Supporting Information

Fragmentation of Carbohydrate Anomeric Alkoxy Radicals. A New Synthesis of Chiral β -Iodo Azides, Vinyl Azides and 2*H*-Azirines

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Structural data and procedures for the synthesis of compounds: β -iodo azides **2**, **6**, **10**, **14**, **18**, vinyl azides **3**, **7**, **11**, **15**, **19** and 2*H*-azirines **4**, **8**, **12**, **16**, **20**.

General Methods. Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in CHCl₃ solutions. IR spectra were recorded in CCl₄ solutions unless otherwise stated. NMR spectra were determined at 500 MHz for ¹H and 125.7 MHz for ¹³C in CDCl₃ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF₂₅₄ were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H₂SO₄–EtOH (4:1) and further heating until development of color.

General procedure for the synthesis of 4-azido-4,5-dideoxy-aldoses.¹ A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in 1,4-dioxane (1.35 mL) containing HgSO₄ (0.047 mmol) and aqueous H₂SO₄ (5 mM, 5.4 mL) was stirred at 30 °C for 1–5 h. Then NaN₃ (10 mmol) and AcOH glacial (1.35 mL) were added and the

stirring continued for 1.5 h. The reaction mixture was then poured into water and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, concentrated under vacuum and the residue purified by column chromatography (hexanes–EtOAc, mixtures), to give the required 4-azido-4,5-dideoxy compounds.

General procedure for the synthesis of β -iodo azide compounds. A solution of the 4-azido-4,5-dideoxy compounds (1 mmol) in CH₂Cl₂ (25 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was stirred at 50 °C for 15–30 min. The reaction mixture was then poured into water and extracted with CH₂Cl₂. The organic layer was washed with 10% aqueous sodium thiosulfate, dried and concentrated in vacuo. Chromatotron chromatography of the residue (hexanes–EtOAc, mixtures) afforded the required iodo-azides.

General procedure for the synthesis of vinyl azide compounds. To a solution of the β -iodo azide (1 mmol) in dry benzene (34 mL) was added DBU (2.5 mmol) and the mixture stirred at 90 °C for 0.5–3 h. After this time the reaction mixture was poured into a saturated solution of NaHSO₄, and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under vacuum. Column chromatography (hexanes–EtOAc, mixtures) of the residue afforded the required vinyl azides.

General procedure for the synthesis of 2*H*-azirine compounds. A solution of the vinyl azide (1 mmol) in dry toluene (12 mL) was heated at reflux temperature, under nitrogen for 2–22 h. After concentration under vacuum, the residue was purified by Chromatotron chromatography (hexanes–EtOAc, mixtures) to give the required 2*H*-azirines.

3,5-Di-*O*-acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-1-iodo-D-arabinitol and 3,5-Di-*O*-acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-1-iodo-D-ribitol (2). From the isomeric

mixture 4,6-di-*O*-acetyl-3-azido-2,3-dideoxy-D-*arabino*-hexopyranose and -D-*ribo*-hexopyranose (**1**)^{1a} (95%, **2-D-Ara:2-D-Rib**, 9:1). Compound **2-D-Ara**: mp 53–53.1 °C (from *n*-hexane–EtOAc); [α]_D +45 (*c* = 1.01); IR 2113, 1741, 1428 cm^{−1}; ¹H NMR δ 2.07 (3H, s), 2.15 (3H, s), 3.24 (1H, dd, *J* = 10.8, 8.2 Hz), 3.28 (1H, dd, *J* = 10.8, 5.9 Hz), 3.71 (1H, ddd, *J* = 8.3, 5.9, 2.5 Hz), 4.21 (1H, dd, *J* = 12.7, 4.7 Hz), 4.35 (1H, dd, *J* = 12.7, 2.7 Hz), 5.42 (1H, ddd, *J* = 10.3, 7.5, 2.7 Hz), 5.44 (1H, dd, *J* = 7.5, 2.6 Hz), 8.09 (1H, s); ¹³C NMR δ 1.0 (CH₂), 20.4 (CH₃), 20.6 (CH₃), 61.3 (CH₂), 62.1 (CH), 69.4 (CH), 70.8 (CH), 159.3 (CH), 169.4 (C), 170.4 (C); MS *m/z* (rel intensity) 400 (M⁺ + H, 3), 340 (3), 203 (78), 115 (100); HRMS calcd for C₁₀H₁₅IN₃O₆ 400.0006, found 399.9984. Anal. Calcd for C₁₀H₁₄IN₃O₆: C, 30.09; H, 3.54; N, 10.53. Found: C, 30.28; H, 3.61; N, 10.51. Compound **2-D-Rib**: [α]_D +36 (*c* = 0.73); IR 2115, 1741, 1429 cm^{−1}; ¹H NMR δ 2.07 (3H, s), 2.12 (3H, s), 3.22 (1H, dd, *J* = 10.9, 8.7 Hz), 3.39 (1H, dd, *J* = 10.9, 3.7 Hz), 3.83 (1H, ddd, *J* = 9.1, 6.1, 3.7 Hz), 4.23 (1H, dd, *J* = 12.4, 6.7 Hz), 4.41 (1H, dd, *J* = 12.4, 3.4 Hz), 5.17 (1H, dd, *J* = 6.0, 4.6 Hz), 5.46 (1H, ddd, *J* = 7.3, 3.9, 3.9 Hz), 8.1 (1H, s); ¹³C NMR δ 2.5 (CH₂), 20.6 (2 × CH₃), 61.7 (CH₂), 62.9 (CH), 69.4 (CH), 72.2 (CH), 159.4 (CH), 169.2 (C), 170.4 (C); MS (rel intensity) 400 (M⁺ + H, 100), 203 (9), 71 (36), 57 (52); HRMS calcd for C₁₀H₁₅IN₃O₆ 400.0006, found 400.0042. Anal. Calcd for C₁₀H₁₄IN₃O₆: C, 30.09; H, 3.54; N, 10.53. Found: C, 30.29; H, 3.55; N, 10.39.

