nature chemistry

Article

https://doi.org/10.1038/s41557-023-01248-4

Efficient platform for synthesizing comprehensive heparan sulfate oligosaccharide libraries for decoding glycosaminoglycan–protein interactions

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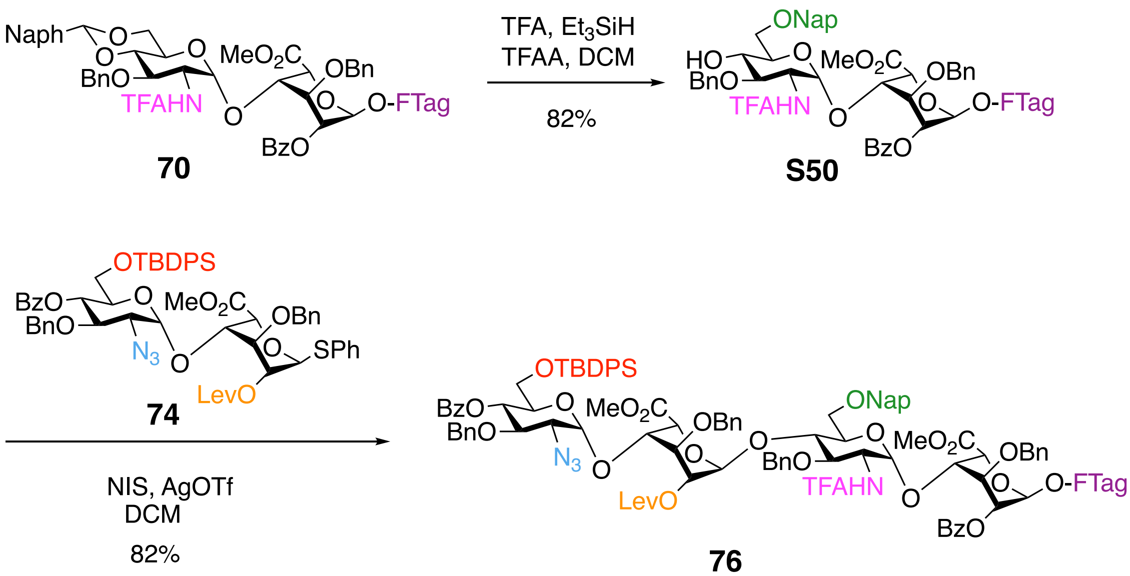
Supplementary Information for

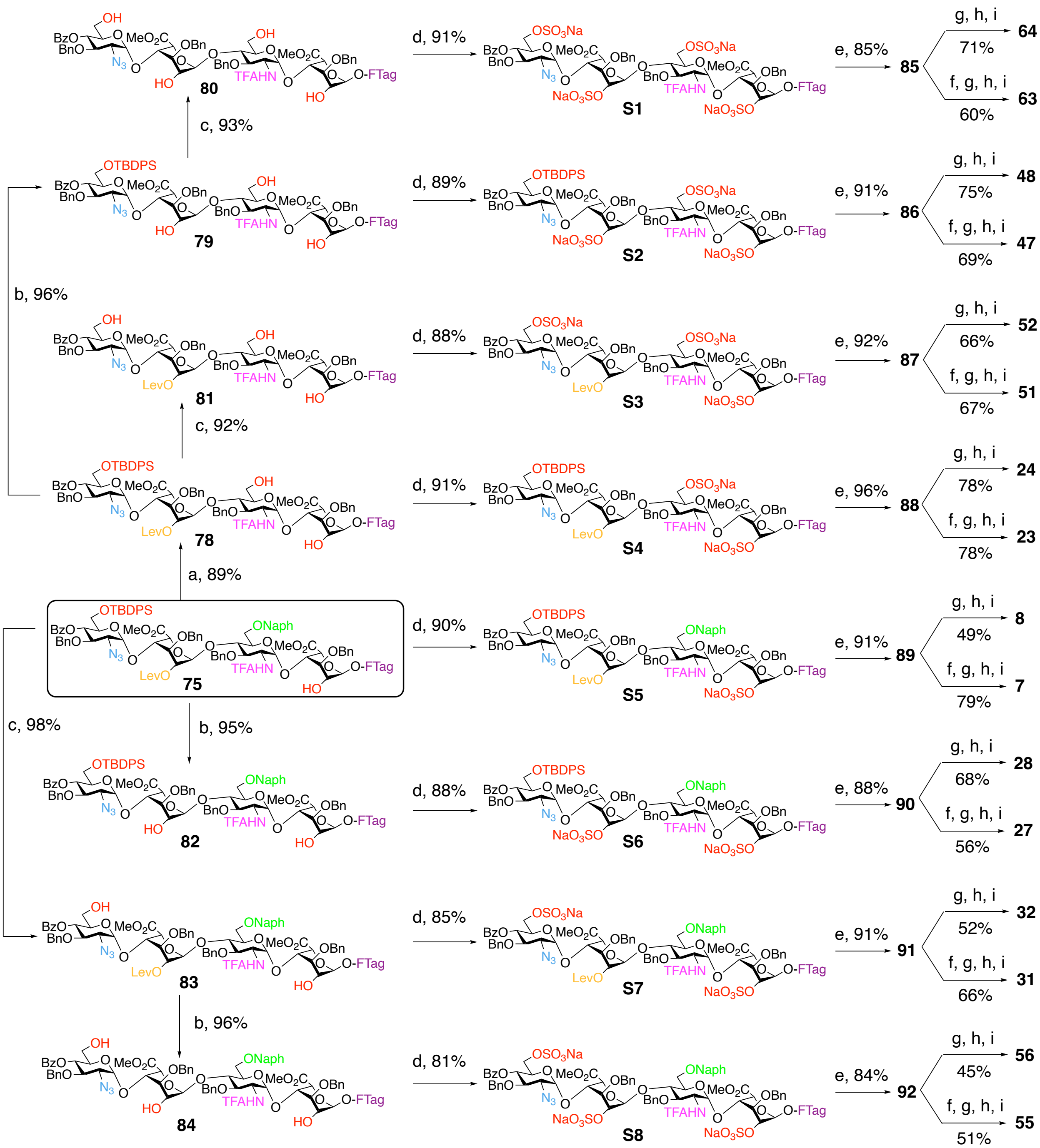
Efficient Platform for Synthesizing Comprehensive Heparan Sulfate Oligosaccharide Libraries for Decoding Glycosaminoglycan-Protein Interactions

Lei Wang[1], Alexander W. Sorum[1], Bo-Shun Huang[1], Mallory K. Kern[2], Guowei Su[3], Nitin Pawar[1], Xuefei Huang[4], Jian Liu[5], Nicola L. B. Pohl[2] and Linda C. Hsieh-Wilson[1]

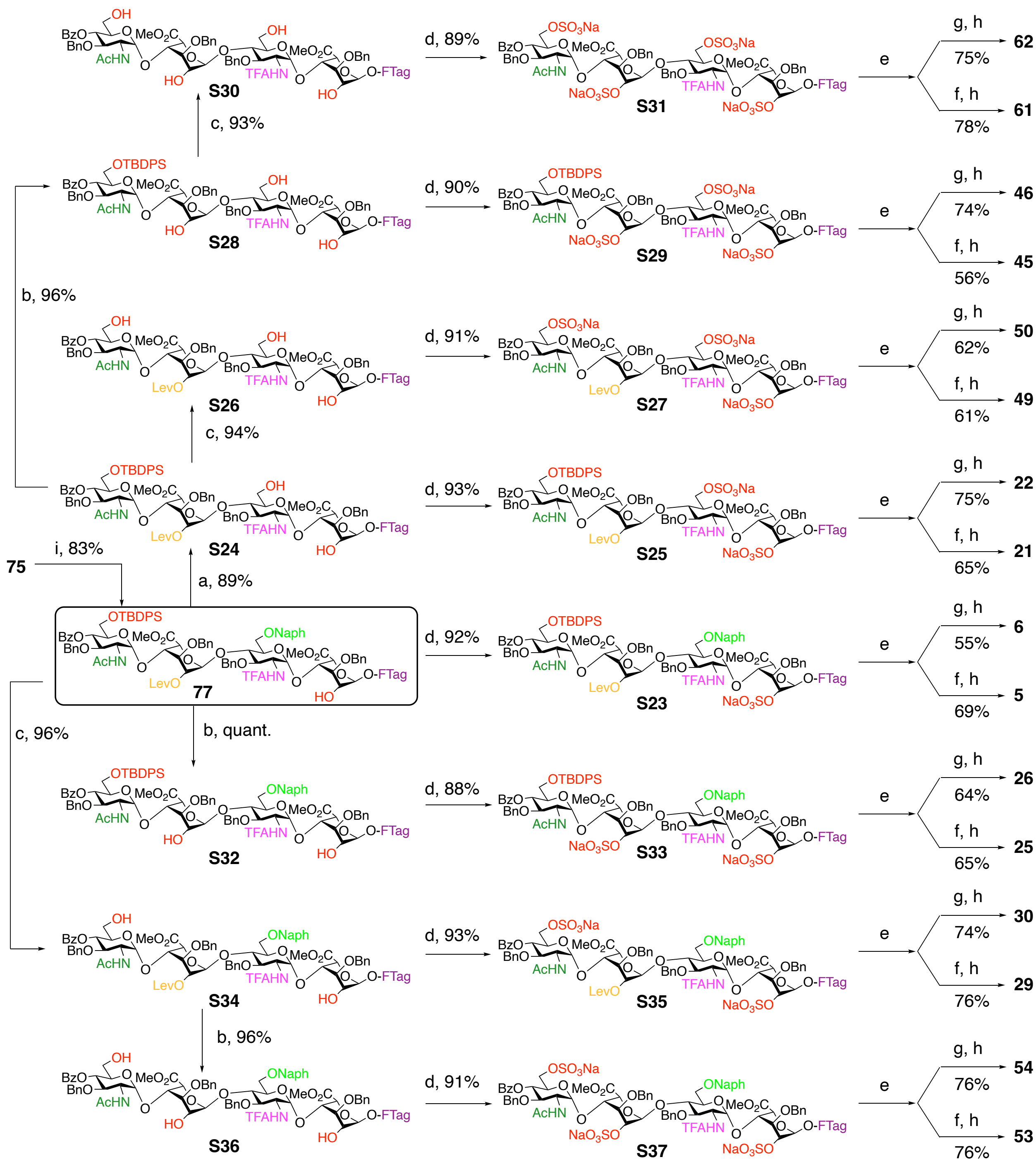
TABLE OF CONTENTS:



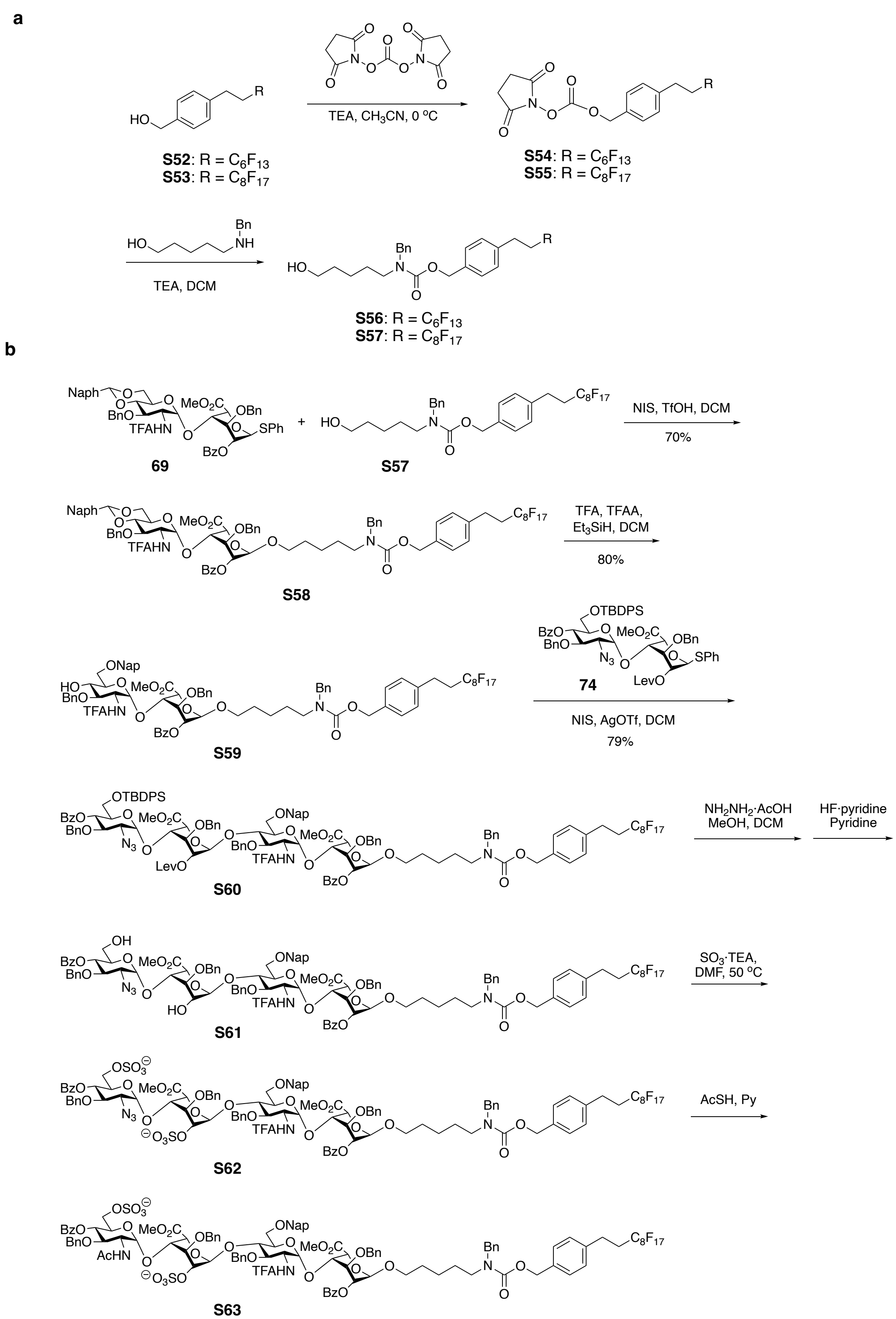
Supplementary Figure 1. Alternative synthetic route to tetrasaccharide **76**.



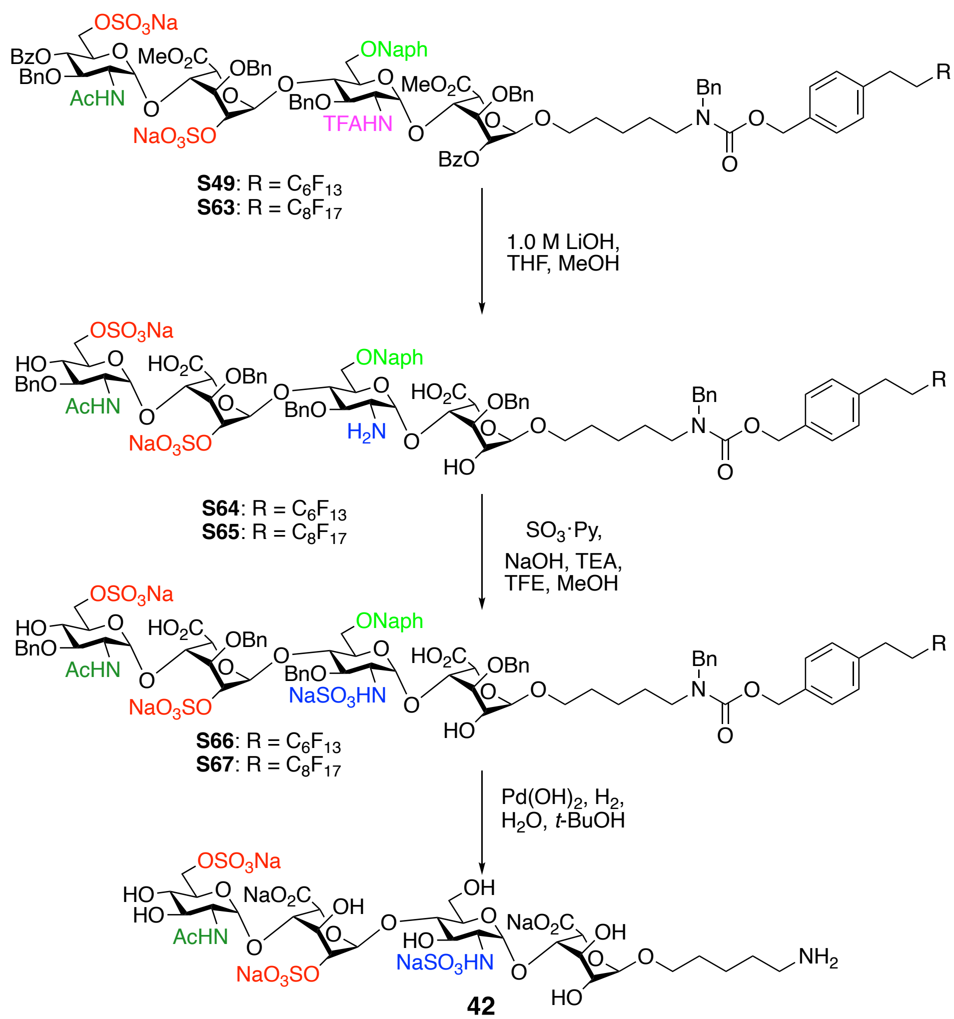
Supplementary Figure 2. Synthesis of HS sub-library NS(2)-2OS(1). Reagents and conditions: (a) DDQ, DCE, MeOH, PBS, rt. (b) hydrazine acetate, MeOH, DCM, rt. (c) HF·Py, pyridine, 0 °C to rt. (d) $SO_3 \cdot Et_3N$, DMF, 50 °C. (e) 1 M LiOH, MeOH, THF, 40 °C. (f) Ac_2O, TEA, MeOH, rt. (g) PMe_3, NaOH, THF, rt. (h) $SO_3 \cdot Py$, NaOH, TEA, TFE, MeOH, rt. (i) $Pd(OH)_2$, H_2, *t*-BuOH, H_2O, rt.



Supplementary Figure 3. Synthesis of HS sub-library NAc(2)-2OS(1). Reagents and conditions: (a) DDQ, DCE, MeOH, PBS, rt. (b) hydrazine acetate, MeOH, DCM, rt. (c) HF·Py, pyridine, 0 °C to rt. (d) $SO_3 \cdot Et_3N$, DMF, 50 °C. (e) 1 M LiOH, MeOH, THF, 40 °C. (f) Ac_2O, TEA, MeOH, rt. (g) $SO_3 \cdot Py$, NaOH, TEA, TFE, MeOH, rt. (h) $Pd(OH)_2$, H_2, *t*-BuOH, H_2O, rt. (i) AcSH, pyridine, rt. 16h.

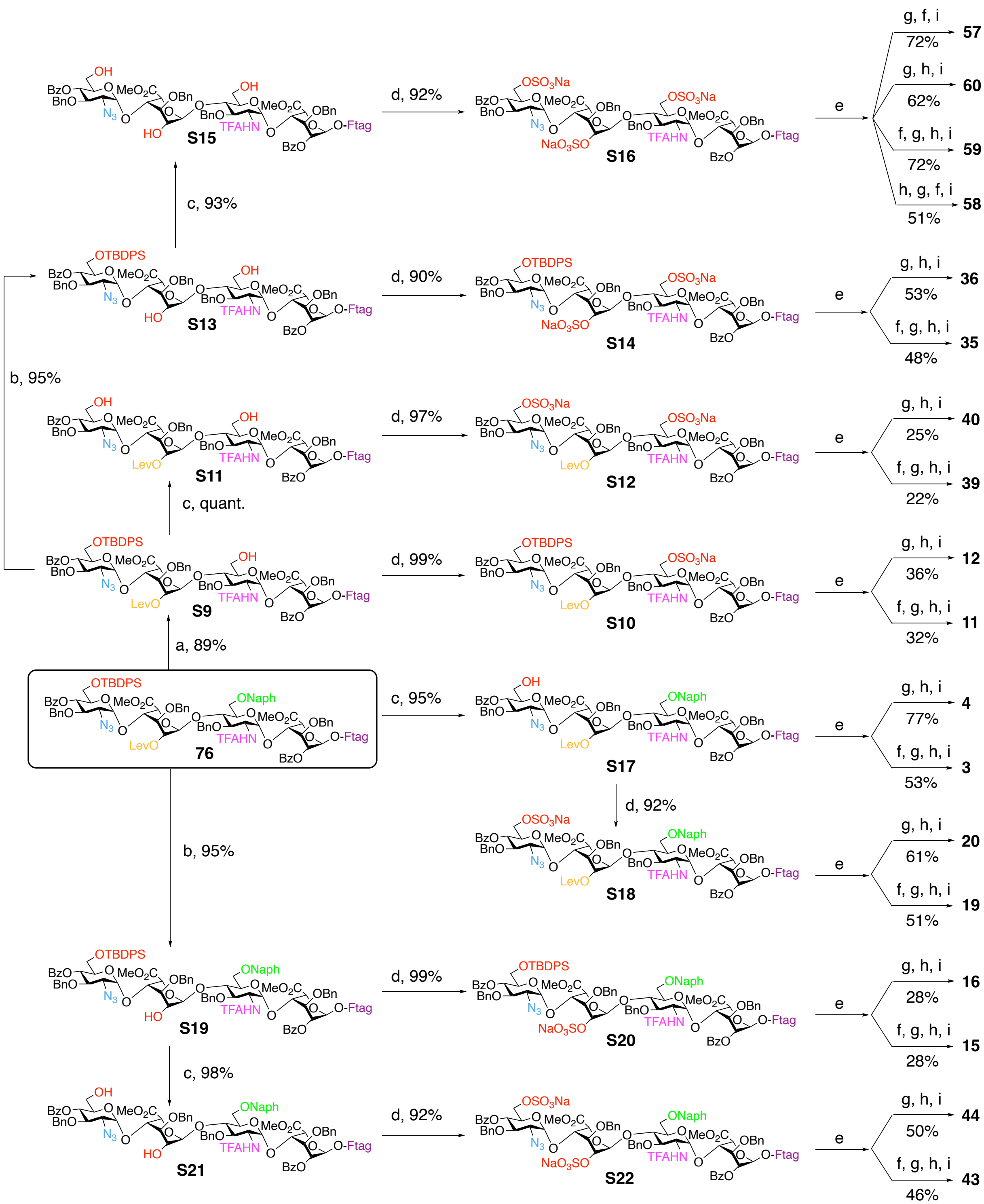


Supplementary Figure 4. (a) Synthesis of the C_6F_{13} linker **S56** and C_8F_{17} linker **S57**. (b) Synthesis of tetrasaccharide **S63** with the C_8F_{17} linker.

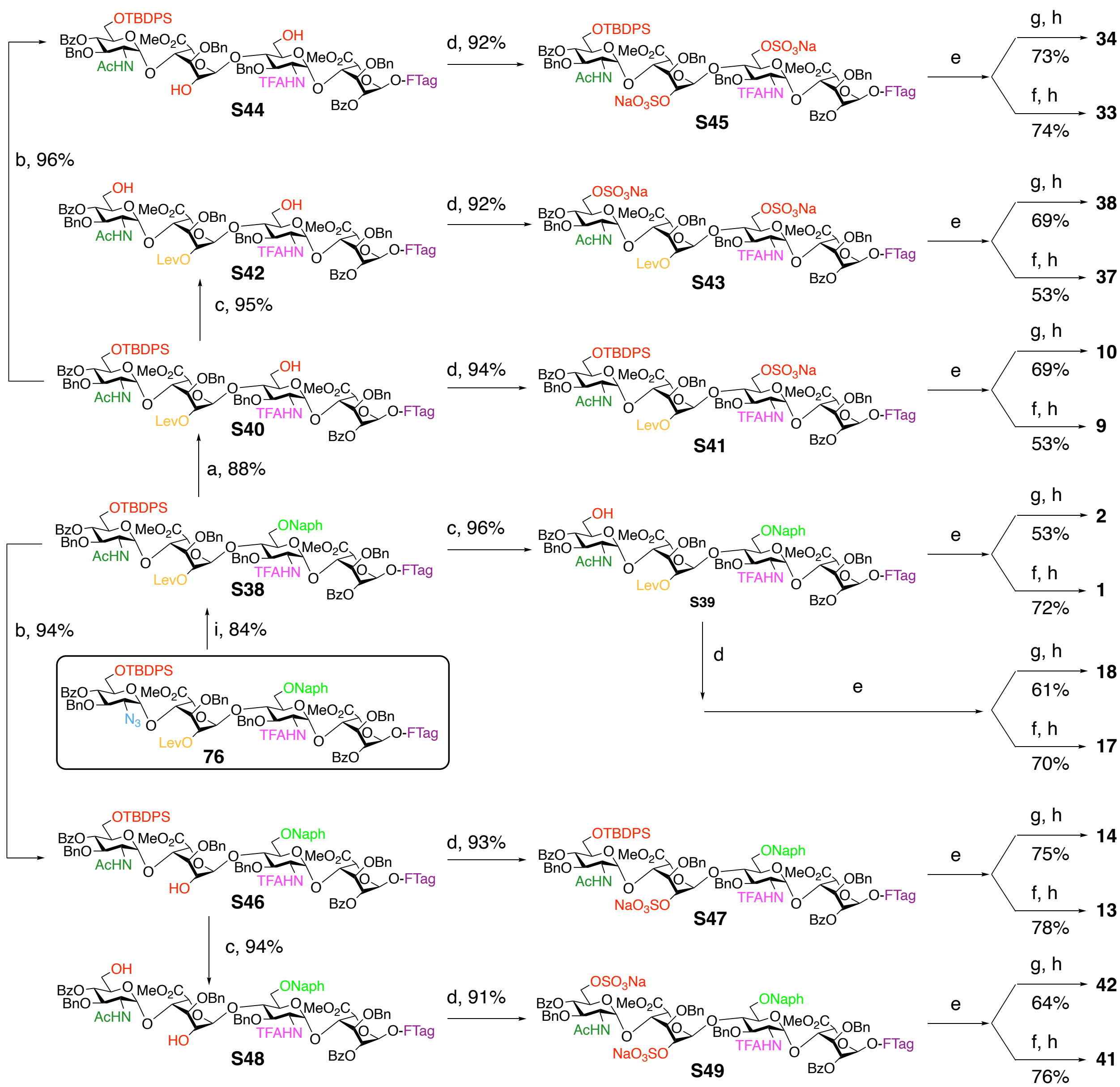


	Reaction time (Hydrolysis)	Reaction time (N-Sulfation)	SO_3Py	Yields (Three steps)
R = C_6F_{13}	24 h	12 h	30 eq	64%
R = C_8F_{17}	35 h	18 h	45 eq	62%

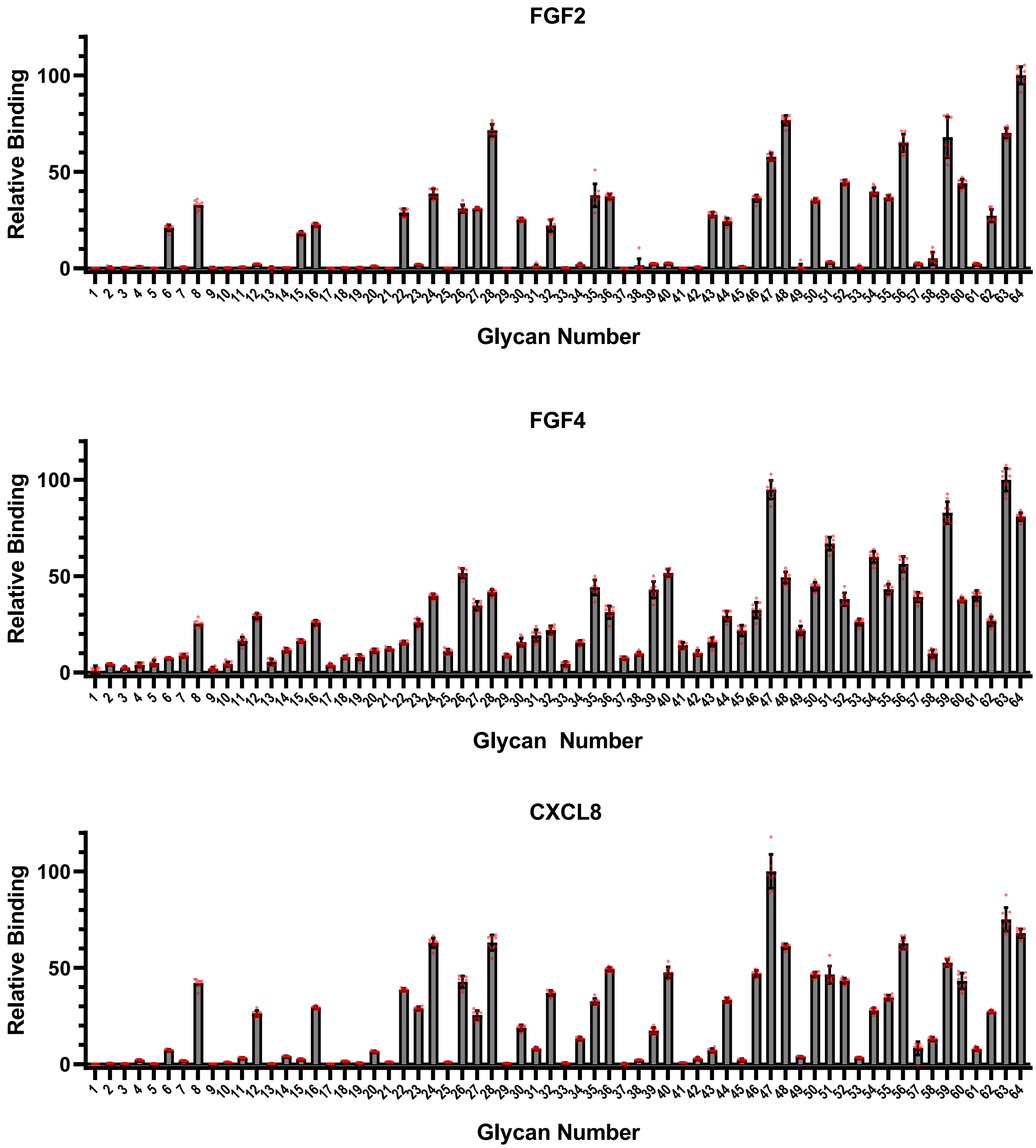
Supplementary Figure 5. Comparison between the C_6F_{13} and C_8F_{17} F-tags.



Supplementary Figure 6. Synthesis of HS sub-library NS(2)-2OH(1) and compounds **57**-**58**. Reagents and conditions: (a) DDQ, DCE, MeOH, PBS, rt. (b) hydrazine acetate, MeOH, DCM, rt. (c) HF·Py, pyridine, 0 °C to rt. (d) $SO_3 \cdot Et_3N$, DMF, 50 °C. (e) 1 M LiOH, MeOH, THF, rt. (f) Ac_2O, TEA, MeOH, 40 °C. (g) PMe_3, NaOH, THF, rt. (h) $SO_3 \cdot Py$, NaOH, TEA, TFE, MeOH, rt. (i) $Pd(OH)_2$, H_2, *t*-BuOH, H_2O, rt.



Supplementary Figure 7. Synthesis of HS sub-library NAc(2)-2OH(1). (a) DDQ, DCE, MeOH, PBS, rt. (b) hydrazine acetate, MeOH, DCM, rt. (c) HF·Py, pyridine, 0 °C to rt. (d) $SO_3 \cdot Et_3N$, DMF, 50 °C. (e) 1 M LiOH, MeOH, THF, 40 °C. (f) Ac_2O, TEA, MeOH, rt. (g) $SO_3 \cdot Py$, NaOH, TEA, TFE, MeOH, rt. (h) $Pd(OH)_2$, H_2, *t*-BuOH, H_2O, rt. (i) AcSH, pyridine, rt, 16 h.



Supplementary Figure 8. Relative binding of FGF2, FGF4 and CXCL8 (from top to bottom) to the tetrasaccharide arrays. The fluorescence intensities were corrected for background and normalized with respect to the highest intensity on the array. Bar graphs represent the mean ± SD for each compound in nonuplicate. Individual data points are shown as red dots.

Supplementary Table 1. Structures and purities of HS tetrasaccharides **1-64**.

Compd. No.	Structure	Purity	Compd. No.	Structure	Purity
1	GlcNAc-IdoA-GlcNAc-IdoA	>95%	**33**	GlcNAc-IdoA2S-GlcNAc6S-IdoA	>95%
2	GlcNAc-IdoA-GlcNS-IdoA	>95%	**34**	GlcNAc-IdoA2S-GlcNS6S-IdoA	>95%
3	GlcNS-IdoA-GlcNAc-IdoA	>95%	**35**	GlcNS-IdoA2S-GlcNAc6S-IdoA	>95%
4	GlcNS-IdoA-GlcNS-IdoA	>95%	**36**	GlcNS-IdoA2S-GlcNS6S-IdoA	90%
5	GlcNAc-IdoA-GlcNAc-IdoA2S	95%	**37**	GlcNAc6S-IdoA-GlcNAc6S-IdoA	95%
6	GlcNAc-IdoA-GlcNS-IdoA2S	95%	**38**	GlcNAc6S-IdoA-GlcNS6S-IdoA	95%
7	GlcNS-IdoA-GlcNAc-IdoA2S	95%	**39**	GlcNS6S-IdoA-GlcNAc6S-IdoA	93%
8	GlcNS-IdoA-GlcNS-IdoA2S	95%	**40**	GlcNS6S-IdoA-GlcNS6S-IdoA	95%
9	GlcNAc-IdoA-GlcNAc6S-IdoA	>95%	**41**	GlcNAc6S-IdoA2S-GlcNAc-IdoA	94%
10	GlcNAc-IdoA-GlcNS6S-IdoA	95%	**42**	GlcNAc6S-IdoA2S-GlcNS-IdoA	95%
11	GlcNS-IdoA-GlcNAc6S-IdoA	94%	**43**	GlcNS6S-IdoA2S-GlcNAc-IdoA	90%
12	GlcNS-IdoA-GlcNS6S-IdoA	95%	**44**	GlcNS6S-IdoA2S-GlcNS-IdoA	92%
13	GlcNAc-IdoA2S-GlcNAc-IdoA	95%	**45**	GlcNAc-IdoA2S-GlcNAc6S-IdoA2S	95%
14	GlcNAc-IdoA2S-GlcNS-IdoA	94%	**46**	GlcNAc-IdoA2S-GlcNS6S-IdoA2S	95%
15	GlcNS-IdoA2S-GlcNAc-IdoA	92%	**47**	GlcNS-IdoA2S-GlcNAc6S-IdoA2S	88%
16	GlcNS-IdoA2S-GlcNS-IdoA	92%	**48**	GlcNS-IdoA2S-GlcNS6S-IdoA2S	>95%
17	GlcNAc6S-IdoA-GlcNAc-IdoA	>95%	**49**	GlcNAc6S-IdoA-GlcNAc6S-IdoA2S	91%
18	GlcNAc6S-IdoA-GlcNS-IdoA	93%	**50**	GlcNAc6S-IdoA-GlcNS6S-IdoA2S	90%
19	GlcNS6S-IdoA-GlcNAc-IdoA	>95%	**51**	GlcNS6S-IdoA-GlcNAc6S-IdoA2S	91%
20	GlcNS6S-IdoA-GlcNS-IdoA	94%	**52**	GlcNS6S-IdoA-GlcNS6S-IdoA2S	>95%
21	GlcNAc-IdoA-GlcNAc6S-IdoA2S	94%	**53**	GlcNAc6S-IdoA2S-GlcNAc-IdoA2S	>95%
22	GlcNAc-IdoA-GlcNS6S-IdoA2S	95%	**54**	GlcNAc6S-IdoA2S-GlcNS-IdoA2S	94%
23	GlcNS-IdoA-GlcNAc6S-IdoA2S	91%	**55**	GlcNS6S-IdoA2S-GlcNAc-IdoA2S	90%
24	GlcNS-IdoA-GlcNS6S-IdoA2S	93%	**56**	GlcNS6S-IdoA2S-GlcNS-IdoA2S	90%
25	GlcNAc-IdoA2S-GlcNAc-IdoA2S	93%	**57**	GlcNAc6S-IdoA2S-GlcNAc6S-IdoA	91%
26	GlcNAc-IdoA2S-GlcNS-IdoA2S	94%	**58**	GlcNAc6S-IdoA2S-GlcNS6S-IdoA	82%
27	GlcNS-IdoA2S-GlcNAc-IdoA2S	95%	**59**	GlcNS6S-IdoA2S-GlcNAc6S-IdoA	94%
28	GlcNS-IdoA2S-GlcNS-IdoA2S	94%	**60**	GlcNS6S-IdoA2S-GlcNS6S-IdoA	90%
29	GlcNAc6S-IdoA-GlcNAc-IdoA2S	86%	**61**	GlcNAc6S-IdoA2S-GlcNAc6S-IdoA2S	94%
30	GlcNAc6S-IdoA-GlcNS-IdoA2S	92%	**62**	GlcNAc6S-IdoA2S-GlcNS6S-IdoA2S	92%
31	GlcNS6S-IdoA-GlcNAc-IdoA2S	95%	**63**	GlcNS6S-IdoA2S-GlcNAc6S-IdoA2S	93%
32	GlcNS6S-IdoA-GlcNS-IdoA2S	95%	**64**	GlcNS6S-IdoA2S-GlcNS6S-IdoA2S	93%

Supplementary Table 2. Structures, relative binding, and standard deviation (s.d.) of HS tetrasaccharides to FGF2, FGF4, and CXCL8.

Cmpd	Structure	FGF2 Rel. binding	s.d.	FGF4 Rel. binding	s.d.	CXCL8 Rel. binding	s.d.
1	GlcNAc-IdoA-GlcNAc-IdoA	0.1	0.1	0.6	2.8	0.1	0.0
2	GlcNAc-IdoA-GlcNS-IdoA	0.4	0.3	4.3	0.4	0.4	0.1
3	GlcNS-IdoA-GlcNAc-IdoA	0.5	0.1	2.4	0.6	0.2	0.1
4	GlcNS-IdoA-GlcNS-IdoA	0.9	0.1	4.0	1.1	2.1	0.3
5	GlcNAc-IdoA-GlcNAc-IdoA2S	0.1	0.1	4.9	1.4	0.2	0.1
6	GlcNAc-IdoA-GlcNS-IdoA2S	20.6	1.3	7.5	0.4	7.4	0.4
7	GlcNS-IdoA-GlcNAc-IdoA2S	0.6	0.2	8.8	0.8	1.7	0.2
8	GlcNS-IdoA-GlcNS-IdoA2S	31.9	1.8	25.3	1.8	41.9	2.3
9	GlcNAc-IdoA-GlcNAc6S-IdoA	0.2	0.3	2.0	0.8	0.1	0.1
10	GlcNAc-IdoA-GlcNS6S-IdoA	0.2	0.1	4.4	1.2	1.0	0.1
11	GlcNS-IdoA-GlcNAc6S-IdoA	0.7	0.1	16.5	2.0	3.3	0.2
12	GlcNS-IdoA-GlcNS6S-IdoA	2.2	0.1	29.2	1.6	26.3	1.4
13	GlcNAc-IdoA2S-GlcNAc-IdoA	0.0	0.7	5.5	1.6	0.2	0.1
14	GlcNAc-IdoA2S-GlcNS-IdoA	0.4	0.1	11.6	0.9	4.1	0.2
15	GlcNS-IdoA2S-GlcNAc-IdoA	17.6	0.8	16.4	0.8	2.6	0.2
16	GlcNS-IdoA2S-GlcNS-IdoA	21.2	0.6	25.9	1.3	29.5	0.6
17	GlcNAc6S-IdoA-GlcNAc-IdoA	0.0	0.1	3.7	0.7	0.1	0.0
18	GlcNAc6S-IdoA-GlcNS-IdoA	0.4	0.1	7.9	0.7	1.6	0.1
19	GlcNS6S-IdoA-GlcNAc-IdoA	0.4	0.2	8.0	1.4	0.6	0.2
20	GlcNS6S-IdoA-GlcNS-IdoA	1.1	0.2	11.3	1.0	6.6	0.3
21	GlcNAc-IdoA-GlcNAc6S-IdoA2S	0.1	0.0	12.3	0.7	1.1	0.1
22	GlcNAc-IdoA-GlcNS6S-IdoA2S	29.2	1.8	15.5	0.8	38.6	0.7
23	GlcNS-IdoA-GlcNAc6S-IdoA2S	2.0	0.1	25.9	1.8	28.9	0.8
24	GlcNS-IdoA-GlcNS6S-IdoA2S	38.2	2.2	39.6	1.2	62.9	2.5
25	GlcNAc-IdoA2S-GlcNAc-IdoA2S	0.2	0.0	10.9	1.3	1.0	0.1
26	GlcNAc-IdoA2S-GlcNS-IdoA2S	30.9	2.2	51.5	2.4	42.7	3.1
27	GlcNS-IdoA2S-GlcNAc-IdoA2S	30.3	0.6	34.6	2.3	25.4	2.4
28	GlcNS-IdoA2S-GlcNS-IdoA2S	68.1	2.5	41.7	1.4	63.0	3.9
29	GlcNAc6S-IdoA-GlcNAc-IdoA2S	0.0	0.0	8.8	0.7	0.4	0.1
30	GlcNAc6S-IdoA-GlcNS-IdoA2S	25.6	1.0	15.8	2.1	18.9	1.5

31	GlcNS6S-IdoA-GlcNAc-IdoA2S	1.0	0.6	19.2	3.0	8.1	0.6
32	GlcNS6S-IdoA-GlcNS-IdoA2S	22.1	2.8	22.0	2.2	36.9	1.3
33	GlcNAc-IdoA2S-GlcNAc6S-IdoA	0.2	0.2	4.5	1.2	0.5	0.3
34	GlcNAc-IdoA2S-GlcNS6S-IdoA	1.9	0.5	15.5	1.2	13.3	0.8
35	GlcNS-IdoA2S-GlcNAc6S-IdoA	38.2	5.4	44.2	3.9	32.6	1.5
36	GlcNS-IdoA2S-GlcNS6S-IdoA	36.3	1.2	31.3	3.2	49.3	1.0
37	GlcNAc6S-IdoA-GlcNAc6S-IdoA	0.0	0.1	7.5	0.7	0.0	0.4
38	GlcNAc6S-IdoA-GlcNS6S-IdoA	1.6	3.6	9.8	0.9	2.1	0.1
39	GlcNS6S-IdoA-GlcNAc6S-IdoA	2.4	0.1	43.0	4.3	17.3	1.6
40	GlcNS6S-IdoA-GlcNS6S-IdoA	2.7	0.1	51.6	1.9	47.6	2.9
41	GlcNAc6S-IdoA2S-GlcNAc-IdoA	0.1	0.0	14.0	1.6	0.8	0.0
42	GlcNAc6S-IdoA2S-GlcNS-IdoA	0.6	0.2	10.1	1.3	2.9	0.5
43	GlcNS6S-IdoA2S-GlcNAc-IdoA	26.0	1.0	15.8	2.3	7.1	0.9
44	GlcNS6S-IdoA2S-GlcNS-IdoA	24.4	1.4	29.3	2.6	33.2	1.1
45	GlcNAc-IdoA2S-GlcNAc6S-IdoA2S	0.9	0.1	21.7	2.8	2.1	0.7
46	GlcNAc-IdoA2S-GlcNS6S-IdoA2S	36.9	1.4	32.3	4.1	47.0	1.6
47	GlcNS-IdoA2S-GlcNAc6S-IdoA2S	57.3	1.8	94.9	4.8	100.0	8.7
48	GlcNS-IdoA2S-GlcNS6S-IdoA2S	76.9	2.5	49.3	3.0	61.2	1.3
49	GlcNAc6S-IdoA-GlcNAc6S-IdoA2S	0.7	1.1	21.8	2.3	3.9	0.2
50	GlcNAc6S-IdoA-GlcNS6S-IdoA2S	35.5	0.9	44.6	2.1	46.5	1.3
51	GlcNS6S-IdoA-GlcNAc6S-IdoA2S	3.2	0.2	66.9	3.3	46.5	4.5
52	GlcNS6S-IdoA-GlcNS6S-IdoA2S	44.6	1.2	38.0	3.2	43.3	1.3
53	GlcNAc6S-IdoA2S-GlcNAc-IdoA2S	0.6	0.4	26.1	1.7	3.4	0.2
54	GlcNAc6S-IdoA2S-GlcNS-IdoA2S	38.2	1.9	59.9	3.0	27.9	1.3
55	GlcNS6S-IdoA2S-GlcNAc-IdoA2S	35.5	1.3	43.2	2.6	34.5	1.3
56	GlcNS6S-IdoA2S-GlcNS-IdoA2S	63.1	4.1	56.3	4.0	62.6	3.0
57	GlcNAc6S-IdoA2S-GlcNAc6S-IdoA	2.5	0.3	39.2	2.4	8.2	3.4
58	GlcNAc6S-IdoA2S-GlcNS6S-IdoA	4.9	2.9	9.8	2.0	13.0	1.0
59	GlcNS6S-IdoA2S-GlcNAc6S-IdoA	67.8	10.4	82.9	5.7	52.5	1.8
60	GlcNS6S-IdoA2S-GlcNS6S-IdoA	38.8	1.8	37.7	1.0	43.1	4.1
61	GlcNAc6S-IdoA2S-GlcNAc6S-IdoA2S	2.2	0.2	39.9	2.6	7.9	0.8
62	GlcNAc6S-IdoA2S-GlcNS6S-IdoA2S	28.1	3.1	26.6	2.3	27.2	0.6
63	GlcNS6S-IdoA2S-GlcNAc6S-IdoA2S	69.6	2.5	100.0	5.9	75.1	6.1
64	GlcNS6S-IdoA2S-GlcNS6S-IdoA2S	100.0	4.2	80.8	2.1	67.9	2.2

3. Synthetic procedures and characterization data

3-1. Materials and methods

Unless stated otherwise, reactions were performed in oven-dried glassware under an argon atmosphere using freshly dried solvents. Solvents were dried via passage through an activated alumina column under argon. All other commercially obtained reagents were used as received unless otherwise noted. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Visualization of the chromatogram was accomplished by UV, cerium ammonium molybdate, or ninhydrin staining as necessary. ICN silica gel (particle size 0.032–0.063 mm) was used for column chromatography. ^{1}H NMR (Varian Inova-500 MHz and Bruker-400 MHz), and ^{13}C NMR (Varian Inova-125 MHz and Bruker-100 MHz) spectra were recorded using $CDCl_3$, CD_3COCD_3, CD_3OD, or D_2O as solvent(s). Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz, and integration. When necessary, proton and carbon assignments were made by means of ^{1}H-^{1}H gCOSY, ^{1}H-^{13}C gHSQCAD and ^{1}H-^{13}C gHMBCAD. Mass spectra were obtained using a Waters LCT Premier XE high-resolution mass spectrometer at the California Institute of Technology. Sodium heparinate was obtained from Smithfield Bioscience. Abbreviations: fluorenylmethyloxycarbonyl (Fmoc); benzenethiol (SPh); levulinoyl (Lev); 2-naphthyl (Naph); (2-naphthyl)methyl (Nap);; trifluoroacetic anhydride (TFAA); trifluoroacetate (TFA); uronic acid (UA).

General synthetic procedures

General procedure of fluorous solid phase extraction (FSPE) for non-sulfated compounds. The crude residue (less than 0.20 g) was dissolved in 0.80 mL of DMF and loaded onto the cartridge filled with fluorous silica gel (10 g). Non-fluorous compounds were eluted with 20 mL of MeOH/H_2O (3:2, v/v) and 10 mL of MeOH/H_2O (7:3, v/v). The fluorous compounds were eluted with 20 mL of acetone, and the fluorous fraction was concentrated to obtain the desired product.

General procedure of FSPE for *O*-sulfation step. The crude reaction mixture (less than 0.20 g) in DMF (0.50 mL) was loaded onto the cartridge filled with fluorous silica gel (10 g). Non-fluorous compounds were eluted with 20 mL of MeOH/H_2O (1:1, v/v), and fluorous compounds were eluted with 20 mL of acetone. The fluorous fraction was collected and passed through a column of Dowex® 50W X8 Na^+ resin. The resulting solution was concentrated to obtain the desired compound as the sodium salt.

General procedure of FSPE for hydrolysis, N_3 to NH_2, *N*-acetylation, and *N*-sulfation steps. The crude reaction mixture (less than 0.20 g) was dissolved in a mixture of MeOH and water (1:1, v/v, 1.0 mL) and loaded onto the cartridge filled with fluorous silica gel (10 g). Non-fluorous compounds were eluted with 20 mL of MeOH/H_2O (3:7, v/v), and fluorous compounds were eluted with 20 mL of MeOH. The fluorous fraction was collected and passed through a column of Dowex® 50W X8 Na^+ resin. The resulting solution was concentrated to obtain the desired compound as the sodium salt.

N_3 to NHAc. To a solution of starting material (0.040 M) in pyridine thioacetic acid (130 eq.) was added at RT. After stirring for 18 h, the mixture was diluted with DCM and washed with saturated aq. $NaHCO_3$ and then brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (elution with 3:2 $\rightarrow$ 1:2 hexane/EtOAc) to obtain the desired compound.

Cleavage of Fmoc group. Piperidine (10 equiv per Fmoc group) was added to a solution of starting material (0.050 M) in DCM at RT. Stirring was continued until TLC (hexane/EtOAc, 2:1, v/v) indicated disappearance of starting material (~1 h). The solvent was then removed under reduced pressure. The resulting crude material was purified by

FSPE for non-sulfated compounds. The fluorous fraction was concentrated to obtain the desired compound.

Cleavage of Lev group. A solution of starting material (0.030 M) and hydrazine acetate (10 equiv per Lev group) in CH_2Cl_2/CH_3OH (9:1, v/v) was stirred at RT. Stirring was continued until TLC (hexane/EtOAc, 2:1, v/v) indicated disappearance of starting material (~1 h). The solvent was then removed under reduced pressure. The resulting crude material was purified by FSPE for non-sulfated compounds. The fluorous fraction was concentrated to obtain the desired compound.

Cleavage of TBDPS group. To a solution of starting material (0.020 M) in pyridine (1.6 mL) in a plastic conical tube was added hydrogen fluoride pyridine (0.60 mL) at 0 °C. After stirring at RT for 2 h, the reaction was quenched with saturated aq. $NaHCO_3$. The mixture was then extracted with EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting crude material was purified by FSPE for non-sulfated compounds. The fluorous fraction was concentrated to obtain the desired compound.

Cleavage of Nap group. DDQ (10 equiv per Nap group) was added to a solution of starting material (8.0 mM) in DCE/MeOH/PBS (16:4:0.25, v/v/v). Stirring was continued until TLC (hexane/EtOAc, 1:1, v/v) indicated disappearance of starting material (~8 h). The reaction mixture was diluted with DCM, and the organic layer was washed with saturated aq. $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting crude material was purified by FSPE for non-sulfated compounds. The fluorous fraction was concentrated to obtain the desired compound.

***O*-Sulfation.** A solution of the starting material (0.050 M) and $SO_3 \cdot Et_3N$ (10 equiv per OH group) in DMF was stirred at 50 ^oC under argon atmosphere. Stirring was continued until TLC (DCM/MeOH, 7:1, v/v) indicated completion of the reaction (~8–10 h). A mixture of triethylamine and MeOH (1:1, v/v, 0.20 mL) was added, and stirring was continued for 30 min. The mixture was directly transferred to a fluorous silica column and purified by FSPE.

Hydrolysis. The starting material (0.010 M) was dissolved in a mixture of THF and MeOH (1:1, v/v, 2 mL), and 1.0 M aq. LiOH (1.0 mL) was added at RT. The reaction was stirred at RT for 1 h and then at 40 °C until TLC (EtOAc:pyridine:H2O:AcOH, 12:5:3:1, v/v) indicated completion of the reaction (~24-36 h). After completion, 1.0 M aq. NH_4Cl (1.0 mL) was added to quench the reaction, and the reaction mixture was concentrated under reduced pressure to remove THF. The resulting solution was transferred to a fluorous silica column and purified by FSPE. The fluorous fraction was collected and passed through a column of Dowex® 50W X8 Na^+ resin. The resulting solution was concentrated to obtain the desired compound as sodium salt.

N_3 to NH_2. To a solution of the starting material (0.020 M) in THF (1.0 mL) was added aqueous NaOH (0.10 M, 0.45 mL) and PMe_3 in THF (1.0 M solution, 10 equiv per N_3 group). The reaction mixture was stirred at RT until completion of the reaction (~1 h), as determined by MALDI-TOF. The reaction mixture was concentrated to remove THF, and the residue was purified by FSPE to obtain the desired compound.

***N*-Acetylation.** The starting material (0.020 M) was dissolved in a mixture of anhydrous MeOH (1.0 mL) and Et_3N (30 equiv per NH_2 group), to which was added acetic anhydride (20 equiv per NH_2 group). The reaction mixture was stirred for 3 h at RT and concentrated under reduced pressure. The residue was purified by FSPE to obtain the desired compound.

***N*-Sulfation.** To a solution of the starting material (0.020 M) in MeOH (1.0 mL) and trifluoroethane (0.15 mL) were added trimethylamine (0.15 mL), aqueous NaOH (0.10 M, 0.40 mL) and SO_3·Py (15 equiv per NH_2 group). After 1 hour, another batch of SO_3·Py (15 equiv per NH_2 group) was added, and stirring was continued until TLC

(EtOAc:pyridine:H_2O:AcOH, 8:5:3:1, v/v) indicated completion of the reaction (~12 h). The reaction mixture was then concentrated under reduced pressure, and the residue was purified by FSPE to obtain the desired compound.

Hydrogenation. The starting material was dissolved in a mixture of *tert*-butanol and H_2O (1:1, v/v, 8.0 mL) to which $Pd(OH)_2$ on carbon (20%, 4 times the weight of starting material) was added. The resulting mixture was placed under an atmosphere of hydrogen and the reaction progress was monitored by Maldi-TOF. After 16 hours, $Pd(OH)_2$ on carbon (20%, 4 times the weight of starting material) was added. After completion of the reaction, the mixture was filtered, and the residue was washed with a mixture of 1:1 *tert*-butanol/H_2O (8.0 mL). The combined solvents were concentrated under reduced pressure, concentrated, and the resulting residue was purified by Sephadex G15 (elution with H_2O) to give target HS tetrasaccharide.

Glycan microarray

Materials. Dulbecco's phosphate buffered saline (DPBS), 1X was purchased from Corning, bovine serum albumin (BSA) from Fisher BioReagents. Tris-buffered saline with 0.1% Tween-20 (TBST) was prepared by mixing 10 X TBS (0.10 L, Fisher BioReagents), Tween-20 (1.0 g, Millipore Sigma) and ddH_2O (0.90 L). Alexa Fluor 647-conjugated streptavidin was purchased from Invitrogen. Recombinant human his-tagged FGF2 protein (>95% purity) was purchased from Sino Biological. 6x-His Tag monoclonal antibody AF647 was purchased from ThermoFisher. Recombinant human FGF4 (>95% purity), biotinylated anti-human FGF4 antibody (>95% purity), recombinant human IL-8 (CXCL8) (77 a.a.) (>95% purity), and biotinylated anti-human IL-8 antibody (CXCL8) (>95% purity) were purchased from Peprotech. Human FGF2, FGF4, and CXCL8 was reconstituted in 0.1% BSA in PBS before use or as recommended by supplier. Schott NEXTERION® 3-D Hydrogel coated microarray slides were purchased from Applied Microarrays Inc.

Heparan sulfate tetrasaccharide microarray fabrication.

HS oligosaccharides were dissolved in sodium phosphate buffer (pH 8.5, 50 mM) in 9 concentrations: 200 μM, 100 μM, 50 μM, 25 μM, 12.5 μM, 6.25 μM, 3.13 μM, 1.57 μM, 0.79 μM. The robotic arrayer SX (from Scienion, Berlin, Germany) delivered 414 pL of the solution containing oligosaccharides (9 spots per concentration) to the array slides using dispensing nozzle PDC80, P-2040, under ~50% relative humidity at 20 ^{o}C. The array spots had an average diameter of about 70 μm with a distance of 260 μm between the centers of adjacent spots. The slides were incubated in a chamber with saturated $(NH_4)_2SO_4$ solution (81% relative humidity) for 24 h at 20 ^{o}C, and unreacted HS oligosaccharides were removed from the slides by rinsing with deionized water. The remaining *N*-hydroxysuccinimide (NHS) ester groups were blocked by placing slides in a solution containing 50 mM ethanolamine in PBST (137 mM NaCl, 13 mM Na_2HPO_4, 1.6 mM NaH_2PO_4, 2.7 mM KCl, 0.010% Tween-20) at 50 °C for 1.5 h. Slides were rinsed several times with deionized water, dried by centrifugation, and stored before use.

HS tetrasaccharide microarray binding assay and array slide processing

The slide was blocked with 10% BSA in TBST (4.0 mL) with gentle rocking at RT for 1 h, followed by submerging in TBST. This condition was empirically determined to reduce nonspecific binding of proteins to the microarray and to provide optimal signal-to-noise ratios. Next, 5.0 μL of the primary detection protein (2.5 μg, 0.50 μg/mL) solution was transferred to 2.5 mL of TBST w/ 1% BSA in a chamber and the slide was incubated with gentle shaking for 1 h at RT. The slide was then washed two times for 5 min each in TBST (4.0 mL) while gently rocking. After the washes, the slide was incubated with the appropriate biotinylated antibody (3.0 μg, 0.50 μg/mL) in 1% BSA in TBST solution (3.0 mL) with gentle rocking for 1 h. The slide was then washed two times for 5 min in TBST (5.0 mL) while gently rocking. Next, the slide was incubated with 4.0 mL of Alexa Fluor

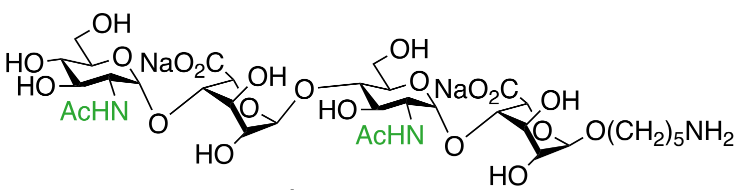
647-conjugated streptavidin detection solution (1.0 μg/mL in TBST w/ 1% BSA) in the dark with gentle rocking for 1 h, washed with TBST (5.0 mL, two times) followed by PBS (45 mL, two times) and ddH_2O (45 mL, two times), and then dried under a gentle stream of 0.2 micron-filtered air. For his-tagged FGF2, detection was accomplished with an AF647-labeled anti-his antibody. All incubations and washes were carried out at RT unless otherwise noted. The microarray was scanned and analyzed at 647 nm using an Agilent G2565CA Microarray Scanner, and fluorescence quantification was performed using ImageJ software with correction for local background. To ensure accurate signal quantification, the average signal intensity was calculated over a fixed area for all spots. Results were plotted with Prism 9 software at a single concentration as background-corrected fluorescence values normalized to the compound with the highest signal. Bar graphs represent the mean ± SD for each compound (50 μM) in nonuplicate. Each experiment was performed 2-3 times. Heat maps were generated in Excel with columns sorted by sulfation status of the amino positions and rows sorted by sulfation status of the 2-*O*- and 6-*O*-hydroxyl groups.

Sulfation Logo Calculations

The sulfation logos were calculated based on methods used to determine DNA consensus sequences for transcription factors that capture enrichment and depletion at each position.[1,2] Each tetrasaccharide was assigned a 6-letter code representing sulfation (S), acetylation (A) or no modification (H) at each position. To generate the logos, the "relative number of binding events" for each compound was calculated by rounding the normalized microarray binding data from the heatmaps down to the nearest integer. This foreground data set was considered to be the number of times a tetrasaccharide sequence appeared in the list of bound sequences and was used to generate a position frequency matrix, where all bound sequences were coded (as described above), and a sum representing the observed frequency of each modification at each position was obtained. From this, a position weight matrix (PWM) was generated by taking the log of the ratio of the observed frequency to the expected frequency. Because our 64-compound library is comprehensitve, the modifications at each position are represented with equal frequency, and the expected frequency for all modifications is 0.5. From the PWMs, sequence logos were visualized as the log likelihood for each modification at each position. The code for generating these logos is publicly available (DOI: 10.5281/zenodo.7787616).

3-2. Synthesis and Characterization of Compounds

1. GlcNAc-IdoA-GlcNAc-IdoA



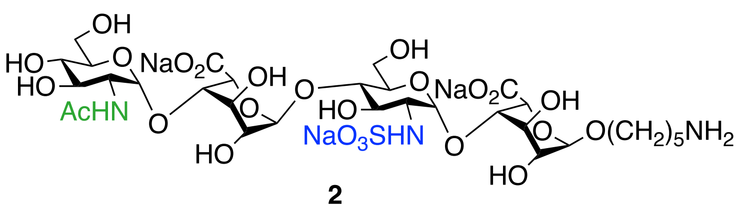
1

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate di sodium salt (1).

Compound **S39** (32 mg, 0.014 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **1** (9.0 mg, 72% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.09 (d, J = 3.6 Hz, 1H, H-1'''), 5.06 (d, J = 3.7 Hz, 1H, H-1'), 4.81 (d, J = 3.7 Hz, 1H, H-1''), 4.76 (d, J = 2.9 Hz, 1H, H-1), 4.64 (d, J = 3.0 Hz, 1H, H-5''), 4.41 (d, J = 2.8 Hz, 1H, H-5), 3.98 (t, J = 3.5 Hz, 1H, H-4''), 3.93 (t, J = 3.1 Hz, 1H, H-4), 3.87–3.81 (m, 3H, H-2', H-2''', H-3), 3.80–3.68 (m, 7H, H-6', H-6''', H-3'', H-5', H-5'''), 3.68–3.47 (m, 7H, H-3''', H-2'', H-4', H-3', H-2, OCH_2), 3.37 (t, J = 9.5 Hz, 1H, H-4'''), 2.89 (t, J = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.91 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6), 174.9 (C-6''), 174.4 (NHC=O), 174.3 (NHC=O), 101.7 (C-1''), 100.7

(C-1), 94.5 (C-1'), 94.3 (C-1'''), 76.7 (C-4'), 74.3 (C-4''), 73.9 (C-4), 71.9 (C-5'''), 71.09 (C-5'), 71.05 (C-3'''), 69.9 (C-5'',C-2''), 69.7 (C-4''', C-3', C-3''), 69.4 (C-2), 68.8 (C-5), 68.6 (C-3), 68.1 (OCH_2), 60.1 (C-6'''), 59.6 (C-6'), 53.7 (C-2'), 53.5 (C-2'''), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.88 (NHC=O*C*H_3), 21.86 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{23}$ [M–2Na+H]$^-$: 860.3148; found: 860.3154.

2. GlcNAc-IdoA-GlcNS-IdoA



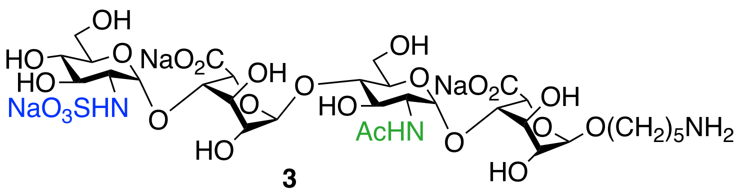
2

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (2).

Compound **S39** (23 mg, 0.010 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **2** (5.0 mg, 53% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.25 (d, *J* = 3.7 Hz, 1H, H-1'), 5.09 (d, *J* = 3.6 Hz, 1H, H-1'''), 4.82 (d, *J* = 3.8 Hz, 1H, H-1''), 4.78 (d, *J* = 2.5 Hz, 1H, H-1), 4.67 (d, *J* = 3.2 Hz, 1H, H-5''), 4.40 (d, *J* = 2.5 Hz, 1H, H-5), 4.03 (t, *J* = 4.0 Hz, 1H, H-3), 3.98 (t, *J* = 3.4 Hz, 1H, H-4''), 3.94 (t, *J* = 2.8 Hz, 1H, H-4), 3.83 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2'''), 3.80–3.70 (m, 7H, H-6', H-6''', H-3'', H-5', H-5'''), 3.68–3.51 (m, 7H, H-3''', H-2'', H-4', H-3', H-2, OCH_2), 3.37 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.14 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2'), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6), 175.0 (C-6''), 174.4 (NHC=O), 101.5 (C-1''), 100.7 (C-1), 95.7 (C-1'), 94.4 (C-1'''), 76.7 (C-4'), 74.8 (C-4), 74.3 (C-4''), 71.9 (C-5'''), 71.0 (C-3'''), 70.9 (C-5'), 69.9 (C-5'',C-2''), 69.7 (C-4''', C-3'), 69.6 (C-3''), 68.9 (C-2), 68.3 (C-5), 68.1 (C-3), 68.0 (OCH_2), 60.1 (C-6' or C-6'''), 59.7 (C-6' or C-6'''), 57.9 (C-2'), 53.5 (C-2'''), 39.3 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9

(NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{25}S$ $[M–3Na+2H]^–$: 898.2611; found: 898.2594.

3. GlcNS-IdoA-GlcNAc-IdoA

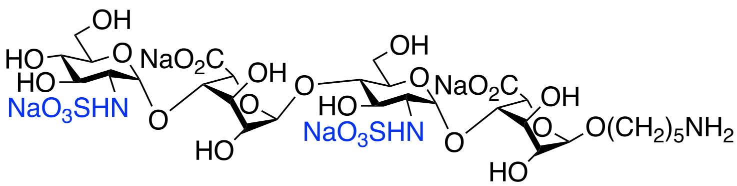


3

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (3).

Compound **S17** (22 mg, 0.0090 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **3** (5.0 mg, 53% for five steps).^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'), 4.84 (d, *J* = 3.2 Hz, 1H, H-1''), 4.76 (d, *J* = 3.0 Hz, 1H, H-1), 4.65 (d, *J* = 2.2 Hz, 1H, H-5''), 4.41 (d, *J* = 2.8 Hz, 1H, H-5), 4.00–3.97 (m, 2H, H-3'', H-4''), 3.93 (t, *J* = 3.1 Hz, 1H, H-4), 3.87–3.81 (m, 2H, H-2', H-3), 3.80–3.61 (m, 10H, H-5', H-6', H-6''', H-5''', H-2'', H-4', H-3', OCH_2), 3.57–3.50 (m, 3H, H-3''', H-2, OCH_2), 3.36 (t, *J* = 9.3 Hz, 1H, H-4'''), 3.11 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6''), 175.0 (C-6), 174.3 (NHC=O), 101.7 (C-1''), 100.8 (C-1), 95.3 (C-1'''), 94.5 (C-1'), 76.9 (C-4'), 74.8 (C-4''), 73.9 (C-4), 71.6 (C-5'''), 71.2 (C-3'''), 71.1 (C-5'), 69.73 (C-4'''), 69.68 (C-3'), 69.4 (C-2), 69.3 (C-5'',C-2''), 68.8 (C-5, C-3''), 68.6 (C-3), 68.1 (OCH_2), 60.2 (C-6'''), 59.6 (C-6'), 57.8 (C-2'''), 53.7 (C-2'), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{25}S$ $[M–3Na+2H]^–$: 898.2611; found: 898.2639.

4. GlcNS-IdoA-GlcNS-IdoA

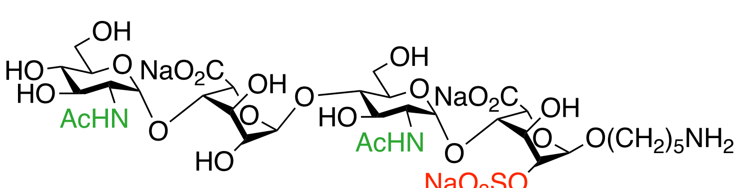


4

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-sulfamino-2-deoxy-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (4).

