CHEMISTRY

A EUROPEAN JOURNAL

Supporting Information

Fragmentation of Carbohydrate Anomeric Alkoxy Radicals: New Synthesis of Chiral 1-Fluoro-1-halo-1-iodo Alditols

Cosme G. Francisco,[a] Concepción C. González,*[a] Alan R. Kennedy,[b] Nieves R. Paz[a] and Ernesto Suárez*[a]

[a]*Instituto de Productos Naturales y Agrobiología del C.S.I.C., Carretera de La Esperanza 3, 38206 La Laguna Tenerife, Spain.*

[b]*WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK.*

General Methods: Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in CCl_4 solutions unless otherwise stated. NMR spectra were determined at 400 MHz for ^1H, 100.6 MHz for ^{13}C in $CDCl_3$ and 376.5 MHz for ^{19}F in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air– or moisture–sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5 % vanillin in H_2SO_4-EtOH (4:1) and further heating until development of color.

General procedure for the synthesis of 2-deoxy-2,2-difluoropyranoses: To a solution of the corresponding 2-deoxy-2-fluor-hex-1-enitol (1 mmol) in nitromethane (10 mL) and H_2O (2 mL) was added F-TEDA-BF_4 (Selectfluor^{TM}) (1.5 mmol) and the mixture was stirred at room temperature until the disappearance of the starting material was observed by TLC (15 h). The reaction mixture was then heated to reflux for 0.5 h, poured into brine and extracted with EtOAc. The organic layer was dried and concentrated *in vacuo*. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required difluorohydrins compounds.

General procedure for the synthesis of 2-deoxy-2,2-chlorofluoropyranoses: A solution of the corresponding 2-deoxy-2-fluor-hex-1-enitol (1 mmol) in THF (20 mL) and H_2O (10 mL), containing *N*-chlorosuccinimide (2 mmol) was heated at 50 ºC for 6–12 h. The reaction mixture was then poured into water and extracted with EtOAc. The organic layer was dried and concentrated *in vacuo*. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required chlorofluorohydrins compounds.

General procedure for the synthesis of 2-deoxy-2,2-bromofluoropyranoses: A solution of the corresponding 2-deoxy-2-fluor-hex-1-enitol (1 mmol) in THF (20 mL) and H_2O (5 mL), containing freshly crystallized *N*-bromoacetamide (1.5 mmol) was stirred at room temperature for 1–7.5 h. The reaction mixture was then poured into

water and extracted with EtOAc. The organic layer was dried and concentrated *in vacuo*. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required bromofluorohydrins compounds.

General procedure for the synthesis of 2-deoxy-2,2-fluoroiodopyranoses: A solution of the corresponding 2-deoxy-2-fluor-hex-1-enitol (1 mmol) in THF (10 mL) and H_2O (5 mL), containing *N*-iodosuccinimide (2 mmol) was stirred at room temperature (without light exposure) for 1–4 h. The reaction mixture was diluted with EtOAc, poured into water and extracted with EtOAc. The organic layer was washed with aqueous sodium thiosulfate, dried and concentrated in vacuo. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required fluoroiodohydrins compounds.

General procedure for the alkoxyl radical fragmentation (ARF) reaction: A solution of the dihalohydrins (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at room temperature. 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*. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the halo-fluoro-iodine compounds. No special precautions need to be taken to exclude light during workup and chromatography, and these compound can be stored indefinitely under nitrogen at −20 ºC in the dark.

3,4-Di-*O*-acetyl-2,6-dideoxy-2-fluoro-a**-L-galactopyranosyl bromide (72S)**:[1] Selecfluor™ (2.7 g, 7.7 mmol, 1.5 equiv) was added to a solution of di-*O*-acetyl-L-fucal (1.1 g, 5.1 mmol, 1 equiv) in dry nitromethane (40 mL) and the reaction was stirred at room temperature for 15 h. $MgBr_2$ anhydrous (964 mg, 5.1 mmol, 2 equiv) was then added and the reaction was refluxed for 30 minutes. Once cooled, was poured into brine and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 anhidro and concentrated under vacuum. The residue was purified by column chromatography (hexanes/EtOAc 8:2) to give **72S** (1.2 g, 3.9 mmol, 77 %) as an oil: $[\alpha]_D$ = –275.4 (*c* = 0.35); ^{1}H NMR: *d* = 1.22 (d, *J* = 6.6 Hz, 3H), 2.06 (s, 3H), 2.17 (s, 3H), 4.44 (ddddd, *J* = 0.8, 1.3, 6.6, 6.6, 6.6 Hz, 1H), 4.73 (ddd, *J* = 4.2, 10.1 Hz, ^2J(F,H) = 50.4 Hz, 1H),

[1] Numbers ending in S refer to products only cited in the Supporting Information.

5.38 (ddd, J = 1.3, 3.4 Hz, ^4J(F,H) = 3.4 Hz, 1H), 5.48 (ddd, J = 3.4, 10.1 Hz, ^3J(F,H) = 10.1 Hz, 1H), 6.60 ppm (dd, J = 0.8, 4.2 Hz, 1H); ^{13}C NMR: d = 15.3 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 69.2 (d, ^2J(F,C) = 17.5 Hz, CH), 69.9 (CH), 70.3 (CH), 84.2 (d, ^1J(F,C) = 194.6 Hz, CH), 87.9 (d, ^2J(F,C) = 25.3 Hz, CH), 169.7 (C), 169.9 ppm (C); ^{19}F NMR: d = –195.7 ppm (dd, ^3J(F,H) = 9.2 Hz, ^2J(F,H) = 50.5 Hz, 1F); IR: $\tilde{n}$ = 2992, 2942, 1756, 1371, 1235, 1104, 1020 cm^{-1}; MS (70 eV, EI): m/z (%): 313/311 (1) [M–1]$^+$, 233 (100), 173 (25), 113 (33); HRMS (EI): m/z calcd for $C_{10}H_{13}{}^{79}BrFO_5$ [M–1]$^+$: 310.9930, found: 310.9920; elemental analysis calcd (%) for $C_{10}H_{14}BrFO_5$ (313.12): C 38.36, H 4.51; found: C 38.20, H 4.46.

3,4-Di-*O*-acetyl-2-deoxy-2-fluoro-b**-L-arabinopyranosyl bromide (73S)**: Selecfluor™ (3.4 g, 9.7 mmol, 1.5 equiv) was added to a solution of di-*O*-acetyl-L-arabinal (1.3 g, 6.5 mmol, 1 equiv) in dry nitromethane (65 mL) and the reaction was stirred at room temperature for 15 h. $MgBr_2$ anhydrous (1.2 g, 6.5 mmol, 2 equiv) was then added and the reaction was refluxed for 30 minutes. Once cooled, was poured into brine and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 anhidro and concentrated under vacuum. The residue was purified by column chromatography (hexanes/EtOAc 8:2) to give **73S** (1.4 g, 4.5 mmol, 70 %) as a crystalline solid: m.p. 110.5–112.0 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = +393.5 (c = 0.10); ^{1}H NMR: d = 2.08 (s, 3H), 2.15 (s, 3H), 3.92 (ddd, J = 1.7, 1.7, 13.4 Hz, 1H), 4.22 (ddd, J = 0.8, 0.8, 13.4 Hz, 1H), 4.78 (ddd, J = 4.2, 9.9 Hz, ^2J(F,H) = 50.3 Hz, 1H), 5.41 (dddd, J = 0.8, 1.7, 3.6 Hz, ^4J(F,H) = 3.4 Hz, 1H), 5.47 (ddd, J = 3.6, 9.9 Hz, ^3J(F,H) = 10.0 Hz, 1H), 6.62 ppm (d, J = 4.2 Hz, 1H); ^{13}C NMR (125.7 MHz): d = 20.6 (CH_3), 20.7 (CH_3), 64.7 (CH_2), 68.3 (CH), 68.6 (d, ^2J(F,C) = 17.5 Hz, CH), 84.3 (d, ^1J(F,C) = 194.5 Hz, CH), 88.3 (d, ^2J(F,C) = 25.1 Hz, CH), 169.78 (C), 169.84 ppm (C); ^{19}F NMR: d = –193.8 ppm (dd, ^3J(F,H) = 9.2 Hz, ^2J(F,H) = 50.4 Hz, 1F); IR: $\tilde{n}$ = 1757, 1371, 1235, 1213, 1091 cm^{-1}; MS (70 eV, EI): m/z (%): 299/297 (16/14) [M–1]$^+$, 219 (22), 159 (10), 116 (100); HRMS (EI): m/z calcd for $C_9H_{11}{}^{79}BrFO_5$ [M–1]$^+$: 296.9774, found: 296.9767; elemental analysis calcd (%) for $C_9H_{12}BrFO_5$ (299.09): C 36.14, H 4.04; found: C 36.10, H 3.84.

3,4-Di-*O*-acetyl-2,6-dideoxy-2-fluoro-a**-L-glucopyranosyl bromide (74S)**: Acetic anhydride (1 mL) was added to a solution of 1,3,4-tri-*O*-acetyl-2,6-dideoxy-2-fluoro-L-glucopyranose (1.0 g, 3.4 mmol, 1 equiv) in 30 % HBr/AcOH (10 mL). The reaction

was stirred at room temperature for 2 h, then poured into ice/water and extracted with ethyl acetate. The organic phase was washed with sodium bicarbonate and brine, dried over sodium sulfate and concentrate under vacuum. The residue was purified by column chromatography (hexanes/EtOAc 7:3) to give the bromide **74S** (979 mg, 3.1 mmol, 92 %) as a crystalline solid. m.p. 114.7–115.7 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = –216.4 (*c* = 0.12); ^{1}H NMR: *d* = 1.26 (d, *J* = 6.4 Hz, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 4.20 (ddddd, *J* = 0.8, 6.4, 6.4, 6.4, 10.0 Hz, 1H), 4.50 (ddd, *J* = 4.2, 9.4 Hz, ^2J(F,H) = 49.7 Hz, 1H), 4.84 (ddd, *J* = 9.4, 10.0 Hz, ^4J(F,H) = 0.5 Hz, 1H), 5.58 (ddd, *J* = 9.4, 9.4, Hz, ^3J(F,H) = 11.2 Hz, 1H), 6.49 ppm (ddd, *J* = 0.8, 4.3 Hz, ^3J(F,H) = 0.8 Hz, 1H); ^{13}C NMR: *d* = 16.8 (CH_3), 20.6 (2 × CH_3), 70.4 (CH), 71.0 (d, ^2J(F,C) = 18.3 Hz, CH), 71.9 (CH), 85.8 (d, ^2J(F,C) = 24.6 Hz, CH), 86.7 (d, ^1J(F,C) = 201.5 Hz, CH), 169.7 ppm (2 × C); ^{19}F NMR: *d* = –188.7 ppm (dd, ^3J(F,H) = 9.2 Hz, ^2J(F,H) = 45.9 Hz, 1F); IR: $\tilde{n}$ = 2942, 1763, 1238, 1212, 1110, 1043 cm^{-1}; MS (70 eV, EI): *m/z* (%): 314/312 (<1) $[M]^+$, 270/268 (3/3), 233 (100), 173 (26), 130 (32), 113 (89); HRMS (EI): *m/z* calcd for $C_{10}H_{14}{}^{81}BrFO_5$ $[M]^+$: 313.9988, found: 314.0004; elemental analysis calcd (%) for $C_{10}H_{14}BrFO_5$ (313.12): C 38.36, H 4.51; found: C 38.46, H 4.50.

General procedure for the synthesis of vinyl fluorides 5, 10 and 11: TEA (3 mmol) was added to a solution of the bromide (1 mmol) in dry acetonitrile (3 mL) and the reaction was refluxed for 1.5 h. Once cooled, the reaction was poured into 10 % HCl solution and extracted with ethyl acetate. The organic phase was washed with sodium bicarbonate, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column (hexanes/EtOAc 8:2) to yield the correspondent vinyl fluorides.

3,4-Di-*O*-acetyl-2,6-anhydro-1,5-dideoxy-5-fluoro-L-*arabino*-hex-5-enitol (5): Volatile crystalline solid (47 %): m.p. 87.0–88.0 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = +6.3 (*c* = 0.22); ^{1}H NMR: *d* = 1.29 (d, *J* = 6.6 Hz, 3H), 2.07 (s, 3H), 2.17 (s, 3H), 4.16 (ddddd, *J* = 1.3, 1.3, 6.6, 6.6, 6.6 Hz, 1H), 5.30 (ddd, *J* = 1.3, 5.0 Hz, ^4J(F,H) = 5.3 Hz, 1H), 5.88 (dddd, *J* = 1.3, 1.3, 5.0 Hz, ^3J(F,H) = 1.3 Hz, 1H), 6.74 ppm (dd, *J* = 1.3 Hz, ^3J(F,H) = 5.0 Hz, 1H); ^{13}C NMR: *d* = 15.7 (CH_3), 20.5 (2 × CH_3), 63.3 (d, ^2J(F,C) = 20.3 Hz, CH), 66.6 (d, ^3J(F,C) = 6.2 Hz, CH), 72.1 (CH), 132.9 (d, ^2J(F,C) = 39.7 Hz, CH), 142.6 (d, ^1J(F,C) = 242.6 Hz, C), 170.1 (C), 170.4 ppm (C); ^{19}F NMR: *d* = –171.7 ppm (s, 1F); IR: $\tilde{n}$ = 2991, 1755, 1371, 1239, 1215, 1174 cm^{-1}; MS (70 eV, EI): *m/z* (%): 233 (54) $[M+1]^+$, 172 (31), 146 (29), 130 (100), 115 (85); HRMS (EI): *m/z* calcd

for $C_{10}H_{14}FO_5$ $[M+1]^+$: 233.0814, found: 233.0825; elemental analysis calcd (%) for $C_{10}H_{13}FO_5$ (232.21): C 51.73, H 5.64; found: C 51.93, H 5.60.

3,4-Di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-2-fluoro-L-*arabino*-hex-1-enitol (10): Oil (83 %): $[\alpha]_D$ = +32.7 (*c* = 0.74); ^{1}H NMR: *d* = 1.31 (d, *J* = 6.9 Hz, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 4.17 (dddd, *J* = 5.8, 6.9, 6.9, 6.9 Hz, 1H), 5.02 (ddd, *J* = 3.4, 5.8 Hz, ^4J(F,H) = 4.2 Hz, 1H), 5.62 (ddd, *J* = 0.8, 3.4 Hz, ^3J(F,H) = 5.0 Hz, 1H), 6.74 ppm (dd, *J* = 0.8 Hz, ^3J(F,H) = 5.0 Hz, 1H); ^{13}C NMR: *d* = 15.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 66.0 (d, ^2J(F,C) = 22.5 Hz, CH), 71.8 (d, ^3J(F,C) = 8.3 Hz, CH), 72.3 (CH), 132.4 (d, ^2J(F,C) = 39.2 Hz, CH), 142.6 (d, ^1J(F,C) = 240.6 Hz, C), 169.5 (C), 170.1 ppm (C); ^{19}F NMR: *d* = –168.3 ppm (s, 1F); IR: $\tilde{n}$ = 2986, 2883, 1754, 1369, 1235, 1172, 1039 cm^{-1}; MS (70 eV, EI): *m/z* (%): 233 (17) $[M+1]^+$, 188 (2), 172 (18), 146 (39), 130 (68), 112 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{14}FO_5$ $[M+1]^+$: 233.0825, found: 233.0834; elemental analysis calcd (%) for $C_{10}H_{13}FO_5$ (232.21): C 51.73, H 5.64. Found: C 51.50, H 5.70.

