

Supporting Information

for

Fragmentation of Carbohydrate Anomeric Alkoxy Radicals.

A New Synthesis of Chiral 1-Halo-1-iodo Alditols

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Structural data and procedures for the synthesis of compounds **1** and **2**.

Structural data for halohydrins **3-18**, **35-60**, and **87-97**.

Structural data for 1-halo-1-iodo compounds **19-21**, **23-25**, **28-30**, **32**, **33**, **61-63**, **65-67**, **70**, **71**, **79**, **81**, **83-85**, **99-101**, **104-106**, and **110**.

2,6-Anhydro-5-deoxy-1,3-O-(tetraisopropylidisiloxane-1,3-diyl)-D-arabino-hex-5-enitol. 1,3-Dichloro-1,1,3,3-tetra-isopropyl-disiloxane (0.77 mL, 2.4 mmol) was added dropwise to a solution of 2,6-anhydro-5-deoxy-D-arabino-hex-5-enitol (292 mg, 2 mmol) in dry pyridine (5 mL) at 0 °C. After 3 hours, the reaction was poured into aqueous HCl (10%) and extracted with CH₂Cl₂. The organic phase was washed with brine and dried over sodium sulfate. The residue was purified by column

chromatography (hexanes-EtOAc, 95:5) to afford the title compound (611 mg, 1.57 mmol, 79%) as an oil: $[\alpha]_D = +28.3$ ($c = 3.4$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): $\delta = 1.04$ – 1.25 (m, 28H), 2.07 (d, $J = 12.0$ Hz, 1H), 3.85 (d, $J = 8.1$ Hz, 2H), 3.94 (t, $J = 8.1$ Hz, 1H), 4.25 (d, $J = 4.8$ Hz, 1H), 4.38 (dd, $J = 4.8$, 12.0 Hz, 1H), 4.64 (dt, $J = 1.8$, 6.2 Hz, 1H), 6.28 (dd, $J = 1.8$, 6.2 Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 12.4$ – 13.7 ($8 \times \text{CH}_3$), 17.1 (CH), 17.2 (CH), 17.3 (CH), 17.5 (CH), 59.2 (CH_2), 63.8 (CH), 64.1 (CH), 75.2 (CH), 103.5 (CH), 144.7 (CH); IR (CCl_4): $\nu = 3578$, 1650, 1465, 1166 cm^{-1} ; MS (70 eV, EI): m/z (%): 345 (100) [$M^+ - \text{C}_3\text{H}_7$], 327 (11), 263 (24), 235 (62), 135 (22), 119 (25), 81 (95); HRMS (EI): calcd for $\text{C}_{15}\text{H}_{29}\text{O}_5\text{Si}_2$ 345.1554; found 345.1529; elemental analysis calcd for $\text{C}_{18}\text{H}_{36}\text{O}_5\text{Si}_2$ (388.6): C 55.64, H 9.35; found: C 55.46, H 9.56.

2,6-Anhydro-5-deoxy-4-O-pivaloyl-1,3-O-(tetraisopropyl-disiloxane-1,3-diyl)-D-arabino-hex-5-enitol (1). Pivaloyl chloride (0.16 mL, 1.33 mmol) was added dropwise to a solution of 2,6-anhydro-5-deoxy-1,3-O-(tetraisopropyl-disiloxane-1,3-diyl)-D-arabino-hex-5-enitol (345 mg, 0.89 mmol) and DMAP (11 mg, 0.09 mmol) in dry pyridine (5 mL). The reaction was allowed to warm up to room temperature and stirred for 24 hours. The reaction was poured into aqueous HCl (10%) and extracted with CH_2Cl_2 . The organic phase was washed with brine and dried over sodium sulfate. The residue was purified by column chromatography (hexanes-EtOAc, 98:2 $\rightarrow$ 95:5) to afford

the title compound (405 mg, 0.86 mmol, 97%) as a crystalline solid: m.p. 65–66.5°C (from *n*-hexane–EtOAc); $[\alpha]_D = +22.2$ ($c = 0.72$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): $\delta = 1.05$ – 1.09 (m, 28H), 1.22 (s, 9H), 3.81–3.89 (m, 2H), 4.06 (dd, $J = 7.7, 8.5$ Hz, 1H), 4.43 (d, $J = 4.0$ Hz, 1H), 4.53 (dd, $J = 1.9, 6.2$ Hz, 1H), 5.47 (ddd, $J = 1.9, 1.9, 4.0$ Hz, 1H), 6.31 (dd, $J = 1.9, 6.2$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 12.9$ (CH), 13.1 (CH), 13.3 (CH), 13.6 (CH), 17.1–17.8 ($8 \times \text{CH}_3$), 27.2 ($3 \times \text{CH}_3$), 38.9 (C), 58.9 (CH_2), 62.4 (CH), 68.2 (CH), 75.6 (CH), 99.5 (CH), 144.2 (CH), 178.7 (C); IR (CCl_4): $\nu = 1728, 1655, 1465, 1280$ cm^{-1} ; MS (70 eV, EI): m/z (%): 429 (4) [$M^+ - \text{C}_3\text{H}_7$], 399 (4), 371 (3), 345 (3), 319 (100), 119 (7), 81 (22); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{37}\text{O}_6\text{Si}_2$: 429.2129; found: 429.2142; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{44}\text{O}_6\text{Si}_2$ (472.8): C 58.43, H 9.38; found: C 58.67, H 9.29.

2,6-Anhydro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-3,4-*O*-isopropylidene- β -arabino-hex-5-enitol (2). To a solution of 2,6-anhydro-5-deoxy-3,4-*O*-isopropylidene- β -arabino-hex-5-enitol (400 mg, 2.15 mmol) in CH_2Cl_2 (100 mL) containing dry pyridine (400 μL , 5 mmol) was added 3,5-dinitrobenzyl chloride (991 mg, 4.3 mmol) and stirred at room temperature for 8h. The reaction mixture was then poured into water and extracted with CH_2Cl_2 . The organic layer was washed with a solution of aqueous HCl (10%) and saturated aqueous NaHCO_3 , dried and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc

80:20) afforded compound **2** (793 mg, 2.1 mmol, 97%). Crystalline solid: m.p. 144–145°C (from *n*-hexane–EtOAc); $[\alpha]_D = +11$ ($c = 0.32$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): $\delta = 1.38$ (s, 3H), 1.49 (s, 3H), 4.32 (ddd, $J = 1.6, 3.3, 7.8$ Hz, 1H), 4.38 (br d, $J = 6.0$ Hz, 1H), 4.71 (dd, $J = 3.4, 12.0$ Hz, 1H), 4.74 (dd, $J = 3.0, 6.0$ Hz, 1H), 4.81 (dd, $J = 7.7, 12.0$ Hz, 1H), 4.90 (ddd, $J = 1.3, 2.8, 6.2$ Hz, 1H), 6.42 (d, $J = 6.4$ Hz, 1H), 9.20 (d, $J = 2.1$ Hz, 2H), 9.24 (dd, $J = 2.1, 2.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 26.9$ (CH_3), 27.9 (CH_3), 66.4 (CH_2), 68.6 (CH), 72.4 (CH), 72.6 (CH), 102.8 (CH), 111.1 (C), 122.5 (CH), 129.6 ($2 \times \text{CH}$), 133.6 (C), 144.5 (CH), 148.7 ($2 \times \text{C}$), 162.4 (C); IR (CHCl_3): $\nu = 3102, 1741, 1550, 1344$ cm^{-1} ; MS (70 eV, EI): m/z (%): 365 (7) [$M^+ - \text{Me}$], 305 (31), 195 (100); HRMS(EI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_9$: 365.0621; found: 365.0611; elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_9$ (380.3): C 50.53, H 4.24, N 7.37; found: C 50.64, H 4.28, N 7.30.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluor- β -glucopyranose and β -mannopyranose (3).^[1] From 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy- β -arabino-hex-1-enitol by reaction with xenon difluoride,^[2] followed by acid hydrolysis of the anomeric fluoride, peracetylation and subsequent selective anomeric *O*-deacetylation with hydrazine acetate.^[3] Oil (four steps, 60%): IR (CHCl_3): $\nu = 3595, 1751$ cm^{-1} ; MS (70 eV, EI): m/z (%): 291 (3) [$M^+ - \text{OH}$], 259 (4), 248 (3), 235 (4), 103 (100); HRMS (EI): calcd for $\text{C}_{12}\text{H}_{16}\text{FO}_7$ 291.0880; found 291.0854; elemental analysis

calcd (%) for $C_{12}H_{17}FO_8$ (308.3): C 46.76, H 5.56; found: C 46.64, H 5.57.

3,4,6-Tri-O-acetyl-2-chloro-2-deoxy-D-glucopyranose and -D-mannopyranose (4).^[4] From 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol. Oil (82%): IR ($CHCl_3$): ν = 3610, 1753 cm^{-1} ; MS (70 eV, EI): m/z (%): 309/307 (<1/1) [M^+ - OH], 259 (4), 229 (14), 120 (92), 103 (100); HRMS (EI): calcd for $C_{12}H_{16}^{35}ClO_7$ 307.0584; found 307.0551; elemental analysis calcd (%) for $C_{12}H_{17}ClO_8$ (324.7): C 44.39, H 5.28; found: C 44.11, H 5.16.

3,4,6-Tri-O-acetyl-2-bromo-2-deoxy-D-glucopyranose and -D-mannopyranose (5).^[5] From 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol. Oil (84%): IR ($CHCl_3$): ν = 3617, 1757 cm^{-1} ; MS (70 eV, EI): m/z (%): 353/351 (1/1) [M^+ - OH], 310/308 (<1/1), 297/295 (2/2), 208/206 (19/19), 164 (48), 145 (53), 115 (78), 103 (100); HRMS (EI): calcd for $C_{12}H_{16}^{81}BrO_7$ 353.0059; found 352.9981; elemental analysis calcd (%) for $C_{12}H_{17}BrO_8$ (369.2): C 39.04, H 4.64; found: C 39.21, H 4.52.

3,4,6-Tri-O-acetyl-2-deoxy-2-iodo-D-glucopyranose and -D-mannopyranose (6).^[6] From 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol. Oil (84%): IR ($CHCl_3$): ν = 3588, 3477, 1744 cm^{-1} ; MS (70 eV, EI): m/z (%): 399 (3) [M^+ - OH], 183 (100); HRMS (EI): calcd for $C_{12}H_{16}IO_7$ 398.9941; found 398.9942; elemental analysis calcd (%) for $C_{12}H_{17}IO_8$ (416.2): C 34.63, H 4.12; found: C 34.86, H 4.15.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-2-fluoro-*D*-mannopyranose and -*D*-glucopyranose (7). From 1,5-anhydro-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-*D*-arabino-hex-1-enitol.^[7] Oil (50%); IR (CCl₄): ν = 3616, 3418, 1253, 1154 cm⁻¹; MS (70 eV, EI): m/z (%): 467 (3) [M^+ - C₄H₉], 449 (1), 375 (3), 335 (14), 115 (20), 73 (100); HRMS (EI): calcd for C₂₀H₄₄FO₅Si₃ 467.2481; found 467.2454; elemental analysis calcd (%) for C₂₄H₅₃FO₅Si₃ (524.9): C 54.91, H 10.18; found: C 54.78, H 10.04.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-chloro-2-deoxy-*D*-mannopyranose and -*D*-glucopyranose (8). From 1,5-anhydro-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-*D*-arabino-hex-1-enitol.^[7] Oil (89%); IR (CCl₄): ν = 3611, 3425, 1472, 1087 cm⁻¹; MS (70 eV, EI): m/z (%): 485/483 (2/5) [M^+ - C₄H₉], 353/351 (3/8), 301 (4), 273 (7), 219 (10), 171 (6), 147 (21), 73 (100); HRMS (EI): calcd for C₂₀H₄₄³⁵ClO₅Si₃ 483.2185; found 483.2145; elemental analysis calcd (%) for C₂₄H₅₃ClO₅Si₃ (541.4): C 53.24, H 9.87; found: C 53.48, H 9.79.

2-Bromo-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-*D*-mannopyranose and -*D*-glucopyranose (9).^[8] From 1,5-anhydro-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-*D*-arabino-hex-1-enitol.^[7] Crystalline solid (83%); IR (CCl₄): ν = 3607, 3416, 1255, 1116 cm⁻¹; MS (70 eV, EI): m/z (%): 529/527 (4/4) [M^+ - C₄H₉], 447 (3), 397/395 (10/10), 315 (10), 171 (14), 73 (100); HRMS (EI): calcd for C₂₀H₄₄⁸¹BrO₅Si₃ 529.1660; found 529.1625;

elemental analysis calcd (%) for $C_{24}H_{53}BrO_5Si_3$ (585.8): C 49.20, H 9.12; found: C 49.28, H 9.31.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-2-iodo- β -mannopyranose and - β -glucopyranose (10).^[8] From 1,5-anhydro-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy- β -*arabino*-hex-1-enitol.^[7] Oil (95%): IR ($CHCl_3$): ν = 3594, 3426, 1259, 1110 cm^{-1} ; MS (70 eV, EI): m/z (%): 575 (4) [M^+ - C_4H_9], 557 (1), 483 (2), 443 (8), 316 (12), 117 (26), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}IO_5Si_3$ 575.1541; found 575.1600; elemental analysis calcd (%) for $C_{24}H_{53}IO_5Si_3$ (632.8): C 45.55, H 8.44; found: C 45.51, H 8.33.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo- β -mannopyranose and - β -glucopyranose (11).^[9] From 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy- β -*arabino*-hex-1-enitol. Oil (100%): IR ($CHCl_3$): ν = 3587, 3388, 1102 cm^{-1} ; MS (70 eV, EI): m/z (%): 560 (1) [M^+], 559 (2), 543 (5), 469 (56), 451 (12), 91 (100); HRMS (EI): calcd for $C_{27}H_{29}IO_5$, 560.1060 found 560.1045; elemental analysis calcd (%) for $C_{27}H_{29}IO_5$ (560.4): C 57.87, H 5.22; found: C 57.81, H 5.47.

3,6-Di-*O*-acetyl-2-deoxy-2-fluoro-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β - β -galactopyranosyl)- β -mannopyranose and - β -glucopyranose (12). From 3,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β - β -galactopyranosyl)- β -*arabino*-hex-1-enitol.^[10] Oil (67%): IR ($CHCl_3$): ν = 3597, 3477, 1752, 1370, 1250 cm^{-1} ; MS (FAB): m/z (%): 619 (13) [M^+ + Na], 463 (11), 385 (15), 331

(100), 241 (31); HRMS (FAB): calcd for $C_{24}H_{33}FNaO_{16}$, 619.1650 found 619.1643; elemental analysis calcd (%) for $C_{24}H_{33}FO_{16}$ (596.5): C 48.32, H 5.58; found: C 48.22, H 5.63.

3,6-Di-O-acetyl-2-chloro-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-mannopyranose and -D-glucopyranose (13).

From 3,6-di-O-acetyl-1,5-anhydro-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-arabino-hex-1-enitol.^[10] Oil (95%): IR ($CHCl_3$): ν = 3593, 3474, 1758, 1369, 1248 cm^{-1} ; MS (FAB): m/z (%): 637/635 (49/100) [M^+ + Na], 615/613 (11/32); HRMS (FAB): calcd for $C_{24}H_{33}^{35}ClNaO_{16}$, 635.1355 found 635.1541; elemental analysis calcd (%) for $C_{24}H_{33}ClO_{16}$ (613.0): C 47.03, H 5.43; found: C 47.11, H 5.60.

2-Bromo-3,6-di-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-mannopyranose and -D-glucopyranose (14).

From 3,6-di-O-acetyl-1,5-anhydro-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-arabino-hex-1-enitol.^[10] Oil (92%): IR ($CHCl_3$): ν = 3591, 3476, 1752, 1370, 1240 cm^{-1} ; MS (FAB): m/z (%): 681/679 (10/8) [M^+ + Na], 639/637 (9/7), 613 (16), 460 (100); HRMS (FAB): calcd for $C_{24}H_{33}^{81}BrNaO_{16}$, 681.0830 found 681.0842; elemental analysis calcd (%) for $C_{24}H_{33}BrO_{16}$ (657.4): C 43.85, H 5.06; found: C 43.85, H 5.34.

3,6-Di-O-acetyl-2-deoxy-2-iodo-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-mannopyranose and -D-glucopyranose (15).

