Adaptable Synthesis of Chondroitin Sulfate Disaccharide Subtypes Preprogrammed for Regiospecific *O*-Sulfation

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Supporting Information 1

Experimental

Table of Contents

General Experimental

Unless otherwise stated, all reagents used in the following experiments were bought commercially from Acros Organics, Alfa Aesar, Apollo Scientific, Biosynth, Fisher Scientific, Fluorochem, Sigma Aldrich or TCI chemicals and were used without further purification. Dry solvents were dried and stored under N_2 in Young's flasks over 4 Å molecular sieves. Anhydrous DMF, pyridine and THF were purchased from Acros Organics, fitted with AcroSeal™ packaging. For reactions that required heating, DrySyn heating blocks were used as the heat source. Reactions were monitored by thin layer chromatography (TLC) using pre-coated 0.25 mm 60 F_{254}silica gel plates (Merck) and eluent systems outlined in the respective experiments. Visualisation was achieved using UV light (λ = 254 nm), and 10% H_2SO_4:EtOH or ninhydrin staining followed by heating. Flash column chromatography was performed using silica gel [high purity grade, 60 Å pore size, 40-63 μm particle size]. NMR spectra were recorded at 400 MHz on a Bruker AVIII400 spectrometer using deuterated solvent. Chemical shifts are reported in parts per million (ppm), coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are abbreviated as; s (singlet), d (doublet), t (triplet) or m (multiplet) or combinations thereof. Chemical shifts were referenced to tetramethylsilane (TMS, where δ = 0.00 ppm). HRMS were recorded on a ThermoScientific LTQ Orbitrap XL at the ESPRC National Mass Spectrometry Facility at Swansea University. Optical rotations were recorded on a Bellingham + Stanley ADP430 (specific rotation, tube length: 50 mm, concentrations in g per 100 mL).

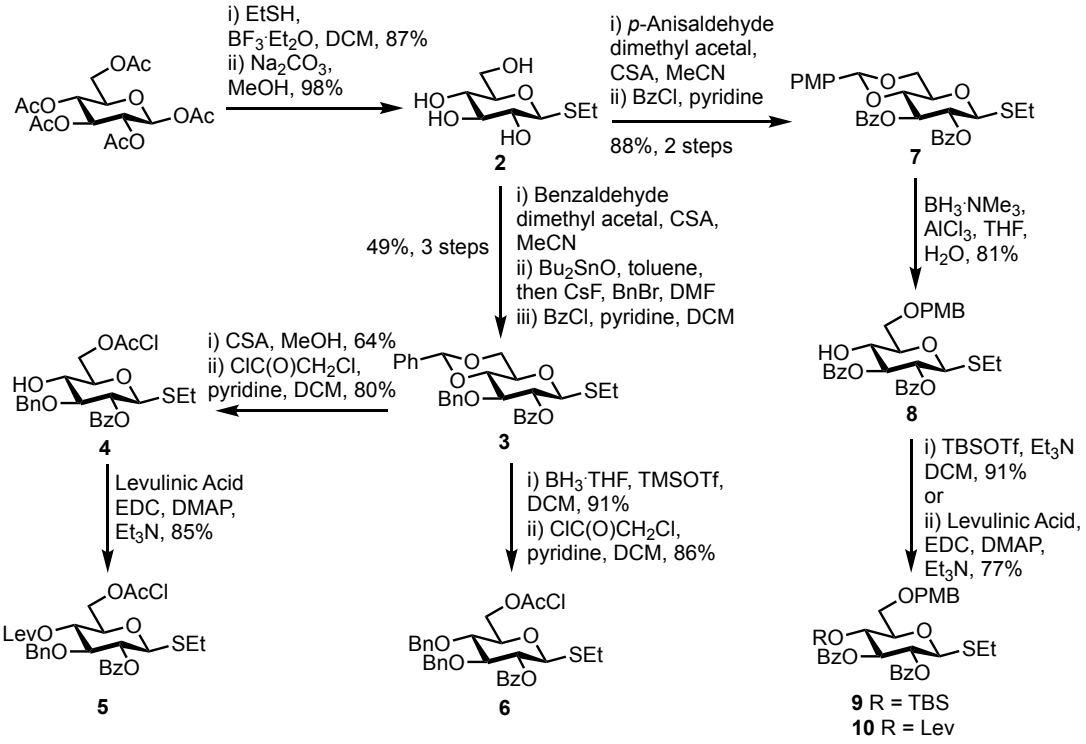
General procedure A – Glycosylation

In a multi-neck flask, glycosyl donor (1.2 equiv.), glycosyl acceptor (1.0 equiv.) and 4 Å M.S. were placed under three cycles of vacuum and N_2. Anhydrous DCM (0.05 M) was added and the solution was pre-dried for 1 h. The solution was cooled to – 35 °C (using IMS and dry ice) and stirred for a further 10 min at this temperature. *N*-iodosuccinimide (1.3 equiv.) and TfOH (0.15 equiv.) were added and the reaction was gradually warmed to 0 °C over approximately 2.5 h. TLC analysis (1:1 Hexane:EtOAc) showed full consumption of the glycosyl acceptor. The reaction was quenched with Et_3N (1 mL) and extracted with sat. aq. $Na_2S_2O_3$ (1 × 50 mL), sat. aq. $NaHCO_3$ (1 × 100 mL) and brine (1 × 100 mL). The organic phase was dried over $MgSO_4$ and filtered. Solvents were removed *in vacuo* and the crude foam was purified *via* manual flash column chromatography (10:1 → 3:1 → 1.5:1, hexane:EtOAc) which afforded the target disaccharide.

General Procedure B – Tempo Oxidation

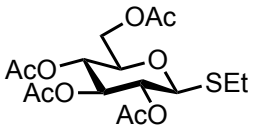
To a vigorously stirred solution of starting material (1.0 equiv.) in DCM:H_2O (2:1 *v/v*, 0.2 M), 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) (0.2 equiv.) and (diacetoxyiodo)benzene (BAIB) (2.5 equiv.) were added at 0 °C. After 10 min., the solution was warmed to RT and stirred for a further 2-3 h. TLC analysis showed formation of the desired product (7:1:1 EtOAc:MeOH:H_2O). The reaction was diluted with EtOAc, quenched with sat. aq. $Na_2S_2O_3$ and the layers were separated. The pH of the aqueous phase was tuned to pH 2 with 1 M HCl then extracted with EtOAc (3 ×). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Under an atmosphere of N_2, the crude material was suspended in anhydrous DMF (0.2 M) and cooled to 0 °C, to which MeI (3.0 equiv.) and K_2CO_3 (3.0 equiv.) were added. The reaction was stirred at RT in the dark for 2 h before dilution with EtOAc and washed with H_2O (2 ×) and brine (1 ×). The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification *via* flash column chromatography (10:1 → 3:1 → 1:1 hexane:EtOAc) afforded the desired product as a white solid.

Synthesis of Thioglycoside Glucosyl Donors



Scheme S1. Synthesis of thioglycoside glucosyl donors **5**, **6**, **9** and **10**.

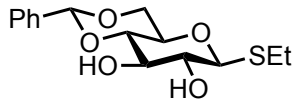
Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside S1



Under an atmosphere of N_2, at 0 °C, ethanethiol (12.3 mL, 167 mmol, 1.3 equiv.) and $BF_3{\cdot}Et_2O$ (32 mL, 256 mmol, 2.0 equiv.) were added successively to a solution of 1,2,3,4-Tetra-*O*-acetyl-β-D-glucopyranose (50.0 g, 128 mmol, 1.0 equiv.) in DCM (250 mL). The reaction mixture was then stirred at RT for a further 3 h before pouring onto sat. aq. $NaHCO_3$ (200 mL) and stirred for 30 min, until effervescence stopped. I_2 (5.60 g, 44.8 mmol, 0.35 equiv.) was added and the solution was stirred for a further 20 min. Subsequently, sat. aq. $Na_2S_2O_3$ (150 mL) was added and following 15 min. of stirring, the organic phase was extracted with DCM (2 × 200 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude product. Recrystallisation with 3:1 *v:v* hexane:EtOH (200 mL) afforded **S1** as colourless crystals (43.4 g, 111 mmol, 87%). Alternatively, the crude syrup can be washed with 10:1 *v:v* petroleum ether:Et_2O (200 mL) then filtered to afford **S1** as a white

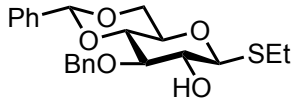
solid. $\mathbf{R_f}$ = 0.38 (2:1, hexane:EtOAc). **m.p.** 82 – 83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.23 (t, *J* = 9.4 Hz, 1H, H3), 5.09 – 5.03 (m, 2H, H2, H4), 4.50 (d, *J* = 10.0 Hz, 1H, H1), 4.25 (dd, *J* = 12.4, 4.9 Hz, 1H, H6a), 4.14 (dd, *J* = 12.4, 2.4 Hz, 1H, H6b), 3.71 (ddd, *J* = 10.0, 5.0, 2.4 Hz, 1H, H5), 2.79 – 2.64 (m, 2H, SC*H*$_2$CH$_3$), 2.08 (s, 3H, C*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 2.03 (s, 3H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 1.28 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7 (C=O), 170.2 (C=O), 169.4 (C=O), 169.4 (C=O), 83.5 (C1), 75.9 (C5), 73.9 (C3), 69.9 (C2), 68.4 (C4), 62.2 (C6), 24.2 (S*C*H$_2$CH$_3$), 20.7 (*C*H$_3$), 20.6 (*C*H$_3$), 20.6 (*C*H$_3$), 14.8 (SCH$_2$*C*H$_3$). **HRMS** m/z (ESI+) Found $(M+NH_4)^+$ 410.1478, $C_{16}H_{24}O_9S$ required $(M+NH_4)^+$, 410.1479. These data are consistent with literature data.[1]

Ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside S2



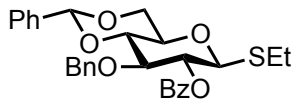
To a stirred solution of thioglycoside **S1** (43.4 g, 111 mmol, 1.0 equiv.) in MeOH (370 mL), Na_2CO_3 (3.53 g, 33.3 mmol, 0.3 equiv.) was added. After stirring for 2 h at RT, TLC analysis (7:1:1 EtOAc:MeOH:H_2O) showed full consumption of the starting material. The solution was neutralised with Dowex® 50W X8 H^+ resin, filtered and concentrated *in vacuo* afforded **the desired product** as a white foam (24.4 g, 109 mmol, 98%) which was used without further purification. Under an atmosphere of N_2, the crude **tetrol** was suspended in MeCN (370 mL) and 10-camphorsulfonic acid (6.43 g, 27.7 mmol, 0.25 equiv.) was added. Benzaldehyde dimethyl acetal (33.0 mL, 222 mmol, 2.0 equiv) was also added and the resultant solution was stirred at 50 °C for 18 h. The reaction was neutralised with Et_3N (3.90 mL, 27.8 mmol, 0.25 equiv.) and solvent removed *in vacuo* to give a crude yellow solid. Trituration with 8:1 *v:v* petroleum ether:Et_2O (250 mL) afforded **S2** as a white solid (25.2 g, 80.7 mmol, 86%). $\mathbf{R_f}$ 0.44 (2:1, hexane:EtOAc). **m.p.** 137–138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H, Ar-H), 7.42 – 7.31 (m, 2H, Ar-H), 5.52 (s, 1H, PhC*H*), 4.43 (d, *J* = 9.8 Hz, 1 H, H1), 4.33 (dd, *J* = 10.5, 4.8 Hz, 1H, H6a), 3.84 – 3.70 (m, 2H, H3, H6b), 3.55 (t, *J* = 9.2 Hz, 1H, H4), 3.51 – 3.42 (m, 2H, H2, H5), 3.12 (d, *J* = 2.3 Hz, 1H, C3-OH), 2.85 (d, *J* = 2.4 Hz, 1H, C2-OH), 2.74 (qd, *J* = 7.4, 2.2 Hz, 2H, SCH$_2$C*H*$_3$), 1.32 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9 (Ar-CH), 129.3 (Ar-CH), 128.4 (Ar-CH), 126.3 (Ar-CH), 101.9 (Ph*C*H), 86.6 (C1), 80.4 (C4), 74.5 (C3), 73.2 (C2), 70.5 (C5), 68.6 (C6), 24.7 (S*C*H$_2$CH$_3$), 15.3 (SCH$_2$*C*H$_3$). **HRMS** m/z (ESI^+) Found $(M+H)^+$ 313.1101, $C_{15}H_{20}O_5S$ required $(M+H)^+$, 313.1109. These data are consistent with literature data.[2]

Ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-1-thio-β-D-glucopyranoside S3



Diol **S2** (20.0 g, 64.0 mmol, 1.0 equiv.) was suspended in anhydrous toluene (250 mL) in a flask fitted with Dean-Stark apparatus. $^{n}Bu_2SnO$ (24.0 g, 96.0 mmol, 1.5 equiv.) was added and the glassware was covered with aluminium foil. The reaction was heated at 130 °C for 7 h, cooled and solvent was removed *in vacuo*. Under an atmosphere of N_2, the crude residue was dissolved in DMF (160 mL) then BnBr (11.4 mL, 96.0 mmol, 1.5 equiv.) and CsF (19 g, 192 mmol, 3.0 equiv.) were added at 0 °C. The reaction was warmed to RT and stirred overnight before diluting in DCM (200 mL), filtering through a silica plug and washing with 10:1 hexane:EtOAc (2 x 200 mL) then 2:1 hexane:EtOAc (4 × 200 mL). The filtrate was concentrated *in vacuo* then washed with 4:1 *v:v* petroleum ether:Et_2O (200 mL) to afford **S3** (21.7 g, 53.4 mmol, 84%) as a white solid. **R_f** 0.50 (2:1, hexane:EtOAc). **m.p.** 94 – 95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H, Ar-H), 7.41 – 7.27 (m, 8H, Ar-H), 5.58 (s, 1H, (PhC*H*), 4.97 (d, *J* = 11.7 Hz, 1H, CH_2, OBn), 4.82 (d, *J* = 11.7 Hz, 1H, CH_2, OBn), 4.46 (d, *J* = 9.7 Hz, 1H, H1), 4.36 (dd, *J* = 10.5, 5.0 Hz, 1H, H6a), 3.81 – 3.73 (m, 1H, H6b), 3.69 (dd, *J* = 17.3, 9.2 Hz, 2H, H3, H4), 3.61 – 3.55 (m, 1H, H2), 3.50 (ddd, *J* = 9.9, 9.0, 5.0 Hz, 1H, H5), 2.75 (qd, *J* = 7.4, 3.0 Hz, 2H, SC$H_2$$CH_3$), 2.51 (d, *J* = 2.0 Hz, 1H, C2-OH), 1.34 – 1.28 (m, 3H, SCH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 137.3 (2 x Ar-C), 129.0 (Ar-CH), 128.5 (Ar-CH), 128.3 (Ar-CH), 128.1 (Ar-CH), 127.9 (Ar-CH), 126.1 (Ar-CH), 101.3 (PhC*H*), 86.6 (C1), 81.6 (C5), 81.3 (C4), 74.7 (C3), 73.1 (C2), 70.8 (CH_2, Bn), 68.7 (C6), 24.6 (S*C*$H_2$$CH_3$), 15.3 ($SCH_2$*C*$H_3$). **HRMS** m/z (ESI+) Found $(M+H)^+$ 425.1396, $C_{22}H_{26}O_5S$ required $(M+H)^+$, 425.1393. These data are consistent with literature data.[3]

