Supporting Information

Synthesis of novel carbohydrate based pyridinium ionic liquids and Cytotoxicity of ionic liquids for mammalian cells

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General information

All reagents and solvents were purchased from commercial sources and used as received without further purification, if not stated otherwise. The NMR spectra were recorded on a Bruker AVANCE 300 III, 250 II or 500. The IR spectra were measured as ATR experiments with a Nicolet 6700 FT-IR spectrometer and a Nicolet 550 FT-IR spectrometer. MS and HRMS were measured by an Agilent 6890 N/5973 GC-MS and an Agilent 1200/6210 Time-of-Flight LC-MS.

General procedure for synthesis of thiophenyl-tri-O-acetyl-pentose glycosides 1-4b.

Peracetylated D-ribose 1a, D-lyxose 2a, D-xylose 3a or L-arabinose 4a (1.20 g, 3.77 mmol) was dissolved in dichloromethane (24 mL) and cooled to 0°C. Grinded molecular sieves (1 spatula tip) and thiophenol (0.46 mL, 4.52 mmol) were added and the reaction was stirred at 0°C for 15 min. BF₃·OEt₂ (2.40 mL, 18.93 mmol) was added slowly and the reaction was stirred further 1 h at 0°C followed by 1 h at room temperature. The reaction was then neutralized with NEt₃ (6 mL) and dichloromethane (100 mL) was added. The reaction was washed with brine (2x 30 mL) and cold water (2x 30 mL), dried and evaporated. Column chromatography (PE/EA 2:1 to 1:1) led to products 1-4b.

Thiophenyl-2,3,5-tri-O-acetyl-α-D-ribofuranoside 1b

Yield: 1.11 g (80 %); Rf = 0.49 (PE/EA 1:1); [α]D²² = -51.4° (c = 1.2, CHCl₃); ¹H NMR (300 MHz, CDCℓ₃): 5 = 7.56‒7.50 (m, 2H, CH₃), 7.36‒7.31 (m, 3H, CH₃), 5.35-5.30 (d, 1H, JH-1,H-2 = 4.91 Hz, H-1), 5.27-5.21 (m, 2H, H-2, H-3), 4.31-4.23 (m, 2H, H-4, H-5a), 4.10 (dd, 1H, H-5b), 2.10 (s, 3H, CH₃), 2.08 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCℓ₃): 5 = 170.5, 169.0, 169.4 (3x C=O), 133.4, 129.2 (CH₃), 131.7 (CH₂), 128.4 (CH₃), 87.9 (C-1), 80.1 (C-4), 73.9, 71.4 (C-2, C-3), 63.4 (C-5), 20.8, 20.5, 20.5 (3x CH₃); HRMS (ESI), m/z calc. for C₁₇H₂₀O₇S [M+Na]⁺: 391.082, found: 391.083; Elemental Analysis for C₁₇H₂₀O₇S: C: 55.42, H: 5.47, found: C: 55.33, H: 5.55.
Thiophenyl-2,3,5-tri-O-acetyl-α-D-lyxofuranoside 2b

Yield: 0.69 g (50 %); R<sub>f</sub> = 0.46 (PE/EA 2:1); [α]<sup>21</sup><sub>D</sub> = -72.6° (c = 1.0, CHCl<sub>3</sub>); ¹H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.57–7.51 (m, 2H, CH<sub>Ar</sub>), 7.37–7.32 (m, 3H, CH<sub>Ar</sub>), 5.50 (d, 1H, H-3), 5.46 (d, 1H, 3J<sub>H1,H2</sub> = 5.99 Hz, H-1), 5.32 (dd, 1H, H-2), 4.51–4.43 (m, 1H, H-4), 4.27 (s, 1H, H-5a), 4.24 (d, 1H, H-5b), 2.11 (s, 3H, CH<sub>3</sub>), 2.08 (s, 6H, CH<sub>3</sub>); ¹³C NMR (75 MHz, CDCl<sub>3</sub>): δ = 170.5, 169.6, 169.3 (3x C=O), 132.8, 129.1, 128.2 (CH<sub>Ar</sub>), 87.7 (C-1), 77.2 (C-<sub>Ar</sub>), 76.4 (C-4), 75.0 (C-2), 70.9 (C-3), 61.7 (C-5), 20.8, 20.5, 20.4 (3x CH<sub>3</sub>); HRMS (ESI), m/z calc. for C<sub>17</sub>H<sub>20</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup>: 391.082, found: 391.082; Elemental Analysis for C<sub>17</sub>H<sub>20</sub>O<sub>7</sub>S: C: 55.42, H: 5.47, S: 8.70, found: C: 55.33, H: 5.64, S: 8.60.

Thiophenyl-2,3,5-tri-O-acetyl-α-D-xylofuranoside 3b

Yield: 1.04 g (74 %); R<sub>f</sub> = 0.60 (PE/EA 1:1); [α]<sup>21</sup><sub>D</sub> = -73.8° (c = 1.0, CHCl<sub>3</sub>); ¹H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.49–7.46 (m, 2H, CH<sub>Ar</sub>), 7.40–7.29 (m, 3H, CH<sub>Ar</sub>), 5.44 (d, 1H, 3J<sub>H1,H2</sub> = 3.15 Hz, H-1), 5.30 (dd, 1H, 3J<sub>H2,H3</sub> = 2.21 Hz, H-3), 5.14 (dd, 1H, H-2), 4.47 (dt, 1H, 3J<sub>H4,H5a</sub> = 4.73 Hz, H-4), 4.25 (dd, 1H, H-5a), 4.13 (dd, 1H, H-5b), 2.08 (s, 3H, CH<sub>3</sub>), 2.03 (s, 3H, CH<sub>3</sub>), 2.02 (s, 3H, CH<sub>3</sub>); ¹³C NMR (125 MHz, CDCl<sub>3</sub>): δ = 169.9, 169.3, 169.1 (3x C=O), 133.3 (C<sub>Ar</sub>), 131.1, 129.1, 127.5 (CH<sub>Ar</sub>), 88.2 (C-1), 79.7 (C-2), 78.1 (C-4), 74.9 (C-3), 61.7 (C-5), 20.5, 20.5, 20.3 (3x CH<sub>3</sub>); HRMS (ESI), m/z calc. for C<sub>17</sub>H<sub>20</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup>: 391.082, found: 391.082; Elemental Analysis for C<sub>17</sub>H<sub>20</sub>O<sub>7</sub>S: C: 55.42, H: 5.47, S: 8.70, found: C: 55.37, H: 5.34, S: 8.80.

Thiophenyl-2,3,5-tri-O-acetyl-α-L-arabinofuranoside 4b

Yield: 1.15 g (83 %); R<sub>f</sub> = 0.47 (PE/EA 1:1); [α]<sup>22</sup><sub>D</sub> = -159.5° (c = 1.0, CHCl<sub>3</sub>); ¹H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.53–7.49 (m, 2H, CH<sub>Ar</sub>), 7.36–7.28 (m, 3H, CH<sub>Ar</sub>), 5.55 (d, 1H, 3J<sub>H1,H2</sub> = 2.08 Hz, H-1), 5.29 (t, 1H, 3J<sub>H2,H3</sub> = 2.27 Hz, H-2), 5.09 (dd, 1H, H-3), 4.54–4.45 (m, 1H, H-4), 4.41 (dd, 1H, 3J<sub>H4,H5a</sub> = 11.90 Hz, H-5a); 4.29 (dd, 1H, H-5b); 2.13 (s, 3H, CH<sub>3</sub>), 2.11 (s, 3H, CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>); ¹³C NMR (75 MHz, CDCl<sub>3</sub>): δ = 170.5, 170.0, 169.5 (3x
C=O), 133.4 (C_{Ar}), 132.0, 129.0, 127.8 (CH_{Ar}), 90.9 (C-1), 81.7 (C-2); 80.0 (C-4), 77.1 (C-3), 62.8 (C-5); 20.7, 20.7, 20.7 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{17}$H$_{20}$NaO$_7$ [M+Na]$^+$: 391.082, found: 391.083; Elemental Analysis for C$_{17}$H$_{20}$O$_7$S: C: 55.42, H: 5.47, S: 8.70, found: C: 55.42, H: 5.49, S: 8.80.

**General procedure for synthesis of tri-O-acetyl-1-deoxy-pentoses 1-4c.**

1-4b (650 mg, 1.76 mmol) was dissolved in toluene (20 mL) and tributyltin hydride (886 µL, 3.35 mmol) and AlBN (68.2 mg) were added. The reaction was heated under reflux for 2.5 h and evaporated afterwards. The crude reaction mixture was dissolved in diethyl ether (100 mL), washed with a 10 % KF solution (2x 30 mL) and cold water (2x 30 mL), dried and evaporated again. Column chromatography (Tol/EA 10:1) led to products 1-4c.

1-Deoxy-2,3,5-tri-O-acetyl-D-ribofuranoside 1c

![Image of 1-Deoxy-2,3,5-tri-O-acetyl-D-ribofuranoside 1c](image)

Yield: 390 mg (85 %); R$_f$ = 0.42 (PE/EA 1:1); $[^{22}\text{D}]$ = 70.7° (c = 1.5, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): δ = 5.37 (dt, 1H, $^3$J$_{H-2,H-3}$ = 5.36 Hz, H-2), 5.14 (dt, 1H, H-3), 4.34 (dt, 1H, H-5a), 4.20–4.08 (m, 2H, H-4, H-5b), 3.88 (dd, 1H, H-1b), 2.10 (s, 3H, CH$_3$), 2.09 (s, 3H, CH$_3$), 2.09 (s, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 170.6, 169.9, 169.8 (3x C=O), 78.0 (C-4), 71.8 (C-2), 71.2 (C-3), 70.8 (C-1), 63.5 (C-5), 20.8, 20.6, 20.5 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{11}$H$_{16}$NaO$_7$ [M+Na]$^+$: 283.079, found: 283.079; Elemental Analysis for C$_{11}$H$_{16}$O$_7$: C: 50.77, H: 6.20, found: C: 50.57, H: 6.29.

1-Deoxy-2,3,5-tri-O-acetyl-D-lyxofuranoside 2c

![Image of 1-Deoxy-2,3,5-tri-O-acetyl-D-lyxofuranoside 2c](image)

Yield: 229 mg (50 %); R$_f$ = 0.41 (PE/EA 1:1); $[^{22}\text{D}]$ = 11.9° (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): δ = 5.49 (t, 1H, $^3$J$_{H-2,H-3}$ = 5.10 Hz, H-3), 5.40 (dd, 1H, $^3$J$_{H-1a,H-2}$ = 6.04 Hz, H-2), 4.32–4.19 (m, 3H, H-4, H-5a, H-5b), 4.09 (dd, 1H, $^3$J$_{H-1a,H-1b}$ = 10.01 Hz, H-1a), 3.92 (dd, 1H, H-1b), 2.11 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 2.07 (s, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 170.7, 169.9, 169.7 (3x C=O), 76.4 (C-4), 71.6, 71.3 (C-2, C-3), 69.6 (C-1), 62.7 (C-5), 20.8, 20.6, 20.4 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{11}$H$_{16}$NaO$_7$ [M+Na]$^+$: 283.079, found: 283.079; Elemental Analysis for C$_{11}$H$_{16}$O$_7$: C: 50.77, H: 6.20, found: C: 50.73, H: 6.26.
1-Deoxy-2,3,5-tri-O-acetyl-D-xylofuranoside 3c

Yield: 320 mg (70 %); R₇ = 0.50 (PE/EA 1:1); [α]²¹_D = 57.5° (c = 1.0, CHCl₃); 'H NMR (300 MHz, CDCl₃): δ = 5.36 (dd, 1H, J_H-2,H-3 = 2.46 Hz, H-3), 5.14 (ddd, 1H, H-2), 4.34–4.23 (m, 3H, H-4, H-1a, H-1b), 4.16 (dd, 1H, H-5a), 3.77 (dd, 1H, H-5b), 2.10 (s, 3H, CH₃), 2.09 (s, 3H, CH₃), 2.08 (s, 3H, CH₃); 'C NMR (75 MHz, CDCl₃): δ = 170.6, 169.8, 169.5 (3x C=O), 77.3 (C-2), 77.3 (C-4), 76.0 (C-3), 71.8 (C-1), 61.9 (C-5), 20.8, 20.8, 20.6 (3x CH₃); HRMS (ESI), m/z calc. for C₁₁H₁₆NaO₇[M+Na]^+: 283.079, found: 283.079; Elemental Analysis for C₁₁H₁₆O₇: C: 50.77, H: 6.20, found: C: 50.54, H: 6.34.

1-Deoxy-2,3,5-tri-O-acetyl-L-arabinofuranoside 4c

Yield: 298 mg (65 %); R₇ = 0.67 (PE/EA 1:1); [α]²³_D = 18.7° (c = 1.5, CHCl₃); 'H NMR (500 MHz, CDCl₃): δ = 5.20–5.17, 5.07–5.04 (2x m, 2H, H-2, H-3), 4.36 (dd, 1H, H-5a), 4.21 (dd, 1H, H-5b), 4.08 (dd, 1H, H-1a), 4.05–3.98 (m, 2H, H-1b, H-4), 2.11 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 2.10 (s, 3H, CH₃); 'C NMR (125 MHz, CDCl₃): δ = 170.6, 170.0, 169.8 (3x C=O), 81.7 (C-4), 78.3, 77.7 (C-2, C-3), 72.1 (C-1), 63.5 (C-5), 20.8, 20.8, 20.7 (3x CH₃); HRMS (ESI), m/z calc. for C₁₁H₁₆NaO₇[M+Na]^+: 283.079, found: 283.079; Elemental Analysis for C₁₁H₁₆O₇: C: 50.77, H: 6.20, found: C: 50.56, H: 6.49.

General procedure for synthesis of 1-deoxy-pentoses 1-4d.

1-4c (520 mg, 2.00 mmol) was dissolved in dry methanol (100 mL) und cooled to 0°C. Sodium was added in small portions until pH was 12. The reaction was stirred at room temperature for 4 hours. The reaction was neutralized with Amberlite H⁺ ion exchange resin, filtrated and evaporated. Column chromatography (CHCl₃/MeOH 10:1 to 5:1) led to products 1-4d.

1-Deoxy-D-ribofuranoside 1d
Yield: 241 mg (90%); m.p. = 95–101°C; R<sub>f</sub> = 0.29 (CHCl<sub>3</sub>/MeOH 4:1); \([\alpha]^{23}_D = 60.6^\circ\) (c = 1.0, MeOH); \(^1\)H NMR (300 MHz, MeOD): \(\delta = 4.14\) (m, 1H), 4.05–3.93 (m, 2H, H-1a, H-1b), 3.80–3.67 (m, 3H), 3.57 (dd, 1H, H-5b); \(^1^3\)C NMR (63 MHz, MeOD): \(\delta = 73.9\) (C-1), 84.3, 73.3, 72.6 (C-2, C-3, C-4), 63.3 (C-5); HRMS (ESI), m/z calc. for C<sub>5</sub>H<sub>10</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 157.047, found: 157.047; Elemental Analysis for C<sub>5</sub>H<sub>10</sub>O<sub>4</sub>: C: 44.77, H: 7.51, found: C: 44.69, H: 7.57.