From 3,6-di-O-acetyl-1,5-anhydro-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-D-arabino-hex-1-enitol.^[10] Oil

(91%): IR (CHCl₃): ν = 3594, 1750, 1370, 1232 cm⁻¹; MS (FAB): m/z (%): 727 (20) [M^+ + Na], 704 (<1) [M^+], 627 (12), 613 (28), 460 (100); HRMS (FAB): calcd for C₂₄H₃₃IO₁₆, 704.0813 found 704.0817; elemental analysis calcd (%) for C₂₄H₃₃IO₁₆ (704.4): C 40.90, H 4.72; found: C 40.87, H 4.82.

2-Chloro-2-deoxy-3-O-methyl-5,6-O-isopropylidene-D-mannofuranose and -D-glucofuranose (16). From 1,4-anhydro-2-deoxy-3-O-methyl-5,6-O-isopropylidene-D-arabino-hex-1-enitol.^[11] Solid (79%): IR (CHCl₃): ν = 3594, 3522, 2990, 2936, 2837 cm⁻¹; MS (70 eV, EI): m/z (%): 239/237 (17/55) [M^+ - CH₃], 101 (100); HRMS (EI): calcd for C₉H₁₄³⁷ClO₅ 239.0500; found 239.0497; elemental analysis calcd (%) for C₁₀H₁₇ClO₅ (252.7): C 47.53, H 6.78; found: C 47.22, H 7.12.

2-Bromo-2-deoxy-3-O-methyl-5,6-O-isopropylidene-D-mannofuranose and -D-glucofuranose (17). From 1,4-anhydro-2-deoxy-3-O-methyl-5,6-O-isopropylidene-D-arabino-hex-1-enitol.^[11] Oil (82%): IR (CHCl₃): ν = 3591, 3520, 2990, 2937 cm⁻¹; MS (70 eV, EI): m/z (%): 283/281 (60/59) [M^+ - CH₃], 101 (100); HRMS (EI): calcd for C₉H₁₄⁸¹BrO₅ 283.0004; found 282.9951; elemental analysis calcd (%) for C₁₀H₁₇BrO₅ (297.1): C 40.42, H 5.77; found: C 40.54, H 5.68.

2-Deoxy-2-iodo-3-O-methyl-5,6-O-isopropylidene-D-mannofuranose and -D-glucofuranose (18). From 1,4-anhydro-2-deoxy-3-O-methyl-5,6-O-isopropylidene-D-arabino-hex-1-enitol.^[11] Solid (80%): IR (CHCl₃): ν = 3594, 3512, 3012, 2990, 2936 cm⁻¹; MS (70 eV, EI):

m/z (%): 420 (60) [M^+ - CH₃], 101 (100); HRMS (EI): calcd for C₉H₁₄IO₅ 328.9886; found 328.9903; elemental analysis calcd (%) for C₁₀H₁₇IO₅ (344.1): C 34.90, H 4.98; found: C 35.01, H 4.75.

2,3,5-Tri-*O*-acetyl-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-D-

arabinitol (19). Crystalline solid (96%): diastereoisomeric mixture (1:1); ¹H NMR (C₆D₆): δ = 1.57 (s, 3H), 1.59 (s, 3H), 1.65 (s, 3H), 1.67 (s, 6H), 1.72 (s, 3H), 4.01 (dd, J = 5.1, 12.5 Hz, 2H), 4.15 (dd, J = 2.9, 12.6 Hz, 1H), 4.16 (dd, J = 3.4, 12.6 Hz, 1H), 5.27 (m, 2H), 5.54 (ddd, J = 2.0, 5.7 Hz, ³ J (F,H) = 12.8 Hz, 1H), 5.60 (ddd, J = 2.5, 4.6 Hz, ³ J (F,H) = 17.9 Hz, 1H), 5.66 (dd, J = 2.6, 8.6 Hz, 1H), 5.83 (ddd, J = 1.6, 8.7 Hz, ⁴ J (F,H) = 1.6 Hz, 1H), 6.46 (dd, J = 4.6 Hz, ² J (F,H) = 49.1 Hz, 1H), 6.51 (dd, J = 5.7 Hz, ² J (F,H) = 48.8 Hz, 1H), 7.35 (s, 1H), 7.40 (s, 1H); ¹³C NMR (C₆D₆): δ = 19.9 (CH₃), 20.0 (2 $\times$ CH₃), 20.1 (3 $\times$ CH₃), 61.4 (2 $\times$ CH₂), 67.3 (2 $\times$ CH), 68.1 (2 $\times$ CH), 68.2 (CH), 68.5 (CH), 69.6 (¹ J (F,C) = 258.3 Hz, CH), 70.5 (¹ J (F,C) = 256.2 Hz, CH), 72.7 (² J (F,C) = 24.4 Hz, CH), 73.2 (² J (F,C) = 18.3 Hz, CH), 168.9 (C), 169.0 (C), 169.1 (C), 169.2 (C), 169.78 (C), 169.8 (C); MS (70 eV, EI): m/z (%): 307 (100) [M^+ - I], 205 (8), 159 (12), 157 (11), 139 (28); HRMS (EI): calcd for C₁₂H₁₆FO₈: 307.0829; found: 307.0852; elemental analysis calcd (%) for C₁₂H₁₆FIO₈ (434.2): C 33.20, H 3.71; found: C 33.49, H 3.48.

2,3,5-Tri-*O*-acetyl-1-chloro-1-deoxy-4-*O*-formyl-1-iodo-D-

arabinitol (20). Crystalline solid (95%): diastereoisomeric

mixture (1:1); ^1H NMR (C_6D_6): δ = 1.59 (s, 3H), 1.60 (s, 3H), 1.66 (s, 6H), 1.73 (s, 6H), 3.97 (dd, J = 5.8, 12.4 Hz, 1H), 3.99 (dd, J = 5.6, 12.5 Hz, 1H), 4.20 (dd, J = 3.2, 12.5 Hz, 2H), 5.26 (m, 1H), 5.29 (m, 1H), 5.53 (d, J = 7.7 Hz, 1H), 5.55 (dd, J = 2.1, 7.8 Hz, 1H), 5.58 (d, J = 6.7 Hz, 1H), 5.66 (dd, J = 3.1, 6.7 Hz, 1H), 5.86 (dd, J = 3.0, 5.1 Hz, 1H), 5.88 (dd, J = 2.1, 4.7 Hz, 1H), 7.42 (s, 1H), 7.44 (s, 1H); ^{13}C NMR (C_6D_6): δ = 20.0 (2 $\times$ CH_3), 20.1 (CH_3), 20.2 (2 $\times$ CH_3), 20.4 (CH_3), 24.6 (CH), 25.3 (CH), 61.6 (2 $\times$ CH_2), 67.8 (CH), 68.4 (CH), 68.5 (CH), 69.3 (CH), 74.1 (2 $\times$ CH), 159.3 (CH), 159.4 (CH), 168.9 (C), 168.95 (C), 168.98 (C), 169.1 (C), 169.8 (C), 169.9 (C); MS (70 eV, EI): m/z (%): 325/323 (32/100) [$M^+ - \text{I}$], 223/221 (85), 175 (38), 157 (27), 139 (79); HRMS (EI): calcd for $\text{C}_{12}\text{H}_{16}^{35}\text{ClO}_8$: 323.0534; found: 323.0526; elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{16}\text{ClIO}_8$ (450.6): C 31.99, H 3.58; found: C 31.95, H 3.28.

2,3,5-Tri-*O*-acetyl-1-bromo-1-deoxy-4-*O*-formyl-1-iodo- β -

arabinitol (21). Crystalline solid (99%): diastereoisomeric mixture (1:1); ^1H NMR (C_6D_6): δ = 1.57 (s, 3H), 1.59 (s, 3H), 1.65 (s, 6H), 1.73 (s, 6H), 3.96 (dd, J = 6.5, 12.9 Hz, 1H), 3.97 (dd, J = 6.3, 13.0 Hz, 1H), 4.20 (dd, J = 3.3, 12.4 Hz, 2H), 5.26 (m, 1H), 5.28 (m, 1H), 5.30 (d, J = 7.5 Hz, 1H), 5.34 (d, J = 6.9 Hz, 1H), 5.57 (dd, J = 2.6, 7.5 Hz, 1H), 5.64 (dd, J = 3.1, 6.9 Hz, 1H), 5.90 (dd, J = 2.7, 7.8 Hz, 2H), 7.38 (s, 1H), 7.39 (s, 1H); ^{13}C NMR (C_6D_6): δ = 6.2 (CH), 6.6

(CH), 20.0 (2 × CH₃), 20.1 (CH₃), 20.2 (2 × CH₃), 20.3 (CH₃), 61.6 (2 × CH₂), 68.48 (CH), 68.5 (CH), 68.6 (CH), 69.5 (CH), 73.77 (CH), 73.8 (CH), 159.0 (CH), 159.1 (CH), 169.0 (3 × C), 169.1 (C), 169.8 (2 × C); MS (70 eV, EI): *m/z* (%): 436/434 (2) [*M*⁺ – AcOH], 369/367 (18), 281/279 (30), 267/265 (100); HRMS (EI): calcd for C₁₀H₁₂⁸¹BrIO₆: 435.8842; found: 435.8872; elemental analysis calcd (%) for C₁₂H₁₆BrIO₈ (495.1): C 29.11, H 3.26; found: C 29.39, H 3.03.

2,3,5-Tris-*O*-[tert-butyl(dimethyl)silyl]-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-D-arabinitol (23). Oil (94%): diastereoisomeric mixture (3:2); ¹H NMR: δ = 0.02 (s, 3H), 0.03 (s, 3H), 0.04 (s, 3H), 0.05 (s, 3H), 0.11 (s, 3H), 0.12 (s, 9H), 0.13 (s, 3H), 0.14 (s, 3H), 0.19 (s, 6H), 0.87 (s, 9H), 0.88 (s, 9H), 0.89 (s, 9H), 0.90 (s, 9H), 0.94 (s, 9H), 0.95 (s, 9H), 3.78–3.88 (m, 5H), 3.99 (dd, *J* = 3.9, 4.5 Hz, 1H), 4.09 (dd, *J* = 3.6 Hz, ³*J*(F,H) = 3.9 Hz, 1H), 4.13 (m, 1H), 5.01–5.03 (m, 1H), 5.11 (ddd, *J* = 3.0, 3.9, 7.0 Hz, 1H), 6.94 (dd, *J* = 3.6 Hz, ²*J*(F,H) = 51.2 Hz, 1H), 6.98 (dd, *J* = 3.4 Hz, ²*J*(F,H) = 48.7 Hz, 1H), 8.09 (s, 2H); ¹³C NMR: δ = –5.4 (CH₃), –5.3 (3 × CH₃), –4.8 (CH₃), –4.6 (CH₃), –4.5 (CH₃), –4.4 (CH₃), –4.3 (3 × CH₃), –4.1 (CH₃), 18.0 (C), 18.1 (C), 18.2 (4 × C), 25.7 (6 × CH₃), 25.8 (6 × CH₃), 25.9 (6 × CH₃), 61.4 (CH₂), 61.8 (CH₂), 71.9 (CH), 72.0 (CH), 73.7 (¹*J*(F,C) = 258.3 Hz, CH), 74.8 (CH), 75.5 (CH), 77.3 (²*J*(F,C) = 17.5 Hz, CH), 79.2 (²*J*(F,C) = 16.0 Hz, CH), 78.8 (¹*J*(F,C) = 253.8 Hz, CH), 160.4 (CH), 160.5 (CH); IR

(CCl₄): ν = 1732, 1257, 1174 cm⁻¹; MS (70 eV, EI): m/z (%): 593 (1) [M^+ - C₄H₉], 473 (18), 389 (18), 347 (17), 301 (29), 297 (15), 115 (32), 73 (100); HRMS (EI): calcd for C₂₀H₄₃FIO₅Si₃: 593.1447; found: 593.1463; elemental analysis calcd (%) for C₂₄H₅₂FIO₅Si₃ (650.8): C 44.29, H 8.06; found: C 44.10, H 8.22.

2,3,5-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-1-chloro-1-deoxy-4-*O*-formyl-1-iodo-*D*-arabinitol (24). Oil (84%): diastereoisomeric mixture (2:1); ¹H NMR: δ = 0.01 (s, 3H), 0.02 (s, 3H), 0.03 (s, 3H), 0.04 (s, 3H), 0.11 (s, 3H), 0.12 (s, 3H), 0.128 (s, 6H), 0.13 (s, 6H), 0.24 (s, 3H), 0.26 (s, 3H), 0.86 (s, 9H), 0.87 (s, 9H), 0.90 (s, 9H), 0.91 (s, 9H), 0.97 (s, 9H), 0.98 (s, 9H), 3.69 (dd, J = 2.6, 5.1 Hz, 1H), 3.74 (dd, J = 6.0, 13.4 Hz, 1H), 3.78 (dd, J = 6.4, 13.4 Hz, 1H), 3.86–3.89 (m, 2H), 3.95 (ddd, J = 5.1, 5.1, 10.3 Hz, 2H), 4.33 (dd, J = 2.6, 5.1 Hz, 1H), 5.13–5.19 (m, 2H), 6.05 (d, J = 2.6 Hz, 1H), 6.12 (d, J = 2.6 Hz, 1H), 8.06 (s, 1H), 8.09 (s, 1H); ¹³C NMR: δ = -5.3 (3 × CH₃), -4.9 (3 × CH₃), -4.7 (CH₃), -4.6 (CH₃), -4.2 (CH₃), -4.1 (CH₃), -3.9 (CH₃), -3.8 (CH₃), 18.0 (2 × C), 18.2 (2 × C), 18.3 (2 × C), 25.6–25.9 (18 × CH₃), 28.7 (CH), 33.6 (CH), 61.8 (CH₂), 62.1 (CH₂), 72.9 (CH), 73.3 (CH), 74.8 (CH), 75.8 (CH), 79.9 (CH), 81.3 (CH), 160.6 (2 × CH); IR (CCl₄): ν = 1731, 1472, 1109 cm⁻¹; MS (70 eV, EI): m/z (%): 611/609 (>1) [M^+ - C₄H₉], 583/581 (>1/1), 565/563 (>1/2), 407/405 (3/8), 301 (29), 147 (15), 115 (22), 73 (100); HRMS (EI): calcd for C₂₀H₄₃³⁵ClIO₅Si₃: 609.1152; found: 609.1112; elemental analysis

calcd (%) for $C_{24}H_{52}ClIO_5Si_3$ (667.3): C 43.20, H 7.85; found: C 43.26, H 7.76.

1-Bromo-2,3,5-tris-*O*-[*tert*-butyl(dimethyl)silyl]-1-deoxy-4-*O*-formyl-1-iodo- β -arabinitol (25). Oil (91%): diastereoisomeric mixture (2:1); 1H NMR: δ = 0.01 (s, 3H), 0.02 (s, 6H), 0.03 (s, 3H), 0.12 (s, 3H), 0.13 (s, 6H), 0.14 (s, 3H), 0.15 (s, 6H), 0.27 (s, 3H), 0.28 (s, 3H), 0.867 (s, 9H), 0.87 (s, 9H), 0.91 (s, 9H), 0.92 (s, 9H), 0.98 (s, 9H), 0.99 (s, 9H), 3.76 (dd, J = 6.3, 11.6 Hz, 1H), 3.79 (dd, J = 6.5, 11.6 Hz, 1H), 3.86–3.92 (m, 5H), 4.34 (dd, J = 2.3, 4.6 Hz, 1H), 5.18–5.21 (m, 2H), 5.92 (d, J = 1.9 Hz, 1H), 5.93 (d, J = 2.3 Hz, 1H), 8.07 (s, 1H), 8.09 (s, 1H); ^{13}C NMR: δ = -5.3 (2 $\times$ CH₃), -4.9 (2 $\times$ CH₃), -4.7 (2 $\times$ CH₃), -4.6 (2 $\times$ CH₃), -4.2 (2 $\times$ CH₃), -3.8 (2 $\times$ CH₃), 11.4 (CH), 15.2 (CH), 18.1 (2 $\times$ C), 18.2 (2 $\times$ C), 18.3 (2 $\times$ C), 25.8 (9 $\times$ CH₃), 25.9 (9 $\times$ CH₃), 61.9 (CH₂), 62.2 (CH₂), 73.7 (CH), 73.8 (CH), 74.3 (CH), 74.5 (CH), 80.3 (CH), 81.2 (CH), 160.5 (2 $\times$ CH); IR (CCl₄): ν = 1731, 1257, 1174 cm⁻¹; MS (70 eV, EI): m/z (%): 655/653 (1/1) [M^+ - C₄H₉], 535/533 (3/3), 523/521 (3/3), 301 (87), 107 (33), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}^{79}BrIO_5Si_3$: 653.0646; found: 653.0642; elemental analysis calcd (%) for $C_{24}H_{52}BrIO_5Si_3$ (711.7): C 40.50, H 7.36; found: C 40.57, H 7.65.

