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Supporting Information

for

Fragmentation of Carbohydrate Anomeric Alkoxy Radicals. A New Synthesis of Chiral 1-Halo-1-iodo Alditols

Concepción C. González, Alan R. Kennedy, Elisa I. León, Concepción Riesco-Fagundo, and Ernesto Suárez*

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*-(tetraisopropyldisiloxane-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 CH_2Cl_2. 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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 12.4–13.7 (8 × 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): ν = 3578, 1650, 1465, 1166 cm^{-1}; MS (70 eV, EI): *m/z* (%): 345 (100) [M^+ – C_3H_7], 327 (11), 263 (24), 235 (62), 135 (22), 119 (25), 81 (95); HRMS (EI): calcd for $C_{15}H_{29}O_5Si_2$ 345.1554; found 345.1529; elemental analysis calcd for $C_{18}H_{36}O_5Si_2$ (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-di-siloxane-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 → 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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 12.9 (CH), 13.1 (CH), 13.3 (CH), 13.6 (CH), 17.1–17.8 (8 × CH_3), 27.2 (3 × 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): ν = 1728, 1655, 1465, 1280 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 429 (4) [M^+ – C_3H_7], 399 (4), 371 (3), 345 (3), 319 (100), 119 (7), 81 (22); HRMS (EI): calcd for $C_{20}H_{37}O_6Si_2$: 429.2129; found: 429.2142; elemental analysis calcd (%) for $C_{23}H_{44}O_6Si_2$ (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-D-*arabino*-hex-5-enitol (2). To a solution of 2,6-anhydro-5-deoxy-3,4-*O*-isopropylidene-D-*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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 × CH), 133. 6 (C), 144.5 (CH), 148.7 (2 × C), 162.4 (C); IR ($CHCl_3$): ν = 3102, 1741, 1550, 1344 cm^{-1}; MS (70 eV, EI): *m/z* (%): 365 (7) [M^+ – Me], 305 (31), 195 (100); HRMS(EI): calcd for $C_{15}H_{13}N_2O_9$: 365.0621; found: 365.0611; elemental analysis calcd (%) for $C_{16}H_{16}N_2O_9$ (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-D-glucopyranose and -D-mannopyranose (3).[1] From 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*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 ($CHCl_3$): ν = 3595, 1751 cm^{-1}; MS (70 eV, EI): *m/z* (%): 291 (3) [M^+ – OH], 259 (4), 248 (3), 235 (4), 103 (100); HRMS (EI): calcd for $C_{12}H_{16}FO_7$ 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 (CCl_4): ν = 3616, 3418, 1253, 1154 cm^{-1}; MS (70 eV, EI): *m/z* (%): 467 (3) [M^+ – C_4H_9], 449 (1), 375 (3), 335 (14), 115 (20), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}FO_5Si_3$ 467.2481; found 467.2454; elemental analysis calcd (%) for $C_{24}H_{53}FO_5Si_3$ (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 (CCl_4): ν = 3611, 3425, 1472, 1087 cm^{-1}; MS (70 eV, EI): *m/z* (%): 485/483 (2/5) [M^+ – C_4H_9], 353/351 (3/8), 301 (4), 273 (7), 219 (10), 171 (6), 147 (21), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}{}^{35}ClO_5Si_3$ 483.2185; found 483.2145; elemental analysis calcd (%) for $C_{24}H_{53}ClO_5Si_3$ (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 (CCl_4): ν = 3607, 3416, 1255, 1116 cm^{-1}; MS (70 eV, EI): *m/z* (%): 529/527 (4/4) [M^+ – C_4H_9], 447 (3), 397/395 (10/10), 315 (10), 171 (14), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}{}^{81}BrO_5Si_3$ 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-D-mannopyranose and -D-glucopyranose (10).[8] From 1,5-anhydro-3,4,6-tris-*O*-[*tert*-butyl(dimethyl)silyl]-2-deoxy-D-*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-D-mannopyranose and -D-glucopyranose (11).[9] From 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*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-D-galactopyranosyl)-D-mannopyranose and -D-glucopyranose (12). 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 (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-gluco-pyranose (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 ($CHCl_3$): 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 $C_{24}H_{33}IO_{16}$, 704.0813 found 704.0817; elemental analysis calcd (%) for $C_{24}H_{33}IO_{16}$ (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 ($CHCl_3$): ν = 3594, 3522, 2990, 2936, 2837 cm^{-1}; MS (70 eV, EI): *m/z* (%): 239/237 (17/55) [$M^+ - CH_3$], 101 (100); HRMS (EI): calcd for $C_9H_{14}{}^{37}ClO_5$ 239.0500; found 239.0497; elemental analysis calcd (%) for $C_{10}H_{17}ClO_5$ (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 ($CHCl_3$): ν = 3591, 3520, 2990, 2937 cm^{-1}; MS (70 eV, EI): *m/z* (%): 283/281 (60/59) [$M^+ - CH_3$], 101 (100); HRMS (EI): calcd for $C_9H_{14}{}^{81}BrO_5$ 283.0004; found 282.9951; elemental analysis calcd (%) for $C_{10}H_{17}BrO_5$ (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 ($CHCl_3$): ν = 3594, 3512, 3012, 2990, 2936 cm^{-1}; MS (70 eV, EI):

