Supporting Information I

for

Synthesis of multiply fluorinated N-acetyl-D-glucosamine and D-galactosamine analogs via the corresponding deoxyfluorinated glucosazide and galactosazide thiodonors

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Experimental procedures
General methods

Chemicals were used as received. DAST was obtained from Acros Organics. Dichloromethane was dried by distillation from CaH$_2$ and stored over molecular sieves 3Å, pyridine was dried by standing over NaOH. Ethyl acetate and petroleum ether (fraction with boiling point 40–65 °C) were distilled before use. TLC was carried out with Sigma-Aldrich TLC Silica gel 60 F254 and spots were detected with an anisaldehyde solution in EtOH/AcOH/H$_2$SO$_4$. UV detection at 254 nm was also used where appropriate. Column chromatography was performed with silica gel 60 (70–230 mesh, Material Harvest). Preparative TLC chromatography was performed using 20 cm × 20 cm glass plates covered with TLC-Silica gel 60 GF$_{254}$ (20 g, mean particle size 15 µm, containing 12–13.5% CaSO$_4$·0.5 H$_2$O and fluorescent indicator, Merck). The maximum loading used was approximately 70 mg per one plate. If necessary, the plates were developed repeatedly. The solutions were concentrated at temperatures below 45 °C. Anhydrous sodium sulfate was used to dry solutions after aqueous workup. Reactions requiring microwave irradiation were conducted using Anton Paar Monowave 300 microwave reactor equipped with simultaneous temperature measurement with IR and a fiber optic sensor. The $^1$H (400.1 MHz), $^{13}$C (100.6 MHz), and $^{19}$F (376.4 MHz) NMR spectra were measured on a Bruker Avance 400 spectrometer at 25 °C. The $^1$H and $^{13}$C NMR spectra were referenced to the line of the solvent (δ/ppm; $\delta^H$/$\delta^C$: CDCl$_3$, 7.26/77.16, MeOH-d$_4$, 3.31/49.00). The $^{19}$F spectra were referenced to the line of internal standard hexafluorobenzene (δ/ppm; −163.00 in CDCl$_3$, −166.62 in MeOH-d$_4$). Structural assignments were made with additional information from COSY, HSQC, and HMBC experiments. HRMS analyses were done using Bruker MicrOTOF-QIII, using APCI ionization in positive mode and a TOF mass analyzer, the m/z value of the [M – N$_2$ + H]$^+$ adduct is reported for 2-azido sugars because the molecular ion adducts were undetectable or extremely weak in abundance. Starting compounds 7–13, and 14–17 were prepared following the published procedures [1,2]. EtOAc stands for ethyl acetate, PE for petroleum ether, MTBE for methyl tert-butyl ether.

General procedure for reactions of 1,6-anhydropyranoses with phenyl trimethylsilyl sulfide

To a solution of the starting deoxyfluorinated 1,6-anhydrohexopyranose in dry 1,2-dichloroethane ($c \approx 0.2–0.3$ mol.dm$^{-3}$) phenyl trimethylsilyl sulfide (PhSTMS, 3.3 equiv) and ZnI$_2$ (1.5 equiv) were added sequentially under argon atmosphere and the reaction was stirred vigorously with the exclusion of light and moisture at rt for about 24–120 h, until TLC indicated full consumption of the starting compound. Spots of C$_6$-OH products in varying intensity can also be detected near the TLC origin. The reaction was diluted with dichloromethane, filtered, washed with water and the water phase was extracted with dichloromethane (3×). The organic extracts were combined, dried and concentrated. The crude product was then dissolved in methanol ($c \approx 0.1$ mmol dm$^{-3}$) acidified by a few drops of AcOH and stirred at rt for about 1–2 h to remove 6-O-trimethylsilyl group (indicated by TLC), concentrated and purified by column chromatography.
**General procedure for C6 or C4 deoxyfluorination**

Diethylaminosulfur trifluoride (1.3 equiv per reacting OH group) and 2,4,6-collidine (2.6 equiv per reacting OH group) were added dropwise to a solution of the starting alcohol in dichloromethane (c 0.1–0.2 mol dm$^{-3}$) and the reaction was stirred, and heated as fast as possible to 80 °C under microwave irradiation, and kept at this temperature for 1 h in a 20 mL sealed glass vial. The reaction mixture was quenched by the addition of MeOH, diluted with dichloromethane and washed with a 1% aqueous solution of HCl. The water phase was extracted with dichloromethane (3×). Organic extracts were combined, dried, and concentrated. The crude product was purified by column chromatography.

**General procedure for thioglycoside hydrolysis**

A solution of the starting phenyl thioglycoside and N-bromosuccinimide (NBS, 4 equiv) in acetone/water 9/1 (c 0.05–0.1 mol dm$^{-3}$) was stirred at rt for about 1 h. The reaction mixture turned red and then gradually became colorless. When TLC indicated full consumption of the starting compound, the reaction was quenched by the addition of an aqueous solution of Na$_2$S$_2$O$_3$, diluted with dichloromethane and washed with water. The water phase was extracted with dichloromethane (3×). Organic extracts were combined, dried, and concentrated. The crude product was purified by column chromatography.

**General procedure for azide/acetamide conversion**

2-Azidohexose was dissolved in pyridine (0.1 mL per 1 mmol of the 2-azidohexose) and thioacetic acid (0.1 mL per 1 mmol of the 2-azidohexose) and the resulting solution was stirred overnight. The reaction mixture may become a thick paste during this period. It was concentrated, co-distilled with toluene and dry-loaded onto a chromatographic column for purification.

**General procedure for debenzylation**

An O-benzylated hexose was dissolved in a given volume of methanol and 10% palladium on carbon was added under argon atmosphere. The reaction mixture was degassed and purged with hydrogen (three cycles). Reaction was stirred under H$_2$ atmosphere until TLC indicated the complete absence of the starting material and the presence of a more polar product (usually for 24–72 h). The reaction mixture was filtered, concentrated and recrystallized.
1,6-Anhydro-2-azido-4-O-benzyl-2,3-dideoxy-3-fluoro-β-D-glucopyranose (7)

![Compound 7](image)

Compound 7 was prepared as described in ref 1.

1,6-Anhydro-2-azido-3-O-benzyl-2,4-dideoxy-4-fluoro-β-D-glucopyranose (8)

![Compound 8](image)

Compound 8 was prepared as described in ref 2.

1,6-Anhydro-2-azido-4-O-benzyl-2,3-dideoxy-3-fluoro-β-D-galactopyranose (9)

![Compound 9](image)

Compound 9 was prepared as described in ref 2.

1,6-Anhydro-2-azido-2,4-dideoxy-4-fluoro-β-D-galactopyranose (10)

![Galactopyranose 10](image)

Galactopyranose 10 was prepared according to ref 2.

1,6-Anhydro-2-azido-2,3-dideoxy-3-fluoro-β-D-glucopyranose (11)

![Glucopyranose 11](image)

Glucopyranose 11 was prepared according to ref 1.
1,6-Anhydro-2-azido-2,3,4-trideoxy-3,4-difluoro-β-D-glucopyranose (12)

Glucopyranose 12 was prepared according to ref 1.

Phenyl 2-Azido-2,3-dideoxy-3-fluoro-4-O-benzyl-1-thio-α/β-D-glucopyranoside (14)

Thioglycoside 14 was prepared from 7 in 77% yield according to ref 2.

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-O-benzyl-1-thio-α/β-D-glucopyranoside (15)

Thioglycoside 15 was prepared from 8 in 76% yield according to ref 2.

Phenyl 2-Azido-2,3-dideoxy-3-fluoro-4-O-benzyl-1-thio-α/β-D-galactopyranoside (16)

Thioglycoside 16 was prepared from 9 in 79% yield according to ref 2.

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-O-benzyl-1-thio-α/β-D-galactopyranoside (17)

Thioglycoside 17 was prepared from 10 in 63% yield according to ref 2. See also the synthesis of compound 20.
Phenyl 2-Azido-2,3-dideoxy-3-fluoro-1-thio-α/β-D-glucopyranoside (18)

Thioglycoside 18 was prepared by the reaction of 11 (1.00 g, 5.29 mmol) with PhSTMS (3.00 mL, 15.84 mmol) and ZnI₂ (2.50 g, 7.83 mmol) in 1,2-dichloroethane (20 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:2) showed the absence of compound 11 (Rf 0.27) and the presence of one major product (Rf 0.80). Chromatography of the residue after work-up (see the general procedure) in EtOAc/PE 2:1 afforded 18 as a colorless gel-like mixture of anomers (1.42 g, 90%), which crystallized after standing in a fridge as a white crystalline solid, mp 82–84 °C (dec, from heptane/MTBE, α/β 3.3:1). NMR data for the α-anomer: 1H NMR (CDCl₃, 400 MHz, 1H {10F}, H-H COSY): δ 7.49–7.47 (m, 2H, CH_arom), 7.36–7.32 (m, 3H, CH_arom), 4.70 (ddd, 1H, J = 52.9, 10.1, 8.6 Hz, H-3), 4.22 (dt, 1H, J = 10.0, 3.4 Hz, H-5), 3.99 (ddd, 1H, J = 11.0, 10.1, 5.7 Hz, H-2), 3.95–3.74 (m, 3H, H-4, 2H-6), 3.23 (br s, 1H, OH), 2.09 (br s, 1H, OH). 13C{1H} NMR (CDCl₃, 101 MHz, HSQC): δ 132.7 (2CH_arom), 132.6 (C₂), 129.4 (2CH_arom), 128.4 (CH_arom), 94.5 (d, J=184.5 Hz, C-3), 86.9 (d, J=8.0 Hz, C-1), 71.9 (d, J=6.8 Hz, C-5), 69.1 (d, J=18.0 Hz, C-2), 62.1 (d, J=1.7 Hz, C-4), 61.5 (d, J=1.3 Hz, C-6). 19F NMR (CDCl₃, 376 MHz): –194.44 (ddd, J=53.0 Hz, J=13.7, 11.0 Hz, J=3.2 Hz). NMR data for the β-anomer: 1H NMR (CDCl₃, 400 MHz, 1H {10F}, H-H COSY): δ 7.55–7.53 (m, 2H, CH_arom), 7.36–7.32 (m, 3H, CH_arom), 4.47 (ddd, 1H, J=10.2, 0.9 Hz, H-1), 4.36 (ddd, 1H, J=51.7, 9.1 Hz, H-3), 3.95–3.74 (m, 3H, H-4, 2H-6), 3.43 (ddd, 1H, J=12.3, 10.2, 9.1 Hz, H-2), 3.35 (ddd, 1H, J=9.8, 4.4, 3.1, 1.2 Hz, H-5), 3.18 (br s, 1H, OH), 1.81 (br s, 1H, OH). 13C{1H} NMR (CDCl₃, 101 MHz, HSQC): δ 133.5 (2CH_arom), 130.9 (C₂), 129.4 (2CH_arom), 128.9 (CH_arom), 96.8 (d, J=187.1 Hz, C-3), 85.9 (d, J=7.1 Hz, C-1), 78.6 (d, J=7.2 Hz, C-5), 68.5 (d, J=18.1 Hz, C-4), 63.3 (d, J=17.4 Hz, C-2), 61.8 (d, J=1.7 Hz, C-6). 19F NMR (CDCl₃, 376 MHz): –189.40 (ddd, J=51.7 Hz, J=13.5, 12.3 Hz). HRMS-APCI (m/z): [M – N₂ + H]⁺ caleqd for C₁₂H₁₅FNO₃S, 272.0751; found, 272.0750.

Phenyl 2-Azido-2,3,4-trideoxy-3,4-difluoro-1-thio-α-D-glucopyranoside (α-19)

Thioglycoside α-19 was prepared by reaction of 12 (670 mg, 3.51 mmol) with PhSTMS (1.65 mL, 8.71 mmol) and ZnI₂ (1.50 g, 4.70 mmol) in 1,2-dichloroethane (12 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:4) showed the absence of 12 (Rf 0.29) and the presence of one major product (Rf 0.65). Chromatography of the residue after workup (see the general procedure) in Et₂O/PE 2:5 → Et₂O/PE
1:1 first afforded the β-anomer of the product β-19 (224 mg, 21%) in 84% purity (due to the presence of an inseparable product of the ring contraction, see below) as a colorless syrup followed by the α-anomer (α-19) (577 mg, 55%) as a thick colorless syrup. Data for α-19: Rf 0.08 (EtOAc/PE 1:4), [α]_D^20 +190 (c 1.44, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.50–7.48 (m, 2H, CH₃, F), 7.36–7.32 (m, 3H, CH₃), 5.58 (dt, 1H, J = 5.7, 2.8 Hz, H-1), 4.89 (ddd, 1H, J = 15.4, 10.0, 8.3 Hz, H-3), 4.70 (ddd, 1H, J = 50.9, 15.2, 9.9, 8.3 Hz, H-4), from ¹H {¹⁹F} 4.39 (ddd, 1H, J = 9.9, 3.6, 2.7 Hz, H-5), 4.03 (ddd, 1H, J = 11.2, 10.0, 5.7, 0.9 Hz, H-2), 3.89–3.80 (m, 2H, H-6), 1.69 (t, 1H, J = 6.5 Hz, OH). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 132.8 (2CH₃), 132.1 (C₆), 129.5 (2CH₃, 128.6 (CH₃), 91.8 (dd, J = 188.9 Hz, J = 19.8 Hz, C-3), 86.7 (dd, J = 186.2 Hz, J = 18.7 Hz, C-4), 86.5 (dd, J = 7.6 Hz, J = 1.0 Hz, C-1), 70.2 (dd, J = 25.2 Hz, J = 6.2 Hz, C-5), 60.7 (dd, J = 17.6 Hz, J = 7.0 Hz, C-2), 60.7 (C-6). ¹⁹F NMR (CDCl₃, 376 MHz): –193.75 (ddddd, J = 53.0 Hz, J = 15.2, 13.6, 11.2 Hz, J = 2.8 Hz, F-3), –199.63 (ddddd, J = 50.9 Hz, J = 15.4, 13.6 Hz, J = 2.8 Hz, F-4). HRMS-APCI (m/z): [M – N₂ + H]^+ calc for C₁₂H₁₄F₂NO₃S, 274.0707; found, 274.0700.

Data for β-19: Rf 0.10 (EtOAc/PE 1:4). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.56–7.54 (m, 2H, CH₃), 7.39–7.35 (m, 3H, CH₃), 4.65–4.47 (m, 2H, H-3, H-4), 4.47 (dd, 1H, J = 10.2, 0.9 Hz, H-1), 3.97 (dt, 1H, J = 12.3, 2.1 Hz, H-6'), 3.79 (dd, 1H, J = 12.3, 3.5 Hz, H-6), 3.51–3.42 (m, 2H, H-2, H-5). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 133.8 (2CH₃), 130.4 (C₆), 129.5 (2CH₃), 129.2 (CH₃), 94.0 (dd, J = 191.5 Hz, J = 19.5 Hz, C-3), 86.0 (dd, J = 186.0 Hz, J = 18.5 Hz, C-4), 85.8 (dd, J = 6.6 Hz, J = 1.4 Hz, C-1), overlapped with CDCl₃ (C-5), 63.2 (dd, J = 18.0 Hz, J = 7.4 Hz, C-2), 61.1 (dd, J = 4.4 Hz, C-6). ¹⁹F NMR (CDCl₃, 376 MHz): –188.79 (m, F-3), –200.73 (m, F-4). HRMS-APCI (m/z): [M – N₂ + H]^+ calc for C₁₂H₁₄F₂NO₃S, 274.0707; found, 274.0703.

The β-anomer was contaminated by a co-eluting product of the ring contraction (approximately 16%) that was assigned the structure of 2,3-dideoxy-2,3-difluoro-C-α- or β-D-arabinofuranosyl-formaldehyde diphenyl dithioacetal S1. The configuration at C1 was not determined.

Data for S1: ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.50–7.46 (m, 3H, CH₃), 7.34–7.31 (m, 7H, CH₃), 5.54 (ddd, 1H, J = 51.8, 16.1, 3.6, 2.7 Hz, H-2), 5.19 (ddd, 1H, J = 52.6, 17.2, 4.7, 2.7 Hz, H-3), 4.53 (d, 1H, J = 7.1 Hz, CH(SPh)₂), 4.36 (ddd, 1H, J = 20.2, 7.1, 3.6 Hz, H-1), 4.24 (ddt, 1H, J = 20.9, 4.7, 4.4 Hz, H-4), 3.87–3.80 (m, 1H, H-5), 3.69 (dd, 1H, J = 12.1, 4.4 Hz, H-5'), 2.00 (br s, 1H, OH). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 133.7, 133.6 (2 × CH₃), 132.7, 132.7 (2 × C₆), 129.3, 129.2 (2 × CH₃), 128.7, 128.5 (2 × CH₃), 97.1 (dd, J = 186.9 Hz, J = 27.5 Hz, C-2), 95.3 (dd, J = 184.8 Hz, J = 28.1 Hz, C-3), 83.9 (dd, J = 26.6 Hz, J = 4.6 Hz, C-1), 82.8 (dd, J = 25.9 Hz, J = 4.3 Hz, C-4), 61.3 (dd, J = 5.8 Hz, J = 0.8 Hz, C-5), 60.4 (d, J = 6.6 Hz, J = 1.5 Hz, CH(SPh)₂). ¹⁹F NMR (CDCl₃, 376 MHz): –191.15 (ddddd, J = 51.8 Hz, J = 20.2, 17.2, 8.7 Hz, F-2), –195.68 (ddddd, J = 52.6 Hz, J = 20.9, 16.1, 8.7 Hz, F-2).

S7
2-O-benzyl-3-deoxy-3-fluoro-C-α-carboxymethyl-lyxofuranosyl-formaldehyde diphenyl dithioacetal (20)

(2,5-Anhydro-4-deoxy-4-fluoro-3-O-benzyl-D-talo-1-thio-α-D-glucopyranoside (200 mg, 0.51 mmol), prepared from α-14 in 94% yield as described in ref 3, was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 22 (129 mg, 85%, 80% over two steps) as a colorless gel, Rf 0.43 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.39–7.30 (m, 5H, CH-arom), 5.35 (q, 1H, J = 3.7 Hz, H-1), 5.05 (ddd, 1H, J = 53.3, 9.6, 8.3, 0.9 Hz, H-3), 4.92 (dd, 1H, J = 11.2, 1.4 Hz, CHH Bn), 4.66 (ddd, 1H, J = 47.3, 10.3, 3.2 Hz, H-6'), 4.65 (d, 1H, J = 11.2 Hz, CHH Bn), 4.57 (ddd, 1H, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 3.7 Hz, H-1), 5.05 (ddd, 1H, J = 53.3, 9.6, 8.3, 0.9 Hz, H-3), 4.92 (dd, 1H, J = 11.2, 1.4 Hz, CHH Bn), 4.66 (ddd, 1H, J = 47.3, 10.3, 3.2 Hz, H-6').

