Supporting Information I

Experimental procedures

The Effect of Deoxyfluorination and O-Acylation on the Cytotoxicity of *N*-Acetyl-D-Gluco- and D-Galactosamine Hemiacetals

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General methods

Chemicals were used as received. $(CH_2Cl)_2$ was dried by distillation from CaH_2 and stored over 3 Å molecular sieves , 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_2SO_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% $CaSO_4 \cdot 0.5\ H_2O$ 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. 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; δ_H/δ_C: $CDCl_3$, 7.26/77.16, methanol-d_4, 3.31/49.00). The ^{19}F spectra were referenced to the line of internal standard hexafluorobenzene (δ/ppm; $CDCl_3$, −163.00, methanol-d_4, −166.62). HRMS analyses were done using Bruker MicrOTOF-QIII, using APCI ionization in positive mode, 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. EtOAc stands for ethyl acetate, PE for petroleum ether.

General acetylation procedure

Acetic anhydride (10 equiv) was added to a solution of the starting alcohol in anhydrous pyridine (*c* 0.1–0.2 mol.dm^{-3}). The reaction mixture was stirred at rt for about 2–4 h when TLC indicated the complete absence of the starting material. The reaction mixture was concentrated and co-distilled with toluene to afford the crude product that was subsequently purified by column chromatography.

General procedure for propionylation or butyrylation

Propionyl or butyryl chloride (1.2–2.0 equiv per OH group) was added dropwise into a cooled (0 °C) solution of the starting alcohol in anhydrous pyridine (*c* 0.1–0.2 mol.dm^{-3}) and a catalytic amount of 4-dimethylaminopyridine was added. The reaction mixture was stirred at rt overnight, concentrated, co-distilled with toluene, diluted with water and extracted with dichloromethane (3×). The organic extracts were combined, dried, concentrated and the crude product was purified by column chromatography.

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

To a solution of the starting deoxyfluorinated 1,6-anhydrohexopyranose in dry 1,2-dichloroethane (*c* ~0.2–0.3 mol dm^{-3}) phenyl trimethylsilyl sulfide (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 h–5 days, until TLC indicated full consumption of the starting compound. Spots of 6-OH products in varying intensity can also be detected near the TLC origin. The reaction was diluted with dichloromethane, 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* ~0.1 mmol.dm^{-3}) acidified by a few drops of AcOH and stirred at rt for about 1 h to remove the 6-*O*-trimethylsilyl group (indicated by TLC), concentrated and purified by column chromatography.

General procedure for C6-OH deoxyfluorination

The procedure is based on the literature report.[1] Diethylaminosulfur trifluoride (DAST, 1.3 equiv) and 2,4,6-collidine (2.6 equiv) 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 under microwave irradiation at 80 °C for 1 h. The reaction mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$, 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 the hydrolysis of phenyl 1-thioglycosides

A solution of the starting phenyl 1-thioglycoside and *N*-bromosuccinimide (4.0 equiv) in acetone/water 9/1 (*c* 0.05 mol.dm^{-3}) was stirred at rt for about 1 h. The reaction mixture turned yellow or red after addition of NBS and gradually became colourless. When TLC indicated full consumption of the starting compound, the reaction was quenched by the addition of a saturated aqueous solution of $Na_2S_2O_3$, 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.

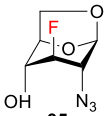
General procedure for azide/acetamide transformation

2-Azidohexose was dissolved in pyridine/thioacetic acid 1:1 (*c* ~5 mol dm^{-3}). The reaction was stirred overnight. During this, it frequently acquired the consistency of thick paste. It was concentrated, co-distilled with toluene and dry-loaded onto silica gel column for chromatographic purification.

General procedure for debenzylation

The benzyl glycoside was dissolved in methanol and 10% palladium on carbon was added under argon atmosphere. The resulting suspension was degassed (3×), purged with hydrogen, and then stirred under H_2 atmosphere for 24–72 h, until TLC indicated complete absence of the starting material and the presence of a more polar product. The reaction mixture was filtered, concentrated and the residue recrystallized.

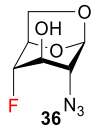
1,6-Anhydro-2-azido-2,3-dideoxy-3-fluoro-β-D-glucopyranose (35)



35

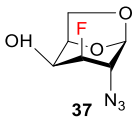
Compound **35** was prepared according to the published procedure.[2]

1,6-Anhydro-2-azido-2,4-dideoxy-4-fluoro-β-D-glucopyranose (36)



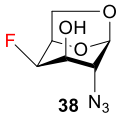
Compound **36** was prepared according to the published procedure.[2]

1,6-Anhydro-2-azido-2,3-dideoxy-3-fluoro-β-D-galactopyranose (37)



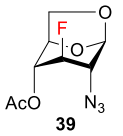
Compound **37** was prepared according to the published procedure.[2]

1,6-Anhydro-2-azido-2,4-dideoxy-4-fluoro-β-D-galactopyranose (38)



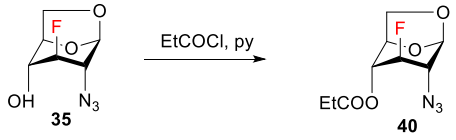
Compound **38** was prepared according to the published procedure.[2]

1,6-Anhydro-4-*O*-acetyl-2-azido-2,3-dideoxy-3-fluoro-β-D-glucopyranose (39)



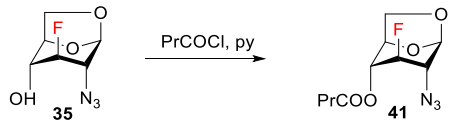
The compound **39** was prepared according to the published procedure.[3]

1,6-Anhydro-2-azido-2,3-dideoxy-3-fluoro-4-*O*-propionyl-β-D-glucopyranose (40)



Compound **40** was prepared according to the general procedure for acylation from **35** (500 mg, 2.64 mmol) and propionyl chloride (280 µL, 3.20 mmol). Chromatography in EtOAc/PE 2:5 afforded **40** as colourless thick syrup (582 mg, 90%), R_f 0.55 (EtOAc/heptane 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.57 (t, 1H, J = 1.8 Hz, H-1), 4.84 (dtt, 1H, J = 15.9, 1.8, 0.7 Hz, H-4), 4.65 (dtd, 1H, J = 5.8, 1.8, 1.1 Hz, H-5), 4.62 (dp, 1H, J = 43.7, 1.8 Hz, H-3), 4.12 (dt, 1H, J = 7.9, 1.1 Hz, H-6^{en}), 3.83 (ddd, 1H, J = 7.9, 5.8, 1.9 Hz, H-6^{ex}), 3.33 (dt, 1H, J = 16.8, 1.8 Hz, H-2), 2.47 (q, 2H, J = 7.5 Hz, CH_2CH$_3$), 1.19 (t, 3H, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.5 (CO), 100.4 (C-1), 88.6 (d, ^1J = 183.8 Hz, C-3), 73.8 (C-5), 69.1 (d, ^2J = 30.5 Hz, C-4), 65.5 (d, ^4J = 3.0 Hz, C-6), 58.7 (d, ^2J = 25.6 Hz, C-2), 27.5 (*C*H$_2$CH$_3$), 9.0 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −180.80 (dddd, ^2J = 43.7 Hz, ^3J = 16.8, 15.9 Hz, ^5J = 1.9 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_9H_{13}FNO_4$, 218.0823; found, 218.0818.

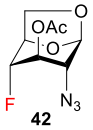
1,6-Anhydro-2-azido-4-*O*-butyryl-2,3-dideoxy-3-fluoro-β-D-glucopyranose (41)



Compound **41** was prepared according to the general procedure for acylation starting from **35** (500 mg, 2.64 mmol) and butyryl chloride (330 µL, 3.18 mmol). Chromatography in EtOAc/PE 2:5 afforded **41** as colourless thick syrup (609 mg, 89%), R_f 0.58 (EtOAc/heptane 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.58 (t, 1H, J = 1.8 Hz, H-1), 4.85 (ddtd, 1H, J = 15.8, 1.8, 1.2, 0.8 Hz, H-4), 4.66 (ddd, 1H, J = 5.8, 1.2, 1.1 Hz, H-5), 4.62 (dq, 1H, J = 43.7, 1.8 Hz, H-3), 4.12 (dt, 1H, J = 7.8, 1.1 Hz, H-6^{en}), 3.83 (ddd, 1H, J = 7.8, 5.8, 1.9 Hz, H-6^{ex}), 3.34 (dt, 1H, J = 17.5, 1.8 Hz, H-2), 2.42 (t, 2H, J = 7.4 Hz, COCH_2), 1.71 (h, 2H, J = 7.4 Hz, CH_2CH$_3$), 0.98 (t, 3H, J = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR

($CDCl_3$, 101 MHz, HSQC): δ 172.7 (CO), 100.4 (C-1), 88.6 (d, ^1J = 183.9 Hz, C-3), 73.7 (C-5), 68.9 (d, ^2J = 30.6 Hz, C-4), 65.5 (d, ^4J = 3.1 Hz, C-6), 58.6 (d, ^2J = 25.6 Hz, C-2), 35.9 ($COCH_2$), 18.4 (CH_2CH_3), 13.7 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −180.60 (dddd, ^2J = 43.7 Hz, ^3J = 17.5, 15.8 Hz, ^5J = 1.9 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{10}H_{15}FNO_4$, 232.0979; found, 232.0980.

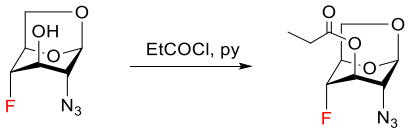
1,6-Anhydro-3-*O*-acetyl-2-azido-2,4-dideoxy-4-fluoro-β-D-glucopyranose (42)



42

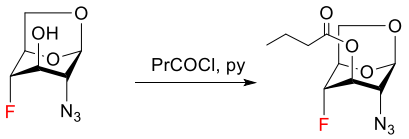
Compound **42** was prepared according to the published procedure.[3]

1,6-Anhydro-2-azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-β-D-glucopyranose (43)



Compound **43** was prepared according to the general procedure for acylation starting from **36** (500 mg, 2.64 mmol) and propionyl chloride (300 μL, 3.43 mmol). Chromatography in EtOAc/PE 1:4 afforded **43** as a colourless thick syrup (470 mg, 73%), R_f 0.19 (EtOAc/heptane 1:5). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.51 (t, 1H, *J* = 1.6 Hz, H-1), 5.07 (dp, 1H, *J* = 16.3, 1.6 Hz, H-3), 4.77 (ddddd, 1H, *J* = 10.5, 5.9, 1.6, 1.1, 0.9 Hz, H-5), 4.42 (dtd, 1H, *J* = 44.4, 1.6, 0.9 Hz, H-4), 4.03 (dt, 1H, *J* = 7.9, 1.1 Hz, H-6^{en}), 3.83 (ddd, 1H, *J* = 7.9, 5.9, 5.0 Hz, H-6^{ex}), 3.21 (q, 1H, *J* = 1.6 Hz, H-2), 2.44−2.34 (m, 2H, CH_2CH_3), 1.17 (t, 3H, *J* = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.7 (CO), 100.4 (C-1), 86.8 (d, ^1J = 182.4 Hz, C-4), 73.8 (d, ^2J = 21.0 Hz, C-5), 69.5 (d, ^2J = 34.1 Hz, C-3), 64.2 (d, ^3J = 8.9 Hz, C-6), 58.8 (d, ^3J = 2.2 Hz, C-2), 27.6 (CH_2CH_3), 9.0 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −185.17 (dddd, ^2J = 44.4 Hz, ^3J = 16.3, 10.5 Hz, ^4J = 5.0 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_9H_{13}FNO_4$, 218.0823; found, 218.0823.

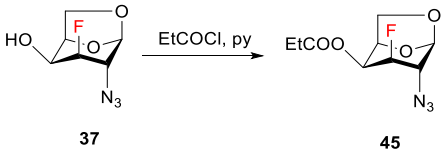
1,6-Anhydro-2-azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-β-D-glucopyranose (44)



36 **44**

Compound **44** was prepared according to the general procedure for acylation starting from **36** (500 mg, 2.64 mmol) and butyryl chloride (350 µL, 3.37 mmol). Chromatography in EtOAc/PE 1:6 → EtOAc/PE 1:4 afforded **44** as a colourless thick syrup (480 mg, 70%), R_f 0.23 (EtOAc/heptane 1:5). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.52 (t, 1H, J = 1.6 Hz, H-1), 5.07 (dp, 1H, J = 16.3, 1.6 Hz, H-3), 4.77 (ddddd, 1H, J = 10.5, 5.9, 1.6, 1.2, 0.9 Hz, H-5), 4.42 (dtd, 1H, J = 44.4, 1.6, 0.9 Hz, H-4), 4.00 (dt, 1H, J = 7.8, 1.2 Hz, H-6^{en}), 3.83 (ddd, 1H, J = 7.8, 5.9, 4.8 Hz, H-6^{ex}), 3.21 (q, 1H, J = 1.6 Hz, H-2), 2.41−2.29 (m, 2H, COCH_2), 1.67 (h, 2H, J = 7.4 Hz, CH_2CH$_3$), 0.97 (t, 3H, J = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.9 (CO), 100.4 (C-1), 86.8 (d, ^1J = 182.5 Hz, C-4), 73.8 (d, ^2J = 21.2 Hz, C-5), 69.4 (d, ^2J = 34.1 Hz, C-3), 64.2 (d, ^3J = 8.8 Hz, C-6), 58.8 (d, ^3J = 2.3 Hz, C-2), 36.1 (COCH_2), 18.4 (CH_2CH$_3$), 13.7 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −185.13 (dddd, ^2J = 44.4 Hz, ^3J = 16.3, 10.5 Hz, ^4J = 4.8 Hz). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for $C_{10}H_{15}FNO_4$, 232.0979; found, 232.0972.

1,6-Anhydro-2-azido-2,3-dideoxy-3-fluoro-4-*O*-propionyl-β-D-galactopyranose (45)

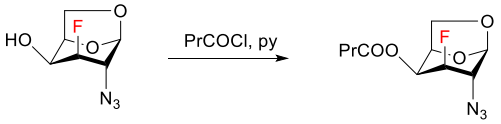


37 **45**

Compound **45** was prepared according to the general procedure for acylation starting from **37** (340 mg, 1.80 mmol) and propionyl chloride (345 µL, 3.95 mmol). Chromatography in EtOAc/PE 1:5 afforded **45** as a colourless thick syrup (345 mg, 78%), R_f 0.23 (EtOAc/PE 1:5). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.52 (t, 1H, J = 1.5 Hz, H-1), 5.04 (ddd, 1H, J = 26.3, 4.5, 4.2 Hz, H-4), 4.94 (dddt, 1H, J = 48.3, 4.5, 1.7, 1.6 Hz, H-3), 4.54 (dddd, 1H, J = 5.1, 4.2, 1.6, 0.8 Hz, H-5), 4.32 (dd, 1H,

J = 7.6, 0.8 Hz, H-6^{en}), 3.76 (ddd, 1H, J = 7.6, 5.1, 1.2 Hz, H-6^{ex}), 3.71 (dt 1H, J = 14.7, 1.6 Hz, H-2), 2.42 (q, 2H, J = 7.6 Hz, CH_2CH$_3$), 1.17 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.2 (CO), 100.0 (C-1), 86.5 (d, ^1J = 189.5 Hz, C-3), 72.2 (d, ^3J = 1.2 Hz, C-5), 66.2 (d, ^2J = 16.1 Hz, C-4), 65.0 (d, ^4J = 3.6 Hz, C-6), 61.4 (d, ^2J = 24.7 Hz, C-2), 27.4 (CH$_2$CH$_3$), 9.1 (CH$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −198.07 (ddd, ^2J = 48.3 Hz, ^3J = 26.3, 14.7 Hz). HRMS-APCI (m/z): [M − N$_2$ + H]$^+$ calcd for C$_9$H$_{13}$FNO$_4$, 218.0823; found, 218.0829.

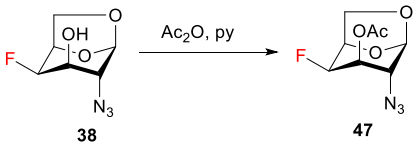
1,6-Anhydro-2-azido-4-*O*-butyryl-2,3-dideoxy-3-fluoro-β-D-galactopyranose (46)



37 **46**

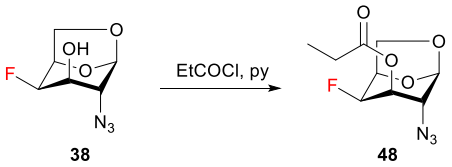
Compound **46** was prepared according to the general procedure for acylation starting from **37** (331 mg, 1.75 mmol) and butyryl chloride (362 μL, 3.49 mmol). Chromatography in EtOAc/PE 1:5 afforded **46** as a colourless thick syrup (376 mg, 83%), R_f 0.26 (EtOAc/PE 1:5). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.52 (t, 1H, J = 1.5 Hz, H-1), 5.04 (dddd, 1H, J = 26.2, 4.9, 4.5, 1.2 Hz, H-4), 4.88 (ddtd, 1H, J = 48.1, 4.5, 1.6, 1.2 Hz, H-3), 4.54 (dddd, 1H, J = 5.1, 4.9, 1.2, 1.1 Hz, H-5), 4.32 (dd, 1H, J = 7.6, 1.1 Hz, H-6^{en}), 3.77 (ddt, 1H, J = 7.6, 5.1, 1.2 Hz, H-6^{ex}), 3.71 (dt 1H, J = 14.7, 1.6 Hz, H-2), 2.43−2.31 (m, 2H, COCH_2), 1.68 (h, 2H, J = 7.4 Hz, CH_2CH$_3$), 0.97 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.4 (CO), 100.0 (C-1), 86.5 (d, ^1J = 189.5 Hz, C-3), 72.2 (d, ^3J = 1.3 Hz, C-5), 66.1 (d, ^2J = 16.1 Hz, C-4), 65.0 (d, ^4J = 3.6 Hz, C-6), 61.4 (d, ^2J = 24.8 Hz, C-2), 35.9 (COCH$_2$), 18.5 (CH$_2$CH$_3$), 13.7 (CH$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −197.95 (ddd, ^2J = 48.1 Hz, ^3J = 26.2, 14.7 Hz). HRMS-APCI (m/z): [M − N$_2$ + H]$^+$ calcd for C$_{10}$H$_{15}$FNO$_4$, 232.0979; found, 232.0980.

1,6-Anhydro-3-*O*-acetyl-2-azido-2,4-dideoxy-4-fluoro-β-D-galactopyranose (47)



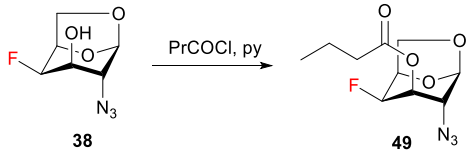
Compound **47** was prepared according to the general procedure for acylation starting from **38** as described in the published procedure.[4]

1,6-Anhydro-2-azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-β-D-galactopyranose (48)



Compound **48** was prepared according to the general procedure for acylation starting from **38** (600 mg, 3.17 mmol) and propionyl chloride (480 µL, 5.49 mmol). Chromatography in EtOAc/PE 1:6 afforded **48** as a colourless thick syrup (590 mg, 76%), R_f 0.65 (EtOAc/PE 1:4). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.43 (ddd, 1H, J = 4.8, 1.7, 1.4 Hz, H-1), 5.38 (dddd, 1H, J = 5.5, 3.3, 1.7, 1.4 Hz, H-3), 4.91 (dddd, 1H, J = 44.3, 5.5, 4.4, 1.1 Hz, H-4), 4.64 (dddd, 1H, J = 5.0, 4.4, 1.3, 0.6 Hz, H-5), 4.43 (dt, 1H, J = 7.7, 0.6 Hz, H-6^{en}), 3.77 (ddd, 1H, J = 7.7, 5.0, 1.7 Hz, H-6^{ex}), 3.59 (dt, 1H, J = 3.6, 1.7 Hz, H-2), 2.43 (q, 2H, J = 7.6 Hz, CH_2CH$_3$), 1.18 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.3 (CO), 100.2 (d, ^4J = 1.4 Hz, C-1), 82.3 (d, ^1J = 194.3 Hz, C-4), 72.2 (d, ^2J = 27.2 Hz, C-5), 67.7 (d, ^2J = 15.2 Hz, C-3), 64.4 (C-6), 62.8 (d, ^3J = 2.2 Hz, C-2), 27.7 (*C*H$_2$CH$_3$), 9.0 (CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −206.36 (dddd, ^2J = 44.3 Hz, ^3J = 3.3 Hz, ^4J = 3.6 Hz, ^5J = 4.8 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_9H_{13}FNO_4$, 218.0823; found, 218.0823.

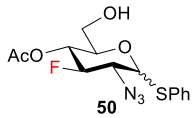
1,6-Anhydro-2-azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-β-D-galactopyranose (49)



38 49

Compound **49** was prepared according to the general procedure for acylation starting from **38** (660 mg, 3.49 mmol) and butyryl chloride (470 μL, 4.53 mmol). Chromatography in EtOAc/PE 1:6 afforded **49** as a colourless thick syrup (631 mg, 70%), R_f 0.68 (EtOAc/PE 1:4). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.43 (dt, 1H, *J* = 4.9, 1.5 Hz, H-1), 5.38 (ddt, 1H, *J* = 5.4, 3.9, 1.5 Hz, H-3), 4.91 (dddd, 1H, *J* = 44.9, 5.4, 4.5, 1.1 Hz, H-4), 4.64 (ddd, 1H, *J* = 5.1, 4.5, 1.3 Hz, H-5), 4.42 (dt, 1H, *J* = 7.7, 1.3 Hz, H-6^{en}), 3.77 (ddd, 1H, *J* = 7.7, 5.1, 1.1 Hz, H-6^{ex}), 3.58 (dt, 1H, *J* = 3.4, 1.5 Hz, H-2), 2.38 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.69 (h, 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.97 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.5 (CO), 100.2 (C-1), 82.3 (d, ^1J = 194.4 Hz, C-4), 72.2 (d, ^2J = 27.2 Hz, C-5), 67.7 (d, ^2J = 15.1 Hz, C-3), 64.4 (C-6), 62.8 (d, ^3J = 2.3 Hz, C-2), 36.2 (COCH_2), 18.4 (CH_2CH$_3$), 13.7 (CH$_2$$CH_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −206.20 (dddd, ^2J = 44.9 Hz, ^3J = 3.9 Hz, ^4J = 3.4 Hz, ^5J = 4.9 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{10}H_{15}FNO_4$, 232.0979; found, 232.0980.

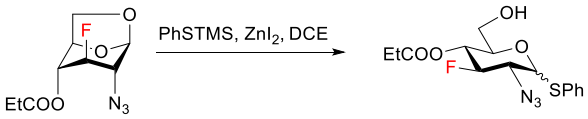
Phenyl 4-*O*-Acetyl-2-azido-2,3-dideoxy-3-fluoro-1-thio-α,β-D-glucopyranoside (50)



50

The compound **50** was prepared according to the published procedure.[3]

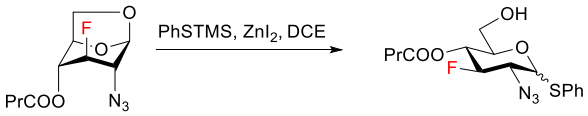
Phenyl 2-Azido-2,3-dideoxy-3-fluoro-4-*O*-propionyl-1-thio-α,β-D-glucopyranoside (51)



40 **51**

Compound **51** was prepared by reaction of **40** (503 mg, 2.05 mmol) with PhSTMS (1.30 mL, 6.86 mmol) and ZnI_2 (1.10 g, 3.45 mmol) in dichloroethane (10 mL) according to the general procedure. The reaction was completed in 24 h when TLC (EtOAc/PE 1:2) showed the absence of **40** (R_f 0.55) and the presence of one major product (R_f 0.7). Chromatography of the residue after work-up (see the general procedure) in EtOAc/PE 1:2 afforded **51** (610 mg, 84%) as a pale orange syrupy mixture of anomers (α/β ≈ 1:0.6), R_f 0.15 (EtOAc/heptane 1:2). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1010. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.57 (m, 1H, CH_{arom}), 7.49–7.47 (m, 2H, CH_{arom}), 7.38–7.30 (m, 2H, CH_{arom}), 5.65 (dd, 1H, *J* = 5.8, 3.1 Hz, H-1), 5.16 (ddd, 1H, *J* = 13.8, 10.2, 8.9 Hz, H-4), 4.83 (ddd, 1H, *J* = 52.6, 9.9, 8.9 Hz, H-3), 4.25 (ddd, 1H, *J* = 10.2, 3.8, 2.3 Hz, H-5), 4.11 (ddd, 1H, *J* = 11.3, 9.9, 5.8 Hz, H-2), 3.77–3.56 (m, 2H, H-6), 2.51–2.25 (m, 3H, C*H*$_2$CH$_3$, O*H*), 1.28–1.14 (m, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.4 (CO), 134.1 (CH_{arom}), 132.4, 129.5 (2 × 2CH_{arom}), 129.2 (C_q), 91.5 (d, ^1J = 189.4 Hz, C-3), 86.4 (d, ^3J = 7.7 Hz, C-1), 70.8 (d, ^3J = 5.8 Hz, C-5), 68.9 (d, ^2J = 17.9 Hz, C-4), 62.4 (d, ^2J = 17.3 Hz, C-2), 60.9 (d, ^4J = 1.1 Hz, C-6), 27.6 (*C*H$_2$CH$_3$), 9.2 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.52 (dddd, ^1J = 52.6 Hz, ^2J = 13.8, 11.3 Hz, ^4J = 3.1 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY) δ 7.38–7.30 (m, 5H, CH_{arom}), 5.03 (ddd, 1H, *J* = 12.4, 10.1, 9.1 Hz, H-4), 4.48 (dt, 1H, *J* = 51.4, 9.1 Hz, H-3), 4.44 (dd, 1H, *J* = 10.2, 0.9 Hz, H-1), 3.77–3.55 (m, 2H, H-6), 3.50 (ddd, 1H, *J* = 12.6, 10.2, 9.1 Hz, H-2), 3.41 (dddd, 1H, *J* = 10.1, 4.9, 2.3, 1.2 Hz, H-5), 2.51–2.25 (m, 3H, C*H*$_2$CH$_3$, O*H*), 1.22–1.14 (m, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.9 (CO), 130.3 (C_q), 129.4 (3CH_{arom}), 128.4 (2CH_{arom}), 93.9 (d, ^1J = 192.1 Hz, C-3), 85.5 (d, ^3J = 6.9 Hz, C-1), 77.8 (d, ^3J = 5.2 Hz, C-5), 68.2 (d, ^2J = 18.2 Hz, C-4), 63.3 (d, ^2J = 17.4 Hz, C-2), 61.4 (d, ^4J = 1.7 Hz, C-6), 27.5 (*C*H$_2$CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −188.68 (dddd, ^1J = 51.4 Hz, ^2J = 12.6, 12.4 Hz, ^5J = 1.2 Hz).

Phenyl 2-Azido-4-*O*-butyryl-2,3-dideoxy-3-fluoro-1-thio-α,β-D-glucopyranoside (52)

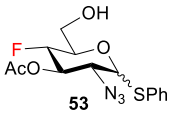


41 52

Compound **52** was prepared by reaction of **41** (537 mg, 2.07 mmol) with PhSTMS (1.30 mL, 6.86 mmol) and ZnI_2 (1.10 g, 3.45 mmol) in dichloroethane (10 mL) according to the general procedure. The reaction was completed in 24 h when TLC (EtOAc/PE 1:2) showed the absence of **41** (R_f 0.58) and the presence of one major product (R_f 0.7). Chromatography of the residue after work-up (see the general procedure) in EtOAc/PE 1:2 afforded **52** (545 mg, 71%) as a reddish syrupy mixture of anomers (α/β 1:0.7), R_f 0.16 (EtOAc/heptane 1:2). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{21}FNO_4S$, 342.1168; found, 342.1156. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.59–7.57 (m, 1H, CH_{arom}), 7.49–7.47 (m, 2H, CH_{arom}), 7.39–7.30 (m, 2H, CH_{arom}), 5.65 (dd, 1H, *J* = 5.8, 3.1 Hz, H-1), 5.16 (ddd, 1H, *J* = 13.8, 10.2, 8.9 Hz, H-4), 4.83 (ddd, 1H, *J* = 52.6, 10.0, 8.9 Hz, H-3), 4.25 (ddd, 1H, *J* = 10.2, 3.8, 2.3 Hz, H-5), 4.11 (ddd, 1H, *J* = 11.4, 10.0, 5.8 Hz, H-2), 3.77–3.55 (m, 2H, H-6), 2.45–2.27 (m, 3H, COCH_2, O*H*), 1.75–1.60 (m, 2H, CH_2CH$_3$), 0.98 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.6 (CO), 134.1 (CH_{arom}), 132.4, 129.5 (2 × 2CH_{arom}), 129.1 (C_q), 91.5 (d, ^1J = 189.4 Hz, C-3), 86.4 (d, ^3J = 7.7 Hz, C-1), 70.8 (d, ^3J = 5.6 Hz, C-5), 68.8 (d, ^2J = 18.1 Hz, C-4), 62.4 (d, ^2J = 17.1 Hz, C-2), 60.9 (d, ^4J = 1.0 Hz, C-6), 36.1 (CO*C*H$_2$), 18.5 (*C*H$_2$CH$_3$), 13.7 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.45 (dddd, ^1J = 52.6 Hz, ^2J = 13.8, 11.4 Hz, ^4J = 3.1 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.39–7.30 (m, 5H, CH_{arom}), 5.03 (ddd, 1H, *J* = 12.3, 10.1, 9.1 Hz, H-4), 4.48 (dt, 1H, *J* = 51.5, 9.1 Hz, H-3), 4.44 (dd, 1H, *J* = 10.2, 0.9 Hz, H-1), 3.77–3.55 (m, 2H, H-6), 3.49 (ddd, 1H, *J* = 12.5, 10.2, 9.1 Hz, H-2), 3.40 (dddd, 1H, *J* = 10.1, 5.0, 2.4, 1.2 Hz, H-5), 2.45–2.27 (m, 3H, COCH_2, O*H*), 1.75–1.60 (m, 2H, CH_2CH$_3$), 0.95 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.1 (CO), 130.3 (C_q), 129.4 (3CH_{arom}), 128.3 (2CH_{arom}), 93.9 (d, ^1J = 192.2 Hz, C-3), 85.5 (d, ^3J = 6.8 Hz, C-1), 77.8 (d, ^3J = 6.2 Hz, C-5), 68.1 (d, ^2J = 18.3 Hz, C-4), 63.3 (d, ^2J = 17.5 Hz, C-2), 61.4 (d, ^4J = 1.5 Hz, C-6),

36.0 ($COCH_2$), 18.5 (CH_2CH_3), 13.6 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −188.61 (dddd, ^1J = 51.5 Hz, ^2J = 12.5, 12.3 Hz, ^5J = 1.2 Hz).

Phenyl 3-*O*-Acetyl-2-azido-2,4-dideoxy-4-fluoro-1-thio-α,β-D-glucopyranoside (53)

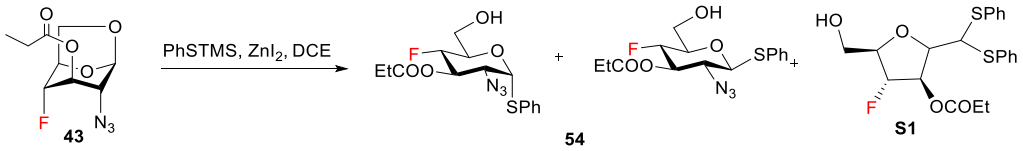


53

The compound **53** was prepared according to the published procedure.[3]

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-1-thio-α-D-glucopyranoside (α-54)

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-1-thio-β-D-glucopyranoside (β-54)

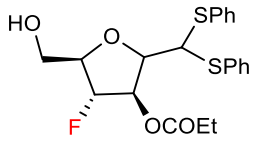


43 **54** **S1**

Thioglycoside **54** was prepared by reaction of **43** (400 mg, 1.63 mmol) with PhSTMS (1.00 mL, 5.28 mmol) and ZnI_2 (0.90 g, 2.82 mmol) in dichloroethane (7 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:5) showed the absence of the **43** (R_f 0.19) and the presence of one major product (R_f 0.75). Chromatography of the residue after work-up (see the general procedure) in Et_2O/PE 3:2 first afforded the β-anomer (β-**54**) (86 mg, 15%) as a colourless syrup. Continued elution gave the α-anomer (α-**54**) (385 mg, 66%) as a colourless syrup in ca 90% purity (by ^{19}F NMR, see below) sufficient for the next deoxyfluorination step. Data for α-**54**: R_f 0.27 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.49 (m, 2H, CH_{arom}), 7.34–7.32 (m, 3H, CH_{arom}), 5.59 (dd, 1H, J = 5.5, 2.7 Hz, H-1), 5.51 (ddd, 1H, J = 13.0, 10.6, 8.7 Hz, H-3), 4.54 (ddd, 1H, J = 50.2, 9.9, 8.7 Hz, H-4), from ^{1}H {^{19}F} 4.44 (dt, 1H, J = 9.9, 3.2 Hz, H-5), 3.94 (ddd, 1H, J = 10.6, 5.5, 1.1 Hz, H-2), 3.78–3.87 (m, 2H, H-6), 2.46 (q, 2H, J = 7.6 Hz, CH_2CH_3), 1.71 (br s, 1H, OH), 1.21 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.2 (CO), 132.8 ($2CH_{arom}$), 132.5 (C_q), 129.4 ($2CH_{arom}$), 128.4 (CH_{arom}), 87.0 (d, ^4J = 1.4 Hz, C-1), 86.9 (d, ^1J = 187.0 Hz, C-4),

71.5 (d, ^{2}J = 19.6 Hz, C-3), 70.5 (d, ^{2}J = 25.0 Hz, C-5), 61.8 (d, ^{3}J = 7.1 Hz, C-2), 60.8 (C-6), 27.6 (*C*H_2CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −199.77 (m). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1009.

The impurity in the α-anomer has been tentatively assigned the following structure: 2,5-Anhydro-4-deoxy-4-fluoro-3-*O*-propionyl-D-mannose/D-glucose diphenyl dithioacetal (**S1**)

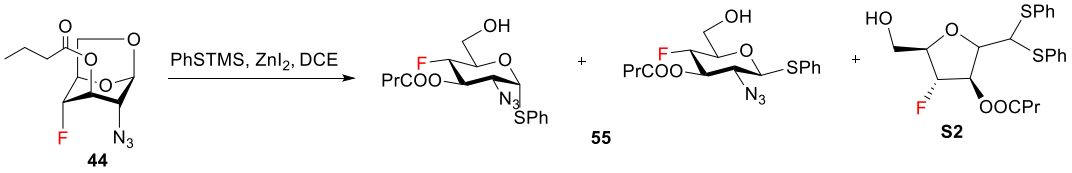


Resolved NMR signals for **S1**: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.77 (ddd, 1H, *J* = 18.4, 4.3, 3.2 Hz, H-3), 5.08 (ddd, 1H, *J* = 53.3, 4.9, 3.2 Hz, H-4), 4.78 (d, 1H, *J* = 5.4 Hz, H-1), 4.28 (ddt, 1H, *J* = 20.1, 4.9, 4.3 Hz, H-5), 4.21 (dd, 1H, *J* = 5.4, 4.3 Hz, H-2), 3.69–3.66 (m, 2H, H-6). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 95.5 (d, ^{1}J = 186.3 Hz, C-4), 84.5 (d, ^{3}J = 4.8 Hz, C-2), 82.9 (d, ^{2}J = 26.0 Hz, C-5), 79.4 (d, ^{2}J = 26.6 Hz, C-3), 61.6 (d, ^{4}J = 0.9 Hz, C-1), 61.1 (d, ^{3}J = 5.2 Hz, C-6). ^{19}F NMR (CDCl$_3$, 376 MHz): −192.89 (ddd, ^{2}J = 53.3 Hz, ^{3}J = 20.1, 18.4 Hz). HRMS-APCI (*m/z*): [M + NH_4]$^+$ calcd for $C_{21}H_{23}FO_4S_2NH_4$, 440.1360; found, 440.1354. The configuration at C2 was not determined.

Data for β-**54**: R_f 0.30 (Et_2O/PE 3:2). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.56–7.54 (m, 2H, CH$_{arom}$), 7.38–7.36 (m, 3H, CH$_{arom}$), 5.25 (ddd, 1H, *J* = 13.6, 9.8, 9.1 Hz, H-3), 4.57 (d, 1H, *J* = 10.1 Hz, H-1), 4.41 (ddd, 1H, *J* = 50.4, 9.7, 9.1 Hz, H-4), 3.95 (dddd, 1H, *J* = 12.3, 5.8, 2.4, 2.2 Hz, H-6), 3.77 (dddd, 1H, *J* = 12.3, 7.3, 4.5, 2.2 Hz, H-6'), 3.58 (dddd, 1H, *J* = 9.7, 4.5, 2.4, 2.8 Hz, H-5), 3.35 (ddd, 1H, *J* = 10.1, 9.8, 0.9 Hz, H-2), 2.43 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.89 (dd, 1H, *J* = 7.3, 5.8 Hz, OH), 1.19 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.3 (CO), 133.7 (2CH$_{arom}$), 130.7 (C$_q$), 129.4 (2CH$_{arom}$), 129.0 (CH$_{arom}$), 86.4 (d, ^{4}J = 1.5 Hz, C-1), 86.2 (d, ^{1}J = 187.0 Hz, C-4), 77.8 (d, ^{2}J = 23.7 Hz, C-5), 73.9 (d, ^{2}J = 19.4 Hz, C-3), 63.1 (d, ^{3}J = 7.4 Hz, C-2), 61.3 (C-6), 27.6 (*C*H_2CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −201.05 (ddddd, ^{2}J = 50.4 Hz, ^{3}J = 13.6, 2.8 Hz, ^{4}J = 2.2, 0.9 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1015.

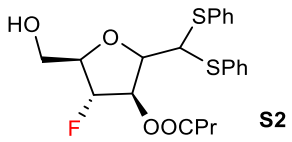
Phenyl 2-Azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-α-D-glucopyranoside (α-55)

Phenyl 2-Azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-β-D-glucopyranoside (β-55)



Thioglycoside **55** was prepared by reaction of **44** (460 mg, 1.77 mmol) with PhSTMS (1.10 mL, 5.81 mmol) and ZnI_2 (1.00 g, 3.13 mmol) in dichloroethane (8 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:5) showed the absence of **44** (R_f 0.23) and the presence of one major product (R_f 0.75). Chromatography of the residue after work-up (see the general procedure) in Et_2O/PE 2:1 → Et_2O/PE 1:1 first afforded the β-anomer β-**55** (83 mg, 13%) as a crystalline solid, followed by the α-anomer α-**55** (320 mg, 49 %) as thick colourless syrup. Both anomers were isolated in ca 90% purity and the impurities were removed in the next step. Data for α-**55** R_f 0.28 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.51–7.49 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.59 (dd, 1H, *J* = 5.5, 2.7 Hz, H-1), 5.50 (ddd, 1H, *J* = 12.9, 10.7, 8.7 Hz, H-3), 4.54 (ddd, 1H, *J* = 49.6, 9.9, 8.7 Hz, H-4), from^{1}H {^{19}F} 4.44 (ddd, 1H, *J* = 9.9, 3.6, 2.6 Hz, H-5), 3.93 (ddd, 1H, *J* = 10.7, 5.5, 1.1 Hz, H-2), 3.88–3.80 (m, 2H, H-6), 2.41 (t, *J* = 7.4 Hz, $COCH_2$), 1.72 (h, 2H, *J* = 7.4 Hz, CH_2CH_3), overlapped 1.71 (br s, 1H, OH), 0.99 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.3 (CO), 132.8 ($2CH_{arom}$), 132.5 (C_q), 129.4 ($2CH_{arom}$), 128.4 (CH_{arom}), 87.0 (d, ^4J = 1.4 Hz, C-1), 86.9 (d, ^1J = 187.0 Hz, C-4), 71.3 (d, ^2J = 19.5 Hz, C-3), 70.5 (d, ^2J = 25.1 Hz, C-5), 61.8 (d, ^3J = 7.1 Hz, C-2), 60.8 (C-6), 36.1 ($COCH_2$), 18.43 (CH_2CH_3), 13.6 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −199.72 (m). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{21}FNO_4S$, 342.1169; found, 342.1171

The impurity in the α-anomer has been tentatively assigned the structure of the ring-contracted product: 2,5-anhydro-4-deoxy-4-fluoro-3-*O*-butyryl-D-mannose/D-glucose diphenyl dithioacetal (**S2**).



