Supporting Information

Stereoselective Protection-Free Modification of 3-Keto-Saccharides

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1. General Information

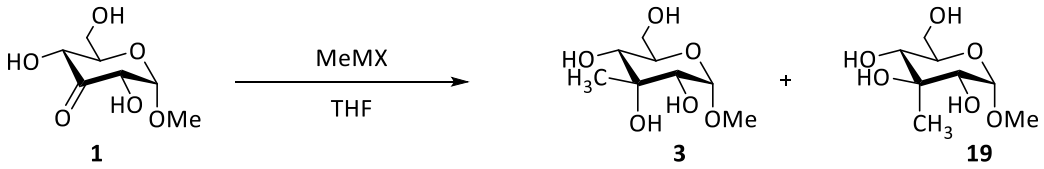
All solvents used for extraction, filtration and chromatography were of commercial grade, and used without further purification. [(neocuproine)PdOAc]$_2$OTf$_2$ was prepared according to literature procedure.[1] Benzoquinone was purified by recrystallization from ethanol (15 g *p*-benzoquinone from 45 mL). Celite (Celite® 545) was purchased from Merck. The palladium on carbon was supplied by Alfa Aesar (Palladium, 10% on carbon, Type 487, dry) and activated charcoal was supplied by Sigma-Aldrich. Other reagents were purchased from Sigma-Aldrich, TCI, Fluorochem and Acros and were used without further purification.

Flash chromatography was performed manually with silica (SiliaFlash P60, 230-400 mesh, Silicycle) or spherical silica (SiliaSphere S10030M, Silicycle), or performed with automated column chromatography using a Reveleris flash chromatography system purchased from Buchi. The diol-coated silica flash columns were purchased from Grace (Reveleris Diol Flash Cartridges, 40 μm) or from BGB Analytics (BGB Scorpius Flash Cartridge, Diol 100Å, Spherical 30 μm). TLC was performed on Merck silica gel 60, 0.25 mm plates and visualization was done by staining with anisaldehyde stain (a mixture of AcOH (300 mL), H_2SO_4 (6 mL) and anisaldehyde (3 mL)) or potassium permanganate stain (a mixture of $KMnO_4$ (3 g), K_2CO_3 (10 g), and water (300 mL)).

^{1}H-, ^{13}C-NMR, NOESY were recorded on a Varian AMX400 (400, 100.6 MHz, respectively) or on a Bruker Avance NEO 600 (600, 150.9 MHz, respectively) at 25 ˚C using MeOD-*d4* or D_2O as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (MeOD-*d4*: δ3.31 for ^{1}H, δ 49.00 for ^{13}C, D_2O: δ 4.79 for ^{1}H, $CDCl_3$: δ 7.26 for ^{1}H, δ 77,16 for ^{13}C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, m = multiplet, br = broad), coupling constants J (Hz), and integration. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL. Optical rotations were measured on a Schmidt+Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL) at ambient temperature (±20 °C).

2. Optimization of Reactions

Table S1. Optimization of methyl addition[a]

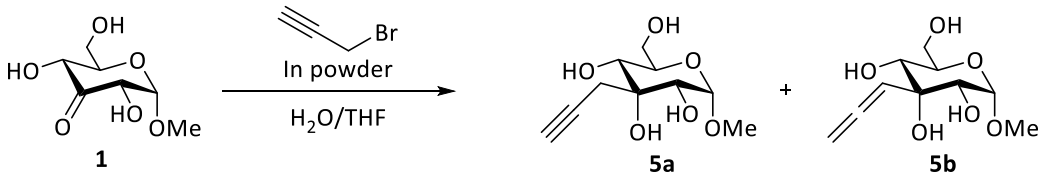


1 **3** **19**

Entry	Organometallic reagent (equiv.)	Purification method	Product ratio (**3**/**19**)	Isolated yield (%)[b]	Purity (wt%)[c]	Corrected yield (%)[d]
1	MeMgBr (7.5)	Silica column chromatography	92/8 [e] 93/7 [f]	264	20	53
2	MeLi (5)	-	80/20 [e]			
3	MeMgBr (5.5)	Precipitation of magnesium salts [g] followed by silica column chromatography	100/0 [f]	48	82	39
4	MeMgBr (5.5)	Ion Exchange [h] followed by silica column chromatography	100/0 [f]	68	78	53
5	**MeMgBr (5.8)**	**Diol-coated silica column chromatography**	**100/0** [f]	**52**	**92**	**48**

[a]Reactions were carried out with keto saccharide **1** (0.25-0.83 mmol) and MeMgBr or MeLi in THF (0.05 M) starting at -78 °C and slowly warming to rt. [b]Isolated yield based on **1**. [c]Determined by quantitative NMR. All impurities were NMR silent. [d]Isolated yield taking purity into account. [e]Determined prior purification by crude NMR. [f]Determined by NMR after purification. [g]Reaction mixture was conc. *in vacuo* and NaOH (2 equiv.) relative to magnesium in water was added. The suspension was centrifuged and supernatant was purified. [h]Reaction was quenched with HCl and the crude was purified by ion exchange (dowex 50WX8, 50-100 mesh, Ca^{2+} form[2]).

Table S2. Optimization of indium mediated propargylation[a]

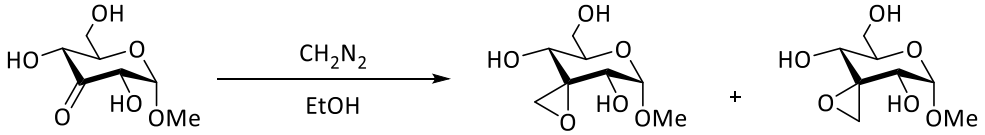


1 **5a** **5b**

Entry	H_2O/THF (v/v)	Indium powder (equiv.)	Propargyl bromide (equiv.)	Product ratio (**5a**/**5b**)[b]	Conversion (%)[b]	Yield (%)[c]
1	9/1	1.4	2.6	10/4	90	n.d. [d]
2	10/0	1	2	10/4	42	n.d. [d]
3	**19/1**	**3**	**3**	**10/2.5**	**96**	**80**

[a]Reactions were carried out with keto saccharide **1** (0.5 mmol), indium powder and propargyl bromide in water/THF (0.1 M) mixtures at rt for two days. [b]Determined by crude NMR. [c]Isolated yield based of **5a** and **5b**. [d]Not determined.

Table S3. Optimization of epoxidation with diazomethane[a]

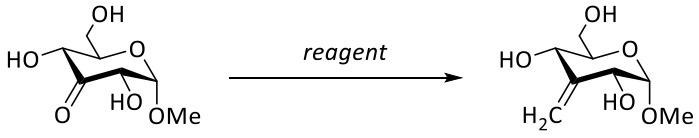


1 **7** **18**

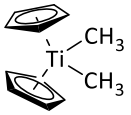
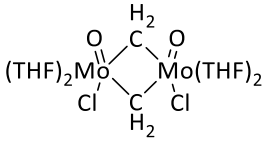
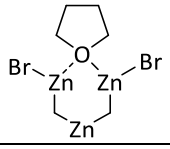
Entry	Solvent	product ratio (**7**/**18**)[b]
1	*i*-PrOH	52/48
2	EtOH	78/22
3	MeOH	86/14
4	**H_2O**[c]	**97/3**

[a]Reactions were carried out with keto saccharide **1** (0.13 or 0.25 mmol) in the indicated solvent and a solution of diazomethane in Et_2O was added at 0 °C. The mixtures were swirled to a homogeneous mixture and kept for 30 minutes at 0 °C. The Et_2O and residual diazomethane were removed by a stream of N_2. [b]Determined by crude NMR. [c]The water/Et_2O mixture was stirred vigorously.

Table S4. Overview of methylenations performed



1 **17**

Entry	Reagent		Result
1	Wittig olefination:	$Ph_3P{=}CH_2$	No product was isolated[a]
2	Peterson olefination:	1) TMS MgCl 2) NaH	9% yield over two steps[a]
3	Petasis olefination:		Compound **17** was not observed and compound **28** was isolated instead.[a]
4	Kauffmann olefination:		15% yield, purity: 32 wt%[a]
5	**Nysted olefination:**		**55% yield**[a]

[a]See Experimental Procedures and Characterization for a detailed procedures and product characterization.

3. Labeling of MBP

Proteins

Maltose binding protein (MBP, MalE(T36C/S352C), 252 µM, in 50 mM Tris-Hcl (pH 8.0); 50 mM KCl; 50% glycerol; 1 mM DTT) was produced in *Escherichia coli* as described previously.[3] Prior each labeling experiment, a new working solution of MBP was prepared by diluting an aliquot of the original stock solution (250 µM) with Tris-buffer (50 mM Tris-HCl (pH 8.0)). Bovine Serum Albumin (BSA) was purchased from Sigma-Aldrich and was dissolved in Tris-buffer (50 mM Tris-HCl (pH 8.0)) prior labeling experiment.

SDS-PAGE, fluorescence scanning

Labeling experiments were resolved on 12% TRIS-glycine type SDS-PAGE according to standard literature procedures. Gels were prepared using acrylamide-bis ready-to-use solution 40% (37.5:1) (Merck Millipore) and separated on a Mini-PROTEAN Tetra cell (Bio-Rad). In-gel fluorescence scanning of the SDS-PAGE gels was performed on a Typhoon FLA 9500 (GE Healthcare) using the Cy2-settings for BODIPY (laser excitation at 473 nm and emission filter 515-545 nm).

Bio-reagents

Stock solutions of SDS (20% w/v) and maltopentaose were prepared in water and stored at rt. Stock solutions of 3,3'-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (probe **12**, 50 mM), iodoacetamide (IAA; 100 mM), THPTA/$CuSO_4$ (20 mM) were prepared in water and stored at -20 °C. Solutions of sodium ascorbate (20 mM) in water were always prepared fresh from the salt. A stock solution of BODIPY-alkyne[4] (5 mM) was prepared in DMSO and stored at -20 °C. Click mixtures for CuAAC reactions were prepared as follows: BODIPY-alkyne (16 μL, 5 mM), DMSO (48 μL), THPTA/$CuSO_4$ (20 μL, 20 mM) and water (20 μL) were added together in this exact order, followed by addition of sodium ascorbate (20 μL, 20 mM; freshly prepared).

Labeling of MBP with a different concentrations of probe 12

To MBP (9 μL, 11 μM) was added water (1 μL, negative control) or probe **12** (1 μL of a 10× stock solution, range of concentrations: 100 μM, 200 μM, 500 μM, 1 mM, 10 mM and 50 mM). The mixtures were incubated for 19 h at rt followed by addition of the SDS solution (0.5 μL) and IAA solution (1 μL). The mixtures were incubated for 1 h, followed by addition of the BODIPY-alkyne click mixture (5 μL) and additional incubation for 1 h. Subsequently, reducing sample buffer (5.5 μL, 4×) was added and half of the samples (11 μL) were loaded and resolved on SDS-PAGE. In-gel fluorescence scanning showed concentration dependent labeling of MBP by **12** (figure S1).

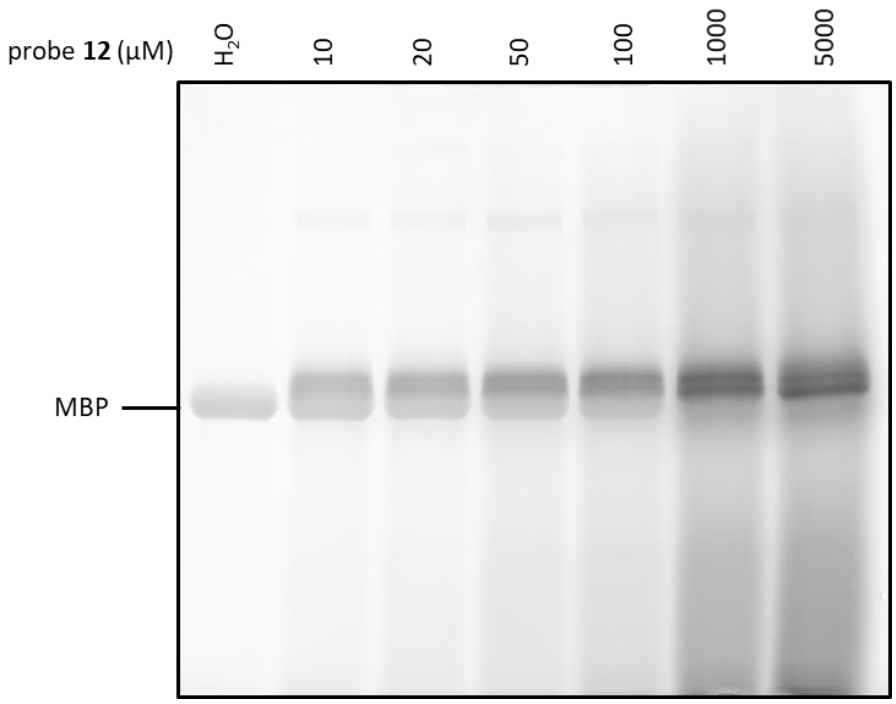


Figure S1 – Concentration dependent labeling of MBP

Control experiments of labeling MBP by probe 12

For the control experiments, each mixture contained MBP (4.5 µL, 22 µM) and BSA (4.5 µL, 22 µM). SDS solution (0.5 µL) was added to mixtures 2 and 4, and IAA solution (1 µL) was added to mixtures 3 and 4. These were then incubated for 1 h. Maltopentaose was added to mixtures 5 (0.5 µL, 10 mM) and 6 (0.5 µL, 100 mM), followed by addition of probe **12** (1 µL, 500 µM) to mixtures 1-6. Water (1 µL) was added to mixture 7 and solely contained MBP and BSA. All were incubated for 19 h at rt followed by addition of the SDS solution (0.5 µL) and/or the IAA solution (1 µL) to the remaining Eppendorf test tubes without SDS and/or IAA. The mixtures were incubated for 30 minutes and diluted with water (0.5 µL or 1 µL) to an equal volume (12.5 µL). The BODIPY-alkyne click mixture (5 µL) was added and the mixtures were incubated again for 1 h. Subsequently, reducing sample buffer (5.8 µL, 4×) was added and the samples (2.5 µL) were loaded and resolved on SDS-PAGE. In-gel fluorescence scanning showed that MBP was labeled by **12** in an affinity based manner (figure S2).

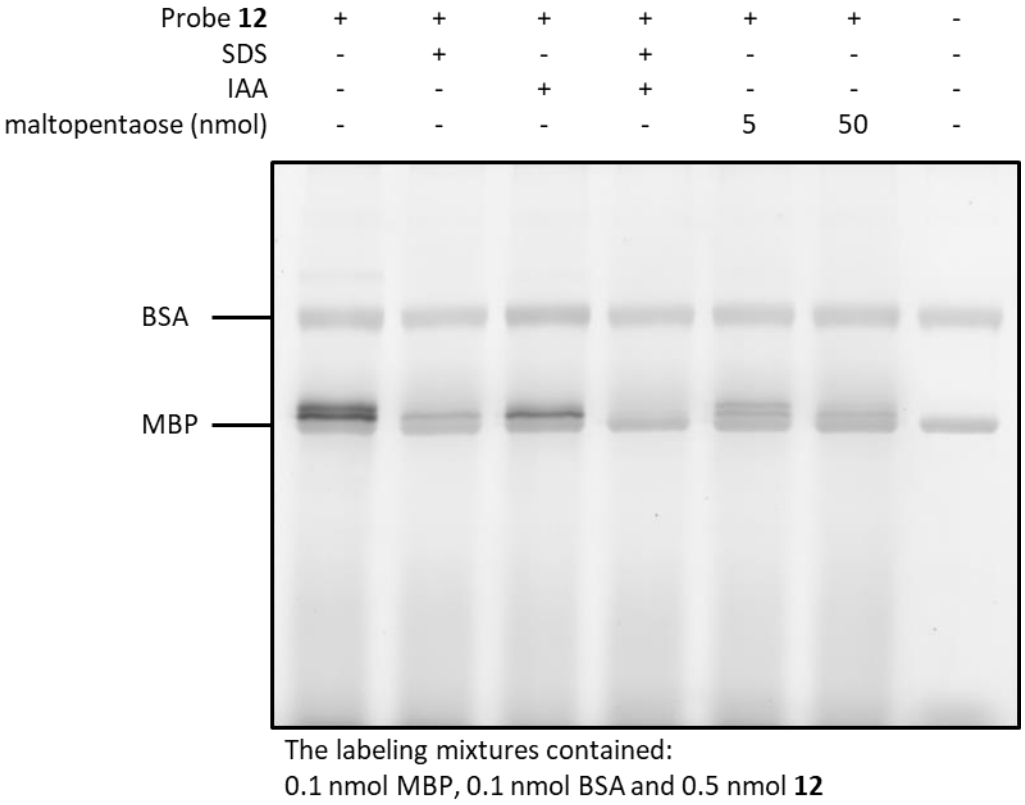


Figure S2 – Control experiments of labeling MBP by probe **12**

In all cases, the fluorescent signal for BSA is comparable to the sample treated with the click mixture in absence of the probe. Denaturation of MBP with SDS showed a significant decrease in labelling (lane 2). Iodoacetamide decreased labelling to a certain extent (lane 3), which indicates that amines can probably react with the probe as well. A combination of SDS and IAA completely removed labelling (lane 4). Competition experiments with maltopentaose showed decreasing fluorescence as well (lanes 5 and 6). These results indicate that MBP could indeed be labeled in an affinity based manner.

4. X-ray crystallography

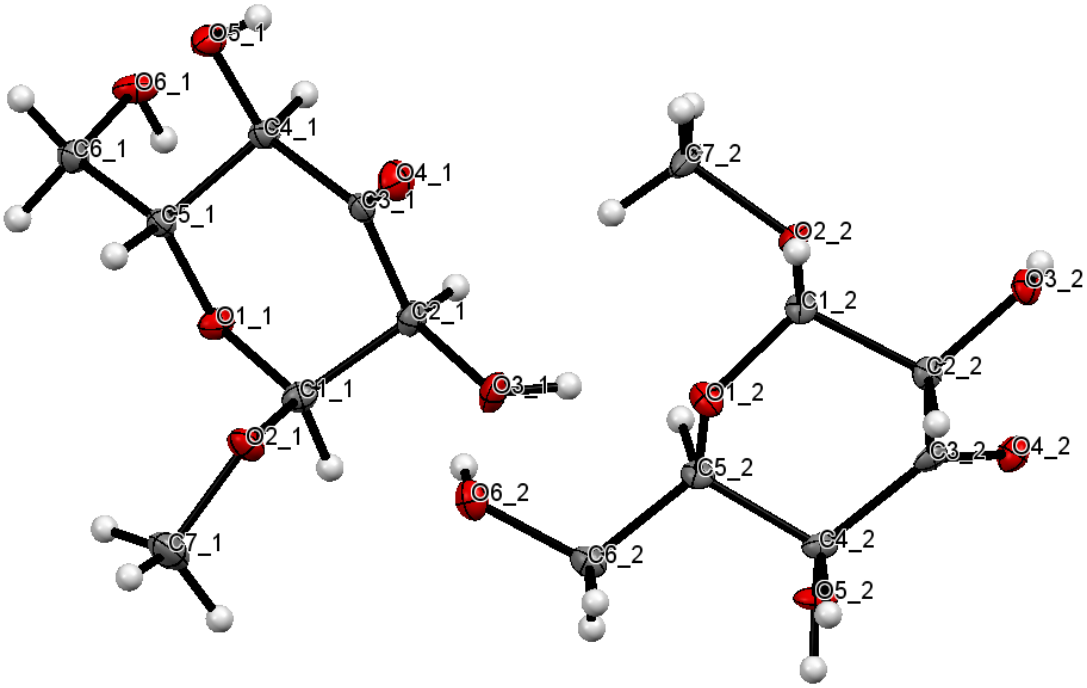


Figure S3 – Molecular structure of methyl α-D-ribo-hex-3-ulopyranoside (**1**), showing 50% probability ellipsoids.

A single crystal of compound **1** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[5] The final unit cell was obtained from the xyz centroids of 9777 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*[6] and refinement of the structure was performed using *SHELXL*.[7] The carbon-bound hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The hydrogen atoms of the OH groups were located from the difference Fourier map and their position refined; their isotropic displacement parameter was related to that of their carrier atoms. The absolute structure was chosen based on the known configuration of the starting material. The asymmetric unit consists of two independent molecules that interact via hydrogen-bonding between OH moieties. Crystal data and details on data collection and refinement are presented in Table S5.

Table S5. Crystallographic data for **1**

chem formula	C7 H12 O6
M_r	192.17
cryst syst	orthorhombic
color, habit	colorless, block
size (mm)	0.49 x 0.45 x 0.12
space group	$P2_12_12_1$
a (Å)	7.6855(3)
b (Å)	8.7667(4)
c (Å)	25.0098(11)
V (Å^3)	1685.07(13)
Z	8
ρ_{calc}, g.cm^{-3}	1.515
μ(Mo K$\overline{\alpha}$), cm^{-1}	0.134
F(000)	816
temp (K)	100(2)
θ range (deg)	3.111 – 28.749
data collected (h,k,l)	-10:10, -11:11, -33:33
no. of rflns collected	30948
no. of indpndt reflns	4367
observed reflns	4241($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	2.59
wR(F^2) (%)	6.64
GooF	1.095
Weighting a,b	0.0360, 0.3582
params refined	255
restraints	0
min, max resid dens	-0.221, 0.275

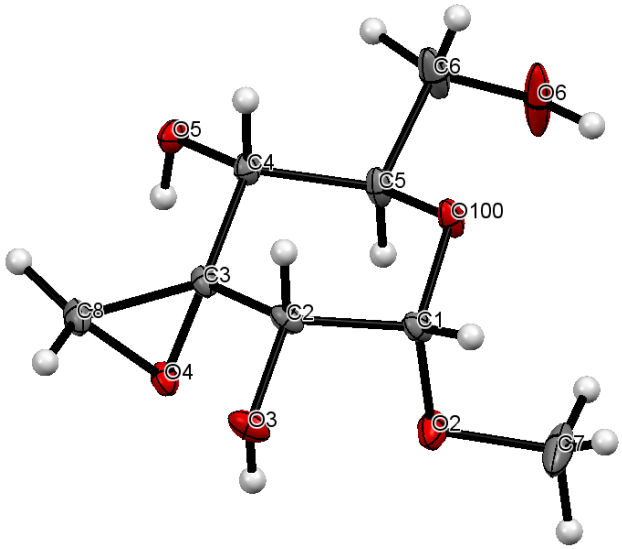


Figure S4 – Molecular structure of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (**7**), showing 50% probability ellipsoids.

A single crystal of compound **7** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[5] The final unit cell was obtained from the xyz centroids of 9954 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*[6] and refinement of the structure was performed using *SHELXL*.[7] The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The absolute structure was chosen based on the known configuration of the sugar unit. Crystal data and details on data collection and refinement are presented in Table S6.

Table S6. Crystallographic data for **7**

chem formula	C8 H14 O6
M_r	206.19
cryst syst	tetragonal
color, habit	colorless, needle
size (mm)	0.58 x 0.20 x 0.20
space group	I4
a (Å)	19.4264(9)
b (Å)	19.4264(9)
c (Å)	4.9922(2)
V (Å^3)	1883.98(19)
Z	8
ρ_{calc}, g.cm^{-3}	1.454
μ(Mo K$\overline{\alpha}$), cm^{-1}	0.126
F(000)	880
temp (K)	100(2)
θ range (deg)	3.316 – 28.745
data collected (h,k,l)	-26:26, -26:26, -6:6
no. of rflns collected	17666
no. of indpndt reflns	2433
observed reflns	2381 ($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	2.69
wR(F^2) (%)	7.27
GooF	1.055
Weighting a,b	0.0343, 0.7468
params refined	134
restraints	1
min, max resid dens	-0.223, 0.445

5. Experimental Procedures and Characterization

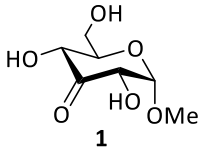
Purity determination with quantitative NMR.

The purity of a sample was determined by dissolving an accurately weighed sample (3.00-5.00 mg) and accurately weighed internal calibrant (IC) 1,3,5-trimethoxybenzene (3.00-5.00 mg, 99.96%) in MeOH-*d4* (0.6-0.7 mL). Thereafter a ^{1}H-NMR was taken with 16 scans (nt=16) and a d1 value of 60 seconds (d1=60). The general calculation of purity (*P*) is as follows:

$$P[\%] = \frac{n_{\mathrm{IC}} \cdot \mathrm{Int_t} \cdot \mathrm{MW_t} \cdot m_{\mathrm{IC}}}{n_{\mathrm{t}} \cdot \mathrm{Int_{IC}} \cdot \mathrm{MW_{IC}} \cdot m_{\mathrm{s}}} \cdot P_{\mathrm{IC}}$$

where Int is the integral, MW is the molecular weight, m is the mass, n is the number of protons, *P* is the purity (in %), IC is the internal calibrant, s is the sample, and t is the target analyte/molecule. For a more detailed description see reference.[8]

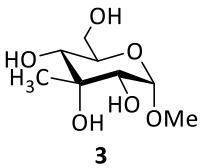
Methyl α-D-*ribo*-hex-3-ulopyranoside (1)



1

Methyl α-D-glucopyranoside (5.00 g, 25.7 mmol, 1 equiv.) and *p*-benzoquinone (2.92 g, 27.0 mmol, 1.05 equiv.) were placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (103 mL, 0.25 M) was added and, after stirring for 15 min, [(2,9-dimethyl-1,10-phenanthroline)Pd(μ-OAc)]$_2$(OTf)$_2$ (135 mg, 129 μmol, 0.5 mol%) was added to the orange solution. No efforts were made to exclude water or oxygen from the reaction. The reaction mixture became darker over time and, after 1 h, the starting material was consumed (TLC, 15% MeOH in DCM). Celite (20 g) was added to the black reaction mixture and the slurry was concentrated to dryness at 40 °C. The resulting green solid Celite-product mixture was pulverized and placed on top of a silica column made of silica (200 g, column volume: ~420 mL, bed volume: 470 mL). Hydroquinone was eluted with 10% pentane in EtOAc (1 L) and subsequent elution with 3% MeOH in EtOAc (2 L) provided keto saccharide **1** (4.56 g, 92%) as a white solid. Some ketone **1** (360 mg) was recrystallized from 8% MeOH in EtOAc (8 mL) to obtain crystals suitable for X-ray analysis.**^{1}H-NMR** (400 MHz, MeOD-*d4*) δ 5.05 (d, J = 4.2 Hz, 1H, H-1), 4.40 (dd, J = 4.3, 1.5 Hz, 1H, H-2), 4.23 (dd, J = 9.7, 1.5 Hz, 1H, H-4), 3.88 (dd, J = 12.0, 2.2 Hz, 1H, H-6a), 3.80 (dd, J = 12.1, 4.6 Hz, 1H, H-6b), 3.65 (ddd, J = 9.7, 4.5, 2.2 Hz, 1H, H-5), 3.40 (s, 3H, OCH_3); **^{13}C-NMR** (100 MHz, MeOD-*d4*) δ 207.0 (C-3), 103.8 (C-1), 76.7 (C-5), 76.1 (C-2), 73.3 (C-4), 62.5 (C-6), 55.7 (OCH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{12}O_6Na^+$: 215.0526; Found: 215.0525; **mp** 120-121 °C (from EtOAc/MeOH).

Methyl 3-*C*-methyl-α-D-allopyranoside (3)

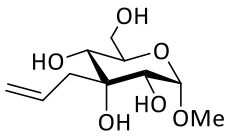


3

Route 1: Keto saccharide **1** (160 mg, 0.83 mmol) was placed in a Schlenk tube and kept under a nitrogen atmosphere using standard Schlenk techniques. Dry THF (17 mL, 0.05 M) was added and the mixture was stirred at rt until everything was dissolved. The solution was cooled to -78 °C and MeMgBr (4.8 mL, 1 M in THF, 5.8 equiv.) was added dropwise over 5 minutes. The suspension was stirred for an additional 30 minutes before it was allowed to warm to rt. The reaction was quenched by adding H_2O (0.15 mL) and transferred with MeOH to a bigger flask. The mixture was concentrated *in vacuo*, loaded onto Celite (2.6 g) and purified by automated column chromatography (40 g Reveleris diol-column, DCM/MeOH gradient: 0% MeOH for 3 CV, 0% to 4% in 4 CV, 4% to 5% in 2 CV and 5% for 10 CV). The allose diastereoisomer (**3**) started to elute at 4% MeOH, followed by elution of the glucose diastereoisomer (**19**) and salts at 5% MeOH. Methyl 3-*C*-methyl-α-D-allopyranoside (**3**) was obtained diastereomerically pure as a white solid (90 mg, 52% yield, purity: 92 wt%).

Route 2: Epoxide **7** (102 mg, 0.50 mmol) was dissolved in MeOH/H_2O (4/1 v/v, 5 mL, 0.1 M). The solution was degassed by two freeze-pump-thaw cycles and palladium on carbon (53 mg, 10 wt% Pd) was added. The black suspension was degassed by one additional freeze-pump-thaw cycle and a hydrogen atmosphere was applied. The mixture was stirred at rt and the starting material was consumed after 16 h. The suspension was filtered over Celite and the Celite was washed with MeOH. The combined filtrates were concentrated *in vacuo* to obtain **3** (103 mg, quantitative yield) as a white solid.
^{1}H-NMR (600 MHz, MeOD-*d4*) δ 4.69 (d, J = 3.8 Hz, 1H, H-1), 3.84 (dd, J = 11.7, 2.3 Hz, 1H, H-6a), 3.72 (dd, J = 11.7, 5.5 Hz, 1H, H-6b), 3.65 (ddd, J = 10.0, 5.4, 2.2 Hz, 1H, H-5), 3.44 (s, 3H, OCH_3), 3.38 (d, J = 3.8 Hz, 1H, H-2), 3.25 (d, J = 10.1 Hz, 1H, H-4), 1.28 (s, 3H, CH_3); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.7 (C-1), 75.3 (C-3), 72.6 (C-2), 71.7 (C-4), 70.5 (C-5), 63.0 (C-6), 56.1 (OCH_3), 21.8 (CH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{16}O_6Na^+$: 231.0839; Found: 231.0839.

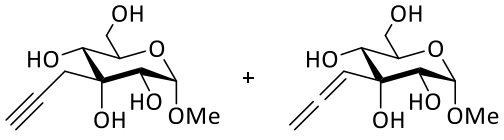
Methyl 3-*C*-allyl-α-D-allopyranoside (4)



4

A mixture of H_2O/THF (9/1 v/v, 7.6 mL) was added to **1** (146 mg, 0.76 mmol) and indium powder (87 mg, 0.76 mmol, 1 equiv.), followed by addition of allylbromide (0.10 mL, 1.14 mmol, 1.5 equiv.). The resulting grey suspension was stirred for 18 h at rt. Upon completion the mixture was concentrated *in vacuo*, loaded onto Celite (0.4 g) and purified by automated column chromatography (12 g Reveleris diol-column, DCM/MeOH gradient: 0% MeOH for 3 CV, 0% to 3% in 3 CV and 3% for 8 CV). Allyl product **4** (151 mg, 85% yield, purity: 95 wt%) was obtained as a white solid. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 5.83 (ddt, J = 17.8, 10.2, 7.7 Hz, 1H, H_2C=C<u>H</u>–), 5.18 (ddt, J = 17.1, 2.5, 1.3 Hz, 1H, <u>H</u>$_2$C=CH–), 5.14 – 5.10 (m, 1H, <u>H</u>$_2$C=CH), 4.70 (d, J = 3.9 Hz, 1H, H-1), 3.86 – 3.81 (m, 1H, H-6a), 3.73 – 3.66 (m, 2H, H-6b + H-5), 3.47 (d, J = 3.9 Hz, 1H, H-2), 3.45 (s, 3H, OCH_3), 3.38 (d, J = 9.8 Hz, 1H, H-4), 2.53 – 2.42 (m, 2H, H_2C=CH–C<u>H</u>$_2$–); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 134.6 (H_2C=<u>C</u>-H–), 119.5 (H_2<u>C</u>=CH–), 102.0 (C-1), 77.4 (C-3), 70.3 (C-5), 69.0 (C-2), 67.8 (C-4), 63.0 (C-6), 56.1 (OCH_3), 38.1 (H_2C=CH–<u>C</u>H_2–); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{18}O_6Na^+$: 257.0996; Found: 257.0995.

Methyl 3-*C*-propargyl-α-D-allopyranoside (5a) & Methyl 3-*C*-allenyl-α-D-allopyranoside (5b)

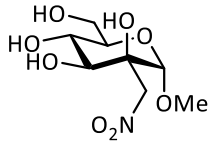


5a **5b**

A mixture of H_2O/THF (19/1 v/v, 11 mL) was added to **1** (107 mg, 0.557 mmol) and indium powder (192 mg, 1.67 mmol, 3 equiv.), followed by addition of propargylbromide (0.19 mL, 1.67 mmol, 3 equiv.). The resulting grey suspension was stirred for 42 h at rt. Upon completion the mixture was concentrated *in vacuo*, loaded onto Celite (0.7 g) and purified by automated column chromatography (20 g BGB diol-column, DCM/MeOH gradient: 0% MeOH for 3 CV, 0% to 3% in 3 CV, 3% for 6 CV and 4% for 8 CV). The product (104 mg, 80% yield) was a white solid and obtained as an inseparable mixture of methyl 3-*C*-(propargyl)-α-D-allopyranoside (**5a**) and methyl 3-*C*-(allenyl)-α-D-allopyranoside (**5b**) with a ratio of 4/1, respectively. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 5.27 (t, J = 6.8 Hz, 0.25H, H_2C=C=C<u>H</u>–), 4.90 (d, J = 6.8 Hz, 0.5H, <u>H</u>$_2$C=C=CH–), 4.74 (d, J = 3.9 Hz, 1H, **5a**:H-1), 4.71 (d, J = 4.0 Hz, 0.25H, **5b**:H-1), 3.88 – 3.83 (m, 1.25H, H-6a), 3.81 (d, J = 4.0 Hz, 1H, **5a**:H-2), 3.75 – 3.67 (m, 3.5H, **5a**:H-4 + H-5 + H-6b), 3.54 (d, J = 4.0 Hz, 0.25H, **5b**:H-2), 3.45 (s, 3H, **5a:**OCH_3), 3.46 – 3.40 (m, 1H, **5b**:H-4 + **5b**:OCH_3), 2f.62 (dd, J = 16.4, 2.7 Hz, 1H, HC≡C–C<u>H</u>$_2$), 2.58 (dd, J = 16.4, 2.7 Hz, 1H, HC≡C–C<u>H</u>$_2$), 2.35 (t, J = 2.7 Hz, 1H, <u>H</u>C≡C–CH_2); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 208.3 (H_2C=<u>C</u>=CH–), 101.8 (**5a**:C-1), 101.5 (**5b**:C-1), 95.5 (H_2C=C=<u>C</u>H–), 81.3 (HC≡<u>C</u>–CH_2), 78.2 (H_2<u>C</u>=C=CH–), 77.1 (**5a**:C-3), 76.8 (**5b**:C-3), 72.3 (**5b**:C-2), 72.0 (H<u>C</u>≡C–CH_2), 71.2 (**5b**:C-4), 70.4 (**5a**:C-5), 70.3 (**5b**:C-5), 68.9 (**5a**:C-2), 67.7 (**5a**:C-4), 63.0 (**5a**:C-6), 62.9 (**5b**:C-

6), 56.1 (**5a**:OCH_3), 56.1 (**5b**:OCH_3), 23.9 (HC≡C–$\underline{C}H_2$); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{16}O_6Na^+$: 255.0839; Found: 255.0841.

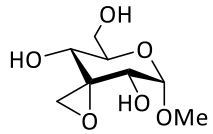
Methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (6)



6

Keto saccharide **1** (363 mg, 1.88 mmol, 1 equiv.) and DBU (0.31 mL, 2.1 mmol, 1.1 equiv.) were stirred at rt for three days in nitromethane (9.4 mL, 0.2 M). The mixture was cooled to 0 °C and acetic acid (0.14 mL) was added. The mixture was loaded on Celite (1.2 g) and purified by column chromatography (60 mL silica, eluent: 1.5 L 4% MeOH in DCM). The product (**6**, 145 mg, 30%) was isolated as an orange syrup. **^{1}H-NMR** (600 MHz, MeOD-d_4) δ 4.80 (s, 1H, H-1), 4.77 (s, 2H, CH_2NO_2), 3.83 (dd, *J* = 11.8, 2.2 Hz, 1H, H-6a), 3.73 (dd, *J* = 11.8, 5.6 Hz, 1H, H-6b), 3.62 (dd, *J* = 9.8, 9.1 Hz, 1H, H-4), 3.56 (ddd, *J* = 10.0, 5.4, 2.2 Hz, 2H, H-5), 3.47 (d, *J* = 8.9 Hz, 1H, H-3), 3.45 (s, 3H, OCH_3). **^{13}C-NMR** (151 MHz, MeOD) δ 101.6 (C-1), 79.4 (CH_2NO_2), 75.5 (C-2), 73.9 (C-5), 73.3 (C-3), 69.0 (C-4), 62.7 (C-6), 55.8 (OCH_3). **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{15}NO_8Na^+$: 276.0690; Found: 276.0690.

Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (7)



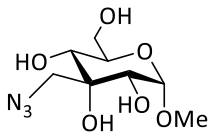
7

Note: Diazomethane is potentially explosive and precautions should be taken, such as working behind a blast shield and using glassware without scratches and without ground joints.

General preparation of diazomethane: The diazomethane was distilled using the Aldrich Mini Diazald®Apparatus.[9] A 100 mL receiving flask was attached to the apparatus and its cold finger was filled with acetone/dry ice slurry and the receiving flask was cooled with an acetone/dry ice bath as well. The apparatus was charged with a solution of KOH (5 g) in water (8 mL) and followed by addition of ethanol (96%, 10 mL). The mixture was heated to 65 °C with a water bath, followed by dropwise addition of a Diazald (5.0 g, 23 mmol) solution in Et_2O (45 mL) over a period of 30 minutes. After full addition, the distillation was continued by slowly adding Et_2O (5 mL). The distillate (~50 mL ethereal diazomethane) was kept in the acetone/dry ice bath and used the same day after preparation.

Keto saccharide **1** was epoxidized by diazomethane in two batches. Batch 1: Ethereal diazomethane (50 mL) was added to a solution of **1** (650 mg, 3.38 mmol) in H_2O (17 mL) in an Erlenmeyer (100 mL) at 0 °C. Batch 2: Ethereal diazomethane (50 mL) was added to a solution of **1** (700 mg, 3.64 mmol) in H_2O (18 mL) in an Erlenmeyer (100 mL) at 0 °C. Both yellow water/Et_2O mixtures were stirred for 1 h at 0 °C by the time which the yellow color had disappeared. Most of the Et_2O was removed by a stream of N_2 and thereafter the mixtures were concentrated *in vacuo* (at 40 °C). The white solids were dissolved in H_2O, combined and then lyophilized. Epoxide **7** (1.45 g, quantitative yield, contains 2% of **18**) was obtained as a white solid. Some epoxide **7** (50 mg) was recrystallized from 9% MeOH in EtOAc (1.1 mL) to obtain crystals suitable for X-ray analysis. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 4.74 (d, J = 3.9 Hz, 1H, H-1), 3.89 (d, J = 3.9 Hz, 1H, H-2), 3.83 (dd, J = 11.7, 2.0 Hz, 1H, H-6a), 3.78 (d, J = 9.9 Hz, 1H, H-4), 3.72 (dd, J = 11.7, 5.3 Hz, 1H, H-6b), 3.68 (ddd, J = 10.0, 5.3, 2.1 Hz, 1H, H-5), 3.43 (s, 3H, OCH_3), 2.83 (d, J = 5.7 Hz, 1H, C$\underline{H}_2$-epoxide), 2.81 (d, J = 5.7 Hz, 1H, C$\underline{H}_2$-epoxide); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.1 (C-1), 72.2 (C-5), 67.0 (C-2), 64.8 (C-4), 62.7 (C-6), 60.7 (C-3), 55.8 (OCH_3), 42.83 ($\underline{C}H_2$-epoxide); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{14}O_6Na^+$: 229.0683, found: 229.0683; **mp** 146-149 °C (from EtOAc/MeOH).

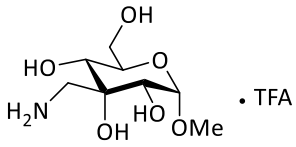
Methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (8)



8

Epoxide **7** (108 mg, 0.52 mmol, 1 equiv.) and sodium azide (36 mg, 0.55 mmol, 1.05 equiv.) were dissolved in H_2O (2.6 mL, 0.2 M). The mixture was stirred for 27 h at 30 °C and subsequently acidified by adding aqueous HCl (0.27 mL, 2 M, 1.05 equiv.). The mixture was concentrated *in vacuo* and the residue was suspended in acetone (10 mL) through sonication. The white suspension was filtered over Celite. The filtrate was concentrated *in vacuo* and azide **8** (106 mg, 81%) was obtained as a syrup. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 4.75 (d, *J* = 4.0 Hz, 1H, H-1), 3.87 – 3.83 (m, 1H, H-6a), 3.75 – 3.70 (m, 2H, H-6b & H-5), 3.58 (d, *J* = 4.0 Hz, 1H, H-2), 3.54 (d, *J* = 11.7 Hz, 1H, CH_2N_3), 3.49 (d, *J* = 9.6 Hz, 1H, H-4), 3.48 (d, *J* = 11.8 Hz, 1H, CH_2N_3), 3.45 (s, 3H, OCH_3); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.8 (C-1), 76.6 (C-3), 70.2 (C-5), 68.1 (C-2), 66.9 (C-4), 62.9 (C-6), 56.2 (OCH_3), 51.7 (CH_2N_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{15}N_3O_6Na^+$: 272.0853; Found: 272.0853.

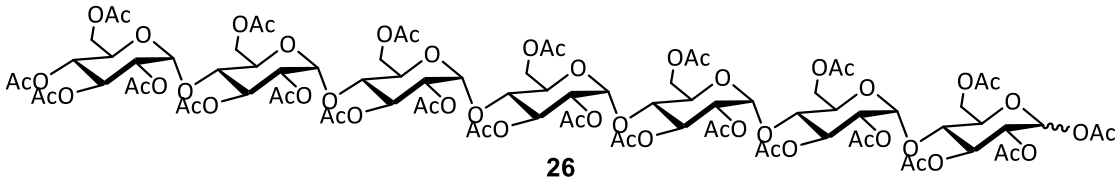
Methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (9)



9

Azide **8** (64 mg, 0.26 mmol, 1 equiv.) and triphenylphosphine (202 mg, 0.77 mmol, 3 equiv.) were dissolved in THF/H_2O (8/1, 1.9 mL, 0.12 M). The solution was stirred for 17 h at rt and then concentrated *in vacuo*. The residue was partitioned between EtOAc (5 mL) and H_2O (5 mL) and the aqueous layer was washed three more times with EtOAc (3× 5 mL). Trifluoroacetic acid (0.04 mL, 0.5 mmol, 2 equiv.) and charcoal were added to the aqueous layer and filtered over Celite, followed by washing with H_2O. The resulting filtrate was freeze dried to obtain desired product (83 mg, 96%) as a white solid. **^{1}H-NMR** (600 MHz, D_2O) δ 4.80 (s, 1H, H-1, overlaps with residual HDO peak), 3.88 (dd, *J* = 12.1, 2.0 Hz, 1H, H-6a), 3.82 (ddd, *J* = 10.0, 5.1, 2.0 Hz, 1H, H-5), 3.79 – 3.75 (m, 2H, H-2 + H-6b), 3.55 (d, *J* = 10.1 Hz, 1H, H-4), 3.44 (s, 3H, OCH_3), 3.34 (d, *J* = 13.3 Hz, 1H, $C\underline{H}_2NH_2$), 3.28 (d, *J* = 13.3 Hz, 1H, $C\underline{H}_2NH_2$); **^{13}C-NMR** (151 MHz, D_2O) δ 163.1 (q, *J* = 35.5 Hz, TFA), 116.4 (q, *J* = 291.6 Hz, TFA), 99.4 (C-1), 72.5 (C-3), 69.7 (C-2), 68.1 (C-4 or C-5), 68.1 (C-4 or C-5), 60.5 (C-6), 55.7 (OCH_3), 44.5 ($\underline{C}H_2NH_2$); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{17}NO_6Na^+$: 246.0948; Found: 246.0947.

Tricosa-*O*-acetyl-D-maltoheptaose (26)

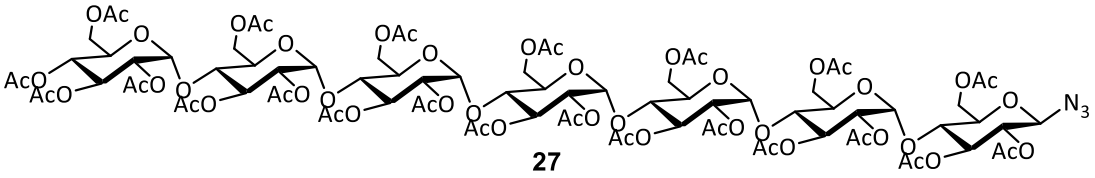


26

Tricosa-*O*-acetyl-D-maltoheptaose was prepared from β-cyclodextrin according to literature procedure.[10] $FeCl_3 \cdot 6H_2O$ (5.82 g, 22.0 mmol) was suspended in Ac_2O (600 mL), β-cyclodextrin (100 g, 88.1 mmol) was added in small portions under cooling (<40 °C) and the mixture was stirred vigorously for 16 h at rt. Then the reaction temperature was raised to 70 °C and the mixture was stirred for another 3.5 h. The mixture was poured into water (6 L). The resulting crystalline product was filtered off, washed with water, dried and crystallized six times from EtOH (0.5-1 L). The product (**26**, 56.9 g, 31%) was isolated as a white powder. NMR data matched those in the literature.[10] **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 6.21 (d, *J* = 3.6 Hz, 1H, H-1α), 5.72 (d, *J* = 8.1 Hz, 0.12H, H-1β), 5.48 (t, *J* = 9.5 Hz, 1H), 5.42 – 5.30 (m, 6H), 5.29 – 5.23 (m, 4H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.92 (dd, *J* = 10.1, 3.8 Hz, 1H), 4.83 (dd, *J* = 10.5, 4.0 Hz, 1H), 4.74 – 4.67 (m, 4H), 4.53 – 4.43 (m, 5H), 4.32 – 4.16 (m, 5H), 4.16 – 4.08 (m, 2H), 4.05 – 4.00 (m, 2H), 3.99 – 3.85 (m, 9H), 2.23 – 1.91 (m, 69H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.8, 170.8, 170.8, 170.6, 170.5, 170.5, 170.5, 170.5, 170.4, 170.0, 169.9, 169.8, 169.8, 169.6, 169.6, 169.1, 96.0,

95.8, 95.8, 95.8, 95.7, 91.4 (C-1β), 88.9 (C-1α), 73.4, 73.3, 73.2, 72.4, 72.3, 71.8, 71.8, 71.8, 71.7, 71.7, 70.6, 70.6, 70.6, 70.5, 70.5, 70.5, 70.3, 70.1, 69.9, 69.4, 69.2, 69.2, 69.1, 69.0, 69.0, 68.5, 68.0, 62.6, 62.5, 62.4, 62.2, 61.4, 21.1, 21.0, 21.0, 20.9, 20.9, 20.8, 20.7, 20.6, 20.5 (signals are missing due to overlap); **HRMS** (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{88}H_{118}O_{59}NH_4^+$: 2136.657; Found: 2136.658.

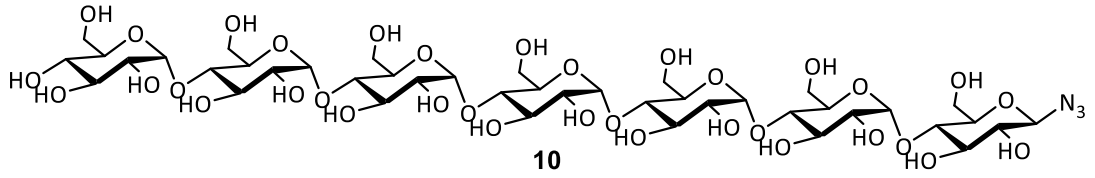
docosa-*O*-acetyl-β-D-maltoheptaosyl azide (27)



27

Docosa-*O*-acetyl-β-D-maltoheptaosyl azide (**27**) was prepared in two steps from **26**. Compound **26** (3.04 g, 1.43 mmol, 1 equiv.) was dissolved in AcOH (9.1 mL, 0.16 M) and cooled to 0 °C. HBr/HOAc (33%, 1.3 mL, 5.3 mmol, 3.7 equiv.) was added and the mixture was stirred for 6 h and then poured onto ice (40 g). The resulting mixture was extracted with DCM (3× 40 mL). The organic layer was successively washed with cold saturated $NaHCO_3$ (2× 50 mL) and brine (50 mL), and dried (Na_2SO_4) and concentrated to give peracetylatedmaltoheptaosyl bromide. All of the bromide (1.43 mmol) was dissolved in EtOAc (18 mL, 0.08 M) and NaN_3 (1.37 g, 21.0 mmol, 14.7 equiv.), tetrabutylammonium hydrogen sulfate (0.95 g, 2.8 mmol, 2 equiv.) and aq. $NaHCO_3$ (18 mL, 0.08 M) were added in sequence. The reaction mixture was stirred vigorously at rt for 15 h at rt. The reaction was diluted with EtOAc (15 mL), washed with water (3× 30 mL) and brine (30 mL). The organic layer was and dried (Na_2SO_4) and concentrated *in vacuo.* The residue was purified by column chromatography (eluted product with 2% *i*PrOH in DCM) and resulted in peracetylated maltoheptaosyl azide (**27**, 1.37 g, 46%) as a white solid. NMR data matched those in the literature.[11] **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 5.43 – 5.31 (m, 6H), 5.31 – 5.23 (m, 5H), 5.06 (t, J = 9.9 Hz, 1H), 4.85 (dd, J = 10.5, 4.0 Hz, 1H), 4.80 – 4.68 (m, 6H), 4.55 – 4.45 (m, 5H), 4.37 (dd, J = 12.4, 3.9 Hz, 1H), 4.33 – 4.19 (m, 4H), 4.19 – 4.13 (m, 1H), 4.07 – 3.87 (m, 11H), 3.81 (dt, J = 9.6, 3.4 Hz, 1H), 2.23 – 1.95 (m, 66H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 170.9, 170.9, 170.8, 170.8, 170.8, 170.7, 170.7, 170.6, 170.6, 170.5, 170.5, 170.5, 170.1, 169.9, 169.8, 169.7, 169.7, 169.6, 169.6, 95.9, 95.9, 95.8, 95.8, 95.8, 87.6, 75.1, 74.4, 73.6, 73.5, 73.3, 73.3, 72.5, 71.9, 71.7, 71.7, 70.7, 70.6, 70.6, 70.5, 70.2, 69.5, 69.2, 69.1, 69.1, 69.1, 68.6, 68.1, 62.7, 62.6, 62.6, 62.5, 62.5, 62.5, 62.5, 62.5, 62.3, 61.5 (signals are missing due to overlap).

β-D-maltoheptaosyl azide (10)

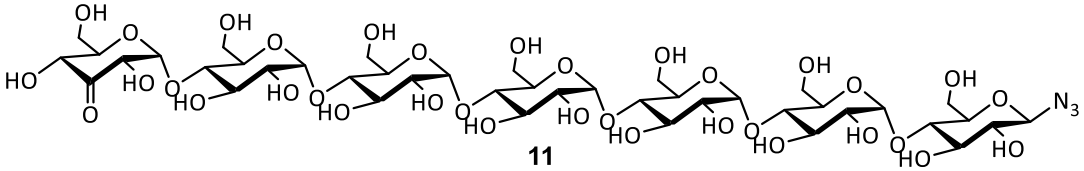


10

Peracetylatedmaltoheptaosyl azide (**27**, 1.36 g, 0.65 mmol) was dissolved in anhydrous methanol (160 mL, 4 mM) and a small lump of sodium was added. The mixture was stirred for 20 h at rt and neutralized by Dowex (H^+, 50WX4). The resin was removed by filtration and washed with water. The filtrate was concentrated *in vacuo*. and freeze dried. The product (**10**, 729 mg, 96%) was obtained as a white powder. **^{1}H-NMR** (600 MHz, D_2O) δ 5.45 – 5.40 (m, 5H), 4.79 – 4.77 (m, 1H, overlaps with HDO peak), 4.01 – 3.94 (m, 5H), 3.92 – 3.77 (m, 16H), 3.75 (ddd, *J* = 10.2, 5.3, 2.3 Hz, 1H), 3.73 – 3.62 (m, 11H), 3.61 (dd, *J* = 9.9, 3.9 Hz, 1H), 3.45 (dd, *J* = 10.0, 9.1 Hz, 1H), 3.33 (dd, *J* = 9.4, 8.8 Hz, 1H); **^{13}C-NMR** (151 MHz, D_2O) δ 99.7, 99.6, 99.6, 99.4, 89.9 (CN_3), 76.8, 76.7, 76.7, 76.7, 76.4, 76.2, 76.2, 73.3, 73.3, 73.3, 73.3, 72.9, 72.7, 72.7, 71.7, 71.5, 71.5, 71.2, 71.2, 69.3, 60.5,

60.4 (15 signals are missing due to overlap); **HRMS** (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{42}H_{71}N_3O_{35}NH_4^+$: 1195.421; Found: 1195.421.