2,3-Di-*O*-acetyl-1,5-anhydro-4-deoxy-4-fluoro-D-*erythro*-pent-4-enitol (11): Crystalline solid (47 %): m.p. 44.3–45.6 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = –153.9 (*c* = 0.35); ^{1}H NMR: *d* = 2.04 (s, 3H), 2.12 (s, 3H), 3.79 (dd, *J* = 10.5, 10.5 Hz, 1H), 3.93 (dd, *J* = 3.9, 10.5 Hz, 1H), 5.20 (ddd, *J* = 3.9, 4.3, 10.5 Hz, 1H), 5.82 (ddd, *J* = 1.2, 4.3 Hz, ^3J(F,H) = 8.1 Hz, 1H), 6.81 ppm (d, ^3J(F,H) = 4.1 Hz, 1H); ^{13}C NMR (125.7 MHz): *d* = 20.5 (CH_3), 20.7 (CH_3), 62.6 (CH_2), 63.4 (d, ^2J(F,C) = 24.3 Hz, CH), 65.3 (CH), 134.6 (d, ^2J(F,C) = 39.8 Hz, CH), 142.7 (d, ^1J(F,C) = 241.9 Hz, C), 169.4 (C), 170.2 ppm (C); ^{19}F NMR: *d* = –166.3 ppm (s, 1F); IR: $\tilde{n}$ = 2935, 1756 1369, 1233, 1074 cm^{-1}; MS (70 eV, EI): *m/z* (%): 219 (22) $[M+1]^+$, 159 (24), 146 (12), 116 (100); HRMS (EI): *m/z* calcd for $C_9H_{12}FO_5$ $[M+1]^+$: 219.0669, found: 219.0666; elemental analysis calcd (%) for $C_9H_{11}FO_5$ (218.18): C 49.55 H 5.08; found: C 49.33, H 5.14.

2,6-Anhydro-5-deoxy-5-fluoro-1,3,4-tri-*O*-methyl-D-*arabino*-hex-5-enitol (3): A suspensión of **1** (1 mmol, 1 equiv) in 3 % MeOH–K_2CO_3 (5 mL) was stirred at room temperature for 1 h. Then, the reaction was neutralized with acid resins Dowex (50 × 8). The resins were separated by filtration and washed several times with MeOH. The filtrate was concentrated under vacuum to yield a white solid which was used without futher purifications. To a solution of the triol **2** (1.1 g, 3.8 mmol, 1 equiv) in DMF (15 mL) was added NaH (60 % suspension oil, 912 mg, 22.8 mmol, 6 equiv) at 0ºC and the

reaction was stirred for 30 minutes. MeI (1.5 mL, 22.8 mmol, 6 equiv) was added to the suspensión and stirred at room temperature for 4 h. The reaction was poured into ice/water and extracted with diehyl ether. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography (hexanes/EtOAc 90:10) to obtain **3** (532 mg, 2.6 mmol, 68 %) as an oil. $[\alpha]_D$ = –47.0 (*c* = 0.46); ^{1}H NMR: *d* = 3.37 (s, 3H), 3.52 (s, 3H), 3.537 (d, ^5J(F,H) = 1.3 Hz, 3H), 3.54 (dd, *J* = 3.3, 10.9 Hz, 1H), 3.73 (dd, *J* = 8.5, 10.9 Hz, 1H), 3.74 (ddd, *J* = 1.1, 5.8 Hz, ^3J(F,H) = 4.9 Hz, 1H), 4.15 (ddd, *J* = 0.8, 5.8 Hz, ^4J(F,H) = 4.5 Hz, 1H), 4.21 (dddd, *J* = 0.8, 1.1, 3.3, 8.5 Hz, 1H), 6.57 ppm (d, ^3J(F,H) = 5.3 Hz, 1H); ^{13}C NMR: *d* = 58.8 (CH_3), 59.03 (CH_3), 59.05 (CH_3), 69.0 (CH_2), 71.7 (d, ^2J(F,C) = 19.4 Hz, CH), 74.9 (CH), 75.0 (CH), 130.3 (d, ^2J(F,C) = 40.3 Hz, CH), 146.0 ppm (d, ^1J(F,C) = 243.2 Hz, C); ^{19}F NMR: *d* = –163.6 ppm (s, 1F); IR: $\tilde{n}$ = 2971, 2928, 1456, 1345, 1134, 1149, 1118 cm^{-1}; MS (70 eV, EI): *m/z* (%): 206 (3) $[M]^+$, 145 (2), 102 (57), 101 (50), 71 (100); HRMS (EI): *m/z* calcd for $C_9H_{15}FO_4$ $[M]^+$: 206.0954, found: 206.0958; elemental analysis calcd (%) for $C_9H_{15}FO_4$ (206.21): C 52.42, H 7.33; found: C 52.50, H 7.02.

2,6-Anhydro-1,3,4-tri-*O*-benzyl-5-deoxy-5-fluoro-D-*arabino*-hex-5-enitol (4): A suspensión of **1** (1 mmol, 1 equiv) in 3 % MeOH–K_2CO_3 (5 mL) was stirred at room temperature for 1 h. Then, the reaction was neutralized with acid resins Dowex (50 × 8). The resins were separated by filtration and washed several times with MeOH. The filtrate was concentrated under vacuum to yield a white solid which was used without futher purifications. To a solution of the triol **2** (282 mg, 1.72 mmol, 1 equiv) in DMF (7 mL) was added NaH (60 % oil suspensión, 413 mg, 10.3 mmol, 6 equiv) at 0 ºC and the reaction was stirred for 30 minutes. Benzyl bromide (1.3 mL, 10.3 mmol, 6 equiv) was added and the suspensión was stirred at room temperature for 2.5 h. The reaction was poured into ice/water and extracted with diehyl ether. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography (hexanes/EtOAc 90:10) to obtain **4** (685 mg, 1.2 mmol, 70 %) as a crystaline solid: m.p. 62.8–64.1 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = –47.3 (*c* = 1.35); ^{1}H NMR: *d* = 3.72 (dd, *J* = 3.8, 10.9 Hz, 1H), 3.88 (dd, *J* = 8.0, 10.9 Hz, 1H), 3.94 (ddd, *J* = 3.8, 4.1 Hz, ^4J(F,H) = 1.7 Hz, 1H), 4.24 (ddd, *J* = 3.8, 3.8, 8.0 Hz, 1H), 4.34 (dd, *J* = 4.1 Hz, ^3J(F,H) = 4.8 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.77 (d, *J* = 11.8 Hz, 1H),

4.79 (d, J = 11.9 Hz, 1H), 6.60 (d, ^3J(F,H) = 5.3 Hz, 1H), 7.26–7.36 ppm (m, 15H); ^{13}C NMR: d = 67.1 (CH_2), 69.9 (d, ^2J(F,C) = 19.5 Hz, CH), 72.5 (d, ^3J(F,C) = 8.7 Hz, CH), 72.7 (CH_2), 73.1 (CH_2), 73.3 (CH_2), 75.7 (CH), 127.6 (4 × CH), 127.8 (2 × CH), 127.9 (3 × CH), 128.3 (4 × CH), 128.4 (2 × CH), 130.5 (d, ^2J(F,C) = 40.6 Hz, CH), 137.6 (C), 138.0 (C), 138.1 (C), 146.1 ppm (d, ^1J(F,C) = 243.9 Hz, C); ^{19}F NMR: d = –164.4 ppm (s, 1F); IR: $\tilde{n}$ = 3032, 2868, 1454, 1156, 1102 cm^{-1}; MS (70 eV, EI): *m/z* (%): 343 (1) [*M*–Bn]$^+$, 253 (4), 220 (4), 163 (14), 91 (100); HRMS (EI): *m*/*z* calcd for $C_{20}H_{20}FO_4$ [*M*–Bn]$^+$: 343.1346, found: 343.1358; elemental analysis calcd (%) for $C_{27}H_{27}FO_4$ (434.51): C 74.64, H 6.26; found: C 74.41, H 6.23.

2,6-Anhydro-5-deoxy-5-fluoro-3,4-*O*-isopropylidene-D-*arabino*-hex-5-enitol (6): To a solution of **2** (74 mg, 0.45 mmol, 1equiv) in 2,2-dimethoxypropane (1 mL) was added CSA (10 mg) and stirred at room temperature for 10 minutes. Water was added to the reaction mixture and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by column chomatography (*n*-hexanes/EtOAc 7:3) to yield **6** (69 mg, 0.34 mmol, 75 %) as a white solid: m.p. 77.7–78.4 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = –20.9 (c = 0.15); ^{1}H NMR (500 MHz): d = 1.41 (s, 3H), 1.52 (s, 3H), 3.86 (dd, J = 4.3, 11.4 Hz, 1H), 3.95 (ddd, J = 1.4, 4.3, 6.7 Hz, 1H), 4.02 (dd, J = 6.7, 11.4 Hz, 1H), 4.43 (ddd, J = 1.4, 6.7 Hz, ^4J(F,H) = 5.3 Hz, 1H), 4.85 (dd, J = 6.7 Hz, ^3J(F,H) = 1.4 Hz, 1H), 6.67 ppm (d, ^3J(F,H) = 4.8 Hz, 1H); ^{13}C NMR (125.7 MHz): d = 26.6 (CH_3), 27.7 (CH_3), 62.3 (CH_2), 69.1 (d, ^2J(F,C) = 21.9 Hz, CH), 74.2 (d, ^3J(F,C) = 6.0 Hz, CH), 76.1 (CH), 111.9 (C), 131.3 (d, ^2J(F,C) = 41.6 Hz, CH), 147.6 ppm (d, ^1J(F,C) = 242.0 Hz, C); ^{19}F NMR: d = –168.1 ppm (s, 1F); IR: $\tilde{n}$ = 3683, 3020, 1521, 1423, 1211, 1175 cm^{-1}; MS (70 eV, EI): *m/z* (%): 204 (21) [*M*]$^+$, 189 (18), 146 (32), 129 (94), 99 (100); HRMS (EI): *m*/*z* calcd for $C_9H_{13}FO_4$ [*M*]$^+$: 204.0798, found: 204.0796; elemental analysis calcd (%) for $C_9H_{13}FO_4$ (204.20): C 52.94, H 6.42; found: C 52.92, H 6.51.

2,6-Anhydro-1-*O*-benzyl-5-deoxy-5-fluoro-3,4-*O*-isopropylidene-D-*arabino*-hex-5-enitol (7): To a solution of **6** (90 mg, 0.44 mmol, 1equiv) in dry DMF (3 mL) was added NaH (60 % oil suspension, 35 mg, 0.88 mmol, 2 equiv) at 0 ºC and the suspension was stirred for 30 minutes. When the hydrogen evolution ceased, benzyl bromide (0.12 mL, 0.88 mmol, 2 equiv) was added amd the mixture was stirred at room temperature for 1 h. MeOH was added to eliminate the excess of NaH, and the resulting

mixture was poured into ice/water and extracted with diethyl ether. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by column chomatography (hexanes/EtOAc 90:10) to yield **7** (111 mg, 0.38 mmol, 86 %) as an oil.: $[\alpha]_D$ = –46.5 (*c* = 0.63); ^{1}H NMR: *d* = 1.39 (s, 3H), 1.49 (s, 3H), 3.74 (dd, *J* = 5.5, 10.1 Hz, 1H), 3.81 (dd, *J* = 7.2, 10.1 Hz, 1H), 4.02 (ddd, *J* = 1.3, 5.5, 7.2 Hz, 1H), 4.42 (ddd, *J* = 1.3, 6.4 Hz, ^4J(F,H) = 5.6 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.81 (dd, *J* = 6.6 Hz, ^3J(F,H) = 1.4 Hz, 1H), 6.62 (d, ^3J(F,H) = 4.8 Hz, 1H), 7.29–7.36 ppm (m, 5H); ^{13}C NMR: *d* = 26.6 (CH_3), 27.8 (CH_3), 69.03 (d, ^2J(F,C) = 22.0 Hz, CH), 69.04 (CH_2), 73.6 (CH_2), 74.0 (d, ^3J(F,C) = 7.0 Hz, CH), 74.9 (CH), 111.7 (C), 127.8 (2 × CH), 127.9 (CH), 128.5 (2 × CH), 131.4 (d, ^2J(F,C) = 41.0 Hz, CH), 137.7 (C), 147.5 ppm (d, ^1J(F,C) = 240.0 Hz, C); ^{19}F NMR: *d* = –168.3 ppm (s, 1F); IR: $\tilde{n}$ = 2990, 2934, 1454, 1382, 1237, 1177, 1100 cm^{-1}; MS (70 eV, EI): *m/z* (%): 294 (2) $[M]^+$, 279 (37), 236 (2), 203 (29), 130 (18), 107 (99), 91 (100); HRMS (EI): *m*/*z* calcd for $C_{16}H_{19}FO_4$ $[M]^+$: 294.1267, found: 294.1259; elemental analysis calcd (%) for $C_{16}H_{19}FO_4$ (294.32): C 65.29, H 6.51; found: C 65.49, H 6.58.

2,6-Anhydro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-5-fluoro-3,4-*O*-isopropylidene-D-*arabino*-hex-5-enitol (8): 3,5-Dinitrobenzoyl choride (203 mg, 0.88 mmol, 2 equiv) and DMAP (23 mg, 0.19 mmol, 0.2 equiv) were added to a solution of **6** (90 mg, 0.44 mmol, 1 equiv) in dry piridine (3 mL), and the suspension was stirred at room temperature for 1.5 h. The reaction was poured into aqueous HCl and extraced with AcOEt, washed with sodium bicarbonate, dried over sodium sulfate and concentrated under vacuum. The residue was purified by column chomatography (hexanes/EtOAc 70:30) to yield **8** (138 mg, 0.35 mmol, 78 %) as a crystalline solid: m.p. 149.5–150.9 ºC (from *n*-hexane/EtOAc); $[\alpha]_D$ = –14.4 (*c* = 0.33); ^{1}H NMR: *d* = 1.43 (s, 3H), 1.53 (s, 3H), 4.25 (ddd, *J* = 1.3, 3.4, 7.7 Hz, 1H), 4.51 (ddd, *J* = 1.3, 6.9 Hz, ^4J(F,H) = 5.0 Hz, 1H), 4.72 (dd, *J* = 3.4, 12.2 Hz, 1H), 4.80 (dd, *J* = 7.7, 12.2 Hz, 1H), 4.91 (dd, *J* = 6.9 Hz, ^3J(F,H) = 1.8 Hz, 1H), 6.66 (d, ^3J(F,H) = 4.8 Hz, 1H), 9.19 (d, *J* = 2.2 Hz, 2H), 9.25 ppm (dd, *J* = 2.2, 2.2 Hz, 1H); ^{13}C NMR: *d* = 26.7 (CH_3), 27.8 (CH_3), 65.7 (CH_2), 69.1 (d, ^2J(F,C) = 23.1 Hz, CH), 73.5 (CH), 74.1 (d, ^3J(F,C) = 7.0 Hz, CH), 112.3 (C), 122.6 (CH), 129.6 (2 × CH), 131.2 (d, ^2J(F,C) = 42.2 Hz, CH), 133.4 (C), 147.6 (d, ^1J(F,C) = 244.4 Hz, C), 148.7 (2 × C), 162.3 ppm (C); ^{19}F NMR: *d* = –167.1 ppm (s, 1F); IR: $\tilde{n}$ = 3103, 2959, 1742, 1550, 1343, 1277, 1264, 1163 cm^{-1}; MS (70 eV, EI): *m/z* (%): 398

(7) $[M]^+$, 383 (21), 323 (42), 195 (100); HRMS (EI): *m*/*z* calcd for $C_{16}H_{15}FN_2O_9$ $[M]^+$: 398.0762, found: 398.0773; elemental analysis calcd (%) for $C_{16}H_{15}FN_2O_9$ (398.30): C 48.25, H 3.80; N, 7.03; found: C 48.54, H 3.72; N, 6.73.

3,4,6-Tri-*O*-acetyl-2-deoxy-2,2-difluoro-α**-D-*lyxo*-hexopyranose (12)**: Oil (43 %); ^{1}H NMR (500 MHz): *d* = 2.06 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 4.16 (d, *J* = 6.7 Hz, 2H), 4.56 (ddd, *J* = 1.2, 6.7, 6.7 Hz, 1H), 5.29 (dd, ^3J(F,H) = 3.4, 5.7 Hz, 1H), 5.42–5.50 ppm (m, 2H); ^{13}C NMR: *d* = 20.4 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 61.4 (CH_2), 65.7 (dd, ^2J(F,C) = 18.3, 18.3 Hz, CH), 66.4 (CH), 67.3 (CH), 91.9 (dd, ^2J(F,C) = 27.4, 30.5 Hz, CH), 114.2 (dd, ^1J(F,C) = 247.2, 253.3 Hz, C), 169.7 (C), 170.5 (C), 170.7 ppm (C); ^{19}F NMR: *d* = –119.9 (dd, ^3J(F,H) = 18.4 Hz, ^2J(F,F) = 252.4 Hz, 1F), –120.7 ppm (dd, ^3J(F,H) = 13.8 Hz, ^2J(F,F) = 252.4 Hz, 1F); IR: $\tilde{n}$ = 3612, 1758, 1371, 1235, 1124 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 327 (<1) $[M+1]^+$, 309 (4), 267 (2), 223 (8), 206 (17), 178 (20), 164 (36), 148 (60), 103 (100); HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}F_2O_8$ $[M+1]^+$: 327.0891, found: 327.0883; elemental analysis calcd (%) for $C_{12}H_{16}F_2O_8$ (326.25): C 44.18, H 4.94; found: C 43.91, H 5.09.