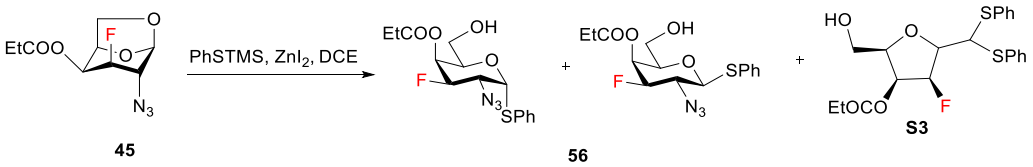
S2

Resolved NMR signals for **S2**: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.77 (ddd, 1H, *J* = 18.4, 4.2, 3.2 Hz, H-3), 5.08 (ddd, 1H, *J* = 53.3, 4.9, 3.2 Hz, H-4), 4.78 (d, 1H, *J* = 5.4 Hz, H-1), 4.28 (ddt, 1H, *J* = 20.1, 4.9, 4.0 Hz, H-5), 4.21 (dd, 1H, *J* = 5.4, 3.2 Hz, H-2), 3.69–3.66 (m, 2H, H-6). ^{19}F NMR ($CDCl_3$, 376 MHz): −192.95 (ddd, ^{2}J = 53.3 Hz, ^{3}J = 20.1, 18.4 Hz). HRMS-APCI (*m/z*): [M + NH_4]$^{+}$ calcd for $C_{22}H_{25}FO_4S_2NH_4$, 454.1516; found, 454.1511. The configuration at C2 was not determined.

Data for β-**55**: mp 83–86 °C (EtOAc/PE), R_f 0.32 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.57–7.54 (m, 2H, CH_{arom}), 7.38–7.36 (m, 3H, CH_{arom}), 5.25 (ddd, 1H, *J* = 13.5, 9.8, 9.1 Hz, H-3), 4.57 (d, 1H, *J* = 10.2 Hz, H-1), 4.41 (ddd, 1H, *J* = 50.5, 9.8, 9.1 Hz, H-4), from ^{1}H {^{19}F} 3.95 (ddd, 1H, *J* = 12.4, 5.9, 2.4 Hz, H-6), from ^{1}H {^{19}F} 3.77 (ddd, 1H, *J* = 12.4, 7.4, 4.5 Hz, H-6), 3.58 (dddd, 1H, *J* = 9.8, 4.5, 3.1, 2.4 Hz, H-5), 3.35 (ddd, 1H, *J* = 10.2, 9.8, 0.9 Hz, H-2), 2.38 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.85 (dd, 1H, *J* = 7.4, 5.9 Hz, OH), 1.70 (h, 2H, *J* = 7.4 Hz, C$H_2$$CH_3$), 0.97 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.4 (CO), 133.8 (2CH_{arom}), 130.7 (C_q), 129.4 (2CH_{arom}), 129.1 (CH_{arom}), 86.5 (d, ^{4}J = 1.1 Hz, C-1), 86.2 (d, ^{1}J = 186.8 Hz, C-4), 77.8 (d, ^{2}J = 23.6 Hz, C-5), 73.8 (d, ^{2}J = 19.5 Hz, C-3), 63.1 (d, ^{3}J = 7.5 Hz, C-2), 61.3 (C-6), 36.1 (COCH_2), 18.5 (CH_2CH_3), 13.6 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −201.00 (ddddd, ^{2}J = 50.5 Hz, ^{3}J = 13.5, 3.1 Hz, ^{4}J = 1.4, 0.9 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^{+}$ calcd for $C_{16}H_{20}FNO_4S$, 342.1169; found, 342.1168.

Phenyl 2-Azido-2,3-dideoxy-3-fluoro-4-*O*-propionyl-1-thio-α-D-galactopyranoside (α-56)

Phenyl 2-Azido-2,3-dideoxy-3-fluoro-4-*O*-propionyl-1-thio-β-D-galactopyranoside (β-56)

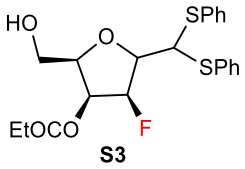


45 **56** **S3**

Thioglycoside **56** was prepared by reaction of **45** (1.016 g, 4.14 mmol) with PhSTMS (2.60 mL, 13.73 mmol) and ZnI_2 (2.30 g, 7.21 mmol) in dichloroethane (20 mL) according to the general procedure. The reaction was completed in 72 h when TLC (EtOAc/PE 1:3) showed the absence of **45** (R_f 0.65) and the presence of one major product (R_f 0.8). Chromatography of the residue after work-up (see the general procedure) in EtOAc/PE 1:3 afforded first the α-anomer α-**56** (744 mg, 51%) as a colourless syrup followed by the β-anomer β-**56** (436 mg, 30%) as a colourless syrup. The α-anomer α-**56** was isolated in 90% purity (^{19}F NMR) due to the presence of the ring-contracted product **S3**. Data for α-**56**: R_f 0.32 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.51–7.47 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.66 (dd, 1H, *J* = 5.7, 4.1 Hz, H-1), 5.56 (ddd, 1H, *J* = 6.5, 3.6, 1.1 Hz, H-4), 4.86 (ddd, 1H, *J* = 47.7, 10.4, 3.6 Hz, H-3), 4.50 (td, 1H, *J* = 6.8, 1.1 Hz, H-5), 4.39 (ddd, 1H, *J* = 10.4, 10.0, 5.7 Hz, H-2), 3.56 (ddd, 1H, *J* = 11.8, 7.0, 6.8 Hz, H-6'), 3.47 (ddd, 1H, *J* = 11.8, 7.0, 6.8 Hz, H-6), 2.52–2.42 (m, 2H, C*H*$_2$CH$_3$), 2.27 (t, *J* = 7.0 Hz, O*H*), 1.20 (t, 3H, *J* = 7.5 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.8 (CO), 133.0 ($2CH_{arom}$), 132.1 (C_q), 129.4 ($2CH_{arom}$), 128.5 (CH_{arom}), 88.4 (d, ^1J = 193.3 Hz, C-3), 86.8 (d, ^3J = 7.4 Hz, C-1), 70.1 (d, ^3J = 4.4 Hz, C-5), 68.1 (d, ^2J = 16.2 Hz, C-4), 60.4 (d, ^4J = 2.4 Hz, C-6), 59.7 (d, ^2J = 18.3 Hz, C-2), 27.5 (*C*H$_2$CH$_3$), 9.2 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −197.94 (dddddd, ^2J = 47.7 Hz, ^3J = 10.0, 6.5 Hz, ^4J = 4.1, 1.6 Hz, ^5J = 1.3 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1015. Data for β-**56**: R_f 0.20 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.58 (m, 2H, CH_{arom}), 7.37–7.34 (m, 3H, CH_{arom}), 5.43 (ddd, 1H, *J* = 6.4, 3.5, 0.9 Hz, H-4), 4.51 (ddd, 1H, *J* = 46.8, 9.5, 3.5 Hz, H-3), 4.44 (dd, 1H, *J* = 10.1, 0.9 Hz, H-1), 3.75 (ddd, 1H, *J* = 11.0, 10.1, 9.5 Hz, H-2), 3.73 from ^{1}H {^{19}F} (dd, 1H, *J* = 11.7, 6.3 Hz, H-6'), 3.63 (dddd, 1H, *J* = 7.0, 6.3, 1.7, 0.9 Hz, H-5), 3.46 (dd, 1H, *J* = 11.7, 7.0 Hz, H-6), 2.41 (q, 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.15 (t, 3H, *J* = 7.5 Hz, C*H*$_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 175.0 (CO), 133.9 ($2CH_{arom}$), 130.7 (C_q), 129.2 ($2CH_{arom}$), 128.9 (CH_{arom}), 90.9 (d, ^{1}J = 195.8 Hz, C-3), 86.0 (d, ^{3}J = 6.6 Hz, C-1), overlapped with $CDCl_3$ (C-5), 67.3 (d, ^{2}J = 16.3 Hz, C-4), 60.8 (d, ^{2}J = 18.3 Hz, C-2), 60.4 (d, ^{4}J = 2.4 Hz, C-6), 27.5 (CH_2CH_3), 9.2 (CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −191.13 (ddd, ^{2}J = 46.8 Hz, ^{3}J = 11.0, 6.4 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1014.

The impurity in the α-anomer has been tentatively assigned the following structure of the ring-contracted by-product: 2,5-anhydro-3-deoxy-3-fluoro-4-*O*-propionyl-D-galactose/D-talose diphenyl dithioacetal:

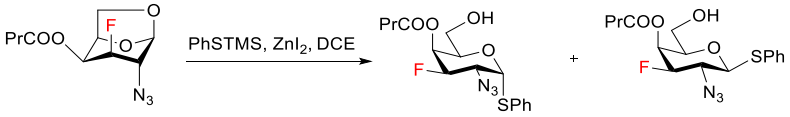


S3

Resolved NMR signals for **S3**: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC): δ 5.49 (ddd, 1H, *J* = 7.5, 4.3, 3.5 Hz, H-4), 5.31 (ddd, 1H, *J* = 45.6, 9.5, 3.5 Hz, H-3), 4.70 (t, 1H, *J* = 1.8 Hz, H-1), 4.13–4.09 (m, 1H, H-2). ^{19}F NMR ($CDCl_3$, 376 MHz): –208.30 (br d, ^{2}J = 45.6 Hz). HRMS-APCI (*m/z*): $[M + NH_4]^+$ calcd for $C_{21}H_{23}FO_4S_2NH_4$, 440.1360; found, 440.1357. The configuration at C2 was not determined.

Phenyl 2-Azido-4-*O*-butyryl-2,3-dideoxy-3-fluoro-1-thio-α-D-galactopyranoside (α-57)

Phenyl 2-Azido-4-*O*-butyryl-2,3-dideoxy-3-fluoro-1-thio-β-D-galactopyranoside (β-57)



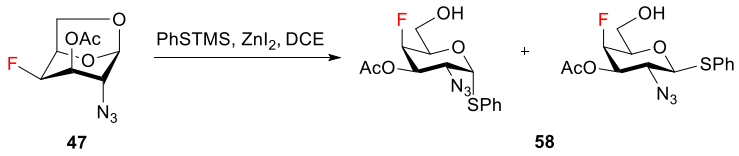
46 **57**

Thioglycoside **57** was prepared by reaction of **46** (656 mg, 2.53 mmol) with PhSTMS (1.60 mL, 8.45 mmol) and ZnI_2 (1.41 g, 4.42 mmol) in dichloroethane (13 mL) according to the general procedure. The reaction was completed in 72 h when TLC (EtOAc/PE 1:3) showed the absence of **46** (R_f 0.68) and the presence of one major product (R_f 0.8). Chromatography of the residue after work-up (see the general procedure) in Et_2O/PE 1:1.2 first afforded the α-anomer (α-**57**) (283 mg, 30%) as a colourless syrup

followed by the β-anomer (β-**57**) (256 mg, 27%) as a thick colourless syrup. Data for α-**57**: R_f 0.20 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.48 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.67 (dd, 1H, *J* = 5.7, 4.1 Hz, H-1), 5.56 (ddd, 1H, *J* = 6.5, 3.6, 1.1 Hz, H-4), 4.87 (ddd, 1H, *J* = 47.4, 10.4, 3.6 Hz, H-3), 4.51 (ddd, 1H, *J* = 7.5, 6.4, 1.1 Hz, H-5), 4.39 (ddd, 1H, *J* = 10.4, 10.2, 5.7 Hz, H-2), 3.56 (dddd, 1H, *J* = 11.8, 7.5, 6.5, 1.5 Hz, H-6), 3.47 (ddd, 1H, *J* = 11.8, 6.4, 6.5 Hz, H-6'), 2.50–2.37 (m, 2H, COCH_2), 2.27 (t, 1H, *J* = 6.5 Hz, O*H*), 1.70 (h, 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.98 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1 (CO), 133.1 ($2CH_{arom}$), 132.1 (C_q), 129.4 ($2CH_{arom}$), 128.5 (CH_{arom}), 88.4 (d, ^1J = 193.4 Hz, C-3), 86.8 (d, ^3J = 7.5 Hz, C-1), 70.1 (d, ^3J = 4.5 Hz, C-5), 68.1 (d, ^2J = 16.2 Hz, C-4), 60.4 (d, ^4J = 2.3 Hz, C-6), 59.7 (d, ^2J = 18.4 Hz, C-2), 36.1 (CO*C*H$_2$), 18.6 (*C*H$_2$CH$_3$), 13.7 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −197.82 (ddd, ^1J = 46.8 Hz, ^2J = 11.5, 6.3 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{21}FNO_4S$, 342.1170; found, 342.1170. Data for β-**57:** R_f 0.17 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.58 (m, 2H, CH_{arom}), 7.38–7.33 (m, 3H, CH_{arom}), 5.43 (ddd, 1H, *J* = 6.3, 3.5, 0.9 Hz, H-4), 4.50 (ddd, 1H, *J* = 46.8, 9.6, 3.5 Hz, H-3), 4.44 (dd, 1H, *J* = 10.0, 0.8 Hz, H-1), 3.76–3.71 (m, 2H, H-2, H-6), 3.63 (dddd, 1H, *J* = 6.7, 6.2, 1.7, 0.9 Hz, H-5), 3.46 (ddd, 1H, *J* = 11.1, 7.0, 6.2 Hz, H-6'), 2.59 (t, 1H, *J* = 7.0 Hz, O*H*), 2.60–2.33 (m, 2H, COCH_2), 1.63 (h, 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.96 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.2 (CO), 134.0 ($2CH_{arom}$), 130.7 (C_q), 129.2 ($2CH_{arom}$), 128.9 (CH_{arom}), 90.9 (d, ^1J = 195.8 Hz, C-3), 85.9 (d, ^3J = 6.5 Hz, C-1), overlapped with $CDCl_3$ (C-5), 67.2 (d, ^2J = 16.5 Hz, C-4), 60.8 (d, ^2J = 18.5 Hz, C-2), 60.4 (d, ^4J = 2.4 Hz, C-6), 30.1 (CO*C*H$_2$), 18.6 (*C*H$_2$CH$_3$), 13.7 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −191.04 (m). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{21}FNO_4S$, 342.1170; found, 342.1173.

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-acetyl-1-thio-α-D-galactopyranoside (α-58)

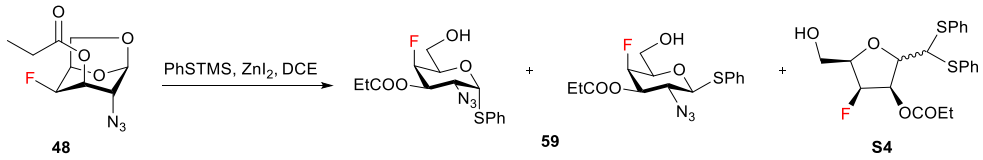
Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-acetyl-1-thio-β-D-galactopyranoside (β-58)



Thioglycoside **58** was prepared by reaction of **47** (804 mg, 3.48 mmol) with PhSTMS (2.50 mL, 13.20 mmol) and ZnI_2 (2.50 g, 7.83 mmol) in dichloroethane (9 mL) according to the general procedure. The details of the synthesis and analytical data of product **58** were published in ref 4.

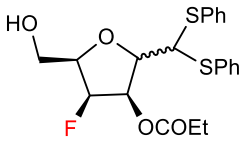
Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-1-thio-α-D-galactopyranoside (α-59)

Phenyl 2-Azido-2,4-dideoxy-4-fluoro-3-*O*-propionyl-1-thio-β-D-galactopyranoside (β-59)



Thioglycoside **59** was prepared by reaction of **48** (590 mg, 2.41 mmol) with PhSTMS (1.50 mL, 7.92 mmol) and ZnI_2 (1.30 g, 4.07 mmol) in dichloroethane (10 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:4) showed the absence of the **48** (R_f 0.65) and the presence of one major product (R_f 0.80). Chromatography of the residue after work-up (see the general procedure) in Et_2O/PE 1:1 first afforded the α-anomer (α-**59**) (305 mg, 36%) obtained in purity ~95% (^{19}F NMR) as a thick colourless syrup, followed by the β-anomer (β-**59**) (335 mg, 39%) as a thick colourless syrup. Data for α-**59**: R_f 0.40 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.53–7.51 (m, 2H, CH_{arom}), 7.36–7.31 (m, 3H, CH_{arom}), 5.67 (d, 1H, J = 5.5 Hz, H-1), 5.10 (ddd, 1H, J = 26.1, 11.1, 2.6 Hz, H-3), 4.97 (ddd, 1H, J = 50.9, 2.6, 0.8 Hz, H-4), 4.50 (ddd, 1H, J = 30.0, 7.4, 5.2 Hz, H-5), 4.38 (dd, 1H, J = 11.1, 5.5 Hz, H-2), 3.82 (ddd, 1H, J = 11.5, 7.4, 1.1 Hz, H-6), 3.74 (dd, 1H, J = 11.5, 5.2 Hz, H-6´), 2.47 (q, 2H, J = 7.5 Hz, CH_2CH_3), 1.61 (br s, 1H, OH), 1.21 (t, 3H, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 173.6 (CO), 133.1 ($2CH_{arom}$), 132.2 (C_q), 129.4 ($2CH_{arom}$), 128.4 (CH_{arom}), 86.9 (C-1), 86.6 (d, ^1J = 184.3 Hz, C-4), 71.0 (d, ^2J = 17.6

Hz, C-3), 70.5 (d, ^{2}J = 17.8 Hz, C-5), 61.1 (d, ^{3}J = 5.6 Hz, C-6), 58.3 (d, ^{4}J = 1.8 Hz, C-2), 27.6 (*C*H_2CH$_3$), 9.0 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −217.90 (ddd, ^{2}J = 50.9 Hz, ^{3}J = 30.0, 26.2 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.1013; found, 328.1015. Data for β-**59**: R_f 0.30 (Et$_2$O/PE 3:2). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.57 (m, 2H, CH$_{arom}$), 7.37–7.34 (m, 3H, CH$_{arom}$), 4.84 (dd, 1H, *J* = 50.7, 2.5 Hz, H-4), 4.82 (ddd, 1H, *J* = 27.0, 10.2, 2.5 Hz, H-3), 4.52 (d, 1H, *J* = 10.1 Hz, H-1), from ^{1}H {^{19}F} 3.93 (dd, 1H, *J* = 11.4, 7.4 Hz, H-6), 3.76–3.70 (m, 2H, H-2, H-6'), 3.67 (ddd, 1H, *J* = 26.7, 7.4, 5.2 Hz, H-5), 2.43 (q, 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.94 (dd, 1H, *J* = 8.4, 3.7 Hz, OH), 1.17 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.7 (CO), 133.5 (2CH$_{arom}$), 130.9 (C$_q$), 129.3 (2CH$_{arom}$), 128.8 (CH$_{arom}$), 86.4 (C-1), 85.6 (d, ^{1}J = 184.1 Hz, C-4), 77.6 (d, ^{2}J = 18.0 Hz, C-5), 73.7 (d, ^{2}J = 17.7 Hz, C-3), 61.2 (d, ^{3}J = 5.0 Hz, C-6), 59.7 (C-2), 27.5 (*C*H$_2$CH$_3$), 9.0 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −218.49 (ddd, ^{2}J = 50.7 Hz, ^{3}J = 27.0, 26.7 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{15}H_{19}FNO_4S$, 328.2013; found, 328.1015. Column chromatography of **59** also gave syrupy by-product **S4** (37 mg) in ca 70% purity (^{19}F NMR), obtained as two inseparable diastereomers. R_f 0.34 (Et$_2$O/PE). HRMS-APCI (*m/z*): [M − SPh]$^+$ calcd for $C_{15}H_{18}FO_4S$, 313.0904; found, 313.0903. The diastereomers were assigned the following structures of 2,5-anhydro-4-deoxy-4-fluoro-3-*O*-propionyl-D-talose and -D-galactose diphenyl dithioacetals.



S4

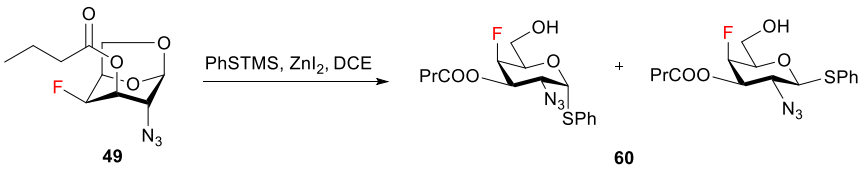
Diastereomer 1: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.47–7.41 (m, 4H, CH$_{arom}$), 7.36–7.22 (m, 6H, CH$_{arom}$), 5.45 (ddd, 1H, *J* = 21.8, 8.0, 4.1 Hz, H-3), 5.30 (ddd, 1H, *J* = 54.7, 4.1, 2.9 Hz, H-4), 4.61 (d, 1H, *J* = 2.9 Hz, H-1), 4.57 (ddd, 1H, *J* = 8.0, 2.9, 0.9 Hz, H-2), 4.39 (dddd, 1H, *J* = 29.0, 5.9, 5.7, 2.9 Hz, H-5), 3.94–3.80 (m, 2H, H-6), 2.42–2.34 (m, 2H, C*H*$_2$CH$_3$), 1.14 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 173.6 (CO), 133.5 (2C$_q$), 133.0, 132.8 (2 × 2CH$_{arom}$), 129.3 (CH$_{arom}$), 129.24 (2CH$_{arom}$), 129.17 (CH$_{arom}$), 129.16 (2CH$_{arom}$), 90.4 (d, ^{1}J = 190.9 Hz, C-4), 81.4 (d, ^{2}J = 17.7 Hz, C-5), 81.0 (C-2), 74.5 (d, ^{2}J = 15.7 Hz, C-3), 62.4 (C-1), 60.6 (d, ^{3}J = 11.9

Hz, C-6), 27.4 (CH_2CH_3), 9.1 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −215.17 (ddd, ^2J = 54.7 Hz, ^3J = 29.0, 21.8 Hz).

Diastereomer 2: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.47–7.41 (m, 4H, CH_{arom}), 7.36–7.22 (m, 6H, CH_{arom}), 5.52 (ddd, 1H, J = 28.4, 10.0, 3.1 Hz, H-3), 5.02 (ddd, 1H, J = 50.2, 4.5, 3.1 Hz, H-4), 4.42 (d, 1H, J = 1.9 Hz, H-1), 4.15 (ddd, 1H, J = 10.0, 1.9, 0.9 Hz, H-2), 4.00–3.80 (m, 3H, H-5, 2H-6), 2.48 (q, 2H, J = 7.6 Hz, CH_2CH_3), 0.97 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 172.8 (CO), 133.5 ($2C_q$), 133.0, 132.9 (2 × $2CH_{arom}$), 129.4 (CH_{arom}), 128.22, 128.20 (2 × $2CH_{arom}$), 128.1 (CH_{arom}), 87.1 (d, ^1J = 180.6 Hz, C-4), 76.6 (d, ^3J = 1.3 Hz, C-2), 67.83 (m, C-3, C-5, C-6), 62.3 (C-1), 27.3 (CH_2CH_3), 8.9 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −206.24 (ddq, ^2J = 50.2 Hz, ^3J = 28.4, 3.5 Hz, ^4J = 3.5 Hz).

Phenyl 2-Azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-α-D-galactopyranoside (α-60)

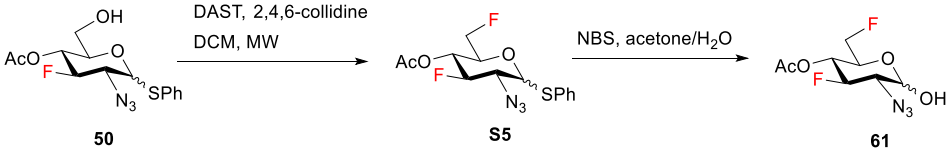
Phenyl 2-Azido-3-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-β-D-galactopyranoside (β-60)



Thioglycoside **60** was prepared by reaction of **49** (590 mg, 2.28 mmol) with PhSTMS (1.40 mL, 7.39 mmol) and ZnI_2 (1.20 g, 3.76 mmol) in dichloroethane (10 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:4) showed the absence of **49** (R_f 0.7) and the presence of one major product (R_f 0.8). Chromatography of the residue after work-up (see the general procedure) in Et_2O/PE 1:1 first afforded the α-anomer (α-**60**) (344 mg, 41%) as a thick colourless syrup, followed by the β-anomer (β-**60**) (410 mg, 49%) as thick colourless syrup. Data for α-**60**: R_f 0.42 (Et_2O/PE 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.54–7.50 (m, 2H, CH_{arom}), 7.36–7.31 (m, 3H, CH_{arom}), 5.68 (d, 1H, J = 5.5 Hz, H-1), 5.10 (ddd, 1H, J = 26.0, 11.1, 2.6 Hz, H-3), 4.99 (ddd, 1H, J = 50.9, 2.6, 0.8 Hz, H-4), 4.51 (ddd, 1H, J = 29.9, 7.5, 5.1 Hz, H-5), 4.38 (dd, 1H, J = 11.1, 5.5 Hz, H-2), 3.83 (ddd, 1H, J = 11.6, 7.5, 1.1 Hz, H-6), 3.75 (dd, 1H, J = 11.6, 5.1 Hz, H-6'), 2.43 (t,

2H, *J* = 7.4 Hz, COC*H*$_2$), 1.73 (h, 2H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.00 (t, 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.8 (CO), 133.1 (2CH$_{arom}$), 132.2 (C$_q$), 129.4 (2CH$_{arom}$), 128.4 (CH$_{arom}$), 86.6 (d, ^1J = 184.4 Hz, C-4), 87.0 (C-1), 70.9 (d, ^2J = 17.6 Hz, C-3), 70.5 (d, ^2J = 17.7 Hz, C-5), 61.2 (d, ^3J = 5.5 Hz, C-6), 58.3 (d, ^3J = 1.7 Hz, C-2), 36.1 (CO*C*H$_2$), 18.4 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −217.84 (ddd, ^2J = 50.9 Hz, ^3J = 29.9, 26.0 Hz). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{16}$H$_{21}$FNO$_4$S, 342.1169; found, 342.1177. Data for **β-60**: R_f 0.33 (Et$_2$O/PE 3:2). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.57 (m, 2H, CH$_{arom}$), 7.37–7.34 (m, 3H, CH$_{arom}$), 4.84 (dd, 1H, *J* = 50.5, 2.6 Hz, H-4), 4.82 (ddd, 1H, *J* = 27.3, 10.2, 2.6 Hz, H-3), 4.52 (dd, 1H, *J* = 10.1, 0.8 Hz, H-1), 3.93 (ddd, 1H, *J* = 11.4, 7.5, 1.1 Hz, H-6), 3.77–3.71 (m, 2H, H-2, H-6), 3.67 (ddd, 1H, *J* = 26.5, 7.5, 5.2 Hz, H-5), 2.39 (t, 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.69 (h, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 0.97 (t, 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.9 (CO), 133.5 (2CH$_{arom}$), 130.9 (C$_q$), 129.3 (2CH$_{arom}$), 128.8 (CH$_{arom}$), 86.5 (C-1), 85.6 (d, ^1J = 184.4 Hz, C-4), 77.6 (d, ^2J = 18.1 Hz, C-5), 73.5 (d, ^2J = 17.7 Hz, C-3), 61.3 (d, ^3J = 5.0 Hz, C-6), 61.3 (C-2), 36.1 (CO*C*H$_2$), 18.5 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −218.44 (ddd, ^2J = 50.5 Hz, ^3J = 27.3, 26.5 Hz). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{16}$H$_{21}$FNO$_4$S, 342.1169; found, 342.1171.

4-*O*-Acetyl-2-azido-3,6-difluoro-2,3,6-trideoxy-D-glucopyranose (61)



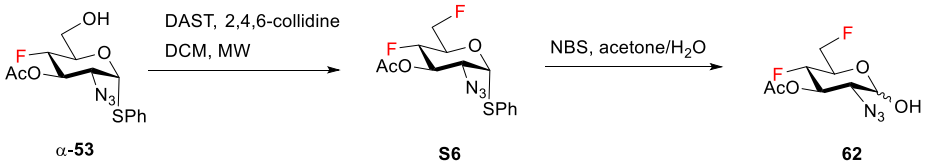
Thioglycoside **50** (340 mg, 1.00 mmol) reacted with diethylaminosulfur trifluoride (170 µL, 1.29 mmol) and 2,4,6-collidine (330 µL, 2.50 mmol) in dichloromethane (7 mL) according to the general procedure. Chromatography of the crude product in Et$_2$O/PE 1:2 first afforded phenyl 4-*O*-acetyl-2-azido-2,3,6-trideoxy-3,6-difluoro-1-thio-α-D-glucopyranoside α-**S5** (165 mg, 48%) as a thick yellowish syrup followed by phenyl 4-O-acetyl-2-azido-2,3,6-trideoxy-3,6-difluoro-1-thio-β-D-glucopyranoside β-**S5** (82 mg, 24%) as a thick yellowish syrup. Data for α-**S5:** R_f 0.54 (EtOAc/heptane 1:3). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.47 (m, 2H, CH$_{arom}$), 7.35–7.31 (m, 3H, CH$_{arom}$), 5.62 (dd,

1H, *J* = 5.7, 3.2 Hz, H-1), 5.23 (ddd, 1H, *J* = 13.4, 10.1, 8.8 Hz, H-4), 4.78 (ddd, 1H, *J* = 53.2, 10.1, 8.9 Hz, H-3), 4.56–4.37 (m, 3H, H-5, 2H-6), 4.11 (ddd, 1H, *J* = 11.1, 10.1, 5.7 Hz, H-2), 2.17 (s, 3H, *Me*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.5 (CO), 132.4 ($2CH_{arom}$), 132.3 (C_q), 129.5 ($2CH_{arom}$), 128.5 (CH_{arom}), 91.7 (dd, ^{1}J = 189.9 Hz, ^{4}J = 1.1 Hz, C-3), 86.6 (d, ^{3}J = 7.7 Hz, C-1), 81.0 (dd, ^{1}J = 176.2, ^{4}J = 1.5 Hz, C-6), 69.3 (dd, ^{2}J = 19.4 Hz, ^{3}J = 6.9 Hz, C-5), 68.0 (dd, ^{2}J = 18.6 Hz, ^{3}J = 6.7 Hz, C-4), 62.2 (d, ^{2}J = 17.2 Hz, C-2), 20.8 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.92 (dddd, ^{2}J = 53.2 Hz, ^{3}J = 13.4, 11.1 Hz, ^{4}J = 3.2 Hz, F-3), −232.99 (ddd, ^{2}J = 47.4, 47.2 Hz, ^{3}J = 23.5 Hz, F-6). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{16}F_2NO_3S$, 316.0813; found, 316.0811. NMR data for β-**S5:** R_f 0.50 (EtOAc/heptane 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, $^{1}H\ \{^{19}F\}$, H-H COSY): δ 7.61–7.59 (m, 2H, CH_{arom}), 7.39–7.36 (m, 3H, CH_{arom}), 5.06 (ddd, 1H, *J* = 11.9, 10.2, 9.1 Hz, H-4), 4.49 (ddd, 1H, *J* = 46.8, 10.5, 2.6 Hz, H-6'), 4.48 (ddd, 1H, *J* = 46.8, 10.5, 4.7 Hz, H-6), 4.57–4.36 (m, 1H, H-3), 4.42 (dd, 1H, *J* = 10.2, 1.0 Hz, H-1), 3.61 (ddddd, 1H, *J* = 20.9, 10.2, 4.7, 2.6, 1.2 Hz, H-5), 3.48 (ddd, 1H, *J* = 12.4, 10.2, 9.1 Hz, H-2), 2.12 (s, 3H, *Me*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.4 (CO), 134.4 ($2CH_{arom}$), 129.9 (C_q), 129.4 ($2CH_{arom}$), 129.3 (CH_{arom}), 93.9 (d, ^{1}J = 192.7 Hz, C-3), 85.5 (d, ^{3}J = 6.8 Hz, C-1), 81.2 (dd, ^{1}J = 176.4, ^{4}J = 1.9 Hz, C-6), 76.0 (dd, ^{2}J = 19.7 Hz, ^{3}J = 7.3 Hz, C-5), 67.5 (dd, ^{2}J = 18.6 Hz, ^{3}J = 6.8 Hz, C-4), 62.0 (d, ^{2}J = 17.5 Hz, C-2), 20.8 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −189.02 (ddd, ^{2}J = 51.3 Hz, ^{3}J = 12.4, 11.9 Hz, F-3), −232.90 (td, ^{2}J = 46.8 Hz, ^{3}J = 20.9 Hz, F-6). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{16}F_2NO_3S$, 316.0813; found, 316.0816.

Compound **61** was prepared according to the general procedure for the thioglycoside hydrolysis starting from **S5** (210 mg, 0.61 mmol). Chromatography in Et_2O/PE 2:1 afforded **61** (123 mg, 80% from **S5**, 58% over two steps) as a colourless thick syrup, R_f 0.17 (Et_2O/PE 2:1). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_8H_{12}F_2NO_4$, 224.0729; found, 224.0729. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, $^{1}H\ \{^{19}F\}$, H-H COSY): δ 5.38 (dd, 1H, *J* = 3.9, 3.5 Hz, H-1), 5.19 (ddd, 1H, *J* = 13.1, 10.4, 8.9 Hz, H-4), 4.94 (ddd, 1H, *J* = 53.1, 9.9, 8.9 Hz, H-3), 4.53–4.39 (m, 2H, H-6), 4.18 (ddt, 1H, *J* = 23.6, 10.4, 3.5 Hz, H-5), 3.58 (ddd, 1H, *J* = 11.9, 9.9, 3.5 Hz, H-2), 3.27 (br s 1H, O*H*), 2.15 (s, 3H, *Me*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (CO), 92.3 (d, ^{3}J = 9.5 Hz, C-1), 90.4 (d, ^{1}J = 187.4 Hz, C-3), 81.3 (dd, ^{1}J = 174.9, ^{4}J = 1.6 Hz, C-6), 68.3 (dd, ^{2}J = 19.4 Hz, ^{3}J = 6.8 Hz, C-5), 68.1 (dd, ^{2}J

= 19.0 Hz, ^{3}J = 6.9 Hz, C-4), 62.0 (d, ^{2}J = 16.5 Hz, C-2), 20.8 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −198.87 (dddd, ^{2}J = 53.1 Hz, ^{3}J = 13.1, 11.9 Hz, ^{4}J = 3.9 Hz, F-3), −233.86 (td, ^{2}J = 47.2 Hz, ^{3}J = 23.6 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.12 (ddd, 1H, *J* = 12.3, 10.3, 9.0 Hz, H-4), 4.68 (d, 1H, *J* = 8.0 Hz, H-1), 4.56–4.37 (m, 2H, H-6), 4.39 (ddd, 1H, *J* = 51.0, 9.6, 9.0 Hz, H-3), 3.78 (br s 1H, O*H*), 3.68–3.53 (m, 2H, H-2, H-5), 2.13 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (CO), 95.8 (d, ^{3}J = 10.4 Hz, C-1), 92.1 (d, ^{1}J = 191.3 Hz, C-3), 81.3 (dd, ^{1}J = 175.3, ^{4}J = 1.5 Hz, C-6), 71.9 (dd, ^{2}J = 19.6 Hz, ^{3}J = 7.8 Hz, C-5), 67.9 (dd, ^{2}J = 18.9 Hz, ^{3}J = 7.2 Hz, C-4), 65.4 (d, ^{2}J = 16.8 Hz, C-2), 20.8 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.15 (ddd, ^{2}J = 51.0 Hz, ^{3}J = 12.9, 12.3 Hz, F-3), −232.55 (td, ^{2}J = 47.0 Hz, ^{3}J = 20.2 Hz, F-6).

2-Azido-3-*O*-acetyl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (62)



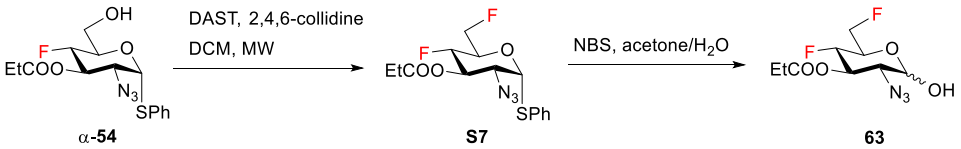
α-**53** **S6** **62**

The α-anomer of thioglycoside **53** (275 mg, 0.81 mmol) was subjected to reaction with diethylaminosulfur trifluoride (140 µL, 1.06 mmol) and 2,4,6-collidine (270 µL, 2.04 mmol) in dichloromethane (5 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:5 afforded phenyl 2-azido-3-*O*-acetyl-2,4,6-trideoxy-4,6-difluoro-1-thio-α-D-glucopyranoside **S6** (225 mg, 81%) as a thick colourless syrup. R_f 0.48 (EtOAc/heptane 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.46 (m, 2H, CH_{arom}), 7.36–7.31 (m, 3H, CH_{arom}), 5.63 (dd, 1H, *J* = 5.5, 2.8 Hz, H-1), 5.49 (ddd, 1H, *J* = 13.1, 10.7, 8.6 Hz, H-3), 4.70 (dddd, 1H, *J* = 46.8, 10.7, 3.0, 1.8 Hz, H-6'), 4.66–4.46 (m, 3H, H-4, H-5, H-6), 3.97 (ddd, 1H, *J* = 10.7, 5.5, 1.1 Hz, H-2), 2.20 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.6 (CO), 132.5 (C_q), 132.2, 129.5 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 87.0 (d, ^{4}J = 1.3 Hz, C-1), 86.2 (dd, ^{1}J = 188.3 Hz, ^{3}J = 7.4 Hz, C-4), 80.6 (d, ^{1}J = 175.8 Hz, C-6), 71.5 (d, ^{2}J = 19.4 Hz, C-3), 69.4 (dd, ^{2}J = 24.2, 18.0 Hz, C-5), 58.2 (d, ^{3}J = 7.0 Hz, C-2), 20.9 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.75 (dd, ^{2}J = 54.0 Hz, ^{3}J = 13.1 Hz, F-

4), −237.04 (ddd, ^{2}J = 48.2, 46.8 Hz, ^{3}J = 26.5 Hz, F-6). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{16}F_2NO_3S$, 316.0813; found, 316.0819.

Compound **S6** (154 mg, 0.45 was subjected to thioglycoside hydrolysis according to the general procedure. Chromatography in EtOAc/PE 1:3 to EtOAc/PE 1:1 afforded **62** (93 mg, 83% from **S6**, 67% over two steps) as a thick colourless syrup, R_f 0.45 (EtOAc/PE 2:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_8H_{12}FNO_4$, 224.0729; found, 224.0733. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.68 (ddd, 1H, *J* = 13.6, 10.6, 8.9 Hz, H-3), 5.41 (dd, 1H, *J* = 3.4, 3.1 Hz, H-1), 4.67 (dddd, 1H, *J* = 46.9, 10.6, 3.2, 1.7 Hz, H-6), 4.62 (ddt, 1H, *J* = 48.1, 10.6, 1.9 Hz, H-6'), 4.53 (ddd, 1H, *J* = 50.5, 10.2, 8.9 Hz, H-4), 4.25 (ddddd, 1H, *J* = 27.1, 10.1, 4.7, 3.2, 1.9 Hz, H-5), 3.30 (ddd, 1H, *J* = 10.6, 3.4, 1.0 Hz, H-2), 2.19 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.1 (CO), 92.4 (d, ^{4}J = 1.5 Hz, C-1), 86.1 (dd, ^{1}J = 188.0 Hz, ^{3}J = 7.6 Hz, C-4), 80.8 (d, ^{1}J = 174.9 Hz, C-6), 70.0 (d, ^{2}J = 19.2 Hz, C-3), 68.4 (dd, ^{2}J = 23.8, 18.0 Hz, C-5), 61.3 (d, ^{3}J = 6.4 Hz, C-2), 20.9 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.88 (dddd, ^{2}J = 50.5 Hz, ^{3}J = 13.6, 4.7 Hz, ^{5}J = 3.3 Hz, F-4), −238.06 (ddd, ^{2}J = 48.1, 46.9 Hz, ^{3}J = 27.1 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.18 (dddd, 1H, *J* = 13.9, 10.4, 9.0, 0.8 Hz, H-3), 4.79 (d, 1H, *J* = 7.9 Hz, H-1), 4.75–4.54 (m, 2H, H-6), 4.48 (ddd, 1H, *J* = 50.3, 10.1, 9.0 Hz, H-4), 3.72 (ddddd, 1H, *J* = 23.8, 10.1, 4.5, 2.0, 1.9 Hz, H-5), 3.42 (ddd, 1H, *J* = 10.4, 7.9, 1.0 Hz, H-2), 2.18 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.9 (CO), 96.4 (d, ^{4}J = 1.4 Hz, C-1), 85.8 (dd, ^{1}J = 187.5 Hz, ^{3}J = 7.7 Hz, C-4), 80.7 (d, ^{1}J = 175.7 Hz, C-6), 72.6 (dd, ^{2}J = 23.9, 18.8 Hz, C-5), 72.0 (dd, ^{2}J = 19.7 Hz, ^{4}J = 0.6 Hz, C-3), 64.7 (d, ^{3}J = 7.7 Hz, C-2), 20.9 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −202.35 (ddd, ^{2}J = 50.3 Hz, ^{3}J = 13.9, 4.5 Hz, F-4), −236.58 (td, ^{2}J = 47.0 Hz, ^{3}J = 23.8 Hz, F-6).

