

Electronic Supporting Information

A Straightforward Synthesis of Man₉, the relevant epitope of the High-Mannose Oligosaccharide

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General. Reagents and solvents were purchased as reagent grade and used without further purification. *p*-Tolyl 4,6-*O*-benzylidene-1-thio- α -D-mannopyranoside (**21**),¹ *p*-tolyl 4,6-*O*-

benzylidene-3-*O*-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (**22**)² compound **6**,³ compound **7**⁴ and compounds **10-11**⁵ were prepared according to the literature. Silica gel 60n (230-400 mesh, 0.015-0.04 mm) for column chromatography was purchased from Merck and Sephadex G25 from GE Healthcare (Barcelona, Spain) for gel filtration. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F₂₅₄ purchased from Merck and visualized by UV light. NMR spectra were recorded on a Bruker AC 400 with solvent peaks as reference. ¹H and ¹³C NMR spectra were obtained from solutions in CDCl₃ and D₂O at 298K. Coupling constants (*J*) are reported in Hz. Splitting patterns are described by using the following abbreviations: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; td, triplet of doublet; dt, doublet of triplet; m, multiplet. ¹H-NMR spectra are reported in this order: chemical shift; multiplicity; coupling constant(s); number(s) of proton. All the assignments were confirmed by one- and two-dimensional NMR experiments (COSY and HSQC). Coupled HSQC NMR experiments were used to verify the stereochemistries of newly created linkage which were unambiguously confirmed by the magnitude of the J_{C,H} coupling constant.⁶ ESI-mass spectra were recorded with an Esquire 6000 ESI-Ion Trap from Bruker Daltonics using CH₂Cl₂/MeOH or MeOH/H₂O as solvent system.

Synthesis and characterization.

¹ Sanapala, S. R.; Kulkarni, S. S. *Chem. Eur. J.* **2014**, *20*, 3578.

² Sun, B.; Srinivasan, B.; Huang, X. *Chem. Eur. J.* **2008**, *14*, 7072.

³ Zhang, Y.; Chen, C.; Jin, L.; Tan, H.; Wang, F.; Cao, H. *Carbohydr. Res.* **2015**, *401*, 109.

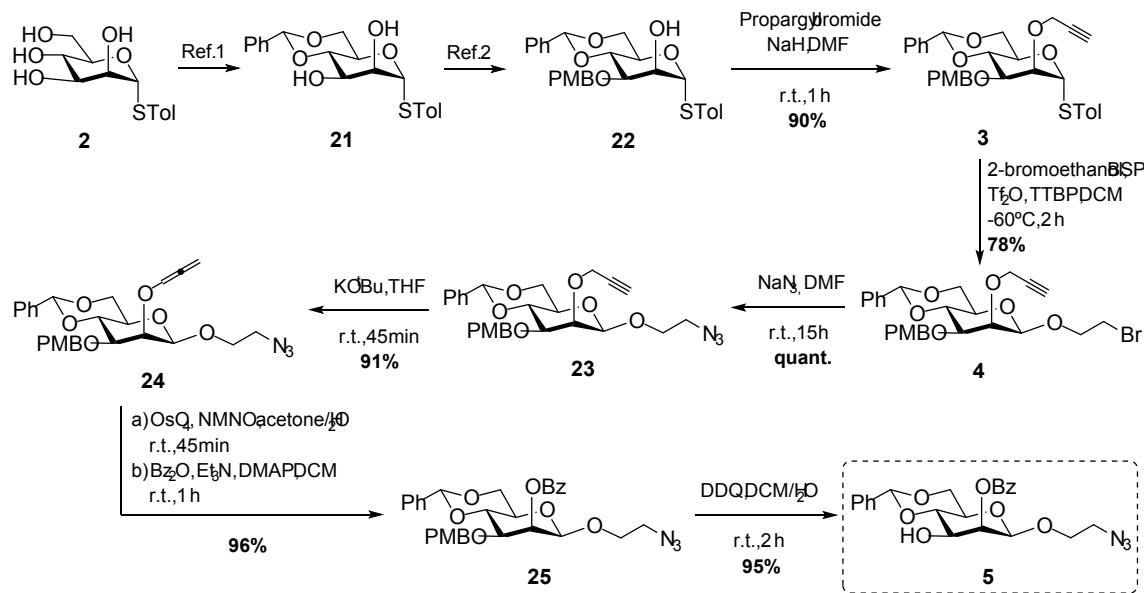
⁴ Reina, J. J.; Di Maio, A.; Ramos-Soriano, J.; Figueiredo, R. C.; Rojo, J. *Org. Biomol. Chem.* **2016**, *14*, 2873.

⁵ Szurmai, Z.; Jánossy, L.; Szilágyi, Z.; Vékey, K. *J. Carbohydr. Chem.* **1998**, *17*, 417.

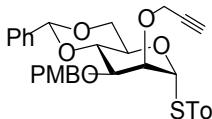
⁶ Bock, K.; Pedersen, C. *J. Chem. Soc. Perkin Trans. 2* **1974**, 293.

SYNTHESIS OF KEY INTERMEDIATE 5.

Stepwise synthesis.



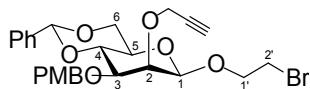
p-Tolyl 4,6-O-benzylidene-2-O-(prop-2-ynyl)-3-O-*p*-methoxybenzyl-1-thio- α -D-mannopyranoside (3).



To a solution of compound **22** (3.7 g, 7.49 mmol) in dry DMF (60 mL) cooled to 0 °C, NaH (450 mg, 11.23 mmol) was added in different portions (30 min). The reaction mixture was stirred for 15 min at 0 °C, and then propargyl bromide (1.25 mL, 11.23 mmol) was added. The reaction mixture was stirred at room temperature for 1h and quenched with methanol. The solvent was removed and the resulting crude was diluted with CH₂Cl₂ and washed with NaHCO₃ sat. aq. soln. The organic layer was dried with anh. MgSO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane 1:8), to give compound **3** (3.59 g, 6.75 mmol, 90%) as a colourless oil. $[\alpha]_D^{20} : +145$ (*c* 1.00, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ 7.54 (m, 2H, H-Ar), 7.44-7.30 (m, 8H, H-Ar, H_{tolyl}), 7.14 (d, *J* = 8.1, 2H, H_{tolyl}), 6.90 (d, *J* = 8.7, 2H, H-Ar), 5.64 (s, 1H, H_{acetal}), 5.56 (d, *J*_{1,2} = 1.3, 1H, H-1), 4.76 (AB system, 2H, CH₂,PMB), 4.42 (AB system, 2H, CH₂CCH), 4.32 (td, *J*_{5,4} = 9.7, *J*_{5,6} = 4.7, 1H, H-5), 4.27-4.18 (m, 3H, H-2, H-4, H_{6a}), 5.00 (dd, *J*_{3,4} = 9.8, *J*_{3,2} = 3.2, 1H, H-3), 4.88 (t, *J*_{6b,6b} = *J*_{6b,5} = 10.2, 1H, H-6b), 3.82 (s, 3H, CH₃,PMB), 2.46 (t, *J*_{CCH,H} = 2.4, 1H, CCH), 2.35 (s,

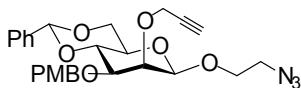
3H, $\text{CH}_3\text{,tolyl}$); ^{13}C -NMR (100 MHz, CDCl_3): δ 159.4 (C_{ipso} -Ar), 138.1 (C_{ipso} -Ar), 137.7 (C_{ipso} -Ar), 132.4 (C-Ar), 130.3 (C_{ipso} -Ar), 130.0 (C-Ar), 129.9 (C_{ipso} -Ar), 129.5 (C-Ar), 129.0 (C-Ar), 128.3 (C-Ar), 126.2 (C-Ar), 113.9 (C-Ar), 101.6 (C_acetal), 87.8 (C-1), 79.6 (CCH), 79.2 (C-4), 77.7 (C-2), 75.8 (CCH), 75.3 (C-3), 73.0 ($\text{CH}_2\text{,PMB}$), 68.6 (C-6), 65.4 (C-5), 58.9 (CH_2CCH), 55.4 ($\text{CH}_3\text{,PMB}$), 21.2 ($\text{CH}_3\text{,tolyl}$); ESI-MS m/z calcd. for $\text{C}_{31}\text{H}_{32}\text{O}_6\text{S}$: 532.2; found: 555.4 $[\text{M}+\text{Na}]^+$; ESI-HRMS m/z calcd. for $\text{C}_{31}\text{H}_{32}\text{O}_6\text{SNa}$ $[\text{M}+\text{Na}]^+$: 555.1812; found: 555.1803.

2-Bromoethyl 4,6-O-benzylidene-2-O-(prop-2-ynyl)-3-O-p-methoxybenzyl- β -D-mannopyranoside (4).



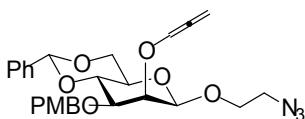
To a solution of donor **3** (1 g, 1.88 mmol), BSP (487 mg, 2.26 mmol), TTBP (722 mg, 2.82 mmol), and 4 Å molecular sieves in dry CH_2Cl_2 (20 mL), at -60 °C, Tf_2O (411 μL , 2.44 mmol) was added. After 30 min of stirring at -60 °C, 2-bromoethanol (421 μL , 5.64 mmol) was added. The reaction mixture was stirred for further 2 h at -60 °C, and allowed to reach room temperature. Then, the reaction mixture was filtered through celite and washed with CH_2Cl_2 and NaHCO_3 sat. aq. soln. The organic layer was separated, dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 1:5 → 1:4) to give the compound **4** (780 mg, 1.47 mmol, 78%) as a white amorphous solid. $[\alpha]_D^{20}$: -56 (c 0.80, CHCl_3); ^1H -NMR (400 MHz, CDCl_3): δ 7.49 (m, 2H, H-Ar), 7.42-7.29 (m, 5H, H-Ar), 6.85 (d, J = 8.6, 2H, H-Ar), 5.59 (s, 1H, H_acetal), 4.75 (AB system, 2H, $\text{CH}_2\text{,PMB}$), 4.58 (AB system, 2H, CH_2CCH), 4.56 (d, $J_{1,2}$ = 0.8, 1H, H-1), 4.30 (dd, 1H, $J_{6a,6b}$ = 10.4, $J_{6a,5}$ = 4.9, H-6a), 4.21 (dd, 1H, $J_{1'a,1'b}$ = 11.0, $J_{1'a,2'}$ = 5.5, H-1'a), 4.17 (m, 1H, H-2), 4.10 (t, $J_{4,3}$ = $J_{4,5}$ = 9.6, 1H, H-4), 3.90 (t, $J_{6b,6a}$ = $J_{6b,5}$ = 10.3, 1H, H-6b), 4.84-3.76 (m, 4H, H-1'b, $\text{CH}_3\text{,PMB}$), 3.61 (dd, 1H, $J_{3,4}$ = 10.0, $J_{3,2}$ = 3.2, H-3), 3.50 (m, 2H, H-2'), 3.32 (td, $J_{5,4}$ = 9.9, $J_{5,6}$ = 4.7, 1H, H-5), 2.48 (t, $J_{\text{CCH},\text{H}}$ = 2.4, 1H, CCH); ^{13}C -NMR (100 MHz, CDCl_3): δ 159.0 (C_{ipso} -Ar), 137.4 (C_{ipso} -Ar), 130.0 (C_{ipso} -Ar), 129.1 (C-Ar), 128.7 (C-Ar), 128.0 (C-Ar), 125.9 (C-Ar), 113.6 (C-Ar), 101.7 (C-1), 101.2 (C_acetal), 80.0 (CCH), 78.0 (C-4), 76.5 (C-3), 75.0 (CCH), 74.9 (C-2), 71.9 ($\text{CH}_2\text{,PMB}$), 69.5 (C-1'), 68.2 (C-6), 67.3 (C-5), 60.0 (CH_2CCH), 55.1 ($\text{CH}_3\text{,PMB}$), 30.2 (C-2'); ESI-MS m/z calcd. for $\text{C}_{26}\text{H}_{29}\text{BrO}_7$: 532.1; found: 555.3 $[\text{M}+\text{Na}]^+$; ESI-HRMS m/z calcd. for $\text{C}_{26}\text{H}_{29}\text{BrO}_7\text{Na}$ $[\text{M}+\text{Na}]^+$: 555.0989; found: 555.0981.

2-Azidoethyl 4,6-O-benzylidene-2-O-(prop-2-ynyl)-3-O-p-methoxybenzyl- β -D-mannopyranoside (23).



To a solution of bromo derivative **4** (560 mg, 1.13 mmol) in DMF (10 mL), NaN_3 (368 mg, 5.65 mmol) was added, and the mixture was stirred at room temperature for 15 h. After evaporation of the solvent, the residue was diluted with CH_2Cl_2 , and washed with water. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum, to give the compound **23** (560 mg, 1.13 mmol, quant.) as a colourless oil. $[\alpha]_D^{20} : -75$ (*c* 0.70, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.49 (m, 2H, H-Ar), 7.42-7.29 (m, 5H, H-Ar), 6.85 (d, *J* = 8.6, 2H, H-Ar), 5.59 (s, 1H, H_{acetal}), 4.75 (AB system, 2H, $\text{CH}_{2,\text{PMB}}$), 4.56 (AB system, 2H, CH_2CCH), 4.55 (m, 1H, H-1), 4.30 (dd, 1H, $J_{6a,6b} = 10.4$, $J_{6a,5} = 4.9$, H-6a), 4.17 (d, 1H, $J_{2,3} = 3.2$, H-2), 4.15-4.05 (m, 2H, H-4, H-1'a), 3.90 (t, $J_{6b,6a} = J_{6b,5} = 10.3$, 1H, H-6b), 3.80 (s, 3H, $\text{CH}_{3,\text{PMB}}$), 3.70-3.59 (m, 2H, H-3, H-1'b), 3.54 (m, 1H, H-2'a), 3.38 (m, 2H, H-5, H-2'b), 2.48 (t, $J_{\text{CCH},\text{H}} = 2.4$, 1H, CCH); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 159.0 ($\text{C}_{ipso}\text{-Ar}$), 137.3 ($\text{C}_{ipso}\text{-Ar}$), 129.9 ($\text{C}_{ipso}\text{-Ar}$), 129.0 (C-Ar), 128.6 (C-Ar), 127.9 (C-Ar), 125.8 (C-Ar), 113.4 (C-Ar), 101.5 (C-1), 101.0 (C_{acetal}), 79.8 (CCH), 77.9 (C-4), 76.5 (C-3), 75.0 (CCH), 74.8 (C-2), 71.7 ($\text{CH}_{2,\text{PMB}}$), 68.5 (C-1'), 68.1 (C-6), 67.2 (C-5), 59.9 (CH_2CCH), 54.9 ($\text{CH}_{3,\text{PMB}}$), 50.4 (C-2'); ESI-MS *m/z* calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_7$: 495.2; found: 518.4 [$\text{M}+\text{Na}$]⁺; ESI-HRMS *m/z* calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_7\text{Na}$ [$\text{M}+\text{Na}$]⁺: 518.1898; found: 518.1889.

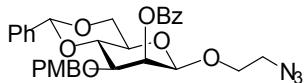
2-Azidoethyl 4,6-O-benzylidene-2-O-allenyl-3-O-p-methoxybenzyl- β -D-mannopyranoside (24).



To a stirred solution of azide derivative **23** (1.00 g, 2.02 mmol) in dry THF (15 mL), KO^tBu (254 mg, 2.22 mmol) was added and stirring was continued at room temperature for 45 min. The reaction mixture was diluted with EtOAc . The organic phase was washed with brine, dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography ($\text{EtOAc}/n\text{-hexane}$ 1:4), to give compound **24** (910 mg, 1.84 mol, 91%) as a colourless oil. $[\alpha]_D^{20} : -70$ (*c* 0.70, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.49 (m, 2H, H-Ar), 7.42-7.34 (m, 3H, H-Ar), 7.30 (d, *J* = 8.6, 2H, H-Ar), 6.94 (t, *J* = 6.0, 1H, $\text{CH}_{\text{allene}}$), 6.85 (d, *J* = 8.6, 2H, H-Ar), 5.60 (s, 1H, H_{acetal}), 5.51 (AB system, 2H, $\text{CH}_{2,\text{allene}}$), 4.69

(s, 2H, $\text{CH}_{2,\text{PMB}}$), 4.58 (d, 1H, $J_{1,2} = 1.0$, H-1), 4.35-4.28 (m, 2H, H-2, H-6a), 4.12 (t, 1H, $J_{4,3} = J_{4,5} = 9.6$, H-4), 4.09 (m, 1H, H-1'a), 3.91 (t, $J_{6b,6a} = J_{6b,5} = 10.3$, 1H, H-6b), 3.80 (s, 3H, $\text{CH}_{3,\text{PMB}}$), 3.71-3.63 (m, 2H, H-3, H-1'b), 3.54 (ddd, 1H, $J_{2'a,2'b} = 13.3$, $J_{2'a,1'b} = 8.7$, $J_{2'a,1'a} = 3.5$, H-2'a), 3.36 (ddd, 1H, $J_{5,6b} = 10.1$, $J_{5,4} = 9.3$, $J_{5,6a} = 4.9$, H-5), 3.30 (ddd, 1H, $J_{2'b,2'a} = 13.3$, $J_{2'b,1'a} = 4.5$, $J_{2'b,1'b} = 3.3$, H-2'b); ^{13}C -NMR (100 MHz, CDCl_3): δ 201.2 (C_{allene}), 159.4 (C_{ipso}-Ar), 137.5 (C_{ipso}-Ar), 130.0 (C_{ipso}-Ar), 129.4 (C-Ar), 129.0 (C-Ar), 128.3 (C-Ar), 126.1 (C-Ar), 124.0 (CH_{allene}), 113.9 (C-Ar), 101.6 (C_{acetal}), 100.9 (C-1), 92.1 (CH_{2,allene}), 78.3 (C-4), 76.3 (C-3), 75.5 (C-2), 72.1 (CH_{2,PMB}), 68.9 (C-1'), 68.5 (C-6), 67.6 (C-5), 55.3 (CH_{3,PMB}), 50.7 (C-2'); ESI-MS m/z calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_7$: 495.2; found: 518.1 [M+Na]⁺; ESI-HRMS m/z calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_7\text{Na}$ [M+Na]⁺: 518.1898; found: 518.1895.

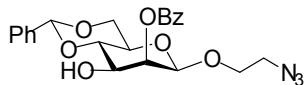
2-Azidoethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl- β -D-mannopyranoside (25).



A solution of allenyl ether **24** (800 mg, 1.62 mmol) in acetone/water (4:1, 25 mL) was treated with OsO_4 (41.5 mg, 0.16 mmol) and *N*-methyl morpholine *N*-oxide (390 mg, 3.23 mmol) and the mixture was stirred for 45 min at room temperature. After completion of the reaction, acetone was removed under vacuum and the residue was dissolved in CH_2Cl_2 and washed with NaHSO_3 sat. aq. soln. The organic phase was separated, dried over anh. MgSO_4 , filtered and concentrated under vacuum. To the resulting mixture containing 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl derivative in CH_2Cl_2 (15 mL) was subsequently added, Bz_2O (769 mg, 3.23 mmol), Et_3N (450 μL , 3.23 mmol) and a catalytic amount of DMAP and the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with HCl 1M, NaHCO_3 sat. aq. soln. and brine. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane 1:4), to give compound **25** (870 mg, 1.55 mmol, 96%) as a colourless oil. $[\alpha]_D^{20} : -114$ (*c* 1.0, CHCl_3); ^1H -NMR (400 MHz, CDCl_3): δ 8.13 (m, 2H, H-Ar), 7.62-7.34 (m, 8H, H-Ar), 7.28 (m, 2H, H-Ar), 6.82 (d, $J = 8.7$, 2H, H-Ar), 5.89 (dd, 1H, $J_{2,3} = 3.4$, $J_{2,1} = 1.1$, H-2), 5.66 (s, 1H, H_{acetal}), 4.74 (d, 1H, $J_{1,2} = 1.3$, H-1), 4.66 (AB system, 2H, $\text{CH}_{2,\text{PMB}}$), 4.39 (dd, 1H, $J_{6a,6b} = 10.5$, $J_{6a,5} = 4.9$, H-6a), 4.12 (t, 1H, $J_{4,3} = J_{4,5} = 9.6$, H-4), 4.05-3.93 (m, 2H, H-6b, H-1'a), 3.82 (dd, 1H, $J_{3,4} = 9.8$, $J_{3,2} = 3.4$, H-3), 3.78 (s, 3H, $\text{CH}_{3,\text{PMB}}$), 3.74 (m, 1H, H-1'b), 3.47 (td, 1H, $J_{5,4} = J_{5,6b} = 9.9$, $J_{5,6a} = 4.9$, H-5), 3.38 (ddd, 1H, $J_{2'a,2'b} = 13.2$, $J_{2'a,1'b} = 7.3$, $J_{2'a,1'a} = 3.9$, H-2'a), 3.30 (ddd, 1H, $J_{2'b,2'a} = 13.3$, $J_{2'b,1'a} = 5.6$, $J_{2'b,1'b} = 3.9$, H-2'b); ^{13}C -NMR (100 MHz, CDCl_3): δ : 165.7 (CO), 159.1 (C_{ipso}-Ar), 137.3 (C_{ipso}-Ar), 132.9 (C_{ipso}-Ar), 129.8 (C-Ar), 129.6 (C-Ar), 129.2 (C-Ar), 128.8 (C-Ar), 129.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 126.0 (C-Ar), 113.6 (C-Ar), 101.4 (C_{acetal}), 99.7 (C-1), 78.0 (C-4), 75.2 (C-3), 71.1 (CH_{2,PMB}), 69.1 (C-2), 68.6 (C-1'), 68.4 (C-6),

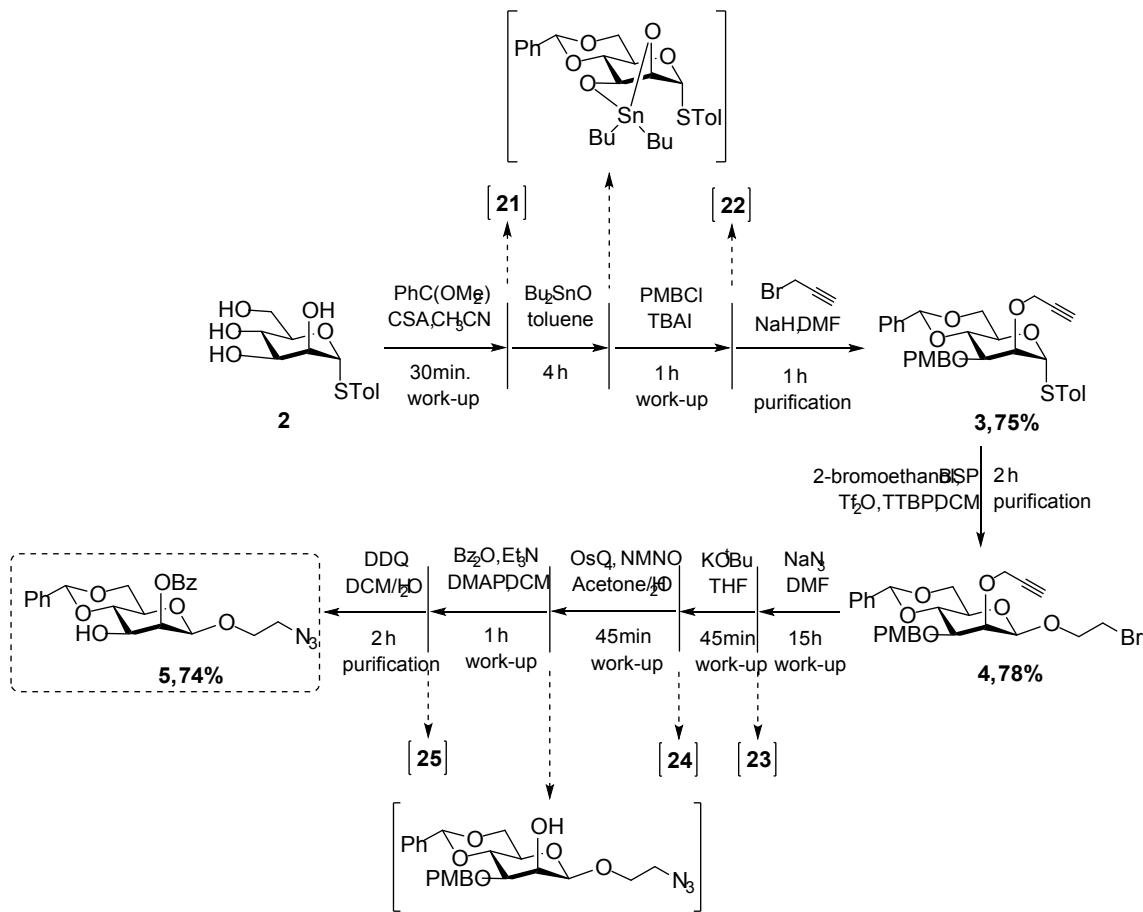
67.2 (C-5), 55.0 (CH₃_{PMB}), 50.4 (C-2'); ESI-MS *m/z* calcd. for C₃₀H₃₁N₃O₈: 561.6; found: 584.2 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₃₀H₃₁N₃O₈Na [M+Na]⁺: 584.2003; found: 584.1998.

