Electronic Supplementary Material (ESI) for Chemical Science.

SELF-PROMOTED AND STEREOSPECIFIC FORMATION OF *N*-GLYCOSIDES

Table of contents

General experimental details

All chemicals used have been used in synthesis purchased at Sigma-Adrich, Fluka, TCI, ABCR, CarboSynth or Merck unless otherwise noted. All solvents used for synthesis were HPLC-grade and obtained dry from an Innovative Technology PS-MD-05 solvent drying system. ROTH silica gel 60 (40-63 mesh) has been used as stationary phase for column chromatography. Merck 60 F254-plates were used for TLC-analysis, visualized by UV and submerged in Ce/Mo-solution (Ce(IV)sulphate (10 g) and $(NH_4)_2MO_4$ (15 g) in 1000 mL 10 % aqueous sulphuric acid), 10 % H_2SO_4 in methanol or vanillin stain (10 g, in 1000 mL 10 % H_2SO_4 in MeOH) followed by heating. All reactions were carried out under an inert nitrogen atmosphere in flame-dried glassware unless otherwise stated.

A Bruker 500 MHz Ultra Shield Plus spectrograph with a cryo probe has been used to obtain ^{1}H-NMR-, ^{13}C-NMR-, COSY- (Correlation Spectroscopy) and HSQC-spectra (Heteronuclear Single Quantum Coherence).

Recorded spectra were referenced to the respective solvent peak as internal standard:

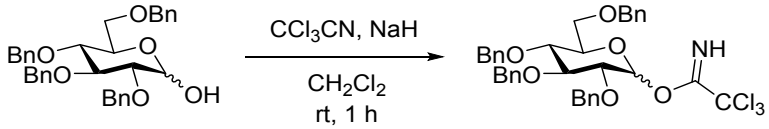
Ref. to solvent:	$CDCl_3$	^{1}H-NMR 7.260 ppm ^{13}C-NMR 77.160 ppm
	CD_2Cl_2	^{1}H-NMR 5.320 ppm ^{13}C-NMR 54.000 ppm
	DMSO-6d	^{1}H-NMR 2.500 ppm ^{13}C-NMR 39.520 ppm
	CD_3CN	^{1}H-NMR 1.940 ppm ^{13}C-NMR 1.320 ppm
	C_6D_6	^{1}H-NMR 7.160 ppm ^{13}C-NMR 128.060 ppm

High-resolution mass spectrometry has been performed on a Bruker SolarX XR 7T E8I/MALDI-FT-ICR-MS instrument.

Experimental procedures

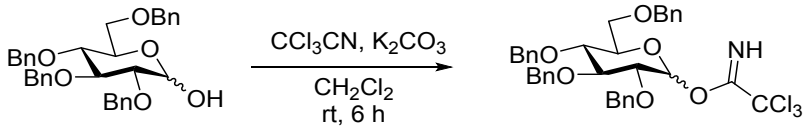
Synthesis of glycosyl donors

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (1)



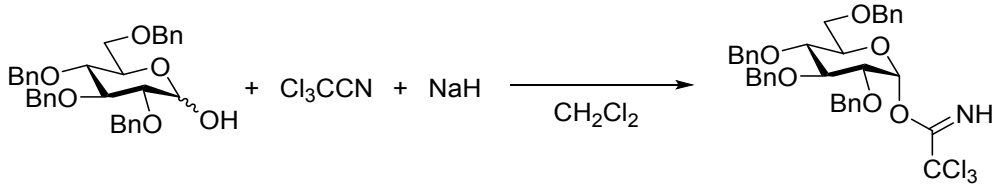
NaH (44.4 mg 60 % in mineral oil, 1.11 mmol) and trichloroacetonitrile (2.3 mL, 23.12 mmol) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (2.50 g, 4.62 mmol) in dry DCM (10 ml). The solution was stirred at RT for 1 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:9→1:8 EtOAc/Heptane + 0.5 % Et_3N) to afford the major anomer (α) of the desired product 1 (2.53 g, 3.69 mmol, 80 %) as a colorless syrup. NMR data of the compound 1 were consistent with the previously reported.[1]

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (1)



K_2CO_3 (2.05 g, 14.80 mmol) and trichloroacetonitrile (1.9 mL, 18.50 mmol) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (2.00 g, 3.70 mmol) in dry DCM (12 ml). The solution was stirred at RT for 6 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:9→1:7 EtOAc/Heptane + 0.5 % Et_3N) to afford the major anomer (*β*) of the desired product 1 (1.86 g, 2.74 mmol, 74 %). NMR data of the compound 1 were consistent with the previously reported.[1]

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (1)

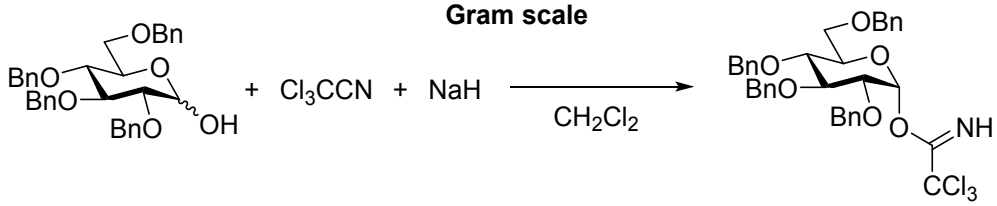


NaH (8 mg 60 % in mineral oil, 0.2 mmol) and trichloroacetonitrile (1.9 mL, 19 mmol) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.03 g, 1.9 mmol) in dry CH_2Cl_2. The solution was stirring at RT overnight and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired product 1 (1.25 g, 1.82 mmol, 96 %) as a mixture of anomers (85:15 α/β). NMR is in accordance with the literature.[2] α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, NH, 1H), 7.34-7.27 (m, Ar, 18H), 7.18-7.16 (m, Ar, 2H), 6.55 (d, H-1. *J*=3.6 Hz, 1H), 4.98 (d, CH_2, *J*=10.9 Hz, 1H), 4.88 (d, CH_2, *J*=10.7 Hz, 1H), 4.84 (d, CH_2, *J*=11.0 Hz, 1H), 4.76 (d, CH_2, *J*=10.7 Hz, 1H), 4.70 (d, CH_2, *J*=10.7 Hz, 1H), 4.63 (d, CH_2, *J*=12 Hz, 1H), 4.55 (d, CH_2, *J*=10.7 Hz, 1H), 4.49 (d, CH_2, *J*=12.1 Hz, 1H), 4.07 (t, H-3, *J*=9.5 Hz, 1H), 4.01

(ddd, H-5, *J*=2.0 Hz, *J*=3.2 Hz, *J*=10.1 Hz, 1H), 3.82-3.77 (m, H-2, H-4, H-6a, 3H), 3.68 (dd, H-6b, *J*=2.0, *J*=11.0 Hz, 1H). β-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, NH, 1H), 7.38-7.28 (m, Ar, 18H), 7.22-7.18 (m, Ar, 2H), 5.85 (d, H-1, *J*=7.1 Hz, 1H), 4.96 (d, CH_2, *J*=10.9 Hz, 1H), 4.92 (d, CH_2, *J*=11.0 Hz, 1H), 4.83 (m, CH_2, 2H), 4.77 (d, CH_2, *J*=10.9 Hz, 1H), 4.63 (d, CH_2, *J*=12.2 Hz, 1H), 4.59 (d, CH_2, *J*=10.8 Hz, 1H), 4.56 (d, CH_2, *J*=12.2 Hz, 1H), 3.85-3.76 (m, H-2, H-3, H-4, H-6a, 5H) 3.66 (m, H-6b, 1H).

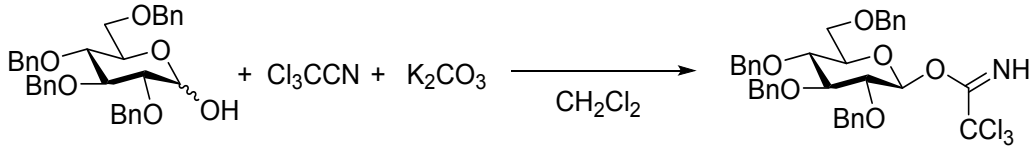
2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (1)

Gram scale



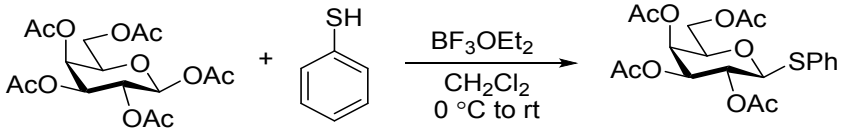
NaH (79.1 mg 60 % in mineral oil, 1.98 mmol) and trichloroacetonitrile (8.00 mL, 79.8 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (8.00 g, 14.80 mmol) in dry CH_2Cl_2 (80 mL). After 2 hr, a further 111.2 mg NaH (60 % dispersion in mineral oil) was added. The reaction was stirred for a total of 4.25 hr and extracted with sat aq. $NaHCO_3$ (2 x 50 mL). The organic phase was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was dissolved in hot EtOAc and added heptane until a white, cloudy precipitation would start forming around the area of contact with heptane. The resulting solution was left covered at -18 °C overnight from which the desired product 1 could be filtered off as an amorphous solid (7.62 g, 75 %, 93:7 α/β). The NMR data is in accordance with what has been reported previously in this SI for an identical compound.

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (1)



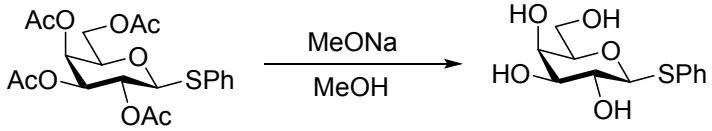
K_2CO_3 (2.56 g, 18.5 mmol) and trichloroacetonitrile (1.9 mL, 19 mmol) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.03 g, 1.9 mmol) in dry DCM. The solution was stirred at RT for 2 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired product 1 (403 mg, 0.72 mmol, 38 %) as a mixture of anomers from which fractions containing primarily the β-anomer could be isolated. This reaction was performed multiple times giving rise to similar yields. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in the literature.[3]

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-thiogalactopyranoside (S1)



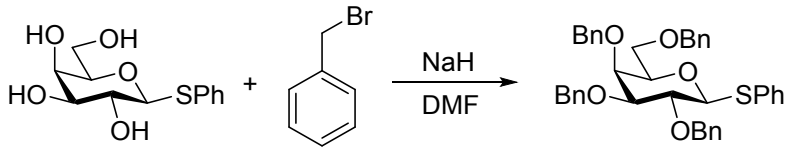
Boron trifluoride diethyl etherate (11.0 mL, 89.1 mmol) was added dropwise at 0 °C to a stirring solution of penta-*O*-acetyl-β-D-galactopyranose (11.6 g, 27.2 mmol) and PhSH (9.0 mL, 88 mmol) in DCM (75 mL). The reaction was allowed to reach rt and was stirred for 2.5 hr until no starting material was left. The reaction was quenched with sat. aq. $NaHCO_3$ (150 mL) and added to a separating funnel with 200 mL Et_2O. The organic layer was washed with sat. aq. $NaHCO_3$ (2 x 50 mL), water (2 x 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was added to a plug of silica and washed with toluene to remove excess PhSH. Afterwards, the silica was washed with EtOAc to yield the desired product, S1, as a colorless syrup. The crude product was used in the next step without any further purification. ^{1}H-NMR and ^{13}C-NMR was in accordance with the literature.[4] Rf = 0.43 (1:4 EtOAc/toluene)

Phenyl β-D-1-thio-galactopyranoside (S2)



The crude phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-thiogalactopyranoside, S1, was dissolved in 200 mL methanol and added NaOMe (25 wt% in methanol, 6 mL). The reaction was stirred at rt for 2.25 hr until no starting material was left. The reaction was neutralized with IR120 Amberlite hydrogen form resin, filtered and evaporated *in vacuo*. The crude product was used in the next step without any further purification or characterization.

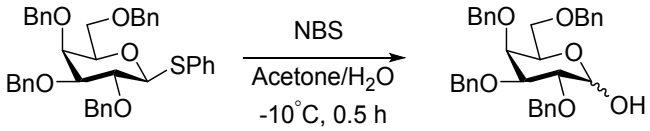
Phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-thiogalactopyranoside (S3)



NaH (15.6 g, 163 mmol) was added in four portions over 0.5 hr to a stirring solution of phenyl β-D-thiogalactopyranoside and benzyl bromide (20 mL, 168 mmol) at 0 °C in DMF (150 mL). The reaction was added a further 20 mL DMF after 1 hr. The reaction was quenched with methanol after 1.5 when all starting material was consumed. The reaction was added 200 mL Et_2O and washed with water (4 x 100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was dissolved in refluxing EtOAc and poured into a stirring solution of petroleum ether to yield the desired product S3 as white crystals (13.66 g, 79.5 % over 3 steps). ^{1}H- and ^{13}C-NMR is in accordance with the literature.[5] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, arom. H, 2H), 7.46 – 7.29 (m, arom. H, 19H), 7.25 – 7.17 (m, arom. H, 2H), 5.01 (d, CH_2^{Bn}, *J* = 11.5 Hz, 1H), 4.83 (d, CH_2^{Bn}, *J* = 10.2 Hz, 1H), 4.80 – 4.73 (m, CH_2^{Bn}, 2H), 4.69 (d, H-1, *J* = 9.7 Hz, 1H), 4.65 (d, CH_2^{Bn}, *J* = 11.5 Hz, 1H), 4.51 (d, CH_2^{Bn}, *J* = 11.7 Hz, 1H), 4.46 (d, CH_2^{Bn}, *J* = 11.7 Hz, 1H), 4.02 (d, H-4, *J* = 2.7 Hz, 1H), 3.98 (t, H-2, *J* = 9.5 Hz, 1H), 3.72 – 3.63 (m, H-3, H-5, H-6a, H-6b, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.87, 138.44, 138.37, 137.99, 134.27, 131.61, 128.89, 128.54, 128.44, 128.30,

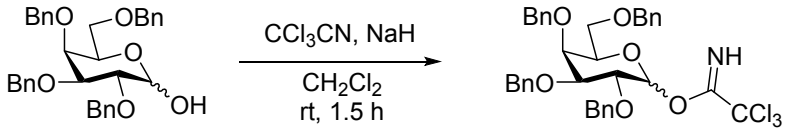
128.03, 127.94, 127.91, 127.85, 127.80, 127.68, 127.58, 127.14, 87.83, 84.30, 77.42, 77.16, 76.91, 75.76, 74.57, 73.69, 72.84, 68.88. Rf = 0.52 (3:7 EtOAc/heptane)

2,3,4,6-Tetra-*O*-benzyl-D-galactopyranose (S4)



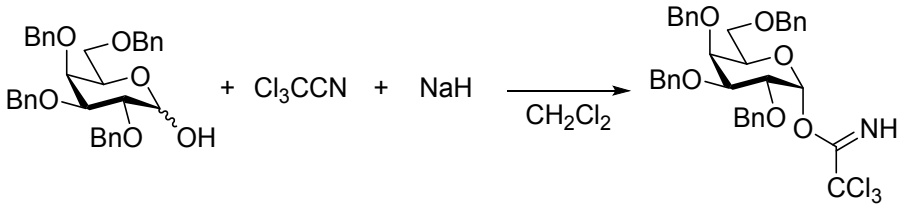
N-Bromosuccinimide (1.01 g, 5.69 mmol) was added in the dark to a stirred solution of Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-galactopyranoside (3.00 g, 4.74 mmol) in a mixture of acetone and water (19:1, 60 ml) at -10°C. The solution was stirred at this temperature for 0.5 h. After completion the reaction mixture was diluted with sat. $NaHCO_3$ solution and extracted with EtOAc (2 x 200 ml). The combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by flash column chromatography (1:3→1:0 EtOAc/Heptane) to yield the desired product S4 (2.49 g, 4.60 mmol, 97 %) as a colorless syrup. NMR data of the compound S4 were consistent with the previously reported.[6]

2,3,4,6-Tetra-*O*-benzyl-D-galactopyranosyl trichloroacetimidate (2)



NaH (12.4 mg 60 % in mineral oil, 0.31 mmol) and trichloroacetonitrile (0.7 mL, 6.47 mmol) was added to a stirred solution of S4 (699.8 mg, 1.29 mmol) in dry DCM (7 ml). The solution was stirred at RT for 1.5 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:9→1:8 EtOAc/Heptane + 0.5 % Et_3N) to yield two anomers (α/β 1:1.6) of the desired product 2 (599.1 mg, 0.87 mmol, 68 %) as a colorless syrup. NMR data of the compound 2 were consistent with the previously reported.[7,8]

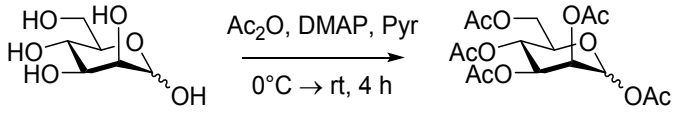
2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl trichloroacetimidate (2)



NaH (18.9 mg, 0.47 mmol, 60 % in mineral oil) was added to a stirring solution of 2,3,4,6-tetrabenzyl-α/β-D-galactopyranose (S4) (303.6 mg, 0.562 mmol) in DCM. The reaction was stirred at rt for 4 hr and evaporated onto celite. The crude product was purified by flash column chromatography (1:10 EtOAc/heptane to 1:4) to yield the desired product, 2 (66.4 mg, 17 %) as a clear syrup. ^{1}H- and ^{13}C-NMR is in accordance with the literature.[9] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, NH, 1H), 7.45

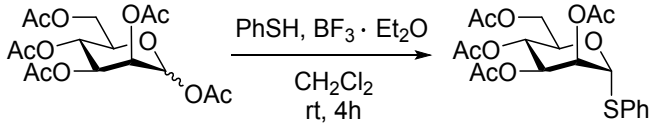
– 7.27 (m, Ar^{Bn}, 20H), 6.53 (d, H-1, *J* = 3.5 Hz, 1H), 4.98 (d, CH_2^{Bn}, *J* = 11.2 Hz, 1H), 4.83 (d, CH_2^{Bn}, *J* = 11.9 Hz, 1H), 4.79 – 4.73 (m, CH_2^{Bn}, 3H), 4.61 (d, CH_2^{Bn}, *J* = 11.3 Hz, 1H), 4.47 (d, CH_2^{Bn}, *J* = 11.7 Hz, 1H), 4.41 (d, CH_2^{Bn}, *J* = 11.8 Hz, 1H), 4.25 (dd, H-2, *J* = 10.0, 3.5 Hz, 1H), 4.17 (ddd, H-5, *J* = 7.2, 5.5, 1.3 Hz, 1H), 4.07 (dd, H-4, *J* = 2.9, 1.3 Hz, 1H), 4.03 (dd, H-3, *J* = 10.0, 2.8 Hz, 1H), 3.62 (dd, H-6a, *J* = 9.3, 7.6 Hz, 1H), 3.56 (dd, H-6b *J* = 9.3, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.41, 138.67, 138.64, 138.55, 137.97, 128.55, 128.45, 128.41, 128.36, 128.29, 128.01, 127.92, 127.77, 127.66, 127.57, 95.33, 91.58, 78.07, 76.03, 75.08, 74.78, 73.59, 73.13, 73.06, 72.31, 68.43. Rf = 0.48 (3:7 EtOAc/heptane)

1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose (S5)



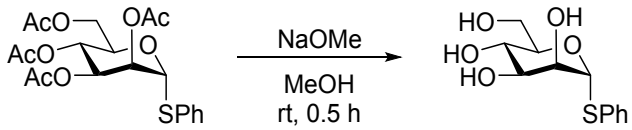
Ac_2O (39.4 ml, 416.3 mmol) was added to a solution of D-mannose (10.00 g, 55.5 mmol) in dry pyridine (60 ml) at 0°C. To the resulting mixture DMAP (0.68 g, 5.55 mmol, 0.10 eq.) was added. The reaction was allowed to warm up slowly to RT and stirred for 4 h. After completion the reaction mixture was diluted with EtOAc (200 ml), washed with 1 M HCl (5 x 200 ml) and brine (1 x 200 ml). The organic layer was dried over Na_2SO_4 and evaporated to dryness to give a mixture of anomers of the desired compound S5 (21.45 g, 54.95 mmol, 99 %) as a colorless syrup. NMR data of the compound S5 were consistent with the previously reported.[10]

Phenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-*α*-D-mannopyranoside (S6)



PhSH (8.6 ml, 83.3 mmol) was added to a solution of S5 (21.67 g, 55.5 mmol) in dry DCM (100 ml), followed by $BF_3{\cdot}Et_2O$ (21 ml, 167 mmol). The resulting solution was stirred at RT for 4 h. After this time the reaction mixture was washed with sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4 and condensed *in vacuo*. The residue was crystallized from EtOH to afford the desired product S6 (17.08 g, 38.8 mmol, 70 %) as a colorless crystalline solid. NMR data of the compound S6 were consistent with the previously reported.[11]

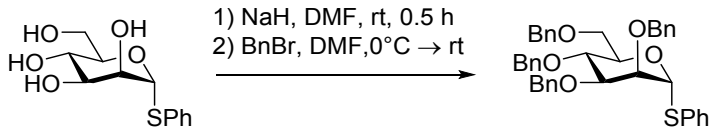
Phenyl 1-thio-*α*-D-mannopyranoside (S7)



A 25% solution of NaOMe in MeOH (5.55 ml, 24.27 mmol) was added dropwise to a solution of S6 (15 g, 34.06 mmol, 1 eq.) in dry MeOH (100 ml). The reaction mixture was stirred at RT for 0.5 h. After completion the solution was neutralized with Amberlite resin IRA-120 (H^+). The filtration and

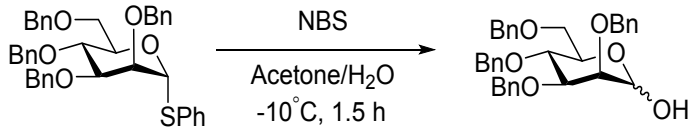
evaporation of solvent afforded the crude product S7 as a white solid which was used in the next step without further purification.[11]

Phenyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-*α*-D-mannopyranoside (S8)



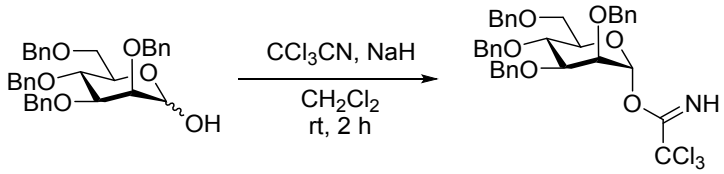
NaH (6.67 g 60 % in mineral oil, 166.8 mmol) was added to a stirred solution of S7 (9.06 g, 33.3 mmol) in dry DMF (100 ml). The resulting suspension was stirred at RT for 0.5 h. Then the mixture was cooled down to 0°C and treated with BnBr (19.8 ml, 166.3 mmol). The suspension was allowed to warm up to RT and stirred overnight. After completion the reaction was quenched with MeOH (20 ml) at 0°C. The solution was diluted with H_2O (500 ml) and extracted with Et_2O (3 x 300 ml). The combined organic layers were dried over Na_2SO_4, and condensed *in vacuo*. The residue was purified by flash column chromatography (1:8→1:4 EtOAc/Heptane) to yield the desired product S8 (16.42 g, 25.95 mmol, 78%) as a colorless syrup. NMR data of the compound S8 were consistent with the previously reported.[11]

2,3,4,6-Tetra-*O*-benzyl-D-mannopyranose (S9)



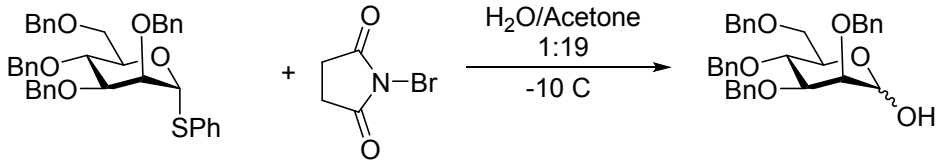
N-Bromosuccinimide (4.22 g, 23.7 mmol) was added in the dark to a stirred solution of S8 (5.00 g, 7.90 mmol) in a mixture of acetone and water (19:1, 200 ml) at -10°C. The solution was stirred at this temperature for 1.5 h. After completion the reaction mixture was diluted with sat. $NaHCO_3$ solution and extracted with EtOAc (3 x 200 ml). The combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by flash column chromatography (1:2→1:0 EtOAc/Heptane) to yield the desired product S5 (3.67 g, 6.79 mmol, 86 %) as a colorless syrup. NMR data of the compound S9 were consistent with the previously reported.[11]

2,3,4,6-Tetra-*O*-benzyl-D-mannopyranosyl trichloroacetimidate (3)



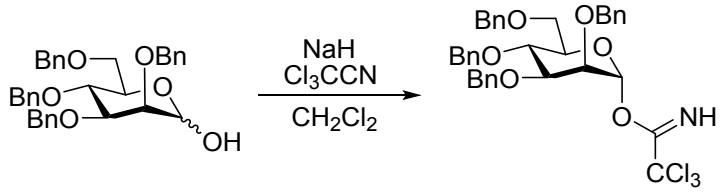
NaH (64.6 mg 60 % in mineral oil, 1.62 mmol) and trichloroacetonitrile (3.4 mL, 33.7 mmol) was added to a stirred solution of S9 (3.64 g, 6.73 mmol) in dry DCM (15 ml). The solution was stirred at RT for 2 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:9→1:8 EtOAc/Heptane + 0.5 % Et_3N) to afford the major anomer (*α*) of the

desired product 7 (2.52 g, 3.68 mmol, 55 %) as a colorless syrup. NMR data of the compound 3 were consistent with the previously reported.[12]



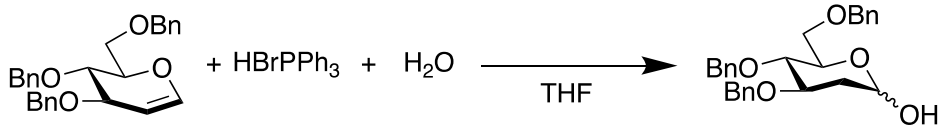
2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose (S9)

NBS (1.45 g, 8.15 mmol) was added to a stirring solution of S8 (3.40 g, 5.37 mmol) in acetone/water 19:1 (50 mL) at -10 °C cooled in a salt/ice-bath. The reaction was stirred for 25 minutes, until a further 0.46 g NBS was added. The reaction was stirred for 2.5 hours until water (50 mL) was added. The aq. phase was extracted with Et_2O (2 x 50 mL). The combined organic phases were washed with water (2 x 50 mL) and brine (1 x 50 mL) and dried over $MgSO_4$. The crude was evaporated *in vacuo* and purified by flash column chromatography, yielding the desired product, S9, as a clear syrup (1.92 g, 66 %). NMR data was in accordance with the literature.[13] Rf = 0.26 (3:7 EtOAc/Heptane)



2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl trichloroacetimidate (3)

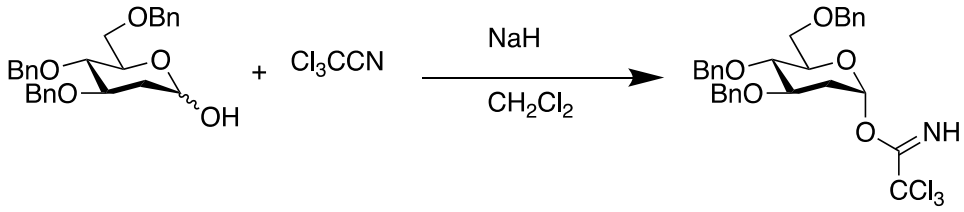
NaH (8.0 mg, 0.20 mmol, 60 % in mineral oil) was added to a stirring solution of (449 mg, 0.831 mmol) in DCM. The reaction was stirred at rt for 1.75 hr and evaporated onto celite. The crude product was purified by flash column chromatography (1:10 EtOAc/heptane to 1:4) to yield the desired product, 3 (288 mg, 51 %) as a clear syrup. ^{1}H- and ^{13}C-NMR is in accordance with the literature.[14]



2-Deoxy-2,3,5-tri-*O*-benzyl-D-glucopyranose (S10)

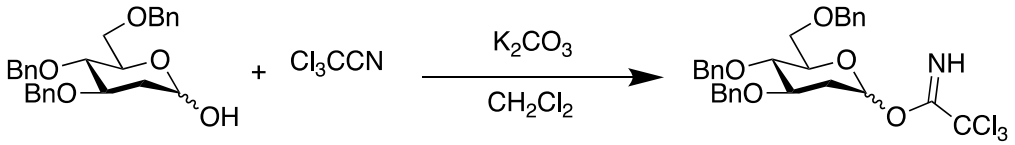
Prepared following an experimental procedure from the literature.[3] $HBr{\cdot}PPh_3$ was added to a solution of 3,4,6-tri-*O*-benzyl-D-glucal (504 mg, 1.21 mmol) in 4.5 mL of THF at r.t. under a nitrogen atmosphere. After stirring for 10 minutes, water (0.55 μL) was added and the solution was stirred until completion. The reaction was quenched with a saturated solution of $NaHCO_3$ (4 mL) and water (1 mL) and extracted with EtOAc (15 mL). The organic phase was washed with brine (10 mL), dried over $MgSO_4$ and evaporated to dryness to yield a slightly pink, white solid as a mixture of anomers (3:1 α/β). The crude product was used without any further purification in the synthesis of 4. ^{1}H NMR

(500 MHz, Chloroform-*d*) δ = 7.37-7.24 (m, Ph, 26H), 7.20-7.16 (m, Ph, 4H), 5.42 (s, br, H-1α, 1H), 4.90 (d, CH_2^{Bn}α, *J*=10.9 Hz, 1H), 4.89 (d, CH_2^{Bn}β, *J*=10.8 Hz, 1H), 4.79 (ddd, H-1β, $J_{1,2a}$=1.8 Hz, $J_{1,OH}$=6.2Hz, $J_{1,2b}$=8.6Hz, 1H), 4.70-4.50 (m, CH_2^{Bn}α/β, 8H), 4.08-4.00 (m, H-3α, H-5α, 2H), 3.75-3.63 (m, H-3β, H-6β, H-6α, 3H), 3.52 (t, H-4α, *J*=9.3 Hz, 1H), 3.48 (m, H-4β, H-5β, 2H), 3.10 (d, -OHβ, 1H), 2.55 (t, -OHα, $J_{1,OH}$=2.5Hz, 1H), 2.40 (ddd, H-2aβ, *J*=12.5 Hz, *J*=5.0 Hz, 1H), 2.30 (ddd, H-2aα, *J*=13.1 Hz, *J*=5.0 Hz, 1H), 1.70 (m, H-2bα, 1H), 1.60 (m, H-2bβ, 1H) ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 138.76 (iPhα), 138.60 (iPhα), 138.39 (iPhβ), 138.37 (iPhβ), 138.17 (iPhα), 138.13 (iPhβ) 128.7-127.7 (Ph), 94.31 (C1β), 92.37 (C1α), 79.30 (C3β), 78.70 (C4α), 77.90 (C5β), 75.16 (C4β), 75.08 (Bn α and β), 73.70 (Bnβ), 73.65 (Bnα), 71.97 (Bnα), 71.67 (Bnβ) 71.06 (C5α), 69.43 (C6α) 69.38 (C6β), 38.13 (C2β), 35.61 (C2α) Rf = 0.14 (EtOAc/heptane 1:4)



2-Deoxy-2,3,5-tri-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate[1] (4)

NaH (3 mg, 60 % in mineral oil, 0.1 mmol) was added to a stirred solution of S10 (100 mg, 0.23 mmol) and trichloroacetonitrile (0.23 mL, 2.3 mmol) in DCM (1 mL) at r.t. under a nitrogen atmosphere. The solution was stirred for 0.5 h and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography with 0.5 vol% triethylamine in the eluent (1:5 ethyl acetate/heptane) to yield the desired product, 4, (105 mg, 0.18 mmol, 79%). ^{1}H NMR (500 MHz, C_6D_6) δ = 8.45 (s, NH, 1H), 6.49 (m, H-1, 1H), 5.02 (d, CH_2^{Bn}, *J*=11.1 Hz, 1H), 4.70 (d, CH_2^{Bn}, *J*=11.2 Hz, 1H), 4.46 (d, CH_2^{Bn}, *J*=12.1 Hz, 1H), 4.43 (s, CH_2^{Bn}, 1H), 4.35 (d, CH_2^{Bn}, *J*=12.1 Hz, 1H), 4.19 (ddd, H-5, $J_{5\text{-}6b}$=1.7 Hz, $J_{5\text{-}6a}$=3.2 Hz, $J_{5\text{-}4}$=10.0 Hz, 1H), 4.12 (ddd, H-3, *J*=4.9 Hz, *J*=9.0 Hz, *J*=11.4 Hz, 1H), 3.89 (t, H-4, *J*=9.5 Hz, 1H) 3.81 (dd, H-6a, $J_{6a\text{-}5}$=3.5 Hz, *J*=10.9 Hz, 1H), 3.66 (dd, H-6b, $J_{6a\text{-}5}$=1.7 Hz, *J*=10.9 Hz, 1H), 2.22 (ddd, H-2a, $J_{a,1}$=1.5 Hz, $J_{a,3}$=5.0 Hz, *J*=13.7 Hz, 1H), 1.59 (ddd, H-2b, $J_{a,1}$=3.4 Hz, $J_{a,3}$=11.5 Hz, *J*=13.8 Hz, 1H) ^{13}C NMR (126 MHz, C_6D_6) δ 169.89, 160.98, 139.23, 138.93, 138.90, 128.10, 127.90, 127.71, 96.33, 78.73, 77.47, 76.45, 74.60, 73.33, 71.17, 69.08, 59.92, 32.11, 29.30, 22.94, 14.20.

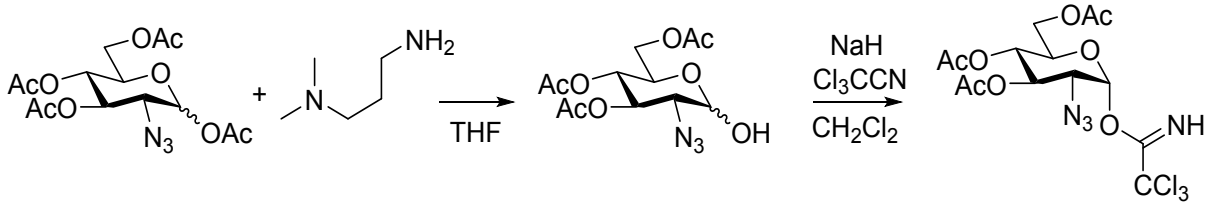


2-Deoxy-2,3,5-tri-*O*-benzyl-D-glucopyranosyl trichloroacetimidate[2] (4)

[1] This compound was used in glycosylations without any further characterization due to the very low stability of the compound. Examples of similar application of 2-deoxy TCA donors is also found in earlier publications in the literature.[30,31]

K_2CO_3 (256 mg, 1.85 mmol) was added to a stirred solution of S10 (110 mg, 0.253 mmol) and trichloroacetonitrile (0.25 mL, 2.5 mmol) and DCM (2 mL) at r.t. under a nitrogen atmosphere. The heterogeneous solution was stirred for 5 h and washed with aq. NaOH (1M) (2x10 mL) before being evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography with 0.5 vol% triethylamine in the eluent (1:5 ethyl acetate/heptane) to yield the desired product, 4, (50 mg, 0.086 mmol, 34 %) as a mixture of anomers (α/β 1:5) containing a small amount of heptane residue. ^{1}H NMR (500 MHz, C_6D_6) δ = 8.53 (s, NHβ, 1H), 8.44 (s, NHα, 1H), 7.28-7.06 (m, Phα/β, 40H), 6.48 (m, H-1α, 1H), 5.87 (dd, H-1β, $J_{1,2a}$=2.4 Hz, $J_{1,2b}$=9.5 Hz, 1H), 4.98 (d, $CH_2^{Bn}\alpha$, *J*=11.2 Hz, 1H) , 4.86 (d, $CH_2^{Bn}\beta$, *J*=11.4 Hz, 1H), 4.68 (d, $CH_2^{Bn}\alpha$, *J*=11.2 Hz, 1H), 4.57 (d, $CH_2^{Bn}\beta$, *J*=11.4 Hz, 1H), 4.45-4.28 (m, $CH_2^{Bn}\alpha/\beta$, 8H) 4.18 (ddd, H-5α, J_{5-6b}=1.7 Hz, J_{5-6a}=3.2 Hz, J_{5-4}=9.8 Hz, 1H), 4.11 (ddd, H-3α, *J*=4.9 Hz, *J*=9.0 Hz, *J*=11.4 Hz, 1H), 3.79 (dd, H-6aα, J_{6a-5}=3.5 Hz, *J*=10.9 Hz, 1H) 3.70 (m, H-4β, H-6aβ, H-6bβ, 3H), 3.64 (dd, H-6bα, J_{6a-5}=1.7 Hz, *J*=10.9 Hz, 1H) 3.48 (ddd, H-5β, *J*=2.6 Hz, *J*=3.8 Hz, *J*=9.3 Hz, 1H) 3.44 (ddd, H-3β, *J*=5.1 Hz, *J*=8.4 Hz, *J*=11.1 Hz, 1H), 2.25 (ddd, H-2aβ, $J_{a,1}$=2.4 Hz, $J_{a,3}$=5.0 Hz, *J*=12.4 Hz, 1H), 2.21 (m, H-2aα, 1H) 1.86 (ddd, H-2bβ, $J_{b,1}$=9.5 Hz, $J_{b,3}$=11.1 Hz, *J*=12.3 Hz, 1H), 1.57 (m, H-2bα, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.60, 139.21, 138.97, 138.91, 97.03, 96.85, 78.14, 77.96, 76.89, 76.70, 74.77, 74.60, 73.42, 73.34, 71.64, 68.95, 34.09.

3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α/β-D-glucopyranosyl trichloroacetimidate (5)

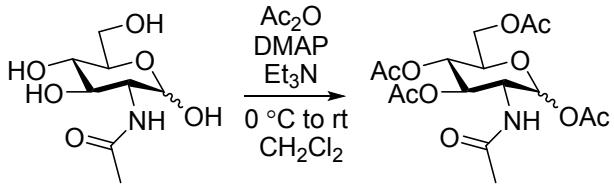


DMAPA (0.84 mL, 6.7 mmol) was added to a solution of 1,3,4,5-tetraacetyl-2-azido-2-deoxy-α/β-d-glucopyranose (500 mg, 1.34 mmol) in dry THF at rt. The reaction was stirred for 1.75 hr and EtOAc (20 mL) was added before the organic phase was extracted with 1M aq. HCl (2 x 20 mL) and washed with brine (20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was used directly in the next step of the synthesis without further purification or characterization. The crude product was dissolved in DCM and added trichloroacetonitrile (0.70 mL, 7.0 mmol) and NaH (31 mg, 0.78 mmol, 60 % in mineral oil). The reaction was stirred at rt for 0.85 hr and evaporated onto celite. The crude product was purified by flash column chromatography (1:10 EtOAc/heptane to 1:3) yielding the desired product, 5 (239 mg, 38 % over two steps), as a colorless syrup containing a small impurity of an unidentified supposedly aromatic compound. ^{1}H- and ^{13}C-NMR is in accordance with the literature.[15] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.83 (s, NH, 1H), 6.49 (d, H-1, *J* = 3.6 Hz, 1H), 5.52 (dd, H-3, *J* = 10.5, 9.3 Hz, 1H), 5.15 (dd, H-4, *J* = 10.3, 9.3 Hz, 1H), 4.27 (dd, H-6a, *J* = 12.4, 4.3 Hz, 1H), 4.21 (ddd, H-5, *J* = 10.4, 4.3, 2.1 Hz, 1H), 4.10 (dd, H-6b, *J* =

[2] This compound was used in glycosylations without any further characterization due to the very low stability of the compound. Examples of similar application of 2-deoxy TCA donors is also found in earlier publications in the literature.[30,31]

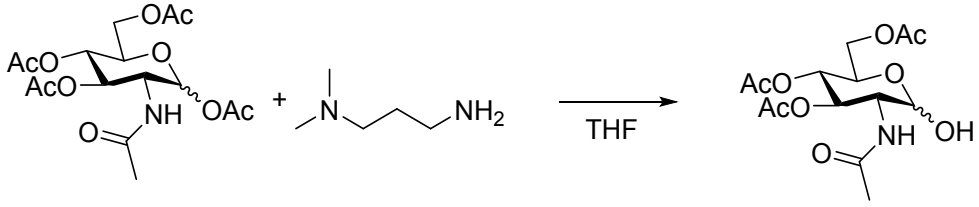
12.4, 2.2 Hz, 1H), 3.77 (dd, H-2 *J* = 10.6, 3.6 Hz, 1H), 2.11 (s, CH_3^{OAc}, 3H), 2.06 (s, CH_3^{OAc}, 3H), 2.06 (s, CH_3^{OAc}, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.50 ($C{=}O^{Ac}$), 169.84 ($C{=}O^{Ac}$), 169.66 ($C{=}O^{Ac}$), 160.56 ($C{=}O^{imidate}$), 94.03 (C-1), 90.53 (CCl_3), 70.68 (C-3), 70.12 (C-5), 67.94 (C-4), 61.40 (C-6), 60.66 (C-2), 20.69 (CH_3^{Ac}), 20.66 (CH_3^{Ac}), 20.59 (CH_3^{Ac}). Rf = 0.61 (1:1 EtOAc/heptane)

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α/β-D-glucopyranose (S11)



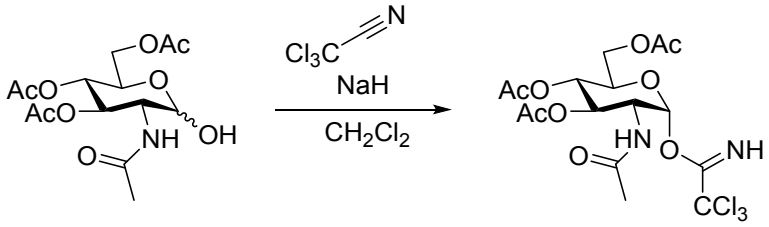
Triethylamine (11.4 mL, 81.8 mmol) was added dropwise at 0 °C over 45 minutes to a stirring solution of 2-acetamido-2-deoxy-D-glucose (2.90 g, 13.6 mmol), DMAP (193 mg, 1.58 mmol) and acetic anhydride (6.4 mL, 67.7 mmol). The reaction was allowed to reach rt after 1 hr. After 3 hr, the reaction was quenched by adding small portions of ice until no further heat development was observed. The reaction was added water (20 mL) and extracted with EtOAc (2 x 20 mL). The combined organic phase was washed with brine (2 x 20 mL) and evaporated *in vacuo*, yielding the desired product S11 as a slightly orange solid (mixture of anomers, α/β 89:11, 4.91 g, 96 %). The crude product was used in the next step without further purification. NMR data was in accordance with reference spectra from the literature.[16,17] Rf = 0.47 (100 % EtOAc)

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α/β-D-glucopyranose (S12)



DMAPA (3.3 mL, 26.2 mmol) was added to a stirring solution of S11 in THF (25 mL). The reaction was stirred for 1 hr and extracted with EtOAc (2 x 50 mL). The combined organic phase was dried over $MgSO_4$ and evaporated *in vacuo* to yield the desired product S12 as an orange, amorphous solid (1.01 g, 57 %). NMR data was in accordance with the literature,[18] albeit a small impurity from acetic acid and acetone was present from the NMR. Rf = 0.34 (100 % EtOAc)

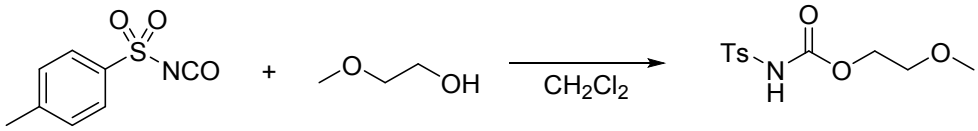
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (6)



NaH (49.9 mg, 1.25 mmol, 60 % dispersion in mineral oil) was added to a stirring solution of S12 and Cl_3CCN (2.0 mL, 20 mmol) in CH_2Cl_2. The reaction was stirred for 4 hours until no starting material was left. The reaction mixture was evaporated onto celite and purified by flash column chromatography (1:5 EtOAc/heptane to 100 % EtOAc), yielding the desired product, 6, as a clear syrup (1.02 g, 71 %). NMR data was in accordance with the literature.[19] Rf = 0.74 (100 % EtOAc)

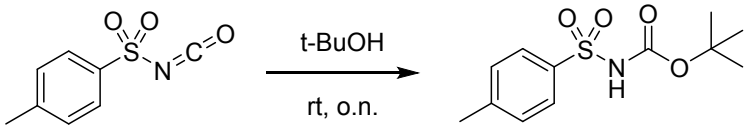
Synthesis of carbamates

2-methoxyethyl *N*-(4-nitrophenylsulfonyl)carbamate (7)



Tosyl isocyanate (10 g, 50.7 mmol, 7.7 mL) was added slowly to a flask, in an ice bath, containing freshly distilled 2-methoxyethanol (20 mL). The reaction mixture was allowed to reach rt and stirred for 3 h. After concentration in vacuo, the solid obtained was crystallized from CH_2Cl_2 and PE resulting in 12.59 g of a white crystalline solid (91%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.99 (s, NH, 1H), 7.78 (d, Ar^{Ts}, J = 8.4 Hz, 1H), 7.43 (d, Ar^{Ts}, J = 7.8 Hz, 1H), 4.21 – 3.88 (m, CH_2, 2H), 3.57 – 3.37 (m, CH_2, 2H), 3.20 (s, CH_3^{OMe}, 3H), 2.40 (s, CH_3^{Ts}, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.12 (C=O), 144.21 (*i*Ar), 136.35 (*i*Ar), 129.59 (Ar), 127.48 (Ar), 69.45 (CH_2), 64.80 (CH_2), 57.94 (CH_3^{OMe}), 21.06 (CH_3^{Ts}). HRMS (MALDI+): Calculated for $C_{11}H_{15}NO_5SNa^+$ m/z 296.05631; found m/z 296.05361.

