Combinatorial Ionic Catch and Release Oligosaccharide Synthesis (Combi-ICROS)

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Experimental Procedures

General. Chemicals were purchased and used without further purification except for benzyl galactal which was passed through a plug of silica before use. 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 through rubber septa; solid reagents were added via Schlenk type adapters. Teflon rings were used between the joints of the condensers and round bottom flasks. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck). 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 *in vacuo* 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. High performance liquid chromatography (HPLC) was performed on a Waters System with a Waters 2707 Autosampler, a Waters 2535 Quarternary Gradient Module, a Waters In-Line Degasser, a Waters Temperature Control Module II, a Waters 2424 ELS Detector and a Waters 2998 Photodiode Array Detector. The used column was the reversed-phase ZORBAX Rx-C18 4.6 mm x 25 cm P.N. 880967.902.

As eluents acetonitrile (MeCN) and water have been used, both containing 0.1 vol.-% of trifluoroacetic acid. The gradient used was 60% MeCN to 0% in 20 mins. Size exclusion column chromatography was performed on Sigma-Aldrich lipophilic Sephadex R LH-20 resin with column dimensions of 26 x 150 mm and with a 1:1 mixture of dichloromethane and methanol as eluent. Rt = Retention time.

¹H NMR and ¹³C NMR spectra were measured in the solvent stated at 400 or 500 MHz. Chemical shifts are quoted in parts per million from residual solvent peak (CDCl₃: ¹H - 7.26 ppm and ¹³C - 77.16 ppm) 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. The units of the specific rotation, (deg·mL)/(g·dm), are implicit and are not included with the reported value. Concentration *c* is given in g/100 mL.

Calibration and Data Acquisition

In order to monitor I-Tag-acceptor **2** by HPLC, a standard concentration curve was constructed for **2** at 4 different concentrations (0.008 mg/mL, 0.04 mg/mL, 0.2 mg/mL and 1 mg/mL). Reaction progress was monitored by HPLC and MALDI-TOF. Final yields were calculated based on isolated products from starting material **2**.



Figure S1. Calibration curve for ITag-acceptor 2.

Sequential Glycosylation Sequence:



General OTIPS Deprotection Procedure of I-Tagged Saccharides

To a solution of 6-OTIPS protected compounds (1 eq.) in DCM, hydrochloric acid (20 equiv., 1.25 M in methanol) was added. The reaction mixture was left stirring at room temperature, until reaction completion was confirmed by MALDI-TOF analysis. The solvent was removed under azeotropic conditions with toluene. The resulting residue was washed three times with water and the aqueous layer extracted three times with DCM. The organic phase was dried over sodium sulfate, the solution was dried under reduced pressure for at least 2 h, before it was washed with a 1:1 mixture of **n**-hexane/diethylether and concentrated under reduced pressure.

General glycosylation procedure for individual glycosylation reactions:

To a solution of trichloroacetimidate donor (2 equiv.) in CH₂Cl₂ (3 mL), acceptor (1 equiv.) and 4 A°

molecular sieves (1-2 g) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40°C. TMSOTf (10% solution in CH_2Cl_2 , 0.2 equiv.) was then added and the reaction was left to warm to room temperature overnight. MALDI-TOF and HPLC 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 corresponding glycoside.

From 2^1 (54 mg, 0.08 mmol) to give 3 (98 mg, 94%) following the general trichloroacetimidate glycosylation procedure.

From **3** (90 mg, 0.07 mmol) to give **4** (4 mg, 97%) following the general OTIPS removal procedure. From **4** (52 mg, 0.05 mmol) to give **5** (75 mg, 94%) following the general trichloroacetimidate glycosylation procedure.