2-Azidoethyl 2-*O*-benzoyl-4,6-*O*-benzylidene- β -D-mannopyranoside (5).



To a stirred solution of the β -mannoside derivative **25** (500 mg, 0.89 mmol) in CH₂Cl₂ (45 mL) and water (1.8 mL) was added DDQ (619 mg, 2.67 mmol) at room temperature. After 2 h, NaHCO₃ sat. aq. soln. was added, and the mixture was extracted with CH₂Cl₂. The extract was washed several times with NaHCO₃ sat. aq. soln. and then dried over anh. MgSO₄, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (EtOAc/n-hexane 1:2 → 1:1) to give the compound **5** (372 mg, 0.84 mmol, 95%) as a white solid. $[\alpha]_D^{20}$: -13 (c 0.50, CHCl₃); ¹H-NMR (400 MHz, CDCl₃) δ : 8.12 (m, 2H, H-Ar), 7.58 (m, 1H, H-Ar), 7.53-7.43 (m, 4H, H-Ar), 7.42-7.35 (m, 3H, H-Ar), 5.76 (dd, 1H, $J_{2,3}$ = 3.5, $J_{2,1}$ = 1.2, H-2), 5.63 (s, 1H, H_{acetal}), 4.76 (d, 1H, $J_{1,2}$ = 1.2, H-1), 4.40 (dd, 1H, $J_{6a,6b}$ = 10.5, $J_{6a,5}$ = 5.0, H-6a), 4.09 (dt, 1H, $J_{3,4}$ = 9.8, $J_{3,2}$ = 3.7, H-3), 4.04-3.92 (m, 3H, H-4, H-6b, H-1'a), 3.75 (ddd, 1H, $J_{1'b,1'a}$ = 10.8, $J_{1'b,2'a}$ = 7.1, $J_{1'b,2'b}$ = 3.9, H-1'b), 3.49 (ddd, 1H, $J_{5,4}$ = 10.0, $J_{5,6b}$ = 9.1, $J_{5,6a}$ = 4.9, H-5), 3.38 (ddd, 1H, $J_{2'a,2'b}$ = 13.2, $J_{2'a,1'b}$ = 7.1, $J_{2'a,1'a}$ = 3.9, H-2'a), 3.31 (ddd, 1H, $J_{2'b,2'a}$ = 13.3, $J_{2'b,1'a}$ = 5.7, $J_{2'b,1'b}$ = 3.9, H-2'b), 2.98 (d, 1H, $J_{OH,3}$ = 3.9, OH); ¹³C-NMR (100 MHz, CDCl₃) δ : 166.1 (CO), 137.1 (C_{ipso}-Ar), 132.9 (C_{ipso}-Ar), 129.8 (C-Ar), 129.6 (C-Ar), 129.0 (C-Ar), 128.1 (C-Ar), 126.2 (C-Ar), 101.6 (C_{acetal}), 99.4 (C-1), 78.5 (C-4), 71.6 (C-2), 69.1 (C-3), 68.5 (C-1'), 68.2 (C-6), 66.7 (C-5), 50.3 (C-2'); ESI-MS *m/z* calcd. for C₂₂H₂₃N₃O₇: 441.2; found: 464.2 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₂₂H₂₃N₃O₇Na [M+Na]⁺: 464.1428; found: 464.1422.

Consecutive approach.

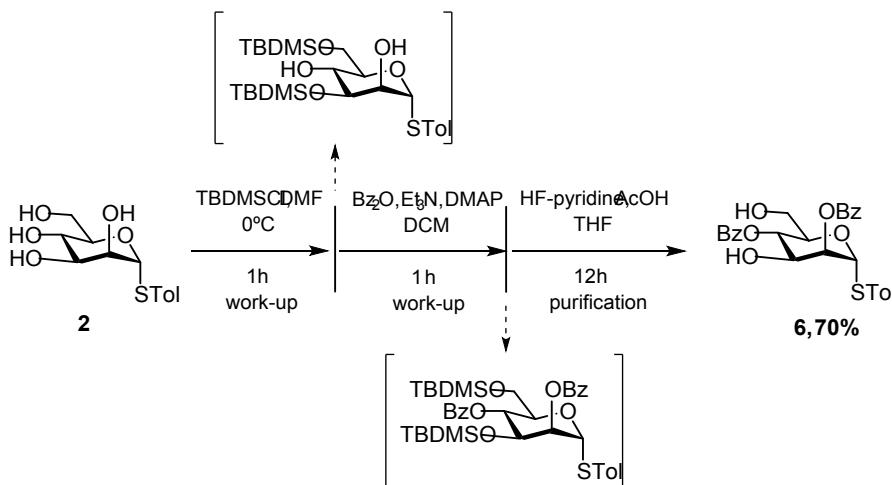


To a suspension of *S*-tolyl α-D-mannopyranose (**2**) (1 g, 3.50 mmol) in CH_3CN (10 mL), CSA (206 mg, 0.87 mmol) and benzaldehyde dimethyl acetal (0.58 mL, 2.84 mmol) were added at room temperature. The reaction mixture became solidified during addition of the reagent, which indicates the progress of the reaction. After 30 min the reaction mixture was quenched with Et_3N (0.3 mL) and dissolved in excess of EtOAc and water. The reaction mixture was extracted twice with EtOAc and the combined organic layers were washed with brine and dried over anh. MgSO_4 , filtered and concentrated under vacuum. After being dissolved in dry toluene (35 mL), dibutyltin oxide (0.96 g, 3.84 mmol) was added to the resulting mixture containing the 4,6-*O*-benzylidene derivative. The reaction mixture was kept under reflux at 110 °C for 4 h, cooled to room temperature and PMBCl (0.52 mL, 3.84 mmol) and TBAI (1.44 g, 3.84 mmol) were added to it under Ar atmosphere. The reaction mixture was kept under reflux at 110 °C for 1 h. After removal the solvent, the crude was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anh. MgSO_4 , filtered and concentrated under vacuum. To the resulting mixture containing 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl derivative in dry DMF (25 mL) cooled to 0 °C, NaH (210 mg, 5.24 mmol) was added in different portions (30 min). The reaction mixture was stirred for 15 min at 0 °C, and then propargyl bromide (0.58 mL, 5.24 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and quenched with methanol. The solvent was removed and the resulting crude was diluted with CH_2Cl_2 and washed with NaHCO_3 sat. aq. soln. The organic layer was dried with anh. MgSO_4 , filtered and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n -

hexane 1:8), to give compound **3** (1.40 g, 2.63 mol, 75%) as a colourless oil. To a solution of donor **3** (1 g, 1.88 mmol), BSP (487 mg, 2.26 mmol), TTBP (722 mg, 2.82 mmol), and 4 Å molecular sieves in dry CH_2Cl_2 (20 mL), at -60 °C, Tf_2O (411 μL , 2.44 mmol) was added. After 30 min of stirring at -60 °C, 2-bromoethanol (421 μL , 5.64 mmol) was added. The reaction mixture was stirred for further 2 h at -60 °C, and allowed to reach room temperature. Then, the reaction mixture was filtered through celite and washed with CH_2Cl_2 and NaHCO_3 sat. aq. soln. The organic layer was separated, dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 1:5 → 1:4) to give the compound **4** (780 mg, 1.47 mmol, 78%) as a white amorphous solid. To a solution of bromo derivative **4** (330 mg, 0.62 mmol) in DMF (4 mL), NaN_3 (202 mg, 3.10 mmol) was added and the mixture was stirred at room temperature for 15 h. After evaporation of the solvent, the residue was diluted with CH_2Cl_2 , and washed with water. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum. To a stirred solution of azide derivative in dry THF (4 mL), $\text{KO}^\ddagger\text{Bu}$ (78 mg, 0.68 mmol) was added and stirring was continued at room temperature for 45 min. The reaction mixture was diluted with CH_2Cl_2 . The organic phase was separated, washed with water, dried over anh. MgSO_4 , filtered and concentrated under vacuum to give the allenyl ether. A solution of allenyl ether in acetone/water (4:1, 5 mL) was treated with OsO_4 (15.6 mg, 0.06 mmol) and *N*-methyl morpholine *N*-oxide (150 mg, 1.24 mmol) and the mixture was stirred for 45 min at room temperature. After completion of the reaction, acetone was removed under vacuum and the residue was dissolved in CH_2Cl_2 and washed with NaHSO_3 sat. aq. soln. The organic phase was separated, dried over anh. MgSO_4 , filtered and concentrated under vacuum. To the resulting mixture containing 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl derivative in CH_2Cl_2 (10 mL) was subsequently added, Bz_2O (296 mg, 1.24 mmol), Et_3N (172 μL , 1.24 mmol) and a catalytic amount of DMAP and the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with HCl 1M, NaHCO_3 sat. aq. soln. and brine. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum. Finally, to a stirred solution of the β -mannoside derivative in CH_2Cl_2 (10 mL) and water (0.4 mL) was added DDQ (430 mg, 1.86 mmol) at room temperature. After 2 h, NaHCO_3 sat. aq. soln. was added, and the mixture was extracted with CH_2Cl_2 . The extract was washed several times with NaHCO_3 sat. aq. soln. and then dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 1:2 → 1:1) to give the compound **5** (203 mg, 0.46 mmol, 74%) as a white solid.

SYNTHESIS OF KEY INTERMEDIATE 6.

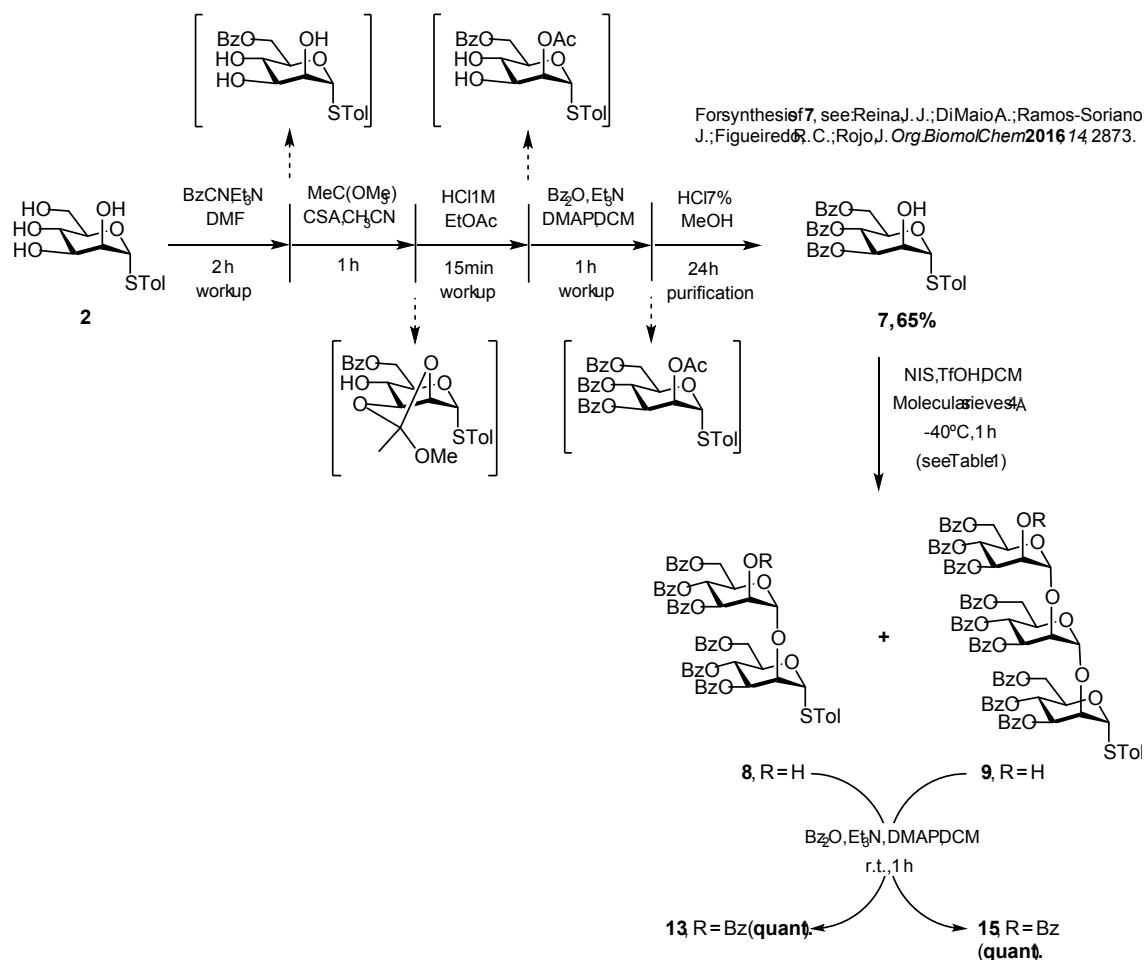
p-Tolyl 2,4-di-*O*-benzoyl-1-thio- α -D-mannopyranoside (6).



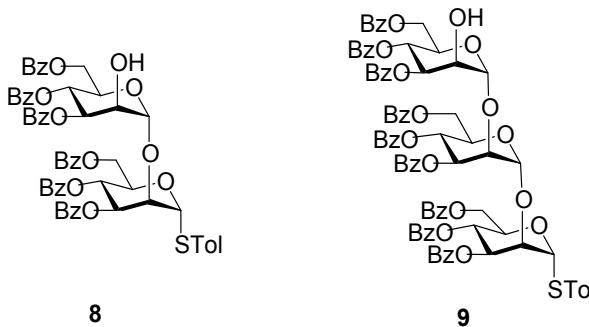
To a solution of *S*-tolyl α -D-mannopyranose (**2**) (1 g, 3.50 mmol) in anhydrous DMF (10 mL) was added TBDMSCl (1.63 g, 10.49 mmol) and imidazole (1.43 g, 20.97 mmol). The reaction mixture was stirred at 0 °C for 1 h. The resulted mixture was diluted with CH₂Cl₂, quenched with NaHCO₃ sat. aq. soln. and washed with H₂O, and the organic layer was dried over anh. MgSO₄, filtered and concentrated. To the resulting mixture containing 3,6-di-*O*-di-*tert*-butyldimethylsilyl derivative in CH₂Cl₂ (15 mL), Bz₂O (3.33 g, 13.98 mmol), Et₃N (1.95 mL, 13.98 mmol) and a catalytic amount of DMAP were subsequently added and the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with HCl 1M, NaHCO₃ sat. aq. soln. and brine. The organic phase was dried over anh. MgSO₄, filtered and concentrated under vacuum. To the resulting mixture containing 2,4-di-*O*-benzoyl-3,6-di-*O*-di-*tert*-butyldimethylsilyl protected mannopyranoside and AcOH (0.5 mL) in THF (10 mL) was slowly added a cold solution of HF-pyridine complex (2 mL). The reaction mixture was stirred at room temperature overnight and the solvent was removed under vacuum. The reaction mixture was diluted with CH₂Cl₂ and washed successively with NaHCO₃ sat. aq. soln. and water. The organic layer was dried over anh. MgSO₄, filtered and concentrated. The crude was purified by column chromatography on silica gel (EtOAc/n-hexane 1:2) to give the key intermediate **6** (1.21 g, 2.45 mmol, 70%) as a white solid. Spectroscopic and physical data matched those reported in the literature.

SYNTHESIS OF DISACCHARIDE **8** AND TRISACCHARIDE **9**.

Consecutive approach.



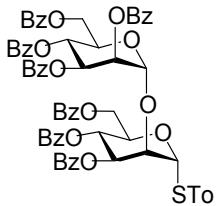
S-Tolyl (3,4,6-tri-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (**8**) and *S*-Tolyl (3,4,6-tri-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (**9**).



To a solution of compound **7** (16 g, 26.75 mmol) in dry CH_2Cl_2 (160 mL) was added 4 Å molecular sieves and the mixture was stirred at room temperature for 1 h. Then, reaction mixture was cooled at -40 °C and NIS (4.12 g, 17.39 mmol) and TfOH (482 μL , 5.35 mmol) were added and the reaction was stirred for 1 h. Then, the reaction was quenched with NaHCO_3 sat. aq. soln. and filtered over a pad of celite. The organic layer was washed with $\text{Na}_2\text{S}_2\text{O}_3$ sat. aq. soln. and dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 1:3 → 2:5) to give the disaccharide **8** (6.3 g, 5.88 mmol, 44%) as a white amorphous solid and the trisaccharide **9** (3.3 g, 2.13 mmol, 24%) as a white amorphous solid. *Compound 8.* $[\alpha]_D^{20} : +89$ (*c* 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.06-7.89 (m, 12H, H_{Bz}), 7.49 (m, 6H, H_{Bz}), 7.43-7.29 (m, 14H, H_{Bz} , H_{tolyl}), 6.95 (d, $J = 8.1$, 2H, H_{tolyl}), 6.03 (t, $J_{4,3} = J_{4,5} = 9.8$, 1H, H-4), 5.94 (t, $J_{4',3'} = J_{4',5'} = 9.8$, 1H, H-4'), 5.83 (dd, $J_{3,4} = 9.8$, $J_{3,2} = 3.1$, 1H, H-3), 5.81-5.76 (m, 2H, H-1, H-3'), 5.20 (d, $J_{1,2} = 1.6$, 1H, H-1'), 4.98 (ddd, $J_{5,4} = 9.8$, $J_{5,6a} = 5.9$, $J_{5,6b} = 3.1$, 1H, H-5), 4.70 (dd, $J_{2,3} = 3.1$, $J_{2,1} = 1.9$, 1H, H-2), 4.66-4.39 (m, 6H, H-2', H-5', H-6', H-6), 2.26 (s, 3H, $\text{CH}_{3,\text{tolyl}}$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 166.3 (CO), 166.2 (CO), 165.6 (CO), 165.6 (CO), 165.4 (CO), 165.3 (CO), 138.2 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 133.2 (C-Ar), 133.0 (C-Ar), 132.9 (C-Ar), 132.5 (C-Ar), 130.1-129.7 (C-Ar), 129.5 (C-Ar), 129.2 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.4-128.2 (C-Ar), 101.5 (C-1'), 87.0 (C-1), 77.3 (C-2), 72.2 (C-3'), 71.6 (C-3), 69.9 (C-2'), 69.8 (C-5), 69.3 (C-5'), 67.7 (C-4), 67.0 (C-4'), 63.7 (C-6), 63.5 (C-6'), 21.1 ($\text{CH}_{3,\text{tolyl}}$); ESI-MS *m/z* calcd. for $\text{C}_{61}\text{H}_{52}\text{O}_{16}\text{S}$: 1072.3; found: 1095.2 [$\text{M}+\text{Na}$] $^+$; ESI-HRMS *m/z* calcd. for $\text{C}_{61}\text{H}_{52}\text{O}_{16}\text{SNa}$ [$\text{M}+\text{Na}$] $^+$: 1095.2868; found: 1095.2860. *Compound 9.* $[\alpha]_D^{20} : +9$ (*c* 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.09-7.85 (m, 18H, H_{Bz}), 7.48 (m, 6H, H_{Bz}), 7.43-7.26 (m, 23H, H_{Bz} , H_{tolyl}), 6.96 (d, $J = 7.9$, 2H, H_{tolyl}), 6.01 (t, $J_{4,3} = J_{4,5} = 9.9$, 1H, H-4), 5.96 (t, $J_{4,3} = J_{4,5} = 9.7$, 1H, H-4), 5.89 (dd, $J_{3,4} = 10.0$, $J_{3,2} = 3.2$, 1H, H-3), 5.82-5.78 (m, 3H, H-1, H-3, H-4), 5.68 (dd, $J_{3,4} = 9.9$, $J_{3,2} = 3.0$, 1H, H-3), 5.51 (d, $J_{1,2} = 1.6$, 1H, H-1), 4.97 (m, 1H, H-5), 4.94 (d, $J_{1,2} = 1.5$, 1H, H-1), 4.65-4.46 (m, 7H, H-2, H-2, H-2, H-6, H-6), 4.39 (m, 2H, H-5, H-5), 4.20 (dd, $J_{6a,6b} = 12.1$, $J_{6a,5} = 3.0$, 1H, H-6a), 4.05 (dd, $J_{6b,6a} = 12.1$, $J_{6b,5} = 5.0$, 1H, H-6b), 2.26 (s, 3H, $\text{CH}_{3,\text{tolyl}}$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 166.3 (CO), 166.3 (CO), 165.9 (CO), 165.7 (CO), 165.5 (CO), 165.4 (CO), 165.3 (CO), 165.2 (CO), 133.5 (C-Ar), 133.4 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 133.3 (C-Ar), 133.1 (C-Ar),

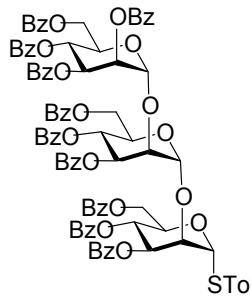
133.0 (C-Ar), 132.9 (C-Ar), 132.5 (C-Ar), 130.1 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.6 (C-Ar), 129.6 (C-Ar), 129.5 (C-Ar), 129.3 (C-Ar), 129.1 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 101.9 (C-1), 100.0 (C-1), 87.1 (C-1), 77.3 (C-2, C-2), 72.3 (C-3), 71.3 (C-3), 70.7 (C-3), 69.7 (C-2, C-5), 69.5 (C-5), 69.2 (C-5), 67.8 (C-4), 67.3 (C-4), 67.0 (C-4), 63.7 (C-6), 63.7 (C-6), 63.7 (C-6), 21.1 (CH_{3,tolyl}); ESI-MS *m/z* calcd. for C₈₈H₇₄O₂₄S: 1546.4; found: 1569.2 [M+Na]⁺.

S-Tolyl (2,3,4,6-tetra-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (13).