Phenyl 2-azido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-1-thio-α-D-glucopyranoside (200 mg, 0.51 mmol), prepared from α-14 in 94% yield as described in ref 3, was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 22 (129 mg, 85%, 80% over two steps) as a colorless gel, Rf 0.43 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.39–7.30 (m, 5H, CH-arom), 5.35 (q, 1H, J = 3.7 Hz, H-1), 5.05 (ddd, 1H, J = 53.3, 9.6, 8.3, 0.9 Hz, H-3), 4.92 (dd, 1H, J = 11.2, 1.4 Hz, CHH Bn), 4.66 (ddd, 1H, J = 47.3, 10.3, 3.2 Hz, H-6'), 4.65 (d, 1H, J = 11.2 Hz, CHH Bn), 4.57 (ddd, 1H, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6), 3.99 (ddt, 1H, J = 28.3, 10.0, 1.5 Hz, H-5), 3.76 (ddd, 1H, J = 13.4, 10.0, 8.3 Hz, J = 48.1, 10.3, 1.9, 1.5 Hz, H-6).
2-Azido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (23)

Thioglycoside 15 (380 mg, 0.98 mmol) was subjected to reaction with diethylaminosulfur trifluoride (170 μL, 1.29 mmol) and 2,4,6-collidine (340 μL, 2.57 mmol) in dichloromethane (8 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 afforded phenyl 2-azido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-1-thio-α/β-D-glucopyranoside (S2) (355 mg, 93%) as a colorless syrup mixture of anomers. Rf 0.83 (EtOAc/PE 1:3). NMR data for the β-anomer: 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.39–7.30 (m, 5H, CHarom), 4.89 (dd, 1H, J = 11.2, 0.7 Hz, CHH Bn), 4.70–7.53 (m, 2H, H-6), 6.62 (d, 1H, J = 8.5 Hz, H-1), 4.63 (d, 1H, J = 11.2 Hz, CHH Bn), 4.50 (dddd, 1H, J1 = 51.1, 9.9, 8.4, 0.8 Hz, H-3), 3.72 (ddd, 1H, J1 = 12.9, 10.0, 8.4 Hz, H-4), 3.54–3.46 (m, 2H, H-2, H-5), 2.99 (dd, 1H, J = 3.7, 1.3 Hz, OH). 13C{1H} NMR (CDCl3, 101 MHz, HSQC, HMBC): δ 137.2 (Cα), 128.7 (2CHarom), 128.4 (CHarom), 128.3 (2CHarom), 96.0 (dd, J1 = 187.8 Hz, J2 = 1.1 Hz, C-3), 95.7 (d, J2 = 10.9 Hz, C-1), 81.4 (dd, J1 = 174.3, J2 = 1.8 Hz, C-6), 74.8 (d, J2 = 2.7 Hz, CH2 Bn), 74.3 (dd, J2 = 17.2 Hz, J3 = 7.0 Hz, C-4), 73.2 (dd, J2 = 18.7 Hz, J3 = 9.9 Hz, C-5), 65.6 (d, J2 = 17.2 Hz, C-2). 19F NMR (CDCl3, 376 MHz): −188.75 (ddd, J2 = 51.1 Hz, J3 = 13.3, 12.9 Hz, F-3), −235.25 (ddd, J2 = 47.6, 47.4 Hz, J3 = 25.4 Hz, F-6). HRMS-APCI (m/z): [M − N2 + H]+ calcd for C13H16F2NO5, 272.1092; found, 272.1091.
75.2 (d, $^2J = 2.3$ Hz, CH$_2$ Bn), 76.4 (dd, $^2J = 23.4$ Hz, $^3J = 18.7$ Hz, C-5), 63.9 (d, $^3J = 9.0$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ −197.07 (dd, $^2J = 50.3$ Hz, $^3J = 14.5$ Hz F-4), −235.99 (td, $^2J = 47.1$ Hz, $^3J = 23.9$ Hz, F-6). HRMS-APCI (m/z): [M − N$_2$ + H]$^+$ calcd for C$_{10}$H$_{20}$F$_2$NO$_2$S, 364.1177; found, 364.1176.

Thioglycoside S2 (350 mg, 0.89 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 23 (201 mg, 75% from S2; 70% over two steps) as a white crystalline solid, mp 97–102 °C (EtOAc/heptane). $R_f$ 0.38 (EtOAc/PE 1:3). NMR data for the α-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F), H-H COSY): $\delta$ 7.43–7.31 (m, 5H, CH$_{arom}$), 6.80 (d, $^1J = 10.9$ Hz, $^2J = 1.9$ Hz, H-6), 4.59 (ddd, 1H, $^1J = 184.6$ Hz, $^3J = 0.8$ Hz, C-3), 75.1 (d, $^1J = 2.9$ Hz, CH$_2$ Bn), 68.6 (dd, $^2J = 24.6$ Hz, $^3J = 18.3$ Hz, C-5), 62.7 (d, $^1J = 8.4$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ −196.09 (ddd, $^2J = 50.5$ Hz, $^3J = 14.1$, 4.9 Hz, $^5J = 3.2$ Hz, F-4), −237.14 (ddd, $^3J = 47.3$, 47.0 Hz, $^2J = 26.3$ Hz, F-6). HRMS-APCI (m/z): [M − N$_2$ + H]$^+$ calcd for C$_{13}$H$_{16}$F$_2$NO$_3$, 272.1092; found, 272.1091. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample dissolution.

2-Azido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-α-D-galactopyranose (24)

Thioglycoside α-16 (245 mg, 0.63 mmol) was subjected to reaction with diethylaminosulfur trifluoride (100 μL, 0.76 mmol) and 2,4,6-collidine (200 μL, 1.51 mmol) in dichloromethane (5 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 afforded phenyl 2-azido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-1-thio-α-D-galactopyranoside (α-S3) (210 mg, 85%) as a colorless syrup.

2-Azido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-β-D-galactopyranose (16) and 2-Azido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-β-D-galactopyranose (β-S3) (210 mg, 85%) as a colorless syrup.
In another experiment, a mixture of anomers of thioglycoside 16 (α/β 3:7, 500 mg, 1.29 mmol) was subjected to reaction with diethylaminosulfur trifluoride (213 μL, 1.61 mmol) and 2,4,6-collidine (425 μL, 3.22 mmol) in dichloromethane (10 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 afforded sequentially 2-azido-4-O-benzyl-2,3,6-trideoxy-3-fluoro-6-S-phenyl-6-thio-α-D-galactopyranosyl fluoride (α-S4) (205 mg, 41%) as a white crystalline solid, phenyl 2-azido-4-O-benzyl-2,3,6-trIDEOXY-3,6-difluoro-1-thio-α-D-galactopyranoside (α-S3) (107 mg, 21%) as a colorless syrup, 2-azido-4-O-benzyl-2,3,6-trideoxy-3-fluoro-6-S-phenyl-6-thio-β-D-galactopyranosyl fluoride (β-S4) (27 mg, 5%) as a colorless syrup and phenyl 2-azido-4-O-benzyl-2,3,6-trIDEOXY-3,6-difluoro-1-thio-β-D-galactopyranoside (β-S3) (90 mg, 18%) as a colorless syrup. Data for α-S3: Rf 0.85 (EtOAc/PE 1:3). 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.50–7.47 (m, 2H, CHarom), 7.40–7.29 (m, 8H, CHarom), 5.62 (dd, 1H, J = 5.6, 4.3 Hz, H-1), 4.92 (d, 1H, J = 11.2 Hz, CHH Bn), 4.49 (ddd, 1H, J = 48.0, 10.4, 3.1 Hz, H-3), 4.60 (d, 1H, J = 11.2 Hz, CHH Bn), 4.60–4.50 (m, 1H, H-5), from 1H 19F 4.52 (dd, 1H, J = 10.4, 5.6 Hz, H-2), 4.47 (ddd, 1H, J = 46.8, 9.3, 6.4, 1.1 Hz, H-6’), 4.41 (ddd, 1H, J = 46.1, 9.4, 5.9 Hz, H-6), 4.11 (ddd, 1H, J = 6.6, 3.1, 1.3 Hz, H-4). 13C 1H NMR (CDCl3, 101 MHz, HSQC): δ 137.4 (Cq), 132.69 (2CHarom), 132.67 (Cq), 129.3, 128.7, 128.5 (3 × 2CHarom), 128.4, 128.3 (2 × CHarom), 91.8 (d, Jf = 190.8 Hz, C-3), 87.3 (d, Jf = 7.7 Hz, C-1), 81.4 (d, Jf = 169.1, Jf = 2.8 Hz, C-6), 75.3 (d, Jf = 4.2 Hz, CH2 Bn), 73.6 (dd, Jf = 15.5 Hz, Jf = 5.4 Hz, C-4), 69.4 (dd, Jf = 24.6 Hz, Jf = 7.0 Hz, C-5), 59.6 (d, Jf = 18.0 Hz, C-2). 19F NMR (CDCl3, 376 MHz): –196.89 (dd, Jf = 48.0 Hz, Jf = 9.6, 6.6 Hz, Jf = 4.3 Hz, F-3), –231.60 (dd, Jf = 46.8, 46.1 Hz, Jf = 11.9 Hz, Jf = 2.0 Hz, F-6). HRMS-APCI (m/z): [M – N2 + H]+ calcd for C19H20F2NO2S, 364.1177; found, 364.1178.

Data for β-S3: Rf 0.42 (Et2O/PE 1:6). 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.59–7.57 (m, 2H, CHarom), 7.37–7.25 (m, 8H, CHarom), 4.87 (d, 1H, J = 11.4 Hz, CHH Bn), 4.58 (ddd, 1H, J = 46.8, 9.3, 6.2, 1.3 Hz, H-6’), 4.57 (d, 1H, J = 11.4 Hz, CHH Bn), 4.49 (ddd, 1H, J = 47.4, 9.6, 3.1 Hz, H-3), 4.41 (dd, 1H, J = 10.1, 0.9 Hz, H-1), 4.43 (ddd, 1H, J = 46.0, 9.3, 6.4 Hz, H-6), 4.00 (ddd, 1H, J = 6.4, 3.1, 1.2 Hz, H-4), 3.92 (ddd, 1H, J = 11.0, 10.1, 9.6 Hz, H-2), 3.71 (ddd, 1H, J = 9.6, 6.4, 6.2, 1.5, 1.2 Hz, H-5). 13C 1H NMR (CDCl3, 101 MHz, HSQC): δ 137.6 (Cq), 133.4 (2CHarom), 131.2 (Cq), 129.2, 128.6 (2 × CHarom), 128.5, 128.1 (2 × CHarom), 128.1 (2CHarom), 94.4 (d, Jf = 193.1 Hz, C-3), 86.2 (d, Jf = 6.9 Hz, C-1), 81.0 (dd, Jf = 169.1, Jf = 2.9 Hz, C-6), 75.6 (dd, Jf = 24.4 Hz, Jf = 7.7 Hz, C-5), 74.8 (d, Jf = 4.0 Hz, CH2 Bn), 72.5 (dd, Jf = 15.8 Hz, Jf = 4.7 Hz, C-4), 60.7 (d, Jf = 18.2 Hz, C-2). 19F NMR (CDCl3, 376 MHz): –190.12 (ddd, Jf = 47.4 Hz, Jf = 11.0, 6.4 Hz, F-3), –231.82 (ddd, Jf = 46.8, 46.0 Hz, Jf = 9.6 Hz, F-6). HRMS-APCI (m/z): [M – N2 + H]+ calcd for C19H20F2NO2S, 364.1177; found, 364.1179.

Data for α-S4: Rf 0.50 (Et2O/PE 1:6). 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.37–7.23 (m, 10H, CHarom), 5.66 (ddd, 1H, J = 52.7, 5.4, 2.8 Hz, H-1), 4.94 (ddd, 1H, J = 48.5, 10.4, 3.0 Hz, H-3), 4.93, 4.54 (2 × d, 2 × 1H, J = 11.1 Hz, CHH Bn), 4.34 (ddd, 1H, J = 7.4, 3.0, 1.3 Hz, H-4), 4.03 (ddd, 1H, J = 25.3, 10.4, 9.6, 2.8 Hz, H-2), from 1H 19F-3 3.99 (ddd, 1H, J = 8.8, 5.4, 1.3 Hz, H-5), 3.20 (ddd, 1H, J = 13.7, 5.4, 2.0 Hz, H-6’), 3.10 (ddd, 1H, J = 13.7, 8.8, 0.8 Hz, H-6). 13C 1H NMR (CDCl3, 101 MHz, HSQC): δ 137.5, 134.8 (2 × Cq), 129.9, 129.4, 128.7, 128.5 (4 × 2CHarom), 128.3, 127.0 (2 × CHarom), 106.6 (d, Jf = 227.3 Hz, Jf = 9.8 Hz, C-1), 90.6 (d, Jf = 189.6 Hz, C-3), 75.4 (d, Jf = 4.2 Hz, CH2 Bn), 73.8 (d, Jf = 15.8 Hz, C-4), 71.9 (dd, Jf = 7.0, 3.3 Hz, C-5), 58.9
Data for β-S4: Rf 0.46 (Et₂O/PE 1:6), 1H NMR (CDCl₃, 400 MHz, ¹H {¹F}, H-H COSY): δ 7.38–7.27 (m, 10H, CH₆arom), 4.93 (d, 1H, J = 11.3 Hz, C/H H Bn), 4.93 (dd, 1H, J = 52.2, 7.4 Hz, H-1), 4.55 (d, 1H, J = 11.3 Hz, C/H H Bn), 4.41 (dddd, 1H, J = 47.2, 10.1, 3.2, 1.1 Hz, H-3), from ¹H {¹F-3} 4.20 (d, 1H, J = 3.2 Hz, H-4), 4.14–3.99 (m, 1H, H-2), from ¹H {¹F-3} 3.47 (dd, 1H, J = 8.8, 5.1 Hz, H-5), 3.25 (dd, 1H, J = 13.9, 5.1, 1.9 Hz, H-6”), 3.15 (dd, 1H, J = 13.9, 8.8 Hz, H-6). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 137.4, 134.7 (2 × C₆arom), 129.8, 129.4, 128.7, 128.5 (4 × 2CH₆arom), 128.3, 127.1 (2 × CH₆arom), 107.7 (dd, 1J = 216.1 Hz, 3J = 11.3 Hz, C-1), 92.7 (dd, 1J = 192.5 Hz, 3J = 10.9 Hz, C-3), 75.3 (d, 1J = 4.1 Hz, CH₂ Bn), 72.8 (dd, 2J = 7.7, 4.3 Hz, C-5), 72.5 (dd, 2J = 15.5 Hz, 3J = 1.0 Hz, C-4), 62.3 (dd, 2J = 22.3, 18.5 Hz, C-2), 33.1 (d, 3J = 2.4 Hz, C-6). ¹⁹F NMR (CDCl₃, 376 MHz): –141.26 (dddd, 2J = 52.2 Hz, 3J = 13.2 Hz, 4J = 3.4, 2.6 Hz, F-1), –197.09 (ddddd, 2J = 47.2 Hz, 3J = 9.0, 5.9 Hz, 4J = 3.4, 1.5 Hz, F-3). HRMS-APCI (m/z): [M – N₂ + H]⁺ calcd for C₁₉H₂₀F₂NO₂S, 364.1177; found, 364.1175.

Thioglycoside S3 (184 mg, 0.47 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 24 (126 mg, 90% from S3; 76% over two steps) as a white crystalline solid, mp 115–119 °C (Et₂O/heptane). Rf 0.40 (EtOAc/PE 1:3). NMR data for the α-anomer: ¹H NMR (CDCl₃, 400 MHz, ¹H {¹F}, H-H COSY): δ 7.40–7.31 (m, 5H, CH₆arom), 3.96 (dd, 1H, J = 52.2 Hz, 7.4 Hz, H-1), 3.46 (d, 1H, J = 8.0, 1.1 Hz, H-1), 4.43 (dd, 1H, J = 47.5, 10.2, 3.3 Hz, H-3), from ¹H {¹F-3} 3.96 (dd, 1H, J = 3.1, 1.6 Hz, H-4), 3.89 (dd, 1H, J = 11.2, 10.2, 8.0 Hz, H-2), 3.69 (dt, 1H, J = 12.2, 6.1, 1.6 Hz, H-5), 3.46 (br s, 1H, OH). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 137.2 (C₆), 128.7 (2CH₆arom), 128.41 (CH₆arom), 128.37 (2CH₆arom), 96.2 (d, 3J = 10.3 Hz, C-1), 92.8 (dd, 1J = 191.7 Hz, 4J = 1.3 Hz, C-3), 81.3 (dd, 1J = 169.2, 4J = 3.2 Hz, C-6), 75.1 (d, 4J = 5.0 Hz, CH₂ Bn), 72.4 (dd, 2J = 15.6 Hz, 3J = 5.4 Hz, C-4), 72.1 (dd, 2J = 24.0 Hz, 3J = 8.1 Hz, C-5), 63.6 (d, 2J = 17.2 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): –195.67 (m, F-3), –231.69 (m, F-6). HRMS-APCI (m/z): [M – N₂ + H]⁺ calcd for C₁₃H₁₆F₂NO₃, 272.1092; found, 272.1091.
Thioglycoside α-17 (345 mg, 0.89 mmol) was subjected to reaction with diethylaminosulfur trifluoride (150 μL, 1.14 mmol) and 2,4,6-collidine (300 μL, 2.27 mmol) in dichloromethane (7 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 afforded phenyl 2-azido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-l-thio-α-D-galactopyranoside (S5) (300 mg, 87%) as a yellowish syrup. Rf 0.78 (EtOAc/PE 1:3). 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.51–7.48 (m, 2H, CH_arom), 7.44–7.30 (m, 8H, CH_arom), 5.61 (d, 1H, J = 5.4 Hz, H-1), 4.90 (dd, 1H, J = 50.3, 2.5 Hz, H-4), 4.80, 4.76 (2 × d, 2 × 1H, J = 11.7 Hz, CH/H Bn), 4.67–4.53 (m, 2H, H-5, H-6´), 4.51 from 1H {19F-6} (dd, 1H, J = 8.1, 1.5 Hz, H-6), 4.30 (dd, 1H, J = 10.6, 5.4 Hz, H-2), 3.76 (ddd, 1H, J = 26.2, 10.6, 2.5 Hz, H-3). 13C {1H} NMR (CDCl3, 101 MHz, HSQC): δ 136.9 (Cq), 132.7 (2CH_arom), 132.6 (Cq), 129.4, 128.8 (2 × 2CH_arom), 128.4, 128.3 (2 × CH_arom), 128.1 (2CH_arom), 87.4 (C-1), 85.0 (dd, J = 185.9 Hz, 3J = 5.0 Hz, C-4), 80.7 (dd, J = 170.0 Hz, 2J = 6.3 Hz, C-6), 75.9 (d, 2J = 17.8 Hz, C-3), 72.1 (CH2 Bn), 68.7 (dd, 2J = 24.6 Hz, 2J = 18.0 Hz, C-5), 59.7 (d, 3J = 1.9 Hz, C-2). 19F NMR (CDCl3, 376 MHz): −218.13 (ddd, 2J = 50.3 Hz, 3J = 30.2, 26.2 Hz, F-4), −232.28 (m, F-6). HRMS-APCI (m/z): [M − N2 + H]+ calcd for C19H20F2NO2S, 364.1177; found, 364.1177.

Thioglycoside S5 (175 mg, 0.45 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded 25 (90 mg, 67% from S5; 58% over two steps) as a white crystalline solid, mp 89–92 °C (MTBE/heptane). Rf 0.36 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.43–7.31 (m, 5H, CH_arom), 5.37 (d, 1H, J = 3.4 Hz, H-1), 4.87 (dd, 1H, J = 50.2, 2.5 Hz, H-4), 4.78, 4.74 (2 × d, 2 × 1H, J = 11.7 Hz, CH/H Bn), 4.58 (dd, 1H, J = 46.1, 9.5, 6.1 Hz, H-6´), 4.53 (ddd, 1H, J = 46.5, 9.5, 6.5, 1.0 Hz, H-6), 4.28 (ddd, 1H, J = 29.6, 12.4, 6.5, 6.1 Hz, H-5), 3.96 (ddd, 1H, J = 26.7, 10.5, 2.5 Hz, H-3), 3.83 (ddd, 1H, J = 10.5, 3.4, 1.0 Hz, H-2). 13C {1H} NMR (CDCl3, 101 MHz, HSQC): δ 137.1 (Cq), 128.8 (2CH_arom), 128.4 (CH_arom), 128.1 (2CH_arom), 92.4 (C-1), 85.2 (dd, J = 185.6 Hz, 3J = 5.1 Hz, C-4), 81.1 (dd, J = 169.4 Hz, 3J = 6.5 Hz, C-6), 74.1 (dd, 2J = 18.0 Hz, 4J = 0.9 Hz, C-3), 72.0 (CH2 Bn), 68.0 (dd, 2J = 23.9 Hz, 2J = 18.0 Hz, C-5), 59.6 (d, 3J = 2.3 Hz, C-2). 19F NMR (CDCl3, 376 MHz): −220.98 (ddd, 2J = 50.2 Hz, 3J = 29.6, 26.7 Hz, F-4), −232.58 (ddd, 2J = 46.5, 46.1 Hz, 3J = 12.4 Hz, F-6). NMR data for the β-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.43–7.31 (m, 5H, CH_arom), 4.78 (d, 1H, J = 11.9 Hz, CH/H Bn), 4.75 (dd, 1H, J = 49.7, 2.6 Hz, H-4), 4.73 (d, 1H, J = 11.9 Hz, CH/H Bn), 4.58 (dd, 1H, J = 8.1, 1.4 Hz, H-1), overlapped with α-anomer (2H, H-6), 3.72 (ddt, 1H, J = 26.7, 10.6, 6.3 Hz, H-5), 3.68 (dd, 1H, J = 10.3, 8.1 Hz, H-2), 3.38 (ddd, 1H, J = 27.3, 10.3, 2.6 Hz, H-3). 13C {1H} NMR (CDCl3, 101 MHz, HSQC): δ 137.1 (Cq), 128.8 (2CH_arom), 128.4 (CH_arom), 128.1 (2CH_arom), 96.3 (C-1), 84.0 (dd, J = 185.5 Hz, 3J = 3.5 Hz, C-4), 80.5 (dd, J = 170.1 Hz, 3J = 6.0 Hz, C-6), overlapped with CDCl3 (C-3), 72.2 (CH2 Bn), 72.0 (dd, 2J = 23.0 Hz, 2J = 18.5 Hz, C-5), 63.8 (d, 3J = 0.8 Hz, C-2). 19F NMR (CDCl3, 376 MHz):
2-Azido-2,3,4,6-tetradeoxy-3,4,6-trifluoro-D-glucopyranose (26)

