Supporting Information

Ionic Catch and Release Oligosaccharide Synthesis (ICROS)

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Supplementary Material (ESI) for Chemical Communications
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Experimental Procedures

General. Chemicals were purchased from Aldrich and Fluka and used without further purification. Preactivated molecular sieves kept in an oven at 150 °C were activated in a standard Microwave (800 W) for 3 minutes (3 x 1 minute) and cooled under vacuum. Dry solvents were obtained by distillation using standard procedures or by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering (University of Bristol) based on the Grubbs’ design. Reactions requiring anhydrous conditions were performed under nitrogen; glassware and needles were either flame dried immediately prior to use or placed in an oven (150 °C) for at least 2 hours and allowed to cool either in a desiccators or under reduced pressure; liquid reagents, solutions or solvents were added via syringe or cannula through rubber septa; solid reagents were added via Schlenk type adapters. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck) and by MALDI-TOF in case with Itag compounds. Detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in ethanol. Flash column chromatography was performed using silica gel [Merck, 230–400 mesh (40–63 µm)]. Extracts were concentrated under reduced pressure using both a Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. 1H NMR and 13C NMR spectra were measured in the solvent stated at 400 or 500 Hz using Varian INOVA instruments. Chemical shifts are quoted in parts per million from SiMe₄ and coupling constants (J) given in Hertz. Multiplicities are abbreviated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. Positive ion Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) mass spectra were recorded using an HP-MALDI instrument using gentisic acid matrix. Elemental analysis was performed by the University of Bristol Microanalysis Service.

Phenyl 2,3,4-tri-O-acetyl-6-O-triisopropylsilyl-1-thio-β-D-galactopyranoside (1) Synthesized following reported procedures. Spectroscopic data in agreement with reported literature. ¹

2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl trichloroacetimidate (2) Synthesized following reported procedures. Spectroscopic data in agreement with reported literature. ²
3-bromopropyl 2,3,4-di-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside (5). To a solution of 1 (300 mg, 0.541 mmol) in dry CH₂Cl₂ (15mL) was added activated 4 Å molecular sieves, N-iodosuccinimide (243 mg, 0.443 mmol, 2 equiv.), 3-bromopropanol (196 µL, 2.2 mmol), and TMSOTf (49 µL, 0.27 mmol) After stirring at -78 ºC and warming to -40 º C over a 2 hour period the reaction mixture was quenched with triethylamine (3 mL). The reaction mixture was then filtered, concentrated *in vacuo*, and the residue purified by silica gel flash column chromatography, with 9:1 hexanes/ethyl acetate as the eluent, to afford 5 as a colourless oil (130 mg, 41%) and 6 as a colourless oil (121 mg, 41%).

Compound 4: ¹H NMR (CDCl₃, 400 MHz, ppm) : δ = 5.52 (d, 1H, J₄,₃ = 3.5 Hz, H-4), 5.19 (dd, 1H, J₂,₁ = 8.0 Hz, J₂,₂ = 10.5 Hz, H-2), 5.05 (dd, 1H, J₃,₄ = 3.0 Hz, J₃,₀ = 10.5 Hz, H-3), 4.48 (d, 1H, J₁,₂ = 8.0 Hz, H-1), 4.05-3.98 (m, 1H, OCH₂), 3.84-3.74 (2H, m, OCH₂, H-6a), 3.66 (dd, 1H, J₆₆,₉₅ = 4.5 Hz, J₆₅,₆₆ = 10.5 Hz, H-6b), 3.58-3.53 (m, 1H, H-5), 3.51-3.48 (m, 2H, CH₂Br),2.23-1.99 (m, 11H in which 2.11 (s, 3H, CH₃Ac), 2.06 (s, 3H, CH₃Ac), 1.97 (s, 3H, CH₃Ac), OCH₂CH₂) 1.11-0.97 (m, 21H, TIPS); ¹³C NMR (CDCl₃, 100 MHz, ppm) : δ = 170.1, 169.9, 169.6 (CO), 101.5 (C-1), 73.6 (C-5), 71.2 (C-3), 69.2 (C-2), 67.2 (OCH₂), 67.0 (C-4), 60.9 (C-6), 32.2 (OCH₂CH₂), 30.2 (CH₂Br), 20.8 (CH₃Ac), 20.7 (CH₃Ac), 20.6 (CH₃Ac), 17.83, 11.8 (TIPS). ESI-HRMS for C₂₄H₄₃BrNaO₉Si⁺ (MNa⁺) calcd: 605.1752, found: 605.1760.

Compound 5: ¹H NMR (CDCl₃, 300 MHz, ppm) : δ = 5.51 (d, 1H, J₄,₃ = 3.5 Hz, H-4), 4.97 (dd, 1H, J₃,₄ = 3.5 Hz, J₃,₀ = 10.5 Hz, H-3), 4.38 (d, 1H, J₃,₀ = 8.0 Hz, H-1), 4.07 (dt, 1H, J = 5.5 Hz, 10.0 Hz, OCH₂), 3.83-3.70 (m, 5H, H-5, H-2, H-6a, H-6b, OCH₂), 3.56-3.51 (m, 2H, CH₂Br), 2.23-2.04 (m, 8H, OCH₂CH₂), and in which 2.11 (s, 3H, CH₃Ac), 2.06 (s, 3H, CH₃Ac), 1.11-1.00 (m, 21H, TIPS); ¹³C NMR (CDCl₃, 75 MHz, ppm) : δ = 170.5, 169.9, 169.5 (CO), 103.5 (C-1), 73.6 (C-5), 71.2 (C-3), 69.2 (C-2), 67.1 (OCH₂), 67.0 (C-4), 61.2 (C-6), 32.6 (OCH₂CH₂), 30.2 (CH₂Br), 20.9 (CH₃Ac), 20.8 (CH₃Ac), 18.0 (TIPS), 11.9 (TIPS). ESI-HRMS for C₂₃H₄₁BrNaO₈Si⁺ (MNa⁺) calcd: 563.1652, found: 563.1656.

3-(3-Methylimidazolium)-1-propyl 2,3,4-di-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside tetrafluoroborate (6). To a solution of 4 (230 mg, 0.424 mmol, 1eq) in MeCN (5 mL) was added N-methylimidazole (122 µL) and the mixture was refluxed for 18 hours, before a further N-methylimidazole
(122 µL) was added and the mixture was refluxed for a further 24 hours. To the reaction mixture was added KBF₄ (60 mg) and the reaction mixture was stirred for 24 hours. The reaction mixture was filtered, concentrated in vacuo, dried under high vacuum and washed with diethyl ether (3 x 15 mL) with sonication.

Decantation of the ether phase followed by drying under vacuum afforded 6 as a light brown oil (258 mg, 90%). ¹H NMR (CDCl₃, 400 MHz, ppm) : δ = 10.3 (s, 1H, NCHN), 7.39 (t, 1H, J = 2.0 Hz, NCHCHN), 7.35 (t, 1H, J = 2.0 Hz, NCHCHN), 5.50 (dd, 1H, J₄₅ = 0.5 Hz, J₄₃ = 3.0 Hz, H-4), 5.08 (dd, 1H, J₂₁ = 8.0 Hz, J₂₃ = 10.5 Hz, H-2), 5.03 (dd, 4.99 (m, 1H, J₃₄ = 3.0 Hz, J₃₂ = 10.5 Hz, H-3), 4.52-4.36 (m, 1H, in which d at 4.46 (1H, J₁₂ = 8.0 Hz, H-1, CH₂N), 4.09 (s, 3H, CH₃N), 3.95-3.89 (m, 1H, OCH₂), 3.81-3.70 (m, 3H, H-6a, H-6b, OCH₂), 3.68-3.62 (m, 1H, H-5), 2.29-2.20 (m, 2H, OCH₂CH₂), 2.13 (s, 3H, CH₃Ac), 2.06 (s, 3H, CH₃Ac), 1.97 (s, 3H, CH₃Ac), 1.04-0.99 (s, 21H, TIPS). ¹³C NMR (CDCl₃, 100 MHz, ppm) : δ = 169.9, 169.8, 169.7 (CO), 137.8 (NCHN), 122.6 (NCHCHN), 122.8 (NCHCHN), 101.1 (C-1), 73.6 (C-2), 70.9 (C-3), 69.1 (C-5), 66.8 (C-4), 65.9 (OCH₂), 60.7 (C-6), 47.3 (CH₂N), 36.7 (CH₃-N), 30.3 (OCH₂CH₂), 21.0 (CH₃Ac), 20.7 (CH₃Ac), 20.6 (CH₃Ac), 17.8, 11.7 (TIPS). ESI-HRMS for C₂₈H₄₉N₂O₉Si⁺ (M⁺), calcd: 585.3202, found: 585.3198.