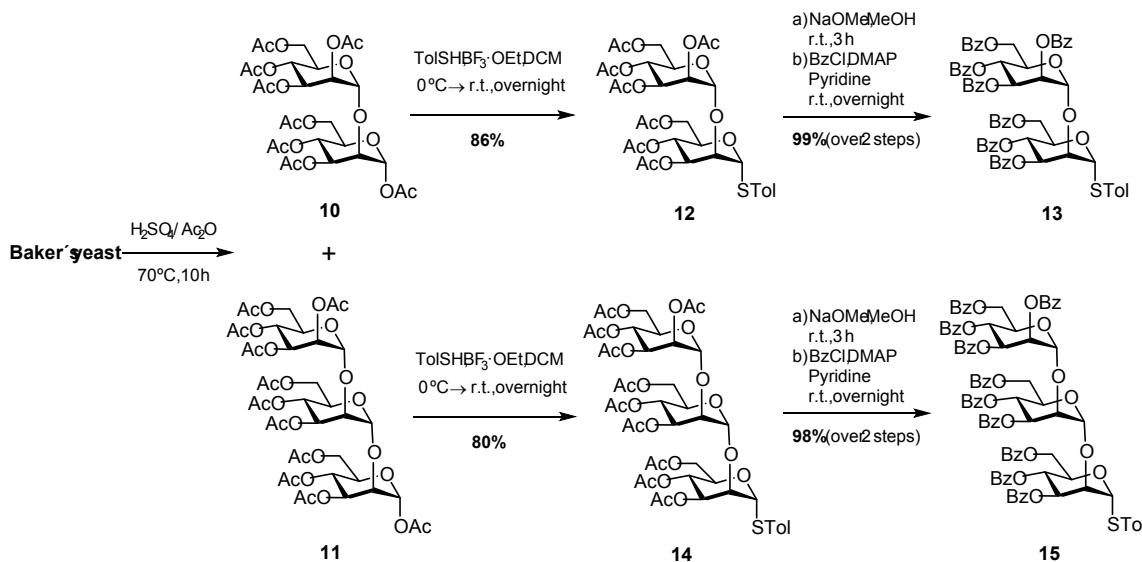
To a solution of compound **8** (5.1 g, 4.76 mmol) in CH₂Cl₂ (70 mL), Bz₂O (2.2 g, 9.51 mmol), Et₃N (1.3 mL, 9.51 mmol) and a catalytic amount of DMAP was subsequently added and the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with HCl 1M, NaHCO₃ sat. aq. soln. and brine. The organic phase was dried over anh. MgSO₄, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (EtOAc/n-hexane, 1:2) to give the disaccharide **13** (5.6 g, 4.76 mmol, quant.) as a white amorphous solid. $[\alpha]_D^{20} +13$ (*c* 1.00, CHCl₃); ¹H-NMR (400 MHz, CDCl₃) δ : 8.14-7.86 (m, 14H, H_{Bz}), 7.61-7.27 (m, 23H, H_{Bz}, H_{tolyl}), 7.00 (d, *J* = 8.0, 2H, H_{tolyl}), 6.17 (t, *J*_{4',3'} = *J*_{4',5'} = 10.0, 1H, H-4'), 6.09 (t, *J*_{4,3} = *J*_{4,5} = 9.8, 1H, H-4), 6.06 (dd, *J*_{3',4'} = 10.0, *J*_{3',2'} = 3.2, 1H, H-3'), 5.98-5.92 (m, 2H, H-2', H-3), 5.85 (d, *J*_{1,2} = 1.5, 1H, H-1), 5.36 (d, *J*_{1',2'} = 1.7, 1H, H-1'), 5.04 (ddd, *J*_{5,4} = 9.8, *J*_{5,6a} = 5.9, *J*_{5,6b} = 3.0, 1H, H-5), 4.73 (dd, *J*_{2,3} = 3.0, *J*_{2,1} = 1.5, 1H, H-2), 4.72-4.59 (m, 4H, H-5', H-6'a, H-6), 4.47 (dd, *J*_{6'b,6'a} = 12.3, *J*_{6'b,5'} = 4.3, 1H, H-6'b), 2.28 (s, 3H, CH_{3,tolyl}); ¹³C-NMR (100 MHz, CDCl₃) δ : 166.4 (CO), 166.2 (CO), 165.7 (CO), 165.6 (CO), 165.4 (CO), 165.2 (CO), 165.0 (CO), 138.5 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 133.2 (C-Ar), 133.1 (C-Ar), 133.1 (C-Ar), 132.7 (C-Ar), 130.2 (C-Ar), 130.1 (C-Ar), 130.0 (C-Ar), 129.9-129.8 (C-Ar), 129.2 (C-Ar), 129.1 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 99.6 (C-1'), 87.3 (C-1), 77.9 (C-2), 71.2 (C-3), 70.2 (C-3'), 70.0 (C-2'), 70.0 (C-5), 69.8 (C-5'), 67.9 (C-4), 66.8 (C-4'), 63.8 (C-6), 62.9 (C-6'), 21.2 (CH_{3,tolyl}); ESI-MS *m/z* calcd. for C₆₈H₅₆O₁₇S: 1176.3; found: 1199.4 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₆₈H₅₆O₁₇SNa [M+Na]⁺: 1199.3130; found: 1199.3135.

S-Tolyl (2,3,4,6-tetra-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (15).



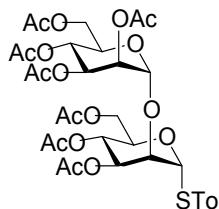
To a solution of compound **9** (3.2 g, 2.07 mmol) in CH_2Cl_2 (50 mL), Bz_2O (986 mg, 4.14 mmol), Et_3N (577 μL , 4.14 mmol) and a catalytic amount of DMAP were subsequently added and the reaction was stirred at room temperature for 1 h. The reaction mixture was washed with HCl 1M, NaHCO_3 sat. aq. soln. and brine. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$, 1:2) to give the trisaccharide **15** (3.4 g, 2.06 mmol, quant.) as a white amorphous solid. $[\alpha]_D^{20} : -4$ (c 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.13-7.82 (m, 20H, H_{Bz}), 7.65-7.26 (m, 30H, H_{Bz} , H_{tolyl}), 7.14 (m, 2H, H_{Bz}), 7.00 (m, 2H, H_{tolyl}), 6.05 (t, $J_{4,3} = J_{4,5} = 9.8$, 1H, H-4), 6.00-5.89 (m, 4H, H-3, H-3, H-4, H-4), 5.79-5.71 (m, 3H, H-1, H-2, H-3), 5.49 (d, $J_{1,2} = 1.5$, 1H, H-1), 5.02-4.93 (m, 2H, H-1, H-5), 4.69 (m, 1H, H-2), 4.67-4.44 (m, 7H, H-2, H-5, H-5, H-6, H-6), 4.33 (m, 1H, H-6a), 4.17 (dd, $J_{6\text{b},6\text{a}} = 12.3$, $J_{6\text{b},5} = 4.3$, 1H, H-6b), 2.27 (s, 3H, $\text{CH}_{3,\text{tolyl}}$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 166.3 (CO), 166.2 (CO), 165.8 (CO), 165.6 (CO), 165.5 (CO), 165.4 (CO), 165.3 (CO), 165.0 (CO), 164.7 (CO), 138.3 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 133.3 (C-Ar), 133.3 (C-Ar), 133.1 (C-Ar), 133.0 (C-Ar), 132.9 (C-Ar), 132.6 (C-Ar), 130.1 (C-Ar), 130.0 (C-Ar), 129.9 (C-Ar), 129.9-129.6 (C-Ar), 129.6 (C-Ar), 129.5 (C-Ar), 129.1 (C-Ar), 129.0 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4-128.3 (C-Ar), 128.2 (C-Ar), 99.9 (C-1), 99.6 (C-1), 87.0 (C-1), 77.8 (C-2), 76.8 (C-2), 71.6 (1C), 70.2 (1C), 70.0 (1C), 69.8 (2C), 69.7 (1C), 69.6 (1C), 67.7 (C-4), 67.4 (C-4), 66.6 (C-4), 63.7 (C-6), 63.6 (C-6), 63.0 (C-6), 21.1 ($\text{CH}_{3,\text{tolyl}}$); ESI-MS m/z calcd. for $\text{C}_{95}\text{H}_{78}\text{O}_{25}\text{S}$: 1651.7; found: 1674.2 $[\text{M}+\text{Na}]^+$.

Baker's yeast approach.



For the acetolysis of baker's yeast see: Szurma Z.; Jánossy L.; Szilágyi Z.; Vékey K. *J. Carbohydr Chem* 1998, 17, 417.

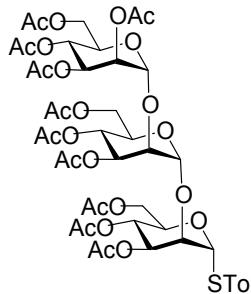
S-Tolyl 2,3,4,6-Tetra-*O*-acetyl- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-acetyl- α -D-mannopyranoside (12).



To a solution of peracetylated *O*- α -D-mannopyranosyl-(1 \rightarrow 2)- α -D-mannopyranoside **10** (600 mg, 0.88 mmol) in dry CH_2Cl_2 (15 mL) cooled at 0°C , TolSH (335 mg, 2.64 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (55 μL , 0.44 mmol) were added. The mixture was allowed to warm to room temperature, and stirred overnight. Then, the reaction mixture was washed with water and a NaHCO_3 sat. aq. soln. The organic layer was dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (EtOAc/n -hexane, 1:1) to give the thiomannoside **12** (564 mg, 0.76 mmol, 86%) as a white amorphous solid. $[\alpha]_D^{20} : +94$ (c 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.37 (d, $J = 8.1$, 2H, H_{tolyl}), 7.12 (d, $J = 8.1$, 2H, H_{tolyl}), 6.57 (d, $J_{1',2'} = 1.9$, 1H, $\text{H-1}'$), 4.48 (ddd, $J_{5,4} = 9.9$, $J_{5,6a} = 4.9$, $J_{5,6b} = 2.3$, 1H, H-5), 4.32 (dd, $J_{2,3} = 3.1$, $J_{2,1} = 1.9$, 1H, H-2), 4.25 (dd, $J_{6a,6b} = 12.3$, $J_{6a,5} = 4.9$, 1H, H-6a), 4.21-4.09 (m, 3H, H-6b , $\text{H-5}'$, $\text{H-6}'$), 4.03 (m, 1H, $\text{H-6}'$), 2.32 (s, 3H, $\text{CH}_{3,\text{tolyl}}$), 2.14 (s, 3H, CH_3 of OAc), 2.10 (s, 6H, CH_3 of OAc), 2.06 (s, 3H, CH_3 of OAc), 2.03 (s, 3H, CH_3 of OAc), 2.00 (s, 3H, CH_3 of OAc), 1.83 (s, 3H, CH_3 of OAc); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 170.5 (CO), 170.3 (CO), 170.1 (CO), 169.6 (CO), 169.5 (CO), 169.3 (CO), 169.2 (CO), 138.2 ($\text{C}_{ipso\text{-tolyl}}$), 132.3 (C_{tolyl}), 129.9 (C_{tolyl}), 128.9 ($\text{C}_{ipso\text{-tolyl}}$), 99.0 (C-1'), 86.6 (C-1), 78.2 (C-2), 70.3 (C-2'), 69.5 (C-5), 69.3 (C-3, C-5'), 68.2 (C-3'), 66.1 (C-4, C-4'), 62.3 (C-6'), 62.0 (C-6), 20.9

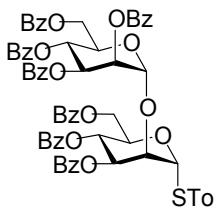
(CH_{3,tolyl}), 20.6 (CH₃ of OAc), 20.5 (CH₃ of OAc), 20.4 (CH₃ of OAc), 20.1 (CH₃ of OAc); ESI-MS *m/z* calcd. for C₃₃H₄₂O₁₇S: 742.2; found: 765.2 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₃₃H₄₂O₁₇SNa [M+Na]⁺: 765.2035; found: 765.2028.

S-Tolyl (2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-acetyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-acetyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-acetyl- α -D-mannopyranoside (14).



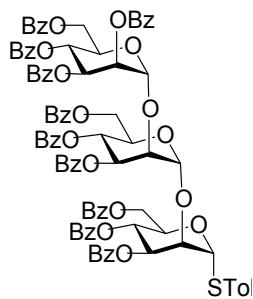
To a solution of peracetylated *O*- α -D-mannopyranosyl-(1 \rightarrow 2)- α -D-mannopyranosyl-(1 \rightarrow 2)- α -D-mannopyranoside **11** (500 mg, 0.52 mmol) in dry CH₂Cl₂ (10 mL) cooled at 0 °C, TolSH (198 mg, 1.56 mmol) and BF₃·Et₂O (35 μ L, 0.28 mmol) were added. The mixture was allowed to warm to room temperature, and stirred overnight. Then, the reaction mixture was washed with water and a NaHCO₃ sat. aq. soln. The organic layer was dried over anh. MgSO₄, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (EtOAc/*n*-hexane, 3:2) to give the thiomannoside **14** (429 mg, 0.42 mmol, 80%) as a white amorphous solid. $[\alpha]_D^{20}$: +40 (*c* 1.00, CHCl₃); ¹H-NMR (400 MHz, CDCl₃) δ : 7.37 (d, *J* = 8.1, 2H, H_{tolyl}), 7.14 (d, *J* = 8.1, 2H, H_{tolyl}), 5.57 (d, *J*_{1,2} = 2.2, 1H, H-1), 5.38 (dd, *J*_{3,4} = 9.9, *J*_{3,2} = 3.3, 1H, H-3), 5.34 (t, *J*_{4,3} = *J*_{4,5} = 9.5, 1H, H-4), 5.32-5.23 (m, 4H, H-2, H-3, H-3, H-4), 5.12 (d, *J*_{1,2} = 2.1, 1H, H-1), 4.94 (d, *J*_{1,2} = 1.8, 1H, H-1), 4.47 (ddd, *J*_{5,4} = 9.6, *J*_{5,6a} = 5.0, *J*_{5,6b} = 2.6, 1H, H-5), 4.30 (m, 1H, H-2), 4.26 (dd, *J*_{6a,6b} = 12.3, *J*_{6a,5} = 5.0, 1H, H-6a), 4.20 (dd, *J*_{6b,6a} = 12.4, *J*_{6b,5} = 5.4, 1H, H-6b), 4.17-4.06 (m, 6H, H-2, H-5, H-6, H-6), 2.33 (s, 3H, CH_{3,tolyl}), 2.15 (s, 3H, CH₃ of OAc), 2.10 (s, 3H, CH₃ of OAc), 2.08 (s, 6H, CH₃ of OAc), 2.07 (s, 3H, CH₃ of OAc), 2.06 (s, 3H, CH₃ of OAc), 2.04 (s, 3H, CH₃ of OAc), 2.02 (s, 3H, CH₃ of OAc), 2.00 (s, 3H, CH₃ of OAc), 1.92 (s, 3H, CH₃ of OAc); ¹³C-NMR (100 MHz, CDCl₃) δ : 170.7 (CO), 170.7 (CO), 170.4 (CO), 170.0 (CO), 169.9 (CO), 169.7 (CO), 169.7 (CO), 169.4 (CO), 169.4 (CO), 169.3 (CO), 138.4 (C_{ipso-tolyl}), 132.3 (C_{tolyl}), 130.0 (C_{tolyl}), 129.0 (C_{ipso-tolyl}), 99.8 (C-1), 99.3 (C-1), 86.7 (C-1), 77.9 (C-2), 77.4 (C-2), 70.5 (C-2), 69.6, 69.5, 69.4, 69.4 (C-3, C-3, C-5, C-5, C-5), 68.3 (C-3), 66.4 (C-4), 66.3 (C-4), 66.0 (C-4), 62.6 (C-6), 62.1 (C-6, C-6), 21.1 (CH_{3,tolyl}), 20.8 (CH₃ of OAc), 20.6 (CH₃ of OAc), 20.5 (CH₃ of OAc), 20.3 (CH₃ of OAc); ESI-MS *m/z* calcd. for C₄₅H₅₈O₂₅S: 1030.3; found: 1053.2 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₄₅H₅₈O₂₅SNa [M+Na]⁺: 1053.2880; found: 1053.2871.

S-Tolyl (2,3,4,6-tetra-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (13).



Sodium methoxide in methanol (1 M, 0.1 eq. per acetyl group) was added to a solution of the acetylated derivative **12** (500 mg, 0.67 mmol) in MeOH (\approx 0.05 M). The reaction mixture was stirred at room temperature for 3 h and, then was neutralized with Amberlite IR-120H $^+$, filtered and concentrated. To a solution of the resulting deprotected derivative and a catalytic amount of DMAP in dry pyridine (10 mL) cooled at 0 °C, was slowly added BzCl (817 μ L, 7.03 mmol). The mixture was allowed to warm to room temperature, and stirred overnight. After removal the solvent, the resulting crude was diluted with CH₂Cl₂ and washed with HCl 1M, NaHCO₃ sat. aq. soln. and brine. The organic phase was dried over anh. MgSO₄, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (EtOAc/n-hexane, 1:2) to give the trisaccharide **13** (780 mg, 0.66 mmol, 99%) as a white amorphous solid.

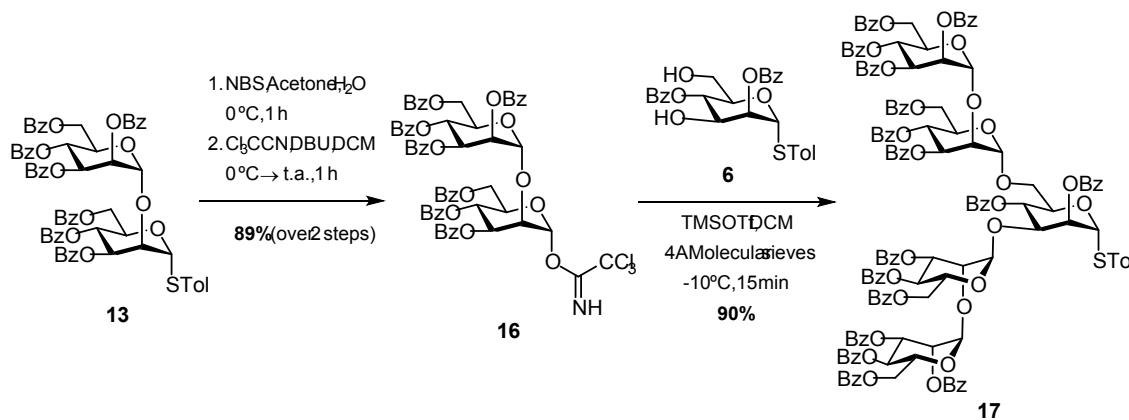
S-Tolyl (2,3,4,6-tetra-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzoyl- α -D-mannopyranosyl)-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside (15).



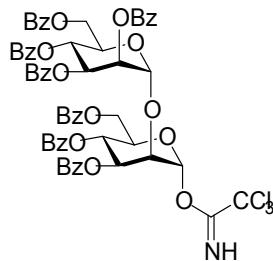
Sodium methoxide in methanol (1 M, 0.1 eq. per acetyl group) was added to a solution of the acetylated derivative **14** (400 mg, 0.39 mmol) in MeOH (\approx 0.05 M). The reaction mixture was stirred at room temperature for 3 h and, then was neutralized with Amberlite IR-120H $^+$, filtered and concentrated. To a solution of the resulting deprotected derivative and a catalytic amount of DMAP in dry pyridine (8 mL) cooled at 0 °C, was slowly added BzCl (679 μ L, 5.85 mmol). The

mixture was allowed to warm to room temperature, and stirred overnight. After removal the solvent, the resulting crude was diluted with CH_2Cl_2 and washed with HCl 1M, NaHCO_3 sat. aq. soln. and brine. The organic phase was dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$, 1:2) to give the trisaccharide **15** (631 mg, 0.38 mmol, 98%) as a white amorphous solid.

SYNTHESIS OF PENTASACCHARIDE 17.



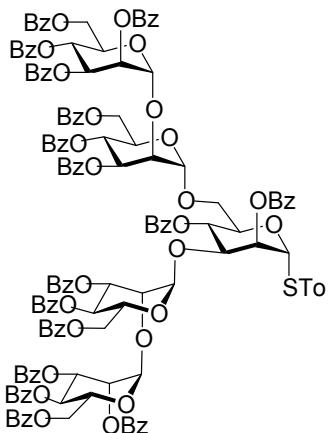
2,3,4,6-Tetra-*O*-benzoyl- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzoyl- α -D-mannopyranoside trichloroacetimidate (16).



To a solution of compound **13** (3 g, 2.55 mmol) in a mixture of acetone/water (9:1, 60 mL), NBS (1.38 g, 7.65 mmol) was added at 0 °C for 1 h when TLC indicated the complete hydrolysis of the thioglycoside. The reaction mixture was quenched with NaHCO_3 sat. aq. soln. and the mixture was extracted with EtOAc . The organic layer was dried over anh. MgSO_4 , filtered and concentrated. The residue was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$, 2:3 \rightarrow 1:1) to give the corresponding hemiacetal (2.73 g, 2.55 mmol, quant.) as a white solid. The hemiacetal was dissolved in dry CH_2Cl_2 (40 mL) and the solution was cooled at 0 °C. Then, trichloroacetonitrile (1.3 mL, 12.7 mmol) and DBU (152 μL , 1.02 mmol) were added to the solution and the reaction mixture was stirred at room temperature for 1 h.

After removal the solvent, the crude was purified by column chromatography on silica gel (EtOAc/n-hexane, 2:3) to give the trichloroacetimidate **16** (2.76 g, 2.27 mmol, 89%) as a white solid. $[\alpha]_D^{20} : -30$ (*c* 1.00, CHCl₃); ¹H-NMR (400 MHz, CDCl₃) δ : 8.71 (s, 1H, NH), 8.09 (m, 4H, H_{Bz}), 8.03 (m, 2H, H_{Bz}), 7.96 (m, 6H, H_{Bz}), 7.88 (m, 2H, H_{Bz}), 7.60-7.27 (m, 21H, H_{Bz}), 6.65 (d, *J*_{1,2} = 2.0, 1H, H-1), 6.16 (t, *J*_{4',3'} = *J*_{4',5'} = 10.1, 1H, H-4'), 6.15 (t, *J*_{4,3} = *J*_{4,5} = 9.8, 1H, H-4), 6.03 (dd, *J*_{3',4'} = 10.1, *J*_{3',2'} = 3.2, 1H, H-3'), 5.98-5.92 (m, 2H, H-2', H-3), 5.35 (d, *J*_{1',2'} = 1.6, 1H, H-1'), 4.73 (dd, *J*_{6'a,6'b} = 12.4, *J*_{6'a,5'} = 2.3, 1H, H-6'a), 4.70-4.61 (m, 4H, H-2, H-5, H-5', H-6a), 4.58 (dd, *J*_{6b,6a} = 11.8, *J*_{6b,5} = 5.2, 1H, H-6b), 4.49 (dd, *J*_{6'b,6'a} = 12.4, *J*_{6'b,5'} = 4.4, 1H, H-6'b); ¹³C-NMR (100 MHz, CDCl₃) δ : 166.1 (CO), 166.0 (CO), 165.5 (CO), 165.4 (CO), 165.1 (CO), 165.0 (CO), 164.8 (CO), 159.9 (CN), 133.4 (C-Ar), 133.3 (C-Ar), 133.1 (C-Ar), 132.0 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.6 (C-Ar), 129.5 (C-Ar), 129.0 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 99.4 (C-1'), 96.1 (C-1), 90.5 (CCl₃), 74.2 (C-2), 71.8 (C-5'), 70.4 (C-5), 70.0 (C-2'), 69.9 (C-3), 69.7 (C-3'), 66.6 (C-4), 66.4 (C-4'), 63.0 (C-6), 62.5 (C-6'); ESI-MS *m/z* calcd. for C₆₃H₅₀Cl₃NO₁₈: 1213.2; found: 1236.2 [M+Na]⁺; ESI-HRMS *m/z* calcd. for C₆₃H₅₀Cl₃NO₁₈Na [M+Na]⁺: 1236.1986; found: 1236.1970.

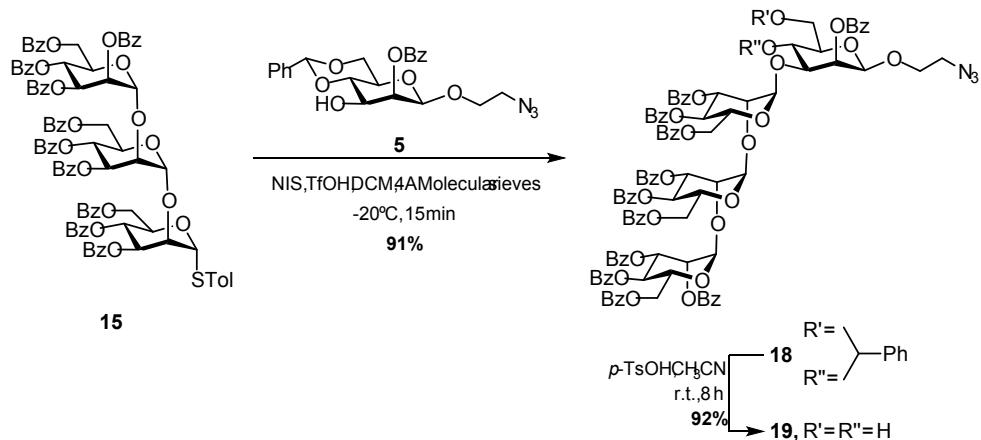
Pentasaccharide **17**.