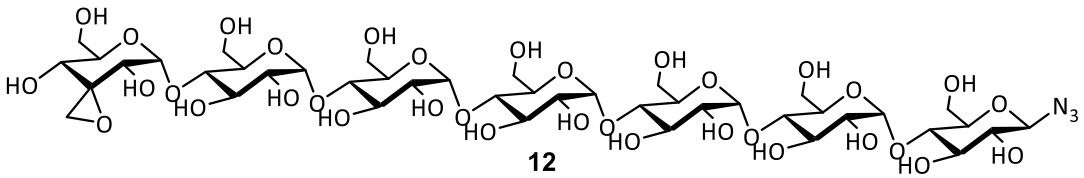
3-keto-β-D-maltoheptaosyl azide (11)



11

Azide **10** (160 mg, 136 µmol, 1 equiv.) and *p*-benzoquinone (26 mg, 0.24 mmol, 1.8 equiv.) were dissolved in DMSO (0.90 mL, 0.15 M) prior addition of $[(2,9\text{-dimethyl-}1,10\text{-phenanthroline})Pd(\mu\text{-OAc})]_2(OTf)_2$ (29 mg, 27 µmol, 20 mol%) to the solution. The brown mixture was stirred for 4 h at rt whereupon ^{1}H-NMR showed full consumption of starting material. The mixture was diluted with water (8 mL) and ammonium pyrrolidinedithiocarbamate[12] (13 mg, 81 µmol) was added to precipitate palladium. The resulting suspension was stirred for 1 h and then further diluted with H_2O/*t*BuOH (9/1 v/v, 5 mL). Activated charcoal (0.7 g) was added and the mixture was filtered over Celite and washed with H_2O/*t*BuOH (9/1 v/v, 10 mL). The filtrate was freeze dried, loaded onto spherical silica and purified by column chromatography (4 g spherical silica). Prior separation, the column was washed with 10% H_2O and 2% AcOH in ACN (25 mL) and then with 10% H_2O in ACN (25 mL). The product was eluted from the column with an ACN/H_2O gradient: first 10% H_2O (25 mL), then 15% H_2O (25 mL) and finally 20% H_2O (100 mL). The fractions containing product were concentrated *in vacuo* and then freeze dried, which resulted in the product (**11**, 95 mg, 60%) as an off white solid. **^{1}H-NMR** (400 MHz, D_2O) δ 5.69 (d, *J* = 4.6 Hz, 1H), 5.30 – 5.23 (m, 5H), 4.64 – 4.61 (m, 1H), 4.52 (d, *J* = 4.4 Hz, 1H), 4.32 (d, *J* = 10.0 Hz, 1H), 3.88 – 3.42 (m, 38H), 3.17 (t, *J* = 9.1 Hz, 1H); **^{13}C-NMR** (101 MHz, D_2O) δ 207.2, 102.1, 99.5, 99.5, 99.3, 89.9, 76.7, 76.5, 76.4, 76.1, 76.1, 76.1, 75.7, 74.6, 73.2, 73.2, 73.0, 72.8, 72.6, 71.5, 71.5, 71.4, 71.1, 71.1, 70.8, 60.4, 60.4, 60.4, 60.3, 60.3, 60.1 (11 signals are missing due to overlap); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{69}N_3O_{35}Na^+$: 1198.360; Found: 1198.360.

3,3'-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (12)



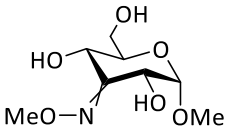
12

*Note: Diazomethane is potentially explosive and precautions should be taken, such as working behind a blast shield and using glassware without scratches and without ground joints. The ethereal diazomethane in this experiment was distilled in the same manner as described in the synthesis of **7** (vide supra).*

Keto-oligosaccharide **11** (80 mg, 68 µmol) was dissolved in H_2O (2.0 mL, 34 mM) and cooled to 0 °C. Ethereal diazomethane (6.2 mL) was added and the mixture was stirred at 0 °C. The yellow color faded over 30 minutes and following ^{1}H-NMR analysis did not show full conversion. The Et_2O was removed by a stream of nitrogen (g) and ethereal diazomethane (4 mL) was added again. The mixture was stirred at 0 °C and the yellow color faded over 30 minutes. ^{1}H-NMR analysis showed full conversion and the mixture was concentrated *in vacuo*. at 35 °C. The residue was freeze dried to obtain the product (76 mg, 94%) as a white powder. An aliquot was freeze dried from D_2O for NMR measurements. **^{1}H-NMR** (600 MHz, D_2O) δ 5.45 (d, *J* = 4.0 Hz, 1H), 5.43 – 5.38 (m, 5H), 4.76 (d, *J* = 8.8 Hz, 1H), 4.14 (d, *J* = 4.0 Hz, 1H), 4.01 – 3.57 (m, 39H), 3.31 (t, *J* = 9.1 Hz, 1H), 2.96 (d, *J*

= 4.5 Hz, 1H), 2.95 (d, *J* = 4.3 Hz, 1H); **^{13}C-NMR** (151 MHz, D_2O) δ 99.7, 99.6, 99.6, 99.6, 99.6, 99.4, 89.9, 76.8, 76.8, 76.7, 76.7, 76.4, 76.1, 73.3, 73.2, 72.7, 71.6, 71.5, 71.4, 71.3, 71.2, 71.1, 65.1, 62.6, 60.7, 60.4, 60.4, 60.2, 60.1, 42.7. (13 signals are missing due to overlap); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{71}N_3O_{35}Na^+$: 1212.376; Found: 1212.376.

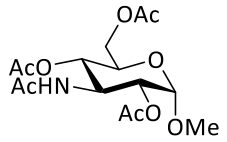
Methyl *E*/*Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (13)



13

Keto saccharide **1** (2.00 g, 10.4 mmol, 1.0 eq), *O*-methylhydroxylamine hydrochloride (956 mg, 11.4 mmol, 1.1 eq) and NaOMe (618 mg, 11.4 mmol, 1.1 eq) were stirred at rt for 17 h in methanol (52 mL, 0.2 M). The mixture was loaded on Celite and purified by column chromatography (100 mL silica, MeOH/DCM gradient: first 3% MeOH (500 mL), then 4% MeOH (500 mL)). The product (**13**, 2.25g, 91% as a mixture of *E*/*Z* isomers) was isolated as a yellow syrup and still contained residual methanol (the yield has been corrected the residual methanol). **^{1}H-NMR** (400 MHz, MeOD-d_4) δ 4.75 (d, *J* = 4.2 Hz, 1H, **13a**:H-1), 4.72 (d, *J* = 3.6 Hz, 0.75H, **13b**:H-1), 4.53 (d, *J* = 3.6 Hz, 0.75H, **13b**:H-2), 4.46 (d, *J* = 9.2 Hz, 1H, **13a**:H-4), 4.27 (d, *J* = 4.1 Hz, 1H, **13a**:H-2), 4.05 (d, *J* = 8.6 Hz, 0.75H, **13b**:H-4), 3.96 (ddd, *J* = 8.7, 5.4, 2.4 Hz, 1H, **13a**:H-5), 3.90 (s, 3H, **13a**:$NOCH_3$), 3.85 (s, 2.25H, **13b**:$NOCH_3$), 3.80 (apparent dd, *J* = 12.5, 2.0 Hz, 1.75H, H-6a), 3.73 (dd, *J* = 11.8, 5.0 Hz, 0.75H, **13b**:H-6b), 3.69 – 3.62 (m, 1.75H, **13a**:H-6b+**13b**:H-5), 3.49 (s, 3H, **13a**:OCH_3), 3.46 (s, 2.25H, **13b**:OCH_3); **^{13}C-NMR** (101 MHz, MeOD-d_4) δ 156.3 (**13a**:C-3), 155.1 (**13b**:C-3), 101.7 (**13b**:C-1), 100.3 (**13a**:C-1), 76.9 (**13b**:C-5), 75.1 (**13a**:C-5), 72.7 (**13b**:C-2), 70.1 (**13a**:C-2), 68.6 (**13b**:C-4), 65.3 (**13a**:C-4), 62.9 (**13b**:NO<u>C</u>H_3), 62.7 (**13a**: NO<u>C</u>H_3), 62.5 (**13a**:C-6), 62.4 (**13b**:C-6), 55.8 (**13b**:OCH_3), 55.7 (**13a**:OCH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{15}NO_6Na^+$: 244.0792; Found: 244.0793.

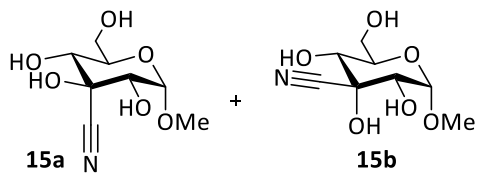
Methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (14)



14

Liquid ammonia (5 mL, 0.1 M) was condensed in a Schlenk containing oxime **13** (115 mg, 0.52 mmol, 1 equiv.) at -78 °C. Ethanol (0.18 mL, 3.1 mmol, 6 equiv.) was added and thereafter sodium (79 mg, 3.4 mmol, 6.6 equiv.) was added in batches. The reaction became dark blue upon addition. The color faded after stirring for 1.5 h at -78 °C and the mixture was allowed to warm to and evaporate at rt. Acetic anhydride (5 mL) was added to the resulting white residue and the mixture was heated to 80 °C for three h with a sand bath. The mixture was concentrated *in vacuo*. and co-evaporated twice with toluene. The crude was loaded onto Celite (1 g) and purified by column chromatography (40 g silica, product eluted with 2% MeOH in DCM (400 mL)). The product (**14**, 118 mg, 63%) was obtained as an orange solid. NMR data matched those in the literature.[13] **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 5.41 (d, J = 9.7 Hz, 1H, NH), 4.89 – 4.82 (m, 2H, H-2+H-4), 4.81 (d, J = 3.6 Hz, 1H, H-1), 4.65 (q, J = 10.1 Hz, 1H, H-3), 4.30 (dd, J = 12.2, 4.5 Hz, 1H, H-6a), 4.09 (dd, J = 12.2, 2.2 Hz, 1H, H-6b), 4.04 (ddd, J = 10.0, 4.4, 2.2 Hz, 1H, H-5), 3.43 (s, 3H, OCH_3), 2.09 (s, 6H), 2.04 (s, 3H), 1.89 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 171.2, 170.8, 170.8, 170.4, 97.1 (C-1), 70.7 (C-2), 68.9 (C-4), 67.8 (C-5), 62.2 (C-6), 55.5 (OCH_3), 50.4 (C-3), 23.4, 20.9, 20.9, 20.8; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{23}NO_9Na^+$: 384.1265; Found: 384.1266.

Methyl 3-*C*-cyano-α-D-glucopyranoside (15a) & Methyl 3-*C*-cyano-α-D-allopyranoside (15b)

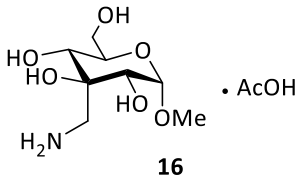


15a **15b**

Keto saccharide **1** (340 mg, 1.77 mmol) and NaCN (356 mg, 7.12 mmol, 4 equiv.) were dissolved in H_2O (1.8 mL, 1 M) and then cooled to 0 °C. HCl (3.5 mL, 2 M in H_2O, 4 equiv.) was added to reach a pH value of 7-8. The last 0.3 mL HCl solution was added dropwise to prevent a pH value lower than 7. The pH was checked regularly with pH paper during addition. The neutral solution was stirred for 2.5 days at rt by the time which nearly all starting

material was consumed (TLC, 0.1% AcOH and 15% MeOH in DCM). Subsequently, the solution was acidified by addition of HCl (2 M, 0.9 mL) before work-up. The mixture was concentrated *in vacuo*, loaded onto Celite (1.1 g) and purified by column chromatography (15 g silica). The products were eluted with a MeOH/DCM gradient containing 0.1% AcOH (first 5% MeOH in DCM (50 mL), then 10% MeOH in DCM (100 mL) and finally 12% MeOH in DCM (100 mL)). The allose diastereoisomer (**15b**) eluted first and the diastereoisomers could be separated partially. The products were isolated as a thick syrup and still contained MeOH and AcOH as impurities, since excessive drying led to decomposition of the cyanohydrin functionality. The first fraction was a mixture of **15a** and **15b** (33:67 / **15a**:**15b**, 91 mg, 18% yield, yield corrected to impurities) and the second fraction contained mainly the glucose diastereoisomer (93:7 / **15a**:**15b**, 290 mg, 55% yield, yield corrected to impurities). **Methyl 3-*C*-cyano-α-D-glucopyranoside (15a):** **^{1}H-NMR** (400 MHz, MeOD-*d4*) δ 4.73 (d, J = 3.8 Hz, 1H, H-1), 3.87 – 3.79 (m, 1H, H-6a), 3.77 – 3.68 (m, 2H, H-6b + H-5), 3.59 (d, J = 3.9 Hz, 1H, H-2), 3.50 (d, J = 9.6 Hz, 1H, H-4), 3.43 (s, 3H, OCH_3); **^{13}C-NMR** (100 MHz, MeOD-*d4*) δ 119.3 (C≡N), 100.2 (C-1), 77.1 (C-3), 74.4 (C-2), 72.4 (C-4), 71.9 (C-5), 62.1 (C-6), 55.65 (OCH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{13}NO_6Na^+$: 242.0635; Found: 242.0633.

Methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (16)



16

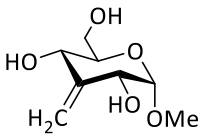
MeOH/H_2O (3/1 v/v, 4.4 mL, 0.2 M) and acetic acid (0.11 mL, 1.85 mmol, 2 equiv.) were added to cyanohydrin **15a** (274 mg, contains MeOH and AcOH as impurities and corresponds to 0.924 mmol). The solution was degassed by two freeze-pump-thaw cycles and palladium on carbon (49 mg, 10 wt% Pd) was added. The black suspension was degassed by one freeze-pump-thaw cycle and a hydrogen atmosphere was applied. The mixture was stirred at rt for 18 h, after which the starting material was consumed (TLC, 0.1% AcOH and 15% MeOH in DCM). The suspension was filtered over Celite and the Celite was washed with MeOH and H_2O. The combined filtrates were concentrated *in vacuo* and then freeze dried to obtain product **16** (276 mg, quantitative yield) as a white solid. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 4.69 (d, J = 3.8 Hz, 1H, H-1), 3.81 (dd, J = 11.9, 2.4 Hz, 1H, H-6a), 3.74 – 3.68 (m, 2H, H-6b + H-2), 3.61 (d, J = 10.2 Hz, 1H, H-4), 3.54 (ddd, J = 10.2, 5.1, 2.5 Hz, 1H, H-5), 3.43 (d, J = 13.4 Hz, 1H, C$H_2$$NH_2$), 3.41 (s, 3H, OCH_3), 3.37 (d, J = 13.3 Hz, 1H, C$H_2$$NH_2$), 1.92 (s, 3H, AcOH); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.1 (C-1), 75.0 (C-2), 73.9 (C-3), 73.8 (C-2), 72.6 (C-5), 62.7 (C-6), 55.8 (OCH_3), 41.9 (C$H_2$$NH_2$, 23.9 (AcOH); **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_{18}NO_6^+$: 224.1129; Found: 224.1127.

Methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (17)

Experimental Procedure for the attempted Wittig olefination

Sodium hydride (33 mg, 0.82 mmol, 2 equiv.) was dissolved in anhydrous DMSO (2 mL) by stirring the mixture at 60 °C for one h. The mixture was allowed to cool to rt and triphenylphosphonium bromide (294 mg, 0.82 mmol, 2 equiv.) in anhydrous DMSO (1 mL) was added. After stirring for 30 minutes, keto saccharide **1** (79 mg, 0.41 mmol, 1 equiv.) dissolved in anhydrous DMSO (0.8 mL) was added. The mixture was stirred for 2 h at rt and full consumption of the starting material was observed (TLC, 15% MeOH in DCM). However, the desired product (**17**) could not be observed or isolated. Additional heating did not result in product formation either.

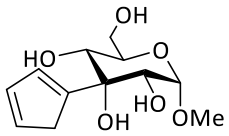
Experimental Procedure for the Peterson olefination[14]



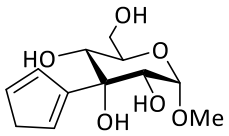
17

Keto saccharide **1** (54 mg, 0.28 mmol, 1 equiv.) was placed in a Schlenk tube and kept under a nitrogen atmosphere using standard Schlenk techniques. Dry THF (5.6 mL, 0.05 M) was added and the mixture was stirred at rt until everything was dissolved. The solution was cooled to -78 °C and trimethylsilylmethylmagnesium chloride (1.5 mL, 1 M in THF, 5.3 equiv.) was added dropwise over 5 minutes. The suspension was stirred for an additional 30 minutes before it was allowed to warm to rt. TLC (15% MeOH in DCM) showed nearly full consumption of the starting material, hence the mixture was cooled to -78 °C again and additional trimethylsilylmethylmagnesium chloride (0.14 mL, 1 M in THF, 0.5 equiv.) was added. The mixture was immediately allowed to warm to rt. The reaction was quenched by adding H_2O (0.05 mL) and transferred with MeOH to a bigger flask. The mixture was concentrated *in vacuo*, loaded onto Celite (0.5 g) and purified by automated column chromatography (12 g Reveleris diol-column, DCM/MeOH gradient: 2% MeOH for 3.5 CV and then 3% for 7 CV). A mixture of Grignard products was isolated and used for the next reaction without further purification. The mixture was dissolved in dry THF (5 mL) using standard Schlenk techniques and sodium hydride (60 wt%, 23 mg, 0.56 mmol, 2 equiv.) was added. It was then stirred at 50 °C for 16 h prior neutralized with acetic acid (0.05 mL). The mixture was loaded onto Celite (300 mg), purified by column chromatography (7 mL silica, eluent: 5% MeOH in DCM (100 mL)) and resulted in **17** (5 mg, 9% over two steps).

Experimental Procedure for the Petasis olefination



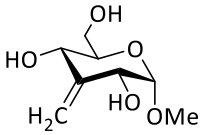
28a



28b

Keto saccharide **1** (50 mg, 0.26 mmol, 1 equiv.) was placed in a Schlenk tube and kept under a nitrogen atmosphere using standard Schlenk techniques. Dry THF (5.2 mL, 0.05 M) was added and the mixture was stirred at rt until everything was dissolved. Petasis reagent[15] (10 wt%, 1.0 g, 0.51 mmol, 2 equiv.) was added and the mixture was heated to 75-80 °C for two h using an oil bath. The mixture was allowed to cool to rt, transferred with MeOH to a bigger flask and then loaded onto Celite (300 mg). Following purification by column chromatography (20 mL silica, eluent: 4% MeOH in DCM (300 mL)) resulted in a 1:1 mixture of cyclopentadiene adducts (**28a** and **28b**, 32 mg, 48%) as a yellow syrup. **^{1}H-NMR** (600 MHz, MeOD-d_4) δ 6.63 (dq, *J* = 5.3, 1.5 Hz, 1H), 6.53 (dq, *J* = 2.6, 1.3 Hz, 1H), 6.46 – 6.44 (m, 1H), 6.43 (ddt, *J* = 5.3, 2.7, 1.4 Hz, 1H), 6.41 (dq, *J* = 3.0, 1.6 Hz, 1H), 6.36 (dq, *J* = 5.3, 1.4 Hz, 1H), 4.78 (d, *J* = 3.9 Hz, 1H), 4.76 (d, *J* = 3.9 Hz, 1H), 3.90 – 3.85 (m, 2H), 3.79 – 3.73 (m, 5H), 3.69 (d, *J* = 3.9 Hz, 1H), 3.65 (d, *J* = 9.8 Hz, 1H), 3.59 (d, *J* = 9.7 Hz, 0H), 3.48 (s, 3H), 3.47 (s, 3H), 3.07 (dq, *J* = 6.1, 1.5 Hz, 2H), 3.01 (d, *J* = 1.5 Hz, 2H); **^{13}C-NMR** (151 MHz, MeOD-d_4) δ 150.8, 149.2, 134.4, 133.1, 132.9, 132.8, 130.2, 101.9, 101.8, 79.2, 78.1, 72.9, 71.8, 71.7, 70.7, 70.6, 70.4, 63.0, 56.2, 42.5, 42.2; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_6Na^+$: 281.0996; Found: 281.0997.

Experimental Procedure of Kauffmann olefination[16]

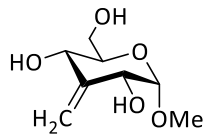


17

Molybdenum(V) chloride (1.1 g, 4.0 mmol, 4 equiv.) was placed in a Schlenk tube and dissolved in dry THF (15 mL) under a nitrogen atmosphere using standard Schlenk techniques. The solution was stirred for 2 h at rt and was then cooled to -78 °C. Methyllithium (7.5 mL, 1.6 M, 12 mmol, 12 equiv.) was added dropwise to the solution over five minutes. After stirring for 1 h at -78 °C, the reaction was allowed to slowly warm to rt. Keto saccharide **1** (192 mg, 1.0 mmol, 1 equiv.) dissolved in EtOH:THF (6 mL, 1:1) was added dropwise when the temperature had reached -40 °C. Upon reaching rt the mixture was stirred for an additional 4 h when and was subsequently kept at 45 °C for three days with a sand bath. The mixture was transferred with acetone to a bigger flask, loaded onto Celite (4 g) and then purified by automated column chromatography (40 g Reveleris

diol-column, DCM/MeOH gradient: 0% MeOH for 7.5 CV and then from 0% to 5% in 20 CV). Obtained impure **17** (28 mg, 15% yield, purity: 32 wt%) as a brown solid.

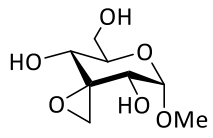
Experimental Procedure for the Nysted olefination



17

Keto saccharide **1** (500 mg, 2.60 mmol) was placed in a Schlenk tube and kept under a nitrogen atmosphere using standard Schlenk techniques. Dry THF (52 mL, 0.05 M) was added and the mixture was stirred at rt until everything had dissolved. The solution was cooled to -78 °C and Nysted reagent (20 wt%, 10.4 mmol, 4 equiv.) was added dropwise over 2 minutes. The suspension was kept in the cooling bath and was allowed to warm to rt over 18 h. The reaction was quenched by addition of MeOH and H_2O and then concentrated *in vacuo*. The crude was suspended in H_2O (100 mL) by sonication for 1 h and the resulting suspension was centrifuged (1 min, 5000 rpm). The supernatant was collected and the process (resuspending residue in 160 mL H_2O by sonication for 15 minutes, centrifuging and decanting) was repeated twice. The combined supernatants were concentrated *in vacuo* and Na_2CO_3 (3.3 g, 31.2 mmol) in H_2O (80 mL) was added to the residue. The white suspension was centrifuged (1 min, 5000 rpm) and the supernatant was collected by decantation. The process of resuspending the residue in H_2O (60 mL) through sonication for 15 minutes, centrifuging and decantation was repeated twice. The combined supernatants were concentrated *in vacuo*, loaded onto Celite (7 g) and purified by automated column chromatography (48 g BGB diol-column, DCM/MeOH gradient: 1% MeOH for 3 CV, 1% to 5% in 10 CV and 5% for 3 CV). The product (**17**, 270 mg, 55% yield) was obtained as a clear syrup. **^{1}H-NMR** (400 MHz, MeOD-*d4*) δ 5.27 – 5.23 (m, 1H, C=C$\underline{H}_2$), 5.19 (apparent q, J = 2.0 Hz, 1H, C=C$\underline{H}_2$), 4.70 (d, J = 3.9 Hz, 1H, H-1), 4.15 – 4.11 (m, 1H, H-2), 3.99 – 3.93 (m, 1H, H-4), 3.83 (dd, J = 11.8, 2.5 Hz, 1H, H-6a), 3.73 (dd, J = 11.8, 5.3 Hz, 1H, H-6b), 3.45 – 3.39 (m, 1H, H-5), 3.39 (s, 3H, OCH_3); **^{13}C-NMR** (100 MHz, MeOD-*d4*) δ 148.6 (C-3), 104.7 (C=$\underline{C}H_2$), 101.4 (C-1), 75.5 (C-5), 71.5 (C-2), 68.8 (C-4), 62.9 (C-6), 55.3 (OCH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{14}O_5Na^+$: 213.0733; Found: 213.0733.

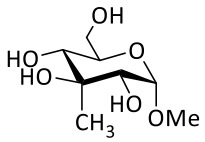
Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (18)



18

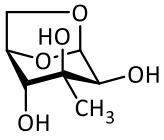
Oxone® (12.5 g) was added slowly to a thoroughly stirred mixture of acetone (15 mL), H_2O (15 mL) and $NaHCO_3$ (12 g) at 0 °C. The cooling bath was removed after 15 minutes, and DMDO was distilled (RT, 200 mbar) from the mixture with acetone using a double U-tube setup which was cooled with a slurry of acetone/N_2 (l) (approx. -90 °C). The condensate was dried with Na_2SO_4 and decanted. The concentration of the DMDO solution was determined by adding 0.1 mL of the solution to thioanisole (5.00 mg) in acetone (0.1 mL) at 0 °C. The mixture was stirred for 10 minutes at 0 °C, then for 10 minutes at rt and finally diluted with $CDCl_3$ (0.5 mL). The concentration of the larger DMDO solution could be calculated from the ratio thioanisole and its sulfoxide, as determined by ^{1}H-NMR.[17] The DMDO solution (7.8 mL, 0.1 M, 2 equiv.) was added to a solution of methylene saccharide **17** (74 mg, 0.39 mmol, 1 equiv.) in acetone (0.8 mL, 0.5 M) at 0 °C and the resulting mixture was stirred for 16 h at rt. The reaction mixture was concentrated *in vacuo* (40 °C), redissolved in H_2O/MeOH (1:1 v/v, 10 mL) and washed with pentane trice (7 mL). The H_2O/MeOH layer was concentrated *in vacuo* (40 °C) and co-evaporated with MeOH and DCM to obtain the product (**18**, 83 mg, quantitative yield) diastereoisomerically pure as a syrup. **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 4.79 (d, J = 3.6 Hz, 1H, H-1), 3.85 (d, J = 3.6 Hz, 1H, H-2), 3.83 (dd, J = 11.9, 2.3 Hz, 1H, H-6a), 3.74 – 3.70 (m, 2H, H-6b + H-4), 3.62 (ddd, J = 9.9, 5.3, 2.3 Hz, 1H, H-5), 3.42 (s, 3H, OCH_3), 3.00 (d, J = 5.8 Hz, 1H, C$\underline{H}_2$-epoxide), 2.96 (d, J = 5.8 Hz, 1H, C$\underline{H}_2$-epoxide); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.6 (C-1), 74.3 (C-5), 68.6 (C-2), 66.2 (C-4), 62.7 (C-6), 62.5 (C-3), 55.6 (OCH_3), 45.6 ($\underline{C}H_2$-epoxide); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{14}O_6Na^+$: 229.0683; Found: 229.0687.

Methyl 3-*C*-methyl-α-D-glucopyranoside (19)


19

$Hg(OAc)_2$ (57 mg, 0.18 mmol, 1.1 equiv.) was added to solution of methylene saccharide **17** (31 mg, 0.16 mmol) in H_2O (1.6 mL, 0.1 M) and the solution was stirred for 1.5 h at rt. Thereafter aqueous NaOH (1M, 0.40 mL, 2.5 equiv.) was added to basify the mixture, followed by addition of $NaBH_4$ (9.2 mg, 0.24 mmol, 1.5 equiv.). The grey suspension was stirred for 30 minutes and then filtered over Celite. The Celite was washed with MeOH and the combined filtrates were concentrated *in vacuo*. The residue was suspended in MeOH and then filtered over a short path of silica. The filtrate was acidified with AcOH and then loaded onto Celite (0.2 g), followed by purified by column chromatography (1.5 mL silica, DCM/MeOH gradient: first 5% MeOH (10 mL), then 8% MeOH (10 mL) and finally 10% MeOH (40 mL)). Methyl 3-*C*-methyl-α-D-glucopyranoside (**19**) was obtained diastereomerically pure as a white solid (25 mg, 74% yield). **^{1}H-NMR** (600 MHz, MeOD-*d4*) δ 4.66 (d, J = 4.3 Hz, 1H, H-1z), 3.82 (dd, J = 11.9, 2.4 Hz, 1H, H-6a), 3.68 (dd, J = 11.9, 5.7 Hz, 1H, H-6b), 3.52 (d, J = 4.3 Hz, 1H, H-2), 3.50 (ddd, J = 10.1, 5.6, 2.4 Hz, 1H, H-5), 3.40 (d, J = 10.2 Hz, 1H, H-4), 3.38 (s, 3H, OCH_3), 1.27 (s, 3H, CH_3); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 101.4 (C-1), 76.6 (C-3), 75.7 (C-2), 74.1 (C-4), 72.6 (C-5), 63.1 (C-6), 55.7 (OCH_3), 15.8 (CH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{16}O_6Na^+$: 231.0839; Found: 231.0841.

1,6-anhydro-3-*C*-methyl-β-D-mannopyranose (22)


22

1,6-anhydro-mannopyranose (587 mg, 3.62 mmol, 1 equiv.) and *p*-benzoquinone (411 mg, 3.80 mmol, 1.05 equiv.) were dissolved in acetonitrile (36 mL, 0.1 M) at 50 °C. [(2,9-dimethyl-1,10-phenanthroline)Pd(μ-OAc)]$_2$(OTf)$_2$ (114 mg, 109 μmol, 3 mol%) was added and in one batch to the solution and mixture was stirred at 50 °C. The reaction mixture became darker over time and the starting material was nearly consumed (TLC, 15% MeOH in DCM) after three h. The mixture was concentrated *in vacuo* and partitioned between H_2O (25 mL) and Et_2O (25 mL). The organic layer was washed once with H_2O (10 mL) and ammonium pyrrolidinedithiocarbamate[12] (53 mg, 0.33 mmol) was added to the combined aqueous layers to precipitate palladium. After stirring for 30 minutes activated charcoal (2.5 g) was added to the suspension. The mixture was stirred for an additional 15 minutes and then filtered over Celite and washed with water. The filtrate was concentrated *in vacuo* and an off white solid was obtained. An aliquot was taken for NMR analysis, which confirmed formation of desired 1,6-anhydro-3-keto-β-D-mannopyranose (**21**) and its dimer. This corresponded to previous reported data as well.[18] The crude keto saccharide was dissolved in H_2O (30 mL) the next day and placed in a scratch free 100 mL Erlenmeyer.

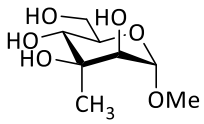
*Note: Diazomethane is potentially explosive and precautions should be taken, such as working behind a blast shield and using glassware without scratches and without ground joints. The ethereal diazomethane in this experiment was distilled in the same manner as described in the synthesis of **7** (vide supra).*

Ethereal diazomethane (43 mL) was added with a plastic pipette to the 100 mL Erlenmeyer containing the crude keto saccharide at 0 °C. The mixture was stirred for 30 minutes whereupon yellow color from the diazomethane had disappeared. Most of the Et_2O and residual diazomethane was removed by a stream of nitrogen (g) through the mixture. ^{1}H-NMR analysis of the aqueous layer did not show full conversion, hence the distillation of diazomethane was repeated and a second batch of ethereal diazomethane (46 mL) was added to the reaction. The reaction was stirred again for 30 minutes at 0 °C, whereupon the yellow color had disappeared again. Having fully converted the starting material (^{1}H-NMR analysis), the Et_2O was removed by a stream of nitrogen (g). The aqueous layer containing the epoxy-saccharide was immediately used for the following reaction.

The crude epoxy-saccharide was transferred to a 100 mL round-bottom flask and the Erlenmeyer containing the aqueous layer was rinsed with methanol (6 mL). Nitrogen (g) was bubbled through the mixture for 15

minutes followed by addition of palladium on carbon (193 mg, 10 wt% Pd). The black suspension was degassed by two freeze-pump-thaw cycles and a hydrogen atmosphere was applied with a balloon. The mixture was stirred at rt and the starting material was consumed after 16 h as observed by ^{1}H-NMR. The suspension was filtered over Celite and washed with MeOH. The filtrate was loaded onto Celite (1.8 g) and purified by column chromatography (32 mL silica, DCM/MeOH gradient: first 4% MeOH (100 mL), then 5% MeOH (250 mL)). The product (**22**, 258 mg, 41% yield) was obtained as a clear syrup. **^{1}H-NMR** (600 MHz, MeOD-*d*$_4$) δ 5.22 (d, *J* = 2.0 Hz, 1H, H-1), 4.45 – 4.42 (m, 1H, H-5), 4.27 (d, *J* = 6.9 Hz, 1H, H-6a), 3.62 (t, *J* = 6.4 Hz, 1H, H-6b), 3.50 (d, *J* = 1.2 Hz, 1H, H-4), 3.36 (d, *J* = 1.9 Hz, 1H, H-2), 1.24 (s, 3H, CH_3); **^{13}C-NMR** (151 MHz, MeOD-*d4*) δ 102.8 (C-1), 79.1 (C-5), 75.7 (C-4), 74.2 (C-3), 72.0 (C-2), 66.2 (C-6), 24.9 (CH_3); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{12}O_5Na^+$: 199.0577; Found: 199.0576.

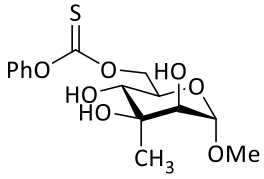
Methyl 3-*C*-methyl-α-D-mannopyranoside (23)



23

Triflic acid (27 µL, 0.30 mmol, 0.1 equiv.) was added to a solution of **22** (528 mg, 3.00 mmol, 1 equiv.) in anhydrous methanol (20 mL). The resulting mixture was stirred for three days at 50 °C and then neutralized by adding Amberlyst® A21 free base resin. The resin was removed by filtration, washed with methanol and the filtrate was concentrated *in vacuo*. The residue was loaded onto silica (640 mg, neutralized with a few drops of Et_3N) and purified by column chromatography (40 mL silica, product was eluted with 500 mL 8% MeOH and 0.1% Et_3N in DCM). The product (**23**, 390 mg, 63% yield) was obtained as a clear syrup. **^{1}H NMR** (600 MHz, MeOD-*d4*) δ 4.66 (d, *J* = 1.1 Hz, 1H, H-1), 3.83 (dd, *J* = 11.7, 2.4 Hz, 1H, H-6a), 3.69 (dd, *J* = 11.7, 6.0 Hz, 1H, H-6b), 3.64 (d, *J* = 10.0 Hz, 1H, H-4), 3.52 – 3.48 (m, 1H, H-5), 3.46 (d, *J* = 1.4 Hz, 1H, H-2), 3.37 (s, 3H, OCH_3), 1.26 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, MeOD-*d4*) δ 103.3 (C-1), 76.1 (C-2), 73.8 (C-3), 73.6 (C-5), 71.3 (C-4), 63.4 (C-6), 55.4 (OCH_3), 19.2 (CH_3); **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_8H_{16}O_6Na^+$: 231.0839; Found: 231.0839.

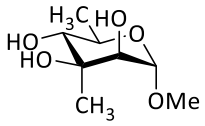
***O*-(6-deoxy-1-*O*,3-*C*-dimethyl-α-D-mannopyranos-6-yl) *O*-phenyl carbonothioate (24)**



24

O-phenyl chlorothionoformate (215 µL, 1.56 mmol, 1.5 equiv.) was added to a solution of **23** (216 mg, 1.04 mmol, 1 equiv.) in anhydrous THF (6.9 mL, 0.15 M) at 0 °C. Pyridine (167 µL, 2.08 mmol, 2 equiv.) was added thereafter and the mixture was stirred for 80 minutes at 0 °C. Upon completion methanol (2 mL) was added and the mixture was stirred at rt for 30 minutes. The mixture was loaded onto Celite (600 mg) and purified by column chromatography (17 mL silica, product was eluted with 300 mL 45% EtOAc in pentane). The product (**24**, 165 mg, 46% yield) was obtained as a white solid. A second batch of product was isolated by flushing the column with EtOAc and combining it with mixed fractions from the first column. The combined fractions were loaded onto Celite (300 mg) and purified by column chromatography (8 mL silica, product was eluted with 150 mL 45% EtOAc in pentane), which resulted in a second batch of product (**24**, 48 mg, 14% yield) as a white foam. The combined yield was 60%. **^{1}H NMR** (400 MHz, MeOD-*d4*) δ 7.45 – 7.39 (m, 2H, *m*-Ph), 7.31 – 7.26 (m, 1H, *p*-Ph), 7.13 – 7.09 (m, 2H, *m*-Ph), 4.80 (dd, *J* = 11.5, 2.0 Hz, 1H, H-6a), 4.68 (d, *J* = 1.6 Hz, 1H, H-1), 4.63 (dd, *J* = 11.5, 6.7 Hz, 1H, H-6b), 3.88 – 3.81 (m, 1H, H-5), 3.72 (d, *J* = 10.0 Hz, 1H, H-4), 3.50 (d, *J* = 1.7 Hz, 1H, H-2), 3.36 (s, 3H, OCH_3), 1.29 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, MeOD-*d4*) δ 196.6 (C=S), 155.0, 130.6, 127.5, 123.0, 103.4 (C-1), 75.8 (C-2), 75.3 (C-6), 73.7 (C-3), 71.1 (C-4), 70.9 (C-5), 55.5 (OCH_3), 19.1 (CH_3); **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{15}H_{20}O_7SNa^+$: 367.0822; Found: 367.0825.

Methyl α-D-evaloside (methyl 6-deoxy-3-*C*-methyl-α-D-mannopyranoside) (25)



25

Carbonothioate **24** (152 mg, 0.441 mmol, 1 equiv.) was co-evaporated with toluene twice and dried *in vacuo* prior to the reaction. AIBN (18 mg, 0.11 mmol, 25 mol%) was added and the solids were dissolved in anhydrous toluene (4 mL). A solution of Bu_3SnH (240 µL, 0.88 mmol, 2 equiv.) in toluene (0.76 mL) was added thereafter over a period of 10 h while heating the reaction mixture to 75 °C with an oil bath. The mixture was concentrated *in vacuo* and partitioned between Et_2O (10 mL) and H_2O (10 mL). The organic layer was washed with H_2O (5 mL) once and the combined aqueous layers were concentrated *in vacuo*. The crude was loaded onto Celite (200 mg) and purified by column chromatography (5 mL silica, DCM/MeOH gradient: first 3% MeOH (50 mL), then 4% MeOH (50 mL)). The product (**25**, 48 mg, 57%) was obtained as a white solid. **^{1}H NMR** (600 MHz, MeOD-*d4*) δ 4.58 (d, *J* = 1.2 Hz, 1H, H-1), 3.56 (dq, *J* = 9.7, 6.1 Hz, 1H, H-5), 3.46 (d, *J* = 1.5 Hz, 1H, H-2), 3.39 (d, *J* = 9.7 Hz, 1H, H-4), 3.34 (s, 3H, OCH_3), 1.25 (d, *J* = 6.2 Hz, 3H, H-6), 1.25 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, MeOD-*d4*) δ 103.3 (C-1), 76.5 (C-4), 76.2 (C-2), 73.6 (C-3), 68.6 (C-5), 55.3 (OCH_3), 19.2 (CH_3), 18.4 (C-6); **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_8H_{16}O_5Na^+$: 215.0890; Found: 215.0892; **mp** 127-129 °C (from DCM), lit.[19] mp 130-131 °C; **$[\alpha]_D^{20}$** +85 (*c* 0.5, MeOH), lit.[19] $[\alpha]_D^{20}$ +89 (*c* 1, MeOH).

6. References

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7. NMR spectra

Methyl α-D-*ribo*-hex-3-ulopyranoside (1)

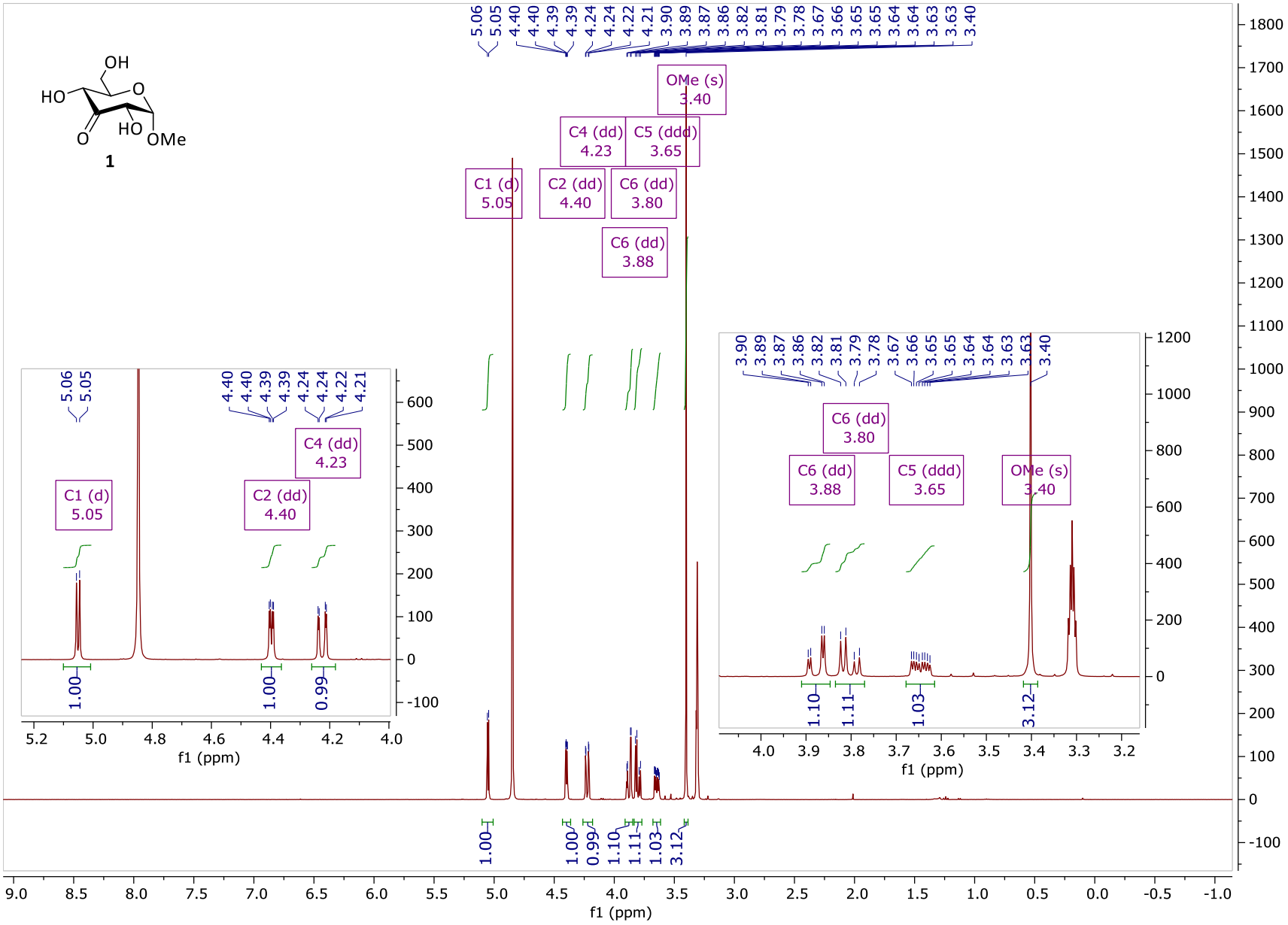

Figure S5 – ^{1}H-NMR (400 MHz, MeOD-*d4*) of methyl α-D-ribo-hex-3-ulopyranoside (**1**)

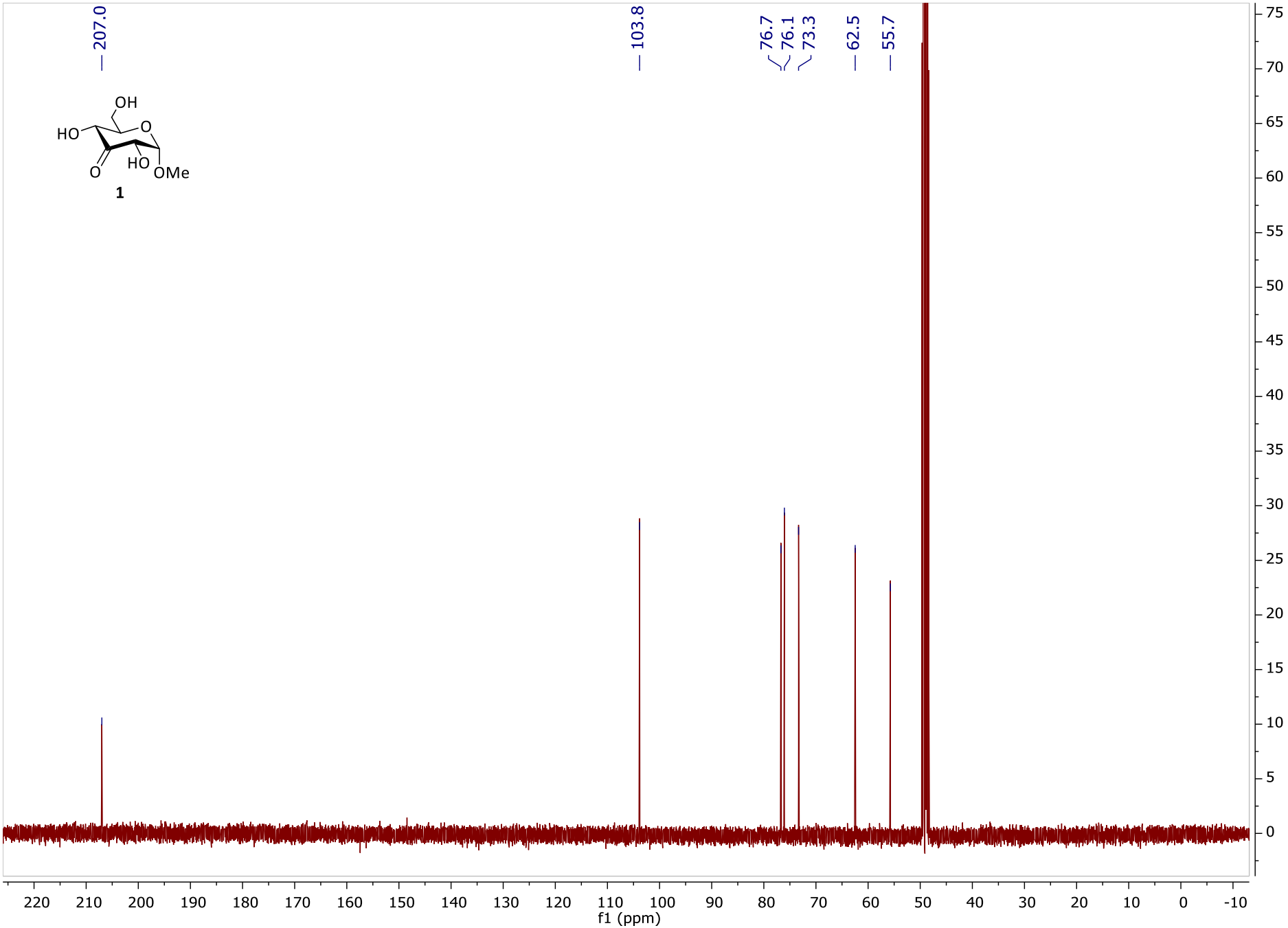

Figure S6 – ^{13}C-NMR (100 MHz, MeOD-*d4*) of methyl α-D-ribo-hex-3-ulopyranoside (**1**)

Methyl 3-*C*-methyl-α-D-allopyranoside (3)

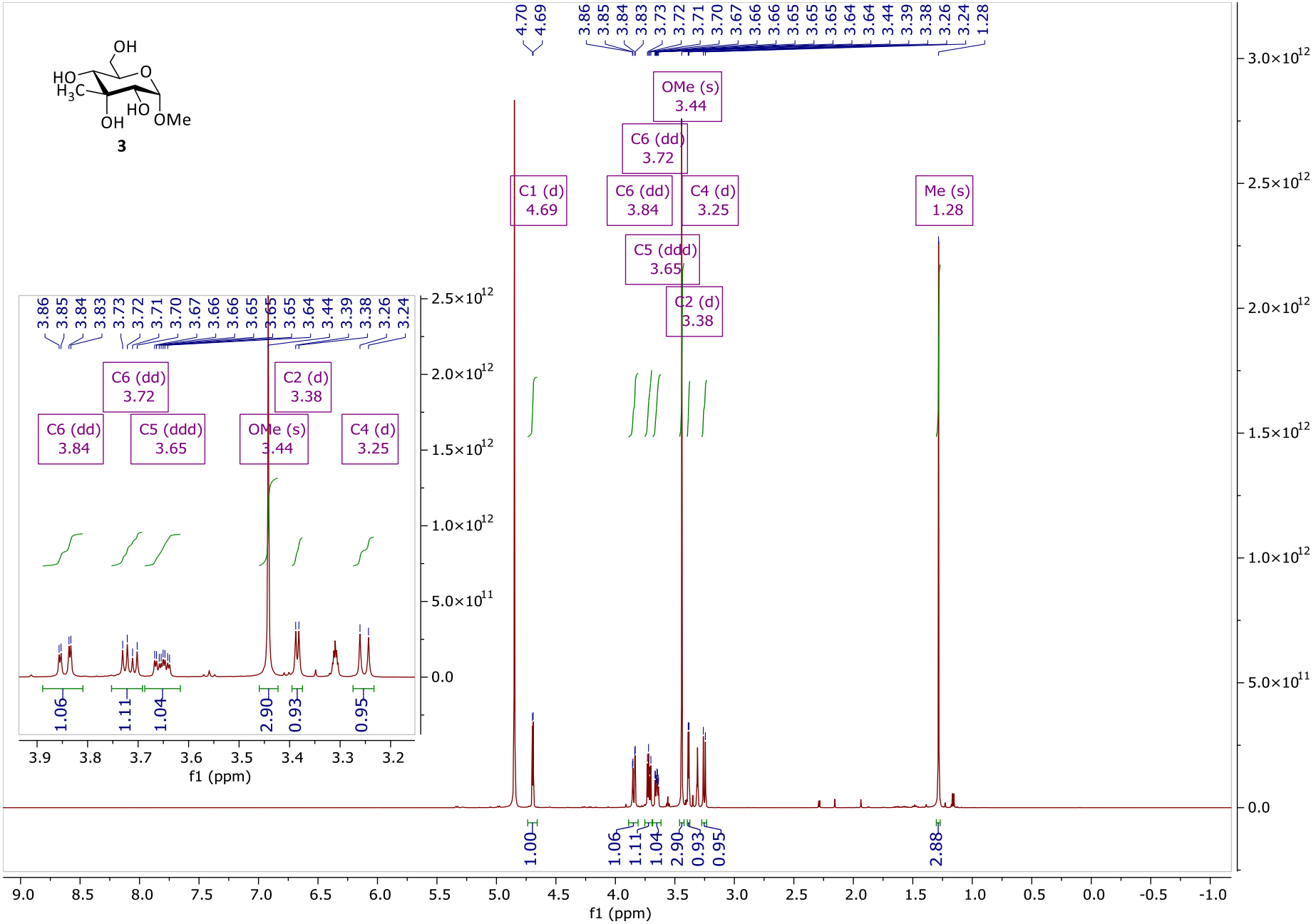

Figure S7 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3-*C*-methyl-α-D-allopyranoside (**3**)

