SUPPLEMENTARY INFORMATION (1)

Synthesis of lactosamine-based building blocks and investigations of their assembly for the preparation of ^{19}F labelled LacNAc oligomers

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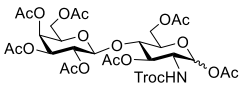
1. General methods

Unless noted, chemical reagents and solvents were used without further purification from commercial sources. Dry solvents as CH_2Cl_2, Et_2O and THF were obtained from a PureSolv-EN^{TM} solvent purification system (Innovation Technology Inc). Concentration *in vacuo* was performed using a Buchi rotary evaporator. The $^{1}H/^{13}C/^{19}F$ NMR spectra (δ in ppm, relative to TMS in $CDCl_3$) were recorded with Varian spectrometers (Varian, Palo Alto, CA, USA) (400/101 MHz or 500/125 MHz) at 25 °C. Assignments were aided by ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments. HRMS spectra were recorded on a micromass LCT instrument from Waters and LaserToF LT3 *Plus* MALDI-TOF (DHAP Matrix). LRMS spectra were recorded on a Waters micromass Quattro Micro LC-MS/MS instrument using electrospray ionisation (ESI) in either positive or negative mode. Optical rotations were recorded on a Perkin-Elmer polarimeter (Model 343) at the sodium D-line (589 nm) at 20°C using a 1 dm cell and are not corrected. Silica gel chromatography was carried out using *Davisil LC60A* (Grace tech., Columbia, MD, USA) SiO_2 (40–63 μm) silica gel. All reactions were monitored by thin-layer chromatography (TLC). TLC was performed on Merck DC-Alufolien plates precoated with silica gel 60 F254. They were visualised with UV-light (254 nm) fluorescence quenching, and/or by charring with an 8% H_2SO_4 dip and/or ninhydrin dip. Deprotected sugars were lyophilised using a freeze-dryer Alpha 1-2 Ldplus (Christ Ltd.), with a pressure of 0.035 mbar and ice condenser temperature -55 °C.

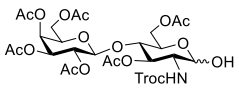
2. Experimental procedures

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranoside (6)



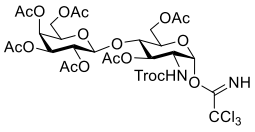
2,2,2,-Trichloroethoxycarbonyl chloride (5.6 mL, 42.8 mmol) was slowly dropped into an ice-cooled solution of lactosamine hydrochloride (10 g, 25.2 mmol) and $NaHCO_3$ (5.9 g, 70.6 mmol) in H_2O (50 mL). The mixture was stirred overnight and checked by TLC analysis (AcOEt/AcOH/MeOH/H_2O, 4:3:3:2, v/v). After complete disappearance of the starting material, the solvent was removed *in vacuo* and the crude residue was acetylated overnight with Ac_2O (47 mL) in pyridine (100 mL). After concentration to dryness, the mixture was diluted with AcOEt (100 mL) and washed with 1M HCl and sat. $NaHCO_3$. Combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Crude was purified by flash column chromatography (Tol/AcOEt, 1:1, v/v) to give **6** (16.5 g, 20.3 mmol, α/β = 2:1, 81%) as a white solid. R_f = 0.44, Tol/AcOEt 1:1; $[\alpha]_D^{20}$= +43.2 (*c* 1.0, $CHCl_3$, α anomer); ^{1}H NMR (500 MHz, $CDCl_3$): δ (α anomer) 6.17 (d, *J* = 3.6 Hz, 1H, H-1α), 5.37 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4'), 5.33 (d, *J* = 9.4 Hz, 1H, N*H*$CO_2CH_2CCl_3$), 5.29 (dd, *J* = 11.0, 8.9 Hz, 1H, H-3), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'), 4.97 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3'), 4.81 (d, *J* = 12.1 Hz, 1H, CH*H*CCl_3), 4.63 (d, *J* = 12.1 Hz, 1H, C*H*$HCCl_3$), 4.52 (d, *J* = 7.9 Hz, 1H, H-1'), 4.41 (dd, *J* = 12.2, 1.8 Hz, 1H, H-6a), 4.18 – 4.05 (m, 4H, H-6b, H-6'a, H-6'b, H-2), 3.94 – 3.82 (m, 3H, H-5, H-4, H-5'), 2.19 (s, 3H, $OCOCH_3$), 2.15 (s, 3H, $OCOCH_3$), 2.12 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.06 (s, 6H, 2 $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.30, 170.27, 170.04, 170.01, 169.2, 168.7 (7 O*C*OCH_3), 154.2 (NH*C*$O_2CH_2CCl_3$), 101.3 (C-1'), 95.2 (CH_2*C*Cl_3), 90.2 (C-1), 75.7 (C-4), 74.6 (*C*H_2CCl_3), 70.9 (C-3'), 70.7 (C-5), 70.4 (C-3, C-5'), 69.1 (C-2'), 66.5 (C-4'), 61.5 (C-6), 60.7 (C-6'), 53.4 (C-2), 21.0, 20.8, 20.7, 20.62, 20.61, 20.5 (7 OCO*C*H_3); HRMS (ESI^+): m/z calcd for $C_{29}H_{38}Cl_3NO_{19}$: 832.1001 $[M+Na]^+$; found: 832.1011.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranose (7)



Glacial AcOH (1.1 mL, 19.7 mmol) was added dropwise to a stirring solution of EDA (1.3 mL, 19.7 mmol) in THF (390 mL), turning the solution cloudy. Compound **6** (16 g, 19.7 mmol) was then added and the reaction was left stirring overnight and checked by TLC analysis (cHex/AcOEt, 1:1, v/v). After reaction completion, the mixture was diluted with H_2O (200 mL) and extracted with CH_2Cl_2. Combined organic layers were washed with 1M HCl, sat. $NaHCO_3$ and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The obtained crude was purified by flash column chromatography (Tol/AcOEt, 1:1, v/v) to afford **7** (11.2 g, 14.6 mmol, 74%, α>>β) as a white foam. R_f = 0.21, Tol/AcOEt 1:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (α anomer) 5.81 (d, *J* = 10.0 Hz, 1H, N*H*$CO_2CH_2CCl_3$), 5.43 (dd, *J* = 10.8, 9.2 Hz, 1H, H-3), 5.36 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4'), 5.27 (*a*t, *J* = 3.9 Hz, 1H, H-1), 5.11 (dd, *J* = 10.5, 7.9 Hz, 1H, H-2'), 4.98 (dd, *J* = 10.5, 3.5 Hz, 1H, H-3'), 4.82 (d, *J* = 12.1 Hz, 1H, C*H*$HCCl_3$), 4.63 (d, *J* = 12.0 Hz, 1H, CH*H*CCl_3), 4.52 – 4.43 (m, H-1', 2H, H-6a), 4.18 – 4.03 (m, 4H, H-6b, H-6'a, H-6'b, H-5'), 3.98 – 3.92 (m, 1H, H-2), 3.88 (ddd, *J* = 7.6, 6.4, 1.3 Hz, 1H, H-5), 3.77 (*a*t, *J* = 9.5 Hz, 1H, H-4), 3.44 (br, 1H, OH), 2.16 (s, 3H, $OCOCH_3$), 2.13 (s, 3H, $OCOCH_3$), 2.06 (s, 6H, 2 $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.2, 170.1, 169.9 (6 O*C*OCH_3), 154.67 (NH*C*$O_2CH_2CCl_3$), 101.08 (C-1'), 95.51 (CH_2*C*Cl_3), 91.64 (C-1), 76.20 (C-4), 74.54 (*C*H_2CCl_3), 70.66 (C-5), 70.59 (C-3'), 70.53 (C-3), 69.40 (C-2'), 68.43 (C-5'), 66.55 (C-4'), 61.98 (C-6), 60.67 (C-6'), 54.40 (C-2), 20.89, 20.87, 20.7, 20.64, 20.62, 20.5 (6 OCO*C*H_3); HRMS (ESI^+): m/z calcd for $C_{27}H_{36}Cl_3NO_{18}$: 790.0896 $[M+Na]^+$; found: 790.0884.

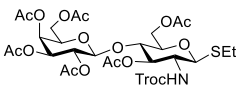
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranosyl trichloroacetimidate (8)



Compound **7** (400 mg, 0.52 mmol) was dissolved in dry CH_2Cl_2 (2 mL) under a N_2 atmosphere. The solution was cooled to 0 °C and trichloroacetonitrile (413 µL, 5.2 mmol) was slowly dropped followed by DBU (15.5 µL, 0.104 mmol). The reaction was left stirring for 45 minutes at RT and monitored by TLC analysis (Tol/AcOEt, 1:1, v/v). The mixture was filtered through a small silica pad (SiO_2 packed with CH_2Cl_2/ Et_3N, 100:1, v/v) and evaporated *in vacuo* at 30 °C. Crude was purified by flash column chromatography (Tol/Acetone, 7:3, v/v, SiO_2 previously packed with Et_3N 1% then flushed with eluent) to afford **8** (400 mg, 0.44 mmol, 85%) as a white solid. R_f = 0.57, Tol/AcOEt 1:1; $[\alpha]_D^{20}$ = +47.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 1H, OC=N*H*CCl_3), 6.36 (d, *J* = 3.7 Hz, 1H, H-1), 5.38 – 5.29 (m, 2H, H-4', H-3), 5.23 (d, *J* = 9.3 Hz, 1H, N*H*$CO_2CH_2CCl_3$), 5.13 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'), 4.97 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3'), 4.72 – 4.69 (m, 2H, CH_2CCl_3), 4.54 (d, *J* = 7.9 Hz, 1H, H-1'), 4.46 (dd, *J* = 12.1, 2.1 Hz, 1H, H-6a), 4.22 – 4.06 (m, 4H, H-2, H-6b, H-6'a, H-6'b), 4.03 (ddd, *J* = 10.1, 4.4, 2.1 Hz, 1H, H-5), 3.96 – 3.84 (m, 2H, H-4, H-5'), 2.15 (s, 3H, $OCOCH_3$), 2.11 (s, 3H, $OCOCH_3$), 2.10 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.8, 170.3, 170.2, 170.1, 170.0, 169.1 (6 O*C*OCH_3), 160.6 (OC=N$HCCl_3$), 154.2 (NH*C*$O_2CH_2CCl_3$), 101.3 (C-1'), 94.8 (CH_2*C*Cl_3), 94.4 (C-1), 90.6 (OC=NH*C*Cl_3), 75.7 (C-4), 74.6 (*C*H_2CCl_3), 71.0 (C-3'), 70.9 (C-5), 70.7 (C-5'), 70.3 (C-3), 69.1 (C-2'), 66.5 (C-4'), 61.5 (C-6), 60.7 (C-6'),

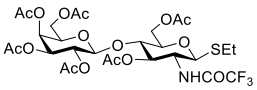
54.1 (C-2), 20.9, 20.8, 20.7, 20.64, 20.62, 20.5 (6 OCO<u>*C*</u>H_3); LRMS (ESI^+): m/z calcd for $C_{29}H_{36}Cl_6N_2O_{18}$: 933.0 $[M+Na]^+$; found: 934.1.

Ethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (9)



To an ice-cooled solution of **8** (13 g, 14.3 mmol) in dry CH_2Cl_2 (280 mL) was added EtSH (10 mL, 143 mmol) under a N_2 atmosphere. Then, $BF_3{\cdot}Et_2O$ (1.7 mL, 14.3 mmol) was slowly dropped in the solution and the reaction was left stirring for 1 hour at RT. Et_3N was then added to quench the reaction which was concentrated to dryness. After flash column chromatography purification, donor **9** (10 g, 12.2 mmol, 85%) was obtained as a white amorphous solid. R_f = 0.53, Tol/Acetone 7:3; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.36 (dd, *J* = 3.5, 1.2 Hz, H-4'), 5.19 (d, *J* = 9.6 Hz, N<u>*H*</u>C$O_2CH_2CCl_3$), 5.15 – 5.08 (m, H-2', H-3), 4.96 (dd, *J* = 10.4, 3.5 Hz, H-3'), 4.81 (d, *J* = 12.1 Hz, C<u>*H*</u>$HCCl_3$), 4.67 (d, *J* = 12.1 Hz, CH<u>*H*</u>CCl_3), 4.52 – 4.44 (m, H-6a, H-1, H-1'), 4.17 – 4.06 (m, H-6b, H-6'a, H-6'b), 3.88 (ddd, *J* = 7.6, 6.3, 1.3 Hz, H-5'), 3.83 – 3.75 (m, H-2, H-4), 3.61 (ddd, *J* = 9.8, 5.5, 2.1 Hz, H-5), 2.76 – 2.64 (m, SC<u>*H*</u>$_2CH_3$), 2.15 (s, 3H, $OCOCH_3$), 2.11 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.05 (s, 3H, $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$), 1.26 (t, *J* = 7.4 Hz, 3H, SCH_2C<u>*H*</u>$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.4, 170.3, 170.1, 170.0, 169.3 (6 O<u>*C*</u>OCH_3), 154.3 (NH<u>*C*</u>$O_2CH_2CCl_3$), 101.1 (C-1'), 95.4 (CH_2<u>*C*</u>Cl_3), 84.7 (C-1), 76.7 (C-5), 76.2 (C-4), 74.6 (<u>*C*</u>H_2CCl_3), 73.5 (C-3), 70.9 (C-3'), 70.7 (C-5'), 69.2 (C-2'), 66.6 (C-4'), 62.4 (C-6), 60.8 (C-6'), 55.3 (C-2), 24.5 (S<u>*C*</u>H_2CH_3), 20.9, 20.7, 20.64, 20.63, 20.62, 20.5 (6 OCO<u>*C*</u>H_3), 14.9 (SCH_2<u>*C*</u>H_3); All analytical data were consistent with literature values.[1]

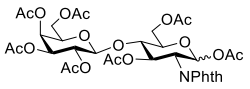
Ethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-trifluoroacetamido-1-thio-β-D-glucopyranoside (10)



To a solution of **9** (400 mg, 0.49 mmol) in CH_3CN/AcOH (16 mL, 4:1, v/v) was added Zn powder (6.4 g, 98.0 mmol) and the reaction was stirred for 2 hours at RT. The mixture was then diluted with water, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Tol/Acetone, 6:4, v/v) gave the free amine derivative (309 mg, 0.44 mmol, 90%) as its acetate salt. The derivative (100 mg, 0.16 mmol) was dissolved in dry CH_2Cl_2 (3 mL) under a stream of N_2. The solution was cooled to 0°C, then TFAA (65 µL, 0.47 mmol) and Et_3N (65 µL, 0.47 mmol) were added and stirring was continued at the same temperature for 3 hours. After solvents removal then solvent was removed under vacuum, the crude residue was purified by flash column chromatography (Tol/AcOEt, 8:2 → 4:6, v/v) to give donor **10** (98 mg, 0.14 mmol, 87%). R_f = 0.63, Tol/AcOEt 1:1; $[\alpha]_D^{20}$= -13.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 9.7 Hz, 1H, $NHCOCF_3$), 5.35 (d, *J* = 3.4 Hz, 1H, H-4'), 5.18 (dd, *J* = 10.1, 8.8 Hz, 1H, H-3), 5.05 (dd, *J* = 10.4, 7.8 Hz, 1H, H-2'), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3'), 4.56 (d, *J* = 10.3 Hz, 1H, H-1), 4.51 (dd, *J* = 12.1, 2.2 Hz, 1H, H-6a), 4.47 (d, *J* = 7.8 Hz, 1H, H-1'), 4.24 – 4.03 (m, 4H, H-2, H-6b, H-6'a, H-6'b), 3.88 (*a*t, *J* = 6.8 Hz, 1H, H-5'), 3.81 (*a*t, *J* = 9.2 Hz, 1H, H-4), 3.63 (ddd, *J* = 9.7, 4.9, 2.2 Hz, 1H, H-5), 2.82 – 2.58 (m, 2H, SC<u>*H*</u>$_2CH_3$), 2.14 (s, 3H, $OCOCH_3$), 2.12 (s, 3H, $OCOCH_3$), 2.06 (s, 6H, 2 $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 1.96 (s, 3H, $OCOCH_3$), 1.26 (t, *J* = 7.4 Hz, 3H, SCH_2C<u>*H*</u>$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 170.5, 170.2, 170.1, 169.3 (6 O<u>*C*</u>OCH_3), 157.5 (*a*d, *J* = 37.6 Hz, NH<u>*C*</u>OCF_3), 115.8 (*a*d, *J* = 287.9 Hz, NHCO<u>*C*</u>F_3), 101.5 (C-1'), 83.6 (C-1), 76.9 (C-5), 76.1 (C-4), 73.9 (C-3), 70.9 (C-3', C-5'), 69.2 (C-2'), 66.7 (C-4'), 62.3 (C-6), 60.9 (C-6'), 53.2 (C-2), 24.3 (S<u>*C*</u>H_2CH_3), 21.0, 20.8, 20.7, 20.6

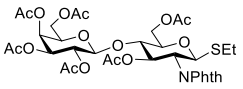
(6 OCO<u>C</u>H$_3$), 15.0 (SCH$_2$<u>C</u>H$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ -76.16 (NHCOCF$_3$); HRMS (ESI$^+$): m/z calcd for $C_{28}H_{38}F_3NO_{16}S$: 754.1761 [M+Na]$^+$; found: 756.1746.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (11)



To a suspension of lactosamine hydrochloride (4 g, 10 mmol) in MeOH (50 mL), was added a freshly prepared solution of MeONa in dry MeOH (1.0 M, 10 mL). Stirring was continued for 30 minutes then phthalic anhydride (814 mg, 5.5 mmol) was added. After 45 min, another aliquot of phthalic anhydride was added (814 mg, 5.5 mmol) together with Et$_3$N (1.4 mL, 10 mmol). Stirring was continued for 1 hour at 50 °C then the solvent was removed under vacuum. Crude residue was dissolved in pyridine (40 mL) and stirred overnight with Ac$_2$O (20 mL). Solvents removal *in vacuo* and precipitation from Et$_2$O gave **11** (4.3 g, 5.6 mmol, 56%, α/β = 3:7) as a white powder. R$_f$ = 0.5, Tol/AcOEt 1:1 (β), 0.35 Tol/AcOEt 1:1 (α); ^{1}H NMR (500 MHz, CDCl$_3$): δ (β anomer) 7.89 – 7.81 (m, 2H, H$_{Ar}$), 7.79 – 7.70 (m, 2H, H$_{Ar}$), 6.49 (d, *J* = 8.9 Hz, H-1), 5.83 (dd, *J* = 10.4, 8.4 Hz, H-3), 5.33 (dd, *J* = 3.4, 1.2 Hz, H-4'), 5.12 (dd, *J* = 10.4, 7.9 Hz, H-2'), 4.95 (dd, *J* = 10.4, 3.4 Hz, H-3'), 4.52 (d, *J* = 7.9 Hz, H-1'), 4.49 (dd, *J* = 12.1, 1.9 Hz, H-6a), 4.36 (dd, *J* = 10.4, 8.9 Hz, H-2), 4.18 (dd, *J* = 12.0, 4.7 Hz, H-6b), 4.13 – 4.07 (m, H-6'a), 4.04 (dd, *J* = 11.2, 7.4 Hz, H-6'b), 3.96 (ddd, *J* = 10.1, 4.7, 1.9 Hz, H-5), 3.92 (*a*t, *J* = 8.4 Hz, H-4), 3.89 – 3.83 (m, H-5'), 2.14 (s, 3H, OCOCH$_3$), 2.13 (s, 3H, OCOCH$_3$), 2.06 (s, 3H, OCOCH$_3$), 2.05 (s, 3H, OCOCH$_3$), 1.97 (s, 3H, OCOCH$_3$), 1.96 (s, 3H, OCOCH$_3$), 1.90 (s, 3H, OCOCH$_3$); ^{13}C NMR (126 MHz, CDCl$_3$): δ 170.4, 170.3, 170.1, 170.0, 169.6, 169.0, 168.5 (7 O<u>C</u>OCH$_3$), 167.5 (2 CO$_{NPhth}$), 134.4 (2 C$_{Ar}$) , 131.3 (C$_{Ar}$), 131.2 (C$_{Ar}$), 123.7 (2 C$_{Ar}$), 100.9 (C-1'), 89.6 (C-1), 76.4 (C-4), 73.3 (C-5), 70.9 (C-3'), 70.8 (C-3), 70.6 (C-5'), 69.0 (C-2)', 66.5 (C-4'), 61.9 (C-6), 60.7 (C-6'), 53.8 (C-2), 20.9, 20.8, 20.62, 20.60, 20.59, 20.49, 20.48 (7 OCO<u>C</u>H$_3$). All analytical data were consistent with literature values.[2]

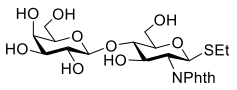
Ethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (12)