3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-D-galactopyranose and 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-D-talopyranose (13): Oil (70 %), mixture of diastereoisomers at C-2 in ratio 3:2; ^{1}H NMR: *d* = 2.06 (s, 6H), 2.11 (s, 3H), 2.13 (s, 3H), 2.146 (s, 3H), 2.150 (s, 3H), 4.17 (d, *J* = 6.7 Hz, 2H), 4.173 (d, *J* = 6.7 Hz, 2H), 4.62 (ddd, *J* = 1.7, 6.7, 6.7 Hz, 2H), 4.94 (d, *J* = 4.5 Hz, 1H), 4.97 (d, *J* = 4.8 Hz, 1H), 5.33–5.48 (m, 5H), 5.66 ppm (dd, *J* = 4.0 Hz, ^3J(F,H) = 9.3 Hz, 1H); ^{13}C NMR: *d* = 20.2 (CH_3), 20.37 (CH_3), 20.42 ($2 \times CH_3$), 20.5 ($2 \times CH_3$), 61.4 ($2 \times CH_2$), 66.0 (CH), 66.2 (CH), 66.8 (d, ^3J(F,C) = 8.6 Hz, CH), 67.4 (CH), 68.0 (d, ^2J(F,C) = 21.5 Hz, CH), 69.0 (d, ^2J(F,C) = 16.1 Hz, CH), 94.5 (d, ^2J(F,C) = 32.2 Hz, CH), 95.3 (d, ^2J(F,C) = 23.6 Hz, CH), 105.8 (d, ^1J(F,C) = 254.6 Hz, C), 107.1 (d, ^1J(F,C) = 252.5 Hz, C), 169.6 (C), 169.7 (C), 170.3 (C), 170.5 (C), 170.6 (C), 171.3 ppm (C); ^{19}F NMR: *d* = –120.4 (s, 1F), –125.6 ppm (d, ^3J(F,H) = 26.3 Hz, 1F); IR: $\tilde{n}$ = 3610, 3431, 2959, 1755, 1371, 1222, 1079 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 327/325 (4/11) $[M–OH]^+$, 239/237 (3/5), 196/194 (4/14), 115 (36), 103 (59), 91 (100); HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}{}^{37}ClFO_7$ $[M–OH]^+$: 327.0461, found: 327.0449; elemental analysis calcd (%) for $C_{12}H_{16}ClFO_8$ (342.71): C 42.06, H 4.71; found: C 42.22, H 4.99.

3,4,6-Tri-*O*-acetyl-2-bromo-2-deoxy-2-fluoro-D-galactopyranose (14): Crystalline solid (76 %), anomeric mixture in ratio 4:1 by NMR, only major isomer described: ^{1}H NMR (500 MHz): *d* = 2.05 (s, 3H), 2.11 (s, 3H), 2.15 (s, 3H), 4.16 (dd, *J* = 1.2, 6.7 Hz, 2H), 4.61 (ddd, *J* = 1.9, 6.7, 6.7 Hz, 1H), 5.43 (ddd, *J* = 1.9, 4.0 Hz, ^{4}J(F,H) = 3.7 Hz, 1H), 5.56 (dd, *J* = 4.0 Hz, ^{3}J(F,H) = 10.8 Hz, 1H), 5.64 ppm (s, 1H); ^{13}C NMR (125.7 MHz): *d* = 20.5 (CH_3), 20.6 ($2 \times CH_3$), 61.4 (CH_2), 66.2 (CH), 66.7 (d, ^{3}J(F,C) = 9.1 Hz, CH), 68.4 (d, ^{2}J(F,C) = 21.1 Hz, CH), 96.2 (d, ^{2}J(F,C) = 22.2 Hz, CH), 100.6 (d, ^{1}J(F,C) = 263.7 Hz, C), 169.7 (C), 170.2 (C), 170.7 ppm (C); ^{19}F NMR: *d* = –119.3 ppm (br s, 1F); IR: $\tilde{n}$ = 3432, 1755, 1372, 1225, 1079 cm^{-1}; MS (70 eV, EI): *m/z* (%): 371/369 (1/1) [*M*–OH]$^{+}$, 277 (56), 159 (29), 145 (41), 115 (61), 103 (100); HRMS (EI): *m/z* calcd for $C_{12}H_{15}{}^{81}BrFO_7$ [*M*–OH]$^{+}$: 370.9965, found: 370.9965; elemental analysis calcd (%) for $C_{12}H_{16}BrFO_8$ (387.16): C 37.23, H 4.17; found: C 37.56, H 4.17.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-2-iodo-D-galactopyranose (15): Oil (90 %), anomeric mixture in ratio 3:1 by NMR, major isomer: ^{1}H NMR (500 MHz): *d* = 2.04 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 4.07–4.18 (d, *J* = 6.6 Hz, 2H), 4.46 (s, 1H), 4.61 (ddd, *J* = 1.9, 6.6, 6.6, 1H), 5.07 (dd, *J* = 4.0 Hz, ^{3}J(F,H) = 12.7 Hz, 1H), 5.41–5.49 (m, 1H), 5.85 ppm (s, 1H); ^{13}C NMR: *d* = 20.7 ($2 \times CH_3$), 20.8 (CH_3), 61.5 (CH_2), 66.0 (CH), 66.7 (CH), 69.2 (d, ^{2}J(F,C) = 20.3 Hz, CH), 83.3 (d, ^{1}J(F,C) = 263.8 Hz, C), 98.5 (d, ^{2}J(F,C) = 22.0 Hz, CH), 169.6 (C), 170.2 (C), 170.8 ppm (C); ^{19}F NMR: *d* = –119.9 ppm (br s, 1F); minor isomer: ^{1}H NMR (500 MHz): *d* = 2.12 (s, 3H), 2.16 (s, 3H), 2.17 (s, 3H), 3.80 (br s, 1H), 4.07–4.18 (m, 3H), 4.90 (dd, *J* = 4.3 Hz, ^{3}J(F,H) = 13.6 Hz, 1H), 5.38–5.39 ppm (m, 1H); ^{13}C NMR: *d* = 20.7 (CH_3), 20.8 ($2 \times CH_3$), 61.2 (CH_2), 66.5 (CH), 72.0 (CH), 72.5 (d, ^{2}J(F,C) = 19.4 Hz, CH), 83.3 (d, ^{1}J(F,C) = 263.8 Hz, C), 95.7 (d, ^{2}J(FC) = 25.0 Hz, CH), 169.5 (C), 170.0 (C), 170.7 ppm (C); ^{19}F NMR: *d* = –118.7 ppm (d, ^{3}J(F,H) = 13.8 Hz, 1F); IR: $\tilde{n}$ = 3468, 1755, 1372, 1235, 1074 cm^{-1}; MS (70 eV, EI): *m/z* (%): 417 (6) [*M*–OH]$^{+}$, 374 (3), 242 (37), 103 (100); HRMS (EI): *m/z* calcd for $C_{12}H_{16}FIO_7$ [*M*–OH]$^{+}$: 416.9847, found: 416.9860; elemental analysis calcd (%) for $C_{12}H_{16}FIO_8$ (434.16): C 33.20, H 3.71; found: C 33.20, H 3.80.

2-Deoxy-2,2-difluoro-3,4,6-tri-*O*-methyl-a**-D-*lyxo*-hexopyranose (16)**: Oil (71 %); ^{1}H NMR: *d* = 3.40 (s, 3H), 3.56 (s, 3H), 3.57–3.58 (m, 2H), 3.62 (s, 3H), 3.63–3.73 (m, 3H), 4.28 (dd, *J* = 4.2, 7.9 Hz, 1H), 5.21 ppm (d, ^{3}J(F,H) = 7.4 Hz, 1H); ^{13}C NMR: *d* = 59.1 (CH_3), 60.0 (d, ^{4}J(F,C) = 2.1 Hz, CH_3), 61.6 (CH_3), 69.3 (CH_2), 71.5 ($2 \times CH$),

77.1 (dd, ^{2}J(F,C) = 31.2, 31.2 Hz, CH), 91.9 (dd, ^{2}J(F,C) = 27.9, 37.6 Hz, CH), 116.7 ppm (dd, ^{1}J(F,C) = 254.6, 250.3 Hz, C); MS (70 eV, EI): *m/z* (%): 243 (<1) $[M+1]^{+}$, 222 (3), 177 (4), 165 (9), 119 (19), 107 (87), 101 (100); HRMS (EI): *m/z* calcd for $C_9H_{17}F_2O_5$ $[M+1]^{+}$: 243.1044, found: 243.1055; elemental analysis calcd (%) for $C_9H_{16}F_2O_5$ (242.22): C 44.63, H 6.66; found: C 44.57, H 6.70.

3,4,6-Tri-*O*-benzyl-2-deoxy-2,2-difluoro-a**-D-*lyxo*-hexopyranose (17)**: Oil (47 %); ^{1}H NMR (500 MHz): *d* = 3.40 (dd, *J* = 5.0, 9.9 Hz, 1H), 3.63 (dd, *J* = 7.0, 9.9 Hz, 1H), 3.86 (br s, 1H), 3.96 (ddd, *J* = 3.8 Hz, ^{3}J(F,H) = 3.8, 22.9 Hz, 1H), 4.21 (ddd, *J* = 1.4, 5.0, 7.0 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.92 (d, *J* = 11.9 Hz, 1H), 4.93 (d, *J* = 11.4 Hz, 1H), 5.21 (d, ^{3}J(F,H) = 7.1 Hz, 1H), 7.25–7.39 ppm (m, 15 H); ^{13}C NMR: *d* = 69.3 (CH_2), 69.8 (CH), 73.5 (CH_2), 74.1 (d, ^{4}J(F,C) = 2.1 Hz, CH_2), 74.4 (CH_2), 74.6 (CH), 74.7 (dd, ^{2}J(F,C) = 18.7, 23.4 Hz, CH), 91.9 (dd, ^{2}J(F,C) = 27.9, 37.6 Hz, CH), 116.8 (dd, ^{1}J(F,C) = 252.5, 253.6 Hz, C), 127.7 (CH), 127.8 (2 × CH), 127.9 (CH), 128.0 (CH), 128.1 (2 × CH), 128.2 (2 × CH), 128.42 (2 × CH), 128.45 (2 × CH), 128.49 (2 × CH), 137.2 (C), 137.5 (C), 138.0 ppm (C); ^{19}F NMR: *d* = –117.4 (d, ^{2}J(F,F) = 252.4 Hz, 1F), –120.0 ppm (dd, ^{3}J(F,H) = 22.9 Hz, ^{2}J(F,F) = 254.2 Hz, 1F); IR: $\tilde{n}$ = 3613, 3400, 3030, 2928, 2872, 1455, 1154, 1110, 1064 cm^{-1}; MS (70 eV, EI): *m/z* (%): 379 (5) $[M–Bn]^{+}$, 271 (6), 211 (1), 197 (3), 181 (4), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{21}F_2O_5$ $[M–Bn]^{+}$: 379.1357, found: 379.1374; elemental analysis calcd (%) for $C_{27}H_{28}F_2O_5$ (470.51): C 68.92, H 6.00; found: C 68.66, H 6.30.

3,4,6-Tri-*O*-benzyl-2-bromo-2-deoxy-2-fluoro-D-galactopyranose and 3,4,6-tri-*O*-benzyl-2-bromo-2-deoxy-2-fluoro-D-talopyranose (18): Oil (64 %), NMR showed a complex mixture of isomers. ^{19}F NMR: *d* = –113.3 (d, ^{3}J(F,H) = 9.2 Hz, 1F), –121.9 ppm (d, ^{3}J(F,H) = 27.5 Hz, 1F); IR: $\tilde{n}$ = 3608, 3404, 3032, 2872, 1454, 1080 cm^{-1}; MS (70 eV, EI): *m/z* (%): 441/439 (1/1) $[M–Bn]^{+}$, 359 (1), 253 (1), 181 (4), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{21}{}^{79}BrFO_5$ $[M–Bn]^{+}$: 439.0556, found: 439.0541; elemental analysis calcd (%) for $C_{27}H_{28}BrFO_5$ (531.42): C 61.02, H 5.31; found: C 61.09, H 5.60.

3,4,6-tri-*O*-benzyl-2-deoxy-2-fluoro-2-iodo-D-galactopyranose (19): Oil (86 %), anomeric mixture in ratio 5:1, only major isomer described; ^{1}H NMR: *d* = 3.47 (dd, *J* = 4.3, 10.2 Hz, 1H), 3.61 (dd, *J* = 3.6 Hz, ^{3}J(F,H) = 11.7 Hz, 1H), 3.69 (dd, *J* = 7.6, 10.0

Hz, 1H), 3.91 (m, 1H), 4.14 (br s, 1H), 4.34 (ddd, J = 2.6, 4.3, 7.6 Hz, 1H), 4.40 (d, J = 11.9 Hz, 1H), 4.50 (d, J = 11.9 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.70 (d, J = 11.4 Hz, 1H), 4.95 (d, J = 11.7 Hz, 1H), 5.00 (d, J = 11.4 Hz, 1H), 5.73 (s, 1H), 7.26–7.44 ppm (m, 15 H); ^{13}C NMR: d = 68.8 (CH_2), 70.2 (CH), 73.5 (CH_2), 73.8 (CH_2), 73.9 (CH_2), 74.4 (d, ^3J(F,C) = 9.2 Hz, CH), 78.6 (d, ^2J(F,C) = 18.3 Hz, CH), 90.4 (d, ^1J(F,C) = 262.4 Hz, C), 97.8 (d, ^2J(F,C) = 21.4 Hz, CH), 127.6–128.5 (15 × CH), 137.4 (C), 137.7 (C), 138.1 ppm (C); ^{19}F NMR: d = –114.3 ppm (br s, 1F); IR: $\tilde{n}$ = 3615, 3384, 3032, 2870, 1497, 1454, 1351 cm^{-1}; MS (70 eV, EI): *m/z* (%): 487 (1) [*M*–Bn]$^+$, 469 (<1), 359 (4), 254 (15), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{21}FIO_5$ [*M*–Bn]$^+$: 487.0418, found: 487.0408; elemental analysis calcd (%) for $C_{27}H_{28}FIO_5$ (578.42): C 56.06, H 4.88; found: C 56.00, H 4.90.

3,4-Di-*O*-acetyl-2,6-dideoxy-2,2-difluoro-b**-L-lyxo-hexopyranose (20)**: Oil (76 %); ^{1}H NMR (500 MHz): d = 1.18 (d, J = 6.6 Hz, 3H), 2.08 (s, 3H), 2.16 (s, 3H), 4.26 (d, J = 3.9 Hz, 1H), 4.50 (dddd, J = 1.6, 6.6, 6.6, 6.6 Hz, 1H), 5.21 (dd, J = 3.9 Hz, ^3J(F,H) = 6.2 Hz, 1H), 5.27 (dd, J = 1.6, 3.9 Hz, 1H), 5.44 ppm (ddd, J = 3.9 Hz, ^3J(F,H) = 6.0, 22.3 Hz, 1H); ^{13}C NMR (125.7 MHz): d = 15.8 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 64.6 (CH), 66.1 (dd, ^2J(F,C) = 19.0, 19.0 Hz, CH), 69.7 (CH), 91.8 (dd, ^2J(F,C) = 28.6, 35.3 Hz, CH), 114.3 (dd, ^1J(F,C) = 252.2, 252.2 Hz, C), 169.9 (C), 171.1 ppm (C); ^{19}F NMR: d = –120.0 (dd, ^3J(F,H) = 24.0 Hz, ^2J(F,F) = 252.3 Hz, 1F), –121.9 ppm (d, ^2J(F,F) = 252.3 Hz, 1F); IR: $\tilde{n}$ = 3610, 2940, 1753, 1368, 1237, 1117, 1090 cm^{-1}; MS (70 eV, EI): *m/z* (%): 251 (5) [*M*–OH]$^+$, 233 (5), 209 (4), 163 (24), 148 (95), 135 (81), 130 (60), 120 (91), 103 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{13}F_2O_5$ [*M*–OH]$^+$: 251.0731, found: 251.0729; elemental analysis calcd (%) for $C_{10}H_{14}F_2O_6$ (268.21): C 44.78, H 5.26; found: C 44.51, H 5.46.