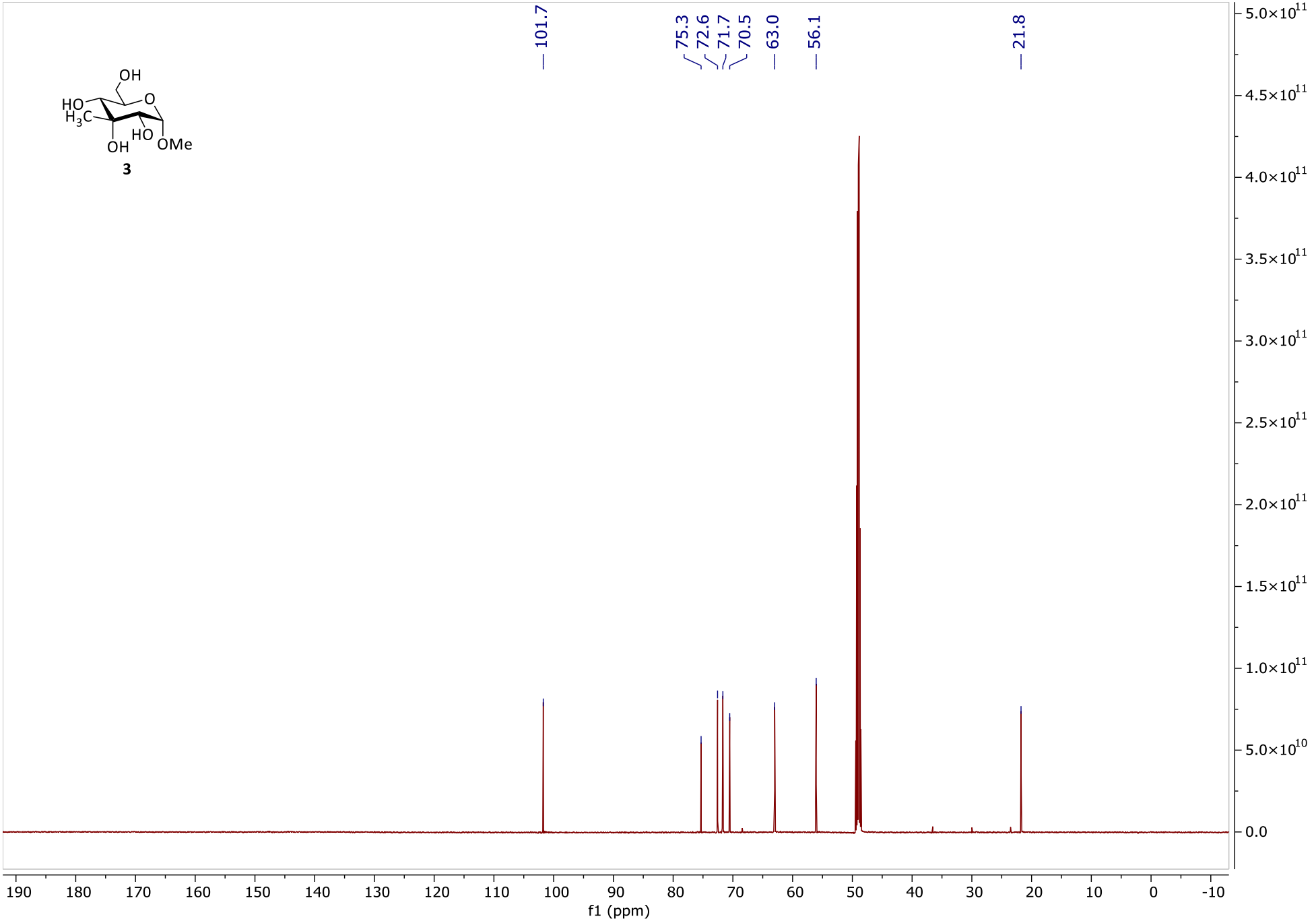

Figure S8 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 3-*C*-methyl-α-D-allopyranoside (**3**)

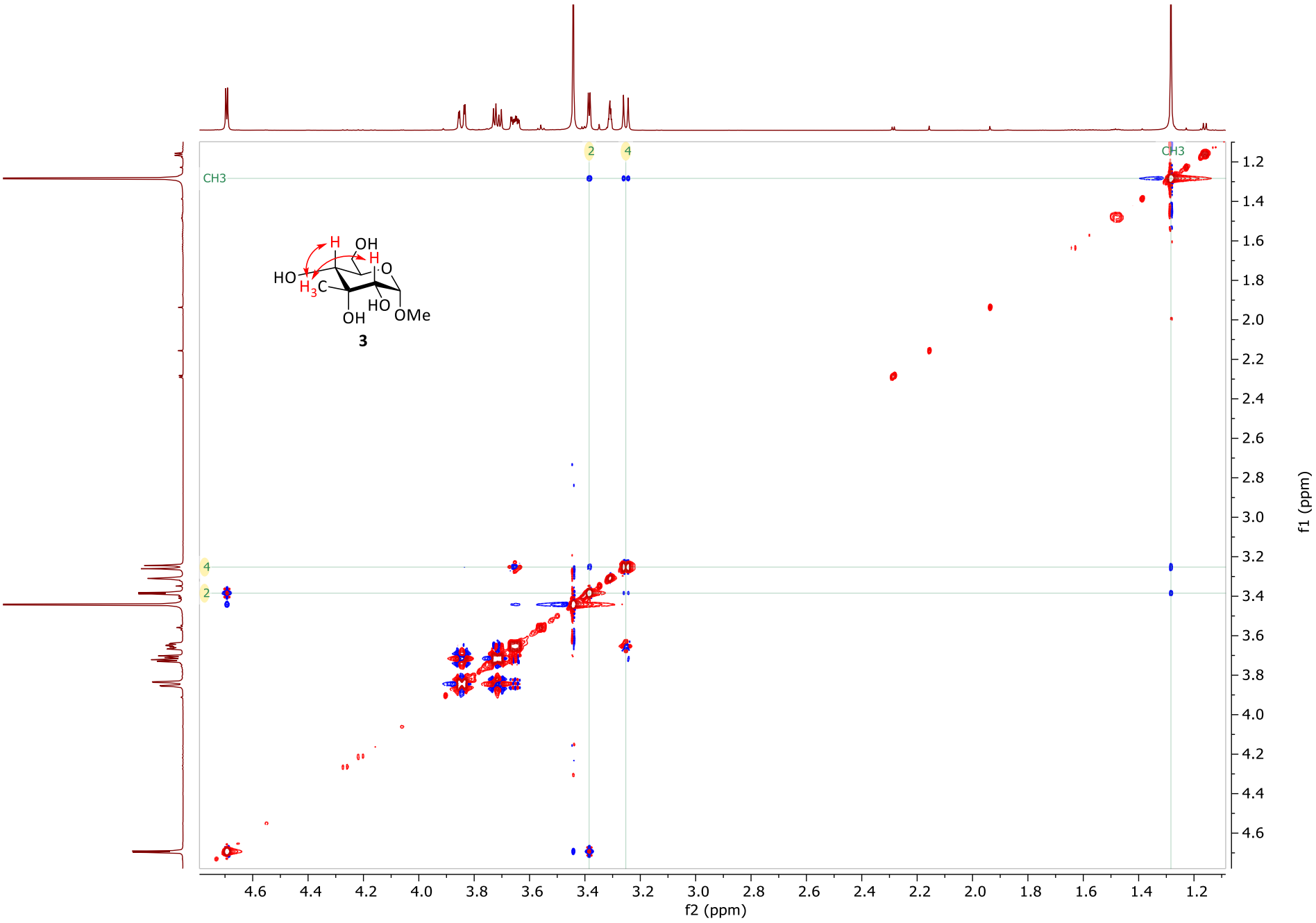

Figure S9 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-methyl-α-D-allopyranoside (**3**)

Methyl 3-*C*-allyl-α-D-allopyranoside (4)

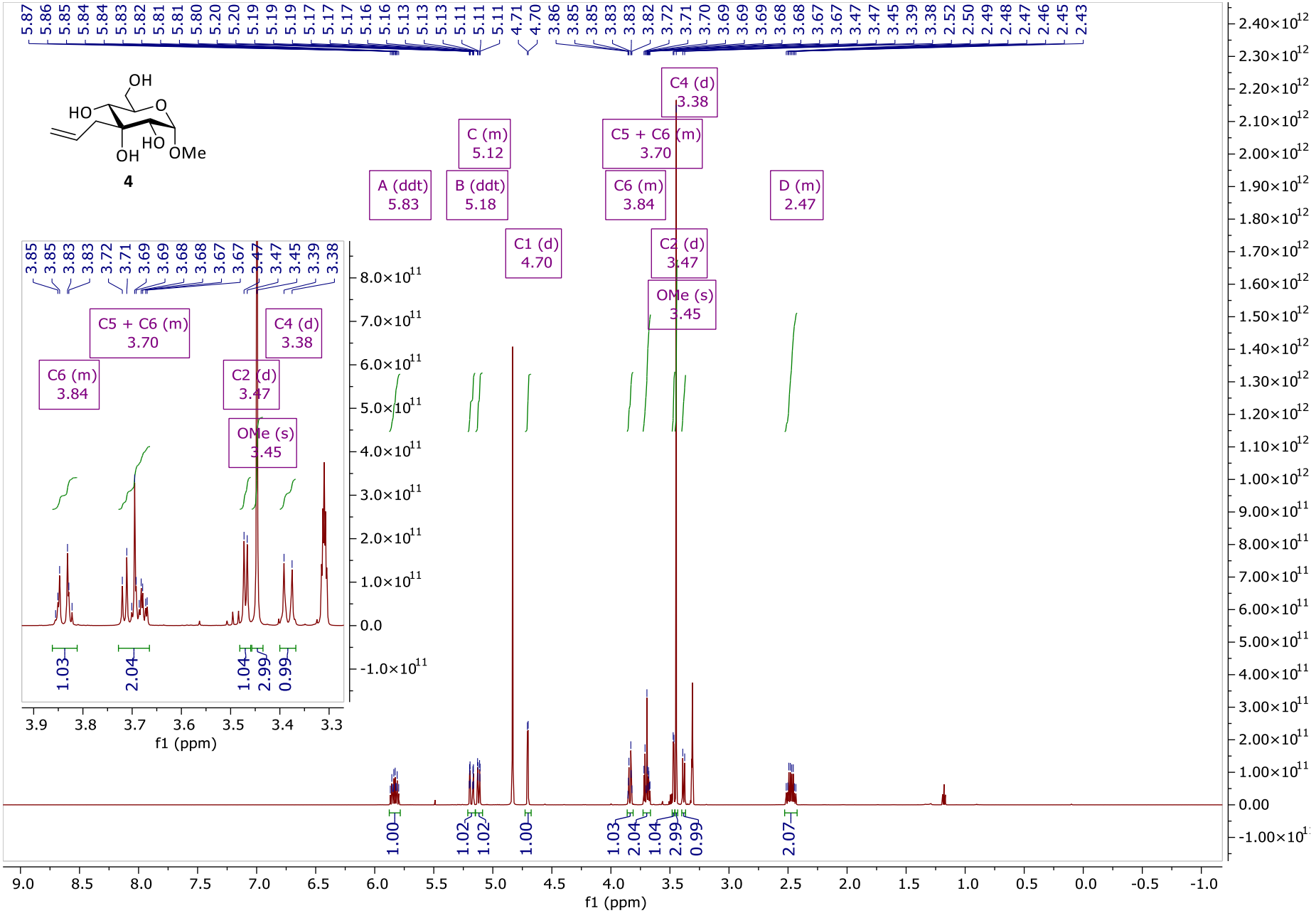

Figure S10 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3-*C*-allyl-α-D-allopyranoside (**4**)

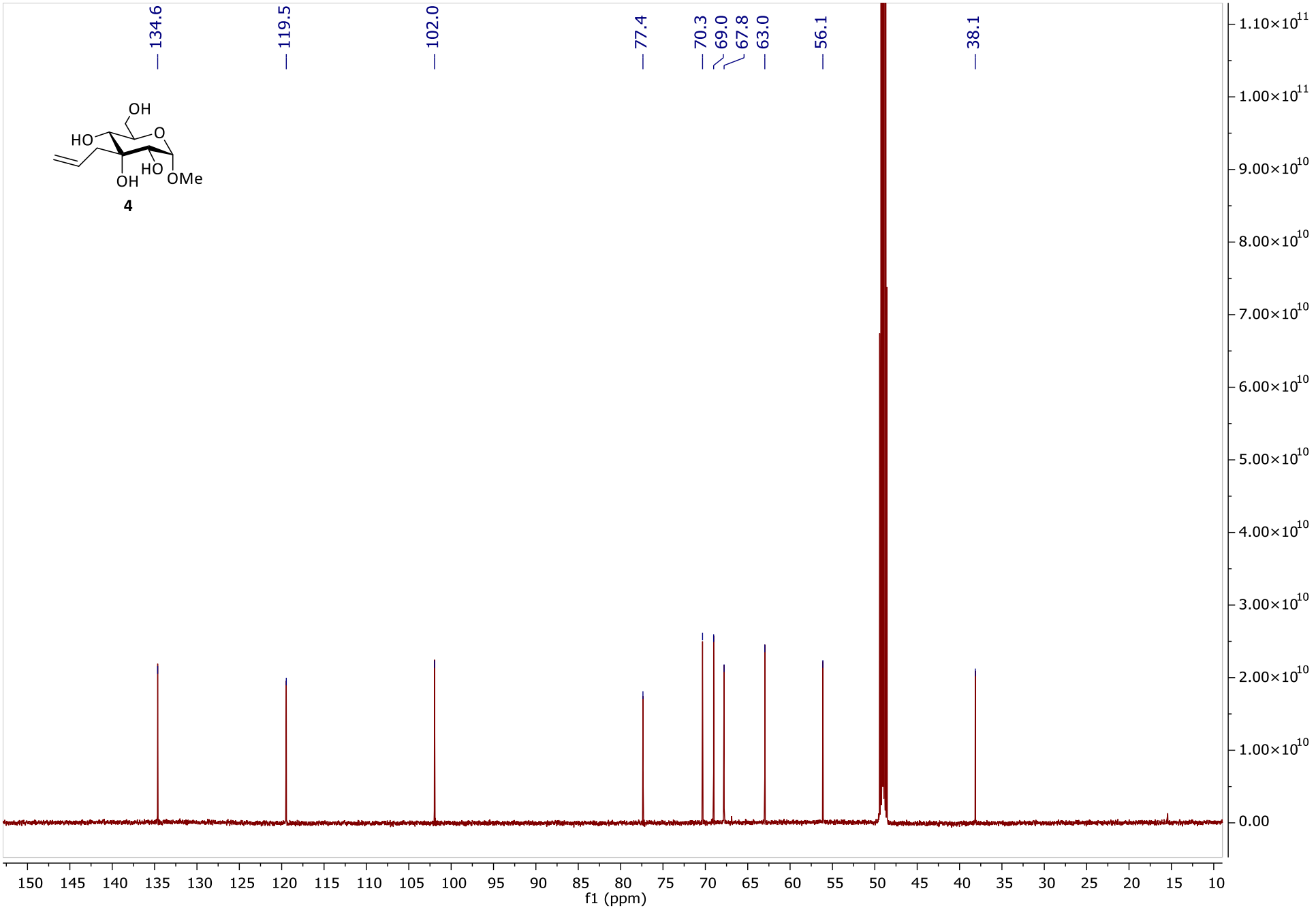

Figure S11 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 3-*C*-allyl-α-D-allopyranoside (**4**)

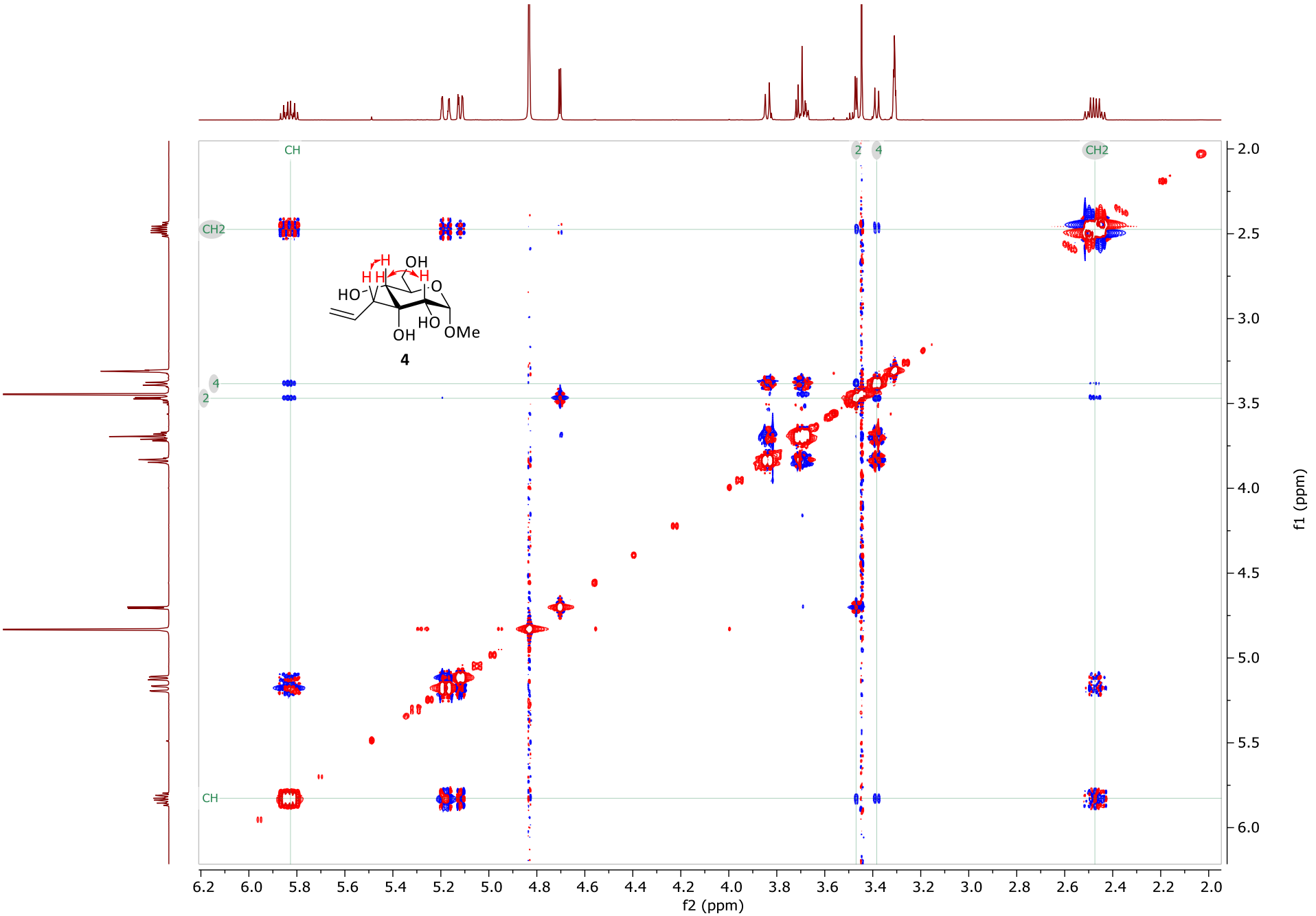

Figure S12 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-allyl-α-D-allopyranoside (**4**)

Methyl 3-*C*-propargyl-α-D-allopyranoside (5a) & Methyl 3-*C*-allenyl-α-D-allopyranoside (5b)

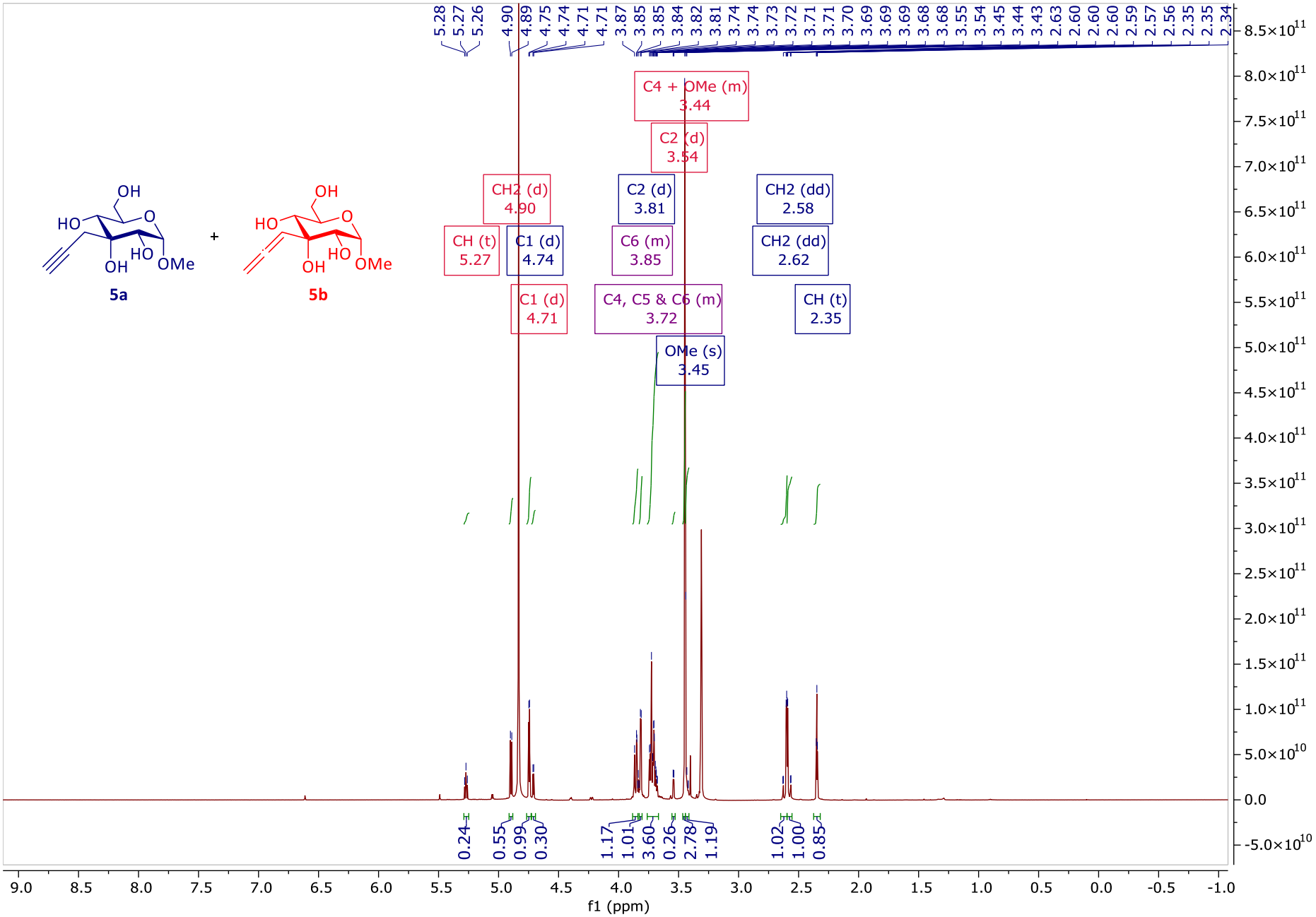

Figure S13 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3-*C*-propargyl-α-D-allopyranoside (**5a**) & methyl 3-*C*-allenyl-α-D-allopyranoside (**5b**)

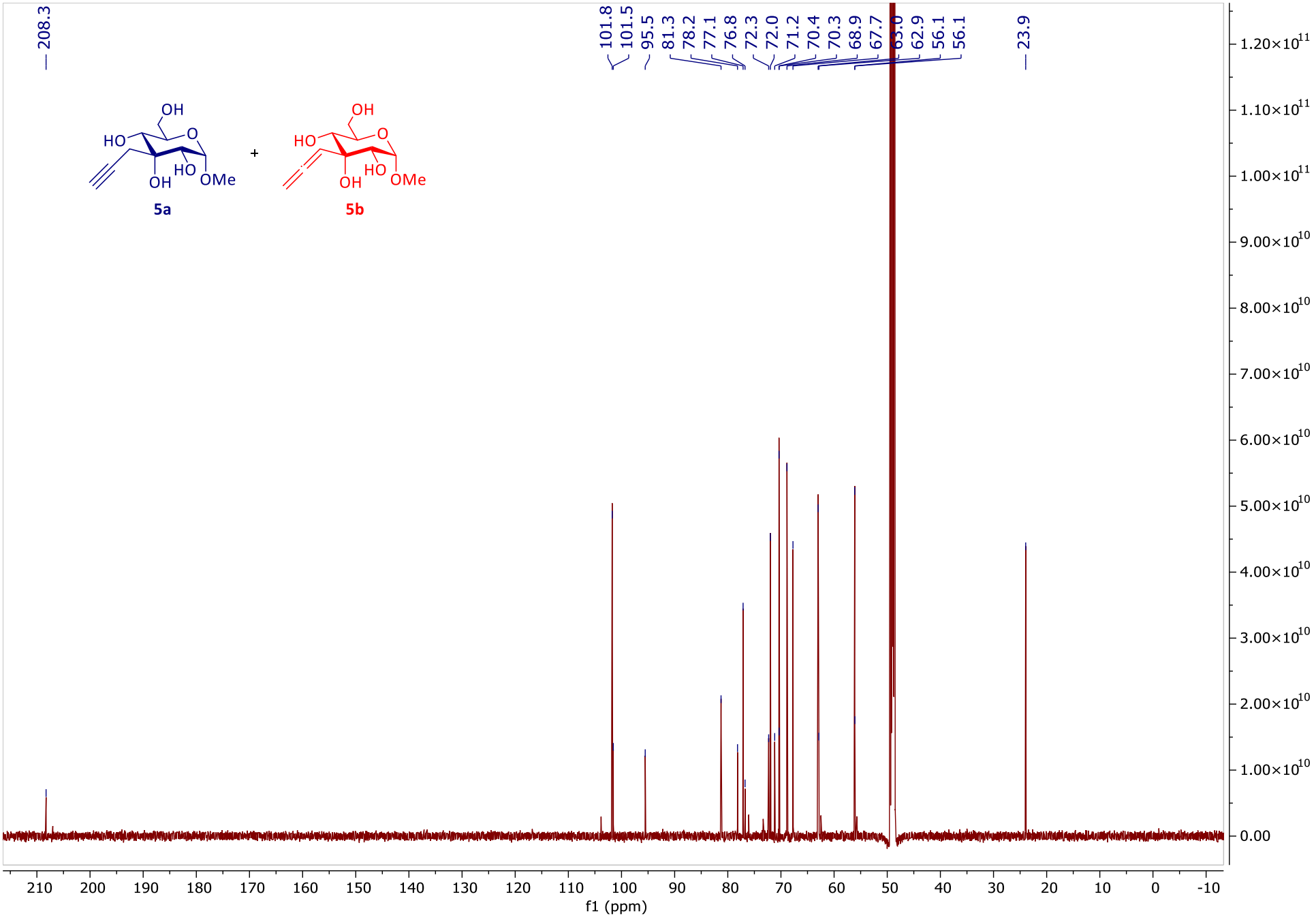

Figure S14 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 3-*C*-propargyl-α-D-allopyranoside (**5a**) & methyl 3-*C*-allenyl-α-D-allopyranoside (**5b**)

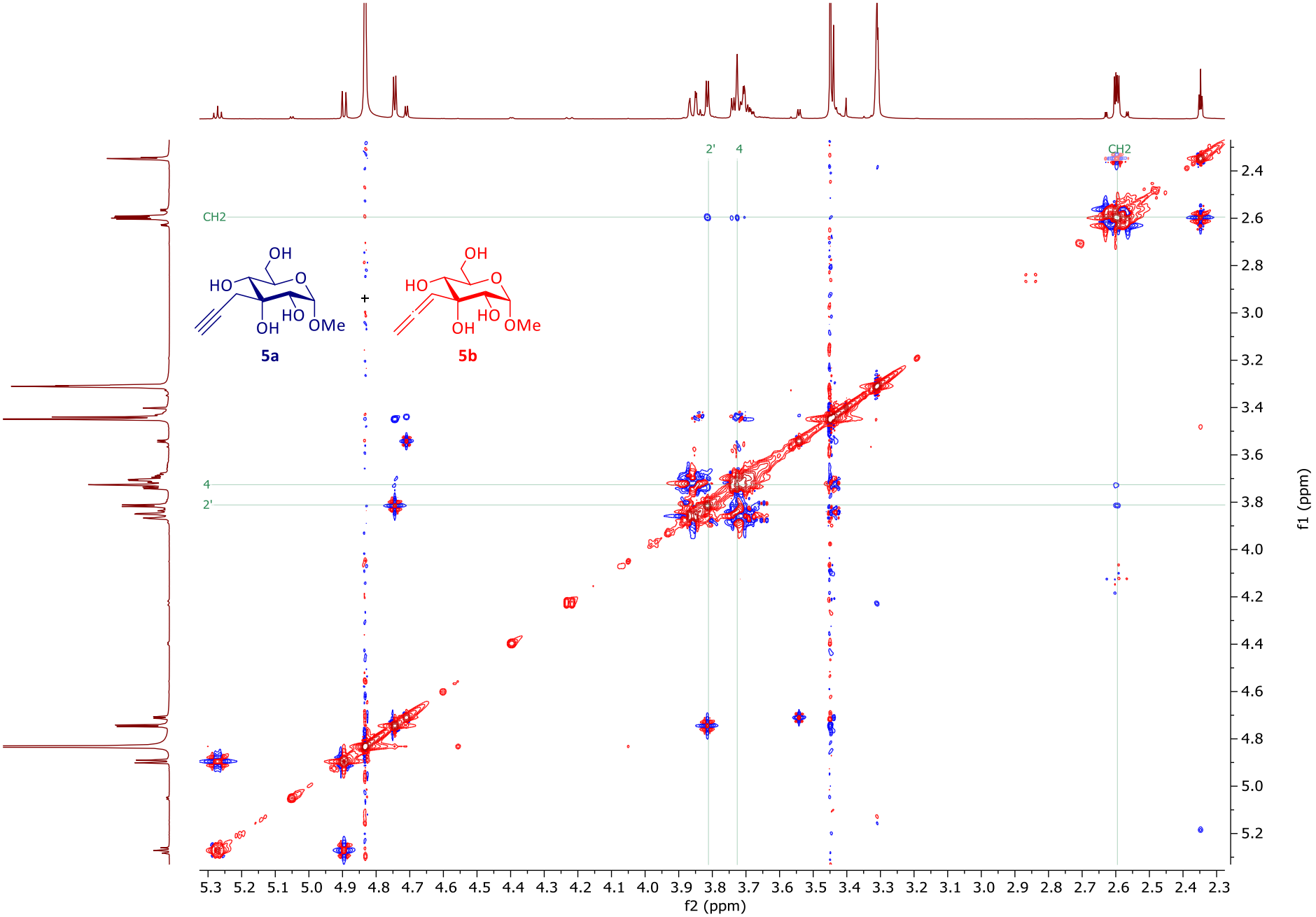

Figure S15 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-propargyl-α-D-allopyranoside (**5a**) & methyl 3-*C*-allenyl-α-D-allopyranoside (**5b**)

Methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (6)

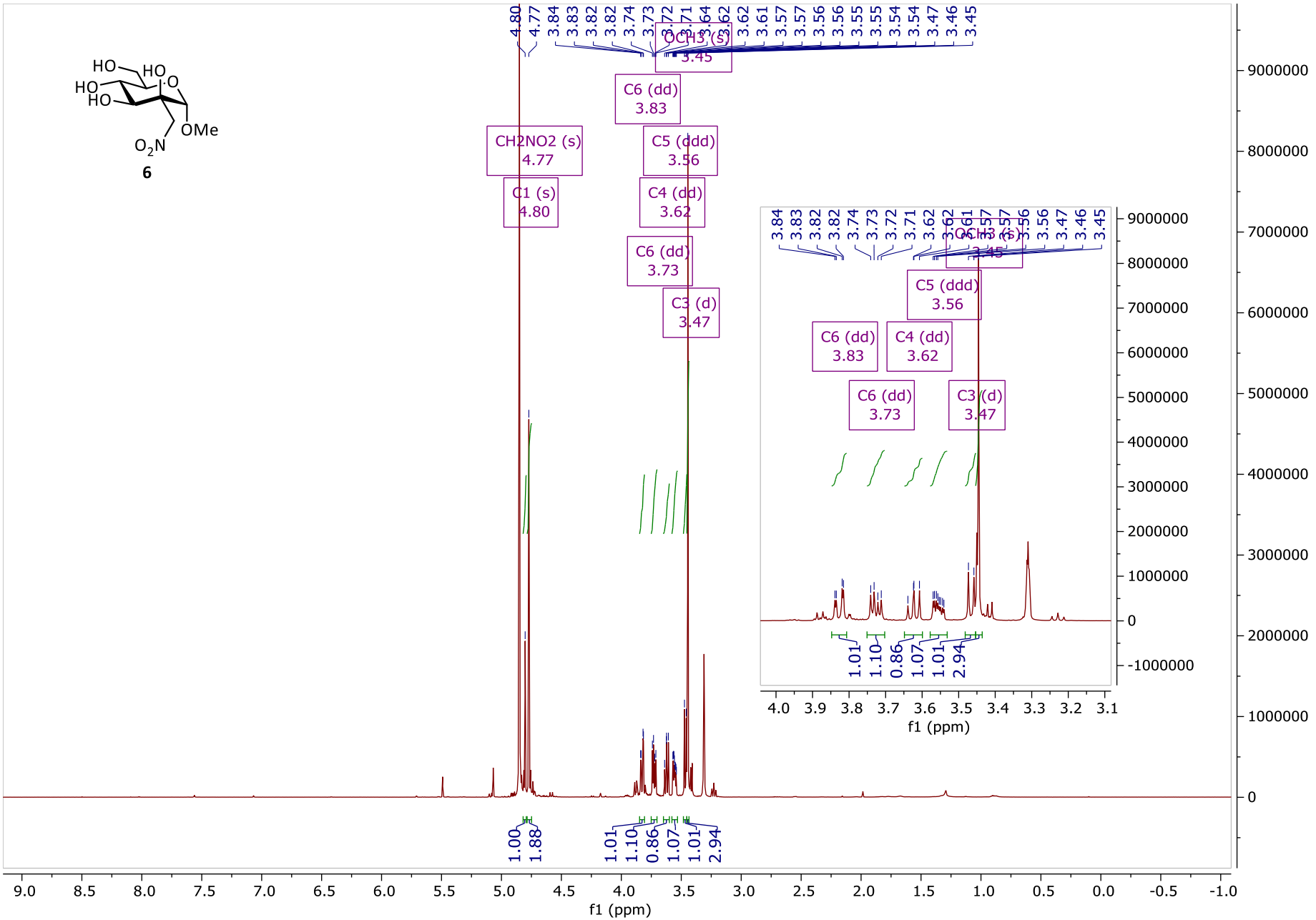

Figure S16 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (**6**)

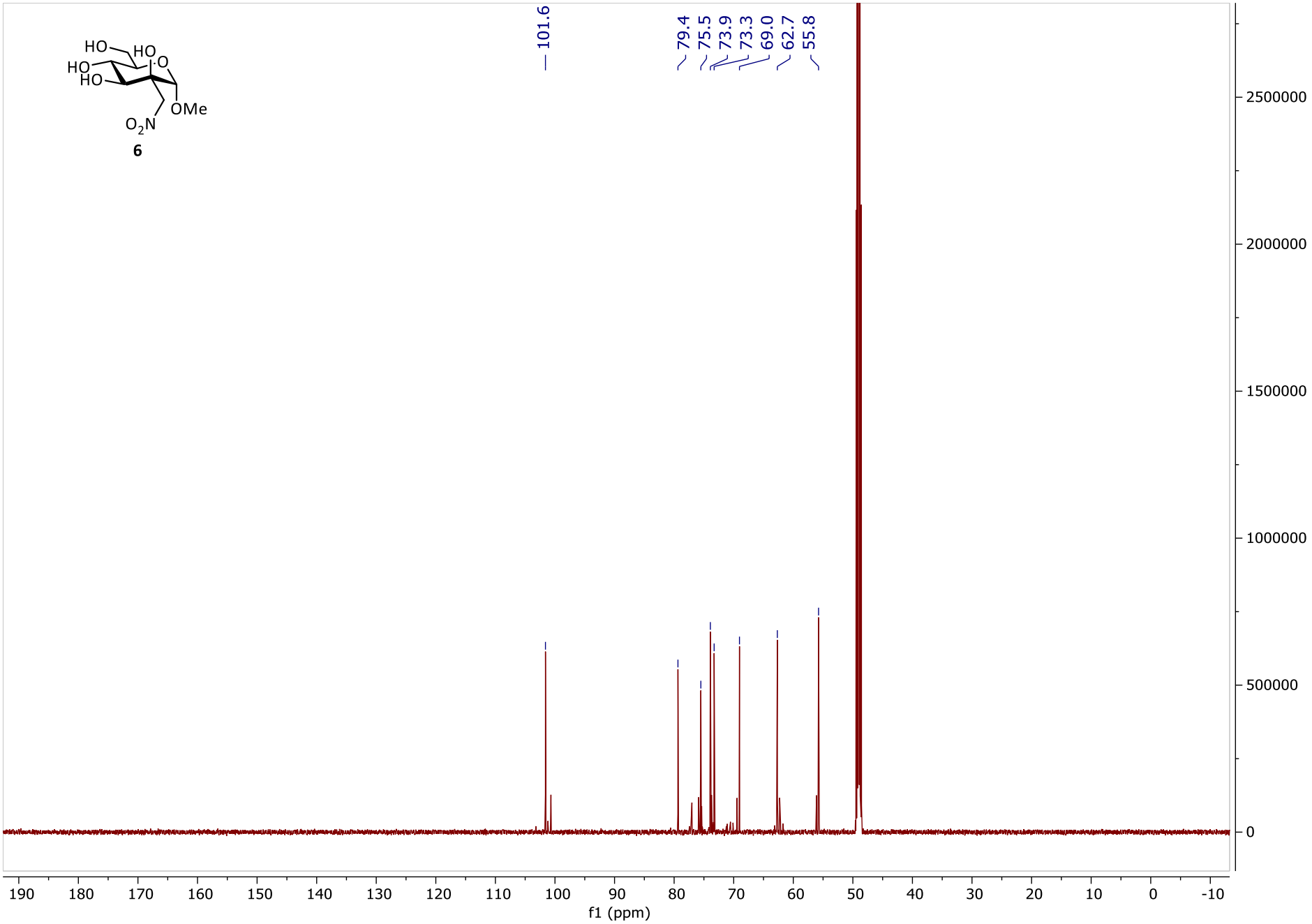

Figure S17 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (**6**)

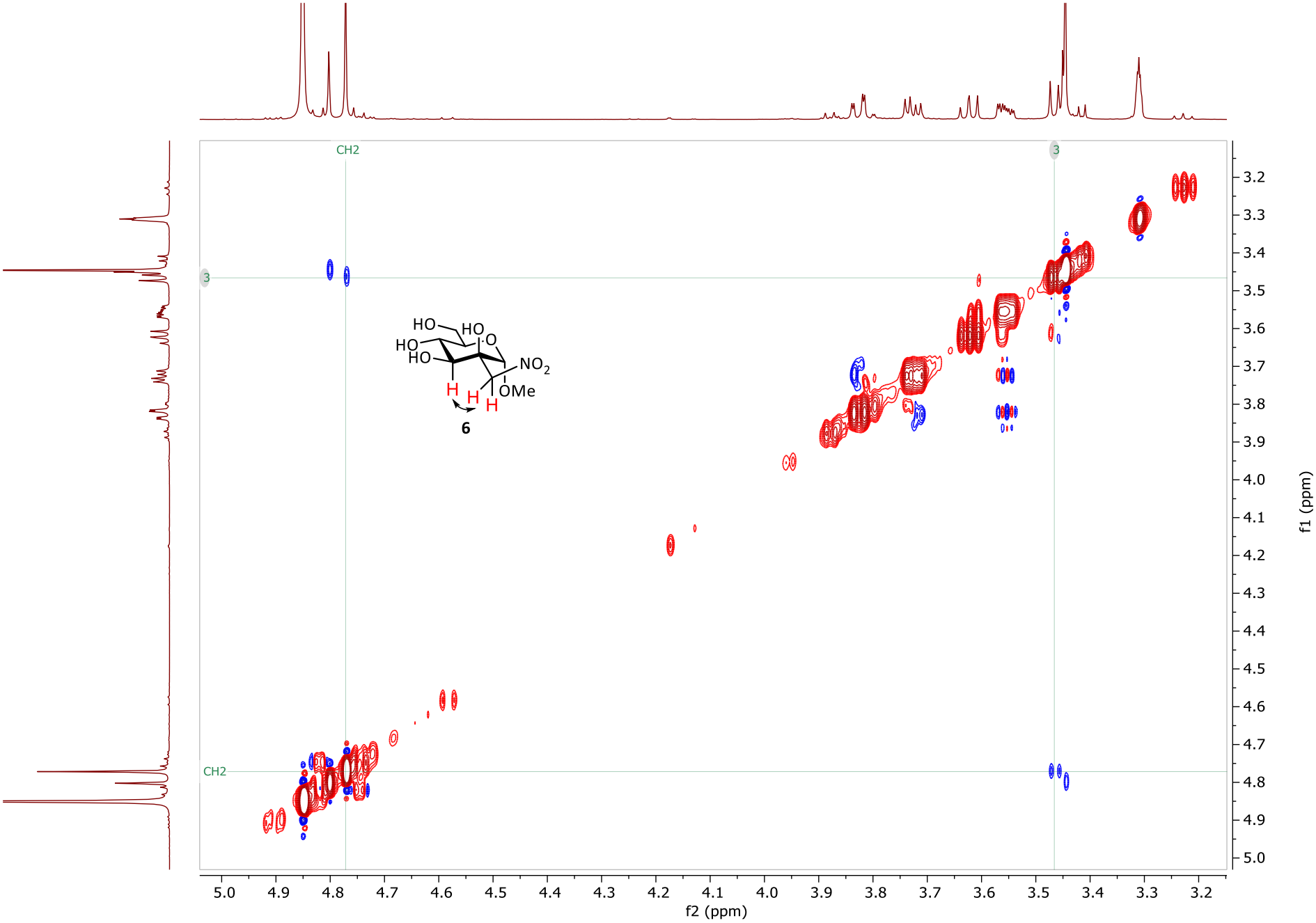

Figure S18 – NOESY (600 MHz, MeOD-*d4*) of methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (**6**)

Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (7)

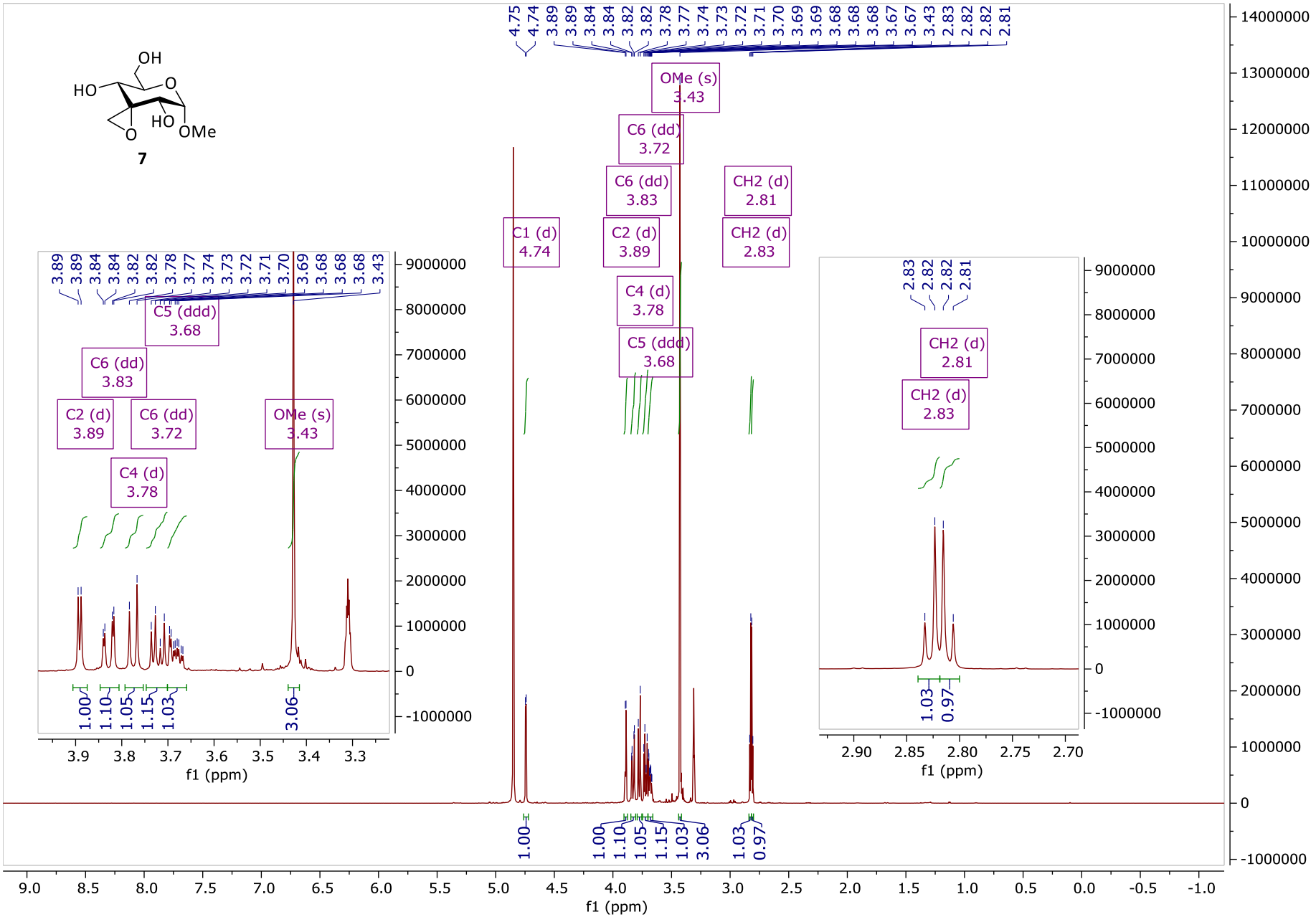

Figure S19 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (**7**)

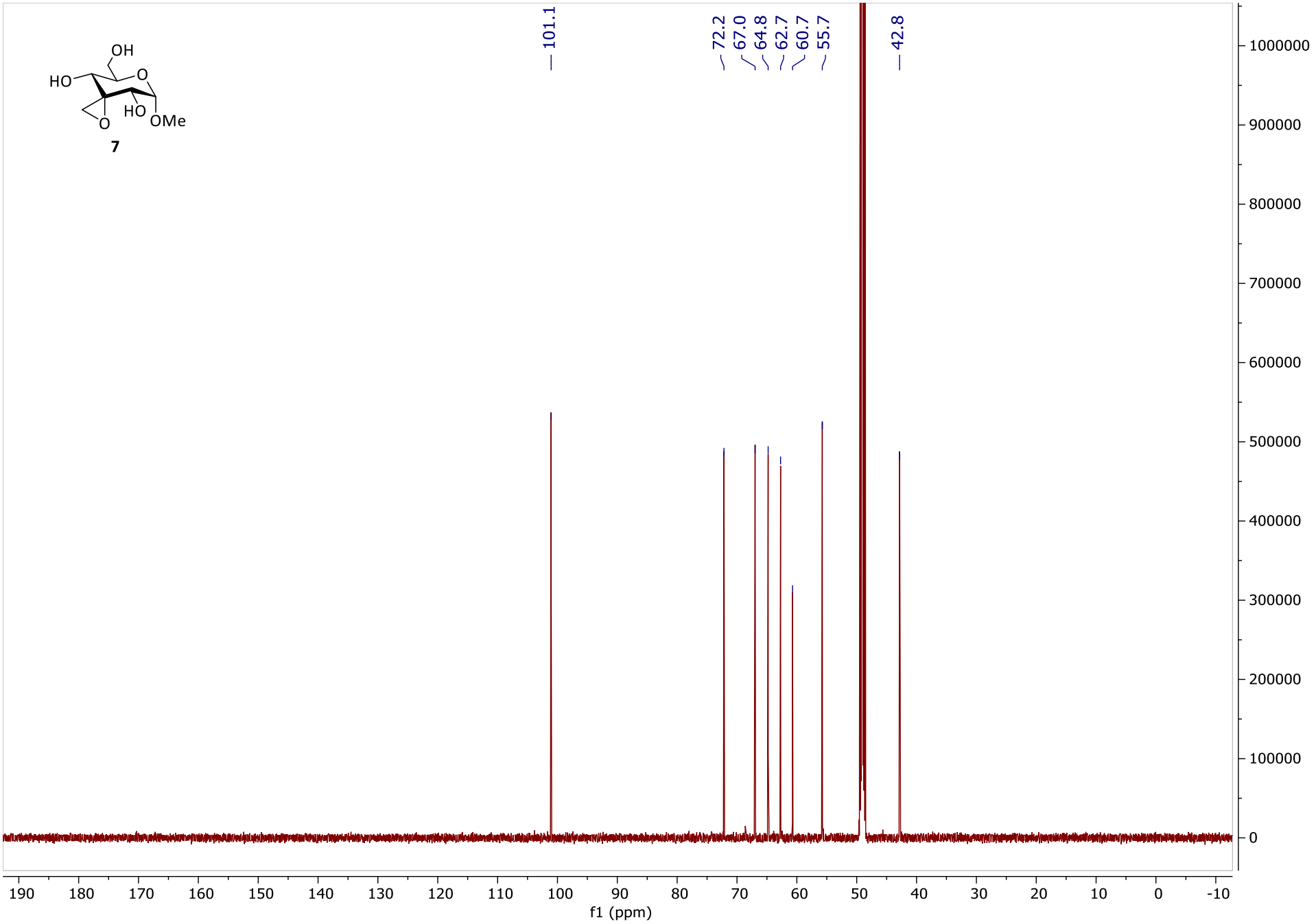

Figure S20 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (**7**)

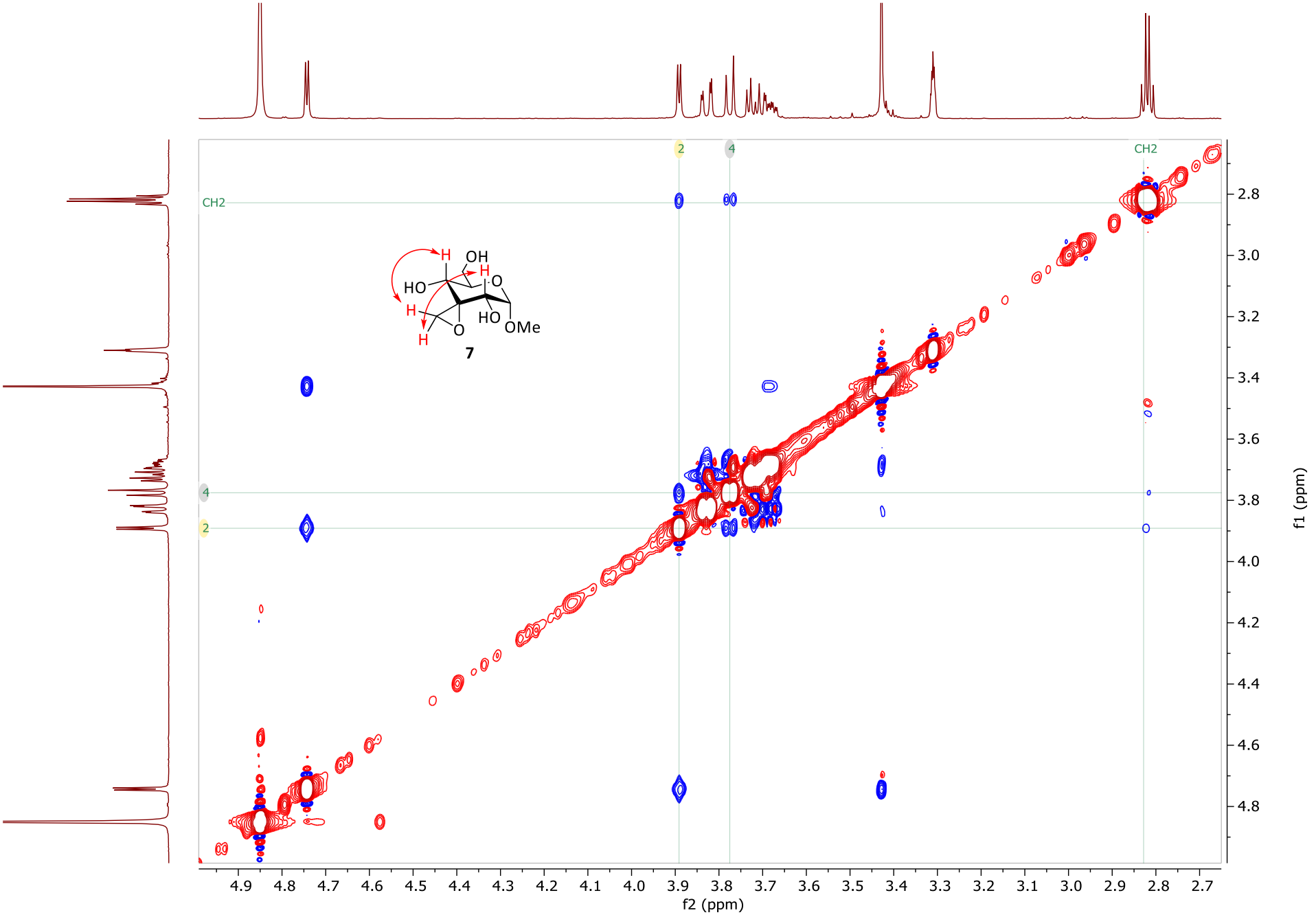

Figure S21 – NOESY (600 MHz, MeOD-*d4*) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (**7**)

Methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (8)

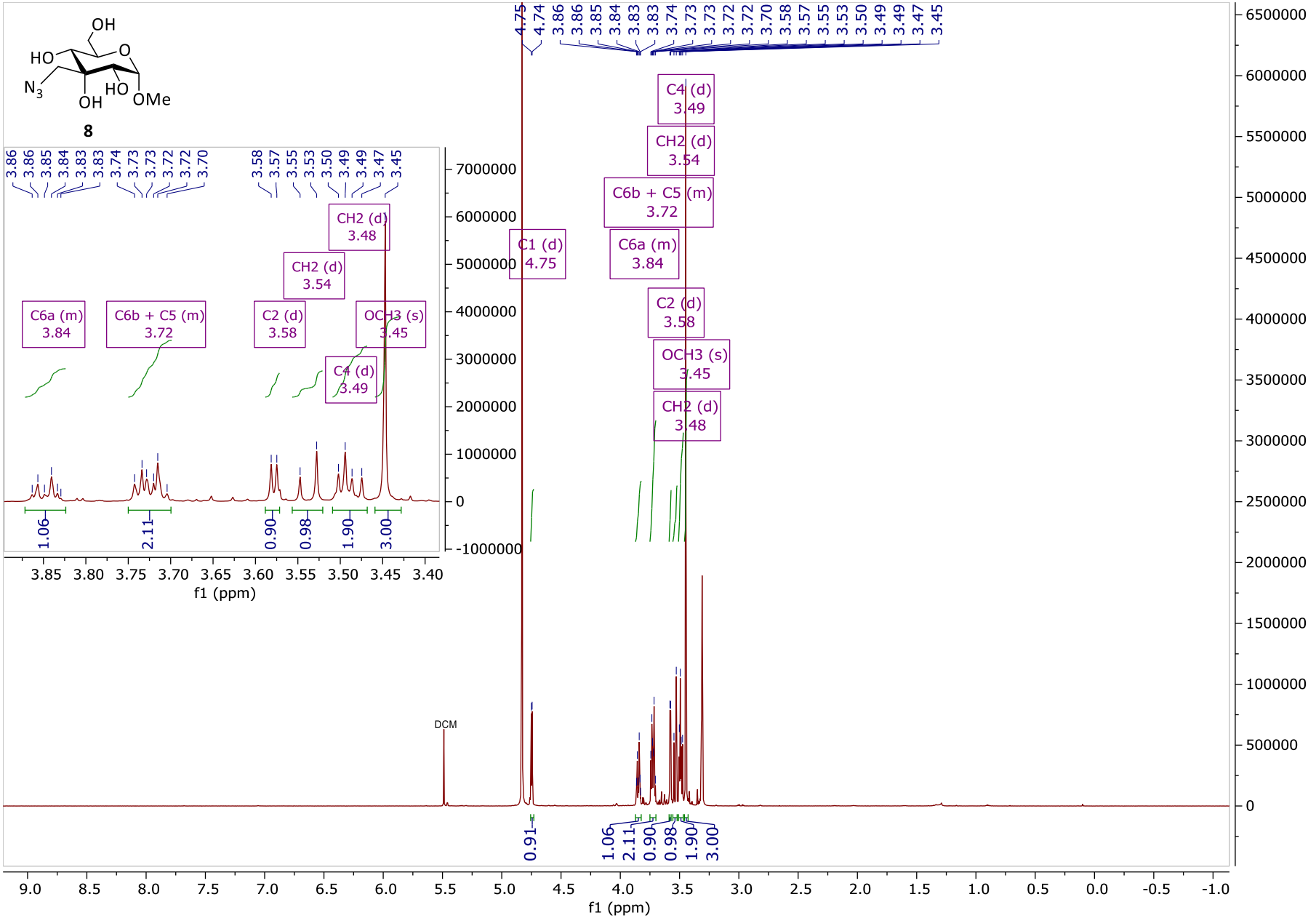

Figure S22 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (**8**)

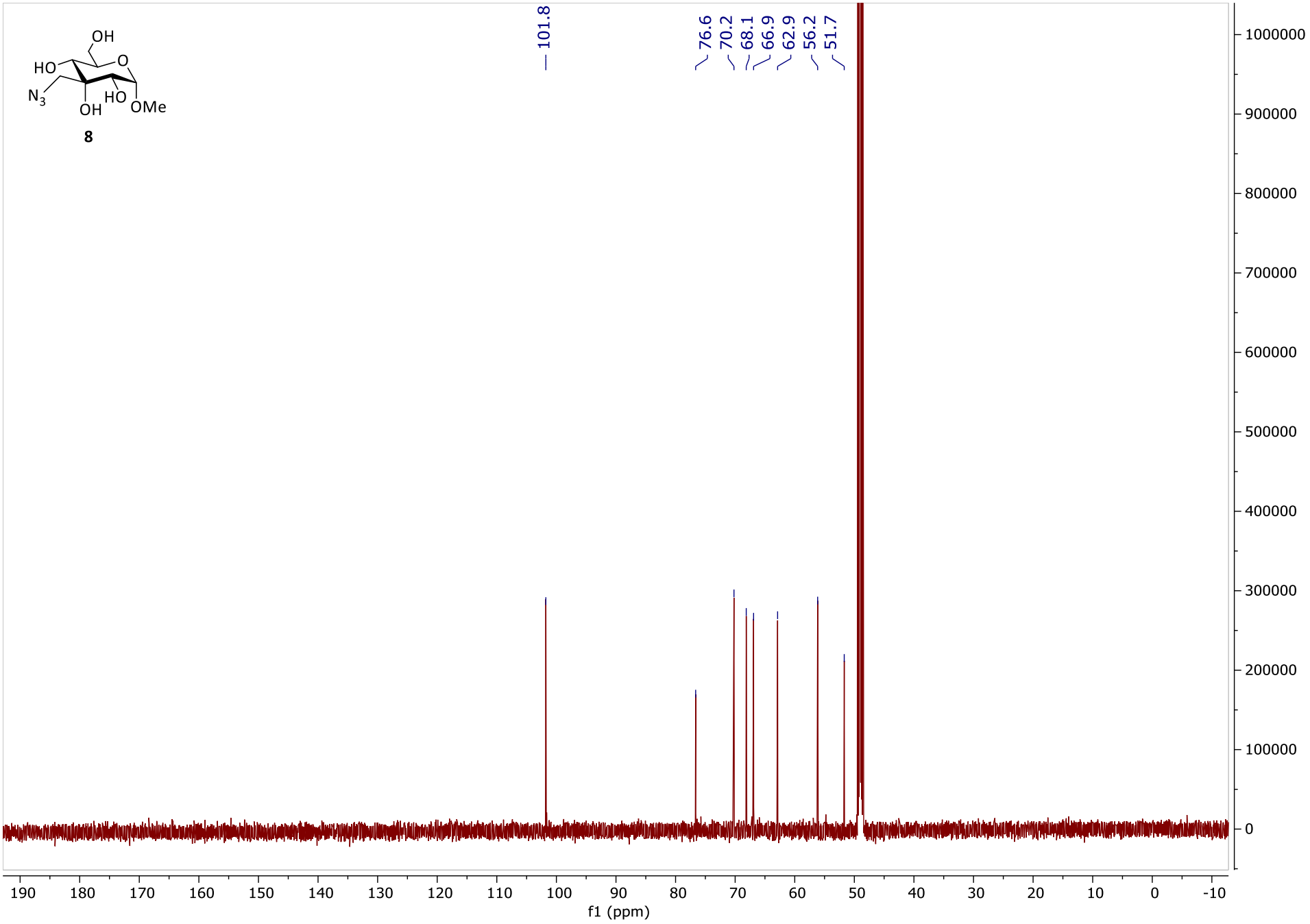

Figure S23 – ^{13}C-NMR (151 MHz, MeOD-*d4*) of methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (**8**)

Methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (9)

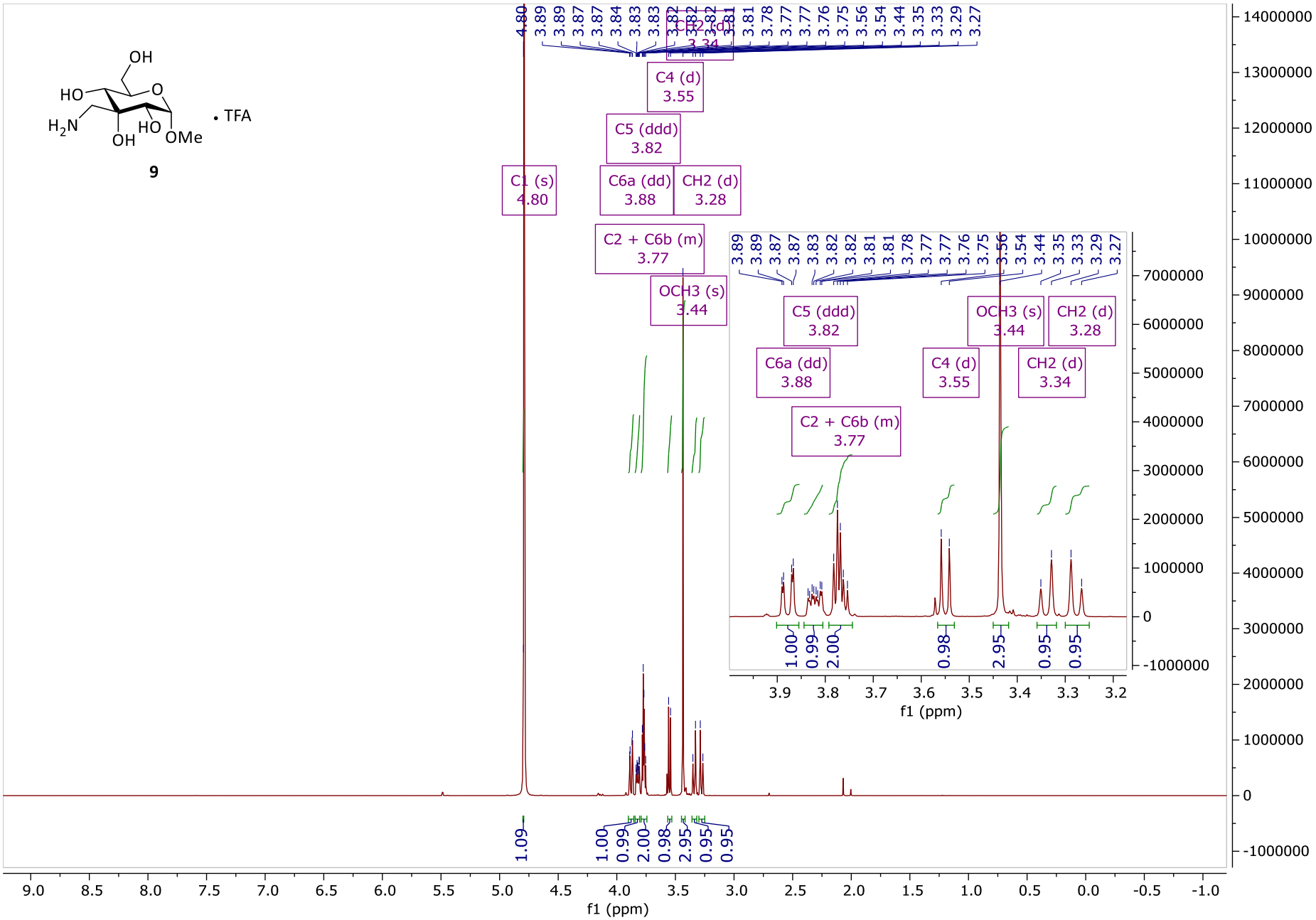

Figure S24 – ^{1}H-NMR (600 MHz, D_2O) of methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (**9**)

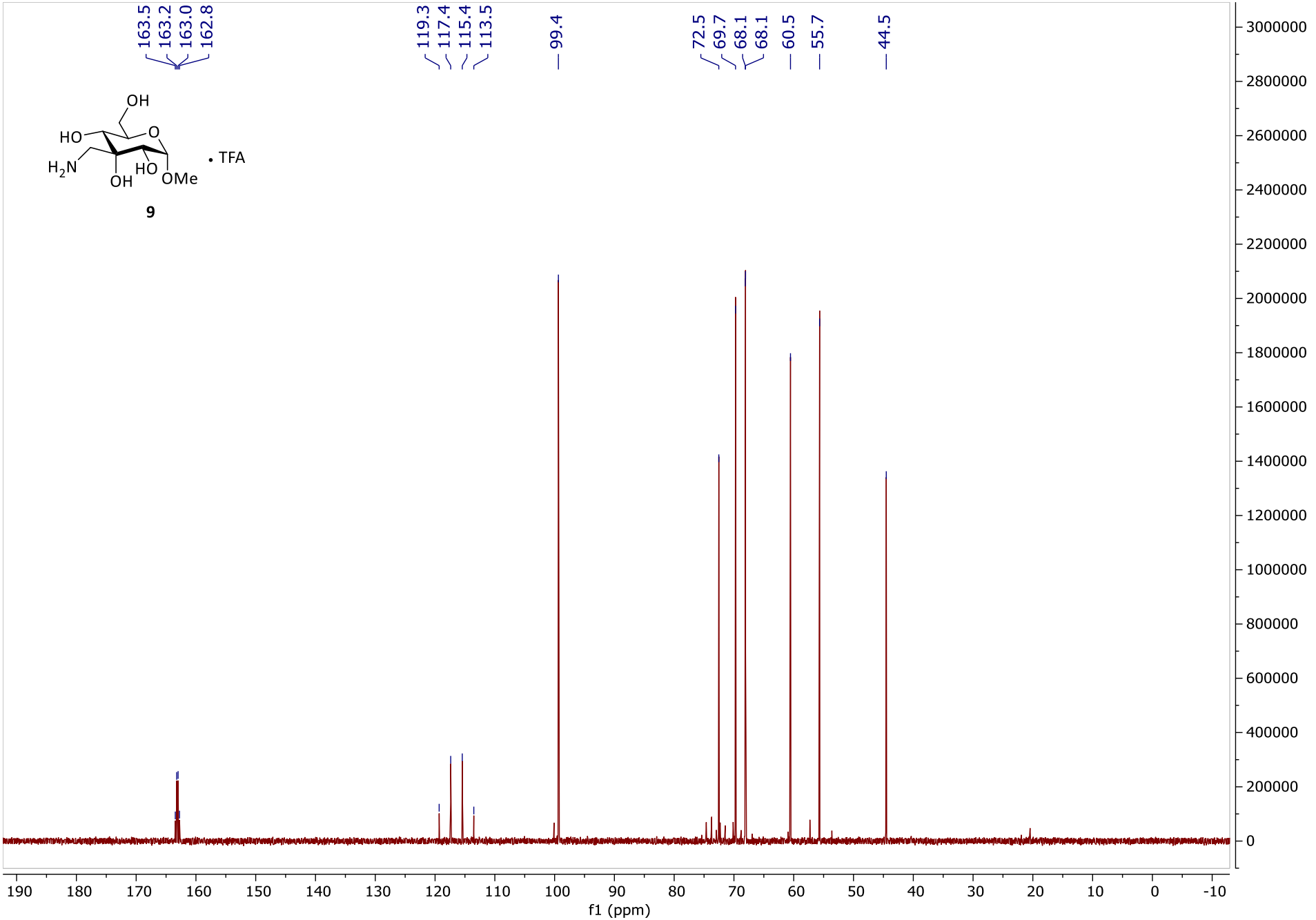

Figure S25 – ^{13}C-NMR (151 MHz, D_2O) of methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (**9**)

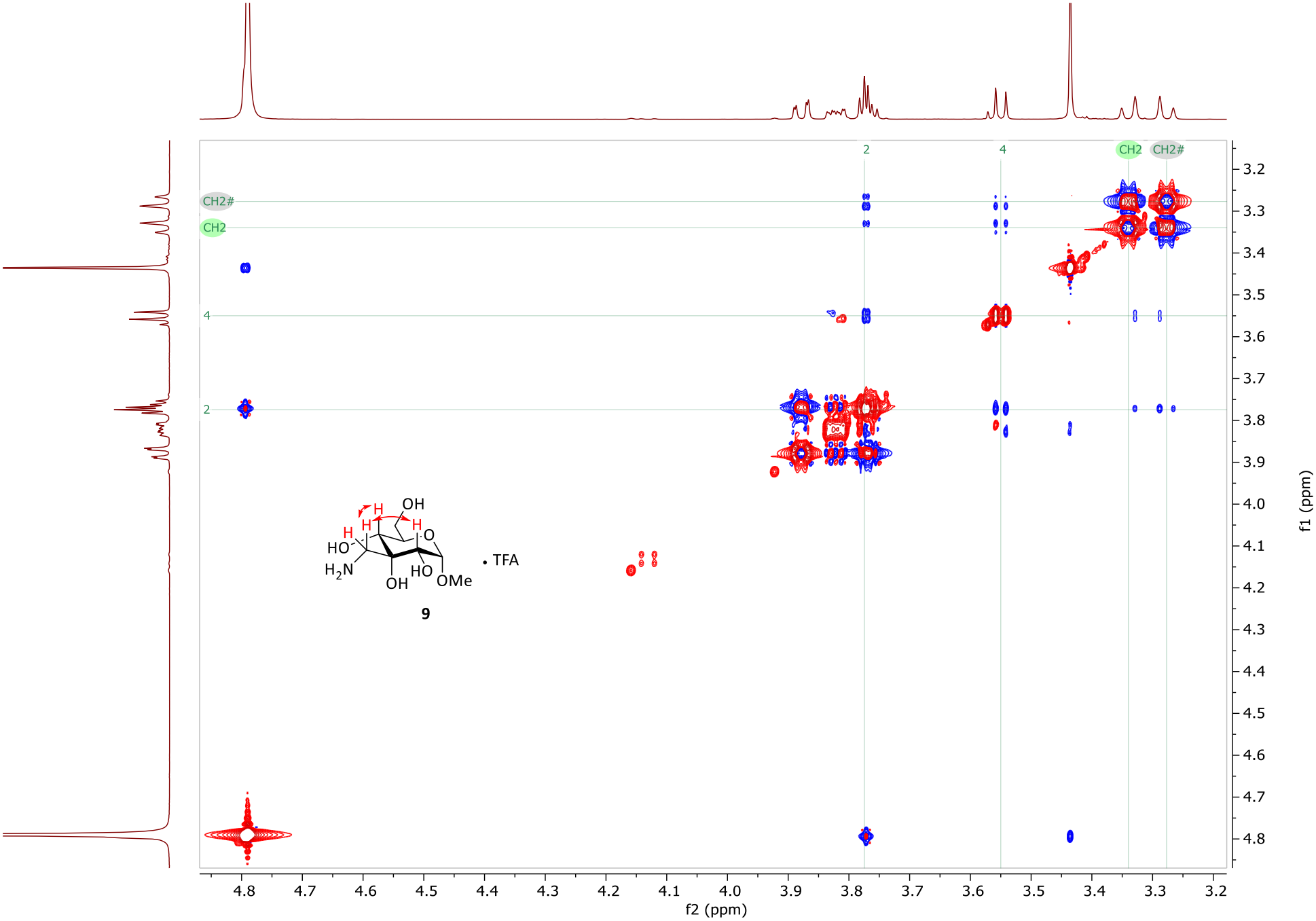

Figure S26 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (**9**)

β-D-maltoheptaosyl azide (10)

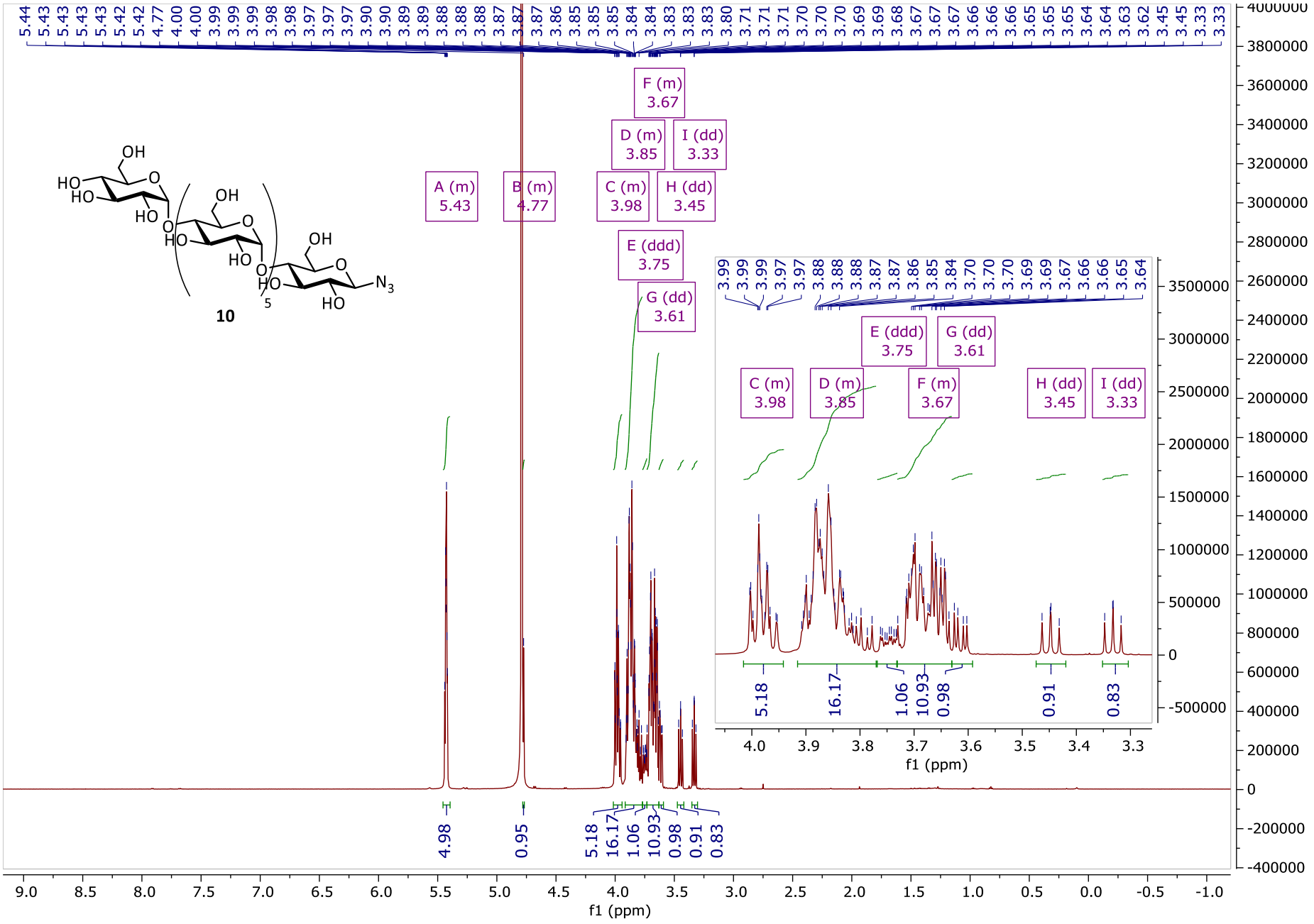

Figure S27 – ^{1}H-NMR (600 MHz, D_2O) of β-D-maltoheptaosyl azide (**10**)

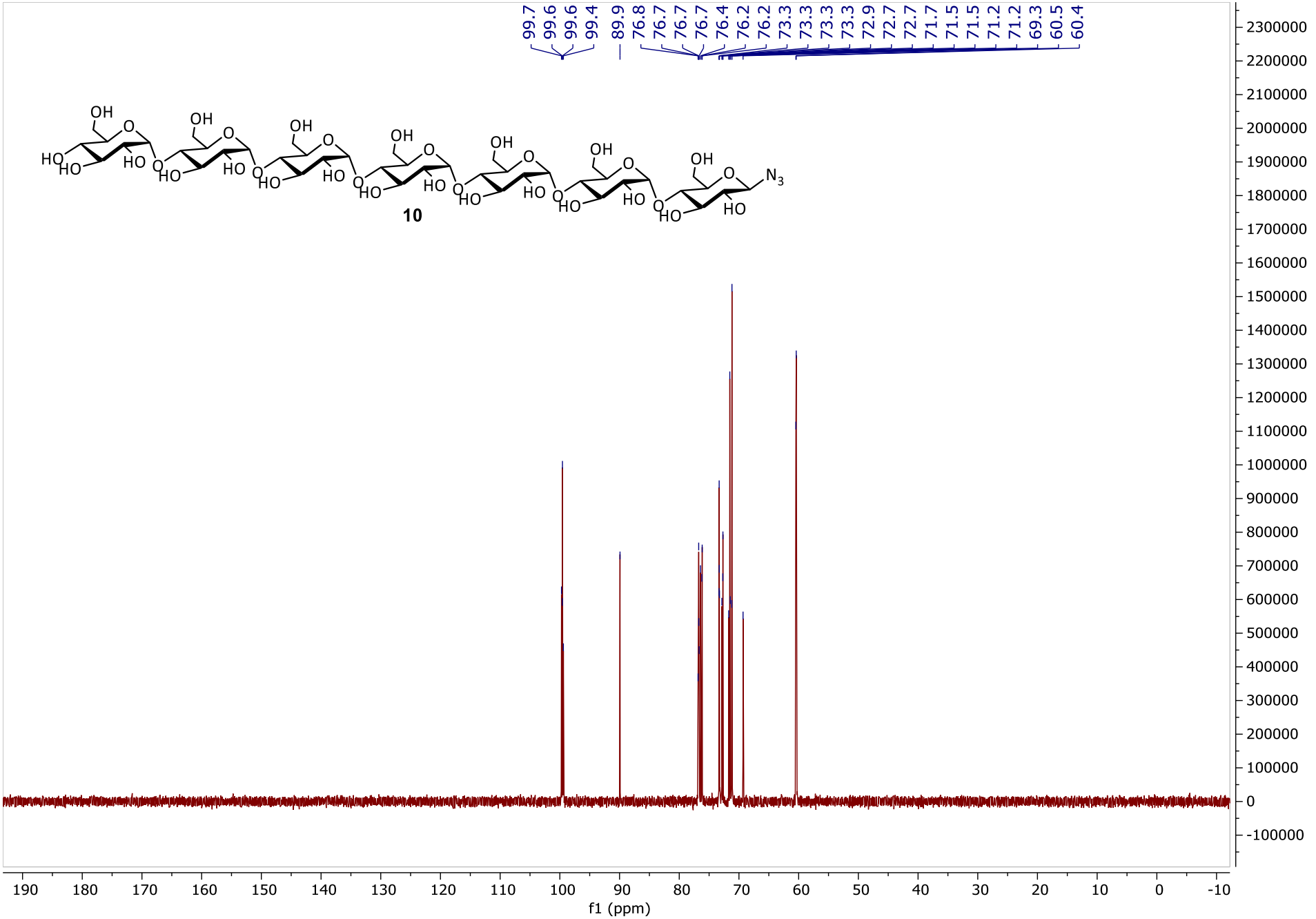

Figure S28 – ^{13}C-NMR (151 MHz, D_2O) of β-D-maltoheptaosyl azide (**10**)

3-keto-β-D-maltoheptaosyl azide (11)

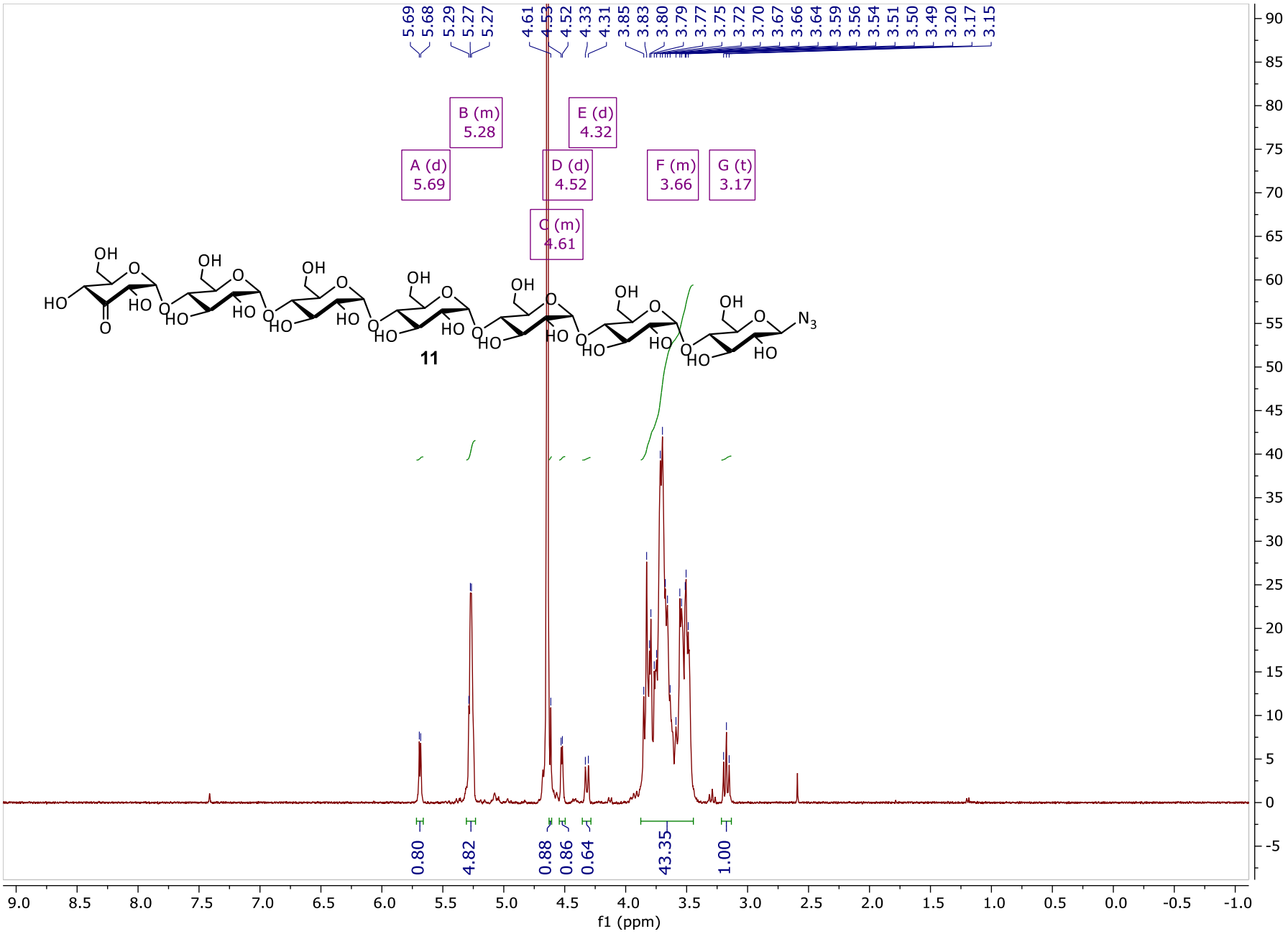

Figure S29 – ^{1}H-NMR (400 MHz, D_2O) of 3-keto-β-D-maltoheptaosyl azide (**11**)

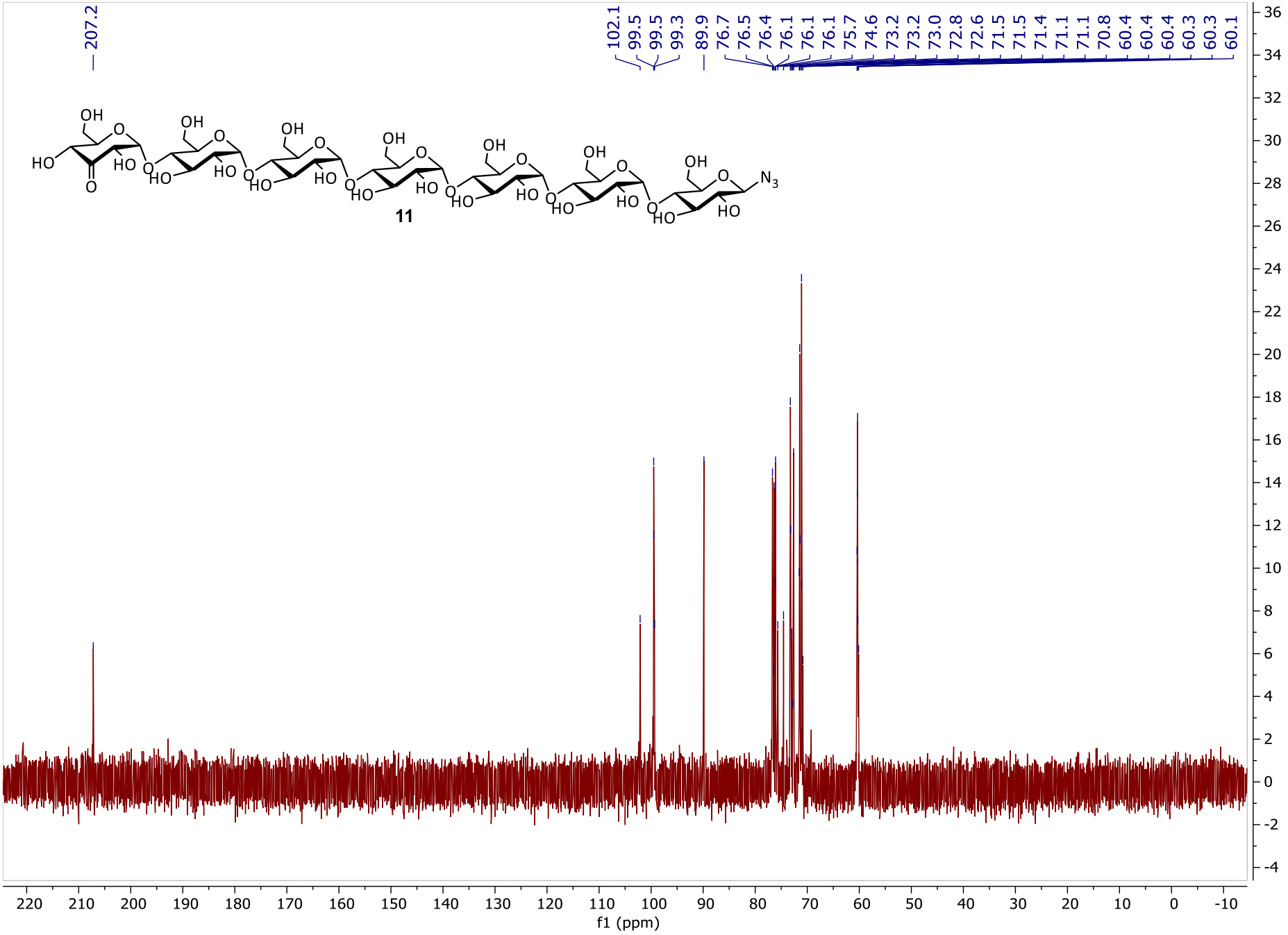

Figure S30 – ^{13}C-NMR (101 MHz, D_2O) of 3-keto-β-D-maltoheptaosyl azide (**11**)

3,3’-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (12)

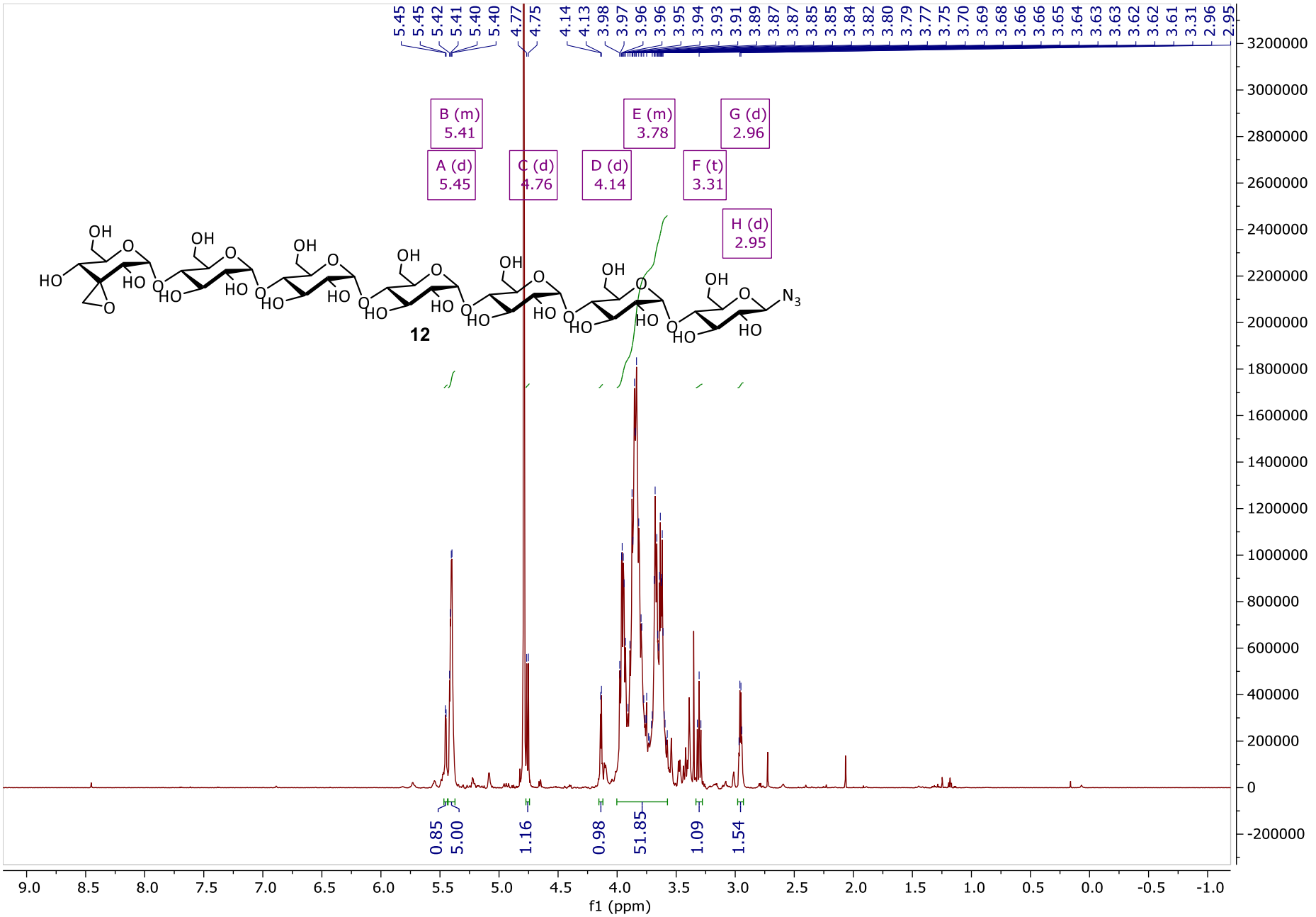

Figure S31 – ^{1}H-NMR (600 MHz, D_2O) of 3,3’-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (**12**)

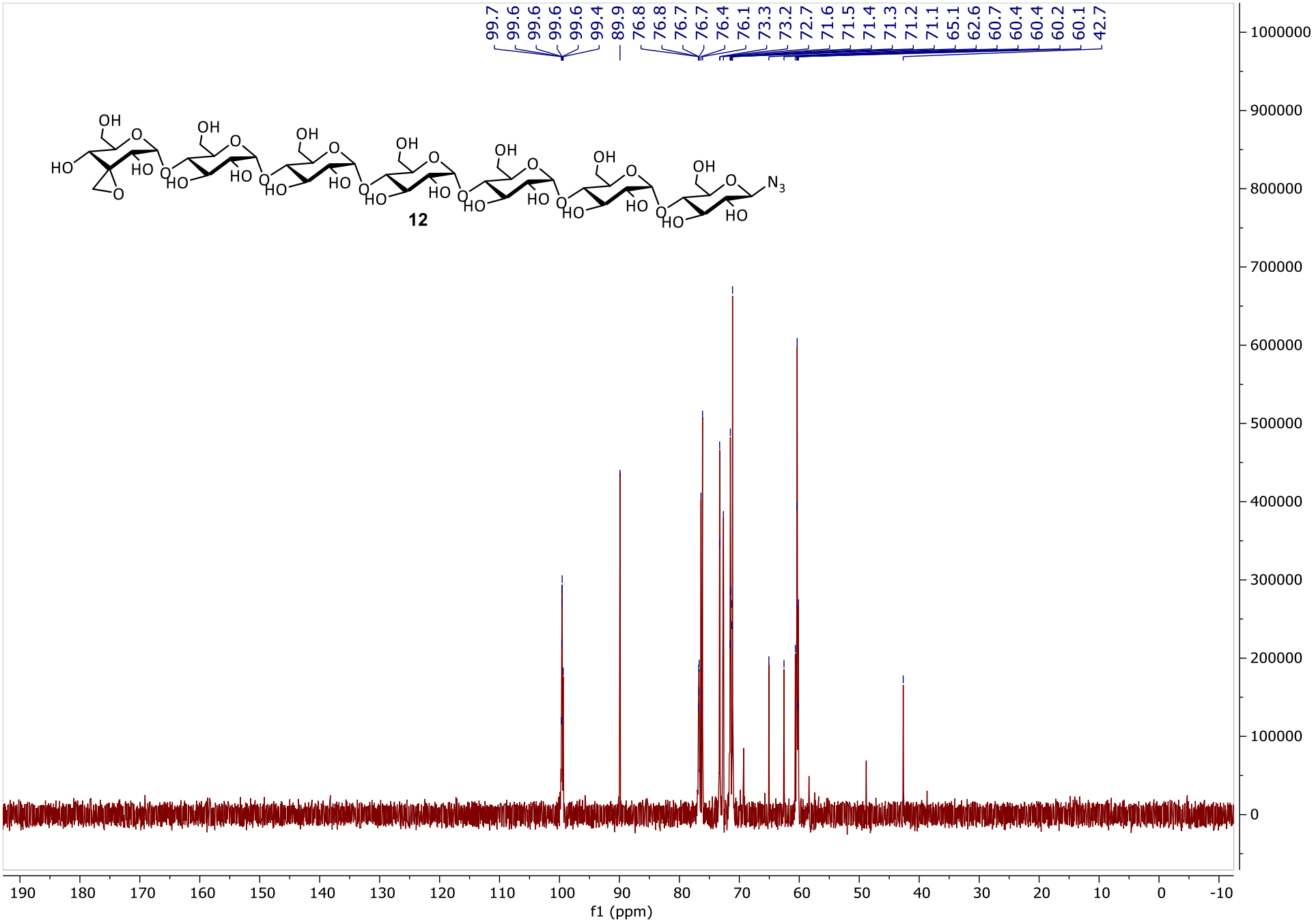

Figure S32 – ^{13}C-NMR (151 MHz, D_2O) of 3,3'-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (**12**)

Methyl *E/Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (13)

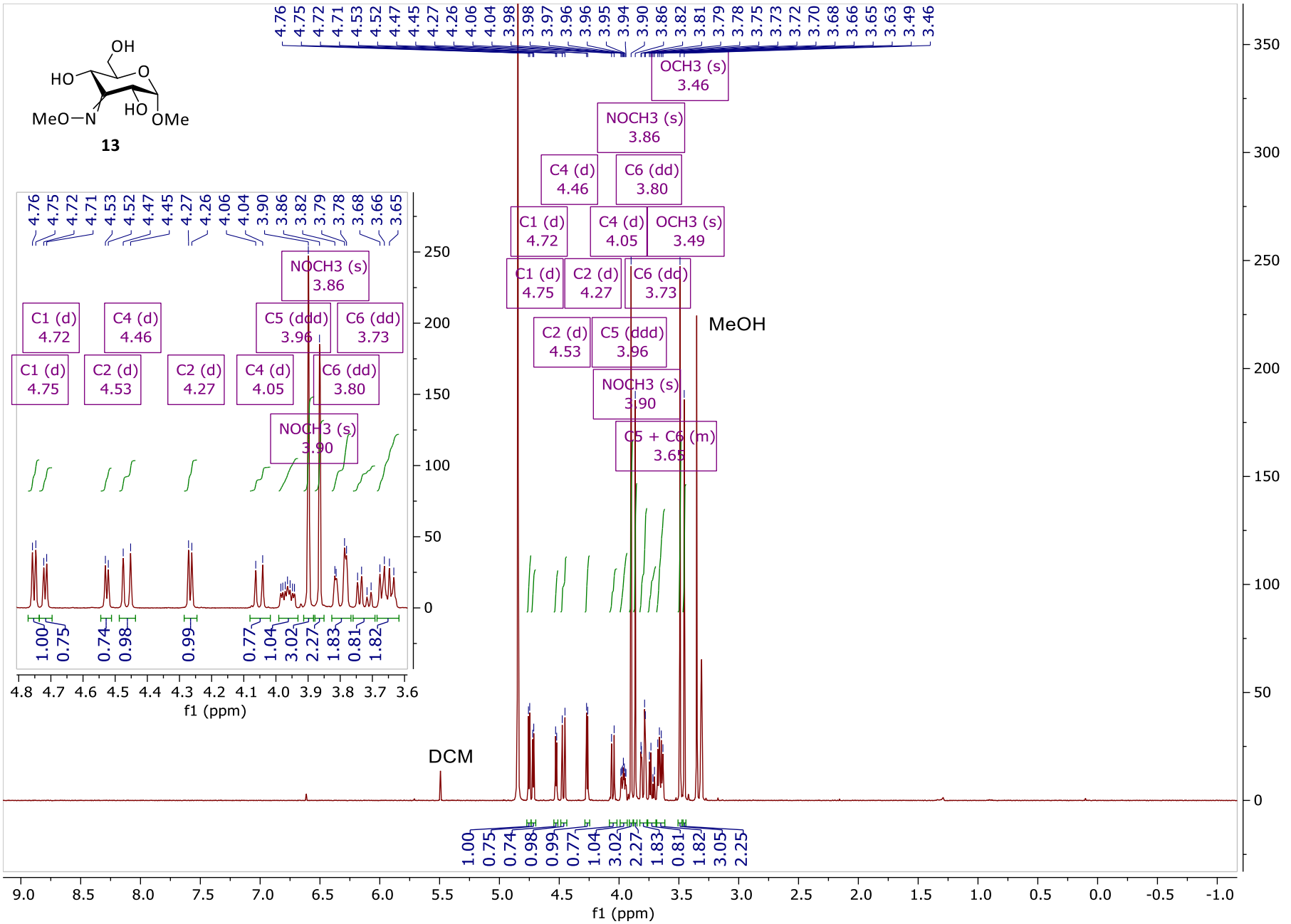

Figure S33 – ^{1}H-NMR (400 MHz, MeOD-d$_4$) of methyl *E/Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (**13**)

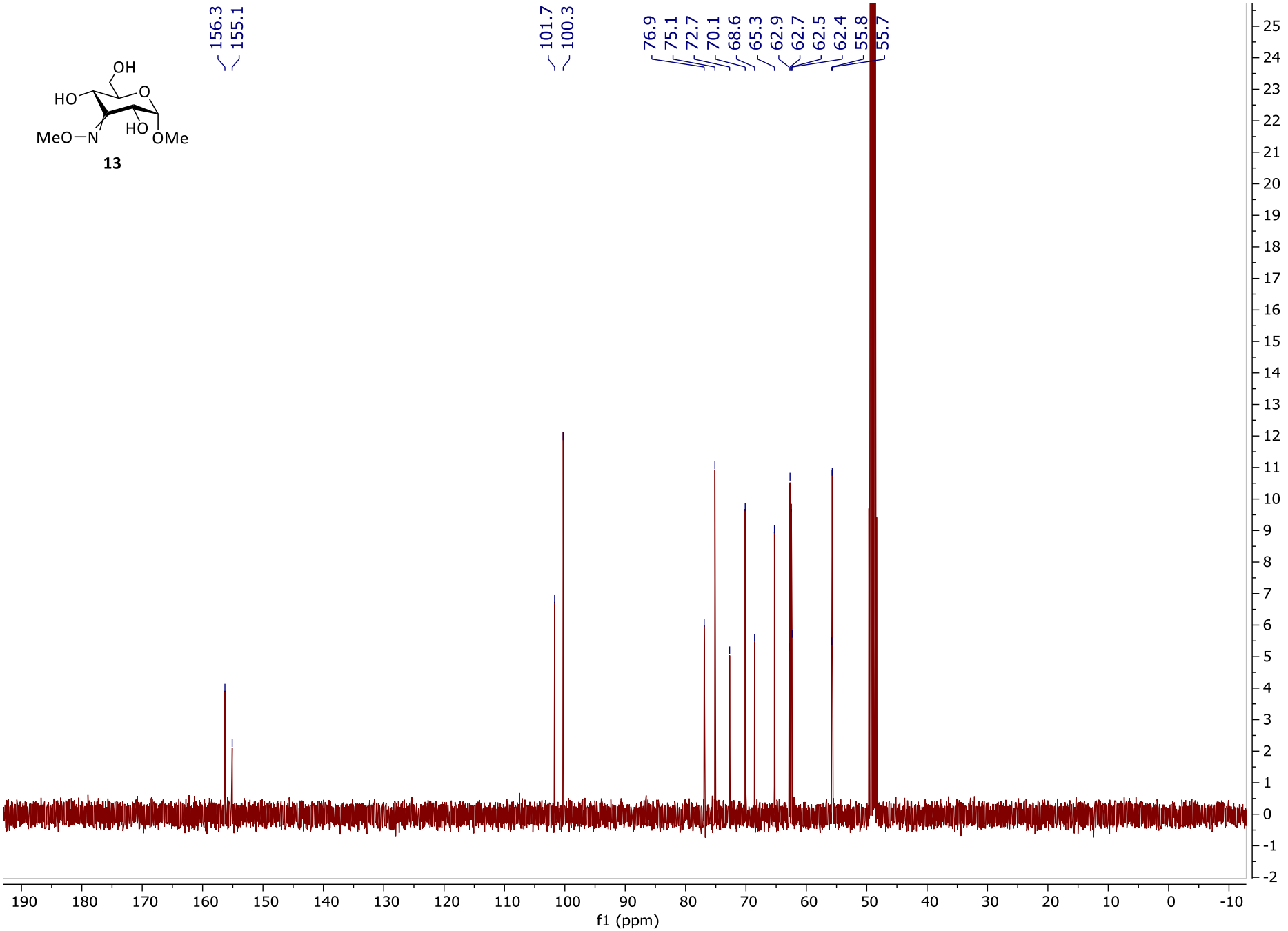

Figure S34 – ^{13}C-NMR (101 MHz, MeOD-d_4) of methyl *E*/*Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (**13**)

Methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (14)