2,5-Di-*O*-acetyl-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-acetyl- β -*D*-galactopyranosyl)- β -arabinitol (28). Crystalline solid (85%): diastereoisomeric mixture

(4:3); ^1H NMR: δ = 1.96 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.067 (s, 3H), 2.074 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.17 (s, 3H), 3.9–4.3 (m, 10H), 4.46–4.60 (m, 4H), 4.95–5.37 (m, 9H), 5.50 (dd, J = 4.3, 9.2 Hz, 1H), 5.59 (ddd, J = 2.6, 6.6 Hz, $^3J(\text{F},\text{H})$ = 13.3 Hz, 1H), 7.038 (dd, J = 9.1 Hz, $^2J(\text{F},\text{H})$ = 47.0 Hz, 1H), 7.042 (dd, J = 6.6 Hz, $^2J(\text{F},\text{H})$ = 50.0 Hz, 1H), 7.97 (s, 1H), 7.99 (s, 1H); ^{13}C NMR: δ = 20.4–21.1 (12 $\times$ CH₃), 61.1 (CH₂), 61.2 (CH₂), 61.3 (CH₂), 61.5 (CH₂), 66.7–76.6 (16 $\times$ CH), 101.7 (CH), 101.9 (CH), 159.4 (2 $\times$ CH), 169.2–170.5 (12 $\times$ C); IR: ν = 1752, 1370, 1228 cm⁻¹; MS (FAB): m/z (%): 745 (6) [M^+ + Na], 721 (2), 694 (1), 664 (4), 331 (100), 169 (75); HRMS (FAB): calcd for C₂₄H₃₁FIO₁₆: 721.0641; found: 721.0567; elemental analysis calcd (%) for C₂₄H₃₂FIO₁₆ (722.4): C 39.90, H 4.46; found: C 40.04, H 4.67.

2,5-Di-*O*-acetyl-1-chloro-1-deoxy-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-arabinitol

(29). Oil (85%): diastereoisomeric mixture (1:1); after careful Chromatotron chromatography (hexanes–EtOAc, 65:35) one enriched diastereoisomer (80:20) could be isolated: ^1H NMR: δ = 1.99 (s, 3H), 2.087 (s, 3H), 2.088 (s, 3H), 2.10 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 3.99 (dd, J = 7.1, 7.1 Hz, 1H), 4.05 (dd, J = 5.7, 12.4 Hz, 1H), 4.21 (dd, J = 7.1, 11.5 Hz, 1H), 4.34 (dd, J = 6.4, 11.3 Hz, 1H), 4.53–4.57 (m, 2H), 4.59 (d, J = 8.0 Hz, 1H), 5.00 (dd, J = 3.5, 10.5 Hz, 1H), 5.14 (m, 1H), 5.22 (dd, J = 8.0, 10.6 Hz, 1H), 5.40 (br d, J = 3.5 Hz, 1H),

5.56 (dd, $J = 2.0, 9.0$ Hz, 1H), 6.06 (d, $J = 9.3$ Hz, 1H), 8.01 (s, 1H); ^{13}C NMR: $\delta = 20.5\text{--}20.7$ ($6 \times \text{CH}_3$), 28.8 (CH), 61.1 (CH₂), 61.3 (CH₂), 66.7 (CH), 66.8 (CH), 69.6 (CH), 70.9 (CH), 71.3 (CH), 74.6 (CH), 76.9 (CH), 101.7 (CH), 159.4 (CH), 169.7–170.3 ($6 \times \text{C}$); the other isomer: ^1H NMR: $\delta = 1.97$ (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.14 (s, 3H), 2.17 (s, 3H), 3.95 (dd, $J = 6.7, 6.7$ Hz, 1H), 4.04 (dd, $J = 5.6, 12.0$ Hz, 1H), 4.18 (d, $J = 6.4$ Hz, 1H), 4.46 (dd, $J = 1.3, 7.4$ Hz, 1H), 4.53–4.57 (m, 3H), 4.97 (dd, $J = 3.6, 10.5$ Hz, 1H), 5.02 (m, 1H), 5.20 (dd, $J = 8.0, 10.4$ Hz, 1H), 5.35 (dd, $J = 1.3, 9.9$ Hz, 1H), 5.35 (br d, $J = 3.5$ Hz, 1H), 6.05 (d, $J = 9.9$ Hz, 1H), 7.98 (s, 1H); ^{13}C NMR: $\delta = 20.5\text{--}21.2$ ($6 \times \text{CH}_3$), 26.9 (CH), 61.1–61.3 ($2 \times \text{CH}_2$), 66.8 (CH), 68.8 (CH), 69.4 (CH), 71.0 (CH), 71.3 (CH), 74.2 (CH), 74.5 (CH), 101.6 (CH), 159.3 (CH), 169.1–170.2 ($6 \times \text{C}$); IR: $\nu = 3566, 3026, 1755, 1371, 1236, 1155, 1077, 1048$ cm⁻¹; MS (70 eV, EI): m/z (%): 680/678 (1) [M^+ – AcOH], 613/611 (11), 391 (18), 331 (100); HRMS (EI): calcd for C₂₄H₃₂³⁵ClIO₁₆: 738.0424; found: 738.0332; elemental analysis calcd (%) for C₂₄H₃₂ClIO₁₆ (738.9): C 39.01, H 4.37; found: C 39.13, H 4.36.

2,5-Di-*O*-acetyl-1-bromo-1-deoxy-4-*O*-formyl-1-iodo-3-*O*-

(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-D-arabinitol

(30). Oil (82%): diastereoisomeric mixture (1:1); ^1H NMR: $\delta = 1.96$ (s, 6H), 2.07–2.08 (s, 18H), 2.15 (s, 3H), 2.16 (s, 3H), 2.176 (s, 3H), 2.18 (s, 3H), 3.95–3.99 (m, 2H), 4.02–4.03 (m,

2H), 4.18–4.24 (m, 3H), 4.32 (dd, $J = 6.3, 11.3$ Hz, 1H), 4.52–4.59 (m, 6H), 4.97–5.01 (m, 2H), 5.03 (m, 1H), 5.10 (m, 1H), 5.18–5.22 (m, 2H), 5.38–5.40 (m, 3H), 5.53 (dd, $J = 2.0, 9.3$ Hz, 1H), 5.80 (d, $J = 8.9$ Hz, 1H), 5.82 (d, $J = 9.6$ Hz, 1H), 7.98 (s, 1H), 8.00 (s, 1H); ^{13}C NMR: $\delta = 9.6$ (CH), 10.7 (CH), 19.1–21.1 ($12 \times \text{CH}_3$), 61.1 ($2 \times \text{CH}_2$), 61.3 ($2 \times \text{CH}_2$), 66.7 (CH), 66.8 (CH), 68.8 ($2 \times \text{CH}$), 69.6 (CH), 69.7 (CH), 70.9 (CH), 71.0 (CH), 71.2 (CH), 71.3 (CH), 73.8 (CH), 74.1 (CH), 75.0 (CH), 76.6 (CH), 101.6 (CH), 101.7 (CH), 159.4 ($2 \times \text{CH}$), 169.5–170.4 ($12 \times \text{C}$); IR: $\nu = 3477, 3026, 1743, 1371, 1232, 1077, 1048$ cm^{-1} ; MS (70 eV, EI): m/z (%): 724/722 (1) [$M^+ - \text{AcOH}$], 657/655 (8), 331 (100); HRMS (EI): calcd for $\text{C}_{22}\text{H}_{28}^{81}\text{BrIO}_{14}$: 723.9687; found: 723.9698; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{32}\text{BrIO}_{16}$ (783.3): C 36.80, H 4.12; found: C 36.66, H 4.36.

1-Chloro-1-deoxy-3-O-formyl-1-iodo-2-O-methyl-4,5-O-isopropylidene-D-arabinitol (32). Oil (83%): diastereoisomeric mixture (3:2); ^1H NMR: $\delta =$ (major): 1.34 (s, 3H), 1.43 (s, 3H), 3.70 (s, 3H), 3.82 (m, 1H), 3.83–3.86 (m, 1H), 3.99–4.02 (m, 1H), 4.18–4.22 (m, 1H), 5.47 (dd, $J = 2.8, 7.9$ Hz, 1H), 5.73 (d, $J = 7.2$, 1H), 8.06 (s, 1H); (minor): 1.34 (s, 3H), 1.43 (s, 3H), 3.70 (s, 3H), 3.71 (dd, $J = 2.3, 7.6$ Hz, 1H), 3.83–3.86 (m, 1H), 3.99–4.02 (m, 1H), 4.18–4.22 (m, 1H), 5.42 (dd, $J = 2.3, 8.4$ Hz, 1H), 5.68 (d, $J = 7.6$ Hz, 1H), 8.06 (s, 1H); ^{13}C NMR: $\delta =$ (major): 25.4 (CH_3), 26.7 (CH_3), 28.1 (CH), 62.3 (CH_3), 66.6 (CH_2), 72.7 (CH), 74.2 (CH), 84.7 (CH), 110.1 (C), 159.8 (CH);

(minor): 25.4 (CH₃), 26.7 (CH₃), 27.6 (CH), 61.8 (CH₃), 67.0 (CH₂), 71.7 (CH), 73.9 (CH), 84.9 (CH), 110.0 (C), 159.7 (CH); IR: ν = 2991, 2938, 1732 cm⁻¹; MS (70 eV, EI): m/z (%): 365/363 (18/55) [M^+ - Me], 221/219 (7/23), 101 (100); HRMS (EI): calcd for C₉H₁₃³⁷ClIO₅: 364.9467; found: 364.9486; elemental analysis calcd (%) for C₁₀H₁₆ClIO₅ (378.6): C 31.73, H 4.26; found: C 31.77, H 4.11.

1-Bromo-1-deoxy-3-O-formyl-1-iodo-2-O-methyl-4,5-O-isopropylidene-D-arabinitol (33). Oil (92%): diastereoisomeric mixture (3:2); ¹H NMR (C₆D₆): δ = (major): 1.26 (s, 3H), 1.40 (s, 3H), 3.44 (s, 3H), 3.71 (dd, J = 3.1, 7.3 Hz, 1H), 3.77 (dd, J = 6.1, 8.8 Hz, 1H), 3.84–3.88 (m, 1H), 3.97–4.03 (m, 1H), 5.41 (d, J = 7.3 Hz, 1H), 5.63 (dd, J = 3.1, 7.9 Hz, 1H), 7.49 (s, 1H); (minor): 1.25 (s, 3H), 1.38 (s, 3H), 3.47 (s, 3H), 3.63 (dd, J = 3.0, 7.5 Hz, 1H), 3.77 (dd, J = 6.1, 8.8 Hz, 1H), 3.84–3.88 (m, 1H), 3.97–4.03 (m, 1H), 5.42 (d, J = 7.5 Hz, 1H), 5.57 (dd, J = 3.0, 8.2 Hz, 1H), 7.48 (s, 1H); ¹³C NMR: δ = (major): 10.0 (CH), 25.4 (CH₃), 26.7 (CH₃), 62.1 (CH₃), 66.7 (CH₂), 72.8 (CH), 74.3 (CH), 84.4 (CH), 110.1 (C), 159.9 (CH); (minor): 9.9 (CH), 25.4 (CH₃), 26.7 (CH₃), 62.0 (CH₃), 66.9 (CH₂), 72.2 (CH), 74.1 (CH), 84.5 (CH), 110.1 (C), 159.8 (CH); IR: ν = 2991, 2938, 1732 cm⁻¹; MS (70 eV, EI): m/z (%): 409/407 (2) [M^+ - Me], 265/263 (43), 184 (51), 101 (100); HRMS (EI): calcd for C₉H₁₃⁸¹BrIO₅: 408.8971; found: 408.8984; elemental

analysis calcd (%) for $C_{10}H_{16}BrIO_5$ (423.0): C 28.39, H 3.81; found: C 28.51, H 3.58.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro- β -galactopyranose (35).^[1]

From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy- β -arabino-hex-5-enitol. Oil (87%); IR (CCl_4): ν = 3615, 1757, 1237, 1081 cm^{-1} ; MS (70 eV, EI): m/z (%): 291 (3) [$M^+ - OH$], 259 (4), 249 (1), 203 (10), 188 (11), 146 (42), 115 (87), 104 (100); HRMS (EI): calcd for $C_{12}H_{16}O_7F$ 291.0880; found 291.0905; elemental analysis calcd (%) for $C_{12}H_{17}FO_8$ (308.3): C 46.76, H 5.56; found: C 46.75, H 5.41.

3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy- β -talopyranose and β -galactopyranose (36).

From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy- β -arabino-hex-5-enitol. Oil (73%); IR ($CHCl_3$): ν = 3610, 1759 cm^{-1} ; MS (70 eV, EI): m/z (%): 309/307 (2/5) [$M^+ - OH$], 264 (1), 229 (19), 176 (54), 115 (62), 103 (100); HRMS (EI): calcd for $C_{12}H_{16}^{35}ClO_7$ 307.0585; found 307.0539; elemental analysis calcd (%) for $C_{12}H_{17}ClO_8$ (324.7): C 44.39, H 5.28; found: C 44.22, H 5.40.

3,4,6-Tri-*O*-acetyl-2-bromo-2-deoxy- β -talopyranose and β -galactopyranose (37).

From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy- β -arabino-hex-5-enitol. Oil (76%); IR ($CHCl_3$): ν = 3590, 1752 cm^{-1} ; MS (70 eV, EI): m/z (%): 353/351 (4/4) [$M^+ - OH$], 267/265 (5/6), 237/235 (28/28), 183 (53), 145 (50), 115 (86), 103 (100); HRMS (EI): calcd for $C_{12}H_{16}^{81}BrO_7$ 353.0059; found

353.0044; elemental analysis calcd (%) for $C_{12}H_{17}BrO_8$ (369.2): C 39.04, H 4.64; found: C 38.98, H 4.72.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-*D*-talopyranose and -*D*-galactopyranose (38). From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy-*D*-arabino-hex-5-enitol. Oil (76%): IR ($CHCl_3$): ν = 3594, 3468, 1750 cm^{-1} ; MS (70 eV, EI): m/z (%): 416 (2) [M^+], 289 (25), 97 (100); HRMS (EI): calcd for $C_{12}H_{17}IO_8$ 415.9968; found 415.9987; elemental analysis calcd (%) for $C_{12}H_{17}IO_8$ (416.2): C 34.63, H 4.12; found: C 34.85, H 3.89.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-2-fluoro-*D*-galactopyranose (39). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-*D*-arabino-hex-5-enitol.^[12] Oil (66%); 1H NMR (500 MHz, $CDCl_3$): δ = 0.06–0.15 (m, 36H), 0.89–0.92 (m, 54H), 3.44 (dd, J = 6.6, 7.0 Hz, 1H), 3.62–3.73 (m, 5H), 3.93 (dd, J = 6.7, 6.7 Hz, 1H), 3.98 (dd, J = 3.0, 3.0 Hz, 1H), 4.02 (dd, J = 2.9, 2.9 Hz, 1H), 4.14 (ddd, J = 2.9, 9.5 Hz, $^3J(F,H)$ = 9.5 Hz, 1H), 4.36 (ddd, J = 7.0, 9.1 Hz, $^2J(F,H)$ = 52.1 Hz, 1H), 4.65 (ddd, J = 3.6, 9.5 Hz, $^2J(F,H)$ = 50.7 Hz, 1H), 4.73 (d, J = 7.0 Hz, 1H), 5.41 (d, J = 3.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –(5.3–4.0) (12 $\times$ CH_3), 18.2 (2 $\times$ C), 18.5 (2 $\times$ C), 18.6 (2 $\times$ C), 25.9 (6 $\times$ CH_3), 26.0 (6 $\times$ CH_3), 26.1 (6 $\times$ CH_3), 61.3 (CH_2), 61.7 (CH_2), 70.2 ($^2J(F,C)$ = 16.1 Hz, CH), 71.3 ($^3J(F,C)$ = 7.8 Hz, CH), 72.4 (2 $\times$ CH), 74.4 ($^2J(F,C)$ = 16.1 Hz, CH), 76.5 (CH), 89.3 ($^2J(F,C)$ = 184.6 Hz, CH), 91.1 ($^2J(F,C)$ = 22.3 Hz, CH), 93.3 ($^1J(F,C)$ = 181.0 Hz,

CH), 95.2 ($^2J(\text{F},\text{C}) = 25.1 \text{ Hz}$, CH); IR (CCl_4): $\nu = 3618, 3451, 1472, 1169, 1098 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 467 (3) [$M^+ - \text{C}_4\text{H}_9$], 335 (7), 273 (5), 203 (10), 147 (20), 73 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{44}\text{FO}_5\text{Si}_3$ 467.2481; found 467.2456; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{53}\text{FO}_5\text{Si}_3$ (524.9): C, 54.91, H 10.18; found: C 54.86, H 10.43.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-chloro-2-deoxy- β -talopyranose and - β -galactopyranose (40). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[12] Oil (74%); IR (CCl_4): $\nu = 3596, 3434, 1472, 1045 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 485/483 (2/5) [$M^+ - \text{C}_4\text{H}_9$], 449/447 (1/4), 353/351 (1/3), 301 (4), 273 (5), 171 (15), 147 (22), 73 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{44}^{35}\text{ClO}_5\text{Si}_3$ 483.2185; found 483.2183; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{53}\text{ClO}_5\text{Si}_3$ (541.4): C 53.24, H 9.87; found: C 53.05, H 10.09.