Combinatorial One-Pot Glycosylation Sequence:

To a solution of trichloroacetimidate donor **1** (1 equiv.) in CH₂Cl₂ (2-6 mL), ITag-acceptor **2** (59 mg, 0.087 mmol, 1 equiv.) and 4 A° molecular sieves (1 g) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40°C. TMSOTf (10% solution in CH₂Cl₂, 0.1 eq) was then added and the reaction was kept at -40°C for another 1h. The reaction process was monitored by MALDI-TOF, HPLC and NMR analysis. When ratio of compounds **2** and **3** was determined by NMR was 1:2. The mixture was concentrated under vacuum and the dried oily residue was washed twice with a 1:1 mixture of n-hexanes/diethylether and NMR. Without further purification, the partially glycosylated mixture of 2 and 3 was redissolved in DCM and hydrochloric acid (20 equiv., 1.25 M in methanol) was added. The reaction mixture was left stirring at room temperature until the reaction complete as determined by MALDI-TOF and HPLC analysis. The ratio of compounds 2 and 4 was determined to be 1:2 by NMR. The solvent was then removed under azeotropic conditions with toluene. The resulting residue was washed three times with water and the aqueous layer extracted three times with DCM. The organic phase was dried over sodium sulfate, the solution was dried under reduced pressure for at least 2 h, before it was washed with a 1:1 mixture of n-hexanes/diethylether and concentrated under reduced pressure and dried under vacuum. The partial glycosylation, de-OTIPS deprotection and n-hexanes/diethylether wash sequence was repeated for 2 more cycles until the final ratio of products 4, 6 and 8 were 1:5:3 as determined by HPLC and NMR. The mixture of compounds was then purified on sephadex LH-20 size exclusion with a 1:1 mixture of DCM:MeOH as the eluent to afford **4** (9 mg, 10%), **6** (42 mg, 30%) and **8** (26 mg, 14%).

General Benzoyl Deprotection and Product Release:

Each ITag-product was dissolved in MeOH (5 mL/mmol), NaOMe (0.5 equiv.) was then added to the solution and left stirring at room temperature for 5 h until TLC (IPA/H₂O/ NH₄OH, 7:3:1, v:v:v) and MALDI-TOF showed completion of the reaction. The mixture was then neutralized with HCl (1M) and concentrated under vacuum. The dried residue was then dissolved in a mixture of MeOH/H₂O (1:1, v:v

5 mL/mmol) and Pd/C (10% weight) was added. The mixture was stirred under hydrogen atmosphere for 18 h. The obtained residue was filtered through celite and purified over silica gel column chromatography with a gradient with DCM/MeOH (9:1, v:v to 8:2, v:v) to give the corresponding β -glucans.

From 4 (8 mg, 0.007 mmol) to 10 (2.2 mg, 90%).

From 6 (32 mg, 0.02 mmol) to 12 (9.5 mg, 95%).

From 8 (10 mg, 0.005 mmol) to 14 (2.8 mg, 85%).

OTIPS -C BzO OB₇ BzQ BzÒ

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 (3). Data

in agreement with reported procedures.¹



4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-*O***-benzoyl-***6***-***O***-(2**,**3**,**4-tri**-*O*-benzoyl-*β*-D-glucopyranoside trifluoromethanesulfonate (4). ¹HNMR (CDCl₃, 500 MHz, ppm) : δ = 9.26 (s, 1H, NC<u>H</u>N), 7.95-7.88 (m, 8H, Ph), 7.81-7.79 (m, 2H, Ph), 7.77-7.75 (m, 2H, Ph), 7.56-7.51 (m, 4H, Ph), 7.48-7.37 (m, 11H, Ph), 7.36-7.15 (m, 9H, Ph + C<u>H</u> *imidazole*), 5.89 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^A) 5.80 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^A) 5.80 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^B), 5.44 (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-4^B), 5.43 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4^A), 5.32 (bs, 2H, C<u>H</u>₂N), 4.92 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^A), 4.73 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^B), 4.63 (d, 1H, J = 13.0 Hz, OC<u>H</u>₂), 4.43 (d, 1H, J = 13.0 Hz, OC<u>H</u>₂), 4.17 (dd, $J_{6a,5} = 1.5$ Hz, H-6^A), 3.80-3.75 (m, 2H, H-5^A, H-6a^B), 3.64 (dd, 1H, $J_{6b,5} = 3.0$ Hz, $J_{6b,6a} = 12.5$ Hz, H-6b^B). ¹³C NMR (CDCl₃, 125 MHz, ppm) : δ = 165.9, 165.6, 165.7, 165.6, 165.2, 165.1, (CO), 138.4, 137.2, 133.7, 133.6, 133.5, 133.4, 133.3, 133.2, 132.1, 131.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.8, 129.8, 128.7, 128.5, 128.4, 128.3, 128.2, 123.5, 121.9, (CH *aromatic*), 100.9 (C-1^A), 99.6 (C-1^B), 74.7 (C-5^A), 73.4 (C-5^B), 72.8 (C-3^A), 72.7 (C-3^B), 71.8 (C-2^A), 71.7 (C-2^B), 70.0 (C-4^B), 69.9 (OCH₂), 69.3 (C-4^A), 68.2 (C-6^A), 61.0 (C-6^B), 53.3 (CH₂N), 36.6 (NCH₃). ESI-HRMS for C66H₅₉N₂O₁₇ (M⁺) calcd: 1151.3808; found: 1151.3808.