Compound **S17** (44 mg, 0.019 mmol) was subjected to hydrolysis, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **4** (15 mg, 77% for four steps).^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.25 (d, *J* = 3.5 Hz, 1H, H-1'), 4.85 (d, *J* = 2.7 Hz, 1H, H-1''), 4.79 (d, *J* = 2.1 Hz, 1H, H-1), 4.69 (1H, H-5''), 4.40 (d, *J* = 2.3 Hz, 1H, H-5), 4.04–3.97 (m, 3H, H-3, H-3'', H-4''), 3.94 (t, *J* = 2.8 Hz, 1H, H-4), 3.76–3.70 (m, 6H, H-6', H-6''', H-5', H-5'''), 3.68–3.60 (m, 4H, H-2'', H-4', H-3', OCH_2), 3.57–3.50 (m, 3H, H-2, H-3''', OCH_2), 3.37 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.14 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'), 3.11 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.28 (C-6), 175.24 (C-6''), 101.5 (C-1''), 100.7 (C-1), 95.6 (C-1'), 95.4 (C-1'''), 77.0 (C-4'), 74.8 (C-4 and C-4''), 71.7 (C-5'''), 71.2 (C-3'''), 70.9 (C-5'), 69.7 (C-4''', C-3'), 69.3 (C-5'',C-2''), 68.9 (C-2), 69.7 (C-3''), 68.3 (C-5), 68.1 (C-3 and OCH_2), 60.2 (C-6'''), 59.7 (C-6'), 57.9 (C-2'), 57.8 (C-2'''), 39.3 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{27}S_2$ $[M–4Na+3H]^–$: 936.2073; found: 936.2062.

5. GlcNAc-IdoA-GlcNAc-IdoA2S

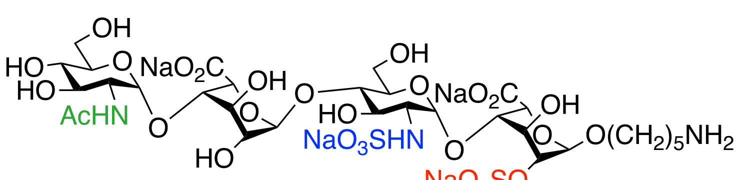


5

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tri sodium salt (5).

Compound **S23** (29 mg, 0.011 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **5** (8.0 mg, 69% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.09 (d, *J* = 3.6 Hz, 1H, H-1'''), 5.02 (d, *J* = 3.7 Hz, 1H, H-1'), 5.01 (s, 1H, H-1), 4.81 (d, *J* = 3.7 Hz, 1H, H-1''), 4.64 (d, *J* = 3.0 Hz, 1H, H-5''), 4.45 (d, *J* = 2.0 Hz, 1H, H-5), 4.15 (t, *J* = 3.5 Hz, 1H, H-3), 4.13–4.12 (m, 1H, H-2), 3.98 (t, *J* = 3.4 Hz, 1H, H-4''), 3.93–3.89 (m, 2H, H-4, H-2'), 3.83 (dd, *J* = 10.5, 3.5 Hz, 1H, H-2'''), 3.81–3.70 (m, 7H, H-6', H-6''', H-3'', H-5', H-5'''), 3.68–3.52 (m, 6H, H-3''', H-2'', H-4', H-3', OCH_2), 3.37 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.96 (s, 3H, $NHC{=}OCH_3$), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6), 174.9 (C-6''), 174.7 (NHC=O), 174.4 (NHC=O), 101.6 (C-1''), 98.5 (C-1), 94.4 (C-1'''), 93.7 (C-1'), 76.7 (C-4'), 74.4 (C-4''), 73.9 (C-2), 71.9 (C-5'''), 71.09 (C-5', C-3'''), 70.9 (C-4), 69.9 (C-5''), 69.8 (C-3',C-2''), 69.7 (C-4''', C-3''), 68.1 (OCH_2), 67.0 (C-5), 64.0 (C-3), 60.1 (C-6'''), 59.7 (C-6'), 53.5 (C-2', C-2'''), 39.4 (NCH_2), 27.7 (CH_2), 26.2 (CH_2), 22.23 (CH_2), 22.16 (NHC=O*C*H_3), 21.86 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{26}S$ $[M{-}3Na{+}2H]^-$: 940.2716; found: 940.2723.

6. GlcNAc-IdoA-GlcNS-IdoA2S

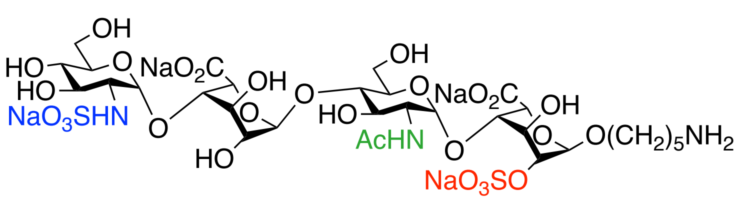


6

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (6).

Compound **S23** (22 mg, 0.0090 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **6** (5.0 mg, 55% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 5.09 (d, *J* = 3.6 Hz, 1H, H-1'''), 5.03 (s, 1H, H-1), 4.82 (d, *J* = 3.8 Hz, 1H, H-1''), 4.67 (d, *J* = 3.2 Hz, 1H, H-5''), 4.39 (d, *J* = 2.5 Hz, 1H, H-5), 4.14–4.13 (m, 2H, H-2, H-3), 3.98 (t, *J* = 3.4 Hz, 1H, H-4''), 3.96–3.95 (m, 1H, H-4), 3.83 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2'''), 3.82–3.75 (m, 3H, H-6', H-3'', H-5'), 3.74–3.69 (m, 4H, H-6''', H-6', H-5'''), 3.69–3.53 (m, 6H, H-3''', H-2'', H-4', H-3', OCH_2), 3.37 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.16 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6''), 174.9 (C-6), 174.4 (NHC=O), 101.4 (C-1''), 98.7 (C-1), 96.9 (C-1'), 94.4 (C-1'''), 76.8 (C-4'), 75.94 (C-4), 75.90 (C-2), 74.3 (C-4''), 71.9 (C-5'''), 71.1 (C-3'''), 70.9 (C-5'), 69.94 (C-5''), 69.90 (C-2''), 69.7 (C-4'''), 69.6 (C-3''), 69.5 (C-3'), 68.6 (C-3), 68.4 (C-5), 68.0 (OCH_2), 60.1 (C-6'''), 59.8 (C-6'), 58.2 (C-2'), 53.5 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ $[M-4Na+3H]^-$: 978.2179; found: 978.2195.

7. GlcNS-IdoA-GlcNAc-IdoA2S



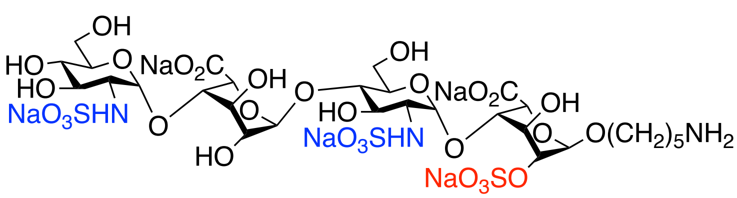
7

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (7).

Compound **89** (25.5 mg, 0.015 mmol) was subjected to *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain

7 (11 mg, 79% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.7 Hz, 1H, H-1'''), 5.02–4.99 (m, 2H, H-1, H-1'), 4.84 (d, *J* = 3.7 Hz, 1H, H-1''), 4.70–4.68 (m, 1H, H-5''), 4.46 (d, *J* = 2.1 Hz, 1H, H-5), 4.18–4.09 (m, 2H, H-2, H-3), 4.03–3.96 (m, 2H, H-3'', H-4''), 3.94–3.89 (m, 2H, H-4, H-2'), 3.82–3.61 (m, 10H, H-3', H-4', H-5', H-6'a, H-6'b, H-2'', H-5''', H-6'''a, H-6'''b, OCH_2), 3.59–3.48 (m, 1H, H-3''', OCH_2), 3.37 (appt, *J* = 9.4 Hz, 1H, H-4'''), 3.10 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.4 Hz, 2H, NCH_2), 1.96 (s, 3H, $C{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.42–1.34 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6), 175.1 (C-6''), 174.7 (*C*ONH), 101.7 (C-1''), 98.5 (C-1), 95.4 (C-1'''), 93.6 (C-1'), 76.9 (C-3'), 74.8 (C-4''), 73.9 (C-2), 71.7 (C-5'''), 71.2 (C-3'''), 71.1 (C-4'), 70.9 (C-4), 69.9 (C-4'''), 69.7 (C-5'), 69.32 (C-2''), 69.28 (C-5''), 68.8 (C-3''), 68.1 (OCH_2), 67.0 (C-5), 64.0 (C-3), 60.2 (C-6'''), 59.7 (C-6'), 57.8 (C-2'''), 53.5 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.24 (CH_2), 22.17 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ $[M{-}4Na{+}3H]^-$: 978.2179; found: 978.2175.

8. GlcNS-IdoA-GlcNS-IdoA2S



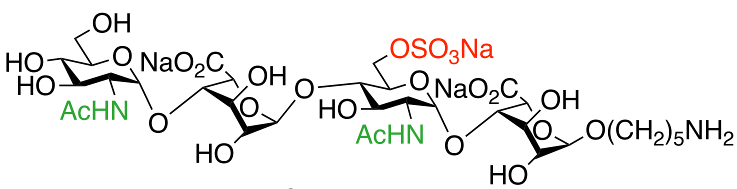
8

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (8).

Compound **89** (38 mg, 0.015 mmol) was subjected to N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **8** (8.2 mg, 49% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.30–5.24 (m, 2H, H-1', H-1'''), 5.06–4.99 (m, 1H, H-1), 4.86 (d, *J* = 3.1 Hz, 1H, H-1''), 4.77 (d, *J* = 2.7 Hz, 1H, H-5''), 4.43 (d, *J* = 2.4 Hz, 1H, H-5), 4.15–4.12 (m, 2H, H-2, H-3), 4.02–3.94 (m, 3H, H-4, H-3'', H-4''), 3.82–3.47 (m, 12H, H-3', H-4', H-5', H-6'a, H-6'b, H-2'', H-3''', H-5''', H-6'''a, H-6'''b, OCH_2), 3.37 (appt, *J*

= 9.6 Hz, 1H, H-4'''), 3.15 (dd, J = 10.1, 3.0 Hz, 1H, H-2'), 3.15 (dd, J = 10.2, 3.5 Hz, 1H, H-2'''), 2.90 (t, J = 7.3 Hz, 2H, NCH_2), 1.63–1.51 (m, 4H, 2 X CH_2), 1.41–1.34 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 174.9 (C-6''), 174.7 (C-6), 101.4 (C-1''), 98.8 (C-1), 97.0 (C-1'''), 95.6 (C-1'), 77.1 (C-3'), 75.9 (C-2, C-4), 74.7 (C-4''), 71.8 (C-5'''), 71.2 (C-3'''), 71.0 (C-4'), 69.7 (C-4'''), 69.5 (C-2''), 69.1 (C-5'), 68.9 (C-5''), 68.52 (C-3''), 68.46 (C-3), 68.3 (C-5), 68.1 (OCH_2), 60.1 (C-6' or C-6'''), 59.8 (C-6' or C-6'''), 58.2 (C-2'), 57.8 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{36}H_{54}N_3O_{30}S_3Na_2$ [M–5Na+4H]$^-$: 1016.1641; found: 1016.1669.

9. GlcNAc-IdoA-GlcNAc6S-IdoA

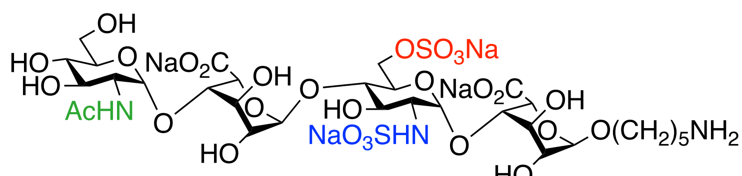


9

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (9).

Compound **S41** (24 mg, 0.0090 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **9** (5.0 mg, 53% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.07 (d, J = 3.5 Hz, 1H, H-1'''), 5.07 (d, J = 3.5 Hz, 1H, H-1'), 4.88 (d, J = 3.3 Hz, 1H, H-1''), 4.76 (d, J = 2.9 Hz, 1H, H-1), 4.66 (d, J = 2.7 Hz, 1H, H-5''), 4.42 (d, J = 2.7 Hz, 1H, H-5), 4.25 (dd, J = 11.3, 2.3 Hz, 1H, H-6'), 4.13 (dd, J = 11.3, 1.5 Hz, 1H, H-6'), 3.98 (t, J = 3.0 Hz, 1H, H-4''), 3.98–3.95 (m, 1H, H-5'), 3.95 (t, J = 3.0 Hz, 1H, H-4), 3.89 (dd, J = 9.8, 3.8 Hz, 1H, H-2'), 3.84–3.79 (m, 3H, H-3'', H-2''', H-3), 3.75–3.70 (m, 3H, H-6', H-6''', H-5'''), 3.69–3.58 (m, 4H, H-3''', H-2'', H-4', H-3', OCH_2), 3.56–3.79 (m, 2H, H-2, OCH_2), 3.37 (t, J = 9.7 Hz, 1H, H-4'''), 2.89 (t, J = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.91 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.01 (C-6''), 174.98 (C-6), 174.5 (NHC=O), 174.3 (NHC=O), 101.9 (C-1''), 100.8 (C-1), 94.5 (C-1' or C-1'''), 94.3 (C-1' or C-1'''), 76.8 (C-4'), 73.95 (C-4''), 73.93 (C-4), 71.9 (C-5'''), 71.1 (C-3'''), 69.8 (C-3'), 69.6 (C-4'''), 69.5 (C-2''), 69.4 (C-5''), 69.3 (C-2), 69.2 (C-5'), 69.0 (C-3''), 68.7 (C-5), 68.5 (C-3), 68.1 (OCH_2), 66.1 (C-6'), 60.1 (C-6'''), 53.5 (C-2' and C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.3 (CH_2), 21.89 (NHC=O*C*H_3 and NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{26}S$ $[M–3Na+2H]^-$: 940.2716; found: 940.2711.

10. GlcNAc-IdoA-GlcNS6S-IdoA



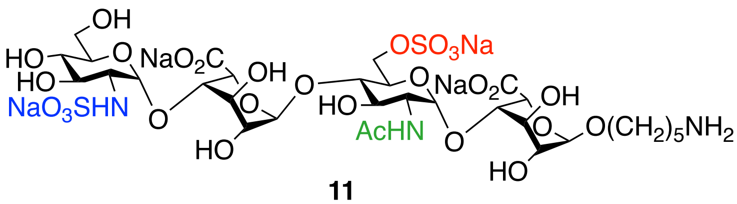
10

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (10).

Compound **S41** (31 mg, 0.012 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **10** (9.0 mg, 69% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.26 (d, J = 3.6 Hz, 1H, H-1'), 5.07 (d, J = 3.6 Hz, 1H, H-1'''), 4.89 (d, J = 3.1 Hz, 1H, H-1''), 4.78 (d, J = 2.3 Hz, 1H, H-1), 4.70 (1H, H-5''), 4.40 (d, J = 2.4 Hz, 1H, H-5), 4.25 (dd, J = 11.2, 2.0 Hz, 1H, H-6'), 4.11 (dd, J = 11.2, 1.5 Hz, 1H, H-6'), 4.02 (t, J = 3.7 Hz, 1H, H-3), 3.98 (t, J = 3.0 Hz, 1H, H-4''), 3.95 (t, J = 2.6 Hz, 1H, H-4), 3.94–3.91 (m, 1H, H-5'), 3.85–3.80 (m, 2H, H-2''', H-3''), 3.75–3.69 (m, 3H, H-6''', H-5'''), 3.67–3.60 (m, 4H, H-3''', H-2'', H-4', OCH_2), 3.59–3.53 (m, 3H, H-3', H-2, OCH_2), 3.37 (t, J = 9.6 Hz, 1H, H-4'''), 3.14 (dd, J = 10.3, 3.5 Hz, 1H, H-2'), 2.90 (t, J = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $NHC=OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6), 175.1 (C-6''), 174.4 (NHC=O), 101.8 (C-1''), 100.7 (C-1), 95.6 (C-1'), 94.3 (C-1'''), 76.8 (C-4'), 74.8 (C-4), 73.9

(C-4''), 71.9 (C-5'''), 71.1 (C-3'''), 69.8 (C-4'''), 69.6 (C-3'), 69.42 (C-2''), 69.36 (C-5''), 78.96 (C-5'), 68.85 (C-3''), 68.82 (C-2), 68.3 (C-5), 68.04 (OCH_2), 68.01 (C-3), 66.2 (C-6'), 60.1 (C-6'''), 57.8 (C-2'), 53.5 (C-2'''), 39.4 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ [M–4Na+3H]$^-$: 978.2179; found: 978.2181.

11. GlcNS-IdoA-GlcNAc6S-IdoA



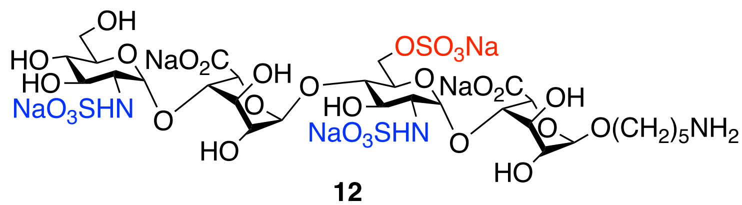
11

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (11).

Compound **S10** (46 mg, 0.019 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **11** (6.3 mg, 32% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.25 (d, *J* = 3.8 Hz, 1H, H-1'''), 5.07 (d, *J* = 3.9 Hz, 1H, H-1'), 4.90 (d, *J* = 2.5 Hz, 1H, H-1''), 4.76 (d, *J* = 3.3 Hz, 1H, H-1), 4.68 (m, 1H, H-5''), 4.42 (d, *J* = 2.9 Hz, 1H, H-5), 4.24 (dd, *J* = 2.6, 11.3 Hz, 1H, H-6'a), 4.13 (dd, *J* = 2.0, 11.3 Hz, 1H, H-6'b), 4.02 (appt, *J* = 4.0 Hz, 1H, H-3''), 3.98–3.93 (m, 3H, H-4, J-5', H-4''), 3.88 (dd, *J* = 3.9, 10.0 Hz, 1H, H-2'), 4.02 (dd, *J* = 3.7, 5.3 Hz, 1H, H-3), 3.74–3.62 (m, 7H, H-3', H-4', H-2'', H-5''', H-6'''a, H-6'''b, OCH_2), 3.57–3.48 (m, 3H, H-2, H-3''', OCH_2), 3.37 (appt, *J* = 9.1 Hz, 1H, H-4'''), 3.09 (dd, *J* = 10.0, 3.8 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.6 Hz, 2H, NCH_2), 1.92 (s, 3H, C=OCH_3), 1.66–1.49 (m, 4H, 2 X CH_2), 1.41–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 175.0 (C-6), 174.3 (*C*ONH), 102.1 (C-1''), 100.8 (C-1), 95.5 (C-1'''), 94.5 (C-1'), 77.4 (C-4'), 74.4 (C-4 or C-4''), 74.0 (C-4 or C-4''), 71.6 (C-5'''), 71.3 (C-3'''), 69.9 (C-3'), 69.7 (C-4'''), 69.4 (C-2), 69.2 (C-5'), 68.8 (C-2''), 68.7 (C-5), 68.64 (C-5''), 68.58 (C-3), 68.1 (OCH_2), 67.9 (C-

3''), 66.2 (C-6'), 60.2 (C-6'''), 57.9 (C-2'''), 53.6 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.3 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ [M–4Na+3H]$^-$: 978.2179; found: 978.2157.

12. GlcNS-IdoA-GlcNS6S-IdoA

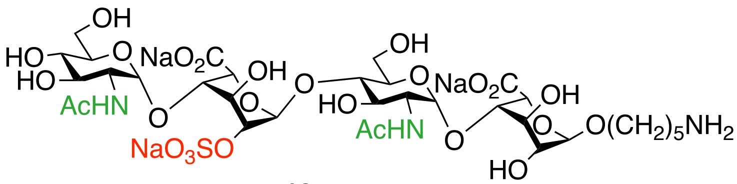


12

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (12).

Compound **S10** (46 mg, 0.019 mmol) was subjected to hydrolysis, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **12** (7.5 mg, 36% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.7 Hz, 1H, H-1'), 5.24 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.91 (d, *J* = 2.5 Hz, 1H, H-1''), 4.78 (d, *J* = 2.7 Hz, 1H, H-1), 4.71 (m, 1H, H-5''), 4.40 (d, *J* = 2.8 Hz, 1H, H-5), 4.24 (dd, *J* = 2.3, 11.3 Hz, 1H, H-6'a), 4.11 (dd, *J* = 2.3, 11.3 Hz, 1H, H-6'b), 4.04–4.00 (m, 1H, H-3, H-3''), 3.98–3.90 (m, 3H, H-4, H-5', H-4''), 3.72–3.51 (m, 10H, H-2, H-3', H-4', H-2'', H-3''', H-5''', H-6'''a, H-6'''b, OCH_2), 3.37 (appt, *J* = 9.5 Hz, 1H, H-4'''), 3.16 (dd, *J* = 10.3, 3.8 Hz, 1H, H-2'), 3.08 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.4 Hz, 2H, NCH_2), 1.92 (s, 3H, C=OCH_3), 1.66–1.49 (m, 4H, 2 X CH_2), 1.41–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.5 (C-6''), 175.2 (C-6), 101.9 (C-1''), 100.7 (C-1), 95.60 (C-1'), 95.56 (C-1'''), 77.5 (C-4'), 74.83 (C-4 or C-4''), 74.33 (C-4 or C-4''), 71.6 (C-5'''), 71.3 (C-3'''), 69.8 (C-3'), 69.7 (C-4'''), 69.0 (C-2), 68.9 (C-5'), 68.6 (C-2'', C-5''), 68.3 (C-5), 68.1 (C-3 or C-3''), 68.0 (C-3 or C-3''), 67.8 (OCH_2), 66.2 (C-6'), 60.2 (C-6'''), 57.9 (C-2 and C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.3 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{30}S_3$ [M–5Na+4H]$^-$: 1016.1641; found: 1016.1660.

13. GlcNAc-IdoA2S-GlcNAc-IdoA

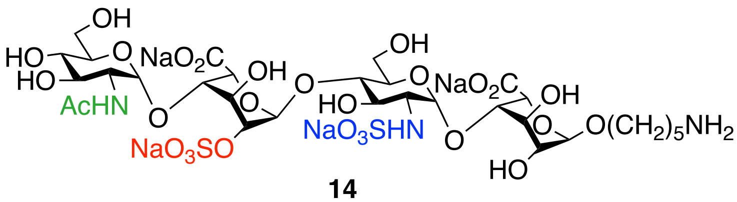


13

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (13).

Compound **S47** (35 mg, 0.014 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **13** (11 mg, 78% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.09 (s, 1H, H-1''), 5.06 (d, *J* = 3.6 Hz, 1H, H-1'), 5.01 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.80 (d, *J* = 1.7 Hz, 1H, H-5''), 4.76 (d, *J* = 3.0 Hz, 1H, H-1), 4.41 (d, *J* = 2.8 Hz, 1H, H-5), 4.23 (s, 1H, H-2''), 4.19 (s, 1H, H-3''), 3.94–3.93 (m, 2H, H-4'', H-4), 3.89–3.81 (m, 3H, H-2', H-2''', H-3), 3.80–3.65 (m, 8H, H-6', H-6''', H-3', H-5', H-5''', OCH_2), 3.65–3.47 (m, 4H, H-3''', H-4', H-2, OCH_2), 3.36 (t, *J* = 9.0 Hz, 1H, H-4'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.91 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.7 (C-6''), 174.9 (C-6), 174.8 (NHC=O), 174.3 (NHC=O), 100.8 (C-1), 99.2 (C-1''), 94.5 (C-1'), 93.5 (C-1'''), 77.1 (C-4'), 73.9 (C-4), 73.3 (C-2''), 71.9 (C-5'''), 71.27 (C-5'), 71.25 (C-3'''), 70.3 (C-4''), 69.7 (C-4'''), 69.6 (C-3'), 69.5 (C-2), 68.9 (C-5), 68.7 (C-3), 68.1 (OCH_2), 67.4 (C-5''), 63.3 (C-3''), 60.2 (C-6'''), 59.6 (C-6'), 53.9 (C-2'), 53.3 (C-2'''), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.23 (CH_2), 22.19 ($NHC{=}O\mathit{C}H_3$), 21.88 ($NHC{=}O\mathit{C}H_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{26}S$ $[M{-}3Na{+}2H]^-$: 940.2716; found: 940.2701.

14. GlcNAc-IdoA2S-GlcNS-IdoA

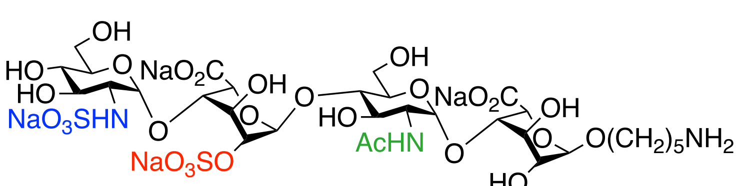


14

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (14).

Compound **S47** (35 mg, 0.014 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **14** (11 mg, 75% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.6 Hz, 1H, H-1'), 5.09 (s, 1H, H-1''), 5.01 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.84 (d, *J* = 1.7 Hz, 1H, H-5''), 4.78 (d, *J* = 2.6 Hz, 1H, H-1), 4.40 (d, *J* = 2.4 Hz, 1H, H-5), 4.22 (s, 1H, H-2''), 4.19 (s, 1H, H-3''), 4.02 (t, *J* = 3.9 Hz, 1H, H-3), 3.94–3.93 (m, 2H, H-4'', H-4), 3.88 (dd, *J* = 10.4, 3.4 Hz, 1H, H-2'''), 3.78–3.64 (m, 7H, H-6', H-6''', H-5', H-5''', OCH_2), 3.64–3.51 (m, 5H, H-3', H-3''', H-4', H-2, OCH_2), 3.36 (t, *J* = 9.3 Hz, 1H, H-4'''), 3.13 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2'), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.8 (C-6''), 175.2 (C-6), 174.8 (NHC=O), 100.7 (C-1), 99.1 (C-1''), 95.6 (C-1'), 93.5 (C-1'''), 77.2 (C-4'), 74.8 (C-4), 73.3 (C-2''), 71.8 (C-5'''), 71.3 (C-3'''), 71.0 (C-5'), 70.3 (C-4''), 69.8 (C-4'''), 69.7 (C-3'), 69.0 (C-2), 68.5 (C-5), 68.3 (C-3), 68.0 (OCH_2), 67.4 (C-5''), 63.2 (C-3''), 60.2 (C-6'''), 59.7 (C-6'), 58.1 (C-2'), 53.3 (C-2'''), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.22 (CH_2), 22.20 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ $[M–4Na+3H]^-$: 978.2179; found: 978.2172.

15. GlcNS-IdoA2S-GlcNAc-IdoA

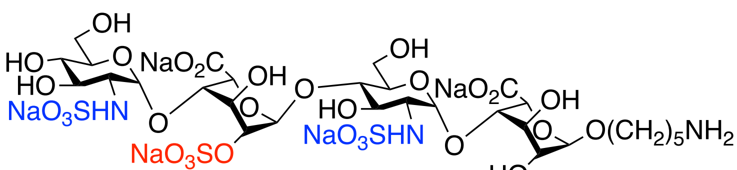


15

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (15).

Compound **S20** (48 mg, 0.019 mmol) was subjected to hydrolysis, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **15** (5.1 mg, 28% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.23 (d, *J* = 3.6 Hz, 1H, H-1'''), 5.13 (d, *J* = 2.6 Hz, 1H, H-1''), 5.06 (d, *J* = 3.6 Hz, 1H, H-1'), 4.76 (d, *J* = 2.7 Hz, 1H, H-1), 4.72 (m, 1H, H-5''), 4.41 (d, *J* = 3.1 Hz, 1H, H-5), 4.24 (dd, *J* = 2.6, 4.4 Hz, 1H, H-2''), 4.14 (appt, *J* = 4.4 Hz, H-3''), 3.97–3.92 (m, 2H, H-4, H-4''), 3.88–3.82 (m, 3H, H-3, H-2', H-6'a), 3.78-3.63 (m, 8H, H-3', H-4', H-5', H-6'b, H-5''', H-6'''a, H-6'''b, OCH_2), 3.59–3.53 (m, 2H, H-3''', OCH_2), 3.49 (dd, *J* = 2.7, 5.6 Hz, 1H, H-2), 3.58 (appt, *J* = 9.7 Hz, 1H, H-4'''), 3.11 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $C{=}OCH_3$), 1.62–1.50 (m, 4H, 2 X CH_2), 1.39–1.30 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6''), 174.9 (C-6), 174.3 (*C*ONH), 100.8 (C-1), 99.2 (C-1''), 97.1 (C-1'''), 94.5 (C-1'), 76.9 (C-4'), 75.6 (C-4''), 75.0 (C-2''), 74.1 (C-4), 71.6 (C-5'''), 71.3 (C-5'), 71.0 (C-3'''), 69.9 (C-4'''), 69.6 (2C, C-2, C-3'), 69.1 (C-5), 68.9 (C-3), 68.4 (C-5''), 68.1 (C-3''), 68.0 (OCH_2), 60.2 (C-6'''), 59.6 (C-6'), 58.1 (C-2'''), 53.8 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ $[M{-}4Na{+}3H]^-$: 978.2179; found: 978.2173.

16. GlcNS-IdoA2S-GlcNS-IdoA

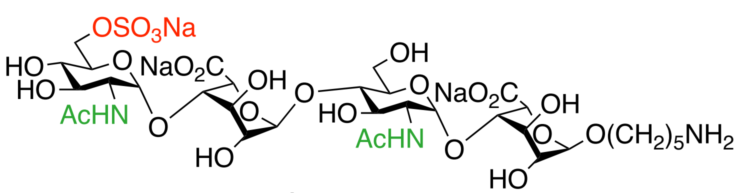


16

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (16).

Compound **S20** (48 mg, 0.019 mmol) was subjected to hydrolysis, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **16** (5.8 mg, 28% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.8 Hz, 1H, H-1'), 5.22 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.15 (bs, 1H, H-1''), 4.78 (d, *J* = 2.9 Hz, 1H, H-1), 4.76 (d, *J* = 2.3 Hz, 1H, H-5''), 4.40 (d, *J* = 2.6 Hz, 1H, H-5), 4.23 (dd, *J* = 1.8, 4.0 Hz, 1H, H-2''), 4.14 (appt, *J* = 4.0 Hz, 1H, H-3''), 4.02 (appt, *J* = 4.0 Hz, 1H, H-3), 3.97–3.91 (m, 2H, H-4, H-4''), 3.83–3.50 (m, 12H, H-2, H-3', H-4', H-5', H-6a', H-6b', H-5''', H-3''', H-6a''', H-6b''', OCH_2), 3.36 (appt, *J* = 8.7 Hz, 1H, H-4'''), 3.17–3.06 (m, 2H, H-2', H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.65–1.49 (m, 4H, 2 X CH_2), 1.41–1.29 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 175.2 (C-6), 100.7 (C-1), 99.1 (C-1''), 97.2 (C-1'''), 95.7 (C-1'), 77.0 (C-4'), 75.6 (C-4''), 74.9 (C-4), 74.7 (C-2''), 71.6 (C-5'), 71.0 (2C, C-3', C-5'''), 69.9 (C-4'''), 69.7 (C-3'''), 69.1 (C-2), 68.5 (C-5), 68.3 (C-3), 68.2 (C-5''), 68.1 (OCH_2), 67.8 (C-3''), 60.2 (C-6'''), 59.7 (C-6'), 58.1 (C-2' or C-2'''), 58.0 (C-2' or C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{30}S_3$ $[M–5Na+4H]^–$: 1016.1641; found: 1016.1647.

17. GlcNAc6S-IdoA-GlcNAc-IdoA



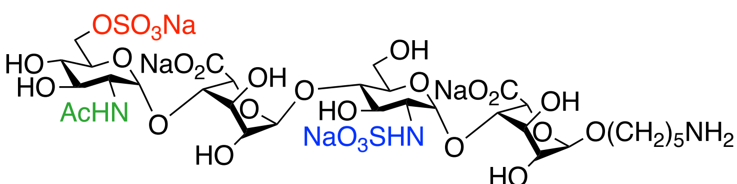
17

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tri sodium salt (17).

Compound **S39** (16 mg, 0.0070 mmol) was subjected to *O*-sulfation, hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **17** (5.0 mg, 70% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.10 (d, *J* =

3.7 Hz, 1H, H-1'''), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'), 4.82 (d, *J* = 3.6 Hz, 1H, H-1''), 4.76 (d, *J* = 3.0 Hz, 1H, H-1), 4.65 (d, *J* = 3.0 Hz, 1H, H-5''), 4.41 (d, *J* = 2.7 Hz, 1H, H-5), 4.25 (dd, *J* = 11.1, 2.9 Hz, 1H, H-6'''), 4.11 (dd, *J* = 11.1, 1.7 Hz, 1H, H-6'''), 4.00 (t, *J* = 3.4 Hz, 1H, H-4''), 3.93 (t, *J* = 2.7 Hz, 1H, H-4), 3.91–3.72 (m, 8H, H-5''', H-2', H-2''', H-3, H-5', H-3'', H-6'), 3.71–3.50 (m, 7H, OCH_2, H-3''', H-3', H-2'', H-4', H-2), 3.47 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $C{=}OCH_3$), 1.92 (s, 3H, $C{=}OCH_3$), 1.64–1.54 (m, 4H, 2 X CH_2), 1.41–1.33 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6), 174.8 (C-6''), 174.34 (*C*ONH), 174.31 (*C*ONH), 101.7 (C-1''), 100.8 (C-1), 94.6 (C-1'), 94.3 (C-1'''), 76.7 (C-4'), 74.3 (C-4''), 74.1 (C-4), 71.1 (C-5'), 71.0 (C-3'''), 70.1 (C-5'''), 69.9 (C-2''), 69.8 (C-5''), 69.6 (C-3''), 69.4 (C-3', C-2), 69.1 (C-4'''), 68.9 (C-5), 68.7 (C-3), 68.1 (OCH_2), 66.4 (C-6'''), 59.6 (C-6'), 53.7 (C-2'), 53.3 (C-2'''), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($CH_3C{=}ONH$, $CH_3C{=}ONH$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{26}S$ $[M–3Na+2H]^-$: 940.2716; found: 940.2693.

18. GlcNAc6S-IdoA-GlcNS-IdoA



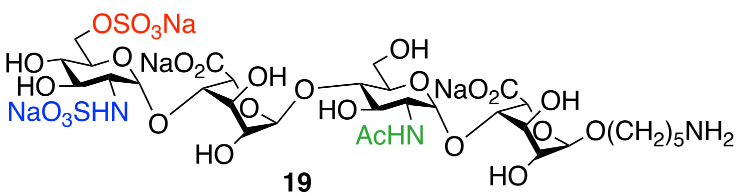
18

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (18).

Compound **S39** (11 mg, 0.0052 mmol) was subjected to *O*-sulfation, hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **18** (3.0 mg, 61% for four steps). ^1H NMR (400 MHz, D_2O): δ 5.27 (d, *J* = 3.5 Hz, 1H, H-1'), 5.12 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.84 (d, *J* = 3.6 Hz, 1H, H-1''), 4.80 (d, *J* = 2.2 Hz, 1H, H-1), 4.65 (d, *J* = 2.1 Hz, 1H, H-5''), 4.41 (d, *J* = 2.2 Hz, 1H, H-5), 4.28 (dd, *J* = 11.2, 2.7 Hz, 1H, H-6'''), 4.12 (dd, *J* = 11.2, 1.7 Hz, 1H, H-6'''), 4.05 (t, *J* = 3.7 Hz, 1H, H-3), 4.02 (t,

J = 3.1 Hz, 1H, H-4''), 3.95 (t, J = 2.7 Hz, 1H, H-4), 3.92–3.88 (m, 1H, H-5'''), 3.87 (dd, J = 10.5, 3.6 Hz, 1H, H-2'''), 3.81–3.74 (m, 4H, H-3'', H-5', H-6'), 3.71–3.53 (m, 7H, OCH_2, H-3''', H-3', H-2'', H-4', H-2), 3.49 (t, J = 9.7 Hz, 1H, H-4'''), 3.16 (dd, J = 10.0, 3.6 Hz, 1H, H-2'), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.94 (s, 3H, $C{=}OCH_3$), 1.64–1.54 (m, 4H, 2 X CH_2), 1.41–1.33 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6), 174.9 (C-6''), 174.3 (*C*ONH), 101.4 (C-1''), 100.7 (C-1), 95.7 (C-1'), 94.3 (C-1'''), 76.8 (C-4'), 74.9 (C-4), 74.3 (C-4''), 71.0 (C-3'''), 70.9 (C-5'), 70.1 (C-5'''), 69.86 (C-5''), 69.84 (C-3'), 69.6 (C-3''), 69.5 (C-2''), 69.1 (C-4'''), 69.0 (C-2), 68.4 (C-5), 68.2 (C-3), 68.0 (OCH_2), 66.3 (C-6'''), 59.7 (C-6'), 57.9 (C-2'), 53.4 (C-2'''), 39.3 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($CH_3C{=}O$); HRMS (ESI-TOF) calcd for $C_{31}H_{49}N_3O_{28}S_2Na_3$ $[M-Na]^-$: 1044.1637; found: 1044.1621.

19. GlcNS6S-IdoA-GlcNAc-IdoA

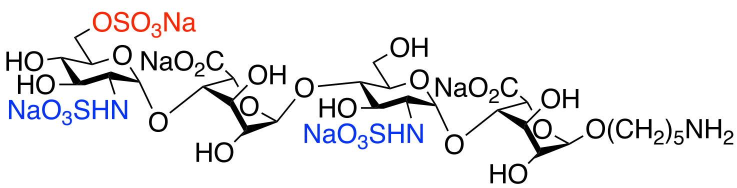


19

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (19).

Compound **S18** (22 mg, 0.0091 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **19** (5.0 mg, 51% for five steps). ^1H NMR (400 MHz, D_2O): δ 5.31 (d, J = 3.3 Hz, 1H, H-1'''), 5.06 (d, J = 3.6 Hz, 1H, H-1'), 4.85 (d, J = 2.9 Hz, 1H, H-1''), 4.77 (d, J = 2.8 Hz, 1H, H-1), 4.67 (d, J = 2.2 Hz, 1H, H-5''), 4.41 (d, J = 2.5 Hz, 1H, H-5), 4.26 (dd, J = 11.1, 2.5 Hz, 1H, H-6'''), 4.09 (dd, J = 11.1, 1.5 Hz, 1H, H-6'''), 4.00–3.99 (m, 2H, H-3'', H-4''), 3.94 (t, J = 2.7 Hz, 1H, H-4), 3.88–3.73 (m, 6H, H-2', H-3, H-5''', H-5', H-6'), 3.71–3.61 (m, 4H, H-2'', H-4', H-3', OCH_2), 3.57–3.44 (m, 4H, H-3''', H-2, OCH_2, H-4'''), 3.14 (dd, J = 9.9, 3.4 Hz, 1H, H-2'''), 2.90 (t, J = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6''), 175.0 (C-6), 174.3 (NHC=O), 101.7 (C-1''), 100.8 (C-1), 95.3 (C-1'''), 94.5 (C-1'), 76.9 (C-4'), 74.8 (C-4''), 74.0 (C-4), 71.1 (C-3''' and C-5'), 69.9 (C-5'''), 69.7 (C-3'), 69.4 (C-2''), 69.3 (C-2), 69.2 (C-5''), 69.1 (C-4'''), 68.9 (C-5), 68.8 (C-3''), 68.7 (C-3), 68.1 (OCH_2), 66.4 (C-6'''), 59.6 (C-6'), 57.7 (C-2'''), 53.7 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{28}S_2$ $[M{-}4Na{+}3H]^-$: 978.2179; found: 978.2166.

20. GlcNS6S-IdoA-GlcNS-IdoA



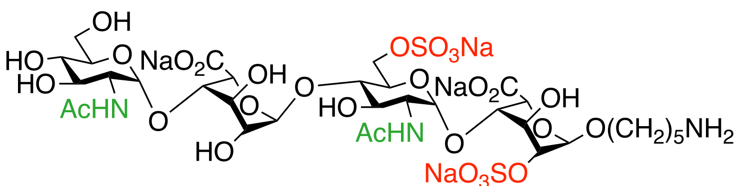
20

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (20).

Compound **S18** (42 mg, 0.017 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **20** (12 mg, 61% for five steps). ^1H NMR (400 MHz, D_2O): δ 5.31 (d, J = 3.5 Hz, 1H, H-1'''), 5.26 (d, J = 3.5 Hz, 1H, H-1'), 4.86 (d, J = 2.9 Hz, 1H, H-1''), 4.79 (d, J = 2.0 Hz, 1H, H-1), 4.70 (1H, H-5''), 4.41 (d, J = 2.1 Hz, 1H, H-5), 4.27 (dd, J = 11.0, 2.5 Hz, 1H, H-6'''), 4.09 (dd, J = 11.0, 1.5 Hz, 1H, H-6'''), 4.03 (t, J = 3.5 Hz, 1H, H-3), 4.01–3.99 (m, 2H, H-3'', H-4''), 3.94 (t, J = 2.7 Hz, 1H, H-4), 3.87–3.84 (m, 1H , H-5'''), 3.78–3.72 (m, 3H, H-6', H-5'), 3.69–3.50 (m, 7H, H-2'', H-4', H-3', OCH_2, H-2, H-3'''), 3.48 (t, J = 9.3 Hz, 1H, H-4'''), 3.15 (dd, J = 10.0, 3.6 Hz, 1H, H-2'), 3.15 (dd, J = 10.0, 3.6 Hz, 1H, H-2'''), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H,

CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6), 175.2 (C-6''), 101.6 (C-1''), 100.7 (C-1), 95.6 (C-1'), 95.4 (C-1'''), 77.1 (C-4'), 74.8 (C-4 and C-4''), 71.1 (C-3'''), 70.9 (C-5'), 69.9 (C-5'''), 69.7 (C-3'), 69.3 (C-2''), 69.2 (C-5''), 69.1 (C-4'''), 68.9 (C-2), 68.7 (C-3''), 68.3 (C-5), 68.1 (C-3 and OCH_2), 66.4 (C-6'''), 59.7 (C-6'), 57.9 (C-2'), 57.7 (C-2'''), 39.4 (NCH_2), 27.9 (CH_2), 26.3 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{28}S_3$ [M–5Na+4H]$^-$: 1016.1641; found: 1016.1664.

21. GlcNAc-IdoA-GlcNAc6S-IdoA2S



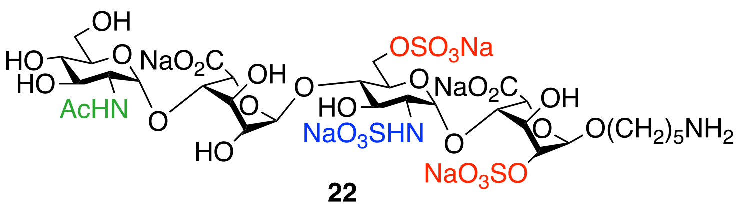
21

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (21).

Compound **S25** (25 mg, 0.010 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **21** (7.0 mg, 65% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.07 (d, J = 3.5 Hz, 1H, H-1'''), 5.02 (d, J = 3.5 Hz, 1H, H-1'), 5.01 (s, 1H, H-1), 4.87 (d, J = 3.1 Hz, 1H, H-1''), 4.67 (d, J = 2.7 Hz, 1H, H-5''), 4.41 (d, J = 1.9 Hz, 1H, H-5), 4.25 (dd, J = 11.2, 2.6 Hz, 1H, H-6'), 4.17 (dd, J = 11.2, 1.4 Hz, 1H, H-6'), 4.15 (s, 1H, H-3), 4.13 (s, 1H, H-2), 3.99–3.92 (m, 4H, H-4'', H-4, H-5', H-2'), 3.85–3.80 (m, 2H, H-2''', H-3''), 3.74–3.53 (m, 9H, H-6''', H-5''', H-3''', H-2'', H-4', H-3', OCH_2), 3.37 (t, J = 9.5 Hz, 1H, H-4'''), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.96 (s, 3H, $NHC{=}OCH_3$), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6), 175.1 (C-6''), 174.7 (NHC=O), 174.4 (NHC=O), 101.8 (C-1''), 98.5 (C-1), 94.3 (C-1'''), 93.7 (C-1'), 76.7 (C-4'), 74.0 (C-4''), 73.9

(C-2), 71.9 (C-5'''), 71.1 (C-3'''), 71.0 (C-4, C-3'), 69.6 (C-4'''), 69.48 (C-2''), 69.45 (C-5''), 69.1 (C-5'), 69.0 (C-3''), 68.1 (OCH_2), 66.9 (C-5), 66.2 (C-6'), 63.9 (C-3), 60.1 (C-6'''), 53.5 (C-2'''), 53.4 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.3 (NHC=OCH_3), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ [M–4Na+3H]$^-$: 1020.2284; found: 1020.2263.

22. GlcNAc-IdoA-GlcNS6S-IdoA2S



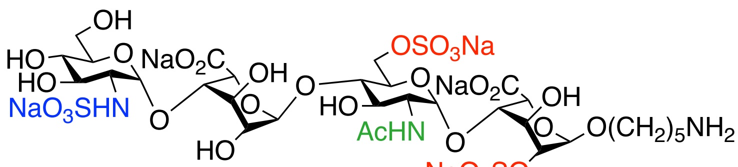
22

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (22).

Compound **S25** (34 mg, 0.014 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **22** (12 mg, 75% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.4 Hz, 1H, H-1'), 5.07 (d, *J* = 3.6 Hz, 1H, H-1'''), 5.05 (s, 1H, H-1), 4.90 (d, *J* = 3.1 Hz, 1H, H-1''), 4.73 (d, *J* = 2.8 Hz, 1H, H-5''), 4.42 (d, *J* = 2.3 Hz, 1H, H-5), 4.25 (dd, *J* = 11.3, 2.0 Hz, 1H, H-6'), 4.16–4.14 (m, 2H, H-6', H-2, H-3), 4.00–3.96 (m, 3H, H-4'', H-4, H-5'), 3.85–3.82 (m, 2H, H-2''', H-3''), 3.74–3.53 (m, 9H, H-6''', H-5''', H-3''', H-2'', H-4', H-3', OCH_2), 3.38 (t, *J* = 9.3 Hz, 1H, H-4'''), 3.19 (dd, *J* = 10.1, 3.4 Hz, 1H, H-2'), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6''), 174.8 (C-6), 174.5 (NHC=O), 101.7 (C-1''), 98.7 (C-1), 97.1 (C-1'), 94.4 (C-1'''), 76.8 (C-4'), 75.9 (C-4), 75.7 (C-2), 73.9 (C-4''), 71.9 (C-5'''), 71.1 (C-3'''), 69.6 (C-4''', C-3'), 69.3 (C-2''), 69.2 (C-5''), 69.1 (C-5'), 68.7 (C-3''), 68.3 (C-3), 68.12 (C-5), 68.08 (OCH_2), 66.2 (C-6'), 60.1 (C-6'''), 58.0 (C-2'), 53.5 (C-2'''), 39.4 (NCH_2), 27.8

(CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ $[M{-}5Na{+}4H]^-$: 1058.1747; found: 1058.1744.

23. GlcNS-IdoA-GlcNAc6S-IdoA2S

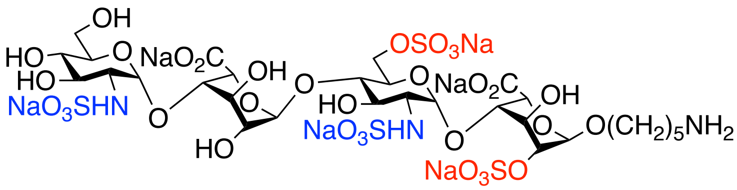


23

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (23).

Compound **88** (30 mg, 0.015 mmol) was subjected to *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **23** (14 mg, 78% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, J = 3.6 Hz, 1H, H-1'''), 5.02 (d, J = 3.5 Hz, 1H, H-1'), 5.02 (s, 1H, H-1), 4.90 (d, J = 2.1 Hz, 1H, H-1''), 4.70 (d, 1H, H-5''), 4.47 (d, J = 2.0 Hz, 1H, H-5), 4.24 (dd, J = 11.2, 2.6 Hz, 1H, H-6'), 4.19–4.13 (m, 3H, H-6', H-2, H-3), 4.03 (t, J = 4.1 Hz, 1H, H-3'') 3.99–3.92 (m, 4H, H-4'', H-4, H-2', H-5'), 3.72–3.61 (m, 7H, H-6''', H-5''', H-2'', H-4', H-3', OCH_2), 3.58–3.52 (m, 2H, H-3''', OCH_2), 3.37 (t, J = 9.2 Hz, 1H, H-4'''), 3.10 (dd, J = 10.3, 3.5 Hz, 1H, H-2'''), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 175.2 (C-6), 174.7 (NHC=O), 102.0 (C-1''), 98.5 (C-1), 95.5 (C-1'''), 93.7 (C-1'), 77.3 (C-4'), 74.4 (C-4''), 73.9 (C-2), 71.6 (C-5'''), 71.3 (C-3'''), 71.0 (C-4), 70.0 (C-3'), 69.7 (C-4'''), 69.1 (C-5'), 68.7 (C-5'',C-2''), 68.1 (OCH_2), 67.9 (C-3''), 66.9 (C-5), 66.2 (C-6'), 63.9 (C-3), 60.2 (C-6'''), 57.8 (C-2'''), 53.4 (C-2'), 39.4 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.3 (NHC=OCH_3), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ $[M{-}5Na{+}4H]^-$: 1058.1747; found: 1058.1744.

24. GlcNS-IdoA-GlcNS6S-IdoA2S

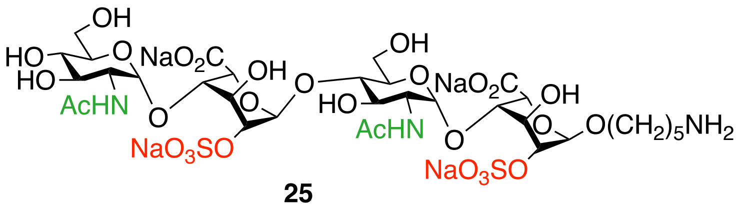


24

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (24).

Compound **88** (25 mg, 0.013 mmol) was subjected to N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **24** (12 mg, 78% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 5.26 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.05 (d, *J* = 1.3 Hz, 1H, H-1), 4.93 (d, *J* = 1.8 Hz, 1H, H-1''), 4.74 (d, *J* = 2.5 Hz, 1H, H-5''), 4.41 (d, *J* = 2.5 Hz, 1H, H-5), 4.25 (dd, *J* = 11.2, 2.0 Hz, 1H, H-6'), 4.17–4.12 (m, 3H, H-6', H-2, H-3), 4.03 (t, *J* = 4.0 Hz, 1H, H-3'') 3.98–3.96 (m, 3H, H-4'', H-4, H-5'), 3.72–3.53 (m, 9H, H-6''', H-5''', H-2'', H-4', H-3', H-3''', OCH_2), 3.38 (t, *J* = 9.3 Hz, 1H, H-4'''), 3.18 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'), 3.10 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.6 (C-6''), 174.8 (C-6), 101.9 (C-1''), 98.7 (C-1), 97.0 (C-1'), 95.5 (C-1'''), 77.5 (C-4'), 75.9 (C-4''), 75.8 (C-2), 74.3 (C-4), 71.6 (C-5'''), 71.3 (C-3'''), 69.7 (C-4'''), 69.6 (C-3'), 69.0 (C-5'), 68.6 (C-2''), 68.5 (C-5''), 68.4 (C-3), 68.2 (C-5), 68.1 (OCH_2), 67.7 (C-3''), 66.3 (C-6'), 60.2 (C-6'''), 58.1 (C-2'), 57.8 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{33}S_4$ $[M{-}6Na{+}5H]^-$: 1096.1198; found: 1096.1209.

25. GlcNAc-IdoA2S-GlcNAc-IdoA2S

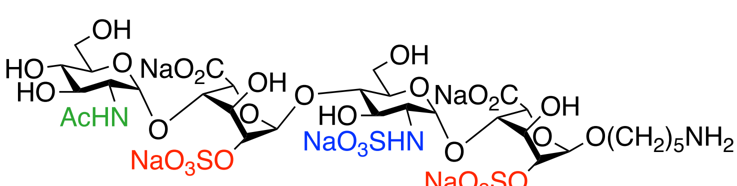


25

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (25).

Compound **S33** (28 mg, 0.011 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **25** (8.0 mg, 65% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.08 (s, 1H, H-1''), 5.02–5.00 (m, 3H, H-1', H-1''', H-1), 4.81 (d, *J* = 1.2 Hz, 1H, H-5''), 4.45 (d, *J* = 1.8 Hz, 1H, H-5), 4.24 (s, 1H, H-2''), 4.20 (s, 1H, H-3''), 4.17 (s, sH, H-3), 4.12 (s, 1H, H-2), 3.94–3.86 (m, 4H, H-4, H-4'', H-2''', H-2'), 3.79–3.67 (m, 6H, H-6', H-6''', H-5', H-5'''), 3.67–3.53 (m, 5H, H-3''', H-4', H-3', OCH_2), 3.36 (t, *J* = 9.2 Hz, 1H, H-4'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.96 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.8 (C-6''), 175.2 (C-6), 174.8 (NHC=O), 174.7 (NHC=O), 99.2 (C-1''), 98.5 (C-1), 93.5 (C-1', C-1'''), 77.2 (C-4'), 73.9 (C-2), 73.2 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 71.2 (C-5'), 70.7 (C-4), 70.3 (C-4''), 69.9(C-3'), 69.7 (C-4'''), 68.1 (OCH_2), 67.3 (C-5''), 67.1 (C-5), 63.8 (C-3), 63.2 (C-3''), 60.2 (C-6'''), 59.7 (C-6'), 53.8 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.24 (NHC=O*C*H_3), 22.20 (CH_2), 22.15 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ $[M–4Na+3H]^–$: 1020.2284; found: 1020.2274.

26. GlcNAc-IdoA2S-GlcNS-IdoA2S

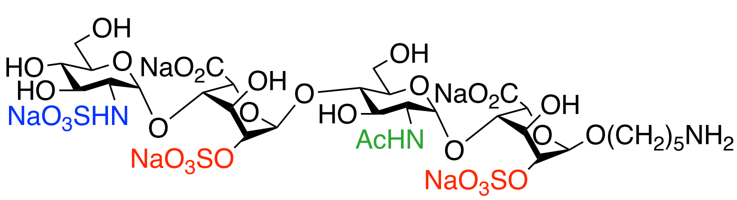


26

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (26).

Compound **S33** (28 mg, 0.011 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **26** (8.0 mg, 64% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'), 5.09 (s, 1H, H-1''), 5.02 (s, 1H, H-1), 5.02 (d, *J* = 3.6 Hz, 1H, H-1'''), 4.86 (d, *J* = 1.8 Hz, 1H, H-5''), 4.40 (d, *J* = 2.7 Hz, 1H, H-5), 4.23 (s, 1H, H-2''), 4.19 (s, 1H, H-3''), 4.15–4.11 (m, 2H, H-2, H-3), 3.96 (t, *J* = 2.6 Hz, 1H, H-4), 3.84 (s, 1H, H-4''), 3.88 (dd, *J* = 10.5, 3.5 Hz, 1H, H-2''',), 3.80–3.67 (m, 6H, H-6', H-6''', H-5', H-5'''), 3.67–3.53 (m, 5H, H-3''', H-4', H-3', OCH_2), 3.37 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.15 (dd, *J* = 9.8, 3.5 Hz, 1H, H-2'), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.8 (C-6''), 174.8 (C-6, NHC=O), 99.1 (C-1''), 98.9 (C-1), 96.7 (C-1'), 93.5 (C-1'''), 77.4 (C-4'), 76.2 (C-2), 75.8 (C-4), 73.2 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 71.0 (C-5'), 70.3 (C-4''), 69.8 (C-4'''), 69.5 (C-3'), 68.8 (C-3), 68.6 (C-5), 68.0 (OCH_2), 67.3 (C-5''), 63.2 (C-3''), 60.2 (C-6'''), 59.7 (C-6'), 58.3 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.20 (CH_2), 22.18 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ $[M{-}5Na{+}4H]^-$: 1058.1747; found: 1058.1742.

27. GlcNS-IdoA2S-GlcNAc-IdoA2S

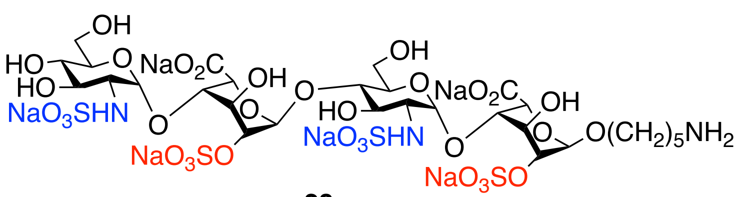


27

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (27).

Compound **90** (18 mg, 0.0081 mmol) was subjected to *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **27** (5.8 mg, 56% for four steps). ^{1}H NMR (400 MHz, D_2O): δ5.21 (d, *J* = 3.4 Hz, 1H, H-1'''), 5.14 (bs, 1H, H-1''), 5.02 (d, *J* = 3.7 Hz, 1H, H-1'), 4.99 (bs, 1H, H-1), 4.74–4.71 (m, 1H, H-5''), 4.45 (d, *J* = 2.0 Hz, 1H, H-5), 4.26–4.23 (m, 1H, H-2''), 4.19–4.09 (m, 3H, H-2, H-3, H-3''), 3.98–3.86 (m, 2H, H-4, H-2', H-4''), 3.83–3.50 (m, 11H, H-3', H-4', H-5', H-6'a, H-6'b, H-3''', H-5''', H-6'''a, H-6'''b, OCH_2), 3.36 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.12 (dd, *J* = 10.3, 3.3 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.96 (s, 3H, $COCH_3$), 1.63–1.51 (m, 4H, 2 X CH_2), 1.40–1.33 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 175.2 (C-6), 174.7 (*C*ONH), 99.2 (C-1''), 98.6 (C-1), 97.3 (C-1'''), 93.4 (C-1'), 77.0 (C-4'), 75.5 (C-4''), 74.6 (C-2''), 74.0 (C-2), 71.6 (C-5'''), 71.3 (C-5'), 71.0 (C-3'''), 70.8 (C-4), 69.89 (C-3' or C-4'''), 69.84 (C-3' or C-4'''), 68.2 (C-5''), 68.1 (OCH_2), 67.7 (C-3''), 67.1 (C-5), 63.9 (C-3), 60.2 (C-6'''), 59.7 (C-6'), 58.2 (C-2'''), 53.6 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.24 (CH_2), 21.9 ($COCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ [M–5Na+4H]$^-$: 1058.1747; found: 1058.1763.

28. GlcNS-IdoA2S-GlcNS-IdoA2S



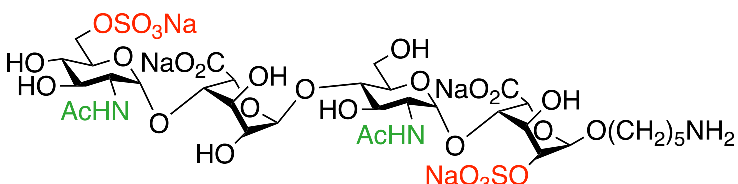
28

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (28).

Compound **90** (22 mg, 0.010 mmol) was subjected to N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **28** (9.0 mg, 68% for three steps). ^{1}H NMR (400 MHz, D_2O): δ5.29 (d, *J* = 3.6 Hz, 1H, H-1'), 5.22 (d, *J*

= 3.5 Hz, 1H, H-1'''), 5.16 (s, 1H, H-1''), 5.02 (d, *J* = 2.0 Hz, 1H, H-1), 4.80 (d, *J* = 2.0 Hz, 1H, H-5''), 4.41 (d, *J* = 2.6 Hz, 1H, H-5), 4.25 (dd, *J* = 3.5, 1.7 Hz, 1H, , H-2''), 4.16–4.11 (m, 3H, H-2, H-3, H-3''), 3.97–3.95 (m, 2H, H-4'', H-4), 3.80–3.70 (m, 6H, H-5', H-5''', H-6''', H-6'), 3.69–3.54 (m, 5H, H-3', H-4', OCH_2, H-3'''), 3.37 (t, *J* = 9.6 Hz, 1H, H-4'''), 3.15 (dd, *J* = 9.4, 3.4 Hz, 1H, H-2'), 3.12 (dd, *J* = 9.5, 3.4 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 174.7 (C-6), 99.0 (C-1''), 98.9 (C-1), 97.4 (C-1'''), 96.7 (C-1'), 77.2 (C-4'), 76.3 (C-2), 75.8 (C-4), 75.5 (C-4''), 74.4 (C-2''), 71.7 (C-5'''), 71.1 (C-5'), 71.0 (C-3'''), 69.9 (C-4'''), 69.5 (C-3'), 68.9 (C-3), 68.6 (C-5), 68.1 (OCH_2, C-5''), 67.6 (C-3''), 60.2 (C-6'''), 59.7 (C-6'), 58.2 (C-2'), 58.1 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 21.9 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{33}S_4$ $[M{-}6Na{+}5H]^-$: 1096.1209; found: 1096.1198.

29. GlcNAc6S-IdoA-GlcNAc-IdoA2S

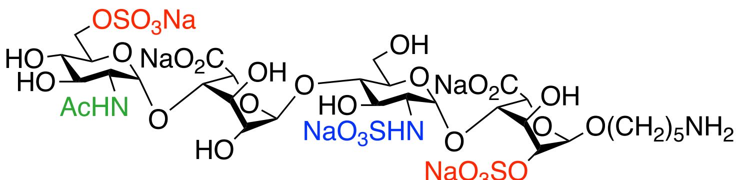


29

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (29).

Compound **S35** (43 mg, 0.018 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **29** (15 mg, 76% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.11 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.02 (d, *J* = 3.5 Hz, 1H, H-1'), 5.01 (s, 1H, H-1), 4.82 (d, *J* = 3.8 Hz, 1H, H-1''), 4.66 (d, *J* = 3.0 Hz, 1H, H-5''), 4.46 (d, *J* = 2.0 Hz, 1H, H-5), 4.26 (dd, *J* = 11.1, 2.1 Hz, 1H, H-6'''), 4.17–4.09 (m, 3H, H-2, H-3, H-6'''), 4.00 (t, *J* = 3.4 Hz, 1H, H-4''), 3.93–3.85 (m, 4H, H-4, H-2', H-2''', H-5'''), 3.81–3.70 (m, 4H, H-6', H-3'', H-5'), 3.68–3.53 (m, 6H, H-3''', H-2'', H-4', H-3', OCH_2), 3.48 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.94 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6), 174.9 (C-6''), 174.7 (NHC=O), 174.4 (NHC=O), 101.6 (C-1''), 98.5 (C-1), 94.4 (C-1'''), 93.7 (C-1'), 76.7 (C-4'), 74.4 (C-4''), 73.9 (C-2), 71.1 (C-5'), 71.0 (C-3'''), 70.9 (C-4), 70.1 (C-5'''), 69.8 (C-5'', C-3',C-2''), 69.6 (C-3''), 69.1 (C-4'''), 68.1 (OCH_2), 67.1 (C-5), 66.4 (C-6'''), 64.0 (C-3), 59.7 (C-6'), 53.5 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 27.7 (CH_2), 26.2 (CH_2), 22.24 (CH_2), 22.18 (NHC=O*C*H_3), 21.9 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ [M–4Na+3H]$^-$: 1020.2284; found: 1020.2266.

30. GlcNAc6S-IdoA-GlcNS-IdoA2S

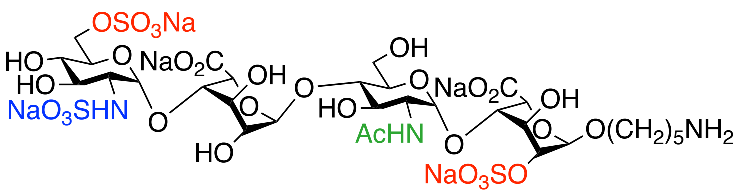


30

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (30).

Compound **S35** (30 mg, 0.013 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **30** (11 mg, 74% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.27 (d, *J* = 3.5 Hz, 1H, H-1'), 5.09 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.03 (s, 1H, H-1), 4.82 (d, *J* = 3.6 Hz, 1H, H-1''), 4.68 (d, *J* = 2.0 Hz, 1H, H-5''), 4.39 (d, *J* = 2.4 Hz, 1H, H-5), 4.26 (dd, *J* = 11.2, 2.9 Hz, 1H, H-6'''), 4.14–4.09 (m, 3H, H-2, H-3, H-6'''), 3.99 (t, *J* = 3.4 Hz, 1H, H-4''), 3.96–3.95 (m, 1H, H-4), 3.90–3.87 (m, 1H, H-5'''), 3.86 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2'''), 3.81–3.70 (m, 4H, H-6', H-3'', H-5'), 3.70–3.53 (m, 6H, H-3''', H-2'', H-4', H-3', OCH_2), 3.37 (t, *J* = 9.6 Hz, 1H, H-4'''), 3.16 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, NHC=OCH$_3$), 1.62–1.52 (m, 4H, 2 X CH$_2$), 1.39–1.31 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, D$_2$O): δ 175.0 (C-6''), 174.9 (C-6), 174.4 (NHC=O), 101.5 (C-1''), 98.7 (C-1), 96.9 (C-1'), 94.4 (C-1'''), 76.9 (C-4'), 75.89 (C-4), 75.86 (C-2), 74.4 (C-4''), 71.0 (C-5'), 70.9 (C-3'''), 70.1 (C-5'''), 69.8 (C-5'', C-2''), 69.5 (C-3'', C-3'), 69.0 (C-4'''), 68.6 (C-3), 68.4 (C-5), 68.0 (OCH$_2$), 66.4 (C-6'''), 59.8 (C-6'), 58.2 (C-2'), 53.4 (C-2'''), 39.4 (NCH$_2$), 27.8 (CH$_2$), 26.2 (CH$_2$), 22.2 (CH$_2$), 21.9 (NHC=O*C*H$_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ [M–5Na+4H]$^-$: 1058.1747; found: 1058.1742.

31. GlcNS6S-IdoA-GlcNAc-IdoA2S



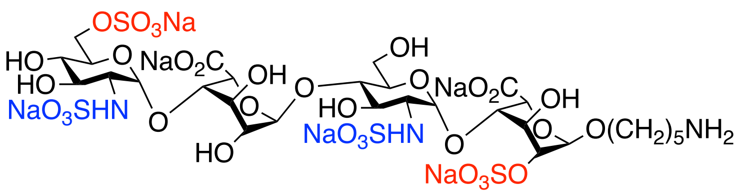
31

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (31).