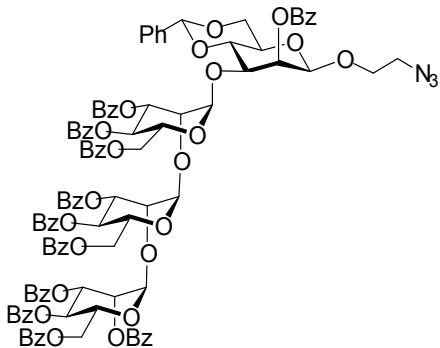
A solution of acceptor **6** (368 mg, 0.74 mmol), donor **16** (2.4 g, 1.94 mmol) and 4 Å molecular sieves in dry CH₂Cl₂ (30 mL) was stirred at -10 °C for 30 min. Then, TMSOTf (41 μ L, 0.22 mmol) was added and the resulting mixture was stirred for 15 min at -10 °C. The reaction was quenched with Et₃N (300 μ L), and the mixture was diluted with CH₂Cl₂, filtered through Celite and washed with CH₂Cl₂. After removal the solvent, the crude was purified by column chromatography on silica gel (EtOAc/n-hexane 2:3 → 4:5) to give the pentasaccharide **17** (1.72 g, 0.67 mmol, 90%) as a white solid. $[\alpha]_D^{20} : -29$ (*c* 1.00, CHCl₃); ¹H-NMR (400 MHz, CDCl₃) δ : 8.31-7.77 (m, 32H, H_{Bz}), 7.62-7.22 (m, 47H, H_{Bz}, H_{tolyl}), 7.11 (m, 2H, H_{tolyl}), 6.96 (m, 2H, H_{Bz}), 6.80 (m, 1H, H_{Bz}), 6.12-5.84 (m, 8H), 5.81-5.76 (m, 2H, H-1), 5.71 (dd, *J* = 9.9, *J* = 3.2, 1H), 5.61 (m, 1H), 5.52 (m, 1H, H-1), 5.19 (m, 1H, H-1), 4.97 (m, 1H, H-1), 4.76 (m, 1H), 4.66 (m,

1H), 4.63-4.47 (m, 6H, H-1), 4.44-4.26 (m, 8H), 4.20 (m, 1H), 4.08 (m, 1H), 4.04 (m, 1H), 3.68 (m, 1H), 2.17 (s, 3H, CH_3 , tolyl); ^{13}C -NMR (100 MHz, CDCl_3) δ : 166.4 (CO), 166.1 (CO), 166.1 (CO), 165.9 (CO), 165.9 (CO), 165.5 (CO), 165.4 (CO), 165.3 (CO), 165.2 (CO), 165.1 (CO), 165.0 (CO), 164.9 (CO), 164.7 (CO), 164.5 (CO), 138.3 (C-Ar), 133.5-132.9 (C-Ar), 132.0 (C-Ar), 131.5 (C-Ar), 130.1 (C-Ar), 129.9-129.6 (C-Ar), 129.1 (C-Ar), 129.0 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.6-128.0 (C-Ar), 100.1 (C-1), 99.9 (C-1), 99.4 (C-1), 98.7 (C-1), 86.5 (C-1), 78.0, 77.6, 77.4, 75.6, 73.4, 72.7, 70.7, 70.3, 70.0, 69.9-69.4, 68.8, 67.1, 67.1, 66.7, 66.6, 66.4, 63.7, 63.3, 62.7, 62.4, 20.9 (CH_3 , tolyl); ESI-MS m/z calcd. for $\text{C}_{149}\text{H}_{122}\text{O}_{41}\text{S}$: 2598.7; found: 2622.3 [$\text{M}+\text{Na}]^+$, 1322.6 [$\text{M}+2\text{Na}]^{+2}$.

SYNTHESIS OF TETRASACCHARIDE 19.



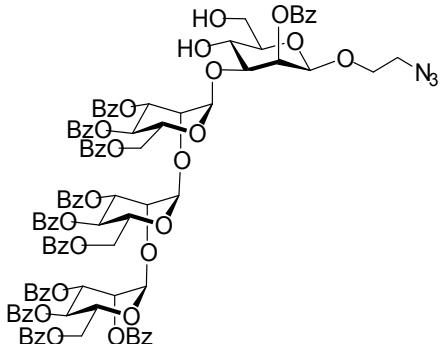
Tetrasaccharide 18.



To a solution of acceptor **5** (253 mg, 0.57 mmol), donor **15** (1.23 g, 0.75 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 (30 mL) was stirred at -20 °C for 30 min. Then, NIS (177 mg, 0.75 mmol) and TfOH (10.4 μL , 0.11 mmol) were added and the reaction was stirred at -20 °C for 15 min. The reaction was quenched with NaHCO_3 sat. aq. soln. The reaction mixture was filtered through Celite and washed several times with CH_2Cl_2 . The organic layer was washed

with $\text{Na}_2\text{S}_2\text{O}_3$ sat. aq. soln. and then dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel (Toluene/Acetone 15:1) to give the tetrasaccharide **18** (1.03 g, 0.52 mmol, 91%) as a white solid. $[\alpha]_D^{20} : -40$ (*c* 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.29-8.20 (m, 2H, H-Ar), 8.19-8.14 (m, 2H, H-Ar), 8.09-7.89 (m, 12H, H-Ar), 7.89-7.81 (m, 4H, H-Ar), 7.77-7.70 (m, 2H, H-Ar), 7.63-7.20 (m, 32H, H-Ar), 7.20-6.98 (m, 5H, H-Ar), 6.80 (m, 1H, H-Ar), 6.03-5.83 (m, 6H), 5.76 (m, 1H), 5.58 (dd, *J* = 9.4, *J* = 3.1, 1H), 5.55 (s, 1H, H-1), 5.53 (s, 1H, H-1), 5.31 (s, 1H, H_{acetal}), 4.93 (s, 1H, H-1), 4.82 (m, 1H), 4.74 (dd, *J* = 12.2, *J* = 2.7, 1H), 4.65 (dd, *J* = 12.2, *J* = 5.4, 1H), 4.60 (m, 1H, H-1_B), 4.42 (m, 1H), 4.39-4.13 (m, 6H), 4.13-3.95 (m, 4H), 3.93-3.77 (m, 2H), 3.70 (ddd, *J* = 10.7, *J* = 6.8, *J* = 4.2, 1H), 3.46-3.27 (m, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 166.2 (CO), 165.7 (CO), 165.6 (CO), 165.4 (CO), 165.3 (CO), 165.2 (CO), 165.1 (CO), 165.0 (CO), 164.7 (CO), 136.8 (C-Ar), 133.4 (C-Ar), 133.2 (C-Ar), 133.1 (C-Ar), 133.0 (C-Ar), 132.8 (C-Ar), 132.7 (C-Ar), 130.1 (C-Ar), 129.8-129.5 (C-Ar), 129.1 (C-Ar), 129.0 (C-Ar), 128.9 (C-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.5-128.1 (C-Ar), 101.5 (C-1), 99.7 (C-1), 99.6 (C-1_B, C_{acetal}), 99.4 (C-1), 78.6, 77.4, 75.5, 73.0, 70.8, 70.3, 69.9, 69.7, 69.6 (2C), 69.5, 69.4 (2C), 68.9, 68.4, 67.0, 66.9, 66.3, 63.7, 63.1, 62.5, 50.5; ESI-MS *m/z* calcd. for $\text{C}_{110}\text{H}_{93}\text{N}_3\text{O}_{32}$: 1967.6; found: 1990.9 $[\text{M}+\text{Na}]^+$.

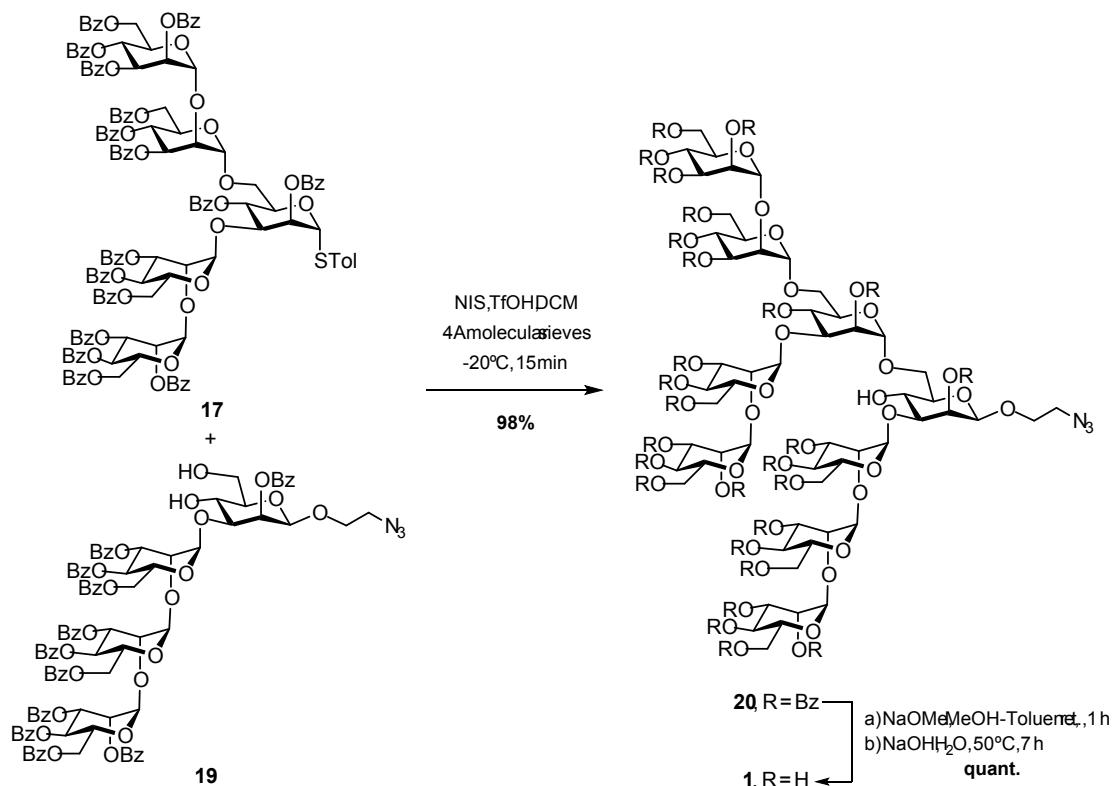
Tetrasaccharide **19**.



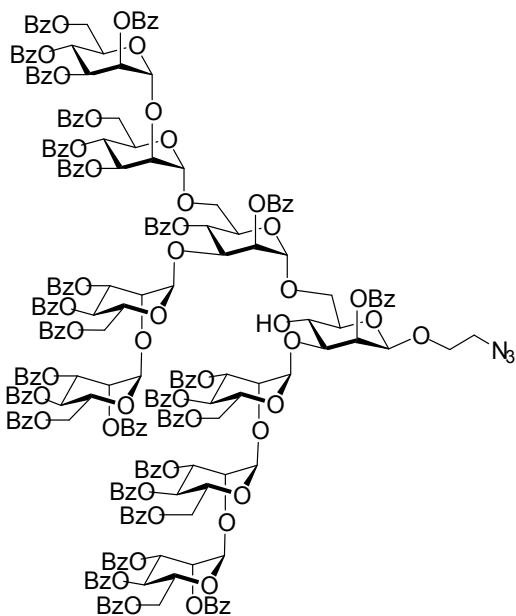
p-Toluenesulfonic acid monohydrate (70 mg, 0.36 mmol) was added to a stirred solution of tetrasaccharide **18** (470 mg, 0.24 mmol) in CH_3CN (18 mL) at room temperature. After 8 h, the reaction mixture was quenched with Et_3N (75 μL) and concentrated under vacuum. The residue was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 3:2) to give the tetrasaccharide **19** (413 mg, 0.22 mmol, 92%) as a white amorphous solid. $[\alpha]_D^{20} : -37$ (*c* 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.21-8.14 (m, 2H, H_{Bz}), 8.08-7.94 (m, 13H, H_{Bz}), 7.93-7.88 (m, 2H, H_{Bz}), 7.87-7.79 (m, 4H, H_{Bz}), 7.60-7.14 (m, 34H, H_{Bz}), 6.13 (t, *J* = 10.1, 1H), 6.01-5.87 (m, 3H), 5.84-5.73 (m, 3H), 5.63-5.54 (m, 2H, H-1), 5.49 (s, 1H, H-1), 5.07 (br s, 1H, H-1), 4.77-4.64 (m, 3H), 4.63 (s, 1H, H-1_B), 4.54-4.40 (m, 4H), 4.34-4.21 (m, 3H), 4.18-3.92 (m, 6H), 3.70 (ddd, *J* = 10.6, *J* = 6.1, *J* = 4.6, 1H), 3.41-3.28 (m, 3H), 2.31 (m, 1H); $^{13}\text{C-NMR}$ (100

MHz, CDCl_3) δ : 166.3 (CO), 166.2 (CO), 166.0 (CO), 165.9 (CO), 165.7 (CO), 165.4 (CO), 165.3 (CO), 165.2 (CO), 165.1 (CO), 164.9 (CO), 164.7 (CO), 133.3 (C-Ar), 133.0 (C-Ar), 129.9 (C-Ar), 129.7 (C-Ar), 129.6 (C-Ar), 129.5 (C-Ar), 129.4 (C-Ar), 129.0 (C-Ar), 128.9 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 100.3 (C-1), 99.3 (C-1, C-1 β), 99.0 (C-1), 78.0, under CDCl_3 (1C), 76.4, 71.1, 70.3, 70.0, 69.7 (2C), 69.5, 69.4, 69.2, 68.4 (2C), 68.1, 67.4, 66.3, 63.5, 63.4, 62.4, 62.0 (2C), 50.4; ESI-MS m/z calcd. for $\text{C}_{103}\text{H}_{89}\text{N}_3\text{O}_{32}$: 1872.5; found: 1902.9 $[\text{M}+\text{Na}]^+$.

SYNTHESIS OF MAN₉(1).

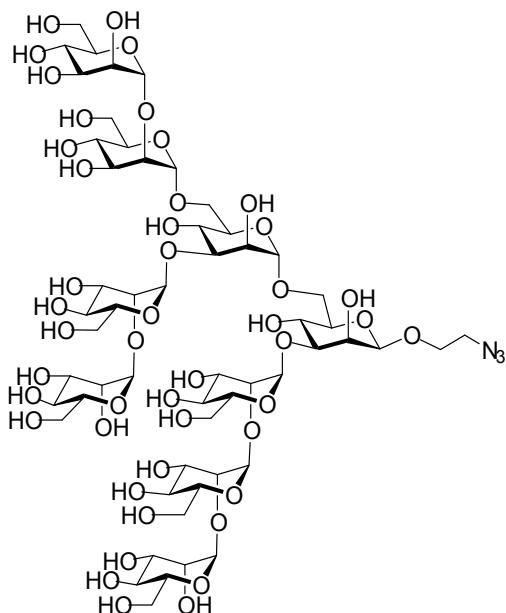


Nonasaccharide 20.



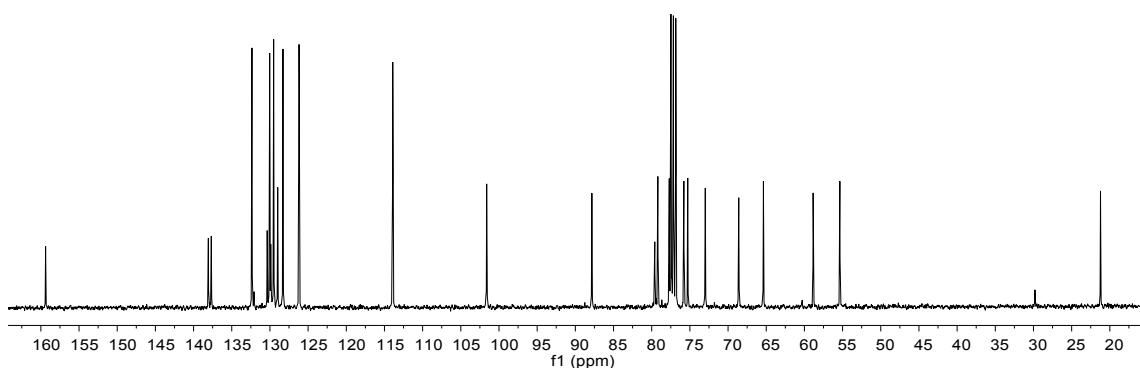
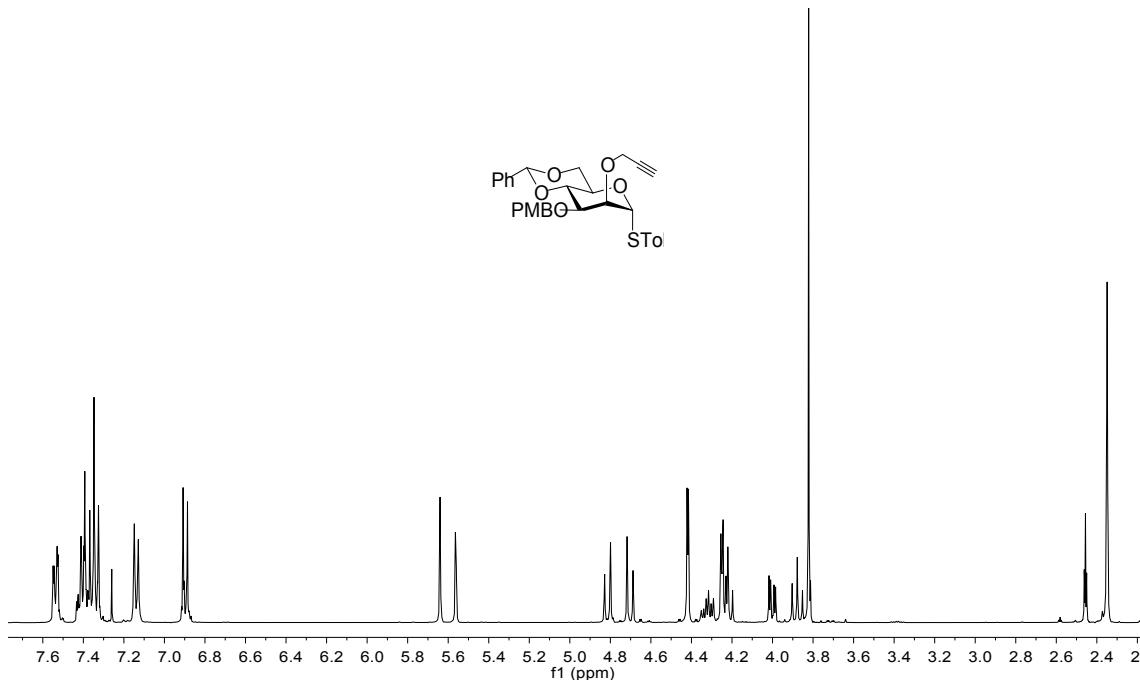
To a solution of acceptor **19** (390 mg, 0.21 mmol), donor **17** (701 mg, 0.27 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 (15 mL) was stirred at -20 °C for 30 min. Then, NIS (63.9 mg, 0.27 mmol) and TfOH (3.7 μL , 41.50 μmol) were added and the reaction was stirred at -20 °C for 15 min. The reaction was quenched with NaHCO_3 sat. aq. soln. The reaction mixture was filtered through Celite and washed several times with CH_2Cl_2 . The organic layer was washed with $\text{Na}_2\text{S}_2\text{O}_3$ sat. aq. soln. and then dried over anh. MgSO_4 , filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel ($\text{EtOAc}/n\text{-hexane}$ 4:5 → 1:1) to give the nonasaccharide **20** (885 mg, 0.20 mmol, 98%) as a white solid. $[\alpha]_D^{20} : -33$ (c 1.00, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.29-7.67 (m, 52H, H_{Bz}), 7.64-7.01 (m, 80H, H_{Bz}), 6.96 (t, $J = 7.8$, 2H, H_{Bz}), 6.79 (t, $J = 7.5$, 1H, H_{Bz}), 6.17-5.74 (m, 16H), 5.68 (dd, $J = 9.9$, $J = 3.3$, 1H), 5.65-5.51 (m, 3H, H-1), 5.48 (s, 1H, H-1), 5.43-5.36 (m, 2H, 2xH-1), 5.33 (s, 1H, H-1), 5.02 (s, 1H, H-1), 4.96 (s, 1H, H-1), 4.85-3.92 (m, 36H, H-1, $\text{H}_{1\beta}$), 3.85 (m, 1H), 3.79 (m, 1H), 3.58 (m, 1H), 3.35 (m, 1H), 3.25 (m, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 166.5 (CO), 166.4 (CO), 166.3 (CO), 166.2 (CO), 166.1 (CO), 166.0 (CO), 165.9 (CO), 165.8 (CO), 165.6 (CO), 165.5 (CO), 165.4 (CO), 165.3 (CO), 165.2 (CO), 165.1 (CO), 165.0 (CO), 164.9 (CO), 164.8 (CO), 164.7 (CO), 164.6 (CO), 164.5 (CO), 133.5 (C_{Bz}), 133.4 (C_{Bz}), 133.3 (C_{Bz}), 133.1 (C_{Bz}), 130.1-129.4 (C_{Bz}), 129.3-128.0 (C_{Bz}), 100.7 (C-1), 100.6 (C-1), 100.0 (C-1), 99.5 (C-1), 99.4 (C-1), 99.3 ($\text{C}-1\beta$), 98.7 (C-1), 97.6 (2xC-1), 78.4, 78.1, under CDCl_3 (2C), 76.1, 75.5, 72.0, 71.3, 70.8, 70.4, 70.1-69.4, 68.9, 68.7, 68.0, 67.7, 67.6, 67.2, 67.1, 66.5, 66.4, 65.6, 63.7, 63.5, 63.3, 62.4, 62.3, 50.5; ESI-MS m/z calcd. for $\text{C}_{245}\text{H}_{203}\text{N}_3\text{O}_{73}$: 4354.2; found: 2200.9 $[\text{M}+2\text{Na}]^{+2}$, 1474.7 $[\text{M}+3\text{Na}]^{+3}$.

Nonasaccharide Man₉ (1).