1-Deoxy-D-lyxofuranoside 2d

Product 2d was not free from impurities after column chromatography. The crude product was directly used for the next reaction, see 2e.

1-Deoxy-D-xylofuranoside 3d

Yield: 201 mg (73%); R<sub>f</sub> = 0.35 (CHCl<sub>3</sub>/MeOH 4:1); \([\alpha]^{23}_D = -15.3^\circ\) (c = 1.0, MeOH); \(^1\)H NMR (300 MHz, MeOD): \(\delta = 4.14\) (m, 1H), 4.15–3.99 (m, 4H, H-1a, H-2, H-3, H-4), 3.80 (dd, 1H, H-5a), 3.72 (dd, 1H, H-5b), 3.65 (m, 1H, H-1b); \(^1^3\)C NMR (75 MHz, MeOD): \(\delta = 82.4, 78.8, 78.3\) (C-2, C-3, C-4), 74.4 (C-1), 61.7 (C-5); HRMS (ESI), m/z calc. for C<sub>5</sub>H<sub>10</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 157.047, found: 157.047; Elemental Analysis for C<sub>5</sub>H<sub>10</sub>O<sub>4</sub>: C: 44.77, H: 7.51, found: C: 44.69, H: 7.70.

1-Deoxy-L-arabinofuranoside 4d

Yield: 233 mg (87%); R<sub>f</sub> = 0.25 (CHCl<sub>3</sub>/MeOH 4:1); \([\alpha]^{18}_D = -16.5^\circ\) (c = 1.0, MeOH); \(^1\)H NMR (500 MHz, MeOD): \(\delta = 4.08–4.03\) (m, 1H, H-2), 3.99–3.92 (m, 2H, H-1a, H-3), 3.82–3.74 (m, 2H, H-1b, H-4), 3.69–3.64 (m, 2H, H-5a, H-5b); \(^1^3\)C NMR (75 MHz, MeOD): \(\delta = 87.9\) (C-4), 80.0 (C-3), 78.9 (C-2), 74.8 (C-1), 63.7 (C-5); HRMS (ESI), m/z calc. for C<sub>5</sub>H<sub>10</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>:
157.047, found: 157.047; Elemental Analysis for C$_5$H$_{10}$O$_4$: C: 44.77, H: 7.51, found: C: 44.49, H: 7.69.
General procedure for synthesis of 5-O-trityl-1-deoxy-pentoses 1-4e.

1-4d (1.34 g, 10.0 mmol), trityl chloride (4.18 g, 15.0 mmol), DMAP (one spatula tip) and NEt$_3$ (6.7 mL) were stirred at room temperature overnight in dichloromethane (25 mL). The reaction mixture was evaporated. Column chromatography (PE/EA 4:1 to EA) led to products 1-4e.

5-O-Trityl-1-deoxy-D-ribofuranoside 1e

Yield: 3.01 g (80 %); m.p. = 143°C; R$_f$ = 0.69 (EA); $[\alpha]^{22}_D$ = 42.5° (c = 1.0, MeOH); $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ = 7.42‒7.23 (m, 15H, CH$_{Ar}$), 4.78 (d, 1H, OH), 4.74 (d, 1H, OH), 4.03‒3.99 (m, 1H, $^3$J$_{H-1a,H-2}$ = 4.73 Hz, H-2), 3.96 (dd, 1H, H-1a), 3.81‒3.74 (m, 2H, H-3,H-4), 3.60 (dd, 1H, $^3$J$_{H-3a,H-4}$ = 9.46 Hz, H-1b), 3.12 (dd, 1H, $^3$J$_{H-5a,H-5b}$ = 9.77 Hz, H-5a), 2.97 (dd, 1H, H-5b); $^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ = 143.8 (C$_{Ar}$), 128.3, 127.8, 126.9 (CH$_{Ar}$), 85.7 (CPh$_3$), 80.8 (C-4), 72.5 (C-1), 72.2, 70.3 (C-2, C-3), 64.6 (C-5); HRMS (ESI), m/z calc. for C$_{24}$H$_{24}$NaO$_4$ [M+Na]$^+$: 399.157, found: 399.157; Elemental Analysis for C$_{24}$H$_{24}$O$_4$: C: 76.57, H: 6.43, found: C: 76.46, H: 6.48.

5-O-Trityl-1-deoxy-D-lyxofuranoside 2e

Yield: 2.07 g (55 %*); R$_f$ = 0.26 (PE/EA 1:1); $[\alpha]^{23}_D$ = 25.9° (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.44‒7.23 (m, 15H, CH$_{Ar}$), 4.30 (t, 1H, $^3$J$_{H-3,H-4}$ = 5.36 Hz, H-3), 4.25 (t, 1H, $^3$J$_{H-4a,H-4}$ = 4.41 Hz, H-2), 4.08‒4.04 (m, 1H, H-4), 3.94 (dd, 1H, H-1a), 3.90 (dd, 1H, H-1b), 3.57 (dd, 1H, H-5a), 3.32 (dd, 1H, H-5b); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 143.2 (C$_{Ar}$), 128.5, 128.1, 127.3 (CH$_{Ar}$), 87.9 (CPh$_3$), 78.6 (C-4), 72.6 (C-3), 72.5 (C-1), 71.9 (C-2), 62.9 (C-5); HRMS (ESI), m/z calc. for C$_{24}$H$_{24}$NaO$_4$ [M+Na]$^+$: 399.157, found: 399.157; Elemental Analysis for C$_{24}$H$_{24}$O$_4$: C: 76.57, H: 6.43, found: C: 76.48, H: 6.49.

*yield over two steps, impure product 2d was used for this reaction.

5-O-Trityl -1-deoxy-D-xylofuranoside 3e
Yield: 3.31 g (88 %); \( R_f = 0.49 \) (EA); \( [\alpha]^{22}_D = 16.3^\circ \ (c = 1.0, \ CHCl_3) \); \( ^1H \) NMR (500 MHz, DMSO-\( d_6 \)): \( \delta = 7.44-7.23 \) (m, 15H, CH\(_{Ar}\)), 5.04 (d, 1H, OH), 4.87 (d, 1H, OH), 4.07 (dd, 1H, H-4), 3.94 (t, 1H, H-2), 3.90 (dd, 1H, H-1a), 3.84 (t, 1H, H-3), 3.49 (d, 1H, H-1b), 3.14-3.10 (m, 2H, H-5a, H-5b); \( ^13C \) NMR (125 MHz, DMSO-\( d_6 \)): \( \delta = 143.9 \) (C\(_{Ar}\)), 128.3, 127.8, 126.9 (CH\(_{Ar}\)), 85.8 (CPh\(_3\)), 79.5 (C-4), 76.6, 76.3 (C-2, C-3), 72.9 (C-1), 62.8 (C-5); HRMS (ESI), m/z calc. for C\(_{24}\)H\(_{24}\)O\(_4\) [M+Na\(^+\)]: 399.157, found: 399.157; Elemental Analysis for C\(_{24}\)H\(_{24}\)O\(_4\): C: 76.57, H: 6.43, found: C: 76.48, H: 6.47.

5-O-Trityl-1-deoxy-L-arabinofuranoside 4e

Yield: 2.82 g (75 %); \( R_f = 0.38 \) (EA); \( [\alpha]^{22}_D = -46.6^\circ \ (c = 1.0, \ CHCl_3) \); \( ^1H \) NMR (300 MHz, DMSO-\( d_6 \)): \( \delta = 7.45-7.20 \) (m, 15H, CH\(_{Ar}\)), 5.15 (d, 1H, OH), 4.92 (d, 1H, OH), 3.96-3.90 (m, 1H, H-3), 3.85 (dd, 1H, H-5a), 3.81-3.72 (m, 2H, H-2, H-4), 3.61 (dd, 1H, H-5b), 3.12-3.01 (m, 2H, H-1a, H-1b); \( ^13C \) NMR (75 MHz, DMSO-\( d_6 \)): \( \delta = 143.9 \) (C\(_{Ar}\)), 128.3, 127.8, 126.9 (CH\(_{Ar}\)), 85.8 (CPh\(_3\)), 84.4, 78.6 (C-2, C-4), 76.9 (C-3), 73.0 (C-1), 64.6 (C-5); HRMS (ESI), m/z calc. for C\(_{24}\)H\(_{24}\)O\(_4\) [M+Na\(^+\)]: 399.157, found: 399.157; Elemental Analysis for C\(_{24}\)H\(_{24}\)O\(_4\): C: 76.57, H: 6.43, found: C: 76.32, H: 6.43.

**General procedure for synthesis of 5-O-trityl-2,3-O-methyl-1-deoxy-pentoses 1-4f as well as ethyl and allyl ethers 1l and 1p**

1-4e (2.07 g, 5.5 mmol) was dissolved in dry DMF (33 mL) and cooled to 0°C. NaH (60 % dispersion in mineral oil, 1.3 eq per OH group) was added in small portions. The reaction was stirred at 0°C for 30 min, then methyl iodide (2.0 eq per OH group) was added and the reaction was stirred over night at room temperature. The solvent was evaporated, dichloromethane (100 mL) was added and the mixture was washed (3x 30 mL). Column chromatography (PE/EA 3:1) led to products 1-4f.

For ethylation, 1e (2.07 g, 5.5 mmol) and ethyl bromide (2.0 eq per OH group) was used, leading to product 1l.

For allylation, 1e (1.69 g, 4.5 mmol) and allyl bromide (1.56 mL, 18.0 mmol) was used, leading to product 1p.
5-O-Trityl-2,3-O-methyl-1-deoxy-D-ribofuranoside 1f

Yield: 2.11 g (95 %); Rf = 0.55 (PE/EA 1:1); $\left(\alpha\right)_D^{22} = 35.4^\circ$ (c = 1.5, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.49–7.45, 7.33–7.29, 7.27–7.22 (m, 15H, CH$_{\text{Ar}}$), 4.11–4.04 (m, 2H, H-1a, H-4), 3.82 (t, 1H, H-3), 3.45 (s, 3H, CH$_3$), 3.38 (s, 3H, CH$_3$), 3.34 (dd, 1H, H-5a), 3.14 (dd, 1H, H-5b); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 143.9 (C$_{\text{Ar}}$), 128.7, 127.8, 127.0 (CH$_{\text{Ar}}$), 86.6 (CPh$_3$), 81.0 (C-3), 80.5 (C-4), 79.3 (C-2), 69.6 (C-1), 64.3 (C-5), 58.0, 57.7 (2x CH$_3$); HRMS (ESI), m/z calc. for C$_{26}$H$_{28}$NaO$_4$ [M+Na]$^+$: 427.188, found: 427.189; Elemental Analysis for C$_{26}$H$_{28}$O$_4$: C: 77.20, H: 6.98, found: C: 77.31, H: 6.85.

5-O-Trityl-2,3-O-methyl-1-deoxy-D-lyxofuranoside 2f

Yield: 2.11 g (95 %); m.p. = 96–99$\degree$C; Rf = 0.74 (PE/EA 1:1); $\left(\alpha\right)_D^{23} = -6.8^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (300 MHz, DMSO-d$_6$): δ = 7.46–7.21 (m, 15H, CH$_{\text{Ar}}$), 4.12 (dt, 1H, 3J$_{H-4,H-5b}$ = 5.10 Hz, H-4), 4.05–3.88 (m, 2H, H-2, H-3), 3.80 (dd, 1H, H-1a), 3.54 (dd, 1H, H-5a), 3.02 (dd, 1H, H-5b); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ = 143.8 (C$_{\text{Ar}}$), 128.2, 127.8, 126.9 (CH$_{\text{Ar}}$), 85.9 (CPh$_3$), 80.0 (C-2), 79.1 (C-3), 78.4 (C-4), 67.9 (C-1), 62.4 (C-5), 58.7, 57.3 (2x CH$_3$); HRMS (ESI), m/z calc. for C$_{26}$H$_{28}$NaO$_4$ [M+Na]$^+$: 427.188, found: 427.188; Elemental Analysis for C$_{26}$H$_{28}$O$_4$: C: 77.20, H: 6.98, found: C: 77.14, H: 7.17.

5-O-Trityl-2,3-O-methyl-1-deoxy-D-xylofuranoside 3f

Yield: 2.11 g (95 %); Rf = 0.80 (PE/EA 1:1); $\left(\alpha\right)_D^{22} = -40.1^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, DMSO-d$_6$): δ = 7.41–7.23 (m, 15H, CH$_{\text{Ar}}$), 4.05–3.89 (m, 1H, H-4), 3.90–3.85 (m, 2H, H-2, H-3), 3.62–3.57 (m, 1H, H-1a), 3.30 (s, 3H, CH$_3$), 3.22 (s, 3H, CH$_3$), 3.13–3.05 (m, 2H, H-5a, H-5b); $^{13}$C NMR (125 MHz, DMSO-d$_6$): δ = 143.7 (C$_{\text{Ar}}$), 128.2, 127.8, 127.0 (CH$_{\text{Ar}}$), 85.9 (CPh$_3$), 83.0 (C-3), 82.6 (C-2), 79.2 (C-4), 70.4 (C-1), 61.5 (C-5), 56.9, 56.3 (2x CH$_3$); HRMS (ESI), m/z calc. for C$_{26}$H$_{28}$NaO$_4$ [M+Na]$^+$: 427.188, found: 427.189; Elemental Analysis for C$_{26}$H$_{28}$O$_4$: C: 77.20, H: 6.98, found: C: 76.94, H: 7.11.
5-O-Trityl-2,3-O-methyl-1-deoxy-L-arabinofuranoside 4f

Yield: 1.94 g (87 %); Rf = 0.59 (PE/EA 1:1); \([\alpha]_{D}^{22} = -3.2^\circ (c = 1.0, \text{CHCl}_3)\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.51–7.44, 7.33–7.19\) (m, 15H, CH\(_{Ar}\)), 4.00–3.93 (m, 1H, \(^3\)J\(_{H-4,H-5}\) = 5.67 Hz, H-4), 3.92–3.85 (m, 2H, \(^3\)J\(_{H-1H-2}\) = 4.15 Hz, H-1a, H-1b), 3.81–3.76 (m, 1H, H-2), 3.74–3.70 (m, 1H, H-3), 3.37 (s, 3H, CH\(_3\)), 3.32 (dd, 1H, H-5a), 3.27 (s, 3H, CH\(_3\)), 3.19 (dd, 1H, H-5b); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 143.9\) (C\(_{Ar}\)), 128.7, 127.8, 126.9 (CH\(_{Ar}\)), 86.6 (CPh\(_3\)), 86.2 (C-3), 85.2 (C-2), 82.7 (C-4), 71.2 (C-1), 63.9 (C-5), 57.4, 56.7 (2x CH\(_3\)); HRMS (ESI), m/z calc. for C\(_{26}\)H\(_{28}\)O\(_4\) Na\([M+Na]\)^+: 427.188, found: 427.188; Elemental Analysis for C\(_{26}\)H\(_{28}\)O\(_4\): C: 77.20, H: 6.98, found: C: 76.91, H: 6.99.