3-(3-Methylimidazolium)-1-propyl 3,4-di-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside tetrafluoroborate (7). To a solution of 5 (300 mg, 0.554 mmol) in MeCN (5 mL) was added N-methylimidazole (159 µL, 2 mmol) and the mixture was refluxed for 18 hours after which the reaction was complete. To the reaction mixture was added KBF₄ (84 mg, 0.67 mmol) and the reaction mixture was stirred for 24 hours. The reaction mixture was filtered, concentrated in vacuo, dried under high vacuum and washed with diethyl ether (3 x 15 mL) with sonication. Decantation of the ether phase followed by drying under vacuum afforded 10 as a light brown oil (252 mg, 84 %). ¹H NMR (CD₃OD, 400 MHz, ppm) : δ = 8.98 (1H, s, NCHN), 7.69, 7.60 (2H, NCHCHN), 5.48 (d, 1H, J₄₃ = 3.5 Hz, H-4), 4.92 (dd, 1H, J₃₄ = 3.5 Hz, J₃₂ = 10.0 Hz, H-3), 4.47 (d, 1H, J₁₂ = 8.0, H-1) 4.42 (m, 2H, CH₃N), 3.96 (s, 3H, CH₃N), 3.88 (m, 1H, H-5), 3.82-3.80 (m, 1H, H-6a), 3.70-3.69 (m, 1H, H-6b), 3.60-3.55 (m, 3H, H-2, OCH₂), 2.21 (m, 2H, OCH₂CH₂), 2.11 (s, 3H, CH₃Ac), 2.01 (s, 3H, CH₃Ac), 1.06 (s 21H, TIPS); ¹³C NMR (CD₃OD, 100 MHz, ppm) : δ = 172.2, 171.9 (CO), 138.4 (NCHN), 124.9 (NCH), 123.9 (NCH), 104.4 (C-1), 75.0 (C-3), 74.3 (C-5), 70.1 (C-2), 68.8 (C-4), 66.8 (OCH₂), 62.2 (C-6), 47.9 (CH₂N), 36.8 (CH₃N), 31.0 (OCH₂CH₂), 21.0 (CH₃Ac), 20.92 (CH₃Ac), 18.5, 13.1 (TIPS). ESI-HRMS for C₂₆H₄₉N₂O₈Si⁺ (M⁺), calcd: 543.3096, found: 543.3121.
Phenyl 2,3,4-tri-O-benzoyl-1-thio-6-O-trisopropylsilyl -β-D-glucopyranoside (8). To a solution of 1,2,3,4,6-O-acetyl-D-glucopyranose A1 (3.12 g, 0.008 mol) in CH₂Cl₂ (60 mL) was added ZnI₂ (7.6 g, 0.023 mol) and TMSSPh (4.5 mL, 0.024 mol). The mixture was then left stirring at room temperature for 2 h. After filtration on celite, the mixture was diluted in DCM (20 mL) and washed with HCl 0.1 M (200 mL), sat NaHCO₃ (2 x 200 mL), sat brine (2 x 100 mL) and H₂O (2 x 250 mL). The organic layer was then dried over MgSO₄, filtered and concentrated under vacuum to give 3.14 g (89%) of clean A2 as observed by NMR. 2.0 g (4.545 mmol) of A2 were dissolved in a mixture of MeOH/Et₃N/H₂O (1/8/1, 50 mL) and left stirring overnight at room temperature. The solution was then co-evaporated with toluene and dried under vacuum to afford A3 (1.5 g) of sufficient purity to be taken into the following step without further purification. The A3 mixture was dissolved in DMF (20 mL) and imidazole (544 mg, 1.5 eq) and triisopropylsilyl chloride (1.6 mL, 1.5 eq) were added. The resulting mixture was left stirring at room temperature for 24h until TLC showed completion of the reaction. The solvent was then evaporated under high pressure and the residue dissolved in EtOAc (100 mL) and washed with water (100 mL). The aqueous layer was then extracted with EtOAc (4 x 100 mL). The collected organic layer was dried over MgSO₄ and then evaporated under vacuum to give A4, which was dissolved in pyridine (50 mL) and BzCl (1.8 mL) and DMAP (61 mg) were added. The solution was stirred overnight. The reaction mixture was then quenched with MeOH at 0 °C. Co-evaporation of the solvent with toluene followed by crystallisation in EtOH gave 8 (2 g) as a white solid, column chromatography of the filtered fraction (petroleum ether/Et₂O : 10/0- 9/1) gave another 1.0 g of 8. Overall, 3.0 g of 8 were obtained in 90 % yield from 3 steps starting from A2. Rf = 0.4 (95/5 : petroleum ether/EtOAc). ¹H NMR (CDCl₃, 400 MHz, ppm) : δ = 8.01-7.98 (m, 2H, Ph), 7.95-7.92 (m, 2H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.51 (m, 4H, Ph), 7.46-7.36 (m, 5H, Ph), 5.91 (t, 1H, J₃,4 = J₃,2 = 9.5 Hz, H-3), 5.57 (t, 1H, J₄,5 = J₄,3 = 9.5 Hz, H-4), 5.50 (dd, 1H, J₂₃ = 9.5 Hz, J₂₁ = 10.0 Hz, H-2), 5.08 (d, 1H, J₁₂ = 10.0 Hz, H-1), 3.98-3.93 (m, 3H, H-6a, H-6b, H-5), 1.15-1.02 (m, 21H, TIPS). ¹³C NMR (CDCl₃, 100 MHz) : δ = 165.9, 165.1 (CO), 133.2, 133.1, 132.6, 132.5 (C₉, Ph), 129.8, 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.4, 128.3, 128.2, 128.0 (CH, Ph), 86.4 (C-1), 79.9 (C-5), 74.6 (C-3), 70.7 (C-2), 69.2 (C-4), 63.0 (C-6), 17.9, 11.9 (TIPS). HRMS-ESI for C₄₂H₄₈NaO₈SSi (MNa⁺) calcd: 763.2764, found: 763.2731.
2,3,4-tri-O-Benzoyl-6-O-triisopropyldisilyl-β-D-glucopyranoside trichloroacetimidate (9)

Method A with K₂CO₃: A solution of thioglycoside 8 (700 mg, 0.94 mmol), NBS (204 mg, 1.13 mmol) in acetone (20 mL) was stirred at room temperature for 30 min. The reaction was quenched dropwise with NaHCO₃ at 0 °C and the acetone was removed under vacuum. CH₂Cl₂ (150 mL) was added to the residue and the organic layer was washed with sat Na₂S₂O₃ (2 x 40 mL), H₂O (2x50 mL), dried with MgSO₄, filtered, and concentrated. The residue was co-evaporated with toluene and dried under vacuum overnight. To the crude mixture, CH₂Cl₂ (8 mL), K₂CO₃ (780 mg, 5.64 mmol) and CCl₃CN (940 µL, 9.4 mmol) were added and the reaction was stirred for 21 h. The mixture was concentrated under vacuum and purified by silica gel chromatography (toluene) to yield 300 mg (47 %) of 9 as an α/β: 1/1 mixture.

