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General Methods:

All reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 coated glass slides. Column chromatography was performed by elution from prepacked (Varian, Inc.) columns of silica gel with the Isolera Flash Chromatograph (Biotage), the latter being connected to the external Evaporative Light Scattering Detector, Model 380-LC (Varian, Inc.). Nuclear magnetic resonance (NMR) spectra were measured at 600 MHz for ^{1}H, 150 MHz for ^{13}C, and 162 MHz for ^{31}P with Bruker Avance spectrometers. Solvent peaks were used as internal reference relative to TMS for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts (ppm) are reported relative to 85% H_3PO_4 in D_2O external reference. Assignments of NMR signals were made by homonuclear and heteronuclear two-dimensional correlation spectroscopy, run with the software supplied with the spectrometers. When reporting assignments of NMR signals, nuclei associated with the spacer are denoted with a prime; sugar residues are serially numbered, beginning with the one bearing the aglycon, and are identified by a Roman numeral superscript in listings of signal assignments, with nuclei of the colitose residues as V and VI (see Figure 1). The density of 2,2,2-trichloroethyl phosphorodichloridate (Aldrich/Sigma, $d \approx 1.7$ g/mL at 20 °C) was determined by weighing of 1 mL of the reagent. Palladium-on-charcoal catalyst (5%, Escat^{TM} 103) was purchased from Engelhard Industries. Solutions in organic solvents were dried with anhydrous Na_2SO_4, and concentrated at 40 °C/2 kPa.

I- Preparation of the Disaccharide Donor Building Block 3:

A solution of 3,4,6-tri-*O*-acetyl-2-*O*-bromoacetyl-α-D-galactopyranosyl bromide (**1**,[13] 5 g, 10.20 mmol) in anhydrous CH_2Cl_2 (15 mL) was added, in one portion, at –30 ºC to a stirred mixture of glycosyl acceptor (**2**,[14] 2.9 g, 6.37 mmol), 1,1,3,3-tetramethylurea (1.5 mL, 12.30 mmol), and powdered AgOTf (2.8 g, 10.83 mmol) in anhydrous CH_2Cl_2 (60 mL). The cooling was removed and, with continued stirring, the mixture was allowed to warm up to room temperature. The stirring was continued until TLC (~6 h, 7:1 toluene–acetone) indicated that all acceptor was consumed. Et_3N (0.5 mL) was added, the mixture was diluted with CH_2Cl_2 (100 mL) and filtered through a Celite pad. The filtrate was washed successively with (1:1) aq. $Na_2S_2O_4$–$NaHCO_3$, brine, and dried. After concentration, chromatography (11:1 toluene–acetone) gave the β-(1→3)-linked disaccharide **3** (4.9 g, 90%). ^{1}H and ^{13}C NMR spectra [page S18], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50–7.38 (m, 5 H, Ph); 7.07 (d, 1 H, J = 8.4 Hz, NH), 5.57 (s, 1 H, PhC*H*), 5.35 (d, 1 H, $J_{3,4}$ = 3.1 Hz, H-4^{II}), 5.24 (dd, 1 H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{II}), 5.06 (d, 1 H, $J_{1,2}$ = 10.4 Hz, H-1^{I}), 4.96 (dd, 1 H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{II}), 4.75 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{II}), 4.46 (t, 1 H, J = 9.4 Hz, H-3^{I}), 4.37 (dd, 1 H, J = 4.8, 10.5 Hz, H-6$^{I}_{a}$), 4.14 (dd, 1 H, J = 6.9, 11.3 Hz, H-6$^{II}_{a}$), 4.05 (dd, 1 H, J = 6.6, 11.3 Hz, H-6$^{II}_{b}$), 3.81–3.77 (m, 2 H, H-6$^{I}_{b}$, H-5^{II}), 3.73 (t, 1 H, J = 9.4 Hz, H-4^{I}), 3.70–3.63 (m, 3 H, H-2^{I}, CH_2Br), 3.56 (m, 1 H, H-5^{I}), 2.73 (m, 2 H, SCH_2), 2.12, 2.03, 1.97 (3 s, 9 H, 3 x COCH_3), 1.28 (t, 3 H, J = 7.4 Hz, SCH_2CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.1, 170.0 (3 O*C*OCH$_3$), 166.2 (*C*OCH_2Br), 161.7 (N*C*OCCl_3), 136.9 (ipso Ph), 129.3, 128.3, 126.0 (Ph), 101.2 (Ph*C*H), 99.4 ($J_{C,H}$ = 165.2 Hz, C-1^{II}), 92.3 (*C*Cl_3), 83.1 ($J_{C,H}$ = 161.0 Hz, C-1^{I}), 78.5 (C-4^{I}), 77.3 (C-3^{I}), 70.8 (C-5^{II}), 70.7 (C-5^{I}), 70.6 (C-3^{II}), 70.2 (C-2^{II}), 68.4 (C-6^{I}), 66.9 (C-4^{II}), 61.2 (C-6^{II}), 57.5 (C-2^{I}), 25.2 (*C*H_2Br), 24.8 (S*C*H_2), 20.7, 20.6, 20.5 (3 x OCO*C*H_3), 15.1 (SCH_2CH_3). HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{31}H_{37}Cl_3NO_{14}SNa$: 886.0081; found: 886.0106.

II- Preparation of the Disaccharide Acceptor Building Block 8:

*i- Zemplén de-O-acylation of **4**:*

A solution of NaOMe in MeOH (1M, 2.5 mL) was added under nitrogen to a solution of **4**[12] (2.5 g, 2.39 mmol) in 1:9 CH_2Cl_2–MeOH (150 mL), and the mixture was stirred overnight at

room temperature. The mixture was neutralized with Amberlite IR-120 (H^+) resin, filtered, and the filtrate was concentrated to give compound **5** as amorphous solid in virtually theoretical yield. For identification and spectral analysis, a portion was purified by chromatography (12:1 CH_2Cl_2–MeOH). ^{1}H and ^{13}C NMR spectra [page S20], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, 1H, $J_{2,NH}$ = 8.4 Hz, NH), 7.37–7.30 (m, 5 H, Ph), 5.04 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H-1^{II}), 4.85 (d, partial overlap, 1 H, $J_{1,2}$ = 8.6 Hz, H-1^{I}), 4.83 (d, partial overlap, 1 H, ^2J = 11.5 Hz, PhC*H*H), 4.70 (br d, 2 H, ^2J = 11.7 Hz, PhCH*H*, 4^{I}-OH), 4.07–4.02 (m, 2 H, H-3^{II}, H-4^{II}), 3.94–3.88 (m, 3 H, H-3^{I}, H-5^{II}, H-1′$_a$), 3.81–3.78 (m, 4 H, H-2^{II}, H-6^{II}, H-1′$_b$), 3.74–3.69 (m, 1 H, H-6$^{I}_a$), 3.68–3.58 (m, 9 H, H-2^{I}, H-2′, H-3′, H-4′, H-5′), 3.52–3.49 (m, 2 H, H-5^{I}, H-4^{I}), 3.48–3.43 (m, 1 H, H-6$^{I}_b$), 3.42–3.37 (m, 3 H, H-6′, 6^{II}-OH), 3.29, 2.35 (2br s, 2H, 3^{II}-OH, 4^{II}-OH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.7 (N*C*OCCl_3), 137.0 (*ipso* Ph), 128.7–128.4 (Ar), 100.0 (C-1^{II}), 99.9 (C-1^{I}), 92.4 (*C*Cl_3), 82.7 (C-3^{I}), 77.0 (C-2^{II}), 74.4 (C-5^{I}), 74.3 (Ph*C*H_2), 73.1 (C-4^{I}), 70.7, 70.5, 70.2 (C-2′, C-3′, C-4′), 70.3 (C-4^{II}), 70.2 (C-5^{II}), 69.8 (C-5′), 69.5 (C-3^{II}), 68.6 (C-1′), 62.0 (C-6^{II}), 57.3 (C-2^{I}), 50.5 (C-6′), 32.6 (C-6^{I}). HRMS (ESI-TOF): *m/z* [M + NH_4]$^+$ calcd for $C_{27}H_{42}Cl_3BrN_5O_{12}$: 812.1073; found: 812.1075.

*ii- p-Methoxybenzylidenation of **5**:*

A solution of **5** in CH_3CN (20 mL) was treated with anisaldehyde dimethyl acetal (612 μL, 3.58 mmol) and CSA (60 mg, 0.24 mmol) for 2 h at room temperature. The reaction was quenched with Et_3N (1.0 mL), concentrated, and chromatography (6:1 chloroform–acetone) afforded **6** (2.0 g, 92%). ^{1}H and ^{13}C NMR spectra [page S21], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 7 H, Ar), 7.08 (d, 1H, $J_{2,NH}$ = 8.9 Hz, NH), 7.88 (d, 2 H, *J* = 8.5 Hz, *p*-MeO$C_6H_2H_2$), 5.45 (s, 1H, *p*-MeOPhC*H*), 5.05 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H-1^{II}), 5.01 (d, 1 H, ^2J = 11.7 Hz, PhC*H*H), 4.95 (br s, 1 H, 4^{I}-OH), 4.75 (d, 1 H, ^2J = 11.7 Hz, PhC*H*H), 4.74 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1^{I}), 4.25–4.20 (m, 3 H, H-4^{II}, H-3^{II}, H-6$^{II}_a$), 3.97 (dd, 1 H, *J* = 1.5, 12.4 Hz, H-6$^{II}_b$), 3.92–3.89 (m, 1 H, H-1′$_a$), 3.87–3.82 (m, 7 H, H-1′$_b$, H-2^{II}, H-5^{II}, H-2^{I}, O*C*H_3), 3.73–3.59 (m, 10 H, H-6$^{I}_a$, H-3^{I}, H-2′, H-3′, H-4′, H-5′), 3.50–3.48 (m, 2 H, H-4^{I}, H-5^{I}), 3.46–3.37 (m, 3 H, H-6$^{I}_b$, H-6′), 2.40 (d, 1 H, *J* = 9.9, 3^{II}-OH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.3 (N*C*OCCl_3), 160.2, 136.8, 129.9 (*ipso* Ar), 128.7–113.6 (Ar), 102.5 (C-1^{II}), 101.0 (*p*-MeOPh*C*H), 100.9 (C-1^{I}), 92.7 (*C*Cl_3), 86.2 (C-3^{I}), 77.1 (C-2^{II}), 76.2 (C-3^{II}), 74.8 (Ph*C*H_2), 74.6, 73.4 (C-4^{I}, C-5^{I}), 71.1, 70.5, 70.3, 70.0 (C-2′, C-3′,

C-4′, C-5′), 69.6 (C-4^{II}), 69.4 (C-6^{II}), 68.3 (C-1′), 63.4 (C-5^{II}), 56.7 (C-2^{I}), 55.3 (OCH_3), 50.5 (C-6′), 32.4 (C-6^{I}). HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{44}BrCl_3N_4O_{13}Na$: 935.1052; found: 935.1060.

iii- Controlled benzylation of ***6****:*

Sodium hydride (170 mg, 4.3 mmol, 60% in oil) was added at –25 °C to a stirred solution of **6** (1.0 g, 1.1 mmol) in DMF-DME (2:1, 30 mL). After 5 min, BnBr (0.5 mL, 4.3 mmol) was added and, with continued stirring, the mixture was allowed to warm to room temperature. After total reaction time of 30 min, the mixture was cooled to –10 °C and excess of reagents was consumed by addition of MeOH (3.0 mL). After warming to room temperature, the mixture was diluted with CH_2Cl_2 (100 mL), washed with brine, and the organic extract was dried and concentrated. Chromatography (6:1, toluene–acetone) gave **7** (1.03 g, 86%) as syrup. ^1H and ^{13}C NMR spectra [page S22], ^1H NMR (600 MHz, $CDCl_3$): δ = 7.56 (d, 1H, $J_{2,NH}$ = 8.4 Hz, NH), 7.43 (d, 2 H, *J* = 8.7 Hz, *p*-$MeOC_6H_2H_2$), 7.39–7.21 (m, 15 H, 3 x Ph), 6.88 (d, 2 H, *J* = 8.8 Hz, *p*-$MeOC_6H_2H_2$), 5.42 (s, 1H, *p*-MeOPhC*H*), 5.21 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1^{II}), 4.89 (d, partial overlap, 1 H, $J_{1,2}$ = 5.9 Hz, H-1^{I}), 4.87 (d, 1 H, ^2J = 11.9 Hz, PhC*H*H), 4.77–7.71 (m, 3 H, PhC*H*H, PhCH_2), 4.60 (d, 1 H, ^2J = 11.5 Hz, PhC*H*H), 4.58 (d, 1 H, ^2J = 11.5 Hz, PhC*H*H), 4.15 (br d, 1 H, $J_{3,4}$ = 3.0 Hz, H-4^{II}), 4.12 (d, 1 H, *J* = 12.5 Hz, H-6^{II}_a), 4.10 (dd, 1 H, $J_{1,2}$ = 3.5, $J_{2,3}$ = 10.2 Hz, H-2^{II}), 4.03 (t, 1 H, *J* = 6.2 Hz, H-3^{I}), 3.96 (dd, 1 H, $J_{2,3}$ = 10.3, $J_{3,4}$ = 3.2 Hz, H-3^{II}), 3.94–3.85 (m, 4 H, H-6^{II}_b, H-$1'_a$, H-5^{I}, H-2^{I}), 3.83 (br s, 1 H, H-5^{II}), 3.80 (s, 3 H, OCH_3), 3.78 (t, 1 H, *J* = 6.0 Hz, H-4^{I}), 3.75 (dd, 1 H, *J* = 5.6, 10.6 Hz, H-6^{I}_a), 3.72–3.68 (m, 1 H, H-$1'_b$), 3.66 (t, 1 H, *J* = 4.9 Hz, H-5′), 3.63–3.49 (m, 7 H, H-6^{I}_b, H-2′, H-3′, H-4′), 3.38 (t, 2 H, *J* = 5.0 Hz, H-6′). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.5 (N*C*OCCl_3), 160.0, 138.5, 138.2, 137.1, 130.4 (*ipso* Ar), 128.5–113.4 (Ar), 100.9 (*p*-MeOPh*C*H), 99.2 (C-1^{I}), 99.0 (C-1^{II}), 92.3 (*C*Cl_3), 76.3 (C-4^{I}), 76.1 (C-3^{I}), 75.7 (C-3^{II}), 75.1 (C-2^{II}), 74.4 (C-5^{I}), 74.3 (C-4^{II}), 74.2 (Ph*C*H_2), 73.2 (Ph*C*H_2), 71.7 (Ph*C*H_2), 70.6, 70.5, 70.4 (C-2′, C-3′, C-4′), 70.0 (C-5′), 69.3 (C-6^{II}), 68.5 (C-1′), 63.5 (C-5^{II}), 55.3 (OCH_3), 54.4 (C-2^{I}), 50.6 (C-6′), 33.0 (C-6^{I}). HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{49}H_{56}BrCl_3N_4O_{13}Na$: 1115.1991; found: 1115.1996.

*iv- Regioselective reductive opening of the p-methoxybenzylidene ring in **7**:*

A mixture of acetal **7** (1.0 g, 0.91 mmol) and freshly activated powdered molecular sieves (3Å, 4.0 g) in dry THF (35 mL) was stirred under nitrogen for 1.5h at room temperature. The solution was cooled to 0 ºC, and $NaCNBH_3$ (0.71 g, 10.95 mmol) was added portion-wise. After stirring for 20 min at 0 ºC, 2 M HCl-Et_2O was added drop-wise at 0 ºC until the effervescence ceased and the pH remained acidic. The mixture was stirred for an additional 15 min at room temperature, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed with cold satd. aq. $NaHCO_3$, brine, and the organic extract was dried and concentrated. Chromatography (6:1 toluene–acetone) afforded **8** (890 mg, 89%). ^{1}H and ^{13}C NMR spectra [page S23], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, 1H, $J_{2,NH}$ = 6.8 Hz, NH), 7.33–7.21 (m, 17 H, Ar), 6.86 (d, 2 H, J = 8.3 Hz, *p*-MeOC$_6$*H*$_2$H$_2$), 4.89 (d, 1 H, $J_{1,2}$ = 7.1 Hz, H-1^{I}), 5.02 (d, 1 H, ^2J = 11.1 Hz, PhC*H*H), 4.90 (br s, 1 H, H-1^{II}), 4.77–4.70 (m, 3 H, PhC*H*$_2$, PhC*H*H), 4.58–4.53 (m, 3 H, 2 x PhC*H*H, *p*-MeOPhC*H*H), 4.36 (d, 1 H, ^2J = 11.8 Hz, *p*-MeOPhC*H*H), 4.32 (t, 1 H, J = 7.7 Hz, H-3^{I}), 4.13 (br d, 1 H, J = 7.4 Hz, H-5^{II}), 3.94 (br s, 1 H, H-4^{II}), 3.91–3.87 (m, 1 H, H-1′$_a$), 3.82 (br s, 2 H, H-2^{II}, H-3^{II}), 3.79 (s, 3 H, OC*H*$_3$), 3.73–3.65 (m, 4 H, H-1′$_b$, H-5^{I}, H-6$^{I}_a$, H-6$^{II}_a$), 3.61–3.56 (m, 9 H, H-2′, H-3′, H-4′, H-5′, H-4^{I}), 3.55–3.48 (m, 2 H, H-6$^{II}_b$, H-6$^{I}_b$), 3.45–3.42 (m, 1 H, H-2^{I}), 3.34 (t, 2 H, J = 5.1 Hz, H-6′), 2.54 (br s, 1 H, 4^{II}-OH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.6 (N*C*OCCl$_3$), 159.3, 138.0, 137.9, 137.7, 129.4 (*ipso* Ar), 129.6–113.8 (Ar), 98.5 (C-1^{I}), 98.3 (C-1^{II}), 92.6 (*C*Cl$_3$), 80.3 (C-3^{I}), 78.3 (C-4^{I}), 76.6, 75.9 (C-2^{II}, C-3^{II}), 74.6 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 73.2 (C-5^{I}), 73.1 (*p*-MeOPh*C*H$_2$), 72.4 (Ph*C*H$_2$), 70.6, 70.5, 70.3, 69.9 (C-2′, C-3′, C-4′, C-5′), 69.6 (C-6^{II}), 69.4 (C-5^{II}), 68.9 (C-1′), 68.2 (C-4^{II}), 58.4 (C-2^{I}), 55.2 (OCH$_3$), 50.6 (C-6′), 33.2 (C-6^{I}). HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd for $C_{49}H_{62}BrCl_3N_5O_{13}$: 1112.2588; found: 1112.2591.

III- Preparation of the Linear Tetrasaccharide 9:

A mixture of the spacer-equipped disaccharide acceptor **3** (0.8 g, 0.73 mmol), the thioglycoside disaccharide donor **8** (1.1 g, 1.31 mmol), and 4Å MS (250 mg) in anhydrous CH_2Cl_2 (12 mL) was stirred under argon for 1h. The mixture was cooled to –25 ˚C and NIS (246 mg, 1.10 mmol) followed by powdered AgOTf (187 mg, 0.73 mmol) was added portion-wise with stirring. After 15 min, the mixture was treated with Et_3N (0.5 mL), diluted with CH_2Cl_2, and filtered through

Celite. The filtrate was washed with (1:1) aq. $Na_2S_2O_4$–$NaHCO_3$, brine, and dried. After concentration, chromatography (2:1 hexane–acetone) gave **9** (1.15 g, 84%). ^{1}H and ^{13}C NMR spectra [page S24], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.21 (d, 1H, $J_{2,NH}$ = 7.1 Hz, 2^{I}-NH), 7.53–7.01 (m, 22 H, Ar), 6.99 (d, 1H, $J_{2,NH}$ = 7.8 Hz, 2^{III}-NH), 6.89 (d, 2 H, J = 8.6 Hz, *p*-MeOC$_6$*H*$_2$H$_2$), 5.56 (s, 1 H, PhC*H*), 5.35 (d, 1 H, $J_{3,4}$ = 3.2 Hz, H-4^{IV}), 5.21 (dd, 1 H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{IV}), 5.12 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1^{I}), 5.02 (d, 1 H, $J_{1,2}$ = 8.5 Hz, H-1^{III}), 4.95–4.91 (m, 2 H, H-3^{IV}, PhC*H*H), 4.90 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1^{II}), 4.78 (d, 1 H, ^2J = 11.8 Hz, PhC*H*H), 4.66–4.62 (m, 3 H, 2 x PhC*H*H, H-1^{IV}), 4.57–4.50 (m, 3 H, 2 x PhC*H*H, *p*-MeOPhC*H*H), 4.33–4.26 (m, 3 H, *p*-MeOPhC*H*H, H-3^{I}, H-3^{III}), 4.20 (dd, 1 H, J = 4.9, 10.5 Hz, H-6^{III}_a), 4.12 (br d, 2 H, J = 6.8 Hz, H-$6^{IV}_{a,b}$), 4.09–4.06 (m, 1 H, H-5^{II}), 3.90–3.85 (m, 1 H, H-1′$_a$), 3.84–3.74 (m, 9 H, H-4^{II}, H-3^{II}, H-5^{IV}, OC*H*$_3$, C*H*$_2$Br, H-2^{II}), 3.72–3.63 (m, 6 H, H-1′$_b$, H-6^{III}_b, H-4^{III}, H-2^{III}, H-5^{I}, H-6^{I}_a), 3.61 (t, 2 H, J = 5.1 Hz, H-5′), 3.59–3.55 (m, 6 H, H-2′, H-3′, H-4′), 3.51–3.47 (m, 2 H, H-4^{I}, H-6^{II}_a), 3.42 (dd, 1 H, J = 5.9, 10.7 Hz, H-6^{I}_b), 3.39–3.34 (m, 3 H, H-5^{III}, H-2^{I}, H-6^{II}_b), 3.63 (t, partial overlap, 2 H, J = 5.0 Hz, H-6′), 2.12, 2.00, 1.97 (3 s, 9 H, 3 COC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.1, 170.0 (3 x O*C*OCH$_3$), 166.3 (*C*OCH$_2$Br), 161.6, 161.5 (2 x N*C*OCCl$_3$), 159.4, 138.0, 137.9, 137.8, 137.0, 129.5 (*ipso* Ar), 129.7–113.8 (Ar), 101.1 (Ph*C*H), 100.4 (C-1^{III}), 99.7 (C-1^{IV}), 98.4 (C-1^{I}), 97.8 (C-1^{II}), 92.7, 92.5 (2 x *C*Cl$_3$), 80.7 (C-3^{I}), 78.5 (C-4^{I}, C-4^{III}), 77.5 (C-2^{II}), 76.5 (C-3^{III}), 76.3 (C-3^{II}), 75.4 (C-4^{II}), 74.8 (Ph*C*H$_2$), 73.7 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 73.1 (C-5^{I}), 73.0 (*p*-MeOPh*C*H$_2$), 70.7 (C-5^{IV}, C-3^{IV}), 70.6, 70.5, 70.4 (C-2′, C-3′, C-4′), 70.3 (C-2^{IV}), 69.9 (C-5′), 69.6 (C-6^{II}), 69.5 (C-5^{II}), 69.0 (C-1′), 68.4 (C-6^{III}), 66.9 (C-4^{IV}), 66.4 (C-5^{III}), 61.0 (C-6^{IV}), 58.8 (C-2^{I}), 58.3 (C-2^{III}), 55.3 (OCH$_3$), 50.6 (C-6′), 33.1 (C-6^{I}), 25.5 (*C*H$_2$Br), 20.7–20.5 (3 x OCO*C*H$_3$). HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd for $C_{78}H_{93}Br_2Cl_6N_6O_{27}$: 1913.2581; found: 1913.2586.

