

The Use of Remote Acyl Groups for Stereoselective 1,2-*cis*-Glycosylation with Fluorinated Glucosazide Thiodonors

Supporting Information

I

Experimental procedures

Vojtěch Hamala,^{1,2} Lucie Červenková Šťastná,¹ Martin Kurfiřt,^{1,2} Petra Cuřínová,¹ Martin Dračínský,³

Jindřich Karban^{1,*}

¹*Institute of Chemical Process Fundamentals of the CAS, v. v. i., Rozvojová 135, 16502 Praha 6, Czech Republic.* ²*University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6, Czech Republic.*

³*Institute of Organic Chemistry and Biochemistry of the CAS, v. v. i., Flemingovo náměstí 542/2, 16000, Praha 6, Czech Republic*

*Email: karban@icpf.cas.cz.

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General methods

Chemicals were used as received. Toluene was dried by distillation from sodium, CH_2Cl_2 and $(\text{CH}_2\text{Cl})_2$ were dried by distillation from CaH_2 and stored over molecular sieves 3 Å. Pyridine was dried by standing over NaOH. Dry DMF was purchased from Acros Organics. Ethyl acetate and petroleum ether (fraction with boiling point 40–65 °C) were distilled before use. TLC was carried out with Merck DC Alufolien with Kiesesyrup F254 and spots were detected with an anisaldehyde solution in $\text{EtOH}/\text{AcOH}/\text{H}_2\text{SO}_4$. UV detection at 254 nm was also used where appropriate. Column chromatography was performed with silica gel 60 (70–230 mesh). Preparative TLC chromatography was performed using 20 cm × 20 cm glass plates covered with TLC-Silica gel 60 GF₂₅₄ (20 g, mean particle size 15 µm, containing 12–13.5% $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ and fluorescent indicator). The maximum loading used was approx. 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 ^1H (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 ^1H and ^{13}C NMR spectra were referenced to the line of the solvent (δ/ppm ; $\delta_{\text{H}}/\delta_{\text{C}}$: CDCl_3 , 7.26/77.16). The ^{19}F spectra were referenced to the line of internal standard hexafluorobenzene (δ/ppm ; –163.00). HRMS analyses were done using Bruker MicrOTOF-QIII, using APCI ionization in positive mode, the m/z value of the $[\text{M} - \text{N}_2 + \text{H}]^+$ adduct is reported for 2-azido sugars because the molecular ion adducts were undetectable or extremely weak in abundance. The optical rotation was measured at 589 nm in a 100 mm cell on a JASCO P-2000 polarimeter; concentration is given in g/100 mL. Fluorosugars **1**,¹ **2**,¹ **6**,² **7**,² **8**,¹ **18**,¹ **19**,¹ and **22**,² and glycosyl acceptors **A**,³ **B**,⁴ **C**,⁴ **D**,⁵ **E**,⁶ were prepared following published procedures. Symbols α or β placed *after* a compound number indicate the anomeric configuration of the newly formed glycosidic bond in the glycosylation of model acceptors. EtOAc stands for ethyl acetate, PE for petroleum ether.

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

To a solution of the starting deoxofluorinated 1,6-anhydrohexopyranose in dry 1,2-dichloroethane ($c \sim 0.2\text{--}0.3 \text{ mol} \cdot \text{dm}^{-3}$) 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 24–48 h, 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, filtered, the organic layer was

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 ($c \sim 0.1 \text{ mmol.dm}^{-3}$) acidified by a few drops of AcOH and stirred at rt for about 1 h to remove 6-*O*-trimethylsilyl group (indicated by TLC), concentrated and purified by column chromatography.

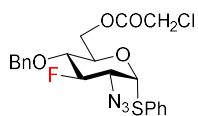
General procedure for 6-*O* chloroacetylation

Chloroacetyl chloride (2 equiv) was dropwise added into a cooled ($-25 \text{ }^{\circ}\text{C}$) solution of the starting alcohol in pyridine ($c \text{ } 0.1\text{--}0.2 \text{ mol.dm}^{-3}$). The reaction mixture was stirred at $-25 \text{ }^{\circ}\text{C}$ for about 1–2 h when TLC indicated the complete absence of the starting material. The reaction mixture was poured onto ice and extracted with dichloromethane (3×). The organic extracts were combined, dried, concentrated, and co-distilled with toluene (at $T \leq 35 \text{ }^{\circ}\text{C}$) to afford crude product that was subsequently purified by column chromatography.

General glycosylation procedure

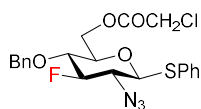
A mixture of thioglycoside donor (0.12 mmol, 1.2 equiv) and glycosyl acceptor (0.1 mmol, 1.0 equiv) was co-distilled with dry toluene (3×) and then dried for 20 min at a vacuum of an oil pump. Dry dichloromethane (1 mL), freshly distilled diethyl ether (1 mL), and 3 Å molecular sieves (0.8 g) were added and the resulting suspension was stirred at room temperature under argon for 1 h and then cooled to $-20 \text{ }^{\circ}\text{C}$. *N*-Iodosuccinimide was added (50 mg, vacuum-dried before use), the mixture was let to stir for about 10 min and triflic acid (4–9 μL , 0.04–0.11 mmol, specified below for each glycosylation) was added dropwise. The reaction turned red in about 5–20 min. The mixture was stirred at $-20 \text{ }^{\circ}\text{C}$ for about 2.5 h in total while monitored by TLC until the absence of the starting material was indicated. The reaction mixture was quenched by sequential addition of a saturated aqueous solution of NaHCO_3 (5 mL) and $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL), diluted with dichloromethane, filtered, and washed with water. The water phase was extracted with dichloromethane (3×). Organic extracts were combined, dried, and concentrated. ^1H NMR and ^{19}F NMR spectra were recorded and the residue was purified by column chromatography or preparative TLC chromatography. To facilitate the NMR assignment, separation of anomers was attempted when possible.

Phenyl 2-Azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro-1-thio- α -D-glucopyranoside (α -9)



Compound α -9 was prepared according to the general procedure for chloroacetylation starting from α -8¹ (740 mg, 1.90 mmol). Chromatography in EtOAc/PE 1:4 gave α -9 as a yellowish oil (754 mg, 85%), R_f 0.5 (EtOAc/heptane 1:3), $[\alpha]_D^{20} +215$ (c 1.42, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.46–7.43 (m, 2H, CH_{arom}), 7.41–7.29 (m, 8H, CH_{arom}), 5.57 (dd, 1H, $J = 5.7, 3.2$ Hz, H-1), 4.92 (ddd, 1H, $J = 52.5, 10.0, 8.2$ Hz, H-3), 4.91 (dd, 1H, $J = 11.3, 1.2$ Hz, CHH Bn), 4.64 (d, 1H, $J = 11.3$ Hz, CHH Bn), 4.43 from $^1\text{H}\{^{19}\text{F}\}$ (ddd, 1H, $J = 9.9, 4.7, 2.2$ Hz, H-5), 4.37 (dd, 1H, $J = 11.8, 4.7$ Hz, H-6'), 4.30 (ddd, 1H, $J = 11.8, 2.2, 1.5$ Hz, H-6), 4.04 (ddd, 1H, $J = 11.5, 10.0, 5.7$ Hz, H-2), 3.90, 3.81 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 15.0$ Hz, CHHCl), 3.65 (ddd, 1H, $J = 13.8, 9.9, 8.2$ Hz, H-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 166.9 (CO), 137.0, 132.44 ($2 \times \text{C}_q$), 132.35, 129.4, 128.8, 128.7 ($4 \times 2\text{CH}_{\text{arom}}$), 128.5, 128.3 ($2 \times \text{CH}_{\text{arom}}$), 95.8 (d, $^1J_{\text{C-F}} = 186.3$ Hz, C-3), 86.2 (d, $^3J_{\text{C-F}} = 8.3$ Hz, C-1), 74.7 (d, $^2J_{\text{C-F}} = 16.6$ Hz, C-4), 74.4 (d, $^4J_{\text{C-F}} = 3.4$ Hz, CH_2 Bn), 69.1 (d, $^3J_{\text{C-F}} = 9.1$ Hz, C-5), 64.1 (d, $^4J_{\text{C-F}} = 1.3$ Hz, C-6), 62.2 (d, $^2J_{\text{C-F}} = 17.6$ Hz, C-2), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): δ -188.91 (dddd, $^2J_{\text{H-F}} = 52.5$ Hz, $^3J_{\text{H-F}} = 13.8, 11.5$ Hz, $^4J_{\text{H-F}} = 3.2$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{FCINO}_4\text{S}$, 438.0936; found, 438.0932.

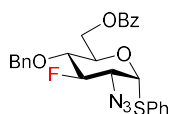
Phenyl 2-Azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro-1-thio- β -D-glucopyranoside (β -9)



Compound β -9 was prepared according to the general procedure for chloroacetylation starting from β -8¹ (506 mg, 1.30 mmol). Chromatography in EtOAc/PE 1:5 followed by crystallization (EtOAc/heptane) to remove impurities gave β -9 (241 mg, 40%), R_f 0.35 (EtOAc/heptane 1:5), mp 72–73 °C (EtOAc/heptane), $[\alpha]_D^{20} +36$ (c 0.85, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.57–7.54 (m, 2H, CH_{arom}), 7.38–7.29 (m, 8H, CH_{arom}), 4.85 (dd, 1H, $J = 11.3, 1.9$ Hz, CHH Bn), 4.59 (ddd, 1H, $J = 51.1, 9.1, 8.1$ Hz, H-3), 4.58 (d, 1H, $J = 11.3$ Hz, CHH Bn), 4.49 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 11.9, 2.1$ Hz, H-6'), 4.38 (dd, 1H, $J = 10.2, 0.9$ Hz, H-1), 4.30 (dd, 1H, $J = 11.9, 4.5$ Hz, H-6), 3.97, 3.92 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 14.9$ Hz, CHHCl), 3.59 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 9.9, 8.1$ Hz, H-4), 3.53 from $^1\text{H}\{^{19}\text{F}\}$ (ddd, 1H, $J = 9.9, 4.5, 2.1$ Hz, H-5), 3.44 (ddd, 1H, $J = 12.9, 10.2, 9.1$ Hz, H-2). $^{13}\text{C}\{^1\text{H}\}$

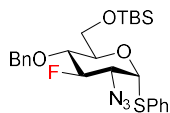
NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 166.9 (CO), 137.0 (C_q), 134.2 (2CH_{arom}), 130.5 (C_q), 129.3 (2CH_{arom}), 129.0 (CH_{arom}), 128.8, 128.6 (2 $\times$ 2CH_{arom}), 128.5 (CH_{arom}), 98.0 (d, $^1J_{(C-F)}$ = 189.1 Hz, C-3), 85.3 (d, $^3J_{(C-F)}$ = 7.3 Hz, C-1), 75.8 (d, $^3J_{(C-F)}$ = 9.6 Hz, C-5), 74.4 (d, $^4J_{(C-F)}$ = 3.4 Hz, CH₂ Bn), 74.1 (d, $^2J_{(C-F)}$ = 16.9 Hz, C-4), 64.1 (d, $^4J_{(C-F)}$ = 1.8 Hz, C-6), 63.3 (d, $^2J_{(C-F)}$ = 18.0 Hz, C-2), 40.7 (CH₂Cl). ¹⁹F NMR (CDCl₃, 376 MHz): δ -184.19 (ddd, $^2J_{(H-F)}$ = 51.1 Hz, $^3J_{(H-F)}$ = 12.9, 11.5 Hz). HRMS-APCI (m/z): [M - N₂ + H]⁺ calcd for C₂₁H₂₂FCINO₄S, 438.0936; found, 438.0944.

Phenyl 2-Azido-4-*O*-benzyl-6-*O*-benzoyl-2,3-dideoxy-3-fluoro-1-thio- α -D-glucopyranoside (**10**)



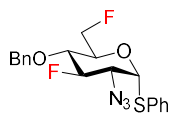
Benzoyl chloride (100 μ L, 0.86 mmol) was added dropwise to a solution of **8**¹ (250 mg, 0.64 mmol) in pyridine (2.5 mL) and the reaction was stirred at rt overnight. TLC in EtOAc/heptane 1:2 indicated the completion of the reaction. The reaction mixture was poured onto ice, extracted with dichloromethane (4 $\times$), the combined extracts were dried and concentrated. Chromatography in EtOAc/PE 1:5 afforded **10** as a colourless syrup (299 mg, 94%), R_f 0.3 (EtOAc/heptane 1:5), $[\alpha]_D^{20}$ +212 (c 1.10, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC, HMBC): δ 7.93–7.90 (m, 2H, CH_{arom}), 7.58–7.56 (m, 1H, CH_{arom}), 7.47–7.40 (m, 4H, CH_{arom}), 7.37–7.29 (m, 4H, CH_{arom}), 7.25–7.17 (m, 4H, CH_{arom}), 5.60 (dd, 1H, J = 5.7, 3.2 Hz, H-1), 4.95 (ddd, 1H, J = 52.6, 10.1, 8.2 Hz, H-3), 4.93 (dd, 1H, J = 11.1, 1.4 Hz, CHH Bn), 4.67 (d, 1H, J = 11.1 Hz, CHH Bn), 4.58 (dt, 1H, J = 9.6, 3.6 Hz, H-5), 4.53–4.52 (m, 2H, H-6), 4.08 (ddd, 1H, J = 11.2, 10.1, 5.7 Hz, H-2), 3.74 (ddd, 1H, J = 14.2, 9.6, 8.2 Hz, H-4). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 166.2 (CO), 137.0 (C_q Bn), 133.3 (CH_{arom}), 132.7 (C_q SPh), 132.2, 129.8 (2 $\times$ 2CH_{arom}), 129.8 (C_q Bz), 129.3, 128.7, 128.6, 128.5 (4 $\times$ 2CH_{arom}), 128.4, 128.1 (2 $\times$ CH_{arom}), 95.7 (d, $^1J_{(C-F)}$ = 186.3 Hz, C-3), 86.3 (d, $^3J_{(C-F)}$ = 8.1 Hz, C-1), 75.6 (d, $^2J_{(C-F)}$ = 16.6 Hz, C-4), 74.7 (d, $^4J_{(C-F)}$ = 3.1 Hz, CH₂ Bn), 69.7 (d, $^3J_{(C-F)}$ = 8.8 Hz, C-5), 63.2 (d, $^4J_{(C-F)}$ = 1.4 Hz, C-6), 62.3 (d, $^2J_{(C-F)}$ = 17.4 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): δ -188.70 (dddd, $^2J_{(H-F)}$ = 52.6 Hz, $^3J_{(H-F)}$ = 14.2, 11.2 Hz, $^4J_{(H-F)}$ = 3.2 Hz). HRMS-APCI (m/z): [M - N₂ + H]⁺ calcd for C₂₆H₂₅FNO₄S, 466.1482; found, 466.1485.

Phenyl 2-Azido-4-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-3-fluoro-1-thio- α -D-glucopyranoside (**11**)



A 50 wt. % solution of TBSCl in toluene (160 μ L, 70 mg TBSCl, 0.46 mmol) was added dropwise to a cooled (0 $^{\circ}$ C) and stirred solution of alcohol ***α*-8¹** (150 mg, 0.39 mmol) and imidazole (65 mg, 0.96 mmol) in anhydrous DMF (2 mL) under argon. The temperature was allowed to reach rt and stirring continued overnight. The reaction was diluted with dichloromethane, washed with water, the water phase reextracted with dichloromethane, and combined extracts dried and concentrated. Chromatography of the residue in EtOAc/PE 1:10 gave **11** (174 mg, 90%) as colourless oil, R_f 0.7 (ethyl acetate/heptane 1:5), $[\alpha]_D^{20} +164$ (c 0.31, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.49–7.47 (m, 2H, CH_{arom}), 7.37–7.28 (m, 8H, CH_{arom}), 5.56 (dd, 1H, $J = 5.7, 3.3$ Hz, H-1), 4.89 (dd, 1H, $J = 11.0, 1.2$ Hz, CHH Bn), 4.87 (ddd, 1H, $J = 52.9, 10.1, 8.4$ Hz, H-3), 4.66 (d, 1H, $J = 11.0$ Hz, CHH Bn), 4.20 (ddd, 1H, $J = 9.6, 3.9, 1.7$ Hz, H-5), 3.99 (ddd, 1H, $J = 11.4, 10.1, 5.7$ Hz, H-2), 3.91 (dd, 1H, $J = 11.6, 3.9$ Hz, H-6'), 3.79 (ddd, 1H, $J = 14.5, 9.6, 8.4$ Hz, H-4), 3.78 (ddd, 1H, $J = 11.6, 1.7, 1.5$ Hz, H-6), 0.90 (s, 9H, CMe_3), 0.04 (s, 6H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 137.9, 133.4 ($2 \times \text{C}_q$), 132.2, 129.2, 128.6, 128.2 ($4 \times 2\text{CH}_{\text{arom}}$), 128.1, 128.0 ($2 \times \text{CH}_{\text{arom}}$), 95.6 (d, $^1J_{\text{C-F}} = 186.0$ Hz, C-3), 86.6 (d, $^3J_{\text{C-F}} = 7.9$ Hz, C-1), 75.8 (d, $^2J_{\text{C-F}} = 16.5$ Hz, C-4), 74.8 (d, $^4J_{\text{C-F}} = 2.5$ Hz, CH_2 Bn), 72.5 (d, $^3J_{\text{C-F}} = 7.8$ Hz, C-5), 62.6 (d, $^2J_{\text{C-F}} = 17.2$ Hz, C-2), 61.9 (C-6), 26.1 (CMe_3), 18.5 (CMe_3), $-5.0, -5.2$ (SiMe_2). ^{19}F NMR (CDCl_3 , 376 MHz): δ -189.30 (dddd, $^2J_{\text{H-F}} = 52.9$ Hz, $^3J_{\text{H-F}} = 14.5, 11.4$ Hz, $^4J_{\text{H-F}} = 3.3$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{35}\text{FNO}_3\text{SSi}$, 476.2085; found, 476.2089.

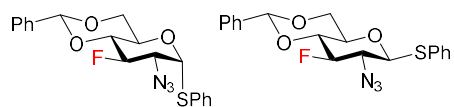
Phenyl 2-Azido-4-*O*-benzyl-2,3-dideoxy-3,6-difluoro-1-thio- α -D-glucopyranoside (**12**)



Diethylaminosulfur trifluoride (220 μ L, 1.66 mmol) and 2,4,6-collidine (530 μ L, 4.01 mmol) were added dropwise into a solution of alcohol ***α*-8¹** (500 mg, 1.28 mmol) in dry dichloromethane (8 mL) and the reaction was stirred under microwave irradiation at 80 $^{\circ}$ C for 1 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NaHCO_3 (2 mL), diluted with dichloromethane and washed with water. The water phase was extracted with dichloromethane (3 $\times$). Organic extracts were combined, dried, and concentrated. Chromatography of the residue

in EtOAc/PE 1:4 gave **12** (471 mg, 94%) as yellowish syrup, R_f 0.7 (EtOAc/heptane 1:3). $[\alpha]_D^{20} +215$ (c 1.27, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.47–7.45 (m, 2H, CH_{arom}), 7.39–7.30 (m, 8H, CH_{arom}), 5.60 (dd, 1H, $J = 5.7, 3.2$ Hz, H-1), 5.16 (ddd, 1H, $J = 13.9, 10.1, 8.4$ Hz, H-4), 4.93 (dd, $J = 11.0, 1.4$ Hz, 1H, CHH Bn), 4.90 (ddd, 1H, $J = 52.7, 10.0, 8.4$ Hz, H-3), 4.70 (ddd, 1H, $J = 46.8, 10.3, 2.9$ Hz, H-6'), 4.67 (d, $J = 11.0$ Hz, 1H, CHH Bn), 4.51 (ddd, 1H, $J = 47.9, 10.3, 1.4$ Hz, H-6), 4.33 (dddt, 1H, $J = 28.9, 10.1, 2.9, 1.4$ Hz, H-5), 4.05 (ddd, 1H, $J = 11.4, 10.0, 5.7$ Hz, H-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 137.3, 137.7 ($2 \times \text{C}_q$), 132.2, 129.4, 128.7 ($3 \times 2\text{CH}_{\text{arom}}$), 128.37 (CH_{arom}), 128.35 (2CH_{arom}), 128.2 (CH_{arom}), 95.4 (d, $^1J = 186.5$ Hz, C-3), 86.6 (d, $^3J = 8.1$ Hz, C-1), 81.4 (d, $^1J = 174.7$ Hz, C-6), 74.8 (d, $^4J = 2.7$ Hz, CH_2 Bn), 75.0 (dd, $^2J = 17.0$ Hz, $^3J = 6.8$ Hz, C-4), 70.6 (dd, $^2J = 18.0$ Hz, $^3J = 8.8$ Hz, C-5), 62.3 (d, $^2J = 17.4$ Hz, C-2). ^{19}F NMR (CDCl_3 , 376 MHz): -189.51 (dddd, $^2J = 52.7$ Hz, $^3J = 13.9, 11.4$ Hz, $^4J = 3.2$ Hz, F-3), -235.49 (ddd, $^2J = 47.9, 46.8$ Hz, $^3J = 28.9$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{F}_2\text{NO}_2\text{S}$, 364.1177; found, 364.1179.

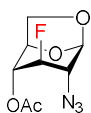
Phenyl 2-Azido-4,6-*O*-benzylidene-2,3-dideoxy-3-fluoro-1-thio- α - and β -D-glucopyranoside (α -13, β -13)



Trimethylsilyl chloride (0.40 mL, 3.15 mmol) was added dropwise to a cooled (0°C) and stirred solution of **7**² (150 mg, 0.79 mmol) and bis(trimethylsilyl)amine (0.83 mL, 3.96 mmol) in pyridine (2 mL). The cooling bath was removed after 0.5 h and stirring continued overnight. The reaction mixture was concentrated and co-distilled with toluene (2 $\times$), the white residue treated with ethyl acetate, the resulting suspension filtered through silica gel and celite and concentrated. The crude product (193 mg, R_f 0.5, EtOAc/heptane 1:5) was reacted with phenyl trimethylsilyl sulfide (0.46 mL, 2.43 mmol) and ZnI_2 (0.40 g, 1.25 mmol) in dichloroethane (2.5 mL) according to the general procedure for 24 h (TLC in EtOAc/heptane 1:7, R_f 0.6 before AcOH treatment). The collected fractions from the chromatography (after workup according to the general procedure) in EtOAc/PE 2:3 were concentrated. A solution of the residue (187 mg, R_f 0.12 and 0.18 in EtOAc/heptane 1:7), benzaldehyde dimethyl acetal (0.21 mL, 1.40 mmol) and camphorsulfonic acid (23 mg, 0.10 mmol) in DMF (2 mL) was heated to 45°C for 4 h. The reaction was quenched by the addition of triethylamine (0.3 mL), diluted with ethyl acetate, washed with saturated aqueous NaHCO_3 and brine, dried, and concentrated. Chromatography of the residue in EtOAc/PE 1:7 afforded first the beta anomer **β -13** as a colourless crystalline solid (39 mg, 13%) followed by the α -anomer **α -13** as a colourless crystalline

solid (89 mg, 29%). Data for **α -13**: R_f 0.19, (EtOAc/heptane 1:7), mp 132–134 °C (EtOAc/heptane), $[\alpha]_D^{20} +217$ (c 1.09, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC): δ 7.57–7.49 (m, 4H, CH_{arom}), 7.43–7.32 (m, 6H, CH_{arom}), 5.62 (dd, 1H, J = 5.9, 2.5 Hz, H-1), 5.59 (s, 1H, CHPh), 4.88 (ddd, 1H, J = 53.4, 9.7, 9.4 Hz, H-3), 4.43 (tdd, 1H, J = 10.0, 4.9, 1.3 Hz, H-5), 4.25 (ddd, 1H, J = 10.4, 4.9, 2.2 Hz, H-6'), 4.12 (ddd, 1H, J = 11.7, 9.7, 5.9 Hz, H-2), 3.85 (ddd, 1H, J = 12.2, 10.0, 9.4 Hz, H-4), 3.81 (dd, 1H, J = 10.3, 10.0 Hz, H-6). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 136.7 (C_q), 132.8 (2CH_{arom}), 132.49 (C_q), 132.51 (CH_{arom}), 129.4, 128.5 (2 $\times$ 2CH_{arom}), 128.4 (CH_{arom}), 126.4 (2CH_{arom}), 102.0 (CHPh), 90.2 (d, ¹ $J_{(C-F)}$ = 190.3 Hz, C-3), 87.6 (d, ³ $J_{(C-F)}$ = 7.2 Hz, C-1), 79.7 (d, ² $J_{(C-F)}$ = 16.9 Hz, C-4), 68.5 (d, ⁴ $J_{(C-F)}$ = 1.0 Hz, C-6), 63.3 (d, ³ $J_{(C-F)}$ = 7.3 Hz, C-5), 63.0 (d, ² $J_{(C-F)}$ = 17.4 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): δ -195.02 (dddddd, ² $J_{(H-F)}$ = 53.4 Hz, ³ $J_{(H-F)}$ = 12.2, 11.7 Hz, ⁴ $J_{(H-F)}$ = 2.5, 1.3 Hz, ⁵ $J_{(H-F)}$ = 2.2 Hz). HRMS-APCI (m/z): [M - N₂ + H]⁺ calcd for C₁₉H₁₉FNO₃S, 360.1064; found, 360.1063. Data for **β -13**: R_f 0.27 (EtOAc/heptane 1:7), 122–124 °C (EtOAc-heptane), $[\alpha]_D^{20} -63$ (c 1.01 CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC): δ 7.59–7.56 (m, 2H, CH_{arom}), 7.49–7.45 (m, 2H, CH_{arom}), 7.40–7.35 (m, 6H, CH_{arom}), 5.56 (s, 1H, CHPh), 4.57 (ddd, 1H, J = 52.3, 9.1, 8.7 Hz, H-3), 4.53 (d, 1H, J = 10.1 Hz, H-1), 4.41 (ddd, 1H, J = 10.6, 5.0, 2.1 Hz, H-6'), 3.81 (dd, 1H, J = 10.6, 9.8 Hz, H-6), 3.72 (ddd, 1H, J = 11.0, 9.5, 9.1 Hz, H-4), 3.51 (ddd, 1H, J = 13.7, 10.1, 8.7 Hz, H-2), 3.45 (dddd, 1H, J = 9.8, 9.5, 5.0, 1.4 Hz, H-5). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 136.6 (C_q), 134.2 (2CH_{arom}), 130.4 (C_q), 129.5 (CH_{arom}), 129.4 (2CH_{arom}), 129.2 (CH_{arom}), 128.5, 128.3 (2 $\times$ 2CH_{arom}), 101.8 (CHPh), 92.6 (d, ¹ $J_{(C-F)}$ = 192.5 Hz, C-3), 86.6 (d, ³ $J_{(C-F)}$ = 6.2 Hz, C-1), 78.5 (d, ² $J_{(C-F)}$ = 17.2 Hz, C-4), 69.7 (d, ³ $J_{(C-F)}$ = 7.8 Hz, C-5), 68.4 (d, ⁴ $J_{(C-F)}$ = 1.5 Hz, C-6), 64.0 (d, ² $J_{(C-F)}$ = 18.0 Hz, C-2). ¹⁹F NMR (CDCl₃, 376 MHz): δ -189.60 (dddddd, ² $J_{(H-F)}$ = 52.3 Hz, ³ $J_{(H-F)}$ = 13.7, 11.0 Hz, ⁴ $J_{(H-F)}$ = 1.4 Hz, ⁵ $J_{(H-F)}$ = 2.1 Hz). HRMS-APCI (m/z): [M - N₂ + H]⁺ calcd for C₁₉H₁₉FNO₃S, 360.1064; found, 360.1060.

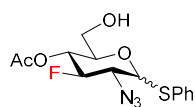
1,6-Anhydro-4-O-acetyl-2-azido-2,3-dideoxy-3-fluoro- β -D-glucopyranose (14)



Acetic anhydride (4.0 mL, 42.3 mmol) and a catalytic amount of 4-dimethylaminopyridine were added to a solution of **6**² (800 mg, 4.23 mmol) in pyridine (10 mL) and the reaction mixture was stirred at rt for 4 h. TLC in EtOAc/PE 1:3 showed the absence of the starting **6** (R_f 0.15) and formation of one major product (R_f 0.5). The reaction mixture was concentrated and co-distilled with toluene (3 $\times$). Column chromatography of the residue in EtOAc/PE 1:4

afforded **14** (919 mg, 94 %) as a colourless syrup. $[\alpha]_D^{20} +8$ (c 3.20, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 5.56 (t, 1H, $J = 1.7$ Hz, H-1), 4.83 (dtd, 1H, $J = 18.8, 1.7, 0.8$ Hz, H-4), 4.66 (ddd, 1H, $J = 5.8, 1.7, 1.1$ Hz, H-5), 4.62 (dp, 1H, $J = 43.7, 1.7$ Hz, H-3), 4.11 (dt, 1H, $J = 7.9, 1.1$ Hz, H-6^{en}), 3.82 (ddd, 1H, $J = 7.9, 5.8, 2.0$ Hz, H-6^{ex}), 3.32 (dtd, 1H, $J = 17.0, 1.7, 0.8$ Hz, H-2), 2.18 (s, 3H, *Me*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.0 (CO), 100.4 (C-1), 88.5 (d, $^1J = 183.8$ Hz, C-3), 73.7 (C-5), 69.2 (d, $^2J = 30.7$ Hz, C-4), 65.4 (d, $^4J = 3.1$ Hz, C-6), 58.7 (d, $^2J = 25.6$ Hz, C-2), 20.9 (Me). ^{19}F NMR (CDCl_3 , 376 MHz): δ -180.72 (ddd, $^2J = 43.7$ Hz, $^3J = 18.8, 17.0$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{11}\text{FNO}_4$, 204.0666; found, 204.0664.

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



Compound **15** was prepared by reaction of **14** (935 mg, 4.04 mmol) with PhSTMS (2.5 mL, 13.2 mmol) and ZnI_2 (2.2 g, 6.9 mmol) in dichloroethane (15 mL) according to the general procedure. The reaction was completed in 48 h when TLC (EtOAc/petroleum ether 1:3) showed the absence of **14** (R_f 0.6) and the presence of one major product (R_f 0.7). Chromatography of the residue in Et₂O/petroleum ether 3:2 afforded **15** (1.22 g, 88%) as a colourless syrupy mixture of anomers. Data: α -anomer: ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.49–7.46 (m, 2H, CH_{arom}), 7.38–7.31 (m, 3H, CH_{arom}), 5.64 (dd, 1H, $J = 5.8, 3.1$ Hz, H-1), 5.15 (ddd, 1H, $J = 13.8, 10.2, 8.9$ Hz, H-4), 4.82 (ddd, 1H, $J = 52.5, 10.0, 8.9$ Hz, H-3), 4.25 (ddd, 1H, $J = 10.2, 3.8, 2.4$ Hz, H-5), 4.10 (ddd, 1H, $J = 11.3, 10.0, 5.8$ Hz, H-2), 3.76–3.58 (m, 2H, H-6), 2.30 (br s, 1H, *OH*), 2.17 (s, 3H, *Me*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.8 (CO), 132.4 (2CH_{arom}), 132.3 (C_q), 129.5 (2CH_{arom}), 128.4 (CH_{arom}), 91.5 (d, $^1J = 189.4$ Hz, C-3), 86.4 (d, $^3J = 7.8$ Hz, C-1), 70.7 (d, $^3J = 5.8$ Hz, C-5), 69.0 (d, $^2J = 18.0$ Hz, C-4), 62.3 (d, $^2J = 17.2$ Hz, C-2), 60.8 (C-6), 20.9 (Me). ^{19}F NMR (CDCl_3 , 376 MHz): δ -193.43 (dddd, $^2J = 52.5$ Hz, $^3J = 13.8, 11.3$ Hz, $^4J = 3.1$ Hz). β -anomer: ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.59–7.56 (m, 2H, CH_{arom}), 7.38–7.31 (m, 3H, CH_{arom}), 5.02 (ddd, 1H, $J = 12.3, 10.1, 9.1$ Hz, H-4), 4.47 (dt, 1H, $J = 51.4, 9.1$ Hz, H-3), 4.44 (dd, 1H, $J = 10.2, 0.9$ Hz, H-1), 3.76–3.58 (m, 2H, H-6), 3.48 (ddd, 1H, $J = 12.5, 10.2, 9.1$ Hz, H-2), 3.41 (dddd, 1H, $J = 10.0, 4.9, 2.3, 1.2$ Hz, H-5), 2.30 (br s, 1H, *OH*), 2.12 (s, 3H, *Me*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.3 (CO), 134.1, 129.4 ($2 \times 2\text{CH}_{\text{arom}}$), 130.2 (C_q), 129.2 (CH_{arom}), 93.8 (d, $^1J = 192.1$ Hz, C-3), 85.4 (d, $^3J = 6.9$ Hz, C-1), 77.8 (d, $^3J = 6.2$ Hz, C-5), 68.3 (d, $^2J = 18.3$ Hz, C-4), 63.3 (d, $^2J = 17.5$ Hz, C-2), 61.4 (d, $^4J = 1.6$ Hz, C-6), 20.8 (Me). ^{19}F NMR

(CDCl₃, 376 MHz): δ -188.61 (ddd, $^2J = 51.4$ Hz, $^3J = 12.5, 12.3$ Hz). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for C₁₄H₁₇FNO₄S, 314.0857; found, 314.0859.