Compound **91** (31 mg, 0.015 mmol) was subjected to *N*-acetylation, N$_3$ to NH$_2$ conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **31** (11 mg, 66% for four steps). ^{1}H NMR (400 MHz, D$_2$O): δ 5.31 (d, *J* = 3.7 Hz, 1H, H-1'''), 5.04–4.99 (m, 2H, H-1, H-1'), 4.84 (d, *J* = 3.4 Hz, 1H, H-1''), 4.66 (d, *J* = 2.4 Hz, 1H, H-5''), 4.45 (d, *J* = 2.3 Hz, 1H, H-5), 4.26 (dd, *J* = 11.1, 2.6 Hz, 1H, H-6'''a), 4.16–4.06 (m, 2H, H-2, H-3, H-6'''b), 4.01–3.97 (m, 2H, H-3'', H-4''), 3.93–3.89 (m, 2H, H-4, H-2'), 3.87–3.82 (m, 1H, H-5'''), 3.81–3.43 (m, 10H, H-3', H-4', H-5', H-6'a, H-6'b, H-2'', H-3''', H-4''', OCH$_2$), 3.13 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.4 Hz, 2H, NCH$_2$), 1.97 (s, 3H, C=OCH$_3$), 1.66–1.52 (m, 4H, 2 X CH$_2$), 1.42–1.32 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, D$_2$O): δ 175.2 (C-6), 175.1 (C-6''), 174.7 (*C*ONH), 101.6 (C-1''), 98.5 (C-1), 95.3 (C-1'''), 93.6 (C-1'), 76.9 (C-3'), 74.8 (C-4''), 74.0 (C-2), 71.12 (C-4' or C-3'''), 71.09 (C-4' or C-3'''), 70.9 (C-4), 69.8

(2C, C-5' and C-5'''), 69.32 (C-4'''), 69.28 (C-5''), 69.1 (C-2''), 68.8 (C-3''), 68.1 (OCH_2), 67.0 (C-5), 66.4 (C-6'''), 64.1 (C-3), 59.7 (C-6'), 57.7 (C-2'''), 53.5 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ [M–5Na+4H]$^-$: 1058.1747; found: 1058.1741.

32. GlcNS6S-IdoA-GlcNS-IdoA2S

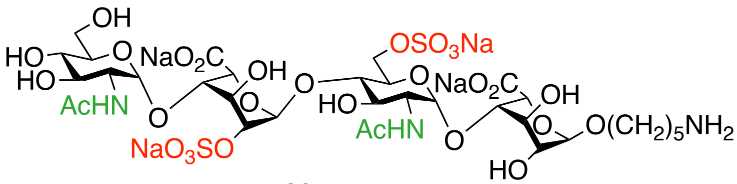


32

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (32).

Compound **91** (21 mg, 0.010 mmol) was subjected to N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **32** (6.3 mg, 52% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.31–5.25 (m, 2H, H-1', H-1'''), 5.02 (bs, 1H, H-1), 4.85 (d, *J* = 3.3 Hz, 1H, H-1''), 4.73–4.68 (m, 1H, H-5''), 4.40 (d, *J* = 2.6 Hz, 1H, H-5), 4.27 (dd, *J* = 11.1, 2.6 Hz, 1H, H-6'''a), 4.15–4.05 (m, 3H, H-2, H-3, H-6'''b), 4.01–3.94 (m, 3H, H-4, H-3'', H-4''), 3.88–3.43 (m, 11H, H-3', H-4', H-5', H-6'a, H-6'b, H-2'', H-3''', H-4''', H-5''', OCH_2), 3.19–3.05 (m, 2H, H-2', H-2'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.61–1.49 (m, 4H, 2 X CH_2), 1.41–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (C-6''), 174.8 (C-6), 101.5 (C-1''), 98.9 (C-1), 96.8 (C-1'''), 95.4 (C-1'), 77.1 (C-3'), 76.3 (C-2), 75.9(C-4), 74.8 (C-4''), 71.1 (C-3'''), 70.9 (C-4'), 69.9 (C-5'''), 69.5 (C-2''), 69.3 (2C, C-5'', C-4'''), 69.1 (C-5'), 68.9 (C-3), 68.7 (C-3''), 68.6 (C-5), 68.0 (OCH_2), 66.4 (C-6'''), 59.8 (C-6'), 58.2 (C-2'), 57.7 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{51}N_3O_{330}S_4$ [M+4H–6Na]$^{2-}$: 547.5566; found: 547.5566.

33. GlcNAc-IdoA2S-GlcNAc6S-IdoA

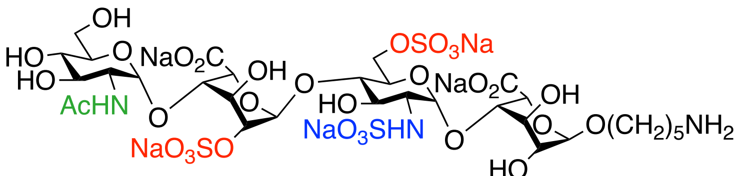


33

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate tetra sodium salt (33).

Compound **S45** (34 mg, 0.013 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **33** (11 mg, 74% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.10 (s, 1H, H-1''), 5.08 (d, *J* = 3.7 Hz, 1H, H-1'), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'''), 4.81 (d, *J* = 2.1 Hz, 1H, H-5''), 4.77 (d, *J* = 3.1 Hz, 1H, H-1), 4.43 (d, *J* = 2.8 Hz, 1H, H-5), 4.25–4.16 (m, 4H, H-2'', H-3'', H-6'), 3.97–3.95 (m, 2H, H-4'', H-4, H-5'), 3.91–3.86 (m, 2H, H-2''', H-2'), 3.84 (dd, *J* = 5.3, 4.0 Hz, 1H, H-3), 3.80–3.66 (m, 6H, H-6''', H-5''', H-3', H-4', OCH_2), 3.63–3.50 (m, 3H, H-3''', H-2, OCH_2), 3.37 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.5 (C-6''), 174.9 (C-6), 174.8 (NHC=O), 174.3 (NHC=O), 100.8 (C-1), 99.1 (C-1''), 94.3 (C-1'), 93.5 (C-1'''), 76.1 (C-4'), 73.9 (C-4), 73.8 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 70.8 (C-4''), 69.8 (C-4''), 69.7 (C-3'), 69.4 (C-2), 69.3 (C-5'), 68.9 (C-5), 68.7 (C-3), 68.1 (OCH_2), 67.9 (C-5''), 66.4 (C-6'), 64.0 (C-3''), 60.3 (C-6'''), 53.6 (C-2'), 53.3 (C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.26 ($NHC{=}OCH_3$), 22.20 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ $[M{-}4Na{+}3H]^{-}$: 1020.2284; found: 1020.2299.

34. GlcNAc-IdoA2S-GlcNS6S-IdoA

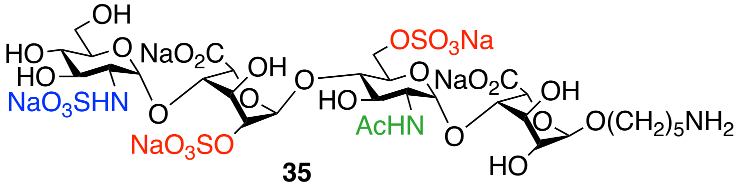


34

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (34).

Compound **S45** (32 mg, 0.013 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **34** (11 mg, 73% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.27 (d, *J* = 3.4 Hz, 1H, H-1'), 5.10 (s, 1H, H-1''), 5.06 (d, *J* = 3.3 Hz, 1H, H-1'''), 4.84 (d, *J* = 1.5 Hz, 1H, H-5''), 4.78 (d, *J* = 2.4 Hz, 1H, H-1), 4.41 (d, *J* = 2.2 Hz, 1H, H-5), 4.25–4.14 (m, 4H, H-2'', H-3'', H-6'), 4.01 (t, *J* = 3.7 Hz, 1H, H-3), 3.97–3.96 (m, 2H, H-4'', H-4), 3.92–3.86 (m, 2H, H-2''', H-5'), 3.79–3.52 (m, 9H, H-6''', H-5''', H-3', H-3''', H-4', H-2, OCH_2), 3.36 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.17 (dd, *J* = 10.3, 3.4 Hz, 1H, H-2'), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.5 (C-6''), 175.1 (C-6), 174.8 (NHC=O), 100.7 (C-1), 99.0 (C-1''), 95.4 (C-1'), 93.5 (C-1'''), 76.1 (C-4'), 74.8 (C-4), 73.8 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 70.7 (C-4''), 69.8 (C-4'', C-3'), 69.1 (C-2, C-5'), 68.5 (C-5), 68.3 (C-3), 68.0 (OCH_2), 67.9 (C-5''), 66.4 (C-6'), 63.9 (C-3''), 60.3 (C-6'''), 57.8 (C-2'), 53.3 (C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.25 (NHC=O*C*H_3), 22.20 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ [M–5Na+4H]$^-$: 1058.1747; found: 1058.1774.

35. GlcNS-IdoA2S-GlcNAc6S-IdoA

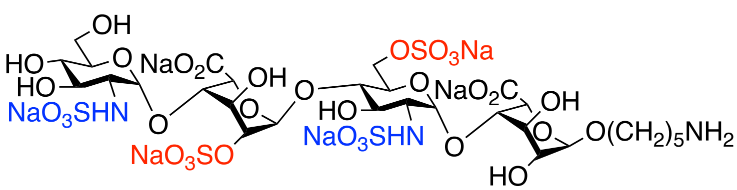


35

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (35).

Compound **S14** (22 mg, 0.0088 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **35** (5.0 mg, 48% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.31 (d, *J* = 3.4 Hz, 1H, H-1'''), 5.11 (d, *J* = 2.6 Hz, 1H, H-1''), 5.07 (d, *J* = 3.6 Hz, 1H, H-1'), 4.76 (d, *J* = 2.5 Hz, 1H, H-1), 4.70 (1H, H-5''), 4.42 (d, *J* = 2.9 Hz, 1H, H-5), 4.32 (dd, *J* = 11.2, 2.9 Hz, 1H, H-6'), 4.25 (dd, *J* = 5.8, 2.9 Hz, 1H, H-2''), 4.17 (dd, *J* = 11.2, 1.5 Hz, 1H, H-6'), 4.12 (dd, *J* = 5.7, 3.6 Hz, 1H, H-3''), 4.00 (t, *J* = 2.9 Hz, 1H, H-4''), 3.97 (t, *J* = 3.4 Hz, 1H, H-4), 3.94–3.87 (m, 1H, H-5', H-2'), 3.83 (dd, *J* = 5.5, 4.1 Hz, 1H, H-3), 3.77–3.65 (m, 5H, H-5''', H-6''', H-4', OCH_2, H-3'), 3.59–3.49 (m, 2H, H-2, OCH_2, H-3'''), 3.35 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.12 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 174.9 (C-6, C-6''), 174.3 (NHC=O), 100.8 (C-1), 99.3 (C-1''), 96.7 (C-1'''), 94.4 (C-1'), 75.8 (C-4' and C-2''), 75.7 (C-4''), 74.1 (C-4), 71.7 (C-5'''), 71.1 (C-3'''), 69.9 (C-4'''), 69.7 (C-3'), 69.6 (C-2), 69.4 (C-5'), 69.2 (C-5''), 69.04 (C-3''), 69.01 (C-5), 68.8 (C-3), 68.1 (OCH_2), 66.4 (C-6'), 60.3 (C-6'''), 58.1 (C-2'''), 53.5 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.3 ($NHC{=}OCH_3$), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ $[M–5Na+4H]^-$: 1058.1747; found: 1058.1740.

36. GlcNS-IdoA2S-GlcNS6S-IdoA

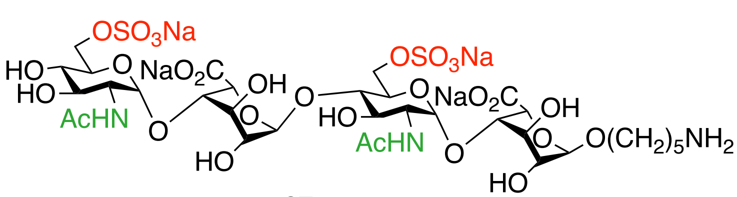


36

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (36).

Compound **S14** (31 mg, 0.012 mmol) was subjected to hydrolysis, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **36** (8.0 mg, 53% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.31 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.27 (d, *J* = 3.6 Hz, 1H, H-1'), 5.12 (d, *J* = 2.3 Hz, 1H, H-1''), 4.78 (d, *J* = 2.6 Hz, 1H, H-1), 4.72 (1H, H-5''), 4.41 (d, *J* = 2.6 Hz, 1H, H-5), 4.31 (dd, *J* = 11.2, 2.3 Hz, 1H, H-6'), 4.24 (dd, *J* = 5.6, 2.7 Hz, 1H, H-2''), 4.16–4.11 (m, 2H, H-6', H-3''), 4.04–3.99 (m, 2H, H-4'', H-3), 3.96 (t, *J* = 2.8 Hz, 1H, H-4), 3.90–3.87 (m, 1H, H-5'), 3.76–3.65 (m, 5H, H-5''', H-6''', H-4', OCH_2), 3.59–3.53 (m, 4H, H-3', H-2, OCH_2, H-3'''), 3.35 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.17 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2'), 3.12 (dd, *J* = 10.4, 3.4 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6), 174.9 (C-6''), 100.7 (C-1), 99.2 (C-1''), 96.8 (C-1'''), 95.5 (C-1'), 75.84 (C-4'), 75.79 (C-2''), 75.69 (C-4''), 74.9 (C-4), 71.7 (C-5'''), 71.0 (C-3'''), 69.9 (C-4'''), 69.7 (C-3'), 69.21 (C-5''), 69.16 (C-2), 69.1 (C-5'), 69.0 (C-3''), 68.6 (C-5), 68.4 (C-3), 68.0 (OCH_2), 66.3 (C-6'), 60.3 (C-6'''), 58.1 (C-2'''), 57.7 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{33}S_4$ $[M–6Na+5H]^-$: 1096.1209; found: 1096.1194.

37. GlcNAc6S-IdoA-GlcNAc6S-IdoA

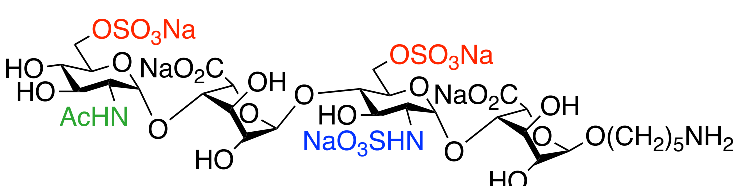


37

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (37).

Compound **S43** (18 mg, 0.0075 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **37** (4.0 mg, 53% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.08 (d, *J* = 3.7 Hz, 1H, H-1'''), 5.07 (d, *J* = 4.0 Hz, 1H, H-1'), 4.88 (d, *J* = 3.0 Hz, 1H, H-1''), 4.77 (d, *J* = 2.8 Hz, 1H, H-1), 4.67 (d, *J* = 2.5 Hz, 1H, H-5''), 4.42 (d, *J* = 2.6 Hz, 1H, H-5), 4.28–4.24 (m, 2H, H-6', H-6'''), 4.15–4.09 (m, 2H, H-6', H-6'''), 4.00–3.95 (m, 3H, H-4'', H-5', H-4), 3.90–3.80 (m, 5H, H-5''', H-2', H-2''', H-3, H-3''), 3.71–3.53 (m, 6H, H-3', H-4', H-2'', OCH_2, H-3'''), 3.51 (dd, *J* = 5.3, 3.0 Hz, 1H, H-2), 3.47 (t, *J* = 9.6 Hz, 1H, H-4'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6 and C-6''), 174.4 (NHC=O), 174.4 (NHC=O), 101.9 (C-1''), 100.8 (C-1), 94.5 (C-1'), 94.3 (C-1'''), 76.7 (C-4'), 74.02 (C-4 or C-4''), 73.99 (C-4 or C-4''), 71.0 (C-3'''), 70.1 (C-5'''), 69.8 (C-3'), 69.42 (C-2''), 69.36 (C-5''), 69.32 (C-2), 69.2 (C-5'), 69.0 (C-4'''), 68.9 (C-3''), 68.8 (C-5), 68.6 (C-3), 68.1 (OCH_2), 66.4 (C-6'''), 66.2 (C-6'), 53.5 (C-2'), 53.4 (C-2'''), 39.3 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.91 ($NHC{=}OCH_3$), 21.89 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ $[M{-}4Na{+}3H]^-$: 1020.2284; found: 1020.2307.

38. GlcNAc6S-IdoA-GlcNS6S-IdoA

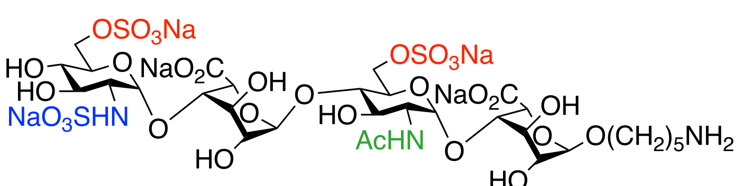


38

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (38).

Compound **S43** (29 mg, 0.012 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **38** (10 mg, 69% for three steps).[1]H NMR (400 MHz, D_2O): δ 5.27 (d, *J* = 3.6 Hz, 1H, H-1'), 5.08 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.90 (d, *J* = 3.0 Hz, 1H, H-1''), 4.79 (d, *J* = 2.4 Hz, 1H, H-1), 4.71 (d, *J* = 2.0 Hz, 1H, H-5''), 4.41 (d, *J* = 2.3 Hz, 1H, H-5), 4.29–4.24 (m, 2H, H-6', H-6'''), 4.13–4.09 (m, 2H, H-6', H-6'''), 4.03 (appt, *J* = 3.8 Hz, 1H, H-3), 4.00 (appt, *J* = 2.9 Hz, 1H, H-4''), 3.96–3.84 (m, 4H, H-4, H-5', H-2''', H-5'''), 3.81 (dd, *J* = 5.5, 3.5 Hz, 1H, H-3''), 3.70–3.52 (m, 7H, OCH_2, H-4', H-3''', H-3', H-2'', H-2), 3.48 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.17 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $C{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6), 175.1 (C-6''), 174.4 (*C*ONH), 101.8 (C-1''), 100.7 (C-1), 95.6 (C-1'), 94.3 (C-1'''), 76.9 (C-4'), 74.8 (C-4), 74.0 (C-4''), 71.0 (C-3'''), 70.1 (C-5'''), 69.8 (C-3'), 69.3 (C-2''), 69.2 (C-5''), 69.00 (C-4'''), 68.97 (C-5'), 68.9 (C-2), 68.7 (C-3''), 68.3 (C-5), 68.1 (OCH_2), 68.0 (C-3), 66.4 (C-6'''), 66.2 (C-6'), 57.8 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{31}S_3$ [M–5Na+4H]$^-$: 1058.1747; found: 1058.1776.

39. GlcNS6S-IdoA-GlcNAc6S-IdoA

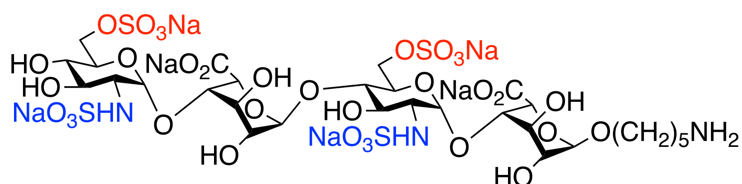


39

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (39).

Compound **S12** (41 mg, 0.017 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **39** (4.5 mg, 22% for five steps). [1]H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.8 Hz, 1H, H-1'''), 5.07 (d, J = 3.8 Hz, 1H, H-1'), 4.90 (d, J = 2.5 Hz, 1H, H-1''), 4.77 (d, J = 2.9 Hz, 1H, H-1), 4.67 (d, J = 2.0 Hz, 1H, H-5''), 4.42 (d, J = 2.9 Hz, 1H, H-5), 4.29–4.22 (m, 2H, H-6a', H-6a'''), 4.17–4.04 (m, 2H, H-6b', H-6b'''), 4.02 (appt, J = 3.9 Hz, 1H, H-3''), 3.99–3.92 (m, 3H, H-4, H-5', H-4''), 3.91–3.80 (m, 3H, H-3, H-2', H-5'''), 3.71–3.62 (m, 4H, H-3', H-4', H-2'', OCH_2), 3.58–3.45 (m, 4H, H-2, H-3''', H-4''', OCH_2,), 3.12 (dd, J = 10.0, 3.6 Hz, 1H, H-2'''), 2.90 (t, J = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $C{=}OCH_3$), 1.66–1.49 (m, 4H, 2 X CH_2), 1.41–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6''), 175.0 (C-6), 174.3 (*C*ONH), 102.1 (C-1''), 100.8 (C-1), 95.5 (C-1'''), 94.5 (C-1'), 77.4 (C-4'), 74.4 (C-4''), 74.0 (C-4), 71.1 (C-3'''), 69.8 (2C, C-3', C-5'''), 69.4 (C-4'''), 69.2 (C-5'), 69.0 (C-2''), 68.8 (C-2), 68.7 (C-5), 68.6 (2C, C-3, C-5''), 68.1 (OCH_2), 67.9 (C-3''), 66.4 (C-6'''), 66.2 (C-6'), 57.7 (C-2'''), 53.6 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{51}N_3O_{31}S_3Na$ $[M{-}4Na{+}3H]^-$: 1080.1566; found: 1080.1571.

40. GlcNS6S-IdoA-GlcNS6S-IdoA

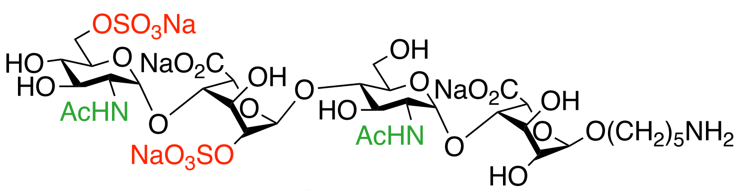


40

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate hexa sodium salt (40).

Compound **S12** (41 mg, 0.017 mmol) was subjected to hydrolysis, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **40** (5.2 mg, 25% for four steps). ^1H NMR (400 MHz, D_2O): δ 5.28–5.24 (m, 2H, H-1', H-1'''), 4.91 (bs, 1H, H-1''), 4.79 (d, J = 2.7 Hz, 1H, H-1), 4.71 (m, 1H, H-5''), 4.40 (d, J = 2.5 Hz, 1H, H-5), 4.30–4.21 (m, 2H, H-6a', H-6a'''), 4.14–4.04 (m, 2H, H-6b', H-6b'''), 4.04–4.00 (m, 2H, H-3, H-3''), 3.99–3.89 (m, 3H, H-4, H-5', H-4''), 3.87–3.82 (m, 1H, H-5'''), 3.73–3.42 (m, 8H, H-2, H-3', H-4', H-2'', H-3''', H-4''', OCH_2), 3.20–3.07 (m, 2H, H-2', H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $C{=}OCH_3$), 1.65–1.49 (m, 4H, 2 X CH_2), 1.41–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.2 (2C, C-6, C-6''), 102.0 (C-1''), 100.7 (C-1), 95.6 (C-1' or C-1'''), 95.5 (C-1' or C-1'''), 77.5 (C-4'), 74.9 (C-4 or C-4''), 74.3 (C-4 or C-4''), 71.1 (C-3'''), 69.85 (C-5'''), 69.81 (C-3'), 69.01 (C-4'''), 68.97 (C-5'), 68.95 (C-2), 68.54 (C-2''), 68.51 (C-5''), 68.4 (C-5), 68.2 (C-3, or C-3''), 68.0 (C-3, or C-3''), 67.7 (OCH_2), 66.4 (C-6' or C-6'''), 66.2 (C-6' or C-6'''), 57.9 (C-2' or C-2'''), 57.7 (C-2' or C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{29}H_{49}N_3O_{33}S_4Na$ $[M{-}5Na{+}4H]^+$: 1118.1029; found: 1118.1029.

41. GlcNAc6S-IdoA2S-GlcNAc-IdoA



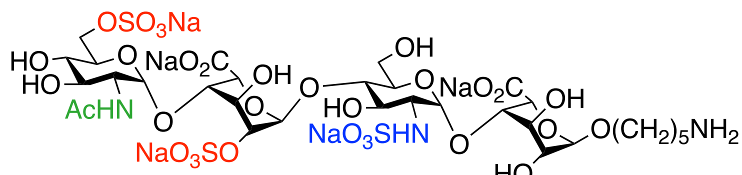
41

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate tetra sodium salt (41).

Compound **S43** (29 mg, 0.012 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **41** (10 mg, 76% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.09 (s, 1H, H-1''), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'), 5.01 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.81 (d, *J* = 2.8 Hz, 1H, H-5''), 4.76 (d, *J* = 1.7 Hz, 1H, H-1), 4.41 (d, *J* = 2.7 Hz, 1H, H-5), 4.24 (dd, *J* = 11.1, 3.0 Hz, 1H, H-6'''), 4.23 (s, 1H, H-2''), 4.19 (s, 1H, H-3''), 4.14 (dd, *J* = 11.1, 1.6 Hz, 1H, H-6'''), 3.96–3.73 (m, 9H, H-4, H-4'', H-2''', H-2', H-5''', H-3, H-5', H-6'), 3.72–3.48 (m, 6H, OCH_2, H-3''', H-3', H-4', H-2), 3.46 (t, *J* = 9.7 Hz, 1H, H-4'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.63–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR

(100 MHz, D_2O): δ 175.7 (C-6), 174.9 (C-6''), 174.8 (NHC=O), 174.3 (NHC=O), 100.8 (C-1), 99.2 (C-1''), 94.5 (C-1'), 93.6 (C-1'''), 77.1 (C-4'), 74.0 (C-4), 73.3 (C-2''), 71.3 (C-5'), 71.2 (C-3'''), 70.5 (C-4''), 70.0 (C-5'''), 69.6 (C-3'), 69.5 (C-2), 69.2 (C-4'''), 69.0 (C-5), 68.8 (C-3), 68.1 (OCH_2), 67.3 (C-5''), 66.5 (C-6'''), 63.3 (C-3''), 59.6 (C-6'), 53.9 (C-2'''), 53.2 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.2 (CH_2, NHC=O*C*H_3), 21.9 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{29}S_2$ $[M{-}4Na{+}3H]^-$: 1020.2284; found: 1020.2276.

42. GlcNAc6S-IdoA2S-GlcNS-IdoA



42

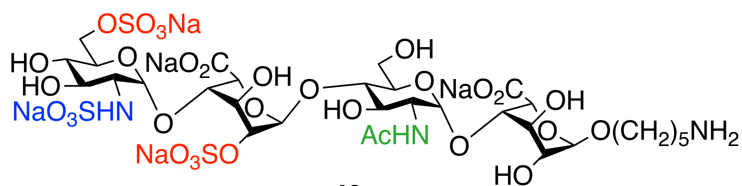
5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-2-*O*-sulfonato-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (42).

Method 1: Compound **S43** (16 mg, 0.0067 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **42** (4.7 mg, 64% for three steps).

Method 2: Compound **S43** (15 mg, 0.0063 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **42** (4.3 mg, 62% for three steps).

^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.7 Hz, 1H, H-1'), 5.09 (s, 1H, H-1''), 5.02 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.85 (d, *J* = 1.8 Hz, 1H, H-5''), 4.78 (d, *J* = 2.7 Hz, 1H, H-1), 4.40 (d, *J* = 2.5 Hz, 1H, H-5), 4.26 (dd, *J* = 11.0, 3.1 Hz, 1H, H-6'''), 4.22 (appt, *J* = 1.0 Hz, 1H, H-2''), 4.19 (appt, *J* = 2.0 Hz, 1H, H-3''), 4.14 (dd, *J* = 11.0, 1.5 Hz, 1H, H-6'''), 4.03 (t, *J* = 4.3 Hz, 1H, H-3), 3.95–3.85 (m, 4H, H-4, H-4'', H-2''', H-5'''), 3.78–3.73 (m, 3H, H-5', H-6'), 3.70–3.53 (m, 6H, OCH_2, H-3''', H-3', H-4', H-2), 3.47 (t, *J* = 9.7 Hz, 1H, H-4'''), 3.13 (dd, *J* = 9.8, 3.5 Hz, 1H, H-2'), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.63–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6), 174.9 (C-6''), 174.3 (NHC=O), 101.4 (C-1''), 100.7 (C-1), 95.7 (C-1'), 94.3 (C-1'''), 76.8 (C-4'), 74.9 (C-4), 73.3 (C-2''), 71.3 (C-3'''), 71.0 (C-5'), 70.4 (C-4''), 70.0 (C-5'''), 69.6 (C-3'), 69.15 (C-2), 69.13 (C-4'''), 68.6 (C-5), 68.4 (C-3), 68.0 (OCH_2), 67.3 (C-5''), 66.4 (C-6'''), 63.2 (C-3''), 59.7 (C-6'), 58.1 (C-2'), 53.2 (C-2'''), 39.3 (NCH_2), 27.9 (CH_2), 26.2 (CH_2), 22.22 (CH_2), 22.19 (NHC=O*C*H_3); HRMS (ESI-TOF) calcd for $C_{31}H_{48}N_3O_{31}S_3Na_4$ $[M–Na]^–$: 1146.1025; found: 1146.1024.

43. GlcNS6S-IdoA2S-GlcNAc-IdoA



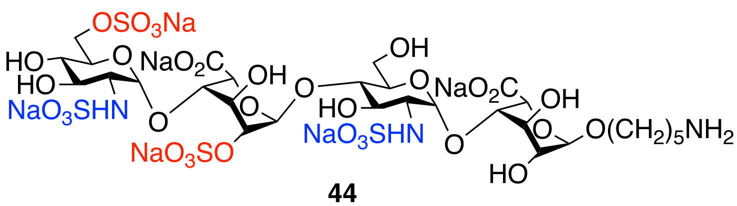
43

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (43).

Compound **S22** (40 mg, 0.017 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **43** (8.9 mg, 46% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.24 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.14 (d, *J* = 2.2 Hz, 1H, H-1''), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'), 4.76 (d, *J* = 3.3 Hz, 1H, H-1), 4.73 (d, *J* = 2.2 Hz, 1H, H-5''), 4.41 (d, *J* = 3.1 Hz, 1H, H-5), 4.29–4.22 (m, 2H, H-2'', H-6a'''), 4.15–4.07 (m, 2H, H-3'', H-6b'''), 3.96 (appt, *J* = 3.0 Hz, 1H, H-4''), 3.94 (appt, *J* = 3.3 Hz, 1H, H-4), 3.89–3.73 (m, 6H, H-3, H-2', H-5', H-6a', H-6b', H-5'''), 3.70–3.61 (m, 3H, H-3', H-4', OCH_2), 3.59–3.52 (m, 2H, H-3''', OCH_2), 3.51–3.42 (m, 2H, H-2, H-4'''), 3.15 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, C=OCH_3), 1.64–1.51 (m, 4H, 2 X CH_2), 1.40–1.30 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6''), 174.9 (C-6), 174.3 (*C*ONH), 100.8 (C-1), 99.2 (C-1''), 97.1 (C-1'''), 94.6 (C-1'), 76.9 (C-4'), 75.6 (C-4''), 75.0 (C-2''), 74.1 (C-4), 71.3 (C-5'), 70.9 (C-3'''), 69.9

(C-5'''), 69.62 (C-3'), 69.58 (C-2), 69.1 (C-4'''), 69.07 (C-5), 68.9 (C-3), 68.4 (C-5''), 68.1 (C-3''), 68.0 (OCH_2), 66.3 (C-6'''), 59.6 (C-6'), 58.0 (C-2'''), 53.8 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{51}N_3O_{31}S_3Na$ $[M–4Na+3H]^–$: 1080.1566; found: 1080.1558.

44. GlcNS6S-IdoA2S-GlcNS-IdoA



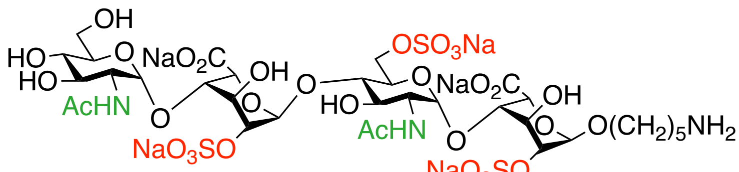
44

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate hexa sodium salt (44).

Compound **S22** (40 mg, 0.017 mmol) was subjected to hydrolysis, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **44** (11 mg, 50% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.26 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.23 (d, *J* = 3.5 Hz, 1H, H-1'), 5.15 (d, *J* = 2.0 Hz, 1H, H-1''), 4.80–4.76 (m, 2H, H-1, H-5''), 4.40 (d, *J* = 2.7 Hz, 1H, H-5), 4.28 (dd, *J* = 2.3, 11.1 Hz, 1H, H-6a'''), 4.24 (dd, *J* = 2.0, 4.0 Hz, 1H, H-2''), 4.14 (appt, *J* = 3.8 Hz, 1H, H-3''), 4.10 (dd, *J* = 2.0, 11.1 Hz, 1H, H-6b'''), 4.02 (appt, *J* = 4.0 Hz, 1H, H-3), 3.96 (appt, *J* = 3.8 Hz, 1H, H-4''), 3.94 (appt, *J* = 4.0 Hz, 1H, H-4), 3.89–3.84 (m, 1H, H-5'''), 3.80–3.71 (m, 3H, H-4', H-6a', H-6b'), 3.70–3.52 (m, 6H, H-2, H-3', H-5', H-3''', OCH_2), 3.48 (appt, *J* = 9.4 Hz, 1H, H-4'''), 3.18–3.10 (m, 2H, H-2', H-2'''), 2.90 (t, *J* = 7.4 Hz, 2H, NCH_2), 1.92 (s, 3H, C=OCH_3), 1.64–1.51 (m, 4H, 2 X CH_2), 1.40–1.30 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.17 (C-6 or C-6''), 175.11 (C-6 or C-6''), 100.7 (C-1), 99.0 (C-1''), 97.3 (C-1'), 95.7 (C-1'''), 77.0 (C-3'''), 75.6 (C-4''), 75.0 (C-4), 74.6 (C-2''), 71.0 (C-4'), 70.9 (C-5'), 69.9 (C-5'''), 69.62 (C-3'), 69.1 (C-4'''), 68.5 (C-5), 68.3 (C-3), 68.2 (C-5''), 68.1 (OCH_2), 67.7 (C-3''), 66.3 (C-6'''), 59.6 (C-6'), 53.8 (C-2' and

C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{29}H_{48}N_3O_{33}S_4Na_2$ [M – 4Na + 3H]$^-$: 1140.0848; found: 1140.0850.

45. GlcNAc-IdoA2S-GlcNAc6S-IdoA2S

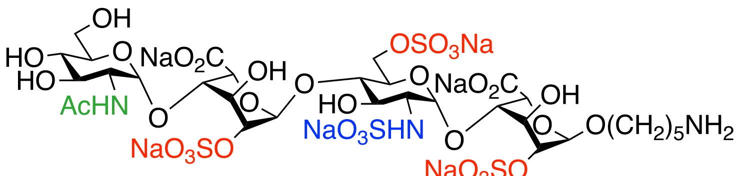


45

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (45).

Compound **S29** (24 mg, 0.0095 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **45** (7.1 mg, 56% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.08 (s, 1H, H-1''), 5.05 (d, J = 3.5 Hz, 1H, H-1'''), 5.02 (d, J = 3.6 Hz, 1H, H-1'), 5.00 (s, 1H, H-1), 4.81 (d, J = 2.1 Hz, 1H, H-5''), 4.47 (d, J = 2.0 Hz, 1H, H-5), 4.25–4.21 (m, 4H, H-2'', H-3'', H-6'), 4.18 (t, J = 2.1 Hz, 1H, H-3), 4.12 (br, 1H, H-2), 3.95–3.92 (m, 4H, H-4'', H-4 , H-5', H-2'), 3.87 (dd, J = 10.5, 3.5 Hz, 1H, H-2'''), 3.78–3.54 (m, 8H, H-6''', H-5''', H-3', H-3''', H-4', OCH_2), 3.36 (t, J = 9.5 Hz, 1H, H-4'''), 2.90 (t, J = 7.5 Hz, 2H, NCH_2), 1.963 (s, 3H, NHC=OCH_3), 1.957 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.6 (C-6''), 175.2 (C-6), 174.8 (NHC=O), 174.7 (NHC=O), 99.2 (C-1''), 98.5 (C-1), 94.5 (C-1'''), 93.3 (C-1'), 76.4 (C-4'), 73.9 (C-2), 73.6 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 70.7 (C-4''), 70.6 (C-4), 70.0 (C-3'), 69.7 (C-4'''), 69.2 (C-5'), 68.1 (OCH_2), 67.8 (C-5''), 67.0 (C-5), 66.5 (C-6'), 63.8 (C-3''), 63.7 (C-3), 60.2 (C-6'''), 53.40 (C-2'), 53.36 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (2 X NHC=OCH_3, CH_2); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{32}S_3$ [M–5Na+4H]$^-$: 1100.1853; found: 1100.1848.

46. GlcNAc-IdoA2S-GlcNS6S-IdoA2S

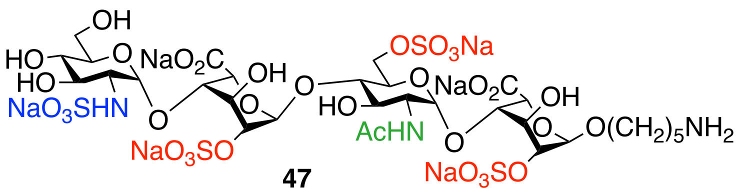


46

5-Aminopentanyl 2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (46).

Compound **S29** (32 mg, 0.013 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **46** (12 mg, 74% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.30 (d, J = 3.3 Hz, 1H, H-1'), 5.11 (s, 1H, H-1''), 5.07 (d, J = 3.5 Hz, 1H, H-1'''), 5.04 (d, J = 1.9 Hz, 1H, H-1), 4.87 (d, J = 1.9 Hz, 1H, H-5''), 4.42 (d, J = 2.6 Hz, 1H, H-5), 4.25–4.20 (m, 4H, H-2'', H-3'', H-6'), 4.14–4.12 (m, 2H, H-2, H-3), 3.94–3.92 (m, 3H, H-4'', H-4 , H-5'), 3.88 (dd, J = 10.5, 3.3 Hz, 1H, H-2'''), 3.79–3.55 (m, 8H, H-6''', H-5''', H-3', H-3''', H-4', OCH_2), 3.37 (t, J = 9.6 Hz, 1H, H-4'''), 3.19 (dd, J = 10.4, 3.5 Hz, 1H, H-2'), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.6 (C-6''), 174.8 (C-6), 174.7 (NHC=O), 98.9 (C-1''), 98.8 (C-1), 96.7 (C-1'), 93.5 (C-1'''), 76.2 (C-2), 76.1 (C-4'), 75.7 (C-4), 73.7 (C-2''), 71.9 (C-5'''), 71.3 (C-3'''), 70.7 (C-4''), 69.8 (C-4'''), 69.6 (C-3'), 69.1 (C-5'), 68.7 (C-3), 68.6 (C-5), 68.1 (OCH_2), 67.8 (C-5''), 66.4 (C-6'), 63.9 (C-3''), 60.3 (C-6'''), 58.0 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.24 ($NHC{=}OCH_3$), 22.21 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M–6Na+5H]^–$: 1138.1315; found: 1138.1337.

47. GlcNS-IdoA2S-GlcNAc6S-IdoA2S

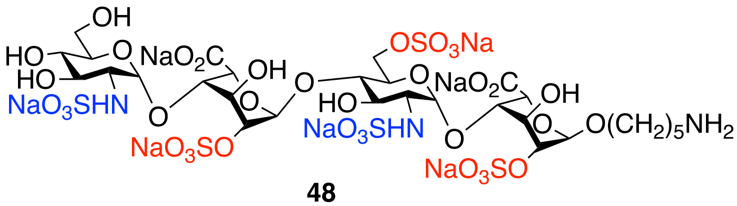


47

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (47).

Compound **86** (26 mg, 0.012 mmol) was subjected to *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **47** (11 mg, 69% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, J = 3.4 Hz, 1H, H-1'''), 5.12 (d, J = 2.4 Hz, 1H, H-1''), 5.03 (d, J = 3.7 Hz, 1H, H-1'), 5.01 (s, 1H, H-1), 4.73 (d, J = 2.6 Hz, 1H, H-5''), 4.48 (d, J = 2.2 Hz, 1H, H-5), 4.30 (dd, J = 11.4, 3.2 Hz, 1H, H-6'), 4.26 (dd, J = 5.2, 2.5 Hz, 1H, H-2''), 4.22–4.11 (m, 4H, H-6', H-3'', H-2, H-3), 4.00 (t, J = 3.0 Hz, 1H, H-4''), 3.96–3.91 (m, 1H, H-5', H-2', H-4), 3.76–3.61 (m, 6H, H-5''', H-6''', H-4', OCH_2, H-3'), 3.60–3.53 (m, 2H, OCH_2, H-3'''), 3.36 (t, J = 9.5 Hz, 1H, H-4'''), 3.12 (dd, J = 10.4, 3.5 Hz, 1H, H-2'''), 2.91 (t, J = 7.5 Hz, 2H, NCH_2), 1.96 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6), 174.9 (C-6''), 174.7 (NHC=O), 99.3 (C-1''), 98.6 (C-1), 96.9 (C-1'''), 93.4 (C-1'), 76.2 (C-4'), 75.7 (C-4''), 75.5 (C-2''), 73.9 (C-2), 71.7 (C-5'''), 71.0 (C-3'''), 70.8 (C-4), 70.0 (C-3'), 69.9 (C-4'''), 69.3 (C-5'), 68.9 (C-5''), 68.7 (C-3''), 68.1 (OCH_2), 67.0 (C-5), 66.5 (C-6'), 63.8 (C-3), 60.3 (C-6'''), 58.1 (C-2'''), 53.3 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.3 ($NHC{=}OCH_3$), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ [M–6Na+5H]$^-$: 1138.1292; found: 1138.1337.

48. GlcNS-IdoA2S-GlcNS6S-IdoA2S

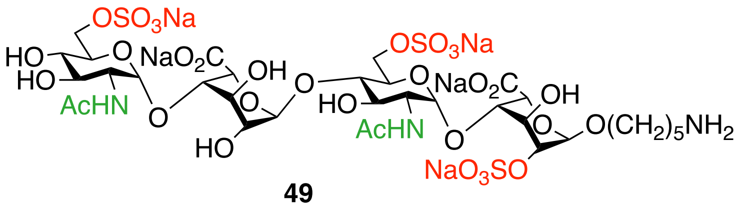


48

5-Aminopentanyl 2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hepta sodium salt (48).

Compound **86** (25 mg, 0.012 mmol) was subjected to N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **48** (12 mg, 75% for three steps).[1]H NMR (400 MHz, D_2O): δ 5.32 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.30 (d, *J* = 3.5 Hz, 1H, H-1'), 5.14 (d, *J* = 2.6 Hz, 1H, H-1''), 5.05 (d, *J* = 2.0 Hz, 1H, H-1), 4.78 (d, *J* = 2.6 Hz, 1H, H-5''), 4.45 (d, *J* = 2.6 Hz, 1H, H-5), 4.32 (dd, *J* = 11.4, 2.3 Hz, 1H, H-6'), 4.26 (dd, *J* = 5.5, 2.8 Hz, 1H, H-2''), 4.20–4.12 (m, 4H, H-6', H-3'', H-2, H-3), 4.02 (t, *J* = 3.0 Hz, 1H, H-4''), 3.99 (t, *J* = 3.0 Hz, 1H, H-4), 3.95–3.92 (m, 1H, H-5'), 3.78–3.65 (m, 5H, H-5''', H-6''', H-4', OCH_2), 3.62–3.54 (m, 3H, OCH_2, H-3''', H-3'), 3.37 (t, *J* = 9.6 Hz, 1H, H-4'''), 3.20 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2'), 3.12 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2'''), 2.92 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); [13]C NMR (100 MHz, D_2O): δ 174.8 (C-6''), 174.5 (C-6), 99.1 (C-1''), 98.9 (C-1), 96.9 (C-1'''), 96.8 (C-1'), 76.1 (C-2), 75.8 (C-4' and C-4''), 75.7 (C-4), 75.6 (C-2''), 71.7 (C-5'''), 71.1 (C-3'''), 69.9 (C-4'''), 69.5 (C-3'), 69.2 (C-5'), 69.1 (C-5''), 68.8 (C-3''), 68.6 (C-3), 68.4 (C-5), 68.1 (OCH_2), 66.3 (C-6'), 60.3 (C-6'''), 58.1 (C-2'''), 57.9 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{36}S_5$ $[M{-}7Na{+}6H]^-$: 1176.0778; found: 1176.0782.

49. GlcNAc6S-IdoA-GlcNAc6S-IdoA2S

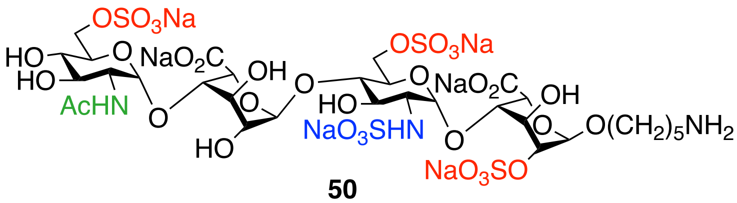


49

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (49).

Compound **S27** (13 mg, 0.0054 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **49** (4.0 mg, 61% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.08 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.02 (d, *J* = 3.5 Hz, 1H, H-1'), 5.02 (s, 1H, H-1), 4.88 (d, *J* = 3.0 Hz, 1H, H-1''), 4.71 (d, *J* = 2.5 Hz, 1H, H-5''), 4.47 (d, *J* = 2.0 Hz, 1H, H-5), 4.28–4.23 (m, 2H, H-6', H-6'''), 4.18–4.09 (m, 4H, H-3, H-6', H-6''', H-2), 4.00–3.93 (m, 4H, H-2', H-4'', H-5', H-4), 3.89–3.85 (m, 5H, H-5''', H-2'''), 3.82 (dd, *J* = 5.8, 3.5 Hz, 1H, H-3''), 3.69–3.54 (m, 6H, H-3', H-4', H-2'', OCH_2, H-3'''), 3.48 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $NHC{=}OCH_3$), 1.93 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6) 174.7 (C-6''), 174.4 (NHC=O), 174.4 (NHC=O), 101.8 (C-1''), 98.5 (C-1), 94.4 (C-1'''), 93.8 (C-1'), 76.7 (C-4'), 74.1 (C-4''), 73.9 (C-2), 71.1 (C-4), 71.0 (C-3'''), 70.1 (C-5'''), 70.0 (C-2''), 69.3 (C-3'), 69.2 (C-5''), 69.1 (C-5'), 69.0 (C-4'''), 68.8 (C-3''), 68.1 (OCH_2), 66.9 (C-5), 66.4 (C-6'''), 66.2 (C-6'), 64.0 (C-3), 53.4 (C-2' and C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.3 ($NHC{=}OCH_3$), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{32}S_3$ $[M{-}5Na{+}4H]^-$: 1100.1853; found: 1100.1846.

50. GlcNAc6S-IdoA-GlcNS6S-IdoA2S

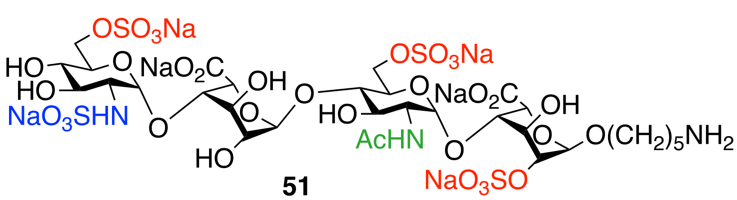


50

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (50).

Compound **S27** (12 mg, 0.0050 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **50** (4.0 mg, 62% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'), 5.08 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.04 (s, 1H, H-1), 4.90 (d, *J* = 2.8 Hz, 1H, H-1''), 4.72 (d, *J* = 2.5 Hz, 1H, H-5''), 4.41 (d, *J* = 2.2 Hz, 1H, H-5), 4.29–4.24 (m, 2H, H-6', H-6'''), 4.17–4.09 (m, 4H, H-6', H-6''', H-3, H-2), 4.01–3.96 (m, 3H, H-4, H-4'', H-5'), 3.89–3.85 (m, 2H , H-2''', H-5'''), 3.82 (dd, *J* = 5.6, 3.5 Hz, 1H, H-3''), 3.69–3.54 (m, 6H, OCH_2, H-4', H-3''', H-3', H-2''), 3.48 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.19 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.93 (s, 3H, $C{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6''), 174.8 (C-6), 174.4 (*C*ONH), 101.8 (C-1''), 98.8 (C-1), 96.9 (C-1'), 94.4 (C-1'''), 76.8 (C-4'), 76.0 (C-2), 75.9 (C-4), 74.0 (C-4''), 71.0 (C-3'''), 70.1 (C-5'''), 69.6 (C-3'), 69.3 (C-2''), 69.2 (C-5''), 69.04 (C-5'), 68.99 (C-4'''), 68.7 (C-3''), 68.6 (C-3), 68.4 (C-5), 68.0 (OCH_2), 66.4 (C-6'''), 66.2 (C-6'), 58.0 (C-2'), 53.4 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M{-}6Na{+}5H]^-$: 1138.1315; found: 1138.1328.

51. GlcNS6S-IdoA-GlcNAc6S-IdoA2S

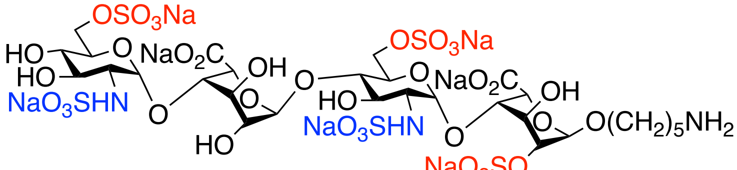


51

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (51).

Compound **87** (27 mg, 0.013 mmol) was subjected to *N*-acetylation, N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **51** (11 mg, 67% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.03 (d, *J* = 3.5 Hz, 1H, H-1'), 5.02 (s, 1H, H-1), 4.91 (d, *J* = 2.0 Hz, 1H, H-1''), 4.77 (d, *J* = 2.3 Hz, 1H, H-5''), 4.49 (d, *J* = 2.0 Hz, 1H, H-5), 4.29–4.23 (m, 2H, H-6', H-6'''), 4.19–4.07 (m, 4H, H-2, H-3, H-6', H-6'''), 4.04 (t, *J* = 3.3 Hz, 1H, H-3''), 4.00–3.93 (m, 4H, H-4, H-4'', H-5', H-2'), 3.84–3.80 (m, 1H, H-5'''), 3.71 (dd, *J* = 4.2, 2.2 Hz, 1H, H-2''), 3.69–3.50 (m, 5H, H-4', OCH_2, H-3''', H-3'), 3.48 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.14 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'''), 2.92 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.98 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6), 175.0 (C-6''), 174.8 (NHC=O), 102.0 (C-1''), 98.5 (C-1), 95.6 (C-1'''), 93.8 (C-1'), 77.3 (C-4'), 74.4 (C-4''), 73.8 (C-2), 71.1 (C-3'''), 71.0 (C-4), 70.0 (C-5'''), 69.6 (C-3'), 69.2 (C-5'), 69.0 (C-4'''), 68.5 (C-2''), 68.3 (C-5''), 68.2 (OCH_2), 67.7 (C-3''), 66.9 (C-5), 66.4 (C-6'''), 66.2 (C-6'), 63.9 (C-3), 57.7 (C-2'''), 53.4 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.3 (CH_2), 22.3 ($NHC{=}OCH_3$), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M{-}6Na{+}5H]^-$: 1138.1315; found: 1138.1313.

52. GlcNS6S-IdoA-GlcNS6S-IdoA2S



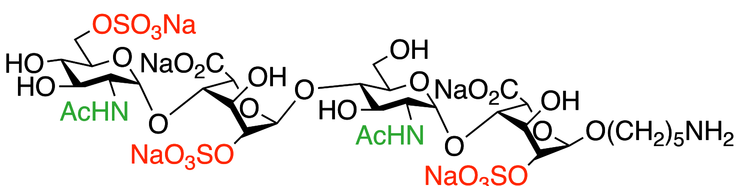
52

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-

glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (52).

Compound **87** (26 mg, 0.013 mmol) was subjected to N_3 to NH_2, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **52** (11 mg, 66% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 5.26 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.05 (s, 1H, H-1), 4.93 (s, 1H, H-1''), 4.81 (d, *J* = 2.2 Hz, 1H, H-5''), 4.44 (d, *J* = 2.4 Hz, 1H, H-5), 4.29–4.23 (m, 2H, H-6', H-6'''), 4.16–4.07 (m, 4H, H-2, H-3, H-6', H-6'''), 4.04 (t, *J* = 3.7 Hz, 1H, H-3''), 3.99–3.95 (m, 3H, H-4, H-4'', H-5'), 3.83–3.79 (m, 1H, H-5'''), 3.71 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2''), 3.68–3.50 (m, 5H, H-4', OCH_2, H-3''', H-3'), 3.48 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.18 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 3.13 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.0 (C-6''), 174.0 (C-6), 101.9 (C-1''), 98.8 (C-1), 97.1 (C-1'), 95.7 (C-1'''), 77.5 (C-4'), 75.9 (C-4), 75.8 (C-2), 74.3 (C-4''), 71.1 (C-3'''), 70.0 (C-5'''), 69.6 (C-3'), 69.1 (C-5'), 69.0 (C-4'''), 68.4 (C-3), 68.3 (C-2''), 68.2 (C-5 and C-5''), 68.1 (OCH_2), 67.5 (C-3''), 66.4 (C-6'''), 66.3 (C-6'), 58.1 (C-2'), 57.7 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{36}S_5$ $[M{-}7Na{+}6H]^-$: 1176.0778; found: 1176.0781.

53. GlcNAc6S-IdoA2S-GlcNAc-IdoA2S

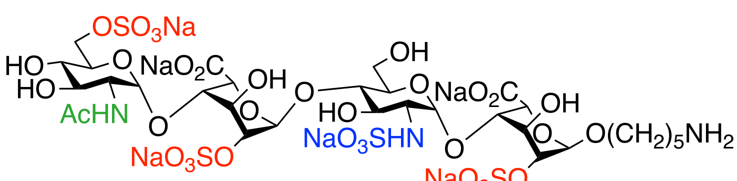


53

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate penta sodium salt (53).

Compound **S37** (29 mg, 0.012 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **53** (11 mg, 76% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.09 (s, 1H, H-1''), 5.03–5.01 (m, 3H, , H-1', H-1''', H-1), 4.82 (d, *J* = 1.8 Hz, 1H, H-5''), 4.46 (d, *J* = 2.5 Hz, 1H, H-5), 4.27–4.24 (m, 2H, H-6''', H-2''), 4.29–4.12 (m, 4H, H-3'', H-6''', H-3, H-2), 3.94–3.86 (m, 5H, H-4, H-4'', H-2''', H-2', H-5'''), 3.81–3.75 (m, 3H, H-5', H-6'), 3.69–3.54 (m, 5H, OCH_2, H-3''', H-3', H-4'), 3.47 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.98 (s, 3H, $NHC{=}OCH_3$), 1.63–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.7 (C-6''), 175.2 (C-6), 174.8 (NHC=O), 174.7 (NHC=O), 99.2 (C-1''), 98.5 (C-1), 93.6 (C-1'''), 93.5 (C-1'), 77.2 (C-4'), 74.0 (C-2), 73.2 (C-2''), 71.2 (C-3''', C-5'), 70.7 (C-4), 70.4 (C-4''), 70.0 (C-5'''), 69.8 (C-3'), 69.1 (C-4'''), 68.1 (OCH_2), 67.3 (C-5''), 67.1 (C-5), 66.4 (C-6'''), 63.9 (C-3), 63.3 (C-3''), 59.7 (C-6'), 53.7 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.24 (CH_2, $NHC{=}OCH_3$), 22.16 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{32}S_3$ $[M{-}5Na{+}4H]^-$: 1100.1853; found: 1100.1869.

54. GlcNAc6S-IdoA2S-GlcNS-IdoA2S



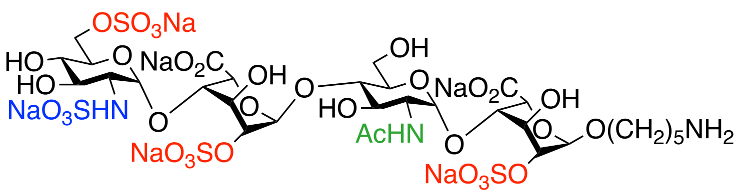
54

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (54).

Compound **S37** (28 mg, 0.012 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **54** (11 mg, 76% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'), 5.10 (s, 1H, H-1''), 5.03 (d, *J* = 2.5 Hz, 1H, H-1), 5.02 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.85 (d, *J* = 1.6

Hz, 1H, H-5''), 4.40 (d, J = 2.5 Hz, 1H, H-5), 4.26 (dd, J = 11.1, 3.1 Hz, 1H, H-6'''), 4.23–4.11 (m, 5H, H-2'', H-3'', H-6''', H-3, H-2), 3.97–3.85 (m, 4H, H-4, H-4'', H-2''', H-5'''), 3.81–3.73 (m, 3H, H-5', H-6'), 3.70–3.54 (m, 5H, OCH_2, H-3''', H-3', H-4'), 3.47 (t, J = 9.6 Hz, 1H, H-4'''), 3.15 (dd, J = 9.6, 3.5 Hz, 1H, H-2'), 2.90 (t, J = 7.5 Hz, 2H, NCH_2), 1.98 (s, 3H, $NHC{=}OCH_3$), 1.63–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.8 (C-6''), 174.81 (C-6), 174.78 (NHC=O), 99.1 (C-1''), 98.8 (C-1), 96.7 (C-1'), 93.6 (C-1'''), 77.4 (C-4'), 76.2 (C-2), 75.8 (C-4), 73.2 (C-2''), 71.2 (C-3'''), 71.0 (C-5'), 70.5 (C-4''), 70.0 (C-5'''), 69.5 (C-3'), 69.1 (C-4'''), 68.8 (C-3), 68.6 (C-5), 68.0 (OCH_2), 67.3 (C-5''), 66.4 (C-6'''), 63.3 (C-3''), 59.7 (C-6'), 58.3 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.23 (CH_2), 22.19 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M{-}6Na{+}5H]^-$: 1138.1315; found: 1138.1334.

55. GlcNS6S-IdoA2S-GlcNAc-IdoA2S

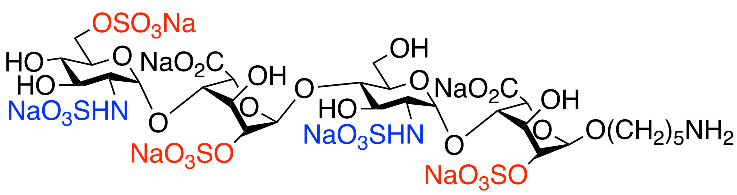


55

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (55).

Compound **92** (32 mg, 0.014 mmol) was subjected to *N*-acetylation, N_3 to NH_2 conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **55** (7.0 mg, 51% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.22 (d, J = 3.5 Hz, 1H, H-1'''), 5.15 (bs, 1H, H-1''), 5.02 (d, J = 3.5 Hz, 1H, H-1'), 5.00 (bs, 1H, H-1), 4.74–4.68 (m, 1H, H-5''), 4.45 (d, J = 2.3 Hz, 1H, H-5), 4.30–4.23 (m, 1H, H-2'', H-6'''a), 4.19–4.06 (m, 3H, H-2, H-3, H-3'', H-6'''b), 3.97–3.74 (m, 7H, H-4, H-2', H-5', H-6'a, H-6'b, H-4'', H-5'''), 3.70–3.53 (m, 5H, H-3', H-4', H-3''', OCH$_2$), 3.49 (t, J = 9.5 Hz, 1H, H-4'''), 3.15 (dd, J = 10.4, 3.4 Hz, 1H, H-2'''), 2.91 (t, J = 7.7 Hz, 2H, NCH$_2$), 1.96 (s, 3H, COCH$_3$), 1.65–1.51 (m, 4H, 2 X CH$_2$), 1.41–1.33 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, D$_2$O): δ 175.2 (2C, C-6 and C-6''), 174.7 (*C*ONH), 99.2 (C-1''), 98.6 (C-1), 97.3 (C-1'''), 93.5 (C-1'), 77.0 (C-4'), 75.5 (C-4''), 74.6 (C-2''), 74.0 (C-2), 71.3 (C-5'), 70.9 (C-3'''), 70.8 (C-4), 69.89 (C-3' or C-5'''), 69.84 (C-3' or C-5'''), 69.1 (C-4'''), 68.1 (2C, C-5'' and OCH$_2$), 67.6 (C-3''), 67.1 (C-5), 66.3 (C-6'''), 63.9 (C-3), 59.7 (C-6'), 58.0 (C-2'''), 53.6 (C-2'), 39.4 (NCH$_2$), 27.8 (CH$_2$), 26.2 (CH$_2$), 22.24 (CH$_2$), 22.16 (COCH$_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{53}N_3O_{34}S_4$ $[M-4Na+2H]^{2-}$: 568.5618; found: 568.5599.

56. GlcNS6S-IdoA2S-GlcNS-IdoA2S

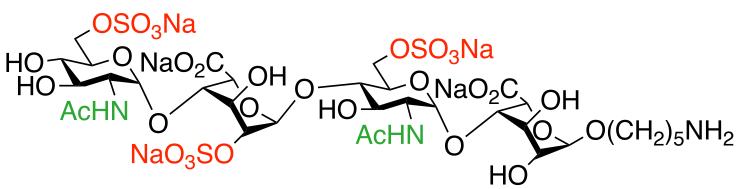


56

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (56).

Compound **92** (24 mg, 0.011 mmol) was subjected to N$_3$ to NH$_2$ conversion, *N*-sulfation and hydrogenation according to the general procedures to obtain **56** (6.5 mg, 45% for three steps). ^{1}H NMR (400 MHz, D$_2$O): δ 5.30 (d, J = 3.6 Hz, 1H, H-1'), 5.22 (d, J = 3.4 Hz, 1H, H-1'''), 5.16 (bs, 1H, H-1''), 5.02 (d, J = 2.7 Hz, 1H, H-1), 4.78 (d, J = 2.4 Hz, 1H, H-5''), 4.40 (d, J = 2.8 Hz, 1H, H-5), 4.30–4.22 (m, 1H, H-2'', H-6'''a), 4.17–4.05 (m, 4H, H-2, H-3, H-3'', H-6'''b), 3.99–3.94 (m, 2H, H-4, H-4''), 3.90–3.83 (m, 1H, H-5''') 3.82–3.74 (m, 3H, H-5', H-6'a, H-6'b), 3.70–3.52 (m, 5H, H-3', H-4', H-3''', OCH$_2$), 3.49 (t, J = 9.4 Hz, 1H, H-4'''), 3.18–3.12 (m, 2H, H-2', H-2'''), 2.91 (t, J = 7.7 Hz, 2H, NCH$_2$), 1.66–1.50 (m, 4H, 2 X CH_2), 1.42–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.3 (C-6''), 174.7 (C-6), 99.0 (C-1''), 98.9 (C-1), 97.3 (C-1'''), 96.7 (C-1'), 77.2 (C-4'), 76.5 (C-2), 75.8 (C-4), 75.6 (C-4''), 74.5 (C-2''), 71.1 (C-5'), 70.9 (C-3'''), 69.9 (C-5'''), 69.5 (C-3'), 69.1 (C-4'''), 69.0 (C-3''), 68.8 (C-5), 68.08 (C-5''), 68.04 (OCH_2), 67.6 (C-3), 66.3 (C-6'''), 59.7 (C-6), 58.2 (C-2' or C-2'''), 58.0 (C-2' or C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{36}S_5$ [M – 7Na + 6H]$^-$: 1176.0778; found 1176.0798.

57. GlcNAc6S-IdoA2S-GlcNAc6S-IdoA

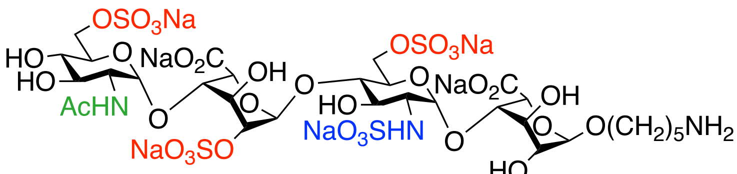


57

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate penta sodium salt (57).

Compound **S37** (38 mg, 0.016 mmol) was subjected to hydrolysis, N_3 to NH_2, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **57** (14 mg, 72% for four steps). ^1H NMR (400 MHz, D_2O): δ 5.10 (s, 1H, H-1''), 5.08 (d, *J* = 3.6 Hz, 1H, H-1'), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.82 (d, *J* = 2.0 Hz, 1H, H-5''), 4.72 (d, *J* = 3.1 Hz, 1H, H-1), 4.43 (d, *J* = 2.8 Hz, 1H, H-5), 4.27–4.14 (m, 6H, H-6', H-6''', H-2'', H-3''), 3.99–3.88 (m, 6H, H-4, H-4'', H-5', H-2''', H-5''', H-2'), 3.83 (dd, *J* = 5.2, 4.0 Hz, 1H, H-3), 3.72–3.50 (m, 6H, OCH_2, H-4', H-3''', H-3', H-2), 3.47 (t, *J* = 9.6 Hz, 1H, H-4'''), 2.91 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, C=OCH_3), 1.93 (s, 3H, C=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.4 (C-6''), 174.9 (C-6), 174.8 (*C*ONH), 174.3 (*C*ONH), 100.8 (C-1), 99.1 (C-1''), 94.4 (C-1'), 93.6 (C-1'''), 76.1 (C-4'), 74.0 (C-4), 73.9 (C-2''), 71.2 (C-3'''), 70.9 (C-4''), 70.0 (C-5'''), 69.7 (C-3'), 69.5 (C-2), 69.3 (C-5'), 69.2 (C-4'''), 69.0 (C-5), 68.8 (C-3), 68.1 (OCH_2), 67.8 (C-5''), 66.5 (C-6'''), 66.4 (C-6'), 64.1 (C-3''), 53.6 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.22 (NHC=OCH_3), 22.20 (CH_2), 21.9 (NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{32}S_3$ $[M–5Na+4H]^-$: 1100.1853; found: 1100.1857.

58. GlcNAc6S-IdoA2S-GlcNS6S-IdoA

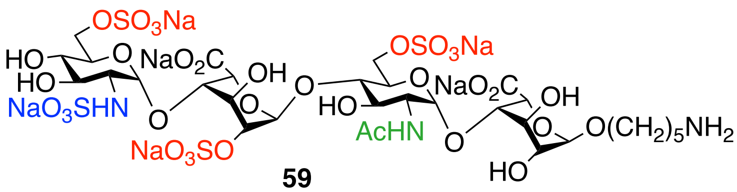


58

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-α-L-idopyranoside uronate hexa sodium salt (58).

Compound **S37** (22 mg, 0.010 mmol) was subjected to hydrolysis, *N*-sulfation, N_3 to NH_2, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **58** (6.1 mg, 51% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 5.10 (s, 1H, H-1''), 5.06 (d, *J* = 3.5 Hz, 1H, H-1'''), 4.85 (d, *J* = 2.1 Hz, 1H, H-5''), 4.78 (d, *J* = 2.8 Hz, 1H, H-1), 4.41 (d, *J* = 2.6 Hz, 1H, H-5), 4.29–4.13 (m, 6H, H-6', H-6''', H-2'', H-3''), 4.02 (appt, *J* = 3.9 Hz, 1H, H-3), 3.97–3.96 (m, 2H, H-4, H-4''), 3.92–3.87 (m, 3H, H-5', H-2''', H-5'''), 3.71–3.53 (m, 6H, OCH_2, H-4', H-3''', H-3', H-2), 3.46 (t, *J* = 9.6 Hz, 1H, H-4'''), 3.17 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2'), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, C=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.6 (C-6''), 175.1 (C-6), 174.9 (*C*ONH), 100.7 (C-1), 99.0 (C-1''), 95.5 (C-1'), 93.6 (C-1'''), 76.1 (C-4'), 74.9 (C-4), 73.8 (C-2''), 71.2 (C-3'''), 70.8 (C-4''), 70.0 (C-5'''), 69.7 (C-3'), 69.2 (C-2), 69.1 (C-4'''), 69.0 (C-5'), 68.7 (C-5), 68.5 (C-3), 68.0 (OCH_2), 67.8 (C-5''), 66.4 (C-6''' and C-6'), 64.0 (C-3''), 57.8 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2 and NHC=OCH_3); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M–6Na+5H]^-$: 1138.1315; found: 1138.1317.