2-Azido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-D-glucopyranose (63)

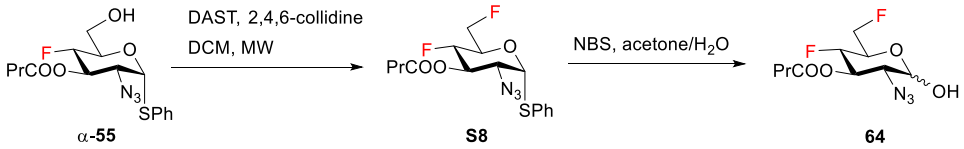


Thioglycoside α-**54** (215 mg, 0.60 mmol) was subjected to reaction with diethylaminosulfur trifluoride (100 µL, 0.76 mmol) and 2,4,6-collidine (200 µL, 1.51 mmol) in dichloromethane (5 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:6 afforded phenyl 2-azido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-1-thio-α-D-glucopyranoside **S7** (158 mg, 73%) as a thick colourless syrup. R_f 0.72 (Et_2O/PE 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.47 (m, 2H, CH_{arom}), 7.36–7.30 (m, 3H, CH_{arom}), 5.62 (dd, 1H, J = 5.5, 2.7 Hz, H-1), 5.51 (ddd, 1H, J = 12.7, 10.7, 8.6 Hz, H-3), 4.74–4.48 (m, 4H, H-4, H-5, 2H-6), 3.98 (ddd, 1H, J = 10.7, 5.5, 1.1 Hz, H-2), 2.47 (q, 2H, J = 7.5 Hz, CH_2CH$_3$), 1.22 (t, 3H, J = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.1 (CO), 132.5 (C_q), 132.2, 129.5 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 87.0 (d, ^4J = 0.9 Hz, C-1), 86.2 (dd, ^1J = 188.3 Hz, ^3J = 7.4 Hz, C-4), 80.6 (d, ^1J = 175.7 Hz, C-6), 71.3 (d, ^2J = 19.4 Hz, C-3), 69.4 (dd, ^2J = 24.3, 17.9 Hz, C-5), 61.6 (d, ^3J = 7.0 Hz, C-2), 27.6 (*C*H$_2$CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.79 (ddd, ^2J = 53.6 Hz, ^3J = 12.7 Hz, ^5J = 2.7 Hz, F-4), −237.00 (td, ^2J = 47.2 Hz, ^3J = 26.8 Hz, F-6). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{15}H_{18}F_2NO_3S$, 330.0969; found, 330.0964.

Thioglycoside **S7** (138 mg, 0.39 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded **63** (79 mg, 77% from **S7**, 56% over two steps) as a white crystalline solid, mp 83–85 °C (EtOAc/PE), R_f 0.45 (EtOAc/PE 2:3). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_9H_{14}F_2NO_4$, 238.0885; found, 238.0881. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.70 (ddd, 1H, J = 13.6, 10.6, 8.9 Hz, H-3), 5.41 (q, 1H, J = 3.4 Hz, H-1), 4.75–4.54 (m, 2H, H-6), 4.52 (ddd, 1H, J = 50.3, 10.1, 8.9 Hz, H-4), 4.31–4.20 (m, 1H, H-5), 3.98 (dd, 1H, J = 10.6, 3.4 Hz, H-2), 3.10 (d, 1H, J = 3.4 Hz, O*H*), 2.46 (q, 2H, J = 7.6 Hz, CH_2CH$_3$), 1.21 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.5 (CO), 92.5 (d, ^4J = 1.6 Hz, C-1), 86.1 (dd, ^1J = 188.0 Hz, ^3J = 7.6 Hz, C-4), 80.8 (d, ^1J = 175.1 Hz, C-6), 69.8 (d, ^2J = 19.2 Hz, C-

3), 68.5 (dd, ^{2}J = 23.6, 18.1 Hz, C-5), 61.4 (d, ^{3}J = 6.6 Hz, C-2), 27.6 (*C*H$_2$CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −199.95 (ddd, ^{2}J = 50.3 Hz, ^{3}J = 13.6 Hz, ^{5}J = 3.4 Hz, F-4), −238.07 (td, ^{2}J = 47.3 Hz, ^{3}J = 27.1 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.20 (dddd, 1H, *J* = 13.9, 10.4, 9.0, 0.8 Hz, H-3), 4.79 (dd, 1H, *J* = 7.9, 3.8 Hz, H-1), 4.75–4.54 (m, 2H, H-6), 4.50 (ddd, 1H, *J* = 50.4, 10.1, 8.9 Hz, H-4), 3.73 (ddddd, 1H, *J* = 23.8, 9.9, 4.4, 2.8, 1.9 Hz, H-5), 3.49 (d, 1H, *J* = 3.8 Hz, O*H*), 3.42 (ddd, 1H, *J* = 10.4, 7.9, 1.0 Hz, H-2), 2.46 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.21 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.4 (CO), 96.4 (d, ^{4}J = 1.4 Hz, C-1), 85.8 (dd, ^{1}J = 187.5 Hz, ^{3}J = 7.6 Hz, C-4), 80.7 (d, ^{1}J = 175.8 Hz, C-6), 72.6 (dd, ^{2}J = 23.8, 18.8 Hz, C-5), 71.8 (d, ^{2}J = 16.7 Hz, C-3), 64.8 (d, ^{3}J = 7.8 Hz, C-2), 27.6 (*C*H$_2$CH$_3$), 9.1 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −202.41 (ddd, ^{2}J = 50.4 Hz, ^{3}J = 13.9, 2.8 Hz, F-4), −236.56 (td, ^{2}J = 47.1 Hz, ^{3}J = 23.8 Hz, F-6).

2-Azido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (64)

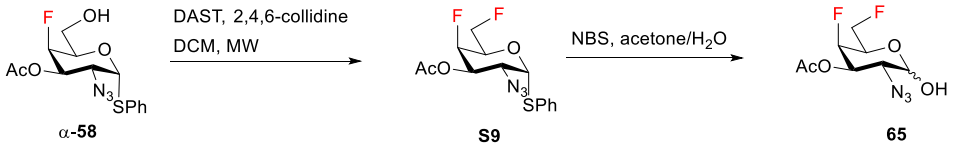


Thioglycoside α-**55** (155 mg, 0.42 mmol) was subjected to reaction with diethylaminosulfur trifluoride (72 μL, 0.54 mmol) and 2,4,6-collidine (144 μL, 1.09 mmol) in dichloromethane (4 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:7 afforded phenyl 2-azido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-1-thio-α-D-glucopyranoside **S8** (137 mg, 88%) as a thick colourless syrup, R_f 0.65 (EtOAc/PE 1:3). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.47 (m, 2H, CH$_{arom}$), 7.35–7.31 (m, 3H, CH$_{arom}$), 5.63 (dd, 1H, *J* = 5.5, 2.8 Hz, H-1), 5.51 (ddd, 1H, *J* = 12.7, 10.7, 8.5 Hz, H-3), from ^{1}H {^{19}F} 4.69 (ddd, 1H, *J* = 10.6, 2.9, 1.4 Hz, H-6), 4.65–4.45 (m, 3H, H-4, H-5, H-6'), 3.97 (ddd, 1H, *J* = 10.7, 5.5, 1.1 Hz, H-2), 2.42 (t, 2H, *J* = 7.3 Hz, COC*H*$_2$), 1.73 (h, 2H, *J* = 7.3 Hz, C*H*$_2$CH$_3$), 1.00 (t, 3H, *J* = 7.3 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.3 (CO), 132.6 (C$_q$), 132.2, 129.5 (2 × 2CH$_{arom}$), 128.3 (CH$_{arom}$), 87.1 (d, ^{4}J = 1.5 Hz, C-1), 86.2 (dd, ^{1}J = 188.3 Hz, ^{3}J = 7.5 Hz, C-4), 80.7 (d, ^{1}J = 175.9 Hz, C-6), 71.1 (d, ^{2}J = 19.4 Hz, C-3), 69.4 (dd, ^{2}J

= 24.3, 18.0 Hz, C-5), 61.6 (d, ^{3}J = 7.0 Hz, C-2), 36.1 (CO*C*H_2), 18.4 (*C*H_2CH$_3$), 13.6 (*C*H_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.75 (ddd, ^{2}J = 53.7 Hz, ^{3}J = 12.7 Hz, ^{5}J = 2.8 Hz, F-4), −237.02 (ddd, ^{2}J = 47.4, 47.1 Hz, ^{3}J = 26.6 Hz, F-6). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{20}F_2NO_3S$, 344.1126; found, 344.1123.

Thioglycoside **S8** (110 mg, 0.30 mmol) was hydrolysed according to the general procedure. Chromatography in Et_2O/PE 2:3 afforded **64** (75 mg, 91% from **S8**; 80% over 2 steps) as a thick colourless gel, R_f 0.10 (Et_2O/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{10}H_{16}F_2NO_4$, 252.1041; found, 252.1046. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.70 (ddd, 1H, *J* = 13.6, 10.6, 8.8 Hz, H-3), 5.41 (dd, 1H, *J* = 3.4, 3.2 Hz, H-1), 4.75–4.54 (m, 2H, H-6), 4.46 (ddd, 1H, *J* = 50.5, 10.1, 8.8 Hz, H-4), 4.31–4.20 (m, 1H, H-5), 3.29 (ddd, 1H, *J* = 10.6, 3.4, 1.0 Hz, H-2), 2.41 (t, 2H, *J* = 7.3 Hz, COCH_2), 1.72 (h, 2H, *J* = 7.3 Hz, CH_2CH$_3$), 0.99 (t, 3H, *J* = 7.3 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.7 (CO), 92.5 (d, ^{4}J = 1.5 Hz, C-1), 86.1 (dd, ^{1}J = 188.0 Hz, ^{3}J = 7.5 Hz, C-4), 80.8 (d, ^{1}J = 174.9 Hz, C-6), 69.7 (d, ^{2}J = 19.1 Hz, C-3), 68.5 (dd, ^{2}J = 23.8, 18.0 Hz, C-5), 61.4 (d, ^{3}J = 6.4 Hz, C-2), 36.2 (CO*C*H_2), 18.5 (*C*H_2CH$_3$), 13.6 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.87 (ddt, ^{2}J = 50.5 Hz, ^{3}J = 13.6, 3.2 Hz, ^{5}J = 3.2 Hz, F-4), −238.04 (td, ^{2}J = 47.2 Hz, ^{3}J = 27.1 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.19 (dddd, 1H, *J* = 13.9, 10.4, 9.0, 0.7 Hz, H-3), 4.79 (d, 1H, *J* = 8.0 Hz, H-1), 4.75–4.54 (m, 2H, H-6), 4.47 (ddd, 1H, *J* = 50.6, 10.0, 9.0 Hz, H-4), 3.78–3.67 (m, 1H, H-5), 3.42 (ddd, 1H, *J* = 10.4, 8.0, 1.0 Hz, H-2), 2.41 (t, 2H, *J* = 7.3 Hz, COCH_2), 1.72 (h, 2H, *J* = 7.3 Hz, CH_2CH$_3$), 0.99 (t, 3H, *J* = 7.3 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.6 (CO), 96.4 (d, ^{4}J = 1.5 Hz, C-1), 85.8 (dd, ^{1}J = 187.5 Hz, ^{3}J = 7.6 Hz, C-4), 80.7 (d, ^{1}J = 175.7 Hz, C-6), 72.6 (dd, ^{2}J = 23.7, 18.8 Hz, C-5), 74.7 (d, ^{2}J = 19.7 Hz, C-3), 64.8 (d, ^{3}J = 7.7 Hz, C-2), 36.1 (CO*C*H_2), 18.5 (*C*H_2CH$_3$), 13.6 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −202.34 (ddd, ^{2}J = 50.6 Hz, ^{3}J = 13.9, 2.4 Hz, F-4), −236.55 (td, ^{2}J = 47.0 Hz, ^{3}J = 23.9 Hz, F-6).

3-*O*-Acetyl-2-azido-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (65)

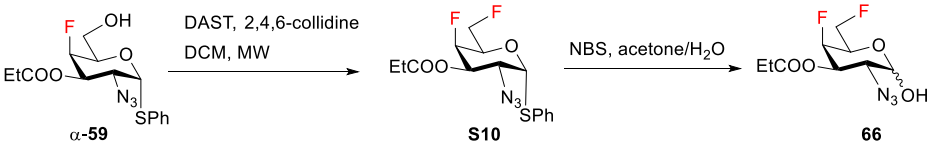


α-**58** **S9** **65**

The α-anomer of thioglycoside **58** (170 mg, 0.50 mmol) was subjected to reaction with diethylaminosulfur trifluoride (80 μL, 0.61 mmol) and 2,4,6-collidine (160 μL, 1.21 mmol) in dichloromethane (4 mL) according to the general procedure. Chromatography in EtOAc/PE 1:6 afforded phenyl 3-*O*-acetyl-2-azido-2,4,6-trideoxy-4,6-difluoro-1-thio-α-D-glucopyranoside **S9** (156 mg, 91%) as colourless syrupy mixture of anomers, R_f 0.74 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{16}F_2NO_3S$, 316.0813; found, 316.0815. ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.51–7.49 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.66 (d, 1H, *J* = 5.4 Hz, H-1), 5.09 (ddd, 1H, *J* = 26.0, 11.1, 2.5 Hz, H-3), 5.00 (dd, 1H, *J* = 50.8, 2.5 Hz, H-4), 4.73 (dddd, 1H, *J* = 29.6, 12.5, 6.6, 5.7 Hz, H-5), 4.59 (ddd, 1H, *J* = 46.3, 9.5, 5.7 Hz, H-6'), 4.51 (dddd, 1H, *J* = 46.3, 9.5, 6.6, 1.1 Hz, H-6), 4.38 (dd, 1H, *J* = 11.1, 5.4 Hz, H-2), 2.20 (s, 3H, *Me*). ^{13}C{^{1}H} ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.5 (CO), 132.8 ($2CH_{arom}$), 132.5 (C_q), 129.5 (CH_{arom}), 128.6 ($2CH_{arom}$), 87.3 (C-1), 86.0 (dd, ^1J = 190.9 Hz, ^3J = 5.6 Hz, C-4), 80.7 (dd, ^1J = 168.3 Hz, ^3J = 6.3 Hz, C-6), 71.0 (dd, ^2J = 16.4 Hz, ^4J = 3.2 Hz, C-3), 68.6 (dd, ^2J = 23.8, 17.2 Hz, C-5), 58.2 (d, ^3J = 2.2 Hz, C-2), 21.3 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): –218.36 (ddd, ^2J = 50.8 Hz, ^3J = 29.6, 26.0 Hz, F-4), –232.53 (td, ^2J = 46.3 Hz, ^3J = 12.5 Hz, F-6). Thioglycoside **S9** (140 mg, 0.41 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded **65** (80 mg, 78% from **S9**, 71% over two steps) as a colourless thick syrup, R_f 0.26 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_8H_{12}F_2NO_4$, 224.0729; found 224.0734. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.44 (dd, 1H, *J* = 3.4 Hz, H-1), 5.33 (ddd, 1H, *J* = 26.7, 11.0, 2.5 Hz, H-3), 4.96 (dd, 1H, *J* = 50.3, 2.5 Hz, H-4), 4.58 (ddd, 1H, *J* = 45.7, 9.6, 5.9 Hz, H-6'), 4.54 (dddd, 1H, *J* = 47.1, 9.6, 6.7, 1.3 Hz, H-6), 4.42 (dddd, 1H, *J* = 29.3, 12.4, 6.7, 5.9 Hz, H-5), 3.83 (dd, 1H, *J* = 11.0, 3.4 Hz, H-2), 2.20 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.4 (CO), 92.4 (C-1), 86.3 (dd, ^1J = 184.5 Hz, ^3J = 5.9 Hz, C-4), 80.9 (dd, ^1J = 170.2 Hz, ^3J = 6.4 Hz, C-6), 69.0 (dd, ^2J = 17.6 Hz, ^4J =

1.0 Hz, C-3), 67.8 (dd, ^{2}J = 23.8, 18.0 Hz, C-5), 57.9 (d, ^{3}J = 2.2 Hz, C-2), 20.9 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): –220.97 (ddd, ^{2}J = 50.3 Hz, ^{3}J = 29.3, 26.7 Hz, F-4), –232.81 (ddd, ^{2}J = 47.1, 45.7 Hz, ^{3}J = 12.4 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY) : δ 4.84 (dd, 1H, *J* = 50.3, 2.6 Hz, H-4), 4.76 (ddd, 1H, *J* = 27.3, 10.8, 2.6 Hz, H-3), 4.72 (dd, 1H, *J* = 7.9, 1.2 Hz, H-1), 4.66–4.44 (m, 2H, H-6), 3.89 (ddt, 1H, *J* = 26.9, 10.8, 6.3 Hz, H-5), 3.74 (ddd, 1H, *J* = 10.8, 7.9, 0.9 Hz, H-2), 2.20 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.4 (CO), 96.5 (C-1), 84.9 (dd, ^{1}J = 185.4 Hz, ^{3}J = 5.5 Hz, C-4), 80.4 (dd, ^{1}J = 170.8 Hz, ^{3}J = 5.9 Hz, C-6), 71.9 (dd, ^{2}J = 24.2, 18.4 Hz, C-5), 71.7 (dd, ^{2}J = 17.7 Hz, ^{4}J = 0.9 Hz, C-3), 61.9 (C-2), 20.9 (Me). ^{19}F NMR ($CDCl_3$, 376 MHz): –218.60 (ddd, ^{2}J = 50.3 Hz, ^{3}J = 27.3, 26.9 Hz, F-4), –232.62 (td, ^{2}J = 46.3 Hz, ^{3}J = 10.8 Hz, F-6).

2-Azido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-D-galactopyranose (66)

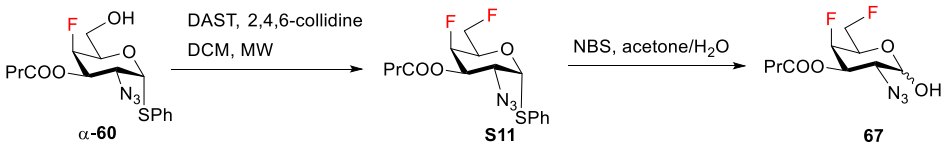


Thioglycoside α-**59** (285 mg, 0.80 mmol) was reacted with diethylaminosulfur trifluoride (140 µL, 1.06 mmol) and 2,4,6-collidine (260 µL, 1.97 mmol) in dichloromethane (6 mL) according to the general procedure. Chromatography of the crude product in Et_2O/PE 1:2 afforded phenyl 2-azido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-1-thio-α-D-galactopyranoside **S10** (263 mg, 92%) as a white crystalline solid, mp 54–57 °C (EtOAc/PE), R_f 0.71 (Et_2O/PE 3:2). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{15}H_{18}F_2NO_3S$, 330.0969; found, 330.0972. ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.52–7.49 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.66 (d, 1H, *J* = 5.4 Hz, H-1), 5.10 (ddd, 1H, *J* = 26.3, 11.1, 2.6 Hz, H-3), 5.01 (dd, 1H, *J* = 50.1, 2.6 Hz, H-4), 4.73 (dddd, 1H, *J* = 28.8, 11.9, 6.6, 5.6 Hz, H-5), 4.59 (ddd, 1H, *J* = 46.0, 9.6, 5.6 Hz, H-6'), 4.51 (dddd, 1H, *J* = 46.7, 9.6, 6.6, 1.0 Hz, H-6), 4.39 (dd, 1H, *J* = 11.1, 5.7 Hz, H-2), 2.49 (q, 2H, *J* = 7.5 Hz, CH_2CH_3), 1.22 (t, 3H, *J* = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.6 (CO), 132.8 ($2CH_{arom}$), 132.3 (C_q), 129.4 ($2CH_{arom}$), 128.4 (CH_{arom}), 87.2 (C-1), 86.0 (dd, ^{1}J = 185.0 Hz, ^{3}J = 5.7 Hz, C-4), 80.6 (dd, ^{1}J =

170.9 Hz, ^{3}J = 6.2 Hz, C-6), 70.7 (d, ^{2}J = 17.5 Hz, C-3), 68.4 (dd, ^{2}J = 24.3, 17.9 Hz, C-5), 58.1 (d, ^{3}J = 1.7 Hz, C-2), 27.6 (*C*H_2CH$_3$), 9.0 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −218.52 (ddd, ^{2}J = 50.1 Hz, ^{3}J = 28.8, 26.3 Hz, F-4), −232.52 (ddd, ^{2}J = 46.7, 46.0 Hz, ^{3}J = 11.9 Hz, F-6).

Thioglycoside **S10** (184 mg, 0.51 mmol) was hydrolysed according to the general procedure. Chromatography in Et$_2$O/PE 1:2 afforded **66** (104 mg, 76% from **S10**, 70% over two steps) as a thick colourless syrup, R_f 0.39 (EtOAc/PE 1:2). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for $C_9H_{14}F_2NO_4$, 238.0885; found, 238.0887. NMR data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.43 (dd, 1H, *J* = 3.4, 2.8 Hz, H-1), 5.33 (ddd, 1H, *J* = 26.7, 11.0, 2.5 Hz, H-3), 4.96 (dd, 1H, *J* = 50.6, 2.5 Hz, H-4), 4.56 (ddd, 1H, *J* = 46.0, 9.6, 5.6 Hz, H-6'), 4.63–4.57 (m, 1H, H-6), from ^{1}H {^{19}F-4} 4.43 (dt, 1H, *J* = 12.2, 6.1 Hz, H-5), 3.84 (dd, 1H, *J* = 11.0, 3.4 Hz, H-2), 3.48 (br s, 1H, O*H*), 2.47 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.20 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.9 (CO), 92.4 (C-1), 86.3 (dd, ^{1}J = 184.4 Hz, ^{3}J = 6.1 Hz, C-4), 81.0 (dd, ^{1}J = 170.2 Hz, ^{3}J = 6.4 Hz, C-6), 68.9 (d, ^{2}J = 17.7 Hz, C-3), 67.8 (dd, ^{2}J = 23.7, 18.0 Hz, C-5), 58.0 (d, ^{3}J = 2.4 Hz, C-2), 27.6 (*C*H_2CH$_3$), 9.0 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −221.05 (ddd, ^{2}J = 50.6 Hz, ^{3}J = 29.7, 26.7 Hz, F-4), −232.71 (td, ^{2}J = 46.3 Hz, ^{3}J = 12.2 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 4.84 (dd, 1H, *J* = 50.0, 2.6 Hz, H-4), 4.77 (ddd, 1H, *J* = 27.2, 10.8, 2.6 Hz, H-3), from ^{1}H {^{19}F- 4} 4.72 (d, 1H, *J* = 9.1 Hz, H-1), 4.67–4.43 (m, 1H, H-6), 4.56 (ddd, 1H, *J* = 46.0, 9.6, 5.6 Hz, H-6'), 4.02 (br s, 1H, O*H*), 3.90 (ddt, 1H, *J* = 27.0, 11.0, 6.5 Hz, H-5), 3.74 (ddd, 1H, *J* = 10.8, 9.1, 0.9 Hz, H-2), 2.47 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.20 (t, 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.9 (CO), 96.4 (C-1), 84.9 (dd, ^{1}J = 185.3 Hz, ^{3}J = 5.7 Hz, C-4), 80.5 (dd, ^{1}J = 170.9 Hz, ^{3}J = 6.0 Hz, C-6), 71.9 (dd, ^{2}J = 23.8, 18.2 Hz, C-5), 71.6 (d, ^{2}J = 17.7 Hz, C-3), 62.0 (C-2), 27.5 (*C*H_2CH$_3$), 9.0 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −218.66 (ddd, ^{2}J = 50.0 Hz, ^{3}J = 27.2, 27.0 Hz, F-4), −232.53 (td, ^{2}J = 46.4 Hz, ^{3}J = 11.0 Hz, F-6).

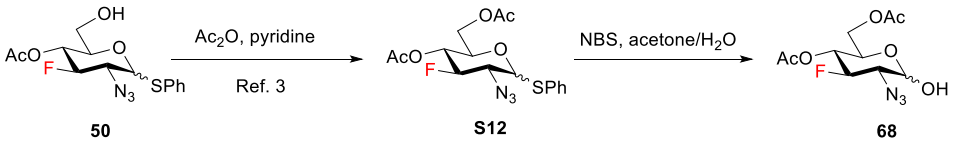
2-Azido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (67)



Thioglycoside α-**60** (316 mg, 0.86 mmol) was reacted 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 1:5 afforded phenyl 2-azido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-1-thio-α-D-galactopyranoside **S11** (295 mg, 93%) as a thick colourless syrup. R_f 0.78 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.52–7.50 (m, 2H, CH_{arom}), 7.35–7.32 (m, 3H, CH_{arom}), 5.66 (d, 1H, *J* = 5.4 Hz, H-1), 5.09 (ddd, 1H, *J* = 26.0, 11.1, 2.4 Hz, H-3), 5.01 (dd, 1H, *J* = 50.4, 2.4 Hz, H-4), 4.73 (dddd, 1H, *J* = 29.5, 12.1, 6.6, 5.6 Hz, H-5), 4.59 (ddd, 1H, *J* = 46.0, 9.6, 5.6 Hz, H-6'), 4.51 (dddd, 1H, *J* = 46.8, 9.6, 6.6, 1.2 Hz, H-6), 4.38 (dd, 1H, *J* = 11.4, 5.4 Hz, H-2), 2.44 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.73 (h, 2H, *J* = 7.4 Hz, CH_2CH$_3$), 1.00 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.8 (CO), 132.8 (2CH_{arom}), 132.3 (C_q), 129.4 (2CH_{arom}), 128.4 (CH_{arom}), 87.3 (C-1), 86.0 (dd, ^1J = 185.0 Hz, ^3J = 5.6 Hz, C-4), 80.6 (dd, ^1J = 171.0 Hz, ^3J = 6.2 Hz, C-6), 70.5 (d, ^2J = 17.4 Hz, C-3), 68.4 (dd, ^2J = 24.3, 18.0 Hz, C-5), 58.2 (C-2), 36.1 (CO*C*H$_2$), 18.4 (*C*H$_2$CH$_3$), 13.6 (*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −218.47 (ddd, ^2J = 50.4 Hz, ^3J = 29.5, 26.0 Hz, F-4), −232.50 (ddd, ^2J = 46.8, 46.0 Hz, ^3J = 12.1 Hz, F-6). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{16}H_{20}F_2NO_3S$, 344.1126; found, 344.1125. Thioglycoside **S11** (265 mg, 0.71 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 2:9 afforded **67** (188 mg, 94% from **S11**, 87% over two steps) as a thick colourless syrup, R_f 0.54 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{10}H_{16}F_2NO_4$, 252.1042; found, 252.1043. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.44 (d, 1H, *J* = 3.4 Hz, H-1), 5.33 (ddd, 1H, *J* = 26.7, 11.0, 2.5 Hz, H-3), 4.96 (dd, 1H, *J* = 51.1, 2.5 Hz, H-4), 4.66–4.46 (m, 2H, H-6), 4.42 (ddt, 1H, *J* = 29.4, 12.4, 6.2 Hz, H-5), 3.83 (dd, 1H, *J* = 11.0, 3.4 Hz, H-2), 2.43 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.77–1.67 (m, 2H, CH_2CH$_3$), 0.99 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.1 (CO), 92.5 (C-1), 86.3 (dd, ^1J = 184.4 Hz, ^3J = 6.0 Hz, C-4), 81.0 (dd, ^1J = 170.2 Hz,

^{3}J = 6.3 Hz, C-6), 68.8 (dd, ^{2}J = 17.6 Hz, ^{4}J = 1.1 Hz, C-3), 67.8 (dd, ^{2}J = 23.5, 18.0 Hz, C-5), 58.0 (d, ^{3}J = 2.2 Hz, C-2), 36.1 (CO*C*H$_2$), 18.5 (*C*H$_2$CH$_3$), 13.6 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −221.06 (ddd, ^{2}J = 51.1 Hz, ^{3}J = 29.4, 26.7 Hz, F-4), −232.75 (td, ^{2}J = 46.3 Hz, ^{3}J = 12.4 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 4.84 (dd, 1H, *J* = 50.7, 2.6 Hz, H-4), 4.77 (ddd, 1H, *J* = 27.2, 10.8, 2.6 Hz, H-3), 5.72 (dd, 1H, *J* = 8.0, 1.1 Hz, H-1), 4.66–4.46 (m, 2H, H-6), 3.87 (ddt, 1H, *J* = 27.0, 10.8, 6.3 Hz, H-5), 3.74 (ddd, 1H, *J* = 10.8, 8.0, 0.9 Hz, H-2), 2.43 (t, 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.77–1.67 (m, 2H, C*H*$_2$CH$_3$), 0.99 (t, 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.1 (CO), 96.5 (C-1), 84.9 (dd, ^{1}J = 185.3 Hz, ^{3}J = 5.7 Hz, C-4), 80.5 (dd, ^{1}J = 170.9 Hz, ^{3}J = 5.9 Hz, C-6), 71.9 (dd, ^{2}J = 23.8, 18.1 Hz, C-5), 71.5 (dd, ^{2}J = 17.8 Hz, ^{4}J = 0.7 Hz, C-3), 62.0 (d, ^{3}J = 2.2 Hz, C-2), 36.0 (CO*C*H$_2$), 18.5 (*C*H$_2$CH$_3$), 13.6 (*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −218.66 (ddd, ^{2}J = 50.7 Hz, ^{3}J = 27.2, 27.0 Hz, F-4), −232.56 (td, ^{2}J = 46.2 Hz, ^{3}J = 10.8 Hz, F-6).

2-Azido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-D-glucopyranose (68)

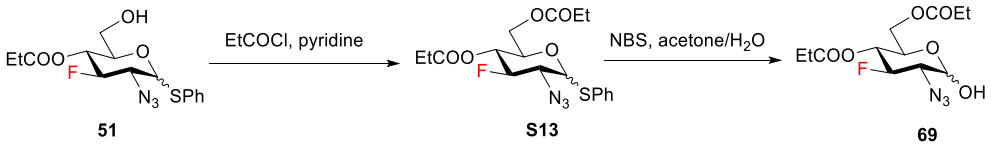


50 **S12** **68**

Compound **68** was prepared according to the general procedure for the thioglycoside hydrolysis starting from phenyl 2-azido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-1-thio-α/β-D-glucopyranoside **S12** (205 mg, 0.53 mmol) that was prepared from **50** by the published procedure in 94% yield.[3] Chromatography in EtOAc/PE 1:2 afforded **68** (120 mg, 77%, 72% over two steps) as a colourless thick syrup, R_f 0.23 (EtOAc/heptane 2:3). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{10}$H$_{15}$FNO$_6$, 264.0878; found, 264.0880. NMR data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.37 (dd, 1H, *J* = 3.8, 3.6 Hz, H-1), 5.21 (ddd, 1H, *J* = 12.9, 10.1, 8.9 Hz, H-4), 4.91 (ddd, 1H, *J* = 53.1, 9.9, 8.9 Hz, H-3), 4.24 (dd, 1H, *J* = 12.0, 4.3 Hz, H-6), 4.21–4.17 (m, 1H, H-5), 4.13 (ddt, 1H, *J* = 12.0, 1.1, Hz, H-6'), 3.58 (ddd, 1H, *J* = 11.1, 9.9, 3.6 Hz, H-2), 2.13, 2.10 (2 × s, 2 × 3H, *Me*). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 171.0 (CO O-6), 169.7 (CO O-4), 92.4 (d, ^{3}J = 9.5 Hz, C-1), 90.5 (d, ^{1}J = 187.4 Hz, C-3), 68.5 (d, ^{2}J = 18.2 Hz, C-4), 67.6 (d, ^{3}J = 7.0 Hz, C-5), 62.1 (d, ^{2}J = 16.5 Hz, C-2), 61.9

(d, ^4J = 1.6 Hz, C-6), 20.9, 20.8 (2 × Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −198.85 (dddd, ^2J = 53.1 Hz, ^3J = 12.9, 11.1 Hz, ^4J = 3.6 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ from ^{1}H {^{19}F} 5.17 (dd, 1H, *J* = 10.1, 9.1 Hz, H-4), 4.66 (d, 1H, *J* = 8.2 Hz, H-1), 4.37 (ddd, 1H, *J* = 51.2, 9.7, 9.1 Hz, H-3), 4.24–4.09 (m, 2H, H-6), from ^{1}H {^{19}F} 3.61 (ddd, 1H, *J* = 10.1, 4.9, 2.5 Hz, H-5), 3.57 (ddd, 1H, *J* = 12.7, 9.7, 8.2 Hz, H-2), 2.12, 2.09 (2 × s, 2 × 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.9 (CO O-6), 169.6 (CO O-4), 95.9 (d, ^3J = 10.4 Hz, C-1), 92.2 (d, ^1J = 190.3 Hz, C-3), 71.3 (d, ^3J = 7.9 Hz, C-5), 68.2 (d, ^2J = 18.6 Hz, C-4), 65.5 (d, ^2J = 16.8 Hz, C-2), 62.0 (d, ^4J = 2.3 Hz, C-6), 20.9, 20.8 (2 × Me). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.28 (ddd, ^2J = 51.2 Hz, ^3J = 12.7, 12.3 Hz).

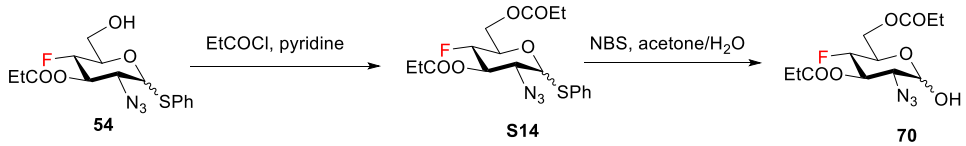
2-Azido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-D-glucopyranose (69)



Compound **51** (560 mg, 1.58 mmol) was O6-propionylated according to the general procedure for acylation using propionyl chloride (220 μL, 2.52 mmol). Chromatography in EtOAc/PE 1:5 afforded phenyl 2-azido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside **S13** (521 mg, 80%) as colourless syrupy mixture of anomers, R_f 0.22 (EtOAc/heptane 1:5). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{18}H_{23}FNO_5S$, 384.1275; found, 384.1289. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.49–7.47 (m, 2H, CH_{arom}), 7.36–7.30 (m, 3H, CH_{arom}), 5.63 (dd, 1H, *J* = 5.7, 3.1 Hz, H-1), 5.22 (ddd, 1H, *J* = 13.2, 10.3, 8.9 Hz, H-4), 4.76 (ddd, 1H, *J* = 52.4, 10.0, 8.9 Hz, H-3), from ^{1}H {^{19}F} 4.51 (ddd, 1H, *J* = 10.3, 5.4, 2.2 Hz, H-5), 4.26 (dd, 1H, *J* = 12.3, 5.4 Hz, H-6), 4.13 (ddd, 1H, *J* = 11.1, 10.0, 5.7 Hz, H-2), 4.06 (ddd, 1H, *J* = 12.3, 2.2, 1.8 Hz, H-6'), 2.45–2.24 (m, 4H, C*H*$_2$CH$_3$), 1.18, 1.11 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1, 173.0 (2 × CO), 132.4 (C_q), 132.2, 129.7 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 91.8 (d, ^1J = 189.5 Hz, C-3), 86.3 (d, ^3J = 7.8 Hz, C-1), 68.7 (d, ^3J = 6.9 Hz, C-5), 68.3 (d, ^2J = 18.2 Hz, C-4), 62.2 (d, ^2J = 17.1 Hz, C-2), 61.8 (d, ^4J = 1.5 Hz, C-6), 27.5, 27.4 (2 × *C*H$_2$CH$_3$), 9.1, 9.0 (2 × *C*H$_3$). ^{19}F NMR

($CDCl_3$, 376 MHz): −194.03 (ddddd, ^1J = 52.4 Hz, ^2J = 13.2, 11.1 Hz, ^4J = 3.1 Hz, ^5J = 1.8 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.58 (m, 2H, CH_{arom}), 7.36–7.30 (m, 3H, CH_{arom}), 5.09 (ddd, 1H, *J* = 11.9, 10.2, 9.1 Hz, H-4), 4.42 (dt, 1H, *J* = 51.4, 9.1 Hz, H-3), 4.41 (dd, 1H, *J* = 10.2, 0.9 Hz, H-1), 4.21–4.19 (m, 2H, H-6), 3.59 (dddd, 1H, *J* = 10.2, 4.7, 2.7, 1.3 Hz, H-5), 3.49 (ddd, 1H, *J* = 12.5, 10.2, 9.1 Hz, H-2), 2.45–2.24 (m, 4H, C*H*$_2$CH$_3$), 1.15, 1.14 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1, 172.9 (2 × CO), 134.2 ($2CH_{arom}$), 130.3 (C_q), 129.3 ($2CH_{arom}$), 129.1 (CH_{arom}), 94.0 (d, ^1J = 192.1 Hz, C-3), 85.4 (d, ^3J = 6.9 Hz, C-1), 75.4 (d, ^3J = 7.4 Hz, C-5), 67.6 (d, ^2J = 18.5 Hz, C-4), 63.1 (d, ^2J = 17.5 Hz, C-2), 61.9 (d, ^4J = 2.0 Hz, C-6), 27.5 (2*C*H$_2$CH$_3$), 9.07, 9.05 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −189.16 (dddd, ^1J = 51.4 Hz, ^2J = 12.5, 11.9 Hz, ^5J = 1.3 Hz). Thioglycoside **S13** (219 mg, 0.53 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:2 afforded **69** (149 mg, 88% from **S13**, 70% over two steps) as a colourless thick syrup, R_f 0.23 (EtOAc/heptane 2:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{12}H_{19}FNO_6$, 292.1190; found, 292.1192. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.34 (dt, 1H, *J* = 3.6, 1.8 Hz, H-1), 5.20 (ddd, 1H, *J* = 14.4, 9.6, 8.9 Hz, H-4), 4.90 (ddd, 1H, *J* = 53.2, 9.9, 8.9 Hz, H-3), 4.24–4.08 (m, 3H, H-5, 2H-6), 3.84 (d, 1H, *J* = 3.6 Hz, OH), from ^{1}H {^{19}F} 3.56 (dd, 1H, *J* = 9.9, 3.6 Hz, H-2), 2.42–2.33 (m, 4H, C*H*$_2$CH$_3$), 1.20–1.11 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.6, 173.24 (2 × CO), 92.3 (d, ^3J = 9.4 Hz, C-1), 90.5 (d, ^1J = 187.2 Hz, C-3), 68.3 (d, ^2J = 18.1 Hz, C-4), 67.6 (d, ^3J = 7.0 Hz, C-5), 62.1 (d, ^2J = 16.3 Hz, C-2), 61.8 (d, ^4J = 1.4 Hz, C-6), 27.52, 27.43 (2 × *C*H$_2$CH$_3$), 9.1, 9.02 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −198.87 (m). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.16 (ddd, 1H, *J* = 12.6, 10.1, 9.0 Hz, H-4), 4.64 (d, 1H, *J* = 8.0 Hz, H-1), 4.35 (ddd, 1H, *J* = 51.3, 9.7, 9.0 Hz, H-3), 4.38 (br s, 1H, O*H*), 4.24–4.08 (m, 2H, 2H-6), 3.61–3.54 (m, 2H, H-2, H-5), 2.42–2.33 (m, 4H, C*H*$_2$CH$_3$), 1.20–1.11 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.5, 173.19 (2 × CO), 95.8 (d, ^3J = 10.3 Hz, C-1), 92.3 (d, ^1J = 190.1 Hz, C-3), 71.3 (d, ^3J = 8.1 Hz, C-5), 68.0 (d, ^2J = 18.5 Hz, C-4), 65.5 (d, ^2J = 16.6 Hz, C-2), 61.8 (d, ^4J = 1.8 Hz, C-6), 27.48, 27.40 (2 × *C*H$_2$CH$_3$), 9.02, 8.98 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −193.18 (dt, ^1J = 51.4 Hz, ^2J = 12.6 Hz).