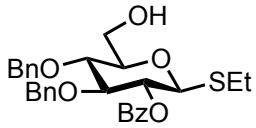
Ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-benzoyl-1-thio-β-D-glucopyranoside 3



Under an atmosphere of N_2, pyridine (7.50 mL, 88.2 mmol, 6.0 equiv.) was added to a solution of **S3** (5.9 g, 14.7 mmol, 1.0 equiv.) in DCM (49 mL) and the reaction was cooled to 0 °C. Subsequently, BzCl (2.60 mL, 22.0 mmol, 1.5 equiv.) was added then the reaction was warmed to RT. After 3 h, TLC analysis (2:1 hexane:EtOAc) showed full consumption of the starting material. The reaction mixture was neutralised with 1 M HCl (30 mL) and the organic phase

was extracted with DCM (2 × 40 mL). The combined organic extracts were washed with sat. aq. $NaHCO_3$ (1 × 50 mL) and brine (1 × 50 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude solid was washed with 8:1 petroleum ether:Et_2O to afford **3** (6.9 g, 13.5 mmol, 92%) as a white solid. $\mathbf{R_f}$ 0.57 (3:1, hexane:EtOAc). **m.p.** 122 – 123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H, Ar-H), 7.63 – 7.39 (m, 8H, Ar-H), 7.18 – 7.06 (m, 5H, Ar-H), 5.63 (s, 1H, PhC*H*, 5.35 (dd, *J* = 10.0, 8.5 Hz, 1H, H2), 4.84 (d, *J* = 11.9 Hz, 1H, CH_2, OBn), 4.71 (d, *J* = 12.0 Hz, 1H, CH_2, OBn), 4.64 (d, *J* = 10.1 Hz, 1H, H1), 4.42 (dd, *J* = 10.5, 5.0 Hz, 1H, H6a), 3.92 – 3.84 (m, 3H, H3, H4, H6b), 3.57 (td, *J* = 9.7, 5.0 Hz, 1H, H5), 2.73 (qd, *J* = 7.4, 3.7 Hz, 2H, SCH_2CH$_3$), 1.24 (t, *J* = 7.5, 3H, SCH$_2$CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2 (C=O), 137.8, 137.6, 133.2 (3 × Ar-C), 130.0, 129.8, 129.1, 128.4, 128.3, 128.2, 128.1, 127.6, 126.1 (9 × Ar-CH), 101.3 (*PhCH*), 84.4 (C1), 81.7, 79.3 (C3, C4), 74.3 (*C*H$_2$, Bn), 71.9 (C2), 70.8 (C5), 68.7 (C6), 24.1 (SCH_2CH$_3$), 14.8 (SCH$_2$CH_3). **HRMS** m/z (ESI+) Found $(M+NH_4)^+$ 524.2102 $C_{29}H_{30}O_6S$ required $(M+NH_4)^+$ 524.2101. These data are consistent with literature data.[4]

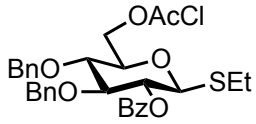
Ethyl 3,4-*O*-benzyl-2-*O*-benzoyl-1-thio-β-D-glucopyranoside S4



Under an atmosphere of N_2, compound **3** (8.0 g, 15.6 mmol, 1.0 equiv.) was dissolved in DCM (60 mL) and cooled to 0 °C. A solution of 1 M BH_3·THF (31 mL, 31.2 mmol, 2.0 equiv.) was added followed by TMSOTf (0.4 mL, 2.34 mmol, 0.15 equiv.). The reaction was warmed to RT and stirred for 4 h then cooled to 0 °C and quenched with sequential additions of Et_3N (2.4 mL, 17.2 mmol, 1.1 equiv.) and MeOH (2.5 mL, 546 mmol, 35 equiv.) until effervescence stopped. The resultant mixture was concentrated *in vacuo* followed by co-evaporation with MeOH (1 × 100 mL). Purification *via* flash column chromatography (10:1 → 7:1 → 4:1 hexane:EtOAc) afforded **S4** (7.2 g, 14.2 mmol, 91%) as a white solid. $\mathbf{R_f}$ 0.48 (2:1, hexane:EtOAc). **m.p.** 84 – 85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H, Ar-H), 7.61 – 7.55 (m, 1H, Ar-H), 7.45 (dd, *J* = 10.7, 4.7, 2H, Ar-H), 7.38 – 7.29 (m, 5H, Ar-H), 7.17 – 7.11 (m, 5H, Ar-H), 5.28 (dd, *J* = 9.9, 9.2 Hz, 1H, H2), 4.87 (d, *J* = 11.0 Hz, 1H, CH_2, OBn), 4.76 (d, *J* = 11.0 Hz, 1H, CH_2, OBn), 4.68 (d, *J* = 11.0 Hz, 2H, CH_2, OBn), 4.58 (d, *J* = 10.0 Hz, 1H, H1), 3.92 (d, *J* = 12.1, 1H, H6a), 3.87 (t, *J* = 9.0 Hz, 1H, H3), 3.76 – 3.73 (m, 1H, H6b), 3.71 (t, *J* = 9.4 Hz, H4), 3.49 (ddd, *J* = 9.7, 4.7, 2.6 Hz, 1H, H5), 2.75 – 2.67 (m, 2H,

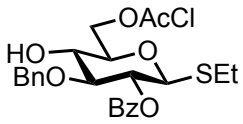
SC*H*$_2$CH$_3$), 1.97 (br s, 1H, C6-OH), 1.25 (m, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3 (C=O), 137.8, 137.7, 133.2 (3 × Ar-C), 129.9, 129.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6 (9 × Ar-CH), 84.2 (C1), 83.8 (C3), 79.8 (C5), 77.7 (C4), 75.3, 75.2 (2 × Ph*C*H$_2$), 72.5 (C2), 62.1 (C6), 24.2 (S*C*H$_2$CH$_3$), 14.9 (SCH$_2$*C*H$_3$). **HRMS** m/z (ESI+) Found $(M+NH_4)^+$ 526.2258, $C_{29}H_{32}O_6S$ required $(M+NH_4)^+$, 526.2258. These data are consistent with literature data.[4]

Ethyl 6-*O*-chloroacetyl-3,4-*O*-benzyl-2-*O*-benzoyl-1-thio-β-D-glucopyranoside 4



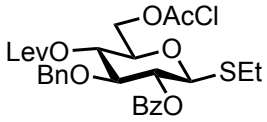
At 0 °C under an atmosphere of N_2, chloroacetyl chloride (0.4 mL, 5.12 mmol, 1.3 equiv.) was added to a stirred solution of **S4** (2.0 g, 3.94 mmol, 1.0 equiv.) and pyridine (1.3 mL, 15.8 mmol, 4.0 equiv.) in anhydrous DCM (20 mL). The reaction was warmed to RT and stirred for 1.5 h. Following completion, as monitored by TLC analysis (2:1 hexane:EtOAc), the reaction was diluted in DCM (20 mL) and washed with 1 M HCl (2 × 50 mL) and brine (1 × 50 mL) before drying over $MgSO_4$, filtering and concentrating *in vacuo*. Purification *via* manual column chromatography (10:1 → 7:1 → 5:1, hexane:EtOAc) afforded **4** (1.9 g, 3.39 mmol, 86%) as a white solid. **R_f** 0.51 (2:1, hexane:EtOAc). **m.p.** 95 – 96 °C. $[\alpha]_D^{22}$= +48.8 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H, Ar-H), 7.62 – 7.54 (m, 1H, Ar-H), 7.45 (dd, *J* = 8.3, 7.1 Hz, 2H, Ar-H), 7.40 – 7.23 (m, 5H, Ar-H), 7.20 – 7.09 (m, 5H, Ar-H), 5.30 (dd, *J* = 10.0, 9.1 Hz, 1H, H2), 4.88 (d, *J* = 11.1 Hz, 1H, C*H*$_2$-OBn), 4.77 – 4.66 (m, 2H, C*H*$_2$-OBn), 4.62 (d, *J* = 11.0 Hz, 1H, C*H*$_2$-OBn), 4.55 (d, *J* = 10.0 Hz, 1H, H1), 4.48 (dd, *J* = 11.8, 1.9 Hz, 1H, H1, H6a), 4.27 (dd, *J* = 11.9, 4.5 Hz, 1H, H6b), 4.06 – 3.94 (m, 2H, C(O)C*H*$_2$Cl), 3.88 (t, *J* = 8.7 Hz, 1H, H3), 3.72 – 3.58 (m, 2H, H4, H5), 2.78 – 2.59 (m, 2H, SC*H*$_2$CH$_3$), 1.22 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0 (C=O), 165.2 (C=O), 137.5, 137.4, 133.3 (3 × Ar-C), 129.8, 129.7, 128.6, 128.5, 128.3, 128.3, 128.2, 128.0, 127.8 (9 × Ar-CH), 84.4 (C3), 83.7 (C1), 76.9 (C4), 76.8 (C5), 75.4 (*C*H$_2$-OBn), 75.0 (*C*H$_2$-OBn), 72.3 (C2), 64.5 (C6), 40.7 (C(O)*C*H$_2$Cl), 24.1 (S*C*H$_2$CH$_3$), 14.9 (SCH$_2$*C*H$_3$). **HRMS** m/z (ESI) Found $(M+NH_4)^+$ 602.1974, $C_{31}H_{33}O_7SCl$ required $(M+NH_4)^+$, 602.1976.

Ethyl 6-*O*-chloroacetyl-3-*O*-benzyl-2-*O*-benzoyl-1-thio-β-D-glucopyranoside 5



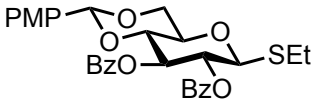
To a solution of **3** (500 mg, 0.987 mmol, 1.0 equiv.**)** in methanol (10 mL), CSA (42 mg, 0.247 mmol, 0.25 equiv.) was added and the reaction was heated to 40 °C for 2 h. When complete, as monitored by TLC analysis (1:1 hexane:EtOAc), the reaction was cooled, diluted in EtOAc (20 mL) then washed with sat. aq. $NaHCO_3$ (1 × 25 mL) and brine (1 × 25 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then placed under an atmosphere of N_2 (g); dissolved in DCM:pyridine (6.3 mL, 5:1 *v:v*) and cooled to – 78 °C. Chloroacetyl chloride (43 μL, 0.538 mmol, 0.85 equiv.) was added and the reaction was stirred at – 78 °C for 45 min then warmed to 0 °C. The reaction was quenched with H_2O (5 mL) and diluted in DCM (10 mL) before washing with sat. aq. $NaHCO_3$ (20 mL), H_2O (20 mL) and brine (20 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification *via* manual flash column chromatography (100% DCM → 7% Et_2O in DCM) afforded **5** (204 mg, 0.411 mmol, 52% over two steps) as a colourless oil. $\mathbf{R_f}$ 0.40 (2:1 hexane:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H, Ar-H), 7.60 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H, Ar-H), 7.50 – 7.44 (m, 2H, Ar-H), 7.24 – 7.17 (m, 5H, Ar-H), 5.28 (dd, *J* = 10.0, 8.7 Hz, 1H, H2), 4.74 (d, *J* = 11.3 Hz, 1H, C*H*$_2$-OBn), 4.62 (d, *J* = 11.4 Hz, 1H, C*H*$_2$-OBn), 4.58 (d, *J* = 10.0 Hz, 1H, H1), 4.48 (qd, *J* = 12.0, 3.4 Hz, 2H, H6a, H6b), 4.11 (s, 2H, C(O)C*H*$_2$Cl), 3.73 – 3.68 (m, 1H, H3), 3.65 (td, *J* = 8.6, 2.7 Hz, 1H, H4), 3.62 – 3.58 (m, 1H, H5), 2.70 (dq, *J* = 8.4, 7.4 Hz, 2H, SC*H*$_2$CH$_3$), 2.62 (d, *J* = 2.9 Hz, 1H, C4-O*H*), 1.23 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6 (C=O), 165.2 (C=O), 137.6 (Ar-C), 133.4 (Ar-C), 129.9, 129.6, 128.6, 128.5, 128.1, 128.1 (6 × Ar-CH), 83.8 (C1), 83.6 (C3), 77.3 (C5), 74.9 (*C*H$_2$-OBn), 72.0 (C2), 69.8 (C4), 64.9 (C6), 40.8 (C(O)*C*H$_2$Cl), 24.2 (S*C*H$_2$CH$_3$), 14.9 (SCH$_2$*C*H$_3$). **HRMS** m/z (ESI) Found $(M+Na)^+$ 517.1044, $C_{24}H_{27}O_7SCl$ required $(M+Na)^+$, 517.1058.

Ethyl 6-*O*-chloroacetyl-3-*O*-benzyl-4-*O*-levulinoyl-2-*O*-benzoyl-1-thio-β-D-glucopyranoside 6



Under an atmosphere of N_2 (g), glycoside **5** (110 mg, 0.222 mmol, 1.0 equiv.) was dissolved in DCM (2.2 mL) and levulinic acid (72 μL, 0.706 mmol, 2.5 equiv.), EDCI·HCl (140 mg, 0.846 mmol, 3.0 equiv.) and DMAP (10 mg, 0.067 mmol, 0.3 equiv.) were added. After 4 h at RT, the reaction mixture was filtered through celite, concentrated *in vacuo* and purified *via* manual flash column chromatography (10% Et_2O in DCM) to afford **6** (115 mg, 0.189 mmol, 85%) as a white foam. $\mathbf{R_f}$ 0.30 (2:1 hexane:EtOAc). $[\alpha]_D^{21}$= +23.3 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H, Ar-H), 7.62 – 7.56 (m, 1H, Ar-H), 7.49 – 7.43 (m, 2H, Ar-H), 7.17 – 7.09 (m, 5H, Ar-H), 5.33 (dd, *J* = 10.1, 9.1 Hz, 1H, H2), 5.17 (dd, *J* = 10.1, 9.3 Hz, 1H, H4), 4.61 – 4.57 (m, 3H, H1, C*H*$_2$-OBn), 4.32 (qd, *J* = 12.3, 3.8 Hz, 2H, H6a, H6b), 4.12 (d, *J* = 1.3 Hz, 2H, C(O)C*H*$_2$Cl), 3.90 (t, *J* = 9.2 Hz, 1H, H3), 3.73 (ddd, *J* = 10.1, 5.1, 2.4 Hz, 1H, H5), 2.76 – 2.65 (m, 4H, SC*H*$_2$CH$_3$, H$_3$CC(O)CH$_2$C*H*$_2$C(O)), 2.50 (dd, *J* = 7.9, 5.4 Hz, 1H, H$_3$CC(O)C*H*$_2$CH$_2$C(O)), 2.38 (ddd, *J* = 17.2, 6.7, 5.8 Hz, 1H, H$_3$CC(O)C*H*$_2$CH$_2$C(O)), 2.16 (s, 3H, C(O)C*H*$_3$), 1.23 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3 (C=O), 171.6 (C=O), 167.1 (C=O), 165.0 (C=O), 137.5 (Ar-C), 133.3 (Ar-C), 129.9, 129.6, 128.5, 128.3, 127.9, 127.7 (6 × Ar-CH), 83.8 (C1), 81.1 (C3), 74.4 (*C*H$_2$-OBn), 71.9 (C5), 69.9 (C4), 64.0 (C6), 40.8 (C(O)*C*H$_2$Cl), 37.8 (H$_3$*C*C(O)CH$_2$CH$_2$C(O)), 29.7 (H$_3$CC(O)CH$_2$*C*H$_2$C(O)), 27.8 (H$_3$CC(O)*C*H$_2$CH$_2$C(O)), 24.1 (SC*H*$_2$CH$_3$), 14.8 (SCH$_2$C*H*$_3$). **HRMS** m/z (ESI) Found $(M+NH_4)^+$ 610.1870, $C_{29}H_{33}O_9SCl$ required $(M+NH_4)^+$, 610.1872.