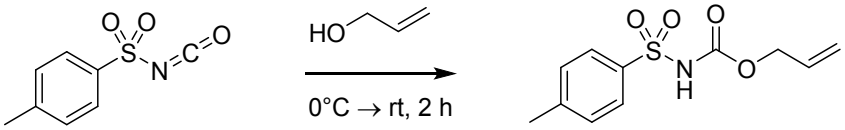
Tert-butyl *N*-(4-methylbenzenesulfonyl)carbamate (8)



t-BuOH (9.6 ml, 101.42 mmol) was stirred at rt. Then p-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. The resulting solution was let to warm up to RT and stirred overnight. After completion an excess of alcohol was removed *in vacuo*. The crude product was purified by crystallization from a mixture Cyclohexane/EtOAc (4:1) to afford the desired product 8 (2.41 g, 8.86 mmol, 87%) as a white crystalline solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.87 (m, Ar, 2H) 7.36-7.31 (m, Ar, 2H), 7.29 (s, *N*H, 1H), 2.45 (s, CH_3^{Ts}, 3H), 1.38 (s, CH_3^{Boc}, 9H) ppm. ^{13}C NMR (126

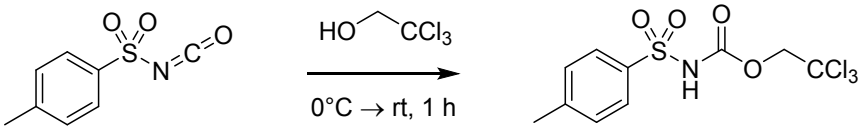
MHz, Chloroform-*d*) δ 149.17 (C=O), 144.90 (iC^{Ts}), 136.08 (iC^{Ts}), 129.65 (*m*-CH, 2C), 128.38 (*o*-CH, 2C), 84.22 (CH^{Boc}), 28.01 (CH_3^{Boc}, 3C), 21.81 (CH_3^{Ts}) ppm. HRMS (MALDI+): Calculated for $C_{12}H_{17}NO_4SNa^+$ m/z 294.0776; found m/z 294.07698. NMR data of the compound 8 were consistent with the previously reported.[20]

Allyl *N*-(4-methylbenzenesulfonyl)carbamate (9)



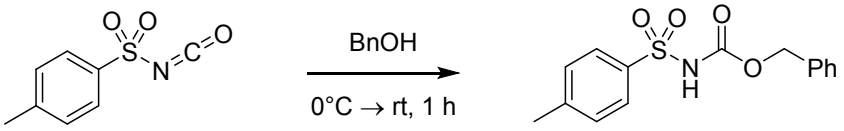
Allyl alcohol (3.4 ml, 50.71 mmol) was cooled down in an ice bath. Then p-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. The resulting solution was let to warm up to RT and stirred for 2h. After completion an excess of alcohol was removed *in vacuo*. The crude product was purified by flash column chromatography with the eluent Petroleum ether/ EtOAc (3:2) to afford the desired product 9 (2.59 g, 10.13 mmol, 99 %) as a white crystalline solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, Ar, *J*= 8.4 Hz, 2H), 7.54 (s, *N*H, 1H), 7.34 (d, Ar, *J*= 8.4 Hz, 2H), 5.86-5.77 (m, CH, 1H), 5.27 (ddt, $=CH_2^{trans}$, *J*= 1.4, *J*= 17.2, ^4J= 1.4 Hz, 1H), 5.23 (ddt, $=CH_2^{cis}$, *J*= 1.4, *J*= 10.5, ^4J= 1.4 Hz, 1H), 4.58-4.55 (m, CH_2, 2H), 2.45 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.23 (C=O), 145.31 (iC^{Ts}), 135.55 (iC^{Ts}), 130.97 (CH), 129.77 (*m*-CH, 2C), 128.57 (*o*-CH, 2C), 119.62 ($=CH_2$), 67.52 (CH_2^{Alloc}), 21.83 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{11}H_{13}NO_4SNa^+$ m/z 278.0463; found m/z 278.0457. NMR data of the compound 9 were consistent with the previously reported.[21]

2,2,2-Trichloroethyl *N*-(4-methylbenzenesulfonyl)carbamate (10)



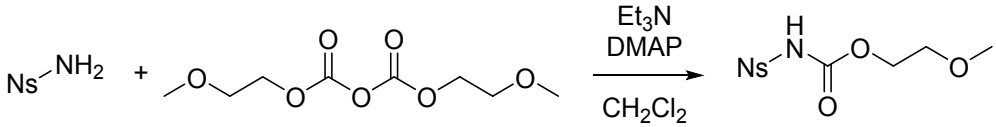
Trichloroethyl alcohol (4.9 ml, 50.71 mmol) was cooled down in an ice bath. Then p-Toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. The resulting solution was let to warm up to RT and stirred for 1 h. After completion an excess of alcohol was removed *in vacuo*. The crude product was purified by crystallization from a mixture Cyclohexane/EtOAc (20:1) to afford the desired product 10 (3.06 g, 8.81 mmol, 87 %) as a white crystalline solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98-7.93 (m, Ar, 2H), 7.64 (s, *N*H, 1H), 7.38-7.34 (m, Ar, 2H), 4.69 (s, CH_2, 2H), 2.45 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.87 (C=O), 145.61 (iC^{Ts}), 134.93 (iC^{Ts}), 129.76 (*m*-CH, 2C), 128.53 (*o*-CH, 2C), 93.95 (CCl_3), 75.25(CH_2), 21.73 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{10}H_{10}Cl_3NO_4SNa^+$ m/z 367.9294; found m/z 367.9287. NMR data of the compound 10 were consistent with the previously reported.[22]

Benzyl *N*-(4-methylbenzenesulfonyl)carbamate (11)



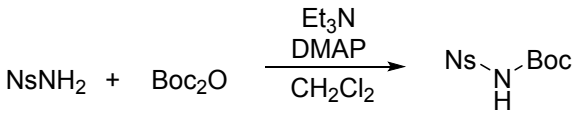
Benzyl alcohol (1.1 ml, 10.7 mmol) was cooled down in an ice bath. Then p-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. The resulting solution was let to warm up to RT and stirred for 1 h. After completion a crystallization was induced at -20°C from a mixture cyclohexane/ DCM (15:1) to afford the desired product 11 (2.94 g, 9.63 mmol, 95 %) as a white crystalline solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91-7.86 (m, Ar^{Ts}, 2H), 7.58 (s, *N*H, 1H), 7.35-7.31 (m, Ar^{Bn}, 3H), 7.31-7.27 (m, Ar^{Ts}, 2H), 7.26-7.22 (m, Ar^{Bn}, 2H), 5.09 (s, CH_2, 2H), 2.44 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.29 (C=O), 145.28 (iC^{Ts}), 135.52 (iC^{Ts}), 134.49 (iC^{Ph}), 129.76, 128.92, 128.80, 128.62, 128.56 (Ar), 68.80 (CH_2), 21.83 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{15}H_{15}NO_4SNa^+$ m/z 328.0620; found m/z 328.0614. NMR data of the compound 11 were consistent with the previously reported.[23]

2-methoxyethyl (4-nitrophenylsulfonyl)carbamate (12)



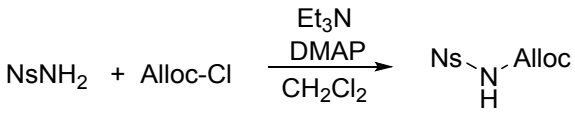
NaH (1.83 g, 60% in mineral oil, 76 mmol) was slowly added to a mixture 2-methoxyethanol (5 mL, 63 mmol) and dry DMF (35 mL) and stirred 1.5 h. CO_2, dried through a pad of dry $CaCl_2$ was bubbled through the resulting heterogeneous solution for 4 h whilst cooled by a water bath at ambient temperature. Methanesulfonyl chloride (2.5 mL) was added and the reaction was stirred at RT overnight. 25 mL was added and the crude product was extracted with Et_2O (2 x 50 mL) and washed with water (2 x 25 mL). The combined organic fractions were dried with $MgSO_4$ and evaporated *in vacuo* to yield a yellow oil (ca. 2.3 g). This solution was slowly added to a stirred solution of 4-nitrophenylsulfonyl amide (290 mg, 1.4 mmol), triethylamine (0.2 mL, 1.43 mmol) and DMAP (10 mg, 0.14 mmol) in dry DCM (2 mL). A development of gas was observed upon addition of the yellow oil. The reaction was stirred overnight until no starting material was left and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography with 5 % acetic acid in the eluent (1:1 EtOAc/Heptane) to yield the desired product, 12, as off-white crystals (422 mg, 97 %). ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.42 (d, Ar^{Ns}, *J*=9 Hz, 2H), 8.24 (d, Ar^{Ns}, *J*=9 Hz, 2H), 4.17 (m, CH_2, 2H), 3.52 (m, CH_2, 2H), 3.29 (s, CH_3, 3H). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.44 (d, Ar^{Ns}, *J* = 8.8 Hz, 2H), 8.14 (d, Ar^{Ns}, *J* = 8.8 Hz, 2H), 4.11 – 4.08 (m, CH_2, 2H), 3.48 – 3.39 (m, CH_2, 2H), 3.19 (s, CH_3, 3H). ^{13}C NMR (126 MHz, DMSO) δ 150.13 (*i*Ns), 144.72 (*i*Ns), 129.08 (Ns), 124.47 (Ns), 69.39 (CH_2), 65.00 (CH_2), 57.90 (CH_3). IR (neat): 3123, 3021, 2965, 2798, 1756. HRMS (MALDI+): Calculated for $C_{10}H_{12}N_2O_7SNa^+$ m/z 327.0257; found m/z 327.0256.

Tert-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (13)



Triethylamine (0.5 mL, 3.6 mmol) was added dropwise over 15 minutes to a stirring solution of 4-nitrophenylsulfonamide (481 mg, 2.38 mmol), Boc anhydride (930 mg, 4.26 mmol) and DMAP (36 mg, 0.29 mmol) at rt. The reaction was stirred for 30 minutes and extracted with 1M aq. HCl (2 x 20 mL) and dried over $MgSO_4$. The crude was evaporated *in vacuo* to yield the desired product, 13, as a white solid (611 mg, 81 %). ^{1}H-NMR is in accordance with the literature.[24] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.40 (d, Ar, *J* = 8.9 Hz, 2H), 8.24 (d, Ar, *J* = 8.8 Hz, 2H), 7.44 (s, NH, 1H), 1.41 (s, 3 x CH3, 9H). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, NH, 1H), 8.47 (d, Ar, *J* = 8.9 Hz, 2H), 8.14 (d, Ar, *J* = 8.9 Hz, 2H), 1.32 (s, 3 x CH_3, 9H). Mp = 126-128 °C HRMS (MALDI+): Calculated for $C_{11}H_{14}N_2O_6SNa^+$ m/z 325.0465; found m/z 325.0469.

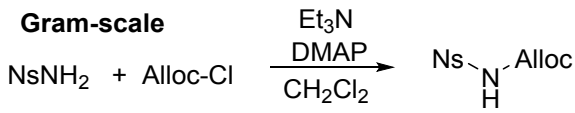
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate (14)



Triethylamine (1.05 mL, 7.5 mmol) was added dropwise over 15 minutes to a stirring solution of allyl chloroformate (0.8 mL, 7.5 mmol), DMAP (54 mg, 0.44 mmol) and 4-nitrophenylsulfonamide (996 mg, 4.93 mmol) in DCM (10 mL). The reaction was stirred for 3.5 hr and extracted with 1M aq. HCl (20 mL). The organic phase was evaporated onto celite and purified by flash column chromatography (1:9 EtOAc/toluene + 2 % formic acid), yielding the desired product 14 as a white solid (944 mg, 67 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 8.15 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 5.82 (ddt, CH^{Allyl}, *J* = 17.3, 10.7, 5.5 Hz, 1H), 5.24 (dq, $CH_2{}^{Allyl}$a, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, $CH_2{}^{Allyl}$b, *J* = 10.4, 1.4 Hz, 1H), 4.51 (dt, OCH_2, *J* = 5.5, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.89, 150.32, 144.37, 131.86, 129.15, 124.63, 118.57, 66.41, 39.52. Mp = 108-118 °C HRMS (MALDI+): Calculated for $C_{10}H_{10}N_2O_6SNa^+$ m/z 309.0152; found m/z 309.0155. Rf = 0.41 (1:9 EtOAc/toluene + 2 % formic acid)

Allyl *N*-(4-nitrophenyl)sulfonylcarbamate (14)

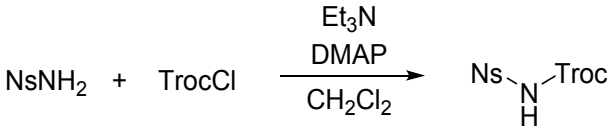
Gram-scale



Triethylamine (11.0 mL, 78.9 mmol) was added dropwise over 30 minutes to a stirring solution of allyl chloroformate (9.5 mL, 74 mmol), DMAP (622 mg, 5.09 mmol) and 4-nitrophenylsulfonamide (9.97 g, 49.3 mmol) in DCM (75 mL) at 0 °C and allowed to reach rt after 1.25 hr. The reaction was stirred over night and extracted with 1M aq. HCl (2 x 100 mL). The organic phase was evaporated *in vacuo* and the crude product was dissolved in hot EtOAc. Heptane was then added to the solution until a cloudy precipitate started forming and the flask was left at 5 °C over night, allowing the

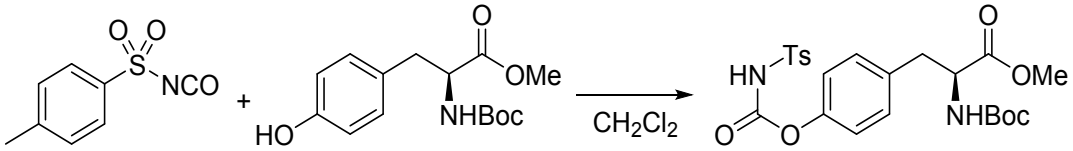
desired product 14 to be filtered off as a white solid (10.04 g, 71 %). The NMR spectrum is in accordance with a spectrum previously reported in this SI for an identical compound.

2,2,2-Trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbamate (15)

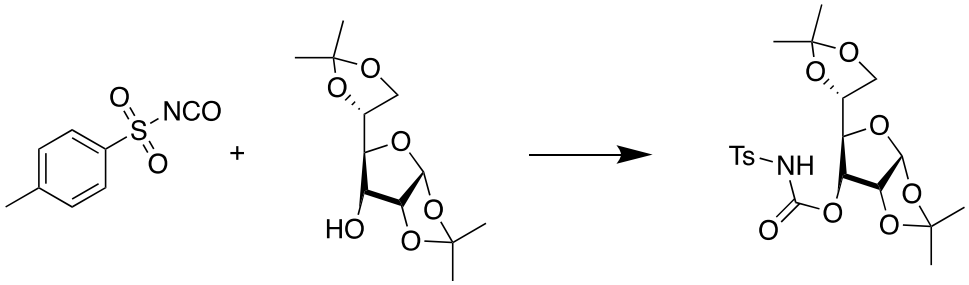


Triethylamine (0.3 mL, 2.15 mmol) was added dropwise over 15 minutes to a stirring solution of DMAP (12.3 mg, 0.10 mmol), 2,2,2-trichloroethyl chloroformate (0.25 mL, 1.88 mmol) and 4-nitrophenylsulfonamide in DCM (20 mL). The reaction was stirred for 30 minutes and added Et_2O (20 mL). The reaction was extracted with 1M aq. HCl (2 x 20 mL) and washed with brine (20 mL). The organic layer was evaporated onto celite and purified by flash column chromatography (1:20 EtOAc/toluene + 2 % formic acid to 1:10 EtOAc/toluene + 2 % formic acid), yielding the desired product 15 as a white solid (336.4 mg, 67 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.44 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 8.16 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 4.82 (s, CH_2^{Troc}, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.41 (C=O), 150.25 (*i*Ar^{Ns}), 144.47 (*i*Ar^{Ns}), 129.13 (Ar^{Ns}), 124.58 (Ar^{Ns}), 94.82 (CCl_3), 74.21 (CH_2). Mp = 136-137 °C HRMS (MALDI+): Calculated for $C_9H_7Cl_3N_2O_6SNa^+$ m/z 398.8983; found m/z 398.8986. Rf = 0.58 (1:10 EtOAc/toluene + 2% formic acid)

N'-Tosyl *O*-(*N*-Boc-tyrosine methyl ester) carbamate (16)

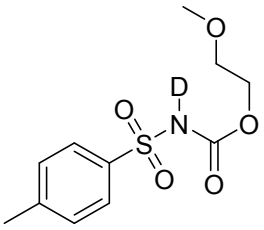


Tosylisocyanate (0.37 mL, 2.54 mmol) was added to a stirring solution of 16 (842.5 mg, 2.85 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction was stirred for 5 hr until no starting material was left. The crude product was evaporated onto celite and purified by flash column chromatography, yielding the desired product 16 (1.021 g, 2.07 mmol, 82 %) as a white solid, containing a tract of EtOAc and a minor, unknown impurity. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, Ar^{Ts}, *J* = 8.4 Hz, 2H), 7.35 (d, Ar^{Ts}, *J* = 8.3 Hz, 2H), 7.09 (d, Ar^{Tyr}, *J* = 8.1 Hz, 2H), 6.97 (d, Ar^{Tyr}, *J* = 8.5 Hz, 1H), 4.96 (d, NH^{Boc}, *J* = 8.3 Hz, 1H), 4.56 (q, C*H*-NH, *J* = 6.6 Hz, 1H), 3.69 (s, OCH_3, 3H), 3.30 – 2.94 (m, CH_2, 2H), 2.45 (s, CH_3^{Tyr}, 2H), 1.41 (s, CH_3^{Boc}, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.13 (C=O^{Boc}), 155.07 (C=$O^{carbamate}$), 148.68 (*i*Ar^{Ts}), 145.42 (*i*Ar^{Ts}), 135.17 (*i*Ar^{Tyr}), 134.40 (*i*Ar^{Tyr}), 130.36 (Ar^{Tyr}), 129.74 (Ar^{Ts}), 128.58 (Ar^{Ts}), 121.21 (Ar^{Tyr}), 80.14 (tert-C^{Boc}), 54.30 (*C*H-NH) 52.33 (OCH_3), 37.67 (CH_2) 28.29 (CH_3^{Boc}), 21.72 (CH_3^{Ts}). HRMS (MALDI+): Calculated for $C_{23}H_{28}N_2O_8SNa^+$ m/z 515.14586; found m/z 515.14586. $[\alpha]_D^{298}$ = +41.4° (c=0.40, $CHCl_3$) Rf = 0.23 (1:1 EtOAc/heptane)



1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl tosylcarbamate (17)

p-Toluenesolfonyl isocyanate (0.84 mL, 5.5 mmol) was added slowly to a stirred solution of 2,3:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1.44 g, 5.5 mmol) in dry DCM (2.5 mL) cooled in an ice bath. The reaction was stirred for four days and purified by flash column chromatography (1:3 EtOAc/Heptane with 2 % formic acid) to yield the desired product, 17, (2.15 g, 85 %) as a clear oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H, Ar), 7.52 (s, 1H, NH), 7.40 – 7.34 (m, 2H, Ar), 5.76 (d, *J* = 3.7 Hz, 1H, H-1), 5.17 (d, *J* = 2.9 Hz, 1H, H-3), 4.42 (d, *J* = 3.7 Hz, 1H, H-2), 4.17 – 4.05 (m, 2H, H-4, Ethyl Acetate), 4.05 – 3.87 (m, 3H, H-5, H-6a, H-6b), 2.46 (s, 3H, Tosyl-CH_3), 1.57 (s, 3H, isopropylidine-CH_3), 1.48 (s, 3H, isopropylidene-CH_3), 1.35 (s, 3H, isopropylidene-CH_3), 1.24 (s, 3H, isopropylidine-CH_3). ^{13}C NMR (126 MHz Chloroform-*d*) δ 149.12 (C-N-O), 145.51, 135.52, 129.85, 128.61 (Ar), 112.67, 109.69 (*C*C_2O_2), 105.06 (C-1), 83.03 (C-2), 79.81 (C-4), 78.72 (C-3), 72.05 (C-5), 67.53 (C-6), 26.96, 26.78, 26.31, 25.22 (isopropylidene-CH_3), 21.85 (Ar-CH_3), 21.21, 14.36. HRMS (MALDI+): Calculated for $C_{20}H_{27}NO_9SNa^+$ m/z 480.1299, found m/z 480.1329. $[\alpha]_D^{298}$ = –29.76 (c=1.0, $CHCl_3$)



2-methoxyethyl deuteriumtosylcarbamate (7-d_1)

A sample containing 7 (100 mg) was dissolved in CD_3OD (0.5 mL) and heated until fully dissolved. The CD_3OD was evaporated under reduced pressure. This cycle was repeated four times and the final product was stored under vacuum. H-NMR data was in accordance with previously reported for the non-deuterated analogue, 7. ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.89 (d, Ar^{Ts}, *J* = 8.4 Hz, 2H), 7.56 (s, NH, 0.5H), 7.37 (d, Ar^{Ts}, *J* = 7.7 Hz, 2H), 4.34 – 3.79 (m, CH_2, 2H), 3.70 – 3.45 (m, CH_2, 2H), 3.29 (s, CH_3^{OMe}, 3H), 2.45 (s, CH_3^{Ts}, 3H).

Glycosylations

General procedure for glycosylations

Procedure 1

Two equivalents of carbamate acceptor were added to a stirred solution of trichloroacetimidate glycosyl donor (100 mg) in dry DCM (2 mL) under a nitrogen atmosphere in flame-dried glassware. The reaction was stirred until no starting material was left. The crude product was extracted with 1M aq. NaOH to remove trichloroacetamide. The products were purified by flash column chromatography and evaporated *in vacuo*.

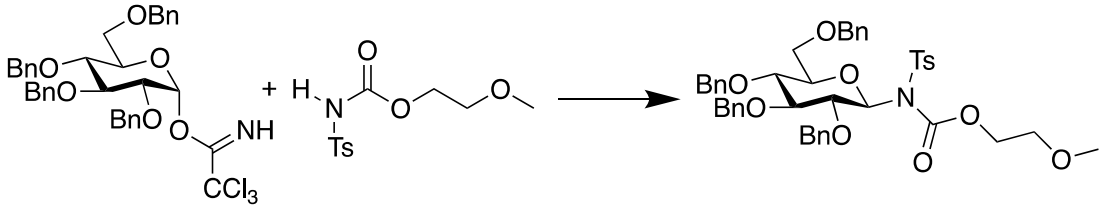
Procedure 2

Two equivalents of carbamate acceptor were added to a stirred solution of trichloroacetimidate glycosyl donor (100 mg) in dry DCM (4 mL) under a nitrogen atmosphere in flame-dried glassware. The reaction was stirred until no starting material was left. The crude product was extracted with 1M aq. NaOH to remove trichloroacetamide. The products were purified by flash column chromatography and evaporated *in vacuo*.

Procedure 3

1. equivalents of carbamate acceptor were added to a stirred solution of trichloroacetimidate glycosyl donor (200 mg) in dry DCM (1,5 mL) under a nitrogen atmosphere in flame-dried glassware. The reaction was stirred until no starting material was left. The crude product was extracted with 1M aq. NaOH to remove trichloroacetamide. The products were purified by flash column chromatography and evaporated *in vacuo*.

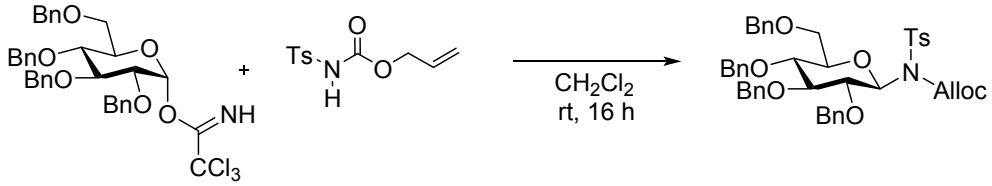
2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl 2-methoxyethyl tosylcarbamate (20)



Following general procedure 1 with 2-methoxyethyl tosylcarbamate 7 (89.5 mg, 0.33 mmol) and 1α (105 mg, 0.15 mmol). All starting material was consumed after stirring overnight. The desired product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired glycoside, 20, as a pale syrup (113 mg, 93 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 2H, Tosyl Ar), 7.38 – 7.26 (m, 18H, Ar), 7.23 – 7.18 (m, 2H, Ar), 7.17 – 7.12 (m, 0H), 7.07 – 7.01 (m, 2H, Tosyl Ar), 5.53 (d, *J* = 9.3 Hz, 1H, H-1β), 4.94 (d, *J* = 11.1 Hz, 1H, Bn-CH_2), 4.88 (d, *J* = 11.1 Hz, 1H, Bn-CH_2), 4.85 (d, *J* = 10.9 Hz, 1H, Bn-CH_2), 4.81 – 4.71 (m, 1H, Bn-CH_2), 4.61 (dt, *J* = 11.1, 6.1 Hz, 2H, Bn-CH_2), 4.55 (dd, *J* = 11.9, 3.1 Hz, 1H, H-2), 4.51 (d, *J* = 12.0 Hz, 2H, Bn-CH_2), 4.15 (dd, *J* = 5.7, 3.8 Hz, 2H, C(O)OCH_2), 3.75 (m, 2H, H-3, H-5, H-6a), 3.65 (m, 2H, H-4 H-6b), 3.41 (dd, *J* = 5.6, 3.8 Hz, 2H,

OCH_2), 3.23 (s, 3H, OCH_3), 2.34 (s, 3H, Tosyl-CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.22 (C=O), 138.56, 138.31, 138.07, 129.11, 128.41, 128.34, 128.28, 128.15, 127.94, 127.79, 127.69, 127.65, 127.57, 127.52 (Ar), 86.64 (C-3), 85.96 (C-1), 77.67 (C-2), 77.19 (C-4, C-5 same as $CDCl_3$), 75.59, 75.06, 73.30 (Ph*C*H_2O), 69.66 (O*C*$H_{2)}$, 68.97 (C-6), 65.97 (C(O)O*C*$H_{2)}$, 58.69 (O*C*$H_{3)}$, 21.60 (Ph*C*H_3). HRMS (MALDI+): Calculated for $C_{45}H_{49}NO_{10}SNa^+$ m/z 818.2969, found m/z 818.2970. $[\alpha]_D^{298}$ = +8.52 (c=1.0, $CHCl_3$)

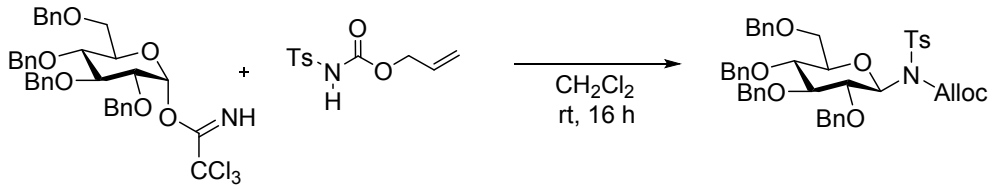
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl allyl *N*-tosylcarbamate (23)



Carbamate 9 (114 mg, 0.45 mmol) was added to a stirred solution of 1α (204 mg, 0.30 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography ((1:7→1:6 EtOAc/Heptane) to yield the *β* anomer of the compound 23 (209 mg, 0.27 mmol, 90 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (broad d, Ar^{Ts}, *J*~ 7.4 Hz, 2H), 7.41-7.16 (m, Ar, 20H), 7.02 (d, Ar^{Ts}, *J* = 7.4 Hz, 2H), 5.71-5.60 (m, =CH, 1H), 5.51 (d, H-1, *J* = 9.3 Hz, 1H), 5.17 (ddt, $=CH_2^{trans}$, *J* = 1.4, *J*= 17.2, ^{4}*J*= 1.4 Hz, 1H), 5.09 (broad ddt, $=CH_2^{cis}$, *J*~ 1.4, *J*~ 10.6, *J*~ 1.4 Hz, 1H), 4.91 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.86 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.83 (d, CH_2^{Bn}, *J* = 11.1 Hz, 1H), 4.78-4.67 (m, CH_2^{Bn}, 2H), 4.58 (d, CH_2^{Bn}, *J* = 11.1 Hz, 2H), 4.54-4.44 (m, H-2, CH_2^{Alloc}, CH_2^{Bn}, 3H), 4.42-4.34 (m, CH_2^{Alloc}, 1H), 3.77-3.66 (m, H-3, H-6, H-6', 3H), 3.68-3.59 (m, H-4, H-5, 2H), 2.31 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.41 (broad C=O), 144.43 (iC^{Ts}), 138.56 (iPh), 138.41 (iPh), 138.20 (iPh), 138.11 (iPh), 136.76 (iC^{Ts}), 130.83 (=CH), 129.27 (CH^{Ts}, 2C), 128.74, 128.57, 128.48, 128.45, 128.34, 128.06, 127.93, 127.81, 127.78, 127.67 (CH^{Ts}, Ar), 119.40 ($=CH_2$), 86.86 (C-3), 86.05 (broad C-1), 77.85, 77.56-76.79 (C-2, C-4, C-5), 75.90 (CH_2^{Bn}), 75.21 (CH_2^{Bn}), 74.69 (CH_2^{Bn}), 73.44 (CH_2^{Bn}), 69.10 (C-6), 67.80 (CH_2^{Alloc}), 21.72 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{45}H_{47}NO_9SNa^+$ m/z 800.2869; found m/z 800.2861. $[\alpha]_D^{298}$=+2.92° (c=0.480, $CHCl_3$).

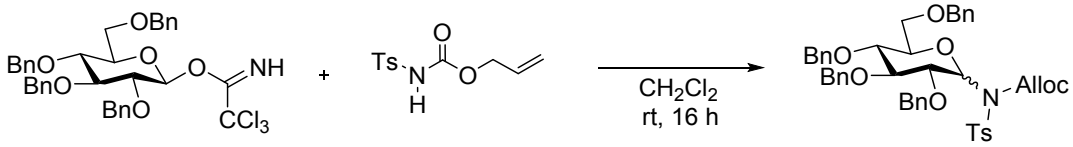
* The obtained compound contains less than 2 % of α anomer; 11 overlapping Ar sygnals with 9 reported in ^{13}C NMR.

2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl allyl *N*-tosylcarbamate (23)



Carbamate 9 (112 mg, 0.439 mmol) was added to a stirred solution of 1α (200 mg, 0.29 mmol) in dry DCM (2.9 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography ((1:7→1:6 EtOAc/Heptane) to yield the *β* anomer of the compound 23 (182 mg, 0.23 mmol, 80 %) as a colorless syrup. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl allyl tosylcarbamate (23)

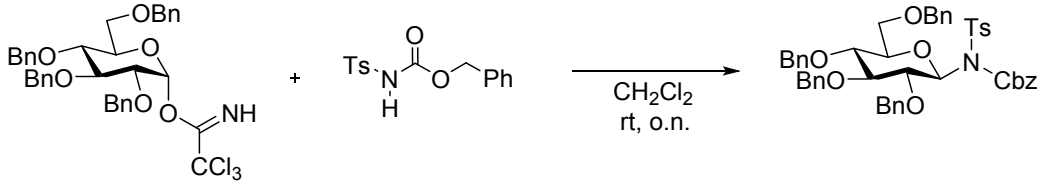


Carbamate 9 (84mg, 0.33 mmol) was added to a stirred solution of 1β (149 mg, 0.22 mmol) in dry DCM (1.1 mL) under a nitrogen atmosphere. The reaction was stirred for 16 h. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the *α*/*β* mixture (1:1.3) of the compound 23 (125.0 mg, 0.16 mmol, 73 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88-7.86 (m, Ar^{Ts}α/β, 4H), 7.37-7.14 (m, Arα/β, 40H), 7.01 (d, Ar^{Ts}β, *J* = 7.5 Hz, 2H), 6.97 (d, Ar^{Ts}α, *J* = 8.1 Hz, 2H), 6.38 (d, H-1, *J* = 8.2 Hz, 1H), 5.69-5.60 (m, =CHβ, 1H), 5.63-5.54 (m, =CHα, 1H), 5.50 (d, H-1, *J* = 9.3 Hz, 1H), 5.19-5.11 (m, $=CH_2^{trans}$α/β, 2H), 5.10-5.05 (m, $=CH_2^{cis}$α/β, 2H), 4.90 (d, CH_2^{Bn}β, *J* = 11.0 Hz, 1H), 4.84 (d, CH_2^{Bn}β, *J* = 11.1 Hz, 1H), 4.83 (d, CH_2^{Bn}α, *J* = 11.1 Hz, 1H), 4.82 (d, CH_2^{Bn}β, *J* = 11.0 Hz, 1H), 4.78 (d, CH_2^{Bn}α, *J* = 11.2 Hz, 1H), 4.76-4.69 (m, CH_2^{Bn}β, 2H), 4.63 (d, CH_2^{Bn}α, *J* = 10.9 Hz, 1H), 4.57 (d, CH_2^{Bn}β, *J* = 11.1 Hz, 2H), 4.55-4.41 (m, H-2β, H-3α, CH_2^{Alloc}α/β, CH_2^{Bn}α/β, 10H), 4.41-4.32 (m, CH_2^{Alloc}α/β, 2H), 4.24 (ddd, H-5α, *J* = 10.1, *J* = 5.0, *J* = 1.7 Hz, 1H), 4.07 (t, H-2α, *J* = 8.2 Hz, 1H), 3.75-3.65 (m, H-3 β, H-6α/β, H-6'β, 4H), 3.66-3.54 (m, H-4α/β, H-5β, H-6'α, 4H), 2.30 (s, CH_3β, 3H), 2.27 (s, CH_3α, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.98 (C=Oα), 151.41 (broad C=Oβ), 144.44 (iC^{Ts}α/β, 2C), 138.98 (iPhα), 138.60 (iPhα), 138.57 (iPhβ), 138.43 (iPhβ), 138.35 (iPhα), 138.21 (iPhβ), 138.12 (iPhβ), 137.37, 137.37 (iPhα), 136.83 (iC^{Ts}α), 136.77 (iC^{Ts}β), 130.84 (=CHβ), 130.83 (=CHα), 129.43 (CH^{Ts}α, 2C), 129.28 (CH^{Ts}β, 2C), 128.74, 128.57, 128.53, 128.52, 128.49, 128.48, 128.47, 128.46, 128.45, 128.41, 128.35, 128.27, 128.07, 127.97, 127.94, 127.92, 127.81, 127.80, 127.78,

127.69, 127.67, 127.65 (CH^{Ts}α/β, Arα/β), 119.40 (=CH_2β), 119.36 (=CH_2β), 86.87 (C-3β), 86.08 (broad C-1β), 82.86 (C-3α), 81.83 (C-1α), 79.04 (C-2α), 78.00 (C-4α), 77.86, 77.56-76.79 (C-2β, C-4β, C-5β), 75.91 (CH_2^{Bn}β), 75.22 (CH_2^{Bn}β), 75.00 (CH_2^{Bn}α), 74.69 (CH_2^{Bn}β), 74.59 (CH_2^{Bn}α), 74.54 (C-5α), 73.76 (CH_2^{Bn}α), 73.64 (CH_2^{Bn}α), 73.45 (CH_2^{Bn}β), 69.98 (C-6α), 69.11 (C-6β), 68.12 (CH_2^{Alloc}α), 67.80 (CH_2^{Alloc}β), 21.73 (CH_3β), 21.67 (CH_3α) ppm*. HRMS (MALDI+): Calculated for $C_{45}H_{47}NO_9SNa^+$ m/z 800.2869; found m/z 800.2856. $[\alpha]_D^{298}$=+12.88° (c=1.025, $CHCl_3$).

* α/β 1:1.3 based on crude ^{1}H NMR; 22 overlapping Ar sygnals with 22 reported in ^{13}C NMR.

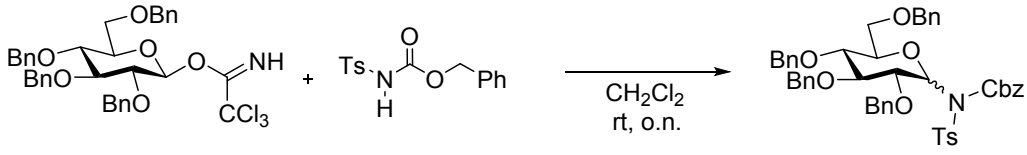
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl benzyl tosylcarbamate (24)



Carbamate 11 (141.6 mg, 0.46 mmol) was added to a stirred solution of 1α (211.8 mg, 0.31 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:6 EtOAc/Heptane) to yield the *β* anomer of the compound 24 (244.4 mg, 0.29 mmol, 93 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (broad d, Ar^{Ts}, *J*~ 7.4 Hz, 2H), 7.45-7.08 (m, Ar, 25H), 6.92 (d, Ar^{Ts}, *J* = 7.4 Hz, 2H), 5.53 (d, H-1, *J* = 9.3 Hz, 1H), 5.05 (d, CH_2^{Cbz}, *J* = 12.1 Hz, 1H), 4.96 (broad d, CH_2^{Cbz}, *J* = 12.1 Hz, 1H), 4.91 (d, CH_2^{Bn}, *J* = 11.1 Hz, 1H), 4.86 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.82 (d, CH_2^{Bn}, *J* = 10.9 Hz, 1H), 4.72-4.54 (m, CH_2^{Bn}, 4H), 4.54-4.46 (m, CH_2^{Bn}, H-2, 2H), 3.79-3.68 (m, H-3, H-6, H-6', 3H), 3.68-3.57 (m, H-4, H-5, 2H), 2.30 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.43 (broad C=O), 144.25 (iC^{Ts}), 138.62 (iPh), 138.43 (iPh), 138.19 (iPh, 2C), 138.13 (iPh), 136.74 (iC^{Ts}), 134.51 (iPh^{Cbz}), 129.22 (CH^{Ts}, 2C), 128.59, 128.57, 128.55, 128.52, 128.49, 128.48, 128.40, 128.27, 128.09, 127.93, 127.89, 127.82, 127.73, 127.70, 127.68 (CH^{Ts}, Ar), 86.83 (C-3), 86.09 (broad, C-1), 77.85, 77.55-76.72 (C-2, C-4, C-5), 75.74 (CH_2^{Bn}), 75.19 (CH_2^{Bn}), 74.59 (CH_2^{Bn}), 73.49 (CH_2^{Bn}), 69.11 (CH_2^{Cbz}), 69.04 (C-6), 21.70 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{49}H_{49}NO_9SNa^+$ m/z 850.3026; found m/z 850.3005. $[\alpha]_D^{298}$=+1.82° (c=1.210, $CHCl_3$).

* The obtained compound contains less than 3 % of α anomer; 12 overlapping Ar sygnals with 15 reported in ^{13}C NMR.

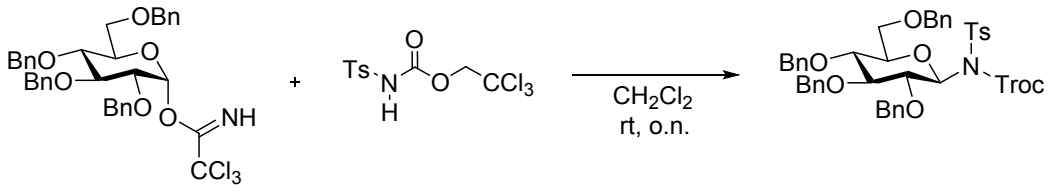
2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl benzyl tosylcarbamate (24)



Carbamate 11 (102 mg, 0.33 mmol) was added to a stirred solution of 1β (152 mg, 0.22 mmol) in dry DCM (1.1 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the *α/β* mixture (1:0.9) of the compound 24 (150 mg, 0.18 mmol, 81 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (broad d, Ar^{Ts}β, *J*~ 7.4 Hz, 2H), 7.69 (d, Ar^{Ts}α, *J* = 8.2 Hz, 2H), 7.42-7.16 (m, Ar, 50 H), 7.14 (d, Ar, *J* = 7.1 Hz, 2H), 7.10 (d, Ar, *J* = 7.3 Hz, 2H), 6.92 (d, Ar^{Ts}β, *J* = 7.4 Hz, 2H), 6.84 (d, Ar^{Ts}α, *J* = 8.2 Hz, 2H), 6.43 (d, H-1α, *J* = 8.2 Hz, 1H), 5.53 (d, H-1β, *J* = 9.3 Hz, 1H), 5.06 (d, CH_2^{Cbz}β, *J* = 12.1 Hz, 1H), 5.02 (d, CH_2^{Cbz}α, *J* = 12.1 Hz, 1H), 4.98 (d, CH_2^{Cbz}α, *J* = 12.1 Hz, 1H), 4.97 (broad d, CH_2^{Cbz}β, *J* ~ 12.1 Hz, 1H), 4.91 (d, CH_2^{Bn}β, *J* = 11.1 Hz, 1H), 4.86 (d, CH_2^{Bn}β, *J* = 11.1 Hz, 1H), 4.83 (d, CH_2^{Bn}β, *J* = 11.1 Hz, 1H), 4.82 (d, CH_2^{Bn}α, *J* = 11.5 Hz, 1H), 4.80 (d, CH_2^{Bn}α, *J* = 11.5 Hz, 1H), 4.72-4.54 (m, CH_2^{Bn}β, 4H), 4.70 (d, CH_2^{Bn}α, *J* = 11.2 Hz, 1H), 4.65 (d, CH_2^{Bn}α, *J* = 10.9 Hz, 1H), 4.59-4.47 (m, H-2β, H-3α, CH_2^{Bn}α/β, 7H), 4.28 (ddd, H-5α, *J* = 10.1 Hz, , *J* = 4.8 Hz, , *J* = 1.6 Hz, 1H), 4.11 (t, H-2α, *J* = 8.2 Hz, Hz, 1H), 3.79-3.68 (m, H-3β, H-6α/β, H-6'β, 4H), 3.69-3.56 (m, H-4α/β, H-5β, H-6'α, 4H), 2.31 (s, CH_3β, 3H), 2.26 (s, CH_3α, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.22 (C=Oα), 151.44 (broad C=Oβ), 144.26 (iC^{Ts}β), 144.21 (iC^{Ts}α), 139.00 (iPhα), 138.62 (iPhβ), 138.60 (iPhα), 138.43 (iPhβ), 138.35 (iPhα), 138.19 (iPhβ), 138.13 (iPhβ), 137.40 (iPhα), 136.74 (iC^{Ts}β), 136.69 (iC^{Ts}α), 134.51 (iPh^{Cbz}β), 134.35 (iPh^{Cbz}α), 129.34 (CH^{Ts}α, 2C), 129.23 (CH^{Ts}β, 2C), 128.74, 128.60, 128.57, 128.56, 128.52, 128.49, 128.47, 128.46, 128.45, 128.44, 128.41, 128.36, 128.28, 128.24, 128.10, 127.94, 127.90, 127.82, 127.78, 127.74, 127.70, 127.69, 127.64 (CH^{Ts}, Ar), 86.83 (C-3β), 86.11 (broad C-1β), 82.82 (C-3α), 81.95 (C-1α), 79.13 (C-2α), 77.97 (C-4α), 77.85, 77.55-76.72 (C-2β, C-4β, C-5β), 75.73 (CH_2^{Bn}β), 75.18 (CH_2^{Bn}β), 74.95 (CH_2^{Bn}α), 74.58 (CH_2^{Bn}β), 74.56 (CH_2^{Bn}α), 74.54 (C-5α), 73.71 (CH_2^{Bn}α), 73.68 (CH_2^{Bn}α), 73.49 (CH_2^{Bn}β), 69.88 (C-6α), 69.38 (CH_2^{Cbz}α), 69.11 (CH_2^{Cbz}), 69.05 (C-6β), 21.70 (CH_3β), 21.64 (CH_3α) ppm*. HRMS (MALDI+): Calculated for $C_{49}H_{49}NO_9SNa^+$ m/z 850.3026; found m/z 850.3010. $[\alpha]_D^{298}$=+17.7° (c=0.825, $CHCl_3$).

* α/β 1:0.9 based on crude ^{1}H NMR; 31 overlapping Ar sygnals with 23 reported in ^{13}C NMR.

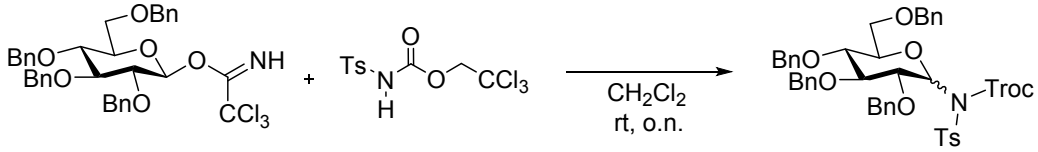
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl 2,2,2-trichloroethyl tosylcarbamate (21)



Carbamate 10 (158 mg, 0.46 mmol) was added to a stirred solution of 1α (208 mg, 0.30 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:6 EtOAc/Heptane) to yield the *β* anomer of the compound 21 (250.4 mg, 0.29 mmol, 95 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (broad d, Ar^{Ts}, *J*~7.5 Hz, 2H), 7.44-7.15 (m, Ar, 20H), 7.04 (d, Ar^{Ts}, *J*= 7.5 Hz, 2H), 5.60 (d, H-1, *J*= 9.3 Hz, 1H), 4.96 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.91 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.85 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.83-4.74 (m, CH_2^{Bn}, 2H), 4.65 (broad d, CH_2^{Troc}, *J*= 11.3 Hz, 1H), 4.61-4.45 (m, H-2, CH_2^{Bn}, CH_2^{Troc}, 5H), 3.78 (t, H-3, *J*= 8.9 Hz, 1H), 3.75 (broad d, H-6, *J*= 10.6 Hz, 1H), 3.72-3.66 (m, H-5, 1H), 3.66-3.55 (m, H-4, H-6', 2H), 2.33 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.51 (broad C=O), 144.82 (iC^{Ts}) , 138.60 (iPh), 138.35 (iPh), 138.05 (iPh), 138.01 (iPh), 136.19 (iC^{Ts}), 129.44 (CH^{Ts}, 2C), 128.59, 128.57, 128.53, 128.45, 128.38, 128.18, 128.02, 127.87, 127.82, 127.80, 127.74 (CH^{Ts}, Ar), 93.95 (CCl_3), 86.86 (C-3), 86.19 (broad C-1), 77.87, 77.69, 77.55-76.75 (C-2, C-4, C-5), 75.85 (CH_2^{Bn}), 75.78 (CH_2^{Troc}), 75.18 (CH_2^{Bn}), 74.66 (CH_2^{Bn}), 73.46 (CH_2^{Bn}), 69.30 (C-6), 21.75 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{44}H_{44}Cl_3NO_9SNa^+$ m/z 890.1700; found m/z 890.1682. $[\alpha]_D^{298}$=+1.36° (c=0.735, $CHCl_3$).