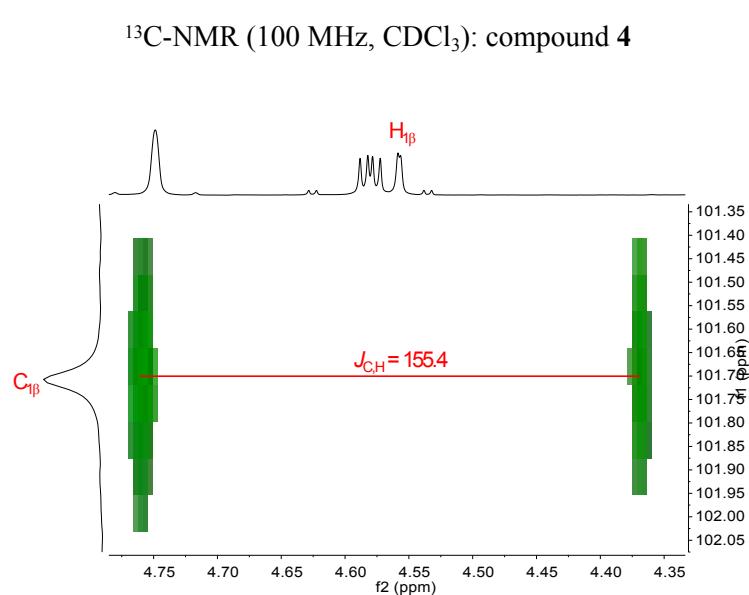
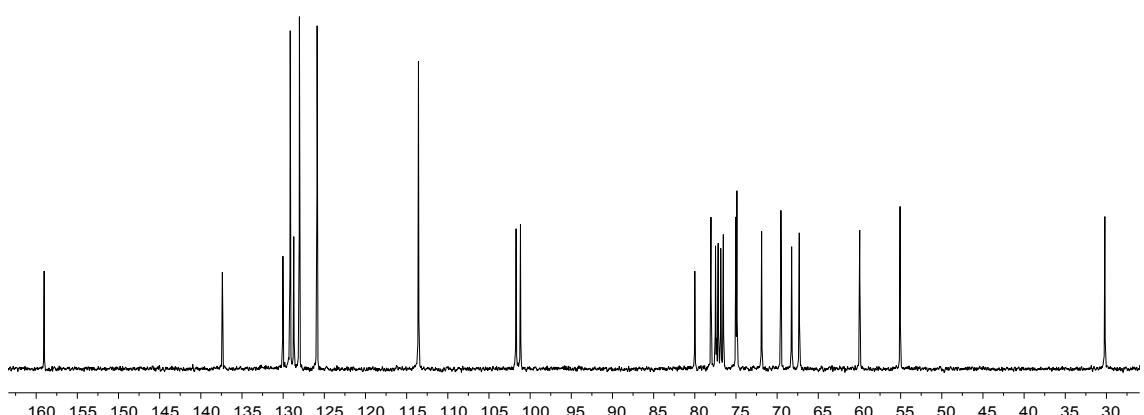
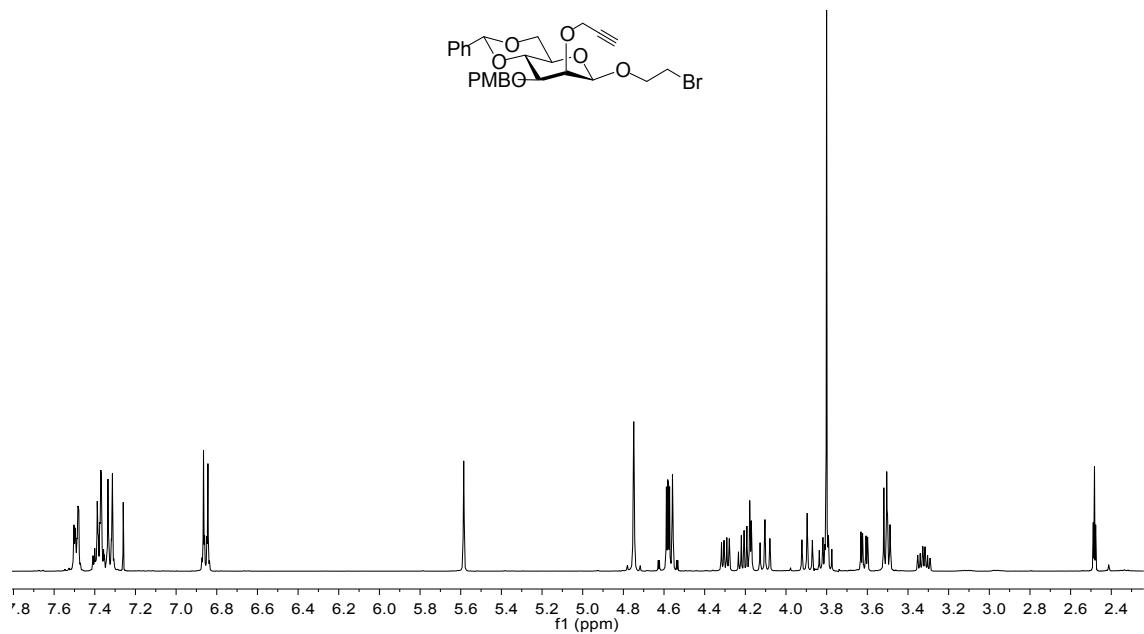


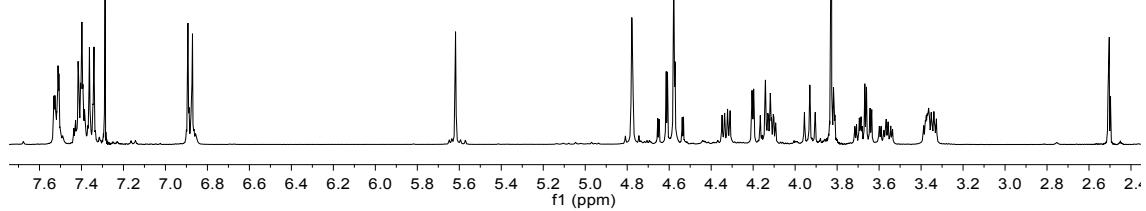
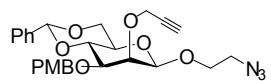
To a solution of compound **20** (750 mg, 0.17 mmol) in MeOH/Toluene (4:1, 7.5 mL), NaOMe (50 mg, 0.93 mmol) was added and the reaction was stirred at room temperature for 1 h. Then, a NaOH 1M solution (3 mL) was added and the reaction mixture was heated at 50 °C for 7 h. After neutralization with Amberlite IR-120H⁺, the solution was filtered and concentrated. The crude was purified by size-exclusion chromatography (Sephadex G-25, H₂O/MeOH 9/1), furnishing Man₉ (**1**) (266 mg, 0.17 mmol, quant.) as a white amorphous solid. $[\alpha]_D^{20} : +58$ (*c* 1.00, H₂O); ¹H-NMR (400 MHz, D₂O) δ : 5.41 (d, *J*_{1,2} = 1.2, 1H, H-1), 5.35 (br s, 1H, H-1), 5.31 (d, *J*_{1,2} = 1.2, 1H, H-1), 5.16 (d, *J*_{1,2} = 1.3, 1H, H-1), 5.07-5.03 (m, 3H, 3xH-1), 4.88 (m, 1H, H-1), 4.74 (d, *J*_{1 β ,2 β} = 0.5, 1H, H-1 β), 4.19 (m, 1H), 4.16 (m, 1H), 4.13-4.09 (m, 3H), 4.09-4.06 (m, 3H), 4.05-3.94 (m, 8H), 3.93-3.68 (m, 36H), 3.68-3.60 (m, 4H), 3.59-3.45 (m, 4H); ¹³C-NMR (100 MHz, D₂O) δ : 102.3 (C-1), 102.1 (2xC-1), 100.7 (2xC-1), 100.5 (C-1), 99.9 (C-1 β), 99.5 (C-1), 97.9 (C-1), 81.0, 78.9, 78.6, 78.5, 78.4, 74.0, 73.2-73.1, 72.6, 71.1, 70.3-69.9, 69.4, 68.4, 66.9-66.8, 65.6-65.4, 61.1-60.9, 50.3; ESI-MS *m/z* calcd. for C₅₆H₉₅N₃O₄₆: 1545.5; found: 1568.9 [M+Na]⁺, 795.5 [M+2Na]⁺².

¹H and ¹³C NMR spectra and selected HSQC and MS spectra

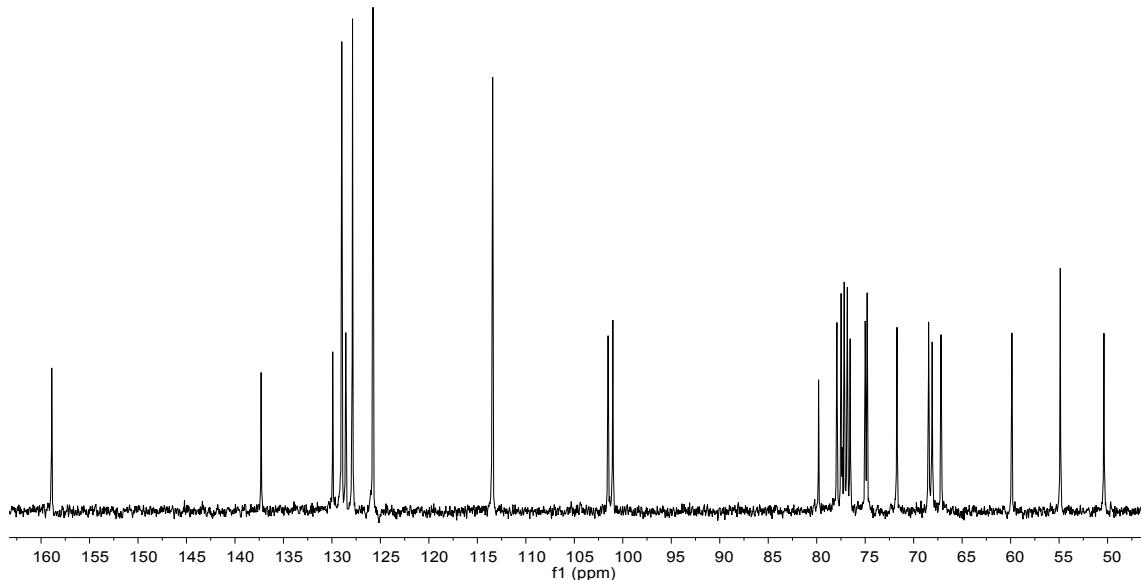


¹³C-NMR (100 MHz, CDCl₃): compound 3

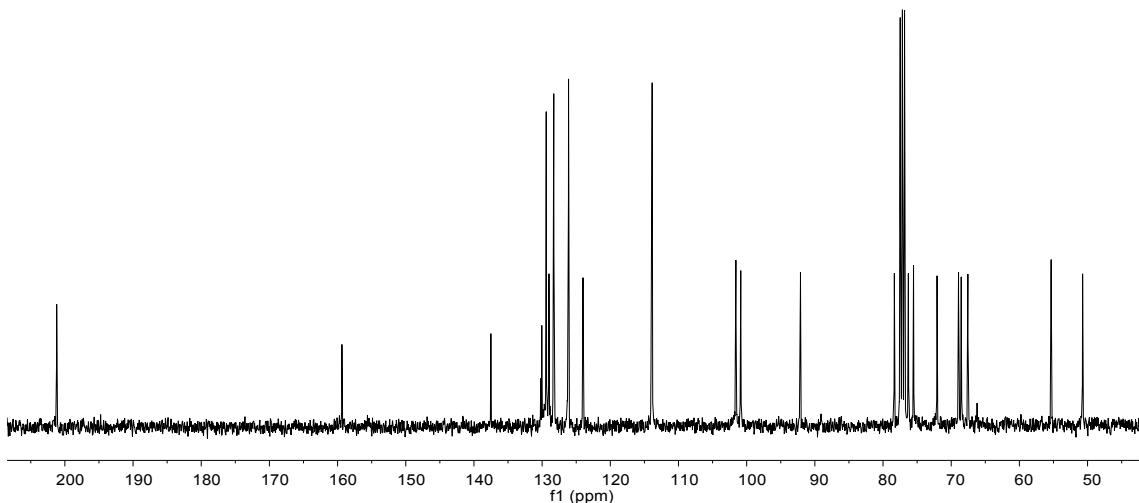
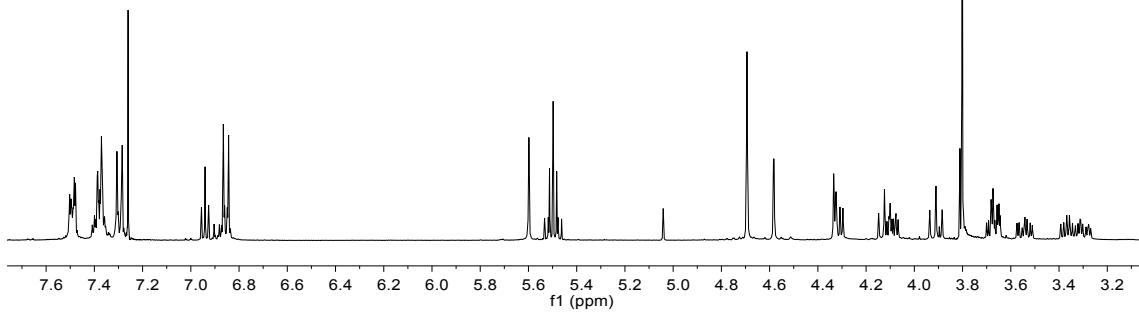
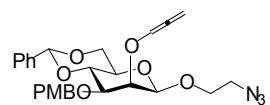


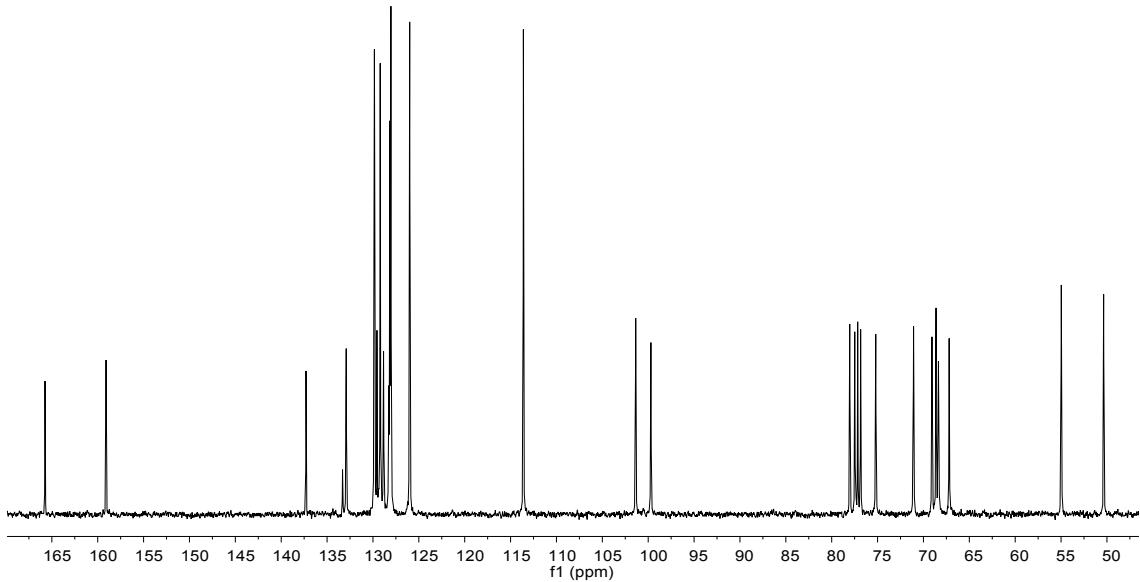
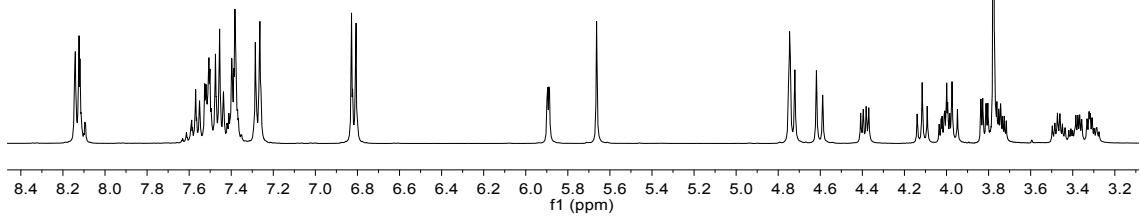
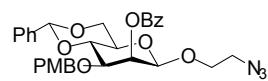


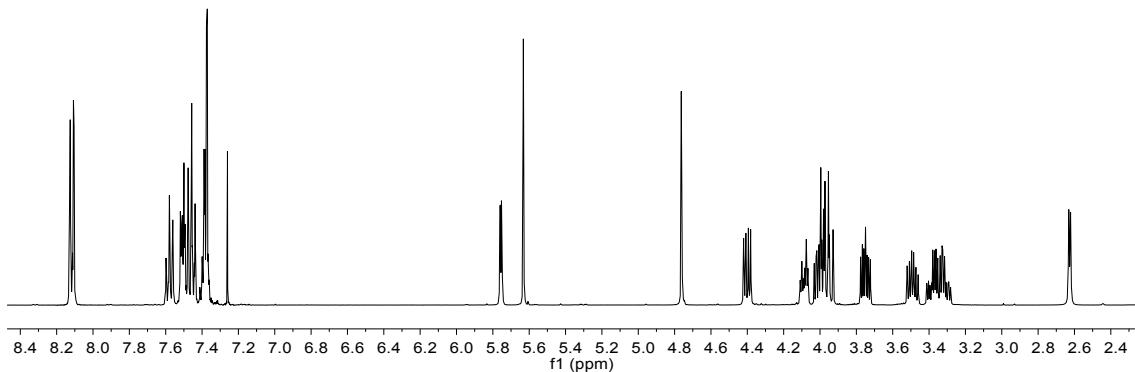
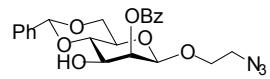
¹H-RMN (400 MHz, CDCl₃): compuesto **23**



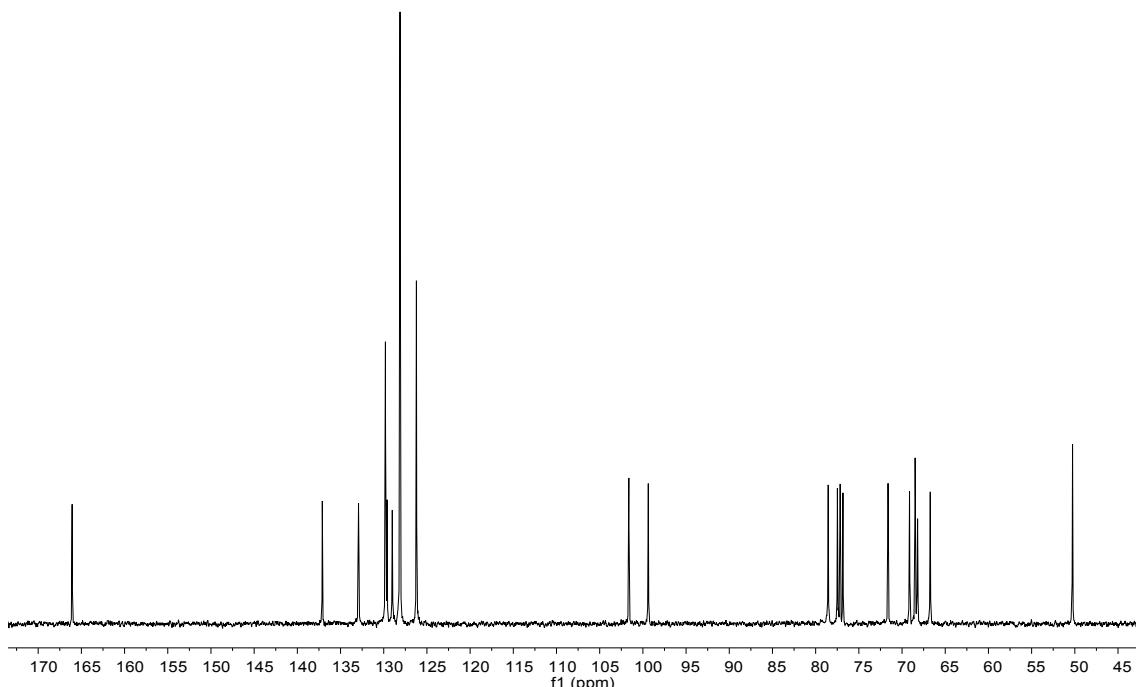
¹³C-RMN (100 MHz, CDCl₃): compuesto **23**



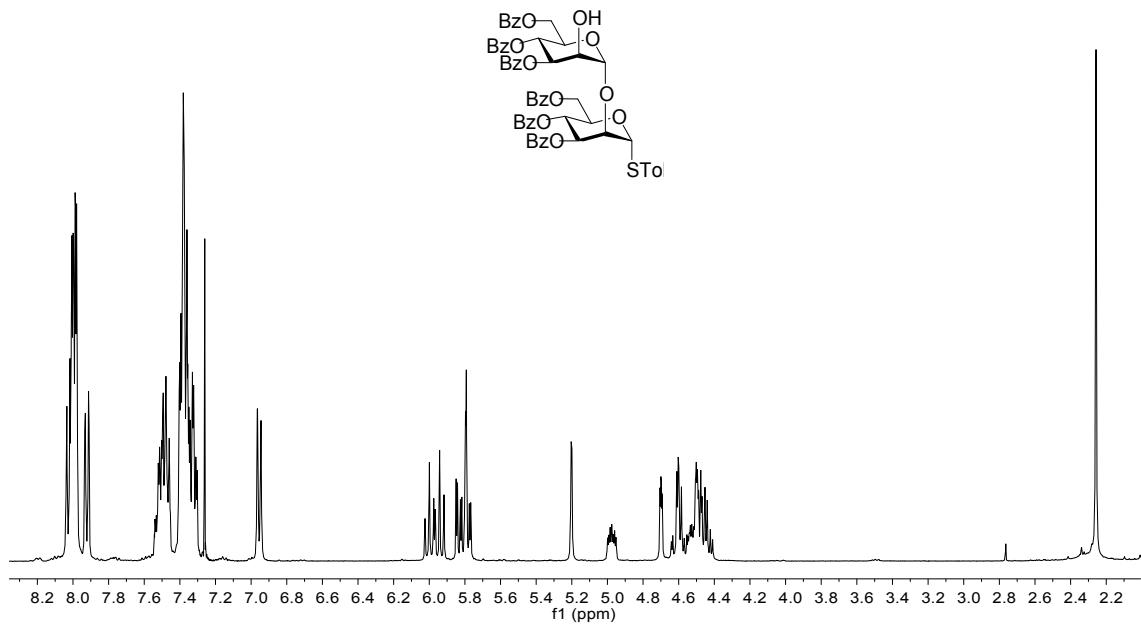




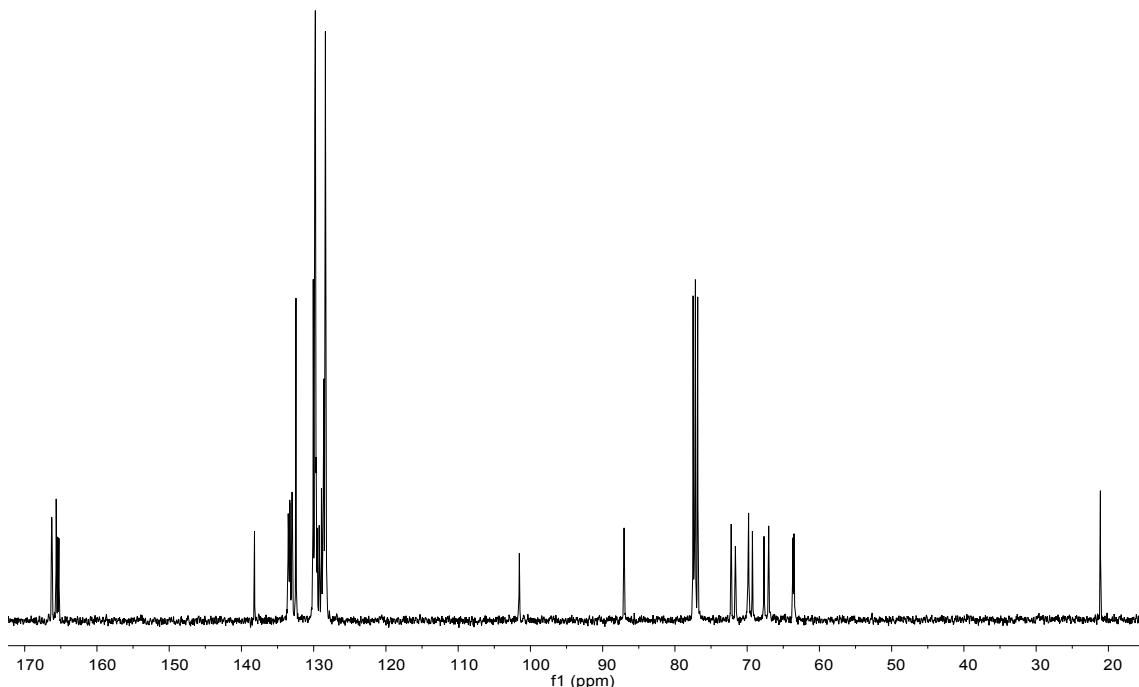
^1H -NMR (400 MHz, CDCl_3): compound **5**