3,5-di-*O*-acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-D-*erythro*-pent-1-enitol (3**).** From the mixture of the isomeric iodo-azides **2** (76%): [α]_D −1 (*c* = 1.34); IR 2115, 1754, 1739, 1717, 1632 cm^{−1}; ¹H NMR δ 2.05 (3H, s), 2.11 (3H, s), 4.23 (1H, dd, *J* = 12.4, 6.5 Hz), 4.33 (1H, dd, *J* = 12.4, 2.8 Hz), 4.93 (1H, d, *J* = 2.5 Hz), 5.12 (1H, d, *J* = 2.6 Hz), 5.35 (1H, d, *J* = 6.1 Hz), 5.41 (1H, ddd, *J* = 6.2, 6.2, 3.4 Hz), 8.03 (1H, s); ¹³C NMR δ

20.6 (CH₃), 20.7 (CH₃), 61.4 (CH₂), 69.4 (CH), 70.6 (CH), 102.3 (CH₂), 141.3 (C), 159.5 (CH), 169.1 (C), 170.5 (C); MS (FAB) (rel intensity) 294 (M⁺ + Na, 2), 221 (33), 207 (22), 73 (100); HRMS calcd for C₁₀H₁₃N₃NaO₆ 294.0702, found 294.0625. Anal. Calcd for C₁₀H₁₃N₃O₆: C, 44.28; H, 4.83; N, 15.49. Found: C, 44.33; H, 5.13; N, 15.18.

(1*S*,2*S*)-3-(Acetyloxy)-1-(2*H*-aziren-3-yl)-2-(formyloxy)propyl acetate (4).

From vinyl azide **3** (85%): [α]_D +45 (*c* = 1.11); IR 1755, 1741 cm⁻¹; ¹H NMR δ 1.63 (1H, d, *J* = 8.4 Hz), 1.65 (1H, d, *J* = 8.4 Hz), 2.02 (3H, s), 2.16 (3H, s), 4.29 (1H, dd, *J* = 12.8, 6.4 Hz), 4.33 (1H, dd, *J* = 12.1, 4.7 Hz), 5.65 (1H, ddd, *J* = 4.6, 4.6, 4.6 Hz), 6.14 (1H, d, *J* = 4.3 Hz), 8.03 (1H, s); ¹³C NMR δ 20.4 (CH₃), 20.5 (CH₃), 21.6 (CH₂), 61.0 (CH₂), 68.6 (CH), 68.8 (CH), 159.4 (CH), 167.4 (C), 169.3 (C), 170.1 (C) MS (rel intensity) 244 (M⁺ + H, 2), 202 (4), 184 (3), 161 (2), 85 (100); HRMS calcd for C₁₀H₁₄NO₆ 244.0821, found 244.0792. Anal. Calcd for C₁₀H₁₃NO₆: C, 49.38; H, 5.39; N, 5.76. Found: C, 49.46; H, 5.66; N, 5.80.