* The obtained compound contains less than 1 % of α anomer; 11 overlapping Ar sygnals with 11 reported in ^{13}C NMR.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl 2,2,2-trichloroethyl tosylcarbamate (21)

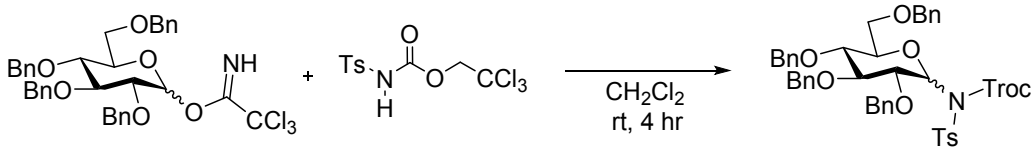


Carbamate 12 (114 mg, 0.33 mmol) was added to a stirred solution of 1β (151 mg, 0.22 mmol) in dry DCM (1.1 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the *α*/*β* mixture (1:1) of the compound 21 (152.2 mg, 0.17 mmol, 80 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, Ar^{Ts}α, *J*=8.4 Hz, 2H), 7.91 (broad d, Ar^{Ts}β, *J*~7.5 Hz, 2H), 7.44-7.16 (m, Ar, 40H), 7.04 (d, Ar^{Ts}, *J*= 7.5 Hz, 2H),

7.02 (d, $Ar^{Ts}\alpha$, *J*=8.4 Hz, 2H), 6.48 (d, H-1α, *J*= 8.0 Hz, 1H), 5.60 (d, H-1β, *J*= 9.3 Hz, 1H), 4.95 (d, $CH_2^{Bn}\beta$, *J*= 11.1 Hz, 1H), 4.90 (d, $CH_2^{Bn}\beta$, *J*= 11.1 Hz, 1H), 4.86 (d, $CH_2^{Bn}\alpha$, *J*= 11.4 Hz, 1H), 4.84 (d, $CH_2^{Bn}\beta$, *J*= 11.0 Hz, 1H), 4.83-4.74 (m, $CH_2^{Bn}\beta$, 2H), 4.81 (d, $CH_2^{Bn}\alpha$, *J*= 11.2 Hz, 1H), 4.77 (d, $CH_2^{Bn}\alpha$, *J*= 11.2 Hz, 1H), 4.72 (d, $CH_2^{Bn}\alpha$, *J*= 11.9 Hz, 1H), 4.68 (d, $CH_2^{Bn}\alpha$, *J*= 11.0, 1H), 4.64 (broad d, $CH_2^{Troc}\beta$, *J*= 11.3 Hz, 1H), 4.61-4.44 (m, H-2β, H-3α, $CH_2^{Bn}\alpha/\beta$, $CH_2^{Troc}\alpha/\beta$, 11H), 4.31 (ddd, H-5α, *J*= 10.1, *J*= 5.1, *J*= 1.7 Hz, 1H), 4.15 (t, H-2α, *J*= 8.0 Hz, 1H), 3.78 (t, H-3β, *J*= 8.9 Hz, 1H), 3.76-3.72 (m, H-6α/β, 2H), 3.72-3.66 (m, H-5β, 1H), 3.66-3.56 (m, H-4α/β, H-6'α/β, 4H), 2.33 (s, $CH_3\beta$, 3H), 2.31 (s, $CH_3\alpha$, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.32 (C=Oα), 150.49 (broad C=Oβ), 144.81 ($iC^{Ts}\beta$), 144.72 ($iC^{Ts}\alpha$), 138.81 (iPhα), 138.60 (iPhβ), 138.47 (iPhα), 138.35 (iPhβ), 138.29 (iPhα), 138.05 (iPhβ), 137.99 (broad iPhβ), 137.23 (iPhα), 136.56 ($iC^{Ts}\alpha$), 136.19 ($iC^{Ts}\beta$), 129.66 ($CH^{Ts}\alpha$, 2C) 129.43 ($CH^{Ts}\beta$, 2C), 128.58, 128.57, 128.55, 128.52, 128.51, 128.45, 128.36, 128.24, 128.17, 128.06, 128.01, 127.94, 127.86, 127.84, 127.82, 127.79, 127.75, 127.73 (CH^{Ts}, Ar), 93.93 ($CCl_3\beta$), 93.91 ($CCl_3\alpha$), 86.86 (C-3β), 86.17 (broad C-1β), 82.70 (C-3α), 82.52 (C-1α), 78.98 (C-2α), 77.94 (C-4α), 77.87, 77.69, 77.55-76.75 (C-2β, C-4β, C-5β), 76.12 ($CH_2^{Troc}\alpha$), 75.85 ($CH_2^{Bn}\beta$), 75.78 (CH_2^{Troc}), 75.19 ($CH_2^{Bn}\beta$), 74.90 (C-5α, $CH_2^{Bn}\alpha$), 74.67 ($CH_2^{Bn}\beta$), 74.58 ($CH_2^{Bn}\alpha$), 73.91 ($CH_2^{Bn}\alpha$), 73.75 ($CH_2^{Bn}\alpha$), 73.46 ($CH_2^{Bn}\beta$), 69.99 (C-6α), 69.30 (C-6β), 21.74 ($CH_3\beta$), 21.68 ($CH_3\alpha$) ppm*. HRMS (MALDI+): Calculated for $C_{44}H_{44}Cl_3NO_9SNa^+$ m/z 890.1700; found m/z 890.1679. $[\alpha]_D^{298}$=+17.47° (c=0.790, $CHCl_3$).

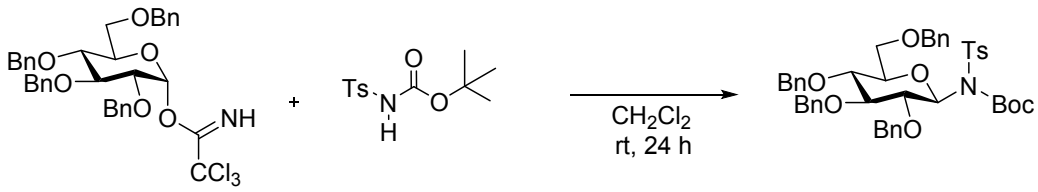
* α/β 1:1 based on crude ^{1}H NMR; 26 overlapping Ar sygnals with 18 reported in ^{13}C NMR.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl 2,2,2-trichloroethyl tosylcarbamate (21)



Carbamate 12 (0.91 g, 2.63 mmol) was added to a stirred solution of 1 (α/β 1:0.7, 1.2 g, 1.75 mmol) in dry DCM (9.0 mL) under a nitrogen atmosphere. The reaction was stirred for 4 h. After completion, the reaction mixture was diluted with DCM (100 ml) and washed with 0.5 M NaOH (100 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the α/β mixture (1:4.3) of the compound 21 (1.51 g, 1.73 mmol, 99 %) as a colorless syrup. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

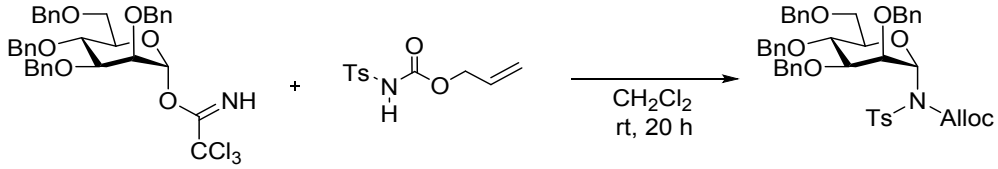
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl *tert*-butyl tosylcarbamate (22)



Carbamate 8 (137 mg, 0.51 mmol) was added to a stirred solution of 1α (231 mg, 0.34 mmol) in dry DCM (3.0 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:6 EtOAc/Heptane) to yield the *β* anomer of the compound 22 (94 mg, 0.12 mmol, 35 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00-7.72 (m, Ar^{Ts}, 2H), 7.35-7.12 (m, Ar, 20H), 7.10-6.92 (m, Ar^{Ts}, 2H), 5.46 (d, H-1β, *J*= 8.8 Hz, 1H), 4.90 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.83 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.81 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.77-4.62 (m, CH_2^{Bn}, 2H), 4.62-4.55 (m, CH_2^{Bn}, 2H), 4.55-4.47 (m, H-2, CH_2^{Bn}, 2H), 3.78-3.65 (m, H-3, H-6, H-6', 3H), 3.67-3.57 (m, H-4, H-5, 2H), 2.30 (s, CH_3^{Ts}, 3H), 1.26 (s, CH_3^{Boc}, 9H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.04 (broad C=O), 143.94 (iC^{Ts}), 138.75 (iPh), 138.51 (iPh), 138.26 (iPh), 138.21 (iPh), 137.58 (iC^{Ts}), 129.23 (CH^{Ts}, 2C), 128.54, 128.51, 128.45, 128.30, 128.11, 127.90, 127.84, 127.82, 127.78, 127.69, 127.61 (CH^{Ts}, Ar), 86.71 (C-3), 85.77 (broad C-1), 85.11 (C^{Boc}), 78.43 (C-2), 77.90, 77.76 (C-4, C-5), 75.76 (CH_2^{Bn}), 75.20(CH_2^{Bn}), 74.80(CH_2^{Bn}), 73.36 (CH_2^{Bn}), 69.00 (C-6), 27.93 (CH_3^{Boc}), 21.70 (CH_3^{Ts}) ppm*. HRMS (MALDI+): Calculated for $C_{46}H_{51}NO_9SNa^+$ m/z 816.3182; found m/z 816.3170. $[\alpha]_D^{298}$=+8.44° (c=0.545, $CHCl_3$).

* The obtained compound contains 2 % of α anomer; 11 overlapping Ar sygnals with 11 reported in ^{13}C NMR.

2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl allyl tosylcarbamate (S13)

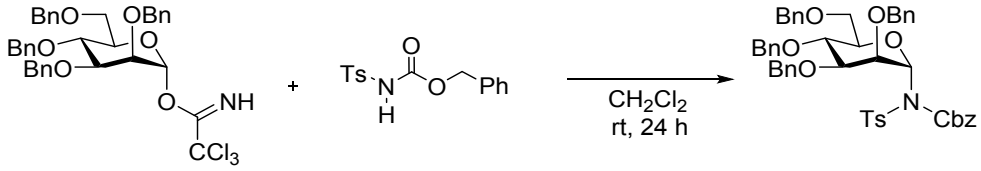


Carbamate 9 (112 mg, 0.44 mmol) was added to a stirred solution of 3α (201 mg, 0.29 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred for 20 h. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:6 EtOAc/Heptane) to yield *α* anomer of the desired product S13 (145.4 mg, 0.19 mmol, 64 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 7.35-7.18 (m, Ar, 20H), 7.04 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 6.28 (d, H-1, *J*= 9.2 Hz, 1H), 5.68-5.59 (m, =CH,

1H), 5.16 (ddt, =CH_2^{trans}, *J* = 1.4, *J*= 17.2, ^4J = 1.4 Hz 1H), 5.05 (ddt, =CH_2^{cis}, *J*= 1.4, *J*= 10.5, ^4J = 1.4 Hz, 1H), 4.76 (dd, H-2, *J*= 9.2, 2.9 Hz, 1H), 4.74 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 4.58 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 4.58-4.45 (m, CH_2^{Bn}, CH_2^{Alloc}, 5H), 4.45-4.33 (m, CH_2^{Bn}, H-5, 4H), 3.96 (t, H-3, *J*= 2.9 Hz, 1H), 3.88 (dd, H-6, *J*= 10.7, *J*= 7.3 Hz, 1H), 3.67 (dd, H-6', *J*= 10.7, *J*= 4.6 Hz, 1H), 3.62 (dd, H-4, *J*= 3.8, 2.9 Hz, 1H), 2.33 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.90 (C=O), 144.10(iC^{Ts}) , 138.50 (iPh), 138.40 (iPh), 138.21 (iPh), 138.06 (iPh), 137.11 (iC^{Ts}), 130.94 (=CH), 129.20 (CH^{Ts}, 2C), 128.70 (CH^{Ts}, 2C), 128.53, 128.51, 128.46, 128.43, 128.18, 128.03, 127.96, 127.88, 127.86, 127.83, 127.75, 127.64 (Ar), 119.12 (=CH_2), 81.27 (C-1), 76.59 (C5), 76.05 (C-4), 75.34 (C-3), 73.56 (C-2), 73.39 (CH_2^{Bn}), 73.19 (CH_2^{Bn}), 72.04(CH_2^{Bn}), 71.56 (CH_2^{Bn}), 69.23 (C-6), 67.68 (CH_2^{Alloc}), 21.70 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{45}H_{47}NO_9SNa^+$ m/z 800.2869; found m/z 800.2860. $[\alpha]_D^{298}$=+16.95° (c=0.755, $CHCl_3$).

* 5.30 ppm signal coming from DCM as reference; 8 overlapping Ar sygnals with 12 reported in ^{13}C NMR.

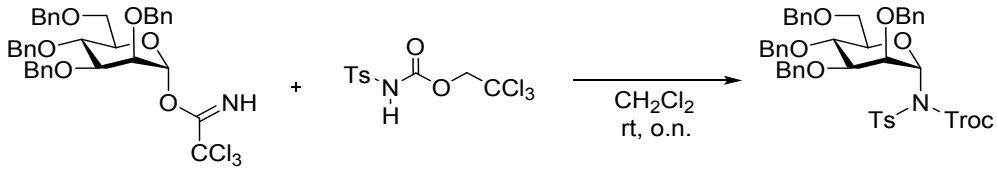
2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl benzyl tosylcarbamate (S14)



Carbamate 11 (137 mg, 0.45 mmol) was added to a stirred solution of 3α (205 mg, 0.30 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:9→1:6 EtOAc/Heptane) to yield *α* anomer of the desired product S14 (179.6 mg, 0.22 mmol, 72 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 7.42-7.08 (m, Ar, 25H), 6.92 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 6.29 (d, H-1, *J*= 9.2 Hz, 1H), 5.02 (d, CH_2^{Cbz}, *J*= 12.1 Hz, 1H), 4.98 (d, CH_2^{Cbz}, *J*= 12.1 Hz, 1H), 4.74 (dd, H-2, *J*= 9.2, 2.8 Hz, 1H), 4.70 (d, CH_2^{Bn}, *J*= 12.3 Hz, 1H), 4.54 (d, CH_2^{Bn}, *J*= 12.3 Hz, 1H), 4.54 (d, CH_2^{Bn}, *J*= 11.8 Hz, 1H) 4.50 (d, CH_2^{Bn}, *J*= 11.8 Hz, 1H), 4.46-4.32 (m, CH_2^{Bn}, H-5, 4H), 4.35 (d, CH_2^{Bn}, *J*= 11.8 Hz, 1H), 3.91 (t, H-3, *J*= 2.8 Hz, 1H), 3.87 (dd, H-6, *J*= 10.7, *J*= 7.3 Hz, 1H), 3.66 (dd, H-6', *J*= 10.7, *J*= 4.6 Hz), 3.61 (dd, H-4, *J*= 3.7, 2.8 Hz, 1H), 2.30 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.98 (C=O), 143.89 (iC^{Ts}) , 138.46 (iPh), 138.34 (iPh), 138.16 (iPh), 138.03 (iPh), 137.00 (iC^{Ts}), 134.51 (iC^{Cbz}), 129.10 (CH^{Ts}, 2C), 128.52, 128.51, 128.49, 128.46, 128.44, 128.39, 128.37, 128.08, 127.96, 127.91, 127.85, 127.82, 127.78, 127.65, 127.59 (Ar, CH^{Ts}), 81.24 (C-1), 76.63 (C5), 75.93 (C-4), 75.34 (C-3), 73.56 (C-2), 73.32(CH_2^{Bn}), 73.08 (CH_2^{Bn}), 71.96 (CH_2^{Bn}), 71.52 (CH_2^{Bn}), 69.13 (C-6), 68.84 (CH_2^{Cbz}), 21.63 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{49}H_{49}NO_9SNa^+$ m/z 850.3026; found m/z 850.3009. $[\alpha]_D^{298}$=+19.64° (c=0.84, $CHCl_3$).

* 5.30 signal coming from DCM as reference; 12 overlapping Ar sygnals with 15 reported in ^{13}C NMR.

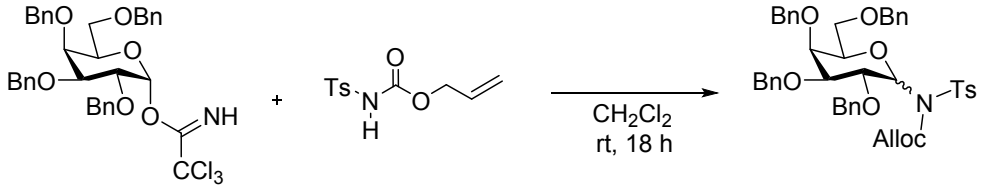
2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl 2,2,2-trichloroethyl tosylcarbamate (S15)



Carbamate 10 (154 mg, 0.44 mmol) was added to a stirred solution of 3α (203 mg, 0.30 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:9→1:6 EtOAc/Heptane) to yield *α* anomer of the desired product S15 (190 mg, 0.22 mmol, 74 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 7.41-7.15 (m, Ar, 20H), 7.02 (d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 6.34 (d, H-1, *J*= 9.3 Hz, 1H), 4.82 (dd, H-2, *J*= 9.3, 2.7 Hz, 1H), 4.72 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 4.65 (d, CH_2^{Troc}, *J*= 11.9 Hz, 1H), 4.62-4.48 (m, CH_2^{Bn}, CH_2^{Troc}, 6H), 4.44-4.39 (m, H-5, CH_2^{Bn}, 2H), 4.36 (d, CH_2Bn, *J*= 12.1 Hz, 1H), 3.99 (t, H-3, *J*= 2.7 Hz, 1H), 3.88 (dd, H-6, *J*= 10.6, *J*= 7.4 Hz, 1H), 3.66 (dd, H-6', *J*= 10.6, *J*= 4.5 Hz, 1H), 3.62 (dd, H-4, *J*= 3.9, 2.7 Hz, 1H), 2.31 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.06 (C=O), 144.42 (iC^{Ts}) , 138.41 (iPh), 138.30 (iPh), 138.13 (iPh), 137.94 (iPh), 136.71 (iC^{Ts}), 129.35 (CH^{Ts}, 2C), 128 (CH^{Ts}, 2C), 128.55, 128.54, 128.49, 128.46, 128.12, 128.02, 127.96, 127.95, 127.89, 127.88, 127.78, 127.69 (Ar), 93.98 (CCl_3), 81.70 (C-1), 76.68 (C-5), 75.95 (C-4), 75.75 (CH_2^{Troc}), 75.21 (C-3), 73.73 (C-2), 73.43 (CH_2^{Bn}), 73.21 (CH_2^{Bn}), 72.02 (CH_2^{Bn}), 71.59 (CH_2^{Bn}), 69.17 (C-6), 21.71 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{44}H_{44}Cl_3NO_9SNa^+$ m/z 890.1700; found m/z 890.1681. $[\alpha]_D^{298}$=+15.71° (c=0.980, $CHCl_3$).

* 8 overlapping Ar sygnals with 12 reported in ^{13}C NMR

2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl allyl tosylcarbamate (S16)

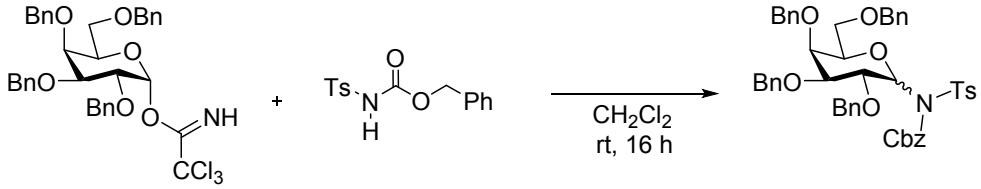


Carbamate 9 (112 mg, 0.44 mmol) was added to a stirred solution of 2α (200 mg, 0.29 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:9→1:4 EtOAc/Heptane) to yield the *α*/*β* mixture (1:2.4) of the desired product S16 (120 mg, 0.15 mmol, 53 %) as a colorless syrup. Anomer α ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (broad d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 7.33-7.16 (m, Ar, 20H), 6.98 (broad d, Ar^{Ts}, *J*= 8.3 Hz, 2H), 6.51-6.46

(m, H-1, 1H), 5.61-5.52 (m, =CH, 1H), 5.12 (ddt, $=CH_2^{trans}$, *J*= 1.4 Hz, *J*= 17.2, ^4J= 1.4 Hz, 1H), 5.07 (ddt, $=CH_2^{cis}$, *J*= 1.4 Hz, *J*= 10.5, ^4J = 1.4 Hz, 1H), 4.91 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.74 (d, CH_2^{Bn}, *J*= 11.9 Hz, 1H), 4.67 (d, CH_2^{Bn}, *J*= 11.9 Hz, 7H), 4.63 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.57 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.55 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.47-4.36 (m, H-2, H-3, H-5, CH_2^{Bn}, CH_2^{Alloc}, 7H), 4.34 (ddt, CH_2^{Alloc}, *J*= 13.1, *J*= 6.0, ^4J = 1.4 Hz, 1H), 3.94 (broad dd, H-4, *J*= 2.4, 1.3 Hz, 1H), 3.60 (dd, H-6, *J*= 10.6 Hz, *J*= 7.4 Hz, 1H), 3.47 (dd, H-6', *J*= 10.6 Hz, *J*= 4.5 Hz, 1H), 2.26 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.06 (C=O), 144.24 (iC^{Ts}) , 138.93 (iPh), 138.78 (iPh), 138.28 (iPh), 137.83 (iPh), 137.06 (iC^{Ts}), 130.87 (=CH), 129.36 (CH^{Ts}, 2C), 128.51, 128.42, 128.39, 128.37, 128.26, 128.25, 128.16, 127.82, 127.70, 127.64, 127.61, 127.54 (CH^{Ts}, Ar), 119.20 ($=CH_2$), 82.68 (C-1), 79.74 (C-3), 75.94 (C-2), 74.77 (C-5), 74.48 (CH_2^{Bn}), 74.32 (CH_2^{Bn}), 74.18 (C-4), 73.63 (CH_2^{Bn}), 72.93 (CH_2^{Bn}), 70.06 (C-6), 67.95 (CH_2^{Alloc}), 21.63 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{45}H_{47}NO_9SNa^+$ m/z 800.2869; found m/z 800.2843. $[\alpha]_D^{298}$=+32.83° (c=0.335, $CHCl_3$). Anomer β ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, Ar^{Ts}, *J*= 8.1 Hz, 2H), 7.34-7.14 (m, Ph, 20H), 6.98 (d, Ar^{Ts}, *J*= 8.1 Hz, 2H), 5.58-5.48 (m, =CH, 1H), 5.43 (d, H-1, *J*= 9.2 Hz, 1H), 5.08 (ddt, $=CH_2^{trans}$, *J*= 1.5, *J*= 17.2, ^4J= 1.5 Hz, 1H), 4.93-4.87 (m, CH_2^{Bn}, $=CH_2^{cis}$, 2H), 4.78-4.71 (m, H-2, CH_2^{Bn}, 2H), 4.70 (s, CH_2^{Bn}, 2H), 4.61 (broad d, CH_2^{Bn}, *J*~ 11.0 Hz, 1H), 4.53 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.45-4.36 (m, CH_2^{Alloc}, CH_2^{Bn}, 3H), 4.30-4.23 (m, CH_2^{Alloc}, 1H), 3.90 (d, H-4, *J*= 2.6 Hz, 1H), 3.70 (t, H-5, *J*= 6.4 Hz, 1H), 3.61 (dd, H-3, *J*= 9.2 Hz, 1H), 3.57 (d, H-6, H-6', *J*= 6.4 Hz, 2H), 2.27 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.46 (C=O), 144.26 (iC^{Ts}), 138.98 (iPh), 138.37 (iPh), 138.35 (iPh), 138.04 (iPh), 136.74 (iC^{Ts}), 130.86 (=CH), 129.18 (CH^{Ts}, 2C), 128.69, 128.56, 128.36, 128.34, 128.25, 127.97, 127.93, 127.90, 127.80, 127.72, 127.61, 127.50 (CH^{Ts}, Ar), 118.96 ($=CH_2$), 86.27 (C-1), 84.85 (C-3), 76.19 (C-5), 75.44 (C-2), 74.85 (CH_2^{Bn}), 74.64 (CH_2^{Bn}), 73.88 (CH_2^{Bn}), 73.58 (C-4), 72.97 (CH_2^{Bn}), 68.80 (C-6), 67.69 (CH_2^{Alloc}), 21.69 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{45}H_{47}NO_9SNa^+$ m/z 800.2869; found m/z 800.2844. $[\alpha]_D^{298}$=-5.96° (c=0.24, $CHCl_3$).

* α/β 1:2.4 based on crude ^{1}H NMR; rotamers of α anomer (signal coming from H-1, m when measured in $CDCl_3$, d when measured in CD_3CN); 10 overlapping Ar sygnals with 12 reported in ^{13}C NMR of α anomer; 10 overlapping Ar sygnals with 12 reported in ^{13}C NMR of β anomer.

2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl benzyl tosylcarbamate (S17)

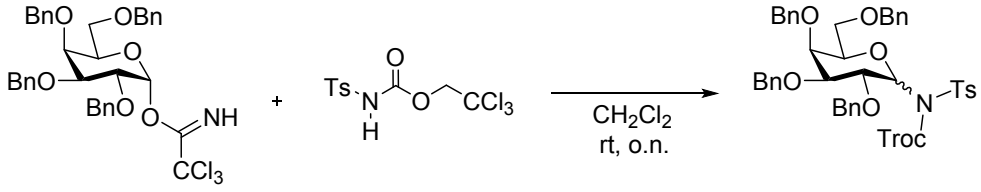


Carbamate 11 (135 mg, 0.44 mmol) was added to a stirred solution of 2α (201 mg, 0.29 mmol) in dry DCM (1.5 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:9→1:5 EtOAc/Heptane) to yield the *α*/*β* mixture (1:1.7) of the desired product

S17 (148.4 mg, 0.18 mmol, 61 %) as a colorless syrup. Anomer α ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, Ar^{Ts}, *J*= 8.0 Hz, 2H), 7.42-7.16 (m, Ar, 25H), 7.10-7.06 (m, Ar^{Cbz}, 2H), 6.85 (d, Ar^{Ts}, *J*= 8.0 Hz, 2H), 6.53 (d, H-1, *J*= 7.1 Hz, 1H), 5.00 (d, CH_2^{Cbz}, *J*= 12.1 Hz, 1H), 4.95 (d, CH_2^{Cbz}, *J*= 12.1 Hz, 1H), 4.94 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.73 (d, CH_2^{Bn}, *J*= 11.9 Hz, 1H), 4.66 (d, CH_2^{Bn}, *J*= 11.9 Hz, 1H), 4.65 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.60 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.58 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.50-4.39 (m, H-2, H-3, H-5, CH_2^{Bn}, 5H), 3.98-3.95 (m, H-4, 1H), 3.64 (dd, H-6, *J*= 9.5, *J*= 6.4 Hz, 1H), 3.50 (dd, H-6', *J*= 9.5, *J*= 6.3 Hz, 1H), 2.25 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.29 (C=O), 144.03 (iC^{Ts}) , 139.02 (iPh), 138.82 (iPh), 138.32 (iPh), 137.93 (iPh), 136.95 (iC^{Ts}), 134.48 (iPh^{Cbz}), 129.29 (CH^{Ts}, 2C), 128.55, 128.52, 128.48, 128.43, 128.38, 128.28, 128.27, 128.24, 128.15, 127.83, 127.70, 127.63, 127.55 (CH^{Ts}, Ar), 82.80 (C-1), 79.80 (C-3), 76.04 (C-2), 74.79 (C-5), 74.48 (CH_2^{Bn}), 74.36 (CH_2^{Bn}), 74.26 (C-4), 73.62 (CH_2^{Bn}), 72.96 (CH_2^{Bn}), 70.01 (C-6), 69.24 (CH_2^{Cbz}), 21.62 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{49}H_{49}NO_9SNa^+$ m/z 850.3026; found m/z 850.3004. $[\alpha]_D^{298}$=+30.31° (c=0.640, $CHCl_3$). Anomer β ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, Ar^{Ts}, *J*= 8.1 Hz, 2H), 7.40-7.07 (m, Ar, 25H), 6.91 (d, Ar^{Ts}, *J*= 8.1 Hz, 2H), 5.46 (d, H-1, *J*= 9.2 Hz, 1H), 5.02 (d, CH_2^{Cbz}, *J*= 12.1 Hz, 1H), 4.96-4.92 (m, CH_2^{Cbz}, CH_2^{Bn}, 2H), 4.83 (broad t, H-2, *J*~ 9.2 Hz, 1H), 4.73 (broad s, CH_2^{Bn}, 2H), 4.65-4.59 (m, CH_2^{Bn}, 2H), 4.48 (d, CH_2^{Bn}, *J*= 11.7 Hz, 1H), 4.45 (d, CH_2^{Bn}, *J*~ 11.8 Hz, 1H), 4.42 (d, CH_2^{Bn}, *J*= 11.7 Hz, 1H), 3.95 (broad d, H-4, *J*= 2.2 Hz, 1H), 3.75 (broad t, H-5, *J*= 6.3 Hz), 3.66-3.60 (m, H-3, H-6, H-6', 3H), 2.29 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.50 (C=O), 144.10 (iC^{Ts}) , 139.02 (iPh), 138.43 (iPh, 2C), 138.09 (iPh), 136.75 (iC^{Ts}), 134.67 (iPh^{Cbz}), 129.15 (CH^{Ts}, 2C), 128.62, 128.58, 128.55, 128.43, 128.32, 128.30, 128.25, 128.02, 127.98, 127.92, 127.78, 127.66, 127.55, 127.54 (CH^{Ts}, Ar), 86.30 (C-1), 84.85 (C-3), 76.28 (C-5), 75.49 (C-2), 74.77 (CH_2^{Bn}), 74.53 (CH_2^{Bn}), 73.75 (CH_2^{Bn}), 73.62 (C-4), 72.93 (CH_2^{Bn}), 68.84 (C-6), 68.76 (CH_2^{Cbz}), 21.68 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{49}H_{49}NO_9SNa^+$ m/z 850.3026; found m/z 850.3001. $[\alpha]_D^{298}$=-6.45° (c=0.620, $CHCl_3$).

* α/β 1:1.7 based on crude ^{1}H NMR; 14 overlapping Ar signals with 13 reported in ^{13}C NMR of anomer α; 13 overlapping Ar signals with 14 reported in ^{13}C NMR of anomer β.

2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl 2,2,2-trichloroethyl tosylcarbamate (S18)

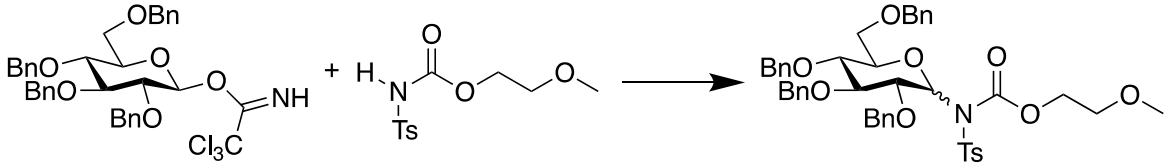


Carbamate 10 (86 mg, 0.25 mmol) was added to a stirred solution of 2α (113 mg, 0.17 mmol) in dry DCM (0.8 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the *α/β* mixture (1:1.4) of the desired product S18 (115.7 mg, 0.13 mmol, 81 %) as a colorless syrup. Anomer α ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, Ar^{Ts}, *J*= 8.4 Hz, 2H), 7.35-7.18 (m, Ar, 20H), 6.99 (d, Ar^{Ts}, *J*= 8.4 Hz, 2H), 6.56 (d, H-1, *J*= 7.8

Hz, 1H), 4.93 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.75 (d, CH_2^{Bn}, *J*= 11.9 Hz, 1H), 4.70 (d, CH_2^{Bn}, *J*= 11.9 Hz, 1H), 4.65 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.64 (d, CH_2^{Troc}, *J*= 11.9 Hz, 1H), 4.60 (d, CH_2^{Bn}, *J*= 11.1 Hz, 1H), 4.58 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.48-4.38 (m, H-2, H-3, H-5, CH_2^{Troc}, CH_2^{Bn}, 6H), 3.97 (dd, H-4, *J*= 2.7, 1.1 Hz, 1H), 3.63 (dd, H-6, *J*= 9.6, *J*= 6.5 Hz, 1H), 3.48 (dd, H-6', *J*= 9.6, *J*= 5.9 Hz, 1H), 2.26 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.33 (C=O), 144.53 (iC^{Ts}), 138.81 (iPh), 138.69 (iPh), 138.25 (iPh), 137.73 (iPh), 136.76 (iC^{Ts}), 129.59 (CH^{Ts}, 2C), 128.53, 128.47, 128.41, 128.35, 128.32, 128.28, 128.26, 128.11, 127.86, 127.77, 127.76, 127.70, 127.65 (Ar), 93.93 (CCl_3), 83.44 (C-1), 79.58 (C-3), 76.05 (C-2, CH_2^{Troc}), 74.89 (C-5), 74.77 (CH_2^{Bn}), 74.52 (CH_2^{Bn}), 74.16 (C-4), 73.63 (CH_2^{Bn}), 72.85 (CH_2^{Bn}), 70.05 (C-6), 21.64 (CH_3) ppm. (MALDI+): Calculated for $C_{44}H_{44}Cl_3NO_9SNa^+$ m/z 890.1700; found m/z 890.1685. $[\alpha]_D^{298}$=+31.64° (c=0.670, $CHCl_3$). Anomer β ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, Ar^{Ts}, *J*= 7.9 Hz, 2H), 7.36-7.14 (m, Ar, 20H), 6.99 (d, Ar^{Ts}, *J*= 7.9 Hz, 2H), 5.50 (d, H-1, *J*= 9.2 Hz, 1H), 4.90 (d, CH_2^{Bn}, *J*= 11.6 Hz, 1H), 4.87 (t, H-2, *J*= 9.2 Hz, 1H), 4.81 (d, CH_2^{Troc}, *J*= 10.9 Hz, 1H), 4.74-4.68 (m, CH_2^{Bn}, CH_2^{Troc}, 3H), 4.58 (d, CH_2^{Bn}, *J*= 11.5 Hz, 1H), 4.56 (d, CH_2^{Bn}, *J*= 11.6 Hz, 1H), 4.45 (broad d, CH_2^{Bn}, *J*~ 11.5 Hz, 1H), 4.44 (d, CH_2^{Bn}, *J*= 11.7 Hz, 1H), 4.40 (d, CH_2^{Bn}, *J*= 11.7 Hz, 1H), 3.90 (d, H-4, *J*= 2.3 Hz, 1H), 3.74 (dd, H-5, *J*= 6.7, 6.0 Hz, 1H), 3.64 (dd, H-3, *J*= 9.2, 2.3 Hz, 1H), 3.60 (dd, H-6, *J*= 9.3, *J*= 6.0 Hz, 1H), 3.55 (dd, H-6', *J*= 9.3, *J*= 6.7 Hz, 1H), 2.28 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.61 (C=O), 144.62 (iC^{Ts}) , 138.81 (iPh), 138.33 (iPh, 2C), 138.06 (iPh), 136.34 (iC^{Ts}), 129.32 (CH^{Ts}, 2C), 128.65, 128.58, 128.57, 128.41, 128.38, 128.32, 128.12, 127.96, 127.92, 127.83, 127.71, 127.68, 127.63 (Ar), 93.96 (CCl_3), 86.57 (C-1), 84.91 (C-3), 76.54 (C-5), 75.62 (C-2), 75.40 (CH_2^{Bn}), 74.97 (CH_2^{Troc}), 74.67 (CH_2^{Bn}), 73.86 (C-4), 73.59 (CH_2^{Bn}), 73.01(CH_2^{Bn}), 68.96 (C-6), 21.70 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{44}H_{44}Cl_3NO_9SNa^+$ m/z 890.1700; found m/z 890.1684. $[\alpha]_D^{298}$=-3.43° (c=0.525, $CHCl_3$).

* α/β 1:1.4 based on crude ^{1}H NMR; 9 overlapping Ar sygnals with 13 reported in ^{13}C NMR.

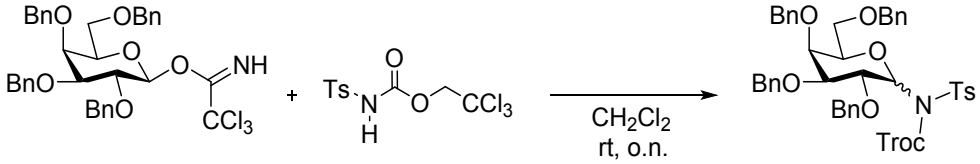
2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl 2-methoxyethyl tosylcarbamate (S19)



Following the general procedure for glycosylations with 2-methoxyethyl tosylcarbamate 7 (46 mg, 0.17 mmol) and 1β (51 mg, 74 µmol). TLC indicated the appearance of the corresponding α-TCA glycosyl donor, 1α, after one day. All starting material was consumed after stirring for four days. The desired product was purified by flash column chromatography (1:6 EtOAc/Heptane) to yield the desired glycoside, S19, (57 mg, 97 %) as a mixture of anomers (a/b 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 6H, Tosyl-Ar), 7.38 – 7.24 (m, 48H, Ar), 7.22 – 7.18 (m, 9H, Ar), 7.17 – 7.10 (m, 2H, Ar), 7.07 – 7.02 (m, 6H, Tosy-Ar), 6.41 (d, *J* = 8.2 Hz, 2H, H-1α), 5.53 (d, *J* = 9.3 Hz, 1H, H-1β), 4.98 – 4.65 (m, 14H, Bn-CH_2), 4.65 – 4.54 (m, 11H, Bn-CH_2, H-2β), 4.53 (d, *J* = 1.9 Hz, 2H, H-3α), 4.52 – 4.47 (m, 3H, Bn-CH_2), 4.27 (ddd, *J* = 10.1, 4.8, 1.9 Hz, 2H, H-5α), 4.17 (t, *J* = 4.7 Hz,

1H), 4.15 (t, *J* = 4.7 Hz, 2H, O-CH_2β), 4.13 – 4.10 (m, 2H, H-2α), 4.09 (t, *J* = 2.4 Hz, 1H), 4.03 (ddd, *J* = 10.1, 3.9, 2.1 Hz, 0H), 3.96 (t, *J* = 9.3 Hz, 0H), 3.75 (m, 2H, H-3β, H-5β, H-6β), 3.72 (dd, *J* = 10.7, 1.8 Hz, 2H, H-6α), 3.66 – 3.62 (m, 5H, H-4α, H-6'α, H-4β H-6'β), 3.40 (ddt, *J* = 7.5, 6.2, 1.8 Hz, 2H, O-CH_2β), 3.36 (t, *J* = 4.8 Hz, 4H, CH_2-Oα), 3.23 (s, 3H, O-CH_3β), 3.20 (s, 6H, O-CH_3α), 2.34 (s, 3H, Tosyl-CH_3β), 2.32 (s, 6H, Tosyl-CH_3α). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.25 (C=Oα), 144.36 (C=Oβ), 139.01, 138.63, 138.36, 137.41, 136.89, 129.40, 129.25, 128.58, 128.56, 128.47, 128.43, 128.39, 128.30, 128.23, 128.21, 128.09, 128.07, 128.01, 127.95, 127.93, 127.82, 127.79, 127.78, 127.71, 127.67, 127.63 (Ar), 82.78 (C-3α), 82.02 (C-1 α), 79.10 (C-2α), 77.98 (C-4α), 77.82, 75.74, 75.21, 74.94 (Ph*C*H_2O), 74.60 (C-5α), 74.47, 73.74, 73.63, 73.47 (Ph*C*H_2O), 69.85, 69.80 (*C*H_2O α/β), 69.76 (C-6α), 66.43(O-CH_2), 58.79 (O*C*H_3), 21.75, 21.70 (Tosyl-CH_3). HRMS (MALDI+): Calculated for $C_{45}H_{49}NO_{10}SNa^+$ m/z 818.2969, found m/z 818.2992.

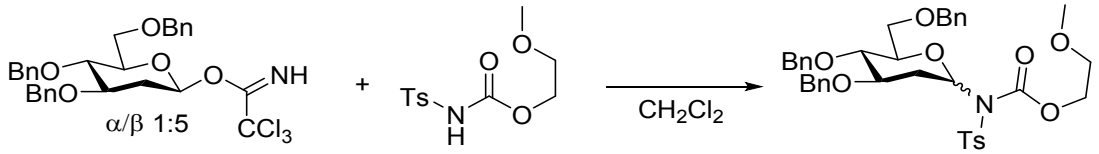
2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl 2,2,2-trichloroethyl tosylcarbamate (S20)



Carbamate 10 (110 mg, 0.32 mmol) was added to a stirred solution of 2β (145 mg, 0.21 mmol) in dry DCM (1.1 mL) under a nitrogen atmosphere. The reaction was stirred overnight. After completion, the reaction mixture was diluted with DCM (35 ml) and washed with 0.5 M NaOH (20 ml). The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and evaporated onto celite. The crude product was purified by flash column chromatography (1:7→1:6 EtOAc/Heptane) to yield the *α/β* (1:0.2) mixture of the desired product S20 (127.8 mg, 0.15 mmol, 69 %) as a colorless syrup. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

* α/β 1:0.2 based on crude ^{1}H NMR; 9 overlapping Ar signals with 13 reported in ^{13}C NMR.

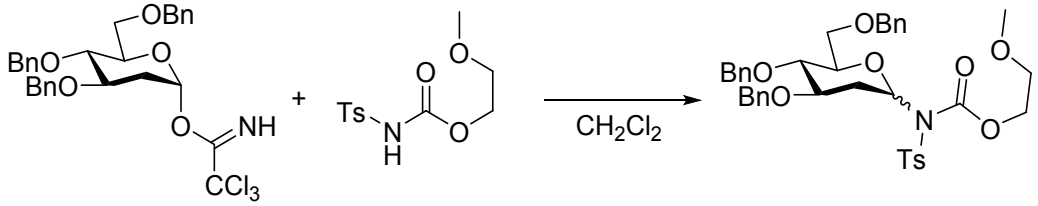
2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl 2-methoxyethyl tosylcarbamate (S21)



42 mg of tosylcarbamate 7 was added to a stirred solution of 4β (α/β 1:5) (48 mg, 0.083 mmol) in dry DCM (1.5 mL) and stirred at RT under a nitrogen atmosphere. No starting material was left after 30 mins according to TLC. The mixture was left stirring overnight and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:10 EtOAc/Heptane) to yield the desired product, S21 (50 mg, 0.072 mmol, 87 %) as a mixture of anomers (67:33 α/β). ^{1}H

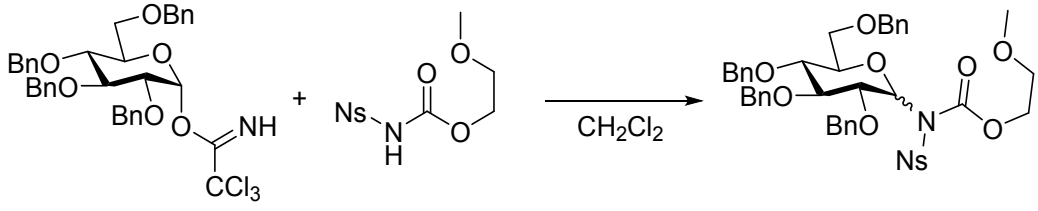
NMR (500 MHz, Benzene-d_6) δ 8.26 (d, $Ar^{Ts}\alpha$, 2H). 8.22 (d $Ar^{Ts}\beta$, 2H), 7.36-7.02 (m, Arα/β, 30H), 6.76 (dd, H-1α, *J*=4.0 Hz, *J*=10.8 Hz, 1H), 6.73 (m, $Ar^{Ts}\alpha/\beta$, 4H), 5.94 (dd, H-1β, α, *J*=2.1 Hz, *J*=11.5 Hz, 1H), 4.96 (d, $CH_2^{Bn}\beta$, *J*=11.5 Hz, 1H), 4.68 (td, H-5α, *J*=6.7 Hz, $J_{5\text{-}6b}$=3.2 Hz, 1H), 4.54 (d, $CH_2^{Bn}\beta$, *J*=11.5 Hz, 1H), 4.44-4.25 (m, $CH_2^{Bn}\alpha/\beta$, 9H), 4.18 (d, $CH_2^{Bn}\alpha$, *J*=11.9 Hz, 1H), 3.95 (dd, H-6aα, *J*=7.0 Hz, *J*=10.7 Hz, 1H), 3.95 (m, H-6aβ, 1H), 3.91 (m, $CH_2^{EtOMe}\alpha$, $CH_2^{EtOMe}\beta$, 4H), 3.87 (m, H-3α, 1H), 3.71 (dd, H-6bα, *J*=3.2 Hz, *J*=10.7 Hz, 1H), 3.67-3.48 (m, H-3β, H-4β, H-5β, H-6aβ. H-6bβ, 5H), 3.56 (dd, H-4α, $J_{4\text{-}5}$=6.6 Hz, $J_{3\text{-}4}$=3.2 Hz, 1H), 3.33 (dq, H-2aα, *J*=14.1 Hz, *J*=11 Hz, *J*=3.2 Hz, 1H), 3.10 (q, H-2aβ, *J*=11.6 Hz, *J*=11.3 Hz, 1H) 3.04-2.92 (m, $CH_2^{EtOMe}\alpha$, $CH_2^{EtOMe}\beta$, 4H), 2.90 (s, $OCH_3\beta$, 3H), 2.87 (s, $OCH_3\alpha$, 3H), 2.28 (ddd, H-2bβ, *J*=12.2 Hz, *J*=4.6 Hz, *J*=2.1 Hz, 1H), 2.14 (dt, H-2bα, *J*=13.6 Hz, *J*=3.5 Hz, *J*=3.5 Hz, 1H), 1.87 (s, $CH_3^{Ts}\beta$, 3H), 1.84 (s, $CH_3^{Ts}\alpha$, 3H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 152.70 (C=Oβ), 152.10 (C=Oα), 143.88 (iPhβ), 143.65 (iPhα), 139.50 (iPhβ), 139.21 (iPhα), 139.18 (iPhβ), 138.85 (iPhα), 138.78 (iPhβ), 138.71 (iPhα), 138.23 (iPhα), 137.98 (iPhβ), 129.35-127.57 (Ph), 83.89 (C-1β), 81.23 (C-3β), 80.25 (C-1α), 78.26+78.09 (C-4β and C-5β), 76.27 (C-4β), 76.26 (C-4α), 75.85 (C-5α), 74.94 ($CH_2^{Bn}\beta$), 73.39 ($CH_2^{Bn}\alpha$), 73.29 ($CH_2^{Bn}\beta$), 71.61 ($CH_2^{Bn}\alpha$), 71.26 ($CH_2^{Bn}\beta$), 70.88 ($CH_2^{Bn}\alpha$), 70.15 (C-6α) 70.11 (C-6β), 69.76 ($CH_2^{EtOMe}\alpha/\beta$), 66.01 ($CH_2^{EtOMe}\beta$), 65.95 ($CH_2^{EtOMe}\alpha$), 58.28 ($OCH_3\beta$) , 58.23 ($OCH_3\alpha$), 35.26 ($CH_2^{EtOMe}\beta$), 30.02 ($CH_2^{EtOMe}\alpha$), 21.23 ($CH_3^{Ts}\beta$), 21.20 ($CH_3^{Ts}\alpha$). HRMS (MALDI+): Calculated for $C_{38}H_{43}NO_9SNa^+$ m/z 712.2551; found m/z 712.2540. $[\alpha]_D^{298}$ = +11.7° (c=0.79, $CHCl_3$)

2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl 2-methoxyethyl tosylcarbamate (S21)



Tosylcarbamate 7 (97 mg, 0.36 mmol) was added to a stirred solution of 4α (α/β 85:15) (105 mg, 0.18 mmol) in dry DCM (3.0 mL) and stirred at RT under a nitrogen atmosphere. No starting material was left after 2 hr according to TLC. The mixture was left stirring overnight and evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired product, S21 (93 mg, 0.14 mmol, 74 %) as a mixture of anomers (69:31 α/β). Spectral data was in accordance with previously reported in this SI for an identical compound.

