Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Regioselective Oxidation of Unprotected 1-4 Linked Glucans

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General Information

Solvents and Reagents

All solvents used for reaction, extraction, filtration and chromatography were of commercial grade, and used without further purification. Reagents were purchased from Sigma-Aldrich, Acros and were used without further purification. Maltotetraose was purchased from Carbosynth, maltopentaose up to maltoheptaose was purchased from TCI Europe. DMC-Cl PF_6 was purchased from AK Scientific. $[(Neocuproine)PdOAc]_2OTf_2$ was prepared according to the literature procedure.[1]

Analysis

TLC was performed on Merck silica gel 60, 0.25 mm plates and visualization was done by staining with anisaldehyde reagent (a mixture of acetic acid (300 ml), H_2SO_4 (6 ml), anisaldehyde (3 ml)) or potassium permanganate stain (a mixture of $KMnO_4$ (3 g), K_2CO_3 (10 g), water (300mL)).
^1H-, ^{13}C-, APT-, COSY-, and HMQC-NMR were recorded on a Varian AMX400 spectrometer (400, 100 MHz, respectively) using CD_3OD or D_2O as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CD_3OD: δ3.31 for ^1H, δ 49.15 for ^{13}C; D_2O: δ4.80 for ^1H). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, t = triplet, appt = apparent triplet, q =quartet, m = multiplet), coupling constants J (Hz), and integration. High Resolution Mass measurements were performed using a ThermoScientific LTQ OribitrapXL spectrometer. Optical rotations were measured on a Schmidt + Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL). Infrared (IR) data were recorded on a Perkin Elmer UATR spectrum two FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1})

Purification: General method for charcoal purification.

Preparation Charcoal column:
Solid loading cartridges (solid loading cartridges for Grace Reveleris automatic column system) were used for performing the columns. One frit was placed on the bottom of the cartridge, followed by the desired amount of charcoal (*DARCO*® activated charcoal, −100 mesh particle size, equal to 10 times the amount of starting material used) Then a second frit is added and pressed firmly together. The charcoal column is washed with ~5 CV of water and stored wet until use.

Performing charcoal column chromatography:
Charcoal columns chromatography is performed with negative pressure (vacuum) in combination with air pressure to maintain an acceptable flow rate (depending on the size of the column, only vacuum can also be sufficient). Before loading, traces of organic solvents are removed *in vacuo* from the sample. The remaining aqueous solution is directly loaded onto the prepared (and washed) charcoal column, and elution starts with pure water to elute salts (if applicable, the presence of salts in eluted fractions is indicated with 0.1 M $AgNO_{3(aq)}$). Upon complete elution of the salts, a gradient of ethanol/water is used to elute the desired product (2 – 4 CV per 2% increase, followed by TLC monitoring for elution of product(s)). When the desired product starts to elute, the polarity of the eluent can be further decreased (to 20 - 30% ethanol/water) to speed up the elution. The fractions containing the product are evaporated or freeze-dried to yield the pure product.
For larger molecules, tert-butanol is more efficient than ethanol.

For purification of the oxidized products, the charcoal chromatography is performed with a small frit of celite on top of the column, to retain the precipitated hydroquinone. Upon complete loading of the product, this frit is removed from the column to ensure an acceptable flow rate, and the elution is continued as stated above.

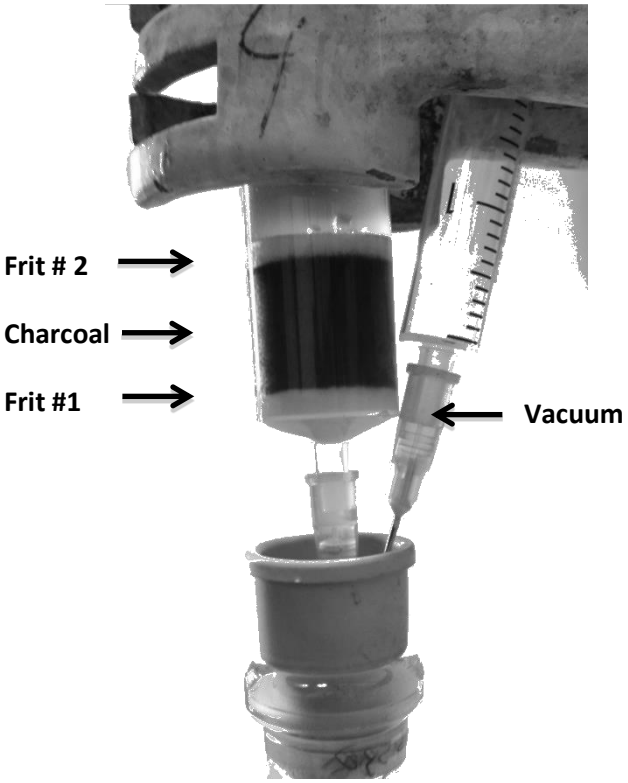


Figure 1, close up charcoal column (~1g)

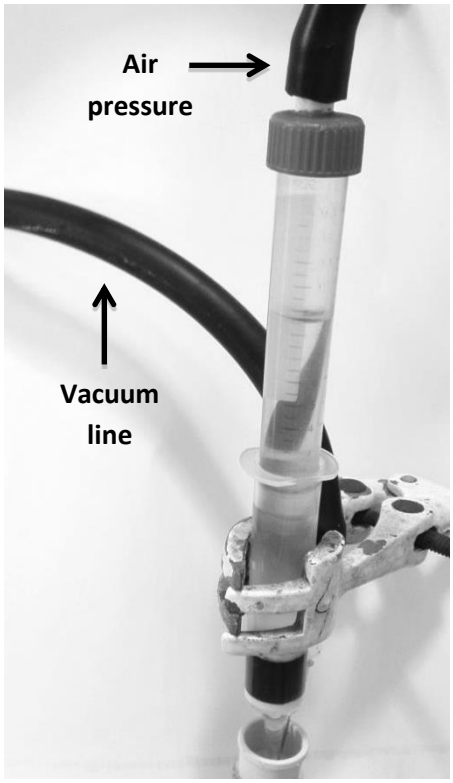
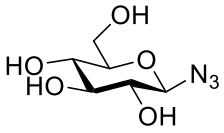


Figure 2, charcoal column vacuum + air pressure, adapter made from 15ml Greiner tube, bottom removed + hole in cap for connection to the air pressure

Synthesis of glycosyl azides

β-D-glucosyl azide (1)

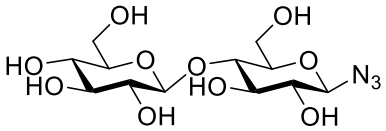


To a solution of glucose (500 mg, 2.78 mmol, 1 eq), sodium azide (1.8 g, 27.8 mmol, 10 eq) and *N*,*N*-diisopropylethylamine (4.4 ml, 25 mmol, 9 eq) in water (4.4 ml) at 0 °C was added DMC-PF_6 (2.3 g, 8.33 mmol, 3 eq). The resulting mixture was stirred at 0 °C until complete conversion of starting material was observed on TLC (eluent: 15% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 50 ml). The resulting water layer was purified by charcoal column chromatography (7% $EtOH/H_2O$ eluted the desired product) and concentrated *in vacuo* to yield 460 mg (2.24 mmol, 81%) of pure β-D-glucosyl azide.

^{1}H-NMR (400 MHz, CD_3OD) δ 4.50 (d, *J* = 8.6 Hz, 1H), 3.87 (dd, *J* = 12.1, 2.1 Hz, 1H), 3.68 (dd, *J* = 12.1, 5.3 Hz, 1H), 3.42 – 3.27 (m, 3H), 3.14 (appt, *J* = 8.9 Hz, 1H). **^{13}C-NMR** (101 MHz, CD_3OD) δ 91.9, 80.0, 78.0, 74.7, 71.0, 62.5.

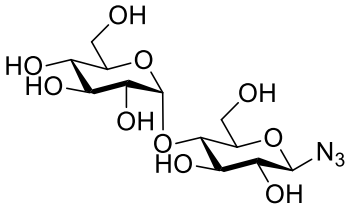
Characterization matches literature.[2]

β-D-cellobiosyl azide (2)



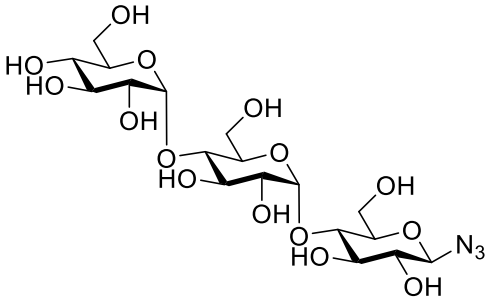
To a solution of cellobiose (100 mg, 0.292 mmol, 1 eq), sodium azide (190 mg, 2.92 mmol, 10 eq) and *N*,*N*-diisopropylethylamine (460 µl, 2.63 mmol, 9 eq) in water (1.1 ml) at room temperature was added DMC-PF_6 (245 mg, 0.88 mmol, 3 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 15% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (14% EtOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 87 mg (0.237 mmol, 81%) of pure β-D-cellobiosyl azide.
^{1}H-NMR (400 MHz, CD_3OD) δ 4.55 (d, J = 8.7 Hz, 1H), 4.42 (d, J = 7.8 Hz, 1H), 3.95 – 3.83 (m, 3H), 3.66 (dd, J = 11.9, 5.5 Hz, 1H), 3.62 – 3.48 (m, 3H), 3.41 – 3.29 (m, 3H, overlapping with CD_3OD), 3.26 – 3.18 (m, 2H). **^{13}C-NMR** (101 MHz, CD_3OD) δ 104.5, 91.8, 80.0, 78.5, 78.0, 77.8, 76.4, 74.8, 74.4, 71.3, 62.4, 61.6.
Characterization matches literature[2]

β-D-maltosyl azide (3)



To a solution of maltose monohydrate (100 mg, 0.278 mmol, 1 eq), sodium azide (180 mg, 2.78 mmol, 10 eq) and *N*,*N*-diisopropylethylamine (440 µl, 2.50 mmol, 9 eq) in water (1.1 ml) at room temperature was added DMC-PF_6 (230 mg, 0.83 mmol, 3 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 20% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (11% EtOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 76 mg (0.207 mmol, 74%) of pure β-D-maltosyl azide.
^{1}H-NMR (400 MHz, CD_3OD) δ 5.18 (d, J = 3.8 Hz, 1H), 4.54 (d, J = 8.6 Hz, 1H), 3.9 (dd, J = 12.39, 1.98 Hz, 1H), 3.86 – 3.80 (m, 2H), 3.71 – 3.63 (m, 3H), 3.63 – 3.54 (m, 2H), 3.50 (td, J = 5.2, 4.8, 1.9 Hz, 1H), 3.46 (dd, J = 9.7, 3.7 Hz, 1H), 3.32 – 3.24 (m, 1H, overlapping with CD_3OD), 3.20 (appt, J = 8.9 Hz, 1H). **^{13}C NMR** (101 MHz,CD_3OD) δ 102.8, 91.9, 80.5, 78.7, 77.8, 75.0, 74.7, 74.3, 74.1, 71.4, 62.7, 61.9.
Characterization matches literature[2]

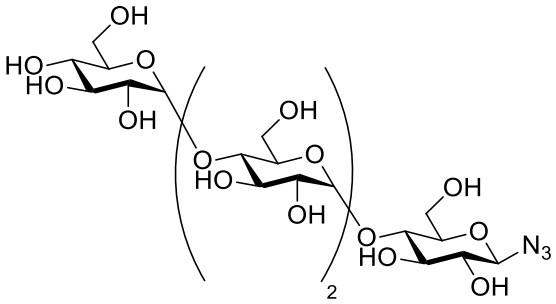
β-D-maltotriosyl azide (4)



To a solution of maltotriose (93% purity, 100 mg, 0.184 mmol, 1 eq), sodium azide (120 mg, 1.84 mmol, 10 eq) and *N*,*N*-diisopropylethylamine (290 µl, 1.66 mmol, 9 eq) in water (0.75 ml) at room temperature was added DMC-PF_6 (155 mg, 0.55 mmol, 3 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting

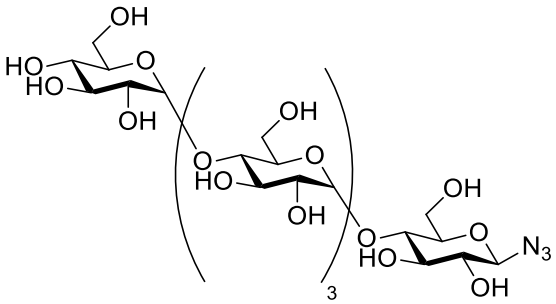
material (eluent: 30% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (12% $EtOH/H_2O$ eluted the desired product) and concentrated *in vacuo* to yield 79 mg (0.149 mmol, 81%) of pure β-D-maltotriosyl azide.
^{1}H-NMR (400 MHz, CD_3OD) δ 5.19 (d, J = 3.8 Hz, 1H), 5.16 (d, J = 3.8 Hz, 1H), 4.55 (d, J = 8.6 Hz, 1H), 3.94 – 3.73 (m, 7H), 3.72 – 3.42 (m, 9H), 3.35 – 3.24 (m, 1H, overlapping with CD_3OD), 3.21 (appt, J = 8.9 Hz, 1H) **^{13}C NMR** (101 MHz,CD_3OD) 102.8, 102.6, 91.9, 81.2, 80.5, 78.6, 77.8, 75.0, 74.9, 74.7, 74.3, 74.1, 73.7, 73.3, 71.4, 62.6, 62.1, 62.0. Characterization matches literature[2]

β-D-maltotetraosyl azide (5)



To a solution of maltotetraose (100 mg, 0.150 mmol, 1 eq), sodium azide (490 mg, 7.5 mmol, 50 eq) and *N*,*N*-diisopropylethylamine (390 µl, 2.25 mmol, 15 eq) in water (1.5 ml) at room temperature was added DMC-PF_6 (210 mg, 0.75 mmol, 5 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 30% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (3 % ^{t}BuOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 79 mg (0.114 mmol, 76%) of pure β-D-maltotetraosyl azide.
^{1}H NMR (400 MHz, D_2O) δ 5.45 – 5.38 (m, 3H), 4.79 (d, J = 8.7 Hz, 1H), 4.01 – 3.91 (m, 3H), 3.92 – 3.77 (m, 9H), 3.77 – 3.55 (m, 10H), 3.43 (appt, *J* = 9.4 Hz, 1H), 3.32 (appt, *J* = 9.1 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 99.7, 99.6, 99.3, 89.8, 76.8, 76.6, 76.4, 76.2, 76.1, 73.3, 73.2, 72.8, 72.6, 71.7, 71.5, 71.4, 71.1, 69.2, 60.4, 60.3. (4 signals are missing due to severe overlap).
Characterization matches literature[2]

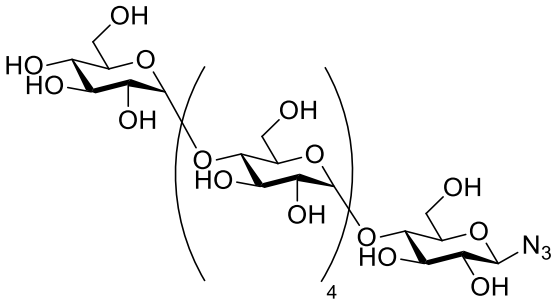
β-D-maltopentaosyl azide (6)



To a solution of maltopentaose (109 mg, 0.132 mmol, 1 eq), sodium azide (428 mg, 6.58 mmol, 50 eq) and *N*,*N*-diisopropylethylamine (350 µl, 1.97 mmol, 15 eq) in water (1.3 ml) at room temperature was added DMC-PF_6 (183 mg, 0.658 mmol, 5 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 30% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (3.5 % ^{t}BuOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 83 mg (0.097 mmol, 74%) of pure β-D-maltopentaosyl azide

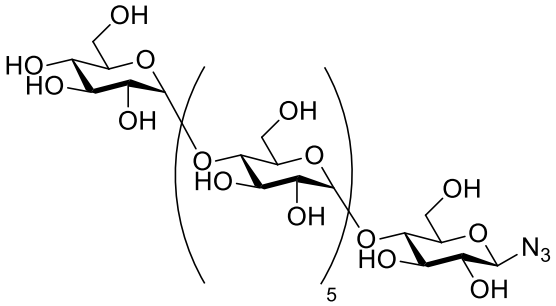
^{1}H NMR (400 MHz, D_2O) δ 5.28 – 5.24 (m, 4H), 4.62 (d, J = 8.9 Hz, 1H), 3.86 – 3.76 (m, 4H), 3.75 – 3.63 (m, 12H), 3.60 – 3.42 (m, 12H), 3.28 (appt, J = 9.4 Hz, 1H), 3.17 (appt, J = 9.1 Hz, 1H).**^{13}C NMR (101 MHz, D_2O)** δ 99.7, 99.5, 99.5, 99.4, 89.8, 76.8, 76.7, 76.6, 76.4, 76.2, 76.1, 73.3, 73.2, 73.2, 72.8, 72.6, 72.6, 71.6, 71.5, 71.4, 71.1, 69.2, 60.4, 60.4, 60.3. (5 signals are missing due to severe overlap).
Characterization matches literature[2]

β-D-maltohexaosyl azide (7)



To a solution of maltohexaose (124 mg, 0.125 mmol, 1 eq), sodium azide (407 mg, 6.26 mmol, 50 eq) and *N*,*N*-diisopropylethylamine (325 µl, 1.875 mmol, 15 eq) in water (1.25 ml) at room temperature was added DMC-PF_6 (174 mg, 0.625 mmol, 5 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 30% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 15 ml). The resulting water layer was purified by charcoal column chromatography (3.75 % ^{t}BuOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 87 mg (0.086 mmol, 69%) of pure β-D-maltohexaosyl azide.
^{1}H NMR (400 MHz, D_2O) δ 5.27 (m, 5H), 4.62 (d, J = 9.1 Hz, 1H), 3.87 – 3.77 (m, 5H), 3.77 – 3.62 (m, 15H), 3.62 – 3.42 (m, 14H), 3.28 (appt, J = 9.3 Hz, 1H), 3.17 (appt, J = 9.1 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 99.7, 99.5, 99.5, 99.5, 99.4, 89.8, 76.8, 76.7, 76.7, 76.6, 76.6, 76.4, 76.2, 76.1, 73.3, 73.2, 73.2, 72.8, 72.6, 71.6, 71.5, 71.4, 71.1, 71.1, 69.2, 60.4, 60.3. (9 signals are missing due to severe overlap).
Characterization matches literature[2]

β-D-maltoheptaosyl azide (8)

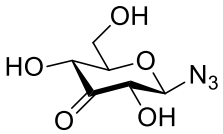


To a solution of maltoheptaose (80% purity, 97 mg, 0.0673 mmol, 1 eq), sodium azide (220 mg, 3.365 mmol, 50 eq) and *N*,*N*-diisopropylethylamine (175 µl, 1.01 mmol, 15 eq) in water (0.7 ml) at room temperature was added DMC-PF_6 (95 mg, 0.337 mmol, 5 eq). The resulting mixture was stirred at room temperature until TLC indicated full conversion of starting material (eluent: 35% H_2O/CH_3CN). Upon complete conversion, the solution was washed with dichloromethane (3 x 20 ml). The resulting water layer was purified by charcoal column chromatography (3.5 % ^{t}BuOH/H_2O eluted the desired product) and concentrated *in vacuo* to yield 39 mg (0.031 mmol, 49%) of pure β-D-maltoheptaosyl azide.
^{1}H NMR (400 MHz, D_2O) δ 5.43 – 5.38 (m, 6H), 4.76 (d, *J* = 9.6 Hz, 1H), 4.01 – 3.92 (m, 6H), 3.90 – 3.77 (m, 17H), 3.77 – 3.55 (m, 17H), 3.43 (appt, *J* = 9.4 Hz, 1H), 3.31 (appt, *J* = 9.1 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 99.7, 99.6, 99.4, 89.9, 76.7, 76.6, 76.4, 76.2, 76.1, 73.3,

73.2, 73.2, 72.8, 72.6, 71.7, 71.5, 71.4, 71.1, 71.1, 69.2, 60.4, 60.4, 60.4, 60.3. (18 signals are missing due to severe overlap).
Characterization matches literature[2]

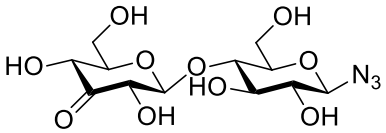
Synthesis of keto-glycosyl azides

β-D-3-ketoglucosyl azide (9)



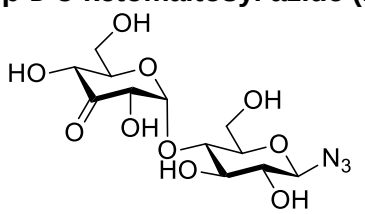
β-D-glucosyl azide (50 mg, 0.243 mmol, 1 eq) was dissolved in a dioxane/DMSO mixture (4:1, 800 µl, 0.3 M), before benzoquinone (80 mg, 0.731 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (20 mg, 18 µmol, 7.5 mol%) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 15% MeOH/CH_2Cl_2)). Upon completion, the reaction mixture was diluted with 10% EtOH/H_2O (7 ml) and the resulting aqueous solution was flushed over a charcoal column and concentrated *in vacuo* to yield β-D-3-ketoglucosyl azide.
*(**9** is highly unstable, flushing over charcoal gave a yielded the product with minor amounts of degradation. Due to this instability a yield of this reaction could not be determined, **9** was only characterized by ^{1}H-NMR.)*
^{1}H NMR (400 MHz, CD_3OD) δ 4.66 (d, J = 8.7 Hz, 1H), 4.29 (dd, J = 10.2, 1.7 Hz, 1H), 4.13 (dd, J = 8.7, 1.6 Hz, 1H), 3.95 (dd, J = 12.2, 2.1 Hz, 1H), 3.81 (dd, J = 12.4, 4.9 Hz, 1H), 3.48 (ddd, J = 10.3, 4.7, 2.0 Hz, 1H).

β-D-3-ketocellobiosyl azide (10)



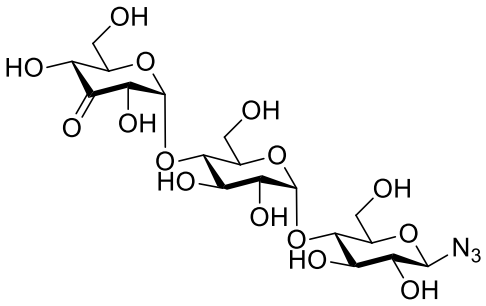
β-D-cellobiosyl azide (40 mg, 0.109 mmol, 1 eq) was dissolved in a dioxane/DMSO mixture (4:1, 370 µl, 0.3 M), before benzoquinone (35 mg, 0.327 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (9 mg, 8.6 µmol, 7.5 mol%, added in 3 portions over 6 h) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: $CHCl_3$:MeOH:EtOAc:H_2O 2:2:4:0.75)). Upon completion, the reaction mixture was diluted with H_2O (7 ml) and the resulting aqueous solution was purified by charcoal column chromatography (12% EtOH/H_2O eluted the desired product). The product was freeze-dried to yield 26 mg (0.071 mmol, 65%) of an off-white solid.
^{1}H NMR (400 MHz, CD_3OD) δ 4.56 (d, *J* = 8.7 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.24 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.97 – 3.86 (m, 3H), 3.78 (dd, *J* = 12.1, 5.0 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.58 (t, *J* = 9.0 Hz, 1H), 3.52 (ddd, *J* = 9.7, 3.7, 2.3 Hz, 1H), 3.38 (ddd, *J* = 10.1, 5.0, 2.1 Hz, 1H), 3.21 (appt, *J* = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD)** δ 206.6, 105.7, 91.9, 79.6, 78.6, 78.2, 78.2, 76.4, 74.5, 73.4, 62.3, 61.3. **HRMS (ESI)** calculated for $C_{12}H_{19}O_{10}N_3Na$ ([M+Na]$^+$): 388.096, found: 388.096 **IR** vmax/cm^{-1}: 3368 (OH), 2888 (C-H), 2118 (N_3), 1734 (C=O), 1028 (C-O) $[\alpha]_D^{20}$ = -20 (c 0.6, H_2O)

β-D-3-ketomaltosyl azide (11)



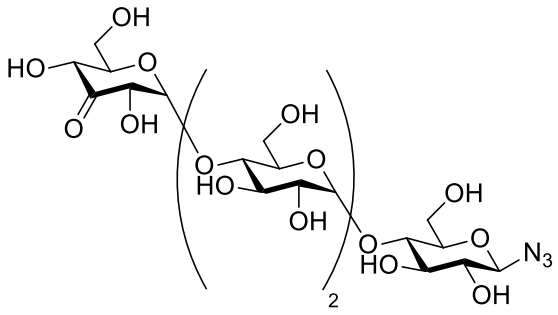
β-D-maltosyl azide (76 mg, 0.207 mmol, 1 eq) was dissolved in a dioxane/DMSO mixture (4:1, 700 µl, 0.3 M), before benzoquinone (67 mg, 0.620 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (16 mg, 15.5 µmol, 7.5 mol%, added in 3 portions over 6h) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: $CHCl_3$:MeOH:EtOAc:H_2O 2:2:4:0.75)). Upon completion, the reaction mixture was diluted with H_2O (14 ml) and the resulting aqueous solution was purified by charcoal column chromatography (7% EtOH/H_2O eluted the desired product). The product was freeze dried to yield 46 mg (0.122 mmol, 59 %) as an off-white solid. (contains ~10% hydroquinone by NMR integration, isolated yield corrected for this value).
^{1}H NMR (400 MHz, CD_3OD) δ 5.64 (d, *J* = 4.5 Hz, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 4.46 (dd, *J* = 4.5, 1.5 Hz, 1H), 4.26 (dd, *J* = 9.5, 1.6 Hz, 1H), 3.91 – 3.76 (m, 5H), 3.64 – 3.58 (m, 2H), 3.43 (ddd, *J* = 9.2, 4.4, 1.9 Hz, 1H), 3.17 (appt, *J* = 8.7 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD)** δ 207.0, 104.7, 91.9, 79.7, 78.4, 77.9, 77.6, 76.5, 74.4, 73.3, 62.5, 61.8. **HRMS (ESI)** calculated for $C_{12}H_{19}O_{10}N_3Na$ ([M+Na]$^+$): 388.096, found: 388.096 **IR** vmax/cm^{-1}: 3343 (OH), 2928 (C-H), 2118 (N_3), 1736 (C=O), 1028 (C-O) $[\alpha]_D^{20}$ = + 89.6 (c 1.00, H_2O)

β-D-3-ketomaltotrioside (12)



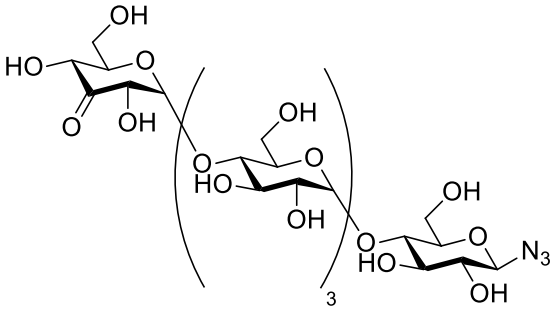
β-D-maltotriosyl azide (190 mg, 0.360 mmol, 1 eq) was dissolved in DMSO (2.4 ml, 0.3 M), before benzoquinone (117 mg, 1.080 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (28 mg, 27 µmol, 7.5 mol%) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 15% H_2O/CH_3CN). Upon completion the reaction mixture was diluted with H_2O (10 ml) and the resulting aqueous solution was purified by charcoal column chromatography (20% EtOH/H_2O eluted the desired product). The product was freeze dried to yield 121 mg (0.23 mmol, 60%) as an off-white solid.
^{1}H NMR (400 MHz, CD_3OD) δ 5.60 (d, *J* = 4.5 Hz, 1H), 5.16 (d, *J* = 3.8 Hz, 1H), 4.51 (d, *J* = 8.6 Hz, 1H), 4.45 (dd, *J* = 4.4, 1.6 Hz, 1H), 4.26 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.93 – 3.71 (m, 8H), 3.65 – 3.43 (m, 6H), 3.18 (appt, *J* = 8.9 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD)** δ 207.1, 104.8, 102.6, 91.9, 80.6, 80.5, 78.7, 77.9, 77.8, 76.6, 74.6, 74.3, 73.7, 73.3, 73.0, 62.5, 62.0, 61.9 **HRMS (ESI)** calculated for $C_{18}H_{29}O_{15}N_3Na$ ([M+Na]$^+$): 550.149, found: 550.148 **IR** vmax/cm^{-1}: 3338 (OH), 2925 (C-H), 2118 (N_3), 1737 (C=O), 1025 (C-O), $[\alpha]_D^{20}$ = + 46.6 (c 1.00, H_2O)

β-D-3-ketomaltoteraosyl azide(13)



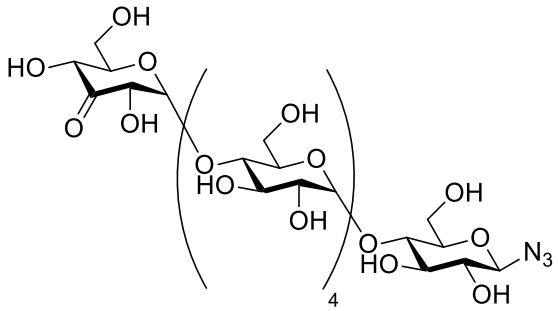
β-D-maltotetraosyl azide (55 mg, 0.08 mmol, 1 eq) was dissolved in DMSO (530 µl, 0.15 M), before benzoquinone (26 mg, 0.240 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (12 mg, 12 µmol, 15 mol%) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 20% H_2O/CH_3CN)). Upon completion the reaction mixture was diluted with H_2O (15 ml) and the resulting aqueous solution was purified by charcoal column chromatography (2.5% ^{t}BuOH/H_2O eluted the desired product). The product was freeze-dried to yield an off white solid containing traces of hydroquinone. Hydroquinone was removed by washing the product in water with diethyl ether to yield 21 mg (0.03 mmol, 38%) of an off-white solid.
^{1}H NMR (400 MHz, D_2O) δ 5.68 (d, J = 4.6 Hz, 1H), 5.27 (d, J = 4.0 Hz, 1H), 5.24 (d, J = 4.1 Hz, 1H), 4.62 (d, J = 9.1 Hz, 1H), 4.52 (dd, J = 4.6, 1.5 Hz, 1H), 4.32 (dd, J = 9.6, 1.5 Hz, 1H), 3.85 – 3.50 (m, 18H), 3.48 (dd, J = 9.8, 4.0 Hz, 2H), 3.17 (appt, J = 9.0 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 207.2, 102.1, 99.5, 99.3, 89.8, 76.7, 76.6, 76.4, 76.2, 76.1, 75.6, 74.6, 73.2, 73.0, 72.6, 71.5, 71.4, 71.4, 71.1, 70.8, 60.4, 60.4, 60.3, 60.1 **HRMS (ESI)** calculated for $C_{24}H_{39}O_{20}N_3Na$ ([M+Na]$^+$): 712.202, found: 712.201 **IR** vmax/cm^{-1}: 3340 (OH), 2932 (C-H), 2121 (N_3), 1738 (C=O), 1027 (C-O), $[\alpha]_D^{20}$= + 102.6 (c 1.00, H_2O)

β-D-3-ketomaltopentaosyl azide (14)



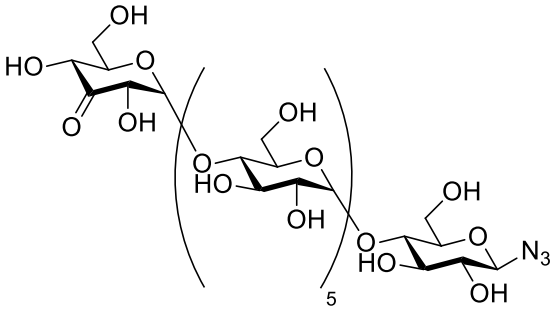
β-D-maltopentaosyl azide (58 mg, 0.068 mmol, 1 eq) was dissolved in DMSO (450 µl, 0.15 M), before benzoquinone (22 mg, 0.20 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (6.8 mg, 11 µmol, 15 mol%,) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 25% H_2O/CH_3CN)). Upon completion the reaction mixture was diluted with H_2O (15 ml) and the resulting aqueous solution was purified by charcoal column chromatography (3.0% ^{t}BuOH/H_2O eluted the desired product). The product was freeze-dried to yield an off white solid containing traces of hydroquinone. Hydroquinone was removed by washing the product in water with diethyl ether to yield 17 mg (0.02 mmol, 30%) of a white solid.
^{1}H NMR (400 MHz, D_2O) δ 5.83 (d, J = 4.7 Hz, 1H), 5.44 – 5.35 (m, 3H), 4.76 (d, J = 8.4 Hz, 1H). 4.66 (d, J = 4.5 Hz, 1H), 4.46 (d, J = 9.6 Hz, 1H), 4.02 – 3.74 (m, 18H), 3.74 – 3.58 (m, 7H), 3.31 (appt, J = 9.0 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 207.1, 102.0, 99.5, 99.4, 99.3, 89.8, 76.7, 76.7, 76.6, 76.5, 76.3, 76.1, 76.0, 75.6, 74.5, 73.2, 73.1, 72.9, 72.5, 71.5, 71.4, 71.3, 71.0, 71.0, 70.8, 60.3, 60.3, 60.2, 60.2, 60.1. **HRMS (ESI)** calculated for $C_{30}H_{49}O_{25}N_3Na$ ([M+Na]$^+$): 874.255, found: 874.253 **IR** vmax/cm^{-1}: 3339 (OH), 2927 (C-H), 2121 (N_3), 1737 (C=O), 1027 (C-O), $[\alpha]_D^{20}$= + 105.6 (c 1.00, H_2O)

β-D-3-ketomaltohexaosyl azide(15)



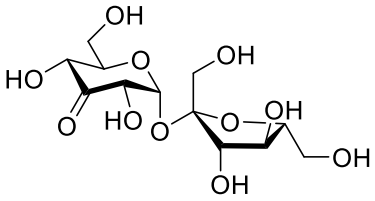
β-D-maltohexaosyl azide (80 mg, 0.079 mmol, 1 eq) was dissolved in DMSO (530 µl, 0.15 M), before benzoquinone (26 mg, 0.240 mmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (13 mg, 12 µmol, 15 mol%,) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 25 % H_2O/CH_3CN)). Upon completion the reaction mixture was diluted with H_2O (15 ml) and the resulting aqueous solution was purified by charcoal column chromatography (3.75 % ^{t}BuOH/H_2O eluted the desired product). The product was freeze dried to yield an off white solid containing traces of hydroquinone. Hydroquinone was removed by washing the product in water with diethyl ether to yield 24 mg (0.024 mmol, 30%) of a white solid.
^{1}H NMR (400 MHz, D_2O) δ 5.60 (d, J = 4.6 Hz, 1H), 5.23 – 5.14 (m, 4H), 4.54 (d, *J* = 9.1 Hz, 1H), 4.44 (dd, J = 4.7, 1.5 Hz, 1H), 4.24 (dd, J = 9.6, 1.6 Hz, 1H), 3.78 – 3.53 (m, 22H), 3.52 – 3.38 (m, 10H), 3.09 (appt, J = 9.0 Hz, 1H). **^{13}C NMR (101 MHz, D_2O)** δ 207.1, 102.0, 99.5, 99.4, 99.4, 99.3, 89.8, 76.7, 76.7, 76.7, 76.6, 76.5, 76.3, 76.2, 76.1, 76.1, 76.0, 75.6, 74.5, 73.1, 73.1, 72.9, 72.5, 71.4, 71.4, 71.3, 71.0, 71.0, 70.7, 69.1, 60.3, 60.3, 60.2, 60.2, 60.2, 60.0 HRMS (ESI) calculated for $C_{36}H_{59}O_{30}N_3Na$ ([M+Na]$^+$): 1036.31, found: 1036.31 **IR** vmax/cm^{-1}: 3340 (OH), 2929 (C-H), 2123 (N_3), 1739 (C=O), 1026 (C-O), $[\alpha]_D^{20}$ = + 122.4 (c 1.00, H_2O)

β-D-3-ketomaltoheptaosyl azide (16)



β-D-maltoheptaosyl azide (62 mg, 52.6 µmol, 1 eq) was dissolved in DMSO (350 µl, 0.15 M), before benzoquinone (17 mg, 158 µmol, 3 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]$_2$(OTf)$_2$ (8 mg, 8 µmol, 15 mol%,) were added. The reaction was stirred at room temperature till complete consumption of starting material (indicated by TLC (eluent: 40% H_2O/CH_3CN)). Upon completion the reaction mixture was diluted with H_2O (5 ml) and the resulting aqueous solution was purified by charcoal column chromatography (3.5 % ^{t}BuOH/H_2O eluted the desired product). The product was freeze-dried to yield an off white solid containing traces of hydroquinone. Hydroquinone was removed by washing the product in water with diethyl ether to yield 29 mg (24.5 µmol, 47%) of an off-white solid.
^{1}H NMR (400 MHz, CD_3OD) δ 5.69 (d, J = 4.6 Hz, 1H), 5.32 – 5.22 (m, 5H), 4.63 (d, J = 8.1 Hz, 1H), 4.53 (dd, J = 4.6, 1.6 Hz, 1H), 4.32 (d, J = 9.8 Hz, 1H), 3.89 – 3.57 (m, 36H), 3.52 (m, 16H), 3.18 (appt, J = 9.1 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD)** δ 207.2, 102.1, 99.5, 99.5, 99.5, 99.3, 89.8, 76.7, 76.5, 76.4, 76.2, 76.1, 75.6, 74.8, 74.6, 73.2, 73.2, 73.0, 72.6, 71.5, 71.5, 71.4, 71.1, 71.1, 70.8, 60.4, 60.4, 60.3, 60.3, 60.1 (12 signals are missing due to severe overlap).
HRMS (ESI) calculated for $C_{42}H_{69}O_{35}N_3Na$ ([M+Na]$^+$): 1198.36, found: 1198.36 **IR** vmax/cm^{-1}: 3343 (OH), 2924 (C-H), 2119 (N_3), 1738 (C=O), 1025 (C-O), $[\alpha]_D^{20}$ = + 120.2 (c 1.00, H_2O)

3-keto-sucrose (17)



Sucrose (62 mg, 0,18 mmol, 1 eq) and benzoquinone (58 mg, 0.54 mmol, 3 eq) were dissolved in DMSO-d_6 (600 µl, 0.3 M) and transferred to a NMR tube. T1 was determined followed by a start NMR to determine the ratio of DMSO : Starting material. $[(Neocuproine)PdOAc]_2OTf_2$ (4.7 mg, 4.5 µmol, 2.5 mol%) was added to the NMR tube, mixed and reacted for 1h. Selectivity towards the desired product: 50 % **^{1}H NMR** (400 MHz, DMSO-d_6) δ 5.60 (d, J = 4.5 Hz, 1H, H1), 4.27 (d, J = 4.4 Hz, 1H, H2), 4.14 (d, J = 9.7 Hz, 1H, H4), 3.94 – 3.86 (m, 2H, H3' + H5), 3.75 – 3.61 (m, 3H, H4' + H6), 3.61 – 3.55 (m, 3H, H5' + H6'), 3.50 – 3.41 (m, 1H, H1a'), 3.40 – 3.32 (m, 1H, H1b').
^{13}C NMR (101 MHz, DMSO-d_6) δ 206.6 (C3), 104.5 (C2'), 94.5 (C1), 82.8 (C5'), 76.2 (C3'), 75.6 (C5), 74.2 (C2), 74.1 (C4'), 71.6 (C4), 62.3 (C6'), 61.8 (C1'), 60.4 (C6).

Cu catalyzed click reaction on the protein 4-OT

The alkyne bearing protein 4-OT[1] (18 µl of a 0.39 mg/ml solution in 50 mM phosphate buffer, pH 8.0) was glycosylated with compound **12** and **16** (0.5 µl of a 10 mM solution in water), respectively, in the presence of $CuSO_4$ (0.5 µl of a 40 mM solution in water), sodium ascorbate (0.5 µl of a 50 mM solution in water) and the ligand THPTA (0.5 µl of a 4 mM solution in water). The reaction was mixed and left for 16 h at rt. The concentrations of the solutes in the resulting solution (20 µl) were as follows: 4-OT, 50 µM; oligomaltoside, 250 µM; $CuSO_4$, 1 mM; sodium ascorbate, 1.25 mM; THPTA, 100 µM. Subsequently, the samples were separated with Tricine SDS-PAGE[2] on a 16% gel and visualized with Coomassie Brilliant Blue R250 staining (AMRESCO, Solon, OH, USA).

Preconjugation with Biotin followed by click reaction

Compounds **12** and **16** were incubated each with hydrazide modified biotin (glycoside: 10 µl of a 10 mM solution in water and biotin hydrazide: 90 µl of a 55 mM solution in DMSO) after thorough mixing by vortexing, for 24 h at rt, to allow acyl hydrazone formation.

The alkyne bearing protein 4-OT[1] (18 µl of a 0.39 mg/ml solution in 50 mM phosphate buffer, pH 8.0) was glycosylated with the biotin bearing compounds **12** and **16** (0.5 µl of a 10 mM solution in water), respectively, using copper catalyzed alkyne azide cycloaddition (CuAAC). Triazole formation was conducted in the presence of $CuSO_4$ (0.5 µl of a 40 mM $CuSO_4$ solution in water), sodium ascorbate (0.5 µl of a 50 mM solution in water) and the ligand THPTA (0.5 µl of a 4 mM solution in water). The reaction was mixed and left for 16 h at rt. The concentrations of the solutes in the resulting solution (20 µl) were as follows: 4-OT, 50 µM; oligomaltoside, 250 µM; $CuSO_4$, 1 mM; sodium ascorbate, 1.25 mM; THPTA, 100 µM. The modified proteins were subjected to Tricine SDS-PAGE and subsequently transferred to a PVDF membrane for visualisation via ECL. To this end the protein samples were separated on a 16% tricine gel, then blotted onto the PVDF membrane (GE Healthcare, Wauwatosa, WI, USA) using a Bio-Rad (Hercules, CA, USA) Mini Trans-Blot system for wet blotting according to the manufacturer's protocol. Electro blotting was followed by blocking the membrane with 5% non-fat dry milk (Sigma-Aldrich St. Louis, MO, USA) in PBS buffer, and then washing 3X for 10 min each with PBS-T. The membrane was probed with HRP-conjugated Streptavidin (ThermoFisher Scientific, Waltham, MA, USA) in 5% non-fat dry milk in PBS-T buffer (1:10,000) for one hour at room temperature. The chemiluminescence signals were recorded subsequent to washing, 3X for 10 min with PBS-T buffer and 2X for 10 min with PBS buffer, using a Bio-Rad ChemiDoc XRS+ system and Clarity Western ECL Substrate according to the manufacturer's protocol.