Thioglycoside α-19 (400 mg, 1.33 mmol) was subjected to reaction with diethylaminosulfur trifluoride (190 μL, 1.44 mmol) and 2,4,6-collidine (380 μL, 2.88 mmol) in dichloromethane (8 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:5 afforded the phenyl 2-azido-2,3,4,6-tetradexo-3,4,6-trifluoro-1-thio-α-D-glucopyranoside (S6) (359 mg, 89%) as a colorless syrup. Rf 0.78 (EtOAc/PE 1:3). 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.48–7.46 (m, 2H, CHα), 7.36–7.32 (m, 3H, CHα), 5.61 (dt, 1H, J = 5.8, 2.8 Hz, H-1), 4.89 (ddd, 1H, J = 52.8, 15.3, 10.1, 8.2 Hz, H-3), from 1H 19F-6) 4.70 (ddd, 1H, J = 10.7, 3.3, 1.5 Hz, H-6), from 1H 19F-6) 4.59 (dq, 1H, J = 10.7, 1.7 Hz, H-6), 4.80–4.42 (m, 2H, H-4, H-5), 4.06 (ddd, 1H, J = 11.1, 10.0, 5.8, 0.9 Hz, H-2). 13C 1H NMR (CDCl3, 101 MHz, HSQC): δ 132.3 (2CH of, 132.2 (Cα), 129.5 (CHα), 91.6 (dd, 1H, J = 189.1 Hz, 2J = 19.7 Hz, 4J = 0.8 Hz, C-3), 86.5 (dd, 1H, J = 7.5 Hz, 4J = 1.3 Hz, C-1), 86.0 (dd, 1H, J = 187.4 Hz, 2J = 17.8 Hz, 3J = 7.7 Hz, C-4), 80.5 (dt, 1H, J = 173.4 Hz, 3J = 0.9 Hz, C-6), 69.0 (ddd, 2J = 24.8, 3J = 18.2 Hz, 5J = 6.9 Hz, C-5), 61.8 (dd, 2J = 17.6 Hz, 3J = 6.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): -193.67 (dddd, 2J = 52.8 Hz, 3J = 14.8, 13.5, 11.1 Hz, 4J = 2.8 Hz, 5J = 1.7 Hz, F-3), -200.64 (ddddd, 2J = 51.0 Hz, 3J = 15.3, 13.5, 3.9 Hz, 5J = 2.8 Hz, F-4), -236.57 (td, 2J = 47.2 Hz, 3J = 26.7 Hz, F-6). Thioglycoside S6 (330 mg, 1.09 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 26 (209 mg, 91% from S6; 81% over two steps) as a colorless gel. Rf 0.32 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 5.37 (dt, 1H, J = 3.6, 3.4 Hz, H-1), 5.05 (ddd, 1H, J = 53.4, 15.4, 10.0, 8.2 Hz, H-3), 4.77–4.53 (m, 3H, H-4, 2H-6), 4.19 (dddd, 1H, J = 26.6, 10.1, 5.4, 2.7, 2.3 Hz, H-5), from 1H 19F-3) 3.52 (dd, 1H, J = 10.0, 3.6 Hz, H-2), 3.16 (br s, 1H, OH). 13C 1H NMR (CDCl3, 101 MHz, HSQC, HMBC): δ 92.3 (dd, 3J = 9.3 Hz, 4J = 1.4 Hz, C-1), 90.4 (ddd, 1H, J = 187.0 Hz, 2J = 19.4 Hz, 4J = 0.6 Hz, C-3), 86.1 (ddd, 2J = 187.1 Hz, 3J = 18.6 Hz, 5J = 7.7 Hz, C-4), 80.7 (dt, 1J = 175.2 Hz, 3J = 0.9 Hz, C-6), 68.1 (ddd, 2J = 23.9 Hz, 3J = 18.2 Hz, 5J = 7.0 Hz, C-5), 61.7 (dd, 2J = 16.9 Hz, 3J = 6.6 Hz, C-2). 19F NMR (CDCl3, 376 MHz): -198.62 (ddddd, 2J = 53.4 Hz, 3J = 13.7, 13.1, 11.0 Hz, 4J = 3.4 Hz, F-3), -199.95 (ddddd, 2J = 51.1 Hz, 3J = 15.4, 13.1, 2.7 Hz, 5J = 3.4 Hz, F-4), -237.44 (td, 2J = 47.2 Hz, 3J = 26.7 Hz, F-6). Resolved signals for the β-anomer: 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 4.77–4.53 (m, 4H, H-1, H-4, 2H-6), 4.52 (dddd, 1H, J = 51.5, 15.9, 9.7, 8.3, 0.8 Hz, H-3), 3.69 (br s, 1H, OH), from 1H 19F-4) 3.64 (ddd, 1H, J = 23.5, 9.9, 4.7, 2.3 Hz, H-5), from 1H 19F-3) 3.54 (dd, 1H, J = 9.7, 8.0 Hz, H-2). 13C 1H NMR (CDCl3, 101 MHz, HSQC, HMBC): δ 95.8 (dd, 3J = 10.2 Hz, 4J = 1.4 Hz, C-1), 92.0 (ddd, 1J = 190.3 Hz, 2J = 19.9 Hz, 3J = 0.8 Hz, C-3), 85.7 (ddd, 1J = 187.0 Hz,
2-J = 19.1 Hz, 3-J = 7.7 Hz, C-4), 80.6 (ddd, 1-J = 175.8 Hz, 3-J = 1.9 Hz, 4-J = 0.4 Hz, C-6), 71.6 (ddd, 2-J = 23.9 Hz, 2-J = 18.8 Hz, 3-J = 7.7 Hz, C-5), 65.1 (dd, 2-J = 17.4 Hz, 2-J = 7.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): -192.87 (ddt, 2-J = 51.5 Hz, 3-J = 13.6, 13.4 Hz, F-3), from 19F 1-H -201.89 (d, 3-J = 13.6 Hz, F-4), -236.13 (ddd, 2-J = 47.0, 47.3 Hz, 3-J = 23.5 Hz, F-6). HRMS-APCI (m/z): [M - N2 + H]+ calcd for C6H9F3NO2, 184.0579; found, 184.0576.

Phenyl 2-azido-4,6-di-O-benzyl-2,3-dideoxy-3-fluoro-1-thio-α/β-D-glucopyranoside (350 mg, 0.73 mmol), prepared from 14 in 81% yield as described in ref 2, was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded 27 (258 mg, 91%, 74% over two steps) as a colorless crystalline material, mp 63–65 °C (MTBE/heptane), Rf 0.2 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}), H-H COSY): δ 7.37–7.29 (m, 10H, CH arom), 5.33 (q, 1H, J = 3.6 Hz, H-1), 5.02 (ddd, 1H, J = 53.5, 10.0, 8.4 Hz, H-3), 4.84 (dd, 1H, J = 11.0, 1.0 Hz, CHH O-4Bn), 4.59 (d, 1H, J = 12.0 Hz, CHH O-6Bn), 4.52 (d, 1H, J = 11.0 Hz, CHH O-4Bn), 4.50 (d, 1H, J = 12.0 Hz, CHH O-6Bn), 4.05 (dd, 1H, J = 10.0, 4.2, 2.4 Hz, H-5), from 1H{19F} 3.73 (dd, 1H, J = 10.0, 8.4 Hz, H-4), 3.73–3.60 (m, 2H, H-6), 3.52–3.43 (m, 1H, H-2), 3.15 (dd, 1H, J = 3.6, 1.4 Hz, OH). 13C{1H} NMR (CDCl3, 101 MHz, HSQC): δ 137.73, 137.66 (2 × Cq), 128.62, 128.58, 128.24, 128.17 (4 × 2CH arom), 128.12, 128.06 (2 × CH arom), 94.3 (d, J = 183.9 Hz, C-3), 92.4 (d, J = 9.7 Hz, C-1), 76.0 (d, J = 16.5 Hz, C-4), 74.7 (d, J = 2.8 Hz, CH2 O-4Bn), 73.7 (CH2 O-6Bn), 69.9 (d, J = 8.3 Hz, C-5), 68.4 (d, J = 0.9 Hz, C-6), 62.2 (d, J = 16.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): δ -192.87 (dt, J = 53.8 Hz, J = 13.3 Hz Hz). Resolved signals for the β-anomer: 1H NMR (CDCl3, 400 MHz, 1H{19F}, H-H COSY, HSQC): δ 7.37–7.29 (m, 10H, CH arom), 4.80 (dd, 1H, J = 11.0, 1.0 Hz, CHH O-4Bn), 4.55 (dd, 1H, J = 7.8, 4.5 Hz, H-1), 4.59 (d, 1H, J = 12.0 Hz, CHH O-6Bn), 4.43 (ddd, 1H, J = 51.4, 9.7, 8.4 Hz, H-3), 3.77–3.60 (m, 4H, OH, H-4, 2H-6), 3.52–3.43 (m, 2H, H-2, H-5). 13C{1H} NMR (CDCl3, 101 MHz, HSQC): δ 137.6, 137.5 (2 × Cq), 128.63, 128.60, 128.27 (3 × 2CH arom), 128.20 (CH arom), 128.18 (2CH arom), 128.1 (CH arom), 96.2 (d, J = 186.8 Hz, C-3), 95.7 (d, J = 10.8 Hz, C-1), 75.5 (d, J = 16.9 Hz, C-4), 74.6 (d, J = 2.8 Hz, CH2 O-4Bn), 73.8 (CH2 O-6Bn), 68.5 (d, J = 1.8 Hz, C-6), 65.7 (d, J = 16.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): δ -187.45 (dt, J = 51.4 Hz, J = 13.3 Hz Hz). HRMS-APCI (m/z): [M - N2 + H]+ calcd for C20H23FNO4, 360.1606; found, 360.1609.
Phenyl 2-azido-3,6-di-O-benzyl-2,4-dideoxy-4-fluoro-D-glucopyranose (28)

Chromatography in EtOAc/PE 1:4 afforded 28 (176 mg, 91%, 78% over two steps) as a colorless syrup. R<sub>f</sub> 0.57 (EtOAc/PE 1:3). NMR data for the α-anomer: ¹H NMR (CDCl<sub>3</sub>, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.43–7.29 (m, 10H, CH<sub>arom</sub>), 5.28 (td, 1H, J = 3.6, 3.2 Hz, H-1), 4.90 (dd, 1H, J = 11.0, 1.1 Hz, CH<sub>H</sub>O3-Bn), 4.78 (d, 1H, J = 11.0 Hz, CH<sub>H</sub>O3-Bn), 4.62, 4.58 (2 × d, 2 × 1H, J = 12.2 Hz, CH<sub>H</sub>O6-Bn), 4.53 (ddd, 1H, J = 50.7, 10.0, 8.4 Hz, H-4), from ¹H {¹⁹F} 4.19 (ddd, 1H, J = 10.0, 5.3, 2.1 Hz, H-5), 4.07 (ddd, 1H, J = 14.2, 10.4, 8.4 Hz, H-3), from ¹H {¹⁹F} 3.72 (dd, 1H, J = 10.9, 2.1 Hz, H-6'), from ¹H {¹⁹F} 3.66 (dd, 1H, J = 10.9, 5.3 Hz, H-6), 3.39 (ddd, 1H, J = 10.4, 3.6, 1.2 Hz, H-2), 3.37 (d, 1H, J = 3.6 Hz, OH<sub>H</sub>). ¹³C {¹H} NMR (CDCl<sub>3</sub>, 101 MHz, HSQC): δ 137.7, 137.6 (2 × C<sub>α</sub>), 128.6 (4CH<sub>arom</sub>), 128.4 (2CH<sub>arom</sub>), 128.2, 128.00 (2 × CH<sub>arom</sub>), 127.97 (2CH<sub>arom</sub>), 92.0 (d, 4J = 1.5 Hz, C-1), 90.9 (d, 1J = 184.0 Hz, C-4), 77.5 (d, 2J = 19.4 Hz, C-3), 75.1 (d, 4J = 2.9 Hz, CH<sub>2</sub>O-3Bn), 73.8 (CH<sub>2</sub>O-6Bn), 68.8 (d, 2J = 24.4 Hz, C-5), 68.4 (C-6), 62.8 (d, 3J = 8.4 Hz, C-2). ¹⁹F NMR (CDCl<sub>3</sub>, 376 MHz): δ −195.45 (dd, 2J = 50.7 Hz, 3J = 14.2 Hz). NMR data for the β-anomer: ¹H NMR (CDCl<sub>3</sub>, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.43–7.29 (m, 10H, CH<sub>arom</sub>), 4.85 (dd, 1H, J = 11.1, 1.0 Hz, CH<sub>H</sub>O3-Bn), 4.76 (d, 1H, J = 11.1 Hz, CH<sub>H</sub>O3-Bn), 4.59 (2 × d, 2 × 1H, J = 12.2 Hz, CH<sub>H</sub>O6-Bn), 4.56 (d, 1H, J = 8.2 Hz, H-1), 4.47 (ddd, 1H, J = 50.3, 9.7, 8.4 Hz, H-4), 3.83 (br s, 1H, OH<sub>H</sub>), from ¹H {¹⁹F} 3.75 (dd, 1H, J = 10.3, 1.7 Hz, H-6'), from ¹H {¹⁹F} 3.64 (dd, 1H, J = 10.3, 6.0 Hz, H-6), from ¹H {¹⁹F} 3.59 (ddd, 1H, J = 9.7, 6.0, 1.7 Hz, H-5), 3.50 (ddd, 1H, J = 14.9, 9.9, 8.4 Hz, H-3), 3.35 (ddd, 1H, J = 9.9, 8.2, 0.8 Hz, H-2). ¹³C {¹H} NMR (CDCl<sub>3</sub>, 101 MHz, HSQC): δ 137.6, 137.5 (2 × C<sub>α</sub>), 128.63, 128.59, 128.3 (3 × 2CH<sub>arom</sub>), 128.2, 128.1 (2 × CH<sub>arom</sub>), 128.0 (2CH<sub>arom</sub>), 96.1 (d, 4J = 1.6 Hz, C-1), 90.2 (d, 1J = 183.9 Hz, C-4), 80.3 (d, 2J = 18.2 Hz, C-3), 74.9 (d, 4J = 2.6 Hz, CH<sub>2</sub>O-3Bn), 73.9 (CH<sub>2</sub>O-6Bn), 73.1 (d, 2J = 24.2 Hz, C-5), 68.5 (C-6), 66.3 (d, 3J = 9.2 Hz, C-2). ¹⁹F NMR (CDCl<sub>3</sub>, 376 MHz): δ −197.68 (dd, 2J = 50.3 Hz, 3J = 14.9, 3.0 Hz). HRMS-APCI (m/z): [M − N<sub>2</sub> + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>22</sub>FNO<sub>4</sub>, 360.1605; found, 360.1608.

2-Azido-4,6-di-O-benzyl-2,3-dideoxy-3-fluoro-D-galactopyranose (29)

Phenyl 2-azido-4,6-di-O-benzyl-2,3-dideoxy-3-fluoro-1-thio-β-D-galactopyranoside (375 mg, 0.78 mmol), prepared from β-16 in 93% yield as described in ref 2 was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 29 (238 mg, 79%, 73% over two steps) as a colorless syrup. R<sub>f</sub> 0.50 (EtOAc/PE 1:3). NMR data for the α-anomer: ¹H NMR (CDCl<sub>3</sub>, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.36–7.25 (m,
10H, CH$_{arom}$), 5.33 (dt, 1H, $J = 5.0$, 3.5 Hz, H-1), 4.97 (ddd, 1H, $J = 49.1$, 10.4, 3.1 Hz, H-3), 4.86 (dd, 1H, $J = 11.4$, 1.8 Hz, CH$_2$O-4Bn), 4.51 (d, 1H, $J = 11.4$, CH$_2$O-4Bn), 4.48, 4.41 (2 × d, 2 × 1H, $J = 11.9$, CH$_2$O-6Bn), from $^1$H $^{19}$F 4.19 (td, 1H, $J = 5.4$, 1.3 Hz, H-5), 4.00 (ddd, 1H, $J = 6.9$, 3.1, 1.3 Hz, H-4), from $^1$H $^{19}$F 3.94 (ddd, 1H, $J = 10.4$, 3.5, 1.3 Hz, H-2), 3.76 (dd, 1H, $J = 3.5$, 1.3 Hz, OH), 3.59 (ddd, 1H, $J = 9.6$, 5.4, 1.1 Hz, H-6), 3.40 (dd, 1H, $J = 9.6$, 5.4 Hz, H-6). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 137.7, 137.5 (2 × C$_aq$), 128.60, 128.55, 128.5, 128.17 (4 × CH$_{arom}$), 128.15, 128.1 (2 × CH$_{arom}$), 92.8 (d, $^J = 9.2$ Hz, C-1), 90.6 (d, $^J = 187.8$ Hz, C-3), 75.0 (d, $^J = 4.1$ Hz, CH$_2$O-4Bn), 74.5 (d, $^J = 15.3$ Hz, C-4), 73.7 (CH$_2$O-6Bn), 69.1 (d, $^J = 7.0$ Hz, C-5), 69.0 (d, $^J = 2.8$ Hz, C-6), 59.5 (d, $^J = 17.2$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): −200.65 (ddd, $^J = 49.1$ Hz, $^J = 10.4$, 6.9 Hz, $^J = 5.0$ Hz). Resolved signals for the β-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F, H-H COSY): δ 7.36–7.25 (m, 10H, CH$_{arom}$), 4.34 (ddd, 1H, $J = 47.7$, 10.1, 3.2 Hz, H-3), from $^1$H $^{19}$F 3.92 (ddd, 1H, $J = 3.2$, 1.3 Hz, H-4), 3.88 (ddd, 1H, $J = 11.1$, 10.1, 7.9 Hz, H-2), 3.61 (ddd, 1H, $J = 8.8$, 6.0, 1.2 Hz, H-6), 3.54 (ddd, 1H, $J = 6.0$, 5.9, 1.7, 1.3 Hz, H-5), 3.47 (dd, 1H, $J = 8.8$, 5.9 Hz, H-6’). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 137.6, 137.5 (2 × C$_aq$), 96.1 (d, $^J = 10.6$ Hz, C-1), 93.1 (d, $^J = 191.0$ Hz, C-3), 75.0 (d, $^J = 4.0$ Hz, CH$_2$O-4Bn), 73.7 (CH$_2$O-6Bn), 73.1 (d, $^J = 15.1$ Hz, C-4), 72.6 (d, $^J = 7.8$ Hz, C-5), 68.4 (d, $^J = 2.9$ Hz, C-6), 63.6 (d, $^J = 17.0$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): −195.39 (ddd, $^J = 47.7$ Hz, $^J = 11.1$, 5.8 Hz). HRMS-APCI (m/z): [M + N$_2$ + H]$^+$ calc'd for C$_{20}$H$_{23}$FNO$_4$, 360.1605; found, 360.1605.

2-Azido-3,6-di-O-benzyl-2,4-dideoxy-4-fluoro-d-galactopyranose (30)

Phenyl 2-azido-3,6-di-O-benzyl-2,4-dideoxy-4-fluoro-1-thio-β-d-galactopyranoside (330 mg, 0.69 mmol), prepared from β-17 in 95% yield as described in ref 2 was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded 30 (201 mg, 75%, 71% over two steps) as a colorless syrup. R$_f$ 0.48 (EtOAc/PE 1:3). NMR data for the α-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F, H-H COSY): δ 7.42–7.29 (m, 10H, CH$_{arom}$), 5.32 (t, 1H, $J = 3.4$ Hz, H-1), 4.83 (dd, 1H, $J = 50.0$, 2.5 Hz, H-4), 4.76, 4.70 (2 × d, 2 × 1H, $J = 11.7$ Hz, CH$_2$H Bn), 4.59, 4.53 (2 × d, 2 × 1H, $J = 12.0$ Hz, CH$_2$H Bn), 4.19 (dt, 1H, $J = 29.5$, 6.5 Hz, H-5), 3.92 (ddd, 1H, $J = 26.8$, 10.6, 2.5 Hz, H-3), 3.79 (ddd, 1H, $J = 10.6$, 3.4, 1.3 Hz, H-2), 3.68–3.61 (m, 2H, H-6), 3.59 (ddd, 1H, $J = 3.4$, 1.3 Hz, OH). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.5, 137.3 (2 × C$_aq$), 128.7, 128.6 (2 × CH$_{arom}$), 128.2, 128.1 (2 × CH$_{arom}$), 128.10, 128.07 (2 × CH$_{arom}$), 92.3 (C-1), 85.9 (d, $^J = 184.7$ Hz, C-4), 74.4 (d, $^J = 18.0$ Hz, C-3), 73.8, 71.9 (2 × CH$_2$ Bn), 68.40 (d, $^J = 18.0$ Hz, C-5), 68.38 (d, $^J = 5.4$ Hz, C-6), 59.7 (d, $^J = 2.2$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): δ −220.71 (ddd, $^J = 50.0$ Hz, $^J = 29.5$, 26.8 Hz). NMR data for the β-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F, H-H COSY): δ 7.42–7.29 (m, 10H, CH$_{arom}$), 4.76 (dd, 1H, $J = 49.7$, 2.6 Hz, H-4), 4.76, 4.69 (2 × d, 2 × 1H, $J = 12.0$ Hz, CH$_2$H Bn), 4.58, 4.53 (2 × d, 2 × 1H, $J = 11.9$ Hz, CH$_2$H Bn), 4.48 (ddd, 1H, $J = 8.1$, 5.6, 1.1 Hz, H-1), 3.98 (d, 1H, $J = 5.6$ Hz, OH), 3.68–3.61 (m, 3H, H-2, H-6), 3.57 (dt, 1H, $J = 26.7$, S17
6.5 Hz, H-5), 3.31 (ddd, 1H, J = 27.5, 10.3, 2.6 Hz, H-3). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.5, 137.1 (2 × C$_q$), 128.72, 128.66 (2 × CH$_{aron}$), 128.3, 128.2 (2 × CH$_{aron}$), 128.1 (4CH$_{aron}$), 96.2 (C-1), 84.6 (dd, $^1$J = 185.5 Hz, C-4), 77.7 (d, $^2$J = 18.1 Hz, C-3), 73.9 (CH$_2$ Bn), 72.6 (d, $^3$J = 18.3 Hz, C-5), 72.1 (CH$_2$ Bn), 67.9 (d, $^3$J = 5.2 Hz, C-6), 63.9 (d, $^3$J = 0.8 Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): δ $^1$F = 218.40 (ddd, $^2$J = 49.7 Hz, $^3$J = 27.5, 26.7 Hz).

