SI Appendix

Synthesis of asymmetrical multi-antennary human milk oligosaccharides

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1. Chemical Synthesis

1.a. Materials and Methods

^{1}H spectra were recorded on a 500 MHz Varian Inova or 600 MHz Agilent DD2. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. NMR data is represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet and / or multiple resonances, br. = broad signal), *J* coupling, integration and peak identity. NMR signals were assigned on the basis of ^{1}H NMR, gCOSY, gHSQC, and zTOCSY, experiments. Mass spectra were collected using an Applied Biosystems SCIEX MALDI TOF / TOF 5800 using 2,5-dihydroxybenzoic acid (DHB) as a matrix. Preparatory HPLC was performed using an Agilent Technologies 1200 Series equipped with a diode array multiple wavelength detector SL for compound visualization. An Eclipse XBD-C18 (21.2 x 250 mm, 7 μm) column was used for separation. Normal phase column chromatography was performed on silica gel G60 (Silicycle, 60 - 2000 μm, 60Å). Thin layer chromatography (TLC) was conducted on Silica gel 60 F_{254} (EMD Chemicals, Inc.) with detection by UV-absorption (254 nm) where applicable. Visualization of TLC plates was accomplished by spraying with 10% sulfuric acid in ethanol, Hanessian's Stain or Ninhydrin, followed by charring at ~150 °C. Reagents were purchased from commercial sources and used without further purification.

1.b. Anomeric Linker Synthesis

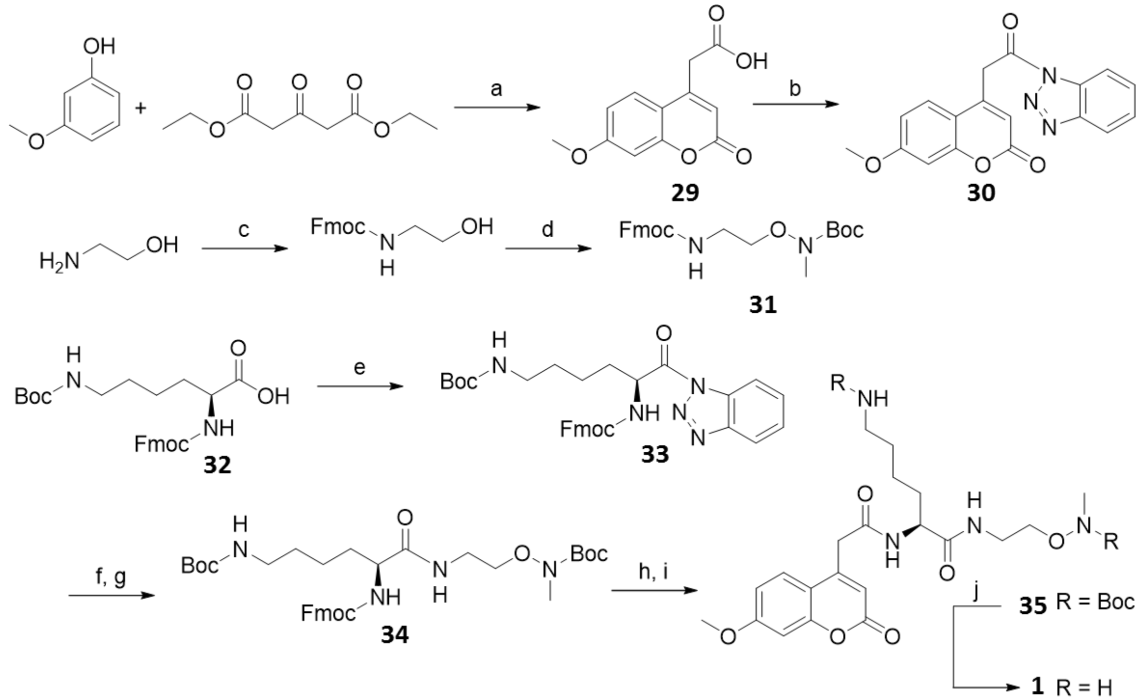
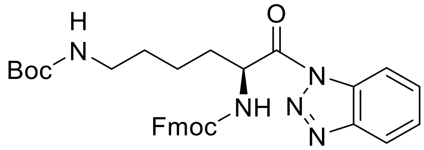
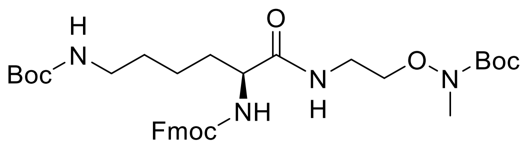


Figure S1: Multifunctional Linker Synthesis.
a) H_2SO_4/H_2O (7:3 v/v); b) $SOCl_2$, benzotriazole; c) Fmoc-Cl, Py; d) DIAD, PPh_3, N-methyl-N-boc-hydroxylamine; e) $SOCl_2$, benzotriazole; f) Piperidine/DMF, **31** g) Py, **33**; h) Piperidine/DMF, **34**; i) Py, **30**; j) 4M HCl in Dioxane.



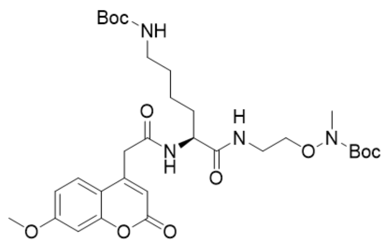
N^{α}-Fmoc-N^{ε}-Boc-L-lysine-(1Hbenzo[1,2,3]triazol-1-yl) (**33)**

Thionyl chloride (0.58 mL, 8 mmol) and benzotriazole (2.54 g, 21.4 mmol) were dissolved in DCM (100 mL). The solution was cooled in an ice bath (0 °C) followed by addition of **32** (2.5 g, 5.85 mmol). Within minutes benzotriazole HCl was formed as a white precipitant. The solution was vigorously stirred for 2 h, after which the solvent was evaporated to yield a light yellow solid that was recrystallized from EtOAc and hexane to yield a white amorphous solid (3.07 g, 92%). ^{1}H (500 MHz, $CDCl_3$) δ ppm: 8.27 (d, *J* = 8.6 Hz, 1H, CH Ar), 8.15 (d, *J* = 8.3 Hz, 1H, CH Ar), 7.82 - 7.47 (m, 6H, Ar), 7.47 - 7.27 (m, 4H, Ar), 5.80 (br. s, 1H, CH(a)), 4.43 (p, 2H, CH_2 Fmoc), 4.25 (t, *J* = 7.0 Hz, 1H, CH Fmoc), 3.12 (br. s, 1H, CH_2(e)), 2.13 (br. m, 1H, CH_2(b)), 2.00 (br. s, 1H, CH_2'(e)), 1.68 - 1.37 (m, 13H, CH_2(d), CH_2(c), 3 x CH_3 boc). ^{13}C NMR-HSQC (125 MHz, $CDCl_3$) δ ppm: 130.96, 127.88, 127.29, 126.77, 125.34, 125.33, 120.58, 120.15, 114.72, 67.42, 54.79, 47.28, 39.87, 32.47, 29.73, 28.51, 22.67. MALDI-MS *m/z* calcd for $C_{32}H_{35}N_5O_5Na$ $(M + Na)^+$ = 592.2536, found 592.2409.



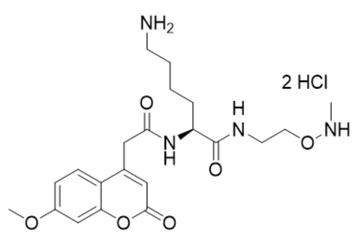
N^{α}-Fmoc-N^{ε}-Boc-L-lysine-(N-**methyl*****(2-(N-Boc-aminooxy)ethyl) (*****34)**

Previously described (1) compound **31** (10 g, 2.4 mmol) was dissolved in a 20% piperidine / DMF solution to remove the Fmoc protecting group. When TLC analysis showed completion of the reaction, the mixture was reduced *in vacuo* and the residue loaded onto a silica gel column which was eluted with 5% ethyl acetate / hexane to remove the 9-methylidene-9H-fluorene by-product. The deprotected amine was eluted with 100% acetone, and fractions containing the compound were concentrated under reduced pressure. The residue was redissolved in DCM (200 mL) and pyridine (3.9 mL, 4.8 mmol). To this mixture, compound **33** (13.67 g, 2.4 mmol) dissolved in DCM (40 mL) was added dropwise over 30 min. The reaction mixture was stirred for 2 h, after which the solvent was removed under reduced pressure. The residue was redissolved in EtOAc (500 mL), washed with saturated ammonium chloride (3 x 100 mL) and the organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (eluent: 40 → 60% EtOAc / Hexane) to yield **34** as a white solid (7.64 g, 49% over two steps). ^{1}H (500 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* = 7.5 Hz, 2H, CH Fmoc), 7.59 (m, 2H, CH Fmoc), 7.37 (dd, *J* = 7.5 Hz, 2H,CH Fmoc), 7.29 (dd, *J* = 7.5 Hz, 2H, CH Fmoc), 4.35 (m, 2H, CH_2 Fmoc), 4.24 (m, 1H, NHCHC(O)), 4.20 (m, 1H, CH Fmoc), 3.87 (m, 2H, CH_2O), 3.45 (m, 2H, CH_2N), 3.10 (m, 2H, Boc-NH-CH_2), 3.06 (s, 3H, N-CH_3), 1.87 (dq, *J* = 13.9, 6.2, 5.6 Hz, 1H, NH-CH_aCH_b -CH_2), 1.70 (dq, 13.9, 6.2, 5.6 Hz, 1H, NH-CH_aCH_b -CH_2), 1.51 (m, 2H, CH-CH_2-CH_2), 1.45 (s, 9H, 3 x CH_3), 1.41 (s, 9H, 3 x CH_3), 1.36 (m, 2H, Boc-NH-CH_2-CH_2), ^{13}C NMR-HSQC (125 MHz, $CDCl_3$) δ ppm119.92, 125.13, 127.61, 126.99, 67.00, 54.77, 47.19, 73.00, 37.81, 40.14, 37.01, 32.78, 29.54, 28.31, 28.40, 28.44, 22.46. MALDI-MS *m/z* calcd for $C_{34}H_{48}N_4O_8Na$ $(M+Na)^+$ = 633.3370; found 633.4843.



***N$^{\alpha}$-((7-methoxy-2-oxo-2H-chromen-4-yl)acetamido)-N$^{\varepsilon}$-Boc-L-lysine-(N-methyl(2-(N-Boc-aminooxy)ethyl))* (35)**

Compound **34** (7.64 g, 11.9 mmol) was dissolved in DMF (24 mL) to which piperidine (6 mL, 59.6 mmol) was added for removal of the Fmoc protecting group. The solution was stirred at room temperature for 2 h which resulted in a change of color from light to dark brown. The solvent was removed *in vacuo* and the residue redissolved in a minimal amount of EtOAc : hexane (1 : 4). The solution was loaded onto a small silica column and eluted with several column volumes of EtOAc : hexane (1 : 4) to remove 9-methylidene-9H-fluorene by-product. Deprotected **34** was eluted off the silica column using 100% acetone and the solvent was removed under reduced pressure to give a brown syrup. Previously reported coumarin-benzotriazole (2) **30** (4.39 g, 13.09 mmol) was added to a solution of **34** dissolved in DCM (130 mL) and pyridine (2.9 mL, 35.7 mmol). The reaction vessel was wrapped in aluminum foil and stirred overnight. The mixture was concentrated under reduced pressure and the resulting solid material was recrystallized from EtOAc / hexane to yield **35** as a rust colored solid (7.56 g, 63% over two steps). ^{1}H (500 MHz, $CDCl_3$) δ ppm 7.59 (d, *J* = 8.8 Hz, 1H, CH coumarin), 6.87 (ddd, *J* = 8.8, 2.5, 0.8 Hz, 1H, CH coumarin), 6.84 (d, *J* = 2.5, 1.0 Hz, 1H, CH coumarin), 6.27 (s, 1H, CH coumarin), 4.50 (q, *J* = 7.4 Hz,1H, NH-CH-C(O)), 3.88 (s, 3H, OCH_3), 3.84 (m, 2H, CH_2-O-N), 3.73 (s, 2H, CH_2-C(O)NH, 3.44 (q, *J* = 5.2 Hz, 2H, NH-CH_2), 3.10(s, 3H, N-CH_3), 3.04 (m, 2H, CH_2-CH_2-NH-Boc), 1.88 (dddd, *J* = 14.1, 7.4, 6.4 Hz, 1H, CH-CH_a-CH_b-CH_2), 1.69 (dddd, *J* = 14.1, 7.4, 6.4 Hz, 1H, CH-CH_a-CH_b-CH_2), 1.49 (s, 9H, 3 x CH_3), 1.46 (m, 2H, CH_2-CH_2-NH-Boc), 1.44 (s, 9H, 3 x CH_3), 1.27 (m, 2H, CH-CH_2-CH_2). ^{13}C NMR-HSQC (125 MHz, $CDCl_3$)) δ ppm 125.91, 112.91, 101.14, 113.64, 53.22, 55.81, 72.84, 40.86, 37.72, 37.02, 40.05, 32.39, 28.35, 29.57, 28.53, 22.22. MALDI-MS *m/z* calcd for $C_{31}H_{46}N_4O_{10}Na$ $(M+Na)^+$ = 657.3112; found 657.1883.



***N$^{\alpha}$-((7-methoxy-2-oxo-2H-chromen-4-yl)acetamido)-L-lysine-(N-methyl-(aminooxy)ethyl)) diammonium chloride (*1)**

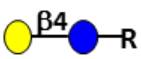
Compound **35** (4.77 g, 7.5 mmol) was dissolved in of 4 M HCl in dioxane (80 mL) and within 1 h a significant amount of solid had precipitated. The light tan solid was filtered, washed with several portions of diethyl ether, and dried in vacuo to yield **1** (3.72 g, 98% yield). ^{1}H (600 MHz, D_2O) δ ppm 7.46 (d, *J* = 8.9 Hz, 1H, CH-coumarin), 6.85 (dd, *J* = 8.9, 2.6, 1H, CH-coumarin), 6.79 (d, *J* = 2.5 Hz, 1H, CH-coumarin), 6.13 (s, 1H, CH-coumarin), 4.12 (dd, *J* 8.9, 5.8 Hz, 1H, NH-CH-C(O)), 4.02 – 3.96 (m, 2H, CH_2-CH_2-O), 3.75 (m, 5H, O-CH_3, NH_2-CH_2), 3.60 (s, 2H, CH_2C(O)), 3.44 – 3.30 (m, 2H, NH-CH_2-CH_2), 2.82 (dq, *J* = 8.4, 5.7, 4.2 Hz, 2H, CH_2-NH_3^+), 2.75 (s, 3H, N-CH_3), 1.74 – 1.59 (m, 2H, CH-CH_a-CH_b-CH_2), 1.57 – 1.49 (m, 2H, CH_2-CH_2-NH_3^+), 1.36 – 1.19 (m, 2H, CH_2- CH_2- CH_2-). ^{13}C NMR-HSQC (150 MHz, D_2O) δ ppm 125.90, 113.05, 100.99, 112.32, 54.09, 72.21, 38.31, 55.88, 67.17, 37.13, 39.13, 34.94, 30.27, 26.09, 21.88. MALDI-MS *m/z* calcd for $C_{21}H_{30}N_4O_6$ $(M+Na)^+$ = 457.2063; found 457.1454.

1.c. Installation of Anomeric Linker

Lactose (2.14 g, 6.25 mmol) and anomeric linker **1** (632 mg, 1.24 mmol) were dissolved in sodium acetate buffer (50 mL, 0.25 M, pH = 4.2) and allowed to mix overnight at 37 °C. The reaction was monitored by reverse phase TLC using an elution system of 40% ACN / H_2O, with 1 drop of acetic acid. When no further linker was detected, the solvent was removed by reduced pressure. The crude product was purified by preparatory HPLC eluting with the following conditions: A = acetonitrile, B = 50 mM ammonium bicarbonate

Time (mins)	%A	%B	Flow Rate (mL / min)
0	0	100	30
20	100	0	30

Fractions containing the product were confirmed by MALDI-MS, pooled, and the solvent was removed using lyophylization to yield a white fluffy powder **3** (423 mg, 42% yield).



3

^{1}H (500 MHz, D_2O): δ (ppm)

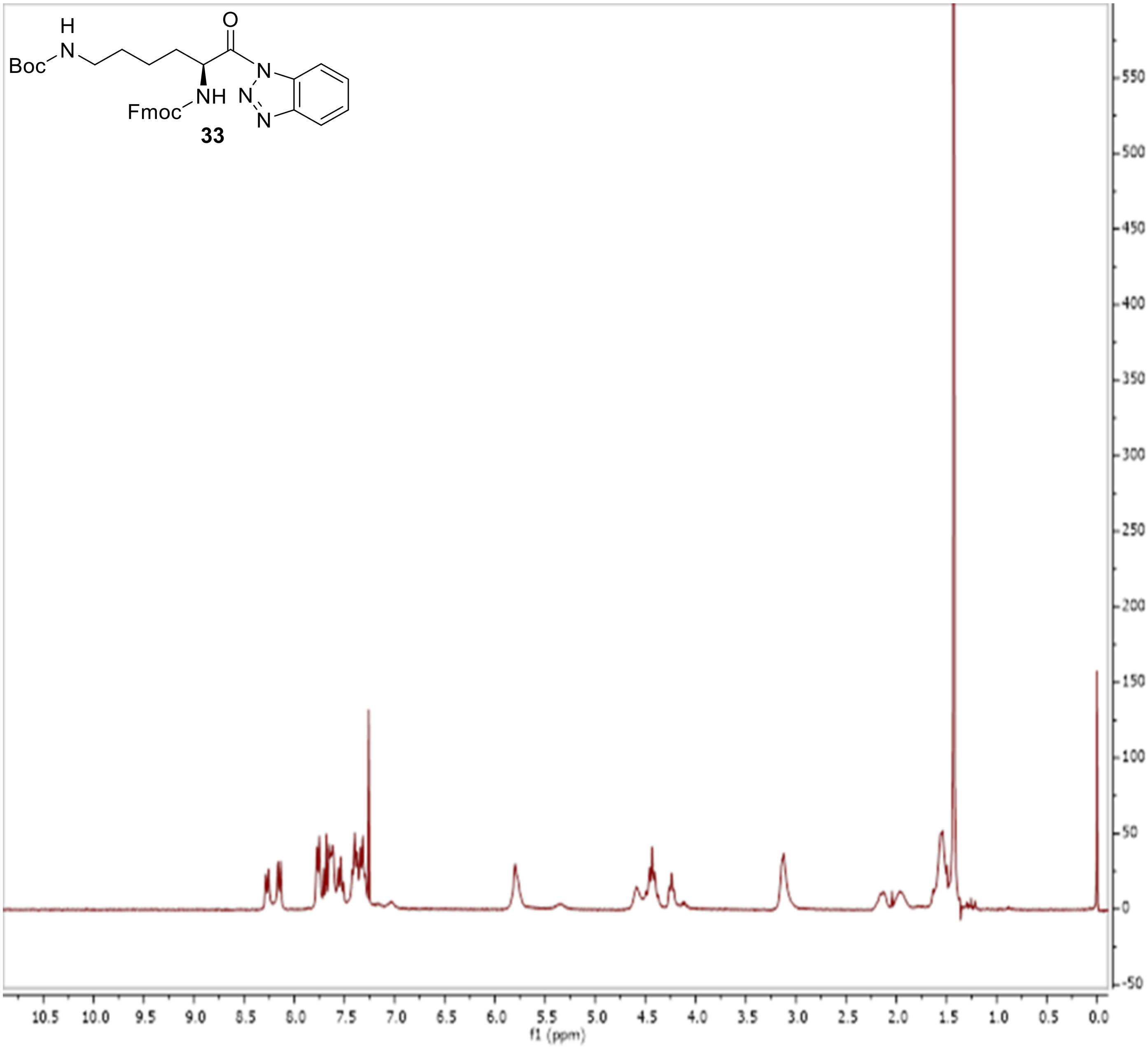
	H1	H2	H3	H4	H5	H6
Glc	4.03 (d, *J* = 9.2 Hz, 1H)	3.39	3.50	3.69	3.28	3.84, 3.69
Gal	4.32 (d, *J* = 7.8 Hz, 1H)	3.41	3.52	3.79	3.54	3.63

Linker

$N\text{-}CH_3$	2.57
$N\text{-}O\text{-}CH_2$	3.70
$CH_2\text{-}NH$	3.28
C(O)-CH-NH	4.18 (dd, *J* = 8.5, 6.0 Hz, 1H)
A	1.71 1.65
B	1.26
C	1.48
D	2.71
E	3.81
F	7.54
G	6.92
H	6.92
I	6.21
$O\text{-}CH_3$	3.80

^{13}C from HSQC (125 MHz, D_2O): δ (ppm) 22.05, 26.83, 30.36, 37.34, 38.18, 38.18, 39.01, 39.14, 53.82, 55.00, 55.14, 55.82, 56.63, 60.05, 60.06, 60.89, 68.42, 69.42, 70.65, 70.81, 72.40, 75.25, 75.52, 76.20, 78.04, 92.90, 101.09, 102.78, 112.48, 113.09, 125.99.

MALDI TOF-MS *m/z* calcd for $C_{33}H_{50}N_4O_{16}Na$ $(M + Na)^+$ 781.3120, found 781.4410.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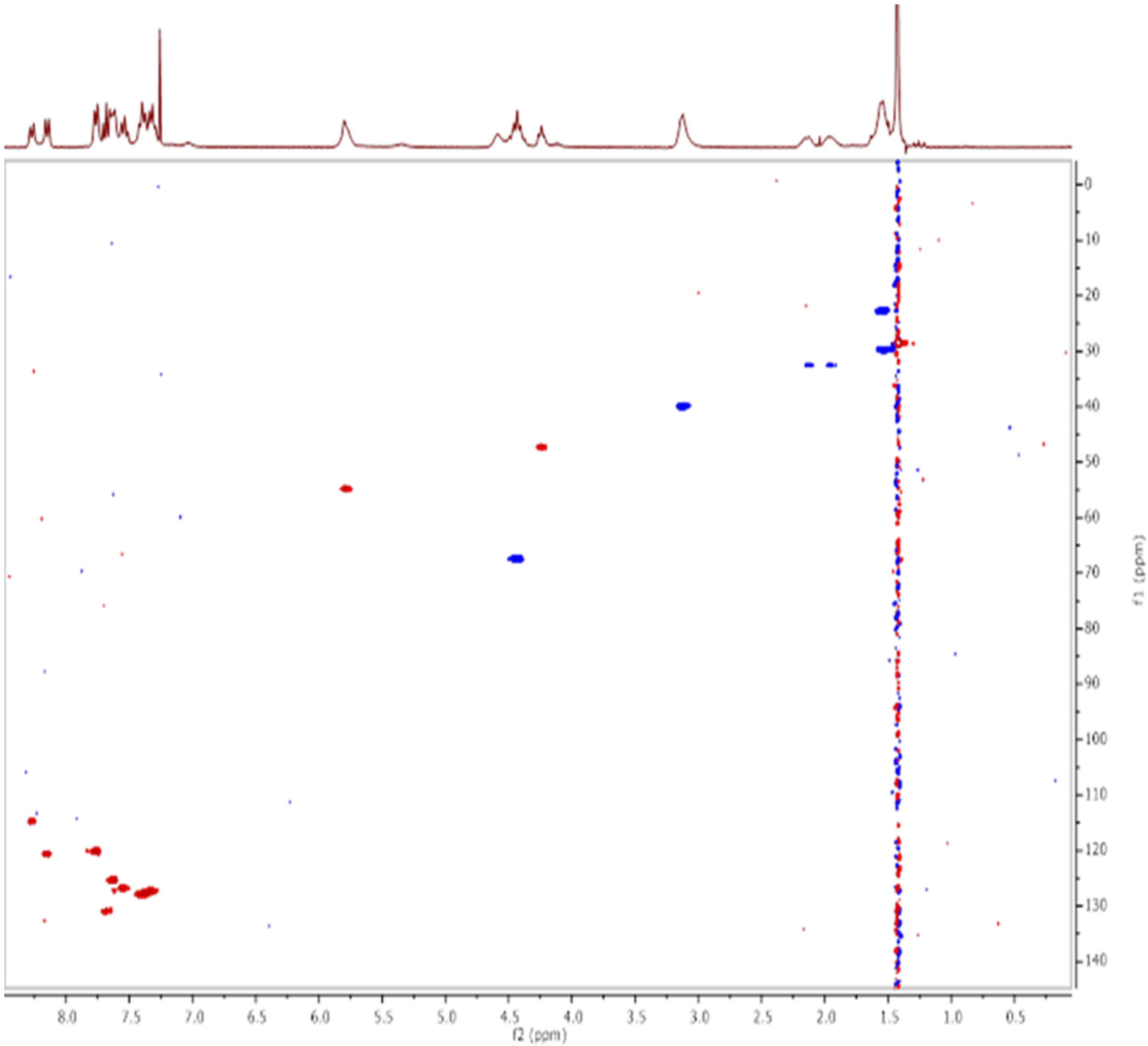
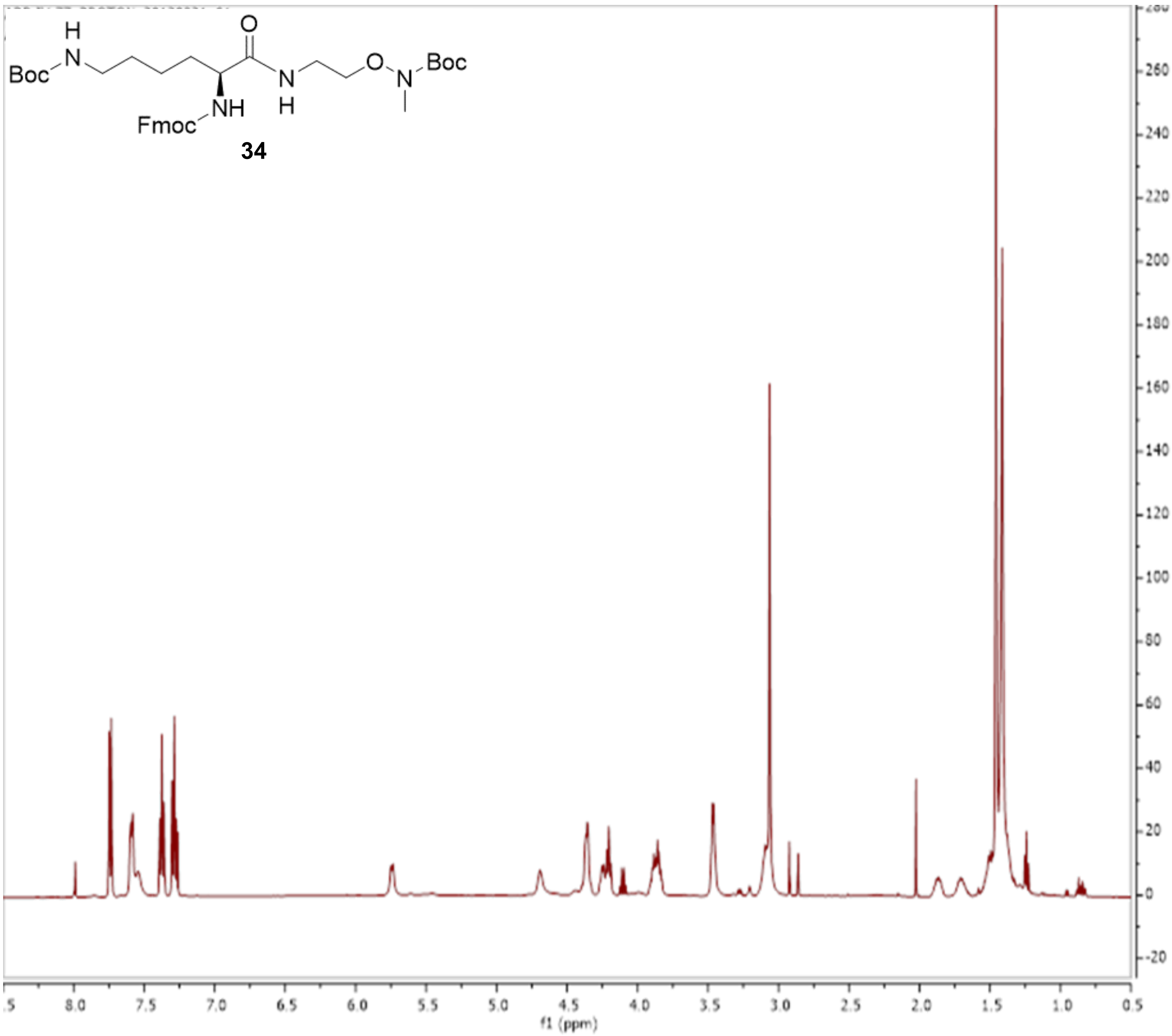
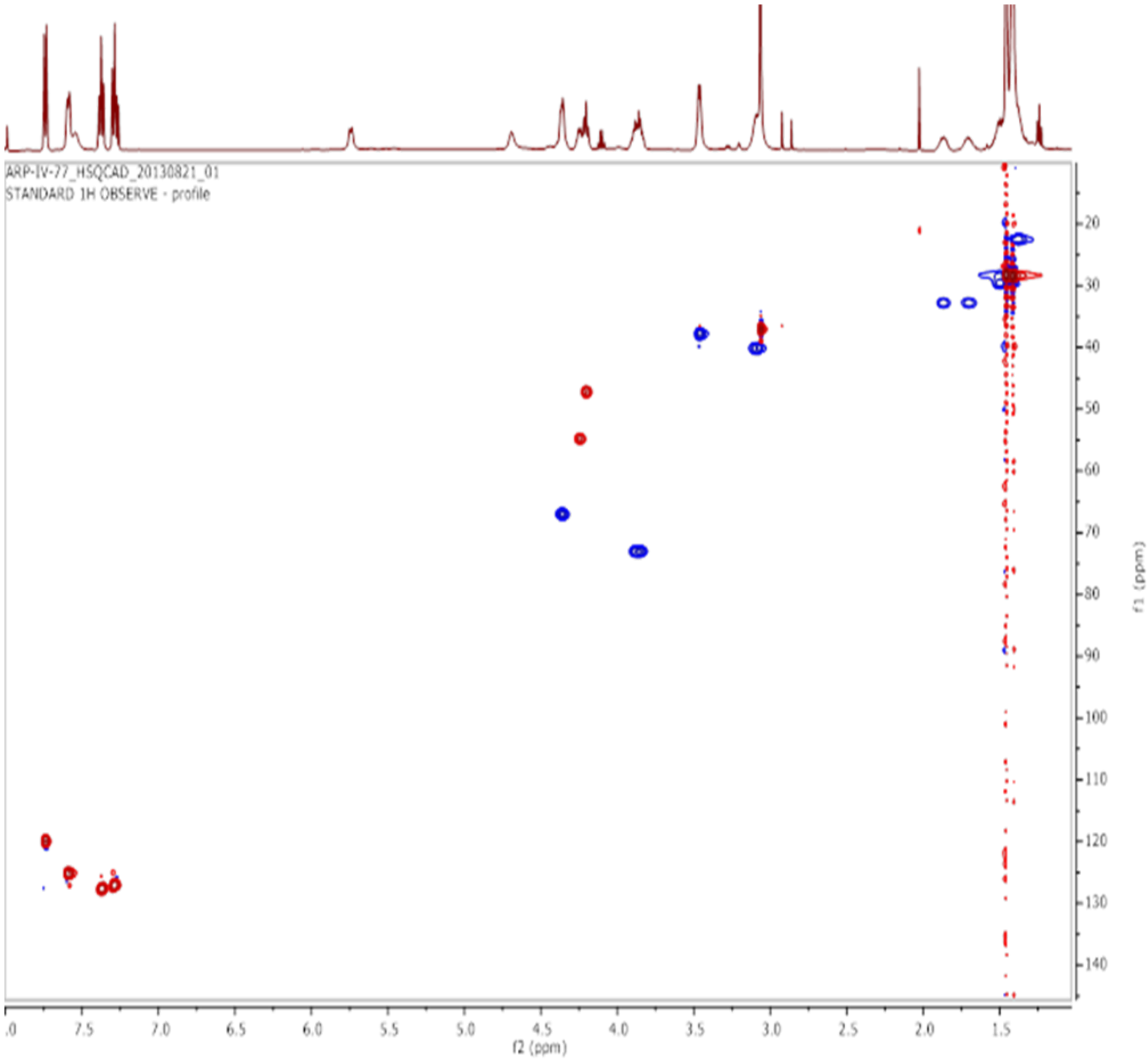
O
Boc
N
N
NH
N
Fmoc
N
N
33
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



f1 (ppm)
f2 (ppm)


Boc
Fmoc
Boc
34
f1 (ppm)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STANDARD 1H OBSERVE - profile
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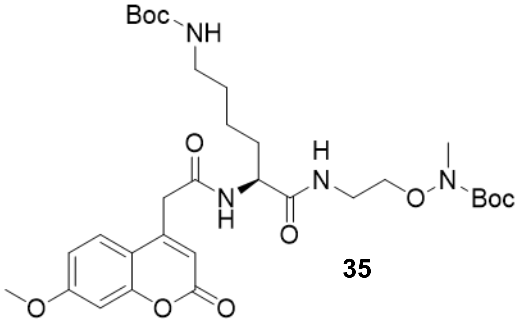
f2 (ppm)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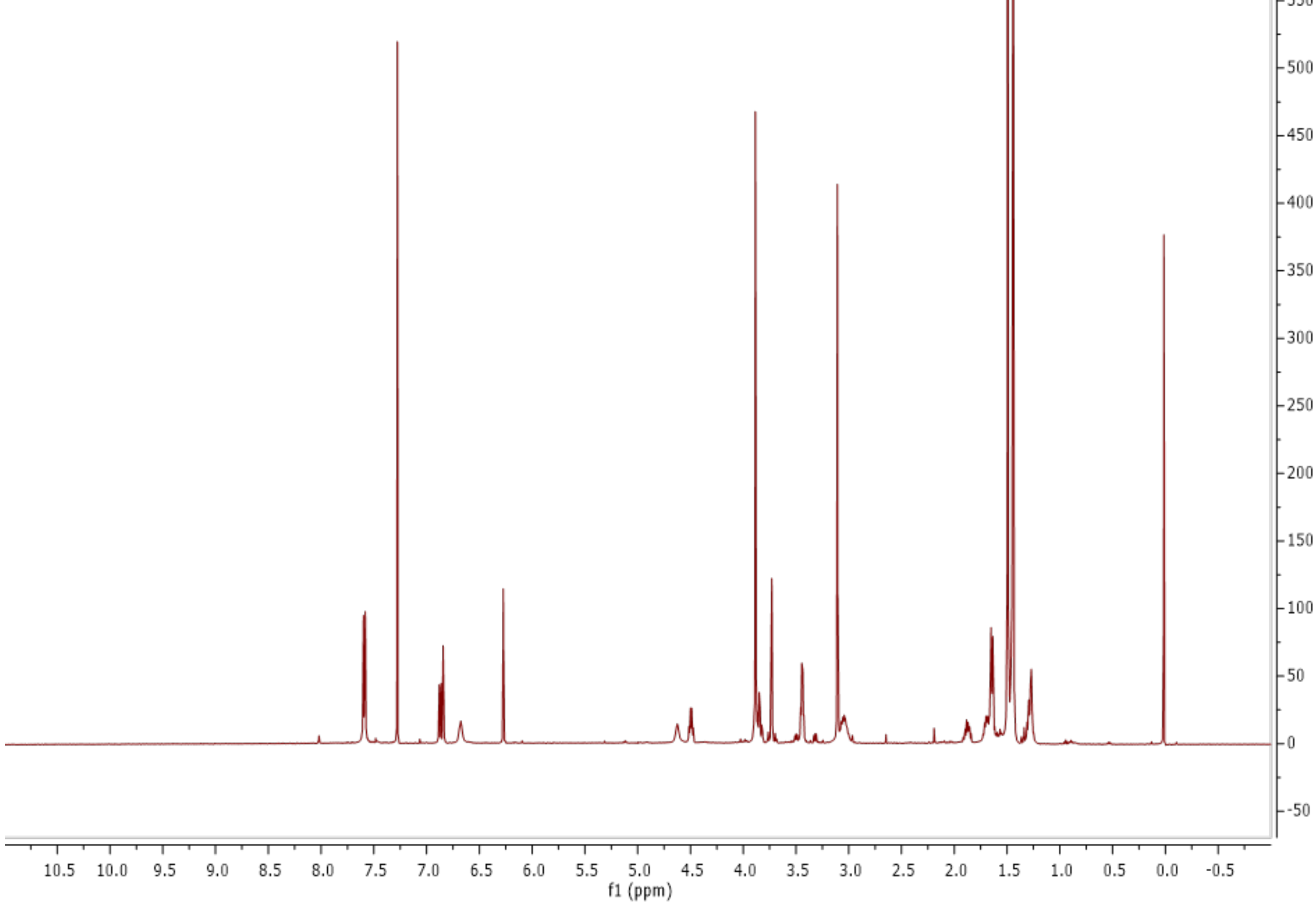
O

35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150
100
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0
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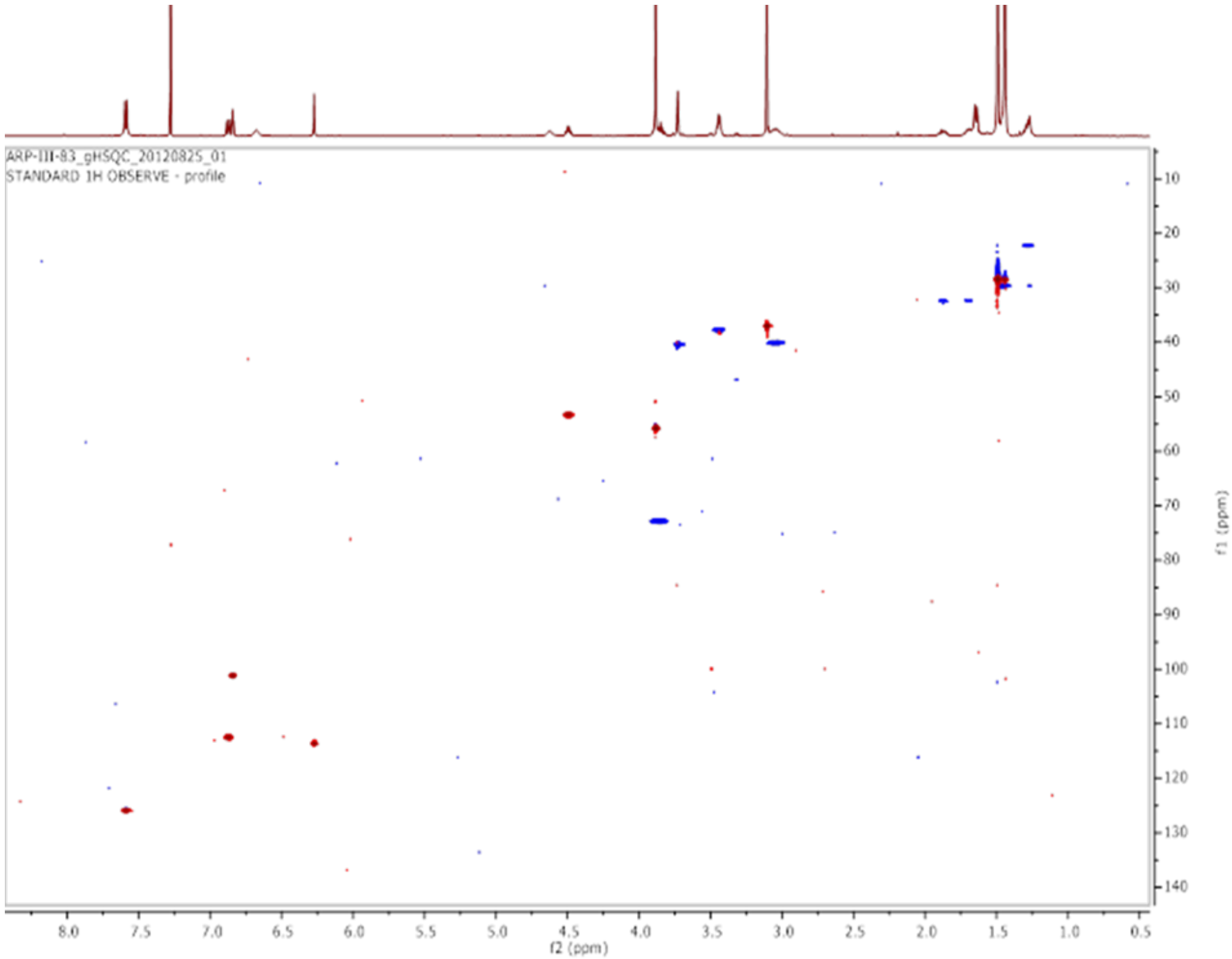
f1 (ppm)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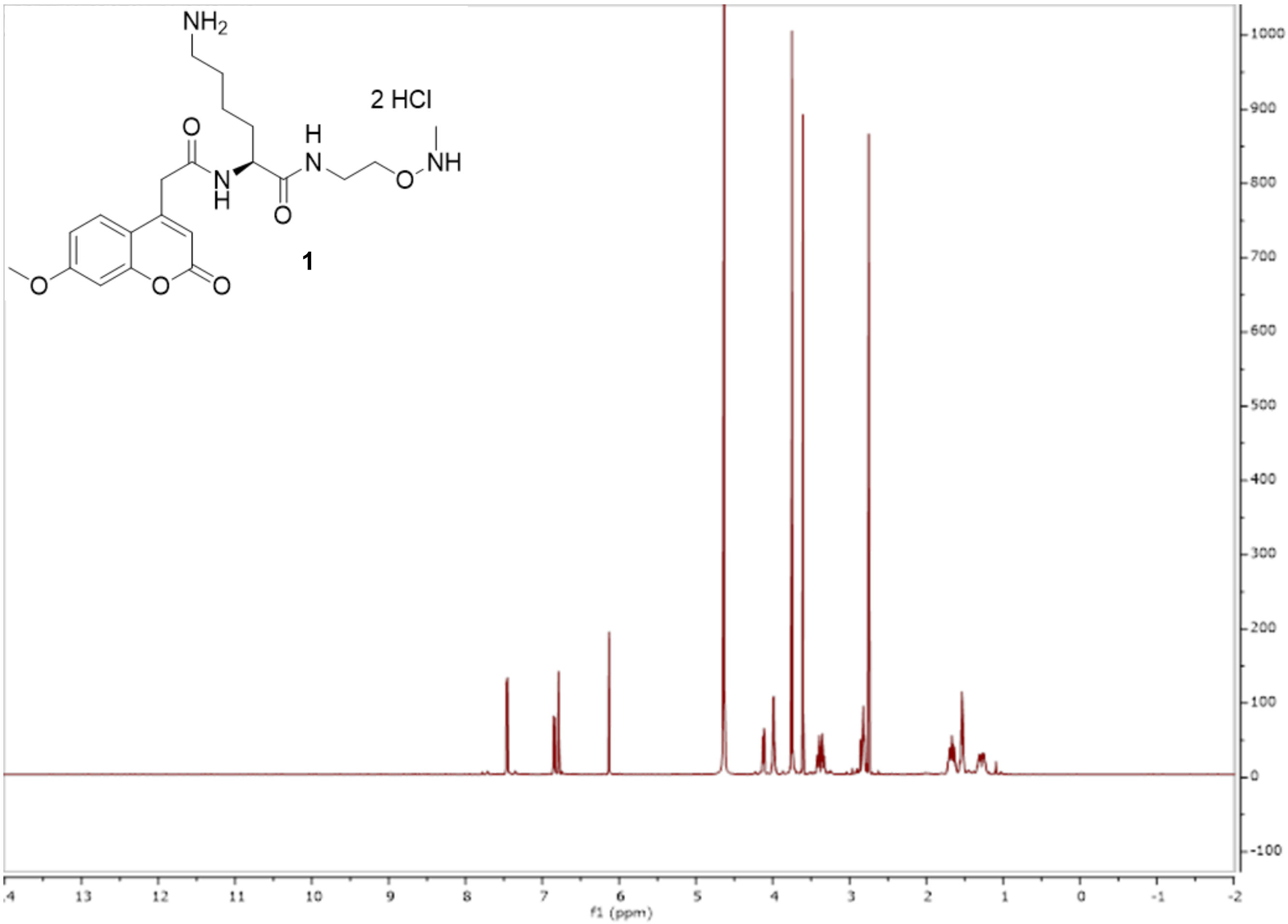
f2 (ppm)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N
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900
800
700
600
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400
300
200
100
0
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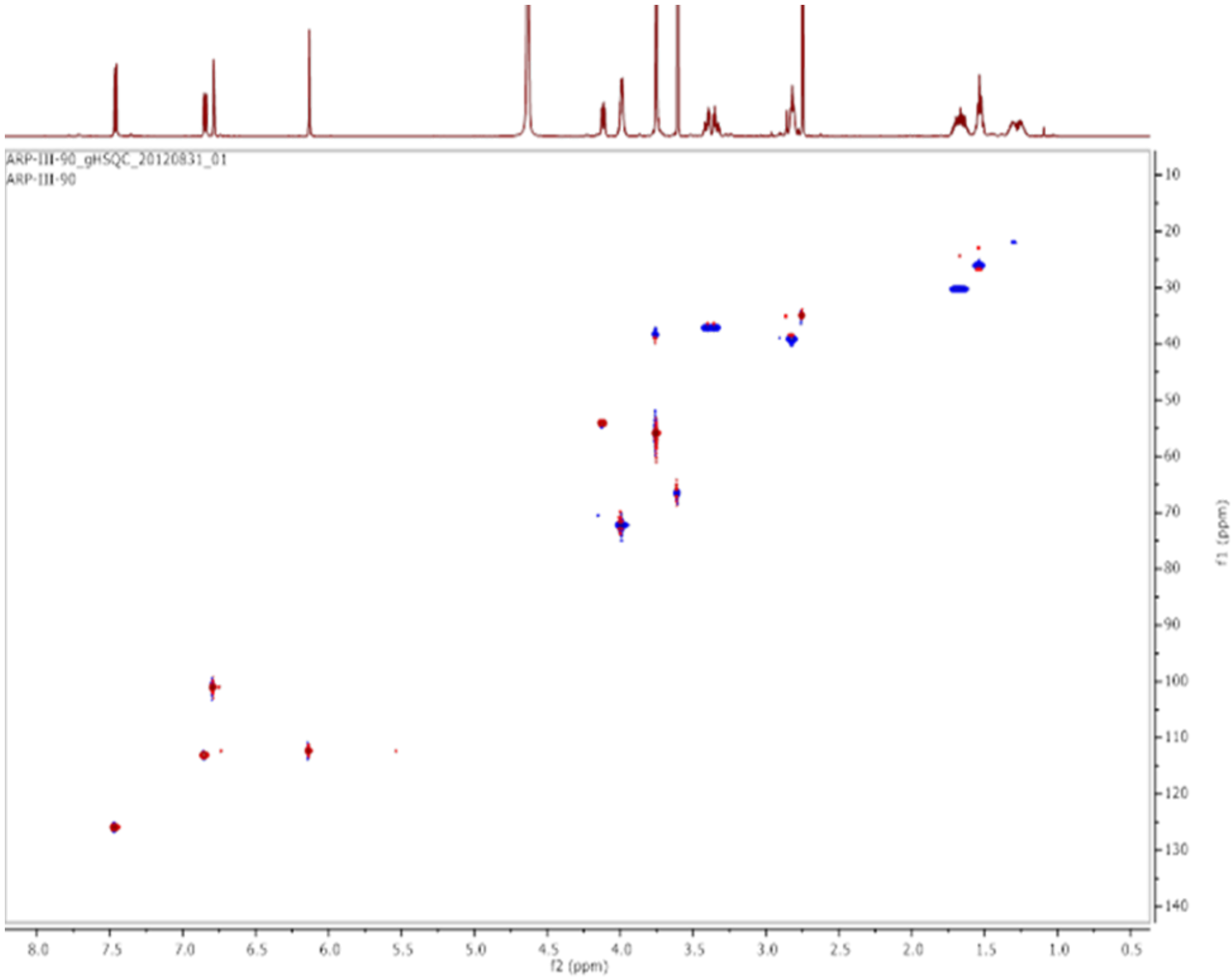
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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f2 (ppm)
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
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30
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70
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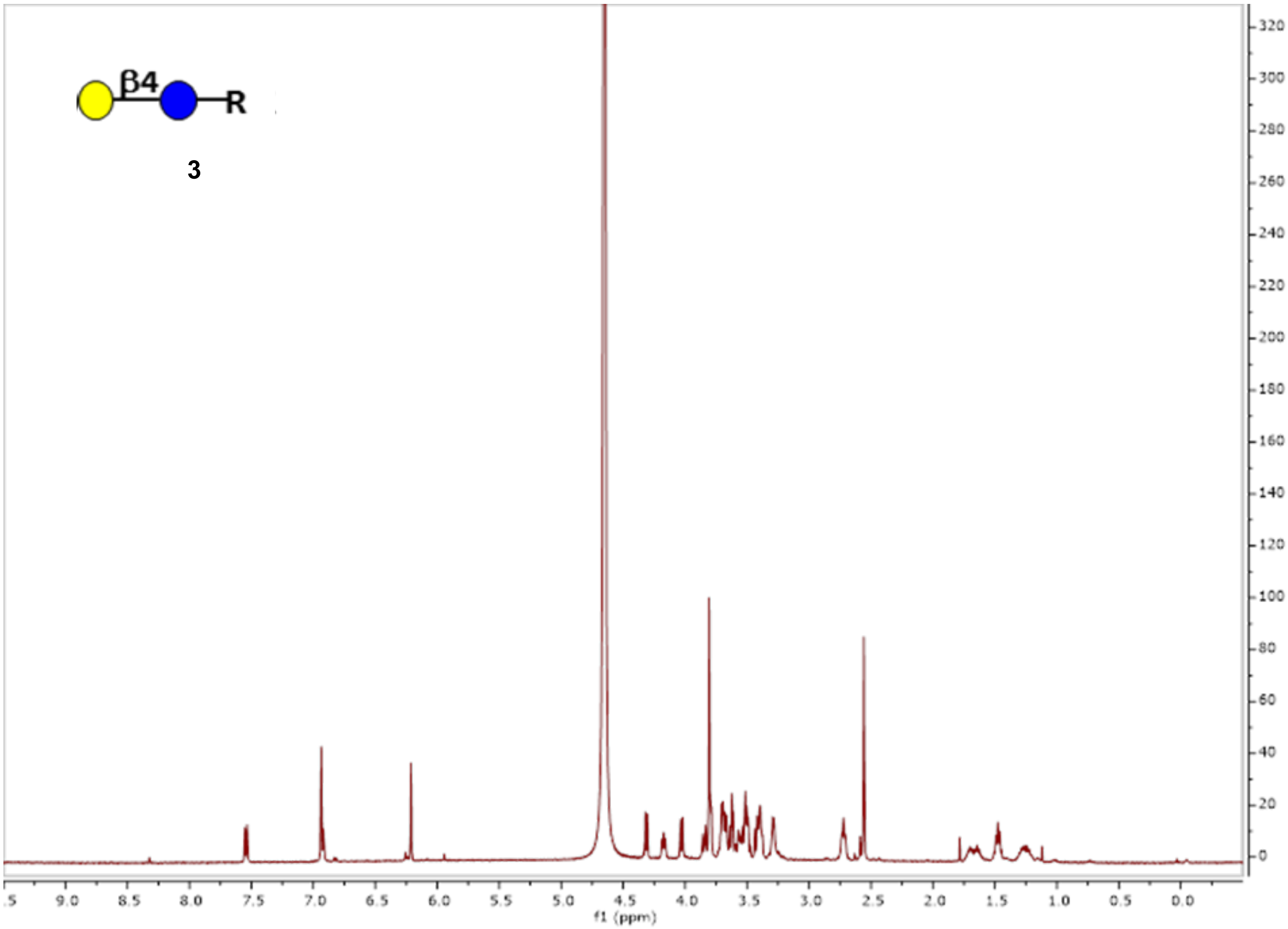
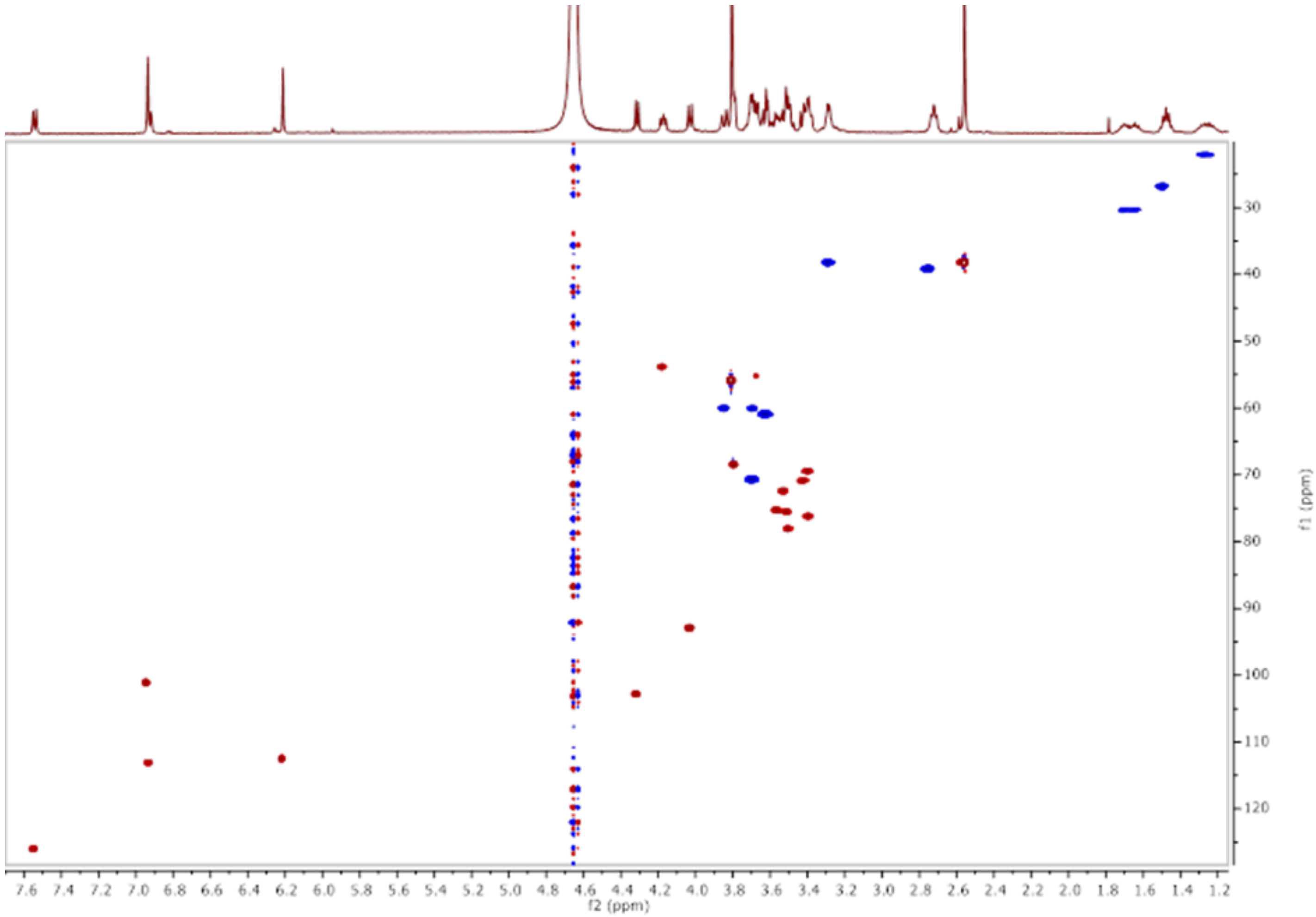
90
100
110
120
130
140


β4
R
3
f1 (ppm)



f2 (ppm)
f1 (ppm)

2. Enzymatic Synthesis

2.a. Materials and Methods

^{1}H spectra were recorded on a 500 MHz Varian Inova, 600 MHz Agilent DD2, 800 MHz Agilent DD2, or an Agilent 900 MHz DD2 spectrometer with a triple resonance (HCN) cryogenically cooled probe spectrometer. Chemical shifts are reported in parts per million (ppm) relative to H1 of reducing glucose which was set to δ 4.00 as the internal standard. NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet and / or multiple resonances, br. = broad signal), *J* coupling, integration, and peak identity. NMR signals were assigned on the basis of ^{1}H NMR, gCOSY, gHSQC, zTOCSY, and NOESY experiments. Enzymatic reactions were monitored by mass spectrometry recorded on an Applied Biosystems SCIEX MALDI TOF / TOF 5800 using 2,5-dihydroxybenzoic acid (DHB) as a matrix or a Shimadzu 20AD UFLC LCMS-IT-TOF. Reverse phase (RP) TLC was performed on glass plates coated with HPTLC Silica gel 69 RP-18 WF_{254S} (EMD Chemicals, Inc.) and developed with 20 - 40% acetonitrile in H_2O. Visualization of TLC plates was accomplished by spraying with 10% sulfuric acid in ethanol, Hanessian's Stain, or ninhydrin followed by charring at ~150 °C. Reagents were purchased from Sigma-Aldrich and used without further purification. HPLC purification of compounds was performed on an Agilent Technologies 1200 Series HPLC equipped with a Halo® RP-Amide 4.6 x 100 mm, 2.7 μm column. HPLC grade acetonitrile and water were purchased from Fischer. Neutral and sialylated samples were eluted in a 50 mM solution of ammonium bicarbonate with a linear gradient of 0 - 50%, or 0 – 25% acetonitrile over 20 min, respectively at 1 mL/min. Spectra were monitored at a wavelength of 324 nm using an Agilent 1200 series diode array with a multiple wavelength detector. GalT1 from bovine milk was purchased from Sigma. Sialidase from *Arthrobacter ureafaciens* was purchased from Roche and 1,2-α-L-fucosidase (microbial) was purchased from Megazyme.

2.b. Human Glycosyl Transferase Expression

The catalytic domains of human glycosyl transferases (as shown in Table S1 below) was expressed as soluble, secreted fusion proteins by transient transfection of HEK293 suspension cultures (3). The coding regions were amplified from Mammalian Gene Collection clones using primers that appended a tobacco etch virus (TEV) protease cleavage site (4) to the NH_2-terminal end of the coding region and attL1 and attL2 Gateway adaptor sites to the 5' and 3' terminal ends of the amplimer products. The amplimers were recombined via BP clonase reaction into the pDONR221 vector and the DNA sequences were confirmed. The pDONR221 clone was then recombined via LR clonase reaction into a custom Gateway adapted version of the pGEn2 mammalian expression vector (3, 5) to assemble a recombinant coding region comprised of a 25 amino acid NH_2-terminal signal sequence from the *T. cruzi* lysosomal α-mannosidase (6) followed by an 8xHis tag, 17 amino acid AviTag (7), "superfolder" GFP (8), the nine amino acid sequence encoded by attB1 recombination site, followed by the TEV protease cleavage site and the respective glycosyltransferase catalytic domain coding region.

Suspension culture HEK293 cells (Freestyle 293-F cells, Life Technologies, Grand Island, NY) were transfected as previously described (3) and the culture supernatant was subjected to Ni-NTA superflow chromatography (Qiagen, Valencia, CA). Enzyme preparations eluted with 300 mM imidazole were concentrated to ~1 mg mL^{-1} using an ultrafiltration pressure cell membrane (Millipore, Billerica, MA) with a 10 kDa molecular weight cutoff.

Table S1: Enzyme expression details

Enzyme	Amino Acid Residues	Uniprot ID
FUT1	26 – 365	P19526
FUT3	40 – 361	P21217
FUT5	40 – 374	Q11128
FUT9	39 – 359	Q9Y231
B3GNT2	35 – 397	Q9NY97
B3GALT5	32 – 310	Q9Y2C3
GCNT2 (Isoform B)	26 - 400	Q06430
ST3GAL4	41 – 333	Q11206
ST6GAL1	75 – 406	P15907
ST6GALNAC5	50 – 336	Q9BVH7

2.c. General Procedures for Enzymatic Synthesis

General procedure for the installation of β1,3 GlcNAc using B3GNT2

HMO acceptor and UDP-GlcNAc (1.5 eq per GlcNAc added) were dissolved at a final HMO concentration of 10 mM in a HEPES buffered solution (50 mM, pH 7.3) containing KCl (25 mM), $MgCl_2$ (2 mM) and DTT (1 mM). Calf intestine alkaline phosphatase (CIAP, 10 U μL^{-1}) and B3GNT2 (8.3 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of B3GNT2 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a. Materials and Methods) provided the desired product.

General procedure for the installation of branching β1,6 GlcNAc using GCNT2

HMO acceptor and UDP-GlcNAc (1.5 eq per GlcNAc added) were dissolved at a final HMO concentration of 10 mM in a MES buffered solution (50 mM, pH 7.0) containing Na_2EDTA (10 mM). CIAP (10 U μL^{-1}) and GCNT2 (7.5 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of GCNT2 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of β1,4 Gal using GalT1 to form Type II LacNAc moieties

HMO acceptor and UDP-Gal (1.5 eq per Gal added) were dissolved at a final HMO concentration of 10 mM in a Tris buffered solution (50 mM, pH 7.3) containing $MnCl_2$ (10 mM) and BSA (0.1% *wt/wt*). CIAP (10 U μL^{-1}) and GalT1 (5 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of GalT1 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of β1,3 Gal using B3GALT5 to form Type I LacNAc moieties

HMO acceptor and UDP-Gal (1.5 eq per Gal added) were dissolved at a final HMO concentration of 10 mM in a sodium cacodylate buffered solution (150 mM, pH 7.5) containing $MnCl_2$ (10 mM) and BSA (0.1% *wt*/*wt*). CIAP (10 U μL^{-1}) and B3GALT5 (8.2 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of B3GALT5 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of α1,2 Fuc using FUT1

HMO acceptor and GDP-Fuc (1.5 eq per Fuc added) were dissolved at a final HMO concentration of 10 mM in a Tris buffered solution (50 mM, pH 7.3) containing $MnCl_2$ (10 mM). CIAP (10 U μL^{-1}) and FUT1 (10 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of FUT1 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of α1,3 Fuc using FUT3

HMO acceptor and GDP-Fuc (1.5 eq per Fuc added) were dissolved at a final HMO concentration of 10 mM in a Tris buffered solution (50 mM, pH 7.3) containing $MnCl_2$ (10 mM). CIAP (10 U μL^{-1}) and FUT3 (10 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of FUT3 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of α1,3 Fuc using FUT5

HMO acceptor and GDP-Fuc (1.5 eq per Fuc added) were dissolved at a final HMO concentration of 10 mM in a Tris buffered solution (50 mM, pH 7.3) containing $MnCl_2$ (10 mM). CIAP (10 U μL^{-1}) and FUT5 (10 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of FUT5 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General Procedure for the installation of α2,3 Neu5Ac using ST3GAL4

HMO acceptor and CMP-Neu5Ac (1.5 eq per Neu5Ac added) were dissolved at a final HMO concentration of 10 mM in a sodium cacodylate buffered solution (50 mM, pH 7.2) containing BSA (0.1% *wt*/*wt*). CIAP (10 U μL^{-1}) and α2,3-sialyltransferase 4 (ST3GAL4, 4 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of ST3GAL4 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of terminal α2,6 Neu5Ac using ST6GAL1

HMO acceptor and CMP-Neu5Ac (1.5 eq per Neu5Ac added) were dissolved at a final HMO concentration of 10 mM in a sodium cacodylate buffered solution (100 mM, pH 6.5) containing BSA (0.1% *wt*/*wt*). CIAP (10 U μL^{-1}) and ST6GAL1 (4.4 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of ST6GAL1 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

General procedure for the installation of internal α2,6 Neu5Ac on GlcNAc using ST6GALNAC5

HMO acceptor and CMP-Neu5Ac (1.5 eq per Neu5Ac added) were dissolved at a final HMO concentration of 10 mM in a sodium cacodylate buffered solution (50 mM, pH 6.5) containing $MgCl_2$ (10 mM) and BSA (0.1% *wt/wt*). CIAP (10 U μL^{-1}) and *N*-acetylgalactosaminide α-2,6-sialyltransferase 5 (ST6GALNAC5, 4.4 μg per μmol HMO) were added, and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS, and if starting material remained after 18 h another portion of ST6GALNAc5 was added until no starting material could be detected. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided the desired product.

Procedure for the cleavage of an α2,6 sialoside using *Arthrobacter ureafaciens* sialidase (compound 19)

HMO **18** (0.5 mg, 0.21 μmol) was dissolved at a final concentration of 10 mM in a sodium acetate buffered solution (50 mM, pH 5.5) containing $CaCl_2$ (5 mM) and BSA (0.1% *wt/wt*). *Arthrobacter ureafaciens* sialidase (2 U μL^{-1}) was added and the reaction mixture was incubated for 4 h at 37 °C with gentle shaking. The reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided **19** (0.4 mg, 89%) as a white solid.

Procedure for the cleavage of an α1,2 fucoside (compound 22)

HMO **21** (0.4 mg, 0.17 μmol) was dissolved at a final concentration of 10 mM in a Tris buffered solution (50 mM, pH 6.5) containing BSA (0.1% *wt/wt)*. Microbial 1,2-α-L-fucosidase (0.5 U μL^{-1}) was added and the reaction mixture was incubated overnight at 37 °C with gentle shaking. Reaction progress was monitored by MALDI-TOF MS and when no starting material could be detected the reaction mixture was centrifuged using a Nanosep® Omega ultrafiltration device (10 kDa

MWCO) to remove enzymes and BSA, and the filtrate was lyophilized. Purification by reverse-phase HPLC (see Section 2.a.) provided **22** (0.3mg, 82%) as a white solid.

2.d. Enzymatic Flowchart of HMO Library Members

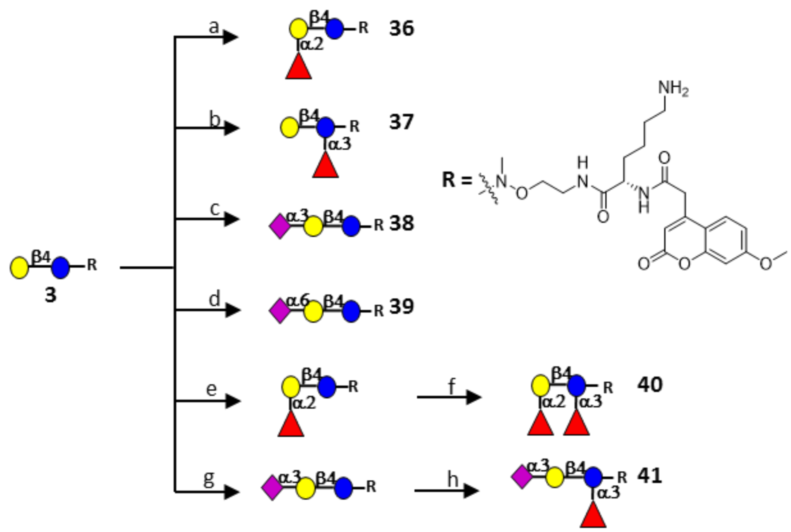


Figure S2: Lactose Modified HMOs.
a) FUT1, GDP-Fuc; b) FUT5, GDP-Fuc; c) ST3GAL4, CMP-Neu5Ac; d) ST6GAL1, CMP-Neu5Ac; e) FUT1, GDP-Fuc; f) FUT3, GDP-Fuc; g) ST3GAL4, CMP-Neu5A; h) FUT3, GDP-Fuc.

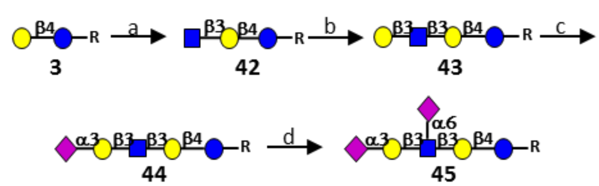


Figure S3: DSLNT Synthesis.
a) B3GNT2, UDP-GlcNAc; b) GalT1, UDP-Gal; c) ST3GAL4, CMP-Neu5Ac; d) ST6GALNAc5, CMP-Neu5Ac

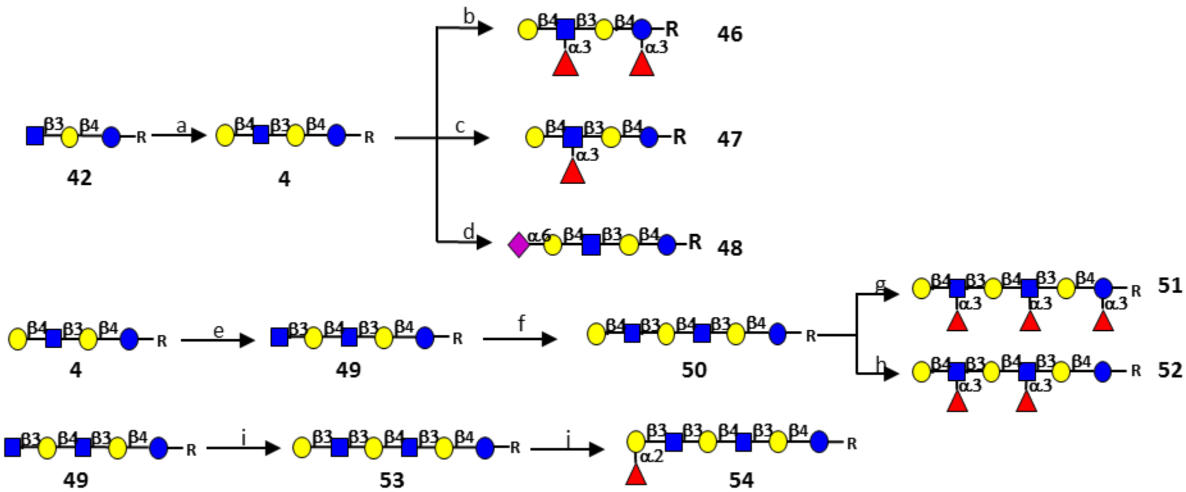


Figure S4: Lacto-N-*neo*tetraose and para-Lacto-N-*neo*hexaose derivatives.
a) GalT1, UDP-Gal; b) FUT5, GDP-Fuc; c) FUT9, GDP-Fuc; d) ST6GAL1, CMP-Neu5Ac; e) B3GNT2, UDP-GlcNAc; f) GalT1, UDP-Gal; g) FUT5, GDP-Fuc; h) FUT9, GDP-Fuc; i) B3GALT5, UDP-Gal; j) FUT1, GDP-Fuc

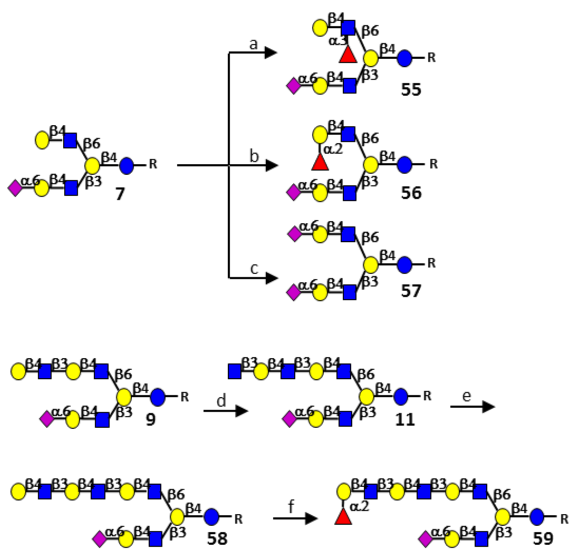


Figure S5: Synthesis of Bi-Antennary HMOs Bearing a β3 6'SialylLacNAc.
a) FUT5, GDP-Fuc; b) FUT1, GDP-Fuc; c) ST6GAL1, CMP-Neu5Ac; d) B3GNT2, UDP-GlcNAc; e) GalT1, UDP-Gal; f) FUT1, GDP-Fuc.

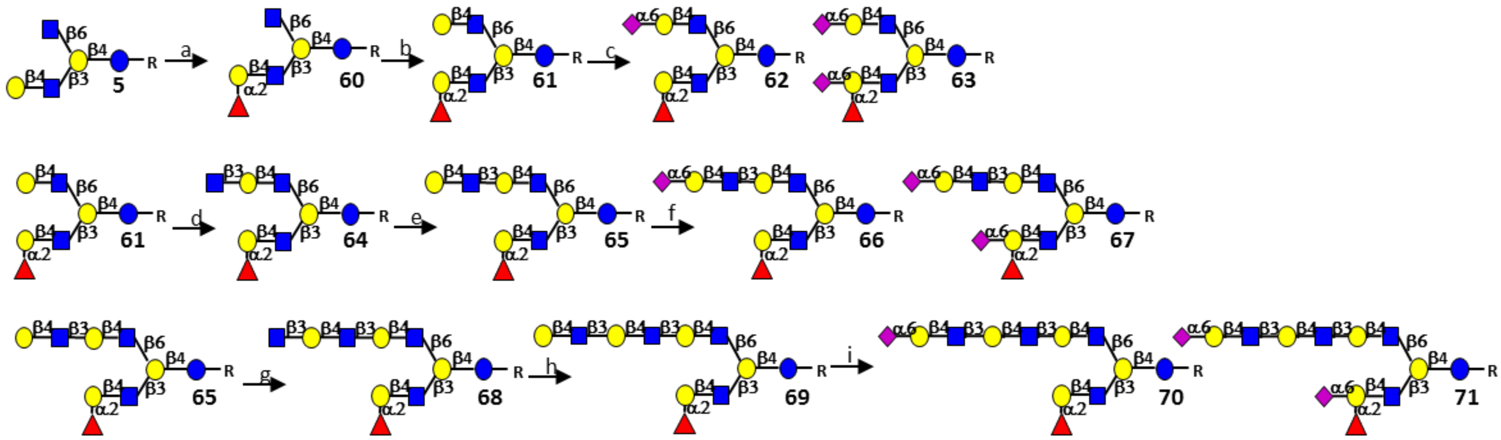


Figure S6: Synthesis of Bi-Antennary HMOs Bearing a β3 H2 Epitope.
a) FUT1, GDP-Fuc; b) GalT1, UDP-Gal; c)ST6GAL1, CMP-Nue5Ac; d) B3GnT2, UDP-GlcNAc; e) GalT1, UDP-Gal; f) ST6GAL1, CMP-Neu5Ac; g) B3GNT2, UDP-GlcNAc; h) GalT1, UDP-Gal; i) ST6GAL1, CMP-Neu5Ac.

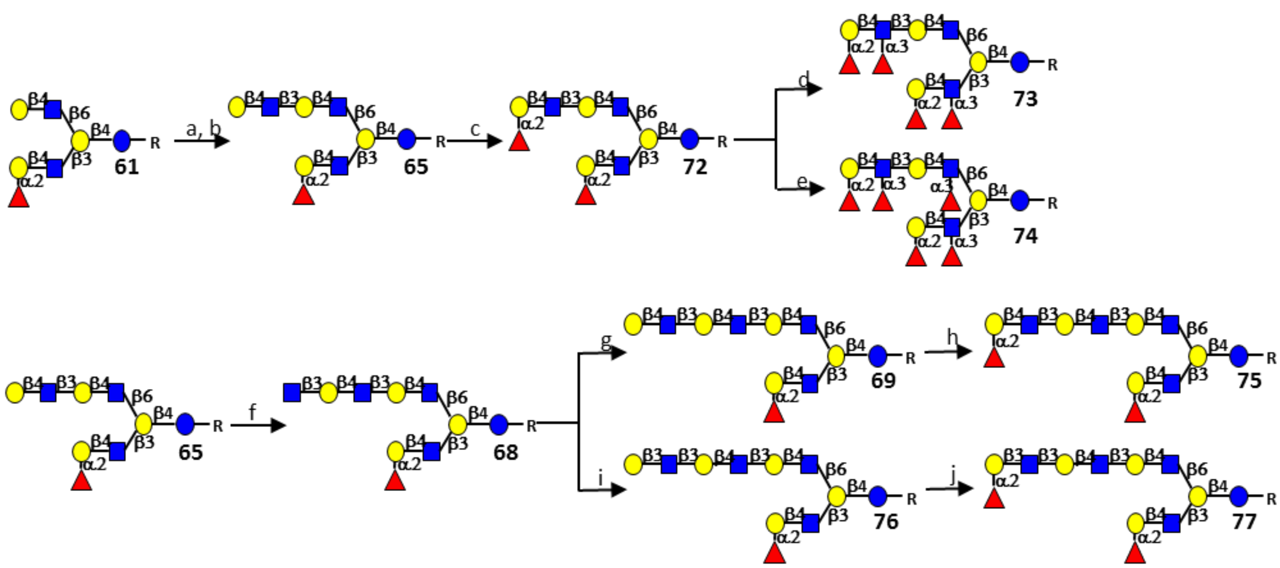


Figure S7: β3 H2 and Le^{y} fucosylated derivatives.
a) B3GNT2, UDP-GlcNAc; b) GalT1, UDP-Gal; c) FUT1, GDP-Fuc; d) FUT3, GDP-Fuc; e) FUT5, GDP-Fuc; f) B3GNT2, UDP-GlcNAc; g) GalT1, UDP-Gal; h) FUT1, GDP-Fuc; i) B3GALT5, UDP-Gal; j) FUT1, GDP-Fuc.

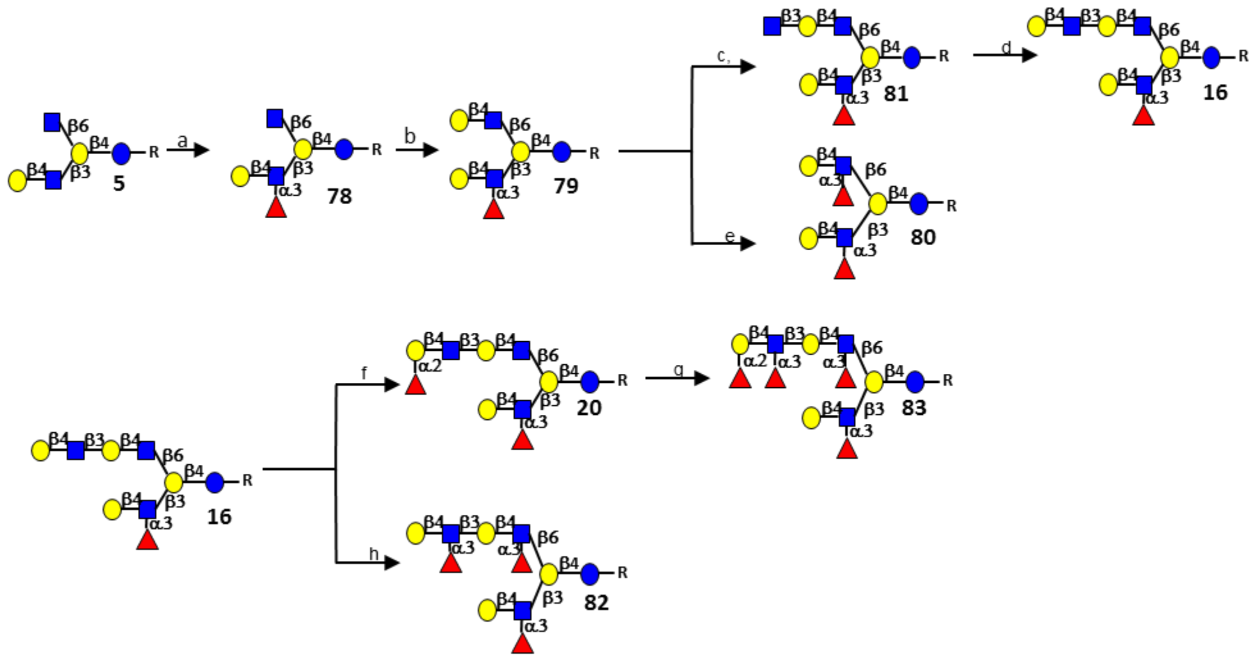


Figure S8: β3 Le^x Derivatives

a) FUT5, GDP-Fuc; b) GalT1, UDP-Gal; c) B3GNT2, UDP-GlcNAc; d) GalT1, UDP-Gal; e) FUT5, GDP-Fuc; f) FUT1, GDP-Fuc; g) FUT5, GDP-Fuc; h) FUT5, GDP-Fuc.

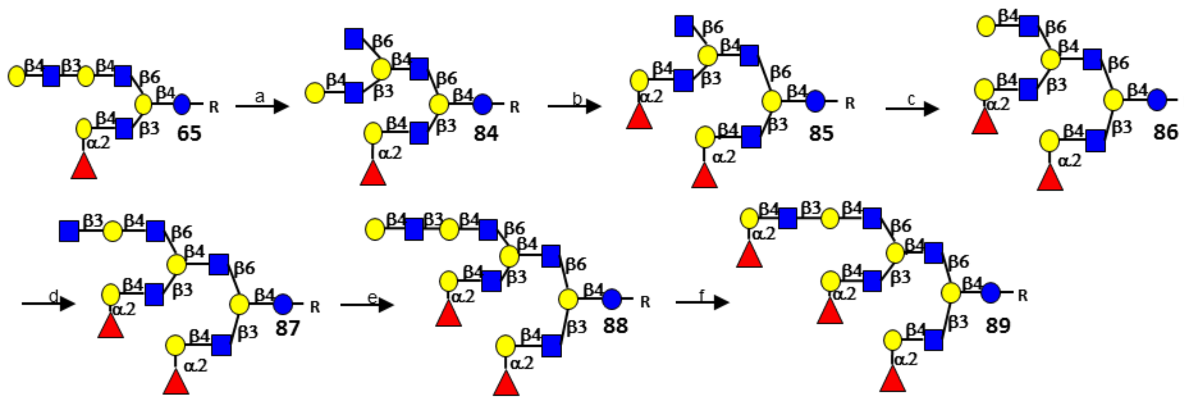


Figure S9: Synthesis of an asymmetric, tri-antennary HMO.

a) GCNT2, UDP-GlcNAc; b) FUT1, GDP-Fuc; c) GalT1, UDP-Gal; d) B3GNT2, UDP-GlcNAc; e) GalT1, UDP-Gal; f) FUT1, GDP-Fuc

2.e. Identification Numbers for Printed HMO Library Members

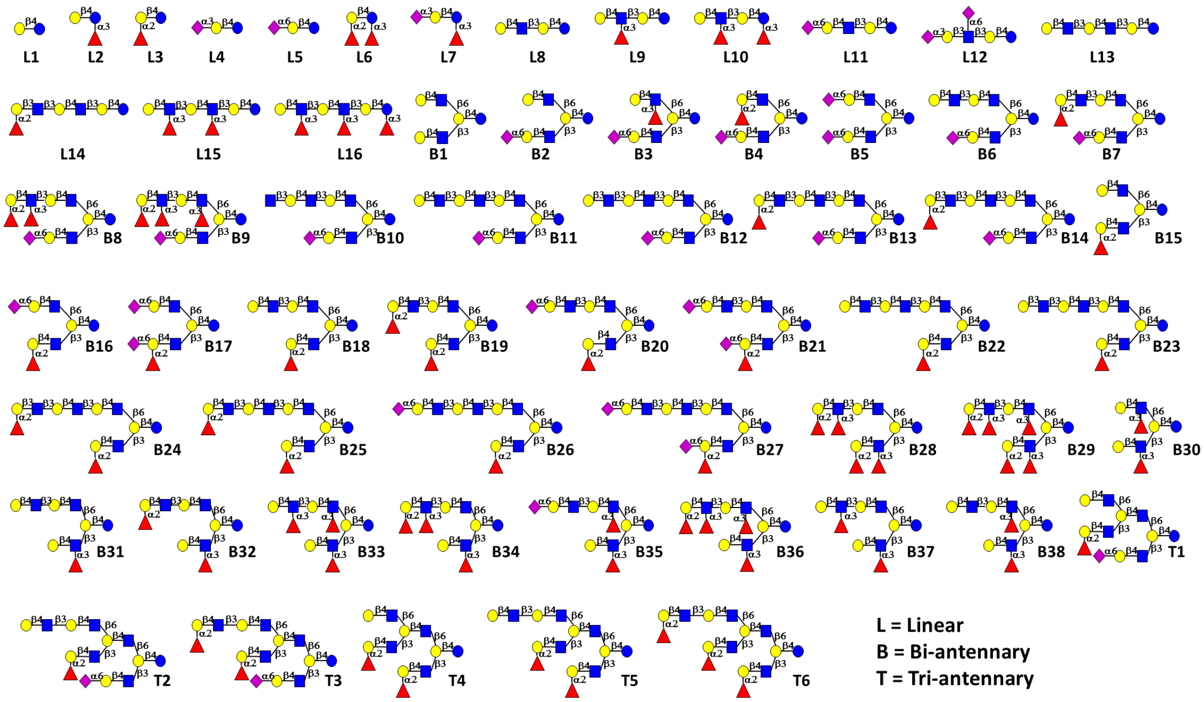


Figure S10: HMO Library Members.

Table S2. Library identifier with corresponding compound synthesis number.

Library Number	Number in Scheme	Library Number	Number in Scheme	Library Number	Number in Scheme	Library Number	Number in Scheme
L1	3	L16	51	B15	61	B30	80
L2	37	B1	n/d	B16	62	B31	16
L3	36	B2	7	B17	63	B32	20
L4	38	B3	55	B18	65	B33	82
L5	39	B4	56	B19	72	B34	21
L6	40	B5	57	B20	66	B35	18
L7	41	B6	9	B21	67	B36	83
L8	4	B7	10	B22	69	B37	22
L9	47	B8	14	B23	76	B38	19
L10	46	B9	15	B24	77	T1	25
L11	48	B10	11	B25	75	T2	27
L12	45	B11	58	B26	70	T3	28
L13	50	B12	12	B27	71	T4	86
L14	54	B13	59	B28	73	T5	88
L15	52	B14	13	B29	74	T6	89

n/d = not described

2.f. HPLC Traces

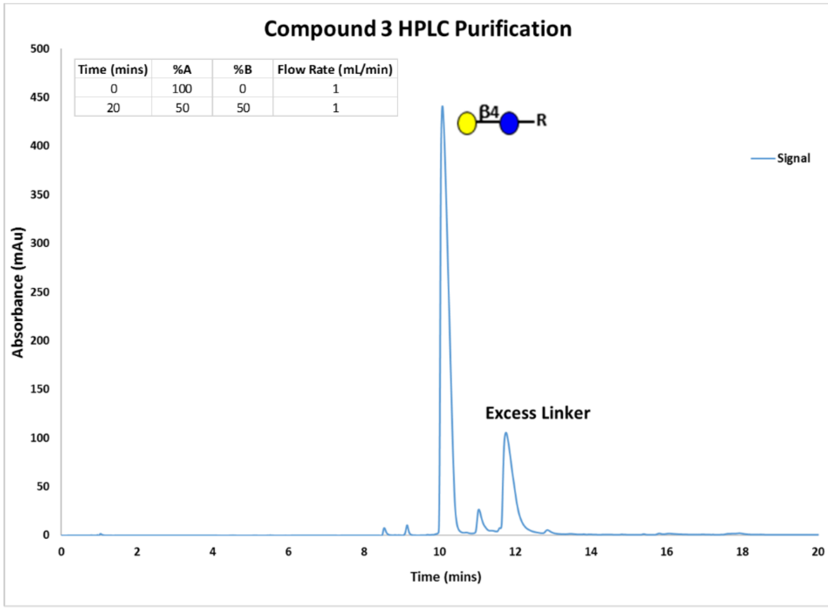


Figure S11: Reverse Phase Analytical Purification of Compound 3.
A = 50mM Ammonium Bicarbonate; B = Acetonitrile.

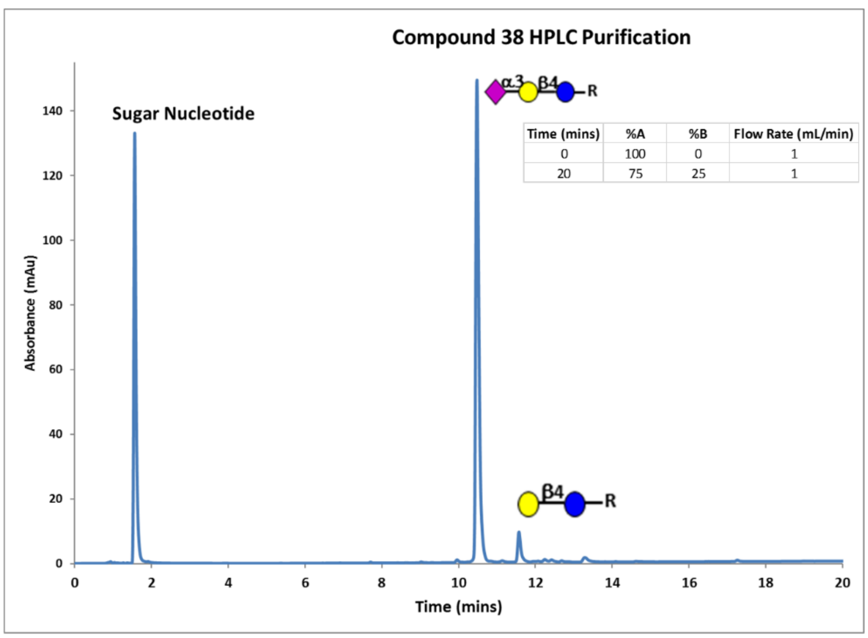


Figure S12: : Reverse Phase Analytical Purification of Compound 38.
A = 50mM Ammonium Bicarbonate; B = Acetonitrile.

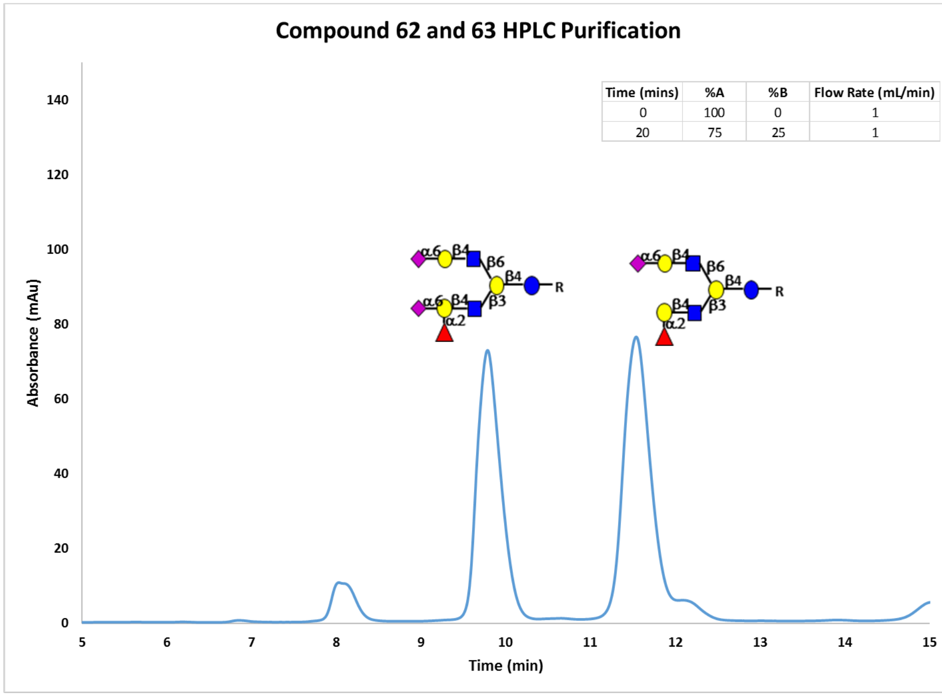
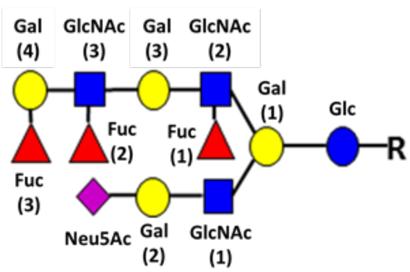


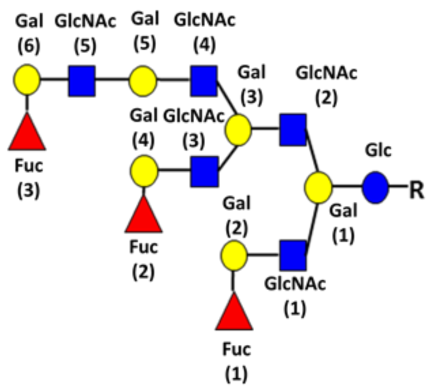
Figure S13: Reverse Phase Analytical Purification of Compound 62 and 63.
A = 50mM Ammonium Bicarbonate; B = Acetonitrile.

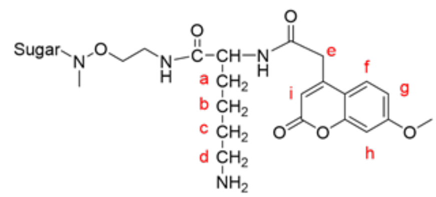
3. NMR and MS

3.a. NMR Nomenclature

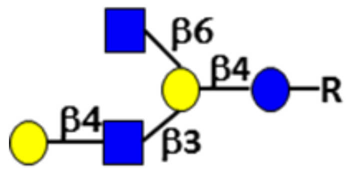
Glycan assignments were made by numbering each monosaccharide starting from the reducing terminus and continuing in sequential order by proceeding to the β3 branch. Once all β3 monosaccharides had been counted, numbering continued on the β6 branch. In the example of a tri-antennary structures, the monosaccharides on the lower β3 branch are counted before residues on the upper β3 branch. Two complex targets are illustrated below in addition to the numbering on the anomeric linker.







3.b. Structure Elucidation of Compound 5 by 1D and 2D NMR Analysis



The reducing H-1 of Glc could be readily assigned due to a large upfield shift in both the ^{1}H and ^{13}C relative to the other anomeric signals which is a result of the *N*-methylhydroxylamine aglycon as seen in the HSQC spectrum in Fig. S14. Additionally, there is a Nuclear Overhauser Effect (NOE) between the anomeric H-1 of Glc and the methyl attached to the nitrogen of the hydroxylamine. The equatorial H-4 of Gal gives a diagnostic downfield signal (δ3.98 and δ3.76) compared

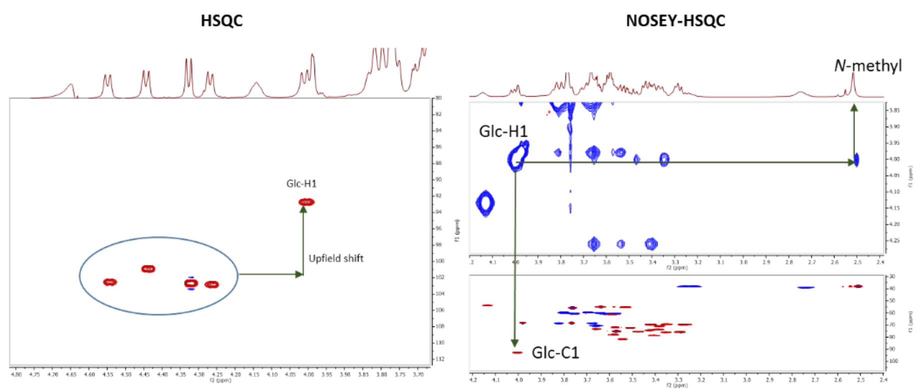


Figure S14: Assignment of reducing Glc H1.

to other the axial H-4 signals of Glc or GlcNAc. As such, the Gal anomeric proton signals could be determined to δ4.32 and δ4.26. Assigning these shifts to a particular Gal was straight forward as the H-4 on the terminal Gal (*i.e.* no glycosidic bond with the H-3 position) is more upfield compared to a H-4 on the penultimate Gal (Fig. S15).

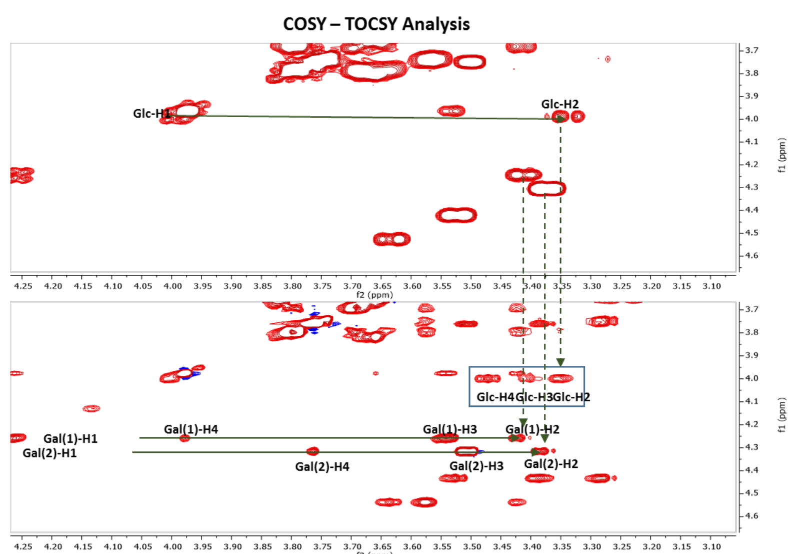


Figure S15: Assignment of both Gal H1→H4 signals.