5-O-Trityl-2,3-O-ethyl-1-deoxy-D-ribofuranoside 1l

Yield: 2.26 g (95 %); Rf = 0.60 (PE/EA 4:1); \([\alpha]_{D}^{25} = 36.4^\circ (c = 1.0, \text{CHCl}_3)\); \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta = 7.44–7.21\) (m, 15H, CH\(_{Ar}\)), 4.05–3.97 (m, 1H, H-2), 3.92 (dd, 1H, H-1a), 3.88–3.77 (m, 2H, H-3, H-4), 3.73 (dd, 1H, H-1b), 3.48–3.36 (m, 4H, 2x CH\(_2\)), 3.12 (dd, 1H, H-5a), 2.94 (dd, 1H, H-5b), 1.12–1.04 (m, 6H, 2x CH\(_3\)); \(^13\)C NMR (75 MHz, DMSO-d\(_6\)): \(\delta = 143.7\) (C\(_{Ar}\)), 128.2, 127.9, 127.0 (CH\(_{Ar}\)), 85.8 (CPh\(_3\)), 79.3, 79.0 (C-3, C-4), 76.7 (C-2), 70.1 (C-1), 64.7, 64.5 (2x CH\(_2\)), 63.8 (C-5), 15.4, 15.2 (2x CH\(_3\)); HRMS (ESI), m/z calc. for C\(_{28}\)H\(_{32}\)NaO\(_4\) Na\([M+Na]\)^+: 455.219, found: 455.220; Elemental Analysis for C\(_{28}\)H\(_{32}\)O\(_4\): C: 77.75, H: 7.46, found: C: 78.03, H: 7.67.

5-O-Trityl-2,3-O-allyl-1-deoxy-D-ribofuranoside 1p

Yield: 1.95 g (95 %); Rf = 0.65 (PE/EA 4:1); \([\alpha]_{D}^{25} = 30.3^\circ (c = 1.0, \text{CHCl}_3)\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.42–7.21\) (m, 15H, CH\(_{Ar}\)), 5.98–5.72 (m, 2H, 2x CH=CH\(_2\)), 5.33–5.05 (m, 4H, 2x CH=CH\(_2\)), 4.10–3.86 (m, 8H, 2x OCH\(_2\), H-1a, H-2, H-3, H-4), 3.77 (dd, 1H, H-1b), 3.15 (dd, 1H, H-5a), 2.97 (dd, 1H, H-5b); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 143.7\) (C\(_{Ar}\)), 135.3, 134.9 (CH=CH\(_2\)), 128.2, 127.8, 127.0 (CH\(_{Ar}\)), 116.5, 116.4 (CH=CH\(_2\)), 85.8 (CPh\(_3\)), 79.5,
78.5, 76.4 (C-2, C-3, C-4), 70.1 (C-1), 70.1, 70.0 (OCH₂), 63.8 (C-5); HRMS (ESI), m/z calc. for C₃₀H₃₂NaO₄ [M+Na]+: 479.219, found: 479.220; Elemental Analysis for C₃₀H₃₂O₄: C: 78.92, H: 7.06, found: C: 79.24, H: 7.17.

General procedure for synthesis of 2,3-O-methyl-1-deoxy-pentoses 1-4g as well as ethyl and allyl ethers 1m and 1q

1-4f, 1l or 1p (4.0 mmol) was heated to 70°C in a 70 % acetic acid solution (20 mL) for 45 min. The solvent was then removed by codistillation with toluene. Column chromatography (PE/EA 3:1 to 1:2) led to products 1-4g, 1m or 1q.

2,3-O-Methyl-1-deoxy-D-ribofuranoside 1g

![structure](image)

Yield: 511 mg (85 %); Rf = 0.16 (EA); [α]₂²₂ = 106.5° (c = 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ = 3.98 (dd, 1H, H-1a), 3.96‒3.89 (m, 3H, H-1b, H-2, H-4), 3.85 (dd, 1H, H-5a), 3.78 (dd, 1H, H-3), 3.63 (dd, 1H, H-5b), 3.46 (s, 3H, CH₃), 3.44 (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃): δ = 80.7, 78.9 (C-2, C-4), 80.3 (C-3), 70.2 (C-1), 62.4 (C-5), 58.1, 57.6 (2x CH₃); HRMS (ESI), m/z calc. for C₇H₁₄NaO₄ [M+Na]+: 185.078, found: 185.079; Elemental Analysis for C₇H₁₄O₄: C: 51.84, H: 8.70, found: C: 51.98, H: 8.75.

2,3-O-Methyl-1-deoxy-D-lyxofuranoside 2g

![structure](image)

Yield: 511 mg (85 %); Rf = 0.18 (EA); [α]₂⁴₂ = 42.0° (c = 1.0, MeOH); ¹H NMR (300 MHz, CDCl₃): δ = 4.13‒4.05 (m, 1H, H-4), 4.03–3.95 (m, 2H, H-2 or H-3, H-1a), 3.90 (dt, 1H, H-2 or H-3), 3.78 (dd, 1H, H-1b), 3.72 (d, 2H, H-5a, H-5b), 3.30 (s, 6H, 2x CH₃); ¹³C NMR (75 MHz, DMSO-d₆): δ = 81.3, 79.0, 78.4 (C-2, C-3, C-4), 68.8 (C-1), 61.6 (C-5), 59.0, 57.7 (2x CH₃); HRMS (ESI), m/z calc. for C₇H₁₄NaO₄ [M+Na]+: 185.078, found: 185.078; Elemental Analysis for C₇H₁₄O₄: C: 51.84, H: 8.70, found: C: 51.85, H: 8.97.

2,3-O-Methyl-1-deoxy-D-xylofuranoside 3g
2,3-O-Methyl-1-deoxy-L-arabinofuranoside 4g

Yield: 511 mg (85 %); R<sub>f</sub> = 0.24 (EA); [α]<sup>22</sup>D = -58.4° (c = 1.8, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, DMSO-<em>d</em><sub>6</sub>): δ = 4.52 (t, 1H, OH), 3.92–3.88 (m, 1H, H-1a), 3.88–3.86 (m, 1H, H-2), 3.80–3.75 (m, 1H, H-4), 3.71 (dd, 1H, H-3), 3.57–3.52 (m, 2H, H-5a, H-1b), 3.47–3.42 (m, 1H, H-5b), 3.31 (s, 6H, 2x CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMSO-<em>d</em><sub>6</sub>): δ = 82.9, 82.8, (C-2, C-3), 81.2 (C-4), 70.2 (C-1), 58.8 (C-5), 57.1, 56.3 (2x CH<sub>3</sub>); HRMS (ESI), m/z calc. for C<sub>7</sub>H<sub>14</sub>O<sub>4</sub> [M+Na]<sup>+</sup>: 185.078, found: 185.079; Elemental Analysis for C<sub>7</sub>H<sub>14</sub>O<sub>4</sub>: C: 51.84, H: 8.70, found: C: 51.22, H: 8.75.

2,3-O-Ethyl-1-deoxy-D-ribofuranoside 1m

Yield: 639 mg (84 %); R<sub>f</sub> = 0.20 (EA); [α]<sup>24</sup>D = 82.5° (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.06–3.77 (m, 6H, H-1a, H-1b, H-2, H-3, H-4, H-5a), 3.73–3.46 (m, 5H, H-5b, 2x CH<sub>2</sub>), 2.07 (s, 1H, OH), 1.23 (t, 6H, 2x CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 80.9, 78.6, 77.3 (C-2, C-3, C-4), 71.2 (C-1), 65.9, 65.5 (2x CH<sub>2</sub>), 62.2 (C-5), 15.3, 15.3 (2x CH<sub>3</sub>); HRMS (ESI), m/z calc. for C<sub>9</sub>H<sub>18</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 213.110, found: 213.110; Elemental Analysis for C<sub>9</sub>H<sub>18</sub>O<sub>4</sub>: C: 56.82, H: 9.54, found: C: 56.61, H: 9.74.

2,3-O-Allyl-1-deoxy-D-ribofuranoside 1q
Yield: 754 mg (88 %); $R_f = 0.22$ (EA); $[\alpha]_D^{24} = 76.3^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 6.07$–5.80 (m, 2H, 2x CH=CH$_2$), 5.36–5.17 (m, 4H, 2x CH=CH$_2$), 4.22–3.80 (m, 10H, H-1a, H-1b, H-2, H-3, H-4, H-5a, 2x OCH$_2$), 3.69–3.55 (m, 1H, H-5b), 1.98 (q, 1H, OH); $^{13}$C NMR (63 MHz, CDCl$_3$): $\delta = 134.6$, 134.5 (2x CH=CH$_2$), 117.5, 117.4 (2x CH=CH$_2$), 80.9, 77.9, 76.7 (C-2, C-3, C-4), 71.5, 71.0, 71.0 (C-1, 2x OCH$_2$), 62.2 (C-5); HRMS (ESI), m/z calc. for C$_{11}$H$_{18}$O$_4$ [M+Na]$^+$: 237.110, found: 237.110; Elemental Analysis for C$_{11}$H$_{18}$O$_4$: C: 61.66, H: 8.47, found: C: 61.56, H: 8.65.

Procedure for the reduction of 2,3-O-allyl-1-deoxy-D-ribofuranoside 1q to the corresponding propyl ether 1t

1q (321 mg, 1.5 mmol) and Pd(OH)$_2$ (20 mg) were dissolved in dry methanol (20 mL) and stirred at room temperature in a closed flask under H$_2$-atmosphere for 12 h. The reaction was filtered afterwards to yield product 1t.

2,3-O-Propyl-1-deoxy-D-ribofuranoside 1t

Yield: 295 mg (90 %); $R_f = 0.34$ (EA); $[\alpha]_D^{24} = 92.8^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 4.02$–3.77 (m, 6H, H-1a, H-1b, H-2, H-3, H-4; H-5a), 3.65–3.38 (m, 5H, H-5b, 2x OCH$_2$), 2.07 (s, 1H, OH), 1.62 (m, 4H, CH$_2$), 0.93 (t, 6H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 80.8$, 78.9, 77.5 (C-2, C-3, C-4), 72.3, 72.0 (2x OCH$_2$), 71.2 (C-1), 62.3 (C-5), 23.0, 23.0 (2x CH$_2$), 10.5, 10.5 (2x CH$_3$); HRMS (ESI), m/z calc. for C$_{11}$H$_{22}$NaO$_4$ [M+Na]$^+$: 241.141, found: 241.141; Elemental Analysis for C$_{11}$H$_{22}$O$_4$: C: 60.52, H: 10.16, found: C: 60.34, H: 9.89.

General two-step procedure for the introduction of the 5-O-triflate group followed by quarternization with pyridine
1-4g, 1m, 1q or 1t (4.5 mmol) was dissolved in dry dichloromethane (18 mL) and cooled to 0°C. Pyridine (1.07 mL, 13.3 mmol) was added. Afterwards, Tf₂O (1.5 mL, 9.0 mmol) was added dropwise and the mixture was stirred for 10 min at 0°C. Dichloromethane (20 mL) was added and the mixture was washed with cold water (15 mL), sat. NaHCO₃ (2x 15 mL) and cold water again (15 mL). The dried organic phase contains the 5-O-triflate intermediates 1-4h, 1n, 1r or 1u, which were directly used in the next step. Pyridine (2.15 mL, 26.6 mmol) was added and the follow-up reaction was performed at the rotary evaporator (40°C, 700 mbar). Further work-up is stated under the respective products 1-4i, 1o, 1s or 1v.

**N-(2,3-O-Methyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1i**

![Diagram of N-(2,3-O-Methyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1i](image)

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vaccum.

Yield: 1.27 g (82 %); m.p. = 48–51°C; Rₜ = 0 (EA); [α]ᵢ²⁴_D = 68.2° (c = 1.0, MeOH); ¹H NMR (500 MHz, MeOD): δ = 8.97 (d, 2H, CH₃Pyr), 8.64 (t, 1H, CH₃Pyr), 8.13 (d, 2H, CH₃Pyr), 4.92 (dd, 1H, 3J_H₅a,H₅b = 13.56 Hz, H-5a), 4.71 (dd, 1H, H-5b), 4.18 (ddd, 1H, 3J_H₄,H₅b = 5.36 Hz, H-4), 4.07 (ddd, 1H, H-2), 4.01 (dd, 1H, H-1a), 3.94 (d, 1H, H-1b), 3.73 (dd, 1H, H-3), 3.48 (s, 3H, CH₃), 3.42 (s, 3H, CH₃); ¹³C NMR (75 MHz, MeOD): δ = 147.5, 146.8, 129.4 (CH₃Pyr), 83.7 (C-3), 79.6, 79.4 (C-2, C-4), 71.9 (C-1), 64.8 (C-5), 58.7, 58.0 (2x CH₃); ¹⁹F NMR (282 MHz, MeOD): δ = -80.06; HRMS (ESI), m/z calc. for C₁₂H₁₉NO₃ [Cation]+: 224.128, found: 224.128, m/z calc. for CF₃O₃S [Anion]⁻: 148.953, found: 148.953; Elemental Analysis for C₁₃H₁₈F₃NO₆S: C: 41.82, H: 4.86, N: 3.75, S: 8.59, found: C: 41.79, H: 4.69, N: 3.74, S: 8.69.

**N-(2,3-O-Methyl-1,5-deoxy-D-lyxofuranoside-5-yl)-pyridinium triflate 2i**

![Diagram of N-(2,3-O-Methyl-1,5-deoxy-D-lyxofuranoside-5-yl)-pyridinium triflate 2i](image)

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of
activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 941 mg (63 %); liquid at room temperature; $R_f = 0$ (EA); $\left[\alpha\right]_{D}^{23} = 31.4^\circ$ (c = 1.1, CHCl$_3$); $^1$H NMR (300 MHz, MeOD): $\delta = 8.90–8.85$ (CH$_2$Pyr), 8.60–8.52 (m, 1H, CH$_2$Pyr), 8.08–8.00 (m, 2H, CH$_2$Pyr), 4.79–4.74 (m, 2H, H-5a, H-5b), 4.52–4.44 (m, 1H, H-4), 4.23 (dd, 1H, H-3), 4.01 (dd, 1H, H-1a), 3.96–3.91 (m, 1H, H-2), 3.76 (dd, 1H, H-1b), 3.50 (s, 3H, CH$_3$), 3.20 (s, 3H, CH$_3$); $^{13}$C NMR (75 MHz, MeOD): $\delta = 147.7$, 146.8, 128.5 (CH$_2$Pyr), 82.8 (C-3), 79.6 (C-2), 77.8 (C-4), 70.8 (C-5), 59.2, 58.1 (2x CH$_3$); $^{19}$F NMR (282 MHz, MeOD): $\delta = -80.06$; HRMS (ESI), m/z calc. for C$_{12}$H$_{18}$NO$_3$ [Cation]$^+$: 224.128, found: 224.128, m/z calc. for CF$_3$O$_3$S [Anion]: 148.953, found: 148.952; Elemental Analysis for C$_{13}$H$_{18}$F$_3$NO$_6$S: C: 41.82, H: 4.86, N: 3.75, S: 8.59, found: C: 41.73, H: 4.95, N: 3.82, S: 8.76.