IV- Preparation of the Tetrasaccharide Diol Acceptor 13:

i- Selective removal of the BrAc group:

A solution of thiourea (61 mg, 0.79 mmol) in methanol (5 mL) was added at 0 ºC to a stirred solution of **9** (0.5 g, 0.26 mmol) and *sym*-collidine (53 μL, 0.40 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred overnight at room temperature, when TLC (7:1, toluene-acetone) showed

that all the starting material was consumed and a single product was formed. The mixture was concentrated, and coevaporated with toluene (twice). The residue was then diluted with CH_2Cl_2 (100 mL), washed with brine, and the organic extract was dried and concentrated. Chromatography (9:1, toluene–acetone) gave **10** (446 mg, 95%). ^{1}H and ^{13}C NMR spectra [page S25], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, 1H, $J_{2,NH}$ = 7.1 Hz, 2^{I}-NH), 7.51–7.12 (m, 23 H, Ar, 2^{III}-NH), 6.89 (d, 2 H, J = 8.6 Hz, *p*-MeOC$_6H_2$H$_2$), 5.57 (s, 1 H, PhC*H*), 5.32 (dd, 1 H, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 1.0 Hz, H-4^{IV}), 5.11 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1^{I}), 5.01 (d, 1 H, $J_{1,2}$ = 8.4 Hz, H-1^{III}), 4.94 (d, 1 H, ^2J = 11.1 Hz, PhC*H*H), 4.92 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1^{II}), 4.81 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{IV}), 4.80 (d, 1 H, ^2J = 11.7 Hz, *p*-MeOPhC*H*H), 4.66 (d, 1 H, ^2J = 11.7 Hz, PhC*H*H), 4.64 (d, 1 H, ^2J = 11.8 Hz, *p*-MeOPhC*H*H), 4.56 (d, 1 H, ^2J = 11.6 Hz, PhC*H*H), 4.55 (d, 1 H, ^2J = 11.7 Hz, PhC*H*H), 4.52 (d, 1 H, ^2J = 11.3 Hz, PhC*H*H), 4.47 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 4.32–4.29 (m, 2 H, PhC*H*H, H-3^{I}), 4.25 (t, 1 H, J = 9.6 Hz, H-3^{III}), 4.21 (dd, 1 H, J = 4.9, 10.4 Hz, H-6^{III}_a), 4.10–4.06 (m, 2 H, H-5^{II}, H-6^{IV}_a), 3.96 (dd, 1 H, J = 6.0, 11.0 Hz, H-6^{IV}_b), 3.90–3.81 (m, 4 H, H-1′$_a$, H-4^{II}, H-3^{II}, H-2^{II}), 3.80 (s, 3 H, OCH_3), 3.79–3.70 (m, 6 H, H-2^{IV}, H-2^{III}, H-5^{IV}, H-1′$_b$, H-6^{III}_b, H-4^{III}), 3.69–3.63 (m, 2 H, H-5^{I}, H-6^{I}_a), 3.61–3.55 (m, 8 H, H-2′, H-3′, H-4′, H-5′), 3.53–3.48 (m, 2 H, H-4^{I}, H-6^{II}_a), 3.45–3.42 (m, 1 H, H-6^{I}_b), 3.40–3.36 (m, 3 H, H-2^{I}, H-5^{III}, H-6^{II}_b), 3.33 (t, 2 H, J = 5.1 Hz, H-6′), 2.54 (d, 1 H, J = 2.6 Hz, 2^{IV}-OH), 2.10, 2.01, 1.96 (3 s, 9 H, 3 COCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.1 (3 x O*C*OCH$_3$), 162.2, 161.5 (2 x N*C*OCCl$_3$), 159.4, 138.0, 137.9, 137.8, 136.7, 129.5 (*ipso* Ar), 129.7–113.8 (Ar), 102.5 (C-1^{IV}), 101.4 (Ph*C*H), 100.6 (C-1^{III}), 98.4 (C-1^{I}), 97.8 (C-1^{II}), 92.7, 92.4 (2 x *C*Cl$_3$), 80.6 (C-3^{I}), 79.3 (C-4^{III}), 78.5 (C-4^{I}), 77.7 (C-3^{III}), 77.5 (C-2^{II}), 76.5 (C-3^{II}), 75.6 (C-4^{II}), 74.8 (Ph*C*H$_2$), 73.8 (*p*-MeOPh*C*H$_2$), 73.2 (Ph*C*H$_2$), 73.1 (C-5^{I}), 73.0 (Ph*C*H$_2$), 72.6 (C-3^{IV}), 70.9 (C-5^{IV}), 70.6, 70.5, 70.3, 70.0 (C-2′, C-3′, C-4′, C-5′), 69.5 (C-6^{II}), 69.4 (C-5^{II}), 69.0 (C-1′), 68.9 (C-2^{IV}), 68.4 (C-6^{III}), 66.8 (C-4^{IV}), 66.3 (C-5^{III}), 61.0 (C-6^{IV}), 58.6 (C-2^{I}), 58.8 (C-2^{III}), 55.3 (OCH$_3$), 50.6 (C-6′), 33.1 (C-6^{I}), 20.7–20.5 (3 x OCO*C*H$_3$). HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd for $C_{76}H_{92}BrCl_6N_6O_{26}$: 1793.3376; found: 1793.3369.

ii- Selective removal of the PMB group:

To a solution of **10** (400 mg, 0.23 mmol) in CH_2Cl_2–H_2O (18:1, *v/v*, 30 mL) was added DDQ (103 mg, 0.45 mmol) at rt. The mixture was stirred for 6h, at which time TLC (1:1, hexane-ehtyl

acetate) indicated the complete consumption of the starting material. The mixture was diluted with CH_2Cl_2 (50 mL), washed with satd. aq. $NaHCO_3$, brine, and the organic extract was dried and concentrated. Chromatography (3:2 hexane–acetone) afforded **11** (328 mg, 88%). ^{1}H and ^{13}C NMR spectra [page S26], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, 1H, $J_{2,NH}$ = 8.4 Hz, 2^{I}-NH), 7.51–7.21 (m, 21 H, Ar, 2^{III}-NH), 5.56 (s, 1 H, PhC*H*), 5.31 (br d, 1 H, *J* = 2.8 Hz, H-4^{IV}), 5.10 (d, 1 H, $J_{1,2}$ = 8.9 Hz, H-1^{III}), 5.02 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1^{II}), 4.92 (d, 1 H, $J_{1,2}$ = 5.7 Hz, H-1^{I}), 4.82–4.80 (m, 2 H, H-3^{IV}, PhC*H*H), 4.74–4.72 (m, 2 H, 2 x PhC*H*H), 4.65 (d, 1 H, ^2J = 11.6 Hz, PhC*H*H), 4.56–4.52 (m, 2 H, 2 x PhC*H*H), 4.47 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 4.32 (dd, 1 H, *J* = 4.9, 10.4 Hz, H-6^{III}_a), 4.27 (t, 1 H, *J* = 9.4 Hz, H-3^{III}), 4.10–4.07 (m, 2 H, H-5^{II}, H-6^{IV}_a), 4.01–3.95 (m, 3 H, H-3^{I}, H-4^{II}, H-6^{IV}_b), 3.92–3.85 (m, 3 H, H-$1'_a$, H-5^{I}, H-3^{II}), 3.84–3.76 (m, 5 H, H-2^{I}, H-2^{II}, H-2^{III}, H-6^{III}_b, H-2^{IV}), 3.75–3.68 (m, 5 H, H-5^{IV}, H-4^{III}, H-6^{I}_a, H-4^{I}, H-$1'_b$), 3.66–3.64 (m, 4 H, H-$6^{II}_{a,b}$, H-5′), 3.63–3.56 (m, 6 H, H-2′, H-3′, H-4′), 3.55 (dd, 1 H, *J* = 5.7, 10.6 Hz, H-6^{I}_b), 3.48–3.44 (m, 1 H, H-5^{III}), 3.38 (t, 2 H, *J* = 5.0 Hz, H-6′), 2.58 (br s, 1 H, 2^{IV}-OH), 2.10, 2.01, 1.97 (3 s, 9 H, 3 COC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.1 (3 x O*C*OCH$_3$), 162.2, 161.6 (2 x N*C*OCCl$_3$), 138.2, 137.9, 137.1, 136.7 (*ipso* Ar), 129.3–125.9 (Ar), 102.6 (C-1^{IV}), 101.3 (Ph*C*H), 100.9 (C-1^{III}), 98.9 (C-1^{I}), 98.7 (C-1^{II}), 92.4 (2 x *C*Cl$_3$), 79.2 (C-4^{III}), 78.1 (C-3^{I}), 77.6 (C-3^{III}), 77.3 (C-2^{II}), 76.4 (C-4^{I}, C-3^{II}), 75.2 (C-4^{II}), 73.9 (Ph*C*H$_2$), 73.8 (C-5^{I}), 73.7 (Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 72.6 (C-3^{IV}), 70.9 (C-5^{IV}), 70.5 (C-5^{II}), 70.6, 70.4, 70.3, 70.0 (C-2′, C-3′, C-4′, C-5′), 69.0 (C-2^{IV}), 68.6 (C-1′), 68.2 (C-6^{III}), 66.8 (C-4^{IV}), 66.5 (C-5^{III}), 61.3 (C-6^{II}), 61.0 (C-6^{IV}), 57.8 (C-2^{III}), 54.9 (C-2^{I}), 50.6 (C-6′), 33.0 (C-6^{I}), 20.7–20.5 (3 x OCO*C*H$_3$). HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd for $C_{68}H_{84}BrCl_6N_6O_{25}$: 1673.2801; found: 1673.2808.

iii- Selective oxidation of the primary hydroxyl group:

To a flask charged with compound **11** (294 mg, 0.18 mmol), TEMPO (17 mg, 0.11 mmol) and BAIB (171 mg, 0.54 mmol) was added CH_2Cl_2–H_2O (2:1, *v/v*, 12 mL), and the two-phase reaction mixture was stirred vigorously at room temperature until TLC (3:2 hexane–acetone) showed complete conversion of the starting material into a slower moving product (~24h). The mixture was diluted with EtOAc (150 mL), and washed with 1:1 (*v/v*) aq $Na_2S_2O_3$ and aq NaH_2PO_4 (2 x 75 mL). The combined aqueous washes were extracted with EtOAc (3 x 100 mL),

the organic phases were combined, dried, and concentrated. Anhydrous K_2CO_3 (32 mg, 0.23 mmol), followed by BnBr (42 μL, 0.27 mmol) was added under argon to a solution of the foregoing material in DMF (10 mL). After stirring for 16 h at room temperature, the mixture was diluted with CH_2Cl_2, and washed with water. The organic layer was dried, concentrated, and coevaporated with toluene (twice). Chromatography (2:1 hexane–acetone) afforded the uronate **12** (278 mg, 89% over two steps). ^{1}H and ^{13}C NMR spectra [page S27], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, 1H, $J_{2,NH}$ = 8.1 Hz, 2^{I}-NH), 7.46–7.14 (m, 26 H, Ar, 2^{III}-NH), 5.46 (s, 1 H, PhC*H*), 5.31 (br d, 1 H, *J* = 3.2 Hz, H-4^{IV}), 5.29 (br s, 1 H, H-1^{II}), 5.26 (d, 1 H, ^2J = 12.6 Hz, COOC*H*HPh), 5.23 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{III}), 4.97 (d, 1 H, ^2J = 12.6 Hz, COOC*H*HPh), 4.93 (d, 1 H, $J_{1,2}$ = 5.8 Hz, H-1^{I}), 4.83–4.79 (m, 3 H, H-3^{IV}, 2 x PhC*H*H), 4.70 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.66–4.63 (m, 2 H, H-5^{II}, PhC*H*H), 4.53–4.50 (m, 3 H, H-1^{IV}, 2 x PhC*H*H), 4.38 (t, 1 H, *J* = 9.4 Hz, H-3^{III}), 4.35 (br s, 1 H, H-4^{II}), 4.10–4.06 (m, 2 H, H-3^{I}, H-6^{IV}_a), 4.05 (dd, 1 H, *J* = 5.1, 10.5 Hz, H-6^{III}_a), 3.96 (dd, 1 H, *J* = 6.1, 10.7 Hz, H-6^{IV}_b), 3.93 (br s, 2 H, H-2^{II}, H-3^{II}), 3.89–3.85 (m, 1 H, H-1′$_a$), 3.83–3.80 (m, 1 H, H-5^{I}), 3.79–3.75 (m, 1 H, H-2^{IV}), 3.79–3.66 (m, 5 H, H-2^{I}, H-4^{I}, H-5^{IV}, H-6^{I}_a, H-1′$_b$), 3.64–3.58 (m, 2 H, H-4^{III}, H-2^{III}), 3.57–3.53 (m, 9 H, H-2′, H-3′, H-4′, H-5′, H-6^{I}_b), 3.52–3.48 (m, 1 H, H-6^{III}_b), 3.35 (t, 2 H, *J* = 5.0 Hz, H-6′), 3.34–3.31 (m, 1 H, H-5^{III}), 2.55 (d, 1 H, *J* = 2.8 Hz, 2^{IV}-OH), 2.08, 2.01, 1.96 (3 s, 9 H, 3 COC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.1 (3 x O*C*OCH$_3$), 167.2 (*C*OOBn), 161.8, 161.7 (2 x N*C*OCCl$_3$), 138.0, 137.7, 137.1, 136.7, 135.1 (*ipso* Ar), 129.3–126.0 (Ar), 102.3 (C-1^{IV}), 101.3 (PhCH), 99.5 (C-1^{III}), 99.0 (C-1^{I}), 98.2 (C-1^{II}), 92.4, 92.2 (2 x *C*Cl$_3$), 79.1 (C-4^{III}), 77.4 (C-3^{I}), 76.9 (C-3^{III}, C-2^{II}), 76.8 (C-4^{I}), 76.1 (C-3^{II}), 74.9 (C-4^{II}), 74.1 (Ph*C*H$_2$), 73.9 (C-5^{I}), 73.8 (Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 72.6 (C-3^{IV}), 70.9 (C-5^{IV}), 70.8 (C-5^{II}), 70.6, 70.4, 70.3, 70.0 (C-2′, C-3′, C-4′, C-5′), 69.0 (C-2^{IV}), 68.5 (C-1′), 68.4 (C-6^{III}), 67.0 (Ph*C*H$_2$OCO), 66.9 (C-4^{IV}), 66.0 (C-5^{III}), 61.1 (C-6^{IV}), 58.4 (C-2^{III}), 55.1 (C-2^{I}), 50.6 (C-6′), 32.9 (C-6^{I}), 20.7–20.5 (3 x OCO*C*H$_3$). HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{75}H_{84}BrCl_6N_5O_{26}Na$: 1782.2617; found: 1782.2633.

iv- Regioselective reductive opening of the benzylidene ring:

A mixture of the acetal **12** (129 mg, 0.07 mmol) and freshly activated powdered molecular sieves (3Å, 350 mg) in dry THF (5 mL) was stirred under argon at room temperature for 1.5h.

$NaCNBH_3$ (60 mg, 0.90 mmol) was added. After stirring for ~20 min, 2 M HCl-Et_2O was added dropwise until the effervescence ceased and the pH remained acidic. The mixture was stirred for an additional 15 min, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed with cold satd. aq. $NaHCO_3$, brine, and the organic extract was dried and concentrated. Chromatography (6:1 toluene–acetone) afforded **13** (110 mg, 85%). ^{1}H and ^{13}C NMR spectra [page S28], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, 1H, $J_{2,NH}$ = 8.1 Hz, 2^{I}-NH), 7.34–7.13 (m, 25 H, Ar), 7.09 (d, 1H, $J_{2,NH}$ = 7.4 Hz, 2^{III}-NH), 5.37 (d, 1 H, ^2J = 12.3 Hz, COOC*H*HPh), 5.36 (br d, 1 H, partial overlap, J = 3.3 Hz, H-4^{IV}), 5.31 (d, 1 H, $J_{1,2}$ = 2.5 Hz, H-1^{II}), 5.04 (d, 1 H, ^2J = 12.2 Hz, COOC*H*HPh), 4.95 (d, 1 H, $J_{1,2}$ = 8.6 Hz, H-1^{III}), 4.91 (d, 1 H, $J_{1,2}$ = 5.5 Hz, H-1^{I}), 4.82 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{IV}), 4.78 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.74 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.72 (d, partial overlap, 1 H, J = 1.5 Hz, H-5^{II}), 4.67 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.65 (d, 1 H, ^2J = 11.3 Hz, PhC*H*H), 4.57 (br s, 1 H, H-4^{II}), 4.54–4.49 (m, 3 H, 3 x PhC*H*H), 4.45 (d, 1 H, ^2J = 12.1 Hz, PhC*H*H), 4.22 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1^{IV}), 4.15–4.08 (m, 3 H, 4^{III}-OH, H-$6^{IV}_{a,b}$), 4.06 (t, 1 H, J = 6.3 Hz, H-3^{I}), 3.98–3.93 (m, 3 H, H-5^{IV}, H-3^{II}, H-2^{II}), 3.87–3.74 (m, 2 H, H-$1'_a$, H-5^{I}), 3.82–3.74 (m, 3 H, H-2^{IV}, H-6^{III}_a, H-2^{I}), 3.73–3.69 (m, 3 H, H-4^{I}, H-6^{I}_a, H-2^{III}), 3.67–3.64 (m, 1 H, H-$1'_b$), 3.62–3.57 (m, 3 H, H-6^{III}_b, H-5′), 3.56–3.50 (m, 9 H, H-2′, H-3′, H-4′, H-6^{I}_b, H-4^{III}, H-3^{III}), 3.38–3.35 (m, 1 H, H-5^{III}), 3.33 (t, 2 H, J = 5.1 Hz, H-6′), 2.83 (d, 1 H, J = 2.2 Hz, 2^{IV}-OH), 2.13–2.02 (3 s, 9 H, 3 COCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.0 (3 x O*C*OCH$_3$), 167.1 (*C*OOBn), 162.9, 161.6 (2 x N*C*OCCl$_3$), 138.2, 137.9, 137.4, 137.0, 135.6 (*ipso* Ar), 128.8–127.4 (Ar), 104.1 (C-1^{IV}), 99.8 (C-1^{III}), 98.9 (C-1^{I}), 98.2 (C-1^{II}), 92.2 (2 x *C*Cl$_3$), 87.3 (C-3^{III}), 77.4 (C-3^{I}), 77.2 (C-3^{II}), 76.7 (C-4^{I}), 76.2 (C-2^{II}), 75.7 (C-5^{III}), 74.4 (C-4^{II}), 74.0 (Ph*C*H$_2$), 73.8 (C-5^{I}), 73.5 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 73.1 (Ph*C*H$_2$), 72.2 (C-3^{IV}), 71.2 (C-5^{IV}), 70.9 (C-5^{II}), 70.6, 70.4, 70.3, 70.0 (C-2′, C-3′, C-4′, C-5′), 69.4 (C-6^{III}), 69.1 (C-4^{III}), 68.6 (C-2^{IV}), 68.4 (C-1′), 67.0 (Ph*C*H$_2$OCO), 66.8 (C-4^{IV}), 61.7 (C-6^{IV}), 56.9 (C-2^{III}), 54.8 (C-2^{I}), 50.6 (C-6′), 32.9 (C-6^{I}), 20.7–20.5 (3 x OCO*C*H$_3$). HRMS (ESI-TOF): *m/z* [M + NH_4]$^+$ calcd for $C_{75}H_{90}BrCl_6N_6O_{26}$: 1779.3219; found: 1779.3225.