Method B with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene): A solution of thioglycoside 8 (1.76 g, 2.38 mmol), NBS (513 mg, 2.85 mmol) in acetone (50 mL) was stirred at room temperature for 30 min. The reaction was quenched dropwise with NaHCO₃ at 0 °C and the acetone was removed under vacuum. CH₂Cl₂ (150 mL) was added to the residue and the organic layer was washed with sat Na₂S₂O₃ (2 x 40 mL), H₂O (2x50 mL), dried with MgSO₄, filtered, and concentrated. The residue was co-evaporated with toluene and dried under vacuum overnight. To the crude residue, CH₂Cl₂ (25 mL), DBU (460 µL, 0.97 mmol) and CCl₃CN (2.4 mL, 23.8 mmol), were added and the reaction was stirred for 1 h. The mixture was concentrated under vacuum and purified by silica gel chromatography to afford 1.36 g (72 %) of 9 as the α isomer. Rf = 0.5 (Toluene). ¹H NMR (CDCl₃, 400 MHz, ppm) :  δ = 8.71 (NH, α), 8.60 (NH, β), 8.00-7.89 (m, 13H, Ph), 7.56-7.27 (m, 17H, Ph), 6.87 (d, 1H, J₁,₂ = 4.0 Hz, H-1α), 6.26 (t, 1H, J₃,₂ = J₃,₄ = 10.0 Hz, H-3α), 6.26 (d, 1H, J₁,₂ = 8.0 Hz, H-1β), 5.96 (t, 1H, J₃,₂ = J₃,₄ = 10.0 Hz, H-3β), 5.81-5.75 [m, 3H, in which dd at 5.79 (1H, J₂,₁ = 8.0 Hz, J₂,₃ = 10.0 Hz, H-2β), H-4α, H-4β], 5.58 (dd, 1H, J₂,₁ = 4.0 Hz, J₂,₃ = 10.0 Hz, H-2α), 4.41 (ddd, 1H, J₅,₆α = 3.5 Hz, J₅,₆b = 4.0 Hz, J₅,₄ = 10.0 Hz, H-5α), 4.11 (ddd, 1H, J₅,₆a =2.0 Hz, J₅,₆b = 4.5 Hz, J₅,₄ = 10.0 Hz, H-5β), 4.05 (dd, 1H, J₆ₐₕ = 2.5 Hz, H-6a β), 4.00-3.93 (m, 3H, H-6a α, H-6b α ,H-6b β), 1.11-1.01 (m, 42H, TIPS). ¹³C NMR (CDCl₃, 100 MHz, ppm) :  δ = 165.7, 165.4, 154.0, 164.8, 164.8 (CO), 160., 160.5 (CO), 133.4, 133.2, 133.1 (C₆, Ph), 129.9, 129.8, 129.7, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, 128.0, 125.7 (C₆H, Ph), 95.7 (C-1β), 93.3 (C-1α), 90.9, 90.4 (C₆Cl₃ α and β), 78.0 (C-5β), 73.8 (C-5α), 73.0 (C-3β), 71.0(C-2α), 70.9 (C-2β), 70.5 (C-3α), 62.4 (C-6β), 62.4 (C-6α), 68.7, 68.6 (C-4 α and β), 17.8, 11.9 (TIPS). HRMS-ESI for C₃₈H₄₄Cl₃NNaO₉Si (MNa⁺), calcd:  814.1761, found: 814.1743.
3-Bromopropyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside (10)

**Method A: trichloroacetimidate donor.** To a solution of 9 (600 mg, 0.76 mmol) in CH₂Cl₂ (6 mL), 3-bromopropan-1-ol (96 µL, 0.99 mmol) and 4 Å molecular sieves (2 g) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40 °C. TMSOTf (10% solution in CH₂Cl₂, 150 µL, 0.052 mmol, 0.1 eq) was then added and the reaction was kept at -40 °C for another 1 h. After quenching with Et₃N (50 µL), the mixture was concentrated under vacuum and the residue purified by silica gel chromatography using toluene as the eluant to give 480 mg (83%) of 10.

**Method B: Thiophenyl donor.** To a solution of 8 (200 mg, 0.268 mmol) in CH₂Cl₂ (1.2 mL), 3-bromopropan-1-ol (48 µL, 0.496 mmol), 2,6-di-tert-butyl-4-methyl-pyridine (55 mg, 0.268 mmol) and 4 Å molecular sieves were added and the mixture was stirred for 30 minutes at room temperature before cooling to 0 °C. Tf₂O/Me₂S₂ (1M solution in CH₂Cl₂ 0.4 mL, 0.4 mmol) was then added and the reaction was kept at 0 °C for another 2 h before being quenched with Et₃N (100 µL). The mixture was concentrated under vacuum and the residue was purified by flash chromatography using toluene as the eluant to give 120 mg (58%) of 10. Rf = 0.28 (Toluene). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 7.99-7.97 (m, 2H, Ph), 7.94-7.92 (m, 2H, Ph), 7.85-7.83 (m, 2H, Ph), 7.45-7.49 (m, 2H, Ph), 7.31-7.25 (m, 2H, Ph), 5.87 (t, 1H, J₃,₄ = J₂,₃ = 9.5 Hz, H-3), 5.56 (t, 1H, J₄,₅ = 9.5 Hz, H-4), 5.47 (dd, 1H, J₂,₁ = 8.0 Hz, J₃,₂ = 9.5 Hz, H-2), 4.83 (d, 1H, J₁,₂ = 8.0 Hz, H-1), 4.04 (dt, 1H, J = 10.0 Hz, CH₂O), 3.95-3.87 (m, 3H, H-6a, H-6b, H-6), 3.73 (dd, 1H, J₂,₃ = 5.0, 8.0 Hz, CH₂O), 3.39-3.35 (m, 2H, CH₂Br), 2.19-1.97 (m, 2H, OCH₂CH₂), 1.07-1.01 (m, 21H, TIPS). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 165.9, 165.2, 165.1 (CO), 133.2, 133.2, 133.1, (Cq, Ph), 129.8, 129.7, 129.3, 129.2, 129.0, 128.4, 128.2, 128.2 (CH, Ph), 101.3 (C-1), 75.6 (C-5), 73.3 (C-3), 72.1 (C-2), 69.5 (C-4), 67.2 (OCH₂), 62.8 (C-6), 32.2 (OCH₂CH₂), 30.1 (CH₂Br). 17.9, 11.9 (TIPS).

ESI-HRMS (MNa⁺) for C₃₉H₄₀BrNaO₉Si⁺ calced. : 791.2221; found : 791.2229.

3-(3-Methylimidazolium)-1-propyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside trifluoromethanesulfonate (11) To a solution of 10 (160 mg, 0.21 mmol) in acetonitrile (20mL) was added 1-methylimidazole (68 µL, 0.84 mmol) and potassium trifluoromethanesulfonate (158 mg, 0.84 mmol) and the mixture was refluxed over night. After filtration of the salts, the solution was evaporated under reduced pressure and the residue redissolved in CH₂Cl₂ and washed with H₂O (5mL) to remove the excess of imidazole.
from the product. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 30 mL). The collected organic fractions were dried with Na$_2$SO$_4$, concentrated and dried under vacuum. The residue was washed with n-hexane (3 x 5 mL) and Et$_2$O (3 x 5 mL) to give 160 mg (83%) of 11. $^1$HNMR (CDCl$_3$, 400 MHz, ppm): $\delta = 9.13$ (s, 1H, NCH$_2$N), 7.97-7.16 (m, 17H, 15H (Ph) + 2H (imidazolium), 5.86 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-2), 4.80 (d, 1H, $J_{i,2} = 8.0$ Hz, H-1), 4.31-4.25 (m, 2H, CH$_2$N), 3.97-3.87 (m, 7H in which s at 3.93, CH$_3$N, H-5, H-6a, H-6b, OCH$_2$), 3.42-3.31 (m, 1H, OCH$_2$), 2.19-2.15 (m, 2H, OCH$_2$CH$_2$), 1.08-0.95 (m, 21H, TIPS). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta = 165.8, 165.4, 165.1$ (CO), 137.0 (NCH$_2$N), 133.7, 133.3, (C$_q$, Ph), 129.7, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 125.3, 122.5, 122.4, 122.2 (CH$_3$, aromatic), 100.9 (C-1), 75.5 (C-5), 73.0 (C-3), 72.2 (C-2), 69.1 (C-4), 65.7 (OCH$_2$), 62.5 (C-6), 47.2 (CH$_2$N), 36.4 (CH$_3$N), 29.9 (OCH$_2$CH$_2$), 17.8, 11.9 (TIPS). $^{19}$F NMR (CDCl$_3$, 400 MHz, ppm): $\delta = -80.3$ (TfO$^-$). HRMS-ESI for C$_{43}$H$_{55}$N$_2$O$_9$Si$^+$ (M$^+$), calcd: 771.3665, found: 771.3671.