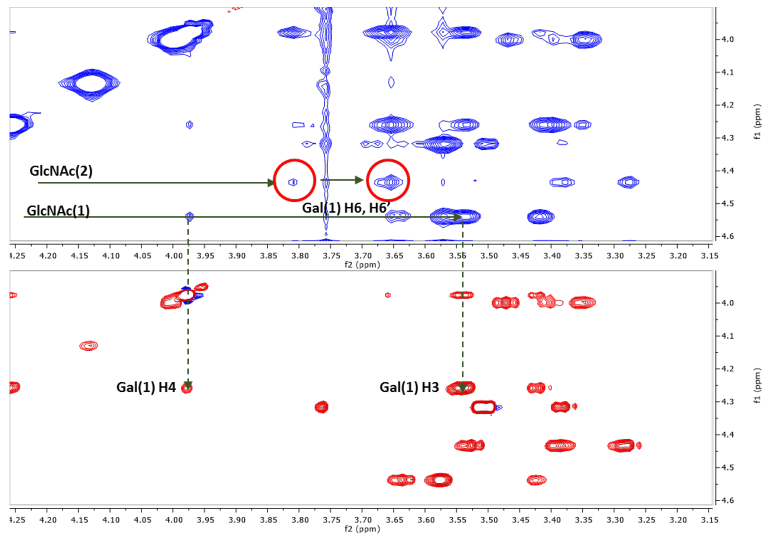


Figure S16: GlcNAc assignment using NOSEY-TOCSY analysis.

Finally, the two GlcNAc residues could be identified by investigating the NOSEY-TOCSY signals of their anomeric peaks. It was expected that GlcNAc(1) H-1 would have a NOE correlation with the penultimate Gal H-3 involved in the glycosidic bond. Fig. S16 shows that, indeed, there is a through space correlation between the GlcNAc anomeric at δ4.26 and the H3 from Gal(1) at δ3.54. Furthermore, there is an additional through space NOE with the H-4 on Gal(1) at δ3.98. The H-1 of GlcNAc(2) shows a through space correlation with δ3.81 and δ3.68 which corresponds to the H-6/6' of Gal(1) that are involved in the β6 glycosidic bond. Finally, investigation of the ^{13}C-^{1}H correlation (Fig. S17) of these two H-6 signals shows a downfield shift in their carbon value compared to other H6/6' positions not involved in a glycosidic bond.

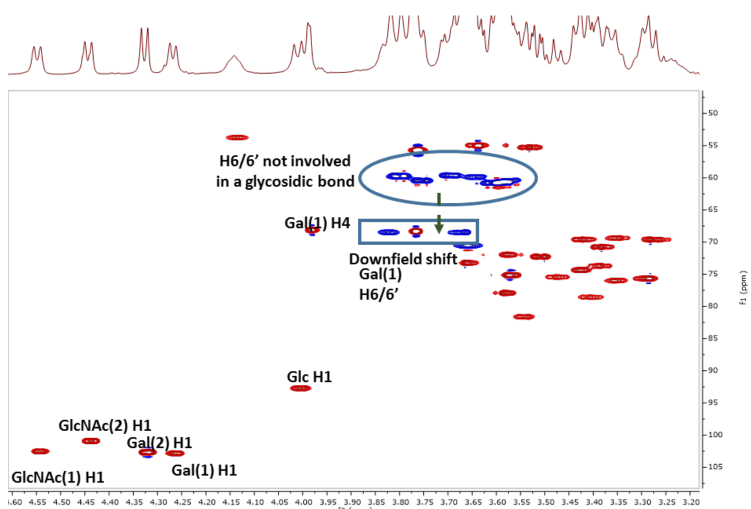
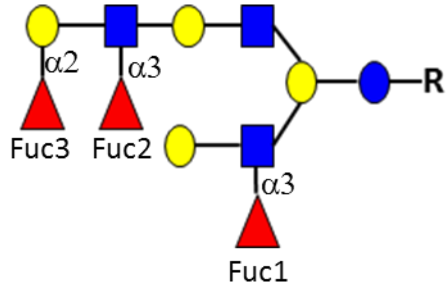


Figure S17: HSQC Analysis.

3.c. NMR Analysis of Fucose Connectivity for Compound 21



The fucose connectivity could be determined by using a combination of 1D and 2D NMR techniques assisted by the presence of reporter signals within the molecule. Fucoside anomeric signals are downfield compared to the Glc, Gal, and GlcNAc peaks as they are the only linkage with an α-configuration. As shown in Fig. S18, the signal at δ5.11 corresponds to the H-1 of the α2 Fucoside whereas the signal at δ4.96 relates to two H-1 signals from both α3 Fucoside moieties, an observation supported by peak area integration.

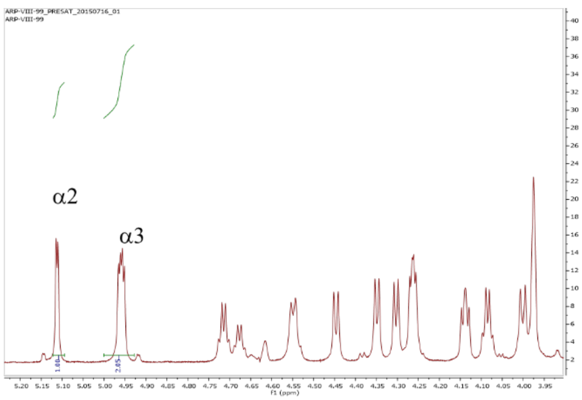


Figure S18: Proton Spectrum of Compound 21.
Fucose anomeric peaks are shifted downfield compared to the other anomeric signals as a result of the α-configuration.

We next looked to confirm this assignment by analyzing glycosidic connectivity of fucose with its corresponding Gal or GlcNAc. As previously mentioned, the Gal TOCSY spectrum shows characteristic downfield shift in the H-4 signal compared to the H-2 and H-3 signal. Furthermore, if the Gal is internal *vs* terminal, the H-4 of the internal will be more downfield than the terminal. An examination of Fig. S19 shows three Gal anomeric signals. δ4.26 corresponds to internal Gal 1 and 3 as indicated by the δ0.24 ppm downfield shift in the H4. Accordingly, the signals at δ4.30 and 4.35 must relate the H-1 of Gal 2 and 4. To uncover the which signal corresponds to a particular Gal, NOSEY-TOCSY analysis can be performed looking at the α2 Fucose anomeric signal.

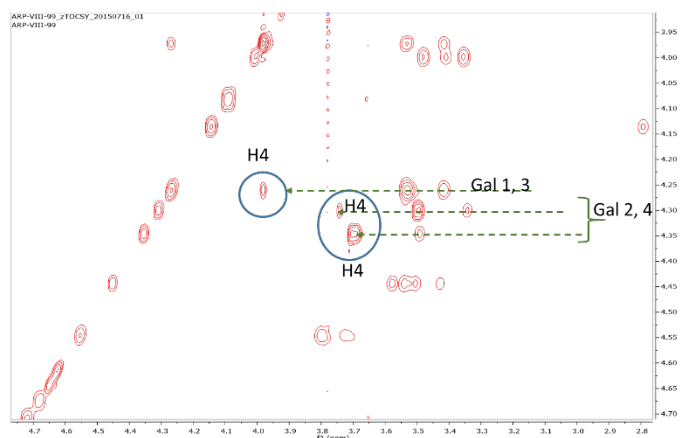


Figure S19: Assignment of Galactose Anomeric Signals Using Characteristic H4 Shift Patterns.

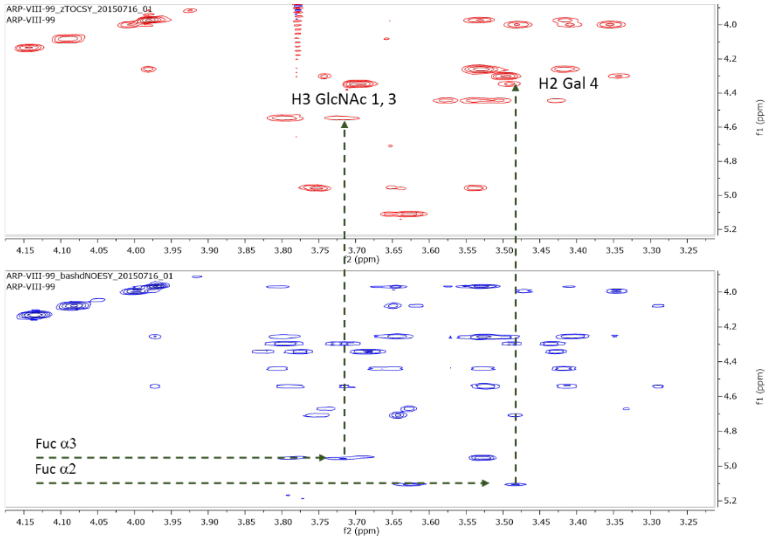


Figure S20: NOSEY-TOCSY Analysis of Anomeric Signals of α2 and α3 Fucose.

Turning our attention to the α2 Fucoside anomeric peak, we observed a through space correlation with the peak at δ3.48 which also gave a through bond TOCSY correlation with the anomeric δ4.35. As such, we could definitively identify the non-reducing, terminal Gal 4 anomeric signal. By process of elimination, the signal at δ4.30 was assigned to the anomeric signal of Gal 2. Additionally, the GlcNAc 1 and 3 anomeric signals could be assigned in a similar method by examining the through space correlation with the anomeric from the two α3 fucose units. Indeed, a through space signal was observed at δ3.72 which was confirmed the be the H3 from GlcNAc 1 and 3. As in the case of the two internal Gal residues, GlcNAc 1 and 3 also have overlapping signals as they have a similar chemical environment. Finally, the anomeric signal of GlcNAc 2 could be assigned to be δ4.44 as it illustrates a diagnostic upfield ^{1}H and ^{13}C signal compared to the H-1 signals for GlcNAc 1 and 3 at δ4.55. Fig. S21 shows the full anomeric assignments of all monosaccharide residues of compound **21.**

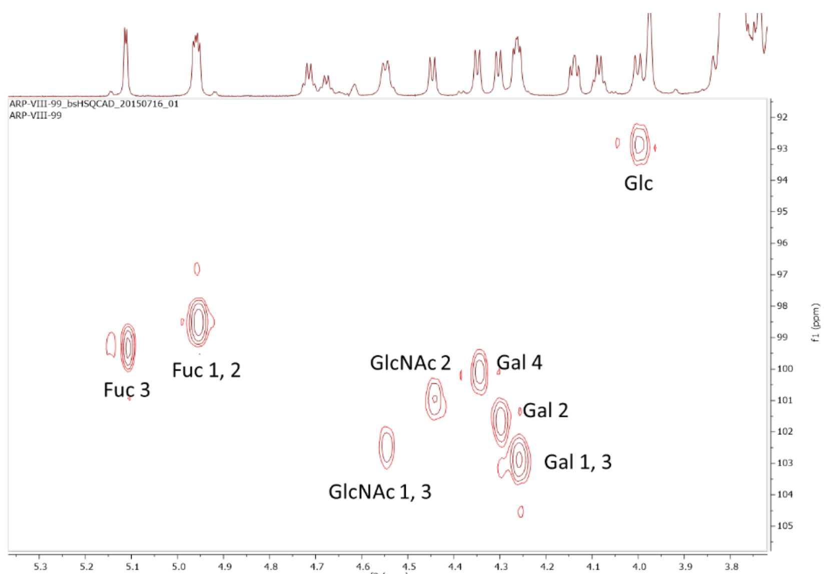
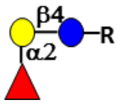


Figure S21: HSQC Spectrum with Anomeric Peak Assignment.

3.d. NMR & MS Data for Library Members



36

^{1}H (600 MHz, D_2O): δ (ppm)

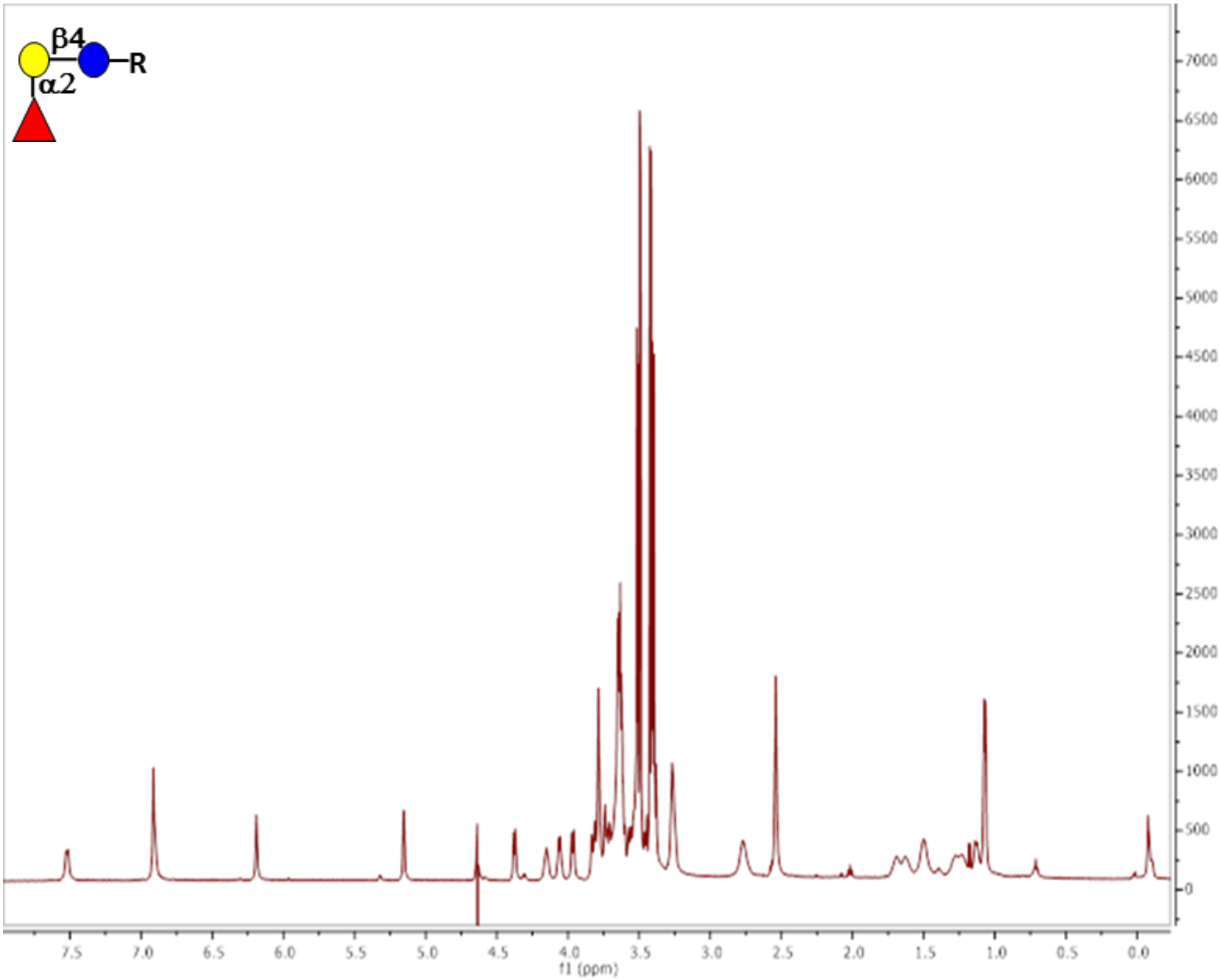
	H1	H2	H3	H4	H5	H6	CH_3
Glc	4.00 (d, *J* = 8.8 Hz, 1H)	3.83	3.43	3.53	3.25	3.85, 3.70	-[b]
Gal	4.38 (d, *J* = 7.6 Hz, 1H)	3.51	n/a[a]	3.74	n/a	3.58	-
Fuc	5.16 (d, *J* = 3.1 Hz, 1H)	3.65	n/a	n/a	4.05	n/a	1.07 (d, *J* = 6.4 Hz, 3H)

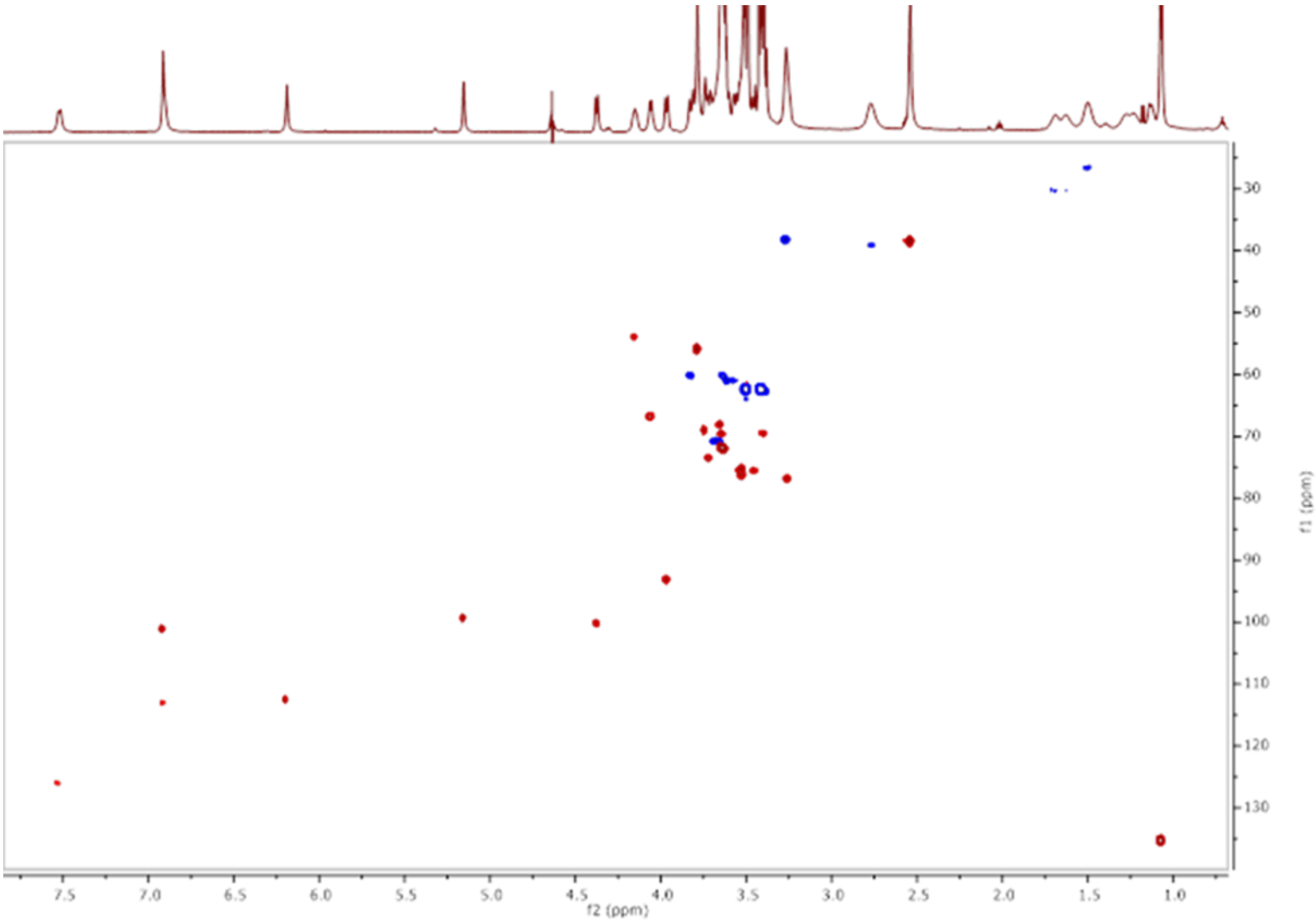
N-CH_3	2.52
N-O-CH_2	3.68
CH_2-NH	3.28
C(O)-CH-NH	4.17 (t, *J* = 5.3 Hz, 1H)
A	1.70, 1.64
B	1.26
C	1.50
D	2.76
E	3.81
F	7.53 (d, *J* = 8.5 Hz, 1H)
G	6.91
H	6.93
I	6.20
O-CH_3	3.78

[a] Not assigned
[b] Not applicable

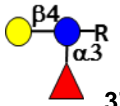
^{13}C from HSQC (150 MHz, D_2O): δ (ppm). 38.2 38.42 53.9 55.84 60.16 60.2 60.84 61.27 62.35 62.36 62.37 66.79 68.05 68.97 69.49 69.54 70.71 71.92 73.47 75.16 75.27 75.58 76.81 93.12 99.32 100.17 101.08 112.5 120.72 135.25

MALDI TOF-MS *m/z* calcd for $C_{39}H_{60}N_4O_{20}Na$ $(M + Na)^+$ exact 927.3699, found 926.1988.


β4
α2
R
f1 (ppm)



f2 (ppm)
f1 (ppm)



37

[1]H (600 MHz, D_2O): δ (ppm)

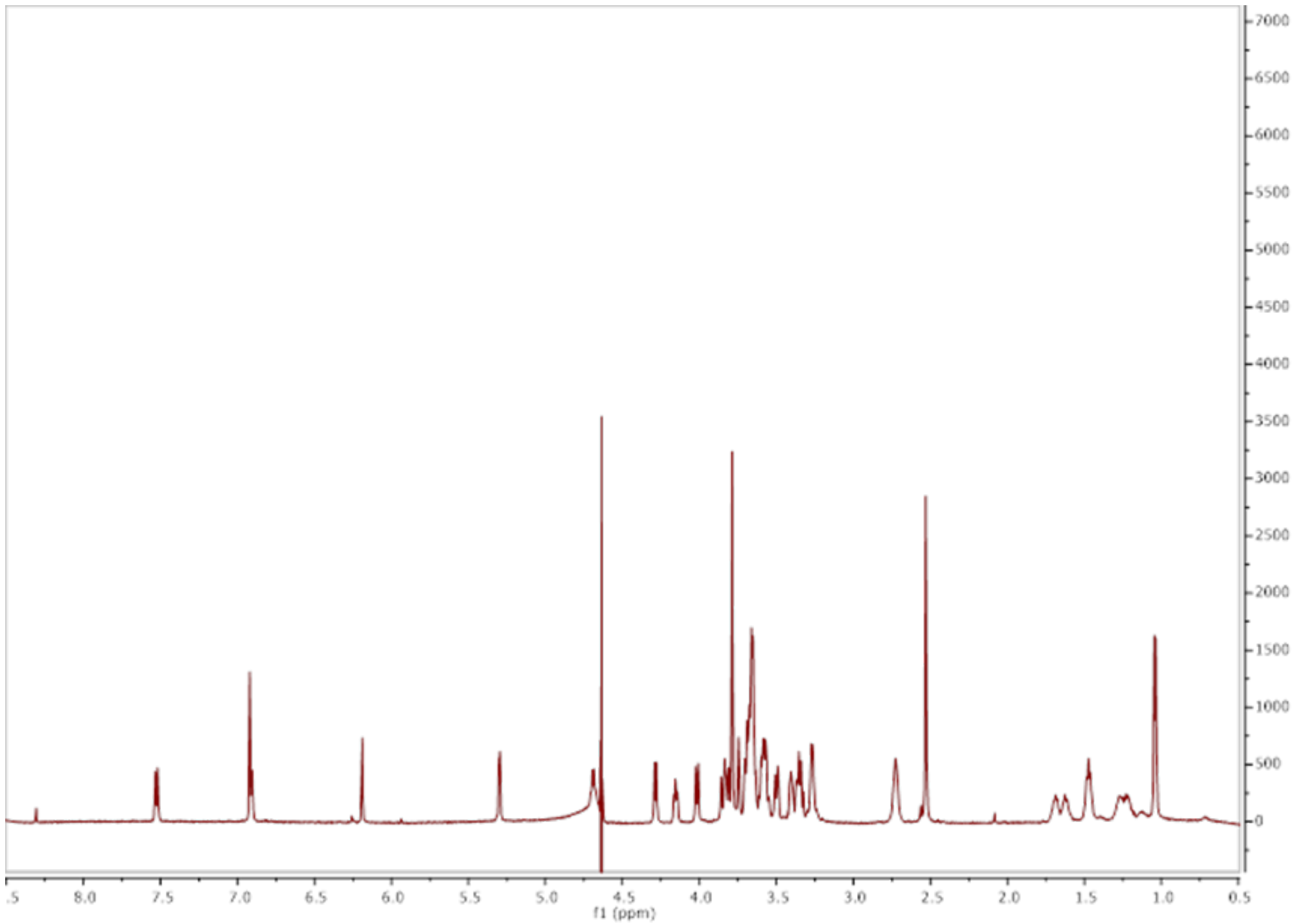
	H1	H2	H3	H4	H5	H6	CH_3
Glc	4.03 (d, *J* = 9.0 Hz, 1H)	3.59	3.36	3.66	n/a[a]	3.85, 3.70	-[b]
Gal	4.29 (d, *J* = 7.7 Hz, 1H)	3.34	3.49	3.74	n/a	3.58	-
Fuc	5.30 (d, *J* = 2.7 Hz, 1H	3.66	3.81	3.65	4.72	n/a	1.04 (d, *J* = 5.5 Hz, 3H)

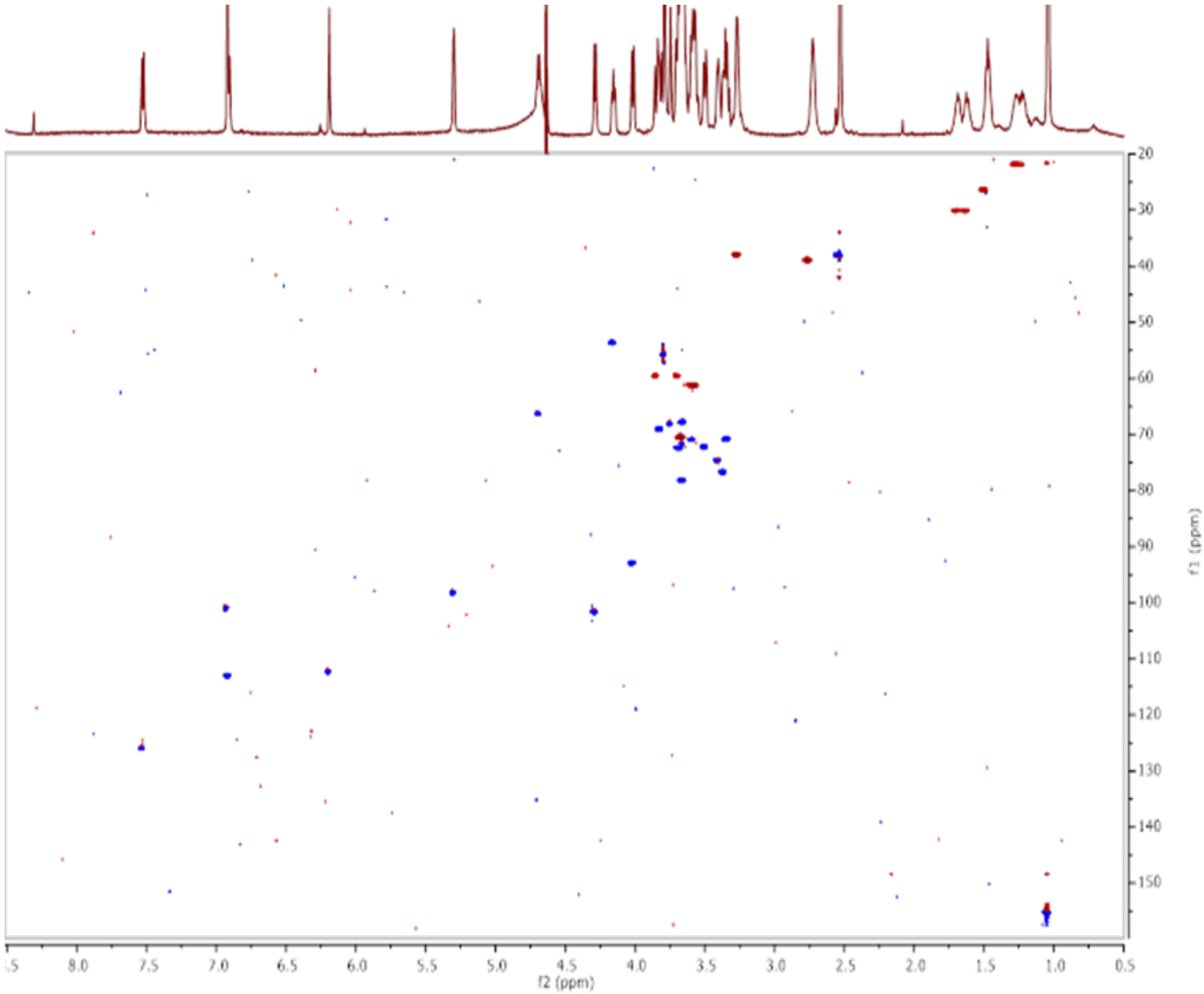
$N-CH_3$	2.52
$N-O-CH_2$	3.68
CH_2-NH	3.28
C(O)-CH-NH	4.17 (t, *J* = 5.3 Hz, 1H)
A	1.70, 1.64
B	1.26
C	1.50
D	2.76
E	3.81
F	7.53 (d, *J* = 8.5 Hz, 1H)
G	6.91
H	6.93
I	6.20
$O-CH_3$	3.78

[a] Not assigned
[b] Not applicable

[13]C from HSQC (150 MHz, D_2O): δ (ppm) 21.81, 26.38, 30.08, 37.93, 37.98, 38.90, 53.63, 55.64, 59.52, 59.55, 61.19, 66.24, 67.78, 67.80, 68.05, 68.97, 70.48, 70.84, 70.89, 70.89, 70.90, 71.66, 72.16, 72.38, 74.61, 76.64, 78.13, 92.90, 98.22, 100.95, 101.59, 112.33, 112.96, 112.98, 125.91, 154.61, 155.17.

MALDI TOF-MS *m/z* calcd for $C_{39}H_{60}N_4O_{20}Na$ $(M + Na)^+$ exact 927.3699, found 926.7706.


7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

38

^{1}H (600 MHz, D_2O): δ (ppm)

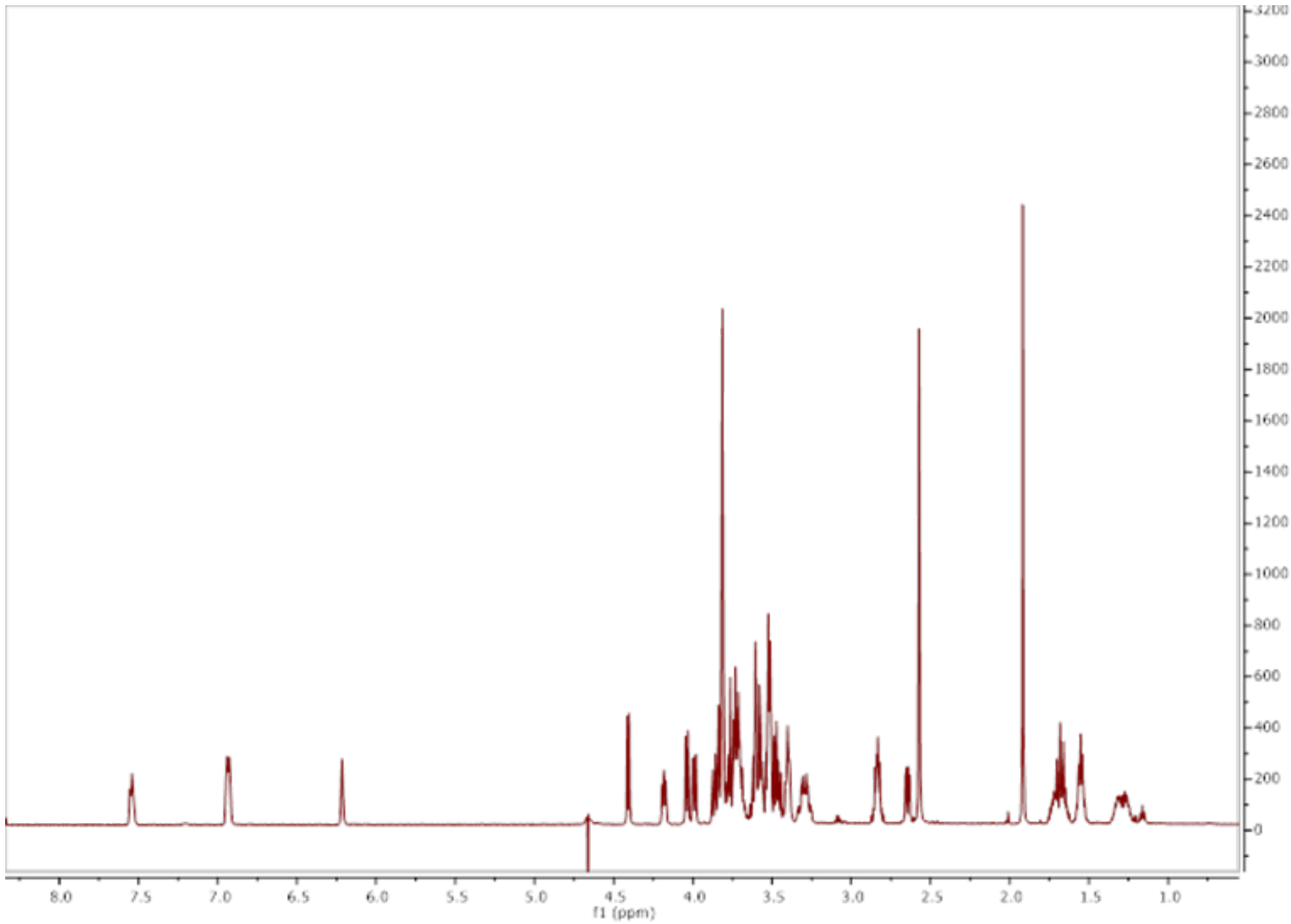
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NH Acetyl
Glc	4.03 (d, J = 9.2 Hz, 1H)	3.39	3.51	3.70	-[a]	3.84, 3.69	n/a[b]	n/a	n/a	n/a
Gal	4.29 (d, J = 7.7 Hz, 1H)	3.34	3.49	3.74	-	3.58	n/a	n/a	n/a	n/a
Neu5Ac	-	-	2.64 - eq (dd, J = 12.4, 4.6 Hz) 1.67 - axial	3.56	3.51	3.73	3.44	3.48	3.75 3.52	1.94

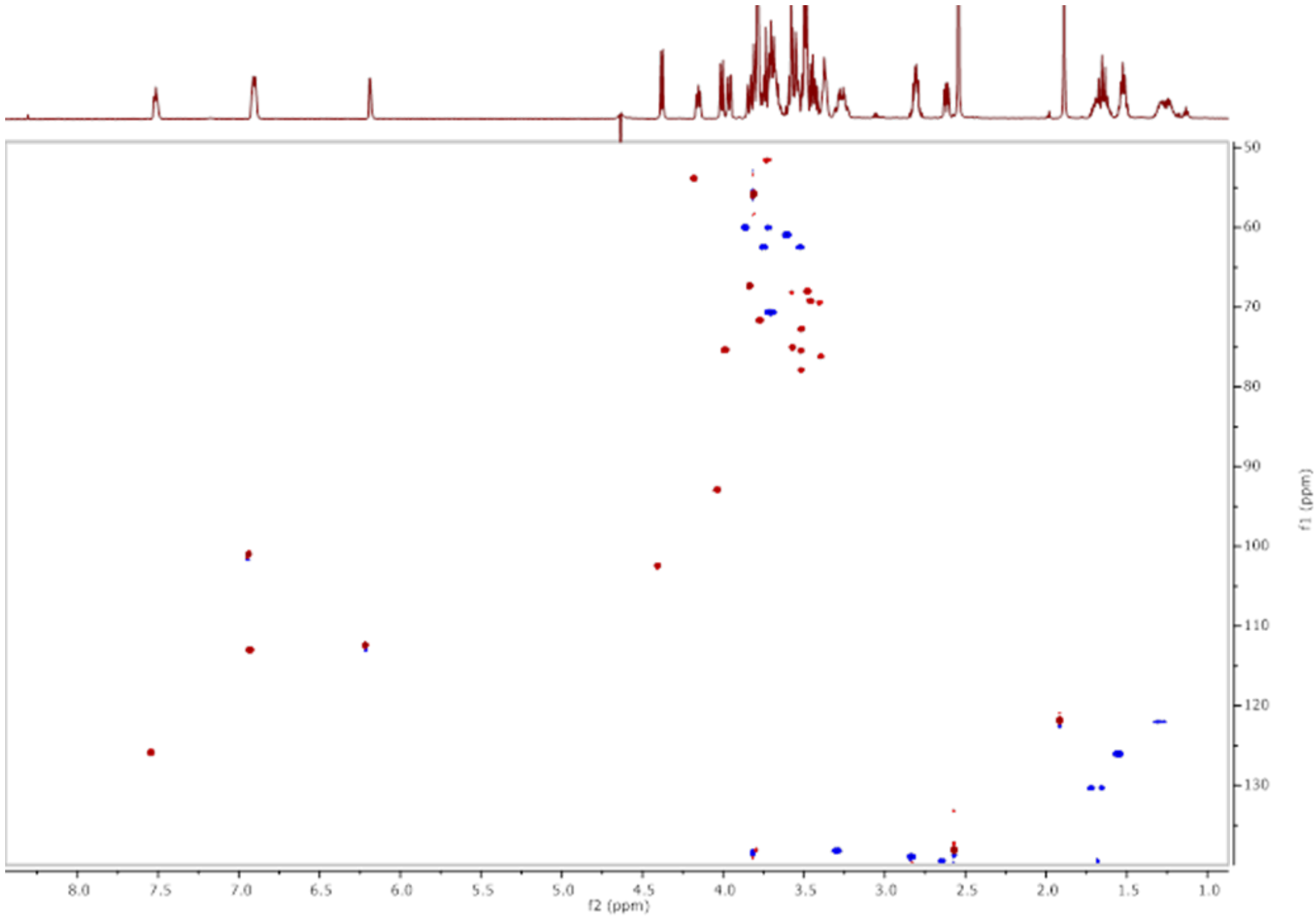
N-CH_3	2.57
N-O-CH_2	3.70
CH_2-NH	3.28 (ddd, J = 20.1, 10.4, 4.2 Hz, 2H)
C(O)-CH-NH	4.18 (dd, J = 8.6, 6.0 Hz, 1H)
A	1.71 1.65
B	1.26
C	1.55
D	2.82 (ddd, J = 13.7, 8.8, 4.9 Hz, 2H)
E	3.81
F	7.54
G	6.93
H	6.94
I	6.21
O-CH_3	3.84

[a] Not assigned
[b] Not applicable

^{13}C from HSQC (150 MHz, D_2O): δ (ppm) 51.54, 53.82, 55.23, 55.82, 56.41, 58.28, 60.00, 60.01, 60.9, 62.44, 62.44, 67.31, 67.95, 68.14, 69.21, 69.40, 70.61, 71.63, 72.74, 75.04, 75.35, 75.42, 76.16, 77.86, 92.89, 101.01, 101.59, 102.41, 112.40, 112.97, 112.99, 120.94, 121.86, 121.99, 122.46, 125.85, 126.01, 126.46, 130.30, 133.18, 133.20, 138.11, 138.17, 138.41, 138.72, 138.95, 139.45, 139.46, 139.52, 139.55.

MALDI TOF-MS *m/z* calcd for $C_{44}H_{66}O_{24}N_5Na_2$ (M + 2Na)$^+$ exact 1094.3899, found 1093.9410.


3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



50
60
70
80
90
100
110
120
130
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

39

^{1}H (600 MHz, D_2O): δ (ppm)

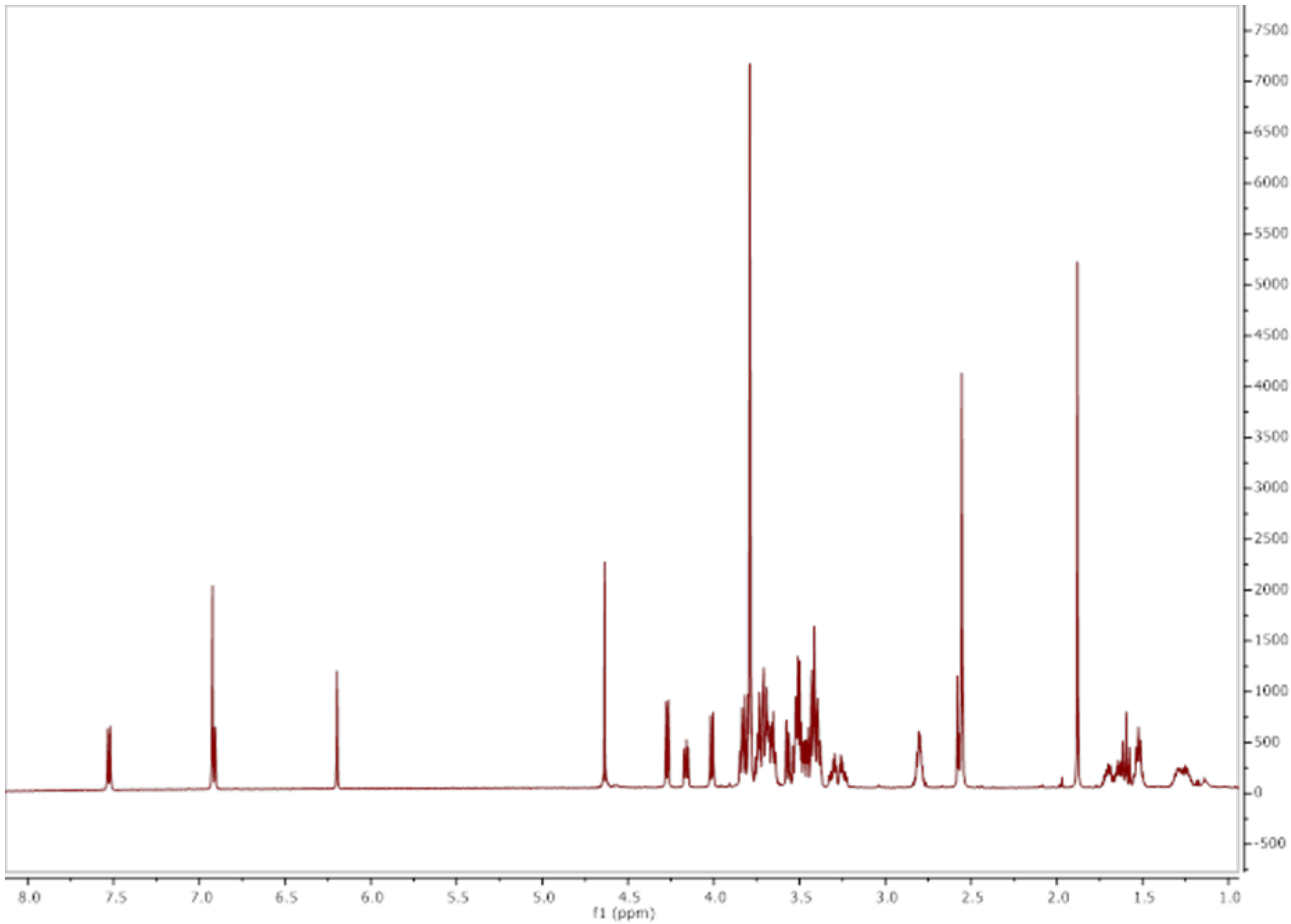
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.01 (d, *J* = 9.2 Hz, 1H)	3.41	3.51	3.74	3.45	3.84 3.46	-[b]	-	-	-
Gal	4.28 (d, *J* = 7.9 Hz, 1H)	3.39	3.51	3.78	n/a[a]	3.84 3.46	-	-	-	-
Neu5Ac	-	-	2.57 - eq 1.57 -axial	3.50	3.66	3.55	n/a	3.42	3.72 3.50	1.88

N-CH_3	2.56
N-O-CH_2	3.70
CH_2-NH	3.28 (ddd, *J* = 20.4, 10.4, 4.2 Hz, 2H)
C(O)-CH-NH	4.16 (dd, *J* = 8.8, 5.9 Hz, 1H)
A	1.70 1.64
B	1.28
C	1.53
D	2.81
E	3.80
F	7.53 (d, *J* = 8.5 Hz, 1H)
G	6.92
H	6.92
I	6.19
O-CH_3	3.79

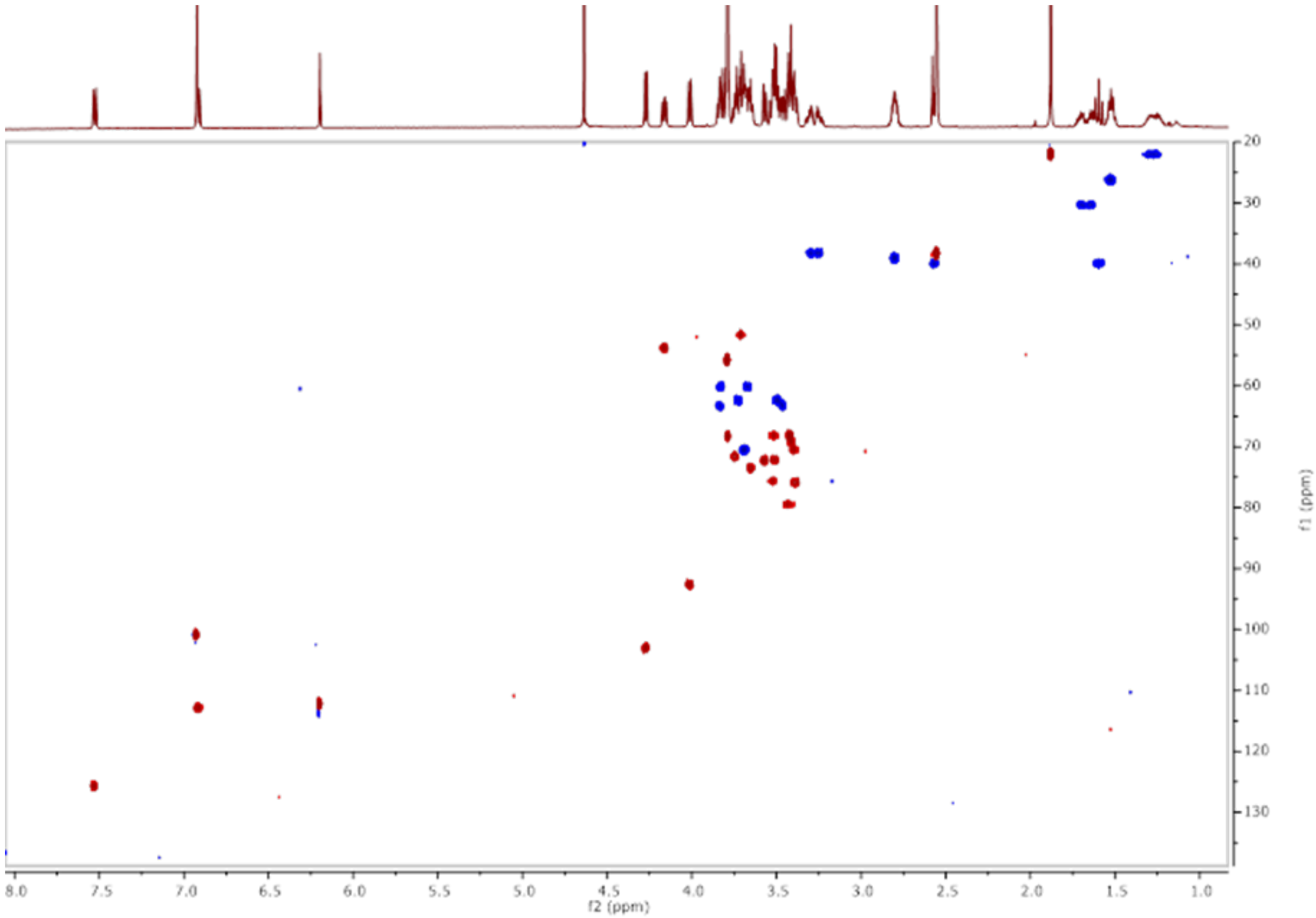
[a] Not assigned
[b] Not applicable

^{13}C from HSQC (150 MHz, D_2O): δ (ppm). 125.80, 100.89, 112.99, 112.26, 102.99, 53.80, 93.13, 63.26, 60.09, 55.68, 68.26, 71.60, 62.45, 51.56, 70.55, 73.50, 72.21, 75.66, 68.14, 72.15, 68.12, 79.50, 68.35, 70.48, 75.85, 38.24, 39.02, 39.78, 38.27, 22.69, 30.27, 26.18, 22.03.

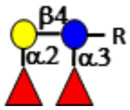
MALDI TOF-MS *m/z* calcd for $C_{44}H_{66}N_5O_{24}Na_2$ $(M + 2Na)^+$ exact 1094.3899, found 1094.3593.



7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)



40

^{1}H (600 MHz, D_2O): δ (ppm)

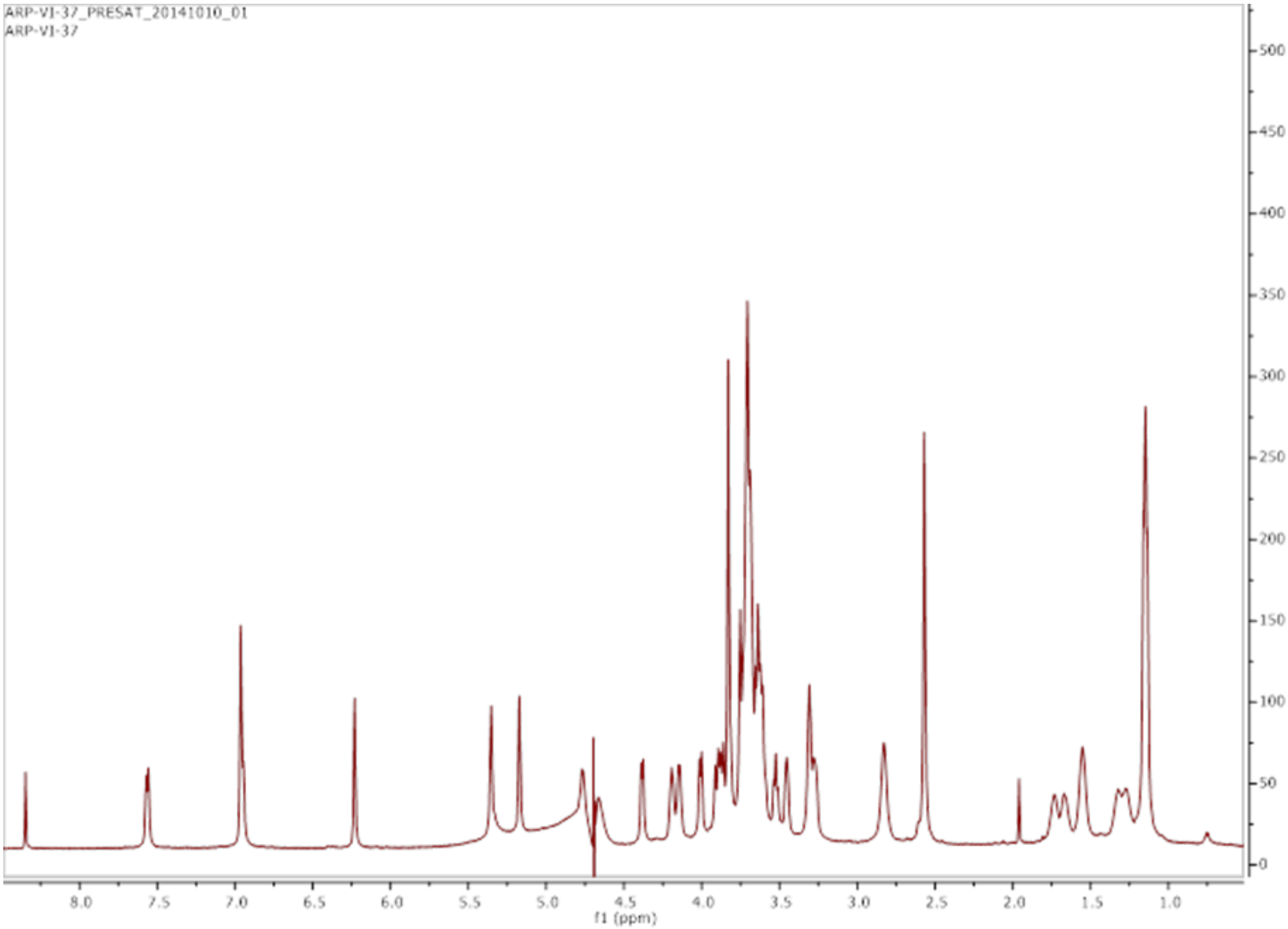
	H1	H2	H3	H4	H5	H6	CH_3
Glc	4.00 (d, *J* = 8.0 Hz, 1H)	3.63	3.26	3.71	n/a[a]	n/a	-
Gal	4.37 (d, *J* = 7.4 Hz, 1H)	3.51	n/a	3.72	n/a	n/a	-
Fuc(1)	5.12	3.68	n/a	n/a	4.14	-	1.14
Fuc(2)	5.35	3.68	3.87	n/a	4.75	-	1.14

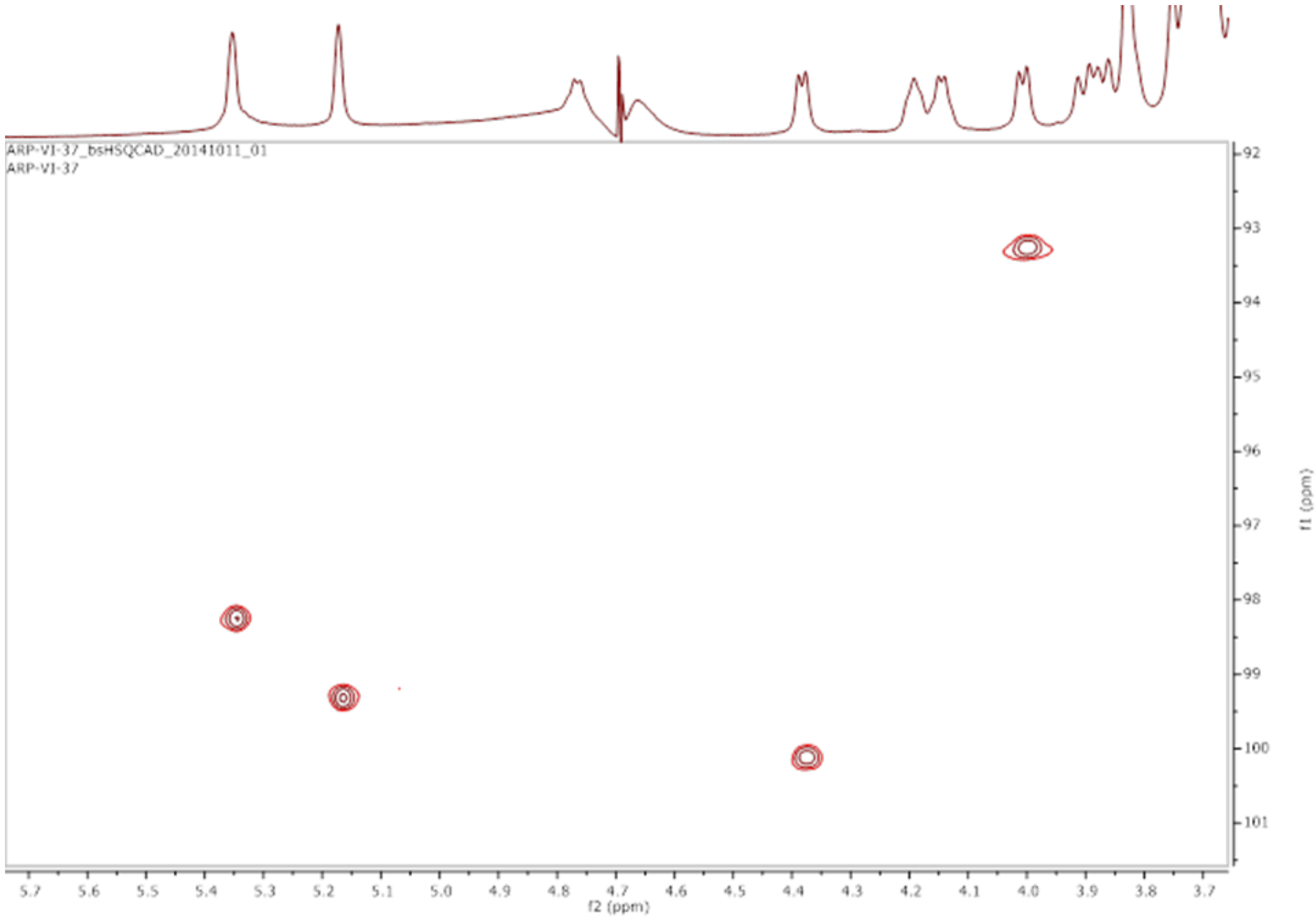
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

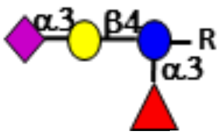
	C1
Glc	93.27
Gal	100.13
Fuc(1)	99.32
Fuc(2)	98.25

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd for $C_{45}H_{70}N_4O_{24}Na$ $(M + Na)^+$ exact 1073.4278, found 1073.8154.


ARP-VI-37_PRESAT_20141010_01
ARP-VI-37
500
450
400
350
300
250
200
150
100
50
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


ARP-VI-37_bsHSQCAD_20141011_01
ARP-VI-37
f2 (ppm)
f1 (ppm)



41

^{1}H (600 MHz, D_2O): δ (ppm)

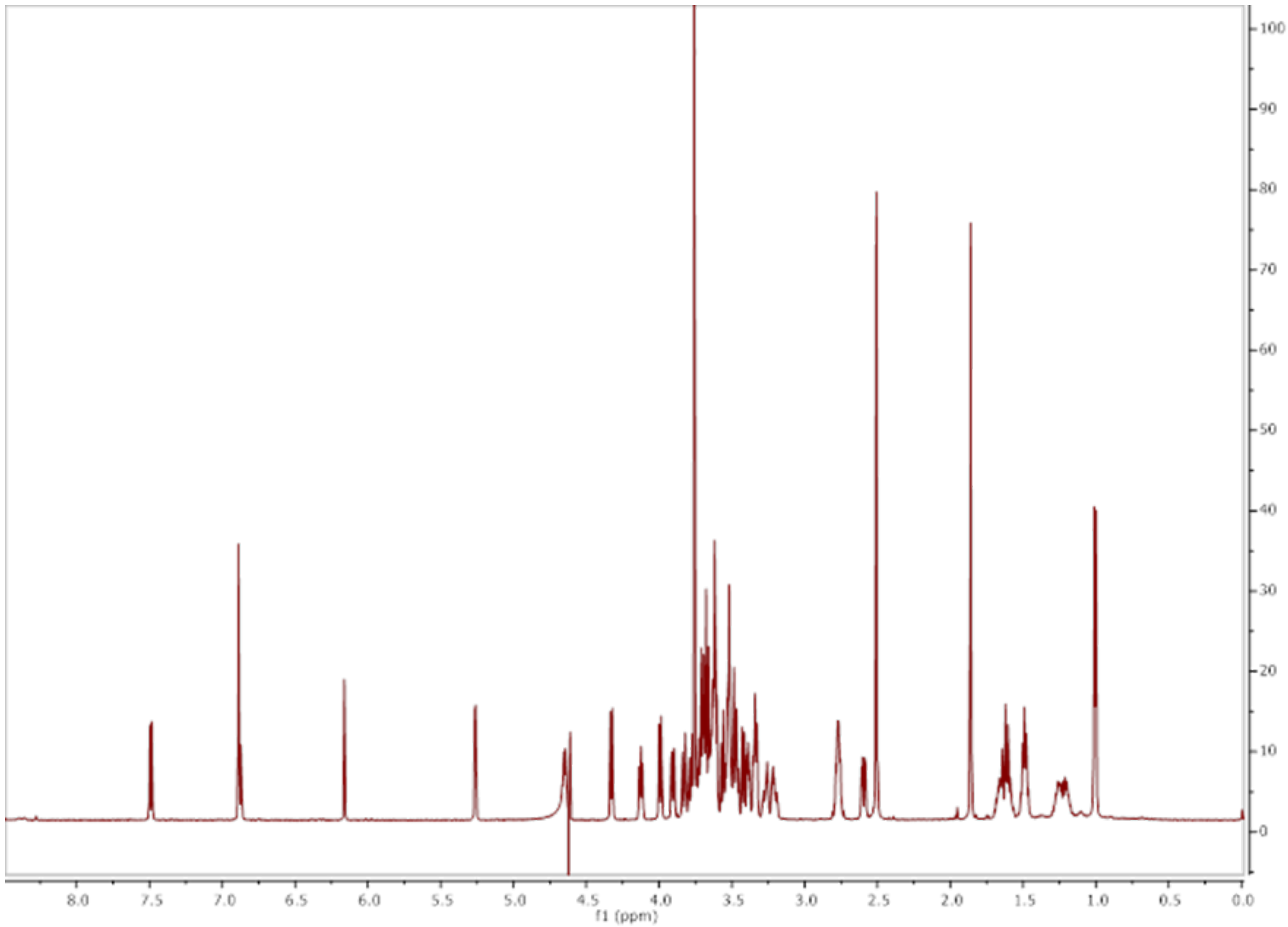
	H1	H2	H3	H4	H5	H6	NHAc	CH_3
Glc	4.00 (d, *J* = 9.1 Hz, 1H)	3.58	3.63	3.69	n/a[a]	n/a	-	-
Gal	4.33 (d, *J* = 7.79 Hz, 1H)	3.35	3.77	3.92 (dd, *J* = 9.8, 2.9 Hz, 1H)	n/a	n/a	-	-
Neu5Ac	-	-	2.61 -eq (dd, *J* = 12.4, 4.5 Hz, 1H) 1.63 - axial	3.52	3.68	n/a	1.86	-
Fuc	5.27 (d, *J* = 3.9 Hz, 1H)	3.63	3.80	3.60	4.66	-	-	1.02 (d, *J* = 6.6 Hz, 3H)

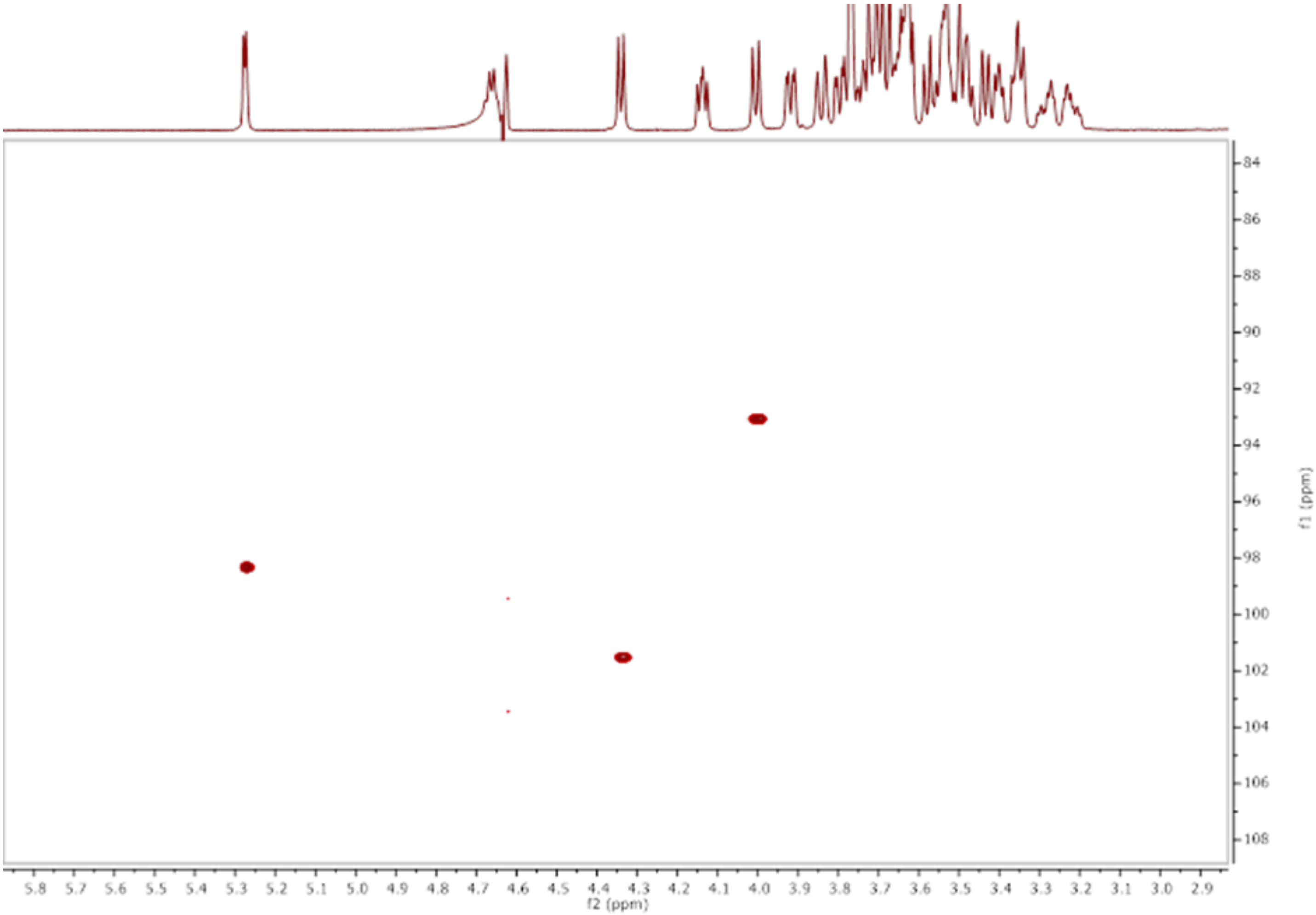
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	93.10
Gal	101.47
Fuc	98.33

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd for $C_{50}H_{76}N_5O_{28}$ Na_2 $(M + 2Na)^+$ exact 1240.4478, found 1240.3639.


100
90
80
70
60
50
40
30
20
10
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



84
86
88
90
92
94
96
98
100
102
104
106
108
f1 (ppm)
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9
f2 (ppm)

42

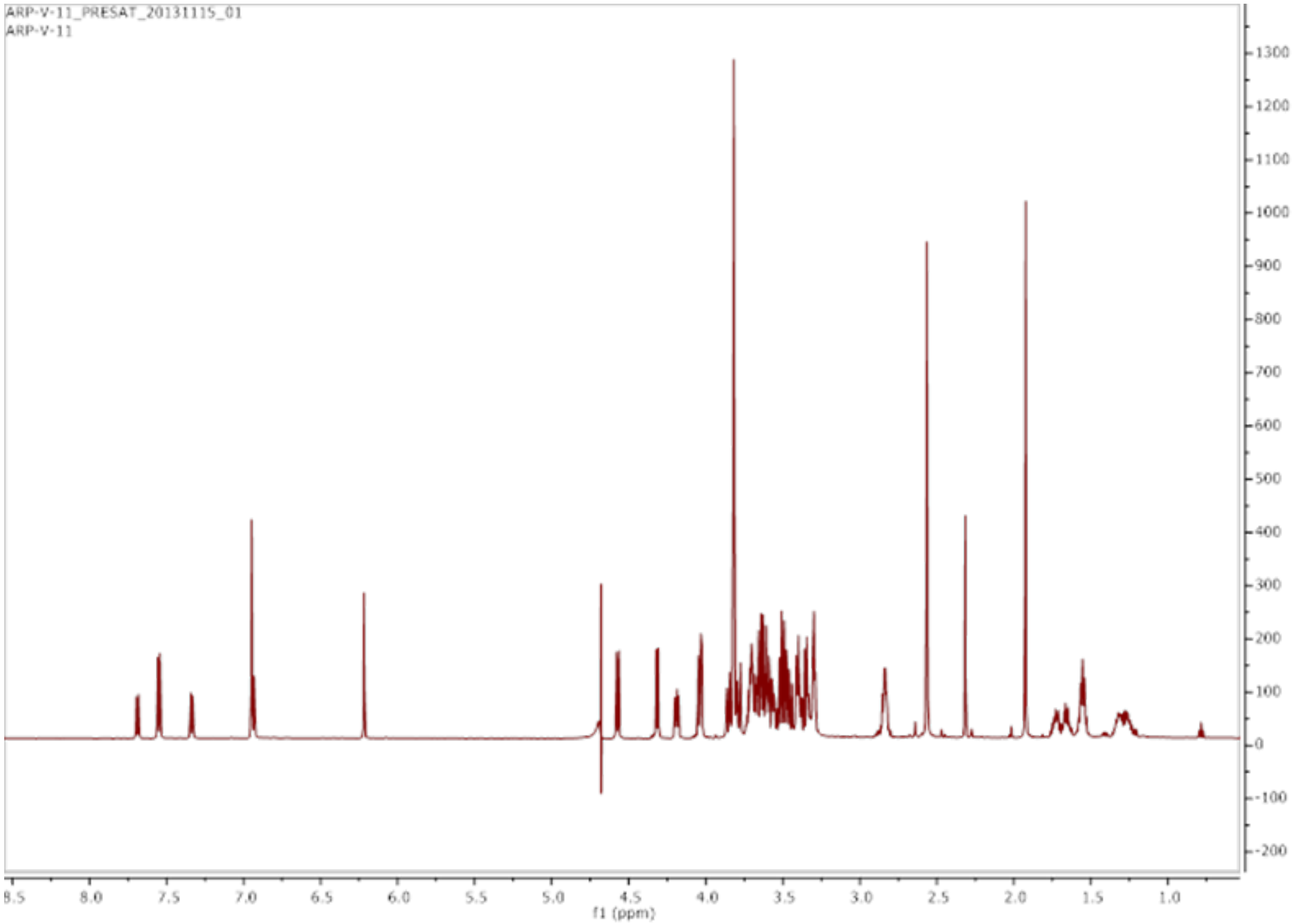
^{1}H (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	NHAc
Glc	4.03	3.39	3.46	3.65	3.34	-[a]	n/a[b]
Gal	4.30 (d, *J* = 7.9 Hz, 1H)	3.45	3.58	4.02	3.55	-	n/a
GlcNAc	4.56 (d, *J* = 8.4 Hz, 1H)	3.63	3.33	3.45	-	-	1.90

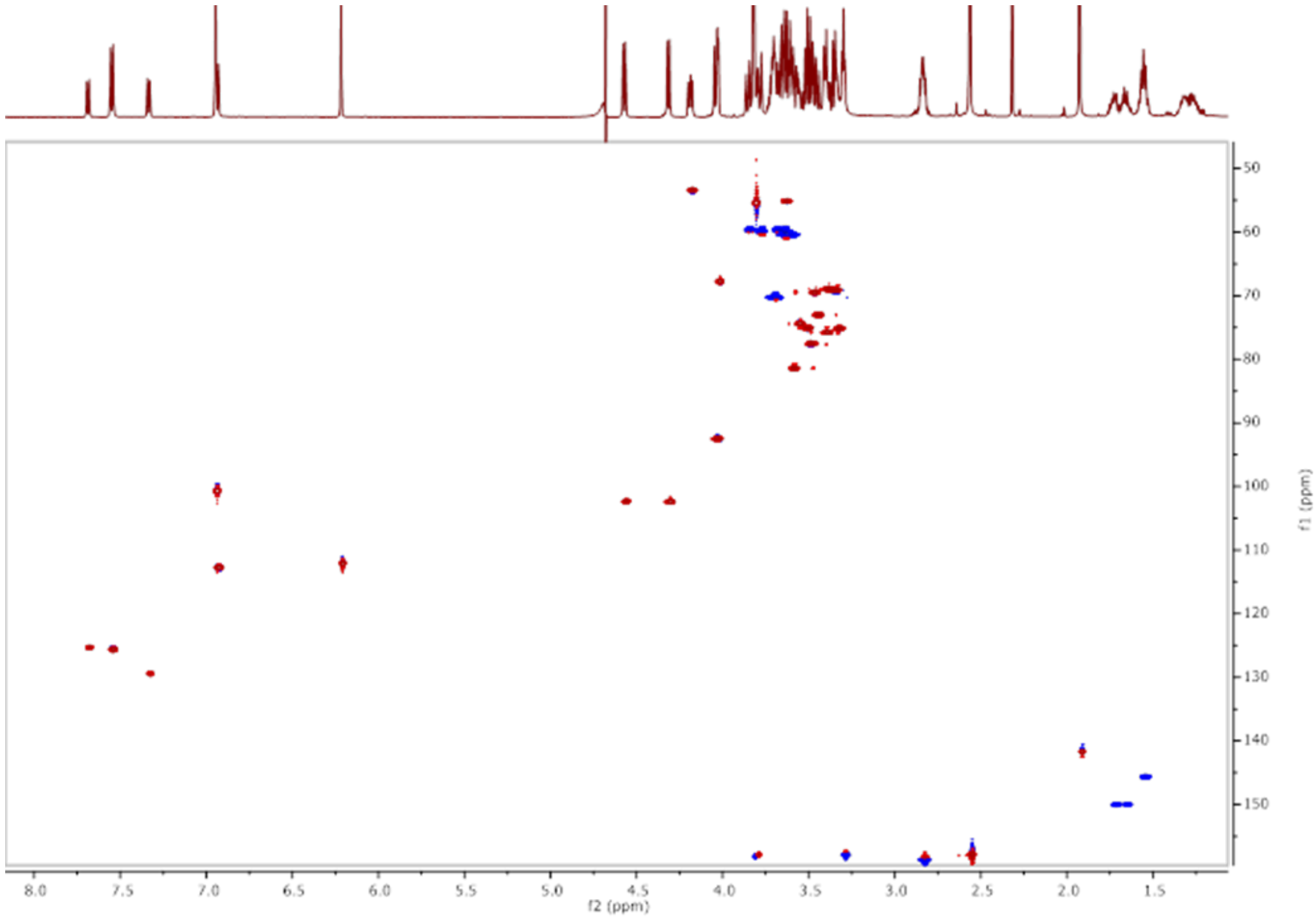
[a] Not assigned
[b] Not applicable

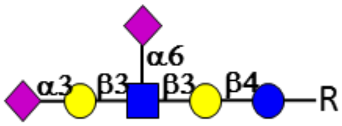
^{13}C from HSQC (150 MHz, D_2O): δ (ppm) 53.38, 54.64, 54.91, 55.11, 55.38, 55.86, 56.45, 59.59, 59.59, 59.60, 59.86, 59.88, 59.88, 60.36, 60.43, 60.92, 67.77, 68.96, 69.03, 69.11, 69.42, 69.46, 70.24, 70.73, 73.00, 74.35, 75.03, 75.07, 75.13, 75.76, 77.52, 77.98, 81.41, 81.41, 92.47, 92.94, 100.66, 101.43, 102.35, 102.38, 112.56, 112.71, 125.59, 141.22, 141.70, 145.67, 150.02, 150.03, 157.88, 157.89, 157.89, 158.14, 158.72.

MALDI TOF-MS *m/z* calcd for $C_{41}H_{63}N_5O_{21}Na$ $(M + Na)^+$ exact 984.3913, found 984.2182.



ARP-V-11_PRESAT_20131115_01
ARP-V-11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


f1 (ppm)
f2 (ppm)



45

^{1}H (800 MHz, D_2O): δ (ppm)

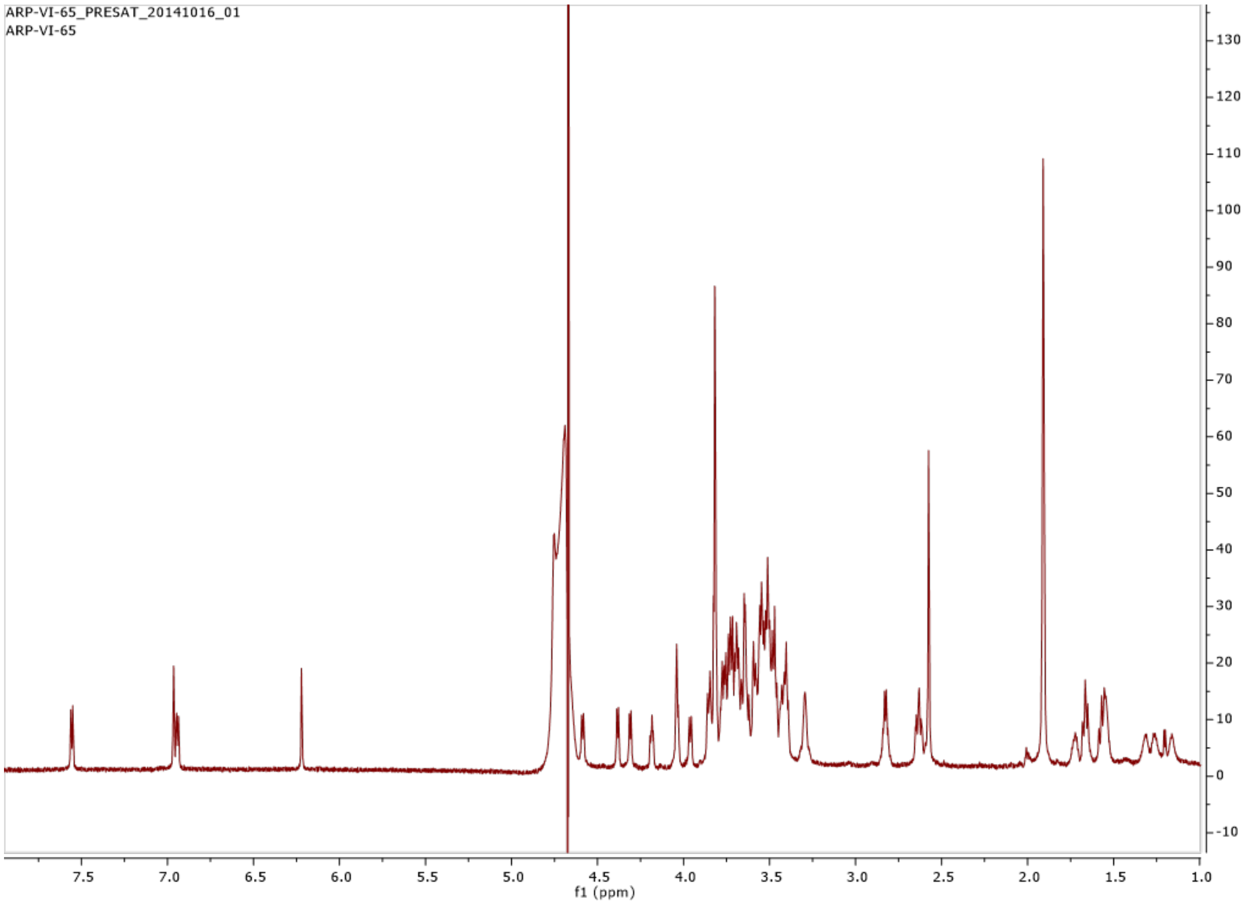
	H1	H2	H3	H4	H5	H6	H9	NHAc
Glc	4.03	3.39	3.46	3.65	3.34	-[a]	n/a	n/a[b]
Gal	4.30	3.45	3.58	4.02	3.53	-	n/a	n/a
GlcNAc	4.58	3.76	3.67	3.43	3.34	-	n/a	1.90 (s, 9H)
Gal(2)	4.37	3.41	3.80	3.95	3.54	-	n/a	n/a
Neu5Ac α2,3	n/a	n/a	2.63 – eq 1.64 - axial	3.54	-	-	3.75 3.52	1.90 (s, 9H)
Neu5Ac α2,6	n/a	n/a	2.63 – eq 1.64 - axial	3.54	-	-	3.75 3.52	1.90 (s, 9H)

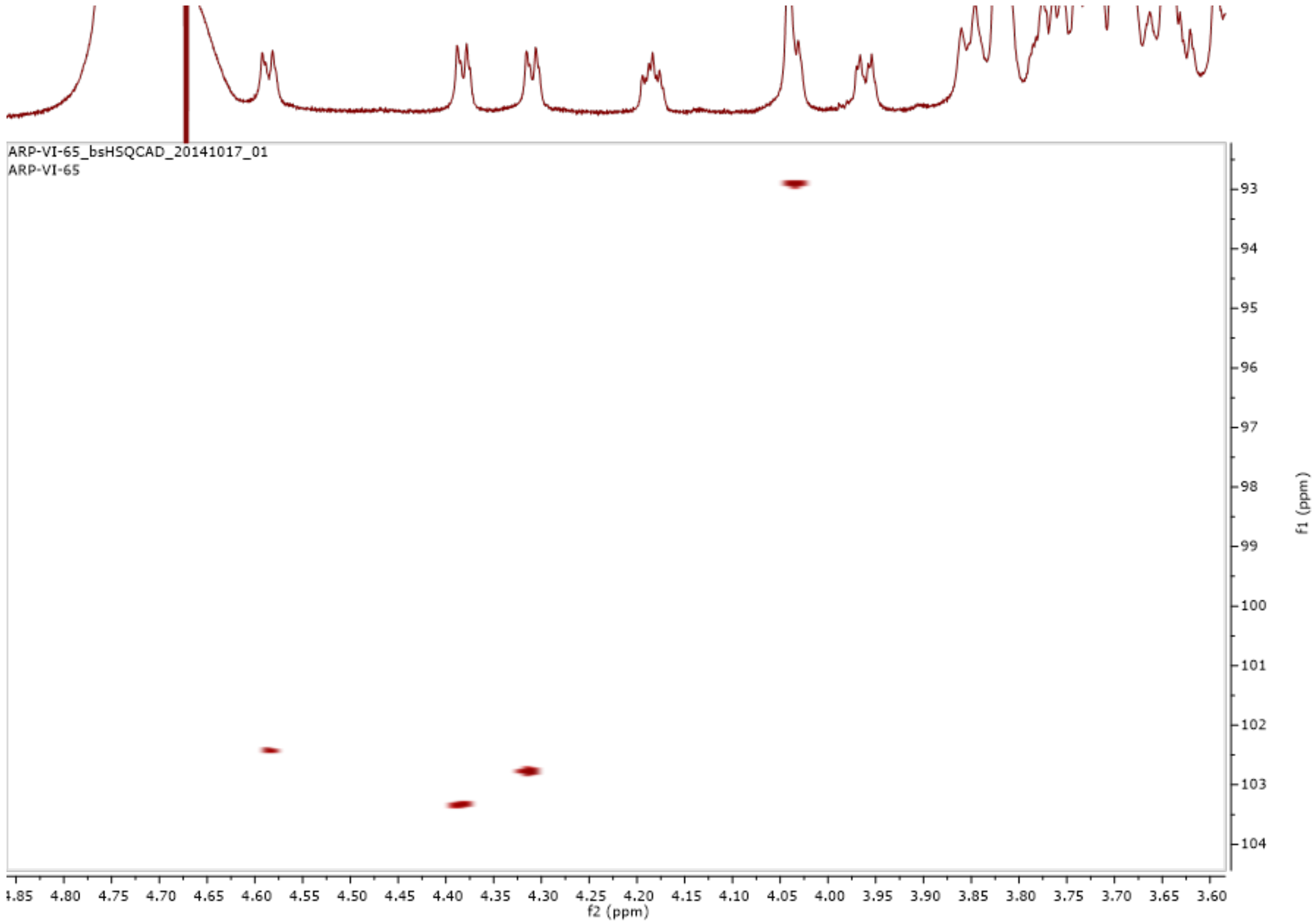
^{13}C (200 MHz, D_2O): δ (ppm)

	C1
Glc	92.87
Gal	102.79
GlcNAc	102.47
Gal(2)	103.34

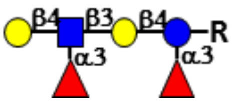
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd for $C_{69}H_{105}N_7O_{42}Na$ $(M -2H + Na)^-$ exact 1726.6193, found 1726.4392.


ARP-VI-65_PRESAT_20141016_01
ARP-VI-65
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



ARP-VI-65_bsHSQCAD_20141017_01
ARP-VI-65
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

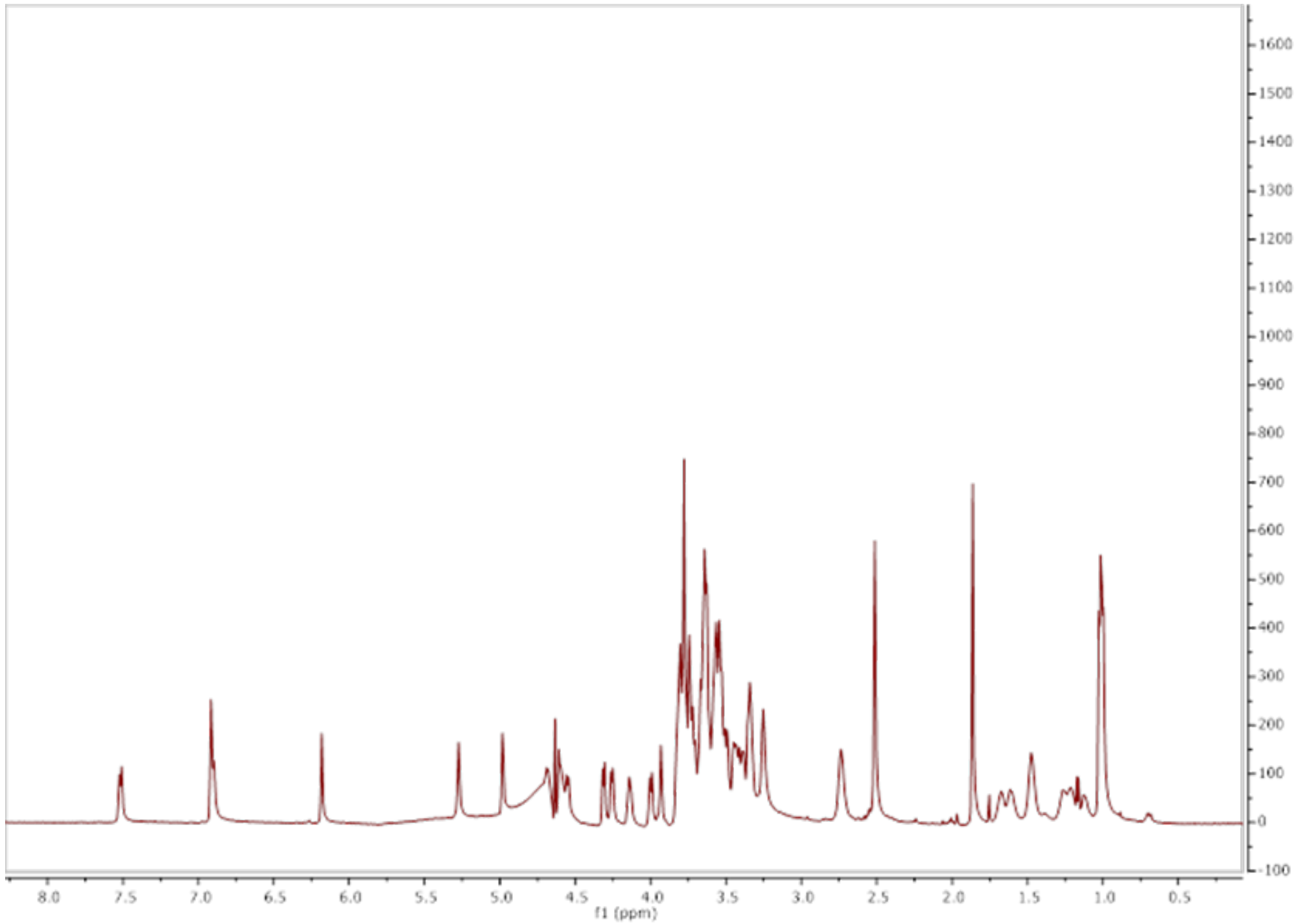
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.8 Hz, 1H)	3.59	3.34	3.64	n/a[a]	n/a	-[b]	-
Gal	4.25 (d, *J* = 7.1 Hz, 1H)	3.31	3.53	3.93	3.39	n/a	-	-
GlcNAc	4.54 (d, *J* = 7.9 Hz, 1H)	3.81	3.87	3.49	n/a	n/a	-	1.85
Gal(2)	4.31 (d, *J* = 7.5 Hz, 1H)	3.32	3.49	3.74	3.45	n/a	-	-
Fuc	5.25	3.61	3.79	3.61	4.67	-	1.01	-
Fuc(2)	4.95	3.52	3.75	3.61	4.67	n/a	1.01	-

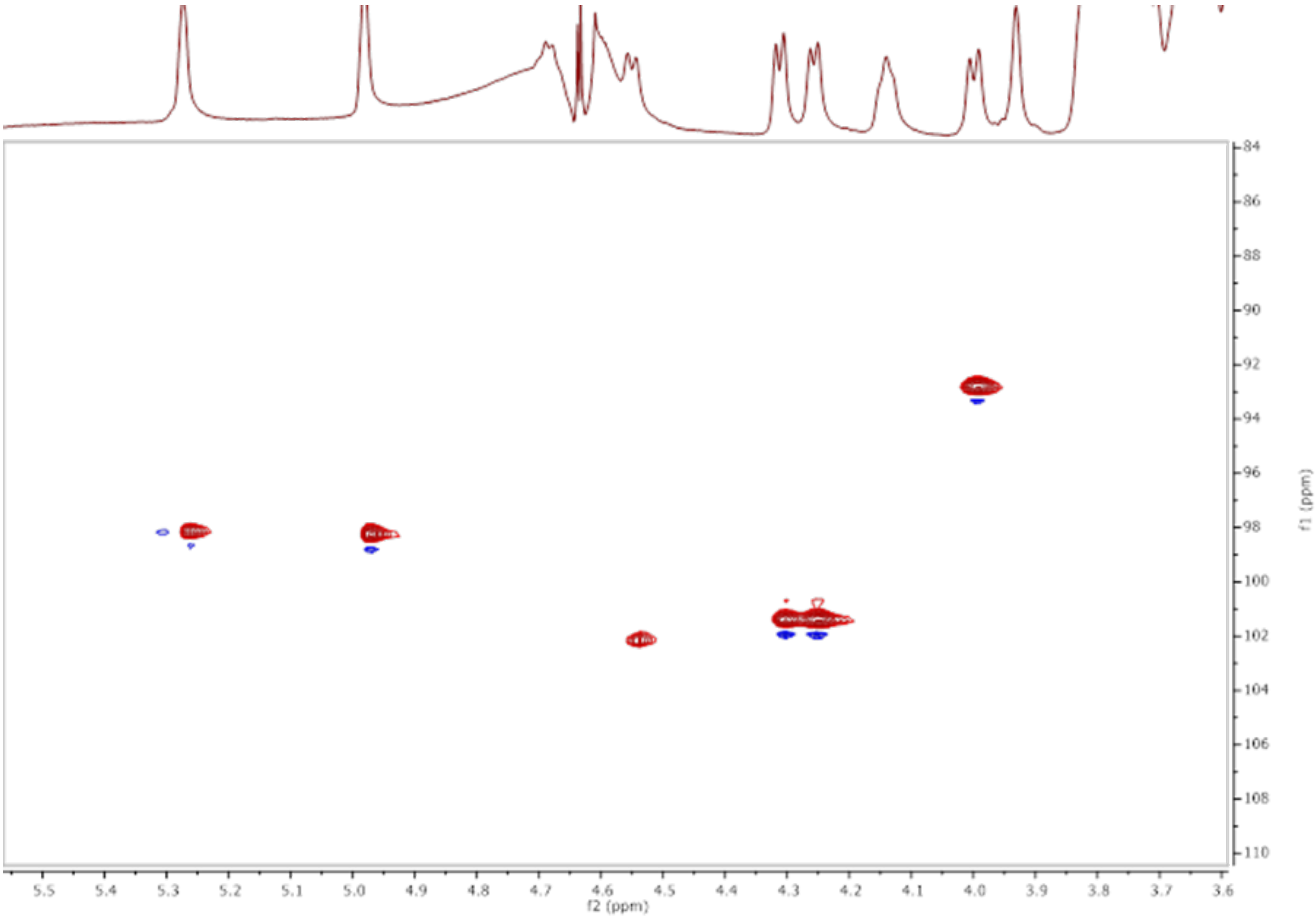
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

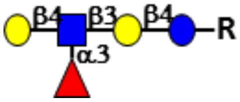
	C1
Glc	92.73
Gal	101.29
GlcNAc	102.17
Gal(2)	101.37
Fuc	98.12
Fuc(2)	98.17

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{59}H_{93}N_5O_{34}Na$ $(M + Na)^+$ exact 1438.5600, found 1438.3550.


f1 (ppm)


f2 (ppm)
f1 (ppm)



47

^{1}H (600 MHz, D_2O): δ (ppm)

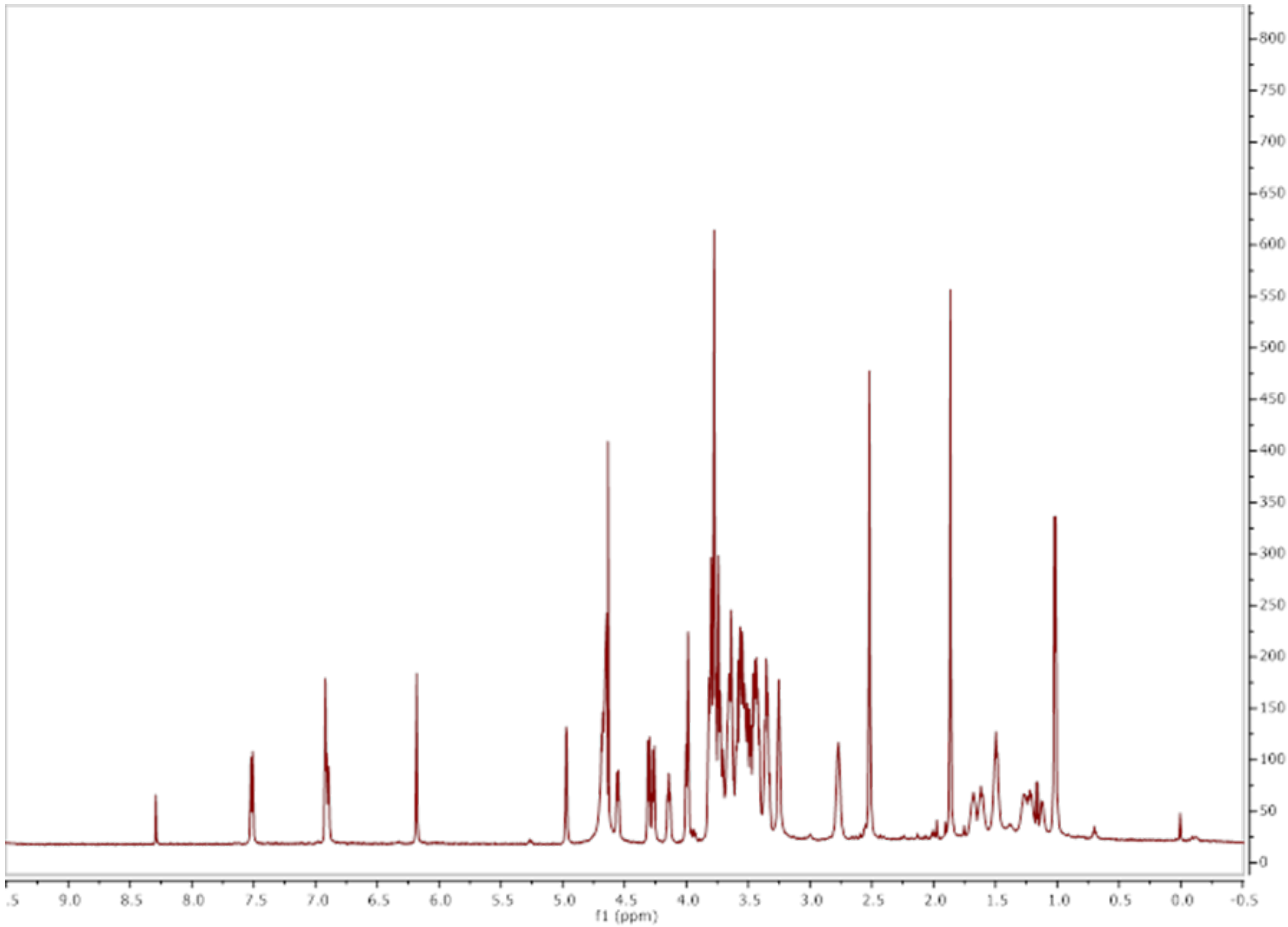
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.54	3.46	n/a[a]	n/a	-[b]	-
Gal	4.27 (d, J = 7.9 Hz, 1H)	3.42	3.54	3.98	n/a	n/a	-	-
GlcNAc	4.56 (d, J = 7.9 Hz, 1H)	3.80	3.72	3.42	n/a	n/a	-	1.86 (s, 3H)
Gal(2)	4.30 (d, J = 7.7 Hz, 1H)	3.33	3.49	3.73	n/a	n/a	-	-
Fuc	4.98 (d, J = 3.4 Hz, 1H)	3.53	3.74	3.63	4.67	-	1.02 (d, J = 6.4 Hz, 3H)	-

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

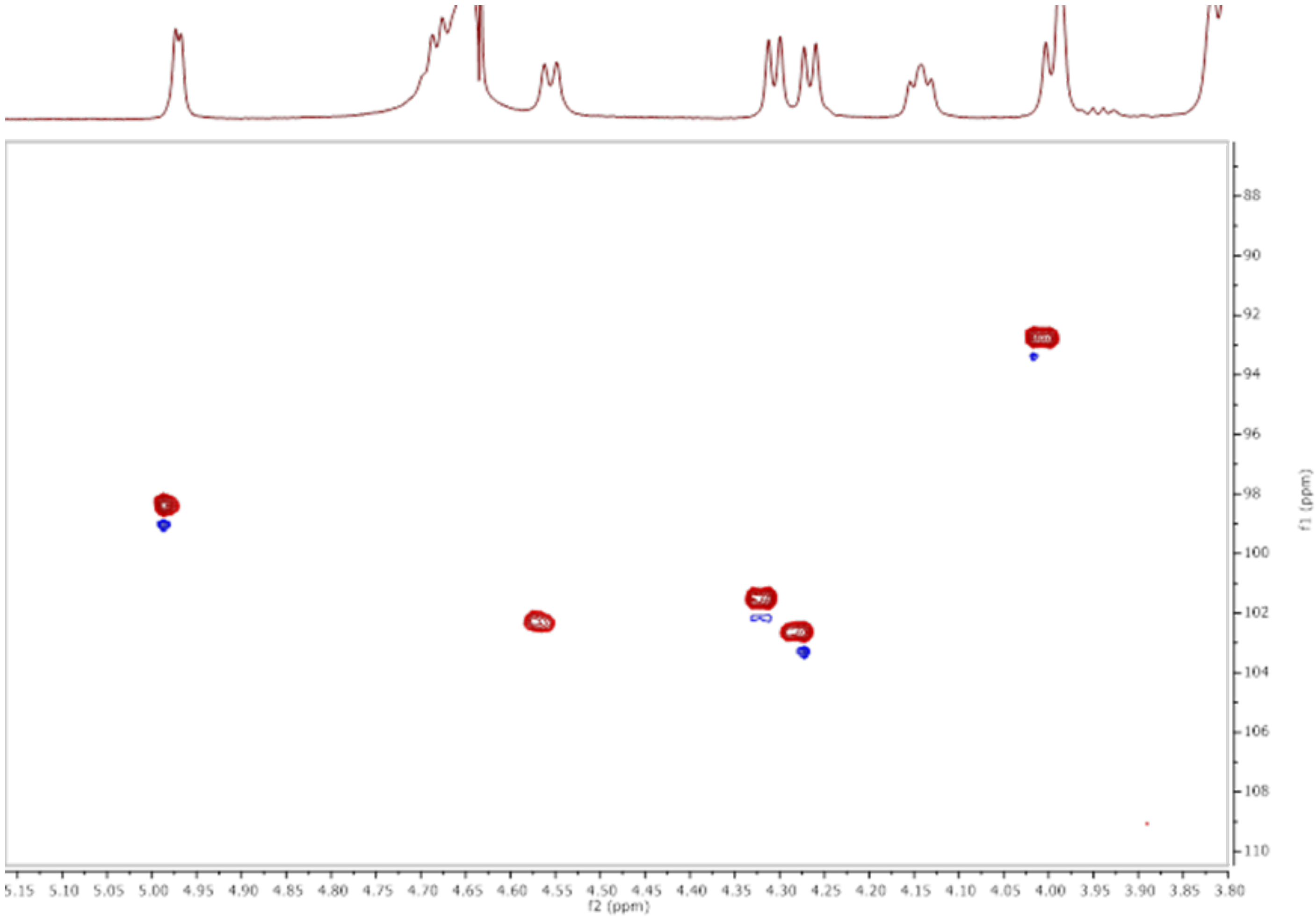
	C1
Glc	92.73
Gal	102.66
GlcNAc	103.38
Gal(2)	101.51
Fuc	93.30

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{53}H_{83}N_5O_{30}Na$ $(M + Na)^+$ exact 1292.5021, found 1292.3600.



f1 (ppm)



88
90
92
94
96
98
100
102
104
106
108
110
f1 (ppm)
5.15 5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80
f2 (ppm)

48

^{1}H (600 MHz, D_2O): δ (ppm)

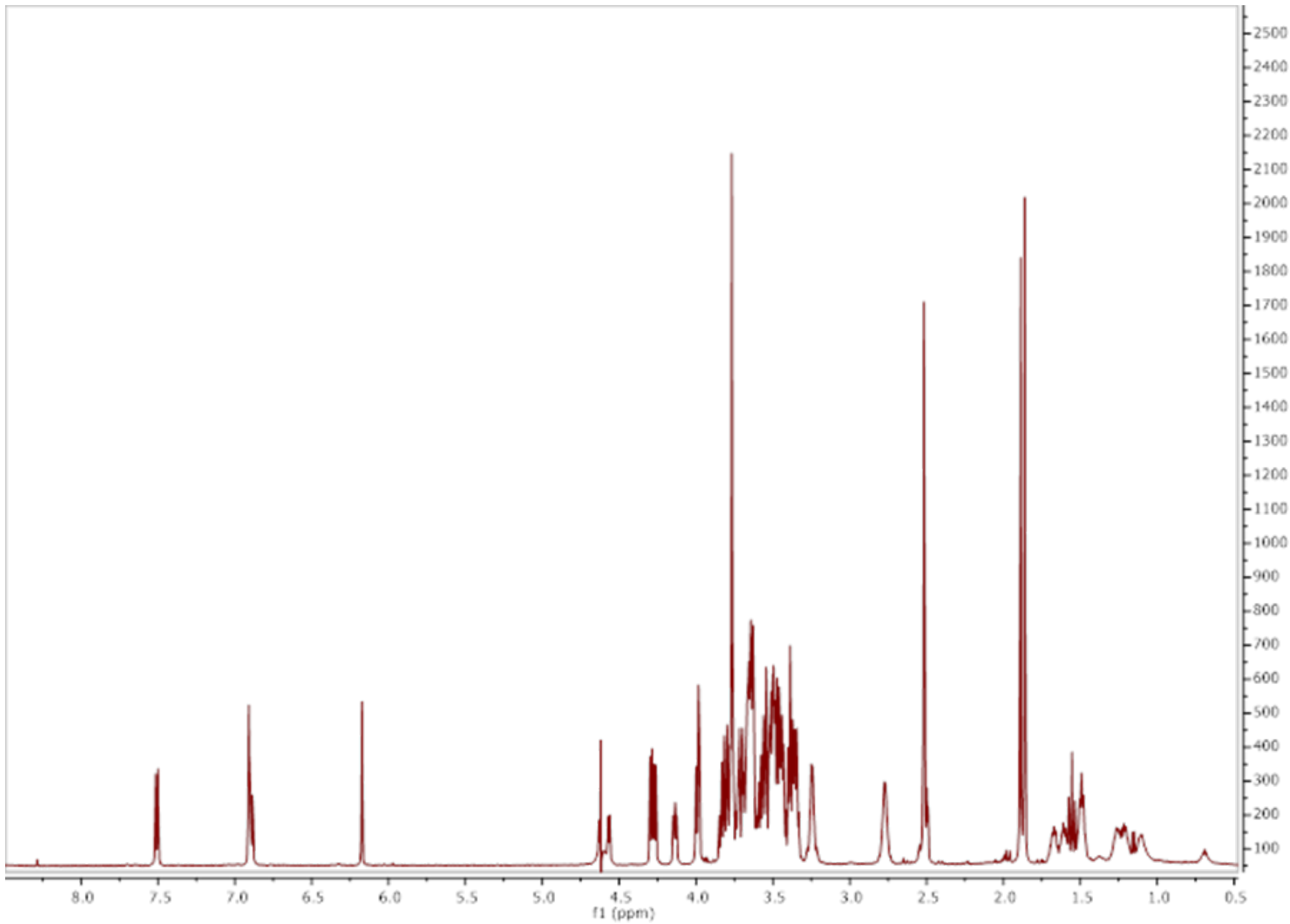
	H1	H2	H3	H4	H5	H6	H9	NHAc
Glc	4.00	3.57	3.46	n/a[a]	n/a	n/a	-	-
Gal	4.28 (d, J = 7.9 Hz, 1H)	3.45	3.56	3.99	n/a	n/a	-	-
GlcNAc	4.58 (d, J = 7.5 Hz, 1H)	3.65	3.51		n/a	n/a	-	1.90 – 1.85 6H
Gal(2)	4.30 (d, J = 7.9 Hz, 1H)	3.83	3.52	3.78	n/a	n/a	-	-
Neu5Ac	-	-	2.52 - eq 1.55 - axial (dd, J = 12.2 Hz, 1H)	3.50	3.66	3.55	3.72 3.49	1.90 – 1.85 6H

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

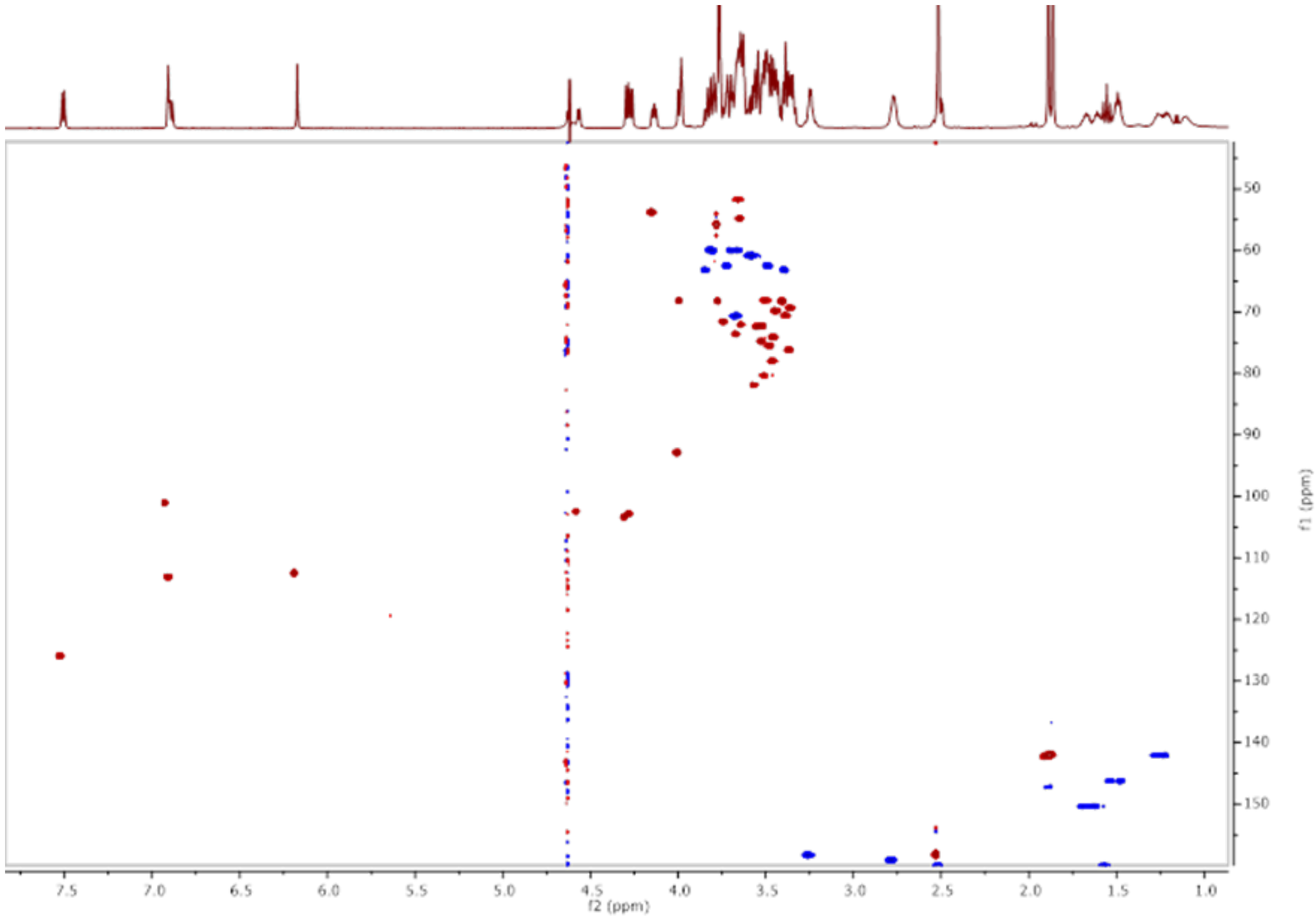
	C1
Glc	92.89
Gal	102.84
GlcNAc	102.47
Gal(2)	103.35

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd for $C_{58}H_{89}N_6O_{34}Na_2$ (M + 2Na)$^{+}$ exact 1459.5221, found 1459.2794.