3,4-Di-*O*-acetyl-2-chloro-2,6-dideoxy-2-fluoro-L-galactopyranose and 3,4-di-*O*-acetyl-2-chloro-2,6-dideoxy-2-fluoro-L-talopyranose (21): Oil (63 %), mixture of two isomers at C-2 in 1:1 ratio. ^{1}H NMR (500 MHz): d = 1.19 (d, J = 6.6 Hz, 3H), 1.20 (d, J = 6.6 Hz, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.159 (s, 3H), 2.161 (s, 3H), 4.02–4.06 (m, 2H), 4.52–4.58 (m, 2H), 5.24 (dd, J = 1.7, 3.8 Hz, 1H), 5.26 (ddd, J = 1.7, 3.7 Hz, ^4J(F,H) = 3.7 Hz, 1H), 5.34 (dd, J = 4.2 Hz, ^3J(F,H) = 6.1 Hz, 1H), 5.41 (d, J = 3.9 Hz, 1H), 5.44 (dd, J = 3.9 Hz, ^3J(F,H) = 26.4 Hz, 1H), 5.65 ppm (dd, J = 4.0 Hz, ^3J(F,H) = 9.6 Hz, 1H); ^{13}C NMR (125.7 MHz): d = 15.6 (CH_3), 15.7 (CH_3), 20.4 (2 × CH_3), 20.6

(2 × CH_3), 64.6 (CH), 64.8 (CH), 68.5 (d, ^2J(F,C) = 21.4 Hz, CH), 69.5 (d, ^2J(F,C) = 15.8 Hz, CH), 69.7 (d, ^4J(F,C) = 7.8 Hz, CH), 70.1 (CH), 94.6 (d, ^2J(F,C) = 32.6 Hz, CH), 95.5 (d, ^2J(F,C) = 23.4 Hz, CH), 105.9 (d, ^1J(F,C) = 253.8 Hz, C), 107.2 (d, ^1J(F,C) = 252.0 Hz, C), 169.7 (C), 169.8 (C), 170.8 (C), 171.0 ppm (C); ^{19}F NMR: d = –120.6 (d, ^3J(F,H) = 9.1 Hz, 1F), –125.1 ppm (d, ^3J(F,H) = 27.5 Hz, 1F); IR: $\tilde{n}$ = 3613, 2958, 2872, 1753, 1369, 1237, 1216, 1079 cm^{-1}; MS (70 eV, EI): *m/z* (%): 269/267 (2/7) $[M–OH]^+$, 219 (10), 189 (21), 152 (100), 136 (87); HRMS (EI): *m/z* calcd for $C_{10}H_{13}{}^{35}ClFO_5$ $[M–OH]^+$: 267.0436, found: 267.0448; elemental analysis calcd (%) for $C_{10}H_{14}ClFO_6$ (284.67): C 42.19, H 4.97; found: C 42.19, H 4.97.

3,4-Di-*O*-acetyl-2-bromo-2,6-dideoxy-2-fluoro-L-galactopyranose (22): Oil (82 %), anomeric mixture in ratio 4:1 by NMR, only major described; ^{1}H NMR: d = 1.18 (d, J = 6.4 Hz, 3H), 2.11 (s, 3H), 2.18 (s, 3H), 4.14 (d, J = 3.0 Hz, 1H), 4.54 (dddd, J = 1.8, 6.4, 6.4, 6.4 Hz, 1H), 5.25 (ddd, J = 1.8, 4.2 Hz, ^4J(F,H) = 3.7 Hz, 1H), 5.53 (dd, J = 4.2 Hz, ^3J(F,H) = 11.1 Hz, 1H), 5.58 ppm (dd, J = 3.0 Hz, 1H); ^{13}C NMR: d = 15.5 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 64.4 (CH), 68.9 (d, ^2J(F,C) = 20.4 Hz, CH), 69.5 (d, ^3J(F,C) = 7.5 Hz, CH), 96.3 (d, ^2J(F,C) = 22.6 Hz, CH), 100.9 (d, ^1J(F,C) = 263.2 Hz, C), 169.8 (C), 170.7 ppm (C); ^{19}F NMR: d = –118.4 ppm (d, ^3J(F,H) = 9.1 Hz, 1F); IR: $\tilde{n}$ = 3612, 3470, 2990, 2941, 1752, 1368, 1236, 1162, 1083 cm^{-1}; MS (70 eV, EI): *m/z* (%): 313/311 (2/2) $[M–OH]^+$, 270/268 (2/2), 255/253 (2/2), 243/241 (4/4), 211 (3), 182/180 (57/57), 153/151 (52/52), 99 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{13}{}^{81}BrFO_5$ $[M–OH]^+$: 312.9910, found: 312.9900; elemental analysis calcd (%) for $C_{10}H_{14}BrFO_6$ (329.12): C 36.49, H 4.29; found: C 36.56, H 4.52.

3,4-Di-*O*-acetyl-2,6-dideoxy-2-fluoro-2-iodo-L-galactopyranose (23): Oil (86 %), anomeric mixture in ratio 2:1; ^{1}H NMR: d = 1.20 (d, J = 6.6 Hz, 3H), 1.24 (d, J = 6.5 Hz, 3H), 2.12 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.26 (s, 3H), 3.21 (d, J = 2.6 Hz, 1H), 3.48 (d, J = 11.4 Hz, 1H), 3.70 (dd, J = 11.4 Hz, ^3J(F,H) = 3.6 Hz, 1H), 3.98 (dddd, J = 1.4, 6.5, 6.5, 6.5 Hz, 1H), 4.57 (dddd, J = 1.8, 6.6, 6.6, 6.6 Hz, 1H), 4.91 (dd, J = 4.0 Hz, ^3J(F,H) = 13.7 Hz, 1H), 5.09 (dd, J = 4.0 Hz, ^3J(F,H) = 13.0 Hz, 1H), 5.26 (ddd, J = 1.4, 4.0 Hz, ^4J(F,H) = 2.5 Hz, 1H), 5.32 (ddd, J = 1.8, 4.0 Hz, ^4J(F,H) = 3.0 Hz, 1H), 5.84 ppm (d, J = 2.6 Hz, 1H); ^{13}C NMR: d = 15.5 (CH_3), 15.6 (CH_3), 20.6 (CH_3), 20.7 (2 × CH_3), 20.8 (CH_3), 64.3 (CH), 69.4 (CH), 69.5 (CH), 69.6 (d, ^2J(F,C) = 20.3 Hz, CH), 70.7 (CH), 72.8 (d, ^2J(F,C) = 19.2 Hz, CH), 83.9 (d, ^1J(F,C) = 262.0 Hz, 2 × C),

95.6 (d, ^{2}J(F,C) = 24.7 Hz, CH), 98.7 (d, ^{2}J(F,C) = 21.2 Hz, CH), 169.6 (C), 169.7 (C), 170.6 ppm (2 × C); ^{19}F NMR: d = –118.5 (d, ^{3}J(F,H) = 13.5 Hz, 1F), –119.6 ppm (br s, 1F); IR: $\tilde{n}$ = 3611, 3523, 2939, 1752, 1372, 1233, 1084 cm^{-1}; MS (70 eV, EI): *m/z* (%): 376 (1) $[M]^{+}$, 316 (43), 254 (18), 243 (55), 228 (64), 199 (94), 189 (76), 127 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{14}FIO_6$ $[M]^{+}$: 375.9819, found: 375.9813; elemental analysis calcd (%) for $C_{10}H_{14}FIO_6$ (376.12): C 31.93, H 3.75; found: C 31.81, H 3.74.

6-*O*-Benzyl-2-bromo-2-deoxy-2-fluoro-3,4-*O*-isopropylidene-D-galactopyranose (24): Oil (55 %), anomeric mixture in ratio 8:1, only major isomer described. ^{1}H NMR (500 MHz): d = 1.33 (s, 3H), 1.53 (s, 3H), 3.67 (dd, *J* = 2.9, 10.4 Hz, 1H), 3.79 (dd, *J* = 8.8, 10.4 Hz, 1H), 4.09 (dd, *J* = 3.0, 5.8 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.59 (ddd, *J* = 2.9, 3.0, 8.8 Hz, 1H), 4.61 (dd, *J* = 5.8 Hz, ^{3}J(F,H) = 19.8 Hz, 1H), 4.73 (d, *J* = 12.2 Hz, 1H), 5.25 (d, *J* = 4.8 Hz, 1H), 5.46 (dd, *J* = 4.8 Hz, ^{3}J(F,H) = 4.8 Hz, 1H), 7.30–7.37 ppm (m, 5H); ^{13}C NMR (125.7 MHz): d = 25.6 (CH_3), 25.7 (CH_3), 66.0 (CH), 69.2 (CH_2), 73.4 (CH), 73.7 (CH_2), 77.2 (d, ^{2}J(F,C) = 15.2 Hz, CH), 94.6 (d, ^{2}J(F,C) = 31.5 Hz, CH), 103.0 (d, ^{1}J(F,C) = 258.7 Hz, C), 110.7 (C), 128.1 (2 × CH), 128.3 (CH), 128.5 (2 × CH), 137.0 ppm (C); ^{19}F NMR: d = –118.6 ppm (d, ^{3}J(F,H) = 22.9 Hz, 1F); IR: $\tilde{n}$ = 3355, 2938, 1455, 1383, 1220, 1149, 1096 cm^{-1}; MS (70 eV, EI): *m/z* (%): 392/390 (1/1) $[M]^{+}$, 377/375 (3/3), 235 (9), 91 (100); HRMS (EI): *m/z* calcd for $C_{16}H_{20}{}^{81}BrFO_5$ $[M]^{+}$: 392.0458, found: 392.0471; elemental analysis calcd (%) for $C_{16}H_{20}BrFO_5$ (391.23): C 49.12, H 5.15; found: C 49.22, H 5.19.

6-*O*-Benzyl-2-deoxy-2-fluoro-3,4-*O*-isopropylidene-2-iodo-D-galactopyranose (25): Crystalline solid (79 %), anomeric mixture in ratio 10:1, only major isomer described. ^{1}H NMR (500 MHz): d = 1.34 (s, 3H), 1.54 (s, 3H), 3.66 (dd, *J* = 2.9, 10.3 Hz, 1H), 3.80 (dd, *J* = 9.0, 10.3 Hz, 1H), 3.98 (dd, *J* = 3.0, 5.6 Hz, 1H), 4.52 (d, *J* = 12.3 Hz, 1H), 4.61 (ddd, *J* = 2.9, 3.0, 9.0 Hz, 1H), 4.72 (dd, *J* = 5.6 Hz, ^{3}J(F,H) = 22.3 Hz, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 5.28 (d, *J* = 4.5 Hz, 1H), 5.58 (dd, *J* = 4.5, ^{3}J(F,H) = 4.3 Hz, 1H), 7.30–7.39 ppm (m, 5H); ^{13}C NMR (125.7 MHz): d = 25.5 (CH_3), 25.8 (CH_3), 65.7 (CH), 69.3 (CH_2), 73.3 (CH), 73.7 (CH_2), 79.4 (d, ^{2}J(F,C) = 14.7 Hz, CH), 88.2 (d, ^{1}J(F,C) = 260.7 Hz, C), 96.2 (d, ^{2}J(F,C) = 28.9 Hz, CH), 110.4 (C), 127.9 (CH), 128.3 (2 × CH), 128.5 (2 × CH), 137.0 ppm (C); ^{19}F NMR: d = –119.0 ppm (d, ^{3}J(F,H) = 22.9 Hz, 1F); IR: $\tilde{n}$ = 3356, 3018, 1550, 1214, 1094 cm^{-1}; MS (70 eV, EI): *m/z* (%): 438 (2) $[M]^{+}$, 423 (4), 380 (1), 332 (2), 253 (4), 235 (5), 189 (2), 149 (3), 107 (78), 91 (100);

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}FIO_5$ $[M]^+$: 438.0340, found: 438.0347; elemental analysis calcd (%) for $C_{16}H_{20}FIO_5$ (438.23): C 43.85, H 4.60; found: C 43.96, H 4.61.

2-Chloro-2-deoxy-6-*O*-(3,5-dinitrobenzoyl)-2-fluoro-3,4-*O*-isopropylidene-a**-D-galactopyranose (26)**: Oil (40 %); ^{1}H NMR: *d* = 1.43 (s, 3H), 1.58 (s, 3H), 3.56 (d, *J* = 5.0 Hz, 1H), 4.41 (ddd, *J* = 1.2, 2.7, 5.8 Hz, 1H), 4.64 (d, *J* = 5.8 Hz, ^3J(F,H) = 17.5 Hz, 1H), 4.70–4.78 (m, 3H), 5.38 (dd, *J* = 5.0 Hz, ^3J(F,H) = 5.8 Hz, 1H), 9.17 (d, *J* = 2.1 Hz, 2H), 9.23 ppm (dd, *J* = 2.1, 2.1 Hz, 1H); ^{13}C NMR: *d* = 25.6 (CH_3), 25.7 (CH_3), 65.3 (CH), 65.6 (CH_2), 73.0 (CH), 76.2 (d, ^2J(F,C) = 17.2 Hz, CH), 93.7 (d, ^2J(F,C) = 33.3 Hz, CH), 106.2 (d, ^1J(F,C) = 251.4 Hz, C), 111.4 (C), 122.6 (CH), 129.5 (2 × CH), 133.5 (C), 148.7 (2 × C), 162.4 ppm (C); ^{19}F NMR: *d* = –121.1 ppm (d, ^3J(F,H) = 18.4 Hz, 1F); IR: $\tilde{n}$ = 3610, 3455, 3102, 2958, 1740, 1549, 1343, 1266, 1154 cm^{-1}; MS (70 eV, EI): *m/z* (%): 437/435 (10/29) $[M–CH_3]^+$, 399 (45), 385 (17), 195 (100), 149 (29); HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}ClFN_2O_{10}$ $[M–CH_3]^+$: 435.0243, found: 435.0220; elemental analysis calcd (%) for $C_{16}H_{16}ClFN_2O_{10}$ (450.76): C 42.63, H 3.58; N, 6.21; found: C 42.46, H 3.53; N, 6.47.

2-Bromo-2-deoxy-6-*O*-(3,5-dinitrobenzoyl)-2-fluoro-3,4-*O*-isopropylidene-a**-D-galactopyranose (27)**: Oil (67 %); ^{1}H NMR (500 MHz, CD_3OD): *d* = 1.40 (s, 3H), 1.50 (s, 3H), 4.45 (dd, *J* = 3.0, 5.6 Hz, 1H), 4.65 (d, *J* = 6.0 Hz, 2H), 4.78–7.82 (m, 2H), 5.28 (d, ^3J(F,H) = 4.6 Hz, 1H), 9.09 (d, *J* = 2.0 Hz, 2H), 9.19 ppm (dd, *J* = 2.0, 2.0 Hz, 1H); ^{13}C NMR (125.7 MHz, CD_3OD**)**: *d* = 26.0 (2 × CH_3), 65.7 (CH), 66.3 (CH_2), 74.9 (d, ^3J(F,C) = 6.1 Hz, CH), 78.7 (d, ^2J(F,C) = 15.3 Hz, CH), 96.0 (d, ^2J(F,C) = 30.5 Hz, CH), 104.7 (d, ^1J(F,C) = 259.4 Hz, C), 111.6 (C), 123.6 (CH), 130.1 (2 × CH), 134.7 (C), 150.2 (2 × C), 164.0 ppm (C); ^{19}F NMR: *d* = –119.3 ppm (d, ^3J(F,H) = 18.4 Hz, 1F); IR: $\tilde{n}$ = 3610, 3405, 3098, 2950, 1741, 1550, 1342, 1280, 1152 cm^{-1}; MS (70 eV, EI): *m/z* (%): 481/479 (13/10) $[M–CH_3]^+$, 399 (70), 385 (29), 195 (100); HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}{}^{79}BrF\ N_2O_{10}$ $[M–CH_3]^+$: 478.9738, found: 478.9737; elemental analysis calcd (%) for $C_{16}H_{16}BrFN_2O_{10}$ (495.21): C 38.81, H 3.26; N, 5.66; found: C 38.56, H 3.22; N, 5.42.