HRMS-APCI ($m/z$): [M − N$_2$ + H]$^+$ calcd for C$_{20}$H$_{25}$FNO$_4$, 360.1605; found, 360.1606.

2-Azido-6-O-benzyl-2,3,4-dideoxy-3,4-difluoro-d-glucopyranose (31)

Thioglycoside 19 (285 mg, 0.95 mmol, a mixture of anomers (α/β ≈10:1) was dissolved in THF/DMF 10:1 (5.5 mL) and the resulting solution was cooled to −25 °C. Sodium hydride (60% suspension in oil, 49 mg, 1.23 mmol) was added, the reaction mixture was stirred for 5 min, and then benzyl bromide (180 μL, 1.51 mmol) and TBAI (cat.) were added. The temperature was allowed to reach rt and the reaction mixture was stirred overnight. TLC (EtOAc/PE 1:4) indicated the absence of the starting material. The reaction was cooled to 0 °C, MeOH (0.3 mL) was added to quench the reaction. After stirring for additional 30 min was the reaction mixture diluted with chloroform, washed with water, the water phase was extracted with chloroform, the combined chloroform phases were dried and concentrated. Chromatography of the residue in EtOAc/PE 2:1 afforded phenyl 2-azido-6-O-benzyl-2,3,4-trideoxy-3,4-difluoro-1-thio-α/β-d-glucopyranoside (S7) (285 mg, 77%) as a colorless syrup, $R_f$ 0.2 (EtOAc/PE 2:1). NMR data for the α-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^1$F), H-H COSY): δ 7.61–7.59 (m, 1H, CH$_{aron}$), 7.51–7.49 (m, 2H, CH$_{aron}$), 7.38–7.27 (m, 7H, CH$_2$ Bn), 5.60 (dt, 1H, J = 5.8, 2.9 Hz, H-1), 4.86 (dddd, 1H, J = 53.0, 15.5, 10.1, 8.2 Hz, H-3), 4.75 from $^1$H $^1$F (dd, 1H, J = 9.9, 8.2 Hz, H-4), 4.64, 4.53 (2 × d, 2 × 1H, J = 12.0 Hz, CH/H Bn), 4.55–4.47 (m, 1H, H-5), 4.06 from $^1$H $^1$F (dd, 1H, J = 10.1, 5.8 Hz, H-2), 3.78 (ddt, 1H, J = 11.2, 9.3, 6.4, 1.1 Hz, H-6’), 3.73 (dd, 1H, J = 11.2, 1.5 Hz, H-6). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 137.7 (C$_q$), 133.9 (CH$_{aron}$), 132.5 (2CH$_{aron}$), 132.4 (C$_q$), 129.4, 128.6 (2 × 2CH$_{aron}$), 128.4 (CH$_{aron}$), 127.8 (2CH$_{aron}$), 91.9 (dd, $^1$J = 188.7 Hz, $^2$J = 19.7 Hz, C-3), 87.0 (dd, $^1$J = 186.6 Hz, $^2$J = 18.2 Hz, C-4), 86.5 (dd, $^1$J = 7.7 Hz, $^2$J = 0.9 Hz,C-1), 73.8 (CH$_2$ Bn), 69.5 (dd, $^2$J = 24.3 Hz, $^3$J = 6.5 Hz, C-5), 67.6 (dd, $^3$J = 1.0, $^4$J = 0.9 Hz, C-6), 62.0 (dd, $^3$J = 17.4 Hz, $^3$J = 6.9 Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): −193.48 (dq, $^2$J = 53.0 Hz, $^3$J = 13.6 Hz, F-3), −199.26 (m, F-4).

NMR data for the β-anomer: $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^1$F), H-H COSY): δ 7.61–7.59 (m, 1H, CH$_{aron}$), 7.38–7.27 (m, 9H, CH$_{aron}$), 4.64, 4.60 (2 × d, 2 × 1H, J = 11.2 Hz, CH/H Bn), 4.73–4.43 (m, 2H, H-3, H-4), 4.43 (dd, 1H, J = 10.2, 0.8 Hz, H-1), 3.84 (ddt, 1H, J = 11.4, 2.3, 2.0 Hz, H-6’), 3.73 (ddd, 1H, J = 11.4, 4.6, 2.3 Hz, H-6), 3.58 (ddddd, 1H, J = 9.1, 4.6, 2.3, 2.0 Hz, H-5), 4.48 (ddd, 1H, J = 13.0, 10.2, 8.8 Hz, H-2). $^{13}$C $^1$H NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 138.0 (C$_q$), 133.9 (CH$_{aron}$), 130.6 (C$_q$), 129.4 (2CH$_{aron}$), 129.0 (CH$_{aron}$), 128.6 (2CH$_{aron}$), 128.0, 127.9 (2 × CH$_{aron}$), 127.7 (2CH$_{aron}$), 94.1 (dd, $^1$J = 191.3 Hz, $^2$J = 19.5 Hz, C-3), 86.3 (dd, $^1$J = 186.7 Hz, $^2$J = 18.4 Hz, C-4), 85.7 (dd, $^3$J = 6.8 Hz, $^4$J = 1.4 Hz, C-1), 76.6 (dd, $^2$J = 22.7 Hz, $^3$J = 6.9 Hz, C-5), 73.8 (CH$_2$ Bn), 68.1
followed by thioglycoside Chromatography of the crude product in EtOAc/PE 1:7 first afforded fluoride (0.17 mmol) and 2,4,6-collidine (41 μL, 0.31 mmol) in dichloromethane (1 mL) according to the general procedure.

NMR data for the Thioglycoside β-

Thioglycoside S7 (268 mg, 0.69 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:5 afforded (268 mg, 0.69 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:5 afforded 31 (156 mg, 76% from S7, 59% over two steps) as a colorless syrup. Rf 0.41 (EtOAc/PE 1:3).

NMR data for the α-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.38–7.31 (m, 5H, CH-arom), 5.32 (tt, 1H, J = 3.6, 3.0 Hz, H-1), 5.00 (dddd, 1H, J = 54.0, 15.4, 10.0, 8.2 Hz, H-3), 5.62, 4.58 (2 × d, 2 × 1H, J = 12.2, CHH Bn), 4.54 (dddd, 1H, J = 51.2, 18.0, 10.0, 8.2 Hz, H-4), 4.18 (dddd, 1H, J = 10.0, 5.4, 4.9, 2.2 Hz, H-5), 3.88 (d, 1H, J = 3.0 Hz, OH), 3.73 (ddt, 1H, J = 10.9, 2.2, 2.0 Hz, H-6), from 1H {19F} 3.68 (dd, 1H, J = 10.9, 5.4 Hz, H-6'), 3.45 (dd, 1H, J = 11.0, 10.0, 3.6 Hz, H-2). 13C{1H} NMR (CDCl3, 101 MHz, HSCQC): δ 137.2 (Cα), 128.6 (2CH-arom), 128.1 (CH-arom), 128.0 (2CH-arom), 92.1 (3J = 9.3 Hz, 4J = 1.3 Hz, C-1), 90.4 (dd, 1J = 186.3 Hz, 2J = 19.3 Hz, C-3), 87.4 (dd, 1J = 186.5 Hz, 2J = 18.1 Hz, C-4), 73.8 (CH2 Bn), 68.1 (dd, 1J = 23.5 Hz, 3J = 6.6 Hz, C-5), 68.0 (t, J = 1.1 Hz, C-6), 61.7 (dd, 1J = 16.6 Hz, 3J = 3.6 Hz, C-2). 19F NMR (CDCl3, 376 MHz): -198.48 (dddd, 2J = 54.0 Hz, 3J = 18.0, 13.2, 11.0 Hz, 4J = 3.0 Hz, F-3), -199.25 (dddd, 2J = 51.2 Hz, 3J = 15.4, 13.2 Hz, F-4). Resolved signals for the β-anomer: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 4.52 (d, 1H, J = 9.3 Hz, H-1), from 1H {19F} 3.76 (dd, 1H, J = 10.7, 2.1 Hz, H-6), from 1H {19F} 3.66 (dd, 1H, J = 10.7, 5.8 Hz, H-6'), 3.56 (dddd, 1H, J = 9.7, 5.4, 2.1, 1.1 Hz, H-5), 3.55 (br s, 1H, OH). 13C{1H} NMR (CDCl3, 101 MHz, HSCQC): δ 137.1 (Cα), 128.6 (2CH-arom), 128.2 (CH-arom), 128.0 (2CH-arom), 95.6 (dd, 3J = 10.2 Hz, 4J = 1.4 Hz, C-1), 92.1 (dd, 1J = 189.3 Hz, 2J = 20.1 Hz, C-3), 86.9 (dd, 1J = 186.3 Hz, 2J = 18.6 Hz, C-4), 73.9 (CH2 Bn), 71.9 (dd, 2J = 23.5 Hz, 3J = 7.6 Hz, C-5), 65.0 (dd, 2J = 17.2 Hz, 3J = 7.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): -192.68 (dq, 2J = 51.7 Hz, 3J = 13.7 Hz, F-3), -201.14 (dddd, 2J = 50.5 Hz, 3J = 16.6, 13.7, 2.9 Hz, F-4). HRMS-APCI (m/z): [M - N2 + H]+ calced for C13H16F2NO3S, 364.1172; found, 364.1171.

Phenyl 2-Azido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-β-D-galactopyranoside (32)

2-Azido-3-O-benzyl-2,4,6-trideoxy-4-fluoro-6-S-phenyl-6-thio-α-D-galactopyranosyl fluoride (33)

Thioglycoside β-17 (50 mg, 0.13 mmol) was subjected to reaction with diethylaminosulfur trifluoride (21 μL, 0.17 mmol) and 2,4,6-collidine (41 μL, 0.31 mmol) in dichloromethane (1 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:7 first afforded fluoride 33 (29 mg, 57%) as a colorless syrup, followed by thioglycoside 32 (17 mg, 34%) as a colorless syrup.
Data for 32: Rf 0.62 (EtOAc/PE 1:3), [α]D20 +62 (c 0.97, CHCl3). 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.58–7.56 (m, 2H, CHarom), 7.38–7.32 (m, 8H, CHarom), 4.79 (dd, 1H, J = 50.0, 2.5 Hz, H-4), 4.77, 4.70 (2 × d, 2 × 1H, J = 11.7 Hz, C2F/H Bn), 4.59 (dddd, 1H, J = 46.4, 9.4, 6.0, 1.0 Hz, H-6), 4.57 (dddd, 1H, J = 46.1, 9.4, 6.6 Hz, H-6), 4.40 (dd, 1H, J = 10.1, 0.8 Hz, H-1), 3.71 (dddd, 1H, J = 26.6, 9.9, 6.6, 6.0 Hz, H-5), 3.66 (ddd, 1H, J = 10.1, 9.7, 1.0 Hz, H-2), 3.42 (ddd, 1H, J = 27.6, 9.7, 2.5 Hz, H-3). 13C {1H} NMR (CDCl3, 101 MHz, HSQC): δ 136.8 (Cg), 133.9 (2CHarom), 130.8 (Cg), 129.3 (2CHarom), 128.8 (3CHarom), 128.5 (CHarom), 128.2 (2CHarom), 86.5 (C-1), 83.9 (dd, 1J = 185.6 Hz, 3J = 4.3 Hz, C-4), 80.3 (dd, 1J = 170.1 Hz, 3J = 5.8 Hz, C-6), 79.1 (d, 2J = 17.9 Hz, C-3), 75.2 (dd, 2J = 24.3 Hz, 3J = 18.2 Hz, C-5), 72.2 (CH2 Bn), 61.0 (d, 3J = 1.1 Hz, C-2). 19F NMR (CDCl3, 376 MHz): –219.21 (ddd, 2J = 50.0 Hz, 3J = 27.6, 26.6 Hz, F-4), –232.58 (ddd, 2J = 46.4, 46.1 Hz, 3J = 9.9 Hz, F-6). HRMS-APCI (m/z): [M − N2 + H]+ calcd for C19H30F2NO2S, 364.1177; found, 364.1179.

Data for 33: Rf 0.67 (EtOAc/PE 1:3). 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.40–7.30 (m, 8H, CHarom), 7.27–7.23 (m, 2H, CHarom), 5.65 (dd, 1H, J = 52.6, 2.1 Hz, H-1), 5.04 (dd, 1H, J = 49.5, 1.9 Hz, H-4), 4.76, 4.71 (2 × d, 2 × 1H, J = 11.6 Hz, C2F/H Bn), 3.94 (ddd, 1H, J = 27.3, 8.6, 5.8 Hz, H-5), 3.89–3.78 (m, 2H, H-2, H-3), 3.66 (dd, 1H, J = 14.1, 5.8, 1.0 Hz, H-6), 3.16 (dd, 1H, J = 14.1, 8.6 Hz, H-6). 13C {1H} NMR (CDCl3, 101 MHz, HSQC): δ 136.8, 134.5 (2 × Cg), 130.0, 129.4, 128.8 (3 × 2CHarom), 128.5 (CHarom), 128.2 (2CHarom), 127.2 (CHarom), 106.2 (d, 1J = 227.7 Hz, C-1), 84.9 (d, 1J = 186.7 Hz, C-4), 74.3 (d, 2J = 18.2 Hz, C-3), 71.9 (CH2 Bn), 71.0 (dd, 2J = 19.9 Hz, 3J = 3.3 Hz, C-5), 58.9 (dd, 2J = 23.6 Hz, 3J = 2.7 Hz, C-2), 32.9 (d, 3J = 4.9 Hz, C-6). 19F NMR (CDCl3, 376 MHz): –148.74 (m, F-1), –221.17 (m, F-4). HRMS-APCI (m/z): [M − N2 + H]+ calcd for C19H30F2NO2S, 364.1177; found, 364.1175.

Deoxyfluorination of the β-anomer of thioglycoside 14

Thioglycoside β-14 (50 mg, 0.13 mmol) obtained from compound 7 as described in ref 2 was subjected to reaction with diethylaminosulfur trifluoride (21 μL, 0.17 mmol) and 2,4,6-collidine (41 μL, 0.31 mmol) in dichloromethane (1 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:7 afforded phenyl 2-azido-4-O-benzyl-2,3,6-trideoxy-3,6-difuoro-β-d-glucopyranoside (34) (43 mg, 85%) as a colorless syrup containing 2-azido-4-O-benzyl-2,3,6-trideoxy-3-fluoro-6-S-phenyl-6-thio-α-β-d-glucopyranosyl fluoride (35) (35/34 ca. 7:93), inseparable under given chromatographic conditions, Rf 0.79 (EtOAc/PE 1:3).

Data for 34: 1H NMR (CDCl3, 400 MHz, 1H {19F}, H-H COSY): δ 7.62–7.60 (m, 2H, CHarom), 7.39–7.32 (m, 8H, CHarom), 4.86 (dd, 1H, J = 11.1, 1.3 Hz, CH/H Bn), 4.64 (dddd, 1H, J = 47.6, 10.3, 2.0, 1.6 Hz, H-6’), 4.62 (d, 1H, J = 11.1 Hz, CH/H Bn), 4.62 (ddd, 1H, J = 46.9, 10.3, 3.4 Hz, H-6), 4.56 (ddd, 1H, J = 51.4, 9.1, 8.6 Hz, H-3), 4.41 (dd, 1H, J = 10.2, 0.8 Hz, H-1), 3.68 (ddd, 1H, J = 12.5, 10.0, 8.6 Hz, H-4), 3.46 (ddd, 1H, J = 13.0, 10.2, 9.1 Hz, H-
2-Azido-2,3,4,6-tetrafluro-3,4,6-trifluoro-D-galactopyranose (36)

Thioglycoside 18 (750 mg, 2.51 mmol) was subjected to reaction with diethylaminosulfur trifluoride (1000 μL, 7.57 mmol) and 2,4,6-collidine (1630 μL, 12.33 mmol) in dichloromethane (15 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 first afforded phenyl 2-azido-2,3,4,6-tetrafluoro-3,4,6-trifluoro-1-thio-D-galactopyranoside (α-S8) (570 mg, 75%) as a colorless syrup followed by phenyl 2-azido-2,3,4,6-tetrafluoro-3,4,6-trifluoro-1-thio-D-galactopyranoside (β-S8) (135 mg, 18%).

Data for α-S8: Rf 0.38 (EtOAc/PE 1:5). 1H NMR (CDCl3, 400 MHz, 1H 19F, H-H COSY): δ 7.50–7.48 (m, 2H, CHarom), 7.36–7.33 (m, 3H, CHarom), 5.66 (dd, 1H, J = 5.6, 4.4 Hz, H-1), 5.06 (dd, 1H, J = 51.0, 7.4, 2.8 Hz, H-4), 4.77 (dddd, 1H, J = 47.0, 25.2, 10.5, 2.8 Hz, H-3), 4.74–4.47 (m, 3H, H-5, H-6, H-2H-6), 4.42 (dddd, 1H, J = 11.0, 10.5, 5.6, 0.9 Hz, H-2). 19F NMR (CDCl3, 101 MHz, HSQC, HMBC): δ 132.8 (2CHarom), 132.0 (Cα), 129.5 (2CHarom), 128.6 (CHarom), 88.4 (dd, J = 179.7 Hz, J = 17.9 Hz, J = 1.0 Hz, C-3), 86.9 (d, J = 7.4 Hz, C-1), 85.8 (dd, J = 187.0 Hz, J = 16.6 Hz, J = 5.4 Hz, C-4), 80.2 (dd, J = 170.8 Hz, J = 6.2 Hz, J = 2.5 Hz, C-6), 68.3 (dd, J = 25.0, J = 18.0 Hz, J = 5.3 Hz, C-5), 59.0 (dd, J = 18.3 Hz, J = 1.8 Hz, C-2). 19F NMR (CDCl3, 376 MHz): from 19F {1H} -199.81 (dd, J = 14.4 Hz, J = 1.9 Hz, F-3), -218.86 (dddd, J = 51.0 Hz, J = 28.5, 25.2, 14.4 Hz, F-4), -232.61 (dddd, J = 51.0 Hz, J = 28.5, 25.2, 14.4 Hz, F-4). HRMS-APCI (m/z): [M - N2 + H]+ calefd for C12H13F3NOS, S21
276.0664; found, 276.0660. Data for β-S8: δ 0.34 (EtOAc/PE 1:5). 1H NMR (CDCl₃, 400 MHz, 1H {¹⁹F}, H-H COSY, HSQC, HMBC): δ 7.60–7.57 (m, 2H, CH₃oxon), 7.38–7.34 (m, 3H, CH₃oxon), 4.95 (ddd, 1H, J = 50.7, 7.1, 2.7 Hz, H-4), 4.64 (dddd, 1H, J = 46.1, 9.4, 6.2, 1.1, 1.1 Hz, H-6), 4.60 (ddd, 1H, J = 46.0, 9.4, 6.7 Hz, H-6'), 4.44 (ddddd, 1H, J = 45.9, 26.6, 9.5, 2.7 Hz, H-3), 4.43 (dd, 1H, J = 10.1, 0.8 Hz, H-1), 3.79 (dddddd, 1H, J = 25.8, 9.8, 6.7, 6.2, 1.9 Hz, H-5), 3.78 (ddddd, 1H, J = 11.0, 10.1, 9.5, 1.1 Hz, H-2). 13C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 133.9 (2CH₃oxon), 130.4 (C₀), 129.4 (2CH₃oxon), 129.1 (CH₃oxon), 90.9 (ddd, 1H, J = 195.8 Hz, 2J = 18.0 Hz, 4J = 0.9 Hz, C-3), 86.1 (d, 3J = 6.5 Hz, C-1), 84.7 (ddd, 1H, J = 186.5 Hz, 2J = 16.7 Hz, 3J = 4.7 Hz, C-4), 79.8 (ddd, 1H, J = 170.9 Hz, 3J = 5.7 Hz, 4J = 2.6 Hz, C-6), 74.4 (ddd, 2J = 24.3, 2J = 18.1 Hz, 3J = 5.8 Hz, C-5), 60.2 (ddd, 2J = 18.4 Hz, 3J = 1.0 Hz, C-2). 19F NMR (CDCl₃, 376 MHz): –193.34 (ddddd, 2J = 49.5 Hz, 3J = 15.7, 11.0, 7.1 Hz, F-3), –219.95 (ddddd, 2J = 50.7 Hz, 3J = 26.6, 25.8, 15.7 Hz, F-4), –232.87 (ddddd, 2J = 46.1, 46.0 Hz, 3J = 9.8 Hz, F-6). HRMS-APCI (m/z): [M – N₂ + H]⁺ calcd for C₁₂H₁₃F₃NOS, 276.0664; found, 276.0660.