2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

50

^{1}H (800 MHz, D_2O): δ (ppm)

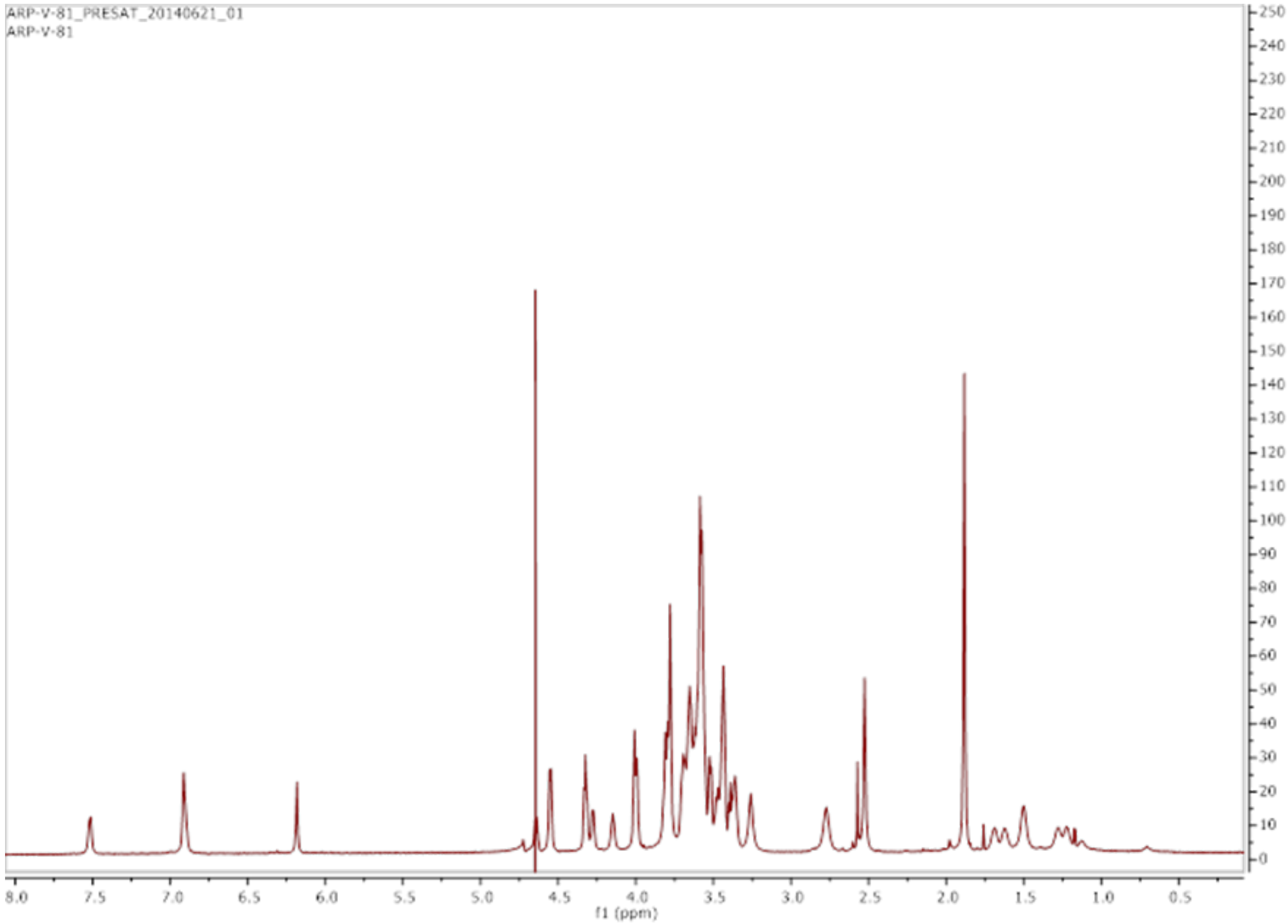
	H1	H2	H3	H4	H5	H6	NHAc
Glc	4.00	3.36	3.45	3.57	n/a[a]	n/a	-[b]
Gal	4.27	3.44	3.56	4.00	n/a	n/a	-
GlcNAc	4.56	3.66	3.58	3.43	n/a	n/a	1.88 (br. s, 6H)
Gal(2)	4.33	3.39	3.51	3.78	n/a	n/a	-
GlcNAc(2)	4.56	3.66	3.58	3.43	n/a	n/a	1.88 (br. S, 6H)
Gal(3)	4.31	3.43	3.58	4.00	n/a	n/a	-

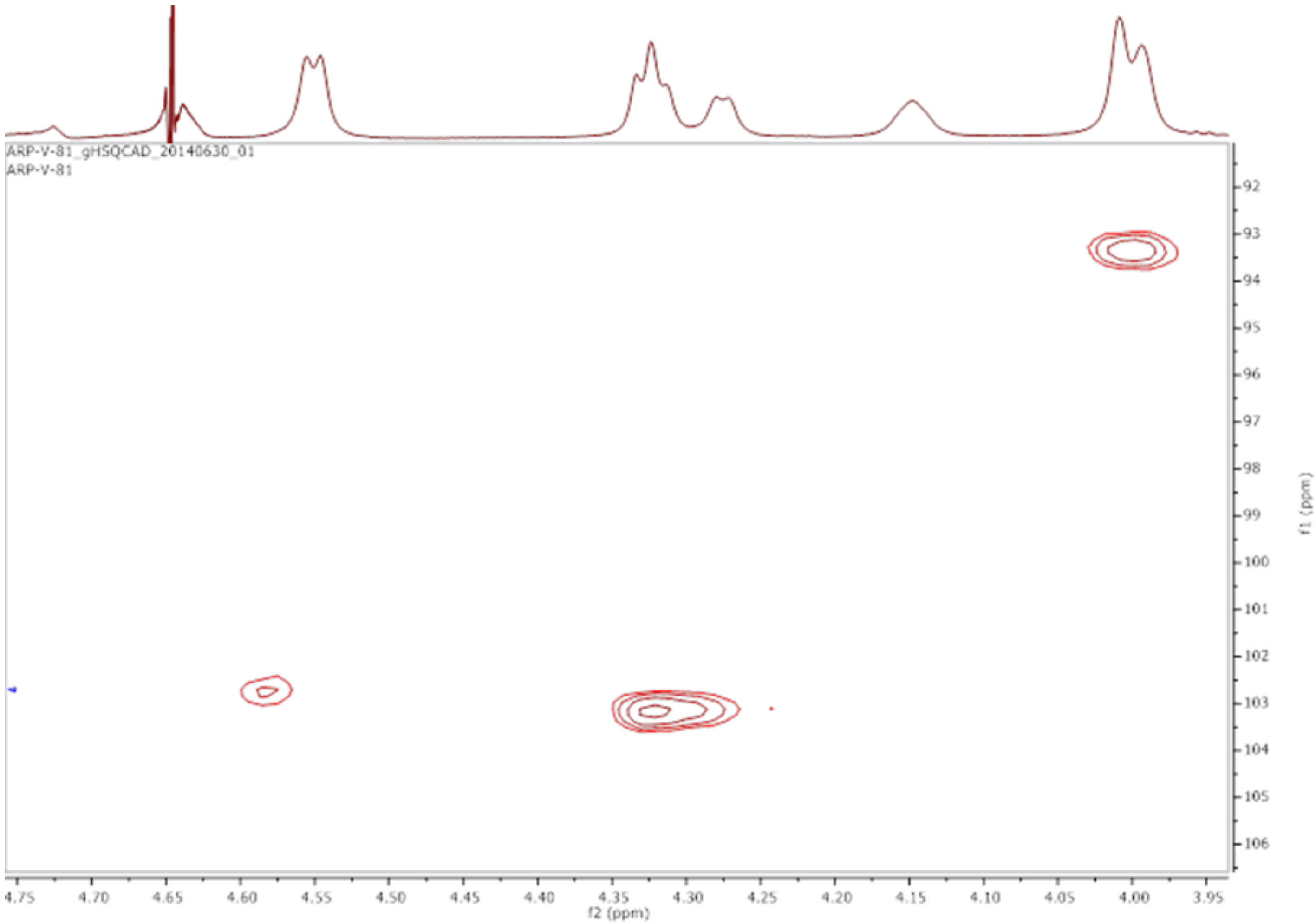
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

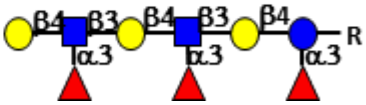
	C1
Glc	93.42
Gal	103.15
GlcNAc	102.69
Gal(2)	103.15
GlcNAc(2)	102.69
Gal(3)	103.15

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{61}H_{96}N_6O_{36}Na$ $(M + Na)^+$ exact 1511.5763, found 1511.4916.


ARP-V-81_PRESAT_20140621_01
ARP-V-81
f1 (ppm)


ARP-V-81_gHSQCAD_20140630_01
ARP-V-81
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
f1 (ppm)
4.75
4.70
4.65
4.60
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
f2 (ppm)



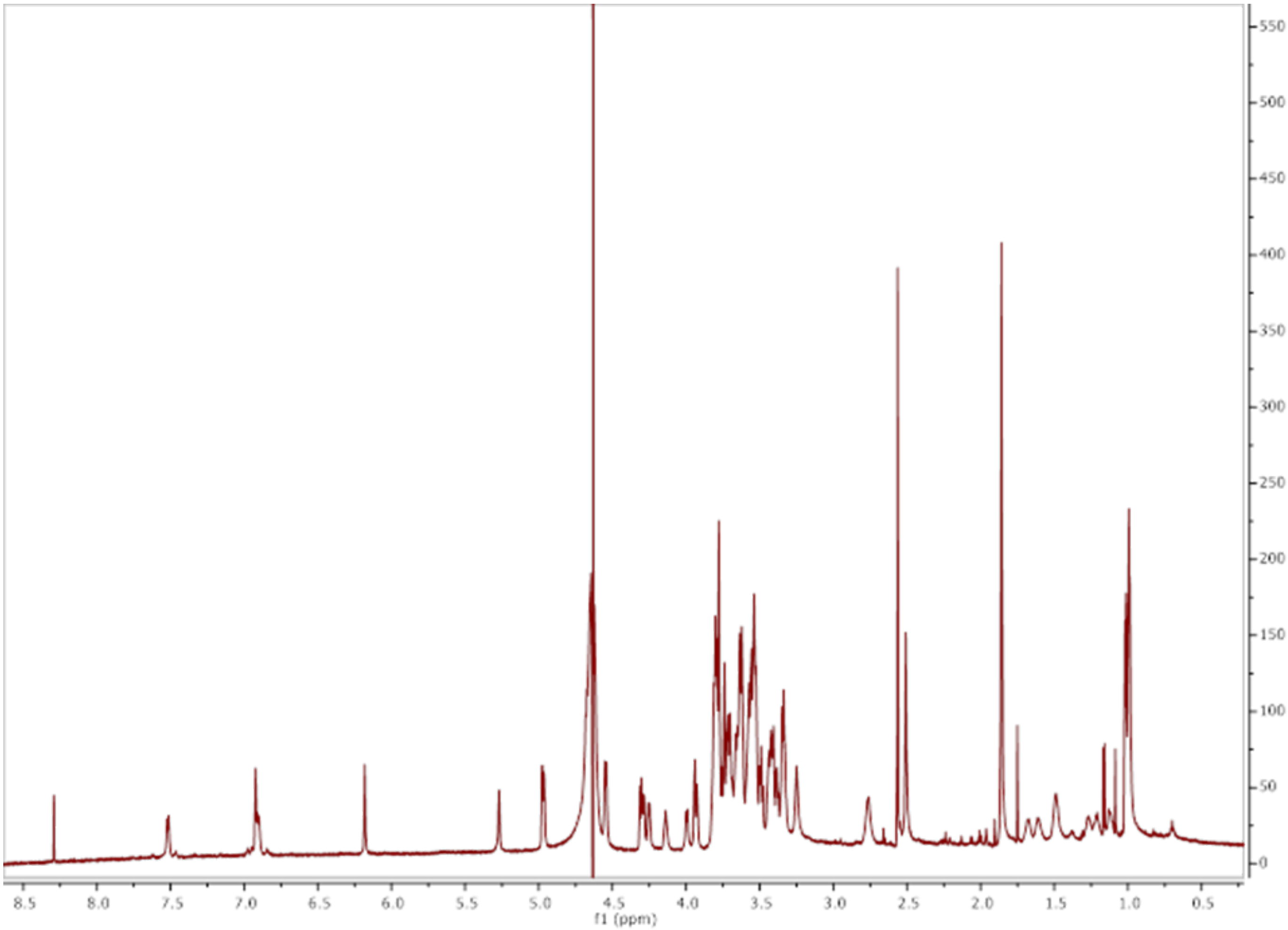
51

^{1}H (800 MHz, D_2O): δ (ppm)

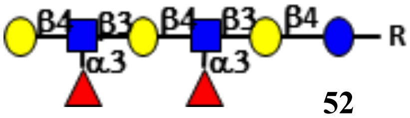
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.6 Hz, 1H)	3.58	3.64	3.68	n/a[a]	n/a	-[b]	-
Gal	4.26	3.35	3.55	3.94	n/a	n/a	-	-
GlcNAc	4.56 (d, *J* = 8.3 Hz, 2H)	3.82	3.73	3.43	n/a	n/a	-	1.86 (s, 6H)
Gal(2)	4.30	3.36	3.56	3.94	n/a	n/a	-	-
GlcNAc(2)	4.56 (d, *J* = 8.3 Hz, 2H)	3.82	3.73	3.43	n/a	n/a	-	1.86 (s, 6H)
Gal(3)	4.32	3.36	3.51	3.75	n/a	n/a	-	-
Fuc(1)	5.27	3.65	3.80	n/a	4.68	-	1.02 – 0.94 (m, 9H)	-
Fuc(2)	4.97	3.55	3.75	3.64	4.68	-	1.02 – 0.94 (m, 9H)	-
Fuc(3)	4.97	3.55	3.75	3.64	4.68	-	1.02 – 0.94 (m, 9H)	-

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{79}H_{126}N_6O_{48}Na$ $(M + Na)^+$ exact 1949.7501, found 1950.0043.



550
500
450
400
350
300
250
200
150
100
50
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



52

^{1}H (800 MHz, D_2O): δ (ppm)

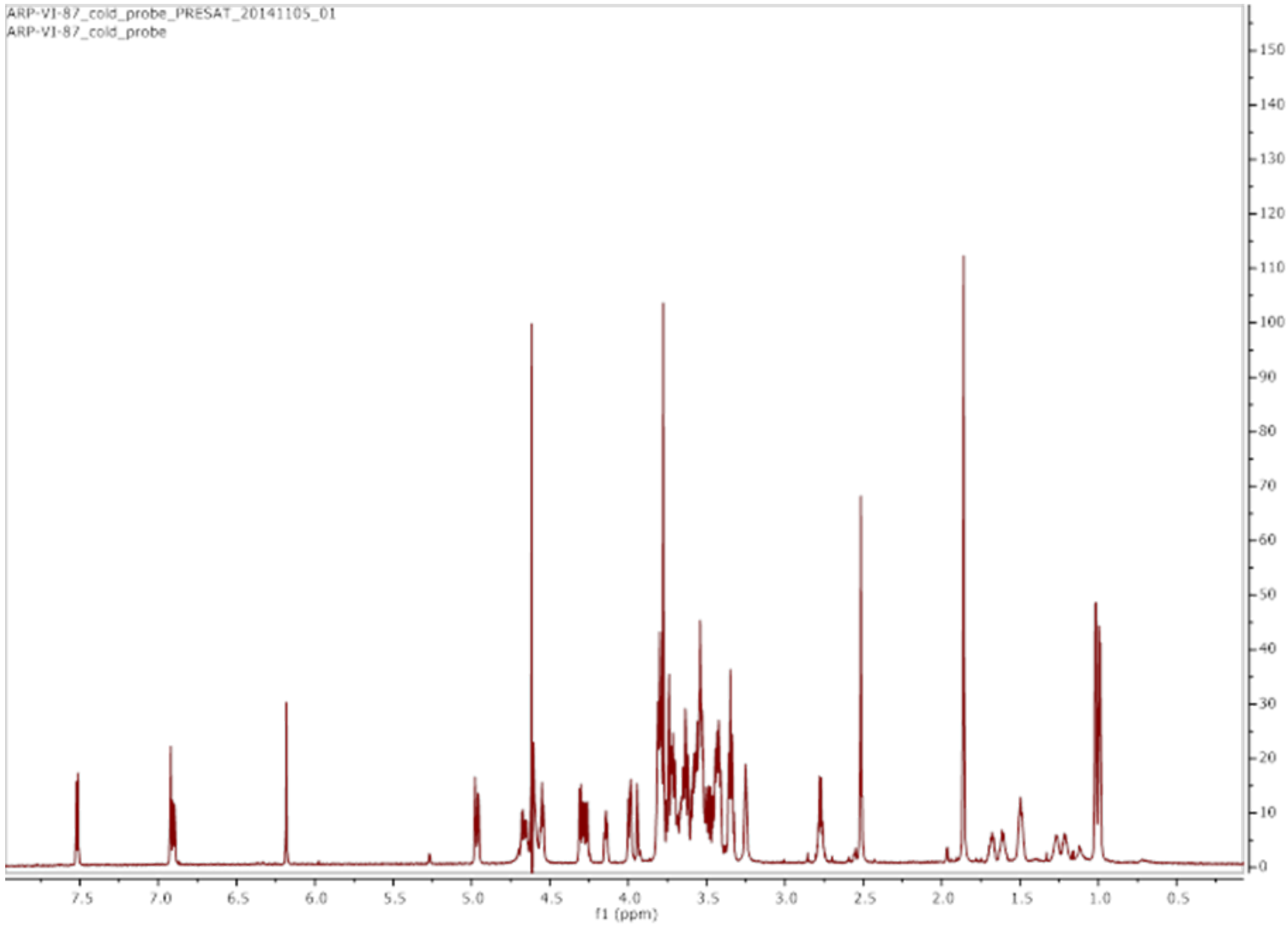
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.45	3.55	n/a[a]	n/a	-[b]	-
Gal	4.27 (d, *J* = 7.9 Hz, 1H)	3.42	3.54	4.00	n/a	n/a	-	-
GlcNAc	4.54	3.80	3.73	3.43	n/a	n/a	-	1.86 (s, 6H)
Gal(2)	4.30 (d, *J* = 7.8 Hz, 1H)	3.35	3.56	3.95 (d, *J* = 2.7 Hz, 1H)	n/a	n/a	-	-
GlcNAc(2)	4.54	3.80	3.73	3.43	n/a	n/a	-	1.86 (s, 6H)
Gal(3)	4.32 (d, *J* = 7.8 Hz, 1H)	3.34	3.50	3.75	n/a	n/a	-	-
Fuc(1)	4.95 (d, *J* = 3.8 Hz, 1H)	3.53	3.74	3.63	4.64	-	0.99 (d, *J* = 6.5 Hz, 3H)	-
Fuc(2)	4.97 (d, *J* = 3.9 Hz, 1H)	3.53	3.76	3.64	4.67	-	1.02 (d, *J* = 6.6 Hz, 3H)	-

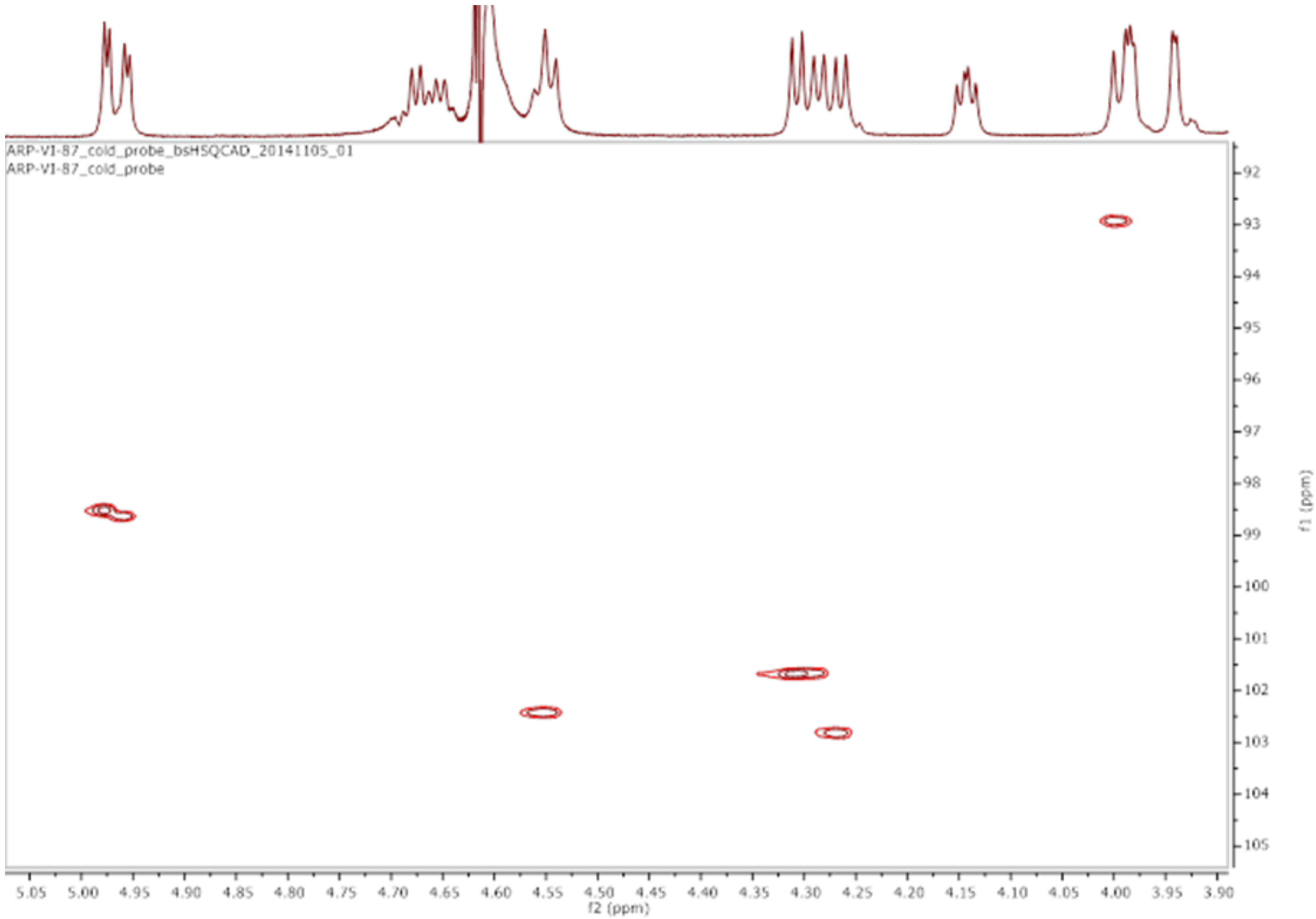
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

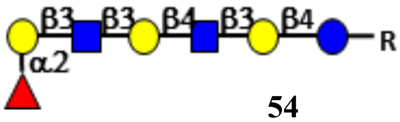
	C1
Glc	93.93
Gal	102.84
GlcNAc	102.43
Gal(2)	101.67
GlcNAc(2)	102.43
Gal(3)	101.67
Fuc(1)	98,62
Fuc(2)	98.52

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{73}H_{116}N_6O_{44}Na$ $(M + Na)^+$ exact 1803.6922, found 1804.2268.


ARP-VI-87_cold_probe_PRESAT_20141105_01
ARP-VI-87_cold_probe
f1 (ppm)


ARP-VI-87_cold_probe_bsHSQCAD_20141105_01
ARP-VI-87_cold_probe
f1 (ppm)
92
93
94
95
96
97
98
99
100
101
102
103
104
105
5.05
5.00
4.95
4.90
4.85
4.80
4.75
4.70
4.65
4.60
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
3.90
f2 (ppm)



54

^{1}H (600 MHz, D_2O): δ (ppm)

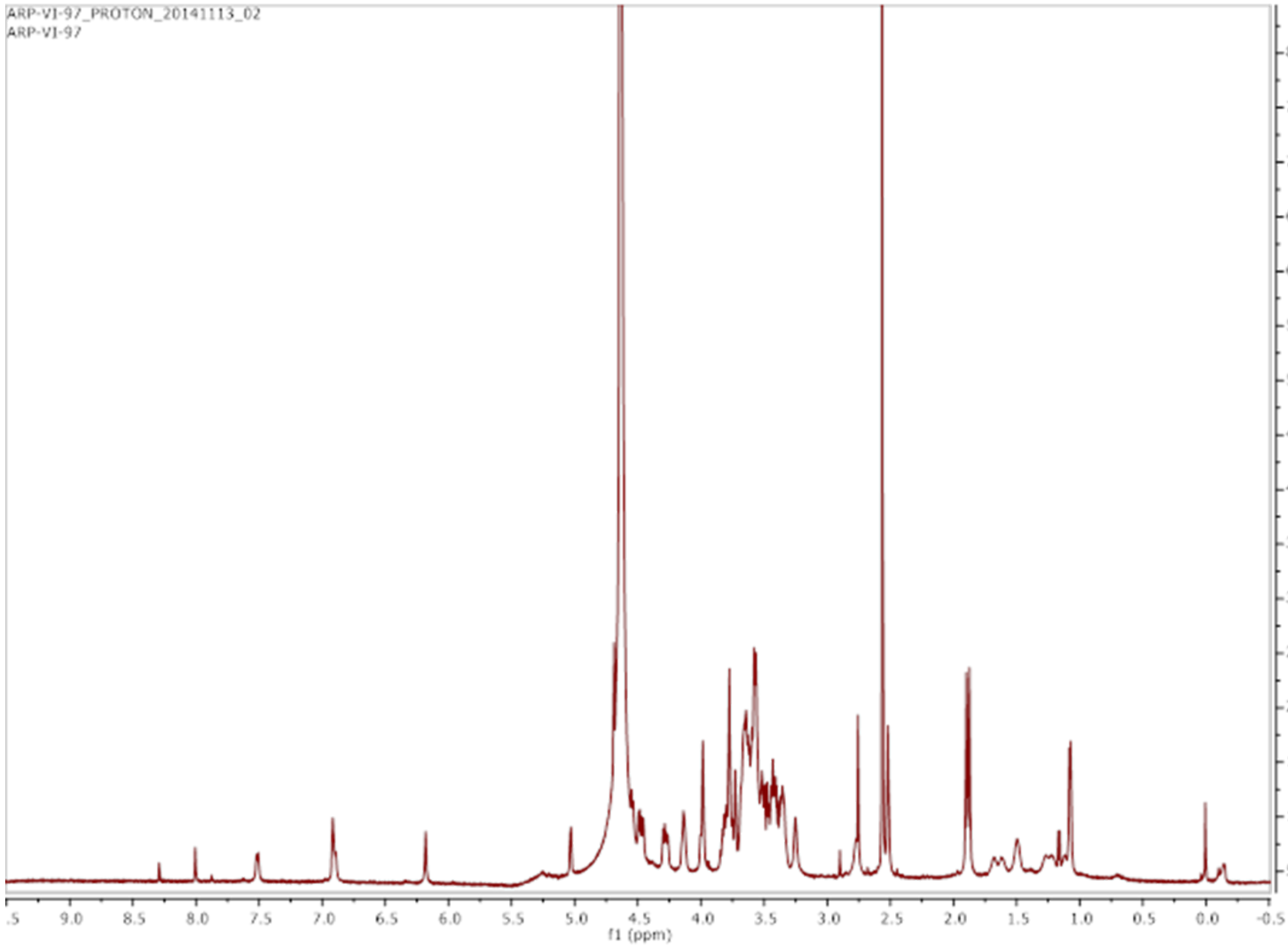
	H1	H2	H3	H4	H5	H6	NHAc	CH_3
Glc	4.00	3.36	3.45	3.57	n/a[a]	n/a	-[b]	-
Gal	4.27	3.41	3.56	3.99	n/a	n/a	-	-
GlcNAc	4.54	3.64	3.57	3.42	n/a	n/a	1.93 – 1.84 (m, 6H)	-
Gal(2)	4.27	3.41	3.56	3.99	n/a	n/a	-	-
GlcNAc(2)	4.45	3.66	3.83	3.34	n/a	n/a	1.93 – 1.84 (m, 6H)	-
Gal(3)	4.48	3.43	3.67	3.73	n/a	n/a	-	-
Fuc	5.03	3.61	3.58	n/a	4.14	-	-	1.08 (d, J = 6.0 Hz, 3H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

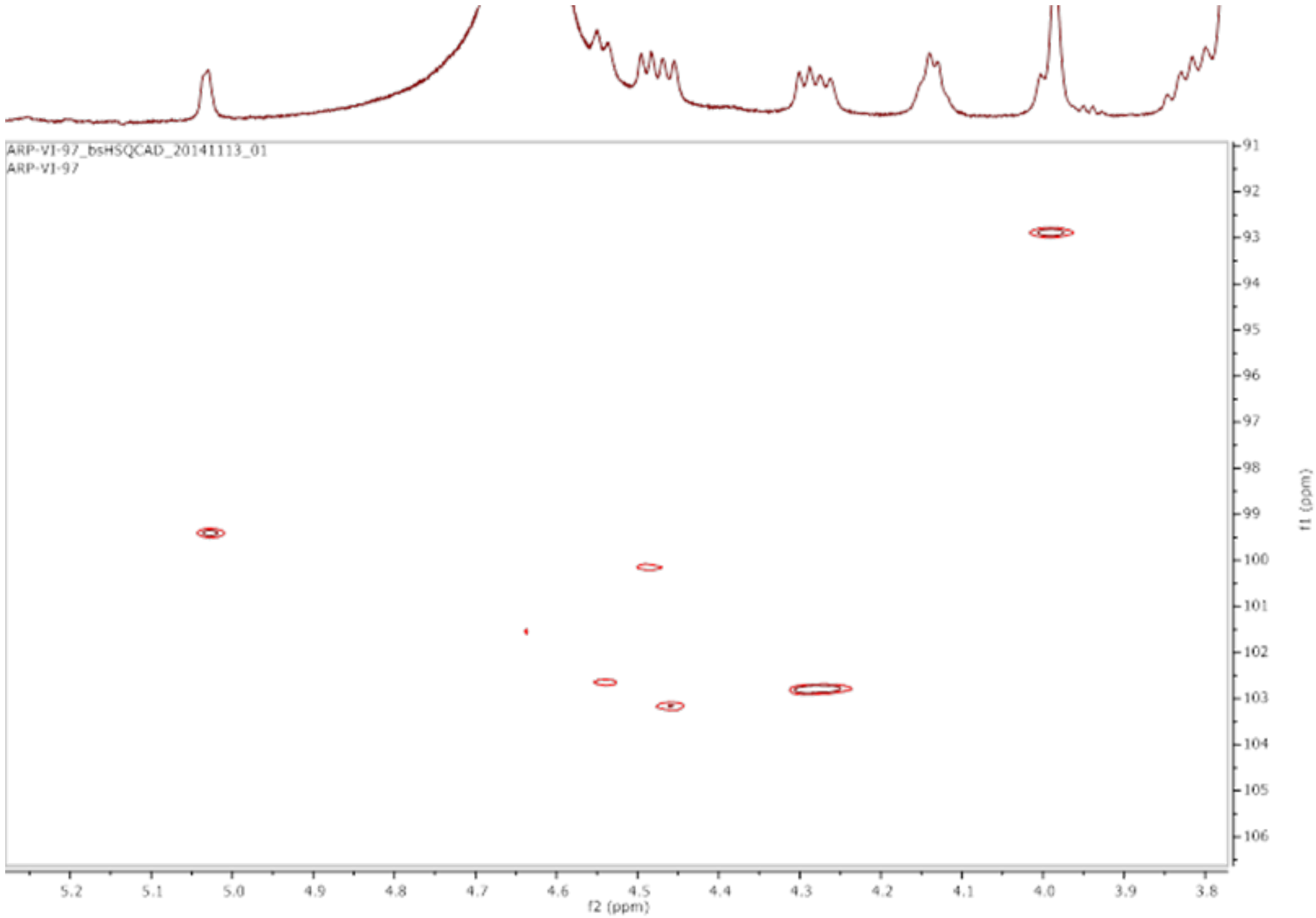
	C1
Glc	92.87
Gal	102.81
GlcNAc	102.64
Gal(2)	102.81
GlcNAc(2)	103.17
Gal(3)	100.20
Fuc	99.41

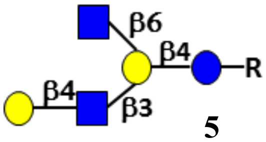
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{67}H_{106}N_6O_{40}Na$ $(M + Na)^+$ exact 1657.6343, found 1657.5427.



ARP-VI-97_PROTON_20141113_02
ARP-VI-97
f1 (ppm)


ARP-VI-97_bsHSQCAD_20141113_01
ARP-VI-97
f2 (ppm)
f1 (ppm)



5

^{1}H (600 MHz, D_2O): δ (ppm)

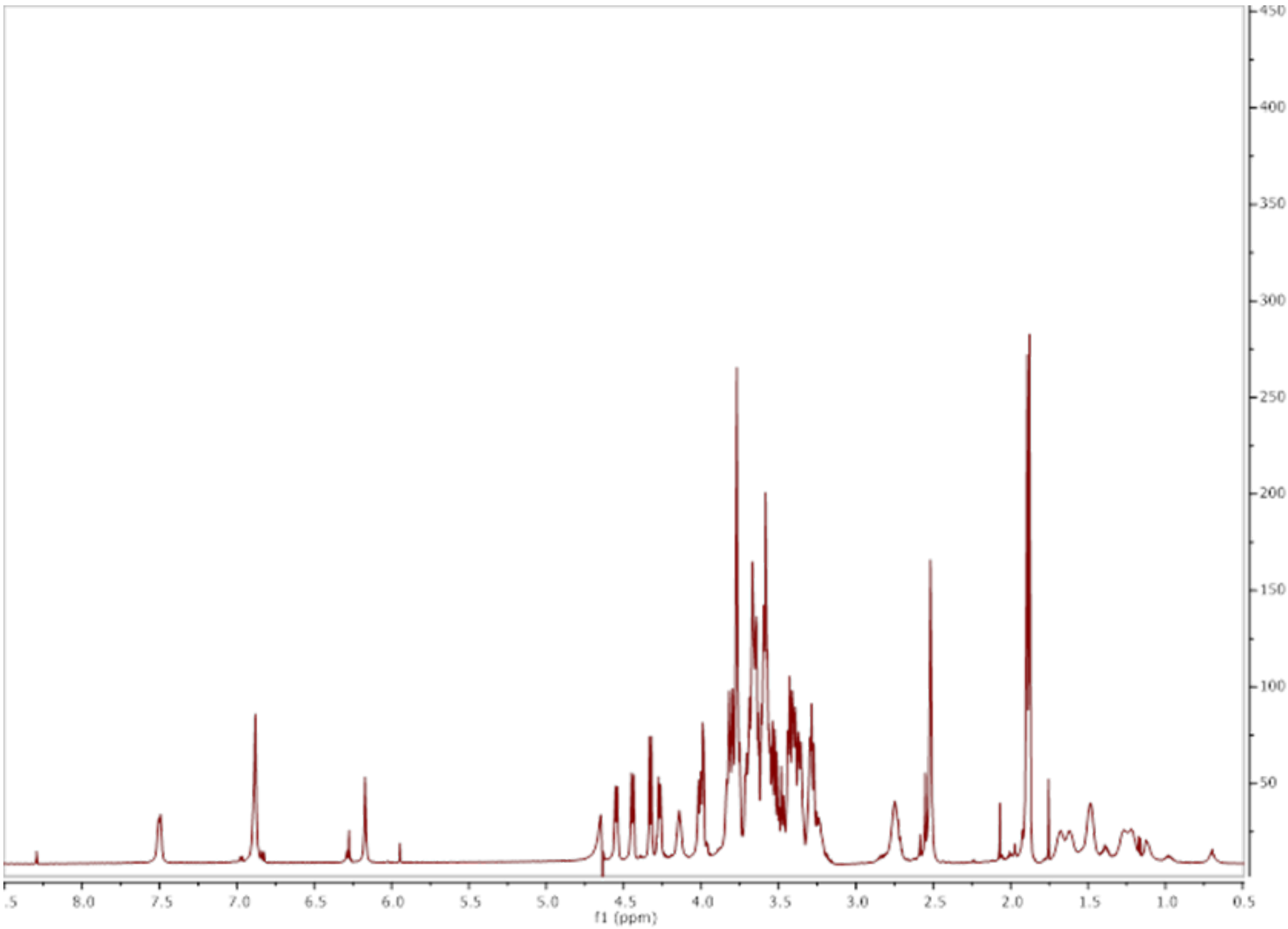
	H1	H2	H3	H4	H5	H6	NHAc
Glc	4.00 (d, *J* = 9.1 Hz, 1H)	3.34	3.47	3.40	n/a[a]	n/a	-[b]
Gal	4.26 (d, *J* = 7.3 Hz, 1H)	3.42	3.54	3.98	n/a	3.81 3.68	-
GlcNAc	4.54 (d, *J* = 8.2 Hz, 1H)	3.63	3.42	3.57	n/a	n/a	1.88 (s, 3H)
Gal(2)	4.32 (d, *J* = 7.8 Hz, 1H)	3.37	3.51	3.76	n/a	n/a	-
GlcNAc(2)	4.44 (d, *J* = 8.4 Hz, 1H)	3.53	3.39	3.28	n/a	n/a	1.89 (s, 3H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

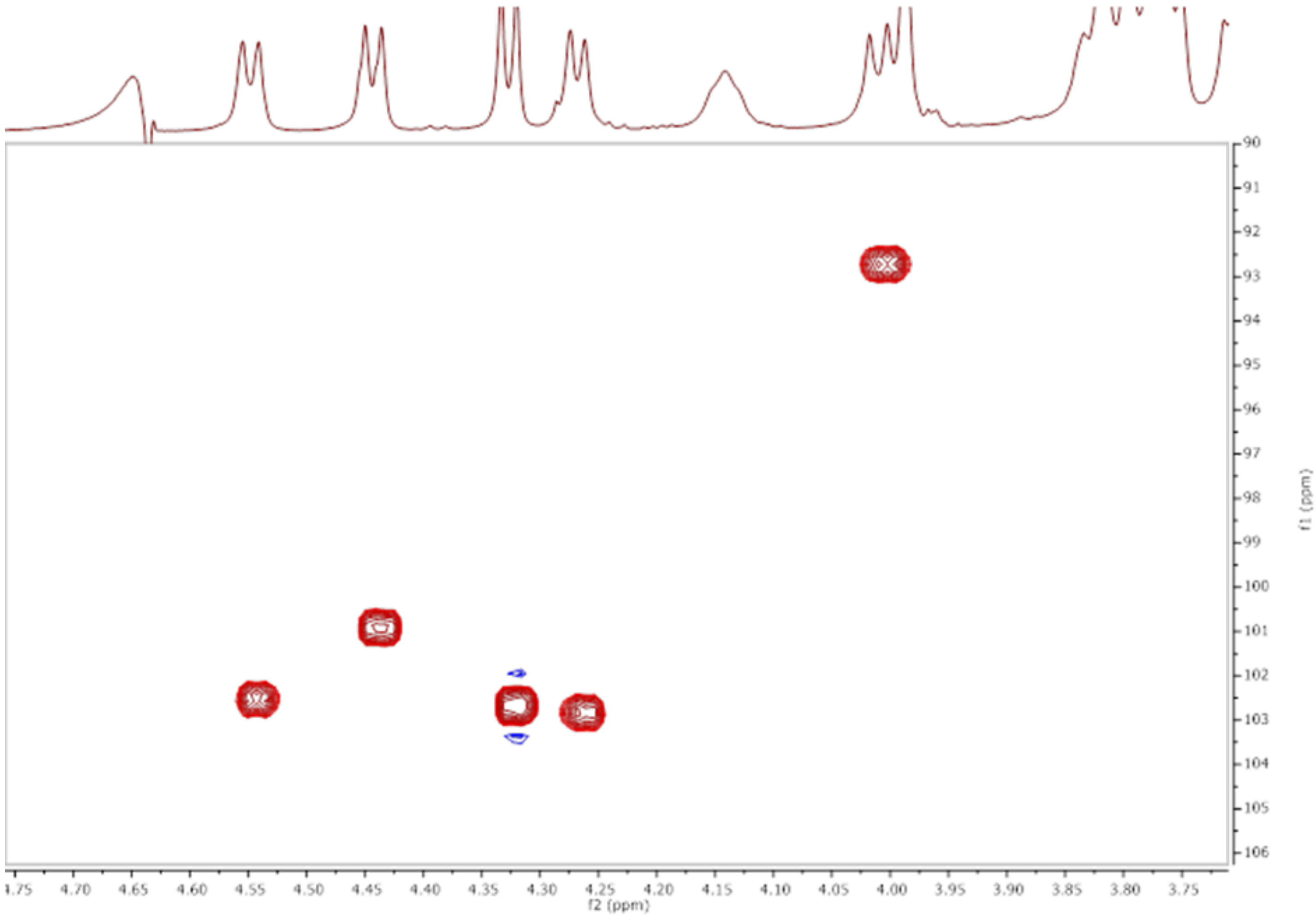
	C1
Glc	92.67
Gal	102.77
GlcNAc	102.46
Gal(2)	102.59
GlcNAc(2)	100.83

[a] Not assigned
[b] Not applicable

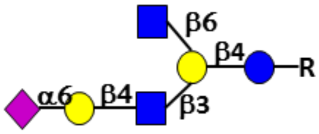
MALDI TOF-MS *m/z* calcd for $C_{55}H_{86}N_6O_{31}Na$ $(M + Na)^+$ exact 1349.5235, found 1349.2135.



450
400
350
300
250
200
150
100
50
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



f1 (ppm)
f2 (ppm)



6

^{1}H (600 MHz, D_2O): δ (ppm)

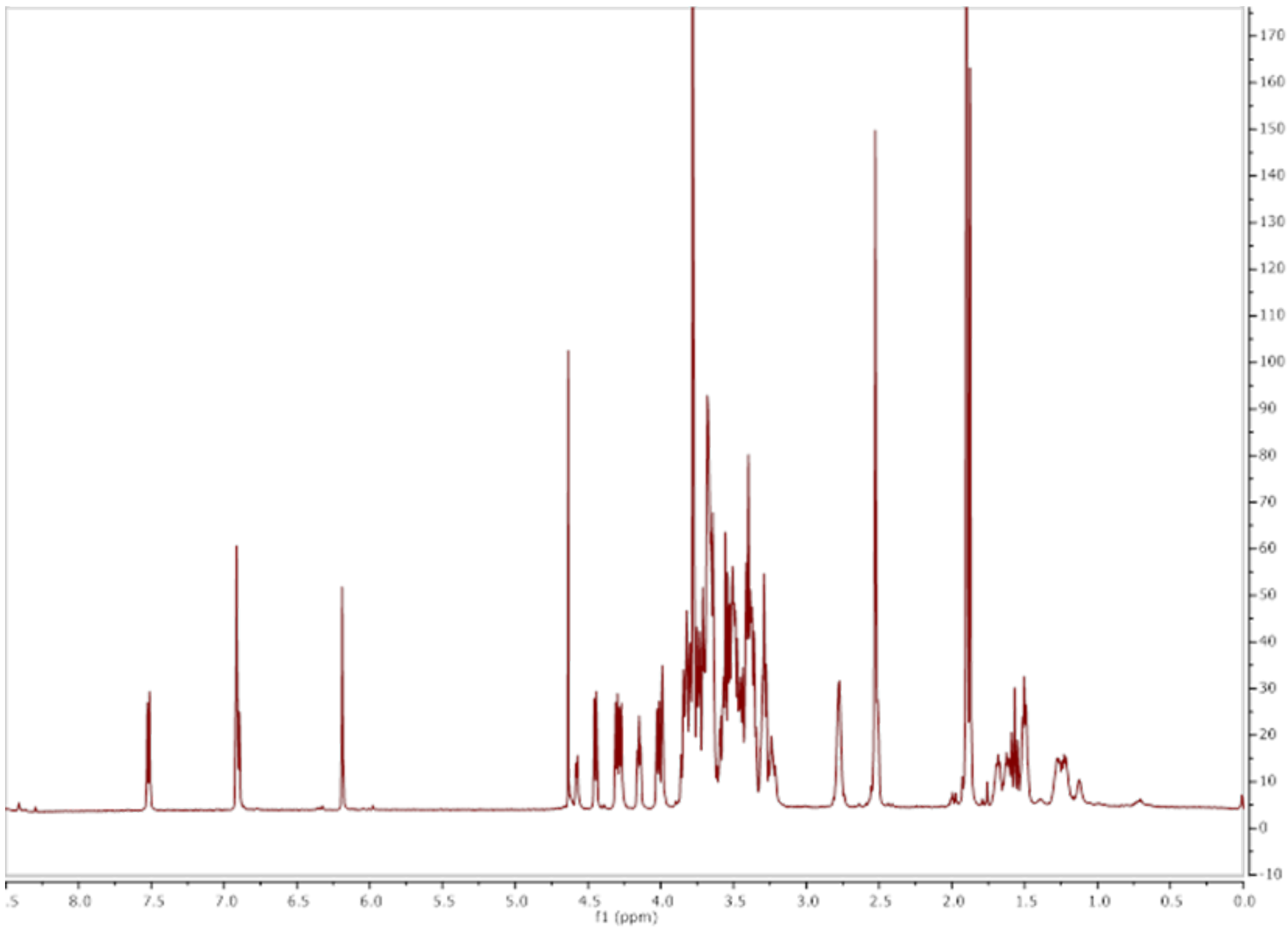
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.34	3.47	3.39	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26 (d, *J* = 7.9 Hz, 1H)	3.41	3.54	3.97	n/a	n/a	-	-	-	-
GlcNAc	4.56 (d, *J* = 7.3 Hz, 1H)	3.62	3.49	n/a	n/a	n/a	-	-	-	1.90 (s, 6H)
Gal(2)	4.28 (d, *J* = 7.8 Hz, 1H)	3.37	3.49	3.75	n/a	n/a	-	-	-	-
GlcNAc(2)	4.43 (d, *J* = 8.3 Hz, 1H)	3.52	3.37	3.27	n/a	n/a	-	-	-	1.90 (s, 6H)
Neu5Ac	-	-	3.49 - eq 1.57 - axial (dd, *J* = 12.1 Hz, 1H)	3.49	3.62	3.51	n/a	n/a	n/a	1.87 (s, 3H)

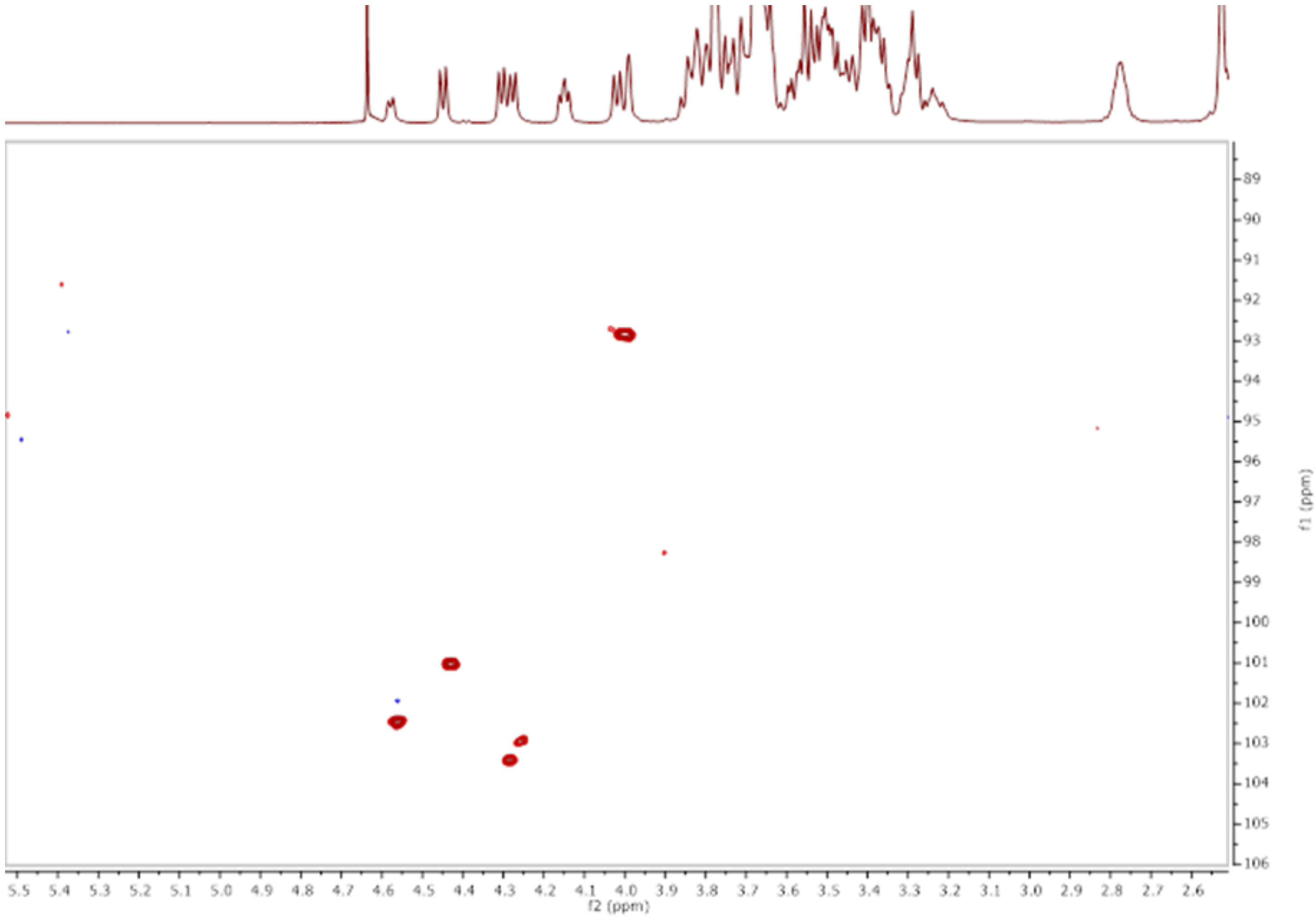
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.86
Gal	102.91
GlcNAc	102.50
Gal(2)	103.43
GlcNAc(2)	101.03

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{66}H_{102}N_7O_{39}$ Na_2 $(M + 2Na)^+$ exact 1662.6014, found 1662.5197.


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
f1 (ppm)
5.5
5.4
5.3
5.2
5.1
5.0
4.9
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4.7
4.6
4.5
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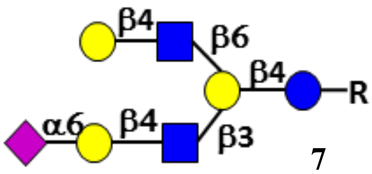
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
f2 (ppm)



7

^{1}H (800 MHz, D_2O): δ (ppm)

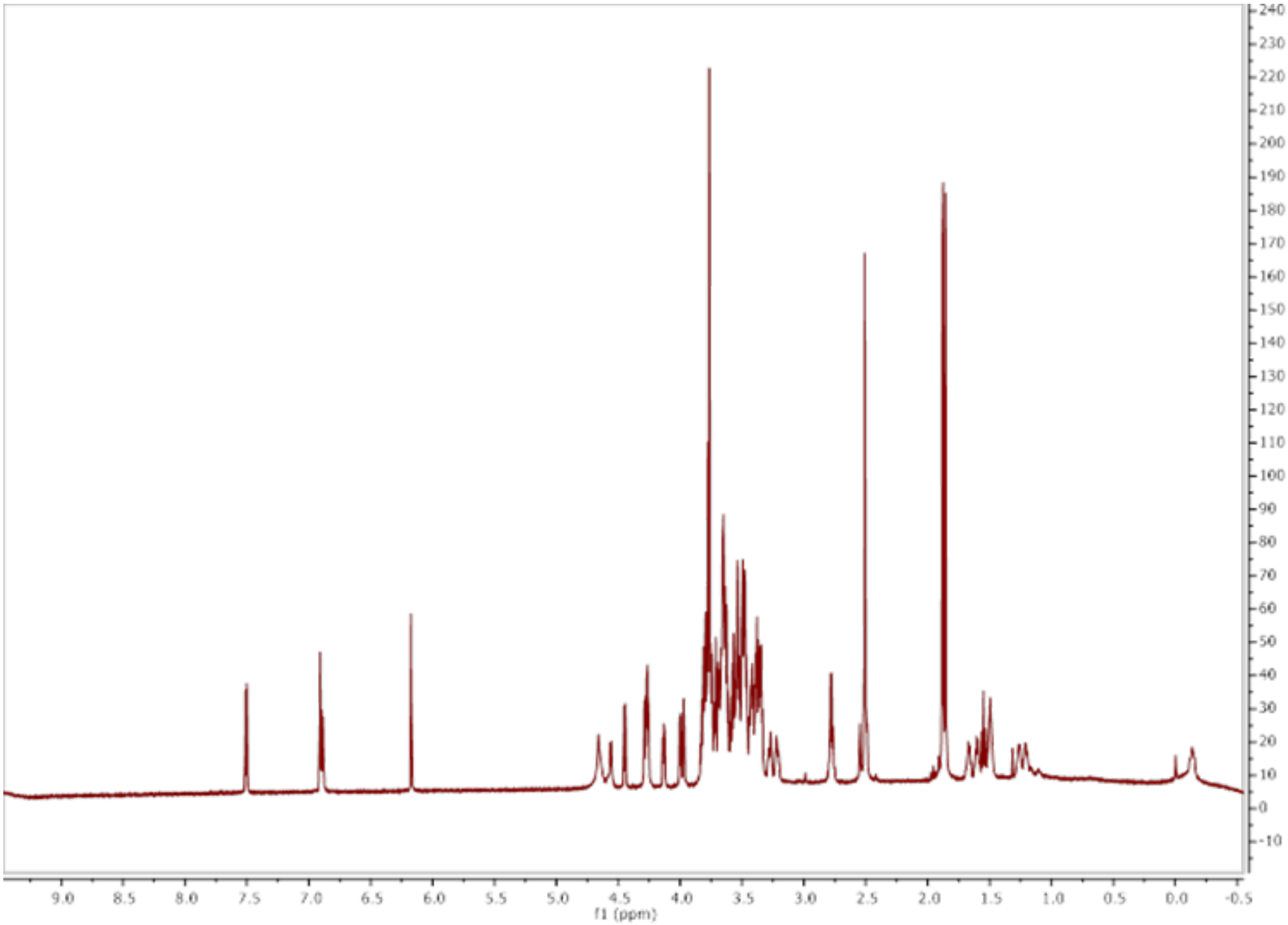
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.34	3.47	3.39	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26 (d, *J* = 7.5 Hz, 1H)	3.42	3.54	3.97 (d, *J* = 2.9 Hz, 1H)	n/a	n/a	-	-	-	-
GlcNAc	4.56 (d, *J* = 8.1 Hz, 1H)	3.62	3.49	3.43	n/a	n/a	-	-	-	1.81 - 1.87 (m, 9H)
Gal(2)	4.28 (d, *J* = 7.9 Hz, 1H)	3.37	3.50	3.76	n/a	n/a	-	-	-	-
GlcNAc(2)	4.45 (d, *J* = 8.2 Hz, 1H)	3.62	3.49	3.43	n/a	n/a	-	-	-	1.81 - 1.87 (m, 9H)
Gal(3)	4.27 (d, *J* = 7.7 Hz, 1H)	3.36	3.48	3.74	n/a	n/a	-	-	-	-
Neu5Ac	-	-	2.50 - eq 1.54 - axial	3.48	3.62	3.51	n/a	n/a	n/a	1.81 – 1.87 (s, 9H)

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

	C1
Glc	92.83
Gal	102.87
GlcNAc	102.42
Gal(2)	103.37
GlcNAc(2)	100.96
Gal(3)	102.87

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{72}H_{112}N_7O_{44}Na_2$ $(M + 2Na)^+$ exact 1824.6543, found 1824.5027.


240
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210
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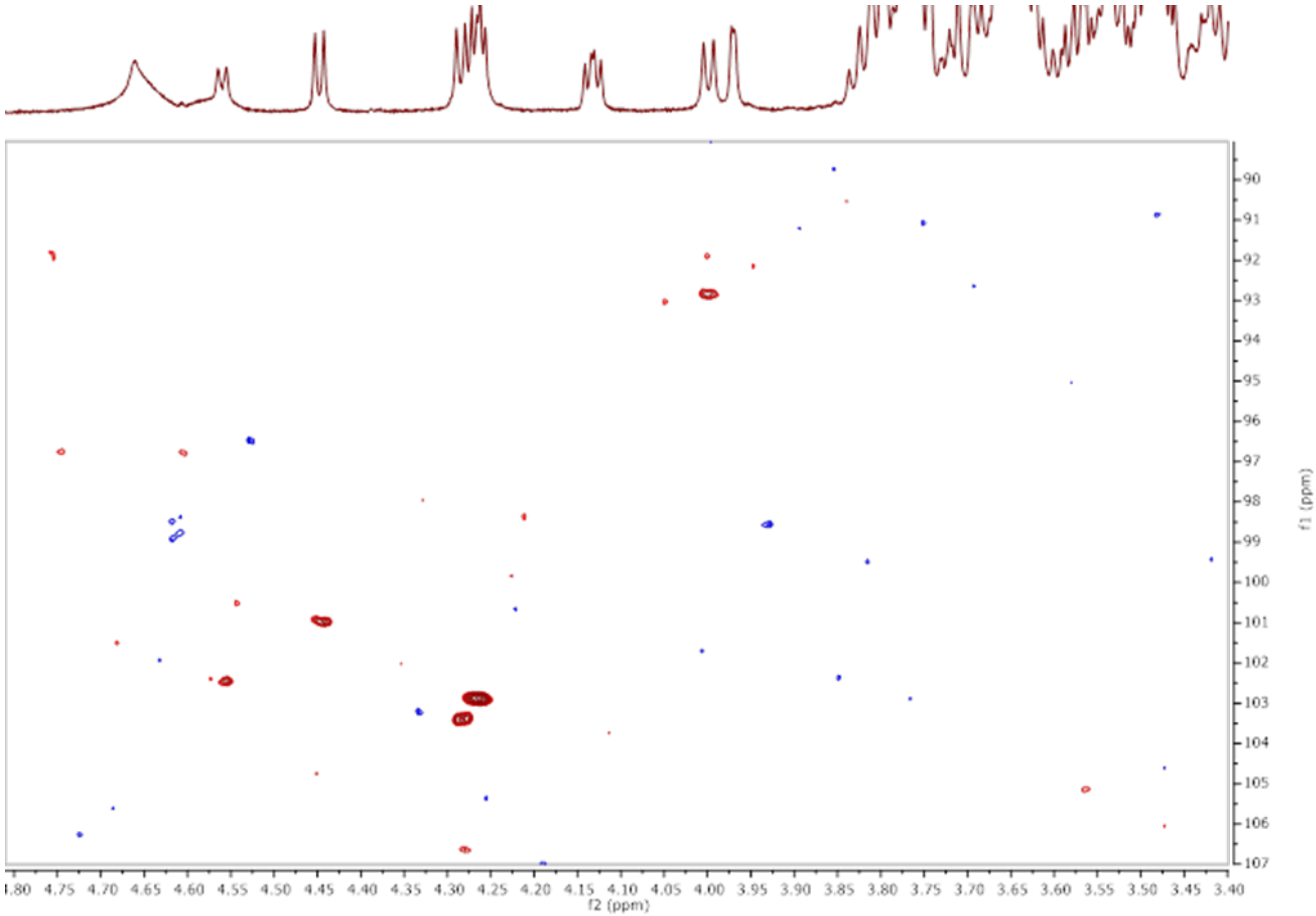
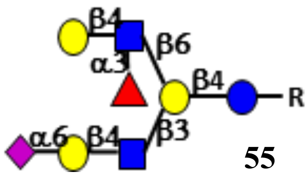
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


f1 (ppm)
f2 (ppm)



55

^{1}H (600 MHz, D_2O): δ (ppm)

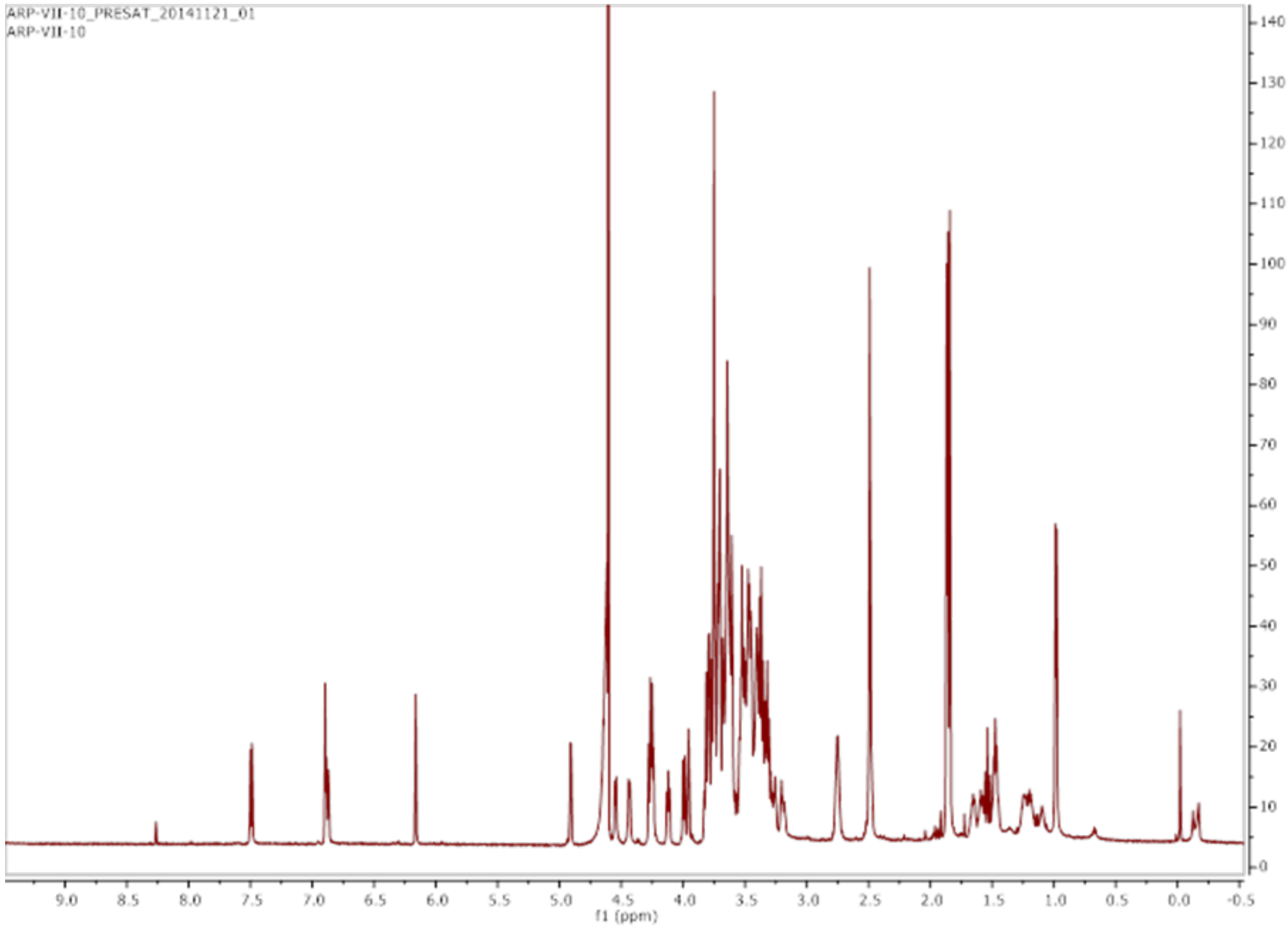
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc	CH₃
Glc	4.00 (d, *J* = 9.0 Hz, 1H)	3.34	3.41	3.47	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.26	3.43	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55 (d, *J* = 7.3 Hz, 1H)	3.64	3.50	3.45	n/a	n/a	-	-	-	1.81 - 1.87 (m, 6H)	-
Gal(2)	4.28	3.37	3.52	3.76	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 6.6 Hz, 1H)	3.74	n/a	3.43	n/a	n/a	-	-	-	1.81 - 1.87 (m, 6H)	-
Gal(3)	4.26	3.33	3.48	3.73	n/a	n/a	-	-	-	-	-
Neu5Ac	-	-	2.50 - eq 1.54 - axial	3.48	3.62	3.51	n/a	n/a	n/a	1.86 (s, 3H)	-
Fuc	4.92 (d, *J* = 3.7 Hz, 1H)	3.52	3.75	3.63	4.66	-	-	-	-	-	0.98 (d, *J* 6.5 Hz, 3H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

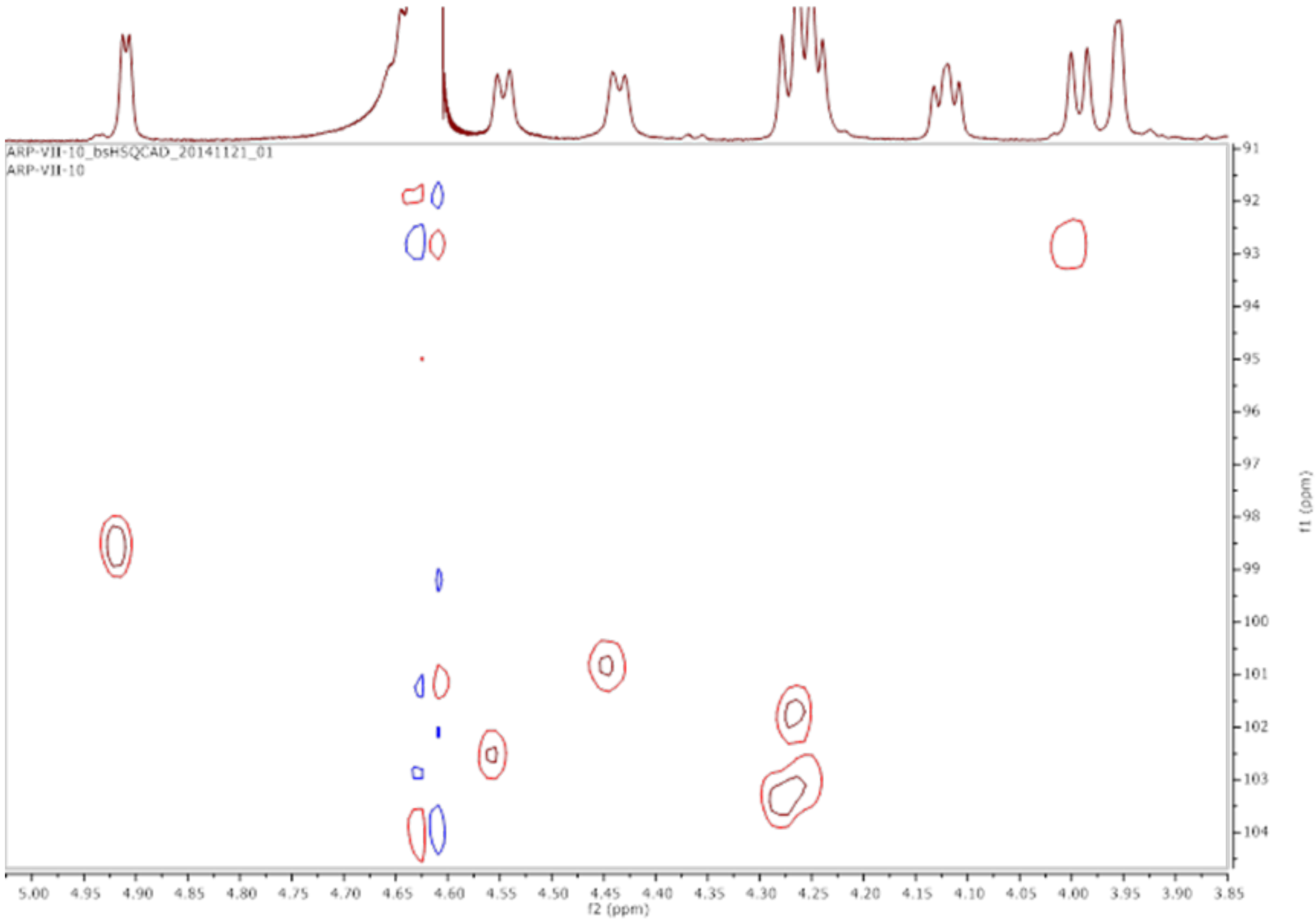
	C1
Glc	92.93
Gal	102.84
GlcNAc	102.42
Gal(2)	103.37
GlcNAc(2)	100.77
Gal(3)	101.67
Fuc	98.47

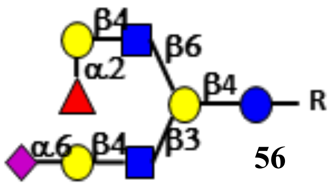
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{78}H_{122}N_7O_{48}Na_2$ $(M + 2Na)^+$ exact 1970.7122, found 1970.3612.



ARP-VII-10_PRESAT_20141121_01
ARP-VII-10
f1 (ppm)


ARP-VII-10_bsHSQCAD_20141121_01
ARP-VII-10
f2 (ppm)
f1 (ppm)



56

^{1}H (600 MHz, D_2O): δ (ppm)

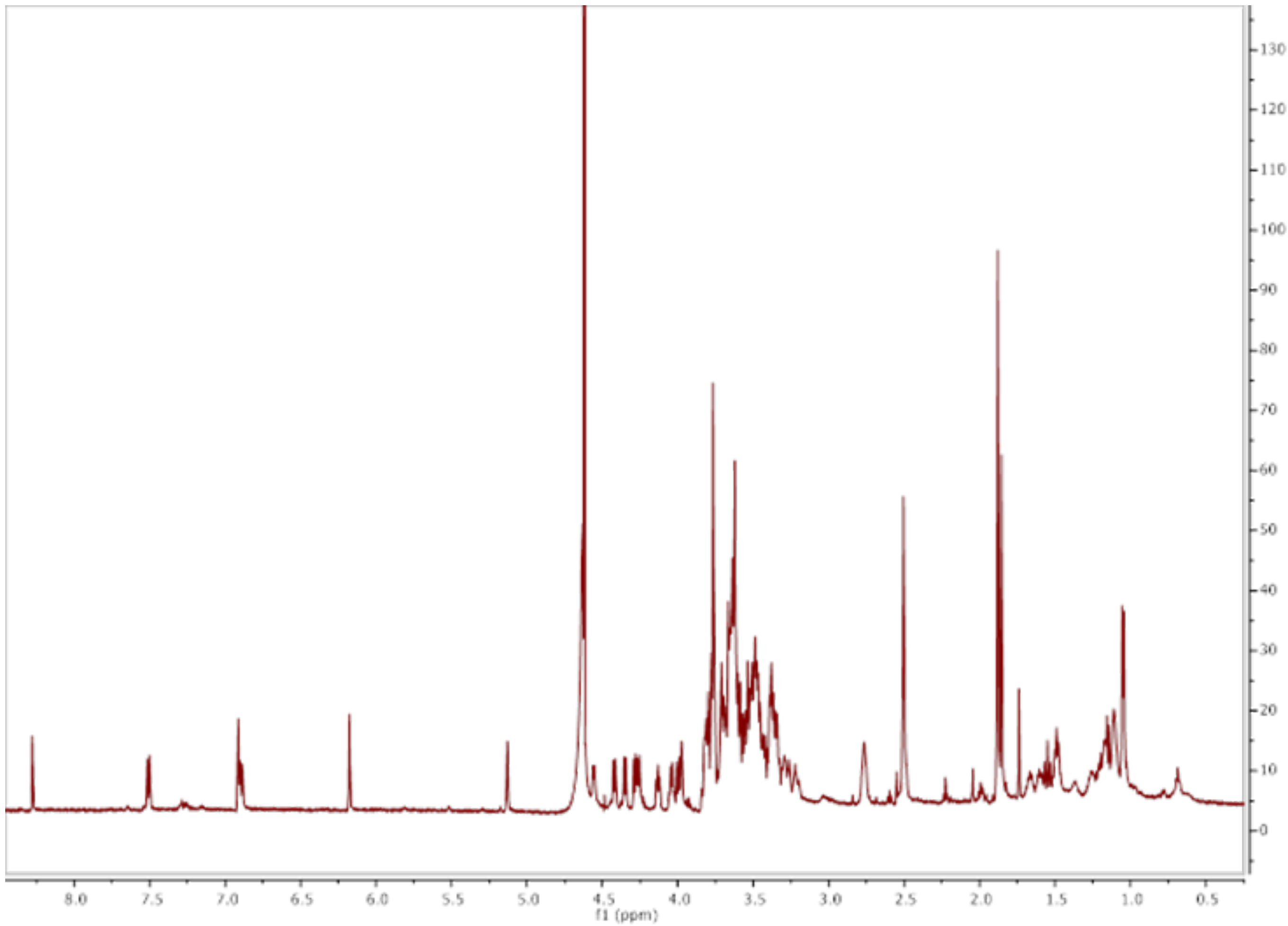
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc	CH_3
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.33	3.46	3.38	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27 (d, *J* = 7.7 Hz, 1H)	3.41	3.54	3.97	n/a	n/a	-	-	-	-	-
GlcNAc	4.56 (d, *J* = 6.6 Hz, 1H)	3.62	3.49	3.43	n/a	n/a	-	-	-	1.88 (s, 6H)	-
Gal(2)	4.29 (d, *J* = 7.8 Hz, 1H)	3.36	3.49	3.75	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.43 (d, *J* = 8.2 Hz, 1H)	3.58	3.51	3.29	n/a	n/a	-	-	-	1.88 (s, 6H)	-
Gal(3)	4.36 (d, *J* = 7.7 Hz, 1H)	3.49	n/a	3.69	n/a	n/a	-	-	-	-	-
Neu5Ac	-	-	2.49 - eq 1.56 - axia (dd, J = 12.2 Hz, 1H)	4.80	3.62	3.51	n/a	n/a	n/a	1.86 (s, 3H)	-
Fuc	5.13 (s, 1H)	3.62	n/a	n/a	4.04 (dd, *J* = 13.5, 6.7 Hz, 1H)	-	-	-	-	-	1.06 (d, *J* = 6.5 Hz, 3H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.84
Gal	102.99
GlcNAc	102.42
Gal(2)	103.39
GlcNAc(2)	101.02
Gal(3)	100.20
Fuc	99.23

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{78}H_{122}N_7O_{48}Na_2$ $(M + 2Na)^+$ exact 1970.7122, found 1970.1387.



130
120
110
100
90
80
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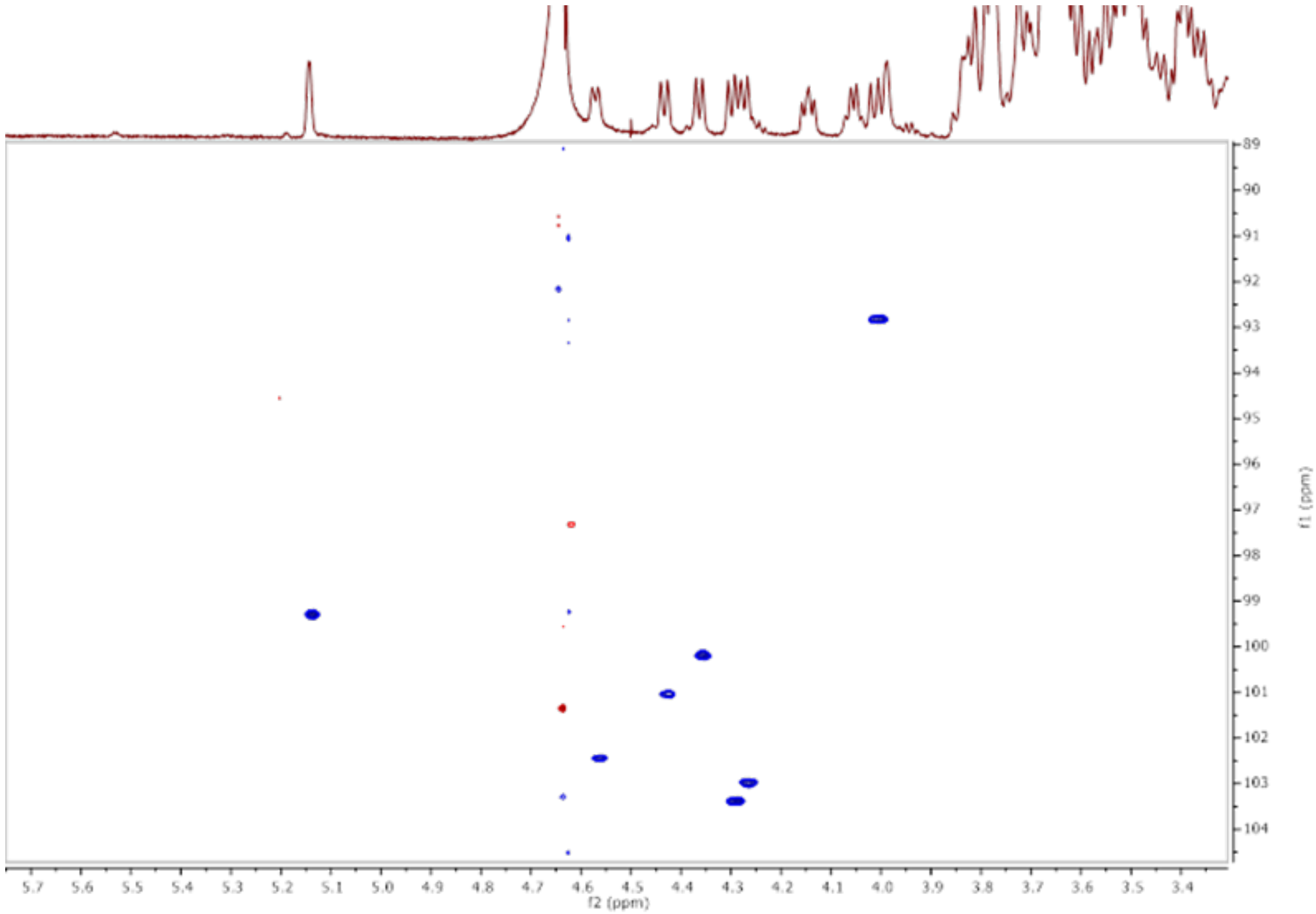
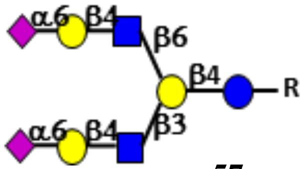
60
50
40
30
20
10
0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


f1 (ppm)
f2 (ppm)



57

^{1}H (800 MHz, D_2O): δ (ppm)

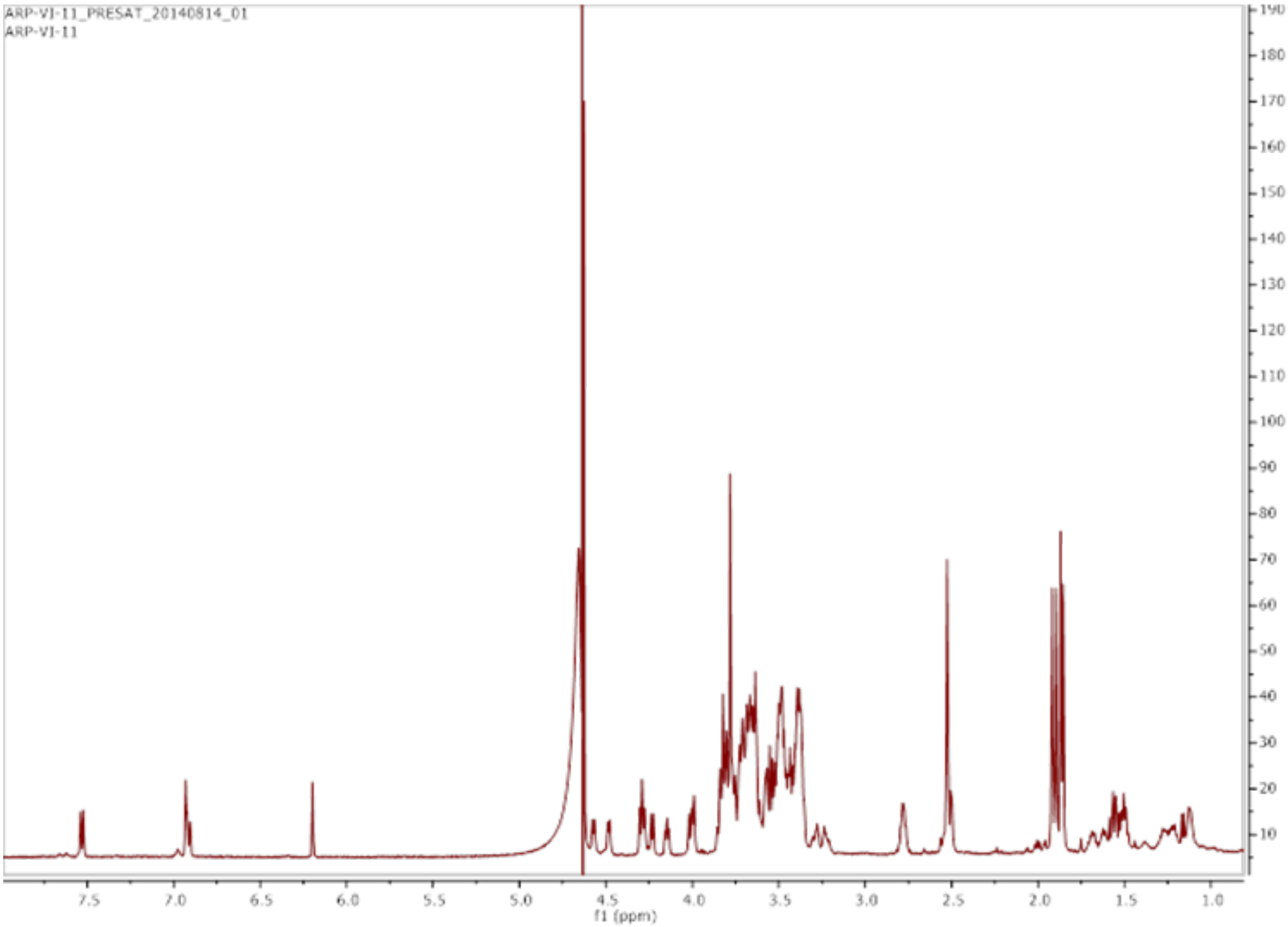
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.37	3.43	3.49	n/a[a]	n/a	-[b]	-	-	-
Gal	4.28	3.44	3.56	3.99	n/a	n/a	-	-	-	-
GlcNAc	4.57 (d, *J* = 7.4 Hz, 1H)	3.64	3.51	3.42	n/a	n/a	-	-	-	1.86 – 1.91 (m, 12H)
Gal(2)	4.30 (d, *J* = 9.0 Hz, 1H)	3.38	3.52	3.76	n/a	n/a	-	-	-	-
GlcNAc(2)	4.48 (d, *J* = 6.8 Hz, 1H)	3.58	n/a	3.43	n/a	n/a	-	-	-	1.86 – 1.91 (m, 12H)
Gal(3)	4.23 (d, *J* = 7.6 Hz, 1H)	3.37	3.48	3.75	n/a	n/a	-	-	-	-
Neu5Ac	-	-	2.50 - eq 1.54 - axial	3.48	3.62	3.51	n/a	n/a	n/a	1.86 – 1.91 (m, 12H)
Neu5Ac	-	-	2.50 - eq 1.54 - axial	3.48	3.62	3.51	n/a	n/a	n/a	1.86 – 1.91 (m, 12H)

13C from BSHSQC (200 MHz, D_2O): δ (ppm)

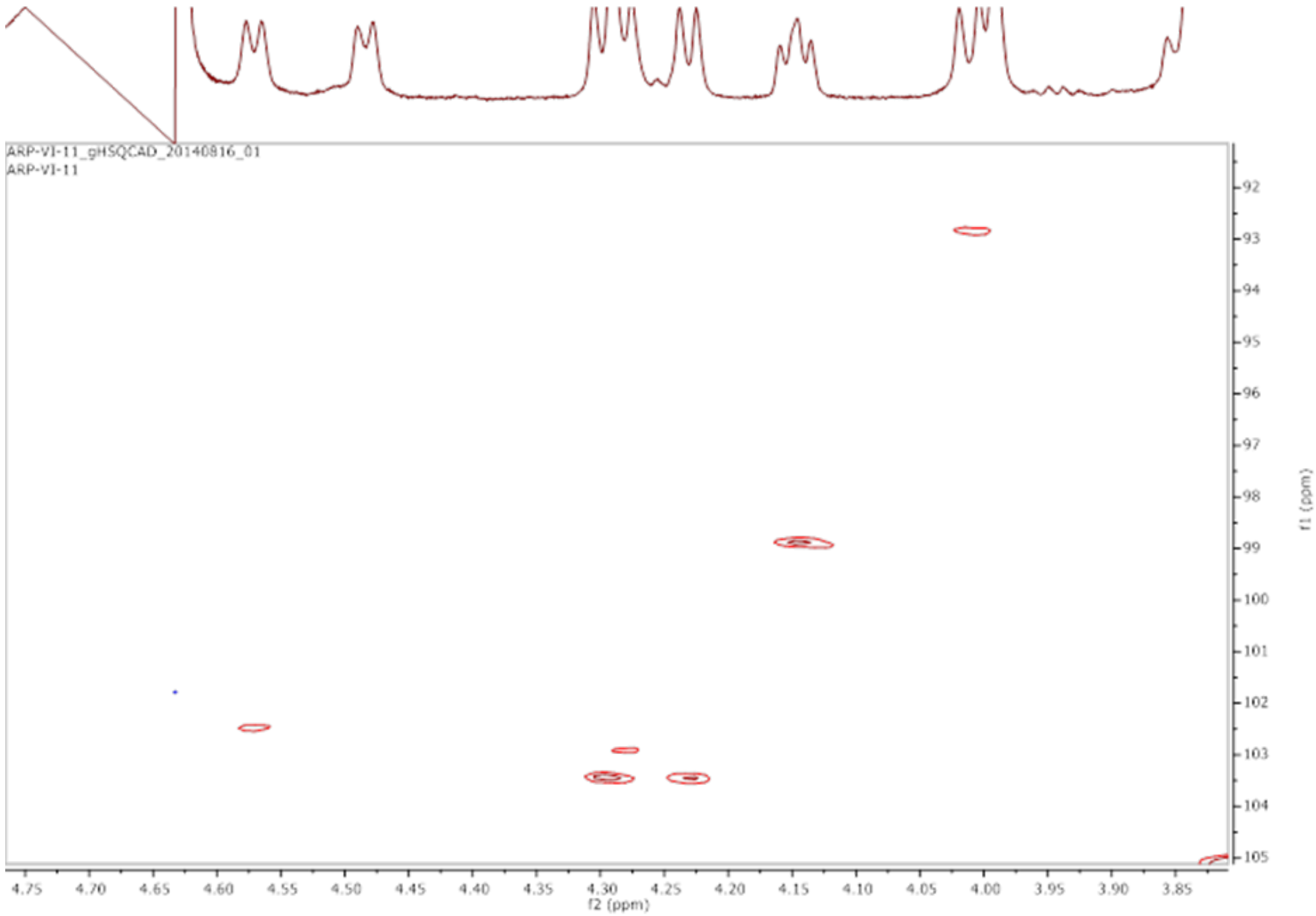
	C1
Glc	92.88
Gal	102.91
GlcNAc	102.55
Gal(2)	103.37
GlcNAc(2)	100.80
Gal(3)	103.38

[a] Not assigned
[b] Not applicable

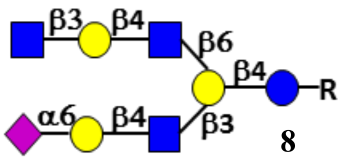
MALDI TOF-MS *m/z* calcd $C_{83}H_{128}N_8O_{52}Na$ $(M + Na)^-$ exact 2091.7526, found 2092.4038.