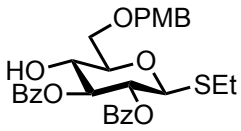
Ethyl 2,3-di-*O*-benzoyl-4,6-*O*-(4-methoxybenzylidine)-1-thio-β-D-glucopyranoside 7



Under an atmosphere of N_2, ethyl 4,6-*O*-4'-methoxybenzylidene-1-thio-β-D-glucopyranoside (3.00 g, 8.80 mmol, 1.0 equiv.) was dissolved in dry DCM (30 mL). Pyridine (4.30 mL, 52.8 mmol, 6.0 equiv.) and BzCl (4.00 mL, 35.0 mmol, 4.0 equiv.) were added sequentially. The reaction was stirred at RT for 2 h. After cooling to 0 °C, methanol (3 mL) was added and then the mixture was concentrated *in vacuo*. The residue was redissolved in DCM (100 mL) and washed with H_2O (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and solvent removed *in vacuo* affording a pale-yellow solid. The solid was washed with petroleum

ether:diethyl ether (100% to 90:10) affording **7** as a white solid (2.35 g, 4.31 mmol, 49%). $\mathbf{R_f}$ 0.25 (7:3, EtOAc:hexane). **m.p.** 163-164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 4H, Ar-H), 7.56 – 7.44 (m, 2H, Ar-H), 7.43 – 7.30 (m, 6H, Ar-H), 6.87 – 6.79 [$(AX)_2$, 2H, Ar-H], 5.79 (t, *J* = 9.4 Hz, 1H, H3), 5.55 – 5.46 (m, 2H, PMPC*H*, H2), 4.81 (d, *J* = 10.0 Hz, 1H, H1), 4.43 (dd, *J* = 10.4, 4.8 Hz, 1H, H6a), 3.96 – 3.80 (m, 2H, H4, H6b), 3.77 (s, 3H, OCH_3), 3.78 – 3.68 (m, 1H, H5), 2.85 – 2.68 (m, 2H, SCH_2), 1.26 (t, *J* = 7.4 Hz, 3H, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6 (C=O), 165.3 (C=O), 160.1 (C=O), 133.3 (Ar-CH), 133.1 (Ar-CH), 129.9 (2 × Ar-CH), 129.8 (2 × Ar-CH), 129.4 (2 × Ar-C), 129.24 (Ar-C), 129.18 (Ar-C), 128.4 (2 × Ar-CH), 128.3 (2 × Ar-CH), 127.5 (2 × Ar-CH), 113.6 (2 × Ar-CH), 101.5 (CH), 84.5 (C1), 78.8 (C4), 73.2 (C3), 71.1 (C5), 71.0 (C2), 68.5 (C6), 55.3 (O*C*H_3), 24.4 (S*C*H_2), 14.8 (*C*H_3). **LCMS** (ES^+-API): 371.1 (20%), 317.3 (5), 245.1 (5), 187.9 (10), 137.1 (10), 102.2 (100). These data are consistent with literature.data.[5]

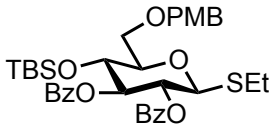
Ethyl 2,3-di-*O*-benzoyl-6-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside 8



Under an atmosphere of N_2, compound **7** (10.3 g, 17.7 mmol, 1.0 equiv.) was dissolved in dry THF (140 mL) and cooled to 0 °C. Borane trimethylamine complex (5.16 g, 70.8 mmol, 4.0 equiv.) was added in one portion followed by careful addition of aluminium chloride (14.2 g, 106.2 mmol, 6.0 equiv.). Once the aluminium chloride was completely dissolved, H_2O (0.64 mL, 35.4 mmol, 2.0 equiv.) was added and the reaction was stirred at RT for 1 h. The reaction was diluted using Et_2O (120 mL). After cooling to 0 °C, H_2O (7.5 mL) was added followed by 1M aq. NaOH (7.5 mL) and a further addition of H_2O (22.5 mL). The mixture was vigorously stirred for 15 min. $MgSO_4$ was added and the mixture was stirred for a further 15 min. After filtration, the solution was concentrated *in vacuo*. Purification *via* flash column chromatography (30:70 to 40:60 EtOAc:hexane + 1% Et_3N) afforded **8** as a colourless oil (7.9 g, 14.3 mmol, 81%). $\mathbf{R_f}$ 0.65 (2:3, EtOAc:hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 4H, Ar-H), 7.53 – 7.45 (m, 2H, Ar-H), 7.40 – 7.31 (m, 4H, Ar-H), 7.31 – 7.23 (m, 2H, Ar-H), 6.93 – 6.84 (m, 2H, Ar-H), 5.53 – 5.39 (m, 2H, H2, H3), 4.69 (d, *J* = 9.4 Hz, 1H, H1), 4.63 – 4.48 (m, 2H, OCH_2), 3.95 (td, *J* = 9.2, 2.7 Hz, 1H, H4), 3.88 – 3.74 (m, 2H, H6), 3.79 (s, 3H, OCH_3), 3.69 (dt, *J* = 9.2, 4.7 Hz, 1H, H5), 3.30 (d, *J* = 3.2 Hz, 1H, OH), 2.83 – 2.65 (m, 2H, SCH_2), 1.25 (t, *J* = 7.3 Hz, 3H, CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1 (*C*=O), 165.5 (*C*=O), 159.5 (Ar*C*OMe), 133.5 (Ar-CH), 134.3 (Ar-CH), 130.1 (2 × Ar-CH), 129.9 (2 × Ar-

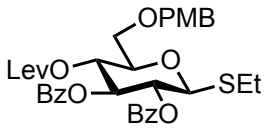
CH), 129.8 (Ar-C), 129.6 (2 × Ar-CH), 129.4 (Ar-C), 129.2 (Ar-C), 128.8 (Ar-C), 128.49 (2 × Ar-CH), 128.47 (2 × Ar-CH), 112.9 (2 × Ar-CH), 83.7 (C1), 78.7 (C5), 77.7 (C3), 73.6 (*C*H$_2$PMP), 71.3 (C4), 70.3 (C2), 70.1 (C6), 55.4 (O*C*H$_3$), 24.3 (S*C*H$_2$), 15.0 (*C*H$_3$). The data are in accordance with the literature.[6]

Ethyl 2,3-di-*O*-benzoyl-4-*O*-tert-butylsimethylsilyl-6-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside 9



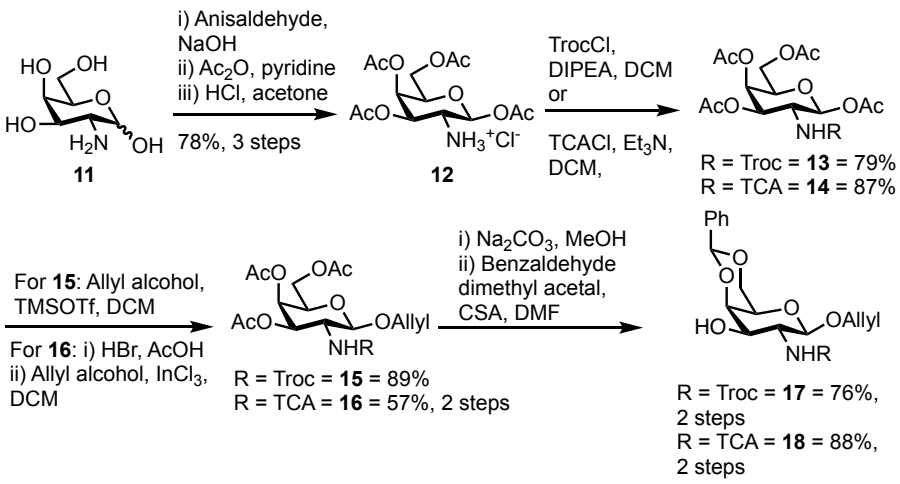
Under an atmosphere of N_2, compound **8** (810 mg, 1.47 mmol, 1.0 equiv.) and Et_3N (0.42 mL, 4.41 mmol, 3.0 equiv.) were dissolved in DCM (15 mL) and cooled to 0 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.84 mL, 3.67 mmol, 2.5 equiv.) was added dropwise then the reaction was warmed to RT and stirred for 1 h. The reaction was quenched using sat. aq. $NaHCO_3$ (10 mL) and the layers were separated. The aqueous layer was extracted using DCM (3 × 15 mL). The combined organic layers were washed using brine (20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification *via* flash column chromatography (20:80 to 30:70 EtOAc:hexane) on silica gel afforded **9** as a colourless oil (890 mg, 0.91mmol, 91%). $\mathbf{R_f}$ 0.63 (3:7, EtOAc:hexane). $[\alpha]_D^{21}$ = + 38.1 (*c* 0.1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H, Ar-H), 7.51 – 7.41 (m, 2H, Ar-H), 7.38 – 7.26 (m, 6H, Ar-H), 6.94 – 6.85 (m, 2H, Ar-H), 5.59 (dd, *J* = 9.7, 9.1 Hz, 1H, H3), 5.35 (t, *J* = 9.7 Hz, 1H, H2), 4.70 (d, *J* = 9.7 Hz, 1H, H1), 4.61 (d, *J* = 11.7 Hz, 1H, C*H*HPMP), 4.51 (d, *J* = 11.7 Hz, 1H, C*H*HPMP), 4.03 (t, *J* = 9.1 Hz, 1H, H4), 3.82 (s, 3H, OC*H*$_3$), 3.78 (dd, *J* = 10.8, 1.9 Hz, 1H, H6a), 3.69 (dd, *J* = 10.8, 5.0 Hz, 1H, H6b), 3.63 (ddd, *J* = 9.3, 5.0, 1.9 Hz, 1H, H5), 2.85 – 2.65 (m, 2H, SC*H*$_2$), 1.27 (t, *J* = 7.5 Hz, 3H, C*H*$_3$), 0.73 [s, 9H, C(C*H*$_3$)$_3$], 0.01 (s, 3H, SiC*H*$_3$), − 0.21 (s, 3H, SiC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0 (*C*=O), 165.5 (*C*=O), 159.3 (Ar-CO), 133.2 (Ar-CH), 133.1 (Ar-CH), 130.5 (Ar-C), 129.9 (2 × Ar-CH), 129.8 (2 × Ar-CH), 129.5 (Ar-C), 129.3 (2 × Ar-CH), 128.39 (2 × Ar-CH), 128.36 (2 × Ar-CH), 113.9 (2 × Ar-CH), 83.4 (C1), 81.0 (C5), 77.4 (C3), 73.2 (O*C*H$_2$), 71.3 (C2), 69.4 (C4), 68.6 (C6), 55.4 (O*C*H$_3$), 25.7 [C(*C*H$_3$)$_3$], 24.2 (S*C*H$_2$), 18.0 [Si*C*(CH$_3$)$_3$], 15.1 (CH$_2$*C*H$_3$), − 4.1 (Si*C*H$_3$), − 4.6 (Si*C*H$_3$). **HRMS** (NSI+) Found $(M+NH_4)^+$ 684.3032, $C_{36}H_{46}O_8SSi$ required $(M+NH_4)^+$ 684.3021.

Ethyl 2,3-di-*O*-benzoyl-4-*O*-levulinoyl-6-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside 10



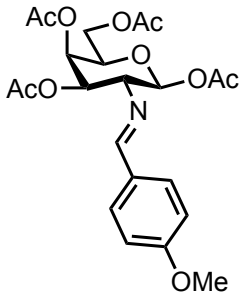
Under an atmosphere of N_2, levulinic acid (0.34 mL, 3.38 mmol, 2.5 equiv.), EDCI.HCl (0.648 g, 3.38 mmol, 2.5 equiv.), Et_3N (0.46 mL, 3.38 mmol, 2.5 equiv.) and DMAP (0.041 g, 0.34 mmol, 0.25 equiv.) were dissolved in DCM (2 mL). Compound **8** (0.748 g, 1.35 mmol, 1.0 equiv.) in DCM (5 mL) was added dropwise and the reaction was stirred at RT for 2 h. After diluting with DCM (10 mL), the mixture was washed with sat. aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification *via* flash column chromatography (35:65 EtOAc:petroleum ether) afforded **10** as a colourless oil (0.68 g, 1.04 mmol, 77%). $\mathbf{R_f}$ 0.50 (2:3, EtOAc:hexane). $[\alpha]_D^{21}$ = + 19.2 (*c* 0.5, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 4H, Ar-H), 7.54 – 7.42 (m, 2H, Ar-H), 7.41 – 7.31 (m, 4H, Ar-H), 7.31 – 7.23 (m, 2H, Ar-H), 6.91 – 6.83 (m, 2H, Ar-H), 5.67 (t, *J* = 9.7 Hz, 1H, H3), 5.44 (t, *J* = 9.7 Hz, 1H, H2), 5.32 (t, *J* = 9.7 Hz, 1H, H4), 4.72 (d, *J* 9.7 Hz, 1H, H1), 4.56 – 4.45 (m, 2H, OC*H*$_2$PMP), 3.89 – 3.77 (m, 1H, H5), 3.80 (s, 3H, OC*H*$_3$), 3.71 – 3.58 (m, 2H, H6), 2.85 – 2.65 (m, 2H, SC*H*$_2$), 2.61 – 2.24 (m, 4H, C*H*$_2$C*H*$_2$), 2.02 (s, 3H, C*H*$_3$), 1.26 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.0 (*C*=O), 171.5 (*C*=O), 165.9 (*C*=O), 165.3 (*C*=O), 159.4 (Ar-CO), 133.4 (Ar-CH), 133.3 (Ar-CH), 130.1 (Ar-C), 130.0 (2 × Ar-CH), 129.9 (2 × Ar-CH), 129.7 (2 × Ar-CH), 129.4 (Ar-C), 129.1 (Ar-C), 128.49 (2 × Ar-CH), 128.46 (2 × Ar-CH), 113.9 (2 × Ar-CH), 83.8 (C1), 77.9 (C5), 74.6 (C3), 73.4 (O*C*H$_2$), 70.7 (C2), 69.5 (C4), 68.9 (C6), 55.4 (O*C*H$_3$), 37.9 (*C*H$_2$), 29.6 (*C*H$_3$), 28.0 (*C*H$_2$), 24.4 (S*C*H$_2$), 15.0 (*C*H$_3$). **HRMS** (ESI+) Found $(M+NH_4)^+$ 668.2518, $C_{35}H_{42}O_{10}NS$ required $(M+NH_4)^+$ 668.2525.