1,3-di-*O*-Acetyl-4-azido-4,5-dideoxy-2-*O*-formyl-5-iodo-D-lyxitol and 3,5-di-*O*-Acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-1-iodo-D-xylitol (6). From the isomeric mixture 4,6-di-*O*-acetyl-3-azido-2,3-dideoxy-D-xylo-hexopyranose and -lyxo-hexopyranose (**5**) (86%, **6-D-Xyl:6-D-Lyx**, 6:4). Compound **6-D-Xyl**: [α]_D -2 (*c* = 0.73); IR 2113, 1759, 1737, 1428 cm⁻¹; ¹H NMR δ 2.09 (3H, s), 2.16 (3H, s), 3.25 (1H, dd, *J* = 10.8, 7.1 Hz), 3.32 (1H, dd, *J* = 10.9, 5.5 Hz), 3.63 (1H, ddd, *J* = 5.2, 5.2, 5.2 Hz), 4.09 (1H, dd, *J* = 12.3, 5.8 Hz), 4.36 (1H, dd, *J* = 12.3, 3.8 Hz), 5.41 (1H, dd, *J* = 4.9, 4.9 Hz), 5.45 (1H, ddd, *J* = 10.0, 5.1, 0.0 Hz), 8.10 (1H, s); ¹³C NMR δ 1.2 (CH₂), 20.4 (CH₃), 20.7 (CH₃), 61.7 (CH₂), 61.7 (CH), 69.4 (CH), 71.9 (CH), 159.6 (CH), 169.5 (C), 170.3 (C); MS (EI) *m/z* (rel intensity) 400 (M⁺ + H, <1), 340 (1), 272 (5), 115 (100); HRMS calcd for C₁₀H₁₅IN₃O₆ 400.0006, found: 399.9954. Anal. Calcd for C₁₀H₁₄IN₃O₆: C, 30.09; H, 3.54; N, 10.53. Found: C, 30.29; H, 3.43; N, 10.22.

Compound **6-D-Lyx**: $[\alpha]_D +5$ ($c = 0.1$); IR 2117, 1757, 1740, 1717, 1429 cm^{-1} ; ^1H NMR δ 2.06 (3H, s), 2.16 (3H, s), 3.22 (1H, dd, $J = 10.9, 8.1$ Hz), 3.33 (1H, dd, $J = 10.9, 3.7$ Hz), 3.72 (1H, ddd, $J = 8.2, 8.2, 3.7$ Hz), 4.03 (1H, dd, $J = 11.8, 7.1$ Hz), 4.28 (1H, dd, $J = 11.8, 5.3$ Hz), 5.07 (1H, dd, $J = 8.2, 2.3$ Hz), 5.61 (1H, ddd, $J = 7.1, 2.2, 2.2$ Hz), 8.15 (1H, s); ^{13}C NMR δ 3.2 (CH_2), 20.6 ($2 \times \text{CH}_3$), 62.0 (CH_2), 62.1 (CH), 68.4 (CH), 71.6 (CH), 159.5 (CH), 169.5 (C), 170.2 (C); MS (EI) m/z (rel intensity) 400 ($\text{M}^+ + \text{H}$, <1), 357 (<1), 340 (<1), 161 (31), 115 (100); HRMS calcd for $\text{C}_{10}\text{H}_{15}\text{IN}_3\text{O}_6$ 400.0006, found: 399.9970. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{IN}_3\text{O}_6$: C, 30.09; H, 3.54; N, 10.53. Found: C, 29.93; H, 3.93; N, 10.17

3,5-Di-*O*-acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-D-*threo*-pent-1-enitol (7).

From the mixture of iodo azides **6** (70%): $[\alpha]_D +7$ ($c = 0.3$); IR 2116, 1755, 1740, 1635 cm^{-1} ; ^1H NMR δ 2.06 (3H, s), 2.11 (3H, s), 4.08 (1H, dd, $J = 12.2, 6.1$ Hz), 4.31 (1H, dd, $J = 12.1, 4.0$ Hz), 4.92 (1H, d, $J = 2.5$ Hz), 5.12 (1H, d, $J = 2.3$ Hz), 5.32 (1H, d, $J = 6.1$ Hz), 5.46 (1H, ddd, $J = 5.9, 5.9, 5.9$ Hz), 8.06 (1H, s); ^{13}C NMR δ 20.6 (CH_3), 20.7 (CH_3), 61.7 (CH_2), 69.3 (CH), 70.8 (CH), 102.1 (CH_2), 141.5 (C), 159.6 (CH), 169.3 (C), 170.3 (C); MS (FAB) m/z (rel intensity) 272 ($\text{M}^+ + \text{H}$, 8), 212 (5), 154 (100), 120 (10); HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}_6$ 272.0883, found: 272.0912 Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_6$: C, 44.28; H, 4.83; N, 15.49. Found: C, 44.43; H, 5.17; N, 15.16.

