SUPPORTING INFORMATION

Sequential acid-catalyzed alkyl glycosylation and oligomerization of unprotected carbohydrates

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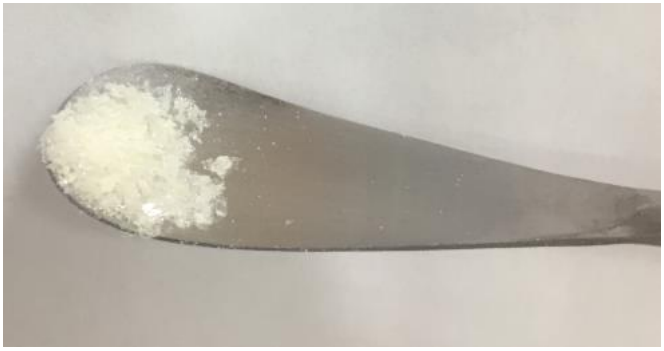


Figure S1. Picture of purified $(PMan)_8$

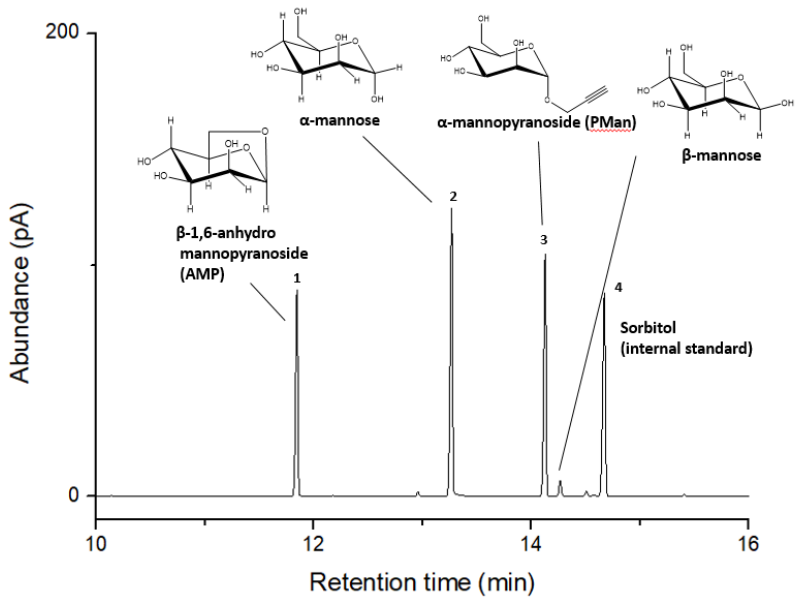


Figure S2. GC-FID spectrum of the sugar standards AMP, mannose, α-propargyl mannopyranoside and the internal standard sorbitol. Column: TRB-5MS (30 m × 0.25 mm × 0.25 mm film thickness) capillary column from Teknokroma with matrix 95% Dimethyl-(5%) diphenyl polysiloxane.

Table S1. Retention times of standards.

Compound	Retention time (t_R) (min)
α-mannose	13.21
β-mannose	14.20
α-propargyl mannopyranoside	14.06
β-propargyl mannopyranoside	14.44
1,6-anhydro mannopyranoside	11.84
Sorbitol	14.59

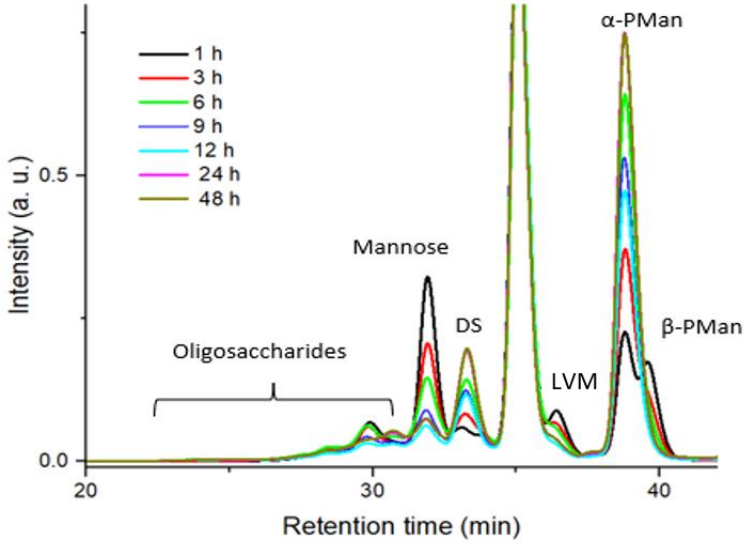


Figure S3. Plot of overlaid SEC (measured against dextran-standards in H_2O at 25 °C) spectra of step 1 over a time period of 48 h. Reaction Conditions step 1: Mannose (1 eq. + PGA (5 eq.) + Amberlyst-15 (4.2 mol%); DS = Disaccharides, LVM = Levomannosane.

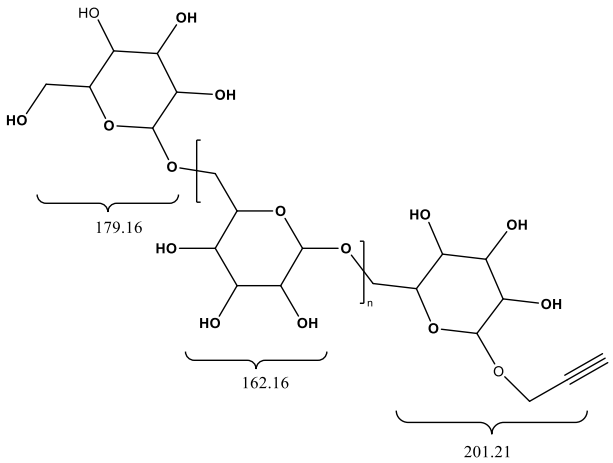


Figure S4. Calculation of the molecular mass of $(PMan)_n$.