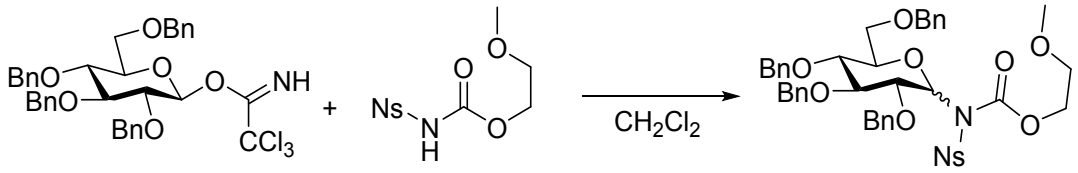
2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl 2-methoxyethyl nosylcarbamate (25)



Carmbamate 12 (49 mg, 0.16 mmol) was added to a stirring solution of 1α (56 mg, 82 µmol) in dry CH_2Cl_2 (2 mL) under a nitrogen atmosphere. The reaction was stirred overnight and evaporated onto

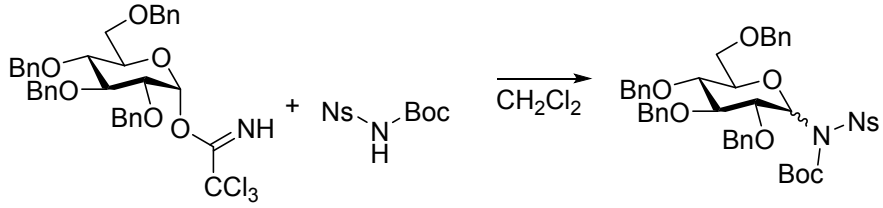
celite. The crude product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired product, 25 (45 mg, 54 µmol, 67 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (br m, *o*-CH^{Ns}, 2H) 7.96 (br m, *m*-CH^{Ns}, 2H), 7.35-7.21 (m, Ph, 20 H), 5.51 (d, H-1, 1H), 4.97-4.82 (m, CH_2^{Bn}, 5H), 4.63-4.50 (m, CH_2^{Bn}, H-2, 6H), 4.18 (br m, $CH_2^{NCO_2CH_2}$, 2H), 3.78-3.59 (m, H-3, H-4, H-5. H-6a, H-6b, 5H), 3.43 (m, $CH_2^{CH_2OCH_3}$, 2H), 3.24 (s, CH_3^{EtOMe}, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.37 (NCO_2), 144.93 (iC^{Ns}), 138.44 (iC^{Ns}), 138.08 (iPh), 137.99 (iPh x2), 137.92 (iPh), 130.08 (br, *o*-CH^{Ns}), 128.58, 128.57, 128.50, 128.16, 128.07, 128.01, 127.96, 127.93, 127.82, 127.79 (Ar), 123.71 (*m*-CH^{Ns}), 86.77 (C-3), 86.31 (br, C-1) 77.77, 77.76 (C-4 and C-5), 75.79 (CH_2^{Bn}), 75.25 (CH_2^{Bn}), 74.85 (CH_2^{Bn}), 73.50 (CH_2^{Bn}), 69.66 (CH_2^{EtOMe}), 69.02 (C-6), 66.67 (CH_2^{EtOMe}), 58.87 (CH_3). *Unknown signal at 58.75. The sample on which the attached HSQC spectrum was recorded from had an impurity of glycosyl trichloroacetamide. The ^{1}H-NMR, ^{13}C-NMR and COSY is however of the pure title compound. HMBC 5.51/86.31 (H-1 $^{1}J_{C1\text{-}H1}$=157.4 Hz). HRMS (MALDI+): Calculated for $C_{44}H_{46}N_2O_{12}SNa^+$ m/z 849.2664; found m/z 849.2658. $[\alpha]_D^{298}$ = +19.9° (c=2.6, $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl 2-methoxyethyl nosylcarbamate (25)



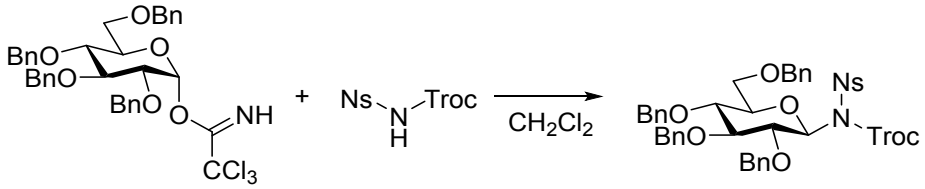
Carmbamate 12 (44 mg, 0.15 mmol) was added to a stirring solution of 1β (55 mg, 82 µmol) in dry DCM (2 mL) under a nitrogen atmosphere. The reaction was stirred overnight and evaporated onto celite. The crude product was purified by flash column chromatography (1:5 EtOAc/Heptane) to yield the desired product, 25 (30 mg, 54 µmol, 45 %). Spectral data for the β-anomer was in accordance with previously reported in this SI for an identical compound. α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.95 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.39 – 7.18 (m, Ar^{Bn}, 20H), 6.39 (d, H-1α, *J* = 8.1 Hz, 1H), 4.99 – 4.76 (m, CH_2^{Bn}, 4H), 4.68 – 4.49 (m, H-3, CH_2^{Bn}, 5H), 4.27 (ddd, H-5, *J* = 10.1, 5.3, 1.9 Hz, 1H), 4.21 – 4.15 (m, $CH_2^{CH2CH2OCH3}$, 2H), 4.31 (t, H-2, *J* = 8.3 Hz, 1H), 3.66 (dd, H-6a, *J* = 10.6, 2.0 Hz, 1H) 3.65 – 3.57 (m, H-6b, H-4, 2H), 3.29 (m, $CH_2^{CH2CH2OCH3}$, 2H), 3.19 (s, CH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.61 (C=0), 150.35 (*i*Ns), 145.21 (*i*Ns), 138.74 (*i*Ns), 138.34 (*i*Bn), 137.98 (*i*Bn), 137.21 (*i*Bn), 129.81 (Ar^{Ns}), 128.66, 128.62, 128.59, 128.56, 128.53, 128.47, 128.28, 128.19, 128.16, 128.12, 128.10, 127.99, 127.96, 127.85, 127.83, 127.77 (Ar^{Bn}), 123.88 (Ar^{Ns}), 82.70 (C-3), 82.46 (C-1), 78.75 (C-2), 77.97 (C-4), 74.91 (CH_2^{Bn}), 74.72 (C-5), 74.66 (CH_2^{Bn}), 73.99 (CH_2^{Bn}), 73.85 (CH_2^{Bn}), 69.93 ($CH_2^{CH2CH2OCH3}$), 69.68 (C-6), 66.95 ($CH_2^{CH2CH2OCH3}$), 58.72 (CH_3). HRMS (MALDI+): Calculated for $C_{44}H_{46}N_2O_{12}SNa^+$ m/z 849.2664; found m/z 849.2648. $[\alpha]_D^{298}$ = +17.9° (c=2.6, $CHCl_3$)

2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl *tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (27)



Tert-butyl *N*-(4-nitrophenyl)sulfonylcarbamate 13 (87 mg, 0.29 mmol) was added to a stirring solution of 1α (99 mg, 0.14 mmol) in CH_2Cl_2 (4 mL). The reaction was stirred over night and evaporated onto celite. The crude product was purified by flash column chromatography (EtOAc/heptane 1:9 to 2:9), yielding the desired product, 27, (α/β 15:85, 94 mg, 79 %) as a colorless syrup. The yield and NMR data can only be approximated due to a lot of overlapping, broad signals from small amounts of unidentified byproducts. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 – 7.91 (m, Ar^{Ns}, 4H), 7.41 – 7.08 (m, Ar, 20H), 5.63 (d, unidentified impurity, *J* = 7.5 Hz, 0.19H), 5.53 (d, unidentified impurity, *J* = 9.4 Hz, 0.21H), 5.47 (d, H-1, *J* = 9.4 Hz, 1H), 5.01 – 4.44 (m, H-2, 4 x CH_2^{Bn}, 9H), 4.17 – 4.06 (m, unidentified impurity, 0.41H), 3.84 – 3.52 (m, H-3, H-4, H-5, H-6a, H-6b, several unidentifiable impurities, 7H), 1.33 (s, *tert*-butyl, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.21 (*i*Ar^{Ns}), 145.95 (*i*Ar^{Ns}), 138.51 (*i*Ar^{Bn}), 137.17 (*i*Ar^{Bn}), 138.07 (*i*Ar^{Bn}), 137.92 (*i*Ar^{Bn}), 128.70, 128.61, 128.59, 128.20, 128.12, 128.03, 127.88, 127.85, 127.75 (15 x Ar^{Bn}, 1 x Ar^{Ns}), 123.81 (Ar^{Ns}), 86.71 (C-3), 86.28 (C^{tBu}), 85.92 (C-1), 77.86, 77.84, 77.72 (C-2, C-4, C-5) 75.87 (CH_2^{Bn}), 75.28 (CH_2^{Bn}), 75.00 (CH_2^{Bn}), 73.49 (CH_2^{Bn}), 69.06 (C-6), 27.96 (CH_3). *C=O signal is missing. HRMS (MALDI+): Calculated for $C_{45}H_{48}N_2O_{11}SNa^+$ m/z 847.28710; found m/z 847.28565. $[\alpha]_D^{298}$ = +17.9° (c=2.6, $CHCl_3$)

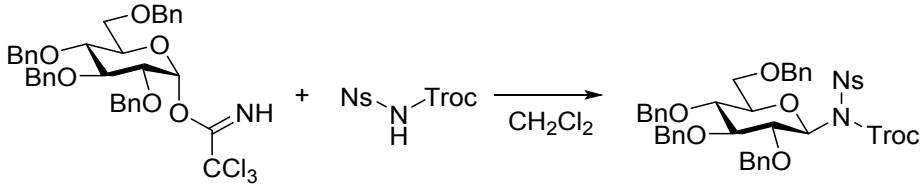
2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl 2,2,2-trichlorethyl *N*-(4-nitrophenyl)sulfonylcarbamate (26)



Following general procedure 2 with glucosyl donor 1α, (103.2 mg, 0.15 mmol), acceptor 15, (103.6 mg, 0.27 mmol). The reaction was stirred for 1 hr when no starting material was left. The eluent for flash column chromatography was 1:10 EtOAc/heptane to 1:4 yielding the desired glycoside 26, as a pure β-anomer (115.6 mg, 85 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (d, Ar^{Ns}, *J* = 9.0 Hz, 2H), 7.97 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.38 – 7.30 (m, Ar, 18H), 7.26 – 7.21 (m, Ar, 2H), 5.59 (d, H-1, *J* = 9.3 Hz, 1H), 5.02 – 4.94 (m, 2H), 4.99 (d, CH_2^{Bn} *J* = 11.0, 1H), 4.96 (d, CH_2^{Bn} *J* = 11.0, 1H), 4.90-4.86 (m, CH_2^{Bn}, 2H) 4.78 – 4.46 (m, 2 x CH_2^{Bn}, CH_2^{Troc}, H-2, 7H), 3.82 (t, H-3 *J* = 9.1 Hz, 1H), 3.77 (dd, H-6a, *J* = 10.5, 1.6 Hz, 1H), 3.74 – 3.71 (m, H-4, 1H), 3.63 (m, H-5, H-6b, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.58 (*i*Ph^{Ns}), 150.16 (br, C=O), 144.47 (*i*Ph^{Ns}), 138.34 (*i*Ph^{Bn}), 137.97 (*i*Ph^{Bn}), 137.83 (*i*Ph^{Bn}), 137.76 (*i*Ph^{Bn}), 130.01 (br, Ar^{Ns}), 129.98-127.79 (Ar), 123.93 (Ar^{Ns}), 93.60 (CCl_3^{Troc}), 86.83 (C-3), 86.33 (br, C-1), 77.83 (C-4), 77.59 (C-5), 76.08 (CH_2^{Bn}), 75.84 (CH_2^{Bn}), 75.23 (CH_2^{Bn}), 74.78 (CH_2^{Troc}), 73.54 (CH_2^{Bn}), 69.25 (C-

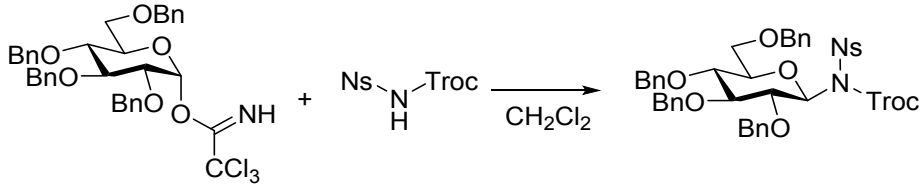
6). HRMS (MALDI+): Calculated for $C_{43}H_{41}Cl_3N_2O_{11}SNa^+$ m/z 921.1389; found m/z 921.1381. $[\alpha]_D^{298}$ = +12.3° (c=4.3, $CHCl_3$) Rf = 0.5 (3:7 EtOAc/heptane)

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl 2,2,2-trichlorethyl *N*-(4-nitrophenyl)sulfonylcarbamate (26)



The reaction was performed following general procedure 3 with glucosyl donor 1α (199 mg, 0.291 mmol) and carbamate 15 (159 mg, 0.422 mmol) in 1.5 mL DCM. The reaction was stirred for 0.75 hr until no starting material was left according to crude NMR. The reaction was added 10 mL Et_2O and extracted with 1M aq. NaOH (10 mL) and dried over $MgSO_4$. The crude was evaporated onto celite and purified by flash column chromatography to yield the desired product 26 as a mixture of anomers (78%, α/β 6:94). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (d, Ar^{Ns}, *J* = 8.8 Hz, 2H), 7.97 (d, Ar^{Ns}, *J* = 8.9 Hz, 1H), 7.41 – 7.30 (m, 18H), 7.25 (m, Ar^{Ns}, 2H), 6.49 (d, H-1α, *J* = 7.8 Hz, 1H), 5.61 (d, H-1β, *J* = 9.3 Hz, 1H), 5.01 (d, Ar^{Bn}α/β, *J* = 11.1 Hz, 2H), 4.97 (d, Ar^{Bn}α/β, *J* = 11.1 Hz, 1H), 4.94 – 4.43 (m, 12 x H-Ar^{Bn}α/β, 4 x H-CH_2^{Troc}α/β, H-2β, H-3α, H-4α, 19H), 4.38 (ddd, H-5α, *J* = 8.2, 4.5, 2.1, 1H), 4.22 (t, H-2α, *J* = 7.9 Hz, 1H), 3.87 – 3.59 (m, H-3β, H-4β, H-5β, H-6β a+b, H-6α a+b, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.54 (*i*Ar^{Ns}α), 150.49 (*i*Ar^{Ns}β), 150.41 (C=Oα), 150.06 (br, C=Oβ), 144.90 (*i*Ar^{Ns}α), 144.38 (*i*Ar^{Ns}β), 138.42 (*i*Ar^{Bn}α), 138.25 (*i*Ar^{Bn}β), 138.08 (*i*Ar^{Bn}α), 137.88 (*i*Ar^{Bn}β), 137.81 (*i*Ar^{Bn}α), 137.73 (*i*Ar^{Bn}β), 137.66 (*i*Ar^{Bn}β), 136.95 (*i*Ar^{Bn}α), 129.92 (br, *i*Ar^{Ns}β), 129.41 (*i*Ar^{Ns}α), 128.56-127.70 (24 x Ar^{Bn}α/β), 124.09 (*i*Ar^{Ns}α), 123.84 (*i*Ar^{Ns}β), 93.50 (CCl_3β), 93.47 (CCl_3α), 86.75 (C-3β), 86.27 (br, C-1β), 83.52 (C-1α), 81.98 (C-3α), 78.43 (C-2α), 77.84 (C-4α), 77.74 (C-4β), 77.50 (C-5β), 76.22 ($CH_2^{Bn/Troc}$α), 75.99 ($CH_2^{Bn/Troc}$β), 75.76 ($CH_2^{Bn/Troc}$β), 75.14 ($CH_2^{Bn/Troc}$β), 75.08 ($CH_2^{Bn/Troc}$α), 74.69 ($CH_2^{Bn/Troc}$β), 74.45 ($CH_2^{Bn/Troc}$α), 74.21($CH_2^{Bn/Troc}$α), 73.76 ($CH_2^{Bn/Troc}$α), 73.46 ($CH_2^{Bn/Troc}$β), 69.98 (C-6α), 69.16 (C-6β). HRMS (MALDI+): Calculated for $C_{43}H_{41}Cl_3N_2O_{11}SNa^+$ m/z 921.1389; found m/z 921.1366. $[\alpha]_D^{298}$ = +15.8° (c=0.68, $CHCl_3$) Rf = 0.34 (1:4 EtOAc/heptane)

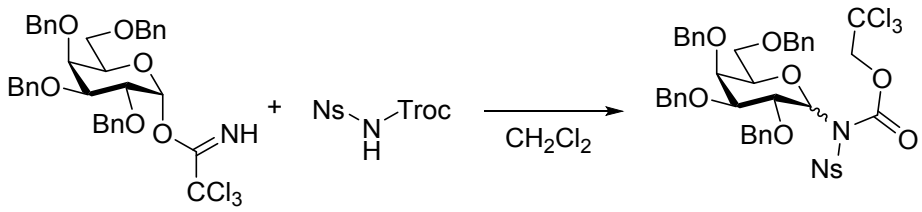
2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl 2,2,2-trichlorethyl nosylcarbamate (26)



The reaction was performed following general procedure 1 with glucosyl donor 1α, (159 mg, 0.23 mmol) in 3 mL DCM, carbamate 15, (163 mg, 0.43 mmol). The reaction was stirred for 1 hr when no starting material was left. The eluent for flash column chromatography was 1:10 EtOAc/heptane to

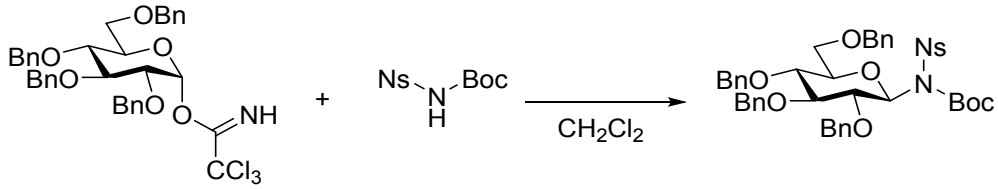
1:4 yielding the desired glycoside 26, (198 mg, 95 %). Spectral data and Rf-value match the previously reported data for the identical compound in this SI.

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl 2,2,2-trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbamate (S22)



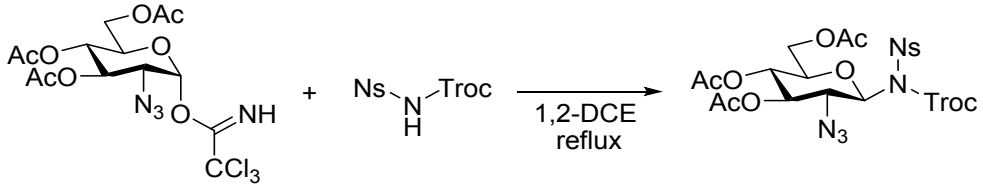
2,2,2-trichloroethyl nosylcarbamate 15 (71 mg, 0.19 mmol) was added to a stirring solution of 2α (66 mg, 0.097 mmol) in DCM (2 mL) following general glycosylation procedure 2. The reaction was stirred for 3 hr until all starting material was consumed. The crude product was purified by flash column chromatography (1:10 EtOAc/heptane to 1:3) to yield the desired product S22 as a mixture of anomers (79 mg, 0.087 mmol, 90%, α/β 26:74). α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.91 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.31 (m, Ar, 20H), 6.57 (d, H-1, *J* = 7.9 Hz, 1H), 4.95 (d, CH_2^{Bn}, *J* = 11.5 Hz, 1H), 4.79 – 4.74 (m, $CH_2^{Bn/Troc}$, 3H), 4.69 (d, $CH_2^{Bn/Troc}$, *J* = 11.1 Hz, 1H), 4.66 (d, $CH_2^{Bn/Troc}$, *J* = 11.9 Hz, 1H), 4.61 (d, $CH_2^{Bn/Troc}$, *J* = 11.5 Hz, 1H), 4.54 – 4.41 (m, $CH_2^{Bn/Troc}$, H-2, H-3, H-5, 6H), 4.00 (dd, H-4, *J* = 3.0, 1.4 Hz, 1H), 3.69 (dd, H-6a, *J* = 9.7, 6.9 Hz, 1H), 3.48 (dd, H-6b, *J* = 9.6, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.73 (*i*Ph^{Ns}), 150.42 (C=O), 145.22 (*i*Ph^{Ns}), 138.53 (*i*Ph^{Bn}), 138.46 (*i*Ph^{Bn}), 137.93 (*i*Ph^{Bn}), 137.56 (*i*Ph^{Bn}), 129.41 (Ar^{Ns}), 128.67-127.78 (15 x Ar^{Bn}), 124.12 (Ar^{Ns}), 93.60 (CCl_3), 84.30 (C-1), 79.47 (C-3), 76.32 ($CH_2^{Bn/Troc}$), 75.82 (C-2), 75.33 (C-5), 74.98 ($CH_2^{Bn/Troc}$), 74.78 ($CH_2^{Bn/Troc}$), 73.88 (C-4), 73.82 ($CH_2^{Bn/Troc}$), 72.78 ($CH_2^{Bn/Troc}$), 70.18 (C-6). HRMS (MALDI+): Calculated for $C_{43}H_{41}Cl_3N_2O_{11}SNa^+$ m/z 921.1389; found m/z 921.1362. $[\alpha]_D^{298}$ = +12.5° (c=0.961, $CHCl_3$) Rf = 0.50 (3:7 EtOAc/heptane) β-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, Ar^{Ns}, *J* = 8.5 Hz, 2H), 7.98 (d, Ar^{Ns}, *J* = 8.4 Hz, 2H), 7.43 – 7.29 (m, Ar^{Bn}, 20H), 5.54 (d, H-1, *J* = 9.3 Hz, 1H), 4.96 (td, *J* = 11.8, 8.3 Hz, 3H), 4.81 (d, *J* = 1.7 Hz, 2H), 4.75 – 4.70 (m, 1H), 4.67 – 4.61 (m, 2H), 4.60 – 4.47 (m, 3H), 3.99 (d, *J* = 2.7 Hz, 1H), 3.83 (t, *J* = 6.3 Hz, 1H), 3.73 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.70 (dd, *J* = 9.5, 6.4 Hz, 1H), 3.61 (dd, *J* = 9.4, 6.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.40 (*i*Ph^{Ns}), 150.18 (br, C=O), 144.62 (*i*Ph^{Ns}), 138.52 (*i*Ph^{Bn}), 138.01 (*i*Ph^{Bn}), 137.99 (*i*Ph^{Bn}), 137.71 (*i*Ph^{Bn}), 129.80 (Ar^{Ns}), 128.59-127.69 (15 x Ar^{Bn}), 123.78 (Ar^{Ns}), 93.52 (CCl_3), 86.70 (br, C-1), 84.82 (C-3), 76.70 (C-5), 75.86 (CH_2^{Bn}), 75.16 (br, C-2), 75.06 (CH_2^{Troc}), 74.64 (CH_2^{Bn}), 73.60 (C-4, CH_2^{Bn}, 2C), 72.87 (CH_2^{Bn}), 68.96 (C6). $Rf_{\alpha\text{-anomer}}$ = 0.62 (3:7 EtOAc/heptane) $Rf_{\beta\text{-anomer}}$ = 0.57 (3:7 EtOAc/heptane) HRMS (MALDI+): Calculated for $C_{43}H_{41}Cl_3N_2O_{11}SNa^+$ m/z 921.1389; found m/z 921.1378. $[\alpha]_D^{298}$ = +6.2° (c=2.78, $CHCl_3$) Rf = 0.44 (3:7 EtOAc/heptane)

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl *tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (27)



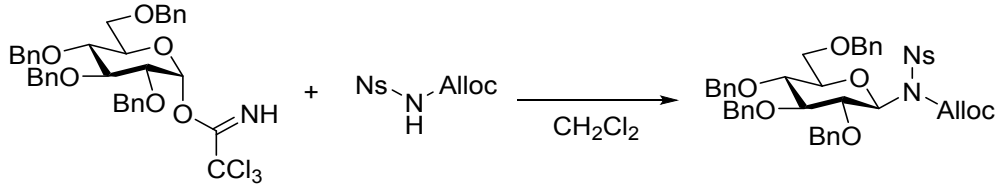
Following general procedure 3 with glucosyl donor 1α, (216 mg, 0.32 mmol), acceptor 13, (142 mg, 0.47 mmol). The reaction was stirred for 4 hr until no starting material was left. The eluent for flash column chromatography was 1:10 EtOAc/heptane to 1:3 yielding the desired glycoside 27, as a pure β-anomer (87 mg, 33 %). NMR-data is in accordance with previously reported for an identical compound in this SI.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl 2,2,2-trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbonate (S23)



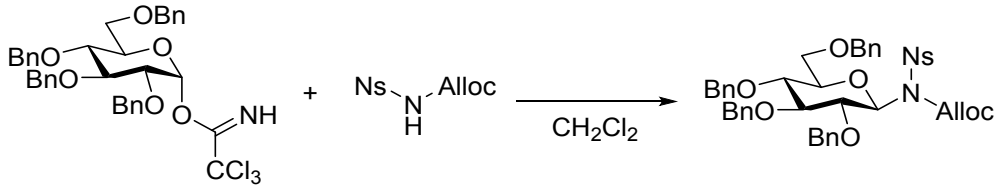
Carbonate 15 (119 mg, 0.314 mmol) was added to a stirring solution of trichloroacetimidate 5 (97 mg, 0.21 mmol) in 1,2-dichloroethane (1 mL). The reaction was stirred under reflux for 3.25 hr before the reaction was allowed to cool down and Et_2O (20 mL) was added. The reaction was extracted with 1M aq. NaOH (2 x 10 mL) and was evaporated onto celite. The crude product was purified by flash column chromatography (1:5 EtOAc/heptane to 1:3), yielding the desired product, S23, as a colorless syrup (100 mg, 70 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 8.25 (d, Ar^{Ns}, *J* = 8.5 Hz, 2H), 5.49 (d, H-1, *J* = 9.9 Hz, 1H), 5.25 (t, H-3, *J* = 9.0 Hz, 1H), 5.09 – 5.02 (m, H-4, 1H), 4.77 (m, H-2, CH_2^{Troc}, 3H), 4.23 (m, H-6a, H-6b, 2H), 3.89 (apprt. d, H-5, *J* = 9.7 Hz, 1H), 2.11 (s, CH_3^{Ac}, 3H), 2.07 (s, CH_3^{Ac}, 3H), 2.04 (s, CH_3^{Ac}, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.35 ($C{=}O^{Ac}$), 169.80 ($C{=}O^{Ac}$), 169.50 ($C{=}O^{Ac}$), 150.87 (*i*Ar^{Ns}), 149.6 (br, $C{=}O^{Carbamate}$), 143.87 (*i*Ar^{Ns}), 130.21 (br, Ar^{Ns}), 124.15 (Ar^{Ns}), 93.30 (CCl_3), 84.58 (br, C-1), 76.35 (CH_2^{Troc}), 75.20 (C-5), 74.30 (C-3), 67.80 (C-4), 61.62 (C-6), 60.41 (br, C-2), 20.74 (CH_3^{Ac}), 20.59 (CH_3^{Ac}), 20.54 (CH_3^{Ac}). HRMS (MALDI+): Calculated for $C_{21}H_{22}N_5O_{13}SNa^+$ m/z 711.9893; found m/z 711.9877. $[\alpha]_D^{298}$ = –0.607° (c=4.28, $CHCl_3$) Rf = 0.56 (1:1 EtOAc/heptane)

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (28)



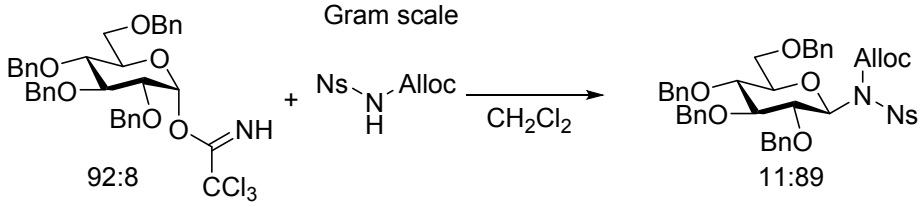
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (133.9 mg, 0.468 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate 1α (207 mg, 0.302 mmol) in CH_2Cl_2 (1.5 mL). The reaction was stirred for 4 hr, added Et_2O (10 mL) and extracted with 1M aq. NaOH (2 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude product was purified by flash column chromatography, yielding the desired product, 28, as a clear syrup (159 mg, 65 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (br s, Ar^{Ns}, 2H), 8.00 (d, Ar^{Ns}, *J* = 8.3 Hz, 2H), 7.38 – 7.20 (m, Ar^{Bn}, 20H), 5.73 (ddt, CH^{allyl}, *J* = 16.4, 10.5, 5.8 Hz, 1H), 5.53 (d, H-1, *J* = 9.3 Hz, 1H), 5.27 (dd, CH_2^{allyl}, *J* = 17.1, 1.4 Hz, 1H), 5.20 (dd, CH_2^{allyl}, *J* = 10.5, 1.3 Hz, 1H), 4.98 (d, CH_2^{Bn}, *J* = 10.9 Hz, 1H), 4.94 (d, CH_2^{Bn}, *J* = 10.9 Hz, 1H), 4.90 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.87 (d, CH_2^{Bn}, *J* = 10.1 Hz, 1H), 4.71 – 4.46 (m, H-2, CH_2^{Bn}, CH_2^{allyl}, 7H), 3.83 – 3.60 (m, H-3, H-4, H-5, H-6a, H-6n, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.30 (C=O), 144.93 (*i*Ar^{Ns}), 138.21 (*i*Ar), 137.95 (*i*Ar), 137.88 (2 x *i*Ar), 137.73 (*i*Ar), 130.24 (CH^{allyl}), 129.92 (br, Ar^{Ns}), 128.52- 127.70 (12 x Ar^{Bn}), 123.67 (Ar^{Ns}), 120.01 (CH_2^{allyl}), 86.74 (br, C-3), 86.13 (br, C-1) 77.71 (br, C-2, C-3, C-5), 75.87 (CH_2^{Bn}), 75.17 (CH_2^{Bn}), 74.79 (CH_2^{Bn}), 73.42 (CH_2^{Bn}), 68.96 (C-6), 68.26 (br, CH_2^{allyl}). HRMS (MALDI+): Calculated for $C_{44}H_{44}N_2O_{11}SNa^+$ m/z 831.25580; found m/z 831.25521. $[\alpha]_D^{298}$ = +26.5° (c=0.66, $CHCl_3$) Rf = 0.44 (3:7 EtOAc/heptane)

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (28)



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (125 mg, 0.437 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate 1α (207 mg, 0.302 mmol) in CH_2Cl_2 (1.5 mL). The reaction was stirred for 1.25 hr, added Et_2O (10 mL) and extracted with 1M aq. NaOH (2 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude product was purified by flash column chromatography (EtOAc/heptane 1:10 to 1:3), yielding the desired product, 28, as a clear syrup (152 mg, 62 %). The NMR-data is identical to what was previously reported in this SI for an identical compound. HRMS (MALDI+): Calculated for $C_{44}H_{44}N_2O_{11}SNa^+$ m/z 831.25580; found m/z 831.25496. $[\alpha]_D^{298}$ = +26.5° (c=0.33, $CHCl_3$)

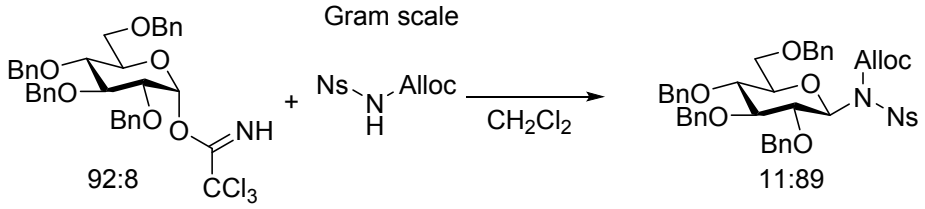
2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (28)



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (1.30 g, 4.54 mmol) was added to a stirring solution of 1α (2.1 g, 3.07 mmol) in CH_2Cl_2 (16 mL). The reaction was stirred for 2 hr, added Et_2O (100 mL) and extracted with 1M aq. NaOH (2 x 50 mL), washed with brine (1 x 50 mL) dried over $MgSO_4$. The crude

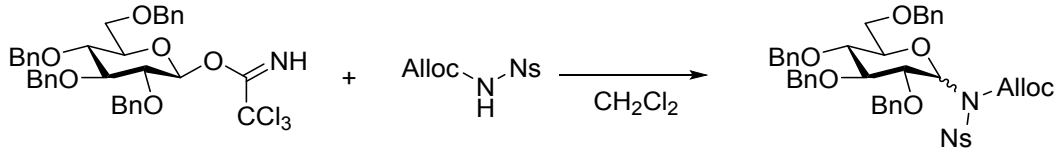
product 28 was (2.16 g, 87 % as a mixture of anomers α/β 11:89) was used further in the next step without any further purification. The NMR-data is identical to what was previously reported in this SI for an identical compound.

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (28)



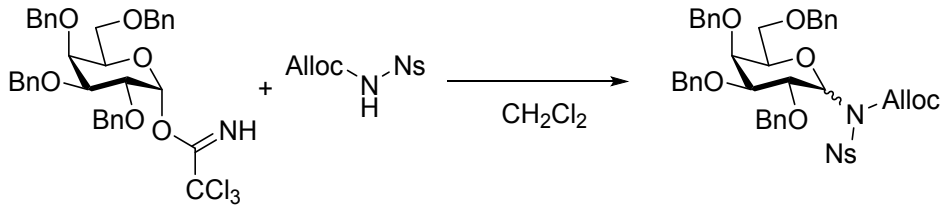
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (1.40 g, 4.90 mmol) was added to a stirring solution of 1α (2.25 g, 3.28 mmol) in CH_2Cl_2 (32 mL). The reaction was stirred for 2 hr, added Et_2O (100 mL) and extracted with 1M aq. NaOH (2 x 50 mL), washed with brine (1 x 50 mL) dried over $MgSO_4$. The crude product 28 was (2.34 g, 88 % as a mixture of anomers α/β 11:89) was used further in the next step without any further purification. The NMR-data is identical to what was previously reported in this SI for an identical compound.

2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (28)



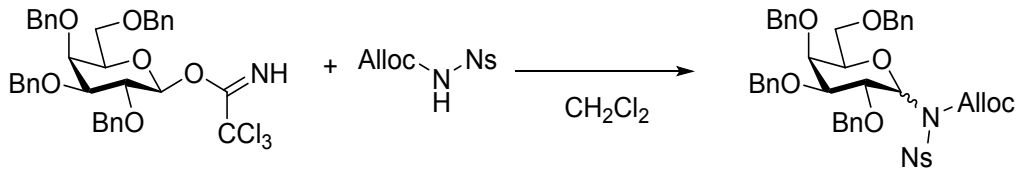
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (135 mg, 0.473 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate 1β (214 mg, 0.313 mmol) in CH_2Cl_2 (1.5 mL). The reaction was stirred for 4.5 hr, added Et_2O (10 mL) and extracted with 1M aq. NaOH (2 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude product was purified by flash column chromatography (EtOAc/heptane 1:10 to 1:3), yielding the desired product, 28, as a clear syrup (198 mg, 62 %, α/β 55:45). The NMR-data for the β-anomer is identical to what was previously reported in this SI for an identical compound. α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, Ar^{Ns}, *J* = 8.8 Hz, 2H), 7.92 (d, Ar^{Ns}, *J* = 8.8 Hz, 2H), 7.39 – 7.17 (m, Ar^{Bn}, 20H), 6.39 (d, H-1, *J* = 8.0 Hz, 1H), 5.76 – 5.58 (m, CH^{allyl}, 1H), 5.32 – 5.11 (m, CH_2^{allyl}, 2H), 4.99 – 4.77 (m, Ar^{Bn}, 6H), 4.74 – 4.37 (m, H-3, Ar^{Bn}, CH_2^{allyl}, 7H), 4.27 (dq, H-5, *J* = 7.6, 2.8, 1.9 Hz, 1H), 4.14 (t, H-2, *J* = 8.2 Hz, 1H), 3.82 – 3.54 (m, H-4, H-6a, H-6b, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.28 (C=O), 150.43 (*i*Ar^{Ns}), 145.30 (*i*Ar^{Ns}), 138.70 (*i*Ar), 138.33 (*i*Ar), 137.98 (*i*Ar), 137.18 (*i*Ar), 130.32 (CH^{allyl}), 129.70 (Ar^{Ns}), 128.68 - 127.79 (12 x Ar^{Bn}), 123.96 (Ar^{Ns}), 120.23 (CH_2^{allyl}), 82.56 (C-3), 82.52 (C-1), 78.72 (C-2), 78.01 (C-4), 76.00 (CH_2^{Bn}), 74.92 (CH_2^{Bn}), 74.63 (C-5) 74.03 (CH_2^{Bn}), 73.55 (CH_2^{Bn}), 70.12 (C-6), 68.61 (CH_2^{allyl}). HRMS (MALDI+): Calculated for $C_{44}H_{44}N_2O_{11}SNa^+$ m/z 831.25580; found m/z 831.25492. $[\alpha]_D^{298}$ = +30.3° (c=0.44, $CHCl_3$)

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (S23)



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (45 mg, 0.159 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl trichloroacetimidate 2α (74 mg, 0.108 mmol) in CH_2Cl_2 (0.6 mL). The reaction was stirred for 2.5 hr, added Et_2O (10 mL), extracted with 1 M aq. NaOH (2 x 10 mL), washed with brine (1 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude was purified by flash column chromatography (heptane/toluene 1:5 to 100 % toluene), yielding the desired product, S23, (α/β 1:3 , 69 mg, 79 %) as a colorless syrup. α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, Ar^{Ns}, *J* = 8.9 Hz, 1H), 7.83 (d, Ar^{Ns}, *J* = 8.9 Hz, 1H), 7.31 – 7.12 (m, 20H), 6.43 (d, H-1, *J* = 7.7 Hz, 1H), 5.54 (ddt, CH^{allyl}, *J* = 17.3, 10.4, 6.0 Hz, 1H), 5.14 – 5.04 (m, CH_2^{allyl}, 2H), 4.94 – 4.32 (m, H-2, H-3, H-5, 8 x CH_2^{Bn}, 2 x CH_2^{allyl}, 13H), 3.91 (dd, H-4, *J* = 3.0, 1.4 Hz, 1H), 3.60 (dd, H-6a, *J* = 9.6, 6.7 Hz, 1H), 3.41 (dd, H-6b, *J* = 9.6, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.38 (C=O), 150.29 (*i*Ar^{Ns}), 145.54 (*i*Ar^{Ns}), 138.68 (iAr^{Bn}), 138.55 (iAr^{Bn}), 137.98 (iAr^{Bn}), 137.71 (iAr^{Bn}), 130.4 (CH^{allyl}) 128.69 (Ar^{Ns}), 127.73-123.86 (12 x Ar^{Bn}), 120.12 (Ar^{Ns}), 83.47 (C-1), 79.52 (C-2/C-3/C-5), 75.72 (C-2/C-3/C-5), 74.92 (C-2/C-3/C-5), 74.76 (CH_2^{Bn}), 74.63 (CH_2^{Bn}), 73.99 (CH_2^{Bn}), 73.85 (C-4), 72.82 (CH_2^{Bn}), 70.18 (C-6), 68.51 (CH_2^{allyl}). β-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (br d, Ar^{Ns}, *J* = 8.6 Hz, 2H), 7.94 (br d, Ar^{Ns}, *J* = 8.5 Hz, 2H), 7.37 – 7.17 (m, Ar^{Bn}, 20H), 5.64 – 5.51 (m, CH^{allyl}, 1H), 5.43 (d, H-1, *J* = 9.2 Hz, 1H), 5.21 – 5.10 (m, $CH2^{allyl}$, 2H), 4.99 – 4.38 (m, H-2, 8 x CH_2^{Bn}, CH_2^{allyl}, 11H), 3.95 (d, H-4, *J* = 2.7 Hz, 1H), 3.76 (apparent t, H-5, *J* = 6.3 Hz, 1H), 3.69 – 3.61 (m, H-6a, H-3, 2H), 3.58 (dd, H-6b, *J* = 9.3, 6.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.06 (C=O), 150.23 (*i*Ar^{Ns}), 145.02 (*i*Ar^{Ns}), 138.69 (*i*Ar^{Bn}), 138.02 (*i*Ar^{Bn}), 137.98 (*i*Ar^{Bn}), 137.72 (*i*Ar^{Bn}), 130.29 (CH^{allyl}), 129.83 (Ar^{Ns}), 128.57-127.56 (12 x Ar^{Bn}), 123.62 (Ar^{Ns}), 119.55 (CH_2^{allyl}), 86.37 (br, C-1), 84.73 (C-3), 79.52 (C-2), 76.32 (C-5), 74.99 (CH_2^{Bn}), 74.61 (CH_2^{Bn}), 73.64 (C-4), 73.58 (CH_2^{Bn}), 72.84 (CH_2^{Bn}), 68.80 (C-6), 68.16 (CH_2^{allyl}). HRMS (MALDI+): Calculated for $C_{44}H_{44}N_2O_{11}SNa^+$ m/z 831.25580; found m/z 831.25478. $[\alpha]_D^{298}$ (1:5 mixture of α/β-anomers) +18.7° (c=1.4, $CHCl_3$) Rf = 0.47 (3:7 EtOAc/heptane)

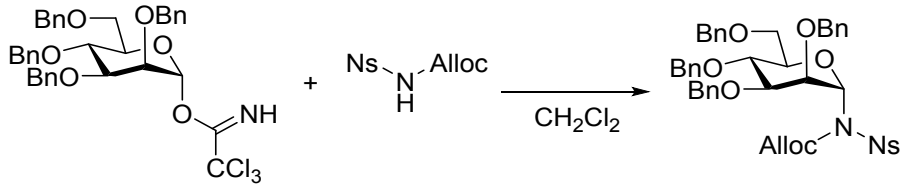
2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (S23)



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (111 mg, 0.389 mmol) was added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl trichloroacetimidate 1α (169 mg, 0.247 mmol) in CH_2Cl_2 (1.5 mL). The reaction was stirred for 2.5 hr, added Et_2O (10 mL), extracted with 1 M aq. NaOH (2 x 10 mL), washed with brine (1 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude was purified by flash column chromatography (heptane/toluene 1:5 to 100 % toluene),

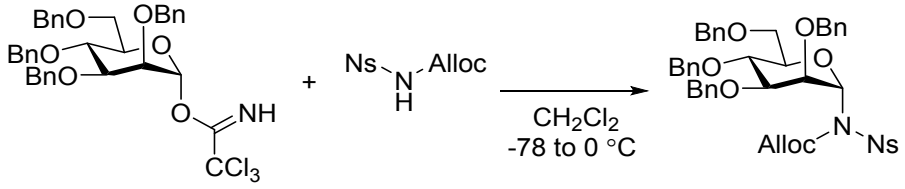
yielding the desired product, S23, (α/β 4:1 , 134 mg, 67 %) as a colorless syrup. The NMR data is in accordance with previously reported data for the same compound. HRMS (MALDI+): Calculated for $C_{44}H_{44}N_2O_{11}SNa^+$ m/z 831.25580; found m/z 831.25486. $[\alpha]_D^{298}$ (4:1 mixture of α/β-anomers) +25.3° (c=1.9, $CHCl_3$)

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (S24)



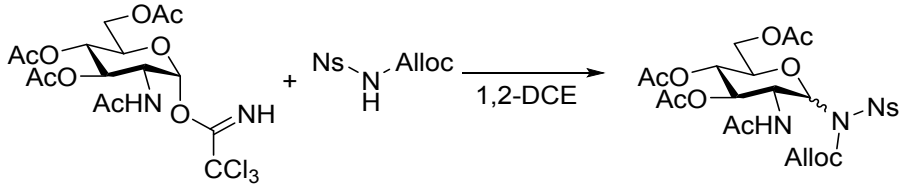
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (83 mg, 0.290 mmol) was added to a stirring solution of 3α (131 mg, 0.191 mmol) in CH_2Cl_2 (1.0 mL). The reaction was stirred for 6.5 hr, added Et_2O (15 mL), extracted with 1 M aq. NaOH (2 x 10 mL), washed with brine (1 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, S24, (122 mg, 79 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.90 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.38 – 7.29 (m, Ar^{Bn}, 14H), 7.26 – 7.06 (m, Ar^{Bn}, 4H), 6.26 (d, H-1, *J* = 9.3 Hz, 1H), 5.64 (ddt, CH^{allyl}, *J* = 16.4, 10.9, 5.8 Hz, 1H), 5.20 (dd, CH_2^{allyl}, *J* = 17.2, 1.5 Hz, 1H), 5.09 (d, CH_2^{allyl}, *J* = 10.5 Hz, 1H), 4.82 – 4.70 (m, H-2, CH_2^{Bn}, 2H), 4.60 (d, CH_2^{Bn}, *J* = 12.1 Hz, 1H), 4.55 – 4.34 (m, H-4, CH_2^{allyl}, CH_2^{Bn}, 10H), 4.05 – 3.93 (m, H-3, H-6a, 2H), 3.72 – 3.57 (m, H-5, H-6b, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 151.45 ($C{=}O^{carbamate}$), 150.25 (*i*Ar^{Ns}), 145.37 (*i*Ar^{Ns}), 138.14 (2 x *i*Ar^{Bn}), 137.86 (*i*Ar^{Bn}), 137.84 (*i*Ar^{Bn}), 130.47 (CH^{allyl}), 129.98 (Ar^{Ns}), 128.62, 128.58, 128.57, 128.55, 128.27, 128.05, 128.04, 128.02, 127.98, 127.85 (15 x Ar^{Bn}), 123.68 (Ar^{Ns}), 119.80 (CH_2^{allyl}), 81.27 (C-1), 76.77 (C-4), 75.79 (C-5), 74.97 (C-3), 73.53 (2 x CH_2^{Bn}), 73.31 (C-2), 72.00 (2 x CH_2^{Bn}), 71.66 (2 x CH_2^{Bn}), 68.94 (C-6), 68.19 (CH_2^{allyl}). HMBC *J* (C1-H1) = 162.4 Hz HRMS (MALDI+): Calculated for $C_{37}H_{38}Cl_3NO_7Na^+$ m/z 831.22580; found m/z 831.25554. $[\alpha]_D^{298}$ = 10.5° (c=0.76, $CHCl_3$) Rf = 0.43 (1:3 acetone/cyclohexane)

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (S24)



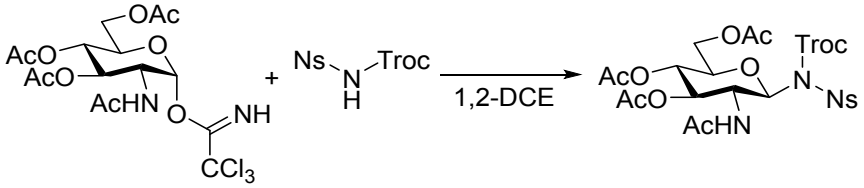
Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (99.9 mg, 0.349 mmol) was added to a stirring solution of 1α (157 mg, 0.230 mmol) in CH_2Cl_2 (1.0 mL). The reaction was stirred overnight, added Et_2O (15 mL), extracted with 1 M aq. NaOH (2 x 10 mL), washed with brine (1 x 10 mL), dried over $MgSO_4$ and evaporated onto celite. The crude was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, S24, (122 mg, 66 %) as a colorless syrup. NMR data is in accordance with previously reported for an identical compound in this SI.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α/β-D-glucopyranosyl allyl *N*-(4-nitrophenyl)sulfonylcarbamate (S25)