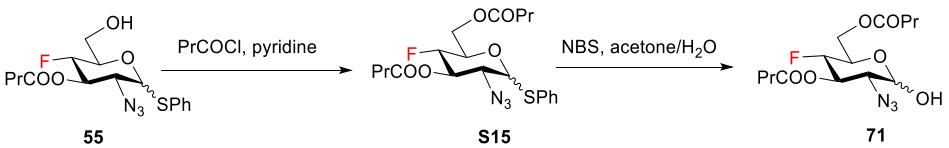
2-Azido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-D-glucopyranose (70)



Compound **54** (180 mg, 0.51 mmol) was O6-propionylated according to the general procedure for acylation using propionyl chloride (60 μL, 0.69 mmol). Chromatography in Et_2O/PE 1:4 afforded phenyl 2-azido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside **S14** (170 mg, 82%) as colourless gel-like mixture of anomers, R_f 0.19 (Et_2O/PE 1:4). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{18}H_{23}FNO_5S$, 384.1275; found, 384.1277. NMR data for the α-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 7.51–7.49 (m, 2H, CH_{arom}), 7.36–7.31 (m, 3H, CH_{arom}), 5.59 (dd, 1H, *J* = 5.6, 2.7 Hz, H-1), 5.49 (ddd, 1H, *J* = 13.2, 10.7, 8.8 Hz, H-3), 4.66 (ddt, 1H, *J* = 10.0, 5.0, 2.9 Hz, H-5), from ^1H {^{19}F} 4.45 (dd, 1H, *J* = 12.0, 2.9 Hz, H-6), from ^1H {^{19}F} 4.41 (dd, 1H, *J* = 10.0, 8.8 Hz, H-4), 4.41–4.19 (m, 1H, H-6'), 3.97 (ddd, 1H, *J* = 10.7, 5.6, 1.1 Hz, H-2), 2.49–2.30 (m, 4H, CH_2CH_3), 1.22, 1.13 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_3). ^{13}C {^1H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.0, 173.2 (2 × CO), 132.52 ($2CH_{arom}$), 132.45 (C_q), 129.4 ($2CH_{arom}$), 128.3 (CH_{arom}), 87.6 (d, ^1J = 188.9 Hz, C-4), 86.8 (d, ^4J = 1.3 Hz, C-1), 71.3 (d, ^2J = 19.6 Hz, C-3), 68.4 (d, ^2J = 23.9 Hz, C-5), 62.1 (C-6), 61.4 (d, ^3J = 7.0 Hz, C-2), 27.6, 27.4 (2 × CH_2CH_3), 9.2, 9.1 (2 × CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −199.16 (dddd, ^2J = 50.7 Hz, ^3J = 13.2, 2.9 Hz, ^5J = 2.7 Hz). NMR data for the β-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 7.58–7.56 (m, 2H, CH_{arom}), 7.36–7.31 (m, 3H, CH_{arom}), 5.23 (ddd, 1H, *J* = 13.5, 9.8, 9.1 Hz, H-3), 4.52 (d, 1H, *J* = 10.1 Hz, H-1), 4.44–4.24 (m, 2H, H-4, H-6), from ^1H {^{19}F} 4.24 (dd, 1H, *J* = 12.2, 5.4 Hz, H-6'), 3.74 (dddd, 1H, *J* = 10.1, 5.4, 2.4, 2.1 Hz, H-5), 3.35 (ddd, 1H, *J* = 10.1, 9.8, 0.8 Hz, H-2), 2.49–2.30 (m, 4H, CH_2CH_3), 1.19, 1.17 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_3). ^{13}C {^1H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.0, 173.2 (2 × CO), 134.1 ($2CH_{arom}$), 130.6 (C_q), 129.2 ($2CH_{arom}$), 129.0 (CH_{arom}), 86.7 (d, ^1J = 188.7 Hz, C-4), 86.2 (d, ^4J = 1.4 Hz, C-1), 75.5 (d, ^2J = 22.5 Hz, C-5), 73.8 (d, ^2J = 19.3 Hz, C-3), 62.9 (d, ^3J = 7.3 Hz, C-2), 62.2 (C-6), 27.6, 27.5 (2 × CH_2CH_3), 9.2, 9.1 (2 × CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −200.46 (ddd, ^2J = 50.6 Hz, ^3J = 13.5, 2.1 Hz).

Thioglycoside **S14** (152 mg, 0.37 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:4 → EtOAc/PE 1:3 afforded **70** (76 mg, 64% from **S14**, 52% over two steps) as a thick colourless syrup, R_f 0.31 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{12}H_{19}FNO_6$, 292.1190; found, 292.1192. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.68 (ddd, 1H, *J* = 13.2, 10.6, 8.8 Hz, H-3), 5.37 (q, 1H, *J* = 3.3 Hz, H-1), 4.49–4.41 (m, 1H, H-6), 4.45 (ddd, 1H, *J* = 50.0, 9.9, 8.8 Hz, H-4), from ^{1}H {^{19}F} 4.32 (ddd, 1H, *J* = 9.9, 4.5, 1.2 Hz, H-5), from ^{1}H {^{19}F} 4.28 (dd, 1H, *J* = 12.1, 4.5 Hz, H-6'), 3.29 (dd, 1H, *J* = 10.6, 3.3 Hz, H-2), 3.23 (d, 1H, *J* = 3.3 Hz, O*H*), 2.48, 2.40 (2 × q, 2 × 2H, *J* = 7.5 Hz, CH_2CH$_3$), 1.23, 1.18 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.3, 173.4 (2 × CO), 92.4 (C-1), 87.3 (d, ^1J = 188.3 Hz, C-4), 69.8 (d, ^2J = 19.2 Hz, C-3), 67.5 (d, ^2J = 23.4 Hz, C-5), 62.0 (C-6), 61.5 (d, ^3J = 6.5 Hz, C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 9.2, 9.1 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −199.47 (m). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.18 (ddd, 1H, *J* = 13.8, 10.4, 9.0 Hz, H-3), 4.78 (d, 1H, *J* = 8.0 Hz, H-1), 4.49–4.32 (m, 2H, H-4, H-6), from ^{1}H {^{19}F} 4.24 (dd, 1H, *J* = 12.3, 5.2 Hz, H-6'), 3.76 (ddt, 1H, *J* = 9.8, 5.2, 2.5 Hz, H-5), 3.64 (br s, 1H, O*H*), 3.41 (ddd, 1H, *J* = 10.4, 8.0, 1.0 Hz, H-2), 2.48, 2.40 (2 × q, 2 × 2H, *J* = 7.5 Hz, CH_2CH$_3$), 1.23, 1.18 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.3, 173.3 (2 × CO), 96.4 (C-1), 87.0 (d, ^1J = 188.1 Hz, C-4), 71.9 (d, ^2J = 19.8 Hz, C-3), 71.7 (d, ^2J = 23.5 Hz, C-5), 64.8 (d, ^3J = 7.8 Hz, C-2), 62.1 (C-6), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 9.13, 9.10 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −201.96 (ddd, ^2J = 50.5 Hz, ^3J = 13.8, 2.5 Hz).

2-Azido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-D-glucopyranose (71)



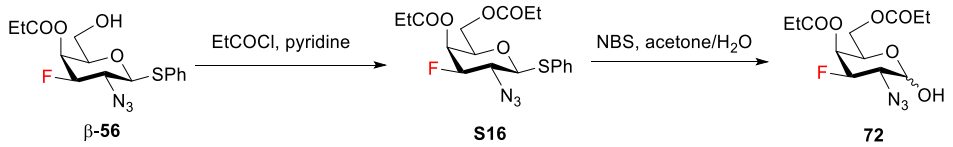
Compound **55** (165 mg, 0.45 mmol) was O6-butyrylated according to the general procedure for acylation using butyryl chloride (60 μL, 0.58 mmol). Chromatography in Et_2O/PE 1:6 afforded phenyl 2-azido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-α/β-D-glucopyranoside **S15** (172 mg, 88%) as colourless

gel-like mixture of anomers, R_f 0.50 (Et_2O/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{20}H_{27}FNO_5S$, 412.1588; found, 412.1590. NMR data for the α-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 7.51–7.49 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.60 (dd, 1H, *J* = 5.5, 2.7 Hz, H-1), 5.49 (ddd, 1H, *J* = 13.2, 10.7, 8.8 Hz, H-3), 4.65 (ddt, 1H, *J* = 10.0, 5.2, 2.6 Hz, H-5), from ^1H {^{19}F} 4.45 (dd, 1H, *J* = 12.2, 2.6 Hz, H-6), from ^1H {^{19}F} 4.40 (dd, 1H, *J* = 10.0, 8.8 Hz, H-4), from ^1H {^{19}F} 4.30 (dd, 1H, *J* = 12.2, 5.2 Hz, H-6'), 3.96 (ddd, 1H, *J* = 10.7, 5.5, 1.1 Hz, H-2), 2.41, 2.28 (2 × t, 2 × 2H, *J* = 7.5 Hz, COCH_2), 1.59–1.17 (m, 4H, CH_2CH$_3$), 0.99, 0.94 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 173.2, 172.2 (2 × CO), 132.50 (C_q), 132.48, 129.4 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 87.6 (d, ^1J = 189.0 Hz, C-4), 86.9 (d, ^4J = 1.3 Hz, C-1), 71.1 (d, ^2J = 19.5 Hz, C-3), 68.4 (d, ^2J = 23.9 Hz, C-5), 62.0 (C-6), 61.7 (d, ^3J = 7.0 Hz, C-2), 36.1, 36.0 (2 × COCH_2), 18.4 (2CH_2CH$_3$), 13.8, 13.6 (2 × CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −199.15 (ddt, ^2J = 50.3 Hz, ^3J = 13.2, 2.7 Hz, ^5J = 2.7 Hz). NMR data for the β-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 7.59–7.56 (m, 2H, CH_{arom}), 7.35–7.31 (m, 3H, CH_{arom}), 5.23 (ddd, 1H, *J* = 13.4, 9.8, 9.1 Hz, H-3), 4.52 (d, 1H, *J* = 10.1 Hz, H-1), from ^1H {^{19}F} 4.34 (dd, 1H, *J* = 12.3, 2.4 Hz, H-6), from ^1H {^{19}F} 4.33 (dd, 1H, *J* = 9.8, 9.1 Hz, H-4), from ^1H {^{19}F} 4.24 (dd, 1H, *J* = 12.3, 5.4 Hz, H-6'), 3.73 (ddt, 1H, *J* = 9.8, 5.4, 2.4 Hz, H-5), 3.34 (ddd, 1H, *J* = 10.1, 9.8, 0.8 Hz, H-2), 2.36, 2.34 (2 × t, 2 × 2H, *J* = 7.5 Hz, COCH_2), 1.59–1.17 (m, 4H, CH_2CH$_3$), 0.99, 0.97 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 173.2, 172.3 (2 × CO), 134.1 (2CH_{arom}), 130.6 (C_q), 129.2 (2CH_{arom}), 129.0 (CH_{arom}), 86.7 (d, ^1J = 188.6 Hz, C-4), 86.3 (d, ^4J = 1.4 Hz, C-1), 75.5 (d, ^2J = 22.4 Hz, C-5), 73.6 (d, ^2J = 19.3 Hz, C-3), 62.9 (d, ^3J = 7.3 Hz, C-2), 62.1 (C-6), 36.09, 36.07 (2 × COCH_2), 18.50, 18.45 (2 × CH_2CH$_3$), 13.8, 13.6 (2 × CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −200.43 (ddd, ^2J = 50.6 Hz, ^3J = 13.4, 2.1 Hz).

Thioglycoside **S15** (145 mg, 0.33 mmol) was hydrolysed according to the general procedure. Chromatography in Et_2O/PE 2:3 afforded **71** (96 mg, 84% from **S15**, 73% over two steps) as a thick colourless syrup, R_f 0.07 (Et_2O/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{23}FNO_6$, 320.1503; found, 320.1506. NMR data for the α-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 5.67 (ddd, 1H, *J* = 13.2, 10.6, 8.6 Hz, H-3), 5.37 (t, 1H, *J* = 3.4 Hz, H-1), from ^1H {^{19}F} 4.44

(dd, 1H, *J* = 12.2, 2.4 Hz, H-6), 4.42 (ddd, 1H, *J* = 49.5, 9.9, 8.6 Hz, H-4), from ^{1}H {^{19}F} 4.32 (ddd, 1H, *J* = 9.9, 4.4, 2.4 Hz, H-5), 4.24 (dd, 1H, *J* = 12.2, 4.4 Hz, H-6'), 3.51 (br s, 1H, O*H*), 3.25 (ddd, 1H, *J* = 10.6, 3.4, 1.0 Hz, H-2), 2.41, 2.34 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.72, 1.67 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.98, 0.95 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.6, 172.7 (2 × CO), 92.4 (d, ^{4}J = 1.5 Hz, C-1), 87.3 (d, ^{1}J = 188.4 Hz, C-4), 69.7 (d, ^{2}J = 19.2 Hz, C-3), 67.4 (d, ^{2}J = 23.5 Hz, C-5), 61.7 (C-6), 61.4 (d, ^{3}J = 6.4 Hz, C-2), 36.2, 36.1 (2 × COCH$_2$), 18.50, 18.49 (2 × CH$_2$CH$_3$), 13.7, 13.6 (2 × CH$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −199.44 (dddd, ^{2}J = 49.5 Hz, ^{3}J = 13.2, 4.2 Hz, ^{5}J = 3.4 Hz). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.17 (ddd, 1H, *J* = 13.8, 10.5, 9.0 Hz, H-3), 4.77 (d, 1H, *J* = 8.0 Hz, H-1), from ^{1}H {^{19}F} 4.45 (dd, 1H, *J* = 12.2, 2.4 Hz, H-6), from ^{1}H {^{19}F} 4.40 (dd, 1H, *J* = 9.8, 9.0 Hz, H-4), 4.21 (ddd, 1H, *J* = 12.2, 5.1, 1.6 Hz, H-6'), 3.94 (br s, 1H, O*H*), 3.75 (dddd, 1H, *J* = 9.8, 5.1, 2.6, 2.4 Hz, H-5), 3.40 (ddd, 1H, *J* = 10.4, 8.0, 1.0 Hz, H-2), 2.40, 2.34 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.71, 1.67 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.98, 0.95 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.6, 172.6 (2 × CO), 96.4 (d, ^{4}J = 1.4 Hz, C-1), 87.0 (d, ^{1}J = 188.0 Hz, C-4), 71.7 (d, ^{2}J = 19.8 Hz, C-3), 71.6 (d, ^{2}J = 23.5 Hz, C-5), 64.8 (d, ^{3}J = 7.7 Hz, C-2), 62.0 (C-6), 36.1, 36.0 (2 × COCH$_2$), 18.49, 18.46 (2 × CH$_2$CH$_3$), 13.7, 13.6 (2 × CH$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −201.94 (ddd, ^{2}J = 50.5 Hz, ^{3}J = 13.8, 2.6 Hz).

2-Azido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-D-galactopyranose (72)



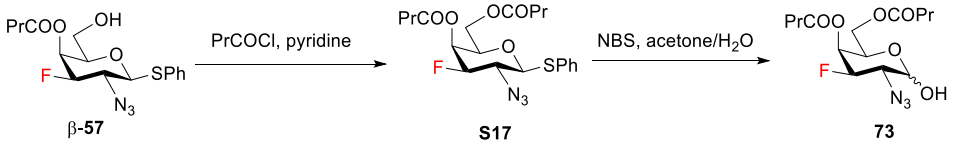
Compound β-**56** (306 mg, 0.86 mmol) was O6-propionylated according to the general procedure for acylation using propionyl chloride (100 μL, 1.14 mmol). Chromatography in EtOAc/PE 1:5 afforded phenyl 2-azido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-1-thio-β-D-galactopyranoside **S16** (278 mg, 78%) as thick colourless syrup. R_f 0.19 (EtOAc/PE 1:5). ^{1}H NMR (CDCl$_3$, 400 MHz, H-H COSY): δ 7.62–7.60 (m, 2H, CH$_{arom}$), 7.37–7.33 (m, 3H, CH$_{arom}$), 5.52 (ddd, 1H, *J* = 6.0, 3.6, 1.1 Hz, H-4), 4.48

(ddd, 1H, *J* = 46.6, 9.5, 3.6 Hz, H-3), 4.43 (dd, 1H, *J* = 10.1, 1.0 Hz, H-1), 4.16–4.14 (m, 2H, H-6), 3.82 (tdd, 1H, *J* = 6.8, 1.6, 1.1 Hz, H-5), 3.69 (ddd, 1H, *J* = 11.5, 10.1, 9.5 Hz, H-2), 2.33 (q, 2 × 2H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.13 (t, 6H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 174.0, 173.2 (2 × CO), 133.9 (2CH$_{arom}$), 130.8 (C$_q$), 129.2 (2CH$_{arom}$), 128.9 (CH$_{arom}$), 91.0 (d, ^1J = 195.8 Hz, C-3), 85.9 (d, ^3J = 6.6 Hz, C-1), 74.3 (d, ^3J = 5.9 Hz, C-5), 66.2 (d, ^2J = 16.8 Hz, C-4), 61.5 (d, ^4J = 2.9 Hz, C-6), 60.6 (d, ^2J = 18.6 Hz, C-2), 27.5, 27.4 (2 × *C*H$_2$CH$_3$), 9.2, 9.1 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −191.99 (dddt, ^2J = 46.6 Hz, ^3J = 11.5, 6.0 Hz, ^4J = 1.0 Hz). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{18}$H$_{23}$FNO$_5$S, 384.1275; found, 384.1268.

Thioglycoside **S16** (260 mg, 0.63 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded **72** (174 mg, 86% from **S16**, 67% over two steps) as a thick colourless syrup, R_f 0.16 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{12}$H$_{19}$FNO$_6$, 292.1190; found, 292.1187. NMR data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.64 (ddd, 1H, *J* = 6.3, 3.7, 1.3 Hz, H-4), 5.42 (td, 1H, *J* = 3.6, 2.6 Hz, H-1), 5.03 (ddd, 1H, *J* = 48.1, 10.4, 3.7 Hz, H-3), 4.40 (ddd, 1H, *J* = 6.8, 6.4, 1.3 Hz, H-5), 4.14 (ddd, 1H, *J* = 11.3, 6.8, 1.1 Hz, H-6), 4.07 (dd, 1H, *J* = 11.3, 6.4 Hz, H-6'), from ^{1}H {^{19}F} 3.80 (dd, 1H, *J* = 10.4, 3.6 Hz, H-2), 3.23 (d, 1H, *J* = 2.6 Hz, O*H*), 2.44, 2.34 (2 × q, 2 × 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.18, 1.13 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 174.2 (CO O-6), 173.5 (CO O-4), 92.8 (d, ^3J = 9.2 Hz, C-1), 87.1 (d, ^1J = 190.4 Hz, C-3), 67.4 (d, ^2J = 16.6 Hz, C-4), 66.9 (d, ^3J = 5.5 Hz, C-5), 61.6 (d, ^4J = 2.6 Hz, C-6), 59.4 (d, ^2J = 17.7 Hz, C-2), 27.5, 27.4 (2 × *C*H$_2$CH$_3$), 9.2, 9.1 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −202.99 (dddd, ^2J = 48.1 Hz, ^3J = 10.9, 6.3 Hz, ^4J = 3.6 Hz). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.52 (ddd, 1H, *J* = 5.1, 3.7, 1.1 Hz, H-4), 4.63 (dd, 1H, *J* = 7.9, 4.6 Hz, H-1), 4.44 (ddd, 1H, *J* = 46.6, 10.1, 3.7 Hz, H-3), 4.17 (dd, 1H, *J* = 11.4, 6.5 Hz, H-6), 4.13 (dd, 1H, *J* = 11.4, 6.4 Hz, H-6'), 3.83 (ddd, 1H, *J* = 6.5, 6.4, 1.1 Hz, H-5), 3.73 (ddd, 1H, *J* = 11.6, 10.1, 7.9 Hz, H-2), 2.46, 2.34 (2 × q, 2 × 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.19, 1.13 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 174.2 (CO O-6), 173.5 (CO O-4), 96.1 (d, ^3J = 10.4 Hz, C-1), 89.5 (d, ^1J = 193.6 Hz, C-3), 70.5 (d, ^3J = 6.3 Hz, C-5), 66.2 (d, ^2J = 16.7 Hz, C-4), 63.5 (d, ^2J = 17.7 Hz, C-2), 61.5 (d, ^4J = 2.9 Hz, C-6), 27.5,

27.4 (2 × *C*H$_2$CH$_3$), 9.2, 9.0 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −197.41 (ddd, ^2J = 46.6 Hz, ^3J = 11.6, 5.1 Hz).

2-Azido-4,6-di-*O*-butyryl-2,3-dideoxy-3-fluoro-D-galactopyranose (73)

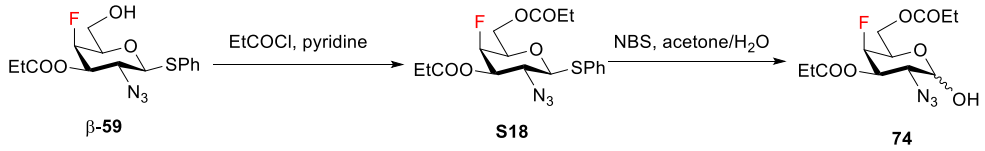


Compound β-**57** (236 mg, 0.64 mmol) was O6-butyrylated according to the general procedure for acylation using butyryl chloride (85 µL, 0.82 mmol). Chromatography in EtOAc/PE 1:6 afforded phenyl 2-azido-4,6-di-*O*-butyryl-2,3-dideoxy-3-fluoro-1-thio-β-D-galactopyranoside **S17** (252 mg, 90%) as a thick colourless syrup. R_f 0.73 (EtOAc/PE 1:3). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.62–7.59 (m, 2H, CH$_{arom}$), 7.37–7.32 (m, 3H, CH$_{arom}$), 5.52 (ddd, 1H, *J* = 6.0, 3.6, 1.0 Hz, H-4), 4.48 (ddd, 1H, *J* = 46.3, 9.5, 3.6 Hz, H-3), 4.42 (d, 1H, *J* = 10.1 Hz, H-1), 4.17 (ddd, 1H, *J* = 11.4, 7.0, 1.0 Hz, H-6), 4.11 (dd, 1H, *J* = 11.4, 6.1 Hz, H-6'), 3.81 (dddd, 1H, *J* = 7.0, 6.1, 1.9, 1.0 Hz, H-5), 3.68 (ddd, 1H, *J* = 11.4, 10.1, 9.5 Hz, H-2), 2.32, 2.29 (2 × t, 2 × 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.62 (h, 4H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.2, 172.3 (2 × CO), 134.0 (2CH$_{arom}$), 130.8 (C$_q$), 129.1 (2CH$_{arom}$), 128.9 (CH$_{arom}$), 91.0 (d, ^1J = 195.3 Hz, C-3), 85.9 (d, ^3J = 6.7 Hz, C-1), 74.2 (d, ^3J = 5.9 Hz, C-5), 66.2 (d, ^2J = 16.8 Hz, C-4), 61.5 (d, ^4J = 2.9 Hz, C-6), 60.7 (d, ^2J = 18.6 Hz, C-2), 36.04, 35.98 (2 × CO*C*H$_2$), 18.5, 18.4 (2 × *C*H$_2$CH$_3$), 13.8, 13.7 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −191.82 (dddd, ^1J = 46.3 Hz, ^2J = 11.4, 6.0 Hz, ^4J = 1.9 Hz). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{20}$H$_{27}$FNO$_5$S, 412.1588; found, 412.1586.

Thioglycoside **S17** (228 mg, 0.52 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded **73** (143 mg, 79% from **S17**, 71% over two steps) as a thick colourless syrup, R_f 0.21 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_{14}$H$_{23}$FNO$_6$, 320.1504; found, 320.1504. NMR data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.64 (ddd, 1H, *J* = 6.3, 3.7, 1.4 Hz, H-4), 5.41 (dd, 1H, *J* = 4.8, 3.6 Hz, H-1), 5.02 (ddd, 1H, *J* = 48.1, 10.3, 3.7 Hz, H-3), from ^{1}H {^{19}F} 4.40 (td, 1H, *J* = 6.6, 1.4 Hz, H-5), 4.14–4.05 (m, 2H, H-6),

from ^{1}H {^{19}F} 3.81 (dd, 1H, *J* = 10.3, 3.6 Hz, H-2), 3.28 (br s, 1H, O*H*), 2.40, 2.29 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.72–1.60 (m, 4H, CH_2CH$_3$), 0.99–0.91 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.4, 172.6 (2 × CO), 92.8 (d, ^{3}J = 9.2 Hz, C-1), 87.1 (d, ^{1}J = 190.4 Hz, C-3), 67.3 (d, ^{2}J = 16.8 Hz, C-4), 68.0 (d, ^{3}J = 5.5 Hz, C-5), 61.6 (d, ^{4}J = 2.6 Hz, C-6), 59.4 (d, ^{2}J = 17.7 Hz, C-2), 36.1, 35.9 (2 × CO*C*H$_2$), 18.6, 18.4 (2 × *C*H$_2$CH$_3$), 13.74, 13.66 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −202.83 (dddd, ^{1}J = 48.1 Hz, ^{2}J = 15.4, 6.3 Hz, ^{4}J = 4.8 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.52 (ddd, 1H, *J* = 5.1, 3.8, 1.1 Hz, H-4), 4.63 (d, 1H, *J* = 7.9 Hz, H-1), 4.44 (ddd, 1H, *J* = 46.8, 10.1, 3.8 Hz, H-3), from ^{1}H {^{19}F} 3.83 (ddd, 1H, *J* = 7.0, 6.3, 1.1 Hz, H-5), 4.14–4.05 (m, 2H, H-6), 3.87 (br s, 1H, O*H*), 3.72 (ddd, 1H, *J* = 11.6, 10.1, 7.9 Hz, H-2), 2.40, 2.29 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.72–1.60 (m, 4H, CH_2CH$_3$), 0.99–0.91 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.4, 172.6 (2 × CO), 96.1 (d, ^{3}J = 10.3 Hz, C-1), 89.4 (d, ^{1}J = 193.6 Hz, C-3), 70.5 (d, ^{3}J = 6.2 Hz, C-5), 66.1 (d, ^{2}J = 16.6 Hz, C-4), 63.5 (d, ^{2}J = 17.6 Hz, C-2), 61.5 (d, ^{4}J = 3.0 Hz, C-6), 36.1, 35.9 (2 × CO*C*H$_2$), 18.6, 18.4 (2 × *C*H$_2$CH$_3$), 13.74, 13.66 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −197.26 (dddd, ^{1}J = 46.8 Hz, ^{2}J = 11.6, 5.1 Hz, ^{4}J = 1.8 Hz).

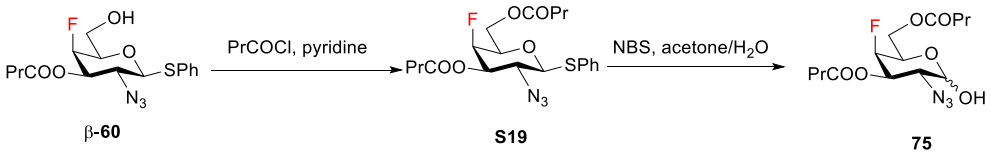
2-Azido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-D-galactopyranose (74)



Compound β-**59** (320 mg, 0.90 mmol) was O6-propionylated according to the general procedure for acylation using propionyl chloride (100 µL, 1.14 mmol). Chromatography in EtOAc/PE 1:7 afforded phenyl 2-azido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-1-thio-β-D-galactopyranoside **S18** (291 mg, 79%) as thick colourless syrup, R_f 0.78 (EtOAc/PE 1:5). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.58 (m, 2H, CH_{arom}), 7.35–7.34 (m, 3H, CH_{arom}), 4.82 (dd, 1H, *J* = 51.0, 2.5 Hz, H-4), 4.81 (ddd, 1H, *J* = 27.0, 10.2, 2.5 Hz, H-3), 4.49 (dd, 1H, *J* = 10.1, 0.8 Hz, H-1), 4.36 (ddd, 1H, *J* = 11.4, 6.7, 1.1 Hz, H-6), 4.22 (dd, 1H, *J* = 11.4, 6.3 Hz, H-6'), 3.79 (ddd, 1H, *J* = 25.7, 6.7, 6.3 Hz, H-5), 3.72 (dd, 1H, *J* = 10.2, 10.3 Hz, H-2), 2.44, 2.35 (2 × q, 2 × 2H, *J* = 7.5 Hz, CH_2CH$_3$), 1.18, 1.14 (2 × t,

2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.0, 173.7 (2 × CO), 133.7 ($2CH_{arom}$), 130.9 (C_q), 129.2 ($2CH_{arom}$), 128.8 (CH_{arom}), 86.5 (C-1), 85.4 (d, ^1J = 185.2 Hz, C-4), 74.7 (d, ^2J = 18.0 Hz, C-5), 73.4 (d, ^2J = 17.6 Hz, C-3), 61.6 (d, ^3J = 5.5 Hz, C-6), 59.5 (C-2), 27.5, 27.4 (2 × *C*H_2CH$_3$), 9.1, 9.0 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −219.14 (ddd, ^2J = 51.0 Hz, ^3J = 27.0, 26.6 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{18}H_{23}FNO_5S$, 384.1275; found, 384.1279. Thioglycoside **S18** (250 mg, 0.61 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:3 afforded **74** (153 mg, 79% from **S18**, 62% over two steps) as a white crystalline solid, mp 145–147 °C (EtOAc/PE), R_f 0.43 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{12}H_{19}FNO_6$, 292.1190; found, 292.1192. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.43 (t, 1H, *J* = 3.4 Hz, H-1), 5.32 (ddd, 1H, *J* = 26.7, 11.0, 2.5 Hz, H-3), 4.93 (dd, 1H, *J* = 50.7, 2.5 Hz, H-4), 4.38–4.19 (m, 3H, H-5, 2H-6), from ^{1}H {^{19}F} 3.85 (dd, 1H, *J* = 11.0, 3.4 Hz, H-2), 3.00 (br s, 1H, O*H*), 2.48, 2.36 (2 × q, 2 × 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.21, 1.15 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1, 173.8 (2 × CO), 92.4 (C-1), 86.7 (d, ^1J = 184.9 Hz, C-4), 69.0 (d, ^2J = 17.6 Hz, C-3), 67.3 (d, ^2J = 18.2 Hz, C-5), 61.8 (d, ^3J = 6.2 Hz, C-6), 58.1 (d, ^3J = 2.2 Hz, C-2), 27.6, 27.5 (2 × *C*H_2CH$_3$), 9.1, 9.0 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −221.26 (ddd, ^2J = 50.7 Hz, ^3J = 29.9, 26.7 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 4.80 (ddd, 1H, *J* = 49.4, 2.6, 0.7 Hz, H-4), 4.76 (ddd, 1H, *J* = 27.2, 10.8, 2.6 Hz, H-3), 4.69 (d, 1H, *J* = 8.0 Hz, H-1), 4.38–4.19 (m, 2H, H-6), from ^{1}H {^{19}F} 3.81 (t, 1H, *J* = 6.5 Hz, H-5), from ^{1}H {^{19}F} 3.74 (dd, 1H, *J* = 10.8, 8.0 Hz, H-2), 3.45 (br s, 1H, O*H*), 2.48, 2.36 (2 × q, 2 × 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.20, 1.14 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1, 173.8 (2 × CO), 96.4 (C-1), 85.3 (d, ^1J = 185.6 Hz, C-4), 71.7 (d, ^2J = 17.6 Hz, C-3), 71.4 (d, ^2J = 18.2 Hz, C-5), 62.1 (C-2), 61.6 (d, ^3J = 5.6 Hz, C-6), 27.5, 27.4 (2 × *C*H_2CH$_3$), 9.1, 9.0 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −218.79 (ddd, ^2J = 49.4 Hz, ^3J = 27.2, 26.6 Hz).

2-Azido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-D-galactopyranose (75)

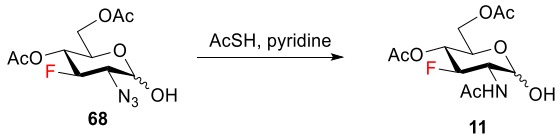


Compound β-**60** (391 mg, 1.06 mmol) was O6-butyrylated according to the general procedure for acylation using butyryl chloride (150 μL, 1.44 mmol). Chromatography in EtOAc/PE 1:6 afforded phenyl 2-azido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-1-thio-β-D-galactopyranoside **S19** (392 mg, 84%) as thick colourless syrup, R_f 0.65 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.62–7.56 (m, 2H, CH_{arom}), 7.36–7.33 (m, 3H, CH_{arom}), 4.81 (dd, 1H, *J* = 50.8, 2.6 Hz, H-4), 4.80 (ddd, 1H, *J* = 27.3, 10.3, 2.6 Hz, H-3), 4.49 (dd, 1H, *J* = 10.1, 0.8 Hz, H-1), 4.36 (ddd, 1H, *J* = 11.4, 6.8, 1.1 Hz, H-6), 4.22 (dd, 1H, *J* = 11.4, 6.3 Hz, H-6'), 3.79 (ddd, 1H, *J* = 26.7, 6.8, 6.3 Hz, H-5), 3.72 (dd, 1H, *J* = 10.3, 10.1 Hz, H-2), 2.39, 2.30 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.69, 1.65 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.97, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.2, 172.9 (2 × CO), 133.8 (2CH_{arom}), 130.9 (C_q), 129.2 (2CH_{arom}), 128.8 (CH_{arom}), 86.5 (C-1), 85.4 (d, ^1J = 185.3 Hz, C-4), 74.7 (d, ^2J = 18.1 Hz, C-5), 73.3 (d, ^2J = 17.7 Hz, C-3), 61.6 (d, ^3J = 5.4 Hz, C-6), 59.5 (C-2), 36.04, 36.00 (2 × CO*C*H_2), 18.5, 18.4 (2 × *C*H_2CH$_3$), 13.8, 13.6 (2 × *C*H_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −219.12 (ddd, ^2J = 50.8 Hz, ^3J = 27.3, 26.7 Hz). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{20}H_{27}FNO_5S$, 412.1588; found, 412.1587.

Thioglycoside **S19** (356 mg, 0.81 mmol) was hydrolysed according to the general procedure. Chromatography in EtOAc/PE 1:4 afforded **75** (205 mg, 73% from **S19**, 61% over two steps) as a white crystalline solid, mp 126–127 °C (EtOAc/PE), R_f 0.41 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{14}H_{23}FNO_6$, 320.1504; found, 320.1504. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.44 (t, 1H, *J* = 3.4 Hz, H-1), 5.34 (ddd, 1H, *J* = 26.7, 11.0, 2.5 Hz, H-3), 4.94 (dd, 1H, *J* = 50.8, 2.5 Hz, H-4), 4.38–4.18 (m, 3H, H-5, 2H-6), from ^{1}H {^{19}F} 3.85 (dd, 1H, *J* = 11.0, 3.4 Hz, H-2), 3.32 (br s, 1H, O*H*), 2.45, 2.34 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.78–1.63 (m, 2 × 2H, CH_2CH$_3$), 1.01, 0.97 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.4, 173.1 (2 × CO), 92.4 (C-1), 86.7 (d, ^1J = 185.0 Hz, C-4), 68.9 (d, ^2J = 17.6 Hz, C-3),

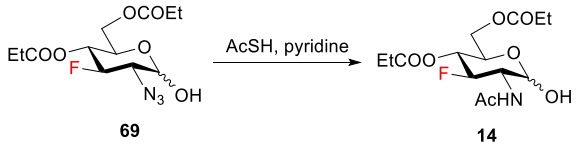
67.2 (d, ^{2}J = 18.0 Hz, C-5), 61.7 (d, ^{3}J = 6.2 Hz, C-6), 58.0 (d, ^{3}J = 2.2 Hz, C-2), 36.1, 36.0 (2 × CO*C*H$_2$), 18.5, 18.4 (2 × *C*H$_2$CH$_3$), 13.7, 13.6 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −221.24 (ddd, ^{2}J = 50.8 Hz, ^{3}J = 30.0, 26.7 Hz). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 4.94 (dd, 1H, *J* = 50.2, 2.5 Hz, H-4), 4.77 (ddd, 1H, *J* = 27.5, 10.8, 2.5 Hz, H-3), from ^{1}H {^{19}F} 4.70 (d, 1H, *J* = 8.0 Hz, H-1), 4.38–4.18 (m, 2H, H-6), from ^{1}H {^{19}F} 3.81 (t, 1H, *J* = 6.5 Hz, H-5), from ^{1}H {^{19}F} 3.75 (dd, 1H, *J* = 10.8, 8.0 Hz, H-2), 3.32 (br s, 1H, O*H*), 2.44, 2.35 (2 × t, 2 × 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.78–1.63 (m, 2 × 2H, C*H*$_2$CH$_3$), 1.01, 0.96 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.5, 173.1 (2 × CO), 96.4 (C-1), 85.4 (d, ^{1}J = 185.8 Hz, C-4), 71.6 (d, ^{2}J = 15.6 Hz, C-3), 71.4 (d, ^{2}J = 18.0 Hz, C-5), 62.1 (C-2), 61.5 (d, ^{3}J = 5.7 Hz, C-6), 36.1, 36.0 (2 × CO*C*H$_2$), 18.44, 18.43 (2 × *C*H$_2$CH$_3$), 13.7, 13.6 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): δ −218.73 (ddd, ^{2}J = 50.2 Hz, ^{3}J = 27.5, 26.8 Hz).

2-Acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-α-D-glucopyranose (11)



Compound **11** was prepared according to the general procedure for the azide reduction and acetylation starting from **68** (110 mg, 0.38 mmol). Chromatography in EtOAc/PE 1:1 → EtOAc afforded **11** (95 mg, 82%) as white crystalline solid, mp 173–177 °C (dec, EtOAc, ref 2 gives 175–182 °C, dec), R_f 0.16 (EtOAc). NMR spectra were in accordance with the literature.[2] NMR signals of the β-anomer were not detected in sufficient intensity within 12 h after sample dissolution in CDCl$_3$.