To a solution of compound **11** (5.2 g, 6.8 mmol) in dry DCE (68 mL) was added EtSH (2.2 mL, 30.6 mmol) under a stream of N$_2$. The mixture was then cooled to 0 °C and BF$_3$·Et$_2$O (1.2 mL, 10.2 mmol) was slowly added. The reaction was stirred at RT for 2 hours then TMSOTf (240 µL, 1.3 mmol) was added and the mixture was stirred overnight. The reaction was then quenched with Et$_3$N and evaporated *in vacuo*. Purification by flash column chromatography (cHex/AcOEt, 1:1, v/v) gave **12** (3.2 g, 4.2 mmol, 62%) as a white solid. R$_f$ = 0.55, Tol/AcOEt 1:1; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.89 – 7.80 (m, H$_{Ar}$), 7.73 (dt, *J* = 5.5, 2.5 Hz, H$_{Ar}$), 5.77 (dd, *J* = 10.1, 8.1 Hz, H-3), 5.48 (d, *J* = 10.6 Hz, H-1), 5.33 (dd, *J* = 3.4, 1.2 Hz, H-4'), 5.12 (dd, *J* = 10.4, 7.9 Hz, H-2'), 4.95 (dd, *J* = 10.4, 3.4 Hz, H-3'), 4.55 – 4.48 (m, H-1', H-6a), 4.27 (a*t*, *J* = 10.4 Hz, H-2), 4.14 (dd, *J* = 11.9, 5.0 Hz, H-6b), 4.09 (dd, *J* = 11.2, 6.2 Hz, H-6a'), 4.04 (dd, *J* = 11.2, 7.6 Hz, H-6b'), 3.89 – 3.77 (m, H-4, H-5, H-5'), 2.71 – 2.56 (m, SC<u>H$_2$</u>CH$_3$), 2.12 (m, 6H, 2 OCOCH$_3$), 2.06 (s, 3H, OCOCH$_3$), 2.04 (s, 3H, OCOCH$_3$), 1.95 (s, 3H, OCOCH$_3$), 1.89 (s, 3H, OCOCH$_3$), 1.20 (t, *J* = 7.4 Hz, 3H, SCH$_2$C<u>H$_3$</u>); ^{13}C NMR (126 MHz, CDCl$_3$): δ 170.4, 170.3, 170.1, 170.0, 169.7, 169.1 (6 O<u>C</u>OCH$_3$), 167.6 (CO$_{NPhth}$), 167.4 (CO$_{NPhth}$), 134.4 (C$_{Ar}$), 134.1 (C$_{Ar}$), 131.6 (C$_{Ar}$), 131.2 (C$_{Ar}$), 123.7 (C$_{Ar}$), 123.6 (C$_{Ar}$), 101.1 (C-1'), 81.1 (C-1), 76.6 (C-5, C-4), 71.9 (C-3), 71.0

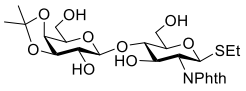
(C-3'), 70.6 (C-5'), 69.1 (C-2'), 66.5 (C-4'), 62.5 (C-6), 60.7 (C-6'), 54.0 (C-2), 24.6 (S<u>*C*</u>H_2CH_3), 20.9, 20.62, 20.60, 20.59, 20.55, 20.5 (6 OCO<u>*C*</u>H_3), 15.0 (SCH_2<u>*C*</u>H_3). All analytical data were consistent with literature values.[3]

Ethyl (β-D-galactopyranosyl)-(1→4)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (13)



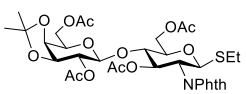
Phthalimido derivative **12** (3.1 g, 4 mmol) was dissolved in MeOH/CH_2Cl_2 (120 mL, 3:1, v/v). A freshly prepared solution of MeONa in MeOH (0.5 M) was slowly added until pH = 8 and stirring was continued for 7 hours at RT. The reaction was quenched with Dowex 50WX8 H^+ resin until pH = 7, filtered and concentrated to dryness. Crude deacetylated product **13** (2 g, 3.9 mmol, 97%) was no further purified. R_f = 0.34, CH_2Cl_2/MeOH 9:1; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.39 – 7.57 (m, 4H, H_{Ar}), 5.20 (d, *J* = 10.5 Hz, 1H, H-1), 5.12 – 5.06 (m, 2H, 2 OH), 4.78 (d, *J* = 5.2 Hz, 1H, OH), 4.67 (t, *J* = 6.0 Hz, 1H, OH), 4.58 (dd, *J* = 5.7, 4.6 Hz, 1H, OH), 4.48 (d, *J* = 4.7 Hz, 1H, OH), 4.26 (d, *J* = 7.2 Hz, 1H, H-1'), 4.25 – 4.19 (m, 1H, H-3), 3.92 (*a*t, *J* = 10.4 Hz, 1H, H-2), 3.82 (ddd, *J* = 12.0, 5.7, 1.8 Hz, 1H, H-6a), 3.72 – 3.64 (m, 1H, H-6b), 3.58 (dd, *J* = 4.8, 2.9 Hz, 1H, H-4'), 3.53 – 3.39 (m, 5H, H-5', H-4, H-5, H-6'a, H-6'b), 3.33 (s, 2H, H-2', H-3'), 2.61 (q, *J* = 7.4 Hz, 2H, SC<u>*H*</u>$_2$$CH_3$), 1.10 (t, *J* = 7.4 Hz, 3H, SCH_2C<u>*H*</u>$_3$), ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ 167.6 (CO_{NPhth}), 167.3 (CO_{NPhth}), 135.0 (2 C_{Ar}), 130.9 (C_{Ar}), 130.7 (C_{Ar}), 123.6 (C_{Ar}), 123.3 (C_{Ar}), 103.9 (C-1'), 80.8 (C-5'), 80.3 (C-1), 79.6 (C-4), 75.6 (C-5), 73.2 (C-3'), 70.6 (C-2'), 70.2 (C-3), 68.2 (C-4'), 60.5 (C-6, C-6'), 55.6 (C-2), 23.3 (S<u>*C*</u>H_2CH_3), 14.9 (SCH_2<u>*C*</u>H_3). All analytical data were consistent with literature values.[4]

Ethyl (3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (14)



To a suspension of compound **13** (2.3 g, 4.5 mmol) in acetone (50 mL), were added 2,2-dimethoxypropane (40 mL, 300 mmol) and *p*-TsOH (167 mg, 0.9 mmol). The mixture was stirred overnight at RT, then the reaction was transferred in a separating funnel and washed with 10% aq. HCl, before extraction with AcOEt. Combined organic layers were washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated to dryness. Crude was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5, v/v) to give **14** (1.9 g, 3.4 mmol, 77%). R_f = 0.24, CH_2Cl_2/MeOH 95:5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (ddd, *J* = 22.5, 6.7, 3.3 Hz, 2H, H_{Ar}), 7.79 – 7.58 (m, 2H, H_{Ar}), 5.35 (d, *J* = 10.6 Hz, 1H, H-1), 4.63 (br, 1H, OH), 4.54 – 4.49 (m, 1H, H-3), 4.46 (d, *J* = 8.0 Hz, 1H, H-1'), 4.23 – 4.12 (m, 3H, H-2, H-2', H-3'), 4.03 – 3.92 (m, 3H, H-5', H-6a, H-6b), 3.91 – 3.78 (m, 3H, H-6'a, H-6'b, OH), 3.78 – 3.71 (m, 1H, H-4), 3.66 – 3.61 (m, 1H, H-5), 3.61 – 3.54 (m, 1H, H-4'), 3.43 (br, 1H, OH), 3.12 (br, 1H, OH), 2.73 – 2.57 (m, 2H, SC<u>*H*</u>$_2$$CH_3$), 1.49 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.17 (t, *J* = 7.4 Hz, 3H, SCH_2C<u>*H*</u>$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3 (CO_{NPhth}), 168.1 (CO_{NPhth}), 134.3 (2 C_{Ar}), 131.9 (C_{Ar}), 131.8 (C_{Ar}), 123.9 (C_{Ar}), 123.4 (C_{Ar}), 110.6 (<u>*C*</u>$(CH_3)_2$), 103.2 (C-1'), 82.1 (C-4), 81.5 (C-1), 79.3 (C-3'), 78.7 (C-5), 74.2 (C-5'), 73.9 (C-2'), 73.5 (C-4'), 71.0 (C-3), 62.2 (C-6), 62.1 (C-6'), 55.5 (C-2), 28.12 (CH_3), 26.36 (CH_3), 24.42 (S<u>*C*</u>H_2CH_3), 15.04 (SCH_2<u>*C*</u>H_3). All analytical data were consistent with literature values.[3]

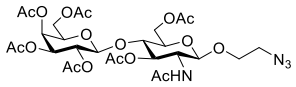
Ethyl (2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-aceyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (15)



Compound **14** (1.9 g, 3.4 mmol) was acetylated with Ac_2O (5 mL) in pyridine (10 mL). The reaction was stirred at RT for 4 hours, then solvents were removed. Purification by flash

column chromatography (cHex/AcOEt, 1:1, v/v) gave **15** (2.3 g, 3.2 mmol, 94%) as a white foam. R_f = 0.27, cHex/AcOEt 1:1; $[\alpha]_D^{20}$= +42.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 11.4, 7.0, 2.6 Hz, 2H, H_{Ar}), 7.76 – 7.67 (m, 2H, H_{Ar}), 5.76 (ddd, *J* = 10.2, 7.3, 1.3 Hz, 1H, H-3), 5.48 (d, *J* = 10.6 Hz, 1H, H-1), 4.87 (dd, *J* = 7.5, 5.8 Hz, 1H, H-2'), 4.48 (dd, *J* = 11.9, 1.5 Hz, 1H, H-6a), 4.39 (d, *J* = 7.5 Hz, 1H, H-1'), 4.35 – 4.18 (m, 4H, H-2, H-6'a, H-6'b, H-6b), 4.17 – 4.10 (m, 2H, H-3', H-4'), 3.93 (ddd, *J* = 7.0, 5.1, 1.8 Hz, 1H, H-5'), 3.85 – 3.77 (m, 2H, H-4, H-5), 2.75 – 2.48 (m, 2H, $SC\underline{H}_2CH_3$), 2.13 – 2.11 (m, 6H, 2 $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 1.90 (s, 3H, $OCOCH_3$), 1.52 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.21 (t, *J* = 7.4 Hz, 3H, $SCH_2C\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 170.7, 170.1, 169.4 (4 $O\underline{C}OCH_3$), 167.8 (CO_{NPhth}), 167.6 (CO_{NPhth}), 134.5 (C_{Ar}), 134.3 (C_{Ar}), 131.8 (C_{Ar}), 131.4 (C_{Ar}), 123.9 (C_{Ar}), 123.7 (C_{Ar}), 111.0 ($\underline{C}(CH_3)_2$), 100.6 (C-1'), 81.3 (C-1), 76.8 (C-4, C-4'), 73.2 (C-3'), 72.8 (C-2'), 71.5 (C-3), 71.0 (C-5'), 63.3 (C-6'), 62.9 (C-6), 54.3 (C-2), 27.4 (CH_3), 26.2 (CH_3), 24.9 ($S\underline{C}H_2CH_3$), 21.03, 21.02, 21.01, 20.7 (4 $OCO\underline{C}H_3$), 15.14 ($SCH_2\underline{C}H_3$); HRMS (ESI$^+$): m/z calcd for $C_{33}H_{41}NO_{15}S$: 746.2095 $[M+Na]^+$; found: 746.2095.

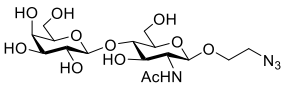
2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (16)



Oxazoline[5] (6 g, 9.7 mmol) was dissolved in dry DCE (80 mL), then 2-chloroethanol (6.5 mL, 97 mmol) and PPTS (487 mg, 1.94 mmol) were added under a N_2 atmosphere. The mixture was stirred for 3 hours at 70 °C then cooled and neutralized with Et_3N. After solvent evaporation, the crude was purified by flash column chromatography (Tol/Acetone, 7:3, v/v) to give 2-chloroethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside as a white foam (5.7 g, 8.1 mmol, 83%). R_f = 0.34, Tol/AcOEt 1:2; $[\alpha]_D^{20}$= -6.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (d, *J* = 9.4 Hz, 1H, $N\underline{H}COCH_3$), 5.35 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4'), 5.15 – 5.05 (m, 2H, H-2', H-3), 4.97 (dd, *J* = 10.5, 3.4 Hz, 1H, H-3'), 4.54 (d, *J* = 7.5 Hz, 1H, H-1), 4.52 – 4.48 (m, 2H, H-1', H-6a), 4.16 – 4.01 (m, 5H, H-6b, H-6'a, H-6'b, H-2, $OCH\underline{H}CH_2Cl$), 3.88 (ddd, *J* = 7.7, 6.4, 1.3 Hz, 1H, H-5'), 3.82 – 3.76 (m, 1H, H-4), 3.75 – 3.70 (m, 1H, $OC\underline{H}HCH_2Cl$), 3.66 – 3.59 (m, 3H, $OCH_2C\underline{H}_2Cl$, H-5), 2.15 (s, 3H, $OCOCH_3$), 2.11 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.05 (s, 3H, $OCOCH_3$), 2.06 – 2.04 (m, 6H, 2 $OCOCH_3$), 1.99 – 1.95 (m, 6H, $OCOCH_3$, $NHCOC\underline{H}_3$), 1.96 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.4, 170.32, 170.30, 170.1, 170.0, 169.3 (7 $\underline{C}OCH_3$), 101.3 (C-1), 100.9 (C-1'), 75.6 (C-4), 72.8 (C-5), 72.0 (C-3), 70.8 (C-3'), 70.7 (C-5'), 69.5 ($O\underline{C}H_2CH_2Cl$), 69.1 (C-2'), 66.6 (C-4'), 62.2 (C-6), 60.8 (C-6'), 53.0 (C-2), 42.9 ($OCH_2\underline{C}H_2Cl$), 23.2 ($NHCO\underline{C}H_3$), 20.84, 20.83, 20.63, 20.62, 20.61, 20.5 (6 $OCO\underline{C}H_3$); HRMS (ESI$^+$): m/z calcd for $C_{28}H_{40}ClNO_{17}$: 720.1882 $[M+Na]^+$; found: 720.1848. To a solution of the chloroethyl derivative (16 g, 23 mmol) in dry DMF (300 mL), was added sodium azide (8.2 g, 126 mmol) and the mixture was heated to 80 °C overnight. Reaction was checked by LRMS and after complete disappearance of the starting material, it was diluted with H_2O (300 mL) and extracted with AcOEt. Combined organic layers were dried over $MgSO_4$, filtered and evaporated. Crude was purified by flash column chromatography (Tol/Acetone, 8:2, v/v) to afford compound **16** as a white solid (12.5 g, 17.7 mmol, 77%). R_f = 0.34, Tol/AcOEt 1:2; $[\alpha]_D^{20}$= -20.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (d, *J* = 9.3 Hz, 1H, $N\underline{H}COCH_3$), 5.35 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4'), 5.19 – 5.06 (m, 2H, H-2', H-3), 4.97 (dd, *J* = 10.5, 3.4 Hz, 1H, H-3'), 4.57 (d, *J* = 7.6 Hz, 1H, H-1), 4.54 – 4.46 (m, 2H, H-1', H-6a), 4.16 – 4.07 (m, 3H, H-6b, H-6'a, H-6'b), 4.06 – 3.95 (m, 2H, $OC\underline{H}HCH_2N_3$, H-2), 3.88 (ddd, *J* = 7.6, 6.4, 1.3 Hz,

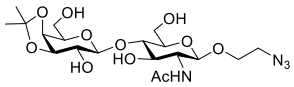
1H, H-5'), 3.80 (*a*t, *J* = 8.5 Hz, 1H, H-4), 3.70 – 3.60 (m, 2H, H-5, OCH*H*CH_2N_3), 3.47 (ddd, *J* = 13.3, 8.3, 3.3 Hz, 1H, $OCH_2CH\underline{H}N_3$), 3.26 (ddd, *J* = 13.4, 4.9, 3.2 Hz, 1H, $OCH_2C\underline{H}HN_3$), 2.15 (s, 3H, $OCOCH_3$), 2.11 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 2.06 – 2.02 (m, 6H, 2 $OCOCH_3$), 1.98 – 1.95 (m, 6H, $OCOCH_3$, $NHCOC\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.4, 170.34, 170.33, 170.1, 170.0, 169.3 (7 $\underline{C}OCH_3$), 101.0 (C-1'), 100.8 (C-1), 75.6 (C-4), 72.8 (C-5), 72.2 (C-3), 70.8 (C-3'), 70.7 (C-5'), 69.1 (C-2'), 68.2 ($O\underline{C}H_2CH_2N_3$), 66.6 (C-4'), 62.1 (C-6), 60.8 (C-6'), 53.3 (C-2), 50.6 ($OCH_2\underline{C}H_2N_3$), 23.3 ($NHCO\underline{C}H_3$), 20.9, 20.8, 20.63, 20.62, 20.61, 20.5 (6 $OCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{28}H_{40}N_4O_{17}$: 727.2286 $[M+Na]^+$; found: 727.2273.

2-Azidoethyl (β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (17)



Methanolic sodium methoxide (0.5 M, 3 mL, 1.5 mmol) was added to a solution of **16** (1.7 g, 2.4 mmol) in MeOH (50 mL). Reaction was followed by TLC analysis (CH_2Cl_2/MeOH, 9:1, v/v). After 4 hours, the mixture was diluted with H_2O, quenched with Dowex 50WX8 H^+ resin, filtered and concentrated *in vacuo* to give **17** (980 mg, 2.2 mmol, 91%). R_f = 0.1, CH_2Cl_2/MeOH 8:2; $[\alpha]_D^{20}$= -32.9 (*c* 0.7, H_2O); ^1H NMR (500 MHz, D_2O): δ 4.62 (d, *J* = 8.3 Hz, 1H, H-1), 4.49 (d, *J* = 7.8 Hz, 1H, H-1'), 4.07 (ddd, *J* = 11.4, 5.6, 3.1 Hz, 1H, OCH*H*CH_2N_3), 4.01 (dd, *J* = 12.4, 2.3 Hz, 1H, H-6a), 3.94 (*a*d, *J* = 3.4 Hz, 1H, H-4'), 3.85 (dd, *J* = 12.4, 5.2 Hz, 1H, H-6b), 3.82 – 3.71 (m, 7H, H-6'a, H-6'b, H-2, $OC\underline{H}HCH_2N_3$, H-4, H-5', H-3), 3.68 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3'), 3.62 (ddd, *J* = 8.3, 5.3, 2.2 Hz, 1H, H-5), 3.55 (dd, *J* = 10.0, 7.8 Hz, 1H, H-2'), 3.50 (ddd, *J* = 13.8, 7.6, 3.0, 1H, $OCH_2CH\underline{H}N_3$), 3.44 (ddd, *J* = 13.8, 5.6, 3.0 Hz, 1H, $OCH_2C\underline{H}HN_3$), 2.06 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, D_2O): δ 174.7 ($NH\underline{C}OCH_3$), 102.9 (C-1'), 101.0 (C-1), 78.5 (C-4), 75.4 (C-5'), 74.8 (C-5), 72.53 (C-3), 72.50 (C-3'), 71.0 (C-2'), 68.8 ($O\underline{C}H_2CH_2N_3$), 68.6 (C-4'), 61.1 (C-6'), 60.1 (C-6), 55.1 (C-2), 50.4 ($OCH_2\underline{C}H_2N_3$), 22.3 ($NHCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{16}H_{28}N_4O_{11}$: 475.1652 $[M+Na]^+$; found: 475.1648.

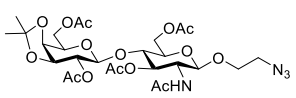
2-Azidoethyl (3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (18)



To a solution of **17** (520 mg, 1.14 mmol) in dry DMF (6 mL) were added 2,2-dimethoxypropane (705 µL, 5.7 mmol) and *p*-TsOH (43 mg, 0.23 mmol). Mixture was heated to 80 °C and followed by TLC analysis (CH_2Cl_2/MeOH, 9:1, v/v). After 20 hours, the reaction was cooled to RT and quenched with Et_3N, then the solvent was evaporated *in vacuo*. Crude syrup was purified by flash column chromatography (CH_2Cl_2/MeOH/ Et_3N, 95:5:0.5, v/v) to give **18** as an amorphous solid (405 mg, 0.82 mmol, 72%). R_f = 0.70 CH_2Cl_2/MeOH, 9:1; $[\alpha]_D^{20}$= -15.0 (*c* 1.0, MeOH); ^1H NMR (500 MHz, CD_3OD): δ 4.53 (d, *J* = 8.3 Hz, 1H, H-1), 4.40 (d, *J* = 8.2 Hz, 1H, H-1'), 4.21 (dd, *J* = 5.5, 2.1 Hz, 1H, H-4'), 4.07 (dd, *J* = 7.4, 5.5 Hz, 1H, H-3'), 4.05 – 4.02 (m, 1H, OCH*H*CH_2N_3), 3.97 – 3.91 (m, 2H, H-5', H-6a), 3.85 (dd, *J* = 12.2, 4.4 Hz, 1H, H-6b), 3.82 – 3.73 (m, 3H, H-2, H-6'a, H-6'b), 3.71 – 3.60 (m, 3H, $OC\underline{H}HCH_2N_3$, H-3, H-4), 3.52 – 3.40 (m, 3H, H-2', H-5, $OCH_2CH\underline{H}N_3$), 3.33 (m, under CD_3OD peak, $OCH_2C\underline{H}HN_3$), 1.98 (s, 3H, $NHCOC\underline{H}_3$), 1.49 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR (126 MHz, CD_3OD): δ 173.6 ($NH\underline{C}OCH_3$), 111.1 ($\underline{C}(CH_3)_2$), 104.2 (C-1'), 102.5 (C-1), 81.2 (C-4), 80.9 (C-3'), 76.6 (C-5), 75.4 (C-5'), 75.1 (C-4'), 74.5 (C-2'), 74.1 (C-3), 69.3 ($O\underline{C}H_2CH_2N_3$), 62.4 (C-6'), 61.9 (C-6), 56.8

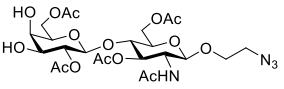
(C-2), 51.8 ($OCH_2\underline{C}H_2N_3$), 28.4 (CH_3), 26.5 (CH_3), 23.1 ($NHCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{19}H_{32}N_4O_{11}$: 493.2146 $[M+H]^+$; found: 493.2141.