m/z (%): 420 (60) [M^+ – CH_3], 101 (100); HRMS (EI): calcd for $C_9H_{14}IO_5$ 328.9886; found 328.9903; elemental analysis calcd (%) for $C_{10}H_{17}IO_5$ (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); ^{1}H NMR (C_6D_6): 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, ^3J(F,H) = 12.8 Hz, 1H), 5.60 (ddd, *J* = 2.5, 4.6 Hz, ^3J(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, ^4J(F,H) = 1.6 Hz, 1H), 6.46 (dd, *J* = 4.6 Hz, ^2J(F,H) = 49.1 Hz, 1H), 6.51 (dd, *J* = 5.7 Hz, ^2J(F,H) = 48.8 Hz, 1H), 7.35 (s, 1H), 7.40 (s, 1H); ^{13}C NMR (C_6D_6): δ = 19.9 (CH_3), 20.0 (2 × CH_3), 20.1 (3 × CH_3), 61.4 (2 × CH_2), 67.3 (2 × CH), 68.1 (2 × CH), 68.2 (CH), 68.5 (CH), 69.6 (^1J(F,C) = 258.3 Hz, CH), 70.5 (^1J(F,C) = 256.2 Hz, CH), 72.7 (^2J(F,C) = 24.4 Hz, CH), 73.2 (^2J(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 $C_{12}H_{16}FO_8$: 307.0829; found: 307.0852; elemental analysis calcd (%) for $C_{12}H_{16}FIO_8$ (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); ^{1}H 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 × CH_3), 20.1 (CH_3), 20.2 (2 × CH_3), 20.4 (CH_3), 24.6 (CH), 25.3 (CH), 61.6 (2 × CH_2), 67.8 (CH), 68.4 (CH), 68.5 (CH), 69.3 (CH), 74.1 (2 × 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^+ – I], 223/221 (85), 175 (38), 157 (27), 139 (79); HRMS (EI): calcd for $C_{12}H_{16}{}^{35}ClO_8$: 323.0534; found: 323.0526; elemental analysis calcd (%) for $C_{12}H_{16}ClIO_8$ (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-D-arabinitol (21). Crystalline solid (99%): diastereoisomeric mixture (1:1); ^{1}H 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 × CH_3), 20.1 (CH_3), 20.2 (2 × CH_3), 20.3 (CH_3), 61.6 (2 × CH_2), 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 $C_{10}H_{12}{}^{81}BrIO_6$: 435.8842; found: 435.8872; elemental analysis calcd (%) for $C_{12}H_{16}BrIO_8$ (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); ^{1}H 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, ^3J(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, ^2J(F,H) = 51.2 Hz, 1H), 6.98 (dd, J = 3.4 Hz, ^2J(F,H) = 48.7 Hz, 1H), 8.09 (s, 2H); ^{13}C NMR: δ = –5.4 (CH_3), –5.3 (3 × CH_3), –4.8 (CH_3), –4.6 (CH_3), –4.5 (CH_3), –4.4 (CH_3), –4.3 (3 × CH_3), –4.1 (CH_3), 18.0 (C), 18.1 (C), 18.2 (4 × C), 25.7 (6 × CH_3), 25.8 (6 × CH_3), 25.9 (6 × CH_3), 61.4 (CH_2), 61.8 (CH_2), 71.9 (CH), 72.0 (CH), 73.7 (^1J(F,C) = 258.3 Hz, CH), 74.8 (CH), 75.5 (CH), 77.3 (^2J(F,C) = 17.5 Hz, CH), 79.2 (^2J(F,C) = 16.0 Hz, CH), 78.8 (^1J(F,C) = 253.8 Hz, CH), 160.4 (CH), 160.5 (CH); IR

(CCl_4): ν = 1732, 1257, 1174 cm^{-1}; MS (70 eV, EI): *m/z* (%): 593 (1) [M^+ – C_4H_9], 473 (18), 389 (18), 347 (17), 301 (29), 297 (15), 115 (32), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}FIO_5Si_3$: 593.1447; found: 593.1463; elemental analysis calcd (%) for $C_{24}H_{52}FIO_5Si_3$ (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); ^{13}C NMR: δ = –5.3 (3 × CH_3), –4.9 (3 × CH_3), –4.7 (CH_3), –4.6 (CH_3), –4.2 (CH_3), –4.1 (CH_3), –3.9 (CH_3), –3.8 (CH_3), 18.0 (2 × C), 18.2 (2 × C), 18.3 (2 × C), 25.6–25.9 (18 × CH_3), 28.7 (CH), 33.6 (CH), 61.8 (CH_2), 62.1 (CH_2), 72.9 (CH), 73.3 (CH), 74.8 (CH), 75.8 (CH), 79.9 (CH), 81.3 (CH), 160.6 (2 × CH); IR (CCl_4): ν = 1731, 1472, 1109 cm^{-1}; MS (70 eV, EI): *m/z* (%): 611/609 (>1) [M^+ – C_4H_9], 583/581 (>1/1), 565/563 (>1/2), 407/405 (3/8), 301 (29), 147 (15), 115 (22), 73 (100); HRMS (EI): calcd for $C_{20}H_{43}{}^{35}ClIO_5Si_3$: 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-D-arabinitol (25). Oil (91%): diastereoisomeric mixture (2:1); ^{1}H 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 × CH_3), –4.9 (2 × CH_3), –4.7 (2 × CH_3), –4.6 (2 × CH_3), –4.2 (2 × CH_3), –3.8 (2 × CH_3), 11.4 (CH), 15.2 (CH), 18.1 (2 × C), 18.2 (2 × C), 18.3 (2 × C), 25.8 (9 × CH_3), 25.9 (9 × CH_3), 61.9 (CH_2), 62.2 (CH_2), 73.7 (CH), 73.8 (CH), 74.3 (CH), 74.5 (CH), 80.3 (CH), 81.2 (CH), 160.5 (2 × CH); IR (CCl_4): ν = 1731, 1257, 1174 cm^{-1}; MS (70 eV, EI): *m/z* (%): 655/653 (1/1) [M^+ – C_4H_9], 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)-D-arabinitol (28). Crystalline solid (85%): diastereoisomeric mixture