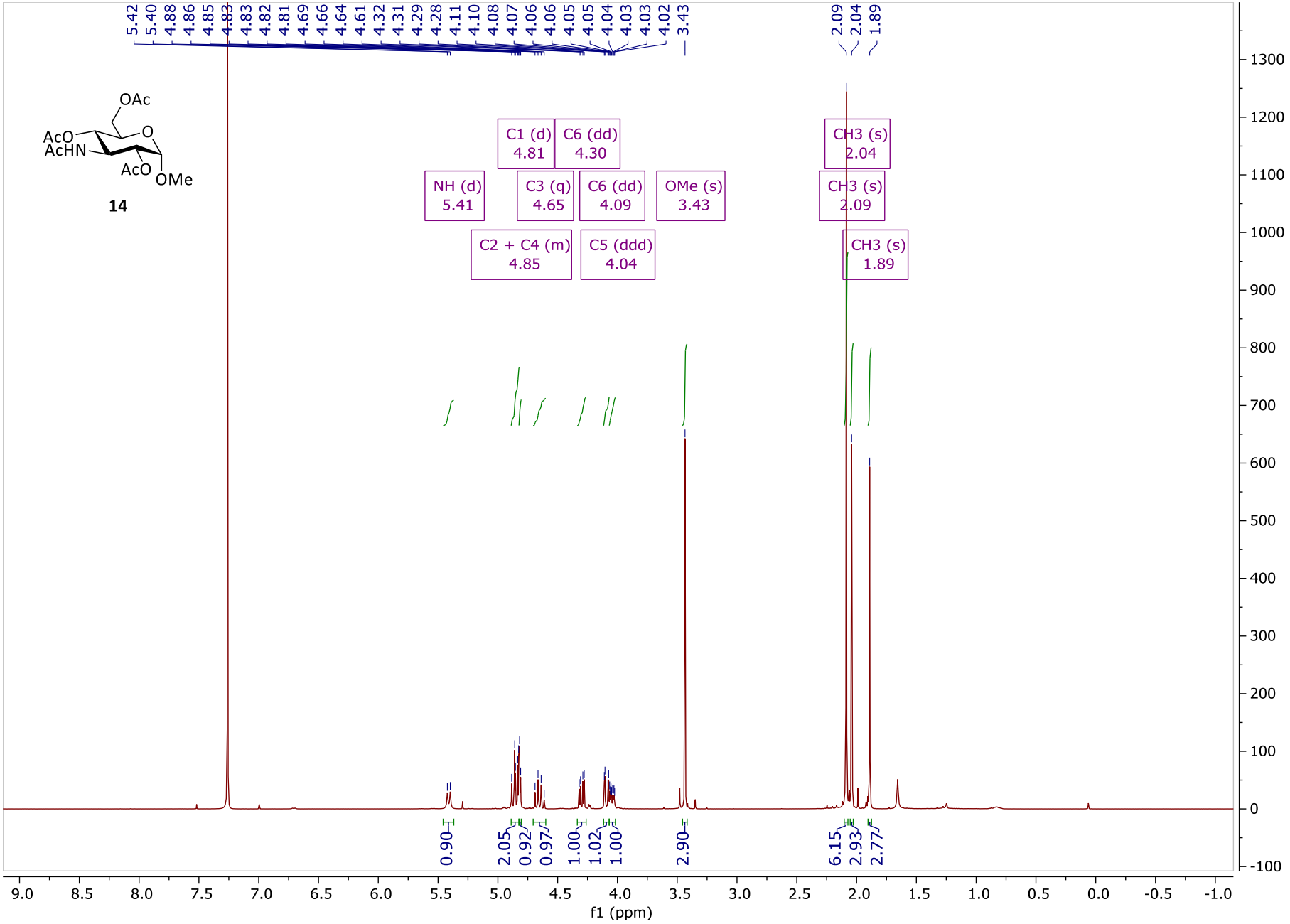

Figure S35 – ^{1}H-NMR (400 MHz, $CDCl_3$) of methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**14**)

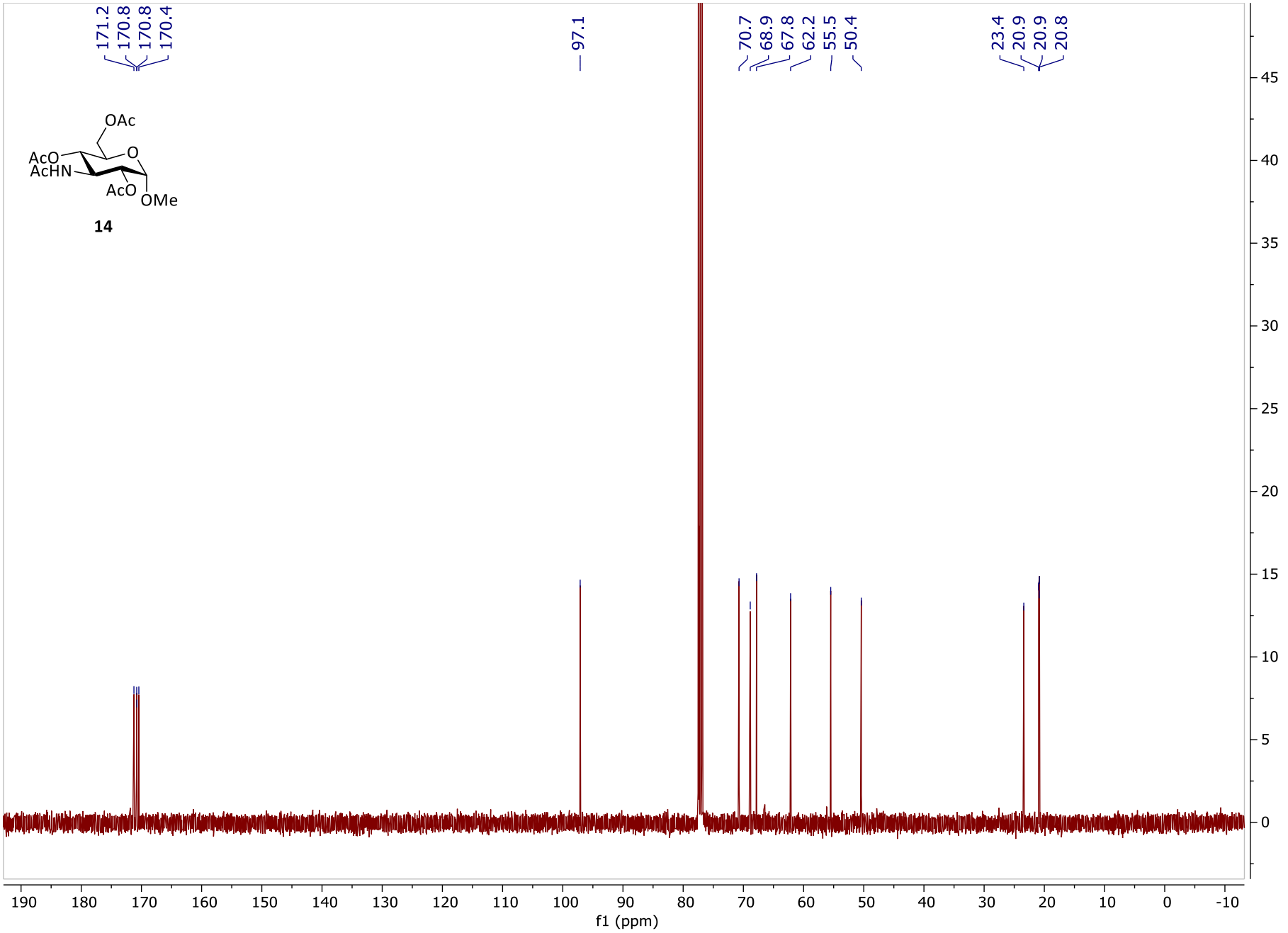

Figure S36 – ^{13}C-NMR (101 MHz, $CDCl_3$) of methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**14**)

Methyl 3-*C*-cyano-α-D-glucopyranoside (15a)

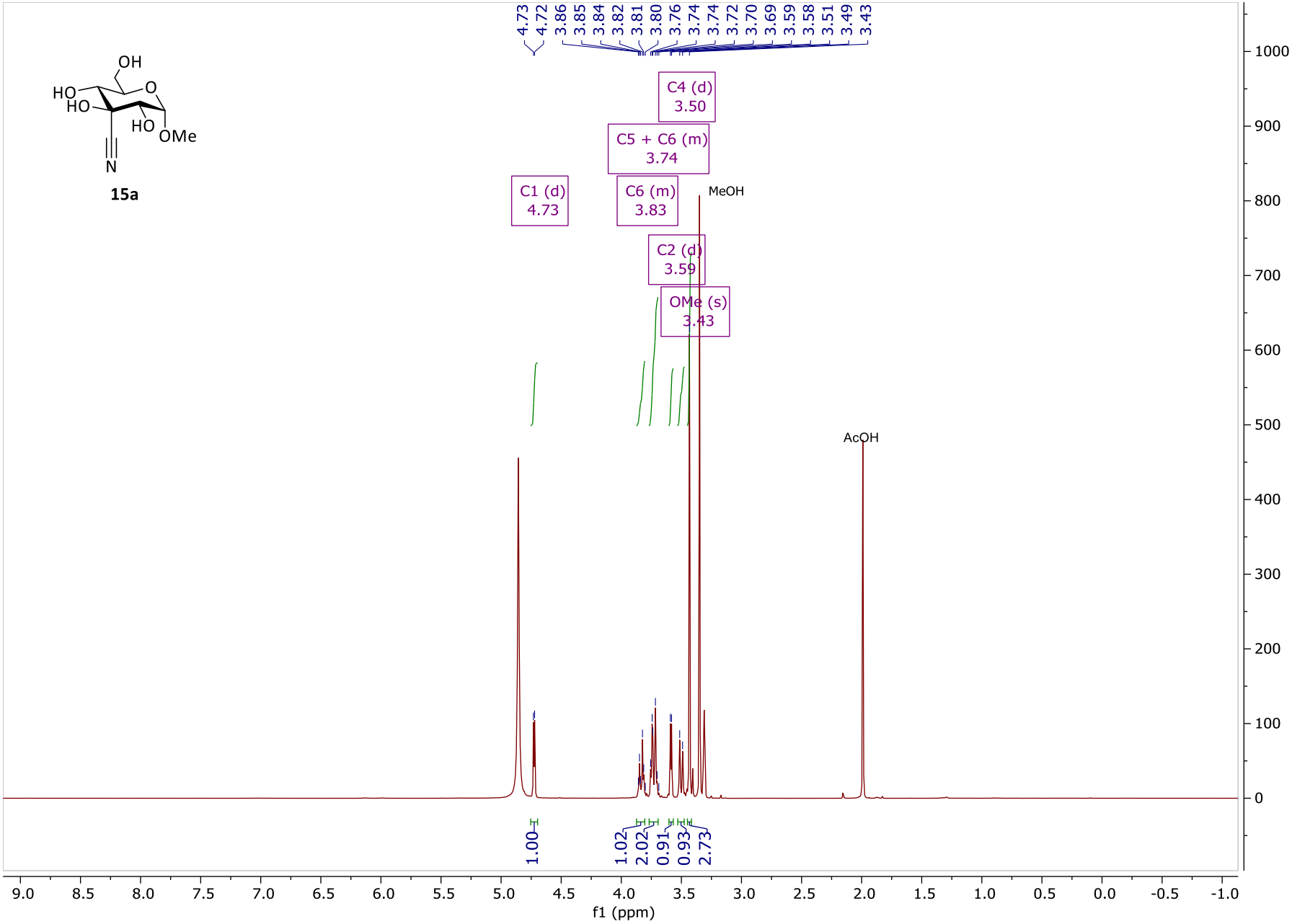

Figure S37 – ^{1}H-NMR (400 MHz, MeOD-d_4) of methyl 3-*C*-cyano-α-D-glucopyranoside (**15a**)

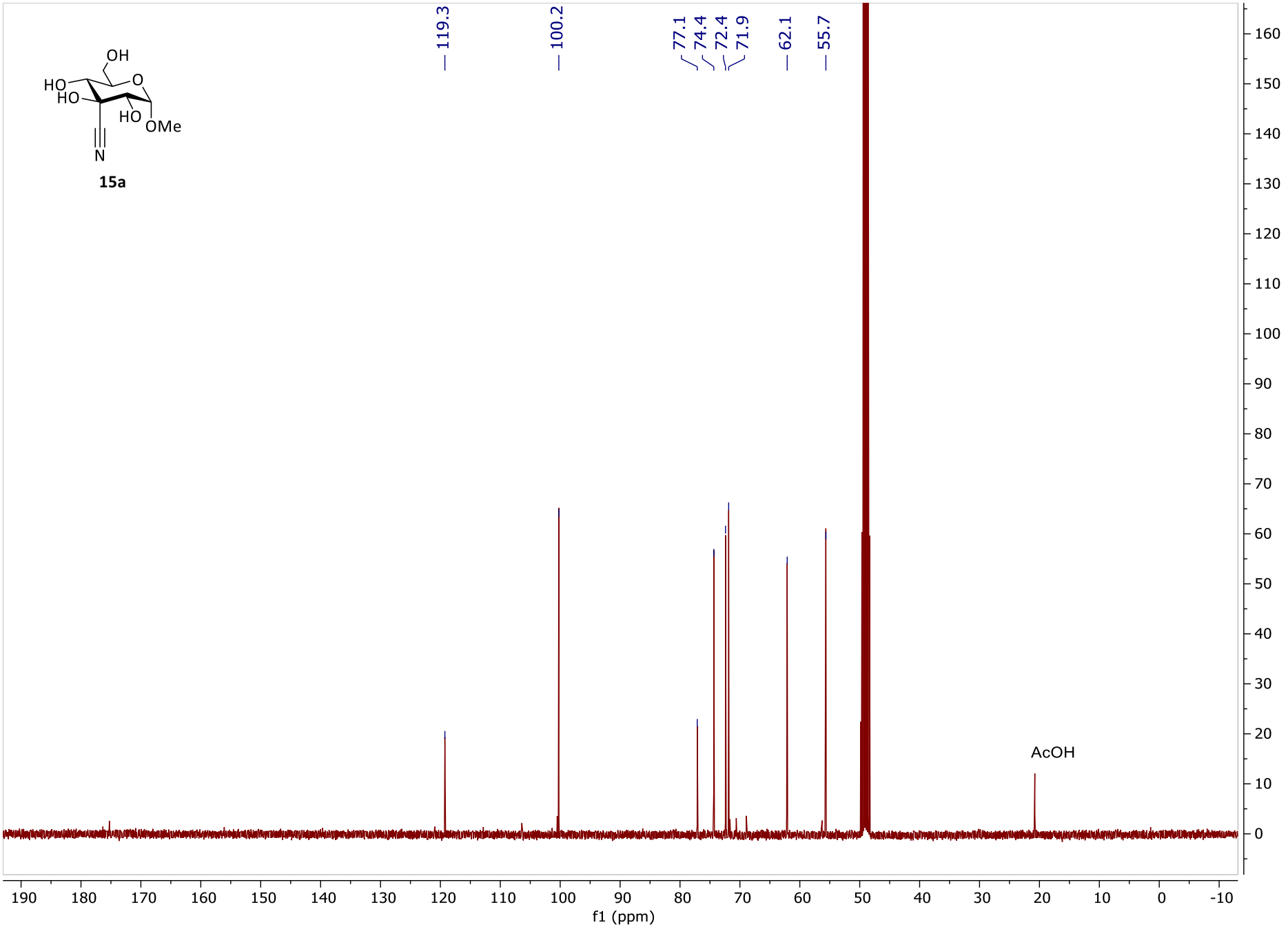

Figure S38 – ^{13}C-NMR (101 MHz, MeOD-d_4) of methyl 3-*C*-cyano-α-D-glucopyranoside (**15a**)

Methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (16)

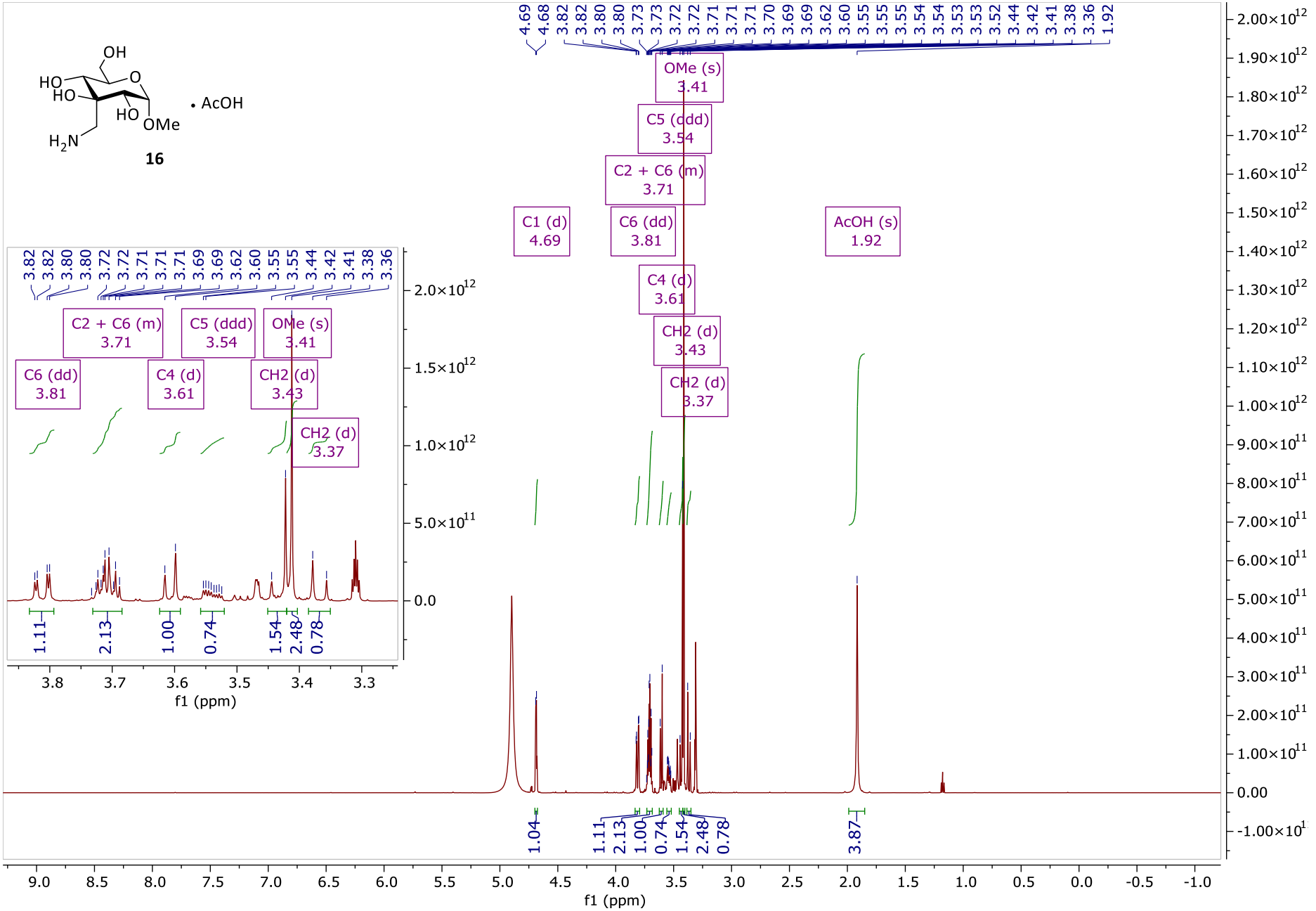

Figure S39 – ^{1}H-NMR (600 MHz, MeOD-d_4) of methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (**16**)

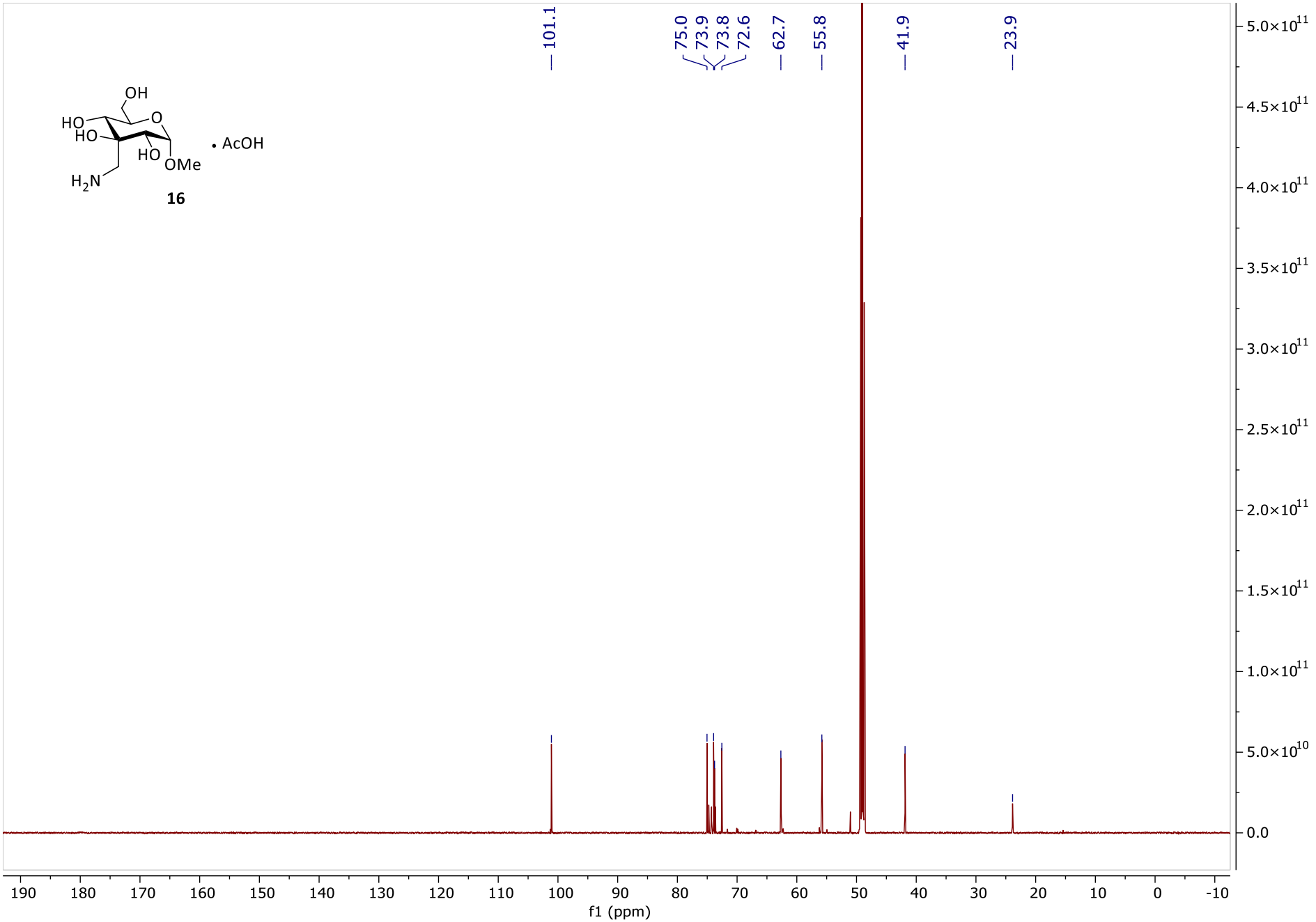

Figure S40 – ^{13}C-NMR (151 MHz, MeOD-d_4) of methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (**16**)

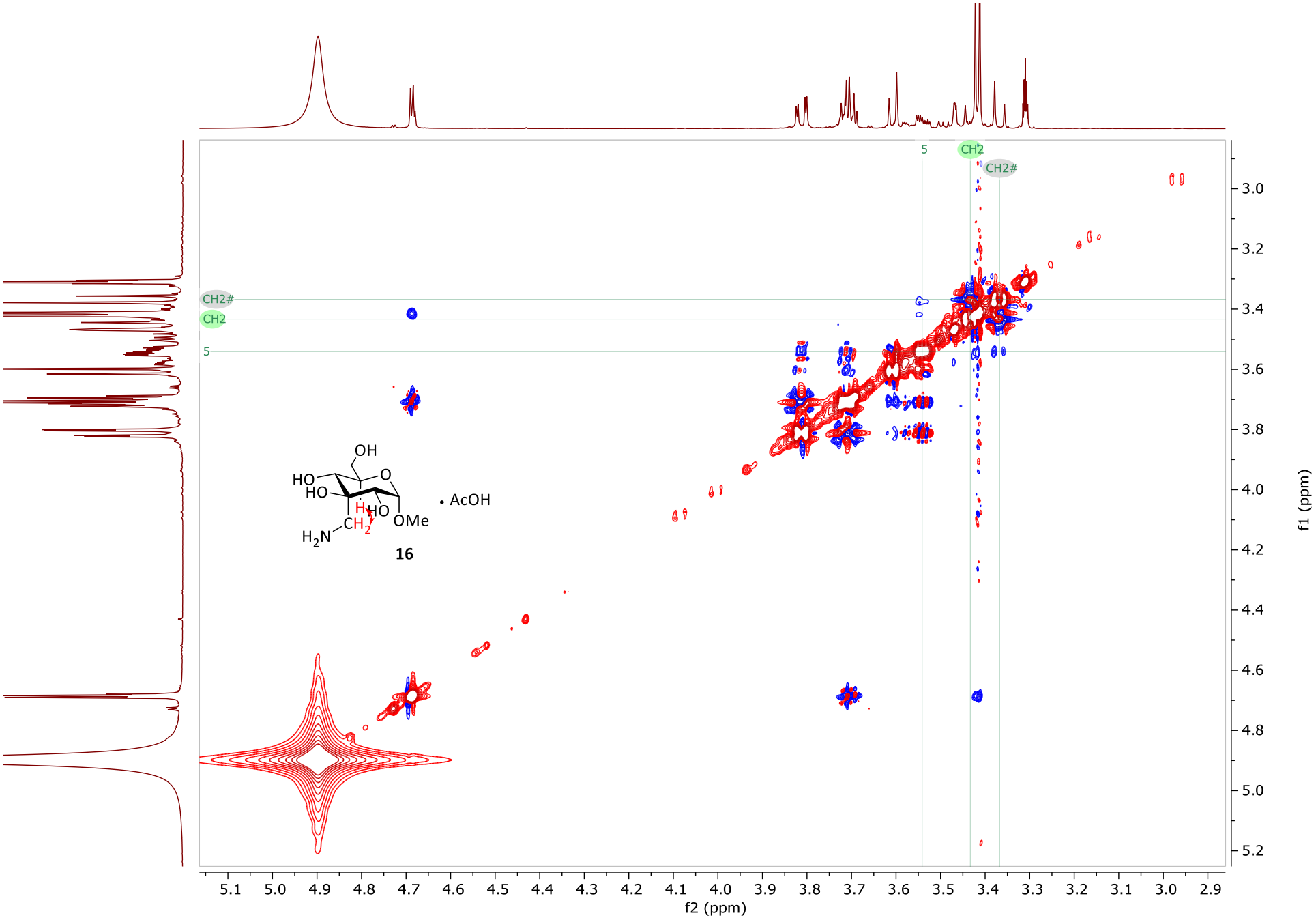

Figure S41 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (**16**)

Methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (17)

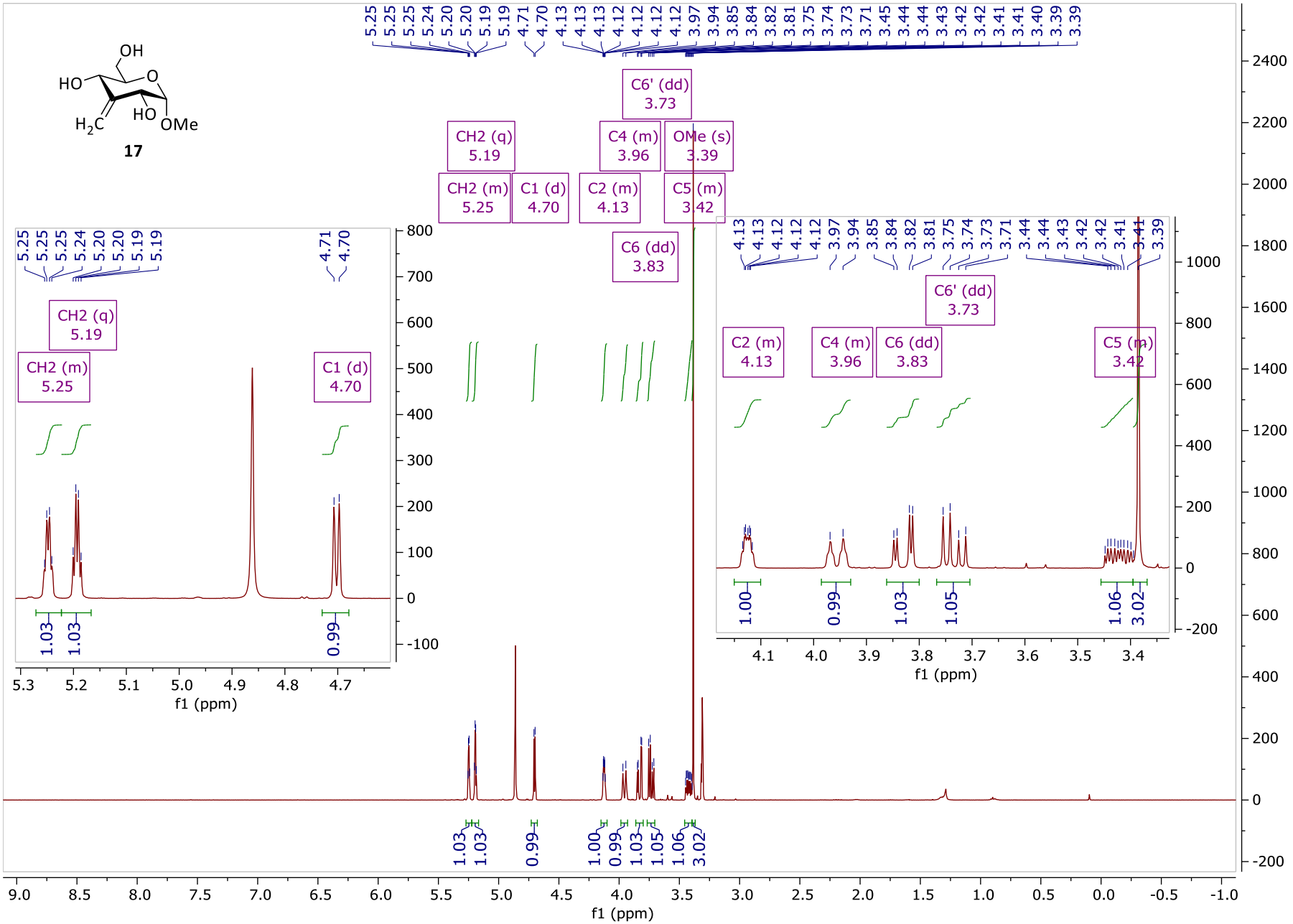

Figure S42 – ^{1}H-NMR (400 MHz, MeOD-*d4*) of methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (**17**)

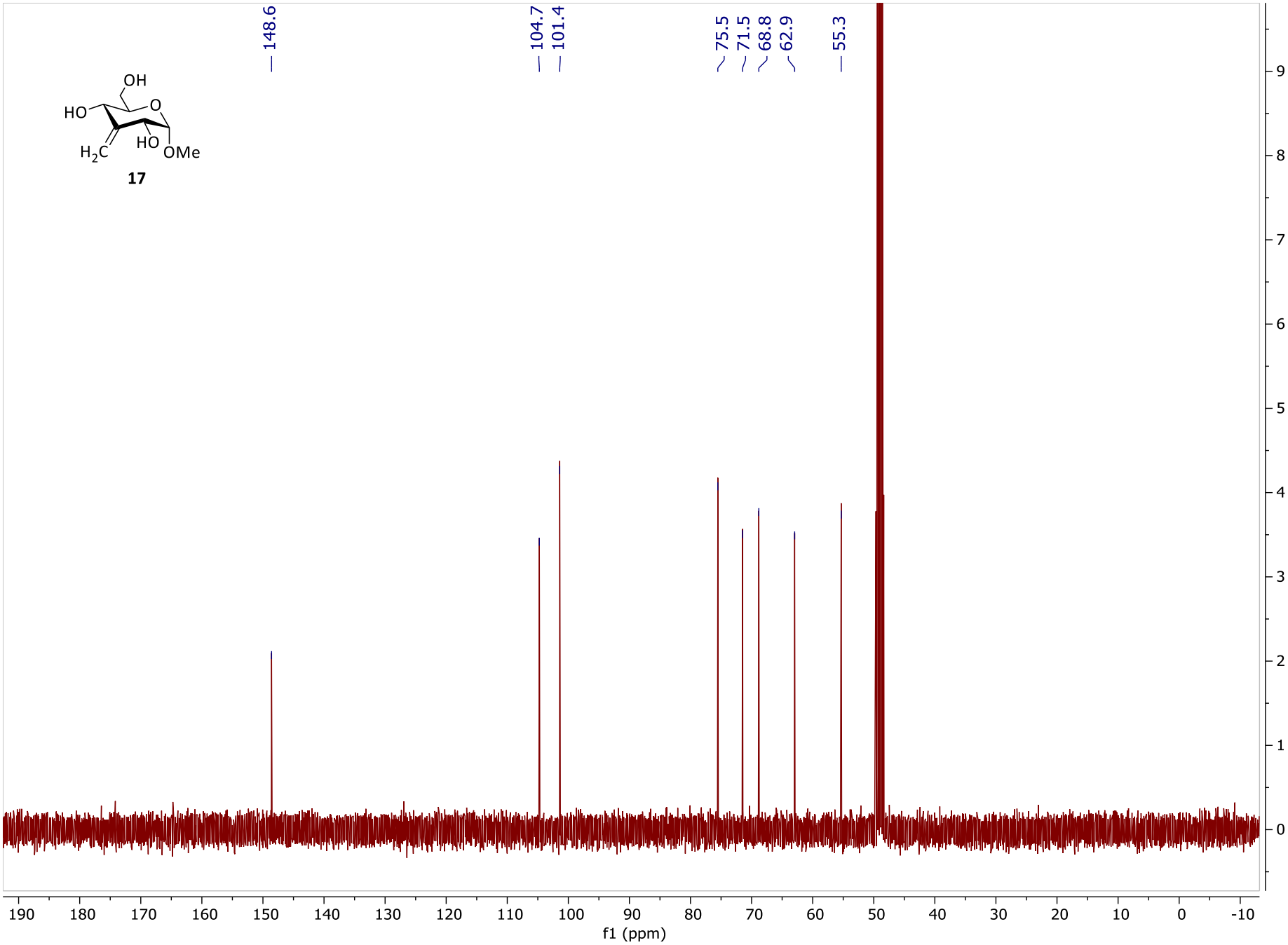

Figure S43 – ^{13}C-NMR (101 MHz, MeOD-*d4*) of methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (**17**)

Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (18)

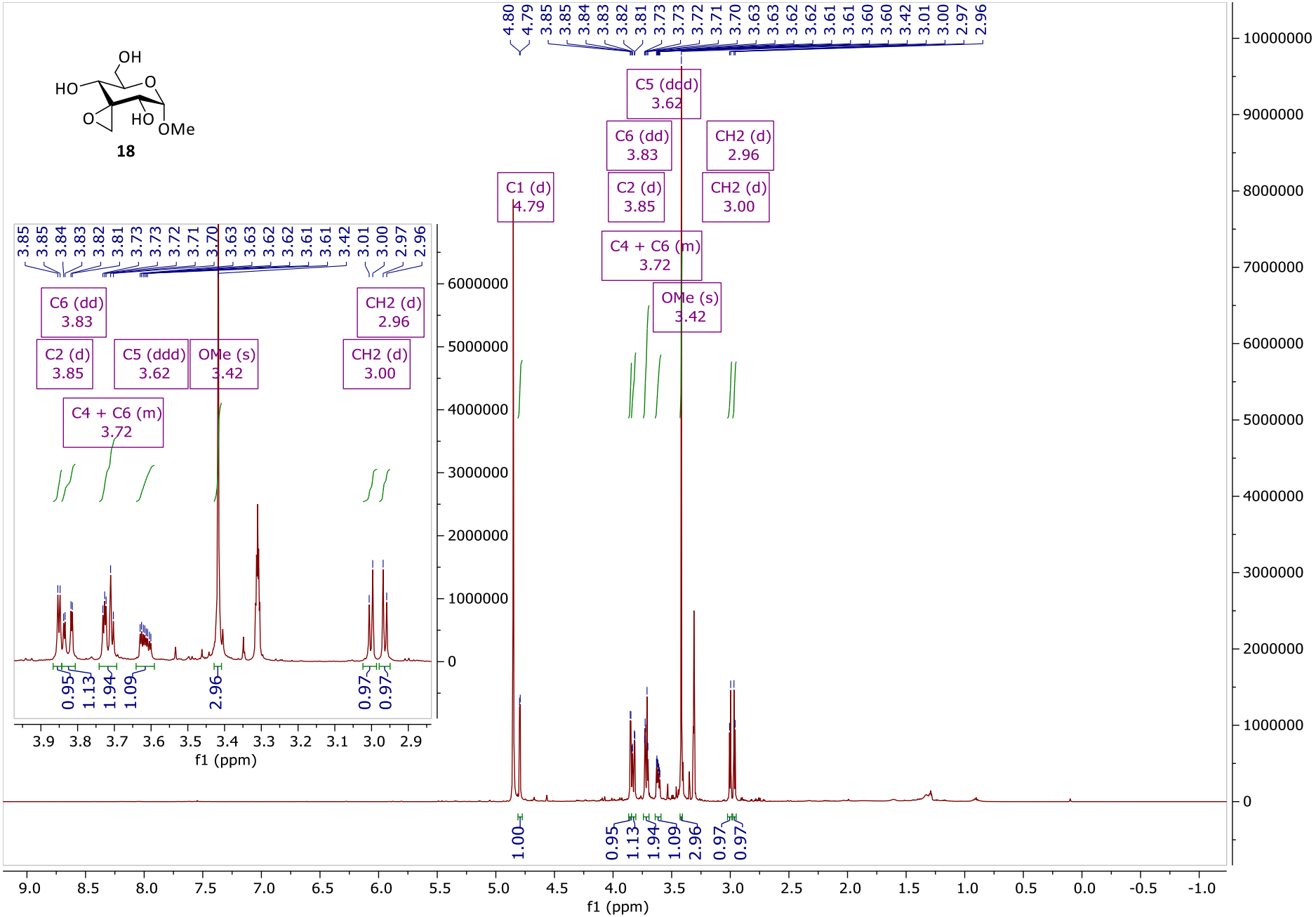

Figure 44 – ^{1}H-NMR (600 MHz, MeOD-d_4) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (**18**)

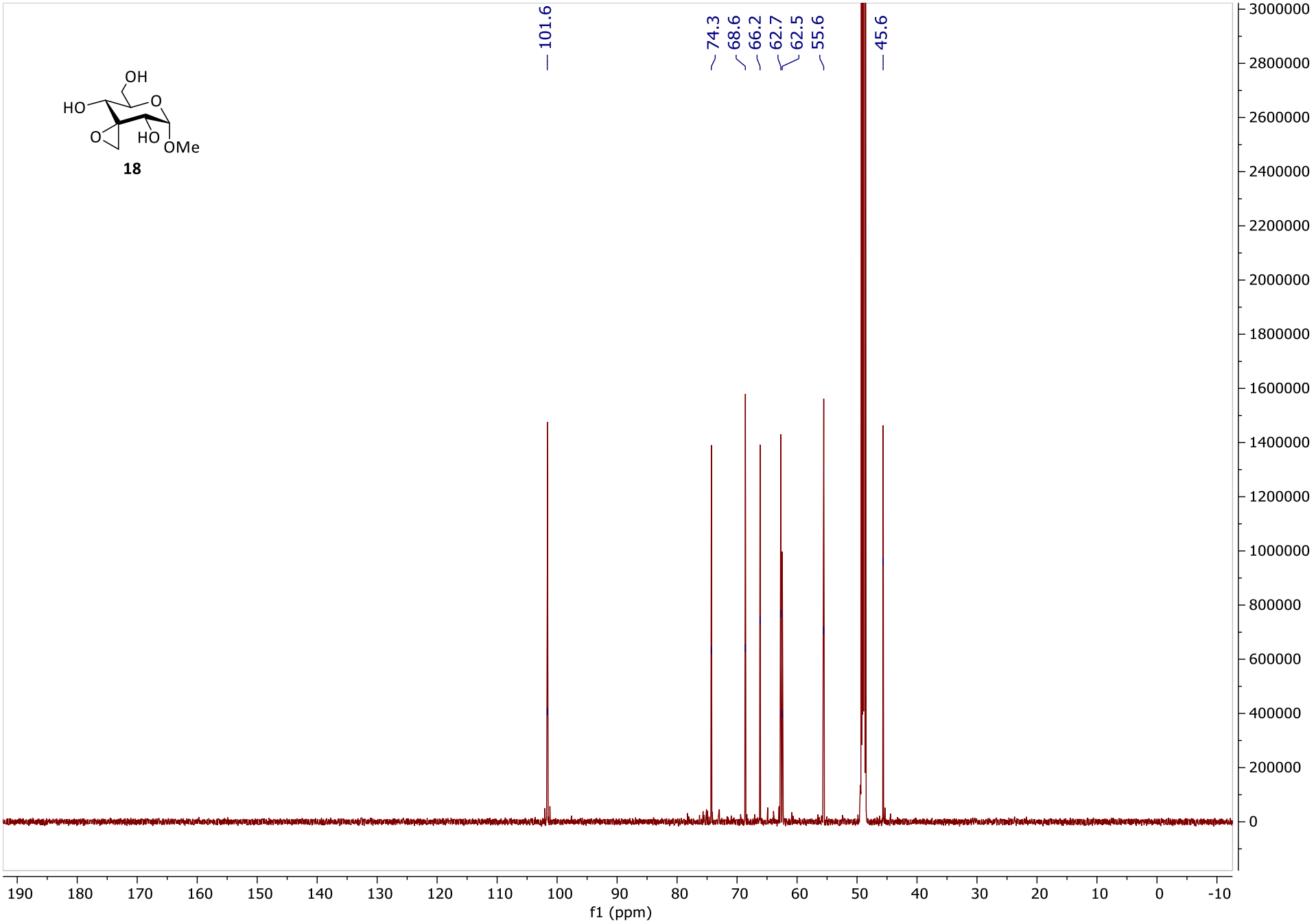

Figure S45 – ^{13}C-NMR (151 MHz, MeOD-d_4) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (**18**)

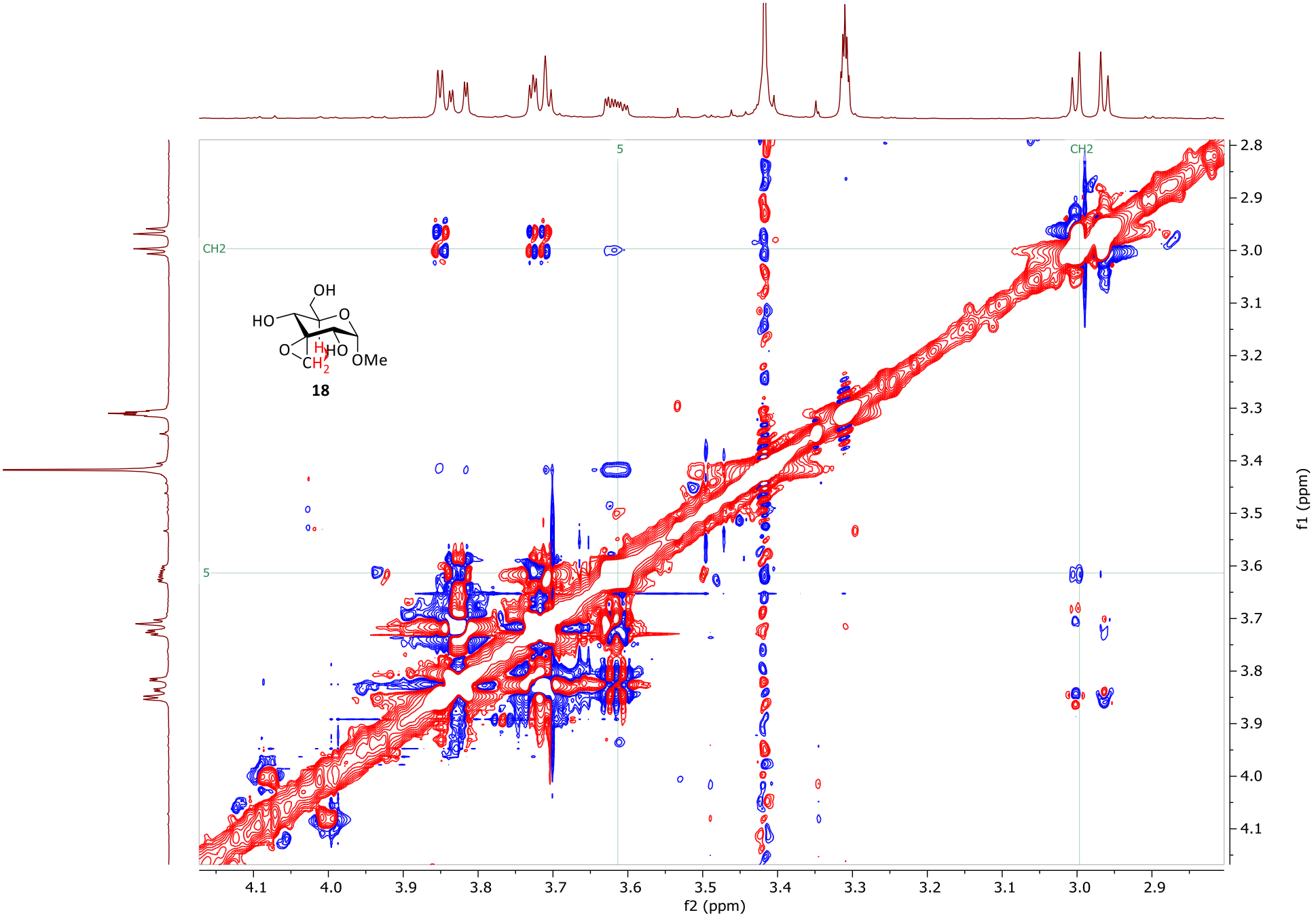

Figure S46 – NOESY (600 MHz, MeOD-*d4*) of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (**18**)

Methyl 3-*C*-methyl-α-D-glucopyranoside (19)

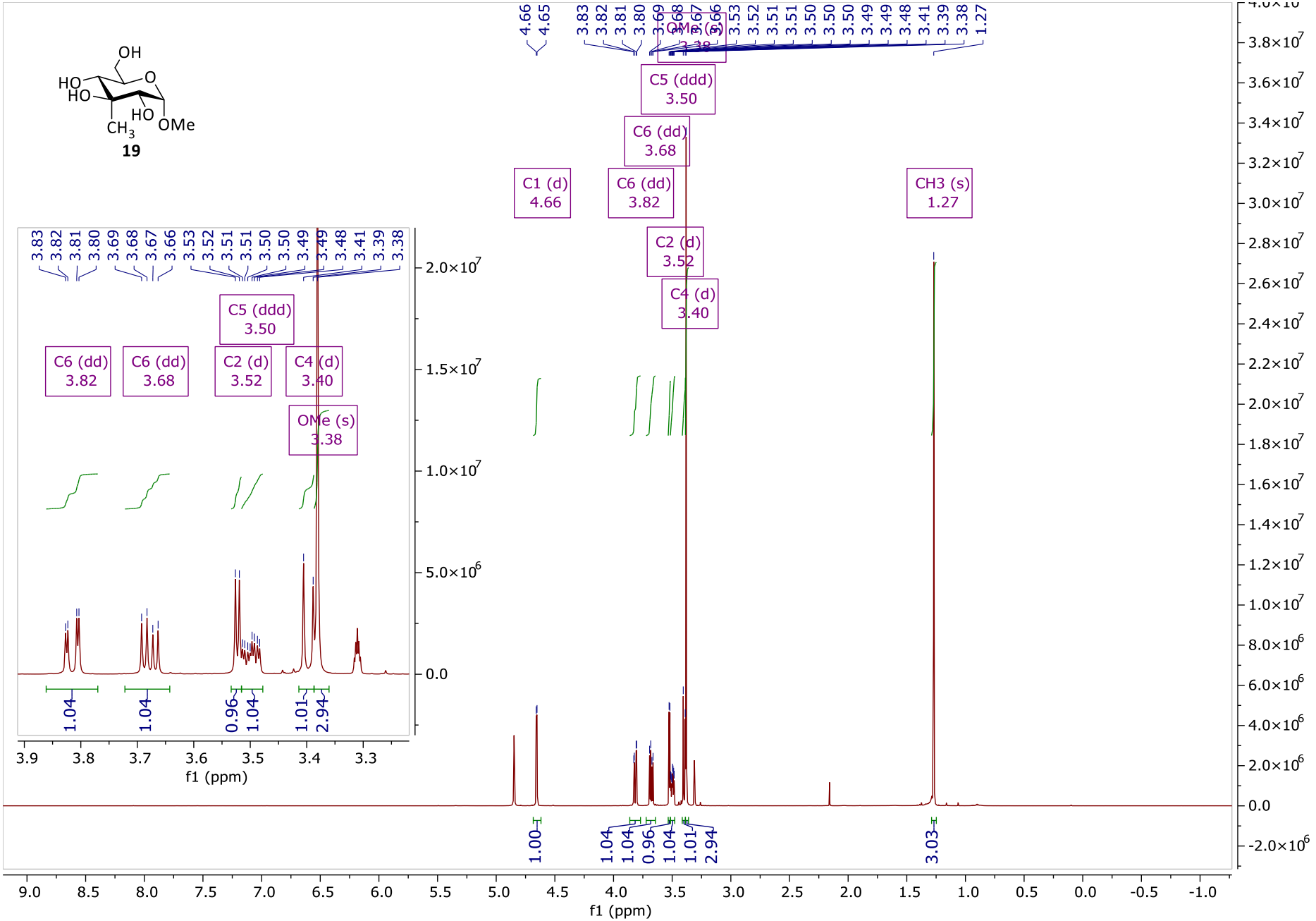

Figure 47 – ^{1}H-NMR (600 MHz, MeOD-d_4) of methyl 3-*C*-methyl-α-D-glucopyranoside (**19**)

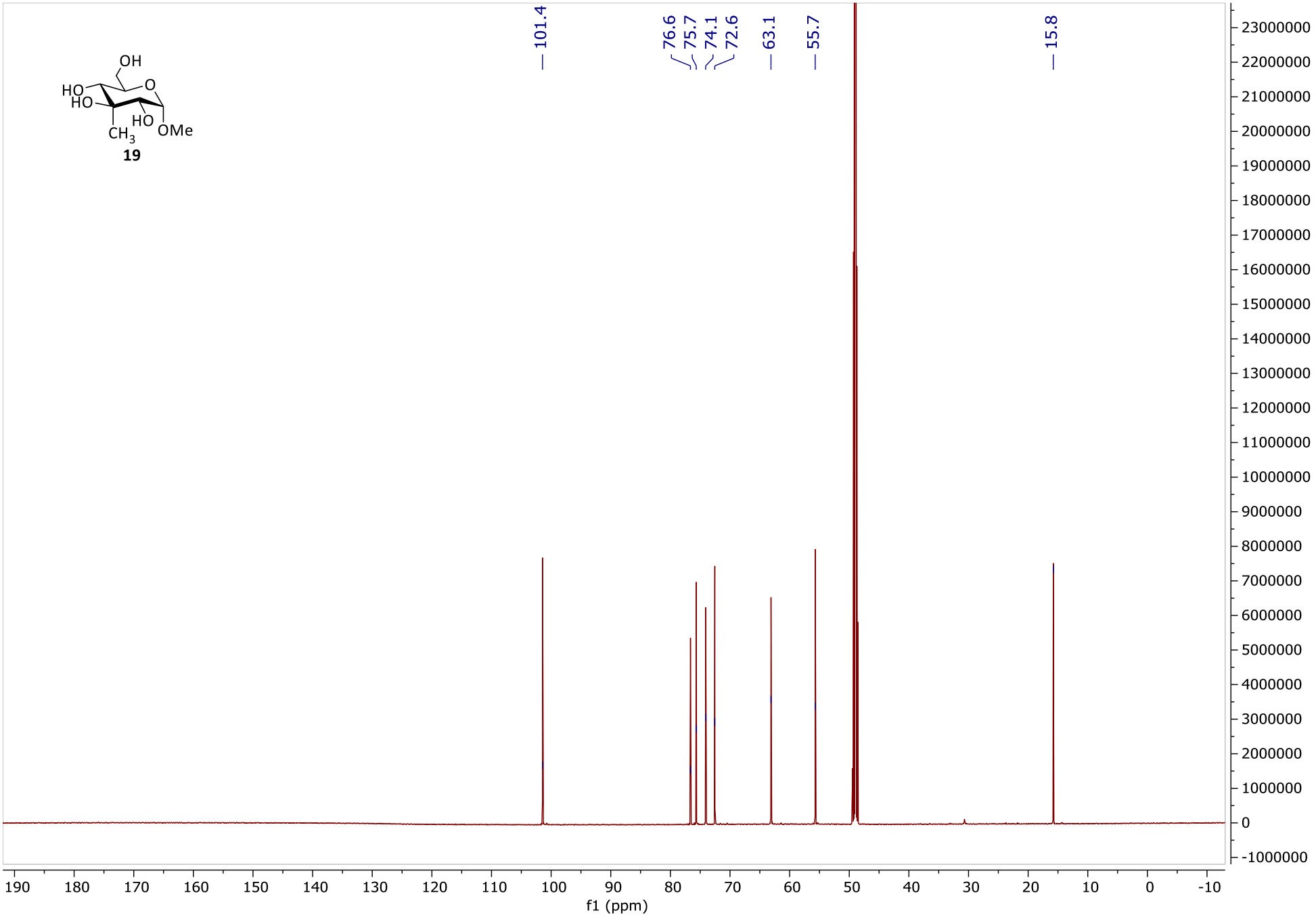

Figure S48 – ^{13}C-NMR (151 MHz, MeOD-d_4) of methyl 3-*C*-methyl-α-D-glucopyranoside (**19**)