Gels and Blots

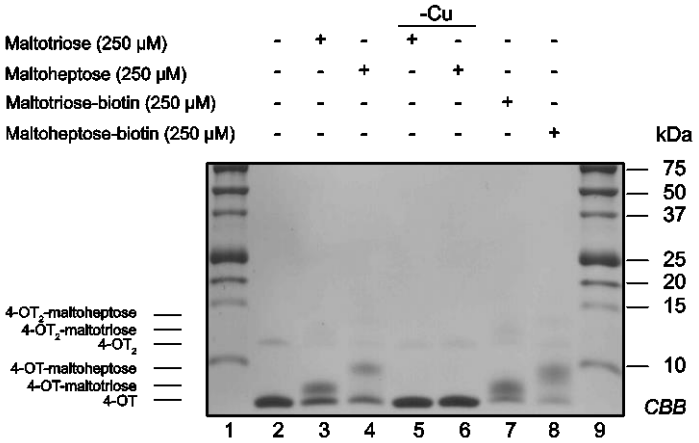


Figure 5, Tricine SDS Page, visualized by Coomassie stain, 4-OT_2 are dimers

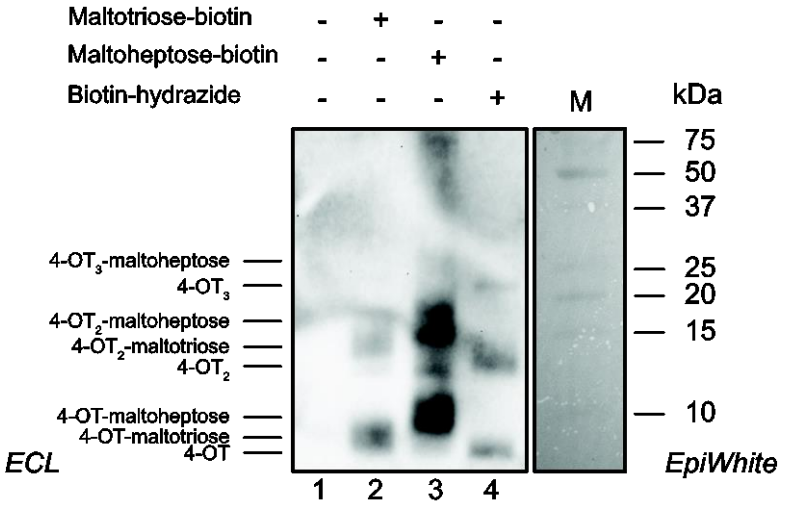


Figure 4, Western Blot using Strep-HRP and ECL, 4-OT_x are dimers/trimers

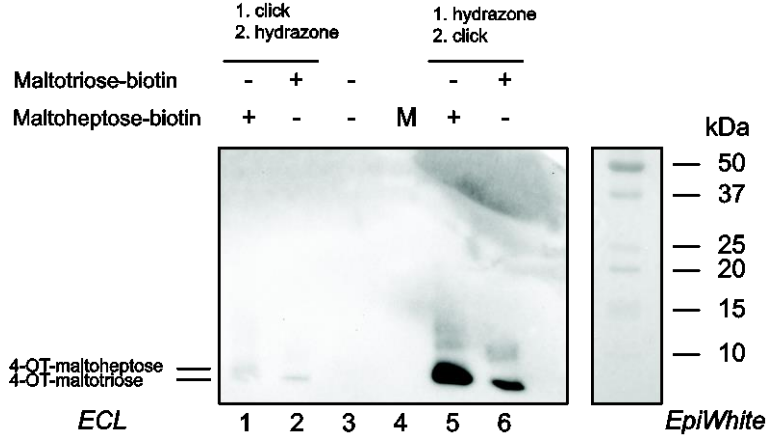


Figure 3, Western Blot using Strep-HRP and ECL, Intensity difference first click followed by hydrazone or first hydrazone formation followed by click

Spectroscopic data

β-D-glucosyl azide (1)

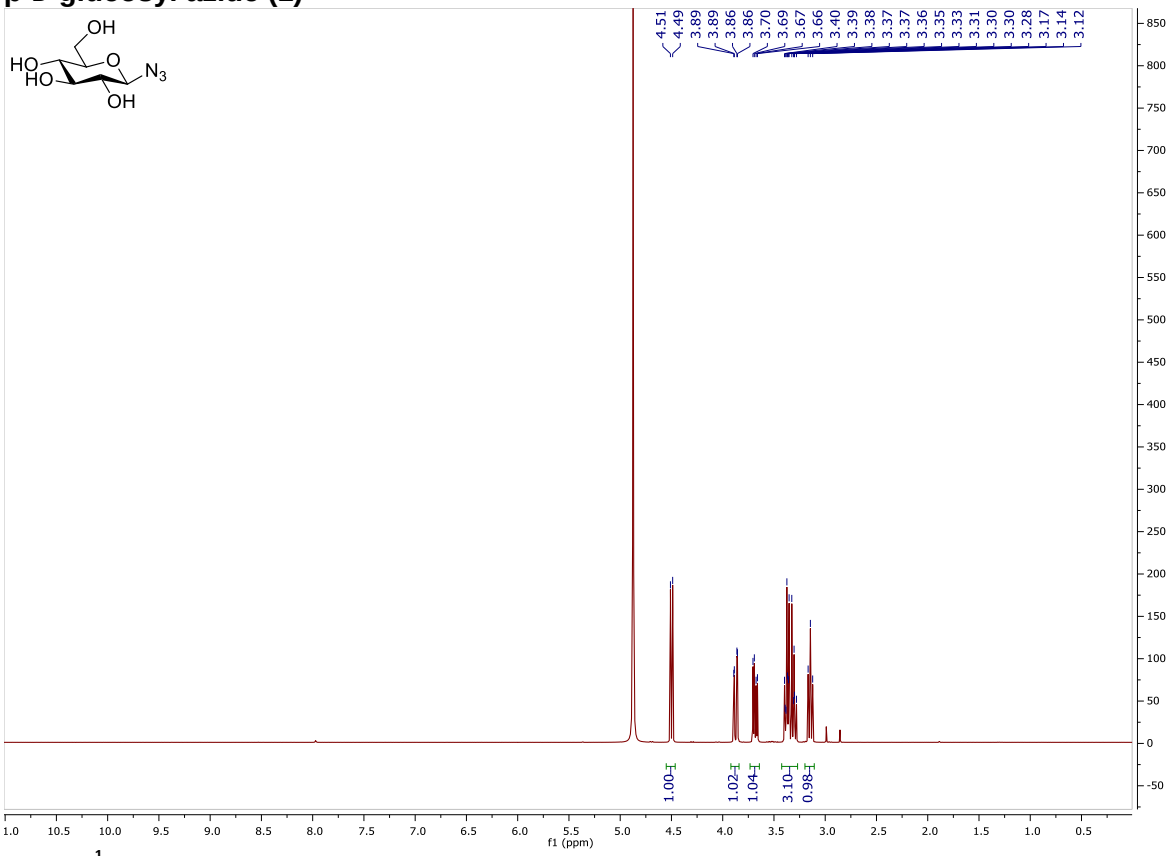


Figure 6, ^{1}H-NMR of β-D-glucosyl azide

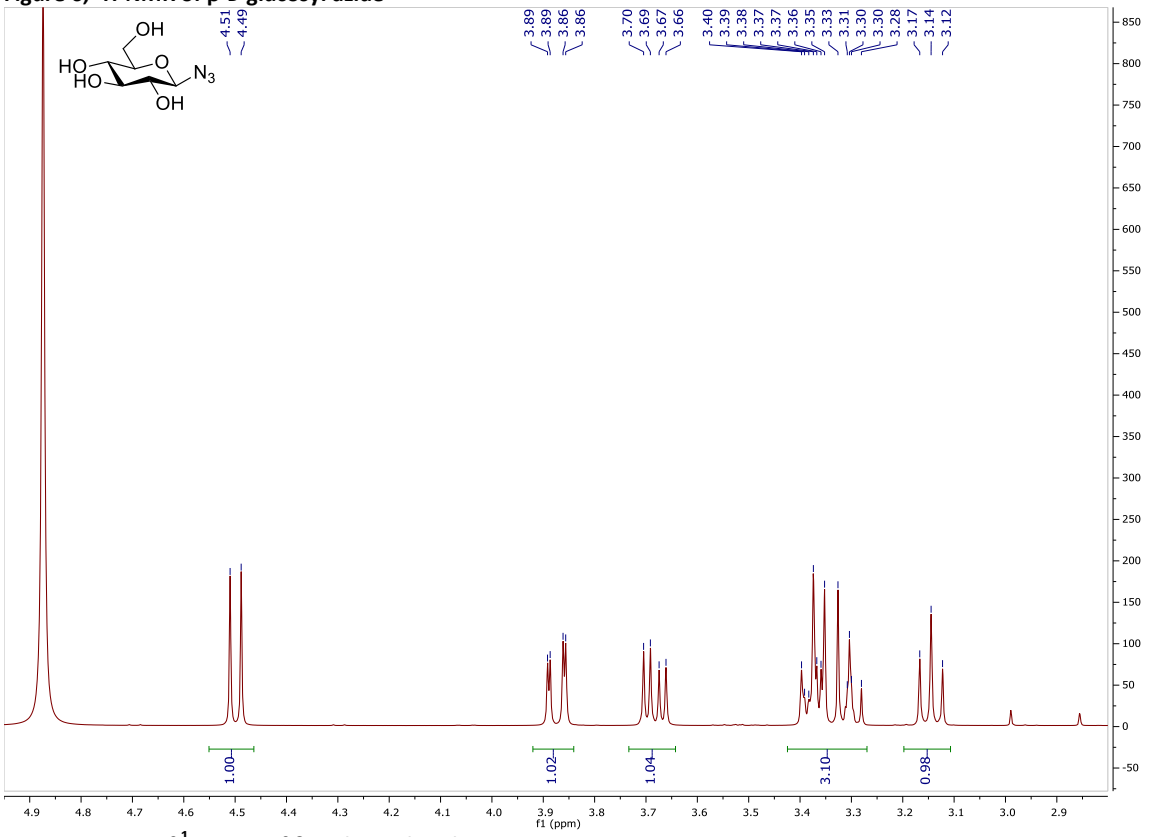


Figure 7, zoom of ^{1}H-NMR of β-D-glucosyl azide

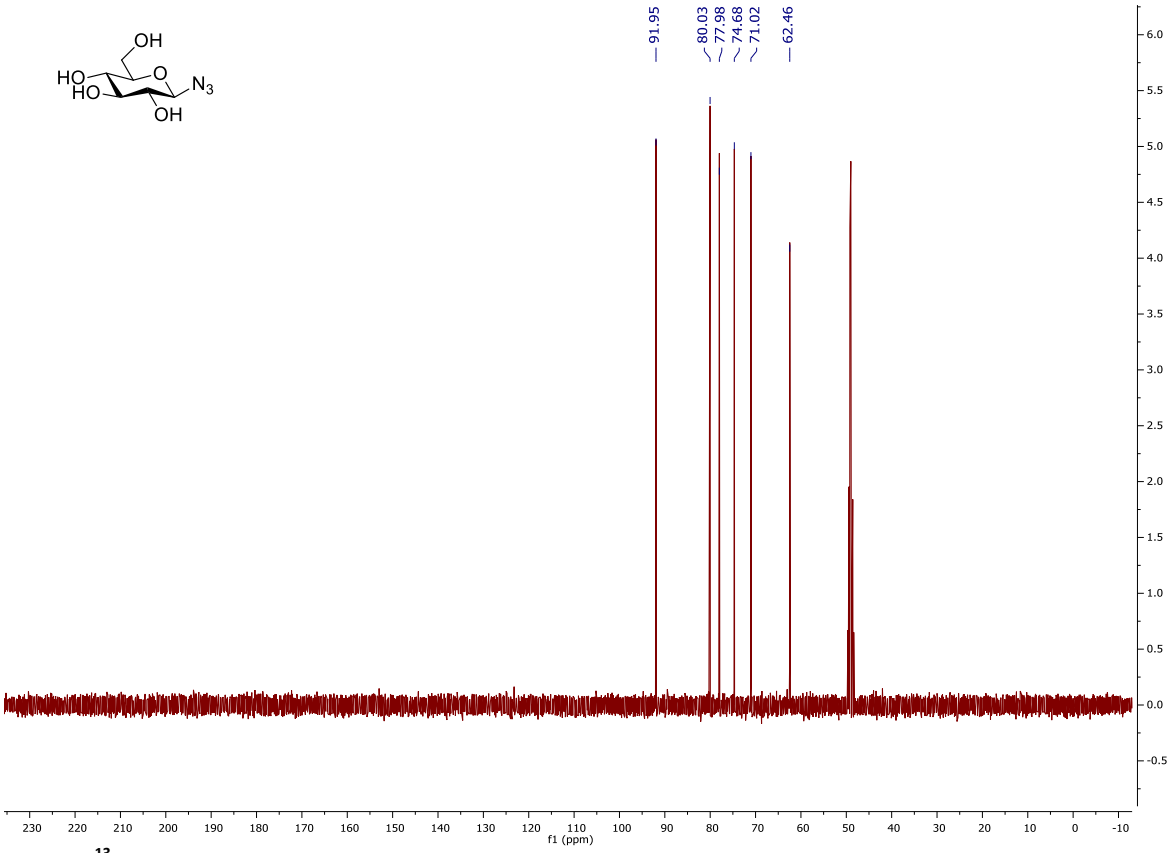


Figure 8, ^{13}C-NMR of β-D-glucosyl azide

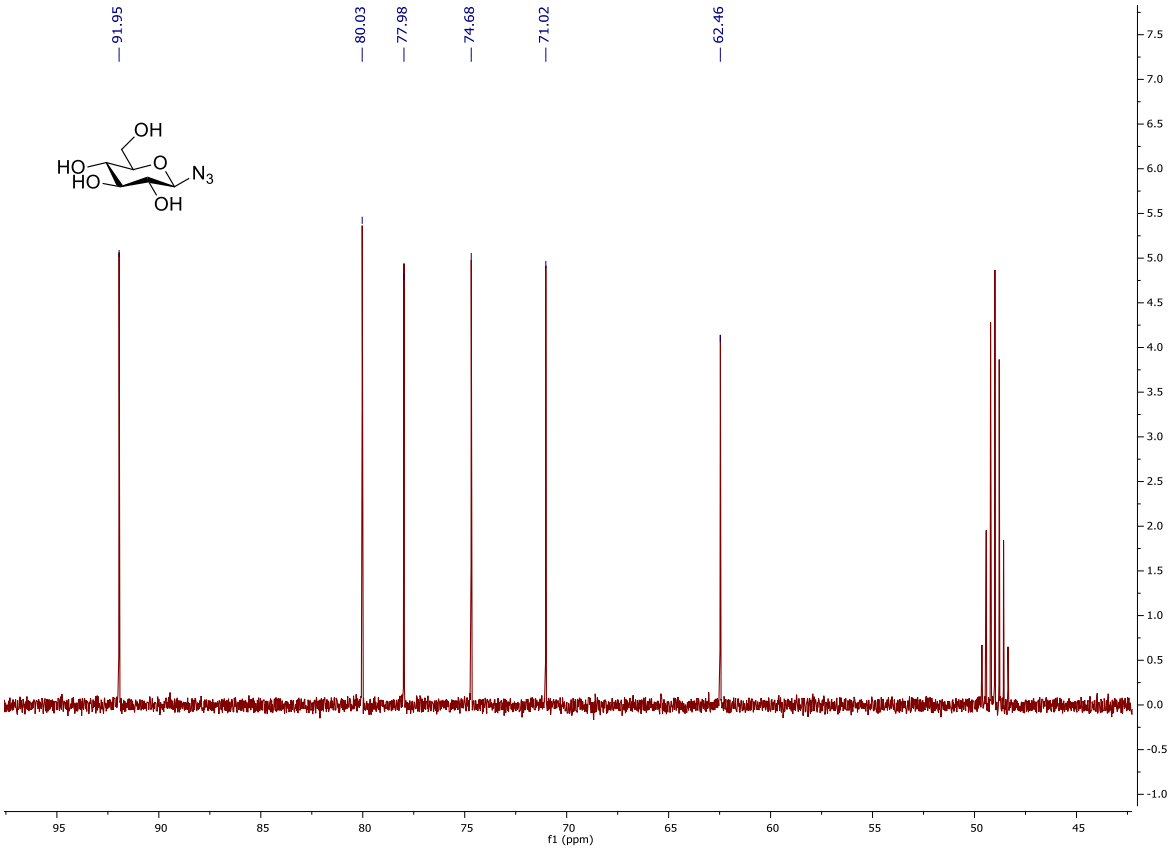


Figure 9, zoom of ^{13}C-NMR of β-D-glucosyl azide

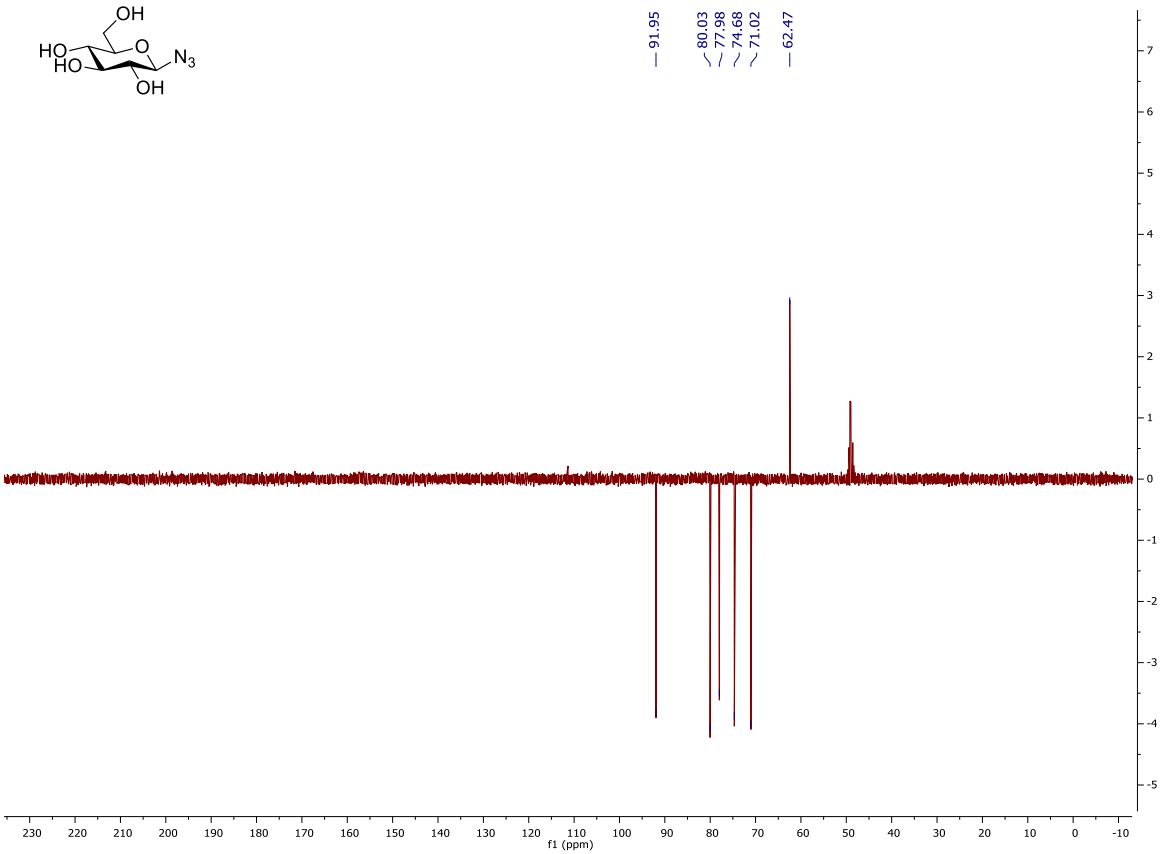


Figure 10, APT of β-D-glucosyl azide

Figure 11, HMQC of β-D-glucosyl azide

B-D-cellobiosyl azide (2)

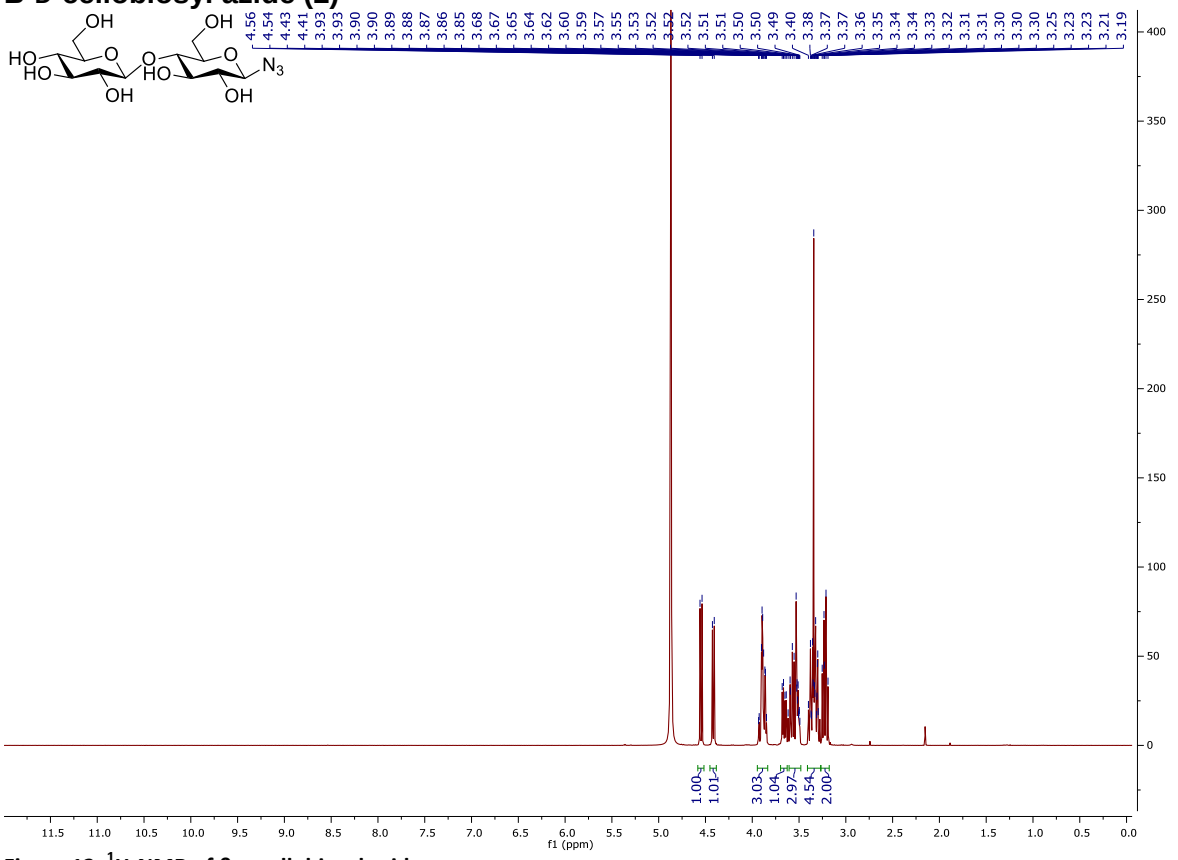


Figure 12, ^{1}H-NMR of β-D-cellobiosyl azide

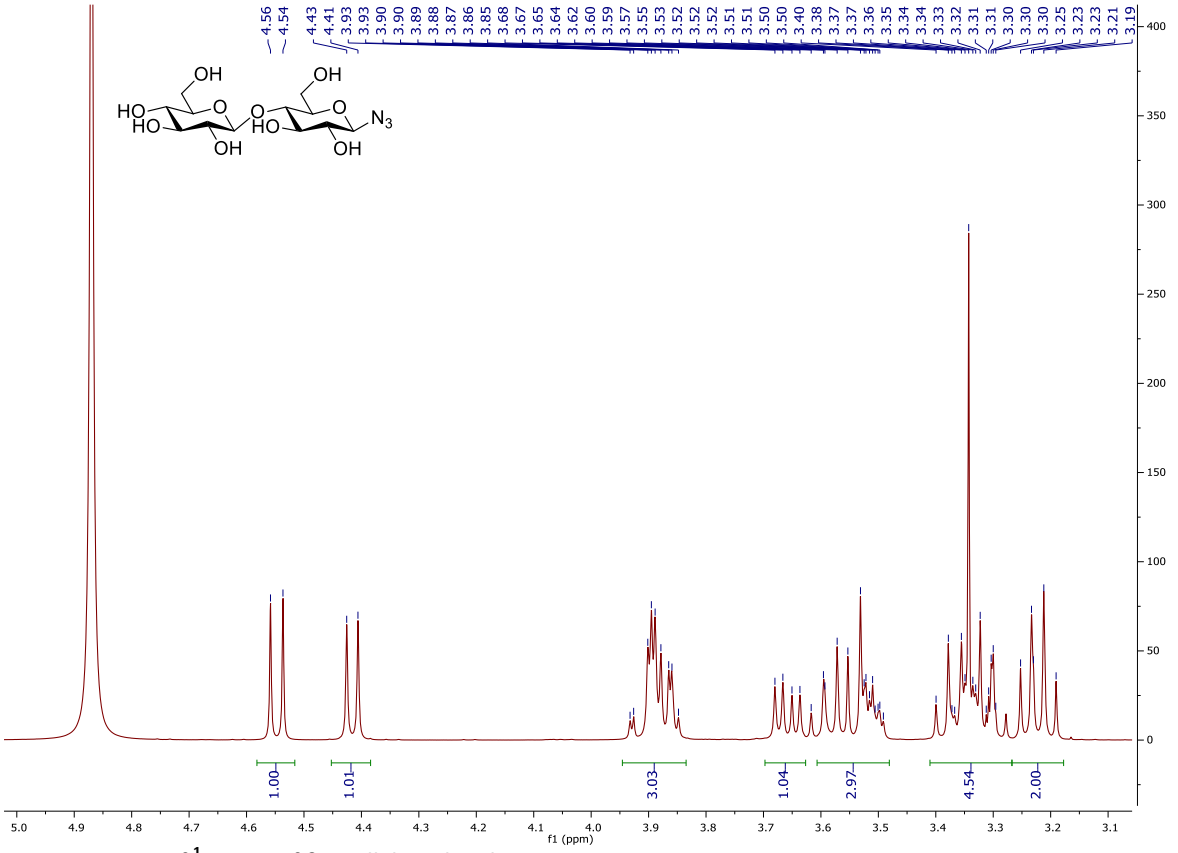


Figure 13, zoom of ^{1}H-NMR of β-D-cellobiosyl azide

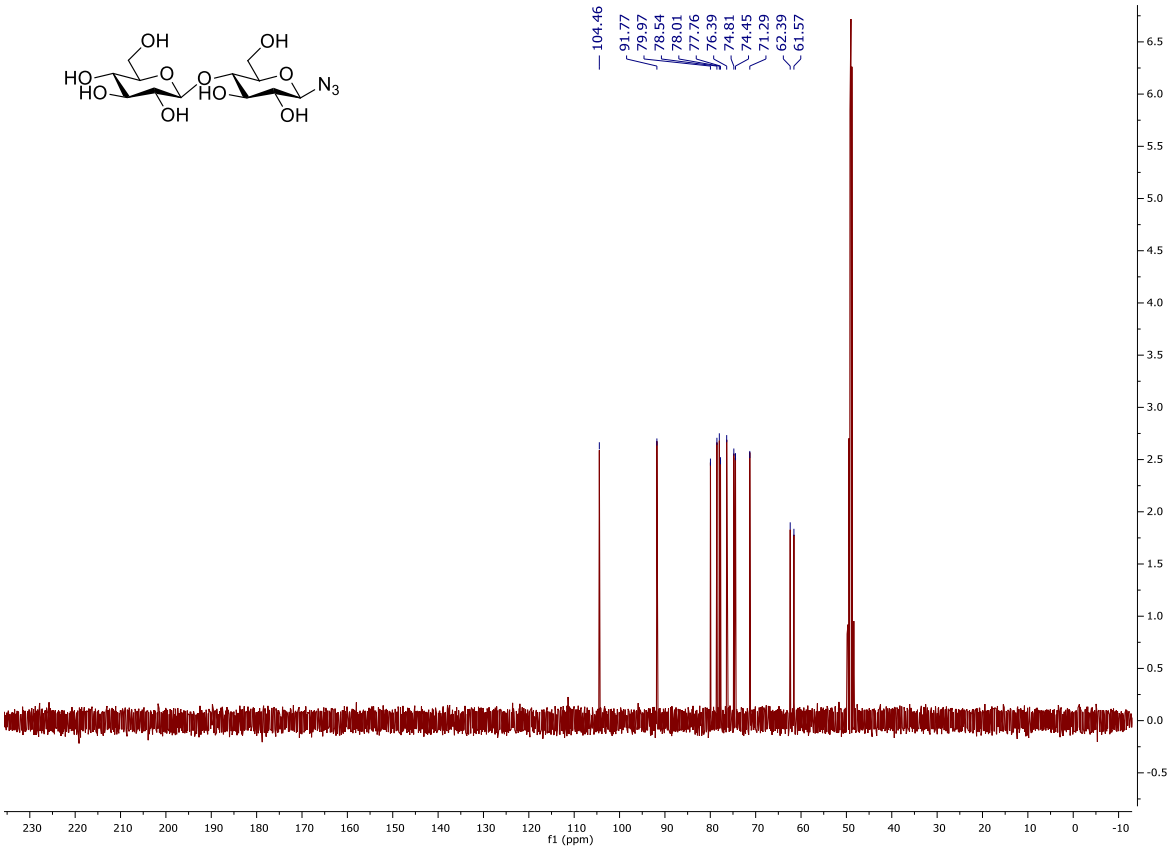


Figure 14, ^{13}C-NMR of β-D-cellobiosyl azide

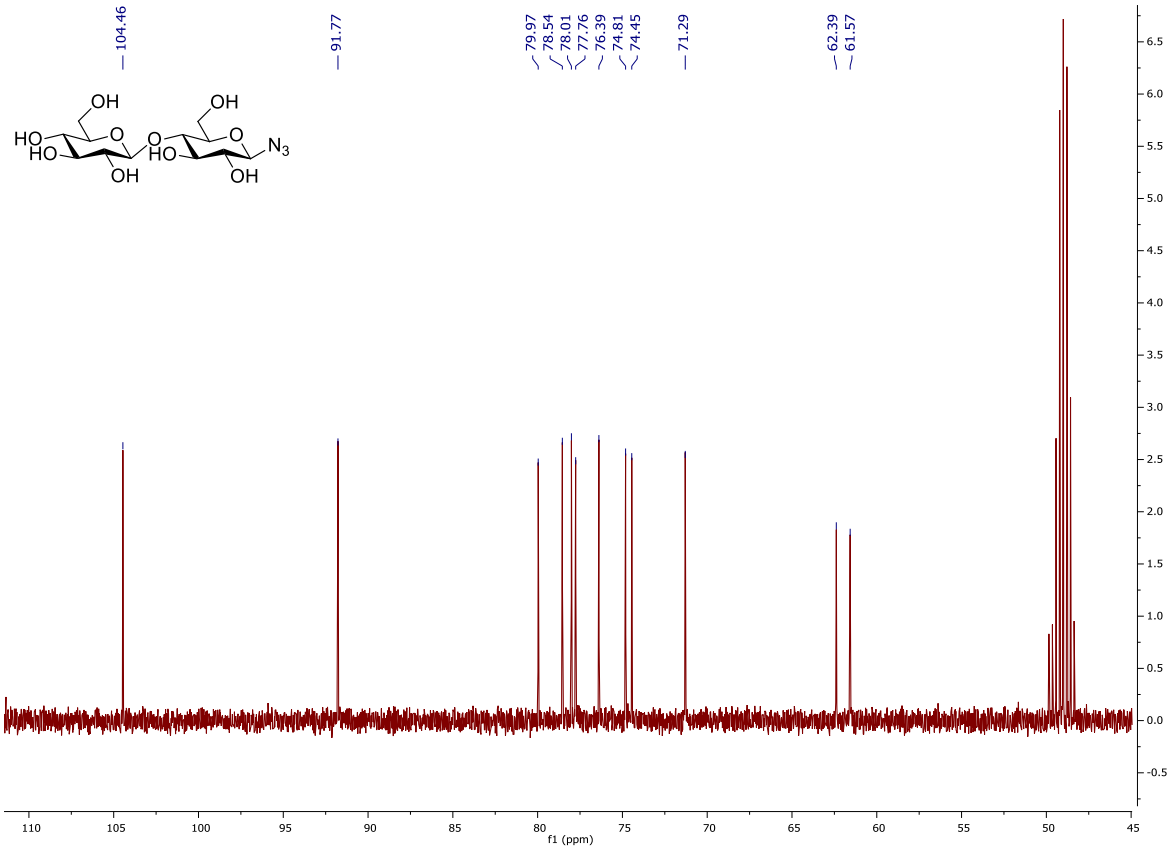


Figure 15, zoom of ^{13}C-NMR of β-D-cellobiosyl azide

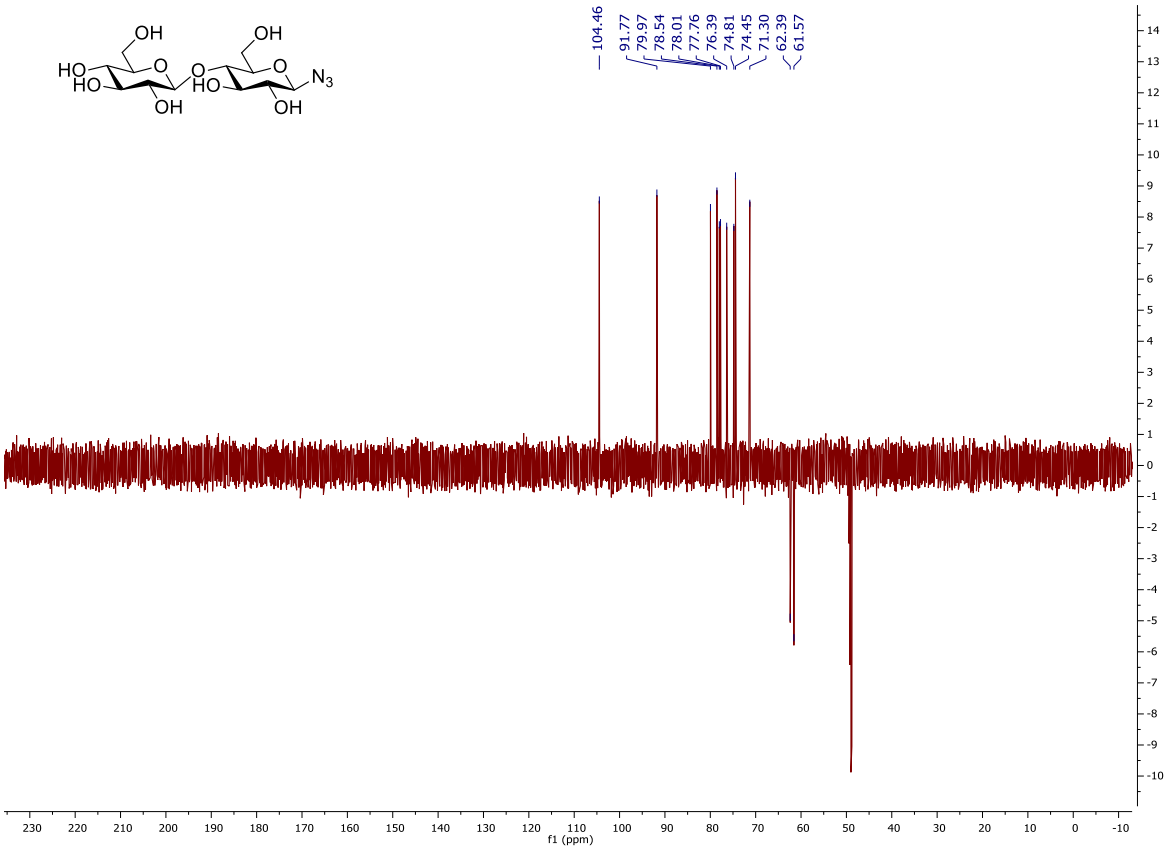


Figure 16, APT of β-D-cellobiosyl azide

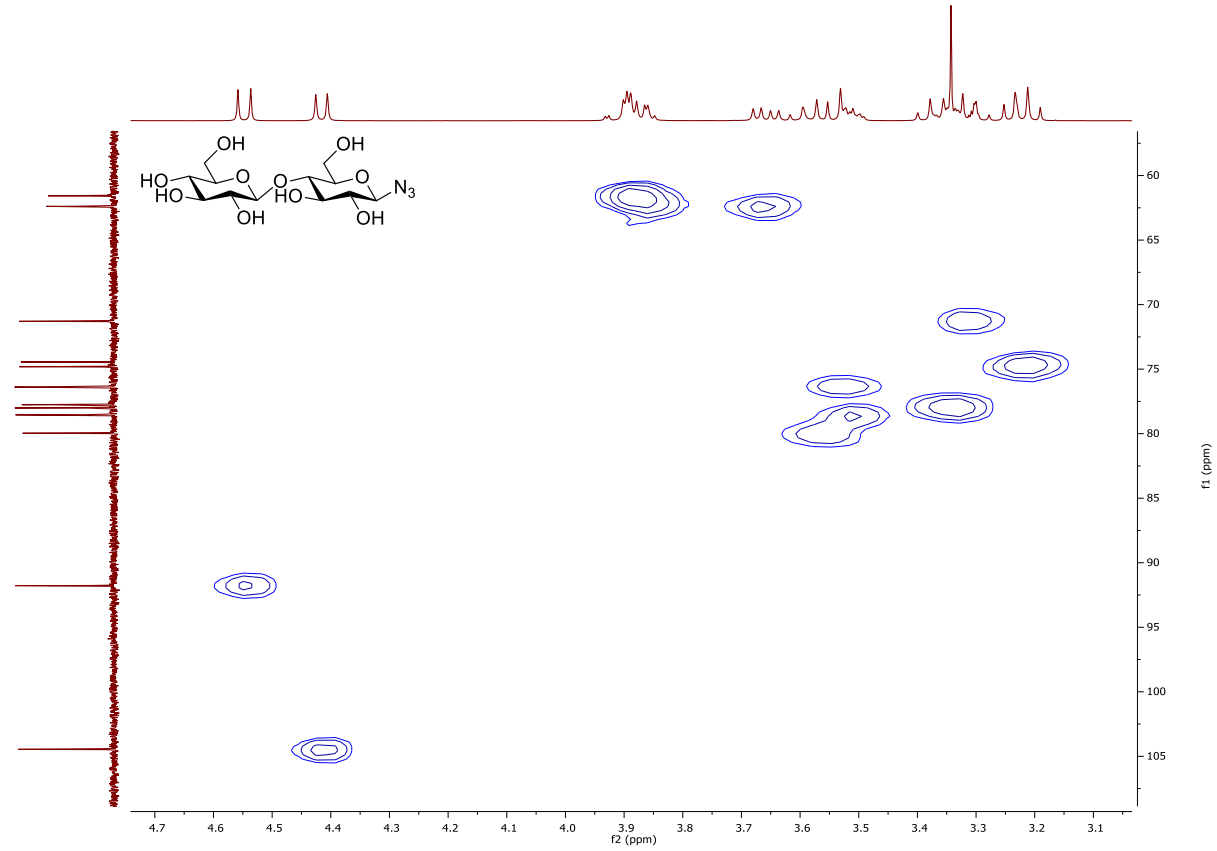


Figure 17, HMQC of β-D-cellobiosyl azide

β-D-maltosyl azide (3)

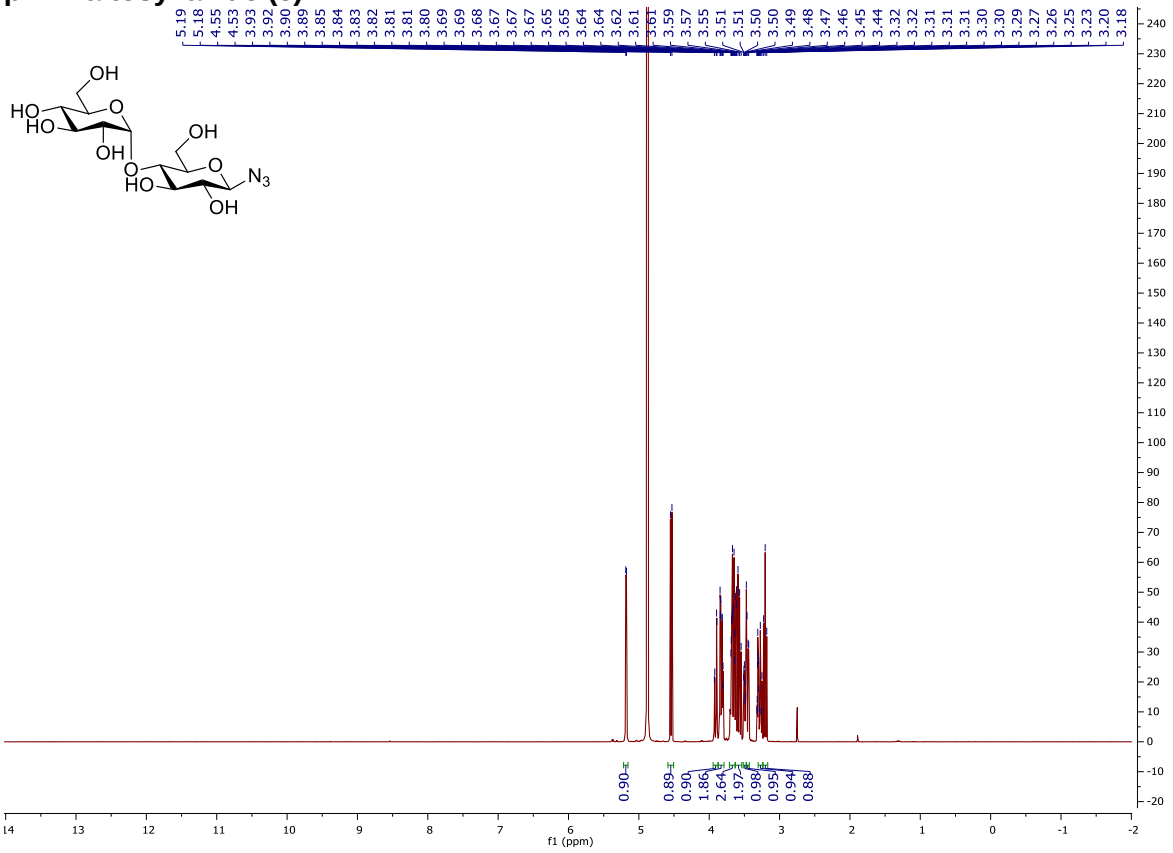


Figure 18, ^{1}H-NMR of β-D-maltosyl azide

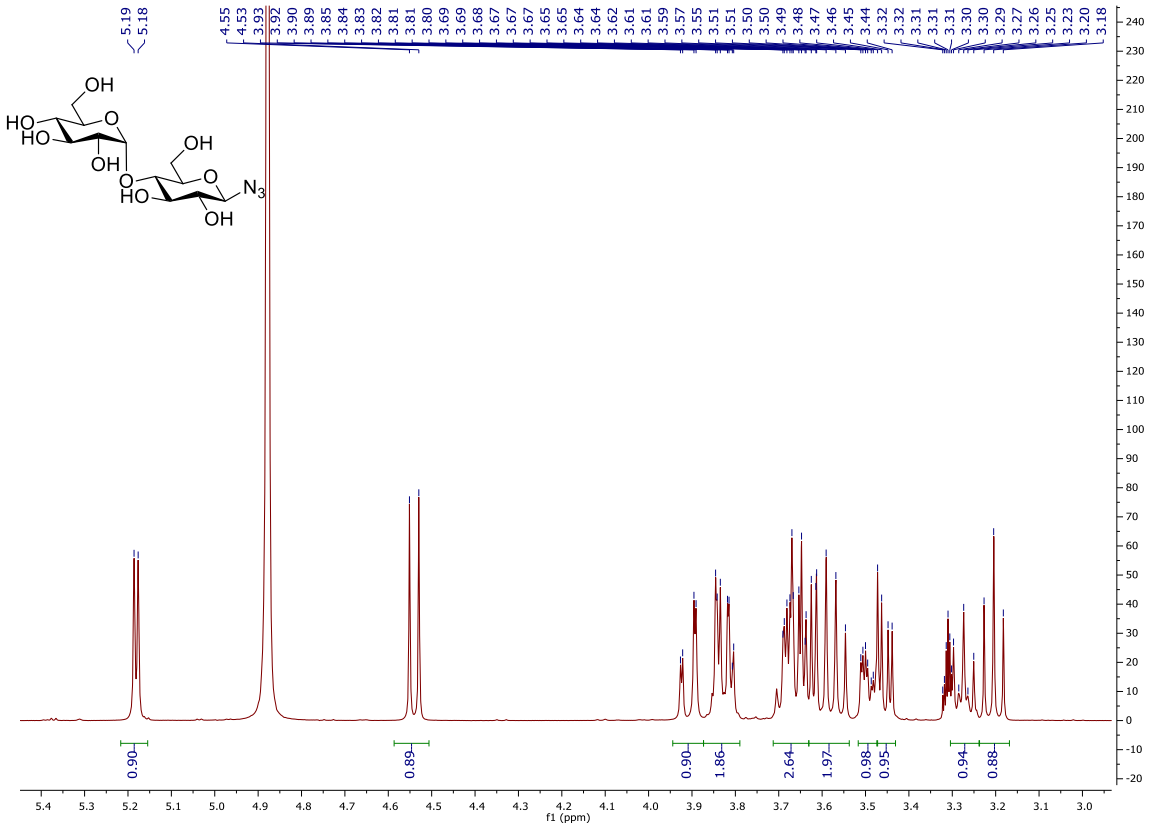


Figure 19, zoom of ^{1}H-NMR of β-D-maltosyl azide

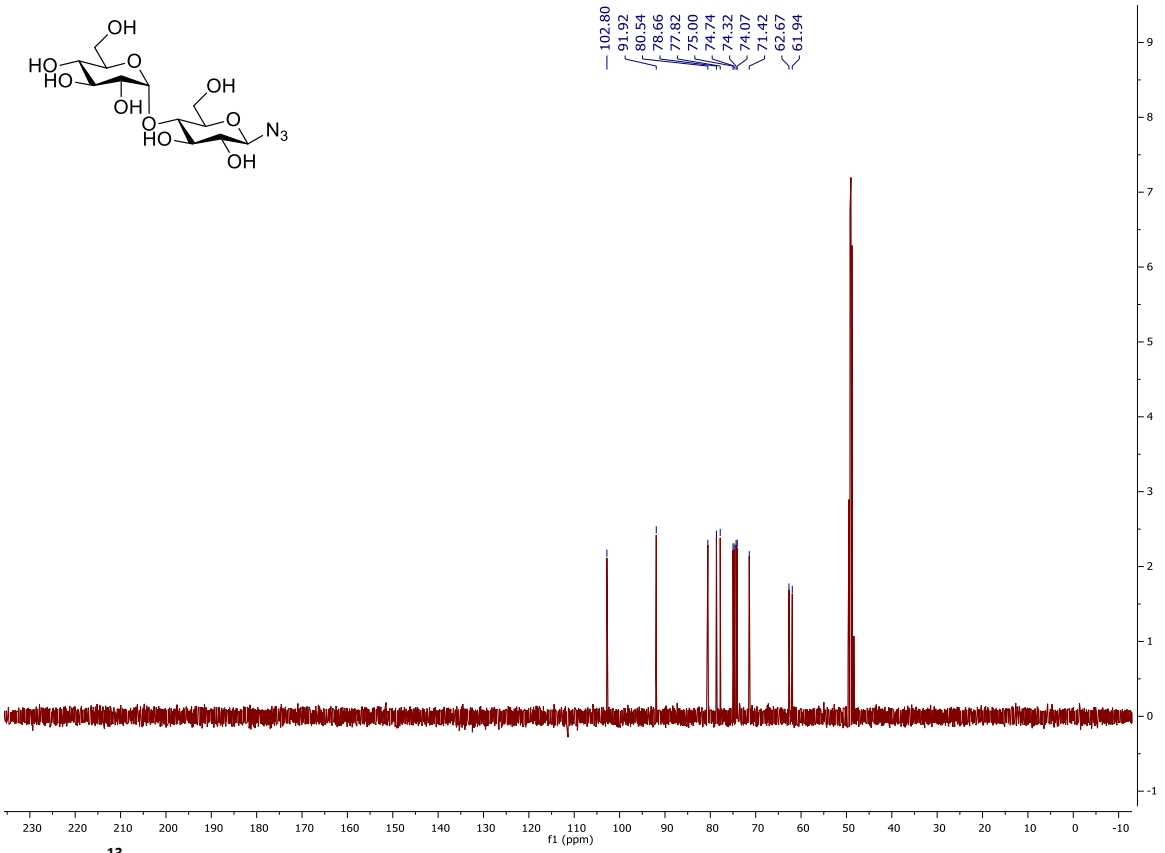


Figure 20, ^{13}C-NMR of β-D-maltosyl azide

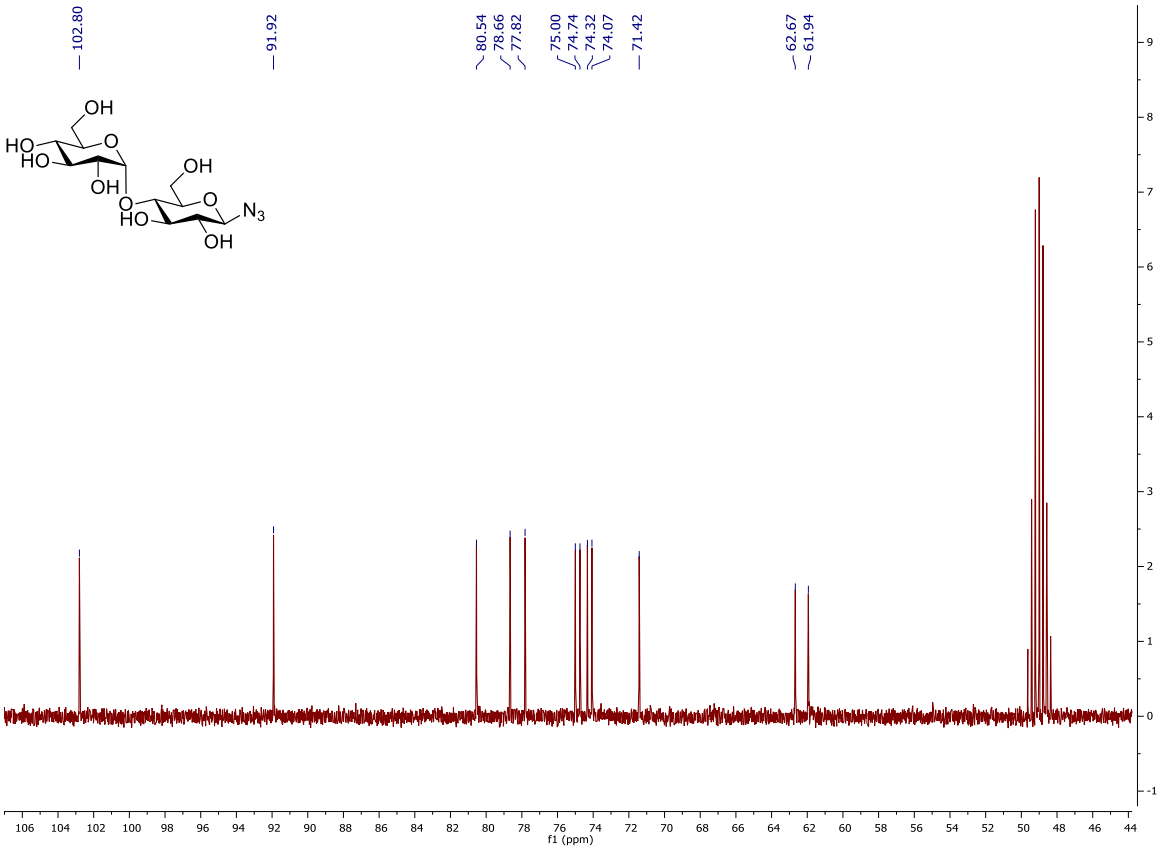


Figure 21, zoom of ^{13}C-NMR of β-D-maltosyl azide

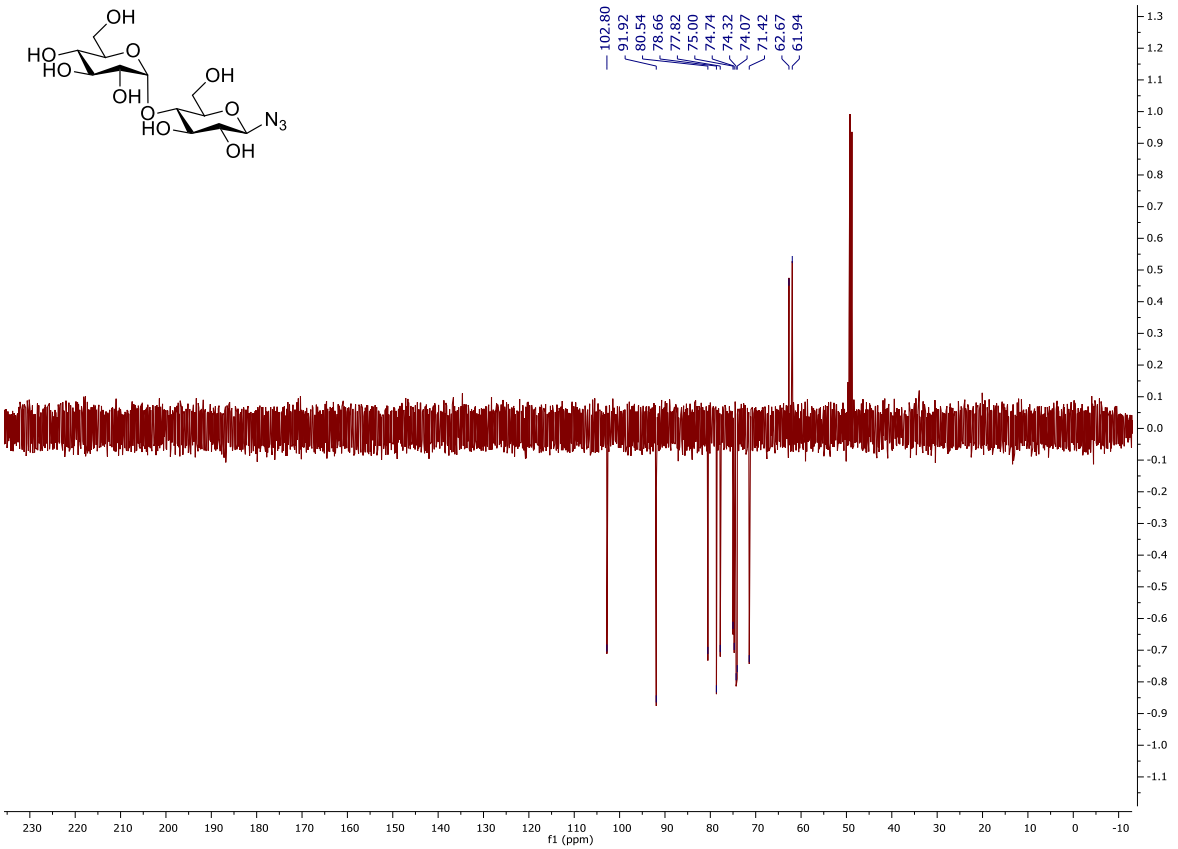


Figure 22, APT of β-D-maltosyl azide

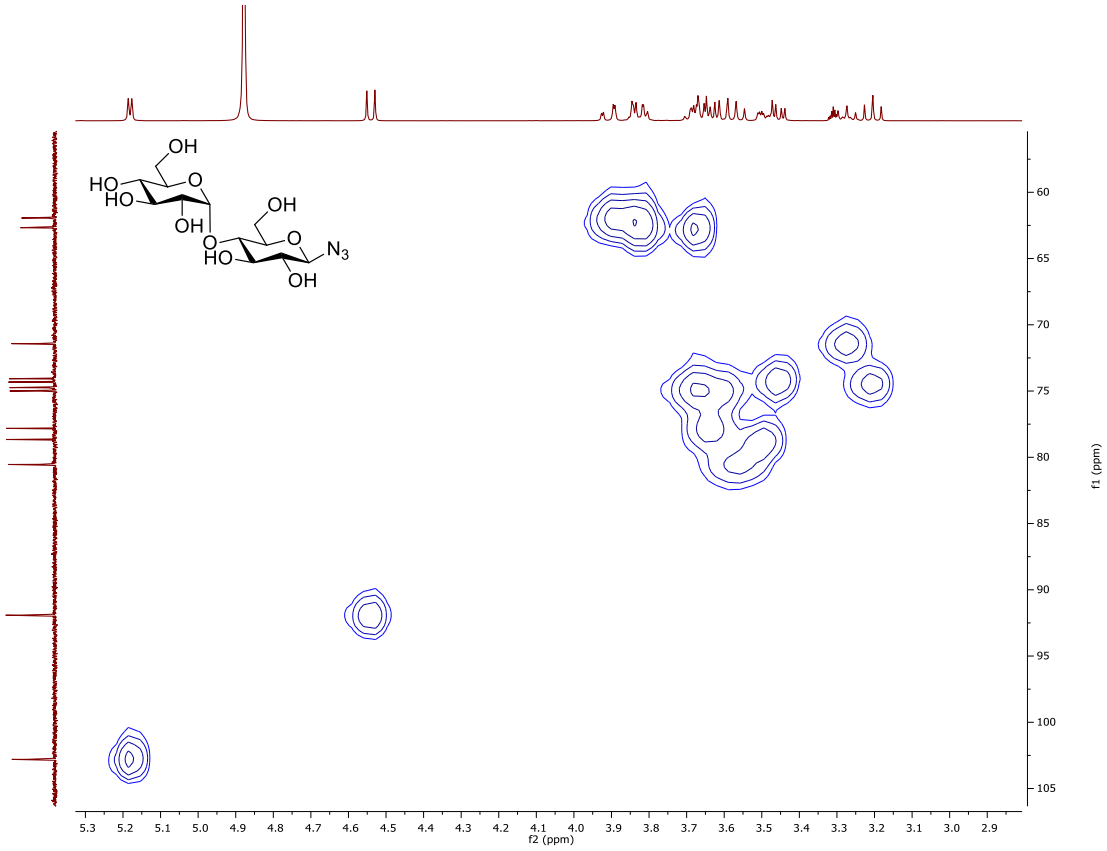


Figure 23, HMQC of β-D-maltosyl azide

β-D-maltotriosyl azide (4)