(1*R*,2*R*)-3-(Acetyloxy)-1-(2*H*-aziren-3-yl)-2-(formyloxy)propyl acetate (8).

From vinyl azide **7** (84%): $[\alpha]_D -21$ ($c = 0.54$); IR 1759, 1741 cm^{-1} ; ^1H NMR δ 1.62 (1H, d, $J = 8.4$ Hz), 1.67 (1H, d, $J = 8.3$ Hz), 2.06 (3H, s), 2.21 (3H, s), 4.21 (1H, dd, $J = 12.0, 6.2$ Hz), 4.46 (1H, dd, $J = 12.1, 4.6$ Hz), 5.71 (1H, ddd, $J = 5.0, 5.0, 5.0$ Hz), 6.16 (1H, d, $J = 4.7$ Hz), 8.03 (1H, s); ^{13}C NMR (50.4 MHz) δ 20.3 (CH_3), 20.5 (CH_3), 22.2 (CH_2), 61.1 (CH_2), 68.0 (CH), 68.7 (CH), 159.2 (CH), 167.6 (C), 169.4 (C), 170.1

(C); MS (rel intensity) 244 ($M^+ + H$, 21), 202 (27), 184 (16), 128 (18), 142 (100); HRMS calcd for $C_{10}H_{14}NO_6$ 244.0821, found 244.0813. Anal. Calcd for $C_{10}H_{13}NO_6$: C, 49.38; H, 5.39; N, 5.76. Found: C, 49.10; H, 5.79; N, 5.94.

5-*O*-Acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-arabinitol and 5-*O*-Acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-ribitol (10). From the diastereoisomeric mixture of 6-*O*-acetyl-3-azido-2,3-dideoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-*arabino*-hexopyranose and -D-*ribo*-hexopyranose (9) (96%, **10-D-Ara:10-D-Rib**, 6:4). Compound **10-D-Ara**: $[\alpha]_D +3$ (*c*, 0.41); IR 2112, 1757, 1428 cm^{-1} ; 1H NMR δ 1.97 (3H, s), 2.05 (3H, s), 2.08 (3H, s), 2.09 (3H, s), 2.15 (3H, s), 3.43 (1H, dd, $J = 9.7, 6.0$ Hz), 3.53 (1H, ddd, $J = 6.0, 6.0, 1.8$ Hz), 3.60 (1H, dd, $J = 9.6, 7.9$ Hz), 3.94 (1H, ddd, $J = 6.6, 6.6, 0.0$ Hz), 4.09 (1H, dd, $J = 12.4, 6.2$ Hz), 4.16 (1H, dd, $J = 11.3, 6.8$ Hz), 4.24 (1H, dd, $J = 11.2, 6.3$ Hz), 4.25 (1H, dd, $J = 6.3, 1.8$ Hz), 4.60 (1H, dd, $J = 11.8, 2.6$ Hz), 4.60 (1H, d, $J = 7.9$ Hz), 5.00 (1H, dd, $J = 10.5, 3.4$ Hz), 5.19 (1H, dd, $J = 10.4, 7.9$ Hz), 5.30 (1H, ddd, $J = 6.1, 6.1, 2.4$ Hz), 5.37 (1H, dd, $J = 3.3, 0.0$ Hz), 8.07 (1H, s); ^{13}C NMR δ 2.7 (CH_2), 20.5 (CH_3), 20.6 ($2 \times CH_3$), 20.7 ($2 \times CH_3$), 61.1 (CH_2), 61.3 (CH_2), 61.7 (CH), 66.7 (CH), 68.8 (CH), 70.7 (CH), 70.8 (CH), 71.1 (CH), 77.9 (CH), 100.9 (CH), 159.3 (CH), 169.1 (C), 169.9 (C), 170.0 (C), 170.1 (C), 170.3 (C). Anal. Calcd for $C_{22}H_{30}IN_3O_{14}$: C, 38.42; H, 4.40; N, 6.11. Found: C, 38.65; H, 4.65; N, 5.88. Compound **10-D-Rib**: $[\alpha]_D +18$ (*c*, 0.53); IR 2115, 1757, 1429 cm^{-1} ; 1H NMR δ 1.97 (3H, s), 2.04 (3H, s), 2.05 (3H, s), 2.07 (3H, s), 2.14 (3H, s), 3.41 (1H, dd, $J = 10.9, 7.0$ Hz), 3.51 (1H, dd, $J = 11.0, 4.4$ Hz), 3.75 (1H, ddd, $J = 7.0, 7.0, 4.3$ Hz), 3.91 (1H, dd, $J = 7.2, 2.8$ Hz), 3.92 (1H, dd, $J = 7.0, 7.0$ Hz), 4.10 (1H, dd, $J = 12.2, 7.5$ Hz), 4.13 (1H, dd, $J = 12.3, 6.5$ Hz), 4.18 (1H, dd, $J = 11.3,$