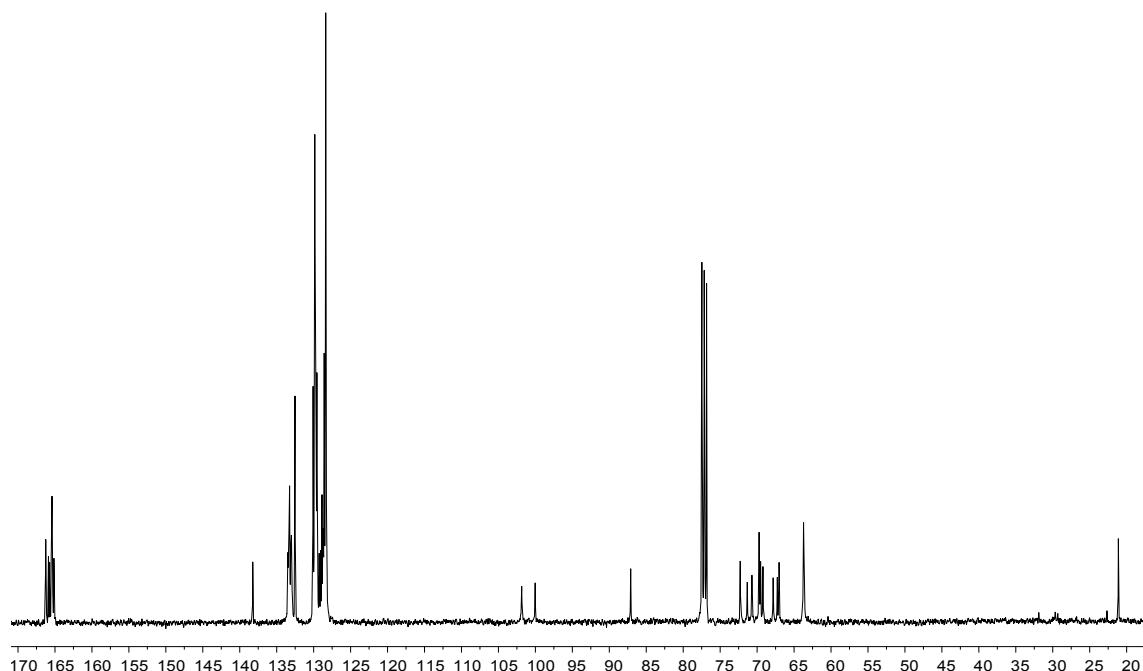
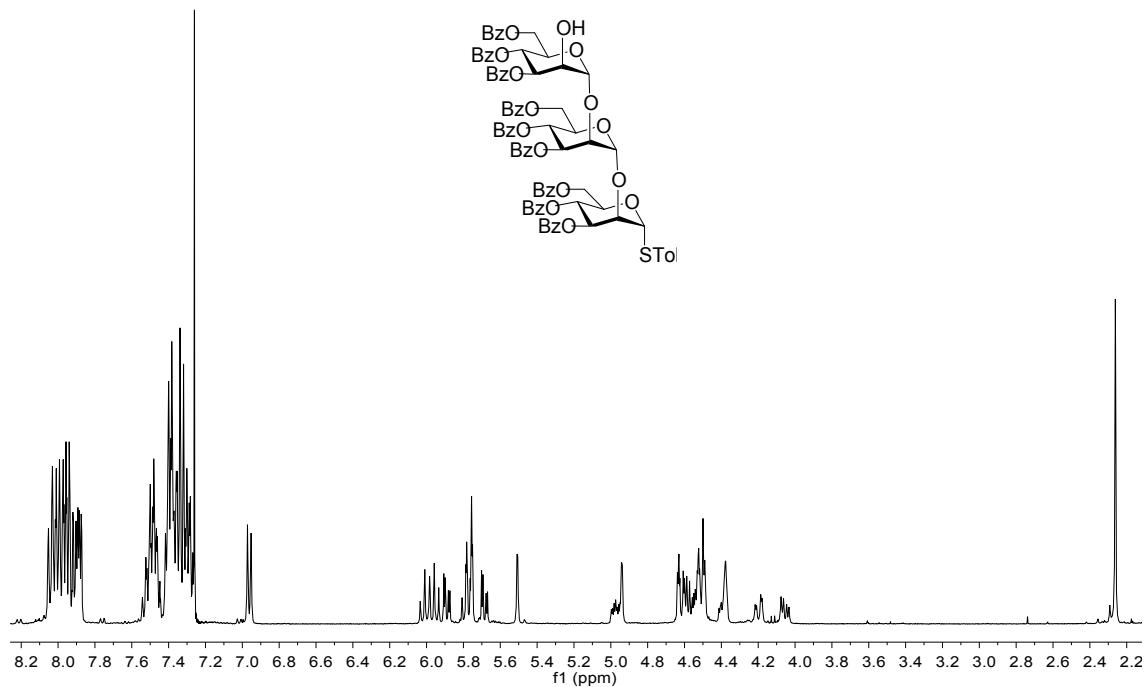
^{13}C -NMR (100 MHz, CDCl_3): compound **5**



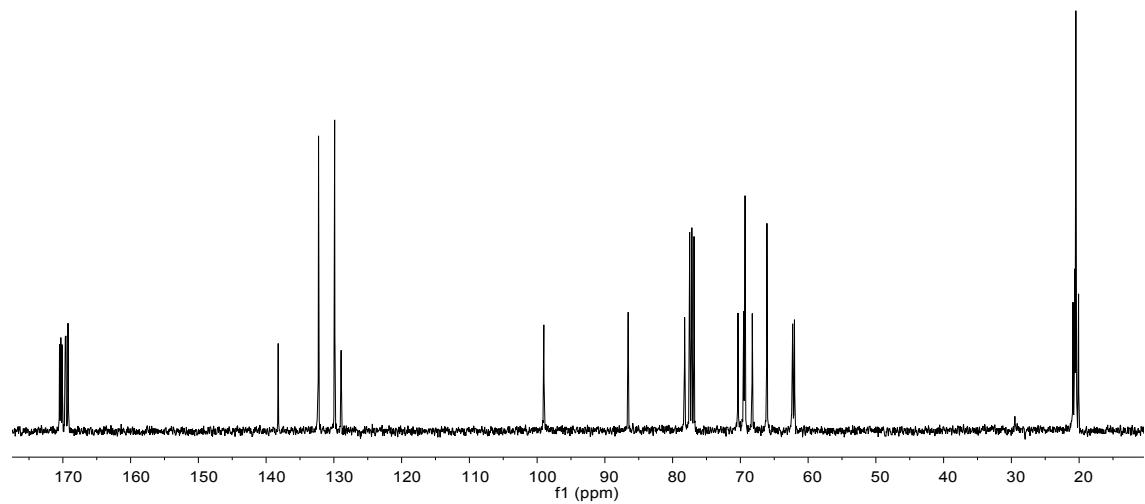
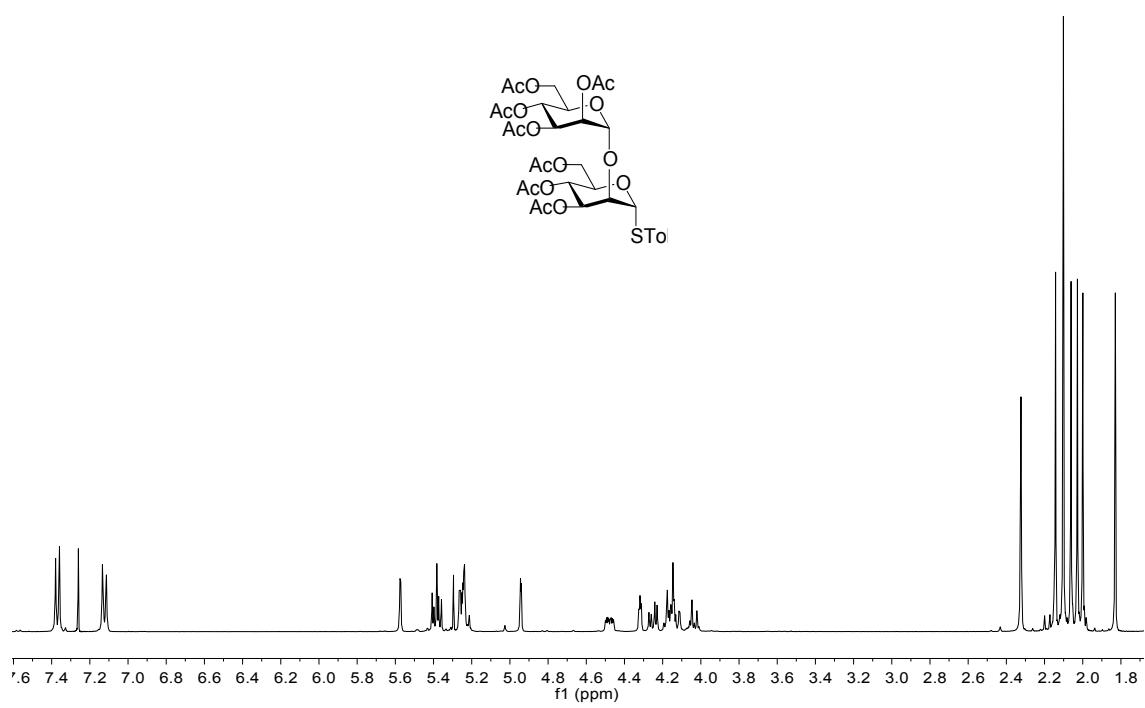
^1H -NMR (400 MHz, CDCl_3): compound 8

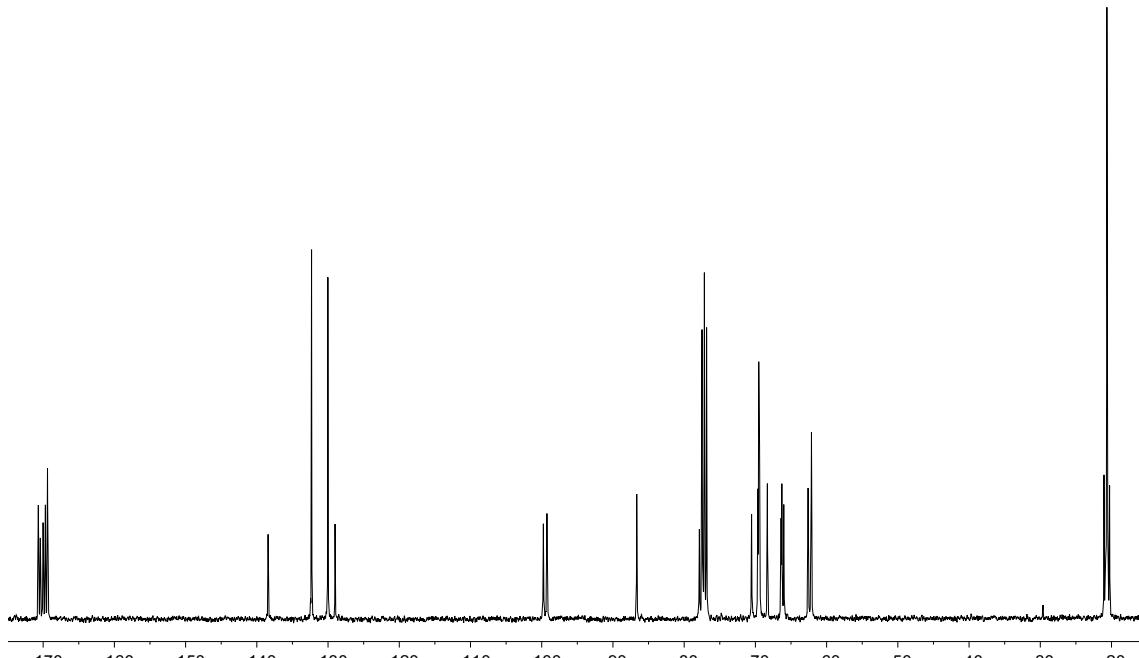
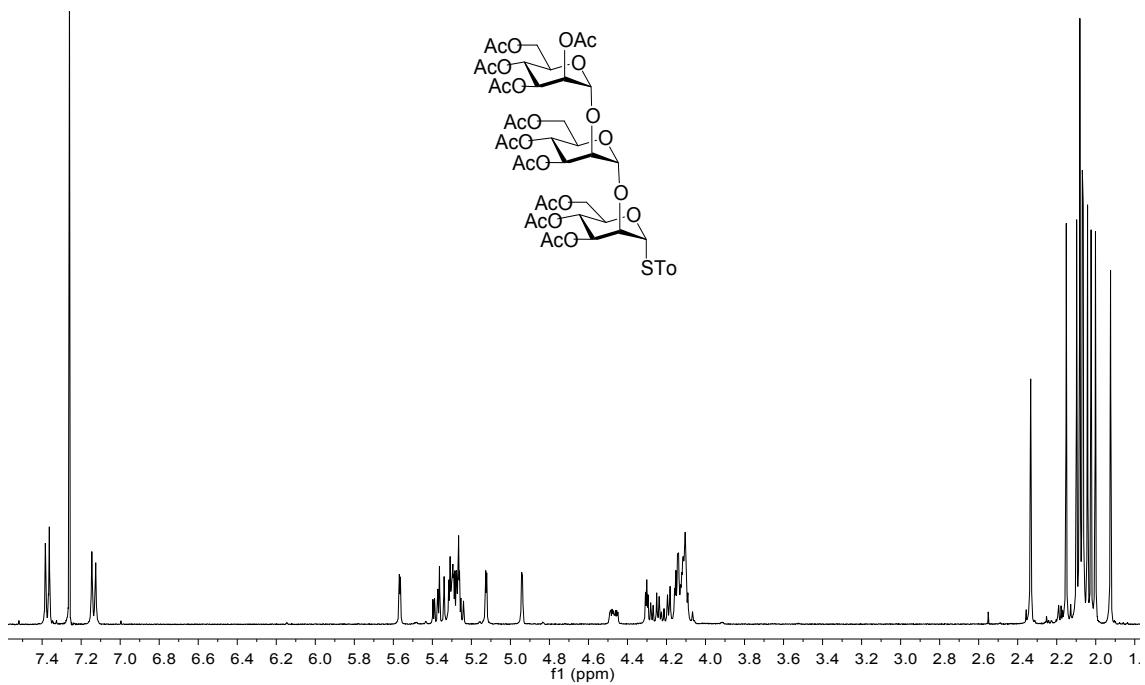


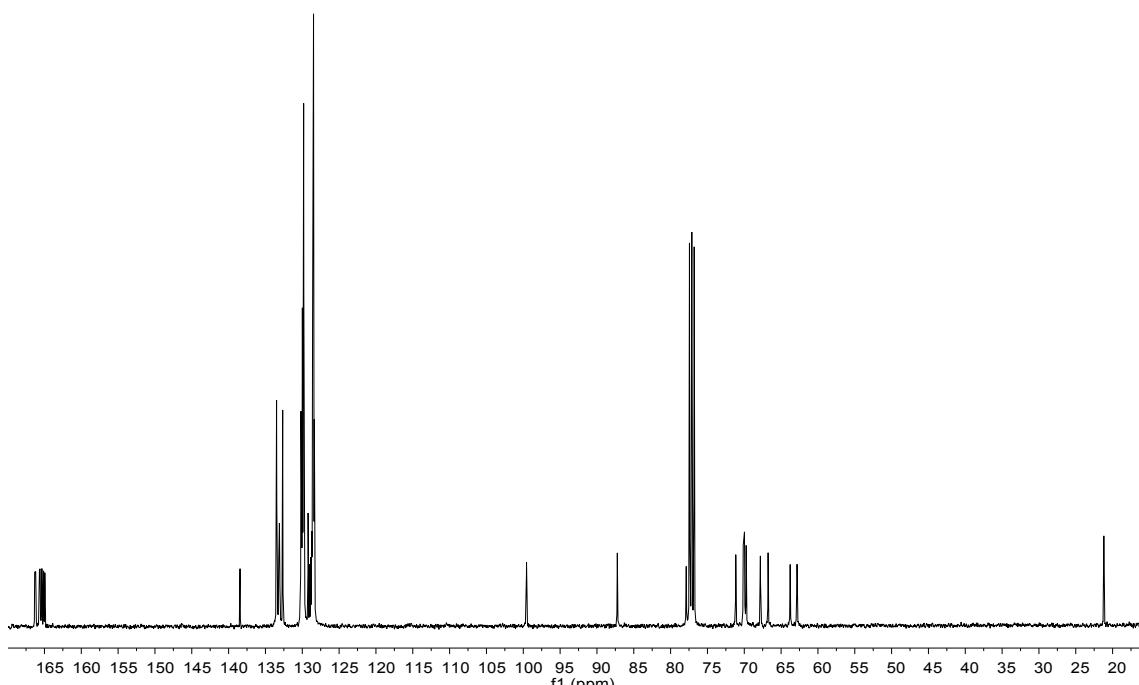
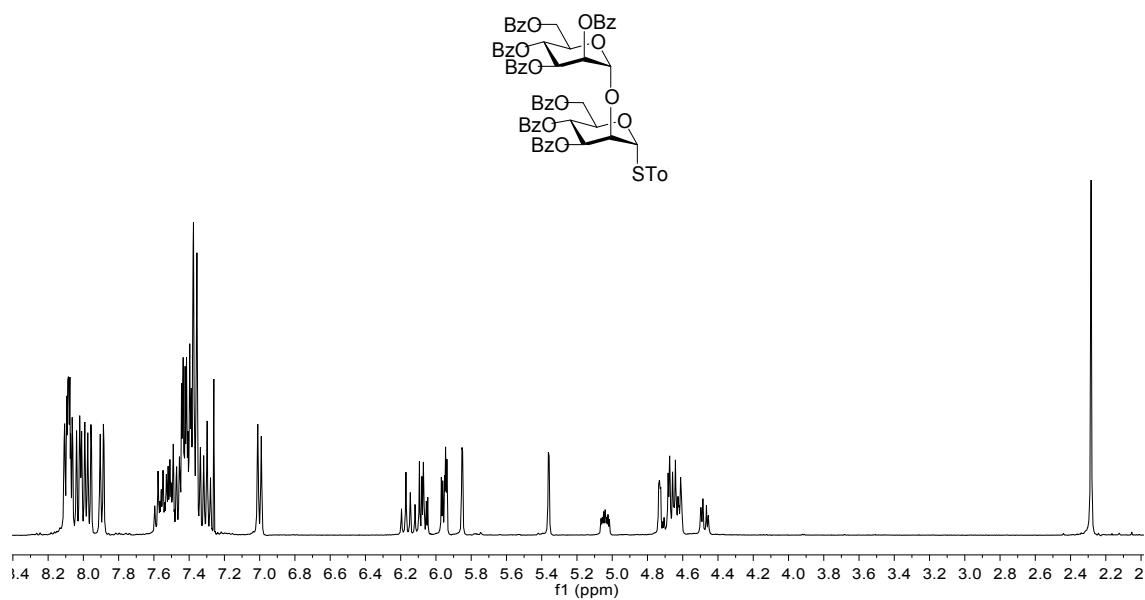
^{13}C -NMR (100 MHz, CDCl_3): compound 8