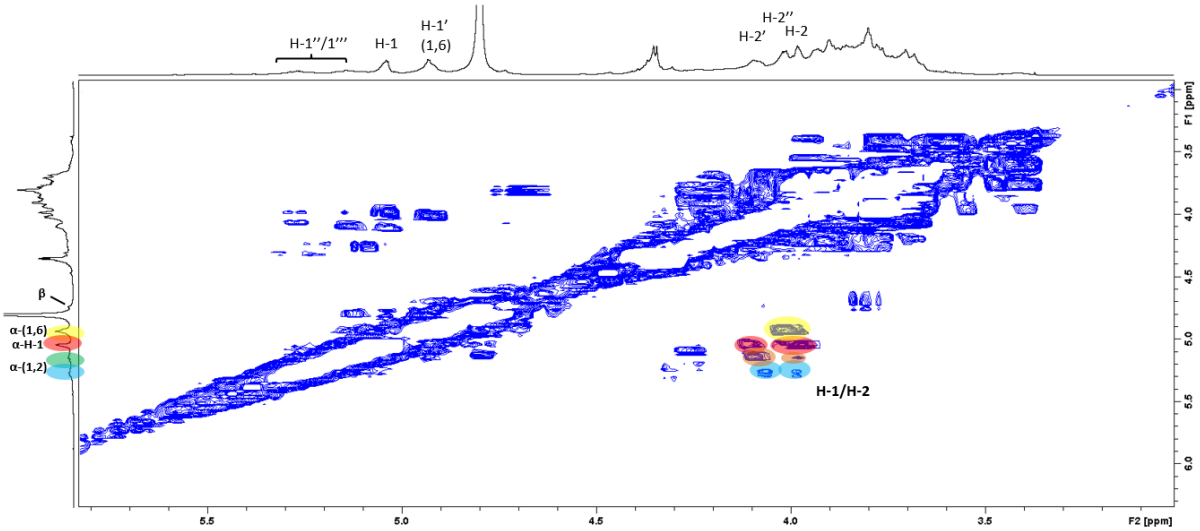


Figure S5. COSY NMR spectrum of $(PMan)_8$.

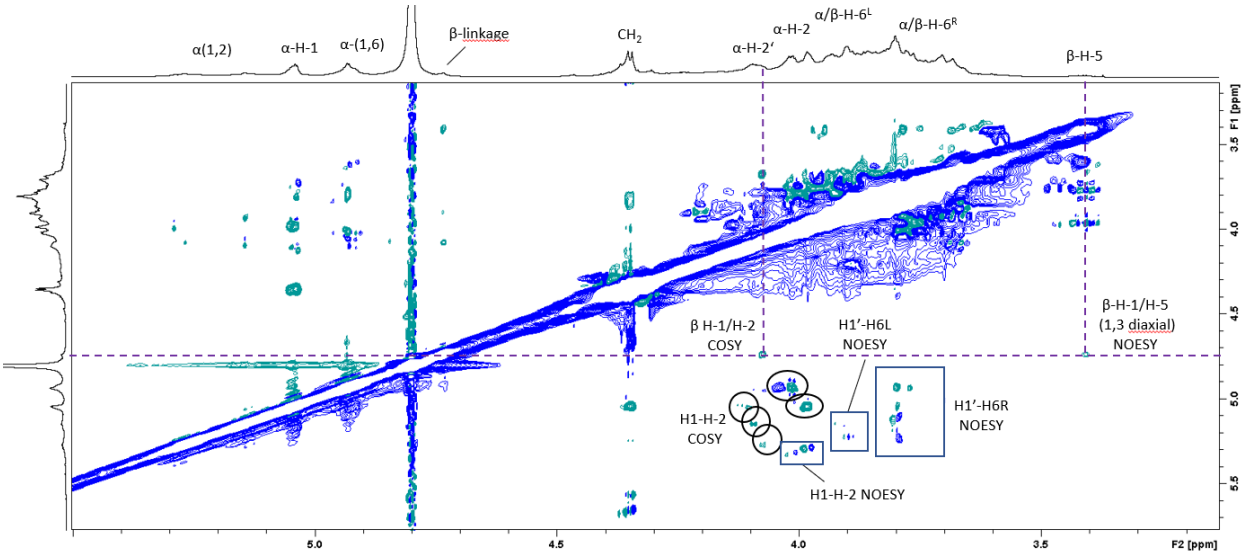


Figure S6. NOESY NMR spectrum of $(PMan)_8$.