V- Preparation of the Branched Hexasaccharide 16 *(α-Colitosylation reaction)*:

Bromine (22 μL, 0.40 mmol) was added to a solution of ethyl 2,4-di-*O*-benzyl-3,6-dideoxy-1-thio-β-L-*xylo*-hexopyranoside **14**[18] (76 mg, 0.20 mmol) in CCl_4 (2 mL). The mixture was shaken gently, and after 5 min, hex-1-ene (100 μL, 0.81 mmol) was added. After concentration and co-evaporation with CCl_4 (twice), a solution of the crude α-colitosyl bromide **15** thus obtained in anhydrous CH_2Cl_2 (2 mL) was added to a stirred mixture of **13** (60 mg, 0.04 mmol), Bu_4NBr (66 mg, 0.20 mmol) and powdered molecular sieves (4Å, 350 mg) in CH_2Cl_2–DMF (3:1, *v/v*, 4 mL). After stirring under argon for 5 days at room temperature, the mixture was diluted with CH_2Cl_2 and filtered through a Celite pad. The combined filtrate and washings were successively washed with satd. aq. $NaHCO_3$ and water, dried, and concentrated. Chromatography (6:1 toluene–acetone) gave first the hexasaccharide **16** (R_f = 0.44, 52.7 mg, 66%). ^{1}H and ^{13}C NMR spectra [page S29], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, 1H, $J_{2,NH}$ = 7.8 Hz, 2^I-NH), 7.35–7.10 (m, 46 H, Ar, 2^{III}-NH), 5.44 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{III}), 5.25 (br d, 1 H, partial overlap, J = 3.5 Hz, H-4^{IV}), 5.24 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1^V), 5.18 (d, 1 H, $J_{1,2}$ = 3.3 Hz, H-1^{II}), 5.07 (d, 1 H, ^2J = 12.5 Hz, COOC*H*HPh), 5.03 (br d, partial overlap, 1 H, H-1^{VI}), 5.01 (d, 1 H, partial overlap, ^2J = 12.5 Hz, COOC*H*HPh), 4.97 (d, 1 H, $J_{1,2}$ = 6.1 Hz, H-1^I), 4.95 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{IV}), 4.78 (d, 1 H, ^2J = 11.6 Hz, PhC*H*H), 4.76 (d, partial overlap, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{IV}), 4.71 (d, 1 H, ^2J = 11.2 Hz, PhC*H*H), 4.65–4.60 (m, 4 H, 2 x PhC*H*H, H-5^{VI}, H-5^{II}), 4.57–4.54 (m, 3 H, 3 x PhC*H*H), 4.53 (br s, 1 H, H-4^{II}), 4.52 (m, 1 H, H-3^{III}), 4.49 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.47 (d, 1 H, ^2J = 11.9 Hz, PhC*H*H), 4.44–4.41 (m, 4 H, 4 x PhC*H*H), 4.39 (d, 1 H, ^2J = 12.4 Hz, PhC*H*H), 4.34 (d, 1 H, ^2J = 11.8 Hz, PhC*H*H), 4.29 (d, 1 H, ^2J = 12.4 Hz, PhC*H*H), 4.22–4.19 (m, 1 H, H-5^{III}), 4.11 (t, 1 H, J = 6.7 Hz, H-3^I), 4.01–4.98 (m, 2 H, H-6$^{IV}_{a,b}$), 3.93 (t, 1 H, J = 8.4 Hz, H-4^{III}), 3.89–3.81 (m, 7 H, H-2^{II}, H-2^{IV}, H-2^V, H-2^{VI}, H-1′$_a$, H-6$^{III}_a$, H-3^{II}), 3.78–3.74 (m, 2 H, H-5^I, H-5^{IV}), 3.69–3.61 (m, 4 H, H-6^I_a, H-1′$_b$, H-6$^{III}_b$, H-4^I), 3.60–3.56 (m, 3 H, H-2^I, H-5′), 3.55–3.51 (m, 9 H, H-2′, H-3′, H-4′, H-5^{III}, H-4^V, H-6^I_b), 3.50–3.47 (m, 1 H, H-2^{III}), 3.33 (t, 2 H, J = 5.2 Hz, H-6′), 2.14–2.11 (m, 2 H, H-3$^V_{eq}$, H-3$^{VI}_{eq}$), 2.01 (s, 3 H, COC*H*$_3$), 1.84 (s, 3 H, COC*H*$_3$), 1.83–1.76 (m, 2 H, H-3$^V_{ax}$, H-3$^{VI}_{ax}$), 1.67 (s, 3 H, COC*H*$_3$), 1.21 (d, 3 H, $J_{5,6}$ = 6.5 Hz, H-6^V), 1.18 (d, 3 H, $J_{5,6}$ = 6.6 Hz, H-6^{VI}). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.3, 169.8, 169.7 (3 x O*C*OCH$_3$), 167.3 (*C*OOBn), 162.6, 161.0 (2 x N*C*OCCl$_3$), 138.6–135.4 (*ipso* Ar), 128.5–127.3 (Ar), 102.0 (C-1^{IV}), 98.8 (C-1^I), 98.3 (C-1^{II}), 97.9 (C-1^{III}),

97.4 (C-1^{V}), 96.7 (C-1^{VI}), 92.6, 92.3 (2 x CCl_3), 78.1 (C-3^{I}), 77.1 (C-4^{I}), 76.8 (C-3^{II}), 76.1 (C-2^{II}), 75.9 (C-4^{V}), 75.6 (C-3^{III}), 75.6 (C-5^{III}, C-4^{VI}), 74.0 (PhCH_2), 73.8 (PhCH_2), 73.7 (C-5^{I}), 73.3 (C-4^{II}, C-2^{IV}), 73.0 (C-4^{III}), 72.8 (PhCH_2), 72.7 (PhCH_2), 72.5 (C-3^{IV}), 71.7 (C-2^{V}), 71.5 (PhCH_2), 71.3 (PhCH_2), 71.2 (C-5^{II}), 71.0 (C-2^{VI}), 70.56 (PhCH_2), 70.54 (PhCH_2), 70.49 (C-5^{IV}), 70.60, 70.47, 70.37, 69.98 (C-2′, C-3′, C-4′, C-5′), 68.6 (C-1′), 67.8 (C-6^{III}), 67.6 (C-5^{V}), 67.5 (C-4^{IV}), 66.9 (PhCH_2OCO), 65.9 (C-5^{VI}), 60.6 (C-6^{IV}), 60.4 (C-2^{III}), 55.9 (C-2^{I}), 50.6 (C-6′), 32.9 (C-6^{I}), 26.6, 26.5 (C-3^{V}, C-3^{VI}), 20.7–20.4 (3 x OCOCH_3), 16.6 (C-6^{V}), 16.5 (C-6^{VI}). HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{115}H_{130}BrCl_6N_5O_{32}Na$: 2404.5911; found: 2404.5901.

Eluted next were the two minor pentasaccharide by-products resulting from monocolitosylation (R_f = 0.33 and 0.30; ~23% combined yield), identified by HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{95}H_{108}BrCl_6N_5O_{29}Na$: 2094.4342; found: 2094.4348 and 2094.4355, respectively.

VI- Preparation of the desired hexasaccharide O-antigen:

*i- Zemplén de-O-acetylation of **16**:*

A solution of NaOMe in MeOH (1 M, ~300 μL) was added under nitrogen to a solution of **16** (44 mg, 18.4 μmol) in 1:8 CH_2Cl_2–MeOH (4 mL), and the mixture was stirred at room temperature for 6 h. The mixture was neutralized with Amberlite IR-120 (H^+) resin, filtered, and the solids were washed with MeOH. The filtrate was concentrated and co-evaporated with toluene (twice) to give triol **17** as an amorphous solid in almost theoretical yield. ^1H and ^{13}C NMR spectra for crude **17** [page S30], HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd for $C_{103}H_{124}BrCl_6N_6O_{29}$: 2197.5727; found: 2197.5732.

*ii- Regioselective phosphorylation of **17**:*

To a solution of the crude **17** and pyridine (20 μL, 0.24 mmol) in CH_2Cl_2 (3 mL), 2,2,2-trichloroethyl phosphorodichloridate (5 μL, 36.8 μmol) was added dropwise at –20 °C. When TLC (~20 min, 4:1 toluene–acetone) indicated complete conversion of **17**, excess of reagent was destroyed by addition of MeOH (400 μL). The mixture was concentrated, and EtOAc (3 mL) was added to the residue. The precipitate was filtered off and washed with EtOAc (2 x 2 mL). The

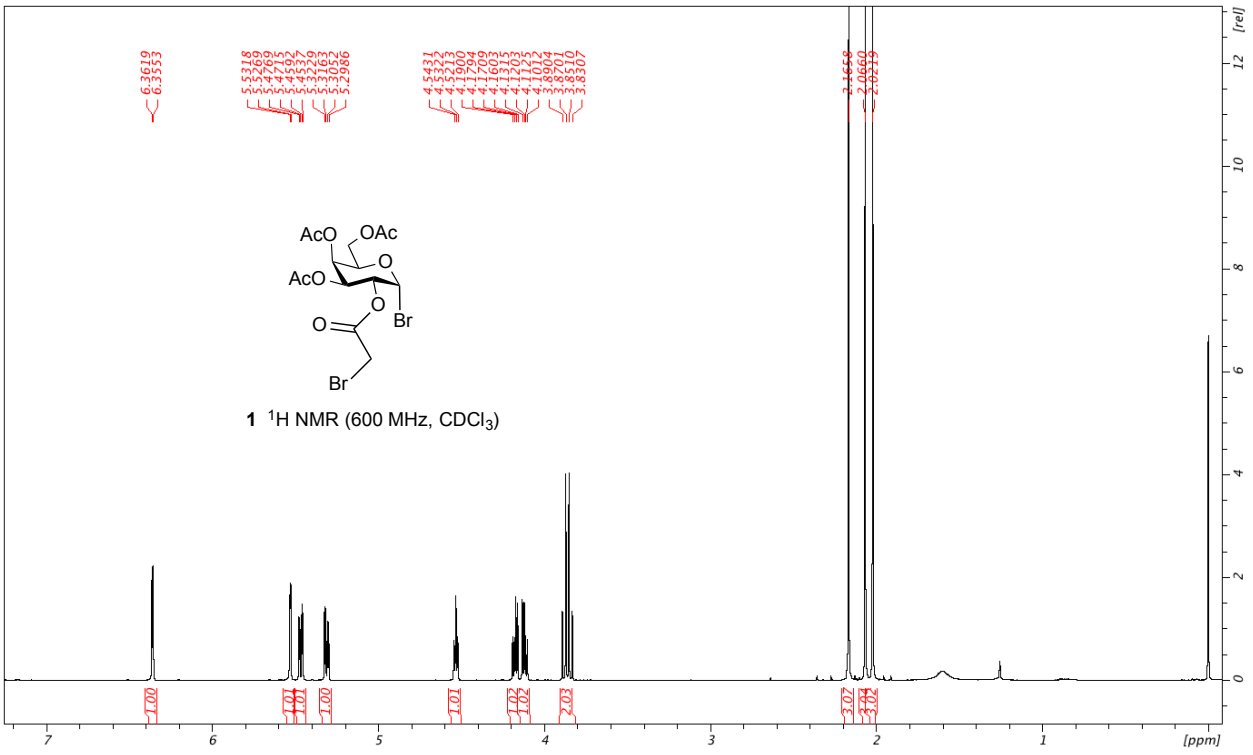
combined filtrates were concentrated and chromatography (4:1 toluene–acetone) gave **18** (36.2 mg) and **19** (4.1 mg) in a combined yield ~91%. ^{31}P NMR for **18** (162 MHz, $CDCl_3$): $\delta = -10.54$, ^{1}H and ^{13}C NMR spectra [page S31], ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, 1H, $J_{2,NH}$ = 7.8 Hz, 2^{I}-NH), 7.39–7.08 (m, 41 H, Ar, 2^{III}-NH), 5.43 (d, 1 H, $J_{1,2}$ = 8.2 Hz, H-1^{III}), 5.23 (d, 1 H, $J_{1,2}$ = 2.9 Hz, H-1^{V}), 5.18 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1^{II}), 5.02 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1^{VI}), 4.98 (d, 1 H, $J_{1,2}$ = 6.0 Hz, H-1^{I}), 4.78 (d, 1 H, ^2J = 11.4 Hz, PhC*H*H), 4.75 (d, 1 H, J = 3.4 Hz, H-4^{IV}), 4.73–4.69 (m, 3 H, PhC*H*H, H-5^{VI}, H-3^{III}), 4.67 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 4.66–4.57 (m, 4 H, 2 x PhC*H*H, C*H*$_2$CCl$_3$), 4.56–4.42 (m, 11 H, 11 x PhC*H*H), 4.40 (d, 1 H, J = 2.8 Hz, 3^{IV}-OH), 4.37 (d, 1 H, ^2J = 12.0 Hz, PhC*H*H), 4.14–4.09 (m, 2 H, H-3^{I}, H-5^{V}), 3.99–3.95 (m, 1 H, H-2^{V}), 3.93 (t, partial overlap, 1 H, J = 9.2 Hz, H-4^{III}), 3.92–3.83 (m, H-4^{VI}, H-2^{VI}, H-6$^{III}_{a}$, H-1′$_a$, H-2^{II}, H-3^{II}), 3.82–3.78 (m, 1 H, H-2^{IV}), 3.77–3.73 (m, 1 H, H-5^{I}), 3.71–3.61 (m, H-1′$_b$, H-3^{IV}, H-6$^{III}_{b}$, H-6$^{I}_{a}$, H-4^{I}, H-5′), 3.60–3.53 (m, H-2^{I}, H-2′, H-3′, H-4′, COOC*H*$_3$), 3.51–3.47 (m, H-6$^{I}_{b}$, H-5^{III}, H-4^{V}, H-5^{IV}), 3.41–3.36 (m, 1 H, H-2^{III}), 3.35 (t, 2 H, J = 5.0 Hz, H-6′), 2.21–2.03 (m, 2 H, H-3$^{V}_{eq}$, H-3$^{VI}_{eq}$), 1.87–1.81 (m, 2 H, H-3$^{V}_{ax}$, H-3$^{VI}_{ax}$), 1.27 (d, 3 H, $J_{5,6}$ = 6.6 Hz, H-6^{VI}), 1.21 (d, 3 H, $J_{5,6}$ = 6.5 Hz, H-6^{V}). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.7 (*C*OOCH$_3$), 161.6, 160.7 (2 x N*C*OCCl$_3$), 139.5–136.7 (*ipso* Ar), 128.7–127.1 (Ar), 101.9 (C-1^{IV}), 99.2 (C-1^{V}), 98.8 (C-1^{I}), 98.3 (C-1^{II}), 96.9 (C-1^{III}), 96.6 (C-1^{VI}), 94.9 (d, $J_{C,P}$ = 9.9 Hz, CH$_2$*C*Cl$_3$), 92.8, 92.3 (2 x *C*Cl$_3$), 78.2 (C-2^{IV}, C-4^{IV}), 78.1 (C-3^{I}), 77.2 (C-4^{I}), 76.8 (C-4^{VI}), 76.7 (C-3^{II}), 76.2 (C-2^{II}), 75.4 (C-3^{III}), 75.2, 75.1 (C-4^{V}, C-5^{III}), 74.1 (Ph*C*H$_2$), 73.8 (Ph*C*H$_2$), 73.7 (C-5^{I}), 72.8 (Ph*C*H$_2$), 72.6 (2 x Ph*C*H$_2$), 72.4 (C-4^{II}), 72.3 (C-4^{III}), 71.9 (C-2^{V}), 71.5 (Ph*C*H$_2$), 71.4 (Ph*C*H$_2$), 71.3 (d, $J_{C,P}$ = 7.3 Hz, C-3^{IV}), 71.1 (C-2^{VI}), 70.9 (C-5^{II}), 70.9 (Ph*C*H$_2$), 70.8 (d, partial overlap, $J_{C,P}$ = 7.0 Hz, C-6^{IV}), 70.6, 70.5, 70.4, 70.0 (C-2′, C-3′, C-4′, C-5′), 68.7 (C-1′), 68.5 (C-5^{V}), 67.7 (C-6^{III}), 66.4 (C-5^{VI}), 66.2 (d, $J_{C,P}$ = 6.7 Hz, C-5^{IV}), 61.3 (C-2^{III}), 56.0 (C-2^{I}), 52.3 (COO*C*H$_3$), 50.6 (C-6′), 33.0 (C-6^{I}), 27.5 (C-3^{VI}), 26.9 (C-3^{V}), 16.8 (C-6^{V}), 16.4 (C-6^{VI}). HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{105}H_{120}BrCl_9N_5O_{31}Na$: 2394.3983; found: 2394.4021. ^{31}P NMR for **19** (162 MHz, $CDCl_3$): $\delta = -2.45$. HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{105}H_{120}BrCl_9N_5O_{31}Na$: 2394.3983; found: 2394.3948.

iii- Global deprotection (hydrogenation/hydrogenolysis):

A mixture of phosphate **18** (10 mg, 4.22 μmol) and Pd/C (10 mg) in a mixture of MeOH (1.5 mL) and 0.1 M potassium phosphate buffer (0.5 mL; pH = 7) was stirred under H_2 (1 atm) at room temperature. After 2 days, when TLC (2:1 *i*PrOH–30% NH_4OH) showed complete conversion of the starting material into a more polar product, the mixture was filtered through a Celite pad, the catalyst was washed with water (3 x 0.5 mL), and the filtrate was concentrated. A solution of the crude product in water (300 μL) was purified by HPLC (SunFire™ C18, 5μm, 4.6x250 mm column) with 5% acetonitrile in water as a mobile phase (several runs, ~0.5 mg each), followed by lyophilization to afford **20** (4.5 mg, 87 %). ^{1}H, ^{13}C and ^{31}P NMR spectra [page S32, S33], ^{31}P NMR (162 MHz, D_2O): δ = –3.73 ($^{3}J_{P,H}$ 21.9 Hz), ^{1}H NMR (600 MHz, D_2O): δ = 5.23 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1^{II}), 4.96 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H-1^{V}), 4.88 (d, 1 H, $J_{1,2}$ = 3.3 Hz, H-1^{VI}), 4.73 (m, overlapped, 1 H, H-5^{VI}), 4.66 (d, 1 H, $J_{1,2}$ = 8.2 Hz, H-1^{IV}), 4.52 (d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4^{IV}), 4.48 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1^{III}), 4.46 (d, 1 H, $J_{1,2}$ = 8.5 Hz, H-1^{I}), 4.47 (m, overlapped, 1 H, H-5^{II}), 4.37–4.27 (m, 2 H, H-$6^{IV}_{a,b}$), 4.31 (br s, partial overlap, 1 H, H-4^{II}), 4.24–4.22 (m, 1 H, H-5^{V}), 4.15 (br s, 1 H, H-4^{VI}), 3.98–3.89 (m, 4 H, H-3^{III}, H-2^{VI}, H-2^{V}, H-3^{II}), 3.88–3.81 (m, 3 H, H-3^{IV}, H-$6^{III}_{a,b}$), 3.79 (br s, 3 H, COOCH_3), 3.77–3.73 (m, 1 H, H-2^{III}), 3.72–3.68 (m, 4 H, H-2^{I}, H-4^{V}, H-5′), 3.67–3.59 (m, 9 H, H-1′, H-2′, H-3′, H-4′, H-4^{III}), 3.58–3.51 (m, 4 H, H-2^{II}, H-2^{IV}, H-5^{IV}, H-3^{I}), 3.46–3.41 (m, 1 H, H-5^{I}), 3.39–3.33 (m, 2 H, H-5^{III}, H-4^{I}), 3.06 (t, 2 H, J = 5.1 Hz, H-6′), 2.01 (s, 3 H, COCH_3), 1.87 (s, 3 H, COCH_3), 2.00–1.77 (m, 4 H, H-3^{V}, H-3^{VI}), 1.24 (d, 3 H, J = 6.4 Hz, H-6^{I}), 1.16, 1.14 (2 d, 6 H, J = 6.1, 6.2 Hz, H-6^{V}, H-6^{VI}). ^{13}C NMR (150 MHz, D_2O): δ = 174.5 (*C*OCH_3), 174.3 (*C*OCH_3), 170.9 (*C*$OOCH_3$), 102.95 (C-1^{III}), 101.17 (C-1^{I}), 101.12 (C-1^{IV}), 100.88 (C-1^{II}), 99.56 (C-1^{V}), 97.76 (C-1^{VI}), 82.5 (C-3^{I}), 78.5 (C-4^{II}), 76.5 (d, $J_{C,P}$ = 4.2 Hz, C-4^{IV}), 76.2 (C-2^{IV}), 75.6, 75.7 (C-4^{I}, C-5^{III}), 75.5 (C-3^{III}), 72.6 (d, $J_{C,P}$ = 7.9 Hz, C-3^{IV}), 72.3 (C-4^{III}), 71.5 (C-5^{I}), 70.8 (C-5^{II}), 69.9–69.3 (C-2′, C-3′, C-4′, C-5′), 68.8 (C-3^{II}, C-4^{V}), 68.7 (d, $J_{C,P}$ = 5.2 Hz, C-6^{IV}), 68.6 (C-2^{II}), 68.5 (C-4^{VI}), 67.6 (C-1′), 67.5 (d, $J_{C,P}$ = 4.2 Hz, C-5^{IV}), 66.8 (C-5^{VI}), 66.3 (C-5^{V}), 63.7, 63.5 (C-2^{V}, C-2^{VI}), 59.8 (C-6^{III}), 55.9 (C-2^{III}), 54.7 (C-2^{I}), 53.2 (COO*C*H_3), 39.4 (C-6′), 32.9, 32.7 (C-3^{V}, C-3^{VI}), 22.6 (CO*C*H_3), 22.3 (CO*C*H_3), 16.7 (C-6^{I}), 15.7, 15.6 (C-6^{V}, C-6^{VI}). HRMS (ESI-TOF): *m/z* $[M - H]^-$ calcd for $C_{47}H_{79}N_3O_{31}P$: 1212.4435; found: 1212.4446.

iv- Saponification of the methyl ester:

Methyl ester **20** (4.4 mg, 3.71 μmol) was dissolved in deionized water (400 μL). 0.1 M KOH aqueous solution (116 μL, 11.5 μmol) was added portionwise at 0 °C until pH = 11, and the reaction mixture was allowed to stir for 12h at room temperature. The mixture was acidified using carbon dioxide gas until pH ~ 6, and then concentrated. A solution of the crude product in water (250 μL) was purified by HPLC (SunFire^{TM} C18, 5μm, 4.6x250 mm column) with 5% methanol in water as a mobile phase (several runs, ~0.5 mg each), followed by lyophilization to afford the desired hexasaccharide **21** (3.7 mg, 83 %). ^{1}H, ^{13}C and ^{31}P NMR spectra [page S34, S35], ^{31}P NMR (162 MHz, D_2O): δ = –3.72 ($^{3}J_{P,H}$ 21.4 Hz), ^{1}H NMR (600 MHz, D_2O): δ = 5.26 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1^{II}), 4.96 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1^{V}), 4.77 (d, overlapped, H-1^{VI}), 4.72 (m, overlapped, 1 H, H-5^{VI}), 4.67 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{IV}), 4.52 (d, 1 H, $J_{3,4}$ = 3.5 Hz, H-4^{IV}), 4.47 (d, 1 H, $J_{1,2}$ = 8.7 Hz, H-1^{I}), 4.45 (d, 1 H, $J_{1,2}$ = 8.5 Hz, H-1^{III}), 4.36–4.27 (m, 2 H, H-6$^{IV}_{a,b}$), 4.25–4.22 (m, 1 H, H-5^{V}), 4.20 (br d, 1 H, $J_{3,4}$ = 2.2 Hz, 1 H, H-4^{II}), 4.15 (br s, 1 H, H-4^{VI}), 4.03 (br s, 1 H, 1 H, H-5^{II}), 3.98–3.88 (m, 3 H, H-3^{III}, H-2^{VI}, H-2^{V}), 3.86–3.82 (m, 3 H, H-3^{IV}, H-3^{II}, H-6$^{III}_{a}$), 3.80–3.76 (m, 1 H, H-2^{III}), 3.72–3.67 (m, 7 H, H-2^{I}, H-4^{V}, H-5′, H-1′, H-6$^{III}_{b}$), 3.65–3.61 (m, 6 H, H-2′, H-3′, H-4′), 3.60–3.59 (m, 1 H, H-2^{II}), 3.58–3.54 (m, 4 H, H-4^{III}, H-2^{IV}, H-5^{IV}, H-3^{I}), 3.47–3.42 (m, 1 H, H-5^{I}), 3.37–3.32 (m, 2 H, H-5^{III}, H-4^{I}), 3.14 (t, 2 H, J = 5.1 Hz, H-6′), 2.01 (s, 3 H, COCH_3), 1.93 (s, 3 H, COCH_3), 2.00–1.77 (m, 4 H, H-3^{V}, H-3^{VI}), 1.25 (d, 3 H, J = 6.2 Hz, H-6^{I}), 1.16 (d, 3 H, J = 6.5 Hz, H-6^{VI}) , 1.14 (d, 3 H, J = 6.6 Hz, H-6^{V}). ^{13}C NMR (150 MHz, D_2O): δ = 175.0 (*C*OOH), 174.7 (*C*OCH$_3$), 174.3 (*C*OCH$_3$), 102.79 (C-1^{III}), 101.31 (C-1^{I}), 101.17 (C-1^{IV}), 100.22 (C-1^{II}), 99.45 (C-1^{V}), 97.94 (C-1^{VI}), 80.7 (C-3^{I}), 79.6 (C-4^{II}), 76.5 (d, $J_{C,P}$ = 4.2 Hz, C-4^{IV}), 76.2 (C-2^{IV}), 76.1 (C-4^{I}), 75.7 (C-5^{III}), 75.6 (C-3^{III}), 72.2 (C-4^{III}), 72.5 (d, $J_{C,P}$ = 5.9 Hz, C-3^{IV}), 71.9 (C-5^{II}), 71.8 (C-5^{I}), 69.9–69.7 (C-2′, C-3′, C-4′), 69.6 (C-3^{II}), 69.2 (C-5′), 68.8 (d, $J_{C,P}$ = 5.3 Hz, C-6^{IV}), 68.7 (C-4^{V}), 68.5 (C-2^{II}, C-4^{VI}), 67.5 (C-5^{IV}), 66.8 (C-5^{VI}), 66.7 (C-1′), 66.3 (C-5^{V}), 63.6 (C-2^{V}), 63.4 (C-2^{VI}), 60.4 (C-6^{III}), 55.9 (C-2^{III}), 54.3 (C-2^{I}), 39.3 (C-6′), 32.8 (C-3^{V}), 32.7 (C-3^{VI}), 22.5 (CO*C*H$_3$), 22.3 (CO*C*H$_3$), 16.6 (C-6^{I}), 15.6, 15.5 (C-6^{V}, C-6^{VI}). HRMS (ESI-TOF): *m/z* [M – H]$^{-}$ calcd for $C_{46}H_{77}N_3O_{31}P$: 1198.4279; found: 1198.4282.