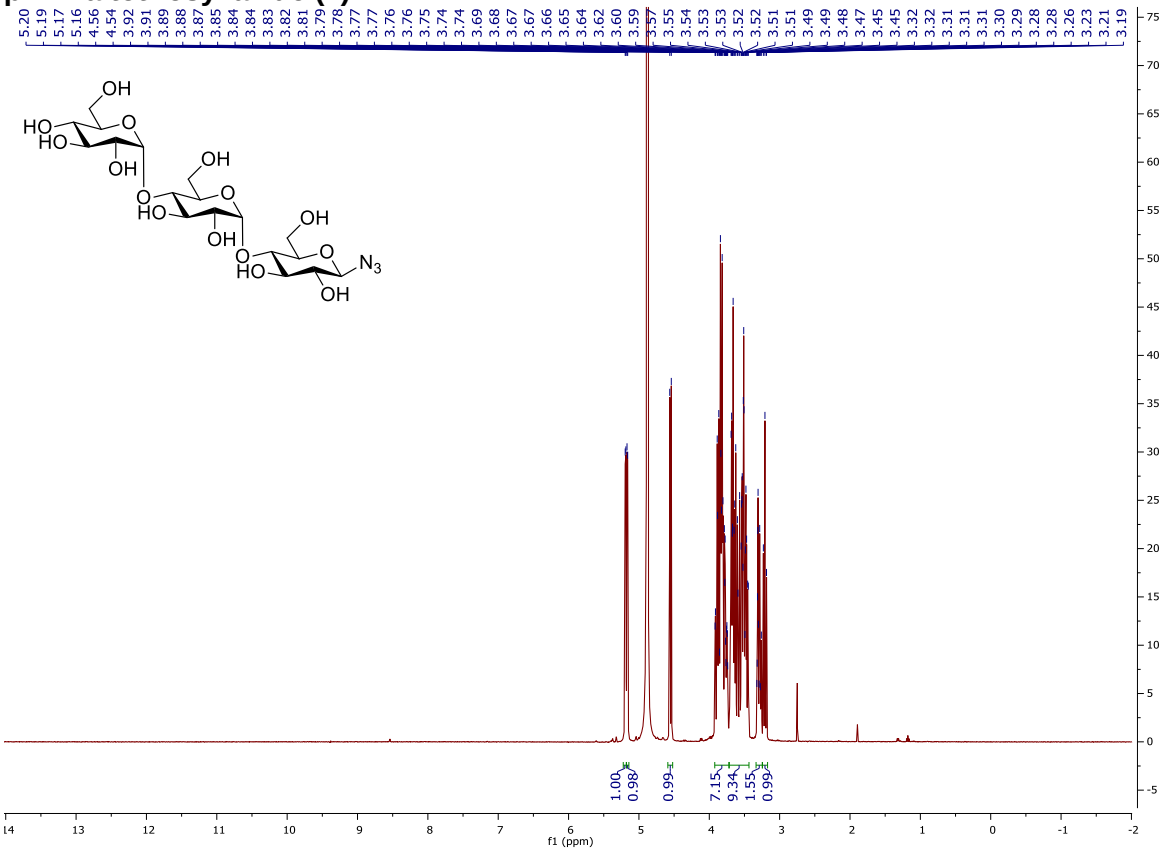


Figure 24, ^{1}H-NMR of β-D-maltotriosyl azide

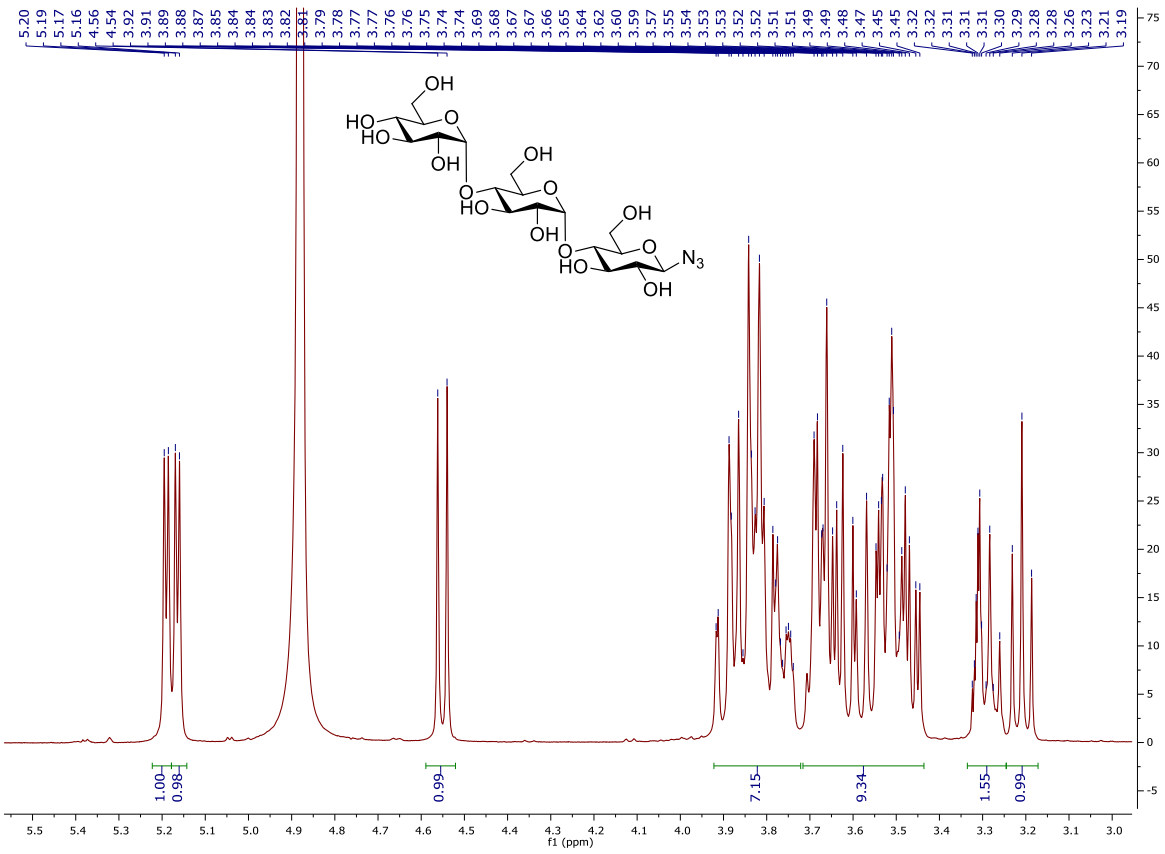


Figure 25, zoom of ^{1}H-NMR of β-D-maltotriosyl azide

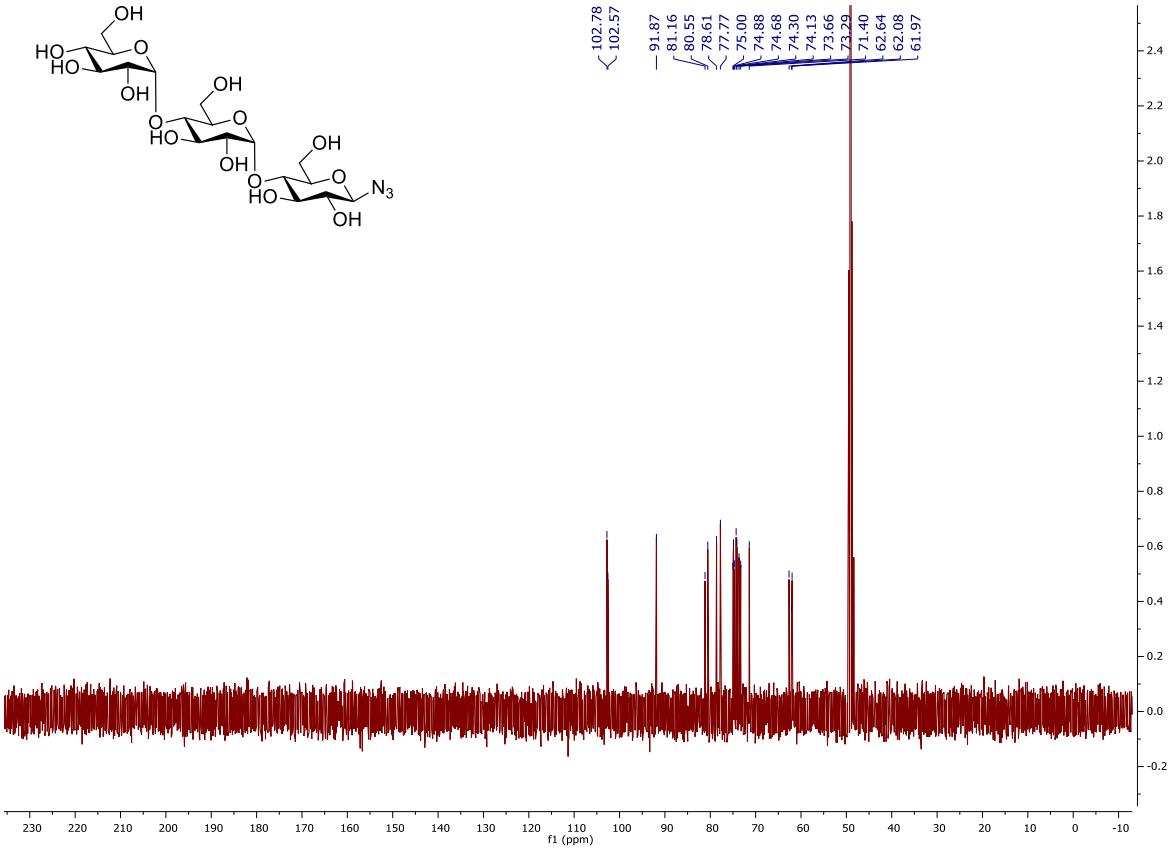


Figure 26, ^{13}C-NMR of β-D-maltotriosyl azide

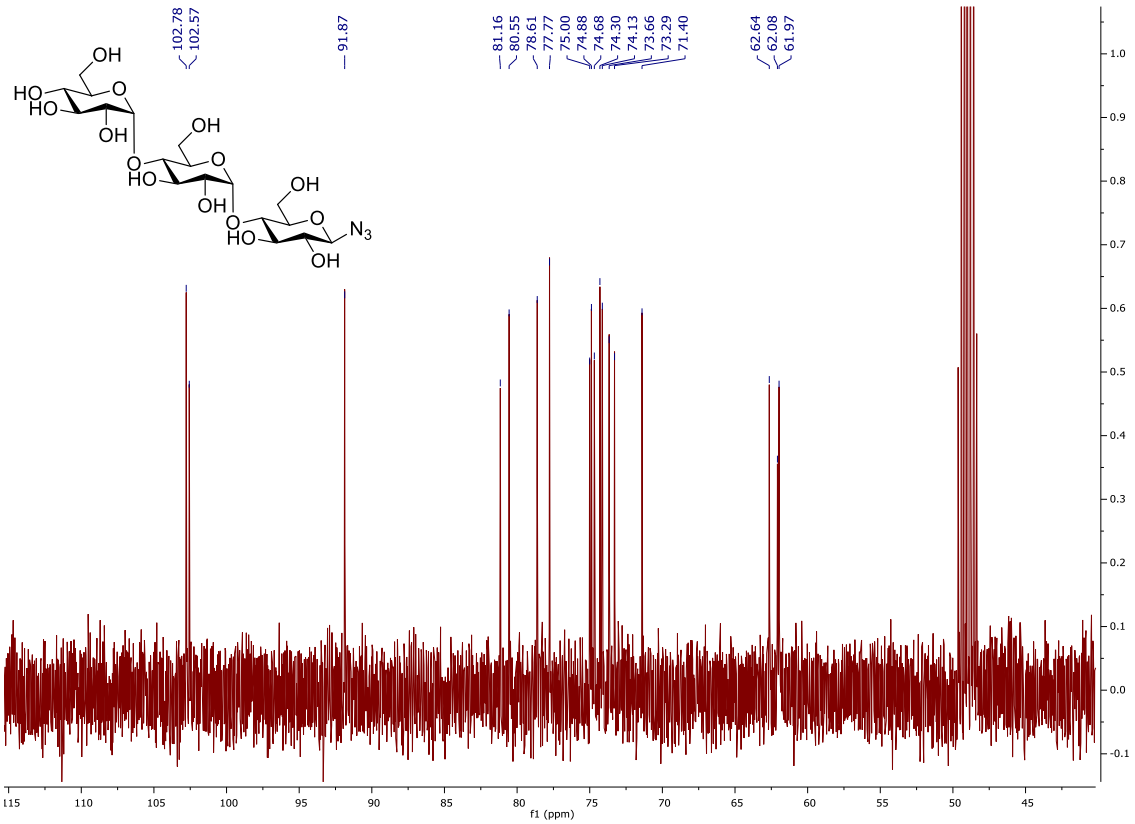


Figure 27, zoom of ^{13}C-NMR of β-D-maltotriosyl azide

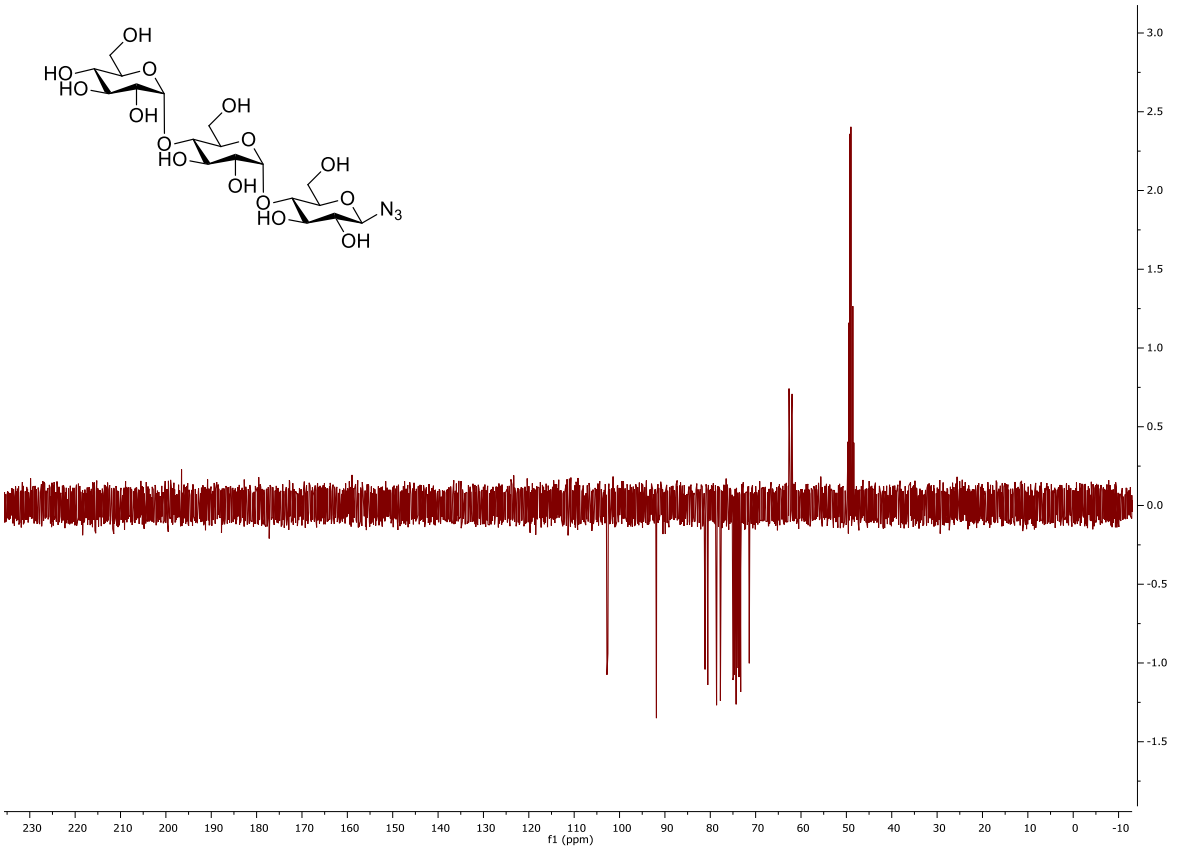


Figure 28, APT of β-D-maltotriosyl azide

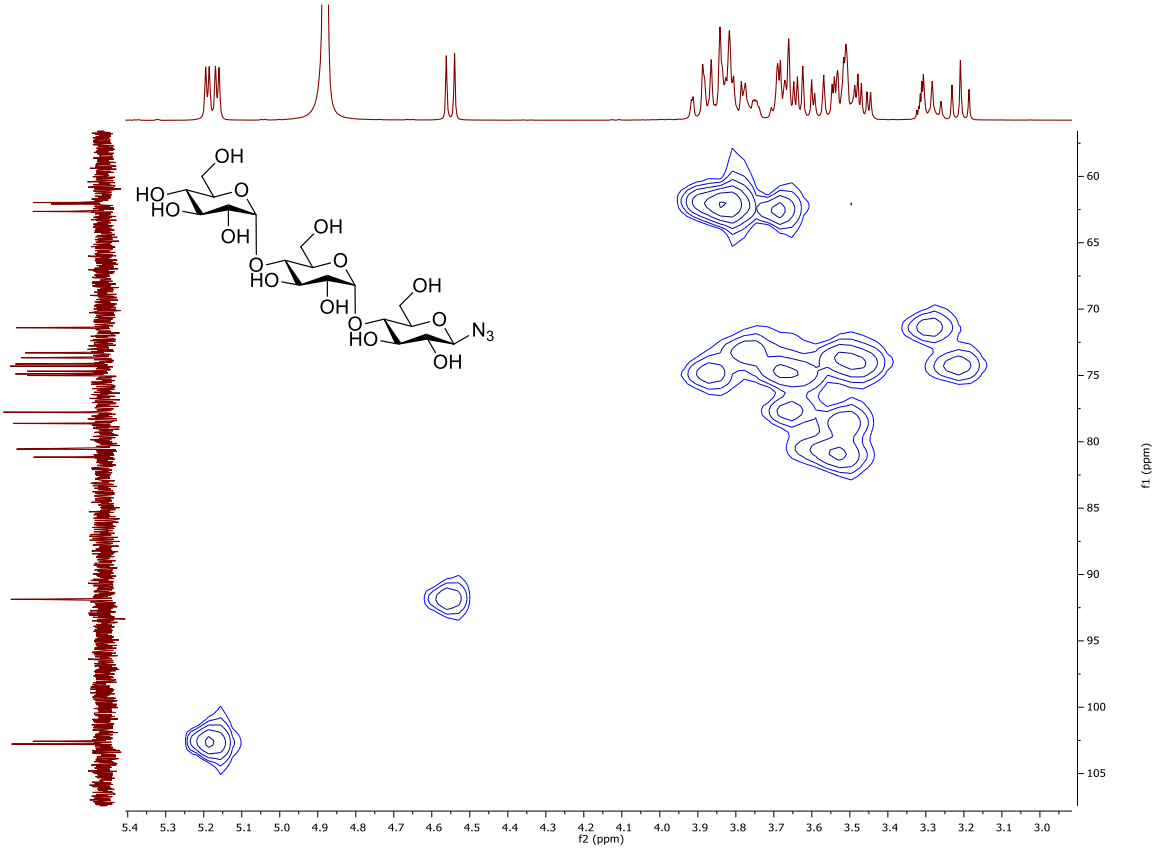


Figure 29, HMQC of β-D-maltotriosyl azide

β-D-maltotetraosyl azide (5)

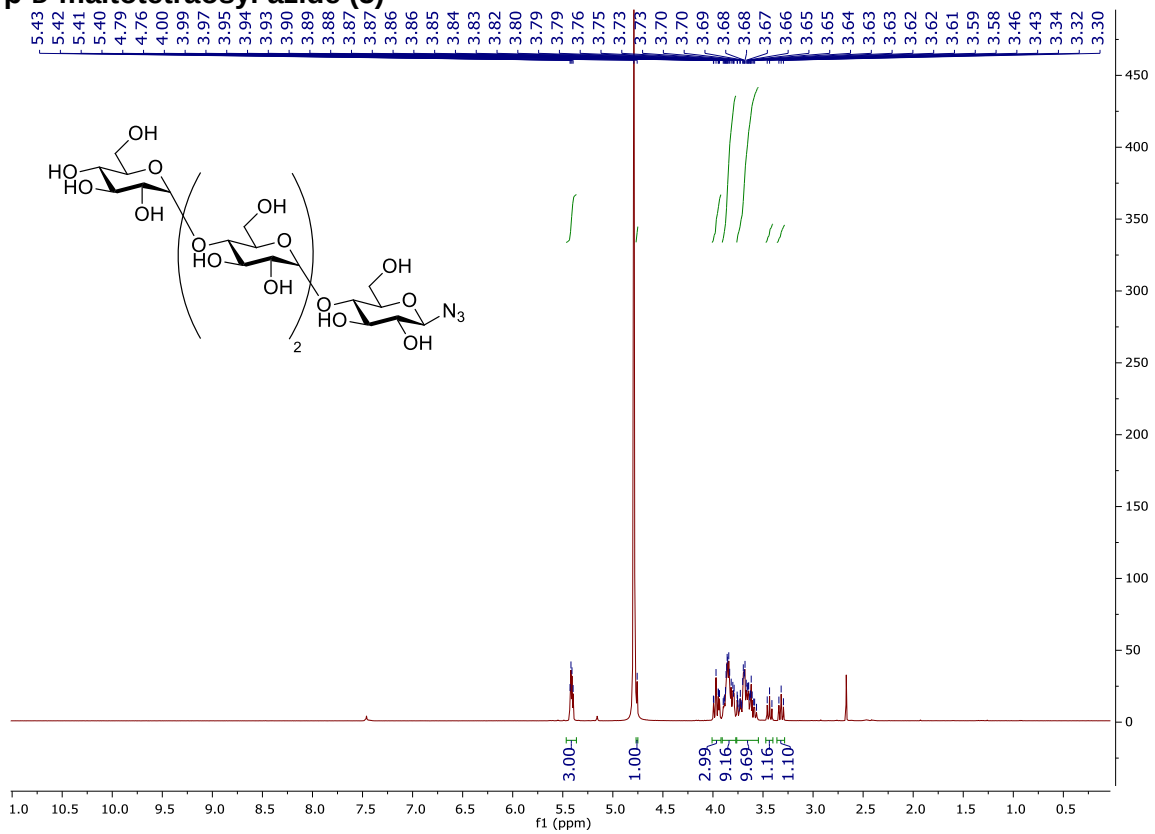


Figure 30, ^{1}H-NMR of β-D-maltotetraosyl azide

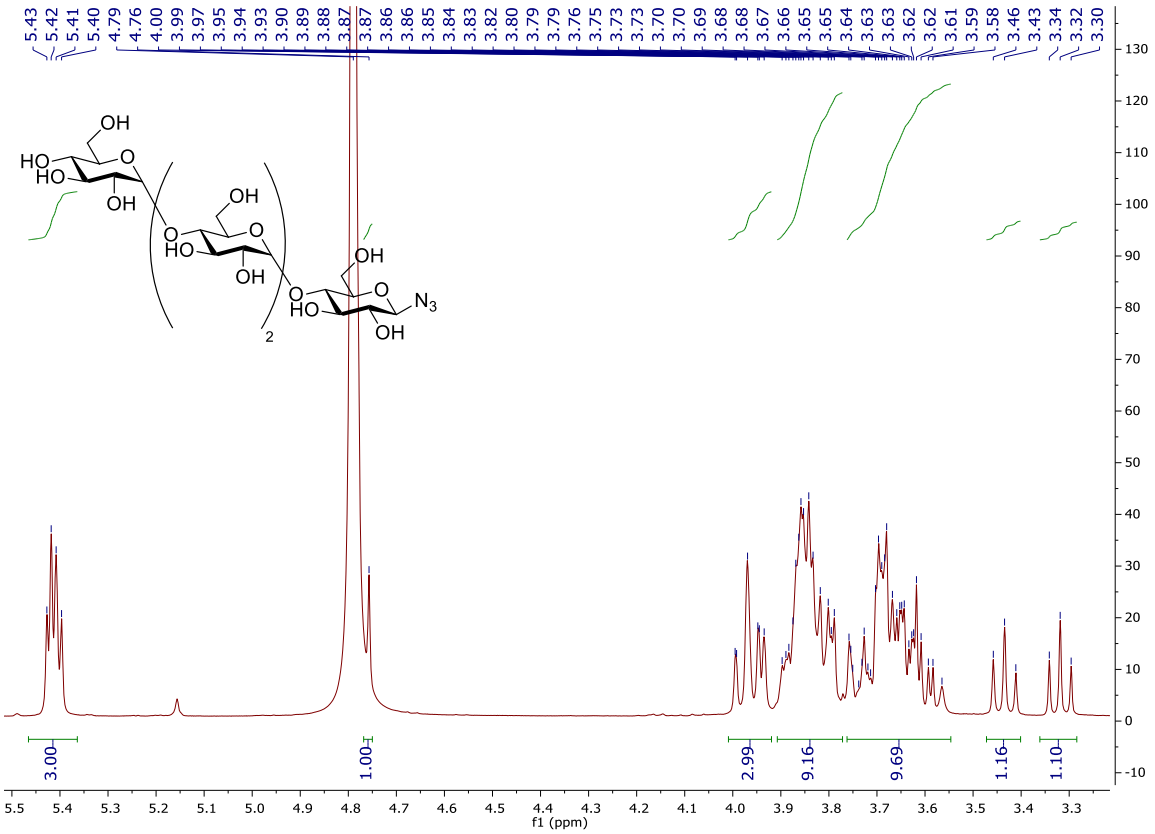


Figure 31, zoom of ^{1}H-NMR of β-D-maltotetraosyl azide

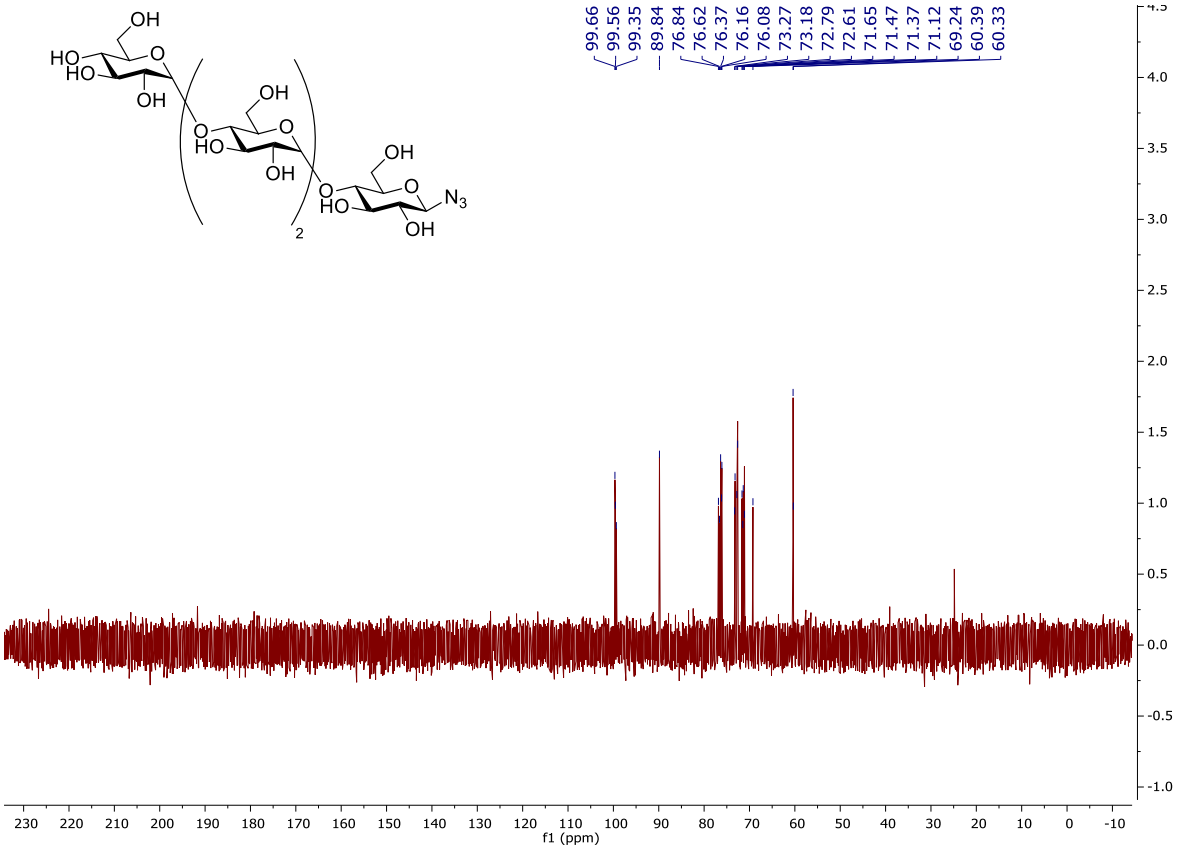


Figure 32, ^{13}C-NMR of β-D-maltotetraosyl azide

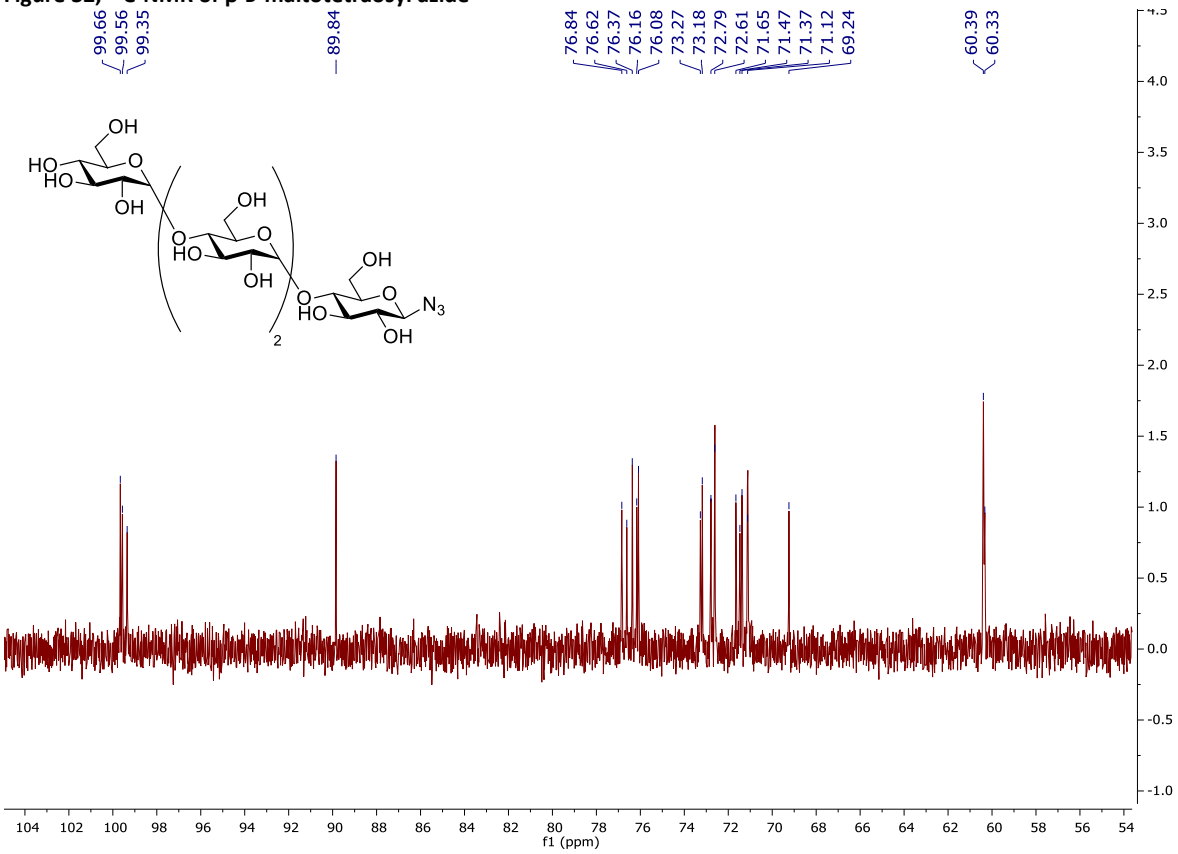


Figure 33, zoom of ^{13}C-NMR of β-D-maltotetraosyl azide

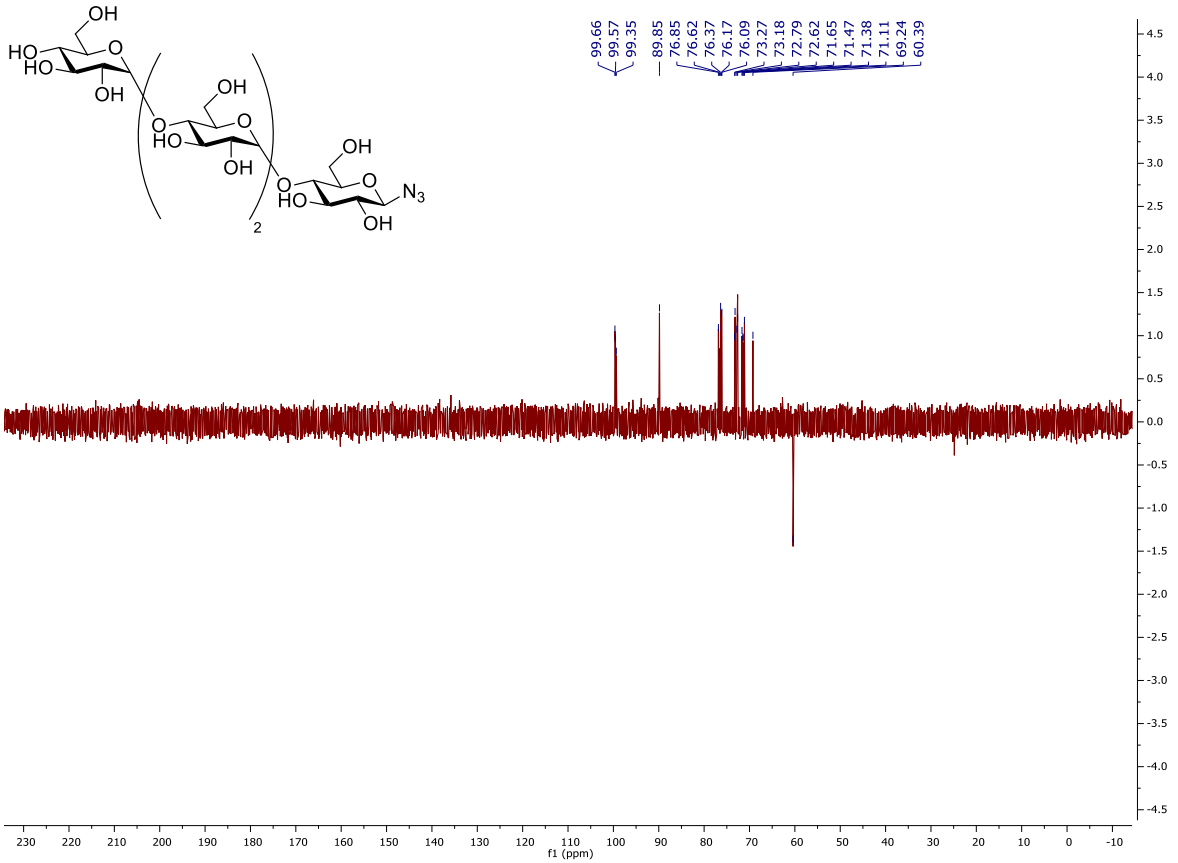


Figure 34, APT of β-D-maltotetraosyl azide

β-D-maltopentaosyl azide (6)

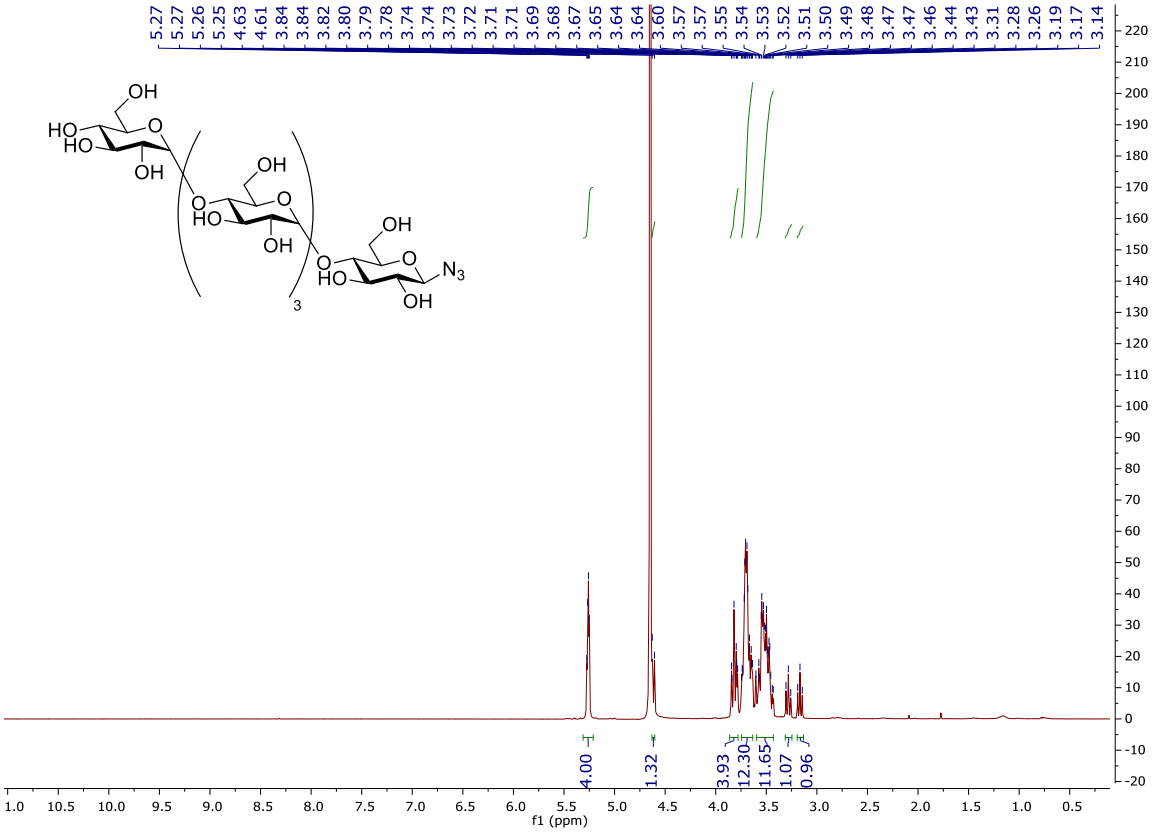


Figure 35, ^{1}H-NMR of β-D-maltopentaosyl azide

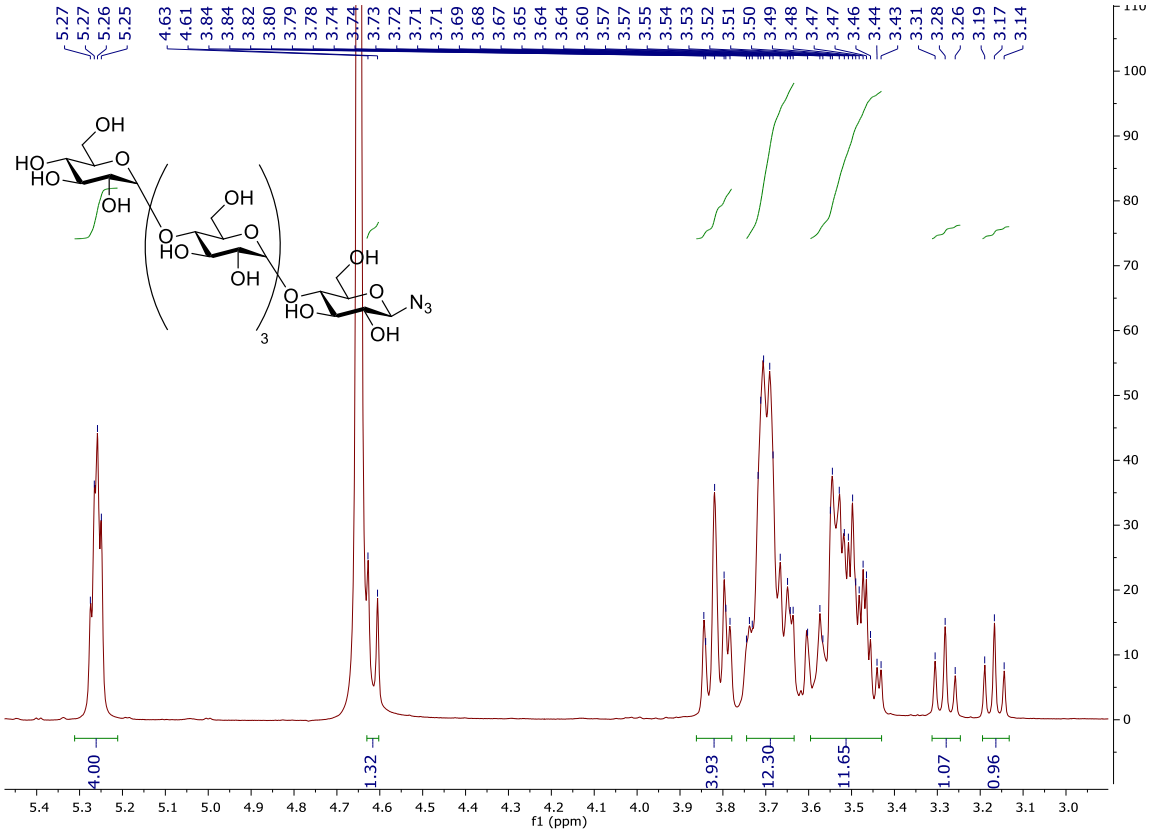


Figure 36, zoom of ^{1}H-NMR of β-D-maltopentaosyl azide

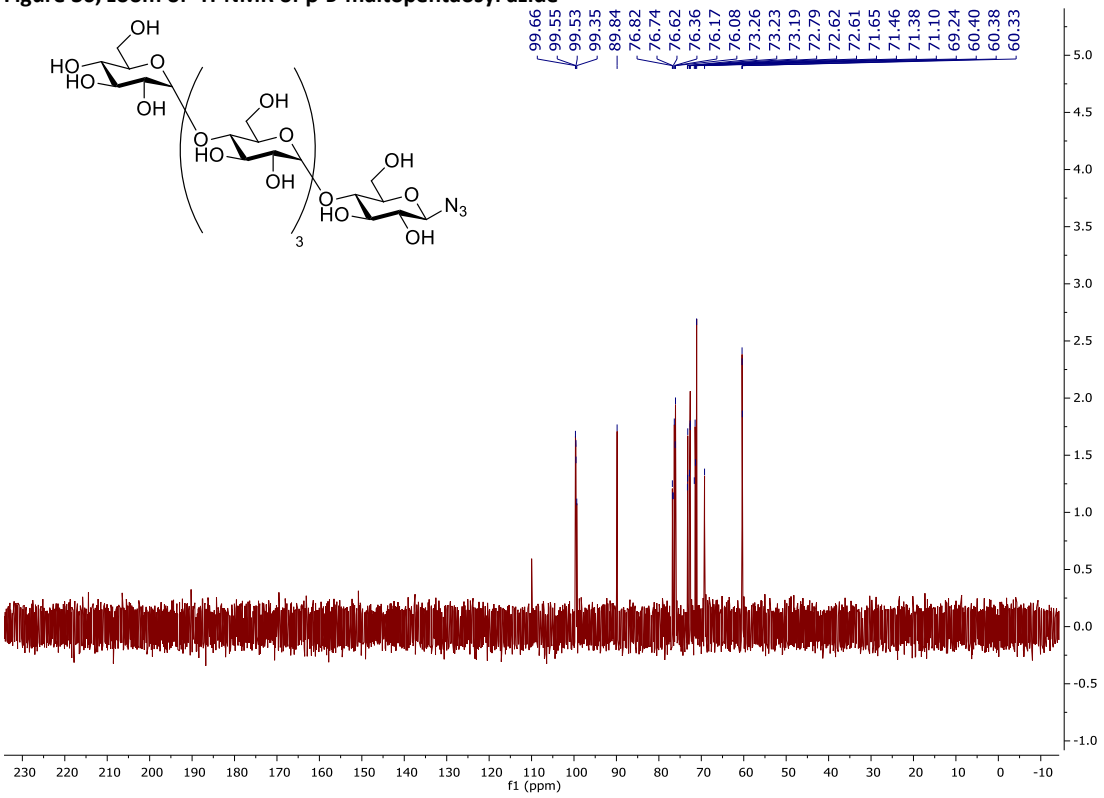


Figure 37, ^{13}C-NMR of β-D-maltopentaosyl azide

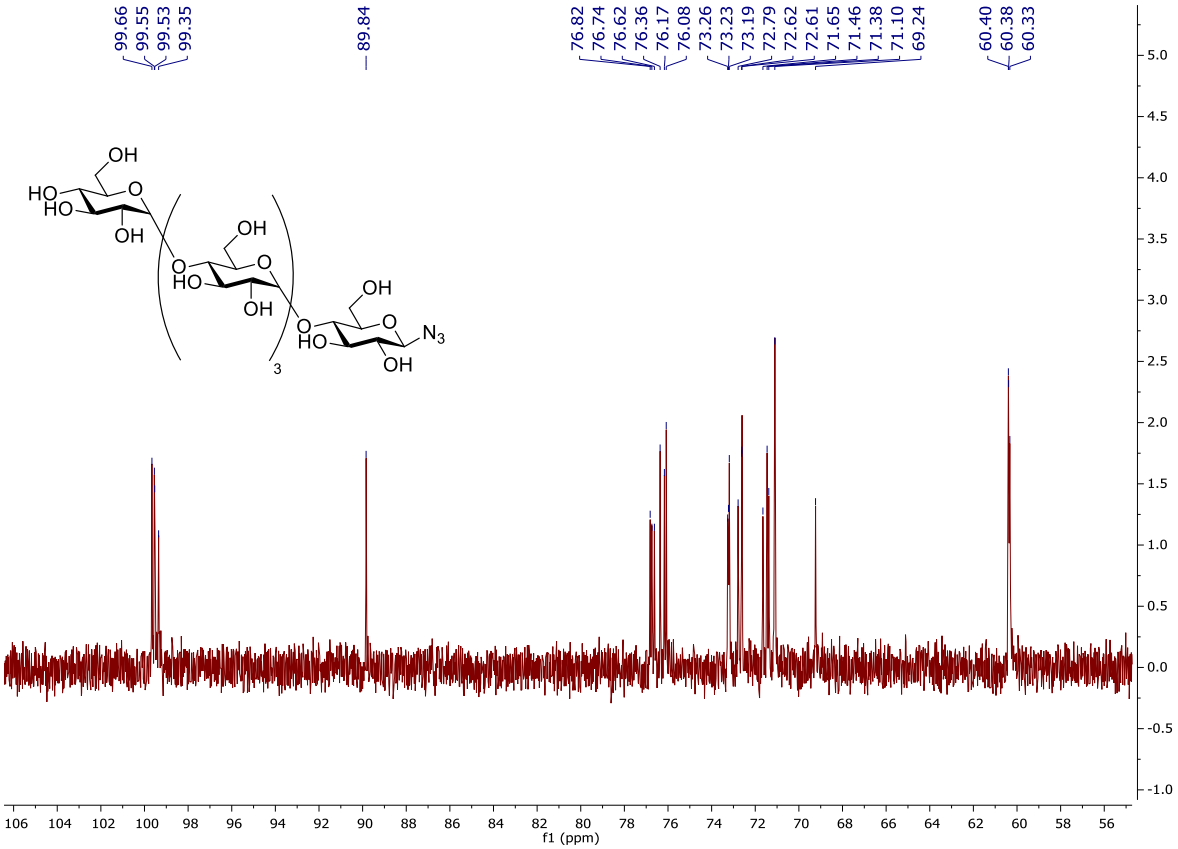


Figure 38, zoom of ^{13}C-NMR of β-D-maltopentaosyl azide

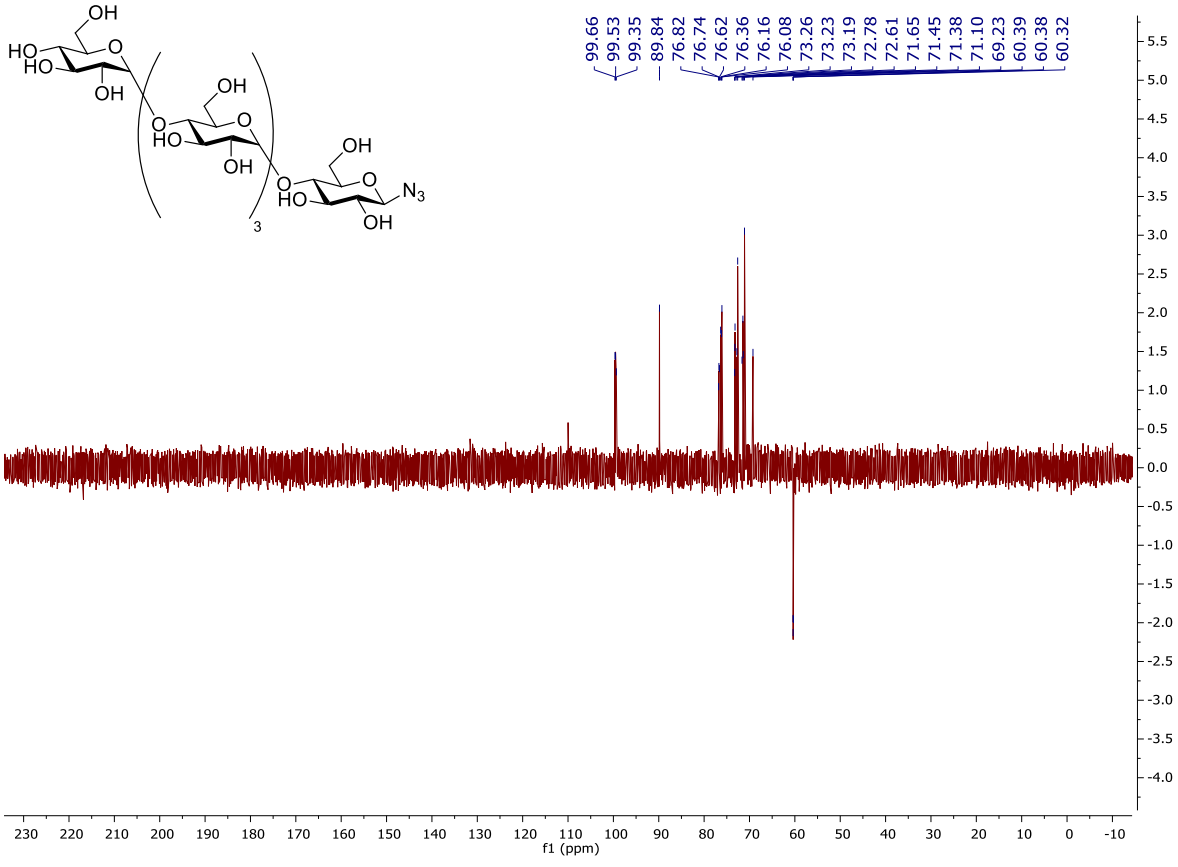


Figure 39, APT of β-D-maltopentaosyl azide

β-D-maltohexaosyl azide (7)