4-(Chloromethyl)benzyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-$\beta$-D-glucopyranoside (13)

To a solution of 9 (210 mg, 0.25 mmol) in CH$_2$Cl$_2$ (2 mL), 4-chloromethyl benzyl alcohol 12 (79 mg, 0.50 mmol) and 4 Å molecular sieves (500 mg) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40 °C. TMSOTf (4 µL, 0.02 mmol) was then added and the reaction was kept at -40°C for another 1h. After quenching with Et$_3$N (20 µL), the mixture was concentrated under vacuum and the residue purified by silica gel chromatography using toluene as the eluant to give 187 mg (94%) of 13. $R_f = 0.3$ (Toluene). $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta = 7.95-7.90$ (m, 4H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.49 (m, 2H, Ph), 7.45-7.35 (m, 4H, Ph), 7.22 (s, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.56 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H-2), 5.54 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 4.92 (d, 1H, $J = 12.5$ Hz, OCH$_2$), 4.81 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.73 (d, 1H, $J = 12.5$ Hz, OCH$_2$), 4.55 (bs, 2H, ClCH$_2$), 3.96 (bs, 2H, H-6a, H-6b), 3.85 (dt, 1H, $J_{5,6a} = J_{5,6b} = 3.5$ Hz, $J_{5,4} = 9.5$ Hz, H-5), 1.09-1.04 (m, 21H, TIPS). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta = 165.8, 165.1$ (CO), 137.1, 137.0 (C$_q$, Ph), 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.2, 129.0, 128.6, 128.3, 128.2, 128.1 (CH, aromatic), 99.2 (C-1), 75.7 (C-5), 73.3 (C-3), 72.0 (C-2), 69.7 (C-4), 69.7 (OCH$_2$), 63.0 (C-6), 45.9 (CH$_2$Cl), 17.9, 12.0 (TIPS). ESI-HRMS (MNa$^+$) for C$_{43}$H$_{55}$ClNaO$_9$Si$^+$ calcd: 809.2889; found: 809.2907.
4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside trifluoromethanesulfonate (14). To a solution of 13 (181 mg, 0.238 mmol) in CH₃CN (5 mL), 1-methyl imidazole (153 µL, 1.922 mmol), potassium trifluoromethylsulfonate (358 mg, 1.904 mmol) were added and the mixture was refluxed for 24 h before being cooled to room temperature. TLC showed completion of the reaction. The solvent was then evaporated to dryness followed by addition of a mixture of H₂O/CH₂Cl₂ (5 mL/15 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL) and EtOAc (2 x 15 mL). The combined organic layer was then dried over Na₂SO₄, filtered and evaporated. The dried residue was washed 3 times with a mixture 1/1 of n-hexane/EtOAc to give 14 (200 mg, 89%) as a yellow foam. ¹H NMR (CDCl₃, 400 MHz, ppm) : δ = 9.20 (s, 1H, NCH₃N), 7.94-7.91 (m, 4H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.51 (m, 2H, Ph), 7.45-7.36 (m, 5H, Ph), 7.31-7.23 (m, 7H, Ph), 7.17 (t, 1H, J = 1.5 Hz, NCHCHN), 5.86 (t, 1H, J₃,₄ = J₃,₂ = 9.5 Hz, H-3), 5.59 (t, 1H, J₄,₃ = J₄,₅ = 9.5 Hz, H-4), 5.55 (dd, 1H, J₂,₁ = 8.0 Hz, J₂,₂ = 9.5 Hz, H-2), 5.31 (bs, 2H, CH₂N), 4.95 (d, 1H, J = 12.0 Hz, OCH₂), 4.87 (d, 1H, J₁,₂ = 8.0 Hz, H-1), 4.70 (d, 1H, J = 12.0 Hz, OCH₃), 3.99-3.96 (m, 2H, H-6a, H-6b), 3.93 (s, 3H, NCH₃N), 3.93-3.88 (m, 1H, H-5), 1.09-1.03 (m, 21H, TIPS). ¹³C NMR (CDCl₃, 100 MHz, ppm) : δ = 165.8, 165.2, 165.1 (CO), 138.6, 137.0 (Cₚ, Ph), 133.4, 133.3, 133.2, 132.1, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, (CH, aromatic), 123.5, 121.8 (CH, imidazolium), 99.7 (C-1), 75.6 (C-5), 73.2 (C-3), 72.0 (C-2), 69.7 (OCH₂), 69.4 (C-4), 62.7 (C-6), 53.1 (CH₂N), 36.4 (NCH₃), 17.8, 11.9 (TIPS). ESI-HRMS (M⁺) for C₄₈H₅₇N₂O₉Si⁺ calcd: 833.3828; found: 833.3828.

General OTIPS deprotection of ITagged saccharides.

Method A: To a solution of 6-OTIPS protected compounds 11, 14, 20 and 22 (1 mmol) in CH₂Cl₂ (10 mL) was added HCl (1.25 M in MeOH, 20 eq) and left stirring at room temperature for 18 h. MALDI-TOF analysis showed completion of the reaction. The mixture was co-evaporated with toluene. CH₂Cl₂ was added to the residue and washed with H₂O (2x2 mL), dried over Na₂SO₄, filtered, concentrated under reduced pressure and dried under vacuum for 2 h. The dried residue was washed twice with Et₂O to give products 19, 21, 23 and 25.

General glycosylation reactions.

Method B: Trichloroacetimidate donor. To a solution of acceptor (1 mmol) and donor (2 mmol) in 5-20 mL of CH₂Cl₂, 4 Å molecular sieves (MS) were added and the mixture was left stirring for 30 minutes at room temperature before cooling to 0 °C. TMSOTf (0.3 mmol) was added at 0 °C. The reaction was left to warm to room temperature overnight. MALDI-TOF analysis showed completion of the reaction. The mixture was then
filtered, concentrated under reduced pressure and dried under vacuum. The obtained oil was then washed twice with n-hexane and n-hexane/Et₂O 1:1 to give the coupling product.

**Method C: Thiophenyl glycoside donor.** To a solution of acceptor (1 mmol) and donor (3 mmol) in 5-20 mL of CH₂Cl₂, 4 Å MS were added and the mixture was left stirring for 30 minutes at room temperature before cooling to 0°C. Tf₂O/Me₂S₂ (1M solution in CH₂Cl₂, 4.5 mL, 4.5 mmol) was then added at 0°C and the reaction was left to warm to room temperature overnight. MALDI-TOF analysis showed completion of the reaction. The mixture was then filtered and the solvent concentrated under reduced pressure. The dried residue was washed with H₂O (10 mL) and the aqueous layer was then extracted twice with abundant quantity of CH₂Cl₂ (2x50 mL). The organic fractions were evaporated and dried under high vacuum. The dried residue was washed three times with a mixture of 1/1 : n-hexane/Et₂O to give the coupling product. Note: Some of the ITag-product will be partially soluble in the water phase. The water fractions must be wash carefully with DCM to ensure most of the product is recovered.

3-(3-Methylimidazolium)-1-propyl 3,4-di-O-acetyl-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-6-O-(triisopropyl)silyl-β-D-galactopyranoside tetrafluoroborate (15)

Following general glycosylation **Method B:** from 7 (30 mg, 0.06 mmol) to give 15 (43.4 mg, 90%).