ARP-VI-11_PRESAT_20140814_01
ARP-VI-11
f1 (ppm)



ARP-VI-11_gHSQCAD_20140816_01
ARP-VI-11
f1 (ppm)
f2 (ppm)



8

^{1}H (600 MHz, D_2O): δ (ppm)

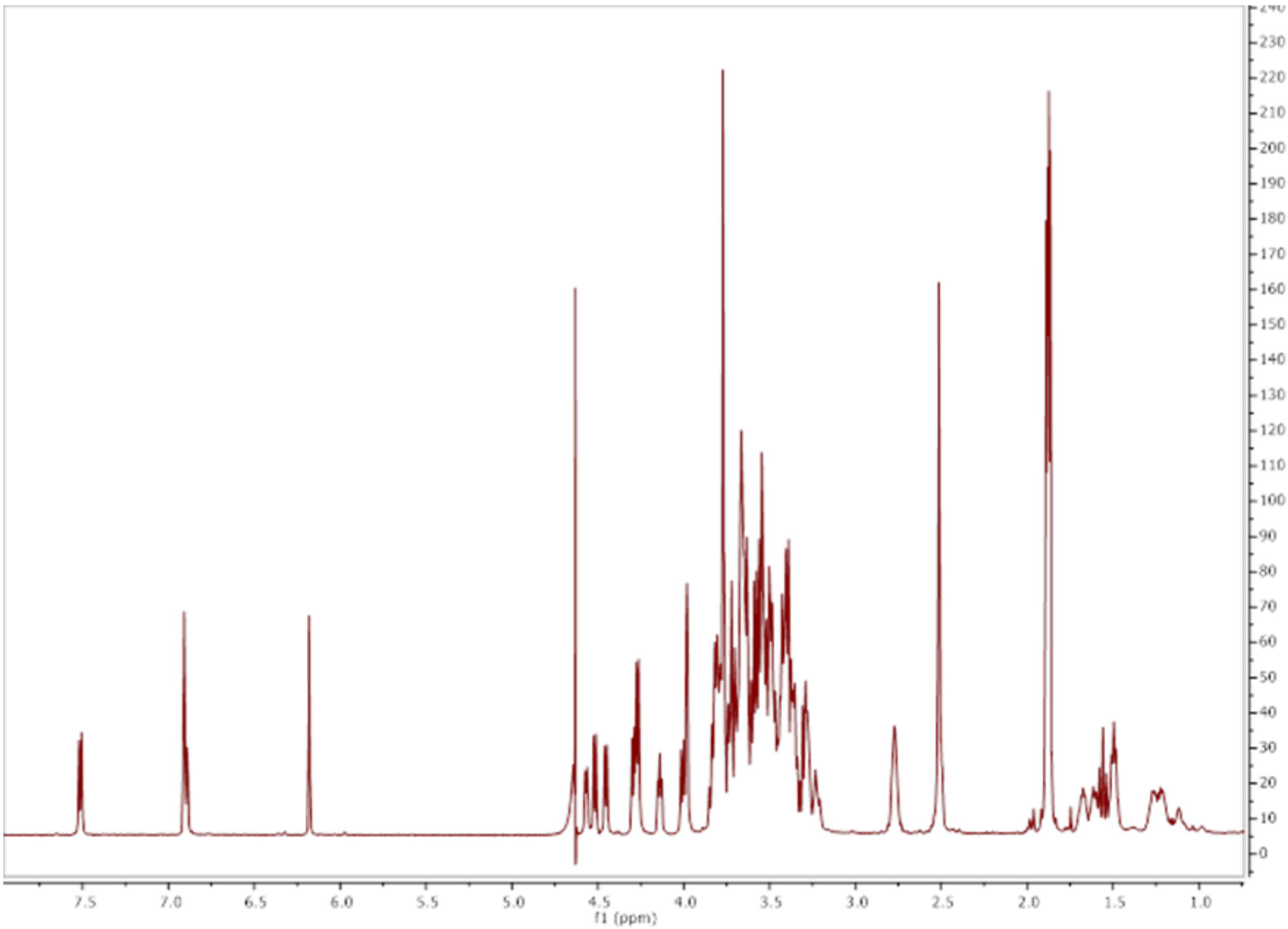
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.36	3.47	3.40	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26 (d, *J* = 7.8 Hz,1H)	3.41	3.55	3.98 (d, *J* = 3.1 Hz, 2H)	n/a	n/a	-	-	-	-
GlcNAc	4.56 (d, *J* = 7.3 Hz, 1H)	3.64	3.49	3.44	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Gal(2)	4.28 d, *J* = 7.8 Hz,1H)	3.38	3.50	3.76	n/a	n/a	-	-	-	-
GlcNAc(2)	4.43 (d, *J* = 7.9 Hz, 1H)	3.57	3.50	3.42	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Gal(3)	4.28 (d, *J* = 7.9 Hz, 1H)	3.38	3.55	3.98 (d, *J* = 3.1 Hz, 2H)	n/a	n/a	-	-	-	-
GlcNAc(3)	4.52 (d, *J* = 8.4 Hz, 1H)	3.60	3.40	3.28	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Neu5Ac	-	-	2.51 - eq 1.56 - axial (dd, *J* = 12.2 Hz, 1H)	3.49	3.62	3.51	n/a	n/a	n/a	1.91 - 1.84 (m, 12H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.84
Gal	102.84
GlcNAc	102.44
Gal(2)	103.39
GlcNAc(2)	100.92
Gal(3)	102.84
GlcNAc(3)	102.70

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{80}H_{125}N_8O_{49}Na_2$ (M + 2Na)$^+$ exact 2027.7336, found 2027.4097.



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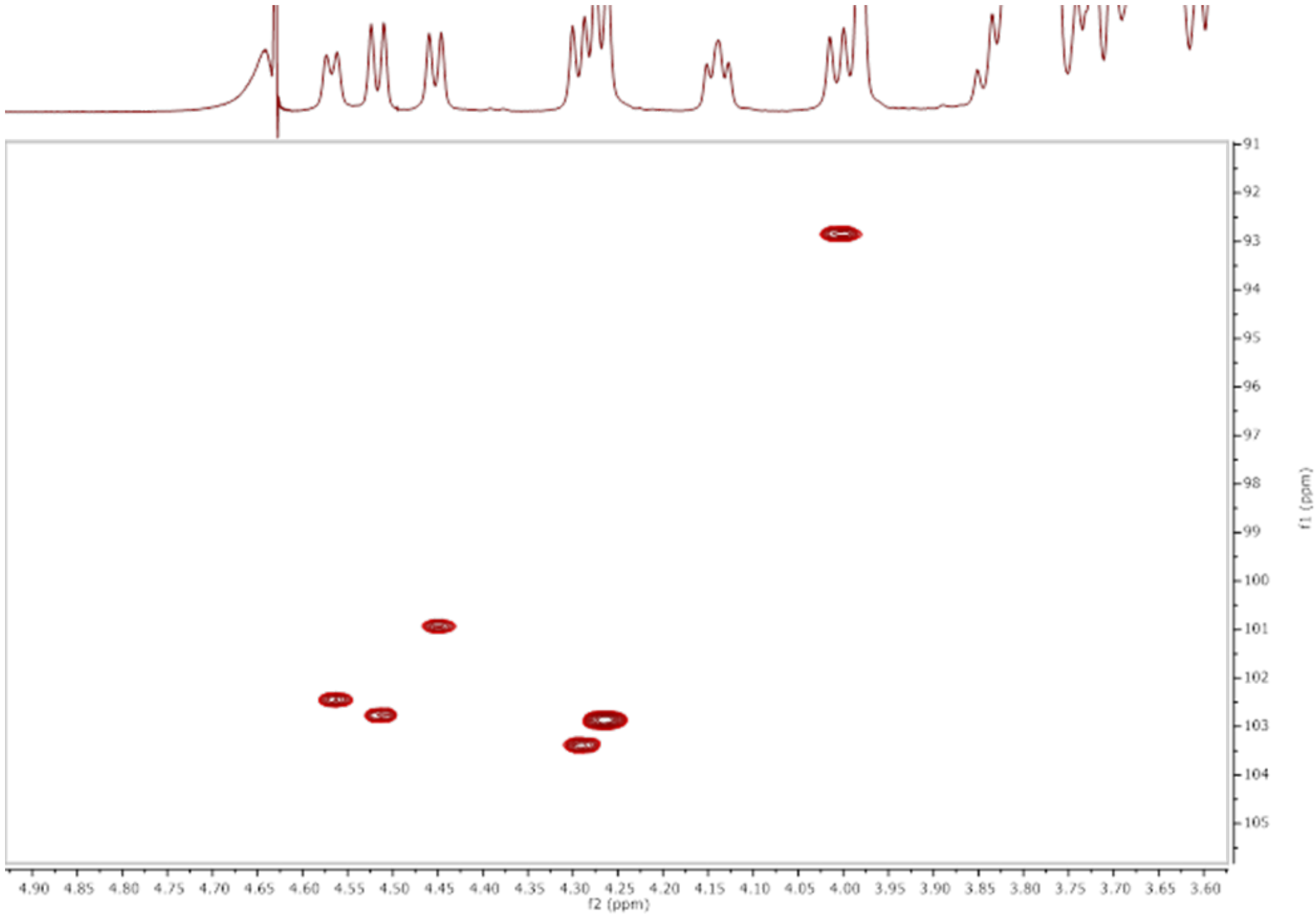
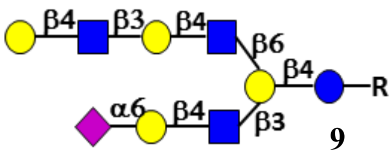
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
f1 (ppm)
4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60
f2 (ppm)



9

^1H (600 MHz, D_2O): δ (ppm)

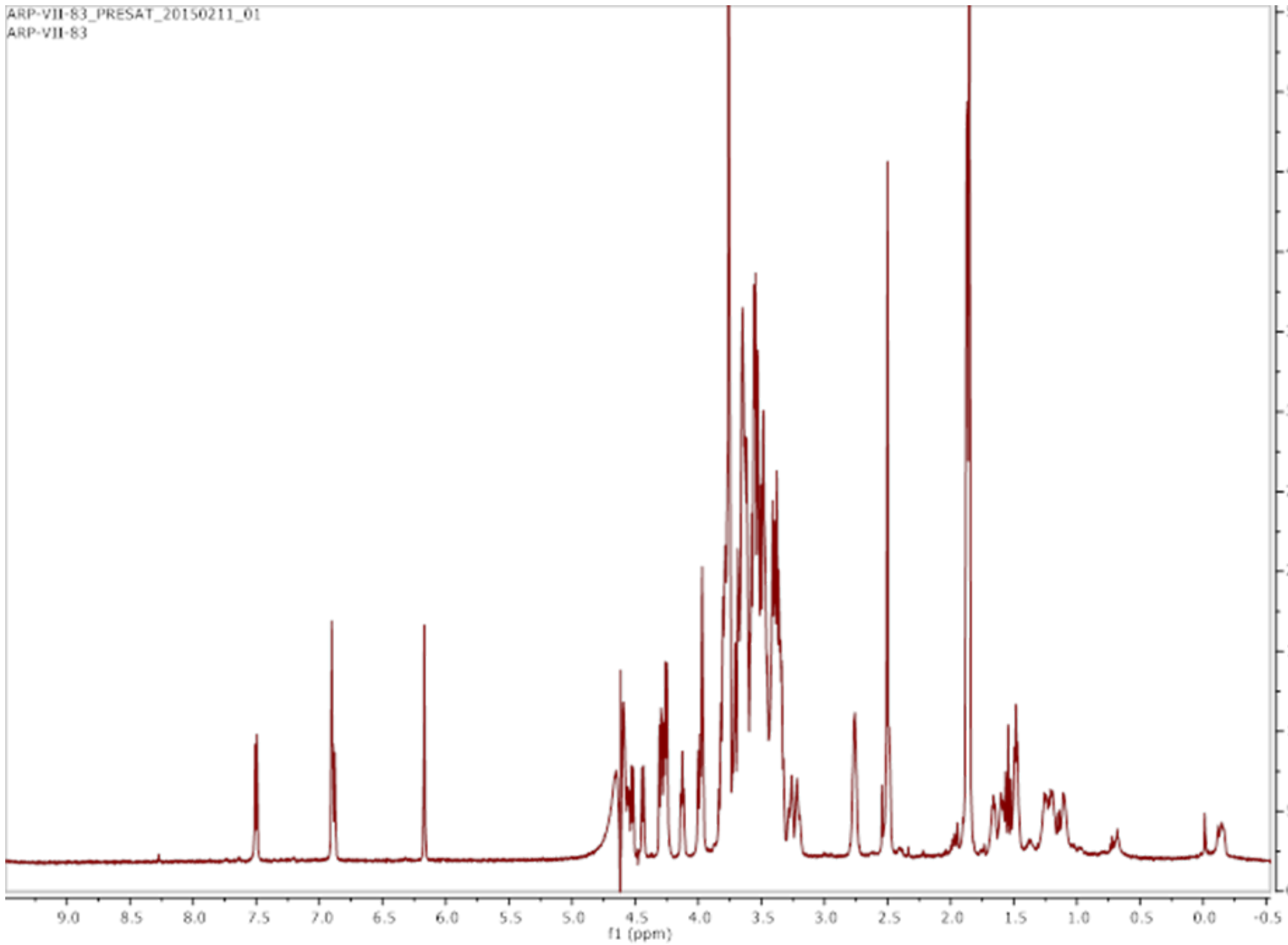
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00	3.35	3.47	3.40	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26	3.41	3.54	3.97	n/a	n/a	-	-	-	-
GlcNAc	4.56 (d, *J* = 6.5 Hz, 1H)	3.64	3.48	3.44	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Gal(2)	4.30	3.37	3.49	3.75	n/a	n/a	-	-	-	-
GlcNAc(2)	4.45 (d, *J* = 8.5 Hz, 1H)	3.56	3.51	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Gal(3)	4.26	3.41	3.54	3.97	n/a	n/a	-	-	-	-
GlcNAc(3)	4.52 (d, *J* = 8.0 Hz, 1H)	3.65	3.56	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 12H)
Gal(4)	4.28	3.37	3.49	3.75	n/a	n/a	-	-	-	-
Neu5Ac	-	-	2.51 – eq 1.56 – axial	3.49	3.62	3.51	n/a	n/a	n/a	1.91 - 1.84 (m, 12H)

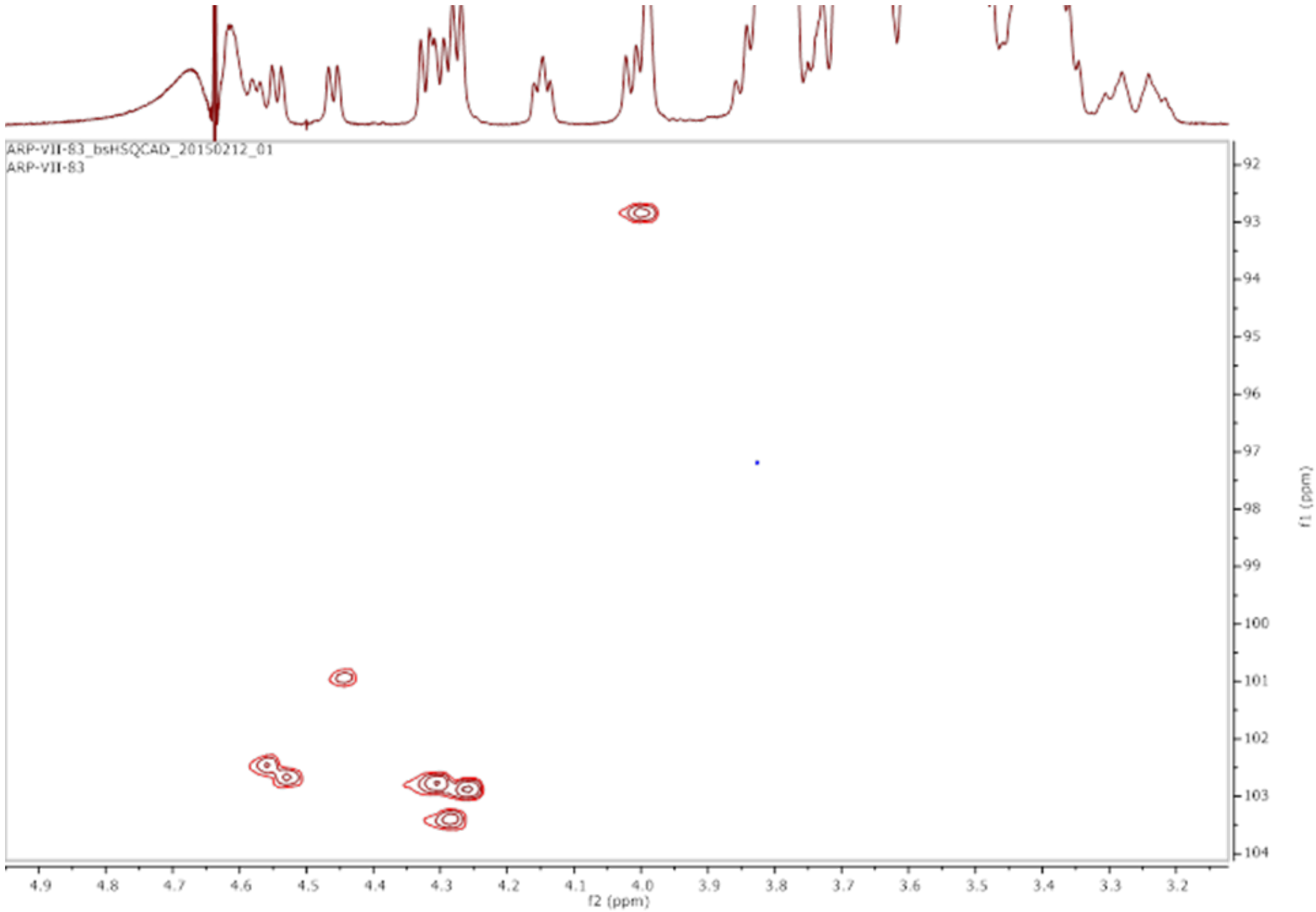
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

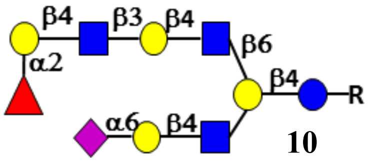
	C1
Glc	92.84
Gal	102.86
GlcNAc	102.53
Gal(2)	102.86
GlcNAc(2)	100.95
Gal(3)	102.86
GlcNAc(3)	102.66
Gal(4)	103.43

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{86}H_{135}N_8O_{54}$ Na_2 $(M + 2Na)^+$ exact 2189.7864, found 2189.6707.


ARP-VII-83_PRESAT_20150211_01
ARP-VII-83
f1 (ppm)


ARP-VII-83_bsHSQCAD_20150212_01
ARP-VII-83
f2 (ppm)
f1 (ppm)
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
92 93 94 95 96 97 98 99 100 101 102 103 104



10

^{1}H (800 MHz, D_2O): δ (ppm)

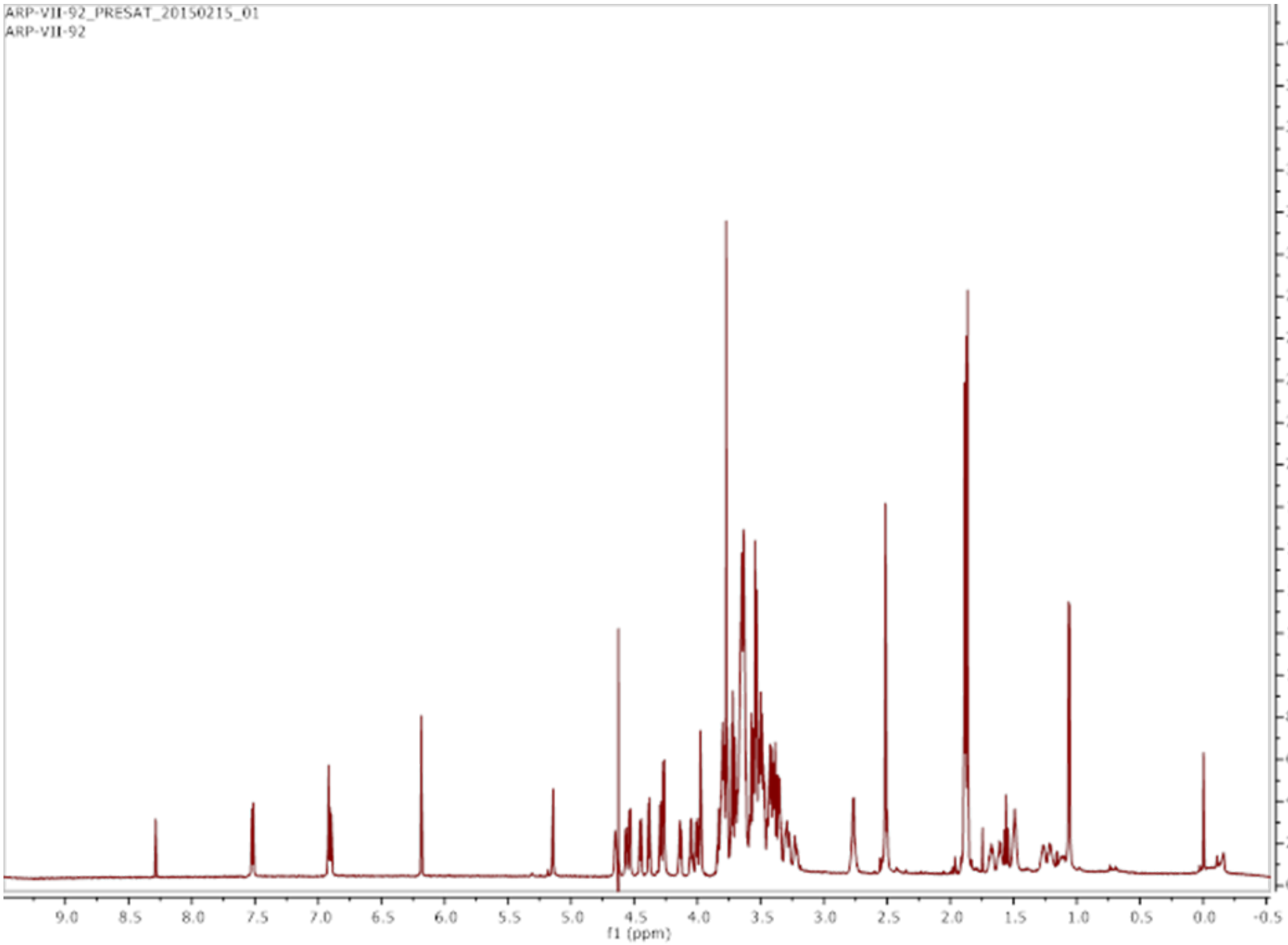
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.34	3.46	3.39	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.26 (d, *J* = 7.9 Hz, 2H)	3.41	3.53	3.96	n/a	3.80 3.66	-	-	-	-	-
GlcNAc	4.56 (d, *J* = 7.5 Hz, 1H)	3.62	3.48	3.43	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(2)	4.28 (d, *J* = 7.9 Hz, 1H)	3.36	3.50	3.75	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.3 Hz, 1H)	3.56	3.49	3.41	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(3)	4.26 (d, *J* = 7.9 Hz, 2H)	3.41	3.53	3.96	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.53 (d, *J* = 8.5 Hz, 1H)	3.64	3.51	3.29	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(4)	4.37 (d, *J* = 7.7 Hz, 1H)	3.56	3.62	3.70	n/a	n/a	-	-	-	-	-
Fuc	5.13 (d, *J* = 3.4 Hz, 1H)	3.62	n/a	n/a	4.04 (q, *J* = 6.6 Hz, 1H)	-	-	-	-	1.06 (d, *J* = 6.6 Hz, 3H)	-
Neu5Ac	-	-	2.49 – eq 1.56 – axial (dd, *J* = 12.2 Hz, 1H)	3.49	3.62	3.51	n/a	n/a	n/a	-	1.91 - 1.84 (m, 12H)

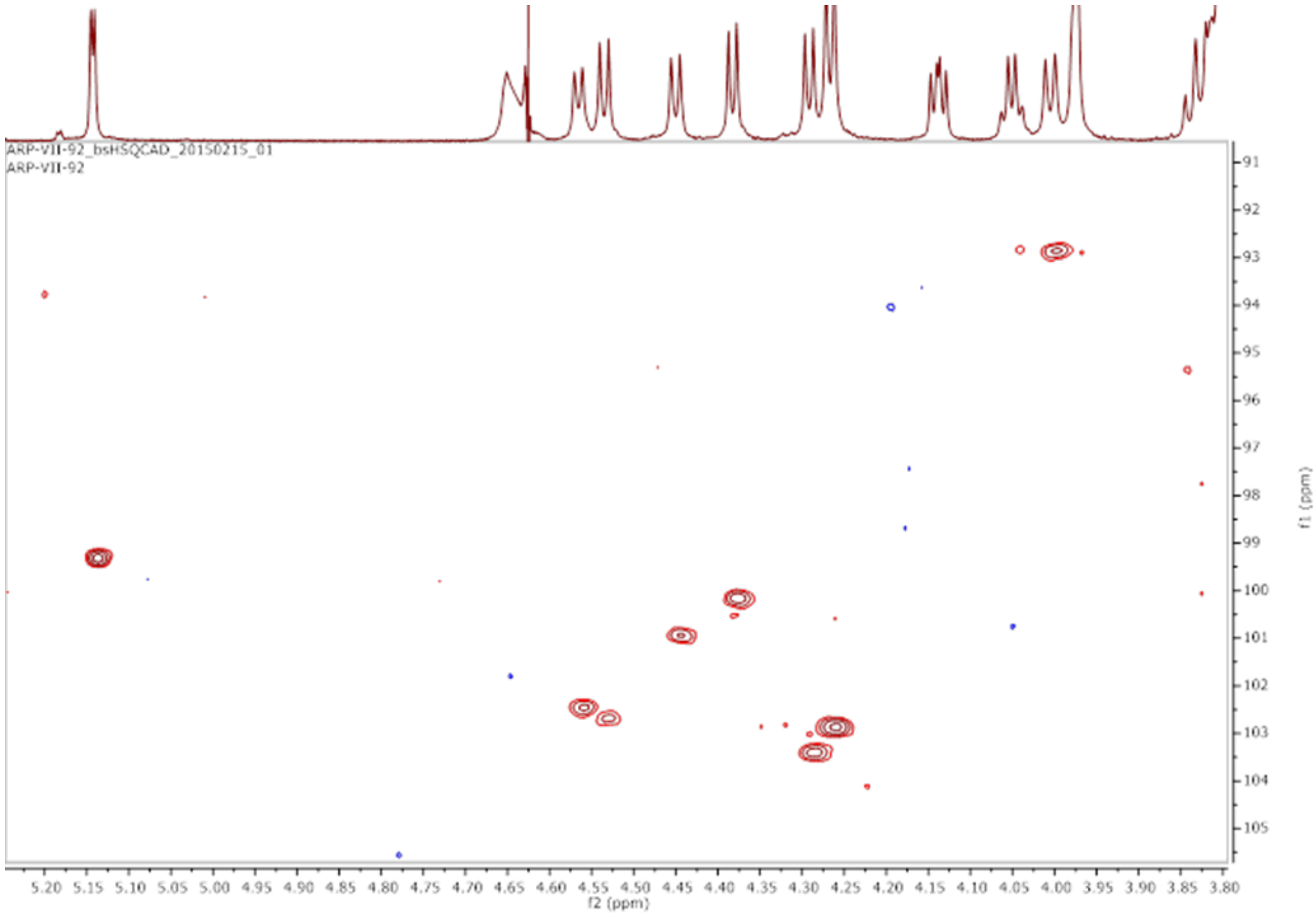
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

	C1
Glc	92.90
Gal	102.84
GlcNAc	102.46
Gal(2)	103.36
GlcNAc(2)	100.87
Gal(3)	102.84
GlcNAc(3)	102.70
Gal(4)	100.17
Fuc	99.27

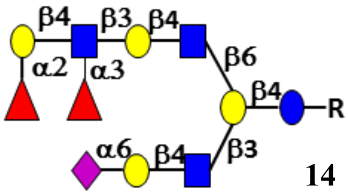
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{86}H_{135}N_8O_{54}$ Na_2 $(M + 2Na)^+$ exact 2335.8444, found 2335.5073.


ARP-VII-92_PRESAT_20150215_01
ARP-VII-92
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



ARP-VII-92_bsHSQCAD_20150215_01
ARP-VII-92
f2 (ppm)
f1 (ppm)



14

^{1}H (800 MHz, D_2O): δ (ppm)

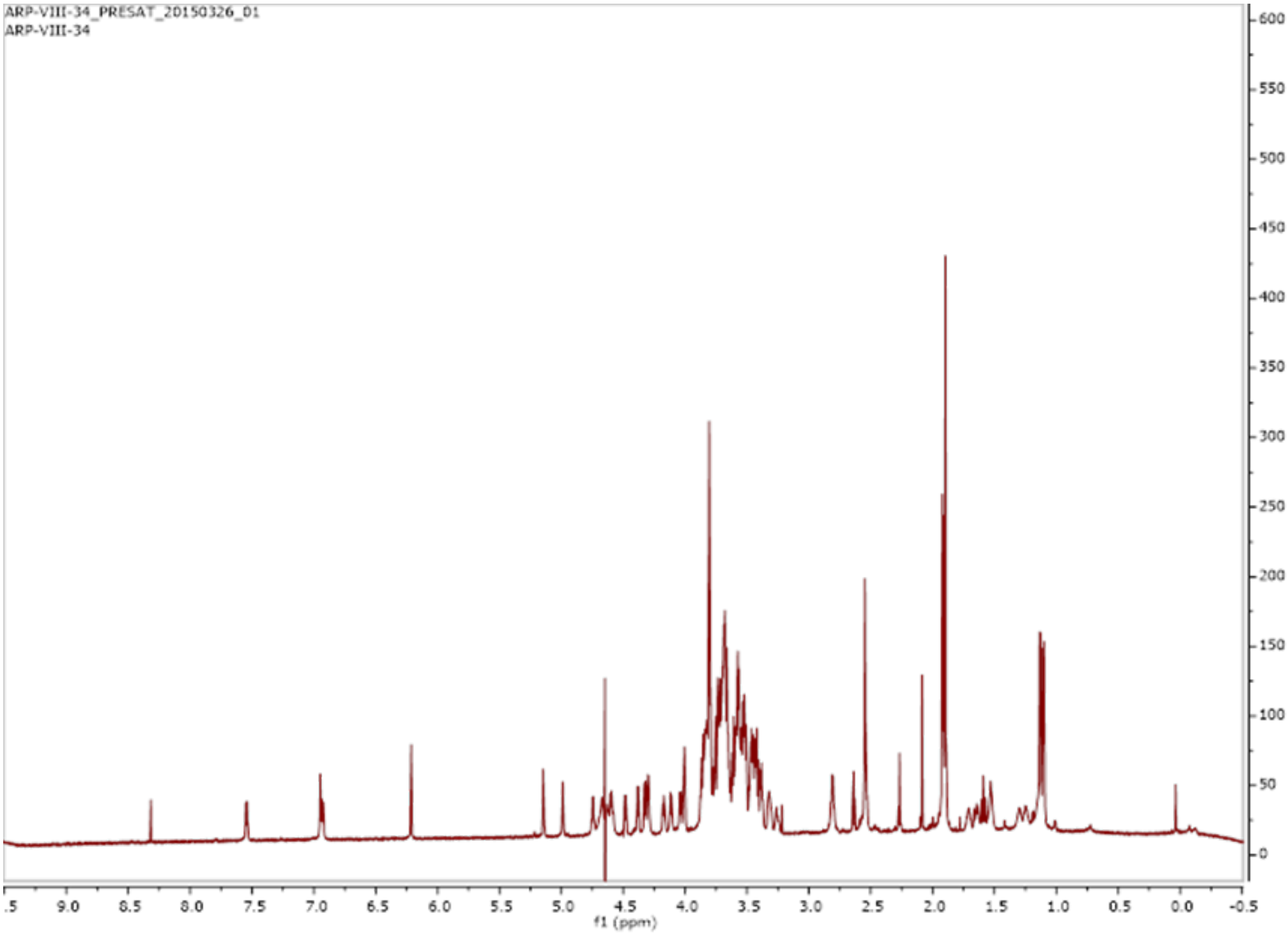
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.34	3.47	3.39	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.26	3.40	3.52	3.96	n/a	n/a	-	-	-	-	-
GlcNAc	4.56	3.63	3.49	3.43	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(2)	4.29	3.36	3.50	3.75	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.3 Hz, 1H)	3.56	3.51	3.41	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(3)	4.26	3.40	3.52	3.96	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.77	3.68	3.28	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(4)	4.37 (d, *J* = 7.7 Hz, 1H)	3.47	n/a	n/a	n/a	n/a	-	-	-	-	-
Fuc (1) (α3)	4.95 (d, *J* = 3.8 Hz, 1H)	3.52	3.75	3.64	4.70	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 3H)	-
Fuc (2) (α2)	5.11 (d, *J* = 3.6 Hz, 1H)	3.62	n/a	n/a	4.06	-	-	-	-	1.10 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac	-	-	1.56 – axial (dd, *J* = 12.2 Hz, 1H) 2.49 – eq	3.49	3.62	3.51	n/a	n/a	n/a	-	1.91 - 1.84 (m, 12H)

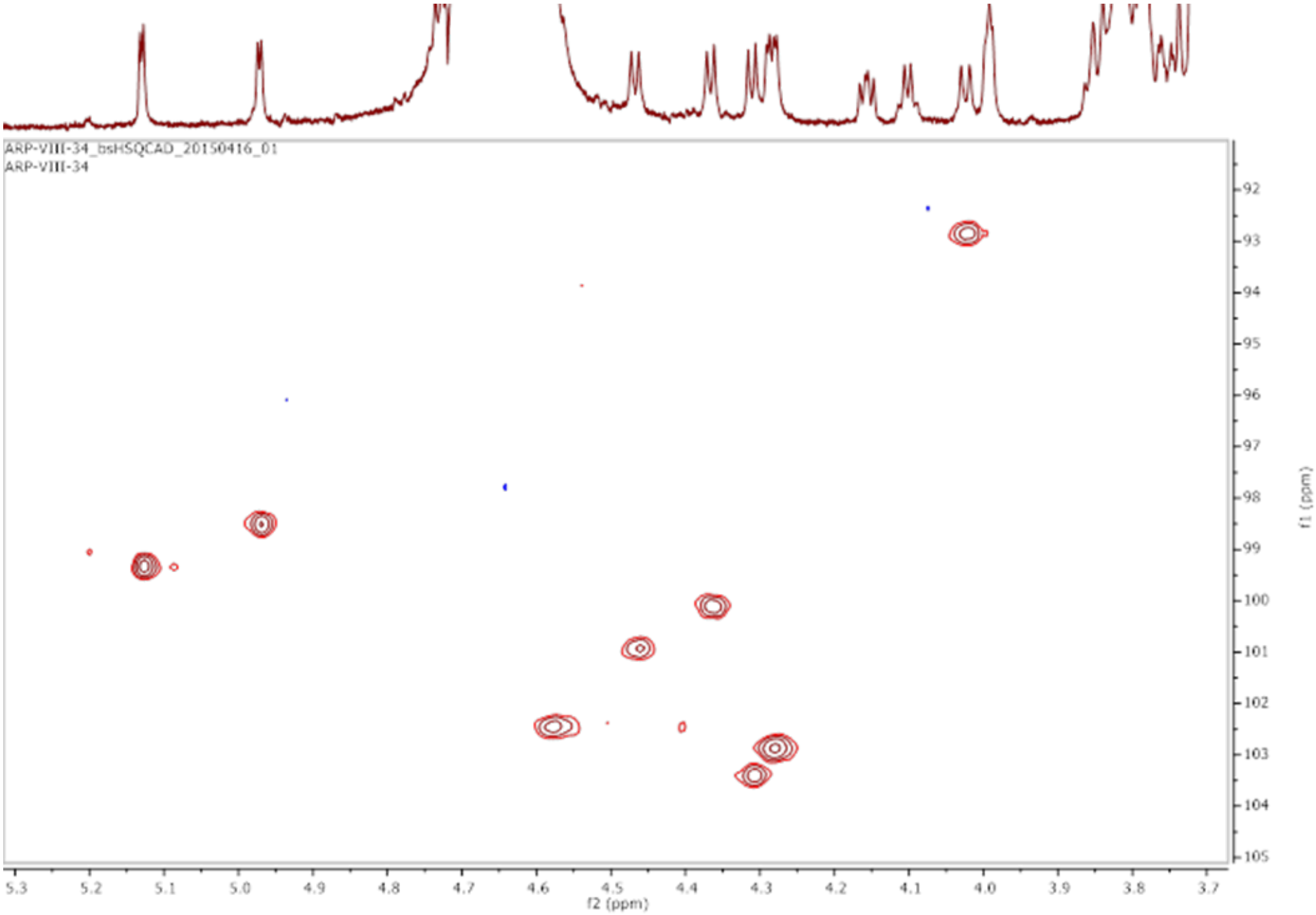
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

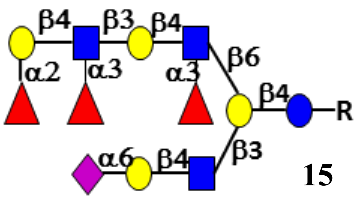
	C1
Glc	92.86
Gal	102.85
GlcNAc	102.43
Gal(2)	103.40
GlcNAc(2)	100.93
Gal(3)	102.85
GlcNAc(3)	102.43
Gal(4)	100.12
Fuc (1) (α3)	98.51
Fuc (2) (α2)	99.38

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{86}H_{135}N_8O_{54}$ Na_2 $(M + 2Na)^+$ exact 2481.9023, found 2481.7117.


ARP-VIII-34_PRESAT_20150326_01
ARP-VIII-34
f1 (ppm)


ARP-VIII-34_bsHSQCAD_20150416_01
ARP-VIII-34
f2 (ppm)
f1 (ppm)
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7
92 93 94 95 96 97 98 99 100 101 102 103 104 105



15

^{1}H (800 MHz, D_2O): δ (ppm)

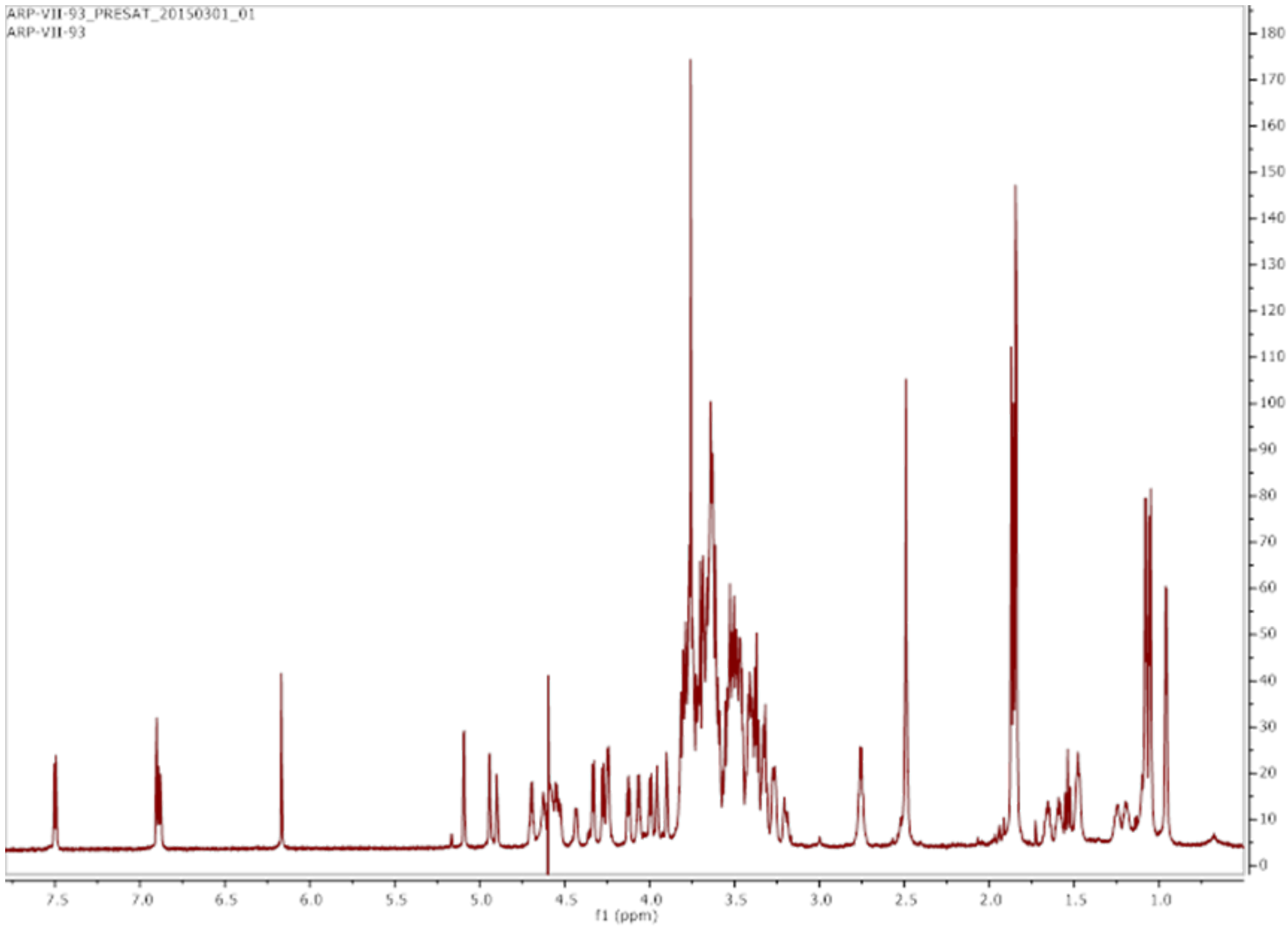
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.31	3.46	3.38	n/a[a]	n/a	-[b]	-	-	-[b]	-
Gal	4.26	3.40	3.52	3.96 (d, *J* = 1.6 Hz, 1H)	n/a	n/a	-	-	-	-	-
GlcNAc	4.56	3.61	3.49	3.42	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(2)	4.28 (d, *J* = 7.8 Hz, 1H)	3.36	3.49	3.75	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 10.3 Hz, 1H)	3.70	3.70	3.40	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(3)	4.24	3.32	3.49	3.90 (d, *J* = 3.1 Hz, 1H)	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.54	3.76	3.64	3.27	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 12H)
Gal(4)	4.33 (d, *J* = 8.0 Hz, 1H)	3.46	n/a	n/a	n/a	n/a	-	-	-	-	-
Fuc (1) (α3)	4.90 (d, *J* = 4.0 Hz, 1H)	3.49	3.69	3.704	4.70 (q, *J* = 7.2 Hz, 1H)	-	-	-	-	1.05 (d, *J* = 6.5 Hz, 3H)	-
Fuc (2) (α3)	4.94 (d, *J* = 3.5 Hz, 1H)	3.56	3.73	3.62	n/a	-	-	-	-	1.08 (d, *J* = 6.5 Hz, 3H)	-
Fuc (3) (α2)	5.09 (d, *J* = 3.6 Hz, 1H)	3.61	n/a	n/a	4.62	-	-	-	-	0.96 (d, *J* = 6.4 Hz, 3H)	
Neu5Ac	-	-	1.54 – axial (dd, *J* = 12.1 Hz, 1H) 2.48 – eq	3.46	3.62	3.51	n/a	n/a	n/a	-	1.91 - 1.84 (m, 12H)

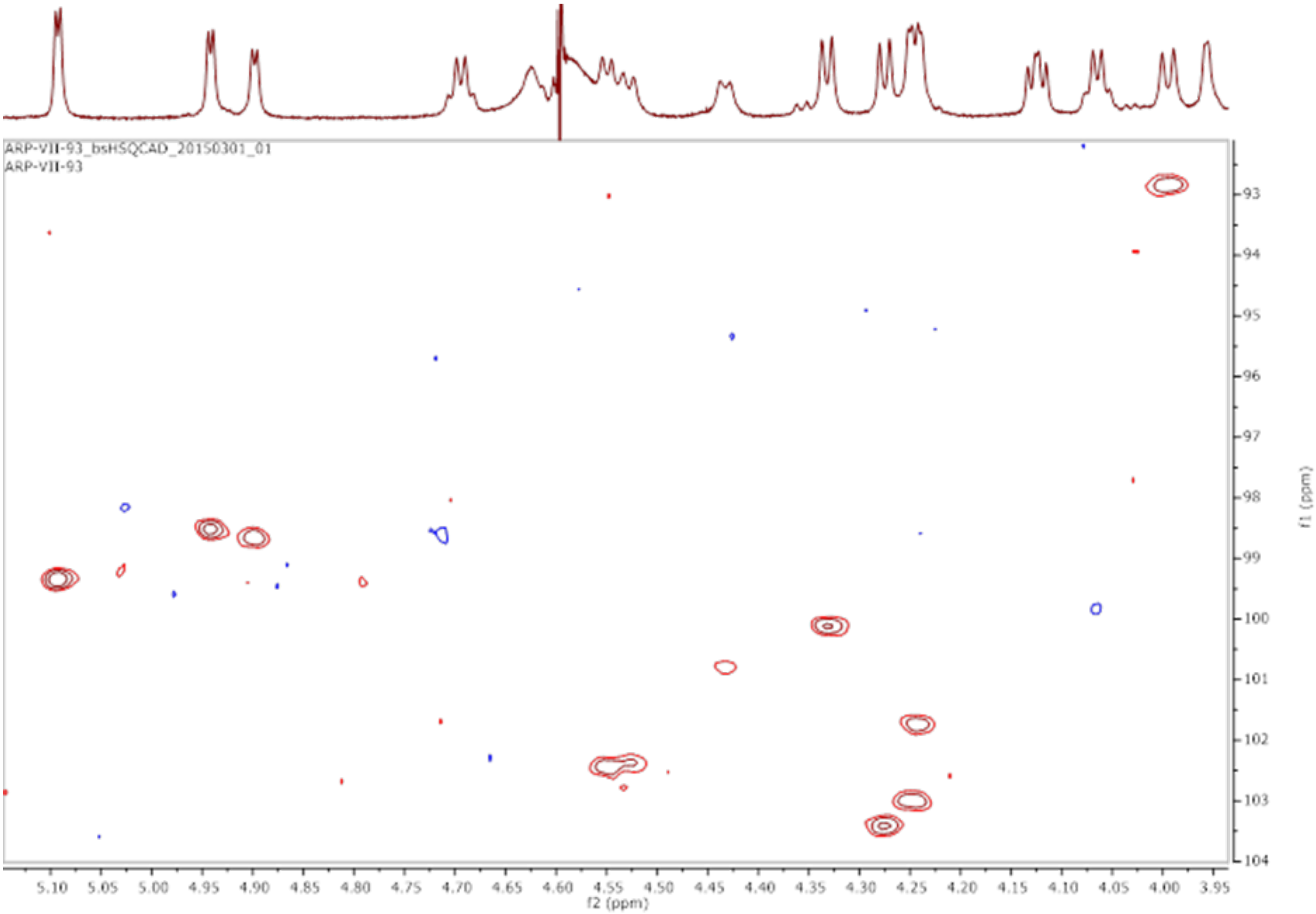
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

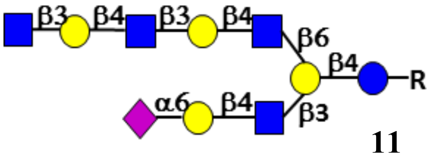
	C1
Glc	98.80
Gal	103.01
GlcNAc	102.41
Gal(2)	103.37
GlcNAc(2)	100.79
Gal(3)	101.74
GlcNAc(3)	102.34
Gal(4)	100.12
Fuc (1) (α3)	98.66
Fuc (2) (α3)	98.56
Fuc (3) (α2)	99.34

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{104}H_{165}N_8O_{66}Na_2$ (M + 2Na)$^+$ exact 2627.9602, found 2627.8804.


ARP-VII-93_PRESAT_20150301_01
ARP-VII-93
f1 (ppm)


ARP-VII-93_bsHSQCAD_20150301_01
ARP-VII-93
f2 (ppm)
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

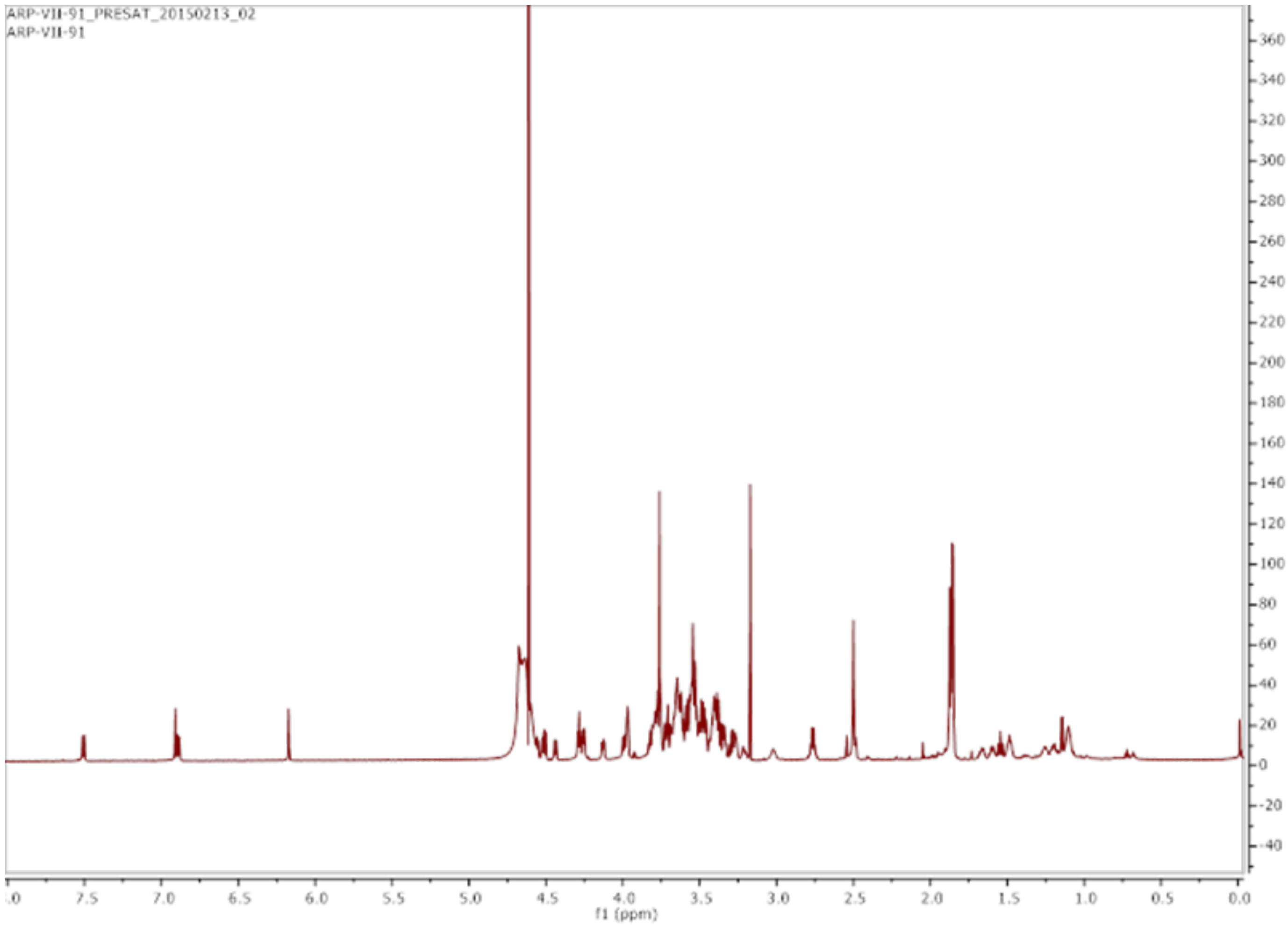
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.36	3.48	3.38	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26 (d, *J* = 7.9 Hz, 2H)	3.41	3.55	3.98 (d, *J* = 1.6 Hz, 1H)	n/a	3.38 3.69	-	-	-	-
GlcNAc	4.56 (d, *J* = 7.8 Hz, 1H)	3.63	3.50	3.45	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(2)	4.29 (d, *J* =7.5 Hz, 1H)	3.341	3.56	3.99	n/a	n/a	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.2 Hz, 1H)	3.56	3.52	3.42	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(3)	4.26 (d, *J* = 7.9 Hz, 2H)	3.41	3.55	3.98	n/a	n/a	-	-	-	-
GlcNAc(3)	4.53 (d, *J* = 8.5 Hz, 1H)	3.62	3.56	n/a	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(4)	4.28 d, *J* =7.5 Hz, 1H)	3.38	3.51	3.77	n/a	n/a	-	-	-	-
GlcNAc(4)	4.52 (d, *J* = 8.5 Hz, 1H)	3.58	3.40	3.29	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Neu5Ac	-	-	1.54 – axial (dd, *J* = 12.1 Hz, 1H) 2.50 – eq	3.48	3.62	3.51	n/a	n/a	n/a	1.91 - 1.84 (m, 15H)

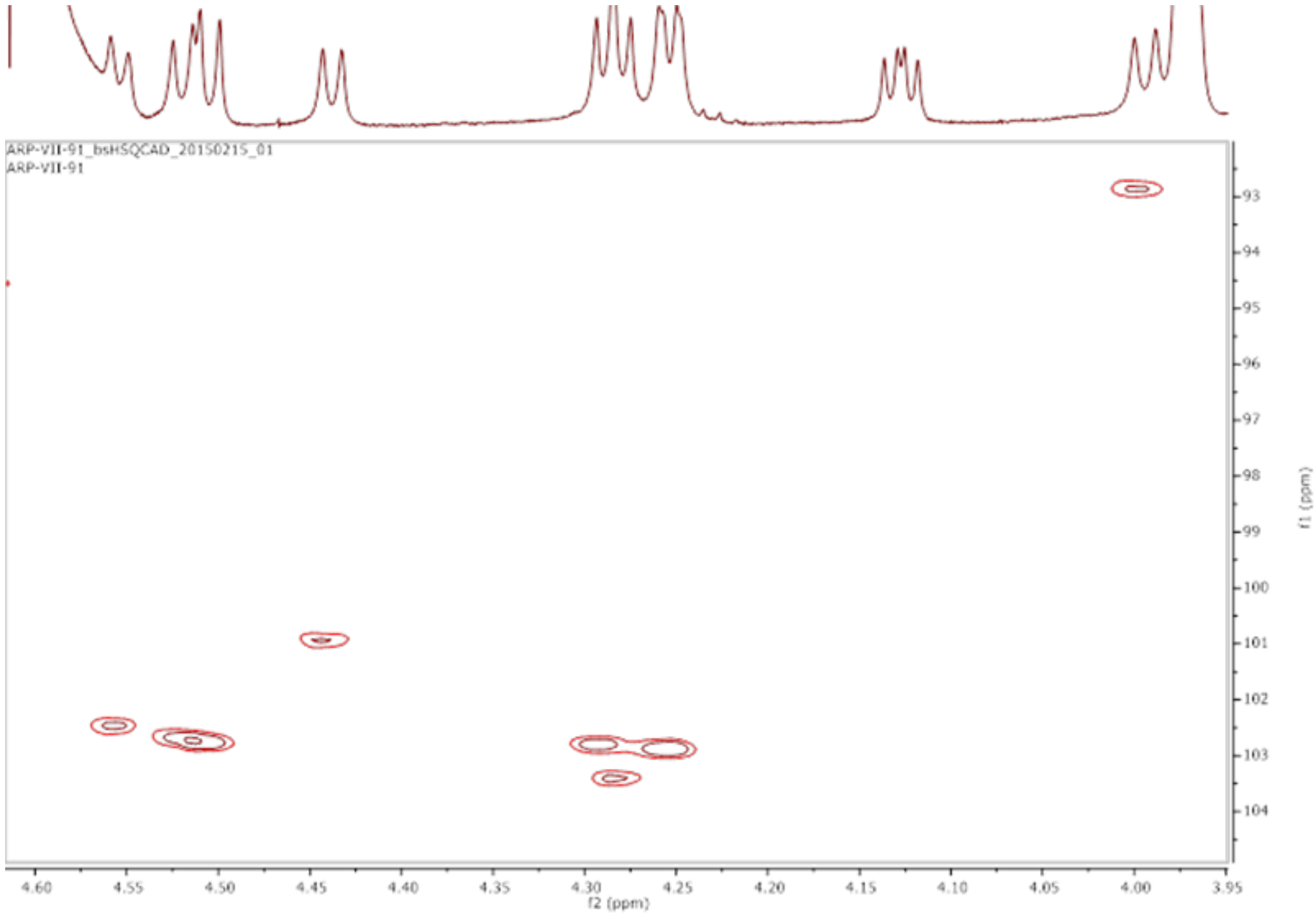
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

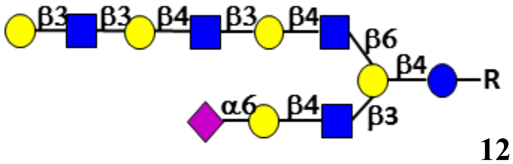
	C1
Glc	92.86
Gal	102.90
GlcNAc	102.445
Gal(2)	102.77
GlcNAc(2)	100.92
Gal(3)	102.90
GlcNAc(3)	102.64
Gal(4)	103.38
GlcNAc (4)	102.77

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{94}H_{148}N_9O_{59}Na_2$- (M + 2Na)$^+$ exact 2392.8658, found 2392.3691.


ARP-VII-91_PRESAT_20150213_02
ARP-VII-91
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ARP-VII-91_bsHSQCAD_20150215_01
ARP-VII-91
f1 (ppm)
93
94
95
96
97
98
99
100
101
102
103
104
4.60
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
f2 (ppm)



12

^{1}H (800 MHz, D_2O): δ (ppm)

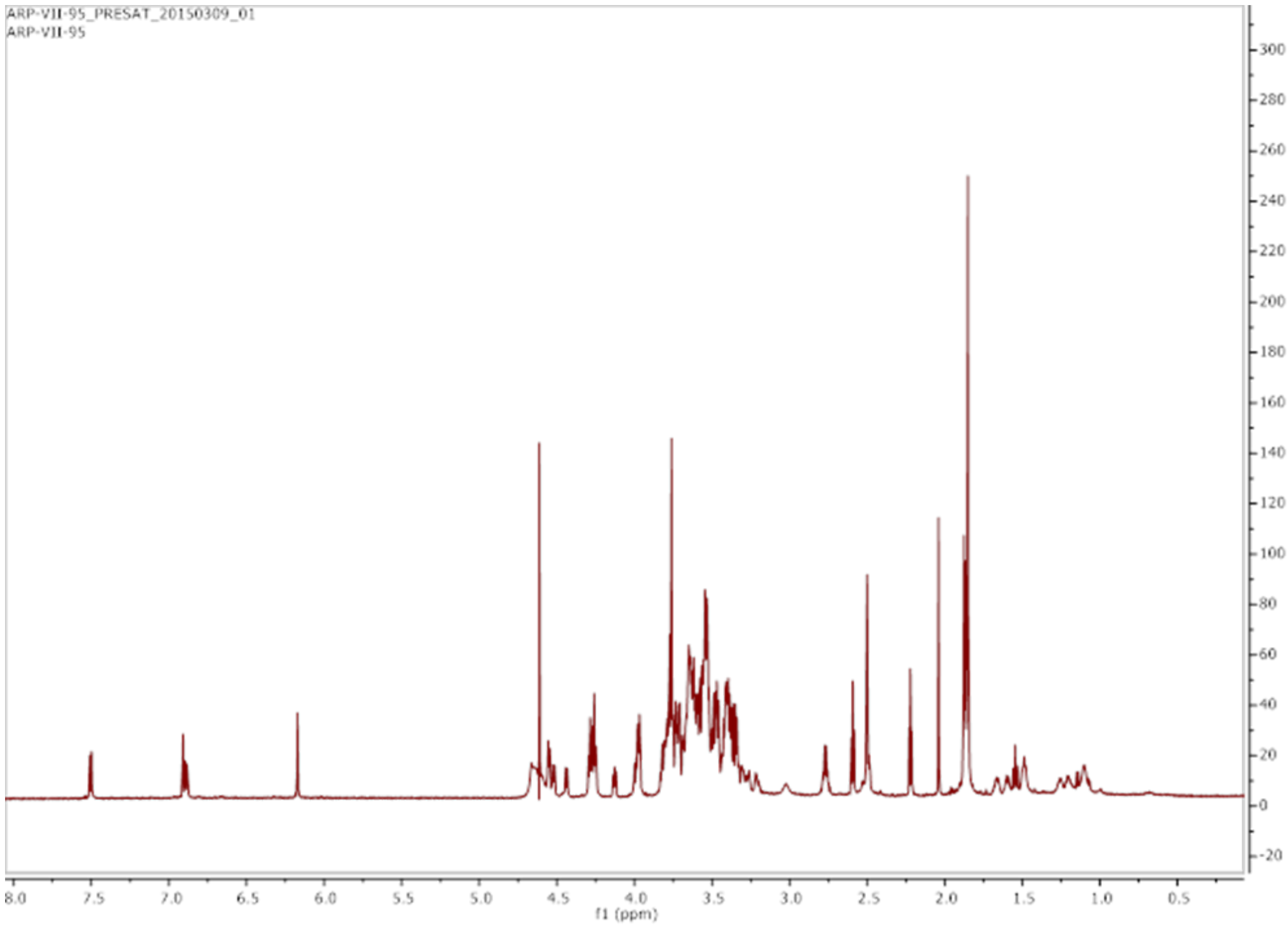
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00	3.34	3.48	3.40	n/a[a]	n/a	-[b]	-	-	-
Gal	4.25 (d, *J* = 8.8 Hz, 2H)	3.40	3.54	3.97	n/a	3.38 3.69	-	-	-	-
GlcNAc	4.55 (d, *J* = 8.3 Hz, 1H)	3.64	3.49	3.44	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(2)	4.30	3.30	3.48	3.75	n/a	n/a	-	-	-	-
GlcNAc(2)	4.45 (d, *J* = 8.5 HZ, 1H)	3.56	3.51	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(3)	4.25 (d, *J* = 8.8 Hz, 2H)	3.40	3.54	3.97	n/a	n/a	-	-	-	-
GlcNAc(3)	4.52 (d, *J* = 8.1 Hz, 1H)	3.63	3.55	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(4)	4.29	3.41	3.57	3.99	n/a	n/a	-	-	-	-
GlcNAc(4)	4.53	3.72	3.40	3.31	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(5)	4.30	3.41	3.57	3.99	n/a	n/a	-	-	-	-
Neu5Ac	-	-	1.54 – axial (dd, *J* = 12.1 Hz, 1H) 2.50 – eq	3.48	3.62	3.51	n/a	n/a	n/a	1.91 - 1.84 (m, 15H)

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

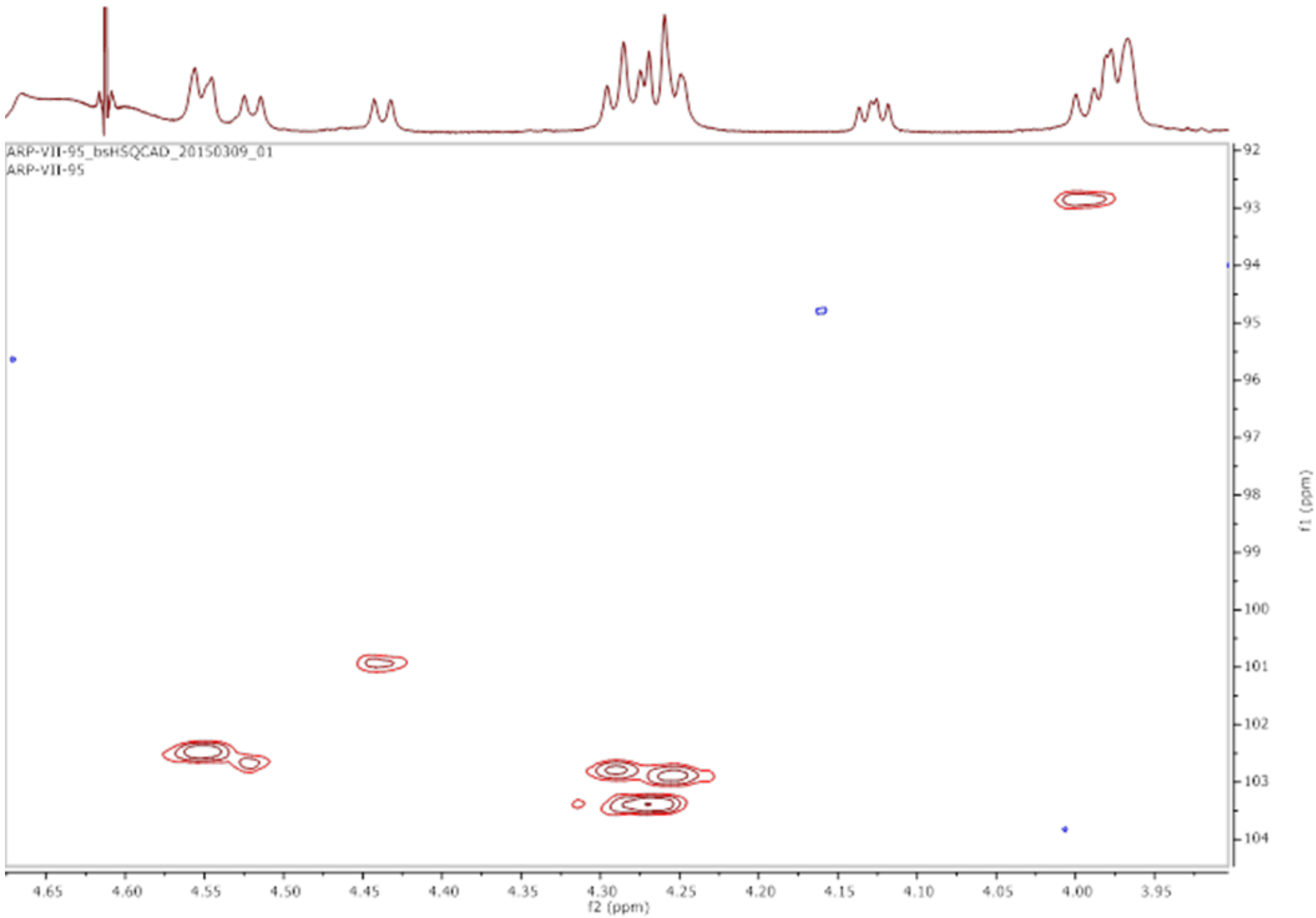
	C1
Glc	92.86
Gal	102.87
GlcNAc	102.49
Gal(2)	102.81
GlcNAc(2)	100.95
Gal(3)	102.87
GlcNAc(3)	102.63
Gal(4)	102.81
GlcNAc (4)	102.49
Gal(5)	103.46

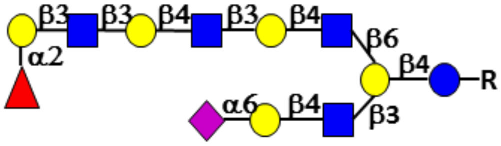
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{100}H_{158}N_9O_{64}Na_2$- $(M + 2Na)^+$ exact 2554.9186, found 2554.7422.



ARP-VII-95_PRESAT_20150309_01
ARP-VII-95
f1 (ppm)


ARP-VII-95_bsHSQCAD_20150309_01
ARP-VII-95
f1 (ppm)
f2 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

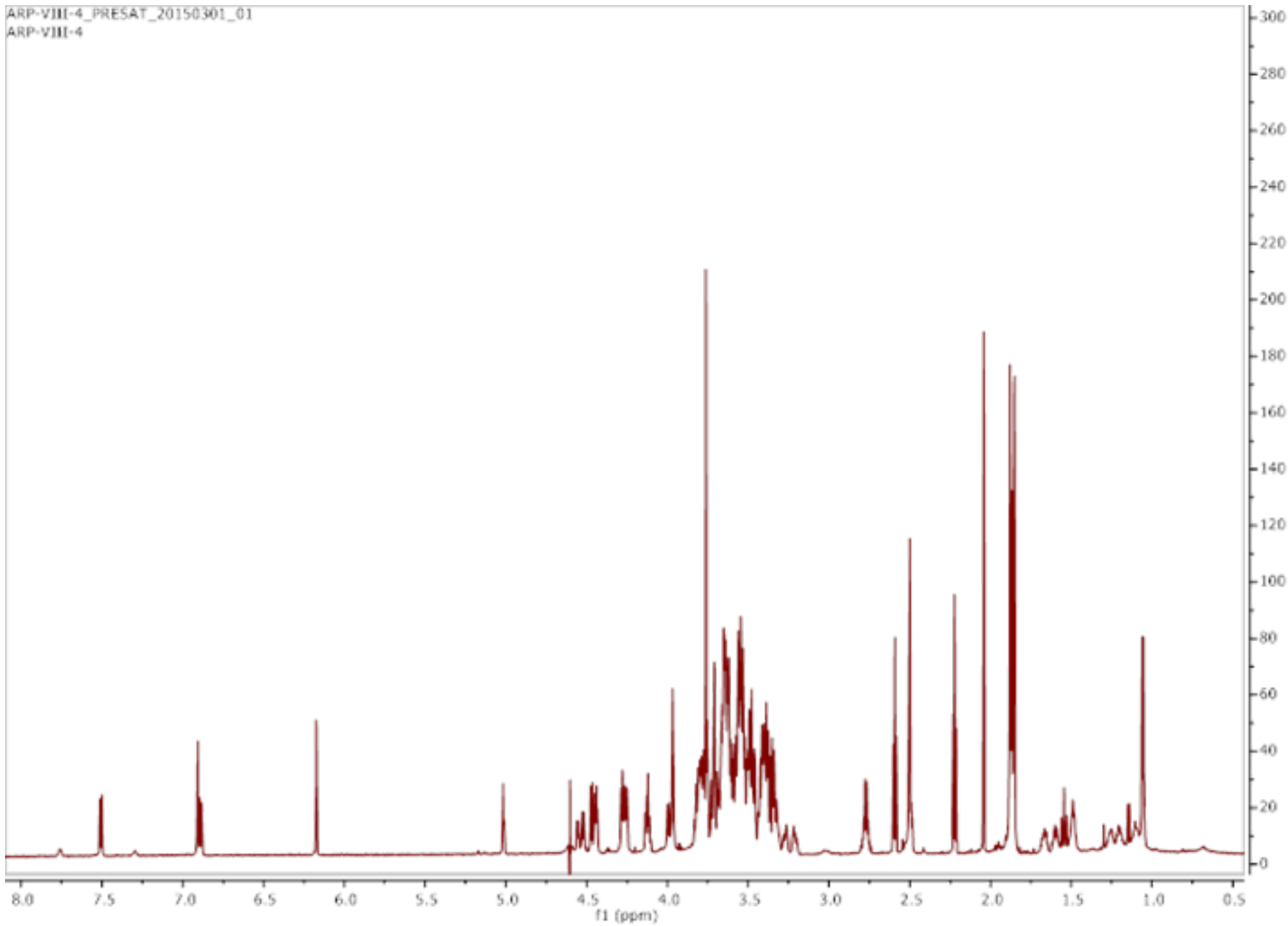
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, J = 9.2 Hz, 1H)	3.35	3.40	3.47	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.26	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc	4.56 (d, J = 7.9 Hz, 2H)	3.63	3.49	3.43	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(2)	4.29	3.38	3.50	3.76	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44	3.57	3.51	3.41	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(3)	4.26	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.52 (d, J = 8.4 Hz, 1H)	3.63	3.55	3.41	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(4)	4.45	3.65	n/a	3.82	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.56 (d, J = 7.9 Hz, 2H)	3.63	3.49	3.43	n/a	n/a	-	-	-	-	1.91-1.84 (m, 15H)
Gal(5)	4.48 (d, J = 7.7 Hz, 1H)	3.42	3.66	3.72	n/a	n/a	-	-	-	-	-
Fuc(α2)	5.02 (d, J = 4.0 Hz, 1H)	3.54	n/a	n/a	4.12 (q, J = 6.4 Hz, 1H)	-	-	-	-	1.07 (d, J = 6.6 Hz, 3H)	-
Neu5Ac	-	-	1.54 – axial (dd, J = 12.1 Hz, 1H) 2.50 – eq	3.48	3.62	3.51	n/a	n/a	n/a	-	1.91 - 1.84 (m, 15H)

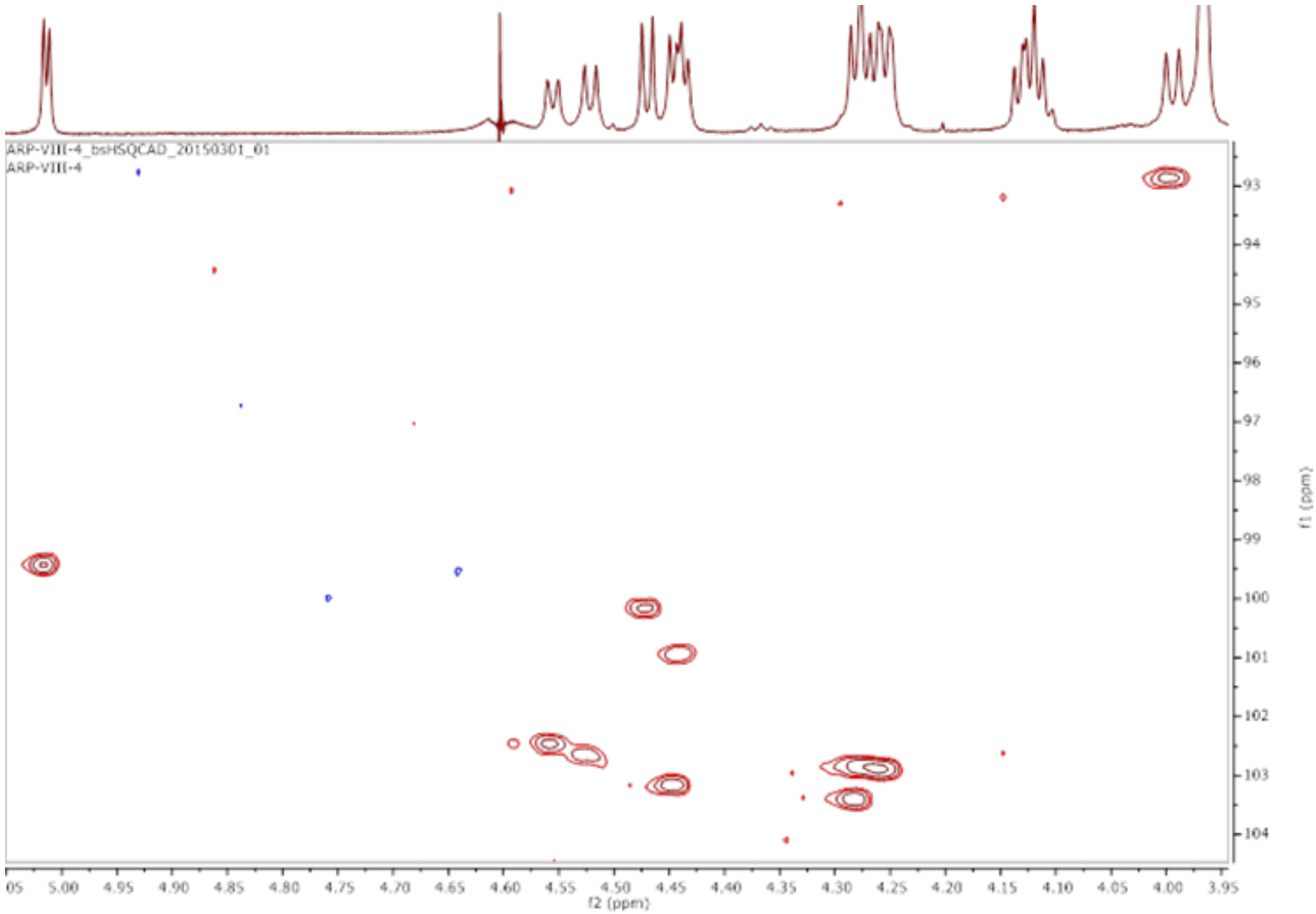
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

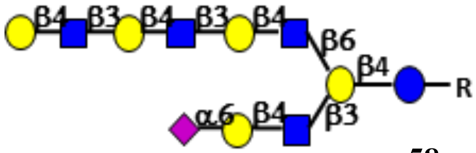
	C1
Glc	92.87
Gal	102.82
GlcNAc	102.43
Gal(2)	103.41
GlcNAc(2)	100.93
Gal(3)	102.82
GlcNAc(3)	102.69
Gal(4)	103.24
GlcNAc (4)	102.43
Gal(5)	100.20
Fuc(α2)	99.42

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{106}H_{168}N_9O_{68}Na_2$- $(M + 2Na)^+$ exact 2700.9766, found 2700.6624.


ARP-VIII-4_PRESAT_20150301_01
ARP-VIII-4
f1 (ppm)


ARP-VIII-4_bsHSQCAD_20150301_01
ARP-VIII-4
f2 (ppm)
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

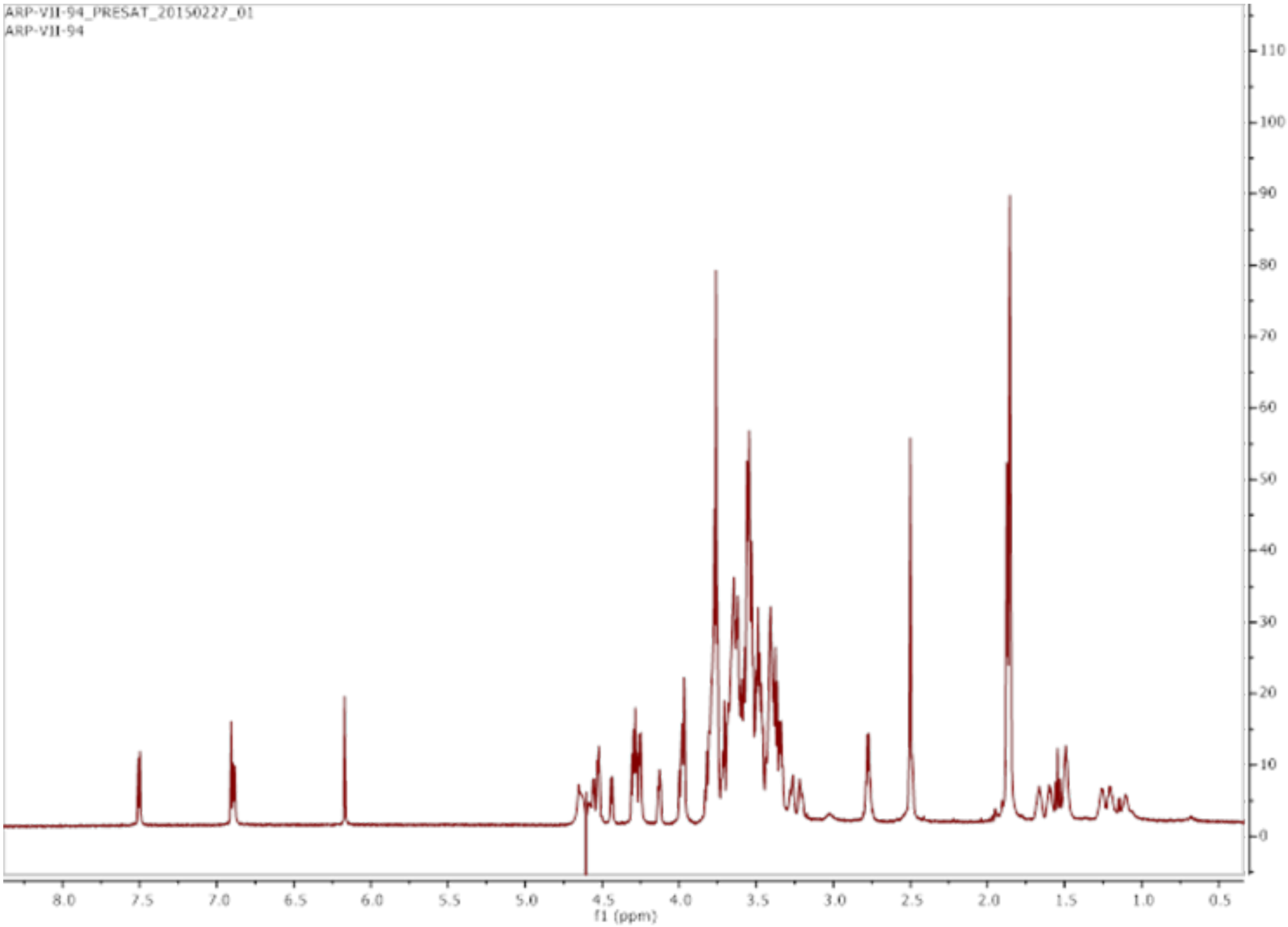
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.00	3.35	3.48	3.39	n/a[a]	n/a	-[b]	-	-	-
Gal	4.26 (d, J = 8.8 Hz, 2H)	3.42	3.54	3.98	n/a	3.38 3.69	-	-	-	-
GlcNAc	4.56 (d, J = 8.3 Hz, 1H)	3.63	3.49	3.44	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(2)	4.30	3.38	3.49	3.76	n/a	n/a	-	-	-	-
GlcNAc(2)	4.44 (d, J = 8.3 HZ, 1H)	3.58	3.51	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(3)	4.26 (d, J = 8.8 Hz, 2H)	3.42	3.54	3.98	n/a	n/a	-	-	-	-
GlcNAc(3)	4.53	3.64	3.56	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(4)	4.30	3.38	3.49	3.76	n/a	n/a	-	-	-	-
GlcNAc(4)	4.53	3.64	3.56	3.41	n/a	n/a	-	-	-	1.91 - 1.84 (m, 15H)
Gal(5)	4.28	3.42	3.56	3.99	n/a	n/a	-	-	-	-
Neu5Ac	-	-	1.54 – axial (dd, J = 12.1 Hz, 1H) 2.50 – eq	3.48	3.62	3.51	n/a	n/a	n/a	1.91 - 1.84 (m, 15H)

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

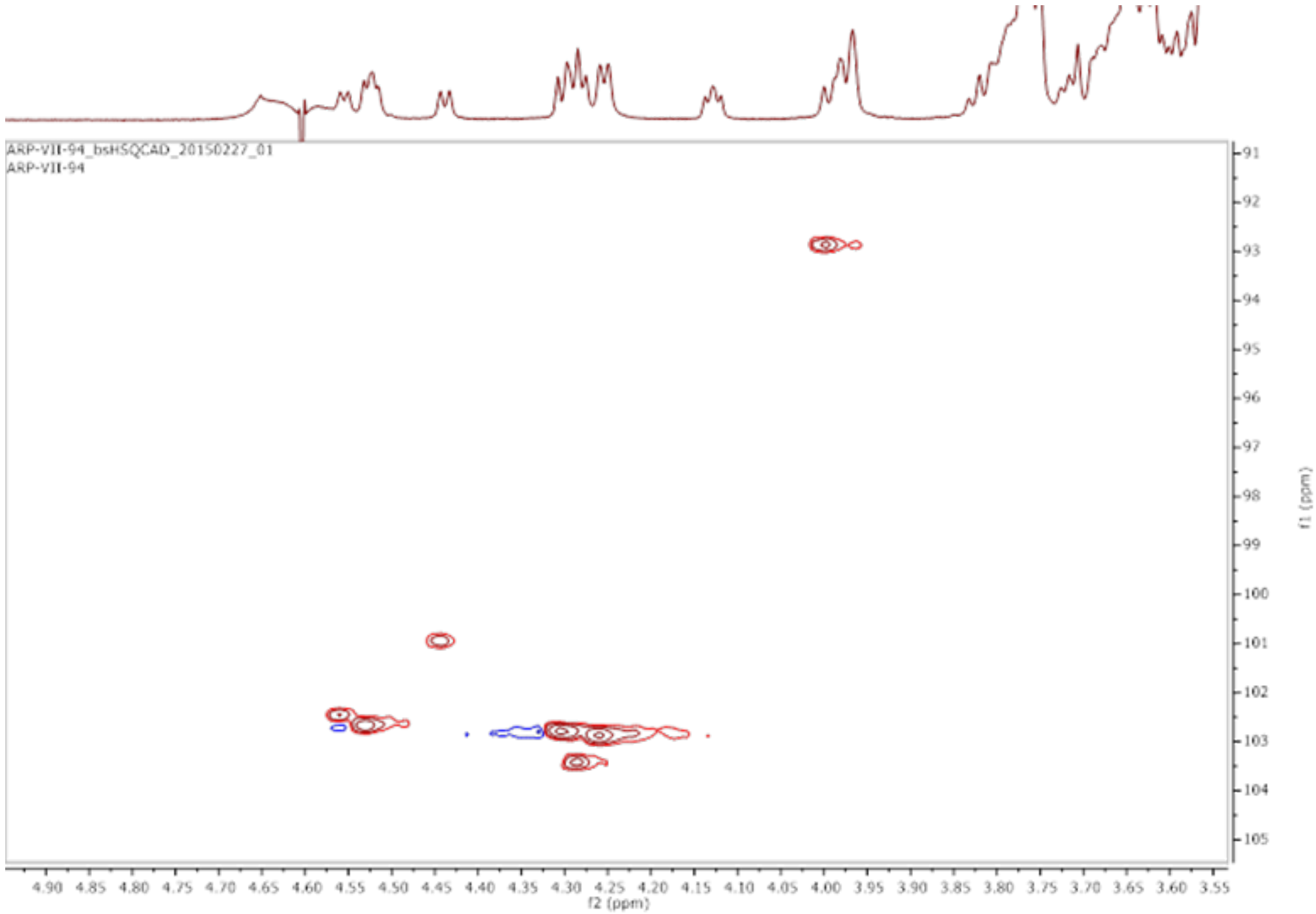
	C1
Glc	92.86
Gal	102.91
GlcNAc	102.51
Gal(2)	102.81
GlcNAc(2)	100.96
Gal(3)	102.98
GlcNAc(3)	102.71
Gal(4)	102.81
GlcNAc (4)	102.71
Gal(5)	103.38

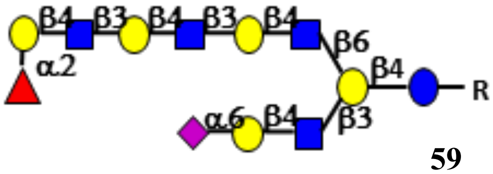
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{100}H_{158}N_9O_{64}Na_2$- $(M + 2Na)^+$ exact 2554.9186, found 2554.2725.



ARP-VII-94_PRESAT_20150227_01
ARP-VII-94
110
100
90
80
70
60
50
40
30
20
10
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ARP-VII-94_bsHSQCAD_20150227_01
ARP-VII-94
f2 (ppm)
f1 (ppm)



59

^{1}H (600 MHz, D_2O): δ (ppm)

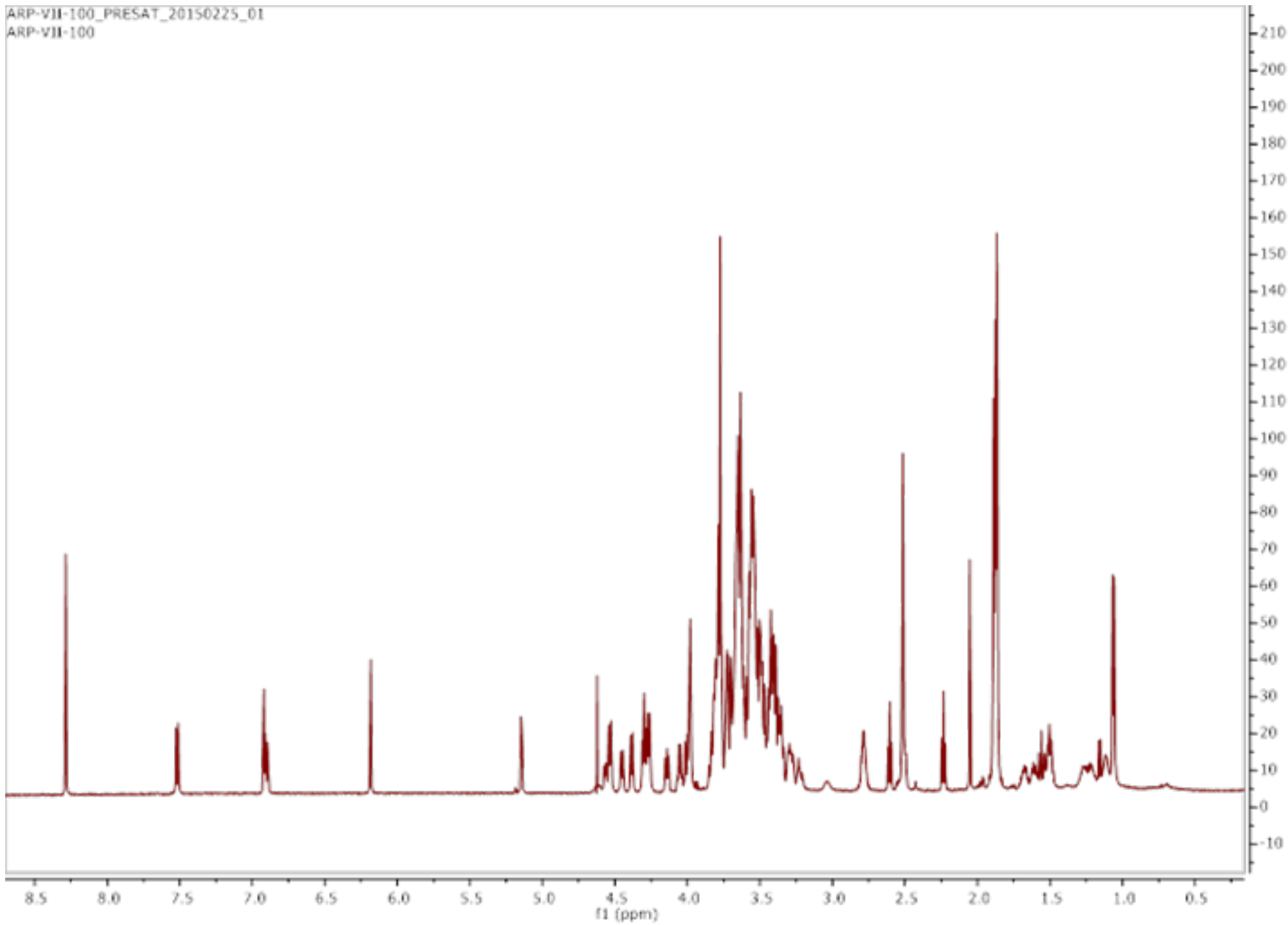
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.31	3.39	3.46	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.26	3.39	3.52	3.95	n/a	3.38 3.69	-	-	-	-	-
GlcNAc	4.57 (d, *J* = 7.6 Hz, 1H)	3.60	3.47	n/a	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(2)	4.28	3.34	3.48	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.2 Hz, 1H)	3.53	3.48	3.39	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(3)	4.26	3.39	3.52	3.95	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.53 (d, *J* = 8.2 Hz, 1H)	3.62	3.52	3.38	n/a	n/a	-	-	-	-	1.91 - 1.84 (m, 15H)
Gal(4)	4.30	3.39	3.57	3.95	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.53 (d, *J* = 8.2 Hz, 1H)	3.62	3.52	3.26	n/a	n/a	-	-	-	-	1.91-1.84 (m, 15H)
Gal(5)	4.38 (d, *J* = 7.7 Hz, 1H)	3.47	n/a	3.69	n/a	n/a	-	-	-	-	-
Fuc(α2)	5.14 (d, *J* = 2.9 Hz, 1H)	3.60	n/a	n/a	4.05 (q, *J* = 6.4 Hz, 1H)	-	-	-	-	1.07 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac	-	-	1.54 – axial (dd, *J* = 12.1 Hz, 1H) 2.50 – eq	3.48	3.62	3.51	n/a	n/a	n/a	-	1.91 - 1.84 (m, 15H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

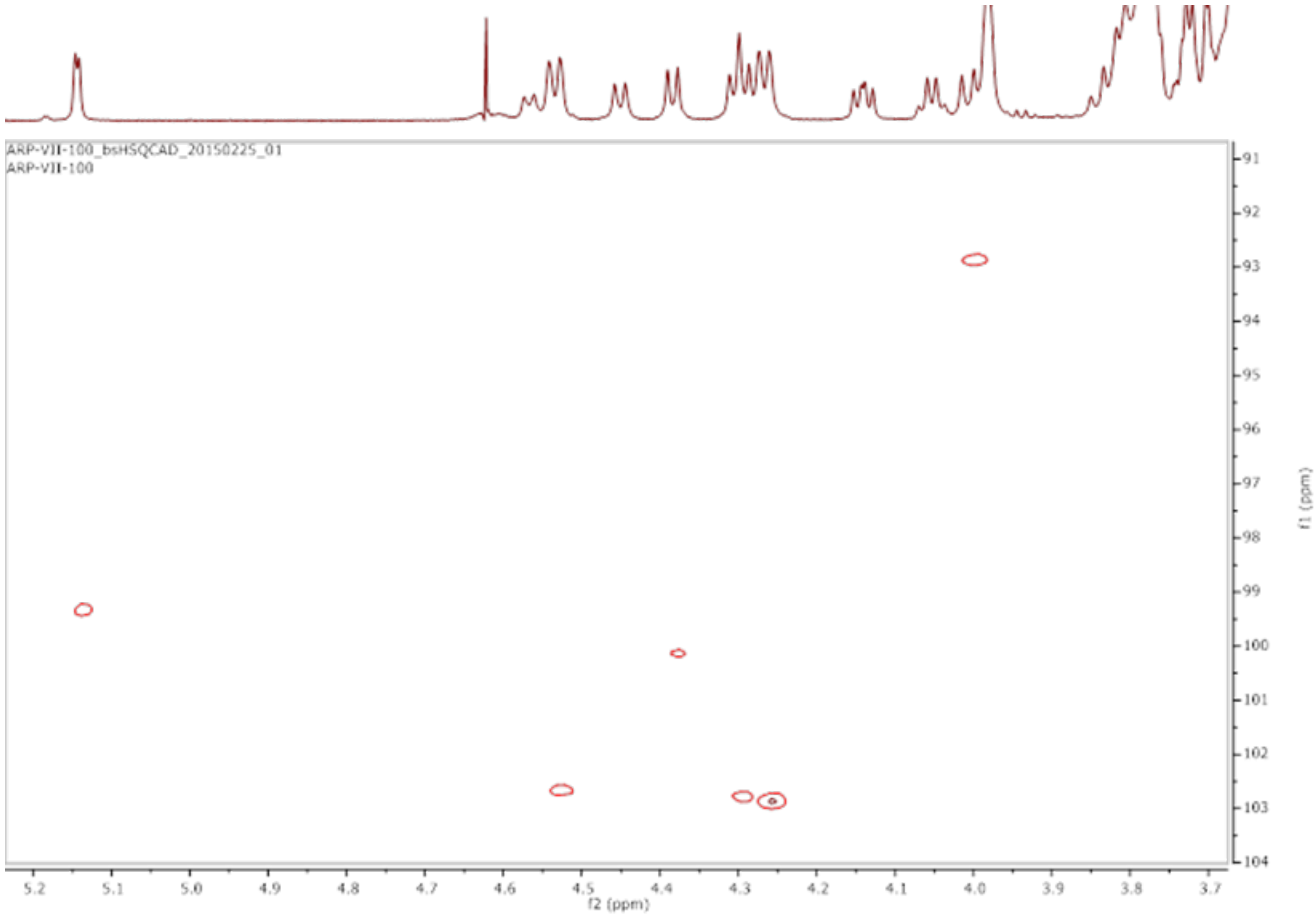
	C1
Glc	92.92
Gal	102.83
GlcNAc	n/a
Gal(2)	103.44
GlcNAc(2)	n/a
Gal(3)	102.83
GlcNAc(3)	102.74
Gal(4)	102.77
GlcNAc (4)	102.74
Gal(5)	100.20
Fuc(α2)	99.32

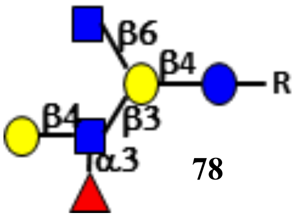
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{106}H_{168}N_9O_{68}Na_2$- $(M + 2Na)^+$ exact 2700.9766, found 2700.7151.