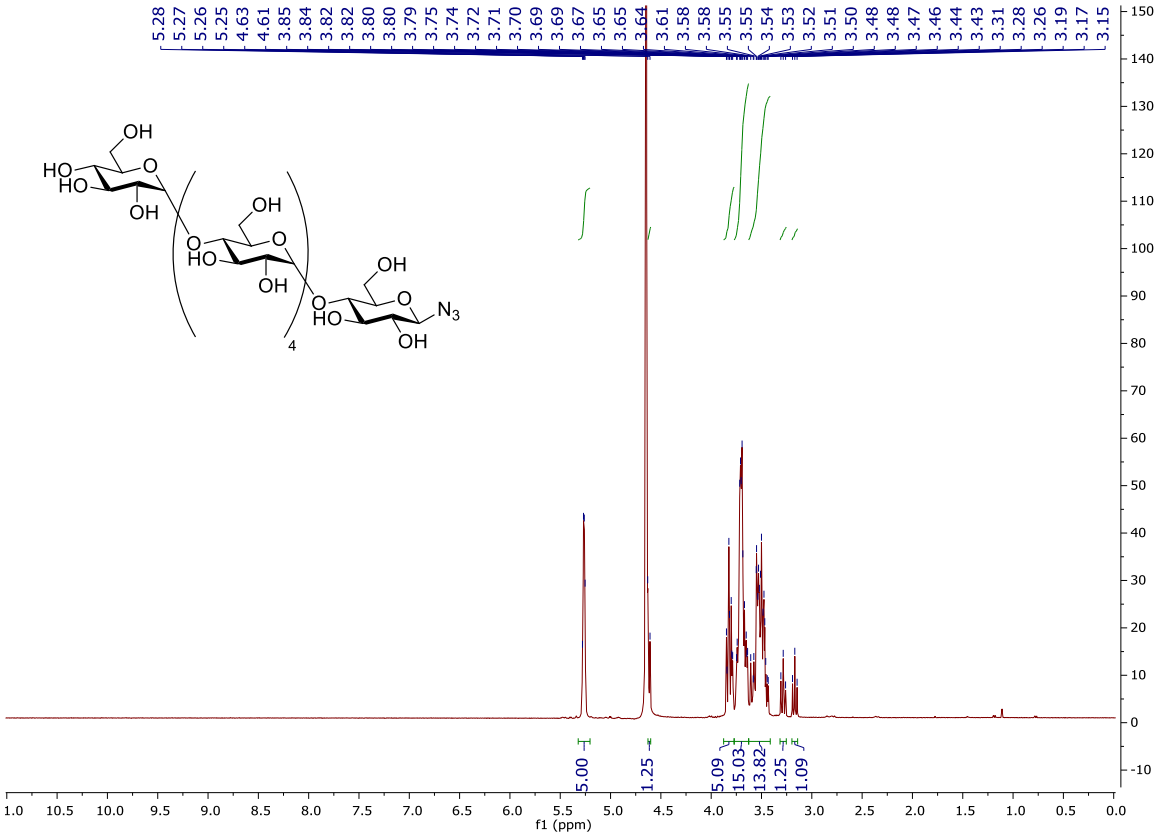


Figure 40, ^{1}H-NMR of β-D-maltohexaosyl azide

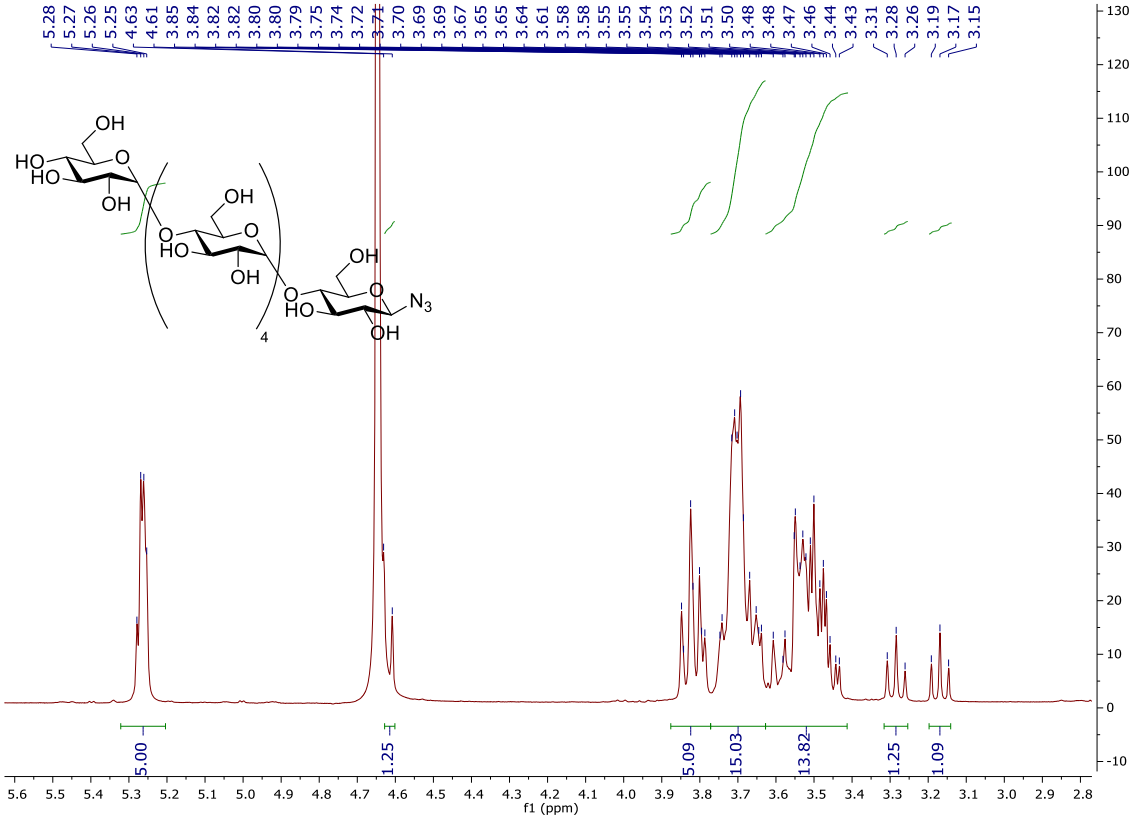


Figure 41, zoom of ^{1}H-NMR of azido-β-D- maltohexaoside

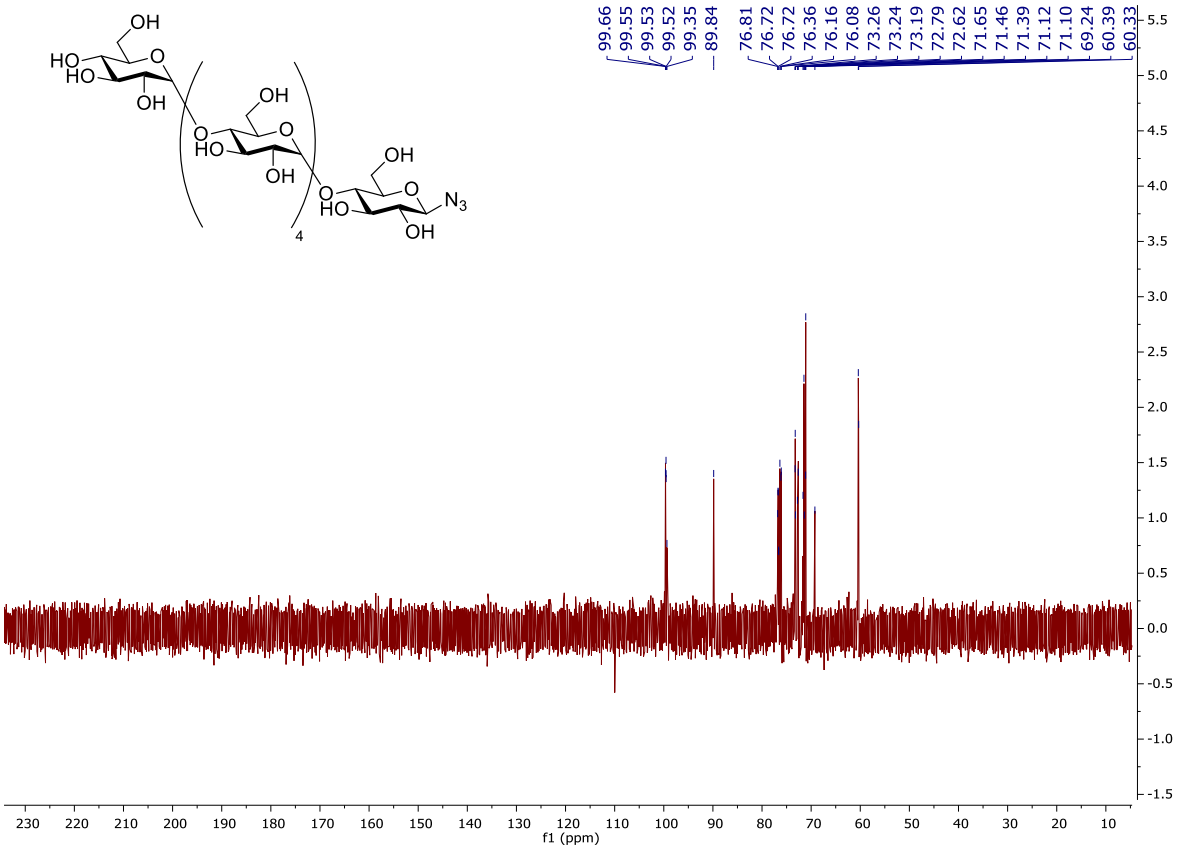


Figure 42, ^{13}C-NMR of azido-β-D- maltohexaoside

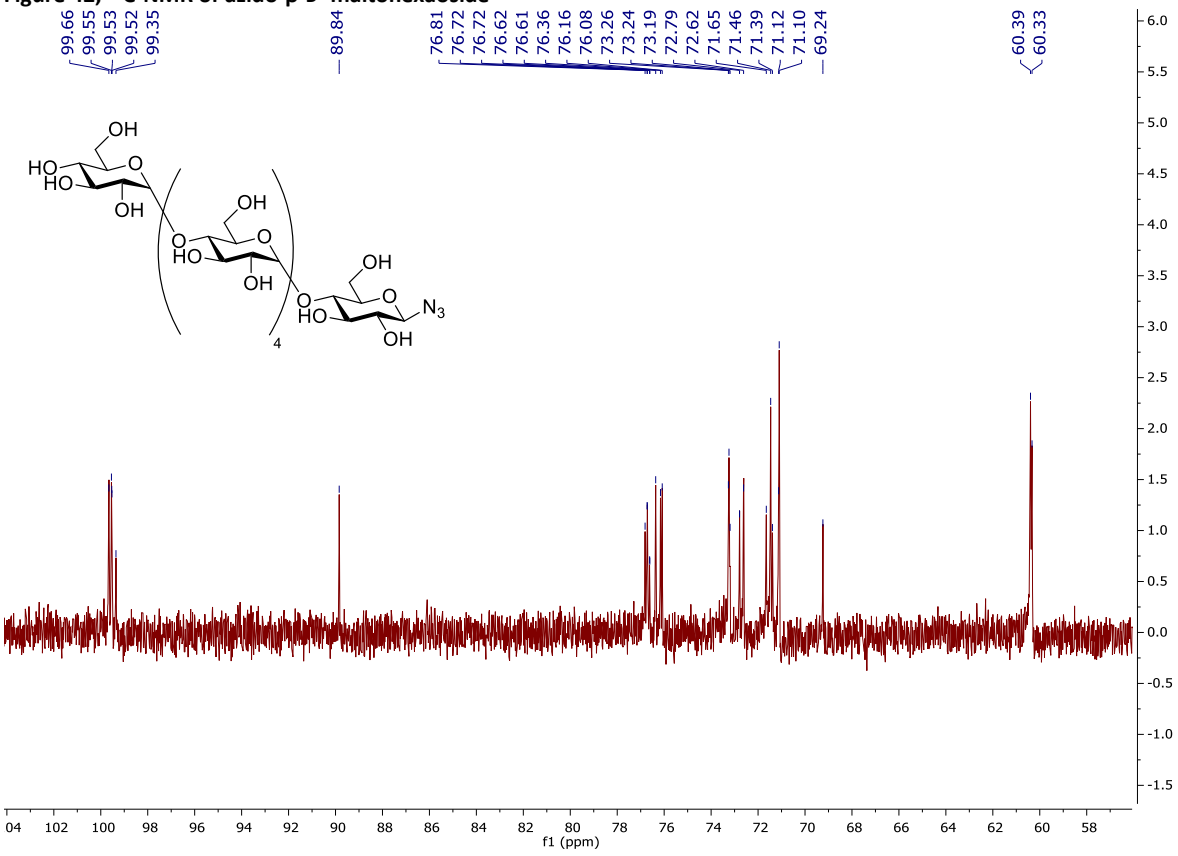


Figure 43, zoom of ^{13}C-NMR of azido-β-D- maltohexaoside

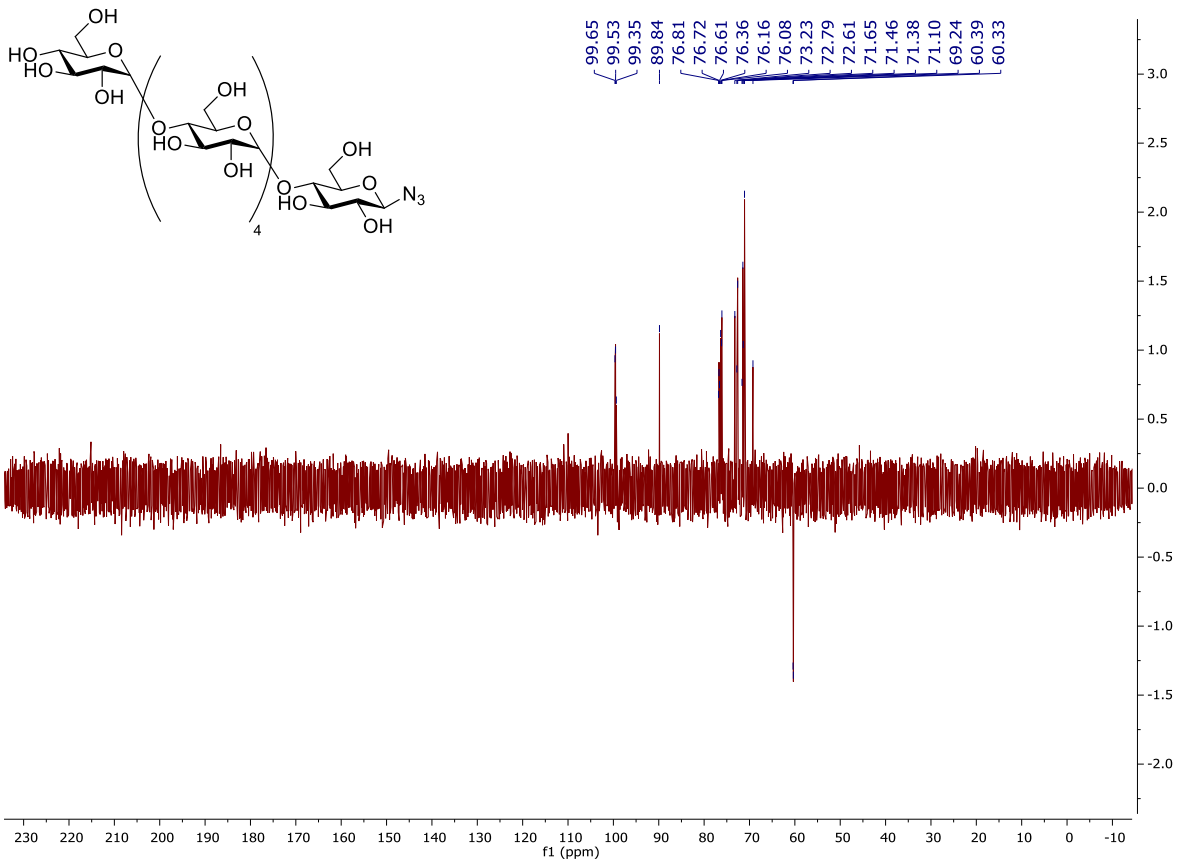


Figure 44, APT of β-D-maltohexaosyl azide

β-D-maltoheptaosyl azide (7)

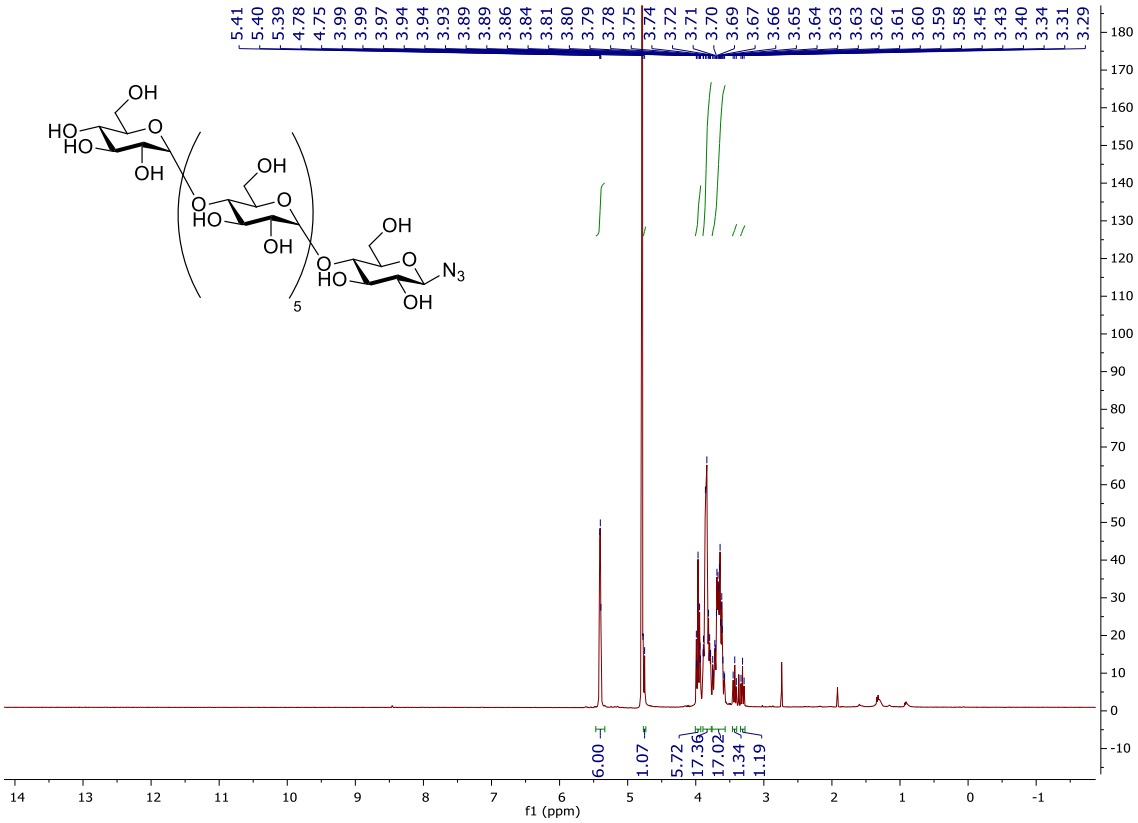


Figure 45, ^{1}H-NMR of β-D-maltoheptaosyl azide

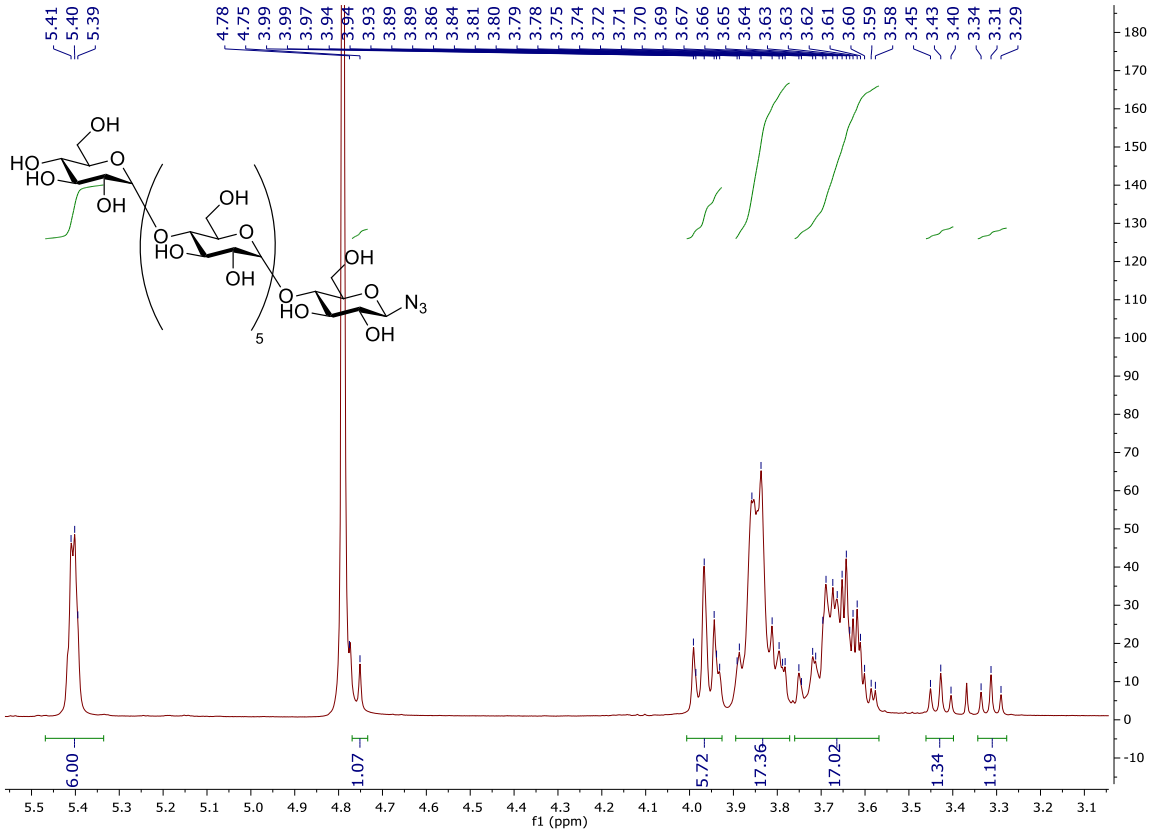


Figure 46, zoom of ^{1}H-NMR of azido-β-D- maltoheptaoside

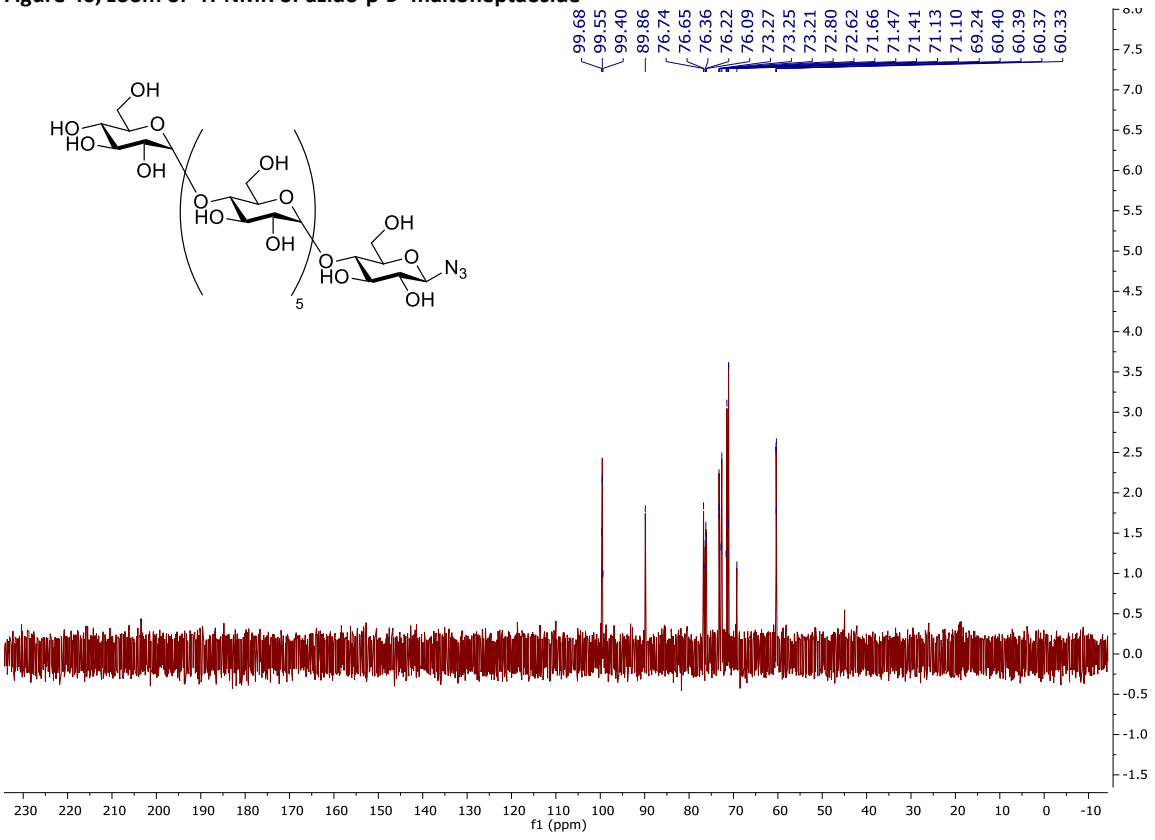


Figure 47, ^{13}C-NMR of azido-β-D- maltoheptaoside

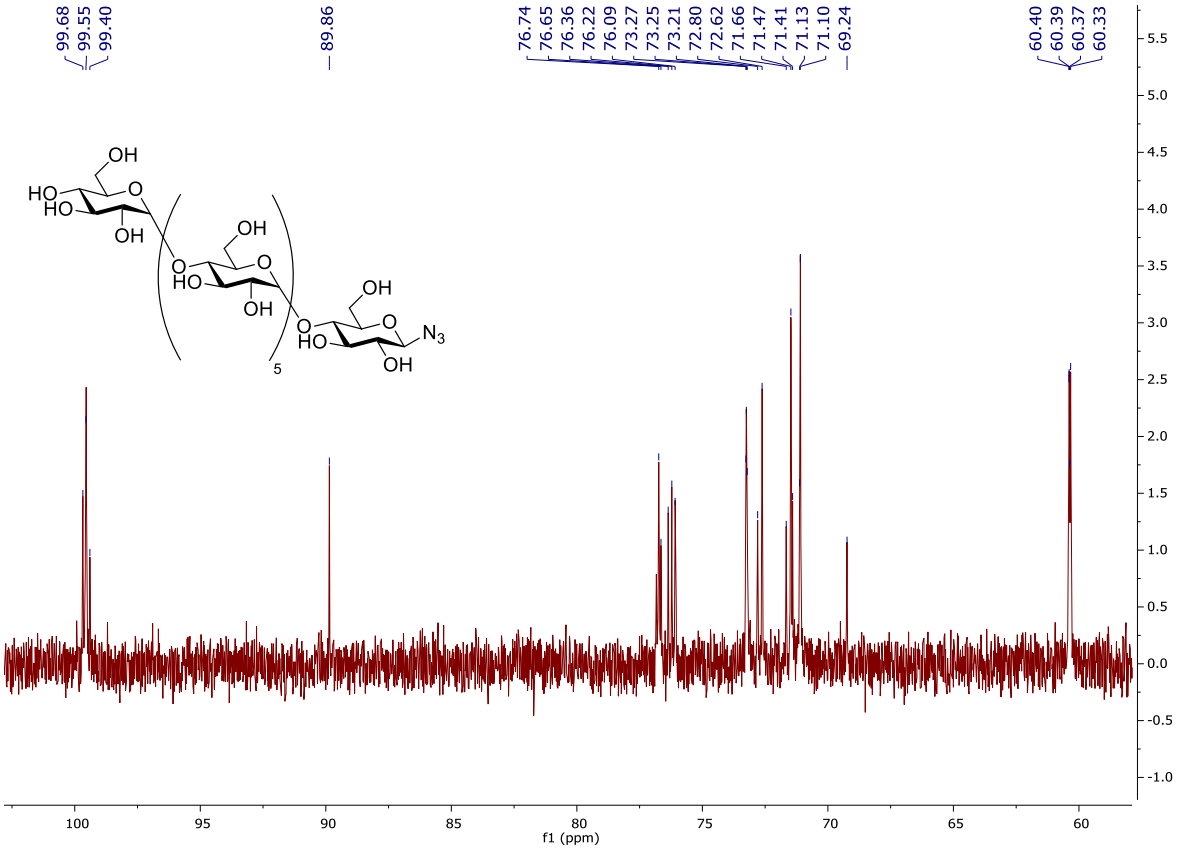


Figure 48, zoom of ^{13}C-NMR of β-D-maltoheptaosyl azide

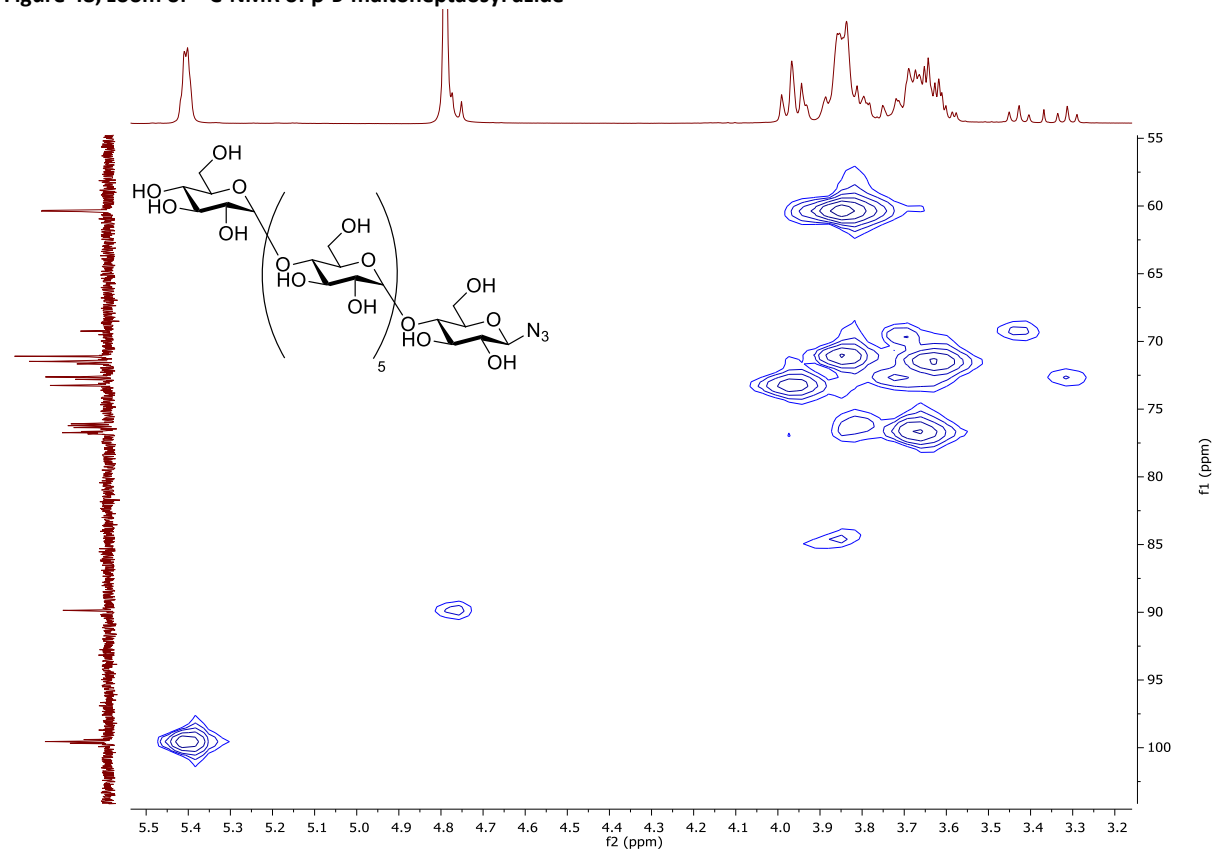


Figure 49, HMQC of β-D-maltoheptaosyl azide

β-D-3-ketoglucosyl azide (9)

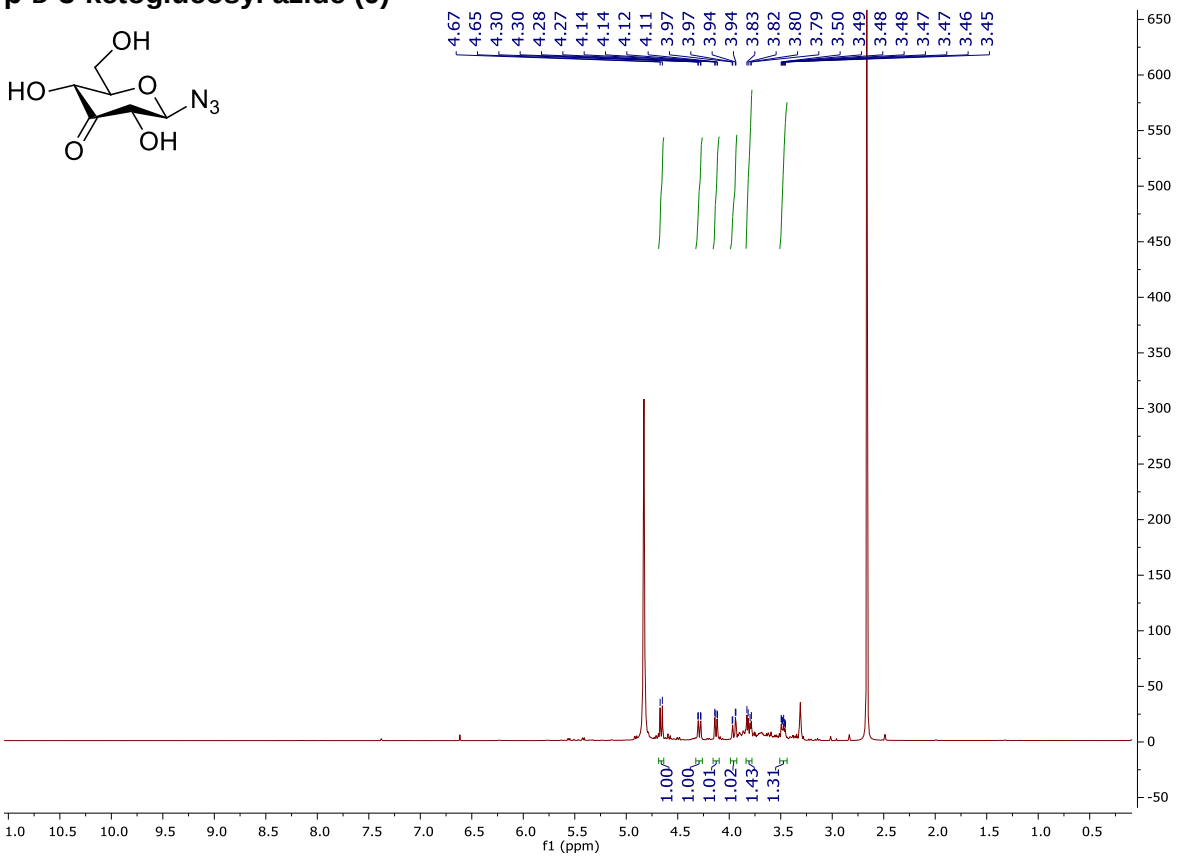


Figure 50, crude ^{1}H-NMR of β-D-3-ketoglucosyl azide

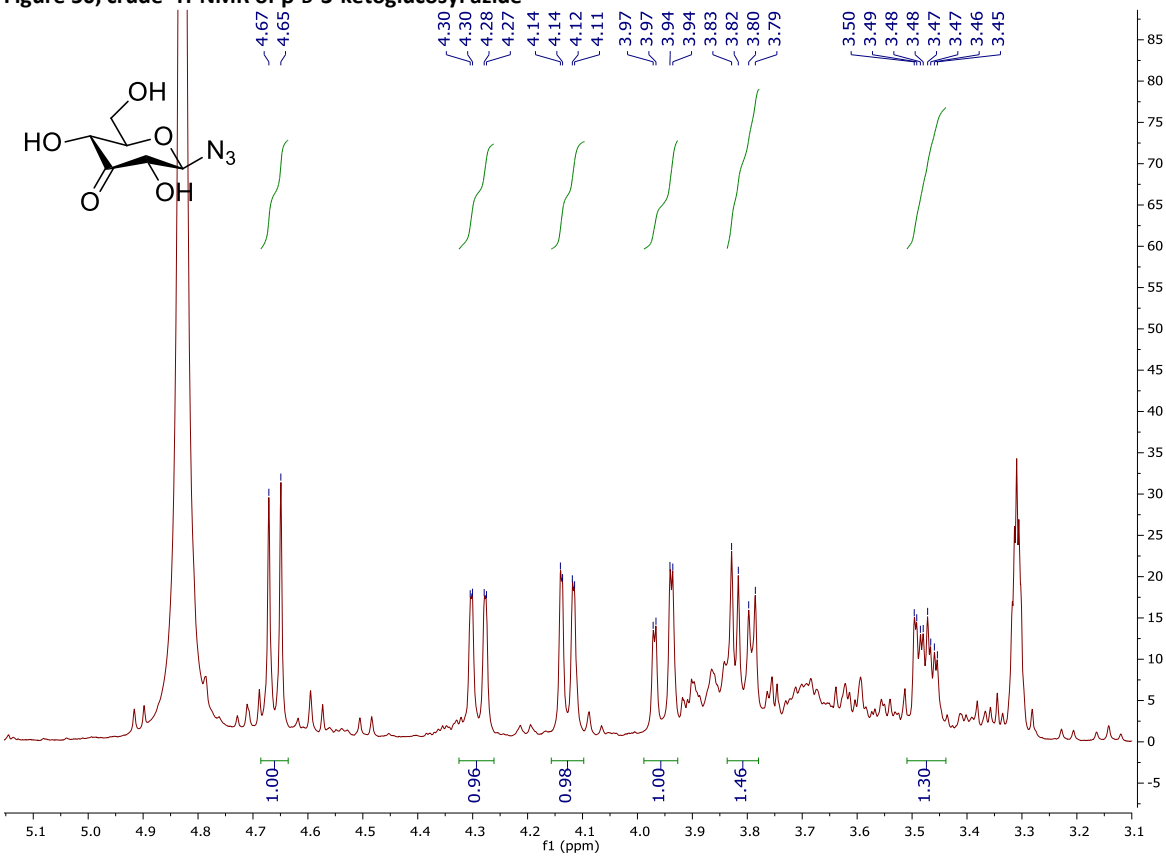


Figure 51, zoom of crude ^{1}H-NMR of β-D-3-ketoglucosyl azide

β-D-3-ketocellobiosyl azide (10)