Thioglycoside S8 (250 mg, 0.82 mmol) was hydrolyzed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded 36 (140 mg, 80% from S8; 74% over two steps) as a colorless gel. Rf 0.29 (EtOAc/PE 1:3). NMR data for the α-anomer: 1H NMR (CDCl₃, 400 MHz, 1H {¹⁹F}, H-H COSY): δ 5.43 (dt, 1H, J = 4.8, 3.5 Hz, H-1), 5.04 (ddd, 1H, J = 51.9, 7.6, 2.7 Hz, H-4), 4.97 (ddddd, 1H, J = 47.4, 25.8, 10.3, 2.7 Hz, H-3); from 1H {¹⁹F-6} 4.62 (dd, 1H, J = 9.5, 6.1 Hz, H-6'). NMR data for the β-anomer: 1H NMR (CDCl₃, 400 MHz, 1H {¹⁹F}, H-H COSY): δ 5.43 (dt, 1H, J = 4.8, 3.5 Hz, H-1), 5.04 (ddd, 1H, J = 51.9, 7.6, 2.7 Hz, H-4), 4.97 (ddddd, 1H, J = 47.4, 25.8, 10.3, 2.7 Hz, H-3), from 1H {¹⁹F-6} 4.62 (dd, 1H, J = 9.5, 6.1 Hz, H-6'). HRMS-APCI (m/z): [M – N₂ + H]⁺ calcd for C₁₂H₁₃F₃NOS, 276.0664; found, 276.0660.
Sodium cyanoborohydride (841 mg, 13.38 mmol) and 3 Å molecular sieves (2 g) were added to a solution of phenyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-3-fluoro-1-thio-α/β-D-glucopyranoside (525 mg, 1.36 mmol, prepared from the 18 as described in ref 3, in anhydrous THF (15 mL) under Ar atmosphere. The mixture was cooled to 0 °C and stirred for 5 min. Hydrogen chloride solution in diethyl ether (1M, 14.0 mL, 14.00 mmol) was carefully added dropwise and the reaction mixture was stirred for 15 min, filtered through a layer of celite, neutralized by saturated aqueous NaHCO₃, extracted with dichloromethane, the dichloromethane solution was dried and concentrated. Chromatography in EtOAc/PE 1:4 first afforded the α-anomer α-37 (290 mg, 55%) as a colorless syrup followed by a mixture of both anomers (α/β 1:5, 145 mg, 27%) as a thick colorless syrup.

Data for α-37: Rf 0.29 (EtOAc/PE 1:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.50–7.48 (m, 2H, CH₃-arom), 7.36–7.27 (m, 8H, CH₃-arom), 5.58 (dt, 1H, J = 5.7, 3.3 Hz, H-1), 4.68 (ddd, 1H, J = 52.8, 10.1, 8.5 Hz, H-3), 4.61, 4.52 (2 × d, 2 × 1H, J = 11.9 Hz, CHH Bn), 4.35 (ddd, 1H, J = 9.8, 4.3, 3.7 Hz, H-5), 4.02 (ddd, 1H, J = 11.1, 10.1, 5.7 Hz, H-2), 3.94 (dd(d, 1H, J = 14.2, 9.8, 8.5, 3.0 Hz, H-4), 3.80 (dd, 1H, J = 10.6, 4.3 Hz, H-6), 3.71 (ddd, 1H, J = 10.6, 3.7, 1.6 Hz, H-6”), 2.78 (d, 1H, J = 3.0 Hz, OHH). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 137.7, 132.9 (2 × Cq), 132.4, 129.3, 128.6 (3 × 2CH₃-arom), 128.11, 128.08 (2 × CH₃-arom), 127.9 (2CH₃-arom), 94.3 (d, 1J = 184.8 Hz, C-3), 86.8 (d, 3J = 8.0 Hz, C-1), 73.8 (CH₂ Bn), 70.7 (d, 3J = 7.2 Hz, C-5), 70.3 (d, 2J = 17.9 Hz, C-4), 69.0 (d, 4J = 1.3 Hz, C-6), 62.1 (d, 2J = 17.0 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): −194.35 (ddd, 3J = 52.8 Hz, 4J = 3.3 Hz). HRMS-APCI (m/z): [M − N₂ + H⁺] calcd for C₁₉H₂₁FNO₃S, 362.1219; found, 362.1215.

Data for β-37: Rf 0.26 (EtOAc/PE 1:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY): δ 7.59–7.56 (m, 2H, CH₃-arom), 7.37–7.28 (m, 8H, CH₃-arom), 4.63, 4.57 (2 × d, 2 × 1H, J = 11.9 Hz, CHH Bn), 4.42 (d, 1H, J = 10.2 Hz, H-1), 4.35 (dt, 1H, J = 51.8, 8.9 Hz, H-3), 3.84–3.76 (m, 3H, H-4, 2H-6), 3.48–3.42 (m, 1H, H-5), from ¹H {¹⁹F} 3.43 (dd, 1H, J = 10.2, 9.0 Hz, H-2), 2.84 (br s, 1H, OHH). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 137.7 (Cq), 133.8 (2CH₃-arom), 130.9 (Cq), 129.3 (2CH₃-arom), 128.8 (CH₃-arom), 128.7 (2CH₃-arom), 128.1 (CH₃-arom), 96.6 (d, 1J = 187.4 Hz, C-3), 85.7 (d, 3J = 7.2 Hz, C-1), 77.3 (d, 2J = 7.7 Hz, C-5), 73.9 (CH₂ Bn), 70.1 (d, 2J = 17.9 Hz, C-4), 69.7 (d, 4J = 1.6 Hz, C-6), 63.1 (d, 2J = 17.6 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): −189.43 (dt, 3J = 51.8 Hz, 2J = 13.0 Hz).
**2-Azido-6-O-benzyl-2,3,4-trideoxy-3,4-difluoro-D-galactopyranose (38)**

Thioglycoside 37 (400 mg, 1.03 mmol) was subjected to reaction with diethylaminosulfur trifluoride (170 μL, 1.29 mmol) and 2,4,6-collidine (340 μL, 2.57 mmol) in dichloromethane (8 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:7 first afforded the phenyl 2-azido-6-O-benzyl-2,3,4-trideoxy-3,4-difluoro-1-thio-α-D-galactopyranoside (α-S9) (276 mg, 69%) in ca. 90% purity (by $^{19}$F NMR) as a colorless syrup followed by the phenyl 2-azido-6-O-benzyl-2,3,4-trideoxy-3,4-difluoro-1-thio-β-D-galactopyranoside β-S9 (63 mg, 16%) in ca 80% purity (by $^{19}$F NMR) as a colorless syrup. The impurities were removed in the next step.

Data for α-S9: $R_f$ 0.78 (EtOAc/PE 1:3). $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F, H-H COSY): δ 7.51–7.49 (m, 2H, CH$_{arom}$), 7.37–7.26 (m, 8H, CH$_{arom}$), 5.64 (ddd, 1H, $J = 5.6, 4.3$ Hz, H-1), 5.08 (ddd, 1H, $J = 50.8, 7.6, 2.7$ Hz, H-4), 4.75 (ddddd, 1H, $J = 47.0, 25.2, 10.6, 2.7$ Hz, H-3), 4.63–4.52 (m, 1H, H-5), 4.54 (s, 2H, CH$_2$ Bn), 4.41 (ddddd, 1H, $J = 10.6, 10.0, 5.6, 0.9$ Hz, H-2), 3.76 (dd, 1H, $J = 9.7, 7.0$ Hz, H-6), 3.64 (ddt, 1H, $J = 9.7, 6.3, 1.4$ Hz, H-6'). $^{13}$C ($^1$H) NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.7 (C$_1$), 132.9 (2CH$_{arom}$), 132.3 (C$_9$), 129.3, 128.6 (2 × 2CH$_{arom}$), 128.4, 128.0 (2 × CH$_{arom}$), 127.8 (2CH$_{arom}$), 88.7 (dd, $^1J = 192.9$ Hz, $^2J = 17.7$ Hz, C-3), 86.8 (d, $^3J = 7.3$ Hz, C-1), 86.4 (dd, $^4J = 186.3$ Hz, $^5J = 16.1$ Hz, C-4), 73.7 (CH$_2$ Bn), 68.9 (dd, $^6J = 18.2$ Hz, $^7J = 5.2$ Hz, C-5), 67.4 (dd, $^8J = 5.3, 2.3$ Hz, C-6), 59.2 (d, $^9J = 18.0$ Hz, $^10J = 1.8$ Hz, C-2). $^{19}$F NMR (CDCl$_3$, 376 MHz): −199.30 (m, F-3), −219.17 (ddddd, $^1J = 50.8$ Hz, $^2J = 29.0, 25.2, 15.1$ Hz, F-4). HRMS-APCI (m/z): [M – N$_2$ + H]$^+$ calcd for C$_{19}$H$_{20}$F$_4$NO$_2$S, 364.1177; found, 364.1176.

Data for β-S9: $R_f$ 0.74 (EtOAc/PE 1:3). $^1$H NMR (CDCl$_3$, 400 MHz, $^1$H $^{19}$F, H-H COSY): δ 7.59–7.57 (m, 2H, CH$_{arom}$), 7.36–7.31 (m, 8H, CH$_{arom}$), 4.99 (ddd, 1H, $J = 50.4, 7.3, 2.7$ Hz, H-4), 4.57 (s, 2H, CH$_2$ Bn), 4.40 (dt, 1H, $J = 10.1, 0.9$ Hz, H-1), 4.39 (ddddd, 1H, $J = 46.3, 26.7, 9.7, 2.7$ Hz, H-3), 3.82–3.68 (m, 3H, H-2, 2H-6), 3.62 (dtd, 1H, $J = 48.0, 25.6, 10.3, 2.8$ Hz, H-3), 3.57 (tt, 1H, $J = 3.5, 2.8$ Hz, H-1), 4.95 (dd, 1H, $J = 51.4, 7.6, 2.8$ Hz, H-4), 4.89 (ddddd, 1H, $J = 48.0, 25.6, 10.3, 2.8$ Hz, H-3), 4.60, 4.54 (2 × d, 2 × 1H, $J = 11.8$ C/H Bn), 4.22 (ddddd, 1H, $J = 29.6, 6.0, 5.8, 2.2$ Hz, H-5), 3.84

**S24**
(ddd, 1H, J = 10.3, 3.5, 1.2 Hz, H-2), 3.71–3.65 (m, 2H, H-6), 3.60 (dd, 1H, J = 3.5, 1.2 Hz, OH). 13C 1H NMR (CDCl3, 101 MHz, HSQC): δ 137.3 (Cδ), 128.7 (2CH arom), 128.3 (CH arom), 128.1 (2CH arom), 92.6 (d, 1J = 9.1 Hz, C-1), 87.3 (dd, 1J = 190.5 Hz, 2J = 18.0 Hz, C-3), 86.9 (dd, 1J = 186.1 Hz, 2J = 16.5 Hz, C-4), 73.9 (CH2 Bn), 68.1 (dd, 2J = 22.0 Hz, 3J = 5.4 Hz, C-5), 68.0 (dd, 3J = 5.5, 1.5 Hz, C-6), 58.9 (dd, 2J = 17.3 Hz, 3J = 2.2 Hz, C-2). 19F NMR (CDCl3, 376 MHz): from 19F 1H NMR (CDCl3, 400 MHz, 1H 13C NMR (CDCl3, 101 MHz, HSQC): δ 137.3 (Cδ), 128.7, 128.1 (2 × CH arom), 95.9 (d, 3J = 10.3 Hz, C-1), 89.6 (dd, 1J = 193.6 Hz, 2J = 18.0 Hz, C-3), 85.4 (dd, 1J = 186.4 Hz, 2J = 16.4 Hz, C-4), 73.9 (CH2 Bn), 71.6 (dd, 2J = 18.2 Hz, 3J = 6.0 Hz, C-5), 67.5 (dd, 3J = 5.1, 2.9 Hz, C-6), 62.9 (dd, 2J = 17.5 Hz, 3J = 0.7 Hz, C-2). 19F NMR (CDCl3, 376 MHz): −198.49 (ddd, 2J = 46.4 Hz, 3J = 15.6, 12.6, 6.6 Hz, F-3), −218.98 (ddd, 2J = 51.3 Hz, 3J = 26.6, 25.5, 15.6 Hz, F-4). HRMS-APCI (m/z): [M − N2 + H]+ calcd for C13H16F2NO3, 272.1092; found, 272.1095.

2-Acetamido-4,6-di-O-benzyl-2,3-dideoxy-3-fluoro-D-glucopyranose (39)

![Reaction Scheme](image)

Compound 39 was prepared from 27 (258 mg, 0.67 mmol) according to the general procedure for azide/acetamide conversion except for the reaction time (6.5 h). Chromatography in EtOAc gave 39 (149 mg, 55%) as white crystalline material, mp 199–201 °C (EtOAc), Rf 0.24 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H 13C NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.5 (CO), 139.5, 139.4 (2 × Cδ), 129.4, 129.3, 129.09, 129.06 (4 × CH arom), 128.8, 128.7 (2 × CH arom), 95.2 (d, 1J = 183.1 Hz, C-3), 92.8 (d, 1J = 9.8 Hz, C-1), 78.0 (d, 2J = 16.3 Hz, C-4), 75.5 (d, 1J = 2.8 Hz, CH2 O-4Bn), 74.4 (CH2 O-6Bn), 70.7 (d, 2J = 8.3 Hz, C-5), 69.9 (d, 4J = 1.2 Hz, C-6), 54.4 (d, 2J = 16.5 Hz, C-2), 22.5 (Me). 19F NMR (MeOH-d4, 376 MHz): δ −197.43 (ddd, 2J = 51.9 Hz, 3J = 12.1 Hz). HRMS-APCI (m/z): [M + H]+ calcd for C22H25FNO5, 404.1867; found, 404.1868.

S25
2-Acetamido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-D-glucopyranose (40)

![Chemical structure of compound 40]

Compound 40 was prepared from 22 (109 mg, 0.36 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 1:1 → EtOAc afforded 40 (83 mg, 72%) as a white crystalline solid, mp 170–180 °C (dec, EtOAc/MeOH). R\text{f} = 0.33 (EtOAc). NMR data for the α-anomer: \textsuperscript{1}H NMR (MeOH-\text{d}_4, 400 MHz, \textsuperscript{1}H \{\textsuperscript{19}F\}, H-H COSY): \(\delta\) 7.35–7.24 (m, 10H, CH\textsubscript{arom}), 5.11 (dd, 1H, \(J = 3.8, 3.6\) Hz, H-1), 4.85 (d, 1H, \(J = 11.2\) Hz, CH/H Bn), 4.80 (ddd, 1H, \(J = 53.4, 10.4, 8.3\) Hz, H-3), 4.64 (d, 1H, \(J = 11.2\) Hz, CH/H Bn), 4.62 (ddd, 1H, \(J = 47.4, 10.3, 3.5\) Hz, H-6\'), 4.52 (ddddd, 1H, \(J = 48.7, 10.3, 1.9, 1.4\) Hz, H-6), 4.12 (ddd, 1H, \(J = 11.0, 10.4, 3.6\) Hz, H-2), 3.99 (ddd, 1H, \(J = 28.3, 10.1, 3.5, 1.4\) Hz, H-5), 3.68 (ddd, 1H, \(J = 13.7, 10.1, 8.3\) Hz, H-4), 2.00 (s, 3H, Me). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (MeOH-\text{d}_4, 101 MHz, HSQC, HMBC): \(\delta\) 173.6 (CO), 139.4 (C\{\textsuperscript{19}F\}), 139.2, 139.1 (2 × C\textsubscript{arom}), 129.9, 129.8, 129.1 (2 × 2CH\textsubscript{arom}), 128.3 (CH\textsubscript{aryl}), 95.1 (dd, \(J = 183.0\) Hz, C-1), 83.1 (dd, \(J = 172.3\) Hz, C-6). \textsuperscript{19}F NMR (MeOH-\text{d}_4, 376 MHz): –192.51 (dt, \(J = 10.0, 4.5, 3.5\) Hz, F-3), –236.49 (ddd, \(J = 11.0, 10.4, 3.6\) Hz, F-6). Resolved signals for the β-anomer: \(\delta\) 173.3 (CO), 139.4 (C\{\textsuperscript{19}F\}), 139.1 (2 × C\textsubscript{arom}), 129.9, 129.8, 129.1 (2 × 2CH\textsubscript{arom}), 128.3 (CH\textsubscript{aryl}), 95.1 (dd, \(J = 183.0\) Hz, C-1), 83.1 (dd, \(J = 172.3\) Hz, C-6). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (MeOH-\text{d}_4, 101 MHz, HSQC, HMBC): \(\delta\) 173.3 (CO), 139.4 (C\{\textsuperscript{19}F\}), 139.1 (2 × C\textsubscript{arom}), 129.9, 129.8, 129.1 (2 × 2CH\textsubscript{arom}), 128.3 (CH\textsubscript{aryl}), 95.1 (dd, \(J = 183.0\) Hz, C-1), 83.1 (dd, \(J = 172.3\) Hz, C-6). HRMS-APCI (m/z): [M + H]\textsuperscript{+} calc for C\textsubscript{15}H\textsubscript{20}F\textsubscript{2}NO\textsubscript{4}, 316.1355; found, 316.1350.

2-Acetamido-3,6-di-O-benzyl-2,4-dideoxy-4-fluoro-D-glucopyranose (41)

![Chemical structure of compound 41]

Compound 41 was prepared from 28 (162 mg, 0.42 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 1:1 → EtOAc afforded 41 (114 mg, 68%) as a white crystalline solid, mp 182–185 °C (dec, EtOAc). R\text{f} = 0.29 (EtOAc). NMR data for the α-anomer: \textsuperscript{1}H NMR (MeOH-\text{d}_4, 400 MHz, \textsuperscript{1}H \{\textsuperscript{19}F\}, H-H COSY): \(\delta\) 7.35–7.24 (m, 10H, CH\textsubscript{arom}), 5.06 (dd, 1H, \(J = 3.5, 3.3\) Hz, H-1), 4.82, 4.64 (2 × d, 2 × 1H, \(J = 11.5\) Hz, CH/H O3-Bn), 4.61, 4.56 (2 × d, 2 × 1H, \(J = 12.0\) Hz, CH/H O6-Bn), 4.51 (ddd, 1H, \(J = 50.9, 10.0, 8.4\) Hz, H-4), 4.17 (ddt, 1H, \(J = 10.0, 4.5, 3.5\) Hz, H-5), 4.06 (ddd, 1H, \(J = 10.7, 3.5, 1.0\) Hz, H-2), 3.93 (ddd, 1H, \(J = 14.6, 10.7, 8.4\) Hz, H-3), 3.93–3.66 (m, 2H, H-6), 1.94 (s, 3H, Me). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (MeOH-\text{d}_4, 101 MHz, HSQC, HMBC): \(\delta\) 173.3 (CO), 139.4 (2 × C\textsubscript{arom}), 129.3, 129.2, 128.8 (3 × 2CH\textsubscript{arom}), 128.7 (CH\textsubscript{aryl}), 128.61 (2CH\textsubscript{arom}), 128.55 (CH\textsubscript{aryl}), 92.6 (d, \(J = 1.6\) Hz, C-1), 92.2 (d, \(J = 181.6\) Hz, C-4), 79.2 (d, \(J = 17.4\) Hz, C-3), 75.5 (d, \(J = 2.3\) Hz, CH2 O-3Bn), 74.5 (CH2 O-6Bn), 69.8 (C-6), 69.7 (d, \(J = 23.7\) Hz, C-5), 54.3 (d, \(J = 9.0\) Hz, C-2), 22.6 (Me). \textsuperscript{19}F NMR (MeOH-
$^1$H NMR (MeOH-d$_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): δ 4.70 (d, 1H, $^1$J = 8.3 Hz, H-1), 1.89 (s, 3H, Me). $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 23.0 (Me). $^{19}$F NMR (CDCl$_3$, 376 MHz): δ −198.67 (dd, $^2$J = 50.8 Hz, $^3$J = 15.0 Hz). HRMS-APCI (m/z): [M + H]$^+$ calcd for C$_{22}$H$_{27}$FNO$_5$, 404.1867; found, 404.1880.