2-Azidoethyl (2,6-di-*O*-acetyl-3,4-*O*-isopropylidene)-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (19)



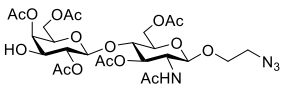
Compound **18** (520 mg, 1.05 mmol) was dissolved in pyridine (3 mL), then Ac_2O (1.5 mL) was slowly dropped under ice cooling. The reaction was stirred overnight at RT and followed by TLC analysis (Tol/Acetone, 6:4, v/v). After solvent evaporation *in vacuo*, the crude residue was purified by flash column chromatography (Tol/Acetone, 6:4, v/v) to give **19** (515 mg, 0.78 mmol, 74%) as a white foam. R_f = 0.4 Tol/Acetone, 6:4; $[\alpha]_D^{20}$ = +4.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (d, *J* = 9.3 Hz, 1H, $N\underline{H}COCH_3$), 5.08 (dd, *J* = 9.6, 8.1 Hz, 1H, H-3), 4.89 – 4.82 (m, 1H, H-2'), 4.54 (d, *J* = 7.5 Hz, 1H, H-1), 4.48 (dd, *J* = 11.9, 2.8 Hz, 1H, H-6a), 4.37 – 4.24 (m, 3H, H-1', H-6a', H-6b'), 4.20 – 4.12 (m, 3H, H-6b, H-3', H-4'), 4.05 (dd, *J* = 9.6, 7.5 Hz, 1H, H-2), 4.01 – 3.91 (m, 2H, $OCH\underline{H}CH_2N_3$, H-5'), 3.74 (*a*t, *J* = 8.4 Hz, 1H, H-4), 3.69 – 3.60 (m, 2H, H-5, $OC\underline{H}HCH_2N_3$), 3.46 (ddd, *J* = 13.3, 8.2, 3.4 Hz, 1H, $OCH_2CH\underline{H}N_3$), 3.26 (ddd, *J* = 13.4, 5.1, 3.3 Hz, 1H, $OCH_2C\underline{H}HN_3$), 2.11 (s, 3H, $OCOCH_3$), 2.10 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 1.95 (s, 3H, $NHCOC\underline{H}_3$), 1.51 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.82, 170.77, 170.5, 170.3, 169.4 (5 $\underline{C}OCH_3$), 110.8 ($\underline{C}(CH_3)_2$), 100.9 (C-1), 100.5 (C-1'), 76.5 (C-4'), 75.5 (C-4), 73.1 (C-5), 72.9 (C-3'), 72.7 (C-2'), 72.0 (C-3), 70.9 (C-5'), 68.2 ($O\underline{C}H_2CH_2N_3$), 63.1 (C-6'), 62.3 (C-6), 53.0 (C-2), 50.6 ($OCH_2\underline{C}H_2N_3$), 27.4 (CH_3), 26.1 (CH_3), 23.2 ($NHCO\underline{C}H_3$), 20.84 (3 $OCO\underline{C}H_3$), 20.78 ($OCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{27}H_{40}N_4O_{15}$: 661.2568 $[M+H]^+$; found: 661.2562.

2-Azidoethyl (2,6-di-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (20)



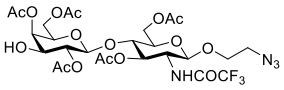
Compound **19** (290 mg, 0.43 mmol) was dissolved in 80% aq. AcOH (9 mL) and heated to 40 °C for 3 hours. Reaction was followed by TLC analysis (CH_2Cl_2/MeOH, 98:2, v/v) and after complete disappearance of the starting material, the solvent was removed under vacuum (co-evaporation with toluene). Crude residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5, v/v) to afford **20** (245 mg, 0.39 mmol, 90%) as a white amorphous solid. R_f = 0.48, CH_2Cl_2/MeOH, 95:5; $[\alpha]_D^{20}$ = -20.1 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 5.09 (dd, *J* = 10.4, 8.8 Hz, 1H, H-3), 4.95 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2'), 4.61 (d, *J* = 8.4 Hz, 1H, H-1), 4.51 (dd, *J* = 11.9, 2.1 Hz, 1H, H-6a), 4.45 (d, *J* = 8.0 Hz, 1H, H-1'), 4.29 – 4.15 (m, 3H, H-6b, H-6'a, H-6'b), 3.95 (ddd, *J* = 11.0, 5.3, 3.2 Hz, 1H, $OCH\underline{H}CH_2N_3$), 3.90 – 3.80 (m, 2H, H-4', H-2), 3.79 – 3.73 (m, 2H, H-4, H-5), 3.72 – 3.64 (m, 2H, $OC\underline{H}HCH_2N_3$, H-5'), 3.62 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3'), 3.44 (ddd, *J* = 13.4, 8.0, 3.2 Hz, 1H, $OCH_2CH\underline{H}N_3$), 3.29 – 3.24 (m, 1H, $OCH_2C\underline{H}HN_3$), 2.10 (s, 3H, $OCOCH_3$), 2.08 (s, 6H, 2 $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.89 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (101 MHz, CD_3OD): δ 173.7 ($NH\underline{C}OCH_3$), 172.7, 172.6, 172.4, 172.1 (4 $O\underline{C}OCH_3$), 102.9 (C-1'), 102.2 (C-1), 78.0 (C-4), 74.8 (C-3), 74.4 (C-5'), 74.2 (C-5), 74.1 (C-2'), 73.3 (C-3'), 70.3 (C-4'), 70.1 ($O\underline{C}H_2CH_2N_3$), 64.5 (C-6'), 63.9 (C-6), 55.6 (C-2), 51.9 ($OCH_2\underline{C}H_2N_3$), 23.1 ($NHCO\underline{C}H_3$), 21.4, 21.3, 21.0, 20.9 (4 $OCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{24}H_{36}N_4O_{15}$: 643.2075 $[M+Na]^+$; found: 643.2047.

2-Azidoethyl (2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (21)



To a solution of **20** (2.8 g, 4.5 mmol) in dry CH_3CN (50 mL), were added $CH_3C(OCH_3)_3$ (1.7 mL, 13.5 mmol) and *p*-TsOH (171 mg, 0.9 mmol). The mixture was checked by TLC analysis (CH_2Cl_2/MeOH, 95:5, v/v, $R_{f\ orthoester}$ = 0.66) and, after 2 hours, it was quenched with Et_3N and evaporated under vacuum. Crude residue was then dissolved in 80% aq. AcOH (50 mL) and the orthoester rearrangement was followed by TLC analysis (CH_2Cl_2/MeOH, 95:5, v/v). After 2 hours, the solvent was removed (co-evaporation with toluene). Crude residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5, v/v) to afford **21** (2.9 g, 4.4 mmol, 98%) as a white foam. R_f = 0.39, CH_2Cl_2/MeOH, 95:5; $[\alpha]_D^{20}$= -21.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 (d, *J* = 9.3 Hz, 1H, N*H*COCH$_3$), 5.30 (dd, *J* = 3.6, 1.1 Hz, 1H, H-4'), 5.13 (dd, *J* = 9.9, 8.3 Hz, 1H, H-3), 4.88 (dd, *J* = 10.0, 7.9 Hz, 1H, H-2'), 4.58 (d, *J* = 7.8 Hz, 1H, H-1), 4.53 (dd, *J* = 11.9, 2.6 Hz, 1H, H-6a), 4.45 (d, *J* = 7.9 Hz, 1H, H-1'), 4.23 – 4.14 (m, 1H, H-6b), 4.13 – 4.06 (m, 2H, H-6'a, H-6'b), 4.04 – 3.94 (m, 2H, H-2, OCH*H*CH$_2$N$_3$), 3.87 – 3.72 (m, 3H, H-3', H-4, H-5'), 3.70 – 3.60 (m, 2H, OC*H*HCH$_2$N$_3$, H-5), 3.48 (ddd, *J* = 13.4, 8.3, 3.3 Hz, 1H, OCH$_2$CH*H*N$_3$), 3.27 (ddd, *J* = 13.4, 4.9, 3.2 Hz, 1H, OCH$_2$C*H*HN$_3$), 2.17 (s, 3H, OCOCH$_3$), 2.13 (s, 3H, OCOCH$_3$), 2.11 (s, 3H, OCOCH$_3$), 2.08 (s, 3H, OCOCH$_3$), 2.07 (s, 3H, OCOCH$_3$), 1.96 (s, 3H, NHCOC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1, 170.7, 170.6, 170.4, 170.3 (6 *C*OCH$_3$), 100.8 (C-1), 100.8 (C-1'), 75.9 (C-4), 73.0 (C-2'), 72.9 (C-5), 72.2 (C-3), 71.5 (C-5'), 71.0 (C-3'), 69.2 (C-4'), 68.2 (O*C*H$_2$CH$_2$N$_3$), 62.2 (C-6), 61.4 (C-6'), 53.5 (C-2), 50.6 (OCH$_2$*C*H$_2$N$_3$), 23.3 (NHCO*C*H$_3$), 20.84, 20.82, 20.81, 20.74, 20.72 (5 OCO*C*H$_3$); HRMS (ESI$^+$): m/z calcd for $C_{26}H_{38}N_4O_{16}$: 685.2181 $[M+Na]^+$; found: 685.2146.

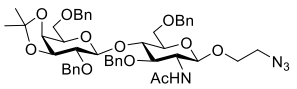
2-Azidoethyl (2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (22)



Compound **21** (280 mg, 0.42 mmol) was dissolved in dry CH_3CN (1.3 mL) and then reacted, in a sealed tube, with trifluoroacetic anhydride (175 µL, 1.26 mmol) at 135 °C for 3 hours. The mixture was then ice-cooled, MeOH was added, and the solvents were removed *in vacuo*. The crude was treated with 80% aq. AcOH (4 mL) for 2 hours at 40 °C then concentrated to dryness. The obtained crude residue was purified by flash column chromatography (cHex/AcOEt, 6:4 → 3:7, v/v) to afford **22** (212 mg, 0.29 mmol, 70%) as an off-white foam. R_f = 0.70, CH_2Cl_2/MeOH, 95:5; $[\alpha]_D^{20}$= -18.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (d, *J* = 9.3 Hz, 1H, N*H*COCH$_3$), 5.32 – 5.28 (m, 1H, H-4'), 5.19 (dd, *J* = 10.1, 8.4 Hz, 1H, H-3), 4.86 (dd, *J* = 10.0, 7.9 Hz, 1H, H-2'), 4.63 (d, *J* = 7.8 Hz, 1H, H-1), 4.53 (dd, *J* = 12.0, 2.6 Hz, 1H, H-6a), 4.44 (d, *J* = 7.9 Hz, 1H, H-1'), 4.18 (dd, *J* = 12.0, 5.1 Hz, 1H, H-6b), 4.14 – 4.03 (m, 3H, H-2, H-6'a, H-6'b), 4.00 (ddd, *J* = 10.9, 5.0, 3.5 Hz, 1H, OCH*H*CH$_2$N$_3$), 3.86 – 3.76 (m, 3H, H-3', H-4, H-5'), 3.74 – 3.63 (m, 2H, OC*H*HCH$_2$N$_3$, H-5), 3.47 (ddd, *J* = 13.4, 8.2, 3.4 Hz, 1H, OCH$_2$C*H*HN$_3$), 3.32 (ddd, *J* = 13.4, 5.0, 3.4 Hz, 1H, OCH$_2$CH*H*N$_3$), 2.56 (br, 1H, OH), 2.17 (s, 3H, OCOCH$_3$), 2.13 (s, 6H, 2 OCOCH$_3$), 2.08 (s, 3H, OCOCH$_3$), 2.06 (s, 3H, OCOCH$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.84, 170.82, 170.42, 170.38 (5 O*C*OCH$_3$), 157.5 (*a*d, *J* = 37.4 Hz, NH*C*OCF$_3$), 115.6 (*a*d, *J* = 287.9 Hz, NHCO*C*F$_3$), 101.0 (C-1'), 100.3 (C-1), 75.8 (C-4), 73.1 (C-5), 72.8 (C-2'), 71.6 (C-3), 71.3 (C-3'), 71.1 (C-5), 69.2 (C-4'), 68.4 (O*C*H$_2$CH$_2$N$_3$), 62.0 (C-6), 61.4 (C-6'), 53.9 (C-2), 50.6

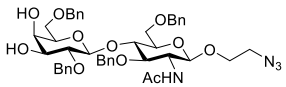
($OCH_2\underline{C}H_2N_3$), 20.82, 20.80, 20.6, 20.5 (5 $OCO\underline{C}H_3$). ^{19}F NMR (376 MHz, $CDCl_3$): δ 76.1 (s, $NHCOCF_3$); HRMS (ESI^+): m/z calcd for $C_{26}H_{35}F_3N_4O_{16}$: 739.1898 $[M+Na]^+$; found: 739.1887.

2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29)



BnBr (2.8 mL, 23.5 mmol) was added to a solution of compound **18** (2 g, 4.1 mmol) in dry DMF (80 mL). The solution was then cooled to -5 °C and NaH (60% dispersion in mineral oil, 0.9 g, 22.3 mmol) was slowly added. The reaction was kept at the same temperature for 2 hours then cooled to -20 °C and quenched with MeOH and AcOH. Solvents were then removed under reduced pressure and the crude residue was purified by flash column chromatography (Tol/AcOEt, 7:3, v/v) to give **29** (2.4 g, 2.8 mmol, 68%) as a clear oil. R_f = 0.38, Tol/AcOEt 6:4; $[\alpha]_D^{20}$= +9.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.19 (m, 20H, H_{Ar}), 5.66 (d, *J* = 7.5 Hz, 1H, $N\underline{H}COCH_3$), 4.98 (d, *J* = 7.5 Hz, 1H, H-1), 4.85 (d, *J* = 11.1 Hz, 1H, $CH\underline{H}Ph$), 4.77 (d, *J* = 11.7 Hz, 1H, $C\underline{H}HPh$), 4.69 (d, *J* = 11.8 Hz, 1H, $C\underline{H}HPh$), 4.58 – 4.49 (m, 3H, $CH\underline{H}Ph$, CH_2Ph), 4.43 – 4.34 (m, 3H, $CH\underline{H}Ph$, $C\underline{H}HPh$, H-1'), 4.13 (dd, *J* = 9.3, 8.0 Hz, 1H, H-3), 4.09 (dd, *J* = 5.6, 1.7 Hz, 1H, H-4'), 4.03 – 3.97 (m, 2H, H-3', $OCH\underline{H}CH_2N_3$), 3.94 (*a*t, *J* = 8.4 Hz, 1H, H-4), 3.83 (dd, *J* = 10.8, 4.2 Hz, 1H, $OC\underline{H}HCH_2N_3$), 3.73 – 3.61 (m, 4H, H-6a, H-6b, H-6'a, H-5'), 3.60 – 3.54 (m, 2H, H-6'b, H-5), 3.44 (ddd, *J* = 13.3, 7.9, 3.4 Hz, 1H, $OCH_2CH\underline{H}N_3$), 3.33 (dd, *J* = 8.0, 6.8 Hz, 1H, H-2'), 3.28 (dt, *J* = 9.4, 7.5 Hz, 1H, H-2), 3.22 (ddd, *J* = 13.3, 5.3, 3.4 Hz, 1H, $OCH_2C\underline{H}HN_3$), 1.84 (s, 3H, $NHCOC\underline{H}_3$), 1.36 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5 ($NH\underline{C}OCH_3$), 138.8 (C_{Ar}), 138.32 (C_{Ar}), 138.28 (C_{Ar}), 138.1 (C_{Ar}), 128.4, 128.32, 128.30, 128.2, 127.9, 127.7, 127.6, 127.54, 127.53 (20 C_{Ar}), 109.8 ($\underline{C}(CH_3)_2$), 102.1 (C-1'), 99.6 (C-1), 80.4 (C-2'), 79.2 (C-3'), 77.6 (C-3), 77.0 (C-4), 75.0 (C-5), 74.2 (CH_2Ph), 73.6 (C-4'), 73.4 (CH_2Ph), 73.2 (2 CH_2Ph), 72.00 (C-5'), 69.0 (C-6'), 68.3 (C-6), 68.2 ($O\underline{C}H_2CH_2N_3$), 56.6 (C-2), 50.6 ($OCH_2\underline{C}H_2N_3$), 27.9 (CH_3), 26.4 (CH_3), 23.6 ($NHCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{47}H_{56}N_4O_{11}$: 875.3843 $[M+Na]^+$; found: 875.3841.

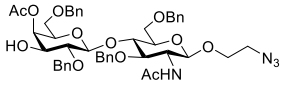
2-Azidoethyl (2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (30)



Compound **29** (2.2 g, 2.5 mmol) was dissolved in AcOH 80% (30 mL) and heated to 60 °C for 2 hours. Then solvent was removed by co-evaporation with toluene to give a crude oil. Purification by flash column chromatography (Tol/AcOEt, 7:3 → 2:8, v/v) gave compound **30** (1.9 g, 2.3 mmol, 92%) as a clear oil. R_f = 0.34, Tol/Acetone 1:1; $[\alpha]_D^{20}$= +11.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 – 6.81 (m, 20H, H_{Ar}), 5.71 (d, *J* = 7.5 Hz, 1H, $N\underline{H}COCH_3$), 5.00 (d, *J* = 7.5 Hz, 1H, H-1), 4.93 (d, *J* = 11.4 Hz, 1H, $CH\underline{H}Ph$), 4.85 (d, *J* = 11.5 Hz, 1H, $C\underline{H}HPh$), 4.67 (d, *J* = 11.5 Hz, 1H, $C\underline{H}HPh$), 4.62 – 4.54 (m, 2H, $CH\underline{H}Ph$, $CH\underline{H}Ph$), 4.48 – 4.39 (m, 4H, CH_2Ph, $C\underline{H}HPh$, H-1'), 4.17 (*a*t, *J* = 8.8 Hz, 1H, H-3), 4.04 – 3.96 (m, 2H, H-4, H-6'a), 3.94 (br, 1H, H-4'), 3.84 (dd, *J* = 10.8, 4.0 Hz, 1H, H-6a), 3.74 (dd, *J* = 10.9, 2.5 Hz, 1H, H-6b), 3.69 – 3.62 (m, 2H, H-6'b, $OCH\underline{H}CH_2N_3$), 3.61 – 3.52 (m, 2H, $OC\underline{H}HCH_2N_3$, H-5), 3.49 – 3.41 (m, 3H, H-2', H-3', $OCH_2CH\underline{H}N_3$), 3.38 (*a*t, *J* = 5.7 Hz, 1H, H-5'), 3.30 (*a*t, *J* = 8.0 Hz, 1H, H-2), 3.24 (dt, *J* = 13.4, 4.3 Hz, 1H, $OCH_2C\underline{H}HN_3$), 2.62 (br, 1H, OH), 2.47 (br, 1H, OH), 1.85 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 ($NH\underline{C}OCH_3$), 139.0 (C_{Ar}), 138.4 (C_{Ar}), 138.3(C_{Ar}), 138.0 (C_{Ar}), 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6 (20 C_{Ar}), 103.0 (C-1'), 99.7 (C-1), 80.0 (C-2'), 77.8 (C-3), 77.3 (C-4), 75.2 (CH_2Ph), 75.1 (C-5), 74.4 (CH_2Ph), 73.7 (CH_2Ph), 73.5

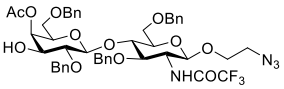
(CH_2Ph), 73.3 (C-3'), 73.1 (C-5'), 69.1 ($O\underline{C}H_2CH_2N_3$), 69.0 (C-4'), 68.5 (C-6'), 68.4 (C-6), 56.8 (C-2), 50.8 ($OCH_2\underline{C}H_2N_3$), 23.7 ($NHCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{44}H_{52}N_4O_{11}$: 835.3530 $[M+Na]^+$; found: 835.3489.