3,4,6-Tri-*O*-acetyl-2-deoxy-2,2-difluoro-a**-D-arabino-hexopyranose (28)**: Crystalline solid (67 %); ^{1}H NMR: *d* = 2.05 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.88 (d, *J* = 4.5 Hz, 1H), 4.19 (dd, *J* = 2.6, 12.4 Hz, 1H), 4.24 (dd, *J* = 4.3, 12.4 Hz, 1H), 4.32 (ddd, *J* = 2.6,

4.3, 10.3 Hz, 1H), 5.23 (ddd, J = 9.8, 10.3 Hz, ^{4}J(F,H) = 1.0 Hz, 1H), 5.27 (dd, J = 4.5 Hz, ^{3}J(F,H) = 5.0 Hz, 1H), 5.61 ppm (ddd, J = 9.8 Hz, ^{3}J(F,H) = 4.8, 20.4 Hz, 1H); ^{13}C NMR: d = 20.3 (CH_3), 20.4 (CH_3), 20.6 (CH_3), 61.8 (CH_2), 67.6 (d, ^{3}J(F,C) = 6.6 Hz, CH), 67.8 (CH), 68.7 (dd, ^{2}J(F,C) = 18.5, 21.0 Hz, CH), 91.2 (dd, ^{2}J(F,C) = 28.5, 35.6 Hz, CH), 115.5 (dd, ^{1}J(F,C) = 245.3, 257.7 Hz, C), 169.5 (C), 169.9 (C), 171.1 ppm (C); ^{19}F NMR: d = –120.9 (d, ^{2}J(F,F) = 252.4 Hz, 1F), –122.5 ppm (dd, ^{3}J(F,H) = 18.3 Hz, ^{2}J(F,F) = 252.3 Hz, 1F); IR: $\tilde{n}$ = 3606, 2955, 1764, 1369, 1224 cm^{-1}; MS (70 eV, EI): *m/z* (%): 309 (3) [*M*–OH]$^{+}$, 291 (1), 206 (17), 164 (33), 145 (62), 103 (100); HRMS (EI): *m/z* calcd for $C_{12}H_{15}F_2O_7$ [*M*–OH]$^{+}$: 309.0786, found: 309.0786; elemental analysis calcd (%) for $C_{12}H_{16}F_2O_8$ (326.25): C 44.18, H 4.94; found: C 44.08, H 5.06.

3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-D-glucopyranose and 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-D-mannopyranose (29): Oil (65 %), diastereoisomeric mixture at C-2 in ratio 3:1, only major isomer described. ^{1}H NMR (500 MHz): d = 2.04 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 4.18 (d, J = 3.4 Hz, 2H), 4.32 (ddd, J = 3.4, 3.4, 10.1 Hz, 1H), 4.86 (d, J = 4.2 Hz, 1H), 5.20 (dd, J = 9.3, 10.1 Hz, 1H), 5.38 (d, J = 4.0 Hz, 1H), 5.78 ppm (dd, J = 9.3 Hz, ^{3}J(F,H) = 7.9 Hz, 1H); ^{13}C NMR (125 MHz): d = 20.4 ($2 \times CH_3$), 20.6 (CH_3), 61.8 (CH_2), 67.9 (d, ^{3}J(F,C) = 5.1 Hz, CH), 68.2 (CH), 70.6 (d, ^{2}J(F,C) = 21.3 Hz, CH), 94.4 (d, ^{2}J(F,C) = 24.3 Hz, CH), 108.4 (d, ^{1}J(F,C) = 259.8 Hz, C), 169.5 (C), 169.9 (C), 171.0 ppm (C); ^{19}F NMR: d = –122.0 ppm (s, 1F); IR: $\tilde{n}$ = 3606, 3471, 2957, 1762, 1370, 1221, 1068, 1048 cm^{-1}; MS (70 eV, EI): *m/z* (%): 327/325 (3/9) [*M*–OH]$^{+}$, 211/209 (5/11), 196/194 (7/20), 153/151 (12/38), 145 (54), 103 (100); HRMS (EI): *m/z* calcd for $C_{12}H_{15}{}^{37}ClFO_7$ [*M*–OH]$^{+}$: 327.0461, found: 327.0460; elemental analysis calcd (%) for $C_{12}H_{16}ClFO_8$ (342.71): C 42.06, H 4.71; found: C 42.05, H 5.04.

3,4,6-Tri-*O*-acetyl-2-bromo-2-deoxy-2-fluoro-D-glucopyranose (30): Oil (72 %), anomeric mixture in ratio 8:1, only major isomer described. ^{1}H NMR (500 MHz): d = 2.04 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 4.15 (dd, J = 4.2, 12.4 Hz, 1H), 4.19 (dd, J = 2.6, 12.4 Hz, 1H), 4.31 (ddd, J = 2.6, 4.2, 10.0 Hz, 1H), 4.67 (br s, 1H), 5.22 (dd, J = 9.5, 10.0 Hz, 1H), 5.54 (s, 1H), 5.61 ppm (dd, J = 9.5 Hz, ^{3}J(F,H) = 9.5 Hz, 1H); ^{13}C NMR (125.7 MHz): d = 20.5 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 61.8 (CH_2), 68.2 (d, ^{3}J(F,C) = 5.3 Hz, CH), 68.4 (CH), 70.9 (d, ^{3}J(F,C) = 19.4 Hz, CH), 95.1 (d, ^{2}J(F,C) = 23.2 Hz, CH), 104.4 (d, ^{1}J(F,C) = 263.7 Hz, C), 169.5 (C), 169.9 (C), 171.1 ppm (C);

^{19}F NMR: d = –120.1 ppm (d, ^{3}J(F,H) = 8.8 Hz, 1F); IR: $\tilde{n}$ = 3607, 3449, 1764, 1221, 1047 cm^{-1}; MS (70 eV, EI): *m/z* (%): 371/369 (14/14) [*M*–OH]$^{+}$, 329/327 (2/2), 277 (23), 240/238 (14/14), 197/195 (18/18), 159 (30), 145 (60), 103 (100); HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}{}^{81}BrFO_7$ [*M*–OH]$^{+}$: 370.9965, found: 370.9967; elemental analysis calcd (%) for $C_{12}H_{16}BrFO_8$ (387.16): C 37.23, H 4.17; found: C 37.14, H 4.25.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-2-iodo-D-glucopyranose (31): Oil (84 %), anomeric mixture in ratio 3:1, major isomer: ^{1}H NMR: d = 2.05 (s, 3H), 2.12 (s, 3H), 2.15 (s, 3H), 3.63 (s, 1H), 4.15 (dd, *J* = 4.5, 12.4 Hz, 1H), 4.21 (dd, *J* = 2.6, 12.4 Hz, 1H), 4.33 (ddd, *J* = 2.6, 4.5, 10.1 Hz, 1H), 5.00 (dd, *J* = 9.3 Hz, ^{3}J(F,H) = 11.1 Hz, 1H), 5.23 (dd, *J* = 9.3, 10.1 Hz, 1H), 5.76 ppm (br s, 1H); ^{13}C NMR: d = 20.5 (CH_3), 20.67 (CH_3), 20.69 (CH_3), 61.7 (CH_2), 68.3 (CH), 69.0 (d, ^{3}J(F,C) = 5.4 Hz, CH), 71.8 (d, ^{2}J(F,C) = 19.4 Hz, CH), 90.0 (d, ^{1}J(F,C) = 270.8 Hz, C), 97.0 (d, ^{2}J(F,C) = 21.5 Hz, CH), 169.5 (C), 169.7 (C), 171.0 ppm (C); ^{19}F NMR: d = –119.9 ppm (d, ^{3}J(F,H) = 9.2 Hz, 1F); minor isomer: ^{1}H NMR: d = 2.05 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 3.55 (d, *J* = 11.1 Hz, 1H), 3.74 (dd, *J* = 11.1 Hz, ^{3}J(F,H) = 2.4 Hz, 1H), 3.83 (ddd, *J* = 3.7, 3.7, 10.1 Hz, 1H), 4.18 (d, *J* = 3.7 Hz, 2H), 4.85 (dd, *J* = 9.5 Hz, ^{3}J(F,H) = 10.4 Hz, 1H), 5.19 ppm (dd, *J* = 9.5, 10.1 Hz, 1H); ^{13}C NMR: d = 20.4 (CH_3), 20.60 (CH_3), 20.63 (CH_3), 61.7 (CH_2), 68.9 (d, ^{3}J(F,H) = 5.4 Hz, CH), 72.8 (CH), 74.3 (d, ^{2}J(F,C) = 19.3 Hz, CH), 90.0 (d, ^{1}J(F,C) = 270.8 Hz, C), 94.6 (d, ^{2}J(F,C) = 23.6 Hz, CH), 169.3 (C), 169.5 (C), 170.9 ppm (C); ^{19}F NMR: d = –119.6 ppm (d, ^{3}J(F,H) = 9.2 Hz, 1F); IR: $\tilde{n}$ = 3607, 3469, 2956, 1758, 1372, 1223, 1050 cm^{-1}; MS (70 eV, EI): *m/z* (%): 417 (4) [*M*–OH]$^{+}$, 374 (5), 307 (5), 287 (72), 277 (30), 247 (67), 115 (100); HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}FIO_7$ [*M*–OH]$^{+}$: 416.9846, found: 416.9832; elemental analysis calcd (%) for $C_{12}H_{16}FIO_8$ (434.16): C 33.20, H 3.71; found: C 33.36, H 3.77.

3,4-Di-*O*-acetyl-2,6-dideoxy-2,2-difluoro-β-L-arabino-hexopyranose (32): Oil (76 %); ^{1}H NMR (500 MHz): d = 1.21 (d, *J* = 6.3 Hz, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 3.92 (br s, 1H), 4.20 (dddd, *J* = 6.3, 6.3, 6.3, 9.9 Hz, 1H), 4.94 (ddd, *J* = 9.9, 9.9 Hz, ^{3}J(F,H) = 1.3 Hz, 1H), 5.16 (dd, ^{3}J(F,H) = 3.7, 5.0 Hz, 1H), 5.55 ppm (ddd, *J* = 9.9 Hz, ^{3}J(F,H) = 4.6, 20.6 Hz, 1H); ^{13}C NMR: d = 17.0 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 65.9 (CH), 68.7 (dd, ^{2}J(F,C) = 19.0, 19.4 Hz, CH), 72.6 (dd, ^{3}J(F,C) = 5.8, 8.5 Hz, CH), 91.2 (dd, ^{2}J(F,C) = 35.4, 36.5 Hz, CH), 115.8 (dd, ^{1}J(F,C) = 244.5, 257.8 Hz, C), 168.8 (C), 170.1 ppm (C); ^{19}F NMR: d = –120.8 (d, ^{2}J(F,F) = 252.0 Hz, 1F), –122.3 ppm (dd, ^{3}J(F,H) =

23.0 Hz, ^{2}J(F,F) = 252.0 Hz, 1F); IR: $\tilde{n}$ = 3615, 3472, 2964, 1764, 1376, 1233, 1078 cm^{-1}; MS (70 eV, EI): *m/z* (%): 269 (<1) [*M*+1]$^{+}$, 251 (8), 181 (11), 164 (11), 135 (69), 148 (44), 103 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{15}F_2O_6$ [*M*+1]$^{+}$: 269.0837, found: 269.0848; elemental analysis calcd (%) for $C_{10}H_{14}F_2O_6$ (268.21): C 44.78, H 5.26; found: C 44.80, H 5.17.

3,4-Di-*O*-acetyl-2-chloro-2,6-dideoxy-2-fluoro-L-glucopyranose and 3,4-di-*O*-acetyl-2-chloro-2,6-dideoxy-2-fluoro-L-mannopyranose (33): Crystalline solid (75 %), mixture of two diastereoisomers at C-2 in ratio 2:1; ^{1}H NMR: δ = 1.22 (d, *J* = 6.4 Hz, 6H), 2.05 (s, 3H), 2.06 (s, 3H), 2.14 (s, 3H), 2.16 (s, 3H), 3.75 (d, *J* = 3.7 Hz, 1H), 3.82 (d, *J* = 3.2 Hz, 1H), 4.20–4.27 (m, 2H), 4.95 (dd, *J* = 9.8, 9.8 Hz, 1H), 4.99 (ddd, *J* = 9.8, 9.8 Hz, ^{4}J(F,H) = 1.6 Hz, 1H), 5.28 (dd, *J* = 3.7 Hz, ^{3}J(F,H) = 3.7 Hz, 1H), 5.34 (d, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 9.8 Hz, ^{3}J(F,H) = 23.4 Hz, 1H), 5.75 ppm (dd, *J* = 9.8 Hz, ^{3}J(F,H) = 8.2 Hz, 1H); ^{13}C NMR: δ = 17.1 (CH_3), 17.2 (CH_3), 20.4 (2 × CH_3), 20.6 (2 × CH_3), 66.1 (CH), 66.4 (CH), 70.6 (d, ^{2}J(F,C) = 21.4 Hz, CH), 72.0 (d, ^{2}J(F,C) = 18.3 Hz, CH), 72.5 (CH), 72.8 (d, ^{3}J(F,C) = 6.1 Hz, CH), 94.0 (d, ^{2}J(F,C) = 30.5 Hz, CH), 94.5 (d, ^{2}J(F,C) = 24.4 Hz, CH), 107.9 (d, ^{1}J(F,C) = 247.2 Hz, C), 108.9 (d, ^{1}J(F,C) = 259.4 Hz, C), 169.7 (2 × C), 169.9 ppm (2 × C); ^{19}F NMR: δ = –121.8 (s, 1F), –127.4 ppm (d, ^{3}J(F,H) = 22.9 Hz, 1F); IR: $\tilde{n}$ = 3612, 3486, 2987, 1764, 1374, 1233, 1213, 1061 cm^{-1}; MS (70 eV, EI): *m/z* (%): 269/267 (8/23) [*M*–OH]$^{+}$, 189 (26), 154/152 (33/100), 136 (86), 103 (51); HRMS (EI): *m/z* calcd for $C_{10}H_{13}{}^{35}ClFO_5$ [*M*–OH]$^{+}$: 267.0436, found: 267.0440; elemental analysis calcd (%) for $C_{10}H_{14}ClFO_6$ (284.67): C 42.19, H 4.96; found: C 42.28, H 4.95.

3,4-Di-*O*-acetyl-2-bromo-2,6-dideoxy-2-fluoro-L-glucopyranose (34): Crystalline solid (79 %), anomeric mixture in ratio 4:1, only major isomer described; ^{1}H NMR: δ = 1.22 (d, *J* = 6.3 Hz, 3H), 2.05 (s, 3H), 2.14 (s, 3H), 3.57 (d, *J* = 3.4 Hz, 1H), 4.24 (dddd, *J* = 6.3, 6.3, 6.3, 9.7 Hz, 1H), 4.98 (dd, *J* = 9.7, 9.7 Hz, 1H), 5.50 (d, *J* = 3.4 Hz, 1H), 5.58 ppm (dd, *J* = 9.7 Hz, ^{3}J(F,H) = 9.7 Hz, 1H); ^{13}C NMR: δ = 17.2 (CH_3), 20.6 (2 × CH_3), 66.5 (CH), 71.1 (d, ^{2}J(F,C) = 21.7 Hz, CH), 73.2 (CH), 95.2 (d, ^{2}J(F,C) = 23.6 Hz, CH), 105.0 (d, ^{1}J(F,C) = 270.2 Hz, C), 169.7 (C), 169.9 ppm (C); ^{19}F NMR: δ = –119.8 ppm (d, ^{3}J(F,H) = 9.2 Hz, 1F); IR: $\tilde{n}$ = 3612, 3490, 2987, 1763, 1430, 1375, 1232, 1054 cm^{-1}; MS (70 eV, EI): *m/z* (%): 313/311 (8/8) [*M*–OH]$^{+}$, 219 (19), 197/195 (27/27), 192 (36), 145 (85), 103 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{13}{}^{79}BrFO_5$

[*M*–OH]$^+$: 310.9930, found: 310.9937; elemental analysis calcd (%) for $C_{10}H_{14}BrFO_6$ (329.12): C 36.49, H 4.29; found: C 36.67, H 4.30.