2-Acetamido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-$	ext{D}$-glucopyranose (42)

Compound 42 was prepared from 23 (140 mg, 0.47 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 1:1 → EtOAc afforded 42 (125 mg, 85%) as a white amorphous solid, $R_f$ 0.45 (EtOAc). NMR data for the $\alpha$-anomer: $^1$H NMR (MeOH-d$_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): δ 7.32–7.30 (m, 5H, CH$_{arom}$), 5.06 (t, 1H, $^1$J = 3.4 Hz, H-1), 4.83 (dd, 1H, $^1$J = 11.5, 1.1 Hz, CH$_2$ Bn), 4.65 (d, 1H, $^1$J = 11.5 Hz, CH$_2$ Bn), 4.60 (dddd, 1H, $^1$J = 47.2, 10.5, 3.9, 1.7 Hz, H-6´), 4.53 (ddt, 1H, $^1$J = 48.1, 10.5, 1.9 Hz, H-6), 4.49 (ddd, 1H, $^1$J = 51.1, 10.1, 3.9, 1.9 Hz, H-5), 4.05 (dd, 1H, $^1$J = 10.8, 3.4 Hz, H-2), 3.96 (ddd, 1H, $^1$J = 14.5, 10.8, 8.2 Hz, H-3), 1.95 (s, 3H, Me). $^{13}$C{$^1$H} NMR (MeOH-d$_4$, 101 MHz, HSQC): δ 173.4 (CO), 139.9 (C$_q$), 129.3, 128.62 (2 × 2CH$_{arom}$), 128.59 (CH$_{arom}$), 96.6 (d, $^4$J = 1.6 Hz, C-1), 82.4 (d, $^4$J = 173.1 Hz, C-6), 81.0 (d, $^2$J = 17.2 Hz, C-3), 75.6 (d, $^2$J = 2.2 Hz, CH$_2$ Bn), 69.3 (dd, $^2$J = 23.8 Hz, $^2$J = 18.3 Hz, C-2), 54.2 (d, $^3$J = 8.8 Hz, C-2), 22.6 (Me). $^{19}$F NMR (MeOH-d$_4$, 376 MHz): −197.18 (dddd, $^2$J = 51.1 Hz, $^3$J = 4.5 Hz, $^5$J = 3.4 Hz, F-4), −238.37 (dd, $^2$J = 48.1, 47.2 Hz, $^3$J = 26.5 Hz, F-6). Resolved signals for the $\beta$-anomer: $^1$H NMR (MeOH-d$_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): δ 7.30–7.24 (m, 5H, CH$_{arom}$), 4.75 (d, 1H, $^1$J = 8.4 Hz, H-1), 3.84 (ddd, 1H, $^1$J = 15.3, 10.4, 8.7 Hz, H-3), 3.86–3.65 (m, 1H, H-5), 3.67 (ddd, 1H, $^1$J = 10.4, 8.4, 0.9 Hz, H-2), 1.91 (s, 3H, Me). $^{13}$C{$^1$H} NMR (MeOH-d$_4$, 101 MHz, HSQC): δ 173.6 (CO), 139.7 (C$_q$), 129.3, 128.8 (2 × 2CH$_{arom}$), 128.7 (CH$_{arom}$), 96.6 (d, $^4$J = 1.6 Hz, C-1), 82.4 (d, $^4$J = 173.1 Hz, C-6), 81.0 (d, $^3$J = 17.2 Hz, C-3), 75.6 (d, $^3$J = 2.2 Hz, CH$_2$ Bn), 57.5 (d, $^3$J = 9.6 Hz, C-2), 23.0 (Me). $^{19}$F NMR (MeOH-d$_4$, 376 MHz): −196.54 (dd, $^2$J = 50.9 Hz, $^3$J = 14.6, 4.5 Hz, $^5$J = 3.3 Hz). Resolved signals for the $\beta$-anomer: $^1$H NMR (MeOH-d$_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): δ 4.70 (d, 1H, $^1$J = 8.3 Hz, H-1), 1.89 (s, 3H, Me). $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 23.0 (Me). $^{19}$F NMR (CDCl$_3$, 376 MHz): δ −196.54 (dd, $^2$J = 50.9 Hz, $^3$J = 14.6, 4.5 Hz, $^5$J = 3.3 Hz). Resolved signals for the $\beta$-anomer: $^1$H NMR (MeOH-d$_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): δ 4.70 (d, 1H, $^1$J = 8.3 Hz, H-1), 1.89 (s, 3H, Me). $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 23.0 (Me). $^{19}$F NMR (CDCl$_3$, 376 MHz): δ −196.54 (dd, $^2$J = 50.9 Hz, $^3$J = 14.6, 4.5 Hz, $^5$J = 3.3 Hz). HRMS-APCI (m/z): [M + H]$^+$ calcd for C$_{22}$H$_{27}$FNO$_5$, 404.1867; found, 404.1880.

2-Acetamido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-$	ext{D}$-glucopyranose (42)
2-Acetamido-6-O-benzyl-2,3,4-trideoxy-3,4-difluoro-D-glucopyranose (43)

Compound 43 was prepared from 31 (120 mg, 0.40 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 3:1 → EtOAc afforded 43 (105 mg, 83%) as a white crystalline solid, mp 192–195 °C (dec, EtOAc). Rf 0.37 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H-19F}, H-H COSY): δ 7.36–7.26 (m, 5H, CHarom), 5.12 (q, 1H, J = 3.4 Hz, H-1), 4.81 (dddd, 1H, J = 54.2, 16.1, 10.4, 8.2 Hz, H-3), 5.61 (d, 1H, J = 12.0 Hz, CHH Bn), 4.58 (dddd, 1H, J = 51.7, 15.1, 10.0, 8.2 Hz, H-4), 4.56 (d, 1H, J = 12.0 Hz, CHH Bn), 4.17–4.10 (m, 2H, H-2, H-5), 3.77–3.70 (m, 2H, H-6), 1.99 (s, 3H, Me). 13C{1H} NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.5 (CO), 139.4 (Cq), 129.4, 128.8 (2 × 2CHarom), 128.7 (CHarom), 92.7 (dd, 3J = 9.4 Hz, 4J = 1.2 Hz, C-1), 90.4 (dd, 1J = 186.3 Hz, 2J = 19.3 Hz, C-3), 89.3 (dd, 1J = 183.2 Hz, 2J = 17.9 Hz, C-4), 74.5 (CH2 Bn), 69.5 (d, J = 1.3 Hz, C-6), 69.2 (dd, 2J = 23.2 Hz, 3J = 6.6 Hz, C-5), 53.9 (dd, 2J = 16.7 Hz, 3J = 7.4 Hz, C-2), 22.5 (Me). 19F NMR MeOH-d4, 376 MHz): –200.23 (dddt, 2J = 51.7 Hz, 3J = 16.1, 13.8, 5.4 Hz, 5J = 3.4 Hz, F-4), –201.68 (ddddd, 2J = 54.2 Hz, 3J = 15.1, 13.8, 10.7 Hz, 5J = 3.4 Hz, F-3). Resolved signals for the β-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H-19F}, H-H COSY): δ 4.72 (d, 1H, J = 8.4 Hz, H-1), 3.86–3.78 (m, 1H, H-2), 3.69–3.64 (m, 1H, H-5), 2.01 (s, 3H, Me). 13C{1H} NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.8 (CO), 139.2 (Cq), 96.1 (dd, 3J = 10.2 Hz, 4J = 1.3 Hz, C-1), 93.0 (dd, 1J = 186.6 Hz, 2J = 19.0 Hz, C-3), 89.0 (dd, 1J = 183.9 Hz, 2J = 18.3 Hz, C-4), 74.6 (CH2 Bn), 73.1 (dd, 2J = 23.5 Hz, 3J = 7.8 Hz, C-5), 57.0 (dd, 2J = 16.9 Hz, 3J = 7.8 Hz, C-2), 22.8 (Me). 19F NMR (MeOH-d4, 376 MHz): –196.48 (dddt, 2J = 52.3 Hz, 3J = 13.6, 12.8 Hz, F-3), –202.19 (ddddd, 2J = 51.4 Hz, 3J = 15.3, 13.6, 1.7 Hz, F-4). HRMS-APCI (m/z): [M + H]+ calcd for C15H29F2NO6, 316.1355; found, 316.1348.

2-Acetamido-4,6-di-O-benzyl-2,3-dideoxy-3-fluoro-D-galactopyranose (44)

Compound 44 was prepared from 29 (225 mg, 0.58 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 44 (178 mg, 76%) as a white crystalline solid, mp 181–183 °C (dec, EtOAc/MeOH). Rf 0.44 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H-19F}, H-H COSY): δ 7.33–7.25 (m, 10H, CHarom), 5.13 (dd, 1H, J = 5.0, 3.6 Hz, H-1), 4.87 (ddd, 1H, J = 48.9, 10.8, 3.1 Hz, H-3), 4.82 (d, 1H, J = 11.3 Hz, CHH O-4Bn), 4.59 (ddd, 1H, J = 10.8, 9.0, 3.6 Hz, H-2), 4.51 (d, 1H, J = 11.3, CHH O-4Bn), 4.49, 4.43 (2 × d, 2 × 1H, J = 11.8, CHH O-6Bn), 4.22 (ddddd, 1H, J = 6.8, 6.2, 2.2, 1.4 Hz, H-5), 4.09 (dd, 1H, J = 7.0, 3.1, 1.4 Hz, H-4), 3.60 (dd, 1H, J = 9.4, 6.8 Hz, H-6), 3.53 (ddd, 1H, J = 9.4, 6.2, 1.4 Hz, S28
H-6\(^{-}\)), 1.99 (s, 3H, Me). \(^{13}\)C\({\{^1}\}H\) NMR (MeOH-\(d_4\), 101 MHz, HSQC): \(\delta\) 173.7 (CO), 139.8, 139.4 (2 \times C\(q\)), 129.4, 129.3, 129.2, 129.0 (4 \times C\(arom\)), 128.8, 128.7 (2 \times C\(arom\)), 93.3 (d, \(^3J = 9.5\) Hz, C-1), 91.5 (d, \(^1J = 187.0\) Hz, C-3), 76.2 (d, \(^2J = 15.2\) Hz, C-4), 75.9 (d, \(^4J = 4.0\) Hz, CH\(2\) O-4Bn), 74.4 (CH\(2\) O-6Bn), 70.0 (d, \(^4J = 2.5\) Hz, C-6), 69.6 (d, \(^3J = 7.1\) Hz, C-5), 51.0 (d, \(^2J = 17.2\) Hz, C-2), 22.6 (Me). \(^{19}\)F NMR (MeOH-\(d_4\), 376 MHz): –202.91 (dddd, \(^2J = 48.9\) Hz, \(^3J = 9.0\), \(^4J = 7.0\) Hz, \(^4J = 5.0\) Hz). HRMS-APCI (\(m/z\)): [M + H]\(^+\) calcd for C\(_{22}\)H\(_{27}\)FNO\(_5\), 404.1867; found, 404.1861.

NMR signals of the \(\beta\)-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

2-Acetamido-4-O-benzyl-2,3,6-trideoxy-3,6-difluoro-\(D\)-galactopyranose (45)

Compound 45 was prepared from 24 (98 mg, 0.33 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 45 (73 mg, 71%) as a white crystalline solid, mp 182–183 °C (dec, EtOAc). \(R_f\) 0.35 (EtOAc). NMR data for the \(\alpha\)-anomer: \(^1\)H NMR (MeOH-\(d_4\), 400 MHz, \(^1\)H \{\(^{19}\)F\}, H-H COSY): \(\delta\) 7.37–7.28 (m, 5H, CH\(arom\)), 5.16 (dd, 1H, \(^1J = 4.9\), 3.6 Hz, H-1), 4.89 (ddd, 1H, \(^3J = 50.6\), 10.9, 3.1 Hz, H-3), 4.85 (d, 1H, \(^1J = 11.3\) Hz, C\(H\) Bn), 4.60 (ddd, 1H, \(^3J = 10.9\), 8.9, 3.6 Hz, H-2), 4.54 (d, 1H, \(^1J = 11.3\) Hz, C\(H\) Bn), 4.51–4.37 (m, 2H, H-6), 4.29 (ddd, 1H, \(^1J = 6.8\), 3.1, 1.4 Hz, H-4), 2.00 (s, 3H, Me). \(^{13}\)C\{\(^1\)H\} NMR (MeOH-\(d_4\), 101 MHz, HSQC): \(\delta\) 173.7 (CO), 139.6 (C\(q\)), 129.4, 129.3 (2 \times C\(arom\)), 128.9 (C\(arom\)), 93.4 (d, \(^3J = 9.4\) Hz, C-1), 91.3 (dd, \(^1J = 187.0\) Hz, \(^4J = 1.4\) Hz, C-3), 83.5 (dd, \(^1J = 167.3\), \(^3J = 3.1\) Hz, C-6), 75.9 (d, \(^4J = 4.3\) Hz, CH\(2\) Bn), 75.8 (dd, \(^3J = 15.3\) Hz, \(^3J = 6.5\) Hz, C-4), 69.6 (dd, \(^3J = 23.3\) Hz, \(^3J = 7.4\) Hz, C-5), 50.8 (d, \(^2J = 17.1\) Hz, C-2), 22.6 (Me). \(^{19}\)F NMR (MeOH-\(d_4\), 376 MHz): –203.45 (ddddd, \(^2J = 50.6\) Hz, \(^3J = 8.9\), \(^4J = 6.8\) Hz, \(^4J = 2.1\) Hz, F-3), –233.00 (tdd, \(^2J = 4.9\) Hz, \(^3J = 13.0\) Hz, \(^3J = 2.3\) Hz, F-6). Resolved signals for the \(\beta\)-anomer: \(^1\)H NMR (MeOH-\(d_4\), 400 MHz, \(^1\)H \{\(^{19}\)F\}, H-H COSY): \(\delta\) from \(^1\)H \{\(^{19}\)F\} 4.72 (dd, 1H, \(^1J = 10.7\), 3.1 Hz, H-3), 4.64 (d, 1H, \(^3J = 7.4\) Hz, H-1), 4.06 (ddd, 1H, \(^1J = 5.2\), 3.1, 2.7 Hz, H-4). \(^{13}\)C\{\(^1\)H\} NMR (MeOH-\(d_4\), 101 MHz, HSQC): \(\delta\) 96.6 (d, \(^3J = 10.4\) Hz, C-1), 54.5 (d, \(^2J = 17.5\) Hz, C-2), 22.9 (Me). \(^{19}\)F NMR (MeOH-\(d_4\), 376 MHz): –199.00 (m, F-3), –232.74 (m, F-6). HRMS-APCI (\(m/z\)): [M + H]\(^+\) calcd for C\(_{15}\)H\(_{26}\)F\(_2\)NO\(_4\), 316.1355; found, 316.1353.
2-Acetamido-3,6-di-O-benzyl-2,4-dideoxy-4-fluoro-D-galactopyranose (46)

Compound 46 was prepared from 30 (185 mg, 0.48 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 46 (162 mg, 84%) as a white crystalline solid, mp 215–217 °C (dec, EtOAc/Methanol). Rf 0.34 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 7.36–7.25 (m, 10H, CH_arom), 5.12 (d, 1H, J = 3.5 Hz, H-1), 4.95 (dd, 1H, J = 50.8, 2.5 Hz, H-4), 4.72, 4.58 (2 × d, 2 × 1H, J = 11.8 Hz, CHH Bn), 4.55 (s, 2H, CH2 Bn), 4.35 (dd, 1H, J = 11.1, 3.5 Hz, H-2), 4.21 (ddd, 1H, J = 29.7, 6.7, 6.5 Hz, H-5), 3.86 (ddd, 1H, J = 26.2, 11.1, 2.5 Hz, H-3), 3.69 (dd, 1H, J = 9.7, 6.7 Hz, H-6’), 3.60 (ddd, 1H, J = 9.7, 6.5, 1.4 Hz, H-6), 1.96 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.5 (CO), 139.7, 139.4 (2 × Cq), 129.4, 129.3, 128.9 (3 × 2CH_arom), 128.8 (CH_arom), 128.74 (2CH_arom), 128.70 (CH_arom), 93.0 (C-1), 87.4 (d, 1J = 182.3 Hz, C-4), 75.6 (d, 2J = 18.4 Hz, C-3), 74.4 (CH2 O-6Bn), 72.5 (CH2 O-3Bn), 69.6 (d, 3J = 5.6 Hz, C-6), 68.9 (d, 2J = 18.0 Hz, C-5), 50.8 (d, 3J = 2.7 Hz, C-2), 22.7 (Me). 19F NMR (MeOH-d4, 376 MHz): δ −223.37 (ddd, 2J = 50.8 Hz, 3J = 29.7, 26.2 Hz). Resolved signals for the β-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ from 1H {19F} 4.91 (d, 1H, J = 2.6 Hz, H-4), 4.71 (d, 1H, J = 11.8 Hz, CHH Bn), 4.55 (s, 2H, CH2 Bn), 4.69 (dd, 1H, J = 7.9, 1.0 Hz, H-1), 3.88 (ddd, 1H, J = 11.0, 7.9 Hz, H-2), 3.77–3.65 (m, 2H, H-3, H-5), 1.94 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.8 (CO), 96.8 (C-1), 86.3 (d, 1J = 182.9 Hz, C-4), 78.4 (d, 2J = 17.8 Hz, C-3), 74.5 (CH2 O-6Bn), 73.4 (d, 2J = 17.9 Hz, C-5), 72.5 (CH2 O-3Bn), 69.4 (d, 3J = 5.1 Hz, C-6), 54.8 (d, 3J = 1.6 Hz, C-2), 23.0 (Me). 19F NMR (MeOH-d4, 376 MHz): δ −221.09 (dt, 2J = 52.0 Hz, 3J = 26.5 Hz). HRMS-APCI (m/z): [M + H]+ calcd for C22H27FNO5 404.1867; found, 404.1862.