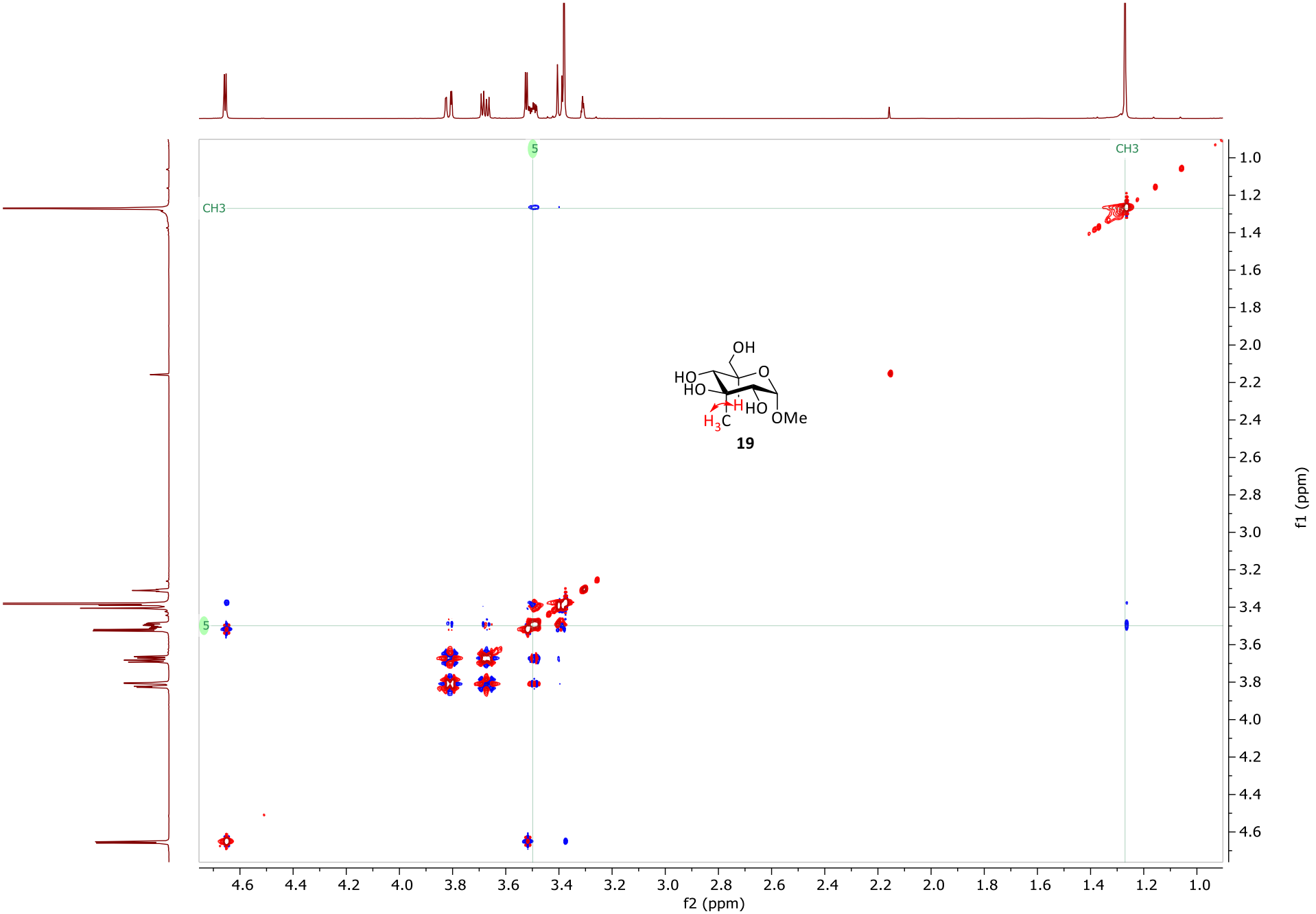

Figure S49 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-methyl-α-D-glucopyranoside (**19**)

1,6-anhydro-3-*C*-methyl-β-d-mannopyranose (22)

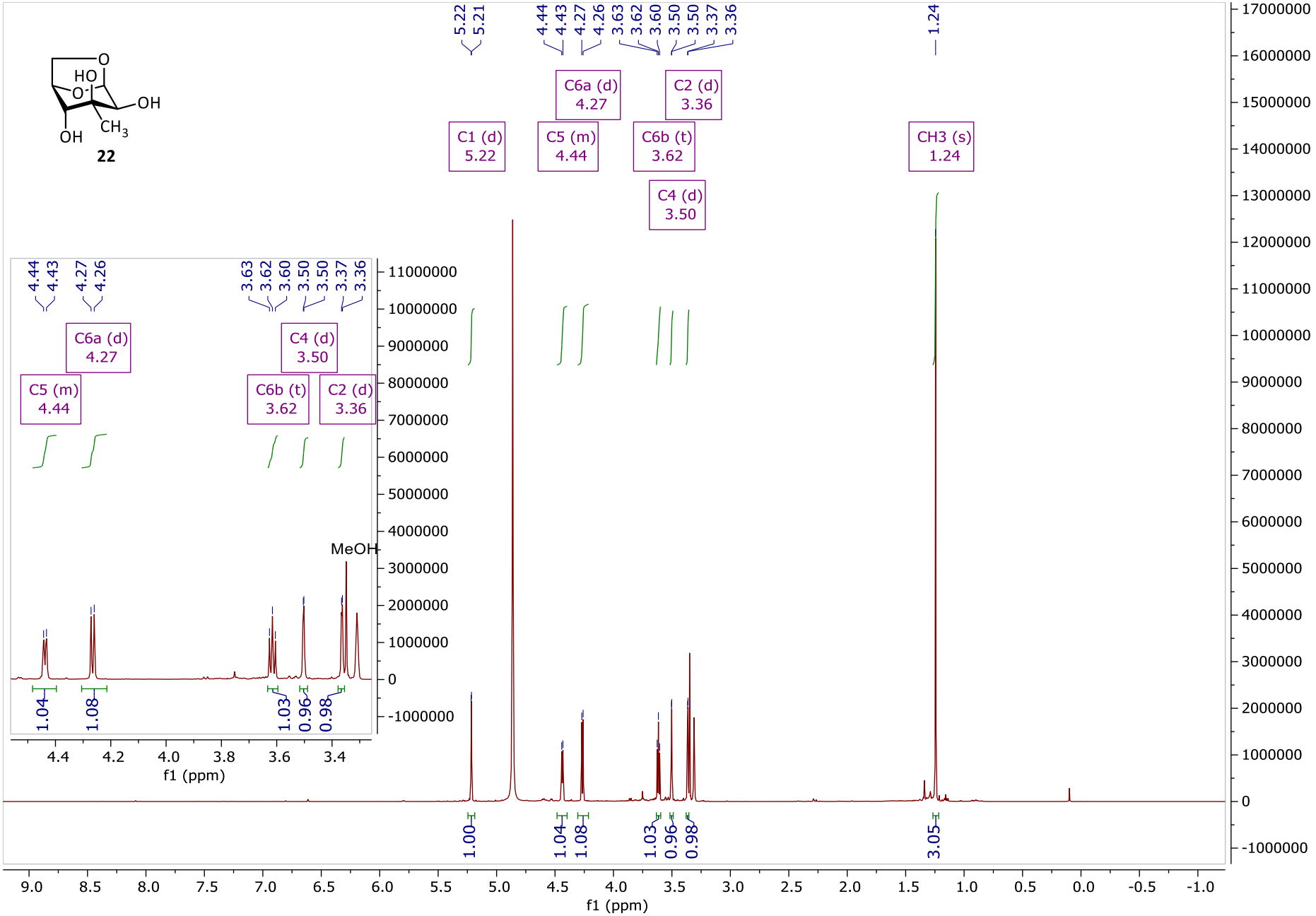

Figure S50 – ^{1}H-NMR (600 MHz, MeOD-d_4) of 1,6-anhydro-3-*C*-methyl-β-D-mannopyranose (**22**)

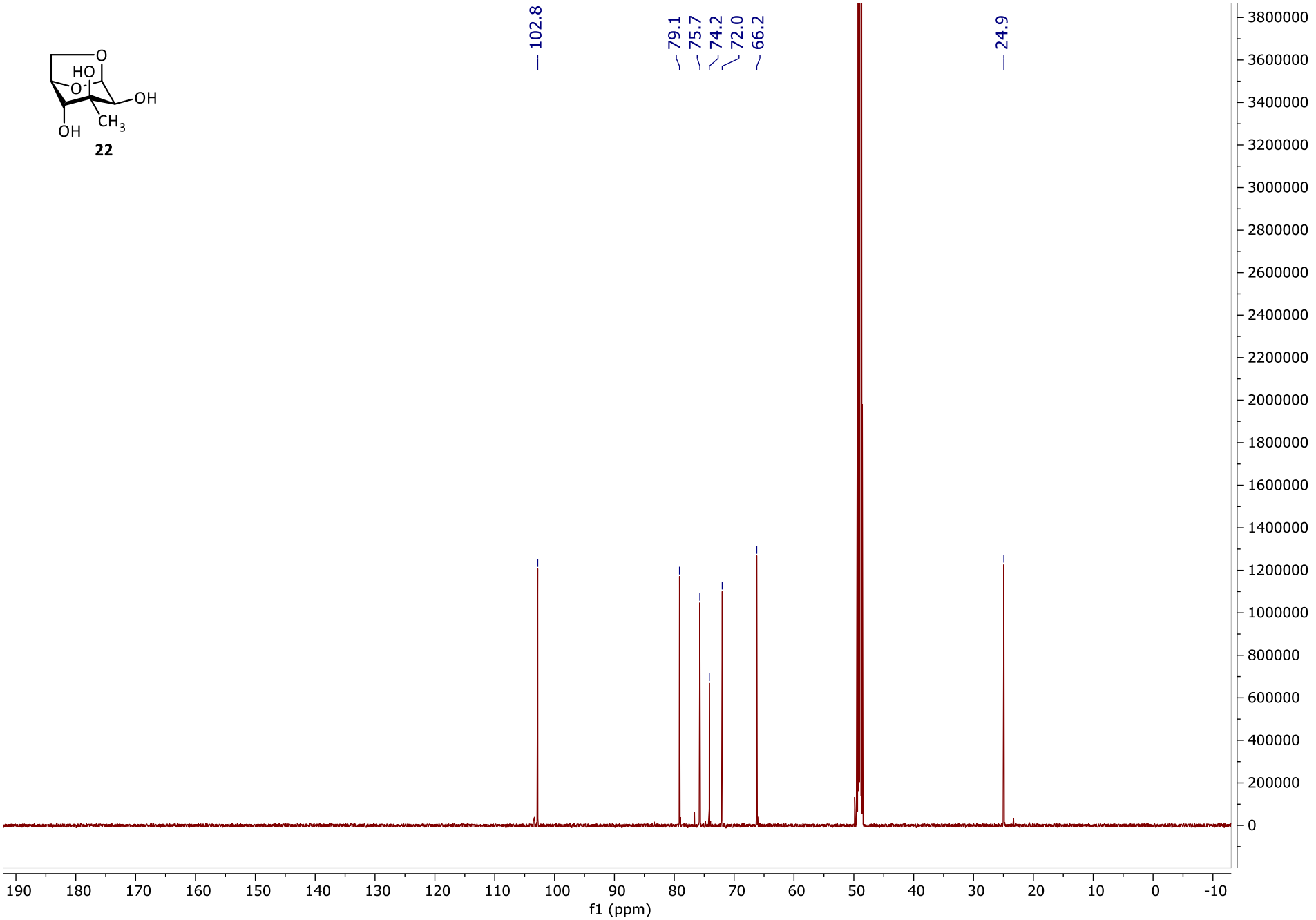

Figure S51 – ^{13}C-NMR (151 MHz, MeOD-d_4) of 1,6-anhydro-3-*C*-methyl-β-D-mannopyranose (**22**)

Methyl 3-*C*-methyl-α-d-mannopyranoside (23)

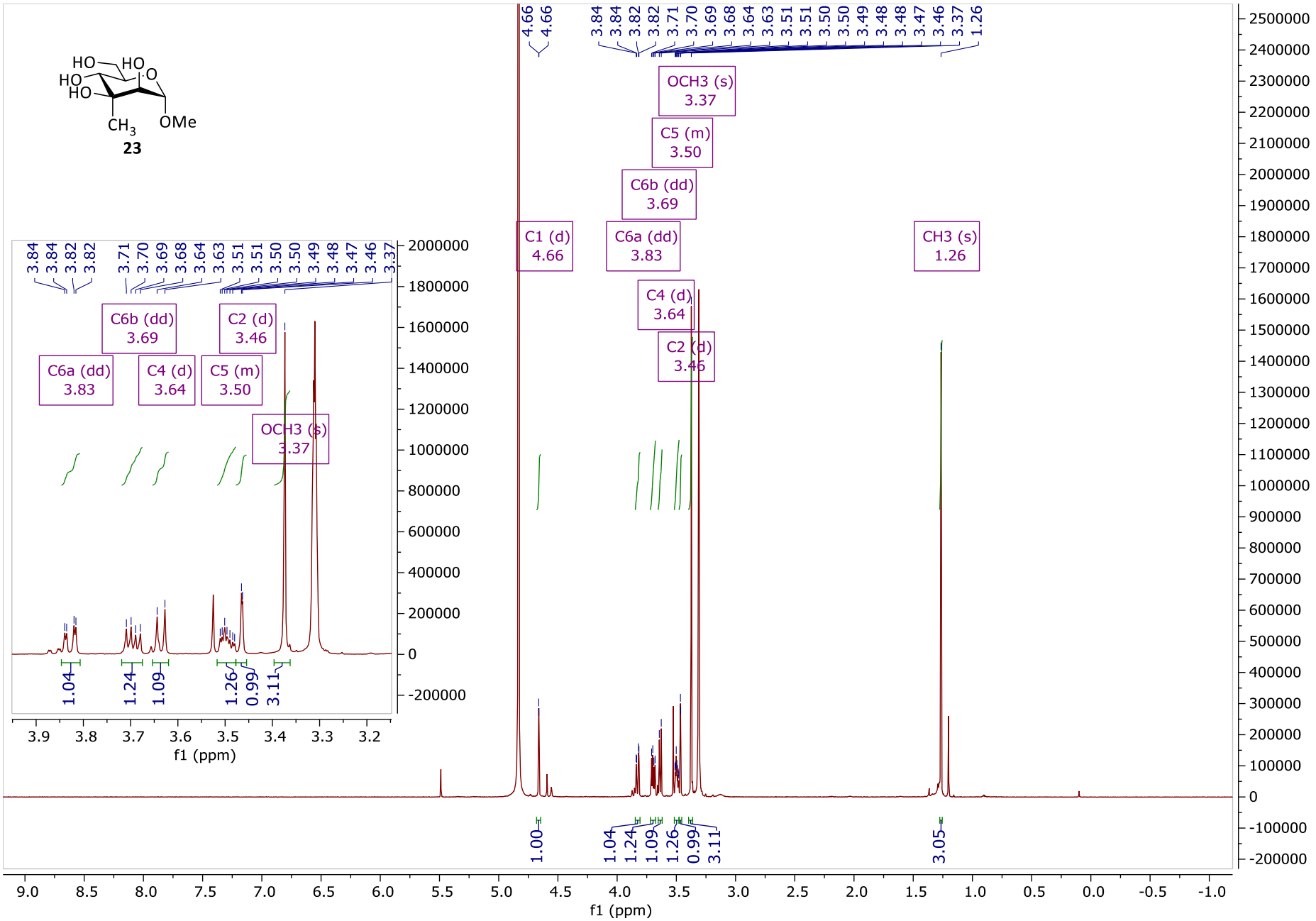

Figure S52 – ^{1}H-NMR (600 MHz, MeOD-d_4) of methyl 3-*C*-methyl-α-D-mannopyranoside (**23**)

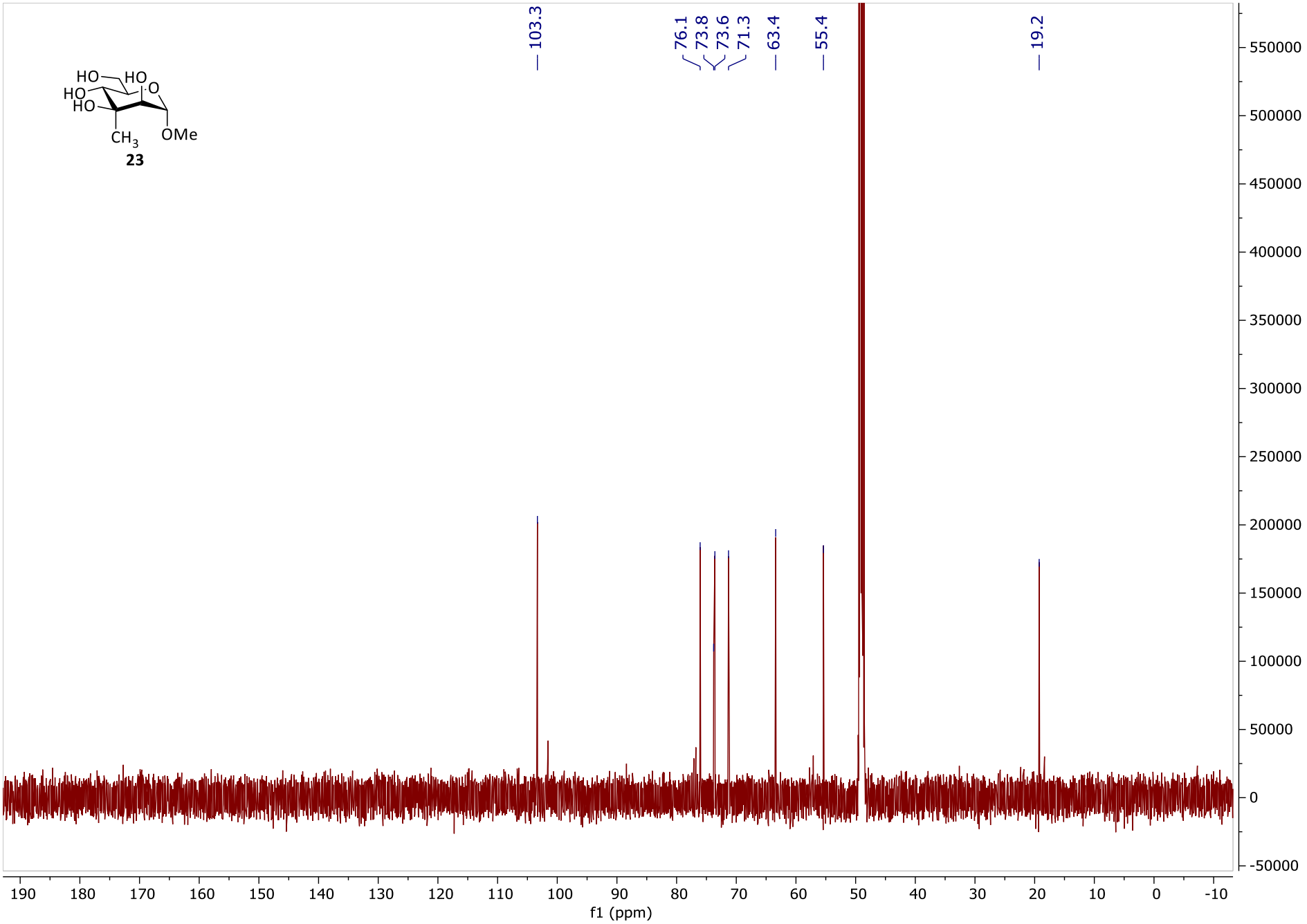

Figure S53 – ^{13}C-NMR (151 MHz, MeOD-d_4) of methyl 3-*C*-methyl-α-D-mannopyranoside (**23**)

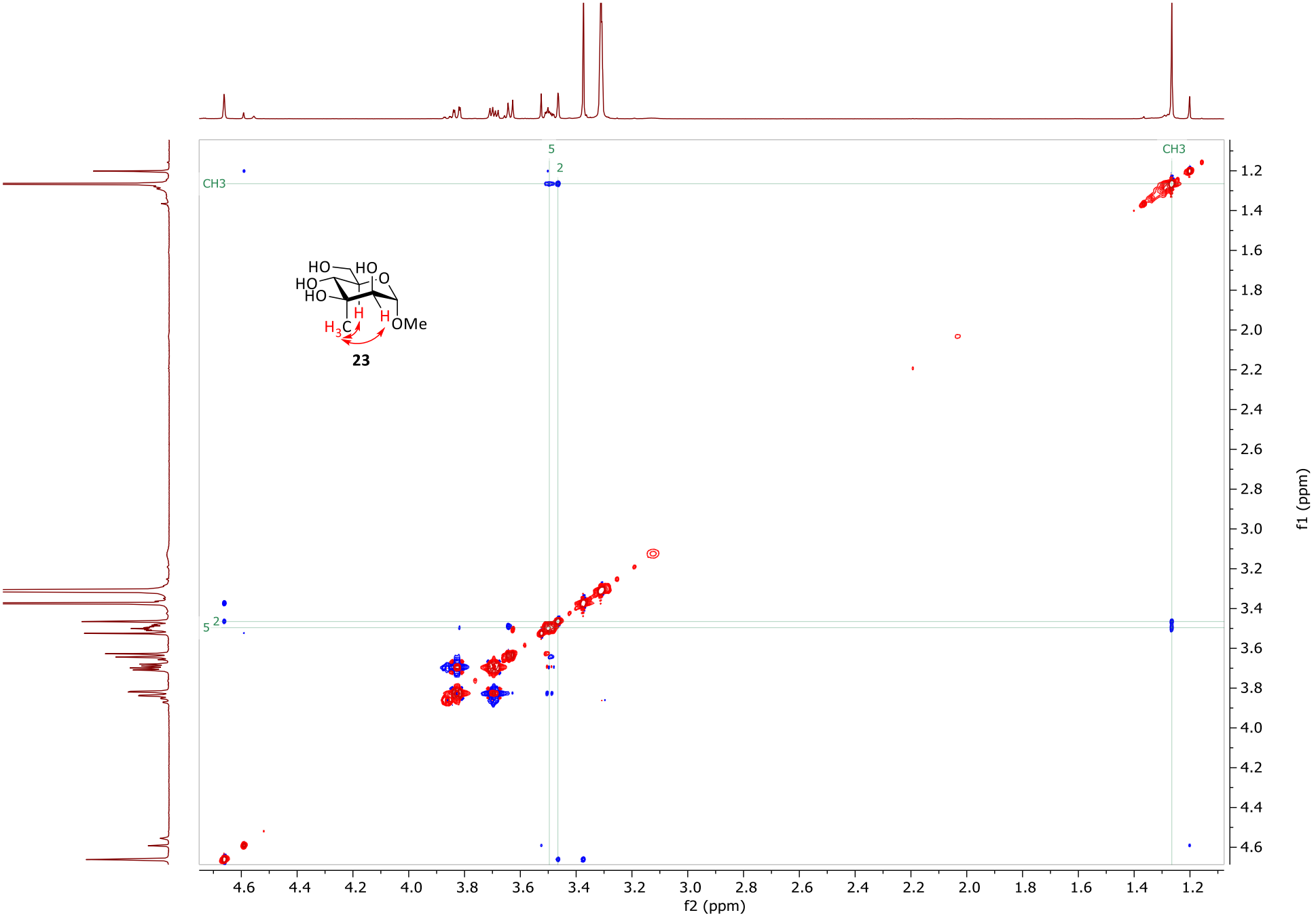

Figure S54 – NOESY (600 MHz, MeOD-*d4*) of methyl 3-*C*-methyl-α-D-mannopyranoside (**23**)

_O_-(6-deoxy-1-_O_,3-_C_-dimethyl-α-d-mannopyranos-6-yl) _O_-phenyl carbonothioate (24)

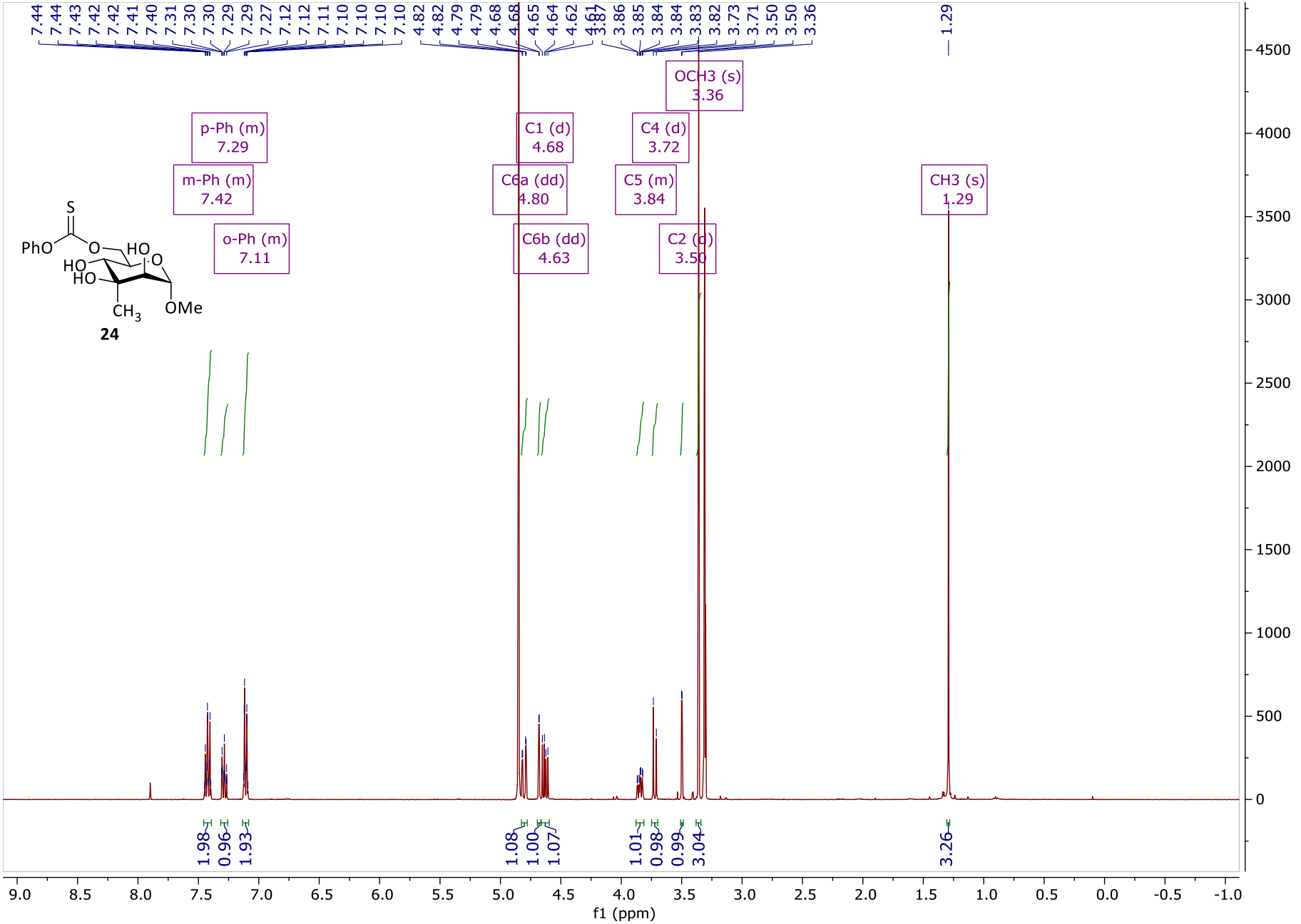

Figure S55 – ^{1}H-NMR (600 MHz, MeOD-d_4) of *O*-(6-deoxy-1-*O*,3-*C*-dimethyl-α-D-mannopyranos-6-yl) *O*-phenyl carbonothioate (**24**)

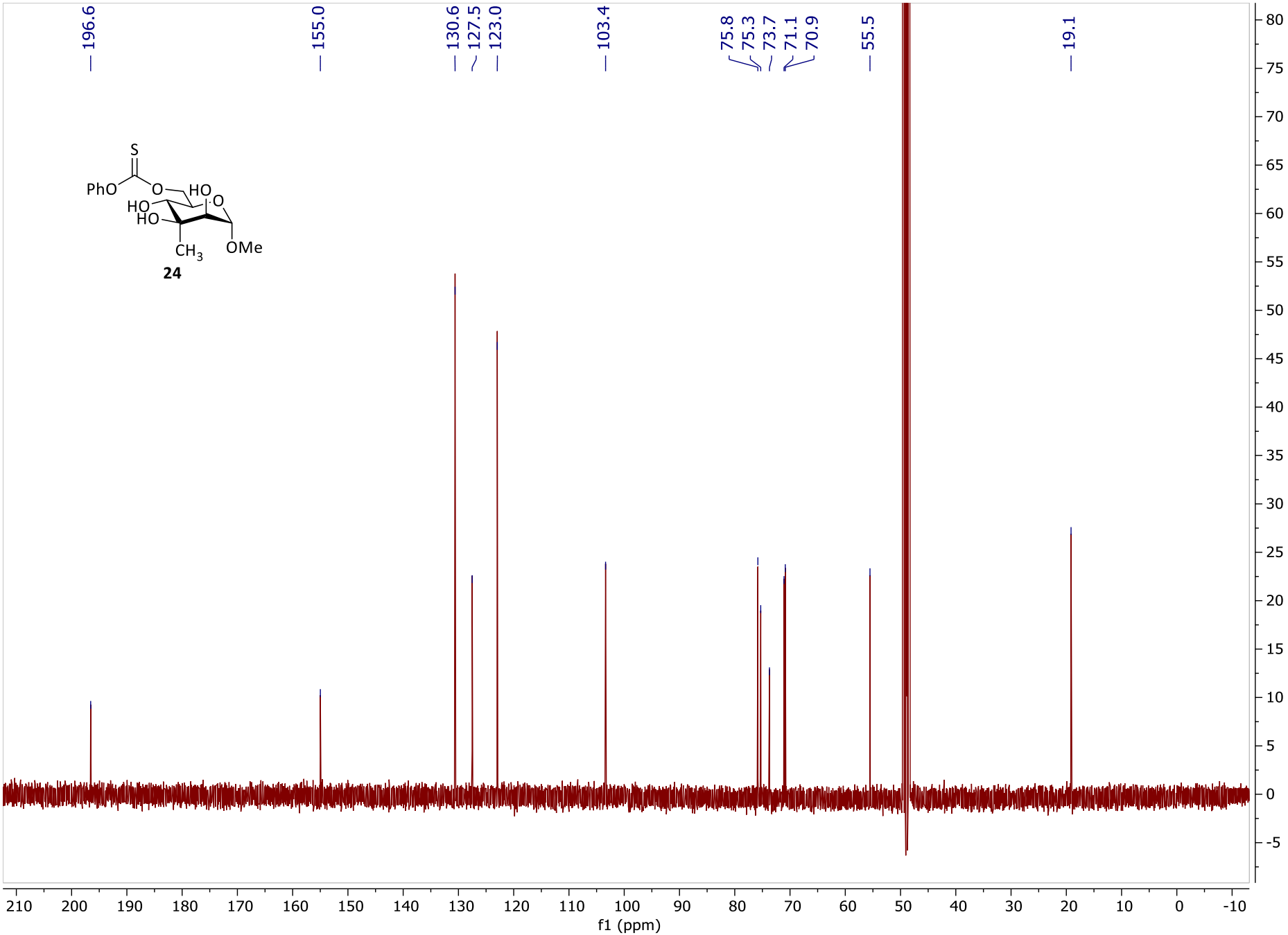

Figure S56 – ^{13}C-NMR (151 MHz, MeOD-d_4) of *O*-(6-deoxy-1-*O*,3-*C*-dimethyl-α-D-mannopyranos-6-yl) *O*-phenyl carbonothioate (**24**)

Methyl α-d-evaloside (methyl 6-deoxy-3-*C*-methyl-α-d-mannopyranoside) (25)

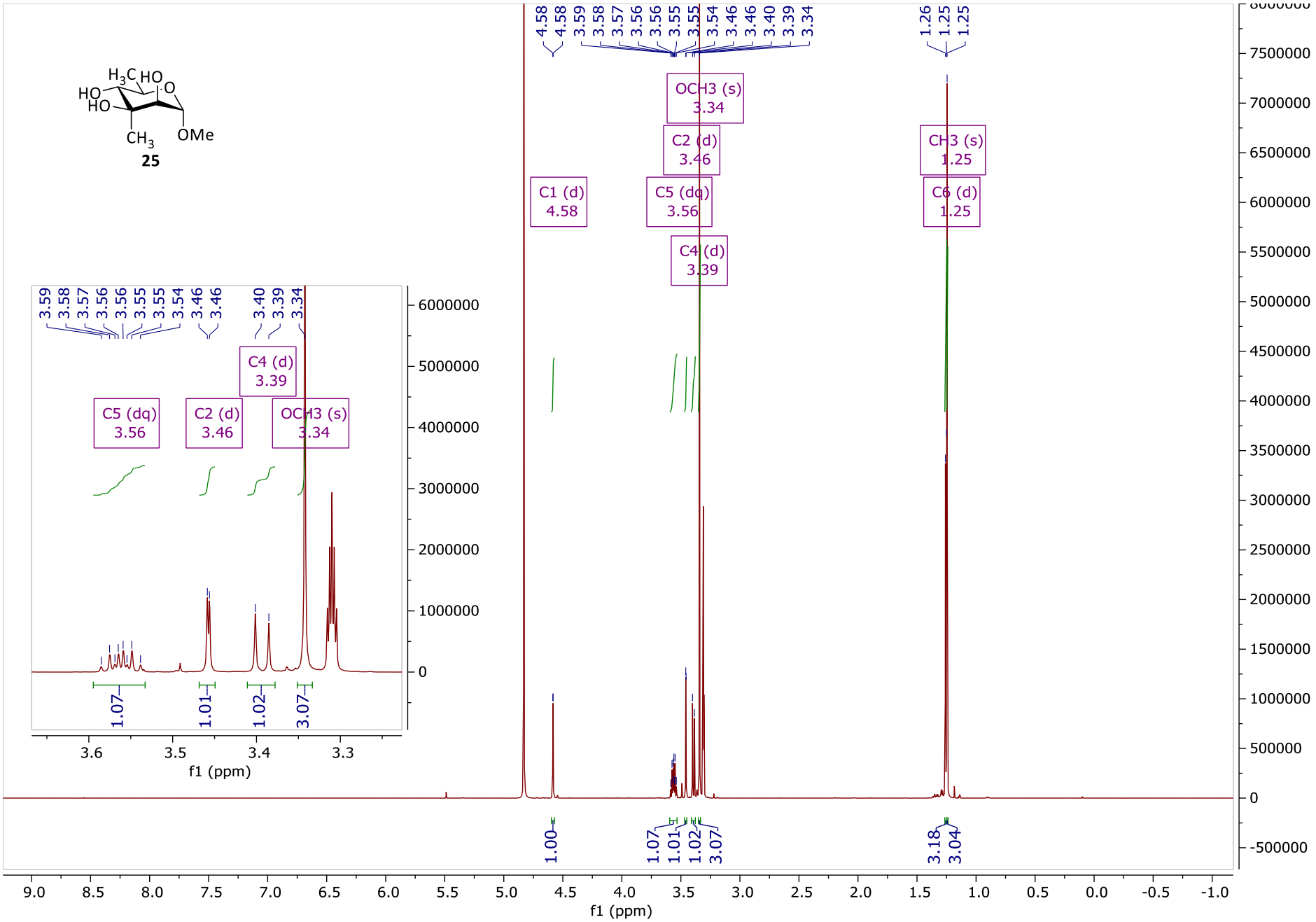

Figure S57 – ^{1}H-NMR (600 MHz, MeOD-d_4) of methyl α-D-evaloside (**25**)

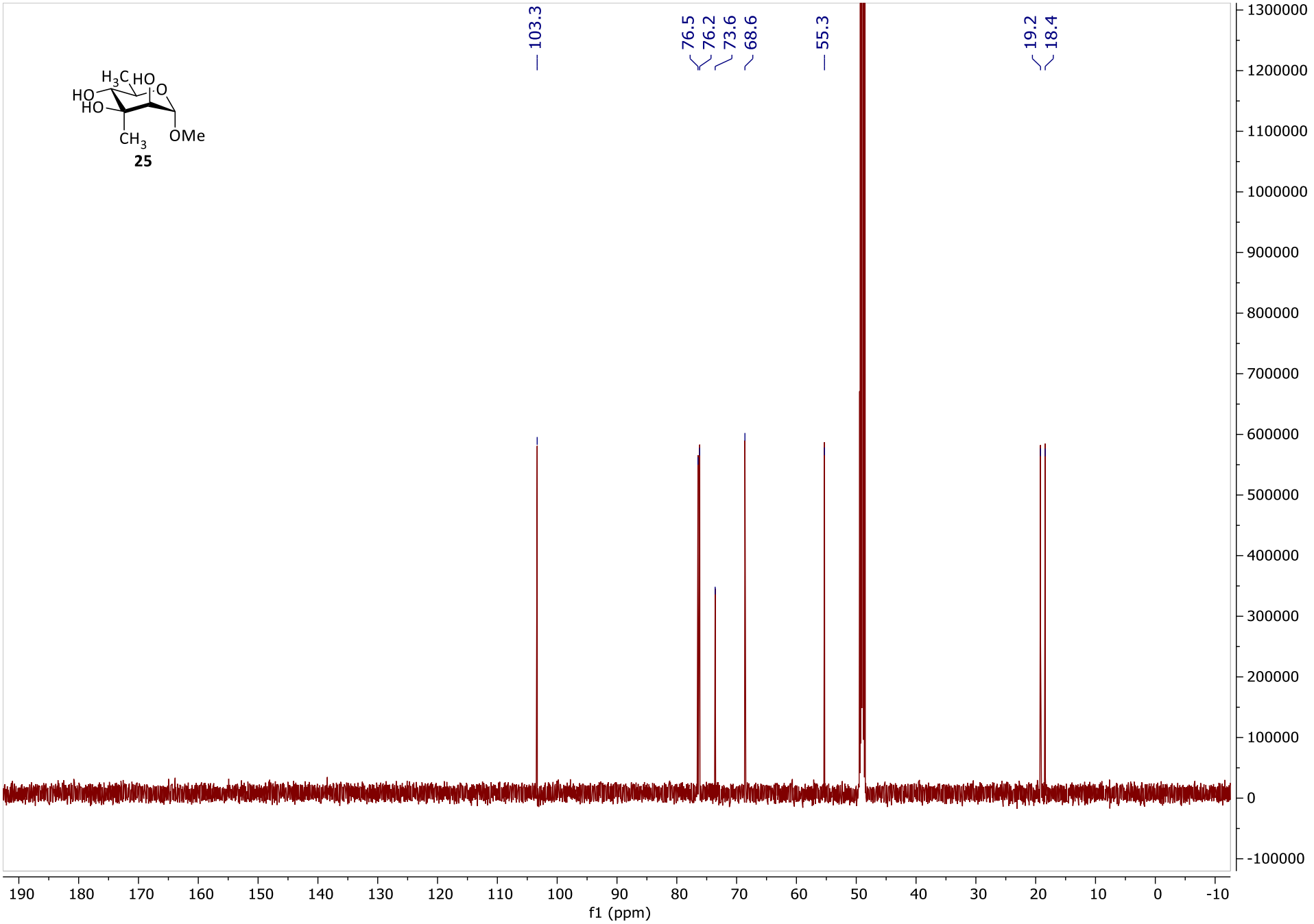

Figure S58 – ^{13}C-NMR (151 MHz, MeOD-d_4) of methyl α-D-evaloside (**25**)

Tricosa-*O*-acetyl-D-maltoheptaose (26)

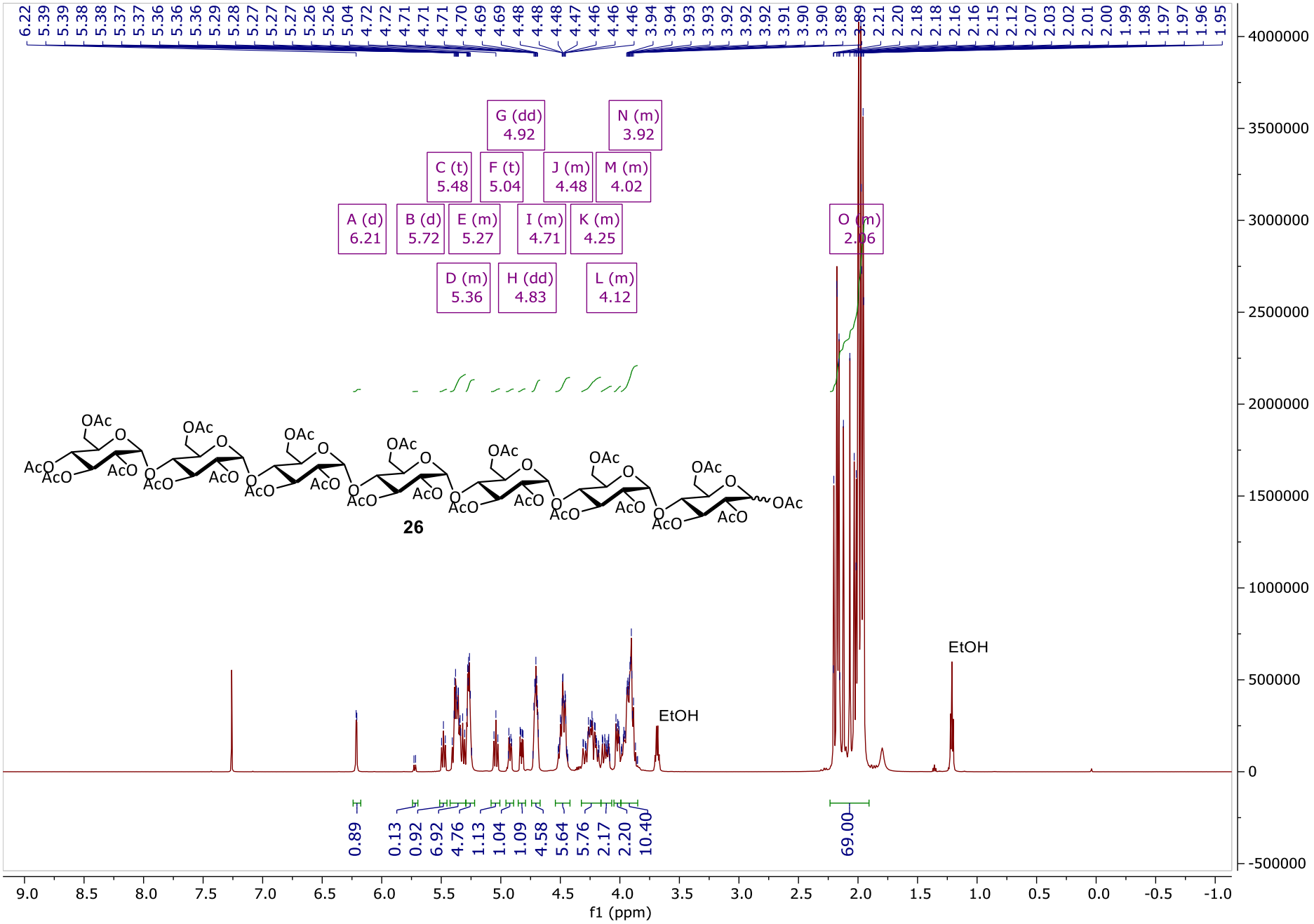

Figure S59 – ^{1}H-NMR (600 MHz, $CDCl_3$) of tricosa-*O*-acetyl-D-maltoheptaose (**26**)

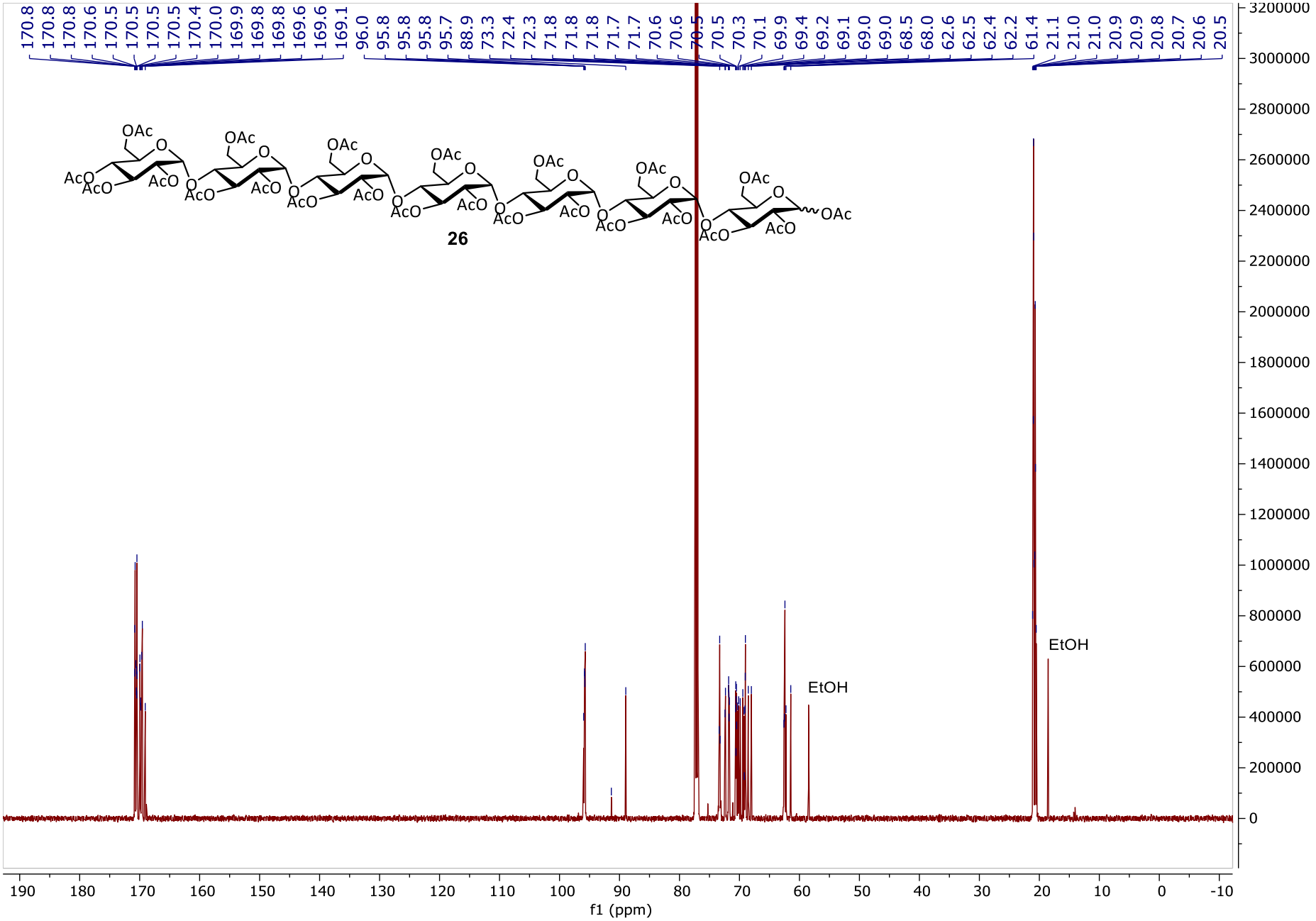

Figure S60 – ^{13}C-NMR (151 MHz, $CDCl_3$) of tricosa-*O*-acetyl-D-maltoheptaose (**26**)

docosa-*O*-acetyl-β-D-maltoheptaosyl azide (27)

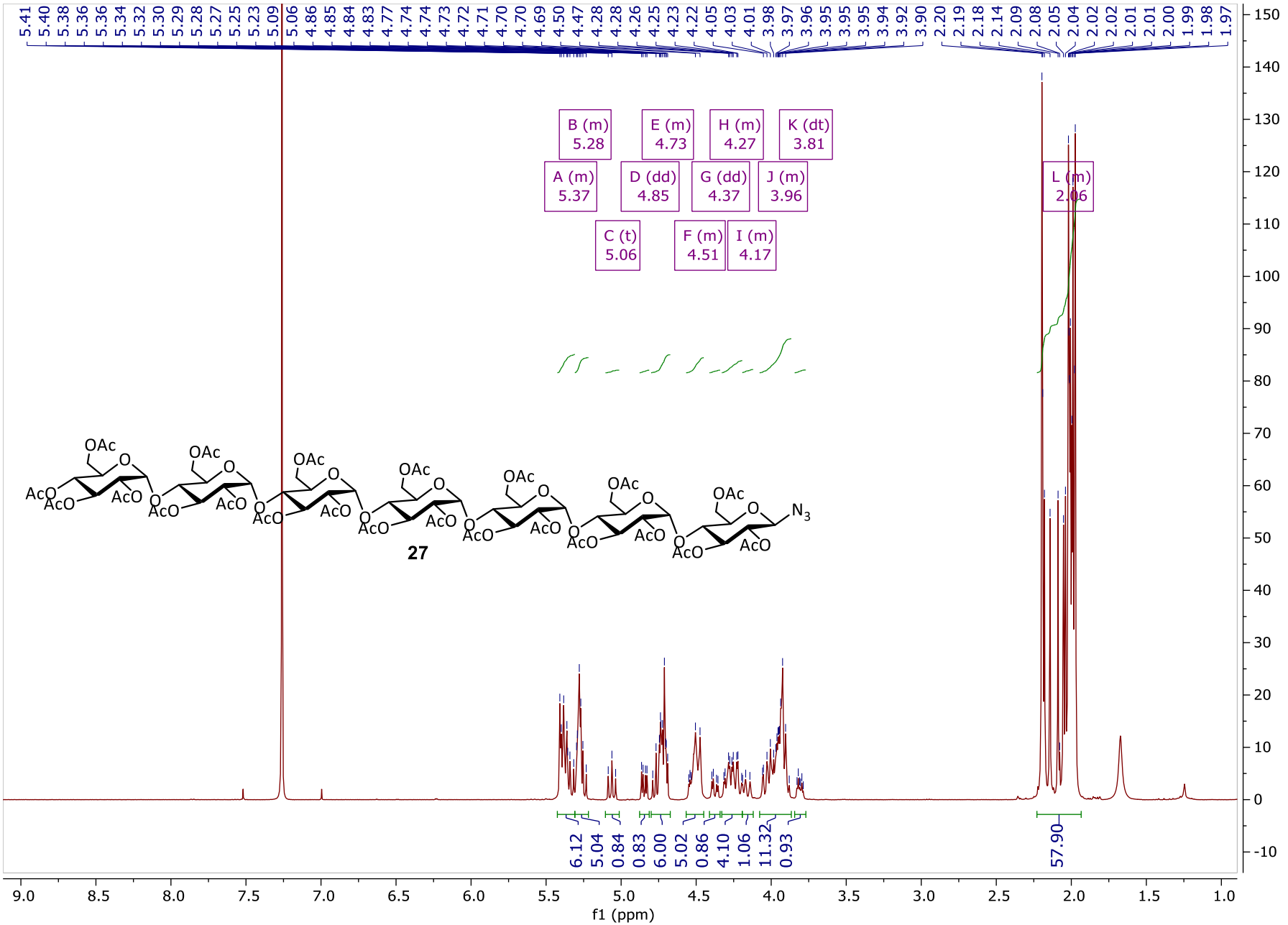

Figure S61 – ^{1}H-NMR (400 MHz, $CDCl_3$) of docosa-*O*-acetyl-β-D-maltoheptaosyl azide (**27**)