3,4-Di-*O*-acetyl-2,6-dideoxy-2-fluoro-2-iodo-L-glucopyranose (35): Oil (74 %), anomeric mixture in ratio 3:2, major isomer: ^{1}H NMR (500 MHz): *d* = 1.20 (d, *J* = 6.3 Hz, 3H), 2.04 (s, 3H), 2.13 (s, 3H), 4.23 (dddd, *J* = 6.3, 6.3, 6.3, 9.2 Hz, 1H), 4.93 (dd, *J* = 9.2, 9.5 Hz, 1H), 4.95 (dd, *J* = 9.5 Hz, ^3J(F,H) = 9.5 Hz, 1H), 5.68 ppm (s, 1H); ^{13}C NMR (125.7 MHz): *d* = 17.4 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 71.4 (CH), 71.9 (d, ^2J(F,C) = 18.8 Hz, CH), 74.0 (CH), 90.8 (d, ^1J(F,C) = 270.2 Hz, C), 97.2 (d, ^2J(F,C) = 21.8 Hz, CH), 169.8 (C), 169.9 ppm (C); ^{19}F NMR: *d* = –119.4 ppm (d, ^3J(F,H) = 8.3 Hz, 1F); minor isomer: ^{1}H NMR (500 MHz): *d* = 1.24 (d, *J* = 6.2 Hz, 3H), 2.04 (s, 3H), 2.15 (s, 3H), 3.67–3.73 (m, 2H), 4.77 (dd, *J* = 9.5 Hz, ^3J(F,H) =11.6 Hz, 1H), 4.91 ppm (dd, *J* = 9.5, 9.5 Hz, 1H); ^{13}C NMR (125.7 MHz): *d* = 17.4 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 66.4 (CH), 73.6 (CH), 74.5 (d, ^2J(F,C) = 19.0 Hz, CH), 94.5 (d, ^2J(F,C) = 23.2 Hz, CH), 100.1 (d, ^1J(F,C) = 269.4 Hz, C), 169.6 (C), 169.7 ppm (C); ^{19}F NMR: *d* = –119.4 ppm (d, ^3J(F,H) = 8.3 Hz, 1F); IR: $\tilde{n}$ = 3610, 3476, 2988, 2941, 1762, 1429, 1376, 1235, 1061 cm^{-1}; MS (70 eV, EI): *m/z* (%): 376 (1) [*M*]$^+$, 359 (2), 243 (17), 229 (28), 189 (38), 147 (45), 127 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{14}FIO_6$ [*M*]$^+$: 375.9819, found: 375.9830; elemental analysis calcd (%) for $C_{10}H_{14}FIO_6$ (376.12): C 31.93, H 3.75; found: C 31.93, H 3.51.

3,4-Di-*O*-acetyl-2-deoxy-2,2-difluoro-β-L-*erythro*-pentopyranose (36): Oil (42 %); ^{1}H NMR (500 MHz): *d* = 2.13 (s, 3H), 2.14 (s, 3H), 3.14 (d, *J* = 5.7 Hz, 1H), 3.80 (dd, *J* = 3.8, 12.9 Hz, 1H), 4.23 (dd, *J* = 2.4, 12.9 Hz, 1H), 5.22 (ddd, *J* = 4.3 Hz, ^3J(F,H) = 4.3, 4.3 Hz, 1H), 5.32 (m, 1H), 5.53 ppm (dd, *J* = 3.8, ^3J(F,H) = 24.8 Hz, 1H); ^{13}C NMR (125.7 MHz): *d* = 20.4 (CH_3), 20.7 (CH_3), 60.7 (CH_2), 65.8 (dd, ^2J(F,C) = 21.4, 21.4 Hz, CH), 67.7 (CH), 91.8 (dd, ^2J(F,C) = 30.5, 30.5 Hz, CH), 114.1 (dd, ^1J(F,C) = 253.3, 253.3 Hz, C), 169.7 (C), 170.5 ppm (C); ^{19}F NMR: *d* = –120.5 (dd, ^3J(F,H) = 18.4 Hz, ^2J(F,F) = 252.4 Hz, 1F), –122.2 ppm (br d, ^2J(F,F) = 252.4 Hz, 1F); IR: $\tilde{n}$ = 3618, 1762, 1549, 1239, 1216, 1005 cm^{-1}; MS (70 eV, EI): *m/z* (%): 237 (55) [*M*–OH]$^+$, 219 (58), 91 (100); HRMS (EI): *m/z* calcd for $C_9H_{11}F_2O_5$ [*M*–OH]$^+$: 237.0575, found: 237.0575; elemental analysis calcd (%) for $C_9H_{12}F_2O_6$ (254.17): C 42.53, H 4.76; found: C 42.38, H 4.98.

3,4-Di-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-L-ribopyranose and 3,4-di-*O*-acetyl-2-chloro-2-deoxy-2-fluoro-L-arabinopyranose (37): Oil (75 %), mixture of diastereoisomers at C-2 in ratio 6:1, only major isomer described; ^{1}H NMR: *d* = 2.10 (s, 3H), 2.14 (s, 3H), 3.77 (dd, *J* = 4.5, 12.8 Hz, 1H), 4.24 (dd, *J* = 2.9, 12.8 Hz, 1H), 5.24–5.31 (m, 2H), 5.55 ppm (dd, *J* = 3.7 Hz, ^{3}J(F,H) = 20.4 Hz, 1H); ^{13}C NMR: *d* = 20.3 (CH_3), 20.6 (CH_3), 61.1 (CH_2), 67.5 (CH), 69.6 (d, ^{2}J(F,C) = 17.2 Hz, CH), 93.8 (d, ^{2}J(F,C) = 31.2 Hz, CH), 107.4 (d, ^{1}J(F,C) = 255.7 Hz, C), 169.5 (C), 170.4 ppm (C); ^{19}F NMR: *d* = –125.9 ppm (d, ^{3}J(F,H) = 18.4 Hz, 1F); IR: $\tilde{n}$ = 3612, 2977, 1762, 1371, 1234, 1120, 1072 cm^{-1}; MS (70 eV, EI): *m/z* (%): 255/253 (2/7) [*M*–OH]$^{+}$, 195 (12), 175 (19), 164 (23), 153/151 (32/100); HRMS (EI): *m/z* calcd for $C_9H_{11}{}^{35}ClFO_5$ [*M*–OH]$^{+}$: 253.0279, found: 253.0294; elemental analysis calcd (%) for $C_9H_{12}ClFO_6$ (270.64): C 39.94, H 4.48; found: C 39.70, H 4.84.

3,4-Di-*O*-acetyl-2-bromo-2-deoxy-2-fluoro-L-ribopyranose and 3,4-di-*O*-acetyl-2-bromo-2-deoxy-2-fluoro-L-arabinopyranose (38): Oil (65 %), NMR showed a complex mixture of isomers; ^{19}F NMR: *d* = –118.8 (s, 1F), –124.0 (s, 1F), –124.0 ppm (br s, 1F); IR: $\tilde{n}$ = 3577, 2938, 1757, 1372, 1234, 1078 cm^{-1}; MS (70 eV, EI): *m/z* (%): 317/315 (<1) [*M*+1]$^{+}$, 299/297 (8/8), 211/209 (6/6), 197/195 (77/77), 168/166 (40/43), 129 (100); HRMS (EI): *m/z* calcd for $C_9H_{13}{}^{79}BrFO_6$ [*M*+1]$^{+}$: 314.9879, found: 314.9879; elemental analysis calcd (%) for $C_9H_{12}BrFO_6$ (315.09): C 34.31, H 3.84; found: C 34.21, H 3.80.

3,4-Di-*O*-acetyl-2-deoxy-2-fluoro-2-iodo-L-ribopyranose (39): Oil (96 %), anomeric mixture in ratio 4:1, only major isomer described. ^{1}H NMR (500 MHz): *d* = 2.04 (s, 3H), 2.20 (s, 3H), 3.51 (d, *J* = 8.8 Hz, 1H), 3.81 (dd, *J* = 9.0, 11.4 Hz, 1H), 4.06 (dd, *J* = 4.3, 11.4 Hz, 1H), 5.23 (dd, *J* = 8.8 Hz, ^{3}J(F,H) = 12.4 Hz, 1H), 5.33 (ddd, *J* = 3.5, 4.3, 9.0 Hz, 1H), 5.66 ppm (dd, *J* = 3.5 Hz, ^{3}J(F,H) = 4.3 Hz, 1H); ^{13}C NMR (125.7 MHz): *d* = 20.6 (CH_3), 20.7 (CH_3), 61.7 (CH_2), 64.8 (CH), 72.3 (d, ^{2}J(F,C) = 30.5 Hz, CH), 88.4 (d, ^{1}J(F,C) = 259.4 Hz, CH), 96.5 (d, ^{2}J(F,C) = 18.3 Hz, C), 168.7 (C), 169.5 ppm (C); ^{19}F NMR: *d* = –119.6 ppm (s, 1F); IR: $\tilde{n}$ = 3577, 3468, 1758, 1371, 1230, 1074 cm^{-1}; MS (70 eV, EI): *m/z* (%): 345 (2) [*M*–OH]$^{+}$, 302 (10), 254 (100); HRMS (EI): *m/z* calcd for $C_9H_{11}FIO_5$ [*M*–OH]$^{+}$: 344.9635, found: 344.9625; elemental analysis calcd (%) for $C_9H_{12}FIO_6$ (362.09): C 29.85, H 3.34; found: C 30.02, H 3.13.

(5*RS*)-1,3,4-Tri-*O*-acetyl-5-chloro-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-D-arabinitol (41): Oil (67 %), mixture of isomers in ratio 1:1; ^{1}H NMR: *d* = 2.04 (s, 6H), 2.13 (s, 3H), 2.14 (s, 3H), 2.17 (s, 3H), 2.18 (s, 3H), 3.88 (dd, *J* = 7.6, 11.7 Hz, 1H), 3.90 (dd, *J* = 7.6, 11.7 Hz, 1H), 4.31 (dd, *J* = 5.0, 11.7 Hz, 2H), 5.20 (dd, *J* = 8.0 Hz, ^{3}J(F,H) = 8.0 Hz, 1H), 5.48 (dd, *J* = 8.0 Hz, ^{3}J(F,H) = 5.4 Hz, 1H), 5.52–5.56 (m, 2H), 5.65 (ddd, *J* = 0.6, 8.0 Hz, ^{4}J(F,H) = 1.8 Hz, 1H), 5.88 (ddd, *J* = 1.9, 8.0 Hz, ^{4}J(F,H) = 0.8 Hz, 1H), 8.00 ppm (s, 2H); ^{13}C NMR (C_6D_6): *d* = 19.9 (CH_3), 20.0 ($3 \times CH_3$), 20.2 (CH_3), 20.3 (CH_3), 61.7 ($2 \times CH_2$), 68.0 (CH), 68.1 (CH), 69.4 (CH), 70.5 (CH), 75.9 (d, ^{2}J(F,C) = 20.4 Hz, CH), 76.1 (d, ^{2}J(F,C) = 23.6 Hz, CH), 78.8 (d, ^{1}J(F,C) = 313.7 Hz, C), 79.5 (d, ^{1}J(F,C) = 314.8 Hz, C), 159.6 (CH), 159.8 (CH), 168.1 (C), 168.2 (C), 169.8 ($2 \times$ C), 169.8 ppm ($2 \times$ C); ^{19}F NMR: *d* = –59.8 (s, 1F), –63.5 ppm (d, ^{3}J(F,H) = 9.0 Hz, 1F); IR: $\tilde{n}$ = 2954, 1763, 1737, 1432, 1197, 1157, 1067 cm^{-1}; MS (70 eV, EI): *m/z* (%): 411/409 (<1) [*M*–OAc]$^{+}$, 299 (3), 281 (3), 277 (4), 264 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{12}{}^{35}ClFIO_6$ [*M*–OAc]$^{+}$: 408.9351, found: 408.9342; elemental analysis calcd (%) for $C_{12}H_{15}ClFIO_8$ (468.60): C 30.77, H 3.23; found: C 30.65, H 3.08.

(5*RS*)-1,3,4-Tri-*O*-acetyl-5-bromo-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-D-arabinitol (42): Oil (60 %), mixture of isomers in ratio 1:1; ^{1}H NMR: *d* = 2.049 (s, 3H), 2.050 (s, 3H), 2.146 (s, 3H), 2.150 (s, 3H), 2.18 (s, 3H), 2.19 (s, 3H), 3.89 (dd, *J* = 5.3, 11.7 Hz, 1H), 3.90 (dd, *J* = 5.2, 11.7 Hz, 1H), 4.32 (dd, *J* = 5.0, 11.7 Hz, 1H), 4.35 (dd, *J* = 4.9, 11.7 Hz, 1H), 5.28 (dd, *J* = 7.4 Hz, ^{3}J(F,H) = 7.4 Hz, 1H), 5.53 (dd, *J* = 8.2 Hz, ^{3}J(F,H) = 5.8 Hz, 1H), 5.53–5.58 (m, 2H), 5.63 (ddd, *J* = 2.0, 7.4 Hz, ^{4}J(F,H) = 1.1 Hz, 1H), 5.67 (ddd, *J* = 1.9, 8.2 Hz, ^{4}J(F,H) = 0.9 Hz, 1H), 8.010 (s, 1H), 8.012 ppm (s, 1H); ^{13}C NMR: *d* = 20.5 ($2 \times CH_3$), 20.6 ($2 \times CH_3$), 20.8 ($2 \times CH_3$), 61.7 ($2 \times CH_2$), 62.4 (d, ^{1}J(F,C) = 321.0 Hz, C), 63.1 (d, ^{1}J(F,C) = 322.0 Hz, C), 67.8 ($2 \times$ CH), 69.8 (CH), 70.5 (CH), 76.4 (d, ^{2}J(F,C) = 21.8 Hz, CH), 76.5 (d, ^{2}J(F,C) = 21.4 Hz, CH), 159.8 ($2 \times$ CH), 168.3 (C), 168.4 (C), 169.2 ($2 \times$ C), 170.3 ppm ($2 \times$ C); ^{19}F NMR: *d* = –62.6 (br s, 1F), –64.7 ppm (d, ^{3}J(F,H) = 9.2 Hz, 1F); IR: $\tilde{n}$ = 2955, 1760, 1736, 1550, 1370, 1217, 1196 cm^{-1}; MS (70 eV, EI): *m/z* (%): 455/453 (<1) [*M*–OAc]$^{+}$, 327/325 (2/2), 291 (8), 277 (5), 263 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{12}{}^{81}BrFIO_6$ [*M*–OAc]$^{+}$: 454.8826, found: 454.8812; elemental analysis calcd (%) for $C_{12}H_{15}BrFIO_8$ (513.05): C 28.09, H 2.95; found: C 28.38, H 2.69.