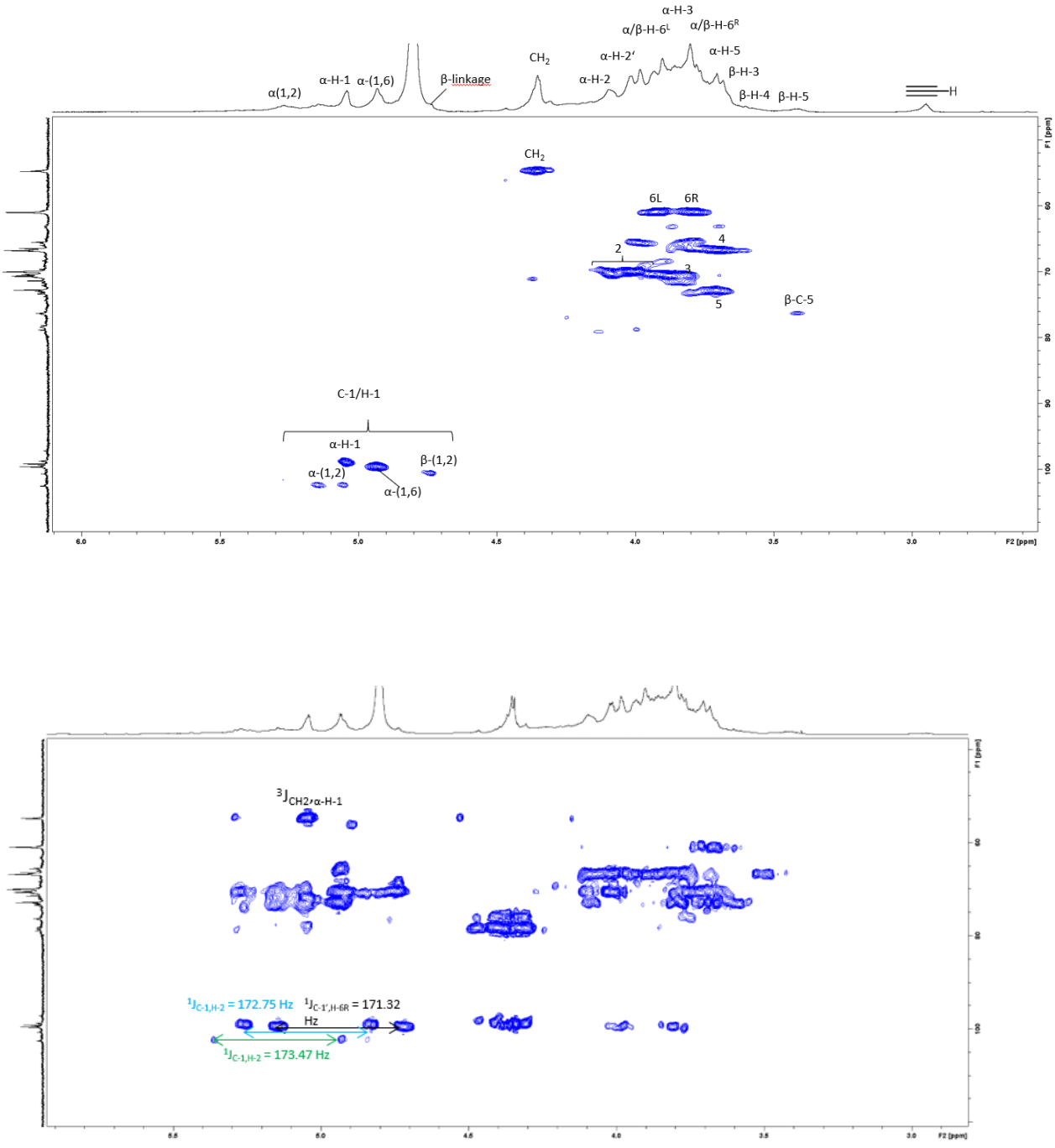


Figure S7: HMBC and HSQC NMR spectrum of $(PMan)_8$.

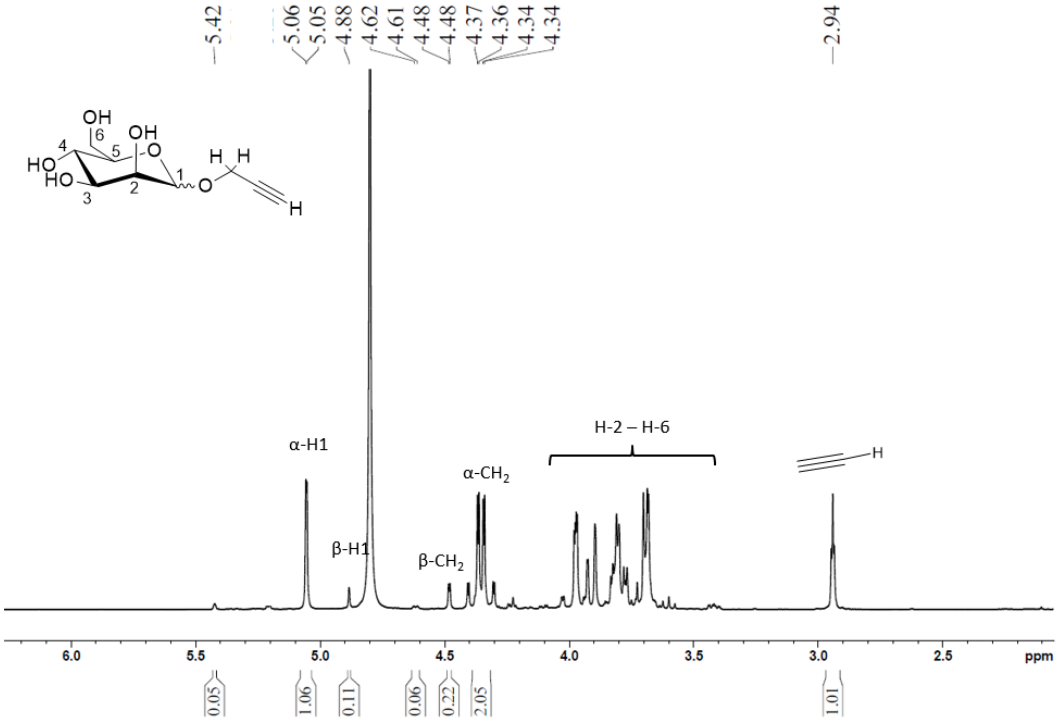


Figure S8. ^{1}H-NMR (400 MHz, D_2O) spectrum of pure PMan.

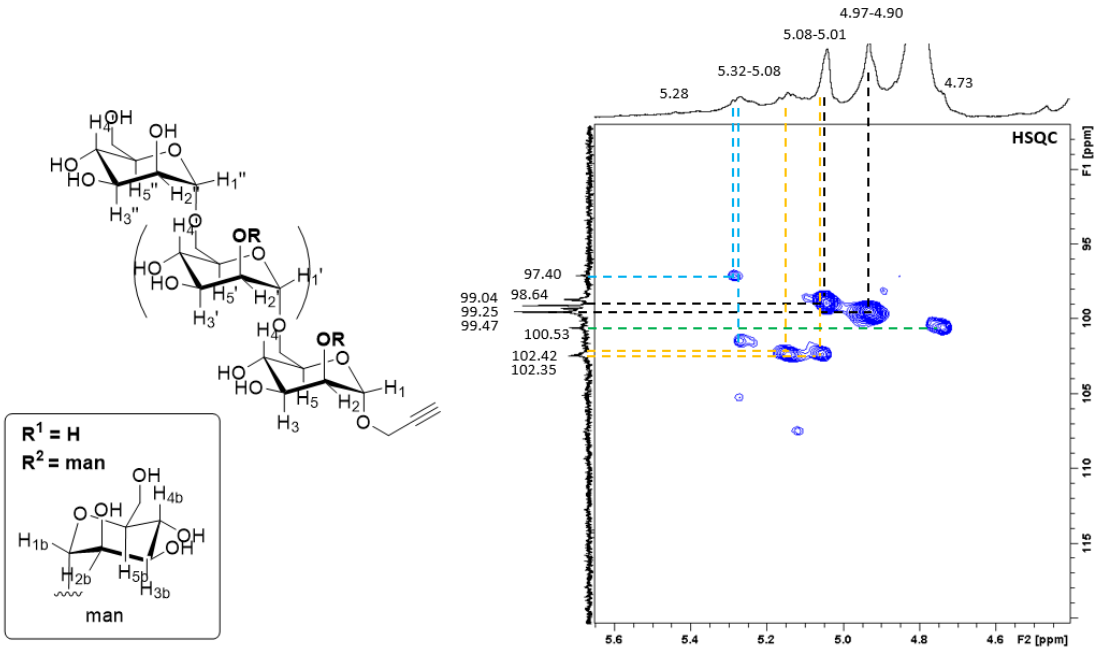


Figure S9. eft = proposed structure of the mannose-oligosaccharides; right = Zoom of the anomeric region of the HSQC NMR.