2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (31)



To a solution of **30** (290 mg, 0.36 mmol) in dry CH_3CN (7 mL), were added $CH_3C(OCH_3)_3$ (135 µL, 1.1 mmol) and *p*-TsOH (7 mg, 0.04 mmol). The reaction was stirred for 40 minutes then quenched with Et_3N and concentrated under reduced pressure. Crude residue was directly dissolved in 80% aq. AcOH (4mL) and stirred at RT for 1 hour. The solvent was then removed by co-evaporation with toluene and the crude residue was purified by flash column chromatography (Tol/Acetone, 9:1 → 1:1, v/v) to give **31** (287 mg, 0.33 mmol, 92%) as a white foam. R_f = 0.28, Tol/AcOEt 6:4; $[\alpha]_D^{20}$= -9.4 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.17 (m, 20H, H_{Ar}), 5.73 (d, *J* = 7.3 Hz, 1H, $N\underline{H}COCH_3$), 5.34 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4'), 5.05 (d, *J* = 7.7 Hz, 1H, H-1), 4.94 (d, *J* = 11.0 Hz, 1H, $CH\underline{H}Ph$), 4.85 (d, *J* = 11.3 Hz, 1H, $C\underline{H}HPh$), 4.67 (d, *J* = 11.4 Hz, 1H, $CH\underline{H}Ph$), 4.62 – 4.55 (m, 2H, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.50 – 4.40 (m, 3H, $C\underline{H}HPh$, $C\underline{H}HPh$, H-1'), 4.28 (d, *J* = 11.9 Hz, 1H, $CH\underline{H}Ph$), 4.24 (dd, *J* = 9.7, 8.3 Hz, 1H, H-3), 4.06 – 3.97 (m, 2H, H-4, $OCH\underline{H}CH_2N_3$), 3.82 (dd, *J* = 10.8, 4.0 Hz, 1H, H-6a), 3.73 (dd, *J* = 10.8, 2.5 Hz, 1H, H-6b), 3.68 (ddd, *J* = 11.0, 8.0, 3.3 Hz, 1H, $OC\underline{H}HCH_2N_3$), 3.65 – 3.60 (m, 1H, H-3'), 3.60 – 3.52 (m, 2H, H-5, H-5'), 3.47 (ddd, *J* = 13.3, 8.0, 3.4 Hz, 1H, $OCH_2CH\underline{H}N_3$), 3.41 (dd, *J* = 9.6, 7.8 Hz, 1H, H-2'), 3.38 – 3.34 (m, 2H, H-6'a, H-6'b), 3.28 – 3.20 (m, 2H, H-2, $OCH_2C\underline{H}HN_3$), 2.28 (br, 1H, OH), 2.01 (s, 3H, $OCOCH_3$), 1.91 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.0 ($O\underline{C}OCH_3$), 170.8 ($NH\underline{C}OCH_3$), 139.0 (C_{Ar}), 138.3 (C_{Ar}), 138.2 (C_{Ar}), 138.0 (C_{Ar}), 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7 (20 C_{Ar}), 102.7 (C-1'), 99.6 (C-1), 80.2 (C-2'), 77.5 (C-3), 77.1 (C-4), 75.3 (C-5), 75.2 (CH_2Ph), 74.4 (CH_2Ph), 73.6 (CH_2Ph), 73.4 (CH_2Ph), 72.4 (C-3'), 72.2 (C-5'), 69.7 (C-4'), 68.5 ($O\underline{C}H_2CH_2N_3$), 68.4 (C-6), 67.6 (C-6'), 57.2 (C-2), 50.8 ($OCH_2\underline{C}H_2N_3$), 23.8 ($NHCO\underline{C}H_3$), 20.9 ($OCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{46}H_{54}N_4O_{12}$: 877.3636 $[M+Na]^+$; found: 877.3657.

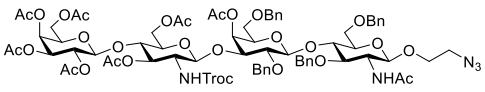
2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (32)



Compound **31** (20 mg, 23 µmol) and Et_3N (20 µL, 0.14 mmol) were dissolved in dry CH_3CN (70 µL). Trifluoroacetic anhydride (10 µL, 70 µmol) was then added, developing smoke and turning the reaction yellow. The reaction vial was then flushed with N_2, sealed and heated to 135 °C for 2 hours. After this time, the mixture was cooled to RT, quenched with MeOH and evaporated to dryness. Crude was purified by flash column chromatography (Tol/Acetone, 9:1 → 7:3, v/v) to give **32** (18 mg, 20 µmol, 86%) as a white-yellow foam. R_f = 0.68, Tol/Acetone 7:3; $[\alpha]_D^{20}$= -12.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.20 (m, 20H, H_{Ar}), 6.80 (d, *J* = 7.6 Hz, 1H, $NHCOCF_3$), 5.33 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 4.94 (d, *J* = 6.9 Hz, 1H, H-1), 4.85 (ad, *J* = 11.1 Hz, 2H, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.70 (d, *J* = 11.3 Hz, 1H, $C\underline{H}HPh$), 4.62 – 4.52 (m, 2H, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.50 – 4.41 (m, 3H, H-1', CH_2Ph), 4.30 (d, *J* = 11.8 Hz, 1H, $CH\underline{H}Ph$), 4.11 (*a*t, *J* = 8.1 Hz, 1H, H-3), 4.06 – 3.98 (m, 2H, H-4, $OCH\underline{H}CH_2N_3$), 3.84 (dd, *J* = 10.6, 4.2 Hz, 1H, H-6a), 3.76 (dd, *J* = 10.6, 3.3 Hz, 1H, H-6b), 3.70 – 3.60 (m, 3H, $OC\underline{H}HCH_2N_3$, H-3', H-5), 3.60 – 3.53 (m, 2H, H-2, H-5'), 3.49 – 3.35 (m, 4H, $OCH_2CH\underline{H}N_3$, H-6'a, H-6'b, H-2'), 3.29 (ddd, *J* = 13.3, 5.4, 3.6 Hz, 1H, $OCH_2C\underline{H}HN_3$), 2.35 – 2.31 (br, 1H, OH),

2.03 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1 ($O\underline{C}OCH_3$), 157.3 (*a*d, *J* = 37.3 Hz, $NH\underline{C}OCF_3$), 138.2 (C_{Ar}), 138.1 (C_{Ar}), 138.0 (C_{Ar}), 137.9 (C_{Ar}), 128.7, 128.58, 128.55, 128.4, 128.1, 128.01, 127.95, 127.89, 127.87 (20 C_{Ar}), 115.8 (*a*d, *J* = 288.5 Hz, $NHCO\underline{C}F_3$), 103.0 (C-1'), 99.1 (C-1), 80.0 (C-2'), 76.7 (C-4), 76.3 (C-3), 75.4 (C-5), 75.3 (CH_2Ph), 74.3 (CH_2Ph), 73.7 (CH_2Ph), 73.4 (CH_2Ph), 72.4 (C-3', C-5'), 69.6 (C-4'), 68.5 ($O\underline{C}H_2CH_2N_3$), 68.4 (C-6), 67.5 (C-6'), 55.9 (C-2), 50.7 ($OCH_2\underline{C}H_2N_3$), 20.8 ($OCO\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.89 ($NHCOCF_3$); HRMS (ESI^+): m/z calcd for $C_{46}H_{51}N_4O_{12}F_3$: 931.3353 $[M+Na]^+$; found: 931.3386.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (33)



Acceptor **31** (47 mg, 55 μmol) and donor **9** (58 mg, 71.0 μmol) were dissolved in dry CH_2Cl_2 (3 mL) together with 4Å molecular sieves (85 mg). The mixture was stirred for 1 hour, then NIS (18 mg, 80 μmol) was added and the mixture was cooled to -20 °C. TfOH (2.4 μL, 27 μmol) was then dropped and the reaction was stirred for 30 minutes at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated *in vacuo*. Purification by flash column chromatography (Tol/Acetone, 9:1 → 7:3, v/v) gave **33** (77 mg, 48 μmol, 87%) as a white foam. R_f = 0.34, Tol/Acetone 7:3; $[\alpha]_D^{20}$= +2.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.20 (m, 20H, H_{Ar}), 5.72 (d, *J* = 7.4 Hz, 1H, $N\underline{H}COCH_3$), 5.38 – 5.33 (m, 2H, H-4', H-4'''), 5.10 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'''), 5.02 (d, *J* = 7.7 Hz, 1H, H-1), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3'''), 4.92 (d, *J* = 10.9 Hz, 1H, $C\underline{H}HPh$), 4.86 (d, *J* = 11.7 Hz, 1H, $CH\underline{H}Ph$), 4.77 – 4.72 (m, 1H, H-3''), 4.67 (dd, *J* = 12.1, 10.2 Hz, 2H, $C\underline{H}HPh$, $CH\underline{H}CCl_3$), 4.61 – 4.38 (m, 11H, H-1'', H-1''', H-1', CH_2Ph, $C\underline{H}HCCl_3$, H-6''a, $N\underline{H}COCH_2CCl_3$, CH_2Ph), 4.31 (d, *J* = 11.8 Hz, 1H, $C\underline{H}HPh$), 4.24 – 4.17 (m, 1H, H-3), 4.09 (d, *J* = 6.8 Hz, 2H, H-6a''', H-6b'''), 4.06 – 3.97 (m, 3H, H-6a'', $OCH\underline{H}CH_2N_3$, H-4), 3.88 – 3.84 (m, 1H, H-5'''), 3.80 (dd, *J* = 10.9, 3.8 Hz, 1H, H-6a), 3.74 (*a*t, *J* = 9.3 Hz, 1H, H-4''), 3.69 – 3.63 (m, 3H, H-6b, $OCH\underline{H}CH_2N_3$, H-3'), 3.61 – 3.54 (m, 2H, H-2'', H-5), 3.53 – 3.42 (m, 4H, $OCH_2CH\underline{H}N_3$, H-5'', H-5', H-2'), 3.36 (*a*dt, *J* = 6.9, 3.1 Hz, 2H, H-6a', H-6b'), 3.27 – 3.17 (m, 2H, $OCH_2CH\underline{H}N_3$, H-2), 2.14 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.05 (s, 3H, $OCOCH_3$), 2.01 (s, 3H, $OCOCH_3$), 1.99 (s, 3H, $OCOCH_3$), 1.97 (s, 3H, $OCOCH_3$), 1.90 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7 ($NH\underline{C}OCH_3$), 170.6, 170.5, 170.4, 170.23, 170.17, 170.0, 169.3 (7 $O\underline{C}OCH_3$), 154.2 ($NH\underline{C}O_2CH_2CCl_3$), 138.9, 138.4, 138.2, 138.1 (4 C_{Ar}), 129.2, 128.9, 128.6, 128.5, 128.31, 128.29, 128.2, 128.1, 128.0, 127.82, 127.80, 127.7, 127.1 (20 C_{Ar}), 102.4 (C-1'), 101.4 (C-1'''), 101.1 (C-1''), 99.6 (C-1), 95.7 ($CH_2\underline{C}Cl_3$), 80.7 (C-2'), 77.4 (H-3), 76.6 (C-3', H-4), 76.3 (H-4''), 75.2 (CH_2Ph), 75.1 (C-5'), 74.4 (CH_2Ph, $\underline{C}H_2CCl_3$), 73.7 (CH_2Ph), 73.6 (CH_2Ph), 72.7 (C-5''), 72.6 (C-5), 72.3 (C-3''), 71.1 (C-3'''), 70.9 (C-5'''), 69.8 (C-4'), 69.3 (C-2'''), 68.5 ($O\underline{C}H_2CH_2N_3$), 68.2 (C-6, C-6'), 66.8 (C-4'''), 61.57 (C-6''), 61.0 (C-6'''), 57.2 (C-2), 56.4 (C-2''), 50.7 ($OCH_2\underline{C}H_2N_3$), 23.8 ($NHCO\underline{C}H_3$), 20.94, 20.89, 20.84, 20.80, 20.78, 20.76, 20.6 (7 $OCO\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{73}H_{88}Cl_3N_5O_{29}$: 1626.4528 $[M+Na]^+$; found 1626.4451.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (34)

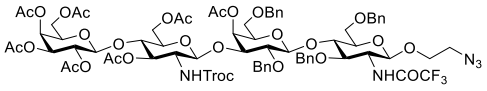
Acceptor **31** (15 mg, 17 μmol) and donor **12** (16 mg, 21 μmol) were dissolved in dry CH_2Cl_2 (1 mL) together with 4Å molecular sieves (25 mg). The mixture was stirred for 1 hour, then NIS (6 mg, 25 μmol) was added and the mixture was cooled to -20 °C. TfOH (1 μL, 9 μmol) was then dropped and the reaction was stirred for 30 minutes at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated. Purification by flash column chromatography (Tol/Acetone, 9:1 → 1:1, v/v) gave **34** (22 mg, 14 μmol, 83%) as a white foam. R_f = 0.47, Tol/Acetone 7:3; $[\alpha]_D^{20}$= +15.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.13 (m, 22H, H_{Ar}), 6.93 (dd, *J* = 6.6, 2.9 Hz, 2H, H_{Ar}), 5.77 (dd, *J* = 10.6, 8.7 Hz, 1H, H-3''), 5.65 (d, *J* = 7.3 Hz, 1H, N*H*COCH$_3$), 5.53 (d, *J* = 8.2 Hz, 1H, H-1''), 5.37 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 5.33 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4'''), 5.13 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'''), 4.97 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3'''), 4.93 (d, *J* = 7.6 Hz, 1H, H-1), 4.84 (d, *J* = 10.9 Hz, 1H, CH*H*Ph), 4.72 (dd, *J* = 11.9, 2.3 Hz, 1H, H-6''a), 4.56 (d, *J* = 7.9 Hz, 1H, H-1'''), 4.50 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.48 – 4.44 (m, 2H, CH*H*Ph, C*H*HPh), 4.35 – 4.22 (m, 4H, H-1' CH*H*Ph, C*H*HPh, CH*H*Ph), 4.13 (dd, *J* = 10.7, 8.4 Hz, 1H, H-2''), 4.10 – 4.02 (m, 5H, H-3, C*H*HPh, H-6'''a, H-6'''b, H-6''b), 3.95 (ddd, *J* = 10.8, 5.2, 3.4 Hz, 1H, OCH*H*CH$_2$N$_3$), 3.92 – 3.83 (m, 3H, H-5''', H-4, H-4''), 3.74 (ddd, *J* = 10.0, 4.2, 2.4 Hz, 1H, H-5''), 3.63 – 3.54 (m, 3H, OC*H*HCH$_2$N$_3$, H-6'a, H-3'), 3.51 (*a*t, *J* = 6.2 Hz, 1H, H-5'), 3.45 – 3.23 (m, 6H, OCH$_2$CH*H*N$_3$, H-6'b, H-6a, H-6b, H-5, H-2'), 3.19 (ddd, *J* = 13.3, 5.2, 3.3 Hz, 1H, OCH$_2$C*H*HN$_3$), 3.11 (dd, *J* = 9.8, 7.6 Hz, 1H, H-2), 2.13 (s, 3H, OCOCH$_3$), 2.09 (s, 3H, OCOCH$_3$), 2.08 (s, 3H, OCOCH$_3$), 2.04 (s, 3H, OCOCH$_3$), 2.00 (s, 3H, OCOCH$_3$), 1.97 (s, 3H, OCOCH$_3$), 1.87 (s, 3H, OCOCH$_3$), 1.85 (s, 3H, NHCOC*H*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.52 (NH*C*OCH$_3$), 170.46, 170.3, 170.2, 170.1, 169.72, 169.66, 169.1 (7 O*C*OCH$_3$), 138.9 (C_{Ar}), 138.1 (C_{Ar}), 138.0 (C_{Ar}), 137.9 (C_{Ar}), 129.0, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.1, 126.7, 125.3 (20 C_{Ar}), 102.1 (C-1'), 101.2 (C-1'''), 99.3 (C-1), 98.1 (C-1''), 78.6 (C-2'), 78.5 (C-3'), 77.2 (C-3), 76.7, 76.4 (C-4'', C-4), 74.8 (C-5), 74.4 CH_2Ph), 74.2 (CH_2Ph), 73.5 (CH_2Ph), 73.1 (CH_2Ph), 72.4 (C-5'', C-5'), 71.0 (C-4'''), 70.9 (C-3''), 70.6 (C-5'''), 70.1 (C-4'), 69.1 (C-2'''), 68.3, 68.2, 67.7 (C-6', C-6, O*C*H$_2$CH$_2$N$_3$), 66.6 (C-4'''), 61.1 (C-6''), 60.6 (C-6'''), 57.1 (C-2), 55.3 (C-2''), 50.6 (OCH$_2$*C*H$_2$N$_3$), 23.6 (NHCO*C*H$_3$), 20.8, 20.74, 20.65, 20.6, 20.5 (7 OCO*C*H$_3$); HRMS (ESI$^+$): m/z calcd for $C_{78}H_{89}N_5O_{29}$: 1560.5721 $[M+H]^+$; found: 1560.5714.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (35)

Acceptor **31** (50 mg, 58 μmol) and donor **10** (52 mg, 70 μmol) were dissolved in CH_2Cl_2 (3 mL) together with 4Å molecular sieves (80 mg). The mixture was stirred for 30 minutes, then NIS (20 mg, 93 μmol) was added and the reaction was cooled to -20 °C before adding TfOH (3 μL, 35 μmol). The reaction was stirred for 90 minutes at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated. Purification by flash column chromatography (Tol/Acetone 9:1 → 6:4, v/v) gave **35** (83 mg, 54 μmol, 93%) as a white foam. R_f = 0.26, Tol/AcOEt 1:1; $[\alpha]_D^{20}$= -0.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.10 (m, 20H, H_{Ar}), 6.22 (d, *J* = 9.5 Hz, 1H, NHCOCF$_3$), 5.74 (d, *J* = 7.4 Hz, 1H, N*H*COCH$_3$), 5.43 – 5.30 (m, 2H, H-4', H-4'''), 5.12 (dd, *J* = 10.5, 7.9 Hz, 1H, H-2'''), 5.02 – 4.96 (m, 2H, H-1, H-3'''), 4.92 – 4.86 (m, 2H, H-3'', C*H*HPh), 4.82 (d, *J* = 11.8 Hz,

1H, CH*H*Ph), 4.71 (d, *J* = 7.8 Hz, 1H, H-1''), 4.68 – 4.62 (m, 2H, C*H*HPh, H-6''a), 4.57 (d, *J* = 11.0 Hz, 1H, CH*H*Ph), 4.53 (d, *J* = 7.9 Hz, 1H, H-1'''), 4.51 – 4.45 (m, 2H, C*H*HPh, CH*H*Ph), 4.44 (d, *J* = 7.8 Hz, 1H, H-1'), 4.40 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.31 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.18 (dd, *J* = 9.6, 8.2 Hz, 1H, H-4), 4.14 – 4.08 (m, 2H, H-6'''a, H-6'''b), 4.06 (dd, *J* = 12.1, 4.4 Hz, 1H, H-6''b), 4.04 – 3.95 (m, 2H, H-3, OCH*H*CH_2N_3), 3.98 – 3.91 (m, 1H, H-2''), 3.91 – 3.86 (m, 1H, H-5'''), 3.82 (*a*t, *J* = 9.0 Hz, 1H, H-4''), 3.77 (dd, *J* = 10.8, 3.9 Hz, 1H, H-6a), 3.73 – 3.62 (m, 3H, H-3', OC*H*HCH_2N_3, H-6b), 3.58 (*a*t, *J* = 6.4 Hz, 1H, H-5'), 3.54 – 3.42 (m, 4H, H-2', H-5, H-5'', OCH_2CH*H*N_3), 3.41 – 3.33 (m, 2H, H-6'a, H-6'b), 3.24 (ddd, *J* = 14.8, 6.2, 3.1 Hz, 1H, OCH_2C*H*HN_3), 2.15 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.07 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.98 (s, 3H, $OCOCH_3$), 1.91 (s, 3H, $NHCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.9, 170.7, 170.53, 170.48, 170.2, 170.14, 170.10, 169.3 (8 *C*OCH_3), 157.1 (*a*d, *J* = 37.3 Hz, NH*C*OCF_3), 138.9, 138.3, 138.2, 138.1 (4 C_{Ar}), 128.7, 128.53, 128.48, 128.31, 128.27, 128.1, 128.04, 127.99, 127.8, 127.7, 127.0 (20 C_{Ar}), 115.7 (*a*d, *J* = 287.7 Hz, NHCO*C*F_3), 102.4 (C-1'), 101.4 (C-1'''), 100.2 (C-1''), 99.6 (C-1), 80.4 (C-2'), 77.4 (C-4), 76.6 (C-3), 76.3 (C-3'), 75.7 (C-4''), 75.1 (C-5), 75.0 (CH_2Ph), 74.3 (CH_2Ph), 73.7 (CH_2Ph), 73.5 (CH_2Ph), 72.9 (C-5''), 72.5 (C-5'), 72.0 (C-3''), 71.0 (C-3'''), 70.9 (C-5'''), 69.8 (C-4'), 69.2 (C-2'''), 68.4 (O*C*$H_2CH_2N_3$), 68.2 (C-6), 68.1 (C-6'), 66.8 (C-4'''), 61.2 (C-6''), 61.0 (C-6'''), 57.0 (C-2), 54.6 (C-2''), 50.7 (OCH_2*C*H_2N_3), 23.7 ($NHCOCH_3$), 20.9, 20.81, 20.79, 20.74, 20.72, 20.63, 20.55 (7 $OCOCH_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.97; HRMS (ESI^+): m/z calcd for $C_{72}H_{86}F_3N_5O_{28}$: 1548.5309 $[M+Na]^+$; found: 1548.5358.