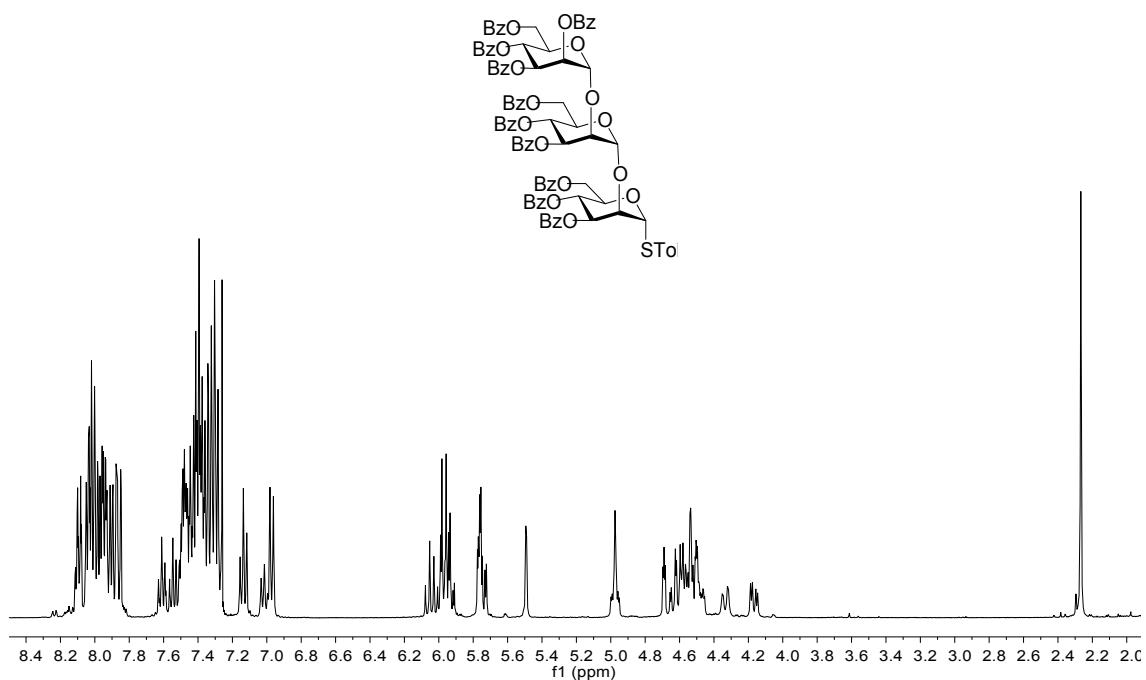


¹³C-NMR (100 MHz, CDCl₃): compound **9**

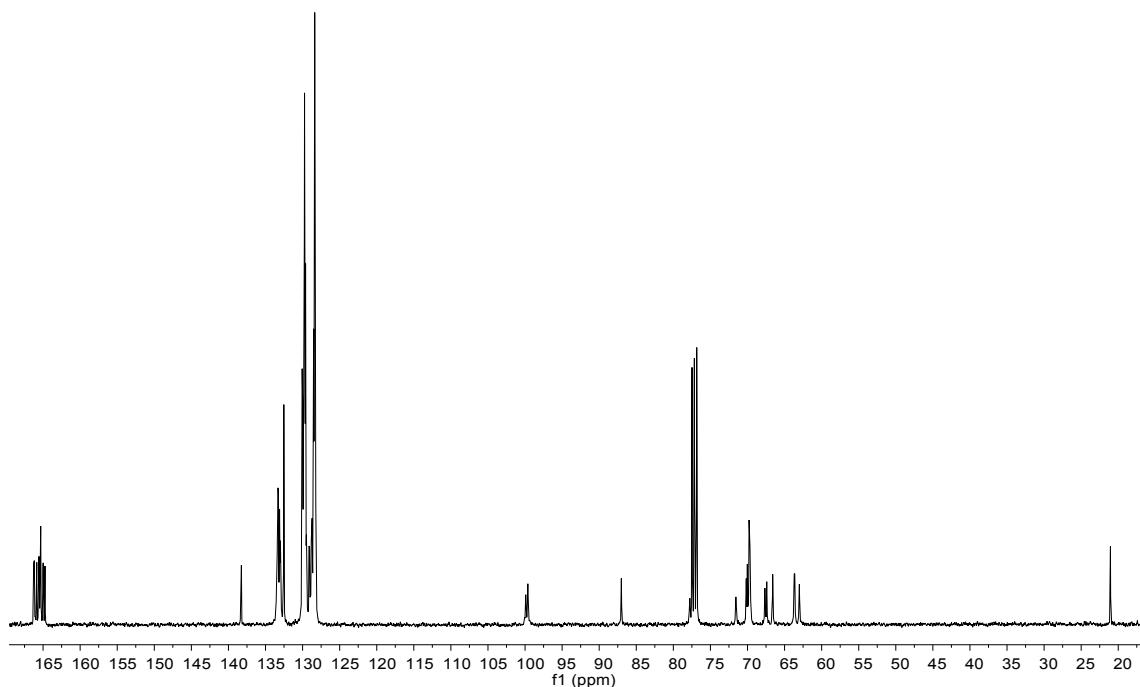




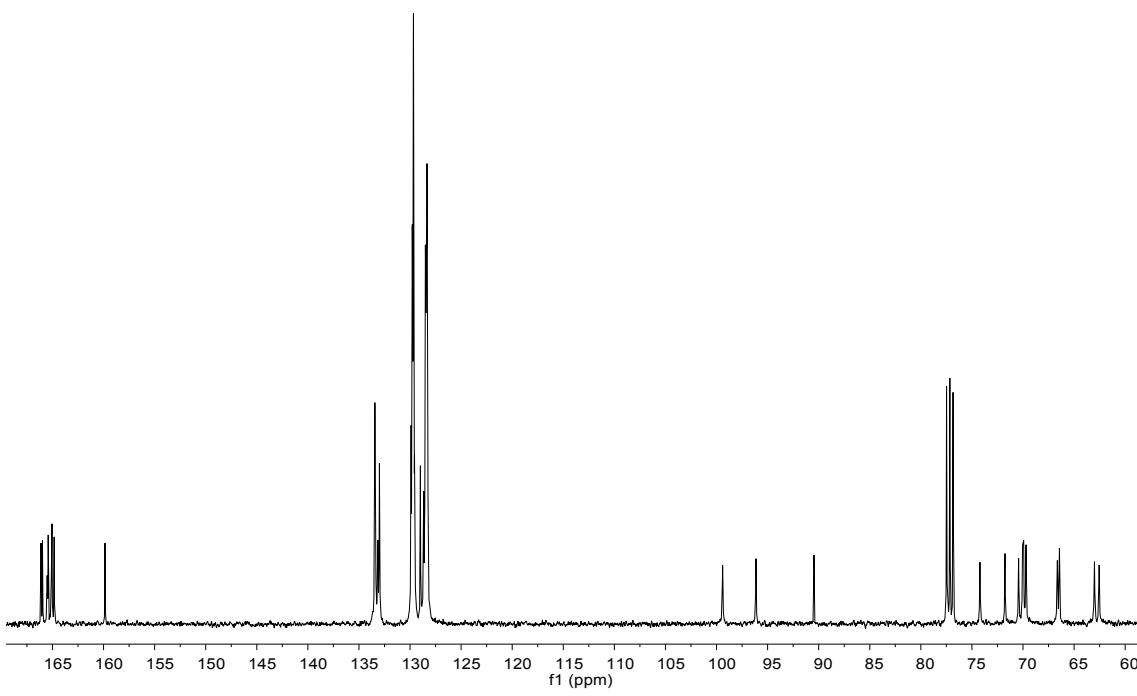
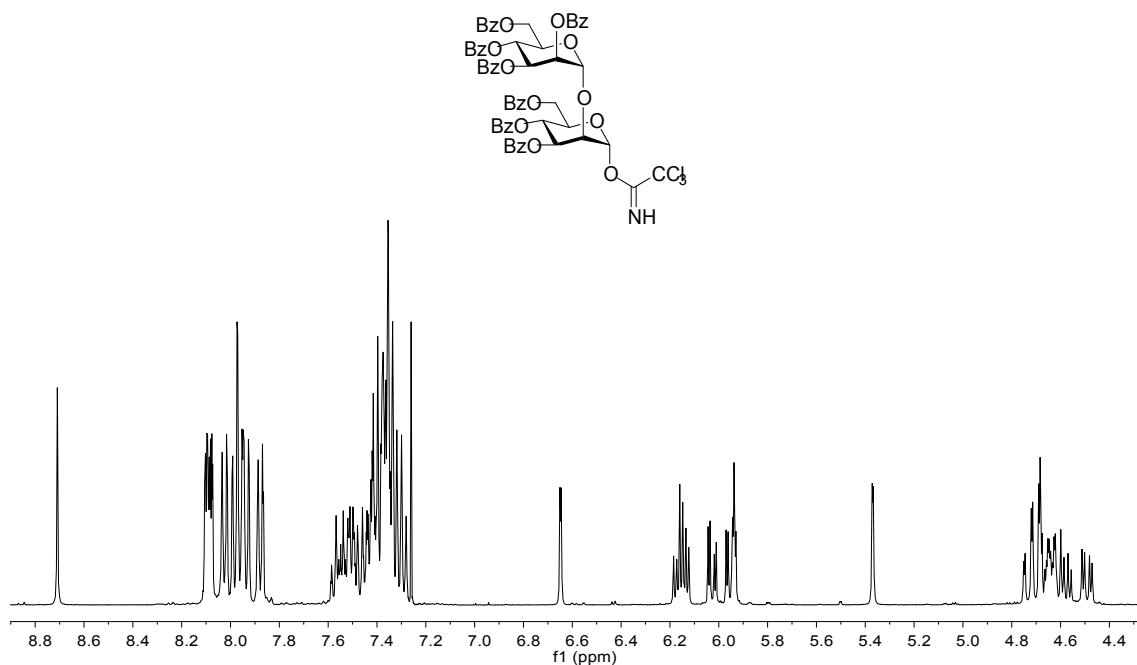


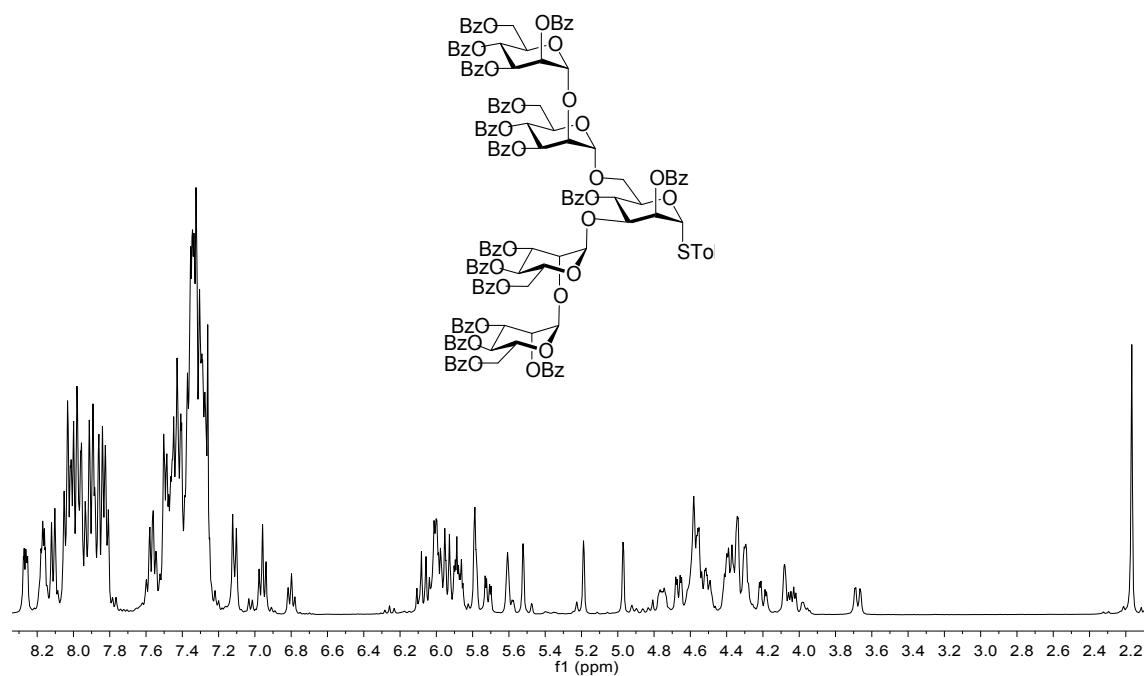


^1H -NMR (400 MHz, CDCl_3): compound **15**

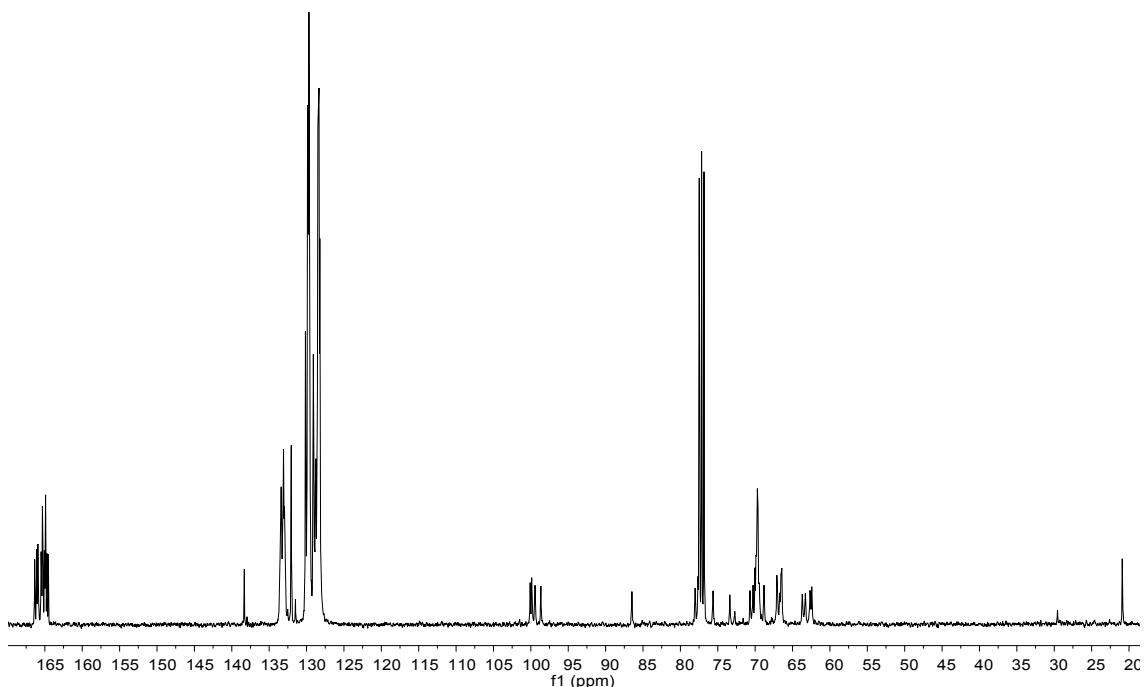


^{13}C -NMR (100 MHz, CDCl_3): compound **15**

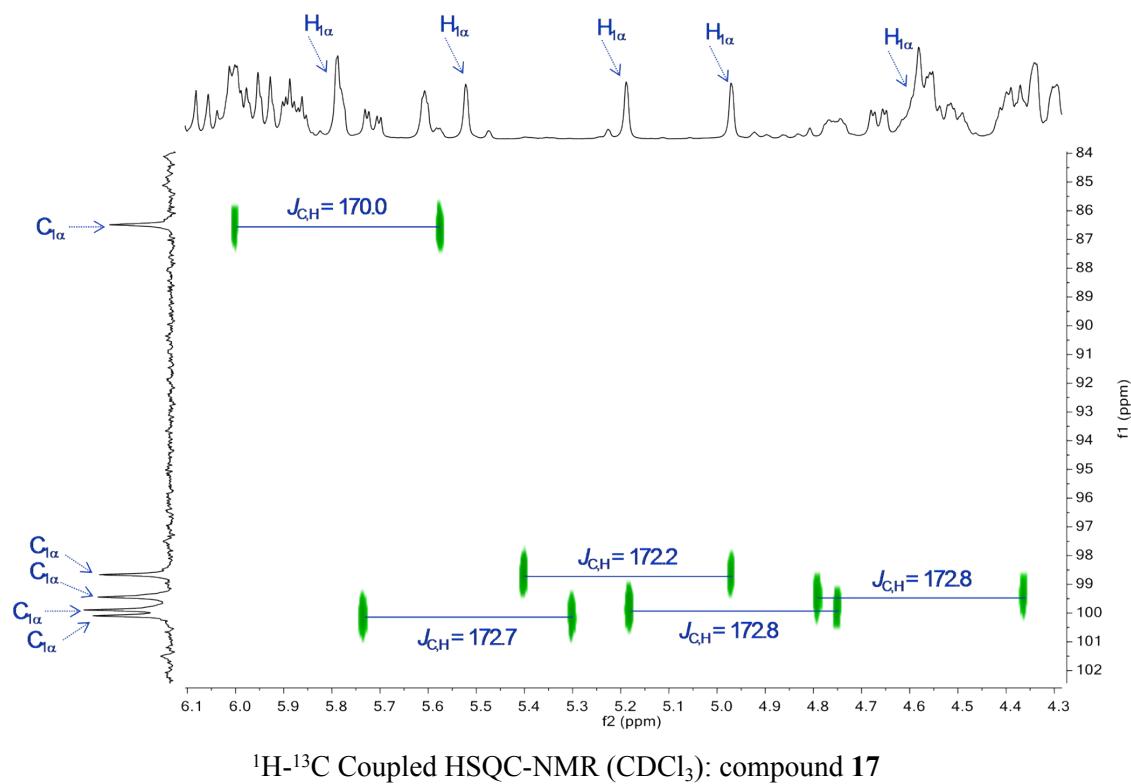




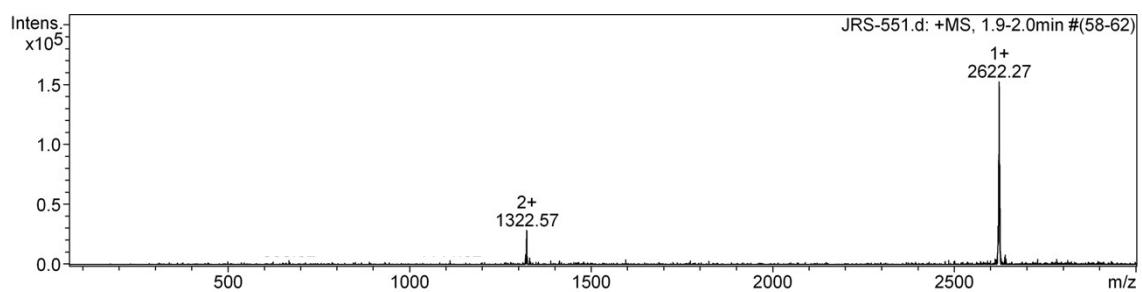
¹H-NMR (400 MHz, CDCl_3): compound **17**



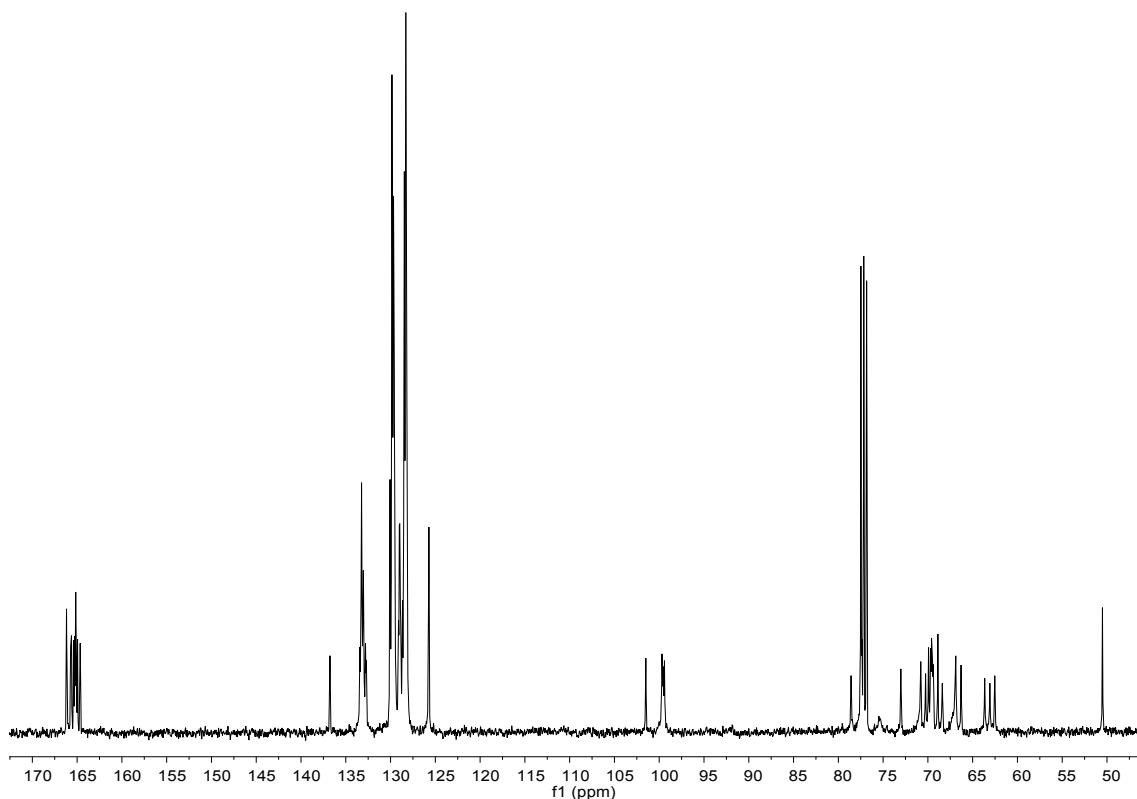
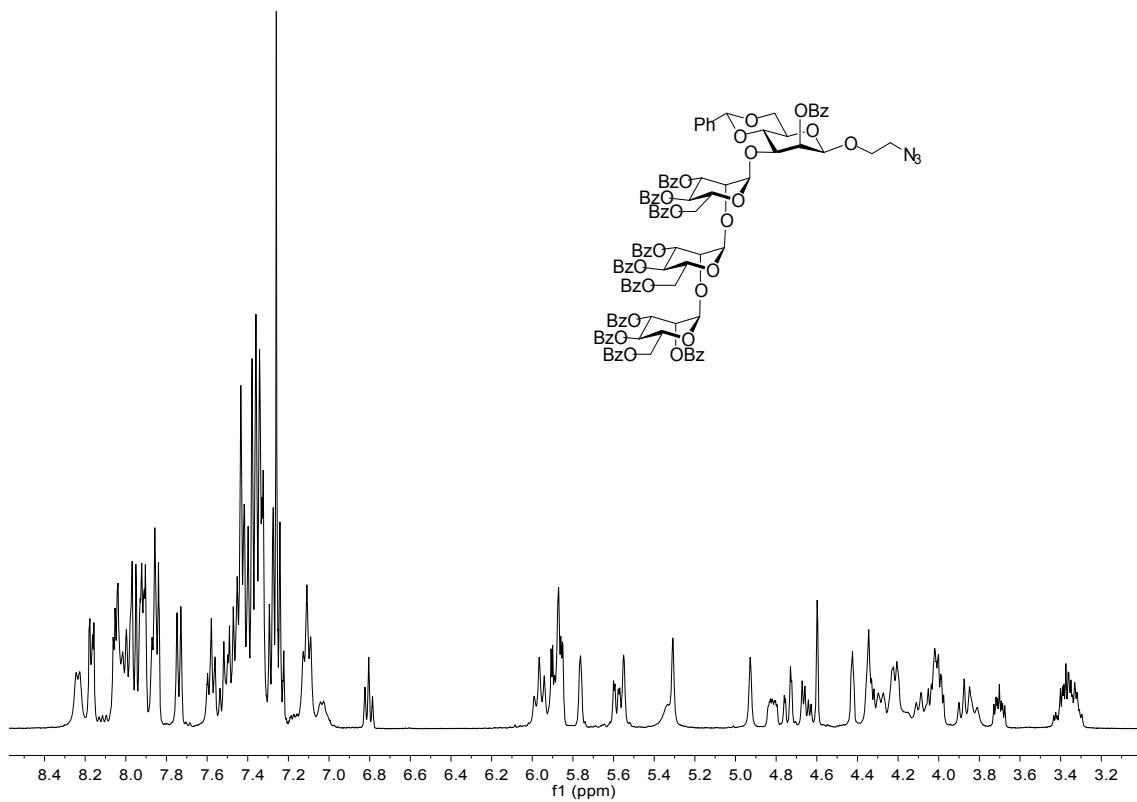
¹³C-NMR (100 MHz, CDCl_3): compound **17**



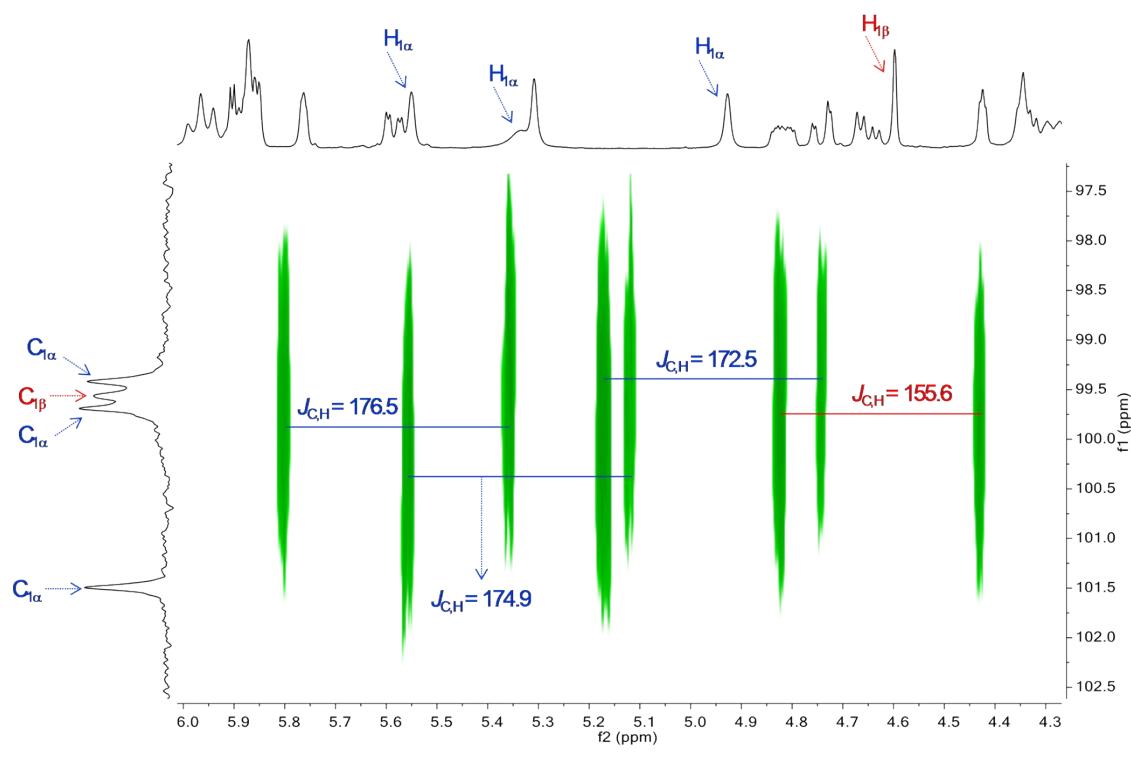
^1H - ^{13}C Coupled HSQC-NMR (CDCl_3): compound **17**