ARP-VII-100_PRESAT_20150225_01
ARP-VII-100
f1 (ppm)


ARP-VII-100_bsHSQCAD_20150225_01
ARP-VII-100
f1 (ppm)
f2 (ppm)



78

^{1}H (600 MHz, D_2O): δ (ppm)

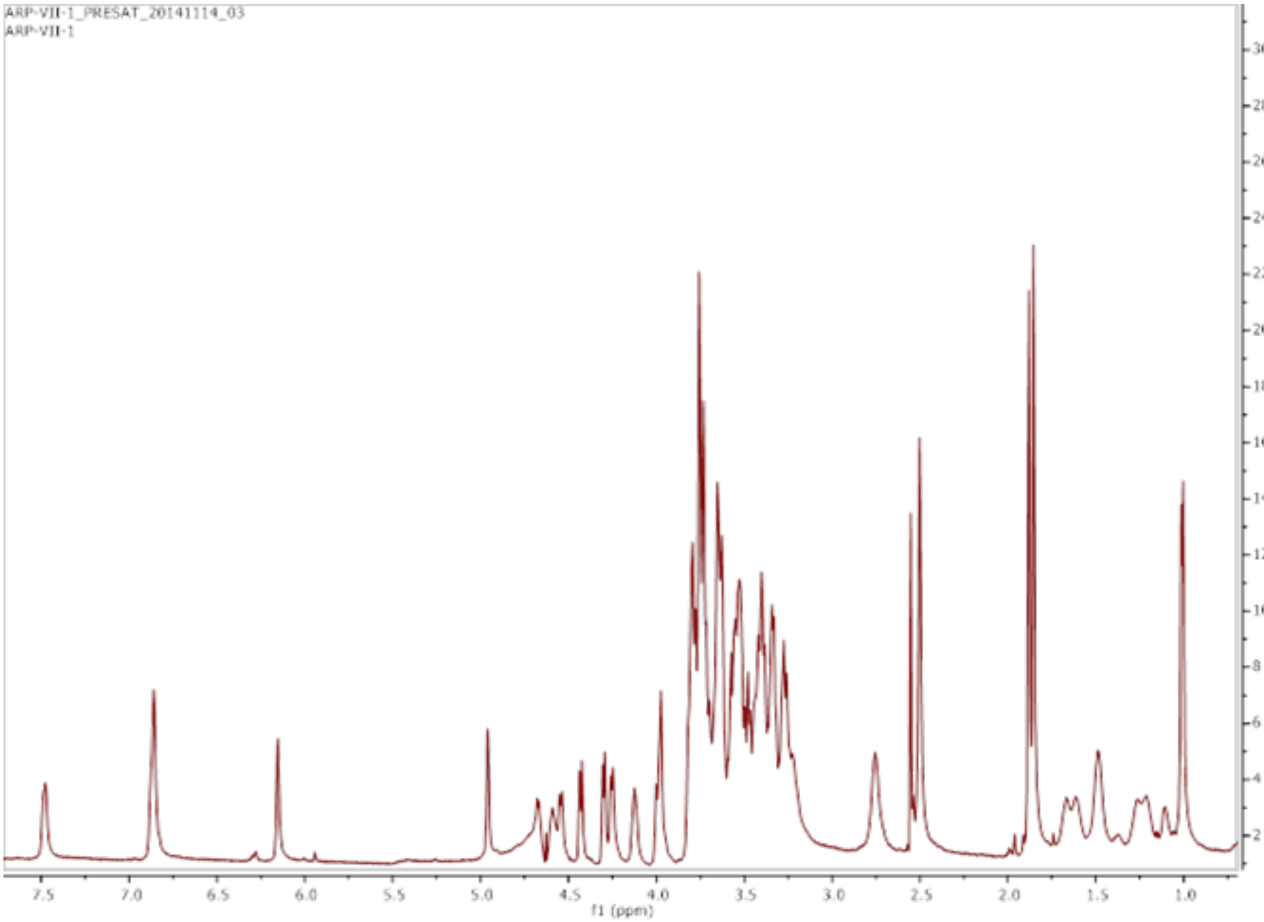
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.36	3.43	3.49	n/a[a]	n/a	-	-
Gal	4.24 (d, *J* = 7.2 Hz, 1H)	3.40	3.54	4.00	n/a	3.82 3.66	-	-
GlcNAc	4.53 (d, *J* = 8.6 Hz, 1H)	3.79	3.73	3.43	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(2)	4.29 (d, *J* = 7.3 Hz, 1H)	3.33	3.51	3.75	n/a	n/a	-	-
GlcNAc(2)	4.42 (d, *J* = 8.1 Hz, 1H)	3.52	3.41	3.30	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Fuc(α3)	4.96	3.53	3.76	3.65	4.68	-	1.01 (d, *J* = 5.9 Hz, 3H)	-

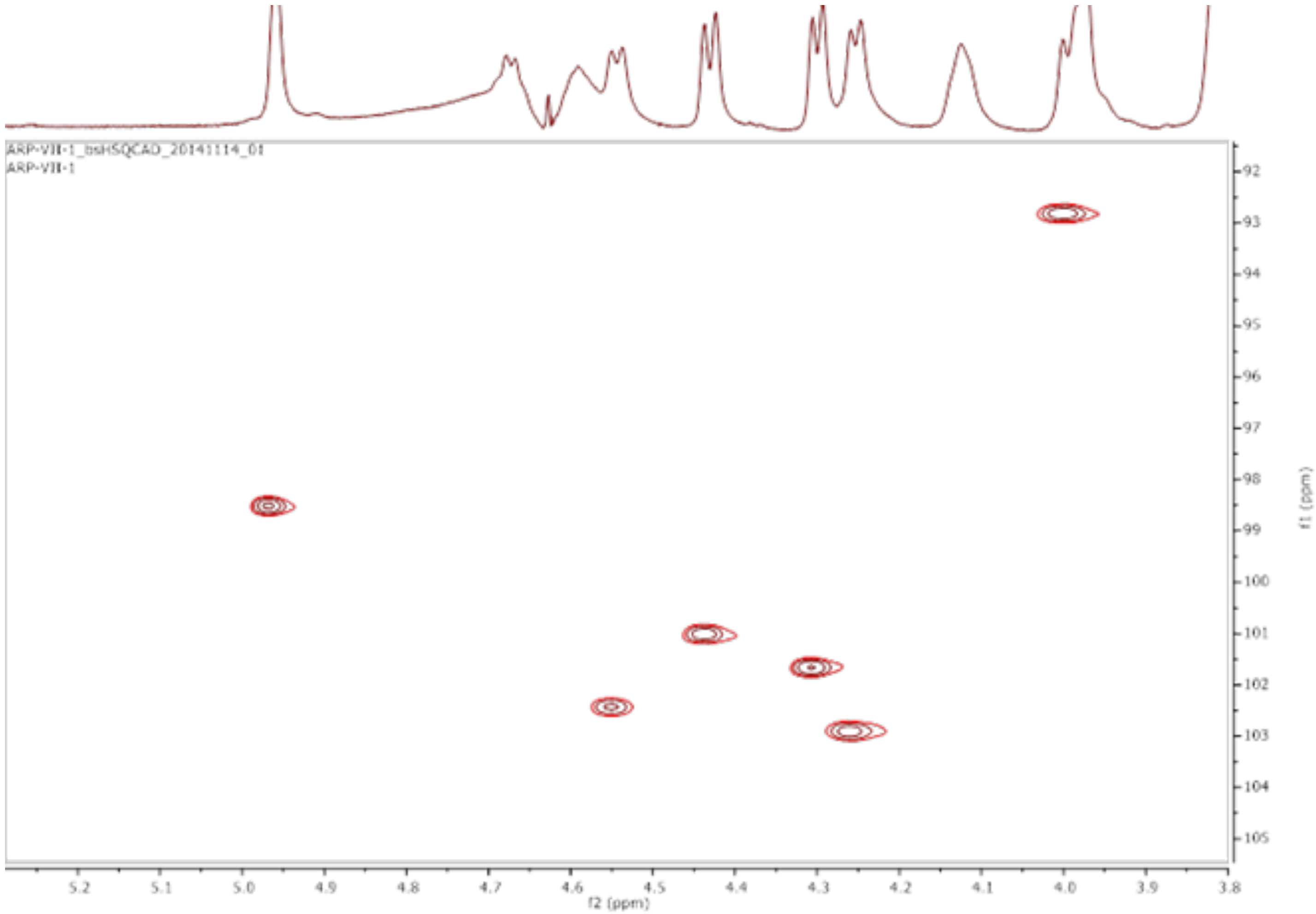
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

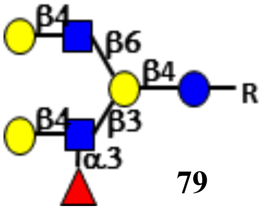
	C1
Glc	92.81
Gal	102.92
GlcNAc	102.47
Gal(2)	101.67
GlcNAc(2)	101.03
Fuc(α3)	98.49

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{61}H_{96}N_6O_{35}Na$- $(M + Na)^+$ exact 1495.5814, found 1495.4545.


ARP-VII-1_PRESAT_20141114_03
ARP-VII-1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2


ARP-VII-1_bsHSQCAD_20141114_01
ARP-VII-1
f2 (ppm)
f1 (ppm)



79

^{1}H (600 MHz, D_2O): δ (ppm)

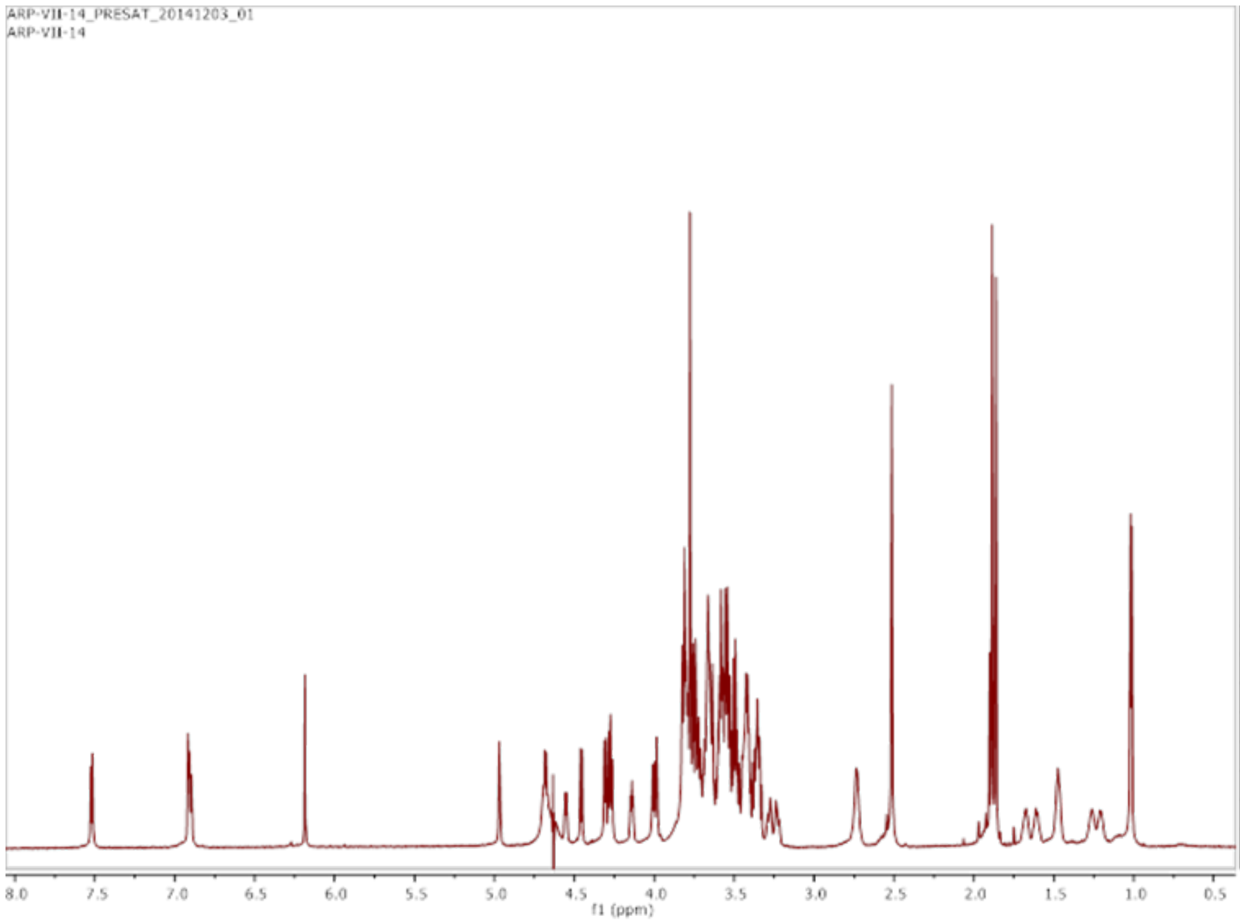
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.34	3.40	3.47	n/a[a]	n/a	-	-
Gal	4.27	3.40	3.53	3.97	n/a	3.82 3.66	-	-
GlcNAc	4.54 (d, *J* = 8.6 Hz, 1H)	3.78	3.71	3.41	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(2)	4.31 (d, *J* = 7.8 Hz, 1H)	3.33	3.49	3.73	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.3 Hz, 1H)	3.56	3.51	3.42	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(3)	4.29	3.35	3.48	3.74	n/a	n/a		
Fuc(α3)	4.96 (d, *J* = 3.9 Hz, 1H)	3.53	3.76	3.65	4.68	-	1.01 (d, *J* = 6.6c Hz, 3H)	-

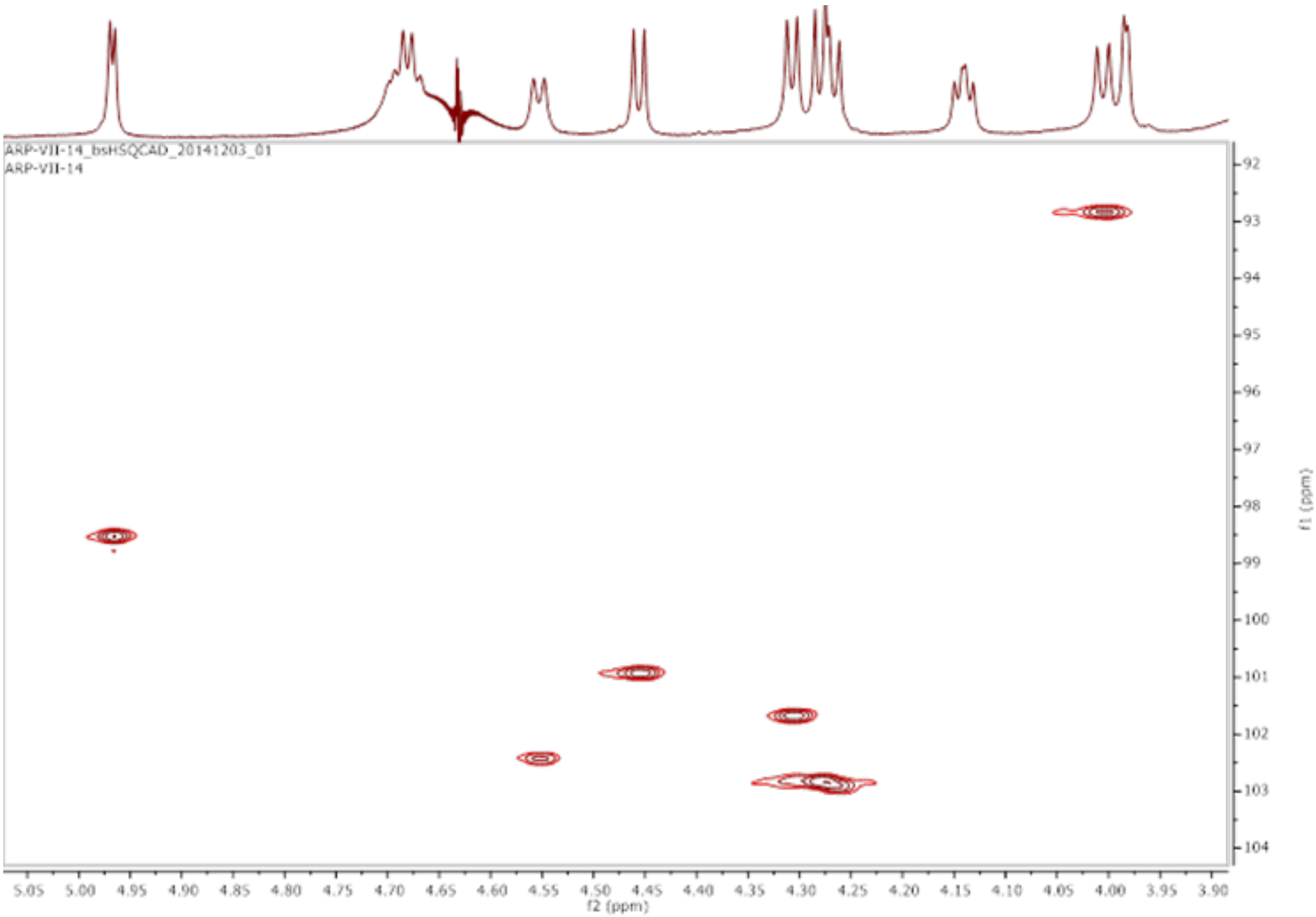
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

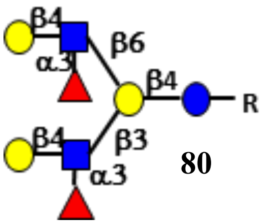
	C1
Glc	92.81
Gal	102.94
GlcNAc	102.44
Gal(2)	101.69
GlcNAc(2)	101.00
Gal(3)	102.82
Fuc(α3)	98.58

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{67}H_{106}N_6O_{40}$- (M + Na)$^+$ exact 1657.6343, found 1657.0420.


ARP-VII-14_PRESAT_20141203_01
ARP-VII-14
f1 (ppm)


ARP-VII-14_bsHSQCAD_20141203_01
ARP-VII-14
5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90
f2 (ppm)
92 93 94 95 96 97 98 99 100 101 102 103 104
f1 (ppm)



80

^{1}H (800 MHz, D_2O): δ (ppm)

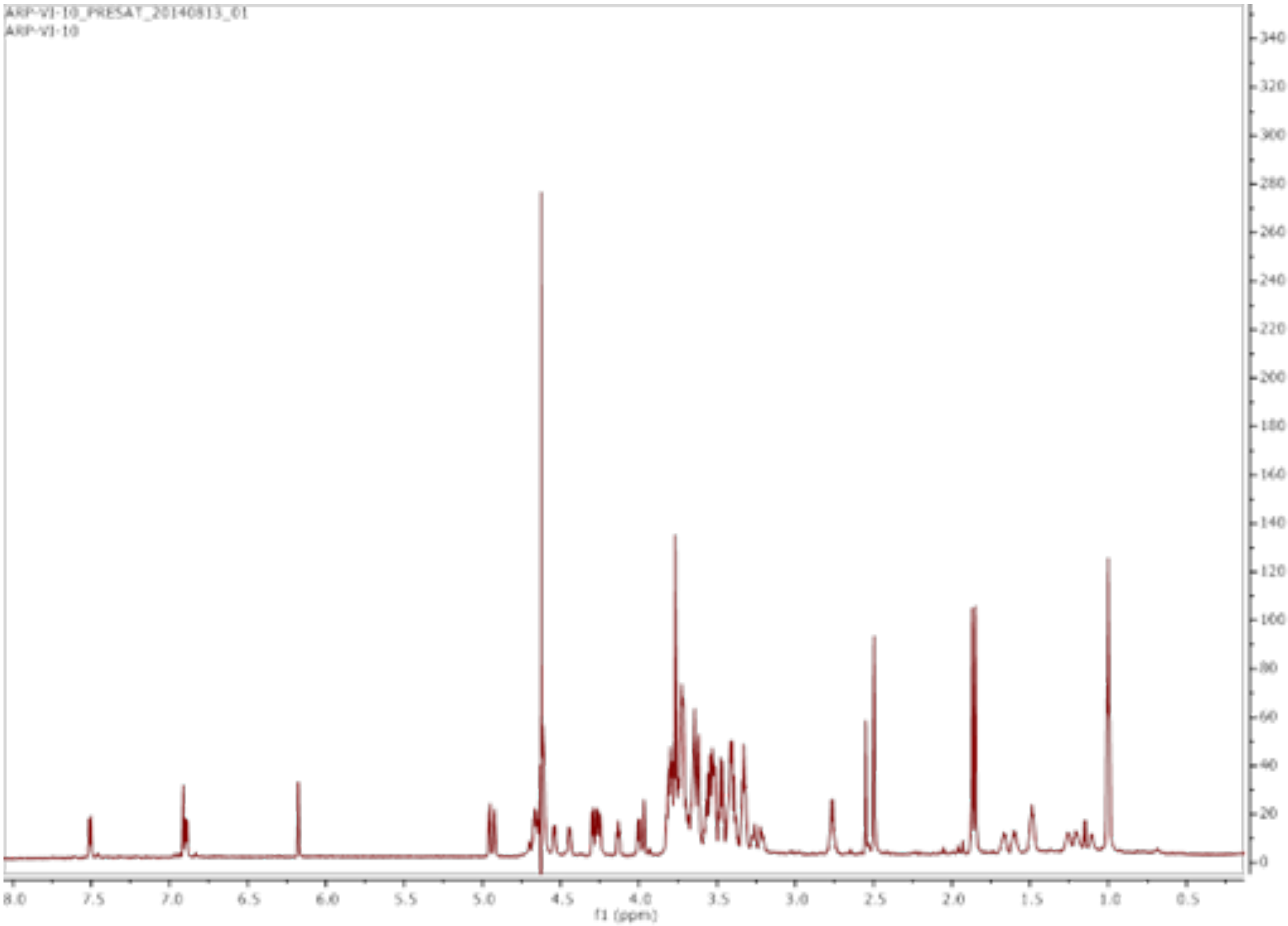
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 9.4 Hz, 1H)	3.32	3.39	3.47	n/a[a]	n/a	-	-
Gal	4.25	3.39	3.51	3.96	n/a	3.82 3.66	-	-
GlcNAc	4.54 (d, *J* = 7.9 Hz, 1H)	3.78	3.71	3.41	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(2)	4.29 (d, *J* = 7.9 Hz, 1H)	3.33	3.47	3.73	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 6.8 Hz, 1H)	3.73	n/a	3.42	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(3)	4.27	3.31	3.46	3.71	n/a	n/a		
Fuc(1)(α3)	4.96 (d, *J* = 3.5 Hz, 1H)	3.51	3.73	3.62	4.66	-	1.01 (d, *J* = 6.6c Hz, 3H)	-
Fuc(2)(α3)	4.92 (d, *J* = 3.5 Hz, 1H)	3.51	3.71	3.61	4.66	-	1.01	-

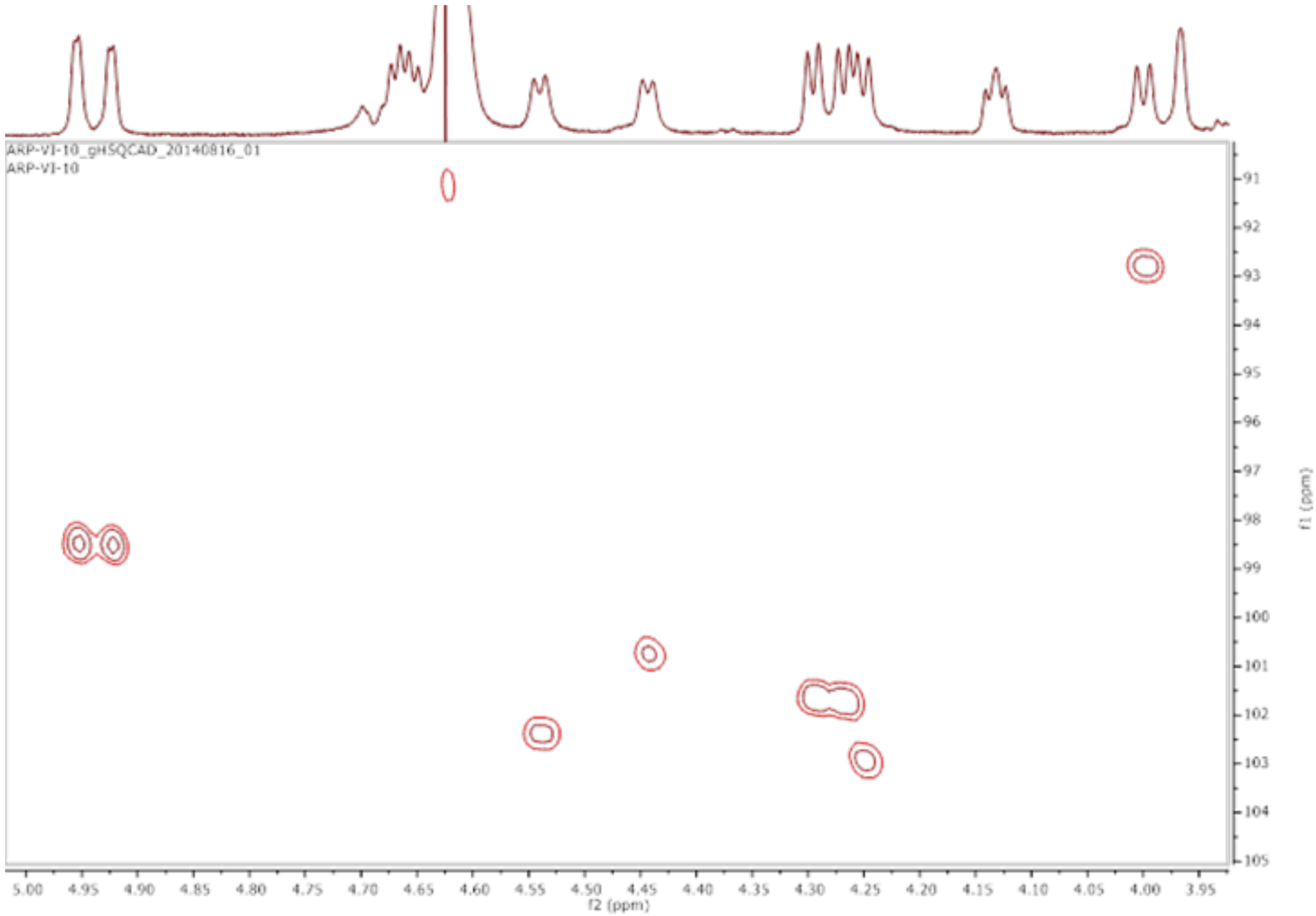
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

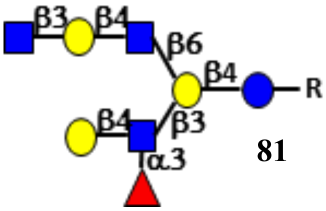
	C1
Glc	92.82
Gal	102.97
GlcNAc	102.38
Gal(2)	101.68
GlcNAc(2)	100.66
Gal(3)	101.68
Fuc(1)(α3)	98.52
Fuc(2)(α3)	98.56

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{73}H_{116}N_6O_{44}Na$- $(M + Na)^+$ exact 1803.6922, found 1804.5262.


ARP-VI-10_PRESAT_20140813_01
ARP-VI-10
f1 (ppm)


ARP-VI-10_gHSQCAD_20140816_01
ARP-VI-10
f2 (ppm)
f1 (ppm)
5.00
4.95
4.90
4.85
4.80
4.75
4.70
4.65
4.60
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105



81

^{1}H (600 MHz, D_2O): δ (ppm)

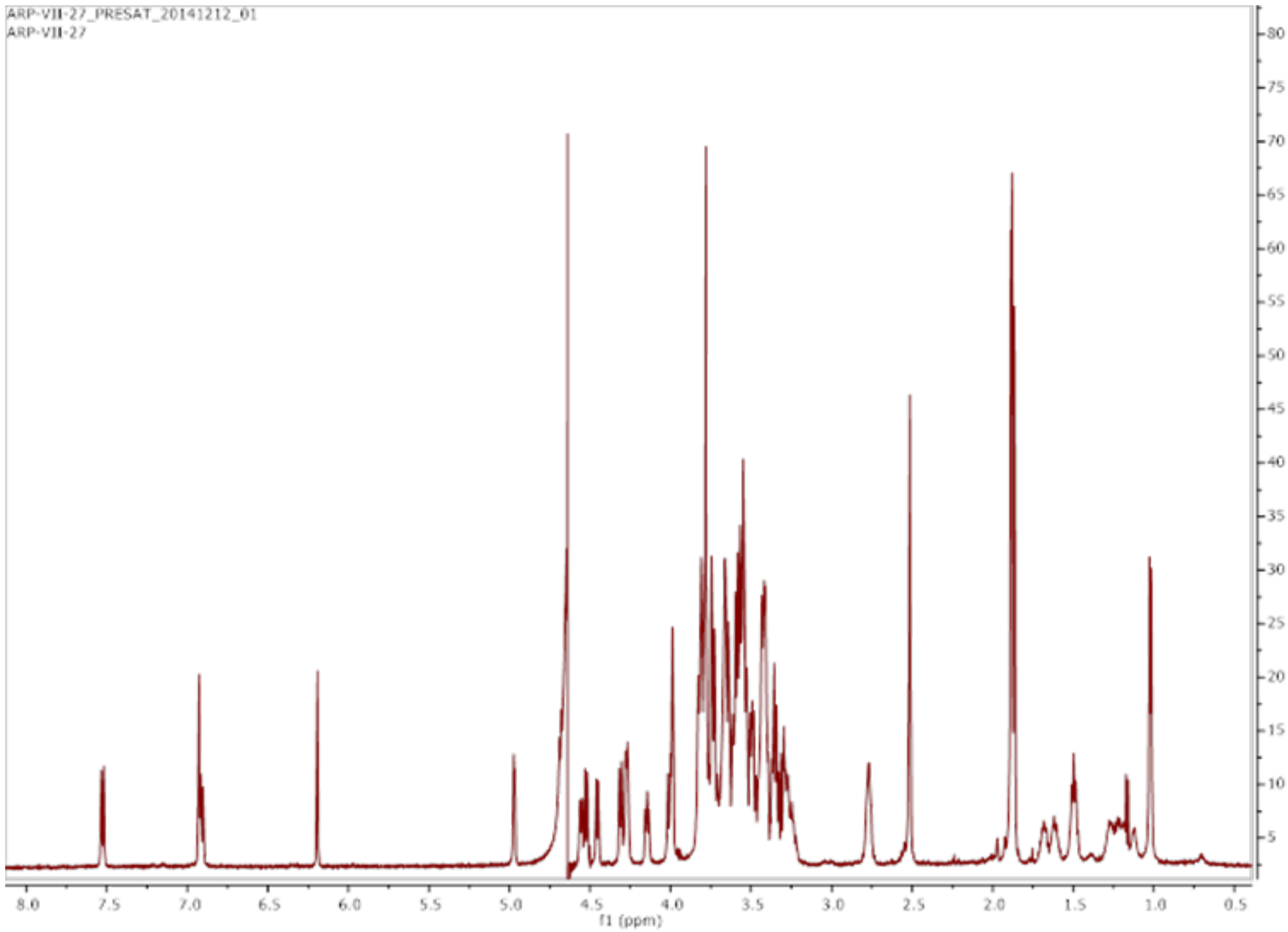
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.31	3.42	3.48	n/a[a]	n/a	-	-
Gal	4.27	3.40	3.56	3.98	n/a	3.82 3.66	-	-
GlcNAc	4.54 (d, *J* = 7.4 Hz, 1H)	3.78	3.71	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.31 (d, *J* = 7.6 Hz, 1H)	3.34	3.49	3.73	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.2 Hz, 1H)	3.56	3.51	3.42	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.27	3.42	3.56	3.98	n/a	n/a		
GlcNAc(3)	4.52 (d, *J* = 8.7 Hz, 1H)	3.58	3.41	3.29	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Fuc(α3)	4.96 (d, *J* = 3.6 Hz, 1H)	3.53	3.76	3.65	4.68	-	1.01 (d, *J* = 6.3 Hz, 3H)	-

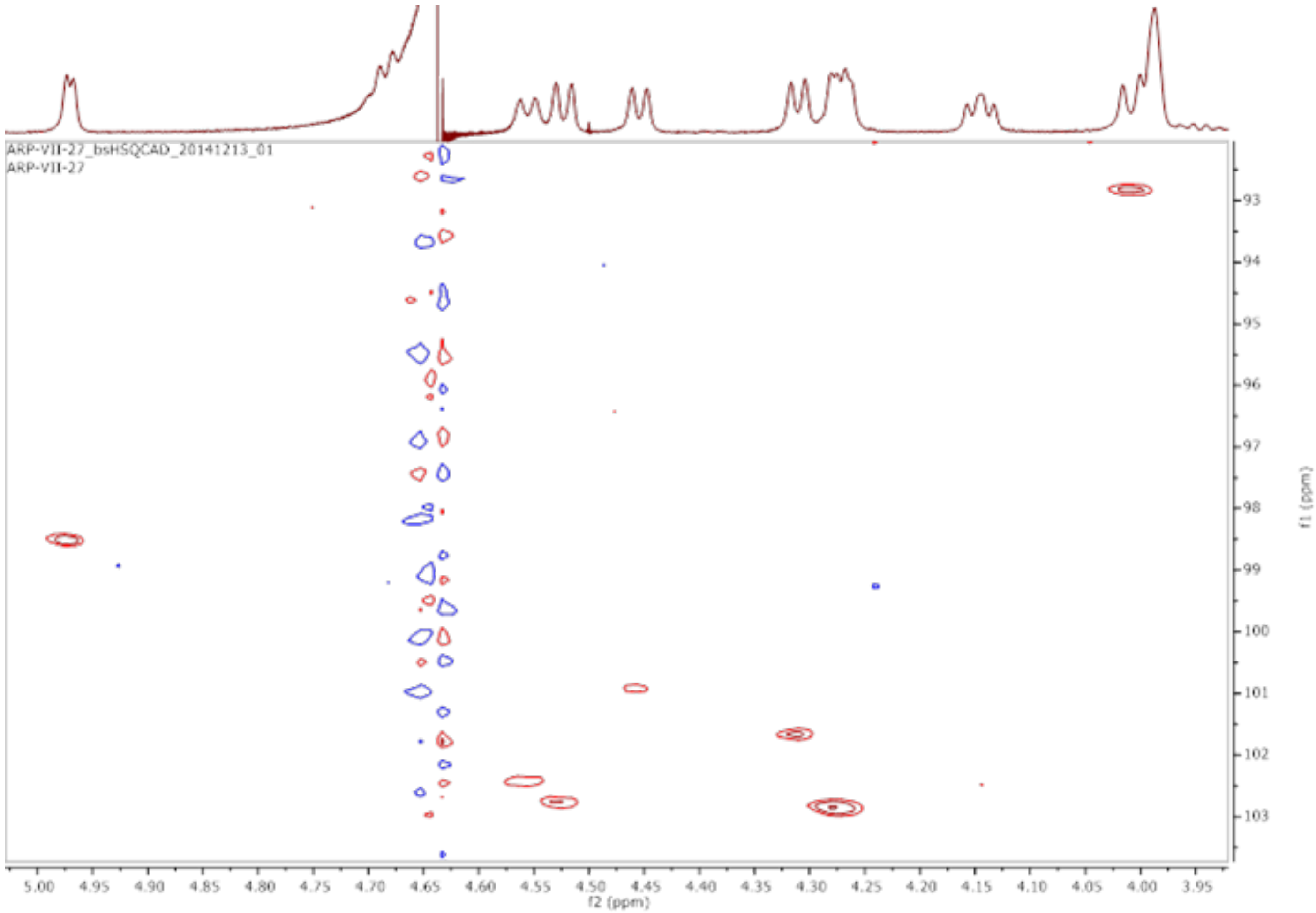
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.79
Gal	102.78
GlcNAc	102.40
Gal(2)	101.69
GlcNAc(2)	101.93
Gal(3)	102.78
GlcNAc(3)	102.78
Fuc(α3)	98.58

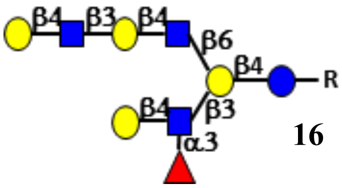
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{75}H_{119}N_7O_{45}Na$- $(M + Na)^+$ exact 1860.7136, found 1860.5052.


ARP-VII-27_PRESAT_20141212_01
ARP-VII-27
f1 (ppm)



ARP-VII-27_bsHSQCAD_20141213_01
ARP-VII-27
f1 (ppm)
f2 (ppm)



16

^{1}H (800 MHz, D_2O): δ (ppm)

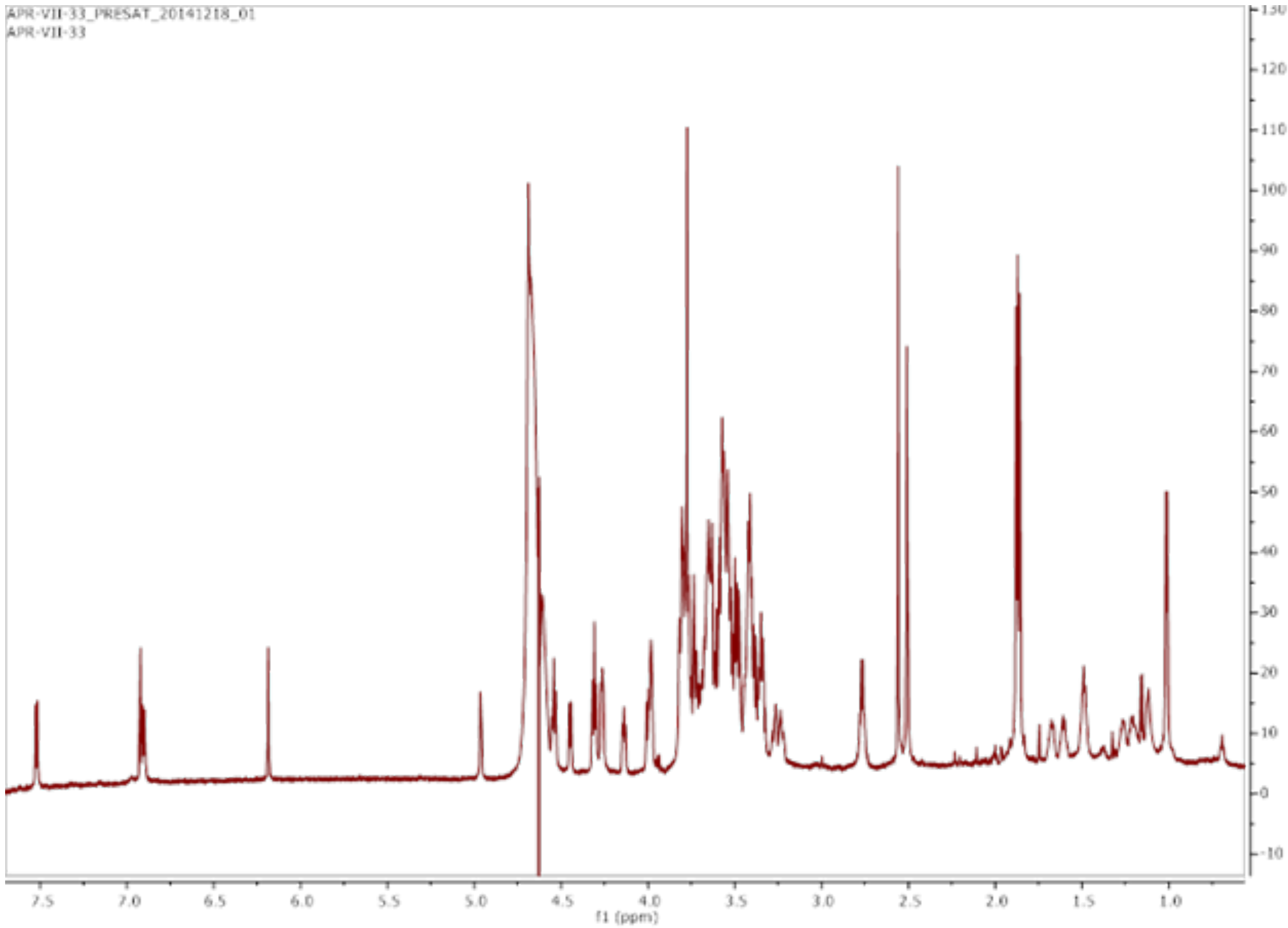
	H1	H2	H3	H4	H5	H6	CH₃	NHAc
Glc	4.00 (d, *J* = 9.3 Hz, 1H)	3.33	3.41	3.48	n/a[a]	n/a	-	-
Gal	4.27	3.40	3.54	3.98	n/a	3.82 3.66	-	-
GlcNAc	4.53	3.78	3.71	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.31 (d, *J* = 7.6 Hz, 1H)	3.36	3.49	3.76	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.4 Hz, 1H)	3.56	3.51	3.42	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.27	3.40	3.54	3.98	n/a	n/a		
GlcNAc(3)	4.54	3.62	3.57	3.42	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.30	3.32	3.49	3.74	n/a	n/a	n/a	n/a
Fuc(α3)	4.96 (d, *J* = 3.7 Hz, 1H)	3.53	3.76	3.65	4.68	-	1.02 (d, *J* = 6.6 Hz, 3H)	-

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

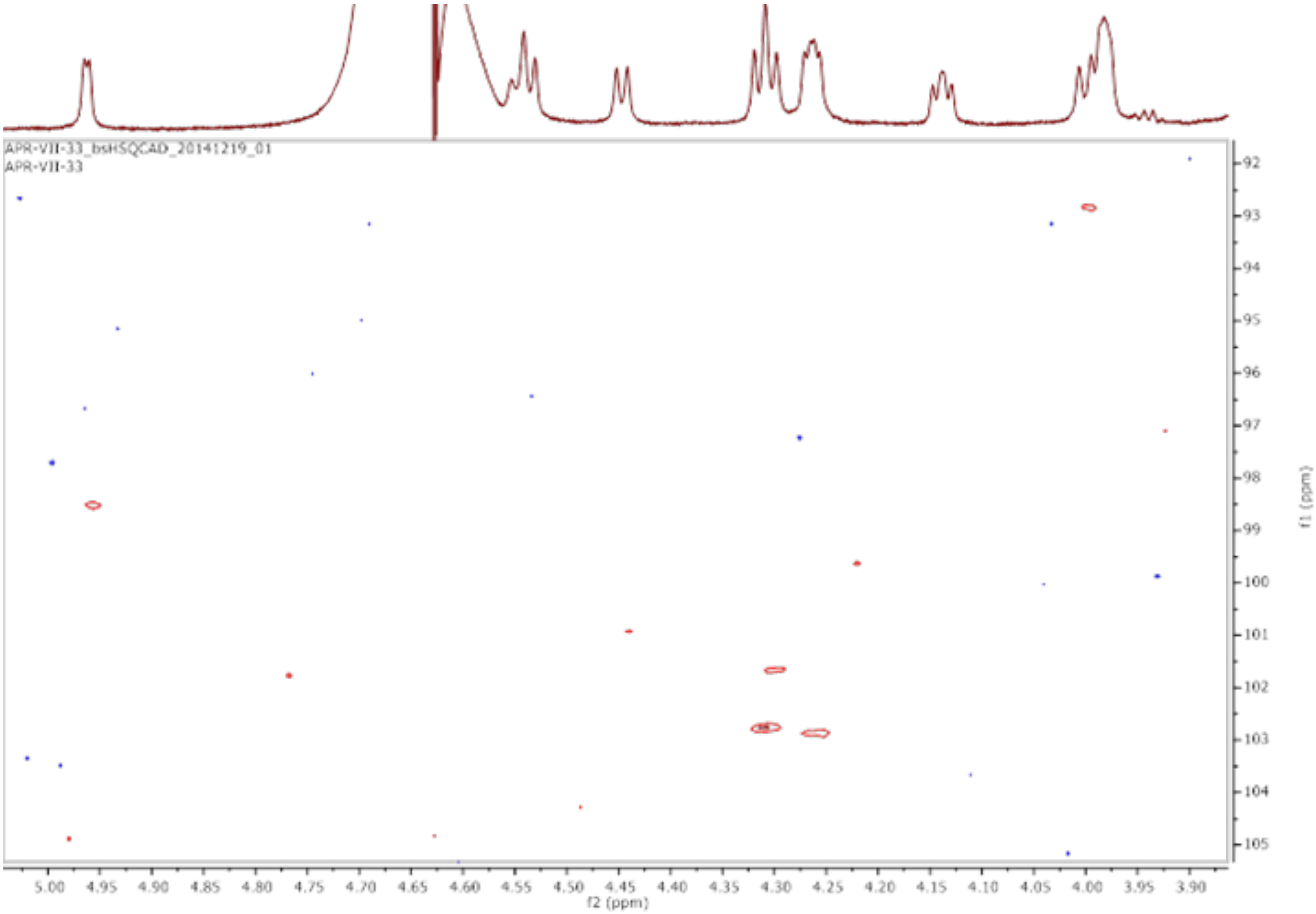
	C1
Glc	92.89
Gal	102.88
GlcNAc	n/a
Gal(2)	101.65
GlcNAc(2)	100.98
Gal(3)	102.88
GlcNAc(3)	n/a
Gal(4)	102.81
Fuc(α3)	98.53

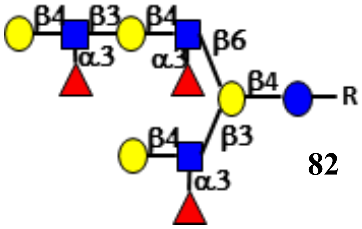
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{81}H_{129}N_7O_{50}Na$- $(M + Na)^+$ exact 2022.7664, found 2023.5796.



APR-VII-33_PRESAT_20141218_01
APR-VII-33
f1 (ppm)


APR-VII-33_bsHSQCAD_20141219_01
APR-VII-33
f2 (ppm)
f1 (ppm)



82

^{1}H (800 MHz, D_2O): δ (ppm)

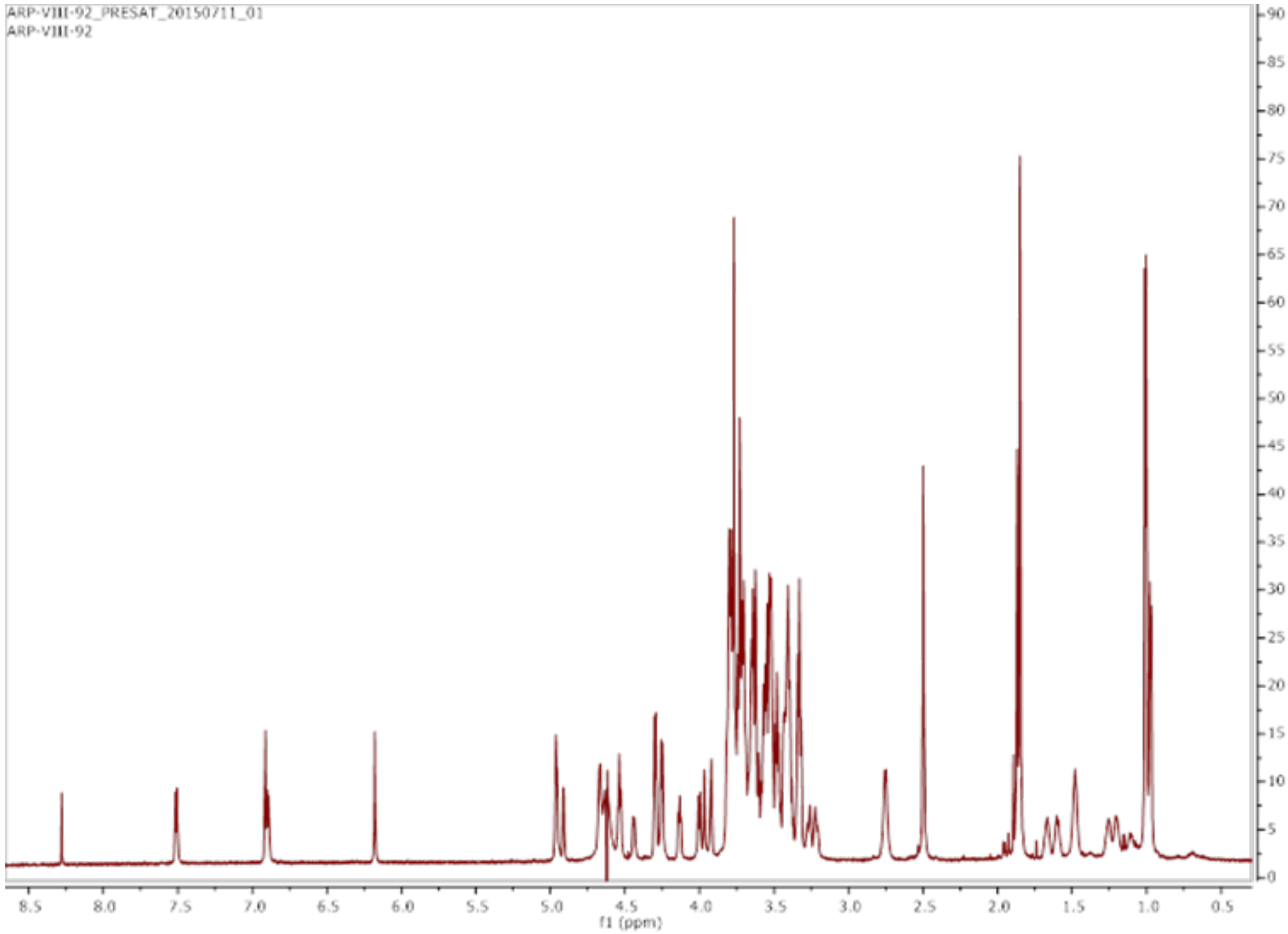
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.9 Hz, 1H)	3.34	3.40	3.48	n/a[a]	n/a	-	-
Gal	4.25 (d, *J* = 7.8 Hz, 1H)	3.41	3.53	3.98	n/a	n/a	-	-
GlcNAc	4.54 (d, *J* = 7.4 Hz, 1H)	3.78	3.71	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.30 (d, *J* = 7.2 Hz, 2H)	3.34	3.49	3.73	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 10.9 Hz, 1H)	3.73	3.71	3.42	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.25 (d, *J* = 7.8 Hz, 1H)	3.33	3.53	3.92	n/a	n/a		
GlcNAc(3)	4.54 (d, *J* = 8.7 Hz, 1H)	3.79	3.71	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.30 (d, *J* = 7.2 Hz, 2H)	3.33	3.49	3.73	n/a	n/a	-	-
Fuc(1)(α3)	4.97	3.53	3.74	3.63	4.68	-	1.00 (d, *J* = 6.4 Hz, 6H)	-
Fuc(2)(α3)	4.91 (d, *J* = 3.4 Hz, 1H)	3.52	3.71	3.60	4.64	-	0.97 (d, *J* = 6.3 Hz, 3H)	-
Fuc(3)(α3)	4.97	3.53	3.74	3.63	4.68	-	1.00 (d, *J* = 6.4 Hz, 6H)	-

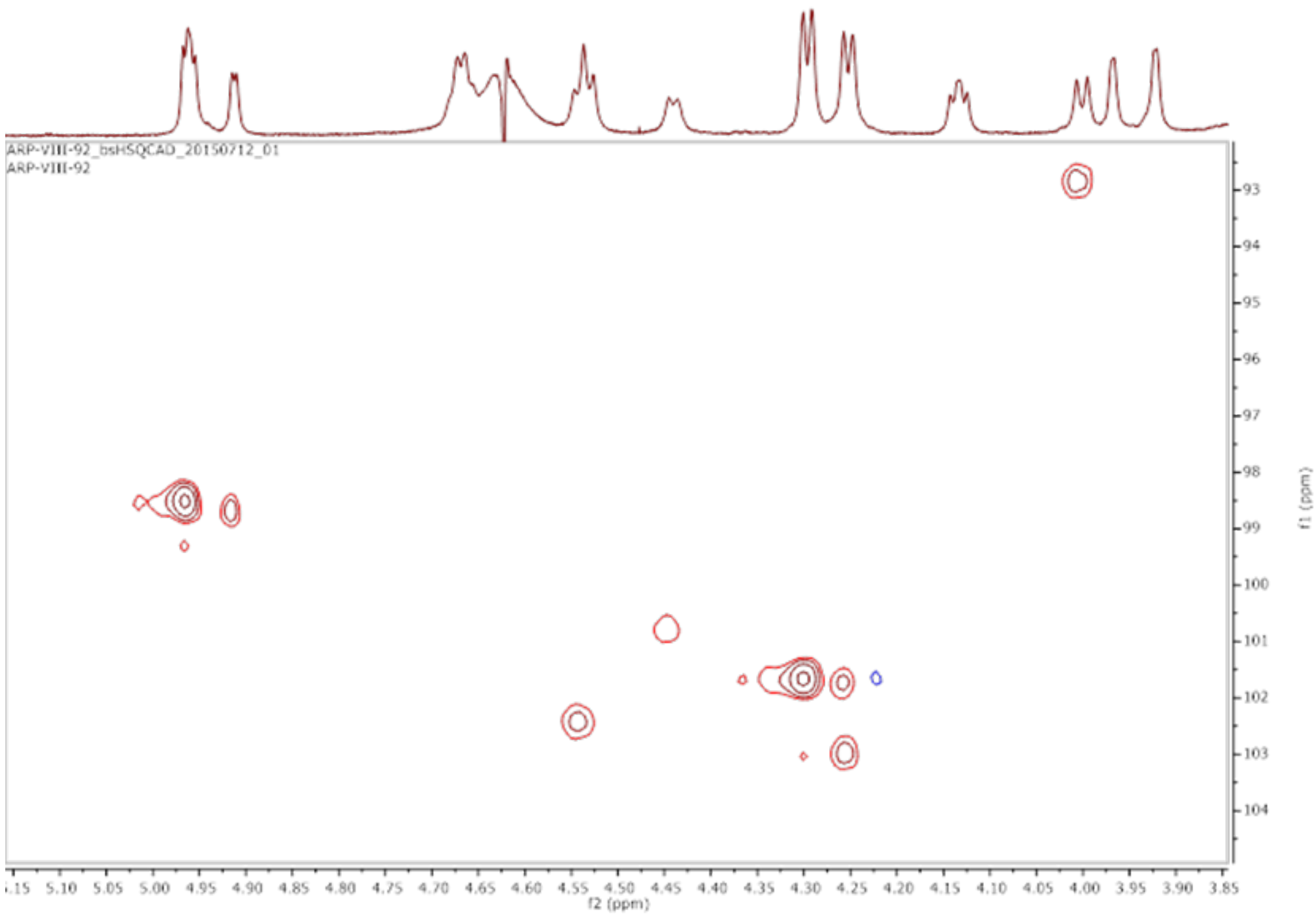
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

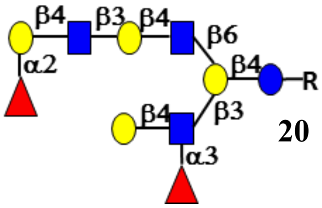
	C1
Glc	92.85
Gal	102.95
GlcNAc	102.44
Gal(2)	101.73
GlcNAc(2)	101.81
Gal(3)	101.73
GlcNAc(3)	102.44
Gal(4)	101.73
Fuc(1)(α3)	98.48
Fuc(2)(α3)	98.77
Fuc(3)(α3)	98.48

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{93}H_{149}N_7O_{58}Na$- $(M + Na)^+$ exact 2314.8823, found 2314.0212.


ARP-VIII-92_PRESAT_20150711_01
ARP-VIII-92
f1 (ppm)


ARP-VIII-92_bsHSQCAD_20150712_01
ARP-VIII-92
f2 (ppm)
f1 (ppm)



20

^{1}H (600 MHz, D_2O): δ (ppm)

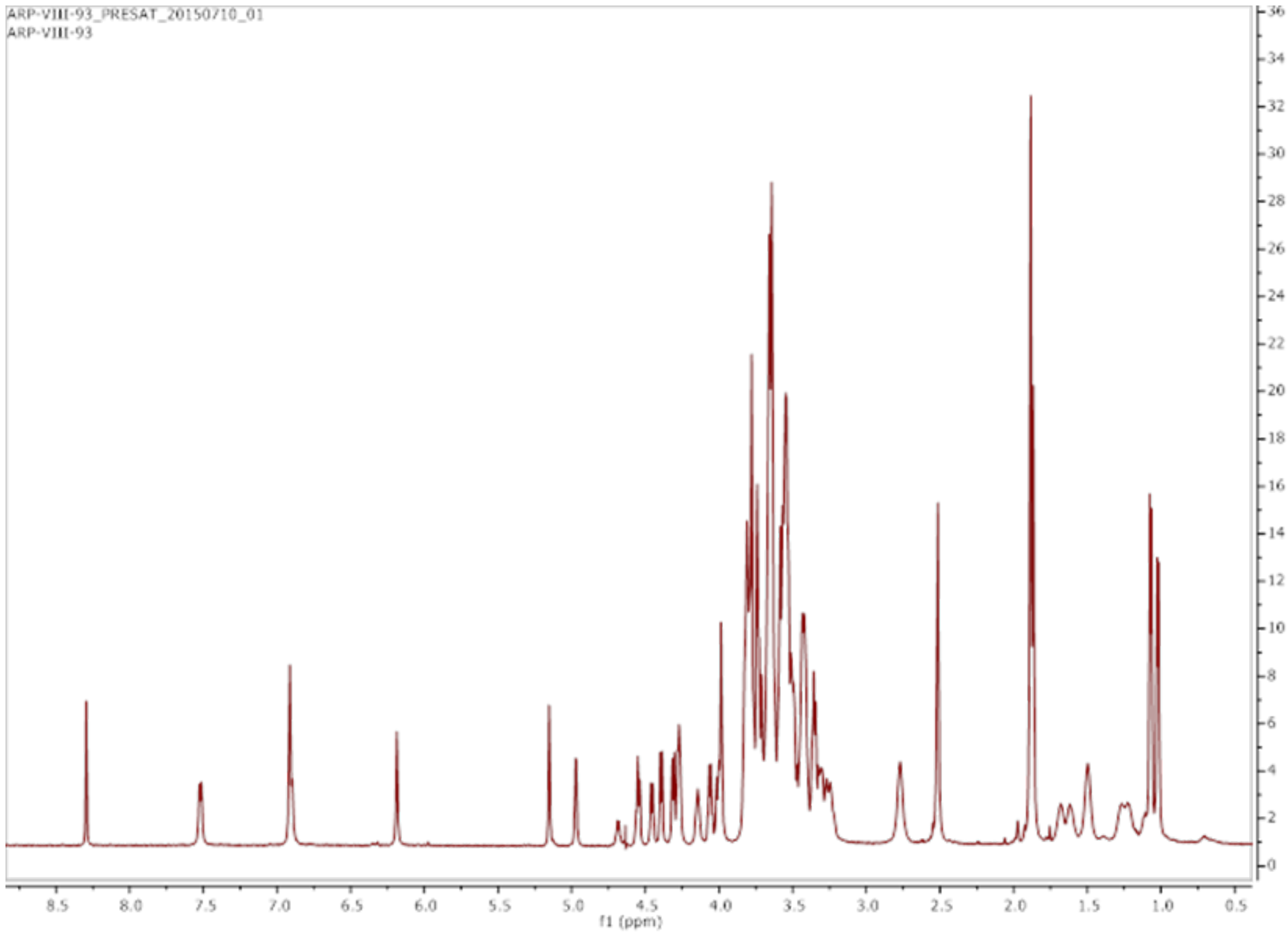
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.36	3.42	3.48	n/a[a]	n/a	-	-
Gal	4.27	3.42	3.54	3.98	n/a	n/a	-	-
GlcNAc	4.54	3.80	3.73	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.31 (d, J = 7.7 Hz, 1H)	3.34	3.50	3.74	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, J = 8.0 Hz, 1H)	3.57	n/a	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.27	3.42	3.54	3.98	n/a	n/a	-	-
GlcNAc(3)	4.54	3.80	3.73	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.40 (d, J = 7.6 Hz, 1H)	3.52	n/a	n/a	n/a	n/a	-	-
Fuc(1)(α3)	4.96	3.55	3.76	3.65	4.69	-	1.02 (d, J = 6.4 Hz, 3H)	-
Fuc(2)(α2)	5.15	3.65	n/a	n/a	4.06 (q, J = 6.4 Hz, 1H)	-	1.08 (d, J = 6.4 Hz, 3H)	-

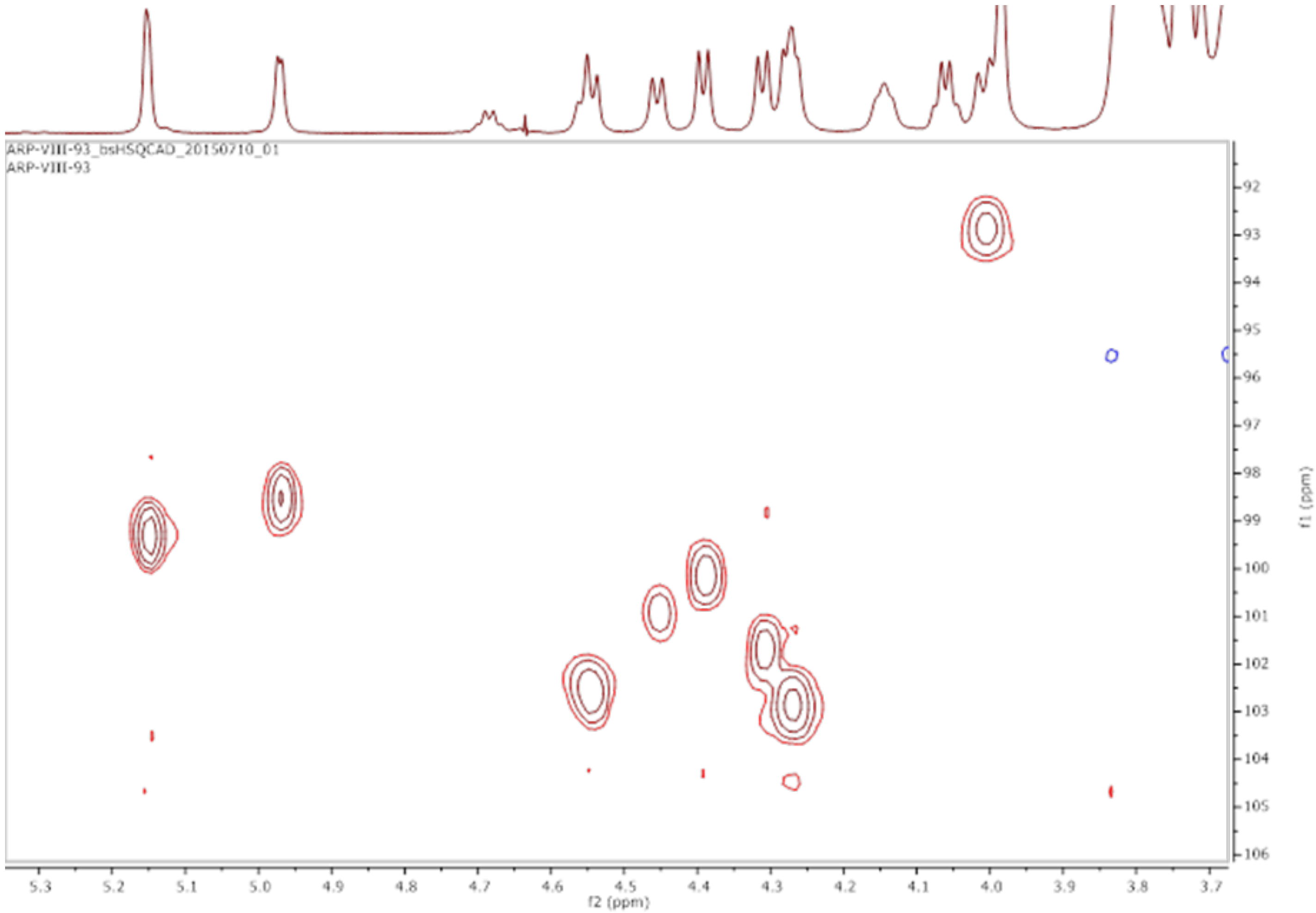
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.91
Gal	102.86
GlcNAc	102.62
Gal(2)	101.66
GlcNAc(2)	100.82
Gal(3)	102.86
GlcNAc(3)	102.62
Gal(4)	100.03
Fuc(1)(α3)	98.55
Fuc(2)(2)	99.34

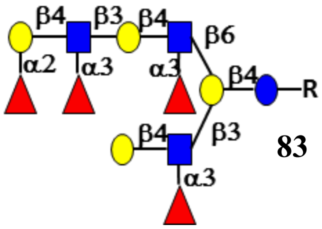
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{87}H_{139}N_7O_{54}Na$- $(M + Na)^+$ exact 2168.8244, found 2167.9634.


ARP-VIII-93_PRESAT_20150710_01
ARP-VIII-93
f1 (ppm)



ARP-VIII-93_bsHSQCAD_20150710_01
ARP-VIII-93
f2 (ppm)
f1 (ppm)



83

^{1}H (600 MHz, D_2O): δ (ppm)

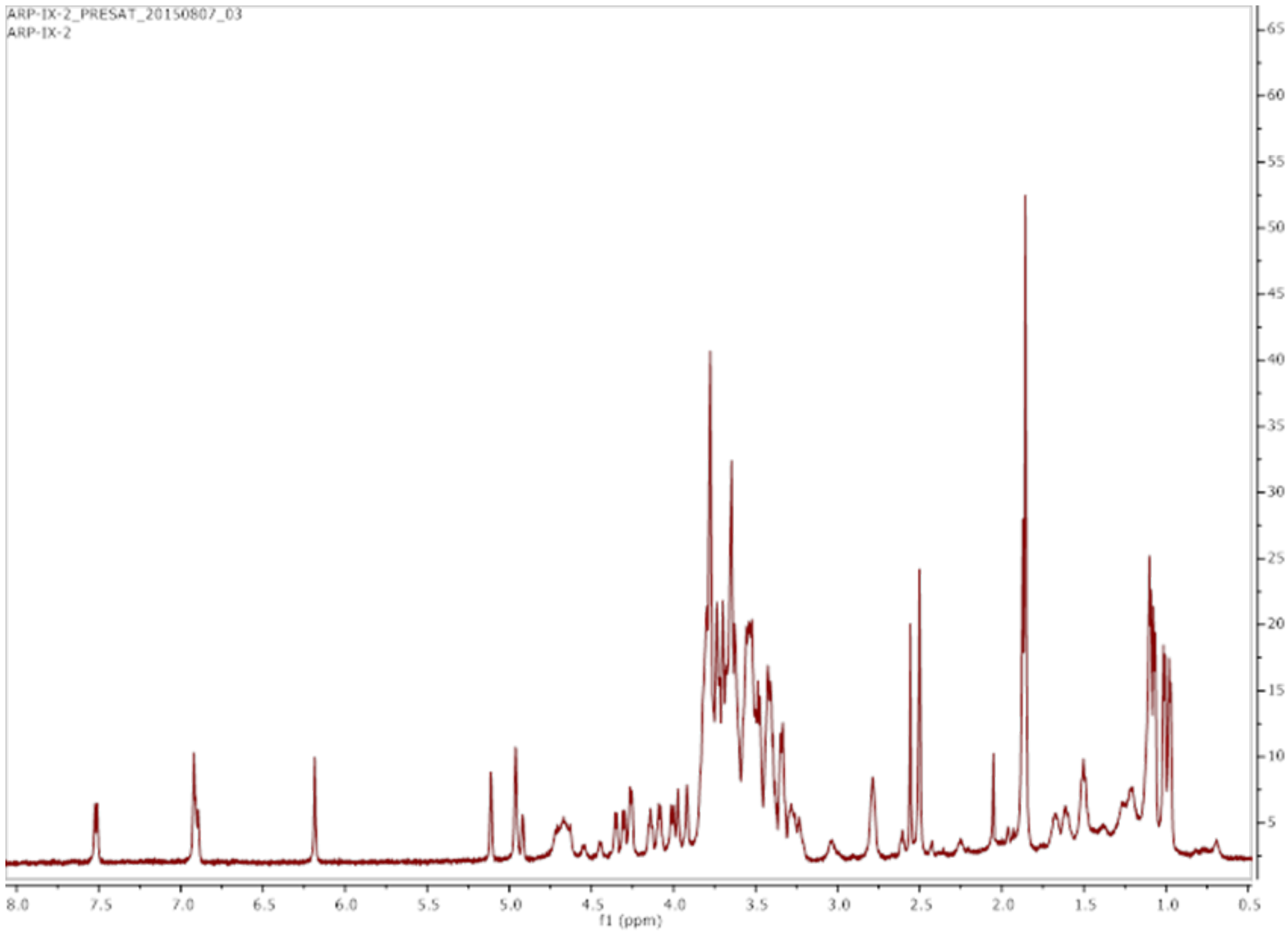
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.1 Hz, 1H)	3.34	3.40	3.46	n/a[a]	n/a	-	-
Gal	4.25 (d, *J* = 7.7 Hz, 2H)	3.41	3.51	3.96	n/a	n/a	-	-
GlcNAc	4.54 (d, *J* = 7.4 Hz, 1H)	3.78	n/a	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.34 (d, *J* = 7.0 Hz, 1H)	3.48	n/a	3.68	n/a	n/a	-	-
GlcNAc(2)	4.45	3.73	n/a1	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.25 (d, *J* = 7.7 Hz, 2H)	3.33	3.51	3.92	n/a	n/a		
GlcNAc(3)	4.54	3.78	n/a	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.30 (d, *J* = 7.8 Hz, 1H)	3.33	3.49	3.73	n/a	n/a	-	-
Fuc(1)(α3)	4.96	3.51	3.73	3.62	4.67	-	1.00 (d, *J* = 6.6 Hz, 3H)	-
Fuc(2)(α3)	4.91	3.50	3.71	3.60	4.64	-	0.97 (d, *J* = 6.2 Hz, 3H)	-
Fuc(3)(α3)	4.96	3.51	3.73	3.62	4.67	-	1.00 (d, *J* = 6.1 Hz, 3H)	-
Fuc(4)(α2)	5.11	3.62	n/a	n/a	4.71	-	1.06 (d, *J* = 6.2 Hz, 3H)	-

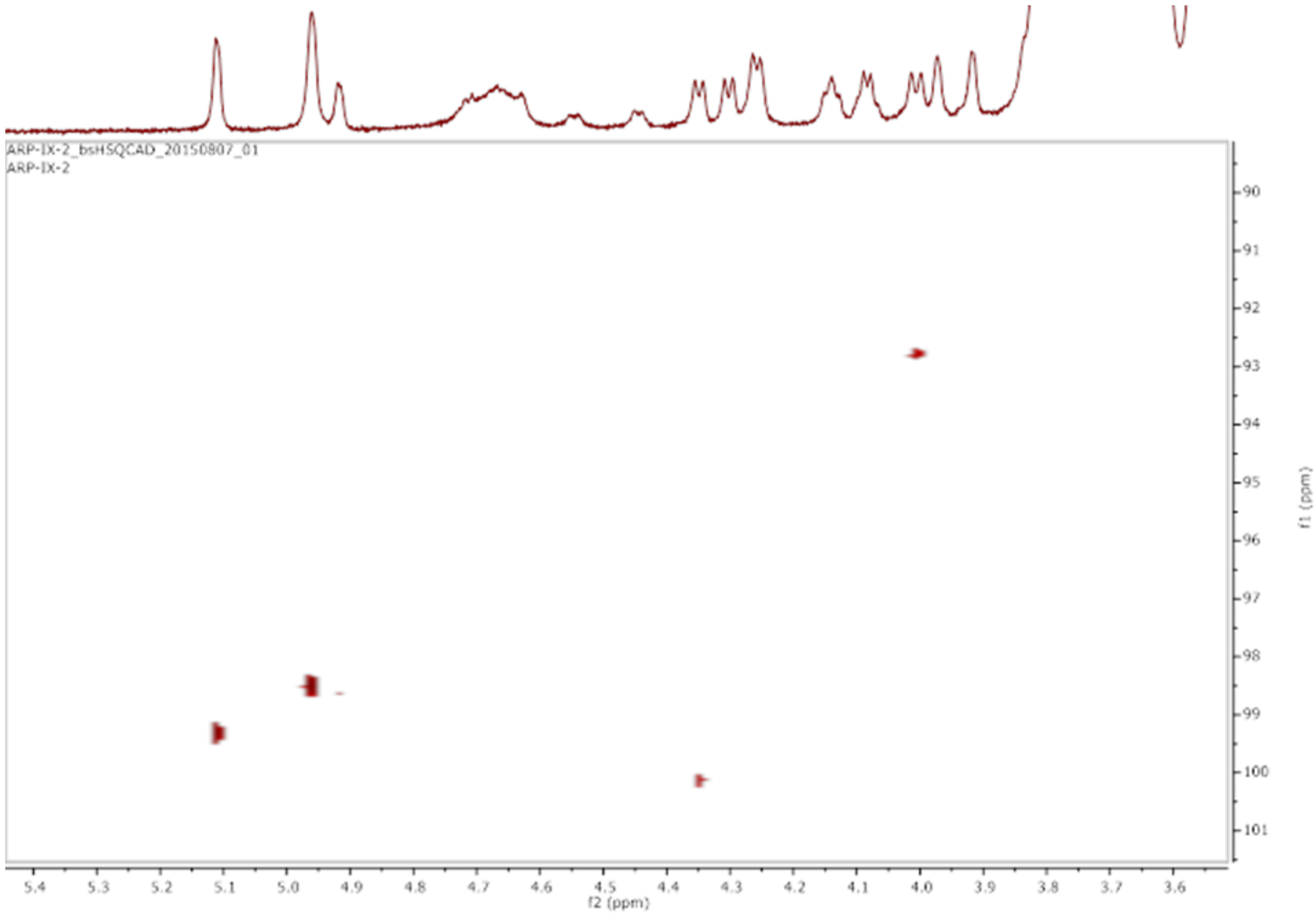
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

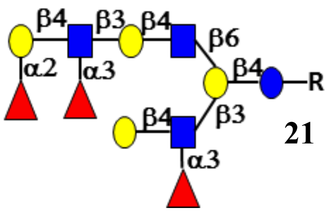
	C1
Glc	92.80
Gal	n/a
GlcNAc	n/a
Gal(2)	100.12
GlcNAc(2)	n/a
Gal(3)	n/a
GlcNAc(3)	n/a
Gal(4)	n/a
Fuc(1)(α3)	98.53
Fuc(2)(α3)	98.64
Fuc(3)(α3)	98.53
Fuc(4)(α2)	99.44

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{99}H_{159}N_7O_{62}Na$- $(M + Na)^+$ exact 2460.9402, found 2460.7825.


ARP-IX-2_PRESAT_20150807_03
ARP-IX-2
65
60
55
50
45
40
35
30
25
20
15
10
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ARP-IX-2_bsHSQCAD_20150807_01
ARP-IX-2
f1 (ppm)
f2 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

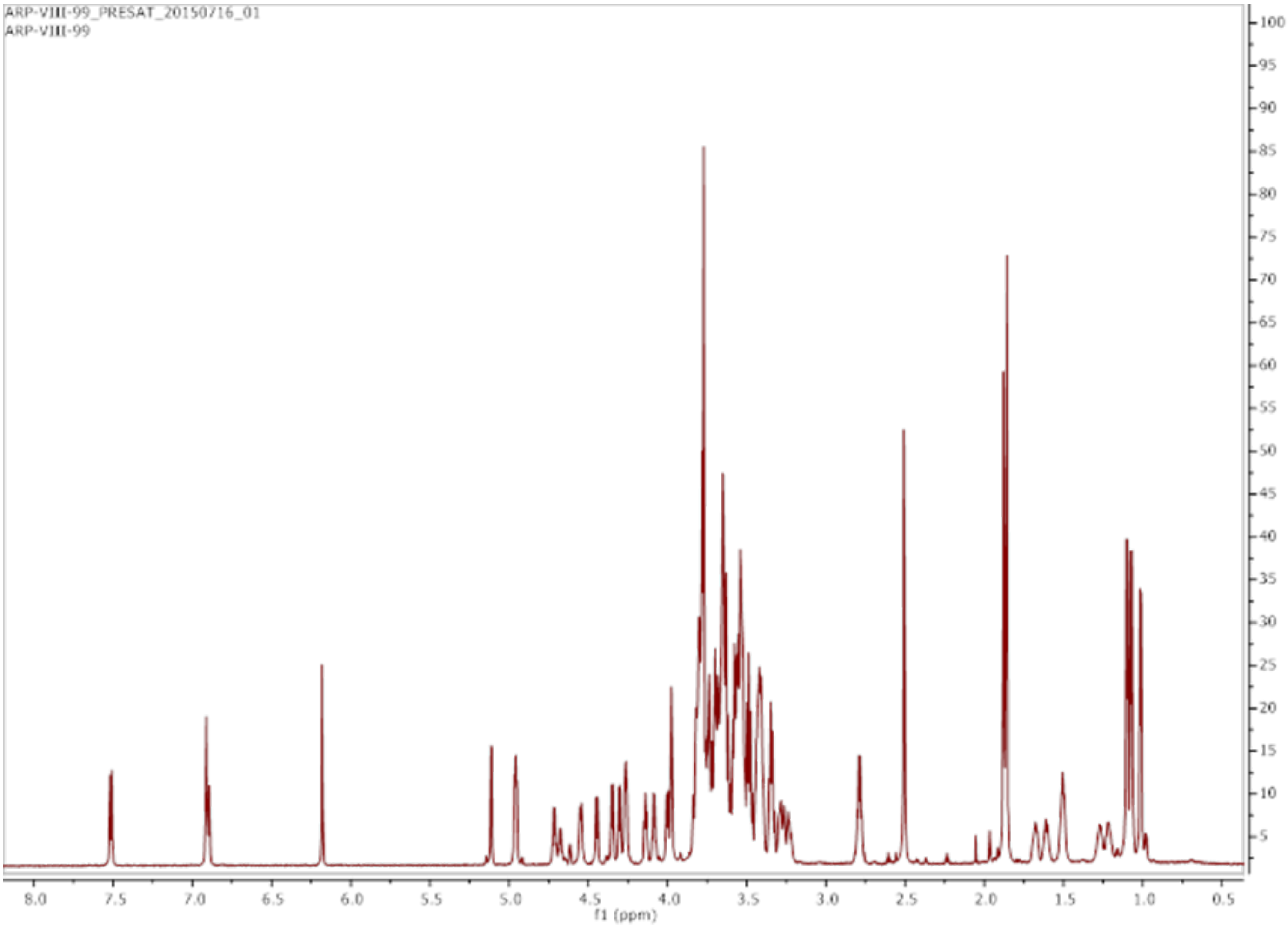
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.8 Hz, 1H)	3.33	3.42	3.48	n/a[a]	n/a	-	-
Gal	4.27	3.41	3.54	3.98	n/a	n/a	-	-
GlcNAc	4.56	3.79	3.73	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.30 (d, *J* = 7.6 Hz, 1H)	3.34	3.50	3.72	n/a	n/a	-	-
GlcNAc(2)	4.44 (d, *J* = 8.3 Hz, 1H)	3.57	3.52	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.27	3.41	3.54	3.98	n/a	n/a	-	-
GlcNAc(3)	4.56	3.79	3.72	3.49	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.34 (d, *J* = 7.8 Hz, 1H)	3.49	n/a	3.70	n/a	n/a	-	-
Fuc(1)(α3)	4.95	3.53	3.76	3.65	4.68 (q, *J* = 7.9, 6.9 Hz, 1H)	-	1.01 (d, *J* = 6.5 Hz, 3H)	-
Fuc(2)(α3)	4.95	3.53	3.76	3.65	4.77 (q, *J* = 5.7, 5.1 Hz, 1H)		1.07 (d, *J* = 6.5 Hz, 3H)	
Fuc(3)(α2)	5.11 (d, *J* = 3.4 Hz, 1H)	3.63	n/a	n/a	4.06 (q, *J* = 6.6, 5.9 Hz, 1H)	-	1.09 (d, *J* = 6.5 Hz, 3H)	-

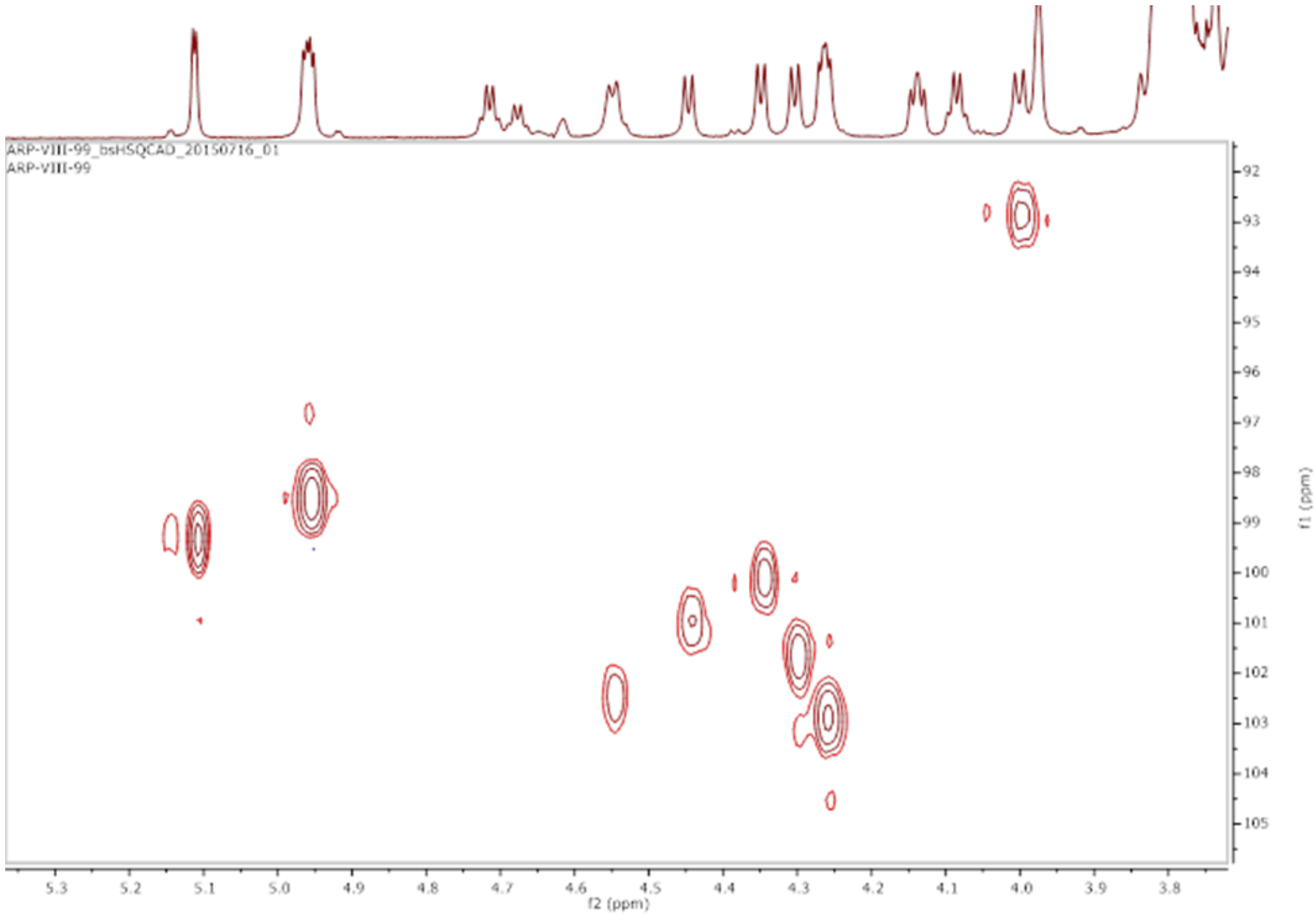
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

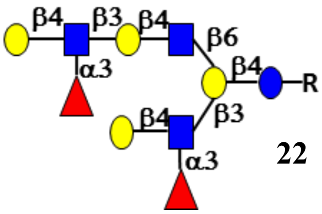
	C1
Glc	92.86
Gal	102.82
GlcNAc	102.53
Gal(2)	101.71
GlcNAc(2)	100.88
Gal(3)	102.82
GlcNAc(3)	102.53
Gal(4)	100.06
Fuc(1)(α3)	98.55
Fuc(2)(α3)	98.55
Fuc(3)(α2)	99.33

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{93}H_{149}N_7O_{58}Na$- $(M + Na)^+$ exact 2314.8823, found 2314.9739.


ARP-VIII-99_PRESAT_20150716_01
ARP-VIII-99
f1 (ppm)


ARP-VIII-99_bsHSQCAD_20150716_01
ARP-VIII-99
f1 (ppm)
f2 (ppm)



22

^{1}H (800 MHz, D_2O): δ (ppm)

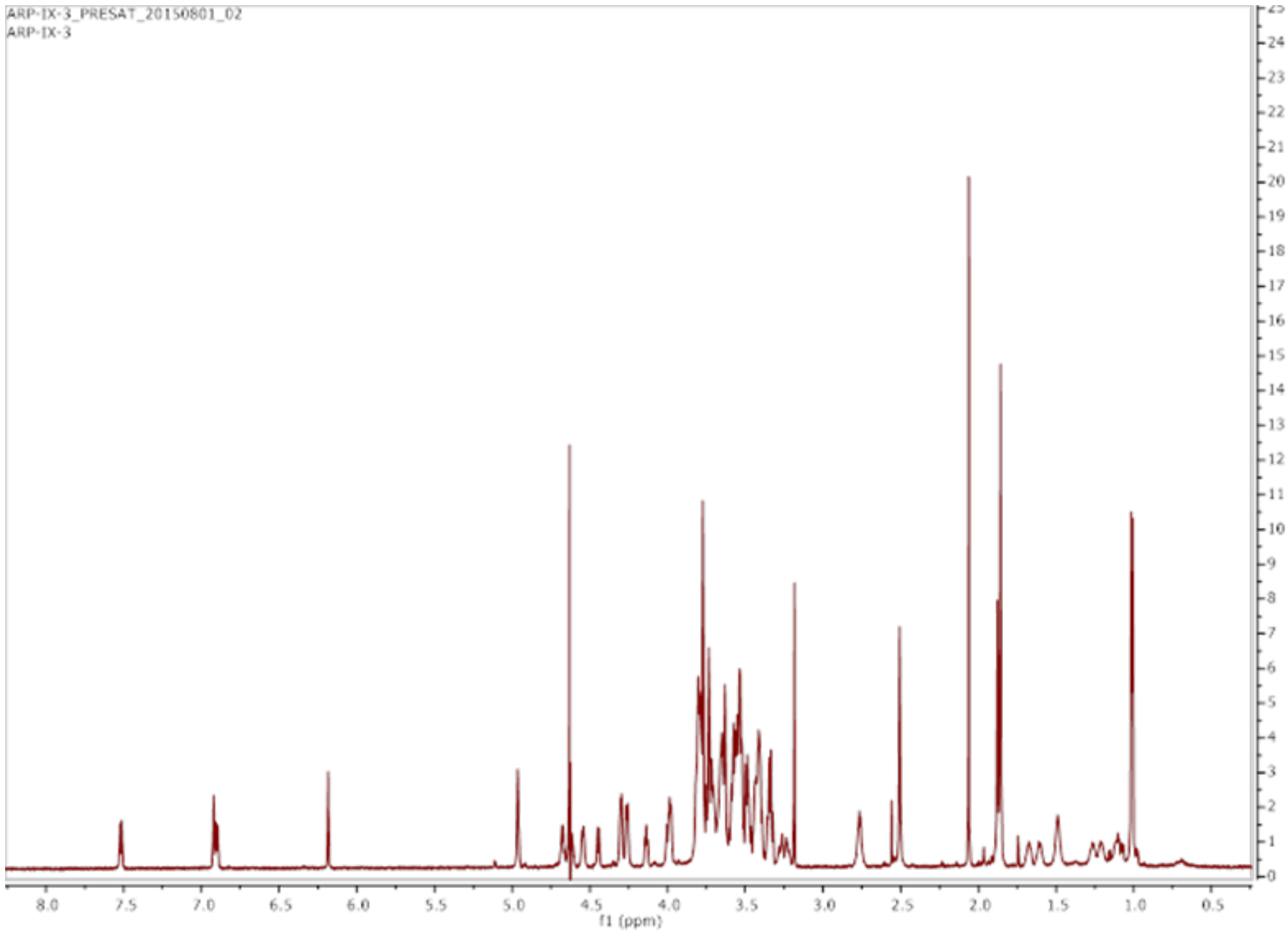
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.1 Hz, 1H)	3.34	3.40	3.46	n/a[a]	n/a	-	-
Gal	4.25	3.41	3.51	3.98	n/a	n/a	-	-
GlcNAc	4.54 (d, *J* = 7.4 Hz, 2H)	3.78	3.71	3.40	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.30 (d, *J* = 8.3 Hz, 2H)	3.32	3.48	3.72	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.3 Hz, 1H)	3.57	3.50	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.25	3.41	3.51	3.98	n/a	n/a	-	-
GlcNAc(3)	4.54 (d, *J* = 7.4 Hz, 2H)	3.78	3.71	3.40	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.30 (d, *J* = 8.3 Hz, 2H)	3.32	3.48	3.72	n/a	n/a	-	-
Fuc(1)(α3)	4.96 (d, *J* = 3.9 Hz, 2H)	3.51	3.73	3.62	4.67 (q, *J* = 6.9 Hz, 2H)	-	1.01 (d, *J* = 6.5 Hz, 6H)	-
Fuc(2)(α3)	4.96 (d, *J* = 3.9 Hz, 2H)	3.51	3.73	3.62	4.67 (q, *J* = 6.9 Hz, 2H)	-	1.01 (d, *J* = 6.5 Hz, 6H)	-

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

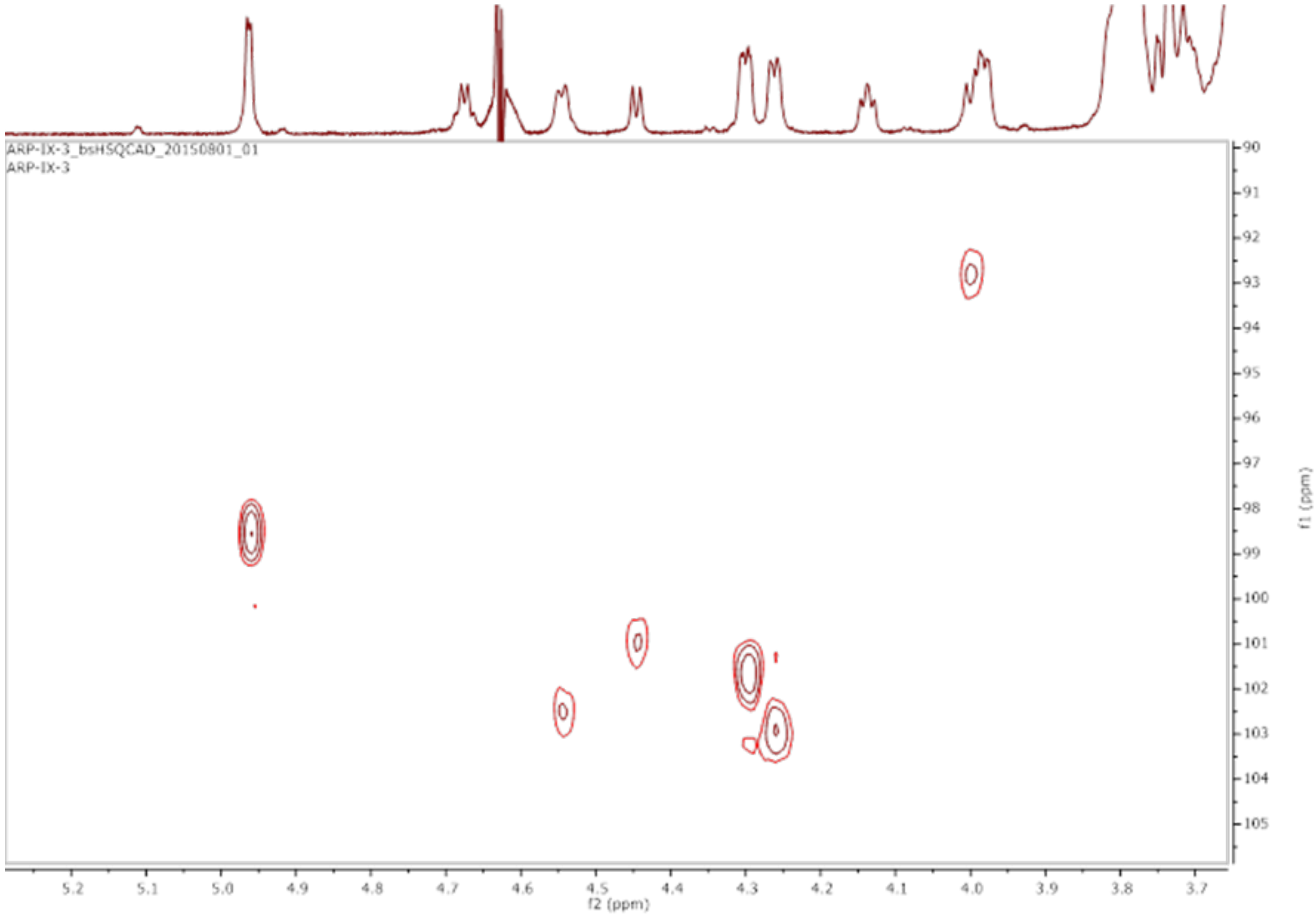
	C1
Glc	92.83
Gal	103.08
GlcNAc	102.50
Gal(2)	101.62
GlcNAc(2)	101.00
Gal(3)	103.08
GlcNAc(3)	102.50
Gal(4)	101.62
Fuc(1)(α3)	98.54
Fuc(2)(α3)	98.54

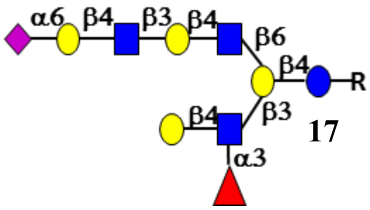
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{87}H_{139}N_7O_{54}Na$- $(M + Na)^+$ exact 2168.8244, found 2168.4053.