2-Bromo-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy- β -talopyranose and - β -galactopyranose (41). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[12] Oil (86%); IR (CHCl_3): $\nu = 3688, 3602, 1472, 1255, 1163 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 529/527 (6/6) [$M^+ - \text{C}_4\text{H}_9$], 447 (4), 429 (3), 397/395 (11), 301 (10), 273 (16), 147 (26), 117 (20), 73 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{44}^{81}\text{BrO}_5\text{Si}_3$ 529.1660; found 529.1602; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{53}\text{BrO}_5\text{Si}_3$ (585.8) C, 49.20, H 9.12; found: C 49.18, H 9.46.

3,4,6-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-2-iodo- β -talopyranose and - β -galactopyranose (42). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[12] Oil (95%); IR: ν = 1724, 1472, 1362, 1258 cm^{-1} ; MS (70 eV, EI) m/z (%): 575 (2) [M^+ - C_4H_9], 557 (2), 447 (4), 431 (4), 73 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{44}\text{IO}_5\text{Si}_3$: 575.1568; found: 575.1541; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{53}\text{IO}_5\text{Si}_3$ (632.8): C 45.55, H 8.44; found: C 45.64, H 8.62.

4-*O*-Acetyl-3,6-bis-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-2-fluoro- β -galactopyranose (43). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[13] Crystalline solid (55%); ^1H NMR (500 MHz, CDCl_3): δ = 0.02 (s, 3H), 0.03 (s, 6H), 0.04 (s, 6H), 0.07 (s, 3H), 0.08 (s, 3H), 0.10 (s, 3H), 0.85 (s, 18H), 0.86 (s, 9H), 0.87 (s, 9H), 2.08 (s, 3H), 2.09 (s, 3H), 3.51–3.69 (m, 5H), 3.86 (ddd, J = 4.2, 9.0 Hz, $^3J(\text{F},\text{H})$ = 13.2 Hz, 1H), 4.20–4.26 (m, 2H), 4.32 (dd, J = 7.9, 8.8 Hz, 1H), 4.53 (ddd, J = 3.6, 9.2 Hz, $^2J(\text{F},\text{H})$ = 49.6 Hz, 1H), 4.76 (dd, J = 3.3, 7.4 Hz, 1H), 5.34 (dd, J = 3.1, 3.1 Hz, 1H), 5.37 (dd, J = 3.3, 3.3 Hz, 1H), 5.45 (d, J = 3.6 Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3): δ = -5.6 (4 $\times$ CH_3), -5.2 (4 $\times$ CH_3), 18.1 (2 $\times$ C), 18.2 (C), 18.3 (C), 20.7 (2 $\times$ CH_3), 25.47 (3 $\times$ CH_3), 25.52 (3 $\times$ CH_3), 25.7 (3 $\times$ CH_3), 25.8 (3 $\times$ CH_3), 61.1 (CH_2), 61.6 (CH_2), 67.5 ($^2J(\text{F},\text{C})$ = 17.9 Hz, CH), 69.6 (CH), 70.1 (br s, CH), 71.3 (br s, CH), 71.7 ($^2J(\text{F},\text{C})$ = 18.2 Hz, CH), 74.1 (CH), 89.3 ($^1J(\text{F},\text{C})$ = 186.3

Hz, CH), 90.9 ($^2J(\text{F},\text{C}) = 22.9$ Hz, CH), 92.9 ($^1J(\text{F},\text{C}) = 183.2$ Hz, CH), 94.9 ($^2J(\text{F},\text{C}) = 23.8$ Hz, CH), 169.8 (C), 169.9 (C); IR (CCl₄): $\nu = 3616, 3446, 1753, 1255, 1229$ cm⁻¹; MS (70 eV, EI): m/z (%): 437 (1) [$M^+ - \text{Me}$], 395 (12), 335 (15), 315 (9), 203 (10), 117 (62), 73 (100); HRMS (EI): calcd for C₁₉H₃₈FO₆Si₂ 437.2191; found 437.2163; elemental analysis calcd (%) for C₂₀H₄₁FO₆Si₂ (452.7): C 53.06, H 9.13; found: C 53.35, H 9.34.

4-*O*-Acetyl-3,6-bis-*O*-[*tert*-butyl(dimethyl)silyl]-2-chloro-2-deoxy- β -talopyranose and - β -galactopyranose (44). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[13] Oil (50%); IR (CHCl₃): $\nu = 3689, 3603, 1744, 1115, 1054$ cm⁻¹; MS (70 eV, EI): m/z (%): 413/411 (1/4) [$M^+ - \text{C}_4\text{H}_9$], 395/393 (1/3), 353/351 (1/4), 259 (5), 219 (12), 117 (64), 75 (100); HRMS (EI): calcd for C₁₆H₃₀³⁵ClO₅Si₂ 393.1320; found 393.1301; elemental analysis calcd (%) for C₂₀H₄₁ClO₆Si₂ (469.2): C 51.20, H 8.81; found: C 51.25, H 8.90.

4-*O*-Acetyl-2-bromo-3,6-bis-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy- β -talopyranose and - β -galactopyranose (45). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy- β -arabino-hex-5-enitol.^[13] Oil (91%). IR (CHCl₃): $\nu = 3692, 3596, 1742, 1472, 1374, 1112$ cm⁻¹; MS (70 eV, EI): m/z (%): 457/455 (3/3) [$M^+ - \text{C}_4\text{H}_9$], 397/395 (3/3), 315 (7), 265/263 (10/10), 184 (15), 129 (16), 117 (97), 73 (100); HRMS (EI): calcd for C₁₆H₃₂⁸¹BrO₆Si₂ 457.0900; found 457.0898; elemental

analysis calcd (%) for $C_{20}H_{41}BrO_6Si_2$ (513.6): C 46.77, H 8.05; found: C 46.91, H 8.04.

6-*O*-Benzyl-2-deoxy-2-fluoro-3,4-*O*-isopropylidene- β -galactopyranose (46). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene- β -arabino-hex-5-enitol.^[14] Oil (47%): IR ($CHCl_3$): ν = 3613, 3416, 3032, 1375, 1219, 1075 cm^{-1} ; MS (70 eV, EI): m/z (%): 312 (1) [M^+], 297 (6), 279 (5), 236 (14), 145 (8), 91 (100); HRMS (EI): calcd for $C_{16}H_{21}FO_5$ 312.1373; found 312.1386; elemental analysis calcd (%) for $C_{16}H_{21}FO_5$ (312.3): C 61.53, H 6.78; found: C 61.62, H 6.67.

6-*O*-Benzyl-2-chloro-2-deoxy-3,4-*O*-isopropylidene- β -talopyranose and - β -galactopyranose (47). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene- β -arabino-hex-5-enitol.^[14] Oil (61%): IR ($CHCl_3$): ν = 3623 cm^{-1} ; MS (70 eV, EI): m/z (%): 330/328 (0.15/0.43) [M^+], 315/313 (1/4), 277 (1), 235 (3), 217 (19), 91 (100); HRMS (EI): calcd for $C_{16}H_{21}^{35}ClO_5$ 328.1078; found 328.1096; elemental analysis calcd (%) for $C_{16}H_{21}ClO_5$ (328.8): C 58.45, H 6.44; found: C 58.12, H 6.44.

6-*O*-Benzyl-2-bromo-2-deoxy-3,4-*O*-isopropylidene- β -talopyranose and - β -galactopyranose (48). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene- β -arabino-hex-5-enitol.^[14] Oil (93%): IR ($CHCl_3$): ν = 3598 cm^{-1} ; MS (70 eV, EI): m/z (%): 374/372 (0.19/0.17) [M^+], 359/357 (1/1), 292 (1), 277 (2), 235 (2), 91 (100); HRMS (EI): calcd for $C_{16}H_{21}^{81}BrO_5$ 374.0552; found

374.0576; elemental analysis calcd (%) for $C_{16}H_{21}BrO_5$ (373.2): C 51.49, H 5.67; found: C 51.32, H 5.66.

6-O-Benzyl-2-deoxy-2-iodo-3,4-O-(1-methylethylidene)-D-talopyranose and -D-galactopyranose (49). From 2,6-anhydro-1-O-benzyl-5-deoxy-3,4-O-isopropylidene-D-arabino-hex-5-enitol.^[14] Oil: (95%): IR ($CHCl_3$): ν = 3592, 3014, 2936 cm^{-1} ; MS (70 eV, EI): m/z (%): 420 (1) [M^+], 405 (1), 91 (100); HRMS (EI): calcd for $C_{16}H_{21}IO_5$ 420.0434; found 420.0426; elemental analysis calcd (%) for $C_{16}H_{21}IO_5$ (420.2): C 45.73, H 5.04; found: C 45.77, H 5.31.

2-Deoxy-6-O-(3,5-dinitrobenzoyl)-2-fluoro-3,4-O-isopropylidene-D-galactopyranose (50). From 2,6-anhydro-5-deoxy-1-O-(3,5-dinitrobenzoyl)-3,4-O-isopropylidene-D-arabino-hex-5-enitol (**2**). Oil (69 %): 1H NMR showed a diastereoisomeric mixture ratio 2.2:1; ^{13}C NMR (100.6 MHz): δ = 25.4 (CH_3), 25.6 (CH_3), 27.0 (CH_3), 27.4 (CH_3), 65.6 (CH_2), 65.8 (CH_2), 66.5 (CH), 70.2 (CH), 73.1 ($^2J(F,C)$ = 26.0 Hz, CH), 73.2 (CH), 73.6 ($^3J(F,C)$ = 6.0 Hz, CH), 75.5 ($^2J(F,C)$ = 25.0 Hz, CH), 88.8 ($^1J(F,C)$ = 194.0 Hz, CH), 89.9 ($^2J(F,C)$ = 32.0 Hz, CH), 91.4 ($^1J(F,C)$ = 180.0 Hz, CH), 94.0 ($^2J(F,C)$ = 26.0 Hz, CH), 110.6 (C), 111.3 (C), 122.5 (2 $\times$ CH), 129.5 (4 $\times$ CH), 133.4 (C), 133.5 (C), 148.6 (4 $\times$ C), 162.4 (2 $\times$ C); IR ν = 3614, 3102, 2990, 1744, 1550, 1343, 1274, 1166 cm^{-1} ; MS (70 eV, EI): m/z (%): 401 (59) [$M^+ - .Me$], 381 (10), 212 (30), 195 (94), 149 (39), 75 (100); HRMS (EI): calcd for $C_{15}H_{14}FN_2O_{10}$: 401.0632;

found: 401.0606; elemental analysis calcd (%) for $C_{16}H_{17}FN_2O_{10}$ (416.3): C 46.16, H 4.12, N 6.73; found: C 46.39, H 4.22, N 6.45.

2-Chloro-2-deoxy-6-O-(3,5-dinitrobenzoyl)-3,4-O-isopropylidene- β -talopyranose and - β -galactopyranose (51). From 2,6-anhydro-5-deoxy-1-O-(3,5-dinitrobenzoyl)-3,4-O-isopropylidene- β -arabino-hex-5-enitol (**2**). Oil (98%): IR ($CHCl_3$): ν = 3688, 3608, 1737, 1549 cm^{-1} ; MS (70 eV, EI): m/z (%): 419/417 (13/36) [M^+ - Me], 381 (24), 367 (13), 195 (100); HRMS (EI): calcd for $C_{15}H_{14}^{37}ClN_2O_{10}$, 419.0307 found 419.0293; elemental analysis calcd (%) for $C_{16}H_{17}ClN_2O_{10}$ (432.8): C 44.41, H 3.96, N 6.47; found: C 44.52, H 4.05, N 6.36.

2-Bromo-2-deoxy-6-O-(3,5-dinitrobenzoyl)-3,4-O-isopropylidene- β -talopyranose and - β -galactopyranose (52). From 2,6-anhydro-5-deoxy-1-O-(3,5-dinitrobenzoyl)-3,4-O-isopropylidene- β -arabino-hex-5-enitol (**2**). Oil (92%): IR ($CHCl_3$): ν = 3613, 1728, 1549 cm^{-1} ; MS (70 eV, EI): m/z (%): 463/461 (24/24) [M^+ - Me], 381 (22), 367 (12), 195 (100); HRMS (EI): calcd for $C_{15}H_{14}^{81}BrN_2O_{10}$, 462.9811 found 462.9817; elemental analysis calcd (%) for $C_{16}H_{17}BrN_2O_{10}$ (477.2): C 40.27, H 3.59, N 5.87; found: C 40.05, H 3.75, N 5.53.

6-O-[tert-Butyl(dimethyl)silyl]-2-deoxy-2-fluoro-3,4-O-(oxomethylene)- β -galactopyranose (53). From 2,6-anhydro-1-O-[tert-butyl(dimethyl)silyl]-5-deoxy-3,4-O-(oxomethylene)- β -arabino-hex-5-enitol.^[15] Crystalline solid (30%); major isomer: 1H NMR

(500 MHz, CDCl₃): δ = 0.08 (s, 6H), 0.89 (s, 9H), 3.78–3.92 (m, 2H), 4.27 (dd, J = 6.9, 6.9 Hz, 1H), 4.72 (ddd, J = 3.9, 5.8, $^2J(\text{F},\text{H})$ = 47.6 Hz, 1H), 4.90–4.95 (m, 1H), 5.03 (ddd, J = 6.4, 6.4 Hz, $^3J(\text{F},\text{H})$ = 12.8 Hz, 1H), 5.39 (dd, J = 3.8, Hz, $^3J(\text{F},\text{H})$ = 7.1 Hz, 1H); major isomer: ^{13}C NMR (125.7 MHz, CDCl₃): δ = -5.6 (2 $\times$ CH₃), 18.2 (C), 25.7 (3 $\times$ CH₃), 61.0 (CH₂), 67.2 (CH), 73.7 ($^2J(\text{F},\text{C})$ = 29.2 Hz, CH), 74.5 ($^3J(\text{F},\text{C})$ = 4.0 Hz, CH), 86.57 ($^1J(\text{F},\text{C})$ = 188.1 Hz, CH), 89.1 ($^2J(\text{F},\text{C})$ = 19.1 Hz, CH), 153.6 (C); IR (CHCl₃): ν = 3595, 3370, 1821, 1113, 1073 cm⁻¹; MS (70 eV, EI): m/z (%): 265 (5) [M^+ - C₄H₉], 217 (1), 203 (12), 175 (23), 117 (89), 75 (100); HRMS (EI): calcd for C₉H₁₄FO₆Si 265.0544; found 265.0534; elemental analysis calcd (%) for C₁₃H₂₃FO₆Si (322.4): C 48.43, H 7.19; found: C 48.45, H 7.03.