59. GlcNS6S-IdoA2S-GlcNAc6S-IdoA

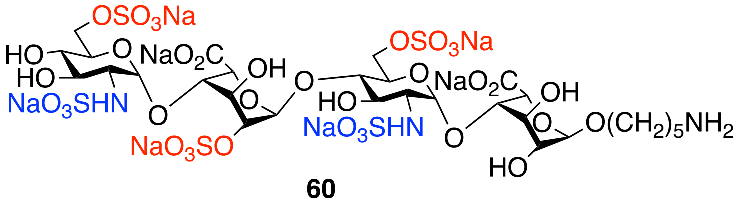


59

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-acetamido-α-L-idopyranoside uronate hexa sodium salt (59).

Compound **S37** (33 mg, 0.014 mmol) was subjected to hydrolysis, *N*-acetylation, N_3 to NH_2, *N*-sulfation, and hydrogenation according to the general procedures to give tetrasaccharide **59** (13 mg, 72% for five steps). ^{1}H NMR (400 MHz, D_2O): δ 5.33 (d, *J* = 3.4 Hz, 1H, H-1'''), 5.12 (d, *J* = 2.5 Hz, 1H, H-1''), 5.08 (d, *J* = 3.7 Hz, 1H, H-1'), 4.76 (d, *J* = 3.0 Hz, 1H, H-1), 4.71 (1H, H-5''), 4.43 (d, *J* = 2.9 Hz, 1H, H-5), 4.34–4.24 (m, 3H, H-6', H-6''', H-2''), 4.19–4.10 (m, 3H, H-6', H-6''', H-3''), 4.04 (t, *J* = 2.9 Hz, 1H, H-4''), 3.97 (t, *J* = 3.3 Hz, 1H, H-4), 3.95–3.88 (m, 2H, H-5', H-5''', H-2'), 3.83 (dd, *J* = 5.4, 4.1 Hz, 1H, H-3), 3.72–3.65 (m, 3H, H-4', OCH_2, H-3'), 3.59–3.45 (m, 4H, H-2, OCH_2, H-3''', H-4'''), 3.15 (dd, *J* = 10.2, 3.4 Hz, 1H, H-2'''), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.92 (s, 3H, $NHC{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 174.8 (C-6), 174.7 (C-6''), 174.3 (NHC=O), 100.8 (C-1), 99.3 (C-1''), 96.7 (C-1'''), 94.4 (C-1'), 75.9 (C-2''), 75.8 (C-4'), 75.7 (C-4''), 74.1 (C-4), 70.9 (C-3'''), 69.9 (C-5'''), 69.7 (C-3'), 69.6 (C-2), 69.4 (C-5'), 69.24 (C-5''), 69.16 (C-4'''), 69.13 (C-3''), 69.0 (C-5), 68.9 (C-3), 68.1 (OCH_2), 66.4 (C-6' and C-6'''), 57.9 (C-2'''), 53.5 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 21.9 ($NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{34}S_4$ $[M{-}6Na{+}5H]^-$: 1138.1315; found: 1138.1312.

60. GlcNS6S-IdoA2S-GlcNS6S-IdoA

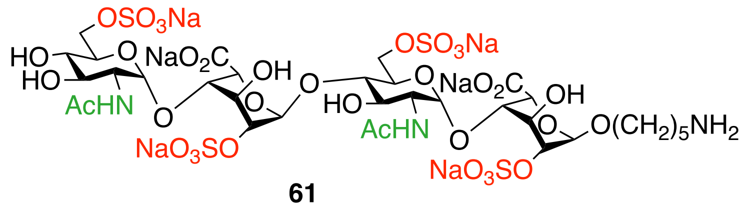


60

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-sulfamino-α-L-idopyranoside uronate hexa sodium salt (60).

Compound **S37** (14 mg, 0.0063 mmol) was subjected to hydrolysis, N_3 to NH_2, *N*-sulfation, and hydrogenation according to the general procedures to give tetrasaccharide **60** (5.1 mg, 62% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.32 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.27 (d, *J* = 3.7 Hz, 1H, H-1'), 5.13 (d, *J* = 2.5 Hz, 1H, H-1''), 4.78 (d, *J* = 2.7 Hz, 1H, H-1), 4.73 (1H, H-5''), 4.41 (d, *J* = 2.5 Hz, 1H, H-5), 4.33–4.23 (m, 3H, H-6', H-6''', H-2''), 4.16–4.10 (m, 3H, H-6', H-6''', H-3''), 4.03–4.00 (m, 2H, H-4'', H-3), 3.96 (t, *J* = 3.0 Hz, 1H, H-4), 3.91–3.88 (m, 2H, H-5', H-5'''), 3.70–3.53 (m, 6H, H-4', OCH_2, H-3', H-2, OCH_2, H-3'''), 3.47 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.17 (dd, *J* = 8.0, 3.5 Hz, 1H, H-2'), 3.15 (dd, *J* = 8.0, 3.5 Hz, 1H, H-2'''), 2.89 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.1 (C-6), 174.8 (C-6''), 100.7 (C-1), 99.2 (C-1''), 96.8 (C-1'''), 95.5 (C-1'), 75.8 (C-4'), 75.7 (C-2'' and C-4''), 74.9 (C-4), 70.9 (C-3'''), 69.9 (C-5'''), 69.7 (C-3'), 69.2 (C-4''' and C-5''), 69.1 (C-2), 69.0 (C-5'), 68.9 (C-3''), 68.5 (C-5), 68.3 (C-3), 68.1 (OCH_2), 66.4 (C-6' and C-6'''), 57.9 (C-2'''), 57.7 (C-2'), 39.4 (NCH_2), 28.0 (CH_2), 26.3 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{36}S_5$ $[M-7Na+6H]^-$: 1176.0778; found: 1176.0786.

61. GlcNAc6S-IdoA2S-GlcNAc6S-IdoA2S

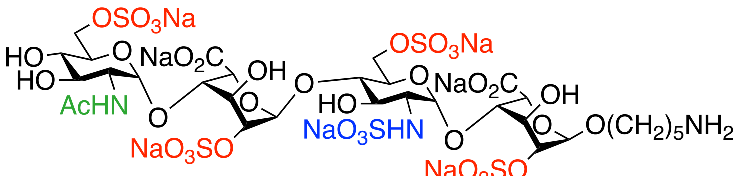


61

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hexa sodium salt (61).

Compound **S31** (32 mg, 0.014 mmol) was subjected to hydrolysis, *N*-acetylation and hydrogenation according to the general procedures to give tetrasaccharide **61** (14 mg, 78% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.09 (s, 1H, H-1''), 5.06 (d, *J* = 3.4 Hz, 1H, H-1'''), 5.03 (d, *J* = 3.7 Hz, 1H, H-1'), 5.01 (s, 1H, H-1), 4.83 (d, *J* = 2.0 Hz, 1H, H-5''), 4.48 (d, *J* = 2.0 Hz, 1H, H-5), 4.28–4.13 (m, 8H, H-6', H-6''', H-2'', H-3'', H-3, H-2), 3.99–3.88 (m, 6H, H-4, H-4'', H-5', H-2''', H-5''', H-2'), 3.72–3.54 (m, 5H, OCH_2, H-4', H-3''', H-3'), 3.47 (t, *J* = 9.5 Hz, 1H, H-4'''), 2.92 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.98 (s, 3H, $C{=}OCH_3$), 1.97 (s, 3H, $C{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.5 (C-6''), 175.2 (C-6), 174.8 (*C*ONH), 174.7 (*C*ONH), 99.2 (C-1''), 98.5 (C-1), 93.6 (C-1'''), 93.4 (C-1'), 76.4 (C-4'), 73.9 (C-2), 73.7 (C-2''), 71.2 (C-3'''), 70.83 (C-4 or C-4''), 70.75 (C-4 or C-4''), 70.03 (C-5'''), 69.99 (C-3'), 69.3 (C-5'), 69.1 (C-4'''), 68.1 (OCH_2), 67.7 (C-5''), 67.0 (C-5), 66.5 (C-6''' and C-6'), 63.9 (C-3''), 63.7 (C-3), 53.4 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.3 (NHC=O*C*H_3), 22.23 (NHC=O*C*H_3), 22.20 (CH_2); HRMS (ESI-TOF) calcd for $C_{33}H_{54}N_3O_{35}S_4$ $[M{-}6Na{+}5H]^-$: 1180.1421; found: 1180.1426.

62. GlcNAc6S-IdoA2S-GlcNS6S-IdoA2S

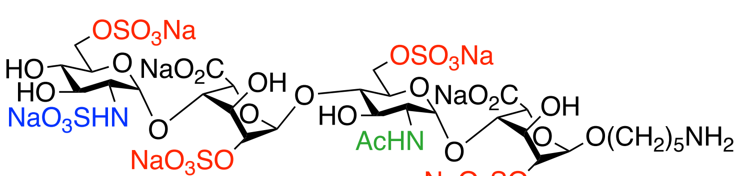


62

5-Aminopentanyl 2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hepta sodium salt (62).

Compound **S31** (30 mg, 0.013 mmol) was subjected to hydrolysis, *N*-sulfation and hydrogenation according to the general procedures to give tetrasaccharide **62** (13 mg, 75% for three steps). ^{1}H NMR (400 MHz, D_2O): δ 5.29 (d, *J* = 3.5 Hz, 1H, H-1'), 5.11 (s, 1H, H-1''), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.04 (s, 1H, H-1), 4.87 (d, *J* = 2.0 Hz, 1H, H-5''), 4.42 (d, *J* = 2.5 Hz, 1H, H-5), 4.27–4.11 (m, 8H, H-6', H-6''', H-2'', H-3'', H-3, H-2), 3.99–3.89 (m, 5H, H-4, H-4'', H-5', H-2''', H-5'''), 3.72–3.55 (m, 5H, OCH_2, H-4', H-3''', H-3'), 3.47 (t, *J* = 9.7 Hz, 1H, H-4'''), 3.19 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'), 2.90 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, $C{=}OCH_3$), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 175.5 (C-6''), 174.8 (*C*ONH), 174.7 (C-6), 98.9 (C-1''), 98.8 (C-1), 96.7 (C-1'), 93.6 (C-1'''), 76.1 (C-4' and C-2), 75.7 (C-4), 73.7 (C-2''), 71.2 (C-3'''), 70.9 (C-4''), 70.0 (C-5'''), 69.6 (C-3'), 69.1 (C-4''' and C-5'), 68.6 (C-3), 68.5 (C-5), 68.1 (OCH_2), 67.8 (C-5''), 66.4 (C-6''' or C-6'), 66.3 (C-6''' or C-6'), 64.0 (C-3''), 58.0 (C-2'), 53.2 (C-2'''), 39.4 (NCH_2), 27.8 (CH_2), 26.3 (CH_2), 22.2 (CH_2 and $NHC{=}OCH_3$); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{37}S_5$ $[M{-}7Na{+}6H]^-$: 1218.0883; found: 1218.0885.

63. GlcNS6S-IdoA2S-GlcNAc6S-IdoA2S

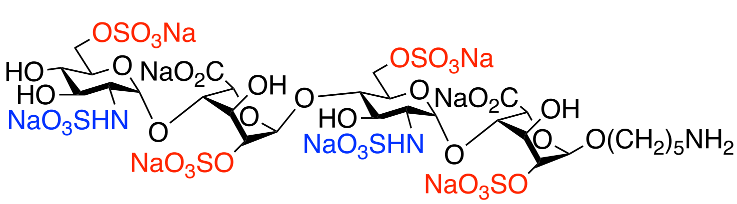


63

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hepta sodium salt (63).

Compound **85** (16 mg, 0.0073 mmol) was subjected to *N*-acetylation, N_3 to NH_2, *N*-sulfation, and hydrogenation according to the general procedures to give tetrasaccharide **63** (6.0 mg, 60% for four steps). ^{1}H NMR (400 MHz, D_2O): δ 5.30 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.14 (d, *J* = 2.1 Hz, 1H, H-1''), 5.04 (d, *J* = 3.5 Hz, 1H, H-1'), 5.03 (s, 1H, H-1), 4.85 (d, *J* = 2.3 Hz, 1H, H-5''), 4.55 (d, *J* = 2.0 Hz, 1H, H-5), 4.29–4.10 (m, 8H, H-6', H-6''', H-2'', H-3'', H-2, H-3), 4.02–3.92 (m, 4H, H-4'', H-4, H-5', H-2'), 3.85–3.82 (m, 1H, H-5'''), 3.70–3.53 (m, 5H, H-4', OCH_2, H-3''', H-3'), 3.48 (t, *J* = 9.4 Hz, 1H, H-4'''), 3.16 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2'''), 2.92 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.97 (s, 3H, NHC=OCH_3), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 174.8 (NHC=O), 174.7 (C-6), 174.0 (C-6''), 99.3 (C-1''), 98.5 (C-1), 97.7 (C-1'''), 93.5 (C-1'), 76.3 (C-4'), 76.1 (C-4''), 75.0 (C-2''), 73.8 (C-2), 70.8 (C-4 and C-3'''), 70.1 (C-5'''), 69.9 (C-3'), 69.4 (C-5'), 69.1 (C-4'''), 68.3 (C-5''), 68.2 (C-3'' and OCH_2), 66.8 (C-5), 66.44 (C-6' or C-6'''), 66.36 (C-6' or C-6'''), 63.6 (C-3), 57.9 (C-2'''), 53.3 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.3 (NHC=O*C*H_3), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{31}H_{52}N_3O_{37}S_5$ $[M–7Na+6H]^–$: 1218.0883; found: 1218.0897.

64. GlcNS6S-IdoA2S-GlcNS6S-IdoA2S

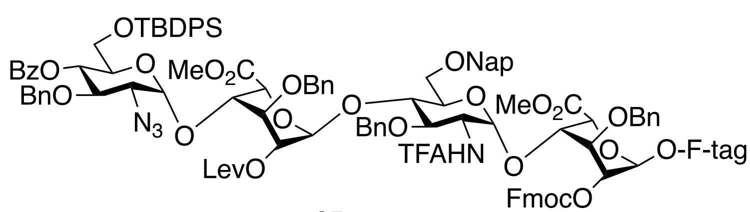


64

5-Aminopentanyl 2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranosyluronate-(1→4)-2-deoxy-2-acetamido-6-*O*-sulfonato-

α-D-glucopyranosyl-(1→4)-2-*O*-sulfonato-α-L-idopyranoside uronate hepta sodium salt (64).

Compound **85** (17 mg, 0.0078 mmol) was subjected to N_3 to NH_2, *N*-sulfation, and hydrogenation according to the general procedures to give tetrasaccharide **64** (8.0 mg, 71% for three steps). ^1H NMR (400 MHz, D_2O): δ 5.33 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.29 (d, *J* = 3.5 Hz, 1H, H-1'), 5.15 (d, *J* = 2.3 Hz, 1H, H-1''), 5.06 (d, *J* = 1.9 Hz, 1H, H-1), 4.79 (d, *J* = 2.6 Hz, 1H, H-5''), 4.45 (d, *J* = 2.5 Hz, 1H, H-5), 4.34–4.26 (m, 3H, H-6', H-6''', H-2''), 4.20–4.11 (m, 5H, H-6', H-6''', H-3'', H-2, H-3), 4.03 (t, *J* = 2.8 Hz, 1H, H-4''), 3.99 (t, *J* = 2.5 Hz, 1H, H-4), 3.95–3.87 (m, 2H, H-5', H-5'''), 3.72–3.55 (m, 5H, H-4', OCH_2, H-3''', H-3'), 3.49 (t, *J* = 9.5 Hz, 1H, H-4'''), 3.20 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2'), 3.17 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2'''), 2.92 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.62–1.52 (m, 4H, 2 X CH_2), 1.39–1.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 174.7 (C-6''), 174.6 (C-6), 99.1 (C-1''), 98.8 (C-1), 97.0 (C-1'''), 96.9 (C-1'), 76.0 (C-2), 75.9 (C-4''), 75.8 (C-4' and C-4), 75.6 (C-2''), 70.9 (C-3'''), 69.9 (C-5'''), 69.5 (C-3'), 69.22 (C-5'), 69.17 (C-4'''), 69.0 (C-5''), 68.8 (C-3''), 68.5 (C-3), 68.3 (C-5), 68.1 (OCH_2), 66.4 (C-6' or C-6'''), 66.3 (C-6' or C-6'''), 57.93 (C-2'''), 57.89 (C-2'), 39.4 (NCH_2), 27.8 (CH_2), 26.2 (CH_2), 22.2 (CH_2); HRMS (ESI-TOF) calcd for $C_{29}H_{50}N_3O_{39}S_6$ $[M–8Na+7H]^–$: 1256.0346; found: 1256.0341.



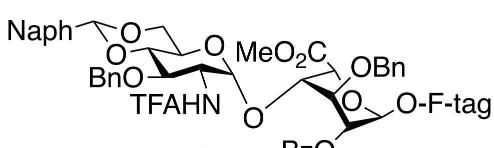
65

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-**

trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl))-α-L-idopyranosyluronate (65).

A mixture of donor **74**[3] (1.7 g, 1.5 mmol), acceptor **72** (1.3 g, 0.75 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous DCM (20 mL) and stirred at RT. After 20 min, NIS (0.42 g, 1.9 mmol) and AgOTf (115 mg, 0.46 mmol) were added. The solution was stirred for another 1 h before pyridine (0.10 mL) was added. The mixture was filtered, and the residue was purified by silica gel column chromatography, eluting first with 3:1 → 2.5:1 hexanes/EtOAc to afford compound **21** (1.6 g, 80%) as a colorless foam. R_f 0.73 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.28 (d, J = 8.0 Hz, 1H, NH), 8.06–7.96 (m, 4H, Ar), 7.93–7.86 (m, 4H, Ar), 7.75–7.55 (m, 10H, Ar), 7.50–7.20 (m, 36H, Ar), 7.13–7.03 (m, 5H, Ar), 5.66 (t, J = 9.6 Hz, 1H, H-4'''), 5.47 (d, J = 4.0 Hz, 1H, H-1''), 5.39 (d, J = 3.4 Hz, 1H, H-1'''), 5.26 (d, J = 3.4 Hz, 1H, H-1'), 5.18 (d, J = 4.5 Hz, 1H, H-1), 5.14 (s, 2H, NCO_2CH_2), 5.07 (t, J = 4.5 Hz, 1H, H-2''), 4.92 (d, J = 4.1 Hz, 1H, H-5), 4.91 (d, J = 11.5 Hz, 1H, CH_2Ph), 4.86 (s, 2H, NapCH_2), 4.83–4.79 (m, 3H, H-2, H-5'', CH_2Ph), 4.78–4.64 (m, 6H, OCH_2Ph), 4.54–4.46 (m, 1H, OCO_2CH_2-Fluoren), 4.50 (s, 2H, NCH_2Ph), 4.35–4.30 (m, 3H, H-4, H-2', OCO_2CH_2-Fluoren), 4.27–4.25 (m, 1H, OCO_2CH_2CH), 4.24 (t, J = 4.5 Hz, 1H, H-4''), 4.20–4.12 (m, 3H, H-3, H-3'', H-5'), 4.10–4.01 (m, 4H, H-4', H-3''', H-5''', H-6'), 3.91–3.84 (m, 2H, H-3', H-6'), 3.81–3.80 (m, 2H, H-6'''), 3.77–3.73 (m, 1H, OCH_2CH_2), 3.74 (s, 3H, OCH_3), 3.51–3.46 (m, 1H, OCH_2CH_2), 3.47 (s, 3H, OCH_3''), 3.23–3.18 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.77–2.74 (m, 2H, CH_2), 2.62–2.47 (m, 4H, CH_2, $PhCH_2CH_2$), 2.10 (s, 3H, CH_3C=O), 1.56–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.6 (CH_3C=OCH_2), 171.8 (CH_2C=O), 169.5 (C=$OOCH_3$), 168.9 (C=$OOCH_3$), 164.7 (C=OPh), 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 155.9 (NCO_2), 154.1 (Fluoren-CH_2OC=O), 143.5 (Ar), 143.3 (Ar), 141.2 (Ar), 138.9 (Ar), 138.7 (Ar), 138.6 (Ar), 138.1 (Ar), 137.1 (Ar), 137.9 (Ar), 137.8 (Ar), 136.2 (Ar), 135.6 (Ar), 135.5 (Ar), 133.5 (Ar), 133.4 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 129.9 (Ar), 129.21 (Ar), 129.67 (Ar), 129.6

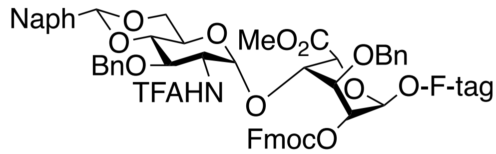
(Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.15 (Ar), 128.08 (Ar), 128.04 (Ar), 128.00 (Ar), 127.99 (Ar), 127.8 (Ar), 127.74 (Ar), 127.69 (Ar), 127.66 (Ar), 127.61 (Ar), 127.58 (Ar), 127.4 (Ar), 127.2 (Ar), 127.1 (Ar), 126.9 (Ar), 126.8 (Ar), 126.4 (Ar), 126.1 (Ar), 126.0 (Ar), 125.8 (Ar), 125.2 (Ar), 125.1 (Ar), 120.1 (Ar), 116.1 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 98.1 (C-1), 98.0 (C-1''), 97.2 (C-1'''), 96.5 (C-1'), 77.8 (C-3', C-3'''), 75.5 (C-3''), 75.2 (C-5'), 74.6 (C-3), 74.2 (CH$_2$Ph), 74.16 (CH$_2$Ph), 73.1 (Nap$C$H$_2$, CH$_2$Ph), 72.9 (CH$_2$Ph), 72.4 (C-4, C-4''), 71.9 (C-5'''), 71.2 (C-4'), 70.4 (C-4'''), 70.0 (C-2''), 69.9 ($CO_2$$CH_2$-Fluoren), 69.7 (C-5, C-5''), 68.5 (OCH$_2$CH$_2$), 68.1 (C-6'), 66.3 (NCO$_2$$CH_2$Ph), 63.0 (C-2'''), 62.1 (C-6'''), 53.4 (C-2'), 51.6 (OCH_3), 51.4 (OCH$_3$''), 49.9 (NCH$_2$Ph), 46.5 (CHCH$_2$, NCH$_2$CH$_2$), 37.3 (CH$_2$C=O), 32.1 (t, $^{2}J_{C,F}$ = 21.6 Hz, CH$_2$CF$_2$), 29.0 (CH$_2$), 28.9 (CH$_3$C=O), 27.7 (CH$_2$C=O), 27.5 (CH$_2$), 26.3 ((CH$_3$)$_3$C), 25.7 (t, $^{3}J_{C,F}$ = 5.0 Hz, CH$_2$CH$_2$CF$_2$), 23.1 (CH$_2$), 18.8 ((CH$_3$)$_3$$C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{138}H_{138}F_{16}N_5O_{29}Si$ 2660.8992; Found 2660.8984. gHSQC 2-D NMR (without ^{1}H decoupling): $^1J_{C1,H1}$ = 172.1 Hz, $^1J_{C1',H1'}$ = 175.7 Hz, $^1J_{C1'',H1''}$ = 173.2 Hz, $^1J_{C1''',H1'''}$ = 176.1 Hz. The coupling constants of $^1J_{C1,H1}$ (172.1 Hz) and $^1J_{C1'',H1''}$ (173.2) Hz are above 170 Hz, which confirms the α configuration of the two IdoA-GlcN linkages.[4] In addition, the coupling constants of $^1J_{C1',H1'}$ (175.7 Hz) and $^1J_{C1''',H1'''}$ (176.1) Hz are greater than 170 Hz, which is indicative of the α configuration for the two GlcN-IdoA linkages.



70

_N_-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-_O_-benzyl-2-deoxy-4,6-_O_-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-2-_O_-benzoyl-3-_O_-benzyl-α-L-idopyranosyluronate (70).

A mixture of donor **69**[3] (0.47 g, 0.48 mmol), the F-tag linker **S56** (0.78 g, 1.2 mmol), and powdered 4 Å molecular sieves was suspended in anhydrous DCM (35 mL) and stirred at RT. After 30 min, NIS (0.21 g, 0.96 mmol) was added and the mixture was cooled to –50 °C for 10 min. Then, TfOH (82 μL, 0.93 mmol) was added via syringe and the solution was slowly warmed up to –20 °C. Et_3N (100 μL) was added to quench the reaction and the mixture was filtered. The filtrate was concentrated, and the resulting residue was purified by silica gel column chromatography (elution with 5:1 → 4:1 hexanes/EtOAc) to afford compound **72** (0.54 g, 72%) as a colorless foam. R_f 0.74 (4:3 hexanes/EtOAc); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.44 (d, *J* = 8.9 Hz, 1H, NH), 8.15–8.12 (m, 3H, Ar), 8.03–7.98 (m, 3H, Ar), 7.78–7.76 (m, 1H, Ar), 7.61–7.58 (m, 2H, Ar), 7.43–7.17 (m, 22H, Ar), 6.00 (s, 1H, NapC*H*), 5.29 (t, *J* = 2.3 Hz, 1H, H-2), 5.26 (d, *J* = 3.6 Hz, 1H, H-1'), 5.23 (s, 1H, H-1), 5.19–5.16 (m, 2H, NCO_2CH_2), 4.95 (s, 1H, H-5), 4.91 (d, *J* = 11.7 Hz, 1H, 3-OCH_2Ph), 4.80 (d, *J* = 11.7 Hz, 1H, 3-OCH_2Ph), 4.75 (d, *J* = 11.7 Hz, 1H, 3'-OCH_2Ph), 4.77 (d, *J* = 11.2 Hz, 1H, 3'-OCH_2Ph), 4.56–4.51 (m, 4H, H-5', H-6', NCH_2Ph), 4.49 (dd, *J* = 3.0, 2.0 Hz, 1H, H-4), 4.32–4.25 (m, 3H, H-3, H-2', 3'-OCH_2Ph), 4.07 (t, *J* = 10.0 Hz, 1H, H-3'), 4.00 (t, *J* = 9.5 Hz, 1H, H-4'), 3.94 (t, *J* = 9.0 Hz, 1H, H-6'), 3.87–3.79 (m, 1H, OC$H_2$$CH_2$), 3.82 (s, 3H, OCH_3), 3.60–3.52 (m, 1H, OC$H_2$$CH_2$), 3.26–3.21 (m, 2H, NCH_2), 3.01–2.97 (m, 2H, PhC$H_2$$CH_2$), 2.65–2.51 (m, 2H, Ph$CH_2CH_2$), 1.66–1.55 (m, 4H, 2 X CH_2), 1.42–1.33 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.2 (*C*=OOCH_3), 165.0 (*C*=OPh), 157.0 (q, $^2J_{C,F}$ = 36.8 Hz, CF_3*C*=O), 155.6 (NCO_2), 139.0 (Ar), 138.9 (Ar), 138.6 (Ar), 138.1 (Ar), 135.7 (Ar), 133.7 (Ar), 133.1 (Ar), 133.0 (Ar), 129.9 (Ar), 129.7 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 127.1 (Ar), 126.8 (Ar), 126.5 (Ar), 126.3 (Ar), 125.6 (Ar), 124.1 (Ar), 116.0 (q, $^1J_{C,F}$ = 287.6 Hz, CF_3), 101.4 (Nap*C*H), 99.4 (C-1), 98.7 (C-1'), 82.9 (C-4'), 75.8 (C-3'), 75.4 (C-3), 75.1 (C-4), 74.0 (3'-O*C*H_2Ph), 71.9 (3-O*C*H_2Ph), 68.4 (C-2), 68.3 (C-6'), 68.0 (O*C*$H_2$$CH_2$), 67.1 (C-5), 66.3 ($NCO_2$*C*$H_2$Ph), 63.8 (C-5'), 54.1 (C-2'), 51.4 (OCH_3), 50.0, 49.8 (N*C*H_2Ph), 46.9, 46.0 (N*C*$H_2$$CH_2$), 32.1 (t, $^2J_{C,F}$ = 21.8 Hz, *C*$H_2$$C_6F_{13}$), 29.0 ($CH_2$), 27.4 ($CH_2$), 25.7 (t, $^3J_{C,F}$ = 4.3 Hz, *C*$H_2$$CH_2$$CF_2$), 23.2 ($CH_2$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{75}H_{71}F_{16}N_2O_{15}$ 1543.4598; Found 1543.4595.

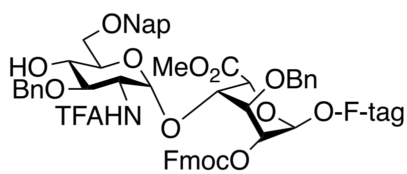


71

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl))-α-L-idopyranosyluronate (71).**

To a mixture of disaccharide **S51** (0.12 g, 0.13 mmol) in pyridine (4.0 mL) at RT was added FmocCl (0.66 g, 2.6 mmol) portion-wise (0.22 g X 3). The reaction was stirred for 2 h, concentrated under reduced pressure, and the resulting residue was dissolved in DCM. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 6:1 → 4:1 hexanes/EtOAc) afforded compound **71** (0.13 g, 90%) as a colorless foam. R_f 0.47 (2:1 hexanes/EtOAc); R_f 0.71 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.23 (d, *J* = 8.0 Hz, 1H, NH), 8.03 (s, 1H, Ar), 7.91–7.89 (m, 3H, Ar), 7.83–7.81 (m, 2H, Ar), 7.66–7.59 (m, 3H, Ar), 7.53–7.51 (m, 2H, Ar), 7.37–7.16 (m, 24H, Ar), 5.26 (d, *J* = 3.6 Hz, 1H, H-1'), 5.14–5.12 (m, 3H, H-1, NCO_2CH_2), 4.96 (d, *J* = 11.2 Hz, 1H, 3'-OCH_2Ph), 4.93 (d, *J* = 4.4 Hz, 1H, H-5), 4.82 (dd, *J* = 5.6, 4.9 Hz, 1H, H-2), 4.81 (s, 2H, NapCH_2), 4.77 (d, *J* = 11.2 Hz, 1H, 3'-OCH_2Ph), 4.72 (s, 2H, 3-OCH_2Ph), 4.52–4.46 (m, 1H, OCO_2CH_2-Fluoren), 4.48 (s, 2H, NCH_2Ph), 4.38–4.32 (m, 2H, H-4, OCO_2CH_2-Fluoren), 4.28–4.23 (m, 2H, H-2', OCO_2CH_2CH), 4.19 (t, *J* = 5.8 Hz, 1H, H-3), 4.08–4.03 (m, 1H, H-5'), 3.95 (dd, *J* = 10.8, 2.1 Hz, 1H, H-6'), 3.88–3.78 (m, 3H, H-3', H-4', H-6'), 3.82 (s, 3H, OCH_3), 3.74 (br, 1H, OCH_2CH_2), 3.46 (br, 1H, OCH_2CH_2), 3.22–3.17 (m, 2H, NCH_2), 2.97–2.93 (m, 2H, $PhCH_2CH_2$), 2.60–2.47 (m, 2H, $PhCH_2CH_2$), 1.56–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.3 (*C*=OOCH$_3$), 156.9 (q, $^2J_{C,F}$ = 36.8 Hz, CF_3C=O), 155.6 (NCO_2), 154.1 (Fluoren-CH_2OC=O), 143.5 (Ar), 143.4 (Ar), 141.2

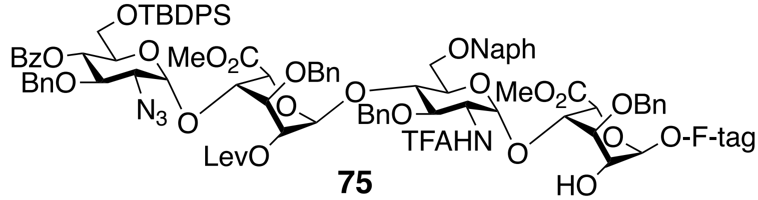
(Ar), 139.1 (Ar), 138.9 (Ar), 138.6 (Ar), 137.9 (Ar), 136.5 (Ar), 133.5 (Ar), 133.0 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 127.94 (Ar), 127.91 (Ar), 127.86 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 127.2 (Ar), 127.1 (Ar), 126.0 (Ar), 125.8 (Ar), 125.7 (Ar), 125.6 (Ar), 125.2 (Ar), 125.1 (Ar), 120.1 (Ar), 116.1 (q, ${}^{1}J_{C,F}$ = 288.0 Hz, CF_3), 98.2 (C-1'), 96.7 (C-1), 79.5 (C-3'), 75.2 (C-3), 74.45 (C-2), 74.40 (3'-O*C*H_2Ph), 73.1 (Nap*C*H_2), 72.86 (3-O*C*H_2Ph), 72.83 (C-5'), 72.5 (C-4), 71.1 (C-4'), 69.94 (C-5), 69.89 (Fluoren-*C*H_2O), 69.6 (C-6'), 68.5 (O*C*H_2CH_2), 66.3 (NCO_2*C*H_2Ph), 53.2 (C-2'), 51.6 (OCH_3), 50.0 49.8 (N*C*H_2Ph), 46.5 (*C*HCH_2, N*C*H_2CH_2), 32.1 (t, ${}^{2}J_{C,F}$ = 21.7 Hz, *C*H_2CF_2), 29.0 (CH_2), 27.8 (CH_2), 25.7 (t, ${}^{3}J_{C,F}$ = 4.2 Hz, *C*$H_2CH_2CF_2$), 23.0 (CH_2); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{83}H_{79}F_{16}N_2O_{16}$ 1663.5175; Found 1663.5189.



72

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl))-α-L-idopyranosyluronate (72).**

To a suspension of compound **71** (1.0 g, 0.60 mmol) in DCM (25 mL) were added triethylsilane (2.5 mL, 16 mmol) and trifluoroacetic anhydride (0.25 g, 1.2 mmol) at 0 °C. After 10 min, trifluoroacetic acid (0.48 g, 4.2 mmol) was added dropwise. The reaction was stirred at RT for 1 h and then quenched with saturated aq. $NaHCO_3$. The resulting mixture was filtered, diluted with DCM (20 mL), and the organic layer was washed with brine, dried over Na_2SO_4, concentratedand purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **72** (0.80 g, 80%) as a colorless foam. R_f 0.48 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.32 (d, *J* = 8.5 Hz, 1H, NH), 7.91–7.86 (m, 6H, Ar), 7.65–7.63 (m, 2H, Ar), 7.56–7.39 (m, 5H, Ar), 7.33–7.20 (m, 21H, Ar), 5.26 (d, J = 3.6 Hz, 1H, H-1'), 5.14–5.12 (m, 3H, H-1, NCO_2CH_2), 4.96 (d, J = 11.2 Hz, 1H, 3'-OCH_2Ph), 4.93 (d, J = 4.4 Hz, 1H, H-5), 4.82 (dd, J = 5.6, 4.9 Hz, 1H, H-2), 4.81 (s, 2H, NapCH_2), 4.77 (d, J = 11.2 Hz, 1H, 3'-OCH_2Ph), 4.72 (s, 2H, 3-OCH_2Ph), 4.52–4.46 (m, 1H, OCO_2CH_2-Fluoren), 4.48 (s, 2H, NCH_2Ph), 4.38–4.32 (m, 2H, H-4, OCO_2CH_2-Fluoren), 4.28–4.23 (m, 2H, H-2', OCO_2CH_2CH), 4.19 (t, J = 5.8 Hz, 1H, H-3), 4.08–4.03 (m, 1H, H-5'), 3.95 (dd, J = 10.8, 2.1 Hz, 1H, H-6'), 3.88–3.78 (m, 3H, H-3', H-4', H-6'), 3.82 (s, 3H, OCH_3), 3.74 (br, 1H, OCH_2CH_2), 3.46 (br, 1H, OCH_2CH_2), 3.22–3.17 (m, 2H, NCH_2), 2.97–2.93 (m, 2H, PhCH_2CH_2), 2.60–2.47 (m, 2H, $PhCH_2CH_2$), 1.56–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.3 (C=$OOCH_3$), 156.9 (q, $^2J_{C,F}$ = 36.8 Hz, CF_3C=O), 155.6 (NCO_2), 154.1 (Fluoren-CH_2OC=O), 143.5 (Ar), 143.4 (Ar), 141.2 (Ar), 139.1 (Ar), 138.9 (Ar), 138.6 (Ar), 137.9 (Ar), 136.5 (Ar), 133.5 (Ar), 133.0 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 127.94 (Ar), 127.91 (Ar), 127.86 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 127.2 (Ar), 127.1 (Ar), 126.0 (Ar), 125.8 (Ar), 125.7 (Ar), 125.6 (Ar), 125.2 (Ar), 125.1 (Ar), 120.1 (Ar), 116.1 (q, $^1J_{C,F}$ = 288.0 Hz, CF_3), 98.2 (C-1'), 96.7 (C-1), 79.5 (C-3'), 75.2 (C-3), 74.45 (C-2), 74.40 (3'-OCH_2Ph), 73.1 (NapCH_2), 72.86 (3-OCH_2Ph), 72.83 (C-5'), 72.5 (C-4), 71.1 (C-4'), 69.94 (C-5), 69.89 (Fluoren-CH_2O), 69.6 (C-6'), 68.5 (OCH_2CH_2), 66.3 (NCO_2CH_2Ph), 53.2 (C-2'), 51.6 (OCH_3), 50.0 49.8 (NCH_2Ph), 46.5 ($CHCH_2$, NCH_2CH_2), 32.1 (t, $^2J_{C,F}$ = 21.7 Hz, CH_2CF_2), 29.0 (CH_2), 27.8 (CH_2), 25.7 (t, $^3J_{C,F}$ = 4.2 Hz, $CH_2CH_2CF_2$), 23.0 (CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{83}H_{79}F_{16}N_2O_{16}$ 1663.5175; Found 1663.5189.

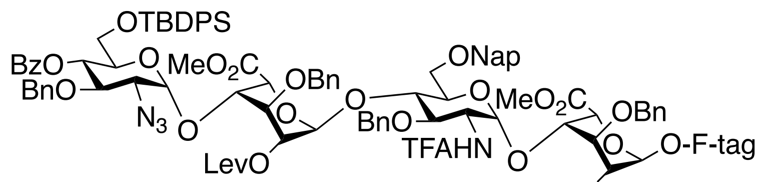


75

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-**

α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (75).

Compound **65** (0.73 g, 0.27 mmol) was treated according to the general procedure for Fmoc deprotection to give tetrasaccharide **75** (0.65 g, 96%); R_f 0.57 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.65 (d, *J* = 8.6 Hz, 1H, NH), 8.03–7.95 (m, 4H, Ar), 7.90–7.81 (m, 2H, Ar), 7.75–7.51 (m, 8H, Ar), 7.47–7.18 (m, 32H, Ar), 7.12–7.03 (m, 5H, Ar), 5.64 (t, *J* = 9.8 Hz, 1H, H-4'''), 5.42 (d, *J* = 3.0 Hz, 1H, H-1''), 5.36 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.21 (d, *J* = 3.5 Hz, 1H, H-1'), 5.15 (br, 2H, NCO_2CH_2), 5.07 (t, *J* = 3.2 Hz, 1H, H-2''), 4.98 (s, 1H, H-1), 4.87 (d, *J* = 1.5 Hz, 1H, H-5), 4.83 (d, *J* = 3.1 Hz, 1H, H-5''), 4.81–4.72 (m, 7H, CH_2Ph, NapCH_2), 4.64 (d, *J* = 11.2 Hz, 1H, OCH_2Ph), 4.63 (d, *J* = 10.9 Hz, 1H, OCH_2Ph), 4.51 (s, 2H, NCH_2Ph), 4.43 (d, *J* = 11.3 Hz, 1H, OCH_2Ph), 4.27–3.98 (m, 9H), 3.91 (s, 1H, H-2), 3.80–3.73 (m, 6H), 3.72 (s, 3H, OCH_3), 3.65 (dd, *J* = 10.3, 4.4 Hz, 1H, H-2'''), 3.50–3.40 (m, 1H, OCH_2CH$_2$), 3.39 (s, 3H, OCH_3''), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, PhCH_2CH$_2$), 2.75–2.71 (m, 2H, CH_2), 2.62–2.49 (m, 4H, CH_2, PhCH$_2$CH_2), 2.07 (s, 3H, CH_3C=O), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.6(CH_3*C*=OCH_2), 172.0 (CH_2*C*=O), 169.9(*C*=OOCH$_3$), 168.8(*C*=OOCH$_3$), 164.7(*C*=OPh), 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 155.9 (NCO_2), 139.0, 138.6, 138.5, 137.9, 137.8, 136.2, 135.6, 135.5, 133.5, 133.4, 133.0, 133.0, 129.9, 129.7, 129.7, 129.6, 128.7, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.0, 126.8, 126.3, 126.1, 126.0, 125.7, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.6 (C-1''), 96.9 (C-1'''), 95.4 (C-1'), 78.3, 77.8, 74.7, 74.4, 74.2, 73.5, 73.4, 73.0, 72.7, 72.2, 72.0, 71.7, 71.6, 71.2, 70.4 (C-4'''), 68.8, 68.7, 68.1, 67.9, 67.3, 66.5 (C-2), 66.3 (NCO_2*C*H$_2$Ph), 63.1 (C-2'''), 62.1, 53.6 (C-2'), 51.6 (OCH_3), 51.2 (OCH_3''), 50.1, 49.8, 46.9, 46.1, 37.3 (CH_2C=O), 32.1 (t, $^2J_{C,F}$ = 21.6 Hz, *C*H$_2$CF$_2$), 29.2 (CH_3C=O), 29.0 (CH_2), 27.7 ($CH_2C=O$), 26.3 ($(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3 (CH_2), 18.8 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M - N_2]^{+2}$ calcd for $C_{123}H_{127}F_{16}N_3O_{27}Si$ 1205.9164; Found 1205.9174.



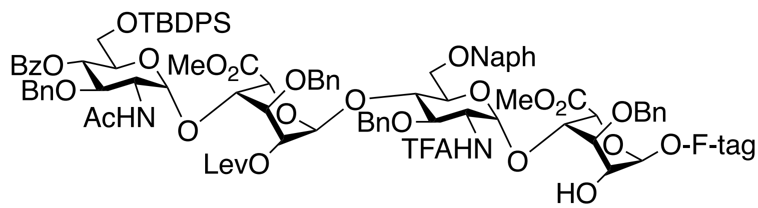
76

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-benzoly-3-*O*-benzyl-α-L-idopyranosyluronate (76).**

Method 1: To a solution of **75** (0.050 g, 0.021 mmol) in pyridine (2.0 mL) was added BzCl (0.30 g, 2.2 mmol) at RT. After stirring overnight, the mixture was concentrated under reduced pressure, and the residue was dissolved in DCM (20 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) gave compound **76** (0.049 g, 95%) as a colorless foam.

Method 2: A mixture of donor **74** (0.72 g, 0.64 mmol), acceptor **S50** (0.50 g, 0.32 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous DCM (8.0 mL) and stirred at RT. After 30 min, NIS (0.22 g, 0.98 mmol) and AgOTf (50 mg, 0.19 mmol) were added. The solution was stirred for another 1 h before Et_3N (0.10 mL) was added. The mixture was filtered, concentrated, and the residue was purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **76** (0.67 g, 82%) as a colorless foam.

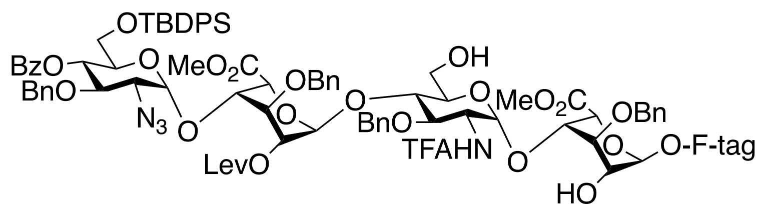
R_f 0.55 (3:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.83 (m, 8H, Ar), 7.66–7.02 (m, 40H, Ar), 6.92–6.90 (m, 2H, Ar), 6.14 (d, J = 8.0 Hz, 1H, NH), 5.59 (t, J = 9.5 Hz, 1H, H-4'''), 5.45 (d, J = 4.7 Hz, 1H, H-1''), 5.18–5.08 (m, 6H, H-1''', H-1', H-1, H-2, NCO_2CH_2), 5.00 (t, J = 5.2 Hz, 1H, H-2''), 4.83–4.71 (m, 6H), 4.65–4.45 (m, 7H), 4.17–3.86 (m, 10H), 3.78–3.62 (m, 5H), 3.59 (s, 3H, OCH_3), 3.51–3.42 (m, 3H), 3.41 (s, 3H, OCH_3), 3.22–3.10 (m, 2H, NCH_2), 2.94–2.91 (m, 2H, $PhC\mathit{H_2}CH_2$), 2.67–2.53 (m, 2H, CH_2), 2.45–2.31 (m, 4H, CH_2, $PhCH_2C\mathit{H_2}$), 2.10 (s, 3H, $CH_3C{=}O$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8 ($CH_3\mathit{C}{=}OCH_2$), 171.9, 169.5, 169.2, 165.4, 164.8, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3\mathit{C}{=}O$), 156.1 (NCO_2), 138.8, 137.7, 137.5, 137.2, 137.1, 135.6, 135.5, 135.3, 133.8, 133.3, 133.1, 133.0, 132.9, 129.7, 129.6, 129.6, 129.2, 129.0, 128.6, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.3, 127.3, 127.2, 127.1, 126.9, 126.5, 126.1, 125.9, 115.5 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0 (C-1), 98.1 (C-1''), 97.8 (C-1'), 97.5 (C-1'''), 75.3, 75.0, 75.0, 74.5, 74.1, 73.9, 73.6, 73.0, 72.7, 72.6, 71.9, 71.4, 70.7 (C-2''), 70.3, 70.2 (C-4'''), 68.9, 68.0, 67.1, 66.8, 62.9, 62.0, 53.5, 52.7 (C-2'), 52.1 (OCH_3), 51.8 (OCH_3), 47.1 ($N\mathit{C}H_2Ph$), 37.7 ($CH_2C{=}O$), 32.9 (t, $^2J_{C,F}$ = 22.3 Hz, $\mathit{C}H_2CF_2$), 29.7, 29.1, 27.7, 26.6 ($(\mathit{C}H_3)_3C$), 26.2 (t, $^3J_{C,F}$ = 4.0 Hz, $\mathit{C}H_2CH_2CF_2$), 23.3, 19.1 ($(CH_3)_3\mathit{C}$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{130}H_{132}F_{16}N_5O_{28}Si$ 2542.8572; Found 2542.7456. gHSQC 2-D NMR (without ^{1}H decoupling): $^1J_{C1,H1}$ = 171.1 Hz, $^1J_{C1',H1'}$ = 172.9 Hz, $^1J_{C1'',H1''}$ = 173.7 Hz, $^1J_{C1''',H1'''}$ = 174.9 Hz. The coupling constants of $^1J_{C1,H1}$ (171.1 Hz) and $^1J_{C1'',H1''}$ (173.7) Hz are above 170 Hz, which confirms the α configuration of the two IdoA-GlcN linkages.[4] In addition, the coupling constants of $^1J_{C1',H1'}$ (172.9 Hz) and $^1J_{C1''',H1'''}$ (174.9) Hz are greater than 170 Hz, which is indicative of the α configuration for the two GlcN-IdoA linkages.



77

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (77).**

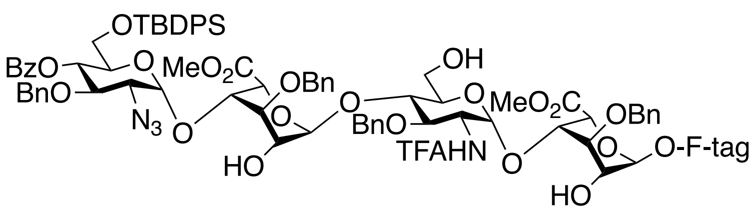
Compound **75** (0.50 g, 0.27 mmol) was treated according to the general procedure for N_3 to NHAc conversion to give tetrasaccharide **77** (0.42 g, 83%); R_f 0.49 (1:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.49 (d, J = 9.5 Hz, 1H, NH), 7.99–7.97 (m, 2H, Ar), 7.90–7.74 (m, 4H, Ar), 7.68–7.61 (m, 4H, Ar), 7.53–7.19 (m, 28H, Ar), 7.12–7.05 (m, 11H, Ar), 5.69 (t, J = 9.6 Hz, 1H, H-4'''), 5.38 (d, J = 2.2 Hz, 1H, H-1''), 5.22 (d, J = 3.2 Hz, 1H, H-1'), 5.19 (d, J = 3.3 Hz, 1H, H-1'''), 5.14 (br, 2H, NCO_2CH_2), 5.07 (t, J = 3.0 Hz, 1H, H-2''), 4.97 (s, 1H, H-1), 4.91 (s, 1H), 4.85–4.63 (m, 10H), 4.54–4.51 (m, 3H, OCH_2Ph, NCH_2Ph), 4.45–4.39 (m, 2H), 4.26 (td, J = 10.3, 3.2 Hz, H-2'), 4.19–4.11 (m, 4H), 4.06–3.99 (m, 3H), 3.93–3.88 (m, 2H), 3.86–3.72 (m, 6H), 3.69 (s, 3H, OCH_3), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.35 (s, 3H, OCH_3''), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.80–2.46 (m, 6H, CH_2, $PhCH_2CH_2$), 2.10 (s, 3H, CH_3C=O), 1.79 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.1 (CH_3C=OCH_2), 171.9, 169.9, 169.2, 168.6, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.6, 138.5, 138.4, 137.9, 136.3, 135.6, 135.5, 133.5, 133.2, 133.1, 133.0, 133.0, 130.1, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.2, 127.1, 127.0, 126.8, 126.1, 126.0, 125.9, 125.8, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.6 (C-1''), 97.4 (C-1'''), 95.8 (C-1'), 78.4, 78.0, 74.5, 74.5, 73.4, 73.1, 72.9, 72.7, 72.5, 72.1, 71.9, 71.6, 71.3, 70.3, 68.8, 68.5, 68.1, 67.9, 67.3, 66.3, 62.2, 54.1, 53.7, 52.5, 51.5, 51.2, 50.0, 49.9, 46.9, 46.0, 37.3 (CH_2C=O), 32.2 (t, ${}^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.0, 27.7 (CH_2C=O), 26.3 ($(CH_3)_3C$), 25.7 (t, ${}^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.3, 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M - 2H]^{+2}$ calcd for $C_{125}H_{131}F_{16}N_3O_{28}Si$ 1227.9294; Found 1227.9275.



78

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (78).**

Compound **75** (0.24 g, 0.097 mmol) was treated according to the general procedure for Nap deprotection to give tetrasaccharide **78** (0.20 g, 89%); R_f 0.51 (2:3 hexanes/EtOAc); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.55 (d, J = 8.9 Hz, 1H, NH), 8.07–8.05 (m, 2H, Ar), 7.73–7.68 (m, 3H, Ar), 7.62–7.54 (m, 4H, Ar), 7.49–7.17 (m, 30H, Ar), 7.12–7.03 (m, 5H, Ar), 5.63 (t, J = 9.6 Hz, 1H, H-4'''), 5.36 (d, J = 3.0 Hz, 1H, H-1''), 5.33 (d, J = 3.4 Hz, 1H, H-1'''), 5.17 (d, J = 3.4 Hz, 1H, H-1'), 5.13 (br, 2H, NCO_2CH_2), 5.07 (dd, J = 4.3, 3.0 Hz, 1H, H-2''), 4.97 (s, 1H, H-1), 4.89–4.77 (m, 6H, CH_2Ph, H-5, H-5''), 4.72–4.62 (m, 3H, CH_2Ph), 4.51 (s, 2H, NCH_2Ph), 4.40 (d, J = 11.1 Hz, 1H, OCH_2Ph), 4.23–4.16 (m, 4H), 4.10–3.98 (m, 4H), 3.92–3.83 (m, 4H), 3.80–3.64 (m, 9H), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.36 (s, 3H, OCH_3''), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.87–2.82 (m, 2H, CH_2), 2.76–2.51 (m, 4H, CH_2, $PhCH_2CH_2$), 2.14 (s, 3H, CH_3C=O), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.00 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.8 ($CH_3\mathit{C}{=}OCH_2$), 171.9, 169.8, 168.7, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3\mathit{C}{=}O$), 138.9, 138.6, 138.5, 138.5, 138.0, 137.9, 135.6, 135.4, 133.4, 133.1, 133.0, 129.9, 129.7, 129.6, 129.6, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 127.0, 126.8, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.7 (C-1''), 96.9 (C-1'''), 95.8 (C-1'), 78.2, 77.9, 74.3, 74.3, 73.8, 73.3, 72.8, 72.6, 72.4, 72.3, 71.6, 71.2, 70.4, 68.8, 68.7, 67.9, 67.4, 66.6, 66.3, 63.1, 62.1, 60.2, 53.6, 53.5, 51.6 (OCH_3), 51.2 (OCH_3''), 50.1, 49.8, 46.9, 46.1, 37.4 ($CH_2C{=}O$), 32.1 (t, $^2J_{C,F}$ = 21.6 Hz, $\mathit{C}H_2CF_2$), 29.2 ($CH_3C{=}O$), 28.8 (CH_2), 27.7 ($CH_2C{=}O$), 26.3 ($(\mathit{C}H_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $\mathit{C}H_2CH_2CF_2$), 23.3 (CH_2), 18.8 ($(CH_3)_3\mathit{C}$); HRMS (ESI-TOF) m/z $[M + N_a]^+$ calcd for $C_{112}H_{119}F_{16}N_5O_{27}SiNa$ 2320.7505; Found 2320.7500.

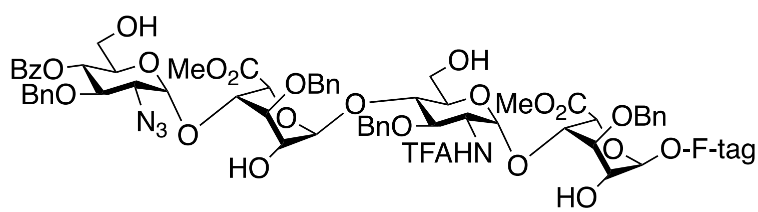


79

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (79).**

Compound **78** (0.13 g, 0.097 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **79** (0.12 g, 96%); R_f 0.64 (2:3 hexanes/EtOAc); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.55 (d, J = 9.0 Hz, 1H, NH), 8.07–8.05 (m, 2H, Ar), 7.73–7.68 (m, 3H, Ar), 7.62–7.50 (m, 6H, Ar), 7.46–7.15 (m, 28H, Ar), 7.10–7.03 (m, 5H, Ar), 5.58 (t, J = 9.6 Hz, 1H, H-4'''), 5.42 (d, J = 3.6 Hz, 1H, H-1'''), 5.38 (d, J = 3.7 Hz, 1H, H-1''), 5.17 (d, J = 3.5 Hz, 1H, H-1'), 5.14 (br, 2H, NCO_2CH_2), 4.96 (s, 1H, H-1), 4.95 (d,

J = 12.5 Hz, 1H, OCH_2Ph), 4.85 (d, J = 1.5 Hz, 1H, H-5), 4.83–4.75 (m, 4H, CH_2Ph, H-5''), 4.70 (d, J = 11.5 Hz, 1H, OCH_2Ph), 4.65–4.61 (m, 2H, CH_2Ph), 4.50 (s, 2H, NCH_2Ph), 4.40–4.33 (m, 2H, OCH_2Ph), 4.25–4.14 (m, 3H), 4.11–3.87 (m, 10H), 3.84–3.65 (m, 10H), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.36 (s, 3H, OCH_3''), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.61–2.48 (m, 2H, $PhCH_2CH_2$), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.7, 169.1, 167.8, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.7, 138.6, 138.5, 138.5, 137.8, 135.6, 135.4, 133.5, 133.1, 133.0, 129.9, 129.7, 129.7, 129.6, 128.8, 128.5, 128.4, 128.4, 128.2, 128.2, 128.1, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 126.9, 126.7, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.3 (C-1), 101.1 (C-1''), 96.2 (C-1'''), 95.8 (C-1'), 78.4, 78.3, 75.5, 75.1, 74.6, 74.3, 73.6, 72.9, 72.3, 71.5, 71.2, 70.4, 69.4, 69.4, 67.9, 67.1, 66.3, 63.2, 62.2, 60.4, 53.6, 53.5, 51.6 (OCH_3), 51.2 (OCH_3''), 50.1, 49.8, 46.9, 46.1, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.2 (CH_3C=O), 27.7 (CH_2), 26.3 ($(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3 (CH_2), 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{107}H_{113}F_{16}N_5O_{25}Si$ 2200.7317; Found 2200.7336.

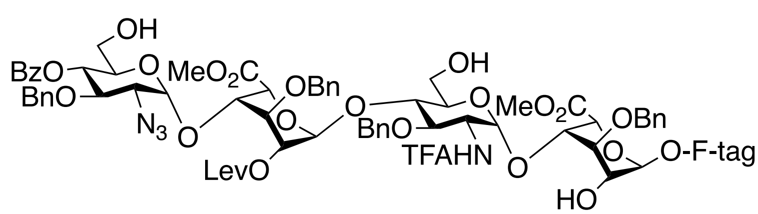


80

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (80).**

Compound **79** (25 mg, 0.011 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **80** (21 mg, 93%); R_f 0.29 (2:3

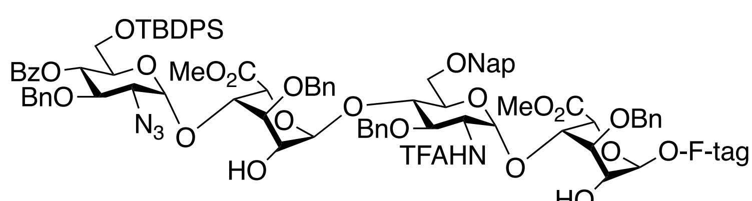
hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.57 (d, J = 9.3 Hz, 1H, NH), 8.07–8.05 (m, 2H, Ar), 7.69–7.66 (m, 1H, Ar), 7.57–7.51 (m, 4H, Ar), 7.46–7.15 (m, 27H, Ar), 5.40 (d, J = 3.8 Hz, 1H, H-1''), 5.37 (d, J = 3.6 Hz, 1H, H-1'''), 5.29 (t, J = 9.8 Hz, 1H, H-4'''), 5.17 (d, J = 3.6 Hz, 1H, H-1'), 5.14 (br, 2H, NCO_2CH_2), 4.97 (s, 1H, H-1), 4.95 (d, J = 11.1 Hz, 1H, OCH_2Ph), 4.86–4.73 (m, 7H, CH_2Ph, H-5'', H-5), 4.64–4.62 (m, 2H, CH_2Ph), 4.50 (s, 2H, NCH_2Ph), 4.41–4.38 (m, 2H), 4.24–4.16 (m, 3H), 4.09–3.83 (m, 9H), 3.82–3.56 (m, 10H), 3.49 (s, 3H, OCH_3), 3.47–3.40 (m, 1H, OCH_2CH_2), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.61–2.48 (m, 2H, $PhCH_2CH_2$), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.7, 169.3, 165.1, 157.0 (q, $^{2}J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.7, 138.6, 138.5, 138.5, 137.8, 133.5, 129.7, 129.6, 128.8, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.2, 126.9, 116.1 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 101.3 (C-1), 101.0 (C-1''), 96.4 (C-1'''), 95.8 (C-1'), 78.4, 78.1, 75.9, 75.1, 74.6, 74.4, 73.6, 73.0, 72.9, 72.3, 71.5, 71.4, 71.0, 69.7, 69.5, 67.9, 67.1, 66.3, 63.2, 60.7, 60.3, 59.7, 54.1, 53.6, 53.5, 51.6, 51.3, 46.9, 46.1, 32.1 (t, $^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 27.7, 25.7 (t, $^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{91}H_{95}F_{16}N_5O_{25}$ 1962.6139; Found 1962.6141.



81

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (81).**

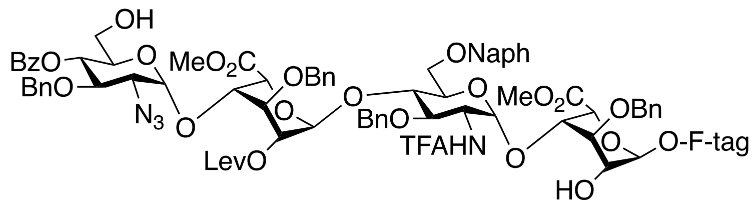
Compound **78** (31 mg, 0.013 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **81** (26 mg, 92%); R_f 0.20 (2:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.58 (d, J = 9.3 Hz, 1H, NH), 8.07–8.05 (m, 2H, Ar), 7.76–7.73 (m, 4H, Ar), 7.69–7.65 (m, 1H, Ar), 7.56–7.43 (m, 12H, Ar), 7.38–7.17 (m, 15H, Ar), 5.39 (d, J = 3.3 Hz, 1H, H-1''), 5.31 (dd, J = 10.1, 9.4 Hz, 1H, H-4'''), 5.26 (d, J = 3.5 Hz, 1H, H-1'''), 5.18 (d, J = 3.5 Hz, 1H, H-1'), 5.15 (br, 2H, NCO_2CH_2), 5.06 (dd, J = 3.8, 3.0 Hz, 1H, H-2''), 4.98 (s, 1H, H-1), 4.89–4.73 (m, 8H, CH_2Ph, OH, H-5, H-5''), 4.69–4.62 (m, 2H, CH_2Ph), 4.51 (s, 2H, NCH_2Ph), 4.42 (d, J = 11.0 Hz, 1H, OCH_2Ph), 4.23–4.15 (m, 4H), 4.09 (dd, J = 10.1, 9.3 Hz, 1H), 4.04 (t, J = 9.5 Hz, 1H), 3.99–3.94 (m, 2H), 3.94–3.84 (m, 3H), 3.82–3.57 (m, 9H), 3.52 (s, 3H, OCH_3), 3.50–3.40 (m, 1H, OC$H_2$$CH_2$), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, PhC$H_2$$CH_2$), 2.87–2.82 (m, 2H, CH_2), 2.76–2.66 (m, 2H, CH_2), 2.60–2.47(m, 2H, $PhCH_2$CH_2), 2.14 (s, 3H, CH_3C=O), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.9 (CH_3*C*=OCH_2), 171.9, 169.9, 169.0, 165.2, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 139.0, 138.6, 138.5, 138.5, 138.0, 137.9, 134.3, 134.2, 133.5, 132.5, 132.4, 130.5, 129.7, 129.6, 128.8, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.5, 127.5, 127.5, 127.3, 126.9, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.7 (C-1''), 97.3 (C-1'''), 95.8 (C-1'), 78.1, 77.7, 74.5, 74.3, 74.0, 73.0, 72.8, 72.8, 72.3, 71.6, 71.5, 71.2, 69.1, 69.0, 67.9, 67.4, 66.7, 66.3, 63.1, 60.7, 60.1, 53.6, 51.6 (OCH_3), 51.3 (OCH_3), 50.1, 49.8, 46.9, 46.1, 37.4 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, *C*H_2CF_2), 27.8, 25.7 (CH_2C=O), 25.4, 23.3; HRMS (ESI-TOF) m/z $[M + N_a]^+$ calcd for $C_{96}H_{101}F_{16}N_5O_{27}Na$ 2082.6326; Found 2082.6340.



82

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (82).**

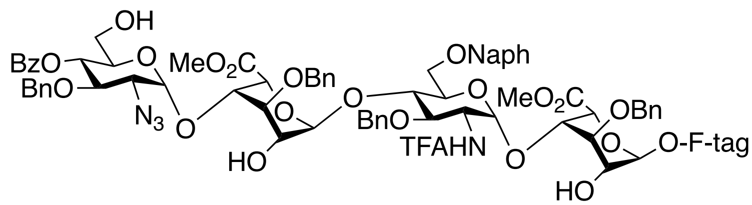
Compound **75** (80 mg, 0.033 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **82** (73 mg, 95%); R_f 0.33 (2:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.46 (d, J = 9.1 Hz, 1H, NH), 8.11–7.85 (m, 6H, ArH), 7.79–7.00 (m, 40H, ArH), 5.63 (app t, J = 9.7 Hz, 1H, H-4'''), 5.47–5.44 (m, 2H, H-1'', H-1'''), 5.22 (d, J = 3.4 Hz, 1H, H-1'), 5.20–5.12 (m, 2H, NCO_2CH_2), 5.01–4.70 (m, 11H), 4.69–4.59 (m, 2H), 4.52 (bs, 2H, NCH_2Ph), 4.42 (d, J = 11.4 Hz, 1H, ArCH_2), 4.33 (d, J = 8.7 Hz, 1H), 4.31–4.20 (m, 2H), 4.19–3.99 (m, 7H), 3.98–3.92 (m, 2H), 3.88–3.66 (m, 11H), 3.52–3.41 (m, 1H, OCH_2), 3.37 (s, 3H, $COOCH_3$), 3.30–3.18 (m, 2H, NCH_2), 3.02–2.92 (m, 2H, PhCH_2CH_2) 2.65–2.47 (m, 2H, PhCH_2CH_2), 1.68–1.49 (m, 4H, 2 X CH_2), 1.41–1.29 (m, 2H, CH_2), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.9 (C=O), 170.5 (C=O), 170.1 (C=O), 165.5 (C=O), 158.0 157.8 (q, J = 36.5 Hz, $COCF_3$), 139.8, 139.53, 139.46, 139.4, 139.3, 138.6, 137.1, 136.5, 136.3, 134.4, 134.3, 133.94, 133.92, 133.8, 130.7, 130.6, 130.54, 130.46, 129.6, 129.34, 129.29, 129.27, 129.1, 129.03, 129.01, 128.9, 128.92, 128.90, 128.87, 128.59, 128.56, 128.52, 128.49, 128.46, 128.44, 128.36, 128.3, 128.0, 127.8, 127.6, 127.2, 126.9, 126.8, 126.6, 117.1 (q, J = 287 Hz, CF_3), 102.1 (C-1), 101.9 (C-1''), 97.2 (C-1'''), 96.6 (C-1'), 79.3, 79.2, 76.6, 76.5, 75.4, 75.1, 74.5, 74.1, 73.8, 73.7, 73.4, 72.8, 72.4, 72.0, 71.2 (C-4'''), 70.4, 70.4, 69.4, 68.7 (OCH_2), 68.0, 67.2 ($NCOCH_2$), 64.1, 63.0, 60.5, 54.4, 52.4 ($COOCH_3$), 52.1 ($COOCH_3$), 50.9, 50.7, 47.8, 46.9, 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.6, 29.5, 29.3, 27.1 ($(CH_3)_3C$), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 24.2, 19.7 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{118}H_{121}F_{16}N_5O_{25}Si$ 2340.7942; Found 2340.7953.