Galactosamine Acceptor Synthesis



Scheme S3. Synthesis of galactosamine acceptors **17** and **18**.

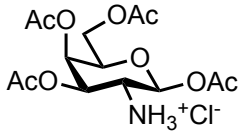
Acetyl 2-deoxy-2-*p*-methoxybenzylidenamino-3,4,6-tri-*O*-acetyl-β-D-galactopyranose S6



D-Galactosamine hydrochloride (50 g, 230 mmol, 1.0 equiv) was dissolved in 1 M aq. NaOH (200 mL). *p*-Anisaldehyde (34 mL, 280 mmol, 1.1 equiv) was added with vigorous stirring and after a few minutes, a white precipitate was formed. After 1 h at 0 °C, the resultant precipitate was then collected by filtration and washed with H_2O (2 × 200 mL) and 1:2 MeOH:Et_2O (1 × 200 mL). The sticky precipitate was then redissolved in MeOH, concentrated *in vacuo* and dried for at least 6 h under vacuum then under N_2, treated with Ac_2O (90 mL), pyridine (400 mL) and DMAP (400 mg, 2.1 mmol, 0.1 equiv) at 0 °C. The reaction mixture was gradually warmed to RT and stirred for 1 h. The solution was diluted with DCM (300 mL) then washed with 1 M HCl (2 × 200 mL), sat. aq. $NaHCO_3$ (300 mL) and brine (300 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **S6** as a white solid that was used without further purification (97 g, 209 mmol, 93%). $\mathbf{R}_f$ 0.50 (1:1, hexane:EtOAc). **m.p.** 178-179 °C. **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.32 (s, 1H, C*H*N), 7.73 – 7.65 (m, 2H, Ar-H), 7.04 – 6.96 (m, 2H, Ar-H), 6.00 (d, J = 8.2 Hz, 1H, H1), 5.36 (dd, J = 10.3, 3.4 Hz, 1H,

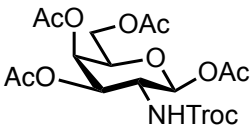
H3), 5.28 (dd, *J* = 3.4, 1.3 Hz, 1H, H4), 4.47 (td, *J* = 6.4, 1.3 Hz, 1H, H5), 4.15 – 4.00 (m, 2H, H6), 3.80 (s, 3H, OC*H*$_3$), 3.53 (dd, *J* = 10.3, 8.2 Hz, 1H, H2), 2.14 (s, 3H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 1.98 (s, 3H, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 170.5 (C=O), 170.4 (C=O), 169.7 (C=O), 169.1 (C=O), 165.1 (C=N), 162.3 (Ar-C), 130.4 (2 × Ar-CH), 128.8 (Ar-C), 114.7 (2 × Ar-CH), 93.2 (C1), 71.4 (C3), 71.2 (C5), 68.9 (C2), 66.5 (C4), 61.9 (C6), 55.8 (O*C*H$_3$), 21.0 (*C*H$_3$), 20.93 (*C*H$_3$), 20.90 (*C*H$_3$), 20.8 (*C*H$_3$). **HRMS**: m/z (ESI+) Found $(M+H)^+$ 466.1698, $C_{22}H_{27}NO_{10}$ required $(M+H)^+$, 466.1713. These data are consistent with the literature.[7]

1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-galactopyranose hydrochloride 12



Compound **S6** (9.10 g, 19.6 mmol, 1.0 equiv.) was dissolved in 50 mL of refluxing acetone and to this solution, 5 M HCl (5 mL) was added dropwise. Upon cooling to RT, a white precipitate formed. This was filtered and washed with ice-cold acetone (150 mL) and Et_2O (2 x 150 mL). The resultant white solid **12** (6.38 g, 16.7 mmol, 85%) was dried under vacuum for 3 h and used without further purification. **R$_f$** 0.00 (1:1, hexane:EtOAc). **^{1}H NMR** (400 MHz, D_2O) δ 5.90 (d, *J* = 8.8 Hz, 1H, H1), 5.47 (d, *J* 3.2 Hz, 1H, H4), 5.27 (dd, *J* = 11.2, 3.2 Hz, 1H, H3), 4.38 – 4.30 (m, 1H, H5), 4.22 – 4.10 (m, 2H, H6), 3.80 (dd, *J* = 11.2, 8.8 Hz, 1H, H2), 2.17 (s, 3H, C*H*$_3$), 2.15 (s, 3H, C*H*$_3$), 2.04 (s, 3H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, D_2O) 173.4 (C=O), 173.0 (C=O), 172.3 (C=O), 171.2 (C=O), 90.7 (C1), 71.8 (C5), 69.4 (C3), 66.4 (C4), 61.6 (C6), 49.6 (C2), 20.2 (*C*H$_3$), 20.1 (*C*H$_3$), 20.0 (*C*H$_3$), 19.8 (*C*H$_3$). **LCMS** (ES^+-API): 370.2 (30), 349.1 (15), 348.0 (90, M+H), 306.1 (5), 288.1 (100), 228.1 (20), 168.0 (25). These data are consistent with literature.[7]

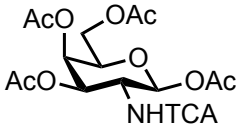
1,3,4,6-Tetra-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranose 13



To a solution of compound **12** (15 g, 49 mmol, 1.0 equiv.) in DCM (150 mL) at 0 °C, DIPEA (17 mL, 98 mmol, 2.5 equiv.) and TrocCl (11 mL, 78 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at RT for 2 h before sat. aq. NH_4Cl (150 mL) was added and the

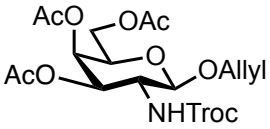
resultant aqueous phase was washed with DCM (100 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified *via* a silica plug (10:1 hexane:EtOAc → 2:1 hexane:EtOAc) to afford **13** as a white foam (17.1 g, 33 mmol, 84%). $\mathbf{R_f}$ 0.72 (1:1 hexane:EtOAc). $\mathbf{[\alpha]_D^{25}}$ = +13.3 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.77 (d, *J* = 8.8 Hz, 1H, H1), 5.44 (d, *J* = 9.6 Hz, 1H, N-H), 5.41 (dd, *J* = 3.4, 1.1 Hz, 1H, H4), 5.16 (dd, *J* = 11.3, 3.3 Hz, 1H, H3), 4.77 – 4.69 (m, 2H, CH2CCl3), 4.18 – 4.07 (m, 4H, H2, H5, H6a, H6b), 2.18 (s, 3H, CH3), 2.13 (s, 3H, CH3), 2.05 (s, 3H, CH3), 2.01 (s, 3H, CH3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 170.5, 170.2, 169.4 (4 × C=O, OAc), 154.4 (C=O, Troc), 95.5 (*C*Cl_3), 92.6 (C1), 74.4 (*C*H_2-Troc), 71.7 (C3), 70.1 (C5), 66.4 (C4), 61.3 (C6), 51.7 (C2), 20.9, 20.7, 20.7, 20.6 (4 × *C*H_3). **HRMS**: m/z (ESI+) Found $(M+NH_4)^+$ 539.0583, $C_{17}H_{22}Cl_3NO_{11}$ required $(M+NH_4)^+$, 539.0602.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranose 14



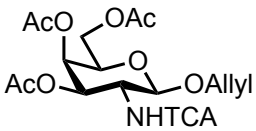
Under an atmosphere of N_2, compound **12** (5.17 g, 13.5 mmol, 1.0 equiv.) was suspended in dry DCM (50 mL) and cooled to 0 °C. Et_3N (3.80 mL, 27.0 mmol, 2.0 equiv.) and trichloroacetyl chloride (2.30 mL, 20.2 mmol, 1.5 equiv.) were added sequentially and the mixture was stirred at 0 °C for 1.5 h. After addition of H_2O (100 mL) to the reaction mixture, the layers were separated, and the aqueous layer was extracted with DCM (2 × 50 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification *via* flash column chromatography on silica gel (40:60, EtOAc:hexane) afforded **14** as a white foam (6.11 g, 12.4 mmol, 92%). $\mathbf{R_f}$ 0.55 (1:1, EtOAc:hexane) $\mathbf{[\alpha]_D^{25}}$ = +2.9 (*c* 1, $CHCl_3$, lit. +4.0, *c* 0.80 in $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 9.0 Hz, 1H, N*H*), 5.84 (d, *J* = 9.0 Hz, 1H, H1), 5.41 (dd, *J* = 3.4, 1.2 Hz, 1H, H4), 5.25 (dd, *J* = 11.3, 3.4 Hz, 1H, H3), 4.44 (dt, *J* = 11.3, 9.0 Hz, 1H, H2), 4.26 – 4.10 (m, 2H, H6), 4.06 (td, *J* = 6.5, 1.2 Hz, 1H, H5), 2.19 (s, 3H, C*H*$_3$), 2.13 (s, 3H, C*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8 (C=O), 170.6 (C=O), 170.2 (C=O), 169.6 (C=O), 162.5 (C=O), 92.5 (C1), 92.3 (*C*Cl_3), 72.3 (C5), 69.9 (C3), 66.4 (C4), 61.4 (C6), 51.9 (C2), 20.9 (*C*H_3), 20.81 (*C*H_3), 20.77 (*C*H_3), 20.66 (*C*H_3). **LCMS** (ES^+-API): 509.1 [100%, $(M+NH_4)$], 511.1 [99, $(M+NH_4)$], 432.0 (95), 434 (94). The data are in accordance with the literature.[8]

Allyl 2-deoxy-2-2,2,2-trichloroethoxycarbonylamino-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside 15



Under an atmosphere of N_2, compound **13** (6.60 g, 11.8 mmol, 1.0 equiv.) and allyl alcohol (2.0 mL, 29.4 mmol, 2.5 equiv.) were dissolved in DCM (80 mL) and stirred in the presence of 4 Å molecular sieves for 1 h. TMSOTf (2.8 mL, 15.3 mmol, 1.3 equiv.) was added then the reaction was stirred at RT for an additional 1 h. When complete, the solution was washed with sat. aq. $NaHCO_3$ (2 × 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification *via* manual flash column chromatography (2:1 hexane:EtOAc (α); 1:1 hexane:EtOAc (β)) afforded β-**15** as a white foam (5.4 g, 10.5 mmol, 89%) and α-**15** as a colourless oil (397 mg, 0.826 mmol, 7%). $\mathbf{R_f}$ 0.38 (β), 0.51 (α) (5% Et_2O in DCM). $\mathbf{[\alpha]_D^{22}}$ = – 5.71 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 17.0, 10.4, 6.4, 5.1 Hz, 1H, OCH_2CHCH_2), 5.38 (dd, *J* = 3.4, 1.1 Hz, 1H, H4), 5.33 – 5.13 (m, 3H, H3, 2 × OCH_2CHCH_2), 4.80 – 4.63 (m, 3H, H1, 2 × $C(O)OCH_2Cl_3$), 4.38 (ddt, *J* = 13.0, 5.1, 1.5 Hz, 1H, OCH_2CHCH_2), 4.22 – 4.08 (m, 3H, H6a, H6b, OCH_2CHCH_2), 3.94 – 3.89 (m, 1H, H5), 3.87 – 3.81 (m, 1H, H2), 2.15 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.00 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5 (C=O), 170.4 (C=O), 170.3 (C=O), 154.1 ($C(O)OCH_2Cl_3$), 133.4 (OCH_2CHCH_2), 118.1 (OCH_2CHCH_2), 100.0 (C1), 95.5 (CCl_3), 74.4 ($C(O)OCH_2Cl_3$) 70.7 (OCH_2CHCH_2), 70.3 (C5), 69.7 (C3), 66.7 (C4), 61.4 (C6), 52.9 (C2), 21.1 (CH_3), 20.7 (CH_3), 20.6 (CH_3). **HRMS**: m/z (ESI+) Found $(M+NH_4)^+$ 537.0782, $C_{18}H_{24}Cl_3NO_{10}$ required 537.0810.

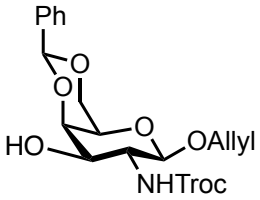
Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranoside 16



Under an atmosphere of N_2, compound **14** (1.94 g, 3.94 mmol, 1.0 equiv.) was dissolved in DCM (16 mL) and cooled to 0 °C in an aluminium foil covered RBF in the dark. HBr (33% in AcOH, 8.6 mL, 0.46 M) was added dropwise and the reaction was slowly warmed to RT. After stirring for 1 h, the mixture was washed with ice H_2O (100 mL) and separated. The organic layer was washed with sat. aq. $NaHCO_3$ (60 mL) until neutralised, then it was washed with brine (60 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Under an atmosphere of N_2,

the off-white foam was dissolved in DCM (24 mL) with 4Å molecular sieves. Allyl alcohol (0.54 mL, 7.88 mmol, 2.0 equiv.) was added and the reaction was stirred for 2 h at RT. Indium chloride (440 mg, 1.97 mmol, 0.5 equiv.) was added and the reaction was stirred overnight at RT. The mixture was filtered through a pad of celite and the celite was washed with DCM (2 × 20 mL). The filtrate was washed with H_2O (60 mL), sat. aq. $NaHCO_3$ (60 mL), and brine (60 mL), and then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification *via* flash column chromatography (40:60, EtOAc:hexane) afforded **16** as a white foam (1.10 g, 2.25 mmol, 57%). $\mathbf{R_f}$ 0.55 (1:1, EtOAc:hexane). $\mathbf{[\alpha]_D^{25}}$ = − 6.5 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.68 (d, *J* 8.7, 1H, N*H*), 5.85 (dddd, *J* = 17.1, 10.4, 6.3, 5.1 Hz, 1H, C=C*H*), 5.40 (dd, *J* = 3.4, 1.2 Hz, 1H, H4), 5.34 (dd, *J* = 11.3, 3.4 Hz, 1H, H3), 5.29 (dq, *J* = 17.1, 1.4 Hz, 1H, C=C*H*H), 5.21 (dq, *J* = 10.4, 1.4 Hz, 1H, C=C*H*H), 4.75 (d, *J* = 8.4 Hz, 1H, H1), 4.38 (ddt, *J* = 12.9, 5.1, 1.4 Hz, 1H, OC*H*H), 4.24 – 4.05 (m, 4H, H2, H6, OC*H*H), 3.94 (td, *J* = 6.7, 1.2 Hz, 1H, H5), 2.16 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.00 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6 (C=O), 170.5 (C=O), 170.3 (C=O), 162.1 (C=O), 133.2 (C=*C*H), 118.5 (C=*C*H_2), 99.6 (C1), 92.4 (*C*Cl_3), 71.0 (C5), 70.5 (O*C*H_2), 69.4 (C3), 66.7 (C4), 61.4 (C6), 53.3 (C2), 20.9 (*C*H_3), 20.8 (*C*H_3), 20.7 (*C*H_3). **HRMS** (ESI+) Found $(M+NH_4)^+$ 507.0689, $C_{17}H_{22}Cl_3NO_9$ required $(M+NH_4)^+$ 507.0704. The data are in accordance with the literature.[9]