6-*O*-[*tert*-Butyl(dimethyl)silyl]-2-chloro-2-deoxy-3,4-*O*-(oxomethylene)- β -talopyranose and - β -galactopyranose (54). From 2,6-anhydro-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-3,4-*O*-(oxomethylene)- β -arabino-hex-5-enitol.^[15] Oil (89%); IR (CCl₄): ν = 3604, 1843, 1110, 1074 cm⁻¹; MS (70 eV, EI): m/z (%): 283/281 (<1/2) ([M^+ - C₄H₉], 219 (13), 191 (23), 155 (12), 117 (100), 75 (80); HRMS (EI): calcd for C₉H₁₄³⁵ClO₆Si 281.0248; found 281.0277; elemental analysis calcd (%) for C₁₃H₂₃ClO₆Si (338.9): C 46.08, H 6.84; found: C 46.22, H 6.58.

2-Bromo-6-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-3,4-*O*-(oxomethylene)- β -talopyranose and - β -galactopyranose (55). From 2,6-anhydro-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-3,4-*O*-

(oxomethylene)-D-arabino-hex-5-enitol.^[15] Oil (84%); IR (CHCl₃): ν = 3692, 3597, 1817, 1113, 1070 cm⁻¹; MS (70 eV, EI): m/z (%): 327/325 (1/1) [M^+ - C₄H₉], 253/251 (2/2), 237/235 (13/13), 155 (13), 139/137 (7/7), 129 (16), 117 (100), 75 (89); HRMS (EI): calcd for C₉H₁₄⁷⁹BrO₆Si 324.9743; found 324.9743; elemental analysis calcd (%) for C₁₃H₂₃BrO₆Si (383.3): C 40.73, H 6.05; found: C 40.71, H 6.04.

6-*O*-[*tert*-Butyl(dimethyl)silyl]-2-deoxy-2-iodo-3,4-*O*-(oxomethylene)-D-talopyranose and -D-galactopyranose (56). From 2,6-anhydro-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-3,4-*O*-(oxomethylene)-D-arabino-hex-5-enitol.^[15] Oil (80%); IR (CHCl₃): ν = 3596, 1816, 1112 cm⁻¹; MS (70 eV, EI): m/z (%): 413 (<1) [M^+ - OH], 373 (1), 355 (1), 317 (100); HRMS (EI): calcd for C₁₃H₂₂IO₅Si 413.0281; found 413.0319; elemental analysis calcd (%) for C₁₃H₂₃IO₆Si (430.3): C 36.29, H 5.39; found: C 36.35, H 5.08.

2-Deoxy-2-fluoro-3-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-D-galactopyranose (57). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-D-arabino-hex-5-enitol (**1**). Oil (72%); ¹H NMR (500 MHz, CDCl₃): δ = 1.13–1.06 (m, 56H), 1.29 (s, 9H), 1.28 (s, 9H), 3.90–3.74 (m, 5H), 4.11 (dd, J = 6.7, 6.7 Hz, 1H), 4.23 (dd, J = 6.2, 9.6 Hz, 1H), 4.45 (dd, J = 2.8, 2.8 Hz, 1H), 4.52 (dd, J = 3.1, 3.3 Hz, 1H), 4.58 (ddd, J = 7.4, 9.9 Hz, ² J (F,H) = 52.5 Hz, 1H), 4.88 (m, 1H), 4.91 (ddd, J = 3.6, 10.2 Hz, ² J (F,H) = 51.1 Hz,

1H), 5.13 (ddd, $J = 2.9, 10.2$ Hz, $^3J(\text{F},\text{H}) = 10.2$ Hz, 1H), 5.47 (br s, 1H), 5.51 (ddd, $J = 2.8, 9.9$ Hz, $^3J(\text{F},\text{H}) = 9.9$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 13.2$ (2 $\times$ CH), 13.7 (4 $\times$ CH), 14.0 (2 $\times$ CH), 17.5 (4 $\times$ CH_3), 17.7 (4 $\times$ CH_3), 18.0 (4 $\times$ CH_3), 18.2 (4 $\times$ CH_3), 27.6 (6 $\times$ CH_3), 39.6 (2 $\times$ C), 59.4 (CH_2), 59.6 (CH_2), 68.5 (CH), 69.3 (CH), 70.3 (CH), 70.8 ($^2J(\text{F},\text{C}) = 15.8$ Hz, CH), 73.9 ($^2J(\text{F},\text{C}) = 16.1$ Hz, CH), 74.7 (CH), 87.2 ($^1J(\text{F},\text{C}) = 187.3$ Hz, CH), 91.3 ($^2J(\text{F},\text{C}) = 20.6$ Hz, CH), 95.5 ($^2J(\text{F},\text{C}) = 22.6$ Hz, CH), 179.0 (2 $\times$ C); IR (CCl_4): $\nu = 3618, 1736, 1464, 1142$ cm^{-1} ; MS (70 eV, EI): m/z (%): 491 (1) [$M^+ - \text{OH}$], 465 (17), 363 (10), 319 (46), 235 (22), 57 (100); HRMS (EI): calcd for $\text{C}_{23}\text{H}_{44}\text{FO}_6\text{Si}_2$ 491.2661; found 491.2639; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{45}\text{FO}_7\text{Si}_2$ (508.8): C 54.30, H 8.92; found: C 54.33, H 8.76.

2-Chloro-2-deoxy-3-O-pivaloyl-1,3-O-(tetraisopropylidisiloxane-1,3-diyl)-D-talopyranose and -D-galactopyranose (58). From 2,6-anhydro-5-deoxy-4-O-pivaloyl-1,3-O-(tetraisopropylidisiloxane-1,3-diyl)-D-arabino-hex-5-enitol (**1**). Oil (76%); IR (CCl_4): $\nu = 3614, 1735, 1039$ cm^{-1} ; MS (70 eV, EI): m/z (%): 483/481 (7/15) [$M^+ - \text{C}_3\text{H}_7$], 407/405 (6/14), 381/379 (8/20), 351/349 (7/16), 319 (99), 277 (17), 235 (50), 57 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{38}^{35}\text{ClO}_7\text{Si}_2$ 481.1845; found 481.1826; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{45}\text{ClO}_7\text{Si}_2$ (525.2): C 52.60, H 8.64; found: C 52.54, H 8.95.

2-Bromo-2-deoxy-3-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-*D*-talopyranose and -*D*-galactopyranose (59). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-*D*-arabino-hex-5-enitol (**1**). Oil (92%). IR (CHCl₃): ν = 3605, 1734, 1465, 1107, 1034 cm⁻¹; MS (70 eV, EI): m/z (%): 527/525 (7/7) [M^+ - C₃H₇], 451/449 (2/2), 425/423 (4/4), 343 (10), 319 (31), 235 (20), 86 (16), 57 (100); HRMS (EI): calcd for C₂₀H₃₈⁸¹BrO₇Si₂ 527.1319; found 527.1330; elemental analysis calcd (%) for C₂₃H₄₅BrO₇Si₂ (569.7): C 48.49, H 7.96; found: C 48.59, H 7.87.

2-Deoxy-2-iodo-3-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-*D*-talopyranose and -*D*-galactopyranose (60). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropylidisiloxane-1,3-diyl)-*D*-arabino-hex-5-enitol (**1**). Oil (83%): IR(CHCl₃): ν = 3592, 3337, 2947, 2868, 1727 cm⁻¹; MS (70 eV, EI): m/z (%): 573 (2) [M^+ - C₃H₇], 555 (<1), 471 (<1), 57 (100); HRMS (EI): calcd for C₂₀H₃₈IO₇Si₂ 573.1201; found 573.1121; elemental analysis calcd (%) for C₂₃H₄₅IO₇Si₂ (616.7): C 44.80, H 7.36; found: C 44.64, H 7.39.

1,3,4-Tri-*O*-acetyl-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-*D*-arabinitol (61). Oil (94%): diastereoisomeric mixture (1:1); ¹H NMR: δ = 2.03 (s, 3H), 2.05 (s, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.17 (s, 3H), 3.91 (dd, J = 7.4, 11.9 Hz, 1H), 3.97 (dd, J = 7.1, 11.9 Hz, 1H), 4.28–4.32 (m, 2H), 5.20 (ddd, J = 3.9, 7.8 Hz, ³ J (F,H) = 11.0 Hz, 1H), 5.33 (ddd, J =

1.8, 10.8 Hz, $^3J(\text{F,H}) = 23.0$ Hz, 1H), 5.36–5.38 (m, 1H), 5.43–5.45 (m, 1H), 5.49–5.53 (m, 2H), 6.85 (dd, $J = 1.8$ Hz, $^2J(\text{F,H}) = 47.7$ Hz, 1H), 6.89 (dd, $J = 1.8$ Hz, $^2J(\text{F,H}) = 48.1$ Hz, 1H), 8.01 (s, 1H), 8.03 (s, 1H); ^{13}C NMR: $\delta = 20.5$ ($2 \times \text{CH}_3$), 20.6 ($2 \times \text{CH}_3$), 20.7 ($2 \times \text{CH}_3$), 61.6 (CH_2), 61.7 (CH_2), 67.3 (CH), 67.4 (CH), 67.9 (CH), 68.5 ($^1J(\text{F,C}) = 265.6$ Hz, CH), 69.6 (CH), 71.0 ($^1J(\text{F,C}) = 254.5$ Hz, CH), 71.02 ($^2J(\text{F,C}) = 22.5$ Hz, CH), 72.0 ($^2J(\text{F,C}) = 18.7$ Hz, CH), 159.6 (CH), 159.7 (CH), 168.8 (C), 169.0 (C), 169.2 ($2 \times \text{C}$), 170.2 ($2 \times \text{C}$); IR (CCl_4): $\nu = 1762$, 1737, 1205, 1156 cm^{-1} ; MS (70 eV, EI): m/z (%): 307 (100) [$M^+ - \text{I}$], 247 (6), 219 (7), 205 (11), 159 (13), 139 (25); HRMS (EI): calcd for $\text{C}_{12}\text{H}_{16}\text{FO}_8$: 307.0829; found: 307.0838; elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{16}\text{FIO}_8$ (434.2): C 33.20, H 3.71; found: C 33.52, H 3.71.

1,3,4-Tri-*O*-acetyl-5-chloro-5-deoxy-2-*O*-formyl-5-iodo- β -

arabinitol (62). Crystalline solid (96%): diastereoisomeric mixture (3:2); ^1H NMR (C_6D_6): $\delta =$ (major): 1.59 (s, 3H), 1.64 (s, 3H), 1.73 (s, 3H), 3.81 (dd, $J = 7.3$, 11.8 Hz, 1H), 4.24 (dd, $J = 4.9$, 11.8 Hz, 1H), 5.14 (dd, $J = 2.7$, 8.7 Hz, 1H), 5.39 (ddd, $J = 0.7$, 2.0, 8.9 Hz, 1H), 5.49 (m, 1H), 5.65 (d, $J = 2.7$ Hz, 1H), 7.54 (s, 1H); (minor): $\delta = 1.56$ (s, 3H), 1.65 (s, 3H), 1.78 (s, 3H), 3.80 (dd, $J = 7.0$, 11.8 Hz, 1H), 4.26 (dd, $J = 5.1$, 11.8 Hz, 1H), 5.45 (m, 1H), 5.54 (ddd, $J = 0.7$, 2.0, 9.1 Hz, 1H), 5.63 (dd, $J = 2.2$, 9.0 Hz, 1H), 5.72 (d, $J = 2.2$ Hz, 1H), 7.58 (s, 1H); ^{13}C NMR (C_6D_6): $\delta = 19.9$ (CH_3), 20.0

(2 × CH₃), 20.1 (CH₃), 20.2 (CH₃), 20.3 (CH₃), 25.1 (CH), 27.6 (CH), 62.1 (2 × CH₂), 67.5 (CH), 67.7 (CH), 69.6 (CH), 71.6 (CH), 73.0 (CH), 73.7 (CH), 159.7 (CH), 159.74 (CH), 168.8 (C), 168.9 (2 × C), 169.0 (C), 169.7 (2 × C); MS (70 eV, EI): *m/z* (%): 392/390 (1.5/5) [*M*⁺ – AcOH], 325/323 (34/100), 223/221 (25/80); HRMS (EI): calcd for C₁₀H₁₂³⁷ClIO₆: 391.9338; found: 391.9404; elemental analysis calcd (%) for C₁₂H₁₆ClIO₈ (450.6): C 31.99, H 3.58; found: C 32.18, H 3.33.

1,3,4-Tri-*O*-acetyl-5-bromo-5-deoxy-2-*O*-formyl-5-iodo-*D*-

arabinitol (63). Crystalline solid (98%): diastereoisomeric mixture (3:2); ¹H NMR (C₆D₆): δ = 1.56 (s, 3H), 1.57 (s, 3H), 1.64 (s, 3H), 1.65 (s, 3H), 1.75 (s, 3H), 1.77 (s, 3H), 3.803 (dd, *J* = 7.4, 11.7 Hz, 1H), 3.805 (dd, *J* = 7.5, 11.7 Hz, 1H), 4.26 (dd, *J* = 4.9, 10.9 Hz, 1H), 4.28 (dd, *J* = 4.9, 10.7 Hz, 1H), 5.23 (dd, *J* = 2.6, 8.7 Hz, 1H), 5.38 (ddd, *J* = 0.7, 2.0, 8.8 Hz, 1H), 5.46 (d, *J* = 2.6 Hz, 1H), 5.46–5.52 (m, 3H), 5.50 (d, *J* = 1.7 Hz, 1H), 5.59 (dd, *J* = 2.2, 8.8 Hz, 1H), 7.53 (s, 1H), 7.55 (s, 1H); ¹³C NMR (C₆D₆): δ = 7.1 (CH), 8.8 (CH), 19.9 (CH₃), 20.0 (CH₃), 20.1 (CH₃), 20.2 (2 × CH₃), 20.3 (CH₃), 62.1 (CH₂), 62.13 (CH₂), 67.5 (CH), 67.7 (CH), 70.9 (CH), 72.1 (CH), 73.0 (CH), 73.5 (CH), 159.69 (CH), 159.74 (CH), 168.7 (C), 168.9 (2 × C), 169.0 (C), 169.7 (2 × C); MS (70 eV, EI): *m/z* (%): 436/434 (16) [*M*⁺ – AcOH], 267/265 (84), 115 (91); HRMS (EI): calcd for C₁₀H₁₂⁸¹BrIO₆: 435.8842; found: 435.8831;

elemental analysis calcd (%) for $C_{12}H_{16}BrIO_8$ (495.1): C 29.11, H 3.26; found: C 29.01, H 3.17.

1,3,4-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-D-arabinitol (65). Oil (95%): diastereoisomeric mixture (1:1); 1H NMR: δ = 0.04 (s, 3H), 0.056 (s, 3H), 0.06 (s, 3H), 0.10 (s, 3H), 0.11 (s, 3H), 0.12 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.18 (s, 3H), 0.193 (s, 3H), 0.195 (s, 3H), 0.20 (s, 3H), 0.87 (s, 9H), 0.90 (s, 18H), 0.91 (s, 18H), 0.95 (s, 9H), 3.61 (ddd, J = 3.6, 5.5 Hz, $^3J(F,H)$ = 9.3 Hz, 1H), 3.71 (dd, J = 5.5, 10.9 Hz, 1H), 3.80 (dd, J = 5.5, 10.9 Hz, 1H), 3.88 (dd, J = 2.5, 12.5 Hz, 1H), 3.92 (dd, J = 5.5, 5.5 Hz, 1H), 3.94 (dd, J = 4.5, 12.5 Hz, 1H), 4.31 (dd, J = 9.0 Hz, $^3J(F,H)$ = 9.0 Hz, 1H), 4.39 (d, J = 6.7 Hz, 1H), 5.05 (ddd, J = 5.5, 5.5, 5.5 Hz, 1H), 5.07–5.11 (m, 1H), 6.81 (dd, J = 9.0 Hz, $^2J(F,H)$ = 51 Hz, 1H), 6.95 (dd, J = 3.6 Hz, $^2J(F,H)$ = 47 Hz, 1H), 8.08 (s, 2H); ^{13}C NMR: δ = -5.4 (3 $\times$ CH₃), -5.1 (CH₃), -4.8 (CH₃), -4.5 (3 $\times$ CH₃), -4.1 (CH₃), -3.97 (CH₃), -3.96 (CH₃), -3.8 (CH₃), 18.06 (C), 18.12 (C), 18.3 (4 $\times$ C), 25.7 (3 $\times$ CH₃), 25.8 (3 $\times$ CH₃), 25.9 (3 $\times$ CH₃), 25.91 (3 $\times$ CH₃), 26.0 (3 $\times$ CH₃), 26.1 (3 $\times$ CH₃), 60.5 (CH₂), 61.8 (CH₂), 70.6 (CH), 71.5 (CH), 73.7 (CH), 75.3 ($^1J(F,C)$ = 254.8 Hz, CH), 76.6 ($^2J(F,C)$ = 20.1 Hz, CH), 76.7 (CH), 81.9 ($^1J(F,C)$ = 251.9 Hz, CH), 82.0 ($^2J(F,C)$ = 19.7 Hz, CH), 160.5 (2 $\times$ CH); IR (CCl₄): ν = 1731, 1257, 1124, 1072 cm⁻¹; MS (70 eV, EI): m/z (%): 593 (1) [M^+ - C₄H₉], 565 (4), 473 (8), 347 (11), 189 (10), 177 (11),

147 (18), 115 (31), 89 (43), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}FIO_5Si_3$: 593.1447; found: 593.1434; elemental analysis calcd (%) for $C_{24}H_{52} FIO_5Si_3$ (650.8): C 44.29, H 8.06; found: C 44.57, H 7.83.