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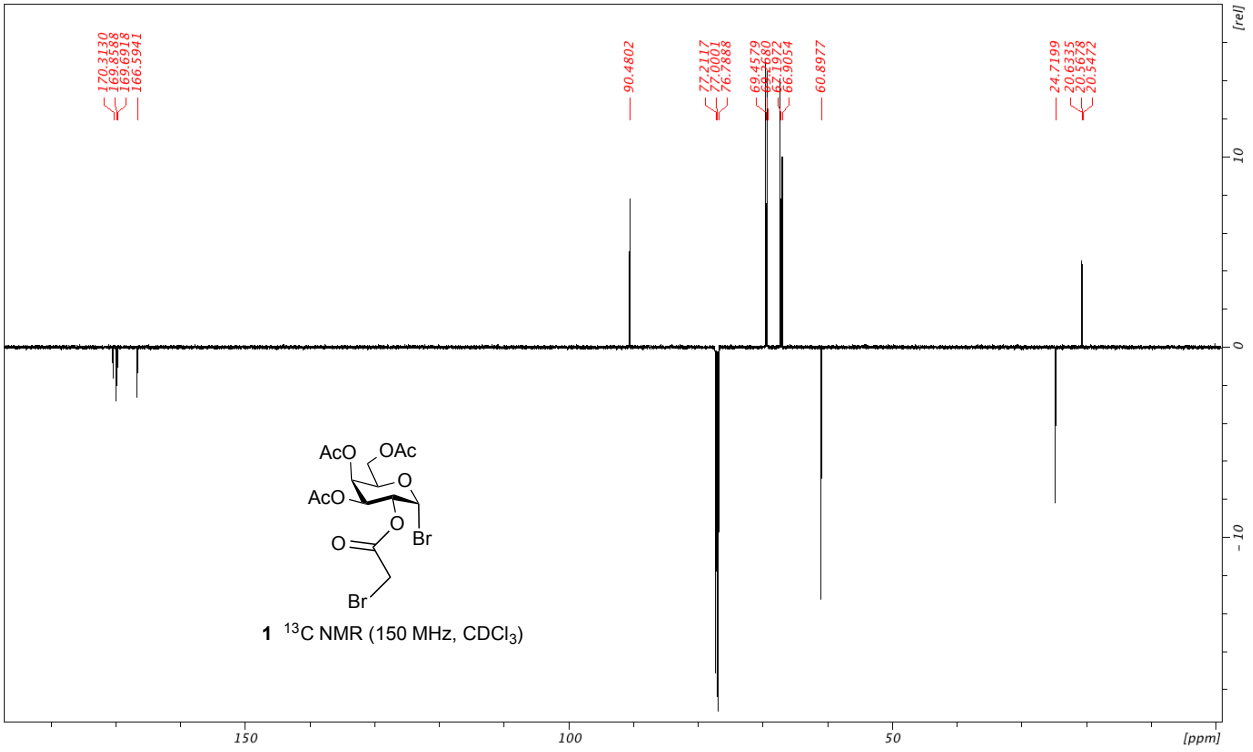
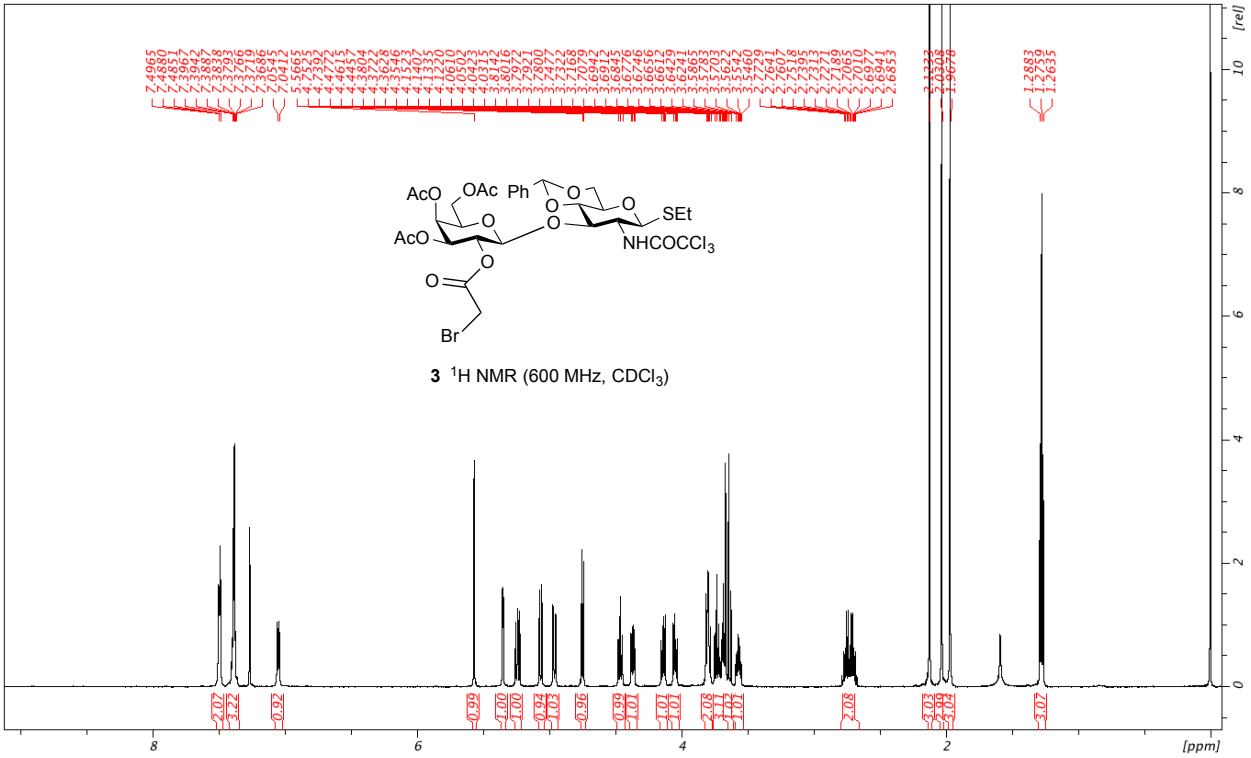
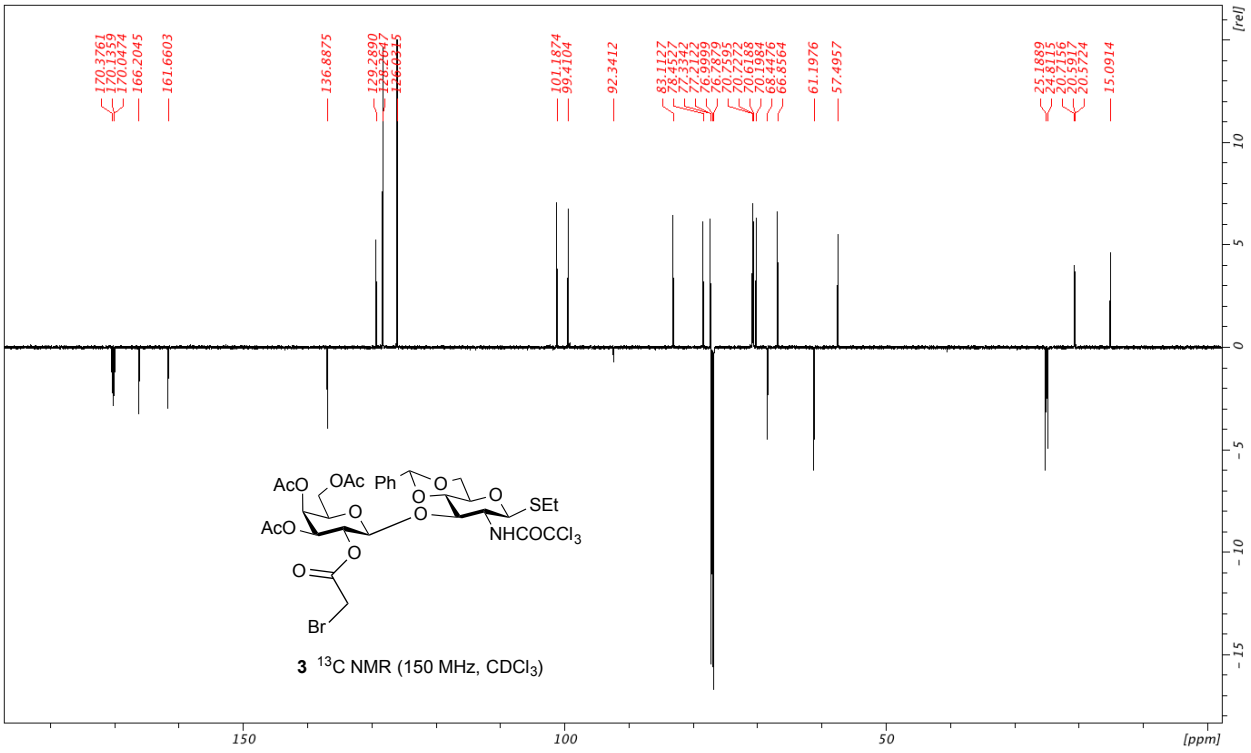


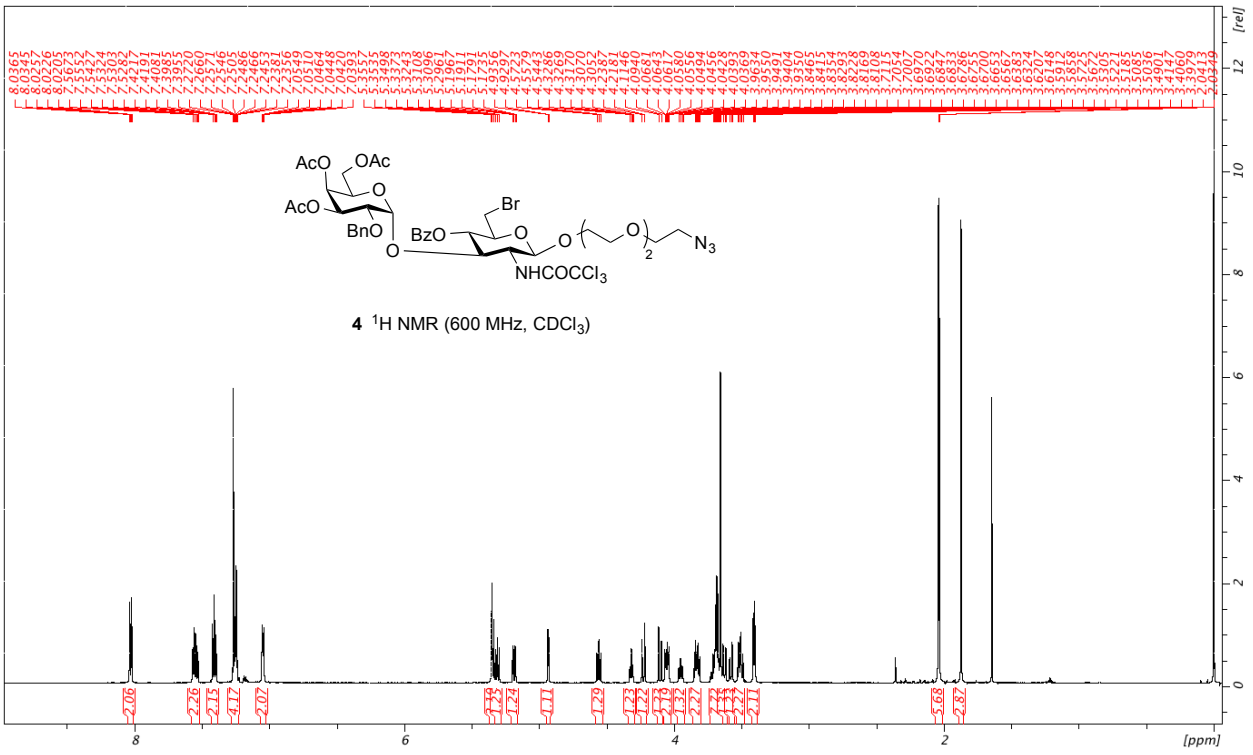
1 ^{13}C NMR (150 MHz, $CDCl_3$)



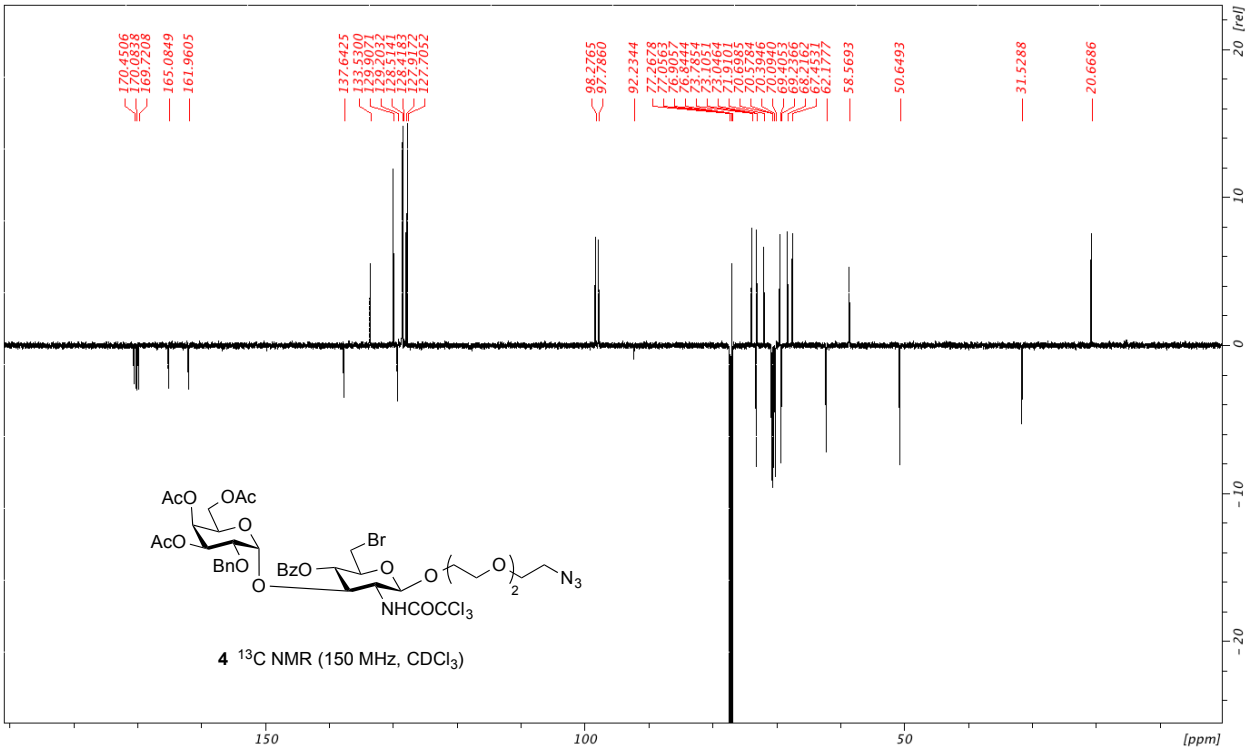
3 ^{1}H NMR (600 MHz, $CDCl_3$)



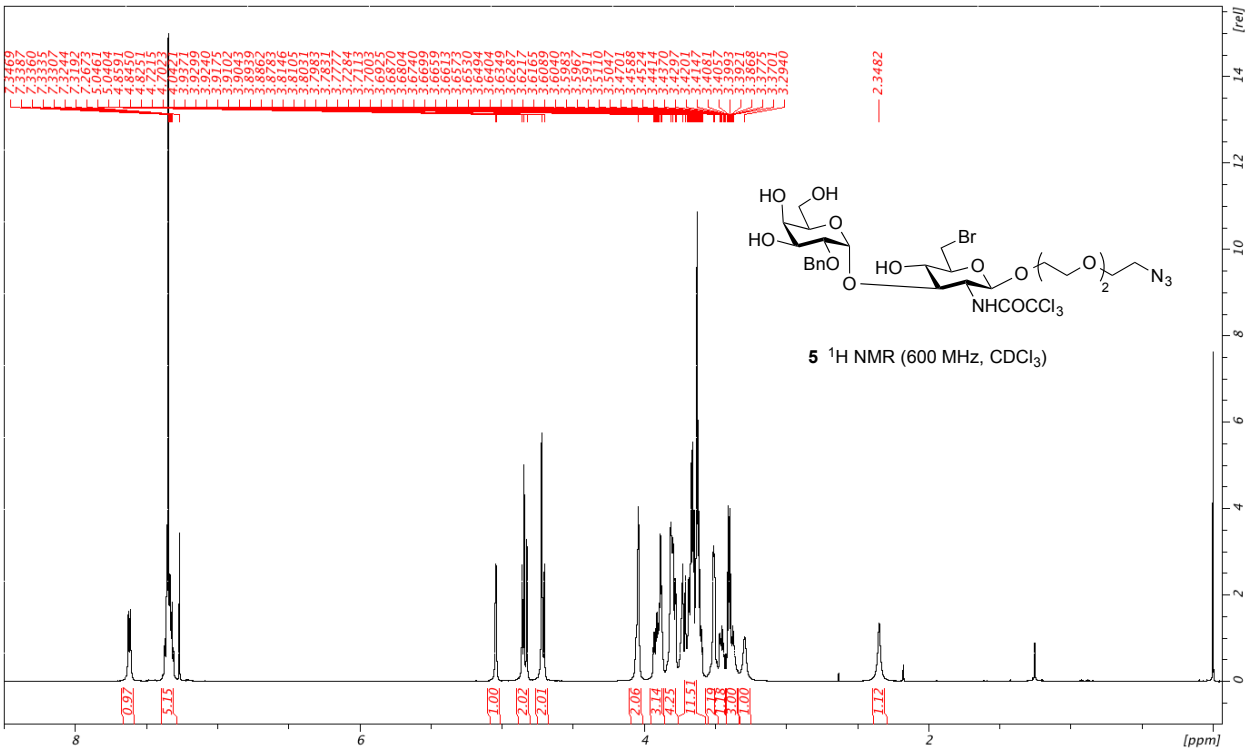
3 ^{13}C NMR (150 MHz, $CDCl_3$)