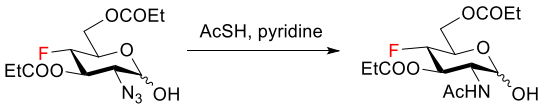
2-Acetamido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-D-glucopyranose (14)



69 **14**

Compound **14** was prepared according to the general procedure for the azide reduction and acetylation starting from compound **69** (105 mg, 0.33 mmol). Chromatography in EtOAc/PE 1:2 → EtOAc afforded **14** (95 mg, 86%) as a white crystalline solid, mp 150–152 °C (EtOAc), R_f 0.26 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1451. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.89 (d, 1H, *J* = 9.1 Hz, N*H*), 5.29 (q, 1H, *J* = 3.6 Hz, H-1), 5.22 (ddd, 1H, *J* = 12.5, 9.9, 9.0 Hz, H-4), 4.68 (ddd, 1H, *J* = 53.2, 10.4, 9.0 Hz, H-3), 4.36 (dddd, 1H, *J* = 10.6, 10.4, 9.1, 3.6 Hz, H-2), 4.22–4.13 (m, 3H, H-5, 2H-6), 4.06 (d, 1H, *J* = 3.6 Hz, O*H*), 2.42–2.04 (m, 4H, C*H*$_2$CH$_3$), 2.05 (s, 3H, *Me* NHAc), 1.15 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 174.5 (CO O-6), 173.0 (CO O-4), 170.8 (CO NHAc), 92.3 (d, ^3J = 9.5 Hz, C-1), 90.3 (d, ^1J = 188.5 Hz, C-3), 68.7 (d, ^2J = 18.1 Hz, C-4), 67.7 (d, ^3J = 6.9 Hz, C-5), 61.9 (d, ^4J = 1.6 Hz, C-6), 52.6 (d, ^2J = 17.0 Hz, C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 23.5 (Me NHAc), 9.14, 9.10 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −201.26 (dddd, ^2J = 53.2 Hz, ^3J = 12.5, 10.6 Hz, ^4J = 3.6 Hz). Resolved NMR signals for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.14 (d, 1H, *J* = 6.4 Hz, N*H*), 5.43 (d, 1H, *J* = 6.8 Hz, O*H*), 3.91–3.81 (m, 1H, H-2), 3.65 (ddd, 1H, *J* = 10.4, 5.2, 2.5 Hz, H-5), 2.08 (s, 3H, *Me* NHAc). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 96.4 (d, ^3J = 8.9 Hz, C-1), 71.2 (d, ^3J = 8.5 Hz, C-5), 68.6 (d, ^2J = 18.3 Hz, C-4), 62.3 (d, ^4J = 1.4 Hz, C-6), 57.7 (d, ^2J = 16.4 Hz, C-2), 27.45, 27.54 (2 × *C*H$_2$CH$_3$), 23.3 (Me NHAc), 9.10, 9.06 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −199.36 (m).

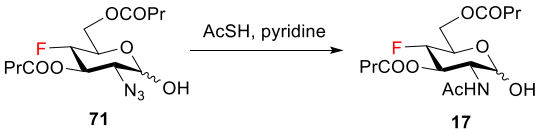
2-Acetamido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-D-glucopyranose (16)



70 **16**

Compound **16** was prepared according to the general procedure for azide reduction and acetylation starting from **70** (67 mg, 0.21 mmol). Chromatography in EtOAc/PE 1:1 → EtOAc afforded **16**[5] (48 mg, 68%) as a colourless gum, R_f 0.19 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1455. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.94 (d, 1H, *J* = 9.4 Hz, N*H*), 5.43 (ddd, 1H, *J* = 14.0, 10.9, 9.0 Hz, H-3), 5.22 (t, 1H, *J* = 3.5 Hz, H-1), 4.52 (ddd, 1H, *J* = 50.7, 9.8, 9.0 Hz, H-4), 4.46 (dt, 1H, *J* = 11.5, 1.7 Hz, H-6), 4.27–4.20 (m, 3H, H-2, H-5, H-6'), 3.75 (br s, 1H, O*H*), 2.39 (q, 2H, *J* = 7.6 Hz, CH_2CH$_3$), 2.44–2.35 (m, 2H, CH_2CH$_3$), 1.96 (s, 3H, *Me* NHAc), 1.16, 1.15 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 175.1 (CO O-3), 174.4 (CO O-6), 170.5 (CO NHAc), 91.8 (d, ^4J = 1.4 Hz, C-1), 86.8 (d, ^1J = 186.4 Hz, C-4), 70.8 (d, ^2J = 18.7 Hz, C-3), 67.4 (d, ^2J = 23.4 Hz, C-5), 62.0 (C-6), 52.2 (d, ^3J = 7.0 Hz, C-2), 27.7, 27.5 (2 × *C*H$_2$CH$_3$), 23.3 (Me NHAc), 9.3, 9.2 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −198.48 (ddt, ^2J = 50.7 Hz, ^3J = 14.0, 3.5 Hz, ^5J = 3.5 Hz). The NMR data for the α-anomer are comparable to those reported.[5] Resolved signals for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.37 (d, 1H, *J* = 6.8 Hz, N*H*), 5.12 (ddd, 1H, *J* = 14.4, 11.0, 8.7 Hz, H-3), 4.63 (d, 1H, *J* = 8.4 Hz, H-1), 3.93 (ddd, 1H, *J* = 11.0, 8.4, 6.8 Hz, H-2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 174.3, 173.9, 171.4 (3 × CO), 98.0 (d, ^4J = 1.4 Hz, C-1), 86.7 (d, ^1J = 187.4 Hz, C-4), 72.3 (d, ^2J = 19.7 Hz, C-3), 71.4 (d, ^2J = 23.3 Hz, C-5), 62.3 (C-6), 57.2 (d, ^3J = 6.8 Hz, C-2), 27.7, 27.5 (2 × *C*H$_2$CH$_3$), 9.2, 9.1 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −200.48 (dd, ^2J = 50.4 Hz, ^3J = 14.4 Hz).

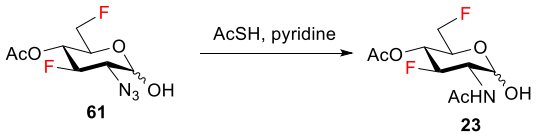
2-Acetamido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-D-glucopyranose (17)



71 17

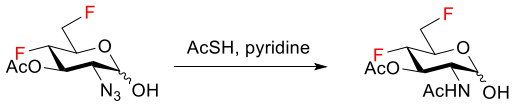
Compound **17** was prepared according to the general procedure for azide reduction and acetylation starting from **71** (76 mg, 0.22 mmol). Chromatography in EtOAc/PE 1:1 → EtOAc afforded **17**[5] (35 mg, 44%) as a colourless gum containing about 5% of inseparable O1-acetate according ^{1}H NMR, R_f 0.59 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1768. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.05 (d, 1H, *J* = 9.4 Hz, N*H*), 5.44 (ddd, 1H, *J* = 14.0, 10.9, 8.9 Hz, H-3), 5.21 (t, 1H, *J* = 3.4 Hz, H-1), 4.51 (ddd, 1H, *J* = 50.5, 9.8, 8.9 Hz, H-4), 4.47–4.42 (m, 1H, H-6), 4.26–4.16 (m, 4H, H-2, H-5, H-6', O*H*), 2.40–2.28 (m, 4H, COCH_2), 1.95 (s, 3H, *Me* NHAc), 1.71–1.59 (m, 4H, CH_2CH$_3$), 0.96, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 174.2 (CO O-3), 173.7 (CO O-6), 170.6 (CO NHAc), 91.7 (C-1), 86.9 (d, ^{1}J = 186.3 Hz, C-4), 70.6 (d, ^{2}J = 19.7 Hz, C-3), 67.3 (d, ^{2}J = 23.4 Hz, C-5), 61.9 (C-6), 52.2 (d, ^{3}J = 7.0 Hz, C-2), 36.2, 36.1 (2 × CO*C*H$_2$), 23.2 (Me NHAc), 18.6, 18.5 (2 × *C*H$_2$CH$_3$), 13.8, 13.6 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −198.48 (ddt, ^{2}J = 50.5 Hz, ^{3}J = 14.0, 3.4 Hz, ^{5}J = 3.4 Hz). The NMR data for the α-anomer are comparable to those reported.[5] Resolved signals for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.41 (d, 1H, *J* = 7.0 Hz, N*H*), 5.14 (ddd, 1H, *J* = 14.4, 11.0, 8.7 Hz, H-3), 4.63 (d, 1H, *J* = 8.4 Hz, H-1), 3.92 (dddd, 1H, *J* = 10.9, 8.4, 7.0, 0.9 Hz, H-2), 3.72 (dddd, 1H, *J* = 9.9, 5.1, 2.8, 2.4 Hz, H-5). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 97.9 (C-1), 86.7 (d, ^{1}J = 186.9 Hz, C-4), 72.2 (d, ^{2}J = 19.8 Hz, C-3), 71.4 (d, ^{2}J = 23.2 Hz, C-5), 62.2 (C-6), 57.0 (d, ^{3}J = 6.6 Hz, C-2), 36.1, 36.0 (2 × CO*C*H$_2$), 23.1 (Me NHAc), 18.51, 18.45 (2 × *C*H$_2$CH$_3$), 13.8, 13.5 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −200.44 (ddd, ^{2}J = 50.9 Hz, ^{3}J = 14.4, 2.8 Hz).

2-Acetamido-4-*O*-acetyl-2,3,6-trideoxy-3,6-difluoro-D-glucopyranose (23)



Compound **23** was prepared from **61** (102 mg, 0.41 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:2 → EtOAc afforded **23** (98 mg, 90%) as a white foam which crystallized overnight, mp 160–162 °C (EtOAc), R_f 0.10 (EtOAc/PE 1:1). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{10}H_{16}F_2NO_5$, 268.0991; found, 268.0994. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.15 (t, 1H, J = 3.6 Hz, H-1), 5.11 (ddd, 1H, J = 13.7, 10.3, 8.9 Hz, H-4), 4.75 (ddd, 1H, J = 53.4, 10.4, 8.9 Hz, H-3), 4.55–4.36 (m, 2H, H-6), 4.16 (ddd, 1H, J = 10.9, 10.4, 3.6 Hz, H-2), 4.13 (ddt, 1H, J = 24.8, 10.4, 3.2 Hz, H-5), 1.99 (s, 3H, *Me* NHAc), 2.11 (s, 3H, *Me* OAc). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 173.5 (CO NHAc), 171.2 (CO OAc), 92.8 (d, ^3J = 9.6 Hz, C-1), 91.4 (dd, ^1J = 185.9 Hz, ^4J = 0.7 Hz, C-3), 82.6 (dd, ^1J = 173.3, ^4J = 1.2 Hz, C-6), 70.1 (dd, ^2J = 18.2 Hz, ^3J = 6.8 Hz, C-4), 69.0 (dd, ^2J = 19.0 Hz, ^3J = 6.9 Hz, C-5), 54.2 (d, ^2J = 16.2 Hz, C-2), 22.5 (Me NHAc), 20.6 (Me OAc). ^{19}F NMR (MeOH-d_4, 376 MHz): −201.89 (dddd, ^2J = 53.4 Hz, ^3J = 13.7, 10.9 Hz, ^4J = 3.6 Hz, F-3), −236.10 (td, ^2J = 47.6 Hz, ^3J = 24.8 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.07 (ddd, 1H, J = 12.8, 10.3, 8.9 Hz, H-4), 4.76 (d, 1H, J = 8.3 Hz, H-1), 4.65 (ddd, 1H, J = 51.5, 10.2, 8.9 Hz, H-3), 4.55–4.36 (m, 2H, H-6), 3.83 (ddd, 1H, J = 12.0, 10.2, 8.3 Hz, H-2), 3.71 (ddddd, 1H, J = 22.7, 10.3, 3.9, 2.3, 1.4 Hz, H-5), 1.99 (s, 3H, *Me* NHAc), 2.11 (s, 3H, *Me* OAc). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 173.8 (CO NHAc), 171.1 (CO OAc), 96.1 (d, ^3J = 10.4 Hz, C-1), 92.8 (dd, ^1J = 187.6 Hz, ^4J = 0.9 Hz, C-3), 82.5 (dd, ^1J = 173.5, ^4J = 1.8 Hz, C-6), 72.8 (dd, ^2J = 19.1 Hz, ^3J = 8.2 Hz, C-5), 69.9 (dd, ^2J = 18.6 Hz, ^3J = 6.8 Hz, C-4), 57.3 (d, ^2J = 16.7 Hz, C-2), 22.8 (Me NHAc), 20.6 (Me OAc). ^{19}F NMR (MeOH-d_4, 376 MHz): −196.70 (ddd, ^2J = 51.5 Hz, ^3J = 12.8, 12.0 Hz, F-3), −235.60 (td, ^2J = 47.2 Hz, ^3J = 22.7 Hz, F-6).

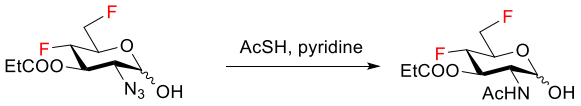
2-Acetamido-3-*O*-acetyl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (20)



62 **20**

Compound **20** was prepared from **62** (80 mg, 0.32 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **20** (79 mg, 93%) as a white crystalline solid, R_f 0.16 (EtOAc), mp 148–151 °C (EtOAc/MTBE). HRMS-APCI (*m/z*): [M + H]$^+$ calcd for $C_{10}H_{16}F_2NO_5$, 268.0991; found, 268.9088. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.43 (ddd, 1H, J = 14.3, 10.8, 8.9 Hz, H-3), 5.08 (dd, 1H, J = 3.5, 3.2 Hz, H-1), 4.63 (dddd, 1H, J = 47.3, 10.5, 3.6, 1.6 Hz, H-6'), 4.57 (ddt, 1H, J = 47.9, 10.5, 1.6 Hz, H-6), 4.49 (ddd, 1H, J = 50.9, 10.1, 8.9 Hz, H-4), 4.21 (ddtd, 1H, J = 26.8, 10.1, 3.6, 1.6 Hz, H-5), 4.14 (ddd, 1H, J = 10.8, 3.5, 1.1 Hz, H-2), 2.05, 1.94 (2 × s, 2 × 3H, *Me*). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 173.5, 172.1 (2 × CO), 92.6 (d, ^4J = 1.5 Hz, C-1), 87.9 (dd, ^1J = 184.9 Hz, ^3J = 8.1 Hz, C-4), 82.4 (d, ^1J = 172.9 Hz, C-6), 72.4 (d, ^2J = 18.4 Hz, C-3), 69.1 (dd, ^2J = 23.1 Hz, ^2J = 18.3 Hz, C-5), 53.4 (d, ^3J = 7.1 Hz, C-2), 22.4, 20.7 (2 × Me). ^{19}F NMR (MeOH-d_4, 376 MHz): −200.37 (dddd, ^2J = 50.9 Hz, ^3J = 14.3, 3.6 Hz, ^5J = 3.2 Hz, F-4), −238.85 (ddd, ^2J = 47.9, 47.3 Hz, ^3J = 26.8 Hz, F-6). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC): 4.83 (d, 1H, J = 8.7 Hz, H-1). ^{19}F NMR (MeOH-d_4, 376 MHz): −202.48 (dd, ^2J = 50.7 Hz, ^3J = 15.0 Hz, F-4), −238.23 (td, ^2J = 47.5 Hz, ^3J = 24.6 Hz, F-6).

2-Acetamido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-D-glucopyranose (21)

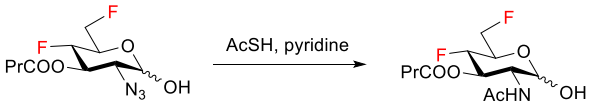


63 **21**

Compound **21** was prepared from **63** (58 mg, 0.22 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **21** (51 mg, 83%) as a white foam, R_f 0.27 (EtOAc). HRMS-APCI (*m/z*): [M + H]$^+$ calcd for $C_{11}H_{18}F_2NO_5$, 282.1147; found,

282.1143. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.45 (ddd, 1H, *J* = 14.4, 10.8, 8.9 Hz, H-3), 5.08 (dd, 1H, *J* = 3.5, 3.3 Hz, H-1), 4.63 (dddd, 1H, *J* = 47.4, 10.2, 3.6, 1.5 Hz, H-6'), 4.58 (dddd, 1H, *J* = 47.9, 10.2, 2.0, 1.6 Hz, H-6), 4.49 (ddd, 1H, *J* = 50.4, 10.0, 8.9 Hz, H-4), 4.21 (ddddd, 1H, *J* = 26.7, 10.0, 4.2, 3.6, 1.6 Hz, H-5), from 4.14 ^{1}H {^{19}F-6} (dd, 1H, *J* = 10.8, 3.5 Hz, H-2), 2.40−2.30 (m, 2H, C*H*$_2$CH$_3$), 1.93 (s, 3H, *Me* NHAc), 1.11 (t, 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 175.5, 173.5 (2 × CO), 92.7 (d, ^{4}J = 1.7 Hz, C-1), 87.9 (dd, ^{1}J = 184.8 Hz, ^{3}J = 8.0 Hz, C-4), 82.5 (d, ^{1}J = 172.8 Hz, C-6), 72.2 (d, ^{2}J = 18.5 Hz, C-3), 69.1 (dd, ^{2}J = 23.2 Hz, ^{2}J = 18.3 Hz, C-5), 53.3 (d, ^{3}J = 6.6 Hz, C-2), 28.4 (*C*H$_2$CH$_3$), 22.4 (Me NHAc), 9.5 (CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): −200.39 (dddd, ^{2}J = 50.4 Hz, ^{3}J = 14.4, 4.2 Hz, ^{5}J = 3.3 Hz, F-4), −238.82 (ddd, ^{2}J = 47.9, 47.4 Hz, ^{3}J = 26.7 Hz, F-6). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.32 (ddd, 1H, *J* = 14.9, 10.7, 8.9 Hz, H-3), 4.82 (d, 1H, *J* = 8.5 Hz, H-1), 3.86–3.74 (m, 2H, H-2, H-5). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 175.3 (CO), 96.5 (d, ^{4}J = 1.5 Hz, C-1), 28.3 (*C*H$_2$CH$_3$), 22.7 (Me NHAc). ^{19}F NMR (MeOH-d_4, 376 MHz): −202.51 (dd, ^{2}J = 50.8 Hz, ^{3}J = 15.0 Hz, F-4), −238.20 (ddd, ^{2}J = 47.5, 47.2 Hz, ^{3}J = 24.5 Hz, F-6).

2-Acetamido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (22)

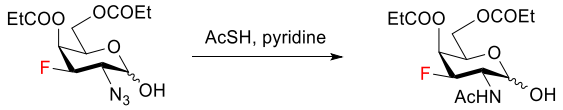


64 **22**

Compound **22** was prepared from **64** (59 mg, 0.21 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **22** (50 mg, 80%) as a colourless gum, R_f 0.45 (EtOAc). HRMS-APCI (*m/z*): [M + H]$^{+}$ calcd for $C_{12}H_{20}F_2NO_5$, 296.1304; found, 296.1303. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.05 (d, 1H, *J* = 9.3 Hz, N*H*), 5.45 (ddd, 1H, *J* = 14.2, 10.9, 8.9 Hz, H-3), 5.25 (dd, 1H, *J* = 3.5, 3.2 Hz, H-1), 4.70–4.57 (m, 2H, H-6), 4.54 (ddd, 1H, *J* = 51.0, 10.1, 9.0 Hz, H-4), 4.27–4.16 (m, 2H, H-2, H-5), 2.42–2.28 (m, 2H, COC*H*$_2$), 1.96 (s, 3H, *Me* NHAc), 1.71–1.58 (m, 2H, C*H*$_2$CH$_3$), 0.94 (t, 3H, *J* =

7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 174.3 (CO O-3), 170.7 (CO NHAc), 91.7 (d, ^4J = 1.4 Hz, C-1), 85.9 (dd, ^1J = 186.1 Hz, ^3J = 7.8 Hz, C-4), 81.2 (d, ^1J = 174.6 Hz, C-6), 70.6 (d, ^2J = 18.7 Hz, C-3), 68.4 (dd, ^2J = 23.4, 18.3 Hz, C-5), 52.2 (d, ^3J = 7.0 Hz, C-2), 36.1 ($COCH_2$), 23.2 (Me NHAc), 18.6 (CH_2CH_3), 13.6 (CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −198.66 (dddd, ^2J = 51.0 Hz, ^3J = 14.2, 4.2 Hz, ^5J = 3.2 Hz, F-4), −236.82 (td, ^2J = 47.3 Hz, ^3J = 25.9 Hz, F-6). Resolved signals for the β-anomer: ^1H NMR ($CDCl_3$, 400 MHz, ^1H $\{^{19}F\}$, H-H COSY): δ 6.40 (d, 1H, *J* = 7.2 Hz, N*H*), 5.17 (ddd, 1H, *J* = 14.5, 11.0, 8.7 Hz, H-3), 4.65 (d, 1H, *J* = 8.3 Hz, H-1), 4.78–4.53 (m, 3H, H-4, 2H-6), 3.94 (ddd, 1H, *J* = 11.0, 8.3, 7.2 Hz, H-2), 3.74–3.57 (m, 1H, H-5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 98.0 (d, ^4J = 1.1 Hz, C-1), 80.6 (d, ^1J = 175.9 Hz, C-6), 72.4 (dd, ^2J = 23.8 Hz, ^2J = 18.7 Hz, C-5), 72.2 (d, ^2J = 18.8 Hz, C-3), 56.9 (d, ^3J = 6.7 Hz, C-2). ^{19}F NMR ($CDCl_3$, 376 MHz): −201.00 (dd, ^2J = 50.6 Hz, ^3J = 14.5 Hz, F-4), −236.88 (td, ^2J = 47.5 Hz, ^3J = 24.5 Hz, F-6).

2-Acetamido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-D-galactopyranose (25)

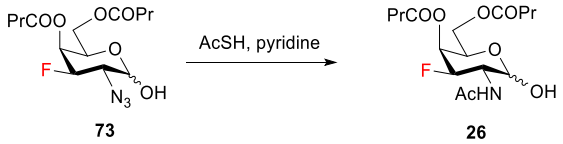


72 **25**

Compound **25** was prepared from **72** (117 mg, 0.37 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **25** (80 mg, 65%) as a colourless gum. R_f 0.32 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1451. Data for the α-anomer: ^1H NMR (MeOH-d_4, 400 MHz, ^1H $\{^{19}F\}$, H-H COSY): δ 5.57 (ddd, 1H, *J* = 6.5, 3.6, 1.3 Hz, H-4), 5.18 (dd, 1H, *J* = 3.6, 5.2 Hz, H-1), 4.90 (ddd, 1H, *J* = 48.0, 10.9, 3.6 Hz, H-3), 4.46–4.40 (m, 2H, H-2, H-5), 4.16 (dd, 1H, *J* = 11.1, 6.6 Hz, H-6), 4.02 (ddd, 1H, *J* = 11.1, 6.7, 1.2 Hz, H-6'), 2.45, 2.33 (2 × q, 2 × 2H, *J* = 7.6 Hz, CH_2CH_3), 1.99 (s, 3H, *Me* NHAc), 1.16, 1.10 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.5 (CO O-6), 175.2 (CO O-4), 173.7 (CO NHAc), 93.3 (d, ^3J = 9.5 Hz, C-1), 88.0 (d, ^1J = 188.7 Hz, C-3), 69.1 (d, ^2J = 16.5 Hz, C-4), 67.3 (d, ^3J = 5.8 Hz, C-5), 63.0 (d, ^4J = 3.3 Hz, C-6), 50.9 (d, ^2J = 17.4 Hz, C-2), 28.2, 28.1 (2 × CH_2CH_3), 22.9 (CH_3 NHAc), 9.5, 9.3 (2 × CH_2CH_3). ^{19}F NMR (MeOH-d_4, 376 MHz):

−205.73 (dddd, ^{2}J = 48.0 Hz, ^{3}J = 10.0, 6.5 Hz, ^{4}J = 5.2 Hz). Data for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.51 (ddd, 1H, *J* = 5.5, 3.6, 1.3 Hz, H-4), 4.73 (ddd, 1H, *J* = 47.2, 10.7, 3.6 Hz, H-3), 4.68 (d, 1H, *J* = 8.5 Hz, H-1), 4.20–4.03 (m, 3H, H-2, 2H-6), 3.96 (ddd, 1H, *J* = 6.6, 4.0, 1.3 Hz, H-5), 2.45, 2.33 (2 × q, 2 × 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.99 (s, 3H, *Me* NHAc), 1.16, 1.10 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.5 (CO O-6), 175.1 (CO O-4), 174.0 (CO NHAc), 96.5 (d, ^{3}J = 10.7 Hz, C-1), 90.1 (d, ^{1}J = 190.5 Hz, C-3), 71.2 (d, ^{3}J = 6.9 Hz, C-5), 68.3 (d, ^{2}J = 16.3 Hz, C-4), 62.7 (d, ^{4}J = 2.7 Hz, C-6), 54.5 (d, ^{2}J = 17.8 Hz, C-2), 28.2, 28.1 (2 × *C*H$_2$CH$_3$), 22.5 (*C*H$_3$ NHAc), 9.5, 9.2 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): −201.06 (ddd, ^{2}J = 47.2 Hz, ^{3}J = 10.8, 5.5 Hz).

2-Acetamido-4,6-di-*O*-butyryl-2,3-dideoxy-3-fluoro-D-galactopyranose (26)

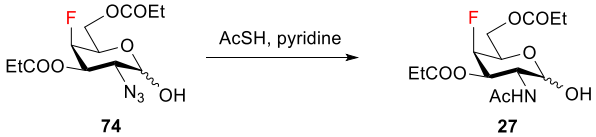


73 **26**

Compound **26** was prepared from **73** (123 mg, 0.35 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **26** (93 mg, 72%) as a thick colourless syrup which crystallized on standing, mp 144–148 °C (EtOAc), R_f 0.34 (EtOAc). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.75 (d, 1H, *J* = 9.1 Hz, N*H*), 5.61 (ddd, 1H, *J* = 6.5, 3.5, 1.3 Hz, H-1), 5.36 (dt, 1H, *J* = 4.4, 3.5 Hz, H-4), 4.79 (ddd, 1H, *J* = 48.0, 10.8, 3.5 Hz, H-3), 4.61 (dddd, 1H, *J* = 10.8, 9.8, 9.1, 3.5 Hz, H-2), 5.36 (ddd, 1H, *J* = 6.8, 6.4, 5.5 Hz, H-5), 4.14 (dd, 1H, *J* = 11.3, 6.4 Hz, H-6), 4.08 (ddd, 1H, *J* = 11.3, 6.8, 1.1 Hz, H-6'), 3.45 (d, 1H, *J* = 1.3 Hz, O*H*), 2.47−2.35 (m, 2H, COC*H*$_2$), 2.29 (t, 2H, *J* = 7.4 Hz, COC*H*$_2$), 2.04 (s, 3H, *Me* Ac), 1.72–1.59 (m, 4H, C*H*$_2$CH$_3$), 0.97, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.3, 172.9, 170.7 (3 × CO), 92.8 (d, ^{3}J = 9.5 Hz, C-1), 86.8 (d, ^{1}J = 191.8 Hz, C-3), 67.2 (d, ^{2}J = 16.8 Hz, C-4), 66.9 (d, ^{3}J = 5.7 Hz, C-5), 61.9 (d, ^{4}J = 2.1 Hz, C-6), 49.2 (d, ^{2}J = 18.3 Hz, C-2), 36.2, 36.0 (2 × CO*C*H$_2$), 23.6 (Me Ac), 18.6, 18.4 (2 × *C*H$_2$CH$_3$), 13.8, 13.7 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −204.28

(m). The β-anomer was not detected in intensity sufficient for characterisation within 24 h after dissolution in $CDCl_3$. HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1766.

2-Acetamido-2,4-dideoxy-4-fluoro-3,6-di-*O*-propionyl-D-galactopyranose (27)

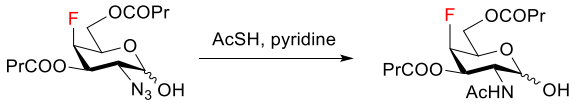


74 **27**

Compound **27** was prepared from **74** (132 mg, 0.41 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **27** (95 mg, 69%) as a white crystalline solid, mp 197–198 °C (EtOAc/PE), R_f 0.14 (EtOAc/PE 1:1). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1450. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.21 (ddd, 1H, J = 27.7, 11.5, 2.5 Hz, H-3), 5.16 (d, 1H, J = 3.4 Hz, H-1), 4.88 (dd, 1H, J = 51.3, 2.5 Hz, H-4), 4.44 (dd, 1H, J = 11.5, 3.4 Hz, H-2), 4.34 (ddd, 1H, J = 28.8, 6.7, 6.2 Hz, H-5), 4.25 (ddd, 1H, J = 11.1, 6.7, 1.4 Hz, H-6'), 4.19 (dd, 1H, J = 11.1, 6.2 Hz, H-6), 2.37, 2.36 (2 × q, 2 × 2H, J = 7.6 Hz, CH_2CH$_3$), 1.94 (s, 3H, *Me* NHAc), 1.12 (2 × t, 2 × 3H, J = 7.6 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.7 (CO O-6), 175.5 (CO O-3), 173.5 (CO NHAc), 93.0 (C-1), 88.2 (d, ^1J = 182.8 Hz, C-4), 70.0 (d, ^2J = 17.9 Hz, C-3), 67.8 (d, ^2J = 17.8 Hz, C-5), 63.4 (d, ^3J = 6.1 Hz, C-6), overlapped with MeOH-d_4 (C-2), 28.3, 28.1 (2 × *C*H$_2$CH$_3$), 22.5 (*Me* NHAc), 9.4, 9.3 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): δ −223.10 (ddd, ^2J = 51.3 Hz, ^3J = 28.8, 27.7 Hz). NMR data for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.08 (ddd, 1H, J = 28.0, 11.2, 2.6 Hz, H-3), 4.82 (dd, 1H, J = 51.3, 2.7 Hz, H-4), 4.77 (d, 1H, J = 8.4 Hz, H-1), overlapped with α anomer (2H, H-6), 4.06 (dd, 1H, J = 11.2, 8.4 Hz, H-2), 3.94 (dt, 1H, J = 27.0, 6.4 Hz, H-5), 2.37, 2.36 (2 × q, 2 × 2H, J = 7.6 Hz, CH_2CH$_3$), 1.92 (s, 3H, *Me* NHAc), 1.12 (2 × t, 2 × 3H, J = 7.6 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.6 (CO O-6), 175.2 (CO O-3), 173.7 (CO NHAc), 96.7 (C-1), 87.4 (d, ^1J = 183.5 Hz, C-4), 72.4 (d, ^2J = 17.8 Hz, C-3), 72.3 (d, ^2J = 17.7 Hz, C-5), 63.2 (d, ^3J = 5.7 Hz, C-6), 53.2 (C-2), 28.2, 28.1 (2

× CH_2CH_3), 22.8 (*Me* NHAc), 9.5, 9.3 (2 × CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −220.51 (ddd, ^2J = 51.3 Hz, ^3J = 28.0, 27.0 Hz).

2-Acetamido-3,6-di-*O*-butyryl-2,4-dideoxy-4-fluoro-D-galactopyranose (28)

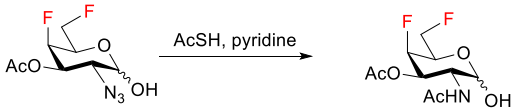


75 **28**

Compound **28** was prepared from **75** (165 mg, 0.48 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 2:3 → EtOAc afforded **28** (150 mg, 87%) as a white crystalline solid, mp 157–160 °C (EtOAc/PE), R_f 0.62 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1764. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.21 (ddd, 1H, *J* = 27.6, 11.5, 2.5 Hz, H-3), 5.15 (d, 1H, *J* = 3.5 Hz, H-1), 4.88 (dd, 1H, *J* = 51.4, 2.5 Hz, H-4), 4.45 (dd, 1H, *J* = 11.5, 3.5 Hz, H-2), 4.34 (ddd, 1H, *J* = 28.9, 6.6, 6.3 Hz, H-5), 4.25 (ddd, 1H, *J* = 11.2, 6.6, 1.3 Hz, H-6'), 4.20 (dd, 1H, *J* = 11.2, 6.3 Hz, H-6), 2.34, 2.32 (2 × t, 2 × 2H, *J* = 7.4 Hz, COCH_2), 1.94 (s, 3H, *Me* NHAc), 1.64 (h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.95 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 174.8, 174.6, 173.5 (3 × CO), 93.0 (C-1), 88.2 (d, ^1J = 182.9 Hz, C-4), 69.9 (d, ^2J = 17.8 Hz, C-3), 67.7 (d, ^2J = 17.8 Hz, C-5), 63.3 (d, ^3J = 6.1 Hz, C-6), 49.3 (d, ^3J = 2.5 Hz, C-2), 36.9, 36.7 (2 × COCH_2), 22.6 (Me NHAc), 19.5, 19.4 (2 × CH_2CH$_3$), 13.88, 13.86 (2 × CH$_2$$CH_3$). ^{19}F NMR (MeOH-$d_4$, 376 MHz): δ −223.03 (ddd, ^2J = 51.4 Hz, ^3J = 28.9, 27.6 Hz). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.08 (ddd, 1H, *J* = 27.9, 11.3, 2.6 Hz, H-3), 4.81 (dd, 1H, *J* = 50.7, 2.6 Hz, H-4), 4.76 (dd, 1H, *J* = 8.4, 1.1 Hz, H-1), 4.06 (dd, 1H, *J* = 11.3, 8.4 Hz, H-2), 3.93 (ddd, 1H, *J* = 26.9, 7.0, 5.9 Hz, H-5), 1.92 (s, 3H, *Me* NHAc). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 174.8, 174.3, 173.6 (3 × CO), 96.7 (C-1), 87.4 (d, ^1J = 183.5 Hz, C-4), 72.30 (d, ^2J = 17.5 Hz, C-3/5), 72.26 (d, ^2J = 17.7 Hz, C-3/5), 63.2 (d, ^3J = 5.5 Hz, C-6), 53.2 (d, ^3J = 1.4 Hz, C-2), 36.8, 36.7 (2 ×

$COCH_2$), 23.2 (Me NHAc), 19.5, 19.4 (2 × CH_2CH_3), 13.88, 13.86 (2 × CH_2CH_3). ^{19}F NMR (MeOH-d_4, 376 MHz): δ −220.53 (ddd, ^2J = 50.7 Hz, ^3J = 27.9, 26.9 Hz).

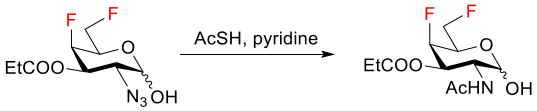
2-Acetamido-3-*O*-acetyl-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (31)



65 **31**

Compound **31** was prepared from **65** (65 mg, 0.26 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 3:1 → EtOAc afforded **31** (47 mg, 68%) as a white crystalline solid, mp 203–205 °C (EtOAc), R_f 0.31 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{10}H_{16}F_2NO_5$, 268.0991; found, 268.0989. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.21 (ddd, 1H, J = 27.5, 11.4, 2.5 Hz, H-3), 5.18 (d, 1H, J = 3.4 Hz, H-1), from ^{1}H {^{19}F-4} 4.92 (d, 1H, J = 2.5 Hz, H-4), 4.58 (ddd, 1H, J = 46.3, 9.5, 5.8 Hz, H-6'), from ^{1}H {^{19}F-6} 4.49 (ddd, 1H, J = 9.5, 6.6, 1.2 Hz, H-6), 4.44 (dd, 1H, J = 11.4, 3.4 Hz, H-2), 4.43 (dddd, 1H, J = 29.3, 12.5, 6.6, 5.8 Hz, H-5), 2.07 (s, 3H, *Me* OAc), 1.95 (s, 3H, *Me* NHAc). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 173.6 (CO NHAc), 172.1 (CO OAc), 92.9 (C-1), 87.8 (dd, ^1J = 182.3 Hz, ^3J = 6.3 Hz, C-4), 82.4 (dd, ^1J = 168.4 Hz, ^3J = 6.4 Hz, C-6), 70.0 (dd, ^2J = 17.8 Hz, ^4J = 1.0 Hz, C-3), 68.5 (dd, ^2J = 23.4, 17.8 Hz, C-5), overlapped with MeOH-d_4 (C-2), 22.5 (Me NHAc), 20.7 (Me OAc). ^{19}F NMR (MeOH-d_4, 376 MHz): –222.99 (ddd, ^2J = 51.3 Hz, ^3J = 29.3, 27.5 Hz, F-4), –234.49 (ddd, ^2J = 46.9, 46.3 Hz, ^3J = 12.5 Hz, F-6). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.08 (ddd, 1H, J = 27.9, 11.3, 2.8 Hz, H-3), 4.85 (dd, 1H, J = 50.5, 2.8 Hz, H-4), 4.79 (dd, 1H, J = 8.6, 1.5 Hz, H-1), 4.67–4.41 (m, 2H, H-6), 4.19–3.93 (m, 1H, H-5), 4.05 (dd, 1H, J = 11.3, 8.6 Hz, H-2). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 96.7 (C-1). ^{19}F{^{1}H} NMR (MeOH-d_4, 376 MHz): –220.44/–220.72 (s, F-4), –234.21/–234.68 (s, F-6).

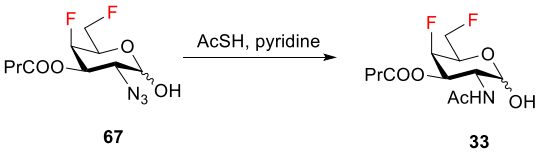
2-Acetamido-2,4,6-trideoxy-4,6-difluoro-3-*O*-propionyl-D-galactopyranose (32)



66 **32**

Compound **32** was prepared from **66** (80 mg, 0.30 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **32** (75 mg, 88%) as a colourless crystalline solid, mp 196−197.5 °C (EtOAc) R_f 0.34 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{11}H_{18}F_2NO_5$, 282.1147; found, 282.1149. NMR data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.22 (ddd, 1H, *J* = 27.7, 11.4, 2.5 Hz, H-3), from ^{1}H {^{19}F-4} 5.17 (d, 1H, *J* = 3.4 Hz, H-1), 4.91 (dd, 1H, *J* = 51.3, 2.5 Hz, H-4), from ^{1}H {^{19}F-6} 4.59 (dd, 1H, *J* = 9.3, 5.5 Hz, H-6'), from ^{1}H {^{19}F-6} 4.49 (dd, 1H, *J* = 9.3, 6.7 Hz, H-6), 4.45 (dd, 1H, *J* = 11.4, 3.4 Hz, H-2), 4.40 (dddd, 1H, *J* = 30.2, 13.4, 6.7, 5.5 Hz, H-5), 2.37 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.94 (s, 3H, *Me* NHAc), 1.12 (t, 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.4 (CO), 173.5 (CO NHAc), 93.0 (C-1), 87.9 (dd, ^1J = 182.3 Hz, ^3J = 6.3 Hz, C-4), 82.5 (dd, ^1J = 168.4 Hz, ^3J = 6.3 Hz, C-6), 69.9 (d, ^2J = 17.7 Hz, C-3), 68.5 (dd, ^2J = 23.4, 17.8 Hz, C-5), overlapped with MeOH-d_4 (C-2), 28.3 (*C*H$_2$CH$_3$), 22.5 (Me NHAc), 9.4 (CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): −223.02 (ddd, ^2J = 51.3 Hz, ^3J = 30.2, 27.7 Hz, F-4), −234.44 (td, ^2J = 46.4 Hz, ^3J = 13.4 Hz, F-6). NMR data for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.09 (ddd, 1H, *J* = 28.0, 11.2, 2.6 Hz, H-3), 4.85 (dd, 1H, *J* = 51.0, 2.7 Hz, H-4), 4.79 (d, 1H, *J* = 8.4 Hz, H-1), 4.68–4.41 (m, 2H, H-6), from ^{1}H {^{19}F-4} 4.07 (dd, 1H, *J* = 11.2, 8.4 Hz, H-2), from ^{1}H {^{19}F-6} 4.01 (dt, 1H, *J* = 27.0, 5.7 Hz, H-5), 2.37 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.93 (s, 3H, *Me* NHAc), 1.12 (t, 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 175.2 (CO), 173.7 (CO NHAc), 96.7 (C-1), 87.1 (dd, ^1J = 182.3 Hz, ^3J = 6.3 Hz, C-4), 82.2 (dd, ^1J = 169.3 Hz, ^3J = 5.7 Hz, C-6), 73.0 (dd, ^2J = 23.1, 17.7 Hz, C-5), 72.3 (d, ^2J = 17.8 Hz, C-3), 53.2 (C-2), 28.2 (*C*H$_2$CH$_3$), 22.8 (Me NHAc), 9.5 (CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): −220.46 (ddd, ^2J = 51.0 Hz, ^3J = 28.0, 27.0 Hz, F-4), −234.16 (ddd, ^2J = 47.2, 46.7 Hz, ^3J = 12.0 Hz, F-6).