(5*RS*)-1,3,4-Tri-*O*-benzyl-5-bromo-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-D-arabinitol (46): Oil (46 %), mixture of isomers in ratio 1:1; ^{1}H NMR: δ = 3.60–3.63 (m, 4H), 3.87 (dd, J = 5.6 Hz, ^{3}J(F,H) = 8.5 Hz, 1H), 3.91 (dd, J = 5.8 Hz, ^{3}J(F,H) = 7.3 Hz, 1H) 4.10 (dd, J = 2.6, 5.8 Hz, 1H), 4.15 (dd, J = 2.6, 5.6 Hz, 1H), 4.44 (d, J = 11.9 Hz, 2H), 4.48 (d, J = 11.9 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 4.56 (d, J = 10.6 Hz, 2H), 4.72 (1H, d, J = 11.4 Hz, 1H), 4.73 (1H, d, J = 11.0 Hz, 1H), 4.82 (1H, d, J = 11.4 Hz, 1H), 4.83 (1H, d, J = 11.0 Hz, 1H), 5.02 (1H, d, J = 10.6 Hz, 1H), 5.04 (1H, d, J = 10.6 Hz, 1H), 5.49 (ddd, J = 2.6, 6.4, 6.4 Hz, 1H), 5.54 (ddd, J = 2.6, 6.4, 6.4 Hz, 1H), 7.24–7.41 (m, 30H), 7.97 ppm (s, 2H); ^{13}C NMR: δ = 67.5 (2 × CH_2), 69.3 (d, ^{1}J(F,C) = 325.6 Hz, C), 69.5 (d, ^{1}J(F,C) = 328.8 Hz, C), 71.2 (2 × CH), 73.2 (2 × CH_2), 74.2 (2 × CH_2), 75.8 (2 × CH_2), 77.7 (CH), 77.8 (CH), 87.4 (d, ^{2}J(F,C) = 18.3 Hz, CH), 88.0 (d, ^{2}J(F,C) = 18.3 Hz, CH), 127.8–128.4 (30 × CH), 136.5 (C), 136.6 (C), 137.27 (C), 137.29 (C), 137.5 (2 × C), 160.3 ppm (2 × CH); ^{19}F NMR: δ = –57.2 (d, ^{3}J(F,H) = 9.2 Hz, 1F), –59.8 ppm (s, 1F); IR: $\tilde{\nu}$ = 3091, 3067, 3033, 2929, 1731, 1455, 1173 cm^{-1}; MS (70 eV, EI): *m/z* (%): 567/565 (1/1) [*M*–Bn]$^{+}$, 461/459 (1/1), 227/225 (1/1), 181 (9), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{20}{}^{79}BrFIO_5$ [*M*–Bn]$^{+}$: 564.9523, found: 564.9547; elemental analysis calcd (%) for $C_{27}H_{27}BrFIO_5$ (657.32): C 49.34, H 4.14; found: C 49.35, H 4.02.

(5*RS*)-3,4-di-*O*-acetyl-5-chloro-1,5-dideoxy-5-fluoro-2-*O*-formyl-5-iodo-L-arabinitol (49): Crystalline solid (79 %), mixture of isomers in ratio 1:1; ^{1}H NMR: δ = 0.92 (d, J = 6.5 Hz, 6H), 1.65 (s, 3H), 1.67 (s, 3H), 1.71 (s, 3H), 1.73 (s, 3H), 5.22 (dddd, J = 1.4, 6.5, 6.5, 6.5 Hz, 1H), 5.23 (dddd, J = 2.0, 6.5, 6.5, 6.5 Hz, 1H), 5.39 (dd, J = 8.4 Hz, ^{3}J(F,H) = 6.9 Hz, 1H), 5.51 (ddd, J = 2.0, 8.4 Hz, ^{4}J(F,H) = 0.7 Hz, 1H), 5.54 (ddd, J = 1.4, 8.6 Hz, ^{4}J(F,H) = 0.7 Hz, 1H), 5.67 (dd, J = 8.6 Hz, ^{3}J(F,H) = 5.1 Hz, 1H), 7.49 ppm (s, 2H); ^{13}C NMR (C_6D_6): δ = 16.2 (2 × CH_3), 20.17 (CH_3), 20.18 (CH_3), 20.25 (CH_3), 20.3 (CH_3), 67.4 (2 × CH), 72.1 (CH), 73.3 (CH), 76.2 (d, ^{2}J(F,C) = 22.8 Hz, CH), 76.4 (d, ^{2}J(F,C) = 26.6 Hz, CH), 79.4 (d, ^{1}J(F,C) = 316.7 Hz, C), 80.0 (d, ^{1}J(F,C) = 316.7 Hz, C), 159.8 (2 × CH), 168.0 (C), 168.1 (C),169.9 ppm (2 × C); ^{19}F NMR: δ = –59.4 (s, 1F), –63.2 ppm (d, ^{3}J(F,H) = 8.3 Hz, 1F); IR: $\tilde{\nu}$ = 2991, 2940, 1760, 1730, 1371, 1199, 1171, 1069, 1050 cm^{-1}; MS (70 eV, EI): *m/z* (%): 367/365 (<1) [*M*–OCOH]$^{+}$, 249 (3), 243/241 (1/3), 205 (100); HRMS (EI): *m/z* calcd for

$C_9H_{12}{}^{35}ClFIO_4$ [*M*–OCOH]$^+$: 364.9453, found: 364.9455; elemental analysis calcd (%) for $C_{10}H_{13}ClFIO_6$ (410.57): C 29.25, H 3.19; found: C 29.13, H 3.14.

(5*RS*)-3,4-Di-*O*-acetyl-5-bromo-1,5-dideoxy-5-fluoro-2-*O*-formyl-5-iodo-L-arabinitol (50): Crystalline solid (72 %), mixture of isomers in ratio 1:1; ^{1}H NMR: *d* = 1.22 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 2.16 (s, 3H), 2.17 (s, 6H), 2.18 (s, 3H), 5.42 (dd, *J* = 8.2 Hz, ^3J(F,H) = 6.5 Hz, 1H), 5.33 (dddd, *J* = 1.0, 6.6, 6.6, 6.6 Hz, 2H), 5.27 (ddd, *J* = 1.0, 8.2 Hz, ^4J(F,H) = 2.0 Hz, 1H), 5.47 (ddd, *J* = 1.0, 8.3 Hz, ^4J(F,H) = 1.8 Hz, 1H), 5.53 (dd, *J* = 8.3 Hz, ^3J(F,H) = 5.2 Hz, 1H), 7.96 ppm (s, 2H); ^{13}C NMR: *d* = 16.3 (2 × CH_3), 20.8 (2 × CH_3), 20.9 (2 × CH_3), 63.1 (d, ^1J(F,C) = 321.4 Hz, C), 63.8 (d, ^1J(F,C) = 323.0 Hz, C), 67.4 (CH), 67.5 (CH), 72.7 (CH), 73.6 (CH), 76.2 (d, ^2J(F,C) = 20.6 Hz, CH), 76.5 (d, ^2J(F,C) = 21.3 Hz, CH), 160.0 (2 × CH), 168.2 (C), 168.3 (C), 169.4 ppm (2 × C); ^{19}F NMR: *d* = –62.0 (br s, 1F), –64.3 ppm (d, ^3J(F,H) = 9.2 Hz, 1F); IR: $\tilde{n}$ = 2938, 1760, 1730, 1370, 1198, 1171, 1068 cm^{-1}; MS (70 eV, EI): *m/z* (%): 411/409 (20/20) [*M*–OCOH]$^+$, 397/395 (17/17), 369/367 (4/4), 287 (11), 205 (100); HRMS (EI): *m/z* calcd for $C_9H_{12}{}^{79}BrFIO_4$ [*M*–OCOH]$^+$: 408.8948, found: 408.8932; elemental analysis calcd (%) for $C_{10}H_{13}BrFIO_6$ (455.02): C 26.40, H 2.88; found: C 26.53, H 2.80.

(1*RS*)-2,3,5-tri-*O*-acetyl-1-chloro-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-D-arabinitol (57): Oil (60 %), mixture of diastereoisomers in ratio 1:1; ^{1}H NMR: *d* = 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 4.14 (dd, *J* = 5.7, 12.7 Hz, 2H), 4.26 (dd, *J* = 4.0, 12.7 Hz, 1H), 4.27 (dd, *J* = 3.0, 12.7 Hz, 1H), 5.11 (dddd, *J* = 0.9, 2.9, 5.6, 8.5 Hz, 1H), 5.15 (dddd, *J* = 0.8, 2.9, 5.8, 8.3 Hz, 1H), 5.52 (dd, *J* = 1.7 Hz, ^3J(F,H) = 18.9 Hz, 1H), 5.55 (dd, *J* = 1.7 Hz, ^3J(F,H) = 21.3 Hz, 1H), 6.01 (dd, *J* = 1.7, 8.3 Hz, 1H), 6.04 (dd, *J* = 1.7, 8.5 Hz, 1H), 8.00 ppm (d, *J* = 0.8 Hz, 2H); ^{13}C NMR (C_6D_6): *d* = 19.8 (CH_3), 20.08 (CH_3), 20.14 (3 × CH_3), 20.3 (CH_3), 61.1 (CH_2), 61.2 (CH_2), 65.7 (CH), 67.4 (CH), 68.5 (CH), 68.6 (CH), 76.2 (d, ^2J(F,C) = 21.5 Hz, CH), 76.7 (d, ^1J(F,C) = 315.9 Hz, C), 76.8 (d, ^2J(F,C) = 20.4 Hz, CH), 77.0 (d, ^1J(F,C) = 319.1 Hz, C), 159.2 (2 × CH), 168.6 (C), 168.7 (3 × C), 169.8 ppm (2 × C); ^{19}F NMR: *d* = –62.4 (d, ^3J(F,H) = 15.9 Hz, 1F), –64.2 ppm (d, ^3J(F,H) = 17.5 Hz, 1F); IR: $\tilde{n}$ = 2951, 1766, 1742, 1371, 1200, 1151, 1047 cm^{-1}; MS (70 eV, EI): *m/z* (%): 425/423 (<1) [*M*–OCOH]$^+$, 307 (1), 301/299 (2/<1), 283/281 (2/<1), 263 (100); HRMS (EI): *m/z*

calcd for $C_{11}H_{14}{}^{35}ClFIO_6$ [*M*–OCOH]$^+$: 422.9508, found: 422.9501; elemental analysis calcd (%) for $C_{12}H_{15}ClFIO_8$ (468.60): C 30.77, H 3.23; found: C 30.78, H 3.16.

(1*RS*)-2,3,5-Tri-*O*-acetyl-1-bromo-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-D-arabinitol (58): Oil (71 %), mixture of isomers in 1:1 ratio; ^{1}H NMR: *d* = 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 2.23 (s, 3H), 2.25 (s, 3H), 4.14 (dd, *J* = 5.2, 12.6 Hz, 2H), 4.26 (dd, *J* = 3.3, 12.6 Hz, 1H), 4.27 (dd, *J* = 3.3, 12.6 Hz, 1H), 5.10 (ddd, *J* = 3.3, 5.2, 8.2 Hz, 1H), 5.14 (ddd, *J* = 3.3, 5.2, 8.3 Hz, 1H), 5.55 (dd, *J* = 1.7 Hz, ^3J(F,H) = 16.4 Hz, 1H), 5.58 (dd, *J* = 1.4 Hz, ^3J(F,H) = 18.0 Hz, 1H), 6.07 (dd, *J* = 1.7, 8.2 Hz, 1H), 6.11 (dd, *J* = 1.4, 8.3 Hz, 1H), 8.01 (s, 1H), 8.02 ppm (s, 1H); ^{13}C NMR: *d* = 20.5 (2 × CH_3), 20.6 (2 × CH_3), 20.8 (2 × CH_3), 60.4 (d, ^1J(F,C) = 324.3 Hz, C), 60.6 (d, ^1J(F,C) = 327.0 Hz, C), 61.0 (2 × CH_2), 65.9 (CH), 67.3 (CH), 68.4 (CH), 68.5 (CH), 76.3 (d, ^2J(F,C) = 20.4 Hz, CH), 76.6 (d, ^2J(F,C) = 20.2 Hz, CH), 159.8 (2 × CH), 168.8 (2 × C), 168.9 (2 × C), 170.4 ppm (2 × C); ^{19}F NMR: *d* = –64.4 (d, ^3J(F,H) = 18.3 Hz, 1F), –65.8 ppm (d, ^3J(F,H) = 18.3 Hz, 1F); IR: $\tilde{n}$ = 2945, 1767, 1740, 1371, 1199, 1152 cm^{-1}; MS (70 eV, EI): *m/z* (%): 469/467 (1/1) [*M*–OCOH]$^+$, 455/453 (1/1), 327/325 (1/1), 263 (100); HRMS (EI): *m/z* calcd for $C_{11}H_{14}{}^{79}BrFIO_6$ [*M*–OCOH]$^+$: 466.9003, found: 466.9000; elemental analysis calcd (%) for $C_{12}H_{15}BrFIO_8$ (513.05): C 28.09, H 2.95; found: C 28.09, H 2.81.

(5*RS*)-3,4-di-*O*-acetyl-5-chloro-1,5-dideoxy-5-fluoro-2-*O*-formyl-5-iodo-L-arabinitol (61): Oil (70 %), mixture of isomers in ratio 1:1; ^{1}H NMR (500 MHz): *d* = 1.28 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 6.4 Hz, 3H), 2.12 (s, 3H), 2.19 (s, 3H), 2.23 (s, 3H), 2.26 (s, 3H), 5.02 (dddd, *J* = 6.4, 6.4, 6.4, 7.4 Hz, 1H), 5.06 (dddd, *J* = 6.4, 6.4, 6.4, 7.0 Hz, 1H), 5.55 (dd, *J* = 2.0 Hz, ^3J(F,H) = 14.0 Hz, 1H), 5.59 (dd, *J* = 1.7 Hz, ^3J(F,H) = 16.5 Hz, 1H), 5.81 (dd, *J* = 2.0, 7.0 Hz, 1H), 5.83 (dd, *J* = 1.7, 7.4 Hz, 1H), 7.99 ppm (s, 2H); ^{13}C NMR (125.7 MHz, C_6D_6): *d* = 15.76 (CH_3), 15.84 (CH_3), 19.8 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.4 (CH_3), 67.7 (CH), 67.8 (CH), 69.5 (CH), 70.8 (CH), 76.2 (d, ^2J(F,C) = 21.5 Hz, CH), 76.7 (d, ^2J(F,C) = 20.4 Hz, CH), 77.3 (d, ^1J(F,C) = 314.8 Hz, C), 77.6 (d, ^1J(F,C) = 319.1 Hz, C), 159.3 (2 × CH), 168.6 (2 × C), 168.8 (C), 168.9 ppm (C); ^{19}F NMR: *d* = –62.0 (d, ^3J(F,H) = 13.9 Hz, 1F), –63.8 ppm (d, ^3J(F,H) = 17.7 Hz, 1F); IR: $\tilde{n}$ = 2992, 2941, 1766, 1736, 1372, 1203, 1163, 1052 cm^{-1}; MS (70 eV, EI): *m/z* (%): 367/365 (<1/2) [*M*–OCOH]$^+$, 339/337 (<1), 219 (7), 205 (100); HRMS (EI): *m/z* calcd for $C_9H_{12}{}^{35}ClFIO_4$ [*M*–OCOH]$^+$: 364.9453, found:

364.9462; elemental analysis calcd (%) for $C_{10}H_{13}ClFIO_6$ (410.57): C 29.25, H 3.19; found: C 29.26, H 3.18.

(1*RS*)-2,3-Di-*O*-acetyl-1-bromo-1,5-dideoxy-1-fluoro-2-*O*-formyl-1-iodo-L-arabinitol (62): Oil (80 %), mixture of isomers in ratio 1:1; ^{1}H NMR: d = 1.28 (d, J = 6.6 Hz, 3H), 1.29 (d, J = 6.5 Hz, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.23 (s, 3H), 2.25 (s, 3H), 5.00 (dddd, J = 6.6, 6.6, 6.6, 6.6 Hz, 1H), 5.04 (dddd, J = 6.5, 6.5, 6.5, 6.5 Hz, 1H), 5.58 (dd, J = 1.9 Hz, ^3J(F,H) = 15.8 Hz, 1H), 5.59 (dd, J = 1.7 Hz, ^3J(F,H) = 17.5 Hz, 1H), 5.86 (dd, J = 1.9, 6.5 Hz, 1H), 5.89 (dd, J = 1.7, 6.6 Hz, 1H), 7.99 ppm (s, 2H); ^{13}C NMR (125.7 MHz): d = 15.9 (2 × CH_3), 20.6 (CH_3), 20.8 (2 × CH_3), 20.9 (CH_3), 61.2 (d, ^1J(F,C) = 326.2 Hz, C), 61.3 (d, ^1J(F,C) = 328.6 Hz, C), 67.9 (2 × CH), 69.5 (CH), 70.6 (CH), 76.2 (d, ^2J(F,C) = 20.7 Hz, CH), 76.5 (d, ^2J(F,C) = 20.2 Hz, CH), 159.6 (2 × CH), 168.9 (2 × C), 169.4 ppm (2 × C); ^{19}F NMR: d = –64.0 (d, ^3J(F,H) = 18.4 Hz, 1F), –65.4 ppm (d, ^3J(F,H) = 18.4 Hz, 1F); IR: $\tilde{n}$ = 2940, 1765, 1736, 1371, 1203, 1163, 1052 cm^{-1}; MS (70 eV, EI): *m/z* (%): 411/409 (1/1) [*M*–OCOH]$^+$, 341/339 (2/2), 241/239 (4/4), 219 (17), 205 (100); HRMS (EI): *m/z* calcd for $C_9H_{12}{}^{79}BrFIO_4$ [*M*–OCOH]$^+$: 408.8948, found: 408.8935; elemental analysis calcd (%) for $C_{10}H_{13}BrFIO_6$ (455.02): C 26.40, H 2.88; found: C 26.24, H 2.82.