6.7 Hz), 4.41 (1H, dd, $J = 12.2, 3.5$ Hz), 4.63 (1H, d, $J = 7.9$ Hz), 5.08 (1H, dd, $J = 10.5, 3.4$ Hz), 5.15 (1H, dd, $J = 10.5, 7.9$ Hz), 5.36 (1H, dd, $J = 3.3, 0.0$ Hz), 5.44 (1H, ddd, $J = 6.8, 3.0, 3.0$ Hz), 8.08 (1H, s); ^{13}C NMR δ 5.3 (CH₂), 20.5 (CH₃), 20.58 (CH₃), 20.62 (2 $\times$ CH₃), 20.7 (CH₃), 61.2 (CH₂), 61.7 (CH₂), 62.9 (CH), 66.7 (CH), 68.7 (CH), 70.5 (CH), 70.8 (CH), 71.0 (CH), 80.1 (CH), 101.6 (CH), 159.4 (CH), 169.4 (C), 169.9 (C), 170.1 (C), 170.2 (C), 170.3 (C). Anal. Calcd for C₂₂H₃₀IN₃O₁₄: C, 38.42; H, 4.40; N, 6.11. Found: C, 38.67; H, 4.74; N, 5.79.

5-*O*-Acetyl-2-azido-1,2-dideoxy-4-*O*-formyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-erythro-pent-1-enitol (11). From the diastereoisomeric mixture of iodo azides (**10**) (85%): $[\alpha]_{\text{D}} -3$ ($c, 0.4$); IR 2114, 1757, 1634 cm⁻¹; ^1H NMR δ 1.94 (3H, s), 2.00 (3H, s), 2.02 (3H, s), 2.04 (3H, s), 2.12 (3H, s); 3.83 (1H, ddd, $J = 6.8, 6.8, 0.0$ Hz), 4.05 (3H, m), 4.13 (1H, d, $J = 5.9$ Hz), 4.39 (1H, dd, $J = 12.4, 2.5$ Hz), 4.56 (1H, d, $J = 8.0$ Hz), 4.87 (1H, d, $J = 2.2$ Hz), 4.98 (1H, dd, $J = 10.5, 3.4$ Hz), 5.15 (1H, d, $J = 2.2$ Hz), 5.20 (1H, dd, $J = 10.5, 7.9$ Hz), 5.30 (1H, ddd, $J = 6.4, 6.4, 2.5$ Hz), 5.33 (1H, dd, $J = 3.4, 0.0$ Hz), 8.00 (1H, s); ^{13}C NMR δ 20.4 (CH₃), 20.5 (4 $\times$ CH₃), 61.3 (CH₂), 61.4 (CH₂), 66.8 (CH), 68.6 (CH), 70.2 (CH), 70.6 (CH), 71.0 (CH), 79.0 (CH), 101.6 (CH), 102.3 (CH₂), 142.6 (C), 159.4 (CH), 169.2 (C), 169.9 (C), 170.1 (C), 170.2 (C), 170.3 (C). Anal. Calcd for C₂₂H₂₉N₃O₁₄: C, 47.23; H, 5.22; N, 7.51. Found: C, 47.43; H, 5.17; N, 7.65.

(2*R*,3*S*)-3-(2*H*-Aziren-3-yl)-2-(formyloxy)-3-[(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)oxy]propyl acetate (12). From the vinyl azide **11** (63%): $[\alpha]_{\text{D}} +11$ ($c, 0.76$); IR (CHCl₃) 1750 cm⁻¹; ^1H NMR δ 1.60 (2H, s), 1.98 (3H, s), 2.04 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 2.14 (3H, s), 3.87 (1H, ddd, $J = 6.4, 6.4, 0.0$ Hz), 4.01 (1H, dd, $J = 11.4, 6.9$ Hz), 4.05 (1H, dd, $J = 11.4, 6.1$ Hz), 4.22 (1H, dd, $J = 12.3, 5.9$ Hz),