Phenyl 2-Azido-4-*O*-acetyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro-1-thio- α -D-glucopyranoside (α -16)

Phenyl 2-Azido-4-*O*-acetyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro-1-thio- β -D-glucopyranoside (β -16)

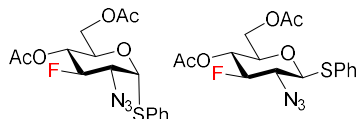


Compounds α - and β -16 were prepared by reaction of **15** (320 mg, 0.94 mmol) with chloroacetyl chloride (0.15 mL 1.88 mmol) according to the general procedure. Column chromatography of the crude product in EtOAc/PE 1:5 afforded first α -16 (187 mg, 48 %) as a colourless syrup. Continued elution afforded β -16 (145 mg, 37 %) as a colourless syrup. Data for α -16: R_f 0.4 (EtOAc/heptane 1:3), $[\alpha]_D^{20} +162$ (c 1.15, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC): δ 7.48–7.46 (m, 2H, CH_{arom}), 7.36–7.32 (m, 3H, CH_{arom}), 5.65 (dd, 1H, $J = 5.7, 3.1$ Hz, H-1), 5.18 (ddd, 1H, $J = 13.3, 10.3, 8.8$ Hz, H-4), 4.78 (ddd, 1H, $J = 52.3, 10.0, 8.8$ Hz, H-3), 4.52 (ddd, 1H, $J = 10.3, 5.5, 2.2$ Hz, H-5), 4.36 (dd, 1H, $J = 12.4, 5.5$ Hz, H-6'), 4.19 (ddd, 1H, $J = 12.4, 2.2, 1.3$ Hz, H-6), 4.13 (ddd, 1H, $J = 11.2, 10.0, 5.7$ Hz, H-2), 4.00, 3.97 (2 $\times$ d, 2 $\times$ 1H, $J = 15.0$ Hz, CHHCl), 2.15 (s, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 169.4, 167.1 (2 $\times$ CO), 132.3 (2CH_{arom}), 132.1 (C_q), 129.5 (2CH_{arom}), 128.4 (CH_{arom}), 91.6 (d, $^1J_{(C-F)} = 189.7$ Hz, C-3), 86.2 (d, $^3J_{(C-F)} = 7.8$ Hz, C-1), 68.5 (d, $^2J_{(C-F)} = 18.3$ Hz, C-4), 68.3 (d, $^3J_{(C-F)} = 6.8$ Hz, C-5), 63.5 (d, $^4J_{(C-F)} = 1.6$ Hz, C-6), 62.2 (d, $^2J_{(C-F)} = 17.2$ Hz, C-2), 40.7 (CH₂Cl), 20.8 (Me). ¹⁹F NMR (CDCl₃, 376 MHz): δ -194.00 (dddd, $^2J_{(H-F)} = 52.3$ Hz, $^3J_{(H-F)} = 13.3, 11.2$ Hz, $^4J_{(H-F)} = 3.0$ Hz). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for C₁₆H₁₈ClFNO₅S, 390.0573; found, 390.0574. Data for β -16: R_f 0.3 (EtOAc/heptane 1:3), $[\alpha]_D^{20} -10$ (c 1.12, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}, H-H COSY, HSQC): δ 7.60–7.57 (m, 2H, CH_{arom}), 7.39–7.35 (m, 3H, CH_{arom}), 5.07 (ddd, 1H, $J = 11.9, 10.2, 9.1$ Hz, H-4), 4.43 (dt, 1H, $J = 51.2, 9.1$ Hz, H-3), 4.41 (dd, 1H, $J = 10.2, 0.9$ Hz, H-1), 4.34–4.31 (m, 2H, H-6), 4.07, 4.97 (2 $\times$ d, 2 $\times$ 1H, $J = 15.2$ Hz, CHHCl), 3.62 (dddd, 1H, $J = 10.2, 4.4, 2.8, 1.2$ Hz, H-5), 3.49 (ddd, 1H, $J = 12.5, 10.2, 9.1$ Hz, H-2), 2.11 (s, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 169.5, 167.1 (2 $\times$ CO), 134.5 (2CH_{arom}), 129.9 (C_q), 129.4 (2CH_{arom}), 129.3 (CH_{arom}), 93.8 (d, $^1J_{(C-F)} = 192.3$ Hz, C-3), 85.4 (d, $^3J_{(C-F)} = 7.0$ Hz, C-1), 75.1 (d, $^3J_{(C-F)} = 7.5$ Hz, C-5), 67.7 (d, $^2J_{(C-F)} = 18.7$ Hz, C-4), 63.5 (d, $^4J_{(C-F)} = 2.0$ Hz, C-6), 63.1 (d, $^2J_{(C-F)} = 17.5$ Hz, C-2), 40.7 (CH₂Cl), 20.8 (Me). ¹⁹F NMR (CDCl₃, 376 MHz):

δ -189.12 (ddd, $^2J_{\text{(H-F)}} = 51.2$ Hz, $^3J_{\text{(H-F)}} = 12.5, 11.9$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{ClFNO}_5\text{S}$, 390.0573; found, 390.0570.

Phenyl 2-Azido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-1-thio- α -D-glucopyranoside (α -17)

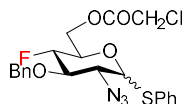
Phenyl 2-Azido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro-1-thio- β -D-glucopyranoside (β -17)



Acetic anhydride (1.2 mL, 12.7 mmol) and 4-dimethylaminopyridine (catalytic amount) were added to a solution of **15** (400 mg, 1.17 mmol) in pyridine (4 mL) and the reaction was stirred at rt for 4 h. It was then concentrated, co-distilled with toluene (2 $\times$), and the residue chromatographed in EtOAc/PE 1:3 to afford first α -**17** (100 mg, 22%) as white crystalline solid, followed by a mixture of α -**17** and β -**17** (277 mg, 61%) and then β -**17** (51 mg, 11%) as a colourless oil. Data for α -**17**: R_f 0.53 (EtOAc/heptane 1:2), mp 78–80 °C (EtOAc-heptane), $[\alpha]_{\text{D}}^{20} +196$ (c 1.06, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.50–7.47 (m, 2H, CH_{arom}), 7.34–7.31 (m, 3H, CH_{arom}), 5.64 (ddd, 1H, $J = 5.8, 3.1, 0.5$ Hz, H-1), 5.21 (ddd, 1H, $J = 13.3, 10.3, 8.9$ Hz, H-4), 4.77 (dddd, 1H, $J = 52.3, 10.0, 8.9, 0.5$ Hz, H-3), 4.51 (ddd, 1H, $J = 10.3, 5.3, 2.3$ Hz, H-5), 4.28 (dd, 1H, $J = 12.4, 5.3$ Hz, H-6'), 4.13 (ddd, 1H, $J = 11.2, 10.0, 5.8$ Hz, H-2), 4.05 (ddd, 1H, $J = 12.4, 2.3, 1.5$ Hz, H-6), 2.15, 2.03 ($2 \times s$, $2 \times 3\text{H}$, *Me*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.6, 169.6 ($2 \times \text{CO}$), 132.4 (2CH_{arom}), 132.3 (C_{q}), 129.4 (2CH_{arom}), 128.4 (CH_{arom}), 91.7 (d, $^1J_{\text{(C-F)}} = 189.6$ Hz, C-3), 86.3 (d, $^3J_{\text{(C-F)}} = 7.9$ Hz, C-1), 68.6 (d, $^3J_{\text{(C-F)}} = 3.1$ Hz, C-5), 68.4 (d, $^2J_{\text{(C-F)}} = 18.4$ Hz, C-4), 62.3 (d, $^2J_{\text{(C-F)}} = 17.1$ Hz, C-2), 61.9 (d, $^4J_{\text{(C-F)}} = 1.6$ Hz, C-6), 20.83, 20.80 ($2 \times \text{Me}$). ^{19}F NMR (CDCl_3 , 376 MHz): δ -193.97 (dddd, $^2J_{\text{(H-F)}} = 52.3$ Hz, $^3J_{\text{(H-F)}} = 13.3, 11.2$ Hz, $^4J_{\text{(H-F)}} = 3.1$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{FNO}_5\text{S}$, 356.0962; found, 356.0965. Data for β -**17**: R_f 0.48 (EtOAc/heptane 1:2), $[\alpha]_{\text{D}}^{20} -14$ (c 0.77, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.60–7.58 (m, 2H, CH_{arom}), 7.04–7.31 (m, 3H, CH_{arom}), 5.07 (ddd, 1H, $J = 11.8, 10.1, 9.1$ Hz, H-4), 4.42 (dt, 1H, $J = 51.3, 9.1$ Hz, H-3), 4.41 (dd, 1H, $J = 10.2, 0.9$ Hz, H-1), 4.23 (dd, 1H, $J = 12.3, 4.9$ Hz, H-6'), 4.18 (ddd, 1H, $J = 12.3, 2.7, 1.2$ Hz, H-6), 3.59 (dddd, 1H, $J = 10.1, 4.9, 2.7, 1.2$ Hz, H-5), 3.49 (ddd, 1H, $J = 12.5, 10.2, 9.1$ Hz, H-2), 2.10, 2.09 ($2 \times s$, $2 \times 3\text{H}$, *Me*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.7, 169.5 ($2 \times \text{CO}$), 134.4 (2CH_{arom}), 130.2 (C_{q}), 129.3 (2CH_{arom}), 129.2 (CH_{arom}), 94.0 (d, $^1J_{\text{(C-F)}} = 192.3$ Hz, C-3), 85.4 (d, $^3J_{\text{(C-F)}} = 6.9$ Hz, C-1), 75.3 (d, $^3J_{\text{(C-F)}} = 7.4$ Hz, C-5), 67.9 (d, $^2J_{\text{(C-F)}} = 18.5$ Hz, C-4), 63.2 (d, $^2J_{\text{(C-F)}} = 17.5$ Hz, C-2), 62.1 (d, $^4J_{\text{(C-F)}} = 1.9$ Hz, C-6), 20.9, 20.8 ($2 \times \text{Me}$).

^{19}F NMR (CDCl_3 , 376 MHz): δ -189.10 (ddd, $^2J_{(\text{H-F})} = 51.3$ Hz, $^3J_{(\text{H-F})} = 12.5, 11.8$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{FNO}_5\text{S}$, 356.0962; found, 356.0962.

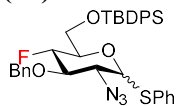
Phenyl 2-Azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro-1-thio- α,β -D-glucopyranoside (**20**)



Compound **20** was prepared according to the general procedure for chloroacetylation starting from **19**¹ (213 mg, 0.55 mmol). Chromatography in EtOAc/PE 1:5 gave **20** as yellowish oil (234 mg, 92%), R_f 0.3 (EtOAc/heptane 1:5).

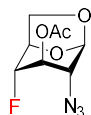
HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{FCINO}_4\text{S}$, 438.0937; found, 438.0941. NMR data for the α -anomer: ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.58–7.56 (m, 2H, CH_{arom}), 7.43–7.23 (m, 8H, CH_{arom}), 5.58 (dd, 1H, $J = 4.7, 3.1$ Hz, H-1), 4.94 (dd, 1H, $J = 10.8, 1.1$ Hz, CHH Bn), 4.85 (d, 1H, $J = 10.8$ Hz, CHH Bn), 4.66–4.34 (m, 4H, H-4, H-5, 2H-6), 4.02 (s, 2H, CH_2Cl), 3.98–3.90 (m, 2H, H-2, H-3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 167.0 (CO), 137.2, 132.5 ($2 \times \text{C}_q$), 132.3, 129.4, 128.7, 128.4 ($4 \times 2\text{CH}_{\text{arom}}$), 128.4, 128.2 ($2 \times \text{CH}_{\text{arom}}$), 90.7 (d, $^1J = 185.8$ Hz, C-4), 86.6 (d, $^4J = 1.0$ Hz, C-1), 79.0 (d, $^2J = 17.8$ Hz, C-3), 75.3 ($\text{CH}_2 \text{Bn}$), 68.1 (d, $^2J = 24.9$ Hz, C-5), 63.8 (C-6), 62.7 (d, $^3J = 8.5$ Hz, C-2), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -195.37 (m). Data for β -anomer: ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.52–7.50 (m, 2H, CH_{arom}), 7.43–7.23 (m, 8H, CH_{arom}), 4.88 (dd, 1H, $J = 10.9, 0.9$ Hz, CHH Bn), 4.79 (d, 1H, $J = 10.9$ Hz, CHH Bn), 4.62–4.57 (m, 1H, H-6), 4.42 (d, 1H, $J = 10.2$ Hz, H-1), 4.52–4.34 (m, 2H, H-4, H-6), 4.11 (s, 2H, CH_2Cl), 3.70 (ddd, 1H, $J = 10.1, 5.4, 2.7$ Hz, H-5), 3.63 (ddd, 1H, $J = 14.5, 9.3, 8.5$ Hz, H-3), 3.70 (ddd, 1H, $J = 10.2, 9.3, 0.8$ Hz, H-2). ^{13}C NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 167.0 (CO), 137.1 (C_q), 134.3 (2CH_{arom}), 130.3 (C_q), 129.2 (2CH_{arom}), 129.1 (CH_{arom}), 128.7, 128.5 ($2 \times 2\text{CH}_{\text{arom}}$), 128.4 (CH_{arom}), 89.6 (d, $^1J = 185.4$ Hz, C-4), 85.9 (d, $^4J = 1.2$ Hz, C-1), 82.0 (d, $^2J = 17.4$ Hz, C-3), 75.4 ($\text{CH}_2 \text{Bn}$), 75.1 (d, $^2J = 23.2$ Hz, C-5), 63.9 (d, $^3J = 8.9$ Hz, C-2), 63.8 (C-6), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -195.37 (dd, $^2J_{(\text{H-F})} = 50.2$ Hz, $^3J_{(\text{H-F})} = 14.5$ Hz).

Phenyl 2-Azido-3-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-2,4-dideoxy-4-fluoro-1-thio- α,β -D-glucopyranoside (21)



tert-Butyldiphenylsilyl chloride (155 μ L, 0.60 mmol) and DMAP (catalytic amount) was added to a cooled (0 $^{\circ}$ C) and stirred solution of **19**¹ (187 mg, 0.48 mmol) in pyridine (2 mL) and the reaction was stirred at rt for 56 h when TLC (EtOAc/heptane 1:5) showed almost complete consumption of **19**. The reaction was poured onto ice, extracted with dichloromethane (4 $\times$), the combined extracts dried and concentrated. Chromatography of the residue in EtOAc/PE 1:8 afforded **21** (281 mg, 93%) as a thick colourless syrup, R_f 0.65 (EtOAc/heptane 1:5). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for $C_{35}H_{39}FNO_3SSi$, 600.2398; found, 600.2396. NMR data for the α -anomer: 1H NMR ($CDCl_3$, 400 MHz, 1H $\{^{19}F\}$, H-H COSY, HSQC, HMBC) δ 7.77–7.60 (m, 6H, CH_{arom}), 7.51–7.23 (m, 14H, CH_{arom}), 5.58 (dd, 1H, $J = 4.7, 3.1$ Hz, H-1), 4.94 (dd, 1H, $J = 10.8, 1.1$ Hz, CHH Bn), 4.83 (d, 1H, $J = 10.8$ Hz, CHH Bn), 4.73 (ddd, 1H, $J = 50.7, 9.9, 8.3$ Hz, H-4), from 1H $\{^{19}F\}$ 4.40 (ddd, 1H, $J = 9.9, 4.1, 1.9$ Hz, H-5), 3.96–3.86 (m, 4H, H-2, H-3, 2H-6), 1.05 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 137.5 (C_q), 135.9, 135.7 ($2 \times 2CH_{arom}$), 133.9 (CH_{arom}), 133.6, 133.4, 133.1 ($3 \times C_q$), 131.9 ($2CH_{arom}$), 129.9, 129.8 ($2 \times CH_{arom}$), 129.2, 128.7, 128.5 ($3 \times 2CH_{arom}$), 128.2 (CH_{arom}), 127.9, 127.8 ($2 \times 2CH_{arom}$), 90.4 (d, $^1J = 183.7$ Hz, C-4), 87.1 (d, $^4J = 1.4$ Hz, C-1), 79.4 (d, $^2J = 18.0$ Hz, C-3), 75.2 (d, $^4J = 2.9$ Hz, CH_2Bn), 71.2 (d, $^2J = 25.0$ Hz, C-5), 62.9 (d, $^3J = 8.7$ Hz, C-2), 62.2 (C-6), 26.9 (CMe_3), 19.5 (CMe_3). ^{19}F NMR ($CDCl_3$, 376 MHz): -195.60 (m). Data for the β -anomer: 1H NMR ($CDCl_3$, 400 MHz, 1H $\{^{19}F\}$, H-H COSY, HSQC, HMBC) δ 7.77–7.60 (m, 4H, CH_{arom}), 7.51–7.23 (m, 16H, CH_{arom}), 4.89 (dd, 1H, $J = 10.8, 0.9$ Hz, CHH Bn), 4.78 (d, 1H, $J = 10.8$ Hz, CHH Bn), 4.64 (ddd, 1H, $J = 50.3, 9.8, 8.6$ Hz, H-4), 4.40 (d, 1H, $J = 10.2$ Hz, H-1), 3.99 (dt, 1H, $J = 10.7, 1.9$ Hz, H-6), 3.96–3.86 (m, 1H, H-6), 3.63 (ddd, 1H, $J = 14.4, 9.3, 8.6$ Hz, H-3), 3.49 (dddd, 1H, $J = 9.8, 4.0, 2.6, 1.9$ Hz, H-5), 3.36 (ddd, 1H, $J = 10.2, 9.3, 0.8$ Hz, H-2), 1.05 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 137.4 (C_q), 135.8, 135.7 ($2 \times 2CH_{arom}$), 133.2, 133.1, 130.8 ($3 \times C_q$), 129.9 ($2CH_{arom}$), 129.24 (CH_{arom}), 129.21 ($2CH_{arom}$), 128.7 ($4CH_{arom}$), 128.3 (CH_{arom}), 127.9 ($4CH_{arom}$), 127.8 ($2CH_{arom}$), 89.2 (d, $^1J = 183.7$ Hz, C-4), 85.9 (d, $^4J = 1.4$ Hz, C-1), 82.6 (d, $^2J = 17.6$ Hz, C-3), 78.3 (d, $^2J = 23.2$ Hz, C-5), 75.3 (d, $^4J = 2.6$ Hz, CH_2Bn), 64.0 (d, $^3J = 8.9$ Hz, C-2), 62.2 (C-6), 26.9 (CMe_3), 19.5 (CMe_3). ^{19}F NMR ($CDCl_3$, 376 MHz): -195.37 (ddd, $^2J_{(H-F)} = 50.3$ Hz, $^3J_{(H-F)} = 14.4, 2.6$ Hz).

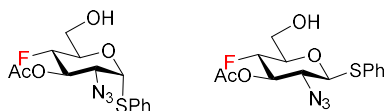
1,6-Anhydro-3-*O*-acetyl-2-azido-2,4-dideoxy-4-fluoro- β -D-glucopyranose (**23**)



Acetic anhydride (2.0 mL, 21.1 mmol) and a catalytic amount of 4-dimethylaminopyridine were added into a solution of **22** (760 mg, 4.02 mmol) in pyridine (5 mL) and the reaction mixture was stirred at rt overnight. The reaction mixture was concentrated and co-distilled with toluene (3 $\times$). Column chromatography of the crude residue in EtOAc/PE 1:3 afforded **23** (799 mg, 86 %) as a colourless syrup R_f 0.2 (EtOAc/heptane 1:3). The NMR data were comparable to those reported.²

Phenyl 2-Azido-3-*O*-acetyl-2,4-dideoxy-4-fluoro-1-thio- α -D-glucopyranoside (α -**24**)

Phenyl 2-Azido-3-*O*-acetyl-2,4-dideoxy-4-fluoro-1-thio- β -D-glucopyranoside (β -**24**)



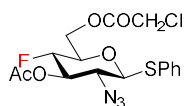
Compound **24** was prepared according to the general procedure by the reaction of **23** (830 mg, 3.59 mmol) with PhSTMS (2.4 mL, 12.7 mmol) and ZnI₂ (2.1 g, 6.6 mmol) in dichloroethane (15 mL). The reaction was completed in 48 h when TLC (EtOAc/PE 1:2) showed the absence of the starting compound and the presence of one major product (R_f 0.8). Chromatography of the residue in Et₂O/PE 1:1 afforded first β -**24** (173 mg, 14%), as a colourless syrup.

Continued elution afforded α -**24** (918 mg, 75%) as a colourless crystalline solid. Data for α -**24**: R_f 0.32

(EtOAc/heptane 1:2), mp 73–76 °C (MTBE/heptane), $[\alpha]_D^{20} +144$ (c 1.15, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC) δ 7.52–7.48 (m, 2H, CH_{arom}), 7.35–7.32 (m, 3H, CH_{arom}), 4.59 (dd, 1H, J = 5.5, 2.7 Hz, H-1), 5.49 (ddd, 1H, J = 13.0, 10.7, 8.7 Hz, H-3), 4.55 (ddd, 1H, J = 49.3, 9.9, 8.7 Hz, H-4), from ¹H {¹⁹F} 4.44 (ddd, 1H, J = 9.9, 3.7, 2.6 Hz, H-5), 3.94 (ddd, 1H, J = 10.7, 5.5, 1.1 Hz, H-2), 3.89–3.79 (m, 2H, H-6), 1.66 (dd, 1H, J = 7.3, 5.8 Hz, OH), 2.19 (s, 3H, Me). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 169.7 (CO), 132.8 (2CH_{arom}), 132.4 (C_q), 129.5 (2CH_{arom}), 128.4 (CH_{arom}), 86.94 (d, ⁴ J = 1.5 Hz, C-1), 86.86 (d, ¹ J = 187.1 Hz, C-4), 71.6 (d, ² J = 19.6 Hz, C-3), 70.5 (d, ² J = 25.0 Hz, C-5), 61.7 (d, ³ J = 7.0 Hz, C-2), 60.9 (C-6), 20.9 (Me). ¹⁹F NMR (CDCl₃, 376 MHz): δ –199.74 (m). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for C₁₄H₁₇FNO₄S, 314.0857; found, 314.0853. Data for β -**24**: R_f 0.46 (EtOAc/heptane 1:2), $[\alpha]_D^{20} -62$ (c 3.66, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC) δ 7.56–7.53 (m, 2H, CH_{arom}), 7.38–7.32 (m, 3H, CH_{arom}), 5.23 (ddd, 1H, J = 13.5, 9.8, 9.2 Hz, H-3),

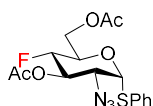
4.56 (d, 1H, $J = 10.1$ Hz, H-1), 4.41 (ddd, 1H, $J = 50.4, 9.7, 9.2$ Hz, H-4), 3.94 (ddd, 1H, $J = 12.5, 2.6, 2.0$ Hz, H-6'), 3.76 (ddd, 1H, $J = 12.5, 4.5, 2.0$ Hz, H-6), 3.57 (dddd, 1H, $J = 9.7, 4.5, 2.6, 2.0$ Hz, H-5), 3.35 (ddd, 1H, $J = 10.1, 9.8, 0.8$ Hz, H-2), 2.04 (br s, 1H, OH), 2.15 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 169.8 (CO), 133.7 (2CH_{arom}), 130.7 (C_q), 129.4 (2CH_{arom}), 129.0 (CH_{arom}), 86.4 (d, $^4J = 1.4$ Hz, C-1), 86.1 (d, $^1J = 187.0$ Hz, C-4), 77.8 (d, $^2J = 23.5$ Hz, C-5), 74.0 (d, $^2J = 19.4$ Hz, C-3), 62.9 (d, $^3J = 7.6$ Hz, C-2), 61.2 (C-6), 20.9 (Me). ^{19}F NMR (CDCl_3 , 376 MHz): δ -200.98 (ddq, $^2J = 50.4$ Hz, $^3J = 13.5, 2.0$ Hz, $^4J = 2.0$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{FNO}_4\text{S}$, 314.0857; found, 314.0860.

Phenyl 2-Azido-3-*O*-acetyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro-1-thio- β -D-glucopyranoside (**25**)



Compound **25** was prepared according to the general procedure for chloroacetylation starting from β -**24** (212 mg, 0.62 mmol). Chromatography in EtOAc/PE 4:1 afforded **25** (190 mg, 73%) as yellow syrup, R_f 0.3 (EtOAc/heptane 1:4) ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.58–7.55 (m, 2H, CH_{arom}), 7.38–7.34 (m, 3H, CH_{arom}), 5.22 (ddd, 1H, $J = 13.4, 9.8, 9.0$ Hz, H-3), 4.56 (ddd, 1H, $J = 12.2, 2.4, 1.8$ Hz, H-6'), 4.52 (d, 1H, $J = 10.1$ Hz, H-1), 4.36 (ddd, 1H, $J = 12.2, 5.0, 1.4$ Hz, H-6), 4.27 (ddd, 1H, $J = 50.6, 10.0, 9.0$ Hz, H-4), 4.09 (s, 2H, CH_2Cl), 3.76 (ddt, 1H, $J = 10.0, 5.0, 2.4$ Hz, H-5), 3.35 (ddd, 1H, $J = 10.1, 9.8, 0.8$ Hz, H-2), 2.15 (s, 3H, Me OAc). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 169.6, 166.9 ($2 \times \text{CO}$), 134.3 (2CH_{arom}), 130.2 (C_q), 129.3 (2CH_{arom}), 129.2 (CH_{arom}), 86.4 (d, $^1J = 188.9$ Hz, C-4), 86.2 (d, $^4J = 1.1$ Hz, C-1), 75.1 (d, $^2J = 22.5$ Hz, C-5), 73.7 (d, $^2J = 19.1$ Hz, C-3), 63.6 (C-6), 62.6 (d, $^3J = 7.2$ Hz, C-2), 40.7 (CH_2Cl), 20.8 (Me OAc). ^{19}F NMR (CDCl_3 , 376 MHz): -204.44 (ddd, $^2J_{(\text{H-F})} = 50.6$ Hz, $^3J_{(\text{H-F})} = 13.4, 2.4$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{ClFNO}_5\text{S}$, 390.0573; found, 390.0577.

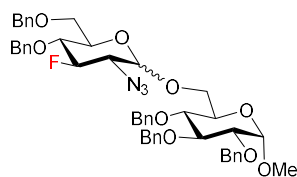
Phenyl 2-Azido-3,6-di-*O*-acetyl-2,4-dideoxy-4-fluoro-1-thio- α -D-glucopyranoside (**26**)



Acetic acid anhydride (0.48 mL, 5.1 mmol) was added to a solution of α -**24** (161 mg, 0.47 mmol) in pyridine (2.5 mL) and the reaction was stirred overnight at rt. The reaction mixture was concentrated and the residue co-distilled

with toluene (2×). Chromatography in EtOAc/PE 4:1 afforded **26** (170 mg, 94%) as yellow syrup, R_f 0.5 (EtOAc/heptane 1:3), $[\alpha]_D^{20} +131$ (c 0.81, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.51–7.49 (m, 2H, CH_{arom}), 7.34–7.32 (m, 3H, CH_{arom}), 5.60 (dd, 1H, $J = 5.6, 2.7$ Hz, H-1), 5.48 (ddd, 1H, $J = 13.0, 10.7, 8.8$ Hz, H-3), 4.65 (dddd, 1H, $J = 10.0, 4.3, 3.9, 3.4$ Hz, H-5), 4.42 (ddd, 1H, $J = 50.4, 10.0, 8.8$ Hz, H-4), 4.32–4.31 (m, 2H, H-6), 3.98 (ddd, 1H, $J = 10.7, 5.6, 1.1$ Hz, H-2), 2.19, 2.05 ($2 \times$ s, $2 \times$ 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.5, 169.5 (CO), 132.6 (2CH_{arom}), 132.3 (C_q), 129.4 (2CH_{arom}), 128.4 (CH_{arom}), 87.5 (d, $^1J = 189.0$ Hz, C-4), 86.7 (d, $^4J = 1.4$ Hz, C-1), 71.4 (d, $^2J = 19.5$ Hz, C-3), 68.2 (d, $^2J = 23.9$ Hz, C-5), 62.2 (C-6), 61.5 (d, $^3J = 6.9$ Hz, C-2), 20.9, 20.8 ($2 \times$ Me). ^{19}F NMR (CDCl_3 , 376 MHz): δ –199.16 (dd, $^2J_{(\text{H-F})} = 50.4$ Hz, $^3J_{(\text{H-F})} = 13.0$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{FNO}_5\text{S}$, 356.0962; found, 356.0966.

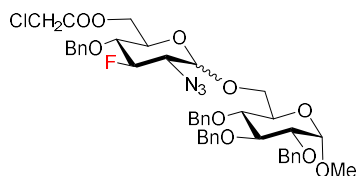
Methyl 6-*O*-(2-azido-4,6-di-*O*-benzyl-2,3-dideoxy-3-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (A1**)**



Compound **A1** was prepared by glycosylation of acceptor **A** with **α-1** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous work-up indicated $\alpha/\beta = 1.2:1.0$. Column chromatography in EtOAc/PE 1:4 afforded a mixture of both anomers of **A1** as a colourless gel (71 mg, 85 %), R_f 0.3 (ethyl acetate/heptane 1:3). NMR spectra of the β -anomer were in accordance with ref.¹ NMR data for the α -anomer are reported here: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.37–7.19 (m, 25H, CH_{arom}), 5.02 (t, 1H, $J = 3.6$ Hz, H-1'), 5.00–4.91 (m, 2H, CHH Bn), 4.91 (ddd, 1H, $J = 53.6, 9.9, 9.0$ Hz, H-3'), 4.84–4.76 (m, 4H, CHH Bn), 4.67–4.42 (m, 5H, H-1, CHH Bn), 3.99 (t, 1H, $J = 9.3$ Hz, H-3), 3.84–3.50 (m, 9H, H-2, H-4, H-5, 2H-6, H-4', H-5', 2H-6'), 3.42–3.37 (m, 1H, H-2'), 3.36 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 138.8, 138.4, 138.2, 137.9, 137.8 (C_q Bn), 128.59, 128.56, 128.53, 128.52, 128.50, 128.3, 128.2, 128.13, 128.07 ($9 \times 2\text{CH}_{\text{arom}}$), 128.05, 128.02, 127.96, 127.82 ($4 \times \text{CH}_{\text{arom}}$), 127.76 (2CH_{arom}), 127.7 (CH_{arom}), 98.4 (d, $^3J_{(\text{C-F})} = 9.6$ Hz, C-1'), 98.1 (C-1), 93.8 (d, $^1J_{(\text{C-F})} = 184.3$ Hz, C-3'), 82.2 (C-3), 80.1 (C-4), 77.8 (C-2), 75.9 (d, $^2J_{(\text{C-F})} = 16.6$ Hz, C-4'), 75.8 (CH_2 C-3Bn), 75.1 (CH_2 Bn), 74.7 (d, $^4J_{(\text{C-F})} = 2.7$ Hz, CH_2 C-4'Bn), 73.7, 73.6 ($2 \times \text{CH}_2$ Bn), 70.01 (C-5), 69.97 (d, $^3J_{(\text{C-F})} = 9.5$ Hz, C-5'),

67.9 (C-6'), 66.7 (C-6), 61.7 (d, $^2J_{(C-F)} = 16.9$ Hz, C-2'), 55.3 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -193.17 (dt, $^2J_{(H-F)} = 53.6$ Hz, $^3J_{(H-F)} = 12.5$ Hz).

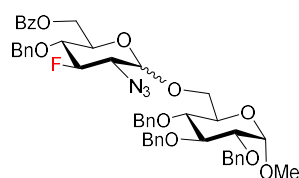
Methyl 6-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (A9)



Compound **A9** was prepared by glycosylation of acceptor **A** with **β-9** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 4.5:1.0$. Column chromatography in EtOAc/PE 1:4 afforded an inseparable mixture of anomers as a colourless gel (68 mg, 83%). Compound **A9** was also prepared by glycosylation of acceptor **A** with **α-9** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 5.2:1.0$. Preparative TLC chromatography in EtOAc/PE 1:4 afforded **A9** as an inseparable mixture of anomers (colourless gel, 65 mg, 78 %), R_f 0.2 (EtOAc/heptane 1:3). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{ClFNO}_{10}$, 792.2945; found, 792.2942. NMR data for α -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.33–7.24 (m, 20H, CH_{arom}), 5.00 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.96 (d, 1H, $J = 11.4$ Hz, CHH O-4Bn), 4.89 (dd, 1H, $J = 11.2, 1.2$ Hz, CHH O-4'Bn), 5.03–4.84 (m, 2H, H-1', H-3'), 4.81 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.79 (d, 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.67 (d, 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.61 (d, 1H, $J = 11.2$ Hz, CHH O-4'Bn), 4.59 overlapped (m, 1H, H-1), 4.58 (d, 1H, $J = 11.4$ Hz, CHH O-4Bn), 4.29 (ddd, 1H, $J = 11.9, 2.2, 1.7$ Hz, H-6'), 4.20 (dd, 1H, $J = 11.9, 4.2$ Hz, H-6'), 4.01 (t, 1H, $J = 9.3$ Hz, H-3), 3.91, 3.84 ($2 \times$ d, $2 \times$ 1H, $J = 14.9$ Hz, CHHCl), 3.83–3.74 (m, 3H, H-5, H-6, H-5'), 3.66–3.49 (m, 4H, H-2, H-4, H-6, H-4'), 3.38 (ddd, 1H, $J = 11.1, 10.0, 3.6$ Hz, H-2'), 3.37 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.9 (CO), 138.7, 138.3, 138.2, 137.2 ($4 \times \text{C}_q$), 128.66, 128.65, 128.58, 128.54, 128.53 ($5 \times 2\text{CH}_{\text{arom}}$), 128.34 (CH_{arom}), 128.25, 128.2 ($2 \times 2\text{CH}_{\text{arom}}$), 128.1, 127.9, 127.8 ($3 \times \text{CH}_{\text{arom}}$), 127.7 (2CH_{arom}), 98.1 (C-1), 98.0 (d, $^3J_{(C-F)} = 10.1$ Hz, C-1'), 94.0 (d, $^1J_{(C-F)} = 184.5$ Hz, C-3'), 82.1 (C-3), 81.1 (C-2), 77.7 (C-4), 75.9 (CH_2 O-3Bn), 75.1 (CH_2 O-4Bn), 74.6 (d, $^2J_{(C-F)} = 16.7$ Hz, C-4'), 74.3 (d, $^4J_{(C-F)} = 3.5$ Hz, CH_2 O-4'Bn), 73.5 (CH_2 O-2Bn), 70.0 (C-5), 68.2 (d, $^3J_{(C-F)} = 8.9$ Hz, C-5'), 66.7 (C-6), 64.0 (d, $^3J_{(C-F)} = 1.2$ Hz, C-6'), 61.5 (d, $^2J_{(C-F)} = 17.1$ Hz, C-2'), 55.3 (MeO), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.63 (dddd, $^2J_{(H-F)} = 53.4$ Hz, $^3J_{(H-F)} = 14.5, 10.9$ Hz, $^4J_{(H-F)} = 2.6$ Hz). Selected NMR

resonances for β -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): 4.45 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 9.6, 8.3$ Hz, H-3'), 4.40 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 11.9, 2.2$ Hz, H-6'), 4.13 (d, 1H, $J = 8.2$ Hz, H-1'), 4.06 (dd, 1H, $J = 10.7, 2.0$ Hz, H-6). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): 167.0 (CO), 138.7, 138.3, 138.2, 137.2 ($4 \times \text{C}_q$), 101.3 (d, $^3J_{(\text{C-F})} = 11.0$ Hz, C-1'), 96.4 (d, $^1J_{(\text{C-F})} = 187.1$ Hz, C-3'), 71.5 (d, $^3J_{(\text{C-F})} = 10.3$ Hz, C-5'), 68.8 (C-6), 64.5 (d, $^2J_{(\text{C-F})} = 17.9$ Hz, C-2'), 63.9 (d, $^3J_{(\text{C-F})} = 1.5$ Hz, C-6'), 55.4 (MeO), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): $\delta -187.88$ (dt, $^2J_{(\text{H-F})} = 51.3$ Hz, $^3J_{(\text{H-F})} = 13.2$ Hz).