(4:3); ^{1}H 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, ^{3}J(F,H) = 13.3 Hz, 1H), 7.038 (dd, J = 9.1 Hz, ^{2}J(F,H) = 47.0 Hz, 1H), 7.042 (dd, J = 6.6 Hz, ^{2}J(F,H) = 50.0 Hz, 1H), 7.97 (s, 1H), 7.99 (s, 1H); ^{13}C NMR: δ = 20.4–21.1(12 × CH_3), 61.1 (CH_2), 61.2 (CH_2), 61.3 (CH_2), 61.5 (CH_2), 66.7–76.6 (16 × CH), 101.7 (CH), 101.9 (CH), 159.4 (2 × CH), 169.2–170.5 (12 × 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 $C_{24}H_{31}FIO_{16}$: 721.0641; found: 721.0567; elemental analysis calcd (%) for $C_{24}H_{32}FIO_{16}$ (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: ^{1}H 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: δ = 20.5–20.7 (6 × CH_3), 28.8 (CH), 61.1 (CH_2), 61.3 (CH_2), 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 × C); the other isomer: ^{1}H NMR: δ = 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, 10.4Hz, 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: δ = 20.5–21.2 (6 × CH_3), 26.9 (CH), 61.1–61.3 (2 × 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 × C); IR: ν = 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 $C_{24}H_{32}{}^{35}ClIO_{16}$: 738.0424; found: 738.0332; elemental analysis calcd (%) for $C_{24}H_{32}ClIO_{16}$ (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); ^{1}H NMR: δ = 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: δ = 9.6 (CH), 10.7 (CH), 19.1–21.1 (12 × CH_3), 61.1 (2 × CH_2), 61.3 (2 × CH_2), 66.7 (CH), 66.8 (CH), 68.8 (2 × 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 × CH), 169.5–170.4 (12 × C); IR: ν = 3477, 3026, 1743, 1371, 1232, 1077, 1048 cm^{-1}; MS (70 eV, EI): m/z (%): 724/722 (1) [M^+ – AcOH], 657/655 (8), 331 (100); HRMS (EI): calcd for $C_{22}H_{28}{}^{81}BrIO_{14}$: 723.9687; found: 723.9698; elemental analysis calcd (%) for $C_{24}H_{32}BrIO_{16}$ (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*-isopropyl-idene-D-arabinitol (32). Oil (83%): diastereoisomeric mixture (3:2); ^{1}H NMR: δ = (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: δ = (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 (CH_3), 26.7 (CH_3), 27.6 (CH), 61.8 (CH_3), 67.0 (CH_2), 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 $C_9H_{13}{}^{37}ClIO_5$: 364.9467; found: 364.9486; elemental analysis calcd (%) for $C_{10}H_{16}ClIO_5$ (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*-isopropyl-idene-D-arabinitol (33). Oil (92%): diastereoisomeric mixture (3:2); ^1H NMR (C_6D_6): 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); ^{13}C NMR: δ = (major): 10.0 (CH), 25.4 (CH_3), 26.7 (CH_3), 62.1 (CH_3), 66.7 (CH_2), 72.8 (CH), 74.3 (CH), 84.4 (CH), 110.1 (C), 159.9 (CH); (minor): 9.9 (CH), 25.4 (CH_3), 26.7 (CH_3), 62.0 (CH_3), 66.9 (CH_2), 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 $C_9H_{13}{}^{81}BrIO_5$: 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-D-galactopyranose (35).[1] From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy-D-*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-D-talopyranose and -D-galactopyranose (36). From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy-D-*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-D-talopyranose and -D-galactopyranose (37). From 1,3,4-tri-*O*-acetyl-2,6-anhydro-5-deoxy-D-*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%); ^{1}H 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 × CH_3),18.2 (2 × C), 18.5 (2 × C), 18.6 (2 × C), 25.9 (6 × CH_3), 26.0 (6 × CH_3), 26.1 (6 × 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 × 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(F,C) = 25.1 Hz, CH); IR (CCl_4): ν = 3618, 3451, 1472, 1169, 1098 cm^{-1}; MS (70 eV, EI): *m/z* (%): 467 (3) [M^+ – C_4H_9], 335 (7), 273 (5), 203 (10), 147 (20), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}FO_5Si_3$ 467.2481; found 467.2456; elemental analysis calcd (%) for $C_{24}H_{53}FO_5Si_3$ (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-D-talopyranose and -D-galactopyranose (40). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol.[12] Oil (74%); IR (CCl_4): ν = 3596, 3434, 1472, 1045 cm^{-1}; MS (70 eV, EI): *m/z* (%): 485/483 (2/5) [M^+ – C_4H_9], 449/447 (1/4), 353/351 (1/3), 301 (4), 273 (5), 171 (15), 147 (22), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}{}^{35}ClO_5Si_3$ 483.2185; found 483.2183; elemental analysis calcd (%) for $C_{24}H_{53}ClO_5Si_3$ (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-D-talopyranose and -D-galactopyranose (41). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol.[12] Oil (86%); IR ($CHCl_3$): ν = 3688, 3602, 1472, 1255, 1163 cm^{-1}; MS (70 eV, EI): *m/z* (%): 529/527 (6/6) [M^+ – C_4H_9], 447 (4), 429 (3), 397/395 (11), 301 (10), 273 (16), 147 (26), 117 (20), 73 (100); HRMS (EI): calcd for $C_{20}H_{44}{}^{81}BrO_5Si_3$ 529.1660; found 529.1602; elemental analysis calcd (%) for $C_{24}H_{53}BrO_5Si_3$ (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-D-talopyranose and -D-galactopyranose (42). From 2,6-anhydro-1,3,4-tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*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 $C_{20}H_{44}IO_5Si_3$: 575.1568; found: 575.1541; elemental analysis calcd (%) for $C_{24}H_{53}IO_5Si_3$ (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-D-galactopyranose (43). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol.[13] Crystalline solid (55%); ^{1}H 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(F,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(F,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 × CH_3),–5.2 (4 × CH_3), 18.1 (2 × C), 18.2 (C), 18.3 (C), 20.7 (2 × CH_3), 25.47 (3 × CH_3), 25.52 (3 × CH_3), 25.7 (3 × CH_3), 25.8 (3 × CH_3), 61.1 (CH_2), 61.6 (CH_2), 67.5 (^2J(F,C) = 17.9 Hz, CH), 69.6 (CH), 70.1 (br s, CH), 71.3 (br s, CH), 71.7 (^2J(F,C) = 18.2 Hz, CH), 74.1 (CH), 89.3 (^1J(F,C) = 186.3