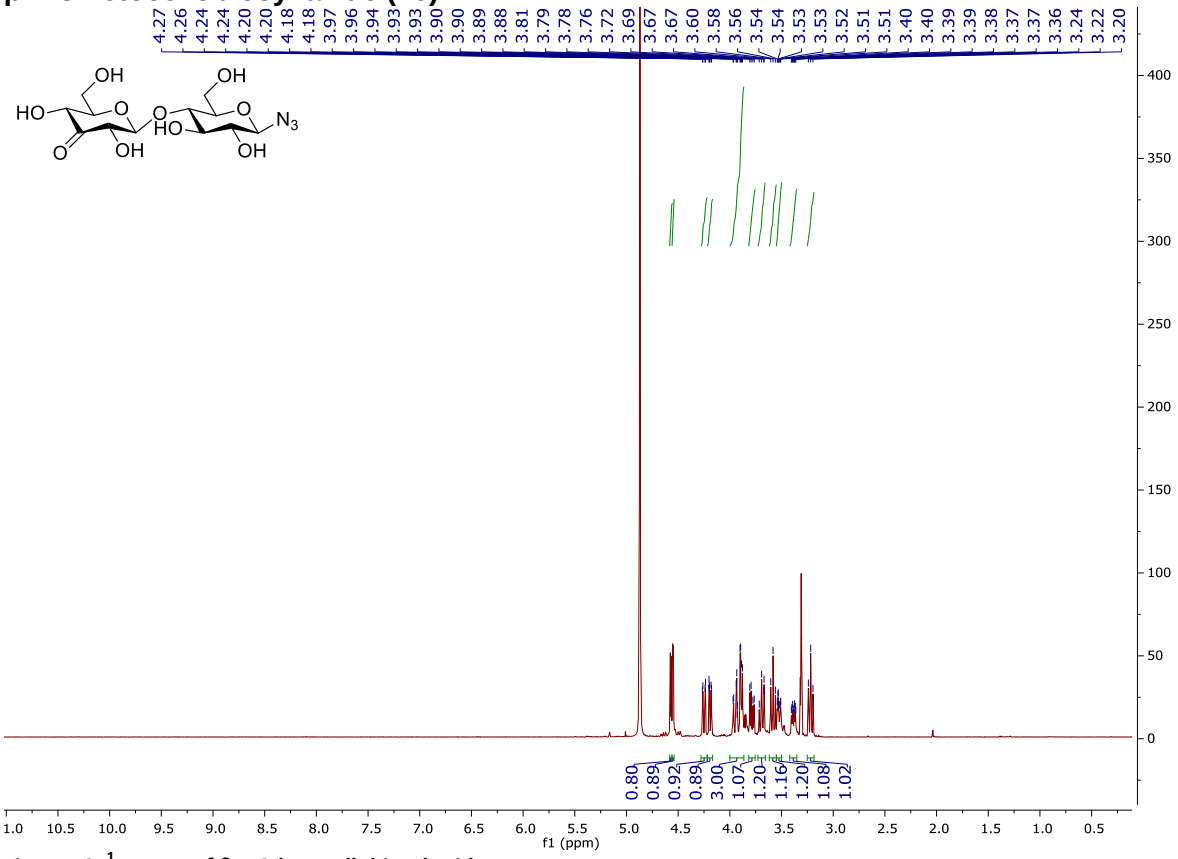


Figure 52, ^{1}H-NMR of β-D-3-ketocellobiosyl azide

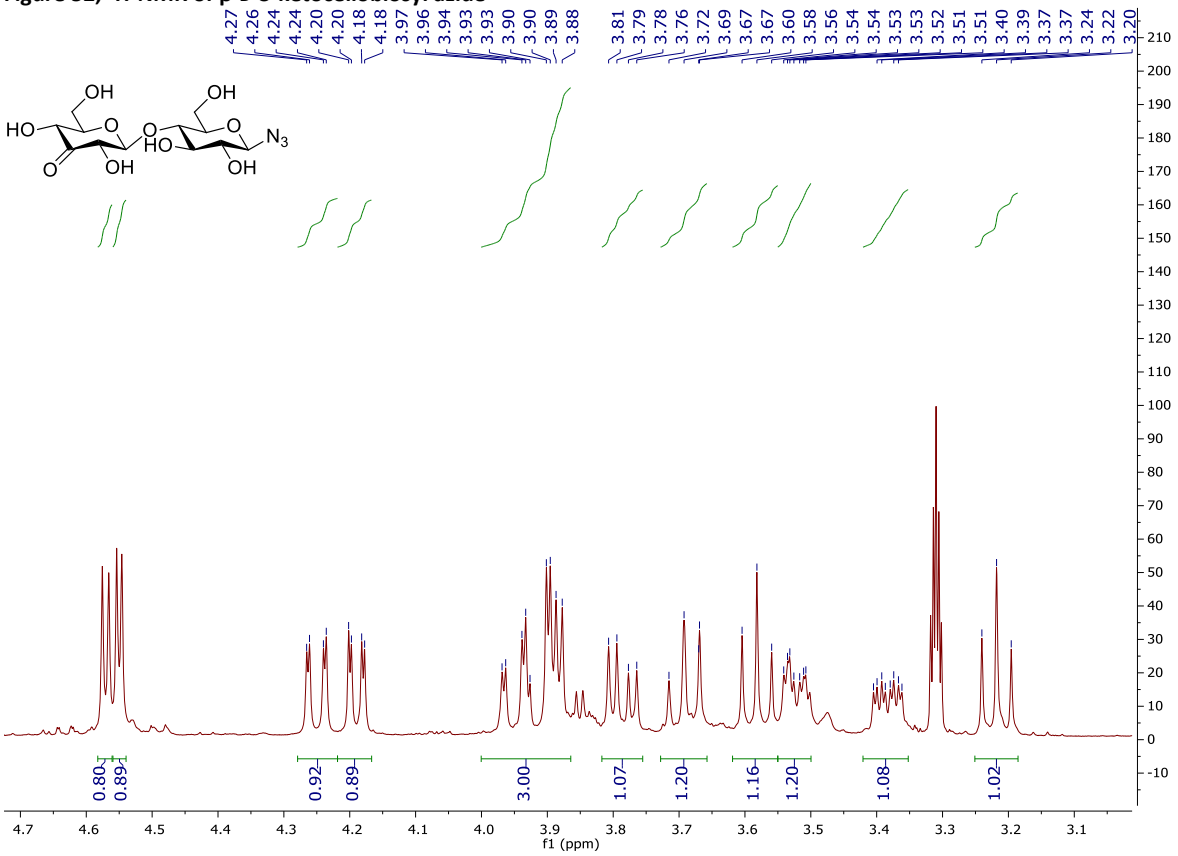


Figure 53, zoom of ^{1}H-NMR of β-D-3-ketocellobiosyl azide

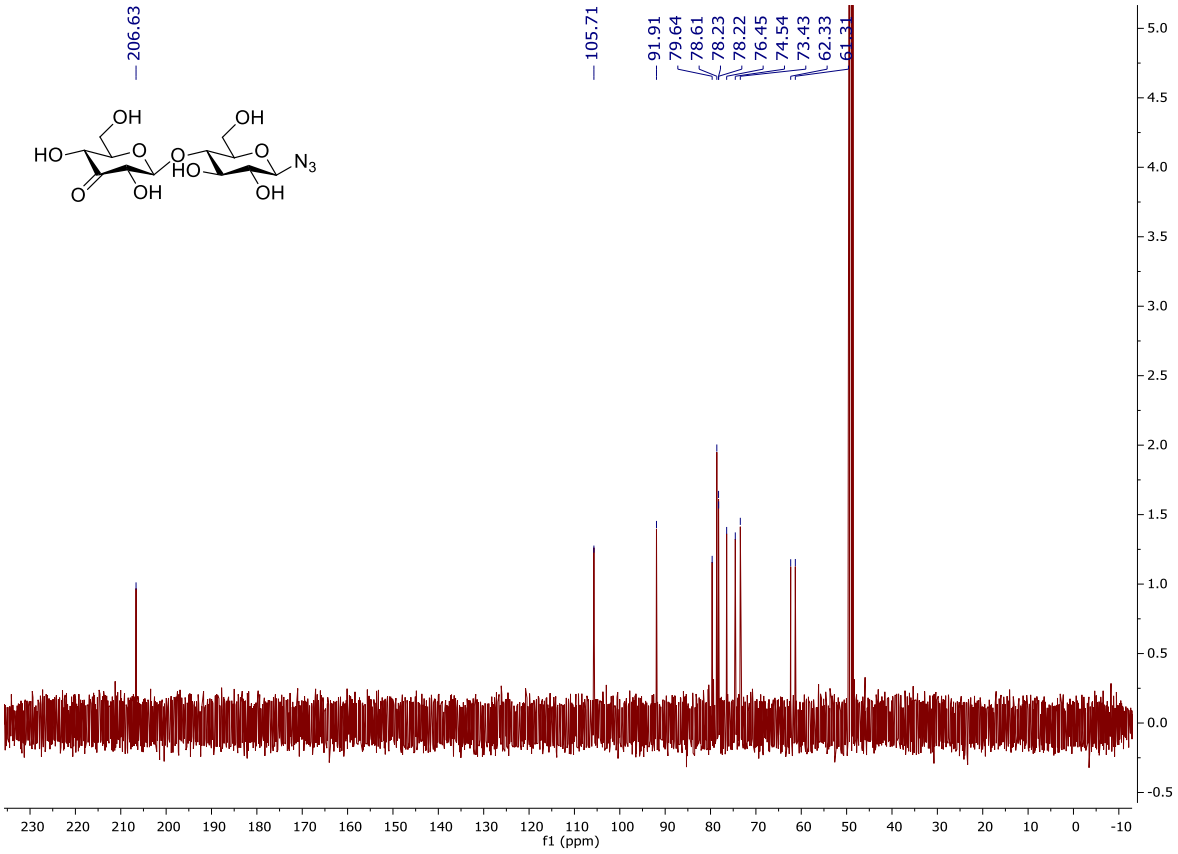


Figure 54, ^{13}C-NMR of β-D-3-ketocellobiosyl azide

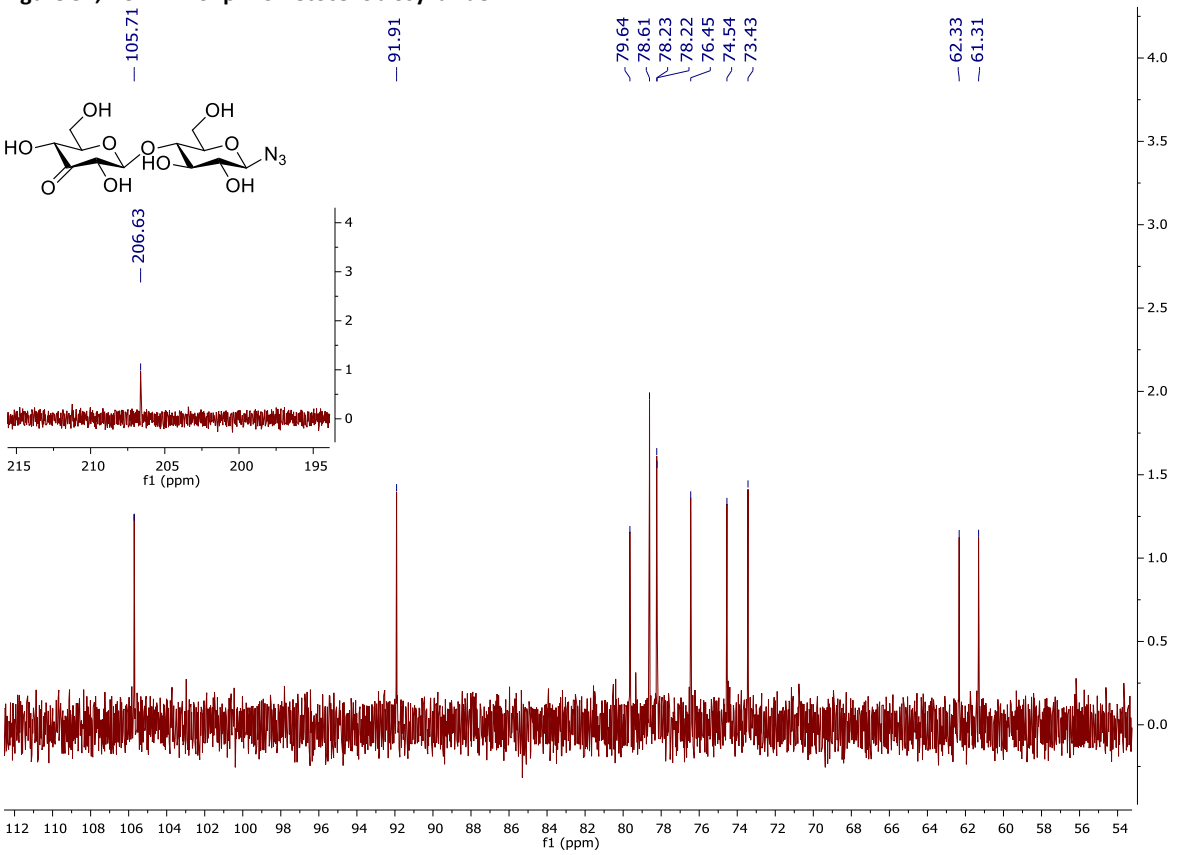


Figure 55, zoom of ^{13}C-NMR of β-D-3-ketocellobiosyl azide

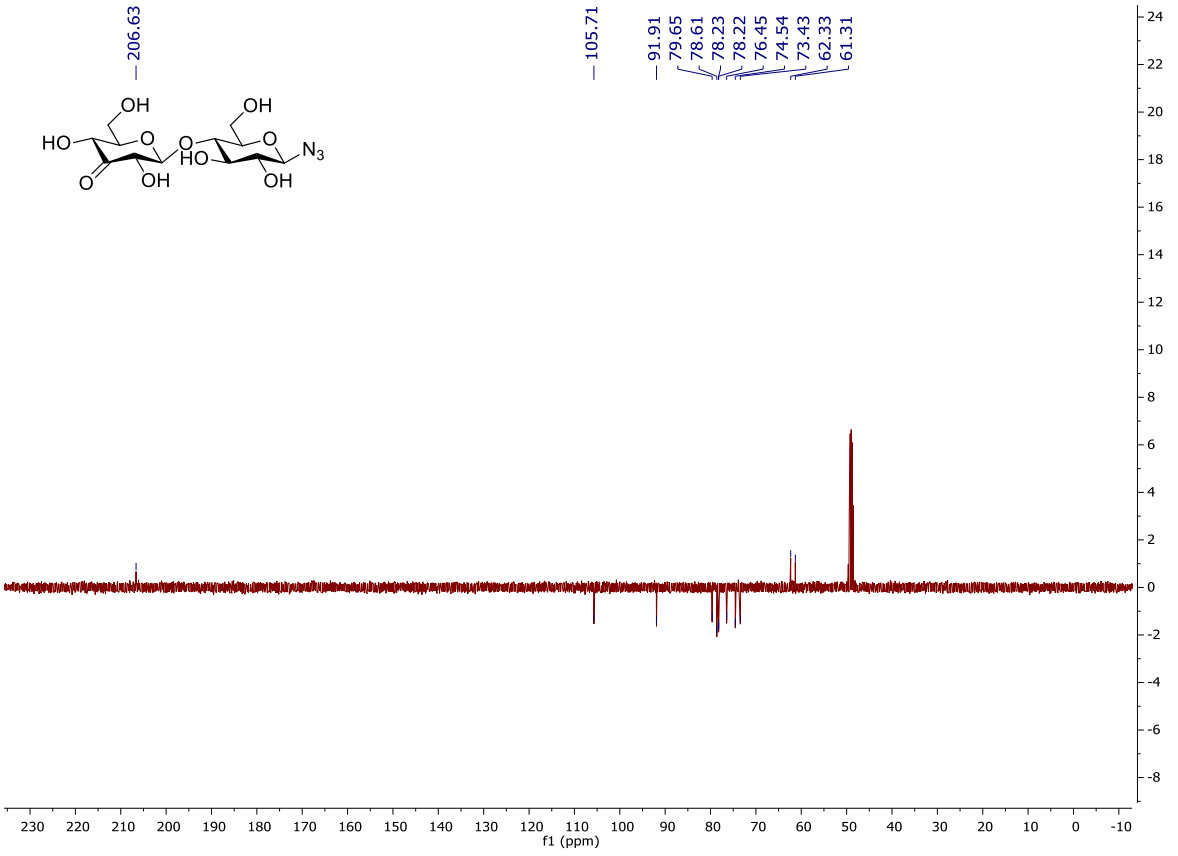


Figure 56, APT of β-D-3-ketocellobiosyl azide

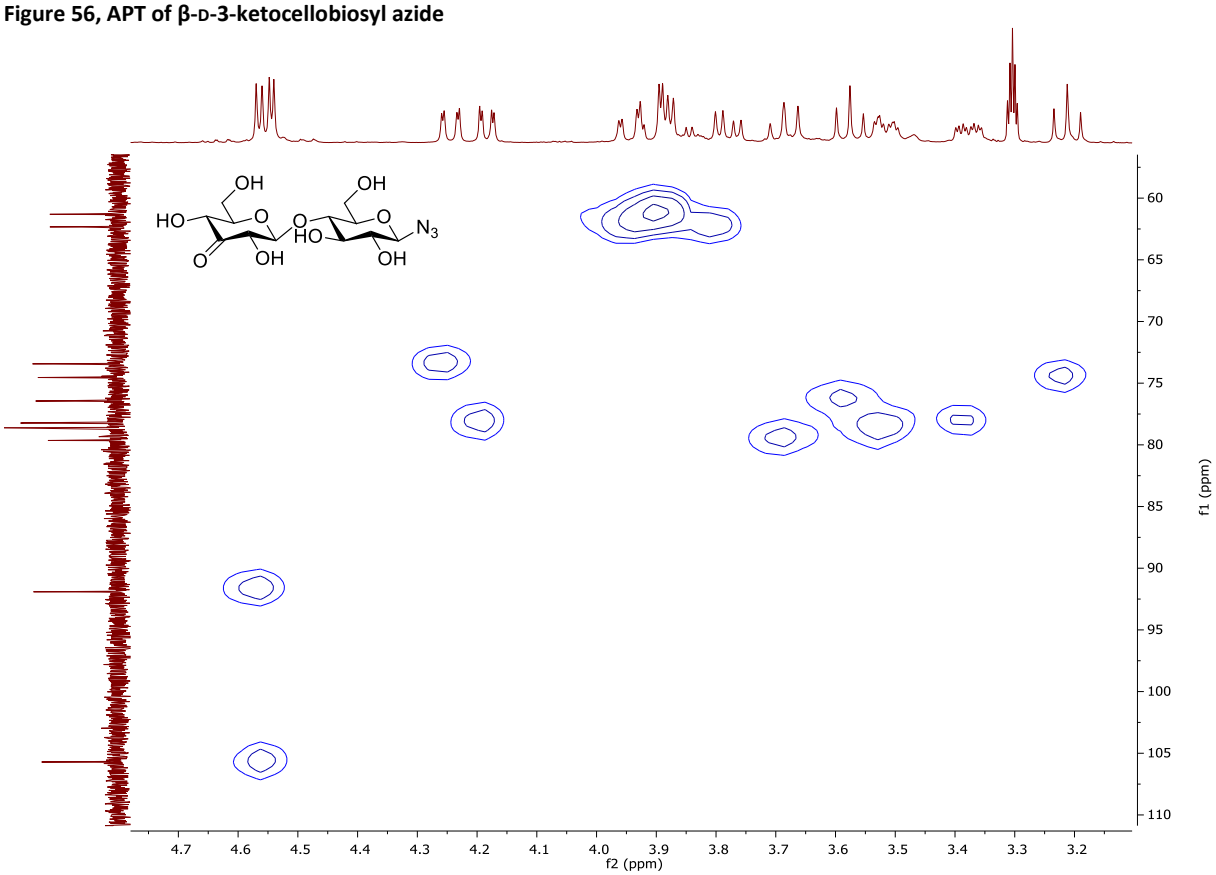


Figure 57, HMQC of β-D-3-ketocellobiosyl azide

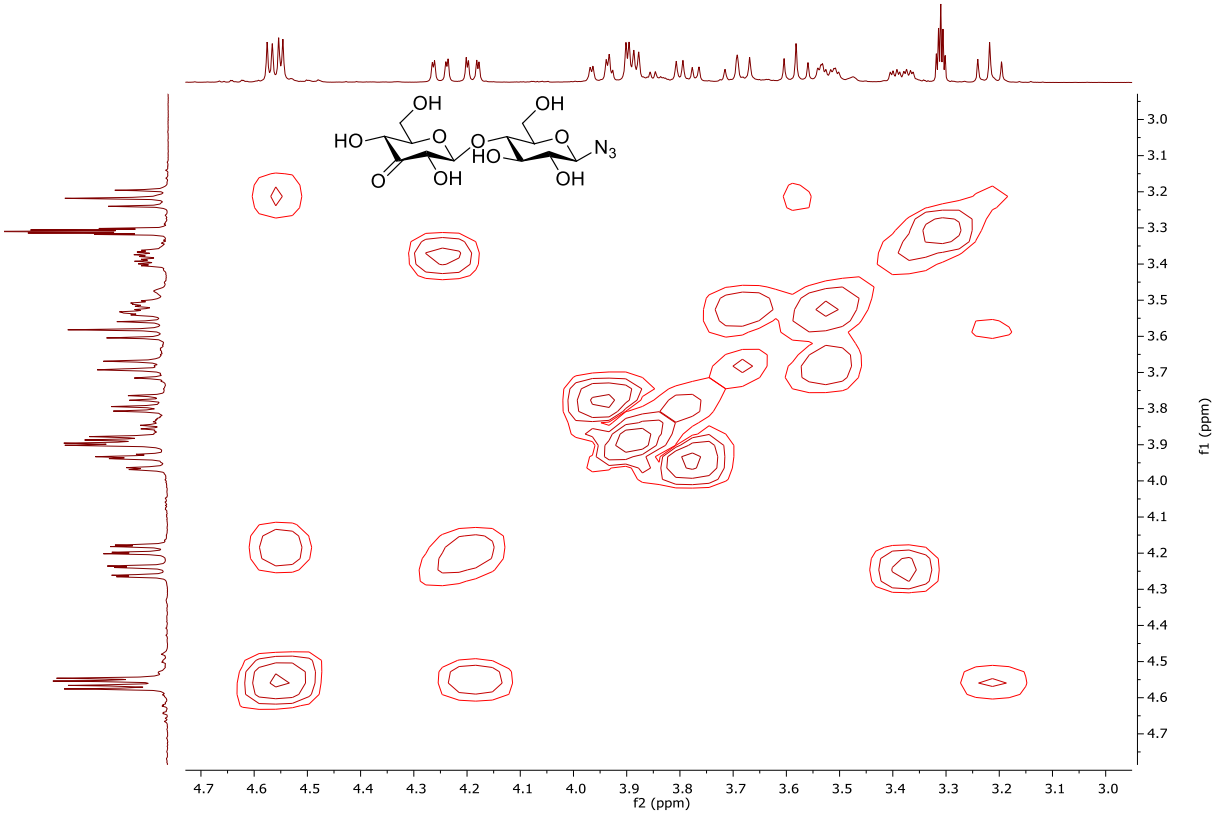


Figure 58, COSY of β-D-3-ketocellobiosyl azide

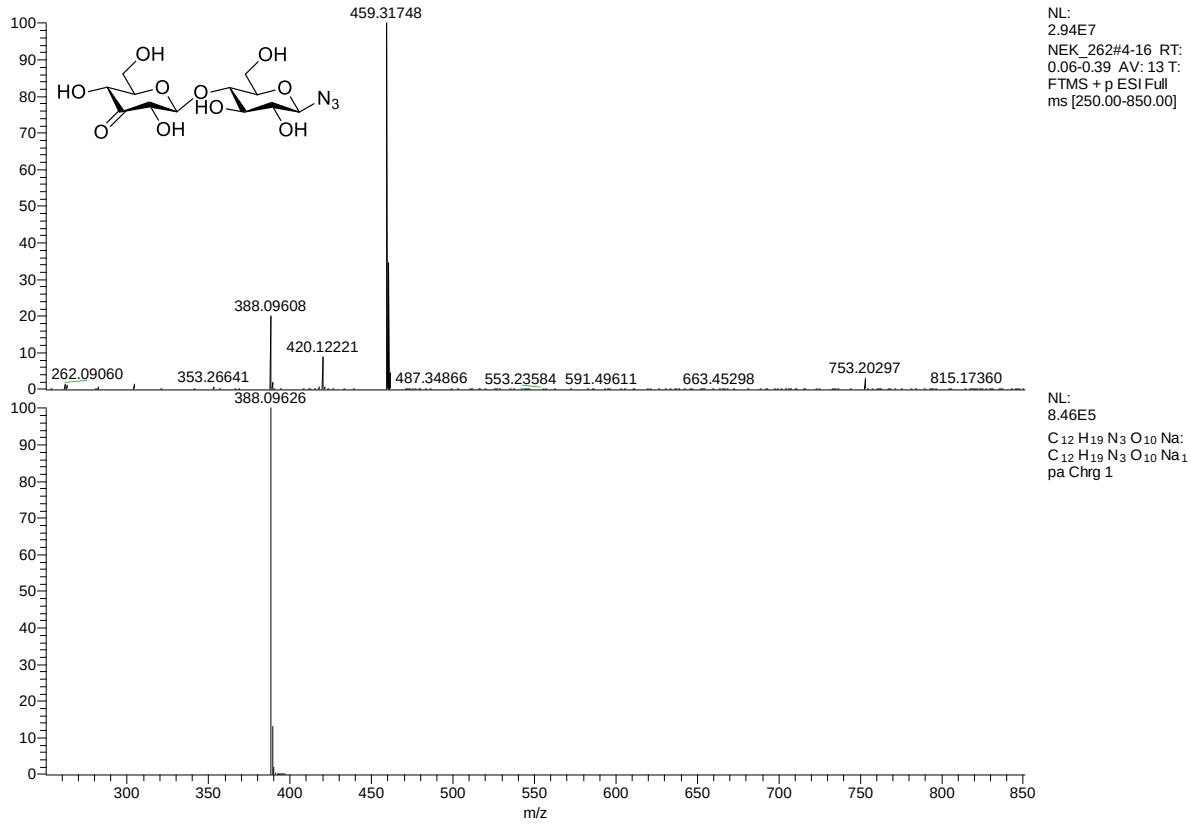


Figure 59, HRMS of β-D-3-ketocellobiosyl azide

β-D-3-ketomaltosyl azide (11)

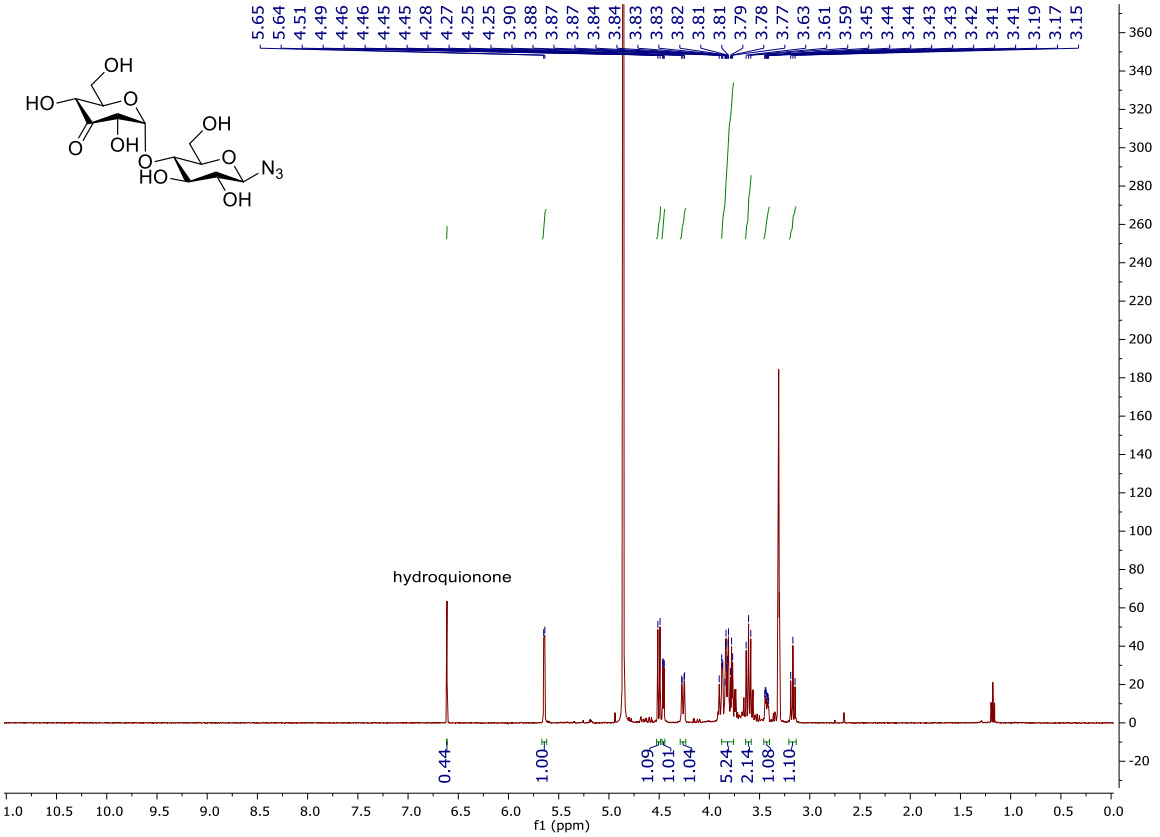


Figure 60, ^{1}H-NMR of β-D-3-ketomaltosyl azide

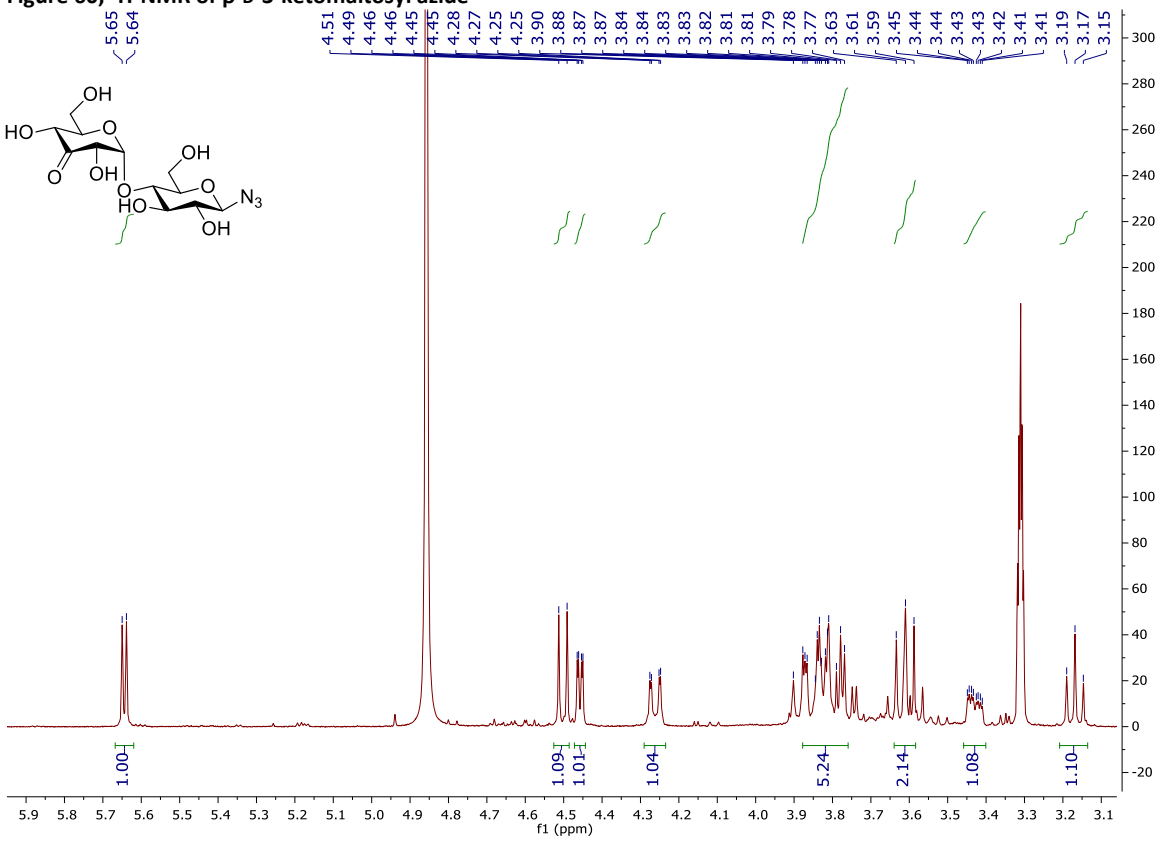


Figure 61, zoom of ^{1}H-NMR of β-D-3-ketomaltosyl azide

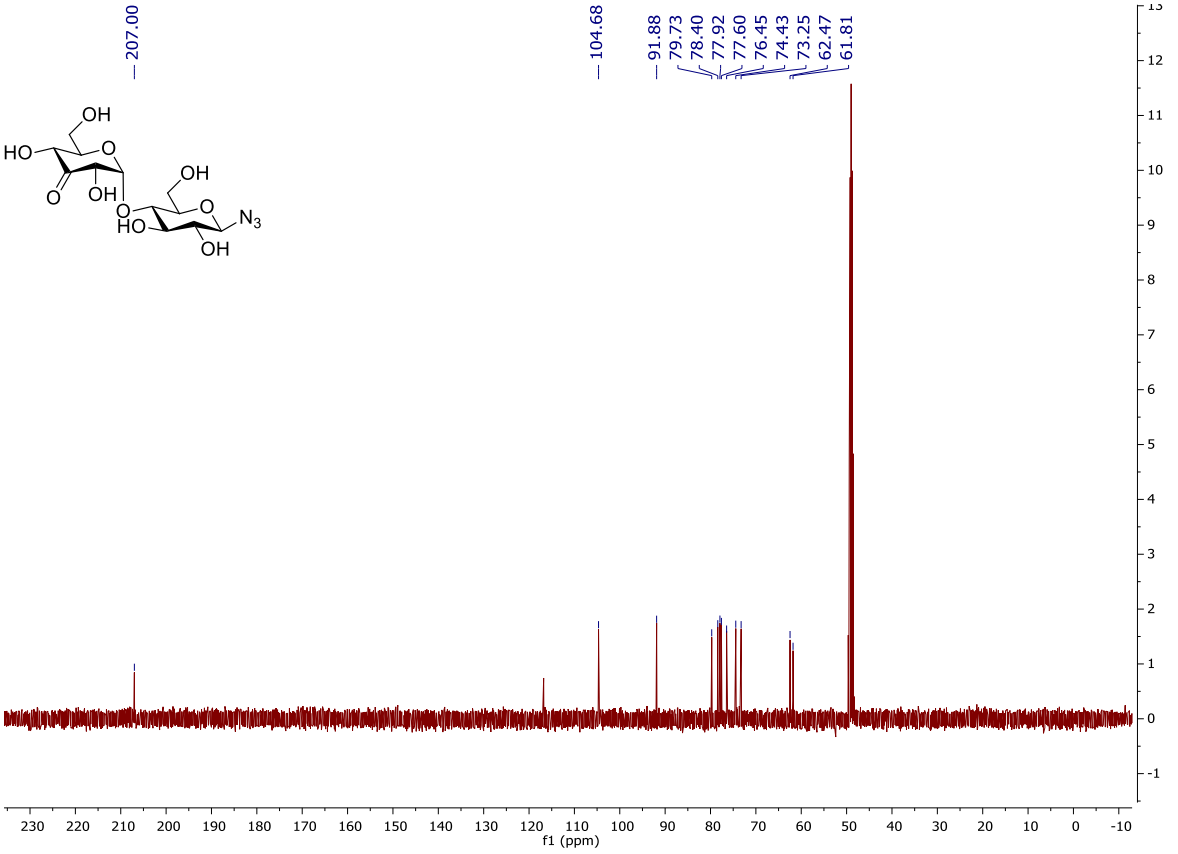


Figure 62, ^{13}C-NMR of β-D-3-ketomaltosyl azide

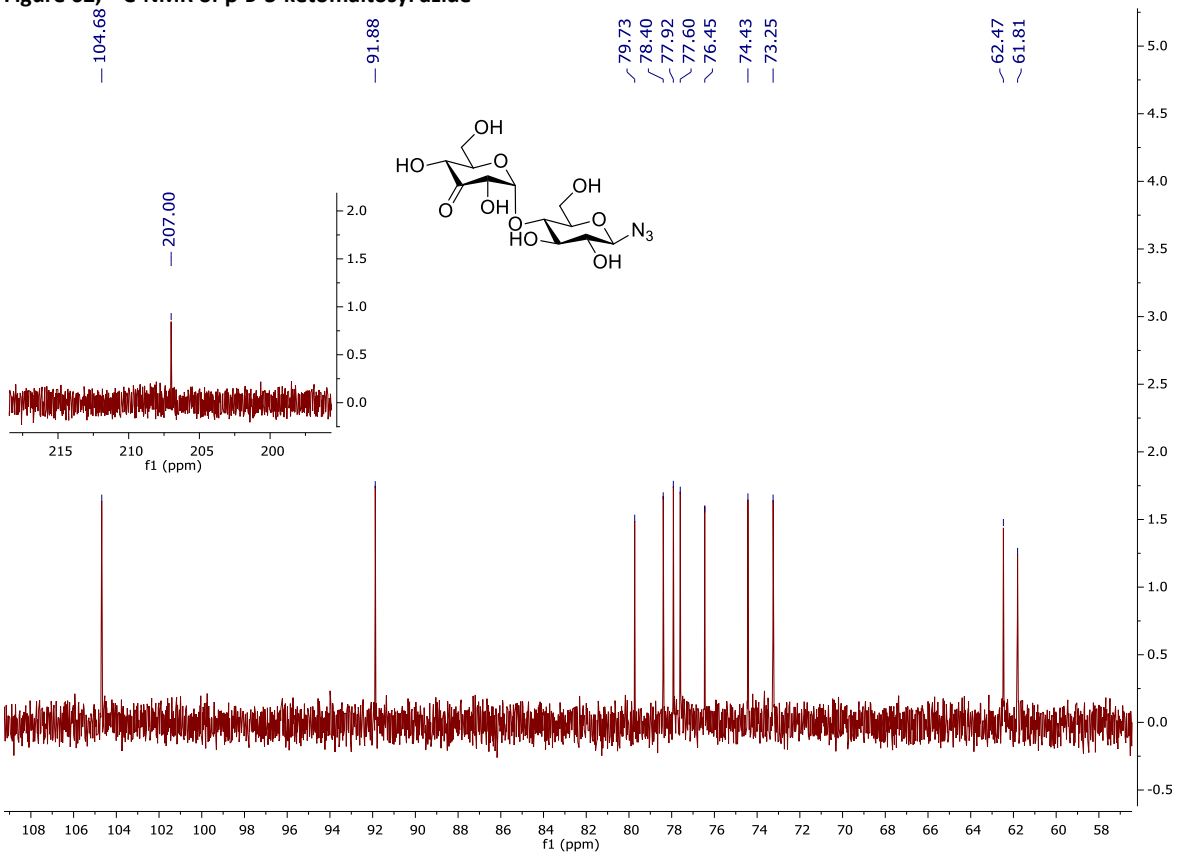


Figure 63, zoom of β-D-3-ketomaltosyl azide

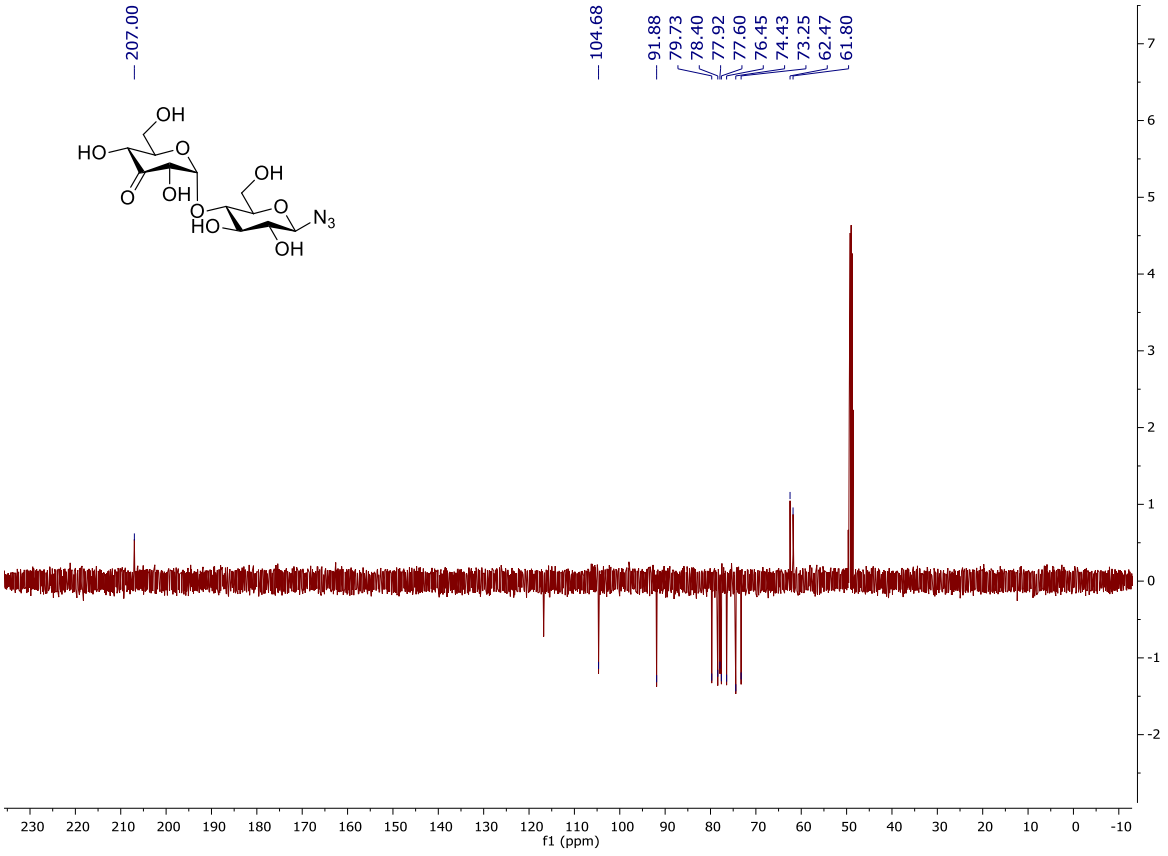


Figure 64, APT of β-D-3-ketomaltosyl azide

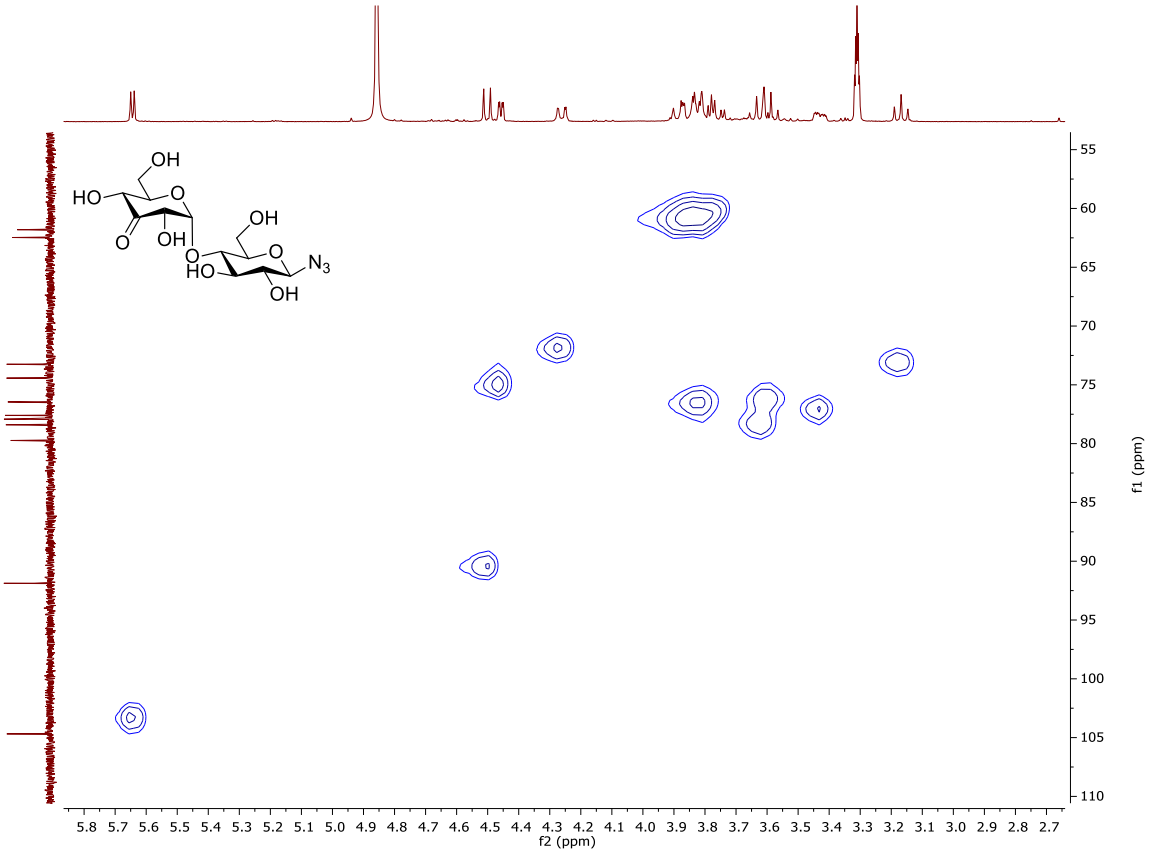


Figure 65, HMQC of β-D-3-ketomaltosyl azide

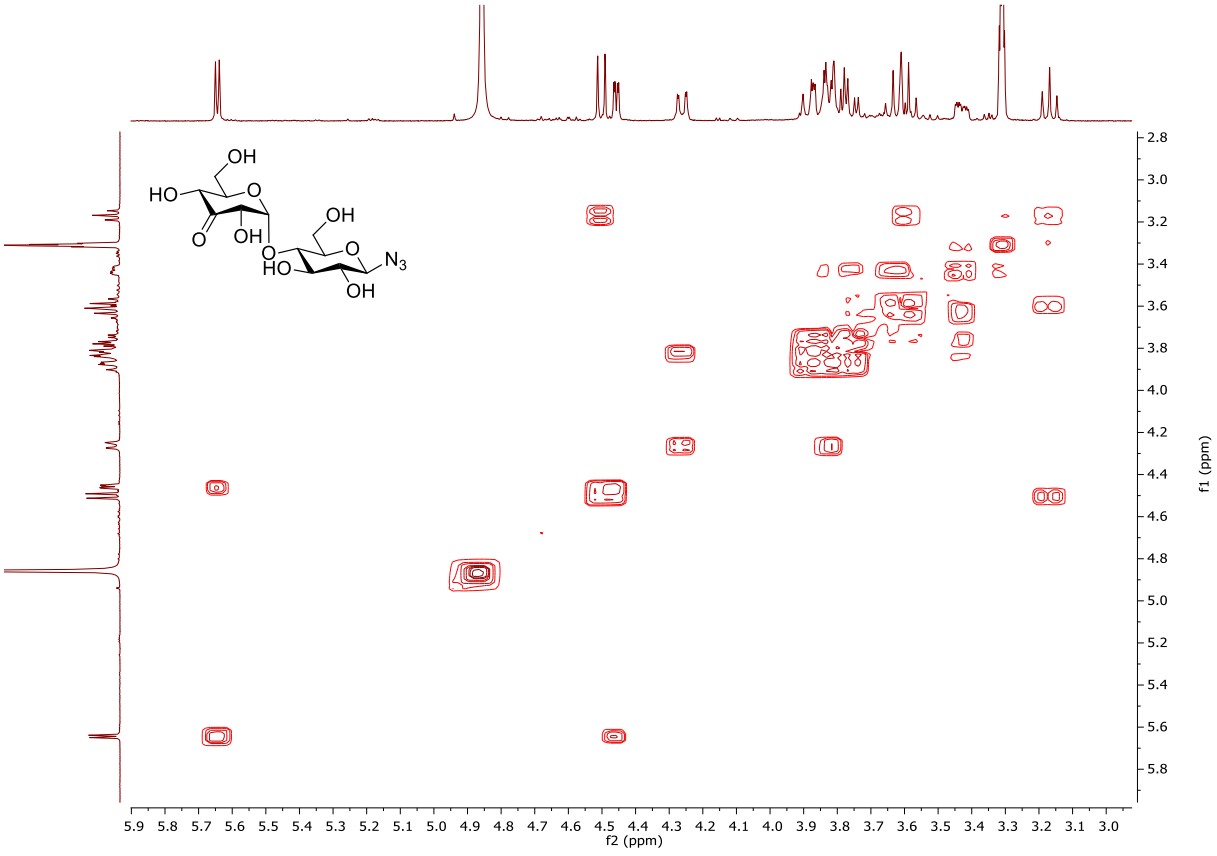


Figure 66, COSY of β-D-3-ketomaltosyl azide

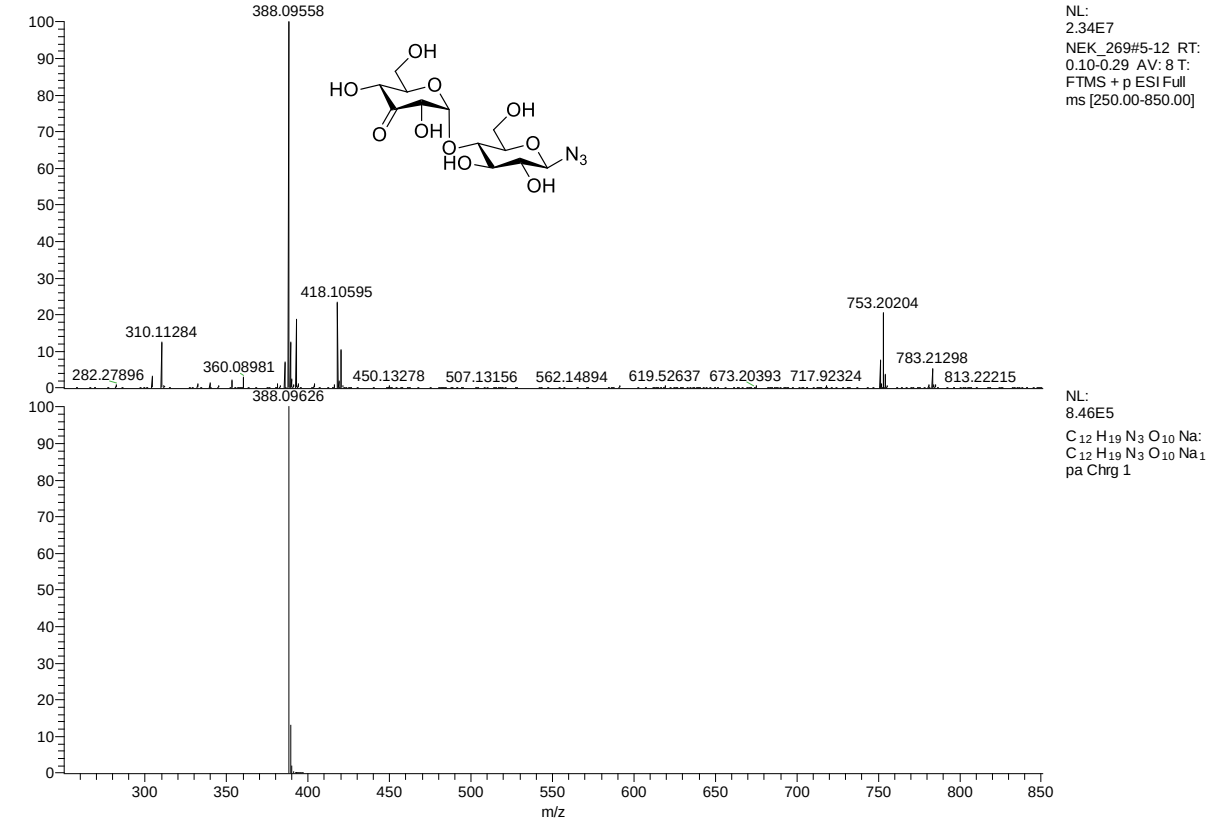


Figure 67, HRMS of β-D-3-ketomaltosyl azide

β-D-3-ketomaltotrioside (12)