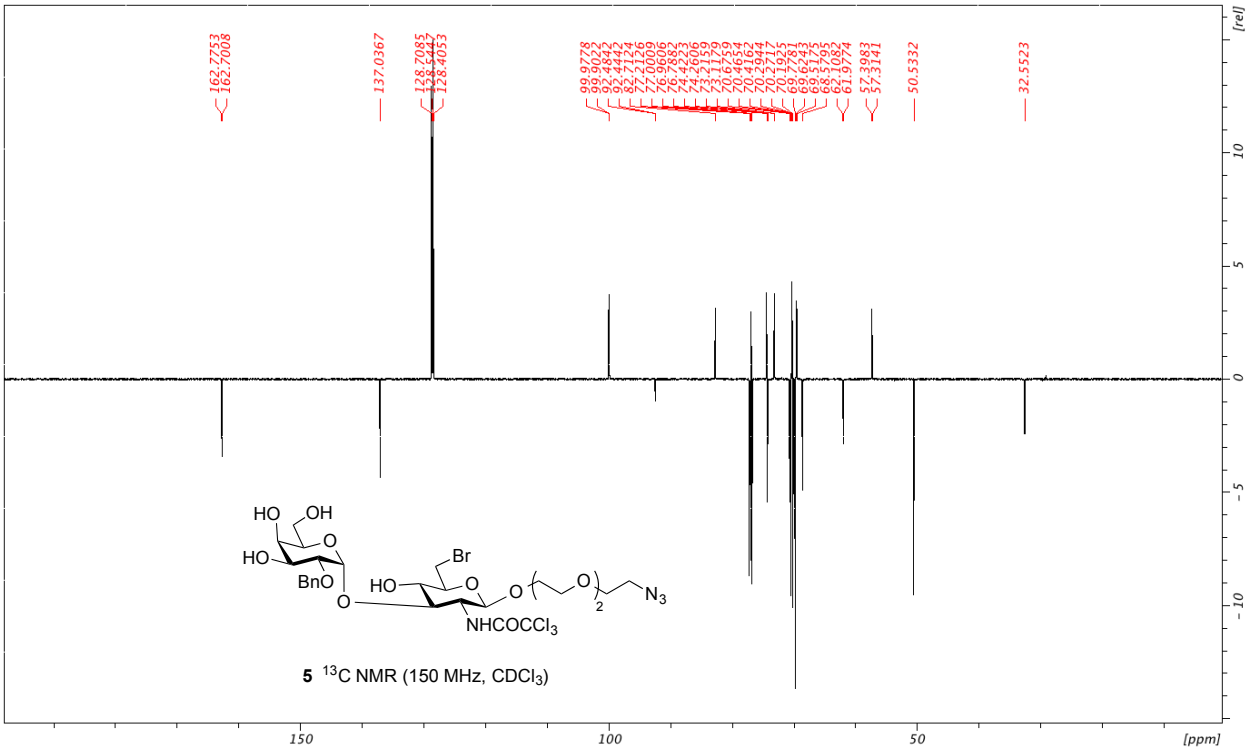
4 ^{1}H NMR (600 MHz, $CDCl_3$)



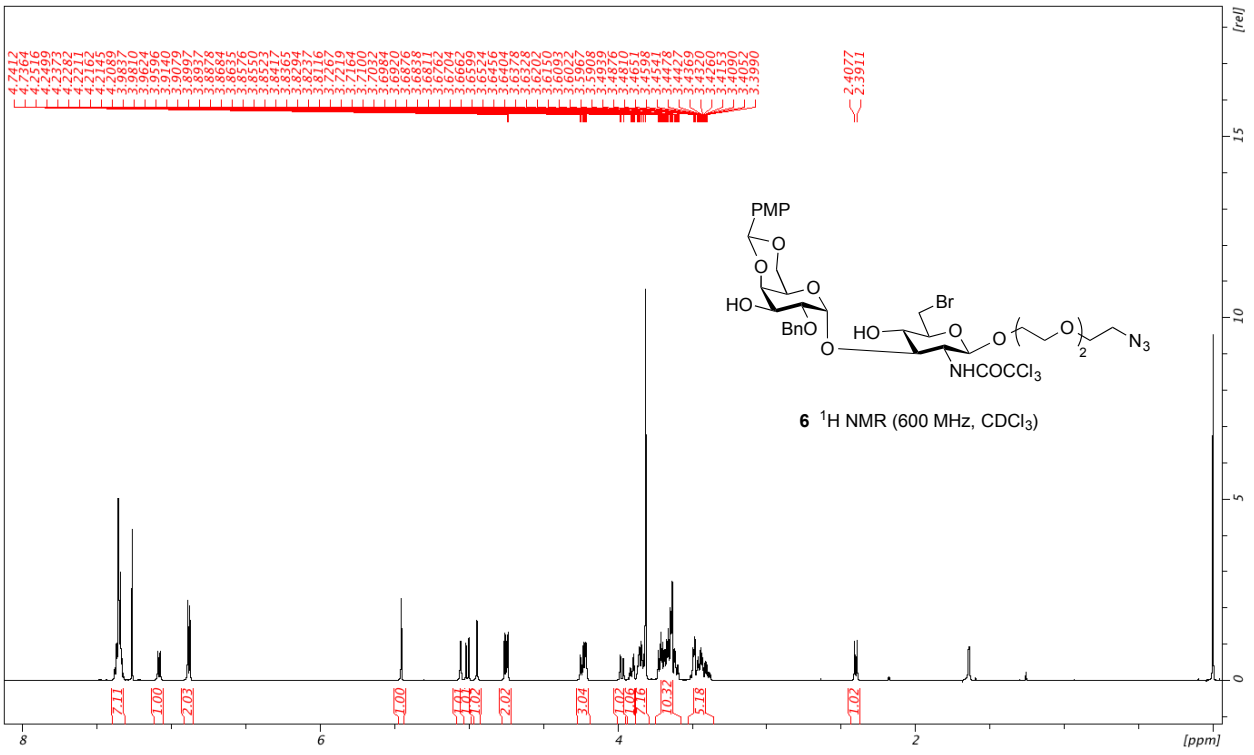
4 ^{13}C NMR (150 MHz, $CDCl_3$)



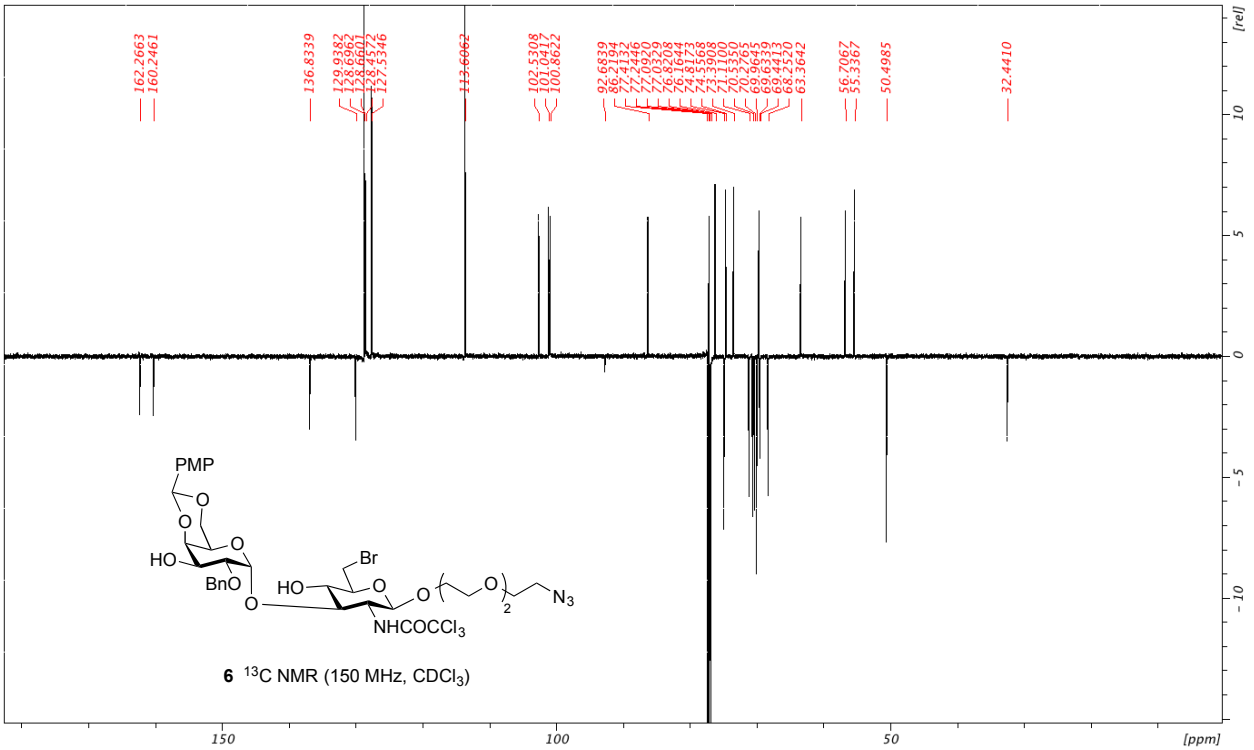
5 ^{1}H NMR (600 MHz, $CDCl_3$)



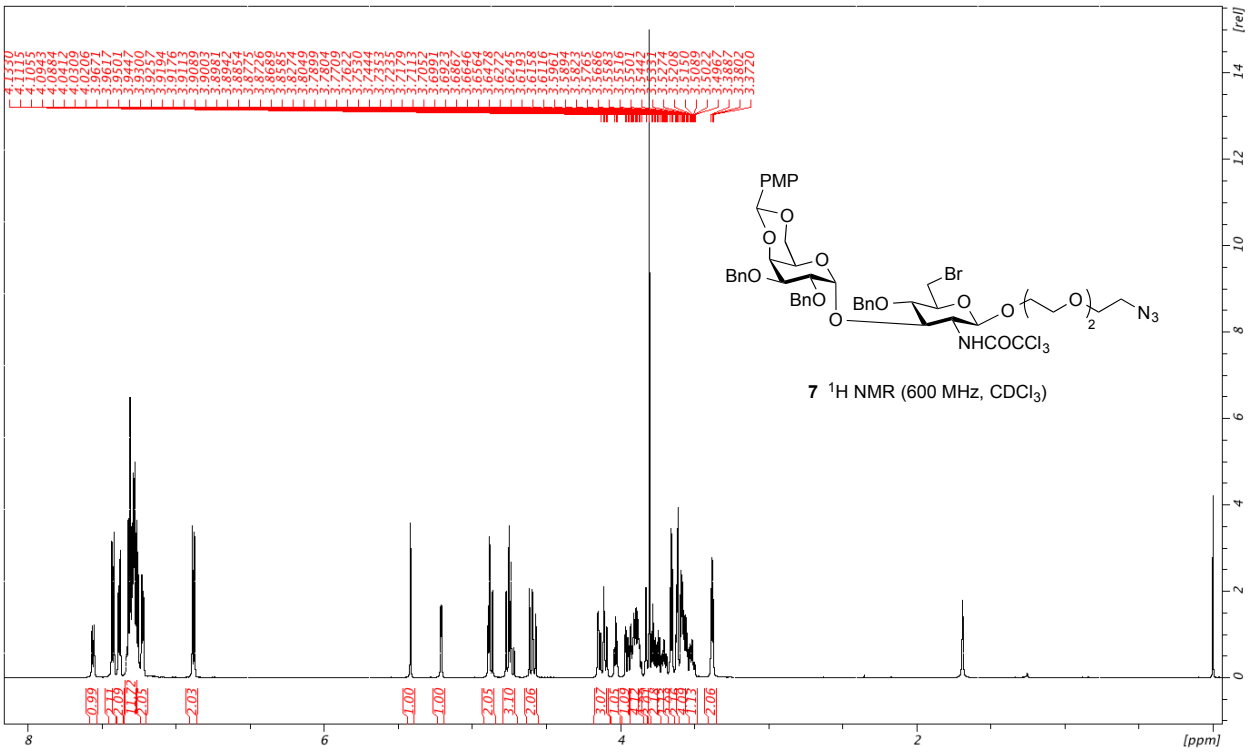
5 ^{13}C NMR (150 MHz, $CDCl_3$)



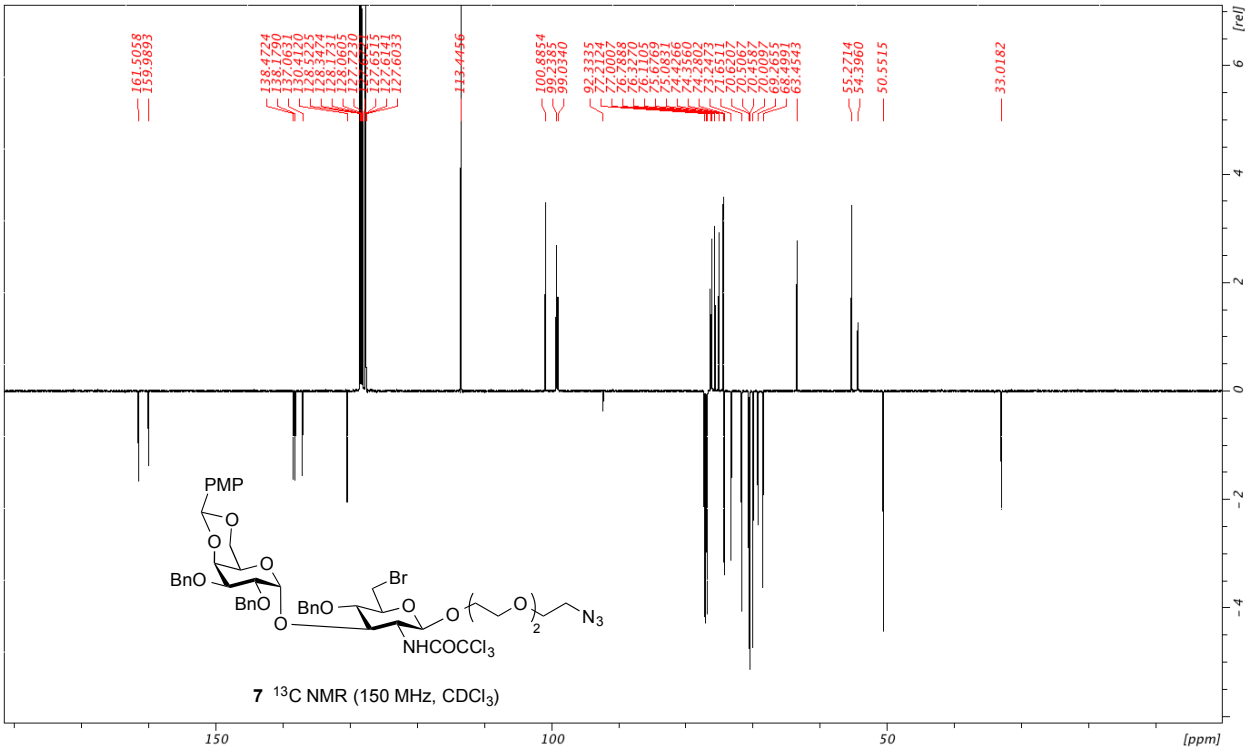
6 ^{1}H NMR (600 MHz, $CDCl_3$)



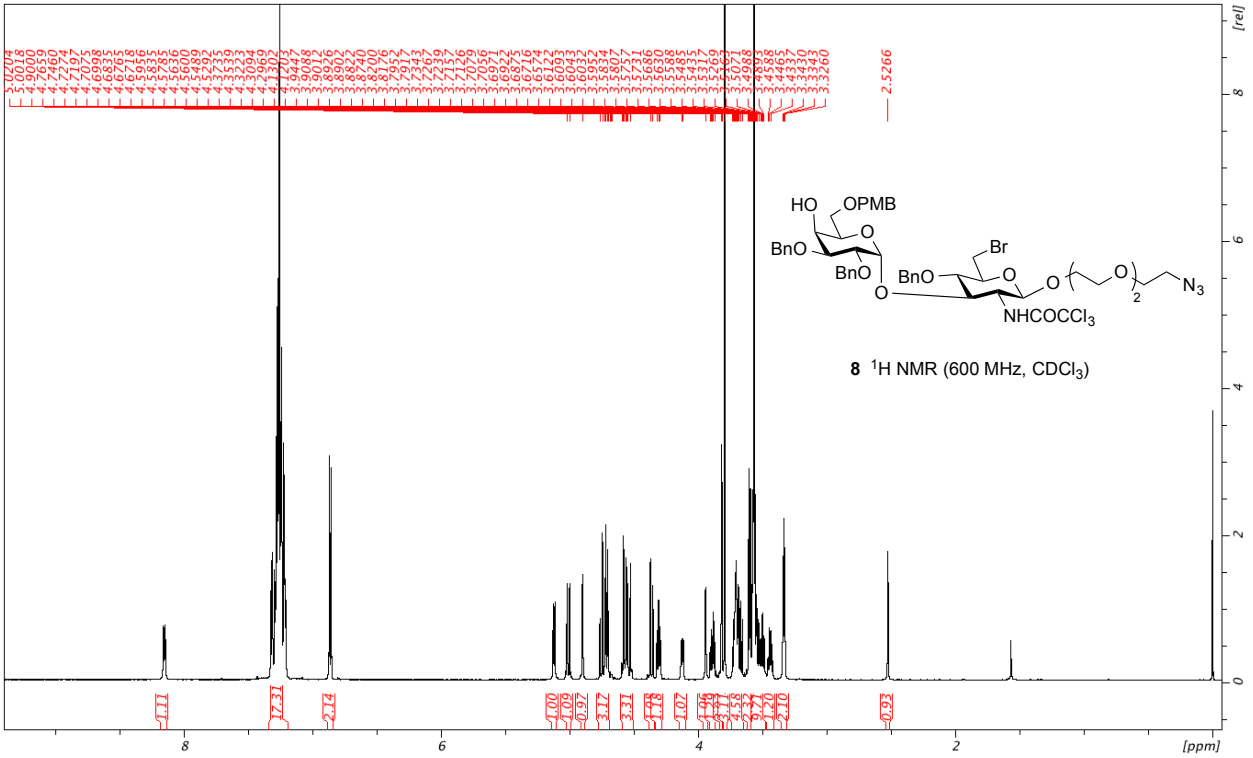
6 ^{13}C NMR (150 MHz, $CDCl_3$)



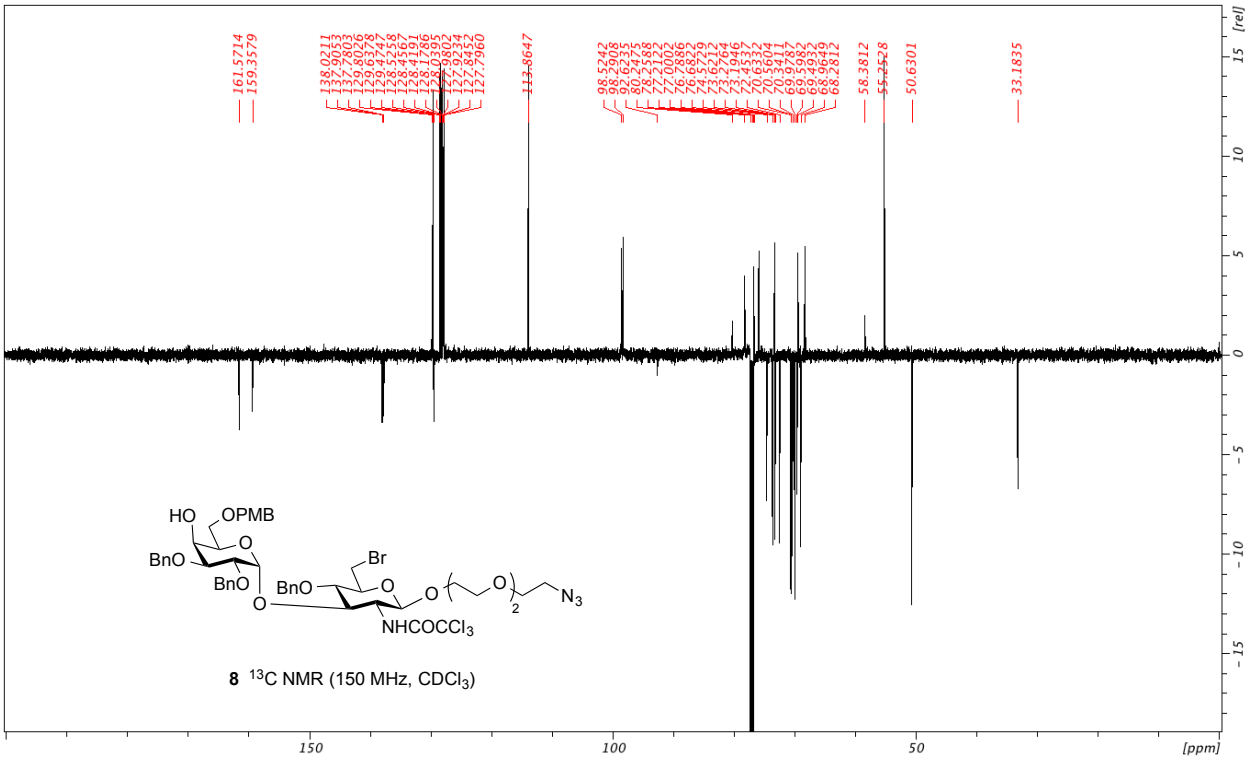
7 ^{1}H NMR (600 MHz, $CDCl_3$)



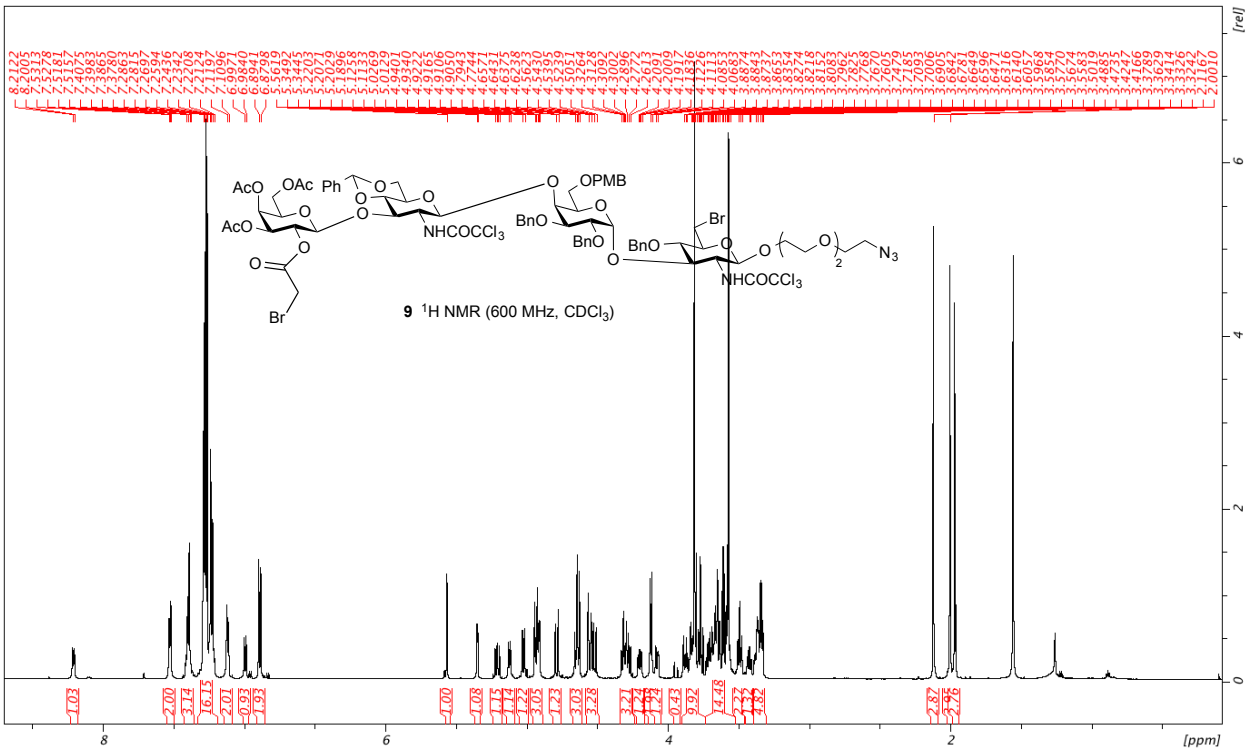
7 ^{13}C NMR (150 MHz, $CDCl_3$)