Table S2: Assignment of the proton and carbon peaks to the corresponding anomeric positon.

Peak (^{1}H-NMR) (ppm)	Peak (^{13}C-NMR) (ppm)	anomeric position
5.28	97.04	β-linkage
5.32-5.08	102.35	H-1b « α-(1,2) linkage » / R^2 = man
5.32-5.08	102.42	H-1b « α-(1,2) linkage » / R^2 = man
5.08-5.01	98.64	H-1 « propargyl-endgroup » / R^1 = H
5.08-5.01	99.04	H-1 « propargyl-endgroup » / R^2 = man
4.97-4.90	99.25	H-1'« α-(1,6) linkage » / R^1 = H
4.97-4.90	99.47	H-1'« α-(1,6) linkage » / R^2 = man
4.73	100.53	β-linkage

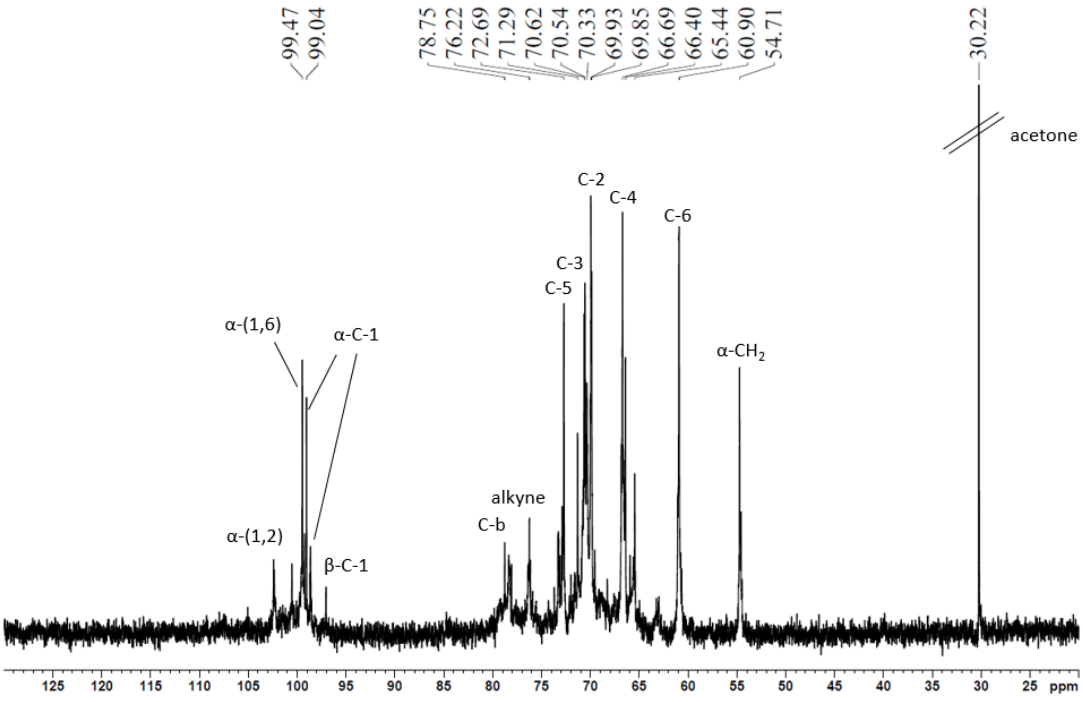


Figure S10. ^{13}C-NMR (100.4 MHz, D_2O) spectrum of $(PMan)_8$.

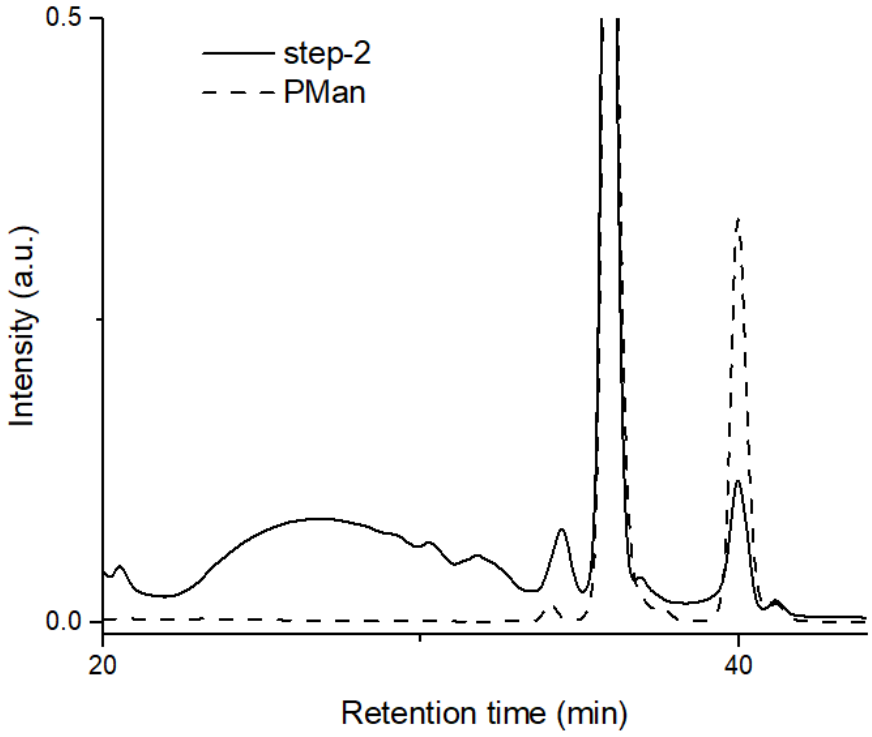


Figure S11: Oligomerization of isolated PMan (after step 2: 100 °C, vacuum, 4 h).