1,3,4-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-D-arabinitol (66). Oil (92%): diastereoisomeric mixture (1:1); 1H NMR: δ = 0.06 (s, 9H), 0.08 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.20 (s, 9H), 0.21 (s, 3H), 0.23 (s, 3H), 0.29 (s, 3H), 0.89 (s, 9H), 0.90 (s, 9H), 0.907 (s, 9H), 0.91 (s, 9H), 0.93 (s, 9H), 0.97 (s, 9H), 3.59 (dd, J = 4.9, 5.0 Hz, 1H), 3.73 (dd, J = 4.9, 11.2 Hz, 1H), 3.80–3.83 (m, 2H), 3.87 (dd, J = 3.8, 12.1 Hz, 1H), 4.09 (dd, J = 4.9, 4.9 Hz, 1H), 4.19 (dd, J = 1.0, 8.6 Hz, 1H), 4.48 (dd, J = 1.0, 6.9 Hz, 1H), 5.07–5.11 (m, 2H), 5.95 (d, J = 8.6 Hz, 1H), 6.03 (d, J = 5.0 Hz, 1H), 8.08 (s, 2H); ^{13}C NMR: δ = -5.4 (CH₃), -5.3 (CH₃), -5.1 (CH₃), -4.7 (CH₃), -4.6 (CH₃), -4.4 (CH₃), -3.8 (2 × CH₃), -3.7 (2 × CH₃), -3.5 (2 × CH₃), 18.11 (C), 18.15 (C), 18.2 (C), 18.5 (3 × C), 25.7 (3 × CH₃), 25.86 (3 × CH₃), 25.9 (3 × CH₃), 26.0 (3 × CH₃), 26.1 (3 × CH₃), 26.4 (3 × CH₃), 32.6 (CH), 36.8 (CH), 60.9 (CH₂), 61.7 (CH₂), 70.9 (CH), 71.4 (CH), 74.2 (CH), 76.2 (CH), 80.8 (CH), 83.0 (CH), 160.4 (CH), 160.5 (CH); IR (CCl₄): ν = 1731, 1472, 1121 cm⁻¹; MS (70 eV, EI): m/z (%): 611/609 (>1) [M^+ - C₄H₉], 583/581 (>1/1), 565/563 (>1/2), 349/347 (1/3), 301 (18), 147 (14), 115 (17), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}^{35}ClIO_5Si_3$: 609.1152; found: 609.1140;

elemental analysis calcd (%) for $C_{24}H_{52}ClIO_5Si_3$ (667.3): C 43.20, H 7.85; found: C 43.16, H 7.69.

5-Bromo-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-2-*O*-formyl-5-iodo-*D*-arabinitol (67). Oil (95%): diastereoisomeric mixture(1:1); 1H NMR: δ = 0.07 (s, 9H), 0.09 (s, 3H), 0.144 (s, 3H), 0.15 (s, 3H), 0.21 (s, 3H), 0.214 (s, 6H), 0.23 (s, 3H), 0.26 (s, 3H), 0.32 (s, 3H), 0.90 (s, 9H), 0.906 (s, 9H), 0.91 (s, 18H), 0.95 (s, 9H), 0.98 (s, 9H), 3.74–3.84 (m, 5H), 4.15 (dd, J = 4.7, 4.7 Hz, 1H), 4.18 (dd, J = 2.1, 8.0 Hz, 1H), 4.44 (dd, J = 2.1, 6.4 Hz, 1H), 5.07–5.11 (m, 2H), 5.78 (d, J = 8.0 Hz, 1H), 5.88 (d, J = 5.7 Hz, 1H), 8.09 (s, 2H). ^{13}C NMR: δ = -5.5 (2 $\times$ CH₃), -5.4 (CH₃), -5.3 (CH₃), -4.48 (CH₃), -4.45 (CH₃), -4.3 (CH₃), -3.75 (CH₃), -3.70 (CH₃), -3.63 (CH₃), -3.3 (CH₃), -3.2 (CH₃), 16.1 (3 $\times$ C), 18.2 (3 $\times$ C), 18.6 (CH), 19.3 (CH), 25.7 (3 $\times$ CH₃), 25.8 (3 $\times$ CH₃), 26.0 (6 $\times$ CH₃), 26.3 (3 $\times$ CH₃), 26.4 (3 $\times$ CH₃), 60.9 (CH₂), 61.5 (CH₂), 70.7 (CH), 70.9 (CH), 74.4 (CH), 75.7 (CH), 81.0 (CH), 82.4 (CH), 160.4 (CH), 160.5 (CH); IR (CCl₄): ν = 1730, 1257, 1178, 1132 cm⁻¹; MS (70 eV, EI): m/z (%): 655/653 (1) [M^+ - C₄H₉], 629/627 (1), 573 (1), 413 (2), 345 (14), 301 (56), 147 (22), 128 (10), 115 (16), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}^{79}BrIO_5Si_3$: 653.0646; found: 653.0609; elemental analysis calcd (%) for $C_{24}H_{52}BrIO_5Si_3$ (711.7): C 40.50, H 7.36; found: C 40.68, H 7.51.

3-*O*-Acetyl-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-*D*-arabinitol (70). Oil (91%):

diastereoisomeric mixture (3:2); ^1H NMR: δ = 0.035 (s, 3H), 0.042 (s, 3H), 0.045 (s, 3H), 0.057 (s, 3H), 0.16 (s, 3H), 0.17 (s, 3H), 0.18 (s, 3H), 0.24 (s, 3H), 0.87 (s, 9H), 0.88 (s, 9H), 0.93 (s, 9H), 0.96 (s, 9H), 2.11 (s, 3H), 2.13 (s, 3H), 3.65–3.72 (m, 5H), 3.95 (t, J = 5.1 Hz, 1H), 5.14 (dd, J = 2.9, 6.6 Hz, 1H), 5.22–5.27 (m, 2H), 5.50 (t, J = 4.2 Hz, 1H), 5.82 (d, J = 5.1 Hz, 1H), 5.87 (d, J = 2.8 Hz, 1H), 8.08 (s, 1H), 8.11 (s, 1H); ^{13}C NMR: δ = -5.5 (3 $\times$ CH₃), -5.4 (CH₃), -4.2 (3 $\times$ CH₃), -3.6 (CH₃), 18.1 (C), 18.3 (2 $\times$ C), 18.5 (C), 20.9 (2 $\times$ CH₃), 25.6 (3 $\times$ CH₃), 25.7 (3 $\times$ CH₃), 25.8 (3 $\times$ CH₃), 25.9 (3 $\times$ CH₃), 31.2 (CH), 32.9 (CH), 61.6 (CH₂), 61.7 (CH₂), 72.2 (3 $\times$ CH), 72.4 (CH), 77.2 (CH), 77.6 (CH), 160.1 (CH), 160.2 (CH), 169.1 (C), 169.2 (C); IR (CCl₄): ν = 1759, 1734, 1470, 1173 cm⁻¹; MS (70 eV, EI): m/z (%): 539/537 (3/6) [M^+ - C₄H₉], 433/431 (1/3), 351/349 (3/6), 319/317 (1/3), 285 (13), 117 (53), 103 (31), 75 (100); HRMS (EI): calcd for C₁₆H₃₁³⁵ClIO₆Si₂: 537.0393; found: 537.0393; elemental analysis calcd (%) for C₂₀H₄₀ClIO₆Si₂ (595.1): C 40.37, H 6.78; found: C 40.48, H 6.94.

3-*O*-Acetyl-5-bromo-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-2-*O*-formyl-5-iodo-D-arabinitol (71). Oil (95%): diastereoisomeric mixture (5:4); ^1H NMR: δ = 0.035 (s, 3H), 0.041 (s, 3H), 0.048 (s, 3H), 0.06 (s, 3H), 0.18 (s, 3H), 0.19 (s, 3H), 0.22 (s, 3H), 0.27 (s, 3H), 0.87 (s, 9H), 0.88 (s, 9H), 0.94 (s, 9H), 0.96 (s, 9H), 2.13 (s, 3H), 2.14 (s, 3H), 3.70

(dd, $J = 5.5, 12.0$ Hz, 2H), 3.87 (dd, $J = 2.8, 6.3$ Hz, 1H), 3.96 (dd, $J = 4.3, 5.2$ Hz, 1H), 5.18 (dd, $J = 3.0, 6.3$ Hz, 1H), 5.22–5.27 (m, 2H), 5.39 (dd, $J = 3.4, 5.2$ Hz, 1H), 5.60 (d, $J = 4.3$ Hz, 1H), 5.70 (d, $J = 2.8$ Hz, 1H), 8.11 (s, 1H), 8.12 (s, 1H); ^{13}C NMR: $\delta = -5.6$ ($2 \times \text{CH}_3$), -5.5 ($2 \times \text{CH}_3$), -4.2 ($2 \times \text{CH}_3$), -4.0 (CH_3), -3.6 (CH_3), 13.6 (CH), 14.7 (CH), 18.1 ($2 \times \text{C}$), 18.4 ($2 \times \text{C}$), 20.9 ($2 \times \text{CH}_3$), 25.8 ($3 \times \text{CH}_3$), 25.86 ($3 \times \text{CH}_3$), 25.9 ($3 \times \text{CH}_3$), 26.1 ($3 \times \text{CH}_3$), 61.6 ($2 \times \text{CH}_2$), 72.2 (CH), 72.3 (CH), 72.4 (CH), 72.6 (CH), 76.7 (CH), 76.8 (CH), 160.1 (CH), 160.2 (CH), 169.1 (C), 169.2 (C); IR: $\nu = 1748, 1427, 1257, 1178$ cm^{-1} ; MS (70 eV, EI): m/z (%): 583/581 (4/4) [$M^+ - \text{C}_4\text{H}_9$], 523/521 (2/2), 477/475 (2/2), 441 (7), 187 (10), 117 (97), 73 (100); HRMS (EI): calcd for $\text{C}_{16}\text{H}_{31}^{81}\text{BrIO}_6\text{Si}_2$: 582.9867; found: 582.9838; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{40}\text{BrIO}_6\text{Si}_2$ (639.5): C 37.56, H 6.30; found: C 37.56, H 6.60.

1-0-[*tert*-Butyl(dimethyl)silyl]-5-deoxy-5-fluoro-2-0-formyl-5-iodo-3,4-0-(oxomethylene)-D-arabinitol (79). Oil (70%): diastereoisomeric mixture (3:2); ^1H NMR: $\delta = 0.11$ (s, 12H), 0.91 (s, 18H), 3.96 (dd, $J = 9.0, 9.4$ Hz, 2H), 3.82 (dd, $J = 5.4, 9.4$ Hz, 1H), 3.84 (dd, $J = 5.4, 9.0$ Hz, 1H), 5.03 (dd, $J = 3.7, 7.4$ Hz, 1H), 5.11 (ddd, $J = 5.5, 7.4$ Hz, $^3J(\text{F},\text{H}) = 16.1$ Hz, 1H), 5.18 (ddd, $J = 6.3, 7.3$ Hz, $^3J(\text{F},\text{H}) = 16.1$ Hz, 1H), 5.27 (d, $J = 7.3$ Hz, 1H), 5.36–5.42 (m, 2H), 6.89 (dd, $J = 6.2$ Hz, $^2J(\text{F},\text{H}) = 49.6$ Hz, 1H), 6.97 (dd, $J = 5.5$ Hz, $^2J(\text{F},\text{H}) = 49.6$ Hz, 1H), 8.02 (s, 1H), 8.07 (s, 1H); ^{13}C NMR: $\delta = -5.6$ (2

$\times \text{CH}_3$), -5.5 ($2 \times \text{CH}_3$), 18.1 (C), 18.2 (C), 25.7 ($3 \times \text{CH}_3$), 25.8 ($3 \times \text{CH}_3$), 59.2 (CH_2), 60.3 (CH_2), 63.7 ($^1J(\text{F}, \text{C}) = 256.9$ Hz, CH), 64.8 ($^1J(\text{F}, \text{C}) = 257.6$ Hz, CH), 68.4 (CH), 69.2 (CH), 74.9 (CH), 75.6 (CH), 79.8 ($^2J(\text{F}, \text{C}) = 25.1$ Hz, CH), 81.0 ($^2J(\text{F}, \text{C}) = 19.1$ Hz, CH), 152.2 ($2 \times \text{C}$), 158.8 (CH), 159.1 (CH); IR (CCl_4): $\nu = 1845, 1737, 1161, 1091$ cm^{-1} ; MS (70 eV, EI): m/z (%): 391 (4) [$M^+ - \text{C}_4\text{H}_9$], 301 (9), 227 (14), 174 (11), 117 (20), 103 (100); HRMS (EI): calcd for $\text{C}_9\text{H}_{13}\text{FIO}_6\text{Si}$: 390.9510; found: 390.9526; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{22}\text{FIO}_6\text{Si}$ (448.3): C 34.82, H 4.95; found: C 34.76, H 5.16.

5-Bromo-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-(oxomethylene)-*D*-arabinitol (81). Crystalline solid (60%): diastereoisomeric mixture (1:1); ^1H NMR: $\delta = 0.09$ (s, 6H), 0.10 (s, 6H), 0.88 (s, 9H), 0.89 (s, 9H), 3.69 (dd, $J = 5.5, 9.4$ Hz, 1H), 3.71 (dd, $J = 5.5, 9.4$ Hz, 1H), 3.78 (dd, $J = 5.5, 9.4$ Hz, 2H), 5.11 (dd, $J = 1.5, 6.9$ Hz, 1H), 5.13 – 5.18 (m, 2H), 5.23 (dd, $J = 6.9, 9.6$ Hz, 1H), 5.33 (d, $J = 10.0$ Hz, 1H), 5.37 (d, $J = 9.6$ Hz, 1H), 5.43 (ddd, $J = 5.5, 5.5, 8.8$ Hz, 1H), 5.47 – 5.50 (m, 1H), 8.03 (s, 1H), 8.09 (s, 1H); ^{13}C NMR: $\delta = -5.6$ ($2 \times \text{CH}_3$), -5.5 (CH_3), -5.4 (CH_3), -2.9 (CH), -0.6 (CH), 18.1 ($2 \times \text{C}$), 25.6 ($6 \times \text{CH}_3$), 59.4 (CH_2), 59.8 (CH_2), 68.2 (CH), 68.5 (CH), 75.0 (CH), 76.3 (CH), 81.7 (CH), 82.2 (CH), 151.2 (C), 151.9 (C), 159.3 ($2 \times \text{CH}$); IR (CCl_4): $\nu = 1842, 1736, 1162$ cm^{-1} ; MS (70 eV, EI): m/z (%): 453/451 (2/2) [$M^+ - \text{C}_4\text{H}_9$], 363/361 (4/4), 289/287 (8/8), 236/234 (5/5), 155 (10),

128 (12), 117 (28), 103 (100); HRMS (EI): calcd for $C_9H_{13}^{79}BrIO_6Si$: 450.8710; found: 450.8719; elemental analysis calcd (%) for $C_{13}H_{22}BrIO_6Si$ (509.2): C 30.66, H 4.35; found: C 30.85, H 4.09.