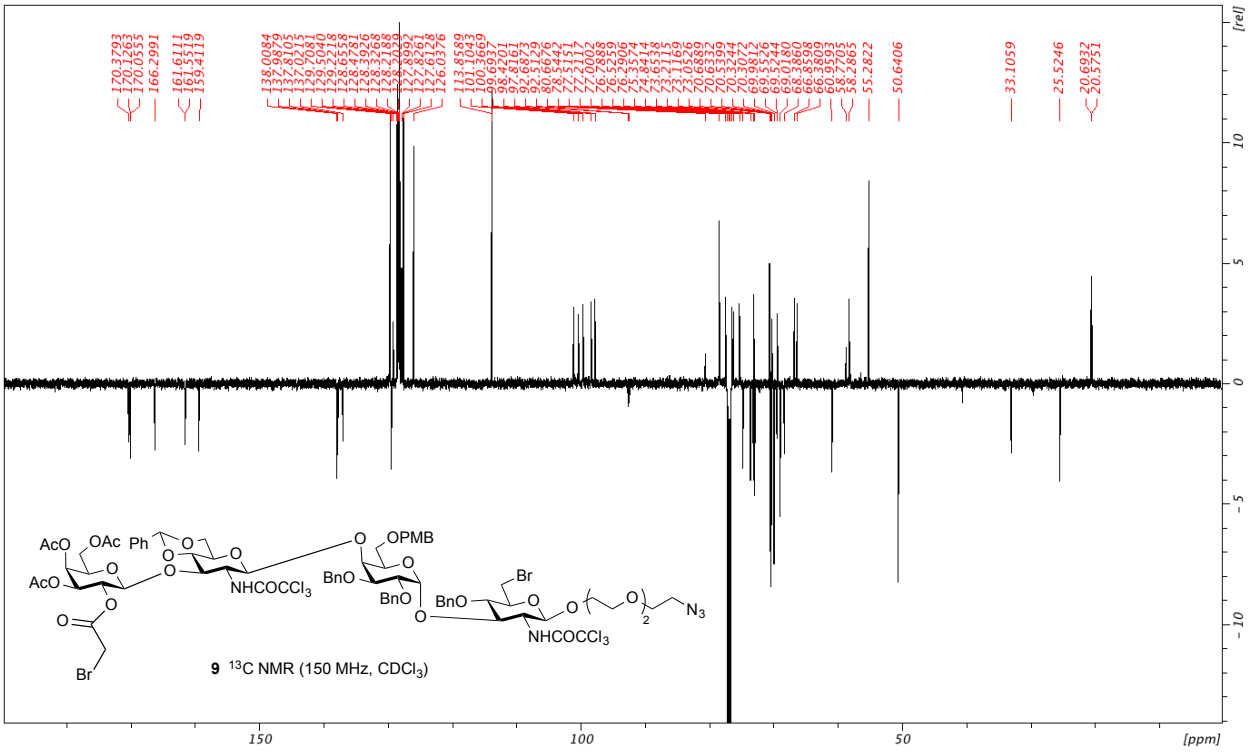


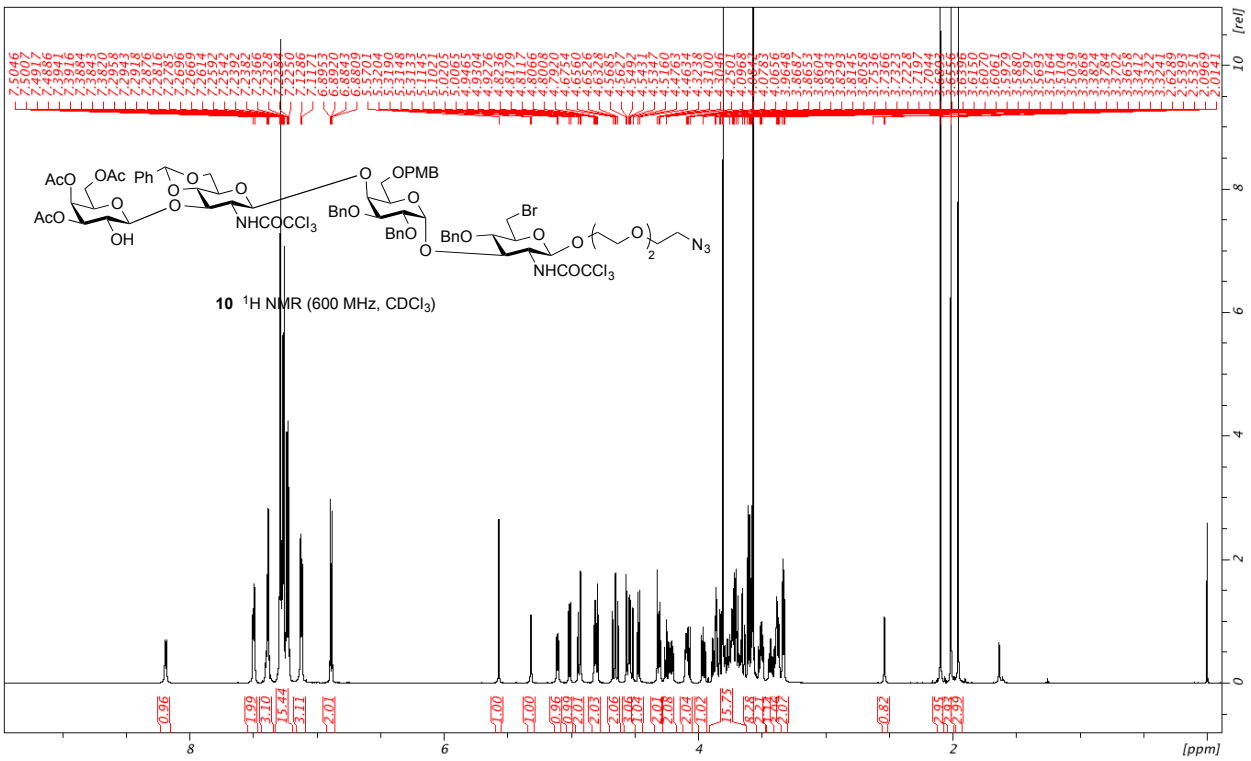
8 ^{1}H NMR (600 MHz, $CDCl_3$)



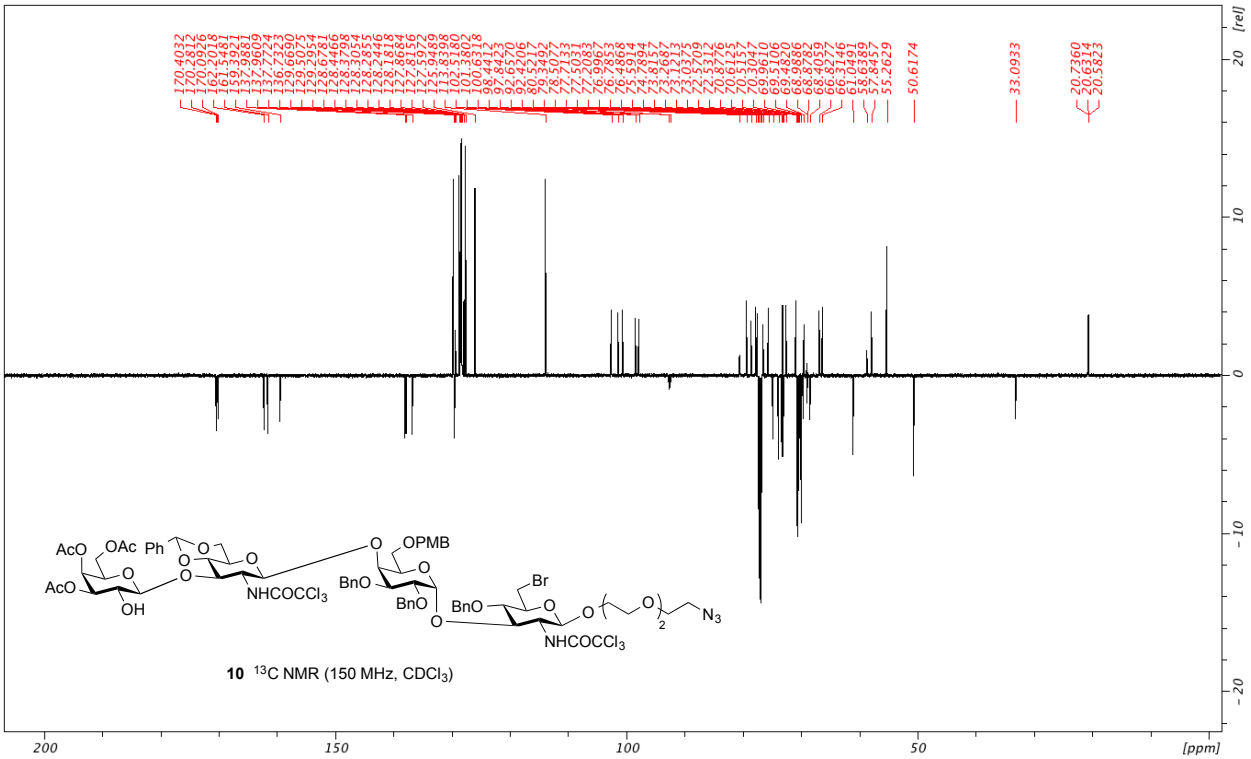
8 ^{13}C NMR (150 MHz, $CDCl_3$)


9 ^{1}H NMR (600 MHz, $CDCl_3$)
[ppm]
[rel]

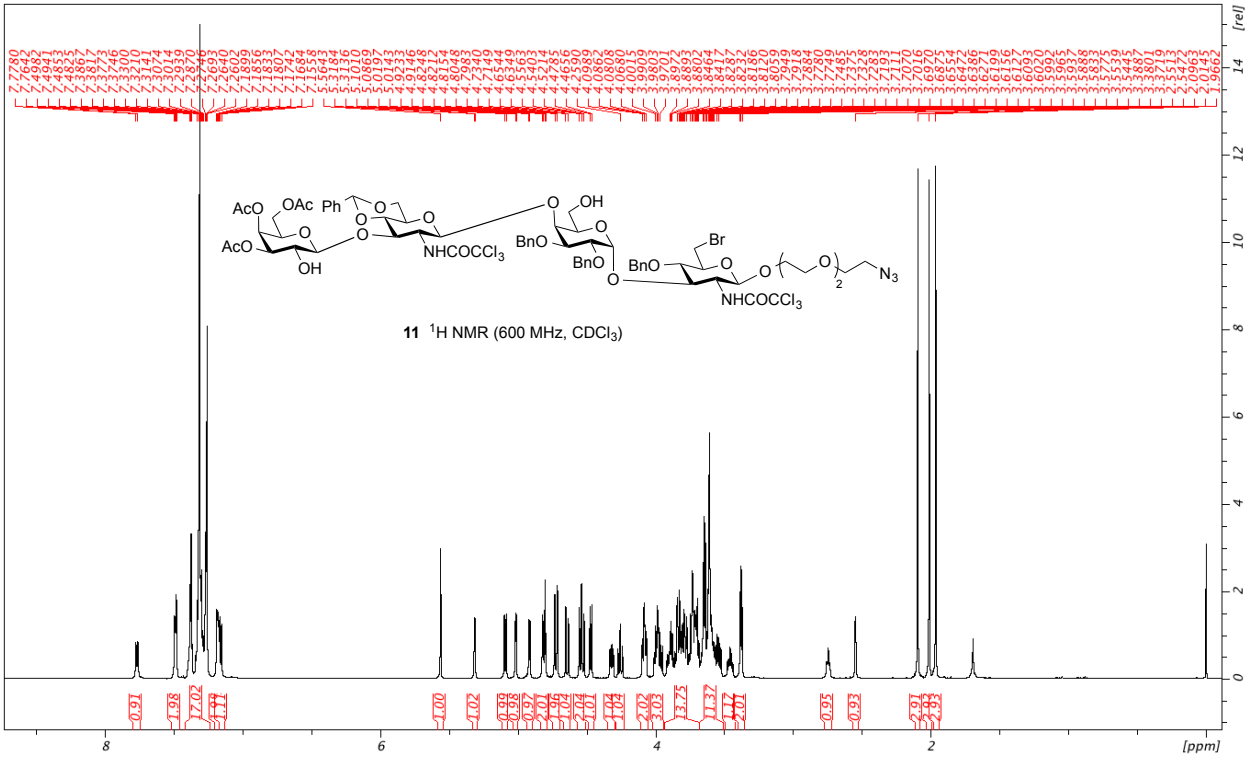

9 ^{13}C NMR (150 MHz, $CDCl_3$)
[ppm]
[rel]

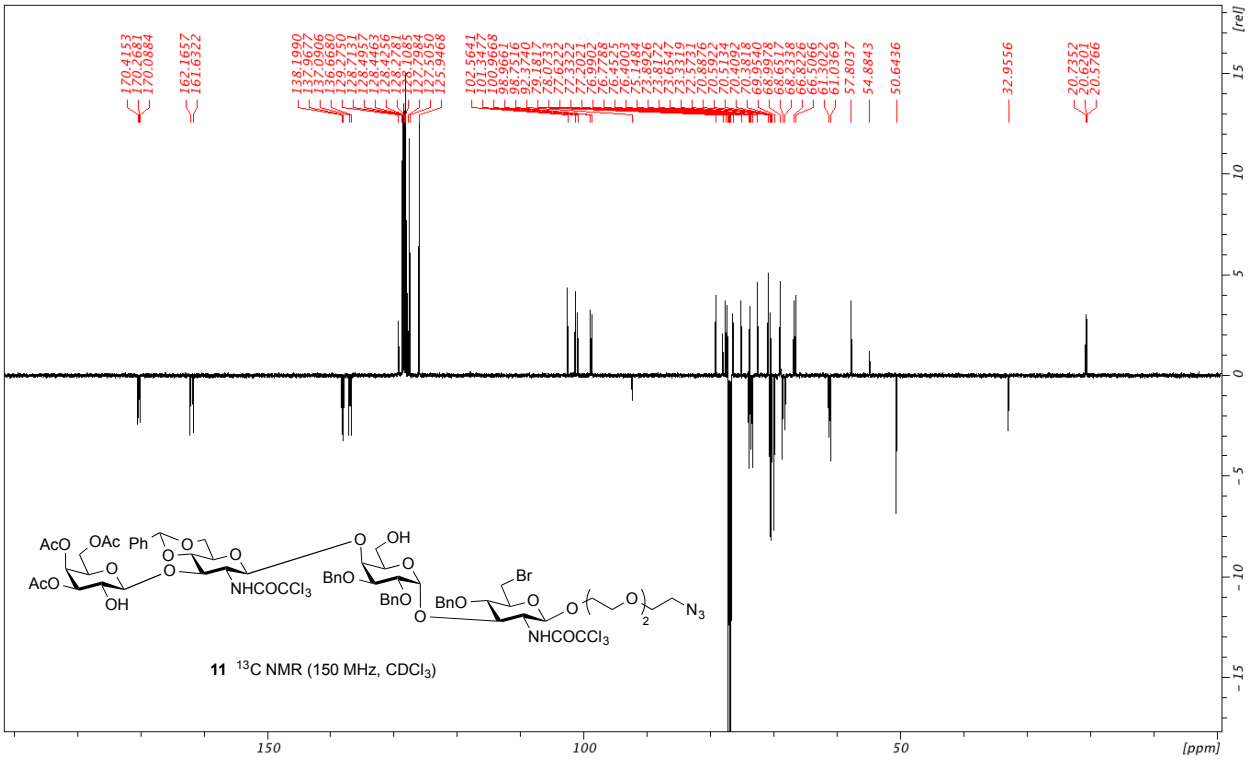


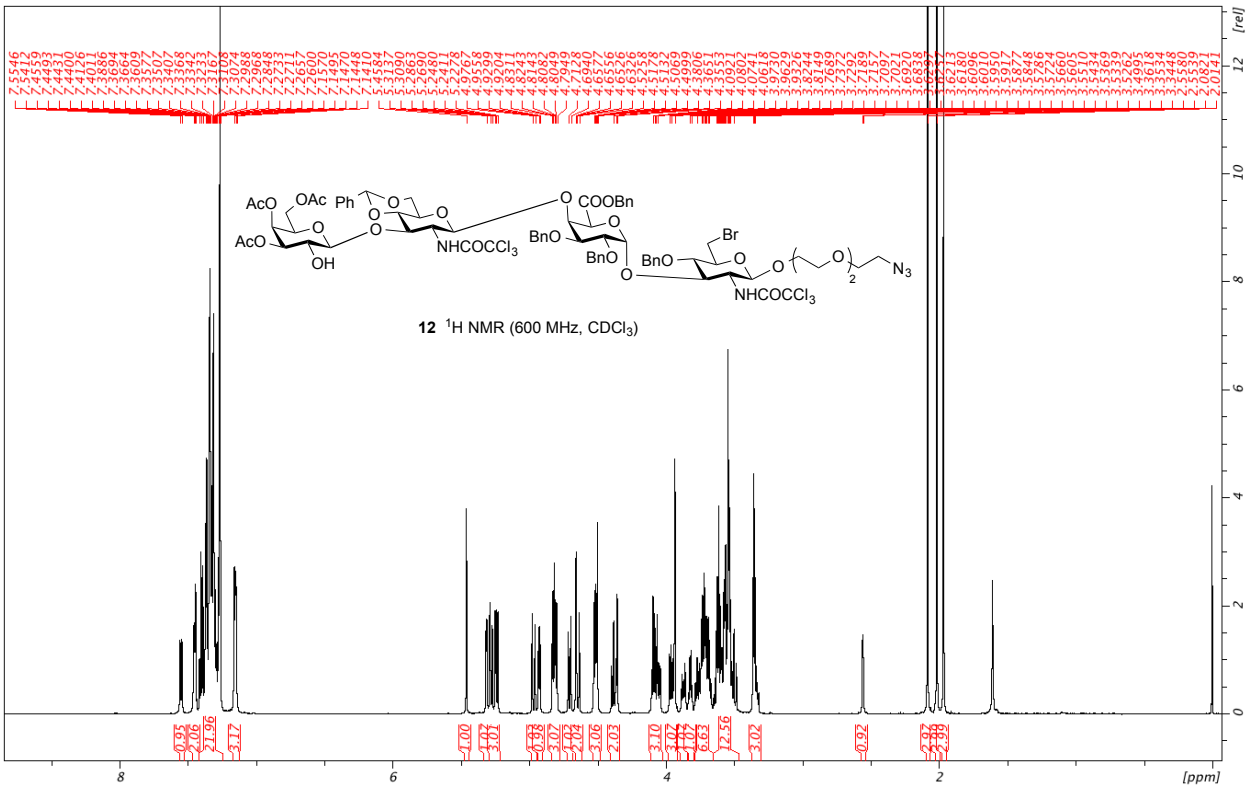
10 ^{1}H NMR (600 MHz, $CDCl_3$)