ARP-IX-3_PRESAT_20150801_02
ARP-IX-3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ARP-IX-3_bsHSQCAD_20150801_01
ARP-IX-3
f2 (ppm)
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

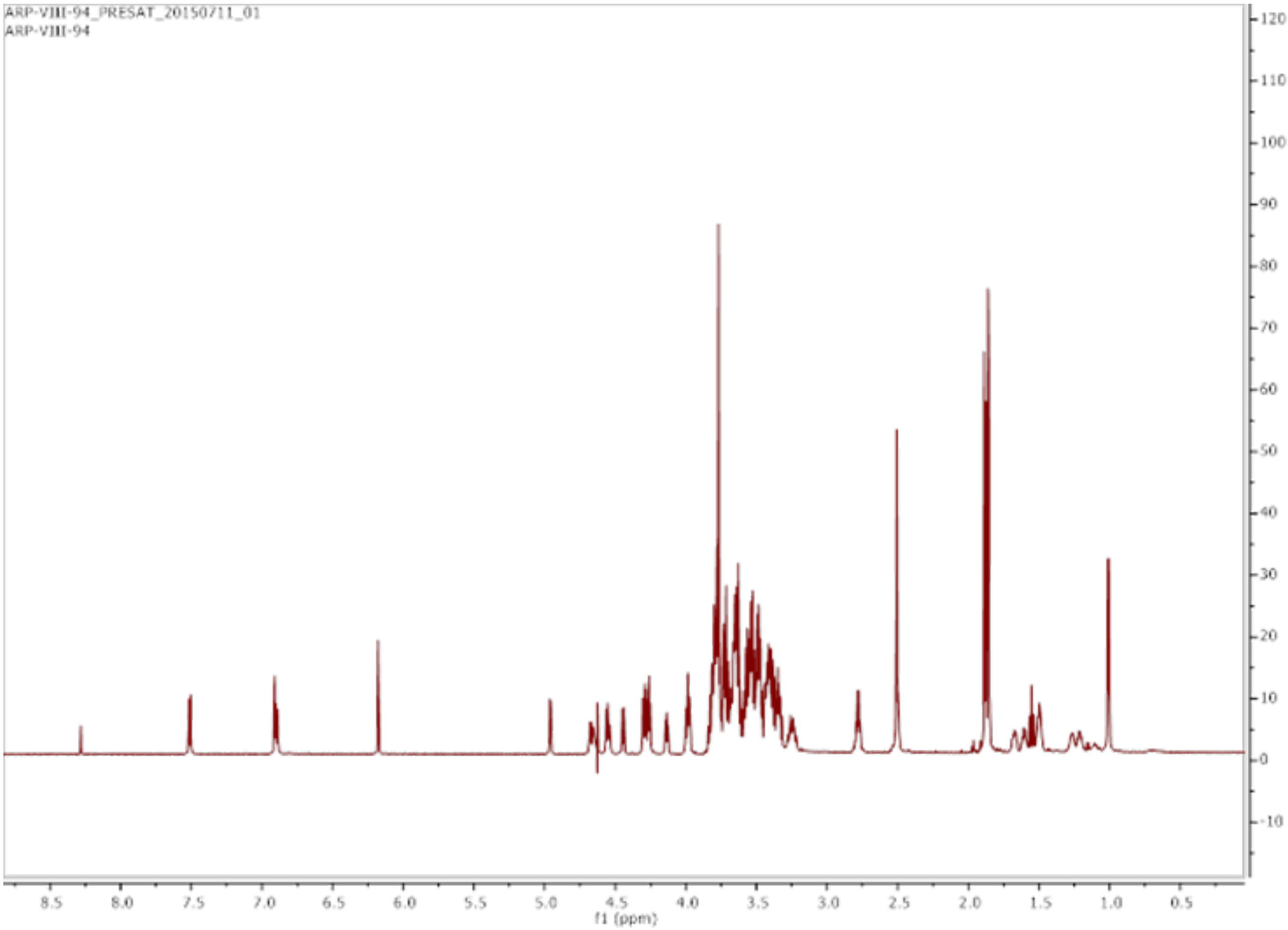
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.36	3.42	3.48	n/a[a]	n/a	-	-	-	-	-
Gal	4.26	3.42	3.54	3.99	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.80	3.73	3.42	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.30	3.33	3.50	3.74	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.3 Hz, 1H)	3.58	3.52	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.26	3.42	3.54	3.99	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.64	3.50	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(4)	4.29	3.38	3.51	3.77	n/a	n/a	-	-	-	-	-
Fuc(1)(α3)	4.96 (d, *J* = 3.9 Hz, 1H)	3.53	3.75	3.64	4.68	-	-	-	-	1.02 (d, *J* = 6.6 Hz, 3H)	-
Neu5Ac	-	-	2.51 – eq 1.56 – axial (dd, *J* = 12.2 Hz, 1H)	3.49	3.62	3.51	n/a	n/a	n/a	n/a	1.91 - 1.81 (m, 12H)

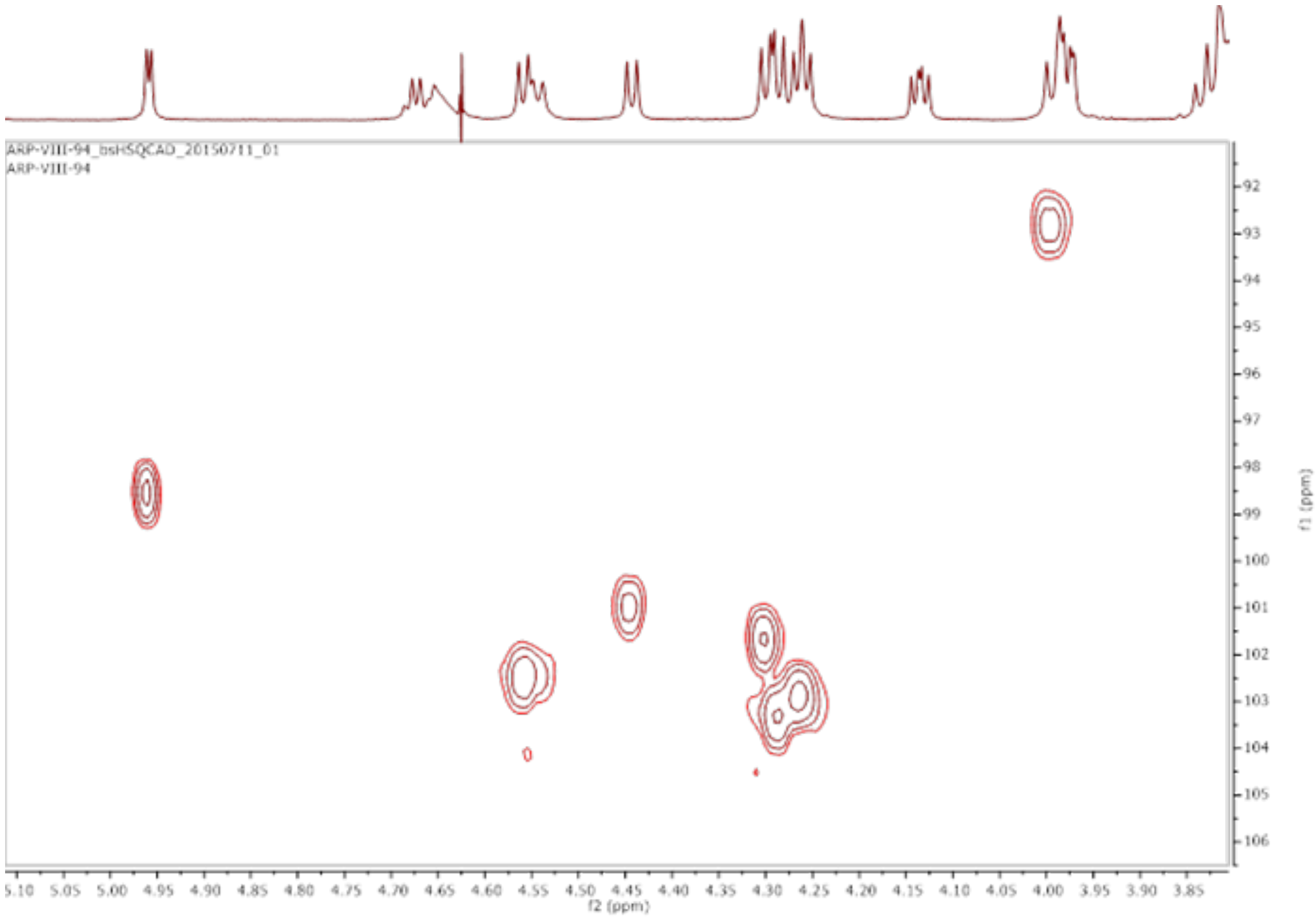
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

	C1
Glc	92.86
Gal	102.97
GlcNAc	102.58
Gal(2)	101.51
GlcNAc(2)	101.02
Gal(3)	102.97
GlcNAc(3)	102.58
Gal(4)	103.22
Fuc(1)(α3)	98.62

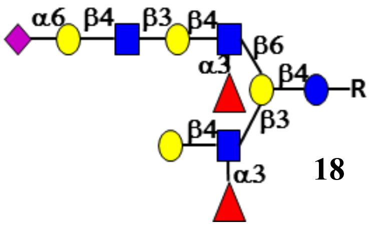
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{92}H_{145}N_8O_{58}Na_2$- $(M + 2Na)^+$ exact 2335.8444, found 2334.8179.


ARP-VIII-94_PRESAT_20150711_01
ARP-VIII-94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
120 110 100 90 80 70 60 50 40 30 20 10 0 -10



ARP-VIII-94_bsHSQCAD_20150711_01
ARP-VIII-94
f2 (ppm)
f1 (ppm)



18

^{1}H (600 MHz, D_2O): δ (ppm)

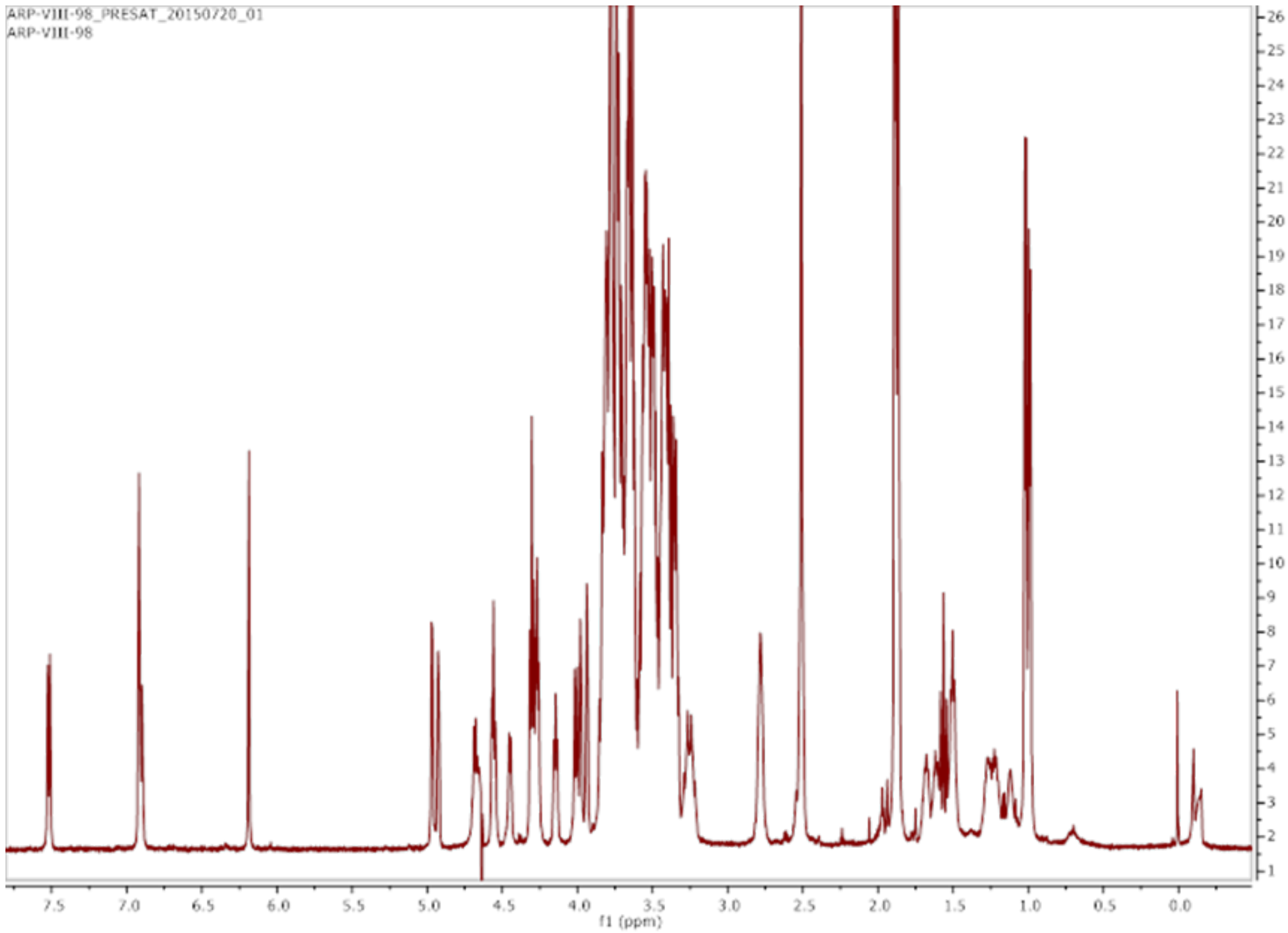
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.35	3.41	3.48	n/a[a]	n/a	-	-	-	-	-
Gal	4.27	3.36	3.54	3.94	n/a	n/a	-	-	-	-	-
GlcNAc	4.56	3.80	3.73	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.31	3.33	3.51	3.74	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.0 Hz, 1H)	3.75	n/a	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.26	3.42	3.54	3.91	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.56	3.64	3.51	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(4)	4.29	3.38	3.52	3.77	n/a	n/a	-	-	-	-	-
Fuc(1)(α3)	4.97 (d, *J* = 3.8 Hz, 1H)	3.53	3.75	3.64	4.69	-	-	-	-	1.02 (d, *J* = 6.5 Hz, 3H)	-
Fuc(2)(α3)	4.93 (d, *J* = 3.6 Hz, 1H)	3.53	3.73	3.63	4.67	-	-	-	-	1.00 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac	-	-	2.51 – eq 1.56 - axial	3.49	3.62	3.51	n/a	n/a	n/a	n/a	1.91 - 1.81 (m, 12H)

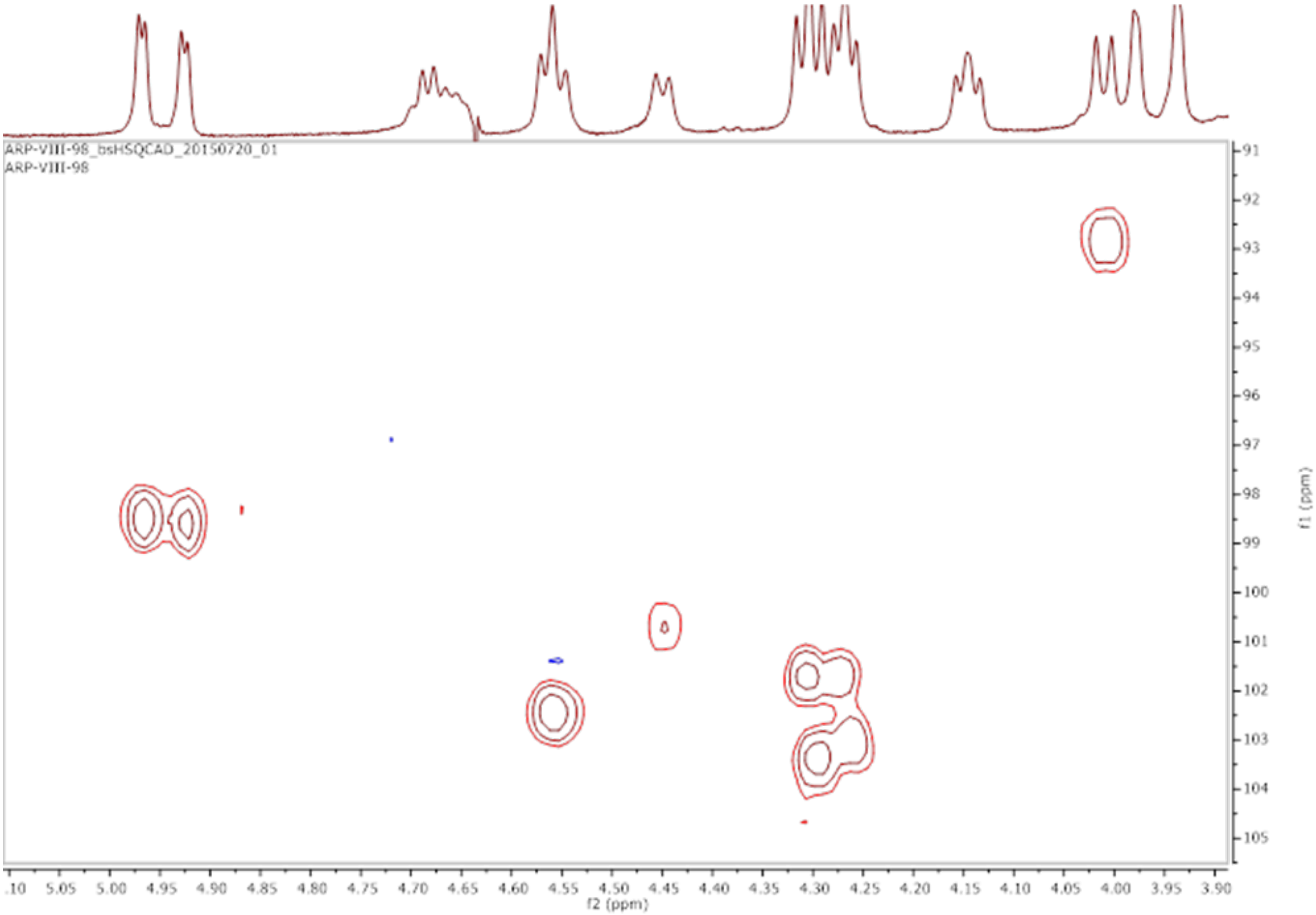
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.90
Gal	101.58
GlcNAc	102.46
Gal(2)	101.68
GlcNAc(2)	100.77
Gal(3)	103.03
GlcNAc(3)	102.46
Gal(4)	103.39
Fuc(1)(α3)	98.45
Fuc(2)(α3)	98.58

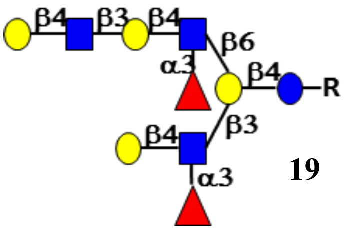
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{98}H_{155}N_8O_{62}Na_2$-- $(M + 2Na)^+$ exact 2481.9023, found 2482.3999.


ARP-VIII-98_PRESAT_20150720_01
ARP-VIII-98
f1 (ppm)



ARP-VIII-98_bsHSQCAD_20150720_01
ARP-VIII-98
f2 (ppm)
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

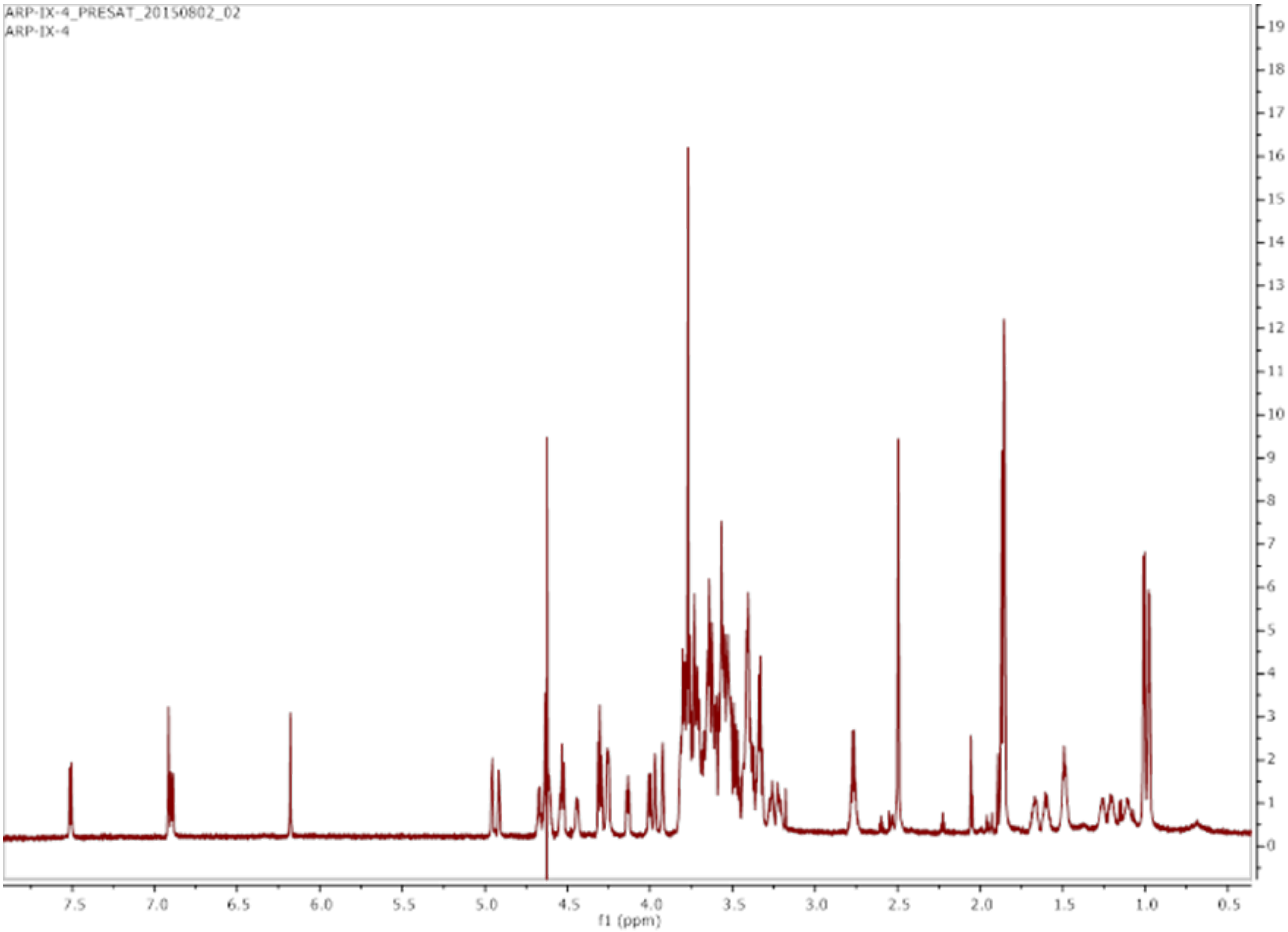
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.8 Hz, 1H)	3.33	3.39	3.44	n/a[a]	n/a	-	-
Gal	4.25	3.41	3.54	3.98	n/a	n/a	-	-
GlcNAc	4.53	3.79	3.71	n/a	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.29	3.34	3.48	3.73	n/a	n/a	-	-
GlcNAc(2)	4.44 (d, *J* = 6.9 Hz, 1H)	3.73	n/a	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.25	3.34	3.52	3.92	n/a	n/a	-	-
GlcNAc(3)	4.53	3.63	3.56	3.41	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(4)	4.31	3.37	3.49	3.76	n/a	n/a	-	-
Fuc(1)(α3)	4.95 (d, *J* = 3.7 Hz, 1H)	3.53	3.73	3.62	4.66	-	1.01 (d, *J* = 6.4 Hz, 3H)	-
Fuc(2)(α3)	4.91 (d, *J* = 3.8 Hz, 1H)	3.51	3.71	3.59	4.63		0.97 (d, *J* = 6.3 Hz, 3H)	

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

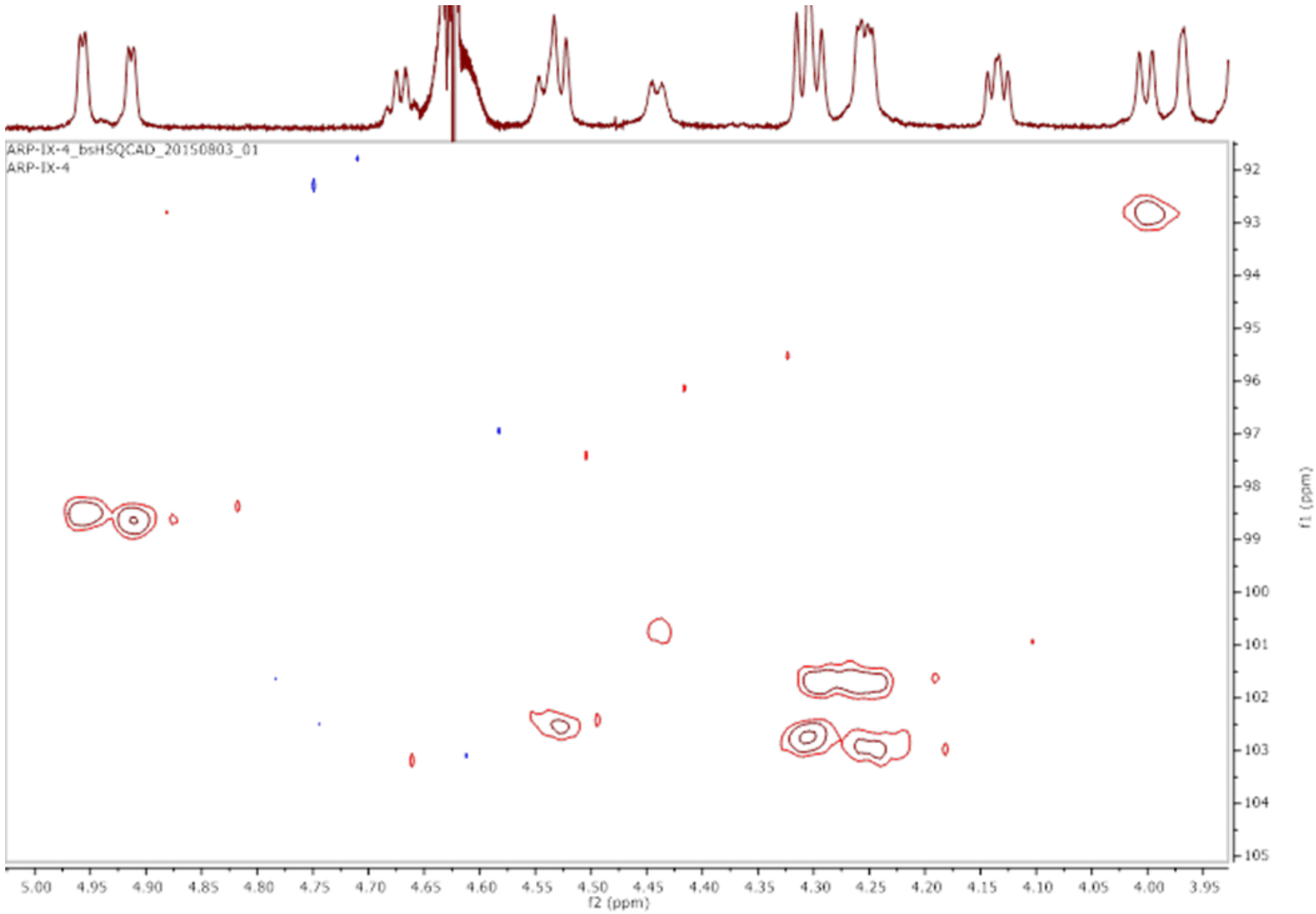
	C1
Glc	92.78
Gal	101.73
GlcNAc	102.55
Gal(2)	101.77
GlcNAc(2)	100.80
Gal(3)	102.89
GlcNAc(3)	102.55
Gal(4)	102.80
Fuc(1)(α3)	98.53
Fuc(2)(α3)	98.74

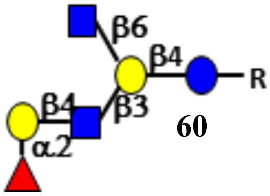
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{87}H_{139}N_7Na_{54}O$- $(M + Na)^+$ exact 2168.8244, found 2169.5872.



ARP-IX-4_PRESAT_20150802_02
ARP-IX-4
f1 (ppm)


ARP-IX-4_bsHSQCAD_20150803_01
ARP-IX-4
f2 (ppm)
f1 (ppm)



60

^{1}H (800 MHz, D_2O): δ (ppm)

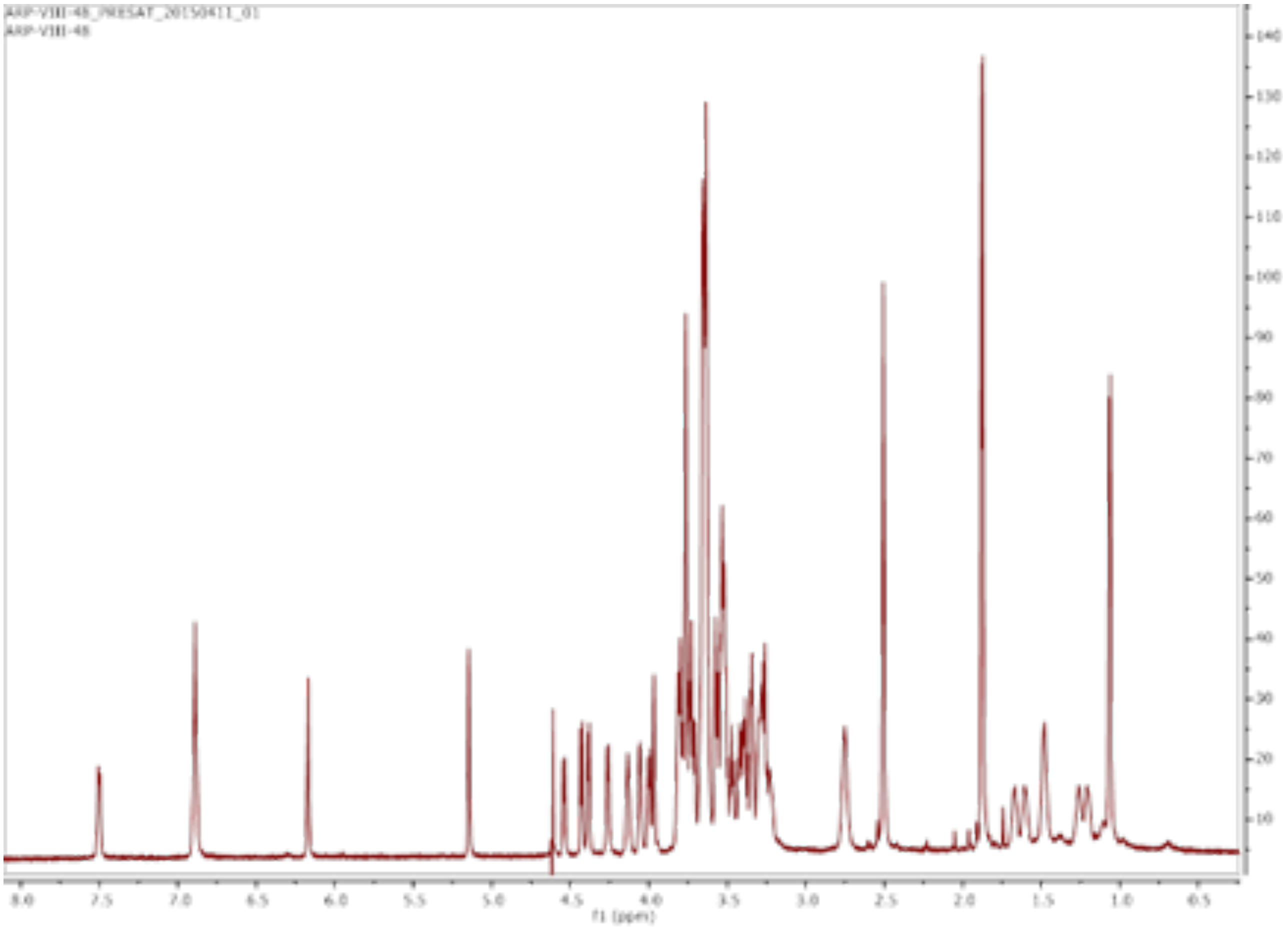
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 10.4 Hz, 1H)	3.34	3.40	3.47	n/a[a]	n/a	-	-
Gal	4.26 (d, *J* = 7.6 Hz, 1H)	3.41	3.52	3.97	n/a	n/a	-	-
GlcNAc	4.53 (d, *J* = 7.7 Hz, 1H)	3.64	3.54	3.31	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(2)	4.39 (d, *J* = 8.2 Hz, 1H)	3.51	3.63	3.72	n/a	n/a	-	-
GlcNAc(2)	4.42 (d, *J* = 8.7 Hz, 1H)	3.52	3.38	3.28	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Fuc(1)(α2)	5.14 (d, *J* = 3.2 Hz, 1H)	3.64	n/a	n/a	4.06 (br q, *J* = 6.1 Hz, 1H)	-	1.07 (d, *J* = 5.8 Hz, 3H)	-

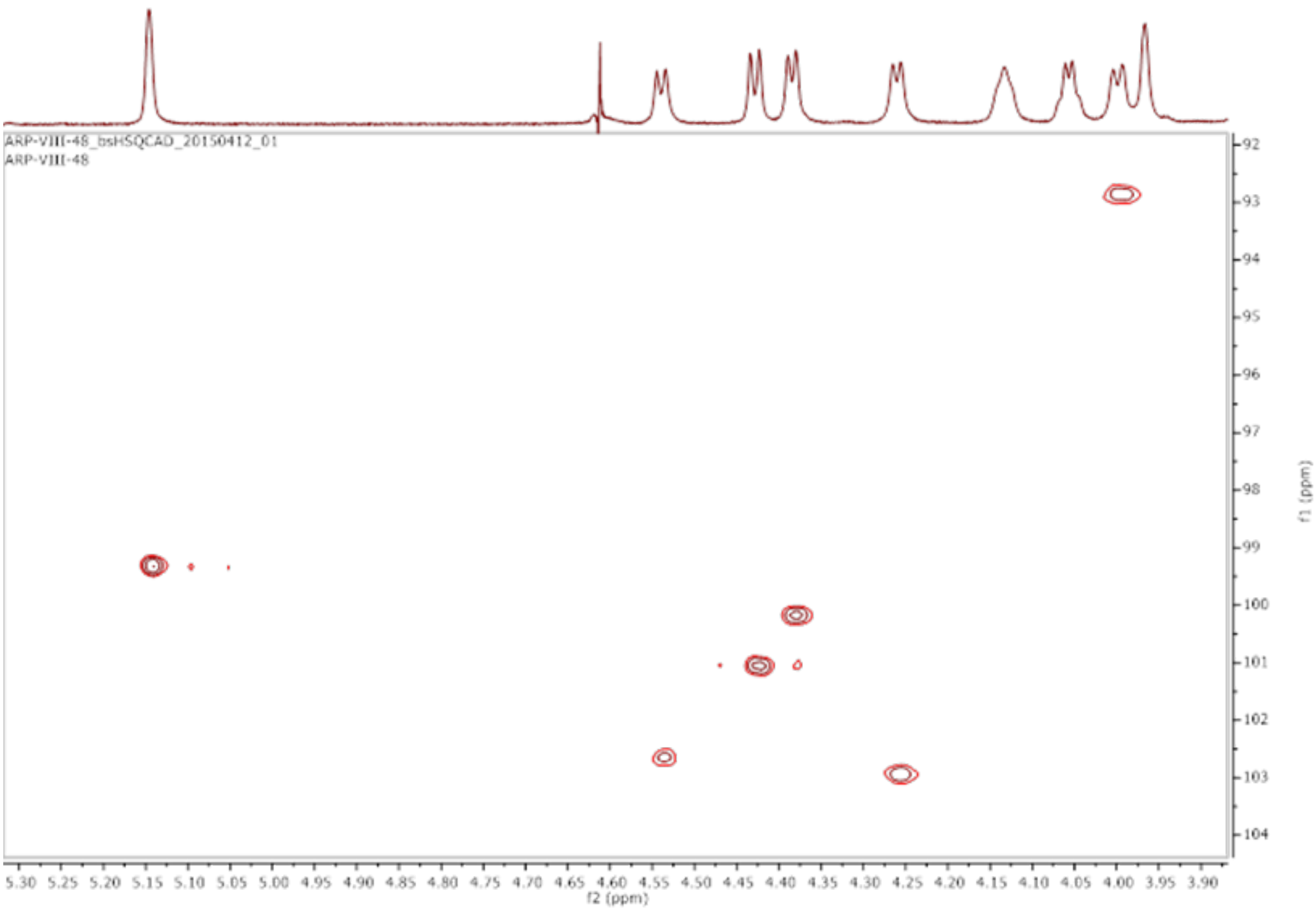
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

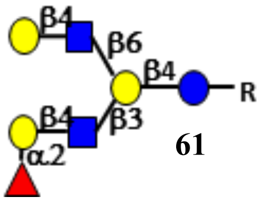
	C1
Glc	92.85
Gal	102.94
GlcNAc	102.66
Gal(2)	100.21
GlcNAc(2)	101.07
Fuc(1)(α2)	99.35

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{61}H_{96}N_6O_{35}Na$-- $(M + Na)^+$ exact 1495.5814, found 1495.2061.


ARP-VIII-48_PRESAT_20150411_01
ARP-VIII-48
f1 (ppm)


ARP-VIII-48_bsHSQCAD_20150412_01
ARP-VIII-48
f1 (ppm)
f2 (ppm)



61

^{1}H (800 MHz, D_2O): δ (ppm)

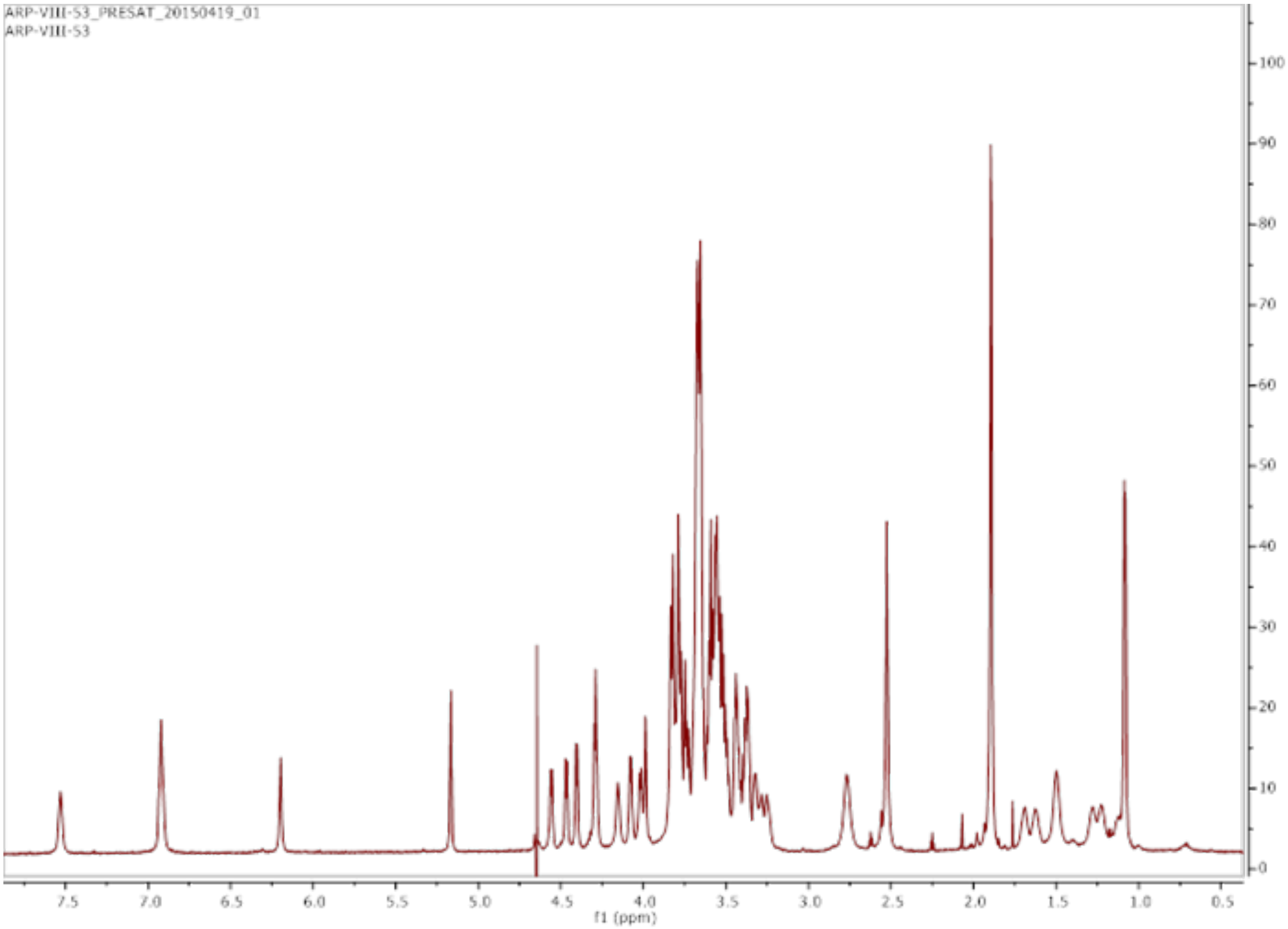
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.5 Hz, 1H)	3.35	3.41	3.48	n/a[a]	n/a	-	-
Gal	4.26 (d, *J* = 7.6 Hz, 1H)	3.41	3.53	3.97	n/a	n/a	-	-
GlcNAc	4.55 (d, *J* = 8.1 Hz, 1H)	3.64	3.54	3.31	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(2)	4.39 (d, *J* = 7.5 Hz, 1H)	3.50	3.64	3.72	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.5 Hz, 1H)	3.56	3.52	3.42	n/a	n/a	-	1.91 - 1.81 (m, 6H)
Gal(3)	4.27	3.37	3.49	3.75	n/a	n/a	-	-
Fuc(1)(α2)	5.14 (d, *J* = 3.1 Hz, 1H)	3.63	n/a	n/a	4.06 (br q, *J* = 6.4 Hz, 1H)	-	1.08 (d, *J* = 6.2 Hz, 3H)	-

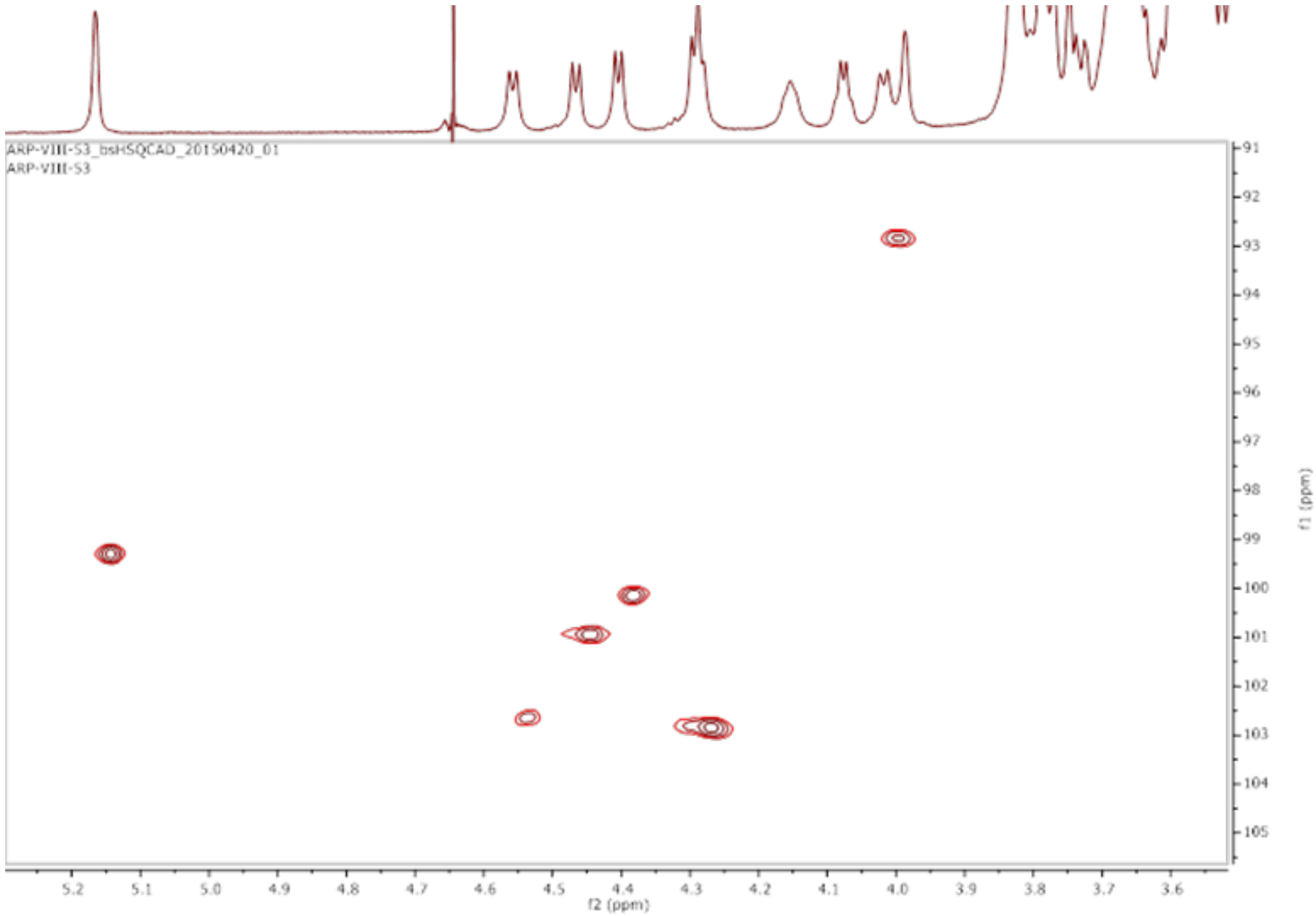
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

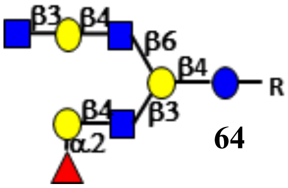
	C1
Glc	92.85
Gal	102.86
GlcNAc	102.67
Gal(2)	100.14
GlcNAc(2)	100.91
Gal(3)	102.83
Fuc(1)(α2)	99.32

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{67}H_{106}N_6O_{40}Na$-- $(M + Na)^+$ exact 1657.6343, found 1657.0045.


ARP-VIII-53_PRESAT_20150419_01
ARP-VIII-53
100
90
80
70
60
50
40
30
20
10
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ARP-VIII-53_bsHSQCAD_20150420_01
ARP-VIII-53
f2 (ppm)
f1 (ppm)



64

^{1}H (800 MHz, D_2O): δ (ppm)

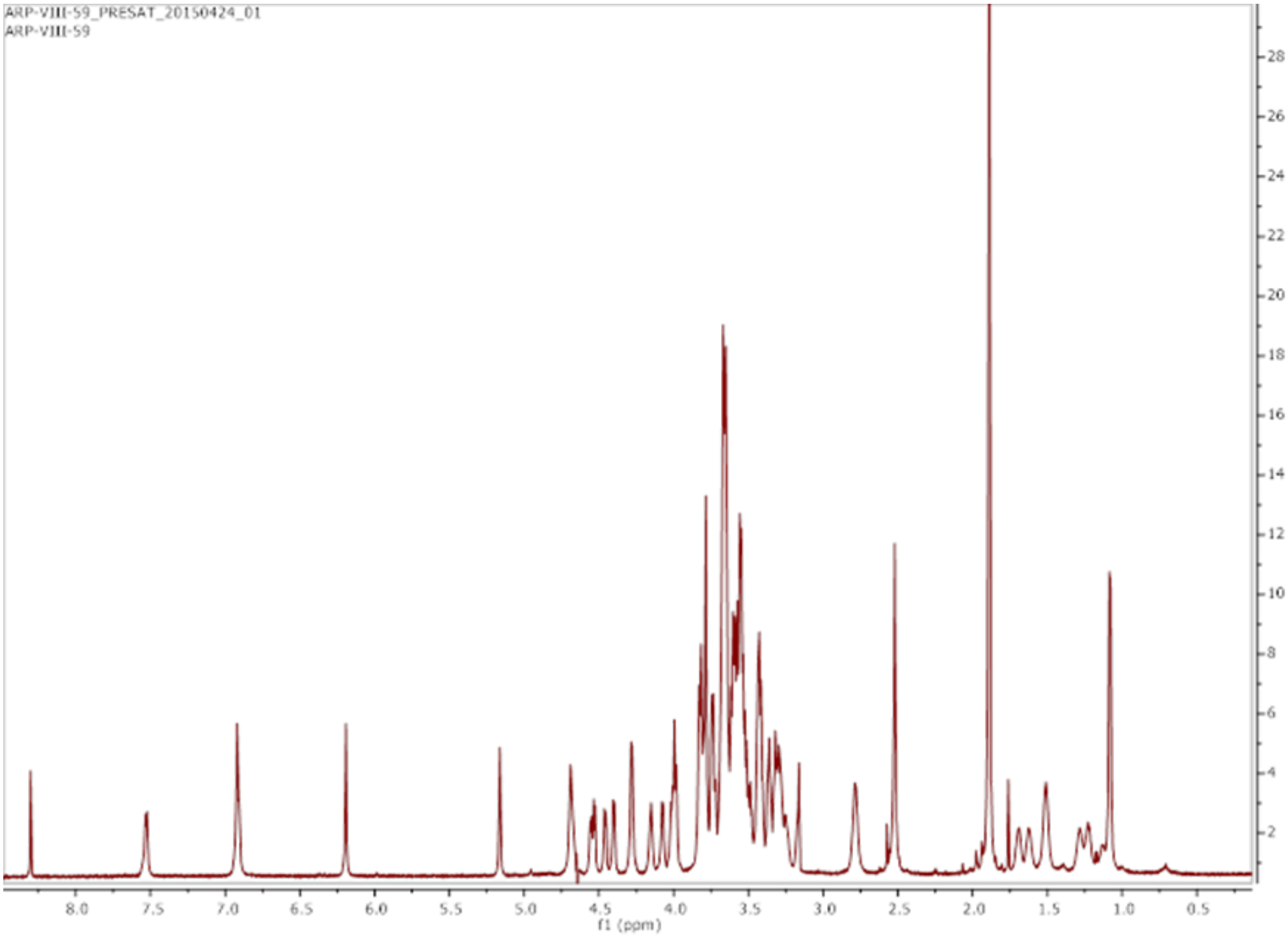
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.5 Hz, 1H)	3.35	3.43	3.48	n/a[a]	n/a	-	-
Gal	4.27 (d, *J* = 7.3 Hz, 2H)	3.41	3.55	3.99	n/a	n/a	-	-
GlcNAc	4.55 (d, *J* = 6.1 Hz, 1H)	3.64	3.54	3.31	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.39 (d, *J* = 7.5 Hz, 1H)	3.52	3.64	3.72	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 7.8 Hz, 1H)	3.56	3.53	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.27 (d, *J* = 7.3 Hz, 2H)	3.41	3.55	3.99	n/a	n/a	-	-
GlcNAc(3)	4.53 (d, *J* = 8.6 Hz, 1H)	3.59	3.41	3.29	n/a	n/a	-	1.91-1.81 (m, 9H)
Fuc(1)(α2)	5.14	3.63	n/a	n/a	4.06 (br q, *J* = 6.6 Hz, 1H)	-	1.08 (d, *J* = 5.9 Hz, 3H)	-

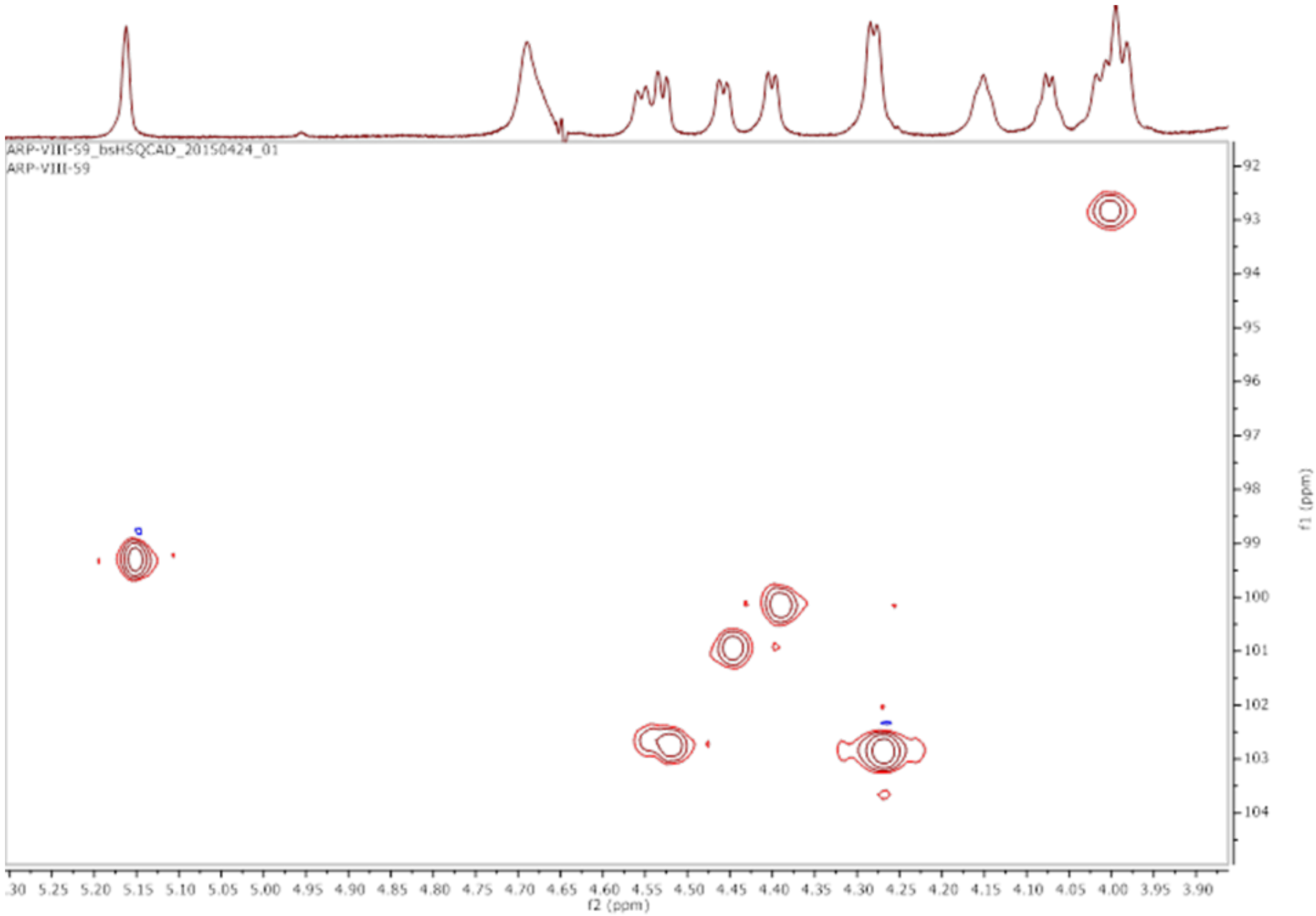
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

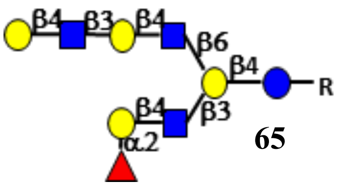
	C1
Glc	92.85
Gal	102.86
GlcNAc	102.73
Gal(2)	100.11
GlcNAc(2)	101.00
Gal(3)	102.87
GlcNAc(3)	102.73
Fuc(1)(α2)	99.35

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{75}H_{119}N_7O_{45}Na$-- $(M + Na)^+$ exact 1860.7136, found 1860.1375.


ARP-VIII-59_PRESAT_20150424_01
ARP-VIII-59
f1 (ppm)


ARP-VIII-59_bsHSQCAD_20150424_01
ARP-VIII-59
f1 (ppm)
f2 (ppm)



65

^{1}H (800 MHz, D_2O): δ (ppm)

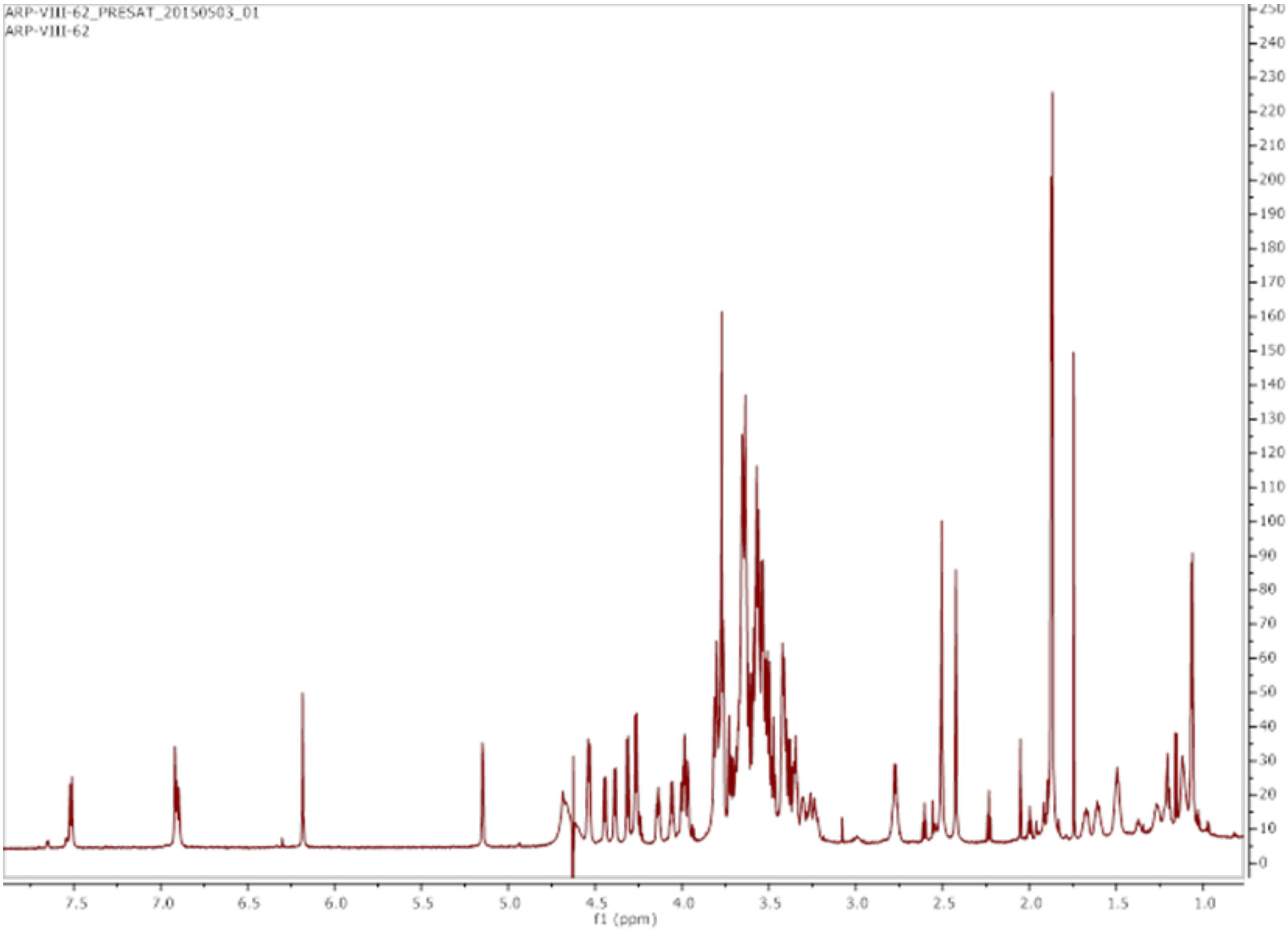
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00 (d, *J* = 8.5 Hz, 1H)	3.35	3.39	3.45	n/a[a]	n/a	-	-
Gal	4.26 (d, *J* = 7.8 Hz, 2H)	3.42	3.55	3.98	n/a	n/a	-	-
GlcNAc	4.54 (d, *J* = 6.1 Hz, 1H)	3.67	3.59	3.31	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.39 (d, *J* = 7.7 Hz, 1H)	3.52	n/a	3.73	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 8.2 Hz, 1H)	3.56	3.53	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.26 (d, *J* = 7.8 Hz, 2H)	3.42	3.55	3.98	n/a	n/a	-	-
GlcNAc(3)	4.53 (d, *J* = 8.6 Hz, 1H)	3.64	3.54	3.42	n/a	n/a	-	1.91-1.81 (m, 9H)
Gal(4)	4.31 (d, *J* = 7.9 Hz, 1H)	3.39	3.51	3.77	n/a	n/a	-	-
Fuc(1)(α2)	5.14 (d, *J* = 2.9 Hz, 1H)	3.62	n/a	n/a	4.06 (br q, *J* = 7.1, 6.4 Hz , 1H)	-	1.07 (d, *J* = 6.5 Hz, 3H)	-

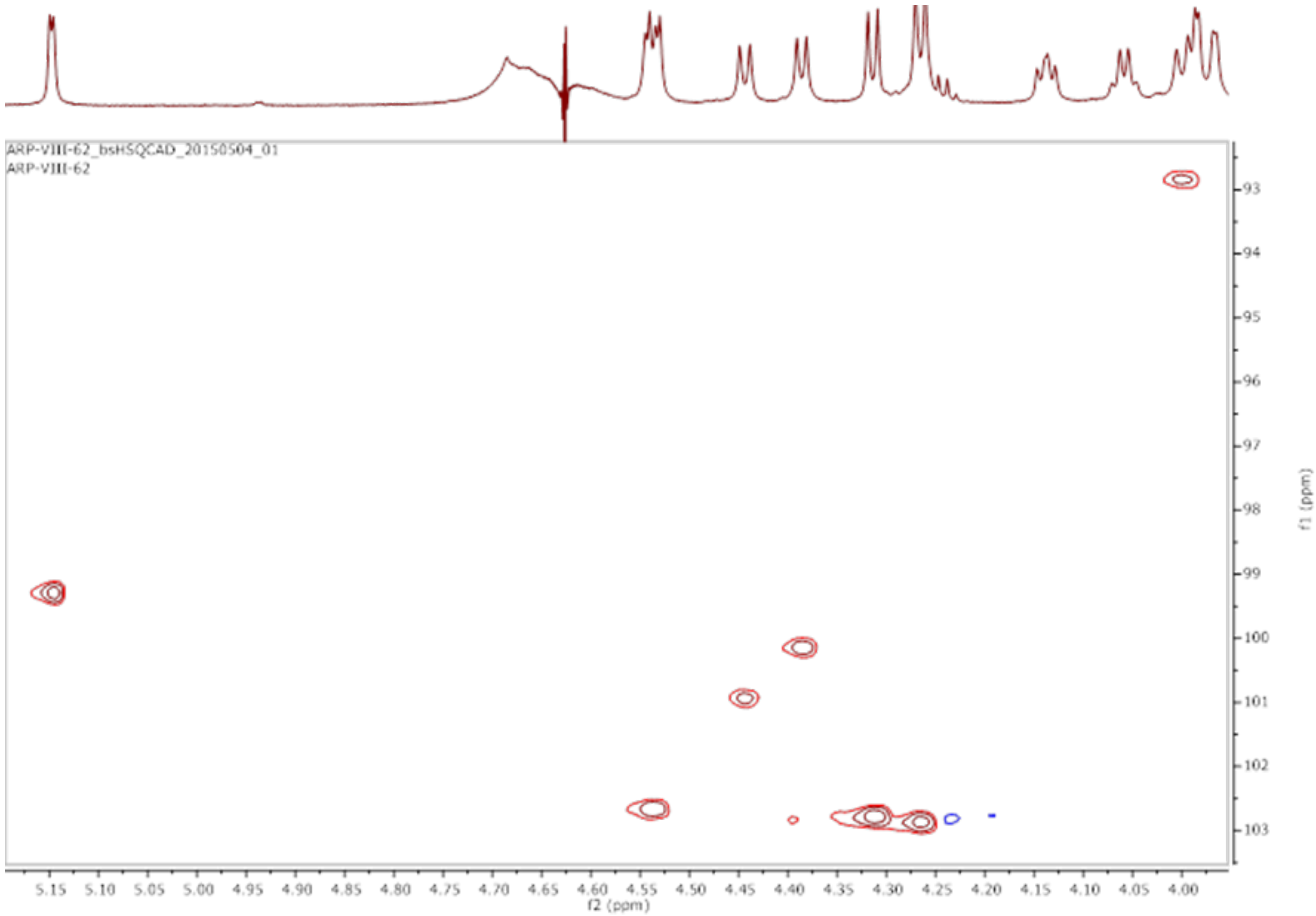
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

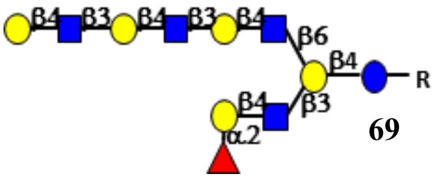
	C1
Glc	92.83
Gal	102.94
GlcNAc	102.68
Gal(2)	100.13
GlcNAc(2)	101.95
Gal(3)	102.94
GlcNAc(3)	102.68
Gal(4)	102.86
Fuc(1)(α2)	99.28

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{81}H_{129}N_7O_{50}Na$-- $(M + Na)^+$ exact 2022.7664, found 2022.0397.


ARP-VIII-62_PRESAT_20150503_01
ARP-VIII-62
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


ARP-VIII-62_bsHSQCAD_20150504_01
ARP-VIII-62
f1 (ppm)
f2 (ppm)



69

[1]H (800 MHz, D_2O): δ (ppm)

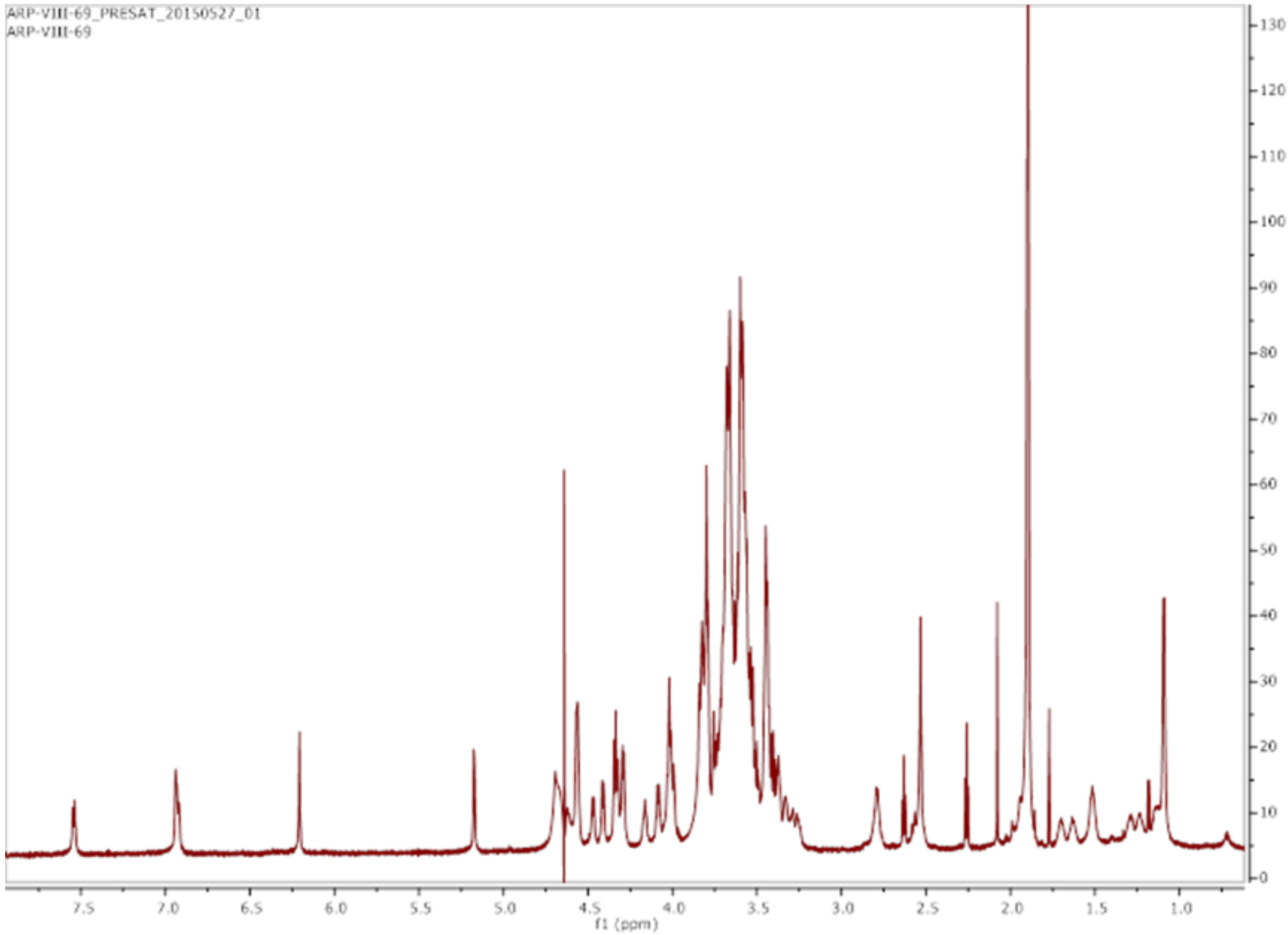
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.43	3.49	n/a[a]	n/a	-	-
Gal	4.26	3.42	3.56	3.90	n/a	n/a	-	-
GlcNAc	4.55	3.65	3.57	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39	3.51	n/a	3.73	n/a	n/a	-	-
GlcNAc(2)	4.44	3.57	3.51	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.26	3.43	3.56	3.99	n/a	n/a	-	-
GlcNAc(3)	4.55	3.65	3.57	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(4)	4.30	3.43	3.58	4.00	n/a	n/a	-	-
GlcNAc(4)	4.55	3.65	3.57	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(5)	4.32	3.38	3.51	3.77	n/a	n/a	-	-
Fuc(1)(α2)	5.15 (d, *J* = 3.2 Hz, 1H)	3.65	n/a	n/a	4.04	-	1.06 (d, *J* = 6.6 Hz, 3H)	-

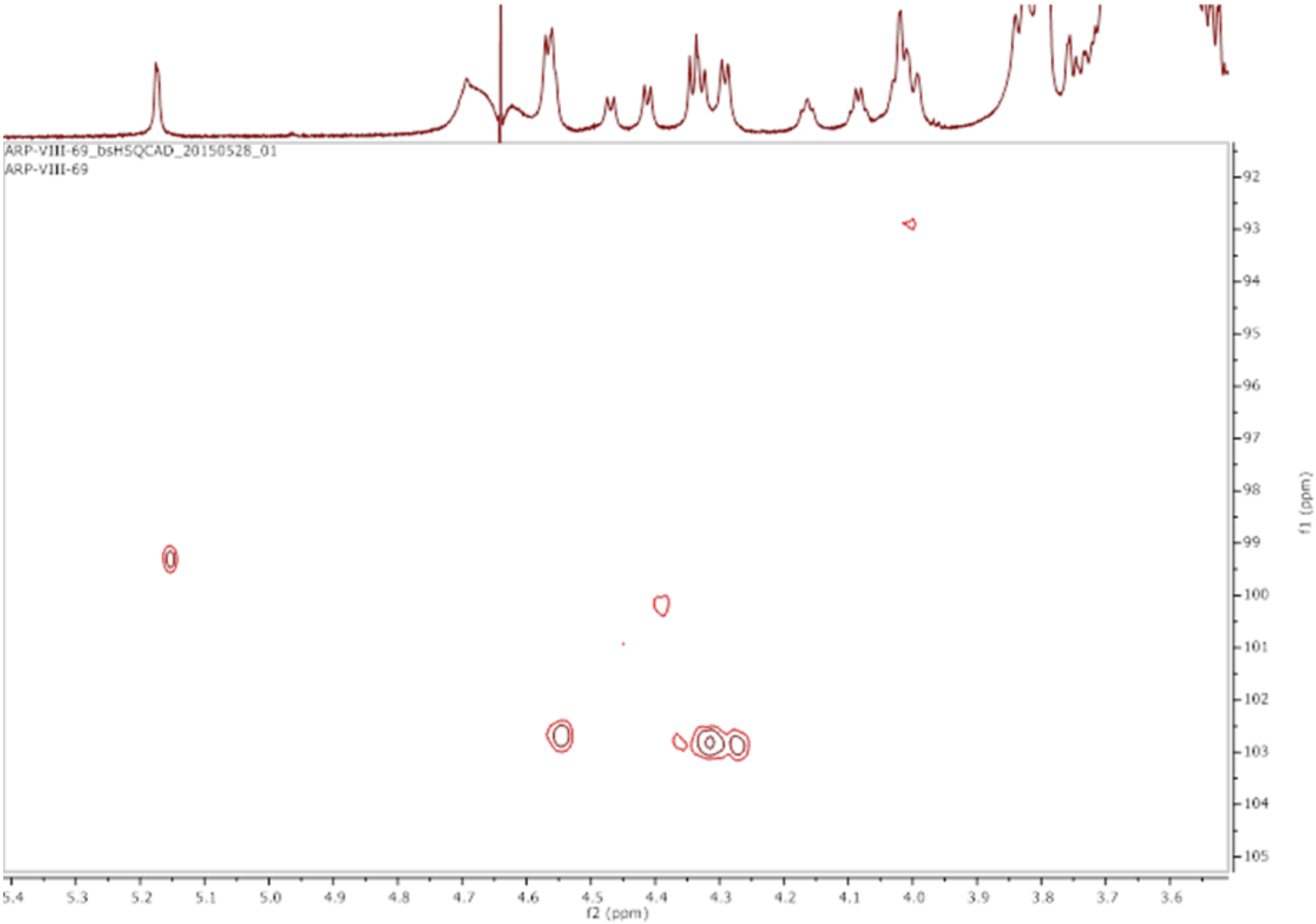
[13]C from BSHSQC (200 MHz, D_2O): δ (ppm)

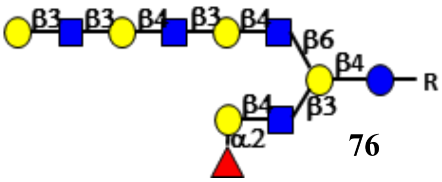
	C1
Glc	92.91
Gal	102.83
GlcNAc	102.74
Gal(2)	100.15
GlcNAc(2)	100.95
Gal(3)	102.83
GlcNAc(3)	102.74
Gal(4)	102.80
GlcNAc(4)	102.74
Gal(5)	102.80
Fuc(1)(α2)	99.36

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{95}H_{152}N_8O_{60}Na$-- $(M + Na)^+$ exact 2387.8986, found 2387.0994.


ARP-VIII-69_PRESAT_20150527_01
ARP-VIII-69
f1 (ppm)


ARP-VIII-69_bsHSQCAD_20150528_01
ARP-VIII-69
f1 (ppm)
f2 (ppm)
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
92
93
94
95
96
97
98
99
100
101
102
103
104
105



76

^{1}H (600 MHz, D_2O): δ (ppm)

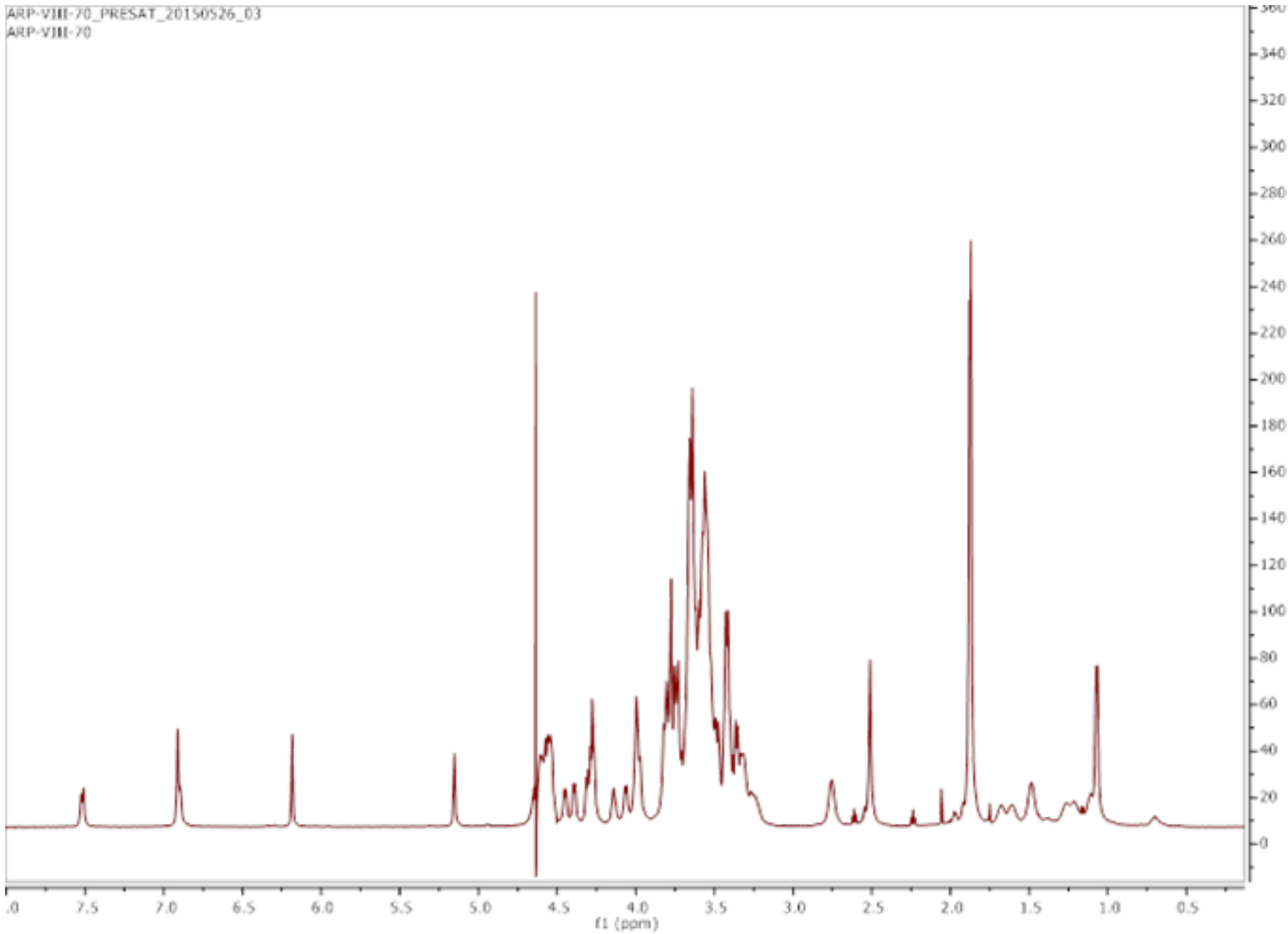
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.43	3.49	n/a[a]	n/a	-	-
Gal	4.26	3.42	3.56	3.99	n/a	n/a	-	-
GlcNAc	4.55	3.65	3.57	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39 (d, *J* = 7.3 Hz, 1H)	3.51	3.64	3.73	n/a	n/a	-	-
GlcNAc(2)	4.44	3.57	n/a	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.26	3.42	3.56	3.99	n/a	n/a	-	-
GlcNAc(3)	4.55	3.65	3.57	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(4)	4.30	3.43	3.58	4.00	n/a	n/a	-	-
GlcNAc(4)	4.55	3.74	n/a	3.32	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(5)	4.28	3.38	3.66	3.75	n/a	n/a	-	-
Fuc(1)(α2)	5.15	3.65	n/a	n/a	4.07	-	1.09 (d, *J* = 5.8 Hz, 3H)	-

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

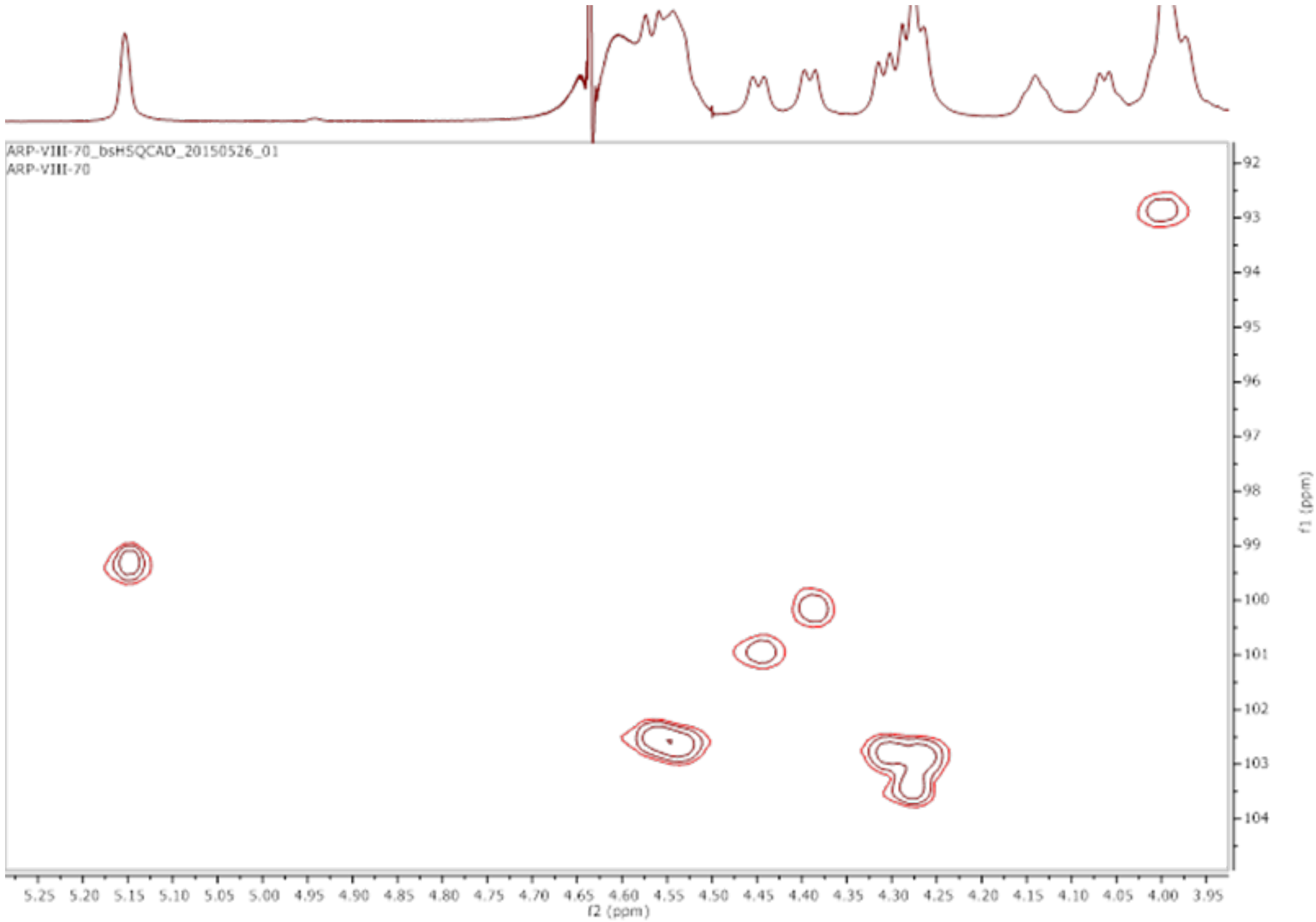
	C1
Glc	92.98
Gal	102.83
GlcNAc	102.53
Gal(2)	100.19
GlcNAc(2)	100.92
Gal(3)	102.83
GlcNAc(3)	102.53
Gal(4)	102.75
GlcNAc(4)	102.53
Gal(5)	103.48
Fuc(1)(α2)	99.31

[a] Not assigned
[b] Not applicable

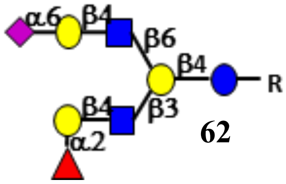
MALDI TOF-MS *m/z* calcd $C_{95}H_{152}N_8O_{60}Na$-- $(M + Na)^+$ exact 2387.8986, found 2387.3384.



ARP-VIII-70_PRESAT_20150526_03
ARP-VIII-70
f1 (ppm)



ARP-VIII-70_bsHSQCAD_20150526_01
ARP-VIII-70
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

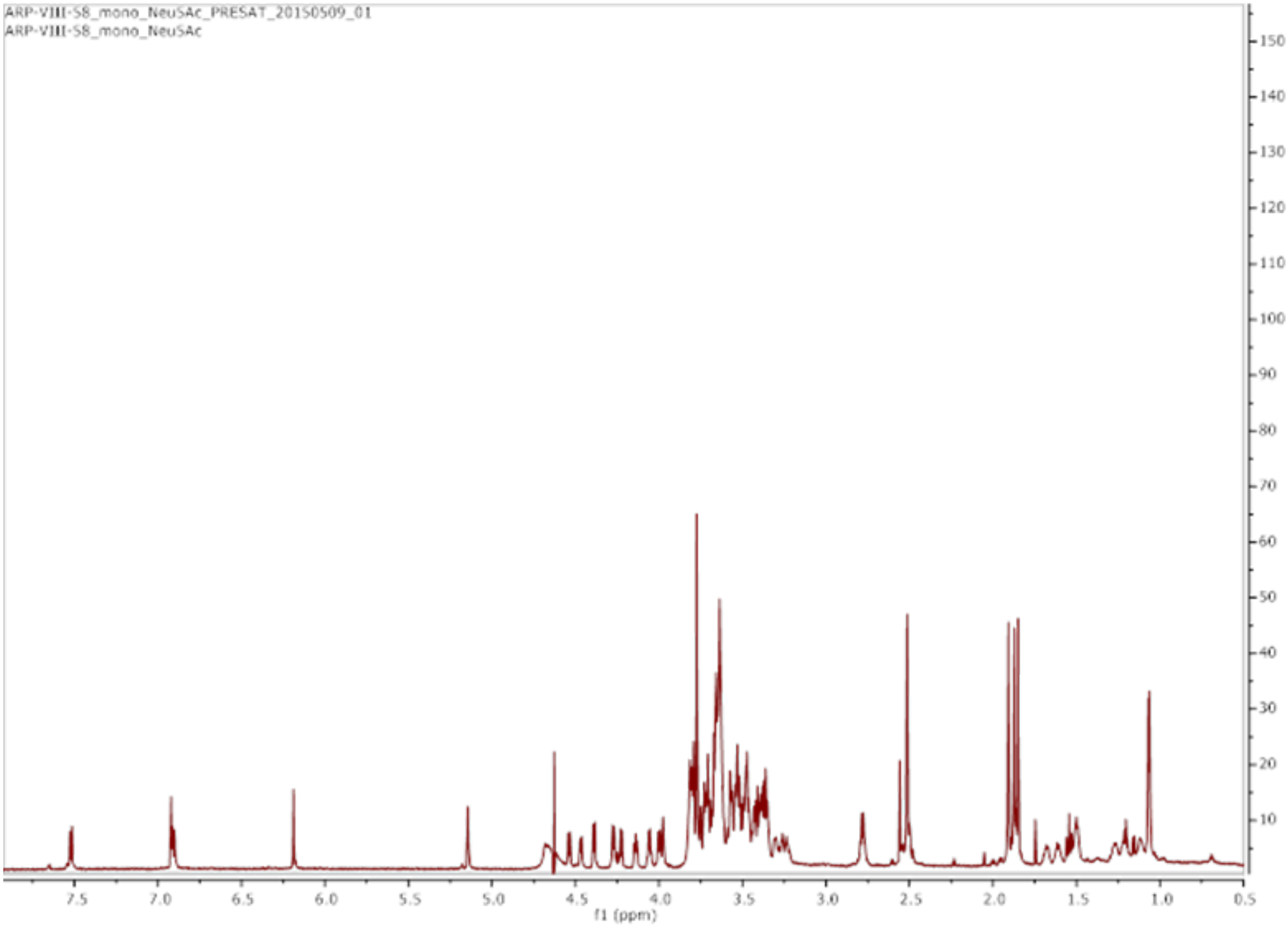
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH$_3$	NHAc
Glc	4.00 (d, *J* = 9.1 Hz, 1H)	3.35	3.41	3.47	n/a[a]	n/a	-	-	-	-	-
Gal	4.27 (d, *J* = 7.8 Hz, 1H)	3.42	3.53	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55 (d, *J* = 8.4 Hz, 1H)	3.65	3.55	3.30	n/a	n/a	-	-	-	-	1.92 - 1.84 (m, 9H)
Gal(2)	4.39 (d, *J* = 7.6 Hz, 1H)	3.50	3.64	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.47 (d, *J* = 7.6 Hz, 1H)	3.57	3.40	3.43	n/a	n/a	-	-	-	-	1.92 - 1.84 (m, 9H)
Gal(3)	4.23 (d, *J* = 7.8 Hz, 1H)	3.36	3.48	3.76	n/a	n/a	-	-	-	-	-
Fuc(1)(α2)	5.15	3.65	n/a	3.60	4.06	-	-	-	-	1.06 (d, *J* = 6.4 Hz, 3H)	-
Neu5Ac	-	-	2.52 – eq. 1.55 - axial	3.47	3.62	3.51	n/a	n/a	3.72 3.48	-	1.92 - 1.84 (m, 9H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

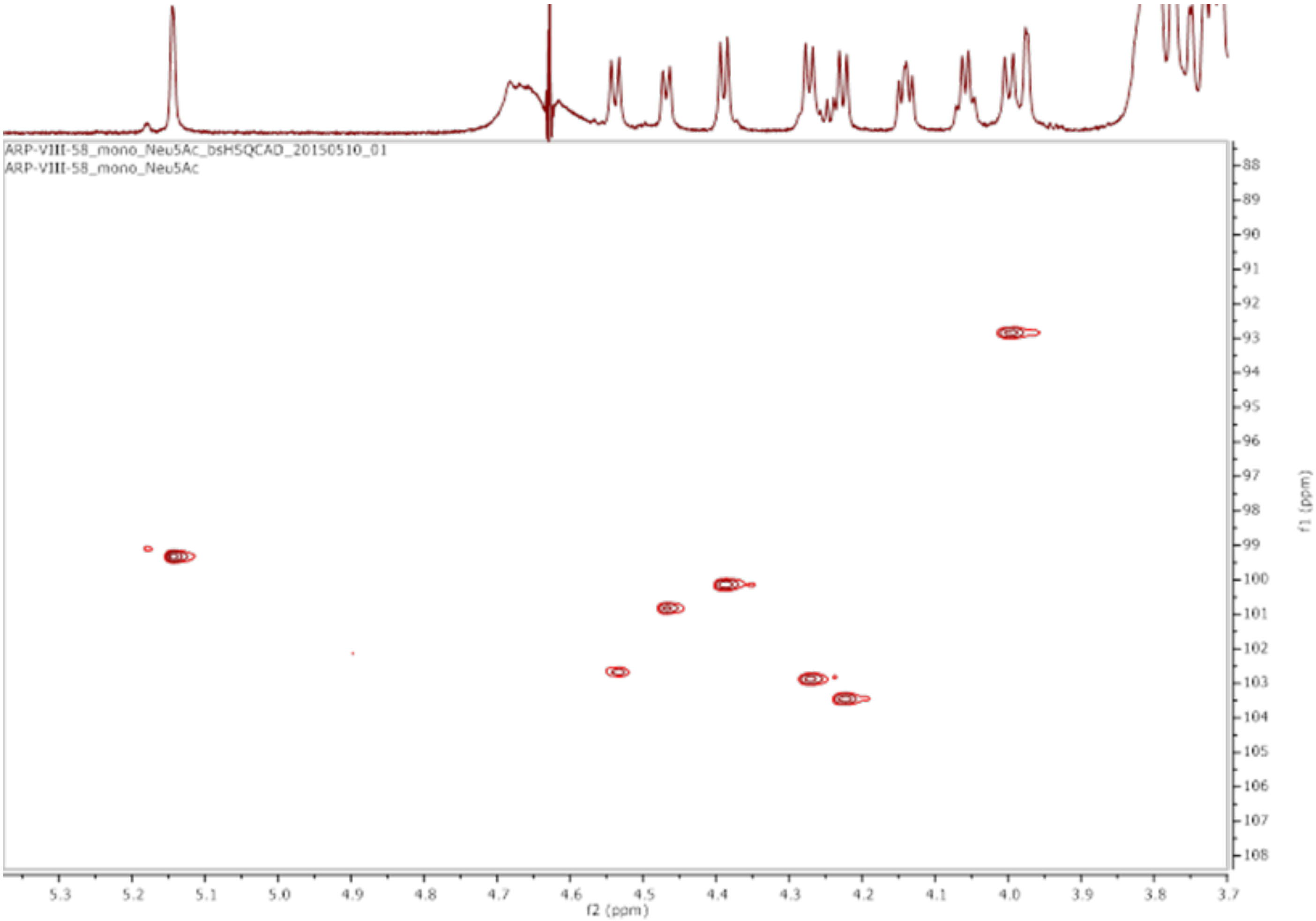
	C1
Glc	92.84
Gal	102.79
GlcNAc	102.69
Gal(2)	100.14
GlcNAc(2)	100.89
Gal(3)	103.42
Fuc(1)(α2)	99.41

[a] Not assigned
[b] Not applicable

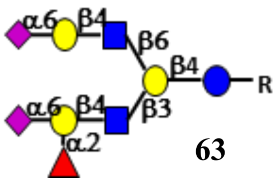
MALDI TOF-MS *m/z* calcd $C_{78}H_{122}N_7O_{48}Na_2$-- (M + 2Na)$^+$ exact 1970.7122, found 1970.2726



ARP-VIII-58_mono_Neu5Ac_PRESAT_20150509_01
ARP-VIII-58_mono_Neu5Ac
f1 (ppm)



ARP-VIII-58_mono_Neu5Ac_bsHSQCAD_20150510_01
ARP-VIII-58_mono_Neu5Ac
f2 (ppm)
f1 (ppm)



63

^{1}H (600 MHz, D_2O): δ (ppm)

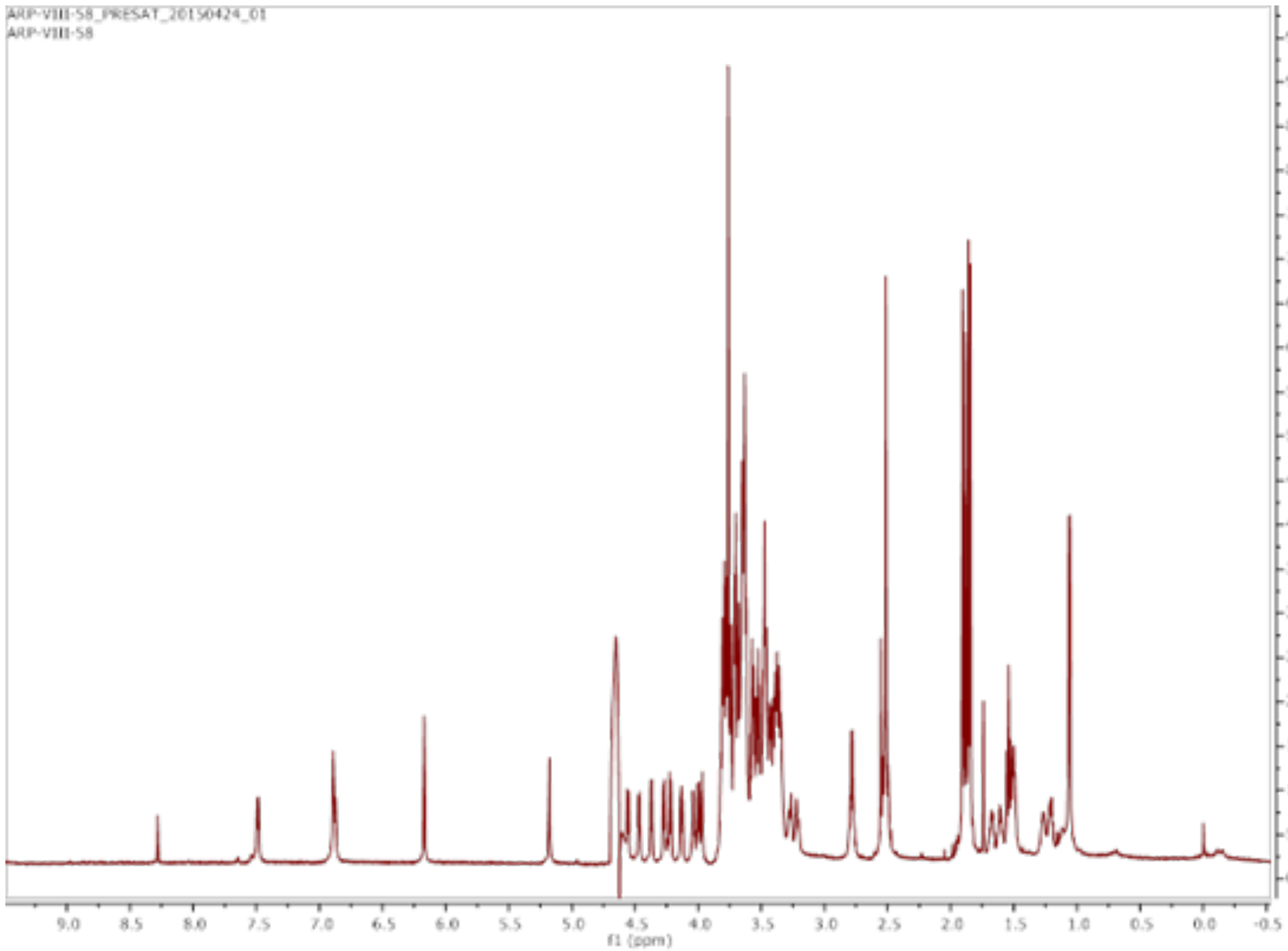
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.1 Hz, 1H)	3.37	3.42	3.43	n/a[a]	n/a	-	-	-	-	-
Gal	4.27 (d, *J* = 8.0 Hz, 1H)	3.42	3.53	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.46 (d, *J* = 7.6 Hz, 1H)	3.56	3.43	3.40	n/a	n/a	-	-	-	-	1.95 - 1.82 (m, 12H)
Gal(2)	4.35 (d, *J* = 7.6 Hz, 1H)	3.52	3.64	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.54 (d, *J* = 8.3 Hz, 1H)	3.63	3.58	3.34	n/a	n/a	-	-	-	-	1.95 - 1.82 (m, 12H)
Gal(3)	4.22 (d, *J* = 7.9 Hz, 1H)	3.36	3.48	3.75	n/a	n/a	-	-	-	-	-
Fuc(1)(α2)	5.15 (d, *J* = 3.2 Hz, 1H)	3.64	n/a	n/a	4.04	-	-	-	-	1.06 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.95 - 1.82 (m, 12H)
Neu5Ac(2)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.95 - 1.82 (m, 12H)

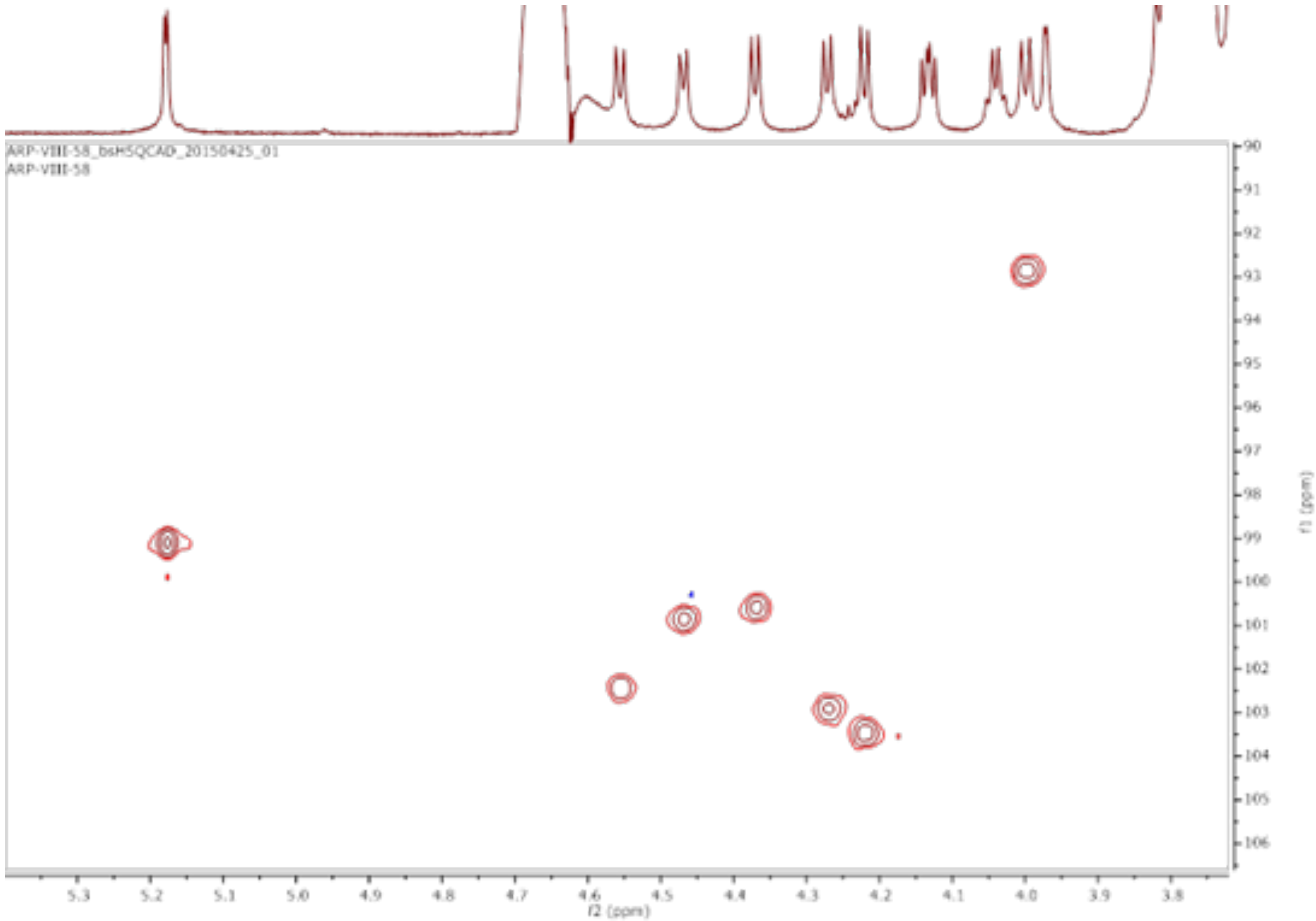
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

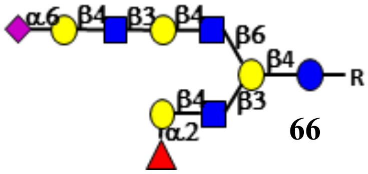
	C1
Glc	92.79
Gal	102.94
GlcNAc	100.81
Gal(2)	100.61
GlcNAc(2)	102.41
Gal(3)	103.48
Fuc(1)(α2)	99.17

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{89}H_{138}N_8O_{56}Na_3$-- $(M + 3Na)^+$ exact 2283.7890, found 2283.2549.