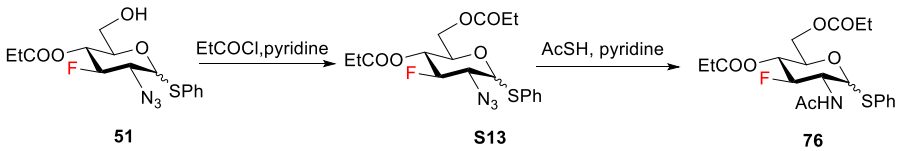
2-Acetamido-3-*O*-butyryl-2,4,6-trideoxy-4,6-difluoro-D-galactopyranose (33)



67 33

Compound **33** was prepared from **67** (164 mg, 0.59 mmol) according to the general procedure for azide reduction and acetylation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded **33** (141 mg, 81%) as a white crystalline solid, mp 167–168 °C (EtOAc), R_f 0.18 (EtOAc/PE 1:1). HRMS-APCI (*m/z*): [M + H]$^+$ calcd for $C_{12}H_{20}F_2NO_5$, 296.1304 found, 296.1307. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.73 (d, 1H, *J* = 9.6 Hz, N*H*), 5.35 (t, 1H, *J* = 3.5 Hz, H-1), 5.26 (ddd, 1H, *J* = 27.9, 11.4, 2.5 Hz, H-3), 4.84 (dd, 1H, *J* = 51.0, 2.5 Hz, H-4), 4.72–4.50 (m, 3H, H-2, 2H-6), 4.38 (ddt, 1H, *J* = 28.8, 12.3, 6.2 Hz, H-5), 3.29 (dd, 1H, *J* = 3.6, 1.6 Hz, O*H*), 2.36 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.97 (s, 3H, CH_3 NHAc), 1.66 (h, 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.95 (t, 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.1, 170.3 (2 × CO), 92.4 (C-1), 86.4 (dd, ^1J = 185.5 Hz, ^3J = 5.7 Hz, C-4), 81.1 (dd, ^1J = 169.5 Hz, ^3J = 6.3 Hz, C-6), 68.0 (d, ^2J = 18.0 Hz, C-3), 67.9 (dd, ^2J = 23.8, 18.1 Hz, C-5), 48.1 (d, ^3J = 2.8 Hz, C-2), 36.2 (CO*C*H$_2$), 23.4 (*C*H$_3$ NHAc), 18.6 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −220.04 (ddd, ^2J = 51.0 Hz, ^3J = 28.8, 27.9 Hz, F-4), −232.79 (ddd, ^2J = 46.3, 46.0 Hz, ^3J = 12.3 Hz, F-6). The signals of the β-anomer were not detected in intensity sufficient for characterisation within 24 h after dissolution in $CDCl_3$.

Phenyl 2-Acetamido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside (76)



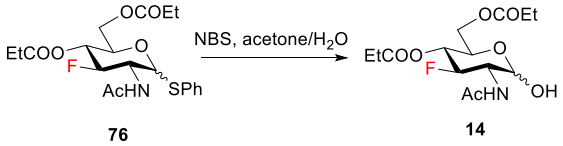
51 S13 76

Compound **51** was O6-propionylated according to the general procedure for acylation to give phenyl 2-azido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside **S13** as described above under the preparation of compound **69**. Compound **S13** (250 mg, 0.61 mmol) was subjected to azide reduction and acetylation according to the general procedure. Chromatography in EtOAc/PE 1:5 →

EtOAc/PE 1:2 afforded first the α-anomer α-**76** (130 mg, 50%, 40% from **51**) as a white gum, followed by mixture of both anomers α/β ca 1:5 (100 mg, 38%) as a white gum. Data for α-anomer: R_f 0.11 (EtOAc/PE 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.45–7.43 (m, 2H, CH_{arom}), 7.33–7.29 (m, 3H, CH_{arom}), 5.73 (dd, 1H, *J* = 5.3, 3.2 Hz, H-1), 5.73 (d, 1H, *J* = 8.2 Hz, N*H*), 5.25 (ddd, 1H, *J* = 13.2, 10.2, 8.6 Hz, H-4), 4.71 (dddd, 1H, *J* = 10.9, 9.9, 8.2, 5.3 Hz, H-2), 4.55 (ddd, 1H, *J* = 52.5, 10.9, 8.6 Hz, H-3), 4.46 (ddd, 1H, *J* = 10.2, 5.1, 2.3 Hz, H-5), 4.26 (dd, 1H, *J* = 12.4, 5.1 Hz, H-6'), 4.13 (ddd, 1H, *J* = 12.4, 2.3, 1.9 Hz, H-6), 2.43–2.30 (m, 4H, C*H*$_2$CH$_3$), 2.07 (s, 3H, *Me* Ac), 1.17, 1.13 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.2, 172.9, 170.1 (3 × CO), 132.7 (C_q), 131.8, 129.5 (2 × 2CH_{arom}), 128.2 (CH_{arom}), 90.2 (d, ^1J = 191.0 Hz, C-3), 87.8 (d, ^3J = 7.5 Hz, C-1), 69.2 (d, ^3J = 6.4 Hz, C-5), 68.7 (d, ^2J = 18.3 Hz, C-4), 61.9 (d, ^4J = 1.0 Hz, C-6), 52.5 (d, ^2J = 17.5 Hz, C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 23.5 (*Me* Ac), 9.0, 9.1 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −197.06 (dddd, ^2J = 52.5 Hz, ^3J = 13.2, 9.9 Hz, ^4J = 3.2 Hz). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{27}FNO_6S$, 428.1538; found, 428.1533. NMR data for the β-anomer: R_f 0.08 (EtOAc/PE 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.52–7.49 (m, 2H, CH_{arom}), 7.32–7.30 (m, 3H, CH_{arom}), 5.73 (d, 1H, *J* = 7.4 Hz, N*H*), 5.40 (d, 1H, *J* = 10.3 Hz, H-1), 5.14 (ddd, 1H, *J* = 40.1, 9.6, 9.1 Hz, H-3), from ^{1}H {^{19}F} 5.10 (dd, 1H, *J* = 9.7, 9.1 Hz, H-4), 4.21–4.15 (m, 2H, H-6), from ^{1}H {^{19}F} 3.74 (ddd, 1H, *J* = 9.7, 5.2, 2.6 Hz, H-5), from ^{1}H {^{19}F} 3.40 (ddd, 1H, *J* = 10.3, 9.6, 7.4 Hz, H-2), 2.43–2.30 (m, 4H, C*H*$_2$CH$_3$), 2.04 (s, 3H, *Me* Ac), 1.14, 1.11 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.2, 173.1, 170.9 (3 × CO), 133.0 (2CH_{arom}), 132.0 (C_q), 129.2 (2CH_{arom}), 128.5 (CH_{arom}), 90.7 (d, ^1J = 188.8 Hz, C-3), 84.1 (d, ^3J = 6.6 Hz, C-1), 75.3 (d, ^3J = 7.7 Hz, C-5), 69.1 (d, ^2J = 18.5 Hz, C-4), 62.3 (d, ^4J = 1.7 Hz, C-6), 56.1 (d, ^2J = 18.0 Hz, C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 23.8 (*Me* Ac), 9.12, 9.10 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −190.77 (m).

2-Acetamido-2,3-dideoxy-3-fluoro-4,6-di-*O*-propionyl-D-glucopyranose (14)

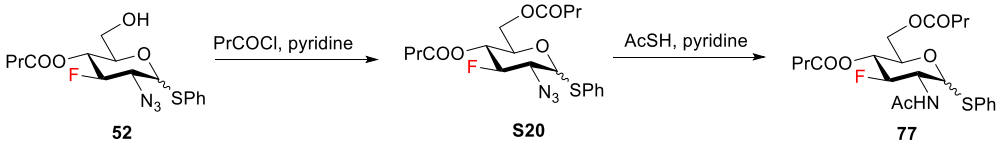
(An alternative to the procedure from **69**)



76 **14**

Compound **14** was also prepared from **76** (160 mg, 0.37 mmol) according to the general procedure for the thioglycoside hydrolysis. The starting compound reacted sluggishly and the reaction mixture had to be stirred for 14 days. A total of 1.0 g of *N*-bromosuccinimide was added in three portions to achieve consumption of the majority of the starting material. Chromatography in EtOAc/PE 1:2 → EtOAc afforded **14** (60 mg, 48%) as a white crystalline solid identical to **14** prepared from compound **69** (see above) according to the NMR data.

Phenyl 2-Acetamido-2,3-dideoxy-3-fluoro-4,6-di-*O*-butyryl-1-thio-α/β-D-glucopyranoside (77)



52 **S20** **77**

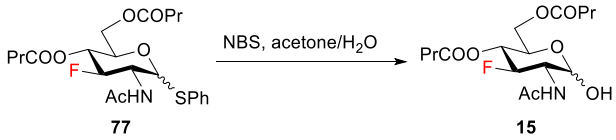
Compound **52** (470 mg, 1.27 mmol) was O6-butyrylated according to the general procedure for acylation using butyryl chloride (200 µL, 1.92 mmol). Chromatography in EtOAc/PE 1:7 afforded phenyl 2-azido-4,6-di-*O*-butyryl-2,3-dideoxy-3-fluoro-1-thio-α/β-D-glucopyranoside **S20** (475 mg, 85%) as a colourless gel-like mixture of anomers, R_f 0.50 (EtOAc/heptane 1:5). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{20}H_{27}FNO_5S$, 412.1588; found, 412.1583. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.50–7.46 (m, 2H, CH_{arom}), 7.38–7.29 (m, 3H, CH_{arom}), 5.63 (dd, 1H, *J* = 5.7, 3.1 Hz, H-1), 5.22 (ddd, 1H, *J* = 13.3, 10.3, 8.9 Hz, H-4), 4.75 (ddd, 1H, *J* = 52.4, 10.0, 8.9 Hz, H-3), from ^{1}H {^{19}F} 4.50 (ddd, 1H, *J* = 10.3, 5.3, 2.2 Hz, H-5), 4.23 (dd, 1H, *J* = 12.4, 5.3 Hz, H-6), 4.12 (ddd, 1H, *J* = 11.0, 10.0, 5.7 Hz, H-2), 4.08 (ddd, 1H, *J* = 12.4, 2.2, 1.8 Hz, H-6'), 2.39–2.19 (m, 4H, COCH_2), 1.73–1.56 (m, 4H, CH_2CH$_3$), 0.90–0.89 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.2, 172.2 (2 × CO), 132.4 (C_q), 132.3, 129.4 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 91.8 (d,

^{1}J = 189.5 Hz, C-3), 86.3 (d, ^{3}J = 7.8 Hz, C-1), 68.7 (d, ^{3}J = 7.0 Hz, C-5), 68.2 (d, ^{2}J = 18.2 Hz, C-4), 62.2 (d, ^{2}J = 17.1 Hz, C-2), 61.7 (d, ^{4}J = 1.5 Hz, C-6), 36.0, 35.9 (2 × CO*C*H$_2$), 18.5, 18.3 (2 × *C*H$_2$CH$_3$), 13.7, 13.6 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −193.95 (ddddd, ^{2}J = 52.4 Hz, ^{3}J = 13.3, 11.0 Hz, ^{4}J = 3.3 Hz, ^{5}J = 1.8 Hz). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.60–7.57 (m, 2H, CH$_{arom}$), 7.38–7.29 (m, 3H, CH$_{arom}$), 5.09 (ddd, 1H, *J* = 11.9, 10.2, 9.2 Hz, H-4), 4.42 (dt, 1H, *J* = 51.4, 9.2 Hz, H-3), 4.40 (dd, 1H, *J* = 10.2, 0.8 Hz, H-1), 4.20–4.18 (m, 2H, H-6), 3.59 (dddd, 1H, *J* = 10.2, 4.4, 3.1, 1.3 Hz, H-5), 3.49 (ddd, 1H, *J* = 12.5, 10.2, 9.2 Hz, H-2), 2.39–2.19 (m, 4H, COC*H*$_2$), 1.73–1.56 (m, 4H, C*H*$_2$CH$_3$), 0.90–0.89 (m, 6H, C*H*$_3$).^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.2, 172.1 (2 × CO), 134.2 (2CH$_{arom}$), 130.2 (C$_q$), 129.2 (2CH$_{arom}$), 129.1 (CH$_{arom}$), 94.0 (d, ^{1}J = 192.1 Hz, C-3), 85.4 (d, ^{3}J = 6.8 Hz, C-1), 75.4 (d, ^{3}J = 7.4 Hz, C-5), 67.6 (d, ^{2}J = 18.4 Hz, C-4), 63.1 (d, ^{2}J = 17.5 Hz, C-2), 61.8 (d, ^{4}J = 1.8 Hz, C-6), 36.04, 35.97 (2 × CO*C*H$_2$), 18.43, 18.38 (2 × *C*H$_2$CH$_3$), 13.8, 13.6 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −198.87 (dddd, ^{2}J = 51.4 Hz, ^{3}J = 12.5, 11.9 Hz, ^{5}J = 1.3 Hz).

Compound **S20** (408 mg, 0.93 mmol) was subjected to azide reduction and acetylation according to the general procedure. Chromatography in EtOAc/PE 1:4 → EtOAc/PE 1:1 afforded **77** (402 mg, 95%, 80% from **52**, α/β 1.4:1) as a colourless thick syrup, R_f 0.17 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): [M + H]$^+$ calcd for C$_{22}$H$_{31}$FNO$_6$S, 456.1851; found, 456.1853. NMR data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.45–7.42 (m, 2H, CH$_{arom}$), 7.33–7.29 (m, 3H, CH$_{arom}$), 5.78 (d, 1H, *J* = 8.3 Hz, N*H*), 5.73 (dd, 1H, *J* = 5.4, 3.3 Hz, H-1), 5.24 (ddd, 1H, *J* = 13.3, 10.2, 8.6 Hz, H-4), 4.71 (dddd, 1H, *J* = 10.9, 9.0, 8.3, 5.4 Hz, H-2), 4.55 (ddd, 1H, *J* = 52.5, 10.9, 8.6 Hz, H-3), 4.45 (ddd, 1H, *J* = 10.2, 5.1, 2.3 Hz, H-5), 4.23 (dd, 1H, *J* = 12.4, 5.1 Hz, H-6), 4.14 (ddd, 1H, *J* = 12.4, 2.3, 1.8 Hz, H-6'), 2.37–2.04 (m, 4H, COC*H*$_2$), 2.07 (s, 3H, *Me* NHAc), 1.72–1.58 (m, 4H, C*H*$_2$CH$_3$), 0.98–0.91 (m, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 173.4 (CO O-6), 172.0 (CO O-4), 170.2 (CO NHAc), 132.7 (C$_q$), 131.8, 129.5 (2 × 2CH$_{arom}$), 128.2 (CH$_{arom}$), 90.2 (d, ^{1}J = 191.0 Hz, C-3), 87.7 (d, ^{3}J = 7.5 Hz, C-1), 69.0 (d, ^{3}J = 6.9 Hz, C-5), 68.6 (d, ^{2}J = 18.3 Hz, C-4), 61.8 (d, ^{4}J = 1.4 Hz, C-6), 52.5 (d, ^{2}J = 17.6 Hz, C-2), 36.10, 36.08 (2 × CO*C*H$_2$), 23.5 (*Me* NHAc), 18.5, 18.4 (2 × *C*H$_2$CH$_3$), 13.8, 13.6 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −196.87 (dddd, ^{2}J = 52.5 Hz, ^{3}J = 13.3, 9.0 Hz, ^{4}J =

3.3 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.52–7.49 (m, 2H, CH_{arom}), 7.33–7.29 (m, 3H, CH_{arom}), 5.82 (d, 1H, *J* = 7.5 Hz, N*H*), 5.37 (dd, 1H, *J* = 10.3, 0.8 Hz, H-1), 5.12 (ddd, 1H, *J* = 45.9, 10.0, 8.9 Hz, H-3), 5.07 (ddd, 1H, *J* = 13.0, 10.0, 8.9 Hz, H-4), 4.18–4.17 (m, 2H, H-6), 3.71 (ddd, 1H, *J* = 10.0, 4.5, 3.2 Hz, H-5), 3.39 (dddd, 1H, *J* = 11.0, 10.3, 10.0, 7.5 Hz, H-2), 2.37–2.04 (m, 4H, COCH_2), 2.07 (s, 3H, *Me* NHAc), 1.72–1.58 (m, 4H, CH_2CH$_3$), 0.98–0.91 (m, 6H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 173.3 (CO O-6), 172.2 (CO O-4), 170.9 (CO NHAc), 133.0 (2CH_{arom}), 132.0 (C_q), 129.1 (2CH_{arom}), 128.4 (CH_{arom}), 90.7 (d, ^{1}J = 188.8 Hz, C-3), 84.1 (d, ^{3}J = 6.8 Hz, C-1), 75.3 (d, ^{3}J = 7.8 Hz, C-5), 69.2 (d, ^{2}J = 18.6 Hz, C-4), 62.3 (d, ^{4}J = 2.0 Hz, C-6), 56.0 (d, ^{2}J = 17.6 Hz, C-2), 36.1, 36.0 (2 × CO*C*H$_2$), 23.8 (Me NHAc), 18.5, 18.4 (2 × *C*H$_2$CH$_3$), 13.8, 13.6 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −190.70 (m).

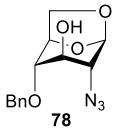
2-Acetamido-4,6-di-*O*-butyryl-2,3-dideoxy-3-fluoro-α-D-glucopyranose (15)



Compound **15** was prepared from **77** (335 mg, 0.74 mmol) according to the general procedure for the thioglycoside hydrolysis. Starting compound reacted very slowly, reaction was stirred for 14 days and a total of 0.8 g of *N*-bromosuccinimide (4.5 mmol) was added in 2 portions. Chromatography in EtOAc/PE 3:2 afforded the unreacted starting material **77** (110 mg, 33%) followed by **15** (142 mg, 53%) as a white crystalline solid, R_f 0.13 (EtOAc/heptane 3:2), mp 153–155 °C (EtOAc/PE). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.88 (d, 1H, *J* = 9.0 Hz, N*H*), 5.29 (ddd, 1H, *J* = 3.7, 3.5, 3.4 Hz, H-1), 5.23 (ddd, 1H, *J* = 12.5, 9.3, 8.9 Hz, H-4), 4.67 (ddd, 1H, *J* = 53.1, 10.4, 8.9 Hz, H-3), 4.36 (dddd, 1H, *J* = 10.5, 10.4, 9.0, 3.7 Hz, H-2), 4.21–4.13 (m, 3H, H-5, 2H-6), 4.02 (br s, 1H, O*H*), 2.36–2.31 (m, 4H, COCH_2), 2.04 (s, 3H, *Me* NHAc), 1.69–1.61 (m, 4H, CH_2CH$_3$), 0.95, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 173.7 (CO O-6), 172.1 (CO O-4), 170.8 (CO NHAc), 92.3 (d, ^{3}J = 9.4 Hz, C-1), 90.3 (d, ^{1}J = 188.6 Hz, C-3), 68.7 (d, ^{2}J = 18.1 Hz, C-4), 67.7 (d, ^{3}J = 7.0 Hz, C-5), 61.8 (d, ^{4}J = 1.5 Hz, C-6), 52.6 (d, ^{2}J = 16.9 Hz, C-2), 36.11, 36.07 (2 × CO*C*H$_2$), 25.5

(Me NHAc), 18.5, 18.4 (2 × CH_2CH_3), 13.8, 13.6 (2 × CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −201.15 (dddd, ^2J = 53.1 Hz, ^3J = 12.5, 10.5 Hz, ^4J = 3.5 Hz). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1766.). The signals of the β-anomer were not detected in intensity sufficient for characterisation within 24 h after sample dissolution in $CDCl_3$

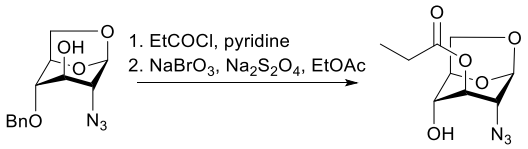
1,6-Anhydro-2-azido-4-*O*-benzyl-2-deoxy-β-D-glucopyranose (78)



78

Compound **78** was prepared according to the published procedure.[6]

1,6-Anhydro-2-azido-2-deoxy-3-*O*-propionyl-β-D-glucopyranose (79)

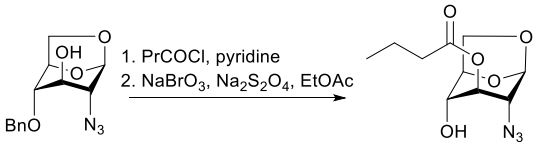


78 **79**

Compound **78** (500 mg, 1.80 mmol) was O3-propionylated according to the general procedure for acylation using propionyl chloride (210 μL, 2.40 mmol). Chromatography in EtOAc/PE 1:3 afforded colourless thick syrup (550 mg) R_f 0.27 (EtOAc/PE 1:3), which was dissolved in EtOAc (24 mL). A solution of $NaBrO_3$ (0.75 g, 4.97 mmol) in water (16 mL) was added, the resulting mixture was stirred vigorously, and a solution of $Na_2S_2O_4$ (0.87 g, 5.00 mmol) in water (35 mL) was added dropwise at rt. The reaction mixture turned orange. Vigorous stirring continued at rt until TLC (EtOAc/PE 1:2) indicated absence of the starting compound (*ca* 2.5 h). The organic phase was separated and the water phase was extracted with EtOAc (3×). EtOAc solutions were combined and washed with $NaHCO_3$ and the water phase was extracted with dichloromethane. Organic phases were combined, dried and concentrated. Chromatography in EtOAc/PE 1:2 afforded **79** (268 mg, 61%) as a thick colourless syrup, R_f 0.1 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 5.43 (t, 1H, J = 1.6 Hz, H-1), 5.07

(tt, 1H, *J* = 1.6, 0.9 Hz, H-3), 4.58 (dddt, 1H, *J* = 5.8, 2.0, 1.1, 0.9 Hz, H-5), 4.11 (dd, 1H, *J* = 7.6, 1.1 Hz, H-6^{en}), 3.82 (dd, 1H, *J* = 7.6, 5.8 Hz, H-6^{ex}), 3.62 (br d, 1H, *J* = 9.0 Hz, H-4), 3.48 (td, 1H, *J* = 1.6, 0.9 Hz, H-2), 2.88 (d, *J* = 9.0 Hz, O*H*), 2.39 (q, 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.15 (t, 3H, *J* = 7.5 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 173.3 (CO), 100.1 (C-1), 76.2 (C-5), 72.1 (C-3), 68.9 (C-4), 65.2 (C-6), 59.4 (C-2), 27.7 (*C*H$_2$CH$_3$), 9.0 (CH$_2$*C*H$_3$). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for C$_9$H$_{14}$NO$_5$, 216.0866; found, 216.0869.

1,6-Anhydro-2-azido-3-*O*-butyryl-2-deoxy-β-D-glucopyranose (80)

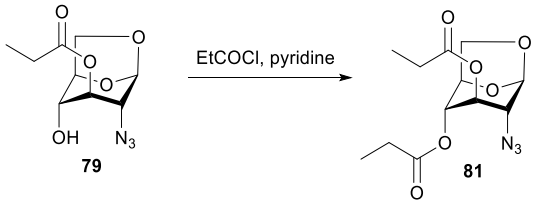


78 80

Compound **78** (645 mg, 2.33 mmol) was O3-butyrylated according to the general procedure for acylation using butyryl chloride (310 μL, 2.99 mmol). Chromatography in EtOAc/PE 1:3 afforded thick colourless syrup (570 mg) R_f 0.33 (EtOAc/PE 1:3), which was dissolved in EtOAc (23 mL). A solution of $NaBrO_3$ (0.72 g, 4.77 mmol) in water (15 mL) was added, the resulting mixture was stirred vigorously, and a solution of $Na_2S_2O_4$ (0.84 g, 4.82 mmol) in water (33 mL) was added dropwise at rt. The reaction mixture turned orange. Vigorous stirring continued at rt until TLC (EtOAc/PE 1:2) indicated the absence of the starting compound (2.5 h). The organic phase was separated and the water phase was extracted with EtOAc (3×). EtOAc solutions were combined and washed with $NaHCO_3$ and the water phase was extracted with dichloromethane. Organic phases were combined, dried and concentrated. Chromatography in EtOAc/PE 1:2 afforded **80** (263 mg, 44%) as a thick colourless syrup, R_f 0.23 (EtOAc/PE 1:2). ^{1}H NMR (CDCl$_3$, 400 MHz, H-H COSY): δ 5.42 (t, 1H, *J* = 1.6 Hz, H-1), 4.85 (p, 1H, *J* = 1.6 Hz, H-3), 4.58 (ddd, 1H, *J* = 5.7, 1.6, 1.1 Hz, H-5), 4.11 (dd, 1H, *J* = 7.6, 1.1 Hz, H-6^{en}), 3.81 (dd, 1H, *J* = 7.6, 5.7 Hz, H-6^{ex}), 3.61 (t, 1H, *J* = 1.6 Hz, H-4), 3.46 (q, 1H, *J* = 1.6 Hz, H-2), 2.93 (br s, 1H, O*H*), 2.34 (t, 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.67 (h, 2H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 0.96 (t, 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.5 (CO), 100.1 (C-1), 76.2 (C-5), 72.0 (C-3),

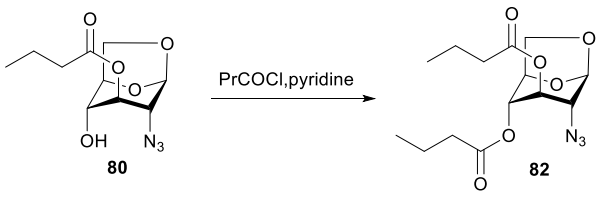
68.9 (C-4), 65.2 (C-6), 59.4 (C-2), 36.3 ($CO\mathit{C}H_2$), 18.4 ($\mathit{C}H_2CH_3$), 13.7 ($CH_2\mathit{C}H_3$). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{10}H_{16}NO_5$, 230.1022; found, 230.1020.

1,6-Anhydro-2-azido-2-deoxy-3,4-di-*O*-propionyl-β-D-glucopyranose (81)



Compound **81** was prepared from **79** (244 mg, 1.00 mmol) according to the general procedure for acylation starting using propionyl chloride (92 μL, 1.05 mmol). Chromatography in EtOAc/PE 1:4 afforded **81** (210 mg, 70%) as thick colourless syrup, R_f 0.44 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 5.51 (t, 1H, *J* = 1.6 Hz, H-1), 4.91 (p, 1H, *J* = 1.6 Hz, H-3), 4.69 (dt, 1H, *J* = 1.6, 1.0 Hz, H-4), 4.65 (dddd, 1H, *J* = 5.7, 1.6, 1.1, 1.0 Hz, H-5), 4.13 (dd, 1H, *J* = 7.8, 1.1 Hz, H-6^{en}), 3.82 (dd, 1H, *J* = 7.8, 5.7 Hz, H-6^{ex}), 3.17 (td, 1H, *J* = 1.6, 1.0 Hz, H-2), 2.46, 2.39 (2 × q, 2 × 2H, *J* = 7.6 Hz, CH_2CH$_3$), 1.18, 1.16 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.6, 172.8 (2 × CO), 100.5 (C-1), 73.8 (C-5), 70.1 (C-3), 69.6 (C-4), 65.4 (C-6), 59.0 (C-2), 27.7, 27.6 (2 × $\mathit{C}H_2CH_3$), 9.01, 8.99 (2 × $CH_2\mathit{C}H_3$). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{12}H_{18}NO_6$, 272.1128; found, 272.1128.

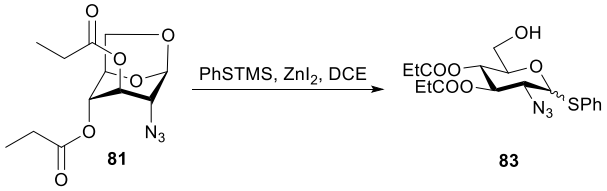
1,6-Anhydro-2-azido-3,4-di-*O*-butyryl-2-deoxy-β-D-glucopyranose (82)



Compound **82** was prepared from **80** (238 mg, 0.93 mmol) according to the general procedure for acylation starting using butyryl chloride (125 μL, 1.20 mmol). Chromatography in EtOAc/PE 1:4 afforded **82** (251 mg, 83%) as thick colourless syrup, R_f 0.52 (EtOAc/PE 1:3). ^{1}H NMR ($CDCl_3$, 400

MHz, H-H COSY): δ 5.51 (t, 1H, *J* = 1.6 Hz, H-1), 4.91 (p, 1H, *J* = 1.6 Hz, H-3), 4.69 (tt, 1H, *J* = 1.6, 0.8 Hz, H-4), 4.64 (dtd, 1H, *J* = 5.7, 1.6, 1.0 Hz, H-5), 4.13 (dd, 1H, *J* = 7.8, 1.0 Hz, H-6^{en}), 3.81 (dd, 1H, *J* = 7.8, 5.7 Hz, H-6^{ex}), 3.17 (td, 1H, *J* = 1.6, 0.8 Hz, H-2), 2.41, 2.34 (2 × t, 2 × 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.70, 1.67 (2 × h, 2 × 2H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 0.98, 0.97 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.8, 172.0 (2 × CO), 100.6 (C-1), 73.9 (C-5), 70.0 (C-3), 69.6 (C-4), 65.4 (C-6), 59.0 (C-2), 36.2, 36.0 (2 × CO*C*H$_2$), 18.43, 18.40 (2 × *C*H$_2$CH$_3$), 13.73, 13.71 (2 × CH$_2$*C*H$_3$). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for $C_{14}H_{22}NO_6$, 300.1441; found, 300.1441.

Phenyl 2-Azido-2-deoxy-3,4-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside (83)



Compound **83** was prepared by reaction of **81** (200 mg, 0.67 mmol) with PhSTMS (0.40 mL, 2.11 mmol) and ZnI$_2$ (0.36 g, 1.13 mmol) in dichloroethane (5 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:3) showed the absence of **81** (R_f 0.44) and the presence of one major product (R_f 0.77). Chromatography of the residue after workup (see the general procedure) in EtOAc/PE 2:5 afforded **83** (256 mg, 94%) as a colourless syrupy mixture of anomers, R_f 0.06 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): [M − N$_2$ + H]$^+$ calcd for $C_{18}H_{24}NO_6S$, 382.1319; found, 382.1320. NMR data for the α- anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, H-H COSY): δ 7.51–7.48 (m, 2H, CH$_{arom}$), 7.39–7.29 (m, 3H, CH$_{arom}$), 5.65 (d, 1H, *J* = 5.5 Hz, H-1), 5.43 (dd, 1H, *J* = 10.6, 9.3 Hz, H-3), 5.04 (dd, 1H, *J* = 10.2, 9.3 Hz, H-4), 4.35 (ddd, 1H, *J* = 10.2, 3.8, 2.4 Hz, H-5), 4.05 (dd, 1H, *J* = 10.6, 5.5 Hz, H-2), 3.66 (dd, 1H, *J* = 12.9, 2.4 Hz, H-6'), 3.57 (dd, 1H, *J* = 12.9, 3.8 Hz, H-6), 2.43–2.25 (m, 4H, C*H*$_2$CH$_3$), 2.19 (br s, 1H, O*H*), 1.16, 1.13 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 174.3, 173.3 (2 × CO), 132.7 (C$_q$), 132.4, 129.4 (2 × 2CH$_{arom}$), 128.2 (CH$_{arom}$), 86.8 (C-1), 71.6 (C-3), 71.0 (C-5), 69.0 (C-4), 62.1 (C-2), 61.1 (C-6), 27.6 (2*C*H$_2$CH$_3$), 9.2, 9.1 (2 × CH$_2$*C*H$_3$). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, H-H COSY): δ 7.59–7.56 (m, 2H, CH$_{arom}$),

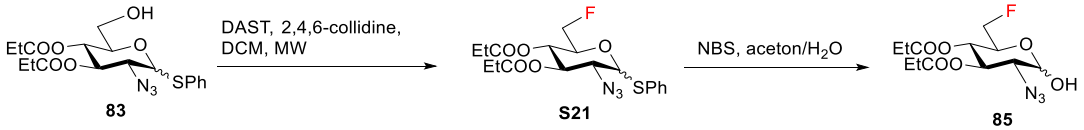
7.39–7.36 (m, 3H, CH_{arom}), 5.16 (dd, 1H, *J* = 9.7, 9.5 Hz, H-3), 4.92 (dd, 1H, *J* = 9.9, 9.5 Hz, H-4), 4.54 (d, 1H, *J* = 10.1 Hz, H-1), 3.73 (dd, 1H, *J* = 12.4, 2.0 Hz, H-6'), 3.57 (dd, 1H, *J* = 12.4, 5.0 Hz, H-6), 3.52 (ddd, 1H, *J* = 9.9, 5.0, 2.0 Hz, H-5), 3.41 (dd, 1H, *J* = 10.1, 9.7 Hz, H-2), 2.43–2.25 (m, 4H, CH_2CH_3), 2.19 (br s, 1H, O*H*), 1.12, 1.09 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.8, 173.5 (2 × CO), 134.0 ($2CH_{arom}$), 130.6 (C_q), 129.4 ($2CH_{arom}$), 129.0 (CH_{arom}), 86.1 (C-1), 78.4 (C-5), 74.2 (C-3), 68.3 (C-4), 63.1 (C-2), 61.6 (C-6), 27.6, 27.5 (2 × CH_2CH_3), 9.2, 9.1 (2 × CH_2CH_3).

Phenyl 2-Azido-3,4-di-*O*-butyryl-2-deoxy-1-thio-α,β-D-glucopyranoside (84)

Compounds **84** was prepared by reaction of **82** (242 mg, 0.74 mmol) with PhSTMS (0.48 mL, 2.53 mmol) and ZnI_2 (0.41 g, 1.28 mmol) in dichloroethane (5 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/PE 1:3) showed the absence of the **82** (R_f 0.52) and the presence of one major product (R_f 0.8). Chromatography of the residue after workup (see the general procedure) in Et_2O/PE 3:2 afforded **84** (284 mg, 88%) as a thick colourless syrup. Careful chromatography allowed collection of a fraction containing enriched α-anomer (α/β ≈ 10:1, R_f 0.45 and 0.49 for the α- and β-anomer, respectively, using Et_2O/PE 3:2) suitable for deoxyfluorination with DAST. HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{20}H_{28}NO_6S$, 410.1632; found, 410.1631. NMR data for the α-anomer: ^1H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 7.50–7.48 (m, 2H, CH_{arom}), 7.37–7.29 (m, 3H, CH_{arom}), 5.66 (d, 1H, *J* = 5.5 Hz, H-1), 5.43 (dd, 1H, *J* = 10.6, 9.3 Hz, H-3), 5.03 (dd, 1H, *J* = 10.2, 9.3 Hz, H-4), 4.33 (ddd, 1H, *J* = 10.2, 3.9, 2.3 Hz, H-5), 4.03 (dd, 1H, *J* = 10.6, 5.5 Hz, H-2), 3.65 (dd, 1H, *J* = 12.9, 2.3 Hz, H-6'), 3.57 (dd, 1H, *J* = 12.9, 3.9 Hz, H-6), 2.38–2.25 (m, 5H, O*H*, $2COCH_2$), 1.69–1.58 (m, 4H, CH_2CH_3), 0.96, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.6, 172.4 (2 × CO), 132.7 (C_q), 132.4, 129.4 (2 × $2CH_{arom}$), 128.2

(CH_{arom}), 86.9 (C-1), 71.2 (C-3), 71.1 (C-5), 68.9 (C-4), 62.2 (C-2), 61.1 (C-6), 36.1 ($2COCH_2$), 18.43, 18.35 ($2 \times CH_2CH_3$), 13.74, 13.70 ($2 \times CH_2CH_3$). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 7.59–7.57 (m, 2H, CH_{arom}), 7.38–7.36 (m, 3H, CH_{arom}), 5.16 (dd, 1H, *J* = 9.8, 9.6 Hz, H-3), 4.92 (dd, 1H, *J* = 9.9, 9.8 Hz, H-4), 4.54 (d, 1H, *J* = 10.2 Hz, H-1), 3.73 (dd, 1H, *J* = 12.4, 2.2 Hz, H-6'), 3.57 (dd, 1H, *J* = 12.4, 4.9 Hz, H-6), 3.51 (ddd, 1H, *J* = 9.9, 4.9, 2.2 Hz, H-5), 3.39 (dd, 1H, *J* = 10.2, 9.6 Hz, H-2), 2.32–2.22 (m, 5H, O*H*, $2COCH_2$), 1.66–1.56 (m, 4H, CH_2CH_3), 0.94, 0.91 ($2 \times$ t, 2×3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.1, 172.5 ($2 \times$ CO), 134.0 ($2CH_{arom}$), 130.6 (C_q), 129.4 ($2CH_{arom}$), 129.0 (CH_{arom}), 86.2 (C-1), 78.5 (C-5), 73.9 (C-3), 68.2 (C-4), 63.3 (C-2), 61.6 (C-6), 36.1, 36.0 ($2 \times COCH_2$), 18.41, 18.39 ($2 \times CH_2CH_3$), 13.73, 13.67 ($2 \times CH_2CH_3$).

2-Azido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-D-glucopyranose (85)

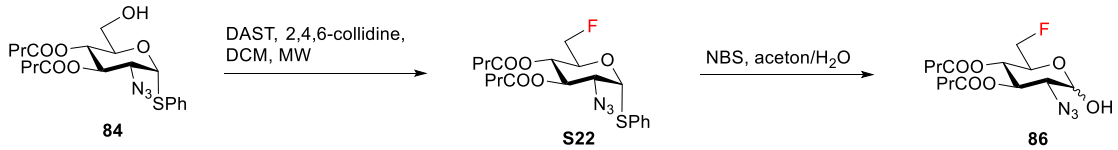


Compounds **83** (270 mg, 0.66 mmol reacted with diethylaminosulfur trifluoride (175 μL, 1.32 mmol) and 2,4,6-collidine (345 μL, 2.61 mmol) in dichloromethane (6 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:4 afforded phenyl 2-azido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-1-thio-α/β-D-glucopyranoside **S21** (190 mg, 70%) as a thick colourless syrupy mixture of anomers, R_f 0.56 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{18}H_{23}FNO_5S$, 384.1275; found, 384.1274. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.51–7.48 (m, 2H, CH_{arom}), 7.38–7.31 (m, 3H, CH_{arom}), 5.64 (d, 1H, *J* = 5.5 Hz, H-1), 5.37 (dd, 1H, *J* = 10.6, 9.2 Hz, H-3), 5.11 (dd, 1H, *J* = 10.3, 9.2 Hz, H-4), 4.57 (dddd, 1H, *J* = 24.7, 10.3, 3.8, 2.3 Hz, H-5), 4.47 (ddd, 1H, *J* = 47.3, 10.5, 3.8 Hz, H-6'), 4.43 (ddd, 1H, *J* = 47.3, 10.5, 2.3 Hz, H-6), 4.07 (dd, 1H, *J* = 10.6, 5.5 Hz, H-2), 2.40–2.25 (m, 4H, CH_2CH_3), 1.17–1.07 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.4, 173.3 ($2 \times$ CO), 132.7 (C_q), 132.3, 129.4 ($2 \times 2CH_{arom}$), 128.2 (CH_{arom}), 87.0 (C-1), 81.2 (d, ^1J = 176.0 Hz, C-6), 72.0 (d, ^4J = 0.8 Hz, C-3), 69.5 (d, ^2J = 18.9 Hz, C-5), 68.1 (d, ^3J = 6.8 Hz, C-4), 61.8 (C-2), 27.6, 27.5 ($2 \times CH_2CH_3$), 9.12, 9.07 ($2 \times CH_3$). ^{19}F NMR

($CDCl_3$, 376 MHz): −233.87 (td, ^2J = 47.3 Hz, ^3J = 24.7 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.61–7.59 (m, 2H, CH_{arom}), 7.38–7.31 (m, 3H, CH_{arom}), 5.13 (dd, 1H, *J* = 9.8, 9.4 Hz, H-3), 4.96 (dd, 1H, *J* = 10.2, 9.4 Hz, H-4), 5.51 (d, 1H, *J* = 10.0 Hz, H-1), 4.56–4.35 (m, 2H, H-6), 3.71 (dddd, 1H, *J* = 22.0, 10.2, 4.5, 2.4 Hz, H-5), 3.41 (dd, 1H, *J* = 10.0, 9.8 Hz, H-2), 2.40–2.25 (m, 4H, C*H*$_2$CH$_3$), 1.17–1.07 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.5, 173.1 (2 × CO), 134.2 ($2CH_{arom}$), 130.3 (C_q), 129.4 ($2CH_{arom}$), 129.1 (CH_{arom}), 86.1 (C-1), 81.3 (d, ^1J = 176.2 Hz, C-6), 76.7 (d, ^2J = 19.6 Hz, C-5), 74.4 (C-3), 67.6 (d, ^3J = 6.9 Hz, C-4), 62.8 (C-2), 27.53, 27.48 (2 × *C*H$_2$CH$_3$), 9.10, 9.08 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −233.63 (td, ^2J = 47.6 Hz, ^3J = 22.0 Hz).