1H NMR (CDCl₃, 400 MHz, ppm) : δ_H = 9.20 (s, 1H, NCH=N), 7.73, 7.38 (2s, 2H, 2 x NC-H), 5.46-5.45 (m, 1H, H-4B), 5.38 (d, 1H, J₄,₃ = 3.0 Hz, H-4A), 5.09 (dd, J₂,₁ = 8.0 Hz, J₂,₃ = 10.5 Hz, H-2B), 5.01 (dd, 1H, J₃,₄ = 3.0 Hz, J₃,₂ = 10.5 Hz, H-3A), 4.98 (dd, 1H, J₃,₂ = 3.0 Hz, J₃,₃ = 10.5 Hz, H-3B), 4.73 (1H, d, J₁,₂ = 8.0 Hz, H-1B), 4.54-4.46 (m, 3H, H-5ₐ, OCH₂CH₂CH₂), 4.34 (1H, d, J₁,₂ = 8.0 Hz, H-1A), 4.30-4.27 (m, 1H, H-6ₐB), 4.10-4.07 (m, 2H, OCH₂CH₂CH₂), 4.06 (s, 3H, CH₃N), 4.01-3.99 (m, 2H, H-5B, H-6bB), 3.90 (dd, 1H, J₂,₁ = 8.0 Hz, J₂,₃ = 10.5 Hz, H-2A), 3.79-3.77 (m, 1H, H-6ₐA), 3.73-3.71 (m, 1H, H-6bA), 2.23-2.18 (m, 2H, OCH₂CH₂CH₂), 2.19 (s, 3H, CH₃Ac), 2.15 (s, 3H, CH₃Ac), 2.06 (s, 3H, CH₃Ac), 2.03 (s, 3H, CH₃Ac), 1.97 (s, 3H, CH₃Ac), 1.95 (s, 3H, CH₃Ac), 2.01 (3H, s), 1.01 (21H, s); ¹³C NMR (CDCl₃, 100 MHz, ppm) : δ = 167-164 (6xCO), 138.0 (NCHN), 124.96 (NC-,H), 123.98 (NC-,H), 100.8 (C-1A), 101.2 (C-1B), 73.5 (C-5ₐ), 70.8 (C-3ₐ), 70.2 (C-3ₐ), 75.2 (C-2ₐ), 68.2 (C-2B), 67.3 (C-4B), 66.9 (C-4ₐ), 65.8 (C-5ₐ), 60.3 (C-6ₐ), 61.5 (OCH₂), 60.7 (C-6ₐ), 45.5 (CH₂N), 36.3 (NCH₃), 29.8 OCH₂CH₂, 17.5, 11.6 (TIPS). HRMS: (ESI⁺) Found M⁺ 873.4053, C₂₆H₄₇O₈N₂Si⁺ requires 873.4047.

S11
2-O-(α/β-D-galactopyranosyl)-β-D-galactopyranose (17). Following general OTIPS removal Method A to remove TIPS group from 15 (10 mg, 0.01 mmol). The resulting product was then dissolved in CH₂Cl₂ (1 mL) and NH₃ (2M solution in MeOH, 10 mL) were added. The solution was heated at 60 °C for 24h. MALDI-TOF showed completion of the reaction. The mixture was co-evaporated with toluene and the dried residue washed with CH₂Cl₂ (3 x 2 mL) to afford 16 that was taken to the next step without further purification. The dried mixture was then redissolved in H₂O (5 mL) and HCl (50 µL, 1M) was added. The mixture was left stirring at reflux for 8 h. TLC showed completion of the reaction. The reaction mixture was then co-evaporated with toluene and the dried residue was purified over reverse phase C-18 column chromatography with a gradient of H₂O/MeOH: 9/1-1/1 to give (3 mg, 77%) of 17 as α/β (5/1) mixture. NMR and MS data in agreement with reported literature.⁴

Methyl 2-O-(α/β-D-galactopyranosyl)-β-D-galactopyranoside (18). Following general OTIPS removal Method A to remove TIPS group from 15 (14 mg, 0.02 mmol). The resulting product was then dissolved in CH₂Cl₂ (1 mL) and NH₃ (2M in MeOH, 10 mL) were added. The solution was heated at 60 °C for 24h. MALDI-TOF showed completion of the reaction. The mixture was co-evaporated with toluene and the dried residue washed with CH₂Cl₂ (3 x 2 mL) to afford 16 that was taken to the next step without further purification. The dried mixture was then redissolved in CH₂Cl₂ (10 mL) and HCl (1.25 M in MeOH, 10 eq) was added. The mixture was left stirring at reflux for 8 h. TLC showed completion of the reaction. The reaction mixture was then co-evaporated with toluene and the dried residue was purified over reverse phase C-18 column chromatography with a gradient of H₂O/MeOH: 9/1-1/1 to give 18 (4.7 mg, 82%) as α/β (9/1) mixture. NMR and MS data in agreement with reported literature.⁵
3-(3-Methylimidazolium)-1-propyl 4,6-O-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside trifluoromethanesulfonate (19). Following general OTIPS removal Method A. From 11 (220 mg, 0.29 mmol) to give 19 (180 mg, 94%). 1H NMR (CDCl3, 400 MHz, ppm) : δ = 9.06 (s, 1H, NCHN), 7.95-7.25 (m, 17H, 15 H (Ph) + 2H (imidazole), 5.89 (t, 1H, J3,4 = J3,2 = 9.5 Hz, H-3), 5.46 (t, 1H, J4,3 = J4,5 = 9.5 Hz, H-4), 5.36 (dd, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2), 4.85 (d, 1H, J1,2 = 8.0 Hz, H-1), 4.35 (t, 2H, J = 6.5 Hz, CH2N), 3.87 (bd, 1H, J = 12.0 Hz, H-6a), 3.83-3.70 (m, 3H, H-6b, H-5, OCH2), 3.42-3.31 (m, 1H, OCH2), 2.71 (bs, 1H, OH), 2.11-2.00 (m, 2H, OCH2CH2). 13C NMR (CDCl3, 100 MHz, ppm) : δ = 165.9, 165.6, 165. (CO), 137.1 (NCHN), 133.6, 133.4, (Cq, Ph), 129.9, 129.7, 129.6, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 125.3, 123.4, 122.6 (CH, aromatic), 100.6 (C-1), 74.6 (C-5), 72.8 (C-3), 71.9 (C-2), 69.5 (C-4), 65.8 (C-6), 60.5 (OCH2), 47.0 (CH2N), 36.4 (NCH3), 29.9 (OCH2CH2). 19F NMR (CDCl3, 400 MHz, ppm): δ = -78.43 (TfO-). HRMS-ESI for C34H35N2O9+ (M+), calcd: 615.2336, found: 615.2337.

3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate (20).

Following general glycosylation Method B. From 19 (140 mg, 0.23 mmol) to give 20 (236 mg, 94%)

Following general glycosylation Method C. From 19 (30 mg, 0.05 mmol) to give 20 (41 mg, 76%)

1HNMR (CDCl3, 400 MHz, ppm) : δ = 9.09 (s, 1H, NCHN), 8.08-7.23 (m, 32H, 30H (Ph) + 2H (imidazole), 5.91 (t, 1H, J3,4 = J3,2 = 9.5 Hz, H-3A), 5.76 (t, 1H, J3,4 = J3,2 = 9.5 Hz, H-3B), 5.54 (t, 1H, J4,3 = J4,5 = 9.5 Hz, H-4A), 5.44 (dd, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2A), 5.30 (t, 1H, J4,3 = J4,5 = 9.5 Hz, H-4B), 5.01 (dd, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2B), 4.89 (d, 1H, J1,2 = 8.0 Hz, H-1A), 4.70 (d, 1H, J1,2 = 8.0 Hz, H-1B), 4.32-4.25 (m, 1H, CH2N), 4.19-4.14 (m, 2H, CH2N + H-6aB), 4.02 (s, 3H, CH3N), 4.01-3.97 (m, 1H, H-5B), 3.88-3.12 (m, 3H, H-5a, 2xH-6a), 3.75 (dd, 1H, J6b,5 = 5.5 Hz, J6b,6a = 12.0 Hz, H-6b), 3.64-3.58 (m, 1H, OCH2), 3.50-3.45 (m, 1H, OCH2), 1.98-1.92 (bs, 2H, OCH2CH2), 0.98-0.91 (m, 1H, TIPS). 13C NMR (CDCl3, 100 MHz, ppm) : δ = 165.7, 165.4, 165.3, 165.0, 164.9 (CO), 137.0 (NCHN), 133.7, 133.6, 133.6, 133.5, 133.5, 133.4, 133.3, 133.2 (Cq, Ph), 130.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.6, 129.0, 128.9, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 125.3, 125.2 (CH, aromatic), 101.8 (C-1A), 100.3 (C-1B), 75.6 (C-5A), 72.9 (C-5B), 72.8 (C-3A), 72.7 (C-3B), 72.2 (C-2A), 71.7
(C-2\(^B\)), 69.2 (C-4\(^A\)), 69.1 (C-4\(^B\)), 67.8 (C-6\(^\alpha\)), 64.7 (OCH\(_2\)H), 64.4 (C-6\(^\beta\)), 46.6 (CH\(_2\)N), 36.3 (NCH\(_3\)), 29.6 (OCH\(_2\)CH\(_2\)), 17.8, 11.7 (TIPS). HRMS-ESI for C\(_{70}\)H\(_{77}\)N\(_2\)O\(_{17}\)Si\(^+\) (M\(^+\)), calcd: 1245.5034, found: 1245.4986.