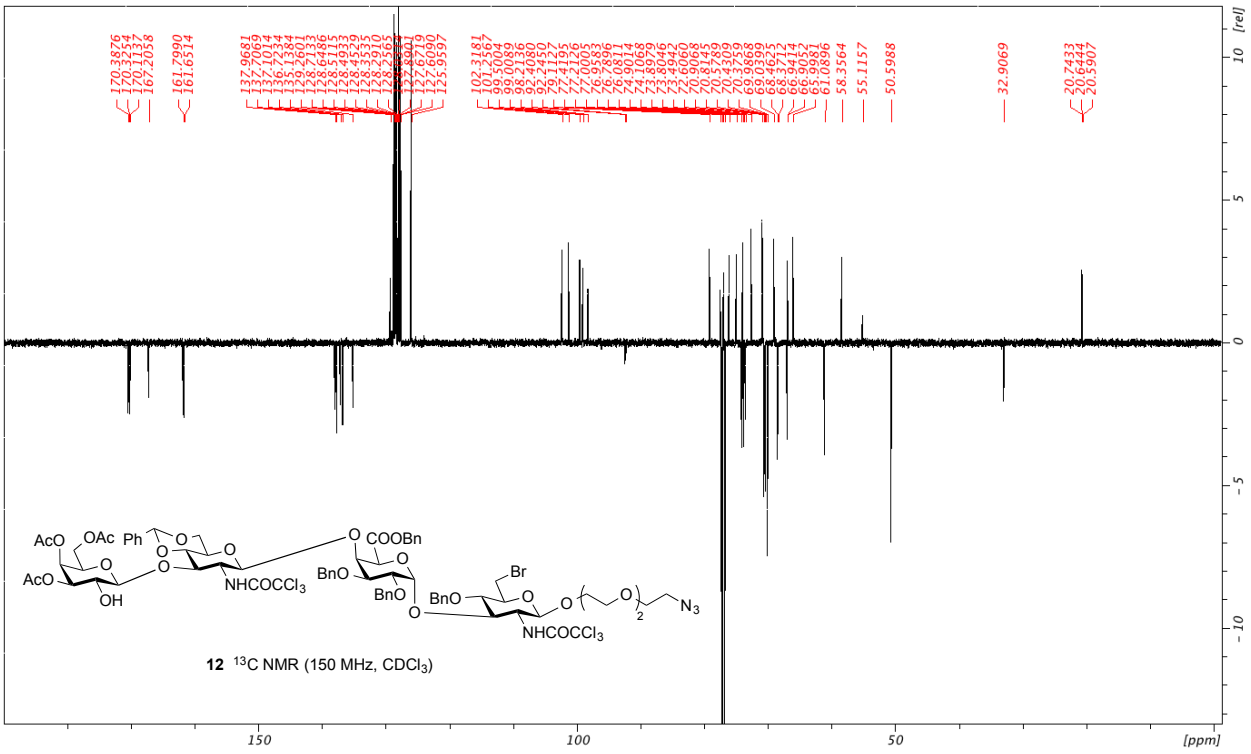


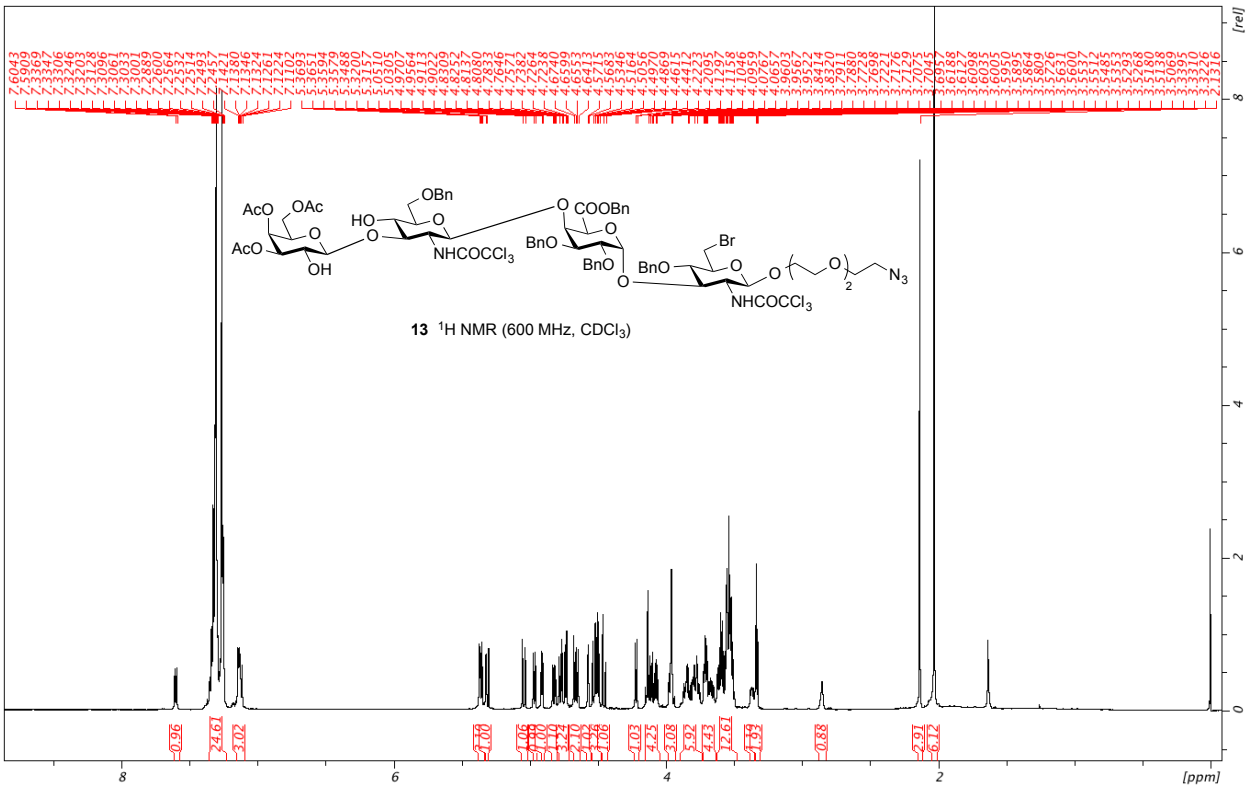
10 ^{13}C NMR (150 MHz, $CDCl_3$)

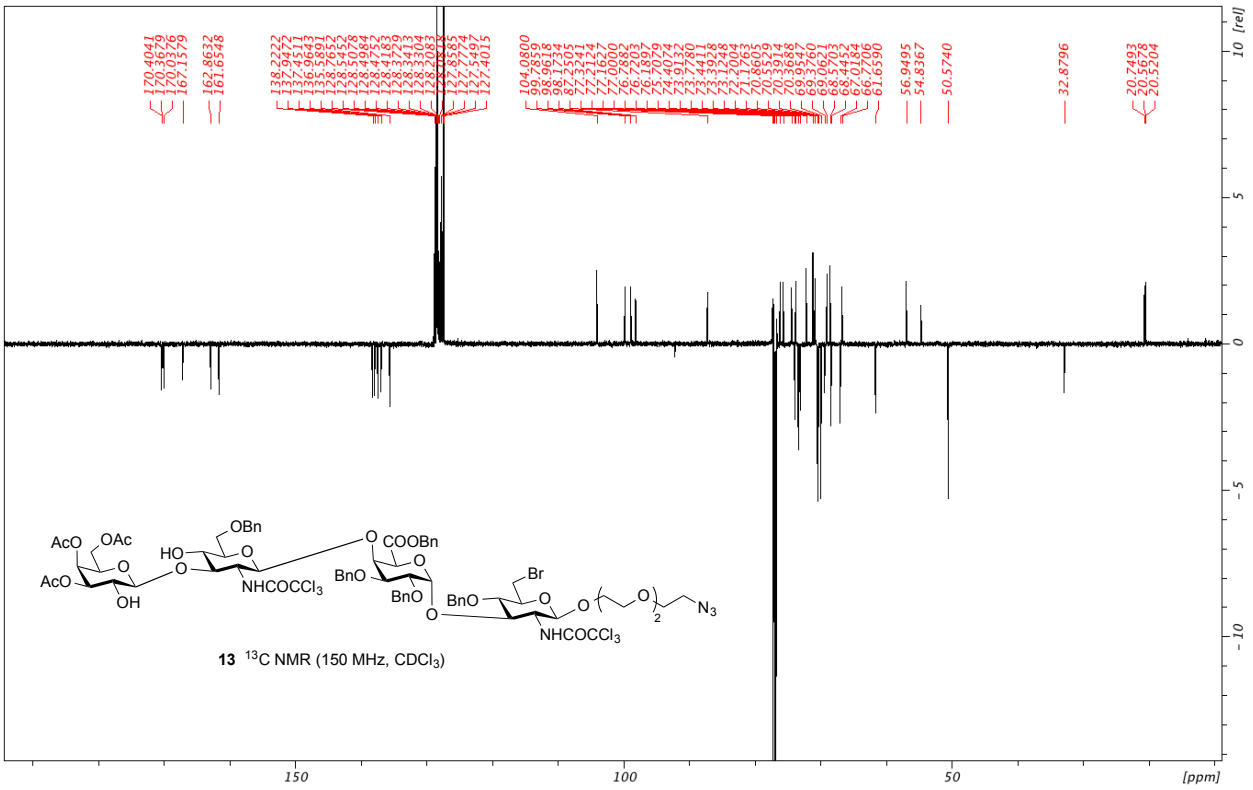

11 ^{1}H NMR (600 MHz, $CDCl_3$)

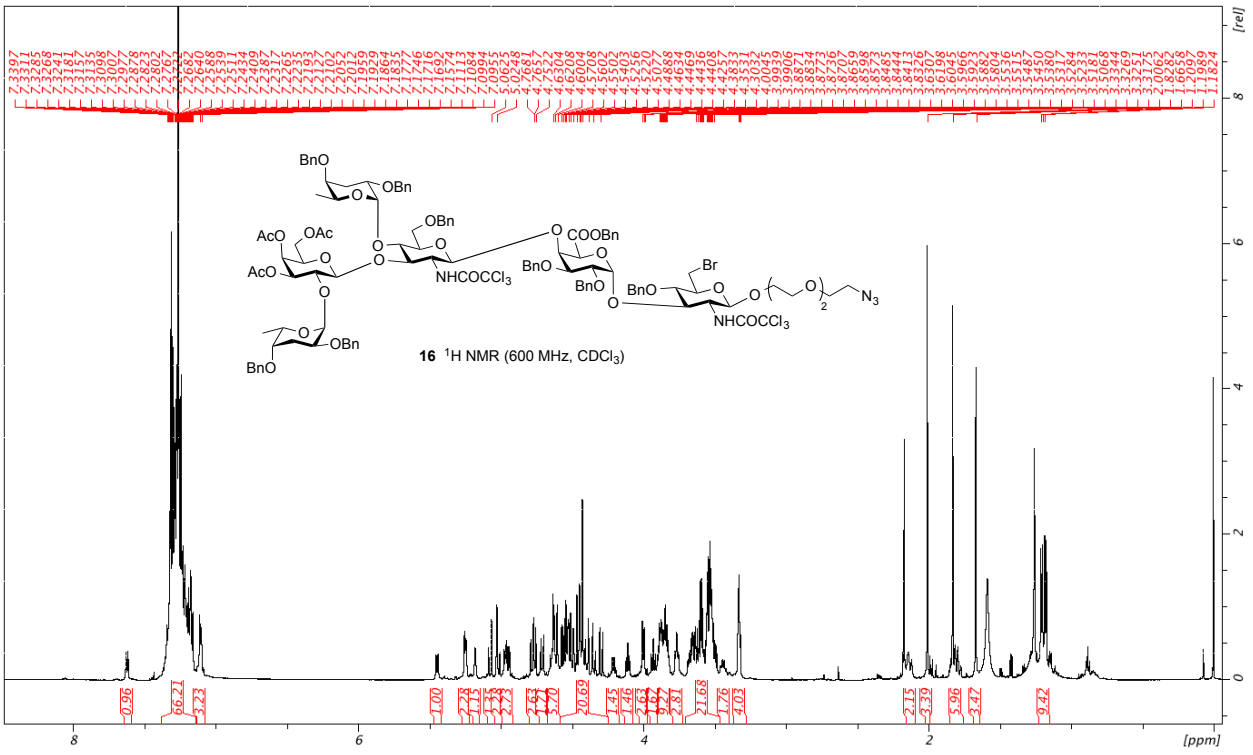

11 ^{13}C NMR (150 MHz, $CDCl_3$)

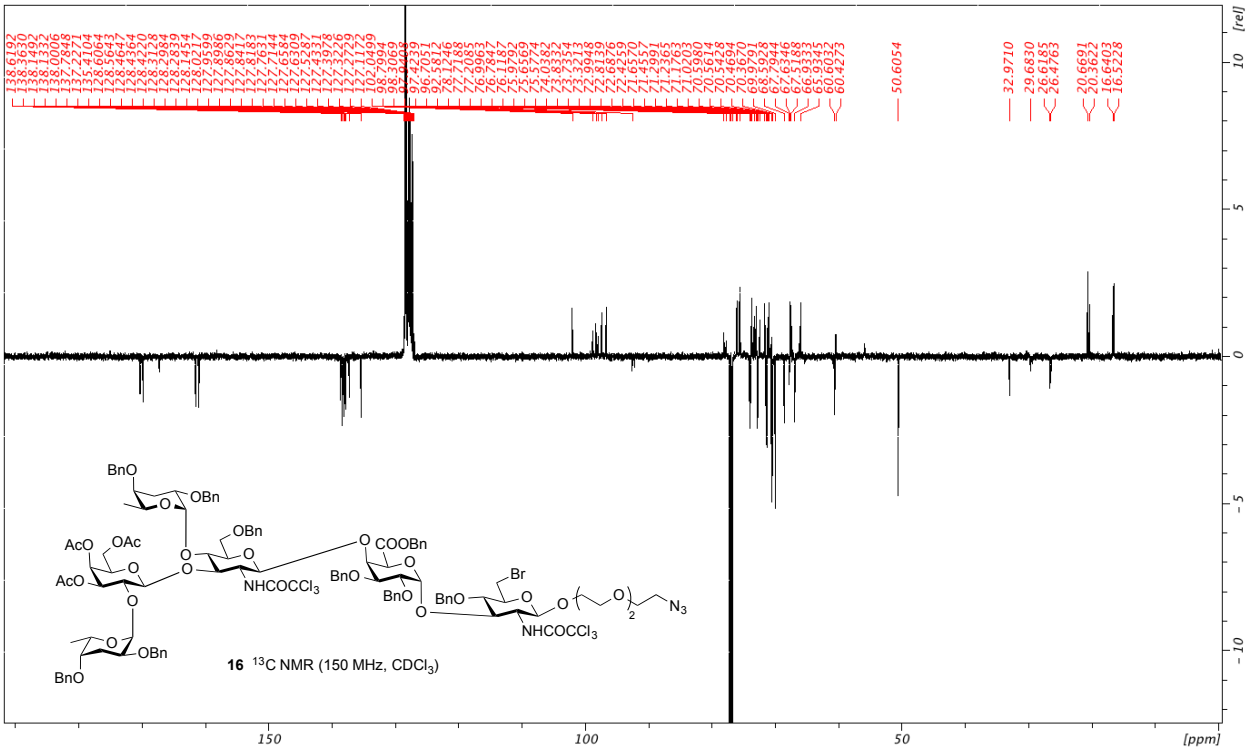

12 ^{1}H NMR (600 MHz, $CDCl_3$)

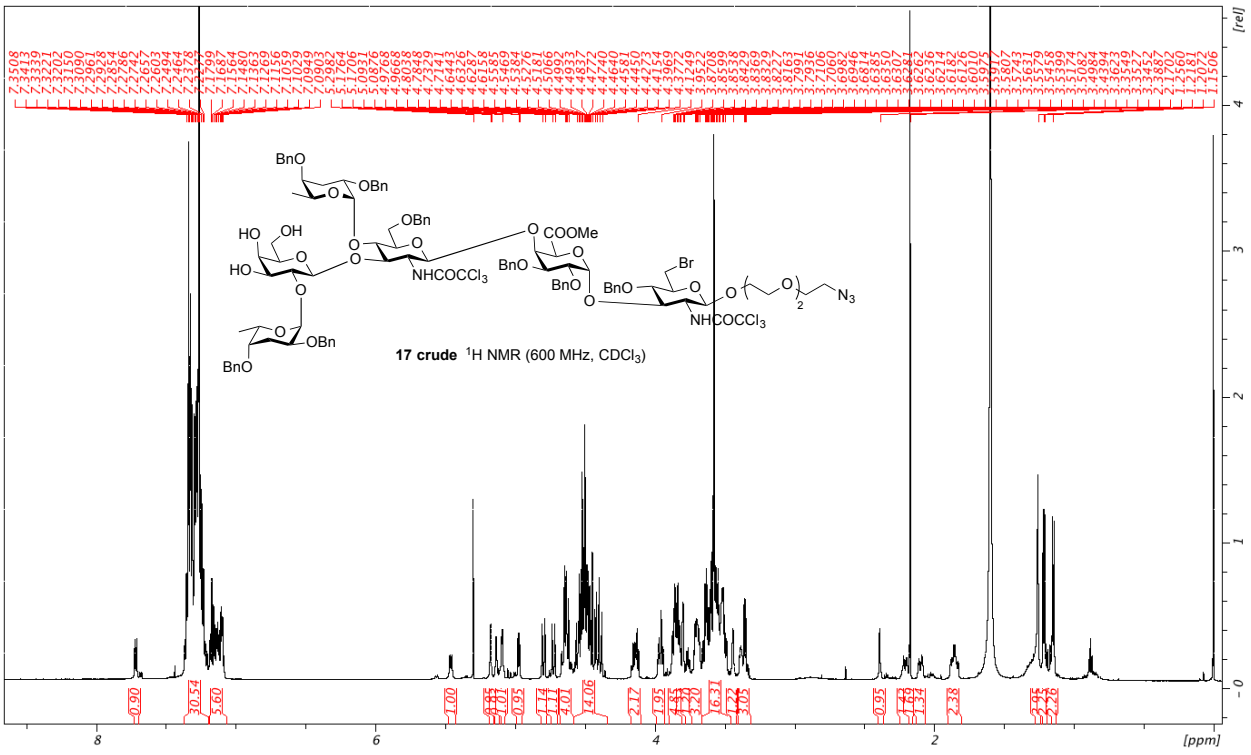

12 ^{13}C NMR (150 MHz, $CDCl_3$)

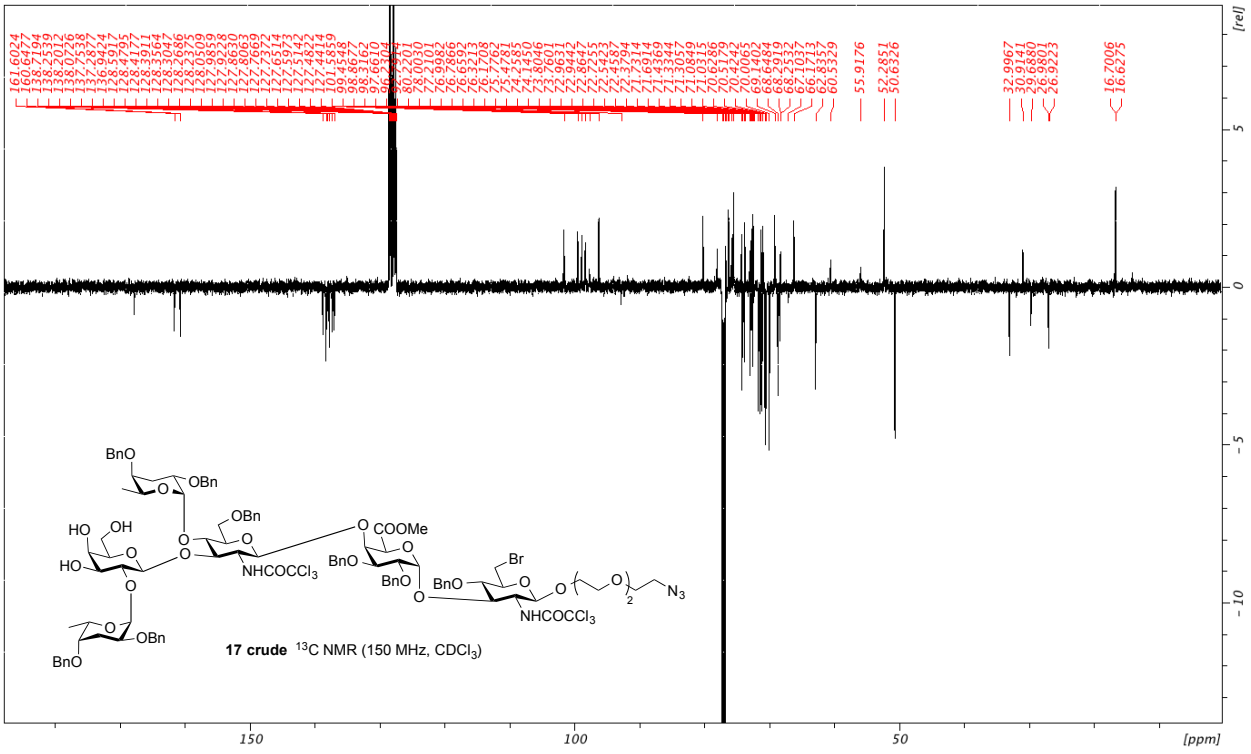

13 ^{1}H NMR (600 MHz, $CDCl_3$)

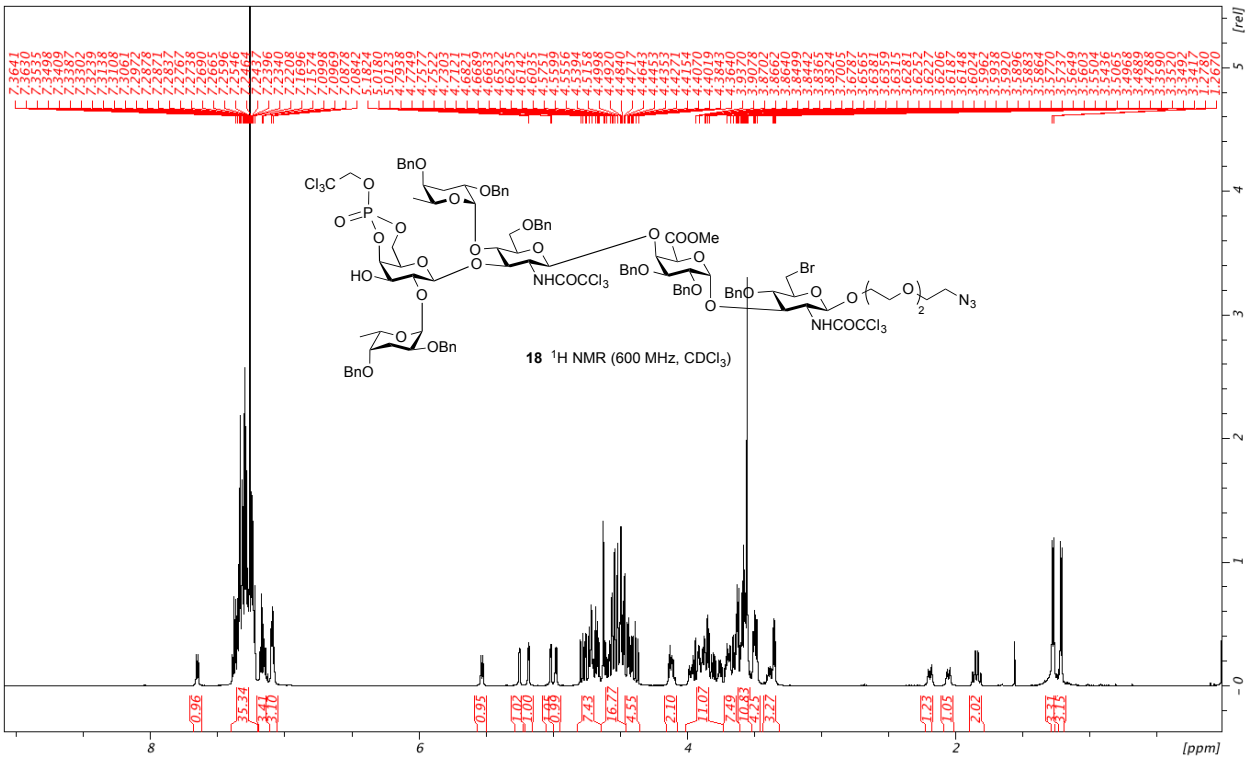

13 ^{13}C NMR (150 MHz, $CDCl_3$)