83

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (83).**

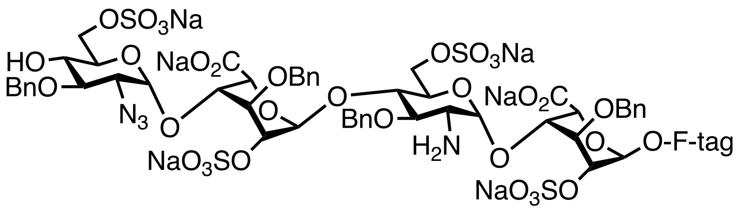
Compound **75** (170 mg, 0.070 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **83** (150 mg, 98%); R_f 0.50 (1:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.52 (d, J = 9.3 Hz, 1H, NH), 8.07–8.03 (m, 2H, ArH), 8.03–7.96 (m, 2H, ArH), 7.94–7.90 (m, 1H, ArH), 7.89–7.83 (m, 1H, ArH), 7.71–7.65 (m, 2H, ArH), 7.57–7.43 (m, 8H, ArH), 7.41–7.15 (m, 20H, ArH), 5.47 (d, J = 3.6 Hz, 1H, H-1''), 5.33 (app t, J = 9.6 Hz, 1H, H-4'''), 5.30 (d, J = 3.6 Hz, 1H, H-1'''), 5.23 (d, J = 3.5 Hz, 1H, H-1'), 5.20–5.12 (m, 2H, NCO_2CH_2), 5.01 (app t, J = 3.6 Hz, 1H, H-2''), 5.00 (bs, 1H, H-1), 4.94–4.74 (m, 10H), 4.70–4.63 (m, 2H), 4.52 (bs, 2H, NCH_2Ph), 4.44 (d, J = 11.4 Hz, 1H, $ArCH_2$), 4.31–3.97 (m, 10H), 3.96–3.91 (m, 1H), 3.86–3.66 (m, 9H), 3.64–3.53 (m, 5H, H-2''', OCH_2, $COOCH_3$), 3.52–3.40 (m, 1H, OCH_2), 3.30–3.16 (m, 2H, NCH_2), 3.02–2.93 (m, 2H, $PhCH_2CH_2$), 2.77–2.68 (m, 2H, $CH_3COCH_2CH_2$), 2.65–2.46 (m, 4H, $CH_3COCH_2CH_2$, $PhCH_2CH_2$), 2.08 (s, 3H, $CH_3COCH_2CH_2$), 1.69–1.50 (m, 4H, 2 X CH_2), 1.43–1.25 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.4 (CH_3C=O), 172.7 (C=O), 170.8 (C=O), 169.9 (C=O), 166.0 (C=O), 157.8 (q, J = 36.5 Hz, $COCF_3$), 139.8, 139.5, 139.4, 138.9, 138.7, 137.0, 134.4, 134.3, 133.9, 130.5, 130.4, 129.6, 129.34, 129.31, 129.29, 129.1, 129.03, 129.00, 128.9, 128.8, 128.74, 128.68, 128.6, 128.44, 128.39, 128.33, 128.30, 128.2, 128.0, 127.8, 127.3, 127.0, 126.8, 126.6, 117.0 (q, J = 288 Hz, CF_3), 102.0 (C-1), 98.6 (C-1''), 98.2 (C-1'''), 96.6 (C-1'), 79.2, 78.4, 75.8, 75.4, 75.1, 75.1, 74.7, 73.9, 73.8, 73.5, 73.2, 72.6, 72.5, 72.4, 72.0 (C-4'''), 70.2 (C-2''), 69.9, 68.9, 68.8 (O*C*H_2), 68.3, 67.6, 67.2 (NCO*C*H_2), 63.8, 61.6, 60.5, 55.0, 54.4, 52.4 (COO*C*H_3), 52.2 (COO*C*H_3), 50.9, 47.8, 46.9, 38.2, 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, *C*H_2CF_2), 28.6, 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, *C*$H_2CH_2CF_2$), 24.2 (*C*H_2); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{107}H_{109}F_{16}N_5O_{27}Na$ 2222.6953; Found 2222.6968.



84

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (84).**

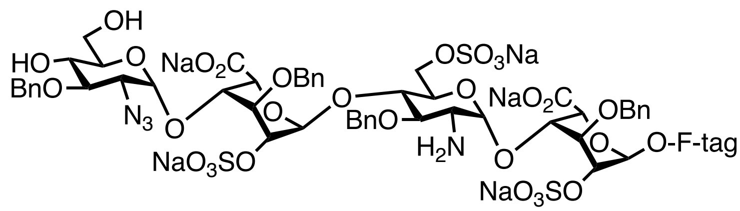
Compound **83** (75 mg, 0.074 mmol) was treated according to the general procedure of Lev deprotection to give tetrasaccharide **84** (69 mg, 96%); R_f 0.52 (1:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.51 (d, *J* = 9.8 Hz, 1H, NH), 8.11–7.86 (m, 6H, ArH), 7.72–7.63 (m, 2H, ArH), 7.60–7.18 (m, 28H, ArH), 5.48 (d, *J* = 4.0 Hz, 1H, H-1''), 5.40 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.32 (app t, *J* = 9.3 Hz, 1H, H-4'''), 5.23 (d, *J* = 3.4 Hz, 1H, H-1'), 5.20–5.12 (m, 2H, NCO_2C*H_2*), 4.99 (bs, 1H, H-1), 4.94 (d, *J* = 10.3 Hz, 1H, ArC*H_2*), 4.91–4.71 (m, 8H), 4.68–4.62 (m, 2H), 4.52 (bs, 2H, NC*H_2*Ph), 4.42 (d, *J* = 11.1 Hz, 1H, ArC*H_2*), 4.32–4.08 (m, 6H), 4.08–3.99 (m, 2H), 3.98–3.94 (m, 1H), 3.91 (ddd, *J* = 9.3, 4.7, 2.5 Hz, 1H, H-5'''), 3.86–3.71 (m, 9H), 3.66–3.60 (m, 2H, H-6'''), 3.54–3.39 (m, 4H, COOC*H_3*, OC*H_2*), 3.29–3.15 (m, 2H, NC*H_2*), 3.01–2.93 (m, 2H, PhC*H_2*CH_2), 2.62–2.46 (m, 2H, PhCH_2C*H_2*), 2.08 (s, 3H, C*H_3*$COCH_2CH_2$), 1.67–1.49 (m, 4H, 2 X CH_2), 1.42–1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.5 (C=O), 170.3 (C=O), 166.0 (C=O), 157.8 (q, J = 36.7 Hz, COCF$_3$), 139.8, 139.5, 139.44, 139.43, 139.3, 138.6, 137.1, 134.4, 133.9, 130.5, 130.4, 129.6, 129.33, 129.29, 129.2, 129.1, 129.03, 129.01, 128.91, 128.88, 128.77, 128.75, 128.7, 128.54, 128.46, 128.42, 128.36, 128.3, 128.2, 128.0, 127.8, 127.2, 126.9, 126.8, 126.6, 117.0 (q, J = 288 Hz, CF$_3$), 102.1 (C-1), 101.9 (C-1''), 97.4 (C-1'''), 96.6 (C-1'), 79.3, 78.9, 77.1, 76.6, 75.4, 75.2, 74.1, 74.0, 73.8, 73.3, 72.8, 72.4 (C-5'''), 72.3, 71.9 (C-4'''), 70.7, 70.6, 69.3, 68.7 (OCH$_2$), 68.0, 67.2 (NCOCH$_2$), 64.0 (C-2'''), 61.6 (C-6'''), 55.4, 54.4, 52.4 (COOCH$_3$), 52.2 (COOCH$_3$), 50.9, 50.7, 47.8, 46.9, 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, CH$_2$CF$_2$), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, CH$_2$CH$_2$CF$_2$), 24.2 (CH$_2$); HRMS (ESI-TOF) m/z [M-H + 2Na]$^+$ calcd for $C_{102}H_{102}F_{16}N_5O_{25}Na_2$ 2146.6404; Found 2146.6406.



85

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (85).**

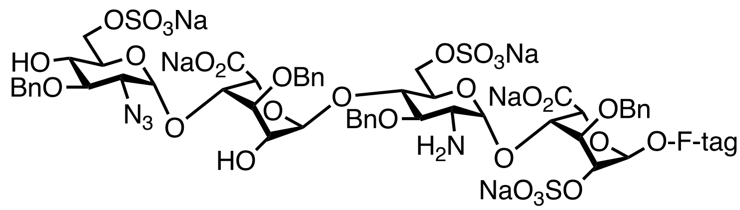
Compound **S1** (77 mg, 0.033 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **85** (60 mg, 85%); R_f 0.65 (8:5:3:1 EtOAc/pyridine/H$_2$O/AcOH); ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.95–7.94 (m, 1H, Ar), 7.43–7.17 (m, 28H, Ar), 5.88 (s, 1H), 5.21–5.02 (m, 8H), 4.84–4.72 (m, 3H), 4.64–4.59 (m, 10H), 4.29–4.27 (m, 2H), 4.17–3.98 (m, 7H), 3.86 (t, J = 9.5 Hz, 1H), 3.73–3.65 (m, 2H), 3.50–3.43 (m, 3H), 3.20–3.10 (m, 2H), 2.94–2.88 (m, 2H, PhCH_2CH$_2$), 2.71 (dd, J = 9.7, 2.9 Hz, 1H), 2.49–2.36 (m, 2H, PhCH$_2$CH_2), 1.63–1.53 (m, 4H, 2 X CH$_2$), 1.40–1.27 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD$_3$OD): δ 129.6, 128.8, 128.4, 127.6, 127.2, 98.9, 95.9, 94.4, 93.8, 80.6, 78.5, 77.6, 75.1, 74.9, 71.5, 71.4, 71.1, 70.3, 70.2, 69.9, 68.5, 68.2, 67.9, 67.8, 67.3, 67.1, 66.8, 63.9, 55.9, 49.9, 46.7, 32.2, 28.9, 27.4, 25.7, 22.9; HRMS (ESI-TOF) m/z $[M -6Na + 5H]^-$ calcd for $C_{80}H_{87}F_{13}N_5O_{35}S_4$ 2052.3857; Found 2052.3872.



86

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (86).**

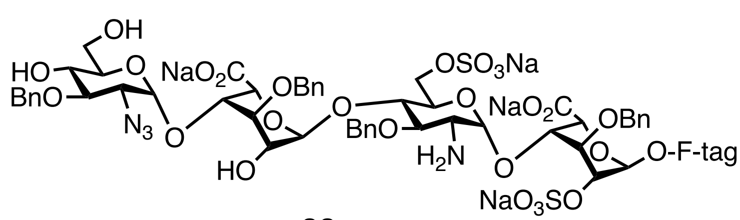
Compound **S2** (71 mg, 0.028 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **86** (53 mg, 91%); R_f 0.47 (12:5:3:1 EtOAc/pyridine/H_2O/AcOH); ^1H NMR (400 MHz, CD_3OD): δ 7.73–7.71 (m, 4H, Ar), 7.43–7.13 (m, 25H, Ar), 5.83 (s, 1H), 5.18–5.02 (m, 8H), 4.92–4.82 (m, 4H), 4.76–4.60 (m, 5H), 4.53–4.44 (m, 5H), 4.25–4.06 (m, 6H), 3.98–3.81 (m, 5H), 3.72–3.64 (m, 2H), 3.53–3.38 (m, 3H), 3.25–3.10 (m, 2H), 2.94–2.88 (m, 2H, $PhCH_2CH_2$), 2.74 (dd, J = 9.6, 3.2 Hz, 1H), 2.50–2.36 (m, 2H, $PhCH_2CH_2$), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 134.6, 128.2, 128.0, 127.4, 127.1, 99.0, 96.0, 94.2, 93.5, 80.8, 78.9, 76.3, 74.9, 72.6, 71.5, 71.3, 71.2, 71.1, 70.1, 70.0, 69.4, 68.3, 68.0, 67.9, 67.5, 67.3, 66.8, 63.8, 61.1, 55.9, 49.9, 46.5, 32.3, 28.9, 27.4, 25.7, 23.4; HRMS (ESI-TOF) m/z $[M -5Na + 4H]^-$ calcd for $C_{80}H_{87}F_{13}N_5O_{32}S_3$ 1972.4288; Found 1972.4264.



87

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (87).**

Compound **S3** (73 mg, 0.031 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **87** (59 mg, 92%); R_f 0.72 (8:5:3:1 EtOAc/pyridine/H_2O/AcOH); ^1H NMR (400 MHz, CD_3OD): δ 7.73–7.71 (m, 1H, Ar), 7.43–7.17 (m, 28H, Ar), 5.36 (s, 1H), 5.31 (d, *J* = 3.6 Hz, 1H), 5.15–5.03 (m, 6H), 4.78–4.56 (m, 8H), 4.51–4.43 (m, 3H), 4.39–4.08 (m, 9H), 4.02–3.98 (m, 1H), 3.92–3.67 (m, 5H), 3.50–3.41 (m, 2H), 3.30–3.26 (m, 1H), 3.20–3.10 (m, 2H), 2.94–2.90 (m, 2H, PhCH_2CH$_2$), 2.51–2.38 (m, 2H, PhCH$_2$CH_2), 1.63–1.53 (m, 4H, 2 X CH$_2$), 1.40–1.27 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD_3OD): δ 134.6, 129.0, 128.4, 127.6, 127.2, 99.0, 98.8, 95.4, 90.6, 80.3, 76.3, 75.0, 74.8, 73.7, 73.1, 72.3, 71.4, 71.1, 70.3, 69.8, 69.6, 69.2, 68.9, 68.5, 67.6, 67.0, 66.8, 66.0, 63.5, 53.8, 49.9, 46.5, 32.2, 28.9, 27.4, 25.7, 23.2; HRMS (ESI-TOF) m/z [M -5Na + 4H]$^-$ calcd for $C_{80}H_{87}F_{13}N_5O_{32}S_3$ 1972.4288; Found 1972.4282.

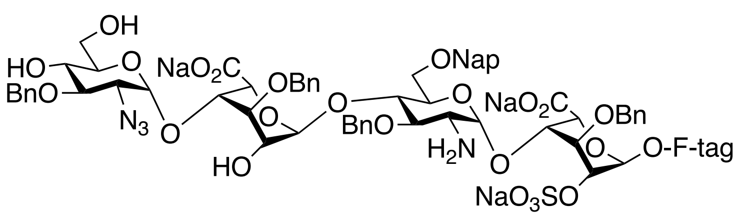


88

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-**

(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (88).

Compound **S4** (72 mg, 0.029 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **88** (55 mg, 96%); R_f 0.55 (12:5:3:1 EtOAc/pyridine/H_2O/AcOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.73–7.71 (m, 3H, Ar), 7.41–7.17 (m, 26H, Ar), 5.35 (d, J = 2.5 Hz, 1H), 5.14–5.01 (m, 7H), 4.81–4.71 (m, 4H), 4.68–4.55 (m, 4H), 4.49–4.45 (m, 3H), 4.38–4.13 (m, 6H), 4.00–3.67 (m, 9H), 3.53–3.43 (m, 3H), 3.30–3.26 (m, 1H), 3.20–3.10 (m, 2H), 2.94–2.90 (m, 2H, $PhCH_2CH_2$), 2.86 (dd, J = 9.9, 3.5 Hz, 1H), 2.51–2.38 (m, 2H, $PhCH_2CH_2$), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 134.6, 129.0, 128.4, 127.6, 127.2, 99.3, 98.9, 95.4, 94.8, 81.1, 80.9, 74.9, 74.7, 74.6, 74.2, 72.7, 72.5, 71.7, 71.6, 71.2, 70.5, 70.4, 70.0, 69.9, 69.8, 68.6, 67.7, 67.4, 66.7, 66.5, 63.7, 55.2, 50.0, 46.5, 32.2, 28.9, 27.4, 25.7, 23.2; HRMS (ESI-TOF) m/z $[M - 4Na + 3H]^-$ calcd for $C_{80}H_{87}F_{13}N_5O_{29}S_2$ 1892.4720; Found 1892.4717.

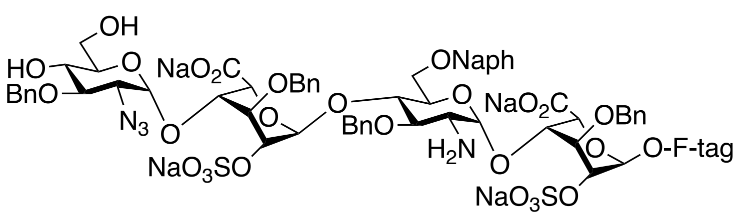


89

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate trisodium salt (89).**

Compound **S5** (70 mg, 0.028 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **89** (51 mg, 91%); R_f 0.65 (7:2:1, EtOAc–CH_3OH–H_2O);

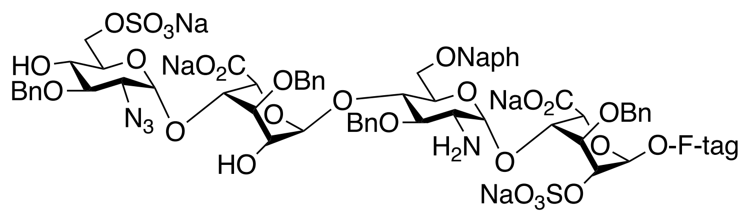
^{1}H NMR (400 MHz, CD_3OD): δ 7.88–7.08 (m, 36H, ArH), 5.38 (d, J = 2.9 Hz, 1H, H-1''), 5.14–5.01 (m, 6H, H-1', H-1''', NCO_2CH_2, H-1, ArCH_2), 4.94 (m, 1H, $ArCH_2$), 4.80–4.54 (m, 10H), 4.52–4.47 (m, 1H), 4.46–4.40 (m, 2H, NCH_2Ph), 4.33–4.28 (m, 1H), 4.28–4.24 (m, 1H), 4.23–4.16 (m, 2H), 3.98 (appt, J = 9.8 Hz, 1H), 3.94–3.78 (m, 8H), 3.76–3.67 (m, 2H), 3.57–3.41 (m, 3H), 3.21–3.06 (m, 2H, NCH_2), 2.96–2.85 (m, 3H, H-2', Ph$CH_2$$CH_2$) 2.52–2.32 (m, 2H, $PhCH_2$$CH_2$) , 1.64–1.40 (m, 4H, 2 X CH_2), 1.35–1.18 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 134.7, 134.5, 132.6, 127.7, 127.7, 127.6, 127.6, 127.4, 126.6, 125.9, 125.6, 125.1, 125.1, 123.5, 98.9 (2C), 94.8 (2C), 80.6, 80.3, 75.8, 75.0, 74.7, 73.9, 73.4, 72.7, 72.4, 71.5, 71.3, 70.3, 70.2, 69.8, 69.0, 68.9, 67.7 (OCH_2), 67.4, 66.8, 63.6, 60.7, 55.1 (C-2'), 50.0, 46.6 (NCH_2), 32.3 (CH_2CF_2), 28.9, 27.8, 25.7 ($CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z [M – 3Na + 2H]$^-$ calcd for $C_{91}H_{95}F_{13}N_5O_{25}S$ 1952.5779; Found 1952.5784.



90

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate tetrasodium salt (90).**

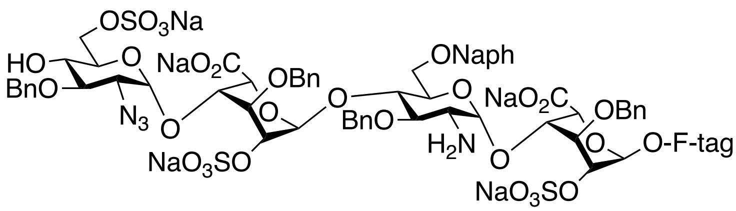
Compound **S6** (54 mg, 0.021 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **90** (40 mg, 88%); R_f 0.59 (7:2:1, EtOAc–CH_3OH–H_2O); ^{1}H NMR (400 MHz, CD_3OD): δ 7.79–7.12 (m, 36H, ArH), 5.81 (bs, 1H, H-1''), 5.25–5.06 (m, 6H, H-1', H-1''', NCO_2CH_2, H-1, ArCH_2), 5.00 (d, J = 10.6 Hz, 1H, $ArCH_2$), 4.74–3.98 (m, 17H), 3.94–3.60 (m, 7H), 3.52–3.30 (m, 4H), 3.27–3.03 (m, 3H), 2.94–2.82 (m, 2H, PhCH_2CH$_2$) 2.51–2.32 (m, 2H, PhCH$_2$CH_2) , 1.58–1.38 (m, 4H, 2 X CH$_2$), 1.34–1.14 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD$_3$COCD$_3$): δ 134.7, 134.7, 134.7, 134.5, 132.6, 129.8, 127.9, 127.9, 127.7, 127.6, 127.6, 127.4, 125.3, 123.4, 98.7, 95.2, 93.4, 91.9, 80.8, 75.2, 75.0, 74.0, 73.4, 72.6, 71.6 (2C), 71.3, 70.2, 70.2, 70.0, 70.0, 69.5, 68.5, 68.4, 66.9, 66.8 (2C), 66.5, 63.9, 60.8, 54.2, 50.0, 46.3 (NCH_2), 32.3 (CH$_2$CF$_2$), 27.6, 27.4, 25.7 (CH$_2$CH$_2$CF$_2$), 23.2; HRMS (ESI-TOF) m/z [M – 4Na + 3H]$^-$ calcd for $C_{91}H_{95}F_{13}N_5O_{29}S_2$ 2032.5347; Found 2032.5358.



91

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate pentasodium salt (91).**

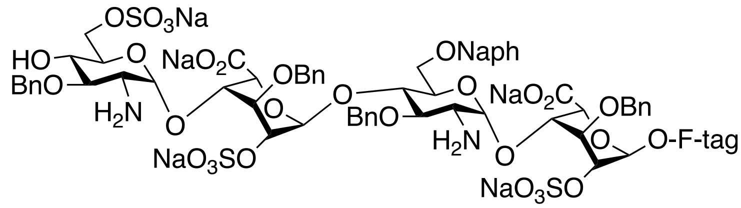
Compound **S7** (70 mg, 0.029 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **91** (56 mg, 91%); R_f 0.68 (7:2:1, EtOAc–CH$_3$OH–H$_2$O); ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.92–7.07 (m, 36H, ArH), 5.39 (d, *J* = 3.7 Hz, 1H), 5.32 (d, *J* = 3.4 Hz, 1H), 5.14–5.02 (m, 5H), 4.84–4.59 (m, 10H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.50–4.40 (m, 3H), 4.40–4.34 (m, 1H), 4.30–4.15 (m, 5H), 4.13–4.00 (m, 2H), 3.96–3.68 (m, 6H), 3.51–3.31 (m, 3H), 3.21–3.07 (m, 2H), 2.94–2.84 (m, 2H, PhCH_2CH$_2$), 2.52–2.31 (m, 2H, PhCH$_2$CH_2) , 1.64–1.41 (m, 4H, 2 X CH$_2$), 1.35–1.23 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD$_3$OD): δ 127.7, 127.7, 127.6, 127.6, 126.6, 126.1, 125.6, 125.1, 99.2, 98.7, 95.3, 91.0, 80.3, 75.8, 75.6, 74.7, 74.2, 73.4, 73.2, 71.8, 71.3, 71.0, 70.8, 70.5, 70.2, 69.5, 68.7, 68.4, 67.7, 67.1, 66.8, 65.8, 63.6, 54.0, 50.0, 46.5 (NCH_2), 32.3 (CH$_2$CF$_2$), 29.0, 27.9, 25.7 ($CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z [M – 4Na + 3H]$^-$ calcd for $C_{91}H_{95}F_{13}N_5O_{29}S_2$ 2032.5347; Found 2032.5325.



92

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate pentasodium salt (92).**

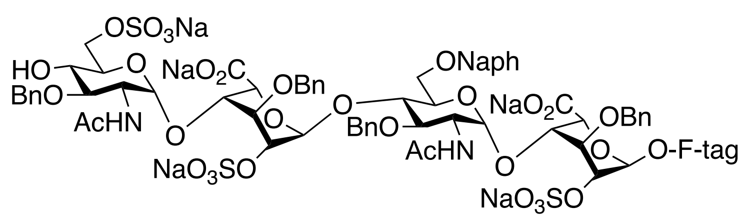
Compound **S8** (64 mg, 0.027 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **92** (49 mg, 84%); R_f 0.51 (7:2:1, EtOAc–CH_3OH–H_2O); ^1H NMR (400 MHz, CD_3OD): δ 7.85–7.08 (m, 36H, ArH), 5.90 (bs, 1H, H-1''), 5.21–5.02 (m, 6H, H-1', H-1''', NCO_2CH_2, H-1, ArCH_2), 4.98–4.87 (m, 2H), 4.84–4.16 (m, 17H), 4.15–4.09 (m, 1H), 4.06–3.86 (m, 5H), 3.80–3.61 (m, 4H), 3.43–3.42 (m, 1H), 3.40–3.35 (m, 1H), 3.24–3.07 (m, 2H), 2.95–2.84 (m, 2H, PhCH_2CH_2), 2.77–2.67 (m, 1H), 2.52–2.33 (m, 2H, PhCH_2CH_2) , 1.69–1.45 (m, 4H, 2 X CH_2), 1.36–1.22 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 127.9, 127.7, 127.7, 127.6, 127.4, 126.9, 125.8, 125.5, 125.5, 125.1, 123.4, 99.0, 96.0, 94.2, 94.0, 80.2, 78.7, 77.2, 74.7 (2C), 73.5, 71.3 (3C), 71.0, 70.8, 70.5, 70.2, 69.8 (2C), 69.7, 69.5, 69.0, 68.4, 67.9, 67.3, 66.8, 66.3, 66.1, 63.6, 56.1, 50.0, 48.6, 46.5 (NCH_2), 32.3 (CH_2CF_2), 28.7, 27.6, 25.7 ($CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z [M – 5Na + 4H]$^-$ calcd for $C_{91}H_{95}F_{13}N_5O_{32}S_3$ 2112.4915; Found 2112.4927.



93

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-amino-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate pentasodium salt (93).**

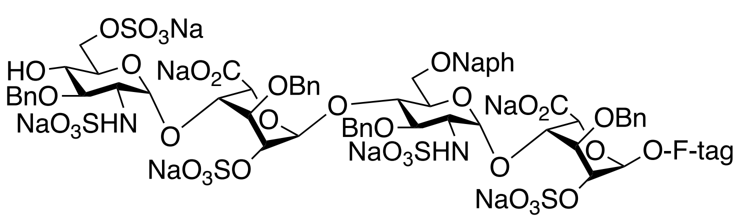
Compound **92** (30 mg, 0.013 mmol) was treated according to the general procedure for N_3 to NH_2 conversion to give tetrasaccharide **93** (28 mg, 95%); R_f 0.54 (7:2:1, EtOAc–CH_3OH–H_2O); ^1H NMR (400 MHz, CD_3OD): δ 7.87–7.77 (m, 4H, ArH), 7.53–7.52 (m, 1H, ArH), 7.43–7.16 (m, 31H, ArH), 5.70 (s, 1H, H-1''), 5.21–5.08 (m, 7H, H-1', H-1''', NCO_2CH_2, H-1, $ArCH_2$), 4.86–4.50 (m, 11H), 4.47–4.38 (m, 4H), 4.26–4.05 (m, 6H), 3.96–3.45 (m, 6H), 3.43–3.42 (m, 1H), 3.35–3.30 (m, 1H), 3.18–3.10 (m, 3H), 2.93–2.88 (m, 2H, $PhCH_2CH_2$), 2.52–2.36 (m, 2H, $PhCH_2CH_2$) , 1.69–1.45 (m, 4H, 2 X CH_2), 1.36–1.22 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 127.9, 127.7, 127.5, 127.2, 126.3, 125.8, 125.5, 103.7, 98.8, 96.1, 91.6, 78.3, 75.4, 74.7 (2C), 73.0, 71.4, 71.0, 70.3, 70.2, 70.0, 69.8, 69.7, 69.3, 69.2, 68.0, 67.7, 67.2, 66.8, 66.4, 65.5, 54.9, 53.9, 50.0, 46.5 (NCH_2), 32.2 (CH_2CF_2), 28.7, 27.4, 25.7 ($CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z [M – 5Na + 4H]$^-$ calcd for $C_{91}H_{97}F_{13}N_3O_{32}S_3$ 2086.5010; Found 2086.4995.



94

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-acetamido-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate pentasodium salt (94).**

Compound **93** (10 mg, 0.0045 mmol) was treated according to the general procedure for *N*-acetylation to give tetrasaccharide **94** (9.7 mg, 94%); R_f 0.37 (12:5:3:1 EtOAc/pyridine/H_2O/AcOH); ^1H NMR (400 MHz, CD_3OD): δ 7.83–7.75 (m, 4H, ArH), 7.50–7.11 (m, 32H, ArH), 6.03 (s, 1H, H-1''), 5.17–5.08 (m, 4H, NCO_2CH_2, H-1, $ArCH_2$), 4.92–4.56 (m, 13H), 4.48–4.35 (m, 6H), 4.31–4.03 (m, 7H), 3.85–3.63 (m, 7H), 3.52–3.45 (m, 1H), 3.19–3.12 (m, 3H), 2.93–2.88 (m, 2H, $PhCH_2CH_2$), 2.50–2.38 (m, 2H, $PhCH_2CH_2$), 2.08 ($NCOCH_3$), 2.06 ($NCOCH_3$), 1.69–1.45 (m, 4H, 2 X CH_2), 1.36–1.22 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 127.9, 127.7, 127.5, 127.2, 126.3, 125.8, 125.5, 99.0, 97.4, 95.5, 93.5, 79.9, 76.0, 74.4, 74.1, 73.9, 73.6, 72.9, 72.1, 71.9, 71.2, 71.0, 70.3, 70.1, 70.0, 69.0, 68.6, 68.5, 67.9, 67.3, 66.8, 66.1, 53.1, 52.6, 50.0, 46.5 (NCH_2), 32.2 (CH_2CF_2), 28.7, 27.4, 25.7 ($CH_2CH_2CF_2$), 23.2, 22.2 ($NCOCH_3$), 22.1 ($NCOCH_3$); HRMS (ESI-TOF) m/z $[M - 5Na + 4H]^-$ calcd for $C_{95}H_{101}F_{13}N_3O_{34}S_3$ 2170.5221; Found 2170.5239.

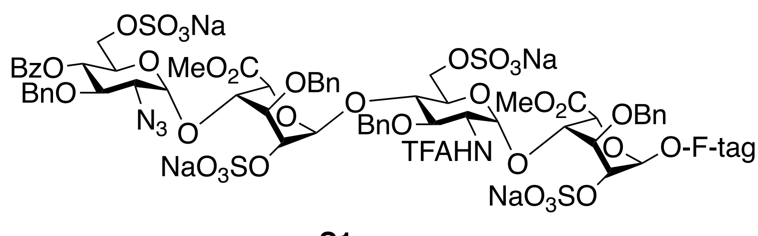


95

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-2-sulfamino-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-**

deoxy-6-*O*-2-naphthylmethyl-2-sulfamino-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate pentasodium salt (95).

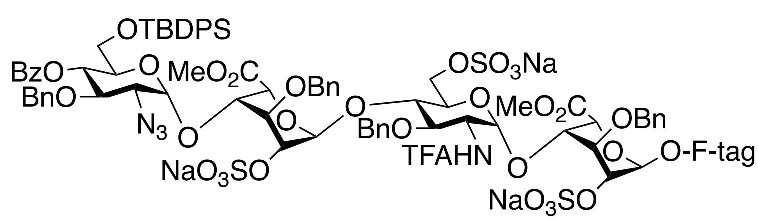
Compound **93** (10 mg, 0.0045 mmol) was treated according to the general procedure for *N*-sulfation to give tetrasaccharide **95** (9.8 mg, 91%); R_f 0.15 (12:5:3:1 EtOAc/pyridine/H_2O/AcOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.81–7.75 (m, 4H, ArH), 7.55–7.10 (m, 32H, ArH), 6.05 (s, 1H, H-1''), 5.38–5.29 (m, 4H, H-1', H-1''', H-1, ArCH_2), 5.15–5.06 (m, 4H, NCO_2CH_2, ArCH_2), 4.97 (d, J = 10.6 Hz, 1H, ArCH_2), 4.88–4.59 (m, 10H), 4.53–4.31 (m, 6H), 4.28–4.00 (m, 6H), 3.87–3.62 (m, 4H), 3.62–3.56 (m, 1H), 3.53–3.48 (m, 1H), 3.41–3.36 (m, 1H), 3.19–3.10 (m, 2H), 2.93–2.89 (m, 2H, PhCH_2CH_2), 2.51–2.37 (m, 2H, PhCH_2CH_2) , 1.69–1.45 (m, 4H, 2 X CH_2), 1.36–1.22 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 127.9, 127.7, 127.5, 127.2, 126.3, 125.8, 125.5, 98.8, 98.3, 96.2, 91.6, 79.6, 75.7, 74.5, 74.0, 73.9, 73.6, 73.3, 71.3, 71.0, 70.7, 70.6, 70.3, 70.1, 68.7, 68.5, 67.5, 67.2, 66.6, 66.5, 66.4, 59.1, 58.0, 50.0, 46.5 (NCH_2), 32.2 (CH_2CF_2), 28.7, 27.4, 25.7 ($CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z $[M - 7Na + 5H]^{-2}$ calcd for $C_{91}H_{98}F_{13}N_3O_{38}S_5$ 1122.7030; Found 1122.7230.



S1

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S1).**

Compound **80** (70 mg, 0.036 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S1** (77 mg, 91%); R_f 0.25 (5:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.98–7.97 (m, 2H, Ar), 7.63–7.56 (m, 3H, Ar), 7.49–7.44 (m, 4H, Ar), 7.37–7.04 (m, 25H, Ar), 5.50 (s, 1H, H-1''), 5.20 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.15–5.07 (m, 5H, H-1''', H-1', H-1, NCO_2CH_2), 4.97 (d, *J* = 1.2 Hz, 1H, H-5''), 4.93–4.74 (m, 5H, CH_2Ph, H-5), 4.65–4.51 (m, 6H), 4.46 (br, 2H, NCH_2Ph), 4.40–4.36 (m, 4H), 4.27 (dd, *J* = 10.7, 3.3 Hz, 1H, H-2'), 4.14–3.95 (m, 7H), 3.89 (s, 3H, OCH_3), 3.88–3.71 (m, 3H), 3.57 (dd, *J* = 10.2, 3.2 Hz, 1H, H-2'''), 3.51–3.46 (m, 1H, OCH_2CH_2), 3.41 (s, 3H, OCH_3), 3.23–3.16 (m, 2H, NCH_2), 2.93–2.90 (m, 2H, PhCH_2CH_2), 2.51–2.37 (m, 2H, $PhCH_2CH_2$), 1.63–1.47 (m, 4H, 2 X CH_2), 1.36–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.8, 170.4, 165.4, 158.4 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 137.9, 137.7, 137.6, 137.4, 133.2, 129.5, 128.5, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.7, 127.4, 127.4, 127.3, 127.2, 126.9, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-1), 97.5 (C-1''), 97.1 (C-1'''), 95.4 (C-1'), 78.0, 77.4, 75.0, 74.9, 72.5, 72.2, 71.7, 71.6, 71.5, 71.1, 70.7, 70.6, 70.1, 69.5, 69.3, 68.0, 66.7, 66.2, 65.9, 65.7, 63.9, 53.9 (C-2'), 52.0 (OCH_3), 51.7 (OCH_3), 50.1, 49.9, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.8, 27.6, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z $[M - Na]^-$ calcd for $C_{91}H_{91}F_{16}N_5O_{37}S_4Na_3$ 2346.3713; Found 2346.3743.

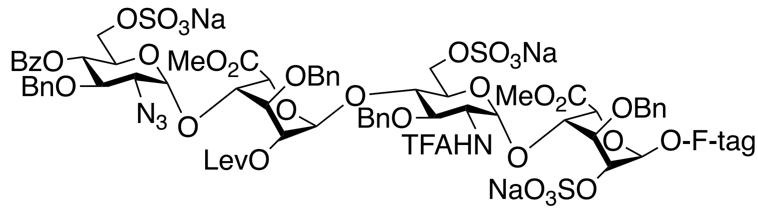


S2

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-**

trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S2).

Compound **79** (70 mg, 0.032 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S2** (71 mg, 89%); R_f 0.63 (5:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.94–7.92 (m, 2H, Ar), 7.73–7.71 (m, 2H, Ar), 7.66–7.64 (m, 3H, Ar), 7.52–7.02 (m, 35H, Ar), 6.97–6.95 (m, 2H, Ar), 5.50 (t, *J* = 9.8 Hz, 1H, H-4'''), 5.48 (s, 1H, H-1''), 5.18 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.14–5.10 (m, 3H, H-1, NCO_2CH_2), 5.07 (d, *J* = 3.3 Hz, 1H, H-1'), 4.94 (d, *J* = 1.3 Hz, 1H, H-5''), 4.91–4.76 (m, 4H, C*H*$_2$Ph, H-5), 4.67–4.51 (m, 7H), 4.46 (s, 2H, NC*H*$_2$Ph), 4.44–4.36 (m, 4H), 4.27 (dd, *J* = 10.6, 3.2 Hz, 1H, H-2'), 4.13 (s, 1H), 4.08 (t, *J* = 9.4 Hz, 1H), 4.03 (t, *J* = 9.7 Hz, 1H), 3.95 (s, 1H), 3.89–3.85 (m, 1H), 3.85 (s, 3H, OCH_3), 3.81–3.70 (m, 3H), 3.67–3.63 (m, 2H), 3.55 (dd, *J* = 10.3, 3.3 Hz, 1H, H-2'''), 3.51–3.46 (m, 1H, OC*H*$_2$CH$_2$), 3.23–3.16 (m, 2H, NCH_2), 3.15 (s, 3H, OCH_3), 2.93–2.90 (m, 2H, PhC*H*$_2$CH$_2$), 2.51–2.39 (m, 2H, PhCH$_2$C*H*$_2$), 1.63–1.47 (m, 4H, 2 X CH_2), 1.36–1.27 (m, 2H, CH_2), 0.96 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.5, 170.4, 165.1, 158.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.0, 137.9, 137.6, 137.4, 135.4, 135.2, 134.5, 132.8, 132.7, 129.7, 129.5, 129.4, 129.4, 129.0, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.4, 127.3, 127.2, 127.2, 126.9, 126.5, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-1), 97.7 (C-1''), 96.4 (C-1'''), 95.4 (C-1'), 78.1, 77.5, 74.8, 74.7, 72.2, 72.0, 71.6, 71.5, 71.4, 71.1, 70.7, 70.5, 70.3, 70.2, 70.1, 69.2, 66.7, 66.2, 65.7, 63.9, 62.1, 53.8 (C-2'), 51.9 (OCH_3), 51.3 (OCH_3), 50.1, 49.9, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, *C*H$_2$CF$_2$), 28.8, 27.5, 25.9 (($CH_3)_3$C), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, *C*H$_2$CH$_2$CF$_2$), 23.2, 22.3, 18.6 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z [M - 3Na + 2H]$^-$ calcd for $C_{107}H_{112}F_{16}N_5O_{34}S_3Si$ 2438.5864; Found 2438.5847.

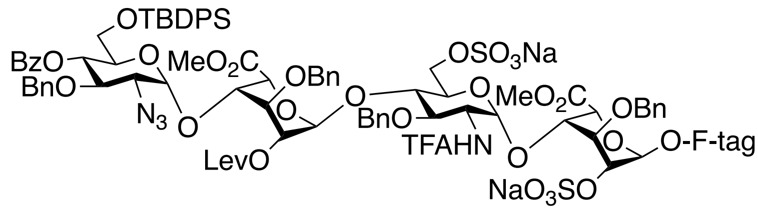


S3

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S3).**

Compound **81** (72 mg, 0.035 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S3** (73 mg, 88%); R_f 0.29 (5:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.98–7.96 (m, 2H, Ar), 7.73–7.71 (m, 2H, Ar), 7.70–7.68 (m, 2H, Ar), 7.64–7.61 (m, 1H, Ar), 7.55–7.07 (m, 29H, Ar), 5.31 (s, 1H, H-1''), 5.27 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.15 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.14–5.10 (m, 3H, H-1, NCO_2CH_2), 5.06 (d, *J* = 3.3 Hz, 1H, H-1'), 5.05 (s, 1H, H-2''), 4.93 (d, *J* = 1.5 Hz, 1H, H-5''), 4.90–4.72 (m, 5H, CH_2Ph, H-5), 4.65–4.52 (m, 5H), 4.46–4.45 (m, 2H, NCH_2Ph), 4.38 (s, 1H), 4.29–4.21 (m, 3H), 4.13–3.96 (m, 8H), 3.86 (s, 3H, OCH_3), 3.85–3.69 (m, 3H), 3.56 (dd, *J* = 10.2, 3.4 Hz, 1H, H-2'''), 3.54–3.46 (m, 1H, OCH_2CH_2), 3.41 (s, 3H, OCH_3), 3.23–3.16 (m, 2H, NCH_2), 3.03–2.69 (m, 6H), 2.51–2.37 (m, 2H, $PhCH_2CH_2$), 2.15 (s, 3H), 1.63–1.47 (m, 4H, 2 X CH_2), 1.36–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 208.4 (C=OCH_3), 172.4, 170.5, 170.4, 165.3, 158.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 137.8, 137.7, 137.4, 137.3, 134.0, 134.0, 133.3, 130.1, 129.5, 129.4, 128.4, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4, 127.2, 127.0, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-1), 97.2 (C-1''), 96.4 (C-1'''), 95.7 (C-1'), 77.6, 77.4, 75.2, 74.3, 72.8, 72.4, 71.8, 71.7, 71.5, 70.6, 70.5, 70.5, 70.2, 69.2, 67.0, 66.6, 66.2, 65.8, 65.3, 63.2, 53.8 (C-2'), 51.9 (OCH_3), 51.7 (OCH_3), 50.1, 49.9, 37.4, 34.4, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.8, 28.4

(C=OCH_3), 27.6, 27.5, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z [M - 3Na + 2H]$^-$ calcd for $C_{96}H_{100}F_{16}N_5O_{36}S_3$ 2298.5054; Found 2298.5039.

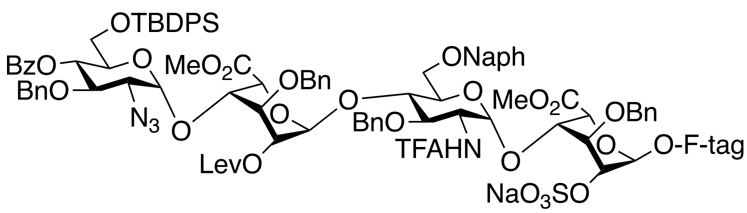


S4

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S4).**

Compound **78** (73 mg, 0.032 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S4** (72 mg, 91%); R_f 0.71 (5:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.94–7.92 (m, 2H, Ar), 7.69–7.63 (m, 3H, Ar), 7.54–7.50 (m, 4H, Ar), 7.45–7.04 (m, 35H, Ar), 5.51 (t, *J* = 9.8 Hz, 1H, H-4'''), 5.32 (s, 1H, H-1''), 5.21 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.14–5.10 (m, 3H, H-1, NCO_2CH_2), 5.07 (s, 1H, H-2''), 5.05 (d, *J* = 3.4 Hz, 1H, H-1'), 4.90–4.73 (m, 5H, CH_2Ph, H-5, H-5''), 4.69–4.54 (m, 6H), 4.51 (s, 1H), 4.46–4.45 (m, 2H, NCH_2Ph), 4.37 (s, 1H), 4.29–4.18 (m, 3H), 4.09–3.95 (m, 3H), 3.87–3.66 (m, 9H), 3.53 (dd, *J* = 10.2, 3.4 Hz, 1H, H-2'''), 3.53–3.43 (m, 1H, OCH_2CH_2), 3.24–3.16 (m, 2H, NCH_2), 3.15 (s, 3H, OCH_3), 3.01–2.69 (m, 6H), 2.49–2.40 (m, 2H, $PhCH_2CH_2$), 2.16 (s, 3H), 1.63–1.47 (m, 4H, 2 X CH_2), 1.36–1.27 (m, 2H, CH_2), 0.96 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 208.5 (C=OCH_3), 172.5, 170.4, 170.1, 165.1, 158.3 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.1, 137.9, 137.4, 135.4, 135.2, 133.3, 132.8, 132.7, 129.5, 129.4, 128.5, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.5, 127.4, 127.4, 127.3, 126.9, 126.7, 126.6, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-

1), 97.6 (C-1''), 96.2 (C-1'''), 95.8 (C-1'), 77.7, 77.5, 74.8, 74.3, 73.6, 72.4, 72.0, 71.7, 71.3, 71.1, 70.8, 70.5, 70.4, 70.3, 70.2, 69.2, 67.3, 66.8, 66.6, 66.2, 65.3, 63.3, 62.2, 54.6, 53.8 (C-2'), 51.9 (OCH_3), 51.3 (OCH_3), 50.1, 49.9, 46.6, 37.4, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.8, 28.3, 27.6, 27.5, 25.9 ($(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2, 18.8 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z [M - 2Na + 2H]$^-$ calcd for $C_{112}H_{118}F_{16}N_5O_{33}S_2Si$ 2456.6665; Found 2456.6628.

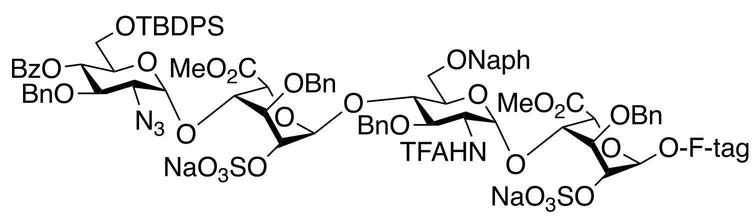


S5

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate monosodium salt (S5).**

Compound **75** (75 mg, 0.031 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S5** (70 mg, 90%); R_f 0.27 (100% EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.05–7.01 (m, 46H, ArH), 5.67 (app t, J = 9.1 Hz, 1H, H-4'''), 5.46 (d, J = 3.1 Hz, 1H, H-1''), 5.34 (d, J = 3.5 Hz, 1H, H-1'''), 5.20–5.12 (m, 2H, NCO_2CH_2), 5.09 (appt, J = 3.1 Hz, 1H, H-2''), 5.03–4.97 (m, 2H, H-1, H-2'), 4.96–4.90 (m, 2H), 4.87–4.71 (m, 6H), 4.65–4.56 (m, 3H), 4.54–4.48 (m, 3H), 4.24–3.92 (m, 9H), 3.85–3.63 (m, 5H), 3.55 (s, 3H, $COOCH_3$), 3.50–3.35 (m, 4H), 3.28–3.15 (m, 2H, NCH_2), 3.02–2.93 (m, 2H, $PhCH_2CH_2$) 2.80–2.71 (m, 2H, $COCH_2CH_2$), 2.66–2.46 (m, 4H, $COCH_2CH_2$, $PhCH_2CH_2$), 2.09 (s, 3H, $CH_3C{=}O$), 1.65–1.48 (m, 4H, 2 X CH_2), 1.41–1.27 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.0, 172.9 (C=O), 170.4

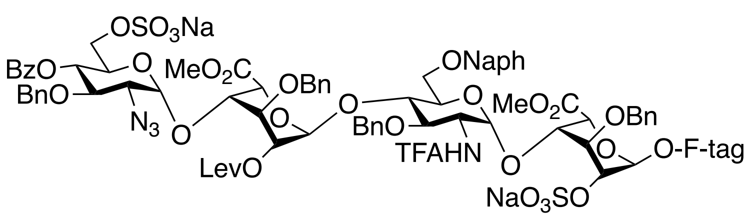
(C=O), 169.7 (C=O), 165.6 (C=O), 140.2, 139.8, 139.6, 139.5, 138.8, 138.7, 137.2, 136.5, 136.3, 134.3, 134.2, 133.93, 133.87, 133.8, 130.8, 130.6, 130.5, 129.6, 129.4, 129.33, 129.28, 129.04, 128.95, 128.9, 128.8, 128.61, 128.56, 128.5, 128.42, 128.39, 128.3, 128.2, 128.1, 127.9, 127.4, 127.2, 127.0, 126.8, 126.5, 100.9 (C-1), 100.4 (C-1'), 98.5 (C-1''), 97.8 (C-1'''), 78.8, 78.2, 77.4, 76.0, 75.6, 75.1, 74.2, 73.7, 73.1, 72.6, 72.2, 72.0, 71.3, 70.7, 69.7 (C-2''), 69.4, 68.5, 67.3, 67.2 (NCO*C*H_2), 64.0 (C-2'''), 63.0, 55.8, 52.0, 52.0, 38.3, 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, *C*H_2CF_2), 28.6 (*C*H_3CO), 27.1 (*C*$H_3)_3$C), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, *C*$H_2CH_2CF_2$), 24.2, 19.7 ($(CH_3)_3$*C*); HRMS (ESI-TOF) m/z [M – Na]$^-$ calcd for $C_{123}H_{126}F_{16}N_5O_{30}SSi$ 2516.7722; Found 2516.7751.



S6

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-*O*-sulfonato-α-L-idopyranosyluronate (S6).**

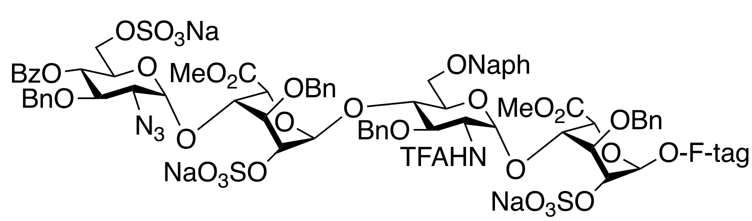
Compound **82** (73 mg, 0.031 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S6** (70 mg, 88%); R_f 0.45 (9:1 EtOAc–CH_3OH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.16 (d, *J* = 8.5 Hz, 1H, NH), 8.10–8.04 (m, 2H, ArH), 8.00–7.96 (m, 1H, ArH), 7.95–7.90 (m, 1H, ArH), 7.88–7.80 (m, 2H, ArH), 7.77–7.67 (m, 3H, ArH), 7.65–7.53 (m, 7H, ArH), 7.48–7.13 (m, 27H, ArH), 7.10–7.00 (m, 3H, ArH), 5.71 (d, *J* = 5.0 Hz, 1H, H-1''), 5.64 (appt, *J* = 9.6 Hz, 1H, H-4'''), 5.51 (d, *J* = 3.8 Hz, 1H, H-1'''), 5.40 (m, 1H, H-1), 5.22–5.11 (m, 3H, ArC*H*$_2$, NCO_2C*H*$_2$), 5.07–4.90 (m, 4H, ArC*H*$_2$, H-1'), 4.87–4.72 (m, 6H), 4.70–4.56 (m, 5H), 3.87–3.74 (m, 3H), 3.69 (dd, J = 10.5, 3.8 Hz, 1H, H-2'''), 3.65–3.54 (m, 4H, OCH_2, COOCH_3), 3.50 (s, 3H, COOCH_3), 3.25–3.08 (m, 2H, NCH_2), 2.99–2.90 (m, 2H, PhCH_2CH$_2$) 2.65–2.44 (m, 2H, PhCH$_2$CH_2), 1.62–1.40 (m, 4H, 2 X CH$_2$), 1.36–1.24 (m, 2H, CH$_2$), 1.01 (s, 9H, (CH$_3$)$_3$C); ^{13}C NMR (100 MHz, CD$_3$COCD$_3$): δ 170.4 (C=O), 165.6 (C=O), 158.4 (q, J = 36.5 Hz, *C*OCF$_3$), 140.6, 139.8, 139.42, 139.38, 139.3, 138.8, 137.7, 136.4, 136.3, 134.3, 134.2, 133.9, 133.82, 133.77, 130.8, 130.6, 130.54, 130.47, 129.6, 129.3, 129.2, 129.0, 128.9, 128.8, 128.60, 128.58, 128.52, 128.47, 128.41, 128.36, 128.23, 128.19, 127.9, 127.4, 126.9, 126.7, 126.4, 117.2 (q, J = 288 Hz, CO*C*F$_3$), 101.9 (C-1'), 100.6 (C-1), 99.4 (C-1''), 97.6 (C-1'''), 78.5, 77.7, 75.6, 75.0, 74.3, 73.5, 72.7, 72.3, 72.2, 71.3, 70.3, 68.9 (O*C*H$_2$), 67.7, 67.2 (NCO*C*H$_2$), 63.8, 63.1, 60.5, 55.7, 52.8 (CO$_2$*C*H$_3$), 52.3 (CO$_2$*C*H$_3$), 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, *C*H$_2$CF$_2$), 27.1 (*C*H$_3$)$_3$C), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, *C*H$_2$CH$_2$CF$_2$), 24.4, 19.7 (CH$_3$)$_3$*C*); HRMS (ESI-TOF) m/z [M – 2Na + H]$^-$ calcd for $C_{118}H_{120}F_{16}N_5O_{31}S_2Si$ 2498.6921; Found 2498.6931.



S7

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S7).**

Compound **83** (75 mg, 0.034 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S7** (70 mg, 85%); R_f 0.65 (4:1 EtOAc–CH$_3$OH); ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.98–7.85 (m, 4H, ArH), 7.83–7.79 (m, 1H, ArH), 7.79–7.74 (m, 1H, ArH) 7.63–7.52 (m, 2H, ArH), 7.51–7.03 (m, 28H, ArH), 5.35–5.25 (m, 2H, H-1'', H-4'''), 5.19–5.04 (m, 5H, H-1, H-1', H-1''', NCO_2CH_2), 5.01 (m, 1H, H-2''), 4.91–4.86 (m, 2H), 4.81–4.64 (m, 7H), 4.58 (d, J = 11.5 Hz, 1H, $ArCH_2$), 4.53–4.46 (m, 3H), 4.46–4.35 (m, 3H), 4.30 (dd, J = 10.5, 3.5 Hz, 1H, H-2'), 4.19–3.96 (m, 8H), 3.91–3.83 (m, 1H), 3.83–3.63 (m, 6H, O*CH₂*, COOC*H₃*), 3.54–3.37 (m, 5H, H-2''', COOC*H₃*, OC*H₂*), 3.21–3.08 (m, 2H, NC*H₂*), 2.93–2.86 (m, 2H, $PhCH_2CH_2$), 2.67–2.60 (m, 2H, $CH_3COCH_2CH_2$), 2.59–2.34 (m, 4H, $CH_3COCH_2CH_2$, $PhCH_2CH_2$), 2.04 (s, 3H, $CH_3COCH_2CH_2$), 1.57–1.39 (m, 4H, 2 X CH_2), 1.35–1.16 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD) δ 208.8 (CH_3C=O), 173.7 (C=O), 171.7 (C=O), 171.1 (C=O), 166.6 (C=O), 139.3, 139.2, 138.9, 138.7, 137.1, 134.8, 134.6, 134.4, 130.8, 130.8, 129.9, 129.68, 129.67, 129.6, 129.50, 129.56, 129.24, 129.21, 129.19, 129.13, 129.10, 129.0, 128.8, 128.75, 128.70, 128.67, 128.4, 128.2, 127.6, 127.2, 127.1, 126.9, 126.3, 101.2 (C-1), 98.9 (C-1''), 97.8 (C-1'''), 96.1 (C-1'), 79.2, 78.7, 76.3, 75.7, 75.4, 74.2, 73.8, 73.2, 73.0, 72.9, 72.8, 71.8, 71.5 (C-4'''), 71.1, 70.5, 69.4 (C-2''), 69.2 (OCH_2), 69.0, 68.1, 67.6 (NCOCH_2), 67.0, 64.3 (C-2'''), 55.1 (C-2'), 53.0 (COOCH_3), 52.8 (COOCH_3), 51.5, 49.6, 49.4, 49.3, 49.2, 49.1, 49.0, 48.8, 48.6, 48.4, 38.5 (CH3COCH_2CH_2), 36.9, 33.6 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 31.6, 30.2 (CH_2), 29.7 (CH_3C=O), 28.8 (CH_2), 28.5 (CH3COCH_2CH_2), 27.0 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 24.6 (CH_2); HRMS (ESI-TOF) m/z [M – 2Na + H]$^-$ calcd for $C_{107}H_{108}F_{16}N_5O_{33}S_2$ 2358.6113; Found 2358.6106.

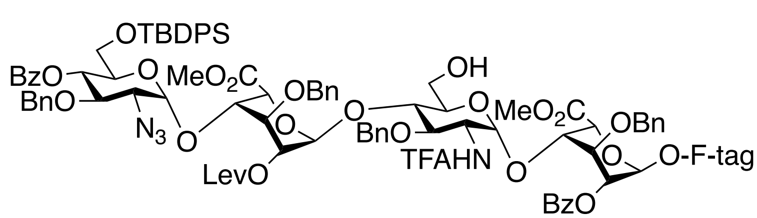


S8

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-**

idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S8).

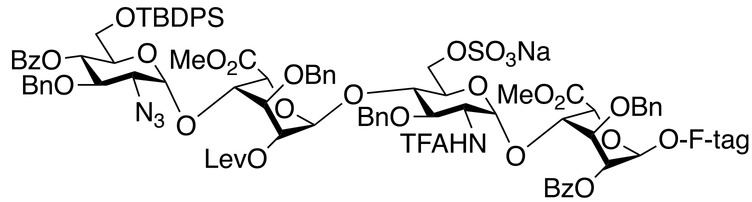
Compound **84** (69 mg, 0.033 mmol) was treated according to the general procedure of TBDPS deprotection to give tetrasaccharide **S8** (64 mg, 81%); R_f 0.61 (4:1 EtOAc–CH_3OH); ^1H NMR (400 MHz, CD_3OD) δ 7.97–7.92 (m, 2H, ArH), 7.88–7.82 (m, 1H, ArH), 7.78–7.71 (m, 2H, ArH), 7.60–7.53 (m, 4H, ArH), 7.50-6.99 (m, 25H, ArH), 5.51 (bs, 1H, H-1''), 5.24 (appt, *J* = 9.6 Hz, 1H, H-4'''), 5.17 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.15–5.04 (m, 4H, H-1, H-1''', NCO_2CH_2), 4.97–4.86 (m, 3H), 4.81–4.63 (m, 13H), 4.32 (dd, *J* = 10.5, 3.3 Hz, 1H, H-2'), 4.19–3.96 (m, 9H), 3.91–3.83 (m, 1H), 3.81–3.66 (m, 6H), 3.52–3.32 (m, 5H, H-2''', OCH_2, $COOCH_3$), 3.22–3.07 (m, 2H, NCH_2), 2.94–2.84 (m, 2H, $PhCH_2CH_2$) 2.52–2.30 (m, 2H, $PhCH_2CH_2$), 1.65–1.40 (m, 4H, 2 X CH_2), 1.36–1.20 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 171.7 (C=O), 166.9 (C=O), 164.8 (C=O), 139.12, 139.10, 139.04, 138.98, 137.1, 134.8, 134.5, 134.4, 130.9, 130.7, 129.64, 129.60, 129.56, 129.4, 129.3, 129.2, 129.1, 129.04, 128.99, 128.64, 128.62, 128.56, 128.2, 127.8, 127.2, 127.0, 126.7, 117.0 (q, *J* = 288 Hz, $COCF_3$), 101.1 (C-1), 100.0 (C-1''), 98.7 (C-1'''), 95.5 (C-1'), 79.3, 79.1, 76.4, 76.2, 75.1, 74.0, 73.9, 73.5, 73.1, 72.9, 72.0 (C-4'''), 71.5, 71.1, 71.1, 70.6, 69.0 (OCH_2), 68.3, 68.1, 67.6, 67.1 ($NCOCH_2$), 65.0 (C-2'''), 55.1 (C-2'), 53.1 ($COOCH_3$), 52.9 ($COOCH_3$), 33.5 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 28.9 (CH_2), 28.5 (CH_2), 27.4 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 24.5 (CH_2); HRMS (ESI-TOF) m/z $[M - 3Na + 2H]^-$ calcd for $C_{102}H_{102}F_{16}N_5O_{34}S_3$ 2340.5313; Found 2340.5317.



S9

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate. (S9).**

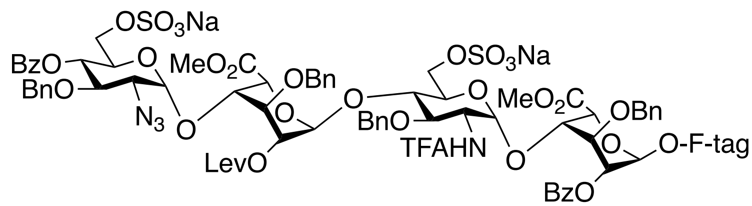
Compound **77** (0.20 g, 0.079 mmol) was treated according to the general procedure for Nap deprotection to give tetrasaccharide **S9** (0.17 g, 89%); R_f 0.38 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.94 (m, 4H, Ar), 7.66–7.44 (m, 10H, Ar), 7.37–7.11 (m, 33H, Ar), 6.94–6.92 (m, 2H, Ar), 6.11 (d, *J* = 8.0 Hz, 1H, NH), 5.55 (t, *J* = 9.5 Hz, 1H, H-4'''), 5.43 (d, *J* = 4.3 Hz, 1H, H-1''), 5.20–5.04 (m, 7H, H-1''', H-1', H-1, H-2, H-2'', NCO_2CH_2), 4.86–4.73 (m, 6H), 4.62–4.46 (m, 5H), 4.19–3.87 (m, 12H), 3.79 (s, 3H, OCH_3), 3.78–3.67 (m, 3H), 3.52–3.44 (m, 3H), 3.46 (s, 3H, OCH_3), 3.25–3.13 (m, 2H, NCH_2), 2.95–2.91 (m, 2H, $PhCH_2CH_2$), 2.82–2.79 (m, 2H, CH_2), 2.65–2.32 (m, 4H, CH_2, $PhCH_2CH_2$), 2.20 (s, 3H, $CH_3C{=}O$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8 ($CH_3C{=}OCH_2$), 172.2, 169.7, 169.4, 165.4, 164.8, 156.4 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C{=}O$), 138.8, 137.5, 137.3, 137.1, 137.1, 135.6, 135.5, 133.8, 133.3, 133.0, 132.9, 129.7, 129.7, 129.6, 129.6, 129.6, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 115.4 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.1 (C-1), 98.1 (C-1''), 97.7 (C-1'), 96.6 (C-1'''), 74.6, 74.1, 73.3, 73.2, 72.6, 71.4, 70.2, 67.9, 66.8, 63.1, 62.2, 60.6, 60.4, 52.9, 52.4, 51.9, 50.5, 50.2, 38.0, 32.9 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 29.8 ($CH_3C{=}O$), 29.1, 27.9, 26.7 ($(CH_3)_3C$), 26.2 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.3, 21.1, 19.1 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{119}H_{123}F_{16}N_5O_{28}Si$ 2402.7947; Found 2402.7932.



S10

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S10).**

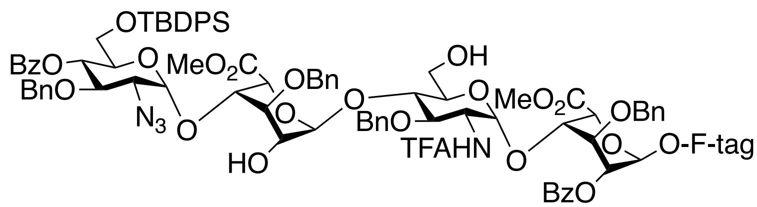
Compound **S9** (90 mg, 0.037 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S1** (93 mg, 99%); R_f 0.21 (13:1 CH_2Cl_2/CH_3OH); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.09–7.99 (m, 4H, ArH), 7.75–7.66 (m, 3H, ArH), 7.63–7.48 (m, 7H, ArH), 7.48–7.42 (m, 2H, ArH), 7.42–7.02 (m, 28H, ArH), 5.66 (t, J = 9.7 Hz, 1H, H-4'''), 5.56 (d, J = 2.7 Hz, 1H, H-1''), 5.32 (d, J = 3.5 Hz, 1H, H-1'''), 5.28–5.16 (m, 4H, H-1, H-2, H-1', H-2''), 5.16–5.09 (m, 2H, NCO_2CH_2), 4.96–4.82 (m, 4H), 4.81–4.70 (m, 4H, $PhCH_2$), 4.64 (d, J = 10.8 Hz, 1H, $PhCH_2$), 4.47 (m, 2H, NCH_2Ph), 4.44–4.37 (m, 2H), 4.33–4.15 (m, 7H), 4.13–4.02 (m, 2H), 3.98–3.92 (m, 1H, H-5'''), 3.86–3.72 (m, 7H), 3.55–3.43 (m, 4H), 3.20–3.08 (m, 2H, NCH_2), 2.98–2.65 (m, 6H, $PhCH_2CH_2$, CH_2) 2.61–2.46 (m, 2H, $PhCH_2CH_2$), 2.08 (s, 3H, CH_3C=O), 1.57–1.43 (m, 4H, 2 X CH_2), 1.31–1.24 (m, 2H, CH_2), 0.99 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.4 (CH_3C=OCH_2), 172.0, 170.0, 169.8, 165.0, 164.7, 138.9, 138.6, 138.5, 138.0, 137.87, 137.86, 135.6, 135.4, 133.4, 133.3, 133.0, 132.9, 129.9, 129.8, 129.7, 129.7, 129.6, 128.8, 128.8, 128.5, 128.41, 128.39, 128.18, 128.15, 128.11, 128.07, 128.0, 127.9, 127.8, 127.70, 127.65, 127.6, 127.5, 127.4, 127.1, 126.8, 126.7, 99.1 (C-1), 97.6 (C-1''), 97.3 (C-1'), 97.1 (C-1'''), 77.9, 77.4, 76.4, 74.3, 74.0, 73.8, 72.9, 72.6, 72.2, 71.3 (C-5'''), 71.2, 70.6 (C-2), 70.2 (C-4'''), 69.1, 68.5, 68.4 (C-2''), 66.3, 64.4, 63.1, 62.0, 53.7, 53.6 (C-2'), 51.9 (OCH_3), 51.8 (OCH_3), 37.6 (CH_2C=O), 32.1 (t, $^2J_{C,F}$ = 21.4 Hz, $\mathit{C}H_2CF_2$), 29.7, 29.1, 27.9, 26.2 ($(\mathit{C}H_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 4.0 Hz, $\mathit{C}H_2CH_2CF_2$), 23.1, 18.8 ($(CH_3)_3\mathit{C}$); HRMS (ESI-TOF) m/z [M – Na]$^-$ calcd for $C_{119}H_{122}F_{16}N_5O_{31}SSi$ 2480.7358; Found 2480.7378.