5-Deoxy-4-O-(2,2-dimethylpropanoyl)-5-fluoro-2-O-formyl-5-iodo-1,3-O-(tetraisopropyldisiloxane-1,3-diyl)-D-arabinitol

(83). Crystalline solid (96%): diastereoisomeric mixture (3:2); 1H NMR: δ = 1.03–1.13 (m, 56H), 1.24 (s, 9H), 1.28 (s, 9H), 3.70 (t, J = 10.4 Hz, 2H), 3.83 (dd, J = 5.8, 10.4 Hz, 2H), 4.25 (d, J = 9.0 Hz, 1H), 4.50 (d, J = 9.2 Hz, 1H), 4.90 (dd, J = 5.8, 10.4 Hz, 1H), 4.99 (dd, J = 9.0 Hz, $^3J(F,H)$ = 10.4 Hz, 1H), 5.06 (dd, J = 5.8, 10.4 Hz, 1H), 5.43 (dd, J = 9.1 Hz, $^3J(F,H)$ = 28.0 Hz, 1H), 7.07 (d, $^2J(F,H)$ = 47 Hz, 1H), 7.18 (d, $^2J(F,H)$ = 48 Hz, 1H), 7.94 (s, 1H), 7.95 (s, 1H); ^{13}C NMR: δ = 12.2 (CH), 12.3 (CH), 13.1 (2 $\times$ CH), 13.2 (2 $\times$ CH), 13.4 (CH), 14.8 (CH), 16.8–17.8 (16 $\times$ CH_3), 27.2 (3 $\times$ CH_3), 29.9 (3 $\times$ CH_3), 38.9 (C), 39.2 (C), 57.3 (CH_2), 57.5 (CH_2), 66.8 (CH), 68.8 ($^1J(F,C)$ = 257.0 Hz, CH), 69.5 (CH), 69.6 (CH), 70.3 (CH), 71.4 ($^2J(F,C)$ = 18.6 Hz, CH), 74.1 ($^2J(F,C)$ = 17.0 Hz, CH), 77.8 ($^1J(F,C)$ = 253.0 Hz, CH), 159.9 (CH), 160.0 (CH), 176.3 (2 $\times$ C); IR (CCl_4): ν = 1749, 1734, 1168, 1145, 1041 cm^{-1} ; MS (70 eV, EI): m/z (%): 633 (1) [$M^+ - H$], 591 (3), 563 (9), 263 (43), 85 (25), 57 (100); HRMS (EI): calcd for $C_{23}H_{43}FIO_7Si_2$: 633.1576; found: 633.1546; elemental analysis calcd (%) for $C_{23}H_{44}FIO_7Si_2$ (634.7): C 43.52, H 6.99; found: C 43.64, H 6.65.

5-Chloro-5-deoxy-4-O-(2,2-dimethylpropanoyl)-2-O-formyl-5-iodo-1,3-O-(tetraisopropyldisiloxane-1,3-diyl)-D-arabinitol

(84). Oil (92%): diastereoisomeric mixture (1:1); ^1H NMR: δ = 1.03–1.15 (m, 56H), 1.27 (s, 9H), 1.29 (s, 9H), 3.68 (t, J = 10.4 Hz, 1H), 3.69 (t, J = 10.4 Hz, 1H), 3.82 (dd, J = 5.9, 10.4 Hz, 1H), 3.83 (dd, J = 5.8, 10.4 Hz, 1H), 4.24 (d, J = 8.6 Hz, 1H), 4.47 (d, J = 8.8 Hz, 1H), 4.84 (dd, J = 1.7, 8.6 Hz, 1H), 4.93 (dd, J = 5.8, 10.4 Hz, 1H), 5.02 (dd, J = 5.9, 10.4 Hz, 1H), 5.65 (d, J = 8.8 Hz, 1H), 6.06 (d, J = 1.7 Hz, 1H), 6.18 (s, 1H), 7.92 (s, 1H), 7.93 (s, 1H); ^{13}C NMR: δ = 12.1 (CH), 12.2 (CH), 13.2 (4 $\times$ CH), 14.2 (CH), 15.0 (CH), 16.9–17.8 (16 $\times$ CH₃), 24.8 (CH), 27.0 (3 $\times$ CH₃), 27.1 (3 $\times$ CH₃), 32.6 (CH), 39.1 (C), 39.2 (C), 57.4 (CH₂), 57.5 (CH₂), 67.9 (CH), 69.7 (CH), 70.0 (CH), 71.0 (CH), 74.3 (CH), 75.4 (CH), 160.1 (2 $\times$ CH), 176.5 (2 $\times$ C); IR (CCl₄): ν = 1749, 1733, 1168, 1147, 1040 cm⁻¹; MS (70 eV, EI): m/z (%): 609/607 (1/3) [M^+ – C₃H₇], 581/579 (2/5), 319 (6), 263 (44), 85 (14), 57 (100); HRMS (EI): calcd for C₂₀H₃₇³⁵ClIO₇Si₂: 607.0811; found: 607.0800; elemental analysis calcd (%) for C₂₃H₄₄ClIO₇Si₂ (651.1): C 42.43, H 6.81; found: C 42.45, H 6.84.

5-Bromo-5-deoxy-4-O-(2,2-dimethylpropanoyl)-2-O-formyl-5-iodo-1,3-O-(tetraisopropyldisiloxane-1,3-diyl)-D-arabinitol (85).

Crystalline solid (92%): diastereoisomeric mixture (4:3); ^1H NMR: δ = 1.04–1.15 (m, 56H), 1.29 (s, 9H), 1.30 (s, 9H), 3.68 (t, J = 10.3 Hz, 2H), 3.83 (dd, J = 5.9, 10.3 Hz, 2H), 4.22

(d, $J = 8.6$ Hz, 1H), 4.39 (d, $J = 8.7$ Hz, 1H), 4.95 (dd, $J = 5.9, 10.3$ Hz, 2H), 4.99 (dd, $J = 2.0, 8.6$ Hz, 1H), 5.57 (dd, $J = 1.7, 8.7$ Hz, 1H), 5.88 (d, $J = 2.0$ Hz, 1H), 5.96 (d, $J = 1.7$ Hz, 1H), 7.927 (s, 1H), 7.93 (s, 1H); ^{13}C NMR: $\delta = 7.9$ (CH), 12.2 (CH), 12.3 (CH), 13.2 ($5 \times \text{CH}$), 14.5 (CH), 15.1 (CH), 17.0–17.9 ($16 \times \text{CH}_3$), 27.08 ($3 \times \text{CH}_3$), 27.13 ($3 \times \text{CH}_3$), 38.9 (C), 39.2 (C), 57.5 ($2 \times \text{CH}_2$), 69.2 (CH), 69.7 (CH), 69.9 ($2 \times \text{CH}$), 74.5 (CH), 75.3 (CH), 160.2 ($2 \times \text{CH}$), 176.5 ($2 \times \text{C}$); IR (CCl_4): $\nu = 1749, 1734, 1167, 1144, 1091 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 653/651 (6/6) [$M^+ - \text{C}_3\text{H}_8$], 625/623 (16/16), 441 (17), 319 (11), 289 (14), 263 (72), 135 (11), 107 (20), 57 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{35}^{81}\text{BrIO}_7\text{Si}_2$: 651.0129; found: 651.0147; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{44}\text{BrIO}_7\text{Si}_2$ (695.6): C 39.72, H 6.38; found: C 39.92, H 6.45.

3,4-di-*O*-Acetyl-2,6-dideoxy-2-fluoro-L-glucopyranose and -L-mannopyranose (87). From 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-arabino-hex-1-enitol.^[10] Oil (85%); IR (CCl_4): $\nu = 3614, 1759, 1239 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 249 (1) [$M^+ - \text{H}$], 233 (10), 172 (4), 144 (21), 130 (40), 117 (100); HRMS (EI): calcd for $\text{C}_{10}\text{H}_{14}\text{FO}_6$ 249.0774; found 249.0789; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{15}\text{FO}_6$ (250.2): C 48.00, H 6.04; found: C 47.79, H 6.37.

3,4-di-*O*-Acetyl-2-chloro-2,6-dideoxy-L-glucopyranose and -L-mannopyranose (88). From 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-arabino-hex-1-enitol.^[10] Oil (86%); IR (CCl_4): $\nu =$

3610, 3481, 1758 cm^{-1} ; MS (70 eV, EI): m/z (%): 251/249 (2/5) [$M^+ - \text{OH}$], 208/206 (2/6), 171 (20), 134 (85), 87 (100); HRMS (EI): calcd for $\text{C}_{10}\text{H}_{14}^{35}\text{ClO}_5$ 249.0530; found 249.0541; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{15}\text{ClO}_6$ (266.6): C 45.04, H 5.67; found: C 45.06, H 5.86.

3,4-di-*O*-Acetyl-2-bromo-2,6-dideoxy-L-glucopyranose and -L-mannopyranose (89). From 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-arabino-hex-1-enitol.^[10] Oil (95%); IR (CHCl_3): ν = 3595, 1751, 1243, 1044 cm^{-1} ; MS (70 eV, EI): m/z (%): 295/293 (1/1) [$M^+ - \text{OH}$], 252/250 (4/4), 209/207 (12/12), 192/190 (15/15), 166/164 (93/96), 141 (23), 127 (82), 99 (100); HRMS (EI): calcd for $\text{C}_{10}\text{H}_{14}^{79}\text{BrO}_5$ 293.0025; found 292.9995; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{15}\text{BrO}_6$ (311.1): C 38.60, H 4.86; found: C 38.85, H 5.07.

3,4-di-*O*-Acetyl-2,6-dideoxy-2-iodo-L-glucopyranose and -L-mannopyranose (90). From 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-arabino-hex-1-enitol.^[10] Oil (82%); IR (CHCl_3): ν = 3592, 3469, 1750, 1240 cm^{-1} ; MS (70 eV, EI): m/z (%): 358 (1) [$M^+ - \text{OH}$], 341 (5), 298 (37), 253 (10), 226 (21), 212 (45), 125 (100); HRMS (EI): calcd for $\text{C}_{10}\text{H}_{15}\text{IO}_6$ 357.9913; found 357.9945; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{15}\text{IO}_6$ (358.1): C 33.45, H 4.22; found: C 33.69, H 4.37.

3-*O*-Acetyl-4,6-*O*-benzylidene-2-bromo-2-deoxy-D-altropyranose and -D-allopyranose (91). From 3-*O*-acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-ribo-hex-1-enitol.^[16] Oil (100%): IR

(CHCl₃): ν = 3586, 3511, 1745, 1231 cm⁻¹; MS (70 eV, EI): m/z (%): 420 (6) [M^+], 345 (25), 271 (40), 235 (16), 211 (17), 179 (17), 149 (21), 107 (100); HRMS (EI): calcd for C₁₅H₁₇IO₆, 420.0070 found 420.0071; elemental analysis calcd (%) for C₁₅H₁₇IO₆ (420.2): C 42.88, H 4.08; found: C 42.76, H 4.24.

3,4-di-O-Acetyl-2-deoxy-2-fluoro-L-ribofuranose (92).^[17] From 2,3-di-O-acetyl-1,5-anhydro-4-deoxy-D-erythro-pent-4-enitol.^[10] Oil (96%); ¹H NMR (500 MHz, CDCl₃): δ = 2.07 (s, 3H), 2.08 (s, 3H), 2.12 (s, 3H), 2.13 (s, 3H), 3.62–3.70 (m, 2H), 3.99 (d, J = 13.4 Hz, 1H), 4.18 (d, J = 13.1 Hz, 1H), 4.49 (ddd, J = 7.2, 9.4 Hz, $^2J(F,H)$ = 51.1 Hz, 1H), 4.77 (ddd, J = 3.5, 10.0 Hz, $^3J(F,H)$ = 50.0 Hz, 1H), 4.81 (m, 1H), 5.12 (ddd, J = 3.5, 9.4 Hz, $^3J(F,H)$ = 12.8 Hz, 1H), 5.28 (br s, 1H), 5.35 (br s, 1H), 5.44 (ddd, J = 3.5, 10.2 Hz, $^3J(F,H)$ = 10.2 Hz, 1H), 5.47 (br s, 1H); ¹³C NMR (125.7 MHz, CDCl₃): δ = 20.7 (2 × CH₃), 20.8 (2 × CH₃), 60.5 (CH₂), 64.0 (CH₂), 67.5 ($^2J(F,C)$ = 19.0 Hz, CH), 68.6 (br s, CH), 69.5 (br s, CH), 70.6 ($^2J(F,C)$ = 20.0 Hz, CH), 86.0 ($^1J(F,C)$ = 189.0 Hz, CH), 89.1 ($^1J(F,C)$ = 186.0 Hz, CH), 90.9 ($^2J(F,C)$ = 21.5 Hz, CH), 95.1 ($^2J(F,C)$ = 23.2 Hz, CH), 170.2 (4 × C); IR (CCl₄): ν = 3614, 1754, 1264 cm⁻¹; MS (70 eV, EI): m/z (%): 235 (1) [$M^+ - H$], 219 (4), 176 (5), 163 (19), 131 (100), 117 (54), 88 (73); HRMS (EI): calcd for C₉H₁₂FO₆ 235.0618; found 235.0620; elemental analysis calcd (%) for C₉H₁₃FO₆ (236.2): C 45.77, H 5.55; found: C 45.64; H 5.69.

3,4-di-O-Acetyl-2-chloro-2-deoxy-L-ribose and **-L-arabinopyranose (93).** From 2,3-di-O-acetyl-1,5-anhydro-4-deoxy-D-erythro-pent-4-enitol.^[10] Oil (95%); IR (CCl₄): ν = 3614, 1755 cm⁻¹; MS (70 eV, EI): m/z (%): 237/235 (2/6) [M^+ - OH], 194/196 (3/10), 171 (13), 157 (49), 146 (53), 133 (78), 71 (100); HRMS (EI): calcd for C₉H₁₂³⁷ClO₅ 237.0344; found 237.0311; elemental analysis calcd (%) for C₉H₁₃ClO₆ (252.6): C 42.79, H 5.19; found: C 42.81, H 5.12.

3,4-di-O-Acetyl-2-bromo-2-deoxy-L-ribose and **-L-arabinopyranose (94).** From 2,3-di-O-acetyl-1,5-anhydro-4-deoxy-D-erythro-pent-4-enitol.^[10] Oil (95%); IR (CHCl₃): ν = 3595, 3467, 1748, 1244, 1074 cm⁻¹; MS (70 eV, EI): m/z (%): 238/236 (3/3) [M^+ - AcOH], 220/218 (5/5), 178/176 (25/25), 166/164 (62/62), 69 (100); HRMS (EI): calcd for C₇H₉⁸¹BrO₄ 237.9664; found 237.9670; elemental analysis calcd (%) for C₉H₁₃BrO₆ (297.1): C 36.38, H 4.41; found: C 36.59, H 4.50.

3,4-di-O-Acetyl-2-deoxy-2-iodo-L-ribose and **-L-arabinopyranose (95).** From 2,3-di-O-acetyl-1,5-anhydro-4-deoxy-D-erythro-pent-4-enitol.^[10] Oil (88%); IR (CHCl₃): ν = 3417, 1747, 1240 cm⁻¹; MS (70 eV, EI): m/z (%): 344 (1) [M^+], 327 (1), 284 (66), 254 (51), 224 (92), 111 (100); HRMS (EI): calcd for C₉H₁₃IO₆ 343.9757; found 343.9798; elemental analysis calcd (%) for C₉H₁₃IO₆ (344.1): C 31.41, H 3.81; found: C 31.74, H 3.87.

4,6-di-*O*-Acetyl-2,3-dideoxy-2-iodo-*D*-arabino-hexopyranose and -*D*-ribo-hexopyranose (96). From 4,6-di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-*D*-erythro-hex-1-enitol.^[18] Oil (75%): IR (CHCl₃): ν = 3592, 3458, 3025, 2957, 1740 cm⁻¹; MS (70 eV, EI): m/z (%): 341 (4) [M^+ - OH], 231 (80), 91 (100); HRMS (EI): calcd for C₁₀H₁₄IO₅, 340.9886 found 340.9838; elemental analysis calcd (%) for C₁₀H₁₅IO₆ (358.1): C 33.54, H 4.22; found: C 33.44, H 4.46.