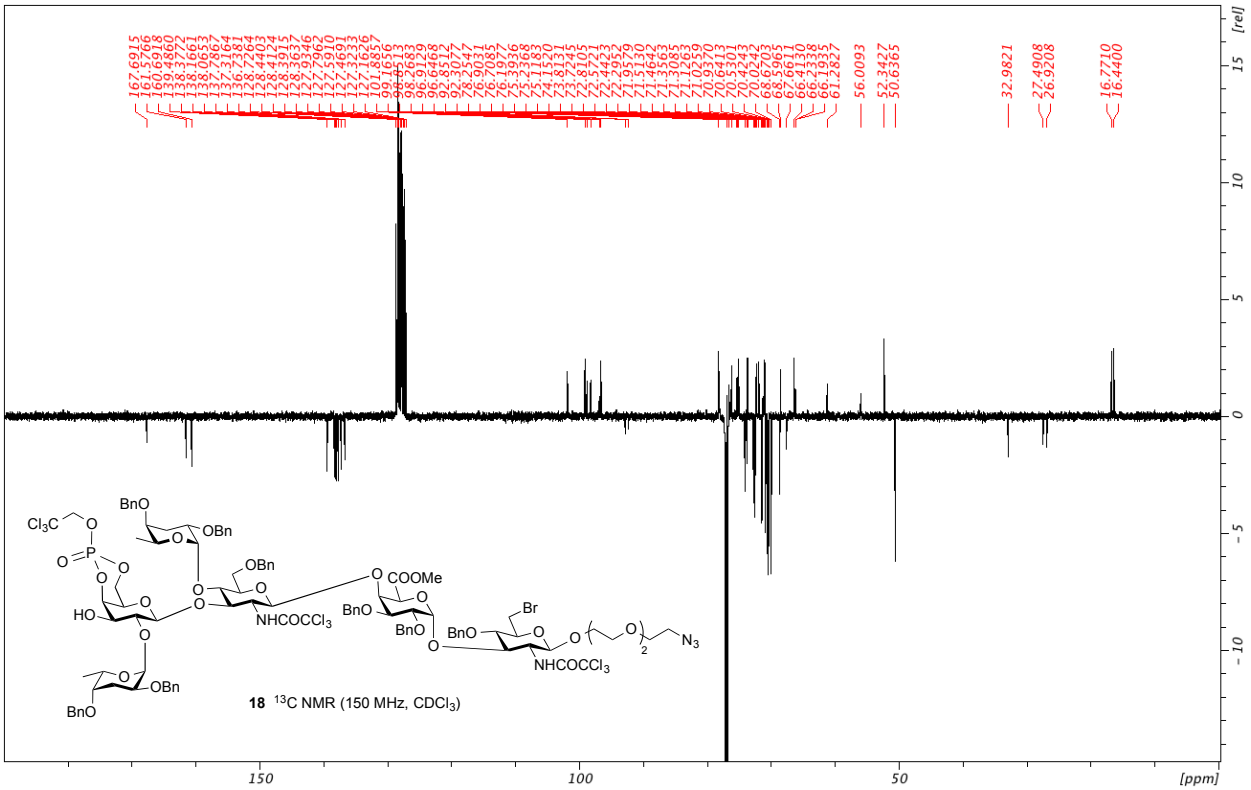

16 ^{1}H NMR (600 MHz, $CDCl_3$)

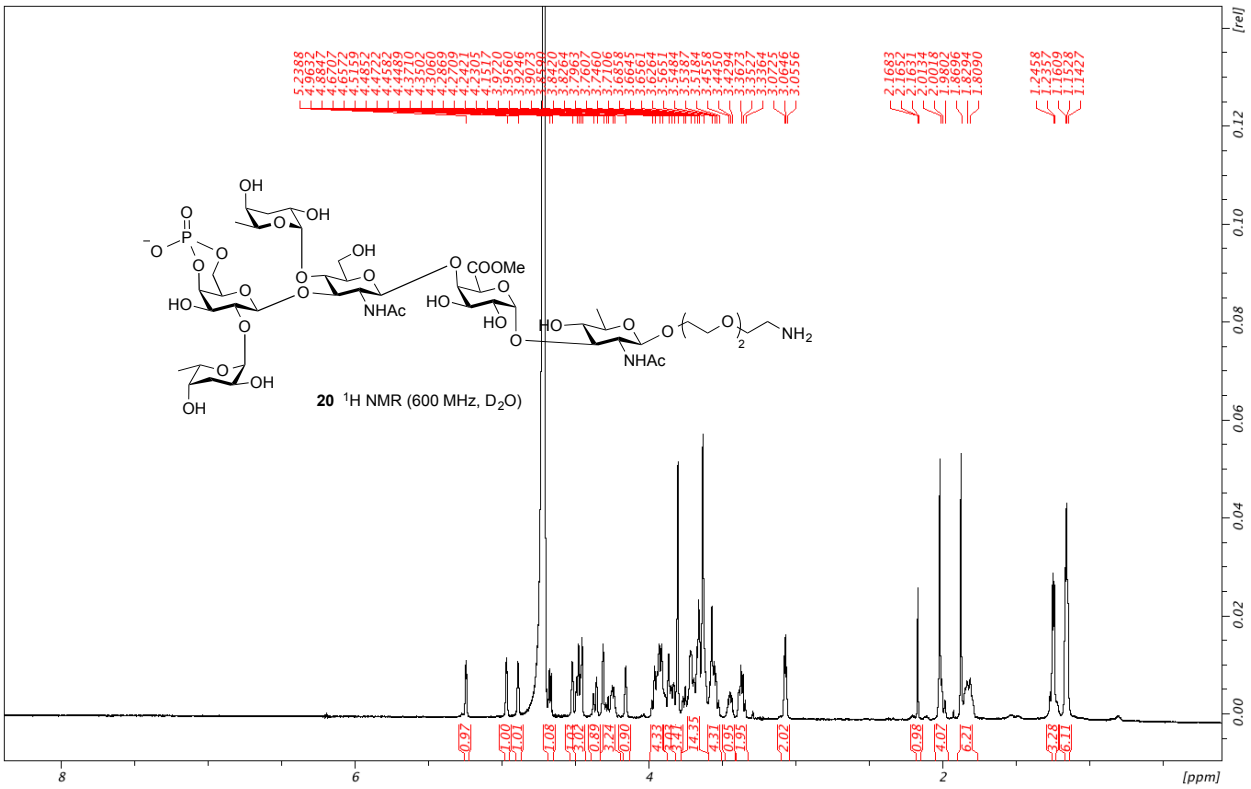

16 ^{13}C NMR (150 MHz, $CDCl_3$)

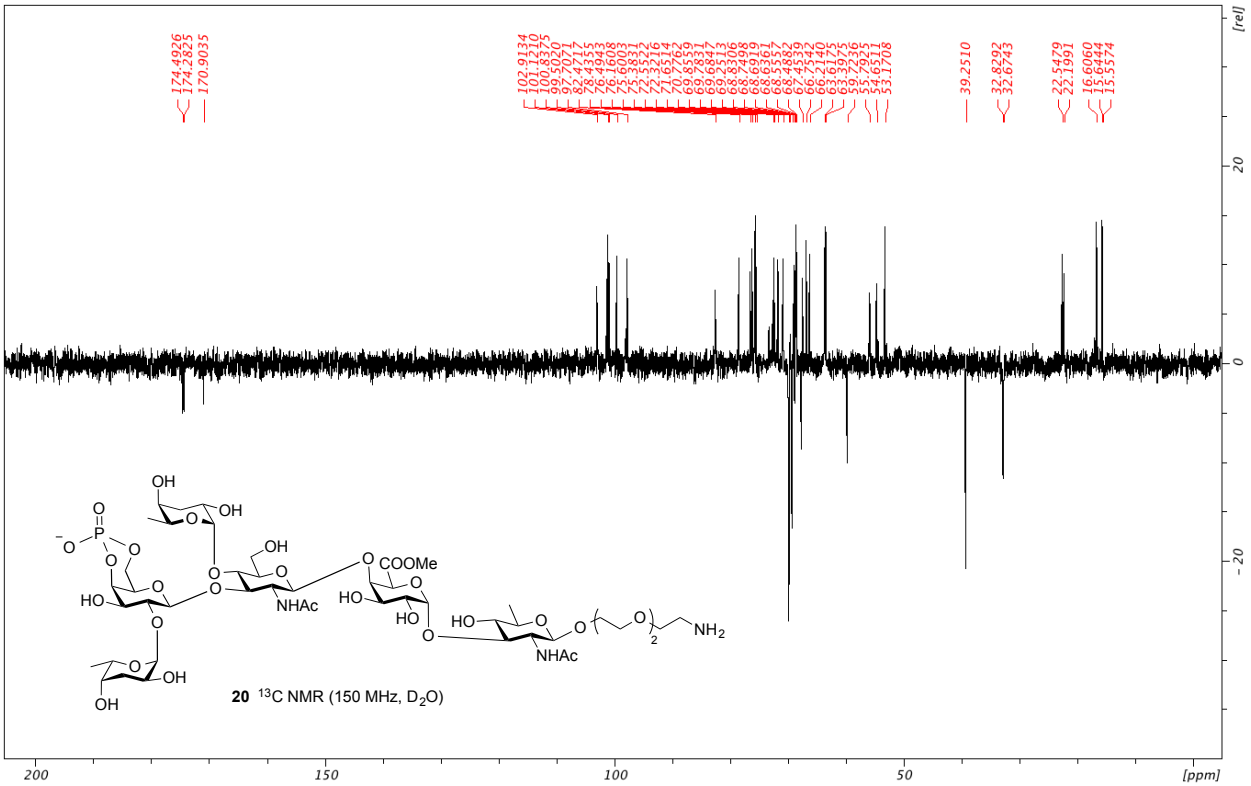

17 crude ^{1}H NMR (600 MHz, $CDCl_3$)
[ppm]
[rel]

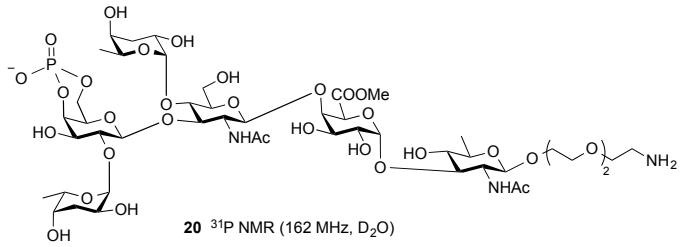

17 crude ^{13}C NMR (150 MHz, $CDCl_3$)
[ppm]
[rel]


18 ^{1}H NMR (600 MHz, $CDCl_3$)
[rel]
[ppm]


18 ^{13}C NMR (150 MHz, $CDCl_3$)
[rel]
[ppm]

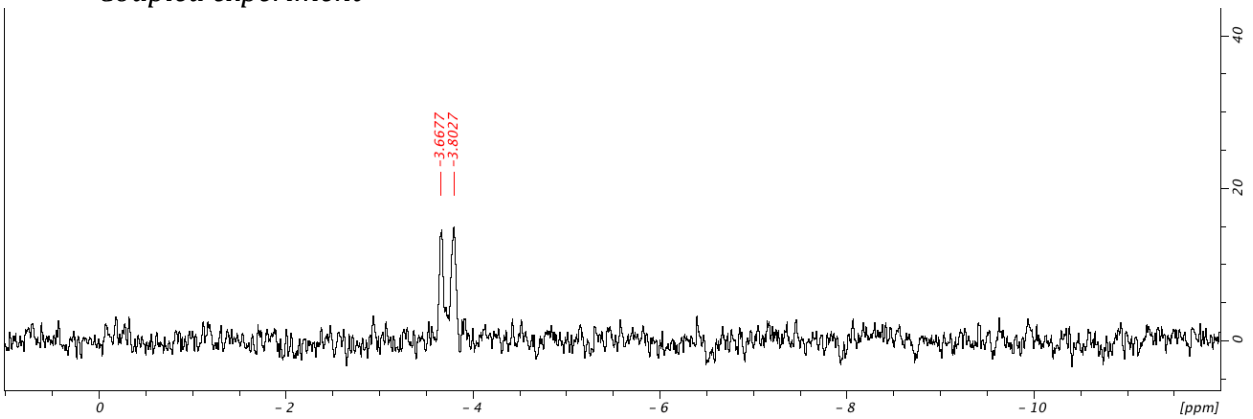

20 ^{1}H NMR (600 MHz, D_2O)


20 ^{13}C NMR (150 MHz, D_2O)

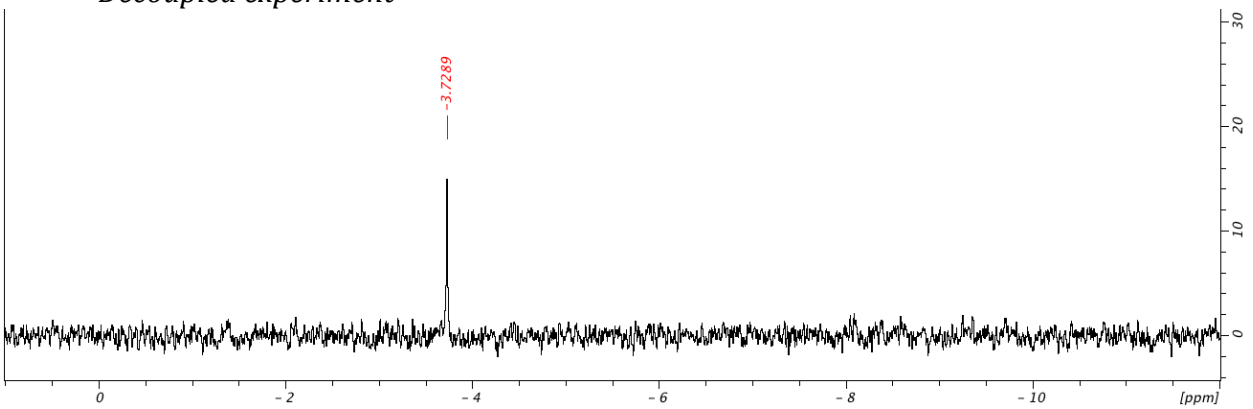


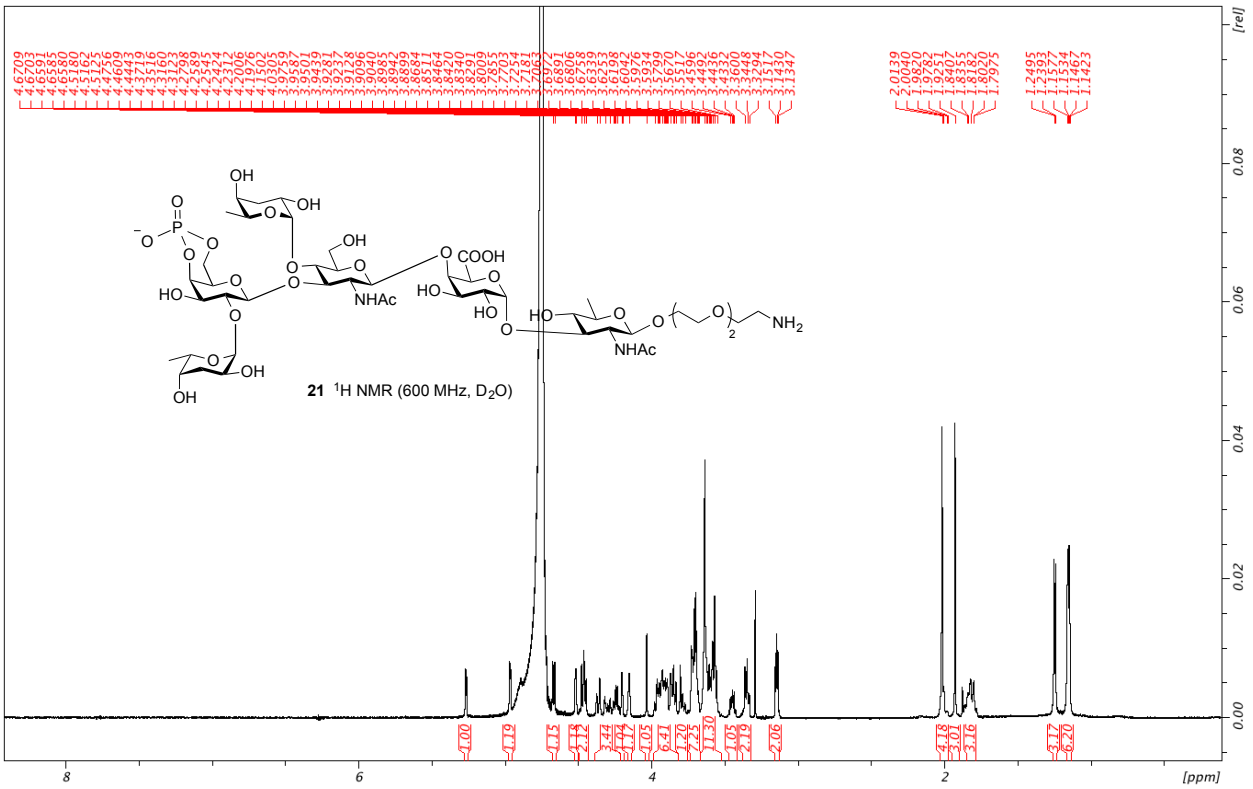
20 ^{31}P NMR (162 MHz, D_2O)

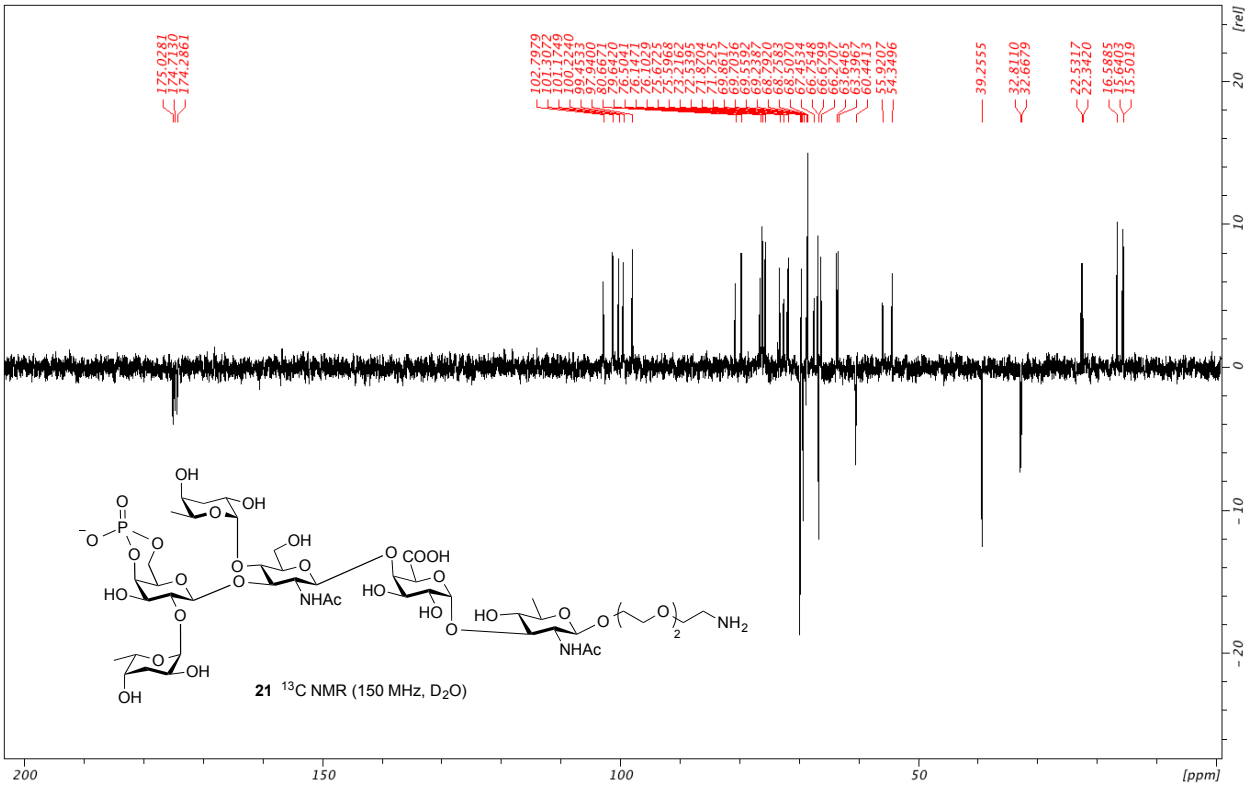
Coupled experiment

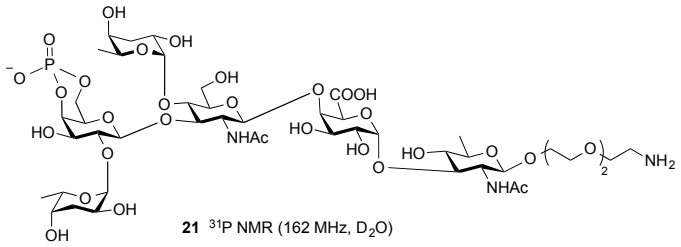


Decoupled experiment



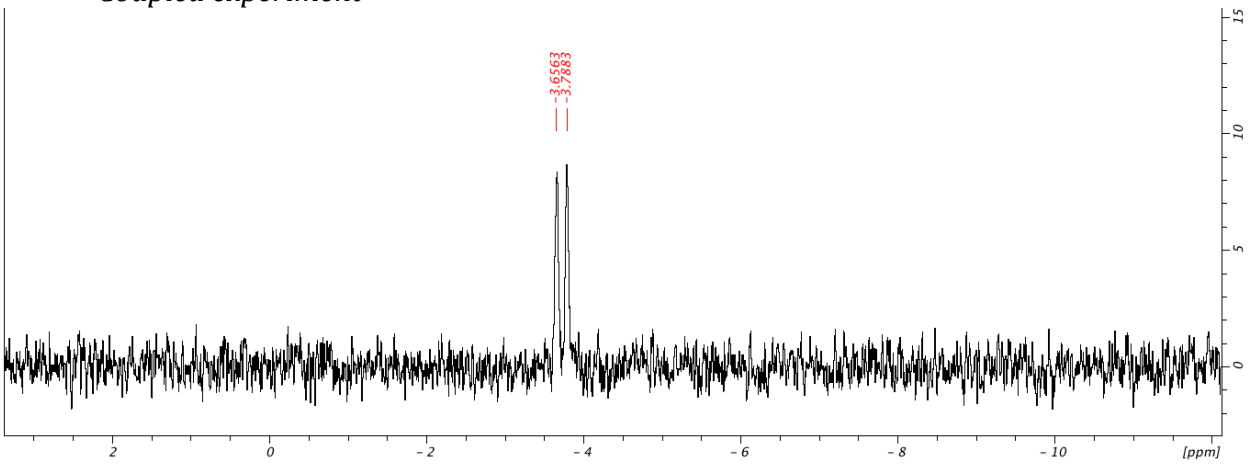

21 ^{1}H NMR (600 MHz, D_2O)


21 ^{13}C NMR (150 MHz, D_2O)



21 ^{31}P NMR (162 MHz, D_2O)

Coupled experiment



Decoupled experiment