3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-\(\beta\)-D-glucopyranosyl)-\(\beta\)-D-glucopyranoside trifluoromethanesulfonate (21). Following general OTIPS removal Method A. From 20 (220 mg, 0.18 mmol) to give 21 (194 mg, 97%). \(^1\)HNMR (CDCl\(_3\), 400 MHz, ppm) : \(\delta = 9.06\) (s, 1H, NCH\(_{\text{N}}\)), 8.05-7.19 (m, 32H, 30H (Ph) + 2H (imidazole), 5.98 (t, 1H, \(J_{3,4} = 9.5\) Hz, H-3\(^A\)), 5.41 (dd, 1H, \(J_{2,1} = 8.0\) Hz, J\(_{2,3} = 9.5\) Hz, H-2\(^A\)), 5.30 (t, 1H, \(J_{4,3} = 9.5\) Hz, H-4\(^B\)), 5.06 (dd, 1H, \(J_{2,1} = 8.0\) Hz, J\(_{2,3} = 9.5\) Hz, H-2\(^B\)), 4.87 (d, 1H, \(J_{4,3} = 8.0\) Hz, H-1\(^A\)), 4.71 (d, 1H, \(J_{4,3} = 8.0\) Hz, H-1\(^B\)), 4.36-4.16 (m, 3H, CH\(_2\)N+H-6), 4.02 (s, 3H, CH\(_3\)N), 3.96-3.56 (m, 9H, 3xH-6, H-5\(^A\), H-5\(^B\), OCH\(_2\)), 3.88-3.82 (m, 3H, H-5\(^A\), 2xH-6\(^A\)), 3.75 (dd, 1H, \(J_{6b,5} = 5.5\) Hz, J\(_{6b,6a} = 12.0\) Hz, H-6\(^b\)), 3.64-3.58 (m, 1H, OCH\(_2\)), 3.50-3.45 (m, 1H, OCH\(_2\)), 1.98-1.92 (bs, 2H, OCH\(_2\)CH\(_2\)), 0.98-0.91 (m, 21H, TIPS). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm) : \(\delta = 165.7, 165.4, 165.3, 165.0, 164.9\) (CO), 137.0 (NC\(_{\text{HN}}\)), 133.7, 133.6, 133.6, 133.5, 133.5, 133.4, 133.3, 133.2 (C\(_q\), Ph), 130.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.6, 129.0, 129.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 125.3, 125.2 (C\(_\text{PH, aromatic}\)), 101.8 (C-1\(^A\)), 100.3 (C-1\(^B\)), 75.6 (C-5\(^A\)), 72.9 (C-5\(^B\)), 72.8 (C-3\(^A\)), 72.7 (C-3\(^B\)), 72.2 (C-2\(^A\)), 71.7 (C-2\(^B\)), 69.2 (C-4\(^A\)), 69.1 (C-4\(^B\)), 67.8 (C-6\(^B\)), 64.7 (OCH\(_2\)), 64.4 (C-6\(^\alpha\)), 46.6 (CH\(_2\)N), 36.3 (NCH\(_3\)), 29.6 OCH\(_2\)CH\(_2\)), 17.8, 11.7 (TIPS). HRMS-ESI for C\(_{61}\)H\(_{57}\)N\(_2\)O\(_{17}\)Si\(^+\) (M\(^+\)), calcd: 1089.3673, found: 1089.3652.

3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-\(\beta\)-D-glucopyranosyl)-\(\beta\)-D-glucopyranosyl)-\(\beta\)-D-glucopyranoside trifluoromethanesulfonate (22) Following general glycosylation Method B. From 21 (240 mg, 0.22 mmol) to give 22 (172 mg, 94%). \(^1\)HNMR (CDCl\(_3\), 500 MHz, ppm) : \(\delta = 9.19\) (s, 1H, NCH\(_{\text{N}}\)), 8.09-7.18 (m, 47H, 45H (Ph) + 2H (imidazole), 5.95 (t, 1H, \(J_{3,4} = J_{3,2} = 9.5\) Hz, H-3), 5.89 (t, 1H, \(J_{3,4} = J_{3,2} = 9.5\) Hz, H-3), 5.87 (t, 1H, \(J_{3,4} = J_{3,2} = 9.5\) Hz, H-3), 5.67 (t, 1H, \(J_{4,3} = J_{4,5} = 9.5\) Hz, H-4), 5.49 (dd, 1H, \(J_{2,1} = 8.0\) Hz, J\(_{2,3} = 9.5\) Hz, H-2), 5.31 (t, 1H, \(J_{4,3} = J_{4,5} = 9.5\) Hz, H-4), 5.28 (dd, 1H, \(J_{2,1} = 8.0\) Hz, J\(_{2,3} = 9.5\) Hz, H-2), 5.23 (t, 1H, \(J_{4,3} = \)
$J_{4,5} = 9.5$ Hz, H-4), 5.12 (dd, 1H, $J_{2,1} = 8.0$ Hz, H-2), 4.91 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.88 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.78 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1$^3$), 4.48-4.23 (m, 2H, CH$_2$N), 4.14-3.62 (m, 14H in which a singulet at 4.07 (3H, CH$_3$N), 3xH-5, 6xH-6, CH$_2$O), 2.19-2.14 (m, 2H, OCH$_2$CH$_2$), 1.05-0.91 (m, 21H, TIPS). 13C NMR (CDCl$_3$, 125 MHz, ppm) : 165.8, 165.7, 165.5, 165.5, 165.4, 165.3, 165.2, 165.1, 165.1, 165.0, (CO), 137.1 (NCHN), 133.6, 133.4, 133.3, 133.2, 133.1 (C$_q$, Ph), 130.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 129.9, 128.8, 128.6, 128.4, 128.4, 128.2, 128.2, 128.1, 123.8, 123. (CH, aromatic), 102.2, 101.9, 100.3 (3 x C-1), 76.1, 73.2, 73.0, 72.4, 72.3, 72.2, 71.8, 71.6, 69.7, 69.5, 69.2, 68.2, 64.6, 62.8, 46.5 (CH$_2$N), 36.4 (NCH$_3$), 29.8 (OCH$_2$CH$_2$), 17.8, 11.7 (TIPS). HRMS-ESI for C$_{97}$H$_{99}$N$_2$O$_{25}$Si$^+$ (M$^+$), calcd : 1719.6325, found: 1719.6301.