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate 14 (170 mg, 0.594 mmol) was added to a stirring solution of 6 (191 mg, 0.389 mmol) in 1,2-DCE (2.0 mL). The reaction was stirred for 1.5 hr when no starting material was left. The crude product was evaporated onto celite and purified by flash column chromatography (1:5 to 1:0 EtOAc/heptane), yielding the desired product, S25 (104 mg, 0.169 mmol, 44 %, α/β 19:81) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 – 8.27 (m, Ar^{Ns}α/β, 4H), 8.21 – 7.99 (m, Ar^{Ns}α/β, 4H), 6.56 (d, H-1α, *J* = 8.3 Hz, 1H), 6.38 – 6.29 (m, NHβ, 1H), 6.14 (d, NHα, *J* = 7.1 Hz, 1H), 5.85 – 5.58 (m, CH^{allyl}α/β, H-1β, H-3α, 4H), 5.37 – 5.19 (m, H-3β, CH_2^{Allyl}α/β, 5H), 5.16 (dd, H-4α, *J* = 10.0, 9.0 Hz, 1H), 5.08 (t, H-4β, *J* = 9.8 Hz, 2H), 4.94 (apparent q, H-2β, *J* = 9.9 Hz, 3H), 4.73 – 4.41 (m, H-2α, CH_2^{Allyl}α/β, 5H), 4.32 – 4.15 (m, H-6aα/β, H-6bβ, 3H), 4.13 (ddd, H-5α, *J* = 10.0, 4.3, 2.3 Hz, 1H), 4.08 (dd, H-6αb, *J* = 11.8, 2.4 Hz, 1H), 3.90 (ddd, H-5β, *J* = 10.1, 4.4, 2.6 Hz, 3H), 2.06 (s, CH_3α, 3H), 2.05 (s, CH_3β, 3H), 2.03 (s, CH_3β, 3H), 2.02 (s, CH_3α, 3H), 2.01 (s, CH_3α/β, 6H), 1.91 (s, CH_3β, 3H), 1.79 (s, CH_3α, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.08 (C=Oα), 171.19 (C=Oβ), 171.07 (C=Oβ), 170.86 (C=Oα), 170.76 (C=Oα), 170.58 (C=Oβ), 169.46 (C=Oα), 169.37 (C=Oβ), 153.12 (*i*Ar^{Ns}α), 150.65 (*i*Ar^{Ns}β), 150.41 ($C=O^{carbamate}$β) 145.04 (*i*Ar^{Ns}α), 144.49 (*i*Ar^{Ns}β), 130.56 (CH^{allyl}β), 130.08 (CH^{allyl}α), 130.01 (Ar^{Ns}β), 129.92 (Ar^{Ns}α), 124.06 (Ar^{Ns}β), 123.98 (Ar^{Ns}α), 121.04 (CH_2^{allyl}α), 119.40 (CH_2^{allyl}β), 84.63 (C-1β), 82.53 (C-1α), 74.66 (C-5β), 72.98 (C-3β), 72.33 (C-3α), 71.80 (C-5α), 69.16 (CH_2^{allyl}α), 68.60 (CH_2^{allyl}β), 68.06 (C-4β), 67.98 (C-4α), 61.92 (C-6α), 61.86 (C-6β), 52.22 (C-2α), 51.28 (C-2β), 23.11 (CH_3β), 22.82 (CH_3α), 20.90 (CH_3α), 20.81 (CH_3α), 20.77 (CH_3β), 20.73 (CH_3β), 20.68 (CH_3α), 20.62 (CH_3β). *$C=O^{carbamate}$ of the α-anomer is too faint to distinguish from noise. HRMS (MALDI+): Calculated for $C_{24}H_{29}N_3O_{14}SNa^+$ m/z 638.12624; found m/z 638.12592. $[\alpha]_D^{298}$ +17.2° (c=5.1, $CHCl_3$) Rf = 0.13 (1:3 acetone/cyclohexane)

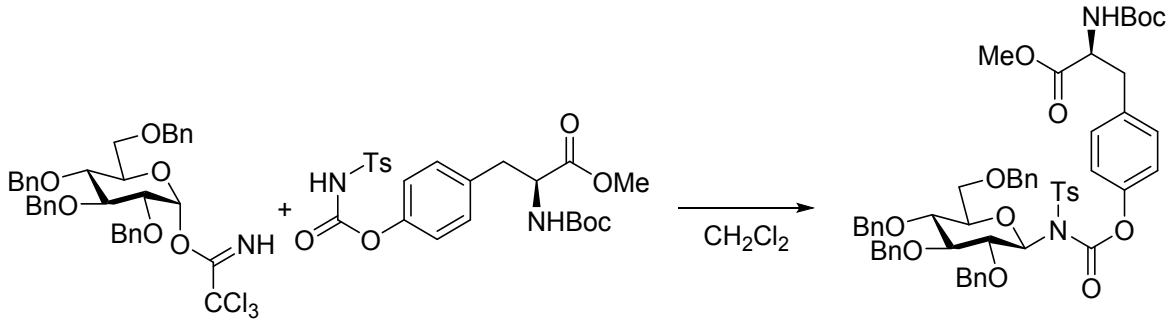
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α/β-D-glucopyranosyl 2,2,2-trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbamate (S26)



2,2,2-trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbamate 15 (162 mg, 0.429 mmol) was added to a stirring solution of 6 (140.6 mg, 0.286 mmol) in 1,2-DCE (2.0 mL). The reaction was stirred for 1.5 hr when no starting material was left. The crude product was evaporated onto celite and purified by flash column chromatography (1:2 to 1:0 EtOAc/heptane), yielding the desired product, S26 (90 mg,

0.128 mmol, 45 %, α/β 5:95) as a colorless syrup containing a small amount of glycosyl acceptor. The α-anomer has only been partially assigned due to a too low signal to noise ratio and broad peaks. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.40 – 8.28 (m, Ar^{Ns}α/β, 2H), 8.24 – 8.17 (m, Ar^{Ns}α/β, 2H), 6.62 (d, H-1α, *J* = 8.2 Hz, 1H), 6.41 (d, NHβ, *J* = 9.1 Hz, 1H), 6.25 (d, NHα, *J* = 6.8 Hz, 0H), 5.83 (dd, H-3α, *J* = 10.1, 9.0 Hz, 0H), 5.62 (d, H-1β, *J* = 8.6 Hz, 1H), 5.30 (t, H-3β, *J* = 9.3 Hz, 1H), 5.11 (m, H-2β, H-4β, H-4α, 3H), 4.86 (d, CH_2^{Troc}α/β, *J* = 12.1 Hz, 1H), 4.80 – 4.57 (m, CH_2^{Troc}α/β, H-2α, 3H), 4.25 (dd, H-6aβ, *J* = 12.6, 5.0 Hz, 1H), 4.21 – 4.15 (m, H-6bβ, H-6abα, H-5α, 4H), 3.93 (ddd, H-5β, *J* = 10.1, 5.1, 2.5 Hz, 1H), 2.11 (s, CH_3α, 3H), 2.07 (s, CH_3β, 3H), 2.04 (s, CH_3β, 3H), 2.02 (s, CH_3β, 3H), 2.00 (s, CH_3α, 3H), 1.98 (s, CH_3α, 3H), 1.97 (s, CH_3α, 3H), 1.93 (s, CH_3β, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.61 (C=Oβ), 171.47 (C=Oα), 171.44 (C=Oβ), 171.28 (C=Oα), 170.81 (C=Oα), 170.69 (C=Oβ), 169.49 (C=Oα), 169.33 (C=Oβ), 150.86 (*i*Ar^{Ns}β), 150.82 (*i*Ar^{Ns}α), 149.57 (C=$O^{carbamate}$β), 144.58 (*i*Ar^{Ns}α), 143.77 (*i*Ar^{Ns}β), 130.08 (Ar^{Ns}β), 129.93 (Ar^{Ns}α), 124.45 (Ar^{Ns}α), 124.20 (Ar^{Ns}β), 93.58 (CCl_3α/β), 84.90 (C-1β), 83.33 (C-1α), 76.57 (CH_2^{allyl}β), 76.52 (CH_2^{allyl}α), 74.88 (C-5β), 72.74 (C-3β), 72.41 (C-5α), 72.09 (C-3α), 68.05 (C-4β), 62.18 (C-6α/β), 52.40 (C-2α), 51.35 (C-2β), 23.08 (CH_3β), 22.83 (CH_3α), 22.73 (CH_3α), 20.90 (CH_3β), 20.82 (CH_3α), 20.76 (CH_3β), 20.69 (CH_3α), 20.62 (CH_3β). HRMS (MALDI+): Calculated for $C_{23}H_{26}Cl_3N_3O_{14}SNa^+$ m/z 728.00933; found m/z 728.00902.$[\alpha]_D^{298}$ +32.4° (c=4.8, $CHCl_3$) Rf = 0.80 (100 % EtOAc)

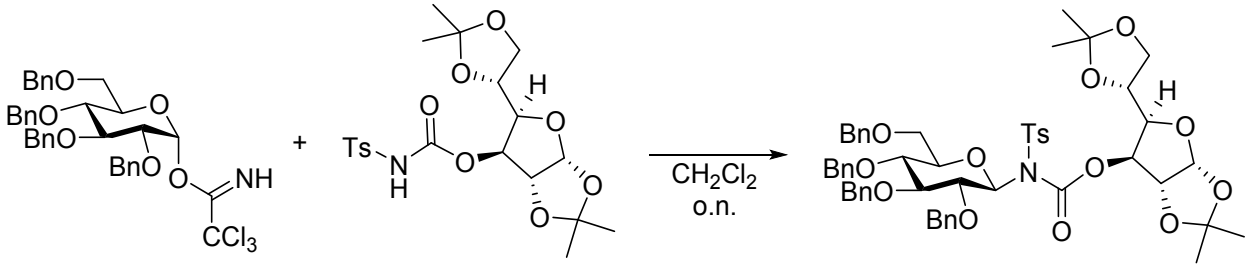
N'-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl) *N*'-tosyl *O*-(*N*-Boc-tyrosine methyl ester) carbamate (18)



16 (213 mg, 0.433 mmol) was added to a stirring solution of 1α (199 mg, 291 mmol) in CH_2Cl_2 (1.5 mL) at room temperature. The reaction was stirred for 4.75 hr and evaporated onto celite. The crude product was purified by flash column chromatography, yielding the desired product, 18 (198 mg, 67%) as a colorless syrup containing a small amount of 16 which has been subtracted from the reported yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 7.88 (m, Ar^{Ts}, 2H), 7.42 – 7.31 (m, Ar^{Bn}, 18H), 7.25 (m, Ar^{Bn}, 2H), 7.11 (d, Ar^{Ts}, *J* = 7.9 Hz, 2H), 7.04 – 6.96 (m, Ar^{Tyr}, 2H), 6.80 (d, Ar^{Tyr}, *J* = 8.1 Hz, 2H), 5.67 (d, H-1, *J* = 9.2 Hz, 1H), 5.02 – 4.81 (m, CH_2^{Bn}, NH^{Boc}, 6H), 4.71 – 4.55 (m, H-2, C*H*-NH, CH_2^{Bn}, 5H), 3.86 – 3.64 (m, H-3, H-4, H-5, H-6a, H-6b, OCH_3, 8H), 3.13 – 2.91 (m, CH_2^{Tyr}, 2H), 2.39 (s, CH_3^{Ts}, 3H), 1.46 (s, CH_3^{Boc}, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.14 (C=O^{Tyr}), 155.12 (C=$O^{carbamate}$), 148.75 (*i*Ar^{Ts}), 144.66 (*i*Ar^{Ts}), 138.38 (*i*Ar^{Bn}), 138.21 (*i*Ar^{Bn}), 138.04 (*i*Ar^{Bn}), 137.95 (*i*Ar^{Bn}) 134.31 (*i*Ar^{Tyr}), 130.41 (*i*Ar^{Tyr}), 130.26 (Ar^{Tyr}), 129.36 (Ar^{Ts}), 128.47 (Ar^{Bn}), 128.43, 128.19, 127.95, 127.80,

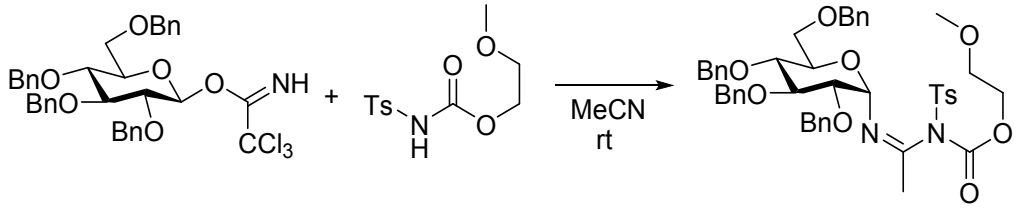
127.72, 126.48 (15 x Ar^{Bn}, Ar^{Ts}), 121.38 (Ar^{Tyr}), 86.60 (C-3), 86.08 (C-1), 80.15 (C^{tertBu}), 78.38 (C-2), 77.74 (C-4), 77.67 (C-5), 75.82 (CH_2^{Bn}), 75.16 (CH_2^{Bn}), 74.81 (CH_2^{Bn}), 73.33 (CH_2^{Bn}), 68.95 (C-6), 54.33 (*C*H-NH), 52.34 (OCH_3), 37.60 (CH_2^{Tyr}), 28.32 (CH_3^{Boc}), 21.66 (CH_3^{Ts}). HRMS (MALDI+): Calculated for $C_{57}H_{62}N_2O_{13}SNa^+$ m/z 1037.38648; found m/z 1037.38521. $[\alpha]_D^{298}$ +7.4° (c=4.2, $CHCl_3$) Rf = 0.53 (1:2 acetone/cyclohexane)

(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) *N*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) *N*-tosyl carbamate (19)



17 (70 mg, 0.154 mmol) was added to a stirring solution of 1α (51 mg, 0.740 mmol) in CH_2Cl_2 (1.5 mL). The reaction was stirred overnight and evaporated *in vacuo*. The crude product was purified by flash column chromatography, yielding the desired product, 19 (47 mg, 0.048 mmol, 64 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.77 (m, Ar^{Ts}, 2H), 7.38 – 7.26 (m, Ar^{Bn}, 18H), 7.23 – 7.18 (m, Ar^{Bn}, 2H), 7.03 (d, Ar^{Ts}, *J* = 17.2 Hz, 2H), 5.53 (d, H-1, *J* = 9.3 Hz, 1H,), 5.50 (d, H-4', *J* = 3.5 Hz, 1H), 5.31 (d, *J* = 2.8 Hz, 1H, H-1'), 4.92 (d, *J* = 11.1 Hz, 1H, Bn-CH_2), 4.86 (d, *J* = 7.5 Hz, 1H, Bn-CH_2), 4.84 (d, *J* = 7.5 Hz, 1H, Bn-CH_2), 4.61 (dq, *J* = 34.2, 11.9, 11.1 Hz, 6H, H-2, Bn-CH_2), 4.02 – 3.97 (m, 1H, H-2'), 3.89 (s, 4H, H-3',H-5', H-6'), 3.75 (ddd, *J* = 26.0, 15.9, 9.2 Hz, 4H, H-3, H-5, H-6), 3.62 (d, *J* = 9.6 Hz, 1H, H-4), 2.34 (s, 3H, Tosyl-CH_3), 1.45 (s, 3H, isopropylidine-CH_3), 1.27 (s, 6H, isopropylidine-CH_3), 1.19 (s, 3H, isopropylidine -CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.42 (C-N), 138.61, 138.49, 138.13 (Ar), 129.54, 128.57, 128.49, 128.45, 128.15, 127.94, 127.84, 127.75, 127.68(Ar-H), 112.44, 109.55 (OCO), 105.21 (C-4'), 86.66 (C-5), 86.32 (C-1), 82.93 (C-5), 79.89 (C-1'), 77.97 (C-4), 77.80 (C-3), 77.41 (C-2), 75.85, 75.21, 74.69, 73.40 (Ar-CH_2), 69.36 (C-6), 67.49 (C-6'), 27.11, 26.74, 26.18, 24.98 (CH_3-isopropylidene), 21.67 (Tosyl-CH_3). HRMS (MALDI+): Calculated for $C_{54}H_{61}NO_{14}SNa^+$ m/z 1002.3705; found m/z 1002.3695. $[\alpha]_D^{298}$ +12.0° (c=1.0, $CHCl_3$)

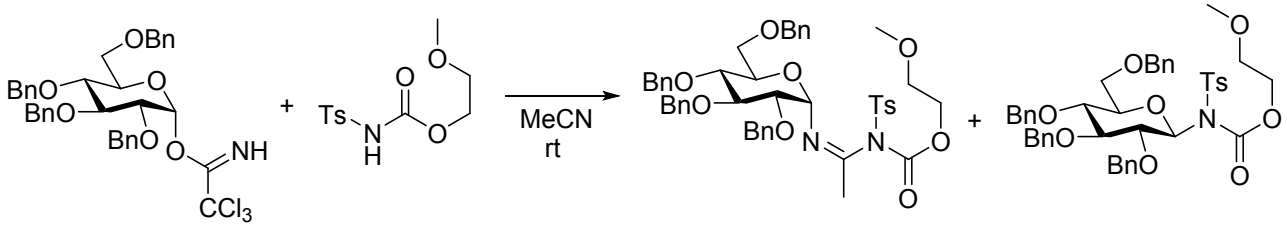
2-Methoxyethyl *N*-(-1-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-imino)ethyl) *N*-tosyl carbamate (33)



7 (50 mg, 0.182 mmol) was added to a stirring solution of 1β (50 mg, 0.073 mmol) in MeCN (2.5 mL). The reaction was stirred overnight and evaporated *in vacuo*. The crude product was purified by flash

column chromatography (1:5 EtOAc/heptane), yielding the desired product, 33 (53 mg, 0.063 mmol, 86%) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, Ar^{Ts}, 2H), 7.37 – 7.27 (m, Ar, 18H), 7.16 (m, Ar, 2H), 7.10 (d, Ar^{Ts}, *J* = 8.0 Hz, 2H), 6.28 (d, H-1, *J* = 6.9 Hz, 1H), 4.73 (d, CH_2^{Bn}, *J* = 11.5 Hz, 1H), 4.69 (d, CH_2^{Bn}, *J* = 11.1 Hz, 1H), 4.62 (d, CH_2^{Bn}, *J* = 11.4 Hz, 1H), 4.55 (d, CH_2^{Bn}, *J* = 12.2 Hz, 1H), 4.50 (m, CH_2^{Bn}, 2H), 4.44 (m, CH_2^{Bn}, 2H), 4.30 – 4.18 (m, H-3, H-5, CH_2, 3H), 4.10 (ddd, CH_2, *J* = 11.9, 5.1, 3.4 Hz, 1H), 3.96 (t, H-2, *J* = 7.2 Hz, 1H), 3.73 – 3.62 (m, H-4, H-6a, 2H), 3.59 (dd, H-6b, *J* = 10.9, 2.1 Hz, 1H), 3.50 – 3.39 (m, CH_2, 2H), 3.27 (s, CH_3^{OMe}, 3H), 2.68 (s, CH_3, 3H), 2.32 (s, CH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.32 (C=N), 155.06 (C=O), 143.30 (*i*Ar), 138.99 (*i*Ar), 138.69 (*i*Ar), 138.61 (*i*Ar), 138.23 (*i*Ar), 137.11 (*i*Ar), 129.45, 128.55, 128.51, 128.48, 128.39, 128.00, 127.97, 127.73, 127.04 ($Ar^{Bn/Ts}$), 82.61 (C-1), 80.69 (C-3), 77.55 (C-4), 77.37 (C-2), 74.16 (CH_2^{Bn}), 74.11 (CH_2^{Bn}), 73.63 (CH_2^{Bn}), 73.58 (CH_2^{Bn}), 73.31 (C-5), 69.68 (CH_2), 68.89 (C-6), 66.83 (CH_2), 58.86 (OCH_3), 23.26 (CH_3), 21.62 (CH_3). HRMS (MALDI+): Calculated for $C_{47}H_{52}NO_{10}SNa^+$ m/z 859.3235; found m/z 859.3234.

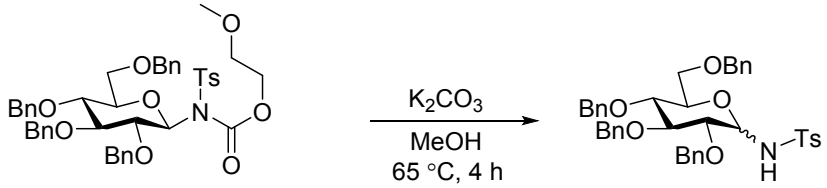
2-Methoxyethyl *N*-(-1-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-imino)ethyl) *N*-tosyl carbamate (33) and 20



7 (69 mg, 0.254 mmol) was added to a stirring solution of 1α (73 mg, 0.107 mmol) in MeCN (3 mL). The reaction was stirred overnight and evaporated *in vacuo*. The crude product was purified by flash column chromatography (1:5 EtOAc/heptane), yielding two products, 33 (30 mg, 33 %) and 20 (55 mg, 65 %). NMR-data is in accordance with previously reported for identical compounds.

N-deprotections

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *p*-toluenesulfonamide (S26)



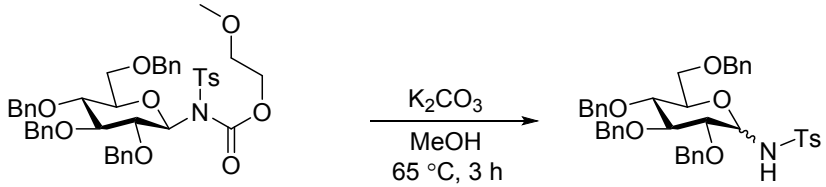
K_2CO_3 (46 mg, 0,33 mmol) was added to a solution of 20 (131 mg, 0.16 mmol) in dry MeOH (10 ml). The resulting mixture was stirred under reflux for 4 h. After this time, the crude product was evaporated *in vacuo* onto celite. The residue was purified by flash column chromatography (50:1 Toluene/Acetone + 1 % HCOOH) to yield two anomers (α/β 1:1.7) of the desired product S26 (73

mg, 0.11 mmol, 65 %) as a colorless syrup (anomer *α*) and a white solid (anomer *β*) [25]. Anomer α ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, Ar^{Ts}, *J*= 8.2 Hz, 2H), 7.36-7.17 (m, Ar, 18H), 7.14 (d, Ar^{Ts}, *J*= 8.2 Hz, 2H), 7.10-7.06 (m, Ar, 2H), 5.34 (d, *N*H, *J*= 2.7 Hz, 1H), 5.31 (dd, H-1, *J*= 5.2, 2.7 Hz, 1H), 4.84 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.74 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.72 (d, CH_2^{Bn}, *J*= 10.7 Hz, 1H), 4.51 (broad s, CH_2^{Bn}, 2H), 4.46 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 4.42 (d, CH_2^{Bn}, *J*= 10.7 Hz, 1H), 4.37 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 3.67 (dd, H-2, *J*= 9.0, 5.2 Hz, 1H), 3.62 (t, H-4, *J*= 9.0 Hz, 1H), 3.57 (t, H-3, *J*= 9.0 Hz, 1H), 3.45 (dd, H-6, *J*= 10.7, 2.6 Hz, 1H), 3.41 (broad ddd, H-5, *J*~ 9.0, 2.6, 1.9 Hz, 1H), 2.95 (dd, H-6', *J*= 10.7, 1.9 Hz, 1H), 2.33 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.78 (iC^{Ts}), 138.48 (iPh), 138.18 (iPh), 137.98 (iPh), 137.36 (iPh), 136.91 (iC^{Ts}), 129.60 (CH^{Ts}, 2C), 128.74, 128.56, 128.52, 128.36, 128.30, 128.04, 128.02, 128.01, 127.91, 127.87, 127.72 (CH^{Ts}, Ar), 82.09 (C-3), 79.73 (C-1), 77.66 (C-2), 76.99 (C-4), 75.83 (CH_2^{Bn}), 75.22 (CH_2^{Bn}), 73.56 (CH_2^{Bn}), 72.75 (CH_2^{Bn}), 70.50 (C-5), 67.39 (C-6), 21.64 (CH_3) ppm*. HRMS (MALDI+): Calculated for $C_{41}H_{43}NO_7SNa^+$ m/z 716.2658; found m/z 716.2650. $[\alpha]_D^{298}$= +54.00° (c=1.100, $CHCl_3$). Anomer β ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76-7.73 (m, Ar^{Ts}, 2H), 7.34-7.20 (m, Ar, 18H), 7.16-7.13 (m, Ar^{Ts}, 2H), 7.13-7.10 (m, Ar, 2H), 4.92 (d, *N*H, *J*= 9.8 Hz, 1H), 4.87 (d, CH_2^{Bn}, *J*= 11.0 Hz, 1H), 4.82-4.78 (m, CH_2^{Bn}, 2H), 4.76 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.72 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.64 (dd, H-1, *J*= 9.8, 8.9 Hz, 1H), 4.49 (d, CH_2^{Bn}, *J*= 10.9 Hz, 1H), 4.39 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 4.31 (d, CH_2^{Bn}, *J*= 12.2 Hz, 1H), 3.66 (t, H-3, *J*= 8.9 Hz, 1H), 3.60-3.54 (m, H-4, H-6, 2H), 3.33-3.27 (m, H-5, H-6', 2H), 3.27 (t, H-2, *J*= 8.9 Hz, 1H), 2.33 (s, CH_3, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.48 (iC^{Ts}), 138.64 (iPh), 138.44 (iPh), 138.14 (iPh), 138.00 (iPh), 137.65 (iC^{Ts}), 129.48 (CH^{Ts}, 2C), 128.68, 128.66, 128.58, 128.54, 128.16, 127.99, 127.97, 127.93, 127.91, 127.88, 127.44 (CH^{Ts}, Ar), 85.74 (C-3), 84.37 (C-1), 80.53 (C-2), 77.36 (C-4), 76.53 (C-5), 75.94 (CH_2^{Bn}), 75.06 (CH_2^{Bn}), 75.04 (CH_2^{Bn}), 73.73 (CH_2^{Bn}), 68.32 (C-6), 21.64 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{41}H_{43}NO_7SNa^+$ m/z 716.2658; found m/z 716.2652. $[\alpha]_D^{298}$= +10.57° (c=0.965, $CHCl_3$). mp= 145-147°C.

* 11 overlapping Ar sygnals with 11 reported in ^{13}C NMR of α anomer

* 11 overlapping Ar sygnals with 11 reported in ^{13}C NMR of β anomer

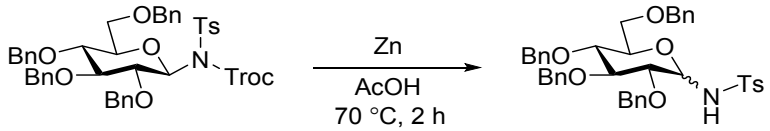
2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *p*-toluenesulfonamide (S26)



K_2CO_3 (1.08 g, 7.81 mmol) was added to a solution of 20 (109 mg, 0.14 mmol) in dry MeOH (10 ml). The resulting mixture was stirred under reflux for 3 h. After this time, the solvent was removed *in vacuo* and the residue diluted with DCM (25 ml). The organic phase was washed with 0.5 M HCl (15 ml), dried over Na_2SO_4 end evaporated to dryness. The crude product was purified by flash column chromatography (50:1→30:1 Toluene/Acetone) to yield two anomers (*α/β* 1:0.9) of the desired product S26 (62 mg, 0.09 mmol, 65 %) as a colorless syrup (anomer *α*) and a white solid (anomer *β*)

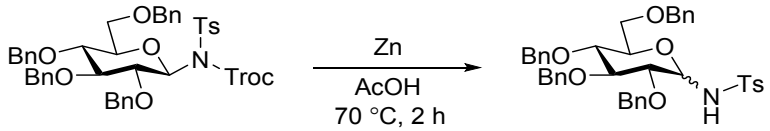
[25]. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *p*-toluenesulfonamide (S26)



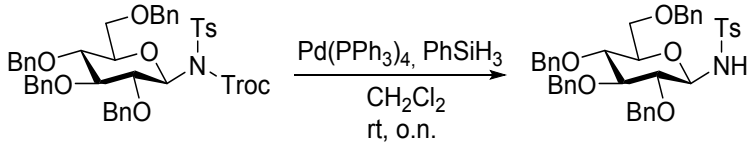
Zn powder (67 mg, 1.03 mmol) was added to a solution of 21 (111 mg, 0.13 mmol) in AcOH (1.1 mL). The resulting suspension was stirred at 70°C for 2 h. After completion the reaction mixture was filtered and the filtrate was evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (100:1→10:1 Toluene/Acetone) to yield two anomers (*α/β* 1:2.6) of the desired product S27 (73 mg, 0.11 mmol, 82 %) as a colorless syrup (anomer *α*) and a white solid (anomer *β*) [26]. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *p*-toluenesulfonamide (S26)



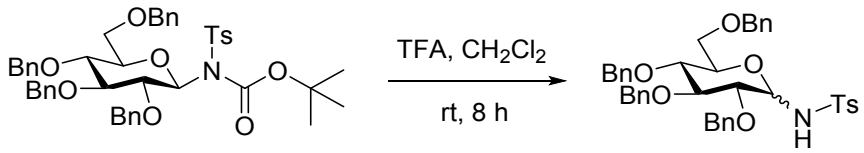
Zn powder (421 mg, 6.44 mmol) was added to a solution of 21 (α/β 1:4.3, 700 mg, 0.81 mmol) in AcOH (7.0 mL). The resulting suspension was stirred at 70°C for 2 h. After completion the reaction mixture was filtered and the filtrate was evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (100:1→10:1 Toluene/Acetone) to yield two anomers (*α/β* 1:1.6) of the desired product S27 (514 mg, 0.74 mmol, 92 %) as a colorless syrup (anomer *α*) and a white solid (anomer *β*) [26]. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl *p*-toluenesulfonamide (S26)



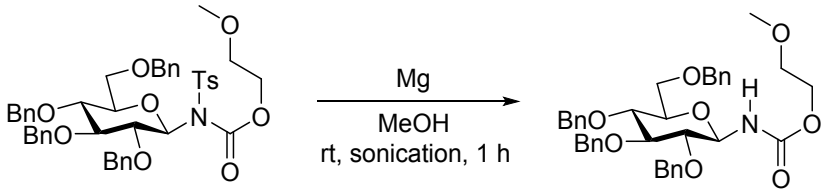
$PhSiH_3$ (0.1 ml, 0.88 mmol) was added to a solution of 21 (172 mg, 0.22 mmol) in dry DCM (3.0 mL) followed by $Pd(Ph_3)_4$ (13 mg, 0.01 mmol). The reaction mixture was stirred at RT overnight and after this time treated with MeOH (2 ml). Then the solution was evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (90:1→40:1 Toluene/Acetone) to yield the *β* anomer of the desired product S28 (136 mg, 0.20 mmol, 89 %) as a white solid [27]. ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl *p*-toluenesulfonamide (S26)



TFA (0.08 ml, 1.05 mmol) was added to a solution of 22 (41 mg, 0.05 mmol) in DCM (2.0 mL). The reaction mixture was stirred at RT for 8 h. After completion the solution was evaporated *in vacuo* onto celite. The crude product was purified by flash column chromatography (100:1→10:1 Toluene/Acetone) to yield two anomers (*α/β* 1:1.8) of the desired product S29 (30 mg, 0.04 mmol, 84 %) as a colorless syrup (anomer *α*) and a white solid (anomer *β*). ^{1}H NMR data is in accordance with the spectrum of the identical compound previously reported in this SI.

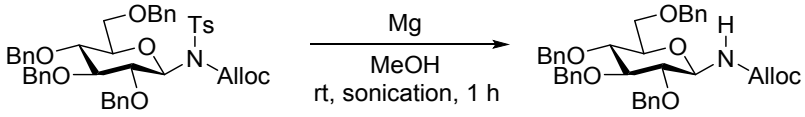
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl 2-methoxyethyl carbamate (S27)



Mg powder (49 mg, 2.00 mmol) was added to a solution of 20 (106 mg, 0.13 mmol) in dry MeOH (1.7 ml). The resulting suspension was sonicated under a nitrogen atmosphere for 1 h. After completion the reaction mixture was diluted with DCM (20 ml) and poured into 0.5 M HCl (10 ml). The organic phase was washed with 1M $NaHCO_3$ (2 x 10 ml), brine (2 x 10 ml) and dried over Na_2SO_4. The crude product was purified by flash column chromatography (3:1→2:1 Heptane/EtOAc) to afford the *β* anomer of the desired compound S27 (68.3 mg, 0.11 mmol, 80 %) as a white solid [28]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40-7.16 (m, Ar, 18H), 7.15-7.07 (m, Ar, 2H), 5.05 (broad d, *N*H, *J*= 9.2 Hz, 1H), 4.91-4.83 (m, H-1, CH_2^{Bn}, 3H), 4.78 (d, CH_2^{Bn}, *J*= 10.8 Hz, 1H), 4.77 (d, CH_2^{Bn}, *J*= 11.3 Hz, 1H), 4.70 (d, CH_2^{Bn}, *J*= 11.3 Hz, 1H), 4.60 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 4.51 (d, CH_2^{Bn}, *J*= 10.8 Hz, 1H), 4.46 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 4.27-4.19 (m, $CH_2^{Carbamate}$, 2H), 3.75-3.65 (m, H-3, H-4, H-6, H-6', 4H), 3.56 (t, $CH_2^{Carbamate}$, *J*= 4.7 Hz, 2H), 3.48 (broad dt, H-5, *J*~ 2.4, 9.2 Hz, 1H), 3.36 (s, CH_3, 3H), 3.30 (t, H-2, *J*= 8.7 Hz, 1H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.68 (broad, C=O), 138.55 (iPh), 138.21 (iPh), 138.02 (iPh), 137.96 (iPh), 128.65, 128.58, 128.54, 128.52, 128.38, 128.15, 128.11, 128.00, 127.96, 127.90, 127.86, 127.84 (Ar), 86.05 (C-3), 81.93 (C-1), 80.66 (C-2), 77.69 (C-4), 76.44 (C-5), 75.84 (CH_2^{Bn}), 75.09 (CH_2^{Bn}), 74.96 (CH_2^{Bn}), 73.72 (CH_2^{Bn}), 70.86 ($CH_2^{Carbamate}$), 68.38 (C-6), 64.44 ($CH_2^{Carbamate}$), 59.08 (CH_3) ppm. HRMS (MALDI+): Calculated for $C_{38}H_{43}NO_8Na^+$ m/z 664.2886; found m/z 664.2872. $[\alpha]_D^{298}$= -4.71° (c=0.765, $CHCl_3$). mp= 104-106 °C.

* 8 overlapping Ar sygnals with 12 reported in ^{13}C NMR

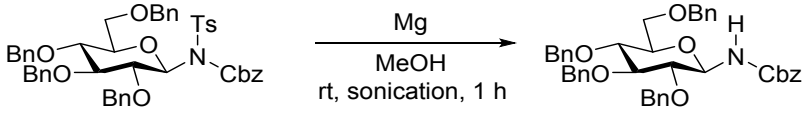
2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl allyl carbamate (S28)



Mg powder (31 mg, 1.29 mmol) was added to a solution of 23 (67 mg, 0.09 mmol) in dry MeOH (1.5 ml). The resulting suspension was sonicated under a nitrogen atmosphere for 1 h. After completion the reaction mixture was diluted with DCM (15 ml) and poured into 0.5 M HCl (6.0 ml). The organic phase was washed with 1M $NaHCO_3$ (2 x 10 ml), brine (2 x 10 ml) and dried over Na_2SO_4. The crude product was purified by flash column chromatography (4:1→2:1 Heptane/EtOAc) to afford the *β* anomer of the desired compound S28 (45 mg, 0.07 mmol, 84 %) as a white solid [28]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37-7.16 (m, Ar, 18H), 7.11-7.04 (m, Ar, 2H), 5.85 (ddt, =CH, *J*= 17.1, 10.6, 5.6 Hz, 1H), 5.25 (ddt, $=CH_2^{trans}$, *J*= 1.5, *J*= 17.1, ^{4}*J*= 1.5 Hz, 1H), 5.17 (broad d, $=CH_2^{cis}$, *J*= 10.6 Hz, 1H), 4.94 (broad d, *N*H, *J*= 8.9 Hz, 1H), 4.87-4.80 (m, H-1, CH_2^{Bn}, 3H), 4.75 (broad d, CH_2^{Bn}, *J*~ 11.1 Hz, 2H), 4.65 (d, CH_2^{Bn}, *J*= 11.4 Hz, 1H), 4.56 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 4.53 (broad t, $=CH_2$, *J*= 5.6 Hz, 2H), 4.47 (d, CH_2^{Bn}, *J*= 10.8 Hz, 1H), 4.41 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 3.71-3.63 (m, H-3, H-4, H-6, H-6‘, 4H), 3.45 (broad dt, H-5, *J*= 9.1, 2.4 Hz, 1H), 3.27 (t, H-2, *J*= 8.6 Hz, 1H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.52 (C=O), 138.52 (iPh), 138.20 (iPh), 137.97 (iPh), 137.90 (iPh), 132.60 (=CH), 128.67, 128.58, 128.53, 128.51, 128.49, 128.16, 127.97, 127.89, 127.86 (Ar), 118.02 (=CH), 86.09 (C-3), 81.86 (C-1), 80.37 (C-2), 77.68 (C-4), 76.38 (C-5), 75.85 (CH_2^{Bn}), 75.07 (CH_2^{Bn}), 74.90 (CH_2^{Bn}), 73.70 (CH_2^{Bn}), 68.32 (C-6), 66.05 (CH_2^{Alloc}) ppm. HRMS (MALDI+): Calculated for $C_{38}H_{41}NO_7Na^+$ m/z 646.2781; found m/z 646.2770. $[\alpha]_D^{298}$= -8.44° (c=0.735, $CHCl_3$). mp= 109-111 °C.

* 11 overlapping Ar sygnals with 11 reported in ^{13}C NMR

2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl benzyl tosylcarbamate (S29)

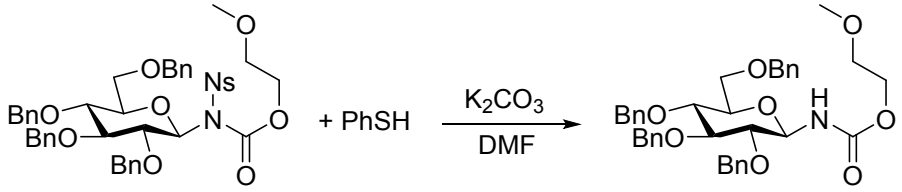


Mg powder (29 mg, 1.20 mmol) was added to a solution of 24 (66 mg, 0.08 mmol) in dry MeOH (1.5 ml). The resulting suspension was sonicated under a nitrogen atmosphere for 1 h. After completion the reaction mixture was diluted with DCM (15 ml) and poured into 0.5 M HCl (6.0 ml). The organic phase was washed with 1M $NaHCO_3$ (2 x 10 ml), brine (2 x 10 ml) and dried over Na_2SO_4. The crude product was purified by flash column chromatography (6:1→5:1 Heptane/EtOAc) to afford the *β* anomer of the desired compound S29 (36 mg, 0.05 mmol, 66 %) as a white solid [28]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35-7.13 (m, Ar, 23H), 7.10-7.04 (m, Ar, 2H), 5.12 (d, CH_2^{Cbz}, *J*= 12.2 Hz, 1H), 5.02 (d, CH_2^{Cbz}, *J*= 12.2 Hz, 1H), 4.96 (broad d, *N*H, *J*= 9.6 Hz, 1H), 4.84-4.81 (m, H-1, CH_2^{Bn}, 3H), 4.75 (d, CH_2^{Bn}, *J*= 10.8 Hz, 1H), 4.73 (d, CH_2^{Bn}, *J*= 11.3 Hz, 1H), 4.63 (d, CH_2^{Bn}, *J*= 11.3 Hz, 1H), 4.56 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 4.47 (d, CH_2^{Bn}, *J*= 10.8 Hz, 1H), 4.42 (d, CH_2^{Bn}, *J*= 12.1 Hz, 1H), 3.71-3.62 (m, H-3, H-4, H-6, H-6‘, 4H), 3.45 (broad d, H-5, *J*= 7.6 Hz, 1H), 3.27 (t, H-2, *J*= 8.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.66 (broad, C=O), 138.52 (iPh), 138.19 (iPh), 137.97 (iPh), 137.84 (iPh), 136.28 (iPh), 128.67, 128.65, 128.59, 128.54, 128.52, 128.49, 128.31, 128.17, 127.98, 127.90, 127.87 (Ar), 86.09 (C-3), 81.89 (C-1), 80.37 (C-2), 77.68 (C-4), 76.40 (C-5), 75.86 (CH_2^{Bn}), 75.08 (CH_2^{Bn}), 74.92

(CH_2^{Bn}), 73.71 (CH_2^{Bn}), 68.33 (C-6), 67.21 (CH_2^{Cbz}) ppm. HRMS (MALDI+): Calculated for $C_{42}H_{43}NO_7Na^+$ m/z 696.2937; found m/z 696.2923. mp= 114-116 °C.