Compound **S21** (170 mg, 0.41 mmol) was then hydrolysed according to the general procedure for thioglycoside hydrolysis. Chromatography in EtOAc/PE 1:3 afforded **85** (80 mg, 61% from **S21**, 43% from **83**) as a thick colourless syrupy mixture of anomers, R_f 0.29 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): $[M - N_2 + H]^+$ calcd for $C_{12}H_{19}FNO_6$, 292.1191; found, 292.1186. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.58 (dd, 1H, *J* = 10.5, 9.3 Hz, H-3), 5.42 (d, 1H, *J* = 3.4 Hz, H-1), 5.08 (dd, 1H, *J* = 10.2, 9.3 Hz, H-4), 4.55–4.36 (m, 2H, H-6), 4.27 (dddd, 1H, *J* = 24.3, 10.2, 4.4, 2.5 Hz, H-5), 3.45 (dd, 1H, *J* = 10.5, 3.4 Hz, H-2), 2.42–2.27 (m, 4H, C*H*$_2$CH$_3$), 1.14, 1.12 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.7, 173.3 (2 × CO), 92.3 (C-1), 81.4 (d, ^1J = 175.0 Hz, C-6), 70.3 (d, ^4J = 0.8 Hz, C-3), 68.6 (d, ^2J = 18.8 Hz, C-5), 68.1 (d, ^3J = 6.9 Hz, C-4), 61.7 (C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 9.15, 9.12 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −234.51 (td, ^2J = 47.2 Hz, ^3J = 24.3 Hz). NMR data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.08 (dd, 1H, *J* = 10.3, 9.3 Hz, H-3), 5.01 (dd, 1H, *J* = 9.9, 9.3 Hz, H-4), 4.77 (d, 1H, *J* = 8.0 Hz, H-1), 4.55–4.36 (m, 2H, H-6), 3.75 (dddd, 1H, *J* = 21.0, 9.9, 4.5, 2.9 Hz, H-5), 3.49 (dd, 1H, *J* = 10.3, 8.0 Hz, H-2), 2.42–2.27 (m, 4H, C*H*$_2$CH$_3$), 1.14, 1.12 (2 × t, 2 × 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.7, 173.3 (2 × CO), 96.3 (C-1), 81.4 (d, ^1J = 175.4 Hz, C-6), 72.9 (d, ^2J = 19.4 Hz, C-5), 72.4 (d, ^4J = 1.1 Hz, C-3), 67.9 (d, ^3J = 6.9 Hz, C-4), 65.0 (C-2), 27.6, 27.5 (2 × *C*H$_2$CH$_3$), 9.12, 9.10 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −233.13 (td, ^2J = 47.1 Hz, ^3J = 21.0 Hz).

2-Azido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-D-glucopyranose (86)

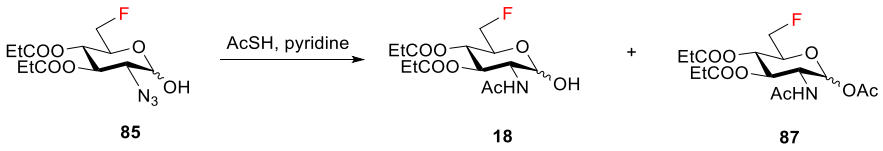


The α-anomer of thioglycoside **84** (153 mg, 0.35 mmol) reacted with diethylaminosulfur trifluoride (62 μL, 0.47 mmol) and 2,4,6-collidine (122 μL, 0.92 mmol) in dichloromethane (3 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:4 afforded phenyl 2-azido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-1-thio-α-D-glucopyranoside **S22** (111 mg, 72%) as a thick colourless syrup, R_f 0.62 (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}), 7.35–7.30 (m, 3H, CH_{arom}), 5.64 (d, 1H, *J* = 5.5 Hz, H-1), 5.37 (dd, 1H, *J* = 10.6, 9.2 Hz, H-3), 5.11 (dd, 1H, *J* = 10.3, 9.2 Hz, H-4), 4.56 (dddd, 1H, *J* = 24.5, 10.3, 3.9, 2.5 Hz, H-5), 4.46 (ddd, 1H, *J* = 47.3, 10.5, 3.9 Hz, H-6'), 4.42 (ddd, 1H, *J* = 47.3, 10.5, 2.5 Hz, H-6), 4.05 (dd, 1H, *J* = 10.6, 5.5 Hz, H-2), 2.37–2.27 (m, 4H, COCH_2), 1.66, 1.63 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.96, 0.94 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.5, 172.4 (2 × CO), 132.7 (C_q), 132.3, 129.4 (2 × 2CH_{arom}), 128.3 (CH_{arom}), 87.0 (C-1), 81.2 (d, ^1J = 176.0 Hz, C-6), 71.6 (d, ^4J = 0.8 Hz, C-3), 69.6 (d, ^2J = 18.0 Hz, C-5), 68.0 (d, ^3J = 6.7 Hz, C-4), 62.0 (C-2), 36.04, 36.01 (2 × CO*C*H$_2$), 18.4, 18.3 (2 × *C*H$_2$CH$_3$), 13.8, 13.7 (2 × *C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −233.65 (td, ^2J = 47.3 Hz, ^3J = 24.5 Hz). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{20}H_{27}FNO_5S$, 412.1588; found, 412.1584.

Thioglycoside **S22** (102 mg, 0.23 mmol) was hydrolysed according to the general procedure for the thioglycoside hydrolysis. Chromatography in EtOAc/PE 1:4 afforded **86** (63 mg, 78% from **S22**, 56% from **84**) as a colourless syrupy mixture of anomer, R_f 0.45 (EtOAc/PE 1:3). HRMS-APCI (*m/z*): [M − N_2 + H]$^+$ calcd for $C_{14}H_{23}FNO_6$, 320.1504; found, 320.1500. NMR data for α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.58 (dd, 1H, *J* = 10.5, 9.3 Hz, H-3), 5.42 (d, 1H, *J* = 3.4 Hz, H-1), 5.08 (dd, 1H, *J* = 10.4, 9.3 Hz, H-4), 4.53–4.35 (m, 2H, H-6), 4.26 (dddd, 1H, *J* = 24.0, 10.4, 3.9, 2.6 Hz, H-5), 3.41 (dd, 1H, *J* = 10.5, 3.4 Hz, H-2), 2.34–2.25 (m, 4H, COCH_2), 1.67–1.59 (m, 4H, CH_2CH$_3$), 0.97–0.90 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.8, 172.5 (2 × CO), 92.3 (C-

1), 81.5 (d, ^{1}J = 174.9 Hz, C-6), 70.0 (d, ^{4}J = 0.8 Hz, C-3), 68.7 (d, ^{2}J = 18.8 Hz, C-5), 67.9 (d, ^{3}J = 6.8 Hz, C-4), 61.8 (C-2), 36.1, 36.0 (2 × CO*C*H$_2$), 18.39, 18.35 (2 × *C*H$_2$CH$_3$), 13.73, 13.69 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −234.26 (td, ^{2}J = 47.2 Hz, ^{3}J = 24.0 Hz). NMR data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.08 (dd, 1H, *J* = 10.1, 9.3 Hz, H-3), 5.01 (dd, 1H, *J* = 9.9, 9.3 Hz, H-4), 4.77 (d, 1H, *J* = 8.0 Hz, H-1), 4.55–4.36 (m, 2H, H-6), 3.74 (dddd, 1H, *J* = 20.9, 9.9, 4.5, 3.0 Hz, H-5), 3.47 (dd, 1H, *J* = 10.1, 8.0 Hz, H-2), 2.34–2.25 (m, 4H, COC*H*$_2$), 1.67–1.59 (m, 4H, C*H*$_2$CH$_3$), 0.97–0.90 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 172.8, 172.4 (2 × CO), 96.3 (C-1), 81.4 (d, ^{1}J = 175.3 Hz, C-6), 73.0 (d, ^{2}J = 19.4 Hz, C-5), 72.1 (d, ^{4}J = 1.0 Hz, C-3), 67.8 (d, ^{3}J = 6.9 Hz, C-4), 65.1 (C-2), 36.1, 36.0 (2 × CO*C*H$_2$), 18.4, 18.3 (2 × *C*H$_2$CH$_3$), 13.70, 13.67 (2 × *C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −232.89 (td, ^{2}J = 47.0 Hz, ^{3}J = 20.9 Hz).

Reaction of 2-azido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-D-glucopyranose (85) with thioacetic acid



85 **18** **87**

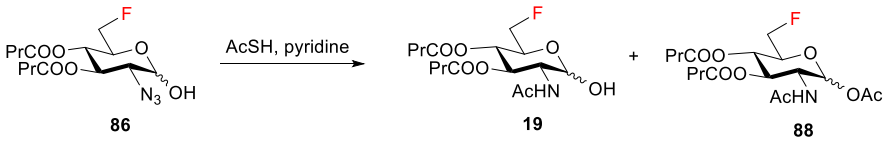
Compound **85** (70 mg, 0.22 mmol) was treated with thioacetic acid according to the general procedure for azide/acetamide transformation. Chromatography in EtOAc/PE 1:1 to EtOAc afforded 2-acetamido-3,4-di-*O*-propionyl-2,6-dideoxy-6-fluoro-D-glucopyranose (**18**) (50 mg) as a colourless syrupy mixture of anomers, R_f 0.40 (EtOAc), HRMS-APCI (*m/z*): [M + H]$^+$ calcd for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1458. Inseparable under given chromatographic conditions was a by-product (approx. 10% by ^{19}F NMR analysis) identified as 2-acetamido-1-*O*-acetyl-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-α/β-D-glucopyranose (**87**, α/β ≈ 2:1). Data for the α-anomer of **18**: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.87 (d, 1H, *J* = 9.4 Hz, N*H*), 5.34 (dd, 1H, *J* = 10.8, 9.5 Hz, H-3), 5.29 (d, 1H, *J* = 3.6 Hz, H-1), 5.08 (dd, 1H, *J* = 10.3, 9.5 Hz, H-4), 4.50–4.36 (m, 2H, H-6), 4.30 (ddd, 1H, *J* = 10.8, 9.4, 3.6 Hz, H-2), 4.23 (ddt, 1H, *J* = 21.9, 10.3, 3.8 Hz, H-5), 2.35–2.26 (m, 4H, C*H*$_2$CH$_3$), 1.95 (s, 3H, *Me* Ac), 1.11, 1.08 (2 × t, 2 × 3H, *J* = 7.6 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 175.1,

173.1, 170.4 (3 × CO), 91.8 (C-1), 81.9 (d, ^{1}J = 174.2 Hz, C-6), 70.7 (d, ^{4}J = 1.1 Hz, C-3), 68.7 (d, ^{2}J = 19.1 Hz, C-5), 68.0 (d, ^{3}J = 7.1 Hz, C-4), 52.3 (C-2), 27.7, 27.6 (2 × CH$_2$CH$_3$), 23.3 (Me Ac), 9.3, 9.2 (2 × CH$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −233.74 (td, ^{2}J = 47.2 Hz, ^{3}J = 21.9 Hz). Resolved signals for the β-anomer of **18**: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 6.27 (d, 1H, J = 6.9 Hz, NH), 5.23 (dd, 1H, J = 10.0, 9.3 Hz, H-3), 5.06 (dd, 1H, J = 10.0, 9.3 Hz, H-4), 4.65 (d, 1H, J = 8.4 Hz, H-1), 4.50–4.36 (m, 2H, H-6), 4.00–3.94 (m, 2H, H-2, H-5). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 97.9 (C-1), 70.6 (d, ^{2}J = 20.6 Hz, C-5), 54.3 (C-2). ^{19}F NMR (CDCl$_3$, 376 MHz): −232.96 (td, ^{2}J = 47.0 Hz, ^{3}J = 21.0 Hz).

Resolved signals for the α-anomer of **87**: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC): δ 6.19 (d, 1H, J = 3.6 Hz, H-1), 5.59 (d, 1H, J = 9.6 Hz, NH), from ^{1}H {^{19}F} 3.69 (ddd, 1H, J = 10.0, 4.4, 2.9 Hz, H-5). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 90.7 (C-1), 72.6 (d, ^{2}J = 19.9 Hz, C-5), 51.2 (C-2). ^{19}F NMR (CDCl$_3$, 376 MHz): −233.63 (td, ^{2}J = 47.9 Hz, ^{3}J = 22.4 Hz). Resolved signals for the β-anomer of **87**: ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC) : δ 5.72 (d, 1H, J = 8.7 Hz, H-1), 5.62 (d, 1H, J = 6.9 Hz, NH), from ^{1}H {^{19}F} 3.81 (ddd, 1H, J = 9.6, 4.4, 2.7 Hz, H-5). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 92.7 (C-1), 73.7 (d, ^{2}J = 19.8 Hz, C-5), 53.2 (C-2). ^{19}F NMR (CDCl$_3$, 376 MHz): −233.28 (td, ^{2}J = 47.0 Hz, ^{3}J = 21.2 Hz). HRMS for compound **87** (measured in mixture with **18**) HRMS-APCI (*m/z*): [M + H]$^{+}$ calcd for $C_{16}H_{25}FNO_8$, 378.1559; found, 378.1565.

Compound **18** (2.0 mg, 0.01 mmol) was dissolved in pyridine (0.2 mL), Ac_2O (0.05 mL) was added and the reaction mixture was stirred at rt for 2 hours, concentrated and co-distilled with toluene. ^{19}F NMR of the crude product revealed the presence of only two substances identical with the anomers of **87**.

Reaction of 2-azido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-D-glucopyranose (86) with thioacetic acid.

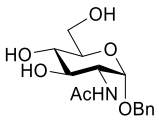


Compound **86** (55 mg, 0.16 mmol) was treated with thioacetic acid according to the general procedure for azide/acetamide transformation. Chromatography in EtOAc/PE 1:1 → EtOAc afforded 2-acetamido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-D-glucopyranose **19** (40 mg) as a colourless syrupy mixture of anomers, R_f 0.42 (EtOAc), HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1761. Inseparable under given chromatographic conditions was a by-product (approx. 36% by ^{19}F NMR analysis) identified as 2-acetamido-1-*O*-acetyl-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-α,β-D-glucopyranose (**88** α/β ≈ 2:1). NMR data for the α-anomer of **19**: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 5.81 (d, 1H, *J* = 9.4 Hz, N*H*), 5.36 (dd, 1H, *J* = 10.9, 9.5 Hz, H-3), 5.30 (d, 1H, *J* = 3.6 Hz, H-1), 5.09 (dd, 1H, *J* = 10.3, 9.5 Hz, H-4), 4.56–4.36 (m, 2H, H-6), 4.30 (ddd, 1H, *J* = 10.9, 9.4, 3.6 Hz, H-2), 4.23 (dddd, 1H, *J* = 21.7, 10.3, 3.8, 3.2 Hz, H-5), 2.31–2.25 (m, 4H, COCH_2), 1.95 (s, 3H, *Me* Ac), 1.66–1.56 (m, 4H, CH_2CH$_3$), 0.93, 0.93 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 174.2, 172.2, 170.3 (3 × CO), 91.8 (C-1), 82.0 (d, ^1J = 174.3 Hz, C-6), 70.4 (d, ^4J = 1.1 Hz, C-3), 68.7 (d, ^2J = 19.3 Hz, C-5), 67.8 (d, ^3J = 7.0 Hz, C-4), 52.4 (C-2), 36.2, 36.1 (2 × COCH_2), 23.3 (Me Ac), 18.52, 18.48 (2 × CH_2CH$_3$), 13.73, 13.70 (2 × CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −232.57 (td, ^2J = 47.2 Hz, ^3J = 21.7 Hz). Resolved signal for the β-anomer of **19**: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY, HSQC): δ 6.27 (d, 1H, *J* = 6.6 Hz, N*H*), 5.21 (t, 1H, *J* = 9.8 Hz, H-3), 5.09 (dd, 1H, *J* = 10.0, 9.8 Hz, H-4), 4.64 (d, 1H, *J* = 8.4 Hz, H-1), 4.56–4.36 (m, 2H, H-6), 4.03–3.93 (m, 2H, H-2, H-5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 98.1 (C-1), 70.8 (d, ^2J = 19.8 Hz, C-5), 57.5 (C-2). ^{19}F NMR ($CDCl_3$, 376 MHz): −232.98 (td, ^2J = 47.0 Hz, ^3J = 21.0 Hz).

Resolved signal for the α-anomer of **88**: ^1H NMR ($CDCl_3$, 400 MHz, ^1H {^{19}F}, H-H COSY): δ 6.20 (d, 1H, *J* = 3.6 Hz, H-1), 5.56 (d, 1H, *J* = 8.9 Hz, N*H*), 3.71–3.62 (m, 1H, H-5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 90.7 (C-1), 51.3 (C-2). ^{9}F NMR ($CDCl_3$, 376 MHz): −233.44 (td, ^2J = 47.0 Hz,

^3J = 22.4 Hz). Resolved signal for the β-anomer of **88**: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.71 (d, 1H, J = 8.7 Hz, H-1), 5.49 (d, 1H, J = 9.4 Hz, N*H*), 3.85–3.74 (m, 1H, H-5). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 92.7 (C-1), 73.8 (d, ^2J = 19.9 Hz, C-5), 53.2 (C-2). ^{19}F NMR ($CDCl_3$, 376 MHz): −233.09 (td, ^2J = 47.5 Hz, ^3J = 21.2 Hz). HRMS for compound **88** (measured in a mixture with **19**) HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{29}FNO_8$, 406.1872; found, 406.1856.

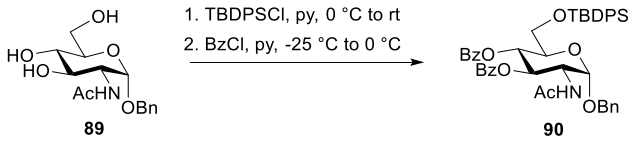
Benzyl 2-Acetamido-α-D-glucopyranoside (89)



89

Glucopyranoside **89** was prepared according to ref 7.

Benzyl 2-Acetamido-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-glucopyranoside (90)

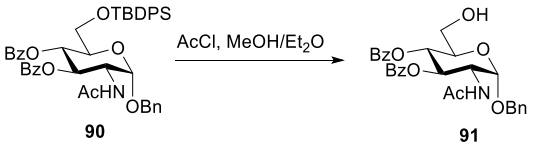


89 **90**

tert-Butyl(chloro)diphenylsilane (1.26 mL, 4.85 mmol) was added dropwise under argon to a stirred and cooled (0 °C) solution of **89**[7] (1.260 g, 4.05 mmol) in dry pyridine (12 mL). The temperature was allowed to reach rt and the reaction was stirred overnight. TLC (EtOAc/MeOH 10:1) indicated only traces of the starting material (R_f 0.1) and one major product (R_f 0.4). Dry pyridine was added (11 mL), the reaction mixture was cooled to −25 °C and benzoyl chloride (0.99 mL, 8.53 mmol) was added dropwise under argon. Immediately a precipitate was formed. The temperature was allowed to reach 0 °C in 1 h and the reaction was stirred at this temperature for 5 h. TLC (EtOAc/heptane 1:2) showed only one product (R_f 0.2). The reaction was poured onto ice, extracted with chloroform (3×), the chloroform extracts were combined, dried, concentrated and co-distilled with toluene (2×) under reduced pressure.

Chromatography of the residue in EtOAc/PE 1:2 afforded **90** (2.67 g, 87%) as white foam, R_f 0.2 (EtOAc/heptane 1:2). ^{1}H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 7.93–7.91 (m, 2H, CH_{arom}), 7.86–7.84 (m, 2H, CH_{arom}), 7.68–7.66 (m, 2H, CH_{arom}), 7.59–7.57 (m, 2H, CH_{arom}), 7.51–7.46 (m, 3H, CH_{arom}), 7.39–7.30 (m, 12H, CH_{arom}), 7.18–7.22 (m, 2H, CH_{arom}), 5.89 (d, 1H, *J* = 9.4 Hz, N*H*), 5.67 (dd, 1H, *J* = 10.3, 9.6 Hz, H-3), 5.62 (t, 1H, *J* = 9.6 Hz, H-4), 5.08 (d, 1H, *J* = 3.7 Hz, H-1), 4.82 (d, 1H, *J* = 11.9 Hz, CH*H* OBn), 4.57 (ddd, 1H, *J* = 10.3, 9.4, 3.7 Hz, H-2), 4.56 (d, 1H, *J* = 11.9 Hz, CH*H* OBn), 4.11 (ddd, 1H, *J* = 9.6, 5.1, 2.2 Hz, H-5), 3.83 (dd, 1H, *J* = 11.5, 5.1 Hz, H-6'), 3.75 (dd, 1H, *J* = 11.5, 2.2 Hz, H-6), 1.04 (s, 9H, C*Me*$_3$), 1.84 (s, 3H, *Me* NHAc). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.1, 167.4, 165.2 (3 × CO), 137.0 (C_q), 135.8, 135.7 (2 × 2CH_{arom}), 133.5 (C_q), 133.3, 133.22, 133.17 (3 × CH_{arom}), 130.3 (C_q), 130.04, 129.88, 129.8, 129.7 (4 × CH_{arom}), 129.5, 129.1 (2 × C_q), 128.8 (2CH_{arom}), 128.6 (CH_{arom}), 128.54, 128.46 (2× 2CH_{arom}), 128.4 (CH_{arom}), 128.3, 127.8, 127.7 (3 × 2CH_{arom}), 96.6 (C-1), 72.3 (C-3), 71.4 (C-5), 69.8 (CH_2 Bn), 69.1 (C-4), 62.9 (C-6), 52.6 (C-2), 26.8 (C*Me*$_3$), 23.3 (*Me* NHAc), 19.3 (*C*Me$_3$). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{45}H_{48}NO_8Si$, 758.3143; found, 758.3146.

Benzyl 2-Acetamido-3,4-di-*O*-benzoyl-2-deoxy-α-D-glucopyranoside (91)

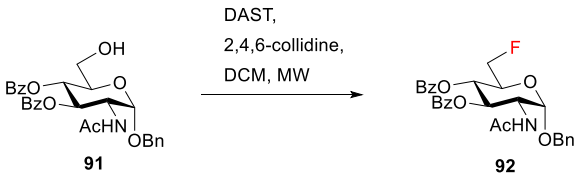


90 **91**

Acetyl chloride (1.0 mL, 14.1 mmol) was added to methanol (25 mL) and the resulting solution was cooled to rt. A volume of 2.0 mL of the solution (containing 1.1 mmol HCl) was added to a solution of the starting compound **90** (650 mg, 0.86 mmol) in diethyl ether (2 mL) and the resulting solution was stirred for 18 h. TLC (EtOAc/PE 1:1) indicated only traces of the starting compound (R_f 0.4). The reaction mixture was neutralized by addition of an anion exchange resin Amberlite IRA-410 (OH^- form), filtered and concentrated. Chromatography in EtOAc/PE 2:1 afforded **91** (308 mg, 69%) as a white foam, R_f 0.4 (EtOAc/PE 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz, H-H COSY): δ 7.95–7.90 (m, 4H, CH_{arom}), 7.54–7.47 (m, 2H, CH_{arom}), 7.41–7.33 (m, 9H, CH_{arom}), 5.82 (d, 1H, *J* = 9.5 Hz, N*H*), 5.76 (dd, 1H, *J* =

10.7, 9.8 Hz, H-3), 5.46 (dd, 1H, *J* = 10.1, 9.8 Hz, H-4), 5.09 (d, 1H, *J* = 3.7 Hz, H-1), 4.79, 4.59 (2 × d, 2 × 1H, *J* = 11.9 Hz, CH*H* OBn), 4.59 (ddd, 1H, *J* = 10.7, 9.5, 3.7 Hz, H-2), 3.98 (ddd, 1H, *J* = 10.1, 3.7, 2.3 Hz, H-5), 3.73 (dd, 1H, *J* = 12.9, 2.3 Hz, H-6'), 3.66 (dd, 1H, *J* = 12.9, 3.7 Hz, H-6), 1.82 (s, 3H, *Me*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.0, 167.2, 166.4 (3 × CO), 136.9 (C_q), 133.8, 133.6 (2 × CH_{arom}), 130.1, 130.0 (2 × 2CH_{arom}), 129.1 (C_q), 128.9 (2CH_{arom}), 128.8 (C_q), 128.63, 128.59 (2 × 2CH_{arom}), 128.5 (CH_{arom}), 128.4 (2CH_{arom}), 97.1 (C-1), 71.5 (C-3), 70.7 (C-5), 70.5 (CH_2 Bn), 69.5 (C-4), 61.2 (C-6), 52.3 (C-2), 23.3 (*Me*). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{29}H_{30}NO_8$, 520.1966; found, 520.1966.

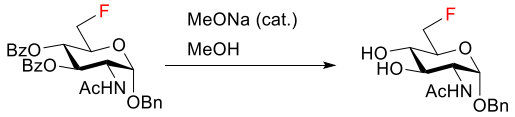
Benzyl 2-Acetamido-3,4-di-*O*-benzoyl-2,6-dideoxy-6-fluoro-α-D-glucopyranoside (92)



Compound **92** was prepared from alcohol **91** (284 mg, 0.55 mmol) according to the general procedure for 6-fluorination using 2,6,4-collidine (174 μL, 1.32 mmol) and DAST (87 μL, 0.66 mmol). Chromatography of the crude product in EtOAc afforded the product that was further purified by recrystallization from EtOAc/heptane giving **92** (202 mg, 70%), mp 181–186 °C (EtOAc/heptane), R_f 0.3 (EtOAc/heptane 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H $\{^{19}F\}$, H-H COSY): δ 7.94–7.89 (m, 4H, CH_{arom}), 7.53–7.47 (m, 2H, CH_{arom}), 7.46–7.32 (m, 9H, CH_{arom}), 5.83 (d, 1H, *J* = 9.4 Hz, N*H*), 5.71 (dd, 1H, *J* = 10.9, 9.5 Hz, H-3), 5.52 (dd, 1H, *J* = 10.3, 9.5 Hz, H-4), 5.09 (d, 1H, *J* = 3.6 Hz, H-1), 4.83, 4.61 (2 × d, 2 × 1H, *J* = 11.9 Hz, CH*H* OBn), 4.61–4.43 (m, 3H, H-2, 2H-6), 4.23 (dddd, 1H, *J* = 22.5, 10.3, 4.8, 2.6 Hz, H-5), 1.81 (s, 3H, *Me*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.0, 167.2, 165.3 (3 × CO), 136.7 (C_q), 133.7, 133.6 (2 × CH_{arom}), 130.0, 129.9 (2 × 2CH_{arom}), 129.0, 128.92 (2 × C_q), 128.85, 128.59, 128.57 (3 × 2CH_{arom}), 128.5 (CH_{arom}), 128.4 (2CH_{arom}), 96.8 (C-1), 81.7 (d, ^{1}J = 174.9 Hz, C-6), 71.7 (C-3), 70.4 (CH_2 Bn), 69.5 (d, ^{2}J = 19.3 Hz, C-5), 68.6 (d, ^{3}J = 6.9 Hz, C-4), 52.3

(C-2), 23.2 (*Me*). ^{19}F NMR ($CDCl_3$, 376 MHz): –232.61 (ddd, ^2J = 47.5, 47.3 Hz, ^3J = 22.5 Hz). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{29}H_{29}FNO_7$, 522.1922; found, 522.1921.

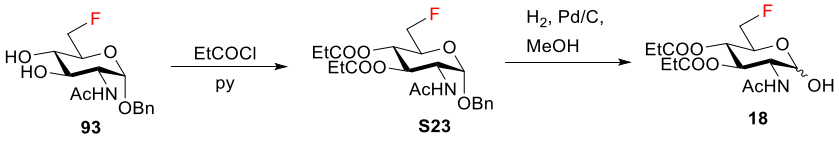
Benzyl 2-Acetamido-2,6-dideoxy-6-fluoro-α-D-glucopyranoside (93)



92 **93**

Sodium methanolate in methanol (1M solution, 0.3 mL) was added to a solution of the starting compound **92** (208 mg, 0.40 mmol) in methanol (9 mL) and the resulting solution was stirred 4 h at rt and then was left to stand overnight at 5 °C. The reaction mixture was neutralized by addition of DOWEX 50W exchange resin, filtered and concentrated. Chromatography of the residue in EtOAc/MeOH 5:1 afforded **93** (117 mg, 93%) as colourless crystalline material, mp 192–194 °C (DCM/EtOAc/EtOH, sub at T ≥ 170 °C), R_f 0.47 (EtOAc/MeOH 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F} H-H COSY): δ 7.41–7.31 (m, 5H, CH_{arom}), 5.90 (d, 1H, *J* = 8.6 Hz, N*H*), 4.90 (d, 1H, *J* = 3.8 Hz, H-1), 4.75 (d, 1H, *J* = 11.8 Hz, CH*H* OBn), 4.65 (ddd, 1H, *J* = 47.4, 10.2, 4.3 Hz, H-6), 4.61 (ddd, 1H, *J* = 47.6, 10.2, 2.1 Hz, H-6'), 4.50 (d, 1H, *J* = 11.8 Hz, CH*H* OBn), 4.09 (ddd, 1H, *J* = 10.3, 8.6, 3.8 Hz, H-2), 3.80 (dddd, 1H, *J* = 25.3, 10.1, 4.3, 2.1 Hz, H-5), 3.80 (d, 1H, *J* = 4.7 Hz, O*H*), 3.71 (ddd, 1H, *J* = 10.3, 9.6, 4.7 Hz, H-3), 3.58 (ddd, 1H, *J* = 10.1, 9.6, 1.9 Hz, H-4), 3.13 (br s, 1H, O*H*), 1.99 (s, 3H, *Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 172.3 (CO), 137.0 (C_q), 128.6 ($2CH_{arom}$), 128.4 (CH_{arom}), 128.3 ($2CH_{arom}$), 96.9 (C-1), 82.3 (d, ^1J = 171.8 Hz, C-6), 74.3 (C-3), 71.0 (d, ^2J = 17.9 Hz, C-5), 70.3 (d, ^3J = 6.9 Hz, C-4), 69.9 (CH_2 Bn), 53.6 (C-2), 23.3 (*Me*). ^{19}F NMR ($CDCl_3$, 376 MHz): – 235.95 (ddd, ^2J = 47.6, 47.4 Hz, ^3J = 25.3 Hz). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{21}FNO_5$, 314.1398; found 314.1393.

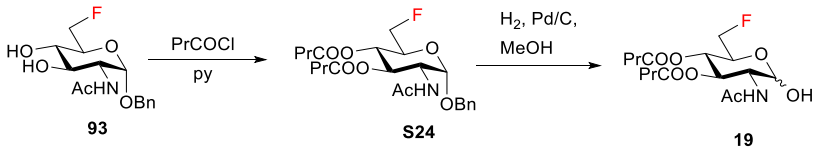
2-Acetamido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-D-glucopyranose (18) from 93



Compound **93** (95 mg, 0.30 mmol) reacted with propionyl chloride (0.07 mL, 0.80 mmol) in pyridine (4 mL) according to the general procedure. Chromatography in EtOAc/PE 1:2 afforded benzyl 2-acetamido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-α-D-glucopyranoside **S23** (118 mg, 91%). NMR data for **S23**: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.41–7.31 (m, 5H, CH_{arom}), 5.66 (d, 1H, *J* = 9.5 Hz, N*H*), 5.28 (dd, 1H, *J* = 10.8, 9.4 Hz, H-3), 5.10 (dd, 1H, *J* = 10.3, 9.4 Hz, H-4), 4.95 (d, 1H, *J* = 3.7 Hz, H-1), 4.75, 4.53 (2 × d, 2 × 1H, *J* = 11.8, C*H*H Bn), 4.49–4.31 (m, 2H, H-6), 4.34 (ddd, 1H, *J* = 10.8, 9.5, 3.7 Hz, H-2), 4.00 (dddd, 1H, *J* = 22.2, 10.3, 4.7, 2.8 Hz, H-5), 2.35–2.22 (m, 4H, C*H*$_2$CH$_3$), 1.88 (s, 3H, *Me* Ac), 1.11, 1.07 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 175.0, 173.0, 170.0 (3 × CO), 137.0 (C_q), 128.8 (2CH_{arom}), 128.5 (CH_{arom}), 128.4 (2CH_{arom}), 96.7 (C-1), 81.7 (d, ^{1}J = 174.6 Hz, C-6), 71.1 (d, ^{4}J = 1.1 Hz, C-3), 70.3 (*C*H$_2$ Bn), 69.0 (d, ^{2}J = 19.4 Hz, C-5), 67.9 (d, ^{3}J = 6.7 Hz, C-4), 51.9 (C-2), 27.7, 27.5 (2 × *C*H$_2$CH$_3$), 23.3 (Me Ac), 9.3, 9.2 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −232.69 (td, ^{2}J = 47.2 Hz, ^{3}J = 22.2 Hz). HRMS-APCI (m/z): [M + H]+ calcd for $C_{21}H_{29}FNO_7$, 426.1923; found, 426.1925. Compound **S23** (110 mg, 0.26 mmol) was debenzylated according to the general procedure using 10% palladium on carbon (50 mg). After 2 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc afforded **18** (72 mg, 83% from **S23**, 76% over 2 steps) as a colourless syrupy mixture of anomers identical to compound **18** prepared from **85**. Here are NMR data for **18** in methanol-d_4, the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.35 (dd, 1H, *J* = 10.9, 9.3 Hz, H-3), 5.11 (d, 1H, *J* = 3.5 Hz, H-1), 5.04 (dd, 1H, *J* = 10.3, 9.3 Hz, H-4), 4.51–4.36 (m, 2H, H-6), 4.20 (ddt, 1H, *J* = 25.2, 10.3, 3.1 Hz, H-5), 4.19 (dd, 1H, *J* = 10.9, 3.5 Hz, H-2), 2.32 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 2.40–2.20 (m, 2H, C*H*$_2$CH$_3$), 1.92 (s, 3H, *Me* Ac), 1.09, 1.06 (2 × t, 2 × 3H, *J* = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.5, 174.7, 173.4 (3 × CO), 92.6 (C-1), 82.8 (d, ^{1}J = 173.1 Hz, C-6), 72.4 (d, ^{4}J = 0.6 Hz, C-3), 69.8 (d, ^{3}J = 6.9 Hz, C-4), 69.2 (d, ^{2}J = 18.8 Hz, C-5), 53.4 (C-2), 28.4, 28.2 (2 × *C*H$_2$CH$_3$), 22.4 (Me Ac), 9.5, 9.4 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz):

δ −236.54 (td, ^{2}J = 47.5 Hz, ^{3}J = 25.2 Hz). Resolved signals for the β-anomer:^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.22 (dd, 1H, *J* = 10.6, 9.3 Hz, H-3), 5.01 (dd, 1H, *J* = 10.2, 9.3 Hz, H-4), 4.81 (d, 1H, *J* = 8.4 Hz, H-1), 4.53–4.41 (m, 2H, H-6), 3.83 (dd, 1H, *J* = 10.6, 8.4 Hz, H-2), 3.79 (dddd, 1H, *J* = 23.0, 10.2, 4.3, 2.7 Hz, H-5), 1.92 (s, 3H, *Me* Ac). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 175.3, 174.6, 173.5 (3 × CO), 96.5 (C-1), 74.3 (C-3), 73.7 (d, ^{2}J = 19.0 Hz, C-5), 56.7 (C-2), 28.3, 28.2 (2 × *C*H$_2$CH$_3$), 22.7 (*Me* Ac). ^{19}F NMR (MeOH-d_4, 376 MHz): δ −235.89 (td, ^{2}J = 47.3 Hz, ^{3}J = 23.0 Hz).

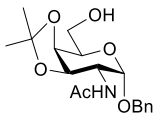
2-Acetamido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-D-glucopyranose (19) from 93



Compound **93** (65 mg, 0.21 mmol) reacted with butyryl chloride (0.057 mL, 0.55 mmol) in pyridine (4 mL) according to the general procedure. Chromatography in EtOAc/PE 1:2 afforded benzyl 2-acetamido-2,6-dideoxy-6-fluoro-3,4-di-*O*-butyryl-α-D-glucopyranoside **S24** (81 mg, 86%). NMR data for **S24**: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.39–7.32 (m, 5H, CH_{arom}), 5.67 (d, 1H, *J* = 9.5 Hz, N*H*), 5.30 (dd, 1H, *J* = 10.8, 9.5 Hz, H-3), 5.10 (dd, 1H, *J* = 10.4, 9.5 Hz, H-4), 4.95 (d, 1H, *J* = 3.7 Hz, H-1), 4.74, 4.53 (2 × d, 2 × 1H, *J* = 11.9, C*H*H Bn), 4.54–4.34 (m, 2H, H-6), from ^{1}H {^{19}F} 4.34 (ddd, 1H, *J* = 10.8, 9.5, 3.7 Hz, H-2), 4.00 (dddd, 1H, *J* = 22.1, 10.4, 4.8, 2.8 Hz, H-5), 2.27–2.21 (m, 4H, COC*H*$_2$), 1.88 (s, 3H, *Me* Ac), 1.64–1.54 (m, 4H, C*H*$_2$CH$_3$), 0.92, 0.89 (2 × t, 2 × 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.2, 172.1, 169.9 (3 × CO), 136.7 (C_q), 128.8 ($2CH_{arom}$), 128.5 (CH_{arom}), 128.4 ($2CH_{arom}$), 96.6 (C-1), 81.8 (d, ^{1}J = 174.6 Hz, C-6), 70.9 (d, ^{4}J = 1.2 Hz, C-3), 70.3 (*C*H$_2$ Bn), 69.1 (d, ^{2}J = 19.5 Hz, C-5), 67.8 (d, ^{3}J = 6.8 Hz, C-4), 52.0 (C-2), 36.2, 36.1 (2 × COC*H*$_2$), 23.3 (Me Ac), 18.51, 18.49 (2 × *C*H$_2$CH$_3$), 13.73, 13.69 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −232.51 (td, ^{2}J = 47.2 Hz, ^{3}J = 22.1 Hz). **S24** (75 mg, 0.16 mmol) was debenzylated according to the general procedure using 10% palladium on carbon (40 mg). After 2 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc afforded **19** (55 mg, 92% from **S23**,

79% over 2 steps) as a colourless syrupy mixture of anomers. NMR data for **19**, the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.35 (dd, 1H, *J* = 10.8, 9.3 Hz, H-3), 5.10 (d, 1H, *J* = 3.5 Hz, H-1), 5.04 (dd, 1H, *J* = 10.3, 9.3 Hz, H-4), 4.50–4.37 (m, 2H, H-6), 4.20 (ddt, 1H, *J* = 25.3, 10.3, 3.1 Hz, H-5), 4.19 (dd, 1H, *J* = 10.8, 3.5 Hz, H-2), 2.53–2.12 (m, 4H, COCH_2), 1.92 (s, 3H, *Me* Ac), 1.57, 1.60 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 0.93, 0.91 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 174.6, 173.7, 173.4 (3 × CO), 92.7 (C-1), 82.8 (d, ^{1}J = 173.4 Hz, C-6), 72.3 (d, ^{4}J = 0.5 Hz, C-3), 69.7 (d, ^{3}J = 6.9 Hz, C-4), 69.2 (d, ^{2}J = 18.9 Hz, C-5), 53.5 (C-2), 37.0, 36.8 (2 × CO*C*H$_2$), 22.5 (Me Ac), 19.4, 19.3 (2 × *C*H$_2$CH$_3$), 13.94, 13.91 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (MeOH-d_4, 376 MHz): δ −236.38 (td, ^{2}J = 47.5 Hz, ^{3}J = 25.3 Hz). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.23 (dd, 1H, *J* = 10.7, 8.9 Hz, H-3), 5.01 (dd, 1H, *J* = 10.1, 8.9 Hz, H-4), 4.81 (d, 1H, *J* = 8.4 Hz, H-1), 4.53–4.41 (m, 2H, H-6), 3.83 (dd, 1H, *J* = 10.7, 8.4 Hz, H-2), from ^{1}H {^{19}F} 3.79 (ddd, 1H, *J* = 10.1, 4.2, 2.1 Hz, H-5), 2.53–2.12 (m, 4H, COCH_2), 1.90 (s, 3H, *Me* Ac). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 96.5 (C-1), 22.8 (Me Ac). ^{19}F NMR (MeOH-d_4, 376 MHz): δ −235.76 (td, ^{2}J = 47.5 Hz, ^{3}J = 23.2 Hz).