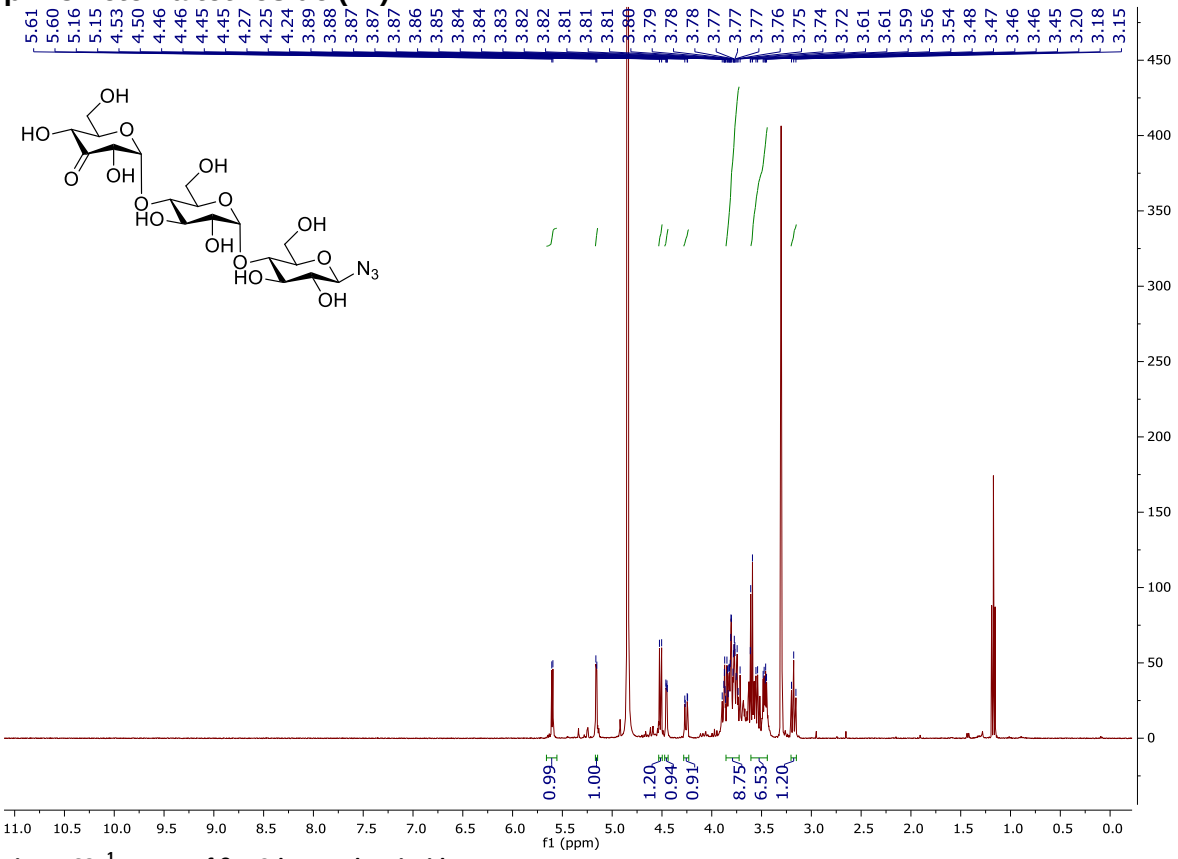


Figure 68, ^{1}H-NMR of β-D-3-ketomaltotrioside

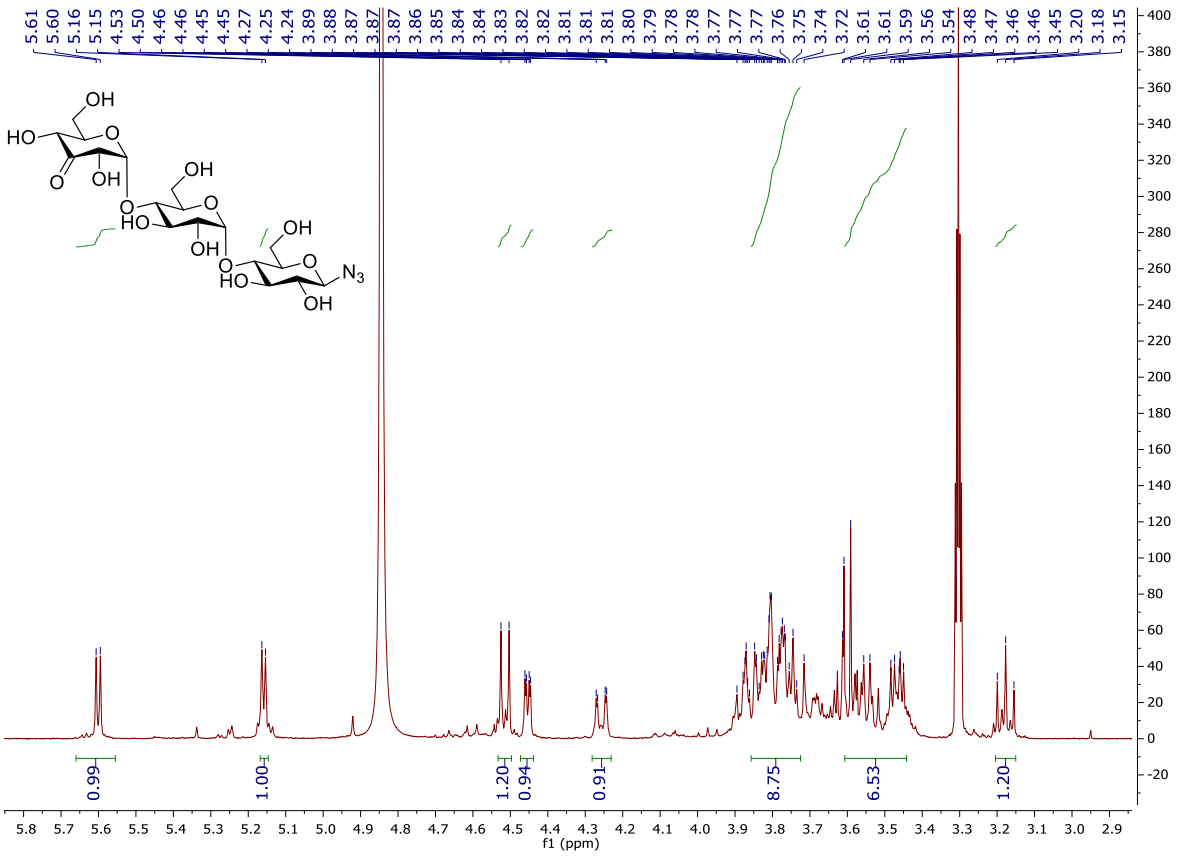


Figure 69, zoom of ^{1}H-NMR of β-D-3-ketomaltotrioside

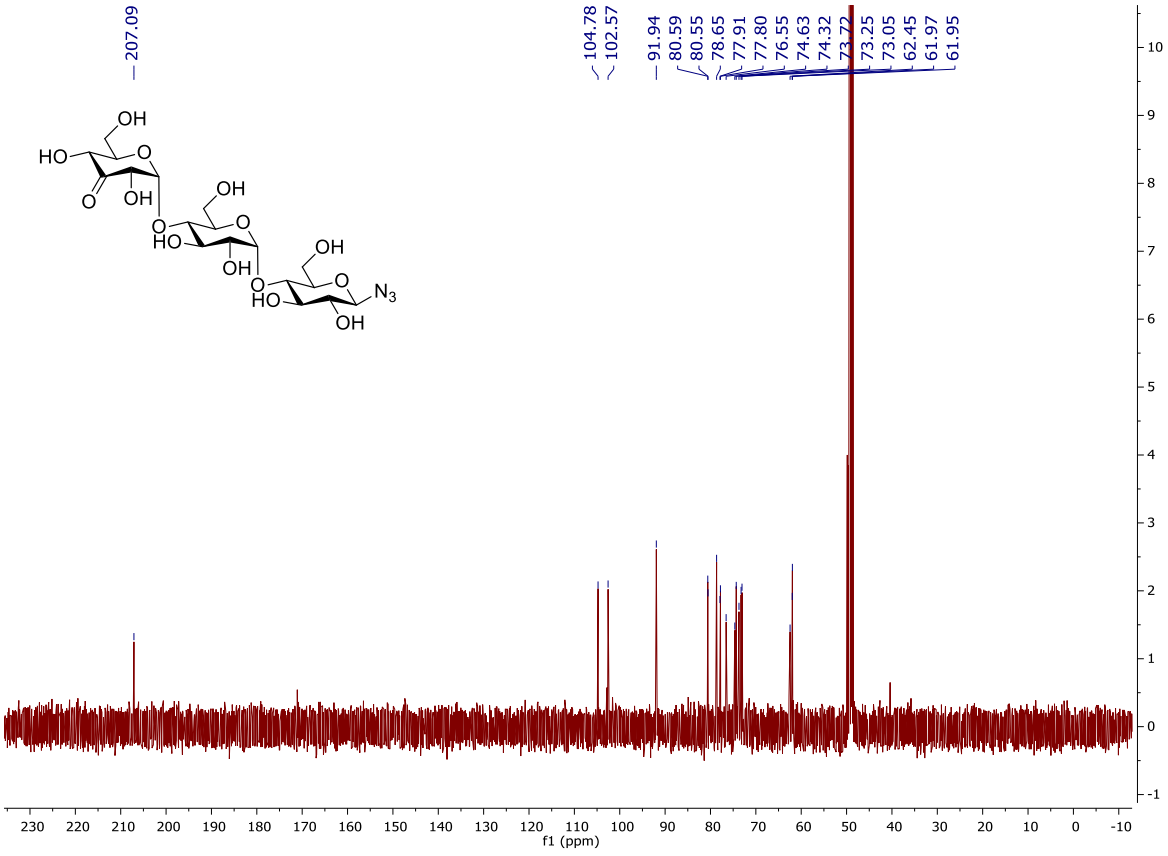


Figure 70, ^{13}C-NMR of β-D-3-ketomaltotrioside

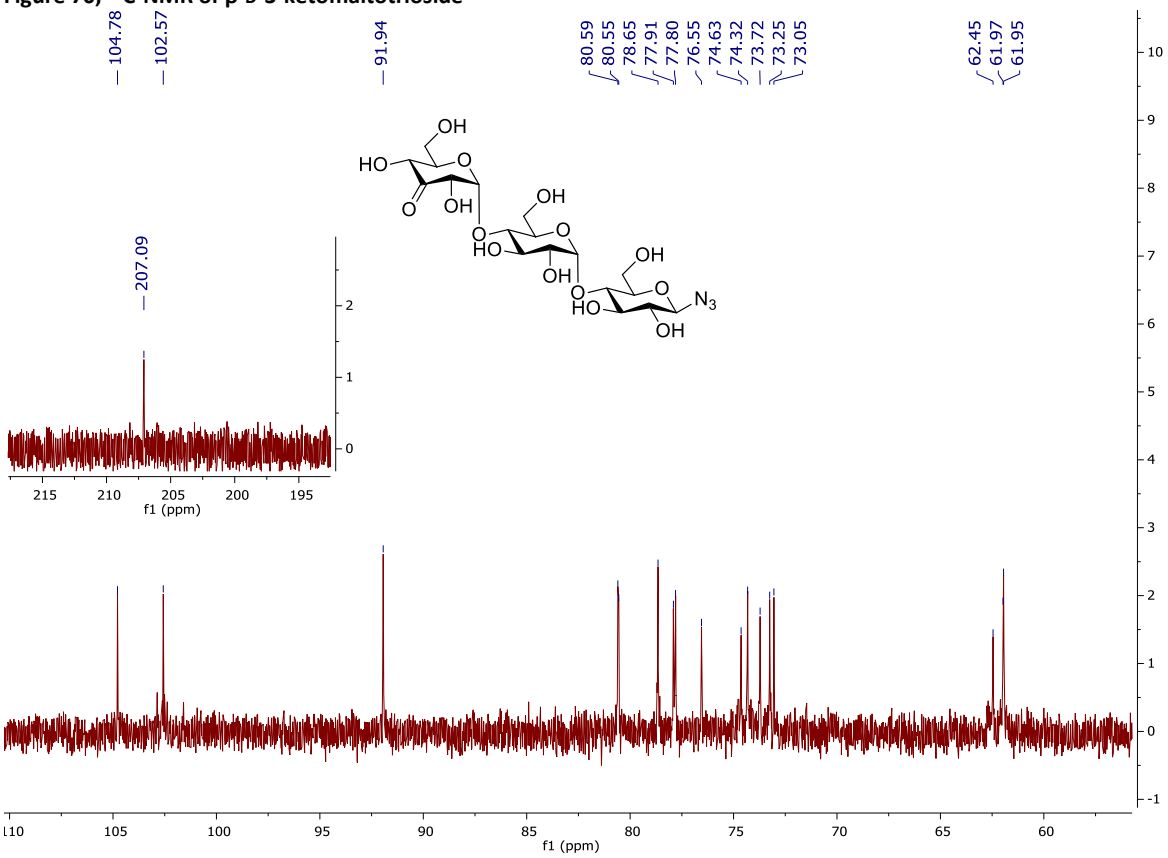


Figure 71, zoom of ^{13}C-NMR β-D-3-ketomaltotrioside

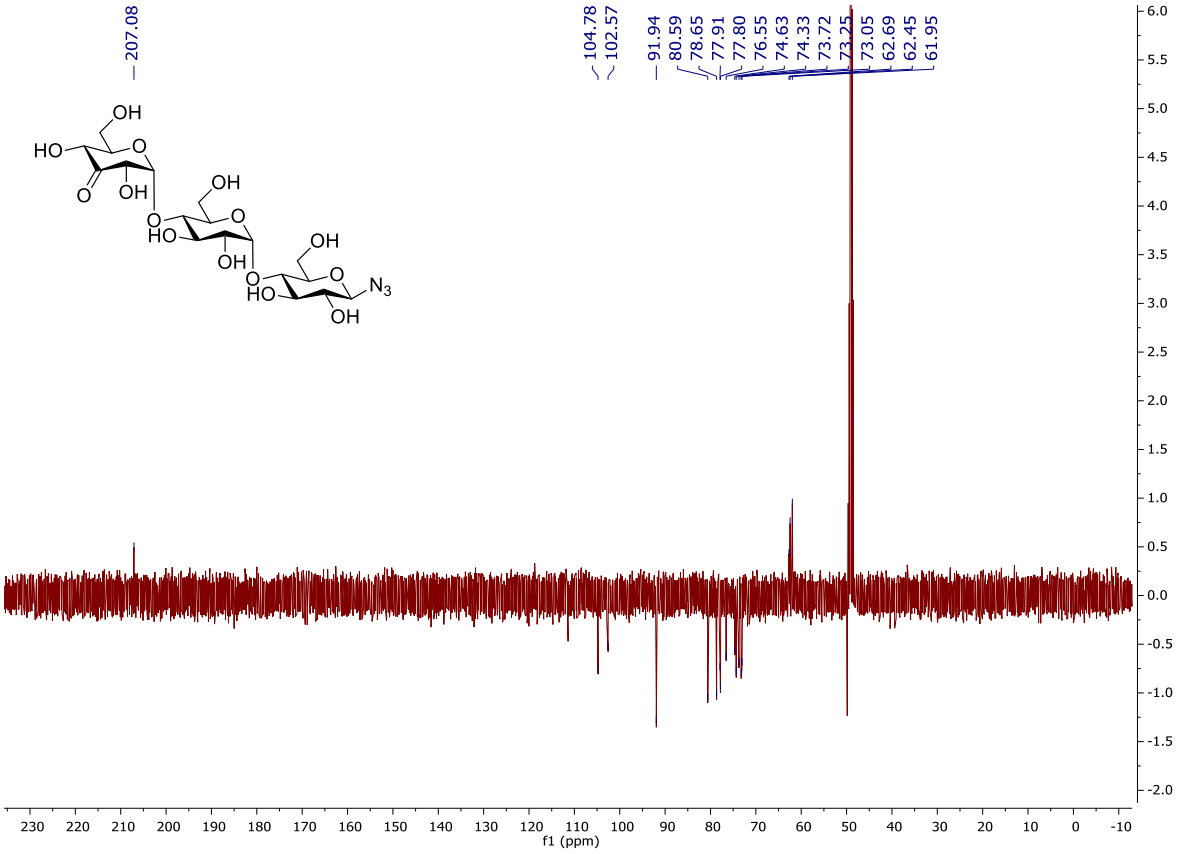


Figure 72, APT of β-D-3-ketomaltotrioside

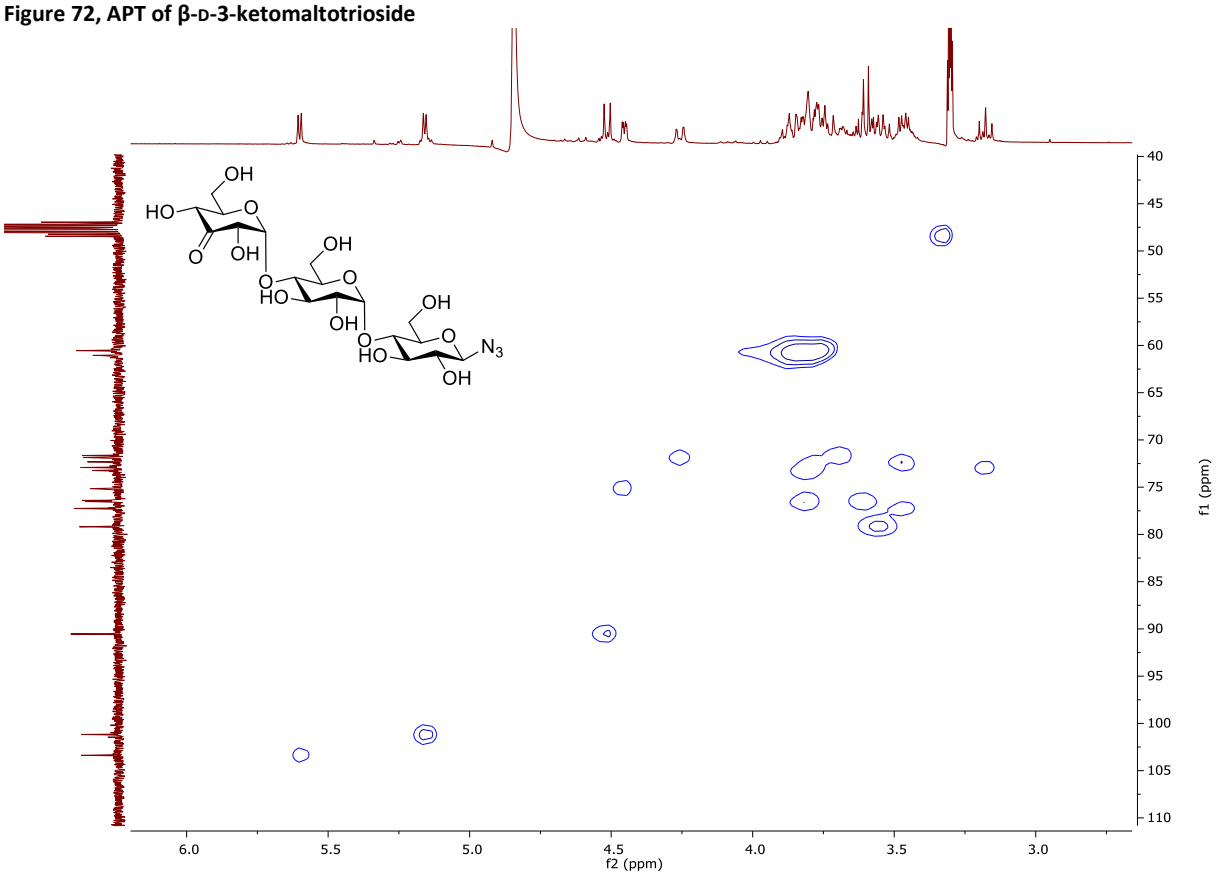


Figure 73, HMQC of β-D-3-ketomaltotrioside

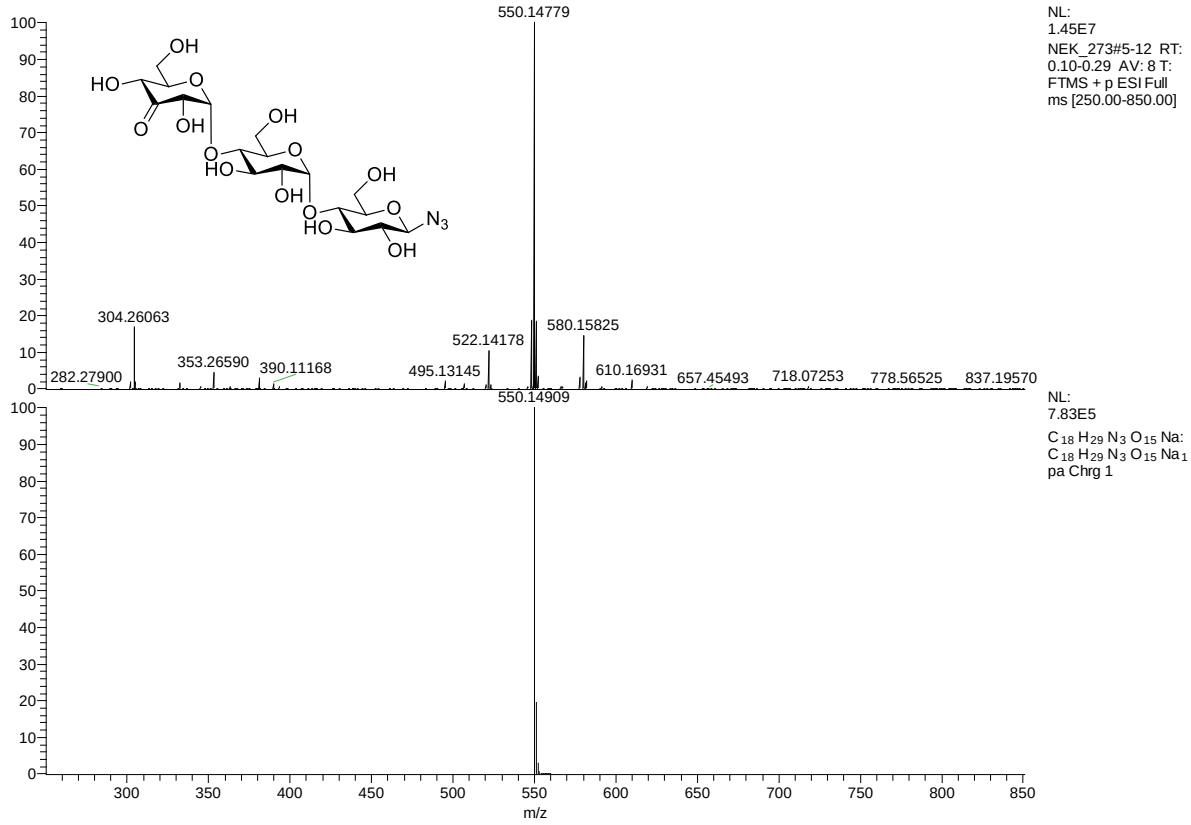


Figure 74, HRMS of β-D-3-ketomaltotrioside

Azido-β-D-3-ketomaltotetraoside (13)

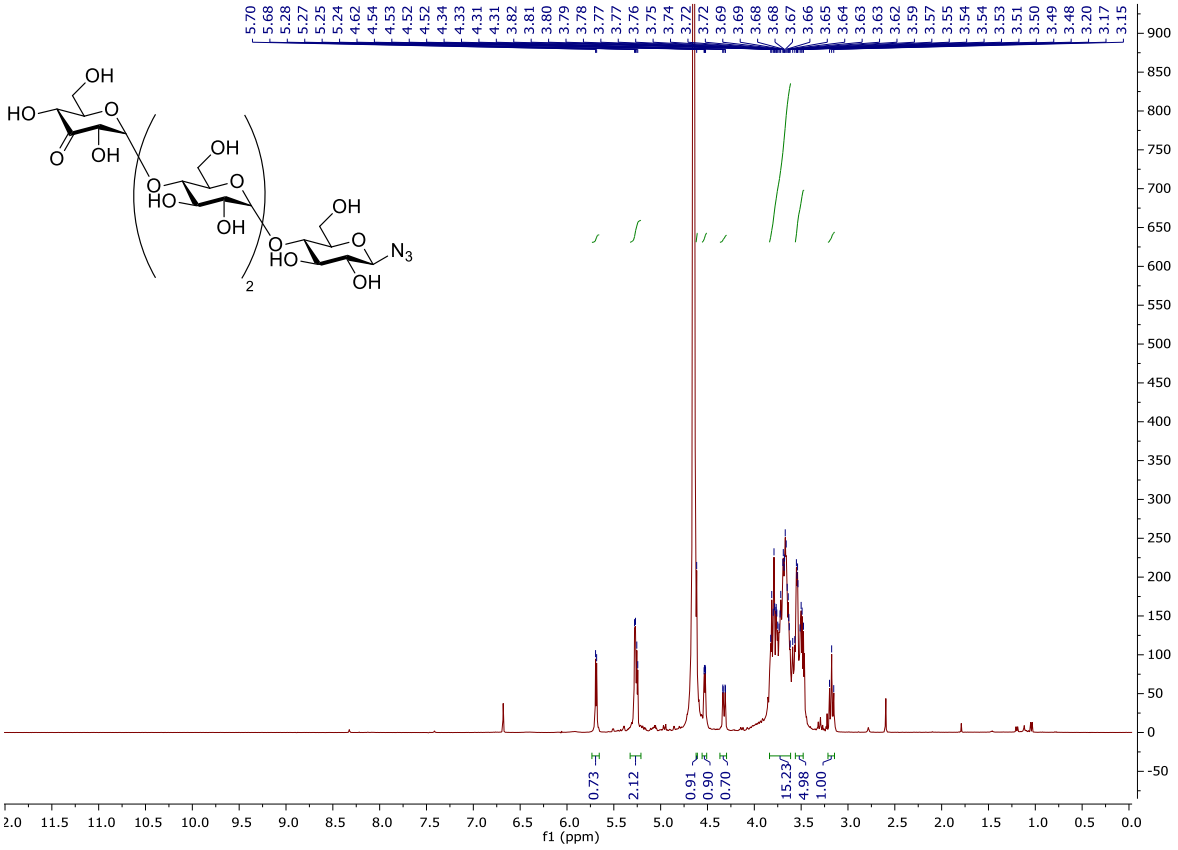


Figure 75, ^{1}H-NMR of azido-β-D-3-ketomaltotetraoside

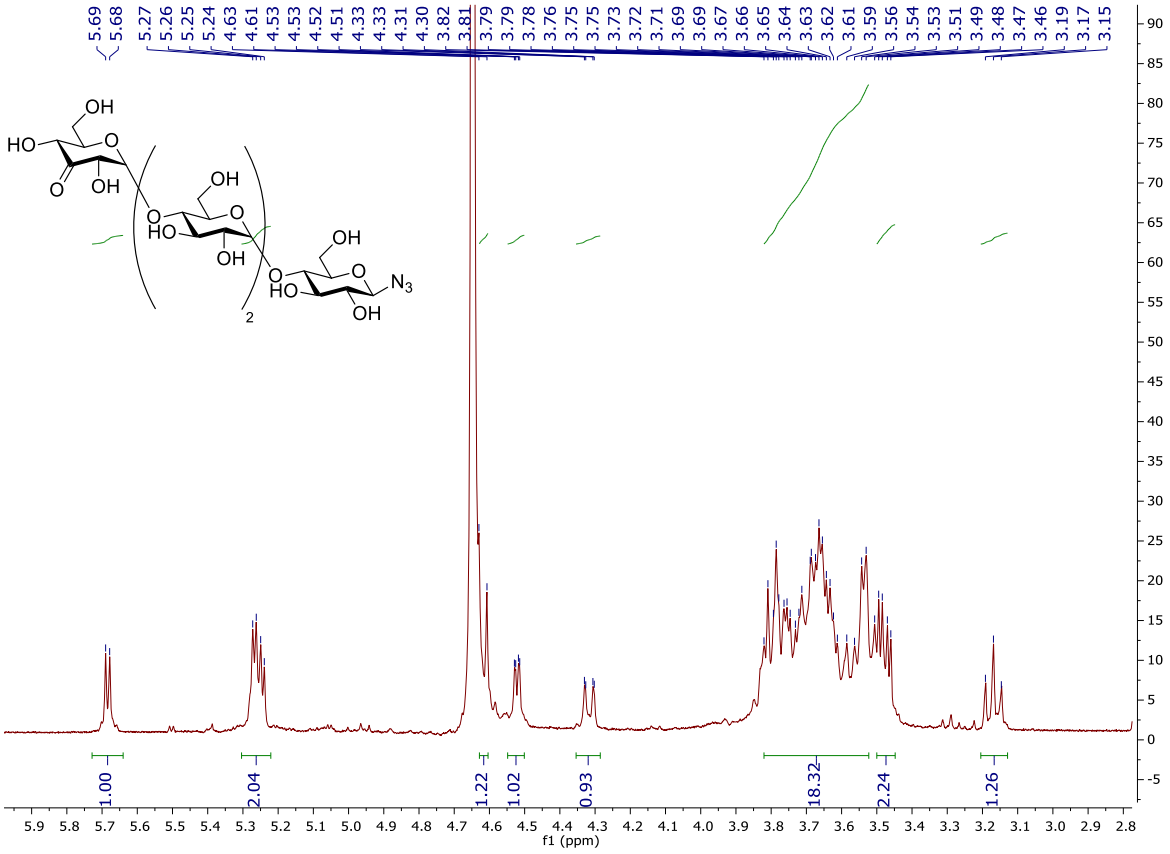


Figure 76, zoom of ^{1}H-NMR of azido-β-D-3-ketomaltotetraoside

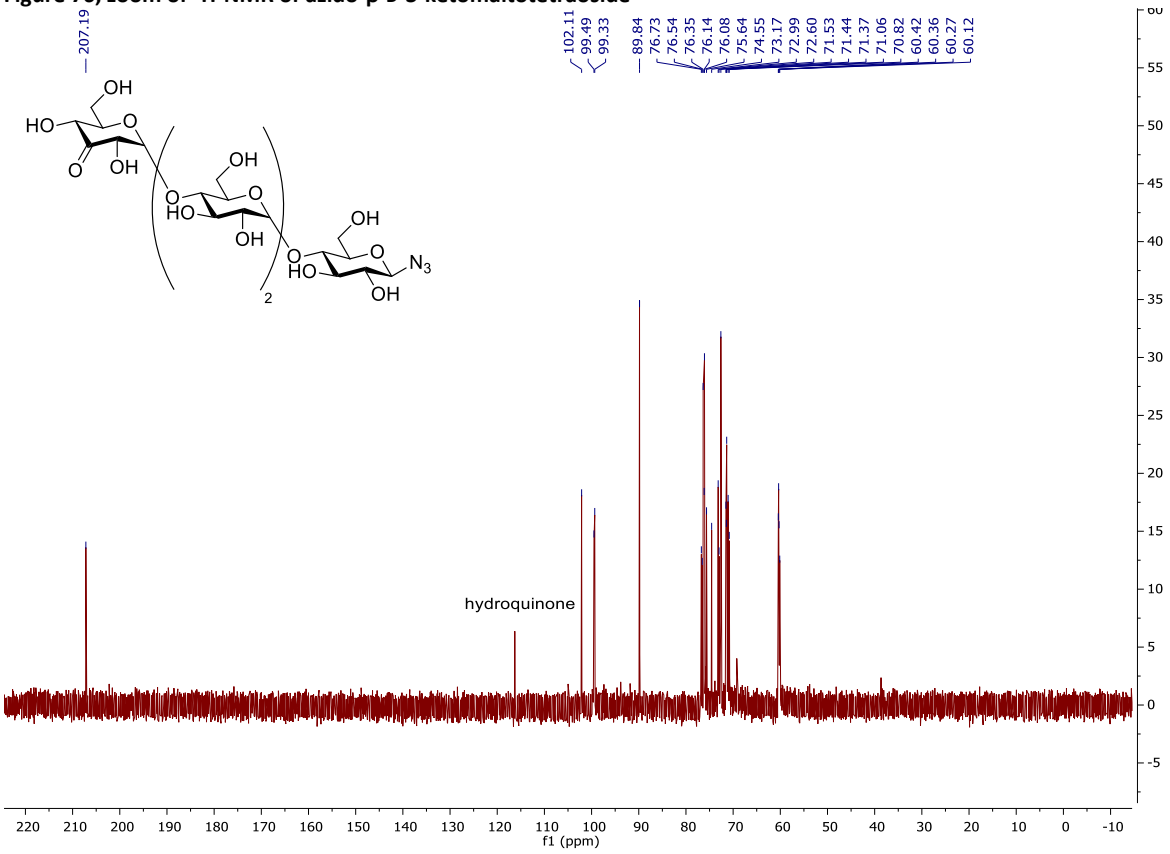


Figure 77, ^{13}C-NMR of azido-β-D-3-ketomaltotetraoside

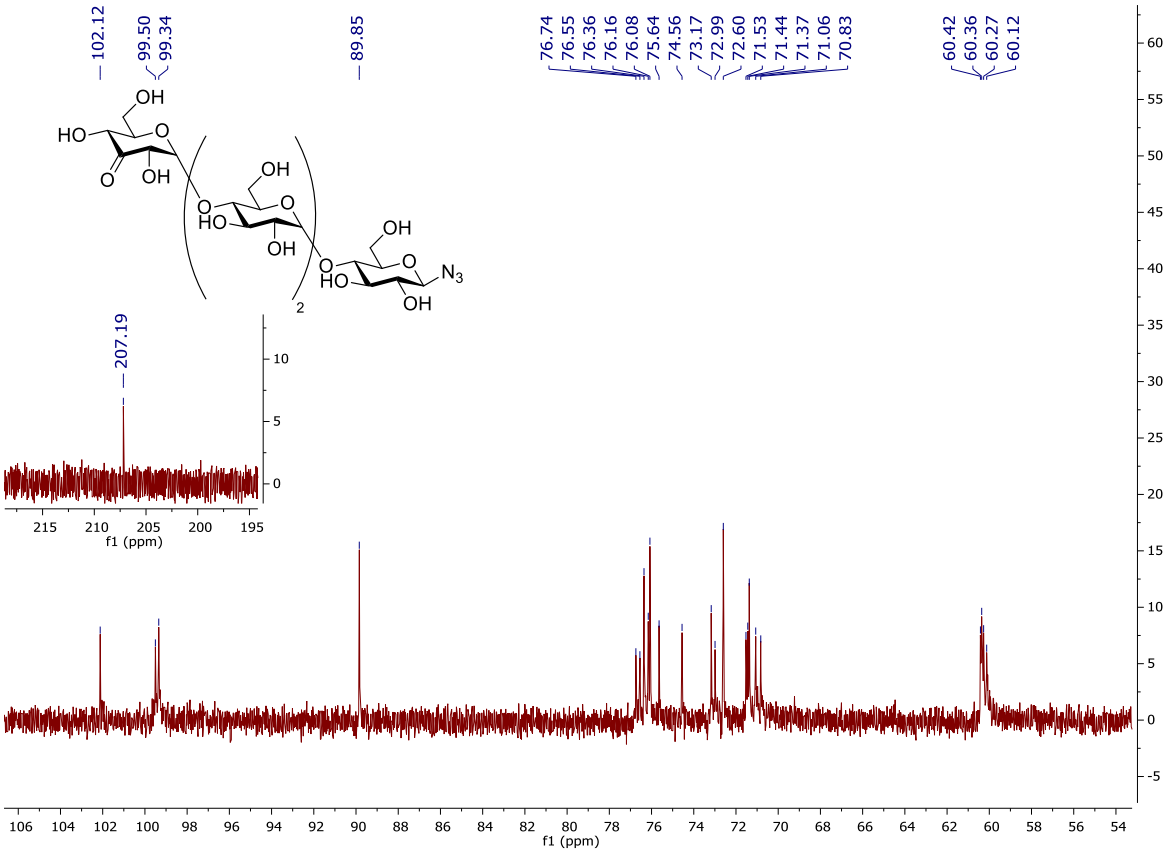


Figure 78, zoom of ^{13}C-NMR of azido-β-D-3-ketomaltotetraoside

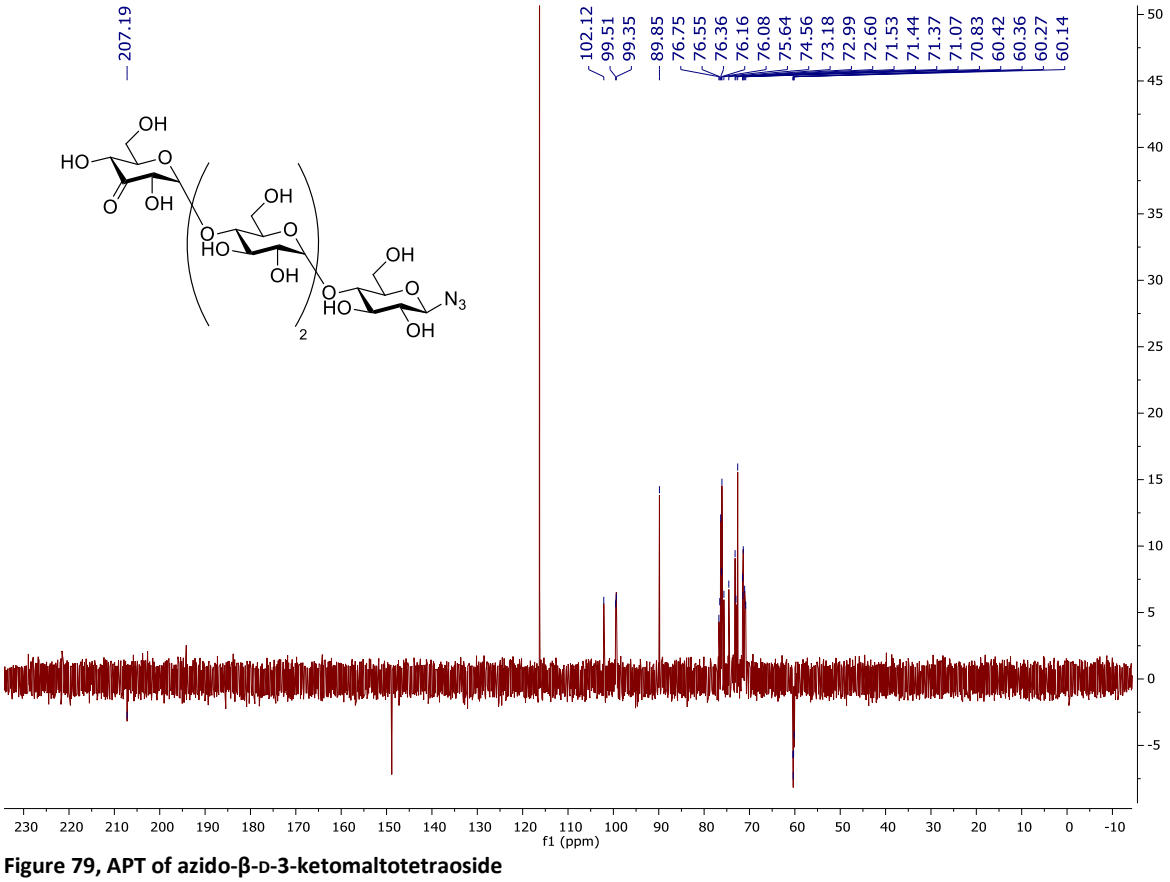


Figure 79, APT of azido-β-D-3-ketomaltotetraoside

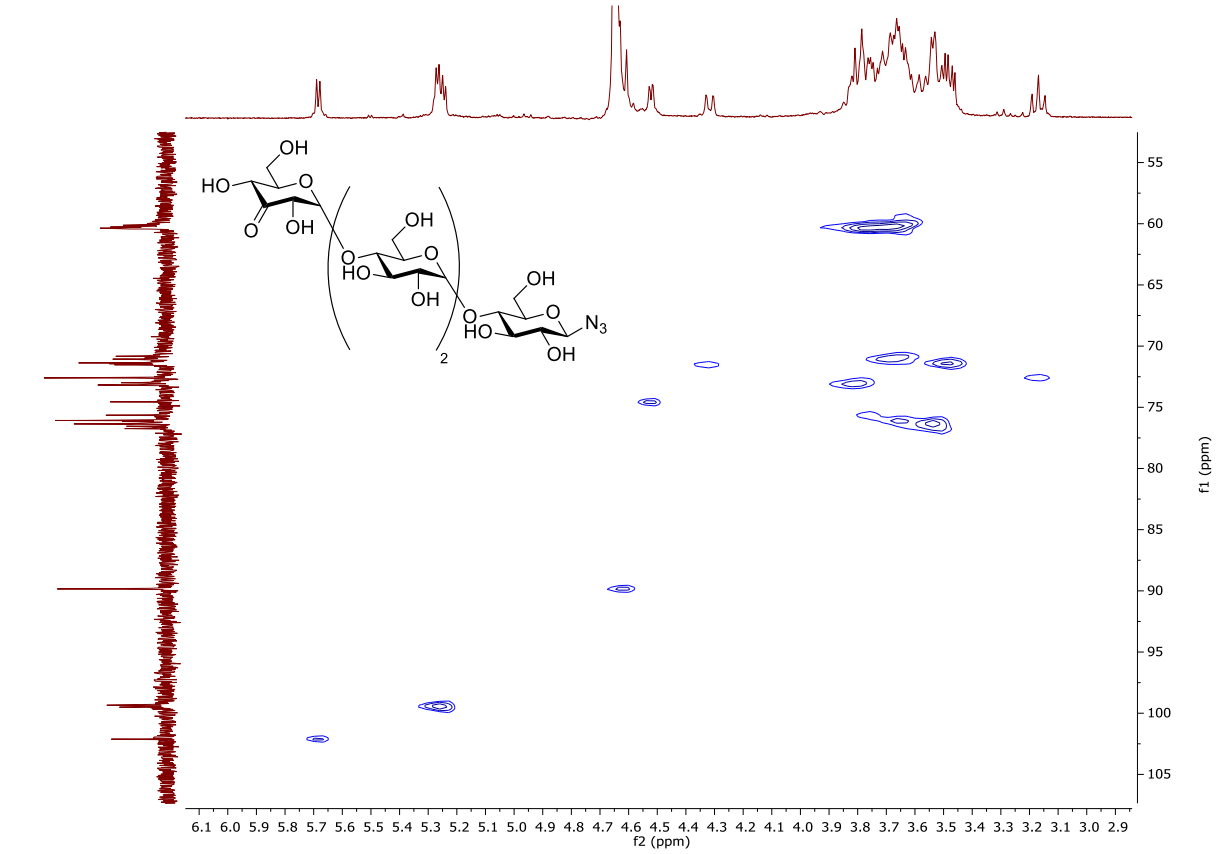


Figure 80, HMQC of azido-β-D-3-ketomaltotetraoside

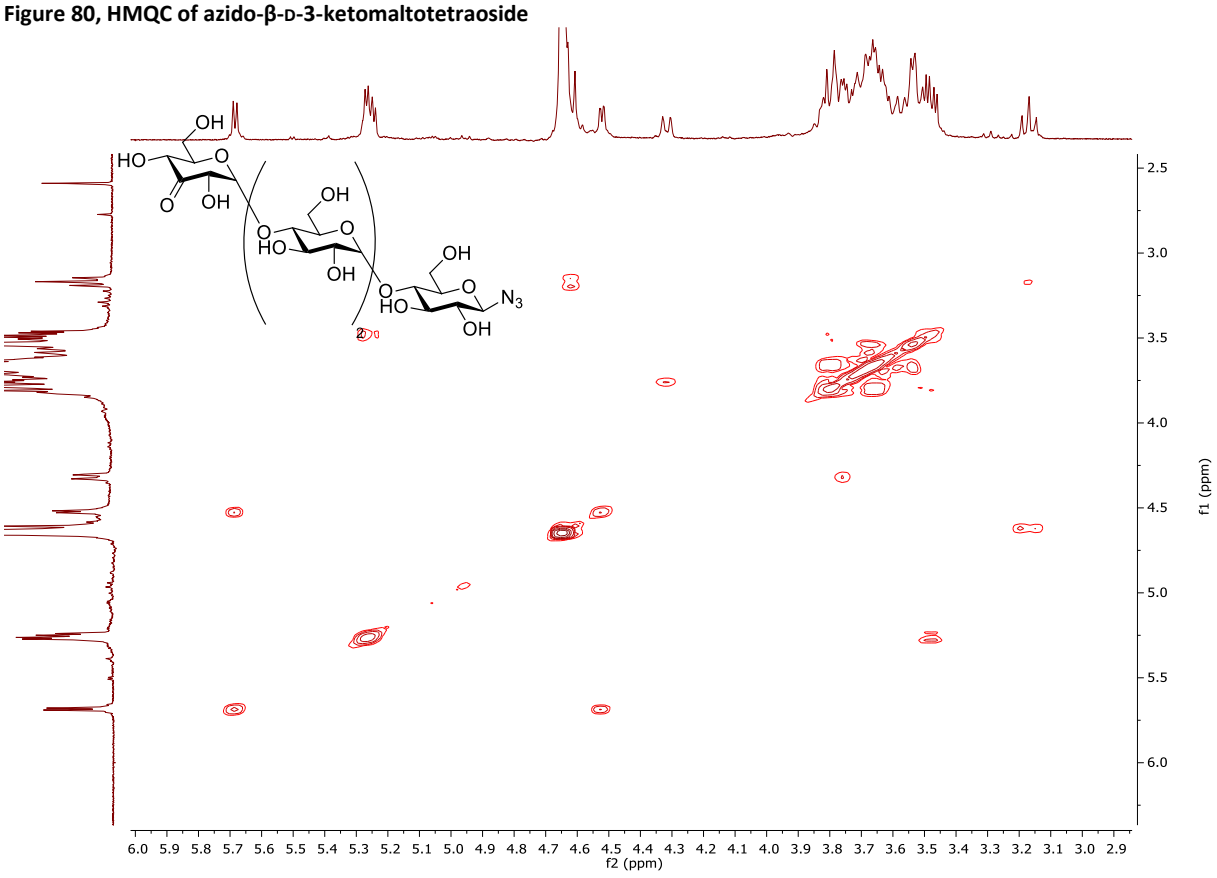


Figure 81, COSY of azido-β-D-3-ketomaltotetraoside

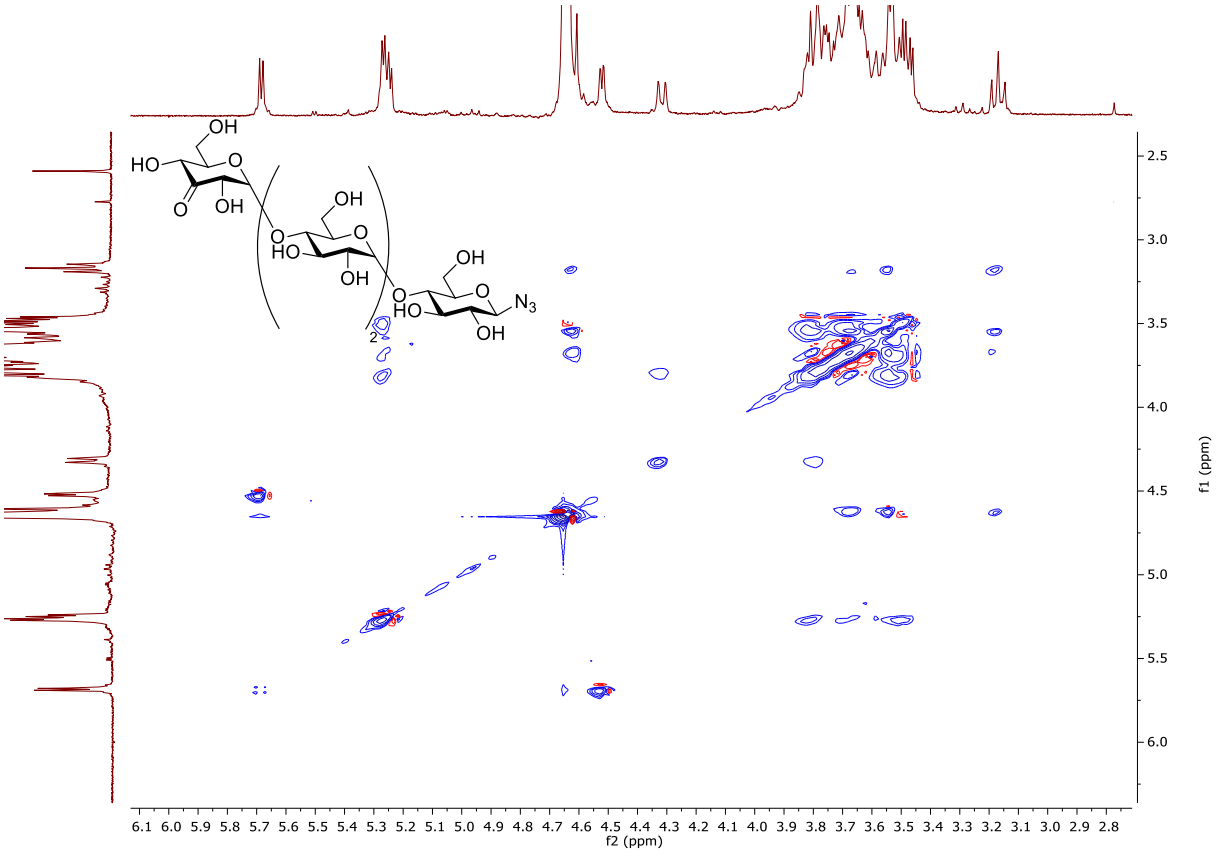


Figure 82, TOCSY of azido-β-D-3-ketomaltotetraoside

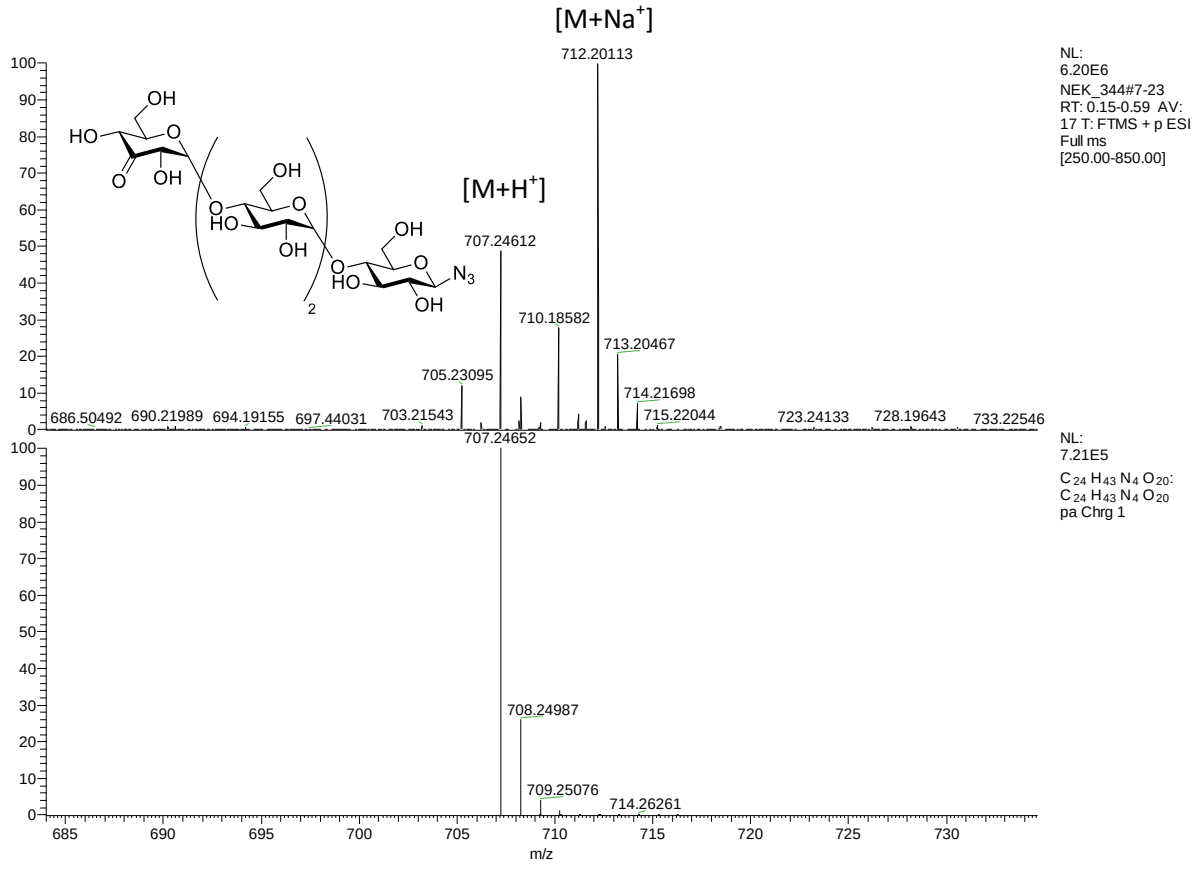


Figure 83, HRMS of azido-β-D-3-ketomaltotetraoside

β-D-3-ketomaltopentaosyl azide (14)