4.42 (1H, dd, $J = 12.3, 3.2$ Hz), 4.63 (1H, d, $J = 7.9$ Hz), 5.00 (1H, dd, $J = 10.3, 3.4$ Hz), 5.02 (1H, d, $J = 6.0$ Hz), 5.26 (1H, dd, $J = 10.5, 8.0$ Hz), 5.36 (1H, dd, $J = 3.2, 0.0$ Hz), 5.54 (1H, ddd, $J = 6.0, 6.0, 3.3$ Hz), 8.00 (1H, s); ^{13}C NMR δ 20.5 (CH₃), 20.6 (4 $\times$ CH₃), 21.3 (CH₂), 61.2 (2 $\times$ CH₂), 66.7 (CH), 68.3 (CH), 68.9 (CH), 70.4 (CH), 71.1 (CH), 74.9 (CH), 101.9 (CH), 159.1 (CH), 168.8 (C), 169.3 (C), 169.9 (C), 170.0 (C), 170.1 (C), 170.4 (C). Anal. Calcd for C₂₂H₂₉NO₁₄: C, 49.72; H, 5.50; N, 2.64. Found: C, 49.75; H, 5.49; N, 2.44.

2-Azido-1,2-dideoxy-3,5-di-*tert*-butylsilanediyl-4-*O*-formyl-1-iodo-D-arabinitol and 2-Azido-1,2-dideoxy-3,5-di-*tert*-butylsilanediyl-4-*O*-formyl-1-iodo-D-ribitol (14).

From the isomeric mixture of 3-azido-3,5-di-*tert*-butylsilanediyl-2,3-dideoxy-D-*arabino*-hexopyranose and -D-*ribo*-hexopyranose (**13**) (91%, **14-D-Ara**:**14-D-Rib**, 7:3).

Compound **14-D-Ara**: $[\alpha]_{\text{D}} -7$ (c , 0.54); IR 2106, 1743, 1472 cm⁻¹; ^1H NMR δ_{H} 1.04 (9H, s), 1.07 (9H, s), 3.45 (1H, dd, $J = 7.6, 3.9$ Hz), 3.54 (1H, dd, $J = 8.0, 8.0$ Hz), 3.56 (1H, m), 3.86 (1H, dd, $J = 10.1, 10.1$ Hz), 4.27 (1H, dd, $J = 10.4, 4.9$ Hz), 4.48 (1H, dd, $J = 9.1, 0.0$ Hz), 5.14 (1H, ddd, $J = 9.4, 9.4, 4.9$ Hz), 8.01 (1H, s); ^{13}C NMR δ 0.4 (CH₂), 20.4 (C), 22.8 (C), 26.8 (3 $\times$ CH₃), 27.4 (3 $\times$ CH₃), 61.9 (CH), 65.1 (CH₂), 67.9 (CH), 75.1 (CH), 159.1 (CH); MS m/z (rel intensity) 456 ($\text{M}^+ + 1$, 2), 428 (1), 410 (41), 147 (100); HRMS calcd for C₁₄H₂₇IN₃O₄Si, 456.0816, found 456.0777. Anal. Calcd for C₁₄H₂₆IN₃O₄Si: C, 36.93; H, 5.76; N, 9.23. Found: C, 37.05; H, 6.03, N, 8.86.

Compound **14-D-Rib**: $[\alpha]_{\text{D}} -40$ (c , 0.32); IR 2107, 1740, 1366 cm⁻¹; ^1H NMR δ 1.02 (9H, s), 1.08 (9H, s), 3.43 (2H, m), 3.50 (1H, dd, $J = 6.7, 0.0$ Hz), 3.92 (1H, dd, $J = 11.0, 8.7$ Hz), 4.19 (1H, dd, $J = 11.0, 4.5$ Hz), 4.29 (1H, dd, $J = 8.3, 3.6$ Hz), 5.07 (1H, ddd, $J = 8.3, 8.3, 4.2$ Hz), 8.04 (1H, s); ^{13}C NMR δ 1.9 (CH₂), 20.5 (C), 22.6 (C), 26.8 (3 $\times$ CH₃), 27.4 (3 $\times$ CH₃), 64.9 (CH₂), 65.0 (CH), 68.4 (CH), 77.4 (CH), 159.3 (CH);

MS (FAB) m/z (rel intensity) 456 ($M^+ + 1$, 23), 259 (43), 147 (62), 137 (100); HRMS calcd for $C_{14}H_{27}IN_3O_4Si$, 456.0816, found 456.0810. Anal. Calcd for $C_{14}H_{26}IN_3O_4Si$: C, 36.93; H, 5.76; N, 9.23. Found: C, 37.29; H, 5.83; N, 8.94.