2-Acetamido-3-O-benzyl-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (47)

Compound 47 was prepared from 25 (74 mg, 0.25 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 47 (62 mg, 80%) as a white crystalline solid, mp 205–206 °C (dec, EtOAc/EtOH), Rf 0.52 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 7.36–7.24 (m, 5H, CH_arom), 5.15 (d, 1H, J = 3.4 Hz, H-1), 4.99 (dd, 1H, J = 51.2, 2.5 Hz, H-4), 4.73 (d, 1H, J = 11.6 Hz, CHH Bn), 4.59 (ddd, 1H, J = 46.3, 9.4, 5.6 Hz, H-6’), 4.58 (d, 1H, J = 11.6 Hz, CHH Bn), 4.49 (ddd, 1H, J = 47.1, 9.4, 6.7, 1.2 Hz, H-6), 4.37 (dd, 1H, J = 11.1, 3.4 Hz, H-2), 4.31 (ddd, 1H, J = 30.1, 12.7, 6.7, 5.6 Hz, H-5), 3.89 (ddd, 1H, J = 27.9, 11.1, 2.5 Hz, H-3), 1.96 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.5 (CO), 139.5 (Cq), 129.3 (2CH_arom), 128.69 (CH_arom), 128.68 (2CH_arom), 93.0 (C-1), 87.0 (dd, S30
Compound 48 was prepared from 38 (160 mg, 0.53 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 48 (105 mg, 62%) as a white crystalline solid, mp 207–208 °C (dec, EtOAc). Rf 0.29 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 7.35–7.24 (m, 5H, CH-arom), 4.94 (dd, 1H, J = 50.8, 2.5 Hz, H-4), 3.95–3.83 (m, 2H, H-2, H-5), 3.76 (ddd, 1H, J = 47.5, 26.8, 10.8 Hz, H-3), 4.58, 4.54 (2 × d, 2 × 1H, J = 12.2, CHH Bn), 4.43 (ddd, 1H, J = 10.8, 9.1, 3.5 Hz, H-2), 4.25 (ddd, 1H, J = 29.0, 6.5, 6.5, 1.8, 0.9 Hz, H-5), 3.71 (dd, 1H, J = 9.7, 6.8 Hz, H-6), 3.71 (dd, 1H, J = 9.7, 6.5, 1.8, 0.9 Hz, H-6'), 1.99 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC, HMBC): δ 173.6 (CO), 139.3 (Cα), 129.4 (2CH-arom), 128.8 (CH-arom), 128.7 (2CH-arom), 96.7 (C-1), 85.3 (dd, 1J = 182.8 Hz), 129.8 (C-2), 22.7 (Me). 19F NMR (MeOH-d4, 376 MHz): δ −220.96 (dt, 2J = 50.8 Hz, 2J = 27.8 Hz, F-4), −233.70 (td, 2J = 46.9 Hz, 3J = 11.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calced for C15H20F2NO4, 316.1355; found, 316.1354.
Compound 49 was prepared from 26 (180 mg, 0.85 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 1:1 → EtOAc afforded 49 (144 mg, 74%) as a white crystalline solid, mp 175–177 °C (dec, sub >160 °C, EtOAc/MTBE), Rf 0.40 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H 19F), H-H COSY): δ 5.12 (q, 1H, J = 3.6 Hz, H-1), 4.84 (dddd, 1H, J = 54.0, 16.4, 10.4, 8.3 Hz, H-3), 4.72–4.50 (m, 2H, H-6), from J12 = 47.3, 26.7, 11.0, 2.8 Hz, H-3), 4.61 (ddd, 1H, J = 47.3, 26.7, 11.0, 2.8 Hz, H-3), 4.61 (ddd, 1H, J = 47.3, 26.7, 11.0, 2.8 Hz, H-3), 2.00 (s, 3H, Me). 13C 1H NMR (MeOH-d₄, 101 MHz, HSQC, HMBC): δ 173.6 (CO), 92.7 (dd, 3J = 9.5 Hz, 4J = 1.5 Hz, C-1), 91.5 (ddd, 1J = 185.0 Hz, 2J = 18.7 Hz, 4J = 0.9 Hz, C-3), 88.3 (ddd, 1J = 183.7 Hz, 2J = 18.3 Hz, 4J = 8.1 Hz, C-4), 82.4 (dd, 1J = 173.4 Hz, C-6), 68.8 (ddd, 2J = 23.2, 2J = 18.5, J = 7.0 Hz, C-5), 53.9 (dd, 2J = 16.6 Hz, 3J = 7.3 Hz, C-2), 22.4 (Me). 19F NMR (MeOH-d₄, 376 MHz): –200.72 (ddddd, 2J = 52.6 Hz, 3J = 16.8, 13.3, 3.6 Hz, 4J = 3.6 Hz, F-4), –201.81 (ddddd, 2J = 54.0 Hz, 3J = 14.2, 13.3, 11.1 Hz, 4J = 3.6 Hz, F-3), –238.52 (td, 3J = 47.7 Hz, 4J = 26.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcd for C₄H₁₁F₃NO₃, 228.0842; found, 228.0846. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

Compound 50 was prepared from 36 (110 mg, 0.52 mmol) according to the general procedure for azide/acetamide conversion. Chromatography in EtOAc/PE 2:1 → EtOAc afforded 50 (101 mg, 85%) as a white crystalline solid, mp 180–205 °C (dec, EtOAc/EtOH), Rf 0.42 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H 19F), H-H COSY): δ 5.19 (dd, 1H, J = 3.5, 5.3 Hz, H-1), 5.03 (ddd, 1H, J = 52.5, 8.2, 2.8 Hz, H-4), 4.84 (dddd, 1H, J = 47.3, 26.7, 11.0, 2.8 Hz, H-3), 4.61 (ddd, 1H, J = 46.2, 9.4, 5.6 Hz, H-6'), 4.61 (ddddd, 1H, J = 47.1, 9.4, 6.6, 1.4, 1.1 Hz, H-6), from 1J = 52.6 Hz, 3J = 16.8, 13.3, 3.6 Hz, 4J = 3.6 Hz, F-4), –201.81 (ddddd, 2J = 54.0 Hz, 3J = 14.2, 13.3, 11.1 Hz, 4J = 3.6 Hz, F-3), –238.52 (td, 3J = 47.7 Hz, 4J = 26.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcd for C₄H₁₁F₃NO₃, 228.0842; found, 228.0846. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.
NMR (MeOH-d₄, 400 MHz, ¹H (¹⁹F), H-H COSY): δ 4.73 (dd, 1H, J = 8.6, 1.0 Hz, H-1), 4.05 (ddd, 1H, J = 11.2, 11.0, 8.6 Hz, H-2), 3.93 (ddd, 1H, J = 11.0, 6.4, 2.0 Hz, H-5). ¹³C{¹H} NMR (MeOH-d₄, 101 MHz, HSQC, HMBC): δ 174.0 (CO), 96.3 (d, J = 10.4 Hz, C-1), 82.1 (ddd, J = 169.4 Hz, J = 5.8 Hz, J = 2.3 Hz, C-6), 72.0 (dd, J = 23.2 Hz, J = 17.8 Hz, J = 6.0 Hz, C-5), 54.2 (dd, J = 17.4 Hz, J = 1.9 Hz, C-2), 22.9 (Me). ¹⁹F NMR (MeOH-d₄, 376 MHz): –202.55 (dddt, J = 46.3 Hz, J = 14.5, 8.6 Hz, J = 1.8 Hz, F-3), –221.98 (dddd, J = 52.6 Hz, J = 28.1, 25.5, 14.5 Hz, F-4), –234.15 (tdd, J = 46.5 Hz, J = 11.8 Hz, J = 1.8 Hz, F-6). HRMS-APCI (m/z): [M + H]⁺ calcd for C₈H₁₃F₃NO₃, 228.0842; found, 228.0846.

2-Acetamido-2,3-dideoxy-3-fluoro-D-glucopyranose (51)

Compound 39 (134 mg, 0.33 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (70 mg) in methanol (9 mL) to afford white crystalline material that was purified by recrystallization to give 51 (50 mg, 68%), mp 178–180 °C (EtOH/MTBE), Rf 0.35 (EtOAc/MeOH 5:1). NMR data for the α-anomer: ¹H NMR (MeOH-d₄, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC): δ 5.12 (dd, 1H, J = 3.8, 3.6 Hz, H-1), 4.57 (ddd, 1H, J = 53.8, 10.4, 8.5 Hz, H-3), 4.06 (ddd, 1H, J = 10.5, 10.4, 3.6 Hz, H-2), 3.84–3.78 (m, 2H, H-5, H-6'), 3.74 (dd, 1H, J = 12.0, 5.1 Hz, H-6), 3.74 (dd, 1H, J = 15.0, 9.8, 8.5 Hz, H-4), 1.99 (s, 3H, Me). ¹³C{¹H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 173.5 (CO), 94.2 (d, J = 182.3 Hz, C-3), 92.9 (d, J = 9.8 Hz, C-1), 72.6 (d, J = 7.1 Hz, C-5), 70.3 (d, J = 17.5 Hz, C-4), 62.3 (d, J = 1.4 Hz, C-6), 54.3 (d, J = 16.4 Hz, C-2), 22.5 (Me). ¹⁹F NMR (MeOH-d₄, 376 MHz): δ –201.21 (ddddd, J = 53.8 Hz, J = 15.0, 10.5 Hz, J = 3.8, 1.1 Hz). Resolved signals for the β-anomer: 4.63 (d, 1H, J = 8.4 Hz, H-1), 4.34 (d, 1H, J = 52.1, 10.2, 8.6 Hz, H-3), 3.87 (dt, 1H, J = 12.0, 1.6 Hz, H-6), 3.59 (ddd, 1H, J = 12.9, 9.7, 8.6 Hz, H-4), 3.28 (ddd, 1H, J = 9.7, 5.5, 2.3, 1.2 Hz, H-5). ¹³C{¹H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 173.8 (CO), 96.3 (d, J = 10.6 Hz, C-1), 95.9 (d, J = 184.7 Hz, C-3), 76.8 (d, J = 8.1 Hz, C-5), 70.1 (d, J = 17.6 Hz, C-4), 62.4 (d, J = 2.0 Hz, C-6), 57.1 (d, J = 17.1 Hz, C-2), 22.8 (Me). ¹⁹F NMR (MeOH-d₄, 376 MHz): δ –196.02 (dt, J = 52.1 Hz, J = 12.9 Hz). HRMS-APCI (m/z): [M + H]⁺ calcd for C₈H₁₃FNO₃, 224.0929; found, 224.0927.
2-Acetamido-2,3,6-trideoxy-3,6-difluoro-D-glucopyranose (52)

Compound 40 (85 mg, 0.27 mmol) was hydrogenated for 2 days according to general procedure for debenzylation using palladium on carbon (40 mg) in methanol (5 mL) to afford the product 52 (58 mg, 94%) as a white crystalline solid, mp 208–210 °C (EtOH), Rf 0.17 (EtOAc). NMR signals of the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 5.12 (dd, 1H, J = 3.8, 3.6 Hz, H-1), 4.66 (ddd, 1H, J = 47.5, 10.2, 4.0 Hz, H-6´), from 1H {19F-3} 4.58 (dd, 1H, J = 10.5, 8.5 Hz, H-3), from 1H {19F-6} 4.56 (ddd, 1H, J = 10.2, 1.6, 1.4 Hz, H-6), 4.06 (ddd, 1H, J = 10.6, 10.5, 3.6 Hz, H-2), 3.94 (dddd, 1H, J = 26.7, 10.2, 4.0, 1.6 Hz, H-5), 3.66 (ddd, 1H, J = 14.7, 10.2, 8.5 Hz, H-4), 1.99 (s, 3H, Me).

13C{1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.5 (CO), 94.0 (dd, 1J = 182.6 Hz, 4J = 0.9 Hz, C-3), 92.9 (d, 3J = 9.8 Hz, C-1), 83.1 (dd, 1J = 171.8, 4J = 1.6 Hz, C-6), 71.4 (dd, 2J = 18.0 Hz, 3J = 7.8 Hz, C-5), 69.3 (dd, 2J = 18.2 Hz, 3J = 7.6 Hz, C-4), 54.2 (d, 2J = 16.5 Hz, C-2), 22.5 (Me).

19F NMR (MeOH-d4, 376 MHz): –201.24 (dddd, 2J = 53.4 Hz, 3J = 14.7, 10.6 Hz, 4J = 3.8 Hz, F-3), –238.19 (ddd, 2J = 48.6, 47.5 Hz, 3J = 26.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcld for C8H14F2NO4, 226.0885; found, 226.0884. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

2-Acetamido-2,4-dideoxy-4-fluoro-D-glucopyranose (53)

Compound 41 (58 mg, 0.14 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (60 mg) in methanol (5 mL) to afford the known product 53 [5] (30 mg, 93%) as a yellowish crystalline solid, mp 183–185 °C (dec, EtOH/EtOAc, ref 5 gives 176–180 °C (dec)), Rf 0.23 (EtOAc/MeOH 5:1). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 5.09 (dd, 1H, J = 3.3, 3.1 Hz, H-1), 4.30 (ddd, 1H, J = 50.9, 9.9, 8.2 Hz, H-4), 4.00–3.92 (m, 1H, H-5), from 1H {19F} 3.96 (dd, 1H, J = 10.7, 8.2 Hz, H-3), 3.88 (dd, 1H, J = 10.7, 3.3 Hz, H-2), 3.84–3.67 (m, 2H, H-6), 1.99 (s, 3H, Me).

13C{1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.7 (CO), 92.4 (d, 4J = 1.5 Hz, C-1), 91.5 (d, 1J = 180.0 Hz, C-4), 70.60 (d, 2J = 19.0 Hz, C-3), 70.58 (d, 2J = 23.8 Hz, C-5), 61.8 (C-6), 55.5 (d, 3J = 8.2 Hz, C-2), 22.5 (Me). 19F NMR (MeOH-d4, 376 MHz): –201.24 (ddd, 2J = 53.4 Hz, 3J = 14.7, 10.6 Hz, 4J = 3.8 Hz, F-3), –238.19 (ddd, 2J = 48.6, 47.5 Hz, 3J = 26.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcld for C8H14F3NO4, 226.0885; found, 226.0884. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

2-Acetamido-2,4-dideoxy-4-fluoro-D-glucopyranose (53)

Compound 41 (58 mg, 0.14 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (60 mg) in methanol (5 mL) to afford the known product 53 [5] (30 mg, 93%) as a yellowish crystalline solid, mp 183–185 °C (dec, EtOH/EtOAc, ref 5 gives 176–180 °C (dec)), Rf 0.23 (EtOAc/MeOH 5:1). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 5.09 (dd, 1H, J = 3.3, 3.1 Hz, H-1), 4.30 (ddd, 1H, J = 50.9, 9.9, 8.2 Hz, H-4), 4.00–3.92 (m, 1H, H-5), from 1H {19F} 3.96 (dd, 1H, J = 10.7, 8.2 Hz, H-3), 3.88 (dd, 1H, J = 10.7, 3.3 Hz, H-2), 3.84–3.67 (m, 2H, H-6), 1.99 (s, 3H, Me).

13C{1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.7 (CO), 92.4 (d, 4J = 1.5 Hz, C-1), 91.5 (d, 1J = 180.0 Hz, C-4), 70.60 (d, 2J = 19.0 Hz, C-3), 70.58 (d, 2J = 23.8 Hz, C-5), 61.8 (C-6), 55.5 (d, 3J = 8.2 Hz, C-2), 22.5 (Me). 19F NMR (MeOH-d4, 376 MHz): –201.24 (ddd, 2J = 53.4 Hz, 3J = 14.7, 10.6 Hz, 4J = 3.8 Hz, F-3), –238.19 (ddd, 2J = 48.6, 47.5 Hz, 3J = 26.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcld for C8H14F3NO4, 226.0885; found, 226.0884. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.
24.2 Hz, C-5), 73.6 (d, $^2J = 18.6$ Hz, C-3), 61.9 (C-6), 58.6 (d, $^3J = 8.6$ Hz, C-2), 22.9 (Me). $^{19}$F NMR (MeOH-$d_4$, 376 MHz): $\delta$ -201.87 (ddd, $^2J = 50.8$ Hz, $^3J = 15.6$, 2.5 Hz).

2-Acetamido-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (54)

Compound 42 (90 mg, 0.29 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (80 mg) in methanol (6 mL) to afford the product 54 (64 mg, 100%) as a white crystalline solid, mp 206–209 °C (dec, EtOH/EtOAc). $R_f$ 0.10 (EtOAc). NMR signals of the $\alpha$-anomer: $^1$H NMR (MeOH-$d_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): $\delta$ 5.09 (t, 1H, $J = 3.3$ Hz, H-1), 4.61 (dddd, 1H, $J = 47.5$, 10.4, 3.9, 1.7 Hz, H-6´), 4.55 (dddd, 1H, $J = 48.1$, 10.4, 1.8, 1.4 Hz, H-6), 4.29 (ddd, 1H, $J = 50.6$, 10.1, 8.3 Hz, H-3), 4.11 (ddddd, 1H, $J = 26.6$, 10.1, 4.1, 3.8 Hz, H-5), 3.97 (ddd, 1H, $J = 14.8$, 10.8, 8.3 Hz, H-3), 3.89 (dd, 1H, $J = 10.8$, 3.3 Hz, H-2), 1.99 (s, 3H, Me). $^{13}$C{${}^1$H} NMR (MeOH-$d_4$, 101 MHz, HSQC): $\delta$ 173.7 (CO), 92.5 (d, $^4J = 1.5$ Hz, C-1), 90.6 (dd, $^1J = 181.2$ Hz, $^3J = 7.4$ Hz, C-4), 82.7 (d, $^1J = 172.5$ Hz, C-6), 70.5 (d, $^2J = 18.5$ Hz, C-3), 69.2 (dd, $^2J = 23.7$ Hz, $^2J = 18.2$ Hz, C-5), 55.3 (d, $^3J = 8.0$ Hz, C-2), 22.6 (Me). $^{19}$F NMR (MeOH-$d_4$, 376 MHz): -199.99 (ddd, $^2J = 50.6$ Hz, $^3J = 14.8$, 4.1 Hz, $^5J = 3.3$ Hz, F-4), -238.52 (ddd, $^2J = 48.1$, 47.5 Hz, $^3J = 26.6$ Hz, F-6). HRMS-APCI (m/z): [M + H]$^+$ caleed for C$_8$H$_{14}$F$_2$NO$_4$, 226.0885; found, 226.0884. NMR signals of the $\beta$-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

2-Acetamido-2,3,4-trideoxy-3,4-difluoro-D-glucopyranose (55)

Compound 43 (85 mg, 0.27 mmol) was hydrogenated for 4 days according to general procedure for debenzylation using palladium on carbon (added in 3 portions, 180 mg in total) in methanol (6 mL) to afford the product 55 (55 mg, 90%) as a white crystalline solid, mp 196–199 °C (dec, EtOH/EtOAc). $R_f$ 0.07 (EtOAc). NMR data for the $\alpha$-anomer: $^1$H NMR (MeOH-$d_4$, 400 MHz, $^1$H {${}^{19}$F}, H-H COSY): $\delta$ 5.12 (dt, 1H, $J = 3.6$, 3.5 Hz, H-1), 4.82 (ddd, 1H, $J = 54.3$, 16.1, 10.5, 8.2 Hz, H-3), 4.59 (ddd, 1H, $J = 51.7$, 15.3, 9.9, 8.2 Hz, H-4), 4.12 (ddd, 1H, $J = 10.9$, 10.5, 3.6 Hz, H-2), 3.99 (ddd, 1H, $J = 9.9$, 4.8, 4.0, 2.4 Hz, H-5), from $^1$H {${}^{19}$F} 3.79 (dd, 1H, $J = 12.4$, 2.4 Hz, H-6), from $^1$H {${}^{19}$F} 3.74 (dd, 1H, $J = 12.4$, 4.1 Hz, H-6´), 2.00 (s, 3H, Me). $^{13}$C{${}^1$H} NMR (MeOH-$d_4$, 101 MHz, HSQC): $\delta$ 173.5 (CO), 92.7 (dd, $^3J = 9.2$ Hz, $^4J = 1.3$ Hz, C-1), 91.7 (dd, $^1J = 184.8$ Hz, $^2J = 18.9$ Hz, C-3), 89.0 (dd, $^1J = 182.3$ Hz, $^2J = 17.7$ Hz, C-4), 70.1 (dd, $^2J = 23.7$ Hz, $^3J = 6.2$ Hz, C-5), 61.4 (C-6), 54.0 (dd, $^2J = 16.5$ Hz, $^3J = 7.4$ Hz, C-
2-Acetamido-2,3-dideoxy-3-fluoro-D-galactopyranose (56)

Compound 44 (125 mg, 0.31 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (70 mg) in methanol (9 mL) to afford the product 56 (65 mg, 94%) as a white foam, which slowly crystallized over a few days into white crystalline material, mp 159–161 °C (dec, EtOH/MTBE). Rf 0.12 (EtOAc/MeOH 10:1). NMR data for the α-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H {¹⁹F}, H-H COSY): δ 5.15 (dd, 1H, J = 4.6, 3.7 Hz, H-1), 4.70 (ddd, 1H, J = 49.1, 10.8, 3.2 Hz, H-3), 4.52 (ddd, 1H, J = 10.8, 9.7, 3.7 Hz, H-2), 4.16 (ddd, 1H, J = 7.7, 3.2, 1.2 Hz, H-4), 4.04 (ddd, 1H, J = 6.2, 2.0, 1.2 Hz, H-5), 3.77–3.71 (m, 2H, H-6), 1.99 (s, 3H, Me). 13C{¹H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 173.6 (CO), 93.2 (d, J = 9.5 Hz, C-1), 90.6 (d, J = 185.0 Hz, C-3), 71.1 (d, J = 6.1 Hz, C-5), 68.4 (d, J = 16.6 Hz, C-4), 62.3 (d, J = 2.9 Hz, C-6), 50.4 (d, J = 17.2 Hz, C-2), 22.6 (Me). ¹⁹F NMR (MeOH-d₄, 376 MHz): –204.16 (ddddd, J = 49.1 Hz, J = 9.7, 7.7 Hz, J = 4.6, 2.0 Hz). NMR data for the β-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H {¹⁹F}, H-H COSY): δ 4.59 (d, 1H, J = 8.4 Hz, H-1), 4.51 (ddd, 1H, J = 48.3, 10.6, 3.3 Hz, H-3), from 1H {¹⁹F} 4.14 (ddd, 1H, J = 10.6, 8.4 Hz, H-2), 4.09 (ddd, 1H, J = 6.7, 3.2, 1.9 Hz, H-4), 3.77–3.71 (m, 2H, H-6), 3.50 (ddd, 1H, J = 5.7, 1.9, 1.5 Hz, H-5), 1.99 (Me). 13C{¹H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 174.0 (CO), 96.8 (d, J = 10.5 Hz, C-1), 92.5 (d, J = 187.0 Hz, C-3), 75.5 (d, J = 7.0 Hz, C-5), 67.6 (d, J = 16.6 Hz, C-4), 62.1 (d, J = 3.4 Hz, C-6), 54.1 (d, J = 17.5 Hz, C-2), 22.9 (Me). ¹⁹F NMR (MeOH-d₄, 376 MHz): –199.96 (ddddd, J = 48.3 Hz, J = 10.0, 6.7 Hz, J = 1.9 Hz). HRMS-APCI (m/z): [M + H]⁺ calecd for C₈H₁₄F₂NO₄, 224.0885; found, 224.0888.
Compound 45 (66 mg, 0.21 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (70 mg) in methanol (9 mL) to afford the product 57 (45 mg, 95%) as a white crystalline solid, mp 169–172 °C (dec, EtOH). R f 0.11 (EtOAc). NMR signals of the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 5.17 (dd, 1H, J = 3.6, 5.0 Hz, H-1), 4.72 (ddd, 1H, J = 49.4, 10.7, 3.1 Hz, H-3), from 1H (19F-6): 4.60 (dd, 1H, J = 9.5, 5.0 Hz, H-6’), 4.52 (dddd, 1H, J = 47.9, 9.5, 6.9, 1.2 Hz, H-6), 4.52 (ddd, 1H, J = 10.7, 10.3, 3.5 Hz, H-2), 4.28 (dddd, 1H, J = 14.1, 6.9, 5.0, 1.3 Hz, H-5), 4.15 (ddd, 1H, J = 7.7, 3.1, 1.3 Hz, H-4), 1.99 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.6 (CO), 93.2 (d, J = 9.4 Hz, C-1), 90.1 (dd, J = 185.0 Hz, 4J = 1.3 Hz, C-3), 83.7 (dd, J = 167.0, 4J = 3.5 Hz, C-6), 69.6 (dd, 4J = 22.6 Hz, 3J = 6.8 Hz, C-5), 68.0 (dd, 2J = 17.2 Hz, 3J = 6.8 Hz, C-4), 50.2 (d, J = 17.3 Hz, C-2), 22.6 (Me). 19F NMR (MeOH-d4, 376 MHz): –204.93 (ddddd, 2J = 49.4 Hz, 3J = 10.3, 7.7 Hz, 4J = 5.0 Hz, 5J = 2.5 Hz, F-3), –233.55 (dddd, 4J = 47.9, 46.1 Hz, 3J = 14.1 Hz, 5J = 2.5 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calc for C8H14F2NO4, 226.0885; found, 226.0880. NMR signals of the β-anomer could not be observed in intensity sufficient for characterization within 12 h after sample preparation.