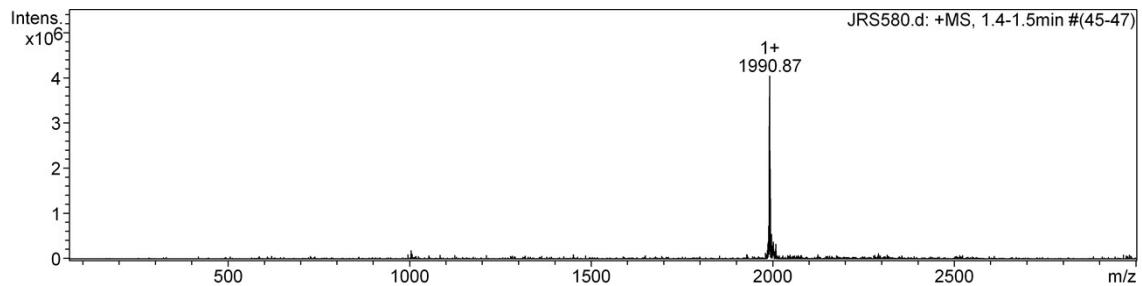
ESI-MS: compound **17**



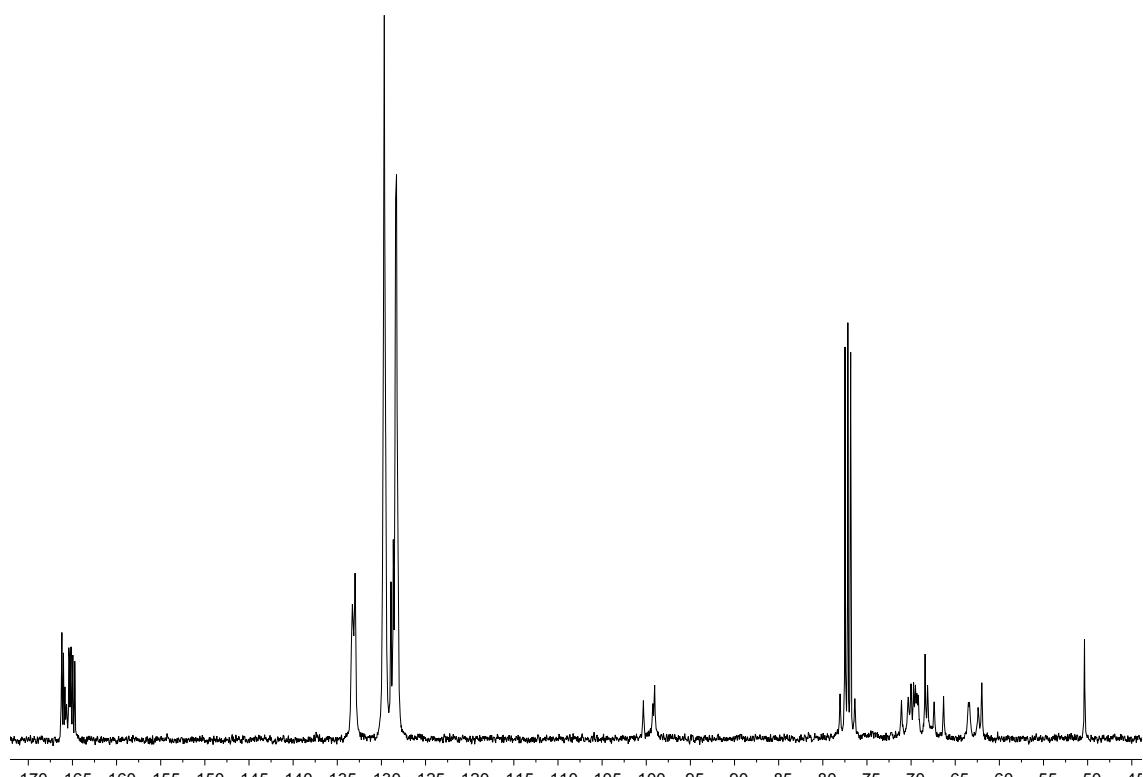
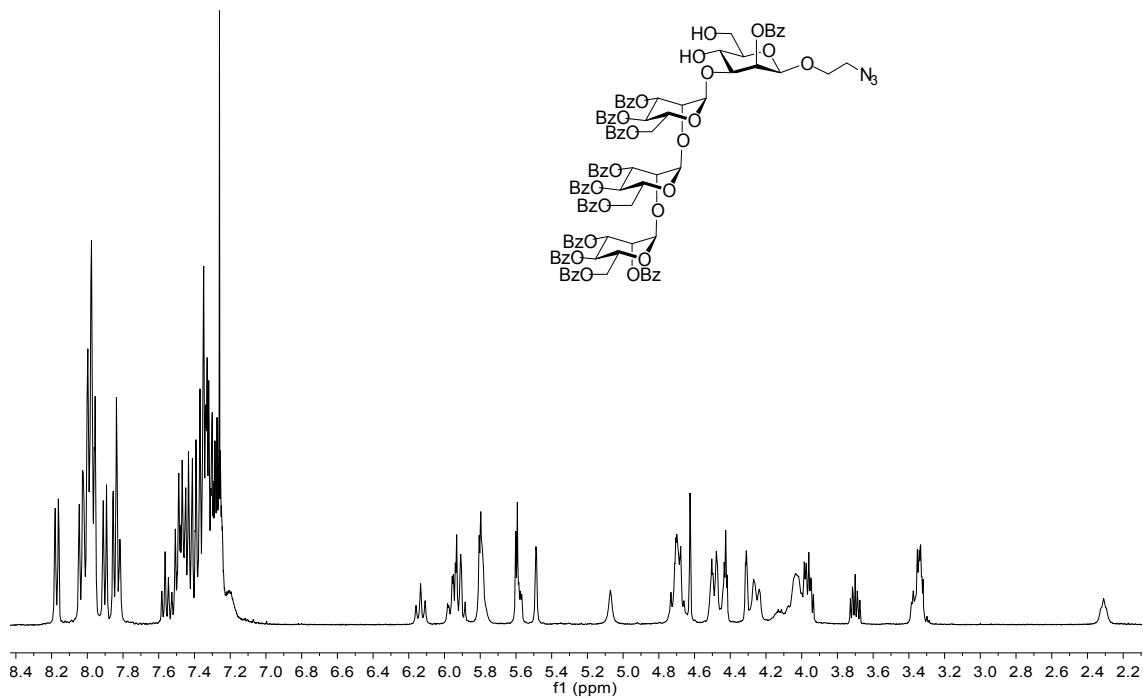
¹³C-NMR (100 MHz, CDCl₃): compound **18**

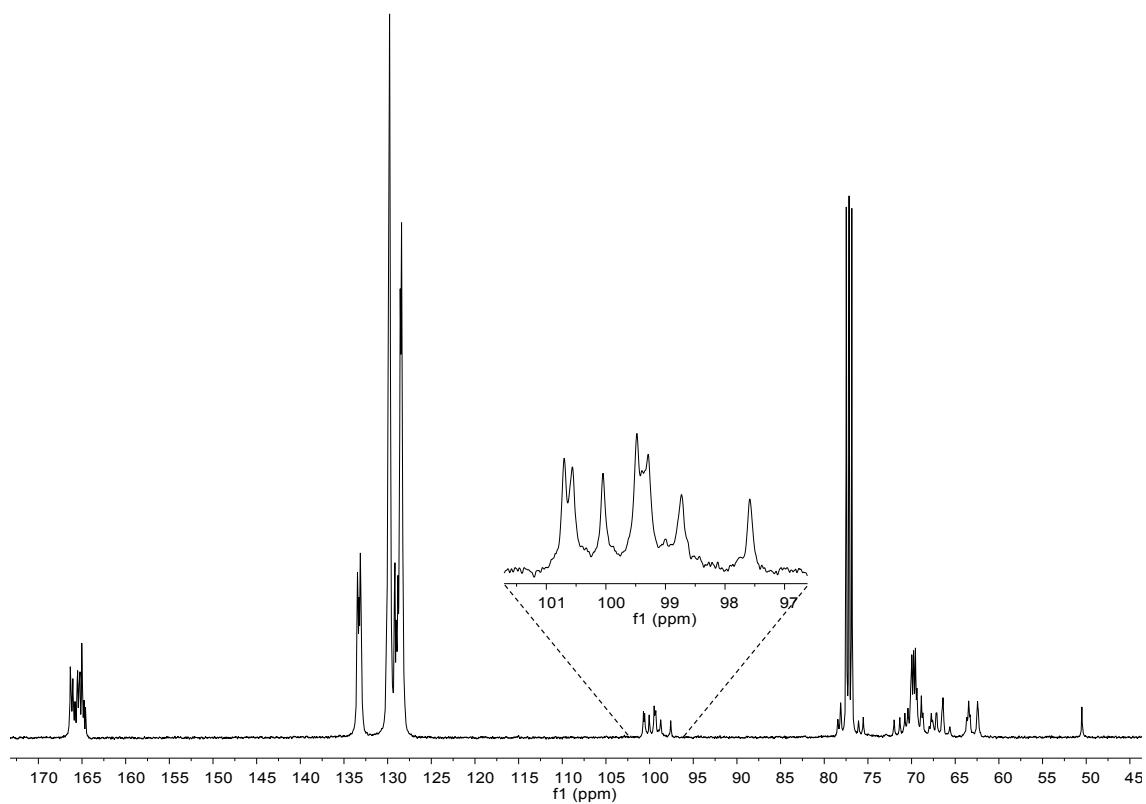
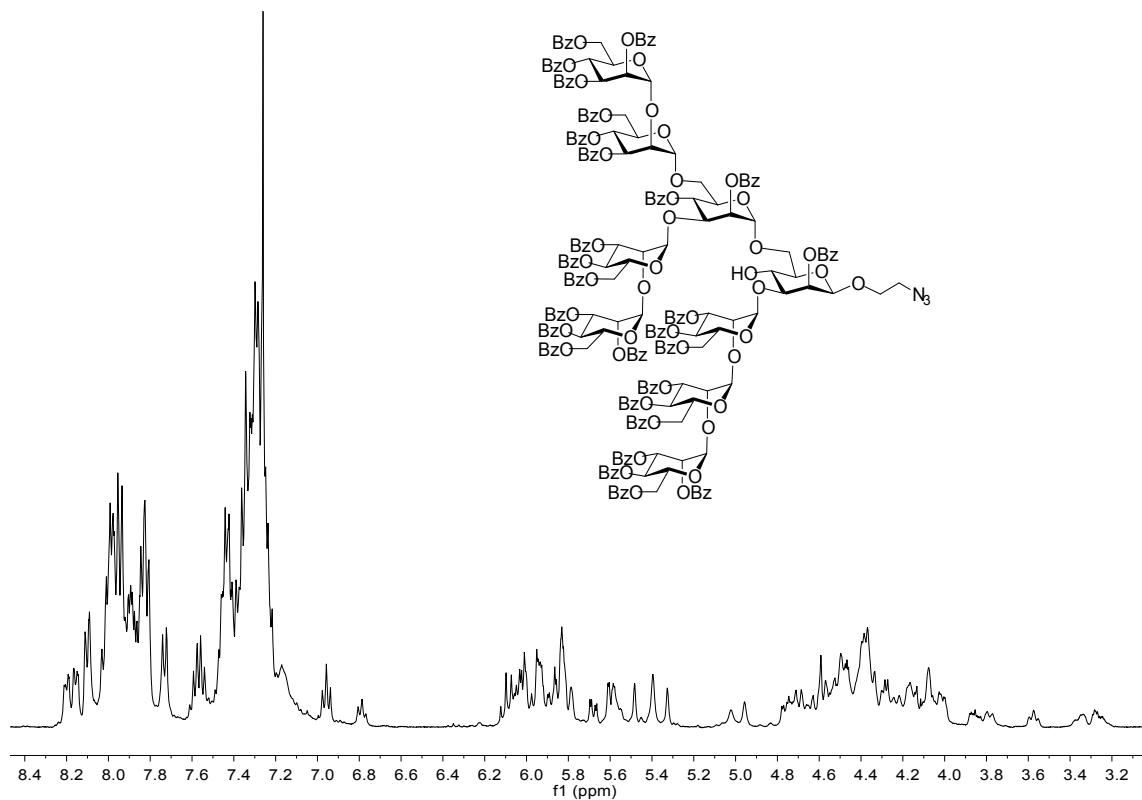


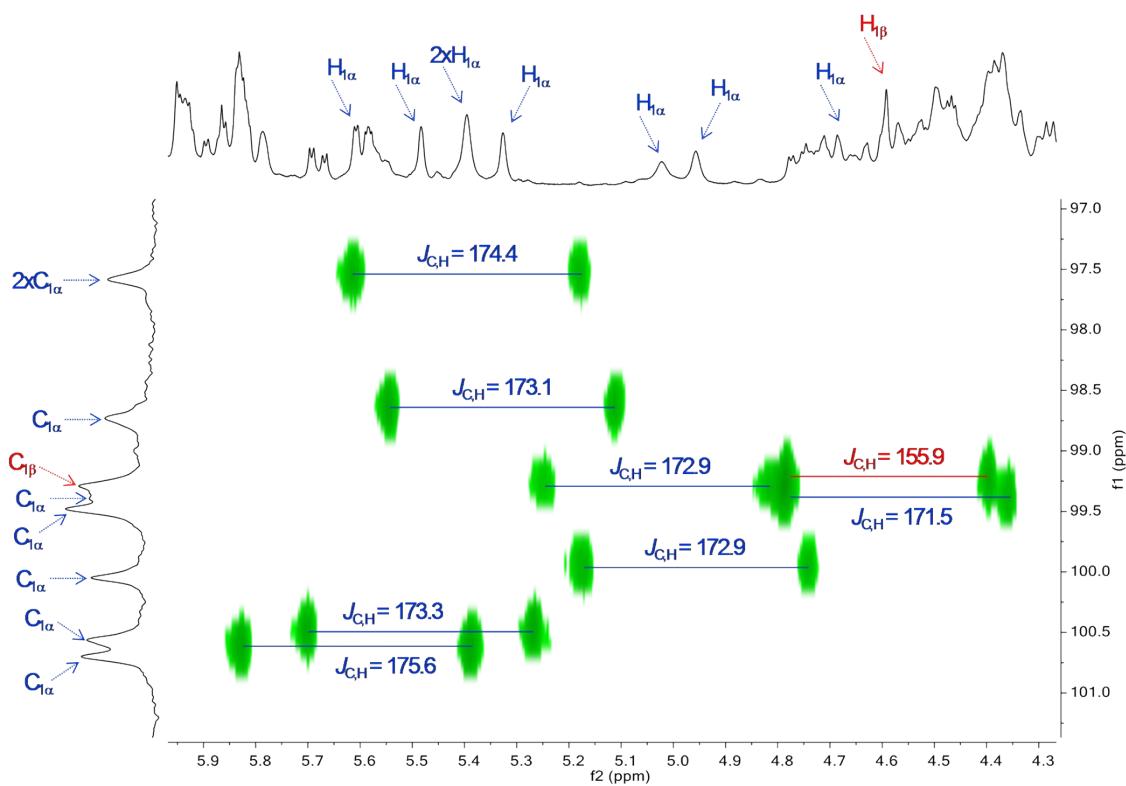
^1H - ^{13}C Coupled HSQC-NMR (CDCl_3): compound **18**



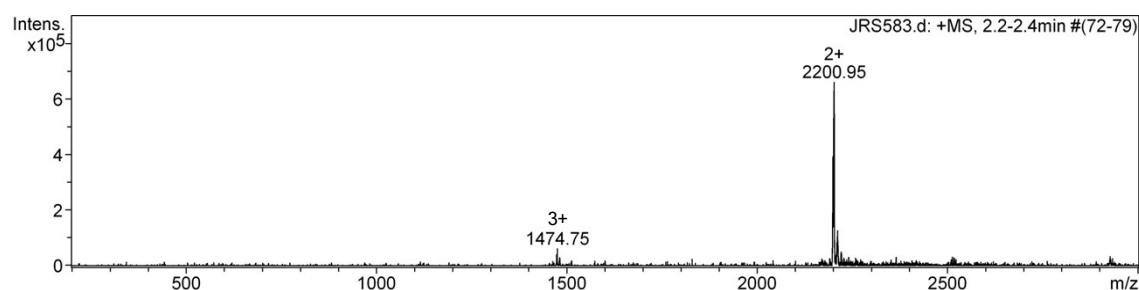
ESI-MS: compound **18**



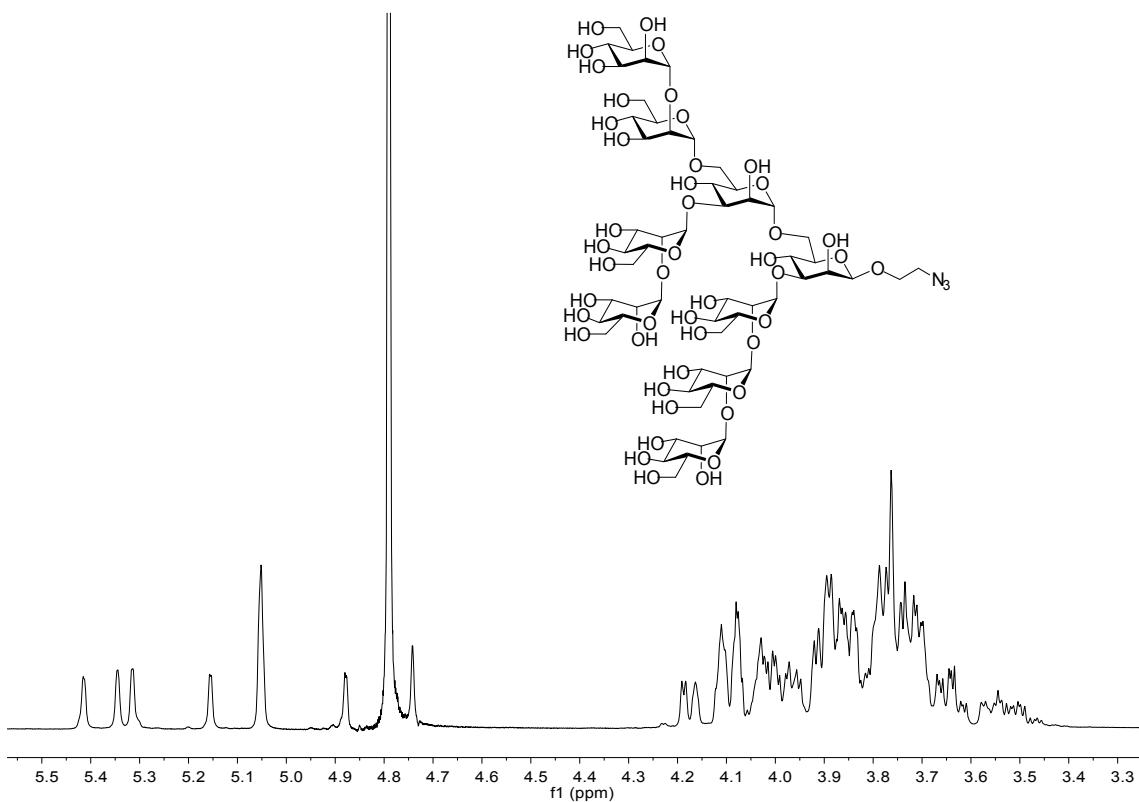




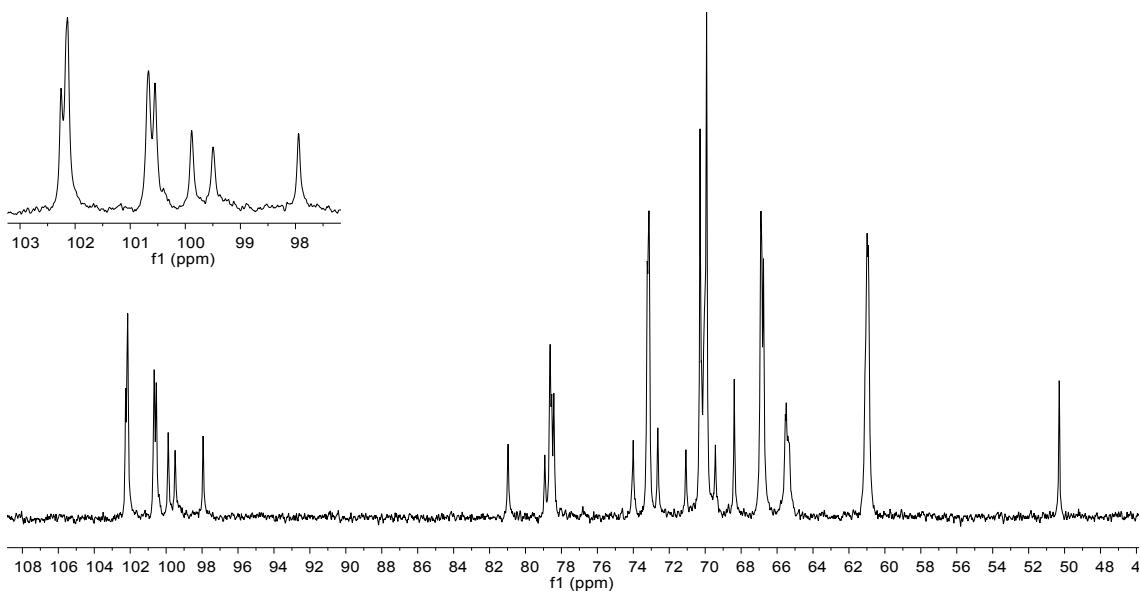
^1H - ^{13}C Coupled HSQC-NMR (CDCl_3): compound **20**



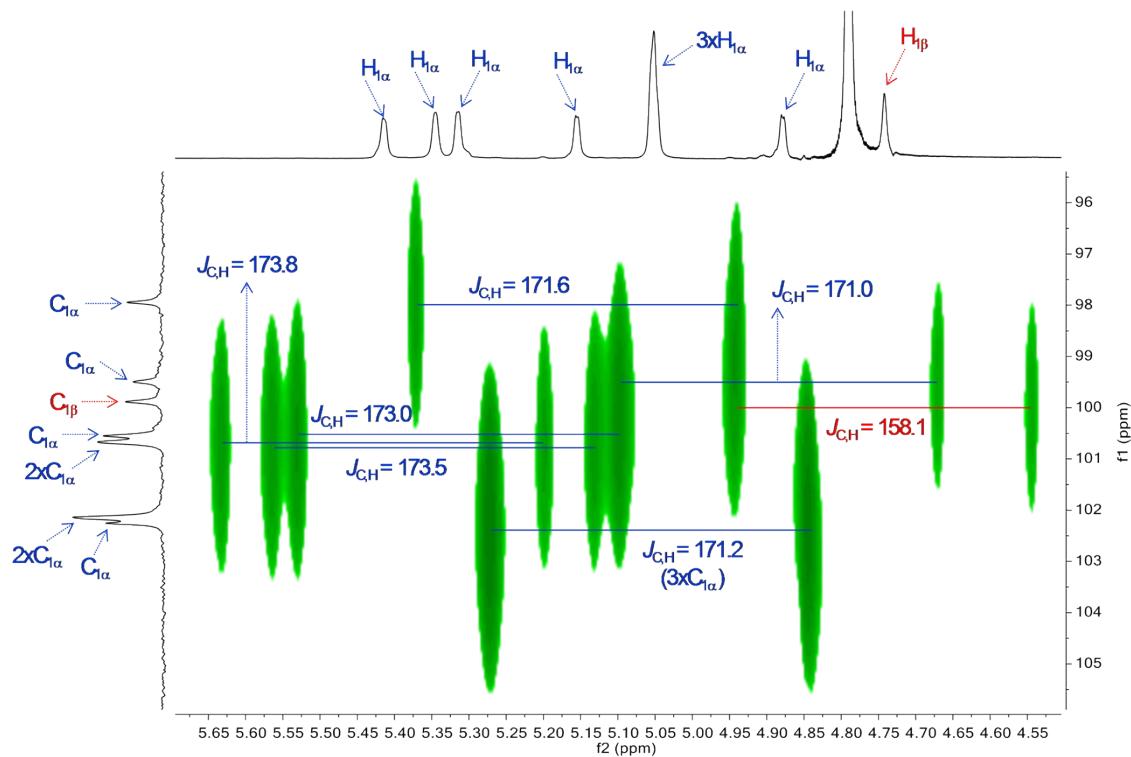
ESI-MS: compound **20**



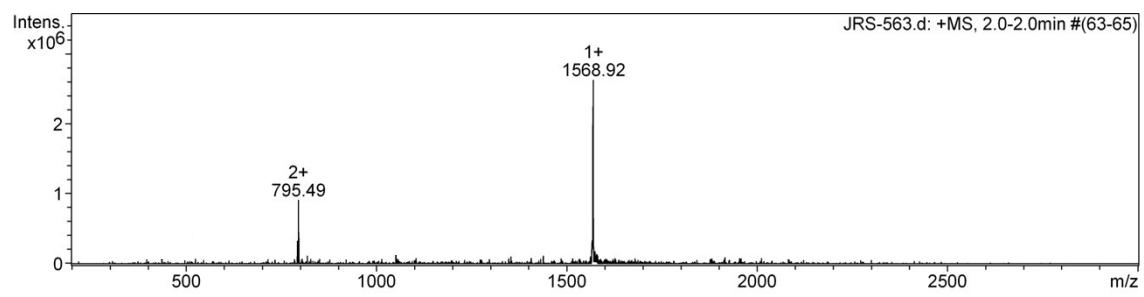
^1H -NMR (400 MHz, D_2O): compound **1**



^{13}C -NMR (100 MHz, D_2O): compound **1**



¹H-¹³C Coupled HSQC-NMR (CDCl_3): compound 1



ESI-MS: compound 1