2-Azido-3,5-di-*tert*-butylsilanediyl-1,2-dideoxy-4-*O*-formyl-D-*erythro*-pent-1-enitol

(15). From the diastereoisomeric mixture of iodo azides **14** (66%): $[\alpha]_D -22$ (c , 0.25); IR 2108, 1741, 1632, 1365 cm^{-1} ; 1H NMR δ 1.06 (18H, s), 3.90 (1H, dd, $J = 10.1$, 10.1 Hz), 4.14 (1H, dd, $J = 10.7$, 4.7 Hz), 4.41 (1H, d, $J = 8.8$ Hz), 4.86 (1H, d, $J = 2.1$ Hz), 5.08 (1H, d, $J = 2.0$ Hz), 5.09 (1H, ddd, $J = 9.2$, 9.2, 4.5 Hz), 7.98 (1H, s); ^{13}C NMR δ 20.4 (C), 22.6 (C), 26.9 ($3 \times CH_3$), 27.3 ($3 \times CH_3$), 64.7 (CH_2), 68.1 (CH), 76.5 (CH), 101.4 (CH_2), 145.1 (C), 159.1 (CH); MS m/z (rel intensity) 328 ($M^+ + H$, 9), 300 (24), 282 (35), 147 (100); HRMS calcd for $C_{14}H_{26}N_3O_4Si$, 328.1693, found 328.1679. Anal. Calcd for $C_{14}H_{25}N_3O_4Si$: C, 51.33; H, 7.70; N, 12.83. Found: C, 51.63; H, 7.87; N, 12.50.

4-(2*H*-Aziren-3-yl)-2,2-di-*tert*-butyl-1,3,2-dioxasilinan-5-yl formate (16). From the vinyl azide **15** (58%): mp 85–86 °C (from *n*-pentane); $[\alpha]_D -13$ (c , 0.6); IR 1744, 1366 cm^{-1} ; 1H NMR δ 1.03 (9H, s), 1.09 (9H, s), 1.61 (1H, d, $J = 8.1$ Hz), 1.63 (1H, d, $J = 8.1$ Hz), 4.23 (1H, dd, $J = 6.8$, 1.6 Hz), 4.10 (1H, dd, $J = 3.4$, 0.0 Hz), 5.29 (2H, m), 8.02 (1H, s); 1H NMR (400 MHz, C_6D_6) δ_H 1.04 (9H, s), 1.05 (9H, s), 1.41 (1H, d, $J = 8.2$ Hz), 1.44 (1H, d, $J = 8.5$ Hz), 3.78 (1H, dd, $J = 11.4$, 7.7 Hz), 3.93 (1H, dd, $J = 11.4$, 4.0 Hz), 5.01 (1H, d, $J = 7.2$ Hz), 5.26 (1H, dddd, $J = 7.9$, 7.2, 3.7 Hz, $J_w = 1.1$ Hz), 7.26 (1H, d, $J_w = 1.1$ Hz); ^{13}C NMR δ 20.5 (CH_2), 20.8 (C), 22.2 (C), 26.8 ($3 \times CH_3$), 27.2 ($3 \times CH_3$), 64.0 (CH_2), 67.2 (CH), 72.7 (CH), 159.1 (CH), 169.3 (C); MS m/z (rel intensity) 300 ($M^+ + H$, 1), 260 (7), 259 (35), 242 (55), 147 (100); HRMS calcd for

C₁₄H₂₆NO₄Si, 300.1631, found 300.1608. Anal. Calcd for C₁₄H₂₅NO₄Si: C, 56.16; H, 8.42; N, 4.68. Found: C, 56.12; H, 8.46; N, 4.66.