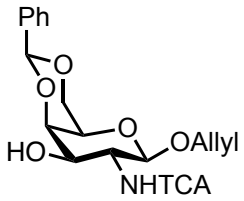
Allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-2,2,2-trichloroethoxycarbonylamino-1-β-D-galactopyranoside 17



To a solution of compound **15** (5.40 g, 10.8 mmol, 1.0 equiv.) in MeOH (100 mL), Na_2CO_3 (1.60 g, 3.24 mmol, 0.3 equiv) was added and the reaction was stirred at RT for 2 h. The reaction mixture was neutralised with Dowex® 50W X8 H^+ resin then filtered, washed with MeOH (3 × 40 mL) and concentrated *in vacuo* to afford a white solid. The crude product was suspended in anhydrous DMF (45 mL) and treated with CSA (400 mg, 2.39 mmol, 0.25 equiv.) and benzaldehyde dimethyl acetal (2.20 mL, 14.3 mmol, 1.5 equiv.). The reaction was stirred at 40 °C for 2 h then diluted with EtOAc (100 mL) before washing with sat. aq. $NaHCO_3$ (3 × 50 mL) and brine (50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was washed with 8:1 petroleum ether:Et_2O (30 mL) to afford **17** as an off-white solid (3.60 g, 8.42 mmol, 78% over 2 steps) as a white solid. $\mathbf{R_f}$

0.38 (2:1 hexane:EtOAc). **[α]$_D^{25}$** –5.49 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$ + 1 drop MeOD) δ 7.56 – 7.52 (m, 2H, Ar-H), 7.48 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.37 (dd, *J* = 5.1, 2.0 Hz, 2H, Ar-H), 5.89 (dddd, *J* = 17.3, 10.5, 6.2, 5.1 Hz, 1H, OCH_3CHCH_2), 5.58 (s, 1H, PhC*H*), 5.29 (dq, *J* = 17.2, 1.7 Hz, 1H, OCH_3CHCH_2), 5.18 (dq, *J* = 10.4, 1.4 Hz, 1H, OCH_3CHCH_2), 4.72 (d, *J* = 1.9 Hz, 2H, $C(O)OCH_2CCl_3$), 4.59 (d, *J* = 8.2 Hz, 1H, H1), 4.39 (ddt, *J* = 13.0, 5.1, 1.6 Hz, 1H, OCH_3CHCH_2), 4.32 (dd, *J* = 12.4, 1.6 Hz, 1H, H6a), 4.19 (dd, *J* = 3.3, 1.1 Hz, 1H, H4), 4.14 – 4.06 (m, 2H, H6b, OCH_3CHCH_2), 3.88 (d, *J* = 10.6 Hz, 1H, H3), 3.71 (d, *J* = 9.2 Hz, 1H, H2), 3.48 (app d, *J* = 1.5 Hz, 1H, H5). **^{13}C NMR** (101 MHz, $CDCl_3$ + 1 drop MeOD) δ 155.1 (C=O), 137.5 (Ar-CH), 133.8 (OCH_2CHCH_2), 129.2 (Ar-CH), 128.2 (Ar-CH), 126.4 (Ar-CH), 117.4 (OCH_2CHCH_2), 101.3 (PhCH), 99.8 (C1), 95.5 (CCl_3), 75.3 (C4), 74.5 ($C(O)CH_2CCl_3$), 69.9 (C3), 69.8 (OCH_2CHCH_2), 69.1 (C6), 55.0 (C2). **HRMS**: m/z (ESI)$^+$ Found $(M+NH_4)^+$ 499.0793, $C_{19}H_{22}Cl_3NO_7$ required $(M+NH_4)^+$ 499.0800.

Allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-trichloroacetamine-1-β-D-galactopyranoside 18

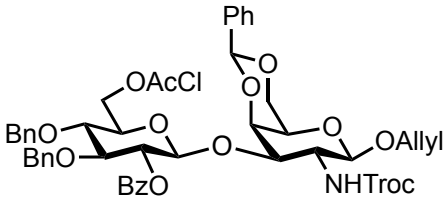


Compound **16** (1.91 g, 3.90 mmol, 1.0 equiv.) was dissolved in methanol (25 mL). Na_2CO_3 (124 mg, 1.20 mmol, 0.3 equiv.) was added in one portion and the reaction was stirred at RT for 1.5 h. After neutralisation using Amberlyst IR-20 H^+ resin, the mixture was filtered and concentrated *in vacuo*. The residue was dissolved in MeCN (50 mL) and CSA (0.226 g, 0.98 mmol, 0.25 equiv.) and benzaldehyde dimethyl acetal (1.2 mL, 7.80 mmol, 2.0 equiv.) were added. The reaction was heated at 50 °C overnight. After cooling to RT, the reaction was neutralised using Et_3N and concentrated *in vacuo*. Purification via flash column chromatography (2% MeOH in DCM + 1% Et_3N) afforded **18** as an off-white solid (1.42 g, 3.43 mmol, 88%). **[α]$_D^{25}$** −4.4 (*c* 1, $CHCl_3$). **m.p.** 142-144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H, Ar-H), 7.48 – 7.32 (m, 3H, Ar-H), 6.84 (d, *J* = 7.3 Hz, 1H, N*H*), 5.89 (dddd, *J* = 17.0, 10.3, 6.3, 5.3 Hz, 1H, $CH=CH_2$), 5.60 (s, 1H, CHPh), 5.30 (dq, *J* = 17.0, 1.4 Hz, 1H, C=CHH), 5.20 (dq, *J* = 10.3, 1.4 Hz, 1H, C=CHH), 4.87 (d, *J* = 8.3 Hz, 1H, H1), 4.46 – 4.33 (m, 2H, OCHH and H6a), 4.27 – 4.19 (m, 2H, H4, H6b), 4.16 – 4.06 (m, 2H, OCHH and H3), 3.82 (ddd, *J* = 10.2, 8.3, 7.3 Hz, 1H, H2), 3.55 (dt, *J* = 2.6, 1.2 Hz, 1H, H5), 2.71 (s,

1H, O*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (C=O), 137.5 (Ar-C), 133.7 (H*C*=C), 129.5 (2 × Ar-CH), 128.4 (2 × Ar-CH), 126.5 (Ar-CH), 118.2 (C=*C*H_2), 101.5 (*C*HPh), 98.7 (C1), 92.6 (*C*Cl_3), 75.1 (C4), 70.2 (O*C*H_2), 69.3 (C3), 69.2 (C6), 66.8 (C5), 56.9 (C2). **HRMS** (ESI+) Found $(M+NH_4)^+$ 469.0691, $C_{18}H_{24}Cl_3NO_6$ required 469.0700.

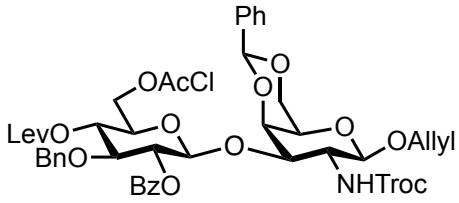
CS Precursor Disaccharide Synthesis

6-*O*-Chloroacetyl-3,4-di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranoside-β(1→3)-Allyl 4,6-*O*-benzylidene-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside 19



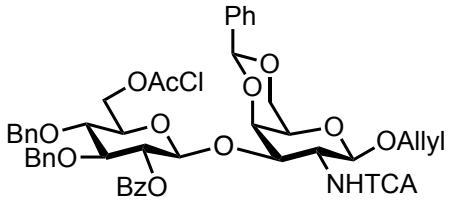
Disaccharide **19** was prepared according to general procedure **A**. Acceptor **17** (1.40 g, 2.66 mmol, 1.0 equiv.) and donor **4** (2.00 g, 3.50 mmol, 1.2 equiv.) afforded **19** (2.20 g, 2.20 mmol, 75%) as a white foam. $\mathbf{R_f}$ 0.61 (1:1 hexane:EtOAc). $[\alpha]_D^{22}$ = + 55.1 (*c* 1, $CHCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H, Ar-H), 7.56 (ddt, *J* = 8.8, 7.0, 1.3 Hz, 1H, Ar-H), 7.45 – 7.38 (m, 3H, Ar-H), 7.35 – 7.25 (m, 9H, Ar-H), 7.14 – 7.10 (m, 5H, Ar-H), 5.82 (dddd, *J* = 16.9, 10.4, 6.4, 5.3 Hz, 1H, OCH_2CHCH_2), 5.48 (s, 1H, PhC*H*), 5.32 – 5.18 (m, 2H, H2', OCH_2CHCH_2), 5.13 – 5.09 (m, 1H, OCH_2CHCH_2), 4.92 – 4.89 (m, 1H, H1), 4.86 (d, *J* = 11.1 Hz, 1H, CH_2-OBn), 4.83 (d, *J* = 8.0 Hz, 1H, H1'), 4.74 – 4.59 (m, 5H, H6a', 4 × CH_2), 4.41 – 4.36 (m, 1 H, H3), 4.32 (ddt, *J* = 12.7, 5.3, 1.5 Hz, 1H, OCH_2CHCH_2), 4.28 – 4.24 (m, 3H, H4, H6a, CH_2), 4.19 (dd, *J* = 11.8, 4.5 Hz, 1H, H6b'), 4.07 – 3.95 (m, 4H, OCH_2CHCH_2, H6b, CH_2Cl), 3.77 (t, *J* = 9.0 Hz, 1H, H3'), 3.66 (t, *J* = 9.2 Hz, 1H, H4'), 3.57 (ddd, *J* = 9.7, 4.5, 2.2 Hz, 1H, H5'), 3.51 – 3.43 (m, 1H, H2), 3.40 (s, 1H, H5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0 (C=O), 165.0 (C=O), 153.8 (C=O), 137.8, 137.4, 137.3 (3 × Ar-C), 133.9 (OCH_2CHCH_2), 133.3 (Ar-C), 129.8, 129.7, 129.6, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 126.3 (12 × Ar-CH), 117.7 (OCH_2CHCH_2), 101.0 (C1'), 100.6 (PhCH), 98.4 (C1), 95.7 (*C*Cl_3), 82.7 (C3'), 76.7 (C4'), 75.5 (C4), 75.3 (*C*H_2) 75.2 (*C*H_2), 75.0 (C3), 73.8 (*C*H_2) 73.4 (C2'), 73.1 (C5'), 70.0 (OCH_2CHCH_2), 69.1 (C6), 66.5 (C5), 63.8 (C6'), 53.8 (C2), 40.7 (*C*H_2Cl). **HRMS**: m/z $(ESI)^+$ Found $(M+NH_4)^+$ 1022.2285, $C_{48}H_{50}Cl_4NO_{14}$ required $(M+NH_4)^+$ 1022.2329.

6-*O*-Chloroacetyl-3-*O*-benzyl-4-*O*-levulinoyl-2-*O*-benzoyl-D-glucopyranoside-β(1→3)-Allyl-4,6-*O*-benzylidene-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside 20



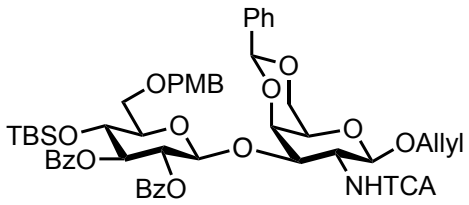
Disaccharide **20** was prepared according to general procedure **A**. Acceptor **17** (50 mg, 0.104 mmol, 1.0 equiv.) and donor **6** (75 mg, 0.125 mmol, 1.2 equiv.) afforded **20** (63 mg, 0.063 mmol, 60%) as a white foam. $\mathbf{R_f}$ 0.52 (2:1 toluene:acetone). $[\alpha]_D^{21}$ = +55.1 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.3 Hz, 2H, Ar-H), 7.60 – 7.55 (m, 1H, Ar-H), 7.54 – 7.50 (m, 1H, Ar-H), 7.48 – 7.40 (m, 3H, Ar-H), 7.37 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.32 (dd, *J* = 5.1, 2.0 Hz, 2H, Ar-H), 7.15 – 7.08 (m, 5H, Ar-H), 5.82 (dddd, *J* = 16.9, 10.3, 6.4, 5.3 Hz, 1H, OCH_2CHCH_2), 5.51 (s, 1H, PhC*H*), 5.31 (dd, *J* = 9.5, 8.0 Hz, 1H, H2'), 5.24 – 5.10 (m, 3H, H4', OCH_2CHCH_2), 4.92 (d, *J* = 8.1 Hz, 1H, H1), 4.88 (d, *J* = 7.9 Hz, 1H, H1'), 4.72 (d, *J* = 12.1 Hz, 1H, CH_2-OBn), 4.55 (br s, 2H, CH_2-OBn, CH_2-Troc), 4.47 – 4.41 (m, 2H, H3, H6a'), 4.36 – 4.25 (m, 5H, H4, H6a, H6b', CH_2-Troc, OCH_2CHCH_2), 4.12 – 4.05 (m, 3H, H6b, $C(O)CH_2Cl$), 4.04 – 3.97 (m, 1H, OCH_2CHCH_2), 3.81 (t, *J* = 9.3 Hz, 1H, H3'), 3.68 (ddd, *J* = 9.9, 5.4, 2.4 Hz, 1H, H5'), 3.51 – 3.41 (m, 2H, H2, H5), 2.78 (ddd, *J* = 18.4, 8.4, 5.3 Hz, 1H, ($H_3CC(O)CH_2CH_2C(O)$), 2.64 (ddd, *J* = 18.5, 6.4, 5.0 Hz, 1H, ($H_3CC(O)CH_2CH_2C(O)$), 2.53 (ddd, *J* = 17.2, 8.4, 5.0 Hz, 1H, ($H_3CC(O)CH_2CH_2C(O)$), 2.35 (ddd, *J* = 17.2, 6.5, 5.3 Hz, 1H, ($H_3CC(O)CH_2CH_2C(O)$), 2.16 (s, 3H, $CH_3C(O)$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3, 171.6, 167.1, 164.7, 153.9 (5 × C=O), 137.8, 137.4, 133.8, 133.8 (4 × Ar-CH), 133.4 (OCH_2CHCH_2), 129.8, 129.3, 128.7, 128.6, 128.3, 128.0, 127.9, 127.7, 126.4, 126.2 (10 × Ar-CH), 117.8 (OCH_2CHCH_2), 101.4 (C1'), 101.2 (PhCH), 100.7 (C1), 79.6 (C3'), 75.6 (C4), 75.0 (C3), 73.9 (CH_2-OBn), 73.9 (CH_2-Troc) 73.1 (C2'), 72.4 (C5'), 70.1 (C4'), 69.9 (OCH_2CHCH_2), 69.1 (C6), 66.6 (C5), 63.6 (C6'), 54.0 (C2), 40.9 ($C(O)CH_2Cl$), 37.8 ($H_3CC(O)CH_2CH_2C(O)$), 29.7 ($CH_3C(O)$), 27.8 ($H_3CC(O)CH_2CH_2C(O)$). **HRMS** m/z $(ESI)^+$ Found $(M+NH_4)^+$ 1031.2148, $C_{46}H_{49}Cl_4NO_{16}$ required $(M+NH_4)^+$ 1031.2114.