Compound 46 (90 mg, 0.22 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (80 mg) in methanol (6 mL) to afford the known product 58 [5] (48 mg, 96%) as a white crystalline solid, mp 210–213 °C (dec, EtOH, ref 5 gives 205–209 °C). R f 0.11 (EtOAc/MeOH 10:1). NMR data for the α-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 5.14 (d, 1H, J = 3.5 Hz, H-1), from 1H (19F) 4.80 (d, 1H, J = 2.6 Hz, H-4), 4.20 (ddd, 1H, J = 11.1, 3.5 Hz, H-2), 4.07 (dt, 1H, J = 30.3, 6.8 Hz, H-5), 3.91 (ddd, 1H, J = 28.9, 11.1, 2.6 Hz, H-3), 3.74–3.62 (m, 2H, H-6), 1.99 (s, 3H, Me). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 173.9 (CO), 92.3 (C-1), 90.5 (d, J = 180.1 Hz, C-4), 70.6 (d, J = 18.1 Hz, C-5), 68.0 (d, J = 19.1 Hz, C-3), 61.3 (d, J = 6.0 Hz, C-6), 52.2 (d, J = 2.9 Hz, C-2), 22.6 (Me). 19F NMR (MeOH-d4, 376 MHz): δ –224.66 (ddd, 2J = 50.5 Hz, 3J = 30.3, 28.9 Hz). Resolved signals for the β-anomer: 1H NMR (MeOH-d4, 400 MHz, 1H {19F}, H-H COSY): δ 4.72 (dd, 1H, J = 50.8, 2.5 Hz, H-4), 4.63 (d, 1H, J = 8.1 Hz, H-1). 13C {1H} NMR (MeOH-d4, 101 MHz, HSQC): δ 97.1 (C-1), 89.5 (d, J = 180.5 Hz, C-4), 56.1 (C-2). 19F NMR (MeOH-d4, 376 MHz): δ –222.05 (dt, J = 50.8 Hz, 3J = 28.4 Hz).
2-Acetamido-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (59)

Compound 47 (48 mg, 0.15 mmol) was hydrogenated overnight according to general procedure for debenzylation using palladium on carbon (70 mg) in methanol (9 mL) to afford the known product 59 [6] (31 mg, 92%) as a white crystalline solid, mp 206–209 °C (dec, EtOH/MTBE, ref 6 gives 205–206 °C (dec)). Rf 0.06 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H {19F}, H-H COSY): δ 5.16 (d, 1H, J = 3.5 Hz, H-1), 4.77 (dd, 1H, J = 51.0, 2.6 Hz, H-4), 4.59 (ddd, 1H, J = 46.2, 9.4, 5.5 Hz, H-6), 4.49 (ddddd, 1H, J = 47.3, 9.4, 6.8, 1.3 Hz, H-6), 4.33 (ddddd, 1H, J = 30.3, 12.7, 6.8, 5.5 Hz, H-5), 4.21 (dd, 1H, J = 11.1, 3.5 Hz, H-2), 3.94 (dd, 1H, J = 28.9, 11.1, 2.6 Hz, H-3), 2.00 (s, 3H, Me). 13C {1H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 173.9 (CO), 92.8 (Hz, C-1), 90.5 (dd, J = 180.1 Hz, 3J = 5.9 Hz, C-4), 82.7 (dd, 1J = 168.1 Hz, 3J = 6.5 Hz, C-6), 68.8 (dd, 2J = 23.1 Hz, 3J = 17.7 Hz, C-5), 67.4 (d, 3J = 18.8 Hz, C-3), 52.8 (d, 3J = 2.7 Hz, C-2), 22.6 (Me). 19F NMR (MeOH-d₄, 376 MHz): -224.17 (ddd, 2J = 100.0 Hz, 3J = 28.9 Hz, F-4), -234.16 (dd, 2J = 51.0 Hz, 3J = 28.9 Hz, F-4), -233.90 (ddd, 2J = 47.0, 46.0 Hz, 3J = 12.7 Hz, F-6). Resolved signal for the β-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H {19F}, H-H COSY): δ 4.67 (d, 1H, J = 8.1 Hz, H-1), 3.95–3.71 (m, 3H, H-2, H-3, H-5). 13C {1H} NMR (MeOH-d₄, 101 MHz, HSQC): δ 174.4 (CO), 97.0 (C-1), 89.5 (dd, 1J = 181.0 Hz, 3J = 6.0 Hz, C-4), 82.4 (dd, 1J = 168.9 Hz, 3J = 6.1 Hz, C-6), 73.1 (dd, 2J = 22.8 Hz, 3J = 17.7 Hz, C-5), 71.3 (d, 2J = 18.7 Hz, C-3), 55.9 (d, 3J = 1.6 Hz, C-2), 22.0 (Me). 19F NMR (MeOH-d₄, 376 MHz): -221.72 (dt, 2J = 51.6 Hz, 3J = 27.9 Hz, F-4), -233.90 (dd, 2J = 47.0, 46.0 Hz, 3J = 12.7 Hz, F-6). HRMS-APCI (m/z): [M + H]+ calcld for C₃H₁₂F₂NO₄, 226.0885; found, 226.0884.

2-Acetamido-2,3,4-trideoxy-3,4-difluoro-D-galactopyranose (60)

Compound 48 (105 mg, 0.33 mmol) was hydrogenated for 4 days according to general procedure for debenzylation using palladium on carbon (added in 2 portions, 120 mg in total) in methanol (8 mL) to afford the product 60 (75 mg, 100%) as a white crystalline solid, mp 150–151 °C (dec, EtOH/MTBE). Rf 0.07 (EtOAc). NMR data for the α-anomer: 1H NMR (MeOH-d₄, 400 MHz, 1H {19F}, H-H COSY): δ 5.16 (d, 1H, J = 5.3, 3.5 Hz, H-1), 5.01 (ddd, 1H, J = 51.8, 8.2, 2.7 Hz, H-4), 4.75 (ddd, 1H, J = 47.7, 26.8, 11.0, 2.7 Hz, H-3), 4.53 (ddd, 1H, J = 11.0, 9.2, 3.5 Hz, H-2), 4.08 (ddd, 1H, J = 29.0, 7.0, 6.7, 1.6 Hz, H-5), 3.73 (dd, 1H, J = 11.0, 7.0 Hz, H-6), 3.66 (dddd, 1H, J = 11.0, 6.7, 1.7, 1.2 Hz, H-6), 1.99 (s, 3H, Me). 13C {1H} NMR (MeOH-d₄, 101 MHz, HSQC, HMBC): δ 173.7 (CO), 93.1 (d, 3J = 9.2 Hz, C-1), 88.3 (dd, 1J = 188.7 Hz, 2J = 18.3 Hz, C-3), 87.8 (dd, 1J = 182.8 Hz, 2J = 16.1 Hz, C-4), 70.2 (dd, 2J = 18.1 Hz, 3J = 5.1 Hz, C-5), 60.9 (dd, 3J = 5.9, 4J = 2.4 Hz, C-6), 50.6 (dd, 2J = 17.4 Hz, 3J = 2.7 Hz, C-2), 50.6.
22.5 (Me). $^{19}$F NMR (MeOH-$d_4$, 376 MHz): $-202.42$ (ddddd, $^2J = 47.7$ Hz, $^3J = 15.0$, $9.2$, $8.2$ Hz, $^4J = 5.3$ Hz, F-3), $-220.90$ (m, F-4). Resolved signals for the β-anomer: $^1$H NMR (MeOH-$d_4$, 400 MHz, $^1$H {$^{19}$F}, H-H COSY): $4.95$ (ddd, $1H$, $J = 52.3$, $7.0$, $2.7$ Hz, H-4), $4.67$ (ddddd, $1H$, $J = 46.5$, $26.8$, $10.9$, $2.7$ Hz, H-3), $4.68$ (d, $1H$, $J = 8.3$ Hz, H-1). $^{19}$F NMR (MeOH-$d_4$, 376 MHz): $-198.00$ (ddd, $^2J = 46.5$ Hz, $^3J = 15.0$, $11.0$, $7.0$ Hz, F-3), $-218.46$ (ddddd, $^2J = 52.3$ Hz, $^3J = 26.8$, $26.5$, $15.0$ Hz, F-4). HRMS-APCI (m/z): [M + H]$^+$ calcd for C$_{8}$H$_{14}$F$_{2}$NO$_{4}$, 226.0885; found, 226.0887.

2-Acetamido-2,6-dideoxy-6-fluoro-$D$-glucopyranose (61)

![61]

Compound 61 was prepared according to ref 7

2-Acetamido-2,6-dideoxy-6-fluoro-$D$-galactopyranose (62)

![62]

Compound 62 was prepared following the published procedure [8], mp 168–171 °C (EtOH), $R_f$ 0.25 (EtOAc/MeOH 20:3). Since NMR data are incomplete in ref 8, we report them here: $^1$H NMR (MeOH-$d_4$, 400 MHz, $^1$H {$^{19}$F}, H-H COSY): $\delta$ 5.14 (d, $1H$, $J = 3.6$ Hz, H-1), 4.58 (ddd, $1H$, $J = 46.4$, 9.5, 4.8 Hz, H-6), 4.50 (ddd, $1H$, $J = 48.1$, 9.5, 7.0 Hz, H-6'), 4.27 (ddddd, $1H$, $J = 14.6$, 7.0, 4.8, 1.3 Hz, H-5), 4.22 (dd, $1H$, $J = 10.9$, 3.6 Hz, H-2), 3.88 (dd, $1H$, $J = 3.3$, 1.3 Hz, H-4), 3.83 (ddd, $1H$, $J = 10.9$, 3.3 Hz, H-3), 1.99 (s, 3H, Me). $^{13}$C{$^1$H} NMR (MeOH-$d_4$, 101 MHz, HSQC): $\delta$ 174.0 (CO), 92.9 (C-1), 84.1 (d, $^1J = 166.8$ Hz, C-6), 70.2 (d, $^2J = 13.0$ Hz, C-5), 70.0 (d, $^3J = 2.5$ Hz, C-4), 69.3 (d, $^4J = 1.1$ Hz, C-3), 51.9 (C-2), 22.7 (Me). $^{19}$F NMR (MeOH-$d_4$, 376 MHz): $-233.19$ (ddd, $^2J = 48.1$, 46.4 Hz, $^3J = 14.6$ Hz). Resolved signals for β-anomer: $^{19}$F NMR (MeOH-$d_4$, 376 MHz): $-232.96$ (ddd, $^2J = 48.0$, 46.5 Hz, $^3J = 13.6$ Hz). HRMS-APCI (m/z): [M + H]$^+$ calcd for C$_{8}$H$_{15}$FNO$_{5}$, 224.0928; found, 224.0928.
Table S1.

The values of $J_{HF}$, $J_{CF}$ and $J_{FF}$ coupling constants extracted from NMR spectra of the target fluoro analogs. (See also refs 9, 10 and 11 for the discussion of the relationship between the values and the spatial orientation of the coupled nuclei)

<table>
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<tr>
<th>Compound</th>
<th>$J_{C3-F}$</th>
<th>$J_{C2-F}$</th>
<th>$J_{C4-F}$</th>
<th>$J_{C1-F}$</th>
<th>$J_{C5-F}$</th>
<th>$J_{C6-F}$</th>
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<td>17.5 Hz</td>
<td>9.8 Hz</td>
<td>7.1 Hz</td>
<td>1.4 Hz</td>
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<tr>
<td>53 $\alpha$</td>
<td>180.0 Hz</td>
<td>19.0 Hz</td>
<td>23.8 Hz</td>
<td>8.2 Hz</td>
<td>8.6 Hz</td>
<td>3.4 Hz</td>
</tr>
<tr>
<td>53 $\beta$</td>
<td>180.9 Hz</td>
<td>18.6 Hz</td>
<td>24.2 Hz</td>
<td>8.6 Hz</td>
<td>8.6 Hz</td>
<td>2.9 Hz</td>
</tr>
<tr>
<td>56 $\alpha$</td>
<td>185.0 Hz</td>
<td>17.2 Hz</td>
<td>16.6 Hz</td>
<td>9.5 Hz</td>
<td>6.1 Hz</td>
<td>2.9 Hz</td>
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</table>

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<th>$J_{H3-F}$</th>
<th>$J_{H4-F}$</th>
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<th>$J_{H1-F}$</th>
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<tbody>
<tr>
<td>51 $\alpha$</td>
<td>53.8 Hz</td>
<td>15.0 Hz</td>
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<td>56 $\alpha$</td>
<td>50.9 Hz</td>
<td>50.8 Hz</td>
<td>50.8 Hz</td>
<td>4.6 Hz</td>
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<th>$J_{C4-F6}$</th>
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<th>$J_{C5-F6}$</th>
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<tr>
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<td>48.2 Hz</td>
<td>48.2 Hz</td>
<td>46.4 Hz</td>
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<tr>
<td>61 $\beta$</td>
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<td>48.2 Hz</td>
<td>48.2 Hz</td>
<td>46.4 Hz</td>
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<td>48.2 Hz</td>
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$^4J_{\text{H5-F}} = 1.9$ Hz

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<th>$^2J_{\text{C3-F}}$</th>
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</tr>
<tr>
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<td>18.2</td>
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<td>7.8</td>
</tr>
<tr>
<td>3</td>
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<td>23.7</td>
<td>8.0</td>
<td>1.5</td>
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<td>1.6</td>
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$^2J_{\text{H6 or H6'-F6}} = 48.0$ Hz

$^2J_{\text{H6 or H6'-F6}} = 46.5$ Hz

$^3J_{\text{H5-F6}} = 13.6$ Hz

$^2J_{\text{H6-F6}} = 48.6$ Hz

$^2J_{\text{H6'-F6}} = 48.1$ Hz

$^3J_{\text{H6-F6}} = 47.5$ Hz

$^3J_{\text{H6'-F6}} = 47.5$ Hz

$^3J_{\text{H5-F6}} = 26.7$ Hz

$^3J_{\text{H5-F6}} = 26.6$ Hz
$J_{C3-F3} = 184.8$ Hz
$J_{C4-F3} = 17.7$ Hz
$J_{C2-F3} = 16.5$ Hz
$J_{C5-F3} = 6.2$ Hz
$J_{C1-F3} = 9.2$ Hz

$J_{C4-F4} = 182.3$ Hz
$J_{C3-F4} = 18.9$ Hz
$J_{C5-F4} = 23.7$ Hz
$J_{C2-F4} = 7.4$ Hz
$J_{C1-F4} = 1.3$ Hz

$J_{C6-F3} = 3.5$ Hz
$J_{C6-F6} = 167$ Hz
$J_{C5-F6} = 22.6$ Hz
$J_{C4-F6} = 6.8$ Hz
$J_{C3-F6} = 1.3$ Hz

$J_{H3-F3} = 54.3$ Hz
$J_{H4-F3} = 15.3$ Hz
$J_{H2-F3} = 10.9$ Hz
$J_{H4-F3} = 13.7$ Hz
$J_{H1-F3} = 3.5$ Hz

$J_{H6-F6} = 47.3$ Hz
$J_{H6'-F6} = 46.2$ Hz
$J_{H5-F6} = 14.1$ Hz
$J_{F3-F6} = 2.5$ Hz
$J_{F1-F3} = 3.5$ Hz

$J_{H1-F3} = 5.0$ Hz
$J_{H3-F4} = 7.7$ Hz
$J_{H2-F4} = 10.3$ Hz
$J_{H4-F4} = 49.4$ Hz
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$J_{H6-F6} = 47.9$ Hz
$J_{H6'-F6} = 46.1$ Hz
$J_{H5-F6} = 14.1$ Hz
$J_{F3-F6} = 2.5$ Hz
$J_{F1-F3} = 3.5$ Hz

$J_{H1-F3} = 5.0$ Hz
$J_{H3-F4} = 7.7$ Hz
$J_{H2-F4} = 10.3$ Hz
$J_{H4-F4} = 49.4$ Hz
$J_{H1-F4} = 51.0$ Hz

$J_{H6-F6} = 47.3$ Hz
$J_{H6'-F6} = 46.2$ Hz
$J_{H5-F6} = 14.1$ Hz
$J_{F3-F6} = 2.5$ Hz
$J_{F1-F3} = 3.5$ Hz

$J_{H1-F3} = 5.0$ Hz
$J_{H3-F4} = 7.7$ Hz
$J_{H2-F4} = 10.3$ Hz
$J_{H4-F4} = 49.4$ Hz
$J_{H1-F4} = 51.0$ Hz

$J_{H6-F6} = 47.3$ Hz
$J_{H6'-F6} = 46.2$ Hz
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$J_{F3-F6} = 2.5$ Hz
$J_{F1-F3} = 3.5$ Hz
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$^{2}J_{C3-F4} = 18.7 \text{ Hz}$
$^{2}J_{C5-F4} = 17.7 \text{ Hz}$
$^{3}J_{C2-F4} = 1.6 \text{ Hz}$
$^{3}J_{C6-F4} = 6.1 \text{ Hz}$

$^{1}J_{C6-F6} = 168.9 \text{ Hz}$
$^{2}J_{C5-F6} = 22.8 \text{ Hz}$
$^{3}J_{C4-F6} = 6.1 \text{ Hz}$

$^{1}J_{C4-F4} = 182.8 \text{ Hz}$
$^{2}J_{C3-F4} = 18.3 \text{ Hz}$
$^{2}J_{C5-F4} = 18.1 \text{ Hz}$
$^{3}J_{C2-F4} = 2.7 \text{ Hz}$
$^{3}J_{C6-F4} = 5.9 \text{ Hz}$
<table>
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<tr>
<th>Chemical Bonding</th>
<th>50 α</th>
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<td>$^1J_{C_3\text{-}F_3}$</td>
<td>189.9 Hz</td>
<td>$^2J_{C_2\text{-}F_3}$</td>
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<tr>
<td>$^2J_{C_2\text{-}F_3}$</td>
<td>17.3 Hz</td>
<td>$^3J_{C_1\text{-}F_3}$</td>
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<td>$^2J_{C_4\text{-}F_3}$</td>
<td>16.5 Hz</td>
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<td>$^3J_{C_1\text{-}F_3}$</td>
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<td>$^3J_{C_5\text{-}F_3}$</td>
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<td>$^4J_{C_6\text{-}F_3}$</td>
<td>2.8 Hz</td>
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<td>$^1J_{C_4\text{-}F_4}$</td>
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<td>$^1J_{C_6\text{-}F_6}$</td>
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<td>$^3J_{C_6\text{-}F_4}$</td>
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References