$N$-(2,3-O-Methyl-1,5-deoxy-D-xylofuranoside-5-yl)-pyridinium triflate 3i

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.27 g (85 %); m.p. = 32–36°C; $R_f = 0$ (EA); $\left[\alpha\right]_{D}^{27} = -2.3^\circ$ (c = 1.1, MeOH); $^1$H NMR (500 MHz, MeOD): $\delta = 9.06–8.97$ (m, 2H, CH$_2$Pyr), 8.70–8.60 (m, 1H, CH$_2$Pyr), 8.19–8.09 (m, 2H, CH$_2$Pyr), 4.98 (dd, 1H, $^3$J$_{H_5A,H_5B} = 13.60$ Hz, H-5a), 4.81 (dd, 1H, H-5b), 4.44–4.37 (m, 1H, H-4), 4.17–4.10 (m, 1H, H-1a), 4.09–4.04 (m, 2H, H-2, H-3), 3.83 (dd, 1H, H-1b), 3.51 (s, 3H, CH$_3$), 3.44 (s, 3H, CH$_3$); $^{13}$C NMR (75 MHz, MeOD): $\delta = 147.3$, 147.0, 129.2 (CH$_2$Pyr), 85.3, 84.4 (C-2, C-3), 80.3 (C-4), 72.6 (C-1), 62.6 (C-5), 58.2, 57.4 (2x CH$_3$); $^{19}$F NMR (282 MHz, MeOD): $\delta = -80.06$; HRMS (ESI), m/z calc. for C$_{12}$H$_{18}$NO$_3$ [Cation]$^+$: 224.128, found: 224.128, m/z calc. for CF$_3$O$_3$S [Anion]: 148.953, found: 148.953; Elemental Analysis for C$_{13}$H$_{18}$F$_3$NO$_6$S: C: 41.82, H: 4.86, N: 3.75, S: 8.59, found: C: 41.87, H: 4.96, N: 3.64, S: 8.31.

$N$-(2,3-O-Methyl-1,5-deoxy-L-arabinofuranoside-5-yl)-pyridinium triflate 4i
Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.34 g (90 %); liquid at room temperature; $R_f = 0$ (EA); $[\alpha]^{23}_D = -97.0^\circ$ (c = 1.0, MeOH);
$^1$H NMR (500 MHz, MeOD): $\delta = 8.94$ (d, 2H, CH$_{Pyr}$), 8.62 (t, 1H, CH$_{Pyr}$), 8.10 (t, 2H, CH$_{Pyr}$), 4.92 (dd, 1H, $^3J_{H-5a,H-5b} = 13.60$ Hz, H-5a), 4.75 (dd, 1H, H-5b), 4.28–4.20 (m, 1H, $^3J_{H-4,H-5b} = 10.39$ Hz, H-4), 4.04 (d, 1H, H-1a), 3.90–3.77 (m, 3H, H-1b, H-2, H-3), 3.46 (s, 3H, CH$_3$), 3.24 (s, 3H, CH$_3$); $^{13}$C NMR (125 MHz, MeOD): $\delta = 147.3, 147.1, 129.1$ (CH$_{Pyr}$), 87.1, 84.6 (C-2, C-3), 83.4 (C-4), 72.9 (C-1), 64.1 (C-5), 58.1, 57.2 (2x CH$_3$); $^{19}$F NMR (282 MHz, MeOD): $\delta = -80.07$; HRMS (ESI), m/z calc. for $C_{12}H_{18}NO_3$ [Cation$^+$]: 224.128, found: 224.128, m/z calc. for CF$_3$O$_3$S [Anion$^-$]: 148.953, found: 148.953; Elemental Analysis for $C_{13}H_{18}F_3NO_6$S: C: 41.82, H: 4.86, N: 3.75, S: 8.59, found: C: 41.48, H: 4.98, N: 3.69, S: 8.43.

$N$-(2,3-O-Ethyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1o

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.17 g (72 %); liquid at room temperature; $R_f = 0$ (EA); $[\alpha]^{24}_D = 61.7^\circ$ (c = 1.0, MeOH);
$^1$H NMR (500 MHz, MeOD): $\delta = 8.97$ (d, 2H, CH$_{Pyr}$), 8.64 (t, 1H, CH$_{Pyr}$), 8.13 (d, 2H, CH$_{Pyr}$), 4.91 (dd, 1H, $^3J_{H-5a,H-5b} = 13.56$ Hz, H-5a), 4.72 (dd, 1H, H-5b), 4.20 (dt, 1H, $^3J_{H-4,H-5b} = 5.04$ Hz, H-4), 4.13 (dt, 1H, H-2), 4.04 (dd, 1H, H-1a), 3.90 (dd, 1H, H-1b), 3.80 (dd, 1H, H-3), 3.75–3.67, 3.66–3.55 (m, 4H, 2x CH$_2$), 1.24 (t, 3H, CH$_3$), 1.20 (t, 3H, CH$_3$); $^{13}$C NMR (75 MHz, MeOD): $\delta = 147.5, 146.8, 129.4$ (CH$_{Pyr}$), 82.3 (C-3), 79.7 (C-4), 78.1 (C-2), 72.8 (C-
1), 67.2, 66.7 (2x CH2), 64.9 (C-5), 15.8, 15.7 (2x CH3); 19F NMR (282 MHz, MeOD): δ = -80.05; HRMS (ESI), m/z calc. for C14H22NO3 [Cation]⁺: 252.159, found: 252.160, m/z calc. for CF3O3S [Anion]: 148.953, found: 148.952; Elemental Analysis for C15H22F3NO6S: C: 44.88, H: 5.52, N: 3.49, S: 7.99, found: C: 44.52, H: 5.49, N: 3.42, S: 7.92.

**N-(2,3-O-Alllyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1s**

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vaccum.

Yield: 1.11 g (64 %); liquid at room temperature; Rf = 0 (EA); [α]25°D = 70.4° (c = 1.1, MeOH); 1H NMR (300 MHz, MeOD): δ = 9.01–8.94 (m, 2H, CHPyr), 8.63 (t, 1H, CHPyr), 8.12 (t, 2H, CHPyr), 6.05–5.85 (m, 2H, 2x CH=CH2), 5.39–5.26 (m, 2H, CH=CH2), 5.26–5.14 (m, 2H, CH=CH2), 4.93 (dd, 1H, 3JH-H5a,H5b = 13.41 Hz, H-5a), 4.72 (dd, 1H, 3JH-H4,H5b = 8.31 Hz, H-5b), 4.27 (ddd, 1H, 3JH-H4,H5a = 3.02 Hz, H-4), 4.24–4.01 (m, 6H, H-1a, H-2, 2x OCH2), 3.93 (dd, 1H, H-1b), 3.86 (dd, 1H, H-3); 13C NMR (75 MHz, MeOD): δ = 147.5, 146.8 (CHPyr), 136.0, 135.6 (2x CH=CH2), 129.4 (CHPyr), 118.4, 117.7 (2x CH=CH2), 81.8 (C-3), 79.7 (C-4), 77.6 (C-2), 72.8, 72.7 (2x OCH2), 72.2 (C-1), 64.8 (C-5); 19F NMR (282 MHz, MeOD): δ = -80.06; HRMS (ESI), m/z calc. for C16H22NO3 [Cation]⁺: 276.159, found: 276.160, m/z calc. for CF3O3S [Anion]: 148.953, found: 148.952; Elemental Analysis for C17H22F3NO6S: C: 48.00, H: 5.21, N: 3.29, S: 7.54, found: C: 47.42, H: 5.10, N: 3.44, S: 7.59.

**N-(2,3-O-Propyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1v**

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify
the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.12 g (65 %); liquid at room temperature; \( \frac{[\alpha]}{D}^{22} = 54.5^\circ \) (c = 1.0, MeOH); \(^1H\) NMR (300 MHz, MeOD): \( \delta = 9.00–8.94 \) (m, 2H, CH\(_{Pyr}\)), 8.63 (t, 1H, CH\(_{Pyr}\)), 8.13 (t, 2H, CH\(_{Pyr}\)), 4.91 (dd, 1H, \(^3J_{H-4,H-5a} = 13.41\) Hz, H-5b), 4.22 (dt, 1H, H-4), 4.11 (dt, 1H, H-2), 3.78 (dd, 1H, H-3), 3.68–3.42 (m, 4H, 2x OCH\(_2\)), 1.72–1.52 (m, 4H, 2x CH\(_2\)), 0.97 (t, 3H, CH\(_3\)), 0.94 (t, 3H, CH\(_3\)); \(^13C\) NMR (75 MHz, MeOD): \( \delta = 147.4, 146.6, 129.2 \) (CH\(_{Pyr}\)), 82.4 (C-3), 79.5 (C-4), 78.1 (C-2), 73.3, 72.9 (2x OCH\(_2\)), 72.6 (C-1), 64.8 (C-5), 24.1, 24.1 (2x CH\(_2\)), 10.9, 10.9 (2x CH\(_3\)); \(^19F\) NMR (282 MHz, MeOD): \( \delta = -80.07 \); HRMS (ESI), m/z calc. for C\(_{16}\)H\(_{26}\)NO\(_3\) [Cation]\+: 280.191, found: 280.191, m/z calc. for CF\(_3\)O\(_3\)S [Anion]-: 148.953, found: 148.953; Elemental Analysis for C\(_{17}\)H\(_{26}\)F\(_3\)NO\(_4\)S: C: 47.54, H: 6.10, N: 3.26, S: 7.47, found: C: 45.97, H: 6.08, N: 3.20, S: 7.54.

Procedure for synthesis of 2,3-O-Isopropylidene-1-deoxy-D-ribofuranoside 1j

1d (872 mg, 6.5 mmol) was suspended in dry acetone (6.0 mL). Dimethoxy propane (1.6 mL, 13.0 mmol) and camphersulfonic acid (154 mg, 0.66 mmol) were added and the reaction was stirred at room temperature for 1.5 h. Afterwards methanol (12 mL) and sat. NaHCO\(_3\) (2 mL) were added and the mixture was evaporated. Column chromatography (PE/EtOAc 1:1, 1 % NE\(_3\)) led to product 1j.

2,3-O-Isopropylidene-1-deoxy-D-ribofuranoside 1j

Yield: 1.09 g (96 %); \( R_i = 0.29 \) (PE/EtOAc 1:1); \( \frac{[\alpha]}{D}^{22} = 37.5^\circ \) (c = 1.0, CHCl\(_3\)); \(^1H\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 4.86–4.81 \) (m, 1H, H-2), 4.67 (dd, 1H, H-3), 4.01 (dt, 1H, H-4), 3.95 (dd, 1H, H-1a), 3.88 (dd, 1H, H-1b), 3.60–3.48 (m, 2H, H-5a, H-5b), 1.46 (s, 3H, CH\(_3\)), 1.32 (s, 3H, CH\(_3\)); \(^13C\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 113.6 \) (C\(_{isopropylidene}\)), 86.8 (C-4), 83.8 (C-3), 82.7 (C-2), 74.2 (C-1), 62.5 (C-5), 27.0, 25.2 (2x CH\(_3\)); HRMS (ESI), m/z calc. for C\(_8\)H\(_{14}\)NaO\(_4\) [M+Na]\+: 197.078, found: 197.079; Elemental Analysis for C\(_8\)H\(_{14}\)O\(_4\): C: 55.16, H: 8.10, found: C: 55.36, H: 8.14.
Procedure for the introduction of the 5-O-triflate group, followed by quarternization with pyridine, followed by 2,3-O-isopropylidene deprotection, leading to product 1k

1j (784 mg, 4.5 mmol) was dissolved in dry dichloromethane (18 mL) and cooled to 0°C. Pyridine (1.07 mL, 13.3 mmol) was added. Afterwards, Tf₂O (1.5 mL, 9.0 mmol) was added dropwise and the mixture was stirred for 10 min at 0°C. Dichloromethane (20 mL) was added and the mixture was washed with cold water (15 mL), sat. NaHCO₃ (2x 15 mL) and cold water again (15 mL). The dried organic phase contains a mixture of the 5-O-triflate intermediates, both 2,3-O-isopropylidene protected and unprotected. The mixture was directly used in the next step. Pyridine (2.15 mL, 26.6 mmol) was added and the follow-up reaction was performed at the rotary evaporator (40°C, 700 mbar). The crude product was dissolved in dest. water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated and the product was dried under high vaccum. This leads to a mixture of both 2,3-O-isopropylidene protected and unprotected pyridinium triflate salts. To achieve pure product 1k, a 70 % acetic acid solution (3 mL) was added and the reaction was stirred for 20 min. The mixture was codistilled with toluene until all acetic acid is removed. The crude product was again dissolved in dest. water (100 mL) and washed with dichloromethane (3x 20 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added. The solvent was evaporated after filtration and the product was dried under high vaccum, leading to 1k.

N-(1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1k

![Chemical structure](image_url)

Yield: 1.01 g (65 %); liquid at room temperature; Rᵣ = 0 (EA); \([\alpha]^{22}_D = 35.8°\) (c = 1.0, MeOH); 

**¹H NMR (300 MHz, MeOD):** δ = 9.00‒8.93 (m, 2H, CH₄Pyr), 8.67‒8.59 (m, 1H, CH₄Pyr), 8.17‒8.07 (m, 2H, CH₄Pyr), 4.93 (dd, 1H, δJ₅a,H₅b = 13.41 Hz, H-5a), 4.71 (dd, 1H, H-5b), 4.18 (dt, 1H, H-2), 4.13‒4.05 (m, 2H, H-1b, H-4), 3.90 (dd, 1H, H-3), 3.75 (dd, 1H, H-1b); 

**¹³C NMR (63 MHz, MeOD):** δ = 147.4, 146.8, 129.4 (CH₄Pyr), 80.8 (C-4), 75.1 (C-3), 74.9 (C-1), 72.3 (C-2), 64.8 (C-5); 

**¹⁹F NMR (282 MHz, MeOD):** δ = -80.04; 

**HRMS (ESI), m/z calc. for C₁₀H₁₄NO₃** [Cation]: 196.097, found: 196.097; 

**m/z calc. for CF₃O₂S [Anion]:** 148.953, found: 148.952;
Elemental Analysis for C₁₁H₁₄NO₆S: C: 38.26, H: 4.09, N: 4.06, S: 9.29, found: C: 38.14, H: 4.13, N: 3.98, S: 8.94.

Procedure for synthesis of 2,3-O-Isopropylidene-5-O-mesyl-1-deoxy-D-ribofuranoside 1w

1j (610 mg, 3.5 mmol) was dissolved pyridine (20 mL) and mesyl chloride (0.39 mL, 5.0 mmol) was added. The reaction was stirred at room temperature overnight. Dichloromethane (100 mL) was added and the mixture was washed with cold water (20 mL), 15% aqueous NaHSO₄ solution (3x 20 mL) and cold water again (20 mL). Column chromatography (PE/EA 2:1) led to product 1w.