Hz, CH), 90.9 (^2J(F,C) = 22.9 Hz, CH), 92.9 (^1J(F,C) = 183.2 Hz, CH), 94.9 (^2J(F,C) = 23.8 Hz, CH), 169.8 (C), 169.9 (C); IR (CCl_4): ν = 3616, 3446, 1753, 1255, 1229 cm^{-1}; MS (70 eV, EI): *m/z* (%): 437 (1) [M^+ – Me], 395 (12), 335 (15), 315 (9), 203 (10), 117 (62), 73 (100); HRMS (EI): calcd for $C_{19}H_{38}FO_6Si_2$ 437.2191; found 437.2163; elemental analysis calcd (%) for $C_{20}H_{41}FO_6Si_2$ (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-D-talopyranose and -D-galactopyranose (44). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol.[13] Oil (50%); IR ($CHCl_3$): ν = 3689, 3603, 1744, 1115, 1054 cm^{-1}; MS (70 eV, EI): *m/z* (%): 413/411 (1/4) [M^+ – C_4H_9], 395/393 (1/3), 353/351 (1/4), 259 (5), 219 (12), 117 (64), 75 (100); HRMS (EI): calcd for $C_{16}H_{30}{}^{35}ClO_5Si_2$ 393.1320; found 393.1301; elemental analysis calcd (%) for $C_{20}H_{41}ClO_6Si_2$ (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-D-talopyranose and -D-galactopyranose (45). From 3-*O*-acetyl-2,6-anhydro-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-D-*arabino*-hex-5-enitol.[13] Oil (91%). IR ($CHCl_3$): ν = 3692, 3596, 1742, 1472, 1374, 1112 cm^{-1}; MS (70 eV, EI): *m/z* (%): 457/455 (3/3) [M^+– C_4H_9], 397/395 (3/3), 315 (7), 265/263 (10/10), 184 (15), 129 (16), 117 (97), 73 (100); HRMS (EI): calcd for $C_{16}H_{32}{}^{81}BrO_6Si_2$ 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-D-galacto-pyranose (46). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene-D-*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-D-talopyranose and -D-galactopyranose (47). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene-D-*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-D-talopyranose and -D-galactopyranose (48). From 2,6-anhydro-1-*O*-benzyl-5-deoxy-3,4-*O*-isopropylidene-D-*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-talo-pyranose 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*-isopropyl-idene-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 diasteroisomeric 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 × CH), 129.5 (4 × CH), 133.4 (C), 133.5 (C), 148.6 (4 × C), 162.4 (2 × C); IR ν = 3614, 3102, 2990, 1744, 1550, 1343, 1274, 1166 cm^{-1}; MS (70 eV, EI): *m/z* (%): 401 (59) [M^+ – $^{\cdot}$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*-isopropyl-idene-D-talopyranose and -D-galactopyranose (51). From 2,6-anhydro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-3,4-*O*-isopropylidene-D-*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-D-talopyranose and -D-galactopyranose (52). From 2,6-anhydro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-3,4-*O*-isopropylidene-D-*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*-(oxo-methylene)-D-galactopyranose (53). From 2,6-anhydro-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-3,4-*O*-(oxomethylene)-D-*arabino*-hex-5-enitol.[15] Crystalline solid (30%); major isomer: ^1H NMR

(500 MHz, $CDCl_3$): 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(F,H) = 47.6 Hz, 1H), 4.90–4.95 (m, 1H), 5.03 (ddd, J = 6.4, 6.4 Hz, ^3J(F,H) = 12.8 Hz, 1H), 5.39 (dd, J = 3.8, Hz, ^3J(F,H) = 7.1 Hz, 1H); major isomer: ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.6 (2 × CH_3), 18.2 (C), 25.7 (3 × CH_3), 61.0 (CH_2), 67.2 (CH), 73.7 (^2J(F,C) = 29.2 Hz, CH), 74.5 (^3J(F,C) = 4.0 Hz, CH), 86.57 (^1J(F,C) = 188.1 Hz, CH), 89.1 (^2J(F,C) = 19.1 Hz, CH), 153.6 (C); IR ($CHCl_3$): ν = 3595, 3370, 1821, 1113, 1073 cm^{-1}; MS (70 eV, EI): m/z (%): 265 (5) [M^+ – C_4H_9], 217 (1), 203 (12), 175 (23), 117 (89), 75 (100); HRMS (EI): calcd for $C_9H_{14}FO_6Si$ 265.0544; found 265.0534; elemental analysis calcd (%) for $C_{13}H_{23}FO_6Si$ (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*-(oxo-methylene)-D-talopyranose and -D-galactopyranose (54). From 2,6-anhydro-1-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-3,4-*O*-(oxomethylene)-D-*arabino*-hex-5-enitol.[15] Oil (89%); IR (CCl_4): ν = 3604, 1843, 1110, 1074 cm^{-1}; MS (70 eV, EI): m/z (%): 283/281 (<1/2) ([M^+ – C_4H_9], 219 (13), 191 (23), 155 (12), 117 (100), 75 (80); HRMS (EI): calcd for $C_9H_{14}{}^{35}ClO_6Si$ 281.0248; found 281.0277; elemental analysis calcd (%) for $C_{13}H_{23}ClO_6Si$ (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*-(oxo-methylene)-D-talopyranose and -D-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 ($CHCl_3$): ν = 3692, 3597, 1817, 1113, 1070 cm^{-1}; MS (70 eV, EI): *m/z* (%): 327/325 (1/1) [M^+ – C_4H_9], 253/251 (2/2), 237/235 (13/13), 155 (13), 139/137 (7/7), 129 (16), 117 (100), 75 (89); HRMS (EI): calcd for $C_9H_{14}{}^{79}BrO_6Si$ 324.9743; found 324.9743; elemental analysis calcd (%) for $C_{13}H_{23}BrO_6Si$ (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 ($CHCl_3$): 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 $C_{13}H_{22}IO_5Si$ 413.0281; found 413.0319; elemental analysis calcd (%) for $C_{13}H_{23}IO_6Si$ (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*-(tetraisopropyldisiloxane-1,3-diyl)-D-galactopyranose (57). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*arabino*-hex-5-enitol (**1**). Oil (72%); ^1H NMR (500 MHz, $CDCl_3$): 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, ^2J(F,H) = 52.5 Hz, 1H), 4.88 (m, 1H), 4.91 (ddd, *J* = 3.6, 10.2 Hz, ^2J(F,H) = 51.1 Hz,