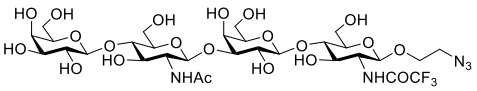
2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (36)



Acceptor **32** (95 mg, 104 μmol) and donor **9** (102 mg, 125 μmol) were dissolved in dry CH_2Cl_2 (6 mL) and stirred with 4Å molecular sieves (200 mg) for 1 hour at RT. NIS (35 mg, 0.156 mmol) was then added and the mixture was cooled to -20 °C before the addition of TfOH (5 μL). After 30 minutes the reaction was quenched with Et_3N and filtered through Celite. Solvent was then removed *in vacuo*. Purification with flash column chromatography (Tol/Acetone, 9:1 → 6:4, v/v) gave **36** (145 mg, 87 μmol, 84%) as a white solid. R_f = 0.33, Tol/Acetone 8:2; $[\alpha]_D^{20}$= +4.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.07 (m, 20H, H_{Ar}), 6.74 (d, *J* = 7.6 Hz, 1H, $NHCOCF_3$), 5.38 – 5.32 (m, 2H, H-4', H-4'''), 5.10 (dd, *J* = 10.5, 7.9 Hz, 1H, H-2'''), 4.96 (dd, *J* = 10.5, 3.4 Hz, 1H, H-3'''), 4.90 (d, *J* = 7.1 Hz, 1H, H-1), 4.86 – 4.73 (m, 3H, C*H*HPh, CH*H*CCl_3, H-3''), 4.71 – 4.38 (m, 12H, C*H*HCCl_3, CH*H*Ph, C*H*HPh, CH_2Ph, CH*H*Ph, C*H*HPh, H-6''a, H-1'', H-1''', H-1', N*H*$CO_2CH_2CCl_3$), 4.31 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.14 – 3.95 (m, 6H, H-6'''a, H-6'''b, H-6''b, OCH*H*CH_2N_3, H-3, H-4), 3.86 (dd, *J* = 6.8, 1.2 Hz, 1H, H-5'''), 3.84 – 3.77 (m, 1H, H-6a), 3.76 – 3.34 (m, 12H, H-6b, H-3', OC*H*HCH_2N_3, H-2'', H-2, H-5, H-5', H-2', H-5'', OCH_2CH*H*N_3, H-6'a, H-6'b), 3.28 (ddd, *J* = 13.2, 5.4, 3.5 Hz, 1H, OCH_2C*H*HN_3), 2.14 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.05 (s, 3H, $OCOCH_3$), 2.02 (m, 6H, 2 $OCOCH_3$), 1.96 (s, 3H, $OCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 170.22, 170.17, 170.0, 169.3 (7 O*C*OCH_3), 157.3 (q, *J* = 37.1 Hz, NH*C*OCF_3), 154.2 (NH*C*$O_2CH_2CCl_3$), 138.3, 138.1, 138.0, 137.9 (4 C_{Ar}), 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.2 (20 C_{Ar}), 115.7 (*a*d, *J* = 288.4 Hz, NHCO*C*F_3), 102.8 (C-1'), 101.4 (C-1'''),

101.2 (C-1’’), 99.2 (C-1), 95.7 $CH_2\underline{C}Cl_3$), 80.5 (C-2’), 76.6 (C-3’), 76.4, 76.3 (C-3, C-4), 76.2 (C-4’’), 75.4 (C-5’), 75.3 (CH_2Ph), 74.4 (CH_2Ph), 74.3 ($\underline{C}H_2CCl_3$), 73.7 (CH_2Ph), 73.6 (CH_2 Ph), 72.8 (C-5), 72.7 (C-5’’), 72.2 (C-3’’), 71.1 (C-3’’’), 70.9 (C-5’’’), 69.7 (C-4’), 69.3 (C-2’’’), 68.5 ($O\underline{C}H_2CH_2N_3$), 68.2 (C-6, C-6’), 66.8 (C-4’’’), 61.5 (C-6’’), 61.0 (C-6’’’), 56.4 (C-2’’), 55.9 (C-2), 50.7 ($OCH_2\underline{C}H_2N_3$), 20.94, 20.88, 20.78, 20.75, 20.62, 20.58, 20.52 (7 $OCO\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.89; HRMS (ESI^+): m/z calcd for $C_{73}H_{85}Cl_3F_3N_5O_{29}$: 1680.4240 $[M+Na]^+$; found: 1680.5447.

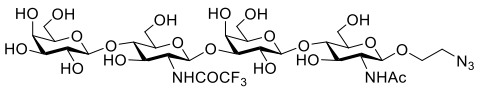
2-Azidoethyl (β-D-galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-(β-D-galactopyranosyl)-(1→4)-(2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside) (1)



To a solution of **36** (110 mg, 66 μmol) in AcOEt (880 μL) was added a solution of $NaBrO_3$ (99 mg, 66 μmol) in water (660 μL). Then a solution of $Na_2S_2O_4$ (108 mg, 0.53 mmol) in water (1.3 mL) was added and the reaction was stirred for 3 hours. The mixture was then quenched with 10% $Na_2S_2O_3$, extracted with AcOEt, dried over $MgSO_4$, filtered and evaporated under vacuum. Purification by flash column chromatography (CH_2Cl_2/MeOH, 98:2 → 85:15, v/v) gave **37** (63 mg, 48 μmol, 73%) as a white amorphous solid. Compound **37** (30 mg, 20.0 μmol) was dissolved in dry THF (300 μL) and then 1M TBAF in THF (150 μL, 150 μmol) was added. The mixture was stirred at RT for 2 hours, diluted with AcOEt, washed with water, dried over $MgSO_4$ and filtered. Solvent was removed under vacuum, then the crude residue was dissolved in pyridine (1 mL) and acetylated with Ac_2O (500 μL). The reaction was stirred for 4 hours then the solvent was removed *in vacuo*. Crude was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5, v/v) to give **38** (23 mg, 17.2 μmol, 85%) as a white foam. R_f = 0.5, CH_2Cl_2/MeOH 95:5; $[\alpha]_D^{20}$= -19 (*c* 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.8 Hz, 1H, $NHCOCF_3$), 5.48 (d, *J* = 8.6 Hz, 1H, $N\underline{H}COCH_3$), 5.34 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4’’’), 5.31 (dd, *J* = 3.6, 1.0 Hz, 1H, H-4’), 5.20 – 5.13 (m, 2H, H-3’’, H-3), 5.10 (dd, *J* = 10.5, 7.9 Hz, 1H, H-2’’’), 4.97 (dd, *J* = 10.5, 3.4 Hz, 1H, H-3’’’), 4.93 (dd, *J* = 10.0, 7.9 Hz, 1H, H-2’), 4.77 (dd, *J* = 12.0, 2.6 Hz, 1H, H-6’’a), 4.67 (d, *J* = 7.8 Hz, 1H, H-1’’), 4.60 (d, *J* = 7.9 Hz, 1H, H-1), 4.54 (d, *J* = 7.9 Hz, 1H, H-1’’’), 4.49 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6a), 4.34 (d, *J* = 7.9 Hz, 1H, H-1’), 4.14 – 4.02 (m, 6H, H-2, H-6b, H-6’a, H-6’b, H-6’’’a, H-6’’’b), 4.02 – 3.92 (m, 2H, H-6’’b, $OC\underline{H}HCH_2N_3$), 3.87 (*a*td, *J* = 6.8, 6.2, 1.3 Hz, 1H, H-5’’’), 3.81 – 3.75 (m, 3H, H-4’’, H-4, H-5’), 3.75 – 3.65 (m, 2H, $OCH\underline{H}CH_2N_3$, H-3’), 3.57 (ddd, *J* = 9.3, 4.6, 2.5 Hz, 1H, H-5), 3.55 – 3.50 (m, 1H, H-2’’), 3.49 – 3.43 (m, 2H, H-5’’, $OCH_2C\underline{H}HN_3$), 3.33 (ddd, *J* = 13.3, 5.2, 3.7 Hz, 1H, $OCH_2CH\underline{H}N_3$), 2.15 – 2.12 (m, 9H, 3 $OCOCH_3$), 2.10 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 2.06 – 2.04 (m, 9H, 3 $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.96 (s, 3H, $OCOCH_3$), 1.86 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 170.6, 170.51, 170.48, 170.4, 170.3, 170.3, 170.08, 170.07, 170.05, 169.5, 169.1, 169.0 (12 $\underline{C}OCH_3$), 157.5 (*a*d, *J* = 37.2 Hz, $NH\underline{C}OCF_3$), 115.7 (q, *J* = 288 Hz, $NHCO\underline{C}F_3$), 101.1 (C-1’’’), 100.87 (C-1’), 100.5 (C-1’’), 100.3 (C-1), 75.8 (C-3’), 75.6 (C-4), 75.3 (C-4’’), 72.9 (C-5), 72.6 (C-5’’), 72.0 (C-3), 71.8 (C-3’’), 71.2 (C-5’), 71.0 (C-2’), 70.8 (C-3’’’), 70.7 (C-5’’’), 69.1 (C-2’’’), 68.8 (C-4’), 68.4 ($O\underline{C}H_2CH_2N_3$), 66.6 (C-4’’’), 61.7 (C-6), 61.5 (C-6’), 60.7 (C-6’’’), 60.2 (C-6’’), 54.9 (C-2’’), 53.5 (C-2), 50.5 ($OCH_2\underline{C}H_2N_3$), 23.1 ($NHCO\underline{C}H_3$), 20.89, 20.85, 20.78, 20.76, 20.7, 20.63, 20.62, 20.60, 20.53, 20.49 (11 $OCO\underline{C}H_3$); ^{19}F NMR (376 MHz MHz, $CDCl_3$): δ -76.1 ($NHCOCF_3$); HRMS (ESI^+): m/z calcd for $C_{52}H_{70}F_3N_5O_{32}$: 1334.4034 $[M+Na]^+$; found: 1334.4087. To a solution of **38** (25 mg, 18.7 μmol) in dry MeOH (1 mL), was added

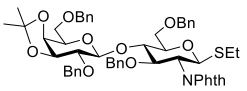
methanolic sodium methoxide (0.5 M) until pH = 8. The reaction was stirred at RT overnight then quenched with Dowex 50WX8 H^+ resin, filtered and concentrated *in vacuo*. The crude residue was purified by Sephadex P-2 size exclusion chromatography to afford **1** (11.5 mg, 12.1 µmol, 70%) as a white amorphous solid. R_f = 0.6, AcOEt/MeOH/AcOH/H_2O 4:3:3:1; $[\alpha]_D^{20}$= +10.1 (*c* 0.4, H_2O); ^{1}H NMR (500 MHz, D_2O): δ 4.72 (m, 2H, H-1, H-1''), 4.51 – 4.46 (m, 2H, H-1''', H-1'), 4.17 (*a*d, *J* = 3.3 Hz, 1H, H-4'), 4.12 – 4.03 (m, 1H, OCH*H*CH_2N_3), 4.04 – 3.95 (m, 2H, H-6a, H-6b), 3.94 (*a*d, *J* = 3.4 Hz, 1H, H-4'''), 3.91 – 3.71 (m, 16H, H-2'', H-2, H-6'a, H-6'b, H-6'''a, H-6'''b, H-6''a, H-6''b, H-3'', H-3, H-5''', H-5', H-4'', H-4, H-3', OC*H*HCH_2N_3), 3.68 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3'''), 3.66 – 3.52 (m, 4H, H-5'', H-5, H-2', H-2'''), 3.52 – 3.44 (m, 2H, $OCH_2C\underline{H}_2N_3$), 2.05 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, D_2O): δ 174.8 ($NHCOCH_3$), 159.5 (*a*d, *J* = 37.6 Hz, $NHCOCF_3$), 115.7 (*a*d, *J* = 286.3 Hz, $NHCOCF_3$), 102.8, 102.9 (C-1', C-1'''), 102.7 (C-1''), 100.2 (C-1), 82.0 (C-3'), 78.2, 78.1 (C-4, C-4''), 75.3 (C-5'''), 74.8 (C-5', C-5''), 74.5 (C-5), 72.4 (C-3'''), 72.1, 71.7 (C-3, C-3'), 70.9, 69.9 (C-2', C-2'''), 68.7 ($OCH_2CH_2N_3$), 68.47 (C-4'''), 68.2 (C-4'), 60.9, 60.9, 59.9, 59.8 (C-6, C-6', C-6'', C-6'''), 55.51 (C-2''), 55.12 (C-2), 50.29 ($OCH_2CH_2N_3$), 22.11 ($NHCOCH_3$); ^{19}F NMR (282 MHz, D_2O): δ -75.8 ($NHCOCF_3$). HRMS (ESI^+): m/z calcd for $C_{30}H_{48}F_3N_5O_{21}$: 894.2692 $[M+Na]^+$; found: 894.2648.

2-Azidoethyl (β-D-galactopyranosyl)-(1→4)-(2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (2)



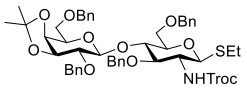
To a solution of fully protected tetrasaccharide **35** (100 mg, 65 µmol) in AcOEt (870 µL) was added a solution of $NaBrO_3$ (99 mg, 0.66 mmol) in water (655 µL). Then a solution of $Na_2S_2O_4$ (90 mg, 0.52 mmol) in water (1.3 mL) was added and the reaction was stirred for 6 hours. The mixture was then quenched with 10% $Na_2S_2O_3$, extracted with AcOEt, dried over $MgSO_4$, filtered and evaporated. Purification by flash column chromatography (CH_2Cl_2/MeOH, 98:2 → 85:15) gave **39** (54 mg, 46 µmol, 71%). Compound **39** (50 mg, 43 µmol) was dissolved in MeOH (2 mL) and solid MeONa was added until pH = 9. The reaction was stirred for 7 hours then quenched with Dowex 50WX8 H^+ resin, filtered and evaporated *in vacuo*. Crude product was purified by size exclusion chromatography (Biogel® P-2, dH_2O:*n*-BuOH, 99:1, v/v) to obtain compound **2** (20 mg, 23 µmol, 53%) as a white solid after freeze-dry. R_f = 0.54, AcOEt/MeOH/AcOH/H_2O 4:3:3:1; $[\alpha]_D^{20}$= -10.7 (*c* 0.69, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.85 (d, *J* = 7.7 Hz, 1H, H-1), 4.62 (d, *J* = 8.1 Hz, 1H, H-1''), 4.51 (d, *J* = 7.8 Hz, 1H, H-1'''), 4.47 (d, *J* = 7.9 Hz, 1H, H-1'), 4.20 (*a*d, *J* = 3.3 Hz, 1H, H-4'), 4.07 (ddd, *J* = 11.4, 5.5, 3.1 Hz, 1H, OCH*H*CH_2N_3), 4.01 (dd, *J* = 5.6, 2.3 Hz, 1H, H-6a), 3.98 (dd, *J* = 5.7, 2.1 Hz, 1H, H-6'a), 3.95 (*a*d, *J* = 3.6 Hz, 1H, H-4'''), 3.93 – 3.84 (m, 4H, H-2, H-6b, H-6'b, H-3''), 3.83 – 3.55 (m, 17H, H-2'', H-6''a, H-6''b, H-6'''a, H-6'''b, OC*H*HCH_2N_3, H-3''', H-5, H-5'', H-5', H-4, H-4'', H-3', H-2', H-2''', H-5''', H-3'), 3.55 – 3.40 (m, 2H, $OCH_2C\underline{H}_2N_3$), 2.06 (s, 3H, $NHCOC\underline{H}_3$); ^{13}C NMR (126 MHz, D_2O) δ 174.6 ($NHCOCH_3$), 159.5 (*a*d, *J* = 37.5 Hz, $NHCOCF_3$), 115.8 (*a*d, *J* = 286.5 Hz, $NHCOCF_3$), 102.9, 102.8 (C-1', C-1'''), 101.9 (C-1), 100.9 (C-1''), 82.4 (C-3'), 78.4 (C-4''), 77.9 (C-4), 75.3, 74.8, 74.7, 74.6 (C-5, C-5', C-5'', C-5'''), 72.5, 72.4, 71.5 (C-3'', C-3''', C-3), 70.9 (C-2'''), 69.8 (C-2'), 68.7 ($OCH_2CH_2N_3$), 68.5 (C-4'''), 68.1 (C-4'), 61.0, 60.9, 60.0, 59.7 (C-6, C-6', C-6'', C-6'''), 55.7 (C-2), 54.9 (C-2''), 50.3 ($OCH_2CH_2N_3$), 22.2 ($NHCOCH_3$); ^{19}F NMR (376 MHz, D_2O) δ -75.65; HRMS (ESI^+): m/z calcd for $C_{30}H_{48}F_3N_5O_{21}$: 894.2692 $[M+Na]^+$; found: 894.2648.

Ethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (40)



Compound **14** (620 mg, 1.12 mmol) was dissolved in dry DMF (28 mL), then BnBr (1 mL, 8.94 mmol) was added followed by TBAI (40 mg, 0.108 mmol). The mixture was cooled to 0 °C and NaH (60% dispersion in mineral oil, 270 mg, 6.72 mmol) was slowly added. Stirring at 0 °C was continued for 15 minutes then the reaction was slowly warmed up to RT. After 3 hours, AcOH and MeOH were added to quench the reaction and solvents were removed *in vacuo*. Purification by flash column chromatography (Tol/AcOEt, 9:1, v/v) afforded compound **40** (560 mg, 0.61 mmol, 54%) as a white foam. R_f = 0.40, Tol/AcOEt 9:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 1H, $H_{ArNPhth}$), 7.70 – 7.57 (m, 3H, $H_{ArNPhth}$), 7.41 – 7.14 (m, 15H, H_{Ar}), 6.99 – 6.89 (m, 2H, H_{Ar}), 6.89 – 6.73 (m, 3H, H_{Ar}), 5.20 (d, *J* = 10.3 Hz, 1H, H-1), 4.79 (dd, *J* = 11.9, 2.9 Hz, 2H, C*H*HPh, CH*H*Ph), 4.70 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.90 – 4.63 (m, 2H, CH*H*Ph, C*H*HPh), 4.44 – 4.34 (m, 4H, H-1', CH_2Ph, CH*H*Ph), 4.30 (dd, *J* = 10.3, 8.4 Hz, 1H, H-3), 4.23 (*a*t, *J* = 10.3 Hz, 1H, H-2), 4.10 – 3.97 (m, 3H, H-4', H-4, H-3'), 3.87 (dd, *J* = 11.0, 3.8 Hz, 1H, H-6a), 3.75 – 3.68 (m, 2H, H-6b, H-5'), 3.64 (dd, *J* = 10.0, 6.1 Hz, 1H, H-6'a), 3.59 – 3.51 (m, 2H, H-5, H-6'b), 3.32 (dd, *J* = 8.1, 6.8 Hz, 1H, H-2'), 2.70 – 2.51 (m, 2H, S*H*$_2$$CH_3$), 1.34 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.14 (t, *J* = 7.4 Hz, 3H, SCH_2C*H*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2 (CO_{NPhth}), 167.6 (CO_{NPhth}), 138.8 (C_{Ar}), 138.60 (C_{Ar}), 138.51 (C_{Ar}), 138.45 (C_{Ar}), 133.9 ($C_{ArNPhth}$), 133.8 ($C_{ArNPhth}$), 131.8 (2 $C_{ArNPhth}$), 128.5, 128.43, 128.36, 128.3, 128.1, 128.0, 127.9, 127.7, 127.64, 127.62, 127.59, 127.1 (20 C_{Ar}), 123.6 ($C_{ArNPhth}$), 123.3 ($C_{ArNPhth}$), 109.9 (*C*$(CH_3)_2$), 102.5 (C-1'), 81.1 (C-1), 80.7 (C-2'), 79.7 (C-5), 79.5 (C-3'), 78.3 (C-4), 78.2 (C-3), 74.7 (CH_2Ph), 73.9 (C-4'), 73.6 (CH_2Ph), 73.5 (CH_2Ph), 73.3 (CH_2Ph), 72.3 (C-5'), 69.3 (C-6'), 68.2 (C-6), 54.9 (C-2), 28.1 (CH_3), 26.5 (CH_3), 23.9 (S*C*H_2CH_3), 15.1 (SCH_2*C*H_3); All analytical data were consistent with literature values.[6]

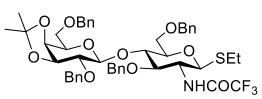
Ethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (41)



Compound **40** (200 mg, 0.22 mmol) was dissolved in EtOH (2.5 mL) and refluxed with hydrazine hydrate (110 μL, 2.2 mmol) for 6 hours. Reaction was then diluted with water and extracted with AcOEt. Organic layers were combined, dried over $MgSO_4$, filtered and evaporated under vacuum. Crude residue was dissolved in THF (2.2 mL) and reacted with 2,2,2-trichloroethyl chloroformate (40 μL, 0.3 mmol) and $NaHCO_3$ (35 mg, 0.44 mmol). After 3 hours the solvent was removed under vacuum and the obtained crude was purified by flash column chromatography (Tol/AcOEt, 9:1, v/v) to give donor **41** (137 mg, 0.14 mmol, 63% over two steps) as a transparent oil. R_f = 0.55, Tol/AcOEt 9:1; $[\alpha]_D^{20}$ = +11.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 20H, H_{Ar}), 5.05 (d, *J* = 8.4 Hz, 1H, N*H*$CO_2CH_2CCl_3$), 4.90 (d, *J* = 10.8 Hz, 1H, CH*H*Ph), 4.80 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.74 – 4.67 (m, 4H, CH_2CCl_3, C*H*HPh, H-1), 4.64 (d, *J* = 10.8 Hz, 1H, CH*H*Ph), 4.57 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.51 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.45 – 4.39 (m, 2H, H-1', CH*H*Ph), 4.35 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.11 (dd, *J* = 5.6, 1.7 Hz, 1H, H-4'), 4.07 – 3.99 (m, 2H, H-3, H-3'), 3.84 (dd, *J* = 11.0, 4.0 Hz, 1H, H-6a), 3.76 – 3.64 (m, 4H, H-6b, H-5', H-4, H-6'a), 3.56 (dd, *J* = 8.8, 5.3 Hz, 1H, H-6'b), 3.50 – 3.43 (m, 2H, H-2, H-5), 3.36 (dd, *J* = 8.0, 6.6 Hz, 1H, H-2'), 2.74 – 2.64 (m, 2H, S*H*$_2$$CH_3$), 1.40 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.29 – 1.22 (m, 3H, SCH_2C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (NH*C*$O_2CH_2CCl_3$), 138.6, 138.53, 138.48, 138.4 (4 C_{Ar}),

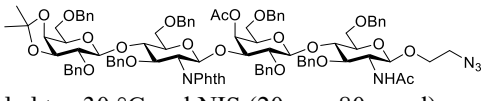
129.2, 128.7, 128.46, 128.45, 128.4, 128.0, 127.9, 127.74, 127.69, 127.6, 125.4 (20 C_{Ar}), 110.0 ($\underline{C}(CH_3)_2$), 102.1 (C-1'), 95.6 ($CH_2\underline{C}Cl_3$), 83.7 (C-1), 80.7 (C-2'), 80.1 (C-4), 79.7 (C-5), 79.5 (C-3'), 76.6 (C-3), 74.6 ($\underline{C}H_2CCl_3$), 74.4 (CH_2Ph), 73.8 (C-4'), 73.6 (2 CH_2Ph), 73.3 (CH_2Ph), 72.3 (C-5'), 69.2 (C-6'), 68.4 (C-6), 56.6 (C-2), 28.1 (CH_3), 26.5 (CH_3), 24.4 ($S\underline{C}H_2CH_3$), 15.1 ($SCH_2\underline{C}H_3$); HRMS (ESI^+): m/z calcd for $C_{48}H_{56}Cl_3NO_{11}S$: 982.2537 $[M+Na]^+$; found: 982.2529.

Ethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-1-thio-β-D-glucopyranoside (42)



Compound **40** (150 mg, 0.16 mmol) was dissolved in EtOH (2 mL) and refluxed with hydrazine hydrate (50 µL, 1.64 mmol) for 10 hours. Reaction was then diluted with water and extracted with AcOEt. Organic layers were combined, dried over $MgSO_4$, filtered and evaporated. Crude residue was dissolved in Py/ CH_2Cl_2 (1:1, 1.64 mL), cooled to 0 °C and reacted with TFAA (46 µL, 0.33 mmol) which was slowly added under vigorous stirring. After 1 hour solvents were removed under vacuum and crude was purified by flash column chromatography (Tol/AcOEt, 9:1, v/v) to give donor **42** (115 mg, 0.13 mmol, 79% over two steps) as a transparent oil. R_f = 0.54, Tol/AcOEt 9:1; $[\alpha]_D^{20}$= +10.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 20H, H_{Ar}), 6.37 (d, *J* = 8.3 Hz, 1H, $NHCOCF_3$), 4.87 – 4.76 (m, 3H, H-1, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.71 (d, *J* = 11.8 Hz, 1H, $CH\underline{H}Ph$), 4.61 – 4.50 (m, 3H, $C\underline{H}HPh$, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.47 – 4.35 (m, 3H, $CH\underline{H}Ph$, $C\underline{H}HPh$, H-1'), 4.11 (dd, *J* = 5.6, 1.6 Hz, 1H, H-4'), 4.08 – 4.01 (m, 2H, H-3, H-3'), 3.91 – 3.82 (m, 2H, H-4, H-6a), 3.77 – 3.66 (m, 4H, H-6b, H-6'a, H-5', H-2), 3.62 – 3.51 (m, 2H, H-6'b, H-5), 3.36 (dd, *J* = 8.0, 6.6 Hz, 1H, H-2'), 2.77 – 2.60 (m, 2H, $SC\underline{H}_2CH_3$), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.26 (t, *J* = 7.4 Hz, 3H, $SCH_2C\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (*a*d, *J* = 37.4 Hz, $NH\underline{C}OCF_3$), 138.5 (C_{Ar}), 138.4 (C_{Ar}), 138.3 (C_{Ar}), 138.1 (C_{Ar}), 129.2, 128.8, 128.49, 128.46, 128.4, 128.1, 128.0, 127.9, 127.74, 127.70, 127.67 (20 C_{Ar}), 115.8 (*a*d, *J* = 288.3 Hz, $NHCO\underline{C}F_3$), 110.0 ($\underline{C}(CH_3)_2$), 102.2 (C-1'), 82.6 (C-1), 80.6 (C-2), 79.7 (C-5), 79.5 (C-4), 79.0 (C-3), 76.5 (C-3'), 74.5 (CH_2Ph), 73.8 (C-4'), 73.6 (CH_2Ph), 73.5 (CH_2Ph), 73.4 (CH_2Ph), 72.4 (C-5'), 69.2 (C-6'), 68.4 (C-6), 55.6 (C-2), 28.1 (CH_3), 26.5 (CH_3), 24.6 ($S\underline{C}H_2CH_3$), 15.1 ($SCH_2\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.89; HRMS (ESI^+): m/z calcd for $C_{47}H_{54}F_3NO_{10}S$: 904.3318 $[M+Na]^+$; found: 904.3312.

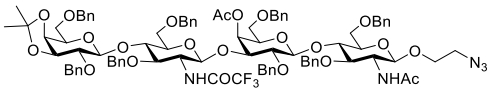
2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (43)



Acceptor **31** (50 mg, 58 µmol) and donor **40** (69 mg, 76 µmol) were dissolved in dry CH_2Cl_2 (3 mL) together with 4Å molecular sieves (120 mg). The mixture was stirred for 1 hour, then the mixture was cooled to -30 °C and NIS (20 mg, 80 µmol) was added followed by TfOH (3 µL, 29 µmol). The reaction was stirred for 90 minutes at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated *in vacuo*. Purification by flash column chromatography (Tol/Acetone, 85:15, v/v) gave **43** (63 mg, 37 µmol, 64%) as an amorphous solid. R_f = 0.86, Tol/Acetone 8:2; $[\alpha]_D^{20}$= +27.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.10 (m, 40H, H_{Ar}), 6.94 (dd, *J* = 6.6, 2.9 Hz, 2H, $H_{ArNPhth}$), 6.90 – 6.84 (m, 2H, $H_{ArNPhth}$), 5.63 (d, *J* = 7.4 Hz, 1H, $N\underline{H}COCH_3$), 5.41 (*a*d, *J* = 3.6 Hz, 1H, H-4'), 5.29 (d, *J* = 8.3 Hz, 1H, H-1''), 4.88 (d, *J* = 7.6 Hz, 1H, H-1), 4.85 – 4.79 (m, 3H, $C\underline{H}HPh$, $CH\underline{H}Ph$, $C\underline{H}HPh$), 4.75 (d, *J* = 11.7 Hz,

1H, CH*H*Ph), 4.65 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.53 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.49 – 4.37 (m, 7H, H-1’’’, C*H*HPh, CH*H*Ph, C*H*HPh, CH*H*Ph, CH*H*Ph, C*H*HPh), 4.36 – 4.26 (m, 3H, H-3’’, CH*H*Ph, C*H*HPh), 4.26 – 4.13 (m, 3H, H-1’, CH*H*Ph, H-2’’), 4.13 – 4.01 (m, 5H, H-4’’, C*H*HPh, H-4’’’, H-3’’’, H-3), 3.96 – 3.89 (m, 2H, H-6a, OCH*H*CH_2N_3), 3.84 (*a*t, *J* = 8.5 Hz, 1H, H-4), 3.82 – 3.78 (m, 1H, H-6b), 3.75 (dd, *J* = 6.4, 2.0 Hz, 1H, H-5’’’), 3.65 (dd, *J* = 9.9, 6.5 Hz, 1H, H-6’’’a), 3.62 – 3.54 (m, 3H, H-5’’, H-6’’’b, OC*H*HCH_2N_3), 3.54 – 3.47 (m, 2H, H-3’, H-6a’’), 3.47 – 3.28 (m, 7H, OCH_2CH*H*N_3, H-5’, H-2’’’, H-2’, H-6’’b, H-6’a, H-6’b), 3.24 – 3.11 (m, 3H, H-5, H-2, OCH_2C*H*HN_3), 2.01 (s, 3H, $OCOCH_3$), 1.85 (s, 3H, NHCOC*H*$_3$), 1.37 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (NH*C*OCH_3), 170.1 (O*C*OCH_3), 167.6 (2 CO_{NPhth}), 139.0, 138.9, 138.8, 138.6, 138.5, 138.4, 138.3, 138.2 (8 C_{Ar}), 133.6 (2 C_{NPhth}), 131.4 (2 C_{NPhth}), 128.50, 128.46, 128.44, 128.39, 128.2, 128.11, 128.08, 128.03, 127.92, 127.87, 127.8, 127.69, 127.67, 127.60, 127.58, 127.5, 127.0, 127.0, 126.6 (40 H_{Ar}) 123.1 (2 C_{NPhth}), 109.8 (*C*$(CH_3)_2$), 102.5 (C-1’’’), 102.3 (C-1’), 99.5 (C-1), 99.2 (C-1’’), 80.7 (C-2’’’), 79.5 (C-3’), 79.3, 78.8, 78.0, 77.4 (C-3’’’, C-4’’’, C-3, C-2’), 77.0 (C-3’’), 76.4 (C-4), 75.4 (C-5’’), 74.9 (C-5), 74.5 (CH_2Ph), 74.4 (CH_2Ph), 74.2 (CH_2Ph), 74.0 (CH_2Ph), 73.68 (CH_2Ph), 73.65 (CH_2Ph), 73.5 (C-4’’), 73.3 (CH_2Ph), 73.2 (CH_2Ph), 72.9 (C-5’), 72.1 (C-5’’’), 70.2 (C-4’), 69.2, 68.9, 68.3, 68.0, 67.9 (O*C*$H_2CH_2N_3$, C-6, C-6’, C-6’’, C-6’’’), 57.0 (C-2), 56.2 (C-2’’), 50.7 (OCH_2*C*H_2N_3), 28.1 (CH_3), 26.5 (CH_3), 23.7 (NHCO*C*H_3), 20.9 (OCO*C*H_3); HRMS (ESI$^+$): m/z calcd for $C_{97}H_{105}N_5O_{23}$; 1730.7098 $[M+Na]^+$; found: 1730.7119.

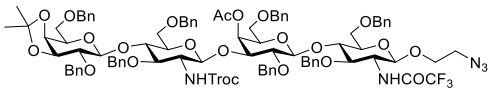
2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (44)



Acceptor **31** (69 mg, 81 μmol) and donor **42** (100 mg, 113 μmol) were dissolved in dry CH_2Cl_2 (4.5 mL) together with 4Å molecular sieves (170 mg). The mixture was stirred for 1 hour, then it was cooled to -25 °C and NIS (25 mg, 113 μmol) was added followed by TfOH (4 μL, 49 μmol), turning the reaction crimson red. Stirring was continued for 20 minutes at the same temperature, then the reaction was quenched with Et_3N, filtered over Celite and evaporated under vacuum. Purification by flash column chromatography (Tol/Acetone, 9:1, v/v) gave **44** (111 mg, 66 μmol, 81%) as an off-white amorphous solid. R_f = 0.65, Tol/Acetone 8:2; $[\alpha]_D^{20}$ = +5.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.14 (m, 40H, H_{Ar}), 6.18 (d, *J* = 7.4 Hz, 1H, NHCOCF_3), 5.79 (d, *J* = 7.4 Hz, 1H, N*H*$COCH_3$), 5.42 (*a*d, *J* = 3.5 Hz, 1H, H-4’), 5.01 (d, *J* = 7.6 Hz, 1H, H-1), 4.96 – 4.89 (m, 2H, H-1’’, C*H*HPh), 4.82 (m, 2H, C*H*HPh, CH*H*Ph), 4.78 (d, *J* = 11.0 Hz, 1H, CH*H*Ph), 4.73 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.63 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.61 – 4.54 (m, 3H, CH_2Ph, C*H*HPh), 4.61 – 4.39 (m, 8H, H-1’’’, H-1’, 3 CH_2Ph), 4.33 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.20 – 4.16 (m, 1H, H-4), 4.14 (dd, *J* = 5.6, 1.9 Hz, 1H, H-4’’’), 4.08 (*a*t, *J* = 6.1 Hz, 1H, H-3’’’), 4.06 – 3.96 (m, 3H, H-4’’, H-3, OCH*H*CH_2N_3), 3.88 (dd, *J* = 10.9, 4.3 Hz, 1H, H-6’’a), 3.78 – 3.63 (m, 9H, H-3’, H-3’’, H-5’’’, H-2’’, H-6’’b, OC*H*HCH_2N_3, H-6’’’a, H-6’’’b, H-6’a), 3.57 (dd, *J* = 9.8, 6.3 Hz, 1H, H-6’b), 3.55 – 3.43 (m, 5H, OCH_2CH*H*N_3, H-5’, H-5, H-5’’, H-2’), 3.40 – 3.33 (m, 3H, H-2’’’, H-6a, H-6b), 3.30 – 3.21 (m, 2H, OCH_2C*H*HN_3, H-2), 1.99 (s, 3H, OCOC*H*$_3$), 1.92 (s, 3H, NHCOC*H*$_3$), 1.40 (s, 3H, CH_3), 1.36 (s, 3H, (CH_3)); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7 (NH*C*OCH_3), 170.1 (O*C*OCH_3), 157.0 (*a*d, *J* = 36.9 Hz, NH*C*OCF_3), 138.9, 138.6, 138.44, 138.42, 138.38, 138.21, 138.19, 138.1 (8 C_{Ar}), 128.6 – 127.6 (m, 39 C_{Ar}), 127.3 (C_{Ar}), 115.7 (*a*d, *J* = 288.7 Hz,

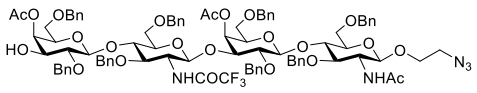
NHCO<u>C</u>F$_3$), 110.0 (<u>C</u>(CH$_3$)$_2$), 102.5 (C-1'), 102.3 (C-1'''), 99.7 (C-1''), 99.6 (C-1), 80.6 (C-2'''), 80.5 (C-2'), 79.4 (C-3'''), 77.6 (C-3''), 77.3 (under CDCl$_3$ peak, C-4), 76.7 (C-3'), 76.6 (C-3), 76.3 (C-4''), 75.5, 75.1, 75.0 (C-5'', C-5, CH$_2$Ph), 74.2 (CH$_2$Ph), 73.8, 73.7, 73.51, 73.47, 73.4, 73.34, 73.30 (6 CH$_2$Ph, C-4'''), 72.7 (C-5'), 72.2 (C-5'''), 69.6 (C-4'), 69.1 (C-6'), 68.4, 68.3, 68.3, 68.1 (C-6'', C-6, C-6''', O<u>C</u>H$_2$CH$_2$N$_3$), 56.9 (C-2), 55.7 (C-2''), 50.7 (OCH$_2$<u>C</u>H$_2$N$_3$), 28.1 (CH$_3$), 26.5 (CH$_3$), 23.7 (NHCO<u>C</u>H$_3$), 20.8 (OCO<u>C</u>H$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ -75.72; HRMS (ESI$^+$): m/z calcd for $C_{91}H_{102}F_3N_5O_{22}$: 1696.6861 [M+Na]$^+$; found: 1696.5470.

2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (45)



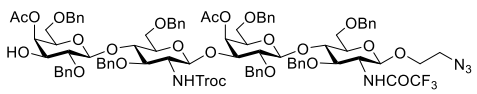
Acceptor **32** (91 mg, 0.1 mmol) and donor **41** (135 mg, 0.14 mmol) were dissolved in dry CH$_2$Cl$_2$ (5.5 mL) together with 4Å molecular sieves (225 mg). The mixture was stirred for 1 hour, then it was cooled to -28 °C and NIS (31 mg, 0.14 mmol) was added followed by TfOH (5 μL, 56 μmol), turning the reaction crimson red. Stirring was continued for 20 minutes at the same temperature, then the reaction was quenched with Et$_3$N, filtered over Celite and evaporated in *vacuo*. Purification by flash column chromatography (cHex/Acetone, 8:2, v/v) gave **45** (96 mg, 53 μmol, 53%) as an off-white amorphous solid and recovered acceptor **32** (40 mg, 44 mmol). R$_f$ = 0.46, Tol/Acetone 9:1; $[\alpha]_D^{20}$= +5.6 (*c* 1.0, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.21 (m, 40H, H$_{Ar}$), 6.72 (d, *J* = 7.6 Hz, 1H, NHCOCF$_3$), 5.43 (*a*d, *J* = 3.6 Hz, 1H, H-4'), 4.90 (d, *J* = 7.0 Hz, 1H, H-1), 4.87 – 4.77 (m, 4H, CH<u>*H*</u>Ph, C<u>*H*</u>HPh, CH<u>*H*</u>Ph, N<u>*H*</u>CO$_2$CH$_2$CCl$_3$), 4.74 – 4.28 (m, 20H, H-1'', H-1''', H-1', CH<u>*H*</u>CCl$_3$, 8 CH<u>*H*</u>Ph), 4.13 (dd, *J* = 5.5, 2.0 Hz, 1H, H-4'''), 4.10 – 3.93 (m, 5H, H-3, H-3''', H-4, H-4'', OC<u>*H*</u>HCH$_2$N$_3$), 3.82 (*a*td, *J* = 10.4, 9.8, 4.3 Hz, 1H, H-6''a), 3.79 – 3.76 (m, 1H, H-6''b), 3.73 (ddd, *J* = 12.9, 5.3, 2.0 Hz, 1H, H-5'''), 3.70 – 3.60 (m, 5H, OCH<u>*H*</u>CH$_2$N$_3$, H-6a, H-6b, H-6'''a, H-3'), 3.59 – 3.49 (m, 5H, H-2, H-6'''b, H-5', H-5, H-2'), 3.49 – 3.34 (m, 7H, OCH$_2$C<u>*H*</u>HN$_3$, H-2'', H-6'a, H-6'b, H-5'', H-3'', H-2'''), 3.28 (ddd, *J* = 13.2, 5.4, 3.5 Hz, 1H, OCH$_2$CH<u>*H*</u>N$_3$), 2.02 (s, 3H, OCOCH$_3$), 1.41 (s, 3H, CH$_3$), 1.36 (s, 3H, CH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.0 (O<u>C</u>OCH$_3$), 157.1 (*a*d, *J* = 37.2 Hz, NH<u>C</u>OCF$_3$), 153.9 (NH<u>C</u>O$_2$CH$_2$CCl$_3$), 138.8, 138.7, 138.5, 138.12, 138.06, 138.0 (8 C$_{Ar}$), 128.7, 128.6, 128.53, 128.47, 128.43, 128.41, 128.37, 128.33, 128.30, 128.2, 128.1, 128.04, 127.99, 127.9, 127.8, 127.68, 127.67, 127.63, 127.56, 127.2 (40 C$_{Ar}$), 115.6 (*a*d, *J* = 288.6 Hz, NHCO<u>C</u>F$_3$), 109.9 (<u>C</u>(CH$_3$)$_2$), 102.9 (C-1'), 102.2 (C-1'''), 101.2 (C-1''), 99.2 (C-1), 95.8 (CH$_2$<u>C</u>Cl$_3$), 80.7 (C-2'''), 80.4 (C-2'), 79.5 (C-3'''), 79.2 (C-3''), 77.4 (C-3'), 76.4, 76.3 (C-3, C-4, C-4''), 75.5, 75.4 (C-5, C-5''), 75.0, 74.33, 74.25, 73.8, 73.5, 73.4, 73.3 (8 CH$_2$Ph, <u>C</u>H$_2$CCl$_3$, C-4'''), 73.1 (C-5'), 72.1 (C-5'''), 69.8 (C-4'), 69.1 (C-6'''), 68.5 (O<u>C</u>H$_2$CH$_2$N$_3$), 68.3, 68.2 (C-6, C-6', C-6''), 57.0 (C-2''), 55.8 (C-2), 50.7 (OCH$_2$<u>C</u>H$_2$N$_3$), 28.1 (CH$_3$), 26.5 (CH$_3$), 20.8 (OCO<u>C</u>H$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ -75.88; HRMS (ESI$^+$): m/z calcd for $C_{92}H_{101}Cl_3F_3N_5O_{23}$: 1828.5797 [M+Na]$^+$; found 1828.4799.