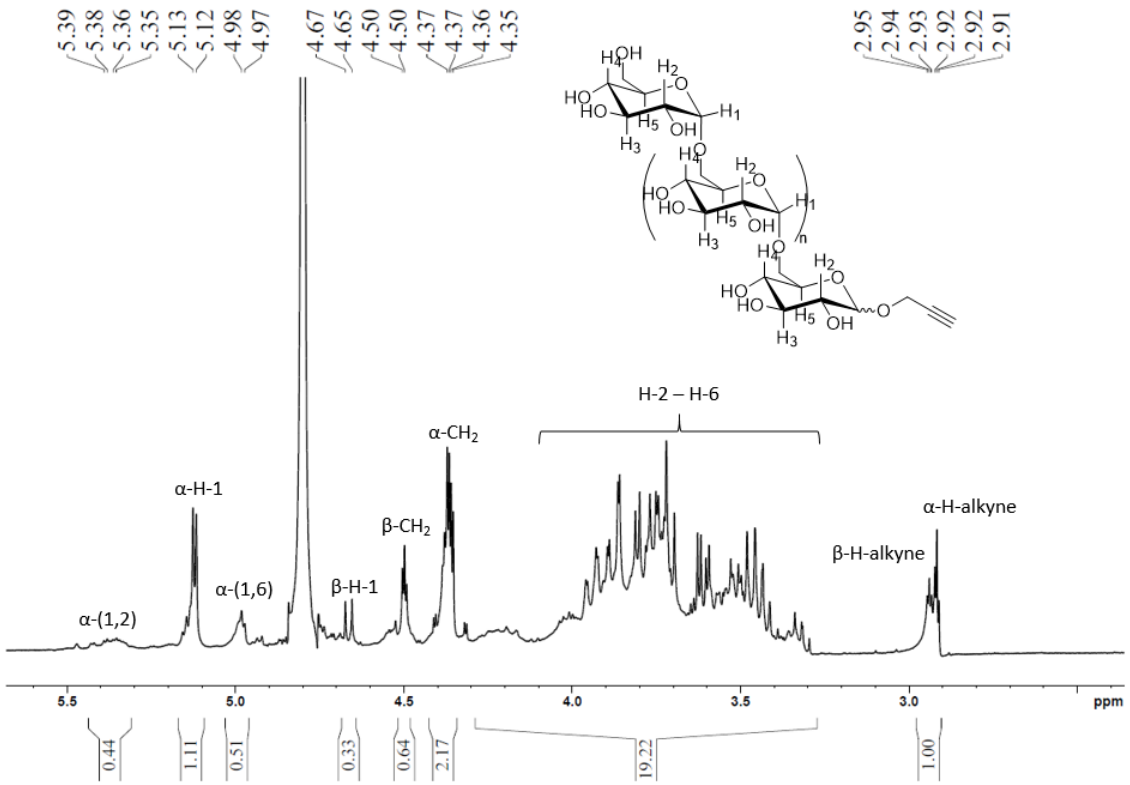


Figure S12. ^{1}H-NMR (400 MHz, D_2O) spectrum of $(PGlu)_n$ (note that peak assignment is inspired from $(PMan)_8$).

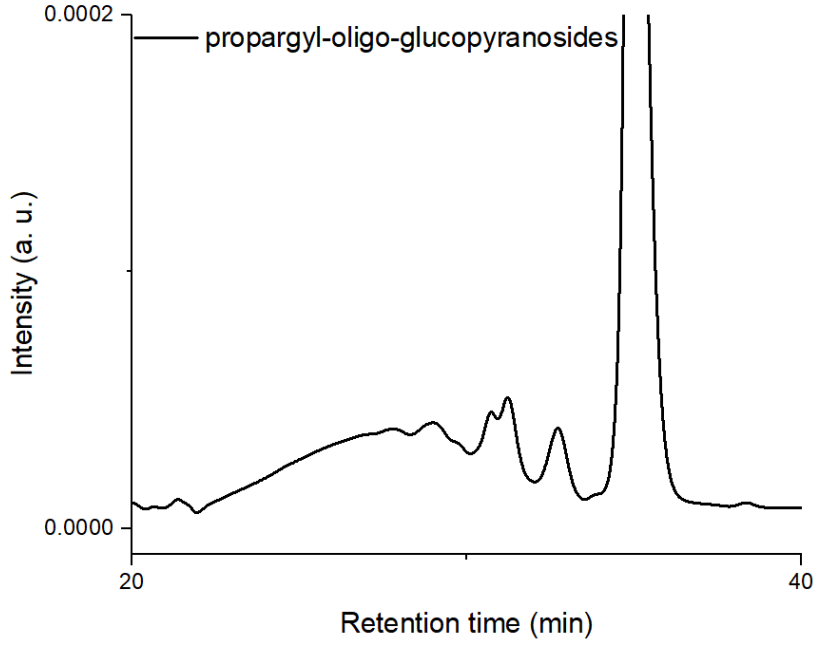


Figure S13. SEC analysis of $(PGlu)_n$

Protocol for the Huisgen Cycloaddition.

Azide functionalization of propyl alcohol.

3-bromo-1-propanol (10 g, 71.94 mmol) and sodium azide (18.7 g, 287.79 mmol) were dissolved in acetone/water (120/20 mL) and refluxed overnight. After removing acetone under reduces pressure, water (100 mL) was added and the mixture was extracted with diethyl ether (3x 100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum to give a colorless oil. (6.24 g, 86 %)**,** ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.74-3.71 (t, J = 6 Hz, 2 H, H-1), 3.45-3.41 (t, J = 6.58 Hz, 2 H, H-3), 2.06 (br, s, 1H, O-H), 1.84-1.78 (qi, J = 6.31, 2 H, H-2); ^{13}C-NMR (100.4 MHz, $CDCl_3$): δ = 59.89 (C-1), 48.54 (C-3), 31.51 (C-2); ATR-IR: 2089 cm^{-1} (N_3 str.) (s).[22-24]