1H), 5.13 (ddd, J = 2.9, 10.2 Hz, ^{3}J(F,H) = 10.2 Hz, 1H), 5.47 (br s, 1H), 5.51 (ddd, J = 2.8, 9.9 Hz, ^{3}J(F,H) = 9.9 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.2 (2 × CH), 13.7 (4 × CH), 14.0 (2 × CH), 17.5 (4 × CH_3), 17.7 (4 × CH_3), 18.0 (4 × CH_3), 18.2 (4 × CH_3), 27.6 (6 × CH_3), 39.6 (2 × C), 59.4 (CH_2), 59.6 (CH_2), 68.5 (CH), 69.3 (CH), 70.3 (CH), 70.8 (^{2}J(F,C) = 15.8 Hz, CH), 73.9 (^{2}J(F,C) = 16.1 Hz, CH), 74.7 (CH), 87.2 (^{1}J(F,C) = 187.3 Hz, CH), 91.3 (^{2}J(F,C) = 20.6 Hz, CH), 95.5 (^{2}J(F,C) = 22.6 Hz, CH), 179.0 (2 × C); IR (CCl_4): ν = 3618, 1736, 1464, 1142 cm^{-1}; MS (70 eV, EI): *m/z* (%): 491 (1) [M^+ – OH], 465 (17), 363 (10), 319 (46), 235 (22), 57 (100); HRMS (EI): calcd for $C_{23}H_{44}FO_6Si_2$ 491.2661; found 491.2639; elemental analysis calcd (%) for $C_{23}H_{45}FO_7Si_2$ (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*-(tetraisopropyldisiloxane-1,3-diyl)-D-talopyranose and -D-galactopyranose (58). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*arabino*-hex-5-enitol (**1**). Oil (76%); IR (CCl_4): ν = 3614, 1735, 1039 cm^{-1}; MS (70 eV, EI): *m/z* (%): 483/481 (7/15) [M^+ – C_3H_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 $C_{20}H_{38}{}^{35}ClO_7Si_2$ 481.1845; found 481.1826; elemental analysis calcd (%) for $C_{23}H_{45}ClO_7Si_2$ (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*-(tetraisopropyldisiloxane-1,3-diyl)-D-talopyranose and -D-galactopyranose (59). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*arabino*-hex-5-enitol (**1**). Oil (92%). IR ($CHCl_3$): ν = 3605, 1734, 1465, 1107, 1034 cm^{-1}; MS (70 eV, EI): *m/z* (%): 527/525 (7/7) [M^+ – C_3H_7], 451/449 (2/2), 425/423 (4/4), 343 (10), 319 (31), 235 (20), 86 (16), 57 (100); HRMS (EI): calcd for $C_{20}H_{38}{}^{81}BrO_7Si_2$ 527.1319; found 527.1330; elemental analysis calcd (%) for $C_{23}H_{45}BrO_7Si_2$ (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*-(tetraisopropyldisiloxane-1,3-diyl)-D-talopyranose and -D-galactopyranose (60). From 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*arabino*-hex-5-enitol (**1**). Oil (83%): IR($CHCl_3$): ν = 3592, 3337, 2947, 2868, 1727 cm^{-1}; MS (70 eV, EI): *m/z* (%): 573 (2) [M^+ – C_3H_7], 555 (<1), 471 (<1), 57 (100); HRMS (EI): calcd for $C_{20}H_{38}IO_7Si_2$ 573.1201; found 573.1121; elemental analysis calcd (%) for $C_{23}H_{45}IO_7Si_2$ (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, ^3J(F,H) = 11.0 Hz, 1H), 5.33 (ddd, *J* =

1.8, 10.8 Hz, ^{3}J(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, ^{2}J(F,H) = 47.7 Hz, 1H), 6.89 (dd, J = 1.8 Hz, ^{2}J(F,H) = 48.1 Hz, 1H), 8.01 (s, 1H), 8.03 (s, 1H); ^{13}C NMR: δ = 20.5 (2 × CH_3), 20.6 (2 × CH_3), 20.7 (2 × CH_3), 61.6 (CH_2), 61.7 (CH_2), 67.3 (CH), 67.4 (CH), 67.9 (CH), 68.5 (^{1}J(F,C) = 265.6 Hz, CH), 69.6 (CH), 71.0 (^{1}J(F,C) = 254.5 Hz, CH), 71.02 (^{2}J(F,C) = 22.5 Hz, CH), 72.0 (^{2}J(F,C) = 18.7 Hz, CH), 159.6 (CH), 159.7 (CH), 168.8 (C), 169.0 (C), 169.2 (2 × C), 170.2 (2 × C); IR (CCl_4): ν = 1762, 1737, 1205, 1156 cm^{-1}; MS (70 eV, EI): m/z (%): 307 (100) [M^+ – I], 247 (6), 219 (7), 205 (11), 159 (13), 139 (25); HRMS (EI): calcd for $C_{12}H_{16}FO_8$: 307.0829; found: 307.0838; elemental analysis calcd (%) for $C_{12}H_{16}FIO_8$ (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-D-arabinitol (62). Crystalline solid (96%): diastereoisomeric mixture (3:2); ^{1}H NMR (C_6D_6): δ = (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): δ = 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): δ = 19.9 (CH_3), 20.0