2,3-O-Isopropylidene-5-O-mesyl-1-deoxy-D-ribofuranoside 1w

Yield: 759 mg (86%); m.p. = 78–80°C; Rᵣ = 0.48 (PE/EA 1:1); [α]₀²² = 39.5° (c = 1.0, CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 4.90–4.80 (m, 1H, H-2), 4.67 (d, 1H, H-3), 4.35 (m, 3H, H-4, H-5a, H-5b), 4.09–3.94 (m, 2H, H-1a, H-1b), 3.07 (s, 3H, SO₂CH₃), 1.53 (s, 3H, CH₃), 1.35 (s, 3H, CH₃); ¹³C NMR (63 MHz, CDCl₃): δ = 113.3 (C_isopropylidene), 82.3 (C-4), 81.8 (C-3), 81.0 (C-2), 73.6 (C-1), 68.6 (C-5), 37.7 (SO₂CH₃), 26.6, 25.0 (2x CH₃); HRMS (ESI), m/z calc. for C₉H₁₆NO₆S [M+Na]⁺: 275.056, found: 275.056; Elemental Analysis for C₉H₁₆O₆S: C: 42.85, H: 6.39, S: 12.71, found: C: 42.91, H: 6.28, S: 12.68.

Procedure for the quarternization of the 5-O-mesylate 1w

1w (757 mg, 3.0 mmol) was dissolved in dry pyridine (5 mL) and heated at 125°C for 5 h. The crude product was dissolved in dest. water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was
added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product 1x was dried under high vacuum.

**N-(2,3-O-Isopropylidene-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium mesylate 1x**

![Chemical structure of N-(2,3-O-Isopropylidene-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium mesylate 1x]

Yield: 845 mg (85 %); m.p. = 92–94°C; Rf = 0 (EA); $[^\alpha]_D^{21} = 99.0^\circ$ (c = 1.0, MeOH); $^1$H NMR (250 MHz, MeOD): $\delta$ = 8.95 (d, 2H, CH$_{Pyr}$), 8.70–8.57 (m, 1H, CH$_{Pyr}$), 8.14 (t, 2H, CH$_{Pyr}$), 4.97 (dd, 1H, $^3$J$_{H-2,H-3} = 6.15$ Hz, H-2), 4.89–4.79 (m, 1H, H-5a), 4.77 (dd, 1H, H-3), 4.65 (t, 1H, H-5b), 4.46–4.36 (m, 1H, H-4), 4.18 (dd, 1H, $^3$J$_{H-1a,H-2} = 3.78$ Hz, H-1a), 4.01 (pd, 1H, H-1b), 2.70 (s, 3H, SO$_3$CH$_3$), 1.45 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 147.4, 146.7, 129.5 (CH$_{Pyr}$), 114.4 (C$_{isopropylidene}$), 85.5 (C-4), 83.9 (C-3), 82.5 (C-2), 73.2 (C-1), 61.2 (C-5), 39.7 (SO$_3$CH$_3$), 26.9, 25.2 (2x CH$_3$); HRMS (ESI), m/z calc. for C$_{13}$H$_{18}$NO$_3$ [Cation]: 236.128, found: 236.128, m/z calc. for CH$_3$O$_3$S [Anion]: 94.981, found: 94.981; Elemental Analysis for C$_{14}$H$_{21}$NO$_6$S: C: 49.40, H: 6.51, N: 4.11, S: 9.42, found: C: 49.27, H: 6.26, N: 4.10, S: 9.22.

**General procedure for synthesis of 6-O-trityl-glucopyranosides 5-8b.**

Methyl-β-D-glucopyranoside 5a, allyl-β-D-glucopyranoside 6a, phenyl-β-D-glucopyranoside 7a or methyl-α-D-glucopyranoside 8a (10.0 mmol), trityl chloride (4.18 g, 15.0 mmol), DMAP (one spatula tip) and NEt$_3$ (6.7 mL) were stirred at room temperature overnight in dichloromethane (25 mL). The reaction mixture was evaporated. Column chromatography (PE/EA 4:1 to EA) led to products 5-8b.

**Methyl-6-O-trityl-β-D-glucopyranoside 5b**

![Chemical structure of Methyl-6-O-trityl-β-D-glucopyranoside 5b]

Yield: 3.80 g (87 %); m.p. = 108–109°C; Rf = 0.25 (EA); $[^\alpha]_D^{25} = -61.3^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 7.46–7.21 (m, 15H, CH$_{Ar}$), 5.09 (d, 1H, OH), 4.95 (d, 1H, OH), 4.84 (d, 1H, OH), 4.14 (d, 1H, H-1), 3.49 (s, 3H, CH$_3$), 3.39–3.22 (m, 2H, H-6a, H-6b), 3.16–2.95 (m, 4H, H-2, H-3, H-4, H-5); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ = 144.0 (C$_{Ar}$), 128.3,
127.8, 126.9 (CH$_{Ar}$), 103.80 (C-1), 85.5 (CPh$_3$), 76.8, 75.1, 73.4, 70.22 (C-2, C-3, C-4, C-5), 63.6 (C-6), 55.6 (CH$_3$); HRMS (ESI), m/z calc. for C$_{28}$H$_{28}$NaO$_6$ [M+Na]$^+$: 459.178, found: 459.178; Elemental Analysis for C$_{28}$H$_{28}$O$_6$: C: 71.54, H: 6.47, found: C: 71.32, H: 6.69.

**Allyl-6-O-trityl-β-D-glucopyranoside 6b**

![Structure](image)

Yield: 3.05 g (66 %); R$_f$ = 0.49 (EA); $[^{23}D] = 41.7^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.47–7.22 (m, 15H, CH$_{Ar}$), 6.07–5.96 (m, 1H, CH$_2$=CH$_2$), 5.37 (d, 1H, CH$_2$=CH$_2$), 5.19 (d, 1H, CH$_2$=CH$_2$), 5.09 (s, 1H, OH), 4.95 (s, 1H, OH), 4.82 (s, 1H, OH), 4.36 (d, 1H, OCH$_2$), 4.28 (t, 1H, H-1), 4.20 (dd, 1H, OCH$_2$), 3.38–3.29 (m, 1H, H-5), 3.29–3.23 (m, 1H, H-6a), 3.18–3.00 (m, 4H, H-2, H-3, H-4, H-6b); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 144.0 (C$_{Ar}$), 135.0 (CH$_{2}$CH$_2$), 128.3, 127.7, 126.9 (CH$_{Ar}$), 116.6 (CH$_{2}$CH$_2$), 102.1 (C-1), 85.5 (CPh$_3$), 76.9, 73.4, 70.2 (C-2, C-3, C-4), 75.2 (C-5), 68.9 (OCH$_2$), 63.6 (C-6); HRMS (ESI), m/z calc. for C$_{28}$H$_{30}$NaO$_6$ [M+Na]$^+$: 485.193, found: 485.193; Elemental Analysis for C$_{28}$H$_{30}$O$_6$: C: 72.71, H: 6.54, found: C: 72.54, H: 6.58.

**Phenyl-6-O-trityl-β-D-glucopyranoside 7b**

![Structure](image)

Yield: 4.25 g (83 %); R$_f$ = 0.45 (CHCl$_3$/MeOH 10:1); $[^{23}D] = -51.2^\circ$ (c = 1.0, CHCl$_3$); $^1$H NMR (300 MHz, DMSO-d$_6$): δ = 7.44–7.02 (m, 20H, CH$_{Ar}$), 5.35 (d, 1H, OH), 5.09 (d, 1H, OH), 4.96 (d, 1H, OH), 4.99 (d, 1H, H-1), 3.66 (t, 1H, H-5), 3.33–3.24 (m, 3H, H-2, H-3, H-6a), 3.06–2.98 (m, 2H, H-4, H-6b); $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ = 157.2, 143.8 (C$_{Ar}$); 129.6, 126.8, 128.3, 127.7, 121.6, 116.3 (CH$_{Ar}$) 100.0 (C-1), 85.6 (CPh$_3$), 76.8, 73.2, (C-2, C-3), 75.2 (C-5), 70.3 (C-4), 63.7 (C-6); HRMS (ESI), m/z calc. for C$_{31}$H$_{30}$NaO$_6$ [M+Na]$^+$: 521.193, found: 521.194; Elemental Analysis for C$_{31}$H$_{30}$O$_6$: C: 74.68, H: 6.07, found: C: 74.82, H: 6.36.

**Methyl-6-O-trityl-α-D-glucopyranoside 8b**

![Structure](image)
Yield: 3.71 g (85%); m.p. = 152–154°C; R_f = 0.35 (EA); \( [\alpha]^{23}_D = 74.2^\circ \) (c = 1.0, CHCl_3); \(^1^H\) NMR (500 MHz, DMSO-\( d_6 \)): \( \delta = 7.43–7.22 \) (m, 15H, CH\(_{Ar}\)), 4.81 (d, 1H, OH), 4.75 (d, 1H, OH), 4.72 (d, 1H, OH), 4.62 (d, 1H, \(^3^J_{H-1,H-2} = 3.47 \) Hz, H-1), 3.62 (t, 1H, H-5), 3.41 (s, 3H, CH\(_3\)), 3.39–3.34 (m, 1H, H-3), 3.29–3.20 (m, 2H, H-2, H-6a), 3.05–2.94 (m, 2H, H-4, H-6b); \(^1^\text{C}\) NMR (125 MHz, DMSO-\( d_6 \)): \( \delta = 144.0 \) (C\(_{Ar}\)), 128.3, 127.8, 126.9 (CH\(_{Ar}\)), 99.6 (C-1), 85.6 (CPh\(_3\)), 73.6 (C-3), 71.9 (C-2), 70.9 (C-5), 70.7 (C-4), 63.8 (C-6), 54.1 (CH\(_3\)); HRMS (ESI), m/z calc. for C\(_{26}\)H\(_{28}\)O\(_6\) [M+Na]^+: 459.178, found: 459.178; Elemental Analysis for C\(_{26}\)H\(_{28}\)O\(_6\): C: 71.54, H: 6.47, found: C: 71.31, H: 6.48.

General procedure for synthesis of 6-O-trityl-2,3,4-O-methyl-glucopyranosides 5-8c and ethyl ether 5g

5-8b (5.5 mmol) was dissolved in dry DMF (33 mL) and cooled to 0°C. NaH (60 % dispersion in mineral oil, 1.3 eq per OH group) was added in small portions. The reaction was stirred at 0°C for 30 min, then methyl iodide (2.0 eq per OH group) was added and the reaction was stirred over night at room temperature. The solvent was evaporated, dichlormethane (100 mL) was added and the mixture was washed (3x 30 mL). Column chromatography (PE/EA 3:1) led to products 5-8c.

For ethylation, 5b and ethyl bromide (33.0 mmol, 2.46 mL) was used, leading to product 5g.

Methyl-6-O-trityl-2,3,4-O-methyl-\( \beta \)-D-glucopyranoside 5c

Yield: 2.45 g (93%); R_f = 0.70 (EA); \( [\alpha]^{25}_D = 50.1^\circ \) (c = 1.0, CHCl\(_3\)); \(^1^H\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.43–7.07 \) (m, 15H, CH\(_{Ar}\)), 4.09 (d, 1H, H-1), 3.51 (s, 3H, CH\(_3\)), 3.50 (s, 3H, CH\(_3\)), 3.34 (dd, 1H, \(^3^J_{H-4,H-5} = 2.08 \) Hz, H-5), 3.28 (d, 1H, H-6), 3.20 (s, 3H, CH\(_3\)), 3.15–3.09 (m, 1H, H-4), 3.03–2.94 (m, 3H, H-2, H-3, H-6); \(^1^\text{C}\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 144.0 \) (C\(_{Ar}\)), 128.7, 127.7, 126.9 (CH\(_{Ar}\)), 104.1 (C-1), 86.63 (CPh\(_3\)), 86.6, 83.8, 74.4 (C-2, C-3, C-4), 79.7 (C-5), 62.3 (C-6), 60.8, 60.5, 60.4, 55.6 (4x CH\(_3\)); HRMS (ESI), m/z calc. for C\(_{28}\)H\(_{30}\)NaO\(_6\) [M+Na]^+: 501.225, found: 501.225; Elemental Analysis for C\(_{28}\)H\(_{30}\)O\(_6\): C: 72.78, H: 7.16, found: C: 72.49, H: 7.24.

Allyl-6-O-trityl-2,3,4-O-methyl-\( \beta \)-D-glucopyranoside 6c
Yield: 2.47 g (89%); R\textsubscript{f} = 0.74 (PE/EA 3:1); \([\alpha]\)\textsubscript{D}^24 = 9.6° (c = 1.0, CHCl\textsubscript{3}); \(^1\)H NMR (500 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 7.46–7.25 (m, 15H, CH\textsubscript{ar}), 6.06–5.97 (m, 1H, CH=CH\textsubscript{2}), 5.35 (dd, 1H, CH=CH\textsubscript{2}), 5.21 (dd, 1H, CH=CH\textsubscript{2}), 4.40 (d, 1H, \(^3\)J\textsubscript{H-1,H-2} = 7.88 Hz, H-1), 4.39–4.34 (m, 1H, OCH\textsubscript{2}), 4.16 (dd, 1H, OCH\textsubscript{2}), 3.49 (s, 3H, CH\textsubscript{3}), 3.48 (s, 3H, CH\textsubscript{3}), 3.35–3.31 (m, 1H, H-5), 3.28–3.21 (m, 2H, H-4, H-6a), 3.19 (s, 3H, CH\textsubscript{3}), 3.11 (t, \(^3\)J\textsubscript{H-2,H-3} = 8.83 Hz, H-3), 3.00 (t, 1H, H-2), 2.94 (dd, 1H, H-6b); \(^{13}\)C NMR (125 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 143.7 (C\textsubscript{Ar}), 134.7 (C=CH\textsubscript{2}), 128.2, 127.8, 127.0 (CH\textsubscript{ar}), 116.5 (CH=CH\textsubscript{2}), 101.6 (C-1), 85.5 (CPh\textsubscript{3}), 85.4 (C-3), 83.3 (C-2), 79.1 (C-4), 73.2 (C-5), 68.9 (OCH\textsubscript{2}), 62.1 (C-6), 59.9, 59.7, 59.4 (3x CH\textsubscript{3}); HRMS (ESI), m/z calc. for C\textsubscript{31}H\textsubscript{36}O\textsubscript{6}Na\textsubscript{6}[M+Na]\textsuperscript{+}: 527.240, found: 527.241; Elemental Analysis for C\textsubscript{31}H\textsubscript{36}O\textsubscript{6}: C: 73.79, H: 7.19, found: C: 73.58, H: 7.11.