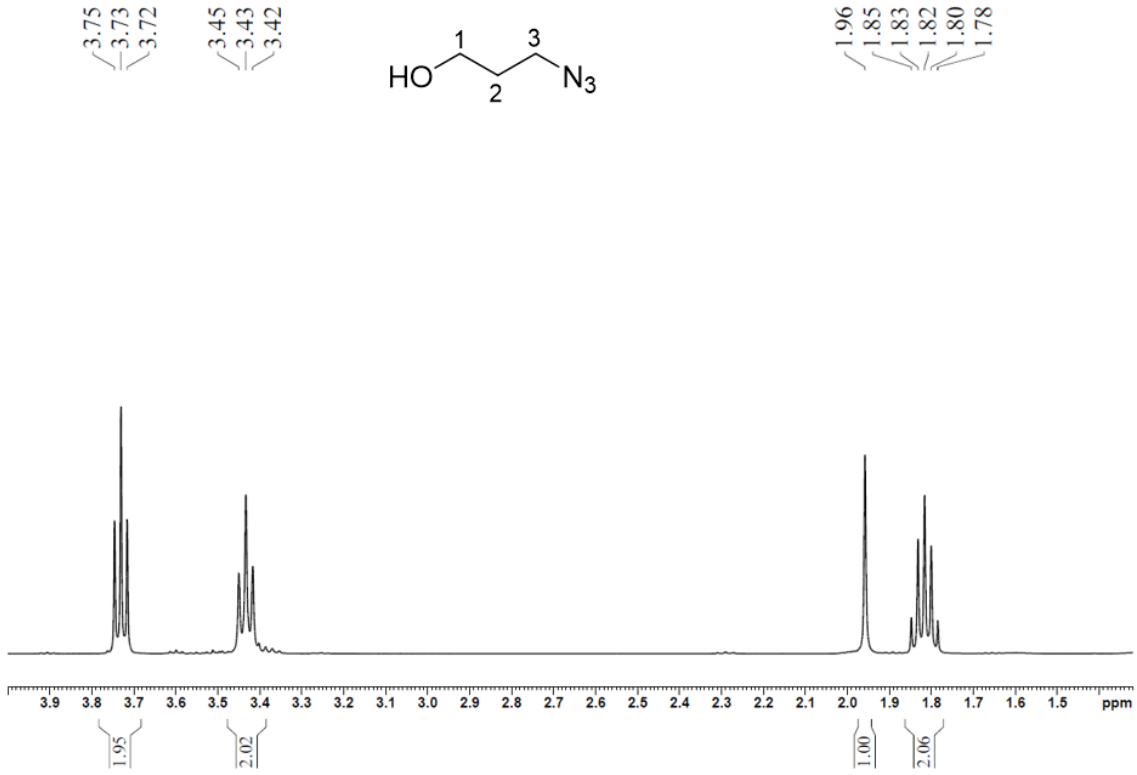


Figure S14. ^{1}H-NMR (400 MHz, D_2O) spectrum of 3-azido-1-propanol.

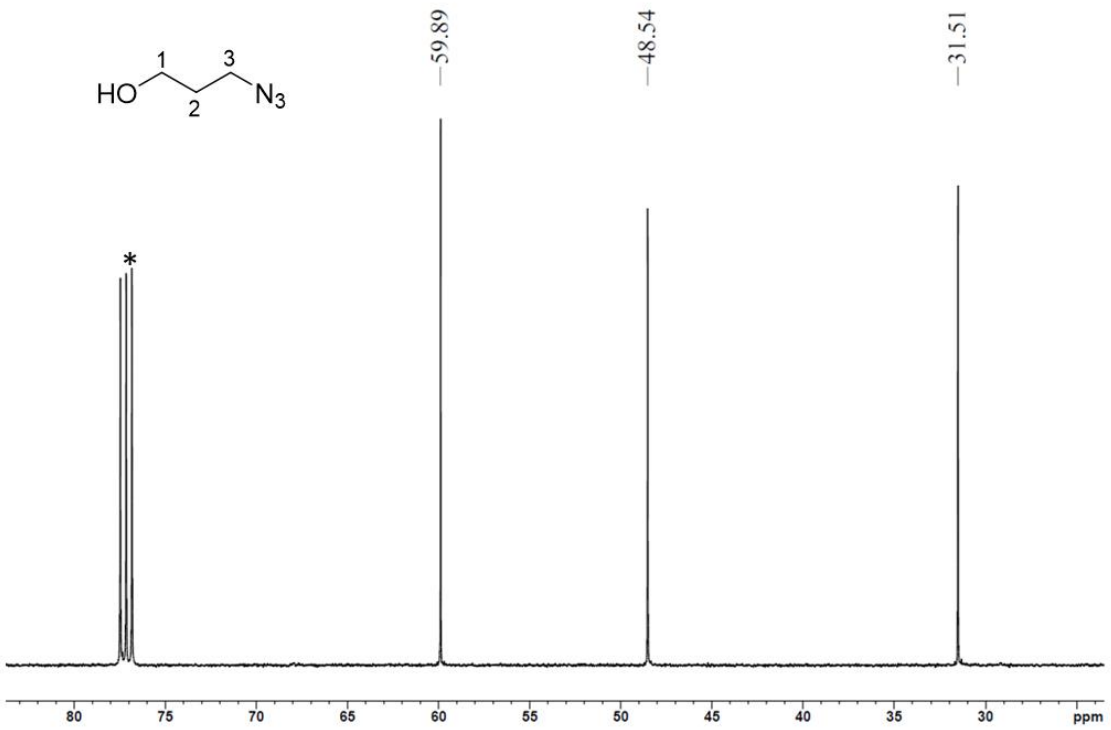


Figure S15. ^{13}C-NMR (100.4 MHz, $CDCl_3$) spectrum of 3-azido-1-propanol.

Transesterification of methyl oleate

In a typical transesterification reaction, fatty acid methyl ester methyl oleate (MeOI, 12 g, 38.43 mmol,) azide-functionalized alcohol (3-azido-1-propanol, 10 eq.) and the catalyst 1,5,7-Triazabicyclo(4.4.0)dec-5-en (TBD, 0.1 eq.) were added in a Schlenk-flask and stirred at 100 °C for 4 h under a gentle flux of nitrogen. The obtained dark solution was then placed for 4 h at 100 °C under vacuum to remove the excess of alcohol. After cooling to room temperature, the residue was dissolved in ethyl acetate (300 mL) and washed four times consecutive with distilled water (30 mL). The organic layer was dried over $MgSO_4$, filtrated and dried under vacuum to obtain a crude orange/yellow oil. Upon purification *via* column chromatography (petroleum ether/ethyl acetate 9:1), azide-functionalized oleate (N_3OI) was obtained as colorless oil (8.54 g, 61 %), ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.34-5.31 (m, 2 H), 4.16-4.13 (t, J = 6.16 Hz, 2 H, H-1), 3.39-3.36 (t, J = 6.7 Hz, 2 H, H-3), 2.30-2.26 (t, J = 7.54 Hz, 2 H), 2.0-1.99 (dd, 4 H), 1.93-1.86 (qi, 2H, H-2), 1.62-1.59 (m, 2 H), 1.29-1.25 (d, br, 20 H), 0.88-0.85 (t, 3 H, CH_3); ^{13}C-NMR (100.4 MHz, $CDCl_3$): δ = 173.87, 130.20, 129.91, 61.27 (C-1), 48.42 (C-3), 34.41, 32.08, 29.94, 29.87, 29.70, 29.50, 29.34, 29.30, 29.27, 28.37 (C-2), 27.40, 27.34, 25.11, 22.86, 14.29; ATR-IR: 2089 cm^{-1} (N3 str.) (s).[25]