(2 × CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 25.1 (CH), 27.6 (CH), 62.1 (2 × CH_2), 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 $C_{10}H_{12}{}^{37}ClIO_6$: 391.9338; found: 391.9404; elemental analysis calcd (%) for $C_{12}H_{16}ClIO_8$ (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); ^{1}H NMR (C_6D_6): 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); ^{13}C NMR (C_6D_6): δ = 7.1 (CH), 8.8 (CH), 19.9 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 20.2 (2 × CH_3), 20.3 (CH_3), 62.1 (CH_2), 62.13 (CH_2), 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 $C_{10}H_{12}{}^{81}BrIO_6$: 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); ^{1}H 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 × CH_3), −5.1 (CH_3), −4.8 (CH_3), −4.5 (3 × CH_3), −4.1 (CH_3), −3.97 (CH_3), −3.96 (CH_3), −3.8 (CH_3), 18.06 (C), 18.12 (C), 18.3 (4 × C), 25.7 (3 × CH_3), 25.8 (3 × CH_3), 25.9 (3 × CH_3), 25.91 (3 × CH_3), 26.0 (3 × CH_3), 26.1 (3 × CH_3), 60.5 (CH_2), 61.8 (CH_2), 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 × CH); IR (CCl_4): ν = 1731, 1257, 1124, 1072 cm^{-1}; MS (70 eV, EI): *m/z* (%): 593 (1) [M^+ − C_4H_9], 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); ^{1}H 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 (CH_3), –5.3 (CH_3), –5.1 (CH_3), –4.7 (CH_3), –4.6 (CH_3), –4.4 (CH_3), –3.8 (2 × CH_3), –3.7 (2 × CH_3), –3.5 (2 × CH_3), 18.11 (C), 18.15 (C), 18.2 (C), 18.5 (3 × C), 25.7 (3 × CH_3), 25.86 (3 × CH_3), 25.9 (3 × CH_3), 26.0 (3 × CH_3), 26.1 (3 × CH_3), 26.4 (3 × CH_3), 32.6 (CH), 36.8 (CH), 60.9 (CH_2), 61.7 (CH_2), 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 (CCl_4): ν = 1731, 1472, 1121 cm^{-1}; MS (70 eV, EI): m/z (%): 611/609 (>1) [M^+ – C_4H_9], 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); ^{1}H 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 × CH_3), –5.4 (CH_3), –5.3 (CH_3), –4.48 (CH_3), –4.45 (CH_3), –4.3 (CH_3), –3.75 (CH_3), –3.70 (CH_3), –3.63 (CH_3), –3.3 (CH_3), –3.2 (CH_3), 16.1 (3 × C), 18.2 (3 × C), 18.6 (CH), 19.3 (CH), 25.7 (3 × CH_3), 25.8 (3 × CH_3), 26.0 (6 × CH_3), 26.3 (3 × CH_3), 26.4 (3 × CH_3), 60.9 (CH_2), 61.5 (CH_2), 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 (CCl_4): ν = 1730, 1257, 1178, 1132 cm^{-1}; MS (70 eV, EI): m/z (%): 655/653 (1) [M^+ – C_4H_9], 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); ^{1}H 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 × CH_3), −5.4 (CH_3), −4.2 (3 × CH_3), −3.6 (CH_3), 18.1 (C), 18.3 (2 × C), 18.5 (C), 20.9 (2 × CH_3), 25.6 (3 × CH_3), 25.7 (3 × CH_3), 25.8 (3 × CH_3), 25.9 (3 × CH_3), 31.2 (CH), 32.9 (CH), 61.6 (CH_2), 61.7 (CH_2), 72.2 (3 × CH), 72.4 (CH), 77.2 (CH), 77.6 (CH), 160.1 (CH), 160.2 (CH), 169.1 (C), 169.2 (C); IR (CCl_4): ν = 1759, 1734, 1470, 1173 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 539/537 (3/6) [M^+ − C_4H_9], 433/431 (1/3), 351/349 (3/6), 319/317 (1/3), 285 (13), 117 (53), 103 (31), 75 (100); HRMS (EI): calcd for $C_{16}H_{31}{}^{35}ClIO_6Si_2$: 537.0393; found: 537.0393; elemental analysis calcd (%) for $C_{20}H_{40}ClIO_6Si_2$ (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); ^{1}H 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: δ = −5.6 (2 × CH_3), −5.5 (2 × CH_3), −4.2 (2 × CH_3), −4.0 (CH_3), −3.6 (CH_3), 13.6 (CH), 14.7 (CH), 18.1 (2 × C), 18.4 (2 × C), 20.9 (2 × CH_3), 25.8 (3 × CH_3), 25.86 (3 × CH_3), 25.9 (3 × CH_3), 26.1 (3 × CH_3), 61.6 (2 × 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: ν = 1748, 1427, 1257, 1178 cm^{-1}; MS (70 eV, EI): m/z (%): 583/581 (4/4) [M^+ − C_4H_9], 523/521 (2/2), 477/475 (2/2), 441 (7), 187 (10), 117 (97), 73 (100); HRMS (EI): calcd for $C_{16}H_{31}{}^{81}BrIO_6Si_2$: 582.9867; found: 582.9838; elemental analysis calcd (%) for $C_{20}H_{40}BrIO_6Si_2$ (639.5): C 37.56, H 6.30; found: C 37.56, H 6.60.

1-*O*-[*tert*-Butyl(dimethyl)silyl]-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-3,4-*O*-(oxomethylene)-D-arabinitol (79). Oil (70%): diastereoisomeric mixture (3:2); ^{1}H NMR: δ = 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(F,H) = 16.1 Hz, 1H), 5.18 (ddd, J = 6.3, 7.3 Hz, ^3J(F,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(F,H) = 49.6 Hz, 1H), 6.97 (dd, J = 5.5 Hz, ^2J(F,H) = 49.6 Hz, 1H), 8.02 (s, 1H), 8.07 (s, 1H); ^{13}C NMR: δ = −5.6 (2