2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (50)



Compound **44** (90 mg, 54 μmol) was stirred in aq. 80% AcOH (3 mL) for 5 hours at 70 °C. After dilution with toluene the solvents were removed and crude was purified by column chromatography (Tol/Acetone, 8:2, v/v) to give diol derivative **47** (75 mg, 46 μmol, 85%). Compound **47** (85 mg, 52 μmol) was then dissolved in CH_3CN (1 mL) and reacted with $CH_3C(OCH_3)_3$ (20 μL, 156 μmol) and *p*-TsOH (1 mg, 5 μmol). After 30 minutes the reaction was quenched with Et_3N and concentrated to dryness. Crude orthoester product was then dissolved in aq. 80% AcOH (1 mL) and stirred for 1 hour at RT. After solvent removal and flash column chromatography purification (Tol/Acetone, 8:2, v/v), acceptor **50** (78 mg, 46 μmol, 88%) was obtained as a white foam. R_f = 0.53, Tol/Acetone 8:2; $[\alpha]_D^{20}$= -2.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 40H, H_{Ar}), 6.26 (d, *J* = 8.2 Hz, 1H, $NHCOCF_3$), 5.76 (d, *J* = 7.4 Hz, 1H, N*H*COCH$_3$), 5.42 (*a*d, *J* = 3.6 Hz, 1H, H-4'), 5.35 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4'''), 5.00 (d, *J* = 7.8 Hz, 1H, H-1), 4.97 (d, *J* = 7.1 Hz, 1H, H-1'), 4.91 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.85 (d, *J* = 11.3 Hz, 1H, CH*H*Ph), 4.88 – 4.71 (m, 2H, CH*H*Ph, C*H*HPh), 4.69 (d, *J* = 11.3 Hz, 1H, CH*H*Ph), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.60 – 4.26 (m, 12H, H-1''', H-1', CH_2Ph, CH_2Ph, CH_2Ph, CH_2Ph, CH_2Ph), 4.18 (dd, *J* = 9.5, 8.2 Hz, 1H, H-3), 4.05 (*a*t, *J* = 8.2 Hz, 1H, H-4''), 4.03 – 3.96 (m, 2H, OCH*H*CH_2N_3, H-4), 3.84 (dd, *J* = 10.9, 4.3 Hz, 1H, H-6''a), 3.79 – 3.62 (m, 8H, H-6''b, H-6a, H-6b, H-3''', H-3', H-3'', H-2'', OC*H*HCH_2N_3), 3.60 – 3.55 (m, 1H, H-5'''), 3.55 – 3.43 (m, 5H, H-5', H-5, H-5'', H-2', OCH_2CH*H*N_3), 3.43 – 3.40 (m, 1H, H-2'''), 3.37 (m, 2H, H-6'a, H-6'b), 3.33 (m, 2H, H-6'''a, H-6'''b), 3.25 3.28 – 3.21 (m, 2H, OCH_2C*H*HN_3, H-2), 2.02 (s, 3H, $OCOCH_3$), 1.99 (s, 3H, $OCOCH_3$), 1.91 (s, 3H, $NHCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.6, 169.9 (3 *C*OCH_3), 156.9 (*a*d, *J* = 36.8 Hz, NH*C*OCF_3), 138.8, 138.4, 138.12, 138.08, 138.07, 138.06, 137.9, 137.7 (8 C_{Ar}), 129.02, 128.96, 128.59, 128.58, 128.56, 128.41, 128.38, 128.37, 128.35, 128.22, 128.17, 128.14, 128.09, 128.0, 127.87, 127.85, 127.81, 127.75, 127.7, 127.64, 127.55, 127.2 (40 C_{Ar}), 115.6 (*a*d, *J* = 288.6 Hz, NHCO*C*F_3), 102.8 (C-1'''), 102.4 (C-1'), 99.5 (C-1), 99.4 (C-1''), 80.3 (C-2'), 79.9 (C-2'''), 77.3 (C-3), 77.2 (C-3''), 76.7 (C-3'), 76.4 (C-4), 76.2 (C-4''), 75.4 (C-5''), 75.1 (CH_2Ph), 74.93, 74.86 (CH_2Ph, C-5'), 74.1, 73.6, 73.46, 73.45, 73.24, 73.19 (6 CH_2Ph), 72.6 (C-5'), 72.3 (C-3'''), 72.1 (C-5'''), 69.54 (C-4'''), 69.47 (C-4'), 68.3 (O*C*$H_2CH_2N_3$), 68.1, 68.0 (C-6, C-6', C-6''), 67.3 (C-6'''), 56.8 (C-2), 55.5 (C-2''), 50.6 ($OCH_2CH_2N_3$), 23.6 ($NHCOCH_3$), 20.7 ($OCOCH_3$), 20.6 ($OCOCH_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.72 ($NHCOCF_3$); HRMS (ESI$^+$): m/z calcd for $C_{90}H_{100}F_3N_5O_{23}$; 1698.6659 $[M+Na]^+$; found 1698.6711.

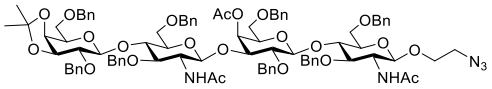
2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (51)



Tetrasaccharide **45** (65 mg, 36 μmol) was stirred in aq. 80% AcOH (2 mL) for 4 hours at 70 °C. After dilution with toluene the solvents were removed *in vacuo* and crude was purified by column chromatography (Tol/Acetone, 8:2, v/v) to give diol derivative **48** (48 mg, 27 μmol, 75%) as a white foam. Compound **48** (48 mg, 27 μmol) was then dissolved in CH_3CN (550 μL) and reacted with $CH_3C(OCH_3)_3$ (10 μL, 81 μmol) and *p*-TsOH (1 mg, 5 μmol). After 30 minutes the reaction was quenched with Et_3N and concentrated to dryness. Crude orthoester product was then dissolved in aq. 80% AcOH (550 μL) and stirred for 1 hour at RT. After solvent removal and flash column

chromatography purification (Tol/Acetone, 8:2, v/v), acceptor **51** (41 mg, 23 µmol, 84%). R_f = 0.75. Tol/Acetone 7:3; $[\alpha]_D^{20}$= +1.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 40H, H_{Ar}), 6.74 (d, *J* = 7.6 Hz, 1H, N*H*COCF$_3$), 5.45 (*a*d, *J* = 3.6 Hz, 1H, H-4'), 5.35 (*a*d, *J* = 3.5 Hz, 1H, H-4'''), 4.90 (d, *J* = 7.1 Hz, 1H, H-1), 4.89 – 4.80 (m, 3H, C*H*HPh, CH*H*Ph, CH*H*CCl$_3$), 4.78 (d, *J* = 7.9 Hz, 1H, H-1''), 4.73 – 4.38 (m, 16H, 6 CH_2Ph, C*H*HCCl$_3$, H-1''', H-1', N*H*CO$_2$CH$_2$CCl$_3$), 4.34 (d, *J* = 11.7 Hz, 1H, CH*H*Ph), 4.24 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.08 (*a*t, *J* = 8.1 Hz, 1H, H-4), 4.04 – 3.96 (m, 3H, H-3, H-4'', OCH*H*CH$_2$N$_3$), 3.82 (dd, *J* = 11.0, 4.4 Hz, 1H, H-6''a), 3.80 – 3.74 (m, 2H, H-6''b, H-6a), 3.71 – 3.60 (m, 4H, H-6b, OC*H*HCH$_2$N$_3$, H-3''', H-3'), 3.59 – 3.51 (m, 6H, H-2, H-5''', H-5', H-5, H-3'', H-2'), 3.47 – 3.40 (m, 5H, OCH$_2$CH*H*N$_3$, H-2'', H-6'a, H-5'', H-2'''), 3.40 – 3.34 (m, 1H, H-6'b), 3.33 – 3.25 (m, 3H, OCH$_2$C*H*HN$_3$, H-6'''a, H-6'''b), 2.03 – 2.00 (m, 6H, 2 OCOCH$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.90 (O*C*OCH$_3$), 169.87 (O*C*OCH$_3$), 157.1 (*a*d, *J* = 37.3 Hz, NH*C*OCF$_3$), 153.8 (NH*C*O$_2$CH$_2$Cl$_3$), 138.61, 138.60, 138.23, 138.16, 138.0, 137.91, 137.88, 137.8 (8 C_{Ar}), 129.0, 128.6, 128.54, 128.48, 128.43, 128.39, 128.38, 128.36, 128.3, 128.0, 127.92, 127.89, 127.87, 127.84, 127.81, 127.75, 127.71, 127.69, 127.65, 127.57, 127.4 (40 C_{Ar}), 115.6 (*a*d, *J* = 288.2 Hz, NHCO*C*F$_3$), 102.7 (C-1'), 102.5 (C-1'''), 100.9 (C-1''), 99.0 (C-1), 95.6 (CH_2*C*Cl$_3$), 80.2 (C-2'), 80.1 (C-2'''), 79.2 (C-3''), 77.7 (C-3'), 76.3, 76.2 (C-3, C-4, C-4''), 75.3, 75.2 (C-5, C-5''), 75.11, 74.12, 73.6, 73.4, 73.3, 73.2 (8 CH_2Ph, *C*H$_2$CCl$_3$), 72.9 (C-5'), 72.4 (C-3'''), 72.0 (C-5'''), 69.6 (C-4'), 69.6 (C-4'''), 68.3 (O*C*H$_2$CH$_2$N$_3$), 68.1, 68.0 (C-6, C-6', C-6''), 67.3 (C-6'''), 57.0 (C-2''), 55.7 (C-2), 50.6 (OCH$_2$*C*H$_2$N$_3$), 20.74 (OCO*C*H$_3$), 20.68 (OCO*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.89 (NHCOCF$_3$); HRMS (ESI$^+$): m/z calcd for $C_{91}H_{99}Cl_3F_3N_5O_{24}$: 1830.5595 $[M+Na]^+$; found: 1830.5514.

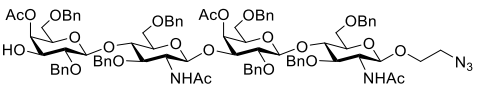
2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (53)



To a solution of tetrasaccharide **43** (160 mg, 94 µmol) in EtOH (2 mL) was added hydrazine hydrate (55 µL, 0.94 mmol) and the reaction was heated to reflux for 8 hours. Solvent was then removed and the crude residue was acetylated overnight with Ac_2O (1.5 mL) in pyridine (3 mL). The reaction was then concentrated to dryness, washed with water and extracted with CH_2Cl_2. Combined organic layers were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Purification by flash column chromatography (Tol/Acetone, 9:1, v/v) gave **53** (140 mg, 86.3 µmol, 92% over two steps) as a white foam. R_f = 0.71, Tol/Acetone 8:2; $[\alpha]_D^{20}$= -0.9 (*c* 1.0 , $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 40H, H_{Ar}), 5.73 (d, *J* = 7.4 Hz, 1H, N*H*COCH$_3$), 5.40 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 5.14 (d, *J* = 8.1 Hz, 1H, N*H*COCH$_3$''), 4.99 (d, *J* = 7.5 Hz, 1H, H-1), 4.97 (d, *J* = 7.5 Hz, 1H, H-1''), 4.91 (d, *J* = 11.1 Hz, 1H, CH*H*Ph), 4.83 – 4.76 (m, 4H, 2 CH_2Ph), 4.72 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.66 – 4.48 (m, 6H, 3 CH_2Ph), 4.46 – 4.29 (m, 6H, H-1''', H-1', 2 CH_2Ph), 4.18 (dd, *J* = 9.4, 8.1 Hz, 1H, H-3), 4.11 (dd, *J* = 5.6, 2.0 Hz, 1H, H-4'''), 4.07 – 4.03 (m, 1H, H-3'''), 4.02 – 3.95 (m, 3H, H-4'', H-4, OCH*H*CH$_2$N$_3$), 3.90 – 3.83 (m, 2H, H-3'', H-6a), 3.79 – 3.73 (m, 2H, H-6b, H-6''a), 3.71 (dd, *J* = 6.3, 2.0 Hz, 1H, H-5'''), 3.69 – 3.64 (m, 3H, H-6''b, H-6'''a, OC*H*HCH$_2$N$_3$), 3.62 (dd, *J* = 9.8, 3.5 Hz, 1H, H-3'), 3.57 – 3.49 (m, 5H, H-6'''b, H-5', H-5, H-5'', H-2'), 3.48 – 3.31 (m, 5H, OCH$_2$CH*H*N$_3$, H-2'', H-6'a, H-6'b, H-2'''), 3.29 – 3.20 (m, 2H, OCH$_2$C*H*HN$_3$, H-2), 1.97 (s, 3H, OCOCH$_3$), 1.89 (s, 3H, NHCOCH$_3$), 1.46 (s, 3H, NHCOC*H*$_3$), 1.37 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (O*C*OCH$_3$), 170.00

(NH*C*OCH$_3$), 169.95 (NH*C*OCH$_3$), 138.89, 138.85, 138.8, 138.5, 138.4, 138.3, 138.11, 138.07 (8 C$_{Ar}$), 128.5 – 126.9 (40 C$_{Ar}$), 109.7 (*C*(CH$_3$)$_2$), 102.4 (C-1'), 102.1 (C-1'''), 100.5 (C-1''), 99.5 (C-1), 80.4 (C-2'''), 79.8 (C-2'), 79.3 (C-3'''), 78.6 (C-3'), 78.4 (C-3''), 77.2 (C-3), 76.6, 76.3 (C-4, C-4''), 75.2, 75.0, 74.9 (C-5, C-5'', CH$_2$Ph), 74.0 (CH$_2$Ph), 73.7 (C-4'''), 73.6, 73.5, 73.4, 73.34, 73.26, 73.1 (6 CH$_2$Ph), 72.9 (C-5'), 71.9 (C-5'''), 69.6 (C-4'), 69.0 (C-6'''), 68.6, 68.3 (C-6, C-6'', C-6', O*C*H$_2$CH$_2$N$_3$), 56.7 (C-2), 56.0 (C-2''), 50.6 (OCH$_2$*C*H$_2$N$_3$), 27.9 (CH$_3$), 26.4 (CH$_3$), 23.6 (NHCO*C*H$_3$), 23.1 (NHCO*C*H$_3$), 20.8 (OCO*C*H$_3$); HRMS (ESI$^+$): m/z calcd for $C_{91}H_{105}N_5O_{22}$: 1620.7329 [M+H]$^+$; found: 1620.7302.

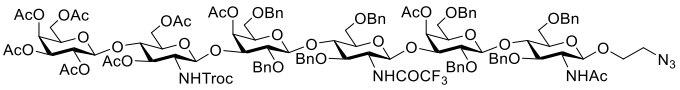
2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (55)



Compound **53** (125 mg, 77 μmol) was dissolved in 80% aq. AcOH (5 mL). The solution was heated at 60 °C for 6 hours then diluted with toluene and concentrated to dryness. Flash column chromatography purification (Tol/Acetone, 7:3, v/v) afforded **54** (104 mg, 66 μmol, 86%) as an amorphous white solid. Compound **54** (40 mg, 25 μmol) was dissolved in CH$_3$CN (500 μL), then CH$_3$C(OCH$_3$)$_3$ (10 μL, 76 μmol) and *p*-TsOH (1 mg, 5 μmol). After 30 minutes the reaction was quenched with Et$_3$N and concentrated *in vacuo*. Crude orthoester product was then dissolved in aq. 80% AcOH (500 μL) and stirred for 1 hour at RT. After solvent removal and flash column chromatography purification (Tol/Acetone, 7:3, v/v), acceptor **55** (38 mg, 23 μmol, 92%) was obtained as a white foam. R$_f$ = 0.23, cHex/Acetone 7:3; $[\alpha]_D^{20}$= +4.9 (*c* 1.0, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.18 (m, 40H, H$_{Ar}$), 5.74 (d, *J* = 7.4 Hz, 1H, N*H*COCH$_3$), 5.41 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 5.34 (dd, *J* = 3.5, 1.0 Hz, 1H, H-4'''), 5.22 (d, *J* = 7.9 Hz, 1H, N*H*COCH$_3$''), 5.03 – 4.98 (m, 2H, H-1, H-1''), 4.91 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.88 – 4.84 (m, 2H, CH*H*Ph, C*H*HPh), 4.81 (d, *J* = 11.6 Hz, 1H, CH*H*Ph), 4.68 – 4.60 (m, 3H, 2 CH$_2$Ph, C*H*HPh), 4.59 – 4.52 (m, 2H, CH$_2$Ph), 4.50 (d, *J* = 7.8 Hz, 1H, H-1'''), 4.47 – 4.36 (m, 5H, H-1', 2 CH$_2$Ph), 4.31 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.26 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.19 (dd, *J* = 9.5, 8.1 Hz, 1H, H-3), 4.06 – 3.95 (m, 4H, H-3'', H-4, H-4'', OC*H*HCH$_2$N$_3$), 3.83 (dd, *J* = 10.8, 4.0 Hz, 1H, H-6a), 3.79 – 3.73 (m, 2H, H-6b, H-6''a), 3.69 – 3.60 (m, 4H, H-6''b, OCH*H*CH$_2$N$_3$, H-3''', H-3'), 3.58 – 3.48 (m, 4H, H-5''', H-5', H-5'', H-2'), 3.48 – 3.30 (m, 7H, OCH$_2$C*H*HN$_3$, H-2'', H-6'''a, H-6'''b, H-6'a, H-6'b, H-2'''), 3.28 – 3.21 (m, 2H, H-2, OCH$_2$CH*H*N$_3$), 2.01 – 1.97 (m, 6H, 2 OCOCH$_3$), 1.89 (s, 3H, NHCOC*H*$_3$), 1.49 (s, 3H, NHCOC*H*$_3$); ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.8 (O*C*OCH$_3$), 170.6 (NH*C*OCH$_3$), 170.2 (NH*C*OCH$_3$), 169.9 (O*C*OCH$_3$), 138.9, 138.8, 138.4, 138.2, 138.1, 137.8 (8 C$_{Ar}$), 128.6 – 127.0 (m, 40 C$_{Ar}$), 102.5 (C-1'''), 102.4 (C-1'), 100.3 (C-1''), 99.5 (C-1), 80.0 (C-2'''), 79.7 (C-2'), 78.8 (C-3'), 78.1 (C-4''), 77.4 (under CDCl$_3$ peak, C-3''), 76.6 (C-3), 76.2 (C-4), 75.11, 75.06, 75.0, 74.9 (2 CH$_2$Ph, C-5'', C-5), 74.1 (CH$_2$Ph), 73.6, 73.4, 73.3, 73.2 (5 CH$_2$Ph), 72.8 (C-5'), 72.3 (C-3'''), 72.0 (C-5'''), 69.6 (C-4', C-4'''), 68.6 (C-6'), 68.3, 68.2 (C-6, C-6'', O*C*H$_2$CH$_2$N$_3$), 67.4 (C-6'''), 56.7 (C-2, C-2''), 50.6 (OCH$_2$*C*H$_2$N$_3$), 23.6 (NHCO*C*H$_3$), 23.1 (NHCO*C*H$_3$), 20.81 (OCO*C*H$_3$), 20.76 (OCO*C*H$_3$); HRMS (ESI$^+$): m/z calcd for $C_{90}H_{103}N_5O_{23}$: 1644.6942 [M+Na]$^+$; found: 1644.7008.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(4-*O*-

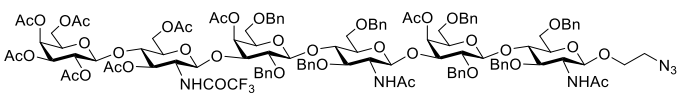
acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (56)



Acceptor **50** (60 mg, 36 μmol) and donor **9** (44 mg, 54 μmol) were dissolved in dry CH_2Cl_2 (2.4 mL) together with 4Å molecular sieves (104 mg). The mixture was stirred for 1 hour, then the mixture was cooled to -20 °C and NIS (12 mg, 54 μmol) was added followed by TfOH (2 μL, 18 μmol). The reaction was stirred for 1 hour at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated. Purification by flash column chromatography (cHex/Acetone 6:4, v/v) gave **56** (50 mg, 20 μmol, 55%). R_f = 0.31, cHex/Acetone 1:1; $[\alpha]_D^{20}$ = +3.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 40H, H_{Ar}), 6.32 (d, *J* = 8.3 Hz, 1H, $NHCOCF_3$), 5.80 (d, *J* = 7.4 Hz, 1H, N*H*$COCH_3$), 5.39 (*a*d, *J* = 3.6 Hz, 1H, H-4'), 5.37 (br, 1H, H-4'''), 5.36 – 5.34 (m, 1H, H-4'''''), 5.10 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'''''), 5.01 – 4.88 (m, 4H, H-3''''', CH*H*Ph, H-1, H-1''), 4.86 – 4.73 (m, 5H, H-3'''', C*H*HPh, CH_2Ph, N*H*$CO_2CH_2CCl_3$), 4.68 (m, 2H, CH*H*CCl_3, C*H*HPh), 4.63 – 4.53 (m, 7H, H-6''''a, C*H*$HCCl_3$, CH_2Ph, CH_2Ph , H-1'''', C*H*HPh), 4.52 – 4.39 (m, 7H, H-1''''', H-1''', C*H*HPh, 2 CH_2Ph), 4.41 – 4.33 (m, 2H, C*H*HPh, H-1'), 4.33 – 4.27 (m, 2H, CH_2Ph), 4.16 (dd, *J* = 9.6, 8.2 Hz, 1H, H-3), 4.12 – 4.09 (m, 2H, H-6'''''a, H-6'''''b), 4.08 – 3.96 (m, 4H, H-6''''b, OC*H*HCH_2N_3, H-4'', H-4), 3.88 (dd, *J* = 6.8, 1.3 Hz, 2H, H-5'''''), 3.82 – 3.56 (m, 12H, H-2'', H-2'''', H-6''a, H-6''b, H-6a, H-6b, OCH*H*CH_2N_3, H-5'''', H-3'', H-3', H-3''', H-4''''), 3.54 – 3.42 (m, 6H, H-5''', H-5', H-5, H-2', H-2''', OCH_2CHHN_3), 3.41 – 3.31 (m, 5H, H-6'''a, H-6'''b, H-6'a, H-6'b, H-5''), 3.27 – 3.20 (m, 2H, H-2, OCH_2CHHN_3), 2.15 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 2.02 (s, 3H, $OCOCH_3$), 1.99 – 1.96 (m, 6H, 2 $OCOCH_3$), 1.91 (s, 3H, $NHCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.54, 170.45, 170.4, 170.2, 170.1, 170.0, 169.9, 169.2 (9 $COCH_3$), 156.9 (*a*d, *J* = 36.9 Hz, $NHCOCF_3$), 154.1 ($NHCO_2CH_2CCl_3$), 138.8, 138.4, 138.3, 138.12, 138.07, 138.0, 137.9, 137.8 (8 C_{Ar}), 128.7, 128.4, 128.4 – 128.2, 128.19, 128.18, 128.15, 128.1, 128.0, 127.87, 127.85, 127.8, 127.71, 127.65, 127.6, 127.5, 127.2, 127.1 (40 C_{Ar}), 115.6 (*a*d, *J* = 288.7 Hz, $NHCOCF_3$), 102.4 (C-1'''), 102.3 (C-1'), 101.2 (C-1'''''), 101.0 (C-1''''), 99.5 (C-1), 99.3 (C-1''), 95.6 (CH_2CCl_3), 80.3 (C-2', C-2'''), 77.3 (C-3), 76.7 (C-4'''', C-3''', C-3'), 76.4 (C-4), 76.1 (C-3''), 75.8 (C-4''), 75.3 (C-5''), 75.1, 74.9, 74.8, 74.3, 74.1, 73.7, 73.51, 73.48, 73.3, 73.2 (8 CH_2Ph, C-5, CH_2CCl_3), 72.5 (C-5', C-5''', C-5''''), 72.3 (C-3''''), 71.0 (C-3'''''), 70.7 (C-5'''''), 69.7, 69.5 (C-4', C-4'''), 69.2 (C-2'''''), 68.2, 68.1, 68.0, 67.8 (C-6'', C-6, C-6', C-6''', O$CH_2CH_2N_3$), 66.66 (C-4'''''), 61.4 (C-6''''), 60.9 (C-6'''''), 56.8 (C-2), 56.3 (C-2''''), 55.8 (C-2''), 50.6 ($OCH_2CH_2N_3$), 23.5 ($NHCOCH_3$), 20.79, 20.77, 20.7, 20.63, 20.61, 20.5 (8 $OCOCH_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.69 ($NHCOCF_3$); HRMS (ESI^+): m/z calcd for $C_{117}H_{134}Cl_3F_3N_6O_{40}$: 2447.7546 $[M+Na]^+$; found: 2447.8903.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (57)

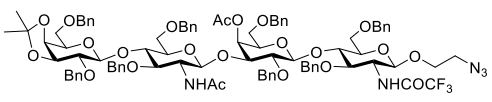
Acceptor **55** (34 mg, 21 μmol) and donor **10** (23 mg, 31 μmol) were dissolved in dry CH_2Cl_2 (1.4 mL) together with 4Å molecular sieves (57 mg).