S12

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S12).**

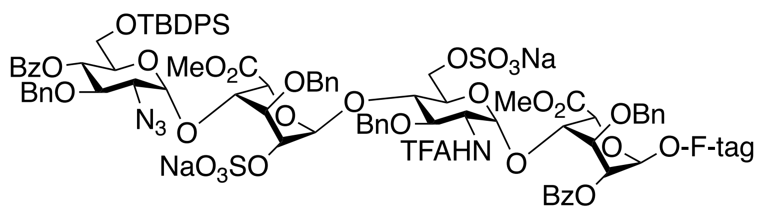
Compound **S9** (85 mg, 0.035 mmol) was treated according to the general procedures for TBDPS deprotection and *O*-sulfation to give tetrasaccharide **S12** (81 mg, 97% over two steps); R_f 0.52 (4:1 EtOAc/CH_3OH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.92–6.92 (m, 34H, ArH), 5.24 (bs, 1H, H-1''), 5.17 (t, *J* = 9.7 Hz, 1H, H-4'''), 5.10–4.93 (m, 7H, , H-1, H-2, H-1', H-2'', H-1''', $NCO_2C\mathit{H_2}$), 4.88–4.73 (m, 3H), 4.67–4.41 (m, 6H, $PhC\mathit{H_2}$), 4.36–4.16 (m, 6H), 4.1–4.06 (m, 1H), 4.04–3.81 (m, 7H), 3.78 (s, 3H, $COOC\mathit{H_3}$), 3.72–3.60 (m, 1H, OCH_2), 3.54 (t, *J* = 9.7 Hz, 1H, H-3''), 3.45 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2'''), 3.38–3.30 (m, 4H, $COOC\mathit{H_3}$, OCH_2), 3.12–2.93 (m, 2H, $NC\mathit{H_2}$), 2.88–2.67 (m, 4H, $PhC\mathit{H_2}CH_2$, CH_2), 2.08 (s, 3H, CH_3C=O), 1.51–1.24 (m, 4H, 2 X CH_2), 1.17–1.02 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 208.3 ($CH_3\mathit{C}$=OCH_2), 172.4, 170.4, 170.1, 165.6, 165.3, 137.59, 137.56, 137.4, 137.3, 134.03, 134.01, 133.3, 133.2, 132.5, 132.3, 130.1, 129.5, 129.41, 129.36, 128.5, 128.4, 128.23, 128.18, 128.12, 128.08, 128.0, 127.9, 127.83, 127.78, 127.7, 127.5, 127.44, 127.38, 127.04, 126.8, 99.0 (C-1), 97.8 (C-1''), 96.2 (C-1'''), 95.7 (C-1'), 77.5 (C-3'''), 77.3 (C-3''), 75.0, 74.3, 74.2, 73.7, 72.7, 72.6, 72.5, 71.6, 71.1, 70.8, 70.5, 69.3, 69.2, 68.5, 67.9, 67.8 (C-2''), 66.8, 65.9, 65.4, 63.1 (C-2'''), 53.3, 52.0 (OCH_3), 51.7 (OCH_3), 37.4 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 28.7, 28.3, 27.6, 25.7 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.0, 18.5 $(CH_3)_3C$); HRMS (ESI-TOF) m/z [M – 2Na + 3H]$^+$ calcd for $C_{103}H_{105}F_{16}N_5O_{34}S_2$ 2324.5906; Found 2324.5930.



S13

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S13).**

Compound **S9** (0.17 g, 0.068 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S13** (0.15 g, 95%); R_f 0.48 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.96 (m, 4H, Ar), 7.68–7.15 (m, 43H, Ar), 6.94–6.92 (m, 2H, Ar), 6.12 (d, *J* = 8.6 Hz, 1H, NH), 5.55 (t, *J* = 9.5 Hz, 1H, H-4'''), 5.34 (d, *J* = 2.1 Hz, 1H, H-1''), 5.22 (t, *J* = 2.8 Hz, 1H, H-2), 5.18–5.15 (m, 2H, NCO_2CH_2), 5.10 (d, *J* = 2.0 Hz, 1H, H-1), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'''), 5.00 (d, *J* = 3.6 Hz, 1H, H-1'), 4.87–4.71 (m, 6H), 4.62–4.46 (m, 5H), 4.20–4.08 (m, 4H), 4.02–3.87 (m, 7H), 3.82 (s, 3H, OCH_3), 3.81–3.67 (m, 6H), 3.55–3.46 (m, 2H), 3.29 (s, 3H, OCH_3), 3.25–3.13 (m, 2H, NCH_2), 2.95–2.91 (m, 2H, $PhCH_2CH_2$), 2.46–2.32 (m, 2H, $PhCH_2CH_2$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 169.4, 165.4, 164.7, 156.6 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.9, 137.4, 137.2, 137.0, 136.9, 135.7, 135.6, 133.8, 133.4, 133.1, 132.9, 129.7, 129.6, 129.6, 129.6, 129.2, 128.9, 128.8, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 127.3, 127.1, 126.7, 115.4 (q, ${}^{1}J_{C,F}$ = 287 Hz, CF_3), 101.5 (C-1''), 99.2 (C-1), 97.9 (C-1'''), 95.6 (C-1'), 78.6, 75.5, 75.2, 74.6, 73.9, 73.3, 73.2, 72.9, 72.7, 72.6, 71.9, 71.4, 70.1, 68.8, 68.5, 67.8, 66.8, 63.3, 61.9, 61.1, 52.7, 52.4, 51.9, 50.5, 50.2, 47.2, 46.1, 32.9 (t, ${}^{2}J_{C,F}$ = 22.3 Hz, $\mathit{C}H_2CF_2$), 29.1, 27.9, 26.7 ($(\mathit{C}H_3)_3C$), 26.2 (t, ${}^{3}J_{C,F}$ = 4.0 Hz, $\mathit{C}H_2CH_2CF_2$), 23.3, 19.2($(CH_3)_3\mathit{C}$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{114}H_{117}F_{16}N_5O_{26}Si$ 2304.7578; Found 2304.7563.

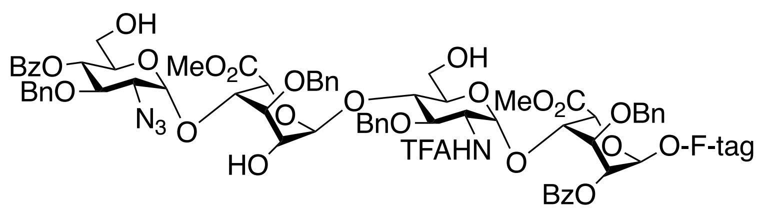


S14

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S14).**

Compound **S13** (67 mg, 0.029 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S14** (66 mg, 90%); R_f 0.19 (14:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 7.97–7.90 (m, 6H, Ar), 7.67–7.63 (m, 3H, Ar), 7.54–7.06 (m, 39H, NH, Ar), 6.96–6.94 (m, 2H, Ar), 5.49 (t, *J* = 9.8 Hz, 1H, H-4'''), 5.47 (s, 1H, H-1''), 5.20–5.09 (m, 6H), 4.98–4.80 (m, 4H), 4.68–4.56 (m, 6H), 4.43–4.32 (m, 8H), 4.15–4.02 (m, 4H), 3.94–3.91 (m, 1H), 3.87 (s, 3H, OCH_3), 3.83–3.71 (m, 2H), 3.68–3.63 (m, 3H), 3.53 (dd, *J* = 10.2, 3.2 Hz, 1H, H-2'''), 3.49–3.40 (m, 1H), 3.18 (s, 3H, OCH_3), 3.14–3.04 (m, 2H, NCH_2), 2.92–2.88 (m, 2H, $PhC\mathit{H}_2CH_2$), 2.50–2.38 (m, 2H, $PhCH_2C\mathit{H}_2$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 0.96 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz,

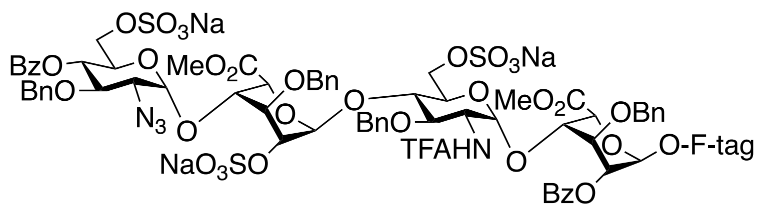
$CDCl_3$): δ 170.4, 170.2, 165.6, 165.2, 157.7 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 137.7, 137.7, 137.6, 137.4, 135.4, 135.3, 133.2, 133.2, 132.8, 132.8, 129.7, 129.5, 129.4, 129.4, 129.3, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 126.9, 126.7, 126.4, 115.7 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 98.9 (C-1''), 98.2 (C-1), 96.5 (C-1'''), 95.1 (C-1'), 78.0, 77.6, 74.7, 74.7, 74.0, 72.7, 72.6, 72.4, 71.8, 71.5, 71.4, 71.2, 71.0, 70.4, 69.9, 69.4, 69.2, 68.5, 67.0, 66.8, 65.8, 63.8, 62.2, 54.7, 53.3, 52.1, 51.3, 50.1, 50.0, 46.1, 32.2 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 28.6, 27.4, 25.9 $(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 22.9, 18.6 $(CH_3)_3C$); HRMS (ESI-TOF) m/z [M - Na]$^-$ calcd for $C_{114}H_{115}F_{16}N_5O_{32}SiNa$ 2484.6377; Found 2484.6377.



S15

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S15).**

Compound **S13** (80 mg, 0.035 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S15** (67 mg, 93%); R_f 0.21 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.98 (m, 4H, Ar), 7.66–7.62 (m, 1H, Ar), 7.50–7.10 (m, 32H, Ar), 6.95–6.93 (m, 2H, Ar), 6.21 (d, *J* = 8.1 Hz, 1H, NH), 5.32 (s, 1H, H-1''), 5.22 (t, *J* = 2.4 Hz, 1H, H-2), 5.20–5.14 (m, 2H, H-4''', NCO_2CH_2), 5.11 (d, *J* = 1.6 Hz, 1H, H-1), 5.04 (d, *J* = 3.7 Hz, 1H, H-1'''), 4.99 (d, *J* = 3.5 Hz, 1H, H-1'), 4.90–4.59 (m, 8H), 4.51–4.47 (m, 3H), 4.23–3.73 (m, 16H), 3.68–3.45 (m, 7H), 3.38 (s, 3H, OCH_3), 3.25–3.13 (m, 2H, NCH_2), 2.94–2.90 (m, 2H, $PhCH_2CH_2$), 2.46–2.32 (m, 2H, $PhCH_2CH_2$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): 169.6, 169.5, 166.4, 165.4, 156.8 (q, $^{2}J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 138.9, 137.9, 137.3, 137.1, 136.9, 136.9, 134.0, 133.8, 129.9, 129.6, 129.2, 128.9, 128.8, 128.8, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.4, 127.1, 126.7, 115.4 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 101.5 (C-1''), 99.2 (C-1), 97.9 (C-1'), 95.8 (C-1'''), 78.3, 77.6, 77.4, 77.3, 77.1, 76.8, 76.7, 75.7, 75.2, 74.2, 74.0, 73.3, 73.2, 72.9, 72.9, 72.6, 72.5, 71.1, 71.0, 68.9, 67.9, 66.8, 63.3, 61.1, 60.6, 52.8, 52.4, 52.1, 50.5, 50.2, 47.1, 46.2, 32.9 (t, $^{2}J_{C,F}$ = 22.3 Hz, *C*H_2CF_2), 29.1, 27.5, 26.2 (t, $^{3}J_{C,F}$ = 4.0 Hz, *C*$H_2CH_2CF_2$), 23.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{98}H_{99}F_{16}N_5O_{26}$ 2066.6401; Found 2066.6401.

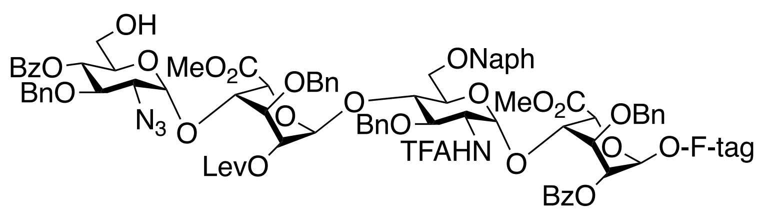


S16

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S16).**

Compound **S15** (70 mg, 0.029 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S16** (74 mg, 92%); R_f 0.38 (6:1 DCM/MeOH); ^1H NMR (400 MHz, CD_3OD): δ 8.19–8.17 (m, 2H, Ar), 8.04–8.02 (m, 3H, Ar), 7.60–7.11 (m, 36H, NH, Ar), 5.77 (s, 1H, H-1''), 5.27–5.23 (m, 3H, H-2, H-1', H-1), 5.13 (br, 2H, NCH_2), 5.07–4.93 (m, 5H, H-1''', H-4''', H-5, H-5'', C*H_2*Ph), 4.66–4.58 (m, 2H), 4.52–4.37 (m, 8H), 4.28–4.14 (m, 5H), 4.06 (dd, *J* = 10.1, 2.7 Hz, 1H, H-2'''), 3.88–3.76 (m, 6H), 3.64 (dd, *J* = 11.9, 2.6 Hz, 1H, H-2'''), 3.53 (s, 3H, OCH_3), 3.53–3.43 (m, 1H), 3.18 (s, 3H, OCH_3), 3.17–3.08

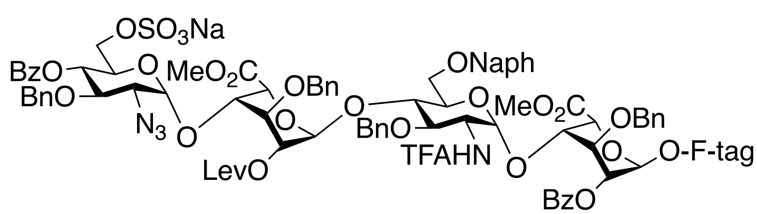
(m, 2H, NCH_2), 2.92–2.88 (m, 2H, $PhCH_2CH_2$), 2.59–2.47 (m, 2H, $PhCH_2CH_2$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.8, 165.6, 165.0, 157.7 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.9, 138.6, 138.3, 138.1, 137.9, 133.4, 133.2, 130.1, 129.8, 129.8, 129.6, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 115.7 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.1 (C-1), 98.1 (C-1''), 97.9 (C-1'''), 97.3 (C-1'), 78.0, 77.4, 76.7, 74.9, 74.2, 73.7, 73.2, 72.8, 72.4, 72.0, 71.9, 71.1, 71.0, 69.7, 69.5, 68.5, 67.3, 66.5, 66.3, 65.8, 64.7, 54.6, 53.8, 52.1, 52.0, 50.0, 49.8, 46.8, 46.0, 32.1 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 29.0, 27.6, 25.7 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.1; HRMS (ESI-TOF) m/z [M - 3Na + 2H]$^-$ calcd for $C_{98}H_{98}F_{16}N_5O_{35}S_3$ 2304.4949; Found 2304.4946.



S17

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S17).**

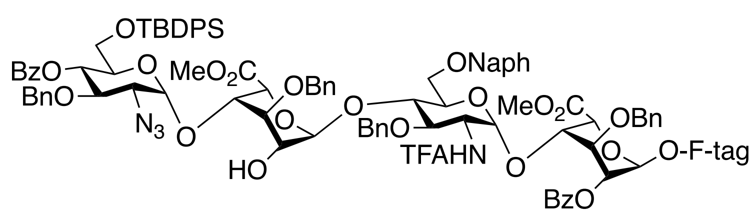
Compound **76** (0.30 g, 0.12 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S17** (0.26 g, 95%); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.38 (d, J = 8.9 Hz, 1H, NH), 8.07–7.87 (m, 8H, Ar), 7.70–7.66 (m, 2H, Ar), 7.58–7.16 (m,36H, Ar), 5.57 (d, J = 5.6 Hz, 1H, H-1''), 5.34–5.28 (m, 3H, H-1''', H-4''', H-1), 5.26 (d, J = 3.6 Hz, 1H, H-1'), 5.21 (dd, J = 5.2, 4.3 Hz, 1H, H-2), 5.13 (br, 2H, NCO_2CH_2), 5.09 (t, J = 5.9 Hz, 1H, H-2''), 4.93–4.66 (m, 11H), 4.47 (s, 2H, NCH_2Ph), 4.41–4.36 (m, 2H), 4.32–4.04 (m, 9H), 3.93 (dd, J = 11.2, 1.3 Hz, 1H), 3.85–3.80 (m, 2H), 3.77–3.74 (m, 1H), 3.74 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.66–3.59 (m, 3H), 3.48–3.43 (m, 1H), 3.17–3.10 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.67–2.37 (m, 6H, CH_2), 2.05 (s, 3H, $CH_3C=O$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.6 ($CH_3C=OCH_2$), 171.6, 169.7, 169.4, 165.2, 165.0, 156.9 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C=O$), 138.9, 138.8, 138.6, 138.3, 138.0, 137.8, 136.3, 133.5, 133.3, 133.1, 129.8, 129.7, 129.6, 129.6, 128.8, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.0, 126.6, 126.4, 126.0, 125.8, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0 (C-1), 98.3 (C-1''), 97.8 (C-1'''), 97.6 (C-1'), 77.5, 77.3, 76.6, 76.4, 76.3, 74.2, 74.2, 73.8, 73.8, 73.3, 73.2, 72.8, 72.0, 71.7, 71.4, 71.2, 70.8, 70.8, 69.3, 68.3, 67.8, 66.3, 62.9, 60.9, 60.8, 53.6 (C-2'), 51.6 (OCH_3), 51.5 (OCH_3), 50.0, 49.8, 37.2 ($CH_2C=O$), 32.2 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 29.5, 29.4, 29.4, 29.1, 29.0, 27.7 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 25.7, 23.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{114}H_{113}F_{16}N_5O_{28}$ 2304.7395; Found 2304.7388.



S18

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S18).**

Compound **S17** (80 mg, 0.035 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S18** (77 mg, 92%); R_f 0.19 (14:1 DCM/MeOH); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.50 (s, 1H, NH), 8.07–7.87 (m, 10H, Ar), 7.68–7.15 (m, 36H, Ar), 5.47 (d, J = 4.0 Hz, 1H, H-1''), 5.36–5.28 (m, 4H, H-1''', H-4''', H-1, H-1''), 5.23 (dd, J = 5.2, 4.3 Hz, 1H, H-2), 5.13 (br, 2H, NCO_2CH_2), 5.11 (t, J = 4.5 Hz, 1H, H-2''), 4.94 (d, J = 2.5 Hz, 1H), 4.90–4.83 (m, 5H), 4.78–4.70 (m, 4H), 4.61 (d, J = 11.2 Hz, 1H), 4.48 (d, J = 11.2 Hz, 1H), 4.47 (s, 2H, NCH_2Ph), 4.41 (t, J = 4.8 Hz, 1H), 4.37 (t, J = 5.0 Hz, 1H), 4.32–4.13 (m, 6H), 4.10–3.86 (m, 6H), 3.85–3.80 (m, 2H), 3.76 (s, 3H, OCH_3), 3.76–3.73 (m, 1H), 3.66–3.62 (m, 1H), 3.61 (s, 3H, OCH_3), 3.52–3.43 (m, 1H), 3.18–3.08 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.75–2.46 (m, 6H), 2.06 (s, 3H, $CH_3C{=}O$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): 205.8 ($CH_3C{=}OCH_2$), 171.8, 169.7, 169.4, 165.3, 165.0, 162.0, 157.1 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C{=}O$), 138.9, 138.6, 138.6, 138.2, 138.0, 137.8, 136.3, 133.5, 133.1, 129.8, 129.7, 129.7, 129.6, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.6, 127.6, 127.5, 127.4, 127.2, 127.0, 126.4, 126.2, 126.0, 125.7, 115.9 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0 (C-1), 98.5 (C-1''), 97.4 (C-1'), 97.2 (C-1'''), 77.5, 77.3, 76.6, 76.0, 75.3, 74.1, 73.7, 73.3, 73.2, 72.8, 72.2, 72.1, 71.1, 71.0, 70.0, 69.6, 68.4, 68.0, 66.3, 65.0, 62.8, 53.6, 51.7, 50.1, 49.8, 46.8, 46.1, 37.3 ($CH_2C{=}O$), 32.2 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 27.8 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 25.7, 23.1; HRMS (ESI-TOF) m/z $[M\ -Na]^-$ calcd for $C_{114}H_{112}F_{16}N_5O_{31}S$ 2382.6807; Found 2382.6821.

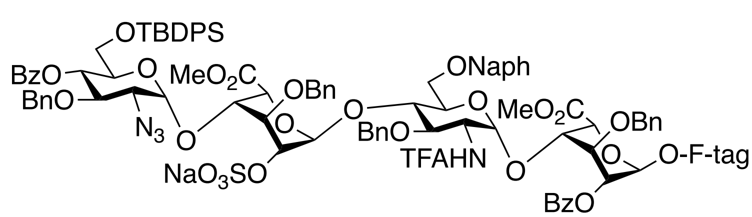


S19

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-**

glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S19).

Compound **76** (0.11 g, 0.045 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S19** (0.10 g, 95%); R_f 0.32 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.11–6.95 (m, 51H, ArH), 5.64 (t, *J* = 9.4 Hz, 1H, H-4'''), 5.52 (d, *J* = 5.4 Hz, 1H, H-1''), 5.47 (d, *J* = 3.8 Hz, 1H, H-1'''), 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 5.27 (appt, *J* = 3.5 Hz, 1H, H-2), 5.20 (d, *J* = 3.5 Hz, 1H, H-1), 5.18–5.10 (m, 2H, NCO_2CH_2), 5.00 (d, *J* = 11.2 Hz, 1H, $ArCH_2$), 4.94–4.70 (m, 9H, $ArCH_2$), 4.63 (d, *J* = 10.6 Hz, 1H, $ArCH_2$), 4.49 (s, 2H, NCH_2Ph), 4.45–4.35 (m, 2H), 4.31–4.10 (m, 7H), 4.08–3.94 (m, 3H), 3.93–3.70 (m, 9H), 3.56–3.41 (m, 4H, OCH_3), 3.24–3.09 (m, 2H, NCH_2), 3.02–2.93 (m, 2H, $PhCH_2CH_2$) 2.64–2.44 (m, 2H, $PhCH_2CH_2$), 2.10 (s, 3H, $CH_3C{=}O$), 1.57–1.43 (m, 4H, 2 X CH_2), 1.34–1.23 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ170.3, 170.2, 165.9, 165.5, 139.84, 139.80, 139.6, 139.5, 138.9, 138.6, 137.3, 136.5, 136.3, 134.4, 134.3, 134.2, 134.0, 133.91, 133.85, 130.8, 130.7, 130.58, 130.55, 130.46, 129.7, 129.6, 129.34, 129.28, 129.1, 129.04, 129.02, 128.94, 128.90, 128.87, 128.8, 128.7, 128.59, 128.56, 128.53, 128.47, 128.4, 128.3, 127.6, 127.5, 127.2, 127.0, 126.8, 126.6, 102.4 (C-1''), 100.0 (C-1), 98.6 (C-1'), 97.9 (C-1'''), 78.9, 78.6, 78.4, 77.7, 77.0, 75.3, 75.2, 74.5, 74.3, 74.1, 73.3, 73.1, 72.5, 72.4, 72.1, 71.7, 71.2 (C-4'''), 70.9 (C-2), 69.6, 69.1, 69.0, 67.1, 64.0, 63.0, 54.6, 54.5, 52.4, 52.3, 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 27.1 $(CH_3)_3C$), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 24.0, 19.7 $(CH_3)_3C$); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{125}H_{125}F_{16}N_5O_{26}Si$ 2444.8206; Found 2444.8201.

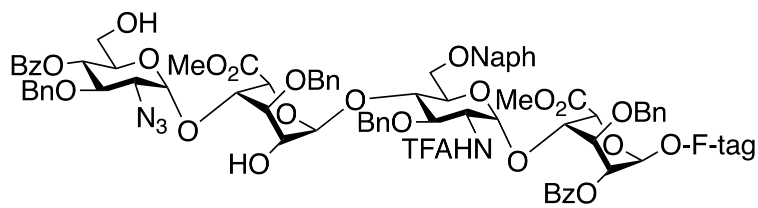


S20

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate, mono sodium salt (S20).**

Compound S**19** (0.10 g, 0.041 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S20** (99 mg, 99%); R_f 0.32 (2:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.07–7.91 (m, 6H, ArH), 7.85–7.77 (m, 2H, ArH), 7.76–7.71 (m, 2H, ArH), 7.70–7.60(m, 4H, ArH), 7.59–7.07 (m, 35H, ArH), 5.64 (bs, 1H, H-1''), 5.57 (appt, J = 9.6 Hz, 1H, H-4'''), 5.48 (d, J = 3.2 Hz, 1H, H-1'''), 5.30 (d, J = 3.6 Hz, 1H, H-1'), 5.28–5.22 (m, 2H, H-1, H-2), 5.17–5.11 (m, 2H, NCO_2CH_2), 5.02–4.92 (m, 4H), 4.88–4.68 (m, 7H), 4.63 (d, J = 10.6 Hz, 1H, ArCH_2), 4.60–4.53 (m, 2H), 4.47 (s, 2H, NCH_2Ph), 4.41 (appt, J = 5.1 Hz, 1H), 4.38–4.26 (m, 3H), 4.23–4.10 (m, 4H), 4.04–3.94 (m, 2H), 3.92–3.84 (m, 1H), 3.82–3.67 (m, 6H, OCH_2, COOCH_3), 3.62 (dd, J = 10.3, 3.4 Hz, 1H, H-2'''), 3.52–3.37 (m, 4H, OCH_2, COOCH_3), 3.18–3.05 (m, 2H, NCH_2), 3.02–2.93 (m, 2H, PhCH_2CH_2) 2.64–2.44 (m, 2H, $PhCH_2$$CH_2$), 2.10 (s, 3H, CH_3C=O), 1.56–1.39 (m, 4H, 2 X CH_2), 1.33–1.15 (m, 2H, CH_2), 1.00 (s, 9H, $(CH_3)_3$C); ^{13}C NMR (100 MHz, CD_3COCD_3): δ170.5 (C=O), 170.3 (C=O), 165.9 (C=O), 165.7 (C=O), 139.78, 139.44, 139.36, 139.2, 138.9, 138.8, 137.5, 136.4, 136.3, 134.4, 134.2, 133.9, 133.84, 133.77, 130.8, 130.7, 130.6, 130.52, 130.50, 130.4, 129.62, 129.55, 129.32, 129.27, 129.1, 129.04, 129.01, 128.98, 128.89, 128.86, 128.7, 128.63, 128.59, 128.56, 128.5, 128.4, 128.34, 128.27, 127.9, 127.6, 127.5, 127.4, 127.3, 126.6, 126.4, 100.1 (C-1''), 99.7 (C-1), 98.1 (C-1'), 96.1 (C-1'''), 78.5, 78.4, 77.3, 76.0, 75.0, 74.33, 74.25, 73.7, 73.6, 73.2, 72.9, 72.6, 72.2 (C-2), 71.5 (C-4'''), 71.1, 70.8, 69.3, 69.0, 68.9 (OCH_2), 67.1 (NCO_2CH_2), 64.0 (C-2'''), 63.3, 54.4, 54.3, 52.6 (COOCH_3), 52.1 (COOCH_3), 50.9 (NCH_2Ph), 47.7 (NCH_2), 33.2 ($PhCH_2CH_2$), 33.0 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 27.1 ($CH_3)_3$C), 26.6 (t, $^3J_{C,F}$ = 4.0 Hz,

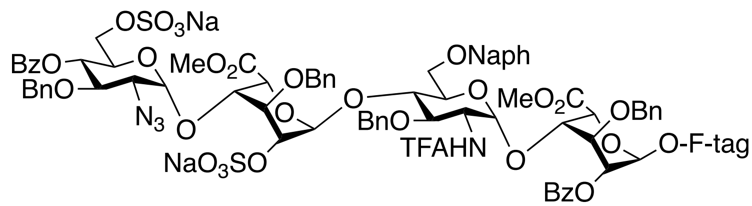
C$H_2CH_2CF_2$), 23.9 (*C*H_2), 19.7 ($(CH_3)_3$*C*); HRMS (ESI-TOF) m/z $[M - Na + 2H]^+$ calcd for $C_{125}H_{124}F_{16}N_5O_{29}SSi$ 2524.7773; Found 2524.7756.



S21

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S21).**

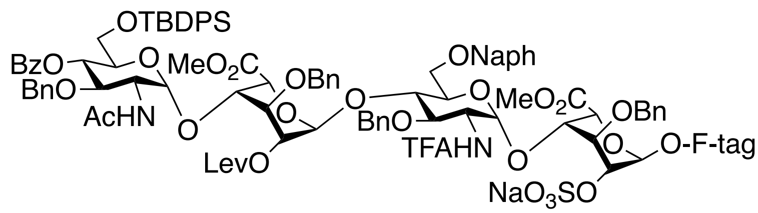
Compound **S19** (85 mg, 0.035 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S21** (75 mg, 98%); R_f 0.52 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.12–7.87 (m, 8H, ArH), 7.73–7.14 (m, 33H, ArH), 5.57 (d, *J* = 5.5 Hz, 1H, H-1''), 5.43 (d, *J* = 3.4 Hz, 1H, H-1'''), 5.35–5.24 (m, 3H, H-4''', H-1', H-2), 5.19 (d, *J* = 3.5 Hz, 1H, H-1), 5.18–5.12 (m, 2H, NCO_2C*H_2*), 5.01 (d, *J* = 11.2 Hz, 1H, ArC*H_2*), 4.97–4.86 (m, 5H, ArC*H_2*), 4.86–4.79 (m, 2H, ArC*H_2*), 4.78–4.72 (m, 2H, ArC*H_2*), 4.66 (d, *J* = 11.0 Hz, 1H, ArC*H_2*), 4.49 (s, 2H, NC*H_2*Ph), 4.43 (appt, *J* = 3.7 Hz, 1H, H-3'), 4.37 (d, *J* = 11.4 Hz, 1H, ArC*H_2*), 4.32–4.21 (m, 5H), 4.19–4.10 (m, 2H), 4.11–3.56 (m, 16H), 3.54–3.40 (m, 1H, OC*H_2*), 3.22–3.09 (m, 2H, NCH_2), 3.00–2.94 (m, 2H, PhC*H_2*CH_2), 2.65–2.46 (m, 2H, $PhCH_2C$*H_2*), 1.65–1.44 (m, 4H, 2 X CH_2), 1.39–1.29 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.5 (C=O), 170.2 (C=O), 166.0 (C=O), 165.9 (C=O), 139.8, 139.8, 139.7, 139.5, 138.9, 138.7, 137.3, 134.4, 134.4, 134.2, 134.0, 130.7, 130.6, 130.5, 129.7, 129.6, 129.3, 129.3, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.8, 128.7, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.2, 127.0, 126.8, 126.6, 102.4 (C-1''), 100.0 (C-1), 98.7 (C-1'), 98.2 (C-1'''), 79.2, 78.6, 78.3, 78.0, 77.0, 75.3 (C-3'), 75.2, 74.8, 74.3, 74.1, 73.3, 73.1, 72.4 (C-4'''), 72.0, 70.8 (C-2), 69.5, 69.1 (O*C*H_2), 69.0, 67.1, 63.9, 61.8, 54.6, 52.4, 52.3, 33.2, 33.0 (t, $^{2}J_{C,F}$ = 21.4 Hz, *C*H_2CF_2), 32.8, 26.6 (t, $^{3}J_{C,F}$ = 4.0 Hz, *C*$H_2CH_2CF_2$), 24.0; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{109}H_{107}F_{16}N_5O_{26}$ 2206.7026; Found 2206.7012.



S22

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate disodium salt (S22).**

Compound **S21** (75 mg, 0.034 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S22** (74 mg, 92%); R_f 0.62 (7:2:1 EtOAc/CH_3OH/H_2O); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.14–8.09 (m, 2H, ArH), 8.05–7.82 (m, 5H, ArH), 7.87–7.79 (m, 2H, ArH), 7.70–7.10 (m, 32H, ArH), 5.64 (bs, 1H, H-1''), 5.36 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.34–5.22 (m, 4H, H-4''', H-1', H-2, H-1), 5.18–5.12 (m, 2H, NCO_2C*H_2*), 5.03–4.93 (m, 4H), 4.92–4.58 (m, 9H, ArC*H_2*), 4.51–4.34 (m, 6H), 4.30 (appt, *J* = 7.6 Hz, 1H), 4.26–4.00 (m, 7H), 4.01–3.88 (m, 2H), 3.82–3.66 (m, 4H, OC*H_2*, COOC*H_3*), 3.64–3.56 (m, 2H), 3.55–3.41 (m, 4H, OC*H_2*, COOC*H_3*), 3.23–2.96 (m, 4H, NC*H_2*, PhC*H_2*CH_2) 2.66–2.46 (m, 2H, PhCH_2C*H_2*), 1.56–1.39 (m, 4H, 2 X CH_2), 1.30–1.15 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ170.7 (C=O), 170.7 (C=O), 166.2 (C=O), 165.9 (C=O), 163.0 (C=O), 139.8, 139.4, 139.3, 139.2, 138.9, 138.7, 137.5, 134.4, 134.3, 134.2, 133.8, 130.7, 130.6, 130.5, 130.4, 129.56, 129.55, 129.51, 129.31, 129.26, 129.1, 129.02, 129.00, 128.98, 128.95, 128.87, 128.84, 128.80, 128.7, 128.6, 128.38, 128.36, 128.31, 128.28, 128.26, 127.9, 127.73, 127.66, 127.3, 127.2, 126.6, 126.4, 100.6 (C-1''), 99.6 (C-1), 97.6 (C-1'), 97.1 (C-1'''), 79.1, 78.1, 77.4, 76.0, 75.0, 73.8, 73.6, 73.3, 72.9, 72.6, 71.9, 71.4, 71.1, 70.4, 69.3, 67.1, 66.3, 63.8, 54.3, 52.5, 47.2, 36.2, 33.0 (t, $^{2}J_{C,F}$ = 21.4 Hz, CH_2CF_2), 26.6 (t, $^{3}J_{C,F}$ = 4.4 Hz, $CH_2CH_2CF_2$), 23.8; HRMS (ESI-TOF) m/z [M – Na]$^-$ calcd for $C_{109}H_{105}F_{16}N_5O_{32}S_2Na$ 2386.5825; Found 2386.5825.

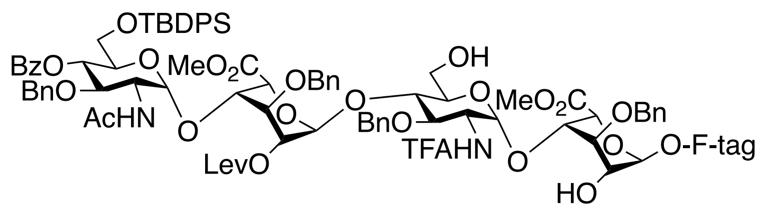


S23

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S23).**

Compound **77** (82 mg, 0.033 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S23** (78 mg, 92%); R_f 0.63 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.98–7.96 (m, 4H, Ar), 7.88–7.85 (m, 1H, Ar), 7.80–7.74 (m, 3H, Ar), 7.67–7.59 (m, 4H, Ar), 7.52–7.03 (m, 39H, Ar), 5.67 (t, J = 9.7 Hz, 1H, H-4'''), 5.40 (d, J = 2.3 Hz, 1H, H-1''), 5.18 (d, J = 3.4 Hz, 1H, H-1'), 5.15–5.13 (br, 2H, NCO_2CH_2), 5.09 (t, J = 2.8 Hz, 1H, H-2''), 5.00–4.98 (m, 5H), 4.85–4.71 (m, 6H), 4.63–4.48 (m, 7H), 4.43–4.38 (m, 1H), 4.19–4.10 (m, 6H), 4.04–3.78 (m, 8H), 3.73–3.64 (m, 1H), 3.53 (s, 3H, OCH_3), 3.47–3.37 (m, 1H), 3.34 (s, 3H, OCH_3), 3.26–3.16 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.76–2.46 (m, 6H, CH_2, $PhCH_2CH_2$), 2.11 (s, 3H, CH_3C=O), 1.80 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$);

^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.4 (CH_3C=OCH_2), 171.9, 169.5, 169.4, 168.7, 164.7, 162.0, 157.7 (q, $^{2}J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.4, 138.7, 138.6, 137.8, 136.4, 135.6, 135.5, 133.5, 133.2, 133.1, 133.0, 133.0, 130.1, 129.7, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.5, 126.2, 126.0, 126.0, 125.7, 116.1 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 100.1, 99.7, 97.6, 97.0, 78.1, 77.3, 76.6, 74.8, 73.2, 72.8, 72.7, 72.3, 71.9, 71.8, 71.3, 70.4, 69.8, 68.8, 68.3, 67.7, 66.4, 66.3, 62.3, 55.0, 54.6, 52.5, 51.2, 51.1, 50.0, 49.8, 47.0, 46.1, 37.3 (CH_2C=O), 32.1 (t, $^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.4, 27.7 (CH_2C=O), 26.3 ($(CH_3)_3C$), 25.7 (t, $^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.2, 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M – Na]^-$ calcd for $C_{125}H_{130}F_{16}N_3O_{31}SSi$ 2532.7922; Found 2532.7915.

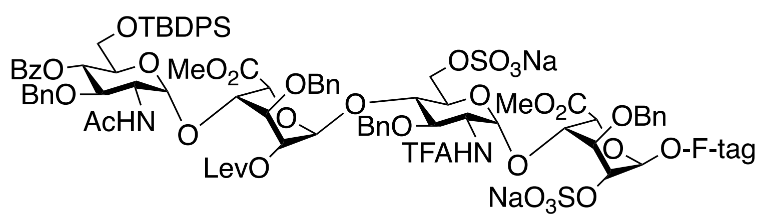


S24

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S24).**

Compound **77** (0.14 g, 0.057 mmol) was treated according to the general procedure for Nap deprotection to give tetrasaccharide **S24** (0.13 g, 89%); R_f 0.18 (1:4 hexanes/EtOAc); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.53 (d, J = 9.3 Hz, 1H, NH), 8.01–8.00 (m, 2H, Ar), 7.73–7.53 (m, 7H, Ar), 7.42–7.21 (m, 25H, Ar), 7.18–7.11 (m, 10H, Ar), 5.61 (t, J = 9.8 Hz, 1H, H-4'''), 5.55 (d, J = 4.5 Hz, 1H, H-1''), 5.21–5.13 (m, 4H, NCO_2CH_2, H-1''', H-1'), 5.07 (dd, J = 3.4, 2.7 Hz, 1H, H-2''), 4.96 (s, 1H, H-1), 4.89–4.77 (m, 5H, C*H*$_2$Ph, H-5, H-5''), 4.72–4.68 (m, 2H, C*H*$_2$Ph), 4.63–4.54 (m, 2H, C*H*$_2$Ph), 4.51 (s, 2H, NC*H*$_2$Ph), 4.50–4.43

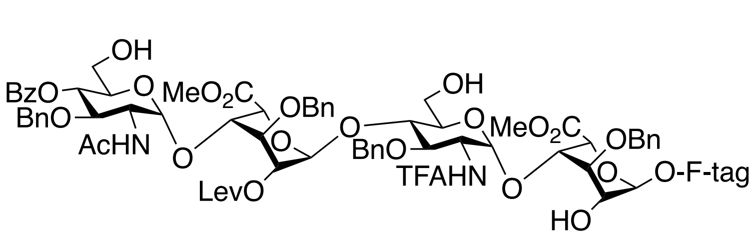
(m, 2H), 4.33 (d, J = 3.7 Hz, 1H), 4.27–4.16 (m, 4H), 4.08–4.03 (m, 1H), 3.99–3.86 (m, 5H), 3.92–3.83 (m, 4H), 3.84–3.65 (m, 8H), 3.52 (s, 3H, OCH_3), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.26–3.17 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.87–2.82 (m, 2H, CH_2), 2.63–2.47 (m, 4H, CH_2, $PhCH_2CH_2$), 2.15 (s, 3H, CH_3C=O), 1.96 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.3 (CH_3C=OCH_2), 171.9, 169.8, 169.4, 169.0, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.8, 138.6, 138.5, 138.5, 138.0, 135.6, 135.4, 133.3, 133.1, 133.0, 130.1, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.7, 127.7, 127.6, 127.5, 127.2, 127.1, 126.9, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.6 (C-1''), 96.5 (C-1'''), 95.8 (C-1'), 78.0, 77.9, 74.8, 74.3, 74.2, 73.5, 72.6, 72.4, 72.2, 71.6, 71.3, 71.1, 70.5, 70.4, 70.2, 67.9, 67.4, 66.7, 66.3, 62.5, 60.1, 54.1, 53.6, 52.5, 51.6, 51.3, 50.1, 49.8, 47.0, 46.1, 37.5 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 28.9, 27.7, 26.3 ($(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.3, 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{114}H_{123}F_{16}N_3O_{28}Si$ 2314.7886; Found 2314.7891.



S25

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S25).**

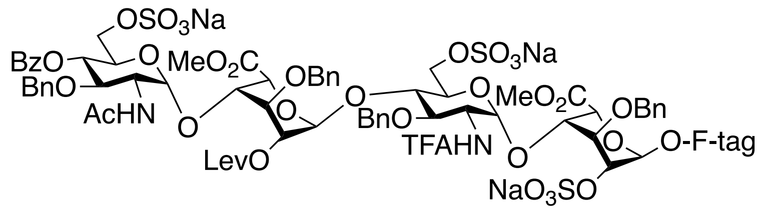
Compound **S24** (60 mg, 0.026 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S25** (61 mg, 93%); R_f 0.63 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.00 (d, *J* = 9.6 Hz, 1H, NH), 8.38 (d, *J* = 9.6 Hz, 1H, NH), 7.87–7.85 (m, 2H, Ar), 7.66–7.63 (m, 2H, Ar), 7.55–7.46 (m, 4H, Ar), 7.35–7.06 (m, 35H, Ar), 5.41 (d, *J* = 2.2 Hz, 1H, H-1''), 5.35 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.18 (d, *J* = 3.3 Hz, 1H, H-1'''), 5.14–5.09 (m, 4H, NCO_2CH_2, H-1, H-2'), 5.06 (d, *J* = 3.2 Hz, 1H, H-1'), 4.89 (d, *J* = 2.8 Hz, 1H), 4.86–4.76 (m, 4H), 4.69–4.55 (m, 4H), 4.51–4.44 (m, 4H, CH_2Ph), 4.37–4.19 (m, 6H), 4.11–4.03 (m, 3H), 3.86–3.65 (m, 10H), 3.52–3.44 (m, 1H, OCH_2CH_2), 3.39 (s, 3H, OCH_3), 3.20–3.13 (m, 2H, NCH_2), 2.98–2.89 (m, 3H), 2.76 (dt, *J* = 18.7, 5.4 Hz, 1H), 2.61 (dt, *J* = 17.1, 5.4 Hz, 1H), 2.54–2.37 (m, 3H, CH_2, $PhCH_2CH_2$), 2.15 (s, 3H, CH_3C=O), 2.03 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 0.95 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3OD): δ 208.3 (CH_3C=OCH_2), 172.4, 172.3, 170.5, 169.9, 165.2, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.3, 137.9, 137.9, 137.4, 135.3, 135.2, 133.2, 132.9, 132.7, 129.6, 129.5, 129.4, 129.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 127.3, 127.2, 126.9, 126.8, 126.6, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-1), 97.7 (C-1''), 96.1 (C-1'), 94.5 (C-1'''), 77.6, 77.4, 74.6, 74.2, 74.1, 72.3, 72.2, 71.7, 71.3, 71.0, 70.5, 70.2, 68.9, 68.5, 68.1, 66.7, 66.2, 64.9, 62.9, 53.8, 52.9, 51.9, 51.4, 50.1, 49.9, 46.6, 46.2, 37.4 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.4, 28.8, 28.2, 25.9 ($(CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2, 22.0, 18.6 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z [M -2Na + H]$^-$ calcd for $C_{114}H_{122}F_{16}N_3O_{34}Si$ 2472.6865; Found 2472.6877.



S26

N-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S26).

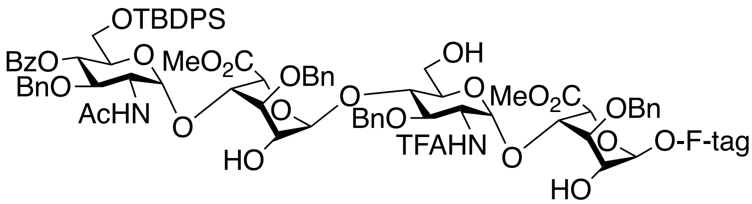
Compound **S24** (73 mg mg, 0.031 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S26** (61 mg, 94%); R_f 0.10 (1:4 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.56 (d, J = 9.0 Hz, 1H, NH), 8.03–8.01 (m, 2H, Ar), 7.76–7.74 (m, 3H, Ar), 7.67–7.64 (m, 1H, Ar), 7.55–7.12 (m, 28H, Ar), 5.51 (d, J = 4.1 Hz, 1H, H-1''), 5.34 (t, J = 9.7 Hz, 1H, H-4'''), 5.19 (d, J = 3.4 Hz, 1H, H-1'), 5.16–5.11 (m, 3H, NCO_2CH_2, H-1'''), 5.06 (t, J = 3.7 Hz, 1H, H-2''), 4.97 (s, 1H, H-1), 4.89–4.75 (m, 6H, CH_2Ph, H-5, H-5''), 4.69–4.61 (m, 2H, CH_2Ph), 4.56 (d, J = 11.2 Hz, 1H, CH_2Ph), 4.51 (s, 2H, NCH_2Ph), 4.46 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.40–4.35 (m, 1H), 4.29 (d, J = 3.7 Hz, 1H), 4.24–4.12 (m, 4H), 4.02–3.85 (m, 6H), 3.83–3.65 (m, 7H), 3.62–3.57 (m, 4H), 3.50–3.40 (m, 1H, OC$H_2$$CH_2$), 3.26–3.17 (m, 2H, NCH_2), 2.98–2.79 (m, 4H, PhC$H_2$$CH_2$, CH_2), 2.65–2.47 (m, 4H, CH_2, PhCH_2CH_2), 2.15 (s, 3H, CH_3C=O), 1.91 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.5 (CH_3*C*=OCH_2), 171.8, 169.8, 169.4, 169.1, 165.2, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 139.0, 138.7, 138.6, 138.6, 138.5, 138.0, 134.3, 134.2, 133.3, 132.5, 132.4, 130.5, 129.9, 129.5, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 127.5, 127.4, 127.2, 127.1, 126.9, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.2 (C-1), 97.7 (C-1''), 97.0 (C-1'''), 95.9 (C-1'), 78.0, 77.7, 74.6, 74.4, 74.4, 74.0, 73.6, 72.7, 72.4, 72.4, 71.9, 71.6, 71.1, 70.2, 69.7, 67.9, 67.4, 66.7, 66.3, 60.9, 60.1, 53.6, 52.5, 51.6, 51.3, 50.1, 49.8, 46.9, 46.1, 37.5 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, *C*$H_2$$CF_2$), 29.1, 28.9, 27.8, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, *C*$H_2$$CH_2$$CF_2$), 23.3, 22.3; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{98}H_{105}F_{16}N_3O_{28}$ 2076.6707; Found 2076.6733.



S27

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S27).**

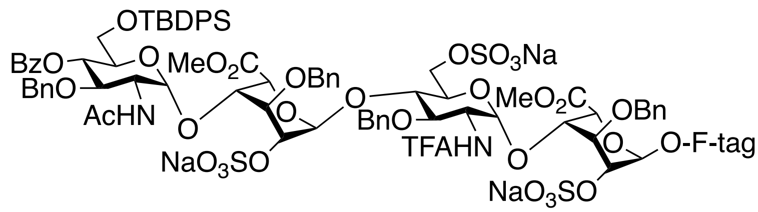
Compound **S26** (60 mg, 0.029 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S27** (63 mg, 91%); R_f 0.12 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.04 (d, J = 9.5 Hz, 1H, NH), 8.28 (d, J = 9.2 Hz, 1H, NH), 7.95–7.93 (m, 2H, Ar), 7.70–7.68 (m, 2H, Ar), 7.64–7.60 (m, 4H, Ar), 7.51–7.06 (m, 29H, Ar), 5.38 (d, J = 1.5 Hz, 1H, H-1''), 5.24 (t, J = 9.3 Hz, 1H, H-4'''), 5.15–5.07 (m, 6H, NCO_2CH_2, H-1, H-2', H-1''', H-1'), 4.94 (d, J = 2.4 Hz, 1H), 4.85–4.70 (m, 4H), 4.64–4.57 (m, 3H), 4.53–4.44 (m, 4H), 4.38 (s, 1H), 4.33–4.21 (m, 5H), 4.13–4.00 (m, 6H), 3.86–3.67 (m, 7H), 3.52–3.44 (m, 4H, OCH_2CH_2, OCH_3), 3.22–3.13 (m, 2H, NCH_2), 2.98–2.89 (m, 3H), 2.75 (dt, J = 18.9, 5.6 Hz, 1H), 2.61 (dt, J = 17.0, 5.4 Hz, 1H), 2.54–2.37 (m, 3H, CH_2, $PhCH_2CH_2$), 2.13 (s, 3H, CH_3C=O), 2.01 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3OD): δ 208.5 (CH_3C=OCH_2), 172.3, 170.5, 170.1, 165.4, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.0, 137.9, 137.8, 137.5, 134.0, 134.0, 130.1, 129.5, 129.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.3, 127.2, 126.9, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.9 (C-1), 97.5 (C-1''), 95.8, 94.9, 77.6, 77.4, 75.0, 74.1, 73.6, 72.2, 71.8, 71.7, 70.9, 70.8, 70.5, 70.3, 70.2, 69.4, 69.2, 68.3, 68.1, 66.8, 66.3, 66.2, 65.0, 53.8, 52.8, 51.9, 51.6, 50.1, 50.0, 46.1, 37.4 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.4, 28.8, 28.3, 27.7, 27.5, 25.7 (t, ${}^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2, 21.9; HRMS (ESI-TOF) m/z [M - 3Na + 2H]$^-$ calcd for $C_{114}H_{122}F_{16}N_3O_{34}Si$ 2314.5256; Found 2314.5244.



S28

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S28).**

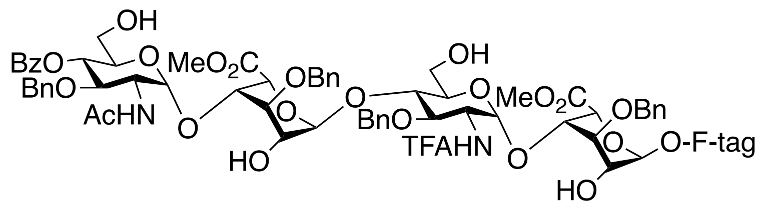
Compound **S24** (80 mg, 0.034 mmol) was treated according to the general procedure for Nap deprotection to give tetrasaccharide **S28** (73 mg, 96%); R_f 0.36 (3:2 hexanes/Acetone); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.60 (d, *J* = 9.0 Hz, 1H, NH), 8.03–8.01 (m, 2H, Ar), 7.77–7.75 (m, 2H, Ar), 7.69–7.62 (m, 3H, Ar), 7.56–7.09 (m, 37H, Ar), 5.63 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.37 (d, *J* = 2.2 Hz, 1H, H-1''), 5.18–5.13 (m, 4H, NCO_2CH_2, H-1''', H-1'), 4.97 (s, 1H, H-1), 4.89–4.85 (m, 3H, CH_2Ph, H-5, H-5''), 4.79–4.61 (m, 5H, CH_2Ph), 4.54 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.50 (s, 2H, NCH_2Ph), 4.40–4.35 (m, 2H), 4.25–4.13 (m, 3H), 4.08–4.04 (m, 2H), 3.99–3.89 (m, 5H), 3.92–3.83 (m, 4H), 3.87–3.64 (m, 10H), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.26–3.17 (m, 5H, OCH_3, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.55–2.47 (m, 2H, $PhCH_2CH_2$), 1.84 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.7, 169.4, 169.2, 164.7, 157.0 (q, ${}^{2}J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.7, 138.6, 138.5, 138.5, 138.3, 135.7, 135.5, 133.2, 133.2, 133.0, 130.2, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 127.1, 126.9, 126.8, 116.1 (q, ${}^{1}J_{C,F}$ = 287 Hz, CF_3), 101.3 (C-1), 100.5 (C-1''), 96.5 (C-1'''), 95.8 (C-1'), 78.3, 74.0, 73.5, 73.0, 72.3, 72.1, 71.9, 71.5, 71.0, 70.3, 68.4, 66.3, 62.2, 55.1, 53.6, 52.4, 51.6, 51.0, 50.0, 49.8, 46.8, 32.1 (t, ${}^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 27.6, 26.2 (($(CH_3)_3C$), 25.7 (t, ${}^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.2, 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{109}H_{1118}F_{16}N_3O_{26}Si$ 2216.7517; Found 2216.7529.



S29

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S29).**

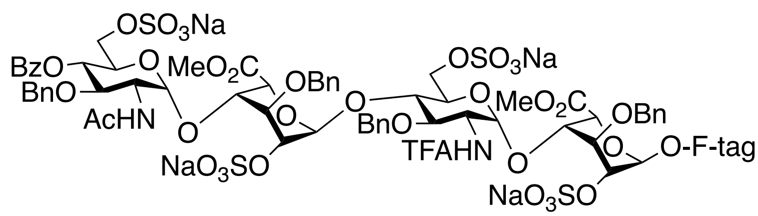
Compound **S28** (66 mg, 0.031 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S29** (68 mg, 90%); R_f 0.53 (4:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.13 (d, *J* = 8.2 Hz, 1H, NH), 8.04–7.98 (m, 2H, Ar), 7.73–7.65 (m, 3H, Ar), 7.60–7.52 (m, 4H, Ar), 7.46–7.09 (m, 34H, Ar), 5.58–5.54 (m, 2H, H-4''', H-1''), 5.16–4.94 (m, 8H, NCO_2CH_2, H-1''', H-1', H-1, CH_2Ph,), 4.89–4.84 (m, 2H, CH_2Ph), 4.80–4.75 (m, 3H), 4.69–4.54 (m, 7H), 4.48 (s, 2H, NCH_2Ph), 4.39–4.37 (m, 3H), 4.26–3.98 (m, 9H), 3.84–3.68 (m, 6H), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.35–3.25 (m, 5H, OCH_3, NCH_2), 2.98–2.94 (m, 2H, PhCH_2CH_2), 2.60–2.47 (m, 2H, $PhCH_2$CH_2), 2.11 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.00 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 135.7, 135.6, 133.3, 129.7, 129.6, 128.8, 128.3, 128.2, 127.8, 127.6, 100.2, 100.0, 98.2, 97.4, 77.4, 77.2, 74.8, 74.4, 73.6, 72.8, 72.5, 72.4, 77.2, 71.9, 71.5, 71.4, 71.1, 70.9, 70.7, 69.7, 68.8, 67.9, 66.6, 66.3, 65.1, 62.3, 54.7, 53.6, 52.1, 51.5, 49.9, 46.8, 32.2, 29.1, 27.6, 26.4, 25.8, 23.3, 22.2; HRMS (ESI-TOF) m/z [M – Na]$^-$ calcd for $C_{109}H_{114}F_{16}N_3O_{35}SiS_3Na_2$ 2498.5703; Found 2498.5728.



S30

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S30).**

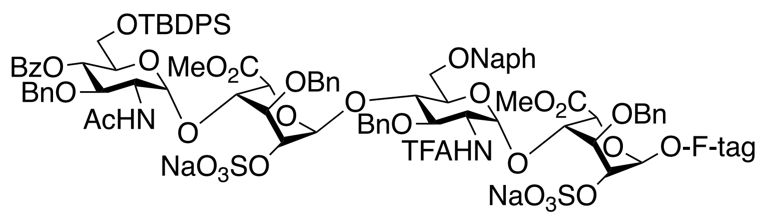
Compound **S28** (75 mg, 0.034 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S30** (62 mg, 93%); R_f 0.17 (3:2 hexanes/Acetone); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.60 (d, *J* = 9.1 Hz, 1H, NH), 8.03–8.01 (m, 2H, Ar), 7.75–7.73 (m, 3H, Ar), 7.67–7.63 (m, 1H, Ar), 7.54–7.13 (m, 28H, Ar), 5.37 (d, *J* = 2.3 Hz, 1H, H-1''), 5.32 (t, *J* = 9.7 Hz, 1H, H-4'''), 5.19 (d, *J* = 3.5 Hz, H-1'), 5.17–5.14 (m, 2H, NCO_2CH_2), 5.09 (d, *J* = 3.5 Hz, H-1'''), 4.98 (s, 1H, H-1), 4.97–4.86 (m, 4H, OH, CH_2Ph, H-5, H-5''), 4.79–4.62 (m, 5H, CH_2Ph), 4.55 (d, *J* = 11.1 Hz, 1H, CH_2Ph), 4.50 (s, 2H, NCH_2Ph), 4.39 (d, *J* = 11.3 Hz, 1H, CH_2Ph), 4.35–4.29 (m, 1H, H-2'''), 4.27–4.21 (m, 1H, H-2'), 4.19 (t, *J* = 2.5 Hz, H-4), 4.15 (t, *J* = 3.1 Hz, H-4''), 4.08 (t, *J* = 9.5 Hz, 1H), 4.03–3.85 (m, 7H), 3.81–3.55 (m, 9H), 3.50–3.40 (m, 4H, OCH_3, OCH_2CH$_2$), 3.26–3.17 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, PhCH_2CH$_2$), 2.60–2.47 (m, 2H, PhCH$_2$CH_2), 1.83 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.8, 169.5, 169.3, 165.2, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.7, 138.6, 138.5, 138.5, 138.3, 134.3, 134.2, 133.3, 130.5, 130.0, 129.5, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.5, 127.1, 127.1, 126.9, 116.1 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 101.3 (C-1), 100.5 (C-1''), 96.6 (C-1'''), 95.8 (C-1'), 78.4, 78.0, 76.4, 74.4, 74.1, 73.5, 73.0, 72.3, 72.2, 71.5, 71.2, 71.0, 68.4, 67.9, 67.2, 66.3, 60.9, 60.3, 55.1, 54.6, 53.6, 52.4, 51.6, 51.2, 50.0, 49.8, 46.9, 46.1, 32.2 (t, $^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.7, 27.9, 25.7 (t, $^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{93}H_{100}F_{16}N_3O_{26}$ 1978.6340; Found 1978.6348.



S31

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S31).**

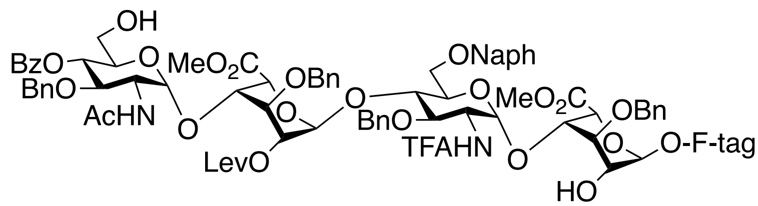
Compound **S30** (62 mg, 0.031 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S31** (66 mg, 89%); R_f 0.15 (4:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.18 (d, J = 8.2 Hz, 1H, NH), 8.08–8.06 (m, 2H, Ar), 7.57–7.71 (m, 3H, Ar), 7.61–7.03 (m, 29H, Ar), 5.63 (s, 1H, H-1''), 5.22–4.71 (m, 10H, NCO_2CH_2, H-4''', H-1, H-1', H-1''', H-5'', CH_2Ph), 4.63–4.36 (m, 6H), 4.21–3.90 (m, 8H), 3.82 (s, 3H, OCH_3), 3.76–3.70 (m, 1H, OCH_2CH_2), 3.59 (s, 3H, OCH_3), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.26–3.17 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.60–2.47 (m, 2H, $PhCH_2CH_2$), 1.95 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 134.3, 133.4, 130.5, 129.8, 128.4, 128.3, 128.2, 128.2, 127.8, 127.5, 100.0, 99.9, 99.5, 97.9, 77.0, 75.1, 74.8, 74.4, 73.5, 72.4, 72.2, 72.0, 71.9, 71.4, 70.8, 70.7, 69.8, 69.3, 68.1, 67.9, 66.6, 66.4, 65.8, 65.5, 54.8, 54.5, 52.3, 52.2, 50.1, 46.6, 32.1, 29.3, 27.7, 25.8, 23.3, 22.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{93}H_{95}F_{16}N_3O_{38}SiS_4Na_3$ 2362.3914; Found 2362.3936.



S33

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S33).**

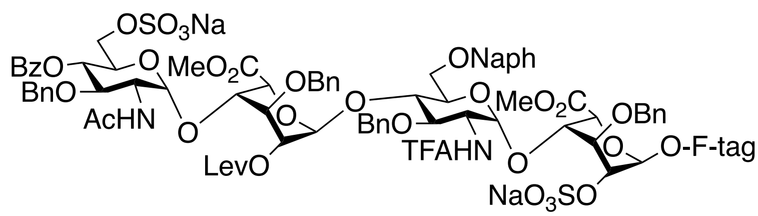
Compound **77** (81 mg, 0.034 mmol) was treated according to the general procedure for Lev deprotection and O-sulfation to give tetrasaccharide **S33** (76 mg, 88%); R_f 0.54 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.03 (d, J = 7.5 Hz, 1H, NH), 8.03–7.93 (m, 4H, Ar), 7.84–7.72 (m, 4H, Ar), 7.66–7.56 (m, 40H, Ar, NH), 5.64–5.59 (m, 2H, H-4''', H-1''), 5.15–5.12 (m, 2H, NCO_2CH_2), 5.01–4.92 (m, 8H, H-1''', H-1', H-1, H-5'', CH_2Ph, CH_2Nap), 4.80–4.67 (m, 6H, H-5, CH_2Ph), 4.61–4.55 (m, 2H), 4.51–4.48 (m, 4H), 4.30–4.24 (m, 2H), 4.19–4.10 (m, 5H), 4.02–3.95 (m, 4H), 3.83–3.68 (m, 4H), 3.51 (s, 3H, OCH_3), 3.47–3.38 (m, 1H, OC$H_2$$CH_2$), 3.23–3.15 (m, 2H, OCH_3, NCH_2), 3.06 (s, 3H, OCH_3), 2.98–2.94 (m, 2H, PhC$H_2$$CH_2$), 2.60–2.47 (m, 2H, Ph$CH_2CH_2$), 1.95 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.00 (s, 9H, $(CH_3)_3$C); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 170.8, 169.3, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 139.3, 139.0, 138.7, 138.6, 138.0, 136.7, 135.7, 135.5, 133.5, 133.1, 133.0, 133.0, 130.3, 129.7, 129.6, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.3, 127.3, 127.1, 126.9, 126.6, 126.5, 126.4, 125.8, 125.5, 116.1 (q, ${}^{1}J_{C,F}$ = 287 Hz, CF_3), 100.0 (C-1), 99.7 (C-1'), 98.7 (C-1'''), 98.4 (C-1''), 77.9, 77.2, 74.7, 74.5, 74.2, 73.9, 72.6, 72.5, 72.2, 71.8, 71.3, 71.0, 70.6, 69.8, 68.7, 67.6, 67.2, 66.5, 66.3, 62.2, 54.6, 54.6, 53.4, 51.3, 50.7, 46.5, 32.1 (t, ${}^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 27.7, 26.3 (($CH_3)_3C$), 25.7 (t, ${}^{3}J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.5, 18.8; HRMS (ESI-TOF) m/z $[M – 2Na]^{2-}$ calcd for $C_{120}H_{125}F_{16}N_3O_{32}SiS_2$ 1256.8523; Found 1256.8502.



S34

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S34).**

Compound **77** (71 mg, 0.27 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S34** (67 mg, 96%); R_f 0.28 (1:4 hexanes/EtOAc); ${}^{1}H$ NMR (400 MHz, CD_3COCD_3): δ 8.60 (d, *J* = 8.9 Hz, 1H, NH), 8.19–8.15 (m, 2H, Ar), 8.07–7.84 (m, 7H, Ar), 7.77–7.21 (m, 31H, Ar), 5.43 (d, *J* = 3.3 Hz, 1H, H-1''), 5.34 (t, *J* = 9.9 Hz, 1H, H-4'''), 5.22 (d, *J* = 3.3 Hz, 1H, H-1'), 5.16–5.13 (m, 2H, NCO_2CH_2), 5.12 (d, *J* = 3.5 Hz, 1H, H-1'''), 5.05 (t, *J* = 3.9 Hz, 1H, H-2''), 5.03 (s, 1H, H-1), 4.89 (d, *J* = 3.3 Hz, 1H), 4.86 (d, *J* =2.0 Hz, 1H), 4.82–4.72 (m, 6H), 4.68–4.63 (m, 2H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.50 (s, 2H, NCH_2Ph), 4.42–4.33 (m, 2H), 4.28–4.23 (m, 2H), 4.19–4.10 (m, 3H), 4.08–3.93 (m, 5H), 3.82–3.70 (m, 8H), 3.60 (dd, *J* = 12.3, 5.0 Hz, 1H), 3.52 (s, 3H, OCH_3), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.80–2.46 (m, 6H, CH_2, $PhCH_2CH_2$), 2.10 (s, 3H, $CH_3C{=}O$), 1.81 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.6 (CH_3*C*=OCH_2), 172.2, 170.3, 169.7, 169.4, 167.2, 165.5, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3*C*=O), 146.0, 140.7, 139.3, 139.0, 138.9, 138.8, 138.4, 136.6, 134.6, 134.6, 133.8, 133.7, 133.4, 133.2, 132.9, 132.7, 130.8, 130.3, 129.9, 129.8, 129.0, 128.8, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 126.5, 126.4, 126.3, 126.1, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.5 (C-1), 98.2 (C-1''), 98.1 (C-1'''), 96.3 (C-1'), 78.7, 78.1, 75.1, 75.0, 74.5, 74.2, 73.7, 73.4, 73.2, 73.0, 72.9, 72.2, 72.1, 72.0, 71.5, 69.7, 69.2, 68.5, 68.3, 67.7, 66.9, 66.7, 61.4, 54.0, 52.9, 51.9, 51.7, 50.4, 50.2, 47.3, 46.5, 37.7 (CH_2C=O), 32.5 (t, $^2J_{C,F}$ = 21.6 Hz, *C*H_2CF_2), 29.2, 29.1, 28.1, 27.8, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, *C*$H_2CH_2CF_2$), 23.7, 22.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{109}H_{113}F_{16}N_3O_{28}$ 2216.7334; Found 2216.7334.

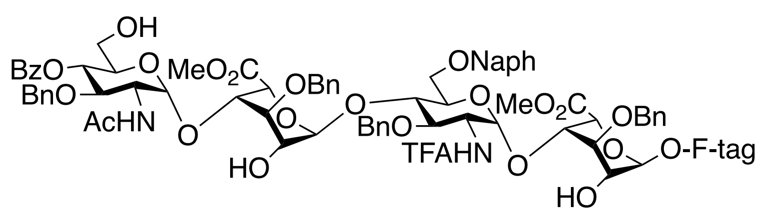


S35

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-2-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S35).**

Compound **S34** (70 mg, 0.031 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S35** (71 mg, 93%); R_f 0.36 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.10 (d, *J* = 9.0 Hz, 1H, NH), 8.21 (d, *J* = 9.0 Hz, 1H, NH), 7.87–7.79 (m, 5H, Ar), 7.70–7.68 (m, 2H, Ar), 7.62–7.52 (m, 3H, Ar), 7.48–7.00 (m, 31H, Ar), 5.23–5.08 (m, 7H, H-1'', H-4''', H-1', NCO_2CH_2, H-1''', H-1), 5.02 (d, *J* = 1.6 Hz, 1H), 4.93

(s, 1H), 4.86 (s, 1H), 4.82–4.68 (m, 5H), 4.64–4.58 (m, 2H), 4.52–4.48 (m, 3H), 4.44–4.31 (m, 6H), 4.19 (s, 1H), 4.13–4.04 (m, 5H), 3.97–3.88 (m, 2H), 3.77–3.64 (m, 8H), 3.50–3.40 (m, 1H, OCH_2CH$_2$), 3.38 (s, 3H, OCH$_3$), 3.21–3.10 (m, 2H, NCH$_2$), 2.91–2.88 (m, 2H, PhCH_2CH$_2$), 2.72–2.67 (m ,2H), 2.48–2.32 (m, 4H, CH$_2$, PhCH$_2$CH_2), 2.11 (s, 3H, CH$_3$C=O), 1.88 (s, 3H, CH$_3$C=ON), 1.63–1.53 (m, 4H, 2 X CH$_2$), 1.40–1.27 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD$_3$COCD$_3$): δ 207.5 (CH$_3$*C*=OCH$_2$), 172.2, 170.3, 169.8, 165.3, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF$_3$*C*=O), 137.8, 137.7, 137.6, 137.5, 135.7, 134.0, 134.0, 133.4, 133.2, 133.1, 130.1, 129.4, 129.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.3, 127.1, 126.9, 126.1, 125.8, 125.6, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF$_3$), 99.9, 97.5, 94.8, 93.8, 77.8, 75.0, 74.1, 74.0, 72.9, 72.4, 71.6, 71.6, 70.7, 70.6, 70.1, 69.8, 69.5, 69.2, 67.8, 67.6, 67.0, 66.8, 66.2, 53.9, 52.5, 51.6, 51.3, 50.1, 37.0 (CH$_2$C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, *C*H$_2$CF$_2$), 28.8, 28.3, 27.4, 27.3, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, *C*H$_2$CH$_2$CF$_2$), 23.2, 21.8; HRMS (ESI-TOF) m/z [M – 2Na + H]$^-$ calcd for $C_{109}H_{112}F_{16}N_3O_{34}S_2$ 2374.6313; Found 2374.6289.