**Phenyl-6-O-trityl-2,3,4-O-methyl-β-D-glucopyranoside 7c**

Yield: 2.59 g (85%); R\textsubscript{f} = 0.62 (PE/EA 1:1); \([\alpha]\)\textsubscript{D}\textsuperscript{25} = -15.9° (c = 1.0, CHCl\textsubscript{3}); \(^1\)H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 7.45–7.00 (m, 20H, CH\textsubscript{ar}), 5.14 (d, 1H, H-1), 3.69 (dd, 1H, H-5), 3.58 (s, 3H, CH\textsubscript{3}), 3.51 (s, 3H, CH\textsubscript{3}), 3.37 (s, 3H, CH\textsubscript{3}), 3.18 (s, 3H, CH\textsubscript{3}), 3.29–3.21 (m, 4H, H-2, H-3, H-5, H-6a), 2.97 (dd, 1H, H-6b); \(^{13}\)C NMR (75 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 156.8, 143.6 (C\textsubscript{Ar}), 129.4, 128.2, 127.8, 127.0 (CH\textsubscript{ar}), 116.5 (CH=CH\textsubscript{2}), 101.6 (C-1), 85.7 (CPh\textsubscript{3}), 85.2, 83.0, 79.2, 73.3 (C-2, C-3, C-4, C-5), 62.3 (C-6), 59.9, 59.8, 59.4 (3x CH\textsubscript{3}); HRMS (ESI), m/z calc. for C\textsubscript{34}H\textsubscript{36}Na\textsubscript{6}O\textsubscript{6}[M+Na]\textsuperscript{+}: 563.240, found: 563.240; Elemental Analysis for C\textsubscript{34}H\textsubscript{36}O\textsubscript{6}: C: 75.53, H: 6.71, found: C: 75.26, H: 6.88.

**Methyl-6-O-trityl-2,3,4-O-methyl-α-D-glucopyranoside 8c**

Yield: 2.47 g (94%); R\textsubscript{f} = 0.73 (PE/EA 1:1); \([\alpha]\)\textsubscript{D}\textsuperscript{23} = 94.2° (c = 1.0, CHCl\textsubscript{3}); \(^1\)H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 7.45–7.22 (m, 15H, CH\textsubscript{ar}), 4.94 (d, 1H, \(^3\)J\textsubscript{H-1,H-2} = 3.21 Hz, H-1), 3.50 (dd, 1H, H-3 or H-4), 3.43 (s, 3H, CH\textsubscript{3}), 3.37 (s, 3H, CH\textsubscript{3}), 3.35 (s, 3H, CH\textsubscript{3}), 3.30–3.09 (m, 4H, H-2, H-5, H-6a, H-3 or H-4), 3.16 (s, 3H, CH\textsubscript{3}), 3.00 (dd, 1H, H-6b); \(^{13}\)C NMR (75 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 143.7 (C\textsubscript{Ar}), 128.2, 127.9, 127.0 (CH\textsubscript{ar}), 96.5 (C-1), 85.6 (CPh\textsubscript{3}),
82.9, 80.9, 79.2, 69.4 (C-2, C-3, C-4, C-5), 62.3 (C-6), 59.9, 59.5, 57.5, 54.2 (4x CH3); HRMS (ESI), m/z calc. for C29H34NaO6 [M+Na]+: 501.225, found: 501.225; Elemental Analysis for C29H34O6: C: 72.78, H: 7.16, found: C: 72.63, H: 7.23.

Methyl-6-O-trityl-2,3,4-O-ethyl-β-D-glucopyranoside 5g

Yield: 2.34 g (82 %); Rf = 0.69 (PE/EA 3:1); [α]D25 = 13.3° (c = 1.0, CHCl3); 1H NMR (500 MHz, DMSO-d6): δ = 7.47–7.24 (m, 15H, CHAr), 4.26 (d, 1H, H-1), 3.81–3.53 (m, 5H, CH2), 3.50 (s, 3H, CH3), 3.29–3.24 (m, 4H, CH2, H-4, H-5, H-6a), 3.14 (t, 1H, JH-2,H-3 = 8.83 Hz, H-3), 3.01 (dd, 1H, H-2), 2.92 (dd, 1H, H-6b), 1.14–1.09 (m, 6H, 2x CH3), 0.78 (t, 3H, CH3); 13C NMR (125 MHz, DMSO-d6): δ = 143.7 (CAr), 128.2, 127.8, 127.0 (CAr), 103.3 (C-1), 85.5 (CPh3), 83.9 (C-3), 81.7 (C-2), 77.4, 73.4 (C-4, C-5), 67.8, 67.2, 67.1 (3x CH2), 62.0 (C-6), 55.7, 5.7, 15.6, 15.4 (4x CH3); HRMS (ESI), m/z calc. for C32H40NaO6 [M+Na]+: 543.272, found: 543.272; Elemental Analysis for C32H40O6: C: 73.82; H: 7.74, found: C: 73.55; H: 7.81.

General procedure for synthesis of 2,3,4-O-methyl-glucopyranosides 5-8d and ethyl ether 5h

5-8c (4.0 mmol) was heated to 70°C in a 70 % acetic acid solution (20 mL) for 1 h. The solvent was then removed by codistillation with toluene. Column chromatography (PE/EA 3:1 to 1:2) led to products 5-8d and 5h.

Methyl-2,3,4-O-methyl-β-D-glucopyranoside 5d

Yield: 756 mg (80 %); m.p. = 90–93°C; Rf = 0.59 (EA); [α]D25 = -24.4° (c = 1.0, MeOH); 1H NMR (300 MHz, CDCl3): δ = 4.21 (d, 1H, JH-1,H-2 = 7.74 Hz, H-1), 3.88 (dd, 1H, JH-6a,H-6b = 11.90 Hz, H-6a), 3.73 (dd, 1H, H-6b), 3.63 (s, 3H, CH3), 3.58 (s, 3H, CH3), 3.56 (s, 3H, CH3), 3.54 (s, 3H, CH3), 3.28–3.21 (m, 1H, JH-5,H-6b = 4.34 Hz, H-5), 3.21–3.15 (m, 2H, H-3,
H-4), 3.00–2.92 (m, 1H, H-2), 2.02 (s, 1H, OH); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 104.4 (C-1), 86.3, 79.4 (C-3, C-4), 83.8 (C-2), 74.8 (C-5), 62.1 (C-6), 60.8, 60.5, 60.5, 57.2 (4x CH$_3$); HRMS (ESI), m/z calc. for C$_{10}$H$_{20}$NaO$_6$ [M+Na]$^+$: 259.115, found: 259.115; Elemental Analysis for C$_{10}$H$_{20}$O$_6$: C: 50.84, H: 8.53, found: C: 51.10, H: 8.65.

**Allyl-2,3,4-O-methyl-β-D-glucopyranoside 6d**

Yield: 944 mg (90 %); m.p. = 48–50°C; $R_f$ = 0.59 (EA); $[^{24}\alpha]_D^2$ = -30.8° (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 5.98–5.89 (m, 1H, CH$_2$=CCH$_3$), 5.33 (dq, 1H, CH=CCH$_3$), 4.38–4.32 (m, 2H, H-1, CH$_2$O), 4.13 (m, 1H, OCH$_3$), 3.86 (dq, 1H, $^3J_{H-6a,H-6b}$ = 2.84 Hz, H-6a), 3.74–3.68 (m, 1H, H-6b), 3.63 (s, 3H, CH$_3$), 3.60 (s, 3H, CH$_3$), 3.55 (s, 3H, CH$_3$), 3.25–3.21 (m, 1H, H-5), 3.19–3.15 (m, 2H, H-3, H-4), 3.03–2.99 (m, 1H, H-2), 1.99 (m, 1H, OH); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 133.9 (C=CH$_2$), 117.3 (CH=CCH$_3$), 102.5 (C-1), 86.4, 79.5 (C-3, C-4), 74.9 (C-5), 70.4 (OCH$_3$), 62.1 (C-6), 60.8, 60.6, 60.5 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{12}$H$_{22}$NaO$_6$ [M+Na]$^+$: 285.131, found: 285.131; Elemental Analysis for C$_{12}$H$_{22}$O$_6$: C: 54.95, H: 8.45, found: C: 54.96, H: 8.35.

**Phenyl-2,3,4-O-methyl-β-D-glucopyranoside 7d**

Yield: 937 mg (75 %); m.p. = 103–105°C; $R_f$ = 0.38 (PE/EA 1:1); $[^{23}\alpha]_D^{23}$ = -109.1° (c = 1.0, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.26–7.20 (m, 2H, CH$_2$Ar), 7.01–6.91 (m, 3H, CH$_3$Ar), 4.87–4.83 (m, 1H, H-1), 3.82 (dd, 1H, $^3J_{H-6a,H-6b}$ = 11.90 Hz, H-6a), 3.65 (dd, 1H, H-6b), 3.59 (s, 3H, CH$_3$), 3.59 (s, 3H, CH$_3$), 3.50 (s, 3H, CH$_3$), 3.35–3.26 (m, 1H, H-5), 3.20–3.12 (m, 3H, H-2, H-3, H-4); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 157.1 (CH$_2$Ar), 129.6, 116.5, 122.7 (CH$_3$Ar), 101.1 (C-1), 86.2, 83.6, 79.2 (C-2, C-3, C-4), 75.2 (C-5), 62.0 (C-6), 60.9, 60.6, 60.6 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{15}$H$_{22}$NaO$_6$ [M+Na]$^+$: 321.131, found: 321.131; Elemental Analysis for C$_{15}$H$_{22}$O$_6$: C: 54.95, H: 8.45, found: C: 54.96, H: 8.35.

**Methyl-2,3,4-O-methyl-α-D-glucopyranoside 8d**

Yield: 893 mg (95 %); m.p. = 68-70°C; $R_f$ = 0.38 (PE/EA 2:1); $[^{22}\alpha]_D^{22}$ = -32.0° (c = 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 5.92–5.83 (m, 2H, CH$_2$OH), 4.60 (s, 3H, CH$_3$), 4.22 (s, 3H, CH$_3$), 3.75 (s, 3H, CH$_3$), 3.60 (s, 3H, CH$_3$), 3.50 (s, 3H, CH$_3$), 3.40–3.32 (m, 1H, H-5), 3.32–3.20 (m, 3H, H-2, H-3, H-4); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 176.6 (CH$_2$OH), 129.6, 116.5, 122.7 (CH$_3$Ar), 101.1 (C-1), 86.2, 83.6, 79.2 (C-2, C-3, C-4), 75.2 (C-5), 62.0 (C-6), 60.9, 60.6, 60.6 (3x CH$_3$); HRMS (ESI), m/z calc. for C$_{12}$H$_{22}$O$_6$ [M+Na]$^+$: 235.131, found: 235.131; Elemental Analysis for C$_{12}$H$_{22}$O$_6$: C: 54.95, H: 8.45, found: C: 54.96, H: 8.35.
Yield: 822 mg (87 %); m.p. = 29‒30°C; \( R_f = 0.40 \) (EA); \( ^1H \) NMR (500 MHz, CDCl₃): \( \delta = 4.80 \) (d, 1H, \( J_{H-1,H-2} = 3.47 \) Hz, H-1), 3.85‒3.80 (m, 1H, H-6a), 3.77‒3.69 (m, 1H, CH₃), 3.63 (s, 3H, CH₃), 3.56 (s, 3H, CH₃), 3.52 (s, 3H, CH₃), 3.41 (s, 3H, CH₃), 3.58‒3.49 (m, 2H, H-4, H-5), 3.17 (dd, 1H, H-2), 3.16‒3.13 (m, 1H, H-3), 1.90 (s, 1H, OH); \( ^13C \) NMR (125 MHz, CDCl₃): \( \delta = 97.5 \) (C-1), 83.4, 70.6 (C-4, C-5), 81.9 (C-2), 79.7 (C-3), 62.0 (C-6), 60.8, 60.5, 59.0, 55.1 (4x CH₃); HRMS (ESI), m/z calc. for C₁₀H₂₀O₆ [M+Na⁺]: 259.115, found: 259.115; Elemental Analysis for C₁₀H₂₀O₆: C: 50.84, H: 8.53, found: C: 50.99, H: 8.30.

**Methyl-2,3,4-O-ethyl-β-D-glucopyranoside 5h**

Yield: 813 mg (73 %); m.p. = 83°C; \( R_f = 0.50 \) (PE/EA 1:1); \( [\alpha]^{21}_D = -13.3^\circ \) (c = 1.0, CHCl₃); \( ^1H \) NMR (300 MHz, CDCl₃): \( \delta = 4.21 \) (d, 1H, \( J_{H-1,H-2} = 7.74 \) Hz, H-1), 3.94‒3.60 (m, 8H, 3x CH₂, H-6a, H-6b), 3.54 (s, 3H, CH₃), 3.31‒3.22 (m, 3H, H-3, H-4, H-5), 3.10‒3.00 (m, 1H, H-2), 1.99 (dd, 1H, OH), 1.26‒1.16 (m, 9H, 3x CH₃); \( ^13C \) NMR (75 MHz, CDCl₃): \( \delta = 104.6 \) (C-1), 82.1, (C-2), 84.5, 77.8, 75.0 (C-3, C-4, C-5), 68.9, 68.3, 68.3 (3x CH₂), 62.1 (C-6), 57.3, 15.8, 15.7, 15.7 (4x CH₃); HRMS (ESI), m/z calc. for C₁₃H₂₆NaO₆ [M+Na⁺]: 301.162, found: 301.162; Elemental Analysis for C₁₃H₂₆O₆: C: 56.10, H: 9.42, found: C: 56.15, H: 9.25.

**General two-step procedure for the introduction of the 6-O-triflate group followed by quaternization with pyridine**

5-8d or 5h (4.5 mmol) was dissolved in dry dichloromethane (18 mL) and cooled to 0°C. Pyridine (1.07 mL, 13.3 mmol) was added. Afterwards, Tf₂O (1.5 mL, 9.0 mmol) was added dropwise and the mixture was stirred for 10 min at 0°C. Dichloromethane (20 mL) was added and the mixture was washed with cold water (15 mL), sat. NaHCO₃ (2x 15 mL) and cold water again (15 mL). The dried organic phase contains the 6-O-triflate intermediates 5-8e or 5i, which were directly used in the next step. Pyridine (2.15 mL, 26.6 mmol) was added and the follow-up reaction was performed at the rotary evaporator (40°C, 700 mbar). Further work-up is stated under the respective products 5-8f or 5j.

**N-(Methyl-6-deoxy-2,3,4-O-methyl-β-D-glucopyranoside-6-yl)-pyridinium triflate 5f**
Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vaccum.