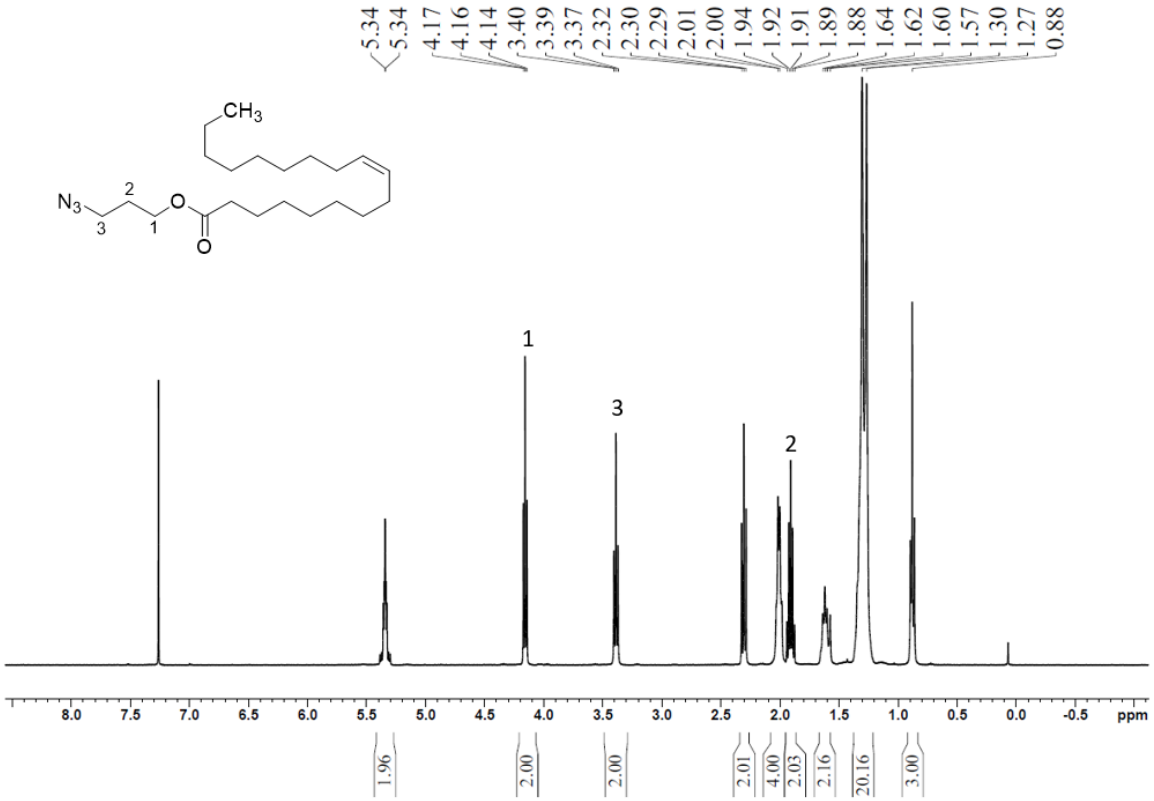


Figure S16. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3-azido-1-propyl oleate.

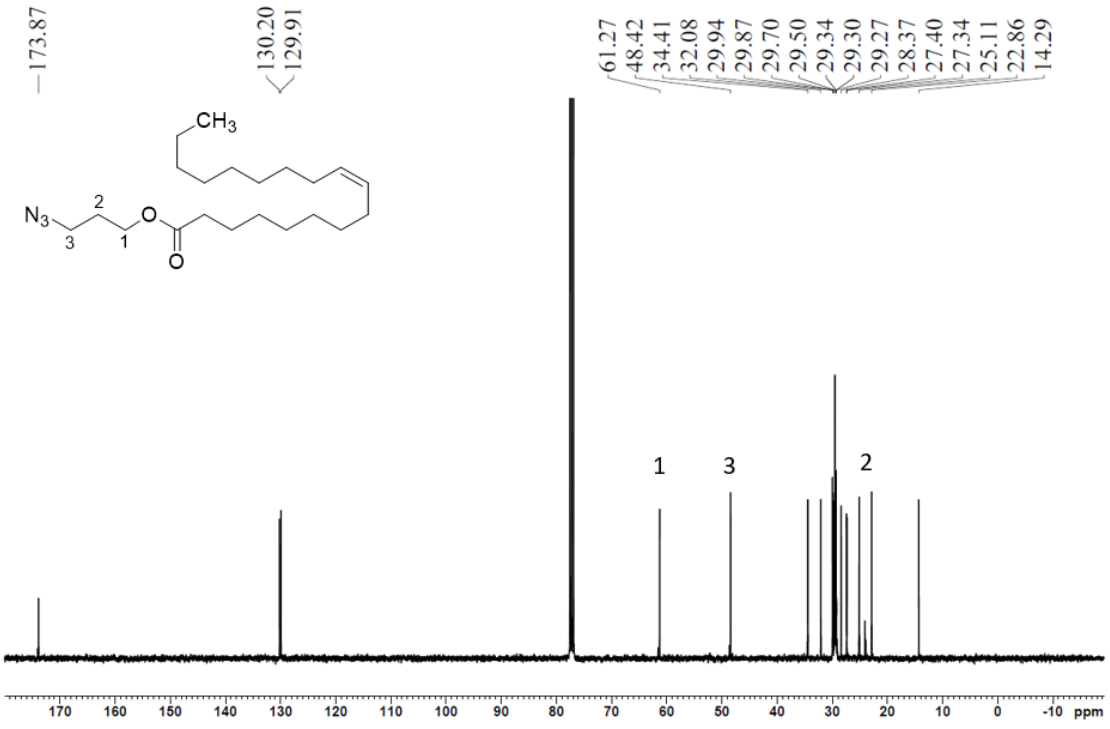
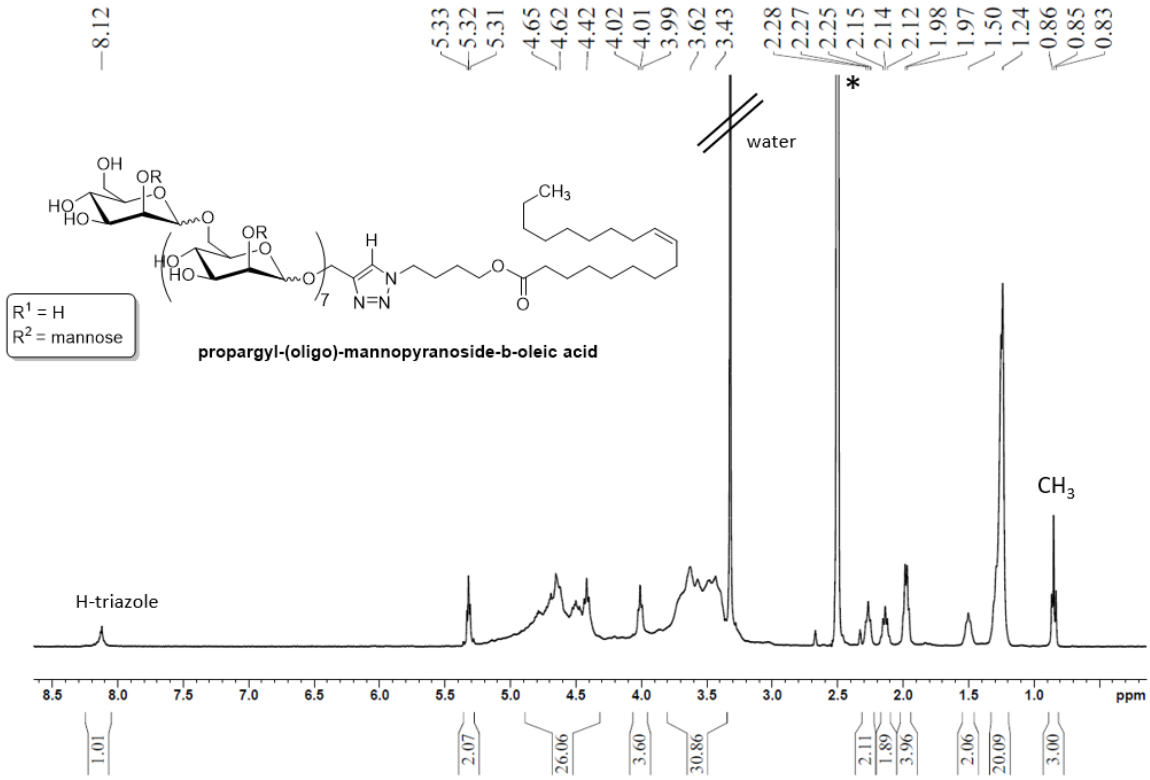