6-*O*-Chloroacetyl-3,4-di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranoside-β(1→3)-Allyl 4,6-*O*-benzylidene-2-deoxy-*N*-trichloroacetamido-1-β-D-galactopyranoside 21



Disaccharide **21** was prepared according to general procedure **A**. Acceptor **18** (600 mg, 1.33 mmol, 1.0 equiv.) and donor **4** (910 mg, 1.60 mmol, 1.2 equiv.) afforded **21** (980 mg, 1.01 mmol, 76%) as a white foam. $\mathbf{R_f}$ 0.42 (2:1, hexane:EtOAc) $[\alpha]_D^{21}$ = +36.8 (*c* 1, $CHCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H, Ar-H), 7.54 (ddt, *J* = 7.8, 7.1, 1.4 Hz, 1H, Ar-H), 7.47 – 7.45 (m, 1H, Ar-H), 7.40 – 7.27 (m, 10H, Ar-H), 7.15 – 7.04 (m, 6H, Ar-H), 5.83 (dddd, *J* = 16.9, 10.3, 6.3, 5.5 Hz, 1H, OCH_2CHCH_2), 5.49 (s, 1H, PhC*H*), 5.33 – 5.28 (m, 1H, H2'), 5.22 (dq, *J* = 17.2, 1.6 Hz, 1H, OCH_2CHCH_2), 5.13 (dd, *J* = 10.3, 1.5 Hz, 1H, OCH_2CHCH_2), 5.10 (d, *J* = 8.2 Hz, 1H, H1), 5.00 (d, *J* = 7.9 Hz, 1H, H1'), 4.85 (d, *J* = 11.1 Hz, 1H, CH_2-OBn), 4.71 (d, *J* = 11.0 Hz, 1H, CH_2-OBn) 4.68 – 4.57 (m, 4H, H3, 2 × CH_2-OBn, H6a'), 4.37 – 4.26 (m, 3H, H4, H6a, OCH_2CHCH_2), 4.17 – 4.04 (m, 3H, H6b, H6b', OCH_2CHCH_2), 4.01 (app. d, *J* = 0.9 Hz, 2H, $C(O)CH_2Cl$) 3.77 (t, *J* = 8.8 Hz, 1H, H3'), 3.72 – 3.57 (m, 3H, H2, H4', H5'), 3.44 (q, *J* = 1.5 Hz, 1H, H5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0 (C=O), 165.1 (C=O), 162.0 (CCl_3CONH), 137.7, 137.3, 133.6 (OCH_2CHCH_2), 133.3, 129.9, 129.5, 128.8, 128.6, 128.5, 128.3, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 126.1, 118.0 (OCH_2CHCH_2), 100.5 (PhCH), 100.2 (C1'), 97.6 (C1), 92.3 (CCl_3CONH), 82.8 (C3'), 76.9 (C4'), 75.9 (C4), 75.2 (CH_2-OBn), 74.9 (CH_2-OBn), 73.4 (C2'), 73.3 (C5'), 72.9 (C3), 70.3 (OCH_2CHCH_2) , 69.1 (C6), 66.6 (C5), 63.9 (C6'), 55.2 (C2), 40.7 ($C(O)CH_2Cl$). **HRMS**: m/z $(ESI)^+$ Found $(M+NH_4)^+$ 993.2145, $C_{47}H_{47}Cl_4NO_{13}$ required $(M+NH_4)^+$ 933.2121.

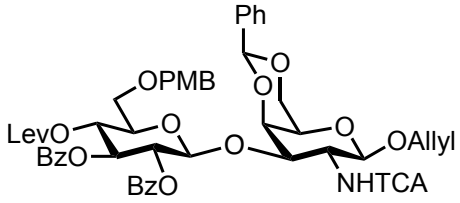
2,3-Di-*O*-benzoyl-4-*O*-tert-butylsimethylsilyl-6-*O*-*p*-methoxybenzyl-β-D-glucopyranoside-(1→3)-allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-trichloroacetamido-1-β-D-galactopyranoside 22



Disaccharide **22** was prepared according to general procedure **A**. Acceptor **18** (0.469 g, 1.04 mmol) and donor **9** (0.830 g, 1.24 mmol) afforded **22** (0.81 g, 74%) as a white foam.

R_f 0.60 (2:3, EtOAc:hexane). **$[\alpha]_D^{25}$** = +50.4 (*c* 0.4, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 4H, Ar-H), 7.62 – 7.55 (m, 2H, Ar-H), 7.49 – 7.36 (m, 5H, Ar-H), 7.34 – 7.19 (m, 6H, Ar-H), 6.92 – 6.83 (m, 2H, Ar-H), 5.83 (ddt, *J* = 17.0, 10.4, 6.2 Hz, 1H, C*H*=CH_2), 5.55 (t, *J* = 9.7 Hz, 1H, H3'), 5.42 (s, 1H, PhC*H*), 5.38 (dd, *J* = 9.7, 7.9 Hz, 1H, H2'), 5.26 (d, *J* = 7.9 Hz, 1H, H1'), 5.22 (qd, *J* = 17.0, 1.4 Hz, 1H, CH=C*H*H), 5.19 (d, *J* = 8.2 Hz, 1H, H1), 5.12 (dq, *J* = 10.4, 1.4 Hz, 1H, CH=C*H*H), 4.70 (dd, *J* = 11.3, 3.6 Hz, 1H, H3), 4.59 (d, *J* = 11.6 Hz, 1H, PMPC*H*H), 4.44 (d, *J* = 11.6 Hz, 1H, PMPC*H*H), 4.39 – 4.30 (m, 2H, OC*H*H and H4), 4.27 (dd, *J* = 12.3, 1.4 Hz, 1H, H6a), 4.06 (ddt, *J* = 12.8, 6.2, 1.4 Hz, 1H, OC*H*H), 3.96 – 3.85 (m, 2H, H4' and H6b), 3.79 (s, 3H, OCH_3), 3.85 – 3.53 (m, 4H, H2, H5', and H6'), 3.39 (t, *J* = 1.4 Hz, 1H, H5), 0.72 [s, 9H, C(CH_3)$_3$], −0.03 (s, 3H, SiCH_3), −0.24 (s, 3H, SiCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7 (C=O), 165.4 (C=O), 162.0 (C=O), 159.4 (Ar-$COCH_3$), 137.8 (Ar-C), 133.8 (H*C*=CH_2), 133.05 (Ar-CH), 133.00 (Ar-CH), 129.82 (Ar-CH), 129.79 (Ar-C), 129.7 (2 × Ar-CH), 129.5 (Ar-CH), 129.3, 128.8, 128.4, 128.3, 128.2, 128.2, 126.1, 126.0, 117.7 (CH=*C*H_2), 114.0 (Ar-CH), 113.9 (Ar-CH), 100.4 (Ph*C*), 100.1 (C1'), 97.6 (C1), 92.3 (*C*Cl_3), 76.4 (C4), 76.0 (C3'), 75.8 (C5'), 73.6 (C3), 73.1 (PMP*C*H_2), 72.3 (C2'), 70.3 (O*C*H_2), 70.0 (C4'), 69.0 (C6), 68.9 (C6'), 66.6 (C5), 55.3 (O*C*H_3), 55.2 (C2), 25.6 [SiC(*C*H_3)$_3$], 17.8 [Si*C*(CH_3)$_3$], −4.2 (Si*C*H_3), −4.7 (Si*C*H_3). **HRMS** (ESI+) Found $(M+NH_4)^+$ 1075.3178, $C_{52}H_{60}Cl_3NO_{13}Si$ required $(M+NH_4)^+$ 1075.7178.

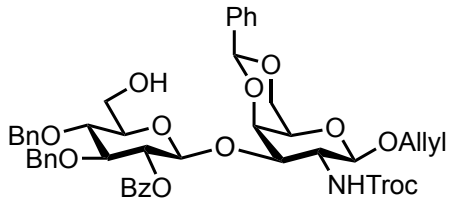
2,3-Di-*O*-benzoyl-4-*O*-levulinoyl-6-*O*-*p*-methoxybenzyl-β-D-glucopyranoside-(1→3)-allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-trichloroacetamido-1-β-D-galactopyranoside 23



Disaccharide **23** was prepared according to general procedure **A**. Acceptor **18** (1.35 g, 2.07 mmol) and donor **10** (0.78 g, 1.73 mmol) afforded **23** (1.14 g, 63%) as a white foam. **R_f** 0.55 (2:3, EtOAc:hexane). **$[\alpha]_D^{25}$** = +29.8 (*c* 0.1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 4H, Ar-H), 7.59 – 7.52 (m, 2H, Ar-H), 7.51 – 7.22 (m, 11H, Ar-H), 7.19 (d, *J* = 6.6 Hz, 1H, N*H*), 6.92 – 6.83 (m, 2H, Ar-H), 5.82 (dddd, *J* = 16.8, 10.4, 6.3, 5.4 Hz, 1H, C*H*=CH_2), 5.62 (t, *J* = 9.6 Hz, 1H, H3'), 5.48 (dd, *J* = 9.6, 7.9 Hz, 1H, H2'), 5.42 (s, 1H, PhC*H*), 5.32 – 5.08 (m, 5H, H1, H1', H4' and CH=CH_2), 4.72 (dd, *J* = 11.3, 3.6 Hz, 1H, H3), 4.38 – 4.29 (m, 2H, H4 and OC*H*H), 4.25 (dd, *J* = 12.3, 1.5 Hz, 1H, H6a), 4.05 (ddt, *J* = 12.7, 6.3, 1.4 Hz, 1H, OC*H*H), 3.78 (s, 3H, OCH_3), 3.91 – 3.57 (m, 5H, H2, H6b, H5' and H6'), 3.40 – 3.36 (m, 1H, H5), 2.66 – 2.39 (m, 3H, CH_2CH_2), 2.36 – 2.24 (m, 1H, C*H*HCH_2), 2.04 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.0 (C=O), 171.6 (C=O), 165.8 (C=O), 165.2 (C=O), 162.1 (C=O), 159.5 (Ar-C), 137.8 (Ar-C), 133.9 (H*C*=CH_2), 133.4 (Ar-CH), 133.4 (Ar-CH), 130.0 (Ar-CH), 129.90 (Ar-CH), 129.88 (Ar-CH), 129.7 (Ar-CH), 129.3 (Ar-C), 129.0 (Ar-C), 128.9 (Ar-C), 128.49 (Ar-CH), 128.46 (Ar-CH), 128.3 (Ar-CH), 126.2 (Ar-CH), 117.9 (CH=*C*H_2), 114.0 (Ar-CH), 100.6 (Ph*C*H), 100.3 (C1'), 97.6 (C1), 92.4 (*C*Cl_3), 76.3 (C4), 73.8 (C3), 73.4 (C5'), 73.4 (C3'), 71.9 (C2'), 70.5 (O*C*H_2), 69.5 (C4'), 69.09 (C6 or C6'), 69.05 (C6 or C6'), 66.7 (C5), 55.4 (O*C*H_3), 55.3 (C2), 37.8 (*C*H_2), 29.7 (*C*H_3), 27.9 (*C*H_2). **HRMS** (ESI+) Found $(M+NH_4)^+$ 1059.2688, $C_{51}H_{52}Cl_3NO_{16}$ required $(M+NH_4)^+$ 1059.2666.

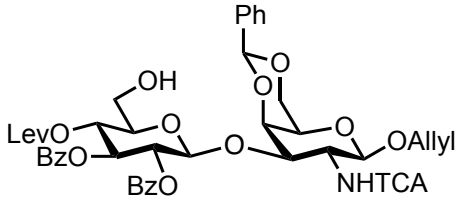
Access to CS precursor disaccharide library

3,4-Di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranoside-β(1→3)-Allyl-4,6-*O*-benzylidene-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside S7



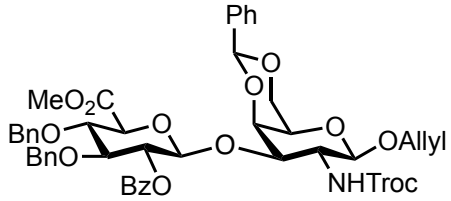
To a stirred solution of **19** (1.40 g, 1.39 mmol, 1.0 equiv.) in absolute EtOH:pyridine (1:1 *v:v*, 48 mL), thiourea (381 mg, 5.00 mmol, 3.5 equiv.) was added. The reaction was stirred at 80 °C for 2 h. Following completion, the reaction mixture was diluted in EtOAc (30 mL) and washed successively with 1 M HCl (1 × 30 mL), sat. aq. $NaHCO_3$ (1 × 30 mL) and brine (1 × 30 mL). The aqueous layer was re-extracted with EtOAc (50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification *via* manual column chromatography (10:1 → 1:1 hexane:EtOAc) afforded **S7** as a white foam (1.07 g, 1.15 mmol, 83%). $\mathbf{R_f}$ 0.28 (1:1 hexane:EtOAc). $\mathbf{[\alpha]_D^{22}}$ = +50.8 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H, Ar-H), 7.57 – 7.52 (m, 1H, Ar-H), 7.43 – 7.37 (m, 2H, Ar-H), 7.34 – 7.27 (m, 7H, Ar-H), 7.26 – 7.19 (m, 3H, Ar-H), 7.11 – 7.08 (m, 5H, Ar-H), 5.82 (dddd, *J* = 16.8, 10.3, 6.2, 5.3 Hz, 1H, OCH_2CHCH_2), 5.47 (br d, *J* = 7.0 Hz, 1H, N-*H*), 5.38 (s, 1H, PhC*H*), 5.28 (dd, *J* = 9.1, 8.0 Hz, 1H, H2'), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H, OCH_2CHCH_2), 5.14 – 5.08 (m, 1H, OCH_2CHCH_2), 4.91 – 4.86 (m, 2H, H1, H1'), 4.83 (d, *J* = 10.9 Hz, 1H, CH_2), 4.75 – 4.58 (m, 4H, 4 × CH_2), 4.50 (d, *J* = 11.2 Hz, 1H, H3), 4.35 – 4.20 (m, 4H, H4, CH_2, H6a, OCH_2CHCH_2), 4.03 – 3.95 (m, 2H, H6b, OCH_2CHCH_2), 3.86 – 3.71 (m, 4H, H3', H4', H6a', H6b'), 3.50 (d, *J* = 7.8 Hz, 1H, H2), 3.45 – 3.40 (m, 1H, H5'), 3.36 (s, 1H, H5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2 (C=O), 154.3 (C=O), 137.7, 137.6, 137.6, 136.1 (4 × Ar-C), 133.8 (OCH_2CHCH_2), 133.3, 129.8, 129.6, 128.8, 128.5, 128.5, 128.2, 128.0, 127.9, 127.7, 126.2, 123.8 (12 × Ar-CH), 117.6 (OCH_2CHCH_2), 100.8 (C1'), 100.1 (PhC*H*), 98.5 (C1), 95.6 (CCl_3), 82.5 (C4'), 77.3 (C3'), 75.8 (C5'), 75.3 (C4), 75.0 (CH_2), 75.0 (CH_2), 73.9 (C2'), 73.3 (CH_2), 72.9 (C3), 70.1 (OCH_2CHCH_2), 69.1 (C6), 66.4 (C5), 61.4 (C6'), 53.9 (C2). **HRMS**: m/z (ESI)$^+$ Found $(M+NH_4)^+$ 945.2528, $C_{46}H_{48}Cl_3NO_{13}$ required $(M+NH_4)^+$ 945.2529.