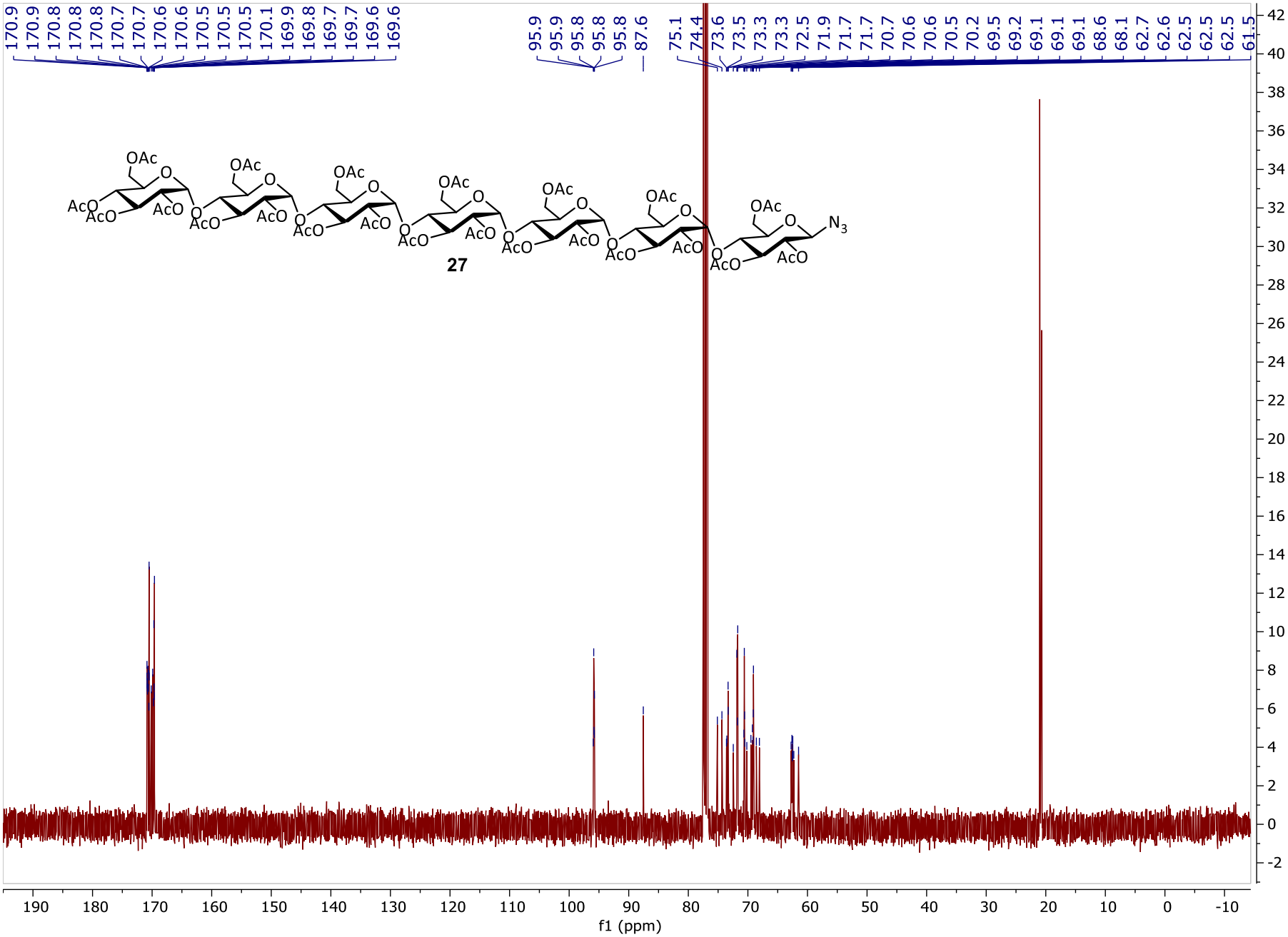

Figure S62 – ^{13}C-NMR (101 MHz, $CDCl_3$) of docosa-*O*-acetyl-β-D-maltoheptaosyl azide (**27**)

Methyl 3-*C*-cyclopentadienyl-α-D-allopyranoside (28)

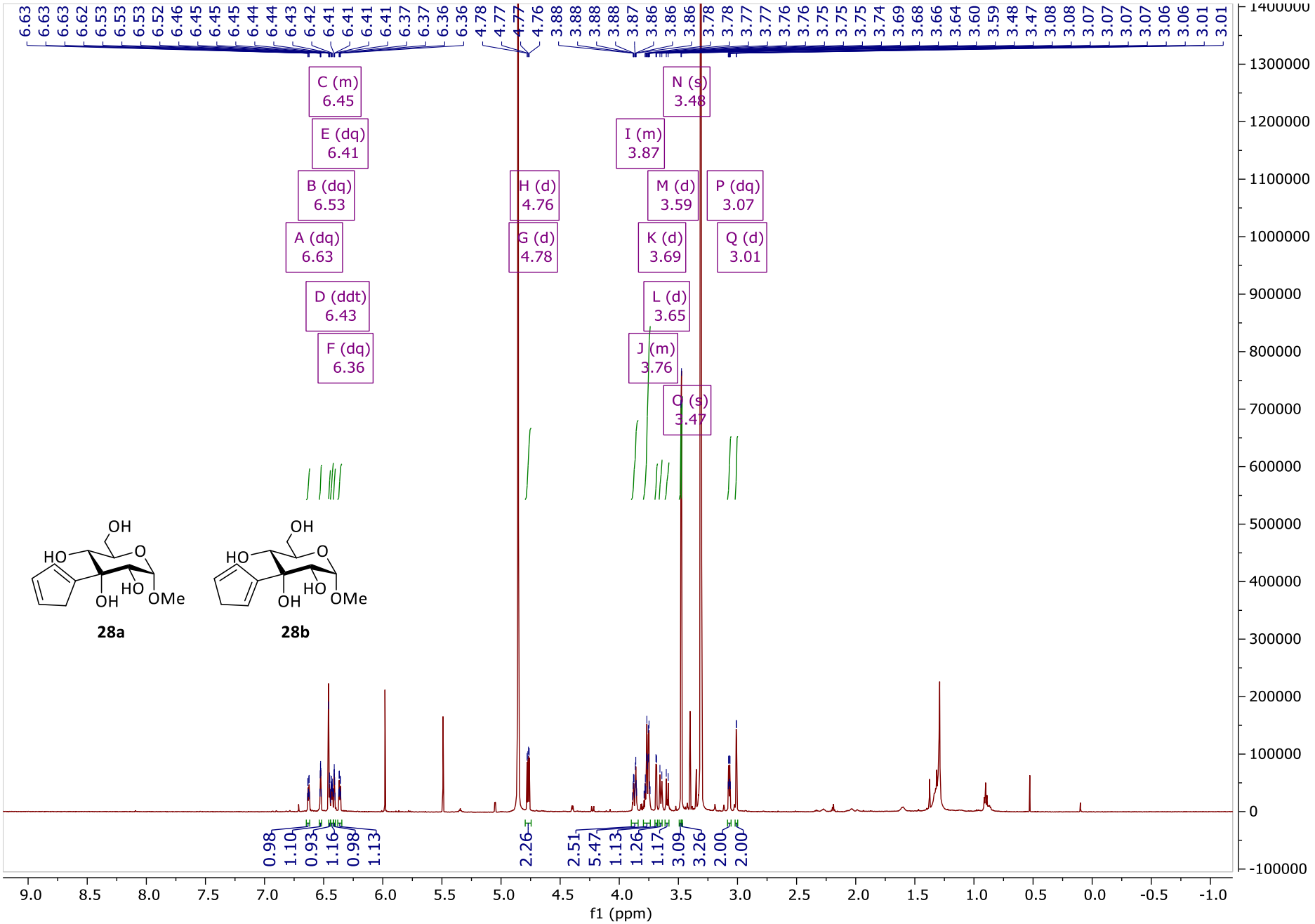

Figure S63 – ^{1}H-NMR (600 MHz, MeOD-*d4*) of methyl 3-*C*-cyclopentadienyl-α-D-allopyranoside (**28**)

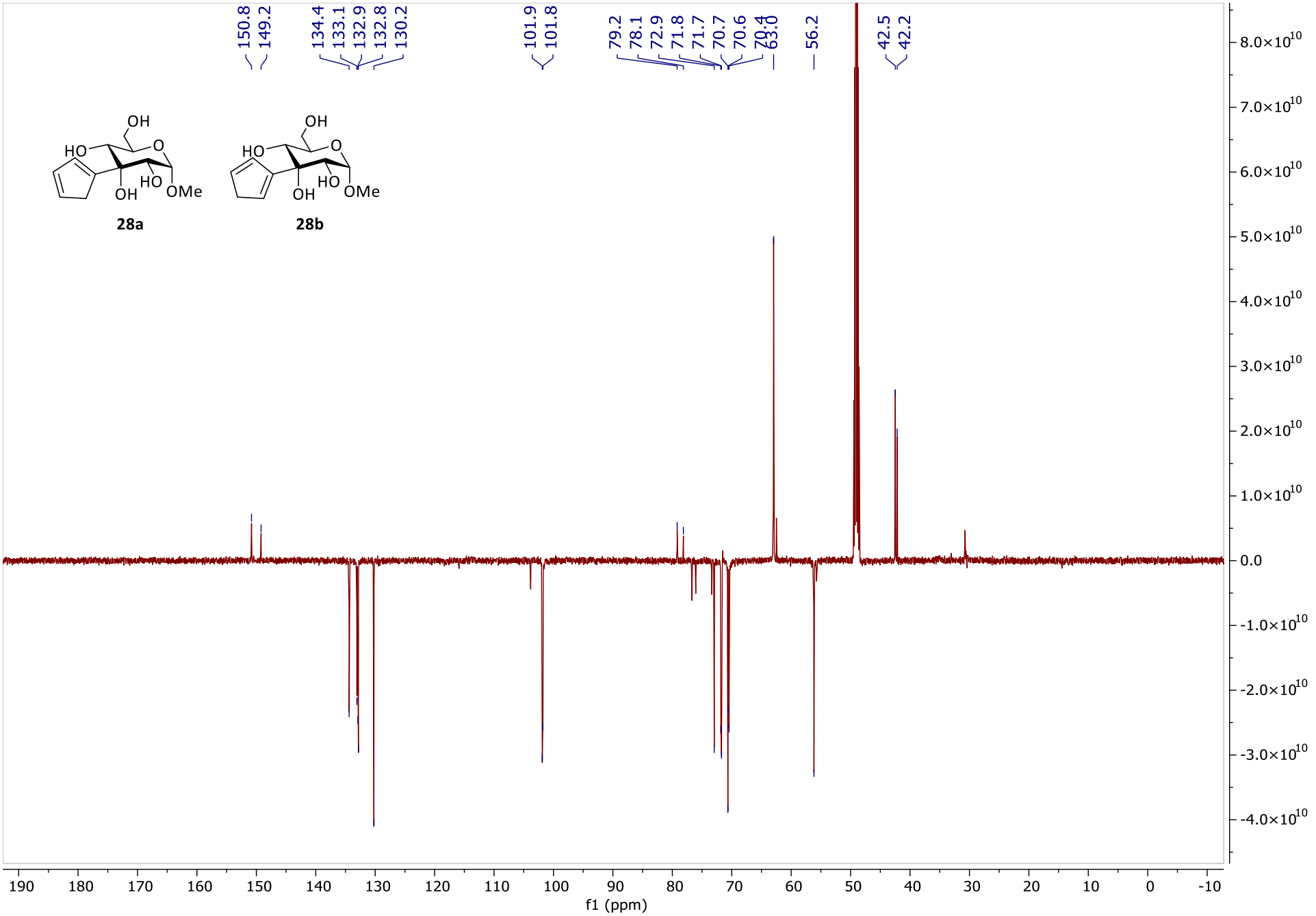

Figure S64 – APT (151 MHz, MeOD-*d4*) of methyl 3-*C*-cyclopentadienyl-α-D-allopyranoside (**28**)

8. HRMS spectra

Methyl α-D-*ribo*-hex-3-ulopyranoside (1)

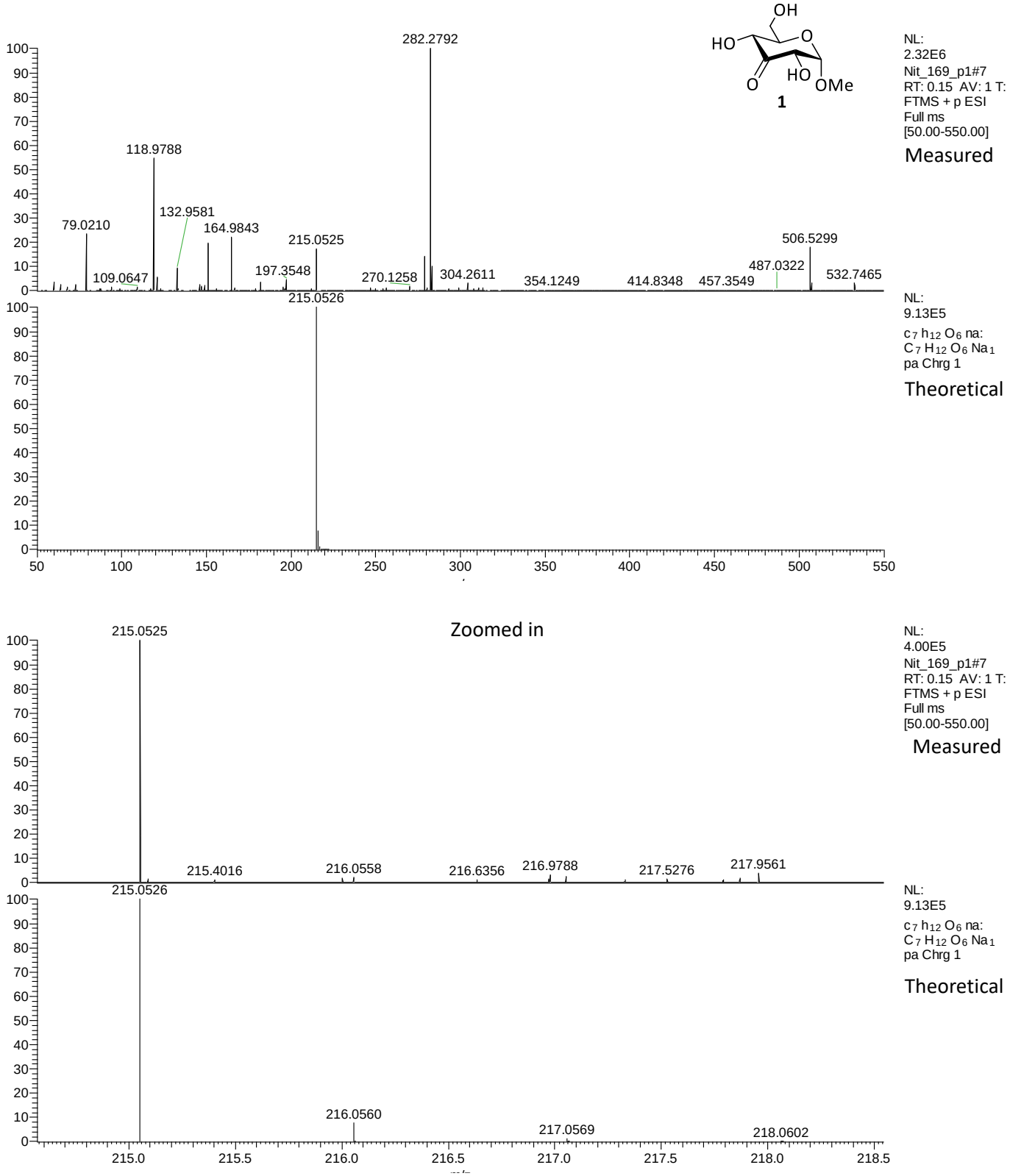

Figure S65 – HRMS of methyl α-D-*ribo*-hex-3-ulopyranoside (**1**)

Methyl 3-*C*-methyl-α-D-allopyranoside (3)

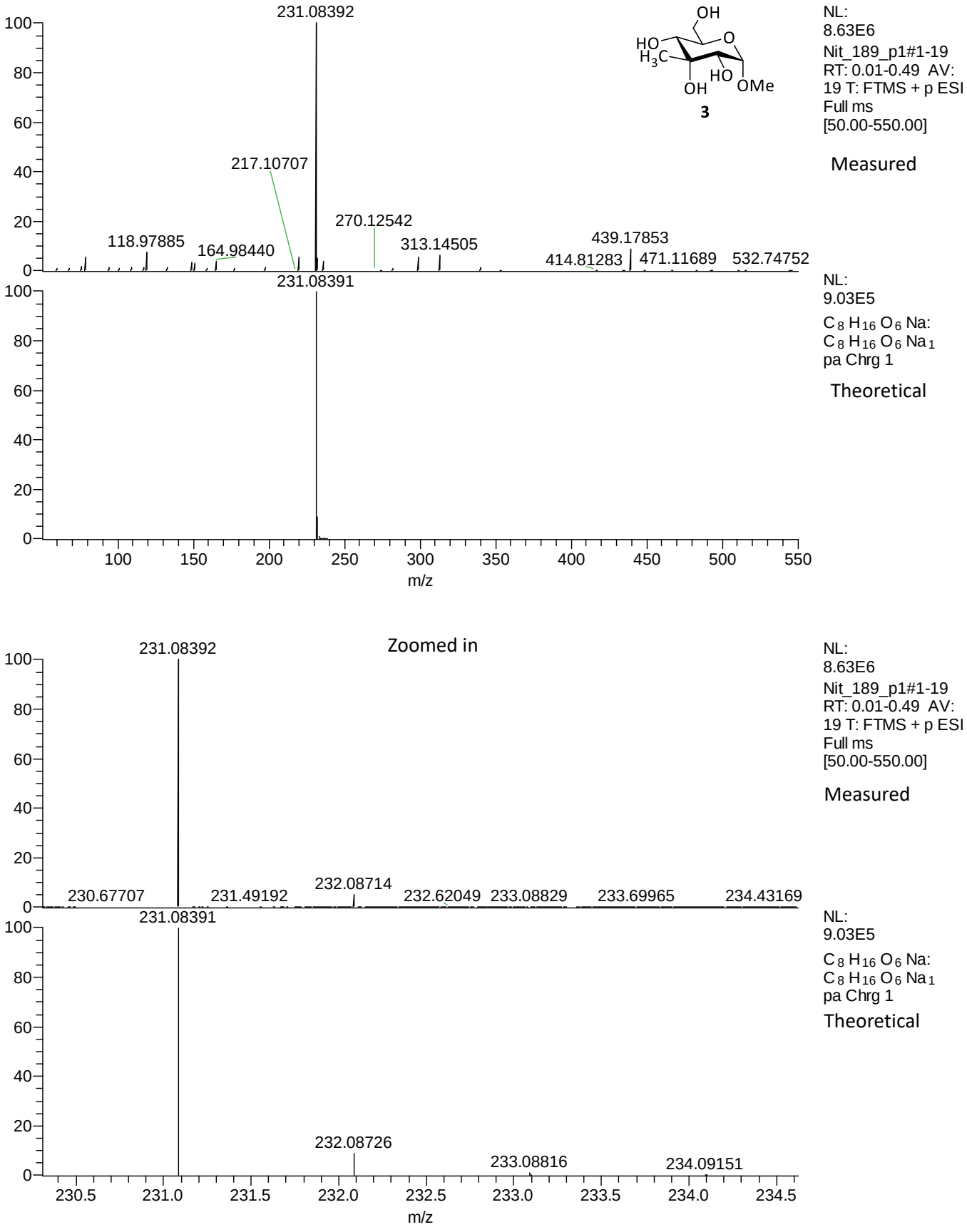

Figure S66 – HRMS of methyl 3-C-methyl-α-D-allopyranoside (**3**)

Methyl 3-*C*-allyl-α-D-allopyranoside (4)

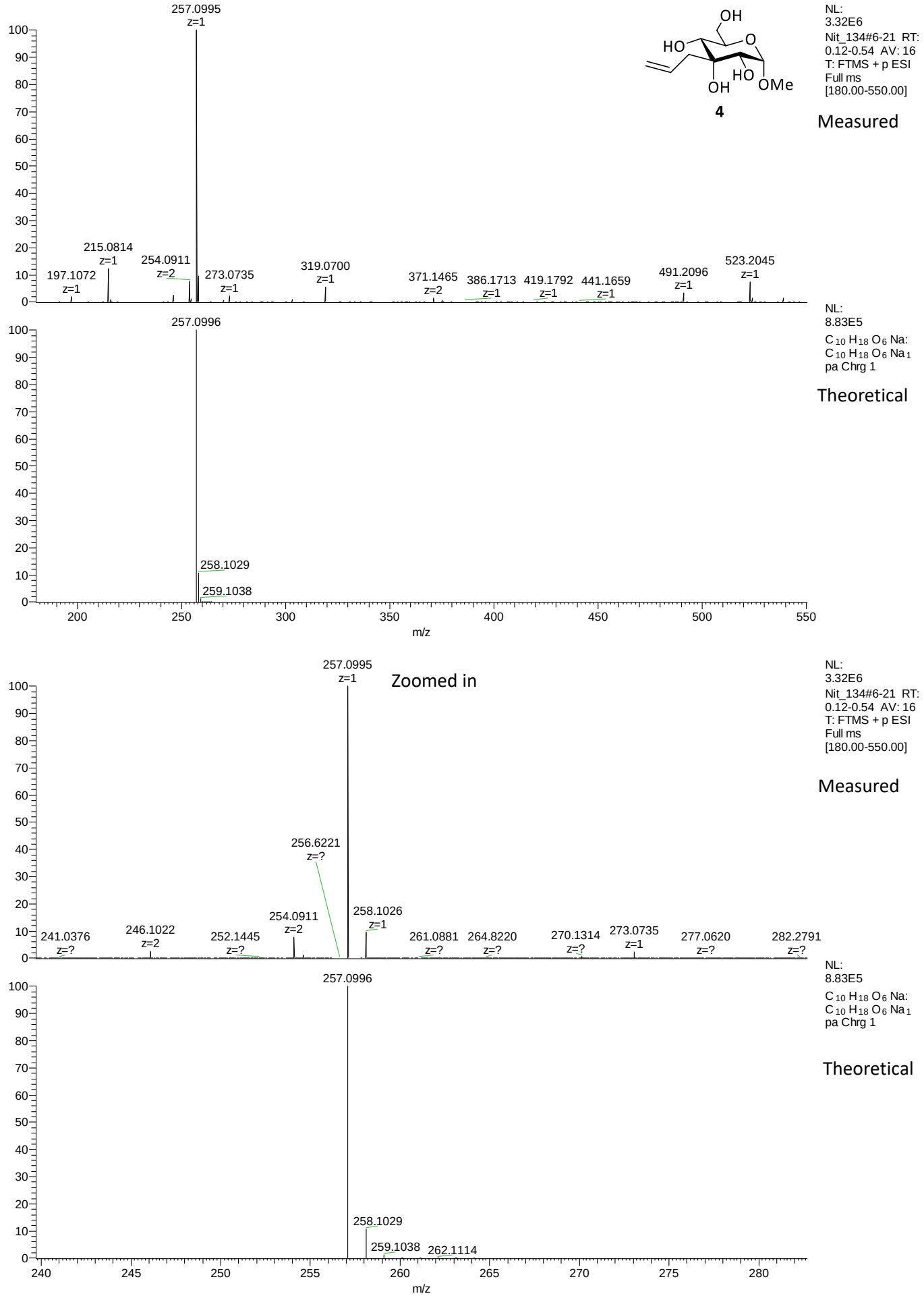

Figure S67 – HRMS of methyl 3-C-allyl-α-D-allopyranoside (**4**)

Methyl 3-*C*-propargyl-α-D-allopyranoside (5a) & Methyl 3-*C*-allenyl-α-D-allopyranoside (5b)

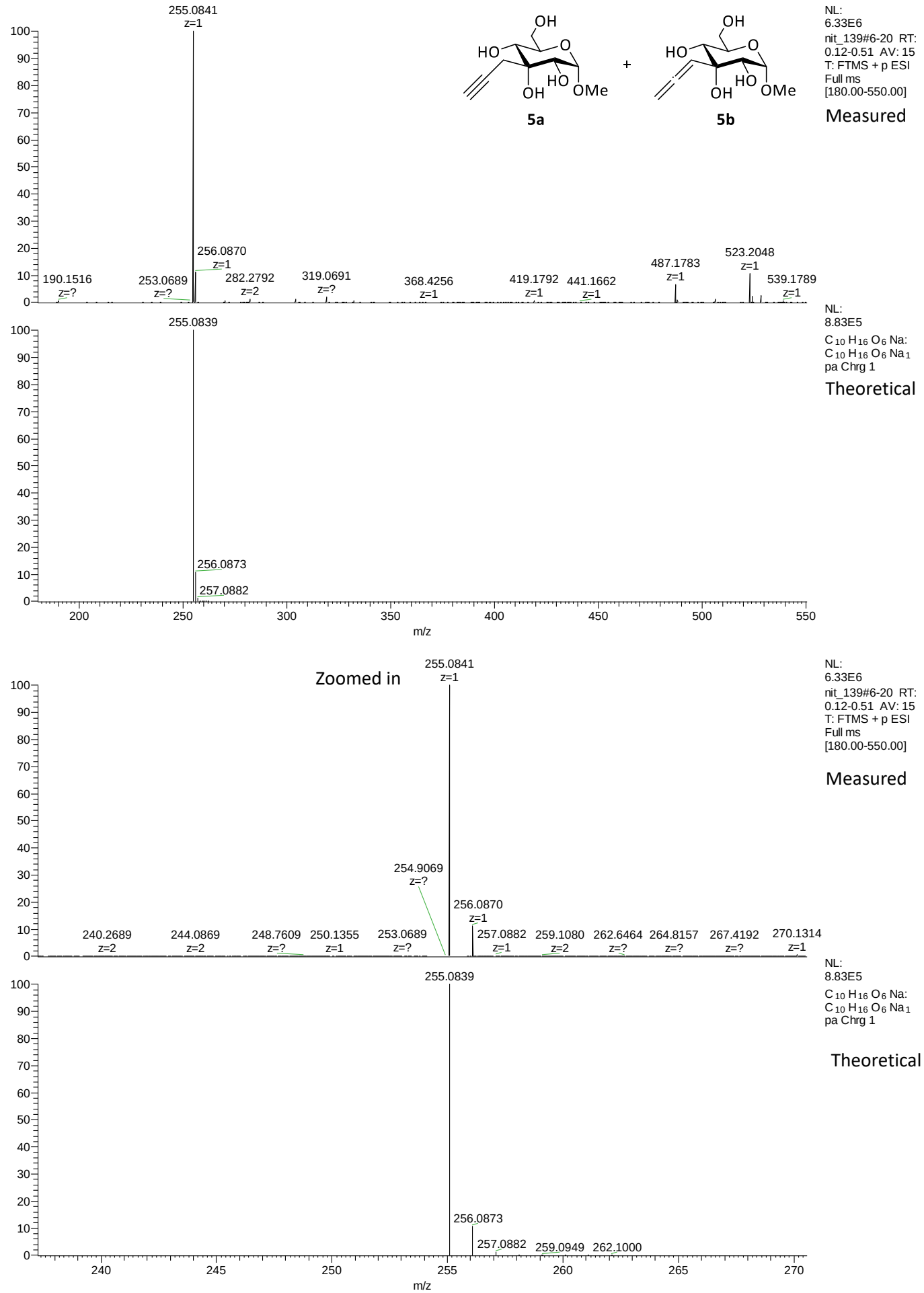

Figure S68 – HRMS of methyl 3-*C*-propargyl-α-D-allopyranoside (**5a**) & methyl 3-*C*-allenyl-α-D-allopyranoside (**5b**)

Methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (6)

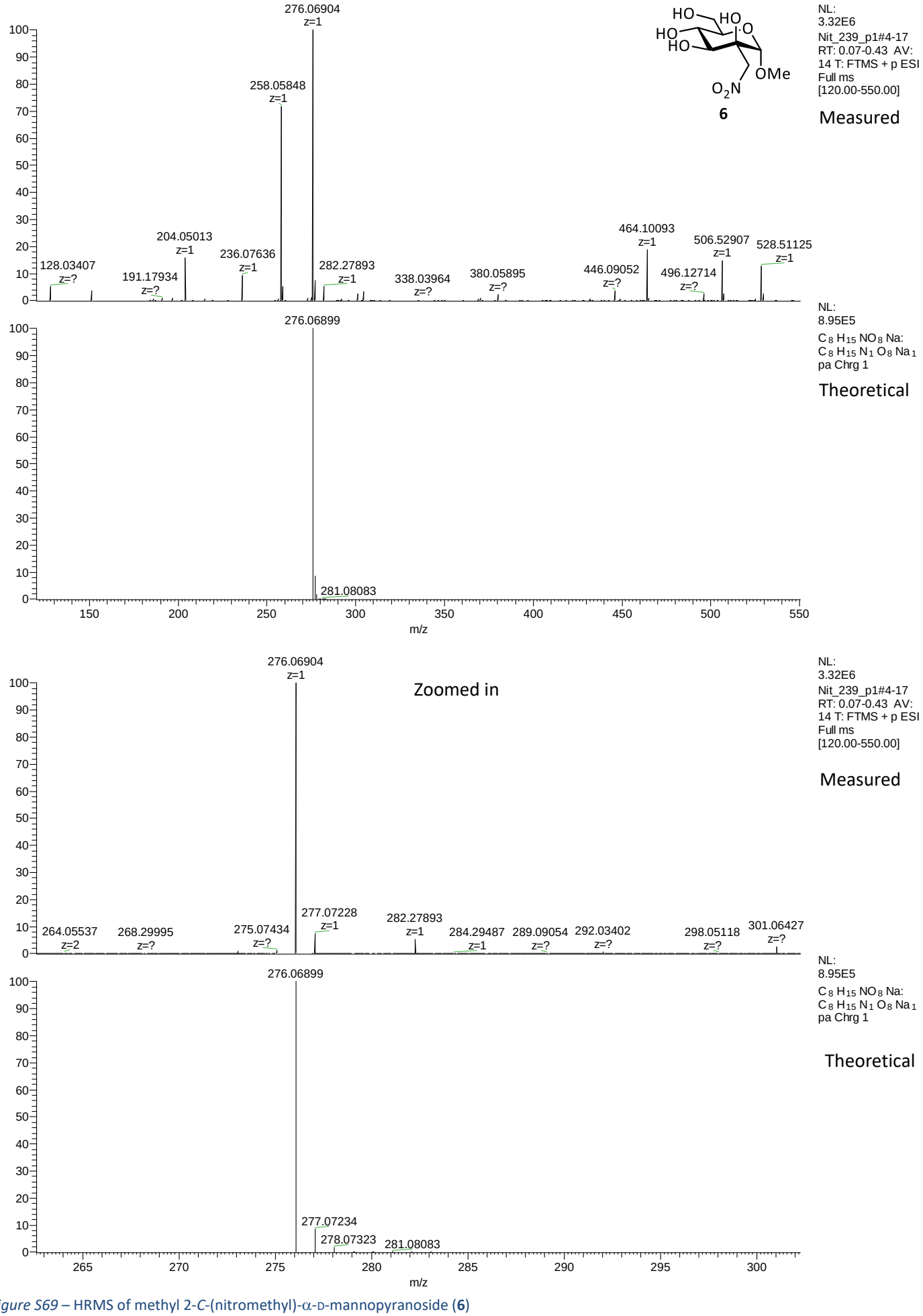

Figure S69 – HRMS of methyl 2-*C*-(nitromethyl)-α-D-mannopyranoside (**6**)

Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (7)

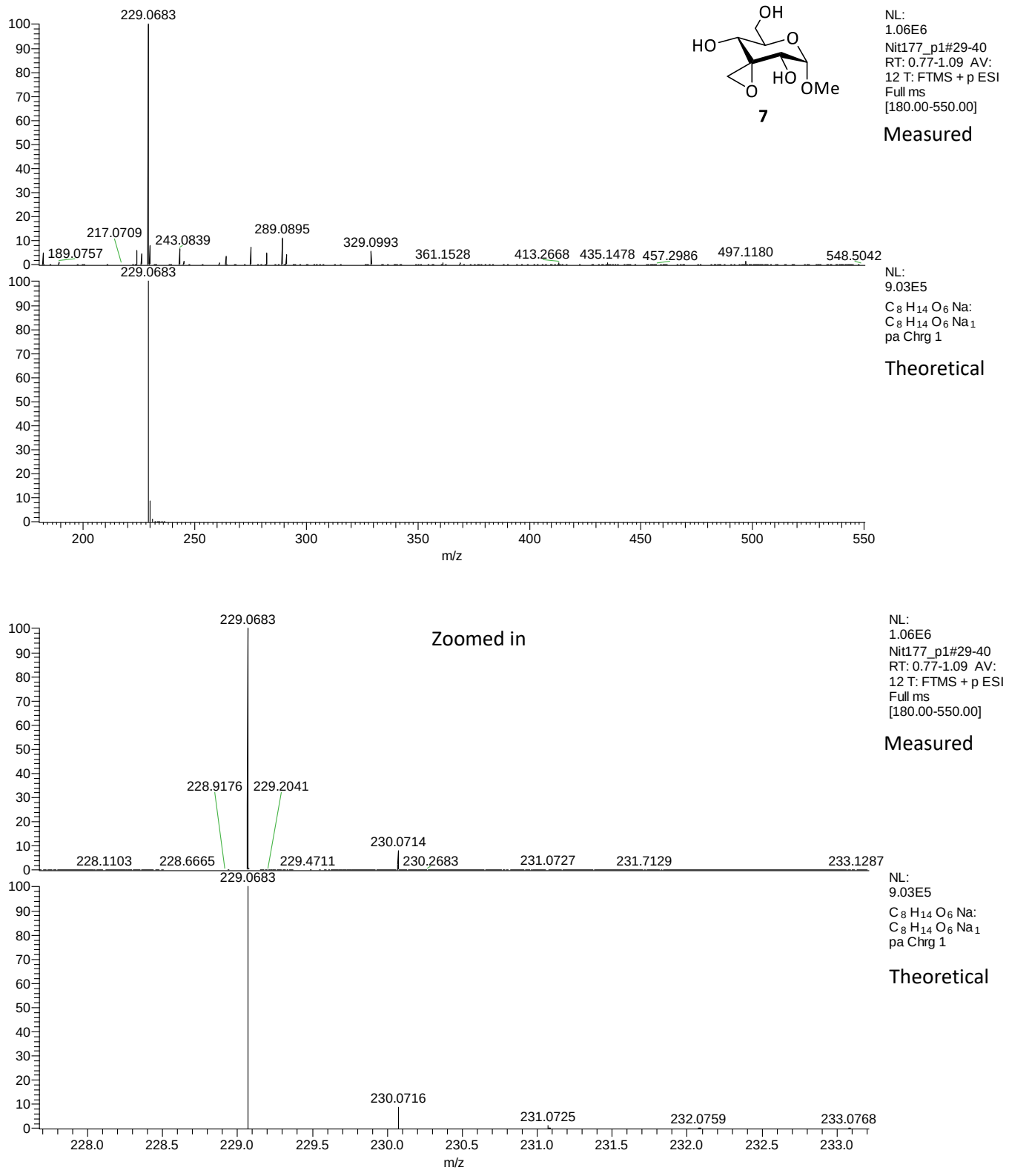

Figure S70 – HRMS of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-allopyranoside (**7**)

Methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (8)

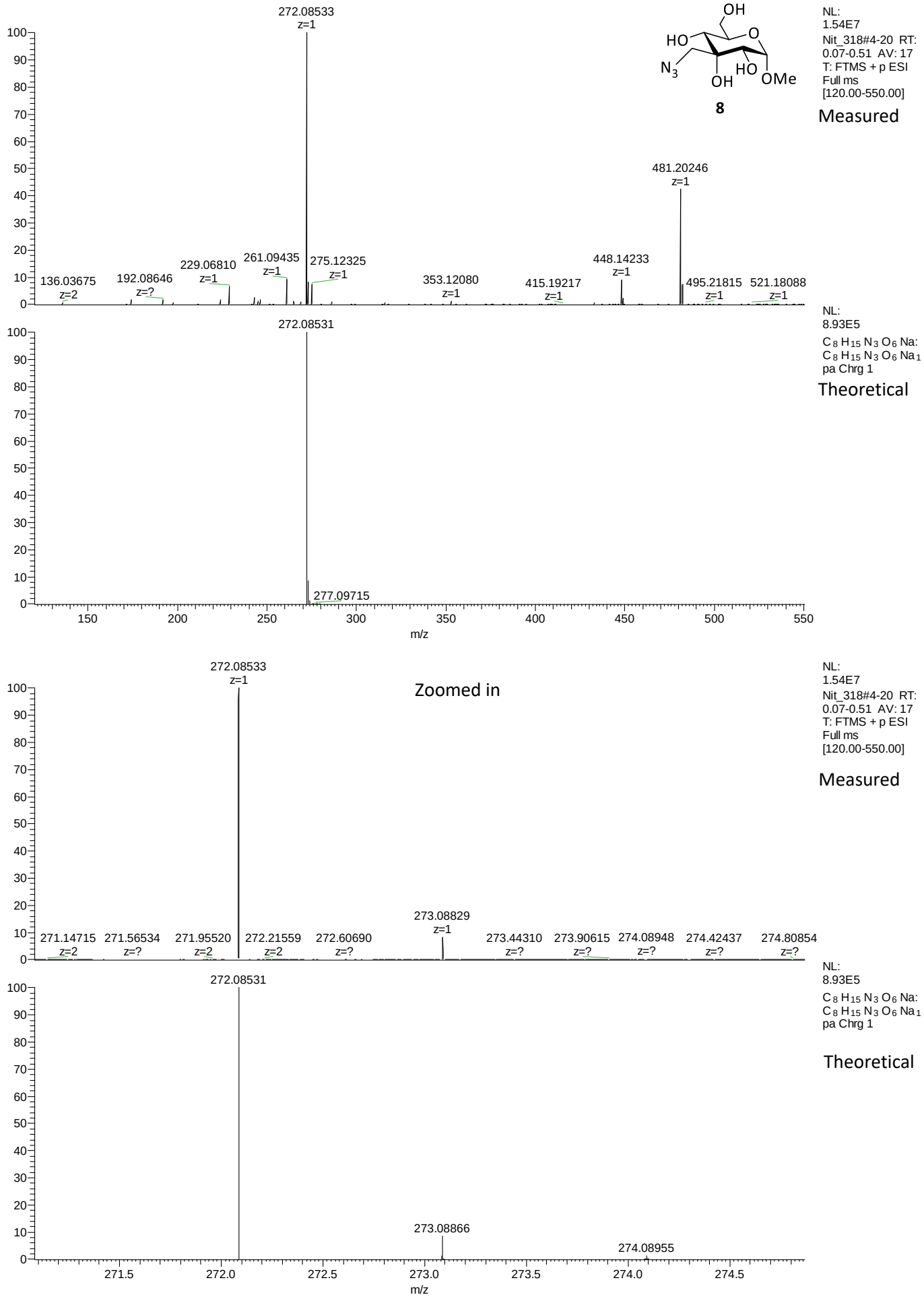

Figure S71 – HRMS of methyl 3-*C*-(azidomethyl)-α-D-allopyranoside (**8**)

Methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (9)

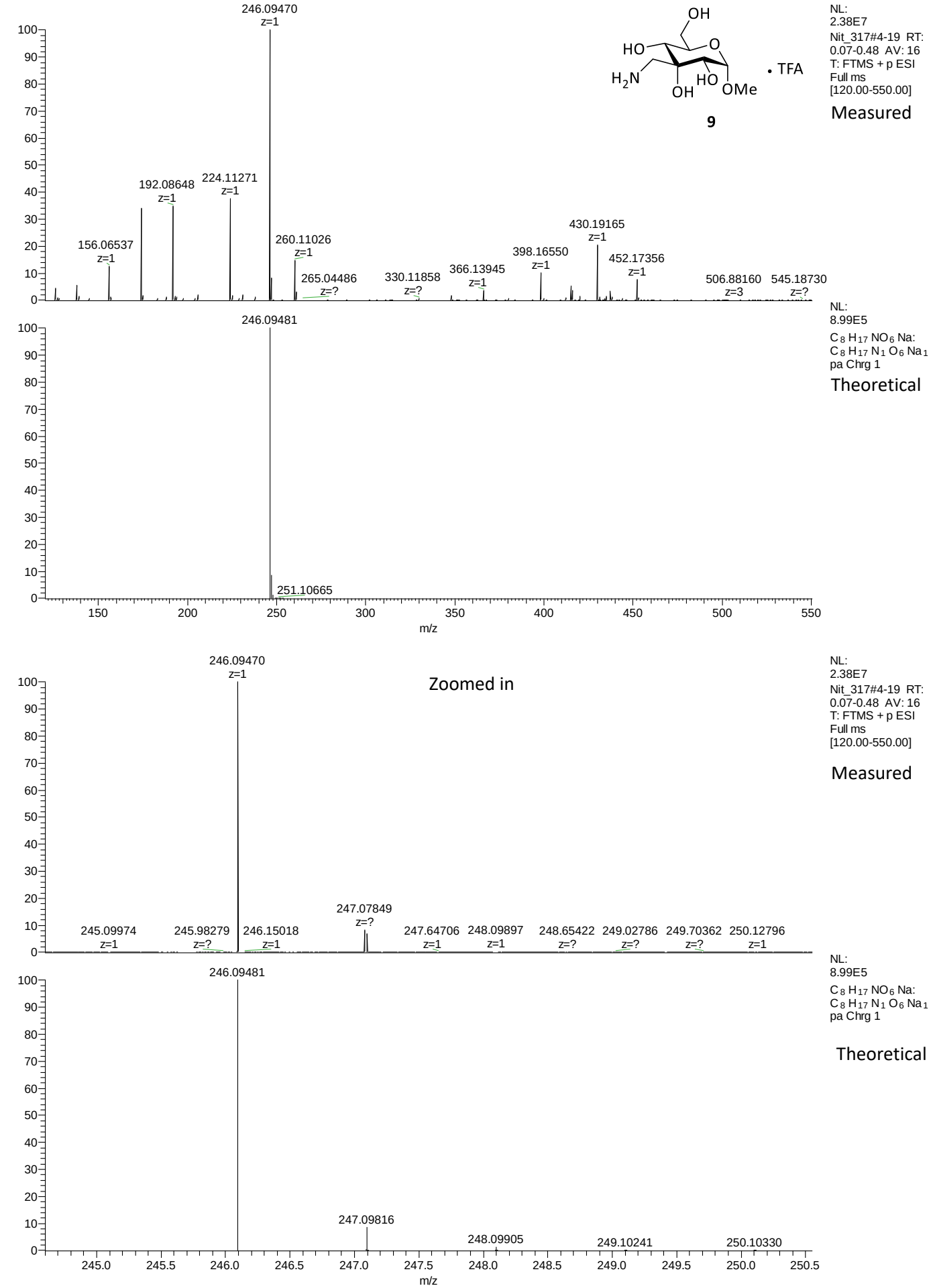

Figure S72 – HRMS of methyl 3-*C*-(aminomethyl)-α-D-allopyranoside · trifluoroacetic acid (**9**)

β-D-maltoheptaosyl azide (10)

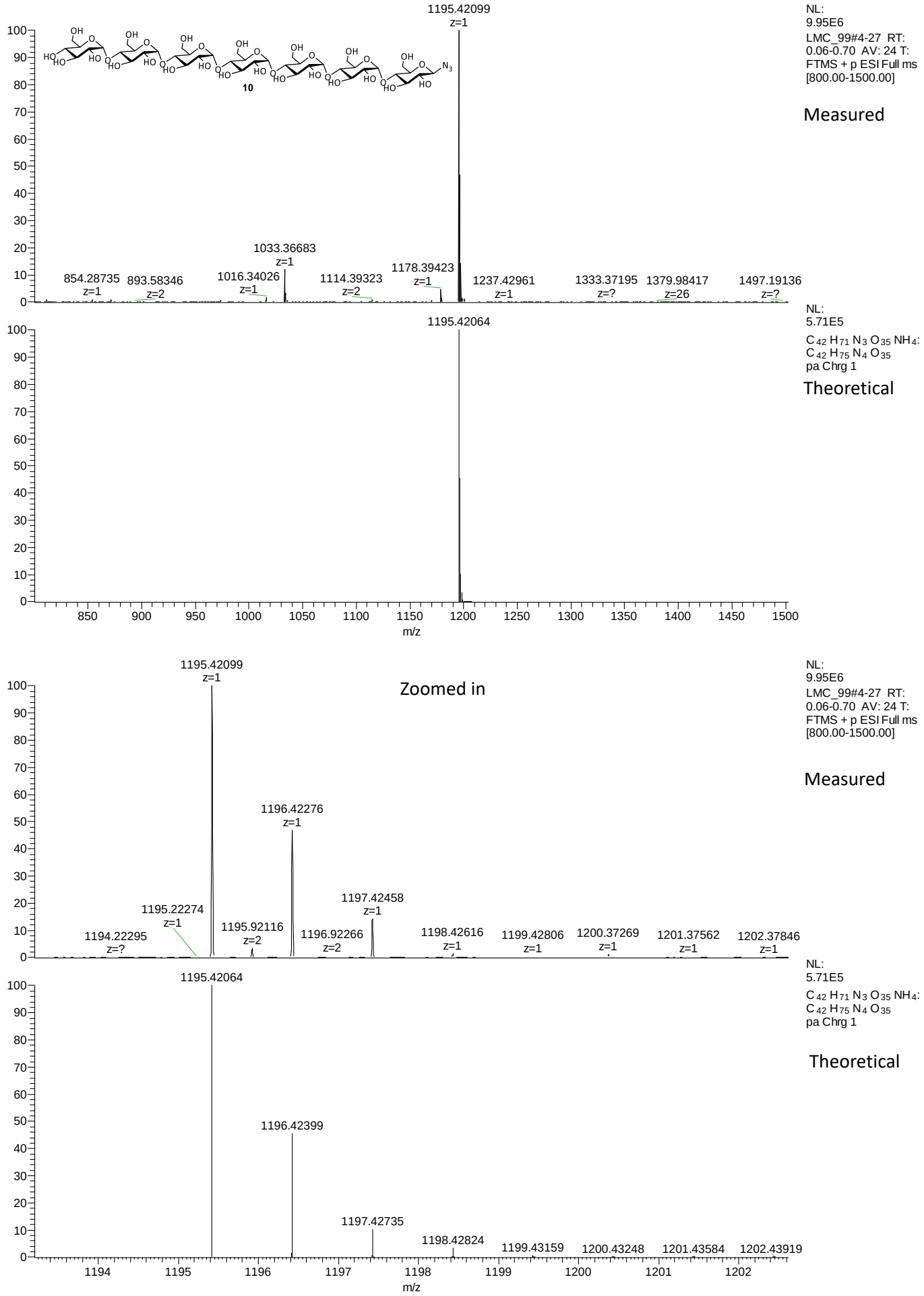

Figure S73 – HRMS of β-D-maltoheptaosyl azide (**10**)

3-keto-β-D-maltoheptaosyl azide (11)

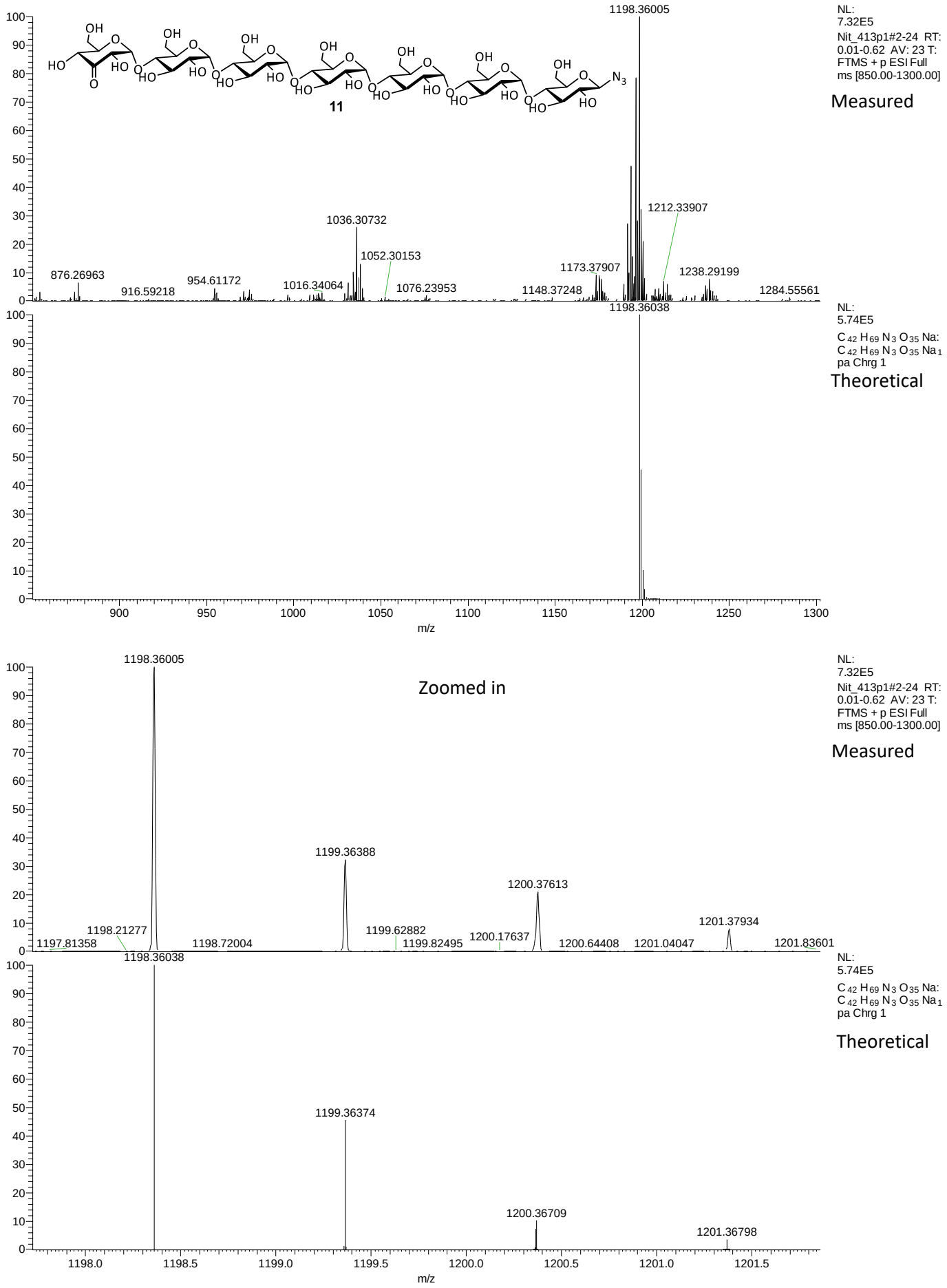

Figure S74 – HRMS of 3-keto-β-D-maltoheptaosyl azide (**11**)

3,3'-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (12)

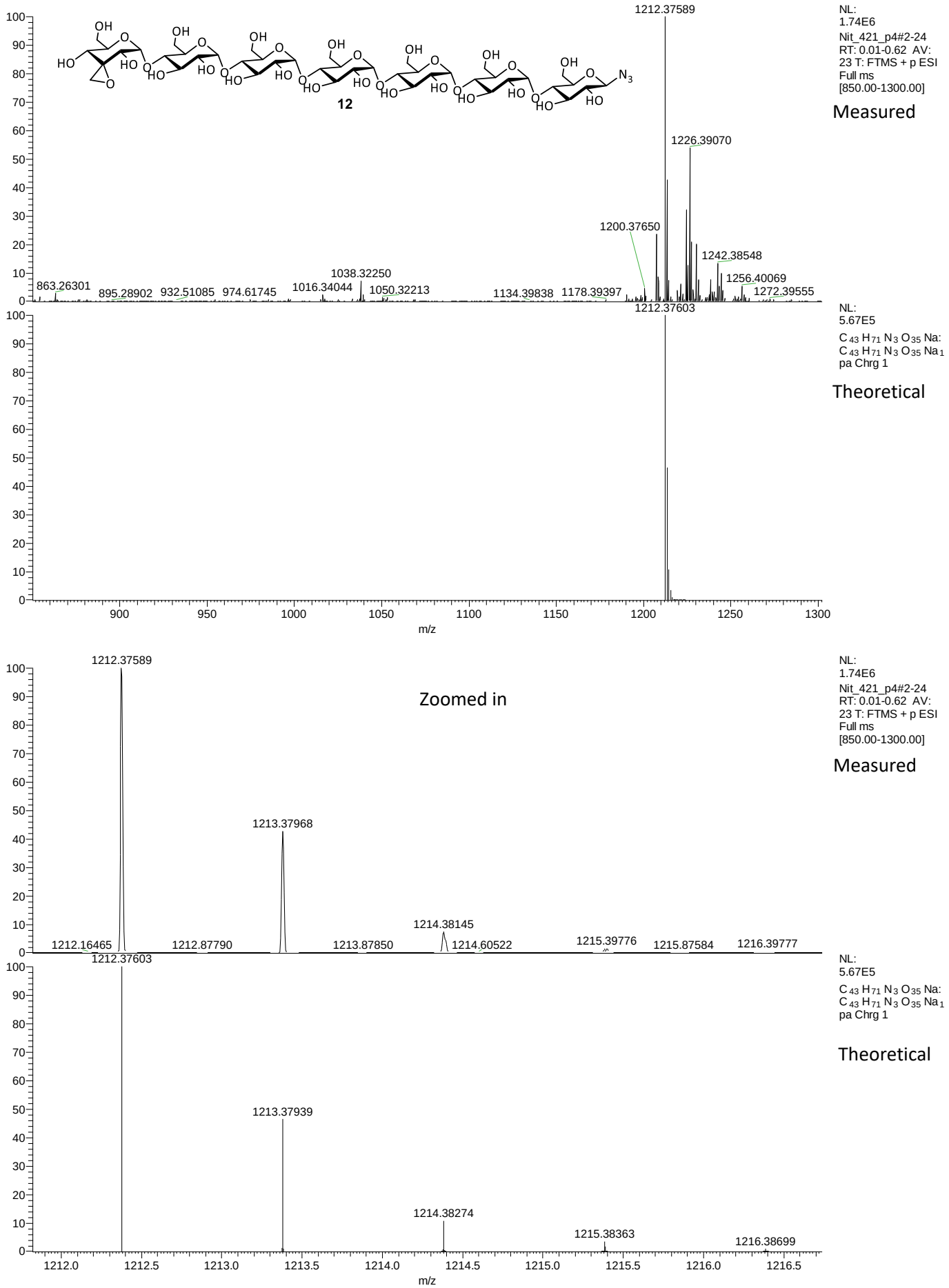

Figure S75 – HRMS of 3,3'-anhydro-3-*C*-(hydroxymethyl)-β-D-maltoheptaosyl azide (**12**)