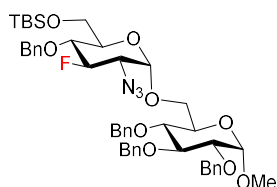
Methyl 6-*O*-(2-azido-4-*O*-benzyl-6-*O*-benzoyl-2,3-dideoxy-3-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (A10**)**



Compound **A10** was prepared by glycosylation of acceptor **A** with **10** according to the general procedure. ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 5.2/1.0$. Column chromatography in EtOAc/PE 1:3 followed by preparative TLC in EtOAc/PE 1:4 afforded **A10** as a mixture of anomers inseparable under given conditions (colourless gel, 70 mg, 82%), R_f 0.3 (EtOAc/heptane 1:3). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{48}\text{H}_{51}\text{FNO}_{10}$, 820.3491; found, 820.3493. NMR data for the α -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.97–7.91 (m, 2H, CH_{arom}), 7.58–7.54 (m, 1H, CH_{arom}), 7.41–7.39 (m, 2H, CH_{arom}), 7.34–7.25 (m, 20H, CH_{arom}), 5.00 (dd, 1H, $J = 3.6, 3.4$ Hz, H-1'), 4.99 (d, 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.97 (ddd, 1H, $J = 53.4, 10.5, 8.3$ Hz, H-3'), 4.93 (d, 1H, $J = 11.4$ Hz, CHH O-4Bn), 4.89 (d, 1H, $J = 11.3$ Hz, CHH O-4'Bn), 4.80 (d, 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.77, 4.66 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 12.3$ Hz, CHH O-2Bn), 4.66 (d, 1H, $J = 11.3$ Hz, CHH O-4'Bn), 4.58 (d, 1H, $J = 3.6$ Hz, H-1), 4.56 (d, 1H, $J = 11.4$ Hz, CHH O-4Bn), 4.49 (ddd, 1H, $J = 12.0, 2.2, 1.8$ Hz, H-6'), 4.39 (dd, 1H, $J = 12.0, 4.4$ Hz, H-6'), 3.99 (t, 1H, $J = 9.2$ Hz, H-3), 3.94 (dddd, 1H, $J = 10.0, 4.4, 2.2, 2.0$ Hz, H-5'), 3.80–3.74 (m, 2H, H-5, H-6), 3.70 (ddd, 1H, $J = 13.5, 10.0, 8.3$ Hz, H-4'), 3.67–3.63 (m, 1H, H-6), 3.40 (ddd, 1H, $J = 10.9, 10.5, 3.6$ Hz, H-2'), 3.36 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.2 (CO), 138.8, 138.3, 138.2, 137.2 ($4 \times \text{C}_q$), 133.3 (CH_{arom}), 129.9 (C_q), 129.7, 128.63 ($2 \times 2\text{CH}_{\text{arom}}$), 128.60, 128.56 ($2 \times 3\text{CH}_{\text{arom}}$), 128.55 (4CH_{arom}), 128.54 (2CH_{arom}), 128.49 (CH_{arom}), 128.3, 128.14 ($2 \times 2\text{CH}_{\text{arom}}$), 128.06 (CH_{arom}), 127.8 (2CH_{arom}), 98.05 (C-1), 98.04 (d, $^3J_{(\text{C-F})} = 9.5$ Hz, C-1'), 94.1 (d, $^1J_{(\text{C-F})} = 184.5$ Hz, C-3'), 82.1 (C-3), 80.1 (C-2), 77.8 (C-4), 75.9 (CH_2 O-

3Bn), 75.4 (d, $^2J_{(C-F)} = 16.6$ Hz, C-4'), 75.2 (CH₂ O-4Bn), 74.6 (d, $^4J_{(C-F)} = 3.2$ Hz, CH₂ O-4'Bn), 73.5 (CH₂ O-2Bn), 70.0 (C-5), 68.6 (d, $^3J_{(C-F)} = 8.8$ Hz, C-5'), 66.6 (C-6), 62.9 (d, $^3J_{(C-F)} = 1.0$ Hz, C-6'), 61.7 (d, $^2J_{(C-F)} = 17.1$ Hz, C-2'), 55.3 (MeO). ^{19}F NMR (CDCl₃, 376 MHz): δ -192.56 (dddd, $^2J_{(H-F)} = 53.4$ Hz, $^3J_{(H-F)} = 13.5, 10.9$ Hz, $^4J_{(H-F)} = 3.4$ Hz). Selected NMR resonances for β -anomer: ^1H NMR (CDCl₃, 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): 4.15 (d, 1H, $J = 8.1$ Hz, H-1'), 4.06 (dd, 1H, $J = 11.0, 2.1$ Hz, H-6), 3.61 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 9.5, 8.1$ Hz, H-2'), 3.34 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz, HSQC, HMBC): 101.6 (d, $^3J_{(C-F)} = 11.1$ Hz, C-1'), 68.8 (C-6), 64.6 (d, $^2J_{(C-F)} = 17.8$ Hz, C-2'), 63.0 (d, $^3J_{(C-F)} = 1.0$ Hz, C-6'), 55.4 (MeO). ^{19}F NMR (CDCl₃, 376 MHz): δ -187.85 (dt, $^2J_{(H-F)} = 51.4$ Hz, $^3J_{(H-F)} = 13.3$ Hz).

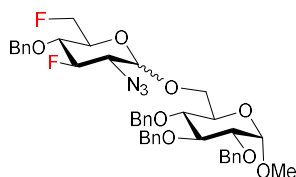
Methyl 6-*O*-(2-azido-4-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (A11)



Compound **A11** was prepared by glycosylation of acceptor **A** with **11** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous work-up revealed the $\alpha/\beta = 4.3/1.0$. Column chromatography in EtOAc/PE 1:7 afforded **A11** as a yellowish gel (56 mg, 65%, with side products in ^{19}F NMR). Separation of anomers by preparative TLC in toluene/Et₂O/heptane 2:3:8, afforded the α -anomer **A11- α** (24 mg, 28%) as a yellowish gel, R_f 0.3 (ethyl acetate/heptane 1:7). The β -anomer could not be purified under these conditions. ^1H NMR (CDCl₃, 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.38–7.23 (m, 20H, CH_{arom} Bn), 4.99 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.98 from $^1\text{H}\{^{19}\text{F}\}$ (d, 1H, $J = 3.6$ Hz, H-1'), 4.93 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 10.1, 8.3$ Hz, H-3'), 4.93 (d, 1H, $J = 11.3$ Hz, CHH O-2Bn), 4.87 (dd, 1H, $J = 11.2, 0.9$ Hz, CHH O-4'Bn), 4.81 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.79, 4.66 ($2 \times$ d, $2 \times$ 1H, $J = 12.0$ Hz, CHH O-4Bn), 4.62 (d, 1H, $J = 11.2$ Hz, CHH O-4'Bn), 4.58 (d, 1H, $J = 11.3$ Hz, CHH O-2Bn), 4.57 (d, 1H, $J = 3.5$ Hz, H-1), 4.00 (dd, 1H, $J = 9.7, 8.9$ Hz, H-3), 3.98–3.63 (m, 6H, H-5, 2H-6, H-4', 2H-6'), 3.60 from $^1\text{H}\{^{19}\text{F}\}$ (ddd, 1H, $J = 9.8, 3.6, 1.7$ Hz, H-5'), 3.55–3.50 (m, 2H, H-2, H-4), 3.38 (s, 3H, MeO), 3.33 (ddd, 1H, $J = 11.0, 10.1, 3.6$ Hz, H-2'), 0.89 (s, 9H, CMe₃), 0.04 (s, 6H, SiMe₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 138.8 (C_q O-3Bn), 138.4 (C_q O-2Bn), 138.3 (C_q O-4Bn), 138.1 (C_q O-4'Bn), 128.6, 128.53 ($2 \times$ 2CH_{arom}), 128.52 (4CH_{arom}), 128.3, 128.1, 128.04 ($3 \times$ 2CH_{arom}), 127.98, 127.83 ($2 \times$ CH_{arom}), 128.78, 127.7 ($2 \times$

2CH_{arom}), 98.3 (d, $^3J_{(C-F)} = 9.2$ Hz, C-1'), 98.1 (C-1), 93.9 (d, $^1J_{(C-F)} = 184.2$ Hz, C-3'), 82.2 (C-3), 80.1 (C-4), 77.8 (C-2), 75.91 (d, $^2J_{(C-F)} = 16.5$ Hz, C-4'), 75.9 (CH₂ O-3Bn), 75.1 (CH₂ O-2Bn), 74.7 (d, $^4J_{(C-F)} = 2.6$ Hz, CH₂ O-4'Bn), 73.6 (CH₂ O-4Bn), 71.3 (d, $^3J_{(C-F)} = 8.1$ Hz, C-5'), 70.1 (C-5), 66.4 (C-6), 61.8 (d, $^2J_{(C-F)} = 16.8$ Hz, C-2'), 61.7 (d, $^4J_{(C-F)} = 0.9$ Hz, C-6'), 55.3 (MeO), 26.0 (CMe₃), 18.5 (CMe₃), -5.0, -5.2 (SiMe₂). ¹⁹F NMR (CDCl₃, 376 MHz): δ -193.02 (dddd, $^2J_{(H-F)} = 54.0$ Hz, $^3J_{(H-F)} = 13.1$, 11.0 Hz, $^4J_{(H-F)} = 3.5$ Hz). HRMS-APCI (*m/z*): [M - N₂ + H]⁺ calcd for C₄₇H₆₁FNO₉Si, 830.4094; found, 830.4098. NMR data for the β-anomer: ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}), H-H COSY, HSQC, HMBC): δ 7.39–7.22 (m, 20H, CH_{arom}), 7.39–7.22 (m, 9H, 4 × CHH Bn, H-1), 4.39 (ddd, 1H, *J* = 51.7, 9.6, 8.5 Hz, H-3'), 4.10 (d, 1H, *J* = 8.1 Hz, H-1'), 4.06 (dd, 1H, *J* = 10.8, 2.0 Hz, H-6), 3.99 (dd, 1H, *J* = 9.7, 8.9 Hz, H-3), 3.84 (ddd, 1H, *J* = 11.5, 2.2, 1.9 Hz, H-6'), 3.81–3.47 (m, 7H, H-2, H-4, H-5, H-6, H-2', H-4', H-6'), 3.38 (s, 3H, MeO), 3.17 from ¹H{¹⁹F} (ddd, 1H, *J* = 9.8, 4.2, 1.9 Hz, H-5'), 0.88 (s, 9H, CMe₃), 0.04 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 138.9, 138.6, 138.3, 137.8 (4 × C_q Bn), 128.60, 128.59 (2 × 2CH_{arom}), 128.58 (4CH_{arom}), 128.53, 128.52 (2 × 2CH_{arom}), 128.3, 128.2 (2 × CH_{arom}), 128.14, 128.13 (2 × 2CH_{arom}), 128.05, 128.0 (2 × CH_{arom}), 101.3 (d, $^3J_{(C-F)} = 10.8$ Hz, C-1'), 98.3 (C-1), 89.0 (d, $^1J_{(C-F)} = 183.5$ Hz, C-3'), 82.3 (C-3), 79.9 (C-4), 77.8 (C-2), 75.9 (CH₂ Bn), 75.4 (d, $^2J_{(C-F)} = 16.8$ Hz, C-4'), 75.0 (CH₂ Bn), 74.7 (CH₂ Bn), 74.8 (d, $^3J_{(C-F)} = 8.8$ Hz, C-5'), 73.6 (CH₂ Bn), 69.8 (C-5), 68.4 (C-6), 64.8 (d, $^2J_{(C-F)} = 17.5$ Hz, C-2'), 61.9 (C-6'), 55.3 (MeO), 26.0 (CMe₃), 18.5 (CMe₃), -5.0, -5.2 (SiMe₂). ¹⁹F NMR (CDCl₃, 376 MHz): δ -188.47 (dt, $^2J_{(H-F)} = 51.7$ Hz, $^3J_{(H-F)} = 13.5$ Hz).

Methyl 6-*O*-(2-azido-4-*O*-benzyl-2,3,6-trideoxy-3,6-difluoro-α,β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (A12)

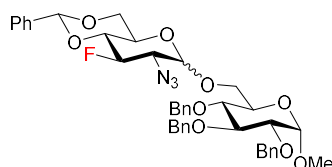


Compound **A12** was prepared by glycosylation of acceptor **A** with **12** according to the general procedure (6 μL TfOH). ¹⁹F NMR after workup revealed the α/β = 1.3/1.0. Column chromatography in EtOAc/PE 1:4 followed by preparative TLC in heptane/Et₂O 6:5 afforded enriched α-anomer (α/β 10:1 36 mg, 48%, containing approx. 20% inseparable side products in ¹⁹F NMR) as a colourless gel. Continued elution gave enriched β-anomer as a colourless gel (α/β 10:1, 29 mg, 39%). Data for the α-anomer: *R_f* 0.5 (heptane/Et₂O 6:5). ¹H NMR (CDCl₃, 400 MHz, ¹H{¹⁹F}),

H-H COSY, HSQC, HMBC): δ 7.39–7.22 (m, 20H, CH_{arom}), 5.01 (dd, 1H, J = 3.7, 3.5 Hz, H-1'), 4.99 (d, 1H, J = 11.0 Hz, CHH O-3Bn), 4.93 overlapped (m, 1H, H-3'), 4.95 (d, 1H, J = 11.3 Hz, CHH O-4Bn), 4.90 (dd, 1H, J = 11.1, 1.2 Hz, CHH O-4'Bn), 4.81 (d, 1H, J = 11.0 Hz, CHH O-3Bn), 4.79, 4.66 (2 $\times$ d, 2 $\times$ 1H, J = 12.0 Hz, CHH O-2Bn), 4.62 (d, 1H, J = 11.1 Hz, CHH O-4'Bn), 4.58 (d, 1H, J = 3.6 Hz, H-1), 4.57 (d, 1H, J = 11.3 Hz, CHH O-4Bn), 4.52 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, J = 10.4, 2.4 Hz, H-6'), 4.44 from $^1\text{H}\{^{19}\text{F}\}$ (dt, 1H, J = 10.4, 1.5 Hz, H-6'), 4.00 (dd, 1H, J = 9.7, 8.9 Hz, H-3), 3.79–3.63 (m, 5H, H-5, 2H-6, H-4', H-5'), 3.55–3.50 (m, 2H, H-2, H-4), 3.39 (ddd, 1H, J = 10.5, 9.8, 3.7 Hz, H-2'), 3.38 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 138.8 (C_q O-3Bn), 138.3 (C_q O-4Bn), 138.2 (C_q O-2Bn), 137.5 (C_q O-4'Bn), 128.63, 128.60 (2 $\times$ 2CH_{arom}), 128.55, 128.27 (2 $\times$ 4CH_{arom}), 128.25 (CH_{arom}), 128.2 (2CH_{arom}), 128.1, 127.9, 127.8 (3 $\times$ CH_{arom}), 127.7 (2CH_{arom}), 98.3 (d, $^3J_{\text{(C-F)}} = 9.4$ Hz, C-1'), 98.1 (C-1), 93.7 (d, $^1J_{\text{(C-F)}} = 184.7$ Hz, C-3'), 82.1 (C-3), 81.4 (d, $^1J_{\text{(C-F)}} = 173.8$ Hz, C-6'), 80.1 (C-2), 77.7 (C-4), 75.9 (CH₂ O-3Bn), 75.1 (CH₂ O-4Bn), 74.87 (dd, $^2J_{\text{(C-F)}} = 16.1$, $^3J_{\text{(C-F)}} = 7.6$ Hz, C-4'), 74.86 (d, $^4J_{\text{(C-F)}} = 3.0$ Hz, CH₂ O-4'Bn), 73.6 (CH₂ O-2Bn), 70.0 (C-5), 69.6 (dd, $^2J_{\text{(C-F)}} = 18.1$, $^4J_{\text{(C-F)}} = 8.7$ Hz, Hz, C-5'), 66.8 (C-6), 61.6 (d, $^2J_{\text{(C-F)}} = 16.9$ Hz, C-2'), 55.3 (MeO). ^{19}F NMR (CDCl₃, 376 MHz): δ -193.24 (ddd, $^2J_{\text{(H-F)}} = 54.1$ Hz, $^3J_{\text{(H-F)}} = 13.3$, 9.8 Hz, F-3'), -235.29 (ddd, $^2J_{\text{(H-F)}} = 48.0$, 47.7 Hz, $^3J_{\text{(H-F)}} = 29.1$ Hz, F-6'). HRMS-APCI (m/z): [M - N₂ + H]⁺ calcd for C₄₁H₄₆F₂NO₈, 718.3186; found, 718.3190. Data for β -anomer: R_f 0.4 (heptane/Et₂O 6:5) ^1H NMR (CDCl₃, 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.39–7.26 (m, 20H, CH_{arom}), 5.00 (d, 1H, J = 10.9 Hz, CHH O-3Bn), 4.94 (d, 1H, J = 10.9 Hz, CHH O-4Bn), 4.86 (dd, 1H, J = 11.1, 1.3 Hz, CHH O-4'Bn), 4.83 (d, 1H, J = 10.9 Hz, CHH O-3Bn), 4.80, 4.65 (2 $\times$ d, 2 $\times$ 1H, J = 11.9 Hz, CHH O-2Bn), 4.63 (d, 1H, J = 10.9 Hz, CHH O-4Bn), 4.60 (d, 1H, J = 11.1 Hz, CHH O-4'Bn), 4.60 (d, 1H, J = 3.5 Hz, H-1), 4.65–4.48 (m, 2H, H-6'), from $^1\text{H}\{^{19}\text{F}\}$ 4.44 (dd, 1H, J = 9.8, 8.4 Hz, H-3'), 4.16 (d, 1H, J = 8.1 Hz, H-1'), 4.09 (dd, 1H, J = 10.8, 2.0 Hz, H-6), 4.01 (dd, 1H, J = 9.7, 8.9 Hz, H-3), 3.81 (ddd, 1H, J = 10.1, 4.7, 2.0 Hz, H-5), 3.70 (dd, 1H, J = 10.8, 4.7 Hz, H-6), from $^1\text{H}\{^{19}\text{F}\}$ 3.65 (dd, 1H, J = 10.0, 8.4 Hz, H-4'), from $^1\text{H}\{^{19}\text{F}\}$ 3.57 (dd, 1H, J = 9.3, 8.1 Hz, H-2'), 3.55–3.50 (m, 2H, H-2, H-4), 3.39 (s, 3H, MeO), 3.39 (dddd, 1H, J = 25.2, 10.0, 3.8, 2.0 Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 138.9 (C_q O-3Bn), 138.5 (C_q O-4Bn), 138.3 (C_q O-2Bn), 137.3 (C_q O-4'Bn), 128.7 (2CH_{arom}), 128.6 (4CH_{arom}), 128.5 (2CH_{arom}), 128.37 (CH_{arom}), 128.36, 128.3, 128.1 (3 $\times$ 2CH_{arom}), 128.1 (CH_{arom}), 127.93 (2CH_{arom}), 127.88, 127.8 (2 $\times$ CH_{arom}), 101.4 (d, $^3J_{\text{(C-F)}} = 10.8$ Hz, C-1'), 98.3 (C-1), 96.2 (d, $^1J_{\text{(C-F)}} = 187.5$ Hz, C-3'), 82.2 (C-3), 81.4 (d, $^1J_{\text{(C-F)}} = 175.7$ Hz, C-6'), 79.9 (C-2), 77.8 (C-4), 75.9 (CH₂ O-3Bn), 75.0 (CH₂ O-4Bn), 74.8 (d, $^4J_{\text{(C-F)}} = 2.7$ Hz, CH₂ O-4'Bn), 74.5 (dd, $^2J_{\text{(C-F)}} = 17.1$, $^4J_{\text{(C-F)}} = 7.0$ Hz, Hz, C-4'), 73.6 (CH₂ O-2Bn), 73.0 (dd, $^2J_{\text{(C-F)}} = 18.9$, $^3J_{\text{(C-F)}} = 9.8$ Hz, C-5'),

69.8 (C-5), 68.9 (C-6), 64.5 (d, $^2J_{\text{C-F}} = 17.6$ Hz, C-2'), 55.4 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -188.26 (dt, $^2J_{\text{H-F}} = 51.3$ Hz, $^3J_{\text{H-F}} = 13.2$ Hz, F-3'), -234.67 (td, $^2J_{\text{H-F}} = 47.3$ Hz, $^3J_{\text{H-F}} = 25.2$ Hz, F-6'). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{46}\text{F}_2\text{NO}_8$, 718.3186; found, 718.3188.

Methyl 6-*O*-(2-azido-4,6-di-*O*-benzylidene-2,3-dideoxy-3-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α,β -D-glucopyranoside (A13)

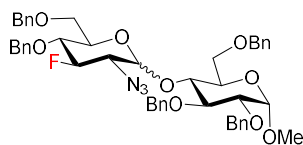


Compound **A13** was prepared by glycosylation of acceptor **A** with **13** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous workup indicated $\alpha/\beta = 1.8/1.0$. Column chromatography in EtOAc/PE 1:3 afforded the mixture of anomers as a colourless gel (72 mg, 86 %), R_f 0.2 (EtOAc/heptane 1:3). An attempt to separate anomers using preparative TLC in Et₂O/PE 5:6 led to their partial decomposition, but NMR data could be extracted. Data for the α -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.51–7.48 (m, 2H, CH_{arom}), 7.40–7.29 (m, 18H, CH_{arom}), 5.57 (s, 1H, CHPh), 5.06 (t, 1H, $J = 3.7$ Hz, H-1'), 5.02 (d, 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.96 (d, 1H, $J = 11.2$ Hz, CHH O-4Bn), from $^1\text{H}\{^{19}\text{F}\}$ 4.91 (dd, 1H, $J = 9.7, 8.6$ Hz, H-3'), 4.84 (d, 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.81, 4.68 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 12.0$ Hz, CHH O-2Bn), 4.64 (d, 1H, $J = 11.2$ Hz, CHH O-4Bn), 4.62 (d, 1H, $J = 3.5$ Hz, H-1), 4.25 (ddd, 1H, $J = 10.3, 4.7, 2.1$ Hz, H-6'), 4.04 (t, 1H, $J = 9.3$ Hz, H-3), 3.89 (td, 1H, $J = 10.0, 4.7$ Hz, H-5'), 3.84–3.68 (m, 5H, H-5, 2H-6, H-4', H-6'), 3.59–3.54 (m, 2H, H-2, H-4), 3.44 (ddd, 1H, $J = 11.0, 9.7, 3.7$ Hz, H-2'), 3.40 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 138.8 (C_q O-3Bn), 138.23, 138.18 (C_q O-2/4Bn), 136.8 (C_q Ph), 129.4 (CH_{arom}), 128.6 (4CH_{arom}), 128.53, 128.45, 128.3, 128.1 ($4 \times 2\text{CH}_{\text{arom}}$), 128.1, 128.00 ($2 \times \text{CH}_{\text{arom}}$), 127.99 (2CH_{arom}), 127.8 (CH_{arom}), 126.3 (2CH_{arom}), 101.9 (CHPh), 99.1 (d, $^3J_{\text{C-F}} = 8.7$ Hz, C-1'), 98.2 (C-1), 88.4 (d, $^1J_{\text{C-F}} = 188.9$ Hz, C-3'), 82.1 (C-3), 80.1 (C-2), 79.9 (d, $^2J_{\text{C-F}} = 16.8$ Hz, C-4'), 77.6 (C-4), 75.9 (CH_2 O-3Bn), 75.1 (CH_2 O-2Bn), 73.6 (CH_2 O-4Bn), 70.1 (C-5), 68.8 (C-6'), 67.0 (C-6), 62.24 (d, $^3J_{\text{C-F}} = 7.2$ Hz, C-5'), 62.23 (d, $^2J_{\text{C-F}} = 16.8$ Hz, C-2'), 55.4 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -198.32 (dtd, $^2J_{\text{H-F}} = 54.2$ Hz, $^3J_{\text{H-F}} = 11.0$ Hz, $^4J_{\text{H-F}} = 3.7$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{45}\text{FNO}_9$, 714.3073; found, 714.3075. Data for the β -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.52–7.46 (m, 2H, CH_{arom}), 7.39–7.28 (m, 18H, CH_{arom}), 5.57 (s, 1H, CHPh), 5.00 (d, 1H, $J = 10.9$

Hz, CHH O-3Bn), 4.96 (d, 1H, $J = 11.3$ Hz, CHH O-4Bn), 4.83 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.81, 4.66 ($2 \times$ d, $2 \times$ 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.65 (d, 1H, $J = 11.3$ Hz, CHH O-4Bn), 4.61 (d, 1H, $J = 3.6$ Hz, H-1), 4.46 (dt, 1H, $J = 52.0, 9.0$ Hz, H-3'), 4.33 (ddd, 1H, $J = 10.7, 5.0, 1.9$ Hz, H-6'), 4.28 (d, 1H, $J = 8.0$ Hz, H-1'), 4.08 (dd, 1H, $J = 10.6, 1.8$ Hz, H-6), 4.01 (t, 1H, $J = 9.3$ Hz, H-3), 3.83–3.71 (m, 4H, H-5, H-6, H-4', H-6'), 3.63 (ddd, 1H, $J = 13.8, 9.0, 8.0$ Hz, H-2'), 3.58–3.51 (m, 2H, H-2, H-4), 3.39 (s, 3H, MeO), 3.32 (tdd, 1H, $J = 9.9, 5.0, 1.4$ Hz, H-5').

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 138.8 (C_q O-3Bn), 138.5 (C_q O-4Bn), 138.2 (C_q O-2Bn), 136.6 (C_q Ph), 128.64, 128.63, 128.56, 128.5, 128.3, 128.1 ($6 \times 2\text{CH}_{\text{arom}}$), 127.94 (CH_{arom}), 127.89 (2CH_{arom}), 127.8, 126.4, 126.3 ($3 \times \text{CH}_{\text{arom}}$), 126.3 (2CH_{arom}), 102.1 (d, $^3J_{\text{(C-F)}} = 9.5$ Hz, C-1'), 101.8 (CHPh), 98.4 (C-1), 91.1 (d, $^1J_{\text{(C-F)}} = 190.7$ Hz, C-3'), 82.2 (C-3), 79.8 (C-2), 78.8 (d, $^2J_{\text{(C-F)}} = 17.1$ Hz, C-4'), 77.7 (C-4), 75.9 (CH_2 O-3Bn), 75.0 (CH_2 O-4Bn), 73.6 (CH_2 O-2Bn), 69.7 (C-5), 69.1 (C-6), 68.4 (C-6'), 65.4 (d, $^2J_{\text{(C-F)}} = 17.6$ Hz, C-2'), 65.3 (d, $^3J_{\text{(C-F)}} = 8.2$ Hz, C-5'), 55.4 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.98 (ddt, $^2J_{\text{(H-F)}} = 52.0$ Hz, $^3J_{\text{(H-F)}} = 13.8, 11.6$ Hz, $J_{\text{(H-F)}} = 1.9$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{45}\text{FNO}_9$, 714.3073; found, 714.3071.

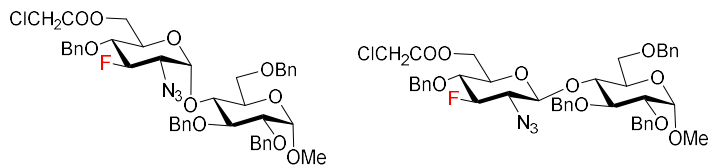
Methyl 4-*O*-(2-azido-4,6-di-*O*-benzyl-2,3-dideoxy-3-fluoro- α,β -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (**B1**)



Compound **B1** was prepared by glycosylation of acceptor **B** with **α -1** according to the general procedure (4 μL TfOH). ^{19}F NMR after workup revealed $\alpha/\beta = 2.0/1.0$. Column chromatography in EtOAc/PE 1:4 afforded the mixture of anomers as a colourless gel (68 mg, 82 %) in about 95% purity by ^{19}F NMR, R_f 0.2 (ethyl acetate/heptane 2:9), the anomers were not separated. NMR spectra were in accordance with ref.¹ Compound **B1** was also prepared by glycosylation of methyl acceptor **B** with **α -1** according to the general procedure with the exception of using 2 mL of dichloromethane as the solvent. ^{19}F NMR after aqueous workup revealed the α/β ratio of 1.0/1.2. Column chromatography of the crude product in EtOAc/PE 1:4 afforded a mixture of anomers as a colourless gel (71 mg, 86 %), R_f 0.2 (ethyl acetate/heptane 2:9). NMR spectra were in accordance with ref.¹

Methyl 4-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (B9- α**)**

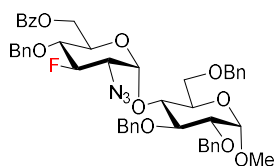
Methyl 4-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- β -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (B9- β**)**



Compounds **B9- α** and **B9- β** were prepared by glycosylation of acceptor **B** with **α -9** according to the general procedure (5 μ L TfOH). ^{19}F NMR after aqueous workup revealed **B9- α /B9- β** = 7.3/1.0. Column chromatography in EtOAc/PE 1:4 afforded first **B9- α** (59 mg, 71%) as a yellowish syrup. Continued elution afforded **B9- β** as a yellowish syrup (10 mg, 12 %). Compounds **B9- α** and **B9- β** were also prepared by glycosylation of acceptor **B** with **β -9** according to the general procedure with the exception of the reaction temperature being set to 0 $^{\circ}\text{C}$, and rt, respectively. ^{19}F NMR after aqueous workup revealed **B9- α /B9- β** = 9.6:1.0 (reaction at 0 $^{\circ}\text{C}$) and 9.7:1.0 (reaction at rt). Column chromatography in EtOAc/PE 1:4 afforded anomeric mixtures (anomers were not separated) of **B9- α** and **B9- β** (62 mg, 75% for the reaction at 0 $^{\circ}\text{C}$, and 57 mg, 70% for the reaction at rt). Data for **B9- α** : R_f 0.2 (EtOAc/heptane 1:4). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.39–7.22 (m, 20H, CH_{arom}), 5.68 (dd, 1H, J = 3.9, 3.5 Hz, H-1'), 5.11 (d, 1H, J = 10.9 Hz, CHH O-3Bn), 4.91 (ddd, 1H, J = 54.1, 10.2, 8.2 Hz, H-3'), 4.85 (d, 1H, J = 11.4 Hz, CHH O-4'Bn), 4.82 (d, 1H, J = 10.9 Hz, CHH O-3Bn), 4.73, 4.61 ($2 \times$ d, $2 \times$ 1H, J = 12.0 Hz, CHH O-2Bn), 4.61 (d, 1H, J = 3.6 Hz, H-1), 4.58 (d, 1H, J = 11.4 Hz, CHH O-4'Bn), 4.53 (m, 2H, CHH O-6Bn), 4.11 (dd, 1H, J = 12.0, 3.5 Hz, H-6'), 4.06 (dd, 1H, J = 9.6, 8.6 Hz, H-3), 4.01 (dt, 1H, J = 12.0, 2.2 Hz, H-6'), 3.85 (dd, 1H, J = 9.9, 8.6 Hz, H-4), 3.85, 3.77 ($2 \times$ d, $2 \times$ 1H, J = 15.0 Hz, CHHCl), 3.7–3.74 (m, 2H, H-5, H5'), 3.68 (dd, 1H, J = 11.1, 4.0 Hz, H-6), 3.61–3.51 (m, 3H, H-2, H-6, H-4'), 3.39 (s, 3H, MeO), 3.30 (ddd, 1H, J = 11.1, 10.2, 3.9 Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.8 (CO), 138.7, 137.94, 137.87, 137.2 ($4 \times$ C_q), 128.8, 128.67, 128.65, 128.6, 128.5 ($5 \times 2\text{CH}_{\text{arom}}$), 128.4 (CH_{arom}), 128.3 (2CH_{arom}), 128.2, 127.9 ($2 \times \text{CH}_{\text{arom}}$), 127.63 (2CH_{arom}), 127.62 (CH_{arom}), 127.55 (2CH_{arom}), 97.8 (C-1), 97.4 (d, $^3J_{(\text{C-F})}$ = 9.4 Hz, C-1'), 94.3 (d, $^1J_{(\text{C-F})}$ = 184.5 Hz, C-3'), 81.0 (C-3), 80.5 (C-2), 75.0 (CH_2 O-3Bn), 74.3 (d, $^4J_{(\text{C-F})}$ = 2.5 Hz, CH_2 O-4'Bn), 74.2 (d, $^2J_{(\text{C-F})}$ = 15.4 Hz, C-4'), 73.7 (CH_2 O-6Bn), 73.4 (CH_2 O-2Bn), 73.2 (C-4), 69.5 (C-5), 69.1 (C-6), 68.6 (d, $^3J_{(\text{C-F})}$ = 8.8 Hz, C-5'), 61.5 (d, $^4J_{(\text{C-F})}$ = 1.8 Hz, C-6'), 61.5 (d, $^2J_{(\text{C-F})}$ = 16.7 Hz, C-2'), 55.5 (MeO), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 ,

376 MHz): δ -192.94 (ddd, $^2J_{\text{H-F}} = 54.1$ Hz, $^3J_{\text{H-F}} = 11.1, 12.1$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{ClFNO}_{10}$, 792.2945 ; found, 792.2943. Data for **B9- β** : R_f 0.17 (EtOAc/heptane 1:4). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.37–7.24 (m, 20H, CH_{arom}), 4.93, 4.80, 4.72 (3 $\times$ d, 3 $\times$ 1H, $J = 11.5$ Hz, CHH Bn), 4.71 (d, 1H, $J = 12.1$ Hz, CHH Bn), 4.70 (d, 1H, $J = 12.3$ Hz, CHH Bn), 4.60 (d, 1H, $J = 3.7$ Hz, H-1), 4.57 (d, 1H, $J = 12.3$ Hz, CHH Bn), 4.54 (d, 1H, $J = 11.5$ Hz, CHH Bn), 4.41 (d, 1H, $J = 12.1$ Hz, CHH Bn), 4.18 (ddd, 1H, $J = 51.7, 9.6, 8.3$ Hz, H-3'), 4.19–4.01 (m, 2H, H-6'), 4.12 (d, 1H, $J = 8.3$ Hz, H-1'), 3.92 (dd, 1H, $J = 10.8, 2.8$ Hz, H-6), 3.89 (dd, 1H, $J = 9.4, 9.1$ Hz, H-4), 3.82 (t, 1H, $J = 9.1$ Hz, H-3), 3.73 (ddd, 1H, $J = 9.4, 2.8, 1.8$ Hz, H-5), 3.67 (dd, 1H, $J = 10.8, 1.8$ Hz, H-6), 3.58–5.47 (m, 1H, H-4'), 3.54 (s, 2H, CH_2Cl), 3.47 (dd, 1H, $J = 9.1, 3.7$ Hz, H-2), 3.38 (s, 3H, MeO), 3.34 (ddd, 1H, $J = 13.5, 9.6, 8.3$ Hz, H-2'), 3.10 (dt, 1H, $J = 9.7, 3.3$ Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.9 (CO), 139.6, 138.3, 137.8, 137.2 (4 $\times$ C_q), 128.8, 128.71, 128.65, 128.49, 128.46 (5 $\times$ 2 CH_{arom}), 128.4 (CH_{arom}), 128.2 (3 CH_{arom}), 128.2 (2 CH_{arom}), 128.0, 127.3 (2 $\times$ CH_{arom}), 127.2 (2 CH_{arom}), 100.2 (d, $^3J_{\text{C-F}} = 11.1$ Hz, C-1'), 98.5 (C-1), 96.8 (d, $^1J_{\text{C-F}} = 186.3$ Hz, C-3'), 80.1 (C-3), 78.8 (C-2), 77.4 (C-4), 75.0 (CH_2 O-3Bn), 73.9 (d, $^2J_{\text{C-F}} = 20.1$ Hz, C-4'), 74.0 (CH_2 O-4'Bn), 73.7 (CH_2 O-6Bn), 73.6 (CH_2 O-2Bn), 71.2 (d, $^3J_{\text{C-F}} = 10.3$ Hz, C-5'), 69.9 (C-5), 68.0 (C-6), 64.9 (d, $^2J_{\text{C-F}} = 17.5$ Hz, C-2'), 64.0 (d, $^4J_{\text{C-F}} = 1.2$ Hz, C-6'), 55.5 (MeO), 40.6 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): δ -187.33 (dt, $^2J_{\text{H-F}} = 51.7$ Hz, $^3J_{\text{H-F}} = 13.5$). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{ClFNO}_{10}$, 792.2945 ; found, 792.2947.