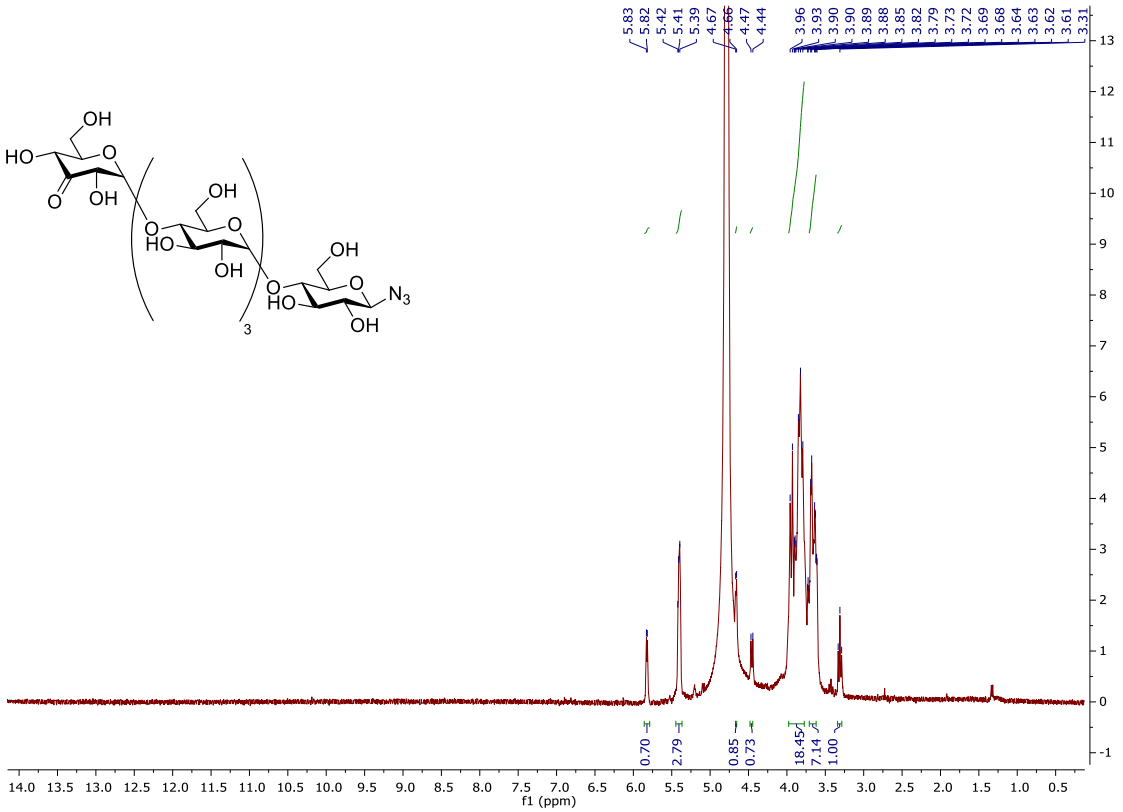


Figure 84, ^{1}H-NMR of β-D-3-ketomaltopentaosyl azide

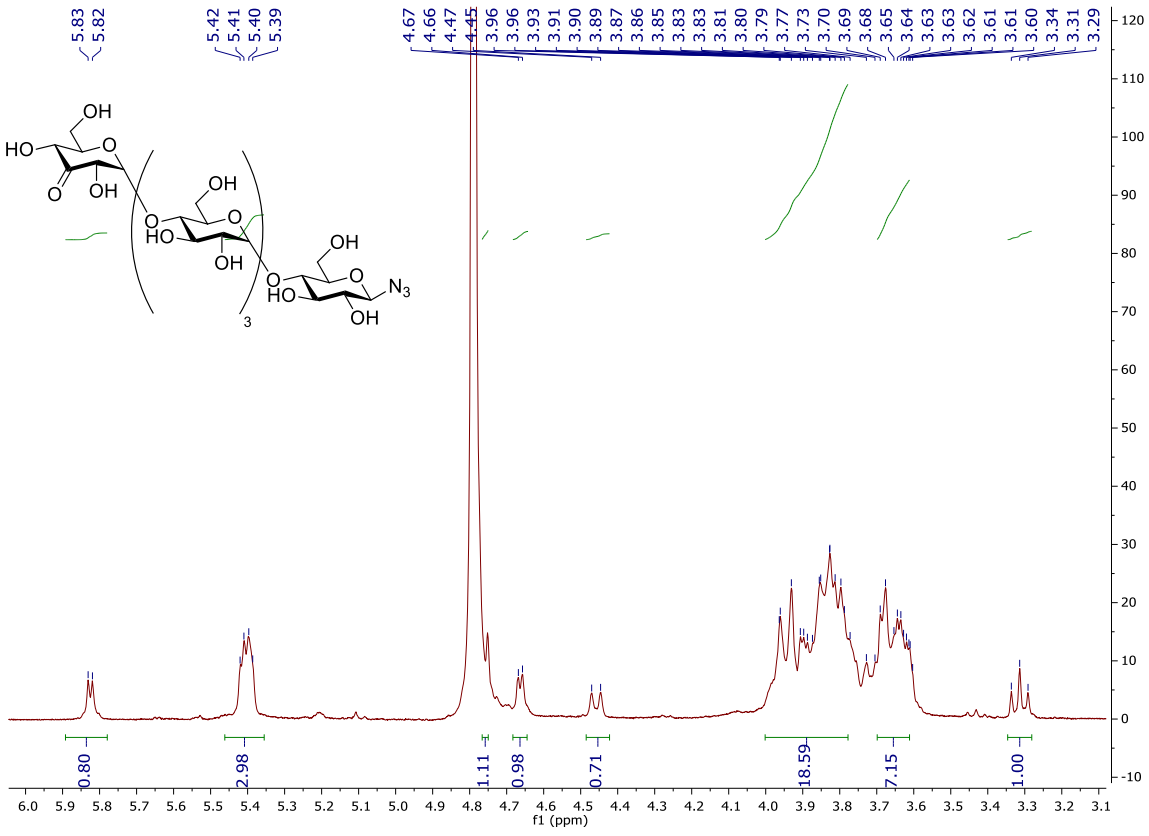


Figure 85, zoom of ^{1}H-NMR of β-D-3-ketomaltopentaosyl azide

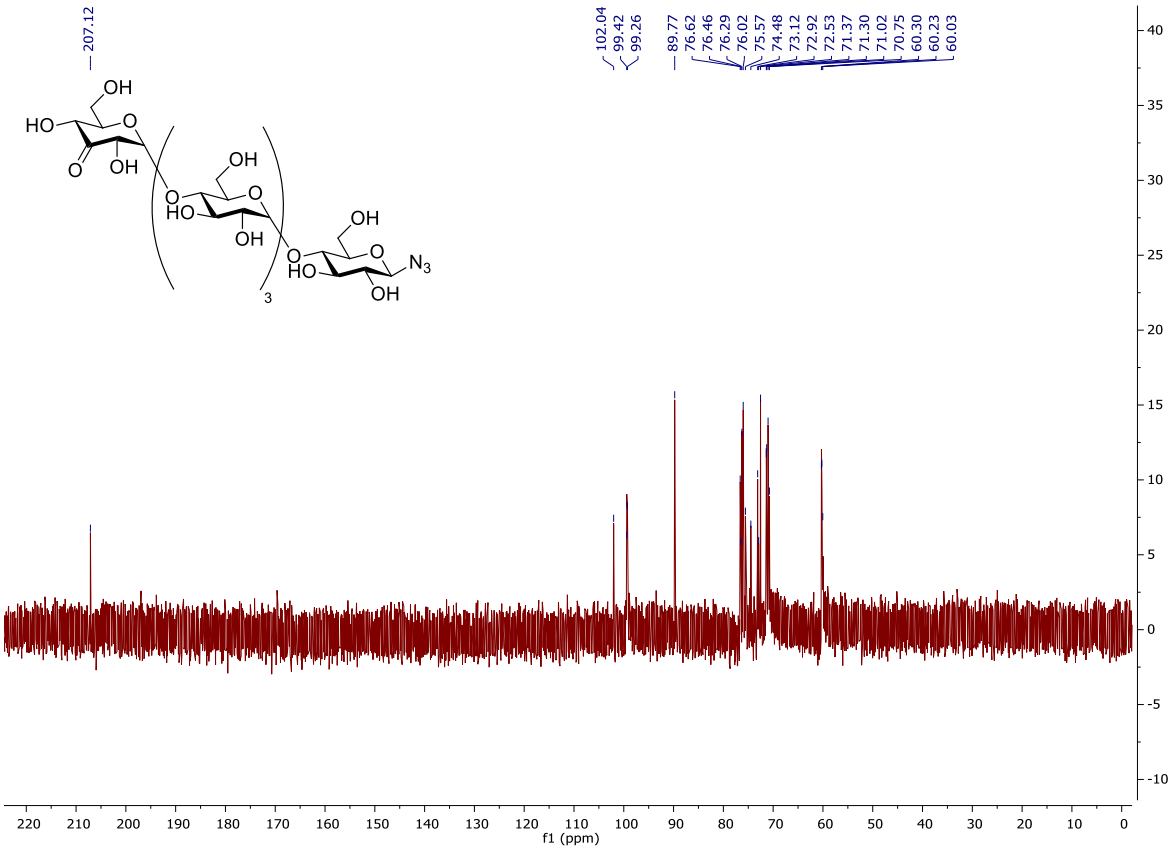


Figure 86, ^{13}C-NMR of β-D-3-ketomaltopentaosyl azide

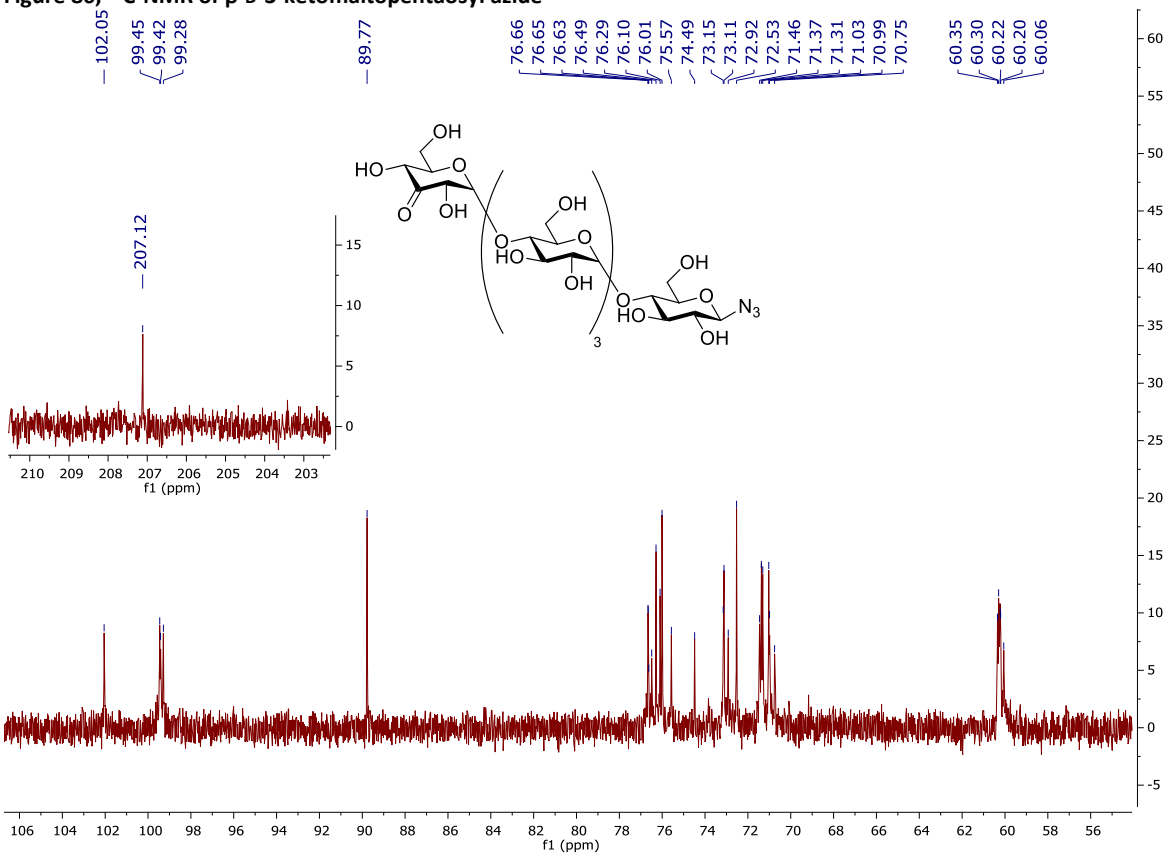


Figure 87, zoom of ^{13}C-NMR of β-D-3-ketomaltopentaosyl azide

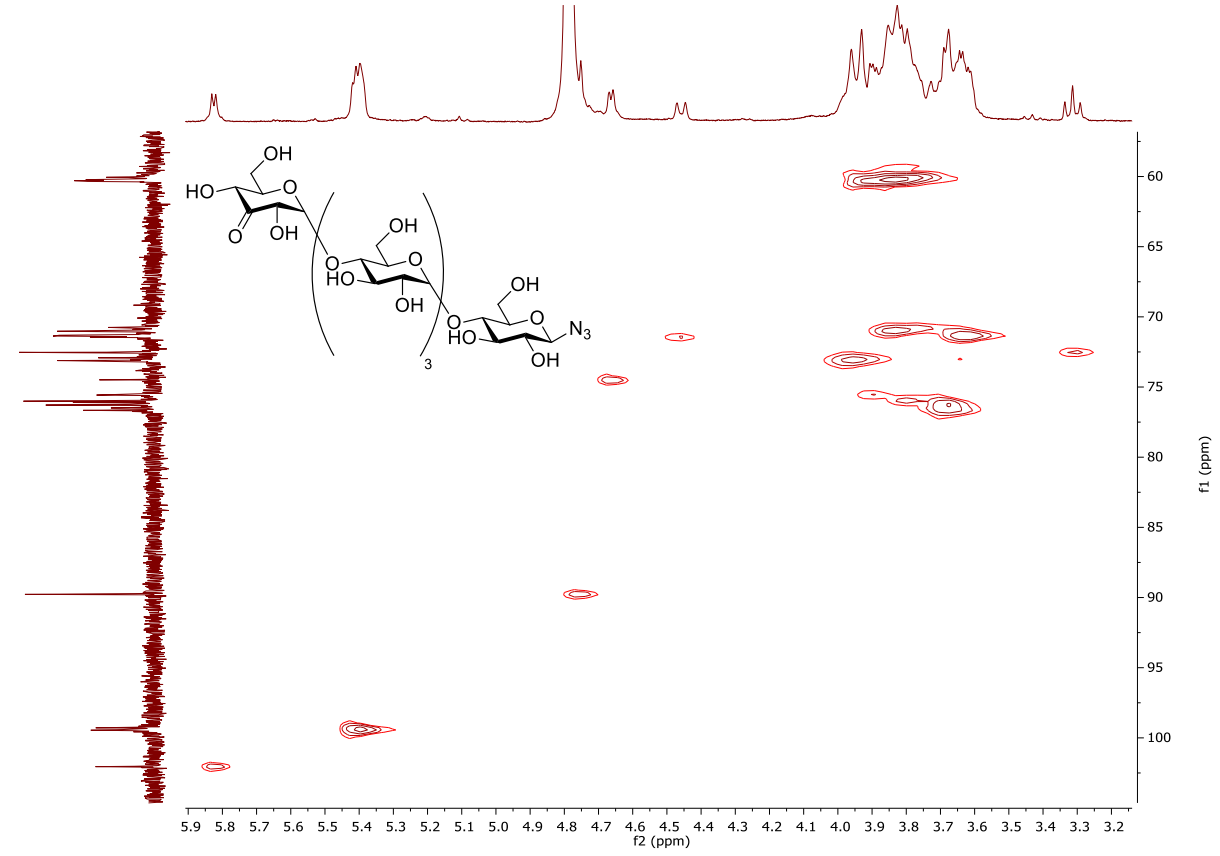


Figure 88, HMQC of β-D-3-ketomaltopentaosyl azide

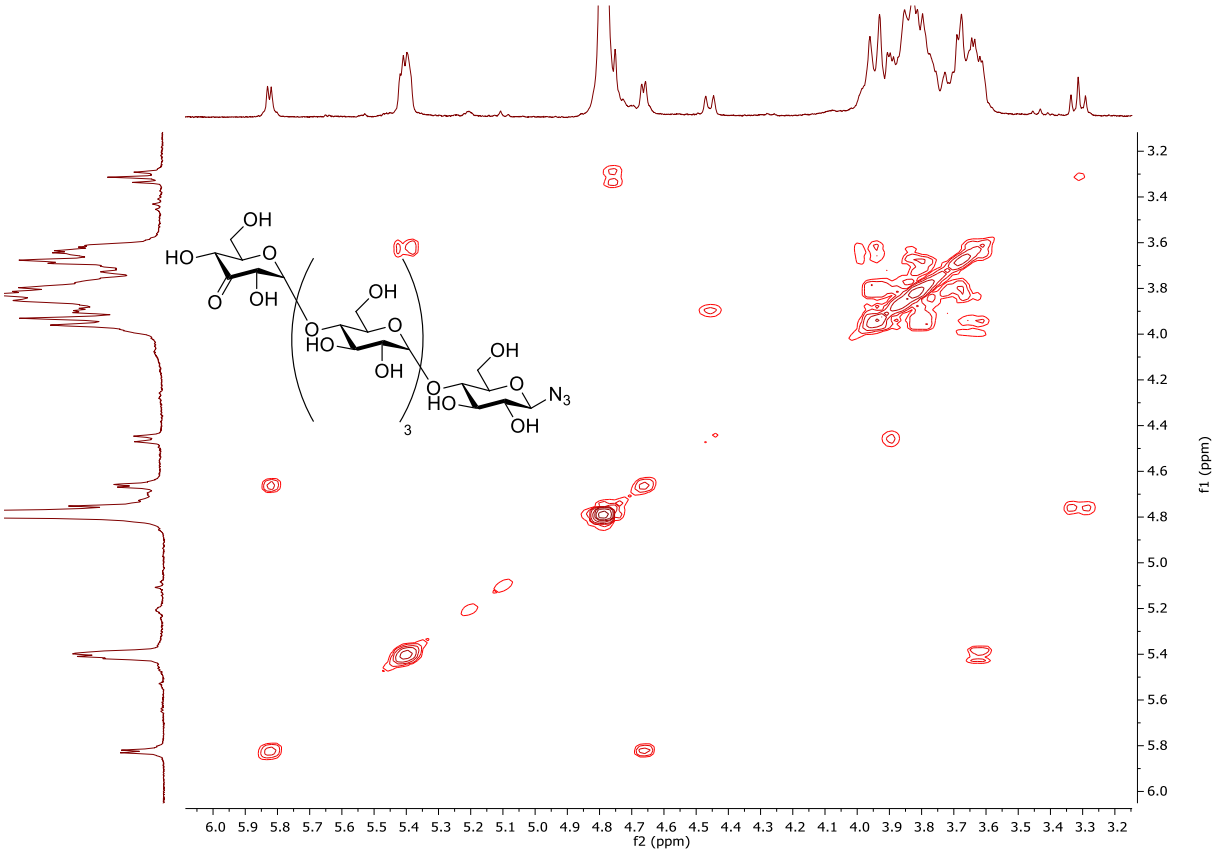


Figure 89, COSY of β-D-3-ketomaltopentaosyl azide

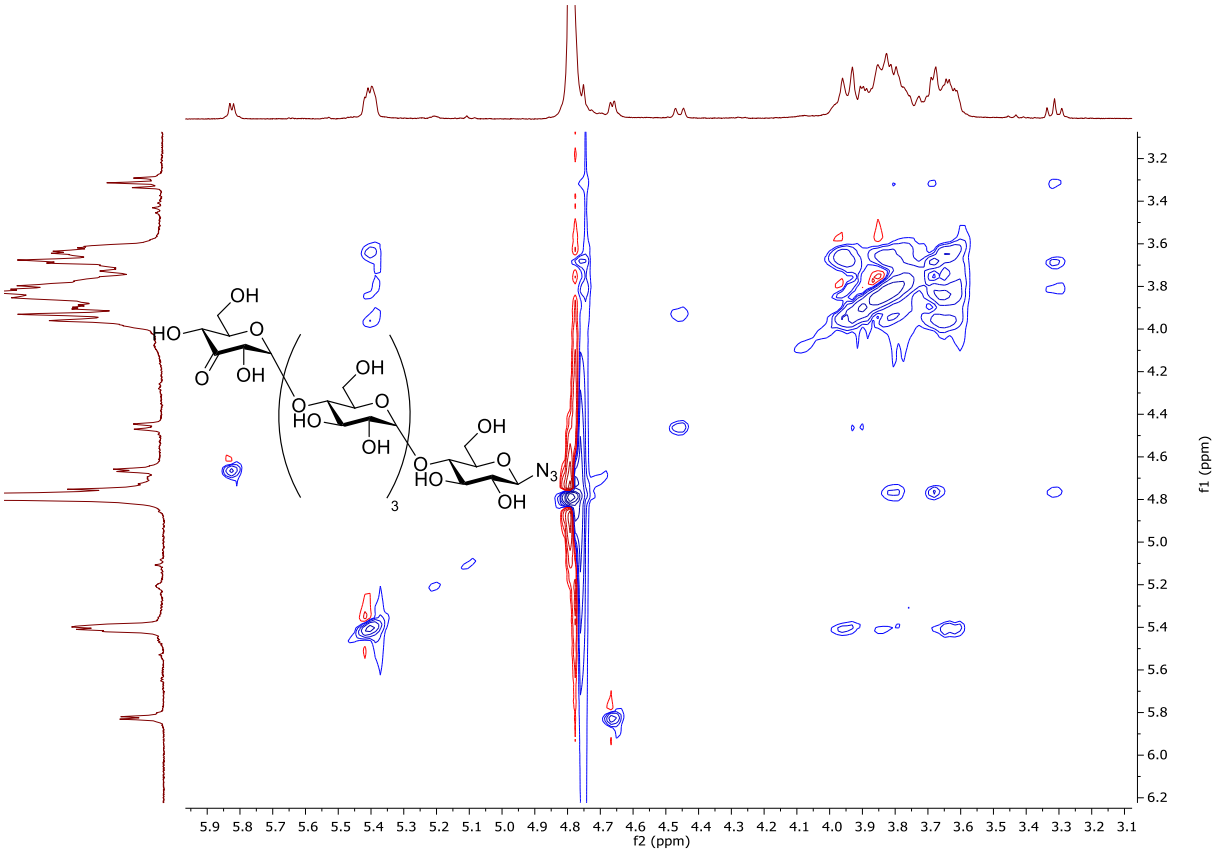


Figure 90, TOCSY of β-D-3-ketomaltopentaosyl azide

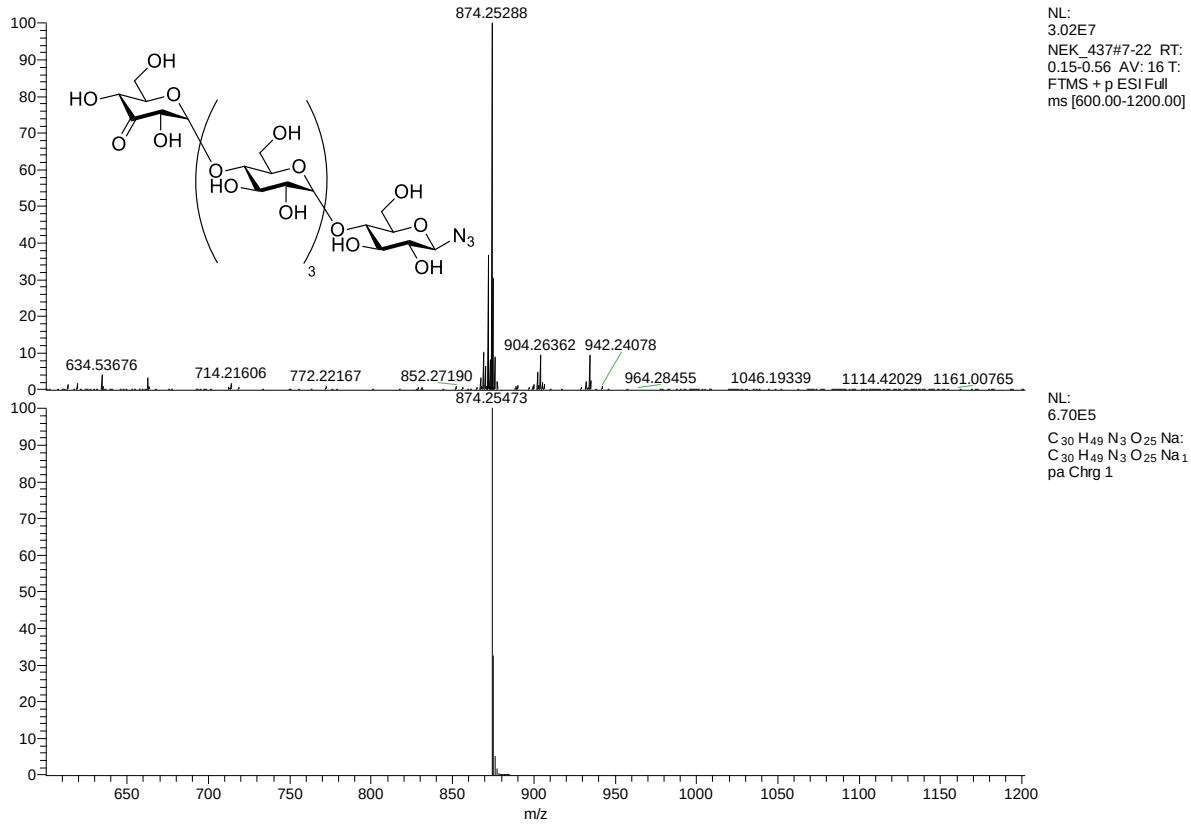


Figure 91, HRMS of β-D-3-ketomaltopentaosyl azide

β-D-3-ketomaltohexaosyl azide(15)

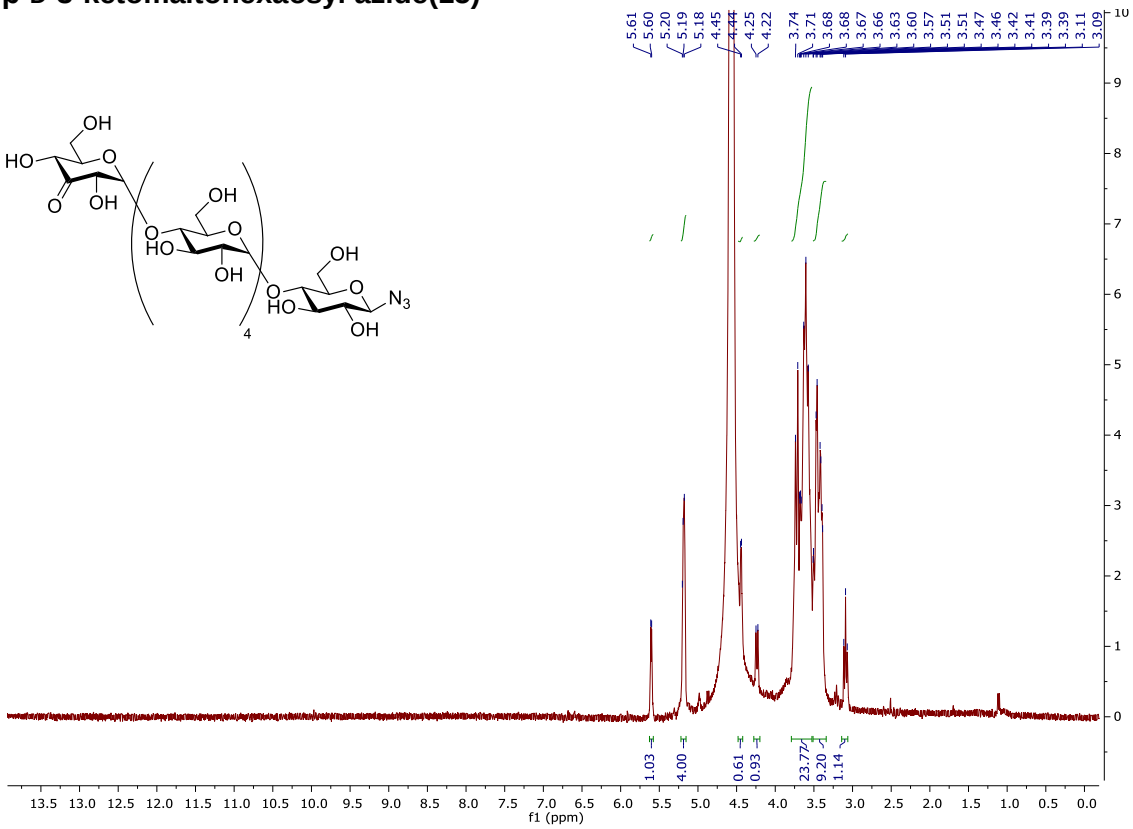


Figure 92, ^{1}H-NMR of β-D-3-ketomaltohexaosyl azide

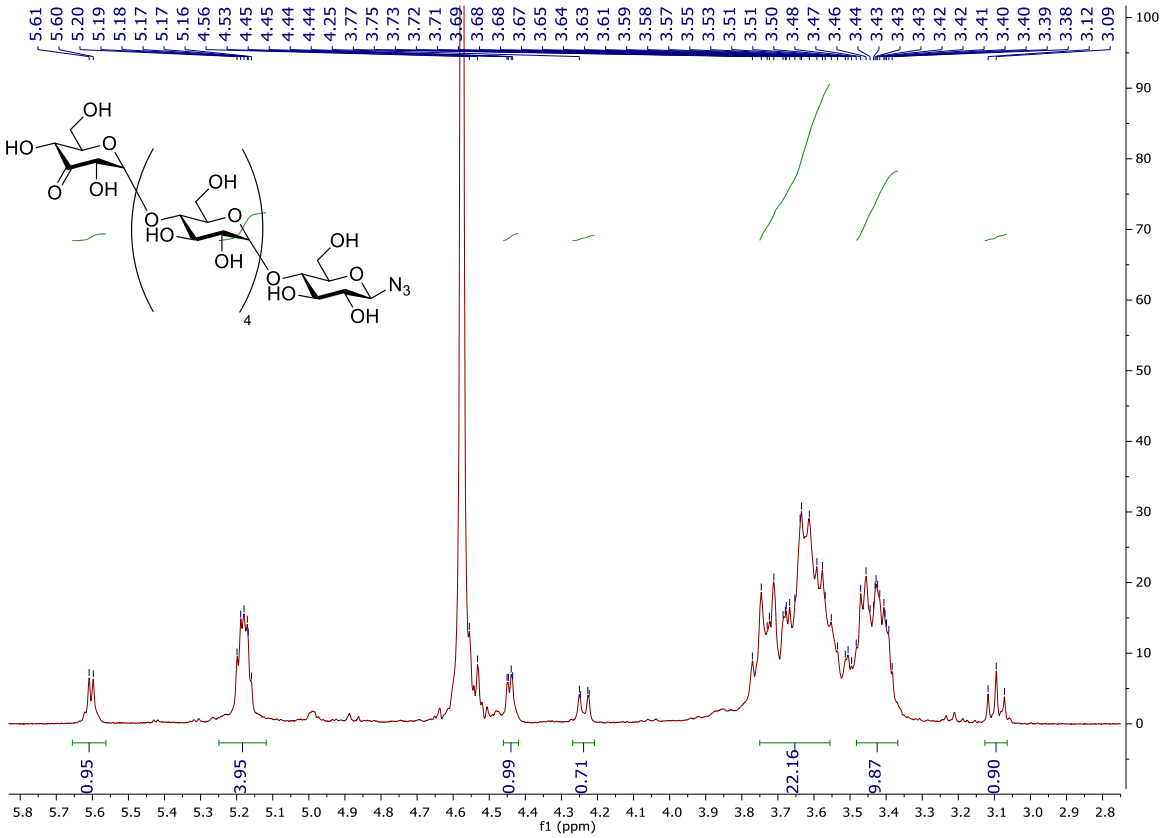


Figure 93, zoom of ^{1}H-NMR of β-D-3-ketomaltohexaosyl azide

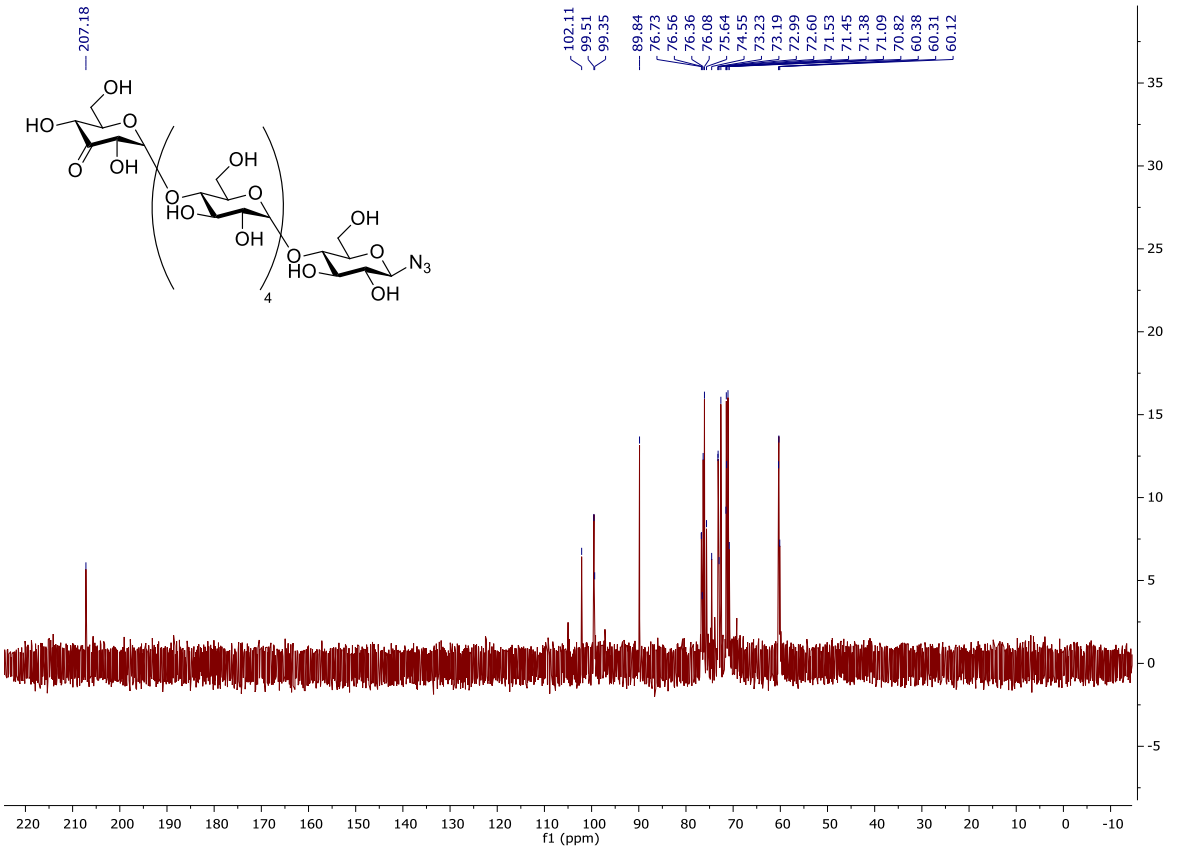


Figure 94, ^{13}C-NMR of β-D-3-ketomaltohexaosyl azide

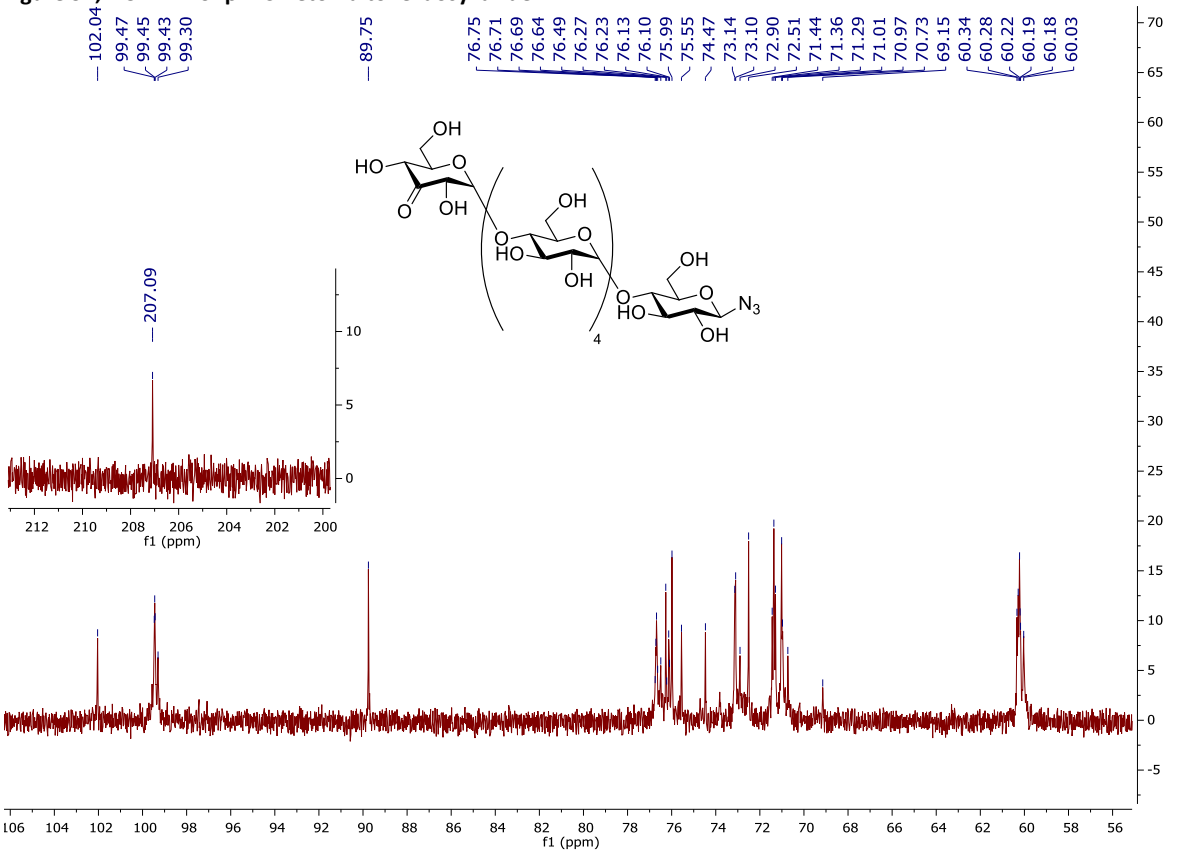


Figure 95, zoom of ^{13}C-NMR of β-D-3-ketomaltohexaosyl azide

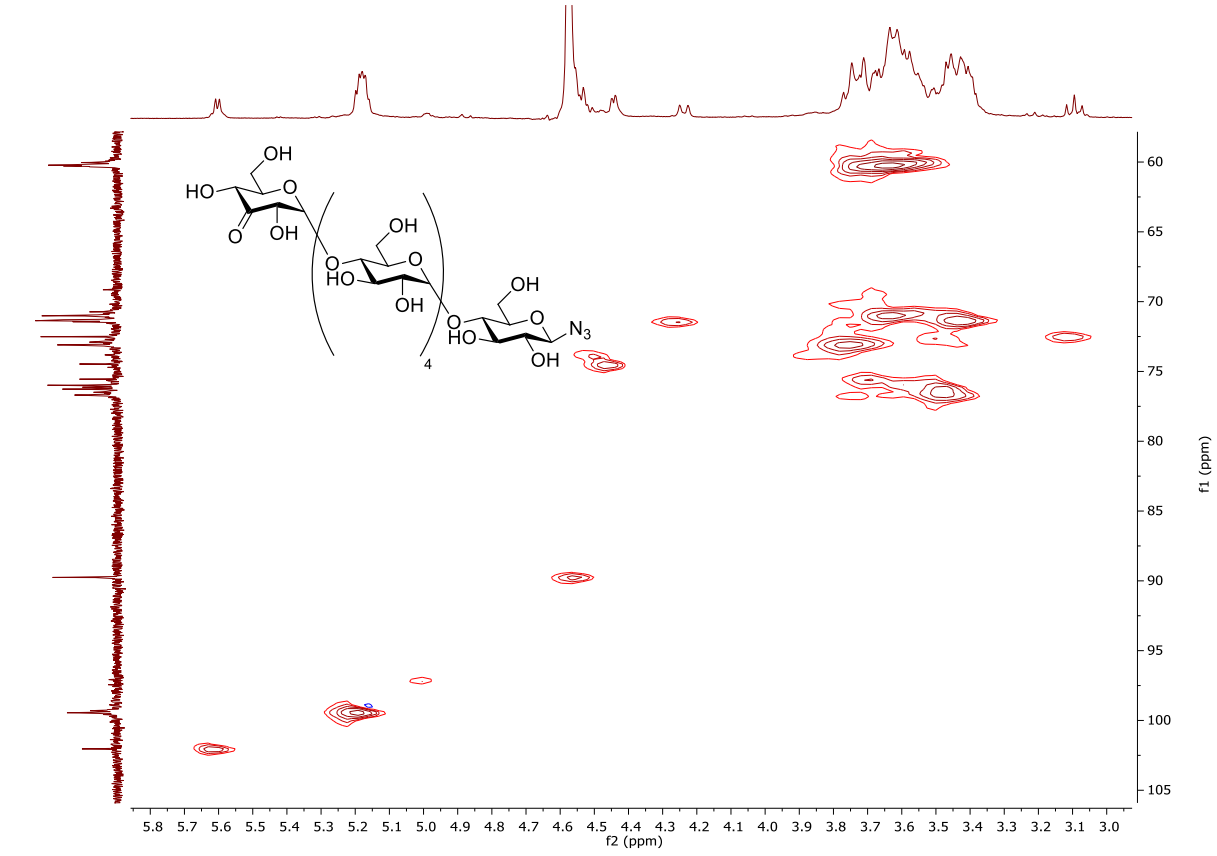


Figure 96, HMQC of β-D-3-ketomaltohexaosyl azide

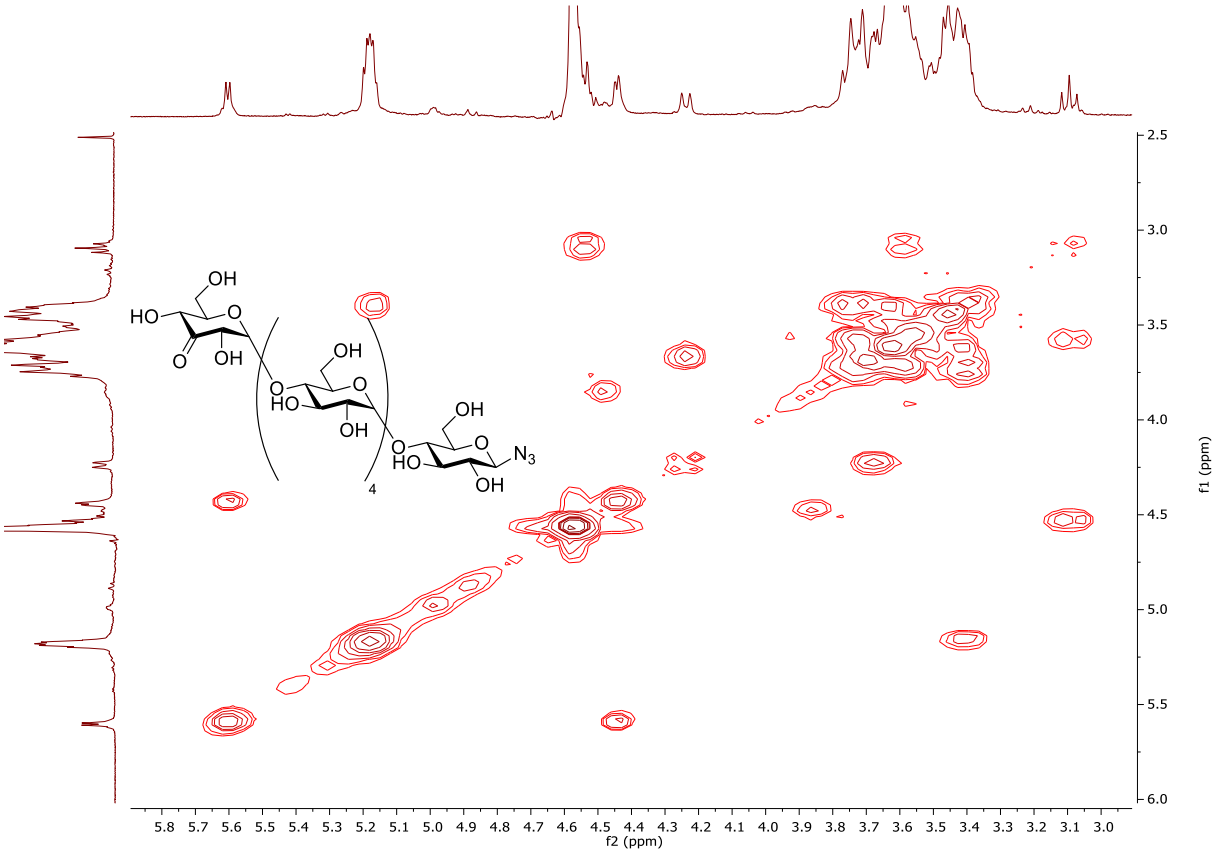


Figure 97, COSY of β-D-3-ketomaltohexaosyl azide

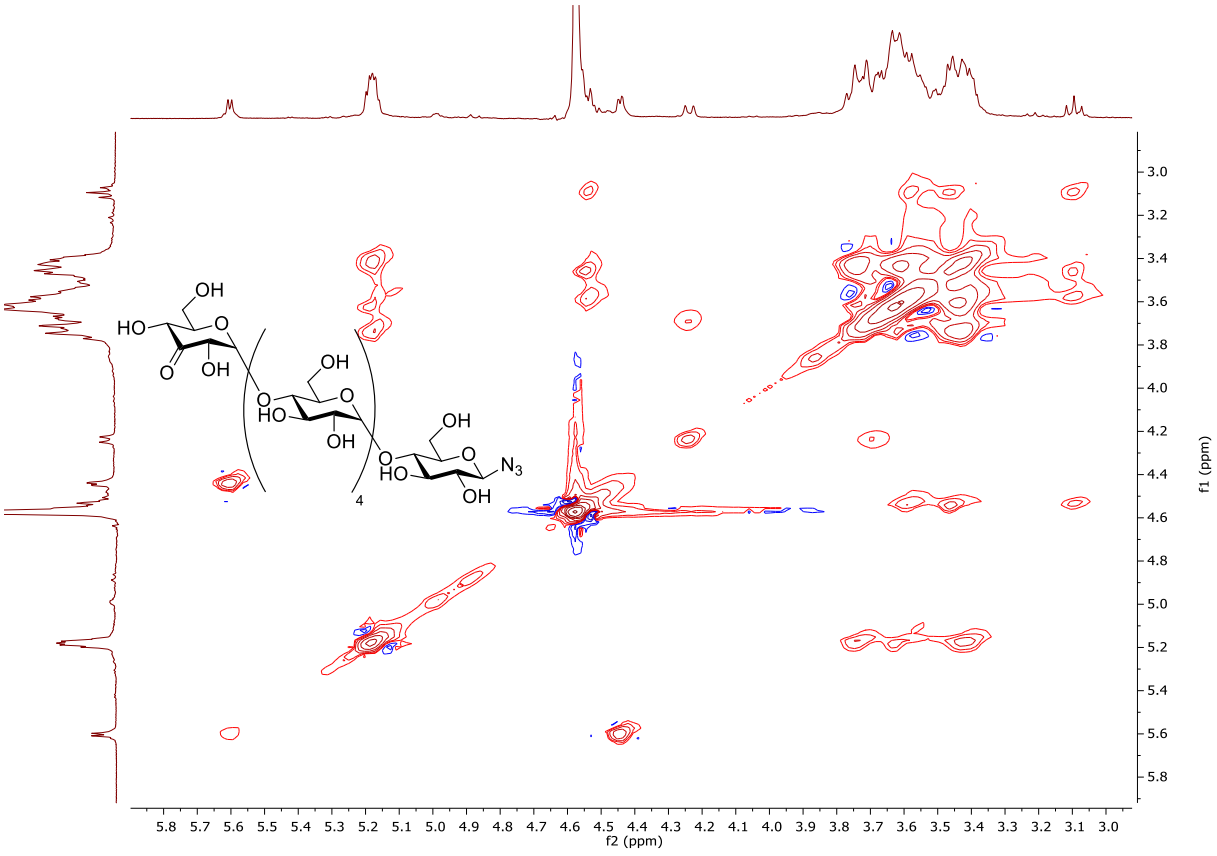


Figure 98, TOCSY of β-D-3-ketomaltohexaosyl azide

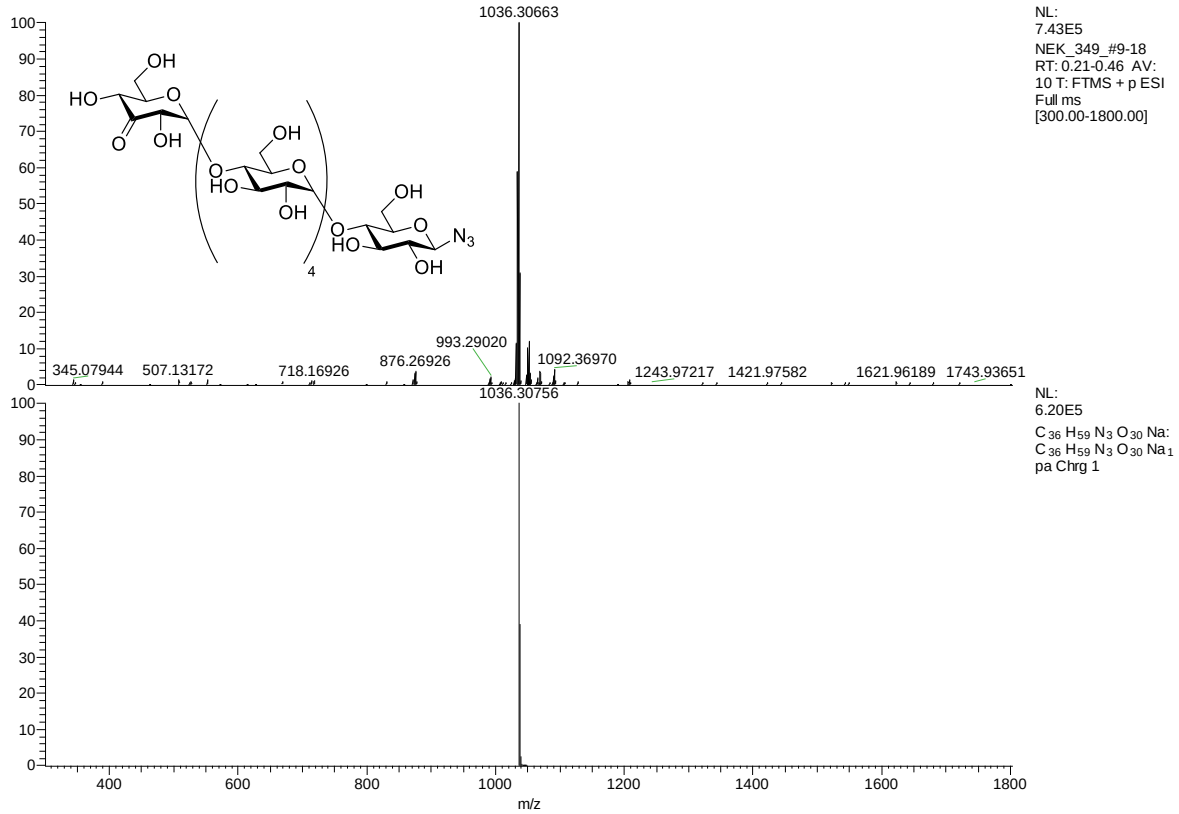


Figure 99, HRMS of β-D-3-ketomaltohexaosyl azide

β-D-3-ketomaltoheptaosyl azide (16)