3-*O*-Acetyl-2-azido-1,2,4-trideoxy-4-*O*-formyl-1-iodo-L-threitol and 3-*O*-Acetyl-2-azido-1,2,4-trideoxy-4-*O*-formyl-1-iodo-L-erythritol (18). From the isomeric mixture 4-*O*-acetyl-3-azido-2,3-dideoxy-L-*threo*-pentopyranose and -L-*erythro*-pentopyranose (**17**) (78%, **18-L-Thr**:**18-L-Ery**, 2:8). Compound **18-L-Thr**: $[\alpha]_D -36$ ($c = 0.84$); IR 2113, 1758, 1739, 1427 cm⁻¹; ¹H NMR δ 2.12 (3H, s), 3.24 (1H, dd, $J = 10.8, 7.4$ Hz), 3.31 (1H, dd, $J = 10.8, 5.5$ Hz), 3.73 (1H, ddd, $J = 7.2, 5.2, 5.2$ Hz), 4.25 (1H, dd, $J = 12.0, 5.6$ Hz), 4.42 (1H, dd, $J = 12.0, 4.5$ Hz), 5.30 (1H, ddd, $J = 5.0, 5.0, 5.0$ Hz), 8.04 (1H, s); ¹³C NMR δ 1.4 (CH₂), 20.6 (CH₃), 61.6 (CH₂), 61.9 (CH), 72.0 (CH), 160.0 (CH), 169.7 (C); MS (EI) m/z (rel intensity) 328 (M⁺ + H, <1), 200 (59), 197 (1), 131 (100); HRMS calcd for C₇H₁₁IN₃O₄ 327.9794, found: 327.9824. Anal. Calcd for C₇H₁₀IN₃O₄: C, 25.71; H, 3.08; N, 12.85. Found: C, 25.90; H, 3.10; N, 12.82. Compound **18-L-Ery**: $[\alpha]_D -56$ ($c = 0.31$); IR 2115, 1759, 1740, 1418 cm⁻¹; ¹H NMR δ 2.11 (3H, s), 3.24 (1H, dd, $J = 10.9, 7.7$ Hz), 3.37 (1H, dd, $J = 10.9, 3.8$ Hz), 3.82 (1H, ddd, $J = 7.5, 7.5, 3.8$ Hz), 4.28 (1H, dd, $J = 12.4, 4.7$ Hz), 4.57 (1H, dd, $J = 12.4, 3.0$ Hz), 5.02 (1H, ddd, $J = 7.5, 4.5, 4.5$ Hz), 8.07 (1H, s); ¹³C NMR δ 3.2 (CH₂), 20.7 (CH₃), 61.0 (CH₂), 62.2 (CH), 72.3 (CH), 160.1 (CH), 169.5 (C); MS (EI) m/z (rel intensity) 328 (M⁺ + H, <1), 283 (3), 200 (64), 141 (92), 131 (100); HRMS calcd for C₇H₁₁IN₃O₄ 327.9794, found: 327.9722. Anal. Calcd for C₇H₁₀IN₃O₄: C, 25.71; H, 3.08; N, 12.85. Found: C, 26.09; H, 3.09; N, 12.55.

(1*R*)-2-Azido-1-[(formyloxy)methyl]-2-propenyl acetate (19). From the mixture of iodo azides **18** (91%): $[\alpha]_D -27$ ($c = 0.33$); IR 2115, 1754, 1737, 1633 cm⁻¹; ¹H NMR δ 2.11 (3H, s), 4.27 (1H, dd, $J = 11.8, 6.9$ Hz), 4.36 (1H, dd, $J = 11.8, 3.9$ Hz), 4.91

(1H, d, J = 2.6 Hz), 5.12 (1H, d, J = 2.5 Hz), 5.34 (1H, dd, J = 6.9, 3.9 Hz), 8.03 (1H, s); ^{13}C NMR δ 20.8 (CH₃), 62.5 (CH₂), 70.3 (CH), 101.1 (CH₂), 141.8 (C), 160.2 (CH), 169.5 (C); MS (EI) m/z (rel intensity) 199 (M^+ , <1), 171 (15), 140 (36), 72 (100); HRMS calcd for C₇H₉N₃O₄ 199.0593, found: 199.0690. Anal. Calcd for C₇H₉N₃O₄: C, 42.21; H, 4.55; N, 21.10. Found: C, 42.35; H, 4.85; N, 20.83.

(1R)-1-(2H-Aziren-3-yl)-2-(formyloxy)ethyl acetate (20). From the vinyl-azide **19**. Compound **20** was unstable on attempted purification by column chromatography (87%, crude yield): IR 1761, 1740 cm⁻¹; ^1H NMR δ 1.63 (1H, d, J = 8.4 Hz), 1.67 (1H, d, J = 8.4 Hz), 2.18 (3H, s), 4.55 (1H, dd, J = 12.1, 5.4 Hz), 4.70 (1H, dd, J = 12.1, 3.6 Hz), 6.13 (1H, dd, J = 4.4, 4.4 Hz), 8.03 (1H, s); ^{13}C NMR δ 20.5 (CH₃), 21.6 (CH₂), 60.7 (CH₂), 68.5 (CH), 159.9 (CH), 167.6 (C), 169.6 (C).

References

1. (a) Dabrowska, A.; Dokurno, P.; Konitz, A.; Smiatacz, Z. *Carbohydr. Res.* **2000**, 323, 230–234. (b) Liberek, B.; Dabrowska, A.; Frankowski, R.; Matuszewska, M.; Smiatacz, Z. *Carbohydr. Res.* **2002**, 337, 1803–1810.