3,4-Dideoxy-2-iodo-6-*O*-(triisopropylsilyl)-*D*-threo-hexopyranose and -*D*-erythro-hexopyranose (97). From 1,5-anhydro-1,2,3,4-tetradeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-hex-1-enitol.^[19] Oil (97%): IR (CHCl₃): ν = 3593, 3507, 2945, 2867, 1113 cm⁻¹; MS (70 eV, EI): m/z (%): 414 (<1) [M^+], 413 (1), 397 (68), 371 (13), 353 (55), 287 (17), 223 (41), 157 (100); HRMS (EI): calcd for C₁₅H₃₁IO₃Si, 414.1087 found 414.1086; elemental analysis calcd (%) for C₁₅H₃₁IO₃Si (414.4): C 43.48, H 7.54; found: C 43.56, H 7.77.

2,3-Di-*O*-acetyl-1,5-dideoxy-1-fluoro-4-*O*-formyl-1-iodo-*L*-arabinitol (99). Oil (90%): diastereoisomeric mixture (1:1); ¹H NMR: δ = 1.25 (d, J = 6.6 Hz, 3H), 1.27 (d, J = 6.6 Hz, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.16 (s, 3H), 5.11 (dddd, J = 6.6, 6.6, 6.6, 13.5 Hz, 2H), 5.46–5.51 (m, 3H), 5.57 (ddd, J = 2.9, 5.4 Hz, ³ J (F,H) = 15.0 Hz, 1H), 6.72 (dd, J = 5.9 Hz, ² J (F,H) = 48.8 Hz, 1H), 6.78 (dd, J = 5.4 Hz, ² J (F,H) = 49.2 Hz, 1H), 7.96 (s, 2H); ¹³C NMR: δ = 16.07 (CH₃), 16.1 (CH₃), 20.5 (2 × CH₃), 20.6 (2 × CH₃), 67.3 (2 × CH), 69.2

($^1J(\text{F},\text{C}) = 258.2 \text{ Hz, CH}$), 70.2 ($^1J(\text{F},\text{C}) = 256.1 \text{ Hz, CH}$), 70.6 (CH), 71.8 (CH), 72.5 ($^2J(\text{F},\text{C}) = 24.0 \text{ Hz, CH}$), 72.8 ($^2J(\text{F},\text{C}) = 18.7 \text{ Hz, CH}$), 159.7 (2 × CH), 169.2 (C), 169.3 (C), 169.5 (C), 169.55 (C); IR (CCl₄): $\nu = 1764, 1735, 1207, 1166 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 303 (1) [$M^+ - \text{C}_3\text{H}_5\text{O}_2$], 253 (14), 249 (100), 161 (17), 147 (11), 99 (95); HRMS (EI): calcd for C₇H₉FIO₄: 302.9530; found: 302.9531; elemental analysis calcd (%) for C₁₀H₁₄FIO₆ (376.1): C 31.92, H 3.75; found: C 31.81, H 3.83.

2,3-Di-O-acetyl-1-chloro-1,5-dideoxy-4-O-formyl-1-iodo-L-

arabinitol (100). Oil (89%): diastereoisomeric mixture (1:1); ^1H NMR: $\delta = 1.26$ (d, $J = 6.4 \text{ Hz, 3H}$), 1.27 (d, $J = 6.5 \text{ Hz, 3H}$), 2.14 (s, 6H), 2.15 (s, 6H), 5.05–5.15 (m, 2H), 5.47 (dd, $J = 2.1, 8.2 \text{ Hz, 1H}$), 5.50 (dd, $J = 2.8, 7.3 \text{ Hz, 1H}$), 5.58–5.60 (m, 2H), 5.62 (d, $J = 8.2 \text{ Hz, 1H}$), 5.68 (d, $J = 7.3 \text{ Hz, 1H}$), 7.96 (s, 2H); ^{13}C NMR: $\delta = 16.1$ (CH₃), 16.2 (CH₃), 20.5 (CH₃), 20.7 (CH₃), 20.8 (CH₃), 20.9 (CH₃), 24.5 (CH), 25.1 (CH), 67.5 (CH), 67.7 (CH), 70.5 (CH), 71.9 (CH), 73.6 (CH), 73.7 (CH), 159.7 (2 × CH), 169.2 (C), 169.3 (C), 169.5 (2 × C); IR (CCl₄): $\nu = 1763, 1734, 1458, 1428, 1371, 1205 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 349/347 (1/3) [$M^+ - \text{OCOH}$], 267/265 (25/75), 225/223 (2/8), 187 (21), 179/177 (14/43), 99 (100); HRMS (EI): calcd for C₉H₁₃³⁵ClIO₄: 346.9547; found: 346.9516; elemental analysis calcd (%) for C₁₀H₁₄ClIO₆ (392.6): C 30.60, H 3.59; found: C 30.67, H 3.41.

2,3-Di-O-acetyl-1-bromo-1,5-dideoxy-4-O-formyl-1-iodo-L-

arabinitol (101). Oil (84%): diastereoisomeric mixture (1:1);

^1H NMR: δ = 1.24 (d, J = 6.4 Hz, 3H), 1.25 (d, J = 6.4 Hz, 3H), 2.12 (s, 6H), 2.13 (s, 3H), 2.14 (s, 3H), 5.02–5.11 (m, 2H), 5.37 (d, J = 8.2 Hz, 1H), 5.42 (d, J = 7.5 Hz, 1H), 5.45 (ddd, J = 2.4, 2.4, 7.5 Hz, 2H), 5.59–5.61 (m, 2H), 7.95 (s, 2H); ^{13}C NMR: δ = 5.9 (CH), 6.4 (CH), 16.0 (CH₃), 16.1 (CH₃), 20.5 (CH₃), 20.7 (CH₃), 20.8 (CH₃), 20.9 (CH₃), 67.7 (CH), 67.8 (CH), 71.0 (CH), 72.0 (CH), 73.3 (CH), 73.4 (CH), 159.6 (CH), 159.7 (CH), 169.2 (C), 169.3 (C), 169.5 (2 $\times$ C); IR (CCl₄): ν = 1755, 1728, 1232, 1174 cm⁻¹; MS (70 eV, EI): m/z (%): 393/391 (2/2) [M^+ – OCOH], 378/376 (8/8), 323/321 (4/4), 311/309 (30/30), 305/303 (22/22), 223/221 (95/100), 209/207 (47/47), 163/161 (47/49), 99 (88); HRMS (EI): calcd for C₈H₁₀⁷⁹BrIO₄: 375.8807; found: 375.8795; elemental analysis calcd (%) for C₁₀H₁₄BrIO₆ (437.0): C 27.48, H 3.24; found: C 27.69, H 3.13.

2,3-Di-O-acetyl-1-fluoro-4-O-formyl-1-iodo-L-erythritol (104).

Crystalline solid (96%): diastereoisomeric mixture (3:2); ^1H NMR: δ = 2.07 (s, 3H), 2.14 (s, 6H), 2.19 (s, 3H), 4.22 (dd, J = 4.9, 12.5 Hz, 1H), 4.28 (dd, J = 5.3, 12.4 Hz, 1H), 4.48 (d, J = 12.4 Hz, 1H), 5.26–5.29 (m, 1H), 5.34–5.30 (m, 2H), 5.45 (ddd, J = 2.1, 7.4 Hz, $^3J(\text{F},\text{H})$ = 24.3 Hz, 1H), 6.88 (dd, J = 3.7 Hz, $^2J(\text{F},\text{H})$ = 48.1 Hz, 1H), 6.98 (dd, J = 2.1 Hz, $^2J(\text{F},\text{H})$ = 48.4 Hz, 1H), 8.00 (s, 1H), 8.02 (s, 1H); ^{13}C NMR: δ = 20.7 (4 $\times$ CH₃), 60.4 (CH₂), 60.6 (CH₂), 68.5 ($J(\text{F},\text{C})$ = 259.2 Hz, CH),

68.8 (CH), 70.1 (CH), 70.8 ($^1J(\text{F},\text{C}) = 255.5 \text{ Hz}$, CH), 72.2 ($^2J(\text{F},\text{C}) = 22.0 \text{ Hz}$, CH), 73.2 ($^2J(\text{F},\text{C}) = 18.3 \text{ Hz}$, CH), 160.2 (2 $\times$ CH), 168.9 (C), 169.1 (C), 169.3 (2 $\times$ C); IR (CCl_4): $\nu = 1762, 1737, 1371, 1208, 1168 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 317 (1) [$M^+ - \text{OCOH}$], 303 (1), 235 (100), 127 (17), 113 (10), 85 (59); HRMS (EI): calcd for $\text{C}_8\text{H}_{11}\text{FIO}_4$: 316.9686; found: 316.9685; elemental analysis calcd (%) for $\text{C}_9\text{H}_{12}\text{FIO}_6$ (362.1): C 29.84, H 3.34; found: C 29.94, H 3.34.

2,3-Di-*O*-acetyl-1-chloro-4-*O*-formyl-1-iodo-L-erythritol (105).

Crystalline solid (73%): diastereoisomeric mixture (3:2); ^1H NMR: $\delta = 2.10$ (s, 3H), 2.19 (s, 6H), 2.23 (s, 3H), 4.16 (dd, $J = 4.0, 12.5 \text{ Hz}$, 1H), 4.21 (dd, $J = 4.4, 12.5 \text{ Hz}$, 1H), 4.50 (dd, $J = 3.2, 12.5 \text{ Hz}$, 2H), 5.13 (dd, $J = 3.8, 7.5 \text{ Hz}$, 1H), 5.20 (ddd, $J = 3.2, 4.0, 7.5 \text{ Hz}$, 1H), 5.29 (ddd, $J = 3.2, 4.4, 8.1 \text{ Hz}$, 1H), 5.61 (dd, $J = 2.8, 8.1 \text{ Hz}$, 1H), 5.88 (d, $J = 3.8 \text{ Hz}$, 1H), 5.98 (d, $J = 2.8 \text{ Hz}$, 1H), 8.03 (s, 1H), 8.04 (s, 1H); ^{13}C NMR: $\delta = 20.6$ (2 $\times$ CH_3), 20.7 (2 $\times$ CH_3), 24.6 (CH), 26.7 (CH), 60.1 (CH_2), 60.4 (CH_2), 69.7 (CH), 71.4 (CH), 73.3 (CH), 74.1 (CH), 160.2 (2 $\times$ CH), 169.0 (2 $\times$ C), 169.2 (2 $\times$ C); IR (CCl_4): $\nu = 1762, 1737, 1371, 1204, 1067 \text{ cm}^{-1}$; MS (70 eV, EI): m/z (%): 320/318 (3/9) [$M^+ - \text{AcOH}$], 253/251 (23/68), 211/209 (4/14), 193/191 (12/35), 85 (100); HRMS (EI): calcd for $\text{C}_7\text{H}_8^{35}\text{ClIO}_4$: 317.9156; found: 317.9151; elemental analysis calcd (%) for $\text{C}_9\text{H}_{12}\text{ClIO}_6$ (378.5): C 28.56, H 3.20; found: C 28.62, H 3.33.

2,3-Di-O-acetyl-1-bromo-4-O-formyl-1-iodo-L-erythritol (106).

Crystalline solid (87%): diastereoisomeric mixture (4:3); ^1H NMR: δ = 2.09 (s, 6H), 2.19 (s, 3H), 2.21 (s, 3H), 4.16 (ddd, J = 3.5, 4.2, 12.7 Hz, 2H), 4.48 (dd, J = 2.4, 12.7 Hz, 2H), 5.13–5.18 (m, 2H), 5.23 (ddd, J = 3.5, 4.0, 7.8 Hz, 1H), 5.53 (dd, J = 3.0, 7.8 Hz, 1H), 5.66 (d, J = 2.9 Hz, 1H), 5.74 (d, J = 3.0 Hz, 1H), 8.02 (s, 1H), 8.03 (s, 1H); ^{13}C NMR: δ = 6.7 (CH), 8.0 (CH), 20.7 ($2 \times \text{CH}_3$), 20.8 ($2 \times \text{CH}_3$), 60.1 (CH_2), 60.3 (CH_2); 70.8 (CH), 71.9 (CH), 73.2 (CH), 73.8 (CH), 160.2 (CH), 160.25 (CH), 169.1 ($2 \times \text{C}$), 169.2 ($2 \times \text{C}$); IR: ν = 1748, 1372, 1232, 1194 cm^{-1} ; MS (70 eV, EI): m/z (%): 364/362 (14/14) [M^+ – AcOH], 254 (43), 209/207 (19/17), 149/147 (11/11), 127 (100), 85 (50); HRMS (EI): calcd for $\text{C}_7\text{H}_8^{81}\text{BrIO}_4$: 363.8630; found: 363.8644; elemental analysis calcd (%) for $\text{C}_9\text{H}_{12}\text{BrIO}_6$ (423.0): C 25.56, H 2.87; found: C 25.79, H 2.61.

3,4,6-Tri-O-benzyl-2-bromo-1-O-[*tert*-butyl(dimethyl)silyl]-2-deoxy-5-O-formyl-2-iodo-D-arabino-hexitol (110).

A solution of 1,5-anhydro-3,4,6-tri-O-benzyl-2-([*tert*-butyl(dimethyl)silyl]oxy)methyl)-2-deoxy-D-arabino-hex-1-enitol (**98**) (100 mg, 0.178 mmol) in THF (4.5 mL) and H_2O (0.5 mL), containing recently crystallized *N*-bromoacetamide (37 mg, 0.267 mmol) was stirred at 0 °C for 3 h. The reaction mixture was then poured into ice-water, extracted with CH_2Cl_2 , and the organic layer dried and concentrated in vacuo. A solution of the crude bromohydrin (117 mg) in CH_2Cl_2 (10 mL) containing DIB

(86 mg, 0.267 mmol) and iodine (68 mg, 0.267 mmol) was stirred at 0 °C for 2.5 h. 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, 94:6) afforded compound **110** (96 mg, 0.122 mmol, 69%, two steps) as a diastereoisomeric mixture (1:1), oil: ¹H NMR: δ = 0.10 (s, 6H), 0.13 (s, 3H), 0.14 (s, 3H), 0.92 (s, 9H), 0.93 (s, 9H), 3.73 (d, *J* = 4.4 Hz, 1H), 3.76 (dd, *J* = 6.8, 11.3 Hz, 2H), 3.89 (dd, *J* = 3.7, 10.8 Hz, 2H), 3.96 (d, *J* = 4.4 Hz, 1H), 4.07 (d, *J* = 11.5 Hz, 1H), 4.10 (d, *J* = 11.9 Hz, 1H), 4.15 (d, *J* = 12.4 Hz, 1H), 4.16 (dd, *J* = 4.2, 4.2 Hz, 1H), 4.20 (dd, *J* = 4.2, 4.2 Hz, 1H), 4.29 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 2H), 4.54 (d, *J* = 12.4 Hz, 2H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.689 (d, *J* = 10.6 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.83 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 11.5 Hz, 1H), 4.99 (d, *J* = 11.5 Hz, 1H), 5.46 (m, 2H), 7.26–7.35 (m, 30H), 8.00 (s, 2H); ¹³C NMR (50.3 MHz): δ = -5.2 (4 × CH₃), 18.3 (2 × C), 25.8 (6 × CH₃), 67.7 (CH₂), 67.8 (CH₂), 72.8 (CH₂), 73.2 (2 × CH₂), 73.5 (CH₂), 74.0 (CH), 74.1 (CH₂), 74.1 (CH), 74.4 (CH₂), 74.9 (CH₂), 75.3 (CH₂), 79.5 (CH), 79.6 (CH), 80.2 (CH), 81.7 (CH), 127.4–128.4 (30 × CH), 137.6 (2 × C), 138.0 (2 × C), 138.2 (2 × C), 160.3 (2 × CH) (two C are missing); IR: ν = 1740, 1731, 1232, 1166 cm⁻¹; MS (70 eV, EI): *m/z* (%): 693/691

(<1) [$M^+ - C_7H_7$], 566/564 (<1), 475/473 (<1), 403 (2); HRMS (EI): calcd for $C_{27}H_{35}^{81}BrIO_6Si$: 691.0411; found: 691.0313; elemental analysis calcd (%) for $C_{34}H_{44}BrIO_6Si$ (783.6): C 52.11, H 5.66; found: C 52.19, H 5.83.

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