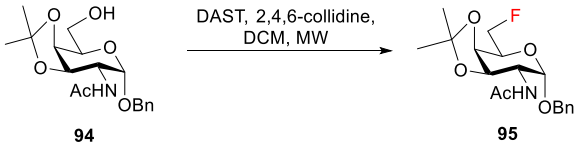
Benzyl 2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-α-D-galactopyranoside (94)



94

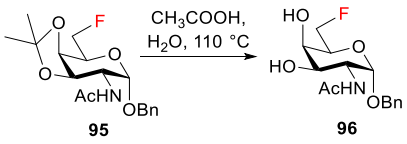
Galactopyranoside **94** was prepared according to ref 8.

Benzyl 2-Acetamido-2,6-dideoxy-6-fluoro-3,4-*O*-isopropylidene-α-D-galactopyranoside (95)



Compound **95** was prepared by reaction of **94** (2.06 g, 5.86 mmol) with diethylaminosulfur trifluoride (1.00 mL, 7.57 mmol) and 2,4,6-collidine (2.00 mL, 15.13 mmol) in dichloromethane (20 mL) according to the general procedure. Chromatography of the crude product in EtOAc/PE 1:1 afforded **95** (1.75 g, 84%) as a thick colourless syrup. R_f 0.25 (EtOAc/PE 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.40–7.29 (m, 5H, CH_{arom}), 5.53 (d, 1H, *J* = 9.5 Hz, N*H*), 4.73 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.90 (d, 1H, *J* = 3.4 Hz, H-1), 4.68 (ddd, 1H, *J* = 46.7, 10.0, 4.9 Hz, H-6), 4.65 (ddd, 1H, *J* = 48.0, 10.0, 6.4 Hz, H-6'), 4.48 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.30 (ddd, 1H, *J* = 9.5, 9.3, 3.4 Hz, H-2), 4.30 (dddd, 1H, *J* = 15.4, 6.4, 4.9, 2.6 Hz, H-5), 4.17 (dd, 1H, *J* = 5.0, 2.6 Hz, H-4), 4.10 (dd, 1H, *J* = 9.3, 5.0 Hz, H-3), 1.97 1.56 (2 × s, 2 × 3H, C*Me*$_2$), 1.32 (s, 3H, C*H*$_3$ NHAc). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.1 (CO), 137.0 (C_q), 128.8 ($2CH_{arom}$), 128.4 (CH_{arom}), 128.2 ($2CH_{arom}$), 110.2 (*C*Me$_2$), 97.3 (C-1), 82.8 (d, ^1J = 169.5 Hz, C-6), 74.6 (C-3), 72.3 (d, ^3J = 7.0 Hz, C-4), 70.1 (*C*H$_2$ Bn), 66.9 (d, ^2J = 22.0 Hz, C-5), 50.5 (C-2), 28.0, 26.7 (2 × C*Me*$_2$), 23.5 (*Me* NHAc). ^{19}F NMR ($CDCl_3$, 376 MHz): −229.21 (ddd, ^2J = 48.0, 46.7 Hz, ^3J = 15.4 Hz). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{25}FNO_5$, calc., 354.1711; found, 354.1706.

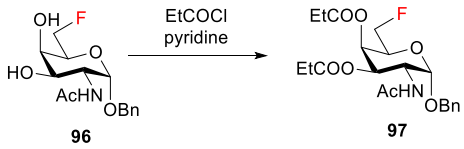
Benzyl 2-Acetamido-2,6-dideoxy-6-fluoro-α-D-galactopyranoside (96)



Compound **96** was prepared by heating a solution of **95** (615 mg, 1.74 mmol) in acetic acid/H_2O 4:1 (15 mL) to 110 °C for 4 h. The reaction mixture was concentrated and recrystallization of the residue from MeOH afforded **96** (470 mg, 86%) as a white crystalline solid, mp 206–210 °C (MeOH), R_f 0.1 (EtOAc). ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.39–7.26 (m, 5H, CH_{arom}), 4.89 (d, 1H, *J* =

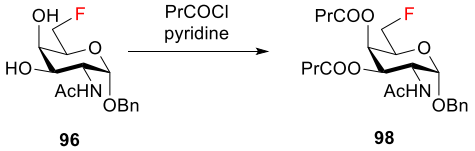
3.7 Hz, H-1), 4.72, 4.50 (2 × d, 2 × 1H, J = 12.0 Hz, C*H*H Bn), 4.59 (ddd, 1H, J = 46.4, 9.6, 4.5 Hz, H-6'), 4.53 (ddd, 1H, J = 48.3, 9.6, 7.1 Hz, H-6), from ^{1}H {^{19}F} 4.27 (dd, 1H, J = 11.1, 3.7 Hz, H-2), 4.12 (dddd, 1H, J = 14.9, 7.1, 4.5, 1.3 Hz, H-5), 3.90 (dd, 1H, J = 3.3, 1.3 Hz, H-4), 3.83 (dd, 1H, J = 11.1, 3.3 Hz, H-3), 1.95 (s, 3H, C*H*$_3$ NHAc). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 173.8 (CO), 138.9 (C$_q$), 129.3, 129.4 (2 × 2CH$_{arom}$), 128.9 (CH$_{arom}$), 97.8 (C-1), 84.1 (d, ^{1}J = 167.0 Hz, C-6), 71.0 (d, ^{2}J = 21.7 Hz, C-5), 70.4 (*C*H$_2$ Bn), 69.9 (d, ^{3}J = 6.6 Hz, C-4), 69.2 (d, ^{4}J = 1.0 Hz, C-3), 51.4 (C-2), 22.6 (*Me* NHAc). ^{19}F NMR (MeOH-d_4, 376 MHz): −232.93 (ddd, ^{2}J = 48.3, 46.4 Hz, ^{3}J = 14.9 Hz). HRMS-APCI (*m/z*): [M + H]$^{+}$ calcd for C$_{15}$H$_{21}$FNO$_5$, 314.1398; found, 314.1399.

Benzyl 2-Acetamido-2,6-dideoxy-6-fluoro-3,4-di-*O*-propionyl-α-D-galactopyranoside (97)



Compound **97** was prepared from **96** (150 mg, 0.48 mmol) according to the general procedure for acylation using propionyl chloride (125 μL, 1.43 mmol). Chromatography in EtOAc/PE 3:2 afforded **97** (160 mg, 79%) as a white crystalline solid, mp 102–103 °C (EtOAc/heptane), R_f 0.75 (EtOAc). ^{1}H NMR (CDCl$_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.41–7.30 (m, 5H, CH$_{arom}$), 5.57 (d, 1H, J = 9.8z Hz, N*H*), 5.43 (dd, 1H, J = 3.3, 1.3 Hz, H-4), 5.22 (dd, 1H, J = 11.3, 3.3 Hz, H-3), 5.00 (d, 1H, J = 3.7 Hz, H-1), 4.74 (d, 1H, J = 11.7 Hz, C*H*H Bn), 4.61 (ddd, 1H, J = 11.3, 9.8, 3.7 Hz, H-2), 4.52 (d, 1H, J = 11.7 Hz, C*H*H Bn), 4.41 (ddd, 1H, J = 46.6, 9.8, 6.3 Hz, H-6), 4.40 (ddd, 1H, J = 46.6, 9.8, 5.0 Hz, H-6'), 4.26 (dddd, 1H, J = 14.6, 6.3, 5.0, 1.3 Hz, H-5), 2.50–2.38 (m, 2H, C*H*$_2$CH$_3$), 2.25 (q, 2H, J = 7.6 Hz, C*H*$_2$CH$_3$), 1.90 (s, 3H, C*H*$_3$ NHAc), 1.18, 1.07 (2 × t, 2 × 3H, J = 7.6 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, HSQC): δ 174.4, 173.9, 170.0 (3 × CO), 136.7 (C$_q$), 128.8 (2CH$_{arom}$), 128.5 (CH$_{arom}$), 128.4 (2CH$_{arom}$), 97.2 (C-1), 81.7 (d, ^{1}J = 171.3 Hz, C-6), 70.3 (*C*H$_2$ Bn), 68.4 (d, ^{4}J = 1.4 Hz, C-3), 68.2 (d, ^{2}J = 22.7 Hz, C-5), 67.4 (d, ^{3}J = 6.6 Hz, C-4), 48.0 (C-2), 27.6, 23.4 (2 × *C*H$_2$CH$_3$), 23.4 (*C*H$_3$ NHAc), 9.4, 9.0 (2 × CH$_2$*C*H$_3$). ^{19}F NMR (CDCl$_3$, 376 MHz): −232.11 (ddd, ^{2}J = 46.7, 46.6 Hz, ^{3}J = 14.6 Hz). HRMS-APCI (*m/z*): [M + H]$^{+}$ calcd for C$_{21}$H$_{29}$FNO$_7$, 426.1923; found, 426.1928.

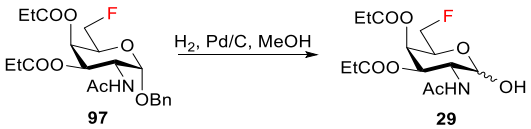
Benzyl 2-Acetamido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-α-D-galactopyranoside (98)



96 **98**

Compound **98** was prepared from **96** (150 mg, 0.48 mmol) according to the general procedure for acylation using butyryl chloride (125 µL, 1.20 mmol). Chromatography in EtOAc/PE 3:2 afforded **98** (155 mg, 71%) as a white crystalline solid, mp 76–79 °C (EtOAc/heptane), R_f 0.77 (EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.41–7.31 (m, 5H, CH_{arom}), 5.58 (d, 1H, *J* = 9.8 Hz, N*H*), 5.42 (dd, 1H, *J* = 3.3, 1.3 Hz, H-4), 5.23 (dd, 1H, *J* = 11.3, 3.3 Hz, H-3), 5.00 (d, 1H, *J* = 3.7 Hz, H-1), 4.74 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.61 (ddd, 1H, *J* = 11.3, 9.8, 3.7 Hz, H-2), 4.52 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.46–4.33 (m, 2H, H-6), 4.27 (dtd, 1H, *J* = 14.6, 5.8, 1.3 Hz, H-5), 2.46–2.32 (m, 2H, COCH_2), 2.21 (t, 2H, *J* = 7.4 Hz, COCH_2), 1.69, 1.57 (2 × h, 2 × 2H, *J* = 7.4 Hz, CH_2CH$_3$), 1.90 (s, 3H, CH_3 NHAc), 0.98, 0.89 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.6, 173.1, 170.1 (3 × CO), 136.7 (C_q), 128.8 (2CH_{arom}), 128.5 (CH_{arom}), 128.4 (2CH_{arom}), 97.2 (C-1), 81.8 (d, ^1J = 171.3 Hz, C-6), 70.3 (*C*H$_2$ Bn), 68.2 (d, ^4J = 4.8 Hz, C-3), 68.1 (d, ^2J = 19.0 Hz, C-5), 67.3 (d, ^3J = 6.6 Hz, C-4), 48.0 (C-2), 36.14, 36.08 (2 × CO*C*H$_2$), 23.4 (*C*H$_3$ NHAc), 18.7, 18.3 (2 × *C*H$_2$CH$_3$), 13.8, 13.7 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −231.99 (td, ^2J = 46.6 Hz, ^3J = 14.6 Hz). HRMS-APCI (*m/z*): [M + H]$^+$ calcd for $C_{23}H_{33}FNO_7$, 454.2235; found, 454.2238.

2-Acetamido-2,6-dideoxy-6-fluoro-3,6-di-*O*-propionyl-D-galactopyranose (29)

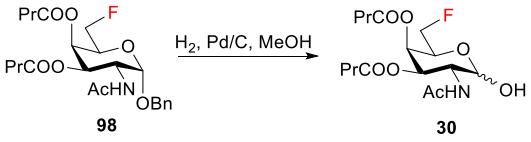


97 **29**

Compound **29** was prepared from **97** (150 mg, 0.35 mmol) according to the general procedure for debenzylation using 10% palladium on carbon (40 mg). After 3 days, the reaction mixture was filtered and concentrated. Chromatography of the residue in EtOAc afforded **29** (71 mg, 60%) as a white crystalline solid, mp 161–163 °C (EtOAc/MeOH), R_f 0.35 (EtOAc). HRMS-APCI (*m/z*): [M + H]$^+$ calcd

for $C_{14}H_{23}FNO_7$, 336.1453; found, 336.1454. NMR data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.79 (d, 1H, *J* = 9.6 Hz, N*H*), 5.44 (dd, 1H, *J* = 3.4, 1.3 Hz, H-4), 5.35 (dd, 1H, *J* = 3.6, 3.4 Hz, H-1), 5.29 (dd, 1H, *J* = 11.3, 3.4 Hz, H-3), 4.58 (ddd, 1H, *J* = 11.3, 9.6, 3.6 Hz, H-2), from ^{1}H {^{19}F} 4.58 (ddd, 1H, *J* = 6.5, 5.5, 1.3 Hz, H-5), 4.52–4.35 (m, 2H, H-6), 3.72 (br s, 1H, O*H*), 2.52–2.40 (m, 2H, C*H*$_2$CH$_3$), 2.30–2.24 (m, 2H, C*H*$_2$CH$_3$), 1.97 (s, 3H, C*H*$_3$ NHAc), 1.19, 1.08 (2 × s, 2 × 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, HSQC): δ 174.4, 173.9, 170.4 (3 × CO), 92.3 (C-1), 81.8 (d, ^1J = 171.2 Hz, C-6), 67.9 (d, ^4J = 1.1 Hz, C-3), 67.7 (d, ^2J = 22.2 Hz, C-5), 67.4 (d, ^3J = 6.8 Hz, C-4), 48.2 (C-2), 27.52, 27.50 (2 × *C*H$_2$CH$_3$), 23.3 (*C*H$_3$ NHAc), 9.9, 9.3 (2 × CH$_2$*C*H$_3$). ^{19}F NMR ($CDCl_3$, 376 MHz): −232.13 (ddd, ^2J = 46.2, 45.9 Hz, ^3J = 15.4 Hz). Resolved NMR signals for the: β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC): δ 6.13 (d, 1H, *J* = 7.1 Hz, N*H*), 5.06 (dd, 1H, *J* = 11.3, 3.4 Hz, H-3), 4.63 (d, 1H, *J* = 8.8 Hz, H-1), 4.16 (ddd, 1H, *J* = 11.3, 8.8, 7.1 Hz, H-2), 3.94 (td, 1H, *J* = 6.1, 1.2 Hz, H-5). ^{19}F NMR ($CDCl_3$, 376 MHz): −232.75 (td, ^2J = 46.5 Hz, ^3J = 11.3 Hz).

2-Acetamido-3,4-di-*O*-butyryl-2,6-dideoxy-6-fluoro-D-galactopyranose (30)

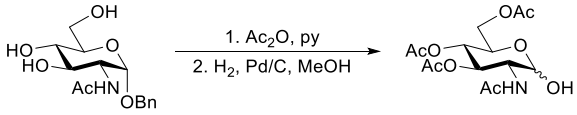


98 **30**

Compound **30** was prepared from **98** (110 mg, 0.24 mmol) according to the general procedure for benzyl deprotection using 10% palladium on carbon (20 mg). After 2 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc/PE 2:1 afforded **30** (70 mg, 79%) as a white crystalline solid, mp 152–154 °C (EtOAc/heptane) R_f 0.55 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}FNO_7$, 364.1766; found, 364.1769. ^{1}H NMR ($CDCl_3$, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.77 (d, 1H, *J* = 9.6 Hz, N*H*), 5.43 (dd, 1H, *J* = 3.3, 1.3 Hz, H-4), 5.36 (t, 1H, *J* = 3.6 Hz, H-1), 5.30 (dd, 1H, *J* = 11.2, 3.3 Hz, H-3), 4.58 (dddd, 1H, *J* = 11.2, 9.6, 3.6, 1.5 Hz, H-2), from ^{1}H {^{19}F} 4.49 (ddd, 1H, *J* = 6.4, 5.0, 1.3 Hz, H-5), 4.52–4.35 (m, 2H, H-6), 3.50 (dd, 1H, *J* = 3.6, 1.5 Hz, O*H*), 2.46−2.34 (m, 2H, COC*H*$_2$), 2.23 (t, 2H, *J* = 7.4 Hz, COC*H*$_2$), 1.69, 1.58 (2 × h, 2 × 2H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.96 (s, 3H,

C*H*$_3$ NHAc), 0.99, 0.90 (2 × t, 2 × 3H, *J* = 7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 173.7, 173.1, 170.4 (3 × CO), 92.4 (C-1), 81.9 (d, ^1J = 171.3 Hz, C-6), 67.9 (d, ^2J = 20.9 Hz, C-5), 67.8 (C-3), 67.5 (d, ^3J = 6.9 Hz, C-4), 48.3 (C-2), 36.2, 36.1 (2 × CO*C*H_2), 23.4 (*Me* NHAc), 18.7, 18.3 (2 × *C*H_2CH_3), 13.8, 13.7 (2 × CH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): −232.05 (ddd, ^2J = 46.3, 46.2 Hz, ^3J = 15.2 Hz). The signals of the β-anomer were not detected in intensity sufficient for characterisation within 24 h after sample dissolution in $CDCl_3$

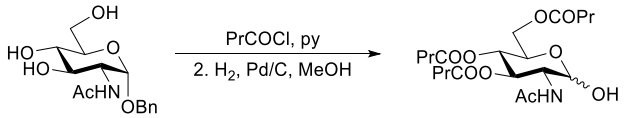
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (99)



89 **99**

Compound **89** (200 mg, 0.64 mmol) reacted with acetic anhydride (0.61 mL, 6.45 mmol) in pyridine (4 mL) according to the general procedure. The reaction mixture product was concentrated and co-distilled with toluene (3×) and the crude product debenzylated according to the general procedure using 10% palladium on carbon (60 mg). After 3 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc/MeOH 20:1 afforded **99** (184 mg, 82%) as a white foam, R_f 0.15 (EtOAc). NMR data were in agreement with ref 9.

2-Acetamido-3,4,6-tri-*O*-butyryl-2-deoxy-α-D-glucopyranose (100)

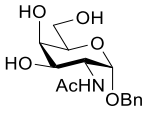


89 **100**

Compound **89** (150 mg, 0.48 mmol) reacted with butyryl chloride (0.20 mL, 1.93 mmol) in pyridine (6 mL) according to the general procedure. Chromatography in EtOAc/PE 1:2 afforded benzyl 2-acetamido-3,4,6-tri-*O*-butyryl-2-deoxy-α-D-glucopyranoside which was debenzylated according to the general procedure using 10% palladium on carbon (100 mg). After 4 days, the reaction mixture was

filtered and concentrated. Chromatography in EtOAc afforded **100** (142 mg, 68%) as a colourless gum, R_f 0.27 (EtOAc). NMR data were in agreement with ref 10.

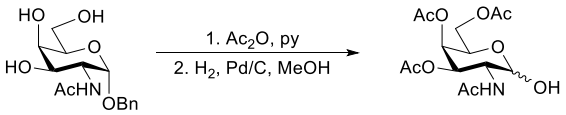
Benzyl 2-Acetamido-2-deoxy-D-galactopyranoside (101)



101

Galactopyranoside **101** was prepared according to ref 11.

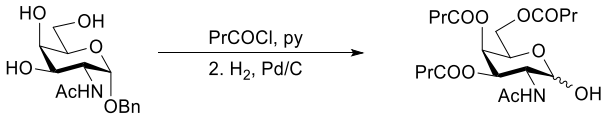
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranose (102)



101 **102**

Compound **101** (400 mg, 1.28 mmol) reacted with acetic anhydride (1.22 mL, 12.91 mmol) in pyridine (4 mL) according to the general procedure. The reaction mixture was concentrated, co-distilled with toluene (3×) and the crude product debenzylated according to the general procedure using 10% palladium on carbon (120 mg). After 3 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc afforded **102** (345 mg, 77%) as a colourless gel, R_f 0.18 (EtOAc). NMR data were in agreement with ref 9.

2-Acetamido-3,4,6-tri-*O*-butyryl-2-deoxy-α-D-galactopyranose (103)

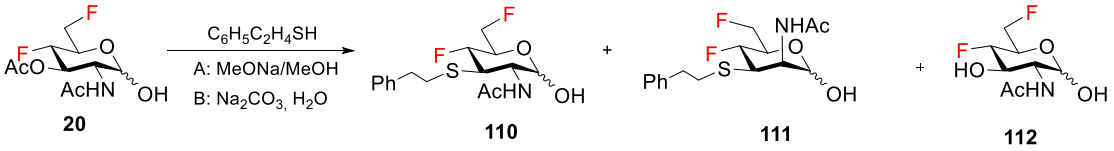


101 **103**

Compound **101** (438 mg, 1.41 mmol) reacted with butyryl chloride (0.50 mL, 4.81 mmol) in pyridine (10 mL) according to the general procedure. Chromatography in EtOAc/PE 1:2 afforded benzyl 2-acetamido-3,4,6-tri-*O*-butyryl-2-deoxy-α-D-galactopyranoside which was debenzylated according to

the general procedure using 10% palladium on carbon (180 mg). After 4 days, the reaction mixture was filtered and concentrated. Chromatography in EtOAc afforded **103** (350 mg, 58%) as a colorless gum, R_f 0.57 (EtOAc). NMR data were in agreement with ref 12.

Reaction of 2-Acetamido-3-*O*-acetyl-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (20) with 2-Phenylethanethiol

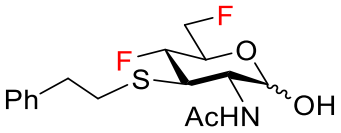


Experiment A

2-Phenylethanethiol (0.05 mL, 0.37 mmol) was added into a solution of **20** (40 mg, 0.15 mmol) in MeOH (3 mL) followed by dropwise addition of 1 M MeONa solution in MeOH until pH ≈ 10 (indicator paper). The reaction mixture was stirred for 24 h, neutralized by addition of DOWEX 50W exchange resin, filtered, concentrated and co-distilled with toluene (3×). Preparative TLC (EtOAc) afforded in the following order: A colourless syrupy mixture of anomers of 2-acetamido-2,3,4,6-tetradeoxy-4,6-difluoro-*S*-(2-phenylethyl)-3-thio-D-mannopyranose (**111**) (10 mg, 19%) with ca 40% of unidentified impurities by NMR analysis, 2-acetamido-2,3,4,6-trideoxy-4,6-difluoro-*S*-(2-phenylethyl)-3-thio-D-glucopyranose (**110**) (8 mg, 15%) in ca 90% purity as a colourless syrupy mixture of anomers, and 2-acetamido-2,4,6-trideoxy-4,6-difluoro-D-glucopyranose (**112**) (10 mg, 30%) as a white crystalline solid.

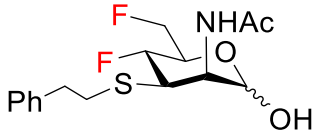
Experiment B

2-Phenylethanethiol (0.05 mL, 0.37mmol) was added into a solution of **20** (40 mg, 0.15 mmol) and anhydrous Na_2CO_3 (17 mg, 0.16 mmol) in water (20 mL). The reaction mixture was stirred for 24 h, neutralized by addition of DOWEX 50W exchange resin, filtered, concentrated, co-distilled with toluene (3×) and analysed by NMR using NMR data from the experiment A.



110

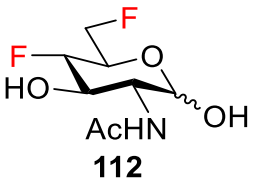
NMR data for the α-anomer of **110**: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.28–7.14 (m, 5H, CH_{arom}), 5.05 (t, 1H, J = 3.4 Hz, H-1), 4.61 (dddd, 1H, J = 47.5, 10.6, 4.1, 1.7 Hz, H-6'), 4.54 (ddt, 1H, J = 47.9, 10.6, 1.6 Hz, H-6), 4.38 (ddd, 1H, J = 48.3, 10.0, 9.8 Hz, H-4), 4.22–4.10 (m, 1H, H-5), 3.94 (ddd, 1H, J = 12.2, 3.4, 1.2 Hz, H-2), 3.19 (ddd, 1H, J = 12.2, 11.7, 10.0 Hz, H-3), 2.93–2.82 (m, 4H, SCH_2CH_2), 1.94 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 173.2 (CO), 141.9 (C_q), 129.6, 129.4 (2 × $2CH_{arom}$), 127.3 (CH_{arom}), 92.0 (d, ^{4}J = 1.6 Hz, C-1), 90.2 (dd, ^{1}J = 181.6 Hz, ^{3}J = 7.6 Hz, C-4), 82.8 (d, ^{1}J = 172.4 Hz, C-6), 70.2 (dd, ^{2}J = 25.7, 18.1 Hz, C-5), 52.4 (d, ^{3}J = 6.2 Hz, C-2), 48.2 (d, ^{2}J = 18.5 Hz, C-3), 37.3 (SCH_2CH_2), 33.6 (d, ^{4}J = 2.2 Hz, SCH_2), 22.5 (Me). ^{19}F NMR (MeOH-d_4, 376 MHz): −188.96 (dd, ^{2}J = 48.3 Hz, ^{3}J = 11.7 Hz, F-4), −237.05 (ddd, ^{2}J = 47.9, 47.5 Hz, ^{3}J = 26.4 Hz, F-6). Resolved signals for the β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY, HSQC): 4.73 (d, 1H, J = 8.7 Hz, H-1), 4.36 (dt, 1H, J = 48.5, 9.8 Hz, H-4), 3.79–3.66 (m, 1H, H-5), 3.57 (dd, 1H, J = 12.2, 8.0 Hz, H-2), 3.07 (ddd, 1H, J = 12.5, 12.2, 9.8 Hz, H-3). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 97.9 (C-1), 90.0 (dd, ^{1}J = 182.5 Hz, ^{3}J = 7.5 Hz, C-4), 82.6 (d, ^{1}J = 172.8 Hz, C-6), 76.2 (dd, ^{2}J = 26.0 Hz, ^{2}J = 18.4 Hz, C-5), 55.6 (d, ^{3}J = 6.3 Hz, C-2), 51.3 (d, ^{2}J = 18.5 Hz, C-3).^{19}F NMR (MeOH-d_4, 376 MHz): −191.60 (dd, ^{2}J = 48.5 Hz, ^{3}J = 12.5 Hz, F-4), −236.27 (td, ^{2}J = 47.6 Hz, ^{3}J = 24.3 Hz, F-6).



111

NMR data of **111** (the major anomer): ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.29–7.15 (m, 5H, CH_{arom}), from ^{1}H {^{19}F} 4.94 (t, 1H, J = 1.5 Hz, H-1), 4.74−4.68 (m, 3H, H-4, 2H-6), 4.36 (dd, 1H, J = 4.6, 1.5 Hz, H-2), 4.23−4.12 (m, 1H, H-5), 3.52 (ddd, 1H, J = 12.0, 10.7, 4.6 Hz, H-3), 2.94–2.79 (m, 4H, SCH_2CH_2), 1.99 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC, HMBC): δ 173.6 (CO), 141.7 (C_q), 129.6, 129.4 (2 × $2CH_{arom}$), 127.3 (CH_{arom}), 94.0 (d, ^{4}J = 1.3 Hz, C-1), 89.2 (dd, ^{1}J = 178.8 Hz, ^{3}J = 7.7 Hz, C-4), 83.0 (d, ^{1}J = 172.6 Hz, C-6), 70.7 (dd, ^{2}J = 25.3 Hz, ^{2}J = 18.4 Hz, C-5), 54.8 (d, ^{3}J = 7.3 Hz, C-2), 45.9 (d, ^{2}J = 18.5 Hz, C-3), 37.4 (SCH_2CH_2), 34.8 (d, ^{4}J = 2.5 Hz, SCH_2), 22.3 (Me). ^{19}F NMR (MeOH-d_4, 376 MHz): −196.50 (dd, ^{2}J = 48.6 Hz, ^{3}J = 12.0 Hz, F-4), −236.76 (td, ^{2}J = 47.7

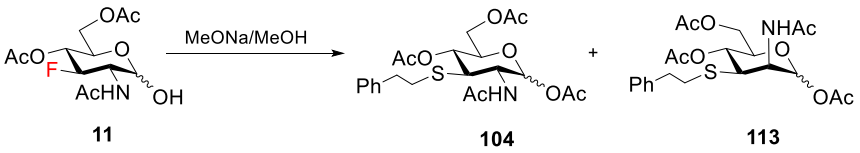
Hz, ^{3}J = 25.4 Hz, F-6). Due to insufficient quantity and purity of **111**, the coupling constant $^{1}J_{C1\text{-}H1}$ and the anomeric configuration were not determined.[13,14]



112

Compound **112**, the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 5.09 (t, 1H, *J* = 3.3 Hz, H-1), 4.61 (ddd, 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-4), 4.11 (ddddd, 1H, *J* = 26.6, 10.1, 4.1, 3.9, 1.8 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): δ 173.7 (CO), 92.5 (d, ^{4}J = 1.5 Hz, C-1), 90.6 (dd, ^{1}J = 181.2 Hz, ^{3}J = 7.4 Hz, C-4), 82.7 (d, ^{1}J = 172.5 Hz, C-6), 70.5 (d, ^{2}J = 18.5 Hz, C-3), 69.2 (dd, ^{2}J = 23.7, 18.2 Hz, C-5), 55.3 (d, ^{3}J = 8.0 Hz, C-2), 22.6 (Me). ^{19}F NMR (MeOH-d_4, 376 MHz): –199.99 (dddd, ^{2}J = 50.6 Hz, ^{3}J = 14.8, 4.1 Hz, ^{4}J = 3.3 Hz, F-4), –238.52 (ddd, ^{2}J = 48.1, 47.5 Hz, ^{3}J = 26.6 Hz, F-6). The β-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ from ^{1}H {^{19}F} 4.69 (d, 1H, *J* = 8.3 Hz, H-1), overlapped with α-anomer (2H, H-6), 4.28 (ddd, 1H, *J* = 50.9, 9.8, 8.5 Hz, H-4), 3.80 (ddd, 1H, *J* = 15.7, 10.5, 8.5 Hz, H-3), 3.68 (ddddd, 1H, *J* = 24.8, 9.8, 4.1, 2.5, 1.7 Hz, H-5), 3.60 (dd, 1H, *J* = 10.5, 8.3 Hz, H-2), 1.99 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 174.1 (CO), 96.9 (d, ^{4}J = 1.5 Hz, C-1), 90.2 (dd, ^{1}J = 181.9 Hz, ^{3}J = 7.2 Hz, C-4), 82.5 (d, ^{1}J = 172.8 Hz, C-6), 73.7 (dd, ^{2}J = 24.0, 18.7 Hz, C-5), 73.4 (d, ^{2}J = 18.3 Hz, C-3), 58.5 (d, ^{3}J = 8.3 Hz, C-2), 22.9 (Me). ^{19}F NMR (MeOH-d_4, 376 MHz): –202.07 (ddd, ^{2}J = 50.9 Hz, ^{3}J = 15.7, 1.7 Hz, F-4), –237.79 (td, ^{2}J = 47.6 Hz, ^{3}J = 24.8 Hz, F-6).

Reaction of 2-Acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-D-glucopyranose (11) with 2-Phenylethanethiol



11 **104** **113**

2-Phenylethanethiol (0.026 mL, 0.19 mmol) was added into a solution of **11** (25 mg, 0.08 mmol) in MeOH (3 mL) followed by dropwise addition of 1 M MeONa solution in MeOH until pH ≈ 10. The reaction mixture was stirred for 24 h, neutralized by addition of DOWEX 50W exchange resin, filtered, concentrated and co-distilled with toluene (3×). Pyridine (2 mL) and acetic anhydride (2 mL) was added and the reaction mixture was stirred for 6 h, concentrated and co-distilled with toluene (3×). Preparative TLC (EtOAc) afforded 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-*S*-(2-phenylethyl)-3-thio-D-mannopyranose (**113**) (2 mg, 5%) as a colourless gum and 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-*S*-(2-phenylethyl)-3-thio-D-glucopyranose (**104**) (19 mg, 50%) in 68% purity as a colourless syrupy mixture of anomers, NMR spectra corresponded to those in ref 15, impurities were not characterized. Data for **113**: R_f 0.30 (EtOAc). HRMS-APCI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{29}NO_8S$, 467.1614; found, 467.1618. ^{1}H NMR (MeOH-d_4, 400 MHz, ^{1}H {^{19}F}, H-H COSY): δ 7.30–7.18 (m, 5H, CH_{arom}), 5.83 (d, 1H, *J* = 1.7 Hz, H-1), 5.10 (dd, 1H, *J* = 11.2, 9.9 Hz, H-4), 4.40 (dd, 1H, *J* = 4.5, 1.7 Hz, H-2), 4.21 (dd, 1H, *J* = 12.3, 6.4 Hz, H-6′), 4.01 (dd, 1H, *J* = 12.3, 3.2 Hz, H-6), 3.96 (ddd, 1H, *J* = 9.9, 6.4, 3.2 Hz, H-5), overlapped wit MeOH-d_4 (H-3), 2.89–2.83 (m, 4H, SCH_2CH_2), 2.14, 2.06 (2 × s, 2 × 3H, *Me*), 2.03 (s, 6H, 2*Me*). ^{13}C{^{1}H} NMR (MeOH-d_4, 101 MHz, HSQC): δ 173.2, 172.5, 171.6, 170.3 (4 × CO), 141.6 (C_q), 129.7, 129.5 (2 × $2CH_{arom}$), 127.4 (CH_{arom}), 92.9 (C-1), 72.4 (C-5), 68.9 (C-4), 64.4 (C-6), 51.8 (C-2), 47.2 (C-3), 37.3 (SCH_2CH_2), 34.6 (SCH_2), 22.2, 20.80, 20.79, 20.6 (4 × Me). Due to insufficient quantity of **113**, the coupling constant $^1J_{C1\text{-}H1}$ and the anomeric configuration were not determined.

Cytotoxicity testing

The cells were maintained at 37 °C in humidified atmosphere with 5% CO_2 in high glucose Dulbecco's modified Eagle's medium (DMEM, all media were from Sigma-Aldrich (St. Louis, MO, USA)). Each media was supplemented with 10% fetal bovine serum (Gibco, ThermoFisher Scientific, Waltham, MA, USA), 300 μg/ml of L-glutamine (Sigma-Aldrich), and 100 μg/ml of HyClone Penicillin–Streptomycin 100X solution (BioSera, Nuaille, France). The culture medium was changed during each cell passage every 2–3 days. Cells were mycoplasma free throughout the experiments. Cells were grown to 60–80% confluence prior to seeding in a 96-well plate at a density of 3000 cells/well for cytotoxicity testing. The next day, these cells were exposed to selected compounds at concentrations from 1 to 500 μM for 72 h. The cell viability was measured using colorimetric MTT assay as described previously.[16] Data from MTT assay were analyzed in GraphPad Prism software and expressed as IC_{50} values (compound concentrations that produce 50% of cell metabolic inhibition). Errors were calculated as standard deviations (SD). All experiments were performed independently at least three times.

***In silico* calculation of membrane permeation**

To simulate permeation of molecules, the COSMOPerm approach was used.[17] As a permeating membranes, dipalmitoylphosphatidylcholine (DPPC) and dioleoylphosphatidylcholine (DOPC) were used as a common model membranes. Using the Gromacs 2018.1 software for molecular dynamics (MD),[18] both membranes were simulated for 50 nm starting from already equilibrated membranes using SLipids force field[19] at 293 K. The membranes were simulated in periodic box containing 64 lipids in each leaflet and approximately 50 water molecules as an TI3P water model.[20] The temperature was kept constant using the Nosé-Hoover thermostat (coupling constant of 0.5 ps).[21,22] The pressure was kept using Parrinello-Rahman barostat (1 atm) and semi-isotropic coupling (coupling constant 5 ps, isothermal compressibility $4.5 \cdot 10^{-5}$ bar^{-1}).[23] The electrostatic interactions were calculated using the Ewald scheme with a 1.2 nm cutoff.[24] The cutoff for Lennard-Jones interactions was set to 1.0 nm. The LINCS algorithm was used to as a bond constrain algoritgm.[25]

From the MD simulations, 5 randomly chosen conformations from last 10 ns were chosen. Using the COSMOThermX 18 software,[17] all 10 membranes were sliced into 50 horizontal layers and electron density and charge of each layer represented by σ-profile was calculated using the COSMO-RS approach.[26]

The molecules are calculated separately to the membrane. The LigPrep and MacroModel packages from Schrodinger were used to generate neutral conformers of compounds in vacuum using the OPLS_2005 force field.[27] For each compound, a maximum of 10 conformers (within 5 kcal/mol of conformer with the lowest energy and RMSD at least 0.2 nm between individual conformers) were selected based on MCMM/LMC2 conformation searching algorithm with Monte Carlo structure selection. For each conformer, a subsequent DFT/B-P/cc-TZVP vacuum and COSMO optimisation with fine grid option were carried out using Turbomole 6.3.

For each combination of lipid membrane (5 DPPC and 5 DOPC) and each conformer of each calculated molecule (8 molecules, 40 conformers in total), the partition coefficient between membrane and water phase and permeation coefficient was calculated using COSMOPerm approach.[17] Finally, the results for each molecule was averaged with the standard deviation for each membrane. Results of the calculations can be seen in Table S1.

From the permeation results, no clear correlation between in vivo toxicity and permeation was observed. According to calculation, the molecules tend to permeate freely through the chosen model membranes considering the free permeation threshold (approximately log Perm = −8)[28] and considering all the molecules neutral in cell cultures. Glucose was used as a confirmation of the used model on a known substance. The permeation coefficient was in agreement with other permeation studies.[29]

Table S1: COSMOPerm calculated partition and permeation coefficients for eight studied molecules and glucose

Compound	IC_{50} (µmol/L) MDA-MB-231	Membrane DPPC		Membrane DOPC	
		log *P* (membrane) /water)	log P_{erm} (cm/s)	log *P* (membrane) /water)	log P_{erm} (cm/s)
99 **(Ac_3-GlcNAc-1-OH)**	96 ± 10	−1.1 ± 0.4	−6.5 ± 0.1	−1.0 ± 0.3	−6.3 ± 0.1
20 **(4,6-F_2-Ac-GlcNAc-1-OH)**	25 ± 10	−0.1 ± 0.1	−2.5 ± 0.1	0.2 ± 0.1	−2.4 ± 0.1
21 **(4,6-F_2-Pr-GlcNAc-1-OH)**	41 ± 7	−0.2 ± 0.3	−4.8 ± 0.1	−0.2 ± 0.3	−4.6 ± 0.1
22 **(4,6-F_2-Bu-GlcNAc-1-OH)**	54 ± 3	0.4 ± 0.2	−2.3 ± 0.3	0.7 ± 0.2	−1.9 ± 0.1
102 **(Ac_3-GalNAc-1-OH)**	414 ± 130	−1.1 ± 0.4	−6.7 ± 0.2	−1.2 ± 0.5	−6.3 ± 0.1
31 **(4,6-F_2-Ac-GalNAc-1-OH)**	61 ± 5	−0.4 ± 0.2	−5.2 ± 0.1	−0.4 ± 0.2	−4.8 ± 0.1
32 **(4,6-F_2-Pr-GalNAc-1-OH)**	20 ± 4	−0.2 ± 0.1	−5.5 ± 0.1	−0.3 ± 0.1	−5.3 ± 0.1
33 **(4,6-F_2-Bu-GalNAc-1-OH)**	54 ± 8	0.0 ± 0.3	−5.7 ± 0.1	0.2 ± 0.2	−5.3 ± 0.1
D-Glucose	Not applicable	−1.5 ± 0.1	−10.8 ± 0.1	−1.2 ± 0.1	−10.5 ± 0.1

Scratch (wound healing) assay

The cells were grown to 100% confluence and scratched in serum-free medium to avoid cellular proliferation as described previously.[30] Cells were left to re-populate the scratched area for 24 h. None of the tested compound showed any inhibitory effect on cell migration.

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