(4*RS*)-2,3-Di-*O*-acetyl-4-chloro-4-deoxy-4-fluoro-1-*O*-formyl-4-iodo-D-erythritol (65): Oil (84 %), mixture of isomers in ratio 1:1; ^{1}H NMR (500 MHz): d = 2.08 (s, 3H), 2.09 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 4.27 (dd, J = 6.2, 12.4 Hz, 1H), 4.29 (dd, J = 6.9, 12.4 Hz, 1H), 4.51 (dd, J = 2.8, 12.4 Hz, 1H), 4.55 (dd, J = 2.6, 12.4 Hz, 1H), 5.51 (dd, J = 4.7 Hz, ^3J(F,H) = 16.1 Hz, 1H), 5.56 (dd, J = 5.5 Hz, ^3J(F,H) = 11.5 Hz, 1H), 5.64 (ddd, J = 2.8, 5.5, 6.2 Hz, 1H), 5.67 (ddd, J = 2.6, 4.7, 6.9 Hz, 1H), 8.03 ppm (s, 2H); ^{13}C NMR (C_6D_6): d = 19.8 (CH_3), 19.9 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 60.7 (CH_2), 60.8 (CH_2), 69.5 (CH), 70.1 (CH), 76.9 (d, ^1J(F,C) = 316.1 Hz, C), 77.2 (d, ^1J(F,C) = 313.8 Hz, C), 77.6 (d, ^2J(F,C) = 22.7 Hz, CH), 78.0 (d, ^2J(F,C) = 21.3 Hz, CH), 159.7 (2 × CH), 168.6 (2 × C), 168.7 (C), 169.8 ppm (C); ^{19}F NMR: d = –61.4 (d, ^3J(F,H) = 17.2 Hz, 1F), –63.1 ppm (d, ^3J(F,H) = 12.9 Hz, 1F); IR: $\tilde{n}$ = 2940, 1763, 1737, 1371, 1226, 1200, 1169, 1072 cm^{-1}; MS (70 eV, EI): *m/z* (%): 297/295 (<1) [*M*–$C_4H_5O_3$], 271/269 (<1), 229/227 (1/3), 211/209 (1/3), 191 (100); HRMS (EI): *m/z* calcd for $C_5H_6{}^{37}ClFIO_3$ [*M*–$C_4H_5O_3$]: 296.9005, found: 296.9019; elemental analysis calcd (%) for $C_9H_{11}ClFIO_6$ (396.54): C 27.26, H 2.80; found: C 27.26, H 2.81.

(4*RS*)-2,3-Di-*O*-acetyl-4-bromo-4-deoxy-4-fluoro-1-*O*-formyl-4-iodo-D-erythritol (66): Oil (65 %), mixture of isomers in ratio 1:1; ^{1}H NMR: *d* = 2.08 (s, 3H), 2.09 (s, 3H), 2.23 (s, 3H), 2.24 (s, 3H), 4.27 (dd, *J* = 6.0, 12.4 Hz, 1H), 4.28 (dd, *J* = 7.4, 12.4 Hz, 1H), 4.51 (ddd, *J* = 1.0, 2.7, 12.4 Hz, 1H), 4.54 (ddd, *J* = 1.0, 2.6, 12.4 Hz, 1H), 5.55 (dd, *J* = 4.7 Hz, ^{3}J(F,H) = 16.6 Hz, 1H), 5.60 (dd, *J* = 5.2 Hz, ^{3}J(F,H) = 13.5 Hz, 1H), 5.67 (ddd, *J* = 2.7, 5.2, 6.0 Hz, 1H), 5.71 (ddd, *J* = 2.6, 4.7, 7.4 Hz, 1H), 8.03 ppm (br s, 2H); ^{13}C NMR: *d* = 20.6 (CH_3), 20.69 (CH_3), 20.7 (2 × H_3), 60.1 (d, ^{1}J(F,C) = 326.4 Hz, C), 60.4 (d, ^{1}J(F,C) = 324.7 Hz, C), 60.8 (d, ^{4}J(F,C) = 2.1 Hz, CH_2), 60.9 (d, ^{4}J(F,C) = 3.2 Hz, CH_2), 69.3 (CH), 70.1 (CH), 77.8 (d, ^{2}J(F,C) = 21.3 Hz, CH), 78.1 (d, ^{2}J(F,C) = 20.0 Hz, CH), 160.1 (2 × CH), 168.3 (C), 168.4 (C), 169.4 (C), 169.5 ppm (C); ^{19}F NMR: *d* = –63.6 (d, ^{3}J(F,H) = 13.8 Hz, 1F), –64.5 ppm (d, ^{3}J(F,H) = 18.4 Hz, 1F); IR: $\tilde{n}$ = 2938, 1760, 1737, 1550, 1371, 1226, 1200, 1070 cm^{-1}; MS (70 eV, EI): *m/z* (%): 383/381 (13/13) [*M*–OAc]$^{+}$, 273 (32), 253 (7), 191 (100); HRMS (EI): *m*/*z* calcd for $C_7H_8{}^{81}BrFIO_4$ [*M*–OAc]$^{+}$: 382.8614, found: 382.8607; elemental analysis calcd (%) for $C_9H_{11}BrFIO_6$ (440.99): C 24.51, H 2.51; found: C 24.70, H 2.45.

1,3,4-Tri-*O*-acetyl-5-deoxy-5,5-difluoro-2-*O*-formyl-D-arabinitol (68): TBTH (0.10 mL, 0.37 mmol, 5 equiv) and AIBN (5 mg, 0.03 mmol, 0.4 equiv) were added to a solution of difluoro derivative **40** (33 mg, 0.073 mmol, 1 equiv) in dry benzene (2 mL). The reaction was refluxing for 30 minutes and then, the solvent was removed under vacuum. The residue was purified by column chromatography (hexanes and gradient elution to 20 % ethyl acetate) to yield **68** (21 mg, 0.064 mmol, 87 %) as an oil; $[\alpha]_D$ = +54.7 (*c* = 0.27); ^{1}H NMR: *d* = 2.07 (s, 3H), 2.12 (s, 3H), 2.15 (s, 3H), 4.03 (dd, *J* = 6.8, 11.9 Hz, 1H), 4.31 (dd, *J* = 4.7, 11.9 Hz, 1H), 5.20–5.28 (m, 1H), 5.50–5.56 (m, 2H), 5.84 (dt, *J* = 3.5 Hz; ^{2}J(F,H) = 54.4 Hz, 1H), 8.05 ppm (s, 1H); ^{13}C NMR: *d* = 20.4 (2 × CH_3), 20.5 (CH_3), 61.5 (CH_2), 67.2 (CH), 67.3 (CH), 67.6 (dd, ^{2}J(F,C) = 23.8, 24.8 Hz, CH), 112.7 (dd, ^{1}J(F,C) = 243.6, 245.4 Hz, CH), 159.6 (CH), 169.0 (C), 169.3 (C), 170.3 ppm (C); ^{19}F NMR: *d* = –128.5 (ddd, ^{3}J(F,H) = 13.8, 55.1 Hz, ^{2}J(F,F) = 293.7 Hz, 1F), –130.1 (ddd, ^{3}J(F,H) = 9.2, 55.1 Hz, ^{2}J(F,F) = 293.7 Hz, 1F); IR: $\tilde{n}$ = 2944, 1761, 1737, 1371, 1206, 1157 cm^{-1}; MS (70 eV, EI): *m/z* (%): 327 (1) [*M*+1]$^{+}$, 281 (2), 267 (13), 253 (6), 203 (82), 178 (58), 131 (69), 115 (100); HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}F_2O_8$ [*M*+1]$^{+}$: 327.0891, found: 327.0907; elemental analysis calcd (%) for $C_{12}H_{16}F_2O_8$ (326.25): C 44.18, H 4.94. Found: C 44.20, H 5.03.

3,4-Di-*O*-acetyl-1,5,6,7,8-pentadeoxy-5,5-difluoro-2-*O*-formyl-L-*arabino*-oct-7-enitol (69): ATBT (0.10 mL, 0.30 mmol, 5 equiv) and AIBN (4 mg, 0.02 mmol, 0.4 equiv) were added to a solution of difluoro derivative **48** (24 mg, 0.061 mmol, 1 equiv) in dry benzene (2 mL). The reaction was refluxing for 1 h and then, the solvent was removed under vacuum. The residue was purified by column chromatography (hexanes and gradient elution to 20 % ethyl acetate) to yield **69** (17 mg, 0.055 mmol, 90 %) as an oil; $[\alpha]_D$ = +26.6 (*c* = 0.25); ^{1}H NMR: *d* = 1.23 (d, *J* = 6.4 Hz, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.63 (ddd, *J* = 7.0 Hz; ^3J(F,H) = 19.0, 19.0 Hz, 2H), 5.20 (dd, *J* = 1.5, 17.0 Hz, 1H), 5.24 (dd, *J* = 1.5, 10.2 Hz, 1H), 5.29–5.35 (m, 2H), 5.44 (ddd, *J* = 0.8, 2.7, 8.2 Hz, 1H), 5.78 (dddd, *J* = 7.0, 7.0, 10.2, 17.0 Hz, 1H), 7.97 ppm (s, 1H); ^{13}C NMR (125.7 MHz): *d* = 16.3 (CH_3), 20.6 (2 × CH_3), 38.4 (t, ^2J(F,C) = 25.0 Hz, CH_2), 67.3 (CH), 68.9 (t, ^2J(F,C) = 28.0 Hz, CH), 70.1 (CH), 121.0 (t, ^1J(F,C) = 246.0 Hz, C), 121.0 (CH_2), 127.6 (CH), 160.0 (CH), 168.9 (C), 169.7 ppm (C); ^{19}F NMR: *d* = –105.5 (dddd, ^3J(F,H) = 9.2, 18.4, 18.4 Hz, ^2J(F,F) = 261.6 Hz, 1F), –107.6 ppm (dddd, ^3J(F,H) = 14.0, 14.0, 14.0 Hz, ^2J(F,F) = 261.6 Hz, 1F); IR: $\tilde{n}$ = 2935, 1757, 1730, 1370, 1209, 1173, 1055 cm^{-1}; MS (70 eV, EI): *m/z* (%): 289 (1) $[M–F]^+$, 262 (7), 248 (14), 193 (33), 145 (100), 103 (67); HRMS (EI): *m/z* calcd for $C_{13}H_{18}FO_6$ $[M–F]^+$: 289.1087, found: 289.1099; elemental analysis calcd (%) for $C_{13}H_{18}F_2O_6$ (308.28): C 50.65, H 5.89. Found: C 50.51, H 5.89.

5,6,8-Tri-*O*-acetyl-4-allyl-1,2,3,4-tetradeoxy-4-fluoro-7-*O*-formyl-D-lyxo-oct-1-enitol (70): ATBT (0.27 mL, 0.89 mmol, 5 equiv) and AIBN (6 mg, 0.04 mmol, 0.4 equiv) were added to a solution of diiodo derivative **43** (50 mg, 0.089 mmol, 1 equiv) in dry benzene (3 mL). The reaction was refluxing for 40 minutes and then, the solvent was removed under vacuum. The residue was purified by column chromatography (hexanes and gradient elution to 20 % ethyl acetate) to yield **70** (30 mg, 0.077 mol, 87 %) as an oil; $[\alpha]_D$ +30.3 (*c* = 0.67, $CHCl_3$); ^{1}H NMR: *d* = 2.08 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.46–2.57 (m, 4H), 4.02 (dd, *J* = 6.6, 11.7 Hz, 1H), 4.28 (dd, *J* = 4.4, 11.7 Hz, 1H), 5.11–5.19 (m, 4H), 5.28 (dd, *J* = 5.7 Hz, ^2J(F,H) = 15.7 Hz, 1H), 5.57–5.59 (m, 4H), 8.05 ppm (s, 1H); ^{13}C NMR: *d* = 20.6 (CH_3), 20.7 (2 × CH_3), 38.4 (d, ^2J(F,C) = 22.7 Hz, CH_2), 39.2 (d, ^2J(F,C) = 22.4, CH_2), 62.2 (CH_2), 68.8 (2 × CH), 71.3 (d, ^2J(F,C) = 24.2 Hz, CH), 97.3 (d, ^1J(F,C) = 180.7 Hz, C), 119.6 (CH_2), 120.2 (CH_2), 130.6 (d, ^3J(F,C) = 7.7 Hz, CH), 131.0 (d, ^2J(F,C) = 7.1 Hz, CH), 159.8 (CH), 169.4

(C), 169.8 (C), 170.4 ppm (C); ^{19}F NMR: d = –162.0 ppm (m, 1F); IR: $\tilde{n}$ = 3081, 2984, 2937, 1754, 1736, 1645, 1370, 1213 cm^{-1}; MS (70 eV, EI): *m/z* (%): 347 (2) [M–C_3H_5]$^+$, 329 (3), 308 (1), 275 (3), 245 (2), 173 (34), 160 (100), 142 (61); HRMS (EI): *m/z* calcd for $C_{15}H_{20}FO_8$ [M–C_3H_5]$^+$: 347.1142, found: 347.1114; elemental analysis calcd (%) for $C_{18}H_{25}FO_8$ (388.39): C 55.67, H 6.49, found: C 55.73, H 6.36.

(1*S*)-1-(1,2,4-Tri-*O*-acetyl-3-*O*-formyl-D-threitol-1-*C*-yl)-1-fluoro-3-cyclopentene (71): Grubbs 1st generation catalyst [$(PCy_3)_2Cl_2Ru$=CHPh] (5 mg) was added, under nitrogen, to a solution of **70** (20 mg, 0.05 mmol, 1 equiv) in dry DCM (2 mL) and the reaction was stirred at room temperature for 1 h, poured into a saturated $NaHCO_3$ solution and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (*n*-hexane/EtOAc, 80.20) to yield **71** (17.5 mg, 0.049 mmol, 94 %) as a white solid; mp 76.2–77.5 ºC (from *n*-hexane:ethyl acetate); $[\alpha]_D$ = +20.1 (c = 0.33); ^{1}H NMR: d = 2.08 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 2.44–2.73 (m, 4H), 3.98 (dd, J = 7.2, 11.8 Hz, 1H), 4.31 (dd, J = 4.6, 11.8 Hz, 1H), 5.33 (dd, J = 7.4 Hz, ^3J(F,H) = 19.1 Hz, 1H), 5.55 (dddd, J = 1.0, 2.8, 4.6, 7.2 Hz, 1H), 5.61 (dd, J = 2.8, 7.4 Hz, ^4J(F,H) = 0.8 Hz, 1H), 5.68 (s, 2H), 8.03 ppm (d, J = 1.0 Hz, 1H); ^{13}C NMR: d = 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 42.4 (d, ^2J(F,C) = 23.6 Hz, CH_2), 42.7 (d, ^2J(F,C) = 22.8Hz, CH_2), 62.2 (CH_2), 68.5 (d, ^4J(F,C) = 2.8 Hz, CH), 68.9 (d, ^2J(F,C) = 2.5 Hz, CH), 71.9 (d, ^2J(F,C) = 24.6 Hz, CH), 103.8 (d, ^1J(F,C) = 184.9 Hz, C), 127.4 (2 × CH), 159.9 (CH), 169.5 (C), 169.9 (C), 170.4 ppm (C); ^{19}F NMR: d = –152.6 ppm (m, 1F); IR: $\tilde{n}$ = 3072, 2937, 1756, 1370, 1214, 1162, 1039 cm^{-1}.; MS (70 eV, EI): *m/z* (%): 315 (1) [M–OCOH]$^+$, 301 (2), 280 (1), 178 (57), 132 (78), 95 (100); HRMS (EI): *m/z* calcd for $C_{15}H_{20}FO_6$ [M–OCOH]$^+$: 315.1244, found: 315.1250; elemental analysis calcd (%) for $C_{16}H_{21}FO_8$ (360.33): C 53.33, H 5.87, found: C 53.36, H 6.07.