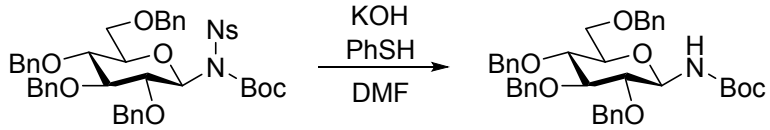
* 14 overlapping Ar sygnals with 11 reported in ^{13}C NMR

2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl 2-methoxyethyl carbamate (S27)



PhSH (7 µL, 65 µmol) was added to a stirred solution of 25 (45 mg, 54 µmol) and K_2CO_3 (14 mg, 0.10 mmol) in dry DMF (1.5 mL) under a nitrogen atmosphere. TLC indicated that the reaction was done after 1 h. Water (5 mL) was added to the reaction mixture and extracted with Et_2O (3 x 10 mL). The combined organic fractions were washed with water (2 x 10 mL) and brine (1 x 10 mL) and dried over $MgSO_4$ and evaporated onto celite. The crude product was purified by flash column chromatography to yield the desired product, S27 (30 mg, 47 µmol, 86 %). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.33-7.26 (m, Ar, 18H), 7.14-7.12 (m, Ar, 2H), 5.09 (m, NH, 1H), 4.89 (m, H-1, CH_2^{Bn}, 3H), 4.81 (m, CH_2^{Bn}, 2H), 4.73 (d, CH_2^{Bn}, *J*=11.3 Hz, 1H), 4.63 (d, CH_2^{Bn}, *J*=12.1 Hz, 1H), 4.54 (d, CH_2^{Bn}, *J*=10.8 Hz, 1H), 4.49 (d, CH_2^{Bn}, *J*=12.1 Hz, 1H), 4.26 (q, CH_2^{EtOMe}, *J*=4.7 Hz, 2H), 3.77-3.67 (m, H-3, H-4, H-5, H-6a, 4H) 3.58 (t, CH_2^{EtOMe}, *J*=4.8 Hz, 2H), 3.50 (m, H-6b, 1H), 3.37 (s, CH_3, 3H), 3.33 (t, H-2, *J*=8.7 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.68 (C=O), 138.53-127.83 (Ar), 86.03 (C-3), 81.92 (C-1), 80.64 (C-2), 77.68 (C-5), 76.42 (C-4), 75.82 (CH_2^{Bn}), 75.07 (CH_2^{Bn}), 74.94 (CH_2^{Bn}), 73.70 (CH_2^{Bn}), 70.85 (CH_2^{EtOMe}), 68.38 (C-6), 64.42 (CH_2^{EtOMe}), 59.06 (CH_3^{EtOMe}). HRMS (MALDI+): Calculated for $C_{38}H_{43}N_2O_8SNa^+$ m/z 664.2881; found m/z 664.2864. $[\alpha]_D^{298}$ = -1.7° (c=1.1, $CHCl_3$)

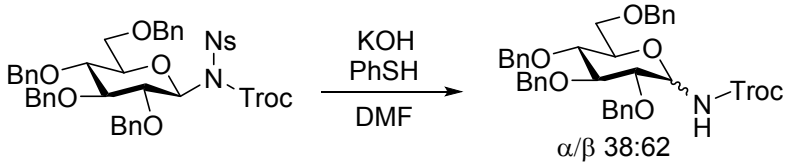
2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl *tert*-butyl carbamate (S30)



PhSH (15 µL, 0.15 mmol) was added to as stirring solution of 27 (41 mg, 0.050 mmol) and KOH (60 mg, 1.1 mmol) in DMF (2 mL). A color change to yellow was observed upon addition of PhSH. The reaction was stirred at rt for 7.5 hr when no starting material was left. All KOH was not dissolved. The reaction mixture was added Et_2O (20 mL) and was washed with 1M aq. HCl (2 x 20 mL) and brine (20 mL). The organic layer was dried with $MgSO_4$ and evaporated *in vacuo*. The crude was purified by flash column chromatography to yield the desired product, S30, (32 mg, 96 %). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36-7.27 (m, Ar, 18H), 7.14-7.13 (m, Ar, 2H), 4.91 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.87 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.86-4.79 (m, H-1, N-*H*, 2 x CH_2^{Bn}, 4H), 4.72 (d, CH_2^{Bn}, *J* = 11.3 Hz, 1H), 4.63 (d, CH_2^{Bn}, *J* = 12.1 Hz, 1H), 4.52 (d, CH_2^{Bn}, *J* = 10.6 Hz, 1H), 4.47 (d, CH_2^{Bn}, *J* = 12.1 Hz, 1H),3.77-3.69 (m, H-3, H-4, H-6a, H-6b, 4H), 3.50-3.48 (m, H-5, 1H), 3.3 (t, H-2, *J*=8.5 Hz, 1H), 1.46 (s, 3 x CH_3^{Boc}, 9H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.88 (C=O), 138.59 (*i*Ph), 138.22 (*i*Ph), 138.05 (*i*Ph), 138.03 (*i*Ph),

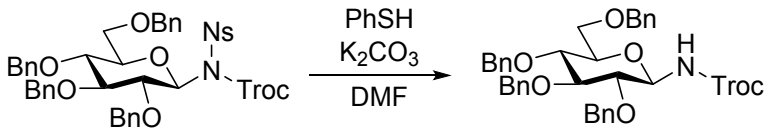
128.65-127.83 (Ar), 86.17 (C-4), 81.50 (br, C-1), 80.57 (br, C-2), 80.32 ($C(CH_3)_3$), 77.77 (C-3), 76.36 (C-5), 75.85 (CH_2^{Bn}), 75.10 (CH_2^{Bn}), 74.92 (CH_2^{Bn}), 73.66 (CH_2^{Bn}), 68.37 (C-6), 28.45 (CH_3^{Boc}). HRMS (MALDI+): Calculated for $C_{39}H_{45}NO_7^+$ m/z 662.3088; found m/z 662.3075. Mp = 118-120 °C $[\alpha]_D^{298}$ = 1.7° (c=0.7, $CHCl_3$) Rf = 0.32 (3:7 EtOAc/Heptane)

2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl 2,2,2-trichloroethylcarbamate (S31)



PhSH (11 mg, 0.10 mmol) and KOH (5.8 mg, 0.10 mmol) was added as a stock solution in DMF (1.8 mL) to carbamate 26 (46 mg, 0.052 mmol). The reaction was stirred over night until no starting material was left. The reaction was added 10 mL Et_2O and extracted with 1M aq. HCl (2 x 10 mL), brine (10 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography to yield the desired product S31 as colorless syrup (23 mg, 63 % estimated by ^{1}H-NMR) as a mixture of anomers (α/β 38:62). The product was contaminated with an unidentified impurity with spectral data very close, but not in accordance, to what would be expected from the corresponding α-anomer of the title compound and the yield is corrected correspondingly. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.19 (m, Ar^{Bn}minor/β 40H), 7.17 – 7.12 (m, Ar^{Bn}minor/β 4H), 5.62 (d, H-1minor *J* = 1.7 Hz, 1H), 5.19 – 5.15 (apprt. d, NHβ 1H), 4.94 – 4.45 (m, NHminor, H-1β, CH_2^{Bn}minor/β, 17H), 4.30 (ddd, H-5minor, *J* = 9.9, 5.2, 1.9 Hz, 1H), 4.08 (t, H-4minor *J* = 9.6 Hz, 1H), 4.01 (dd, H-2α, *J* = 2.6 Hz, 1.7 Hz, 1H), 3.88 (dd, H-3minor *J* = 9.5, 2.9 Hz, 1H), 3.86 (dd, H-6aminor, *J* = 11.8, 5.1 Hz, 1H), 3.79-3.68 (m, H-3β, H-4β, H-6bminor, H-6aβ, H-6bβ, 5H), 3.52 (apprt. d, H-5β *J* = 8.7 Hz, 1H), 3.35 (t, H-2β, *J* = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.01 (C=Oβ), 138.58 (*i*Ar minor), 138.50 (*i*Ar minor), 138.42 (*i*Ar β), 138.32 (*i*Ar minor), 138.13 (*i*Ar β), 138.05 (*i*Ar minor), 137.90 (*i*Ar β), 137.66 (Ar β), 134.53 (*i*Ar minor), 131.78 (Ar minor), 129.12-127.51 (24 x Ar minor/β), 95.31 (CCl_3β), 86.14 (C-3β), 85.88 (C-1 minor), 81.83 (C-1β), 80.32 (C-3 minor), 79.52 (C-2β), 77.64 (C-4β), 76.50 (C-5β), 76.39 (C-2 minor), 75.91 (CH_2^{Bn}β), 75.33 ($CH_2^{Bn/Troc}$ minor), 75.13 (C-4minor), 75.11 (CH_2^{Bn}β), 74.84 (2 x C, CH_2^{Bn}, CH_2^{Troc}β), 73.72 (CH_2^{Bn}β), 73.41 (CH_2^{Bn}minor), 72.90 (C-5minor), 72.24 (2 x C, $CH_2^{Bn/Troc}$ minor), 72.05 ($CH_2^{Bn/Troc}$ minor), 69.33 (C-6minor), 68.24 (C-6β). HRMS (MALDI+): Calculated for $C_{37}H_{38}Cl_3NO_7Na^+$ m/z 736.1606; found m/z 736.1581. Rf = 0.52 (1:19 EtOAc/toluene)

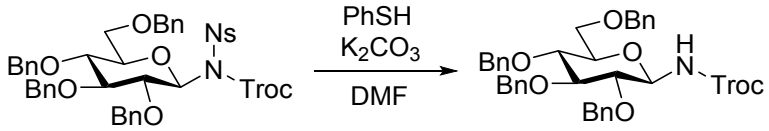
2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl *O*-2,2,2-trichloroethylcarbamate (S31)



K_2CO_3 (46 mg, 0.33 mmol) and PhSH (0.04 mL, 0.39 mmol) was added to a stirring solution of carbamate 26 (139 mg, 0.155 mmol) in DMF (5 mL). The reaction was stirred at rt for 3 hr before

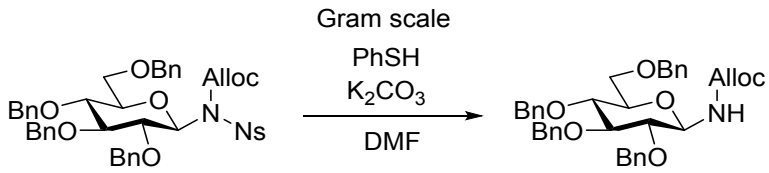
Et_2O (20 mL) was added. The reaction was extracted with 1M aq. HCl (2 x 20 mL), washed with brine (20 mL) and evaporated onto celite. The crude product was purified by flash column chromatography (100 % toluene to 1/10 EtOAc/toluene) to yield the desired product, S31 (64.6 mg, 58 %), as a clear syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, Ar^{Bn}, 18H), 7.16 – 7.12 (m, Ar^{Bn}, 2H), 5.17 (d, NH, *J* = 9.6 Hz, 1H), 4.96 – 4.79 (m, H-1, CH_2^{Bn}, 6H), 4.72 (d, CH_2^{Bn}, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 3.80 – 3.65 (m, H-3, H-4, H-6a, H-6b, 4H), 3.54 – 3.46 (m, H-5, 1H), 3.35 (t, H-2, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.01 (C=O), 138.42 (*i*Ar^{Bn}), 138.13 (*i*Ar^{Bn}), 137.90 (*i*Ar^{Bn}), 137.65 (*i*Ar^{Bn}), 128.83-127.90 (12 x Ar^{Bn}), 95.31 (CCl_3), 86.14 (C-3), 81.83 (C-1), 79.52 (C-2), 77.64 (C-4), 76.50 (C-5), 75.91 (CH_2^{Bn}), 75.11 (CH_2^{Bn}), 74.84 (2 x C, CH_2^{Bn}, CH_2^{Troc}), 73.72 (CH_2^{Bn}), 68.24 (C-6). HRMS (MALDI+): Calculated for $C_{37}H_{38}Cl_3NO_7Na^+$ m/z 736.1606; found m/z 736.1590. $[\alpha]_D^{298}$ = –13.4° (c=2.91, $CHCl_3$) Mp = 112-114 °C Rf = 0.54 (1:9 EtOAc/toluene)

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl *O*-2,2,2-trichloroethylcarbamate (S31)



K_2CO_3 (42 mg, 0.31 mmol) and PhSH (0.09 mL, 0.88 mmol) was added to a stirring solution of carbamate 26 (130 mg, 0.144 mmol) in DMF (5 mL). The reaction was stirred at rt for 20 min before Et_2O (20 mL) was added. The reaction was extracted with 1M aq. HCl (2 x 20 mL), washed with brine (20 mL) and evaporated onto celite. The crude product was purified by flash column chromatography (100 % toluene to 1/10 EtOAc/toluene) to yield the desired product, S31 (59 mg, 57 %), as a clear syrup. ^{1}H- and ^{13}C-NMR data is identical to previously reported in this SI for the similar compound.

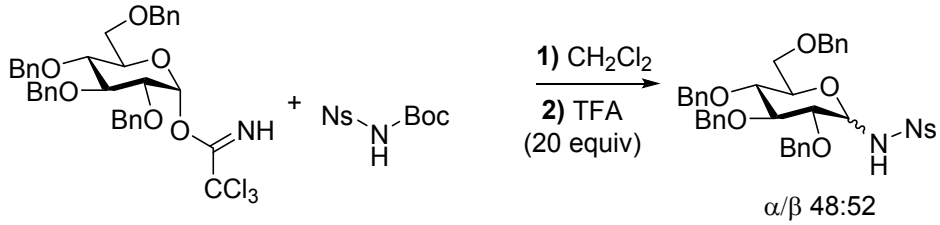
2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl *O*-allyl carbamate (30)



K_2CO_3 (758 mg, 5.49 mmol) and PhSH (0.35 mL, 3.4 mmol) was added to a stirring solution of 28 (2.16 g, 2.67 mmol) in DMF (70 mL). The reaction was stirred at rt for 4 hr min before Et_2O (200 mL) was added. The reaction was extracted with 1M aq. HCl (2 x 50 mL), washed with brine (50 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography (1:9 to 1:1 EtOAc/heptane) to yield the desired product, 30 (1.26 g, 76 %), as a clear syrup with a minor impurity of an unidentified compound in the aromatic region. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, Ar^{Bn}, 18H), 7.16 – 7.08 (m, Ar^{Bn}, 2H), 5.91 (ddt, CH^{allyl}, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.31 (dq, CH_2^{allyl} *J* = 17.2, 1.6 Hz, 1H), 5.22 (d, CH_2^{allyl} *J* = 9.9 Hz, 1H), 5.00 – 4.94 (m, NH, 1H), 4.92 – 4.49 (m, 4 x CH_2^{Bn}, CH_2^{allyl}, 10H), 3.79 – 3.65 (m, H-3, H-4, H-6a, H-6b, 4H), 3.51 – 3.46 (m, H-5, 1H), 3.32 (dd, H-2, *J* =

9.4, 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.53 (*i*Ar^{Bn}), 138.21 (*i*Ar^{Bn}), 137.97 (*i*Ar^{Bn}), 137.89 (*i*Ar^{Bn}), 132.60 (CH^{allyl}), 128.69, 128.60, 128.54, 128.52, 128.17, 127.98, 127.87 (15 x Ar^{Bn}), 118.03 (CH_2^{allyl}), 86.11 (C-3), 81.89 (C-1), 80.38 (C-2), 77.69 (C-4), 76.39 (C-5), 75.87 (CH_2^{Bn}), 75.08 (CH_2^{Bn}), 74.91 (CH_2^{Bn}), 73.72 (CH_2^{Bn}), 68.33 (C-6), 66.07 (CH_2^{allyl}). *C=O^{carbamate} missing. HRMS (MALDI+): Calculated for $C_{38}H_{41}NO_7Na^+$ m/z 646.27752; found m/z 646.27871. $[\alpha]_D^{298}$ = –0.4° (c=0.52, $CHCl_3$) Rf = 0.52 (1:3 acetone/cyclohexane)

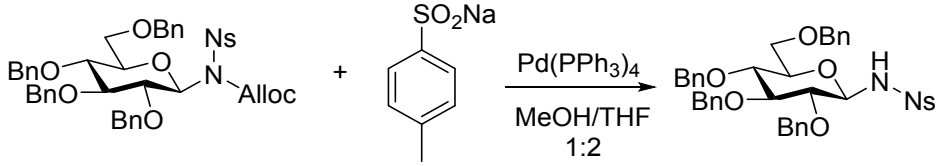
N-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy-2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranoside (29)



α/β 48:52

Tert-butyl *N*-(4-nitrophenyl)sulfonylcarbamate 13 (81 mg, 0.27 mmol) was added to a stirring solution of 1α (92 mg, 0.13 mmol) in CH_2Cl_2 (4 mL). The reaction was stirred for 26 hours, added 15 mL CH_2Cl_2 and extracted with 1 M aq. NaOH (1 x 15 mL), washed with brine (1 x 15 mL) and dried over $MgSO_4$ and reduced to approx. 5 mL and TFA (20 equiv.) was added. The reaction was then stirred overnight and evaporated onto celite. The crude product was purified by flash column chromatography (EtOAc/heptane 1:10 + 5% formic acid), yielding the desired product, 29, (α/β 48:52, 68 mg, 70 %) as a colorless syrup. The NMR spectra of both anomers are identical to previously reported for an identical compound in this SI.

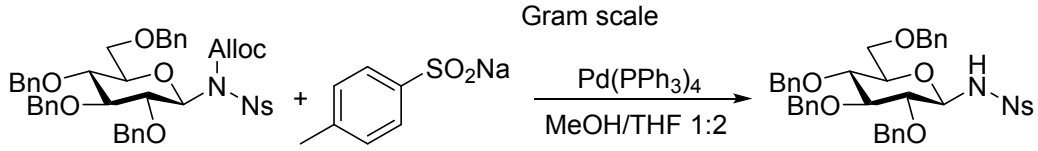
N-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy-2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (29)



Sodium *p*-toluenesulfinate (37 mg, 0.208 mmol) and $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) was added to a stirring solution of 28 (151.6 mg, 0.187 mmol) in MeOH/THF (1:2, 15 mL). The solvent was degassed with an argon balloon for 20 minutes prior to the reaction. The reaction was stirred for 50 minutes until EtOAc (10 mL) was added and the reaction mixture was extracted with NH_4Cl (2 x 10 mL), washed with water (10 mL), brine (10 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, 29 (98 mg, 77 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, Ar^{Ns} *J* = 8.9 Hz, 2H), 8.01 (d, Ar^{Ns}, *J* = 8.9 Hz, 2H), 7.38 – 7.15 (m, Ar^{Bn}, 18H), 7.16 – 7.09 (m, Ar^{Bn}, 2H), 5.07 (d, NH, *J* = 9.1 Hz, 1H), 4.89 (d, CH_2^{Bn}, *J* = 10.9 Hz, 1H), 4.85 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.81 (d, CH_2^{Bn}, *J* = 11.2 Hz, 1H), 4.78 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.74 – 4.68 (m, H-1, CH_2^{Bn}, 2H), 4.50 (d, CH_2^{Bn}, *J* = 10.9 Hz, 1H), 4.39 (d, CH_2^{Bn}, *J* = 12.1 Hz, 1H), 4.36 (d, CH_2^{Bn}, *J* = 12.1 Hz, 1H), 3.71 (t, H-3, *J* = 8.9 Hz, 1H), 3.59 – 3.51 (m, H-4, H-6a, 2H), 3.44 – 3.37 (m, H-5, H-6b, 2H), 3.30 (t, H-2, *J* = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.03 (*i*Ns),

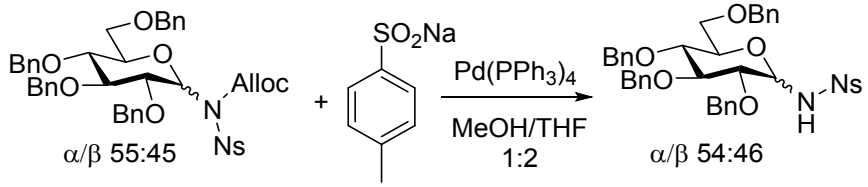
147.14 (*i*Ns), 138.18 (*i*Bn), 137.89 (*i*Bn), 137.56 (*i*Bn), 137.38 (*i*Bn), 128.84, 128.68, 128.66, 128.64, 128.61, 128.58, 128.45, 128.13, 128.07, 128.02, 127.96 (15 x Ar^{Bn}, 1 x Ar^{Ns}), 124.03 (Ar^{Ns}), 85.73 (C-3), 84.10 (C-1), 79.91 (C-2), 77.17 (C-4) 76.45 (C-5), 76.01 (CH_2^{Bn}), 75.15 (CH_2^{Bn}), 75.01 (CH_2^{Bn}), 73.68 (CH_2^{Bn}), 68.36 (C-6). HRMS (MALDI+): Calculated for $C_{40}H_{40}N_2O_9SNa^+$ m/z 747.23467; found m/z 747.23448. $[\alpha]_D^{298}$ = +33.1° (c=0.25, $CHCl_3$) Rf = 0.50 (2:3 EtOAc/heptane)

N-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy-2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (29)



Sodium *p*-toluenesulfinate (567 mg, 3.18 mmol) and $Pd(PPh_3)_4$ (334 mg, 0.289 mmol) was added to a stirring solution of 28 (2.34 g, as 2.89 mmol α/β 11:89) in MeOH/THF (1:2, 230 mL). The solvent was degassed with an argon balloon for 45 minutes prior to the reaction. The reaction was stirred for 1 hr until EtOAc (100 mL) was added and the reaction mixture was extracted with NH_4Cl (2 x 100 mL), washed with water (100 mL), brine (100 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, 29 (1.71 g, 82 %). Spectral data was in accordance with previously reported for an identical compound in this SI.

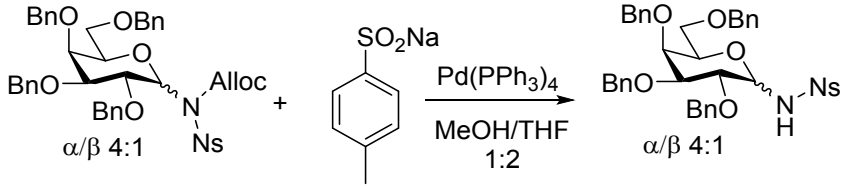
N-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy-2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranoside (29)



Sodium *p*-toluenesulfinate (43 mg, 0.244 mmol) and $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) was added to a stirring solution of 28 (165 mg, as 0.204 mmol α/β 55:45) in MeOH/THF (1:2, 15 mL). The solvent was degassed with an argon balloon for 30 minutes prior to the reaction. The reaction was stirred for 1.5 hr until EtOAc (10 mL) was added and the reaction mixture was extracted with NH_4Cl (2 x 10 mL), washed with water (10 mL), brine (10 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, 29 (128 mg, 86 %). A minor impurity of allyl *p*-tolylsulfone (14 mg) has been subtracted from the reported yield. The NMR-spectrum of the β-anomer is in accordance with what was previously reported in this SI. α-anomer: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (m, Ar^{Ns}, 4H), 7.40 – 7.25 (m, Ar^{Bn}, 18H), 7.10 (m, Ar^{Bn}, 2H), 6.02 (d, NH, *J* = 4.3 Hz, 1H), 5.45 (t, H-1, *J* = 4.8 Hz, 1H), 4.85 (d, CH_2^{Bn}, *J* = 11.0 Hz, 1H), 4.74 (m, CH_2^{Bn}, 2H), 4.61 (s, CH_2^{Bn}, 2H), 4.49 – 4.36 (m, CH_2^{Bn}, 3H), 3.76 (dd, H-2, *J* = 9.3, 5.4 Hz, 1H), 3.65 (t, H-3, *J* = 9.0 Hz, 1H), 3.58 (t, H-4, *J* = 9.3 Hz, 1H), 3.44 (dd, H-6a, *J* = 10.5, 3.5 Hz, 1H), 3.37 – 3.27 (m, H-5, 1H), 3.00 (dd, H-6b, *J* = 10.6, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.00 (*i*Ar^{Ns}), 146.24 (*i*Ar^{Ns}), 138.26 (*i*Ar^{Bn}), 137.84 (*i*Ar^{Bn}), 137.54 (*i*Ar^{Bn}), 136.79 (*i*Ar^{Bn}), 128.56,

128.53, 128.50, 128.48, 128.39, 128.24, 128.04, 128.00, 127.94, 127.90, 127.86 (1 x C, Ar^{Ns}, 15 x C Ar^{Bn}), 124.09 (Ar^{Ns}), 81.51 (C-3), 79.72 (C-1), 77.43 (C-2), 76.81 (C-4), 75.63 (CH_2^{Bn}), 75.15 (CH_2^{Bn}), 73.48 (CH_2^{Bn}), 72.93 (CH_2^{Bn}), 70.86 (C-5), 67.49 (C-6). HRMS (MALDI+): Calculated for $C_{40}H_{40}N_2O_9SNa^+$ m/z 747.23467; found m/z 747.23428. $[\alpha]_D^{298}$ = +39.5° (c=4.2, $CHCl_3$) Rf = 0.31 (1:3 acetone/cyclohexane) Allyl *p*-tolylsulfone:
^{13}C-NMR (126 MHz, $CDCl_3$): 144.79 (*i*Ar^{Ts}), 135.38 (*i*Ar^{Ts}), 129.73 (2 x Ar^{Ts}), 128.71 (2 x Ar^{Ts}), 124.86, 124.62, 60.95, 21.68.

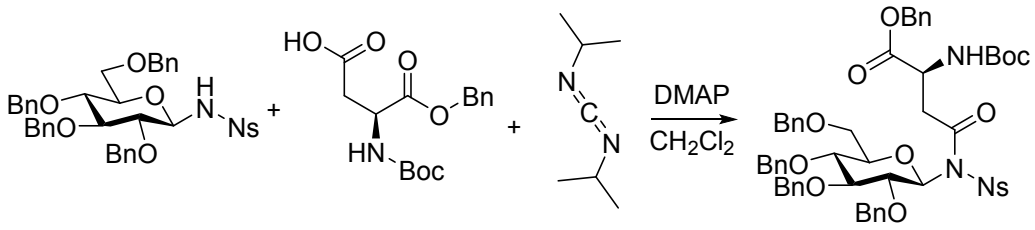
N-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy-2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranoside (S32)



Sodium *p*-toluenesulfinate (33 mg, 0.185 mmol mmol) and $Pd(PPh_3)_4$ (20 mg, 0.020 mmol) was added to a stirring solution of S23 (118 mg, 0.146 mmol as a 4:1 mixture of α/β-anomers) in MeOH/THF (1:2, 10 mL). The solvent was degassed with an argon balloon for 30 minutes prior to the reaction. The reaction was stirred for 1.5 hr until EtOAc (10 mL) was added and the reaction mixture was extracted with NH_4Cl (2 x 10 mL), washed with water (10 mL), brine (2 x 10 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography (1:10 to 1:3 EtOAc/heptane), yielding the desired product, S32, (79 mg, 75 % α/β 4:1) containing a minor impurity of *p*-tolyl sulfone.[29] C-NMR peaks for allyl *p*-tolyl sulfone are reported in the following. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.05 (m, Ar^{Ns}α/β, 4H), 8.01 (s, Ar^{Ns}β, 2H), 7.79 (d, Ar^{Ns}α, *J* = 8.3 Hz, 2H), 7.44 – 7.22 (m, Ar^{Bn}α/β, 30H), 5.97 (d, NHα, *J* = 4.7 Hz, 1H), 5.46 (t, H-1α, *J* = 4.7 Hz, 1H), 5.01 – 4.50 (m, H-1β, CH_2^{Bn}α/β, 13H), 4.37 (m, CH_2^{Bn}α/β, 4H), 4.12 (dd, H-2α, *J* = 9.0, 4.9 Hz, 1H), 3.93 (t, H-4α/β, *J* = 2.5 Hz, 1H), 3.78 (t, H-2β, *J* = 9.0 Hz, 1H) 3.77 – 3.64 (m, H-3α, H-5α, H-3β, 3H), 3.60 (broad apparent t, H-5b, *J* = 6.3 Hz, 1H) 3.48 (dd, H-6aα, *J* = 9.5, 6.7 Hz, 1H), 3.35 (dd, H-6ab, *J* = 9.6, 6.7 Hz, 1H) 3.27 (m, H-6bα, H-6bβ, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.97 (*i*Ar^{Ns}α), 149.76 (*i*Ar^{Ns}β), 147.15 (*i*Ar^{Ns}β), 146.20 (*i*Ar^{Ns}α), 138.19 (*i*Ar^{Bn}α), 138.14 (*i*Ar^{Bn}β), 138.09 (*i*Ar^{Bn}α), 137.95 (*i*Ar^{Bn}β), 137.81 (*i*Ar^{Bn}β), 137.59 (*i*Ar^{Bn}α), 137.52 (*i*Ar^{Bn}β), 137.17 (*i*Ar^{Bn}α), 128.79, 128.63, 128.60, 128.57, 128.51, 128.37, 128.25, 128.12, 128.08, 128.04, 128.00, 127.83, 127.80, 127.54 (30 x C Bnα/β, 4 x Nsα/β), 124.00 (Ar^{Ns}α), 123.78 (Ar^{Ns}β), 84.43 (C-1β), 83.21 (C-3β), 79.51 (C-1α), 77.71 (C-3α), 77.25 (C-2β), 75.15 (C-2α), 74.92 (3 x C, CH_2^{Bn}, C-3β), 74.89 (CH_2^{Bn}), 74.35 (CH_2^{Bn}), 73.60 (2 x C CH_2^{Bn}), 73.44 (4 x C, C-4α/β, CH_2^{Bn}), 72.94 (2 x C, CH_2^{Bn}), 70.70 (C-5α), 68.27 (C-6β), 67.80 (C-6α), 60.94. HRMS (MALDI+): Calculated for $C_{40}H_{40}N_2O_9SNa^+$ m/z 747.23467; found m/z 747.23426. $[\alpha]_D^{298}$ = +15.2° (c=2.9, $CHCl_3$) Rf = 0.56 (2:3 EtOAc/heptane) Allyl *p*-tolylsulfone:
^{13}C-NMR (126 MHz, $CDCl_3$): 144.79 (*i*Ar^{Ts}), 135.38 (*i*Ar^{Ts}), 129.73 (2 x Ar^{Ts}), 128.54 (2 x Ar^{Ts}), 124.84, 124.61, 60.94, 21.67.

N-functionalization

N'-(4-nitrophenyl)sulfonyl *N*-Boc-asparagine benzyl ester *N*'-1-deoxy-2,3,4,6-Tetra-O-benzyl-β-D-glucopyranoside (32)

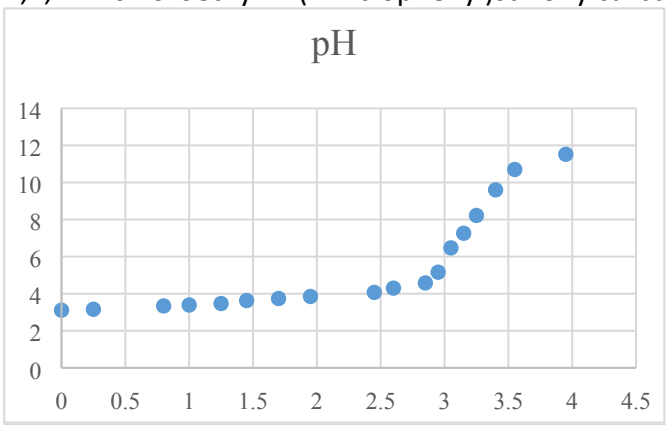


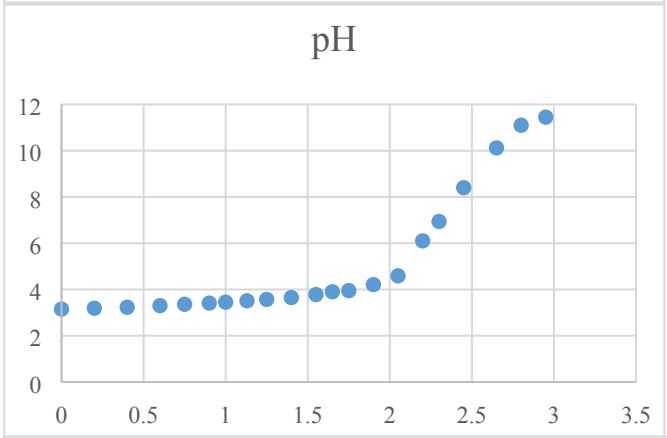
DIC (0.043 mL, 0.278 mmol), DMAP (3 mg, 0.025 mmol), *N*-Boc-aspartic acid benzyl ester (66 mg, 0.204 mmol) was stirred for 5 minutes in CH_2Cl_2 (3 mL) at rt. Then, 29 (99.5 mg, 0.137 mmol) was added and the reaction was stirred at rt for 1.15 hr when no starting material was left. The reaction was added Et_2O (10 mL), extracted with H_2O (5 x 5 mL), washed with brine (10 mL) and dried over $MgSO_4$ and evaporated onto celite. The crude product was purified by flash column chromatography (1:8 to 1:3 EtOAc/heptane), yielding the desired product 32 (117 mg, 0.113 mmol, 83 %) as a colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.34 – 7.84 (m, Ar^{Ns}, 4H), 7.49 – 7.00 (m, Ar^{Bn}, 25H), 5.63 – 5.30 (m, H-1, NH, 2H), 5.09 (d, *J* = 12.5 Hz, CH_2Bn, 1H), 4.95 – 4.77 (m, CH_2^{Bn}, 5H), 4.71 – 4.40 (m, CH_2^{Bn}, 6H), 3.83 – 3.57 (m, H-2, H-3, H-4, H-5, H-6a, H-6b, 6H), 3.36 – 3.00 (br m, C*H*$_2$C=ON, 2H) 1.38 (s, CH_3, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.20 ($C=O^{Boc}$), 170.80 ($C=O^{Bn}$), 155.55 ($C=O^{amide}$), 150.41 (*i*Ar^{Ns}), 144.80 (*i*Ar^{Ns}), 138.25 (*i*Ar^{Bn}), 137.92 (*i*Ar^{Bn}), 137.87 (*i*Ar^{Bn}), 137.58 (*i*Ar^{Bn}), 135.29 (*i*Ar^{Bn}), 129.80 (Ar^{Ns}), 128.72, 128.63, 128.61, 128.38, 128.14, 128.10, 128.08, 127.90, 127.84, 127.80 (18 x C Ar^{Bn}), 123.88 (Ar^{Ns}), 86.56 (C-3), 86.24 (C-1), 80.38 (C^{tertBu}), 77.97-77.37 (3 x C, C-2, C-4, C-5), 75.90 (CH_2^{Bn}), 75.34 (CH_2^{Bn}), 75.15 (CH_2^{Bn}), 73.60 (CH_2^{Bn}), 68.74 (C-6), 67.39 ($CH_2^{Bn\text{-}ester}$) 50.00 (*C*H-NHBoc) 28.34 (CH_3). **C*H_2C=ON missing. HRMS (MALDI+): Calculated for $C_{56}H_{59}N_3O_{14}SNa^+$ m/z 1052.36100; found m/z 1052.35980. $[\alpha]_D^{298}$ = +32.6° (c=1.1, $CHCl_3$) Rf = 0.44 (3:7 EtOAc/heptane)

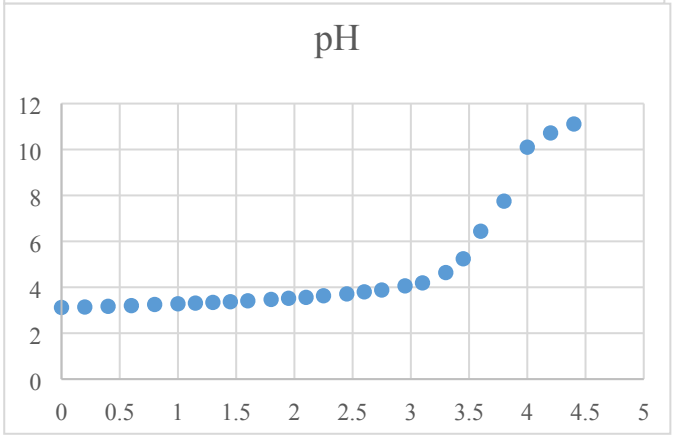
Titrations

General procedure for titrations
0.1-0.2 mmol of carbamate was dissolved in 5 mL of 40 % (V/V) DMSO in water. The solution was titrated under stirring with a 0.01M NaOH solution in 40 % (V/V) DMSO in water.

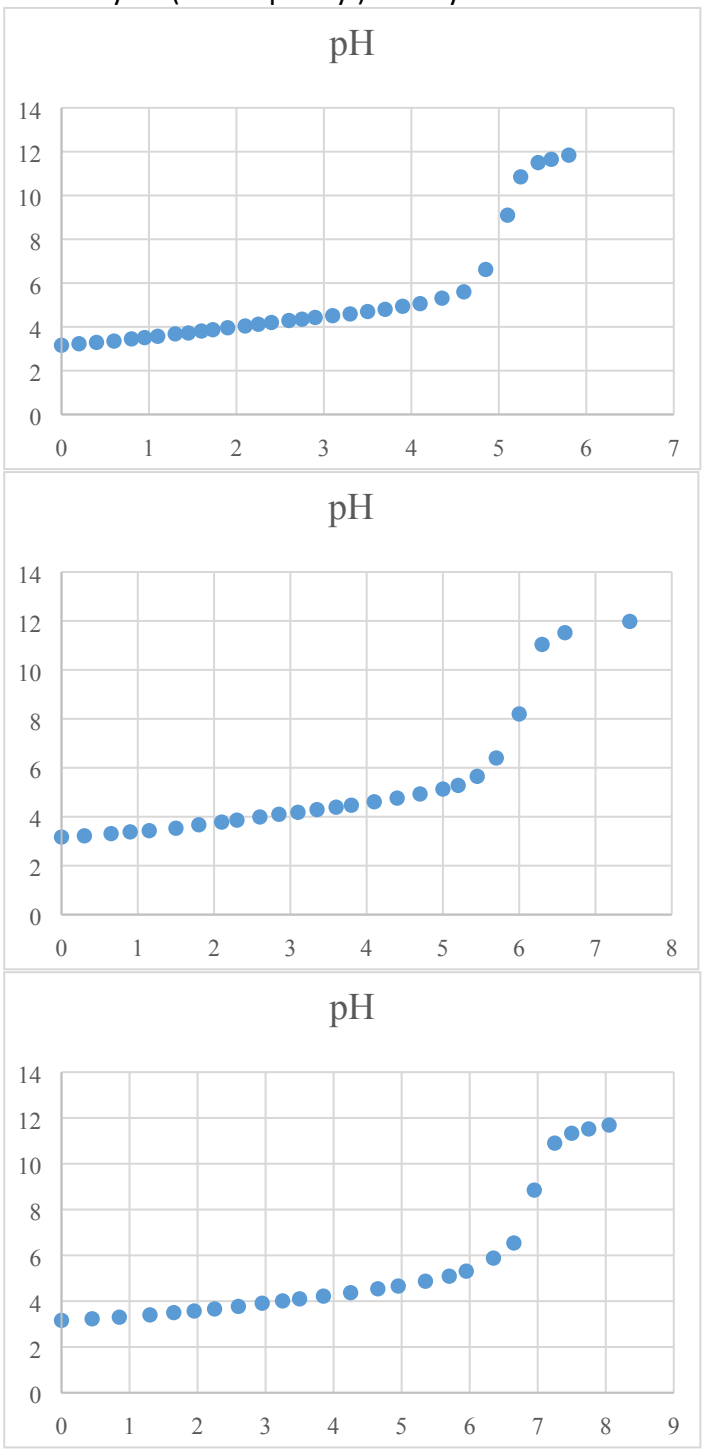
2,2,2-Trichloroethyl *N*-(4-nitrophenyl)sulfonylcarbamate



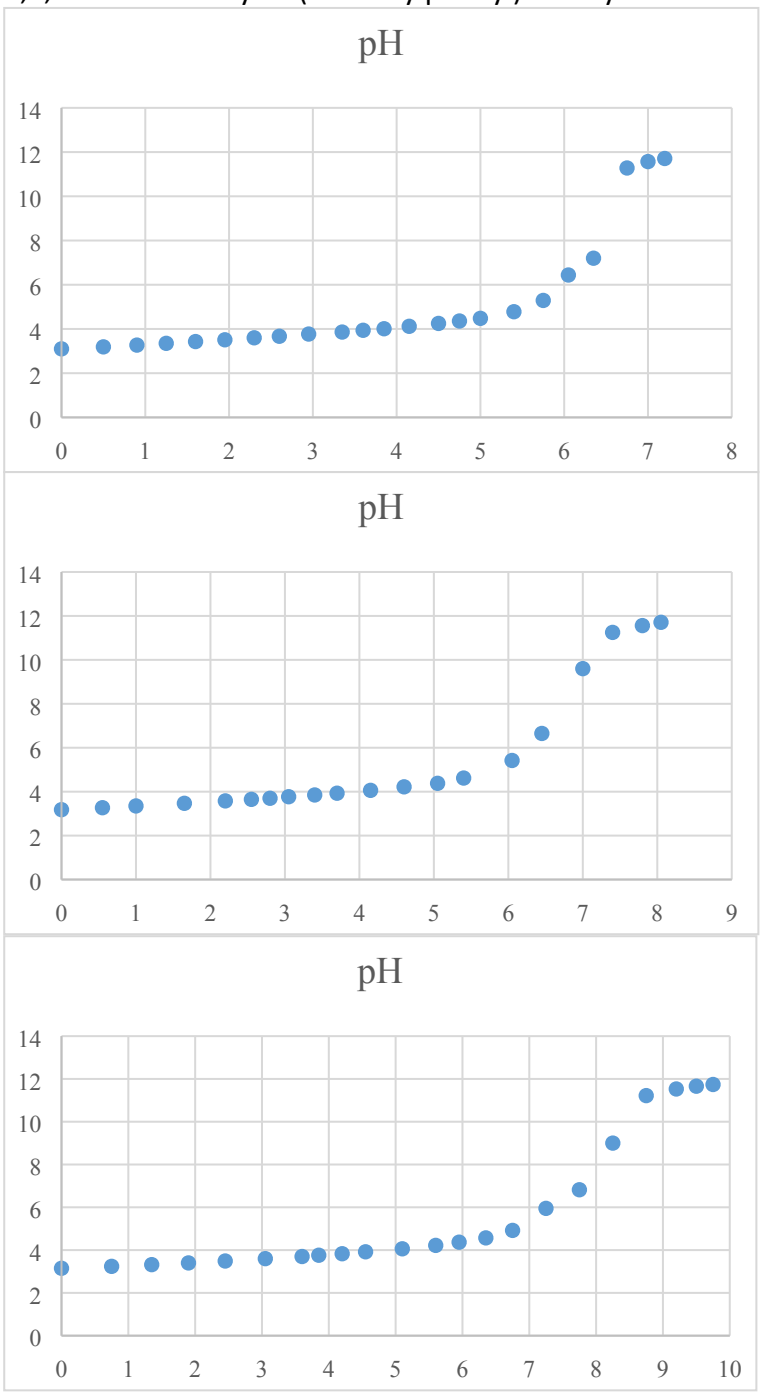




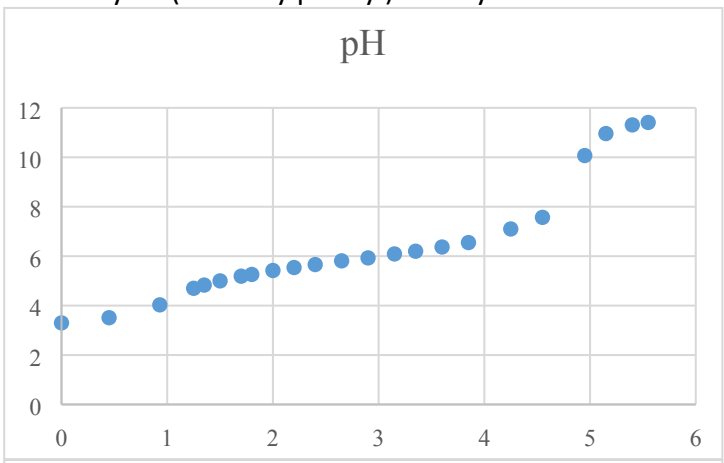
Tert-butyl *N*-(4-nitrophenyl)sulfonylcarbamate

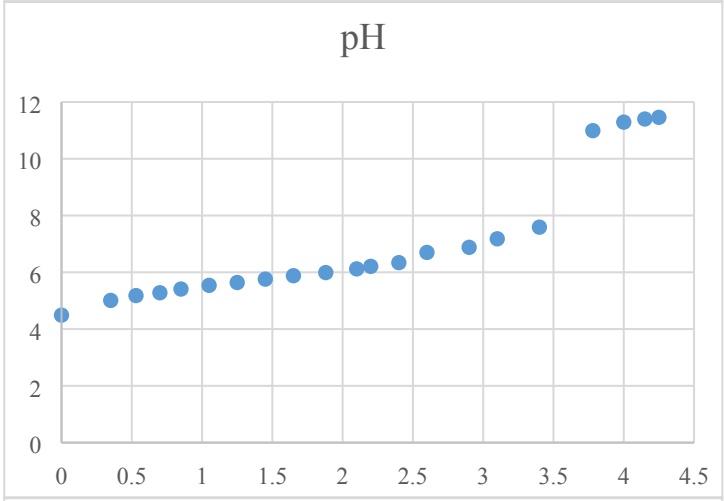


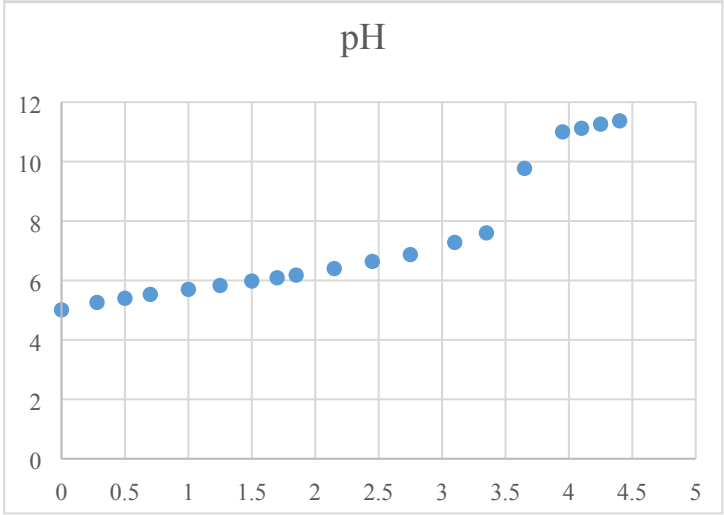
2,2,2-Trichloroethyl *N*-(4-methylphenyl)sulfonylcarbamate



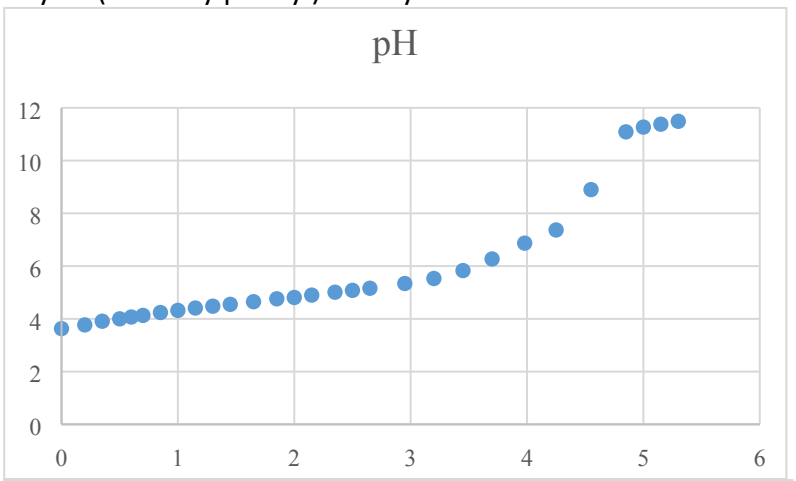
Tert-butyl *N*-(4-methylphenyl)sulfonylcarbamate

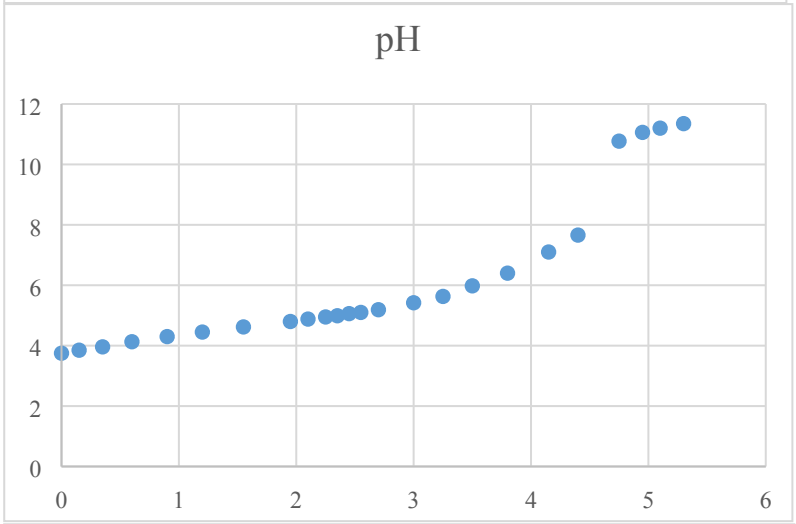


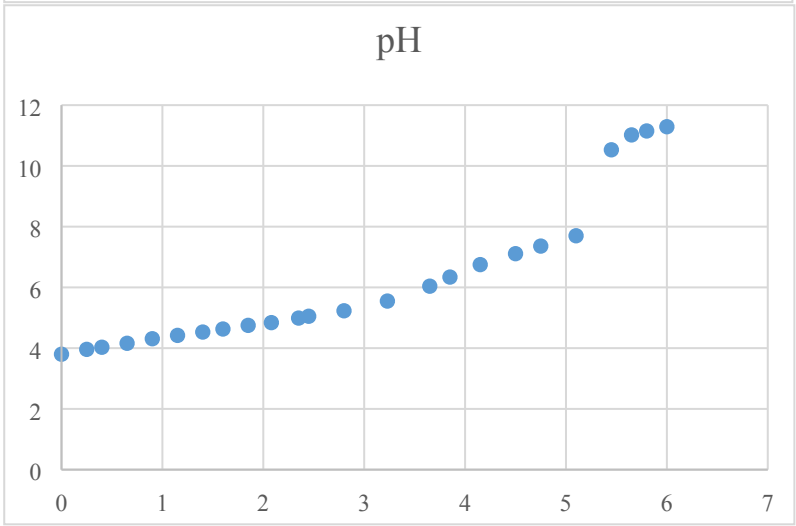




Allyl *N*-(4-methylphenyl)sulfonylcarbamate

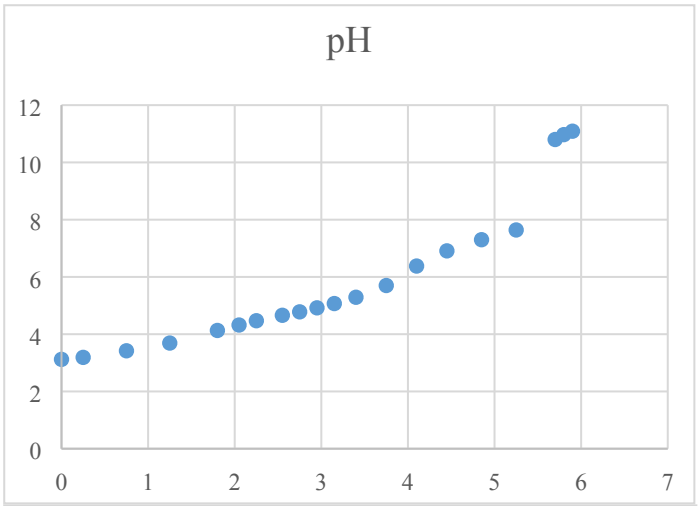


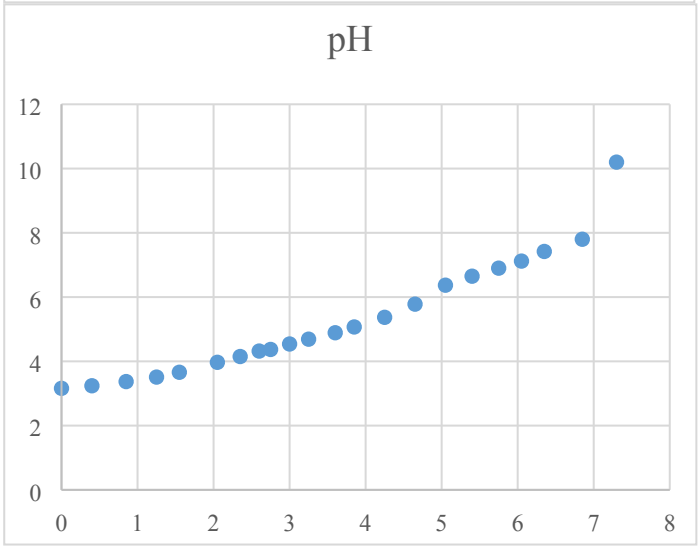




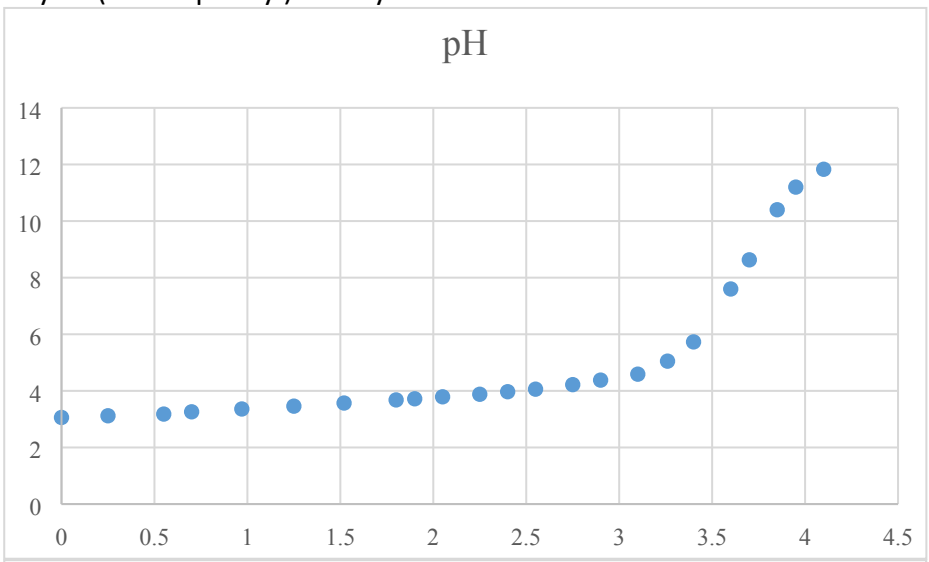
Benzyl *N*-(4-methylphenyl)sulfonylcarbamate

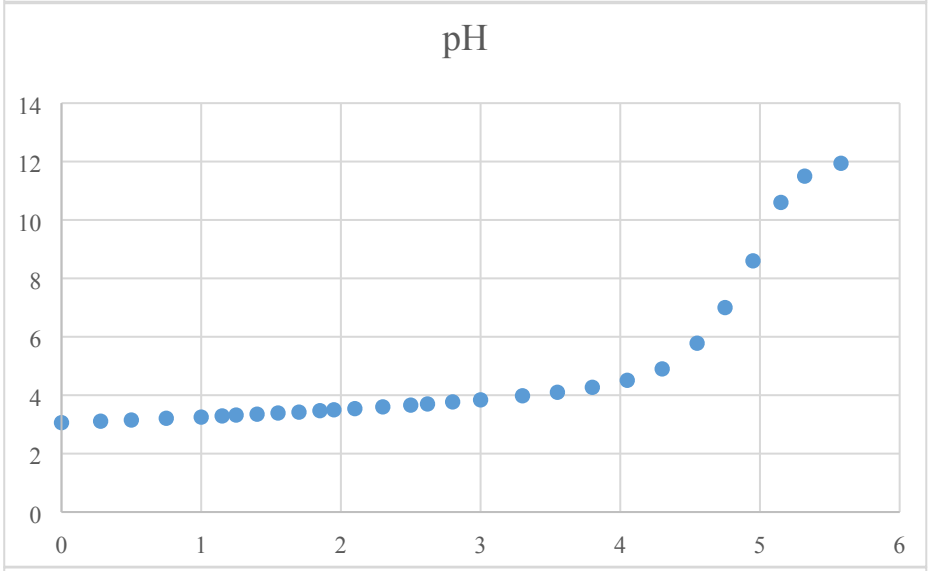
Note: The following titration was only performed twice due to the very low solubility of the carbamate in the 40 % (V/V) DMSO in water solution.