The mixture was stirred for 1 hour, then the mixture was cooled to -20 °C and NIS (7 mg, 31 μmol) was added followed by TfOH (1 μL, 17 μmol). The reaction was stirred for 1 hour at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated *in vacuo*. Purification by flash column chromatography (cHex/Acetone 7:3, v/v) gave **57** (38 mg, 17 μmol, 80%). R_f = 0.40, cHex/Acetone 1:1; $[\alpha]_D^{20}$= +5.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.10 (m, 40H, H_{Ar}), 6.18 (d, *J* = 9.6 Hz, 1H, $NHCOCF_3$), 5.72 (d, *J* = 7.4 Hz, 1H, N*H*COCH$_3$), 5.40 – 5.34 (m, 3H, H-4’’’’’, H-4’, H-4’’’), 5.17 (d, *J* = 7.9 Hz, 1H, N*H*COCH$_3$), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2’’’’’), 5.01 – 4.95 (m, 3H, H-1, H-1’’, H-3’’’’’), 4.92 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.90 – 4.80 (m, 4H, H-3’’’’, CH*H*Ph, CH_2Ph), 4.72 – 4.61 (m, 4H, H-1$_V$, CH_2Ph, H-6’’’’a), 4.60 – 4.36 (m, 11H, H-1’’’, H-1’’’’’, H-1’, 4 CH_2Ph), 4.32 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.28 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.19 (dd, *J* = 9.4, 8.1 Hz, 1H, H-3’’), 4.12 – 4.09 (m, 2H, H-6’’’’’a, H-6’’’’’b), 4.09 – 3.90 (m, 6H, H-6’’’’b, OCH*H*CH_2N_3, H-4, H-3, H-4’’, H-2’’’’), 3.90 – 3.86 (m, 1H, H-5’’’’’), 3.84 – 3.74 (m, 3H, H-6a, H-6’’a, H-4’’’’), 3.74 – 3.63 (m, 4H, H-6b, H-6’’b, H-3’’’, OC*H*HCH_2N_3), 3.62 – 3.58 (m, 2H, H-5’’’’, H-3’), 3.58 – 3.41 (m, 6H, H-5’, H-5, H-5’’, H-2’, H-2’’’, OCH_2CH*H*N_3), 3.41 – 3.29 (m, 5H, H-2, H-6’a, H-6’b, H-6’’’a, H-6’’’b), 3.24 (m, 2H, H-2’’, OCH_2C*H*HN_3), 2.15 (s, 3H, $OCOCH_3$), 2.09 – 2.06 (m, 9H, 3 $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.98 (s, 6H, 2 $OCOCH_3$), 1.89 (s, 3H, NHCOC*H*$_3$), 1.49 (s, 3H, NHCOC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.5, 170.40, 170.36, 170.12, 170.06, 170.01, 169.95, 169.9, 169.2 (10 $COCH_3$), 157.0 (q, J = 37.3 Hz, NH*C*OCF_3), 138.9, 138.8, 138.7, 138.4, 138.13, 138.05, 138.0, 137.9 (8 C_{Ar}), 128.6, 128.4, 128.32, 128.30, 128.12, 128.08, 128.06, 128.0, 127.9, 127.81, 127.77, 127.64, 127.61, 127.57, 127.5, 127.4, 127.0, 126.8 (40 C_{Ar}), 115.5 (*q*d, J = 288.3 Hz, NHCO*C*F_3), 102.4 (C-1’), 102.22 (C-1’’’), 101.2 (C-1’’’’’), 100.4 (C-1), 100.1 (C-1’’’’), 99.5 (C-1’’), 80.2 (C-2’’’), 79.7 (C-2’), 78.8 (C-3’), 78.0 (C-4’’), 77.2 (C-3’’), 76.6 (C-3), 76.1 (C-3’’’), 75.9 (C-4), 75.6 (C-4’’’’), 75.1, 75.0, 74.9 (CH_2Ph, CH_2Ph, H-5’’, H-5), 74.0 (CH_2Ph), 73.53, 73.49, 73.3, 73.2 (5 CH_2Ph), 72.8, 72.7 (C-5’, C-5’’’), 72.3 (C-5’’’’), 71.9 (C-3’’’’), 70.9 (C-3’’’’’), 70.8 (C-5’’’’’), 69.7 (C-4’, C-4’’’), 69.1 (C-2’’’’’), 68.5 (C-6’), 68.3 (O*C*$H_2CH_2N_3$), 68.2, 68.0, 67.9 (C-6, C-6’’, C-6’’’), 66.6 (C-4’’’’’), 61.1 (C-6’’’’), 60.9 (C-6’’’’’), 56.7 (C-2’’), 56.4 (C-2), 54.5 (C-2’’’’), 50.6 (OCH_2*C*H_2N_3), 23.6 (NHCO*C*H_3), 23.1 (NHCO*C*H_3), 20.79, 20.75, 20.63, 20.59, 20.5 (8 OCO*C*H_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.95 ($NHCOCF_3$); HRMS (ESI$^+$): m/z calcd for $C_{116}H_{135}F_3N_6O_{39}$: 2315.8609 [M+Na]$^+$; found: 2315.8827.

2-Azidoethyl (2,6-di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-[2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (46)

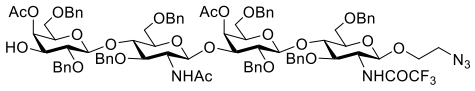
Tetrasaccharide **45** (73 mg, 40 μmol) was dissolved in THF (800 μL) and reacted with a solution of TBAF in THF (1M, 202 μL). The reaction was stirred at RT for 8 hours, then solvent was removed and



the crude residue was acetylated with Ac_2O (250 μL) in pyridine (500 μL). The reaction was stirred overnight, then concentrated to dryness. Purification by flash column chromatography (Tol/Acetone, 8:2, v/v) afforded the desired tetrasaccharide **46** (50 mg, 30 μmol, 75%) and unreacted starting material **57** (15 mg, 8 μmol). R_f = 0.22, Tol/Acetone

8:2; $[\alpha]_D^{20}$= +15.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 40H, H_{Ar}), 6.81 (d, *J* = 7.6 Hz, 1H, N*H*COCF$_3$), 5.41 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 5.01 (d, *J* = 6.1 Hz, 1H, H-1''), 4.89 (d, *J* = 6.8 Hz, 1H, H-1), 4.85 – 4.71 (m, 5H, 2 CH_2Ph, C*H*HPh), 4.69 – 4.49 (m, 5H, 2 CH_2Ph, CH*H*Ph), 4.48 – 4.38 (m, 6H, H-1''', H-1', 2 CH_2Ph), 4.39 – 4.29 (m, 2H, CH_2Ph), 4.13 (dd, *J* = 5.6, 2.0 Hz, 1H, H-4'''), 4.10 – 4.04 (m, 2H, H-3''', H-3), 4.03 – 3.97 (m, 3H, OCH*H*CH_2N_3, H-4, H-4''), 3.92 (*a*d, *J* = 8.8 Hz, 1H, H-3''), 3.90 – 3.83 (m, 1H, H-6''a), 3.82 – 3.61 (m, 8H, H-6''b, H-6a, H-6b, H-6'''a, OC*H*HCH_2N_3, H-5''', H-3', H-2), 3.60 – 3.52 (m, 5H, H-6'''b, H-5', H-5, H-5'', H-2'), 3.47 – 3.39 (m, 3H, OCH_2C*H*HN_3, H-2'', H-6'a), 3.38 – 3.33 (m, 2H, H-6'b, H-2'''), 3.29 (ddd, *J* = 13.3, 5.5, 3.5 Hz, 1H, OCH_2CH*H*N_3), 2.00 (s, 3H, $OCOCH_3$), 1.48 (s, 3H, NHCOC*H*$_3$), 1.39 (s, 3H, CH_3), 1.36 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 170.0 (2 O*C*OCH_3), 157.1 (*a*d, *J* = 37.1 Hz, NH*C*OCF_3), 138.8, 138.7, 138.5, 138.4, 138.3, 137.99, 137.98, 137.9 (8 C_{Ar}), 129.0, 128.58, 128.55, 128.44, 128.41, 128.36, 128.3, 128.24, 128.21, 128.16, 127.9, 127.83, 127.81, 127.76, 127.7, 127.6, 127.52, 127.46, 127.1 (40 C_{Ar}), 115.6 (*a*d, *J* = 288.5 Hz, NHCO*C*F_3), 109.8 (*C*$(CH_3)_2$), 102.8 (C-1'), 102.1 (C-1'''), 100.4 (C-1''), 99.0 (C-1), 80.4 (C-2'''), 79.6 (C-2'), 79.3 (C-3'''), 78.6 (C-3'), 78.3 (C-3''), 76.4, 76.3, 76.1 (C-4, C-3, C-4''), 75.3, 75.2 (C-5, C-5''), 75.0 (CH_2Ph), 73.9 (CH_2Ph), 73.7 (C-4'''), 73.6, 73.4, 73.3, 73.3, 73.1 (6 CH_2Ph), 73.0 (C-5'), 71.9 (C-5'''), 69.5 (C-4'), 69.0 (C-6'''), 68.6 (C-6'), 68.3 (C-6'', C-6, O*C*$H_2CH_2N_3$), 56.1 (C-2''), 55.3 (C-2), 50.6 (OCH_2*C*H_2N_3), 27.9 (CH_3), 26.4 (CH_3), 23.1 (NHCO*C*H_3), 20.7 (OCO*C*H_3); HRMS (ESI$^+$): m/z calcd for $C_{91}H_{102}F_3N_5O_{22}$; 1696.6861 $[M+Na]^+$; found 1696.7732.

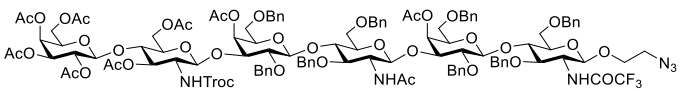
2-Azidoethyl (4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (52)



Tetrasaccharide **46** (50 mg, 30 μmol) was stirred in aq. 80% AcOH (500 μL) for 4 hours at 60 °C. After dilution with toluene the solvents were removed and crude was purified by column chromatography (Tol/Acetone, 8:2, v/v) to give corresponding diol derivative **49** (27 mg, 17 μmol, 56%). Diol **49** (25 mg, 15 μmol) was then dissolved in CH_3CN (500 μL) and reacted with $CH_3C(OCH_3)_3$ (6 μL, 46 μmol) and *p*-TsOH (1 mg, 5 μmol). After 30 minutes the reaction was quenched with Et_3N and concentrated *in vacuo*. Crude orthoester product was then dissolved in aq. 80% AcOH (500 mL) and sirred for 1 hour at RT. After solvent removal and flash column chromatography purification (Tol/Acetone, 7:3, v/v), acceptor **52** (22 mg, 13 μmol, 76%) was obtained as a white foam. R_f = 0.43, Tol/Acetone 7:3; $[\alpha]_D^{20}$= +3.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 40H, H_{Ar}), 6.82 (d, *J* = 7.6 Hz, 1H, NHCOCF_3), 5.41 (*a*d, *J* = 3.5 Hz, 1H, H-4'), 5.35 (*a*d, *J* = 3.5 Hz, 1H, H-4'''), 5.26 (d, *J* = 7.8 Hz, 1H, N*H*$COCH_3$), 5.06 (d, *J* = 7.5 Hz, 1H, H-1''), 4.91 – 4.84 (m, 3H, H-1, CH_2Ph), 4.83 – 4.76 (m, 2H, CH_2Ph), 4.70 – 4.60 (m, 3H, CH_2Ph, CH*H*Ph), 4.59 – 4.52 (m, 3H, C*H*HPh, CH_2Ph), 4.51 (d, *J* = 7.8 Hz, 1H, H-1'''), 4.48 – 4.38 (m, 5H, H-1', 2 CH_2Ph), 4.34 (d, *J* = 11.7 Hz, 1H, CH*H*Ph), 4.28 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.11 – 3.94 (m, 5H, H-3'', H-3, H-4, H-4'', OCH*H*CH_2N_3), 3.86 – 3.75 (m, 3H, H-6''a, H-6''b, H-6a), 3.71 (dd, *J* = 10.6, 3.5 Hz, 1H, H-6b), 3.68 – 3.50 (m, 9H, OC*H*HCH_2N_3, H-2, H-6b, H-3''', H-3', H-5''', H-5', H-5'', H-2'), 3.47 – 3.39 (m, 3H, OCH_2CH*H*N_3, H-6'a, H-2'''), 3.39 – 3.33 (m, 4H, H-2'', H-6'b, H-6'''a, H-6'''b), 3.29 (m, 1H, OCH_2C*H*HN_3), 2.01 (s, 6H, 2 $OCOCH_3$), 1.52 (s, 3H, NHCOC*H*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.2, 170.0 (3 *C*OCH_3), 157.1 (*a*d, *J* = 37.2 Hz, NH*C*OCF_3), 138.9, 138.7, 138.3, 138.1, 137.99, 137.95, 137.9, 137.8 (8 C_{Ar}),

128.6, 128.43, 128.41, 128.36, 128.24, 128.22, 128.20, 128.12, 128.08, 127.9, 127.8, 127.71, 127.69, 127.63, 127.55, 127.5, 127.2 (40 C_{Ar}), 115.6 (*a*d, *J* = 288.6 Hz, NHCO$\underline{C}F_3$), 102.8 (C-1'), 102.5 (C-1'''), 100.2 (C-1''), 99.0 (C-1), 80.0 (C-2'''), 79.5 (C-2'), 78.8 (C-3'), 78.0 (C-3''), 76.4, 76.3, 76.1 (C-3, C-4, C-4''), 75.3 (C-5), 75.09 (C-5''), 75.06 (CH_2Ph), 75.0 (CH_2Ph), 73.9 (CH_2Ph), 73.6 (2 CH_2Ph), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 73.2 (CH_2Ph), 73.0 (C-5'), 72.3 (C-3'''), 72.0 (C-5'''), 69.54 (C-4'''), 69.46 (C-4'), 68.6 (C-6'), 68.3 (O$\underline{C}H_2CH_2N_3$, C-6), 68.2 (C-6''), 67.4 (C-6'''), 56.6 (C-2''), 55.4 (C-2), 50.6 (OCH$_2\underline{C}H_2N_3$), 23.2 (NHCO$\underline{C}H_3$), 20.8 (2 OCO$\underline{C}H_3$); HRMS (ESI$^+$): m/z calcd for $C_{90}H_{100}F_3N_5O_{23}$; 1698.7 $[M+Na]^+$; found 1698.0.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside]-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranoside (59)



Acceptor **52** (23 mg, 12 μmol) and donor **9** (15 mg, 19 μmol) were dissolved in dry CH_2Cl_2 (800 μL) together with 4Å molecular sieves (38 mg). The mixture was stirred for 1 hour, then it was cooled to -20 °C and NIS (4 mg, 19 μmol) was added followed by TfOH. The reaction was stirred for 1 hour at the same temperature, then quenched with Et_3N, filtered over Celite and evaporated *in vacuo*. Purification by flash column chromatography (cHex/Acetone 6:4, v/v) gave **59** (17 mg, 7 μmol, 58%). R_f = 0.20, Tol/Acetone 8:2; $[\alpha]_D^{20}$= +6.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.16 (m, 40H, H_{Ar}), 6.81 (d, *J* = 7.7 Hz, 1H, NHCOCF_3), 5.40 – 5.33 (m, 3H, H-4'''', H-4', H-4'''), 5.25 (d, *J* = 8.0 Hz, 1H, N$\underline{H}$COCH$_3$), 5.11 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2''''), 5.03 (d, *J* = 7.9 Hz, 1H, H-1''), 4.97 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3''''), 4.91 – 4.84 (m, 3H, H-1, CH_2Ph), 4.83 – 4.76 (m, 2H, CH_2Ph), 4.75 – 4.63 (m, 4H, H-3'''', CH_2Ph, C$\underline{H}$HCCl$_3$), 4.61 – 4.36 (m, 15H, H-6''''a, CH$\underline{H}$CCl$_3$, 4 CH_2Ph, H-1'''', H-1''''', H-1''', H-1', N$\underline{H}$CO$_2$CH$_2$CCl$_3$), 4.35 – 4.27 (m, 2H, CH_2Ph), 4.13 – 4.08 (m, 2H, H-6''''a, H-6''''b), 4.08 – 3.95 (m, 6H, H-6''''b, OC*H*$\underline{H}$CH$_2$N$_3$, H-3, H-4, H-4'', H-3''), 3.87 (*a*t, *J* = 6.9 Hz, 1H, H-5'''''), 3.83 – 3.48 (m, 14H, H-2, H-2'''', H-6''a, H-6''b, H-6a, H-6b, OC$\underline{H}$*H*CH$_2$N$_3$, H-5'''', H-5''', H-5, H-4''', H-3''', H-3', H-2'), 3.49 – 3.38 (m, 5H, CH$_2$C*H*$\underline{H}$N$_3$, H-6'a, H-5', H-5'', H-2'''), 3.38 – 3.25 (m, 5H, H-2'', OCH$_2$C$\underline{H}$*H*N$_3$, H-6'''a, H-6'''b, H-6'b), 2.15 (s, 3H, OCOCH$_3$), 2.09 – 2.05 (m, 12H, 4 OCOCH$_3$), 2.02 (s, 3H, OCOCH$_3$), 2.01 (s, 3H, OCOCH$_3$), 2.00 (s, 3H, OCOCH$_3$), 1.98 (s, 3H, NHCOC$\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.4, 170.3, 170.1, 170.03, 169.99, 169.2, 169.94, 169.93 (9 $\underline{C}$OCH$_3$), 156.7 (*a*d, *J* = 37.4 Hz, NH$\underline{C}$OCF$_3$), 154.1 (NH$\underline{C}$O$_2$CH$_2$CCl$_3$), 138.8, 138.6, 138.4, 138.3, 138.0, 137.92, 137.89 (8 C_{Ar}), 128.7, 128.4, 128.3, 128.22, 128.18, 128.1, 127.9, 127.81, 127.79, 127.73, 127.66, 127.6, 127.54, 127.47, 127.1, 127.0 (40 C_{Ar}), 115.6 (*a*d, *J* = 286.9 Hz, NHCO$\underline{C}F_3$), 102.8 (C-1'), 102.1 (C-1'''), 101.2 (C-1'''''), 101.0 (C-1''''), 100.3 (C-1''), 99.0 (C-1), 95.6 (CH$_2\underline{C}$Cl$_3$), 80.6 (C-2'''), 79.4 (C-2'), 77.9 (C-3'), 77.2 (C-3''), 76.3, 76.1, 76.0 (C-3''', C-4'''', C-4'', C-4, C-3), 75.3, 75.0 (C-5, C-5'', CH_2Ph, CH_2Ph), 74.3 ($\underline{C}H_2CCl_3$), 73.9, 73.6, 73.5, 73.33, 73.26 (6 CH_2Ph), 73.0, 72.5, 72.3 (C-5'''', C-5''', C-5'), 72.1 (C-3''''), 71.0 (C-3'''''), 70.7 (C-5'''''), 69.7, 69.4 (C-4', C-4'''), 69.1 (C-3'''''), 68.6 (C-6'), 68.3 (C-6'', C-6, O$\underline{C}$H$_2$CH$_2$N$_3$), 67.9 (C-6'''), 66.6 (C-4'''''), 61.5 (C-6''''), 61.4 (C-6'''''), 56.7 (C-2''), 56.2 (C-2''''), 55.4 (C-2), 50.6 (OCH$_2\underline{C}$H$_2$N$_3$), 23.1 (NHCO$\underline{C}$H$_3$), 20.8, 20.74,

20.73, 20.69, 20.65, 20.63, 20.61, 20.5 (8 OCO<u>C</u>H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.88 ($NHCOCF_3$); HRMS (ESI^+): m/z calcd for $C_{117}H_{134}Cl_3F_3N_6O_{40}$: 2450.7 $[M+Na]^+$; found: 2450.7.

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