Methyl 4-*O*-(2-azido-4-*O*-benzyl-6-*O*-benzoyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (B10- α**)**

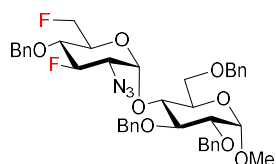


Compound **B10- α** was prepared by glycosylation of acceptor **B** with **10** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 6.6:1.0$. Column chromatography in EtOAc/PE 1:4 followed by preparative TLC in EtOAc/PE 1:4 afforded **B10- α** (61 mg, 71%). The β -anomer could not be purified under given conditions but NMR data were extracted. Data for **B10- α** : R_f 0.35 (ethyl acetate/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.93–7.91 (m, 2H, CH_{arom}), 7.58–7.54 (m, 1H, CH_{arom}), 7.43–7.39 (m, 2H, CH_{arom}), 7.32–7.19 (m, 20H, CH_{arom}), 5.68 (dd, 1H, $J = 3.9, 3.7$ Hz, H-1'), 5.10 (d, 1H, $J = 11.0$ Hz, CHH O-

3Bn), 4.95 (ddd, 1H, $J = 53.1, 10.2, 8.3$ Hz, H-3'), 4.86 (d, 1H, $J = 10.9$ Hz, CHH O-4'Bn), 4.84 (d, 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.72 (d, 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.60 (d, 1H, $J = 3.5$ Hz, H-1), 4.60 (d, 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.60 (d, 1H, $J = 10.9$ Hz, CHH O-4'Bn), 4.55, 4.50 ($2 \times$ d, $2 \times$ 1H, $J = 12.1$ Hz, CHH O-6Bn), 4.33 (dd, 1H, $J = 12.1, 3.6$ Hz, H-6'), 4.29 (ddd, 1H, $J = 12.1, 2.3, 2.1$ Hz, H-6'), 4.07 (dd, 1H, $J = 9.6, 8.6$ Hz, H-3), 3.86 (dd, 1H, $J = 9.9, 8.6$ Hz, H-4), 3.87 (ddd, 1H, $J = 10.0, 3.6, 2.3$ Hz, H-5'), 3.77 (ddd, 1H, $J = 9.9, 4.3, 2.1$ Hz, H-5), 3.68 (ddd, 1H, $J = 12.5, 10.0, 8.3$ Hz, H-4'), 3.68 (dd, 1H, $J = 11.0, 4.3$ Hz, H-6), 3.62 (dd, 1H, $J = 11.0, 2.1$ Hz, H-6), 3.55 (dd, 1H, $J = 9.6, 3.5$ Hz, H-2), 3.39 (s, 3H, MeO), 3.35 (ddd, 1H, $J = 11.1, 10.2, 4.0$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.1 (CO), 138.8, 138.0, 137.9, 137.3 ($4 \times \text{C}_q$), 131.2 (CH_{arom}), 129.9 (C_q), 129.8, 128.64, 128.60, 128.59, 128.52 ($5 \times 2\text{CH}_{\text{arom}}$), 128.48 (4CH_{arom}), 128.30 (2CH_{arom}), 128.27, 128.2, 127.8 ($3 \times \text{CH}_{\text{arom}}$), 127.6, 127.53 ($2 \times 2\text{CH}_{\text{arom}}$), 127.52 (CH_{arom}), 97.8 (C-1), 97.5 (d, $^3J_{(\text{C-F})} = 9.4$ Hz, C-1'), 94.3 (d, $^1J_{(\text{C-F})} = 184.3$ Hz, C-3'), 81.9 (C-3), 80.5 (C-2), 75.2 (d, $^2J_{(\text{C-F})} = 16.5$ Hz, C-4'), 74.6 (d, $^4J_{(\text{C-F})} = 3.2$ Hz, CH_2 O-4'Bn), 73.7 (C-4), 73.6 ($2 \times \text{CH}_2$ O-3Bn, O-6Bn), 73.4 (CH_2 O-2Bn), 69.5 (C-5), 69.2 (d, $^3J_{(\text{C-F})} = 8.8$ Hz, C-5'), 69.1 (C-6), 62.7 (d, $^4J_{(\text{C-F})} = 0.9$ Hz, C-6'), 61.7 (d, $^2J_{(\text{C-F})} = 16.7$ Hz, C-2'), 55.5 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.91 (ddd, $^2J_{(\text{H-F})} = 53.1$ Hz, $^3J_{(\text{H-F})} = 12.5, 11.1$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{48}\text{H}_{51}\text{FNO}_{10}$, 820.3491; found, 820.3493. Data for β -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.93–7.90 (m, 2H, CH_{arom}), 7.55–7.51 (m, 1H, CH_{arom}), 7.46–7.41 (m, 2H, CH_{arom}), 7.36–7.22 (m, 18H, CH_{arom}), 7.07–7.04 (m, 2H, CH_{arom}), 4.94 (d, 1H, $J = 11.3$ Hz, CHH O-3Bn), 4.79 (dd, 1H, $J = 1.3, 11.2$ Hz, CHH O-4'Bn), 4.71 (d, 1H, $J = 11.3$ Hz, CHH O-3Bn), 4.70 (d, 2H, $J = 12.0$ Hz, CHH O-2/6Bn), 4.61 (d, 1H, $J = 3.7$ Hz, H-1), 4.54 (d, 1H, $J = 12.0$ Hz, CHH O-2Bn), 4.53 (d, 1H, $J = 11.2$ Hz, CHH O-4'Bn), 4.41 (d, 1H, $J = 12.0$ Hz, CHH O-6Bn), 4.38 (dt, 1H, $J = 12.0, 1.9$ Hz, H-6'), 4.30 (dd, 1H, $J = 12.0, 4.4$ Hz, H-6'), 4.22 (ddd, 1H, $J = 51.6, 9.6, 8.4$ Hz, H-3'), 4.19 (d, 1H, $J = 8.2$ Hz, H-1'), 3.97–3.92 (m, 2H, H-4, H-6), 3.88 (dd, 1H, $J = 9.4, 9.0$ Hz, H-3), 3.79–3.73 (m, 1H, H-5), 3.68 (dd, 1H, $J = 11.0, 1.9$ Hz, H-6), 3.63 from $^1\text{H}\{^{19}\text{F}\}$ (dd, 1H, $J = 9.8, 8.2$ Hz, H-4'), 3.46 (dd, 1H, $J = 9.4, 3.7$ Hz, H-2), 3.63 from $^1\text{H}\{^{19}\text{F}\}$ 3.42 (dd, 1H, $J = 9.6, 8.2$ Hz, H-2'), 3.38 (s, 3H, MeO), 3.22 (ddt, 1H, $J = 9.8, 4.4, 1.9$ Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.1 (CO), 139.2, 138.4, 137.8, 137.2 ($4 \times \text{C}_q$), 133.2 (CH_{arom}), 129.9 (C_q), 129.8, 128.8 ($2 \times 2\text{CH}_{\text{arom}}$), 128.7 (CH_{arom}), 128.6, 128.54, 128.48 ($3 \times 2\text{CH}_{\text{arom}}$), 128.46 (CH_{arom}), 128.4 (2CH_{arom}), 128.2 (4CH_{arom}), 128.1 (2CH_{arom}), 127.9 (CH_{arom}), 127.5 (2CH_{arom}), 127.2 (CH_{arom}), 100.4 (d, $^3J_{(\text{C-F})} = 11.0$ Hz, C-1'), 98.5 (C-1), 96.7 (d, $^1J_{(\text{C-F})} = 186.3$ Hz, C-3'), 80.1 (C-3), 79.0 (C-2), 77.4 (C-4), 75.3 (CH_2 O-3Bn), 74.9 (d, $^2J_{(\text{C-F})} = 16.6$ Hz, C-4'), 74.3 (d, $^4J_{(\text{C-F})} = 3.0$ Hz, CH_2 O-4'Bn), 73.70, 73.65 (CH_2 O-2Bn/O-6Bn),

71.9 (d, $^3J_{\text{C-F}} = 10.1$ Hz, C-5'), 69.6 (C-5), 68.1 (C-6), 65.0 (d, $^2J_{\text{C-F}} = 17.5$ Hz, C-2'), 63.1 (C-6'), 55.5 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -187.26 (dt, $^2J_{\text{H-F}} = 51.6$ Hz, $^3J_{\text{H-F}} = 13.4$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{48}\text{H}_{51}\text{FNO}_{10}$, 820.3491; found, 820.3492.

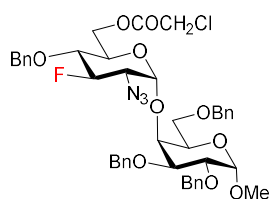
Methyl 4-*O*-(2-azido-4-*O*-benzyl-2,3,6-trideoxy-3,6-difluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (B12- α**)**



Compound **B12- α** was prepared by glycosylation of acceptor **B** with **12** according to the general procedure (4 μL TfOH). ^{19}F NMR after aqueous workup revealed $\alpha/\beta = 3.0/1.0$. Column chromatography followed by preparative TLC in EtOAc/PE 1:4 afforded **B12- α** (39 mg, 52%) as a colourless gel. The β -anomer (R_f 0.3, EtOAc/heptane 1:3) was isolated under these conditions in purity sufficient for NMR characterization. Data for **B12- α** : R_f 0.4 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.42–7.22 (m, 20H, CH_{arom}), 5.78 (dd, 1H, $J = 3.9, 3.3$ Hz, H-1'), 5.13 (d, 1H, $J = 10.8$ Hz, CHH O-3Bn), 4.92 (ddd, 1H, $J = 53.2, 10.1, 7.9$ Hz, H-3'), 4.89 (dd, 1H, $J = 11.1, 1.2$ Hz, CHH O-4'Bn), 4.85 (d, 1H, $J = 10.8$ Hz, CHH O-3Bn), 4.77, 4.64 ($2 \times$ d, $2 \times$ 1H, $J = 12.1$ Hz, CHH O-2Bn), 4.63 (d, 1H, $J = 3.1$ Hz, H-1), 4.62 (d, 1H, $J = 11.1$ Hz, CHH O-4'Bn), 4.54, 4.47 ($2 \times$ d, $2 \times$ 1H, $J = 12.1$ Hz, CHH O-6Bn), 4.33 (ddd, 1H, $J = 47.1, 10.4, 2.1$ Hz, H-6'), 4.20 (ddt, 1H, $J = 48.1, 10.4, 1.3$ Hz, H-6'), 4.09 (dd, 1H, $J = 9.4, 8.8$ Hz, H-3), 3.94 (dd, 1H, $J = 9.7, 8.8$ Hz, H-4), 3.76 (ddd, 1H, $J = 9.7, 3.7, 1.9$ Hz, H-5), 3.71 (dd, 1H, $J = 11.3, 3.7$ Hz, H-6), 3.76–3.62 (m, 2H, H-4', H-5'), 3.61–3.58 (m, 2H, H-2, H-6), 3.40 (s, 3H, MeO), 3.33 (ddd, 1H, $J = 11.0, 10.1, 3.9$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 138.6 (C_q O-3Bn), 137.98, 137.96 (C_q O-2Bn/O-6Bn), 137.5 (C_q O-4'Bn), 128.64, 128.59, 128.54, 128.47, 128.34, 128.28 ($6 \times 2\text{CH}_{\text{arom}}$), 128.24, 128.16, 127.8 ($3 \times \text{CH}_{\text{arom}}$), 127.68 (2CH_{arom}), 127.67 (CH_{arom}), 127.4 (2CH_{arom}), 97.9 (C-1), 97.6 (d, $^3J_{\text{C-F}} = 9.3$ Hz, C-1'), 93.8 (d, $^1J_{\text{C-F}} = 184.6$ Hz, C-3'), 82.1 (C-3), 81.2 (d, $^1J_{\text{C-F}} = 173.5$ Hz, C-6'), 80.6 (C-2), 75.1 (CH_2 O-3Bn), 74.9 (d, $^4J_{\text{C-F}} = 2.7$ Hz, CH_2 O-4'Bn), 74.7 (dd, $^2J_{\text{C-F}} = 16.9, ^4J_{\text{C-F}} = 6.7$ Hz, H-4'), 73.6 (CH_2 O-6Bn), 73.4 (CH_2 O-2Bn), 72.8 (C-4), 70.0 (dd, $^2J_{\text{C-F}} = 17.9, ^3J_{\text{C-F}} = 8.5$ Hz, C-5'), 69.5 (C-5), 69.0 (C-6), 61.5 (d, $^2J_{\text{C-F}} = 16.7$ Hz, C-2'), 55.5 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -194.59 (ddd, $^2J_{\text{H-F}} = 53.2$ Hz, $^3J_{\text{H-F}} = 11.6, 11.0$ Hz, F-3'), -238.15 (ddd, $^2J_{\text{H-F}} = 48.1, 47.1$ Hz, $^3J_{\text{H-F}} = 30.1$ Hz, F-6'). HRMS-APCI (m/z): $[\text{M} -$

$\text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{46}\text{F}_2\text{NO}_8$, 718.3186; found, 718.3184. Data for β -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.43–7.24 (m, 20H, CH_{arom}), 4.92 (d, 1H, $J = 10.7$ Hz, CHH O-3Bn), 4.84 (dd, 1H, $J = 11.1, 1.3$ Hz, CHH O-4'Bn), 4.78 (d, 1H, $J = 10.7$ Hz, CHH O-3Bn), 4.77 (d, 1H, $J = 11.5$ Hz, CHH O-2Bn), 4.70 (d, 1H, $J = 12.0$ Hz, CHH O-6Bn), 4.61 (d, 1H, $J = 11.5$ Hz, CHH O-2Bn), 4.61 (d, 1H, $J = 11.1$ Hz, CHH O-4'Bn), 4.59 (d, 1H, $J = 3.7$ Hz, H-1), 4.54–4.41 (m, 2H, H-6'), 4.40 (d, 1H, $J = 12$ Hz, CHH O-6Bn), 4.19 (ddd, 1H, $J = 51.8, 9.6, 8.4$ Hz, H-3'), 4.16 (d, 1H, $J = 8.2$ Hz, H-1'), 3.95 (dd, 1H, $J = 10.0, 8.9$ Hz, H-4), 3.95 (dd, 1H, $J = 10.9, 2.8$ Hz, H-6), 3.86 (dd, 1H, $J = 9.5, 8.9$ Hz, H-3), 3.76 (ddd, 1H, $J = 10.0, 2.8, 1.9$ Hz, H-5), 3.73–3.66 (m, 1H, H-4'), 3.68 (dd, 1H, $J = 10.9, 1.9$ Hz, H-6), 3.51 (dd, 1H, $J = 9.5, 3.7$ Hz, H-2), 3.39 (s, 3H, MeO), 3.38 (ddd, 1H, $J = 13.4, 9.6, 8.2$ Hz, H-2'), 3.00 (ddd, 1H, $J = 27.8, 8.7, 1.8$ Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 139.2 (C_q O-3Bn), 138.4 (C_q O-2Bn), 137.9 (C_q O-6Bn), 137.6 (C_q O-4'Bn), 128.72 (2CH_{arom}), 128.7 (CH_{arom}), 128.6, 128.5, 128.32, 128.29 ($4 \times 2\text{CH}_{\text{arom}}$), 128.26, 128.25 ($2 \times \text{CH}_{\text{arom}}$), 128.23, 128.18 ($4 \times 2\text{CH}_{\text{arom}}$), 128.15, 128.0, 127.5 ($3 \times \text{CH}_{\text{arom}}$), 100.4 (d, $^3J_{(\text{C-F})} = 10.9$ Hz, C-1'), 98.5 (C-1), 96.3 (d, $^1J_{(\text{C-F})} = 186.6$ Hz, C-3'), 81.0 (d, $^1J_{(\text{C-F})} = 171.9$ Hz, C-6'), 80.2 (C-3), 79.4 (C-2), 77.3 (C-4), 75.8 (CH_2 O-3Bn), 74.7 (d, $^4J_{(\text{C-F})} = 2.6$ Hz, CH_2 O-4'Bn), 74.4 (dd, $^2J_{(\text{C-F})} = 17.0$, $^4J_{(\text{C-F})} = 7.2$ Hz, H-4'), 73.7 (CH_2 O-2Bn), 73.6 (CH_2 O-6Bn), 72.9 (dd, $^2J_{(\text{C-F})} = 18.8$, $^3J_{(\text{C-F})} = 9.9$ Hz, C-5'), 69.7 (C-5), 68.1 (C-6), 65.0 (d, $^2J_{(\text{C-F})} = 17.4$ Hz, C-2'), 55.5 (MeO). ^{19}F NMR (CDCl_3 , 376 MHz): δ -188.03 (dt, $^2J_{(\text{H-F})} = 51.8$ Hz, $^3J_{(\text{H-F})} = 13.4$ Hz, F-3'), -235.26 (td, $^2J_{(\text{H-F})} = 47.4$ Hz, $^3J_{(\text{H-F})} = 27.8$ Hz, F-6'). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{46}\text{F}_2\text{NO}_8$, 718.3186; found, 718.3185.

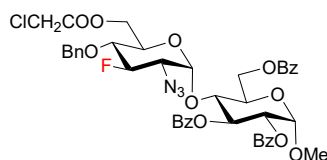
Methyl 4-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (C9- α)



Compound **C9- α** was prepared by glycosylation of acceptor **C** with **β -9** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous workup revealed $\alpha/\beta = 8.7/1.0$. Column chromatography in EtOAc/PE 1:4 followed by preparative TLC (EtOAc/PE 1:4) afforded **C9- α** as a colourless gel (56 mg, 68%), the β -anomer could not be isolated under these conditions. Data for **C9- α** : R_f 0.3 (EtOAc/heptane 1:4). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.40–7.21 (m, 20H, CH_{arom}), 4.92 (ddd, 1H, $J = 53.9, 10.1, 8.3$ Hz, H-3'), 4.88 (dd, 1H,

$J = 3.7, 3.3$ Hz, H-1'), 4.85 (dd, 1H, $J = 10.9, 0.9$ Hz, CHH O-4'Bn), 4.82 (d, 1H, $J = 11.7$ Hz, CHH O-2Bn), 4.79, 4.69 ($2 \times$ d, $2 \times$ 1H, $J = 11.0$ Hz, CHH O-3Bn), 4.67 (d, 1H, $J = 3.5$ Hz, H-1), 4.64 (d, 1H, $J = 11.7$ Hz, CHH O-2Bn), 4.59 (d, 1H, $J = 10.9$ Hz, CHH O-4'Bn), 4.56, 4.49 ($2 \times$ d, $2 \times$ 1H, $J = 11.8$ Hz, CHH O-6Bn), 4.33 (dt, 1H, $J = 10.1, 2.2$ Hz, H-5'), 4.13 (d, 1H, $J = 1.5$ Hz, H-4), 3.89–3.81 (m, 5H, H-2, H-3, H-5, H-6, H-6'), 3.87, 3.78 ($2 \times$ d, $2 \times$ 1H, $J = 14.9$ Hz, CHHCl), 3.70 (ddd, 1H, $J = 12.3, 2.4, 2.2$ Hz, H-6'), 3.59 (ddd, 1H, $J = 13.5, 10.1, 8.3$ Hz, H-4'), 3.51 (dd, 1H, $J = 8.4, 5.1$ Hz, H-6), 3.35 (s, 3H, MeO), 3.31 (ddd, 1H, $J = 11.0, 10.1, 3.7$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.7 (CO), 138.3, 138.1, 137.59, 137.55 ($4 \times \text{C}_q$ Bn), 128.68, 128.66, 128.64, 128.63, 128.62, 128.51 ($6 \times 2\text{CH}_{\text{arom}}$), 128.3 (CH_{arom}), 128.19 (2CH_{arom}), 128.16, 128.1, 128.0 ($3 \times \text{CH}_{\text{arom}}$), 127.7 (2CH_{arom}), 98.6 (C-1), 98.2 (d, $^3J_{\text{C-F}} = 9.5$ Hz, C-1'), 94.5 (d, $^1J_{\text{C-F}} = 183.8$ Hz, C-3'), 76.8 (C-2), 75.8 (C-3), 75.4 (C-4), 74.4 (d, $^2J_{\text{C-F}} = 19.1$ Hz, C-4'), 74.3 (CH_2 O-4'Bn), 73.8 (CH_2 O-2Bn), 73.6 (CH_2 O-6Bn), 73.4 (CH_2 O-3Bn), 68.6 (C-5), 68.1 (d, $^3J_{\text{C-F}} = 8.7$ Hz, C-5'), 67.1 (C-6), 63.5 (C-6'), 62.2 (d, $^2J_{\text{C-F}} = 16.7$ Hz, C-2'), 55.6 (MeO), 40.8 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.78 (ddd, $^2J_{\text{H-F}} = 53.9$ Hz, $^3J_{\text{H-F}} = 13.5, 10.6$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{ClFNO}_{10}$, 792.2945; found, 792.2945. ^{19}F NMR (CDCl_3 , 376 MHz) δ -187.68 (dt, $^2J_{\text{H-F}} = 51.2$ Hz, $^3J_{\text{H-F}} = 13.2$ Hz) in crude product was tentatively assigned for β -anomer.

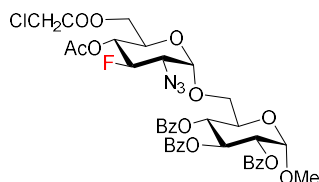
Methyl 4-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzoyl- α -D-glucopyranoside (D9- α)



Compound **D9- α** was prepared by glycosylation of acceptor **D** with **9- β** (93 mg 0.2 mmol, 2 equiv) according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous workup revealed $\alpha/\beta = 17.0:1.0$. Column chromatography in EtOAc/PE 1:3 followed by preparative TLC in EtOAc/PE 1:4 afforded **D9- α** as a colourless gel (52 mg, 59%) with traces of the β -anomer ($\sim 5\%$ by ^{19}F NMR), R_f 0.3 (EtOAc/heptane 1:4). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 8.10–8.07 (m, 2H, CH_{arom}), 8.01–7.97 (m, 4H, CH_{arom}), 7.62–7.58 (m, 1H, CH_{arom}), 7.53–7.46 (m, 4H, CH_{arom}), 7.41–7.28 (m, 9H, CH_{arom}), 6.09 (dd, 1H, $J = 10.0, 8.7$ Hz, H-3), 5.15 (dd, 1H, $J = 3.9, 3.6$ Hz, H-1'), 5.15 (d, 1H, $J = 3.6$ Hz, H-1), 5.11 (dd, 1H, $J = 10.0, 3.6$ Hz, H-2), 4.95 (ddd, 1H, $J = 53.4, 10.1, 8.3$ Hz, H-3'), 4.84 (d, 1H, $J = 11.3$ Hz, CHH O-4'Bn), 4.67 (dd, 1H, $J = 12.1, 2.0$ Hz, H-6), 4.57 (d, 1H, $J = 11.3$ Hz, CHH O-

4'Bn), 4.54 (dd, 1H, $J = 12.1, 4.1$ Hz, H-6), 4.33–4.27 (m, 2H, H-6'), 4.16 (ddd, 1H, $J = 9.9, 4.1, 2.0$ Hz, H-5), 4.09 (dd, 1H, $J = 9.9, 8.7$ Hz, H-4), 3.99 (ddd, 1H, $J = 9.9, 2.8, 2.8$ Hz, H-5'), 3.95, 3.88 ($2 \times d, 2 \times 1H, J = 14.9$ Hz, CHHCl), 3.54 (ddd, 1H, $J = 13.1, 9.9, 8.3$ Hz, H-4'), 3.44 (s, 3H, MeO), 3.31 (ddd, 1H, $J = 11.2, 10.1, 3.9$ Hz, H-2'). $^{13}C\{^1H\}$ NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 166.9 (CO O-3Bz), 166.3 (CO O-2Bz), 166.1 (CO O-6Bz), 166.5 (CO COCH₂), 137.0 (C_q O-4'Bn), 133.5 (3CH_{arom}), 133.2 (CH_{arom}), 130.1 (2CH_{arom}), 130.0 (C_q), 129.9 (2CH_{arom}), 129.7 (C_q), 129.6 (2CH_{arom}), 129.1 (C_q), 128.8, 128.72, 128.69 ($3 \times 2CH_{arom}$), 128.61 (CH_{arom}), 128.55 (2CH_{arom}), 128.4 (CH_{arom}), 99.7 (d, $^3J_{(C-F)} = 9.8$ Hz, C-1'), 96.9 (C-1), 94.4 (d, $^1J_{(C-F)} = 184.4$ Hz, C-3'), overlapped with CDCl₃ (C-4), 74.3 (d, $^4J_{(C-F)} = 3.5$ Hz, CH₂ O-4'Bn), 74.2 (d, $^2J_{(C-F)} = 16.8$ Hz, C-4'), 72.3 (C-2), 72.1 (C-3), 69.6 (d, $^3J_{(C-F)} = 8.9$ Hz, C-5'), 68.2 (C-5), 64.0 (C-6'), 63.5 (C-6), 61.7 (d, $^2J_{(C-F)} = 17.2$ Hz, C-2'), 55.7 (MeO), 40.7 (CH₂Cl). ^{19}F NMR (CDCl₃, 376 MHz): δ -192.88 (dddd, $^2J_{(H-F)} = 53.4$ Hz, $^3J_{(H-F)} = 13.1, 11.2$ Hz, $^4J_{(H-F)} = 3.6$ Hz). HRMS-APCI (m/z): $[M - N_2 + H]^+$ calcd for C₄₃H₄₂ClFNO₁₃, 834.2323; found, 834.2321. Selected NMR resonances for the β -anomer: 1H NMR (CDCl₃, 400 MHz, $^1H\{^{19}F\}$, H-H COSY, HSQC, HMBC): δ 4.37 (d, 1H, $J = 7.8$ Hz, H-1'). ^{19}F NMR (CDCl₃, 376 MHz): δ -187.72 (dt, $^2J_{(H-F)} = 51.8$ Hz, $^3J_{(H-F)} = 13.3$ Hz).

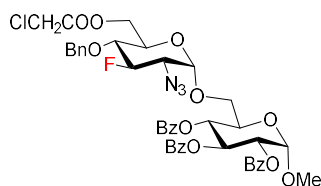
Methyl 6-*O*-(2-azido-4-*O*-acetyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (E16- α)



Compound **E16- α** was prepared by glycosylation of acceptor **E** with **16** according to the general procedure (9 μ L TfOH). ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 4.6/1.0$. Preparative TLC in EtOAc/PE 1:3 afforded the **E16- α** as a colourless gel (40 mg, 49%), and the mixture of both anomers of **E16** as a colourless gel (17 mg, with unidentified byproducts, by ^{19}F NMR). Data for **E16- α** : R_f 0.20 (EtOAc/heptane 1:3). 1H NMR (CDCl₃, 400 MHz, $^1H\{^{19}F\}$, H-H COSY, HSQC): δ 7.99–7.95 (m, 4H, CH_{arom}), 7.88–7.85 (m, 2H, CH_{arom}), 7.55–7.49 (m, 2H, CH_{arom}), 7.43–7.36 (m, 5H, CH_{arom}), 7.31–7.27 (m, 2H, CH_{arom}), 6.16 (ddd, 1H, $J = 11.3, 9.6, 1.6$ Hz, H-3), 5.63 (dd, 1H, $J = 10.2, 9.6$ Hz, H-4), 5.28–5.24 (m, 2H, H-1, H-2), 5.14 (ddd, 1H, $J = 13.0, 10.3, 8.9$ Hz, H-4'), 5.01 (dd, 1H, $J = 3.7, 3.3$ Hz, H-1'), 4.99 (ddd, 1H, $J = 53.0, 9.8, 8.9$ Hz, H-3'), 4.27 (ddd, 1H, $J = 10.2, 5.2, 2.0$ Hz, H-5), 4.19 (dd, 1H, $J = 12.3, 5.2$ Hz, H-6'), 4.07 (ddd, 1H, $J = 12.3, 2.1, 1.5$ Hz, H-6'), 4.02 (d, 1H, $J = 15.1$ Hz, CHHCl), 3.99 (ddd, 1H, $J =$

10.3, 5.2, 2.1 Hz, H-5'), 3.97 (d, 1H, $J = 15.1$ Hz, CHHCl), 3.90 (dd, 1H, $J = 11.1, 5.2$ Hz, H-6), 3.67 (dd, 1H, $J = 11.1, 2.0$ Hz, H-6), 3.49 (s, 3H, OMe), 3.48 (ddd, 1H, $J = 11.3, 9.8, 3.7$ Hz, H-2'), 2.16 (s, 3H, Me OAc). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 169.7, 167.0, 165.93, 165.92, 165.5 ($5 \times \text{CO}$), 133.9, 133.5, 133.3 ($3 \times \text{CH}_{\text{arom}}$), 130.1, 130.0, 129.8 ($3 \times 2\text{CH}_{\text{arom}}$), 129.3, 129.1, 128.8 ($3 \times \text{C}_q$), 128.7, 128.6, 128.4 ($3 \times 2\text{CH}_{\text{arom}}$), 98.2 (d, $^3J_{(\text{C-F})} = 9.4$ Hz, C-1'), 97.2 (C-1), 89.7 (d, $^1J_{(\text{C-F})} = 188.1$ Hz, C-3'), 72.1 (C-2), 70.4 (C-3), 69.2 (C-4), 68.4 (d, $^2J_{(\text{C-F})} = 18.9$ Hz, C-4'), 68.3 (C-5), 67.5 (d, $^3J_{(\text{C-F})} = 7.0$ Hz, C-5'), 66.9 (C-6), 63.3 (d, $^4J_{(\text{C-F})} = 1.3$ Hz, C-6'), 61.5 (d, $^2J_{(\text{C-F})} = 16.9$ Hz, C-2'), 55.8 (OMe), 40.7 (CH_2Cl), 20.9 (Me OAc). ^{19}F NMR (CDCl_3 , 376 MHz): δ -197.72 (dddd, $^2J_{(\text{H-F})} = 53.0$ Hz, $^3J_{(\text{H-F})} = 13.0, 11.3$ Hz, $^4J_{(\text{H-F})} = 3.3$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{38}\text{ClFNO}_{14}$, 786.1959; found, 786.1963. Data for the β -anomer: R_f 0.17 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.98–7.95 (m, 4H, CH_{arom}), 7.86–7.84 (m, 2H, CH_{arom}), 7.56–7.49 (m, 2H, CH_{arom}), 7.44–7.36 (m, 5H, CH_{arom}), 7.30–7.26 (m, 2H, CH_{arom}), 6.17 (ddd, 1H, $J = 11.4, 9.4, 1.8$ Hz, H-3), 5.51 (dd, 1H, $J = 10.2, 9.4$ Hz, H-4), 5.26–5.24 (m, 2H, H-1, H-2), 5.10 (ddd, 1H, $J = 12.6, 10.2, 9.0$ Hz, H-4'), 4.43 (d, 1H, $J = 8.3$ Hz, H-1'), 4.40–4.19 (m, 4H, H-5, H-3', 2H-6'), 4.08 (dd, 1H, $J = 11.3, 2.4$ Hz, H-6), 4.04 (s, 2H, CH_2Cl), 3.78 (dd, 1H, $J = 11.3, 6.5$ Hz, H-6), 3.61–3.53 (m, 2H, H-2', H-5'), 3.50 (s, 3H, OMe), 2.11 (s, 3H, Me OAc). ^{13}C NMR (CDCl_3 , 101 MHz, HSQC): δ 169.5, 167.2, 166.0, 165.9, 165.7 ($5 \times \text{CO}$), 133.8, 133.5, 133.3 ($3 \times \text{CH}_{\text{arom}}$), 130.1, 130.0, 129.8 ($3 \times 2\text{CH}_{\text{arom}}$), 129.3, 129.2, 128.9 ($3 \times \text{C}_q$), 128.7, 128.6, 128.4 ($3 \times 2\text{CH}_{\text{arom}}$), 101.9 (d, $^3J_{(\text{C-F})} = 10.5$ Hz, C-1'), 97.1 (C-1), 91.8 (d, $^1J_{(\text{C-F})} = 190.8$ Hz, C-3'), 72.1 (C-2), 70.9 (d, $^3J_{(\text{C-F})} = 8.0$ Hz, C-5'), 70.3 (C-3), 69.9 (C-4), 68.9 (C-6), 68.3 (C-5), 68.1 (d, $^2J_{(\text{C-F})} = 18.8$ Hz, C-4'), 64.5 (d, $^2J_{(\text{C-F})} = 17.3$ Hz, C-2'), 63.4 (d, $^4J_{(\text{C-F})} = 1.0$ Hz, C-6'), 55.9 (OMe), 40.7 (CH_2Cl), 20.8 (Me OAc). ^{19}F NMR (CDCl_3 , 376 MHz): δ -193.02 (ddd, $^2J_{(\text{H-F})} = 51.1$ Hz, $^3J_{(\text{H-F})} = 13.0, 12.6$ Hz).