Yield: 1.73 g (86 %); liquid at room temperature; R<sub>t</sub> = 0 (EA); \([\alpha]_{D}^{21} = -15.7^\circ\) (c = 1.0, MeOH);

1H NMR (300 MHz, MeOD): \(\delta = 8.99–8.93\) (m, 2H, CH<sub>Pyr</sub>), 8.65 (t, 1H, CH<sub>Pyr</sub>), 8.19–8.10 (m, 2H, CH<sub>Pyr</sub>), 5.07 (dd, 1H, \(3\)J<sub>H-6a,H-5</sub> = 2.64 Hz, H-6a), 4.76 (dd, 1H, H-6b), 4.12 (d, 1H, \(3\)J<sub>H-1,H-2</sub> = 7.74 Hz, H-1), 3.74 (dt, 1H, \(3\)J<sub>H-4,H-5</sub> = 9.44 Hz, H-5), 3.62 (s, 3H, CH<sub>3</sub>), 3.61 (s, 3H, CH<sub>3</sub>), 3.50 (s, 3H, CH<sub>3</sub>), 3.26 (s, 3H, CH<sub>3</sub>), 2.94 (t, 1H, H-2);

13C NMR (75 MHz, MeOD): \(\delta = 147.7, 147.1, 129.3\) (CH<sub>Pyr</sub>), 105.5 (C-1), 87.3 (C-3), 85.0 (C-2), 82.0 (C-4), 74.1 (C-5), 63.7 (C-6), 61.3, 61.0, 60.9, 57.3 (4x CH<sub>3</sub>);

19F NMR (282 MHz, MeOD): \(\delta = -78.85\); HRMS (ESI), m/z calc. for C<sub>15</sub>H<sub>24</sub>NO<sub>5</sub> [Cation]*: 298.165, found: 298.165, m/z calc. for CF<sub>3</sub>O<sub>3</sub>S [Anion]: 148.953, found: 148.953; Elemental Analysis for C<sub>16</sub>H<sub>24</sub>F<sub>3</sub>NO<sub>8</sub>S: C: 42.95, H: 5.41, N: 3.13, found: C: 43.15, H: 5.63, N: 2.87.

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**N-(Allyl-6-deoxy-2,3,4-O-methyl-β-D-glucopyranoside-6-yl)-pyridinium triflate 6f**

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vaccum.
Yield: 1.81 g (85 %); m.p. = 66–70°C; R\textsubscript{f} = 0 (EA); $[\alpha]_{D}^{22} = -19.4^\circ$ (c = 1.1, MeOH); \(^1\)H NMR (500 MHz, MeOD): $\delta$ = 8.96–8.93 (m, 2H, CH\textsubscript{Pyr}), 8.68–8.63 (m, 1H, CH\textsubscript{Pyr}), 8.18–8.13 (m, 1H, CH\textsubscript{Pyr}), 5.84–5.75 (m, 1H, CH=CH\textsubscript{2}), 5.14 (dq, 1H, CH=CH\textsubscript{2}), 5.09–5.04 (m, 2H, CH=CH\textsubscript{2}, H-6a), 4.75 (dd, 1H, $^3$J\textsubscript{H-6a,H-6b} = 7.65 Hz, H-1), 4.02 (m, 1H, OCH\textsubscript{3}), 3.87 (m, 1H, OCH\textsubscript{3}), 3.74 (dt, 1H, $^3$J\textsubscript{H-4,H-5} = 9.56 Hz, H-5), 3.62 (s, 3H, CH\textsubscript{3}), 3.61 (s, 3H, CH\textsubscript{3}), 3.53 (s, 3H, CH\textsubscript{3}), 3.25 (t, 1H, H-3), 3.07 (t, 1H, H-4), 2.99 (dd, 1H, H-2); \(^13\)C NMR (125 MHz, MeOD): $\delta$ = 147.7, 147.1 (CH\textsubscript{Pyr}), 135.4 (CH=CH\textsubscript{2}), 129.3 (CH\textsubscript{Pyr}), 117.4 (CH=CH\textsubscript{2}), 103.8 (C-1), 87.3 (C-3), 85.1 (C-2), 82.0 (C-4), 74.2 (C-5), 71.5 (OCH\textsubscript{3}), 63.7 (C-6), 61.2, 61.0, 61.0 (3x CH\textsubscript{3}); \(^19\)F NMR (282 MHz, MeOD): $\delta$ = -80.08; HRMS (ESI), m/z calc. for C\textsubscript{17}H\textsubscript{26}NO\textsubscript{5}[Cation]\textsuperscript{+}: 324.181, found: 324.180, m/z calc. for CF\textsubscript{3}O\textsubscript{3}S [Anion]\textsuperscript{−}: 148.953, found: 148.953; Elemental Analysis for C\textsubscript{18}H\textsubscript{26}F\textsubscript{3}NO\textsubscript{8}S: C: 45.66, H: 5.54, N: 2.96, S: 6.77, found: C: 45.61, H: 5.52, N: 2.75, S: 6.91.

\textit{N-(Phenyl-6-deoxy-2,3,4-O-methyl-\textbeta-D-glucopyranoside-6-yl)-pyridinium triflate 7f}

\begin{center}
\includegraphics[width=0.2\textwidth]{n-pyridinium-triflate-7f}
\end{center}

Work-up: The crude product was dissolved in dichloromethane (100 mL) and washed with cold water (2x 10 mL). The organic phase was evaporated and the product was crystalized from ethanol.

Yield: 1.10 g (48 %); m.p. = 164–172°C; R\textsubscript{f} = 0 (EA); $[\alpha]_{D}^{22} = 41.5^\circ$ (c = 0.7, acetone); \(^1\)H NMR (300 MHz, MeOD): $\delta$ = 8.86 (dd, 2H, CH\textsubscript{Pyr}), 8.64–8.57 (m, 1H, CH\textsubscript{Pyr}), 8.01 (dd, 2H, CH\textsubscript{Pyr}), 7.16–7.07 (m, 2H, CH\textsubscript{Ar}), 7.01–6.94 (m, 1H, CH\textsubscript{Ar}), 6.61–6.55 (m, 2H, CH\textsubscript{Ar}), 5.10 (dd, 1H, $^3$J\textsubscript{H-6a,H-6b} = 13.41 Hz, H-6a), 4.89 (d, 1H, $^3$J\textsubscript{H-1,H-2} = 7.55 Hz, H-1), 4.74 (dd, 1H, $^3$J\textsubscript{H-6a,H-6b} = 9.82 Hz, H-6b), 3.94 (dt, 1H, H-5), 3.66 (s, 6H, 2x CH\textsubscript{3}), 3.63 (s, 3H, CH\textsubscript{3}), 3.37 (q, 1H, $^3$J\textsubscript{H-3,H-4} = 8.69 Hz, H-3), 3.29–3.25 (m, 1H, H-2), 3.21 (q, 1H, H-4); \(^13\)C NMR (75 MHz, MeOD): $\delta$ = 158.0 (C\textsubscript{Ar}), 147.6, 147.0, 129.2 (CH\textsubscript{Pyr}), 129.5, 123.9, 117.7 (CH\textsubscript{Ar}), 101.4 (C-1), 87.4 (C-3), 83.9 (C-2), 82.1 (C-4), 74.4 (C-5), 63.5 (C-6), 61.9, 61.1 (3x CH\textsubscript{3}); \(^19\)F NMR (282 MHz, MeOD): $\delta$ = -80.08; HRMS (ESI), m/z calc. for C\textsubscript{20}H\textsubscript{26}NO\textsubscript{5}[Cation]\textsuperscript{+}: 360.181, found: 360.180, m/z calc. for CF\textsubscript{3}O\textsubscript{3}S [Anion]\textsuperscript{−}: 148.953, found: 148.953; Elemental Analysis for C\textsubscript{21}H\textsubscript{26}F\textsubscript{3}NO\textsubscript{8}S: C: 45.66, H: 5.54, N: 2.96, S: 6.91.

\textit{N-(Methyl-6-deoxy-2,3,4-O-methyl-\textalpha-D-glucopyranoside-6-yl)-pyridinium triflate 8f}
Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.69 g (84 %); liquid at room temperature; $R_f = 0$ (EA); $[^{23}\alpha]_D^\text{MeOH} = 75.1^\circ$ (c = 1.0, MeOH); $^1$H NMR (500 MHz, MeOD): $\delta = 9.01$–8.96 (m, 2H, CH$_2$Pyr), 8.68–8.63 (m, 1H, CH$_2$Pyr), 8.17–8.12 (m, 2H, CH$_2$Pyr), 5.05 (dd, 1H, $^3J_{H-6a,H-5} = 2.68$ Hz, H-6a), 4.82 (d, 1H, $^3J_{H-1,H-2} = 3.44$ Hz, H-1), 3.90 (dt, 1H, H-5), 3.63 (s, 3H, CH$_3$), 3.58 (s, 3H, CH$_3$), 3.45 (s, 3H, CH$_3$), 3.48–3.42 (m, 1H, H-3), 3.24 (dd, 1H, H-2), 3.05 (dd, 1H, H-4), 2.94 (s, 3H, CH$_3$); $^{13}$C NMR (125 MHz, MeOD): $\delta = 147.7$ (CH$_2$Pyr), 147.1 (CH$_2$Pyr), 129.4 (CH$_2$Pyr), 98.9 (C-1), 84.6 (C-3), 82.8 (C-2), 82.0 (C-4), 71.0 (C-5), 63.6 (C-6), 61.2, 61.1, 59.1, 55.6 (4x CH$_3$); $^{19}$F NMR (282 MHz, MeOD): $\delta = -80.06$; HRMS (ESI), m/z calc. for C$_{15}$H$_{24}$NO$_5$ [Cation]$^+$: 298.165, found: 298.165; m/z calc. for CF$_3$O$_3$S [Anion]: 148.953, found: 148.953; Elemental Analysis for C$_{16}$H$_{24}$F$_3$NO$_8$S: C: 42.95, H: 5.41, N: 3.13, found: C: 42.87, H: 5.67, N: 3.10.

**N-(Methyl-6-deoxy-2,3,4-O-ethyl-β-D-glucopyranoside-6-yl)-pyridinium triflate 5j**

Work-up: The crude product was dissolved in dest. Water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product was dried under high vacuum.

Yield: 1.81 g (82 %); m.p. = 114–116°C; $R_f = 0$ (EA); $[^{23}\alpha]_D^\text{MeOH} = -18.0^\circ$ (c = 1.0, MeOH); $^1$H NMR (300 MHz, MeOD): $\delta = 8.97$ (dd, 2H, CH$_2$Pyr), 8.68–8.61 (m, 1H, CH$_2$Pyr), 8.15 (dd, 2H, CH$_2$Pyr), 5.07 (dd, 1H, $^3J_{H-6a,H-6b} = 13.41$ Hz, H-6a), 4.75 (dd, 1H, H-6b), 4.09 (d, 1H, $^3J_{H-1,H-2} = 7.74$ Hz, H-1), 4.02–3.56 (m, 7H, 3x CH$_2$, H-5), 3.34–3.28 (m, 1H, H-3), 3.22 (s, 3H, CH$_3$), 3.17 (t, 1H, H-4), 3.03 (dd, 1H, H-2), 1.27 (t, 3H, CH$_3$), 1.21 (t, 3H, CH$_3$), 1.14 (t, 3H, CH$_3$); $^{13}$C NMR
(75 MHz, MeOD): δ = 147.7, 147.1, 129.2 (CHPy), 105.6 (C-1), 85.6 (C-3), 83.4 (C-2), 80.7 (C-4), 74.3 (C-5), 70.1, 69.7, 69.4 (3x CH2), 63.9 (C-6), 57.38, 16.3, 16.2, 16.1 (4x CH3); 19F NMR (282 MHz, MeOD): δ = -80.06; HRMS (ESI), m/z calc. for C18H30NO5 [Cation]+: 340.212, found: 340.212, m/z calc. for CF3O3S [Anion]-: 148.953, found: 148.953; Elemental Analysis for C18H30F3NO8S: C: 46.62, H: 6.18, N: 2.86, found: C: 46.51, H: 6.09, N: 2.99.

Procedure for the introduction of the 6-O-mesylate group on 5d

5d (827 mg, 3.5 mmol) was dissolved in dry pyridine (20 mL), mesyl chloride (0.39 mL, 5.0 mmol) was added and the reaction was stirred at room temperature for 12 h. Dichloromethane (100 mL) was added and the mixture was washed with cold water (20 mL), 15 % aqueous NaHSO4 solution (3x 20 mL) and cold water again (20 mL). Column chromatography (PE/EA 2:1) led to product 5k.

Methyl-2,3,4-O-methyl-6-O-mesyl-β-D-glucopyranoside 5k

Yield: 1.05 g (95 %); Rf = 0.60 (EA); [α]D23 = -17.7° (c = 1.0, CHCl3); 1H NMR (500 MHz, CDCl3): δ = 4.48 (dd, 1H, JH-6a,H-5 = 2.21 Hz, H-6a), 4.38 (dd, 1H, JH-6a,H-6b = 11.35 Hz, H-6b), 4.18 (d, 1H, JH-1,H-2 = 7.88 Hz, H-1), 3.62 (s, 3H, CH3), 3.56 (s, 3H, CH3), 3.56 (s, 3H, CH3), 3.52 (s, 3H, CH3), 3.40 (ddd, 1H, JH-4,H-5 = 9.77 Hz, H-5), 3.18 (t, 1H, JH-3,H-4 = 8.83 Hz, H-3), 3.10 (t, 1H, H-4), 3.06 (s, 3H, SO2CH3), 2.96 (t, 1H, H-2); 13C NMR (125 MHz, CDCl3): δ = 104.2 (C-1), 86.3 (C-3), 83.6 (C-2), 78.7 (C-4), 72.7 (C-5), 68.5 (C-6), 60.8, 60.5, 60.4, 57.1 (4x CH3), 37.7 (SO2CH3); HRMS (ESI), m/z calc. for C11H22NaO8S [M+Na]+: 337.093, found: 337.093; Elemental Analysis for C11H22O8S: C: 42.03, H: 7.05, S: 10.20, found: C: 42.21, H: 7.08, S: 10.08.

Procedure for the quarternization of the 6-O-mesylate 5k

5k (944 mg, 3.0 mmol) was dissolved in dry pyridine (5 mL) and heated at 125°C for 3 h. The crude product was dissolved in dest. water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product 5l was dried under high vaccum.
N-(Methyl-6-deoxy-2,3,4-O-methyl-β-D-glucopyranoside-6-yl)-pyridinium mesylate 5l

Yield: 1.11 g (94%); m.p. = 60–63°C; Rf = 0 (EA); \([\alpha]^D_{27} = -23.2^\circ\) (c = 1.0, MeOH); \(^1\)H NMR (300 MHz, MeOD): \(\delta = 9.03–8.98\) (d, 2H, CH\(_{\text{Pyr}}\)), 8.73–8.65 (m, 1H, CH\(_{\text{Pyr}}\)), \(J = 8.23–8.15\) (m, 2H, CH\(_{\text{Pyr}}\)), 5.11 (d, 1H, \(J = 2.83\) Hz, H-6a), 4.81 (d, 1H, \(J = 9.25\) Hz, H-6b), 4.16 (d, 1H, \(J = 7.74\) Hz, H-1), 3.78 (dt, 1H, \(J = 9.44\) Hz, H-5), 3.66 (s, 3H, CH\(_3\)), 3.64 (s, 3H, CH\(_3\)), 3.54 (s, 3H, CH\(_3\)), 3.29 (s, 3H, CH\(_3\)), 3.32-3.24 (m, 1H, H-3), 3.10 (dd, 1H, H-4), 2.98 (dd, 1H, H-2), 2.73 (s, 3H, SO\(_2\)CH\(_3\)); \(^13\)C NMR (75 MHz, MeOD): \(\delta = 147.7, 147.1, 129.3\) (CH\(_{\text{Pyr}}\)), 105.5 (C-1), 87.4 (C-3), 85.1 (C-2), 74.2 (C-5), 63.7 (C-6), 61.3, 61.0, 60.9, 57.3 (4x CH\(_3\)), 39.6 (SO\(_2\)CH\(_3\)); HRMS (ESI), m/z calc. for C\(_{15}\)H\(_{24}\)NO\(_5\) [Cation]\(^+\): 298.165, found: 298.165, m/z calc. for CH\(_3\)O\(_3\)S [Anion]\(^-\): 94.981, found: 94.981; Elemental Analysis for C\(_{16}\)H\(_{27}\)NO\(_8\)S: C: 48.84, H: 6.92, N: 3.56, S: 8.15, found: C: 48.65, H: 7.14, N: 3.49, S: 8.07.