2,3-Di-*O*-benzoyl-4-*O*-levulinoyl-β-D-glucopyranoside-(1→3)-allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-trichloroacetamido-1-β-D-galactopyranoside S8



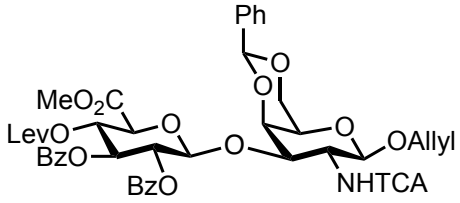
Disaccharide **23 (**2.41 g, 2.31 mmol, 1.0 equiv.) was dissolved in DCM (70 mL) and cooled to 0 °C. DDQ (620 mg, 2.73 mmol, 1.2 equiv.) was added followed by H_2O (2 mL). The reaction was slowly warmed to RT and stirred overnight. The reaction was quenched using sat. aq. $NaHCO_3$ (100 mL) and the layers were separated. The aqueous layer was extracted using EtOAc (4 × 70 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification *via* flash column chromatography (3% MeOH in DCM + 1% Et_3N) afforded **S8** as an off white solid (1.61 g, 1.76 mmol, 76%). **R_f** 0.26 (3% MeOH in DCM). **$[\alpha]_D^{25}$** +40.3 (*c* 0.1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 4H, Ar-H), 7.53 – 7.39 (m, 4H, Ar-H), 7.37 – 7.27 (m, 7H, Ar-H), 7.05 (d, *J* = 6.9 Hz, 1H), 5.84 (dddd, *J* = 17.0, 10.4, 6.3, 5.4 Hz, 1H, C*H*=CH_2), 5.63 (t, *J* = 9.5 Hz, 1H, H3'), 5.48 (s, 1H, PhC*H*), 5.48 (dd, *J* = 9.5, 7.8 Hz, 1H, H2'), 5.37 – 5.27 (m, 1H, H4'), 5.23 (dq, *J* = 17.0, 1.4 Hz, 1H, CH=C*H*H), 5.19 (d, *J* = 7.8 Hz, 1H, H1'), 5.15 (dq, *J* = 10.4, 1.4 Hz, 1H, CH=C*H*H), 5.08 (d, *J* = 8.2 Hz, 1H, H1), 4.79 (dd, *J* = 11.2, 3.5 Hz, 1H, H3), 4.42 – 4.27 (m, 3H, H4, H6a and OC*H*H), 4.11 – 4.01 (m, 2H, H6b and OC*H*H), 3.88 (d, *J* = 12.7 Hz, 1H, H6a'), 3.82 – 3.62 (m, 3H, H2, H5' and H6b'), 3.51 (q, *J* = 1.5 Hz, 1H, H5), 2.75 – 2.63 (m, 1H, C$H_2$$CH_2$), 2.63 – 2.45 (m, 2H, C$H_2$$CH_2$), 2.40 – 2.27 (m, 1H, C$H_2$$CH_2$), 2.07 (s, 3H, C$H_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.5 (C=O), 172.4 (C=O), 165.8 (C=O), 165.3 (C=O), 162.5 (C=O), 137.7 (Ar-C), 133.8 (H*C*=CH_2), 133.50 (Ar-CH), 133.47 (Ar-CH), 130.0 (Ar-CH), 129.9 (Ar-CH), 129.2 (Ar-C), 129.0 (Ar-C), 128.9 (Ar-C), 128.55 (Ar-CH), 128.52 (Ar-CH), 128.2 (Ar-CH), 126.3 (Ar-CH), 118.1 (CH=*C*H_2), 100.7 (Ph*C*), 99.9 (C1'), 97.8 (C1), 92.5 (CCl_3), 75.9 (C4), 74.8 (C5'), 73.2 (C3'), 72.5 (C3), 71.9 (C2'), 70.5 (O*C*H_2), 69.2 (C6), 68.9 (C4'), 66.7 (C5), 61.0 (C6'), 55.4 (C2), 38.0 (*C*H_2), 29.7 (*C*H_3), 28.0 (*C*H_2). **HRMS** (ESI+) Found $(M+NH_4)^+$ 939.2095, $C_{43}H_{44}Cl_3NO_{15}$ required $(M+NH_4)^+$ 939.2091.

Methyl(3,4-di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranosyl)uronate-β(1→3)-Allyl-4,6-*O*-benzylidene-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside 24



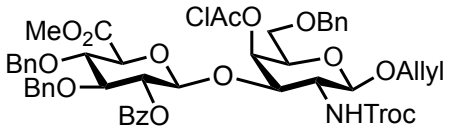
Disaccharide **24** was prepared according to general procedure **B**. Compound **S7** (745 mg, 0.803 mmol, 1.0 equiv.) afforded **24** (645 mg, 0.674 mmol. 85% over two steps) as a white solid. $\mathbf{R_f}$ 0.60 (1:1 hexane:EtOAc). $\mathbf{[\alpha]_D^{22}}$ = +62.9 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H, Ar-H), 7.58 – 7.53 (m, 1H, Ar-H), 7.46 (dd, *J* = 6.6, 3.0 Hz, 2H, Ar-H), 7.41 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.33 – 7.26 (m, 6H, Ar-H), 7.23 – 7.19 (m, 2H, Ar-H), 7.12 (s, 5H, Ar-H), 5.82 (dddd, *J* = 16.8, 10.3, 6.3, 5.2 Hz, 1H, OCH_2CHCH_2), 5.49 (s, 1H, PhC*H*), 5.32 (dd, *J* = 8.3, 7.2 Hz, 1H, H2'), 5.25 – 5.18 (m, 1H, OCH_2CHCH_2), 5.11 (dq, *J* = 10.4, 1.4 Hz, 1H, OCH_2CHCH_2), 4.90 (dd, *J* = 10.9, 7.5 Hz, 2H, H1, H1'), 4.72 (dd, *J* = 11.1, 6.3 Hz, 2H, CH_2), 4.66 – 4.61 (m, 2H, CH_2), 4.56 (d, *J* = 10.9 Hz, 1H, CH_2), 4.51 – 4.39 (m, 1H, H3), 4.35 – 4.23 (m, 4H, H4, CH_2, H6a, OCH_2CHCH_2), 4.05 – 3.98 (m, 4H, H4', H5', H6b, OCH_2CHCH_2), 3.76 (dt, *J* = 8.2, 4.1 Hz, 1H, H3'), 3.69 (s, 3H, OCH_3), 3.53 – 3.46 (m, 1H, H2), 3.40 (s, 1H, H5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9 (C=O), 164.8 (C=O), 153.8 (C=O, Troc), 137.8, 137.5, 137.5 (3 × Ar-C), 133.9 (OCH_2CHCH_2), 133.3 (Ar-C), 129.8, 128.7, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.7, 126.2 (12 × Ar-CH), 117.6 (OCH_2CHCH_2), 101.0 (C1'), 100.6 (PhCH), 98.5 (C1), 95.7 (CCl_3), 81.9 (C3'), 79.0 (C4'), 75.4 (C4), 74.9 (C3), 74.8 (CH_2-OBn), 74.6 (CH_2-OBn), 74.2 (C5'), 73.9 (CH_2-Troc), 73.0 (C2'), 69.9 (OCH_2CHCH_2), 69.1 (C6), 66.5 (C5), 53.9 (C2), 52.5 (OCH_3). **HRMS**: m/z (ESI+) Found $(M+NH_4)^+$ 973.2448, $C_{47}H_{48}Cl_3NO_{14}$ required 973.2484.

Methyl 2,3-Di-*O*-benzoyl-4-*O*- levulinoyl-β-D-glucopyranosyluronate-(1→3)-allyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-trichloroacetamido-1-β-D-galactopyranoside 25



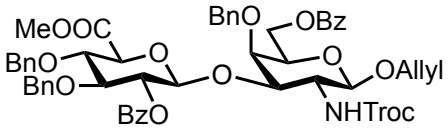
Disaccharide **25** was prepared according to general procedure **B**. Compound **S8** (385 mg, 0.420 mmol, 1.0 equiv.) afforded **25** (240 mg, 0.252 mmol, 60%) as a white solid. $\mathbf{R_f}$ 0.36 (3:2, EtOAc:hexane). $\mathbf{[\alpha]_D^{25}}$ = +48.0 (*c* 0.4, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 4H, Ar-H), 7.57 – 7.45 (m, 4H, Ar-H), 7.42 – 7.29 (m, 7H, Ar-H), 6.99 (d, *J* = 6.7 Hz, 1H, N*H*), 5.84 (dddd, *J* = 17.0, 10.4, 6.4, 5.5 Hz, 1H, C*H*=CH_2), 5.63 (t, *J* = 9.1 Hz, 1H, H3'), 5.56 (s, 1H, PhC*H*), 5.55 – 5.43 (m, 2H, H2' and H4'), 5.23 (dq, *J* = 17.0, 1.6 Hz, 1H, CH=C*H*H), 5.19 (d, *J* = 7.3 Hz, 1H, H1'), 5.15 (dq, *J* = 10.4, 1.3 Hz, 1H, CH=C*H*H), 5.11 (d, *J* = 8.3 Hz, 1H, H1), 4.78 (dd, *J* = 11.2, 3.5 Hz, 1H, H3), 4.48 (d, *J* = 3.5 Hz, 1H, H4), 4.40 – 4.28 (m, 2H, H6a and OC*H*H), 4.21 (d, *J* = 10.0 Hz, 1H, H5'), 4.12 – 4.01 (m, 2H, H6b and OC*H*H), 3.77 (s, 3H, OCH_3), 3.73 (ddd, *J* = 11.2, 8.2, 6.7 Hz, 1H, H2), 3.51 (q, *J* = 1.5 Hz, 1H, H5), 2.67 – 2.47 (m, 3H, CH_2), 2.46 – 2.32 (m, 1H, CH_2), 2.05 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.6 (C=O), 171.3 (C=O), 167.2 (C=O), 165.5 (C=O), 164.9 (C=O), 162.3 (C=O), 137.7 (Ar-C), 133.6 (H*C*=CH_2), 133.43 (Ar-CH), 133.40 (Ar-CH), 129.9 (Ar-CH), 129.8 (Ar-CH), 129.0 (Ar-C), 128.8 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-CH), 128.1 (Ar-CH), 126.2 (Ar-CH), 118.0 (CH=*C*H_2), 100.6 (Ph*C*H), 100.2 (C1'), 97.5 (C1), 92.1 (*C*Cl_3), 75.8 (C4), 73.5 (C3), 72.5 (C3'), 72.1 (C5'), 71.4 (C2'), 70.4 (O*C*H_2), 69.4 (C4'), 69.0 (C6), 66.6 (C5), 55.4 (C2), 53.1 (O*C*H_3), 37.5 (*C*H_2), 29.6 (*C*H_3), 27.7(*C*H_2). **HRMS (ESI+)** Found $(M+NH_4)^+$ 967.2049, $C_{44}H_{44}Cl_3NO_{16}$ required $(M+NH_4)^+$ 967.2136.

Methyl(3,4-di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranosyl)uronate-β(1→3)-Allyl-4-*O*-chloroacetyl-6-*O*-benzyl-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside 26



Under an atmosphere of N_2, a solution of **24** (100 mg, 0.105 mmol, 1.0 equiv.) in DCM (1.1 mL) was cooled to 0 °C and Et_3SiH (84 μL, 0.523 mmol, 5.0 equiv.) and trifluoroacetic acid (40 μL, 0.523 mmol, 5.0 equiv.) were added. The reaction was stirred for 1 h then neutralised with Et_3N. The solution was diluted in DCM (10 mL), extracted with sat. aq. $NaHCO_3$ (10 mL) and brine (10 mL) before drying over $MgSO_4$, filtering and concentrating *in vacuo*. The crude residue was then placed under an atmosphere of N_2 and redissolved in DCM (1 mL) and pyridine (46 μL, 79.1 mmol, 6.0 equiv.), to which chloroacetyl chloride (10 μL, 0.124 mmol, 1.3 equiv.) was added at 0 °C. After 30 min, the reaction was diluted in DCM (10 mL) and washed successively with 1 M HCl (5 mL), sat. aq. $NaHCO_3$ (5 mL) and brine (5 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Manual flash column chromatography (100% DCM → 5% Et_2O in DCM) afforded **26** (65 mg, 0.063 mmol, 60%) as a white foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H, Ar-H), 7.61 – 7.56 (m, 1H, Ar-H), 7.45 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.34 – 7.29 (m, 7H, Ar-H), 7.25 – 7.21 (m, 3H, Ar-H), 7.12 (dd, *J* = 3.9, 1.9 Hz, 5H, Ar-H), 5.80 (dddd, *J* = 17.0, 10.3, 6.5, 5.3 Hz, 1H, OCH_2CHCH_2), 5.51 (d, *J* = 3.3 Hz, 1H, H4), 5.23 – 5.10 (m, 3H, H2', OCH_2CHCH_2), 4.85 (d, *J* = 8.2 Hz, 1H, H1), 4.76 (d, *J* = 10.9 Hz, 1H, CH_2-OBn), 4.72 – 4.59 (m, 4H, H1', 3 × CH_2-OBn), 4.51 – 4.47 (m, 2H, H3, CH_2-Troc), 4.32 – 4.25 (m, 1H, OCH_2CHCH_2), 4.14 – 4.07 (m, 2H, $C(O)CH_2Cl$), 4.05 – 3.92 (m, 3H, H4', H5', OCH_2CHCH_2), 3.81 – 3.69 (m, 5H, H3', H5, OCH_3), 3.54 (dd, *J* = 6.0, 1.8 Hz, 2H, H6a, H6b), 3.21 (d, *J* = 9.1 Hz, 1H, H2). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4 (C=O), 166.8 (C=O), 164.8 (C=O), 153.6 (C=O), 137.8, 137.6, 137.5 (3 × Ar-CH), 133.4 (OCH_2CHCH_2), 129.8, 129.5, 128.6, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.9, 127.8, 127.8, 126.2 (15 × Ar-CH), 118.2 (OCH_2CHCH_2), 100.9 (C1'), 98.2 (C1), 95.5 (CCl_3), 81.4 (C3'), 78.9 (C4'), 75.1 (C5'), 74.7 (CH_2-OBn), 74.4 (CH_2-OBn), 73.7 (CH_2-Troc), 73.3 (C2'), 72.5 (C5), 71.0 (C4), 70.5 (OCH_2CHCH_2), 68.7 (C6), 55.2 (C2), 52.7 (OCH_3), 40.9 ($C(O)CH_2Cl$). **HRMS**: m/z (ESI+) Found $(M+NH_4)^+$ 1053.2358, $C_{49}H_{51}Cl_4NO_{15}$ required 1053.2333.