Methyl 6-*O*-(2-azido-4-*O*-benzyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (E9- α)



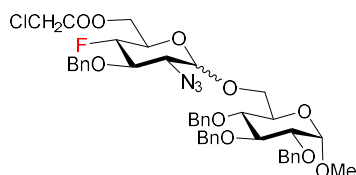
Compounds **E9- α** and **E9- β** were prepared by glycosylation of acceptor **E** with **9** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous workup revealed the $\alpha/\beta = 7.6/1.0$. Preparative TLC in EtOAc/PE 1:3 afforded

E9- α as a colourless gel (58 mg, 67 %), and the β -anomer of the product as a colourless gel (1.5 mg) in purity sufficient for NMR characterization. Data for **E9- α** : R_f 0.15 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.99–7.92 (m, 4H, CH_{arom}), 7.88–7.85 (m, 2H, CH_{arom}), 7.53–7.49 (m, 2H, CH_{arom}), 7.44–7.26 (m, 12H, CH_{arom}), 6.16 (ddd, 1H, $J = 11.3, 9.6, 1.6$ Hz, H-3), 5.52 (dd, 1H, $J = 10.2, 9.6$ Hz, H-4), 5.26–5.23 (m, 2H, H-1, H-2), 5.11 (ddd, 1H, $J = 53.4, 10.0, 8.2$ Hz, H-3'), 4.94 (t, 1H, $J = 3.6$ Hz, H-1'), 4.92 (dd, 1H, $J = 11.4, 0.9$ Hz, CHH Bn), 4.62 (d, 1H, $J = 11.4$ Hz, CHH Bn), 4.27–4.23 (m, 2H, H-5, H-6'), 4.18 (dd, 1H, $J = 11.9, 4.5$ Hz, H-6'), 3.92–3.80 (m, 2H, H-6, H-5'), 3.88, 3.82 ($2 \times \text{d}, 2 \times 1\text{H}, J = 15.0$ Hz, CHHCl), 3.62 (dd, 1H, $J = 11.1, 2.1$ Hz, H-6), 3.59 (ddd, 1H, $J = 13.1, 10.0, 8.2$ Hz, H-4'), 3.47 (s, 3H, MeO), 3.38 (ddd, 1H, $J = 11.1, 10.0, 3.6$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 166.9, 165.94, 165.93, 165.4 ($4 \times \text{CO}$), 137.4, 133.7, 133.5, 133.2 ($4 \times \text{C}_q \text{ Bz}$), 130.07, 130.06, 129.8 ($3 \times 2\text{CH}_{\text{arom}}$), 129.3, 129.2 128.9 ($3 \times \text{CH}_{\text{arom}}$), 128.7 (4CH_{arom}), 128.60, 128.55, 128.4 ($4 \times 2\text{CH}_{\text{arom}}$), 128.3 (CH_{arom}), 98.2 (d, $^3J_{(\text{C-F})} = 9.5$ Hz, C-1'), 97.2 (C-1), 93.9 (d, $^1J_{(\text{C-F})} = 184.4$ Hz, C-3'), 74.7 (d, $^2J_{(\text{C-F})} = 16.7$ Hz, C-4'), 74.3 (d, $^4J_{(\text{C-F})} = 3.5$ Hz, $\text{CH}_2 \text{ Bn}$), 72.2 (C-2), 70.5 (C-3), 69.2 (C-4), 68.4 (C-5), 68.3 (d, $^3J_{(\text{C-F})} = 9.0$ Hz, C-5'), 68.8 (C-6), 64.0 (d, $^4J_{(\text{C-F})} = 1.6$ Hz, C-6'), 61.5 (d, $^2J_{(\text{C-F})} = 17.5$ Hz, C-2'), 55.8 (MeO), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): δ –192.65 (dddd, $^2J_{(\text{H-F})} = 53.4$ Hz, $^3J_{(\text{H-F})} = 13.1, 11.1$ Hz, $^4J_{(\text{H-F})} = 3.6$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{42}\text{FCINO}_{13}$, 834.2323; found, 834.2317. Data for the β -anomer: R_f 0.17 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC): δ 7.97–7.94 (m, 4H, CH_{arom}), 7.86–7.84 (m, 2H, CH_{arom}), 7.53–7.49 (m, 2H, CH_{arom}), 7.42–7.28 (m, 12H, CH_{arom}), 6.16 (ddd, 1H, $J = 11.4, 9.4, 1.8$ Hz, H-3), 5.52 (dd, 1H, $J = 10.3, 9.4$ Hz, H-4), 5.25–5.21 (m, 2H, H-1, H-2), 4.85 (dd, 1H, $J = 11.3, 0.9$ Hz, CHH Bn), 4.59 (d, 1H, $J = 11.3$ Hz, CHH Bn), 4.46 (ddd, 1H, $J = 51.2, 9.6, 8.2$ Hz, H-3'), 4.38 (d, 1H, $J = 8.1$ Hz, H-1'), 4.37 (dd, 1H, $J = 11.9, 2.3$ Hz, H-6'), 4.32–4.26 (m, 1H, H-5), 4.25 (dd, 1H, $J = 11.9, 4.7$ Hz, H-6'), 4.05 (dd, 1H, $J = 11.3, 2.4$ Hz, H-6), 3.93, 3.84 ($2 \times \text{d}, 2 \times 1\text{H}, J = 15.0$ Hz, CHHCl), 3.75 (dd, 1H, $J = 11.3, 6.3$ Hz, H-6), 3.59 (ddd, 1H, $J = 12.8, 9.9, 8.2$ Hz, H-4'), 3.54–3.46 (m, 2H, H-2', H-5'), 3.49 (s, 3H, MeO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 167.0 (COCH_2Cl), 166.0, 165.9 ($2 \times \text{CO Bz}$), 165.6 (CO Bn), 137.0 ($\text{C}_q \text{ Bn}$), 133.7, 133.5, 133.3 ($3 \times \text{C}_q \text{ Bz}$), 130.1, 130.0, 129.8 ($3 \times 2\text{CH}_{\text{arom}}$), 129.3, 129.2 128.9 ($3 \times \text{CH}_{\text{arom}}$), 128.74, 128.71, 128.64, 128.56 ($4 \times 2\text{CH}_{\text{arom}}$), 128.5 (CH_{arom}), 128.4 (2CH_{arom}), 101.8 (d, $^3J_{(\text{C-F})} = 11.0$ Hz, C-1'), 97.1 (C-1), 96.0 (d, $^1J_{(\text{C-F})} = 187.1$ Hz, C-3'), 74.4 (d, $^2J_{(\text{C-F})} = 17.0$ Hz, C-4'), 74.3 (d, $^4J_{(\text{C-F})} = 3.4$ Hz, $\text{CH}_2 \text{ Bn}$), 72.1 (C-2), 71.6 (d, $^3J_{(\text{C-F})} = 10.3$ Hz, C-5'), 70.4 (C-3), 69.8 (C-4), 68.9 (C-5, C-6), 64.6 (d, $^2J_{(\text{C-F})} = 17.8$ Hz, C-2'), 64.0 (C-6'), 55.9

(MeO), 40.7 (CH₂Cl). ¹⁹F NMR (CDCl₃, 376 MHz): δ -187.87 (ddd, ²J_(H-F) = 51.2 Hz, ³J_(H-F) = 13.3, 12.8 Hz).

HRMS-APCI (*m/z*): [M - N₂ + H]⁺ calcd for C₄₃H₄₂FCINO₁₃, 834.2323; found, 834.2325.

Methyl 6-*O*-(2-azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (A20)

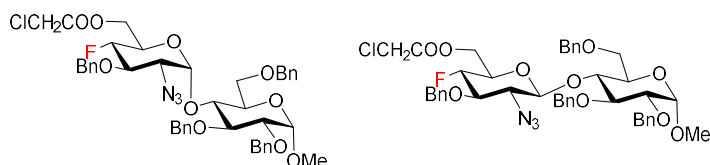


Compound **A20** was prepared by glycosylation of acceptor **A** with **20** according to the general procedure (6 μ L TfOH). ¹⁹F NMR after aqueous workup revealed α/β = 2.9/1.0. Column chromatography in EtOAc/PE 1:3 followed by preparative TLC in EtOAc/PE 2:7 afforded the mixture of anomers inseparable under given conditions as a colourless gel (52 mg, 63 %), *R_f* 0.25 (EtOAc/heptane 1:3). HRMS-APCI (*m/z*): [M - N₂ + H]⁺ calcd for C₄₃H₄₈FCINO₁₀, 792.2946; found, 792.2949. NMR data for the α -anomer: ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.42–7.26 (m, 20H, CH_{arom}), 5.00 (d, 1H, *J* = 10.8 Hz, CHH O-3Bn), 4.96 (d, 1H, *J* = 11.4 Hz, CHH Bn), 4.92 (dd, 1H, *J* = 3.6, 3.2 Hz, H-1'), 4.88 (d, 1H, *J* = 10.8 Hz, CHH Bn), 4.81 (d, 1H, *J* = 11.8 Hz, CHH O-2Bn), 4.81 (d, 1H, *J* = 10.8 Hz, CHH O-3Bn), 4.79 (d, 1H, *J* = 10.8 Hz, CHH Bn), 4.68 (d, 1H, *J* = 11.8 Hz, CHH O-2Bn), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 4.58 (d, 1H, *J* = 11.4 Hz, CHH Bn), 4.46 (ddd, 1H, *J* = 50.7, 10.1, 8.3 Hz, H-4'), 4.43 (ddd, 1H, *J* = 12.0, 2.3, 1.9 Hz, H-6'), 4.23 (ddd, 1H, *J* = 12.0, 5.0, 1.4 Hz, H-6'), 4.02 (s, 2H, CH₂Cl), 3.99–3.90 (m, 3H, H-3, H-3', H-5'), 3.79–3.67 (m, 3H, H-5, 2H-6), 3.56 (dd, 1H, *J* = 10.0, 8.5 Hz, H-4), 3.54 (dd, 1H, *J* = 9.5, 3.5 Hz, H-2), 3.36 (s, 3H, CH₃, OMe), 3.29 (ddd, 1H, *J* = 10.2, 3.6, 1.1 Hz, H-2'). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 167.0 (CO), 138.7 (C_q O-3Bn), 138.3 (C_q), 138.2 (C_q O-2Bn), 137.4 (C_q), 128.63, 128.60, 128.58, 128.56, 128.4, 128.24, 128.22 (7 $\times$ 2CH_{arom}), 128.13, 128.07, 128.0, 127.8 (4 $\times$ CH_{arom}), 127.8 (2CH_{arom}), 98.1 (C-1), 97.6 (d, ⁴*J* = 1.4 Hz, C-1'), 90.6 (d, ¹*J* = 185.0 Hz, C-4'), 82.2 (C-3), 80.1 (C-2), 77.7 (C-4), 76.8 (d, ²*J* = 17.7 Hz, C-3'), 75.9 (CH₂ O-3Bn), 75.00 (CH₂ O-4Bn), 74.95 (d, ⁴*J* = 2.7 Hz, CH₂ O-3'Bn), 73.5 (CH₂ O-2Bn), 70.0 (C-5), 67.1 (d, ²*J* = 24.5 Hz, C-5'), 66.8 (C-6), 63.6 (C-6'), 62.2 (d, ³*J* = 8.2 Hz, C-2'), 55.3 (CH₃ OMe), 40.7 (CH₂Cl). ¹⁹F NMR (CDCl₃, 376 MHz): -195.54 (dd, ²*J* = 50.7 Hz, ³*J* = 14.4 Hz). Selected NMR data for the β -anomer: ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.42–7.26 (m, 20H, CH_{arom}), overlapped with α -anomer (8 $\times$ 1H, CHH Bn), 4.60 (d, 1H, *J* = 3.6 Hz, H-1), 4.46 (ddd, 1H, *J* = 50.6, 10.1, 8.3 Hz,

H-4'), 4.51 (dd, 1H, $J = 12.1, 2.4$ Hz, H-6'), 4.30 (ddd, 1H, $J = 12.1, 5.3, 1.5$ Hz, H-6'), 4.14 (d, 1H, $J = 7.7$ Hz, H-1'), 4.07 (dd, 1H, $J = 10.2, 2.0$ Hz, H-6), 4.06 (s, 2H, CH₂Cl), 3.99–3.90 (m, 1H, H-3), 3.80–3.70 (m, 2H, H-5, H-6), 3.58–3.42 (m, 5H, H-2, H-4, H-2', H-3', H-5'), 3.38 (s, 3H, CH₃, OMe). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 167.1 (CO), overlapped with α -anomer (C Bn), 102.0 (d, $^4J = 1.5$ Hz, C-1'), 98.4 (C-1), 89.9 (d, $^1J = 184.9$ Hz, C-4'), 82.2 (C-3), 80.1 (d, $^2J = 18.1$ Hz, C-3'), 79.9 (C-2), 77.7 (C-4), 75.9 (CH₂ Bn), 75.01 (d, $^4J = 2.6$ Hz, CH₂ O-3'Bn), 74.96, 73.6 (2 $\times$ CH₂ Bn), 71.0 (d, $^2J = 24.6$ Hz, C-5'), 70.0 (C-5), 68.8 (C-6), 65.1 (d, $^3J = 9.2$ Hz, C-2'), 63.7 (C-6'), 55.4 (CH₃, OMe), 40.7 (CH₂Cl). ¹⁹F NMR (CDCl₃, 376 MHz): -198.21 (dd, $^2J = 50.6$ Hz, $^3J = 13.6$ Hz).

Methyl 4-*O*-(2-azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (B20- α)

Methyl 4-*O*-(2-azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- β -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (B20- β)

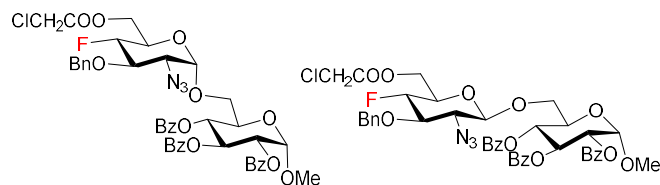


Compounds **B20- α** and **B20- β** were prepared by glycosylation of acceptor **B** with **20** according to the general procedure (6 μ L TfOH). ¹⁹F NMR after aqueous workup revealed $\alpha/\beta = 3.3/1.0$. Preparative TLC in EtOAc/PE 1:4 afforded **B20- α** as a colourless gel (43 mg, 52 %), and **B20- β** as a colourless gel (14 mg, 17 %). Data for **B20- α** : R_f 0.35 (EtOAc/heptane 1:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.42–7.27 (m, 20H, CH_{arom}), 5.65 (dd, 1H, $J = 3.8, 3.3$ Hz, H-1'), 5.11 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.87 (dd, 1H, $J = 10.9, 1.1$ Hz, CHH O-3'Bn), 4.82 (d, 1H, $J = 10.9$ Hz, CHH O-3Bn), 4.75 (d, 1H, $J = 10.9$ Hz, CHH O-3'Bn), 4.75, 4.63 (2 $\times$ d, 2 $\times$ 1H, $J = 12.1$ Hz, CHH O-2Bn), 4.62 (d, 1H, $J = 3.5$ Hz, H-1), 4.58 (s, 2H, CHH O-6Bn), 4.43 (ddd, 1H, $J = 50.7, 10.0, 8.4$ Hz, H-4'), 4.16–4.12 (m, 2H, H-6'), 4.07 (dd, 1H, $J = 9.6, 8.3$ Hz, H-3), 4.01, 3.97 (2 $\times$ d, 2 $\times$ 1H, $J = 14.2$ Hz, CHHCl), 3.97–3.80 (m, 4H, H-4, H-5, H-3', H-5'), 3.71 (dd, 1H, $J = 11.1, 3.7$ Hz, H-6), 3.65 (dd, 1H, $J = 11.1, 1.8$ Hz, H-6), 3.57 (dd, 1H, $J = 9.6, 3.5$ Hz, H-2), 3.41 (s, 3H, CH₃, OMe), 3.21 (ddd, 1H, $J = 10.3, 3.8, 1.1$ Hz, H-2'). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 166.9 (CO), 138.7 (C_q O-3Bn), 137.94 (C_q O-3'Bn), 137.91 (C_q O-6Bn), 137.4 (C_q O-2Bn), 128.7, 128.63, 128.61, 128.5, 128.32, 128.30 (6 $\times$ 2CH_{arom}), 128.22, 128.18,

128.0 ($3 \times \text{CH}_{\text{arom}}$), 127.64 (2CH_{arom}), 127.63 (CH_{arom}), 127.62 (2CH_{arom}), 97.8 (C-1), 97.0 (d, $^4J = 1.1$ Hz, C-1'), 90.4 (d, $^1J = 184.8$ Hz, C-4'), 81.9 (C-3), 80.5 (C-2), 77.3 (d, $^2J = 17.7$ Hz, C-3'), 75.12 (d, $^4J = 2.9$ Hz, CH_2 O-3'Bn), 75.06 (CH_2 O-3Bn), 73.7 (CH_2 O-6Bn), 73.6 (C-4), 73.4 (CH_2 O-2Bn), 69.5 (C-5), 69.3 (C-6), 67.5 (d, $^2J = 24.5$ Hz, C-5'), 63.5 (C-6'), 62.0 (d, $^3J = 8.1$ Hz, C-2'), 55.5 (CH_3 , OMe), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -195.34 (ddd, $^2J = 50.7$ Hz, $^3J = 24.3$, 4.6 Hz, $^5J = 3.8$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{FCINO}_{10}$, 792.2945; found, 792.2941. Data for **B20- β** : R_f 0.30 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.40–7.24 (m, 20H, CH_{arom}), 4.91 (d, 1H, $J = 11.5$ Hz, CHH O-3Bn), 4.82 (dd, 1H, $J = 11.1$, 1.1 Hz, CHH O-3'Bn), 4.75 (d, 1H, $J = 11.5$ Hz, CHH O-3Bn), 4.74 (d, 1H, $J = 12.1$ Hz, CHH O-6Bn), 4.73 (d, 1H, $J = 12.1$ Hz, CHH O-2Bn), 4.71 (d, 1H, $J = 11.1$ Hz, CHH O-3'Bn), 4.61 (d, 1H, $J = 3.7$ Hz, H-1), 4.60 (d, 1H, $J = 12.1$ Hz, CHH O-2Bn), 4.38 (d, 1H, $J = 12.1$ Hz, CHH O-6Bn), from ^1H $\{^{19}\text{F}\}$ 4.33 (dd, 1H, $J = 9.9$, 7.7 Hz, H-4'), 4.22 (ddd, 1H, $J = 12.0$, 2.5, 2.2 Hz, H-6'), 4.11 (ddd, 1H, $J = 12.0$, 4.9, 1.5 Hz, H-6'), 4.09 (d, 1H, $J = 7.9$ Hz, H-1'), 3.87 (dd, 1H, $J = 10.8$, 2.8 Hz, H-6), 3.87 (dd, 1H, $J = 9.7$, 8.0 Hz, H-4), 3.86 (d, 1H, $J = 15.1$ Hz, CHHCl), 3.83 (dd, 1H, $J = 9.3$, 8.0 Hz, H-3), 3.78 (d, 1H, $J = 15.1$ Hz, CHHCl), 3.74 (ddd, 1H, $J = 9.7$, 2.8, 1.9 Hz, H-5), 3.68 (dd, 1H, $J = 10.8$, 1.9 Hz, H-6), 3.49 (dd, 1H, $J = 9.3$, 3.7 Hz, H-2), 3.39 (s, 3H, CH_3 , OMe), 3.22–3.17 (m, 2H, H-2', H-3'), from ^1H $\{^{19}\text{F}\}$ 3.16 (ddd, 1H, $J = 9.9$, 4.9, 2.5 Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 167.1 (CO), 139.6 (C_q O-3Bn), 138.3 (C_q O-2Bn), 138.0 (C_q O-6Bn), 137.4 (C_q O-3'Bn), 128.8, 128.63, 128.62, 128.5, 128.30, 128.26, 128.25, 128.2 ($8 \times 2\text{CH}_{\text{arom}}$), 128.0, 127.4 ($2 \times \text{CH}_{\text{arom}}$), 127.3 (2CH_{arom}), 100.7 (d, $^4J = 1.3$ Hz, C-1'), 98.5 (C-1), 90.0 (d, $^1J = 184.6$ Hz, C-4'), 80.1 (d, $^2J = 18.8$ Hz, C-3'), 80.0 (C-3), 78.9 (C-2), 75.1 (CH_2 O-3Bn), 77.1 (C-4), 74.8 (d, $^4J = 2.6$ Hz, CH_2 O-3'Bn), 73.7, 73.6 (CH_2 O-2/6Bn), 70.5 (d, $^2J = 24.3$ Hz, C-5'), 69.6 (C-5), 68.1 (C-6), 65.5 (d, $^3J = 9.0$ Hz, C-2'), 63.8 (C-6'), 55.5 (CH_3 , OMe), 40.6 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -198.09 (dd, $^2J = 50.7$ Hz, $^3J = 12.8$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{48}\text{FCINO}_{10}$, 792.2945; found, 792.2944.

Methyl 6-*O*-(2-azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (E20- α**)**

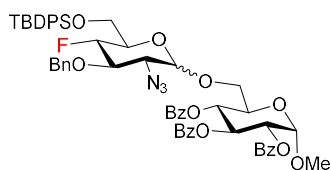
Methyl 6-*O*-(2-azido-3-*O*-benzyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- β -D-glucopyranoside (E20- β**)**



Compounds **E20- α** and **E20- β** were prepared by glycosylation of acceptor **E** with **20** according to the general procedure (6 μ L TfOH). ^{19}F NMR after aqueous workup revealed $\alpha/\beta = 5.6/1.0$. Preparative TLC in EtOAc/PE 1:3 afforded enriched anomers, first **E20- β** as a colourless gel (11 mg, 13 %, β/α 10:1), and then **E20- α** as a colourless gel (51 mg, 59 %, α/β 10:1). Data for **E20- α** : R_f 0.15 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 8.00–7.96 (m, 4H, CH_{arom}), 7.89–7.86 (m, 2H, CH_{arom}), 7.54–7.50 (m, 2H, CH_{arom}), 7.46–7.27 (m, 12H, CH_{arom}), 6.17 (dd, 1H, $J = 10.1, 9.5$ Hz, H-3), 5.63 (dd, 1H, $J = 10.2, 9.5$ Hz, H-4), 5.29 (dd, 1H, $J = 10.1, 3.7$ Hz, H-2), 5.25 (d, 1H, $J = 3.7$ Hz, H-1), 4.94 (d, 1H, $J = 10.9$ Hz, CHH O-3'Bn), 4.90 (t, 1H, $J = 3.5$ Hz, H-1'), 4.85 (d, 1H, $J = 10.9$ Hz, CHH O-3'Bn), 4.47 (ddd, 1H, $J = 50.5, 10.1, 8.3$ Hz, H-4'), 4.36 (dt, 1H, $J = 12.1, 2.2$ Hz, H-6'), 4.28 (ddd, 1H, $J = 10.2, 5.3, 2.1$ Hz, H-5), 4.22 (dd, 1H, $J = 12.1, 5.5$ Hz, H-6'), from ^1H $\{^{19}\text{F}\}$ 4.15 (dd, 1H, $J = 10.3, 8.3$ Hz, H-3'), 4.11–4.01 (m, 1H, H-5'), 3.99, 3.94 ($2 \times \text{d}, 2 \times 1\text{H}, J = 15.0$ Hz, CHHCl), 3.91 (dd, 1H, $J = 11.0, 5.3$ Hz, H-6), 3.67 (dd, 1H, $J = 11.0, 2.1$ Hz, H-6), 3.46 (s, 3H, CH_3 , OMe), 3.31 (ddd, 1H, $J = 10.3, 3.5, 1.1$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 166.9 (CO), 165.88 (CO O-2Bz), 165.86 (CO O-3Bz), 165.4 (CO O-4Bz), 137.4 (C_q , O-3'Bn), 133.7, 133.4, 133.2 ($3 \times \text{CH}_{\text{arom}}$), 130.0, 129.9, 129.7 ($3 \times 2\text{CH}_{\text{arom}}$), 129.2, 129.1, 128.8 ($3 \times \text{C}_q$ Bz), 128.60, 128.55, 128.5, 128.4, 128.3 ($5 \times 2\text{CH}_{\text{arom}}$), 128.1 (CH_{arom}), 97.7 (d, $^4J = 1.3$ Hz, C-1'), 97.1 (C-1), 90.5 (d, $^1J = 185.6$ Hz, C-4'), overlapped with CDCl_3 (C-3'), 75.0 (d, $^4J = 2.7$ Hz, CH_2 O-3'Bn), 72.0 (C-2), 70.5 (C-3), 69.2 (C-4), 68.2 (C-5), 67.2 (d, $^2J = 24.4$ Hz, C-5'), 66.7 (C-6), 63.6 (C-6'), 62.0 (d, $^3J = 8.1$ Hz, C-2'), 55.7 (CH_3 , OMe), 40.5 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -195.88 (dddd, $^2J = 50.5$ Hz, $^3J = 14.1, 3.7$ Hz, $J = 3.7$ Hz).. HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{42}\text{FCINO}_{13}$, 834.2323; found, 834.2319. Data for **E20- β** : R_f 0.18 (EtOAc/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.99–7.95 (m, 4H, CH_{arom}), 7.87–7.84 (m, 2H, CH_{arom}), 7.53–7.49 (m, 2H, CH_{arom}), 7.42–7.28 (m, 12H, CH_{arom}), 6.17 (dd, 1H, $J = 10.2, 9.5$ Hz, H-3), 5.53 (dd, 1H, $J = 10.2, 9.5$ Hz, H-4), 5.30–5.22 (m, 2H, H-2, H-1), 4.84, 4.79 ($2 \times \text{d}$,

2 × 1H, $J = 11.1$ Hz, *CHH* O-3'Bn), from $^1\text{H} \{^{19}\text{F}\}$ 4.48 (dd, 1H, $J = 12.1, 2.3$ Hz, H-6'), from $^1\text{H} \{^{19}\text{F}\}$ 4.43 (dd, 1H, $J = 9.9, 8.3$ Hz, H-4'), 4.41 (d, 1H, $J = 8.0$ Hz, H-1'), 4.37–4.26 (m, 2H, H-5, H-6'), 4.07–4.03 (m, 3H, H-6, CH_2Cl), 3.76 (dd, 1H, $J = 11.3, 6.4$ Hz, H-6), 3.63 (dddd, 1H, $J = 9.9, 5.5, 2.5, 2.3$ Hz, H-5), from $^1\text{H} \{^{19}\text{F}\}$ 3.52 (dd, 1H, $J = 10.0, 8.3$ Hz, H-3'), 3.50 (s, 3H, CH_3 , OMe), 3.41 (dd, 1H, $J = 10.0, 8.0$ Hz, H-2'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 167.1 (CO), 166.0 (CO O-2Bz), 165.9 (CO O-3Bz), 165.6 (CO O-4Bz), 137.5 (C_q , O-3'Bn), 133.7, 133.5, 133.2 ($3 \times \text{CH}_{\text{arom}}$), 130.1, 130.0, 129.8 ($3 \times 2\text{CH}_{\text{arom}}$), 129.3, 129.2, 129.0 ($3 \times \text{C}_q$ Bz), 128.64, 128.61, 128.56, 128.4, 128.3 ($5 \times 2\text{CH}_{\text{arom}}$), 128.2 (CH_{arom}), 102.4 (d, $^4J = 1.4$ Hz, C-1'), 97.1 (C-1), 89.8 (d, $^1J = 185.0$ Hz, C-4'), 79.9 (d, $^2J = 18.2$ Hz, C-3'), 75.1 (d, $^4J = 2.2$ Hz, CH_2 O-3'Bn), 72.1 (C-2), 71.1 (d, $^2J = 24.5$ Hz, C-5'), 70.4 (C-3), 69.8 (C-4), 68.93 (C-5), 68.86 (C-6), 65.4 (d, $^3J = 9.2$ Hz, C-2'), 63.8 (C-6'), 55.8 (CH_3 , OMe), 40.7 (CH_2Cl). ^{19}F NMR (CDCl_3 , 376 MHz): -198.36 (dd, $^2J = 50.6$ Hz, $^3J = 14.7$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{42}\text{FCINO}_{13}$, 834.2323; found, 834.2325.

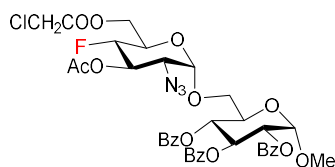
Methyl 6-*O*-(2-azido-3-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-2,4-dideoxy-4-fluoro- α,β -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (E21)



Compound **E21** was prepared by glycosylation of acceptor **E** with **21** according to the general procedure (6 μL TfOH). ^{19}F NMR after aqueous workup revealed α/β 6.1/1.0. Preparative TLC in EtOAc/PE 1:5 afforded a mixture of anomers, inseparable under given conditions, as a colourless gel (58 mg, 56%), R_f 0.55 (EtOAc/heptane 1:3). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{57}\text{H}_{59}\text{FNO}_{12}\text{Si}$, 996.3785; found, 996.3782. NMR data for the α -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H} \{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 8.00–7.86 (m, 6H, CH_{arom}), 7.67–7.63 (m, 4H, CH_{arom}), 7.53–7.27 (m, 20H, CH_{arom}), 6.15 (dd, 1H, $J = 10.0, 9.4$ Hz, H-3), 5.60 (dd, 1H, $J = 10.4, 9.4$ Hz, H-4), 5.25 (dd, 1H, $J = 10.0, 3.6$ Hz, H-2), 5.22 (d, 1H, $J = 3.6$ Hz, H-1), 4.96 (d, 1H, $J = 11.1$ Hz, *CHH* O-3'Bn), 4.92 (t, 1H, $J = 3.5$ Hz, H-1'), 4.84 (d, 1H, $J = 11.1$ Hz, *CHH* O-3'Bn), 4.69 (ddd, 1H, $J = 50.5, 9.8, 8.4$ Hz, H-4'), 4.27 (ddd, 1H, $J = 10.4, 5.8, 2.1$ Hz, H-5), 4.15 (ddd, 1H, $J = 14.0, 10.3, 8.4$ Hz, H-3'), 3.90 (dd, 1H, $J = 11.0, 5.8$ Hz, H-6), from $^1\text{H} \{^{19}\text{F}\}$ 3.82 (ddd, 1H, $J = 9.8, 3.6, 1.9$ Hz, H-5'), from $^1\text{H} \{^{19}\text{F}\}$ 3.77 (dd, 1H, $J = 11.4, 3.6$ Hz, H-6'), 3.71 (ddd, 1H, $J = 11.4, 2.3, 1.9$ Hz, H-6'), 3.63 (dd, 1H, $J = 11.0, 2.1$ Hz, H-6), 3.44 (s, 3H, CH_3 , OMe), 3.32 (ddd, 1H, J

= 10.3, 3.5, 1.0 Hz, H-2'), 1.04 (s, 9H, CM_{E3}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.0, 165.9 (CO O-2/3Bz), 165.4 (CO O-4Bz), 137.8 (C_q , O-3'Bn), 135.8, 135.7 ($2 \times 2CH_{arom}$), 133.6, 133.5 ($2 \times CH_{arom}$), 133.4, 133.3 ($2 \times C_q$), 133.2 (CH_{arom}), 130.1, 130.0 ($2 \times 2CH_{arom}$), 129.82 (CH_{arom}), 129.80 ($2CH_{arom}$), 129.4, 129.2, 129.0 ($3 \times C_q$), 128.59 ($3CH_{arom}$), 128.57, 128.5, 128.44, 128.40 ($4 \times 2CH_{arom}$), 128.1 (CH_{arom}), 127.81, 127.76 ($2 \times 2CH_{arom}$), 97.8 (d, $^4J = 1.5$ Hz, C-1'), 97.1 (C-1), 90.4 (d, $^1J = 183.5$ Hz, C-4'), 77.3 (d, $^2J = 17.8$ Hz, C-3'), 75.0 (d, $^4J = 2.9$ Hz, CH_2 O-3'Bn), 72.2 (C-2), 70.6 (C-3), 70.1 (d, $^2J = 24.5$ Hz, C-5'), 69.4 (C-4), 68.4 (C-5), 66.5 (C-6), 62.4 (d, $^3J = 8.4$ Hz, C-2'), 61.9 (C-6'), 55.6 (CH_3 , OMe), 26.9 (CM_{E3}), 19.5 (CM_{E3}). ^{19}F NMR ($CDCl_3$, 376 MHz): -196.22 (dd, $^2J = 50.5$ Hz, $^3J = 14.0$ Hz). Selected NMR resonances the β -anomer: 1H NMR ($CDCl_3$, 400 MHz, $^1H\{^{19}F\}$, H-H COSY, HSQC, HMBC) δ 6.21 (dd, 1H, $J = 10.0, 9.4$ Hz, H-3), 5.58 (dd, 1H, $J = 10.0, 9.4$ Hz, H-4), 5.29 (d, 1H, $J = 3.6$ Hz, H-1), 5.25 (dd, 1H, $J = 10.0, 3.6$ Hz, H-1), 4.88, 4.81 ($2 \times$ d, $2 \times$ 1H, $J = 11.3$ Hz, CHH O-3'Bn), 4.63 (ddd, 1H, $J = 50.3, 9.8, 8.3$ Hz, H-4'), 4.41 (d, 1H, $J = 7.9$ Hz, H-1'), 4.33 (ddd, 1H, $J = 10.0, 6.3, 2.2$ Hz, H-5), 4.11 (dd, 1H, $J = 11.5, 2.2$ Hz, H-6), 3.90–3.70 (m, 3H, H-6, 2H-6'), 3.54 (s, 3H, CH_3 , OMe), 3.55–3.42 (m, 3H, H-2', H-3', H-5'), 1.02 (s, 9H, CM_{E3}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 102.4 (d, $^4J = 1.2$ Hz, C-1'), 97.1 (C-1), 89.7 (d, $^1J = 183.1$ Hz, C-4'), 80.5 (d, $^2J = 18.5$ Hz, C-3'), 75.0 (d, $^4J = 2.3$ Hz, CH_2 O-3'Bn), 74.2 (d, $^2J = 24.6$ Hz, C-5'), 72.2 (C-2), 70.5 (C-3), 69.7 (C-4), 69.1 (C-5), 68.4 (C-6), 65.7 (d, $^3J = 9.2$ Hz, C-2'), 62.3 (C-6'), 55.8 (CH_3 , OMe), 26.8 (CM_{E3}), 19.4 (CM_{E3}). ^{19}F NMR ($CDCl_3$, 376 MHz): -198.50 (dd, $^2J = 50.3$ Hz, $^3J = 14.8$ Hz).