4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-0-benzoyl-6-O-(2,3 tri-O-benzoyl-6-O-triisopropylsilyl- β -D-glucopyranosyl)- β -D-glucopyranosyl trifluoromethanesulfonate (5). ¹HNMR (CDCl₃, 500 MHz, ppm) : $\delta = 9.26$ (s, 1H, NCHN), 8.03-8.01 (m, 2H, Ph), 7.98-7.95 (m, 6H, Ph) 7.92-7.89 (m, 4H, Ph), 7.59-7.21 (m, 33H, Ph + CH imidazol), 5.02 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^A) 5.90 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^B) 5.78 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3^C), 5.63 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4^A), 5.52 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H-2^A), 5.50 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H-2^B), 5.41 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4^B), 5.36 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H- 2^{C}), 5.34 (bs, 2H, CH₂N), 5.23 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4^C), 4.98 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^A), 4.84 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^B), 4.81 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^C), 4.56 (d, 1H, J = 13.0 Hz, OCH₂), 4.76 (d, 1H, J = 13.0 Hz 13.0 Hz, OCH₂), 4.40-3.91 (m, 7H, in which s at 3.92 (NCH₃), 3.84-3.80 (m, 1H), 3.69-3.65 (m, 1H), 1.00-0.99 (m, 21H, *TIPS*). ¹³C NMR (CDCl₃, 125 MHz, ppm): $\delta = 165.8$, 165.7, 165.6, 165.4, 165.3, 165.1, 165.0, (CO), 138.7, 137.0, 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 132.0, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 123.4, 121.7, (CH aromatic), 101.7 (C-1^A), 101.1 (C-1^C), 100.1 (C-1^B), 75.7, 73.8, 73.4 (3xC-5), 73.1 (C-3^A), 72.8 (C-3^B), 72.7 (C-3^C), 72.3, (C-2^A), 72.0 (C-2^B), 71.8 (C-2^C), 70.2, (C-4^B), 70.1(OCH₂), 69.8 (C-4^C), 69.4 (C-4^A), 68.9, 68.6, 62.8 (3xC-6), 53.2 (CH₂N), 36.4 (NCH₃), 17.8, 11.8 (*TIPS*). ESI-HRMS for $C_{102}H_{101}N_2O_{25}Si^+$ (M⁺) calcd: 1781.6457; found: 1781.6443.