× CH_3), −5.5 (2 × CH_3), 18.1 (C), 18.2 (C), 25.7 (3 × CH_3), 25.8 (3 × CH_3), 59.2 (CH_2), 60.3 (CH_2), 63.7 (^1J(F,C) = 256.9 Hz, CH), 64.8 (^1J(F,C) = 257.6 Hz, CH), 68.4 (CH), 69.2 (CH), 74.9 (CH), 75.6 (CH), 79.8 (^2J(F,C) = 25.1 Hz, CH), 81.0 (^2J(F,C) = 19.1 Hz, CH), 152.2 (2 × C), 158.8 (CH), 159.1 (CH); IR (CCl_4): ν = 1845, 1737, 1161, 1091 cm^{-1}; MS (70 eV, EI): *m/z* (%): 391 (4) [M^+ − C_4H_9], 301 (9), 227 (14), 174 (11), 117 (20), 103 (100); HRMS (EI): calcd for $C_9H_{13}FIO_6Si$: 390.9510; found: 390.9526; elemental analysis calcd (%) for $C_{13}H_{22}FIO_6Si$ (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: δ = 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: δ = −5.6 (2 × CH_3), −5.5 (CH_3), −5.4 (CH_3), −2.9 (CH), −0.6 (CH), 18.1 (2 × C), 25.6 (6 × 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 × CH); IR (CCl_4): ν = 1842, 1736, 1162 cm^{-1}; MS (70 eV, EI): *m/z* (%): 453/451 (2/2) [M^+ − C_4H_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); ^{1}H 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 × CH), 13.2 (2 × CH), 13.4 (CH), 14.8 (CH), 16.8–17.8 (16 × CH_3), 27.2 (3 × CH_3), 29.9 (3 × 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 × 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); ^{1}H 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 × CH), 14.2 (CH), 15.0 (CH), 16.9–17.8 (16 × CH_3), 24.8 (CH), 27.0 (3 × CH_3), 27.1 (3 × CH_3), 32.6 (CH), 39.1 (C), 39.2 (C), 57.4 (CH_2), 57.5 (CH_2), 67.9 (CH), 69.7 (CH), 70.0 (CH), 71.0 (CH), 74.3 (CH), 75.4 (CH), 160.1 (2 × CH), 176.5 (2 × C); IR (CCl_4): ν = 1749, 1733, 1168, 1147, 1040 cm^{-1}; MS (70 eV, EI): m/z (%): 609/607 (1/3) [M^+ – C_3H_7], 581/579 (2/5), 319 (6), 263 (44), 85 (14), 57 (100); HRMS (EI): calcd for $C_{20}H_{37}{}^{35}ClIO_7Si_2$: 607.0811; found: 607.0800; elemental analysis calcd (%) for $C_{23}H_{44}ClIO_7Si_2$ (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); ^{1}H 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: δ = 7.9 (CH), 12.2 (CH), 12.3 (CH), 13.2 (5 × CH), 14.5 (CH), 15.1 (CH), 17.0–17.9 (16 × CH_3), 27.08 (3 × CH_3), 27.13 (3 × CH_3), 38.9 (C), 39.2 (C), 57.5 (2 × CH_2), 69.2 (CH), 69.7 (CH), 69.9 (2 × CH), 74.5 (CH), 75.3 (CH), 160.2 (2 × CH), 176.5 (2 × C); IR (CCl_4): ν = 1749, 1734, 1167, 1144, 1091 cm^{-1}; MS (70 eV, EI): m/z (%): 653/651 (6/6) [M^+ – C_3H_8], 625/623 (16/16), 441 (17), 319 (11), 289 (14), 263 (72), 135 (11), 107 (20), 57 (100); HRMS (EI): calcd for $C_{20}H_{35}{}^{81}BrIO_7Si_2$: 651.0129; found: 651.0147; elemental analysis calcd (%) for $C_{23}H_{44}BrIO_7Si_2$ (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): ν = 3614, 1759, 1239 cm^{-1}; MS (70 eV, EI): m/z (%): 249 (1) [M^+ – H], 233 (10), 172 (4), 144 (21), 130 (40), 117 (100); HRMS (EI): calcd for $C_{10}H_{14}FO_6$ 249.0774; found 249.0789; elemental analysis calcd (%) for $C_{10}H_{15}FO_6$ (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): ν =

3610, 3481, 1758 cm^{-1}; MS (70 eV, EI): *m/z* (%): 251/249 (2/5) [M^+ – OH], 208/206 (2/6), 171 (20), 134 (85), 87 (100); HRMS (EI): calcd for $C_{10}H_{14}{}^{35}ClO_5$ 249.0530; found 249.0541; elemental analysis calcd (%) for $C_{10}H_{15}ClO_6$ (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^+ – 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 $C_{10}H_{14}{}^{79}BrO_5$ 293.0025; found 292.9995; elemental analysis calcd (%) for $C_{10}H_{15}BrO_6$ (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^+ – OH], 341 (5), 298 (37), 253 (10), 226 (21), 212 (45), 125 (100); HRMS (EI): calcd for $C_{10}H_{15}IO_6$ 357.9913; found 357.9945; elemental analysis calcd (%) for $C_{10}H_{15}IO_6$ (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

($CHCl_3$): 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 $C_{15}H_{17}IO_6$, 420.0070 found 420.0071; elemental analysis calcd (%) for $C_{15}H_{17}IO_6$ (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-ribopyranose (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, $CDCl_3$): 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.7 (2 × CH_3), 20.8 (2 × CH_3), 60.5 (CH_2), 64.0 (CH_2), 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 (CCl_4): 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 $C_9H_{12}FO_6$ 235.0618; found 235.0620; elemental analysis calcd (%) for $C_9H_{13}FO_6$ (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-ribopyranose and -L-arabinopyranose (93). From 2,3-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*erythro*-pent-4-enitol.[10] Oil (95%); IR (CCl_4): 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 $C_9H_{12}{}^{37}ClO_5$ 237.0344; found 237.0311; elemental analysis calcd (%) for $C_9H_{13}ClO_6$ (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-ribopyranose and -L-arabinopyranose (94). From 2,3-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*erythro*-pent-4-enitol.[10] Oil (95%); IR ($CHCl_3$): 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 $C_7H_9{}^{81}BrO_4$ 237.9664; found 237.9670; elemental analysis calcd (%) for $C_9H_{13}BrO_6$ (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-ribopyranose and -L-arabinopyranose (95). From 2,3-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*erythro*-pent-4-enitol.[10] Oil (88%); IR ($CHCl_3$): 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 $C_9H_{13}IO_6$ 343.9757; found 343.9798; elemental analysis calcd (%) for $C_9H_{13}IO_6$ (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 ($CHCl_3$): 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 $C_{10}H_{14}IO_5$, 340.9886 found 340.9838; elemental analysis calcd (%) for $C_{10}H_{15}IO_6$ (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 ($CHCl_3$): 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 $C_{15}H_{31}IO_3Si$, 414.1087 found 414.1086; elemental analysis calcd (%) for $C_{15}H_{31}IO_3Si$ (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, ^3J(F,H) = 15.0 Hz, 1H), 6.72 (dd, J = 5.9 Hz, ^2J(F,H) = 48.8 Hz, 1H), 6.78 (dd, J = 5.4 Hz, ^2J(F,H) = 49.2 Hz, 1H), 7.96 (s, 2H); ^{13}C NMR: δ = 16.07 (CH_3), 16.1 (CH_3), 20.5 (2 × CH_3), 20.6 (2 × CH_3), 67.3 (2 × CH), 69.2