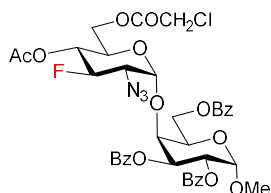
Methyl 6-*O*-(2-azido-3-*O*-acetyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (E25- α)



Compound **E25- α** was prepared by glycosylation of acceptor **E** with **25** according to the general procedure (9 μ L TfOH). ^{19}F NMR after aqueous workup revealed $\alpha/\beta > 20.0:1.0$. Preparative TLC chromatography in EtOAc/PE 1:3 afforded **E25- α** as a colourless foam (62 mg, 76 %) containing traces of the β -anomer and two unidentified byproducts (approx. 15% by ^{19}F NMR) inseparable under given conditions, R_f 0.15 (EtOAc/heptane 1:3). 1H NMR ($CDCl_3$, 400 MHz, $^1H\{^{19}F\}$, H-H COSY, HSQC, HMBC) δ 7.99–7.95 (m, 4H, CH_{arom}), 7.89–7.86 (m, 2H, CH_{arom}), 7.55–7.48 (m, 2H, CH_{arom}), 7.44–7.34 (m, 5H, CH_{arom}), 7.31–7.27 (m, 2H, CH_{arom}), 6.18 (dd, 1H, $J = 11.2, 9.5$ Hz, H-

3), 5.69 (ddd, 1H, $J = 13.6, 10.7, 8.7$ Hz, H-3'), 5.56 (dd, 1H, $J = 10.5, 9.5$ Hz, H-4), 5.27–5.24 (m, 2H, H-1, H-2), 4.98 (dd, 1H, $J = 3.5, 3.1$ Hz, H-1'), 4.55–4.23 (m, 5H, H-5, H-4', H-5', 2H-6'), 4.03, 3.99 ($2 \times$ d, $2 \times$ 1H, $J = 14.9$ Hz, CHHCl), 3.93 (dd, 1H, $J = 10.7, 6.2$ Hz, H-6), 3.67 (dd, 1H, $J = 10.7, 2.1$ Hz, H-6), 3.51 (s, 3H, CH₃ OMe), 3.17 (dd, 1H, $J = 10.7, 3.5$ Hz, H-2'), 2.18 (s, 3H, CH₃ OAc). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 169.8 (CO OAc), 166.9 (COCH₂Cl), 165.94 (CO O-3Bz), 165.89 (CO O-2Bz), 165.5 (CO O-4Bz), 133.8, 133.5, 133.3 ($3 \times$ CH_{arom}), 130.1, 130.0, 129.8 ($3 \times$ 2CH_{arom}), 129.5, 129.3, 129.2 ($3 \times$ C_q), 128.7, 128.5, 128.4 ($3 \times$ 2CH_{arom}), 98.0 (d, $^4J = 1.3$ Hz, C-1'), 97.1 (C-1), 87.1 (d, $^1J = 188.9$ Hz, C-4'), 72.2 (C-2), 70.4 (C-3), 69.9 (d, $^2J = 19.3$ Hz, C-3'), 69.5 (C-4), 68.4 (C-5), 67.2 (d, $^2J = 23.5$ Hz, C-5'), 67.0 (C-6), 63.6 (C-6'), 60.8 (d, $^3J = 6.2$ Hz, C-2'), 55.9 (CH₃ OMe), 40.7 (CH₂Cl), 20.9 (CH₃ OAc). ¹⁹F NMR (CDCl₃, 376 MHz): –199.16 (dd, $^2J = 50.2$ Hz, $^3J = 13.6, 3.0$ Hz). HRMS-APCI (m/z): [M – N₂ + H]⁺ calcd for C₃₈H₃₈FCINO₁₄, 786.1959; found, 786.1951. Selected NMR resonances for the β -anomer: ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 4.78/4.54 (d, 1H, $J = 8.3$ /cca10 Hz, H-1'). ¹⁹F NMR (CDCl₃, 376 MHz): –201.79/–201.92 (dd, $^2J = 51.0/50.3$ Hz, $^3J = 13.8/13.5$ Hz).

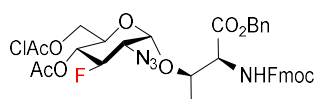
Methyl 4-*O*-(2-azido-3-*O*-acetyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-2,3,6-tri-*O*-benzoyl- α -D-glucopyranoside (D25- α)



Compound **D25- α** was prepared by glycosylation of acceptor **D** with **25** according to the general procedure (6 μ L TfOH). ¹⁹F NMR after aqueous workup revealed the $\alpha/\beta = 1:0$. Preparative TLC chromatography in EtOAc/PE 1:3 afforded unreacted acceptor **D** (15 mg, 36%) and **D25- α** as a colourless gel (38 mg, 46 %, 66 % recalculated on reacted acceptor), R_f 0.2 (EtOAc/heptane 1:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 8.13–8.10 (m, 2H, CH_{arom}), 7.99–7.96 (m, 4H, CH_{arom}), 7.64–7.60 (m, 1H, CH_{arom}), 7.53–7.48 (m, 4H, CH_{arom}), 7.40–7.35 (m, 4H, CH_{arom}), 6.15 (dd, 1H, $J = 10.1, 8.7$ Hz, H-3), 5.54 (ddd, 1H, $J = 12.5, 10.8, 8.8$ Hz, H-3'), 5.27 (dd, 1H, $J = 3.9, 2.9$ Hz, H-1'), 5.16 (d, 1H, $J = 3.6$ Hz, H-1), 5.12 (dd, 1H, $J = 10.1, 3.6$ Hz, H-2), 4.71 (dd, 1H, $J = 12.1, 2.1$ Hz, H-6), 4.60 (dd, 1H, $J = 12.1, 4.7$ Hz, H-6), from ¹H {¹⁹F} 4.41 (dd, 1H, $J = 12.3, 2.2$ Hz, H-6'), 4.43–4.10 (m, 5H, H-4, H-5, H-4', H-5', H-6'), 4.07 (s, 2H, CH₂Cl), 3.46 (s, 3H, CH₃ OMe), 3.12 (ddd, 1H, $J = 10.8, 3.9, 1.0$ Hz, H-2'), 2.1 (s, 3H, CH₃ OAc). ¹³C{¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 169.4 (CO OAc), 166.9 (COCH₂Cl),

166.3 (CO O-6), 166.1 (CO O-2), 165.2 (CO O-3), 133.6, 133.5 ($2 \times \text{CH}_{\text{arom}}$), 133.2 (C_{q}), 130.2, 129.9 ($2 \times 2\text{CH}_{\text{arom}}$), 129.8 (C_{q}), 129.6 (2CH_{arom}), 129.0 (C_{q}), 128.8 (3CH_{arom}), 128.63, 128.54 ($2 \times 2\text{CH}_{\text{arom}}$), 99.2 (d, $^4J = 1.2$ Hz, C-1'), 96.9 (C-1), 86.8 (d, $^1J = 189.4$ Hz, C-4'), 76.7 (C-4), 72.4 (C-3), 72.3 (C-2), 69.7 (d, $^2J = 19.1$ Hz, C-3'), 68.5 (d, $^2J = 23.8$ Hz, C-5'), 68.1 (C-5), 63.5 (C-6), 63.4 (C-6'), 60.5 (d, $^3J = 6.4$ Hz, C-2'), 55.8 ($\text{CH}_3 \text{ OMe}$), 40.7 (CH_2Cl), 20.8 ($\text{CH}_3 \text{ OAc}$). ^{19}F NMR (CDCl_3 , 376 MHz): -199.30 (ddd, $^2J = 50.0$ Hz, $^3J = 12.5$, 5.5 Hz, $^5J = 2.9$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{38}\text{FCINO}_{14}$, 786.1959; found, 786.1958.

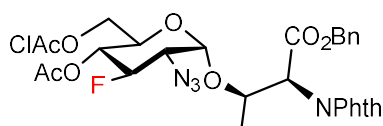
***N*-[(9*H*-fluoren-9-yl)-methoxycarbonyl]-*O*-(2-azido-4-*O*-acetyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester (**28**)**



Compound **28** was prepared by glycosylation of *N*-[(9*H*-fluoren-9-yl)-methoxycarbonyl]-L-threonine benzyl ester (111 mg, 0.26 mmol) with **16** (73 mg, 0.17 mmol) following the general procedure (12 μL TfOH; 75 mg NIS, 0.33 mmol; 3 mL DCM/ Et_2O 1:1). ^{19}F NMR after aqueous workup revealed the $\alpha/\beta = 2.1:1$. Column chromatography in EtOAc/PE 1:3 $\rightarrow$ 1:1 followed by preparative TLC chromatography in EtOAc/PE 1:3 afforded **28- α** as yellowish crystals (35 mg, 28%), R_f 0.17 (ethyl acetate/heptane 1:3). The β -anomer was obtained under these conditions as an inseparable mixture with unreacted acceptor (28 mg). Data for **28- α** : R_f 0.17 (EtOAc/heptane 1:3), mp 139–140 $^\circ\text{C}$ (EtOAc/heptane). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.78, 7.61 ($2 \times \text{d}$, $2 \times 2\text{H}$, $J = 7.6$ Hz, CH_{arom}), 7.43–7.29 (m, 9H, CH_{arom}), 5.64 (d, 1H, $J = 9.4$ Hz, NH), 5.27, 5.21 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 12.0$ Hz, CHH Bn), 5.12 (ddd, 1H, $J = 12.6$, 10.3, 8.9 Hz, H-4), 4.81 (ddd, 1H, $J = 53.0$, 10.3, 8.9 Hz, H-3), 4.80 (dd, 1H, $J = 3.8$, 3.3 Hz, H-1), 4.51–4.44 (m, 2H, CHNH, COOCHHCH), 4.41 (dd, 1H, $J = 6.5$, 2.3 Hz, CHMe), 4.36 (dd, 1H, $J = 10.6$, 7.4 Hz, COOCHHCH), 4.30 (dd, 1H, $J = 12.3$, 5.2 Hz, H-6), 4.25 (dd, 1H, $J = 7.9$, 7.4 Hz, 1H, COOCH₂CH), 4.20 (ddd, 1H, $J = 12.3$, 2.3, 1.5 Hz, H-6'), 4.08 (s, 2H, CH_2Cl), 3.97 (ddd, 1H, $J = 10.3$, 5.2, 2.3 Hz, H-5), 3.40 (ddd, 1H, $J = 11.0$, 10.0, 3.8 Hz, H-2), 2.15 (s, 3H, Me OAc), 1.30 (d, 3H, $J = 6.5$ Hz, CHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 170.0 (COOBn), 169.6 (CO OAc), 167.1 (COCH₂Cl), 156.8 (COOCH₂CH), 144.0, 143.8, 141.5, 141.4, 135.0 ($5 \times \text{C}_{\text{q}}$), 128.9 (3CH_{arom}), 128.8, 127.9 ($2 \times 2\text{CH}_{\text{arom}}$), 127.3, 127.2, 125.3, 125.2, 120.2, 120.1 ($6 \times \text{CH}_{\text{arom}}$), 98.7 (d, $^3J = 9.4$ Hz, C-1), 90.0 (d, $^1J = 188.3$ Hz, C-3), 77.4 (CHMe), 68.3 (d, $^2J = 18.6$ Hz, C-4), 68.0 ($\text{CH}_2 \text{ Bn}$), 67.9 (d, $^3J = 6.9$ Hz, C-5), 67.5 (COOCH₂CH), 63.5 (d, $^4J = 1.6$ Hz, C-6), 61.9 (d, $^2J = 16.8$ Hz, C-2), 58.7

(CHNH), 47.3 (COOCH₂CH), 40.7 (CH₂Cl), 20.8 (Me OAc), 18.8 (CHMe). ¹⁹F NMR (CDCl₃, 376 MHz): −197.65 (dddd, ²*J* = 53.0 Hz, ³*J* = 12.6, 11.0 Hz, ⁴*J*_(H-F) = 3.3 Hz). HRMS-APCI (*m/z*): [M − N₂ + H]⁺ calcd for C₃₆H₃₇ClFN₂O₁₀, 711.2115; found, 711.2112. Data for the β-anomer: *R*_f 0.15 (ethyl acetate/heptane 1:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.77, 7.61 (2 × d, 2 × 2H, *J* = 7.6 Hz, CH_{arom}), 7.43–7.29 (m, 9H, CH_{arom}), 5.61 (d, 1H, *J* = 8.8 Hz, NH), 5.24, 5.20 (2 × d, 2 × 1H, *J* = 12.3 Hz, CHH Bn), 5.04 (ddd, 1H, *J* = 12.5, 9.9, 8.9 Hz, H-4), 4.55–4.52 (m, 2H, MeCHCHNH), 4.46–4.38 (m, 2H, COOCH₂CH), 4.25–4.03 (m, 4H, H-3, 2H-6, COOCH₂CH), 4.23 (d, 1H, *J* = 8.0 Hz, H-1), 4.01 (s, 2H, CH₂Cl), 3.42 (ddd, 1H, *J* = 12.9, 9.7, 8.0 Hz, H-2), 3.29 (ddd, 1H, *J* = 9.9, 4.8, 2.0 Hz, H-5), 2.12 (s, 3H, Me OAc), 1.33 (d, 3H, *J* = 6.2 Hz, CHMe). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 169.9 (COOBn), 169.5 (CO OAc), 167.2 (COCH₂Cl), 156.8 (COOCH₂CH), 143.8, 143.7, 141.44, 141.42, 135.5 (5 × C_q), 128.82 (3CH_{arom}), 128.79, 128.7 (2 × 2CH_{arom}), 128.6, 128.4, 127.9, 127.2, 125.3, 120.1 (6 × CH_{arom}), 99.1 (d, ³*J* = 10.6 Hz, C-1), 91.4 (d, ¹*J* = 190.8 Hz, C-3), 75.4 (CHMe), 70.7 (d, ³*J* = 8.0 Hz, C-5), 68.0 (d, ²*J* = 18.9 Hz, C-4), 67.5 (CH₂ Bn), 67.4 (COOCH₂CH), 64.0 (d, ²*J* = 17.3 Hz, C-2), 63.1 (C-6), 58.4 (CHNH), 47.2 (COOCH₂CH), 40.7 (CH₂Cl), 20.8 (Me OAc), 16.8 (CHMe). ¹⁹F NMR (CDCl₃, 376 MHz): −192.92 (dt, ²*J* = 51.3 Hz, ³*J* = 12.9 Hz). HRMS-APCI (*m/z*): [M − N₂ + H]⁺ calcd for C₃₆H₃₇ClFN₂O₁₀, 711.2115; found, 711.2119.

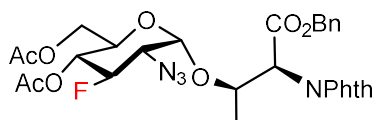
***N*-Phthaloyl-*O*-(2-azido-4-*O*-acetyl-6-*O*-chloroacetyl-2,3-dideoxy-3-fluoro-α-*D*-glucopyranosyl)-*L*-threonine benzyl ester (**29**)**



Compound **29** was prepared by glycosylation of *N*-phthaloyl-*L*-threonine benzyl ester with **16** according to the general procedure (8 μL TfOH). ¹⁹F NMR after aqueous work-up revealed α/β = 5.1/1.0. Column chromatography in toluene/Et₂O/PE 2:2:3 followed by preparative TLC in toluene/Et₂O/PE 2:2:3 afforded the α-anomer **29** as colourless syrup (47 mg, 71%), and a syrupy mixture of both anomers (5 mg), *R*_f 0.1 (toluene/Et₂O/PE 2:2:3). Data for **29**: *R*_f 0.12 (toluene/Et₂O/PE 2:2:3). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.89, 7.73 (2 × dd, 2 × 2H, *J* = 5.4, 3.1 Hz, CH_{arom}), 7.32–7.24 (m, 5H, CH_{arom}), 5.20, 5.15 (2 × d, 2 × 1H, *J* = 12.3 Hz, CHH Bn), 5.03 (ddd, 1H, *J* = 12.8, 10.3, 9.0 Hz, H-4), 4.87 (dd, 1H, *J* = 3.8, 3.4 Hz, H-1), 4.80 (d, 1H, *J* = 9.5 Hz, CHCOOBn), 4.60 (ddd, 1H, *J* = 53.2, 10.4, 9.5 Hz, H-3), 4.57 (dd, 1H, *J* = 9.5, 6.1 Hz, CHMe), 4.28 (dd, 1H, *J* = 12.3, 5.4 Hz, H-

6'), 4.17 (ddd, 1H, $J = 12.3, 2.3, 1.3$ Hz, H-6), 4.09, 4.05 ($2 \times$ d, $2 \times$ 1H, $J = 14.7$ Hz, CHHCl), 4.01 (ddd, 1H, $J = 10.3, 5.4, 2.3$ Hz, H-5), 3.45 (ddd, 1H, $J = 11.4, 9.8, 3.8$ Hz, H-2), 2.09 (s, 3H, Me OAc), 1.54 (d, 3H, $J = 6.1$ Hz, CHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 169.6 (CO OAc), 167.9 (2CO), 167.2, 167.1 ($2 \times$ CO), 135.0 (C_q), 134.3 (2CH_{arom}), 132.2 (2C_q), 128.7 (2CH_{arom}), 128.6 (CH_{arom}), 128.3 123.5 ($2 \times 2\text{CH}_{\text{arom}}$), 99.4 (d, $^3J = 9.5$ Hz, C-1), 91.2 (d, $^1J = 187.2$ Hz, C-3), 75.6 (CHMe), 68.2 (d, $^2J = 15.9$ Hz, C-4), 67.83 (d, $^3J = 6.5$ Hz, C-5), 67.80 (CH_2 Bn), 63.6 (d, $^4J = 1.5$ Hz, C-6), 62.2 (d, $^2J = 16.5$ Hz, C-2), 56.2 (CHCOOBn), 40.7 (CH_2Cl), 21.1 (CHMe), 20.8 (Me OAc). ^{19}F NMR (CDCl_3 , 376 MHz): δ -197.34 (dddt, $^2J = 53.2$ Hz, $^3J = 12.8, 11.4$ Hz, $^4J = 3.4$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{29}\text{ClF}_2\text{N}_2\text{O}_{10}$, 619.1489 ; found, 619.1487. NMR data for the β -anomer: ^1H NMR (CDCl_3 , 400 MHz, $^1\text{H}\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.81, 7.74 ($2 \times$ dd, $2 \times$ 2H, $J = 5.4, 3.1$ Hz, CH_{arom}), 7.40–7.28 (m, 5H, CH_{arom}), 5.19, 5.14 ($2 \times$ d, $2 \times$ 1H, $J = 12.2$ Hz, CHH Bn), 4.84 (d, 1H, $J = 9.7$ Hz, CHCOOBn), 4.72 (ddd, 1H, $J = 12.6, 10.2, 9.0$ Hz, H-4), 4.56 (dd, 1H, $J = 9.7, 6.2$ Hz, CHMe), 4.21 (dd, 1H, $J = 8.1, 0.9$ Hz, H-1), 4.18 (ddd, 1H, $J = 51.0, 9.6, 9.0$ Hz, H-3), 4.15, 3.85 ($2 \times$ d, $2 \times$ 1H, $J = 15.3$ Hz, CHHCl), 3.77–3.70 (m, 2H, H-6), 3.40 (ddd, 1H, $J = 10.2, 5.1, 2.8$ Hz, H-5), 3.32 (ddd, 1H, $J = 13.1, 9.6, 8.1$ Hz, H-2), 2.02 (s, 3H, Me OAc), 1.59 (d, 3H, $J = 6.2$ Hz, CHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 169.5 (CO OAc), 167.4 (2CO), 167.3, 167.1 ($2 \times$ CO), 135.9 (C_q), 134.3 (2CH_{arom}), 132.0 (2C_q), 129.1 (2CH_{arom}), 128.7 (CH_{arom}), 128.4 123.6 ($2 \times 2\text{CH}_{\text{arom}}$), 100.5 (d, $^3J = 10.6$ Hz, C-1), 91.7 (d, $^1J = 190.7$ Hz, C-3), 74.5 (CHMe), 70.4 (d, $^3J = 8.2$ Hz, C-5), 67.9 (d, $^2J = 13.4$ Hz, C-4), 67.70 (CH_2 Bn), 63.9 (d, $^2J = 17.3$ Hz, C-2), 63.5 (d, $^4J = 1.6$ Hz, C-6), 55.9 (CHCOOBn), 40.9 (CH_2Cl), 20.7 (CHMe), 19.3 (Me OAc). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.80 (ddd, $^2J = 51.0$ Hz, $^3J = 13.1, 12.6$ Hz).

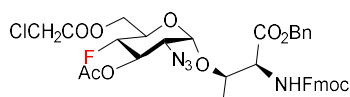
***N*-Phthaloyl-*O*-(2-azido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester (30)**



Compound **30** was prepared by glycosylation of *N*-phthaloyl-L-threonine benzyl ester (110 mg, 0.32 mmol) with **17** (150 mg, 0.39 mmol) according to the general procedure (25 μL TfOH, 0.28 mmol; 175 mg NIS, 0.78 mmol; 7 mL DCM/Et₂O 1:1) with the exception of the reaction temperature being set to 0 °C. ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 7.4/1.0$. Column chromatography in EtOAc/PE 1:3 afforded α -anomer **30** as a yellowish syrup (133

mg, 67%), followed by a mixture of both anomers and then β -anomer as a yellowish syrup (15 mg). Data for **30**: R_f 0.25 (EtOAc/PE 1:3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.88, 7.73 ($2 \times \text{dd}$, $2 \times 2\text{H}$, $J = 5.5, 3.0$ Hz, CH_{arom}), 7.33–7.24 (m, 5H, CH_{arom}), 5.20, 5.15 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 12.3$ Hz, CHH Bn), 5.04 (ddd, 1H, $J = 12.7, 10.3, 9.0$ Hz, H-4), 4.86 (dd, 1H, $J = 3.8, 3.5$ Hz, H-1), 4.80 (d, 1H, $J = 9.6$ Hz, CHCOOBn), 4.59 (ddd, 1H, $J = 52.8, 9.8, 9.0$ Hz, H-3), 4.57 (dq, 1H, $J = 9.7, 6.0$ Hz, CHMe), 4.19 (dd, 1H, $J = 12.3, 5.4$ Hz, H-6), 4.05 (ddd, 1H, $J = 12.3, 2.3, 1.3$ Hz, H-6'), 3.98 (ddd, 1H, $J = 10.3, 5.4, 2.3$ Hz, H-5), 3.46 (ddd, 1H, $J = 11.5, 9.8, 3.8$ Hz, H-2), 2.09, 2.05 ($2 \times \text{s}$, $2 \times 3\text{H}$, Me Ac), 1.54 (d, 3H, $J = 6.1$ Hz, CHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 170.6, 169.6 ($2 \times \text{CO Ac}$), 167.9 (2CO), 167.2 (CO), 135.0 (C_q), 134.2 (2CH_{arom}), 132.2 (2C_q), 128.7 (2CH_{arom}), 128.6 (CH_{arom}), 128.3, 123.4 ($2 \times 2\text{CH}_{\text{arom}}$), 99.5 (d, $^3J = 9.6$ Hz, C-1), 91.4 (d, $^1J = 187.1$ Hz, C-3), 75.5 (CHMe), 68.3 (d, $^2J = 18.2$ Hz, C-4), 68.0 (d, $^3J = 6.9$ Hz, C-5), 67.8 ($\text{CH}_2 \text{Bn}$), 62.3 (d, $^2J = 16.5$ Hz, C-2), 62.0 (d, $^4J = 1.5$ Hz, C-6), 56.2 (CHCOOBn), 21.0 (CHMe), 20.78, 20.77 ($2 \times \text{Me OAc}$). ^{19}F NMR (CDCl_3 , 376 MHz): δ -197.27 (dddd, $^2J = 52.8$ Hz, $^3J = 12.7, 11.5$ Hz, $^4J = 3.3$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{30}\text{FN}_2\text{O}_{10}$, 585.1879; found, 585.1879. Data for the β -anomer: R_f 0.2, EtOAc/PE 1:3. ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC) δ 7.82, 7.72 ($2 \times \text{dd}$, $2 \times 2\text{H}$, $J = 5.5, 3.1$ Hz, CH_{arom}), 7.30–7.24 (m, 5H, CH_{arom}), 5.20, 5.13 ($2 \times \text{d}$, $2 \times 1\text{H}$, $J = 12.3$ Hz, CHH Bn), 4.85 (d, 1H, $J = 9.7$ Hz, CHCOOBn), 4.76 (ddd, 1H, $J = 12.6, 10.1, 9.0$ Hz, H-4), 4.58 (dq, 1H, $J = 9.7, 6.1$ Hz, CHMe), 4.21 (d, 1H, $J = 8.1$ Hz, H-1), 4.17 (ddd, 1H, $J = 51.0, 9.7, 9.0$ Hz, H-3), 3.69 (dd, 1H, $J = 12.2, 5.3$ Hz, H-6), 3.58 (ddd, 1H, $J = 12.3, 2.4, 1.2$ Hz, H-6'), 3.40–3.31 (m, 2H, H-2, H-5), 2.01, 1.94 ($2 \times \text{s}$, $2 \times 3\text{H}$, Me Ac), 1.59 (d, 3H, $J = 6.1$ Hz, CHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 170.7, 169.4 ($2 \times \text{CO Ac}$), 167.4 (2CO), 167.1 (CO), 135.1 (C_q), 134.2 (2CH_{arom}), 132.1 (2C_q), 128.7 (2CH_{arom}), 128.6 (CH_{arom}), 128.4, 123.6 ($2 \times 2\text{CH}_{\text{arom}}$), 100.5 (d, $^3J = 10.6$ Hz, C-1), 91.9 (d, $^1J = 190.7$ Hz, C-3), 74.6 (CHMe), 70.7 (d, $^3J = 8.0$ Hz, C-5), 68.0 (d, $^2J = 18.7$ Hz, C-4), 67.7 ($\text{CH}_2 \text{Bn}$), 64.1 (d, $^2J = 17.3$ Hz, C-2), 61.9 (d, $^4J = 1.8$ Hz, C-6), 56.0 (CHCOOBn), 21.0, 20.7 ($2 \times \text{Me OAc}$), 19.3 (CHMe). ^{19}F NMR (CDCl_3 , 376 MHz): δ -192.80 (ddd, $^2J = 51.1$ Hz, $^3J = 13.0, 12.6$ Hz).

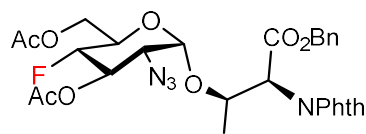
***N*-[(9*H*-fluoren-9-yl)-methoxycarbonyl]-*O*-(2-azido-3-*O*-acetyl-6-*O*-chloroacetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester (**31**)**



Compound **31** was prepared by glycosylation of *N*-[(9*H*-fluoren-9-yl)-methoxycarbonyl]-L-threonine benzyl ester (54 mg, 0.13 mmol) with **25** (56 mg, 0.13 mmol) according to the general procedure (9 μ L TfOH; 55 mg NIS, 0.24 mmol). ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 6.6:1.0$. Preparative TLC in EtOAc/PE 1:3 afforded **31** as a yellowish syrup (51 mg, 53%, with inseparable side-products detected in ^{19}F NMR, approx. 17%) and the mixture of anomers as a yellowish syrup (10 mg), R_f 0.22 (EtOAc/heptane 1:3). Data for **31**: R_f 0.25 (ethyl acetate/heptane 1:3). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.78, 7.62 (2 $\times$ d, 2 $\times$ 2H, $J = 7.5$ Hz, CH_{arom}), 7.42–7.28 (m, 9H, CH_{arom}), 5.71 (d, 1H, $J = 9.5$ Hz, *NH*), 5.55 (ddd, 1H, $J = 13.3, 10.8, 8.8$ Hz, H-3), 5.28, 5.17 (2 $\times$ d, 2 $\times$ 1H, $J = 12.0$ Hz, *CHH* Bn), 5.27 (dd, 1H, $J = 3.9, 3.1$ Hz, H-1), 4.52–4.28 (m, 7H, *MeCHCHNH*, *COOCHHCH*, H-4, 2H-6), 4.25 (t, 1H, $J = 7.3$ Hz, 1H, *COOCH₂CH*), 4.13–4.09 (m, 1H, H-5), 4.09 (s, 2H, CH_2Cl), 3.12 (ddd, 1H, $J = 10.8, 3.9, 0.8$ Hz, H-2), 2.19 (s, 3H, CH_3 OAc), 1.34 (d, 3H, $J = 6.4$ Hz, *CHMe*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 170.0 (*COOBn*), 169.8 (*CO* OAc), 167.0 (*COCH₂Cl*), 156.9 (*COOCH₂CH*), 144.0, 143.9, 141.44, 141.40, 135.0 (5 $\times$ C_q), 128.84, 128.82, 128.80, 127.9, 127.3 (5 $\times$ 2 CH_{arom}), 125.4, 120.11, 120.09 (3 $\times$ CH_{arom}), 98.7 (C-1), 87.2 (d, $^1J = 189.1$ Hz, C-4), 77.0 (*CHMe*), 69.7 (d, $^2J = 19.2$ Hz, C-3), 67.9 (CH_2 Bn), 67.8 (*COOCH₂CH*), 67.6 (d, $^2J = 23.2$ Hz, C-5), 63.6 (C-6), 61.1 (d, $^3J = 6.1$ Hz, C-2), 58.8 (*CHNH*), 47.2 (*COOCH₂CH*), 40.6 (CH_2Cl), 20.9 (CH_3 OAc), 18.8 (*CHMe*). ^{19}F NMR (CDCl_3 , 376 MHz): -199.04 (dd, $^2J = 50.8$ Hz, $^3J = 13.5$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{37}\text{ClFN}_2\text{O}_{10}$, 711.2115; found, 711.2110. NMR data for the β -anomer: ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC, HMBC) δ 7.76, 7.60 (2 $\times$ d, 2 $\times$ 2H, $J = 7.6$ Hz, CH_{arom}), 7.40–7.27 (m, 9H, CH_{arom}), 5.58 (d, 1H, $J = 9.6$ Hz, *NH*), 5.21, 5.17 (2 $\times$ d, 2 $\times$ 1H, $J = 12.2$ Hz, *CHH* Bn), 4.97 (ddd, 1H, $J = 13.8, 10.5, 8.9$ Hz, H-3), 4.57–4.20 (m, 8H, *MeCHCHNH*, *COOCHHCH*, H-4, 2H-6), 4.40 (d, 1H, $J = 7.9$ Hz, H-1), 4.09 (s, 2H, CH_2Cl), 3.38 (ddd, 1H, $J = 10.0, 4.7, 2.1$ Hz, H-5), 3.31 (dd, 1H, $J = 10.5, 7.9$ Hz, H-2), 2.17 (s, 3H, CH_3 OAc), 1.33 (d, 3H, $J = 6.4$ Hz, *CHMe*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC, HMBC): δ 169.9 (*COOBn*), 169.6 (*CO* OAc), 167.0 (*COCH₂Cl*), 156.8 (*COOCH₂CH*), 144.1, 143.8, 141.5, 141.4, 135.0 (5 $\times$ C_q), 128.9, 128.8, 128.6, 127.9, 127.2 (5 $\times$ 2 CH_{arom}), 125.3, 121.8, 120.3 (3 $\times$ CH_{arom}), 99.6 (C-1), 86.7 (d, $^1J = 187.9$ Hz, C-4), 75.5 (*CHMe*), 71.3 (d, $^2J = 20.0$ Hz, C-3), 71.0 (d, $^2J = 23.8$ Hz, C-5), 67.53, 67.52 (CH_2 Bn/ *COOCH₂CH*), 63.3 (d, $^3J = 7.9$ Hz, C-2), 63.3 (C-6), 58.3 (*CHNH*), 47.2 (*COOCH₂CH*), 40.7 (CH_2Cl), 20.9 (CH_3 OAc), 17.0 (*CHMe*). ^{19}F NMR (CDCl_3 , 376 MHz): -202.14 (dd, $^2J = 50.5$ Hz, $^3J = 13.8$ Hz).

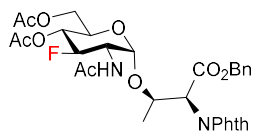
***N*-Phthaloyl-*O*-(2-azido-3,6-di-*O*-acetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester**

(32)



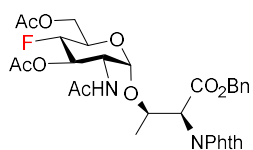
Compound **32** was prepared by glycosylation of *N*-phthaloyl-L-threonine benzyl ester (78 mg, 0.23 mmol) with **26** (107 mg, 0.28 mmol) according to the general procedure (20 μ L TfOH, 0.23 mmol; 130 mg NIS, 0.58 mmol) with the exception of the reaction temperature being set to 0 °C. ^{19}F NMR after aqueous work-up revealed $\alpha/\beta = 18.0/1.0$. Column chromatography in EtOAc/PE 1:3 followed by recrystallization from EtOAc/heptane afforded **32** as white crystals (69 mg, 49 %), R_f 0.25 (Et₂O/PE 3:2), mp 133–135 °C (EtOAc/heptane). ^1H NMR (CDCl₃, 400 MHz, ^1H { ^{19}F }, H-H COSY, HSQC, HMBC) δ 7.87, 7.71 (2 $\times$ dd, 2 $\times$ 2H, $J = 5.5, 3.0$ Hz, CH_{arom}), 7.30–7.24 (m, 5H, CH_{arom}), 5.32 (ddd, 1H, $J = 12.9, 10.5, 8.8$ Hz, H-3), 5.20, 5.14 (2 $\times$ d, 2 $\times$ 1H, $J = 12.3$ Hz, CHH Bn), 4.89 (dd, 1H, $J = 3.8, 3.4$ Hz, H-1), 4.85 (d, 1H, $J = 9.3$ Hz, CHCOOBn), 4.63 (dq, 1H, $J = 9.3, 6.1$ Hz, CHMe), from ^1H { ^{19}F } 4.31 (dd, 1H, $J = 12.1, 2.3$ Hz, H-6), from ^1H { ^{19}F } 4.26 (dd, 1H, $J = 10.0, 8.8$ Hz, H-4), from ^1H { ^{19}F } 4.21 (dd, 1H, $J = 12.1, 5.4$ Hz, H-6'), from ^1H { ^{19}F } 4.12 (ddd, 1H, $J = 10.0, 5.4, 2.3$ Hz, H-5), 3.30 (ddd, 1H, $J = 10.5, 3.8, 1.0$ Hz, H-2), 2.07, 2.02 (2 $\times$ s, 2 $\times$ 3H, Me Ac), 1.57 (d, 3H, $J = 6.1$ Hz, CHMe). ^{13}C { ^1H } NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 170.6, 169.2 (2 $\times$ CO Ac), 167.8 (2CO), 167.4 (CO), 135.1 (C_q), 134.1 (2CH_{arom}), 132.2 (2C_q), 128.7 (2CH_{arom}), 128.6 (CH_{arom}), 128.3, 123.5 (2 $\times$ 2CH_{arom}), 98.9 (C-1), 87.4 (d, $^1J = 189.0$ Hz, C-4), 74.9 (CHMe), 70.9 (d, $^2J = 19.3$ Hz, C-3), 67.8 (CH₂ Bn), 67.7 (d, $^2J = 23.2$ Hz, C-5), 62.2 (C-6), 61.3 (d, $^3J = 6.6$ Hz, C-2), 56.3 (CHCOOBn), 21.0 (CHMe), 20.8, 20.7 (2 $\times$ Me OAc). ^{19}F NMR (CDCl₃, 376 MHz): δ -199.45 (dd, $^2J_{(\text{H-F})} = 50.5$ Hz, $^3J_{(\text{H-F})} = 12.9$ Hz). HRMS-APCI (m/z): $[\text{M} - \text{N}_2 + \text{H}]^+$ calcd for C₂₉H₃₀FN₂O₁₀, 585.1879; found, 585.1871. Selected NMR resonances for the β -anomer: ^1H NMR (CDCl₃, 400 MHz, ^1H { ^{19}F }, H-H COSY, HSQC, HMBC) δ 5.75 (p, 1H, $J = 6.3$ Hz, CHMe), 5.58 (d, 1H, $J = 8.5$ Hz, H-1), 5.26, 5.13 (2 $\times$ d, 2 $\times$ 1H, $J = 12.2$ Hz, CHH Bn), 4.92 (d, 1H, $J = 6.3$ Hz, CHCOOBn), from ^1H { ^{19}F } 4.44 (dd, 1H, $J = 9.9, 8.9$ Hz, H-4), 3.84 (ddt, 1H, $J = 9.9, 4.9, 2.5$ Hz, H-5), 3.60 (ddd, 1H, $J = 10.3, 8.5, 0.9$ Hz, H-2), 1.39 (d, 3H, $J = 6.3$ Hz, CHMe). ^{19}F NMR (CDCl₃, 376 MHz): δ -202.01 (dd, $^2J_{(\text{H-F})} = 50.2$ Hz, $^3J_{(\text{H-F})} = 13.6$ Hz).