4-(1-Methyl-3-methyleneimidazolium)-benzyl 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 (6). ¹H NMR (500 MHz, CD₃CN, ppm): $\delta = 8.53$ (bs, 1H, NC<u>H</u>N), 7.96-7.85 (m, 9H, Ph), 7.81-7.75 (m, 5H, Ph), 7.69-7.65 (m, 5H, Ph), 7.60-7.47 (m, 9H, Ph), 7.44-7.37 (m, 9H, Ph), 7.37-7.30 (m, 9H, Ph), 7.30-7.21 (m, 3H, Ph + 2H, NC<u>H</u>C<u>H</u>N), 5.87 (d, 1H, $J_{3,2} = J_{3,4} = 9.6$ Hz, H-3^C), 5.82 (d, 1H, $J_{3,2} = J_{3,4} = 9.6$ Hz, H-3^B), 5.76 (d, 1H, $J_{3,2} = J_{3,4} = 9.6$ Hz, H-3^A), 5.46 (d, 1H, $J_{4,3} = J_{4,5} = 9.7$ Hz, H-4^C), 5.42 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, J_{4,3} = J_{4,5} = 9.9 Hz, H-4^B), 5.37 (dd, 1H, $J_{2,1} = 7.8, J_{2,3} = 9.6$ Hz, H-2^C), 5.36 (d, 1H, J_{4,3} = J_{4,5} = 9.9 Hz, H-4^B), 5.37 (dd, 1H, J_{2,1} = 7.8, J_{2,3} = 9.6 Hz, H-2^C), 5.36 (d, 1H, J_{4,3} = J_{4,5} = 9.9 Hz, H-4^B), 5.37 (dd, 1H, J_{4,3} = J_{4,5} = 9.9 Hz, H-4^C)</sup>, 5.36 (d, 1H, J_{4,3} = J_{4,5} = 9.9 Hz, H-4^B), 5.37 (dd, 1H, J_{4,3} = J_{4,5} = 9.6 Hz, H-3^C)</sup>, 5.36 (d, 1H, J_{4,5} = 9.6

 $J_{4,5} = 9.9$ Hz, H-4^A), 5.34 (dd, 1H, $J_{2,1} = 8.0$, $J_{2,3} = 9.8$ Hz, H-2^B), 5.29 (dd, 1H, $J_{2,1} = 8.0$, $J_{2,3} = 9.9$ Hz, H-2^A), 5.26 (bs, 2H, CH₂N), 4.99 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1^C), 4.98 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^B), 4.88 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1^A), 4.81 (d, 1H, J = 12.4 Hz, OCH₂), 4.60 (d, 1H, J = 12.4 Hz, OCH₂), 4.10-4.00 (m, 4H, H-5^A, H-5^B, H-6^A, H-6^B), 3.92 (ddd, 1H, $J_{5,4} = 9.8$, $J_{5,6} = 2.4$, $J_{5,6} = 5.1$ Hz, H-5^C), 3.80 (dd, 1H, $J_{6,5} = 5.9$, $J_{6,6} = 12.1$ Hz, H-6^A), 3.79 (s, 3H, NCH₃), 3.72-3.68 (m, 1H, H-6^C), 3.66 (dd, 1H, $J_{6,5} = 5.4$, $J_{6,6} = 11.6$ Hz, H-6^A), 3.61 (dd, 1H, $J_{6,5} = 5.4$, $J_{6,6} = 12.5$ Hz, H-6^C), 3.19 (bs, 1H, OH). ¹³C NMR (126 MHz, CD₃CN, ppm): $\delta = 166.4$, 166.3, 166.3, 164.2, 166.0, 166.0, 166.0, 165.9, 165.9 (C=O), 139.4, 137.1, 134.6, 134.5, 134.5, 134.39, 134.4, 130.4, 130.3, 130.3, 130.3, 130.1, 130.1, 130.1, 130.0, 129.9, 129.8, 129.6, 129.5, 129.5, 129.5, 129.4, 124.9, 123.2 (CH, *aromatic*), 101.7, 101.5, 100.8 (C-1^{A/B/C}), 75.3 (C-5^C), 74.5, 74.3, 74.3 (C-3^{A/B/C}), 73.8, 73.6 (C-5^{A/B}), 73.0, 72.9, 72.8 (C-2^{A/B/C}), 71.3 (OCH₂), 70.4, 70.4, 70.3 (C-4^{A/B/C}), 68.9 (C-6^A), 68.8 (C-6^B), 61.6 (C-6^C), 53.3 (CH₂N), 36.9 (NCH₃) ppm. High resolution ESI: m/z = 1625.5090, [M]⁺-Ion (calc.: m/z = 1625.5103) for C₉₃H₈₁N₂O₂₅⁺. HPLC (conditions according to section XY, 313 K): Rt = 12.47 min.