Methyl *E*/*Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (13)

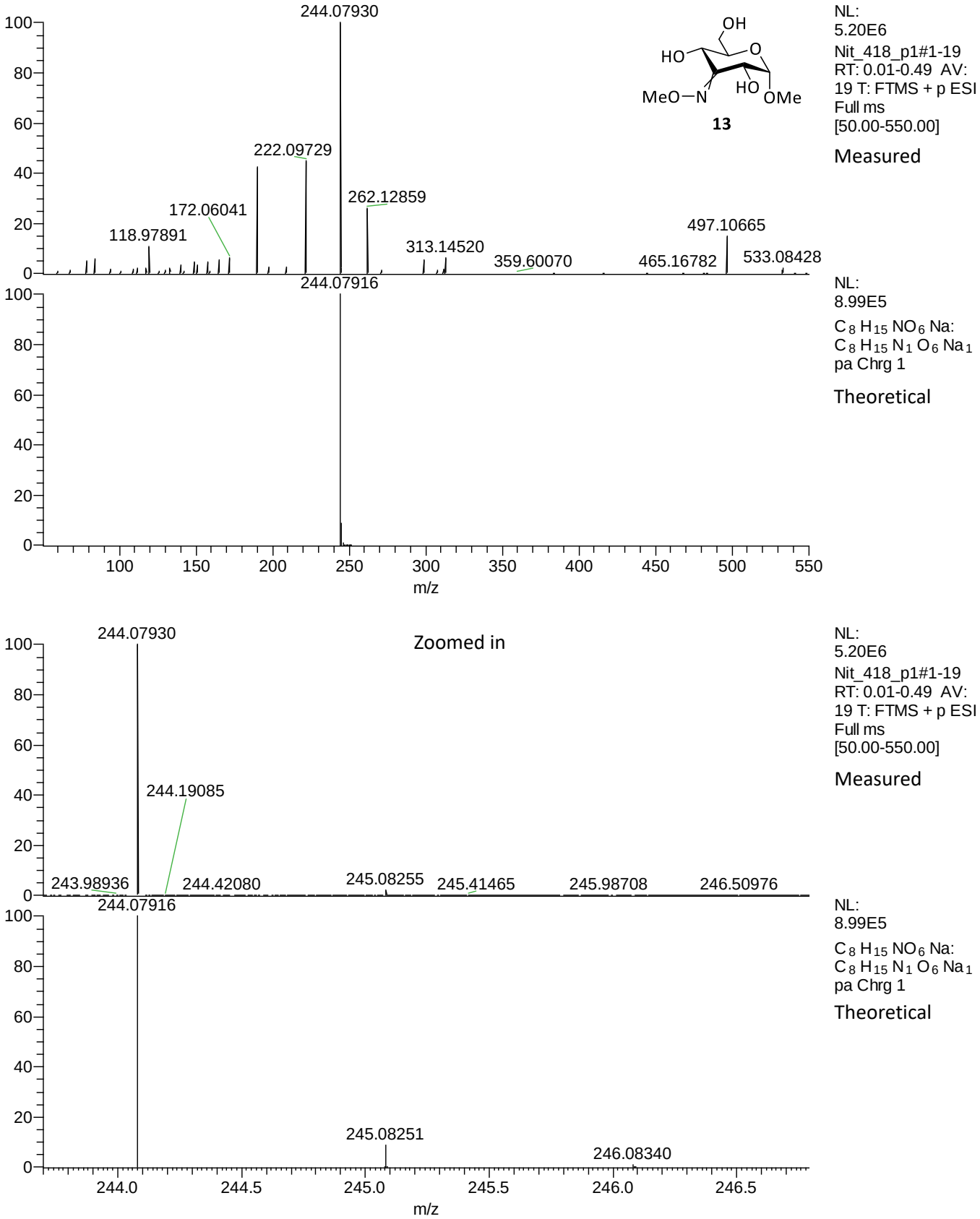

Figure S76 – HMRS of methyl *E*/*Z*-3-deoxy-3-methoxyimino-α-D-*ribo*-hexopyranoside (**13**)

Methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (14)

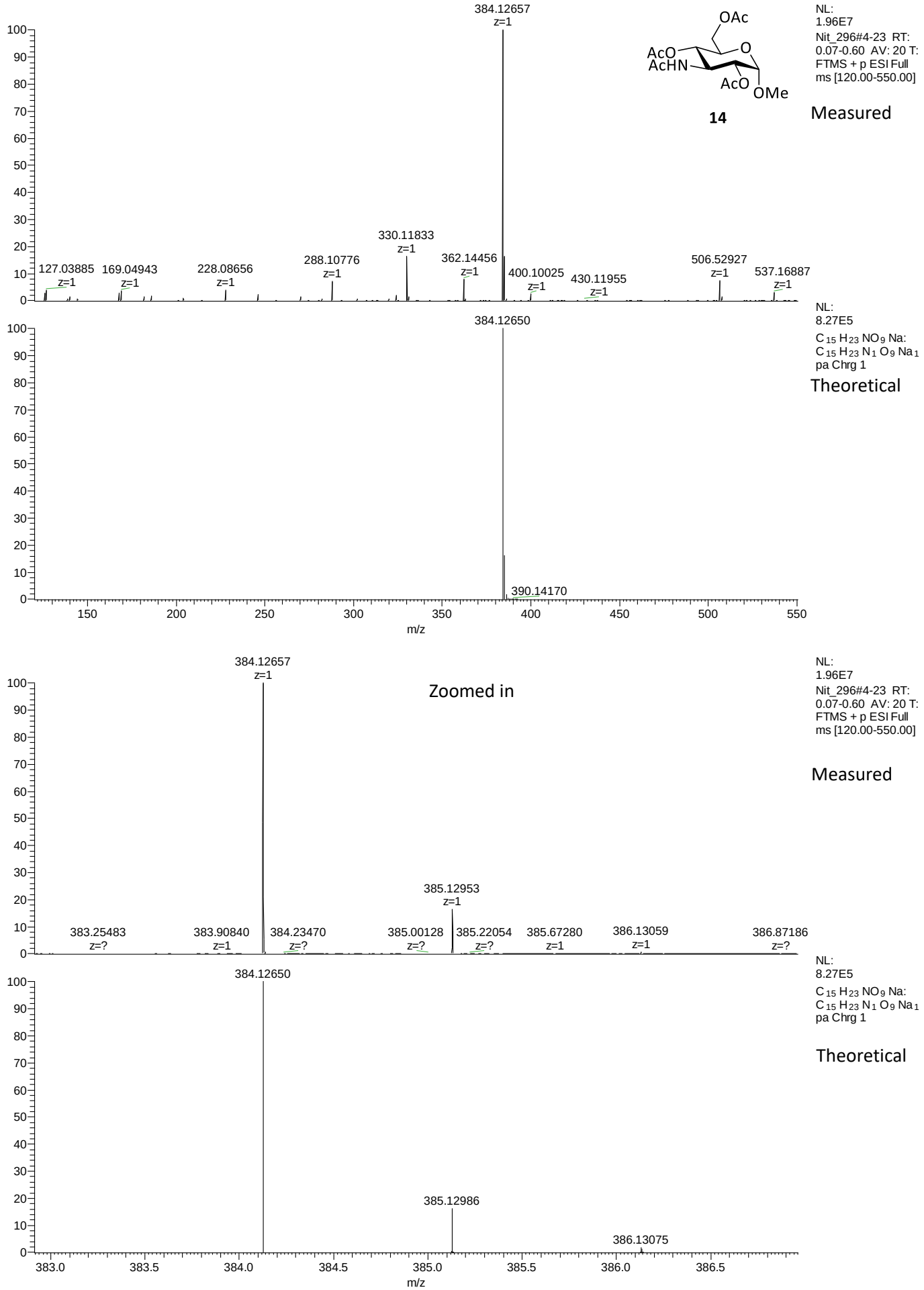

Figure S77 – HRMS of methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**14**)

Methyl 3-*C*-cyano-α-D-glucopyranoside (15a) & Methyl 3-*C*-cyano-α-D-allopyranoside (15b)

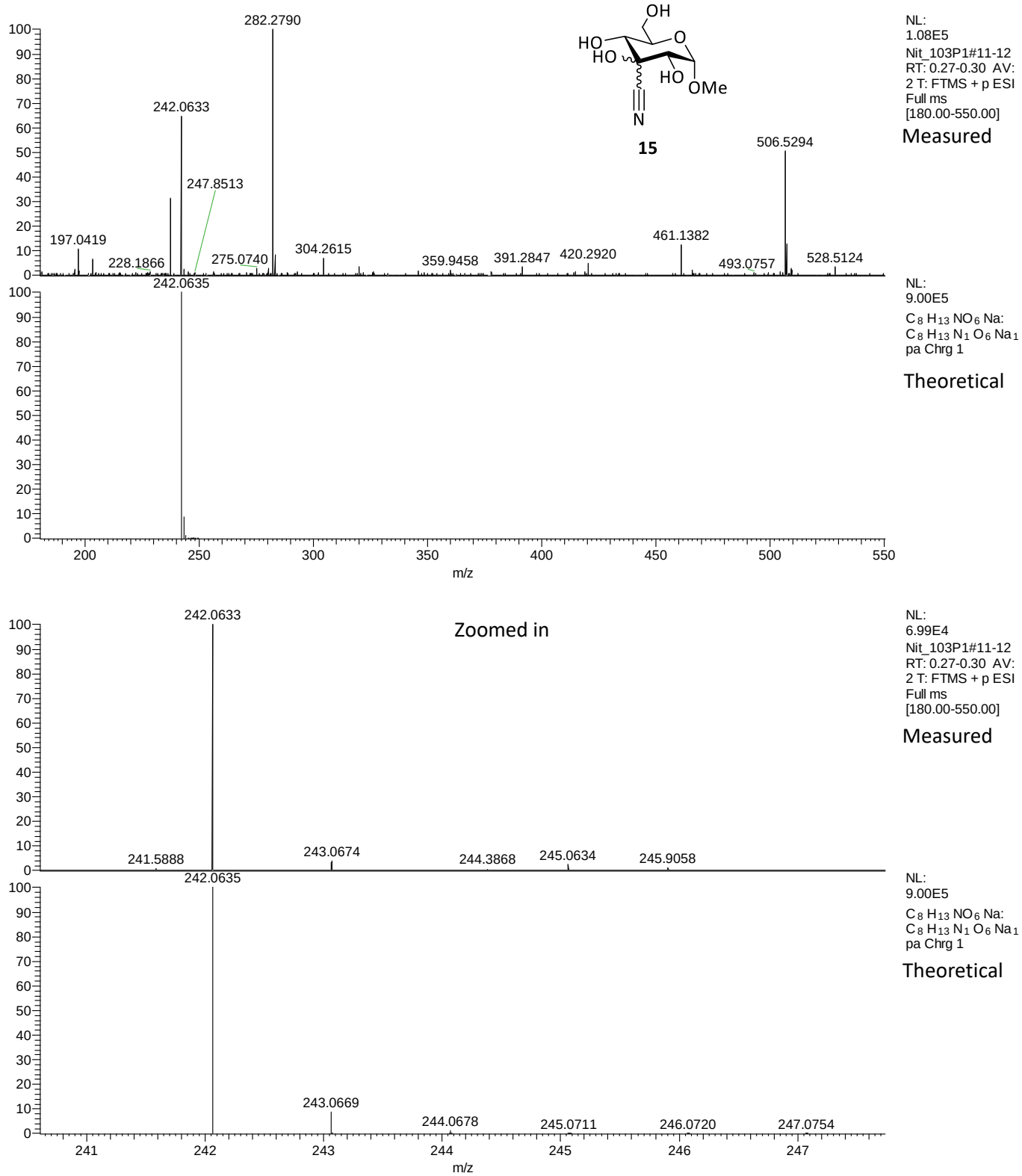

Figure S78 – HRMS of methyl 3-*C*-cyano-α-D-glucopyranoside (**15a**) & methyl 3-*C*-cyano-α-D-allopyranoside (**15b**)

Methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (16)

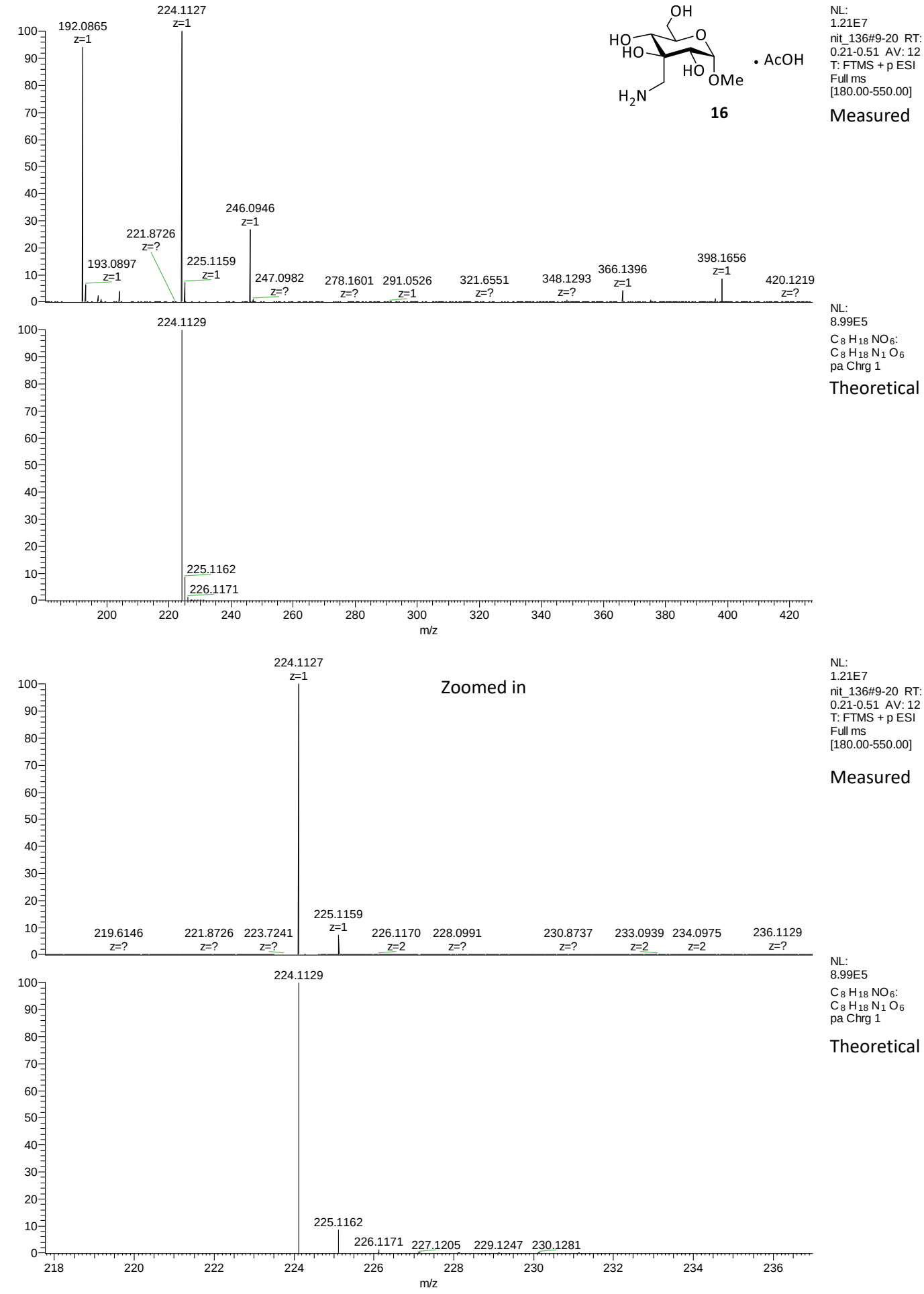

Figure S79 – HRMS of methyl 3-*C*-(aminomethyl)-α-D-glucopyranoside · acetic acid (**16**)

Methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (17)

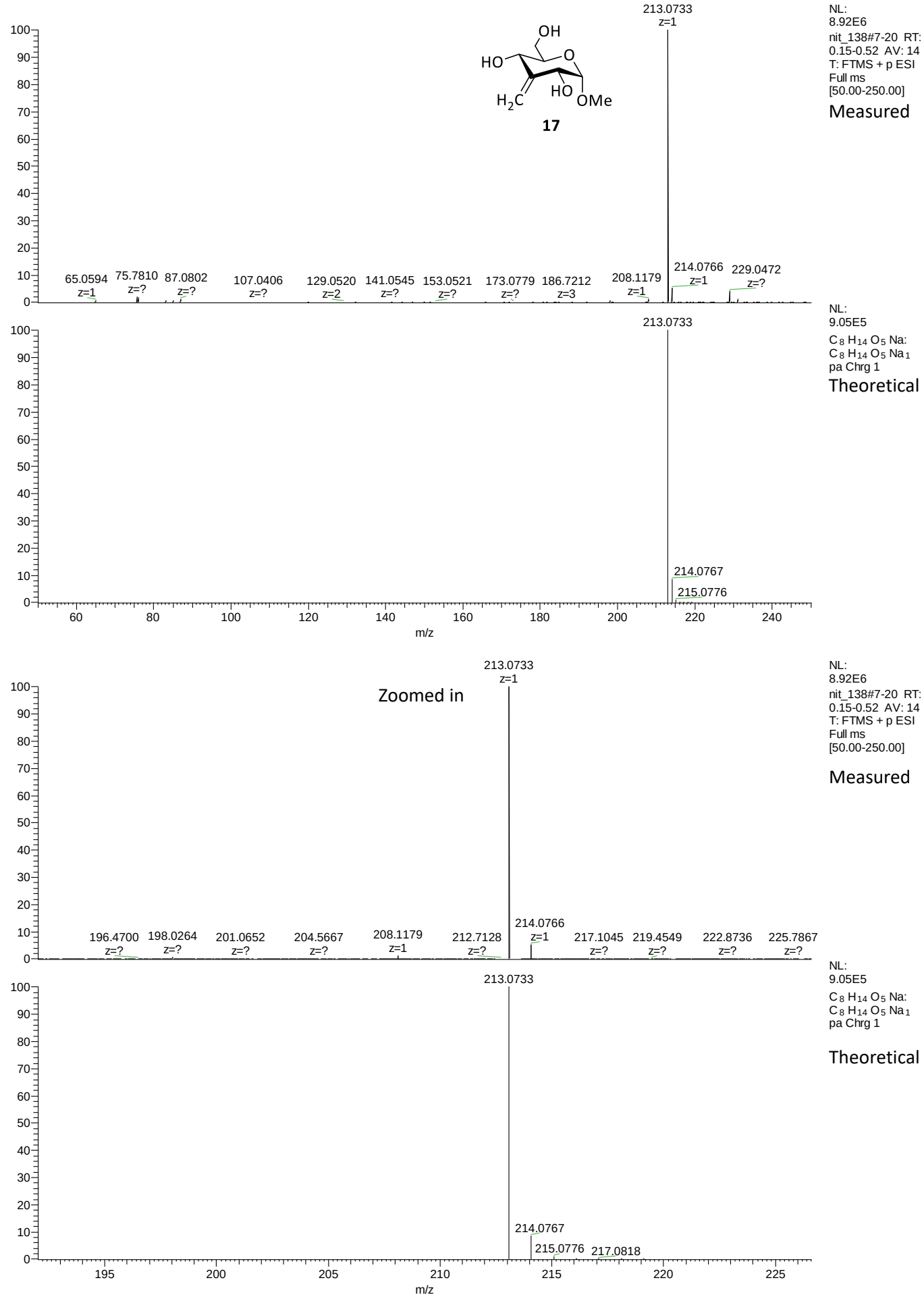

Figure S80 – HRMS of methyl 3-deoxy-3-*C*-methylene-α-D-*ribo*-hexopyranoside (**17**)

Methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (18)

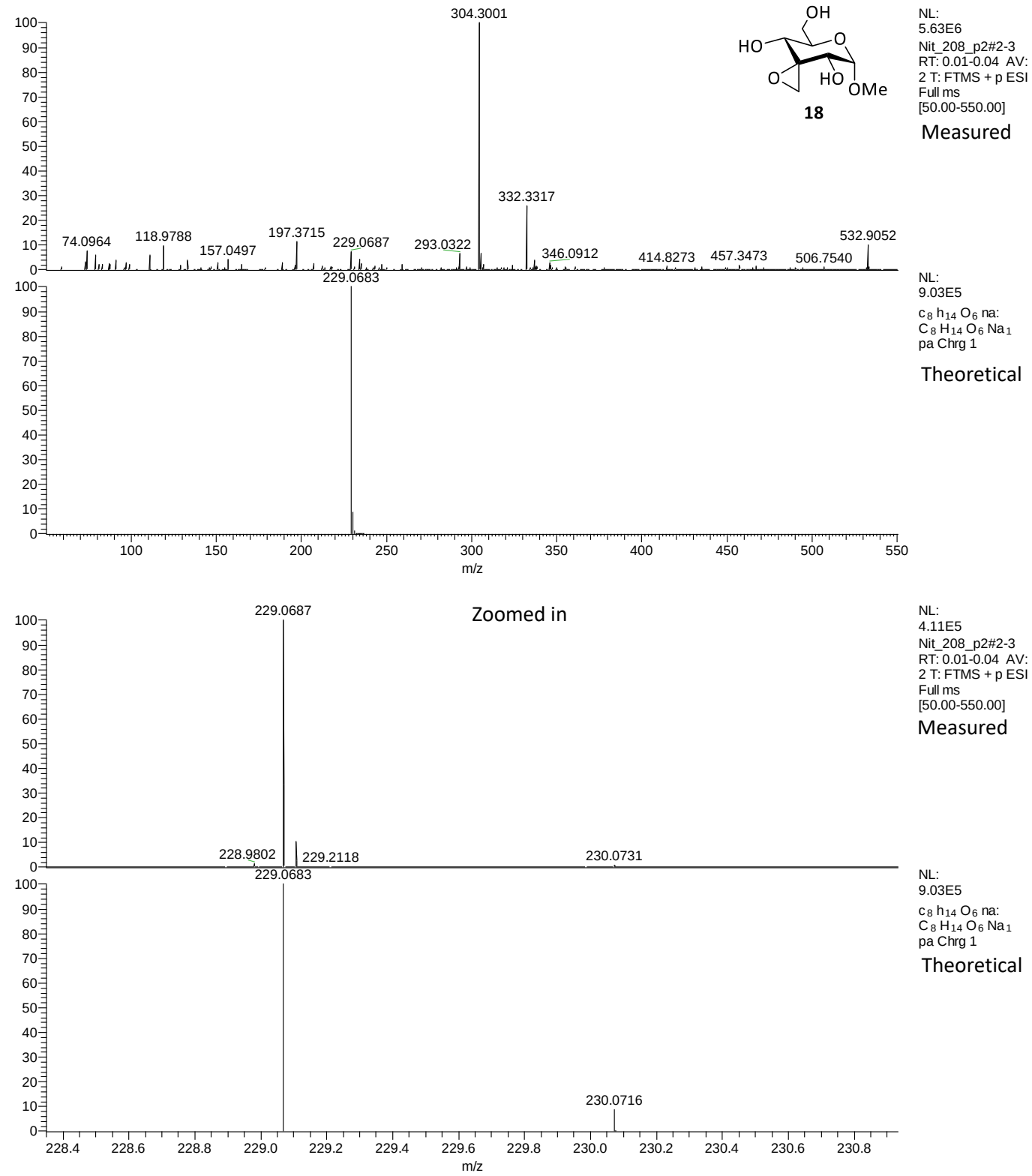

Figure S81 – HRMS of methyl 3,3'-anhydro-3-*C*-(hydroxymethyl)-α-D-glucopyranoside (**18**)

Methyl 3-*C*-methyl-α-D-glucopyranoside (19)

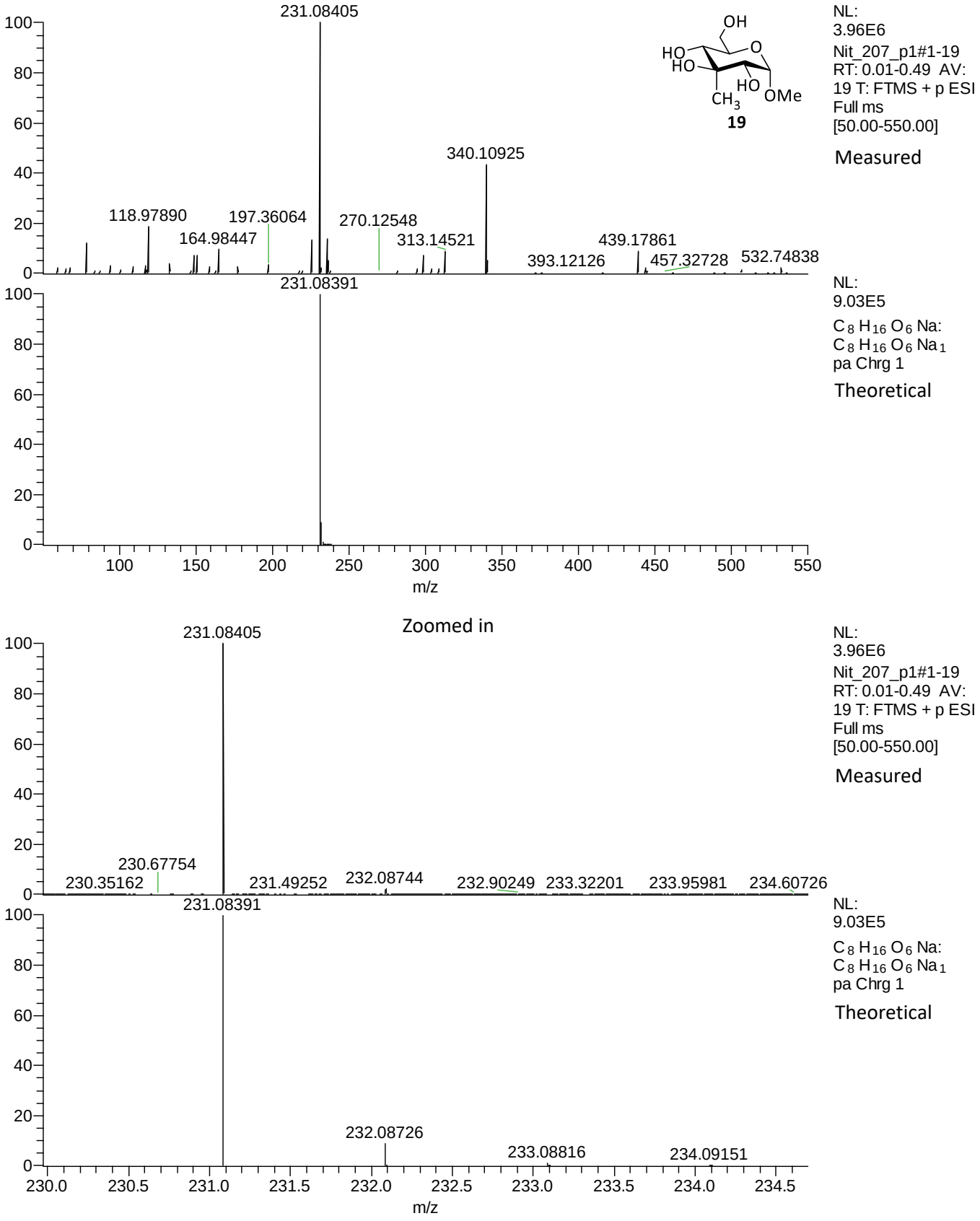

Figure S82 – HRMS of methyl 3-*C*-methyl-α-D-glucopyranoside (**19**)

1,6-anhydro-3-*C*-methyl-β-D-mannopyranose (22)

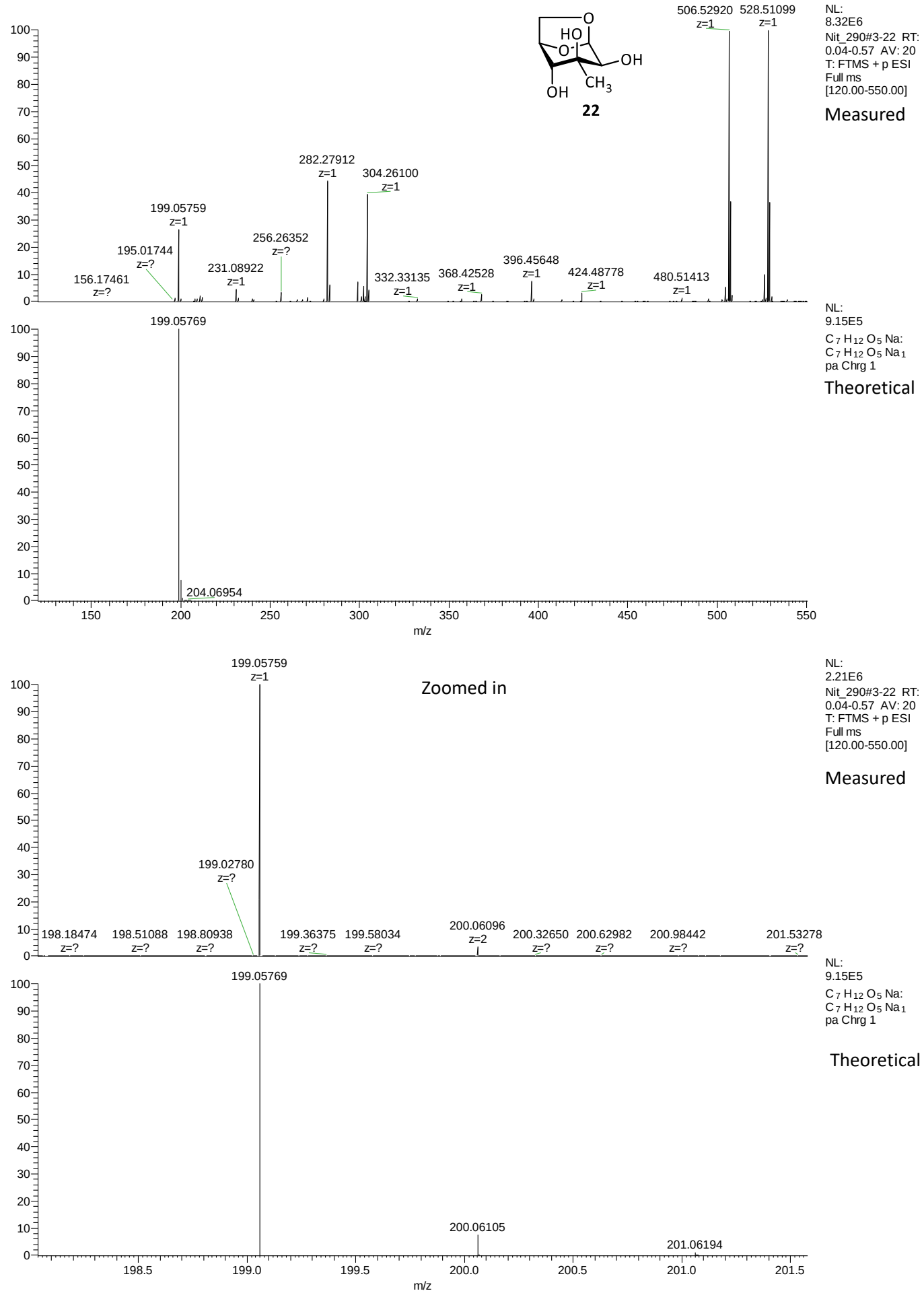

Figure S83 – HRMS of 1,6-anhydro-3-*C*-methyl-β-D-mannopyranose (**22**)

Methyl 3-*C*-methyl-α-D-mannopyranoside (23)

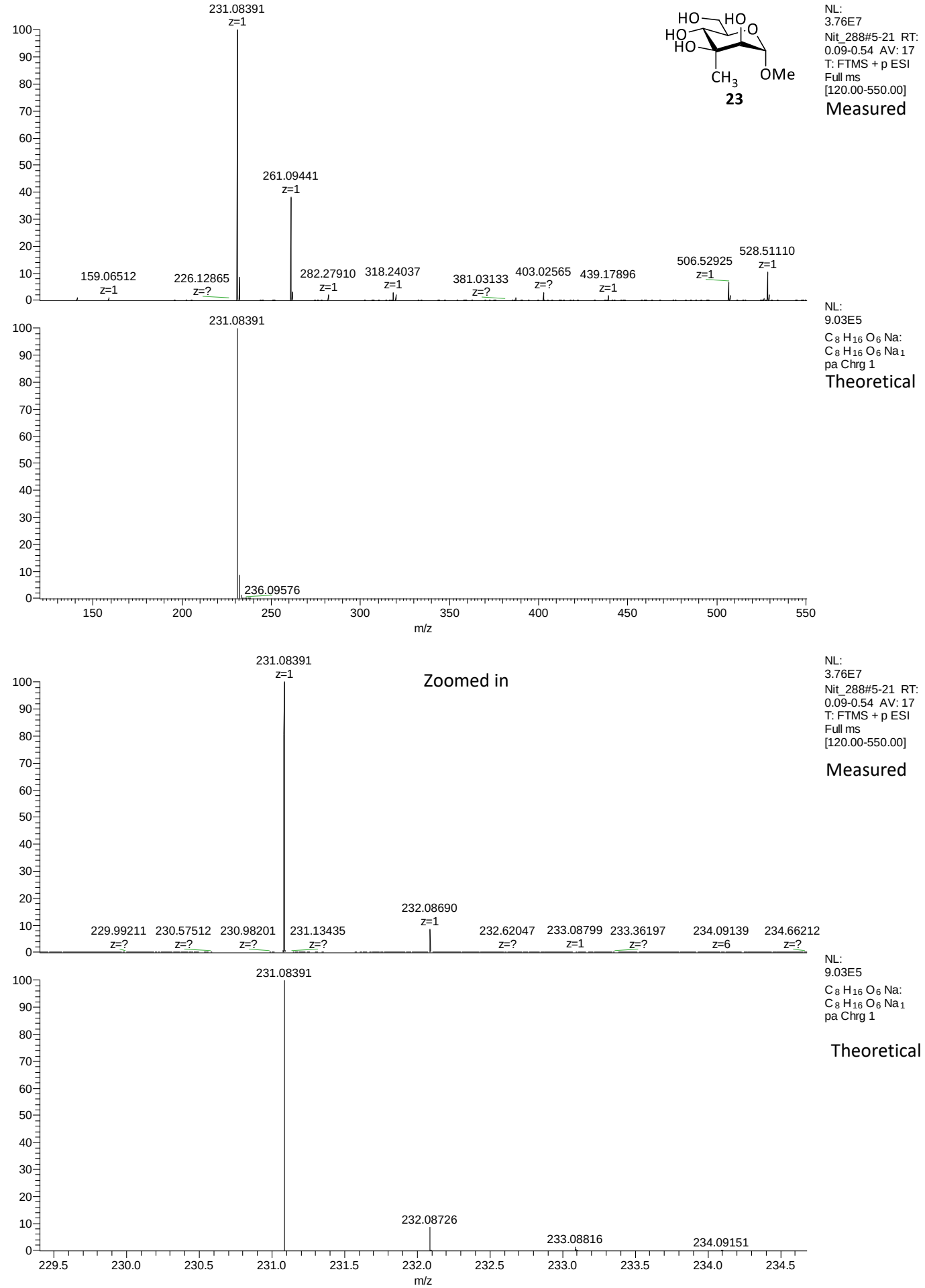

Figure S84 – HRMS of methyl 3-*C*-methyl-α-D-mannopyranoside (**23**)

***O*-(6-deoxy-1-*O*,3-*C*-dimethyl-α-D-mannopyranos-6-yl) *O*-phenyl carbonothioate (24)**

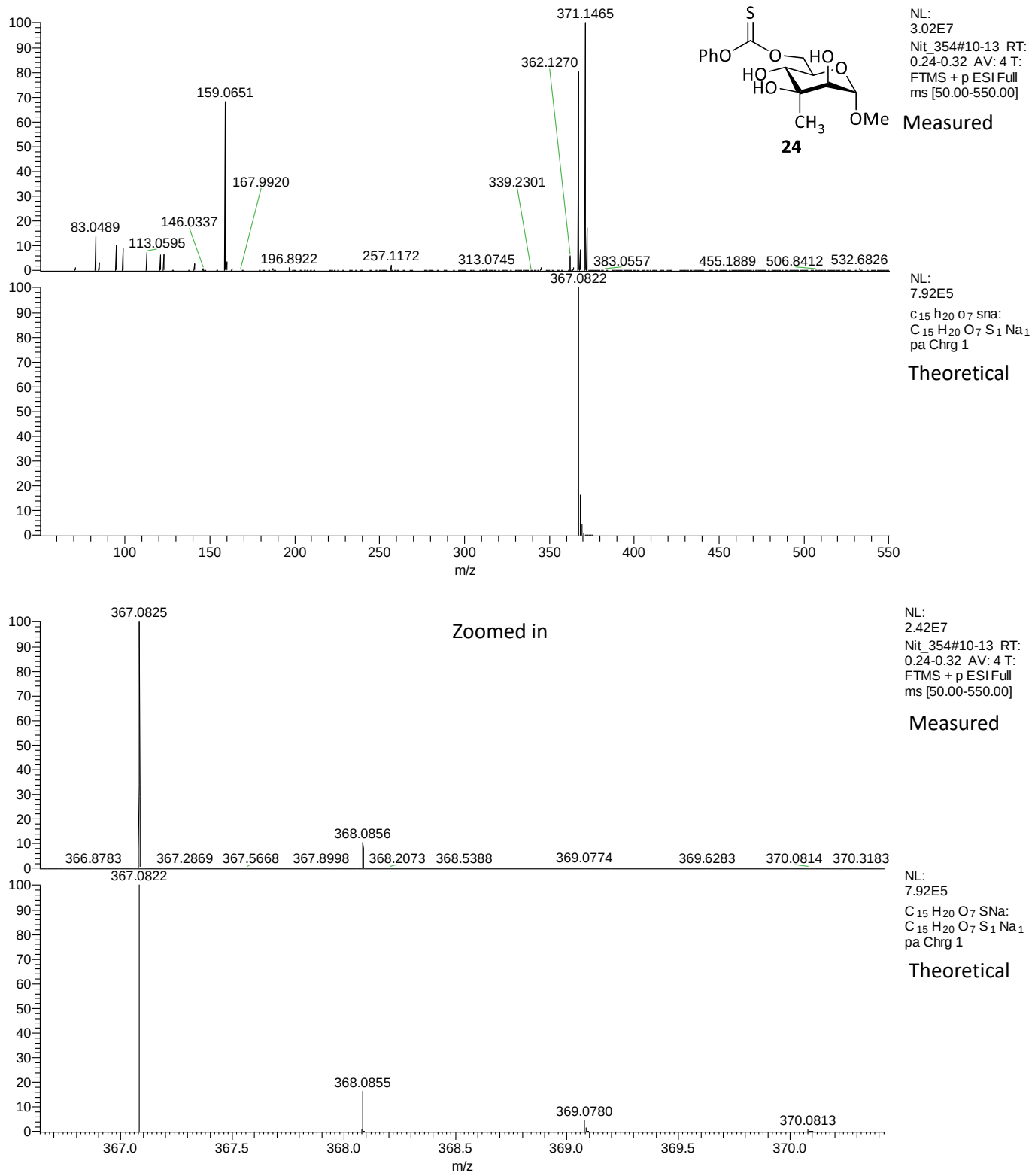

Figure S85 – HRMS of *O*-(6-deoxy-1-*O*,3-*C*-dimethyl-α-D-mannopyranos-6-yl) *O*-phenyl carbonothioate (**24**)

Methyl α-D-evaloside (methyl 6-deoxy-3-*C*-methyl-α-D-mannopyranoside) (25)

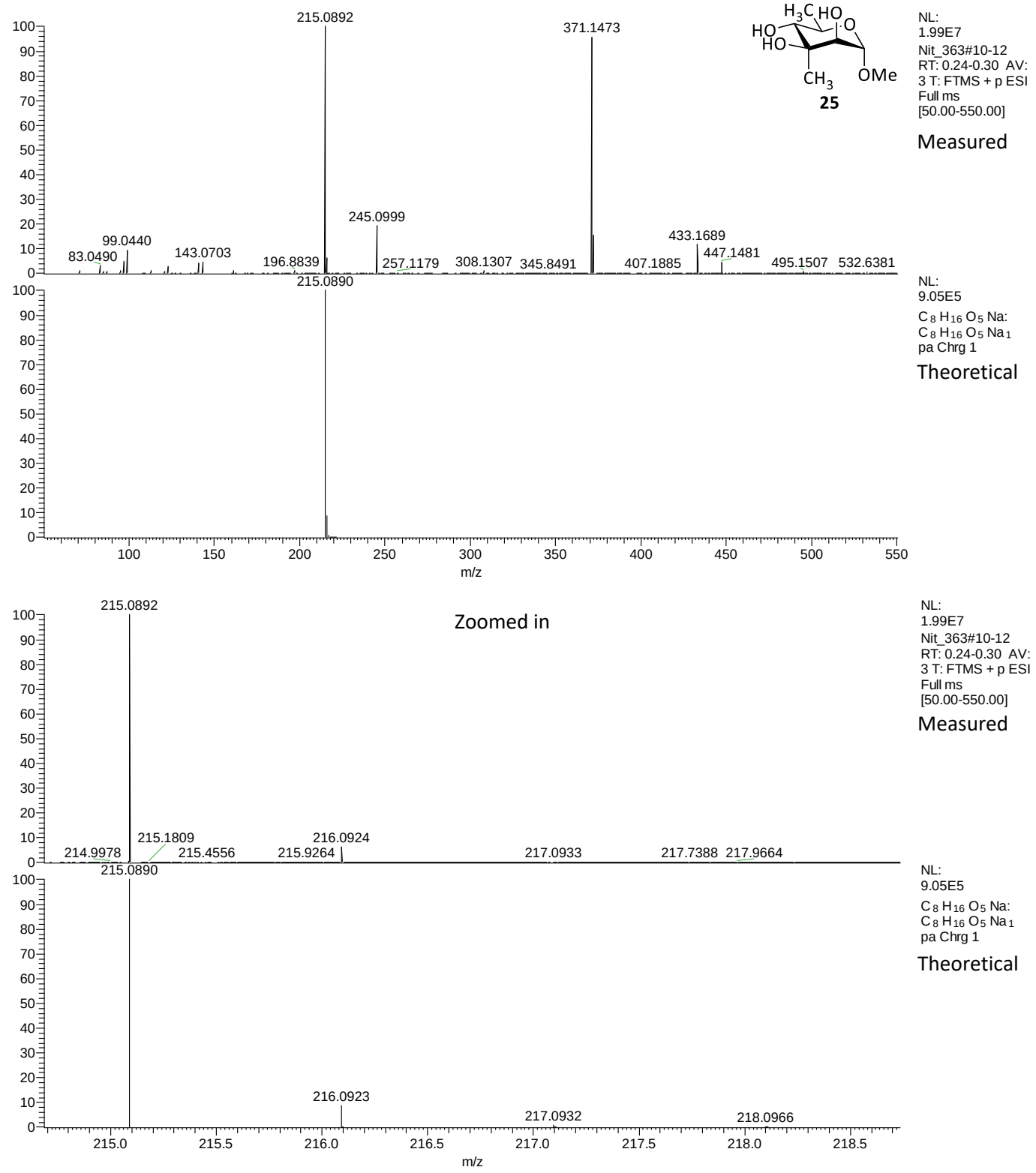

Figure S86 – HRSM of methyl α-D-evaloside (**25**)

Tricosa-*O*-acetyl-D-maltoheptaose (26)

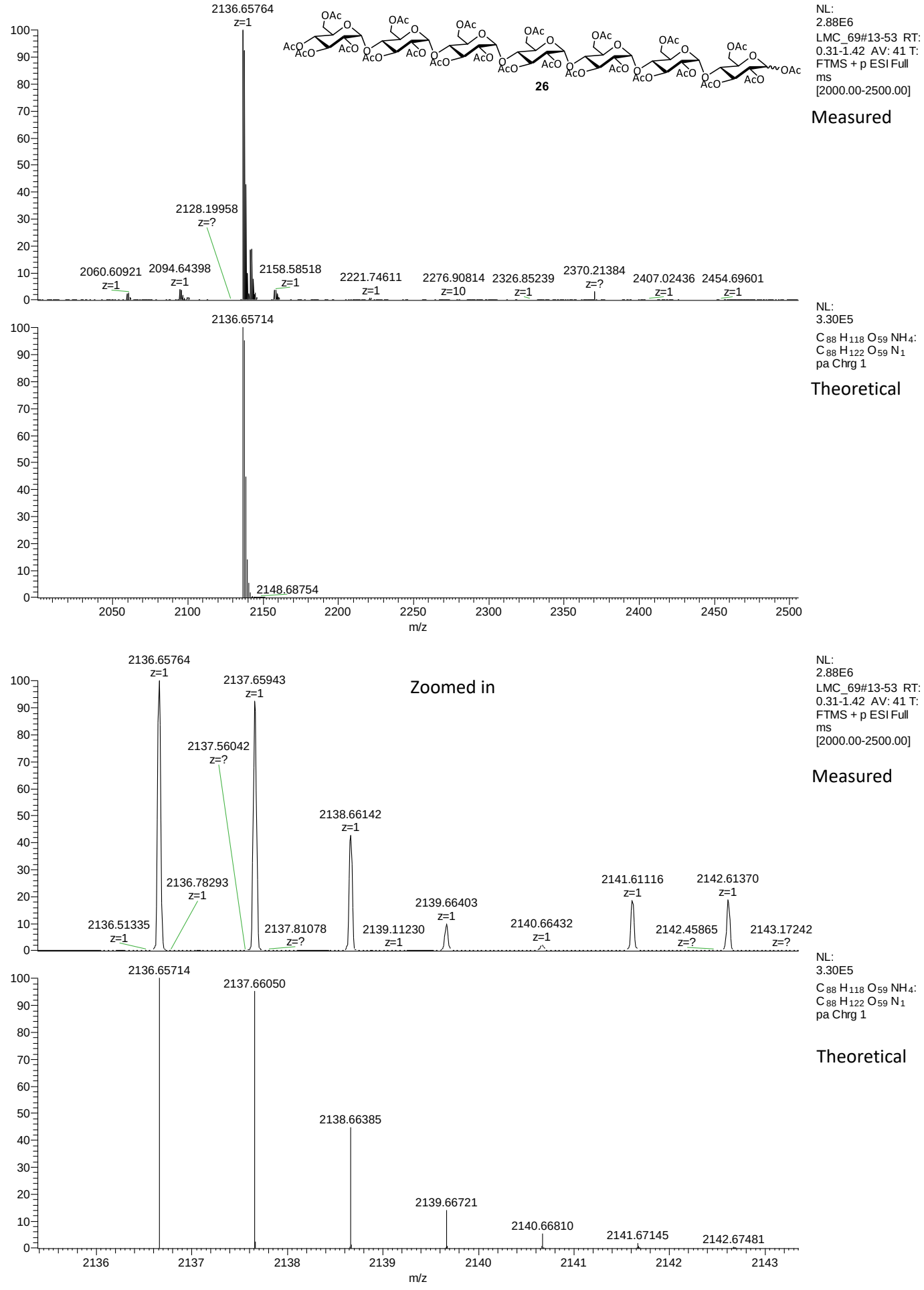

Figure S87 – HRMS of tricosa-*O*-acetyl-D-maltoheptaose (**26**)

Methyl 3-*C*-cyclopentadienyl-α-D-allopyranoside (28)

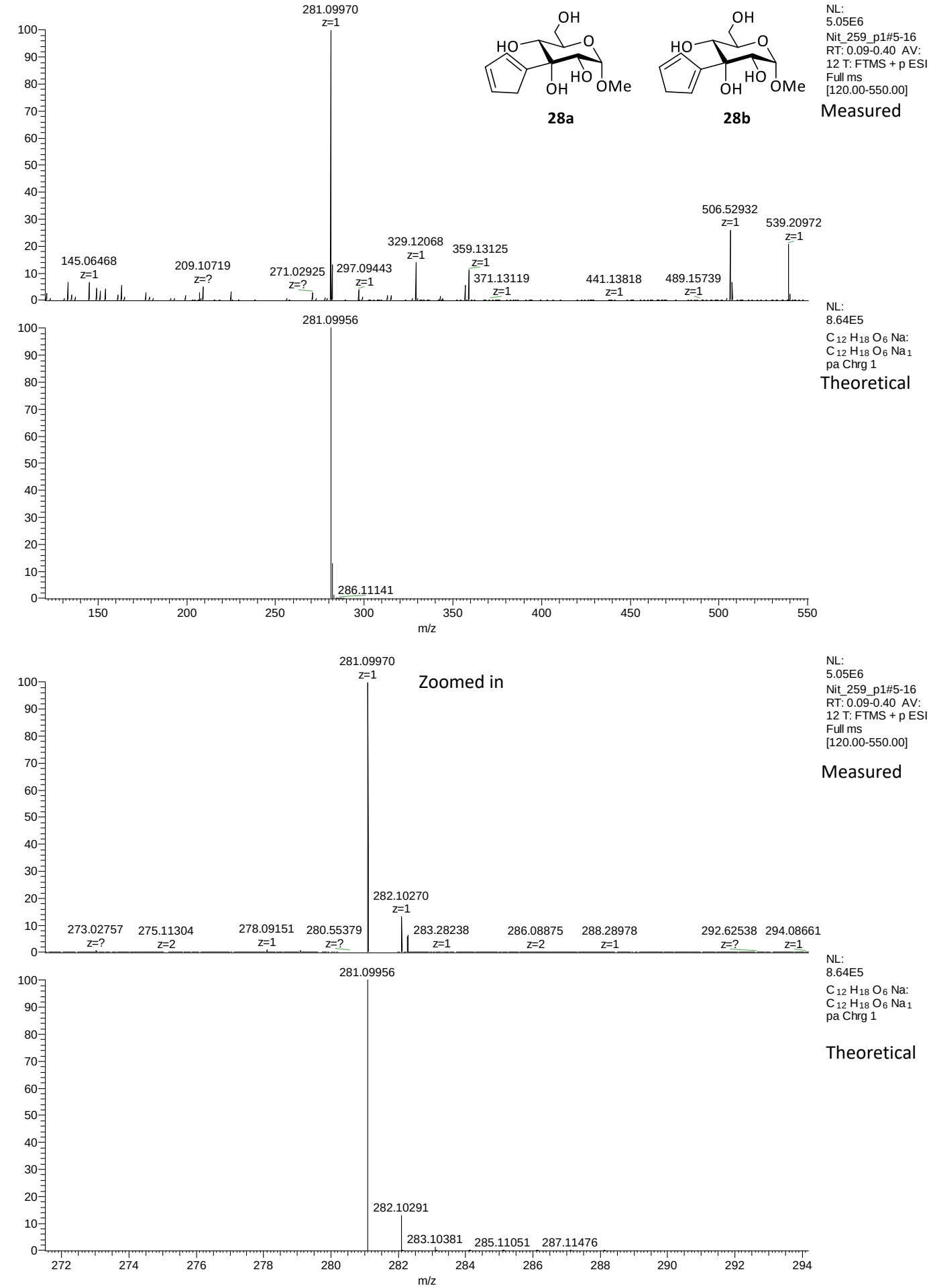

Figure S88 – HRMS of methyl 3-*C*-cyclopentadienyl-α-D-allopyranoside (**28**)