***N*-Phthaloyl-*O*-(2-acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-3-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester (**33**)**



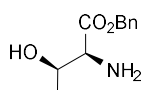
Azide **30** (90 mg, 0.15 mmol) was dissolved in THF (4.5 mL) under argon atmosphere. Zn (300 mg, 4.59 mmol), AcOH (1.5 mL, 26 mmol), and Ac₂O (0.9 mL, 9.5 mmol) were added sequentially, and the reaction mixture was stirred at rt for 4 hours when TLC in EtOAc/PE 3:2 indicated the absence of the starting material and formation of the product. The reaction was diluted with saturated aqueous NaHCO₃, the water phase was extracted with EtOAc (3×), the organic extracts were combined, dried, concentrated and the residue co-distilled with toluene (3×). Column chromatography in EtOAc/PE 3:2 afforded **33** (50 mg, 54 %) as colourless gum, *R*_f 0.3 (EtOAc/PE 3:2). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.81, 7.74 (2 × dd, 2 × 2H, *J* = 5.4, 3.1 Hz, CH_{arom}), 7.40 (d, 1H, *J* = 9.6 Hz, NH), 7.33–7.23 (m, 5H, CH_{arom}), 5.20 (dd, 1H, *J* = 3.9, 3.3 Hz, H-1), 5.16 (d, 1H, *J* = 12.0 Hz, CHH Bn), 5.13 (ddd, 1H, *J* = 12.0, 10.4, 9.0 Hz, H-4), 5.12 (d, 1H, *J* = 12.0 Hz, CHH Bn), 4.86 (d, 1H, *J* = 1.9 Hz, CHCOOBn), 4.65 (qd, 1H, *J* = 6.6, 1.9 Hz, CHMe), 4.52 (dddd, 1H, *J* = 12.0, 10.3, 9.6, 3.9 Hz, H-2), 4.38 (ddd, 1H, *J* = 52.4, 10.3, 9.0 Hz, H-3), 4.13 (dd, 1H, *J* = 12.3, 5.1 Hz, H-6), 4.08 (ddd, 1H, *J* = 12.3, 2.7, 1.5 Hz, H-6'), 3.83 (ddd, 1H, *J* = 10.4, 5.1, 2.7 Hz, H-5), 2.11, 2.05, 2.03 (3 × s, 3 × 3H, Me Ac), 1.22 (d, 3H, *J* = 6.6 Hz, CHMe). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 170.8, 170.7, 169.3 (3 × CO Ac), 168.0 (2CO), 166.8 (2 × CO), 134.9 (2CH_{arom}), 134.5 (C_q), 131.7 (2C_q), 129.0 (CH_{arom}), 128.9, 128.8, 124.1 (3 × 2CH_{arom}), 101.2 (d, ³*J* = 9.8 Hz, C-1), 90.8 (d, ¹*J* = 189.3 Hz, C-3), 76.3 (CHMe), 69.0 (d, ²*J* = 18.3 Hz, C-4), 68.2 (d, ³*J* = 7.0 Hz, C-5), 68.2 (CH₂ Bn), 62.3 (d, ⁴*J* = 1.7 Hz, C-6), 57.1 (CHCOOBn), 51.5 (d, ²*J* = 17.6 Hz, C-2), 23.3 (Me OAc), 20.8 (2Me OAc), 19.5 (CHMe). ¹⁹F NMR (CDCl₃, 376 MHz): δ -200.04 (dtd, ²*J* = 52.4 Hz, ³*J* = 12.0 Hz, ⁴*J* = 3.3 Hz). HRMS-APCI (*m/z*): [M + H]⁺ calcd for C₃₁H₃₄FN₂O₁₁, 629.2141; found, 629.2141.

***N*-Phthaloyl-*O*-(2-acetamido-3,6-di-*O*-acetyl-2,4-dideoxy-4-fluoro- α -D-glucopyranosyl)-L-threonine benzyl ester (**34**)**



Azide **34** (55 mg, 0.09 mmol) was dissolved in pyridine (1 mL) under an argon atmosphere, AcSH (1 mL, 14 mmol) was added and the reaction was stirred at rt overnight. TLC EtOAc/PE 3:2 indicated the absence of the starting material and formation of the product. The reaction was diluted with saturated aqueous NaHCO₃, the water phase was extracted with dichloromethane (3×), the organic extracts were combined, dried, concentrated and the residue co-distilled with toluene (3×). Column chromatography in EtOAc/PE 3:2 afforded **34** (47 mg, 83%) as a white foam, *R_f* 0.2 (EtOAc/PE 3:2). ¹H NMR (CDCl₃, 400 MHz, ¹H {¹⁹F}, H-H COSY, HSQC, HMBC) δ 7.96, 7.80 (2 × dd, 2 × 2H, *J* = 5.5, 3.1 Hz, CH_{arom}), 7.33 (d, 1H, *J* = 9.6 Hz, NH), 7.31–7.29 (m, 3H, CH_{arom}), 7.24–7.21 (m, 2H, CH_{arom}), 5.22–5.16 (m, 2H, H-1, H-3), 5.14, 5.10 (2 × d, 2 × 1H, *J* = 12.0 Hz, CHH Bn), 4.84 (d, 1H, *J* = 1.8 Hz, CHCOOBn), 4.67 (qd, 1H, *J* = 6.6, 1.8 Hz, CHMe), 4.42 (ddd, 1H, *J* = 51.0, 10.0, 9.0 Hz, H-4), 4.38–4.30 (m, 2H, H-2, H-6), 4.17 (ddd, 1H, *J* = 12.1, 5.4, 1.5 Hz, H-6), 3.96 (ddd, 1H, *J* = 10.0, 5.4, 2.2 Hz, H-5), 2.10, 2.07, 2.05 (2 × s, 2 × 3H, Me Ac), 1.25 (d, 3H, *J* = 6.6 Hz, CHMe). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 170.8, 170.73, 170.65 (3 × CO Ac), 168.1 (2CO), 167.0 (CO), 134.9 (2CH_{arom}), 134.6 (C_q), 131.7 (2C_q), 128.9 (CH_{arom}), 128.8, 128.7, 124.2 (3 × 2CH_{arom}), 98.9 (d, ⁴*J* = 1.5 Hz, C-1), 87.2 (d, ¹*J* = 186.7 Hz, C-4), 76.1 (CHMe), 71.2 (d, ²*J* = 18.0 Hz, C-3), 68.04 (CH₂ Bn), 67.95 (d, ²*J* = 23.2 Hz, C-5), 62.4 (C-6), 56.9 (CHCOOBn), 51.1 (d, ³*J* = 7.4 Hz, C-2), 23.2, 21.0, 19.6 (3 × Me OAc), 21.0 (CHMe). ¹⁹F NMR (CDCl₃, 376 MHz): δ –198.61 (dd, ²*J*_(H-F) = 51.0 Hz, ³*J*_(H-F) = 14.0 Hz). HRMS-APCI (*m/z*): [M – N₂ + H]⁺ calcd for C₃₁H₃₄FN₂O₁₁, 629.2141; found, 629.2144.

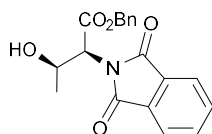
L-Threonine benzyl ester



It was prepared by a modification of the reported procedure.⁷ A solution of L-threonine (2.0 g, 16.8 mmol), *p*-toluenesulfonic acid monohydrate (3.55 g, 18.6 mmol) and benzyl alcohol (25 mL, 242 mmol) in benzene (80 mL) was refluxed for 36 h under Dean-Stark apparatus. Benzene was removed under reduced pressure, the residue dissolved in EtOAc (50 mL) and extracted with water (3×50 mL). The water phase was saturated by NaHCO₃ and the liberated amine was extracted to EtOAc (5×40 mL). EtOAc was removed under reduced pressure, the residue dissolved in Et₂O and the product was precipitated as hydrochloride by addition of hydrogen chloride solution in cyclopentyl methyl ether. The precipitate was filtered off, dissolved in water, the water solution saturated by NaHCO₃, and the liberated amine extracted to EtOAc (5×40 mL), dried and concentrated. Recrystallization

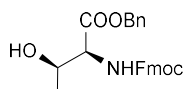
(Et₂O/PE) afforded the product as a white solid (0.8 g, 23%), mp 58–61 °C, HRMS-APCI (*m/z*): [M + H]⁺ calcd for C₁₁H₁₆NO₃, 210.1124; found, 210.1127. NMR spectra were comparable to those in ref.⁷

***N*-Phthaloyl-L-threonine benzyl ester (Phth-Thr-OBn)**



A solution of L-threonine benzyl ester (0.50 g, 2.39 mmol) and phthalic anhydride (460 mg, 3.11 mmol) in benzene (70 mL) was refluxed for 20 h until TLC (dichloromethane/methanol 20:1, visualization by KMnO₄ staining solution) indicated the absence of the starting compound. The reaction was concentrated, the residue dissolved in EtOAc, the resulting solution washed with saturated aqueous NaHCO₃. The water phase was extracted with EtOAc (3×) and the organic extracts were combined, dried, and concentrated. Chromatography in EtOAc/PE 1:2 furnished **Phth-Thr-OBn**⁸ (480 mg, 59 %) as a colourless syrup. ¹H NMR (CDCl₃, 400 MHz, H-H COSY, HSQC) δ 7.91–7.89, 7.79–7.77 (2 × m, 2 × 2H, CH_{arom}), 7.35–7.32 (m, 5H, CH_{arom}), 5.25, 5.21 (2 × d, 2 × 1H, *J* = 12.5 Hz, CHH Bn), 5.04 (d, 1H, *J* = 4.2 Hz, CHCOOBn), 4.70 (ddd, 1H, *J* = 10.4, 6.6, 4.2 Hz, CHMe), 4.15 (d, 1H, *J* = 10.4 Hz, OH), 1.22 (d, 3H, *J* = 6.6 Hz, CHMe). ¹³C {¹H} NMR (CDCl₃, 101 MHz, HSQC): δ 168.9, 167.9 (2 × CO), 135.2 (C_q), 134.8 (2CH_{arom}), 131.8 (2C_q), 128.7 (2CH_{arom}), 128.5 (CH_{arom}), 128.3, 124.1 (2 × 2CH_{arom}), 67.9 (CH₂ Bn), 66.9 (CHMe), 59.6 (CHCOOBn), 20.4 (CHMe). HRMS-APCI (*m/z*): [M + H]⁺ calcd for C₁₉H₁₈NO₅, 340.1179; found, 340.1179.

***N*-[(9*H*-fluoren-9-yl)methoxycarbonyl]-L-threonine benzyl ester (Fmoc-Thr-OBn)**



Benzyl bromide (695 µl, 5.84 mmol, 2.0 equiv) was added into stirred solution of *N*-Fmoc-L-threonine (1.00 g, 2.93 mmol) and Cs₂CO₃ (1.96 g, 6.02 mmol, 2.05 equiv) in DMF (12 mL). The addition resulted in the formation of white precipitate. The reaction mixture was stirred for 3 h until TLC (EtOAc/PE 1:1) indicated the absence of the starting compound. The reaction was quenched with saturated aqueous NH₄Cl (75 mL). The water phase was extracted by EtOAc (3×). Organic extracts were combined, dried, and concentrated. Chromatography in EtOAc/PE 1:2 followed by recrystallization from EtOAc gave **Fmoc-Thr-OBn** (0.90 g, 71 %) as white crystalline solid, *R*_f 0.5 (EtOAc/PE

1:1), mp 118–122 °C (EtOAc/heptane). ^1H NMR (CDCl_3 , 400 MHz, ^1H $\{^{19}\text{F}\}$, H-H COSY, HSQC): δ 7.77, 7.60 (2 $\times$ d, 2 $\times$ 2H, J = 7.5 Hz, CH_{arom}), 7.41–7.29 (m, 9H, CH_{arom}), 5.56 (d, 1H, J = 9.3 Hz, NH), 5.25, 5.20 (2 $\times$ d, 2 $\times$ 1H, J = 12.3 Hz, CHH Bn), 4.43–4.38 (m, 4H, CHCHMe , COOCHHCH), 4.23 (t, 1H, J = 7.2 Hz, COOCH_2CH), 1.82 (d, 1H, J = 4.9 Hz, OH), 1.24 (d, 3H, J = 6.5 Hz, CHMe). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, HSQC): δ 171.1 (COOBn), 158.9 (CO), 144.0, 143.8, 141.45, 141.43, 135.3 (5 $\times$ C_q), 128.8 (3 CH_{arom}), 128.7 (CH_{arom}), 128.4, 127.9, 127.2 (3 $\times$ 2 CH_{arom}), 125.3 (CH_{arom}), 120.1 (2 CH_{arom}), 68.2 (CHMe), 67.6 (COOCH_2CH), 67.4 (CH_2 Bn), 59.3 (CHCOOBn), 47.3 (COOCH_2CH), 20.1 (CHMe). HRMS-APCI (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_5$, 432.1805; found, 432.1806.

DFT calculations

The DFT calculations were performed utilizing widely used B3LYP functional^{9, 10}, standard Ahlrichs Def2SVP basis set¹¹ and the empirical dispersion correction according to Grimme.¹² The calculations were generally performed without solvation and the most stable intermediates were further optimized with implicit diethyl ether solvation utilizing polarizable continuum model (IFPPCM).^{13, 14} All additional calculation variables such as convergence criteria were set to default. The free-Gibbs energies and vibration frequencies were calculated for all the optimized structures to introduce thermal corrections to electronic energies and to evaluate the character of the stationary points (confirmation of minimum), respectively. The Gaussian09 program package was used throughout this study.

The initial screening of possible geometries was performed on 3F oxocarbenium ion, input geometries were chosen to be $^3\text{H}_4$, $^4\text{H}_3$, ^4E , E_4 , E_3 , $^{2,5}\text{B}$, $\text{E}_3/^{2,5}\text{B}$ identified as the most stable conformers of D-*gluco*-configured oxocarbenium ions according to Hansen et al.¹⁵ These geometries were optimized with an arbitrary chosen C5/C6 conformation (*gt*, *gt*, *gt*, *gt*, *gt*, *gt*, and *gg*, respectively) which led to three local minima. Subsequently, all possible C5/C6 conformers (*gg*, *gt*, *tg*) of these three local minima ions were constructed as input geometries for further calculations to examine the effect of C5/C6 conformation. By this manner, we obtained final reported structures **TC9-TC17**. The most stable 3F *gg* conformations **TC9** ($^5\text{H}_4$), **TC12** ($^2\text{S}_0$), and **TC16** ($^5\text{H}_4$) were further optimized with consideration of implicit diethyl ether solvation, which resulted in final 3F conformers **TC3** ($^5\text{H}_4$) and **TC4** ($^2\text{H}_3$) (optimization of **TC16** led to **TC3**). The conformers **TC3** and **TC4** were subsequently used for the construction of input geometries for 4F oxocarbenium ions (by an exchange of OMe and F positions) as similar conformation behaviour of 3F and 4F ions was expected based on our previous work.¹ Again, all possible C5/C6 conformers (*gg*, *gt*, *tg*) of these 4F ions were examined which furnished structures **TC18-TC23**. The most stable 4F *gg* conformers **TC18** ($^5\text{H}_4$) and **TC21** ($^2\text{S}_0/{}^2\text{H}_3$) were further

optimized with consideration of implicit diethyl ether solvation, which resulted in final conformers **TC7** (5H_4) and **TC8** (2H_0). The input geometries for bridged dioxolenium ions **TC1**, **TC2**, **TC5**, **TC6** were constructed from the most stable oxocarbenium ions **TC3**, **TC4**, **TC7** and **TC8**, respectively. Their optimization led to the $B_{3,O}/^1S_3$ and 1C_4 conformations with comparable energies. All bridged dioxolenium ions were calculated with consideration of implicit diethyl ether solvation.

Table S1. Relative energies (kcal/mol) of geometry-optimized conformers of cationic species derived from 6-OAc–OMe analogues of 9 and 20, with consideration of Et₂O solvation.

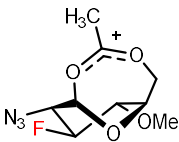
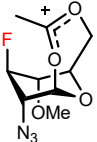
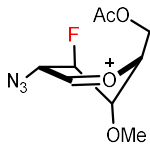
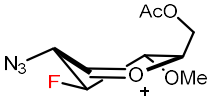
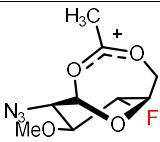
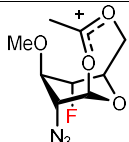
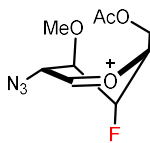
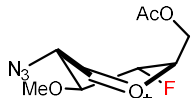
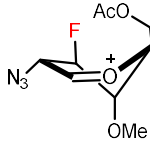
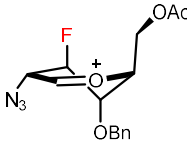
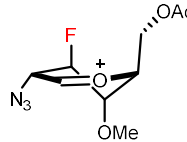
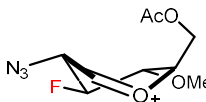
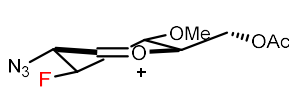
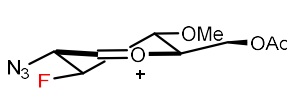
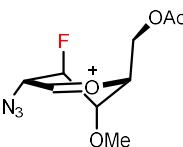
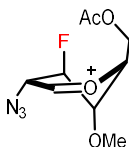
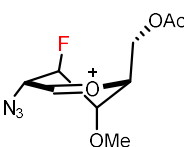
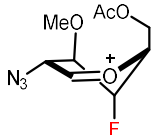
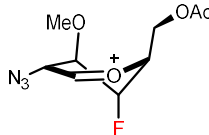
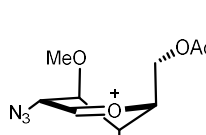
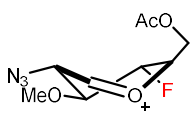
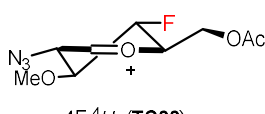
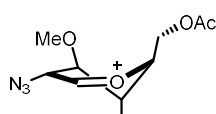
Configuration	Conformations and Energies	
2-Azido-3F-GlucO		
	3F $B_{3,O}/^1S_3$ Bridged dioxolenium ion (TC1) 2.6 Kcal/mol	3F 1C_4 Bridged dioxolenium ion (TC2) 0.0 Kcal/mol
		
	3F 5H_4 (TC3) 10.2 kcal/mol	3F 2H_3 (TC4) 11.8 kcal/mol
2-Azido-4F-GlucO		
	4F $B_{3,O}/^1S_3$ Bridged dioxolenium ion (TC5) 4.8 kcal/mol	4F 1C_4 Bridged dioxolenium ion (TC6) 0.0 Kcal/mol
		
	4F 5H_4 (TC7) 11.5 kcal/mol	4F 2H_0 (TC8) 12.8 kcal/mol

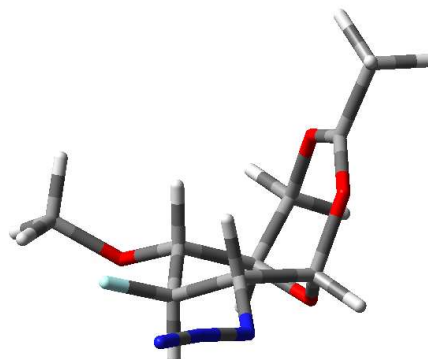
Table S2. Relative energies (kcal/mol) of geometry-optimized conformers of oxocarbenium ions derived from 6-OAc-OMe analogues of 9 and 20, without solvation.

Configuration	Conformations and Energies		
2-Azido-3F-Gluco			
			
3F ⁵ H ₄ (TC9) 0.0 kcal/mol	3F E ₄ (TC10) 7.9 kcal/mol	3F E ₄ (TC11) 7.0 kcal/mol	
			
3F ² S _O (TC12) 2.9 kcal/mol	3F E ₃ (TC13) 11.9 kcal/mol	3F ⁴ H ₃ (TC14) 10.3 kcal/mol	
			
3F E ₄ (TC15) 8.0 kcal/mol	3F ⁵ H ₄ (TC16) 1.0 kcal/mol	3F ³ H ₄ /E ₄ (TC17) 7.8 kcal/mol	
2-Azido-4F-Gluco			
			
4F ⁵ H ₄ (TC18) 0.0 kcal/mol	4F E ₄ / ⁵ H ₄ (TC19) 9.1 kcal/mol	4F E ₄ (TC20) 8.9 kcal/mol	
			
3F ² S _O / ⁴ H ₃ (TC21) 2.4 kcal/mol	4F ⁴ H ₃ (TC22) 10.2 kcal/mol	3F E ₄ / ⁵ H ₄ (TC23) 8.0 kcal/mol	

Cartesian coordinates (Angstroms). Computed total energy values E (E_h), computed sum of electronic and thermal free energies G (E_h) and number of imaginary frequencies of all optimized conformers.

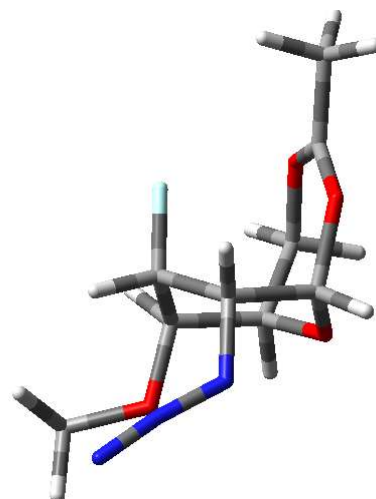
2-Azido-3-Fluoro Glc (bridged dioxolenium-type ion) **TC1**

Conformation: $B_{3,0}/^1S_3$		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	1.242395	0.737567	0.238849
C	-0.112914	1.408157	0.02997
C	-1.073689	0.924851	1.141278
C	1.082128	-0.782739	0.116373
H	-1.039881	1.681119	1.938166
H	-0.486525	1.104519	-0.969954
H	1.651836	1.008463	1.225093
H	0.8972	-1.010196	-0.947869
O	-0.681913	-0.310669	1.757515
N	2.245975	-1.514304	0.608256
N	3.270952	-1.476435	-0.075926
N	4.270215	-1.534768	-0.607689
F	2.142372	1.141616	-0.730223
O	-0.091686	2.800858	0.13409
C	0.272109	3.514621	-1.043729
H	0.153113	4.581544	-0.81327
H	1.314882	3.316765	-1.335262
H	-0.393327	3.253194	-1.887538
C	-2.510163	0.794779	0.700075
H	-3.152349	0.472634	1.530586
H	-2.882928	1.732166	0.271251
O	-2.716443	-0.192533	-0.367399
C	-2.184184	-1.339025	-0.576909
O	-1.138392	-1.823179	-0.02855
C	-2.874517	-2.201156	-1.570831
H	-3.660349	-2.75767	-1.029934
H	-3.362538	-1.580153	-2.332486
H	-2.173463	-2.919025	-2.011513
C	-0.132318	-1.247838	0.955548
H	0.117385	-2.130487	1.553266
E			-914.821846
G			-914.630663
Number of imaginary frequencies			0



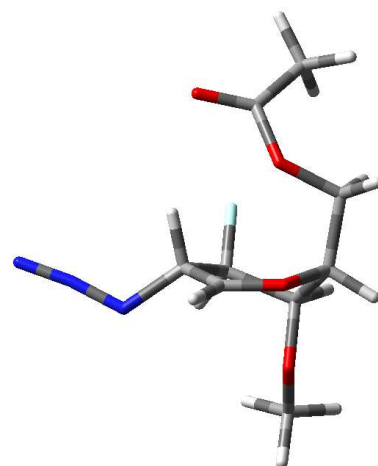
2-Azido-3-Fluoro Glc (bridged dioxolenium-type ion) **TC2**

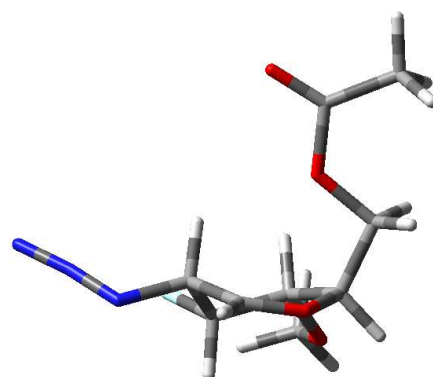
Conformation: 1C_4		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	0.551665	0.158694	1.010486
C	0.696765	-1.190273	0.292213
C	-0.258856	-1.345803	-0.904948
C	0.450931	1.33439	0.025132
H	0.195517	-2.117046	-1.543723
H	0.47121	-1.992978	1.018415
H	1.392319	0.301969	1.705328
H	0.069925	2.210013	0.577507
O	-0.340515	-0.175935	-1.731456
N	1.686354	1.67112	-0.674505
N	2.769836	1.486216	-0.128605
N	3.832453	1.364126	0.250642
F	-0.618686	0.151205	1.771838
O	2.005416	-1.288611	-0.21423
C	2.958715	-1.87564	0.661439
H	3.922067	-1.863413	0.135794
H	3.067772	-1.305772	1.601427
H	2.687358	-2.91853	0.905573
C	-1.668181	-1.837033	-0.638845
H	-2.187361	-1.982528	-1.596106
H	-1.671618	-2.775274	-0.072383
O	-2.539056	-0.956619	0.139517
C	-2.66206	0.31434	0.113066
O	-1.91964	1.147522	-0.50839
C	-3.773099	0.885037	0.914029
H	-4.566054	0.144164	1.06512
H	-3.343823	1.160615	1.893174
H	-4.149118	1.79897	0.437409
C	-0.536841	1.008763	-1.11029
H	-0.544407	1.803026	-1.864015
E			-914.828191
G			-914.634866
Number of imaginary frequencies			0



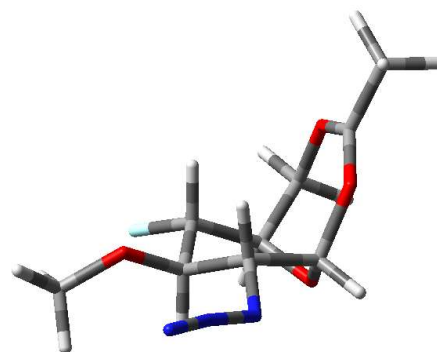
2-Azido-3-Fluoro Glc (*gg* conformation) **TC3**

Conformation: 5H_4		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	-0.695443	-0.073691	-0.885676
C	-0.686943	-1.560113	-0.514359
C	0.245049	-1.871346	0.651582
C	-0.802246	0.815356	0.389079
H	0.090148	-2.910087	0.964696
H	-0.344785	-2.147274	-1.386041
H	-1.566498	0.138742	-1.52001
H	0.130223	1.426732	0.423783
O	-0.248499	-1.0898	1.823499
C	-0.724409	0.05759	1.671796
H	-1.095364	0.531789	2.592386
N	-2.008105	1.630517	0.442973
N	-1.9162	2.800854	0.051465
N	-1.980521	3.879905	-0.280668
F	0.442773	0.237752	-1.603844
O	-1.96912	-1.91291	-0.068831
C	-2.904539	-2.294158	-1.073428
H	-3.846339	-2.519179	-0.557208
H	-3.085147	-1.485771	-1.802917
H	-2.55875	-3.193909	-1.611405
C	1.73772	-1.566783	0.507609
H	2.301839	-2.098993	1.287838
H	2.066056	-1.9308	-0.477946
O	1.896611	-0.170388	0.680088
C	2.710416	0.652804	-0.053751
O	2.530224	1.833521	0.079266
C	3.729952	0.010347	-0.948481
H	4.286149	-0.784711	-0.430362
H	3.220175	-0.432659	-1.819407
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E	-914.806221		
G	-914.618564		
Number of imaginary frequencies			
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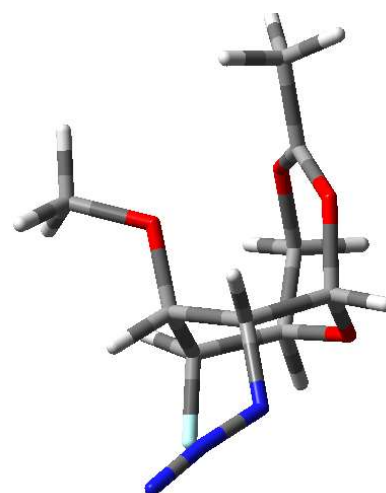


2-Azido-3-Fluoro Glc (*gg* conformation) **TC4**

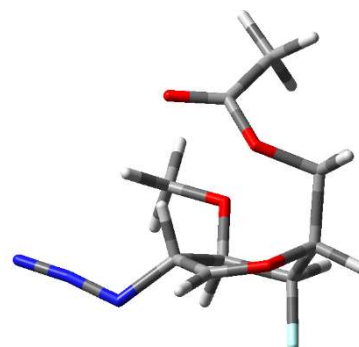
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Atom	x	y	z
O	-0.376805	0.235953	2.08154
C	-0.788268	1.258338	1.06044
C	0.430416	-0.687262	1.84452
C	0.249446	1.483865	-0.064683
H	-0.881999	2.173448	1.656117
H	0.577448	-1.413936	2.657799
C	1.525211	0.650755	0.108296
H	-0.191059	1.142747	-1.021517
H	2.204925	1.131842	0.831009
F	2.173881	0.544345	-1.099516
O	0.487831	2.859345	-0.075378
C	1.037907	3.382271	-1.28276
H	0.411565	3.11222	-2.152391
H	1.052616	4.474196	-1.172911
H	2.063371	3.018678	-1.457648
C	-2.134684	0.767338	0.565872
H	-2.833884	0.643087	1.407351
H	-2.534427	1.526483	-0.126639
O	-1.858516	-0.467647	-0.077923
C	-2.811773	-1.25486	-0.687547
C	-4.226704	-0.747414	-0.665229
H	-4.579672	-0.619382	0.369864
H	-4.299134	0.229894	-1.166659
H	-4.866655	-1.470882	-1.182319
O	-2.431964	-2.277243	-1.182906
C	1.187832	-0.782816	0.576945
H	0.457771	-1.213523	-0.147243
N	2.348074	-1.620576	0.786174
N	2.861149	-2.129431	-0.217828
N	3.429853	-2.658354	-1.03934
E			-914.802762
G			-914.616051
Number of imaginary frequencies			0

2-Azido-4-Fluoro Glc (bridged dioxolenium-type ion) **TC5**

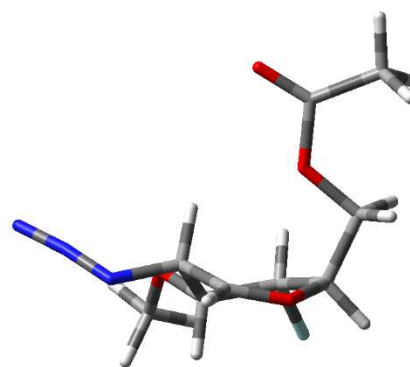
Conformation: $B_{3,0}/^1S_3$		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	1.192558	0.618487	0.084807
C	-0.041645	1.470656	-0.194197
C	-1.074256	1.30817	0.941249
C	0.757724	-0.855383	0.162678
H	-0.909278	2.13733	1.644722
H	-0.455884	1.188792	-1.178068
H	1.612066	0.918259	1.064187
H	0.549314	-1.19294	-0.866638
O	-0.896777	0.105273	1.702169
N	1.774061	-1.700608	0.781639
N	2.841167	-1.839339	0.180362
N	3.861157	-2.064349	-0.260093
C	-2.516903	1.36988	0.499297
H	-3.194842	1.234401	1.352786
H	-2.742582	2.31041	-0.016916
O	-2.882494	0.336324	-0.473717
C	-2.551319	-0.899874	-0.550868
O	-1.610655	-1.490264	0.075601
C	-3.364306	-1.731594	-1.475064
H	-4.245682	-2.08165	-0.9097
H	-3.720721	-1.121768	-2.314903
H	-2.791897	-2.602848	-1.812828
C	-0.521018	-0.999218	1.018259
H	-0.440417	-1.839946	1.714568
F	0.293257	2.809053	-0.265871
O	2.144004	0.696285	-0.934469
C	3.137526	1.707409	-0.793659
H	3.819862	1.599836	-1.647144
H	2.693175	2.714976	-0.80399
H	3.710079	1.571596	0.141719
E	-914.822415		
G	-914.630655		
Number of imaginary frequencies			
0			

2-Azido-4-Fluoro Glc (bridged dioxolenium-type ion) **TC6**

Conformation: 1C_4		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	0.701709	0.692286	0.585106
C	0.551876	-0.605193	1.397353
C	-0.320124	-1.673452	0.725833
C	0.970948	0.375929	-0.900352
H	-0.024423	-2.629535	1.184135
H	0.138463	-0.380758	2.393618
H	1.562041	1.245756	1.002032
H	0.813519	1.30005	-1.481625
O	-0.062229	-1.829507	-0.674029
N	2.290023	-0.201571	-1.147506
N	3.276164	0.440068	-0.791292
N	4.260592	0.929104	-0.510003
C	-1.82168	-1.590344	0.930519
H	-2.294964	-2.467352	0.468085
H	-2.087162	-1.549252	1.993328
O	-2.501328	-0.433247	0.35405
C	-2.279665	0.190633	-0.738473
O	-1.332484	-0.017651	-1.572066
C	-3.243826	1.259135	-1.098771
H	-4.137949	1.211347	-0.468588
H	-2.722445	2.218548	-0.947263
H	-3.496165	1.181189	-2.165522
C	-0.000259	-0.69745	-1.418522
H	0.233301	-0.976082	-2.451343
O	-0.473667	1.466526	0.637666
C	-0.597616	2.336732	1.758448
H	0.222642	3.074742	1.772035
H	-1.555422	2.862283	1.651781
H	-0.599878	1.7839	2.71339
F	1.81672	-1.140743	1.562858
E			-914.830844
G			-914.638280
Number of imaginary frequencies			0