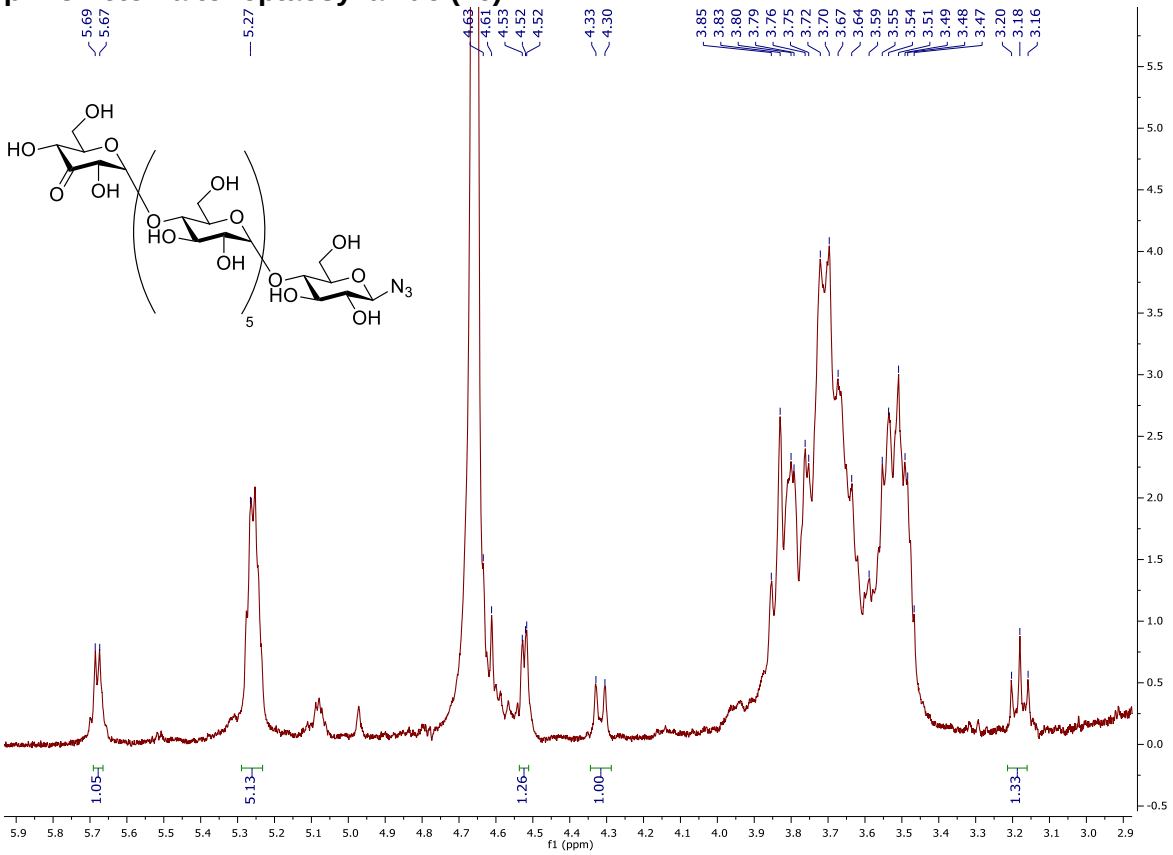


Figure 100, crude 1H-NMR of β-D-3-ketomaltoheptaosyl azide

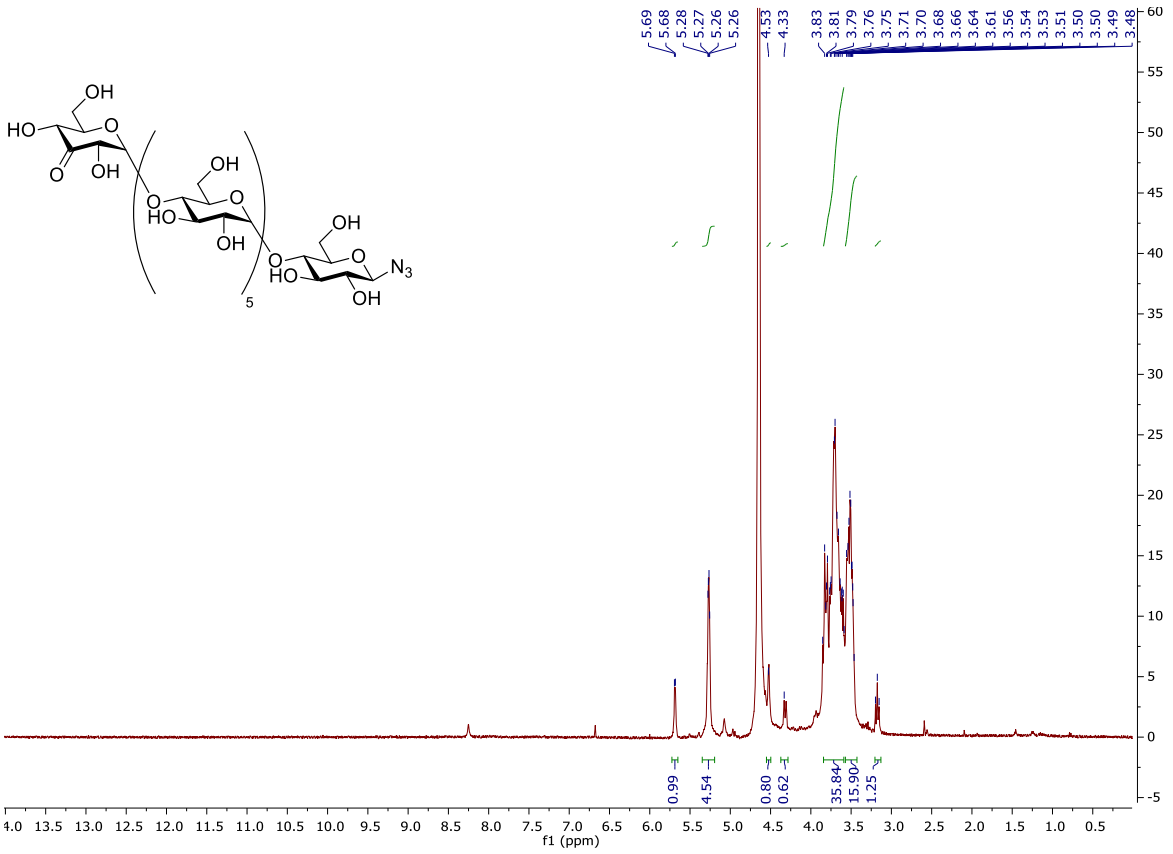


Figure 101, ^{1}H-NMR of β-D-3-ketomaltoheptaosyl azide

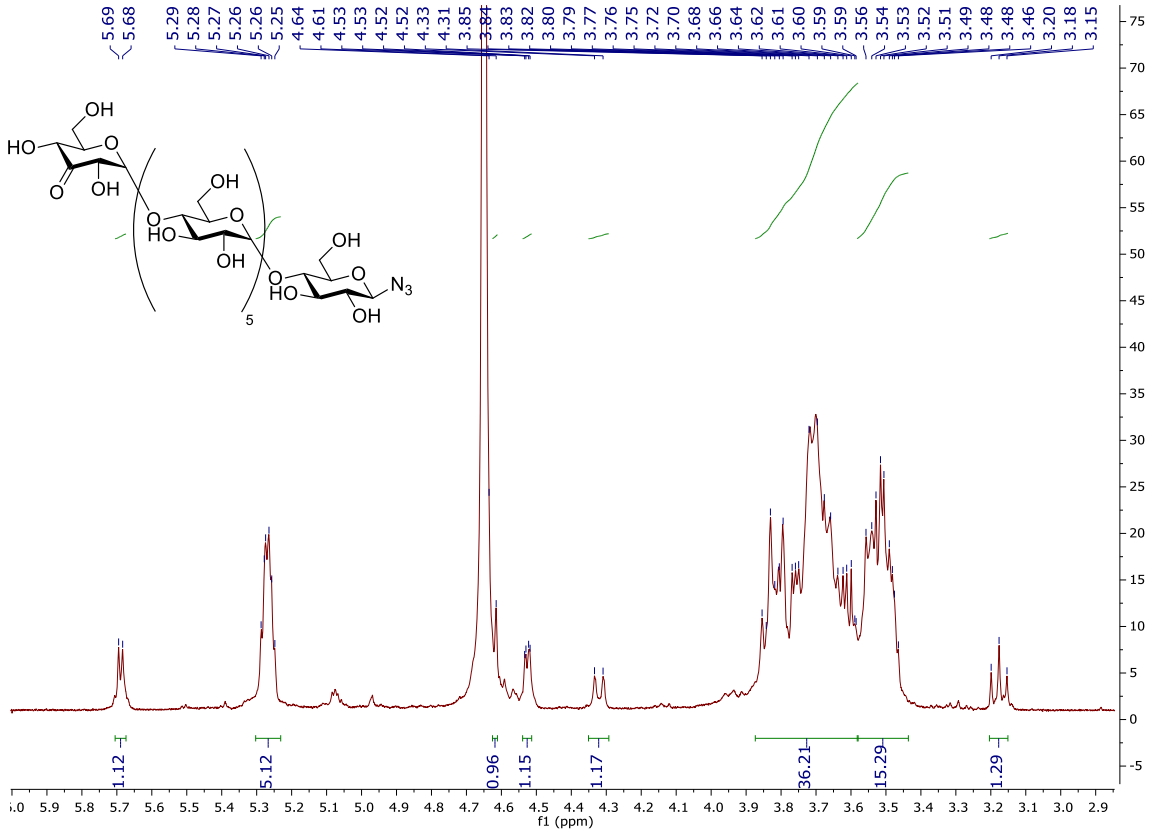


Figure 102, zoom of ^{1}H-NMR of β-D-3-ketomaltoheptaosyl azide

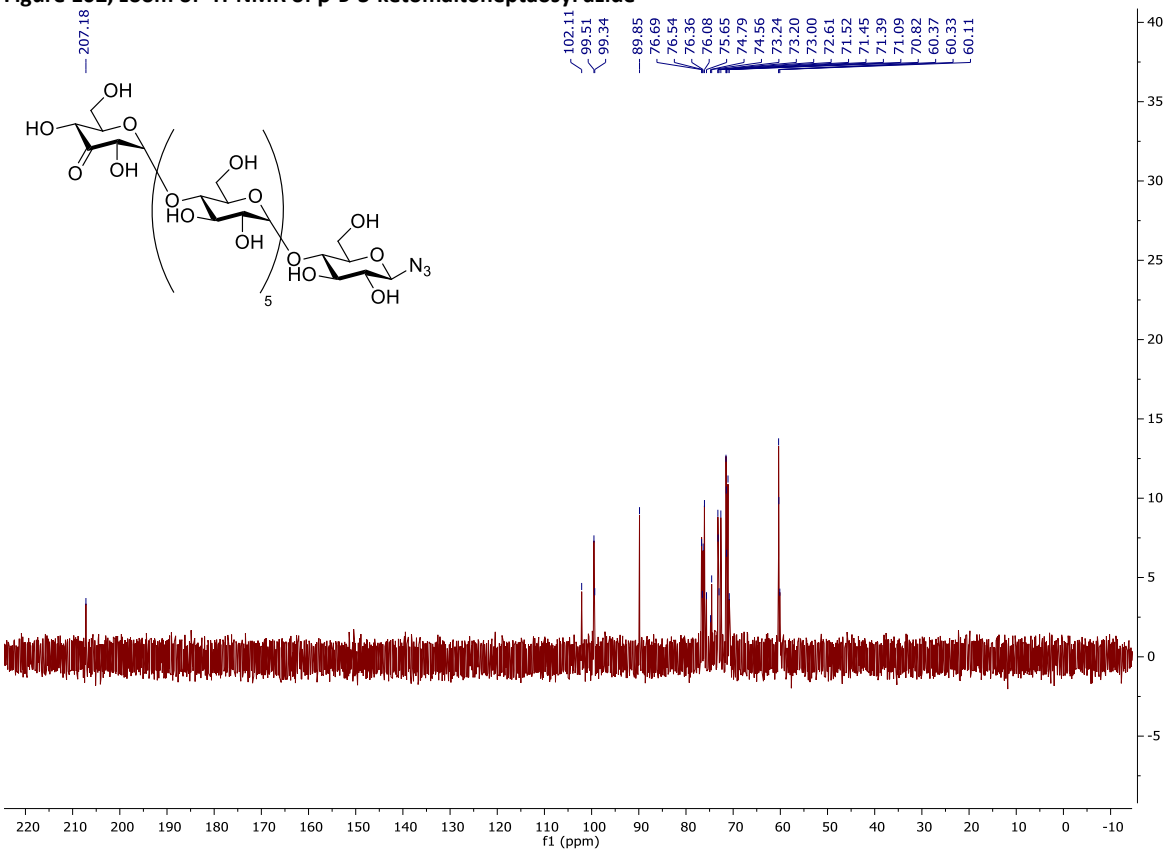


Figure 103, ^{13}C-NMR of β-D-3-ketomaltoheptaosyl azide

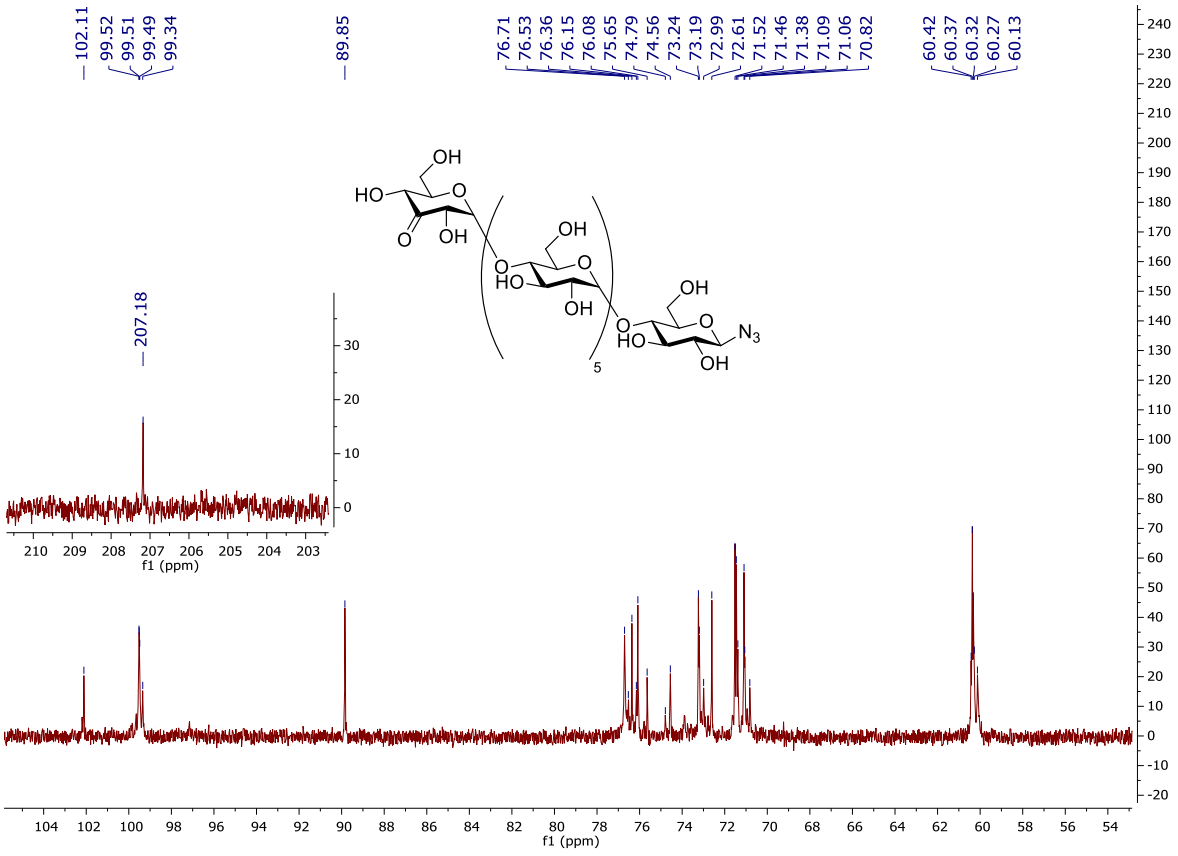


Figure 104, zoom of ^{13}C-NMR of β-D-3-ketomaltoheptaosyl azide

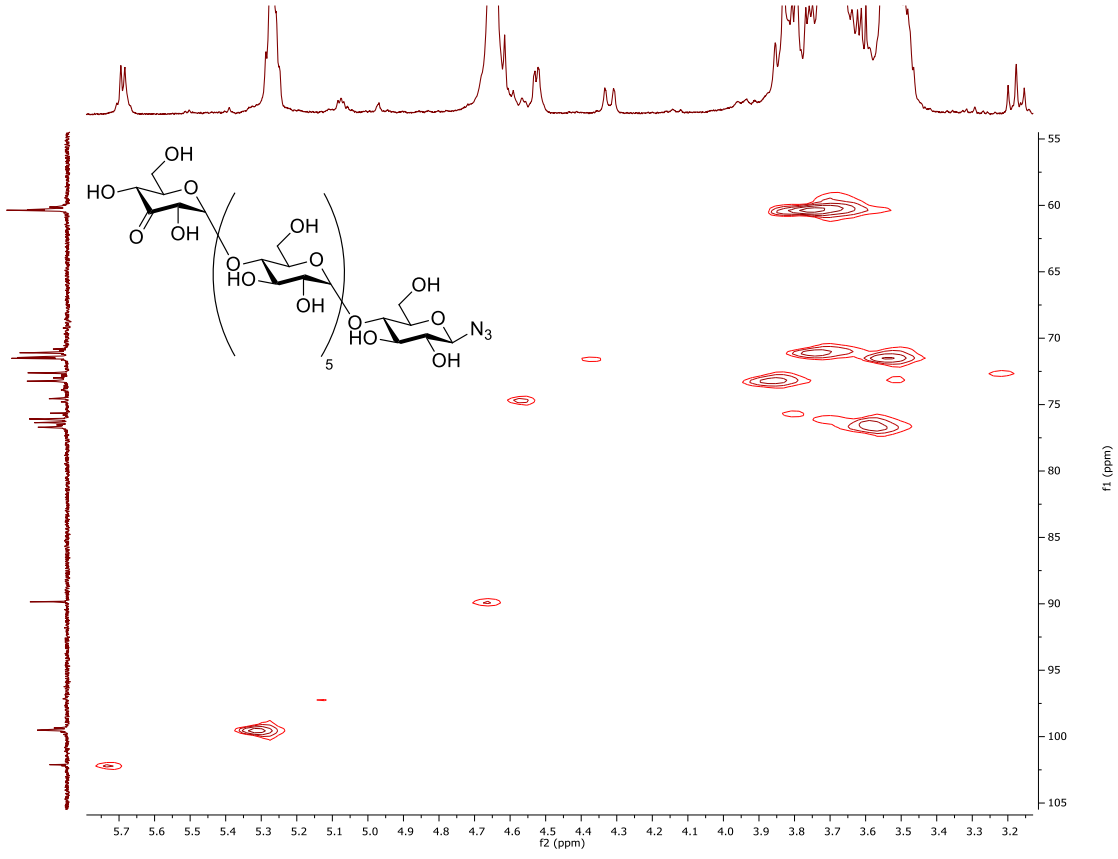


Figure 105, HMQC of β-D-3-ketomaltoheptaosyl azide

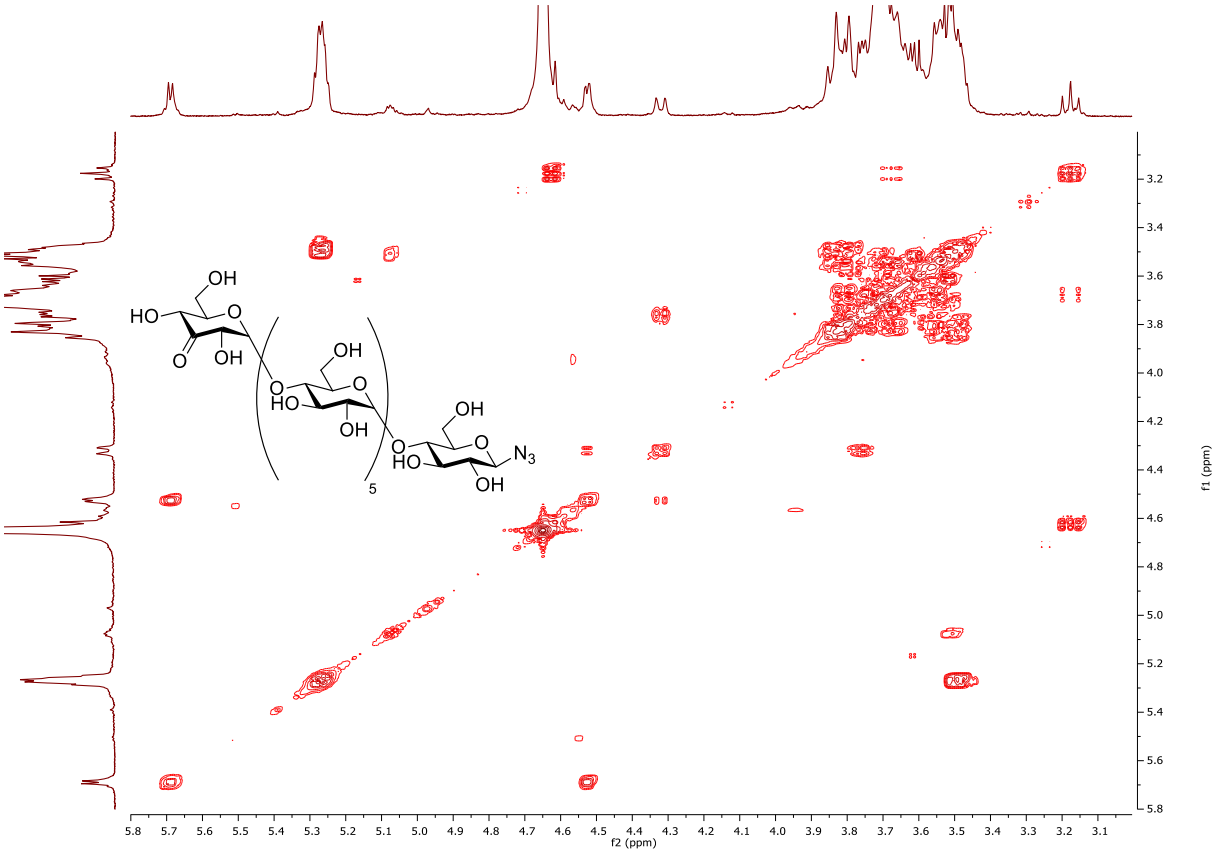


Figure 106, COSY of β-D-3-ketomaltoheptaosyl azide

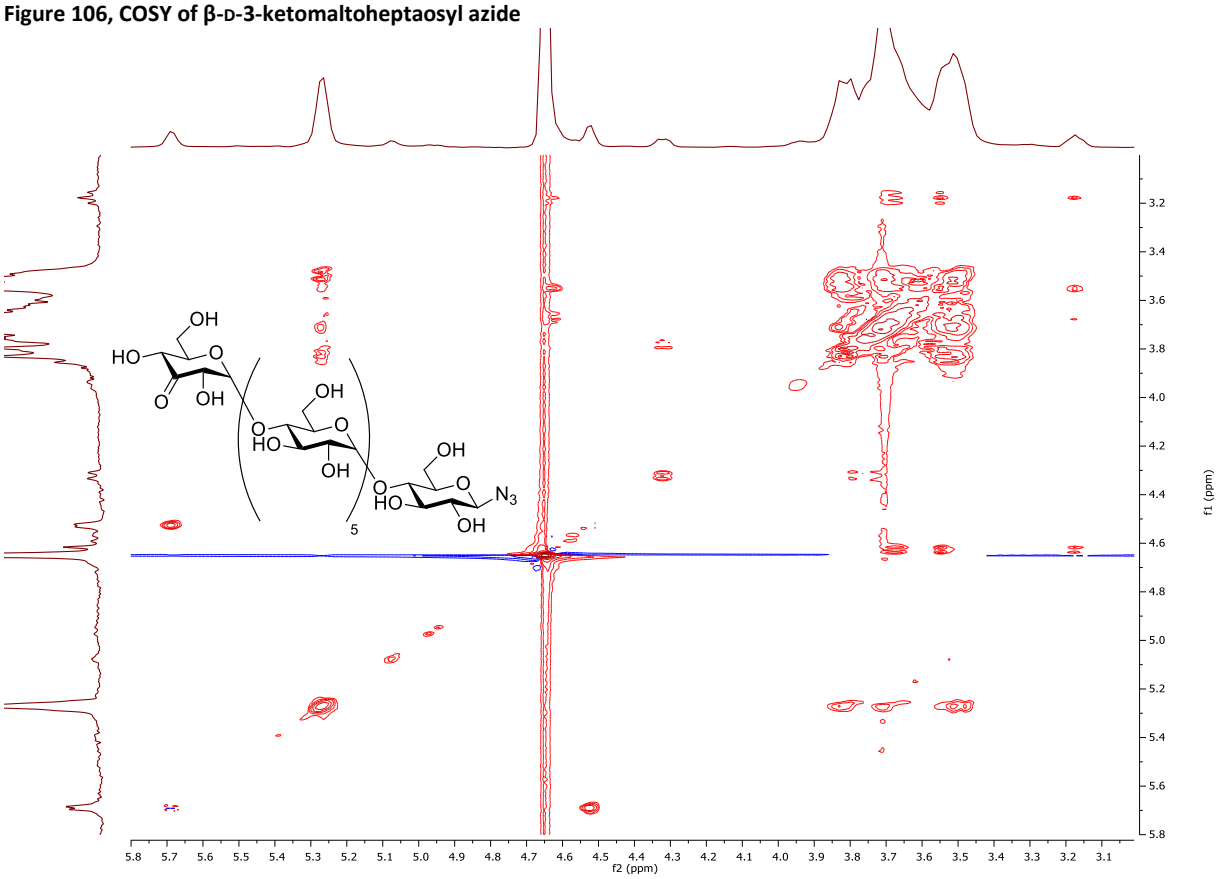


Figure 107, TOCSY of β-D-3-ketomaltoheptaosyl azide

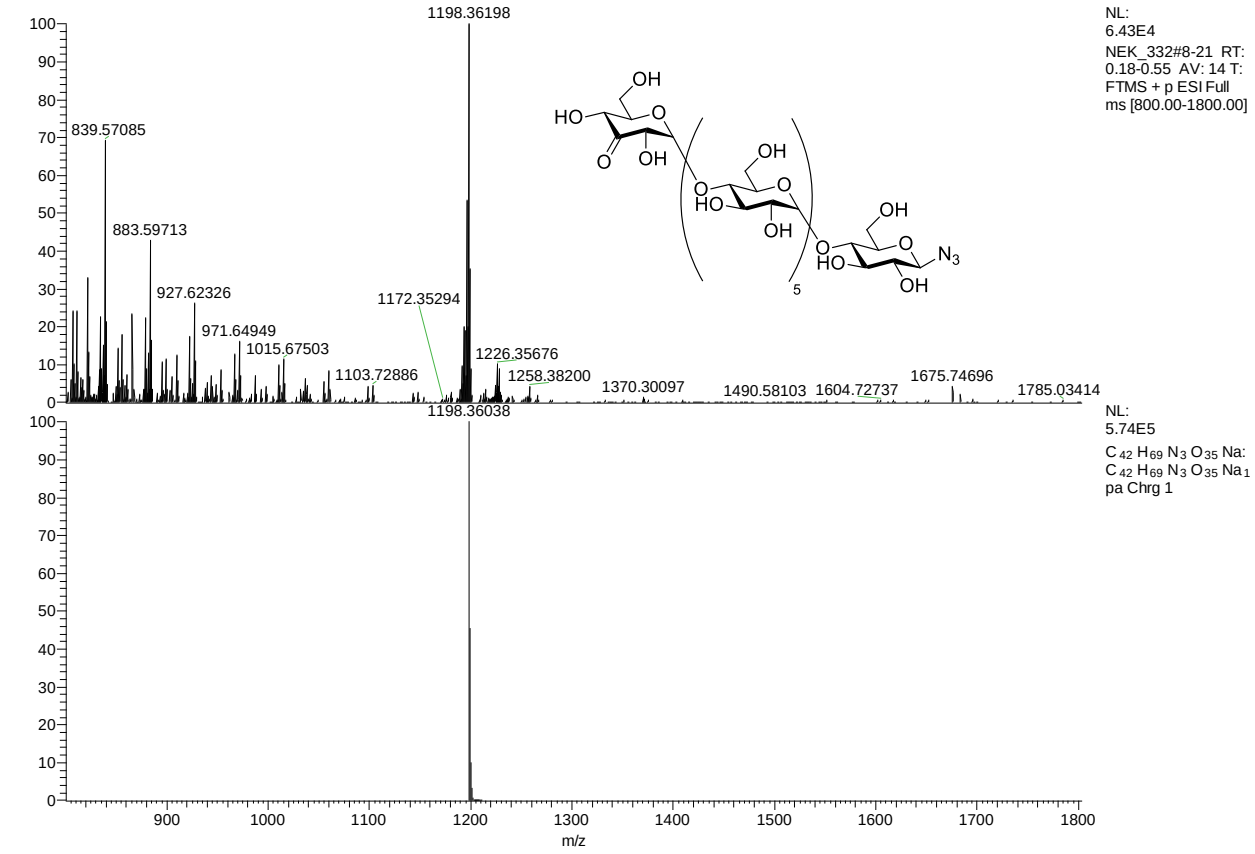


Figure 108, HRMS of β-D-3-ketomaltoheptaosyl azide

Keto-sucrose

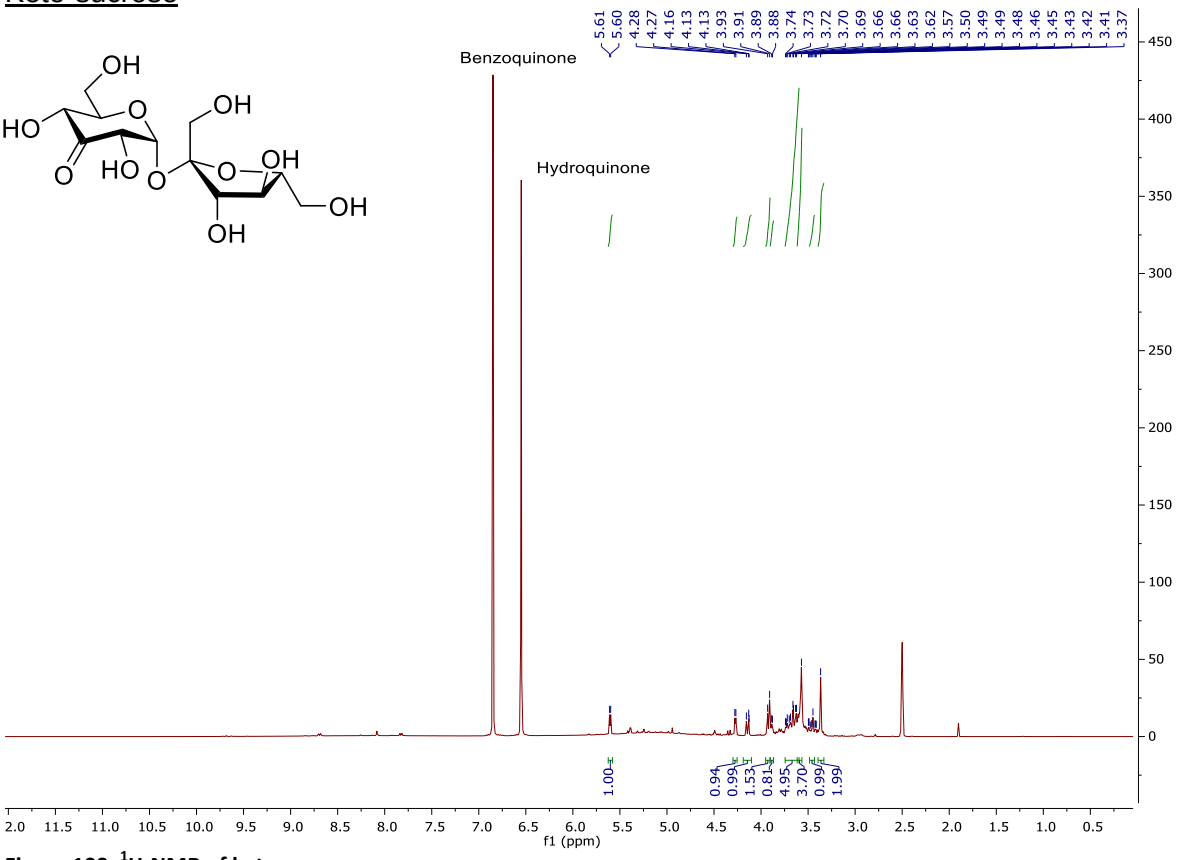


Figure 109, ^{1}H-NMR of keto-sucrose

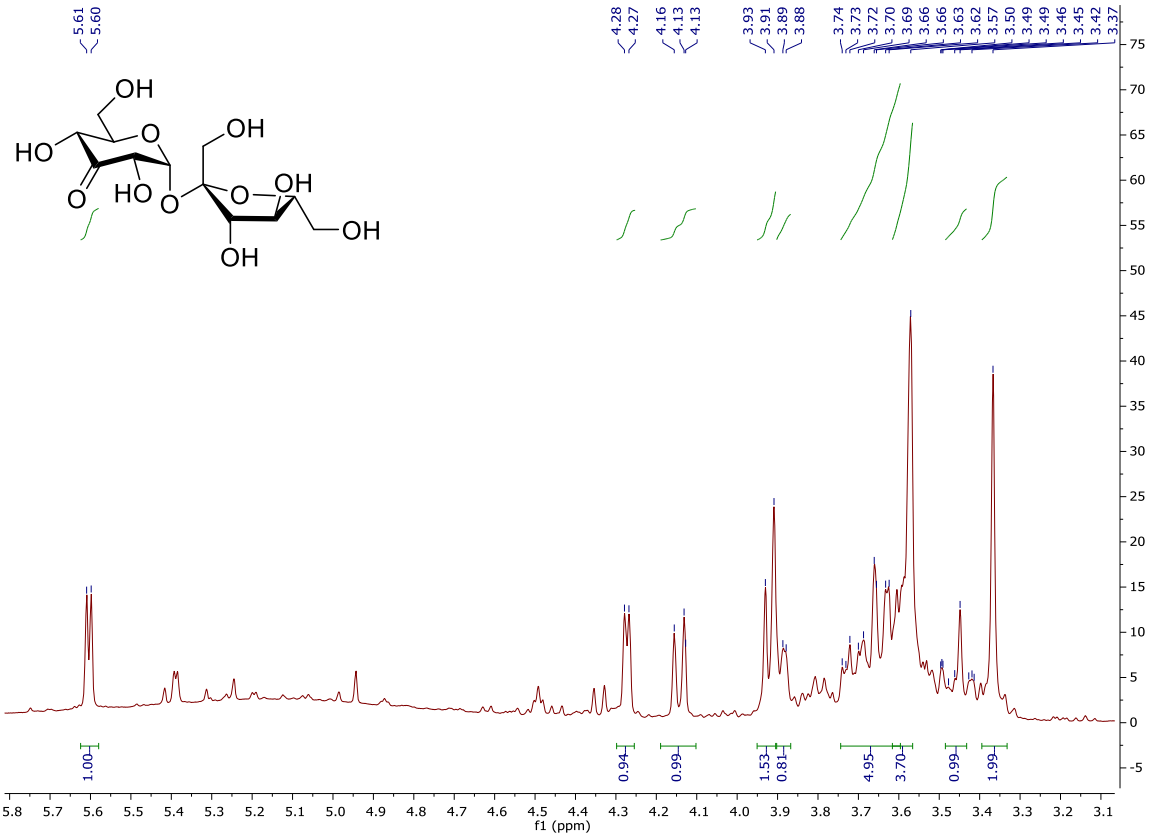


Figure 110, zoom of ^{1}H-NMR of keto-sucrose

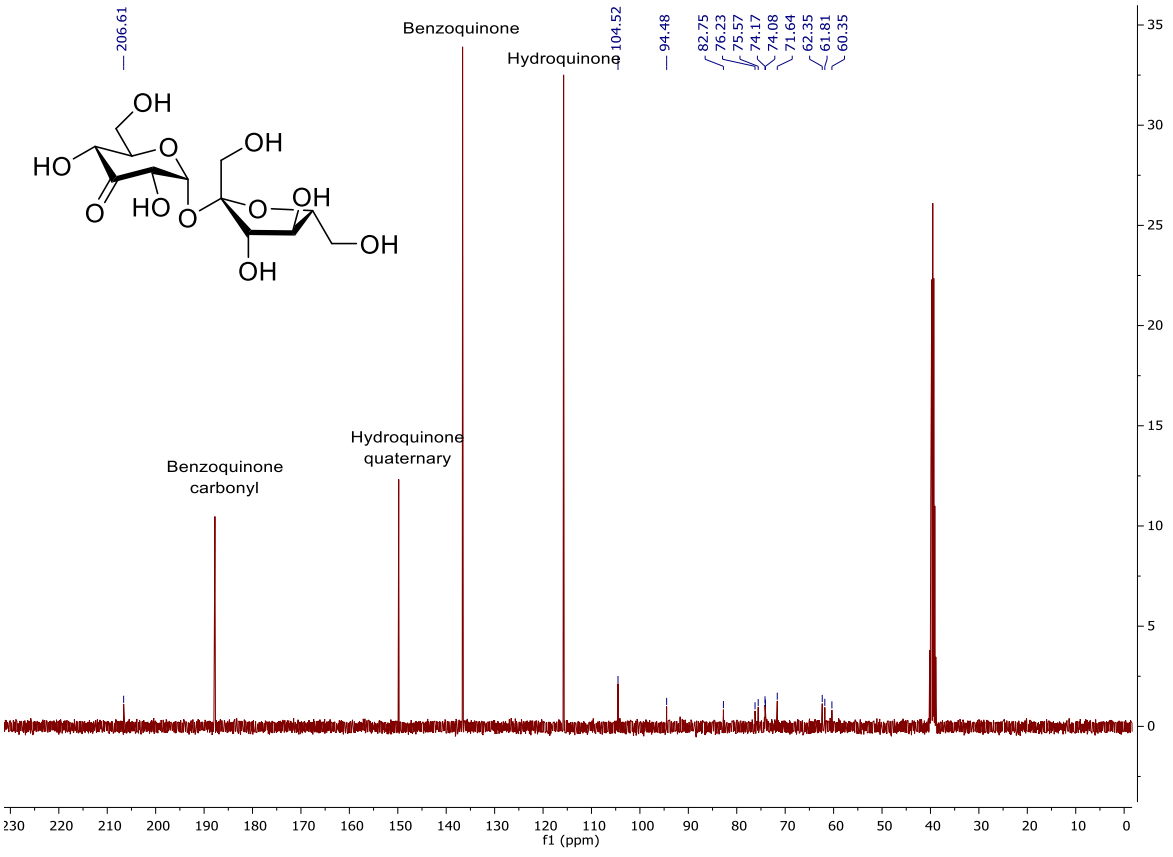


Figure 111, ^{13}C-NMR of keto-sucrose

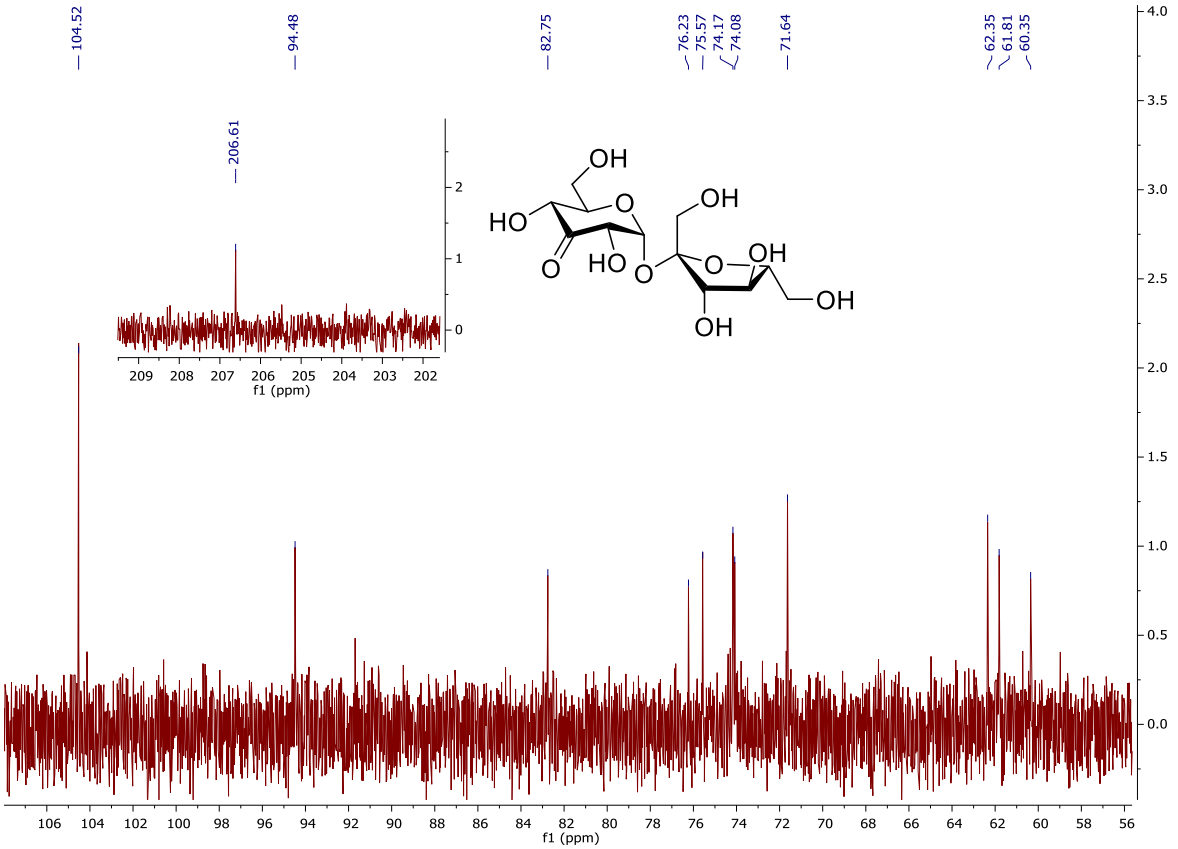


Figure 112, zoom of ^{13}C-NMR of keto-sucrose