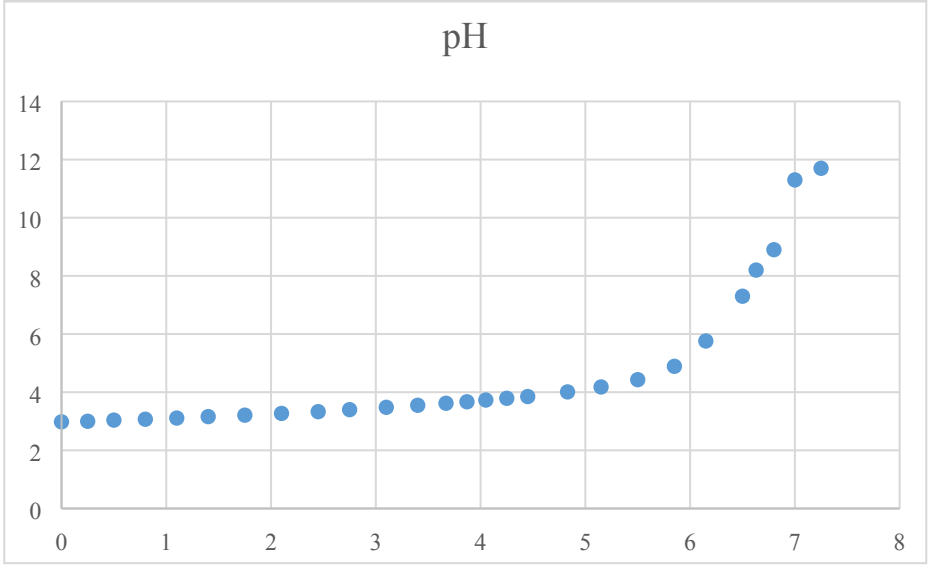




Allyl *N*-(4-nitrophenyl)sulfonylcarbamate





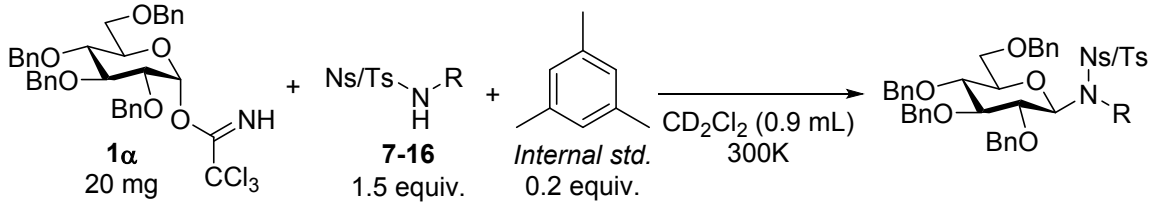


NMR experiments

General information

Reaction kinetics

General reaction scheme for the NMR-experiments conducted on glycosyl acceptors 7-16:



TCA donor 1α and mesitylene (0.2 equiv.) was dissolved in CD_2Cl_2 (0.45 mL) and an NMR-spectrum was recorded to confirm the purity of the starting material. Then, 1.5 equiv. of glycosyl acceptor (7-16) was added as a solution in CD_2Cl_2 (0.45 mL) and the NMR tube was sealed with a new cap and immediately inserted into the NMR spectrograph for data acquisition. The time dilation between mixing and the recording of the first spectrum was approximately two minutes. The sample was monitored by frequent ^{1}H-NMR spectrums at set intervals for up to 10 h or until no starting material was left. All integrals were normalized according to the mesitylene peak (CH_3) in order to avoid an increase in peak intensity due to evaporation of the solvent.

Anomerization studies

The experiment was carried out in an NMR tube. To a solution of the compound 24 (pure anomer *β*, 22 mg, 0.03 mmol) in DMSO-d6 (0.7 ml), K_2CO_3 (8 mg, 0.06 mmol) was added at room temperature. Immediately, after adding the base, ^{1}H NMR was taken, which indicated only *β* anomer. Then, the sample was heated up to 50°C and stored at this temperature for 96 h. The progress of the anomerization was monitored by ^{1}H NMR, which was run every 24 h. After 96 h the experiment was completed, since no change in *α*/*β* ratio was observed, suggesting an equilibrium.

TOCSY experiments

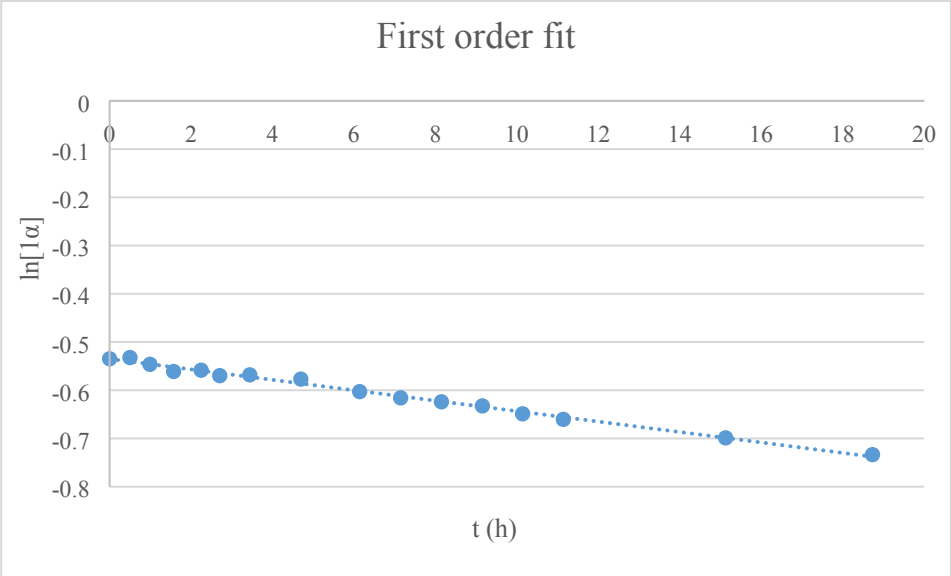
For all *α* anomers of the fully protected *N*-glucosides the unusual, relatively high coupling constants of dublets coming from H-1 were observed (8.0-8.2 Hz). In order to establish the conformation of the obtained *N*-glucosides the other couplings within the sugar ring were determined. As the anomeric mixtures of D-glucose derivatives were inseparable by employing a flash column chromatography, TOCSY experiments were performed. For this purpose a sample of 16 (*α*/*β* 1:3.4) in CD_3CN was used (CD_3CN gave better signals resolution compared to $CDCl_3$). The reported TOCSY experiments were carried out under the same conditions at 26.85°C.

NOESY experiments

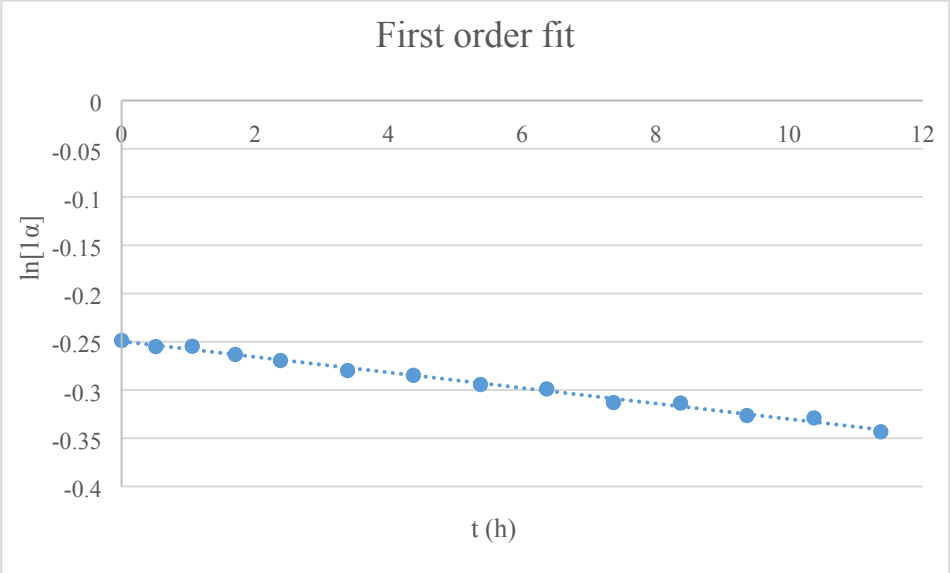
Additionally, NOESY experiments (1D Selective Gradient and 2D) were employed in the conformation studies. Similarly to the TOCSY experiments, the samples of 16 (α/β 1:3.4) in CD_3CN and $CDCl_3$ were used. 1D spectra were measured at 26.85°C, whereas 2D at room temperature. The results obtained for 1D Selective Gradient NOESY and 2D NOESY were coherent, indicating the same key correlations.

Reaction rate and kinetics

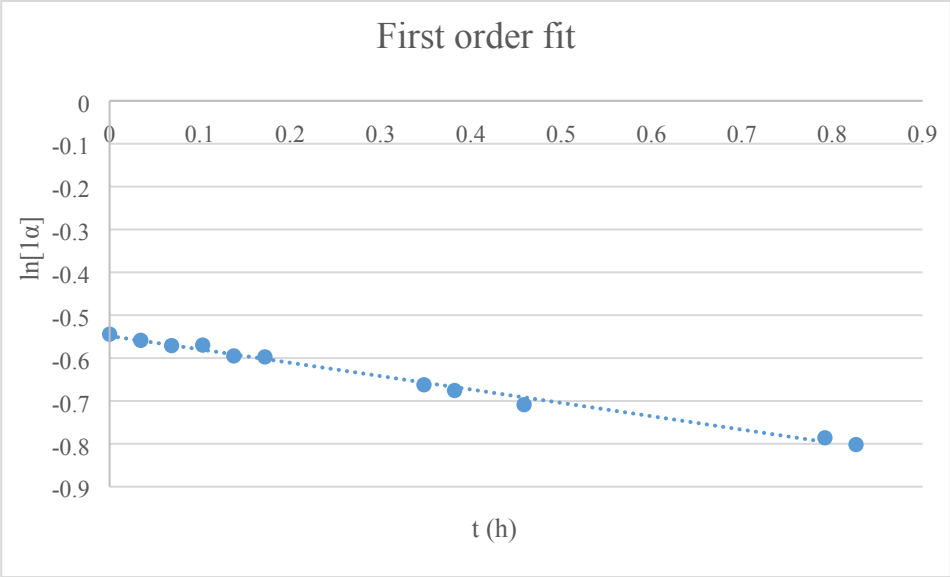
First order fit for reaction with acceptor 7



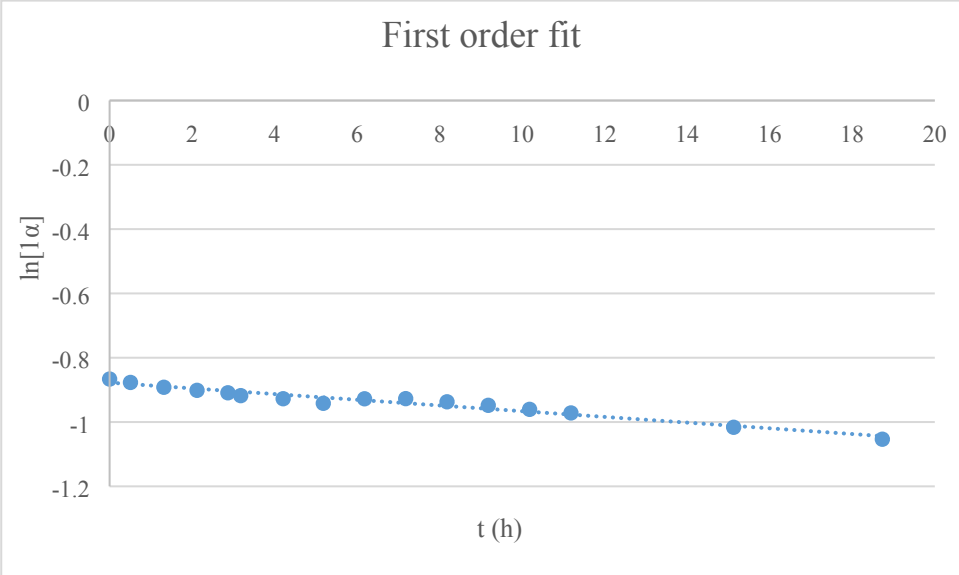
First order fit for reaction with acceptor 9



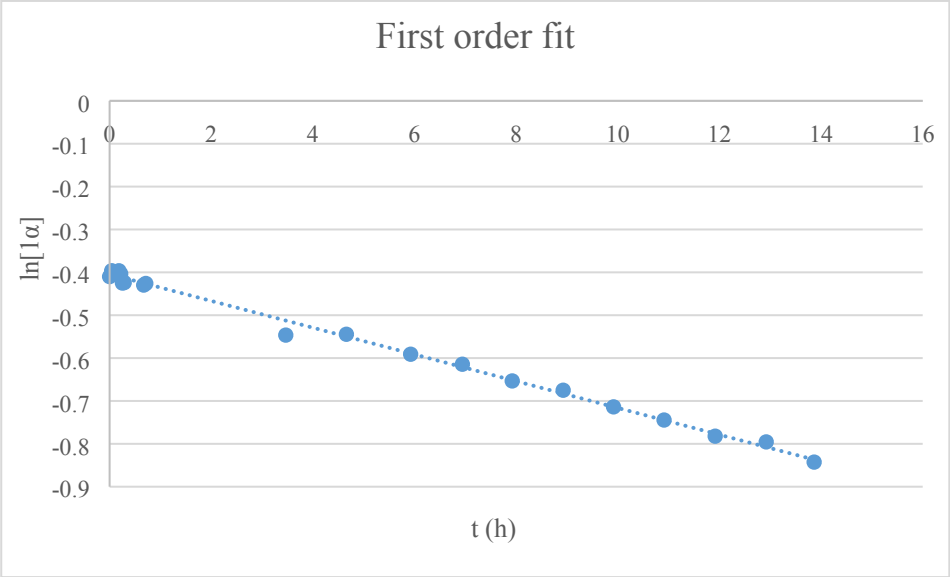
First order fit for reaction with acceptor 10



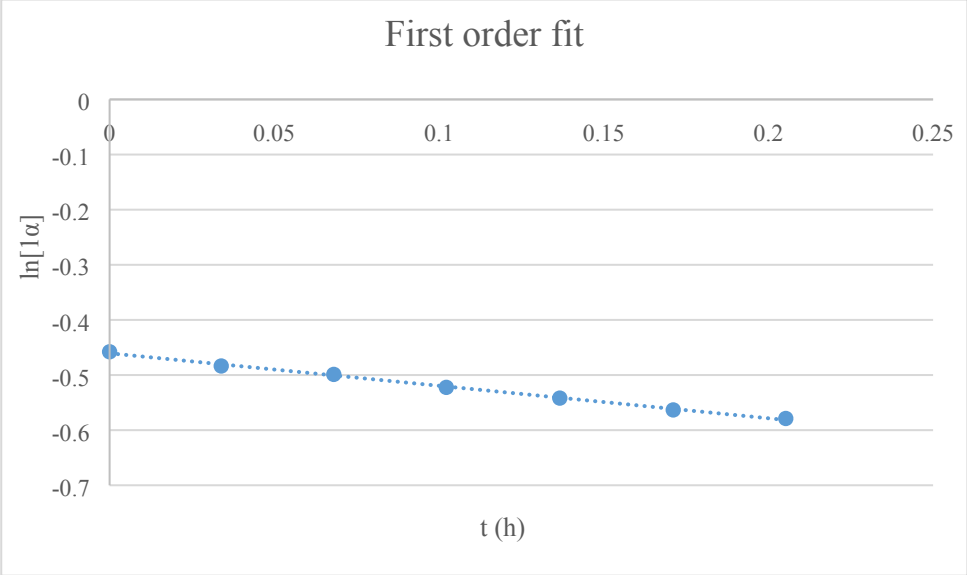
First order fit for reaction with acceptor 11



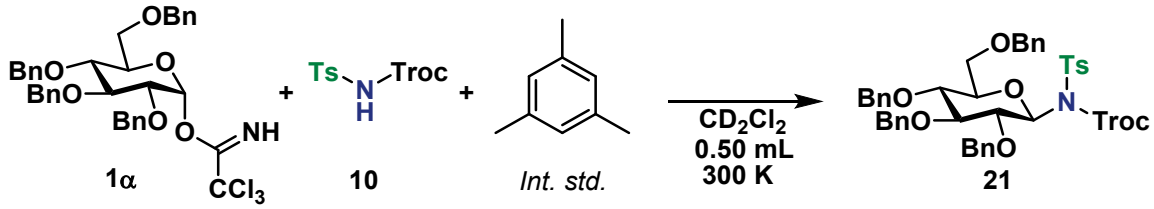
First order fit for reaction with acceptor 13



First order fit for reaction with acceptor 14

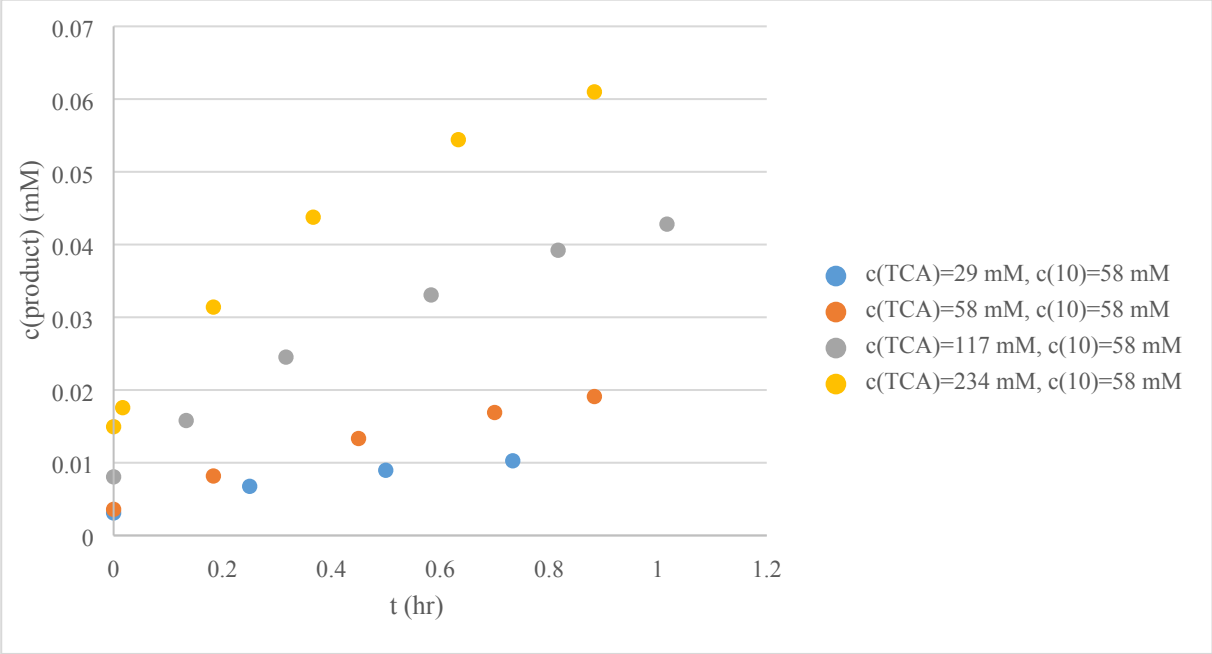


Determination of overall reaction order

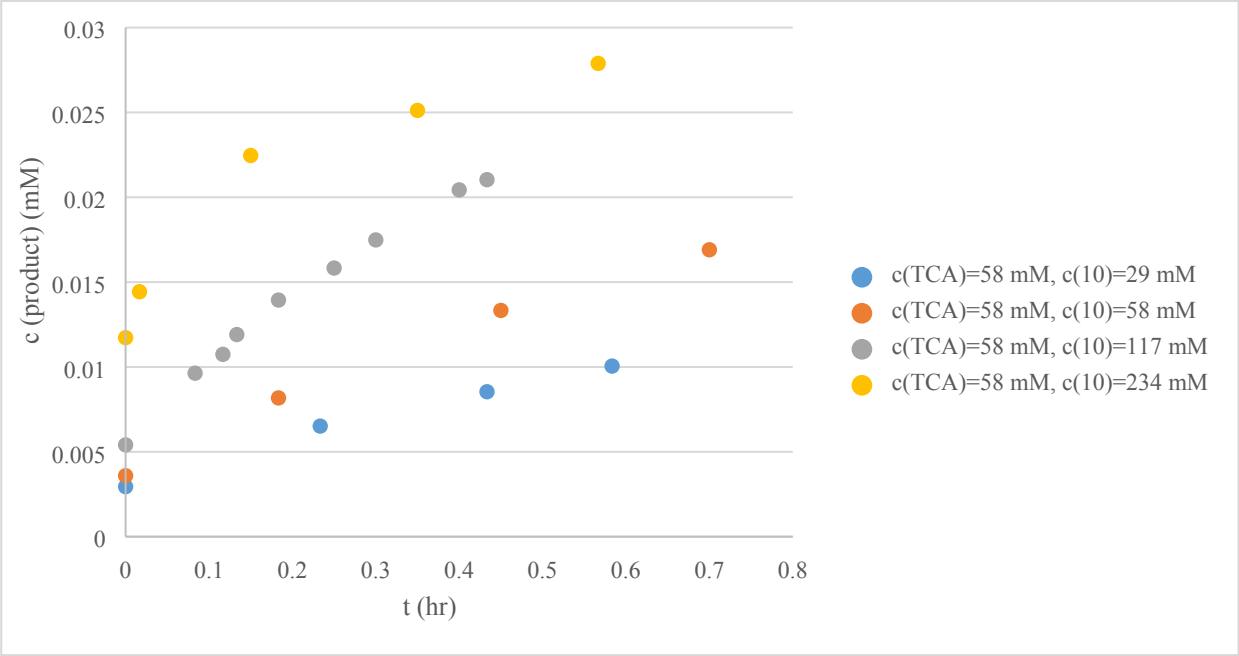


The approximated initial rate for the glycosylation reaction at varying conditions was determined by linear regression of the first two data points obtained from ^{1}H-NMR spectroscopy. The concentration of the product was determined by using a known concentration of mesitylene as an internal standard. Standard solutions of 1α + mesitylene and 10 was prepared in order to perform the glycosylations under comparable conditions in the NMR-tube.
In the following two plots, the formation of product over time is illustrated depending on the starting conditions.

Graph S1 Product formation with varying donor concentration

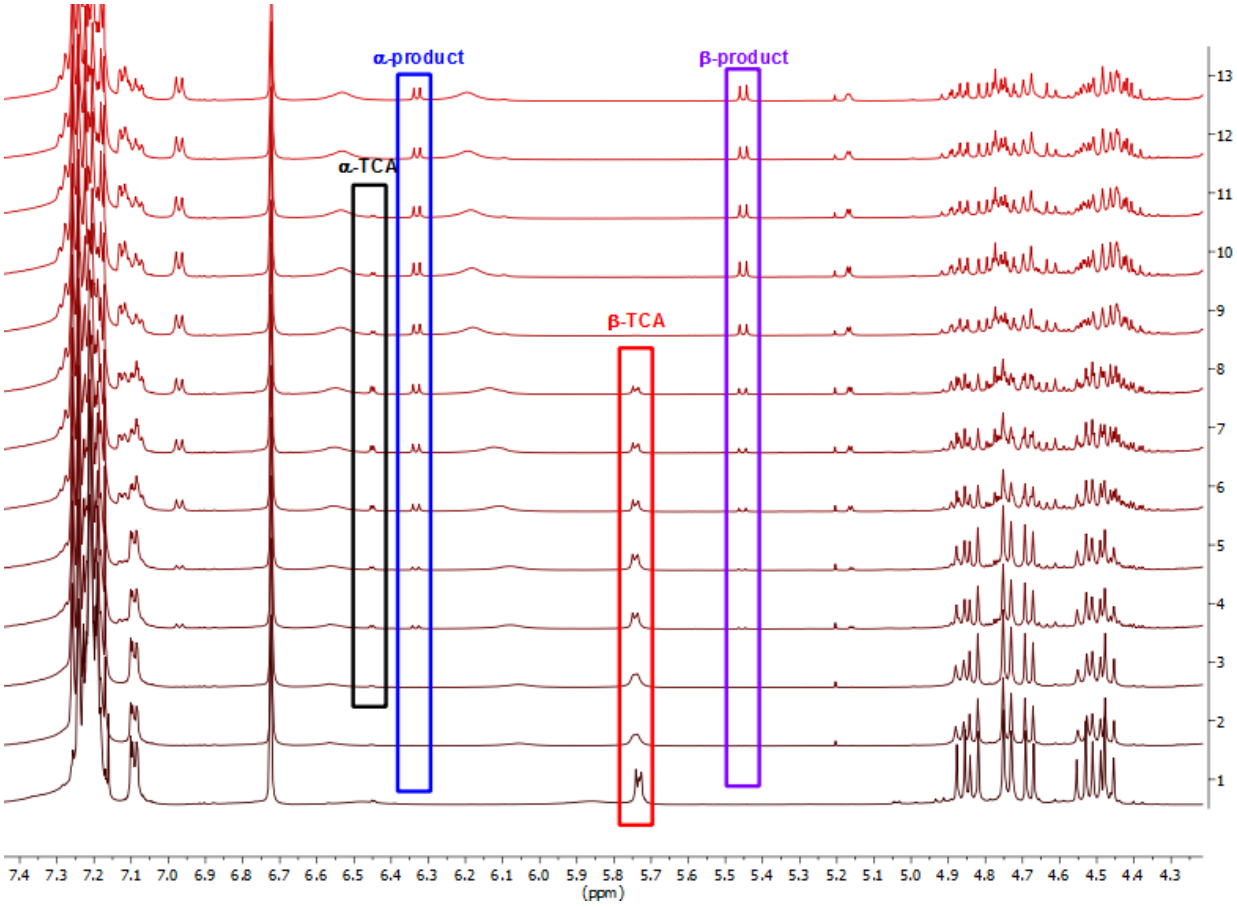


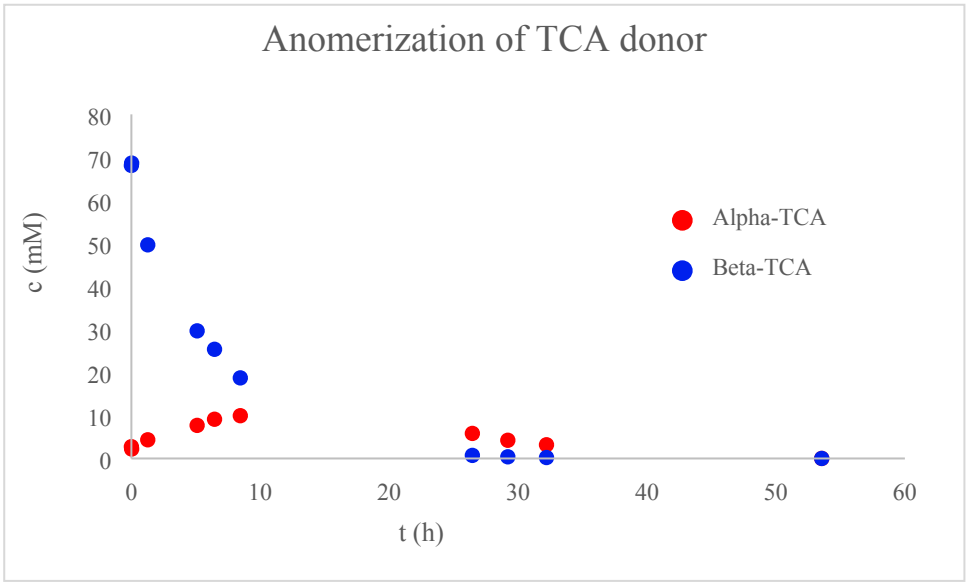
Graph S2 Product formation with varying acceptor concentration

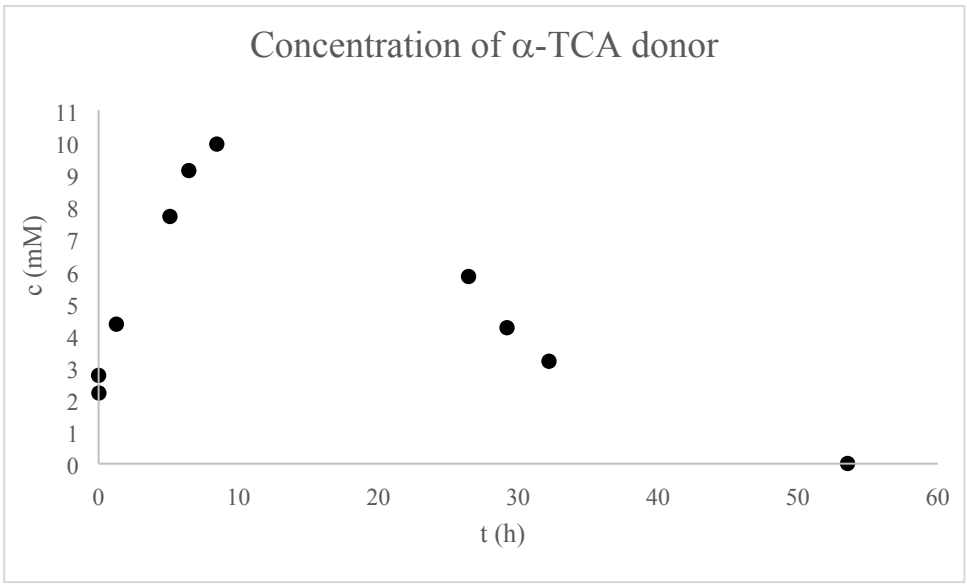


Anomerization of β-TCA donor to α-TCA donor

Conditions: 1β (35 mg) was dissolved in $CDCl_3$ (0.75 mL) (neutralized by passing it through a plug of basic Al_2O_3 that was dried in an oven at 200 degrees for several weeks). Mesitylene (4.3 mg) was added and a starting point was recorded. Then, 7 (40 mg) was added and ^{1}H-NMR data acquisition was started within one minute.






Concentration of α-TCA donor
c (mM)
t (h)
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1
2
3
4
5
6
7
8
9
10
11
0
10
20
30
40
50
60

Anomerization of *N*-glycoside

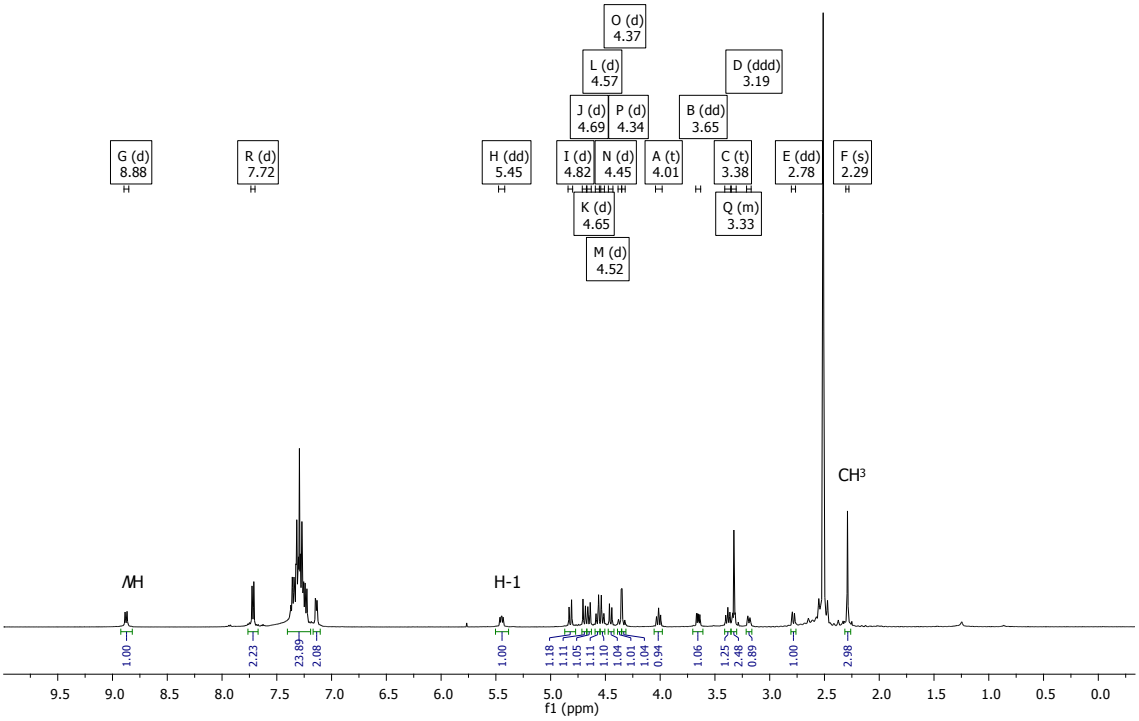


Figure 1. ^{1}H NMR spectrum of the compound 24 (anomer *α*) in DMSO-d6 at room temperature.

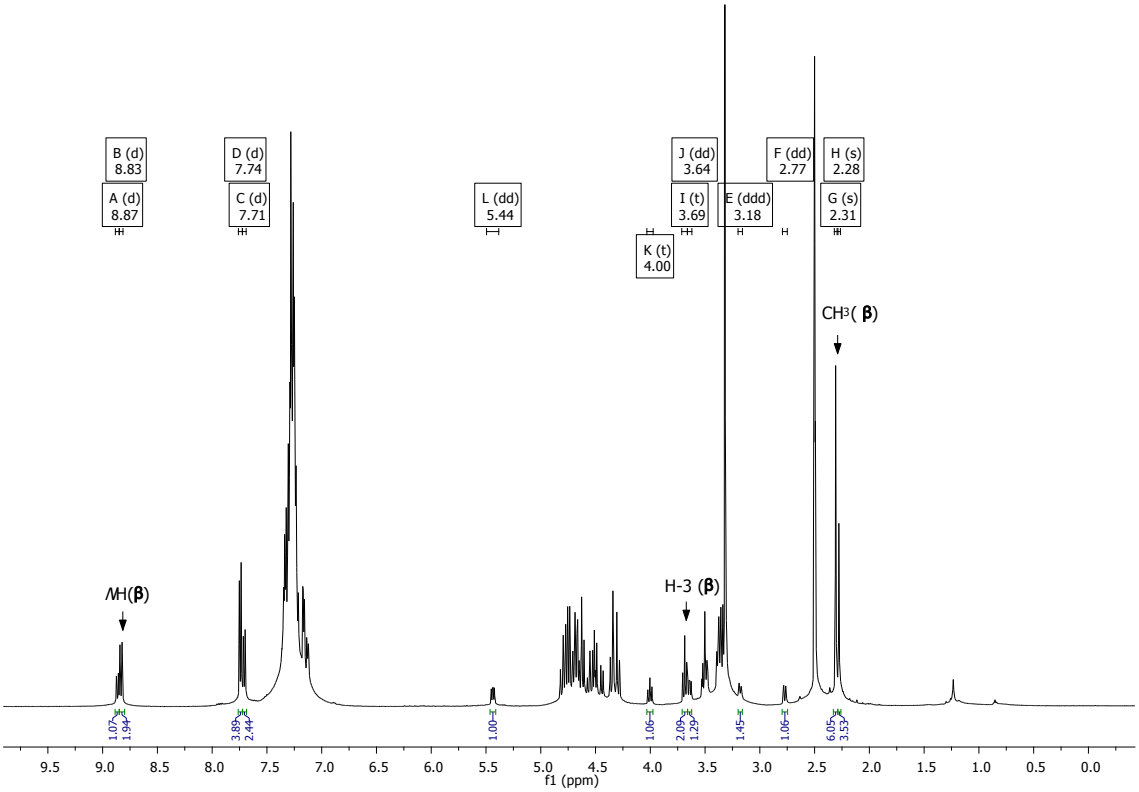


Figure 2. ^{1}H NMR spectrum of the compound 24 (*α*/*β*) in DMSO-d6 at room temperature.

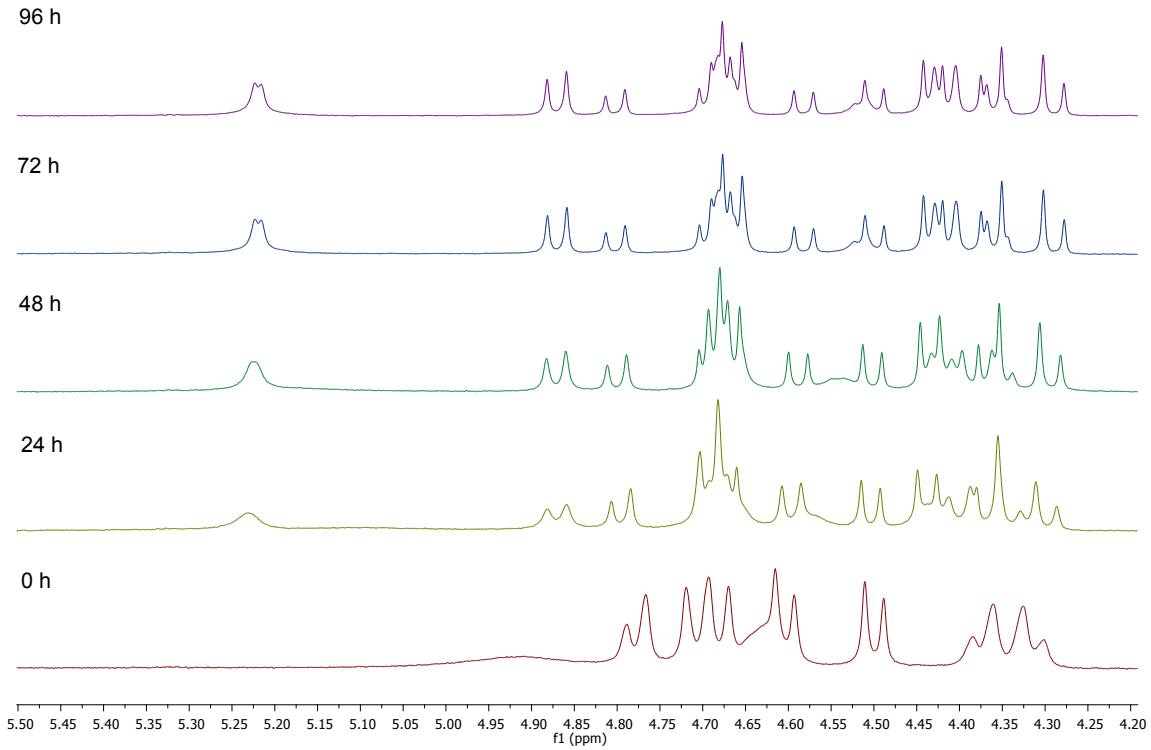


Figure 3. ^{1}H NMR spectra in the range 4.20-5.50 ppm, demonstrating the most pronounced differences observed over the anomerization experiment.

Table 1. Correlation between a sample heating time and *α/β* ratio determined based on ^{1}H NMR.

Sample heating time [h]	α/β
0	0:1
24	1:1
48	1:0.7
72	1:0.6
96	1:0.6

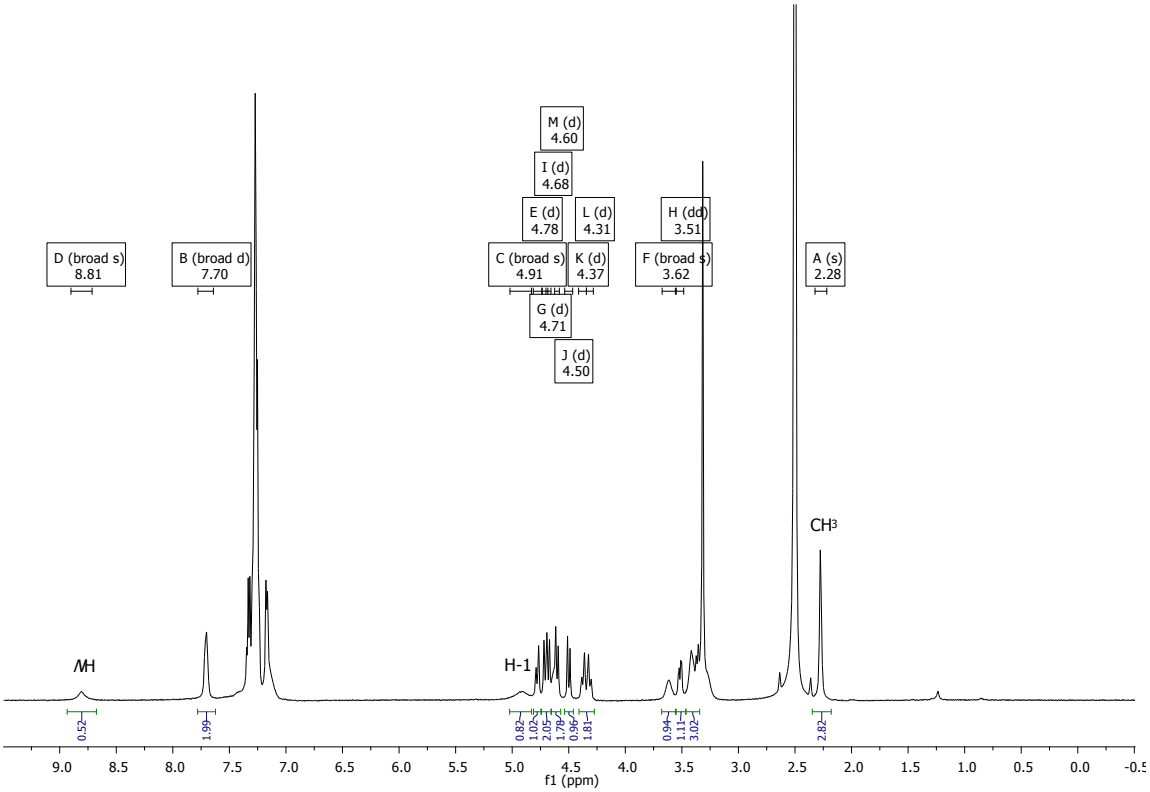


Figure 4. ^{1}H NMR spectrum of the anomerization experiment sample, run directly after adding the base at room temperature.

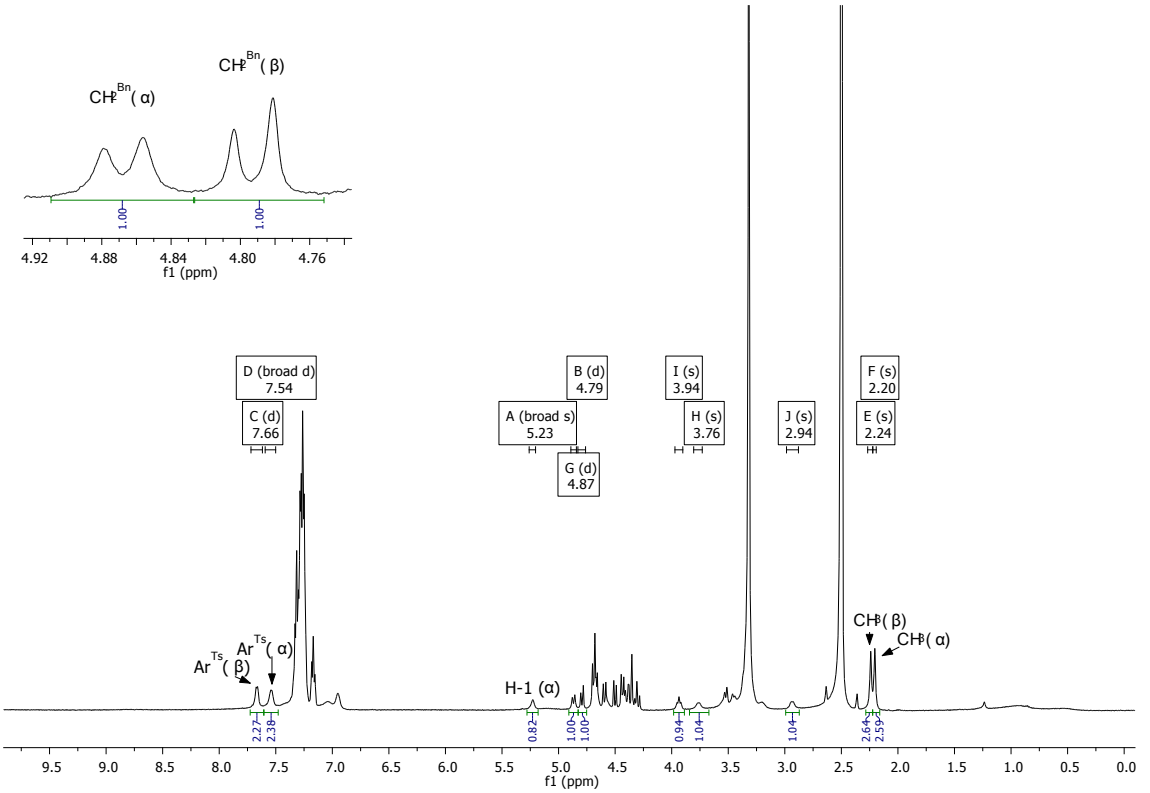


Figure 5. ^{1}H NMR spectrum of the anomerization experiment sample, measured after 24 h of heating at 50°C.