3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate (23). Following general OTIPS removal. From 22 (228 mg, 0.13 mmol) to give 23 (200 mg, 97%). 1HNMR (CDCl$_3$, 400 MHz, ppm) : $\delta = 9.14$ (s, 1H, NCH$_2$N), 8.02-7.24 (m, 47H, 45H (Ph) + 2H (imidazole), 5.90 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.89 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.74 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.44 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 5.41 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 5.33 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 5.30 (dd, 1H, $J_{2,1} = 8.0$ Hz, H-2), 5.27 (dd, 1H, $J_{2,1} = 8.0$ Hz, H-2), 4.97 (dd, 1H, $J_{2,1} = 8.0$ Hz, H-2), 4.85 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.84 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.74 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1) 4.52-4.39 (m, 2H), 4.14-3.62 (m, 14H in which s at 4.07 (3H, CH$_3$N), 2.12 (bs, 2H, OCH$_2$CH$_2$). 13C NMR (CDCl$_3$, 125 MHz, ppm) : $\delta = 165.8$, 165.7, 165.5, 165.5, 165.4, 165.0, 165.0, 164.9, 164.8 (CO), 137.8 (NCHN), 133.6, 133.4, 133.3, 133.3, 133.2, 133.1, 133.0 (C$_q$, Ph), 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 123.7, 123.10 (CH, aromatic), 101.6, 101.0, 100.3 (3xC-1), 77.2, 74.7, 72.9, 72.8, 72.4, 72.3, 71.8, 71.7, 71.6, 69.3, 69.1, 68.7, 67.4, 65.5, 60.7, 47.3 (CH$_2$N), 37.1 (NCH$_3$), 29.6 (OCH$_2$CH$_2$). HRMS-ESI for C$_{88}$H$_{79}$N$_2$O$_{25}$Si$^+$ (M$^+$), calcul : 1563.4964, found: 1563.4966.
3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate (24). Following general glycosylation Method B. From 23 (60 mg, 0.04 mmol) to give 24 (85 mg, 88%). $^1$HNMR (CDCl$_3$, 500 MHz) : 9.13 (s, 1H, NCH$_3$N), 8.02-7.24 (m, 62H, 60 H (Ph) + 2H (imidazole), 5.94 (t, 1H, J = 9.5 Hz), 5.88 (t, 1H, J = 9.5 Hz), 5.87 (t, 1H, J = 9.5 Hz), 5.84 (t, 1H, J = 9.5 Hz), 5.67 (t, 1H, J = 9.5 Hz), 5.49 (t, 1H, J = 9.5 Hz), 5.45 (dd, 1H, J = 8.0, 9.5 Hz) 5.39 (dd, 1H, J = 8.0, 9.5 Hz), 5.24 (dd, 1H, J = 8.0, 9.5 Hz), 5.19-5.11 (m, 3H), 5.04 (d, J = 8.0 Hz) 5.03 (d, J = 8.0 Hz), 5.75 (d, J = 8.0 Hz), 5.44 (d, J = 8.0 Hz), 4.94-4.42 (m, 1H), 4.32-4.30 (m, 2H), 4.15 (t, 2H, J = 9.0 Hz, CH$_2$N), 4.04 (s, 3H, CH$_3$N), 4.00-3.95 (m, 2H), 3.84-3.63 (m, 9H), 3.52-3.48 (m, 1H), 2.11 (bs, 2H, OCH$_2$CH$_2$), 0.88-0.81 ( m, 21H, TIPS). $^{13}$C NMR (CDCl$_3$, 125 MHz) : 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.0, 164.9, 164.7 (CO), 137.2 (NCH$_3$), 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 132.7 (C$_q$, Ph), 130.1, 130.0, 129.9, 129.8, 129.8, 129.8, 129.8, 129.7, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 123.8, 123.7 (CH$_2$ aromatic), 102.9, 102.3, 101.9, 100.2 (4 x C-1), 76.3, 73.7, 72.9, 72.8, 72.6, 72.5, 72.3, 72.1, 72.0, 71.8, 71.7, 71.6, 71.1, 71.0, 70.4, 70.2, 69.9, 69.8, 69.6, 69.3, 64.7, 63.0, 46.9 (CH$_2$N), 36.6 (NCH$_3$), 29.0 (OCH$_2$CH$_2$), 17.9, 11.7 (TIPS). HRMS-ESI for C$_{88}$H$_{79}$N$_2$O$_{25}$ (M$^+$), calcd: 2193.76155, found: 2193.76154. Elemental analysis (C$_{125}$H$_{121}$F$_3$N$_2$O$_{36}$SSi): (%) Calculated: C, 64.04; H, 5.20; N, 1.19 S, 1.37; Found: C, 64.13; H, 5.32; N, 1.28; S, 1.42.

4-(1-Methyl-3-methyleneimidazolium)benzyl 2,3,4-tri-O-benzoyl-6-β-D-glucopyranoside trifluoromethanesulfonate (25)

Following Method A for TIPS deprotection: from 14 (186 mg, 0.19 mmol) to give 25 (150 mg, 95%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) : δ = 9.09 (s, 1H, NCH$_3$N), 7.95-7.94 (m, 4H, Ph), 7.85-7.83 (m, 2H, Ph), 7.56-7.52 (m, 2H, Ph), 7.46-7.38 (m, 5H, Ph), 7.31-7.26 (m, 8H, Ph + 2H imidazolium), 5.84 (t, 1H, J$_{3,4}$ = J$_{3,2}$ = 9.5 Hz, H-3), 5.54 (dd, 1H, J$_{2,1}$ = 8.0 Hz, J$_{2,3}$ = 9.5 Hz, H-2), 5.52 (t, 1H, J$_{4,3}$ = J$_{4,5}$ = 9.5 Hz, H-4), 5.29 (bs, 2H, CH$_2$N), 4.95 (d, 1H, J$_{1,2}$ = 8.0 Hz, H-1), 4.93 (d, 1H, J = 12.0 Hz, OCH$_3$), 4.73 (d, 1H, J = 12.0 Hz, OCH$_3$)}.

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3.89-3.84 (m, 6H, H-6a, H-5 + 3.89 s, CH$_3$N), 3.75 (dd, 1H, J$_{1H,2H}$ = 11.0 Hz, H-6b). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm) : δ = 166.0, 165.7, 165.2 (CO), 138.4, 136.6 (C$_q$, Ph), 133.7, 133.5, 133.3, 132.4, 129.9, 129.7, 129.6, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3 (CH, aromatic), 123.7, 122.1 (CH, imidazolium), 100.3 (C-1), 74.6 (C-5), 72.8 (C-3), 71.9 (C-2), 70.7 (OCH$_2$), 69.4 (C-4), 61.2 (C-6), 53.1 (CH$_2$N), 36.5 (NCH$_3$). ESI-HRMS (M+) for C$_{39}$H$_{37}$N$_2$O$_9$+: calcd: 677.2494; found: 677.2493.