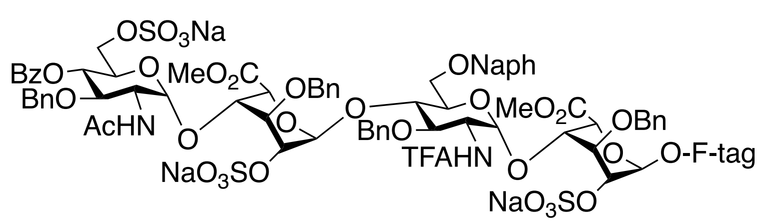


S36

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S36).**

Compound **S34** (63 mg, 0.028 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S36** (58 mg, 96%); R_f 0.22 (1:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.02–7.95 (m, 3H, Ar), 7.92–7.73 (m, 6H, Ar), 7.67–

7.05 (m, 33H, Ar), 5.42 (d, *J* = 2.3 Hz, 1H, H-1''), 5.32 (t, *J* = 9.6 Hz, 1H, H-4'''), 5.23 (d, *J* = 3.4 Hz, 1H, H-1'), 5.15–5.13 (m, 2H, NCO_2CH_2), 5.11 (d, *J* = 3.8 Hz, 1H, H-1'''), 4.98 (s, 1H, H-1), 4.93 (d, *J* = 3.3 Hz, 1H), 4.88–4.85 (m, 4H), 4.79–4.73 (m, 3H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.50 (s, 2H, NCH_2Ph), 4.39 (d, *J* = 11.2 Hz, 1H), 4.35–4.26 (m, 2H), 4.21 (t, *J* = 2.5 Hz, 1H), , 4.16–4.09 (m, 3H), 4.04–3.88 (m, 5H), 3.83–3.71 (m, 5H), 3.70 (s, 3H, OCH_3), 3.66–3.57 (m, 2H), 3.50–3.40 (m, 4H, OCH_3, OCH_2CH_2), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.60–2.47 (m, 2H, $PhCH_2CH_2$), 1.76 (s, 3H, $CH_3C{=}ON$), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.8, 169.3, 169.2, 165.1, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C{=}O$), 149.4, 138.9, 138.6, 138.6, 138.5, 138.5, 138.3, 136.3, 136.3, 134.2, 134.2, 133.5, 133.3, 133.0, 132.3, 130.5, 130.0, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.2, 127.1, 126.9, 126.2, 126.0, 125.9, 125.7, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 101.3 (C-1), 100.6 (C-1''), 96.9 (C-1'''), 95.7 (C-1'), 78.5, 78.0, 74.7, 74.6, 74.5, 73.5, 73.3, 73.2, 72.5, 72.4, 72.3, 72.1, 71.5, 71.3, 70.9, 68.5, 68.4, 68.0, 67.9, 67.1, 66.3, 60.9, 53.6, 52.3, 52.2, 51.6, 51.2, 46.9, 46.1, 32.1 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 27.5, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.3, 22.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{104}H_{108}F_{16}N_3O_{26}$ 2118.6966; Found 2118.6951.

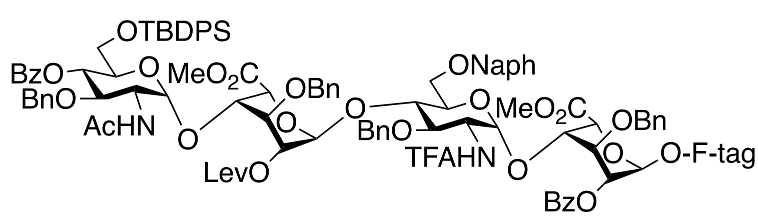


S37

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-**

trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate (S37).

Compound **S36** (60 mg, 0.028 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S37** (63 mg, 91%); R_f 0.30 (4:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.09 (d, *J* = 9.6 Hz, NH), 7.97–7.76 (m, 5H, Ar), 7.71–7.54 (m, 7H, Ar), 7.49–7.02 (m, 29H, Ar), 5.57 (s, 1H, H-1''), 5.22 (t, *J* = 9.5 Hz, 1H, H-4'''), 5.17 (d, *J* = 3.4 Hz), 5.13–5.08 (m, 3H, H-1, NCO_2CH_2), 4.96–4.93 (m, *3*H), 4.90–4.85 (m, 3H), 4.80–4.66 (m, 4H), 4.64–4.53 (m, 3H), 4.49–4.30 (m, 7H), 4.26–3.81 (m, 11H), 3.77–3.61 (m, 6H), 3.50–3.40 (m, 1H, OCH_2CH_2), 3.31 (s, 3H, OCH_3), 3.20–3.10 (m, 2H, NCH_2), 2.93–2.89 (m, 2H, $PhCH_2CH_2$), 2.48–2.39 (m, 2H, $PhCH_2CH_2$), 2.02 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 172.7, 170.3, 170.1, 165.4, 157.2 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.0, 137.9, 137.8, 137.5, 135.9, 134.0, 134.0, 133.5, 133.1, 133.0, 132.5, 132.3, 130.1, 129.6, 129.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 126.8, 126.7, 126.4, 125.9, 125.6, 125.4, 111.7 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.8, 98.5, 97.4, 94.4, 77.9, 77.8, 74.9, 74.8, 73.3, 72.6, 72.5, 72.0, 71.7, 71.6, 71.1, 70.7, 70.2, 69.9, 69.5, 69.1, 67.6, 66.8, 66.5, 66.2, 65.8, 53.9, 53.1, 51.7, 51.5, 50.5, 49.9, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.8, 27.5, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.2, 22.0; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{109}H_{113}F_{16}N_3O_{28}$ 2216.7334; Found 2216.7346.

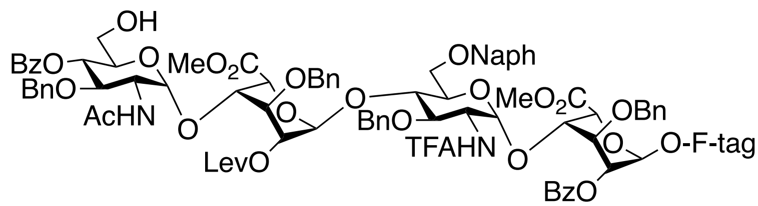


S38

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-**

L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoly-α-L-idopyranosyluronate (S38).

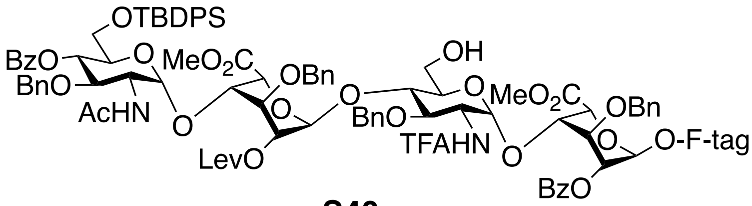
Compound **76** (0.34 g, 0.13 mmol) was treated according to the general procedure for N_3 to NHAc conversion to give tetrasaccharide **S38** (0.29 g, 84%); R_f 0.66 (1:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.33 (d, J = 9.4 Hz, 1H, NH), 8.03–7.96 (m, 6H, Ar), 7.92–7.83 (m, 2H, Ar), 7.76–7.62 (m, 6H, Ar), 7.58–7.42 (m, 7H, Ar), 7.39–6.98 (m, 34H, Ar), 5.69 (t, J = 9.7 Hz, 1H, H-4'''), 5.50 (d, J = 4.8 Hz, 1H, H-1''), 5.28–5.20 (m, 4H, H-1', H-1''', H-2'', H-1), 5.15–5.12 (m, 3H, H-2, NCO_2CH_2), 4.91–4.70 (m, 9H, H-5, H-5'', CH_2Ph, CH_2Nap), 5.61 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.51–4.38 (m, 6H), 4.29–4.14 (m, 6H), 4.10–4.04 (m, 2H), 3.96–3.88 (m, 2H), 3.85–3.64 (m, 7H), 3.50–3.40 (m, 4H, OCH_2CH_2, OCH_3), 3.19–3.08 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.74–2.69 (m, 2H), 2.60–2.36 (m, 4H, CH_2, $PhCH_2CH_2$), 2.07 (s, 3H, CH_3C=O), 1.80 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.02 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.0 (CH_3C=OCH_2), 171.7, 169.5, 169.3, 168.9, 165.0, 164.7, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.9, 138.8, 138.6, 138.5, 138.0, 138.0, 136.3, 135.6, 135.5, 133.5, 133.3, 133.1, 133.0, 130.1, 129.8, 129.7, 129.6, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.2, 127.1, 126.8, 126.3, 126.1, 126.0, 125.8, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0, 98.2, 97.7, 97.6, 77.9, 77.5, 76.5, 75.9, 75.5, 74.1, 73.9, 73.3, 73.3, 73.0, 72.7, 72.5, 72.2, 71.4, 70.9, 70.7, 70.2, 69.2, 68.3, 67.8, 66.3, 62.2, 59.7, 53.7, 52.3, 51.5, 51.4, 50.1, 49.8, 46.9, 46.0, 37.3 (CH_2C=O), 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.0, 28.9, 27.7 (CH_2C=O), 27.5, 26.2 (($CH_3)_3C$), 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.1, 22.2, 18.9 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{132}H_{136}F_{16}N_3O_{29}Si$ 2558.8773; Found 2558.8794.



S39

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S39).**

Compound **S38** (80 mg, 0.031 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S39** (70 mg, 96%); R_f 0.19 (1:2 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.40 (d, J = 8.6 Hz, 1H, NH), 8.03–7.84 (m, 9H, Ar), 7.75–7.73 (m, 3H, Ar), 7.69–7.63 (m, 1H, Ar), 7.60–7.07 (m, 33H, Ar), 5.56 (d, J = 5.0 Hz, 1H, H-1''), 5.33–5.27 (m, 3H), 5.22 (dd, J = 5.2, 4.4 Hz, 1H), 5.21 (dd, J = 5.2, 4.3 Hz, 1H, H-2), 5.19 (d, J = 3.3 Hz, 1H), 5.16–5.10 (m, 3H), 4.93–4.71 (m, 9H), 4.64 (d, J = 11.2 Hz, 1H), 4.54 (d, J = 11.2 Hz, 1H), 4.47 (s, 2H, NCH_2Ph), 4.44–4.37 (m, 3H), 4.34–4.07 (m, 8H), 3.97–3.91 (m, 2H), 3.84 (dd, J = 10.6, 8.8 Hz, 1H), 3.77–3.69 (m, 5H), 3.65–3.61 (m, 4H), 3.50–3.40 (m, 1H), 3.17–3.10 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.74–2.37 (m, 6H, CH_2), 2.07 (s, 3H, CH_3C=O), 1.80 (s, 3H, CH_3C=ONH), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.0, 171.6, 169.6, 169.4, 169.3, 165.2, 165.0, 156.9 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 149.0, 138.9, 138.7, 138.6, 138.5, 138.1, 138.0, 137.0, 136.4, 134.3, 134.2, 133.5, 133.4, 133.3, 133.1, 132.5, 132.4, 130.5, 129.9, 129.8, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.2, 127.1, 127.0, 126.3, 126.1, 126.0, 125.8, 124.2, 115.8 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0, 98.3, 97.9, 97.6, 77.8, 77.4, 76.6, 76.1, 76.0, 74.3, 73.8, 73.6, 73.3, 73.3, 72.8, 72.8, 72.2, 71.8, 71.3, 71.1, 70.8, 70.4, 69.3, 68.3, 67.8, 66.3, 61.1, 53.8, 52.4, 51.5, 50.1, 49.8, 46.9, 46.0, 37.3, 32.2 (t, $^{2}J_{C,F}$ = 22.3 Hz, CH_2CF_2), 29.1, 29.0, 27.7, 27.5, 25.7 (t, $^{3}J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.1, 22.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{116}H_{118}F_{16}N_3O_{29}$ 2320.7596; Found 2320.7573.

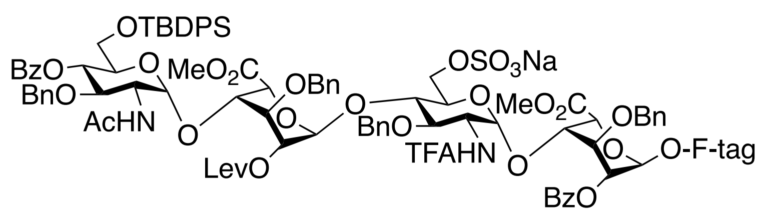


S40

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S40).**

Compound **S38** (0.18 g, 0.069 mmol) was treated according to the general procedure for Nap deprotection to give tetrasaccharide **S40** (0.15 g, 88%); R_f 0.31 (3:2 hexanes/acetone); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.44 (d, *J* = 8.9 Hz, 1H, NH), 8.05–8.00 (m, 4H, Ar), 7.75–7.63 (m, 5H, Ar), 7.57–7.52 (m, 5H, Ar), 7.39–7.09 (m, 35H, Ar), 5.70 (d, *J* = 5.9 Hz, 1H, H-1''), 5.59 (t, *J* = 9.9 Hz, 1H, H-4'''), 5.26–5.13 (m, 7H, NCO_2CH_2, H-1''', H-1', H-2'', H-1, H-2), 4.96–4.91 (m, 2H, CH_2Ph), 4.88 (d, *J* = 3.7 Hz, 1H, H-5), 4.82 (d, *J* = 4.5 Hz, 1H, H-5''), 4.81–4.69 (m, 4H, CH_2Ph), 4.57–4.43 (m, 5H), 4.42–4.26 (m, 5H), 4.24–4.02 (m, 6H), 3.93 (dd, *J* = 10.6, 9.4 Hz, 1H), 3.86 (dd, *J* = 10.6, 9.3 Hz, 1H), 3.82–3.73 (m, 6H), 3.69 (s, 3H, OCH_3), 3.52–3.43 (m, 1H, OCH_2CH_2), 3.20–3.09 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.87–2.82 (m, 2H, CH_2), 2.70–2.47 (m, 4H, CH_2, $PhCH_2CH_2$), 2.13 (s, 3H, CH_3C=O), 1.96 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.2 (CH_3C=OCH_2), 171.9, 169.5, 169.5, 169.3, 165.0, 164.8, 157.0 (q, $^{2}J_{C,F}$ = 37.0 Hz,

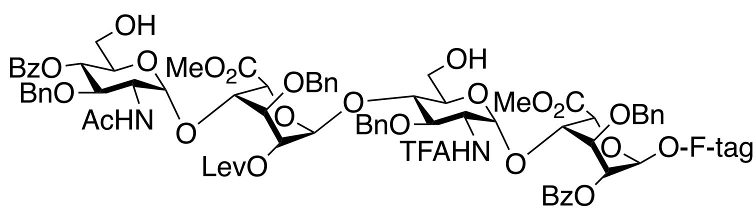
CF_3C=O), 139.1, 138.9, 138.6, 138.5, 138.1, 138.0, 135.6, 135.4, 133.3, 133.1, 133.0, 130.1, 129.8, 129.7, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.8, 116.1 (q, ${}^1J_{C,F}$ = 287 Hz, CF_3), 99.1 (C-1), 98.0 (C-1''), 97.9 (C-1'), 96.3 (C-1'''), 77.8, 76.9, 76.6, 76.2, 75.4, 74.2, 73.9, 73.6, 73.1, 72.7, 72.4, 72.0, 71.6, 71.4, 70.8, 70.5, 69.0, 68.3, 66.3, 62.6, 60.1, 59.7, 54.1, 53.9, 52.4, 51.6, 51.5, 50.1, 49.8, 46.9, 46.0, 37.5 (CH_2C=O), 32.2 (t, ${}^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.1, 28.8, 27.8, 27.4, 26.2 ($(CH_3)_3C$), 25.7 (t, ${}^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.1, 22.3, 18.9; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{121}H_{127}F_{16}N_3O_{29}SiNa$ 2440.7966; Found 2440.7954.



S41

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S41).**

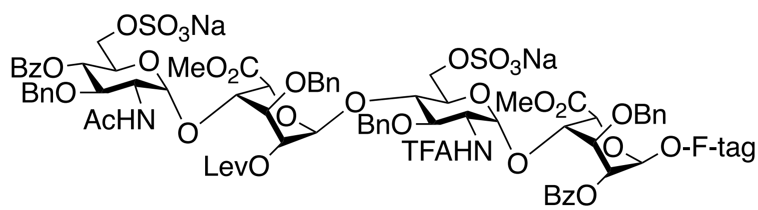
Compound **S40** (60 mg, 0.025 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S41** (59 mg, 94%); R_f 0.42 (8:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.00 (d, J = 9.6 Hz, 1H, NH), 7.97–7.87 (m, 6H, Ar), 7.66–7.40 (m, 10H, Ar), 7.35–7.00 (m, 33H, Ar), 5.50 (d, J = 3.5 Hz, 1H), 5.35 (t, J = 9.7 Hz, 1H), 5.20–5.06 (m, 7H), 4.94–4.90 (m, 1H), 4.83–4.80 (m, 2H), 4.74–4.59 (m, 5H), 4.52–4.07 (m, 13H), 4.00–3.64 (m, 10H), 3.55–3.38 (m, 4H), 3.15–3.04 (m, 2H, NCH_2), 2.92–2.88 (m, 2H), 2.84–2.37 (m, 6H), 2.13 (s, 3H, CH_3C=O), 2.04 (s, 3H, CH_3C=ON), 1.63–1.53 (m, 4H, 2 X CH_2), 1.40–1.27 (m, 2H, CH_2), 0.95 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3OD): δ 207.9, 172.4, 170.4, 169.8, 165.6, 165.2, 163.5, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.1, 138.0, 137.6, 137.5, 135.3, 135.3, 135.2, 135.2, 133.2, 133.0, 132.7, 129.6, 129.4, 129.4, 129.4, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.1, 126.9, 126.7, 126.5, 116.1 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0, 97.9, 96.2, 94.7, 77.5, 77.2, 75.0, 74.4, 74.3, 73.5, 73.0, 72.5, 72.4, 72.3, 71.4, 71.0, 70.9, 70.7, 69.7, 69.1, 68.9, 66.8, 64.9, 62.9, 53.1, 52.9, 52.0, 51.6, 50.1, 49.9, 46.1, 37.3, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.7, 28.2, 27.5, 27.3, 25.9, 25.7(t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 23.0, 21.9, 18.6; HRMS (ESI-TOF) m/z [M - Na]$^{-1}$ calcd for $C_{121}H_{126}F_{16}N_3O_{32}SSi$ 2496.7559; Found 2496.7532.



S42

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S42).**

Compound **S40** (60 mg, 0.025 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S42** (51 mg, 95%); R_f 0.10 (1:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.41 (d, *J* = 9.0 Hz, 1H, NH), 8.04–8.02 (m, 4H, Ar), 7.68–7.64 (m, 1H, Ar), 7.56–7.50 (m, 5H, Ar), 7.43–7.10 (m, 29H, Ar), 5.66 (d, *J* = 6.0 Hz, 1H, H-1''), 5.34 (t, *J* = 9.8 Hz, 1H, H-4'''), 5.26–5.12 (m, 7H, H-1''', H-1', H-1, H-2, H-2'', NCO_2CH_2), 4.95–4.87 (m, 4H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 11.0 Hz, 1H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.47–4.34 (m, 6H), 4.28–4.01 (m, 7H), 3.96 (dd, J = 10.7, 9.4 Hz, 1H), 3.88 (dd, J = 10.5, 9.0 Hz, 1H), 3.79 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.74–3.59 (m, 3H), 3.52–3.42 (m, 1H), 3.17–3.09 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.86–2.82 (m, 2H, CH_2), 2.70–2.47 (m, 4H), 2.12 (s, 3H, CH_3C=O), 1.93 (s, 3H, CH_3C=O), 1.56–1.43 (m, 4H, 2 X CH_2), 1.33–1.23 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.2, 171.8, 169.6, 169.4, 169.4, 165.1, 165.0, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 139.0, 138.9, 138.6, 138.5, 138.2, 138.0, 133.3, 133.3, 129.9, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4, 127.4, 127.3, 126.9, 116.0 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.1, 98.1, 97.9, 96.9, 77.7, 76.9, 76.7, 76.4, 76.2, 75.9, 74.1, 74.0, 73.6, 73.2, 72.8, 72.7, 72.1, 71.7, 71.6, 71.4, 71.1, 70.5, 69.1, 68.3, 66.3, 61.0, 60.9, 60.1, 60.0, 54.1, 53.8, 52.4, 51.6, 51.5, 50.1, 49.8, 46.8, 46.0, 37.5, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 27.8, 25.7 (t, $^3J_{C,F}$ = 4.1 Hz, $CH_2CH_2CF_2$), 23.1, 22.3; HRMS (ESI-TOF) m/z $[M + 2H]^{+2}$ calcd for $C_{105}H_{111}F_{16}N_3O_{29}$ 1090.8524; Found 1090.8552.

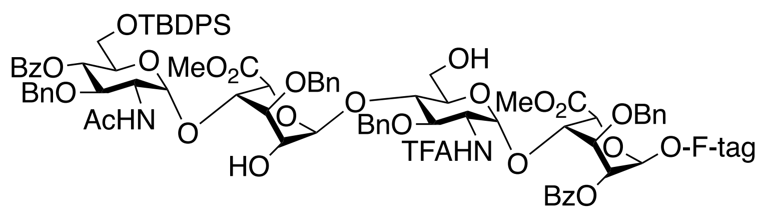


S43

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxyl-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S43).**

Compound **S42** (57 mg, 0.025 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S43** (57 mg, 92%); R_f 0.53 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.33 (d, J = 9.0 Hz, 1H, NH), 8.08–8.04 (m, 4H, Ar), 7.64–7.44

(m, 8H, Ar), 7.35–7.08 (m, 27H, Ar), 5.71 (d, J = 4.1 Hz, 1H, H-1''), 5.31–5.11 (m, 8H, H-1''', H-1', H-1, H-2, H-2'', H-4''', NCO_2CH_2), 4.94–4.73 (m, 8H, H-5', H-2, 3XCH_2Ph), 4.57 (d, J = 11.0 Hz, 1H), 4.48 (s, 2H, N-CH_2Ph), 4.43–4.24 (m, 9H), 4.20–4.16 (m, 2H), 4.11–4.01 (m, 3H), 3.87–3.75 (m, 8H), 3.53–3.46 (m, 1H), 3.19–3.12 (m, 2H, NCH_2), 2.97–2.94 (m, 2H, PhCH_2CH_2), 2.90–2.48 (m, 6H), 2.70–2.47 (m, 4H), 2.11 (s, 3H, CH_3C=O), 1.97 (s, 3H, CH_3C=O), 1.56–1.43 (m, 4H, 2 X CH_2), 1.33–1.23 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.7, 172.1, 170.5, 169.8, 165.5, 165.1, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.9, 138.9, 138.7, 138.6, 138.2, 138.0, 133.3, 133.3, 130.0, 129.8, 129.7, 129.6, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 127.3, 127.1, 127.0, 116.0 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.1, 97.7, 97.1, 97.0, 77.1, 76.4, 74.9, 74.3, 74.2, 74.0, 73.3, 72.5, 72.2, 71.6, 71.1, 70.2, 69.5, 68.7, 68.3, 66.3, 65.8, 64.4, 53.6, 52.9, 52.4, 51.9, 50.1, 49.8, 46.3, 37.5, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 29.0, 25.7 (t, $^3J_{C,F}$ = 4.1 Hz, $CH_2CH_2CF_2$), 23.1, 22.3. HRMS (ESI-TOF) m/z [M - Na]$^-$ calcd for $C_{105}H_{107}F_{16}N_3NaO_{35}S_2$ 2360.5769; Found 2360.5784.

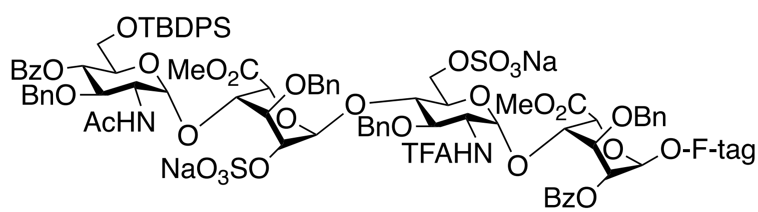


S44

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S44).**

Compound **S40** (80 mg, 0.033 mmol) was treated according to the general procedure for TBDPS deprotection to give tetrasaccharide **S44** (74 mg, 96%); R_f 0.26 (3:2

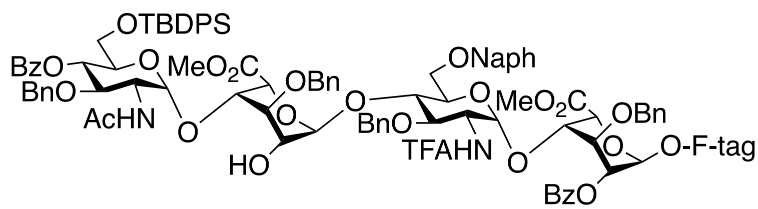
hexanes/acetone); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.34 (d, J = 9.4 Hz, 1H, NH), 8.05–8.01 (m, 4H), 7.77–7.75 (m, 2H), 7.70–7.63 (m, 3H), 7.59–7.46 (m, 7H), 7.43–7.09 (m, 33H), 5.64 (t, J = 9.7 Hz, 1H), 5.43 (d, J = 4.0 Hz, 1H), 5.24–5.10 (m, 6H), 4.93 (d, J = 11.5 Hz, 1H), 4.87–4.81 (m, 4H), 4.78 (d, J = 11.5 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.69 (d, J = 11.0 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.47 (s, 2H), 4.44–4.37 (m, 3H), 4.27–4.21 (m, 3H), 4.17–3.98 (m, 6H), 3.96–3.86 (m, 3H), 3.82–3.73 (m, 6H), 3.51–3.43 (m, 1H), 3.39 (s, 3H, OCH_3), 3.18–3.10 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.61–2.47 (m, 2H), 1.83 (s, 3H, $CH_3C{=}O$), 1.56–1.43 (m, 4H), 1.33–1.23 (m, 2H), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 135.7, 135.5, 133.3, 133.2, 129.6, 129.5, 128.8, 128.3, 128.0, 127.9, 127.6, 126.8, 101.2, 99.1, 97.9, 96.9, 78.2, 77.5, 76.7, 75.9, 75.6, 74.3, 73.6, 73.6, 73.4, 72.7, 72.5, 72.1, 71.1, 70.3, 70.2, 70.0, 69.5, 69.1, 68.4, 66.3, 53.7, 52.4, 51.7, 51.1, 50.0, 46.4, 32.1, 29.2, 27.5, 26.3, 25.8, 23.2, 22.1; HRMS (ESI-TOF) m/z $[M + H]^{+1}$ calcd for $C_{116}H_{122}F_{16}N_3O_{27}Si$ 2320.7778; Found 2320.7788.



S45

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-benzoyl-α-L-idopyranosyluronate (S45).**

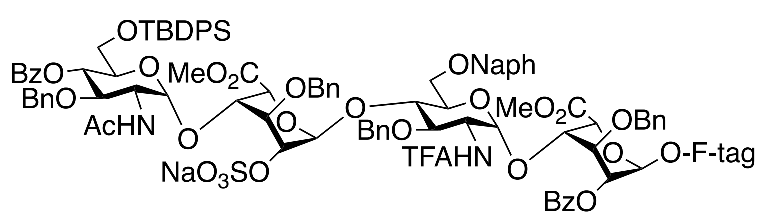
Compound **S44** (74 mg, 0.032 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S45** (74 mg, 92%); R_f 0.26 (8:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.30 (d, J = 9.0 Hz, 1H, NH), 8.06–8.01 (m, 8H), 7.74–7.52 (m, 10H), 7.46–7.07 (m, 31H), 5.60–5.55 (m, 2H), 5.24–5.23 (m, 3H), 5.14–5.12 (m, 2H), 5.02 (d, J = 3.3 Hz, 1H), 4.99 (d, J = 12.0 Hz, 1H), 4.94 (d, J = 2.5 Hz, 1H), 4.90 (d, J = 2.8 Hz, 1H), 4.88–4.72 (m, 6H), 4.56 (d, J = 11.0 Hz, 1H), 4.48 (s, 2H), 4.46–4.39 (m, 5H), 4.27–4.13 (m, 6H), 4.07 (dd, J = 10.5, 9.3 Hz, 1H), 4.02 (dt, J = 10.2, 2.1 Hz, 1H), 3.85–3.69 (m, 7H), 3.51–3.43 (m, 1H), 3.32 (s, 3H, OCH_3), 3.18–3.10 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhC\mathit{H_2}CH_2$), 2.61–2.47 (m, 2H), 2.14 (s, 3H, $CH_3C{=}O$), 1.56–1.43 (m, 4H), 1.33–1.23 (m, 2H), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 135.7, 135.5, 133.4, 133.2, 129.7, 129.6, 128.8, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 99.0, 98.8, 98.2, 97.5, 77.7, 77.5, 76.3, 74.3, 74.2, 74.0, 73.7, 73.5, 72.5, 72.5, 72.0, 71.0, 70.9, 70.6, 69.1, 68.7, 68.4, 66.3, 64.9, 62.3, 53.5, 52.1, 51.4, 49.9, 46.6, 32.2, 31.1, 29.0, 27.5, 26.3, 25.7, 23.2; HRMS (ESI-TOF) m/z $[M - 2Na + H]^{-1}$ calcd for $C_{116}H_{120}F_{16}N_3O_{33}S_2Si$ 2478.6760; Found 2478.6760.



S46

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoly-α-L-idopyranosyluronate (S46).**

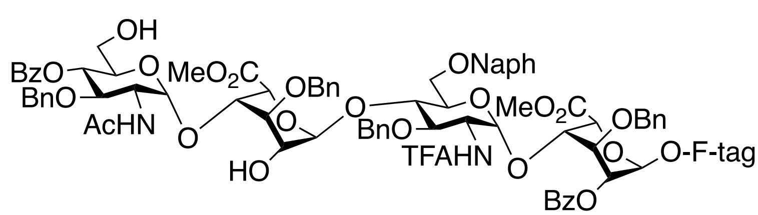
Compound **S38** (0.10 g, 0.039 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S46** (90 mg, 94%); R_f 0.44 (3:2 hexanes/acetone); ^1H NMR (400 MHz, CD_3COCD_3): δ 8.25 (d, J = 9.4 Hz, 1H, NH), 8.06–7.85 (m, 7H, Ar), 7.68–7.76 (m, 2H, Ar), 7.70–7.05 (m, 47H, Ar), 5.67 (t, J = 9.6 Hz, 1H, H-4'''), 5.46 (d, J = 3.6 Hz, 1H, H-1''), 5.28 (d, J = 3.5 Hz, 1H), 5.24 (t, J = 4.2 Hz, 1H), 5.20–5.12 (m, 4H), 4.94 (d, J = 11.5 Hz, 1H), 4.90–4.80 (m, 6H), 4.79 (d, J = 11.5 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.0 Hz, 1H), 4.52 (d, J = 11.0 Hz, 1H), 4.47–4.39 (m, 5H), 4.35–4.07 (m, 7H), 3.99–3.86 (m, 5H), 3.82–3.72 (m, 3H), 3.72 (s, 3H, OCH_3), 3.51–3.43 (m, 1H), 3.37 (s, 3H, OCH_3), 3.18–3.10 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, $PhCH_2CH_2$), 2.61–2.47 (m, 2H), 1.77 (s, 3H, CH_3C=O), 1.56–1.43 (m, 4H, 2 X CH_2), 1.33–1.23 (m, 2H, CH_2), 1.03 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.3, 169.3, 165.0, 164.7, 157.0 (q, $^{2}J_{C,F}$ = 37.0 Hz, CF_3C=O), 138.9, 138.8, 138.6, 138.4, 138.0, 136.4, 135.7, 135.5, 133.5, 133.4, 133.2, 133.1, 133.1, 133.0, 130.2, 129.8, 129.7, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.2, 127.1, 126.8, 126.7, 126.2, 126.0, 125.9, 125.7, 116.0 (q, $^{1}J_{C,F}$ = 287 Hz, CF_3), 101.3, 99.1, 97.8, 97.3, 78.2, 77.8, 76.3, 76.1, 75.9, 74.3, 73.7, 73.3, 73.2, 72.9, 72.6, 72.4, 71.1, 70.3, 70.2, 69.8, 69.5, 68.9, 68.3, 68.2, 66.3, 62.2, 54.1, 53.7, 53.6, 52.3, 51.5, 51.2, 50.0, 49.8, 46.0, 32.2 (t, $^{2}J_{C,F}$ = 21.6 Hz, CH_2CF_2), 26.2, 25.7 (t, $^{3}J_{C,F}$ = 4.1 Hz, $CH_2CH_2CF_2$), 23.1, 22.1; HRMS (ESI-TOF) m/z $[M + Na]^{+1}$ calcd for $C_{127}H_{129}F_{16}N_3NaO_{27}Si$ 2482.8225; Found 2482.8225.



S47

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoly-α-L-idopyranosyluronate (S47).**

Compound **S46** (74 mg, 0.028 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S47** (70 mg, 93%); R_f 0.44 (8:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ 9.11 (d, J = 9.2 Hz, 1H, NH), 7.97–7.86 (m, 5H), 7.84–7.72 (m, 4H), 7.65–7.57 (m, 4H), 7.54–6.95 (m, 43H), 5.55 (s, 1H, H-1'''), 5.47 (t, J = 9.7 Hz, 1H, H-4'''), 5.18 (d, J = 3.5 Hz, 1H), 5.14–5.08 (m, 4H), 4.99 (d, J = 1.6 Hz, 1H), 4.95–4.84 (m, 4H), 4.79 (d, J = 12.0 Hz, 1H), 4.70–4.52 (m, 6H), 4.46 (d, J = 11.1 Hz, 1H), 4.41–4.35 (m, 4H), 4.29–4.23 (m, 3H), 4.18–4.06 (m, 3H), 4.01 (s, 1H), 3.92–3.61 (m, 11H), 3.49–3.40 (m, 1H), 3.14–3.04 (m, 2H, NCH_2), 2.96 (s, 3H), 2.91–2.87 (m, 2H, $PhCH_2CH_2$), 2.48–2.35 (m, 2H), 2.03 (s, 3H, CH_3C=O), 1.56–1.43 (m, 4H), 1.33–1.23 (m, 2H), 0.96 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3OD): 170.3, 169.8, 165.7, 165.2, 163.5, 157.8 (q, $^2J_{C,F}$ = 36.8 Hz, CF_3C=O), 138.1, 137.8, 137.5, 137.3, 135.8, 135.5, 135.3, 133.5, 133.2, 133.1, 133.0, 132.9, 132.8, 129.8, 129.4, 129.3, 129.3, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 127.4, 127.3, 127.2, 127.0, 126.6, 126.4, 126.0, 125.9, 125.6, 125.4, 115.8 (q, $^1J_{C,F}$ = 288.0 Hz, CF_3), 98.8, 97.3, 95.3, 78.0, 77.9, 74.6, 73.9, 73.5, 72.8, 72.6, 72.2, 72.1, 72.1, 71.7, 71.4, 71.2, 70.6, 70.1, 69.3, 68.5, 67.8, 66.6, 62.2, 53.5, 53.3, 51.9, 51.0, 50.1, 49.9, 32.2 (t, $^2J_{C,F}$ = 21.6 Hz, CH_2CF_2), 28.6, 25.9, 25.7 (t, $^3J_{C,F}$ = 5.0 Hz, $CH_2CH_2CF_2$), 22.9, 21.9, 18.6; HRMS (ESI-TOF) m/z [M - Na]$^{-1}$ calcd for $C_{127}H_{128}F_{16}N_3O_{30}SSi$ 2538.7817; Found 2538.7839.

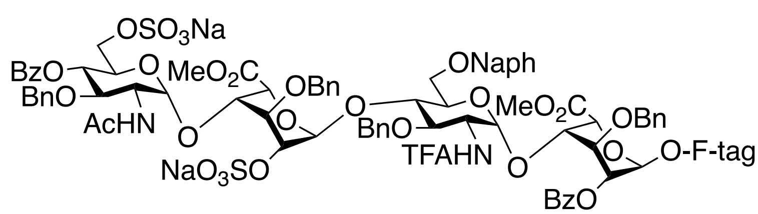


S48

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-**

***O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoly-α-L-idopyranosyluronate (S48).**

Compound **S46** (80 mg, 0.039 mmol) was treated according to the general procedure for Lev deprotection to give tetrasaccharide **S48** (68 mg, 94%); R_f 0.20 (3:2 hexanes/acetone); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.31 (d, J = 9.2 Hz, 1H, NH), 8.06–7.85 (m, 7H, Ar), 7.79–7.74 (m, 3H, Ar), 7.67–7.05 (m, 36H, Ar), 5.50 (d, J = 3.9 Hz, 1H, H-1''), 5.32 (t, J = 9.8 Hz, 1H, H-4'''), 5.28 (d, J = 3.5 Hz, 1H), 5.24 (t, J = 4.0 Hz, 1H), 5.19 (d, J = 3.5 Hz, 1H), 5.14–5.11 (m, 3H), 4.95–4.78 (m, 8H), 4.72 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 11.2 Hz, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.47 (s, 2H), 4.43–4.15 (m, 8H), 4.06 (t, J = 5.0 Hz, 1H), 3.98–3.88 (m, 4H), 3.79–3.72 (m, 4H), 3.66–3.62 (m, 2H), 3.52 (s, 3H, OCH_3), 3.51–3.43 (m, 1H), 3.18–3.10 (m, 2H, NCH_2), 2.98–2.93 (m, 2H, $PhCH_2CH_2$), 2.61–2.47 (m, 2H), 1.75 (s, 3H, $CH_3C{=}O$), 1.56–1.43 (m, 4H), 1.33–1.23 (m, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 134.4, 133.4, 130.4, 129.7, 128.8, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.1, 126.2, 126.0, 125.9, 101.4, 99.1, 97.8, 97.4, 77.9, 76.4, 76.3, 76.3, 74.6, 73.7, 73.4, 73.1, 72.6, 71.5, 71.0, 70.3, 70.2, 69.7, 68.9, 68.3, 68.2, 66.3, 61.1 ,53.7, 52.2, 51.5, 51.3, 50.0, 46.2, 32.2, 29.1, 27.6, 25.7, 23.1, 22.1; HRMS (ESI-TOF) m/z $[M + H]^{+1}$ calcd for $C_{111}H_{112}F_{16}N_3O_{27}$ 2222.7227; Found 2222.7212.

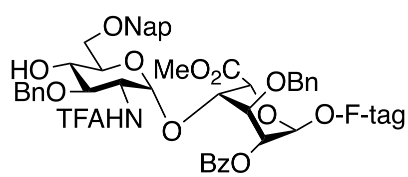


S49

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-**

trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoly-α-L-idopyranosyluronate (S49).

Compound **S48** (60 mg, 0.026 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S49** (59 mg, 91%); R_f 0.32 (6:1 DCM/MeOH); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.53 (d, J = 8.5 Hz, 1H, NH), 8.00–7.96 (m, 5H), 7.86–7.73 (m, 4H), 7.66–7.64 (m, 1H), 7.67–7.05 (m, 36H, Ar), 5.62 (s, 1H), 5.30 (d, J = 3.6 Hz, 1H), 5.27–5.21 (m, 3H), 5.12 (s, 2H), 4.99 (d, J = 12.4 Hz, 1H), 4.95–4.85 (m, 5H), 4.84–4.67 (m, 6H), 4.54 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 11.0 Hz, 1H), 4.45 (s, 2H), 4.42–4.33 (m, 2H), 4.30–4.26 (m, 2H), 4.24–4.13 (m, 4H), 4.10 (s, 1H), 4.07–3.91 (m, 5H), 3.89–3.71 (m, 5H), 3.48–3.43 (m, 1H), 3.41 (s, 3H, OCH_3), 3.14–3.05 (m, 2H, NCH_2), 2.98–2.93 (m, 2H, PhC$H_2$$CH_2$), 2.61–2.47 (m, 2H), 2.00 (s, 3H, CH_3C=O), 1.56–1.43 (m, 4H), 1.33–1.23 (m, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 134.3, 133.3, 130.4, 129.7, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 126.7, 126.5, 126.3, 125.7, 99.0, 98.9, 98.8, 97.0, 77.8, 77.4, 76.6, 74.5, 74.3, 73.8, 73.1, 73.0, 72.8, 72.7, 72.6, 71.9, 71.6, 70.3, 70.1, 69.4, 68.5, 68.3, 67.1, 66.3, 65.2, 53.7, 53.3, 51.7, 51.6, 49.9, 46.3, 32.3, 28.8, 27.4, 25.7, 23.0, 22.4; HRMS (ESI-TOF) m/z [M - 2Na + H]$^{-1}$ calcd for $C_{111}H_{110}F_{16}N_3O_{33}S_2$ 2380.6208; Found 2380.6416.

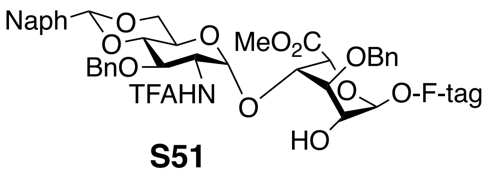


S50

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate (S50).**

To a suspension of compound **70** (1.4 g, 0.93 mmol) in DCM (40 mL) were added triethylsilane (2.5 mL, 15 mmol) and trifluoroacetic anhydride (0.25 g, 1.2 mmol) at 0 °C.

After 10 min, trifluoroacetic acid (0.48 g, 4.2 mmol) was added and the reaction was stirred at RT for 1 h. The reaction was quenched with saturated aq. $NaHCO_3$, and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (elution with 3:1 $\rightarrow$ 2:1 hexanes/EtOAc) afforded compound **S50** (1.2 g, 82%) as a colorless foam. R_f 0.52 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.45 (d, J = 9 Hz, 1H, NH), 8.12–8.10 (m, 2H, Ar), 7.95–7.90 (m, 4H, Ar), 7.68–7.63 (m, 1H, Ar), 7.60–7.50 (m, 5H, Ar), 7.40–7.19 (m, 19H, Ar), 5.31 (d, J = 3.6 Hz, 1H, H-1'), 5.28 (dd, J = 4.9, 4.2 Hz, 1H, H-2), 5.24 (d, J = 3.4 Hz, 1H, H-1), 5.17 (s, 2H, NCO_2CH_2), 5.04 (d, J = 4.2 Hz, 1H, OH), 4.97 (d, J = 3.8 Hz, 1H, H-5), 4.92 (d, J = 11.3 Hz, 1H, 3'-OCH_2Ph), 4.86 (d, J = 12.5 Hz, 1H, NapCH_2), 4.83 (d, J = 12.5 Hz, 1H, 3-OCH_2Ph), 4.82 (d, J = 12.5 Hz, 1H, NapCH_2), 4.78 (d, J = 12.5 Hz, 1H, 3-OCH_2Ph), 4.59 (d, J = 11.3 Hz, 1H, 3'-OCH_2Ph), 4.50 (s, 2H, NCH_2Ph), 4.47 (dd, J = 5.3, 4.1 Hz, 1H, H-4), 4.34 (t, J = 5.3 Hz, 1H, H-3), 4.01–3.89 (m, 4H, H-3', H-4', H-6'), 3.82 (s, 3H, OCH_3), 3.82–3.73 (m, 1H, OCH_2CH_2), 3.54–3.46 (m, 1H, OCH_2CH$_2$), 3.19–3.15 (m, 2H, NCH_2), 3.01–2.97 (m, 2H, PhCH_2CH$_2$), 2.56–2.51 (m, 2H, PhCH$_2$CH_2), 1.58–1.46 (m, 4H, 2 X CH_2), 1.35–1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.4 (C=OOCH$_3$), 165.0 (C=OPh), 157.0 (q, $^2J_{C,F}$ = 36.9 Hz, CF$_3$$C$=O), 156.2 ($NCO_2$), 139.2 (Ar), 138.9 (Ar), 138.6 (Ar), 138.0 (Ar), 136.6 (Ar), 133.5 (Ar), 133.0 (Ar), 129.9 (Ar), 129.7 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar),128.1 (Ar), 127.94 (Ar), 127.91 (Ar), 127.86 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.13 (Ar), 127.09 (Ar), 126.0 (Ar), 125.9 (Ar), 125.7 (Ar), 116.0 (q, $^1J_{C,F}$ = 286.0 Hz, CF_3), 99.0 (C-1), 97.8 (C-1'), 79.2 (C-3'), 76.4 (C-3), 74.2 (3'-OCH$_2$Ph), 74.0 (C-4), 73.2 (Nap$C$H$_2$), 72.8 (C-5'), 72.7 (3-OCH$_2$Ph), 71.3 (C-4'), 70.6 (C-2), 69.3 (C-5, C-6'), 68.3 (OCH$_2$CH$_2$), 66.3 (NCO$_2$$CH_2$Ph), 53.6 (C-2'), 51.5 ($OCH_3$), 50.0, 49.8 (N$CH_2$Ph), 46.8, 46.0 (N$CH_2CH_2$), 32.1 (t, $^2J_{C,F}$ = 21.7 Hz, CH$_2$CF$_2$), 29.0 (CH_2), 27.7 (CH_2), 25.7 (t, $^3J_{C,F}$ = 4.2 Hz, CH$_2$CH$_2$CF$_2$), 23.1 (CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{75}H_{73}F_{16}N_2O_{15}$ 1545.4756; Found 1545.4767.

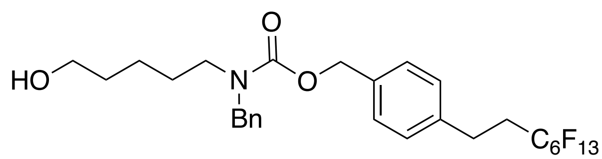


S51

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate (S51)**.

To a solution of disaccharide **70** (0.20 g, 0.13 mmol) in anhydrous DCM (10 mL) was added the solution of NaOMe in MeOH (0.05 M, 5.0 mL) at RT. After stirring for 6 h, the reaction was quenched with saturated aq. NH_4Cl. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel column chromatography (elution with 4:1 → 2:1 hexanes/EtOAc) afforded compound **S51** (0.17 g, 91%) as a colorless foam. R_f 0.59 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.58 (d, J = 9.0 Hz, 1H, NH), 8.04 (s, 1H), 7.97–7.92 (m, 3H, Ar), 7.67–7.64 (m, 1H, Ar), 7.56–7.53 (m, 2H, Ar), 7.40–7.22 (m, 19H, Ar), 5.90 (s, 1H, NapC*H*), 5.28 (d, J = 3.7 Hz, 1H, H-1'), 5.14–5.12 (m, 2H, NCO_2CH_2), 4.93 (s, 1H, H-1), 4.91 (d, J = 11.7 Hz, 1H, CH_2Ph), 4.87 (d, J = 1.2 Hz, 1H, H-5), 4.78 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.75 (br, 1H, OH), 4.68 (d, J = 11.7 Hz, 1H, CH_2Ph), 4.65 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.51 (s, 2H, NCH_2Ph), 4.36–4.30 (m, 2H, H-2', H-6'), 4.23 (t, 1H, J = 2.0 Hz, H-4), 3.99 (t, 1H, J = 2.5 Hz, H-4), 4.19 (t, J = 5.8 Hz, 1H, H-3), 3.97–3.89 (m, 4H, H-2', H-3', H-4', H-6'), 3.84 (s, 3H, OCH_3), 3.84–3.79 (m, 1H, H-5'), 3.72 (br, 1H, OC$H_2$$CH_2$), 3.44 (br, 1H, OC$H_2$$CH_2$), 3.26–3.19 (m, 2H, NCH_2), 2.98–2.94 (m, 2H, PhC$H_2$$CH_2$), 2.62–2.48 (m, 2H, $PhCH_2$CH_2), 1.56–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 169.7 (*C*=$OOCH_3$), 157.1 (q, $^2J_{C,F}$ = 36.8 Hz, CF_3*C*=O), 155.7 (NCO_2), 139.0 (Ar), 138.9 (Ar), 138.6 (Ar), 138.5 (Ar), 135.5 (Ar), 133.7 (Ar), 133.0 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.50 (Ar), 127.48 (Ar), 127.21 (Ar), 127.16 (Ar), 126.4 (Ar), 126.2 (Ar), 125.5 (Ar), 124.0 (Ar), 116.1 (q, $^1J_{C,F}$ = 287.3 Hz, CF_3), 101.3 (NapCH), 101.2 (C-1), 96.3 (C-1'), 82.3 (C-4'), 76.8 (C-3'), 74.1

(CH_2Ph), 73.7 (C-3), 72.8 (C-4), 71.5 (OCH_2Ph), 68.3 (C-6'), 67.9 (OCH_2CH_2), 67.1 (C-5), 66.3 (NCO_2CH_2Ph), 66.2 (C-2), 63.6 (C-5'), 53.3 (C-2'), 51.6 (OCH_3), 50.0 and 49.8 (NCH_2Ph), 46.9 and 46.1 (NCH_2CH_2), 32.1 (t, $^2J_{C,F}$ = 21.2 Hz, CH_2CF_2), 29.0 (CH_2), 27.8 (CH_2), 25.7 (t, $^3J_{C,F}$ = 4.2 Hz, $CH_2CH_2CF_2$), 23.3 (CH_2); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{68}H_{66}F_{16}N_2O_{14}Na$ 1461.4175; Found 1461.4175.

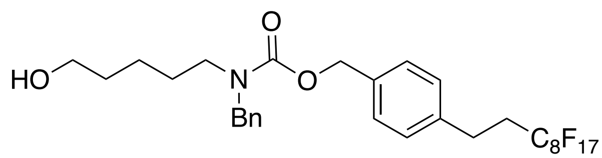


S56

(4-(8,8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-3,5,7-triyn-1-yl)phenyl)methyl benzyl(5-hydroxypentyl)carbamate (S56)

A solution of **S52** (5.2 g, 11 mmol) in acetonitrile (200 mL) was treated at RT with triethylamine (3.3 g, 33 mmol) and cooled to 0 °C. At 0 °C, *N,N*'-disuccinimidyl carbonate (DSC) (5.9 g, 22 mmol) was added. The reaction mixture was stirred at RT for 2 h and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **S54** (5.8 g, 85%). A solution of compound **S54** (5.8 g, 9.7 mmol) in CH_2Cl_2 (100 mL) was added and triethylamine (3.3 g, 33 mmol) and 5-benzylamino-1-pentanol (2.9 g, 15 mmol) at 0 ^oC. The solution was stirred for 1 h at RT, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (elution with 2:1 → 1:1 hexanes/EtOAc) to afford compound **S56** (6.4 g, 96%). R_f 0.35 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3CN): δ 7.36–7.24 (m, 9H, Ar), 5.12 (s, 2H, OCH_2Ph), 4.49 (s, 2H, NCH_2Ph), 3.44 (br, 2H, CH_2OH), 3.24 (br, 2H, NCH_2CH_2), 2.96–2.92 (m, 2H, $CH_2CH_2C_6F_{13}$), 2.57–2.45 (m, 3H, OH, $CH_2CH_2C_6F_{13}$), 1.56–1.42 (m, 4H, 2 X CH_2), 1.31–1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3CN): δ 138.8 (Ar), 138.3 (Ar), 135.4 (Ar), 128.2 (Ar), 128.1 (Ar), 127.7 (Ar), 126.8 (Ar), 66.0 (OCH_2Ph), 61.0 (CH_2OH), 49.8 (C=ONCH_2Ph atropisomer 1), 49.5 (C=ONCH_2Ph atropisomer 2), 46.8 (C=ONCH_2CH_2 atropisomer 1), 46.1, (C=ONCH_2CH_2

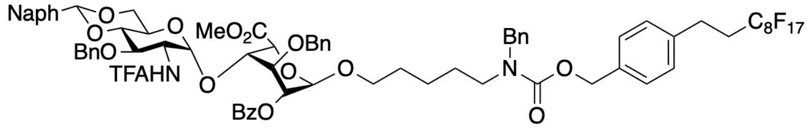
atropisomer 2), 31.9 (CH_2), 31.7 (t, ${}^2J_{C,F}$ = 21.4 Hz, $CH_2\mathit{C}H_2CF_2$), 27.5 ($NCH_2\mathit{C}H_2$, atropisomer 1), 27.0 ($NCH_2\mathit{C}H_2$, atropisomer 2), 25.3 (t, ${}^3J_{C,F}$ = 4.5 Hz, $\mathit{C}H_2CH_2CF_2$), 22.5 (CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{28}F_{13}NO_3$ 674.1940; Found 674.1944.



S57

(4-(8,8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-3,5,7-triyn-1-yl)phenyl) methyl benzyl(5-hydroxypentyl)carbamate (S57)

Compound **S53** (0.61 g, 1.1 mmol) was treated according to the procedure of C_6F_{13} linker preparation to give tetrasaccharide **S57**[5] (0.69 g, 81%); R_f 0.34 (4:3 hexanes/EtOAc); ^{1}H NMR (400 MHz, CD_3CN): δ 7.35–7.25 (m, 9H, Ar), 5.12 (br, 2H, OCH_2Ph), 4.49 (s, 2H, NCH_2Ph), 3.45 (br, 2H, $C\mathit{H_2}OH$), 3.24 (br, 2H, $NC\mathit{H_2}CH_2$), 2.96–2.92 (m, 2H, $C\mathit{H_2}CH_2C_6F_{13}$), 2.57–2.45 (m, 3H, OH, $CH_2C\mathit{H_2}C_6F_{13}$), 1.56–1.42 (m, 4H, 2 X CH_2), 1.31–1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_3CN): δ 138.9 (Ar), 138.4 (Ar), 129.3 (Ar), 129.2 (Ar), 128.8 (Ar), 127.9 (Ar), 67.1 ($O\mathit{C}H_2Ph$), 62.2 ($\mathit{C}H_2OH$), 50.9 ($C{=}ON\mathit{C}H_2Ph$ atropisomer 1), 50.6 ($C{=}ON\mathit{C}H_2Ph$ atropisomer 2), 47.9 ($C{=}ON\mathit{C}H_2CH_2$ atropisomer 1), 47.3, ($C{=}ON\mathit{C}H_2CH_2$ atropisomer 2), 33.0 (CH_2), 32.8 (t, ${}^2J_{C,F}$ = 21.4 Hz, $CH_2\mathit{C}H_2CF_2$), 28.7 ($NCH_2\mathit{C}H_2$, atropisomer 1), 28.2 ($NCH_2\mathit{C}H_2$, atropisomer 2), 26.4 (t, ${}^3J_{C,F}$ = 4.5 Hz, $\mathit{C}H_2CH_2CF_2$), 22.6 (CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{30}H_{29}F_{17}NO_3$ 774.1876; Found 774.1860.



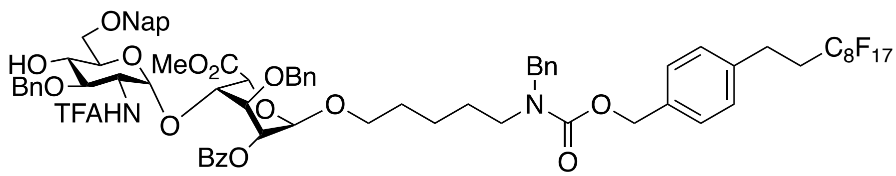
S58

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-4,6-*O*-2-naphthylidene-2-**

trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate (S58).

A mixture of donor **69** (0.40 g, 0.41 mmol), the F-tag linker **S57** (0.79 g, 1.0 mmol), and powdered 4 Å molecular sieves was suspended in anhydrous DCM (30 mL) and stirred at RT. After 30 min, NIS (0.18 g, 0.82 mmol) was added, and the mixture was cooled to –50 °C for 10 min. TfOH (70 μL, 0.79 mmol) was then added via syringe and the solution was slowly warmed up to –20 °C. Et_3N (100 μL) was added to quench the reaction, and the mixture was filtered. The filtrate was concentrated, and the resulting residue was purified by silica gel column chromatography (elution with 5:1 → 4:1 hexanes/EtOAc) to afford compound **S58** (0.46 g, 69%) as a colorless foam. R_f 0.73 (4:3 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–7.89 (m, 6H, Ar), 7.64–7.62 (m, 1H, Ar), 7.55–7.53 (m, 2H, Ar), 7.38–6.98 (m, 22H, Ar), 6.19 (d, *J* = 7.8 Hz, 1H, NH), 5.73 (s, 1H, NapC*H*), 5.20–5.01 (m, 5H, NCO_2CH_2, H-2, H-1', H-1), 4.87–4.82 (m, 2H, H-5, CH_2Ph), 4.64–4.61 (m, 2H, CH_2Ph), 4.50–4.46 (m, 3H, H-6', NCH_2Ph), 4.15–4.03 (m, 4H, CH_2Ph, H-5', H-4, H-2'), 3.93 (t, *J* = 3.2 Hz, 1H, H-3), 3.78 (s, 3H, OCH_3), 3.78–3.74 (m, 3H, OC$H_2$$CH_2$, H-4', H-6'), 3.52 (t, *J* = 9.5 Hz, 1H, H-3'), 3.50–3.44 (m, 1H, OC$H_2$$CH_2$), 3.24–3.13 (m, 2H, NCH_2), 2.93–2.90 (m, 2H, PhC$H_2$$CH_2$), 2.42–2.31 (m, 2H, Ph$CH_2CH_2$), 1.66–1.51 (m, 4H, 2 X CH_2), 1.34–1.25 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3 (*C*=$OOCH_3$), 165.4 (*C*=OPh), 157.0 (q, $^2J_{C,F}$ = 37.3 Hz, CF_3*C*=O), 138.4 (Ar), 137.7 (Ar), 137.1 (Ar), 134.8 (Ar), 133.7 (Ar), 132.9 (Ar), 129.7 (Ar), 129.3 (Ar), 128.5 (Ar), 128.43 (Ar), 128.38 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.3 (Ar), 126.5 (Ar), 126.3 (Ar), 125.7 (Ar), 123.7 (Ar), 115.4 (q, $^1J_{C,F}$ = 285.3 Hz, CF_3), 101.6 (Nap*C*H), 99.2 (C-1), 98.7 (C-1'), 82.3 (C-4'), 76.0 (C-3'), 75.8 (C-4), 74.3 (O*C*H_2Ph), 74.1 (C-3), 72.5 (O*C*H_2Ph), 68.7 (O*C*$H_2$$CH_2$), 68.5 (C-6'), 68.4 (C-2), 67.4 (C-5), 66.8 (NCO_2*C*H_2Ph), 63.7 (C-5'), 53.5 (C-2'), 52.2 (OCH_3), 50.5, 50.3 (N*C*H_2Ph), 47.2, 46.1 (N*C*$H_2$$CH_2$), 32.9 (t, $^2J_{C,F}$ = 22.4 Hz, *C*$H_2$$C_6F_{13}$), 29.1 ($CH_2$), 27.5 ($CH_2$), 26.2 (t, $^3J_{C,F}$ = 4.3 Hz, *C*$H_2$$CH_2CF_2$), 23.4

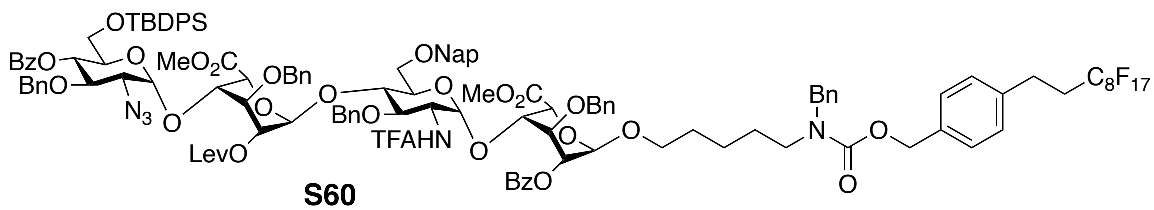
(CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{77}H_{71}F_{20}N_2O_{15}$ 1643.4535; Found 1643.4523.



S59

***N*-(Benzyl)- 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-((9*H*-fluoren-9-yl)methoxycarbonyl))-α-L-idopyranosyluronate (S59).**

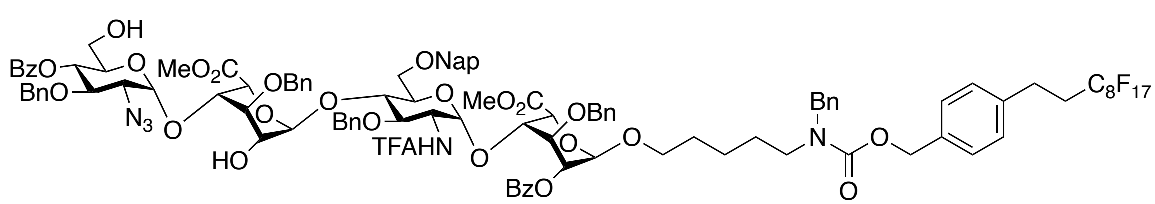
To a suspension of compound **S58** (0.46 g, 0.27 mmol) in DCM (15 mL) were added triethylsilane (1.2 mL, 8.0 mmol) and trifluoroacetic anhydride (0.13 g, 0.60 mmol) at 0 °C. After 10 min, trifluoroacetic acid (0.24 g, 2.1 mmol) was added dropwise. The reaction was stirred at RT for 1 h and then quenched with saturated aq. $NaHCO_3$. The resulting mixture was filtered, diluted with DCM (20 mL), and the organic layer was washed with brine, dried over Na_2SO_4, concentrated and purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **S59** (0.37 g, 81%) as a colorless foam. R_f 0.47 (4:3 hexanes/EtOAc); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 2H, Ar), 7.86–7.80 (m, 4H, Ar), 7.54–7.41 (m, 6H, Ar), 7.34–7.09 (m, 19H, Ar), 6.34 (br, 1H, NH), 5.19 (t, *J* = 2.7 Hz, 1H, H-2), 5.17–5.14 (m, 2H, NCO_2CH_2), 5.10 (s, 1H, H-1), 5.05 (d, *J* = 2.1 Hz, 1H, H-1'), 4.85 (d, *J* = 4.4 Hz, 1H, H-5), 4.80–4.73 (m, 3H, CH_2Ph, $NapCH_2$), 4.60 (d, *J* = 11.5 Hz, 1H, OCH_2Ph), 4.53 (d, *J* = 11.5 Hz, 1H, OCH_2Ph), 4.48–4.46 (m, 2H, NCH_2Ph), 4.23 (d, *J* = 11.5 Hz, 1H, OCH_2Ph), 4.17–4.07 (m, 2H, H-4, H-2'), 3.94 (t, *J* = 3.7 Hz, 1H, H-3), 3.91–3.82 (m, 3H, H-4', H-5', H-6'), 3.78–3.72 (m, 2H, OCH_2CH_2, H-6'), 3.71 (s, 3H, OCH_3), 3.50–3.45 (m, 1H, OCH_2CH_2), 3.42 (dd, *J* = 10.5, 8.5 Hz, 1H, H-3'), 3.24–3.13 (m, 2H, NCH_2), 2.94–2.90 (m, 2H, $PhCH_2CH_2$), 2.78 (br, 1H, OH), 2.45–2.31 (m, 2H, $PhCH_2CH_2$), 1.66–1.51 (m, 4H, 2 X CH_2), 1.34–1.25 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8 (Ar), 129.6 (Ar), 128.9 (Ar), 128.4 (Ar), 128.1 (Ar), 127.6 (Ar), 126.8 (Ar), 126.2 (Ar), 99.1 (C-1), 97.7 (C-1'), 78.9 (C-3'), 74.7 (C-4), 74.3 (O*C*H_2Ph), 74.0 (Nap*C*H_2, C-3), 72.5 (O*C*H_2Ph), 72.3 (C-4), 70.8 (C-5'), 69.8 (C-6'), 68.8 (C-2, O*C*H_2CH_2), 67.8 (C-5), 66.8 (NCO_2*C*H_2Ph), 52.9 (C-2'), 52.2 (OCH_3), 50.3 (N*C*H_2Ph), 47.2, 46.1 (N*C*H_2CH_2), 32.9 (*C*$H_2C_6F_{13}$), 29.1 (CH_2), 27.5 (CH_2), 26.2 (*C*$H_2CH_2CF_2$), 23.4 (CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{77}H_{73}F_{20}N_2O_{15}$ 1645.4692; Found 1645.4678.



S60

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-benzoly-3-*O*-benzyl-α-L-idopyranosyluronate (S60).**

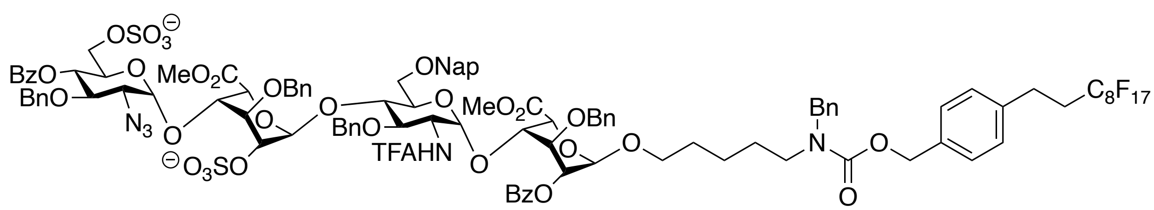
A mixture of donor **74** (0.33 g, 0.30 mmol), acceptor **S59** (0.25 g, 0.15 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous DCM (4.0 mL) and stirred at RT. After 30 min, NIS (0.15 g, 0.66 mmol) and AgOTf (24 mg, 0.090 mmol) were added. The solution was stirred for another 1 h before Et_3N (0.10 mL) was added. The mixture was filtered, concentrated, and the residue was purified by silica gel column chromatography (elution with 3:1 → 2:1 hexanes/EtOAc) to afford compound **S60** (0.32 g, 80%) as a colorless foam. R_f 0.54 (3:2 hexanes/EtOAc); ^1H NMR (400 MHz, $CDCl_3$): δ 8.01–7.83 (m, 8H, Ar), 7.66–7.02 (m, 46H, Ar), 6.92–6.90 (m, 2H, Ar), 6.20 (d, *J* = 7.7 Hz, 1H, NH), 5.59 (t, *J* = 9.5 Hz, 1H, H-4'''), 5.45 (d, *J* = 4.7 Hz, 1H, H-1''), 5.18–5.08 (m, 6H, H-1''', H-1', H-1, H-2, NCO_2CH_2), 5.00 (t, J = 5.2 Hz, 1H, H-2''), 4.83–4.71 (m, 6H), 4.65–4.45 (m, 7H), 4.17–3.86 (m, 10H), 3.78–3.62 (m, 5H), 3.59 (s, 3H, OCH_3), 3.51–3.42 (m, 3H), 3.41 (s, 3H, OCH_3), 3.22–3.10 (m, 2H, NCH_2), 2.94–2.91 (m, 2H, $PhCH_2CH_2$), 2.67–2.53 (m, 2H, CH_2), 2.45–2.31 (m, 4H, CH_2, $PhCH_2CH_2$), 2.10 (s, 3H, $CH_3C{=}O$), 1.60–1.48 (m, 4H, 2 X CH_2), 1.35–1.27 (m, 2H, CH_2), 1.01 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8 ($CH_3C{=}OCH_2$), 171.9, 169.5, 169.2, 165.4, 164.8, 157.0 (q, $^2J_{C,F}$ = 37.0 Hz, $CF_3C{=}O$), 156.1 (NCO_2), 138.8, 137.7, 137.5, 137.2, 137.1, 135.6, 135.5, 135.3, 133.8, 133.3, 133.1, 133.0, 132.9, 129.7, 129.6, 129.6, 129.2, 129.0, 128.6, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.3, 127.3, 127.2, 127.1, 126.9, 126.5, 126.1, 125.9, 115.5 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 99.0 (C-1), 98.1 (C-1''), 97.8 (C-1'), 97.5 (C-1'''), 75.3, 75.0, 75.0, 74.5, 74.1, 73.9, 73.6, 73.0, 72.7, 72.6, 71.9, 71.4, 70.7 (C-2''), 70.3, 70.2 (C-4'''), 68.9, 68.0, 67.1, 66.8, 62.9, 62.0, 53.5, 52.7 (C-2'), 52.1 (OCH_3), 51.8 (OCH_3), 47.1 (NCH_2Ph), 37.7 ($CH_2C{=}O$), 32.9 (t, $^2J_{C,F}$ = 22.3 Hz, CH_2CF_2), 29.7, 29.1, 27.7, 26.6 ($(CH_3)_3C$), 26.2 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.3, 19.1 ($(CH_3)_3C$); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{132}H_{132}F_{20}N_5O_{28}Si$ 2642.8509; Found 2642.8531. gHSQC 2-D NMR (without ^1H decoupling): $^1J_{C1,H1}$ = 170.6 Hz, $^1J_{C1',H1'}$ = 172.5 Hz, $^1J_{C1'',H1''}$ = 173.3 Hz, $^1J_{C1''',H1'''}$ = 173.3 Hz. The coupling constants of $^1J_{C1,H1}$ (170.6 Hz) and $^1J_{C1'',H1''}$ (173.3) Hz are above 170 Hz, which confirms the α configuration of the two IdoA-GlcN linkages.[4] In addition, the coupling constants of $^1J_{C1',H1'}$ (172.5 Hz) and $^1J_{C1''',H1'''}$ (173.3) Hz are greater than 170 Hz, which is indicative of the α configuration for the two GlcN-IdoA linkages.