2-Azido-4-Fluoro Glc (*gg* conformation) **TC7**

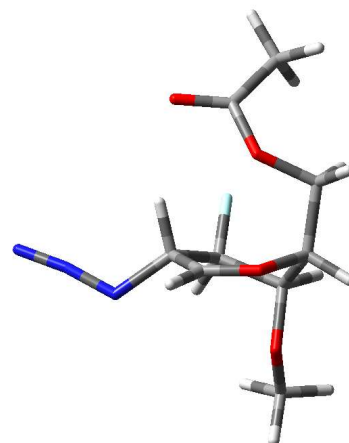
Conformation: 5H_4		Solvation: Diethyl ether (PCM)	
Atom	x	y	z
C	-0.52844	0.486187	1.033219
C	0.457343	1.650439	1.122113
C	1.372486	1.805114	-0.083556
C	-1.12176	0.374219	-0.429599
H	1.900259	2.763996	-0.012772
H	1.06536	1.542721	2.033643
H	-1.380885	0.742901	1.687161
H	-0.701114	-0.562731	-0.871166
O	0.497234	1.990312	-1.274484
C	-0.599435	1.388256	-1.375281
H	-1.186555	1.646948	-2.268788
N	-2.575294	0.408139	-0.493827
N	-3.165709	-0.677427	-0.50456
N	-3.827217	-1.595701	-0.50747
C	2.357518	0.67901	-0.402344
H	3.108962	1.041904	-1.118136
H	2.867876	0.393872	0.528933
O	1.62591	-0.374206	-1.001536
C	1.630443	-1.686335	-0.615362
O	0.710614	-2.357647	-1.008785
C	2.763384	-2.169427	0.240652
H	3.737874	-1.833511	-0.14287
H	2.633401	-1.778333	1.262217
H	2.729959	-3.264162	0.276824
O	0.132496	-0.66036	1.461349
C	-0.698447	-1.776303	1.768937
H	-0.052061	-2.538138	2.22211
H	-1.490377	-1.491104	2.482619
H	-1.151661	-2.206649	0.859446
F	-0.292454	2.811718	1.181862
E			-914.809548
G			-914.619943
Number of imaginary frequencies			0

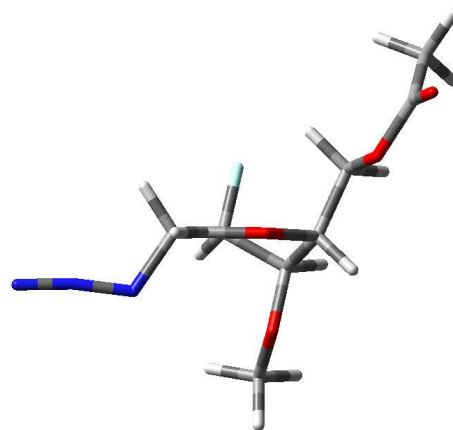
2-Azido-4-Fluoro Glc (*gg* conformation) **TC8**

Conformation: 2H_0		Solvation: Diethyl ether (PCM)		
Atom	x	y	z	
O	0.622916	-0.78239	1.974915	
C	0.947842	-1.597951	0.759947	
C	-0.148711	0.20346	1.949549	
C	-0.17994	-1.601726	-0.292589	
H	1.072867	-2.608063	1.167344	
H	-0.242432	0.751856	2.899136	
C	-1.387175	-0.707139	0.029789	
H	0.227353	-1.271518	-1.260423	
H	-2.046926	-1.273694	0.716066	
C	2.264524	-1.036265	0.258761	
H	3.01666	-1.045783	1.063027	
H	2.616059	-1.676848	-0.566925	
O	1.959015	0.282262	-0.166563	
C	2.881438	1.173325	-0.673214	
C	4.290325	0.674694	-0.830535	
H	4.710201	0.376263	0.142691	
H	4.32106	-0.204197	-1.492747	
H	4.900999	1.477062	-1.25894	
O	2.4782	2.267449	-0.946908	
C	-0.929445	0.585788	0.756108	
H	-0.201934	1.104898	0.090693	
N	-2.022258	1.435071	1.175138	
N	-2.600091	2.084132	0.295764	
N	-3.217031	2.736744	-0.391033	
O	-2.059277	-0.291135	-1.110611	
C	-3.057697	-1.1808	-1.610287	
H	-3.510271	-0.686211	-2.479027	
H	-2.619367	-2.143103	-1.920344	
H	-3.836618	-1.364909	-0.849251	
F	-0.625087	-2.90191	-0.433579	
E				-914.804679
G				-914.617903
Number of imaginary frequencies				0

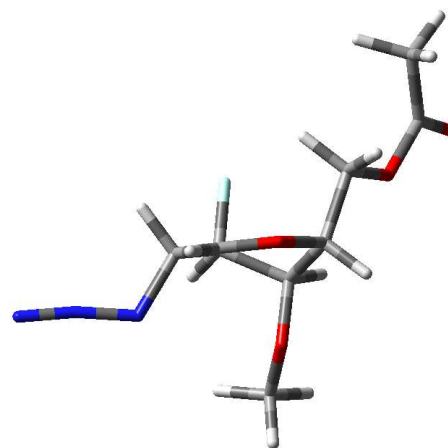
2-Azido-3-Fluoro Glc (*gg* conformation) TC9

Conformation: 5H_4		Solvation: None	
Atom	x	y	z
C	-0.686427	-0.047543	-0.898909
C	-0.800706	-1.529906	-0.527767
C	0.119771	-1.911496	0.630333
C	-0.712053	0.850245	0.376401
H	-0.107967	-2.938711	0.940367
H	-0.518077	-2.140294	-1.40687
H	-1.540731	0.241762	-1.526872
H	0.273997	1.381013	0.404869
O	-0.31402	-1.103046	1.80375
C	-0.690149	0.083767	1.651579
H	-1.021326	0.582968	2.574911
N	-1.843519	1.761767	0.438909
N	-1.637222	2.93289	0.074116
N	-1.601309	4.01907	-0.233235
F	0.470057	0.153883	-1.624785
O	-2.096959	-1.781248	-0.063014
C	-3.08523	-2.078422	-1.047961
H	-4.028013	-2.234849	-0.508889
H	-3.220505	-1.250025	-1.765229
H	-2.824839	-2.998059	-1.600645
C	1.636252	-1.701144	0.48644
H	2.162642	-2.301359	1.244881
H	1.944159	-2.047714	-0.512676
O	1.886582	-0.331016	0.713616
C	2.670867	0.510798	-0.049876
O	2.436381	1.681353	0.060016
C	3.717349	-0.113257	-0.923779
H	4.259856	-0.9183	-0.406624
H	3.234943	-0.532954	-1.822114
H	4.415788	0.668888	-1.244285
E			-914.746283
G			-914.559713
Number of imaginary frequencies			0

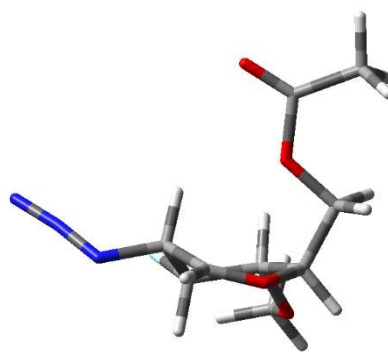


2-Azido-3-Fluoro Glc (*gt* conformation) **TC10**

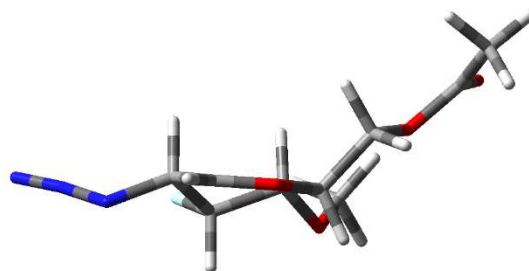
Conformation: E_4		Solvation: None	
Atom	x	y	z
C	-1.230256	0.36238	1.144159
C	-0.506859	1.390241	0.254803
C	0.677591	0.756546	-0.464562
C	-1.718035	-0.825731	0.293608
H	0.983749	1.398204	-1.300413
H	-0.120784	2.210333	0.891916
H	-2.092403	0.810552	1.657971
H	-1.685416	-1.724701	0.94094
O	0.18423	-0.46518	-1.213733
C	-0.829425	-1.110619	-0.885141
H	-1.090032	-1.935925	-1.567193
N	-3.032352	-0.585457	-0.299006
N	-3.91371	-1.442341	-0.094054
N	-4.810375	-2.120689	0.009371
F	-0.34793	-0.117427	2.093518
O	-1.355614	1.834137	-0.761581
C	-2.37722	2.762838	-0.402902
H	-2.796972	3.142065	-1.343192
H	-3.185412	2.282087	0.173412
H	-1.959426	3.607473	0.172928
C	1.902052	0.339371	0.331413
H	2.223993	1.229875	0.902771
H	1.648156	-0.446235	1.060145
O	2.851978	-0.086336	-0.611176
C	4.138266	-0.478215	-0.257308
O	4.839764	-0.900118	-1.121791
C	4.521372	-0.315766	1.193827
H	4.467048	0.741101	1.500233
H	3.855762	-0.893116	1.854671
H	5.550379	-0.671759	1.318818
E			-914.731286
G			-914.547132
Number of imaginary frequencies			0

2-Azido-3-Fluoro Glc (*tg* conformation) **TC11**

Conformation: E_4		Solvation: None	
Atom	x	y	z
C	0.814644	0.008885	-0.928057
C	0.092387	1.021503	-0.023254
C	-0.626239	0.324376	1.123993
C	1.831247	-0.795981	-0.091256
H	-0.869178	1.075485	1.886194
H	-0.6753	1.56801	-0.600604
H	1.34673	0.512049	-1.747924
H	1.85832	-1.818043	-0.523055
O	0.356502	-0.548626	1.856731
C	1.408878	-0.978464	1.336752
H	2.071965	-1.524651	2.026214
N	3.147388	-0.170617	-0.014319
N	4.107776	-0.809483	-0.485538
N	5.067876	-1.257668	-0.875929
F	-0.097411	-0.877568	-1.466373
O	1.040396	1.847477	0.592912
C	1.571451	2.919078	-0.184759
H	2.166268	3.536722	0.499937
H	2.230299	2.554866	-0.99133
H	0.760899	3.531597	-0.616162
C	-1.850659	-0.538525	0.808879
H	-1.558217	-1.419109	0.215613
H	-2.298554	-0.883142	1.757045
O	-2.690433	0.333853	0.096414
C	-3.927418	-0.050477	-0.41829
O	-4.522985	0.756212	-1.058717
C	-4.379714	-1.454152	-0.10508
H	-3.680495	-2.197023	-0.520642
H	-4.443327	-1.618705	0.982009
H	-5.369288	-1.604344	-0.551727
E	-914.732029		
G	-914.548542		
Number of imaginary frequencies			
0			

2-Azido-3-Fluoro Glc (*gg* conformation) **TC12**

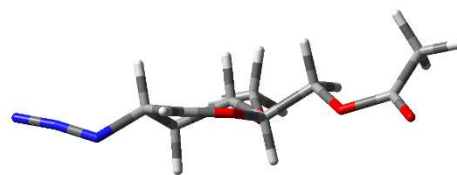
Conformation: 2S_0		Solvation: None	
Atom	x	y	z
O	0.369051	0.342178	-2.086255
C	0.778733	1.336027	-1.031276
C	-0.399125	-0.619318	-1.857939
C	-0.262926	1.516822	0.098804
H	0.861673	2.271588	-1.597247
H	-0.546825	-1.319539	-2.696151
C	-1.498563	0.614539	-0.050974
H	0.204155	1.208585	1.056132
H	-2.225188	1.086531	-0.734284
F	-2.094323	0.440446	1.171211
O	-0.575142	2.874472	0.090193
C	-1.188075	3.383418	1.276149
H	-0.566165	3.168644	2.164273
H	-1.268288	4.469521	1.142779
H	-2.192517	2.958097	1.433778
C	2.127938	0.829921	-0.550653
H	2.836206	0.74585	-1.391771
H	2.522058	1.564553	0.173239
O	1.843802	-0.425945	0.032394
C	2.769708	-1.254438	0.665642
C	4.181159	-0.745142	0.746997
H	4.593376	-0.565517	-0.258593
H	4.223502	0.20481	1.303188
H	4.793687	-1.493947	1.262298
O	2.347508	-2.287585	1.08352
C	-1.129019	-0.791524	-0.584065
H	-0.372347	-1.226852	0.111484
N	-2.265733	-1.648334	-0.820549
N	-2.75122	-2.219896	0.170681
N	-3.293785	-2.800788	0.972018
E			-914.739881
G			-914.555037
Number of imaginary frequencies			0

2-Azido-3-Fluoro Glc (*tg* conformation) **TC13**

Conformation: E_3		Solvation: None	
Atom	X	y	z
O	-0.36856	-1.947946	-0.826301
C	0.55363	-0.750426	-0.890975
C	-1.542243	-1.926957	-0.399069
C	-0.063364	0.553473	-0.338178
H	0.71193	-0.629281	-1.971589
H	-2.086258	-2.88483	-0.449358
C	-1.590396	0.558529	-0.44938
H	0.194063	0.656567	0.732976
H	-1.892426	0.652593	-1.506069
F	-2.093911	1.620943	0.251442
O	0.462569	1.580269	-1.109946
C	1.04825	2.686658	-0.411041
H	1.955539	2.371326	0.128767
H	1.321389	3.419076	-1.181118
H	0.319775	3.144481	0.278407
C	1.828105	-1.218912	-0.178607
H	1.553837	-1.653822	0.802191
H	2.326907	-2.001988	-0.77431
O	2.5932	-0.053934	-0.035939
C	3.843262	-0.012527	0.570515
C	4.509235	-1.335482	0.843139
H	3.900232	-1.959512	1.516341
H	4.659964	-1.89522	-0.093765
H	5.48162	-1.144606	1.311453
O	4.286576	1.067908	0.808275
C	-2.200963	-0.72111	0.157536
H	-1.890481	-0.742601	1.234225
N	-3.625701	-0.872332	-0.009052
N	-4.354393	-0.148312	0.692783
N	-5.13623	0.436284	1.258627
E			-914.725205
G			-914.540706
Number of imaginary frequencies			0

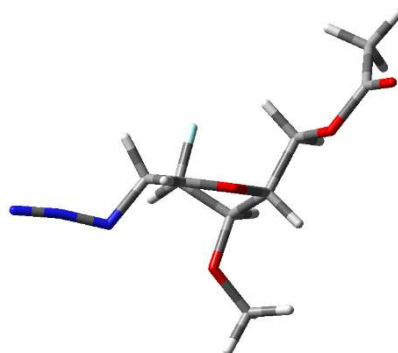
2-Azido-3-Fluoro Glc (*gt* conformation) **TC14**

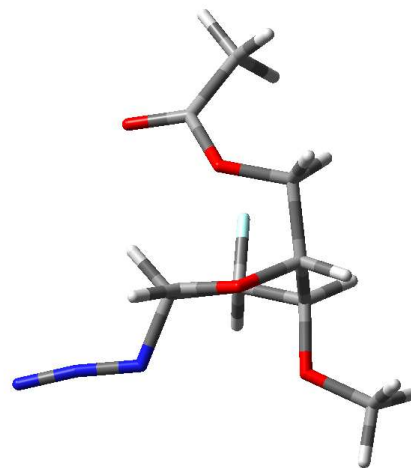
Conformation: 4H_3		Solvation: None	
Atom	X	y	z
O	0.28718	-1.414014	-0.035745
C	0.693707	0.008892	-0.342185
C	-0.885563	-1.789782	0.157087
C	-0.390178	1.013409	0.069166
H	0.809594	-0.008293	-1.435981
H	-1.02209	-2.875201	0.29565
C	-1.769471	0.504218	-0.366523
H	-0.399073	1.130228	1.174634
H	-1.819068	0.449319	-1.467146
F	-2.755112	1.349468	0.078753
O	-0.018128	2.188078	-0.572691
C	-0.511035	3.414409	-0.020443
H	-0.223367	3.508724	1.042162
H	-0.040147	4.220874	-0.596155
H	-1.605144	3.485065	-0.111285
C	2.046283	0.219136	0.302248
H	2.303601	1.275837	0.112751
H	1.969052	0.073859	1.396389
O	2.925429	-0.690692	-0.300819
C	4.295054	-0.69816	-0.054983
C	4.825899	0.383327	0.853879
H	4.636383	1.382873	0.431028
H	4.353461	0.341167	1.847966
H	5.907028	0.239978	0.962536
O	4.940096	-1.547862	-0.58281
C	-2.057773	-0.878799	0.245416
H	-2.141399	-0.723063	1.35178
N	-3.206198	-1.567509	-0.295142
N	-4.324228	-1.189226	0.099739
N	-5.396856	-0.956203	0.361326
E			-914.726735
G			-914.543240
Number of imaginary frequencies			0



2-Azido-3-Fluoro Glc (*gt* conformation) **TC15**

Conformation: E_4		Solvation: None	
Atom	X	y	z
O	0.077942	-0.20971	-1.244315
C	0.619464	0.794107	-0.253486
C	-0.939992	-0.902038	-1.041307
C	-0.538663	1.290921	0.617291
H	0.965136	1.585492	-0.930655
C	-1.816012	-0.853687	0.177657
H	-1.222188	-1.558746	-1.879527
C	-1.298476	0.122948	1.254422
H	-0.114458	1.920778	1.42247
H	-1.800777	-1.865807	0.628663
H	-2.148085	0.497684	1.842405
N	-3.120117	-0.478562	-0.361578
N	-4.018047	-1.341449	-0.326224
N	-4.93064	-2.006117	-0.355491
F	-0.434662	-0.579536	2.073396
O	-1.479774	1.955014	-0.169714
C	-1.259385	3.34432	-0.398534
H	-2.088106	3.695825	-1.025811
H	-1.259448	3.905094	0.552651
H	-0.308458	3.531191	-0.929812
C	1.830355	0.166029	0.416556
H	2.180662	0.88855	1.177153
H	1.546339	-0.757267	0.946332
O	2.769605	-0.060784	-0.602553
C	4.038405	-0.574272	-0.357456
C	4.414224	-0.793501	1.088141
H	4.391436	0.153327	1.651005
H	3.724645	-1.495956	1.582277
H	5.42998	-1.203919	1.11977
O	4.731901	-0.792829	-1.300185
E			-914.730427
G			-914.546943
Number of imaginary frequencies			0

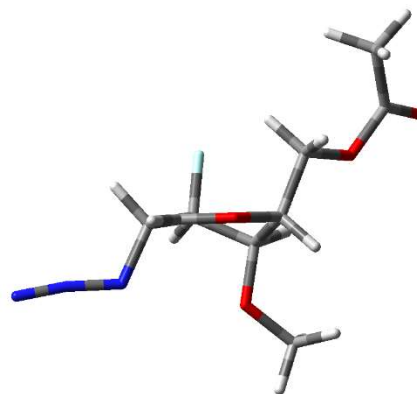


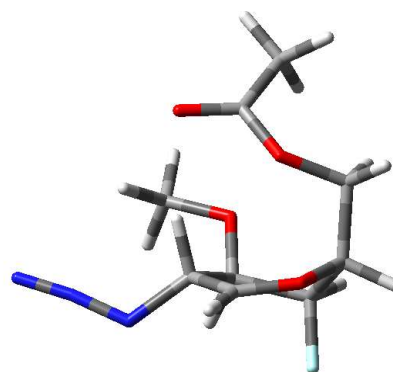
2-Azido-3-Fluoro Glc (*gg* conformation) **TC16**

Conformation: 5H_4		Solvation: None		
Atom	X	y	z	
O	0.419231	0.740256	1.701925	
C	-0.117824	1.706625	0.726374	
C	0.541706	-0.460289	1.336633	
C	0.661243	1.542539	-0.590027	
H	0.091445	2.684314	1.175128	
C	0.684443	-0.954727	-0.077035	
H	0.724385	-1.165697	2.159692	
C	0.491721	0.131825	-1.160683	
H	0.251024	2.263096	-1.324347	
H	-0.064996	-1.751994	-0.236904	
H	1.237298	-0.027731	-1.951698	
N	2.074945	-1.425618	-0.060345	
N	2.254118	-2.657097	-0.011404	
N	2.570227	-3.740924	0.021566	
F	-0.773756	0.030445	-1.710029	
O	2.027211	1.699702	-0.362197	
C	2.525798	3.032041	-0.324457	
H	3.612755	2.958324	-0.193182	
H	2.309935	3.563653	-1.268421	
H	2.109498	3.611506	0.519857	
C	-1.642802	1.437731	0.701881	
H	-2.11979	1.917502	1.570134	
H	-2.05748	1.8671	-0.222442	
O	-1.808041	0.036003	0.785182	
C	-2.700515	-0.753196	0.062886	
C	-3.853312	-0.051047	-0.589523	
H	-4.32795	0.673996	0.087978	
H	-3.492468	0.484925	-1.482688	
H	-4.583532	-0.804175	-0.908482	
O	-2.458913	-1.922506	0.037667	
E				-914.744826
G				-914.558159
Number of imaginary frequencies				0

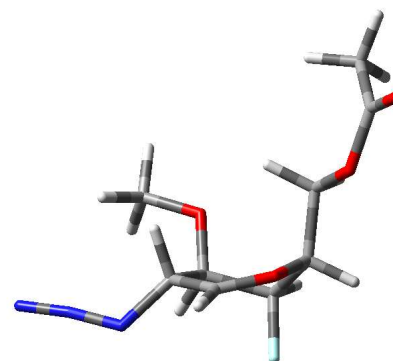
2-Azido-3-Fluoro Glc (*tg* conformation) **TC17**

Conformation: ${}^3H_4/E_4$		Solvation: None	
Atom	x	y	z
O	0.492034	-0.48461	1.710063
C	-0.523278	0.307946	0.938012
C	1.526241	-0.97914	1.206805
C	0.118207	0.913055	-0.313013
H	-0.770004	1.110154	1.645011
C	1.980936	-0.808527	-0.212059
H	2.168515	-1.516286	1.921992
C	0.922128	-0.128178	-1.097513
H	-0.708204	1.28141	-0.946475
H	2.167634	-1.813443	-0.636007
H	1.411858	0.342911	-1.961793
N	3.196996	-0.016025	-0.033399
N	4.283683	-0.587806	-0.248689
N	5.337997	-0.95594	-0.416215
F	0.070195	-1.130958	-1.524724
O	1.033152	1.902293	0.054965
C	0.522437	3.231346	0.127653
H	1.354	3.873157	0.444946
H	0.155406	3.568251	-0.857512
H	-0.297946	3.318182	0.86323
C	-1.74349	-0.599466	0.753098
H	-1.477453	-1.484398	0.153219
H	-2.098131	-0.934201	1.743392
O	-2.665345	0.236243	0.098677
C	-3.943398	-0.178904	-0.271556
C	-4.341657	-1.575053	0.134542
H	-3.66141	-2.325582	-0.297851
H	-4.320665	-1.688878	1.229971
H	-5.359531	-1.76082	-0.226931
O	-4.614254	0.599584	-0.871252
E	-914.731369		
G	-914.547250		
Number of imaginary frequencies			
0			



2-Azido-4-Fluoro Glc (*gg* conformation) **TC18**

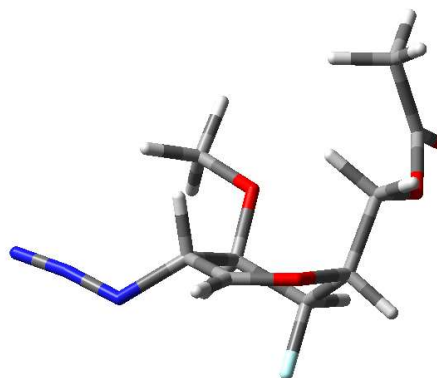
Conformation: 5H_4		Solvation: none	
Atom	x	y	z
C	-0.513726	0.513511	1.026859
C	0.520065	1.633826	1.133187
C	1.471545	1.736533	-0.051695
C	-1.08053	0.424657	-0.452145
H	2.042331	2.670731	0.031683
H	1.09876	1.506577	2.062298
H	-1.371008	0.813466	1.656943
H	-0.682928	-0.535769	-0.877779
O	0.633617	1.963171	-1.258891
C	-0.490097	1.409321	-1.380507
H	-1.046769	1.699826	-2.284776
N	-2.525619	0.517753	-0.561043
N	-3.156425	-0.550183	-0.52723
N	-3.849158	-1.442999	-0.494737
C	2.406242	0.557443	-0.353393
H	3.206377	0.891722	-1.031287
H	2.862426	0.22077	0.590568
O	1.639654	-0.434751	-1.001981
C	1.50696	-1.747954	-0.61744
O	0.50558	-2.302831	-0.984912
C	2.60799	-2.357266	0.197536
H	3.601847	-2.092108	-0.192036
H	2.527268	-1.995947	1.235778
H	2.48221	-3.446456	0.196568
O	0.084822	-0.657346	1.476126
C	-0.807454	-1.726228	1.791606
H	-0.204255	-2.520969	2.247896
H	-1.577087	-1.393443	2.509433
H	-1.286302	-2.133375	0.884876
F	-0.174424	2.825997	1.160458
E			-914.749382
G			-914.560710
Number of imaginary frequencies			0

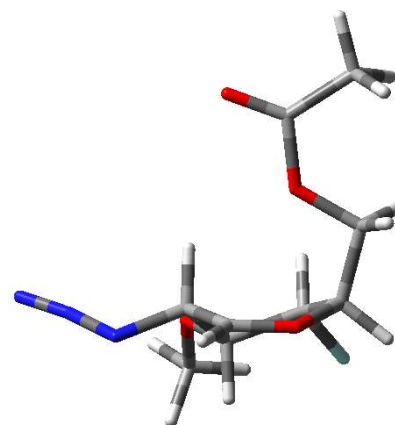
2-Azido-4-Fluoro Glc (*gt* conformation) **TC19**

Conformation: $E_4/^5H_4$		Solvation: none	
Atom	x	y	z
C	-1.406706	-0.242552	0.852918
C	-0.437861	0.681644	1.591632
C	0.815299	1.00395	0.796521
C	-1.65543	0.310998	-0.607944
H	1.372501	1.82504	1.26614
H	-0.158057	0.231128	2.557371
H	-2.375863	-0.193995	1.38183
H	-1.2978	-0.501467	-1.288098
O	0.363043	1.662522	-0.483227
C	-0.742648	1.415883	-1.007335
H	-1.014276	2.057377	-1.861508
N	-3.001347	0.739394	-0.923839
N	-3.831233	-0.153442	-1.153994
N	-4.681277	-0.866293	-1.372031
C	1.762156	-0.133763	0.45811
H	2.059431	-0.59255	1.419243
H	1.243968	-0.91441	-0.122794
O	2.831138	0.446803	-0.241389
C	3.9649	-0.269689	-0.613604
O	4.772194	0.293259	-1.282629
C	4.061736	-1.691483	-0.115866
H	4.085073	-1.722365	0.98532
H	3.206526	-2.298101	-0.452929
H	4.989085	-2.127807	-0.504368
O	-0.854783	-1.518579	0.845
C	-1.77661	-2.591517	0.662259
H	-1.199029	-3.523099	0.707746
H	-2.54121	-2.594187	1.458219
H	-2.281747	-2.534847	-0.320588
F	-1.099262	1.875423	1.791253
E			-914.729612
G			-914.546141
Number of imaginary frequencies			0

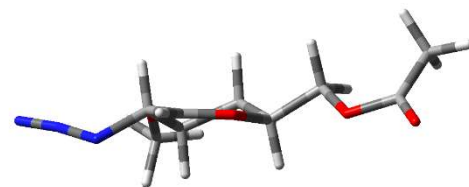
2-Azido-4-Fluoro Glc (*tg* conformation) **TC20**

Conformation: E_4		Solvation: none	
Atom	X	y	z
C	0.752902	0.237615	0.638231
C	-0.01682	-0.989629	1.124856
C	-0.650657	-1.789978	-0.000125
C	1.765581	-0.210495	-0.49088
H	-1.003452	-2.754363	0.388138
H	-0.801541	-0.698446	1.839066
H	1.357945	0.602256	1.487279
H	1.48575	0.408971	-1.380443
O	0.444885	-2.211383	-0.930809
C	1.515627	-1.56973	-1.037646
H	2.2992	-2.060136	-1.637337
N	3.17789	-0.128584	-0.1903
N	3.679364	1.006414	-0.188616
N	4.252203	1.97996	-0.143045
C	-1.741504	-1.079768	-0.811269
H	-1.288697	-0.27741	-1.411863
H	-2.230584	-1.800308	-1.488643
O	-2.627139	-0.59491	0.164074
C	-3.273759	0.633707	0.066993
O	-3.741138	1.085237	1.064253
C	-3.336188	1.260738	-1.303905
H	-2.350016	1.66686	-1.580659
H	-3.639903	0.535188	-2.073666
H	-4.056527	2.086458	-1.26936
O	-0.152716	1.185635	0.17209
C	0.272099	2.544754	0.264386
H	-0.549525	3.16399	-0.116759
H	0.479358	2.822275	1.311742
H	1.175734	2.731659	-0.346155
F	0.915693	-1.819047	1.719078
E	-914.730263		
G	-914.546571		
Number of imaginary frequencies			
0			

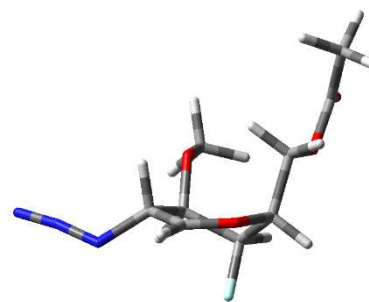


2-Azido-4-Fluoro Glc (*gg* conformation) **TC21**

Conformation: $^2S_0/{}^2H_3$		Solvation: none	
Atom	x	y	z
O	0.609538	-0.778447	1.987076
C	0.954998	-1.598782	0.778616
C	-0.160076	0.211925	1.940314
C	-0.156583	-1.598338	-0.293445
H	1.06647	-2.609934	1.190473
H	-0.270661	0.764212	2.887436
C	-1.377619	-0.718304	0.021979
H	0.260831	-1.24649	-1.25039
H	-2.030863	-1.290196	0.712161
C	2.279888	-1.031798	0.296769
H	3.029257	-1.05638	1.105804
H	2.637839	-1.664322	-0.534741
O	1.971128	0.286936	-0.103651
C	2.870647	1.192956	-0.668482
C	4.267643	0.692054	-0.904604
H	4.734512	0.362487	0.037027
H	4.263723	-0.164382	-1.597608
H	4.860943	1.50497	-1.338931
O	2.438348	2.275705	-0.913115
C	-0.936114	0.587974	0.744749
H	-0.210218	1.106139	0.074313
N	-2.034076	1.421861	1.166683
N	-2.604237	2.084564	0.284358
N	-3.214358	2.741272	-0.401409
O	-2.050489	-0.318036	-1.117462
C	-3.060388	-1.206842	-1.606004
H	-3.507683	-0.717785	-2.480238
H	-2.630039	-2.176745	-1.902519
H	-3.839986	-1.370598	-0.840959
F	-0.582	-2.898798	-0.454599
E			-914.741661
G			-914.556835
Number of imaginary frequencies			0

2-Azido-4-Fluoro Glc (*gt* conformation) **TC22**

Conformation: ⁴ H ₃		Solvation: none	
Atom	X	y	z
O	0.538636	-1.340814	-0.080011
C	0.854951	0.116645	-0.286679
C	-0.614346	-1.793213	0.088957
C	-0.282478	1.005908	0.221793
H	0.944772	0.19244	-1.380819
H	-0.686489	-2.892158	0.14008
C	-1.652146	0.492346	-0.234553
H	-0.270576	1.088044	1.32375
H	-1.675644	0.492538	-1.34333
C	2.204547	0.369809	0.347557
H	2.381268	1.45762	0.258521
H	2.16507	0.120274	1.424913
O	3.132844	-0.407798	-0.355712
C	4.504941	-0.35171	-0.119324
C	4.973962	0.651276	0.905622
H	4.705844	1.677459	0.607569
H	4.524346	0.456856	1.892198
H	6.064357	0.575241	0.986018
O	5.195921	-1.090893	-0.745293
C	-1.827096	-0.959315	0.264913
H	-1.889567	-0.891864	1.383458
N	-2.953229	-1.667603	-0.291728
N	-4.08075	-1.322064	0.104927
N	-5.160535	-1.122098	0.363508
O	-2.711097	1.195832	0.315886
C	-3.148458	2.367328	-0.383908
H	-4.032078	2.73457	0.152664
H	-2.368785	3.143892	-0.390586
H	-3.431077	2.117463	-1.421841
F	-0.044838	2.251657	-0.308309
E			-914.727951
G			-914.544434
Number of imaginary frequencies			0

2-Azido-4-Fluoro Glc (tg conformation) **TC23**

Conformation: $E_4/{}^5H_4$		Solvation: none	
Atom	x	y	z
O	0.53289	-2.253508	-0.586186
C	-0.512183	-1.653863	0.300874
C	1.605609	-1.656593	-0.842352
C	0.17907	-0.695087	1.255988
H	-0.873045	-2.531365	0.853043
H	2.351972	-2.247945	-1.396418
C	0.959218	0.415761	0.537886
H	-0.573513	-0.282981	1.943033
H	1.610767	0.890604	1.295232
C	-1.607126	-1.052307	-0.586663
H	-1.147813	-0.417207	-1.362363
H	-2.176575	-1.861323	-1.074153
O	-2.383948	-0.288934	0.303111
C	-3.435695	0.519106	-0.116743
C	-4.020336	0.215802	-1.470374
H	-3.281017	0.391608	-2.268214
H	-4.342546	-0.83546	-1.532499
H	-4.881659	0.874072	-1.632235
O	-3.792207	1.372811	0.635117
C	1.887112	-0.234313	-0.539154
H	1.537229	0.231408	-1.498894
N	3.314898	-0.102643	-0.362457
N	3.793847	1.031378	-0.530237
N	4.359656	2.003149	-0.6383
O	0.146414	1.332907	-0.127201
C	-0.487201	2.327036	0.689506
H	-0.915448	3.065818	0.000442
H	-1.304036	1.90055	1.293049
H	0.253191	2.824729	1.339664
F	1.114188	-1.438351	1.953858
E			-914.733610
G			-914.547974
Number of imaginary frequencies			0

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