Procedure for the introduction of the 6-O-tosylate group on 5d

5d (827 mg, 3.5 mmol) was dissolved in dry pyridine (25 mL), tosyl chloride (950 mg, 5.0 mmol) was added and the reaction was stirred at room temperature for 12 h. Dichloromethane (100 mL) was added and the mixture was washed with cold water (20 mL), 15% aqueous NaHSO\(_4\) solution (3x 20 mL) and cold water again (20 mL). Column chromatography (PE/EA 2:1) led to product 5m.

Methyl-2,3,4-O-methyl-6-O-tosyl-β-D-glucopyranoside 5m

Yield: 1.23 g (90%); m.p. = 65–68°C; Rf = 0.61 (PE/EA 1:1); \([\alpha]^D_{22} = -12.4^\circ\) (c = 1.0, CHCl\(_3\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.85–7.78\) (m, 2H, CH\(_{\text{Ar}}\)), 7.38–7.31 (m, 2H, CH\(_{\text{Ar}}\)), 4.27 (d, 1H, \(J = 10.58\) Hz, H-6a), 4.19 (dd, 1H, \(J = 5.10\) Hz, H-6b), 4.09 (d, 1H, \(J = 7.74\) Hz, H-1), 3.60 (s, 3H, CH\(_3\)), 3.54 (s, 3H, CH\(_3\)), 3.48 (s, 3H, CH\(_3\)), 3.53 (s, 3H, CH\(_3\)), 3.48 (s, 3H, CH\(_3\)).
3.35 (dt, 1H, 3J_{H4,H5} = 9.63 Hz, H-5), 3.14 (t, 1H, 3J_{H2,H3} = 8.69 Hz, H-3), 3.03 (dd, 1H, 3J_{H3,H-4} = 8.88 Hz, H-4), 2.97 (dd, 1H, H-2), 2.45 (s, 3H, Tos-CH$_3$); $^{13}$C NMR (63 MHz, CDCl$_3$): δ = 144.8, 133.0 (C$_{Ar}$), 129.8, 128.0 (CH$_{Ar}$), 103.9 (C-1), 86.3 (C-3), 83.4 (C-2), 78.8 (C-4), 72.5 (C-5), 68.7 (C-6), 60.7, 60.4, 60.4, 56.8 (4x CH$_3$), 21.6 (Tos-CH$_3$); HRMS (ESI), m/z calc. for C$_{17}$H$_{26}$NaO$_8$S [M+Na]$^+$: 413.124, found: 413.124; Elemental Analysis for C$_{17}$H$_{26}$O$_8$S: C: 52.29, H: 6.71, S: 8.21, found: C: 52.34, H: 6.70, S: 8.18.

**Procedure for the quarternization of the 6-O-tosylate 5m**

5m (1.17 g, 3.0 mmol) was dissolved in dry pyridine (5 mL) and heated at 125°C for 3 h. The crude product was dissolved in dest. water (100 mL) and washed with dichloromethane (4x 10 mL) and diethyl ether (2x 10 mL). The aqueous phase was evaporated. The product was then dissolved in dry methanol (10 mL) and a small amount of activated charcoal was added to further purify the product from remaining pyridine. The solvent was evaporated after filtration and the product 5n was dried under high vaccum. The product was crystalized from dichloromethane.

**N-(Methyl-6-deoxy-2,3,4-O-methyl-β-D-glucopyranoside-6-yl)-pyridinium tosylate 5n**

Yield: 1.06 g (75 %); m.p. = 135–137°C; R$_f$ = 0 (EA); $^{[\alpha]}_D^{21}$ = -19.8° (c = 1.0, MeOH); $^1$H NMR (500 MHz, MeOD): δ = 8.98‒8.91 (m, 2H, CH$_{Pyr}$), 8.65 (t, 1H, CH$_{Pyr}$), 8.19‒8.08 (m, 2H, CH$_{Pyr}$), 7.74‒7.66 (m, 2H, CH$_{Ar}$), 7.26‒7.20 (m, 2H, CH$_{Ar}$), 5.06 (dd, 1H, 3J$_{H6a,H5}$ = 2.83 Hz, H-6a), 4.76 (dd, 1H, 3J$_{H6b,H5}$ = 9.25 Hz, H-6b), 4.11 (d, 1H, 3J$_{H1,H2}$ = 7.74 Hz, H-1), 3.73 (dt, 1H, 3J$_{H4,H5}$ = 9.44 Hz, H-5), 3.62 (s, 3H, CH$_3$), 3.60 (s, 3H, CH$_3$), 3.50 (s, 3H, CH$_3$), 3.25 (s, 3H, CH$_3$), 3.28–3.19 (m, 1H, 3J$_{H3,H4}$ = 8.83 Hz, H-3), 3.05 (dd, 1H, H-2), 2.93 (dd, 1H, H-2), 2.37 (s, 3H, Tos-CH$_3$); $^{13}$C NMR (75 MHz, MeOD): δ = 147.7, 147.1 (CH$_{Pyr}$), 143.9, 147.8 (C$_{Ar}$), 129.9 (CH$_{Ar}$), 129.2 (CH$_{Pyr}$), 127.1 (CH$_{Ar}$), 105.4 (C-1), 87.3 (C-3), 85.0 (C-2), 82.0 (C-4), 74.1 (C-5), 63.7 (C-6), 61.2, 61.0, 60.9, 57.3 (4x CH$_3$), 21.5 (Tos-CH$_3$); HRMS (ESI), m/z calc. for C$_{15}$H$_{26}$NO$_5$ [Cation]$^+$: 298.165, found: 298.165, m/z calc. for C$_{17}$H$_{26}$O$_8$S [Anion]$^-$: 171.012, found: 171.012; Elemental Analysis for C$_{22}$H$_{31}$NO$_8$S: C: 56.27, H: 6.65, N: 2.98, found: C: 56.07, H: 6.67, N: 2.83.
NMR Spectra of all final pentose based ionic products

$N$-(2,3-$O$-Methyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate $1i$

Figure 1: $^1H$ spectrum of compound $1i$ (500 MHz, MeOD).

Figure 2: $^{13}C$ spectrum of compound $1i$ (125 MHz, MeOD).
Figure 3: $^{19}$F spectrum of compound 1i (282 MHz, MeOD).

$N$-(2,3-O-Methyl-1,5-deoxy-D-lyxofuranoside-5-yl)-pyridinium triflate 2i

Figure 4: $^1$H spectrum of compound 2i (300 MHz, MeOD).
Figure 5: $^{13}$C spectrum of compound 2i (75 MHz, MeOD).

Figure 6: $^{19}$F spectrum of compound 2i (282 MHz, MeOD).
$N$-(2,3-O-Methyl-1,5-deoxy-D-xylofuranoside-5-yl)-pyridinium triflate 3i

Figure 7: $^1$H spectrum of compound 3i (300 MHz, MeOD).

Figure 8: $^{13}$C spectrum of compound 3i (75 MHz, MeOD).
Figure 9: $^{19}$F spectrum of compound 3i (282 MHz, MeOD).

**N-(2,3-O-Methyl-1,5-deoxy-L-arabinofuranoside-5-yl)-pyridinium triflate 4i**

Figure 10: $^1$H spectrum of compound 4i (500 MHz, MeOD).
Figure 11: $^{13}$C spectrum of compound 4i (125 MHz, MeOD).

Figure 12: $^{19}$F spectrum of compound 4i (282 MHz, MeOD).
**N-(2,3-O-Ethyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1o**

Figure 13: $^1$H spectrum of compound 1o (500 MHz, MeOD).

Figure 14: $^{13}$C spectrum of compound 1o (75 MHz, MeOD).
Figure 15: $^{19}$F spectrum of compound 1o (282 MHz, MeOD).

$N$-(2,3-O-Allyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1s

Figure 16: $^1$H spectrum of compound 1s (300 MHz, MeOD).
Figure 17: $^{13}$C spectrum of compound 1s (75 MHz, MeOD).

Figure 18: $^{19}$F spectrum of compound 1s (282 MHz, MeOD).
$N$-(2,3-O-Propyl-1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate $1v$

Figure 19: $^1$H spectrum of compound $1v$ (300 MHz, MeOD).

Figure 20: $^{13}$C spectrum of compound $1v$ (75 MHz, MeOD).
Figure 21: $^{19}$F spectrum of compound 1v (282 MHz, MeOD).

$N$-(1,5-deoxy-D-ribofuranoside-5-yl)-pyridinium triflate 1k

Figure 22: $^1$H spectrum of compound 1k (300 MHz, MeOD).
Figure 23: $^{13}$C spectrum of compound 1k (63 MHz, MeOD).

Figure 24: $^{19}$F spectrum of compound 1k (282 MHz, MeOD).
Figure 25: $^1$H spectrum of compound 1x (250 MHz, MeOD).

Figure 26: $^{13}$C spectrum of compound 1x (75 MHz, MeOD).
NMR Spectra of all final glucose based ionic products

\[ N-(\text{Methyl-6-deoxy-2,3,4-O-methyl-}\beta-D-\text{glucopyranoside-6-yl})-\text{pyridinium triflate 5f} \]

Figure 27: \(^1\text{H NMR spectrum of compound 5f (300 MHz, MeOD).}\)

Figure 28: \(^{13}\text{C spectrum of compound 5f (75 MHz, MeOD).}\)
Figure 29: $^{19}$F spectrum of compound 5f (282 MHz, MeOD).

$N$-(Methyl-6-deoxy-2,3,4-O-ethyl-$\beta$-D-glucopyranoside-6-yl)-pyridinium triflate 5j

Figure 30: $^1$H spectrum of compound 5j (300 MHz, MeOD).
Figure 31: $^{13}$C spectrum of compound 5j (75 MHz, MeOD).

Figure 32: $^{19}$F spectrum of compound 5j (282 MHz, MeOD).
**Figure 33:** $^1$H spectrum of compound 5l (300 MHz, MeOD).

**Figure 34:** $^{13}$C spectrum of compound 5l (75 MHz, MeOD).
$\text{N-(Methyl-6-deoxy-2,3,4-O-methyl-}\beta\text{-D-glucopyranoside-6-yl)-pyridinium tosylate 5n}$

Figure 35: $^1\text{H}$ spectrum of compound 5n (500 MHz, MeOD).

Figure 36: $^{13}\text{C}$ spectrum of compound 5n (75 MHz, MeOD).
$N$-(Allyl-6-deoxy-2,3,4-O-methyl-$\beta$-D-glucopyranoside-6-yl)-pyridinium triflate 6f

Figure 37: $^1$H spectrum of compound 6f (300 MHz, MeOD).

Figure 38: $^{13}$C spectrum of compound 6f (75 MHz, MeOD).
Figure 39: $^{19}$F spectrum of compound 6f (282 MHz, MeOD).

$N$-(Phenyl-6-deoxy-2,3,4-O-methyl-β-D-glucopyranoside-6-yl)-pyridinium triflate 7f

Figure 40: $^1$H spectrum of compound 7f (300 MHz, MeOD).
Figure 41: $^{13}$C spectrum of compound 7f (75 MHz, MeOD).

Figure 42: $^{19}$F spectrum of compound 7f (282 MHz, MeOD).
\[ N-(\text{Methyl-6-deoxy-2,3,4-O-methyl-\(\alpha\)-D-glucopyranoside-6-yl})-\text{pyridinium triflate} \ 8f \]

Figure 43: \(^1\text{H}\) spectrum of compound 8f (500 MHz, MeOD).

Figure 44: \(^{13}\text{C}\) spectrum of compound 8f (125 MHz, MeOD).
Figure 45: $^{19}$F spectrum of compound 8f (282 MHz, MeOD).
NMR spectra of key pentose intermediates

5-O-Trityl-1-deoxy-D-ribofuranoside 1e

Figure 46: $^1$H spectrum of compound 1e (300 MHz in DMSO-d$_6$).

Figure 47: $^{13}$C spectrum of compound 1e (75 MHz, DMSO-d$_6$).
5-O-Trityl-1-deoxy-D-lyxofuranoside 2e

Figure 48: $^1$H spectrum of compound 2e (500 MHz, CDCl$_3$).

Figure 49: $^{13}$C spectrum of compound 2e (125 MHz, CDCl$_3$).
5-O-Trityl-1-deoxy-D-xylofuranoside 3e

Figure 50: $^1$H spectrum of compound 3e (500 MHz, DMSO-d6)

Figure 51: $^{13}$C spectrum of compound 3e (125 MHz, DMSO-d6).
5-O-Trityl-1-deoxy-L-arabinofuranoside 4e

Figure 52: $^1$H spectrum of compound 4e (300 MHz, DMSO-d$_6$).

Figure 53: $^{13}$C spectrum of compound 4e (75 MHz, DMSO-d$_6$).
2,3-O-Isopropylidene-1-deoxy-D-ribofuranoside 1j

Figure 54: $^1$H spectrum of compound 1j (300 MHz, CDCl$_3$).

Figure 55: $^{13}$C spectrum of compound 1j (75 MHz, CDCl$_3$).
NMR Spectra of key glucoside intermediates

Methyl-2,3,4-O-methyl-β-D-glucopyranoside 5d

Figure 56: $^1$H spectrum of compound 5d (300 MHz, CDCl$_3$).

Figure 57: $^{13}$C spectrum of compound 5d (75 MHz, CDCl$_3$).
Allyl-2,3,4-O-methyl-β-D-glucopyranoside 6d

Figure 58: $^1$H spectrum of compound 6d (500 MHz, CDCl$_3$).

Figure 59: $^{13}$C spectrum of compound 6d (125 MHz, CDCl$_3$).
Phenyl-2,3,4-O-methyl-β-D-glucopyranoside 7d

Figure 60: $^1$H spectrum of compound 7d (300 MHz, CDCl$_3$).

Figure 61: $^{13}$C spectrum of compound 7d (75 MHz, CDCl$_3$).
Methyl-2,3,4-O-methyl-α-D-glucopyranoside 8d

Figure 62: $^1$H spectrum of compound 8d (500 MHz, CDCl$_3$).

Figure 63: $^{13}$C spectrum of compound 8d (125 MHz, CDCl$_3$).
Methyl-2,3,4-O-ethyl-β-D-glucopyranoside 5h

Figure 64: $^1$H spectrum of compound 5h (300 MHz, CDCl$_3$).

Figure 65: $^{13}$C spectrum of compound 5h (75 MHz, CDCl$_3$).