ARP-VIII-58_PRESAT_20150424_01
ARP-VIII-58
f1 (ppm)


ARP-VIII-58_bsHSQCAD_20150425_01
ARP-VIII-58
f2 (ppm)
f1 (ppm)



66

^{1}H (600 MHz, D_2O): δ (ppm)

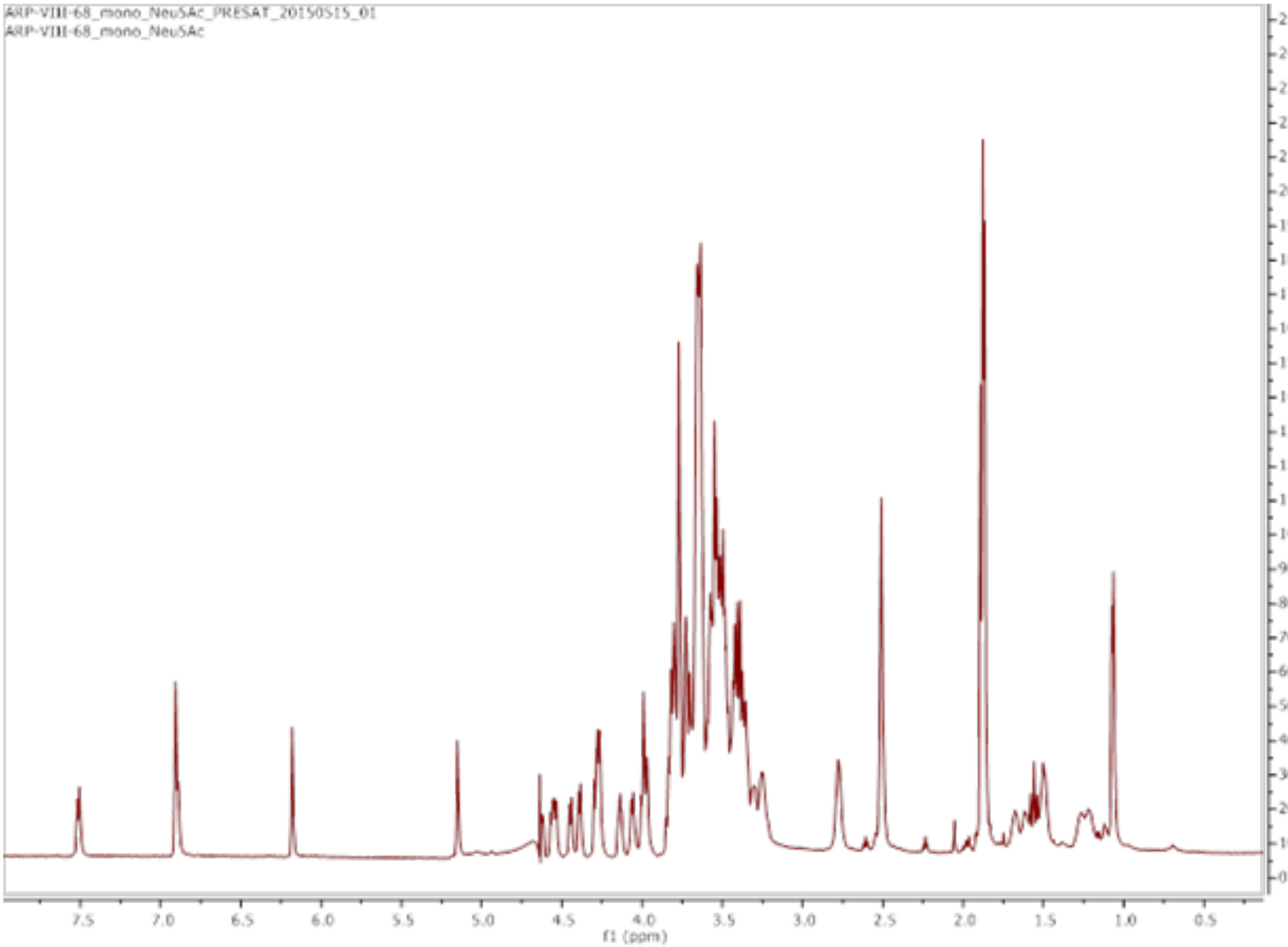
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.35	3.42	3.47	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.42	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.64	3.54	3.31	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 12H)
Gal(2)	4.38 (d, *J* = 7.4 Hz, 1H)	3.52	n/a	3.71	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 7.7 Hz, 1H)	3.56	3.53	3.42	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 12H)
Gal(3)	4.27	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.64	3.50	3.44	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 12H)
Gal(4)	4.29	3.37	3.51	3.77	n/a	n/a	-	-	-	-	-
Fuc(1)(α2)	5.15	3.64	n/a	n/a	4.04	-	-	-	-	1.06 (d, *J* = 6.1 Hz, 3H)	-
Neu5Ac	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 12H)

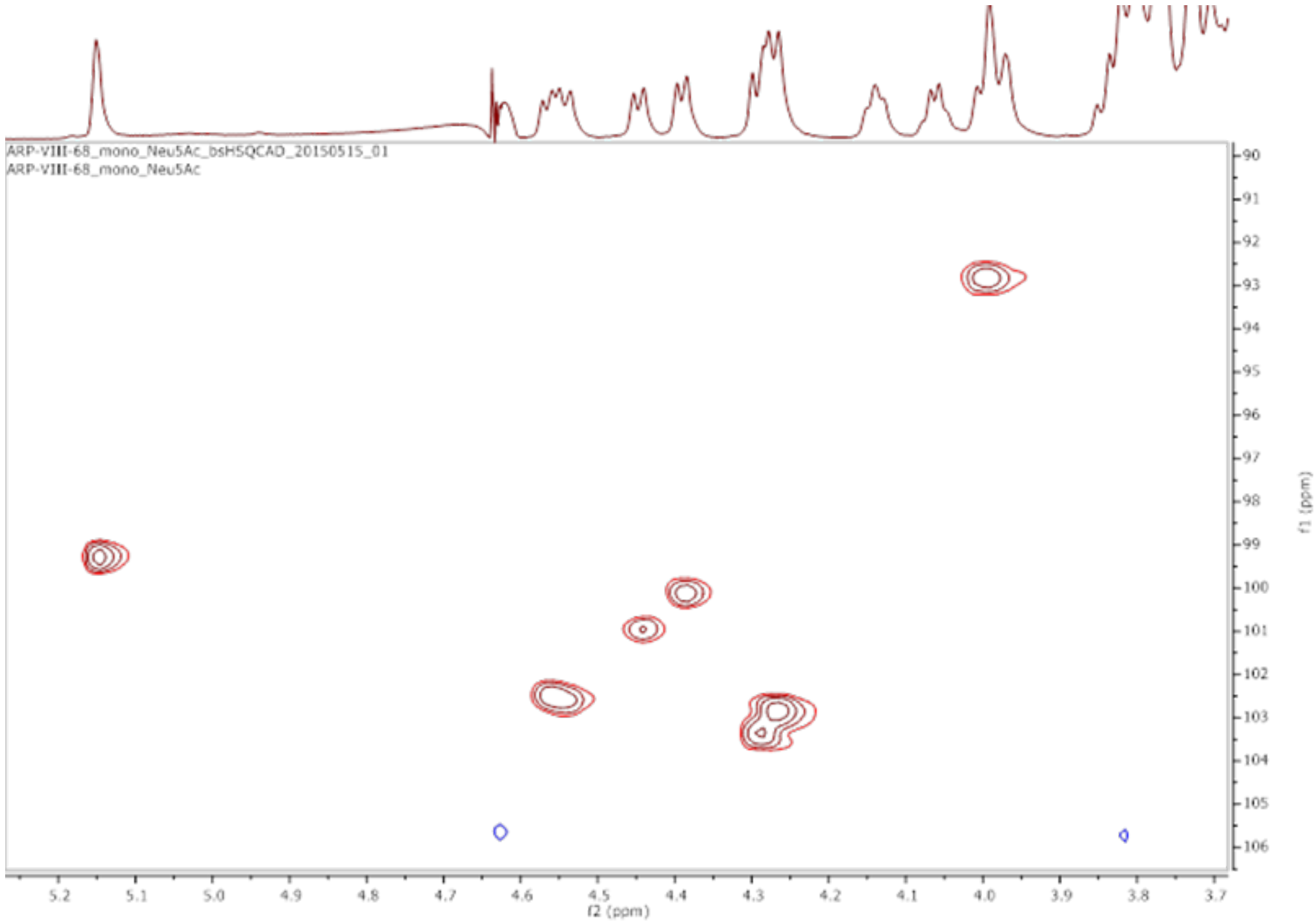
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.87
Gal	102.84
GlcNAc	102.57
Gal(2)	100.07
GlcNAc(2)	100.91
Gal(3)	102.84
GlcNAc(3)	102.57
Gal(4)	103.41
Fuc(1)(α2)	99.29

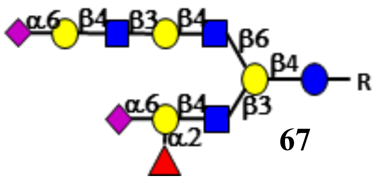
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{89}H_{138}N_8O_{56}$-- (M - H)$^-$ exact 2289.8648, found 2289.3418.


ARP-VIII-68_mono_Neu5Ac_PRESAT_20150515_01
ARP-VIII-68_mono_Neu5Ac
f1 (ppm)



ARP-VIII-68_mono_Neu5Ac_bsHSQCAD_20150515_01
ARP-VIII-68_mono_Neu5Ac
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
f2 (ppm)
f1 (ppm)
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106



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^{1}H (600 MHz, D_2O): δ (ppm)

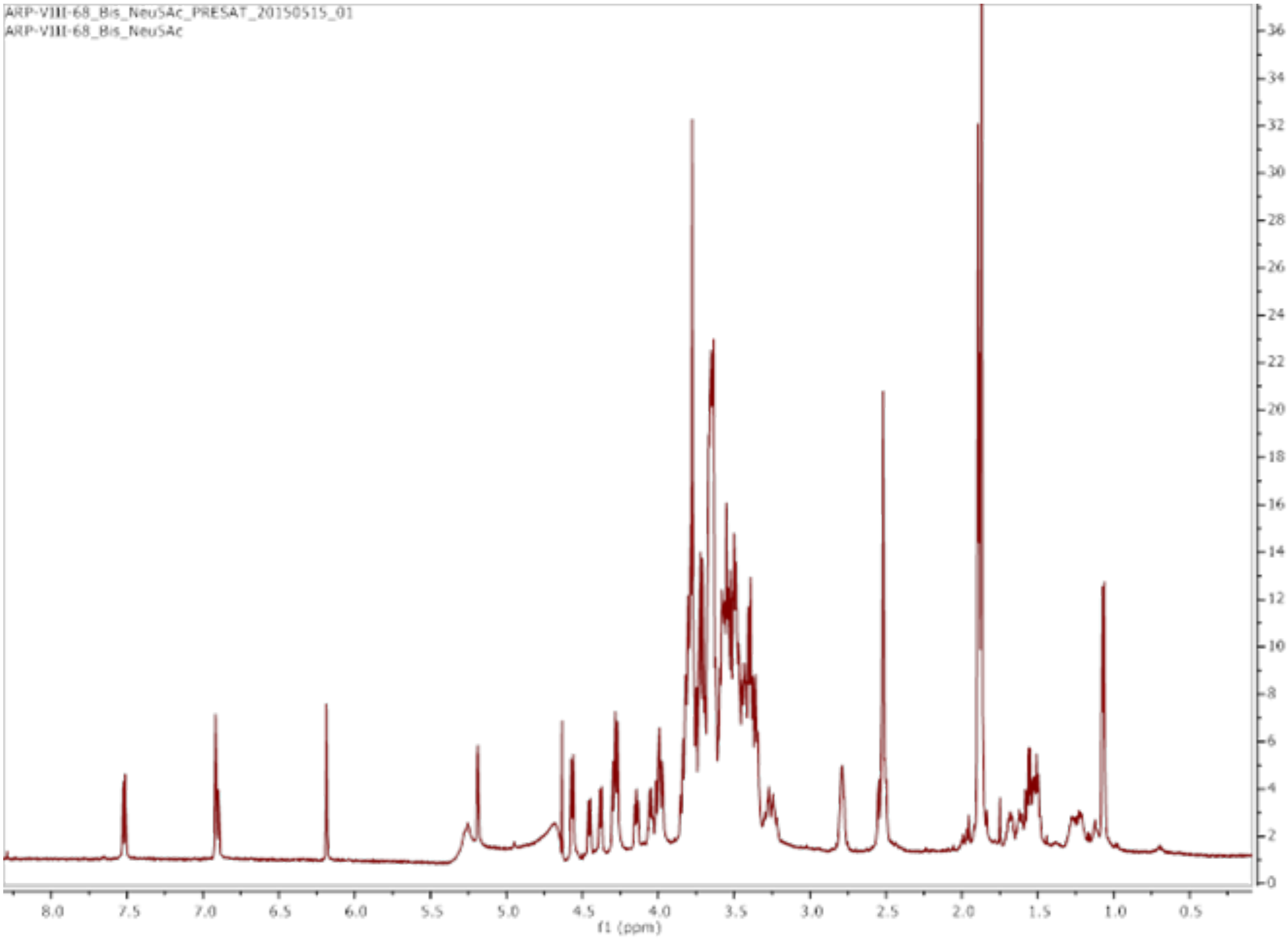
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.35	3.42	3.49	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.42	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55 (d, *J* = 7.9 Hz, 2H)	3.64	3.58	3.35	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 15H)
Gal(2)	4.38 (d, *J* = 7.6 Hz, 1H)	3.52	3.65	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 7.7 Hz, 1H)	3.56	3.50	3.42	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 15H)
Gal(3)	4.27	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55 (d, *J* = 7.9 Hz, 2H)	3.64	3.50	3.44	n/a	n/a	-	-	-	-	1.92 - 1.82 (m, 15H)
Gal(4)	4.29	3.37	3.51	3.77	n/a	n/a	-	-	-	-	-
Fuc(1)(α2)	5.19	3.65	n/a	n/a	4.04	-	-	-	-	1.06 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 15H)
Neu5Ac(2)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 15H)

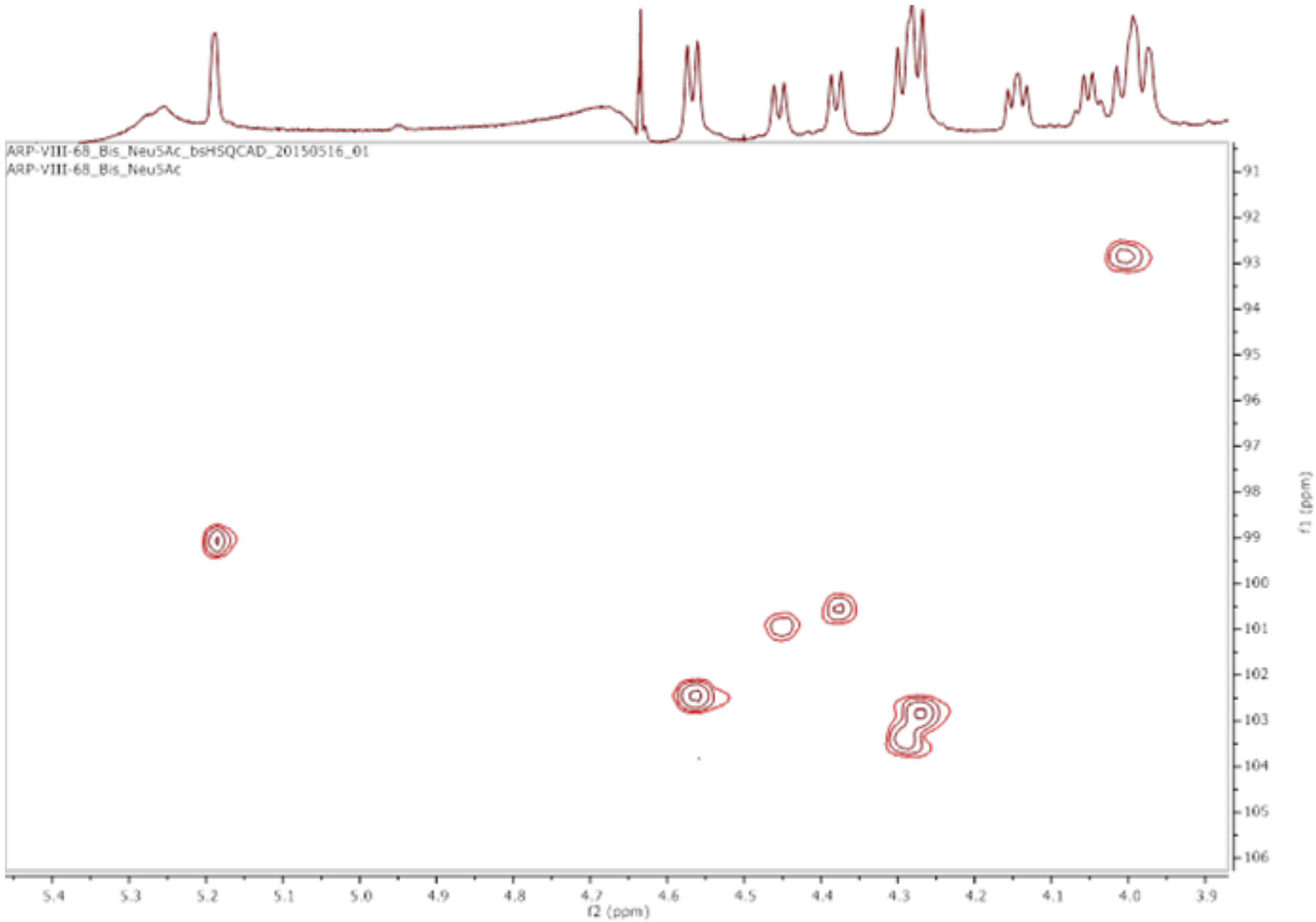
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

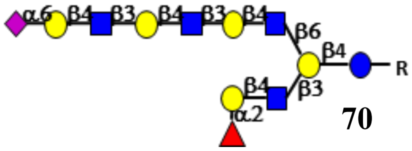
	C1
Glc	92.90
Gal	102.84
GlcNAc	102.49
Gal(2)	100.49
GlcNAc(2)	100.96
Gal(3)	102.84
GlcNAc(3)	102.49
Gal(4)	103.47
Fuc(1)(α2)	99.04

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{103}H_{161}N_9O_{66}Na$-- (M - H)$^-$ exact 2602.9427, found 2602.4346.


ARP-VIII-68_Bis_NeuSAc_PRESAT_20150515_01
ARP-VIII-68_Bis_NeuSAc
f1 (ppm)


ARP-VIII-68_Bis_Neu5Ac_bsHSQCAD_20150516_01
ARP-VIII-68_Bis_Neu5Ac
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

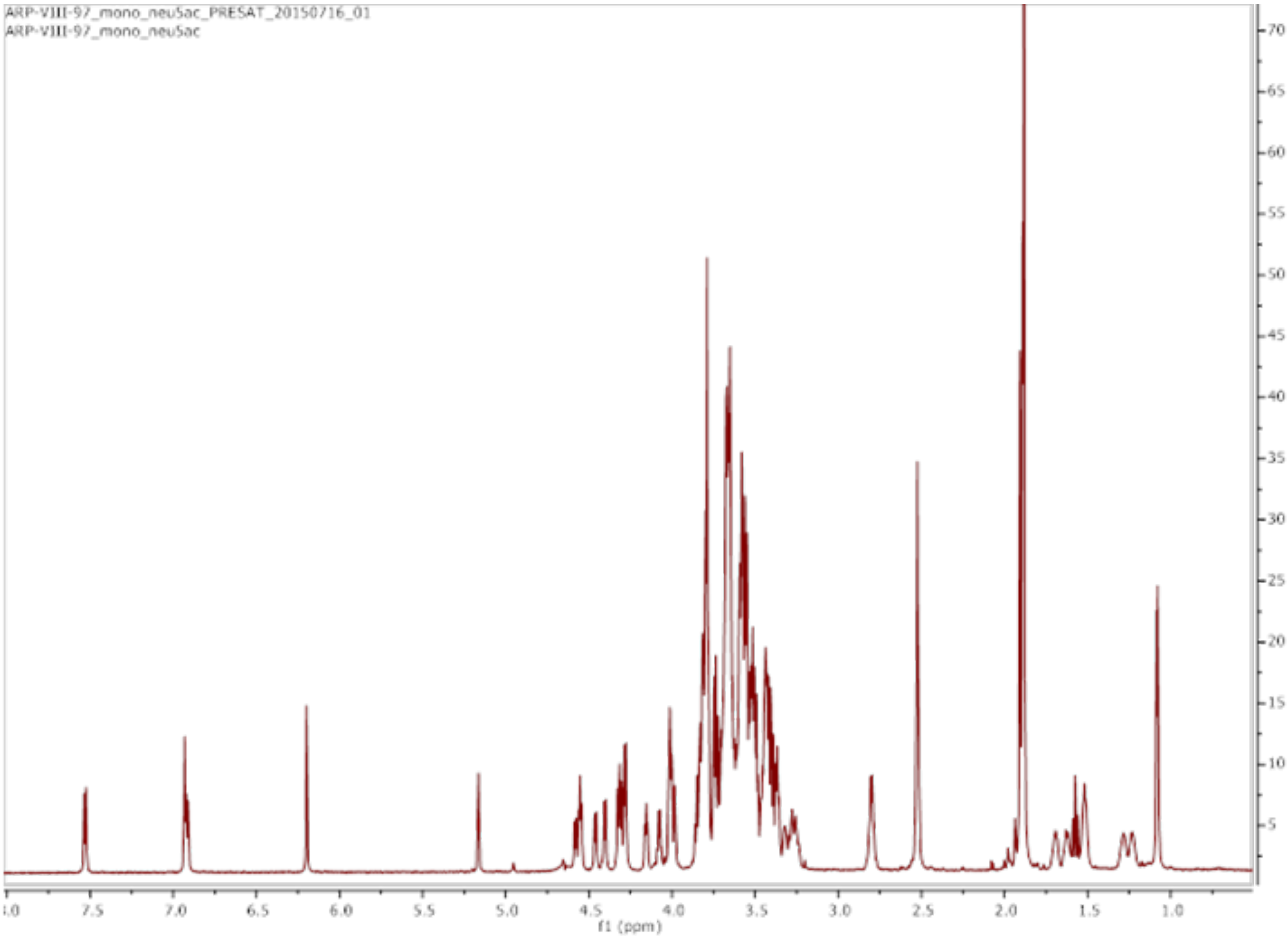
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.35	3.42	3.49	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.44	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.64	3.58	3.43	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 15H)
Gal(2)	4.40 (d, *J* = 7.5 Hz, 1H)	3.52	3.65	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 7.7 Hz, 1H)	3.59	3.53	3.44	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 15H)
Gal(3)	4.27	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.64	3.54	3.32	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 15H)
Gal(4)	4.32	3.44	3.58	4.01	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.58 (d, *J* = 7.8 Hz, 1H)	3.66	3.51	3.46	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 15H)
Gal(5)	4.32	3.39	3.52	3.78	n/a	n/a	-	-	-	-	-
Fuc(1) (α2)	5.19	3.65	n/a	n/a	4.08	-	-	-	-	1.08 (d, *J* = 6.4 Hz, 3H)	-
Neu5Ac	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 15H)

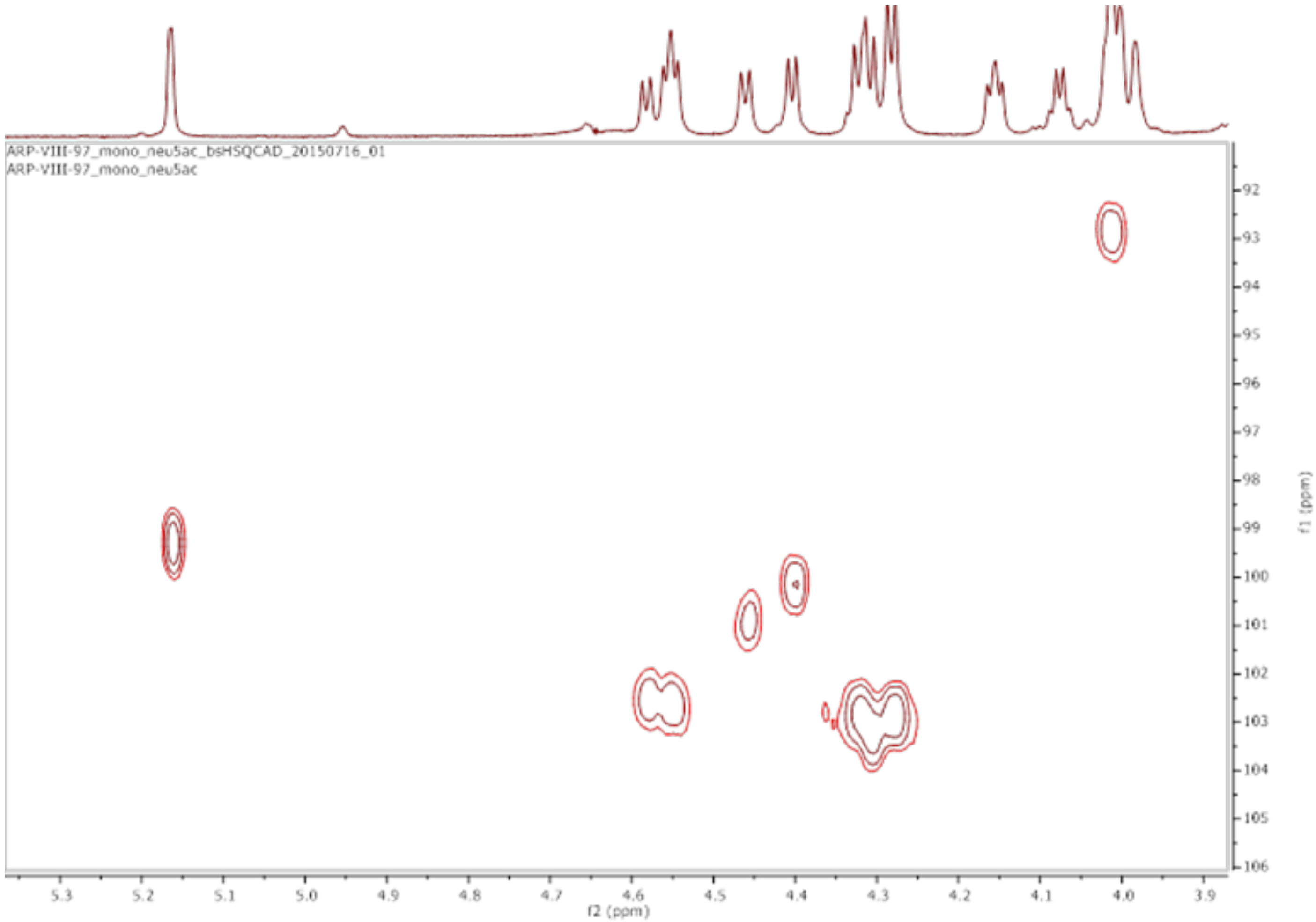
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

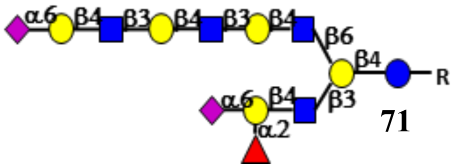
	C1
Glc	92.79
Gal	102.84
GlcNAc	102.62
Gal(2)	100.04
GlcNAc(2)	100.93
Gal(3)	102.84
GlcNAc(3)	102.62
Gal(4)	102.79
GlcNAc(4)	102.54
Gal(5)	103.31
Fuc(1)(α2)	99.18

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{106}H_{168}N_9 O_{68}Na_2$-- $(M + 2Na)^+$ exact 2700.9766, found 2700.2908.


ARP-VIII-97_mono_neu5ac_PRESAT_20150716_01
ARP-VIII-97_mono_neu5ac
f1 (ppm)


ARP-VIII-97_mono_neu5ac_bsHSQCAD_20150716_01
ARP-VIII-97_mono_neu5ac
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

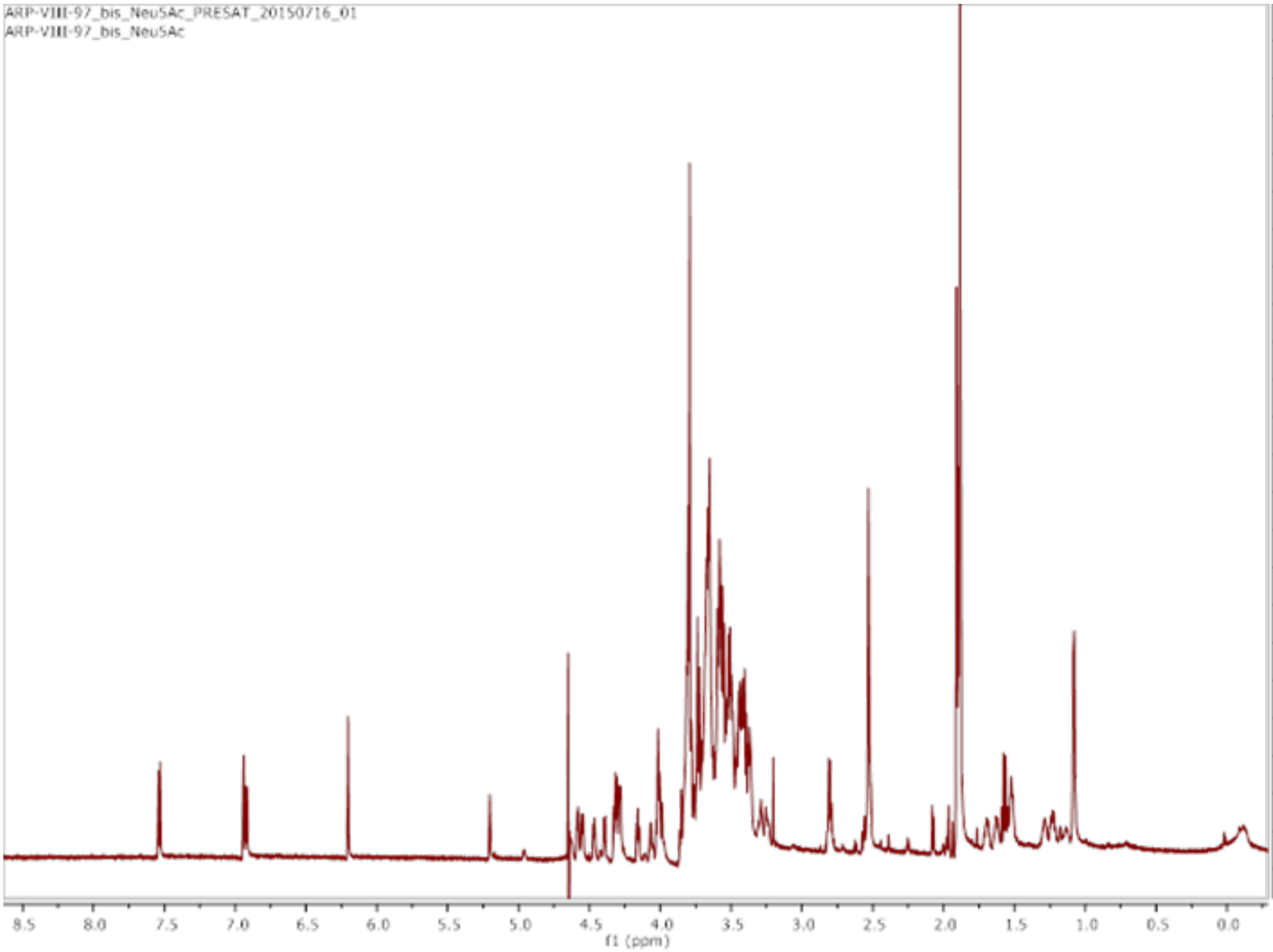
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.35	3.42	3.49	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.44	3.55	4.00	n/a	n/a	-	-	-	-	-
GlcNAc	4.55 (d, *J* = 8.1 Hz, 1H)	3.64	3.58	3.43	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 18H)
Gal(2)	4.40 (d, *J* = 7.4Hz, 1H)	3.54	3.73	3.77	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46	3.59	3.53	3.44	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 18H)
Gal(3)	4.27	3.43	3.55	4.00	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.58	3.64	3.59	3.36	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 18H)
Gal(4)	4.32	3.44	3.58	4.01	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.58	3.66	3.51	3.46	n/a	n/a	-	-	-	-	1.92 - 1.85 (m, 18H)
Gal(5)	4.32	3.39	3.52	3.78	n/a	n/a	-	-	-	-	-
Fuc(1)(α2)	5.19 (d, *J* = 2.7 Hz, 1H)	3.65	n/a	n/a	4.08	-	-	-	-	1.08 (d, *J* = 6.5 Hz, 3H)	-
Neu5Ac(1)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 18H)
Neu5Ac(2)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.92 - 1.82 (m, 18H)

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

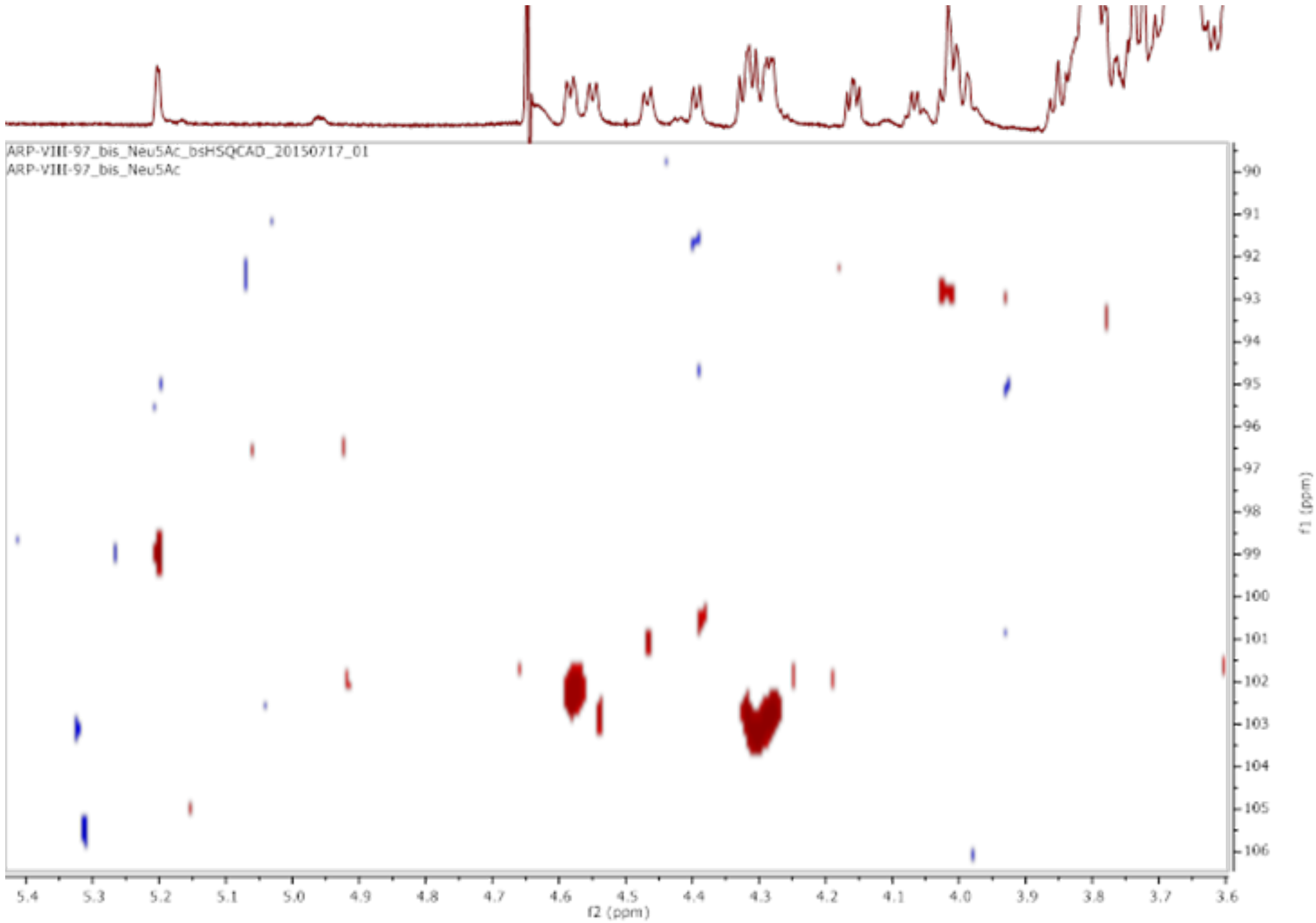
	C1
Glc	92.90
Gal	102.84
GlcNAc	103.17
Gal(2)	100.66
GlcNAc(2)	101.32
Gal(3)	102.85
GlcNAc(3)	102.42
Gal(4)	102.93
GlcNAc(4)	102.42
Gal(5)	103.29
Fuc(1)(α2)	99.06

[a] Not assigned
[b] Not applicable

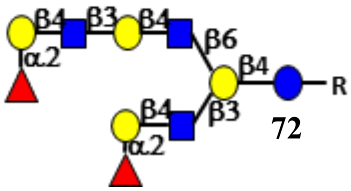
MALDI TOF-MS *m/z* calcd $C_{106}H_{168}N_9\ O_{68}Na_2$-- $(M + 2Na)^+$ exact 2700.9766, found 2700.2908.



ARP-VIII-97_bis_Neu5Ac_PRESAT_20150716_01
ARP-VIII-97_bis_Neu5Ac
f1 (ppm)



ARP-VIII-97_bis_Neu5Ac_bsHSQCAD_20150717_01
ARP-VIII-97_bis_Neu5Ac
f2 (ppm)
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

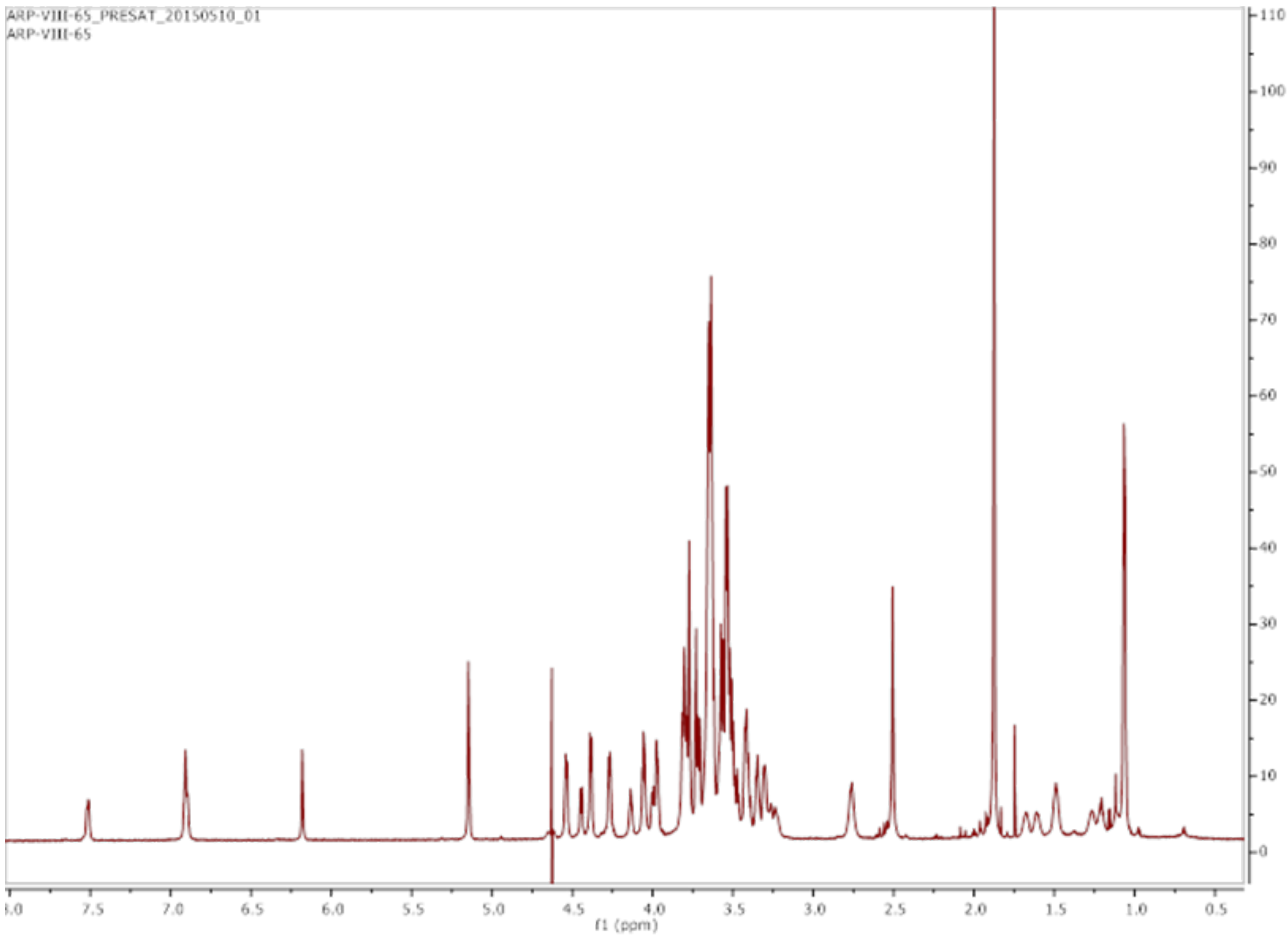
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.39	3.47	n/a[a]	n/a	-	-
Gal	4.26 (d, *J* = 6.0 Hz, 2H)	3.42	3.53	3.98	n/a	n/a	-	-
GlcNAc	4.53	3.64	3.53	3.31	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.39 (d, *J* = 7.6 Hz, 2H)	3.50	3.64	3.72	n/a	n/a	-	-
GlcNAc(2)	4.45 (d, *J* = 7.9 Hz, 1H)	3.56	3.51	3.43	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.26 (d, *J* = 6.0 Hz, 2H)	3.42	3.53	3.98	n/a	n/a	-	-
GlcNAc(3)	4.53	3.64	3.53	3.31	n/a	n/a	-	1.91-1.81 (m, 9H)
Gal(4)	4.39 (d, *J* = 7.6 Hz, 2H)	3.50	3.64	3.72	n/a	n/a	-	-
Fuc(1)(α2)	5.14	3.62	n/a	n/a	4.05	-	1.06	-
Fuc(2)(α2)	5.14	3.62	n/a	n/a	4.05	-	1.06	-

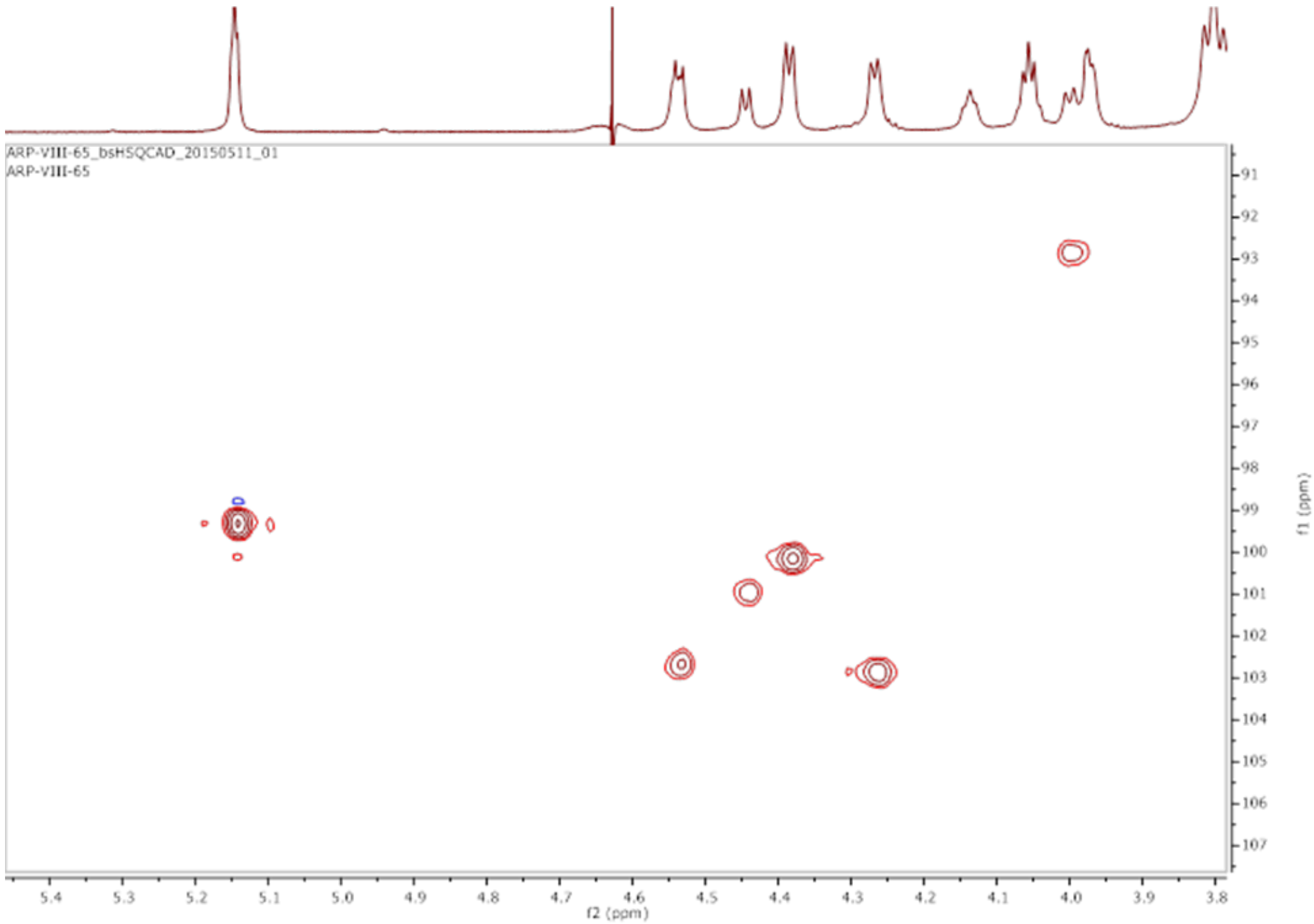
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

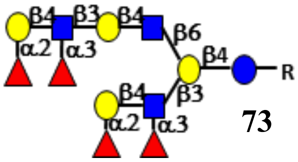
	C1
Glc	92.86
Gal	102.91
GlcNAc	102.59
Gal(2)	100.13
GlcNAc(2)	101.05
Gal(3)	102.91
GlcNAc(3)	102.59
Gal(4)	100.13
Fuc(1)(α2)	99.42
Fuc(2)(α2)	99.42

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{87}H_{139}N_7O_{54}Na$-- $(M + Na)^+$ exact 2168.8244, found 2168.2302.


ARP-VIII-65_PRESAT_20150510_01
ARP-VIII-65
f1 (ppm)


ARP-VIII-65_bsHSQCAD_20150511_01
ARP-VIII-65
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

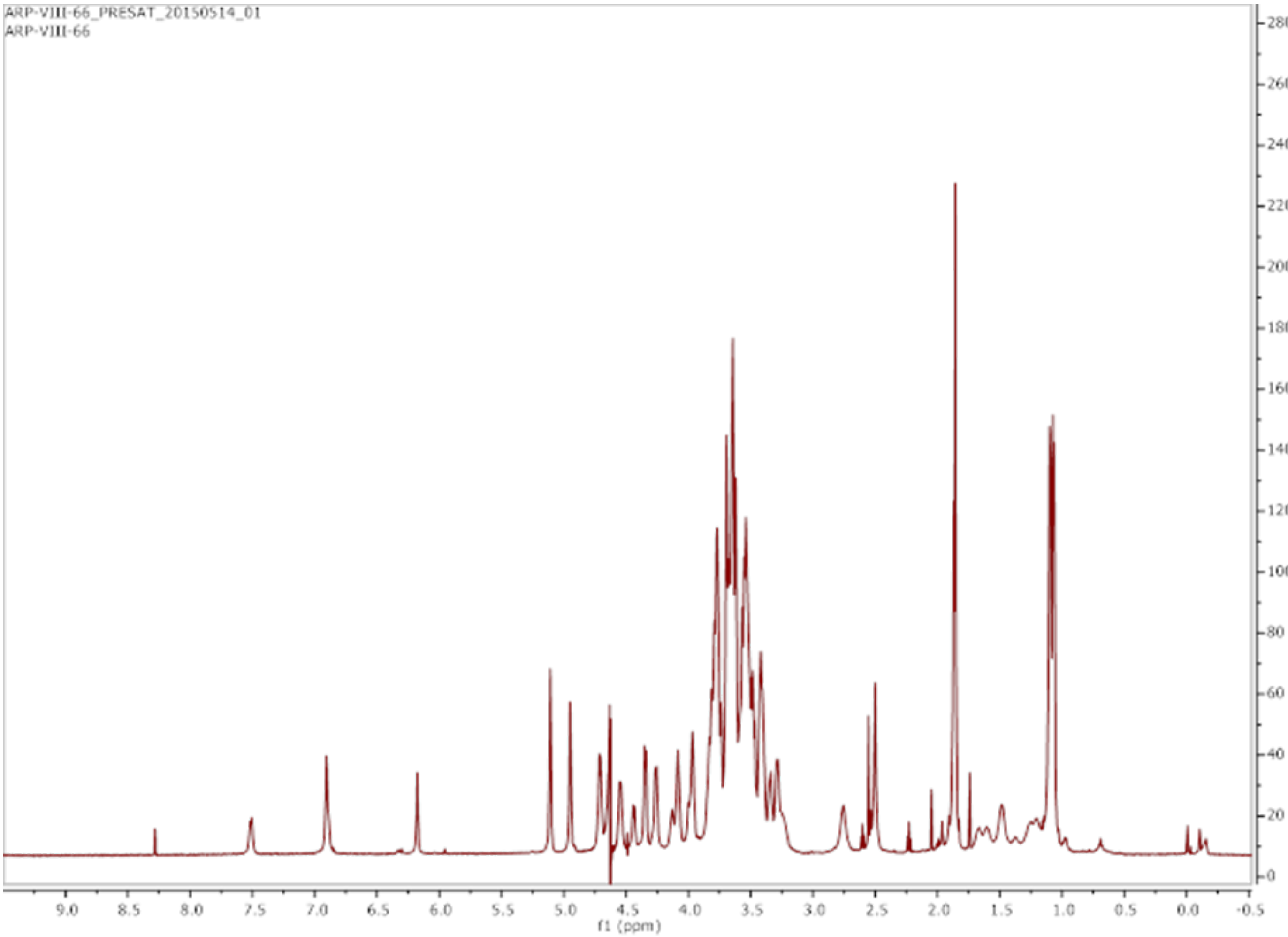
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.37	3.43	3.50	n/a[a]	n/a	-	-
Gal	4.26	3.42	3.55	3.98	n/a	n/a	-	-
GlcNAc	4.55	3.81	3.71	3.31	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.34 (d, *J* = 7.1 Hz, 2H)	3.50	n/a	3.72	n/a	n/a	-	-
GlcNAc(2)	4.44 (d, *J* = 6.8 Hz, 1H)	3.59	3.54	3.44	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.26	3.42	3.55	3.98	n/a	n/a	-	-
GlcNAc(3)	4.55	3.81	3.71	3.31	n/a	n/a	-	1.91-1.81 (m, 9H)
Gal(4)	4.34 (d, *J* = 7.1 Hz, 2H)	3.50	n/a	3.72	n/a	n/a	-	-
Fuc(1)(α3)	4.94	3.56	3.77	3.67	4.74	-	1.10	-
Fuc(2)(α2)	5.11	3.65	n/a	n/a	4.11	-	1.12	-
Fuc(3)(α3)	4.94	3.56	3.77	3.67	4.74	-	1.10	-
Fuc(4)(α2)	5.11	3.65	n/a	n/a	4.11	-	1.12	-

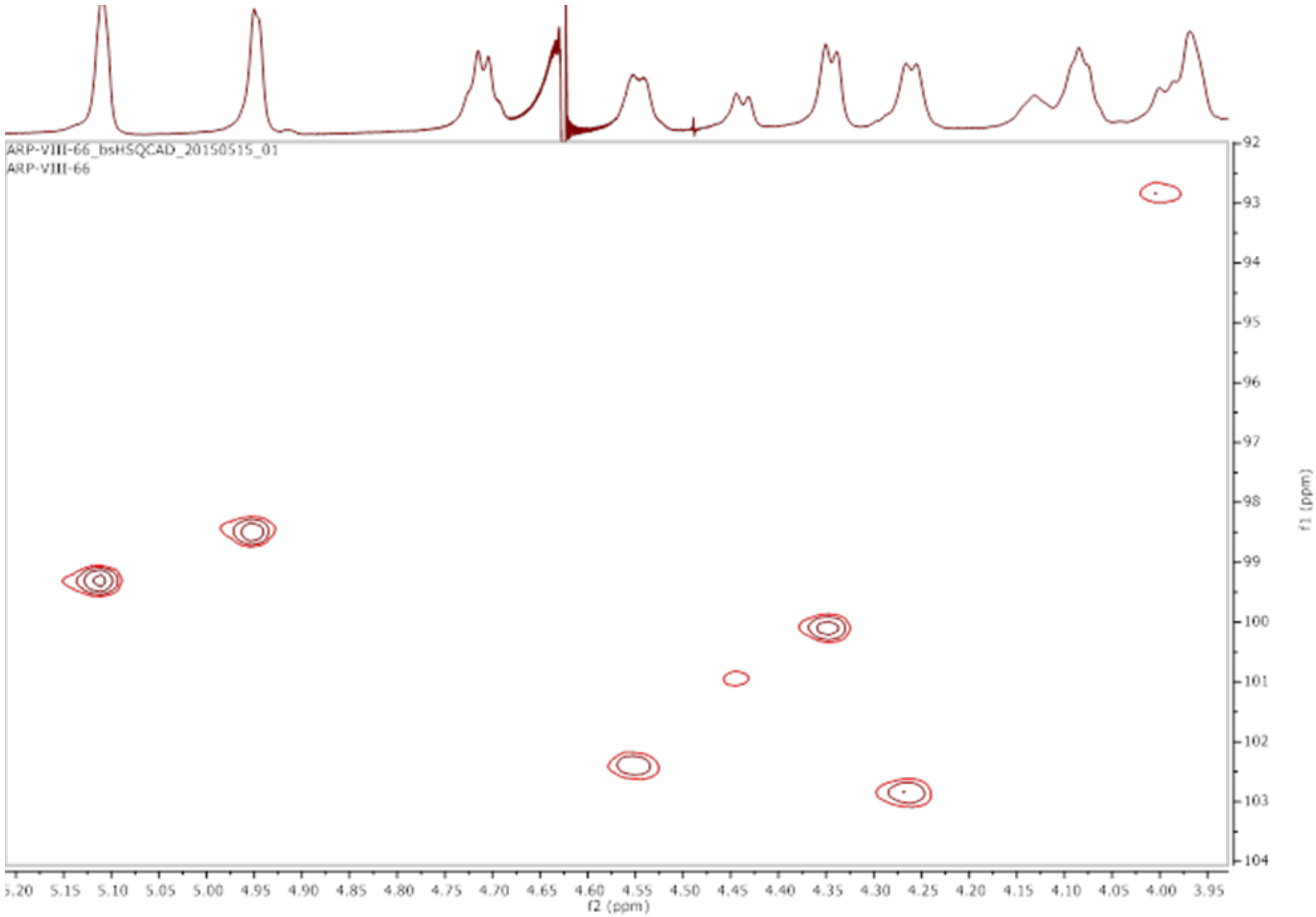
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

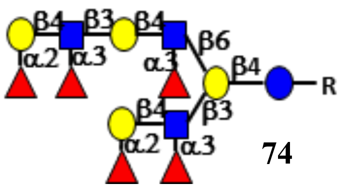
	C1
Glc	92.82
Gal	102.95
GlcNAc	102.39
Gal(2)	100.13
GlcNAc(2)	100.93
Gal(3)	102.95
GlcNAc(3)	102.39
Gal(4)	100.13
Fuc(1)(α3)	98.42
Fuc(2)(α2)	99.36
Fuc(3)(α3)	98.42
Fuc(4)(α2)	99.36

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{99}H_{159}N_7O_{62}Na$-- $(M + Na)^+$ exact 2460.9402, found 2460.6555.


ARP-VIII-66_PRESAT_20150514_01
ARP-VIII-66
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ARP-VIII-66_bsHSQCAD_20150515_01
ARP-VIII-66
f2 (ppm)
f1 (ppm)



74

^1H (600 MHz, D_2O): δ (ppm)

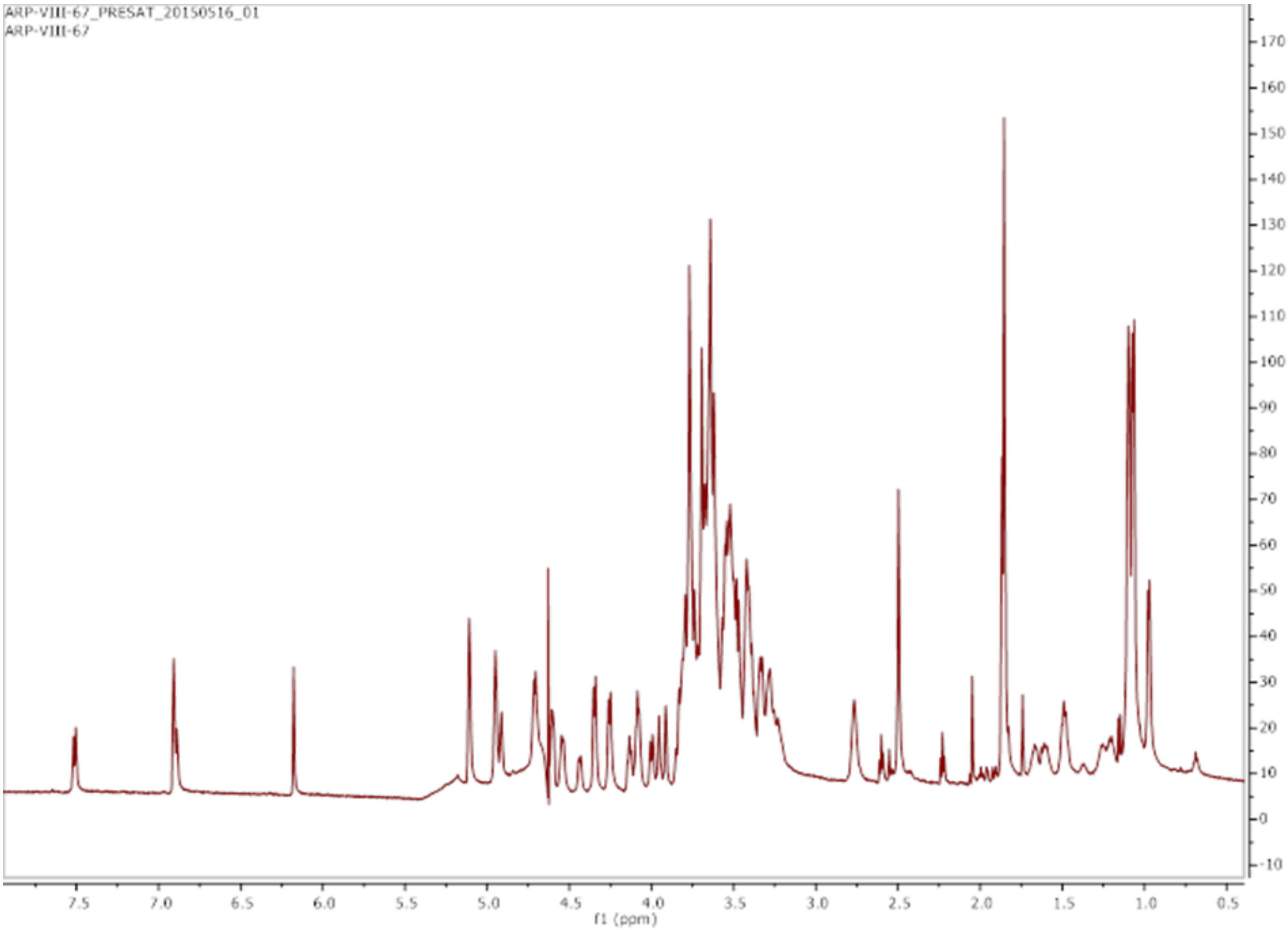
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.33	3.40	3.47	n/a[a]	n/a	-	-
Gal	4.26 (d, *J* = 7.5 Hz, 2H)	3.42	3.52	3.96	n/a	n/a	-	-
GlcNAc	4.53	3.79	3.68	3.29	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(2)	4.34 (d, *J* = 7.4 Hz, 2H)	3.48	n/a	3.70	n/a	n/a	-	-
GlcNAc(2)	4.44 (d, *J* = 5.4 Hz, 1H)	3.73	n/a	3.42	n/a	n/a	-	1.91 - 1.81 (m, 9H)
Gal(3)	4.26 (d, *J* = 7.5 Hz, 2H)	3.34	3.51	3.92	n/a	n/a	-	-
GlcNAc(3)	4.53	3.79	3.68	3.29	n/a	n/a	-	1.91-1.81 (m, 9H)
Gal(4)	4.34 (d, *J* = 7.4 Hz, 2H)	3.48	n/a	3.70	n/a	n/a	-	-
Fuc(1)(α3)	4.94	3.54	3.75	3.64	4.70	-	1.06	-
Fuc(2)(α2)	5.10	3.63	n/a	n/a	4.11	-	1.09	-
Fuc(3)(α3)	4.91	3.52	3.71	3.63	4.70	-	0.98 (d, *J* = 5.9 Hz, 3H)	-
Fuc(4)(α3)	4.94	3.54	3.75	3.64	4.70	-	1.06	-
Fuc(5)(α2)	5.10	3.63	n/a	n/a	4.11	-	1.09	-

^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

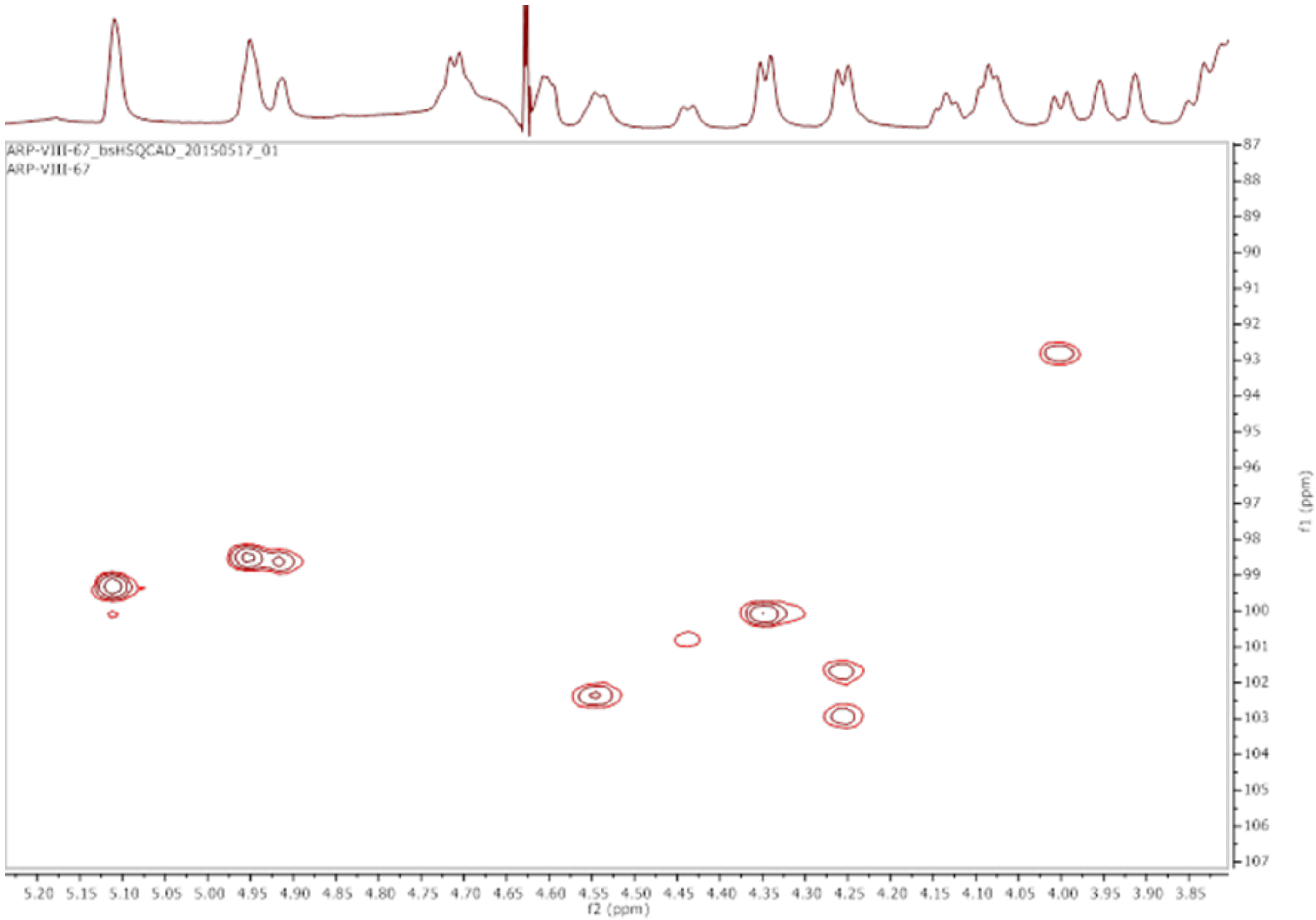
	C1
Glc	92.88
Gal	102.96
GlcNAc	102.41
Gal(2)	100.14
GlcNAc(2)	100.74
Gal(3)	101.62
GlcNAc(3)	102.41
Gal(4)	100.14
Fuc(1)(α3)	98.47
Fuc(2)(α2)	99.30
Fuc(3)(α3)	98.66
Fuc(4)(α3)	98.47
Fuc(5)(α2)	99.30

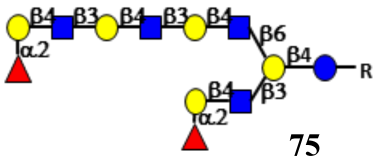
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{105}H_{169}N_7O_{66}Na$-- $(M + Na)^+$ exact 2606.9981, found 2606.3372.



ARP-VIII-67_PRESAT_20150516_01
ARP-VIII-67
f1 (ppm)


ARP-VIII-67_bsHSQCAD_20150517_01
ARP-VIII-67
f2 (ppm)
f1 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

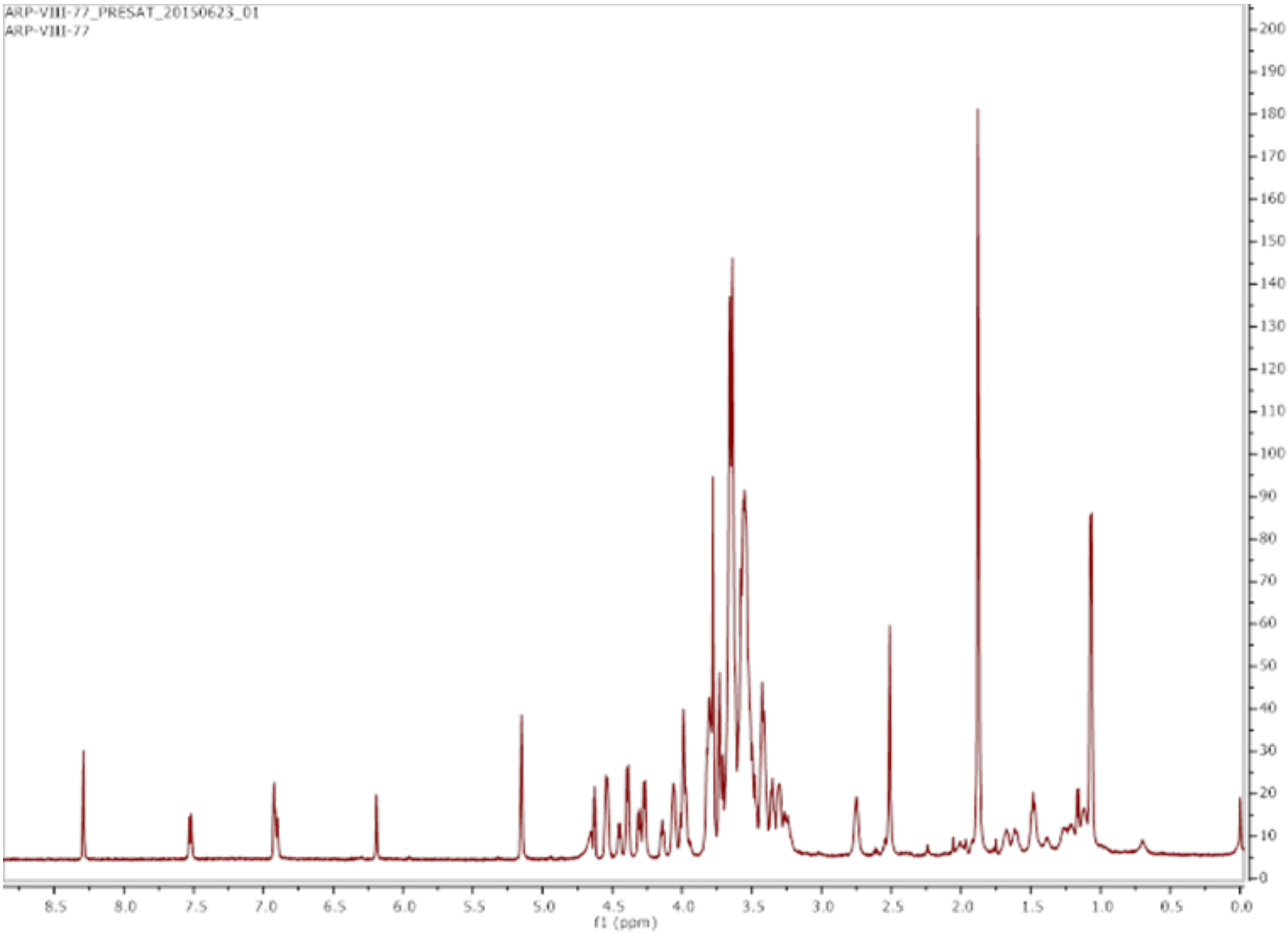
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.43	3.49	n/a[a]	n/a	-	-
Gal	4.26	3.42	3.56	3.99	n/a	n/a	-	-
GlcNAc	4.53 (d, *J* = 9.0 Hz, 1H)	3.65	3.55	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39 (d, *J* = 7.6 Hz, 2H)	3.51	3.64	3.73	n/a	n/a	-	-
GlcNAc(2)	4.44	3.57	3.51	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.26	3.42	3.56	3.99	n/a	n/a	-	-
GlcNAc(3)	4.53	3.65	3.55	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(4)	4.30	3.43	3.58	3.99	n/a	n/a	-	-
GlcNAc(4)	4.53	3.65	3.55	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(5)	4.39 (d, *J* = 7.6 Hz, 2H)	3.51	3.64	3.73	n/a	n/a	-	-
Fuc(1)(α2)	5.15	3.65	n/a	n/a	4.04	-	1.06 (d, *J* = 6.0 Hz, 6H)	-
Fuc(2)(α2)	5.15	3.65	n/a	n/a	4.04	-	1.06 (d, *J* = 6.0 Hz, 6H)	-

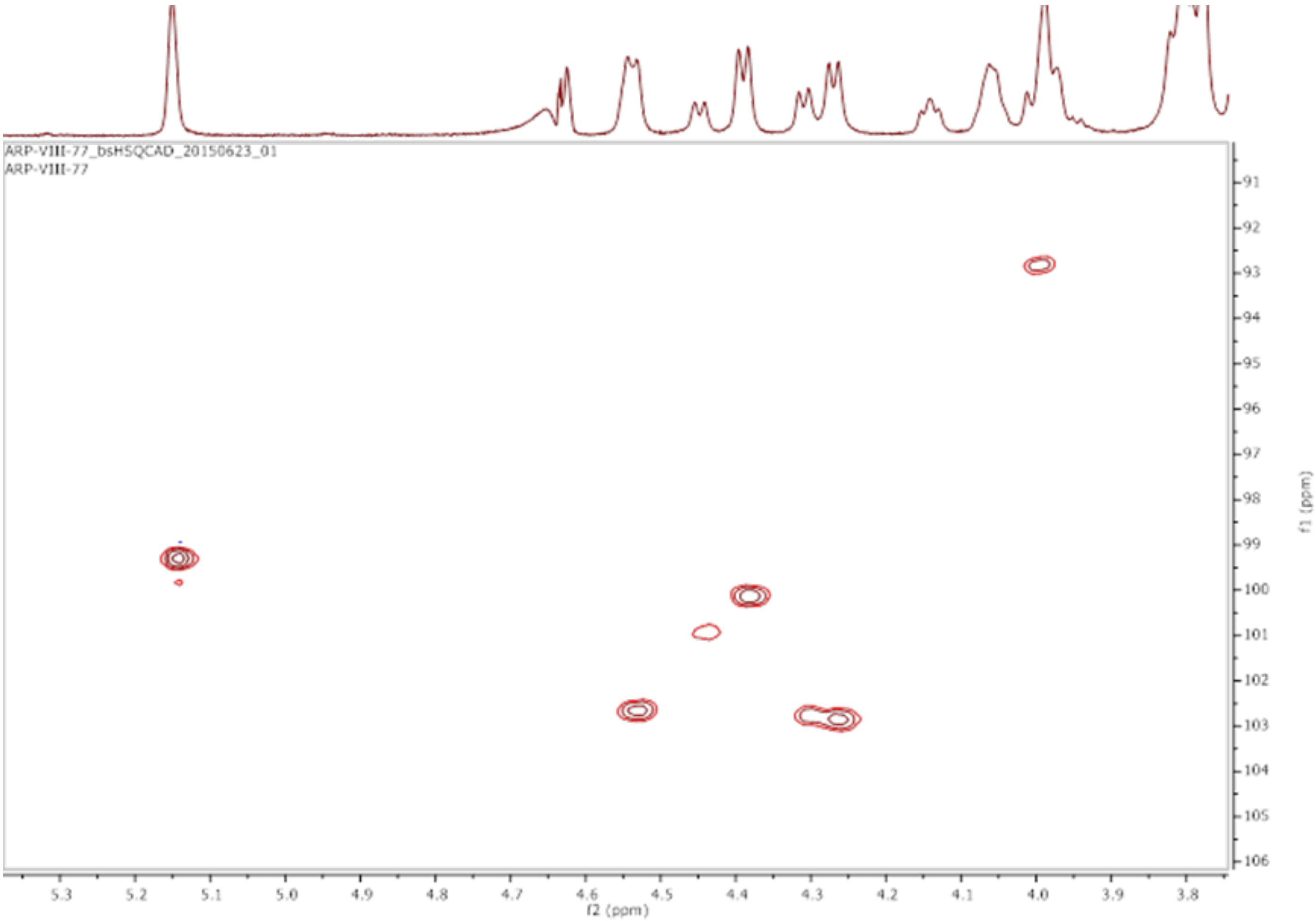
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

	C1
Glc	92.80
Gal	102.85
GlcNAc	102.66
Gal(2)	100.13
GlcNAc(2)	100.97
Gal(3)	102.85
GlcNAc(3)	102.66
Gal(4)	102.82
GlcNAc(4)	102.66
Gal(5)	100.13
Fuc(1)(α2)	99.36
Fuc(2)(α2)	99.36

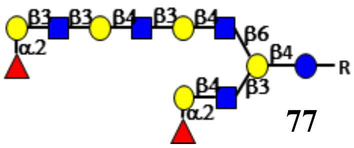
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{101}H_{162}N_8O_{64}Na$-- $(M + Na)^+$ exact 2533.9566, found 2533.0864.


ARP-VIII-77_PRESAT_20150623_01
ARP-VIII-77
f1 (ppm)



ARP-VIII-77_bsHSQCAD_20150623_01
ARP-VIII-77
f1 (ppm)
f2 (ppm)



77

^{1}H (600 MHz, D_2O): δ (ppm)

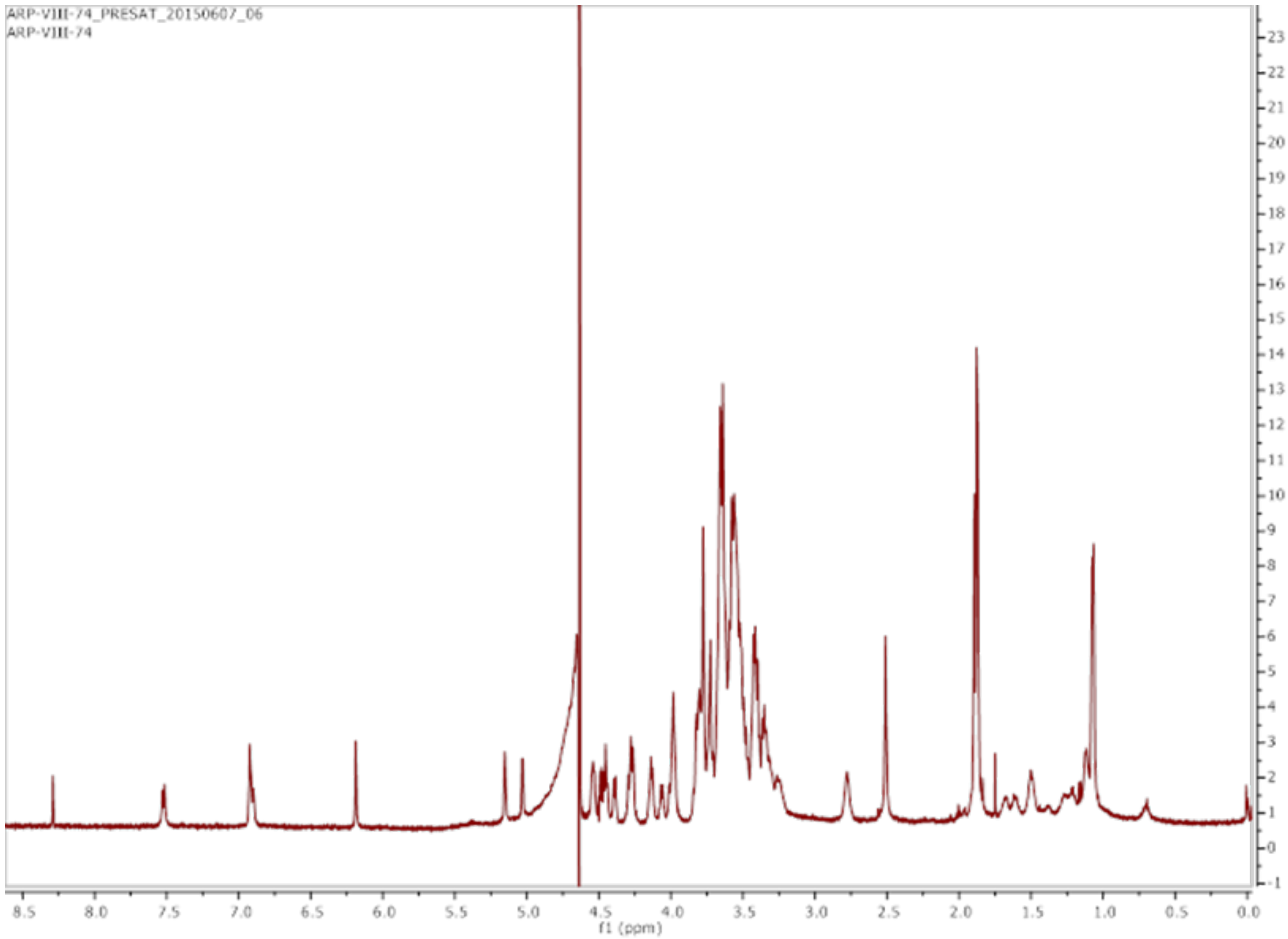
	H1	H2	H3	H4	H5	H6	CH_3	NHAc
Glc	4.00	3.35	3.41	3.49	n/a[a]	n/a	-	-
Gal	4.28	3.42	3.56	3.98	n/a	n/a	-	-
GlcNAc	4.53 (d, *J* = 9.0 Hz, 1H)	3.65	3.55	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39 (d, *J* = 7.5 Hz, 1H)	3.52	3.64	3.73	n/a	n/a	-	-
GlcNAc(2)	4.44	3.57	n/a	3.43	n/a	n/a	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.28	3.42	3.56	3.99	n/a	n/a	-	-
GlcNAc(3)	4.53	3.65	3.55	3.43	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(4)	4.28	3.43	3.58	3.99	n/a	n/a	-	-
GlcNAc(4)	4.46	3.65	3.55	3.35	n/a	n/a	-	1.91-1.81 (m, 12H)
Gal(5)	4.49 (d, *J* = 7.3 Hz, 1H)	3.43	3.68	3.72	n/a	n/a	-	-
Fuc(1)(α2)	5.15	3.65	3.50	3.66	4.14	-	1.08	-
Fuc(2)(α2)	5.04 (d, *J* = 3.8 Hz, 1H)	3.61	3.51	3.57	4.07	-	1.08	-

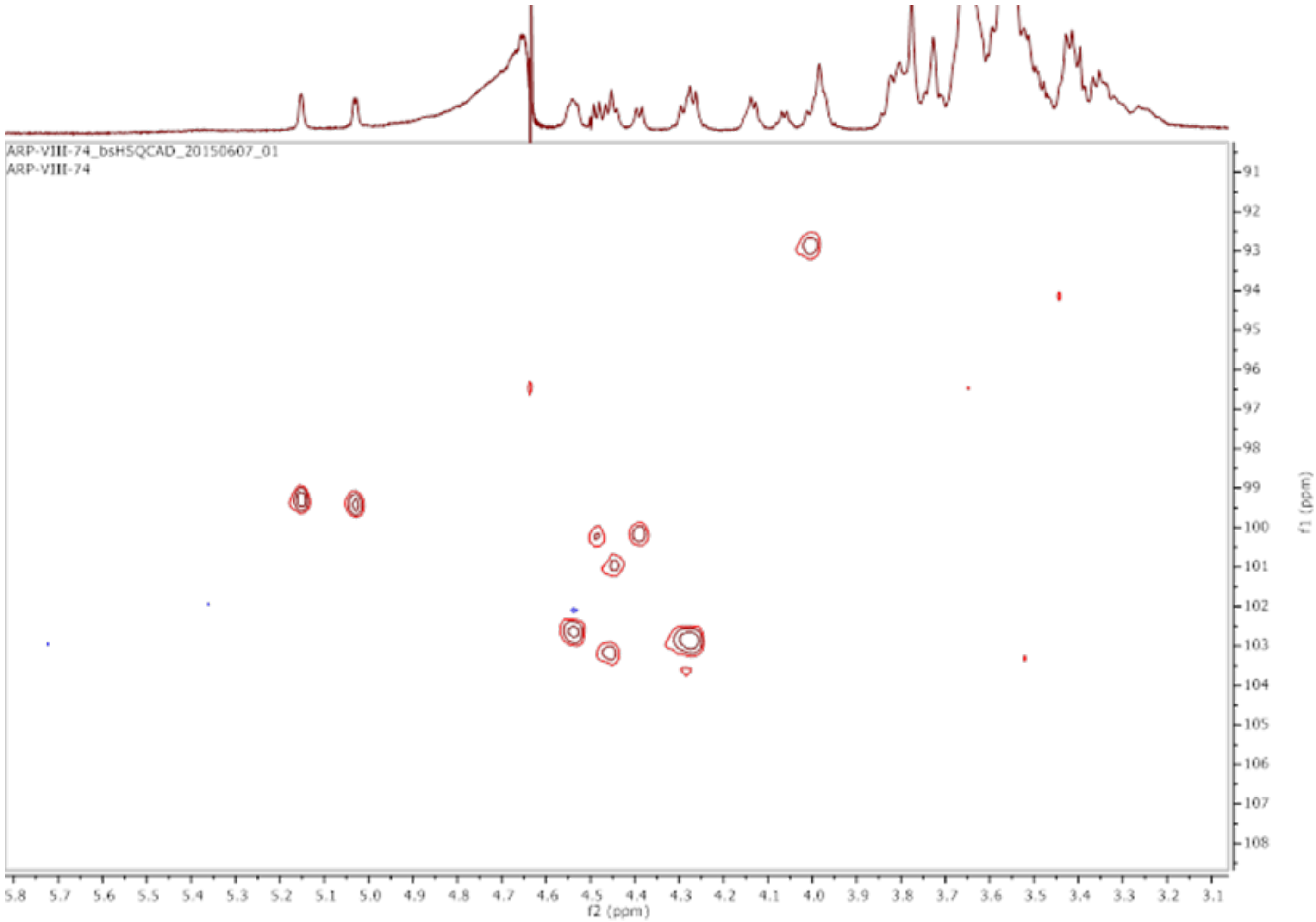
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

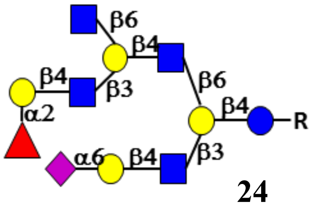
	C1
Glc	92.84
Gal	102.91
GlcNAc	102.73
Gal(2)	100.08
GlcNAc(2)	100.89
Gal(3)	102.91
GlcNAc(3)	102.73
Gal(4)	102.91
GlcNAc(4)	103.12
Gal(5)	100.17
Fuc(1)(α2)	99.41
Fuc(2)(α2)	99.37

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{101}H_{162}N_8O_{64}Na$-- $(M + Na)^+$ exact 2533.9566, found 2534.3401.


ARP-VIII-74_PRESAT_20150607_06
ARP-VIII-74
f1 (ppm)


ARP-VIII-74_bsHSQCAD_20150607_01
ARP-VIII-74
f1 (ppm)
f2 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

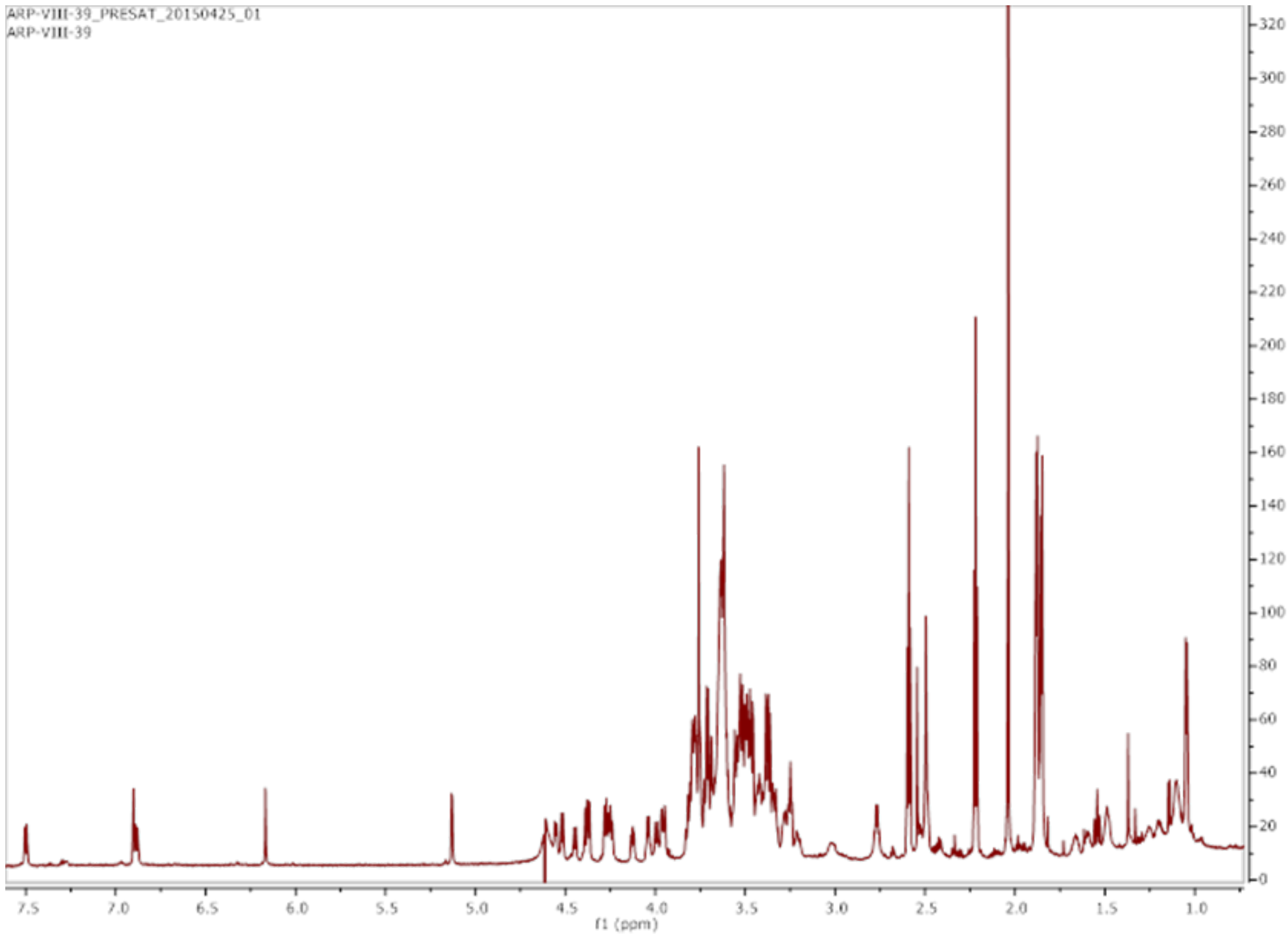
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.1 Hz, 1H)	3.35	3.42	3.53	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.41	3.51	3.97	n/a	n/a	-	-	-	-	-
GlcNAc	4.55 (d, *J* = 7.4 Hz, 1H)	3.62	n/a	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(2)	4.29	3.38	3.49	3.75	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.44 (d, *J* = 8.5 Hz, 1H)	3.58	3.53	3.42	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(3)	4.27	3.43	3.51	3.97	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.52 (d, *J* = 8.4 Hz, 1H)	3.64	3.53	3.29	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(4)	4.38 (d, *J* = 7.7 Hz, 1H)	3.50	3.63	3.70	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.42 (d, *J* = 8.2 Hz, 1H)	3.56	3.52	3.39	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(5)	4.28	3.37	3.49	3.75	n/a	n/a	-	-	-	-	-
Fuc	5.15 (d, *J* = 3.2 Hz, 1H)	3.65	n/a	n/a	4.07	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 3H)	-
Neu5Ac(1)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.91 - 1.81 (m, 15H)

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

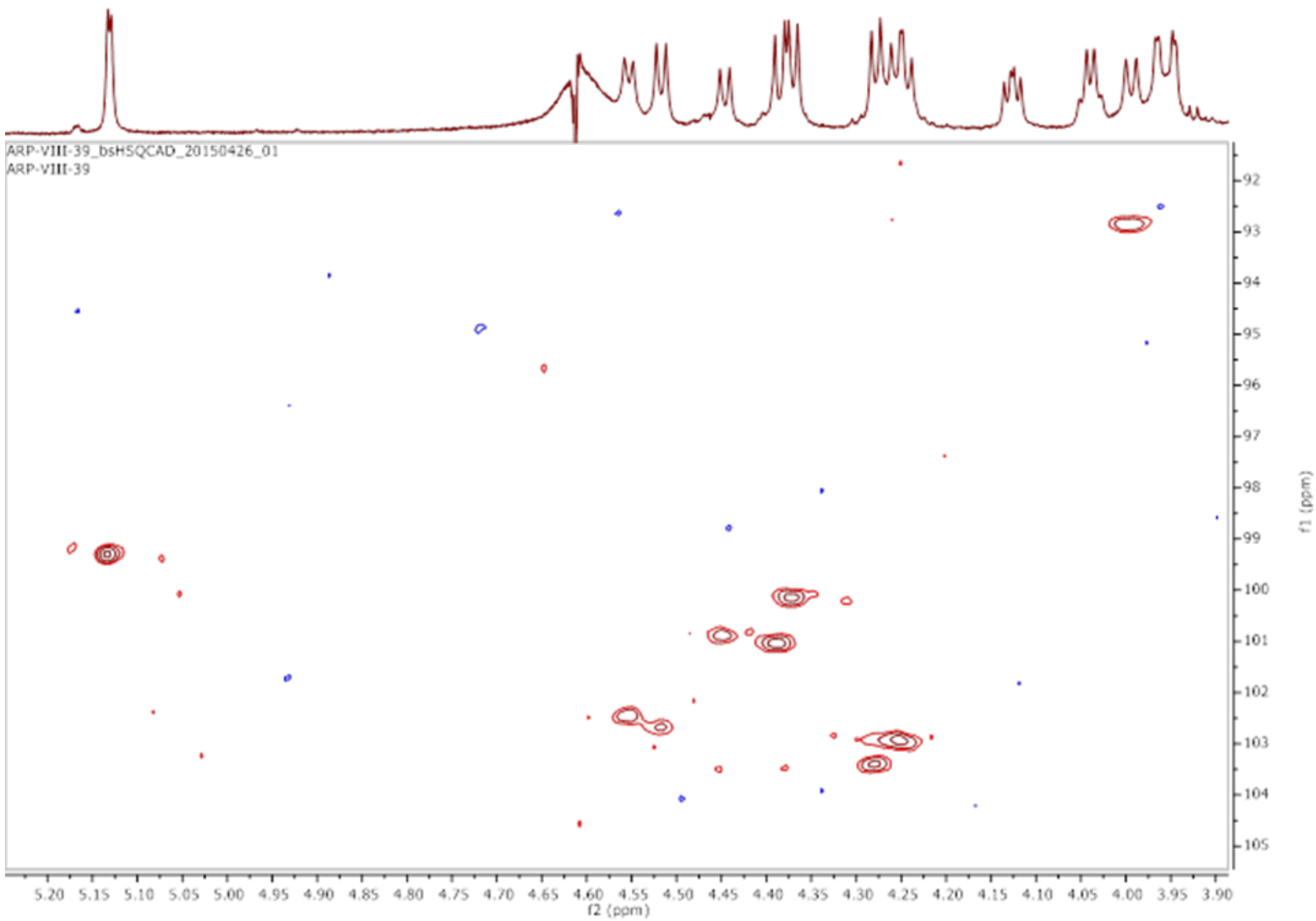
	C1
Glc	92.85
Gal	102.88
GlcNAc	102.47
Gal(2)	103.45
GlcNAc(2)	100.90
Gal(3)	102.88
GlcNAc(3)	n/a
Gal(4)	100.14
GlcNAc(4)	100.87
Gal(5)	102.79
Fuc	99.36

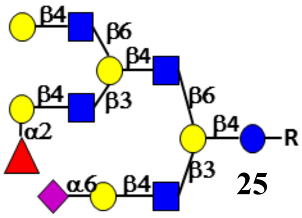
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{106}H_{168}N_9O_{68}Na_2$-- $(M + 2Na)^+$ exact 2700.9766, found 2700.4026.