(^1J(F,C) = 258.2 Hz, CH), 70.2 (^1J(F,C) = 256.1 Hz, CH), 70.6 (CH), 71.8 (CH), 72.5 (^2J(F,C) = 24.0 Hz, CH), 72.8 (^2J(F,C) = 18.7 Hz, CH), 159.7 (2 × CH), 169.2 (C), 169.3 (C), 169.5 (C), 169.55 (C); IR (CCl_4): ν = 1764, 1735, 1207, 1166 cm^{-1}; MS (70 eV, EI): *m/z* (%): 303 (1) [M^+ – $C_3H_5O_2$], 253 (14), 249 (100), 161 (17), 147 (11), 99 (95); HRMS (EI): calcd for $C_7H_9FIO_4$: 302.9530; found: 302.9531; elemental analysis calcd (%) for $C_{10}H_{14}FIO_6$ (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); ^{1}H NMR: δ = 1.26 (d, *J* = 6.4 Hz, 3H), 1.27 (d, *J* = 6.5 Hz, 3H), 2.14 (s, 6H), 2.15 (s, 6H), 5.05–5.15 (m, 2H), 5.47 (dd, *J* = 2.1, 8.2 Hz, 1H), 5.50 (dd, *J* = 2.8, 7.3 Hz, 1H), 5.58–5.60 (m, 2H), 5.62 (d, *J* = 8.2 Hz, 1H), 5.68 (d, *J* = 7.3 Hz, 1H), 7.96 (s, 2H); ^{13}C NMR: δ = 16.1 (CH_3), 16.2 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 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 (CCl_4): ν = 1763, 1734, 1458, 1428, 1371, 1205 cm^{-1}; MS (70 eV, EI): *m/z* (%): 349/347 (1/3) [M^+ – OCOH], 267/265 (25/75), 225/223 (2/8), 187 (21), 179/177 (14/43), 99 (100); HRMS (EI): calcd for $C_9H_{13}{}^{35}ClIO_4$: 346.9547; found: 346.9516; elemental analysis calcd (%) for $C_{10}H_{14}ClIO_6$ (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); ^{1}H 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 (CH_3), 16.1 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 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 × C); IR (CCl_4): 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 $C_8H_{10}{}^{79}BrIO_4$: 375.8807; found: 375.8795; elemental analysis calcd (%) for $C_{10}H_{14}BrIO_6$ (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); ^{1}H 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(F,H) = 24.3 Hz, 1H), 6.88 (dd, J = 3.7 Hz, ^2J(F,H) = 48.1 Hz, 1H), 6.98 (dd, J = 2.1 Hz, ^2J(F,H) = 48.4 Hz, 1H), 8.00 (s, 1H), 8.02 (s, 1H); ^{13}C NMR: δ = 20.7 (4 × CH_3), 60.4 (CH_2), 60.6 (CH_2), 68.5 (J(F,C) = 259.2 Hz, CH),

68.8 (CH), 70.1 (CH), 70.8 (^1J(F,C) = 255.5 Hz, CH), 72.2 (^2J(F,C) = 22.0 Hz, CH), 73.2 (^2J(F,C) = 18.3 Hz, CH), 160.2 (2 × CH), 168.9 (C), 169.1 (C), 169.3 (2 × C); IR (CCl_4): ν = 1762, 1737, 1371, 1208, 1168 cm^{-1}; MS (70 eV, EI): *m/z* (%): 317 (1) [M^+ – OCOH], 303 (1), 235 (100), 127 (17), 113 (10), 85 (59); HRMS (EI): calcd for $C_8H_{11}FIO_4$: 316.9686; found: 316.9685; elemental analysis calcd (%) for $C_9H_{12}FIO_6$ (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); ^{1}H NMR: δ = 2.10 (s, 3H), 2.19 (s, 6H), 2.23 (s, 3H), 4.16 (dd, *J* = 4.0, 12.5 Hz, 1H), 4.21 (dd, *J* = 4.4, 12.5 Hz, 1H), 4.50 (dd, *J* = 3.2, 12.5 Hz, 2H), 5.13 (dd, *J* = 3.8, 7.5 Hz, 1H), 5.20 (ddd, *J* = 3.2, 4.0, 7.5 Hz, 1H), 5.29 (ddd, *J* = 3.2, 4.4, 8.1 Hz, 1H), 5.61 (dd, *J* = 2.8, 8.1 Hz, 1H), 5.88 (d, *J* = 3.8 Hz, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 8.03 (s, 1H), 8.04 (s, 1H); ^{13}C NMR: δ = 20.6 (2 × CH_3), 20.7 (2 × 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 × CH), 169.0 (2 × C), 169.2 (2 × C); IR (CCl_4): ν = 1762, 1737, 1371, 1204, 1067 cm^{-1}; MS (70 eV, EI): *m/z* (%): 320/318 (3/9) [M^+ – AcOH], 253/251 (23/68), 211/209 (4/14), 193/191 (12/35), 85 (100); HRMS (EI): calcd for $C_7H_8{}^{35}ClIO_4$: 317.9156; found: 317.9151; elemental analysis calcd (%) for $C_9H_{12}ClIO_6$ (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); ^{1}H 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 × CH_3), 20.8 (2 × 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 × C), 169.2 (2 × 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 $C_7H_8{}^{81}BrIO_4$: 363.8630; found: 363.8644; elemental analysis calcd (%) for $C_9H_{12}BrIO_6$ (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 CH_2Cl_2. 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: ^{1}H 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); ^{13}C NMR (50.3 MHz): δ = –5.2 (4 × CH_3), 18.3 (2 × C), 25.8 (6 × CH_3), 67.7 (CH_2), 67.8 (CH_2), 72.8 (CH_2), 73.2 (2 × CH_2), 73.5 (CH_2), 74.0 (CH), 74.1 (CH_2), 74.1 (CH), 74.4 (CH_2), 74.9 (CH_2), 75.3 (CH_2), 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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