Methyl(3,4-di-*O*-benzyl-2-*O*-benzoyl-D-glucopyranosyl)uronate-β(1→3)-Allyl-4-*O*-benzyl-6-*O*-benzoyl-2-deoxy-*N*-2,2,2-trichloroethoxycarbonylamino-β-D-galactopyranoside 27

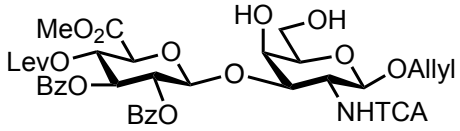


In a multi-neck flask, disaccharide **24** (1.00 g, 1.05 mmol, 1.0 equiv.) and 4 Å molecular sieves were placed under three cycles of vacuum and N_2. Anhydrous DCM (52.5 mL) was added and the solution was pre-dried for 1 h. The reaction was cooled to – 78 °C (using acetone and dry ice) and Et_3SiH (0.17 mL, 1.05 mmol, 1.0 equiv.) was added. The reaction was stirred for 15 minutes before $PhBCl_2$ (0.5 mL, 3.68 mmol, 3.5 equiv.) was added dropwise. The reaction was stirred at – 75 °C for 15 min before quenching with Et_3N (1.6 mL) and MeOH (1.6 mL). After diluting with DCM (20 mL), the organic phase was washed successively with sat. aq. $NaHCO_3$ (50 mL), H_2O (2 × 50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was dissolved in anhydrous DCM (10 mL) and pyridine (0.5 mL, 6.30 mmol, 6.0 equiv.) was added. The solution was cooled to 0 °C and BzCl (0.2 mL, 1.58 mmol, 1.5 equiv.) was added. The reaction was warmed to RT and stirred for 2 h before diluting with DCM (20 mL) and washing successively with 1 M HCl (30 mL), sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude syrup was purified *via* manual flash column chromatography (100% DCM → 5% Et_2O in DCM) then washed with 10:1 petroleum ether:Et_2O to afford **27** as a white solid (815 mg, 0.882 mmol, 84% over two steps). $\mathbf{R_f}$ 0.61 (4:1 toluene:acetone). $\mathbf{[\alpha]_D^{22}}$ = +16.7 (*c* 1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H, Ar-H), 7.93 – 7.89 (m, 2H, Ar-H), 7.62 – 7.52 (m, 2H, Ar-H), 7.49 – 7.39 (m, 6H, Ar-H), 7.34 – 7.19 (m, 6H, Ar-H), 7.12 (br s, 5H, Ar-H), 5.78 (dddd, *J* = 17.0, 10.3, 6.5, 5.3 Hz, 1H, OCH_2CHCH_2), 5.38 (dd, *J* = 9.4, 7.9 Hz, 1H, H2'), 5.17 – 5.05 (m, 2H, OCH_2CHCH_2), 4.97 (d, *J* = 11.5 Hz, 2H, CH_2), 4.87 (br d, *J* = 9.3 Hz, 1H, H1), 4.79 (d, *J* = 10.9 Hz, 1H, CH_2), 4.76 – 4.69 (m, 2H, CH_2, H1'), 4.68 – 4.60 (m, 3H, 3 × CH_2), 4.50 (d, *J* = 8.2 Hz, 1H, H3), 4.41 (dd, *J* = 11.1, 6.7 Hz, 1H, H6a), 4.27 – 4.16 (m, 2H, H6b, OCH_2CHCH_2), 4.05 – 3.94 (m, 4H, H4, H5', H4', OCH_2CHCH_2), 3.81 – 3.72 (m, 2H, H3', H5), 3.66 (s, 3H, OCH_3), 3.33 (d, *J* = 13.8 Hz, 1H, H2). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5 (C=O), 166.0 (C=O), 165.9 (C=O), 164.9 (C=O), 153.8 (C=O), 138.1, 137.6, 137.4, 133.7, 133.4 (5 × Ar-C), 133.0 (OCH_2CHCH_2), 129.9, 129.8, 129.6, 129.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.4 (15 ×

Ar-CH), 117.9 (OCH_2CHCH_2), 102.3 (C1'), 97.9 (C1), 95.7 (CCl_3), 81.5 (C3'), 79.5 (C4'), 77.2 (C3), 75.2 (CH_2), 75.1 (CH_2), 74.5 (CH_2), 74.4 (CH_2), 74.3 (C4), 74.0 (C5'), 73.4 (C2'), 71.9 (C5), 70.1 (OCH_2CHCH_2), 63.1 (C6), 55.2 (OCH_3), 52.5 (C2). **HRMS**: m/z (ESI+) Found $(M+NH_4)^+$ 1079.2817, $C_{54}H_{58}Cl_3N_2O_{15}$ required 1079.2903.

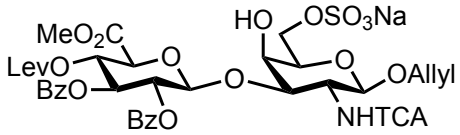
Exemplar synthesis of CS-C

Methyl 2,3-Di-*O*-benzoyl-4-*O*-levulinoyl-β-D-glucopyranosyluronate-(1→3)-allyl 2-deoxy-2-*N*-trichloroacetamido-1-β-D-galactopyranoside 28



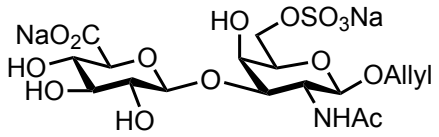
Disaccharide **25 (**0.40 g, 0.42 mmol, 1.0 equiv.) was dissolved in MeOH:DCM (2:1, 15 mL). TsOH (7 mg, 0.04 mmol, 0.1 equiv.) was added and the reaction was heated at reflux for 2 h. After cooling to RT, the reaction was diluted with EtOAc (20 mL) and neutralised using sat. aq. $NaHCO_3$ (2 mL). After diluting with H_2O (10 mL), the layers were separated, and the aqueous layer was extracted using EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo.* Purification via flash column chromatography (5% MeOH in DCM) afforded **28** as a white solid (0.27 g, 0.319 mmol, 76%). **R_f** 0.25 (5% MeOH in DCM). **$[\alpha]_D^{25}$** = +31.7 (*c* 0.1, $CHCl_3$). **^{1}H NMR** (400 MHz, d^6-acetone) δ 8.09 (d, $J_{NH\text{-}H2}$ 9.0, 1H, NH), 7.91 – 7.81 (m, 4H, Ar-H), 7.62 – 7.49 (m, 2H, Ar-H), 7.47 – 7.35 (m, 4H, Ar-H), 5.83 (dddd, *J* = 17.3, 10.6, 5.7, 5.0 Hz, 1H, C*H*=CH_2), 5.74 – 5.67 (m, 1H, H2' or H3'), 5.53 – 5.31 (m, 3H, H1', H4', H2' or H3'), 5.22 (dq, *J* = 17.3, 1.6 Hz, 1H, CH=C*H*H), 5.05 (dq, *J* = 10.5, 1.6 Hz, 1H, CH=C*H*H), 4.66 (d, *J* = 8.2 Hz, 1H, H1), 4.56 (t, *J* = 10.3 Hz, 1H, H5'), 4.39 – 4.29 (m, 1H, H3), 4.29 – 4.21 (m, 2H, H5' and OC*H*H), 4.21 – 4.08 (m, 1H, H2), 4.03 (ddt, *J* = 13.3, 5.7, 1.6 Hz, 1H, OC*H*H), 3.93 (d, *J* = 3.7 Hz, 1H, OH), 3.80 – 3.75 (m, 2H, H6), 3.74 (s, 3H, OCH_3), 3.56 – 3.50 (m, 1H, H5), 2.62 (td, *J* = 6.5, 2.5 Hz, 1H, C*H*H), 2.52 – 2.30 (m, 2H, CH_2), 2.26 – 2.10 (m, 1H, C*H*H), 1.99 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, d^6-acetone) δ 172.5 (C=O), 172.1 (C=O), 168.2 (C=O), 166.1 (C=O), 165.6 (C=O), 162.4 (C=O), 135.5 (H*C*=CH_2), 134.2 (Ar-CH), 134.0 (Ar-CH), 130.7 (Ar-CH), 130.43 (Ar-CH), 130.37 (Ar-C), 130.1 (Ar-C), 129.4 (Ar-CH), 129.3 (Ar-CH), 129.2 (Ar-CH), 116.7 (CH=*C*H_2), 101.2 (C1'), 101.0 (C1), 79.7 (C3), 76.0 (C5), 73.8, 72.72, 72.67, 70.4, 70.1 (O*C*H_2), 68.6 (C5'), 62.2 (C6), 54.4 (C2), 53.2 (*C*H_3), 37.9 (*C*H_2), 29.4 (*C*H_3), 29.3 (*C*H_2).

Methyl 2,3-Di-*O*-benzoyl-4-*O*-levulinoyl-β-D-glucopyranosyluronate-(1→3)-allyl 2-deoxy-6-*O*-sulfonato-2-*N*-trichloroacetamido-1-β-D-galactopyranoside S9



Under an atmosphere of N_2, diol **28 (**137 mg, 0.16 mmol, 1.0 equiv.) was dissolved in anhydrous DMF (4.5 mL). SO_3.TMA (55 mg, 0.40 mmol, 2.5 equiv.) was added and the reaction was heated at 50 °C for 2 h. After cooling to RT, the reaction was concentrated *in vacuo*. Purification via flash column chromatography (10% to 12% MeOH in DCM) afforded **S9** as a flaky white solid (141 mg, 0.150 mmol, 94%). $\mathbf{R_f}$ 0.35 (15:85, MeOH:DCM). **^{1}H NMR (400 MHz**, MeOD**)** δ 7.90 – 7.77 (m, 4H, Ar-CH), 7.56 – 7.46 (m, 2H, Ar-CH), 7.40 – 7.30 (m, 4H, Ar-CH), 5.82 (dddd, *J* = 17.3, 10.6, 5.9, 5.1 Hz, 1H, C*H*=CH_2), 5.73 (t, *J* = 9.5 Hz, 1H, H3'), 5.52 – 5.34 (m, 2H, H2' and H4'), 5.23 (dq, *J* = 17.3, 1.7 Hz, 1H, CH=C*H*H), 5.22 (d, *J* = 7.8 Hz, 1H, H1'), 5.08 (dq, *J* = 10.6, 1.6 Hz, 1H, CH=C*H*H), 4.63 – 4.52 (m, 2H, H1 and ?), 4.49 (d, *J* = 9.9 Hz, 1H, H5'), 4.33 – 4.16 (m, 4H, H4, H6 and OC*H*H), 4.15 – 4.08 (m, 2H, H2 and H3), 4.04 (ddt, *J* = 13.1, 5.9, 1.6 Hz, 1H, OC*H*H), 3.85 (td, *J* = 6.1, 1.1 Hz, 1H, H5), 3.79 (s, 3H, OCH_3), 2.73 – 2.55 (m, 2H, CH_2), 2.54 – 2.34 (m, 2H, CH_2), 1.99 (s, 3H, CH_3). **^{13}C NMR (101 MHz**, MeOD**)** δ 208.5 (C=O), 173.0 (C=O), 169.3 (C=O), 167.0 (C=O), 166.8 (C=O), 164.1 (C=O), 135.2 (H*C*=CH_2), 134.6 (Ar-CH), 134.5 (Ar-CH), 131.2 (Ar-CH), 130.7 (Ar-CH), 130.3 (Ar-C), 130.2 (Ar-C), 129.5 (Ar-CH), 129.4 (Ar-CH), 117.5 (CH=*C*H_2), 102.2 (C1'), 101.6 (C1), 93.9 (*C*Cl_3), 80.4 (C3), 74.1 (C3'), 74.0 (C5), 73.1 (C2'), 73.0 (C5'), 71.1 (O*C*H_2), 70.8 (C4'), 69.0 (C4), 67.9 (C6), 54.5 (C2), 53.7 (O*C*H_3), 38.3 (*C*H_2), 29.4 (CH_2), 28.8 (*C*H_3). **HRMS (NSI):** Found $(M-Na)^-$ 940.0905, $C_{37}H_{39}Cl_3NO_{19}S$ required $(M-Na)^-$ 940.0883.

Sodium β-D-glucopyranosyluronate-(1→3)-allyl 2-deoxy-6-*O*-sulfonato-2-*N*-acetamine-1-β-D-galactopyranoside 29



Disaccharide **S9** (110 mg, 0.12 mmol, 1.0 equiv.) was dissolved in THF (9 mL) and cooled to 0 °C. 30% aq. H_2O_2 (0.03 mL, 0.24 mmol, 2.0 equiv.) and 0.7 M aq. LiOH (0.34 mL, 0.24 mmol, 2.0 equiv.) were added and the reaction was slowly warmed to RT and stirred overnight. MeOH (4 mL) and 4 M aq. NaOH (0.60 mL, 2.40 mmol, 20 equiv.) was added. After stirring at RT for 24 h, the reaction was neutralised using Amberlyst IR-20 H^+ resin. The mixture was filtered and concentrated *in vacuo*. The residue was redissolved in MeOH (8 mL) and cooled to 0 °C. Et_3N (0.15 mL, 1.20 mmol, 10 equiv.) and Ac_2O (0.05 mL, 0.48 mmol, 4.0 equiv.) were added and the reaction was stirred at 0 °C for 1 h. The mixture was concentrated *in vacuo* and co-evaporated with toluene (2 × 10 mL). Purification using Sephadex G25 column afforded **29** as a flaky white solid (13 mg, 0.023 mmol, 19% over three steps). **^{1}H NMR** (400 MHz, D_2O) δ 5.92 (ddt, *J* = 16.5, 11.0, 5.4 Hz, 1H, C*H*=CH_2), 5.38 – 5.24 (m, 2H, CH=CH_2), 4.56 (d, *J* = 8.5 Hz, 1H, H1'), 4.52 (d, *J* = 8.0 Hz, 1H, H1), 4.36 (dd, *J* = 13.2, 5.4 Hz, 1H, OC*H*H), 4.29 – 4.15 (m, 4H, H4, H6 and OC*H*H), 4.05 (dd, *J* = 10.8, 8.5 Hz, 1H, H2'), 3.93 (dd, *J* = 7.6, 4.4 Hz, 1H, H5), 3.86 (dd, *J* = 10.8, 3.1 Hz, 1H, H3'), 3.77 – 3.67 (m, 1H, H5'), 3.55 – 3.44 (m, 2H, H3 and H4'), 3.35 (t, *J* = 8.0 Hz, 1H, H2), 3.21 (q, *J* = 7.3 Hz, 4H, NCH_2), 2.03 (s, 3H, CH_3), 1.29 (t, *J* = 7.3 Hz, 3H, NCH_2CH_3). **^{13}C NMR** (101 MHz, D_2O) δ 174.8 (C=O), 133.3 (H*C*=CH_2), 118.4 (CH=*C*H_2), 104.1 (C1), 100.2 (C1'), 80.0 (C3), 76.2 (C5'), 75.3 (C3'), 72.7 (C2'), 72.6 (C5), 71.8 (C4'), 70.5 (O*C*H_2), 67.7 (C4), 67.6 (C6), 51.0 (C2), 46.7 (N*C*H_2), 22.2 (*C*H_3), 8.2 (NCH_2CH_3). **HRMS** (TOF ES-) Found $(M+H)^-$ 516.1024, $C_{17}H_{26}NO_{15}S$ required $(M+H)^-$ 516.1023.

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