ARP-VIII-39_PRESAT_20150425_01
ARP-VIII-39
f1 (ppm)


ARP-VIII-39_bsHSQCAD_20150426_01
ARP-VIII-39
f1 (ppm)
f2 (ppm)



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^{1}H (600 MHz, D_2O): δ (ppm)

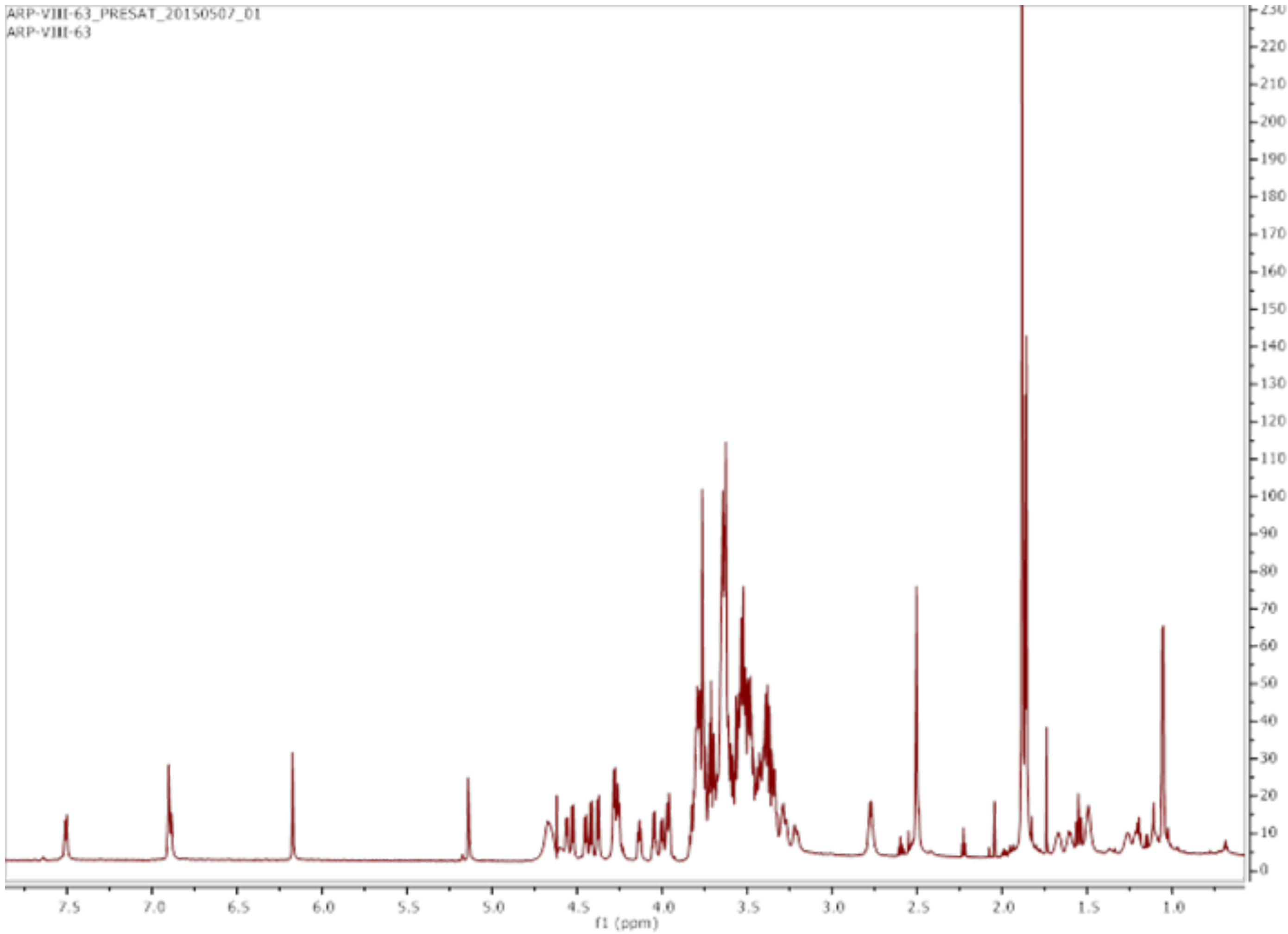
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.35	3.42	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc	4.57 (d, *J* = 8.1 Hz, 1H)	3.64	3.50	3.45	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(2)	4.29	3.42	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.2 Hz, 1H)	3.58	3.53	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(3)	4.27	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.54 (d, *J* = 8.45Hz, 2H)	3.64	3.53	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(4)	4.38 (d, *J* = 7.6 Hz, 1H)	3.52	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.42	3.58	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(5)	4.28	3.42	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.54 (d, *J* = 8.45Hz, 2H)	3.64	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(6)	4.31	3.38	3.51	3.76	n/a	n/a	-	-	-	-	-
Fuc	5.15	3.65	n/a	n/a	4.07	-	-	-	-	1.07 (d, *J* = 6.4 Hz, 3H)	-
Neu5Ac(1)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.91 - 1.81 (m, 18H)

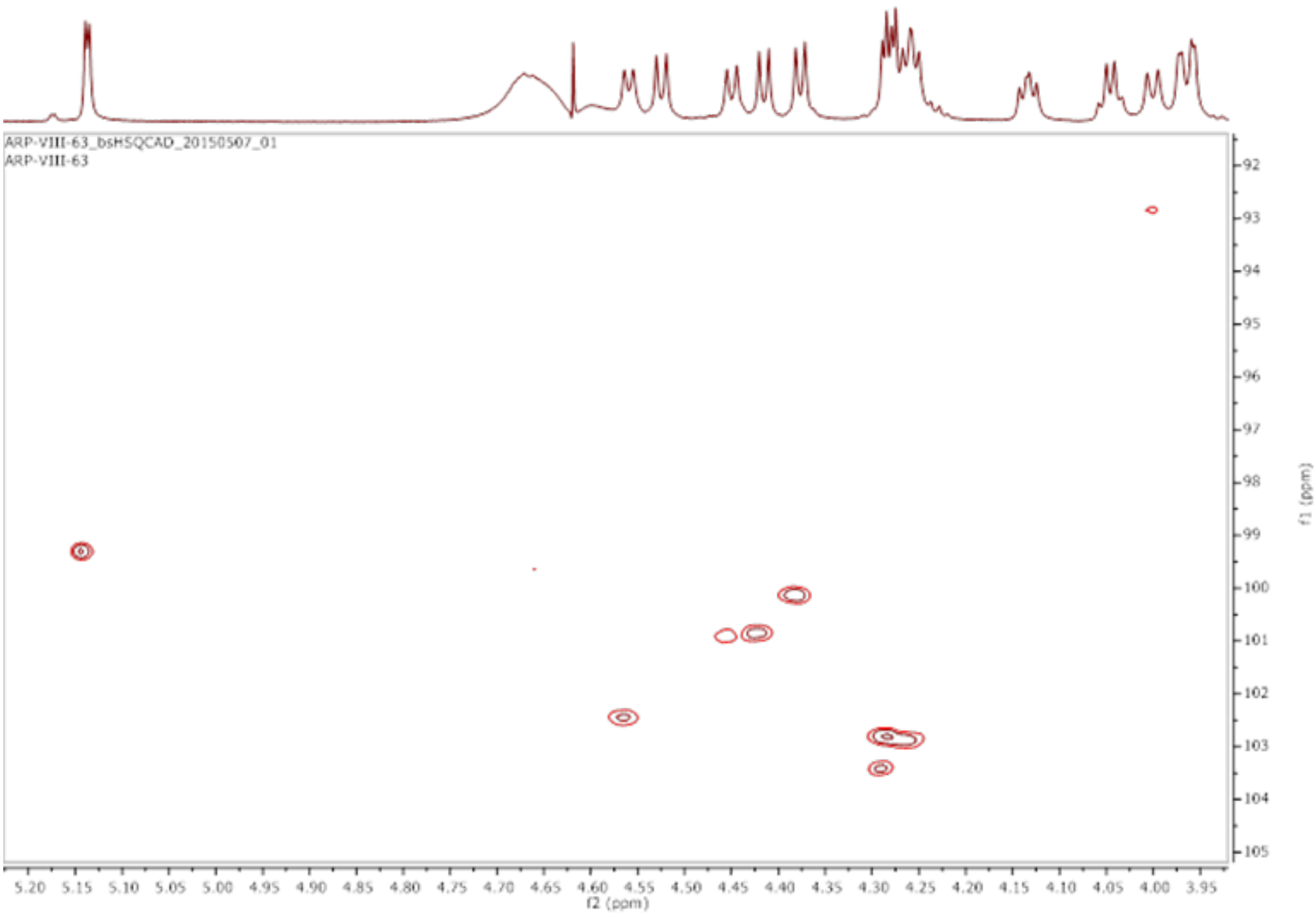
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

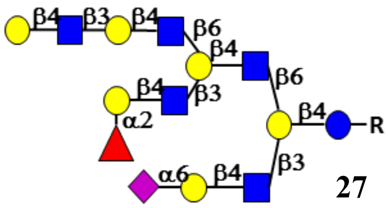
	C1
Glc	92.85
Gal	102.88
GlcNAc	102.36
Gal(2)	103.45
GlcNAc(2)	100.90
Gal(3)	102.88
GlcNAc(3)	102.61
Gal(4)	100.12
GlcNAc(4)	100.94
Gal(5)	102.86
GlcNAc(5)	102.61
Gal(6)	102.65
Fuc	99.37

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{120}H_{191}N_{10}O_{78}Na_2$-- (M + 2Na)$^{+}$ exact 3066.1087, found 3067.1699.


ARP-VIII-63_PRESAT_20150507_01
ARP-VIII-63
f1 (ppm)


ARP-VIII-63_bsHSQCAD_20150507_01
ARP-VIII-63
f2 (ppm)
f1 (ppm)



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[1]H (800 MHz, D_2O): δ (ppm)

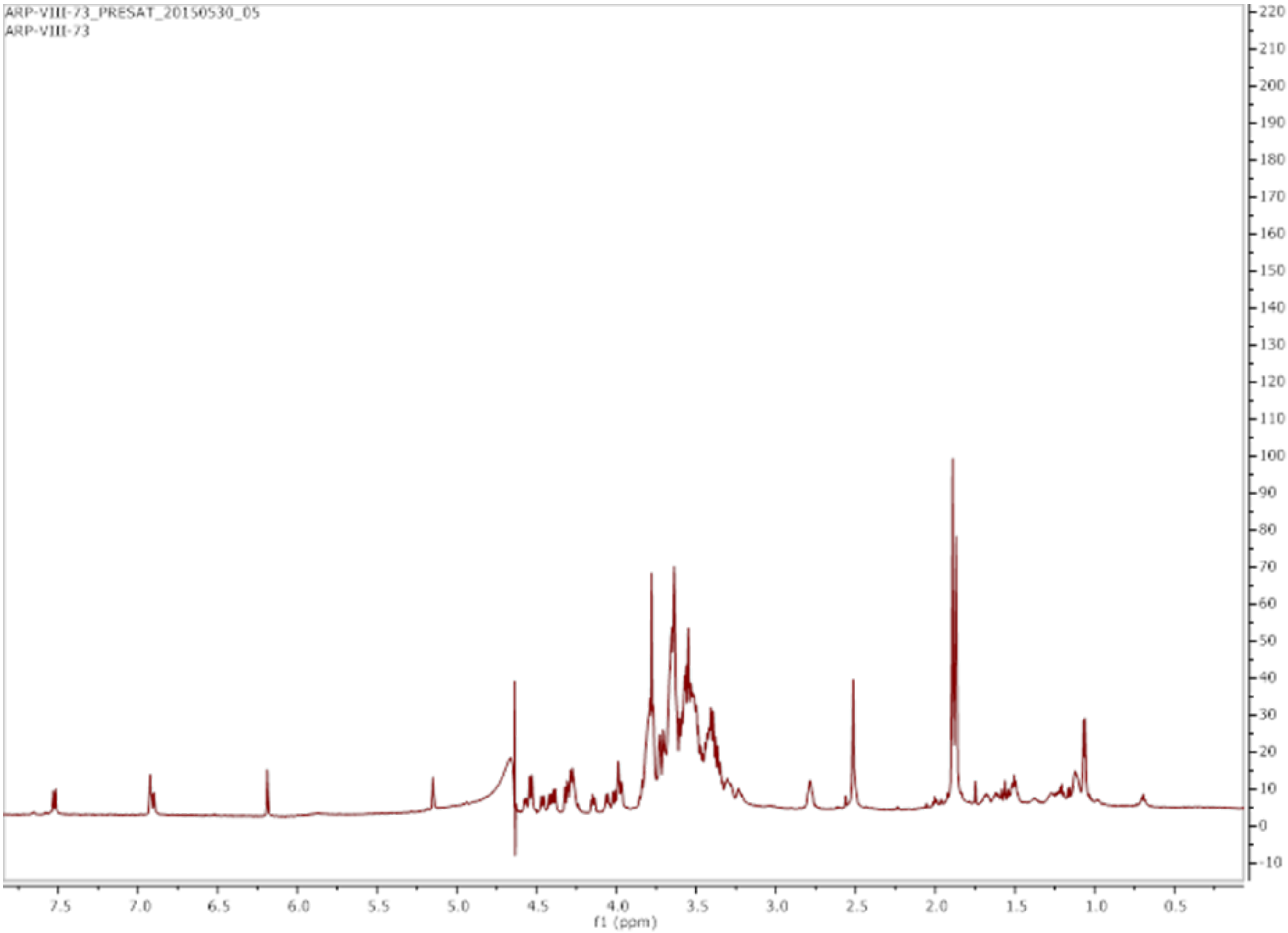
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.28	3.43	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.65	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(2)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46	3.60	3.54	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(3)	4.28	3.41	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(4)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.41	3.52	n/a	3.41	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(5)	4.28	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.55	3.65	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(6)	4.33	3.39	3.52	3.78	n/a	n/a	-	-	-	-	-
Fuc((1)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-
Fuc(2)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-
Neu5Ac(1)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.91 - 1.81 (m, 18H)

[13]C from BSHSQC (200 MHz, D_2O): δ (ppm)

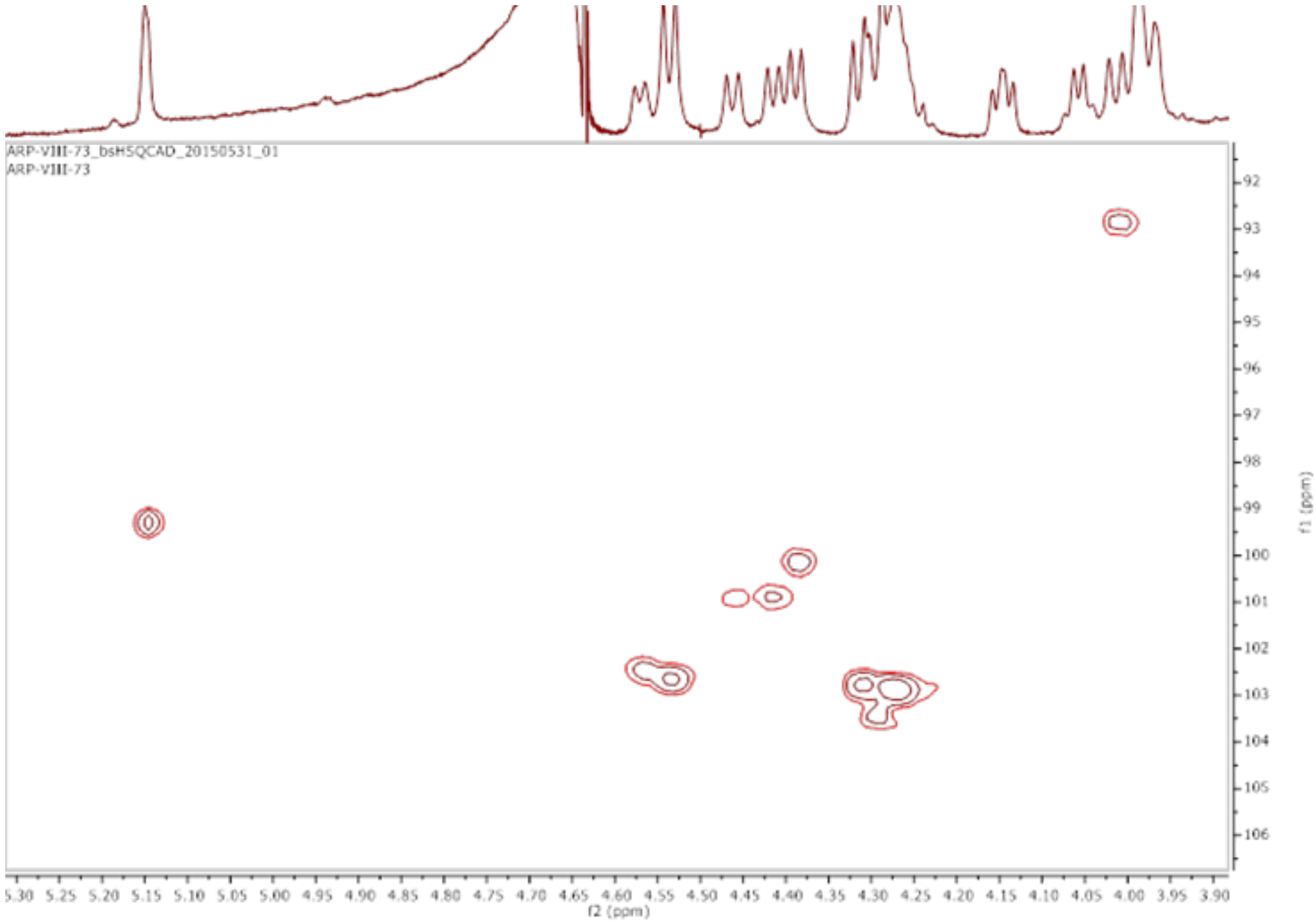
	C1
Glc	92.77
Gal	102.89
GlcNAc	102.69
Gal(2)	100.18
GlcNAc(2)	101.97
Gal(3)	102.89
GlcNAc(3)	102.69
Gal(4)	100.18
GlcNAc(4)	100.97
Gal(5)	102.89
GlcNAc(5)	102.69
Gal(6)	102.82
Fuc(1)	99.37
Fuc(2)	99.37

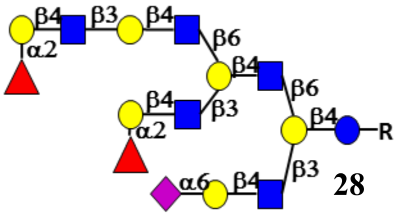
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{115}H_{185}N_9O_{74}Na$- $(M + Na)^+$ exact 2899.0887, found 2900.7866.



ARP-VIII-73_PRESAT_20150530_05
ARP-VIII-73
f1 (ppm)


ARP-VIII-73_bsHSQCAD_20150531_01
ARP-VIII-73
f2 (ppm)
f1 (ppm)



28

[1]H (900 MHz, D_2O): δ (ppm)

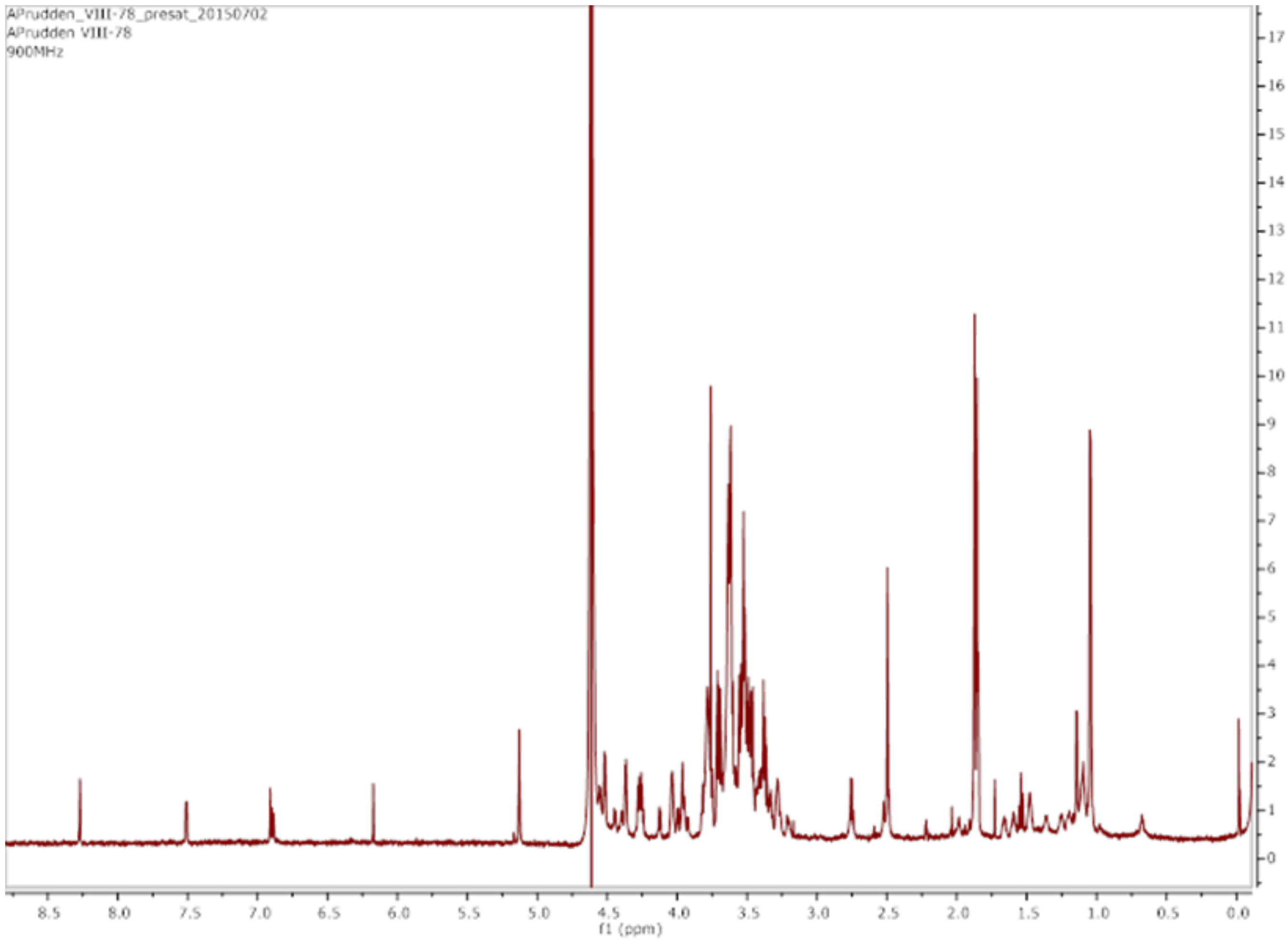
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.35	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc	4.56 (d, *J* = 6.2 Hz, 1H)	3.64	3.50	3.45	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(2)	4.29	3.37	3.51	3.76	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.2 Hz, 1H)	3.58	3.53	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(3)	4.27	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.54 (d, *J* = 8.5Hz, 2H)	3.64	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(4)	4.38	3.52	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.42 (d, *J* = 7.8 Hz, 1H)	3.55	n/a	3.39	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(5)	4.26	3.41	3.55	3.97	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.54 (d, *J* = 8.5Hz, 2H)	3.64	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 18H)
Gal(6)	4.31	3.50	n/a	3.71	n/a	n/a	-	-	-	-	-
Fuc(1)	5.14	3.61	n/a	n/a	4.05	-	-	-	-	1.04 (d, *J* = 6.4 Hz, 6H)	-
Fuc(2)	5.14	3.61	n/a	n/a	4.05	-	-	-	-	1.04 (d, *J* = 6.4 Hz, 6H)	-
Neu5Ac(1)	-	-	2.52 – eq. 1.55 - axial	3.49	3.62	3.51	n/a	n/a	3.69 3.48	-	1.91 - 1.81 (m, 18H)

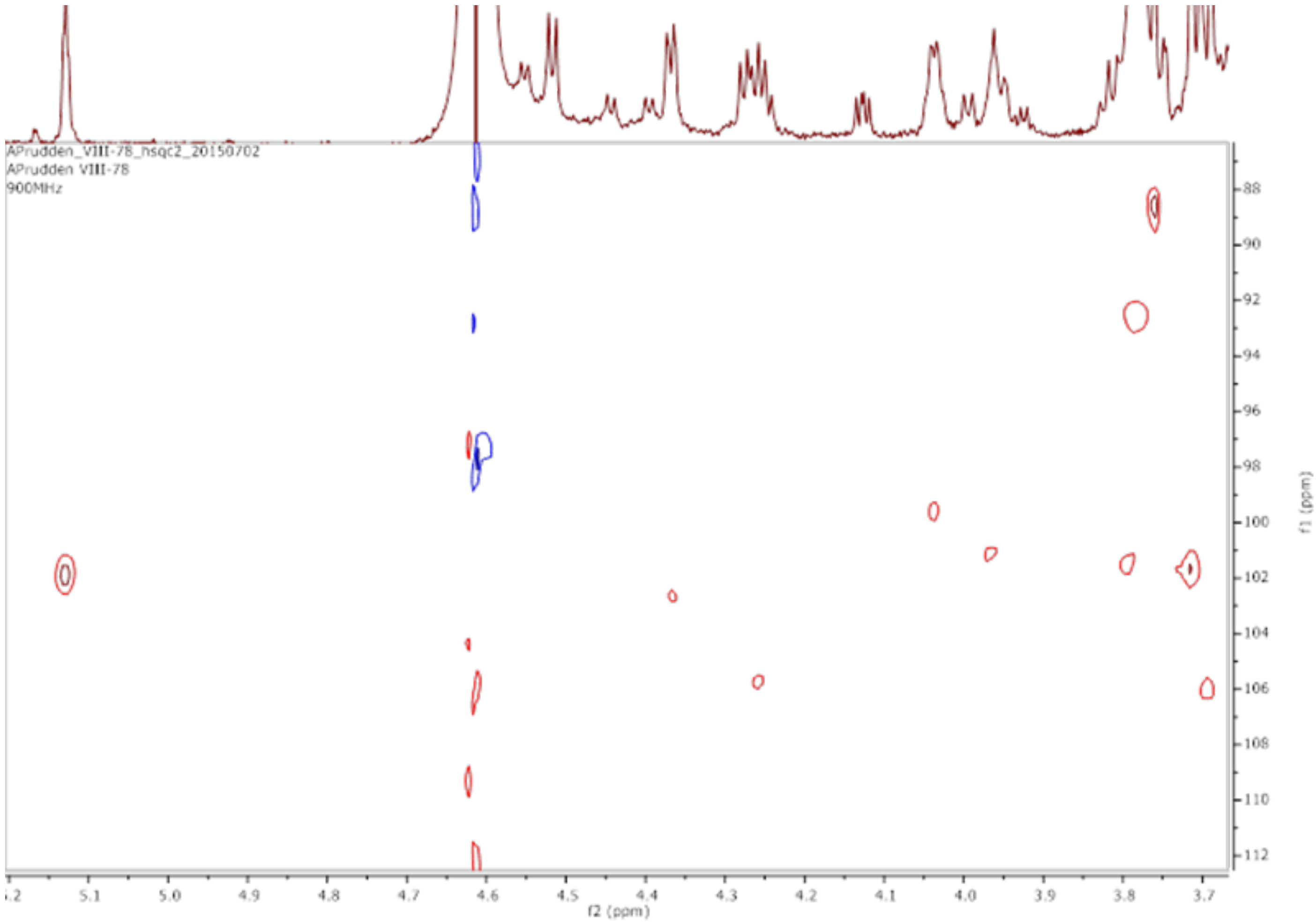
[13]C from BSHSQC (225 MHz, D_2O): δ (ppm)

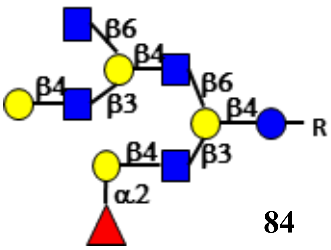
	C1
Glc	n/a
Gal	105.75
GlcNAc	n/a
Gal(2)	n/a
GlcNAc(2)	n/a
Gal(3)	105.75
GlcNAc(3)	n/a
Gal(4)	102.69
GlcNAc(4)	n/a
Gal(5)	105.75
GlcNAc(5)	n/a
Gal(6)	102.69
Fuc(1)	101.79
Fuc(2)	101.79

[a] Not assigned
[b] Not applicable

ESI-MS m/z calcd C126H199N10 O82Na2- (M – 2H)-2 exact 1582.5897, found 1582.5869.


APrudden_VIII-78_presat_20150702
APrudden VIII-78
900MHz
f1 (ppm)


APrudden_VIII-78_hsqc2_20150702
APrudden VIII-78
900MHz
f2 (ppm)
f1 (ppm)



84

^{1}H (600 MHz, D_2O): δ (ppm)

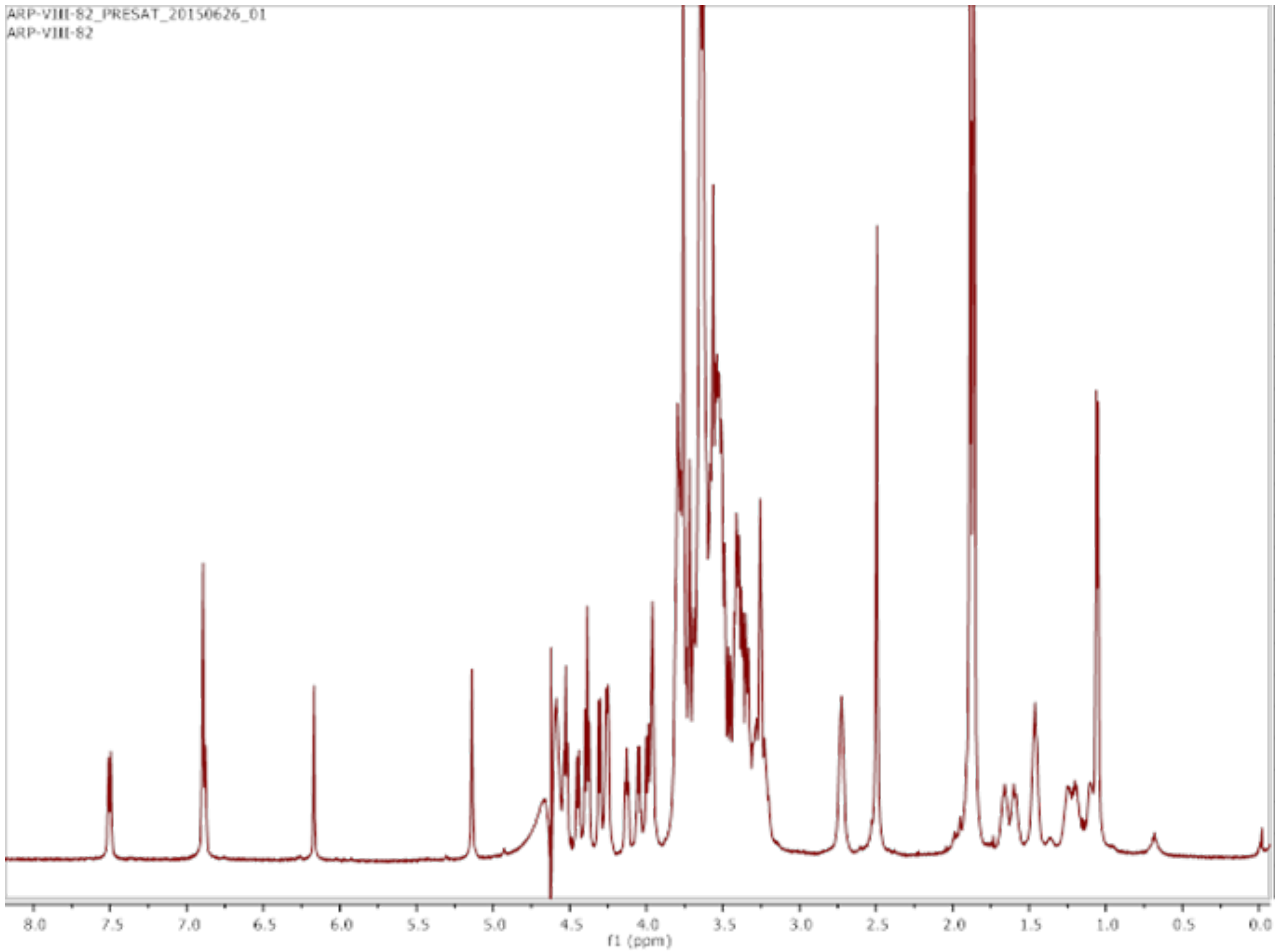
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.37	3.42	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.43	3.55	3.99	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.66	3.58	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39	3.54	n/a	3.74	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.4 Hz, 1H)	3.63	3.56	3.45	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.27	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.54	3.66	3.59	3.32	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(4)	4.32 (d, *J* = 7.7 Hz, 1H)	3.40	3.53	3.78	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.42	3.53	3.39	3.28	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Fuc	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07 (d, *J* = 6.4 Hz, 3H)	-

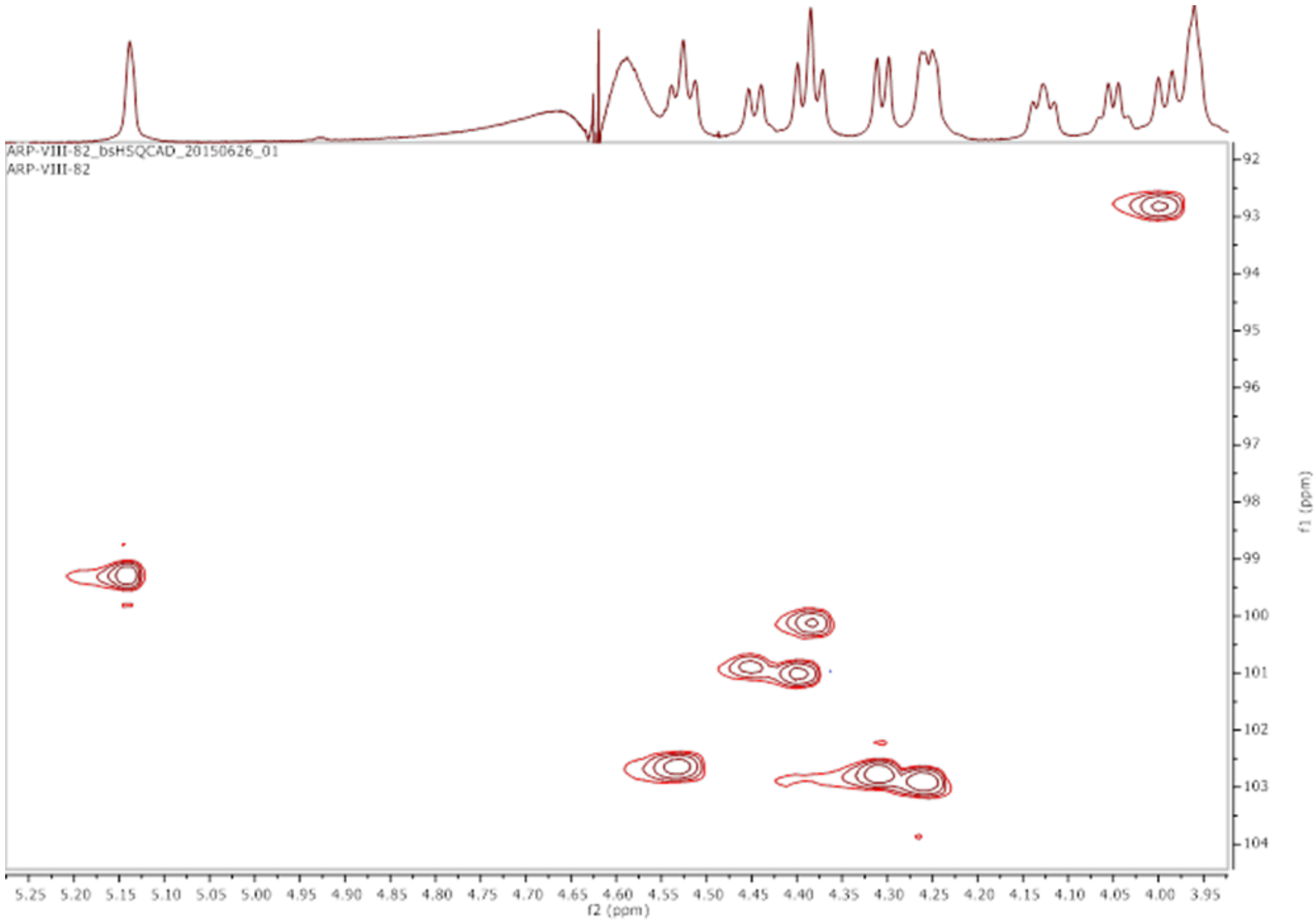
^{13}C from BSHSQC (150 MHz, D_2O): δ (ppm)

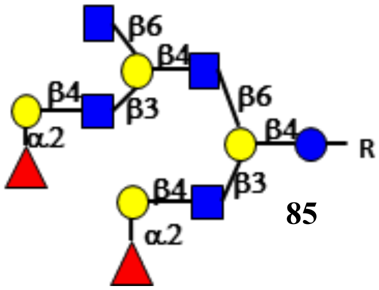
	C1
Glc	92.89
Gal	102.93
GlcNAc	102.66
Gal(2)	100.13
GlcNAc(2)	101.03
Gal(3)	102.93
GlcNAc(3)	102.66
Gal(4)	102.84
GlcNAc(4)	101.03
Fuc	99.34

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{89}H_{142}N_8O_{55}Na$-- (M + Na)$^+$ exact 2225.8458, found 2225.1235.


ARP-VIII-82_PRESAT_20150626_01
ARP-VIII-82
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
26
24
22
20
18
16
14
12
10
8
6
4
2
0


ARP-VIII-82_bsHSQCAD_20150626_01
ARP-VIII-82
f1 (ppm)
f2 (ppm)



85

[1]H (600 MHz, D_2O): δ (ppm)

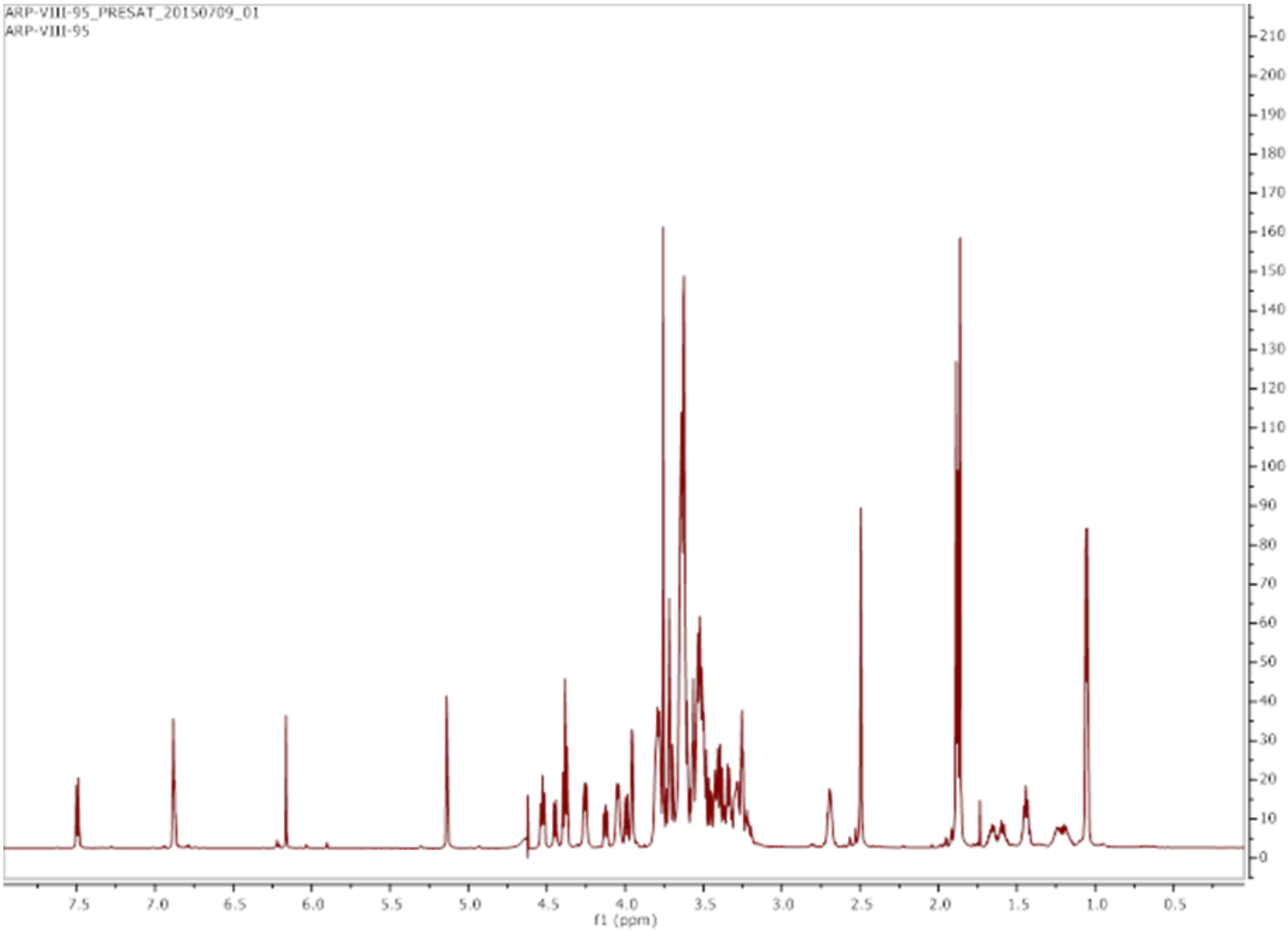
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.2 Hz, 1H)	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.40	3.54	3.97 (d, *J* = 3.2 Hz, 2H)	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.64	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.39	3.51	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.3 Hz, 1H)	3.60	3.54	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.27	3.40	3.54	3.97 (d, *J* = 3.2 Hz, 2H)	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.56	3.64	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(4)	4.39	3.51	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.40	3.51	3.38	3.28	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Fuc((1)	5.15 (d, *J* = 2.2 Hz, 2H)	3.65	n/a	n/a	4.09	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 6H)	-
Fuc(2)	5.15 d, *J* = 2.2 Hz, 2H)	3.65	n/a	n/a	4.09	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 6H)	-

[13]C from BSHSQC (150 MHz, D_2O): δ (ppm)

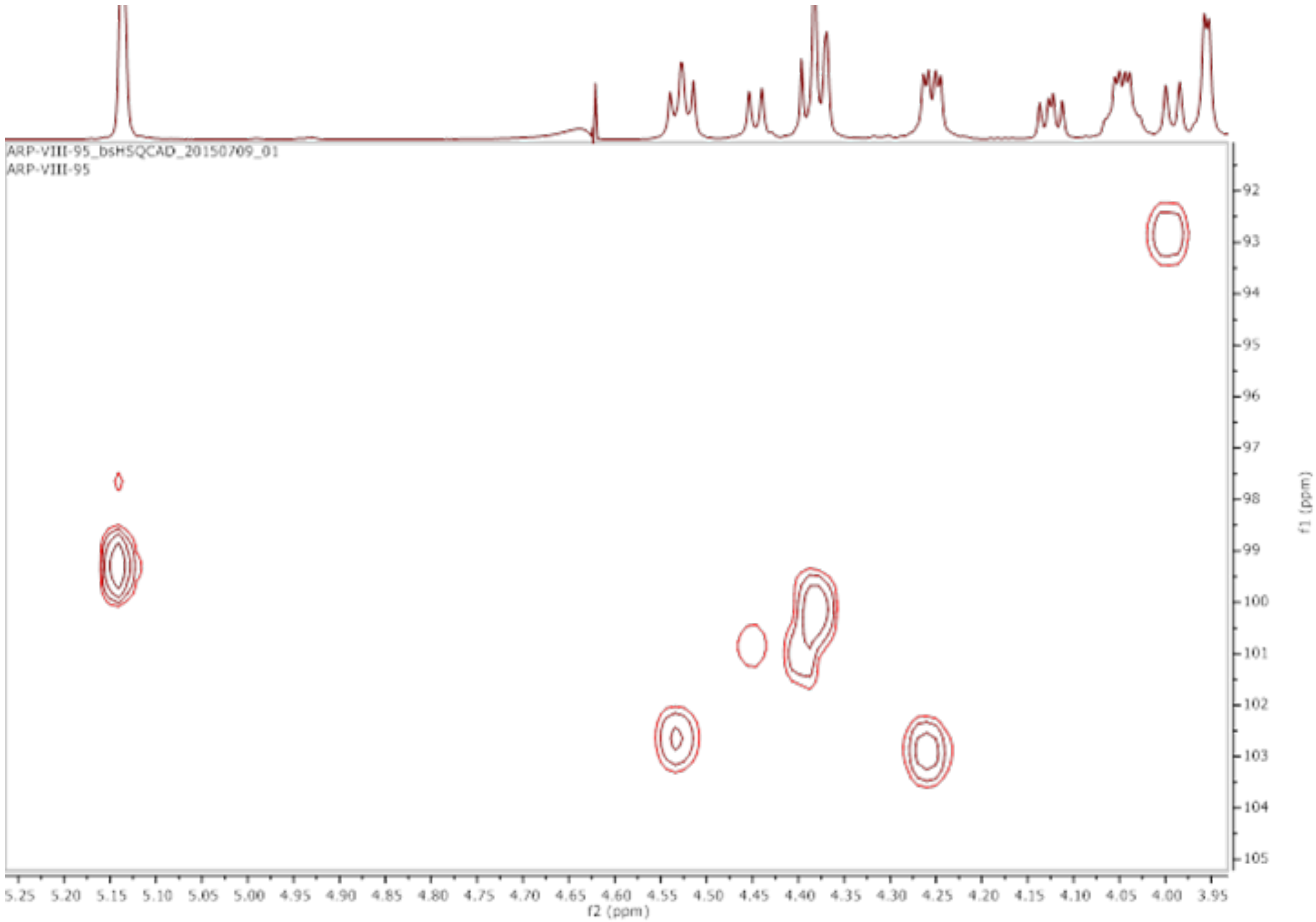
	C1
Glc	92.70
Gal	102.79
GlcNAc	102.59
Gal(2)	100.17
GlcNAc(2)	100.84
Gal(3)	102.79
GlcNAc(3)	102.59
Gal(4)	100.17
GlcNAc(4)	101.01
Fuc(1)	99.29
Fuc(2)	99.29

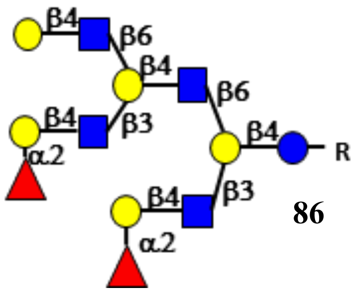
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{95}H_{152}N_8O_{59}Na$-- $(M + Na)^+$ exact 2371.9037, found 2370.7754.



ARP-VIII-95_PRESAT_20150709_01
ARP-VIII-95
f1 (ppm)


ARP-VIII-95_bsHSQCAD_20150709_01
ARP-VIII-95
f2 (ppm)
f1 (ppm)



86

^{1}H (800 MHz, D_2O): δ (ppm)

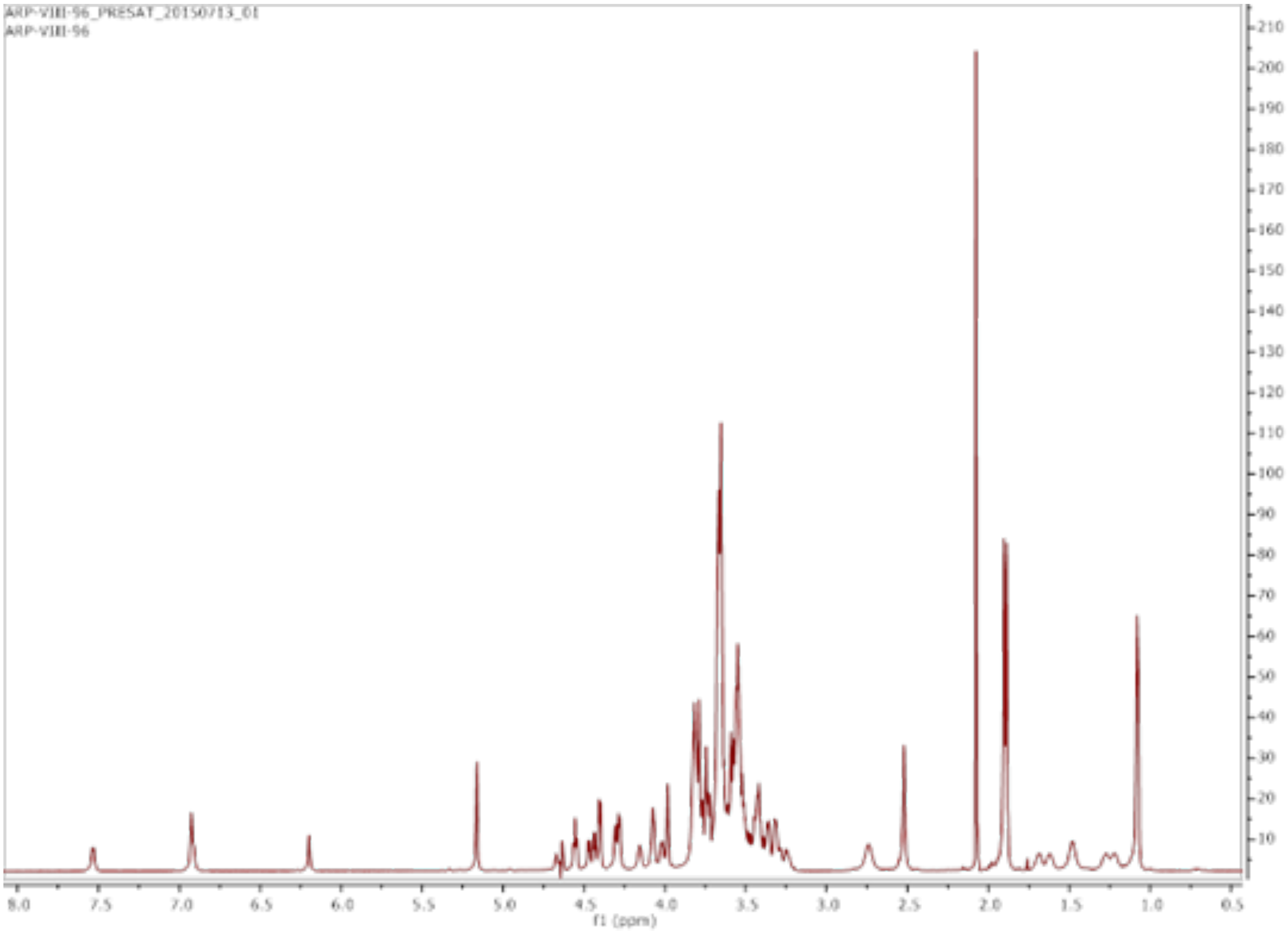
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 8.3 Hz, 1H)	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.28	3.43	3.54	3.97 (d, *J* = 3.2 Hz, 2H)	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.66	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(2)	4.41 (d, *J* = 7.2 Hz, 2H)	3.51	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.2 Hz, 1H)	3.60	3.56	3.43	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(3)	4.27	3.43	3.54	3.97 (d, *J* = 3.2 Hz, 2H)	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.56	3.64	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(4)	4.41 (d, *J* = 7.2 Hz, 2H)	3.51	n/a	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.44 (d, *J* = 8.1 Hz, 1H)	3.58	3.54	3.42	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 12H)
Gal(5)	4.31	3.39	3.51	3.77	n/a	n/a	-	-	-	-	-
Fuc((1)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 6H)	-
Fuc(2)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07 (d, *J* = 6.6 Hz, 6H)	-

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

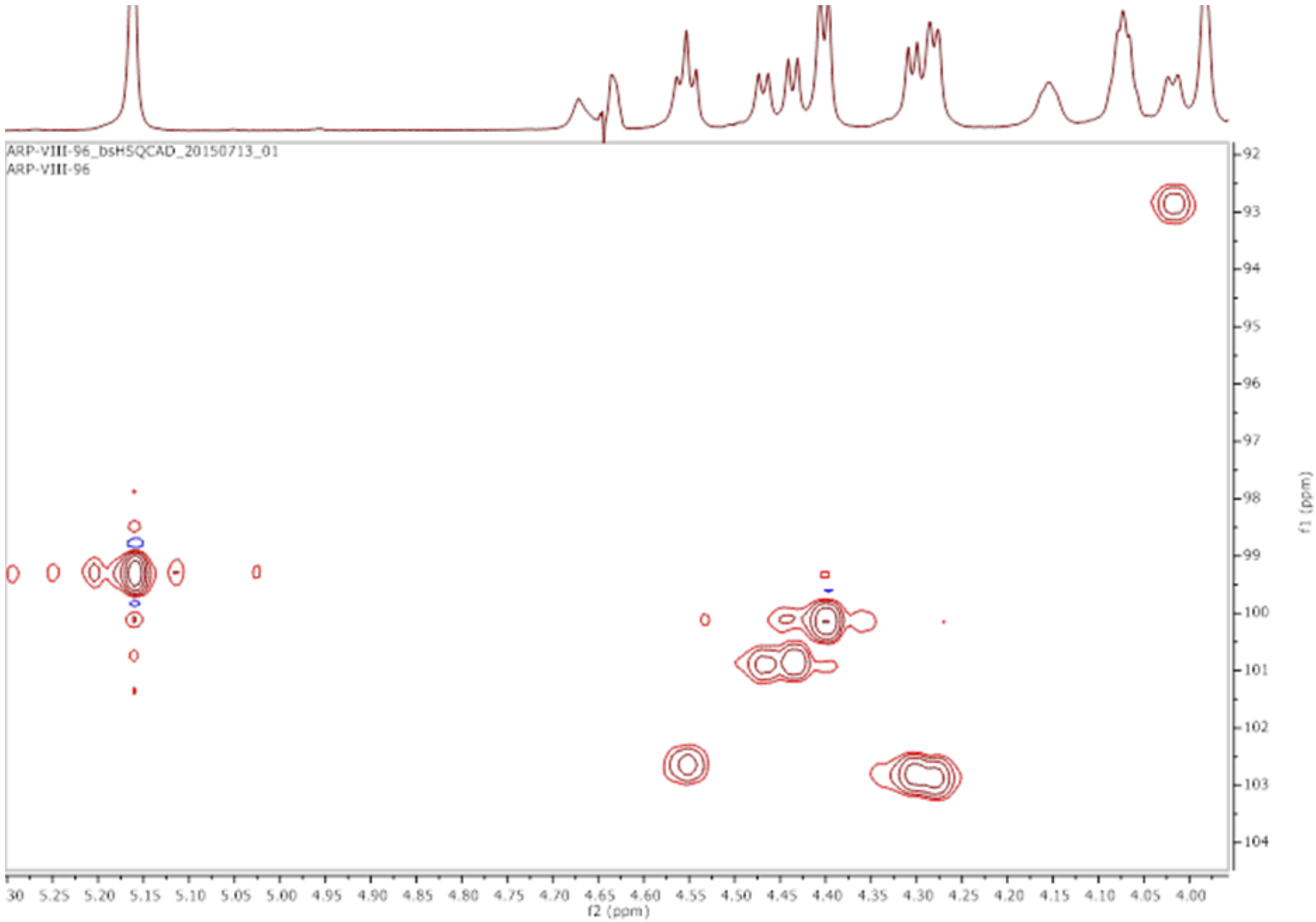
	C1
Glc	92.88
Gal	102.89
GlcNAc	102.62
Gal(2)	100.16
GlcNAc(2)	100.94
Gal(3)	102.89
GlcNAc(3)	102.62
Gal(4)	100.16
GlcNAc(4)	100.91
Gal(5)	102.77
Fuc(1)	99.29
Fuc(2)	99.29

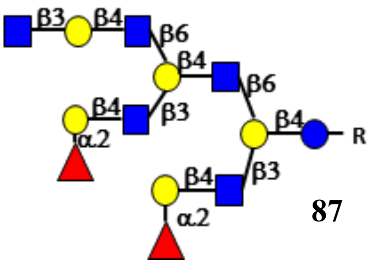
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{101}H_{162}N_8O_{64}Na$- $(M + Na)^+$ exact 2533.9566, found 2534.6438.



ARP-VIII-96_PRESAT_20150713_01
ARP-VIII-96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ARP-VIII-96_bsHSQCAD_20150713_01
ARP-VIII-96
f1 (ppm)
f2 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

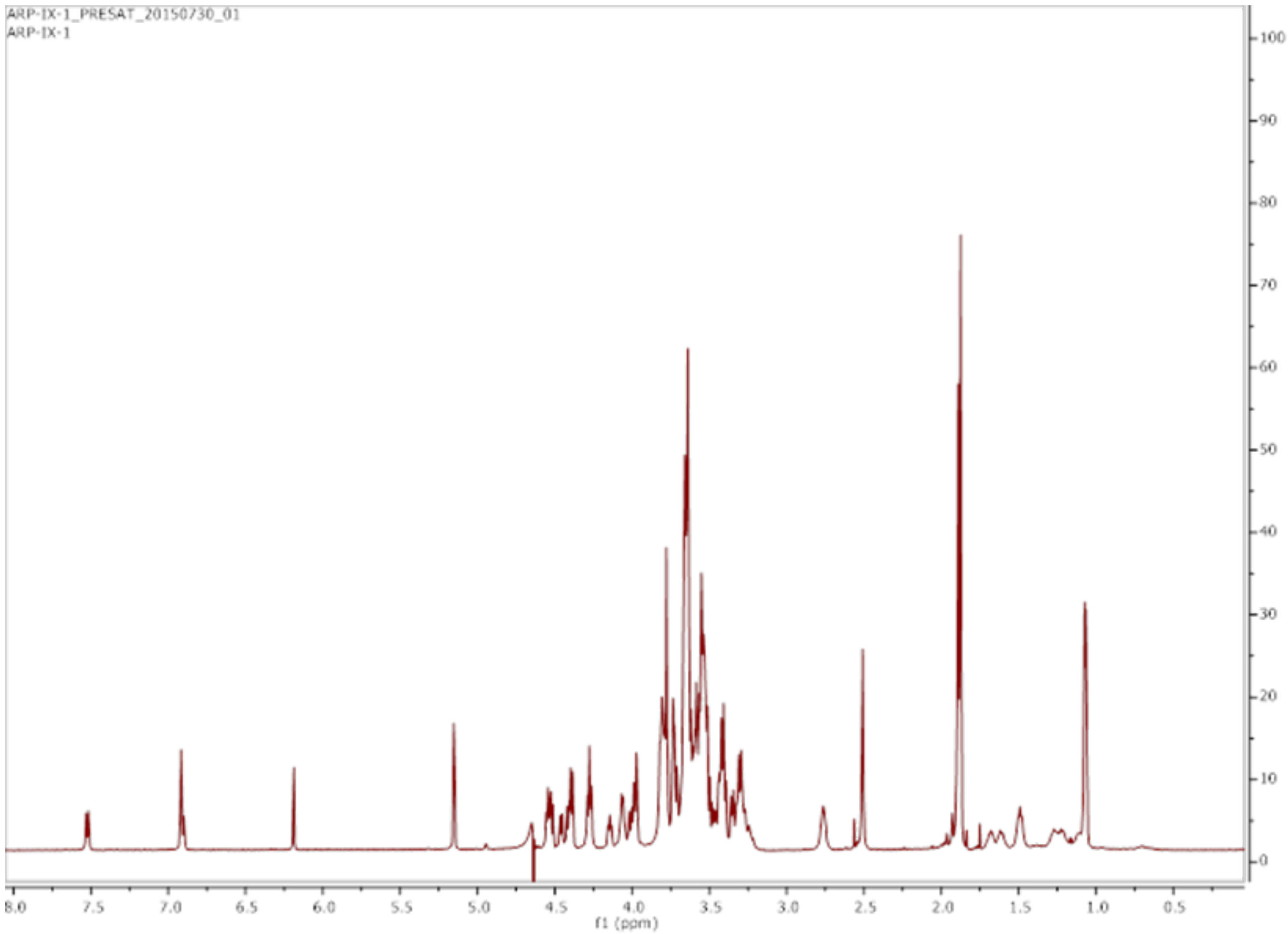
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.28	3.41	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(2)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.2 Hz, 1H)	3.60	3.54	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(3)	4.28	3.41	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(4)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.41	3.56	n/a	3.41	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(5)	4.28	3.41	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.52	3.59	3.41	3.29	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Fuc((1)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-
Fuc(2)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-

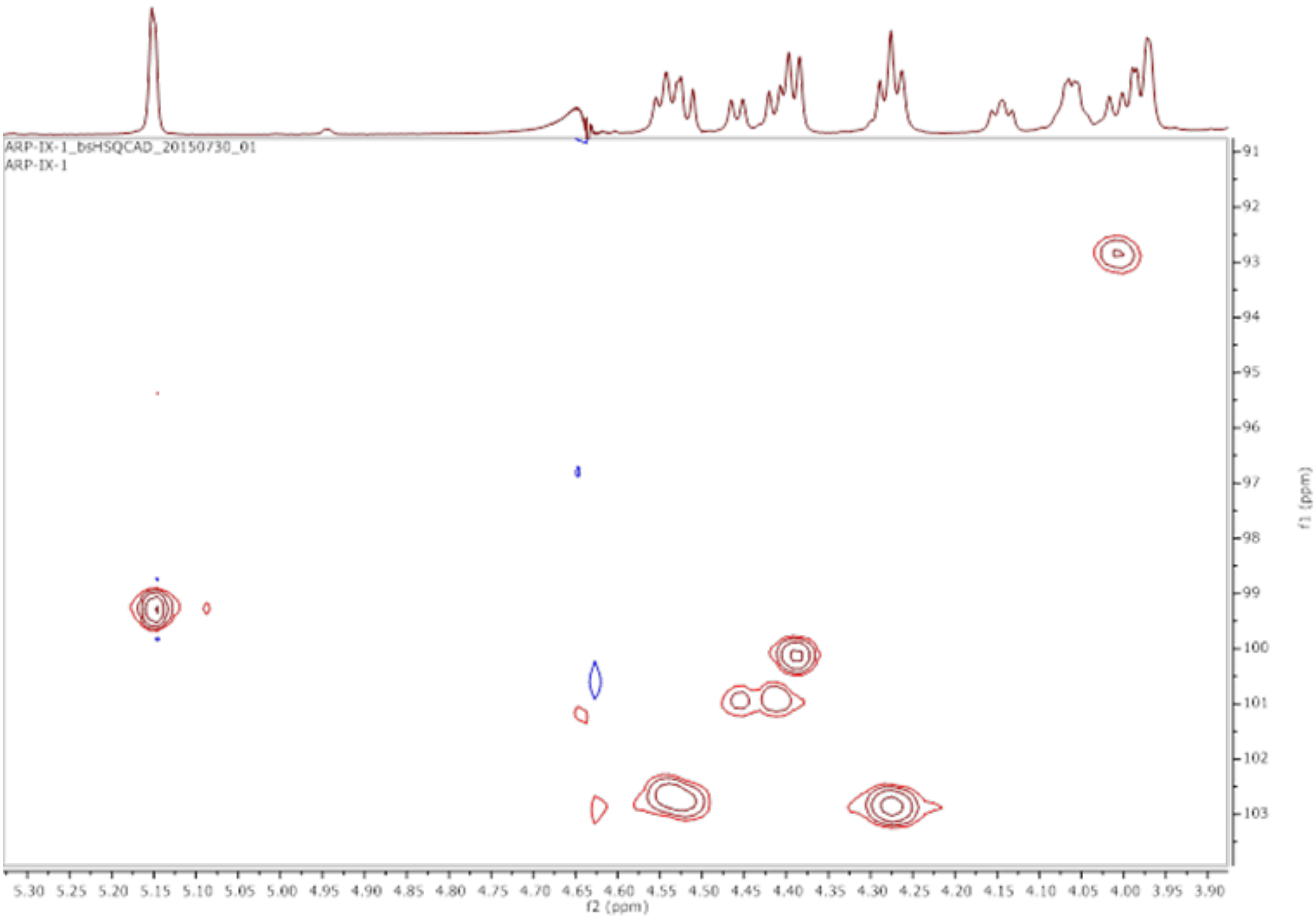
^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

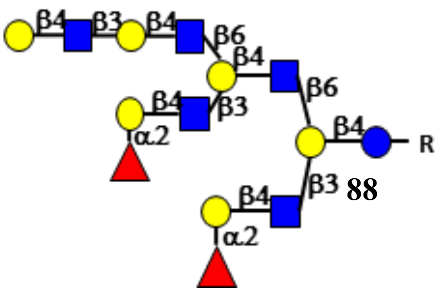
	C1
Glc	92.81
Gal	102.95
GlcNAc	102.62
Gal(2)	100.11
GlcNAc(2)	101.00
Gal(3)	102.95
GlcNAc(3)	102.63
Gal(4)	100.11
GlcNAc(4)	100.92
Gal(5)	102.95
GlcNAc(5)	102.84
Fuc(1)	99.37
Fuc(2)	99.37

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{109}H_{175}N_9O_{69}Na$- $(M + Na)^+$ exact 2737.0359, found 2736.4907.


ARP-IX-1_PRESAT_20150730_01
ARP-IX-1
f1 (ppm)


ARP-IX-1_bsHSQCAD_20150730_01
ARP-IX-1
5.30 5.25 5.20 5.15 5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90
f2 (ppm)
91
92
93
94
95
96
97
98
99
100
101
102
103
f1 (ppm)



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^{1}H (800 MHz, D_2O): δ (ppm)

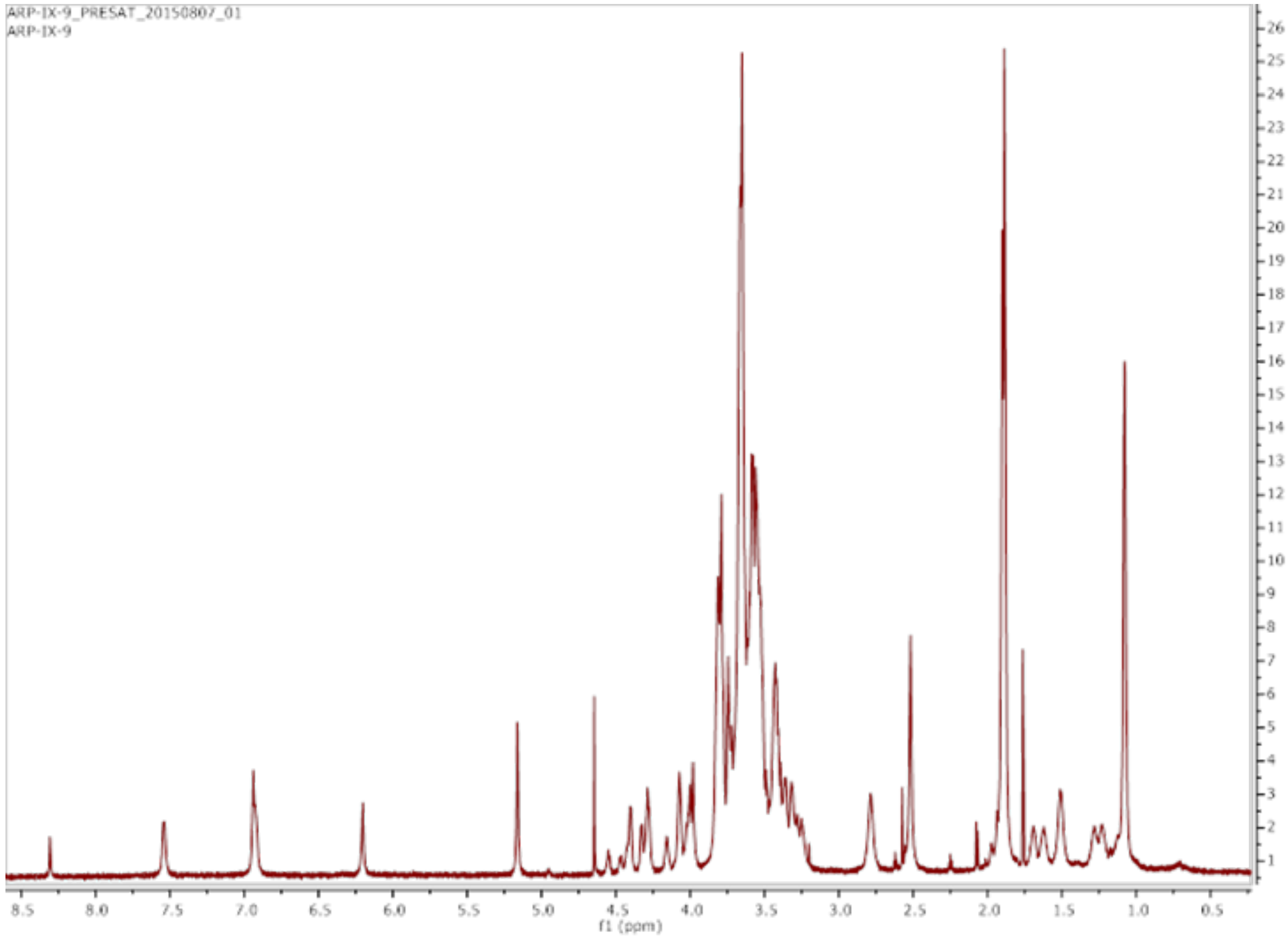
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.28	3.43	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.55	3.65	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(2)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46	3.60	3.54	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(3)	4.28	3.41	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.55	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(4)	4.39	3.52	3.65	3.72	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.41	3.52	n/a	3.41	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(5)	4.28	3.43	3.55	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.55	3.65	n/a	n/a	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(6)	4.33	3.39	3.52	3.78	n/a	n/a	-	-	-	-	-
Fuc((1)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-
Fuc(2)	5.15	3.65	n/a	n/a	4.09	-	-	-	-	1.07	-

^{13}C from BSHSQC (200 MHz, D_2O): δ (ppm)

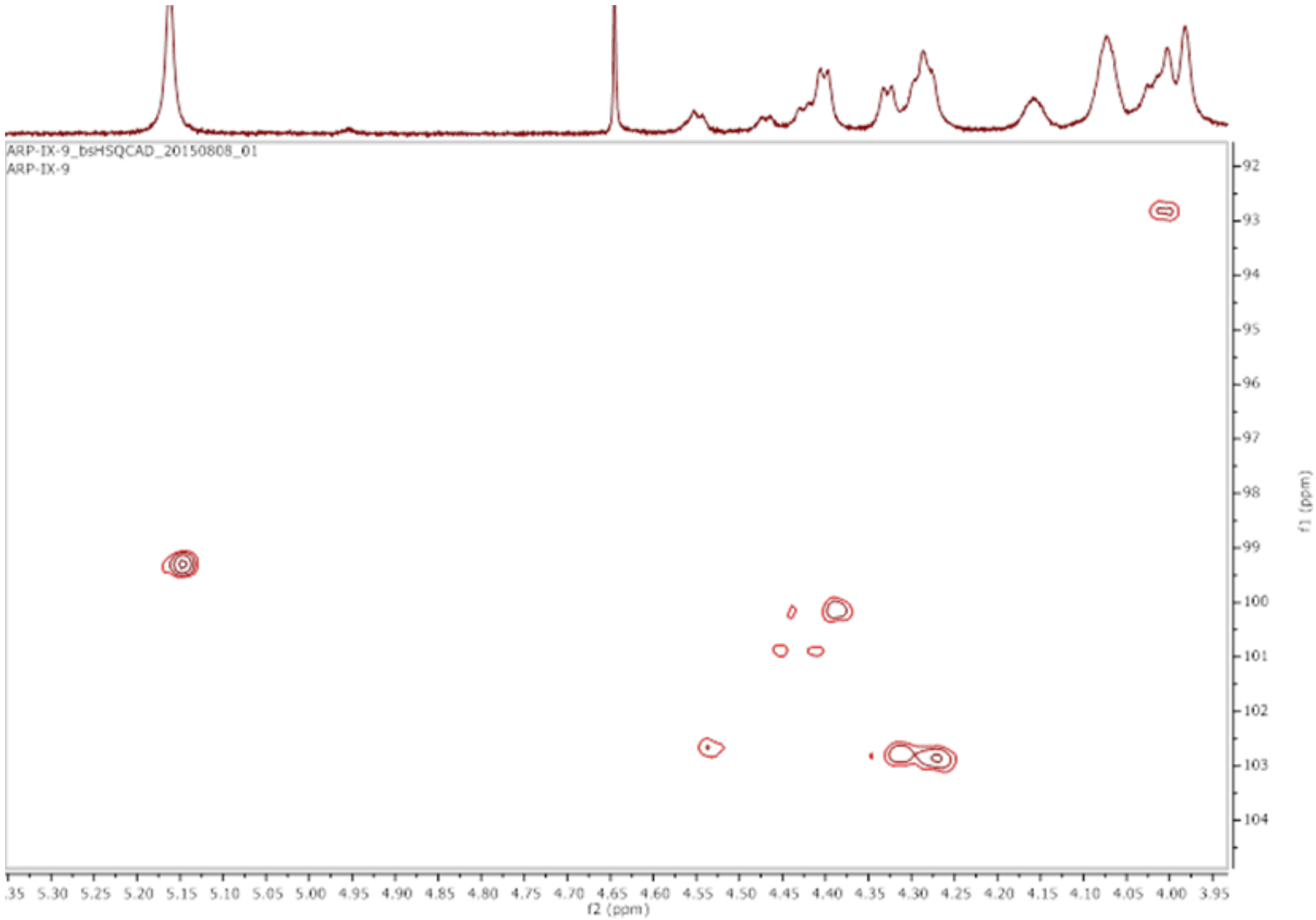
	C1
Glc	92.77
Gal	102.89
GlcNAc	102.69
Gal(2)	100.18
GlcNAc(2)	101.97
Gal(3)	102.89
GlcNAc(3)	102.69
Gal(4)	100.18
GlcNAc(4)	100.97
Gal(5)	102.89
GlcNAc(5)	102.69
Gal(6)	102.82
Fuc(1)	99.37
Fuc(2)	99.37

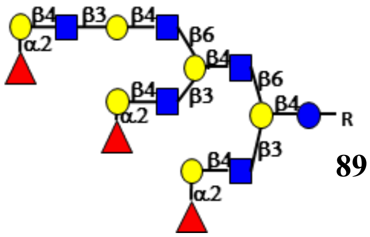
[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{115}H_{185}N_9O_{74}Na$- $(M + Na)^+$ exact 2899.0887, found 2900.7866.



ARP-IX-9_PRESAT_20150807_01
ARP-IX-9
f1 (ppm)


ARP-IX-9_bsHSQCAD_20150808_01
ARP-IX-9
f2 (ppm)
f1 (ppm)



89

^{1}H (900 MHz, D_2O): δ (ppm)

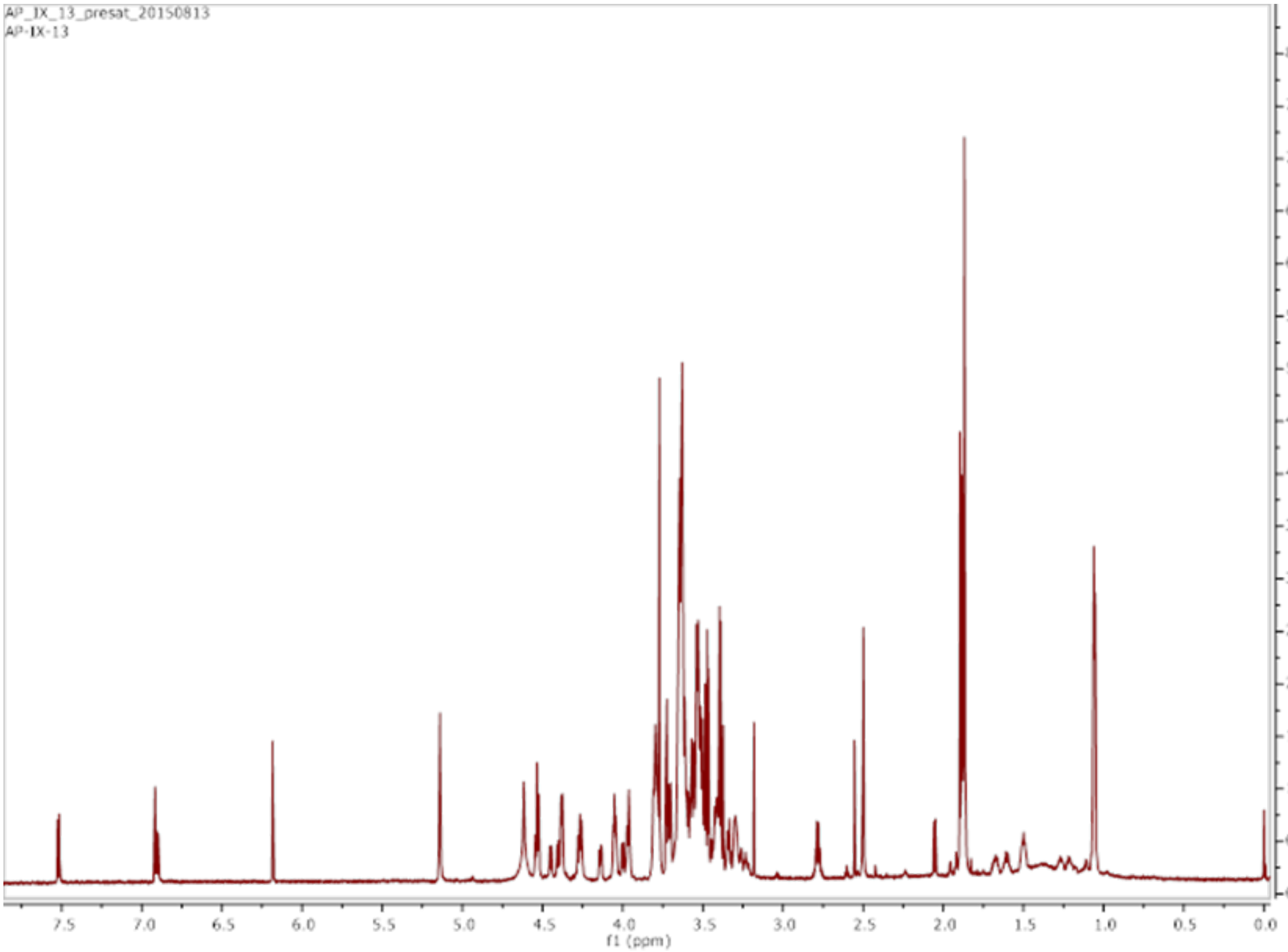
	H1	H2	H3	H4	H5	H6	H7	H8	H9	CH_3	NHAc
Glc	4.00 (d, *J* = 9.6 Hz, 1H)	3.34	3.41	3.48	n/a[a]	n/a	-[b]	-	-	-	-
Gal	4.27	3.42	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc	4.53	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(2)	4.38	3.52	n/a	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(2)	4.46 (d, *J* = 8.2 Hz, 1H)	3.60	3.54	3.44	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(3)	4.27	3.42	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(3)	4.53	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(4)	4.38	3.52	n/a	3.73	n/a	n/a	-	-	-	-	-
GlcNAc(4)	4.40 (d, *J* = 8.0 Hz, 1H)	3.57	3.52	3.41	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(5)	4.27	3.42	3.54	3.98	n/a	n/a	-	-	-	-	-
GlcNAc(5)	4.53	3.65	3.54	3.31	n/a	n/a	-	-	-	-	1.91 - 1.81 (m, 15H)
Gal(6)	4.38	3.52	n/a	3.73	n/a	n/a	-	-	-	-	-
Fuc((1)	5.15	3.65	n/a	n/a	4.06	-	-	-	-	1.07	-
Fuc(2)	5.15	3.65	n/a	n/a	4.06	-	-	-	-	1.07	-
Fuc(3)	5.15	3.65	n/a	n/a	4.06	-	-	-	-	1.07	-

^{13}C from BSHSQC (225 MHz, D_2O): δ (ppm)

	C1
Glc	95.50
Gal	105.63
GlcNAc	105.30
Gal(2)	102.94
GlcNAc(2)	103.63
Gal(3)	105.63
GlcNAc(3)	105.30
Gal(4)	102.94
GlcNAc(4)	103.56
Gal(5)	105.63
GlcNAc(5)	105.30
Gal(6)	102.94
Fuc(1)	101.99
Fuc(2)	101.99
Fuc(3)	101.99

[a] Not assigned
[b] Not applicable

MALDI TOF-MS *m/z* calcd $C_{121}H_{195}N_9O_{78}Na$ $(M + Na)^+$ exact 3045.1467, found 3045.0764.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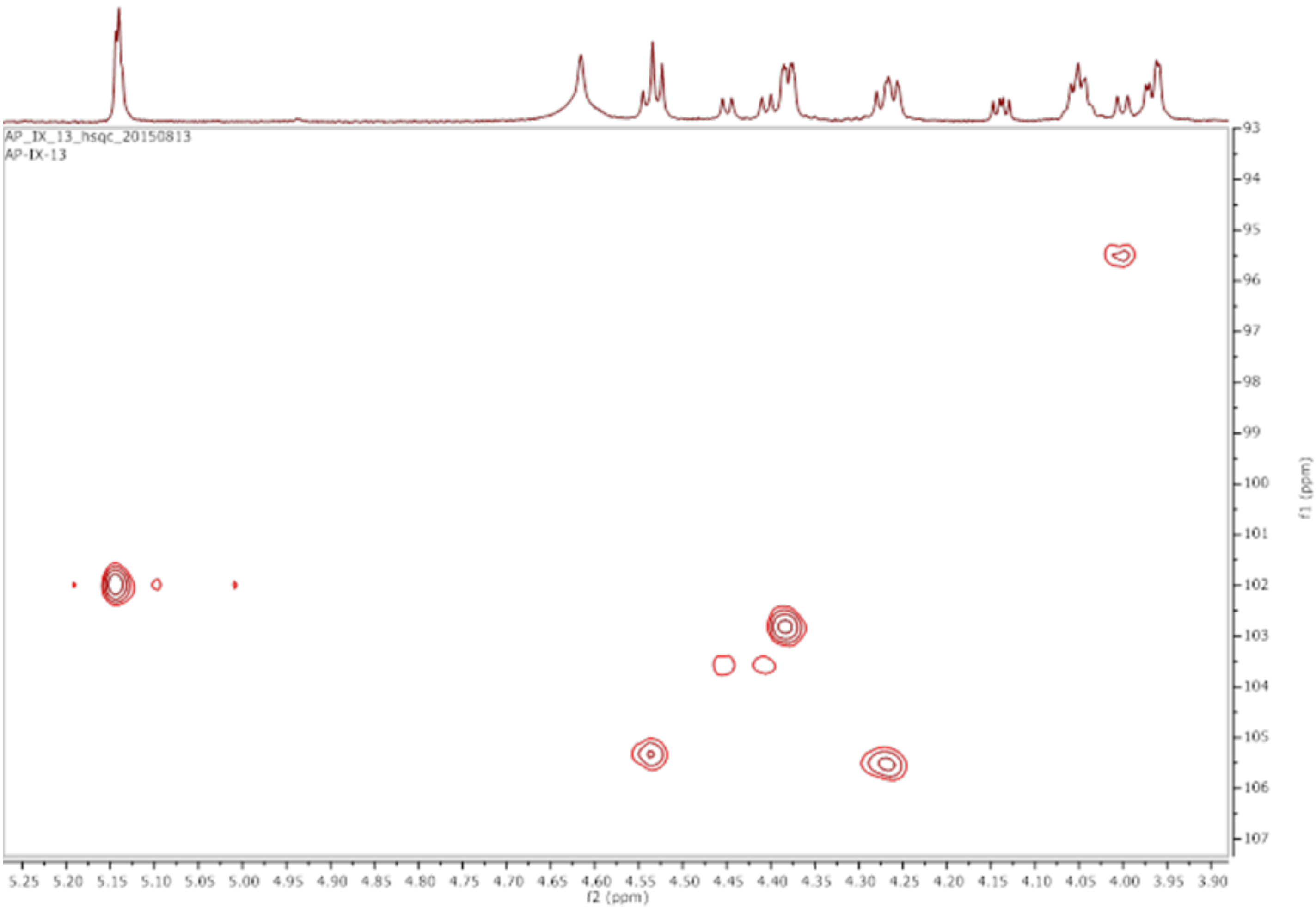
AP-IX-13
f1 (ppm)



AP_IX_13_hsqc_20150813
AP-IX-13
f2 (ppm)
f1 (ppm)

4. Microarray Procedure

4.a. Materials and Methods

All compounds were printed on NHS-activated Nexterion® slides purchased from Schott using a Scienion S3 non-contact microarray printer. Biotinylated plant lectins *Aleuria Aurantia* (AAL), *Ulex Europaeus* Agglutinin I (UEA), and *Sambucus Nigra* Agglutinin (SNA) were purchased from Vector Labs. Human galectin-9 was purchased from R&D Systems. Biotinylated mouse anti-galectin-9 antibody was purchased from PeproTech. Biotinylated Cholera Toxin B (CTB) was purchased from Sigma, biotinylated anti-GST antibody was purchased from Abcam, and streptavidin-AlexaFluor® 635 conjugate was purchased from Thermo Fisher. Stained slides were analyzed using a GenePix 4000B plate reader manufactured by Axon Instruments.

Individual targets were dissolved in a sodium phosphate buffer (pH 9.0, 50 mM) and were printed in replicates of six at a concentration of 100 μM with spot volume ~400 pL. Slides were printed with 24 subarrays (3 x 8) containing 396 spots (18 x 22). Post printing, slides were incubated in a humidity chamber for 24 h and then blocked for 1 h with a 5 mM ethanolamine in a Tris buffer (pH 9.0, 50 mM). Blocked slides were rinsed with DI water, spun dry, and kept in a desiccator at room temperature for future use.

4.b. VP8* Expression

The VP8* sequences (amino acids 64-224) of the Australian CRW-8 porcine (GenBank accession: L07888) were synthesized by GenScript (GenScript USA Inc., Piscataway, NJ) and then sub-cloned into the expression vector pGEX-4T- between the BamH I and EcoRI restriction sites. After confirmation of the inserts through DNA sequencing, the GST-VP8* fusion protein was expressed in *E. coli* BL21 with induction of IPTG (0.4 mM) at room temperature (22 °C) overnight. The GST-VP8* fusion protein was purified using Glutathione Sepharose 4 Fast Flow (GE Healthcare Life Sciences,Piscataway, NJ) according to the manufacturer's protocol.

4.c. Screening Procedure

Plant Lectins: Screening solutions of biotinylated UEA, SNA, and AAL were created by premixing streptavidin-AlexaFluor® 635 at a 1:3 ratio in TSM binding buffer (20 mM Tris Cl, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween, and 1 g/L BSA, pH 7.4). Final lectin concentrations were 10 μg mL^{-1}, 10 μg mL^{-1}, and 1 μg mL^{-1}, respectively. Plant lectin stock solution (100 μL) was added to each subarray and was allowed to incubate at room temperature in the dark for 1 h, after which the slide was washed consecutively with TSM wash buffer (20 mM Tris Cl, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, and 0.05% Tween, pH 7.4), TSM buffer (20 mM Tris Cl, 50 mM NaCl, 2 mM $CaCl_2$, 2 mM, and $MgCl_2$, pH 7.4), and DI water, and spun dry as described in the literature (9). The slides were stored in the dark prior to analysis.

Galectins-9: Galectin-9 solutions were made by dissolving the lectin in a TBS buffer (25 mM Tris, 0.15 M NaCl, pH 7.2) with 0.1% BSA and 0.05% Tween. Antibody and fluorophore solutions (5 μg mL^{-1}) were created by dissolving biotinylated anti-Gal-9 antibody and the AlexaFluor in a TBS buffer containing 0.1% BSA and 0.05% Tween; *these solutions were not premixed*. For galectin staining, galectin solution (100 μL) was added to a subarray and was allowed to incubate at room temperature for 1 h. After this time, the lectin was washed away using the same protocol as used for the plant lectins. To the dried plate anti-Gal-9 antibody (100 μL) was added and incubated for 1 h. Following washing the plate, streptavidin fluorophore (100 μL, 5 μg mL^{-1}) was added and incubated for 1 h.

Cholera Toxin B: Working solutions of biotinylated CTB were made by dissolving the appropriate amount of the protein in a PBS (10 mM, pH 7.4) buffer containing 0.1% BSA and 0.05% Tween. A streptavidin fluorophore working solution (5 μg mL^{-1}) was prepared in the same buffer. To screen the array, CTB solution (100 μL) was added to a subarray and incubated for 1 h. The plate was washed and next the fluorophore (100 μL) was added. After incubation of 1 h, the plate was washed, dried, and analyzed.

Adhesion VP8 from Porcine CRW-8:* Stock solution of VP8* was made by dissolving an appropriate amount of freshly expressed and purified VP8* adhesion protein in TSM binding buffer to a final concentration of 200 μg mL^{-1} protein. Biotinylated anti-GST antibody and the streptavidin fluorophore were mixed in the same vial containing TSM binding buffer to a final concentration of 1 μg mL^{-1} and 3 μg mL^{-1}, respectively. To screen the array, 100 μL of VP8* solution was added to a subarray and incubated for 1 h. The plate was washed, after which the antibody/fluorophore solution (100 μL) was added. The plate was incubated in the dark for 1 h before being washed, dried, and analyzed.

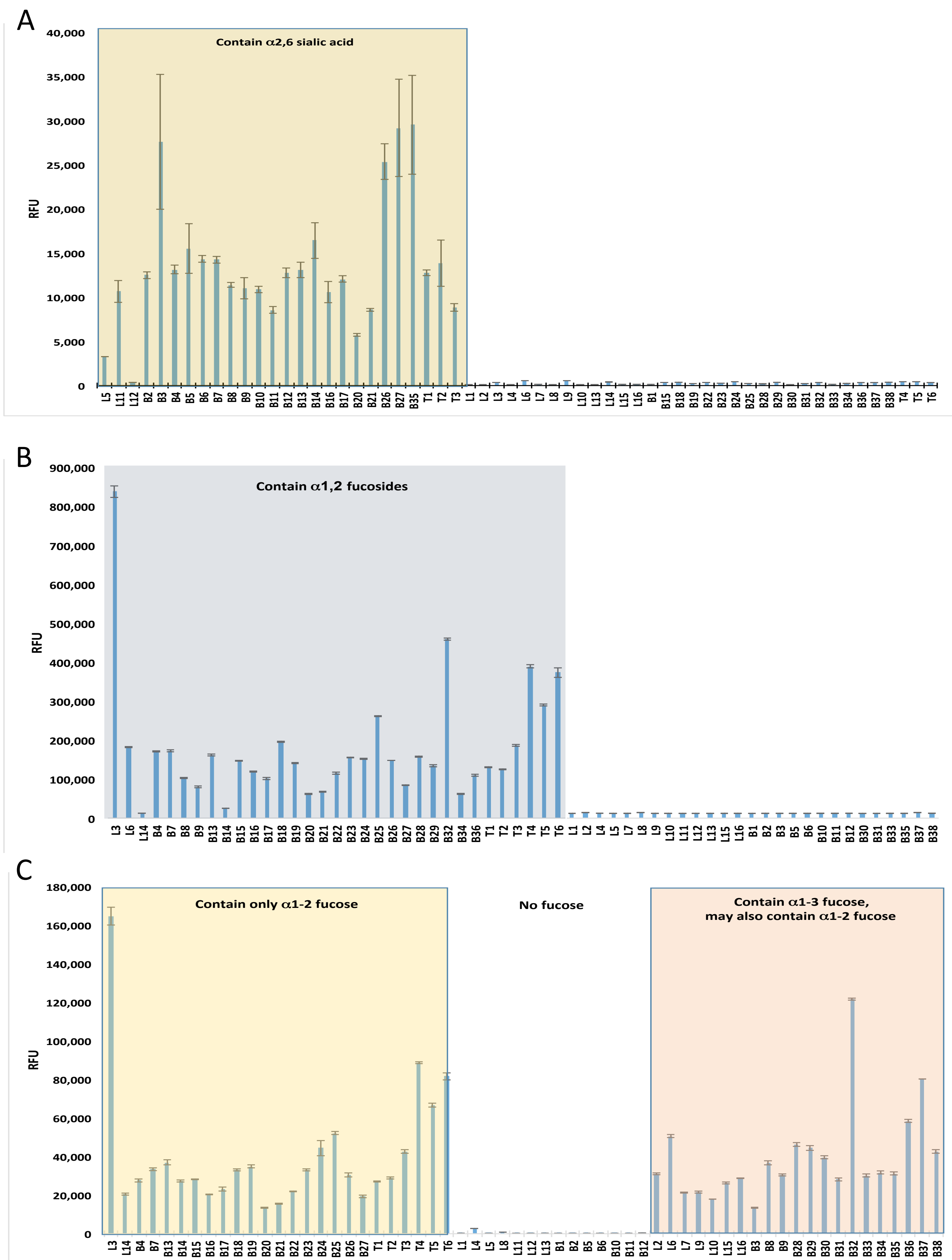


Fig. S22. Screening of the HMO library. Microarray results of the HMO library at 100 μM. (*A*) *Sambucus nigra* agglutinin (SNA; 10 μg mL^{-1}) for α2,6 sialic acid detection. (*B*) *Ulex europaeus* agglutinin I (UEA; 10 μg mL^{-1}) for α1,2-fucose detection. (*C*) *Aleuria aurantia* lectin (AAL; 1 μg mL^{-1}) for α1,2- α1,3- and α1-6 fucose detection.

5. References

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6. Abbreviations

AAL	*Aleuria aurantia* lectin
B3GALT5	β1,3-galactosyltransferase, polypeptide 5
B3GNT2	β1,3-*N*-acetylglucosaminyltransferase 2
CMP-Neu5Ac	cytidine-5'monophospho-*N*-acetylneuraminic acid
FUT1	galactoside α2-fucosyltransferase 1
FUT3 and FUT5	lactosamine α1,3-4 fucosyltransferase 3 and 5
FUT9	lactosamine α1,3-fucosyltransferase 9
Gal	galactose
GalT1	β1,4-galactosyltransferase
GCNT2	*N*-acetyllactosaminide β1,6-*N*-acetylglucosaminyltransferase
GDP-Fuc	guanosine 5'-diphospho-β-L-fucose
GlcNAc	*N*-acetyl-glucosamine
HMO	human milk oligosaccharide
LacNAc	*N*-acetyl-lactosamine
LN*n*T	lacto-*N*-*neo*tetraose
MS	mass spectrometry
NHS	N-hydroxysuccinimide
NOE	nuclear Overhauser effect
SNA	*Sambucus nigra* agglutinin
ST3GAL4	β-galactoside α2,3-sialyltransferase 4
ST6GAL1	β-galactoside α2,6-sialyltransferase 1
ST6GALNAc5	*N*-acetylgalactosaminide α2,6-sialyltransferase 5
Type 1 LacNAc	Galβ1,3GlcNAc, 1 lacto-*N*-biose
Type 2 LacNAc	Galβ1,4GlcNAc; *N*-acetyllactosamine
UDP	uridine-5'-diphosphate
UEA	*Ulex europaeus* agglutinin I