4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate (26). Following general Glycosylation Method B: From 25 (58 mg, 0.09 mmol) to give 26 (100 mg, 98%). $^1$HNMR (CDCl$_3$, 500 MHz, ppm) : δ = 9.26 (s, 1H, NCH$_2$N), 7.93-7.86 (m, 8H, Ph), 7.81-7.80 (m, 2H, Ph), 7.77-7.75 (m, 4H, Ph), 7.55-7.49 (m, 4H, Ph), 7.45-7.35 (m, 12H, Ph), 7.29-7.24 (m, 4H, Ph), 7.21 (t, 1H, J = 1.5 Hz, NCH$_2$N), 7.19 (d, 2H J = 8.5 Hz, CH$_2$ OCH$_2$Ph), 7.13 (t, 1H, J = 1.5 Hz, NCH$_2$N), 7.09 (d, 2H J = 8.5 Hz, CH$_2$ OCH$_2$Ph), 5.85 (t, 1H, J$_{3,4}$= J$_{3,2}$ = 9.5 Hz, H-3$^A$) 5.79 (t, 1H, J$_{3,4}$= J$_{3,2}$ = 9.5 Hz, H-3$^B$), 5.56 (t, 1H, J$_{4,3}$= J$_{4,5}$ = 9.5 Hz, H-4$^A$), 5.50 (dd, 1H, J$_{2,1}$ = 8.0 Hz, J$_{2,3}$ = 9.5 Hz, H-2$^A$), 5.43 (dd, 1H, J$_{2,1}$ = 8.0 Hz, J$_{2,3}$ = 9.5 Hz, H-2$^B$), 5.34 (t, 1H, J$_{4,3}$= J$_{4,5}$ = 9.5 Hz, H-4$^B$), 5.31 (bs, 2H, CH$_2$N), 4.93 (d, 1H, J$_{1,2}$ = 8.0 Hz, H-1$^A$), 4.68 (d, 1H, J$_{1,2}$ = 8.0 Hz, H-1$^B$), 4.50 (d, 1H, J = 13.0 Hz, OCH$_2$), 4.28 (d, 1H, J = 13.0 Hz, OCH$_2$), 4.12 (dd, J$_{6a,5}$ = 1.5 Hz, J$_{6a,6b}$ = 10.5 Hz, H-6a$^A$), 4.03 (dt, J$_{5,6a}$= J$_{5,6b}$ = 2.0 Hz, J$_{5,4}$ = 9.5 Hz, H-5$^B$), 3.93 (s, 3H, CH$_3$N), 3.89-3.83 (m, 3H, H-5$^A$, H-6a$^B$, H-6b$^B$), 3.81 (dd, 1H, J$_{6b,5}$ = 8.0 Hz, J$_{6b,6a}$ = 10.5 Hz, H-6b$^A$), 0.95-0.88 (m, 21H, TIPS).$^{13}$C NMR (CDCl$_3$, 125 MHz, ppm) : δ = 165.9, 165.6, 165.3, 165.2, 165.1, 165.0, (CO), 138.4, 137.2, 133.5, 133.4, 133.3, 133.1, 133.1, 133.0, 131.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 129.8, 128.7, 128.6, 128.4, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 123.4, 121.7 (CH, aromatic), 101.2 (C-1$^A$), 99.4 (C-1$^B$), 75.4 (C-5$^A$), 73.7 (C-5$^B$) 73.3 (C-3$^A$), 72.8 (C-3$^B$), 72.2 (C-2$^A$), 71.8 (C-2$^B$), 69.8 (C-4$^B$), 69.6 (OCH$_2$), 69.2 (C-4$^A$), 68.7 (C-6$^A$), 62.5 (C-6$^B$), 53.2 (CH$_2$N), 36.5 (NCH$_3$), 17.7, 11.7 (TIPS). ESI-HRMS for C$_{75}$H$_{79}$N$_2$O$_{17}$Si$^+$ (M$^+$) calcd: 1307.5143; found: 1307.5142. Elemental analysis (C$_{76}$H$_{79}$F$_3$N$_2$O$_{20}$SSi): (%) Calculated: C, 62.62; H, 5.46; N, 1.92; S, 2.20; Found: C, 62.77; H, 5.56; N, 1.98; S, 2.32.
2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranose (27). To a solution of 26 (60 mg, 0.05 mmol) in HCOOH/EtOH (0.3 mL/6 mL) was added black Pd/C and the mixture was stirred under hydrogen atmosphere for 2 days. The obtained residue was filtered through celite and purified over silica gel column chromatography with a gradient from 9/1 to 7/3 (n-hexane/EtOAc) to give 26 (33 mg, 70%) as α/β (3.3/1) mixture. Rf = 0.3 (n-hexane/EtOAc: 7/3). (CDCl3, 500 MHz, ppm) : δ = 7.97-7.16 (m, 39 H, Ph), 6.02 (t, 1H, J3,4 = J3,2 = 9.5 Hz, H-3α), 5.81 (t, 0.3H, J3,4 = J3,2 = 9.5 Hz, H-3β), 5.79 (t, 0.3H, J4,3 = J4,5 = 9.5 Hz, H-4β), 5.48 (t, 0.3H, J4,3 = J4,5 = 9.5 Hz, H-4α), 5.45 (t, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2α), 5.37 (dd, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2β), 5.26 (t, 0.3H, J4,3 = J4,5 = 9.5 Hz, H-4β), 5.23 (d, 1H, J1,2 = 3.5 Hz, H-1α), 5.22 (t, 1H, J4,3 = J4,5 = 9.5 Hz, H-4α), 5.13 (dd, 1H, J2,1 = 8.0 Hz, J2,3 = 9.5 Hz, H-2β), 5.02 (dd, 1H, J2,1 = 3.5 Hz, J2,3 = 9.5 Hz, H-2α), 4.88 (d, 1H, J1,2 = 8.0 Hz, H-1β), 4.85 (d, 1H, J1,2 = 8.0 Hz, H-1β), 7.45 (d, 0.3 H, J1,2 = 8.0 Hz, H-1β), 4.38 (brt, 1H, J = 9.0 Hz, H-5α), 4.07-4.03 (m, 0.3H, H-5β), 3.99 (brd, 0.3H, J6a,6b = 11.5 Hz, H-6aβ), 3.97 (brd, 1H, J6a,6b = 11.5 Hz, H-6aα), 3.89-3.86 (m, 0.3H, H-5β), 3.84-3.77 (m, 3.6H, H-6aB, H-6bB, H-5Bα, H-6aB, H-6bB), 3.72 (dd, 0.3 H, J6b,5 = 7.5 Hz, J6b,6a = 11.5 Hz, H-6bβ), 3.68 (dd, 0.3 H, J6b,5 = 8.5 Hz, J6b,6a = 11.5 Hz, H-6bα), 0.95-0.88 (m, 27.3 H, TIPS).

13C NMR (CDCl3, 125 MHz, ppm) : δ = 166.2, 165.8, 165.7, 165.4, 165.3, 165.1 (CO), 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.2 (CH, aromatic), 102.0 (C-1β), 101.7 (C-1β), 95.6 (C-1α), 90.1 (C-1α), 75.6 (C-5β), 75.5 (C-5β), 74.1, 73.8, 72.9, 72.4, 72.3, 70.0, 69.7, 69.5, 69.4, 69.3, 68.9, 65.8, 62.9, 62.8, 17.8, 11.9 (TIPS). HRMS-ESI for C63H66NaO17Si+ (MNa+) calcd: 1145.3967; found: 1145.3961.

2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranosyl trichloroacetimidate (28). To a solution of hemiacetal 27 (30 mg, 0.03 mmol) in dry CH2Cl2
(1 mL) was respectively added trichloroacetonitrile (27 µL, 10 eq), DBU (4 µL, 1 eq) and the solution was stirred for 10 h at room temperature. After evaporation of the solvent, the residue was purified by flash chromatography (8/2 : n-hexane/EtOAc) to give 28 (28 mg, 83%). $R_f = 0.6$ (7/3:n-hexane/EtOAc). 1H NMR (CDCl₃, 500 MHz, ppm): $\delta = 8.19$ (s, 1H, NH), 7.99-7.72 (m, 10H, Ph), 7.46-7.11 (m, 20H, Ph), 6.59 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1A), 6.09 (t, 1H, $J_{3,4} = J_{3,2} = 10.0$ Hz, H-3A), 5.75 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3B), 5.45-5.42 (m, 2H, H-4A, H-4B), 5.38 (dd, 1H, $J_{1,2} = 8.0$ Hz, H-1B), 4.40-4.36 (m, 1H, H-5B) 4.04 (brd, 1H, $J_{6a,6b} = 10.5$ Hz, H-6aB), 3.83-3.71 (m, 21H, TIPS). 13C NMR (CDCl₃, 125 MHz, ppm): $\delta = 165.9$, 165.6, 165.3, 165.2, 165.1, 165.0, 164.3 (CO), 160.2 (C=NH), 133.5, 133.4, 133.3, 133.2, 133.0, 132.9 (C₂₉ Ph), 130.0, 129.9, 129.9 129.8, 129.7, 129.6, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (CH, aromatic), 100.8 (C-1B), 92.8 (C-1A), 75.5 (C-5A), 73.3 (C-3B), 72.0 (C-5B), 71.9 (C-2B), 70.7 (C-2A) 70.1 (C-3A), 69.5 (C-4A) 68.7 (C-4B), 67.4 (C-6A), 62.7 (C-6B), 17.8, 11.8 (TIPS). ESI-HRMS for C₆₅H₆₆Cl₃NNaO₁₇Si⁺ (MNa⁺) calcd: 1288.0363; found: 1288.0359.

References
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