4-(1-Methyl-3-methyleneimidazolium)benzyl 2,3,4-tri-0-benzoyl-6-0-(2,3,4-tri-0-benzoyl-6-0-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-tri-isopropylsilyl-β-D-glucopyranosyl)-β-Dglucopyranosyl)- β -D-glucopyranosyl)- β -D-glucopyranoside triuoromethanesulfonate (8). ¹H NMR (600 MHz, CD3CN, ppm): δ = 8.42 (bs, 1H, NCHN), 7.96-7.84 (m, 15H, Ph), 7.84-7.75 (m, 8H, Ph), 7.73-7.70 (m, 2H, Ph), 7.69-7.65 (m, 5H, Ph), 7.63-7.47 (m, 9H, Ph), 7.47-7.23 (m, 25H, Ph), 7.23-7.19 (m, 2H, NCHCHN), 5.94 (d, 1H, $J_{3,2} = J_{3,4} = 9.7$ Hz, H-3^C), 5.88 (d, 1H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3^D), 5.82 (d, 1H, $J_{3,2} = J_{3,4} = 9.6$ Hz, H-3^A), 5.81 (d, 1H, $J_{3,2} = J_{3,4} = 9.8$ Hz, H-3^B), 5.52 (d, 1H, $J_{4,3} = J_{4,5} = 9.7$ Hz, H-4), 5.47 (d, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4), 5.42-5.32 (m, 5H, H-2^{B/C/D}, H-4^{A/B}), 5.23 (bs, 2H, CH₂N), 5.04 (d, 1H, $J_{1,2} =$ 8.1 Hz, H-1^D), 5.01 (d, 1H, $J_{1,2} = 8.1$ Hz, H-1^C), 4.96 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1^B), 4.89 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1^A), 4.85 (d, 1H, J = 12.5 Hz, OCH₂), 4.62 (d, 1H, J = 12.8 Hz, OCH₂), 4.42-3.40 (m, 15H, H-5^{A/B/C/D}, H- $6^{A/B/C/D}$, H- $6^{A/B/C/D}$, NCH₃). ¹³C NMR (151 MHz, CD₃CN, ppm): $\delta = 166.4$, 166.3, 166.3, 164.2, 166.0, 166.0, 166.0, 165.9, 165.9 (C=O), 133.6, 133.6, 129.5, 129.5, 129.1, 129.1, 128.6, 128.5 (CH, aromatic), 101.0 (C-1^B), 100.7 (C-1^A), 100.6 (C-1^C), 100.1 (C-1^D), 74.4, 72.9, 72.8, 72.4 (C-5^{A/B/C/D}), 73.5, 73.5, 73.5, 73.4 (C-3^{A/B/C/D}), 72.2, 72.2, 72.1, 72.0 (C-2^{A/B/C/D}), 70.4 (OCH₂), 69.6, 69.6, 69.5, 69.5 (C-4^{A/B/C/D}), 68.5, 68.3, 68.2, 60.8 (C-6^{A/B/C/D}), 52.4 (CH₂N), 33.6 (NCH₃) ppm. High resolution ESI: m/z = 2099.6351, $[M]^+$ -Ion (calc.: m/z = 2099.6438) for $C_{120}H_{103}N_2O_{33}^+$. HPLC (313 K): Rt = 15.29 min.

HPLC traces of compounds **4**, **6** and **8** prepared using the one pot Combi-ICROS method and after size exclusion chromatography.



References:

(1) Tran, A. T.; Burden, R.; Racys, D. T.; Galan, M. C. Chem Commun **2011**, 47, 4526.

SPECTRAL DATA



Expansion of anomeric region





Expansion of anomeric region



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Expansion of anomeric region





Expansion of anomeric region





Expansion of anomeric region







Expansion of anomeric region



f1 (ppm)