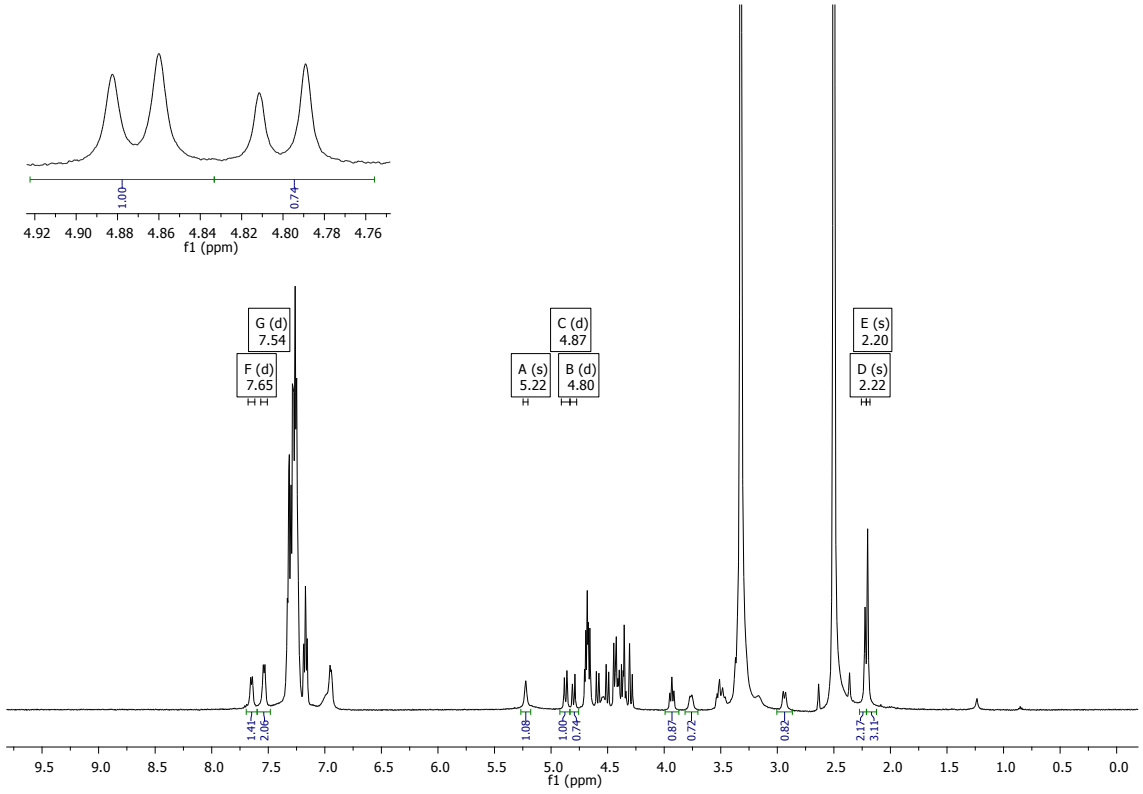


Figure 6. ^{1}H NMR spectrum of the anomerization experiment sample, measured after 48 h of heating at 50°C.

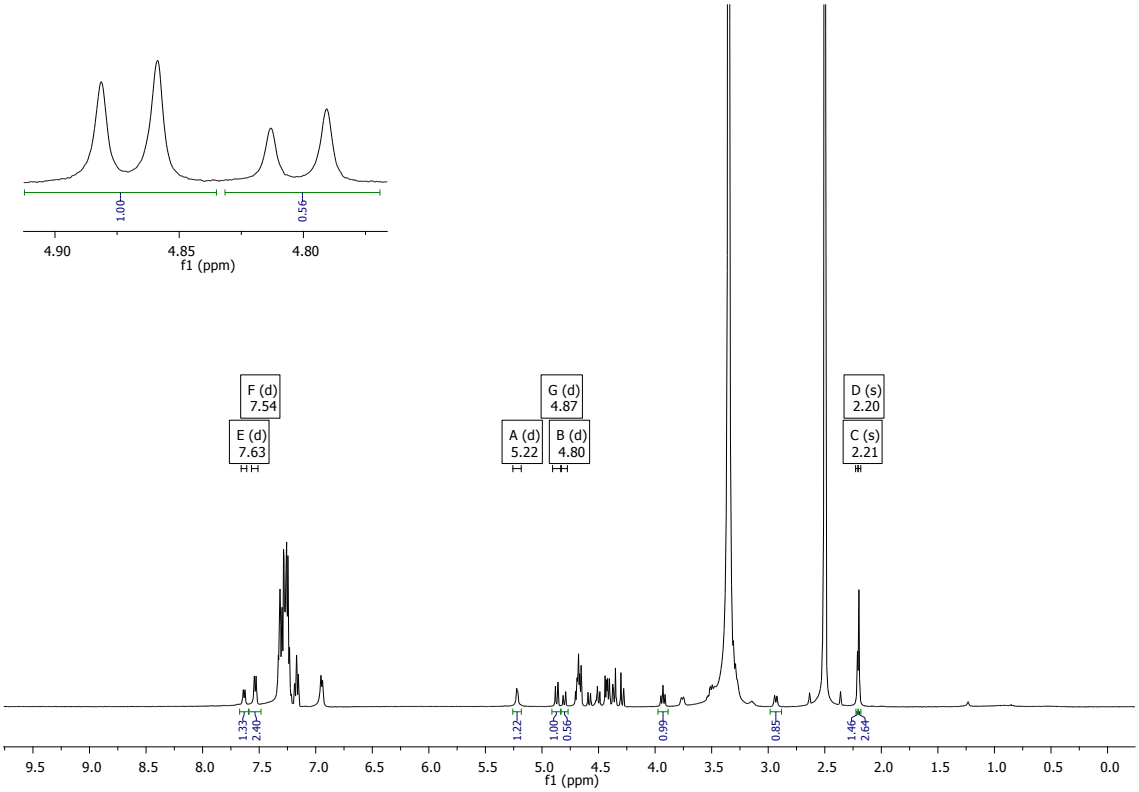


Figure 7. ^{1}H NMR spectrum of the anomerization experiment sample, measured after 72 h of heating at 50°C.

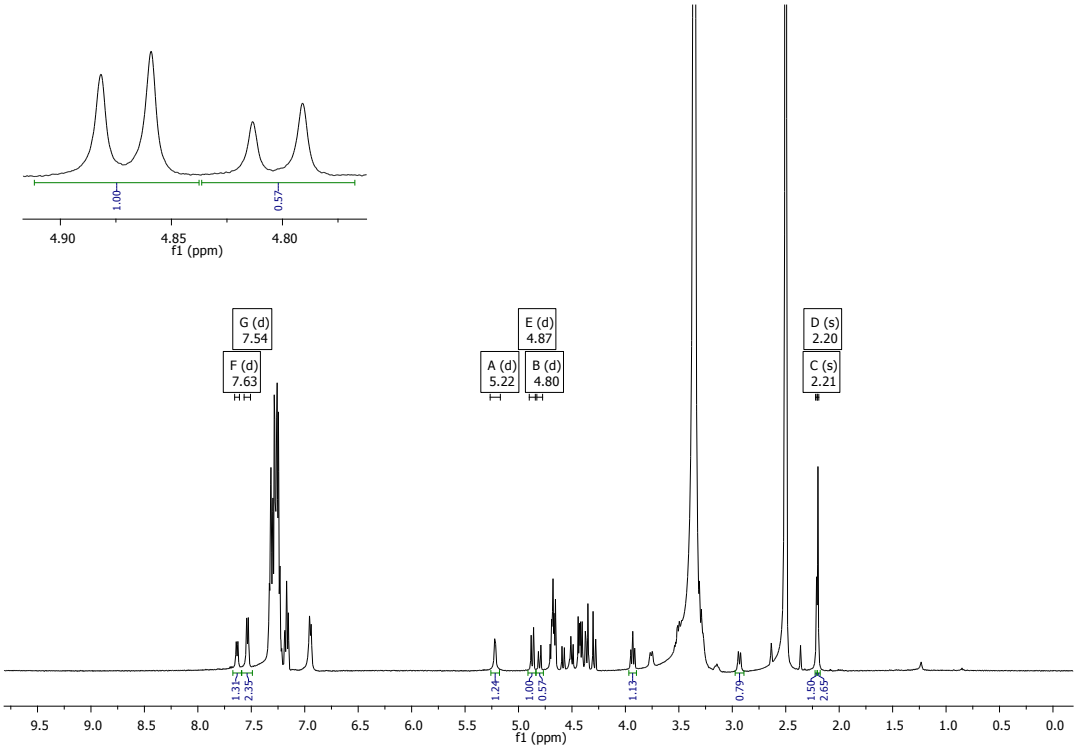


Figure 8. ^{1}H NMR spectrum of the anomerization experiment sample, measured after 96 h of heating at 50°C.

TOCSY experiments

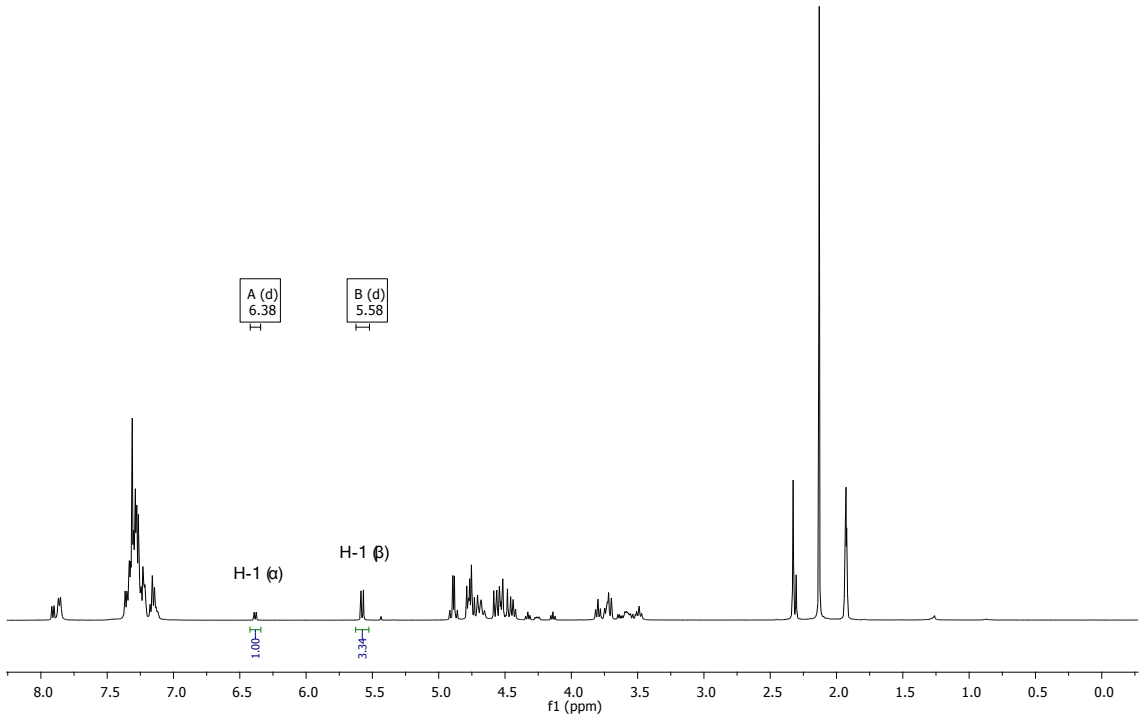


Figure 9. ^{1}H NMR spectrum of 16 (α/β) in CD_3CN at room temperature.

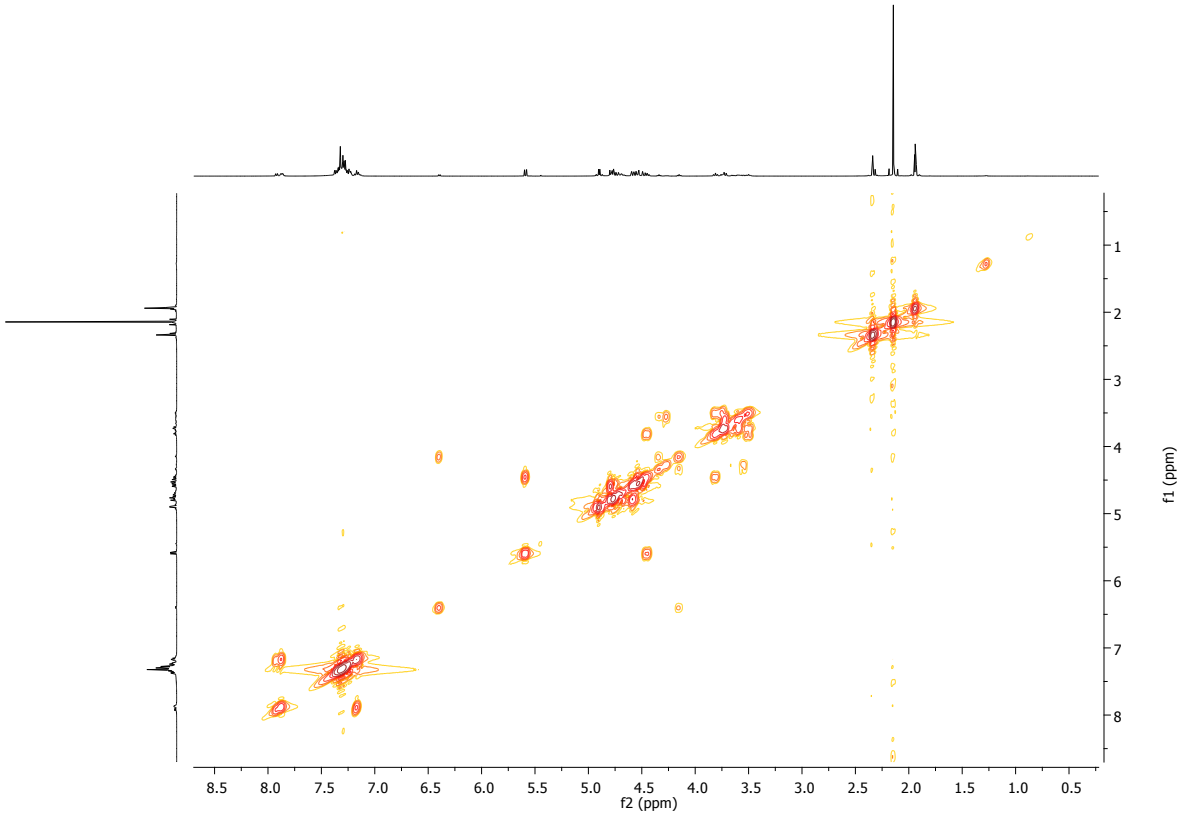


Figure 10. COSY spectrum of 16 (α/β) in CD_3CN at room temperature.

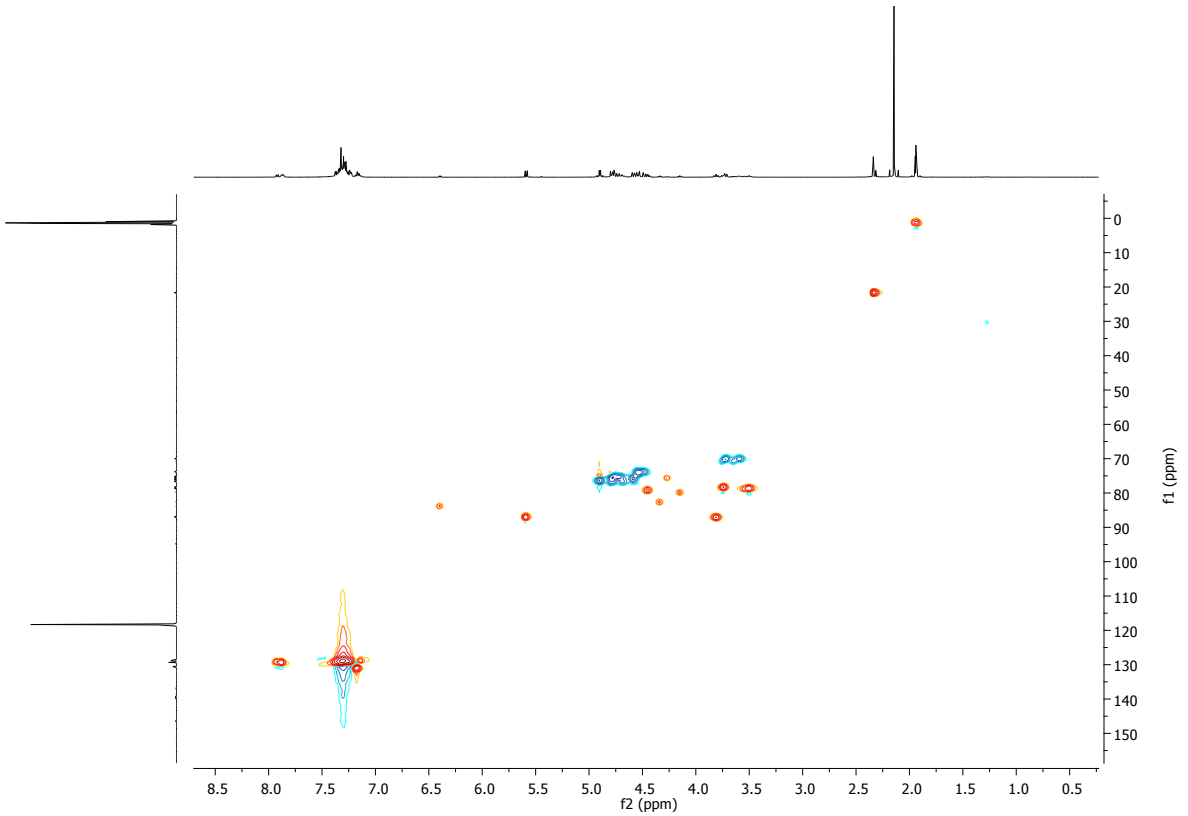


Figure 11. HSQC spectrum of 16 (α/β) in CD_3CN at room temperature.

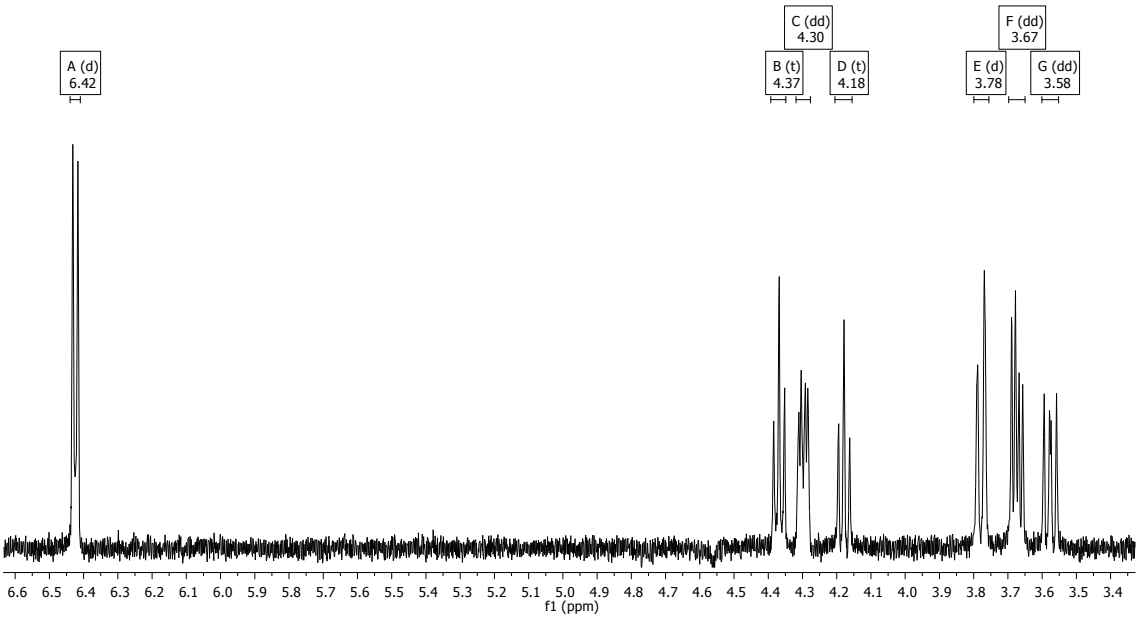


Figure 12. 1D Selective TOCSY of 16 in CD_3CN at 26.85°C, demonstrating signals coming from sugar ring of the *α* anomer.

Table 2. 1D Selective TOCSY chemical shifts *δ*H (ppm) and the proton coupling constants *J*(Hz) of 16 (anomer α) in CD_3CN at room temperature.

No. atom	Chemical shift [ppm]	Multiplicity	^3J [Hz]
H-1	6.42	d	7.6
H-3	4.37	t	8.1
H-5	4.30	broad dd	10.1, ~5.5
H-2	4.18	dd (t)	8.1, 7.6
H-6	3.78	broad d	10.8
H-6’	3.67	dd	10.8, 5.5
H-4	3.58	dd	10.1, 8.1

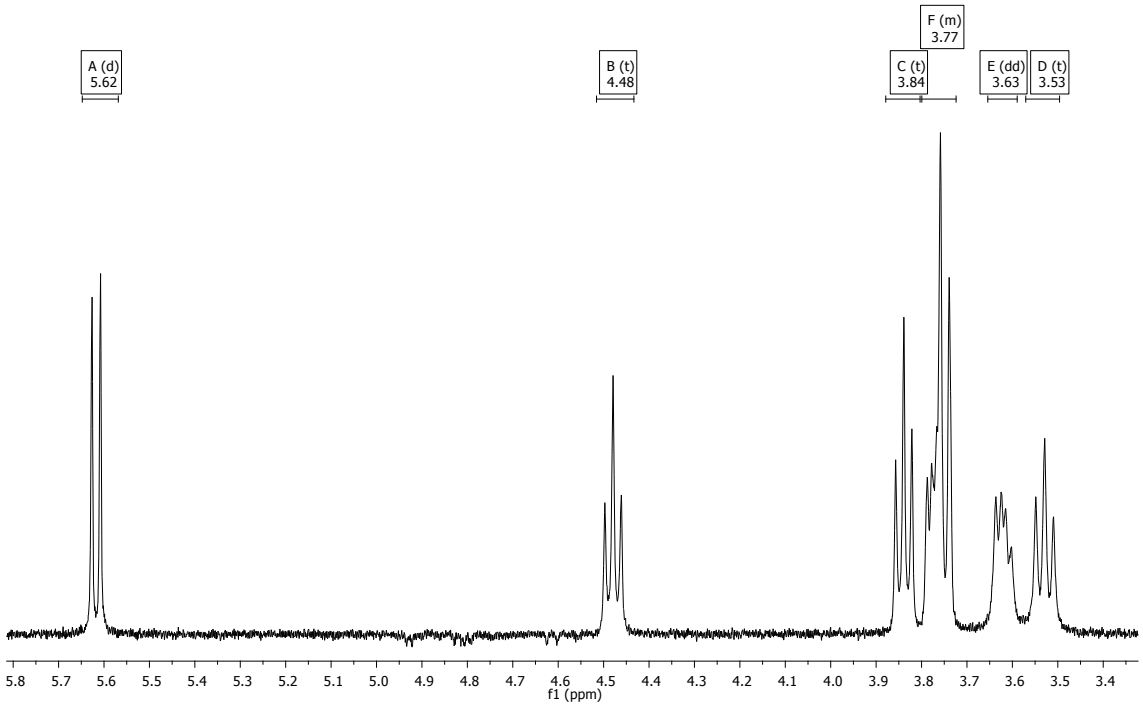


Figure 13. 1D Selective TOCSY of 16 in CD_3CN at 26.85°C, demonstrating signals coming from sugar ring of the *β* anomer.

Table 3. 1D Selective TOCSY chemical shifts *δ*H (ppm) and the proton coupling constants *J*(Hz) of 16 (anomer *β*) in CD_3CN at room temperature.

No. atom	Chemical shift [ppm]	Multiplicity	^3J [Hz]
H-1	5.62	d	9.3
H-2	4.48	dd (t)	9.3, 8.8
H-3	3.84	t	8.8
H-5, H-6	3.72-3.80	m	-

H-6’	3.62	dd	10.8, 6.1
H-4	3.53	dd (t)	10.6, 8.8

NOESY experiments

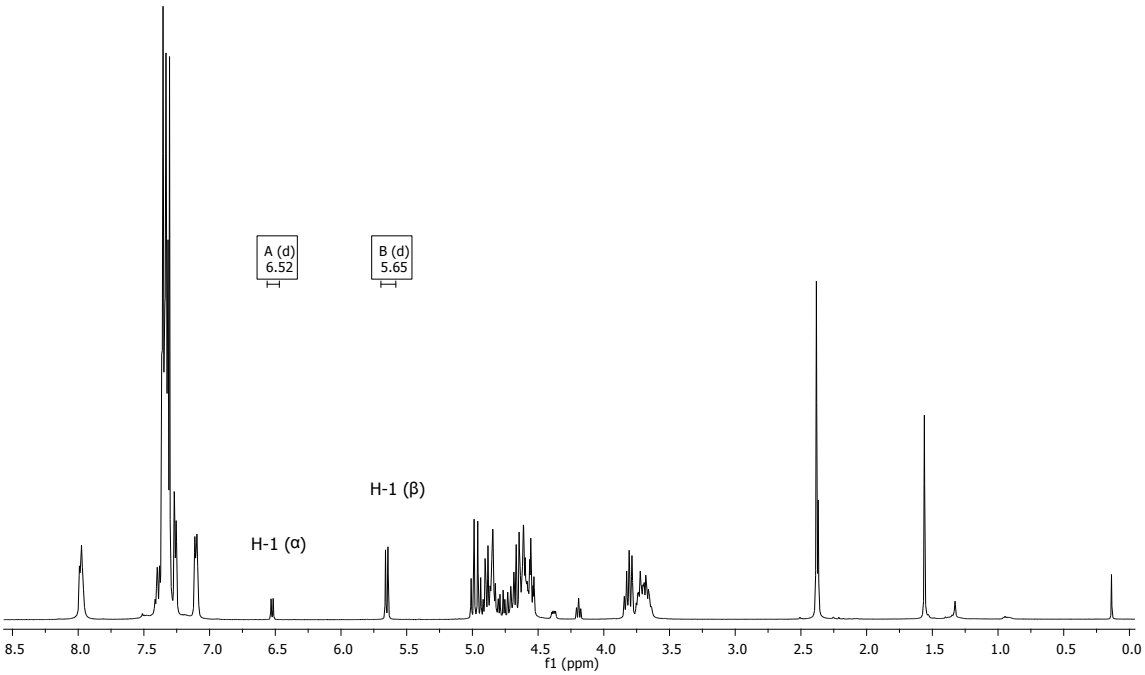


Figure 14. ^{1}H NMR spectrum of 16 (α/β) in $CDCl_3$ at room temperature.

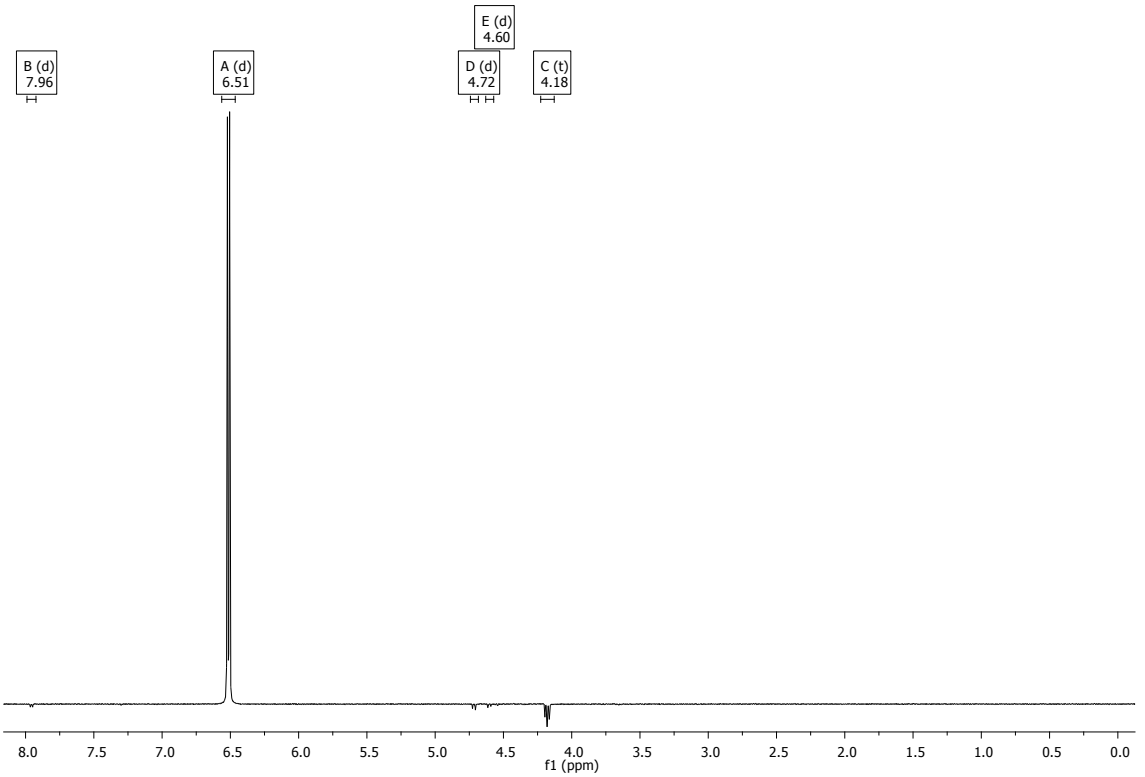


Figure 15. 1D Selective Gradient NOESY of 16 in $CDCl_3$ at 26.85°C, demonstrating correlations between H-1*α* and protons reported in the Table 4.

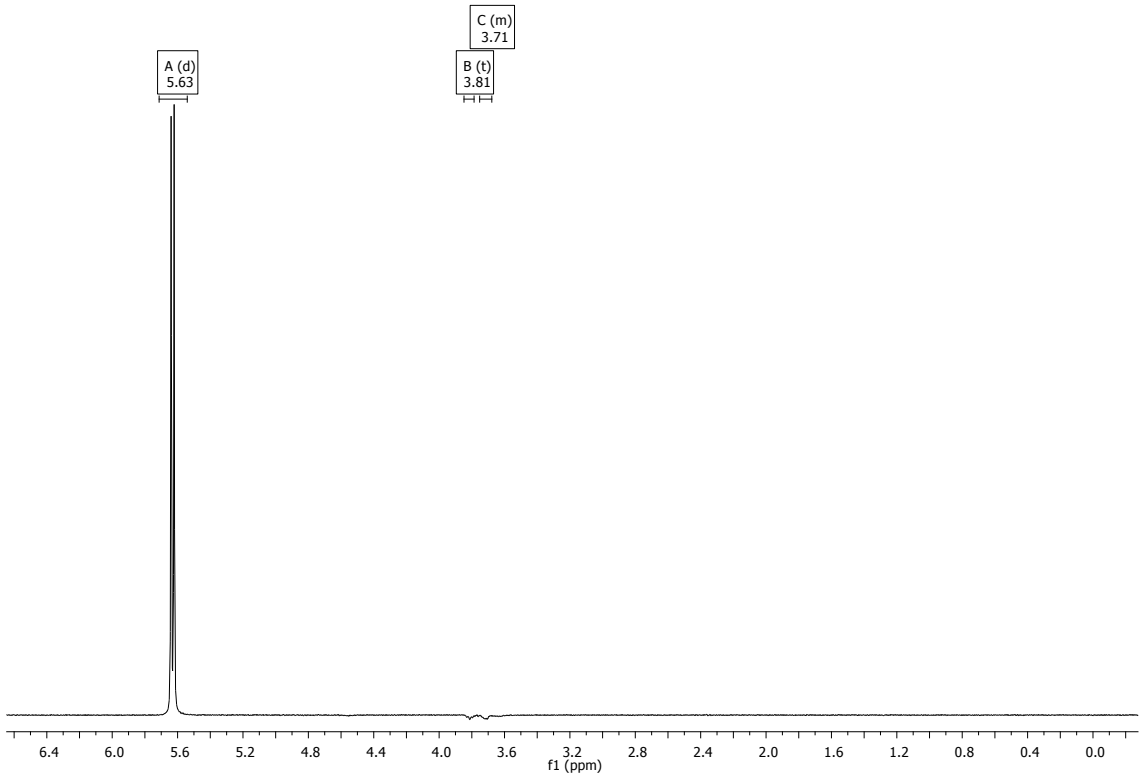


Figure 16. 1D Selective Gradient NOESY of 16 in $CDCl_3$ at 26.85°C, demonstrating correlations between H-1*β* and protons reported in the Table 4.

Table 4. Correlations observed for anomeric protons in 1D Selective Gradient NOESY spectra (Figure 15-16) with chemical shifts *δ*H (ppm) of the coupled protons.

H-1α correlations		H-1β correlations	
Chemical shift [ppm]	Correlated protons	Chemical shift [ppm]	Correlated protons
4.18	H-2	3.81	H-3
4.72	CH_2	3.71	H-5
4.60	CH_2	-	-
7.96	Ar^{Ts}	-	-

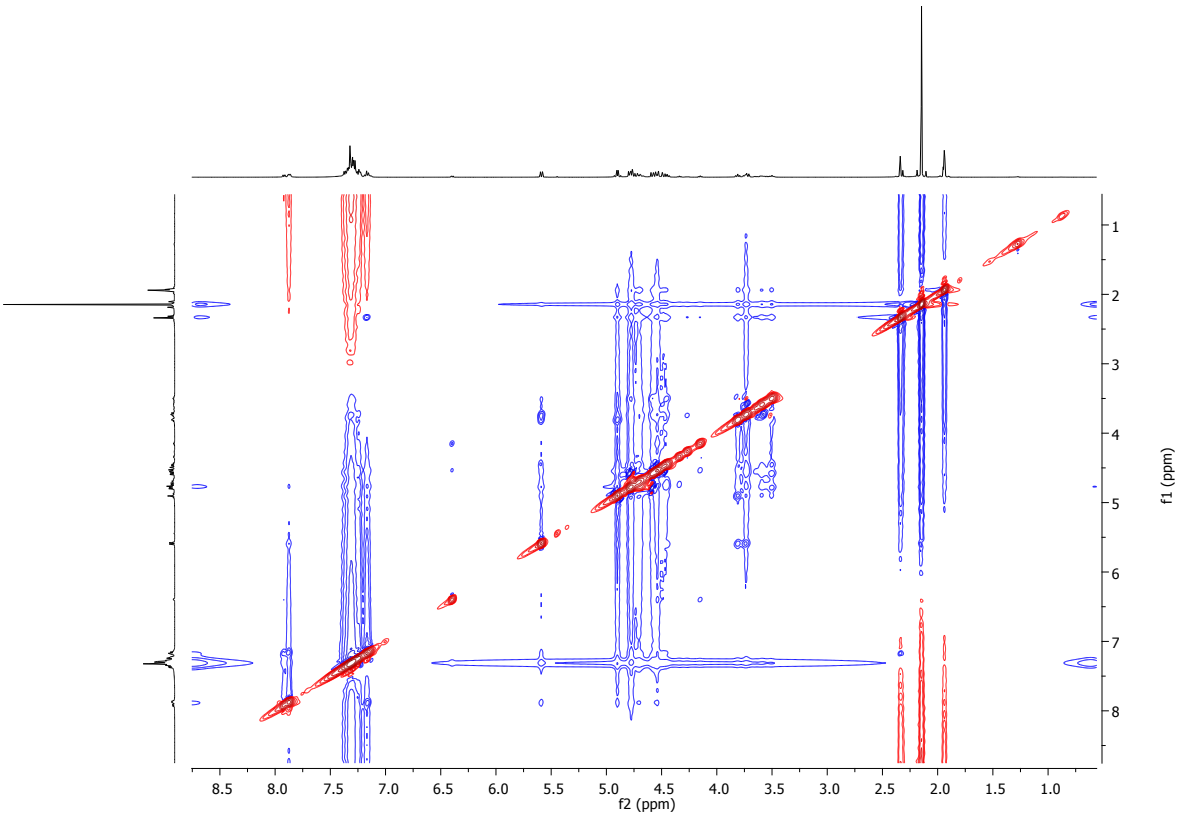
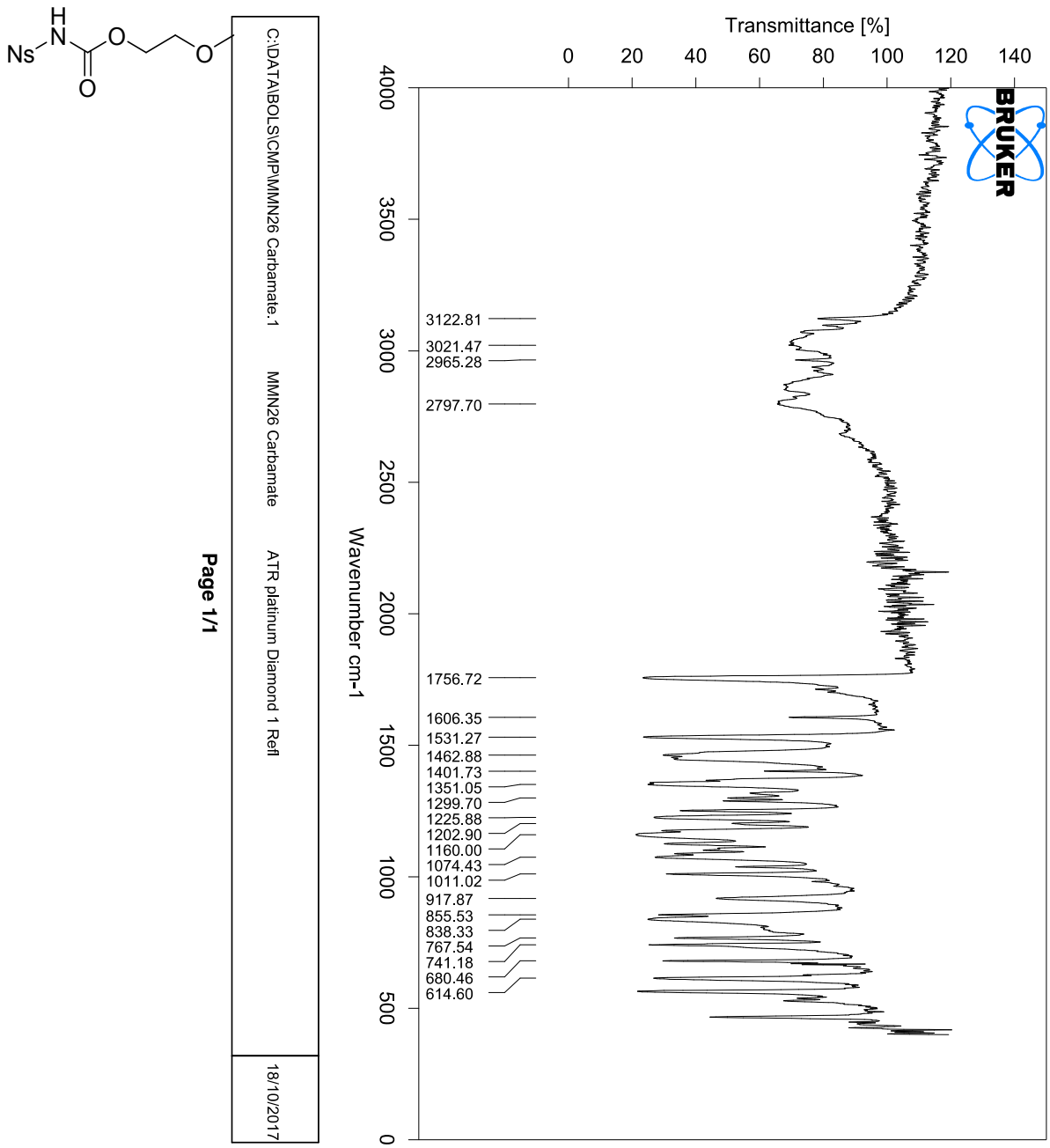


Figure 17. 2D NOESY of 16 (*α*/*β*) in $CDCl_3$ solution at 26.85°C.

Table 5. Correlations between sugar ring protons in 2D NOESY spectrum (Figure 17) with chemical shifts *δ*H (ppm) of these protons.

No. atom	Chemical shift [ppm]	Correlated protons
H-1α	6.39	H-2
H-2α	4.15	H-1
H-3α	4.34	-
H-4α	3.54	n.d.
H-5α	4.27	H-6
H-6α	3.74	n.d.
H-6'α	3.64	H-6
H-1β	5.59	H-2
		H-3
		H-5
H-2β	4.45	H-1
		H-4
H-3β	4.81	H-1
H-4β	3.51	H-2
H-5β	3.74	H-1
H-6β	3.72	H-6'
H-6'β	3.59	H-6

IR spectra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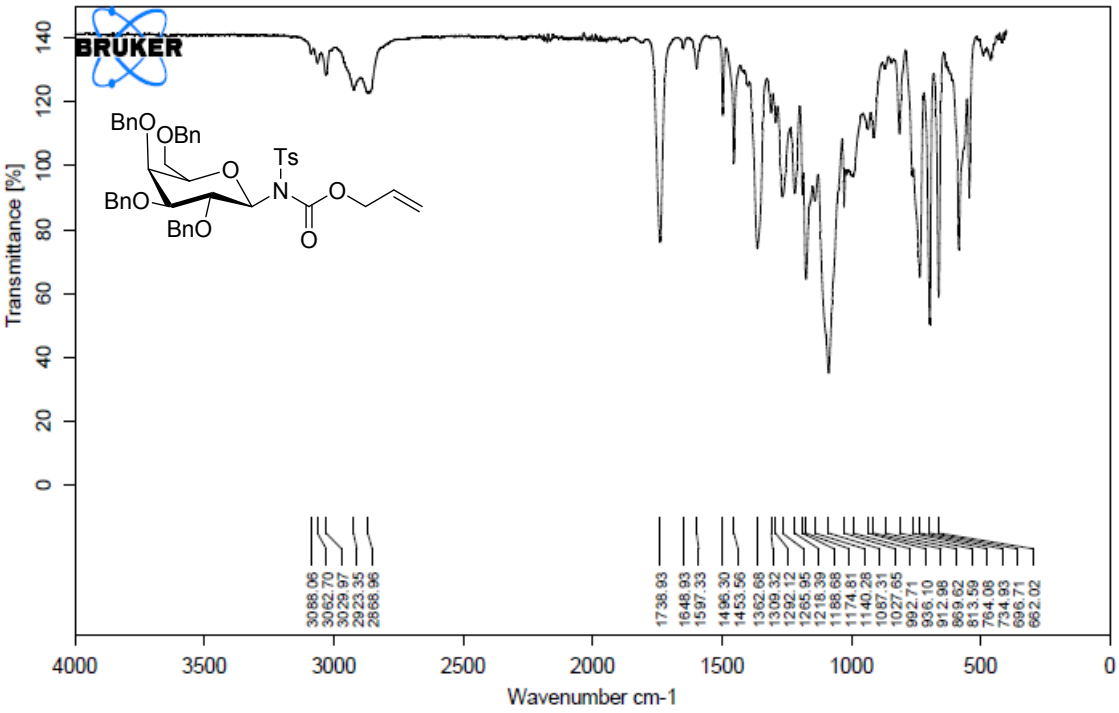
BRUKER


BRUKER
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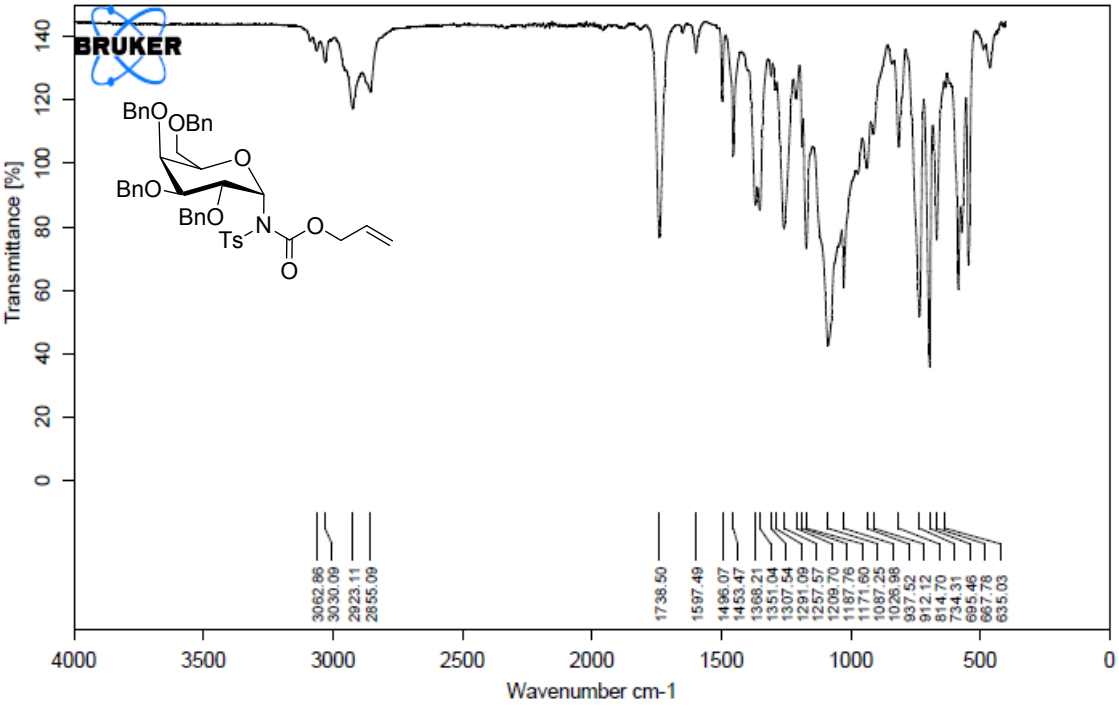
BRUKER
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O
O
Transmittance [%]
0
20
40
60
80
100
120
140
3062.86
3030.09
2923.11
2855.09
1738.50
1597.49
1496.07
1453.47
1368.21
1351.04
1307.54
1291.09
1257.57
1209.70
1187.76
1171.60
1087.25
1026.98
937.52
912.12
814.70
734.31
695.46
667.78
635.03
4000
3500
3000
2500
2000
1500
1000
500
0
Wavenumber cm-1

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