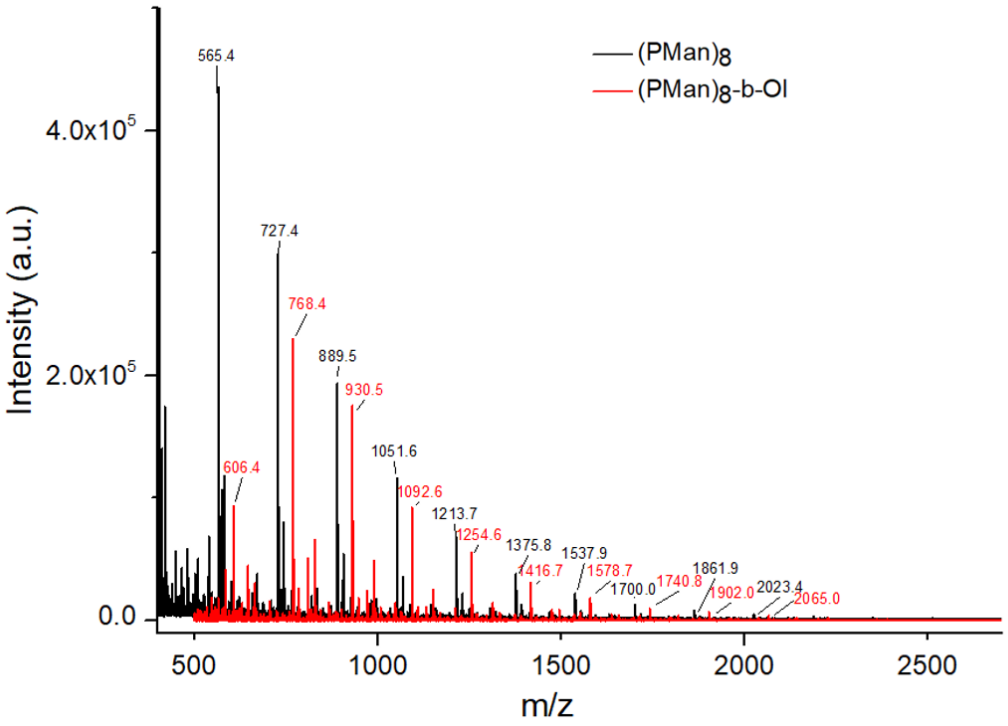
Figure S17. ^{13}C-NMR (100.4 MHz, D_2O) spectrum of 3-azido-1-propyl oleate.

Click reaction

For the click reaction between the azide functionalized fatty acid and the alkyne functionalized oligosaccharides, 2.5 g of $(PMan)_8$ were dissolved in 20 mL of DMSO and stirred at 30 °C overnight. Then, N_3OI (1,2 eq.) was added and the mixture was stirred for 15 minutes. After that, sodium ascorbate (1 eq.) was added and after 15 min. $CuSO_4$ (1 eq.) was introduced and the mixture was stirred for 24 h at 30 °C. 20 mL of dist. The crude product was precipitated in EtOAc and separated by centrifugation. The residue was dissolved in dist. water, Cuprisorb was added and the mixture stirred overnight. The beads were separated by filtration and the obtained solution was dialyzed (MWCO: 100 - 500 Da) against dist. water for 4 d. After freeze-drying, a pale beige-white powder was obtained (1.29 g, 43 %), HRMS (MALDI-tof, m/z): $[M + Na]^+$ calcd for = 1718.89 g/mol; found = 1740.8 g/mol, ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.12 (s, 1 H, triazole), 5.33-5.31 (t, 2 H), 5.12-4.30 (m, 26 H), 4.02-3.99 (t, 4 H), 3.8-3.36 (m, 30 H), 2.28-2.25 (t, 2 H), 2.15-2.12 (t, 2 H), 1.98-1.97 (m, 4 H), 1.5 (m, 2 H), 1.24 (s, br, 20 H), 0.86-0.83 (t, 3 H, CH_3).[25]



S18: ^{1}H-NMR (400 MHz, D_2O) spectrum of amphiphile $(PMan)_8$ clicked with oleic acid.



S19: MALDI-TOF spectrum of amphiphile $(PMan)_8$ clicked with oleic acid.