S61

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate (S61).**

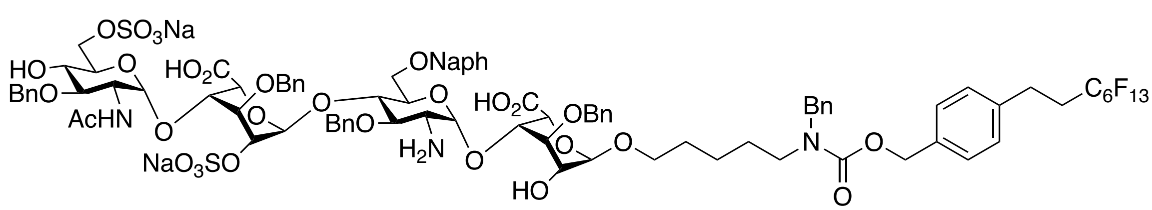
Compound **S60** (50 mg, 0.019 mmol) was treated according to the general procedures for Lev deprotection and TBDPS deprotection to give tetrasaccharide **S61** (38 mg, 86%); R_f 0.50 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.83 (m, 7H, ArH), 7.65–7.09 (m, 37H, ArH), 6.94–6.92 (m, 2H, ArH), 6.24 (br, 1H, NH), 5.37 (s, 1H, H-1''), 5.22–5.12 (m, 4H, H-4''', H-2, NCO_2CH_2), 5.09 (s, 1H, H-1), 5.04 (d, J = 3.8 Hz, 1H, H-1'''), 5.01 (s, 1H, H-1'), 4.94–4.88 (m, 2H), 4.82–4.63 (m, 7H), 4.56 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.47–4.42 (m, 3H, NCH_2Ph, CH_2Ph), 4.27 (td, J = 10.5, 3.5 Hz, 1H, H-2'), 4.17–4.04 (m, 5H), 3.91–3.87 (m, 2H), 3.82–3.42 (m, 12H), 3.28 (s, 3H, OCH_3), 3.23–3.13 (m, 2H, NCH_2), 2.94–2.90 (m, 2H, PhCH_2CH_2), 2.70 (br, 1H, OH), 2.44–2.31 (m, 2H, PhCH_2CH_2), 1.65–1.44 (m, 4H, 2 X CH_2), 1.39–1.29 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6 (C=O), 169.5 (C=O), 166.4 (C=O), 165.4 (C=O), 137.4, 137.2, 137.0, 136.9, 135.0, 134.0, 133.8, 133.3, 133.1, 129.8, 129.6, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.1, 101.8 (C-1''), 99.0 (C-1), 98.2 (C-1'), 95.7 (C-1'''), 78.3, 77.6, 75.7, 75.4, 74.5, 73.8, 72.9, 72.8, 72.5, 72.2, 71.4, 71.2, 70.9, 68.7, 67.7, 67.6, 66.8, 63.3, 60.6, 60.4, 52.0, 50.2, 47.1, 33.2, 32.9 (t, $^2J_{C,F}$ = 21.4 Hz, CH_2CF_2), 29.1, 27.8, 26.2 (t, $^3J_{C,F}$ = 4.0 Hz, $CH_2CH_2CF_2$), 23.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{111}H_{108}F_{20}N_5O_{26}$ 2306.6963; Found 2306.6932.



S62

N-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-azido-3-*O*-benzyl-4-*O*-benzoyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-trifluoroacetamido-α-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-O-benzoyl-α-L-idopyranosyluronate disodium salt (S62).

Compound **S61** (38 mg, 0.016 mmol) was treated according to the general procedure for *O*-sulfation to give tetrasaccharide **S62** (39 mg, 95%); R_f 0.60 (7:2:1 EtOAc/CH_3OH/H_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (br 1H, NH), 8.03–7.75 (m, 7H, ArH), 7.57–7.03 (m, 39H, ArH), 5.58 (s, 1H, H-1''), 5.32–5.02 (m, 7H, H-4''', H-1', H-2, H-1, H-1''', NCO_2CH_2), 4.95–4.69 (m, 8H), 4.59–4.42 (m, 5H), 4.33–3.95 (m, 11H), 3.88–3.39 (m, 12H), 3.18–3.08 (m, 2H, NCH_2), 2.95–2.88 (m, 2H, $PhCH_2CH_2$), 2.44–2.30 (m, 2H, $PhCH_2CH_2$), 1.56–1.39 (m, 4H, 2 X CH_2), 1.30–1.15 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6, 129.7, 128.6, 128.2, 128.0, 127.7, 127.3, 126.8, 126.4, 125.8, 99.0 (C-1''), 98.8 (C-1), 96.8 (C-1'), 97.1 (C-1'''), 77.9, 77.1, 74.3, 74.1, 73.7, 73.0, 72.8, 72.5, 71.6, 70.9, 70.4, 69.8, 69.0, 68.9, 68.6, 68.0, 67.6, 66.7, 65.8, 62.8, 52.4, 52.2, 51.9, 50.4, 46.9, 46.4, 32.9, 29.2, 27.6, 26.1, 23.2; HRMS (ESI-TOF) m/z $[M-Na]^-$ calcd for $C_{109}H_{105}F_{16}N_5O_{32}S_2Na$ 2486.5762; Found 2486.5725.

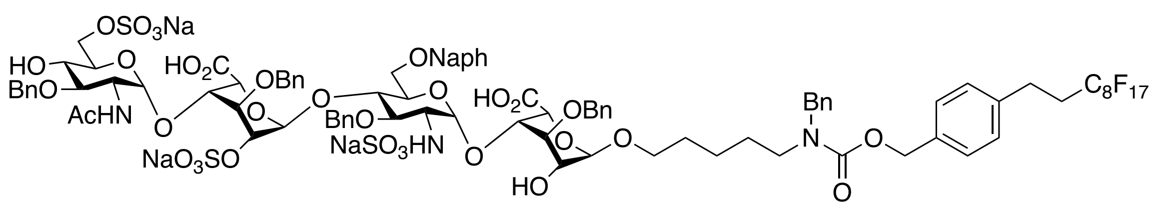


S64

N-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-

α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-α-L-idopyranosyluronate disodium salt (S64).

Compound **S49** (30 mg, 0.012 mmol) was treated according to the general procedure for hydrolysis to give tetrasaccharide **S64** (25 mg, 93%); R_f 0.38 (12:5:3:1 EtOAc/Py/H_2O/AcOH); ^1H NMR (400 MHz, CD_3OD): δ 7.86–7.70 (m, 5H, ArH), 7.53–7.50 (m, 1H, ArH), 7.39–7.17 (m, 30H, ArH), 5.70 (s, 1H, H-1''), 5.22–5.07 (m, 4H), 4.87–4.53 (m, 13H), 4.41 (s, 2H), 4.33–4.15 (m, 5H), 4.09–3.78 (m, 9H), 3.73–3.62 (m, 3H), 3.44–3.36 (m, 1H), 3.18–3.08 (m, 3H, H-2', NC*H*$_2$), 2.90–2.86 (m, 2H, PhC*H*$_2$CH$_2$), 2.48–2.35 (m, 2H, PhCH$_2$C*H*$_2$), 1.98 (s, 3H, COC*H*$_3$), 1.56–1.39 (m, 4H, 2 X CH$_2$), 1.30–1.15 (m, 2H, CH$_2$); ^{13}C NMR (100 MHz, CD_3OD): δ 134.6, 129.0, 128.0, 127.7, 127.4, 126.5, 126.0, 125.5, 101.1, 97.1, 97.0, 91.9, 80.2, 76.3, 74.8, 74.6, 74.0, 73.0, 72.4, 72.0, 71.6, 71.3, 70.6, 69.9, 67.9, 66.7, 67.6, 67.5, 66.7, 66.1, 65.9, 54.1, 52.8, 50.4, 46.7, 46.4, 32.2, 29.0, 27.3, 25.6, 23.2, 22.0; HRMS (ESI-TOF) m/z $[M - Na]^-$ calcd for $C_{93}H_{96}F_{13}N_3O_{30}S_2Na_3$ 2114.5006; Found 2114.5037.



S67

***N*-(Benzyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorooctyl-benzyloxycarbonyl-5-aminopentyl (2-acetamido-3-*O*-benzyl-2-deoxy-6-*O*-sulfonato-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfonato-α-L-idopyranosyluronate)-(1→4)-(3-*O*-benzyl-2-deoxy-6-*O*-2-naphthylmethyl-2-sulfamino-α-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-α-L-idopyranosyluronate disodium salt (S67).**

Compound **S63** (30 mg, 0.012 mmol) was treated according to the general procedure for hydrolysis and *N*-sulfation to give tetrasaccharide **S67** (19 mg, 70%); ^1H NMR (400 MHz,

CD_3OD): δ 7.82–7.73 (m, 4H, ArH), 7.54–7.44 (m, 3H, ArH), 7.40–7.03 (m, 29H, ArH), 5.95 (s, 1H), 5.38 (d, *J* = 3.4 Hz, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 5.13–5.09 (m, 2H), 4.99 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 1.5 Hz, 1H), 4.72–4.64 (m, 6H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.43 (s, 2H), 4.38–4.34 (m, 2H), 4.25–4.22 (m, 2H), 4.14–4.04 (m, 5H), 3.88 (s, 1H), 3.79–3.64 (m, 6H), 3.53–3.50 (m, 1H), 3.44–3.36 (m, 1H), 3.18–3.11 (m, 3H, H-2', NCH_2), 2.92–2.89 (m, 2H, $PhCH_2CH_2$), 2.51–2.37 (m, 2H, $PhCH_2CH_2$), 2.06 (s, 3H, $COCH_3$), 1.56–1.39 (m, 4H, 2 X CH_2), 1.30–1.15 (m, 2H, CH_2); HRMS (ESI-TOF) m/z $[M – Na]^-$ calcd for $C_{95}H_{95}F_{17}N_3O_{33}S_3Na_4$ 2316.4239; Found 2316.4285.

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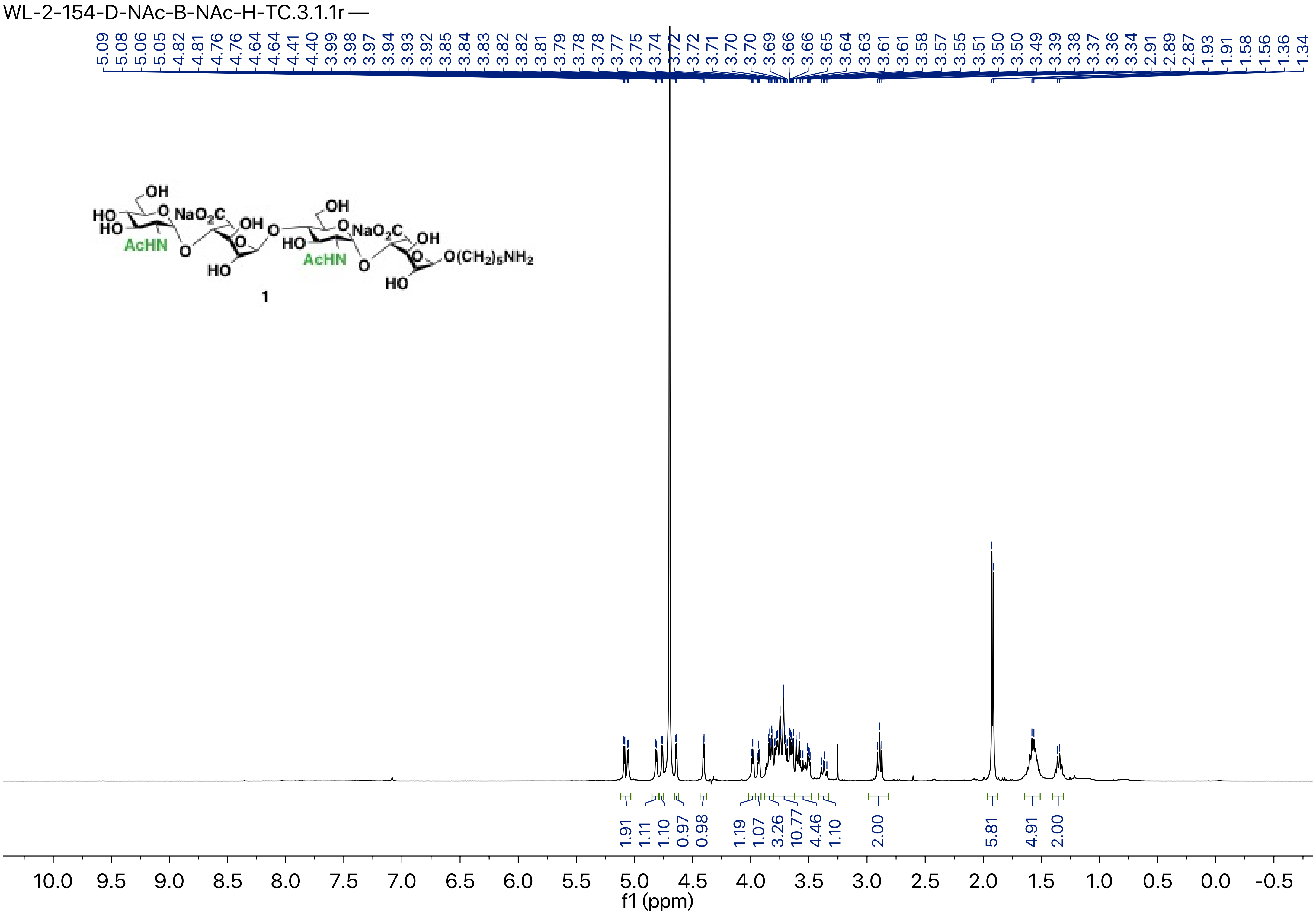
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AcHN
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1.91 1.11 1.10 0.97 0.98 1.19 1.07 3.26 10.77 4.46 1.10 2.00 5.81 4.91 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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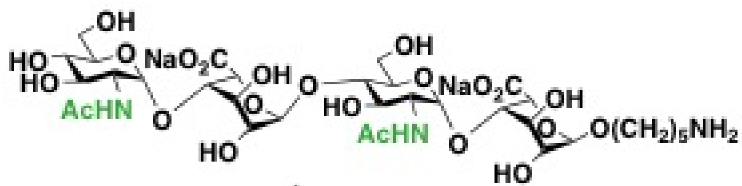

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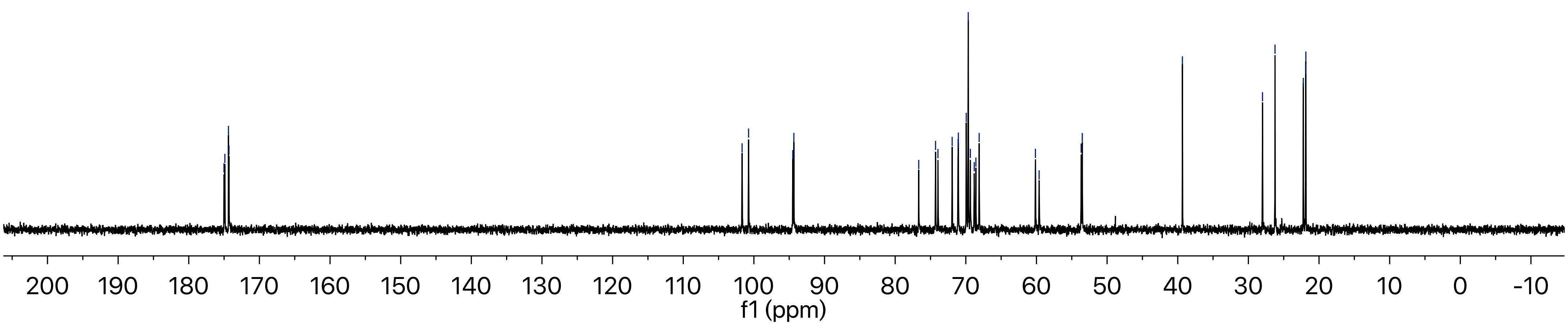

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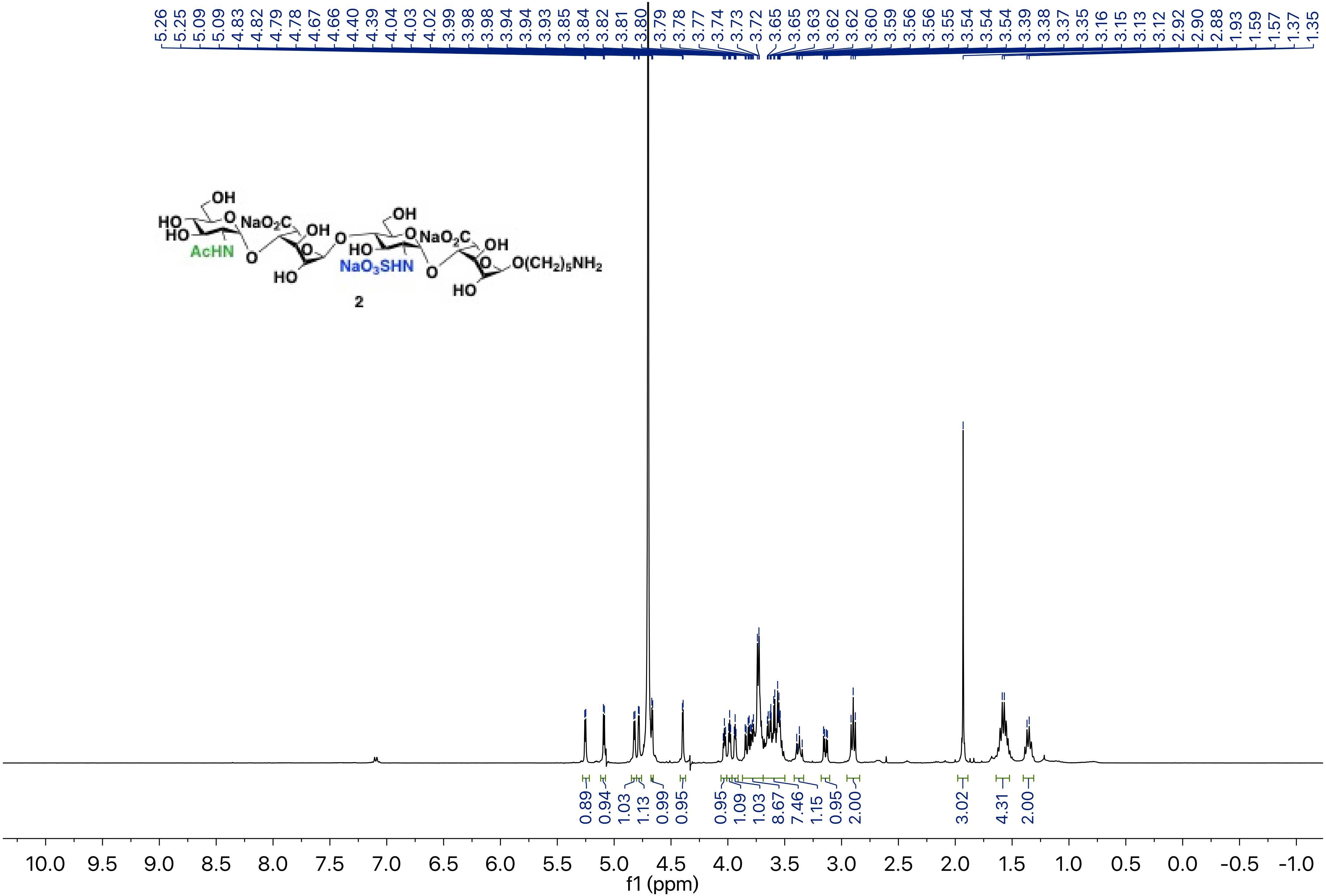

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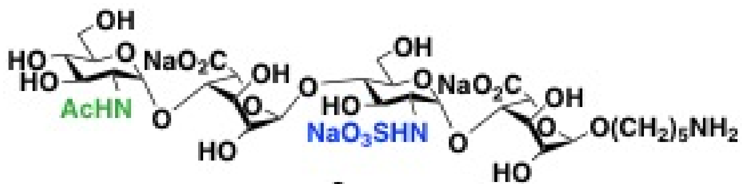
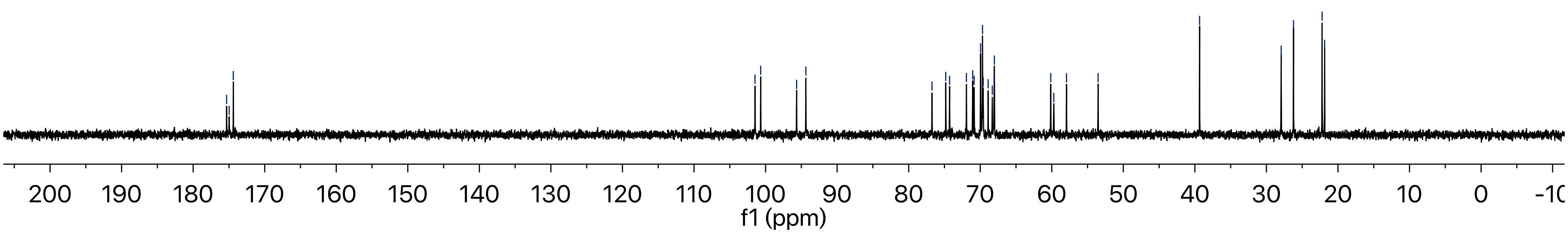
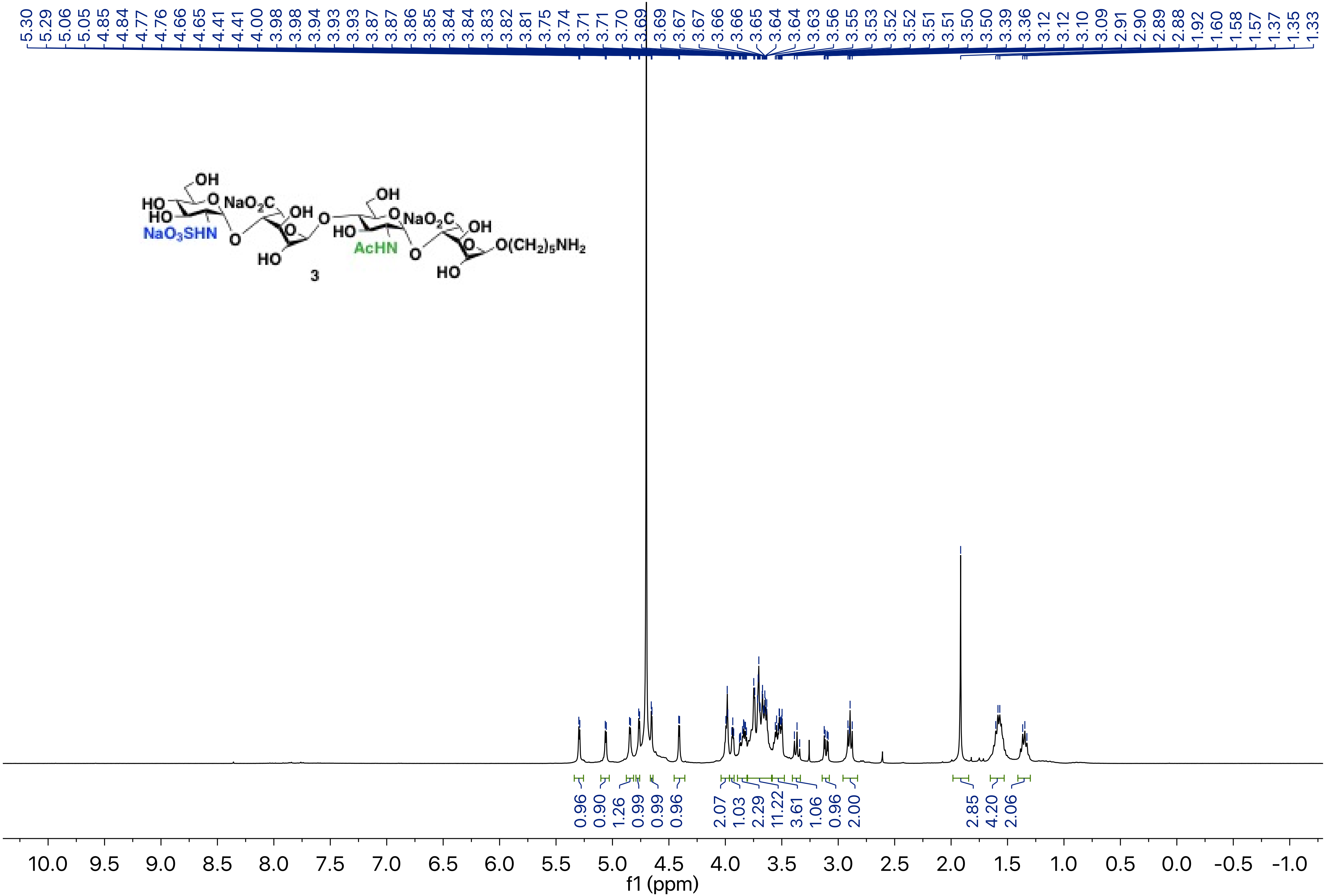


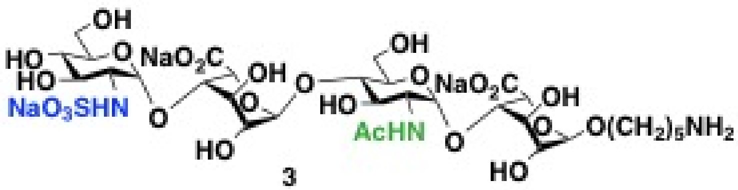
2



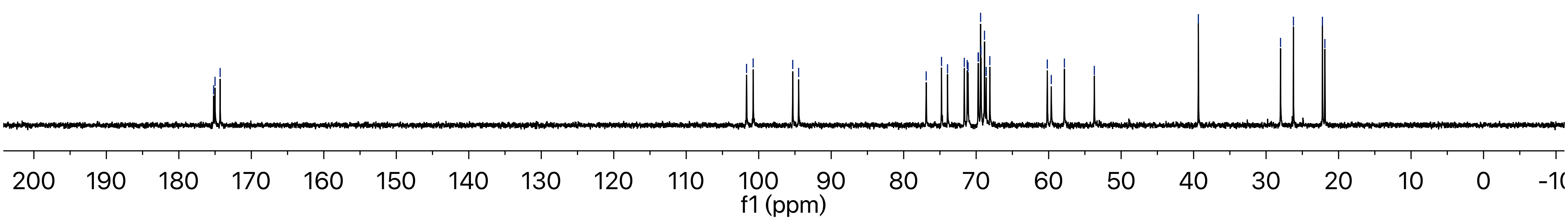
WL-2-238-GlcNS-IdoA-GlcNAc-IdoA-Prod-H-TC.8.1.1r —



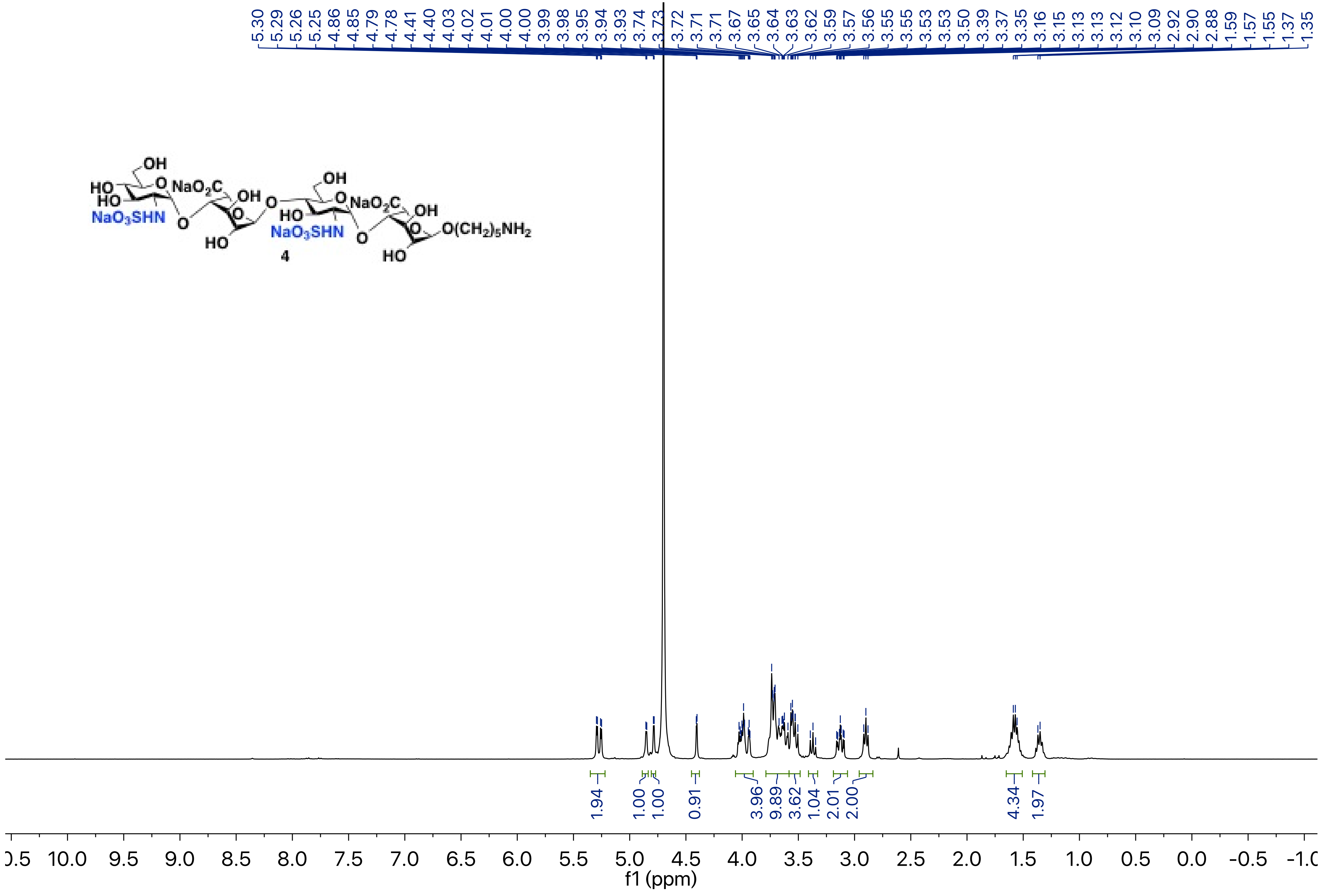
WL-2-238-GlcNS-IdoA-GlcNAc-IdoA-Prod-C-TC.7.1.1r



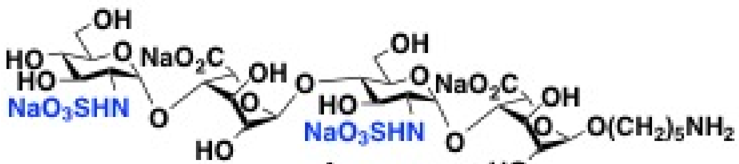
3



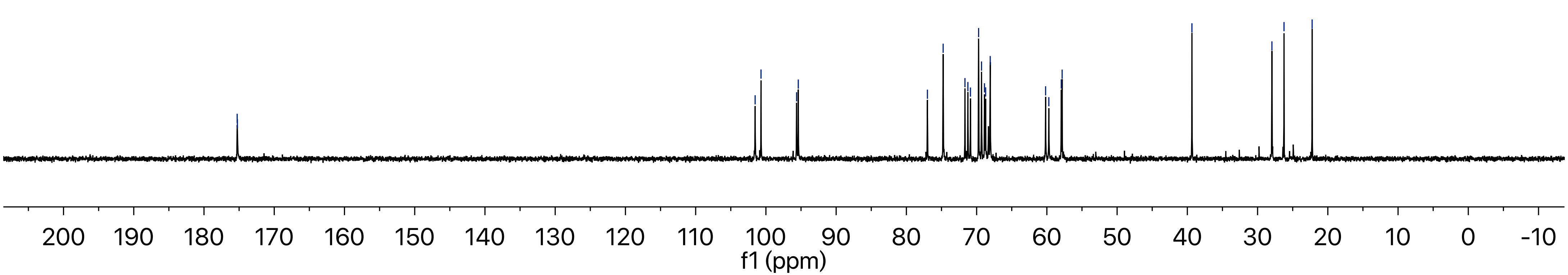
WL-2-244-None-OS-D-NS-B-NS-Prod-H-TC.7.fid —



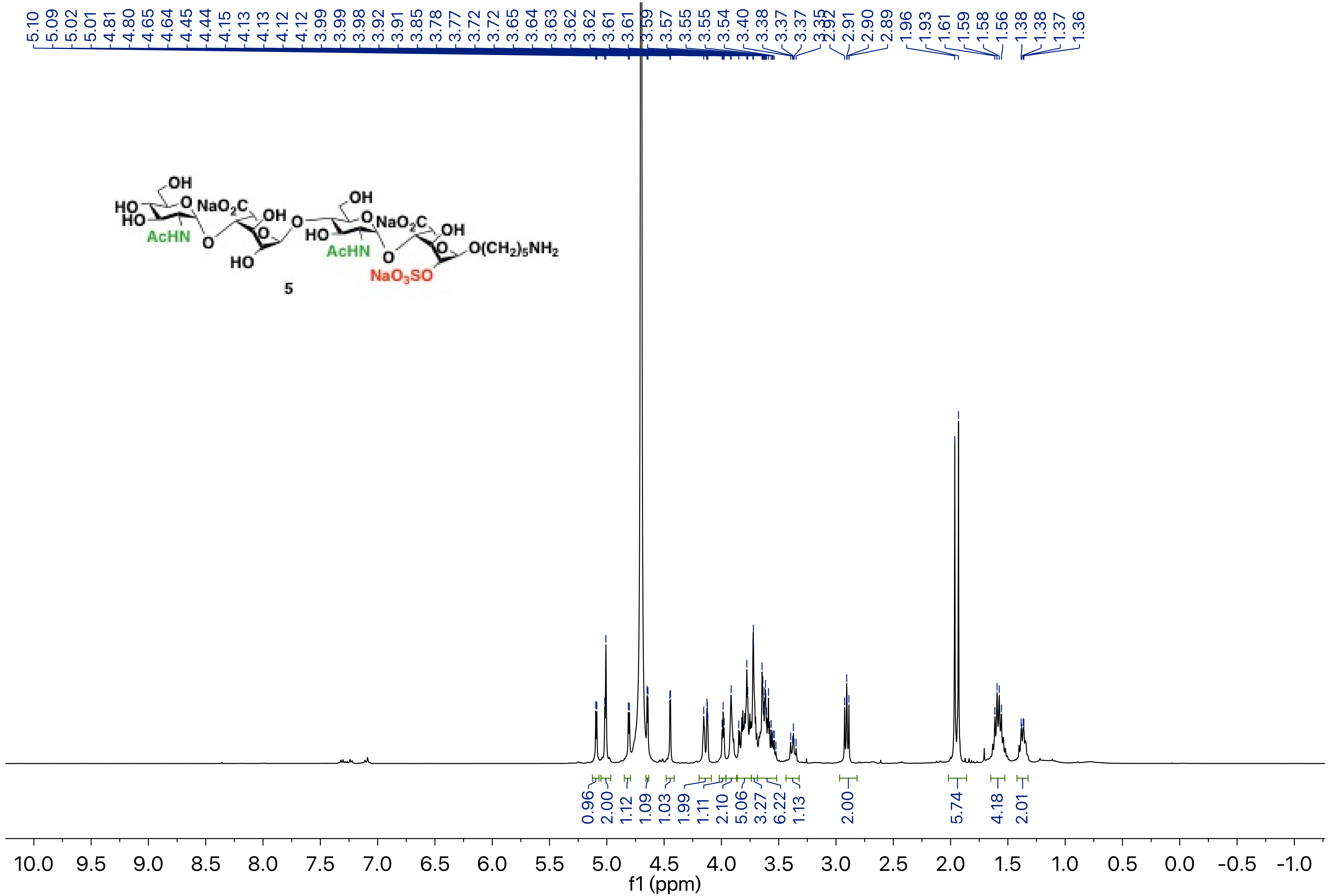
WL-2-244-None-OS-D-NS-B-NS-Prod-C-TC.1.1.1r



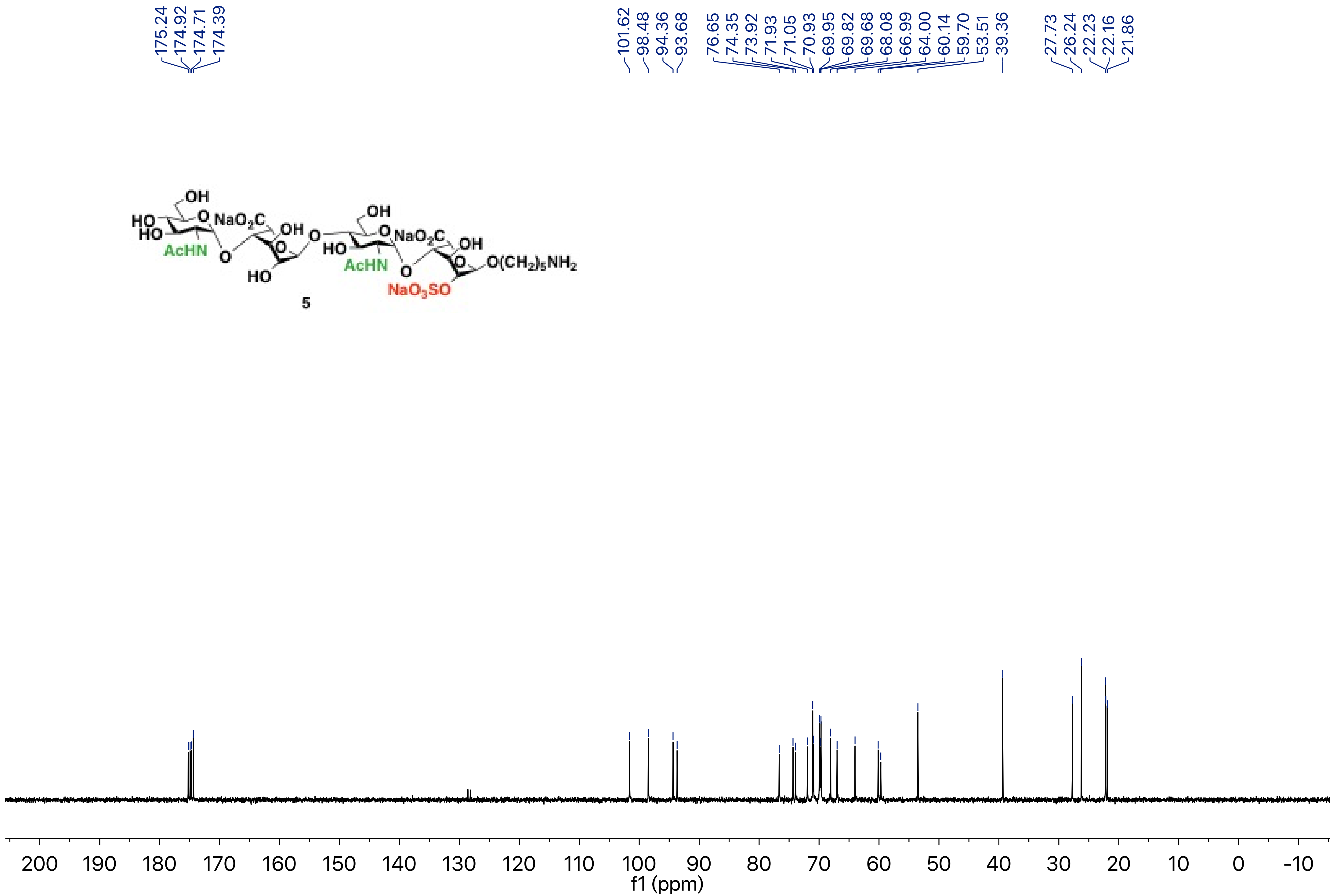
4



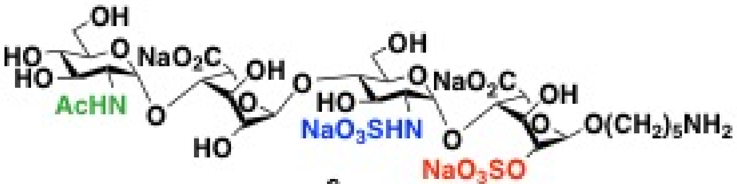
WL-2-135-D-NAc-B-NAc-A-2SO3-prod.1.1.1r —



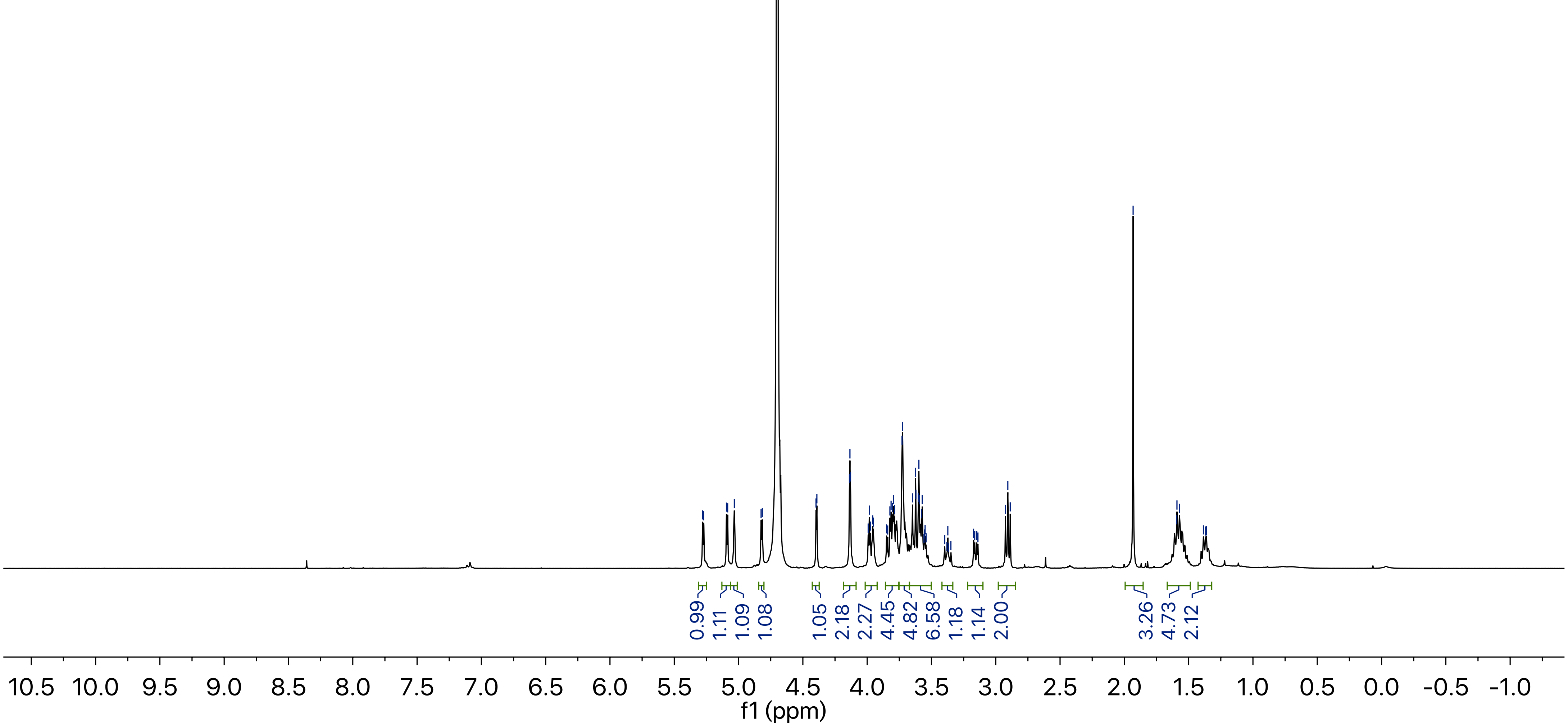
WL-2-135-C.1.1.1r —



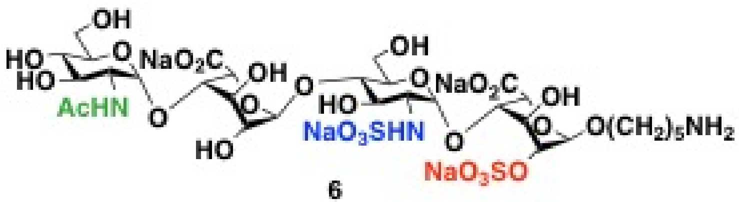
wl-2-131-prod.1.1.1r —



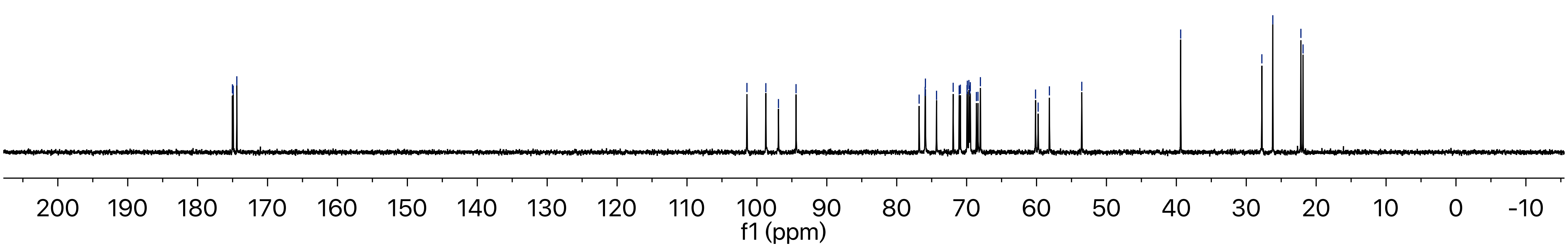
6



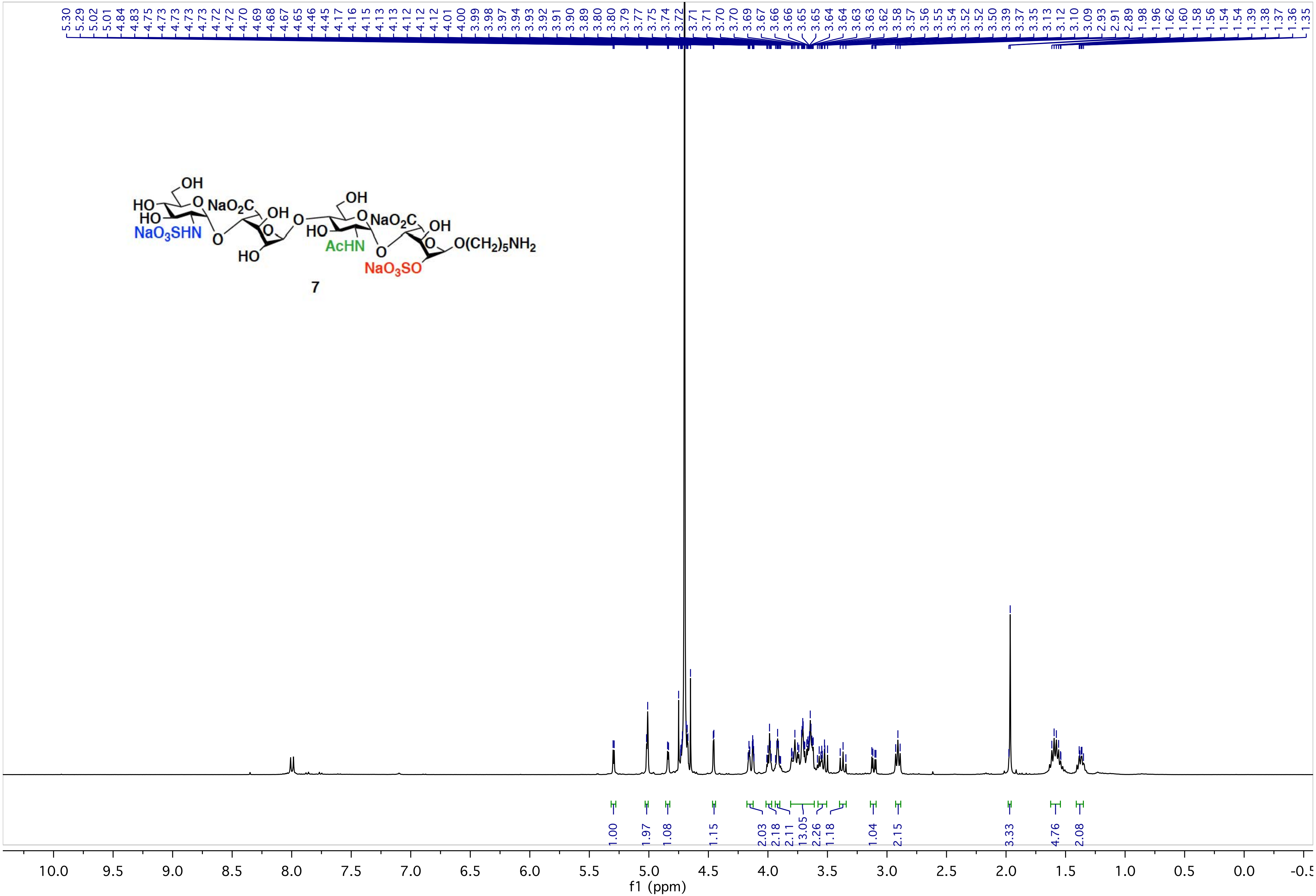
WL-2-131-C.3.1.1r



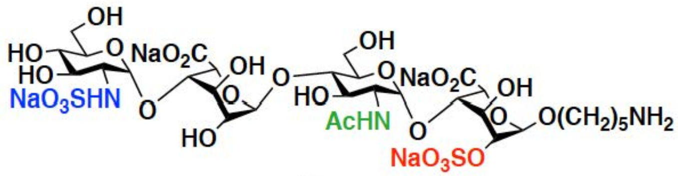
6



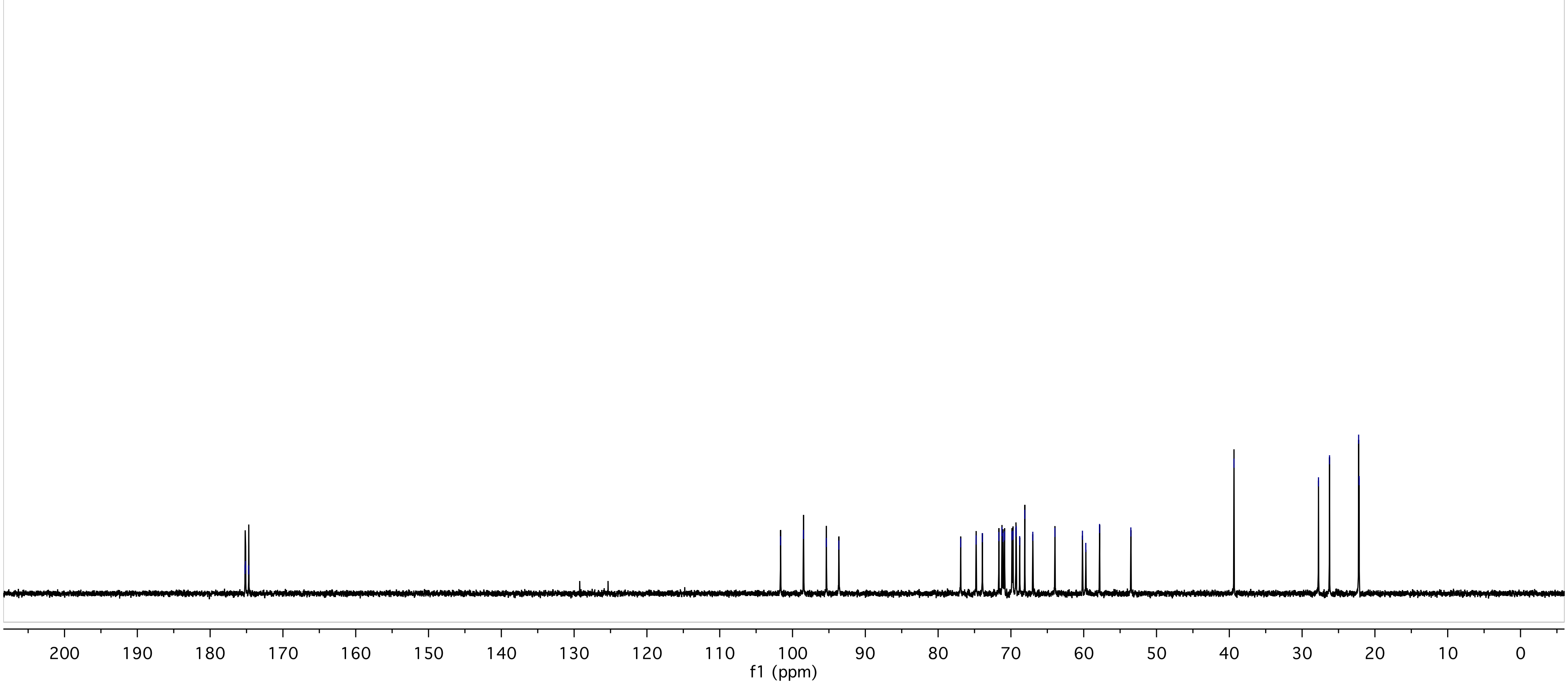
BSH-02-30.1.fid —



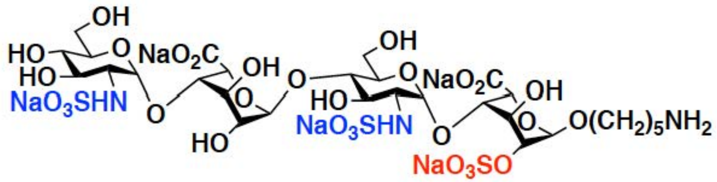
BSH-02-30.2.fid —



7



BSH-02-28-pure.1.fid —



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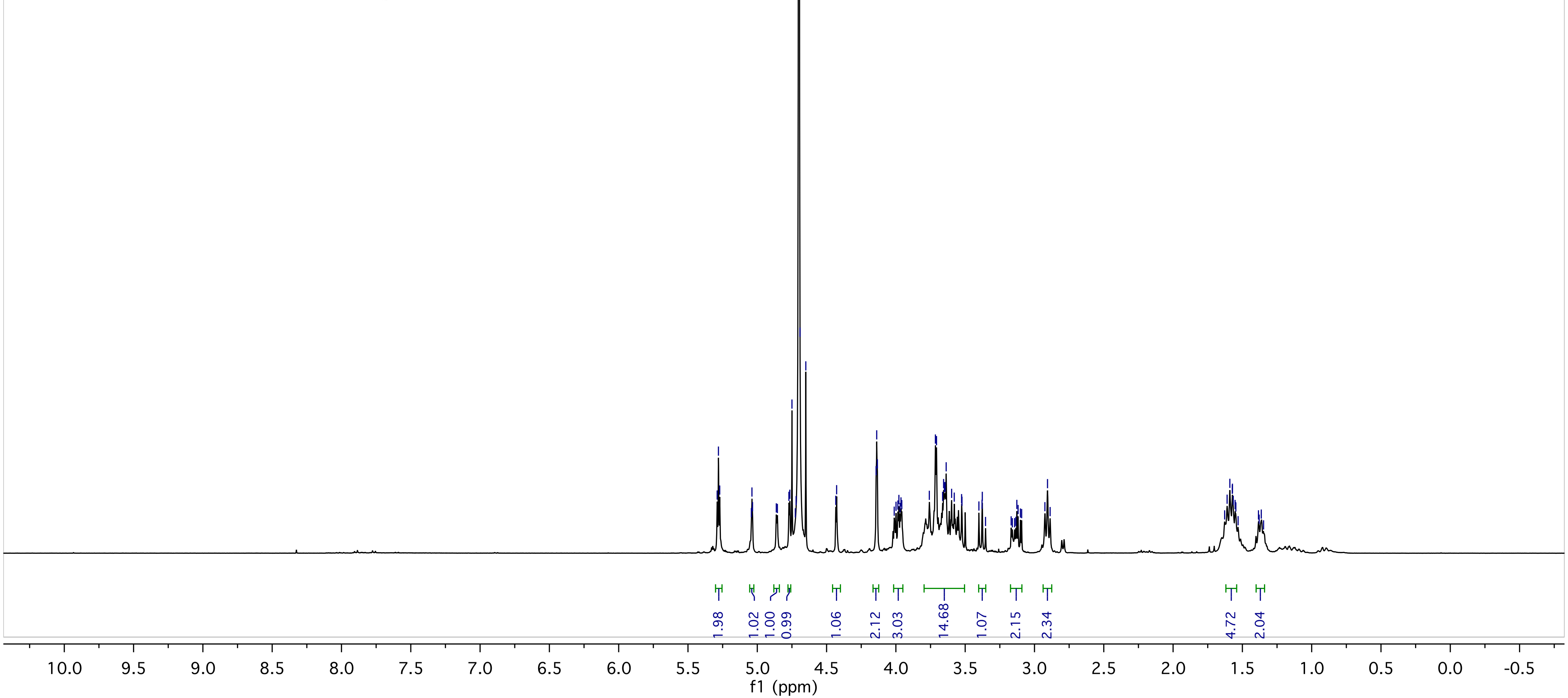
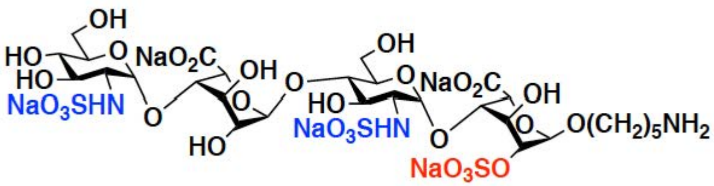
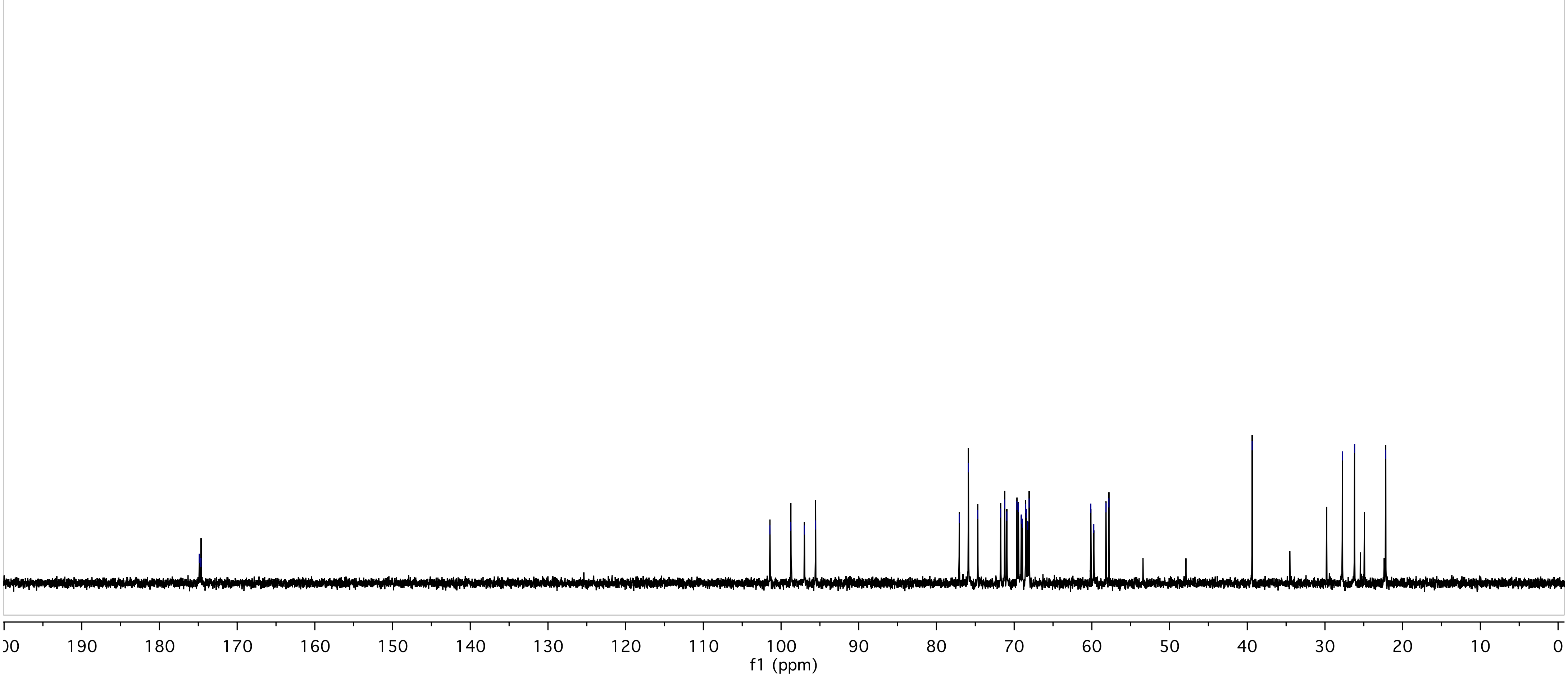
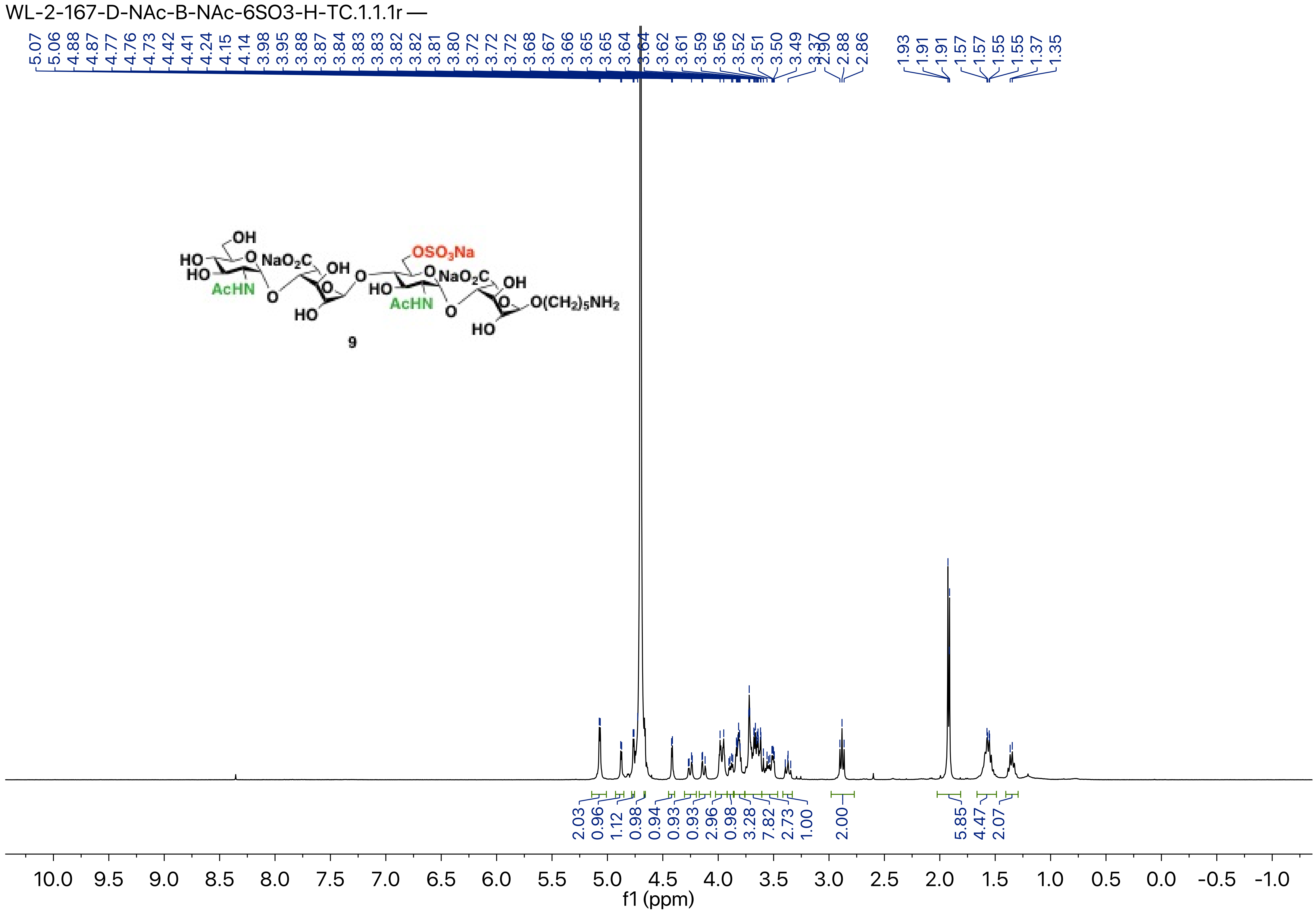


BSH-02-28-pure.2.fid —

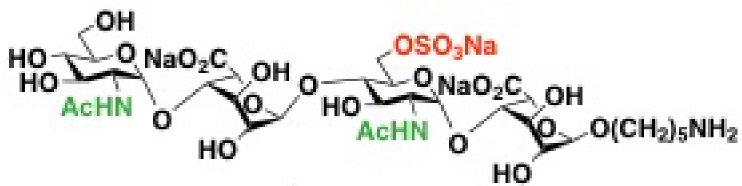


8

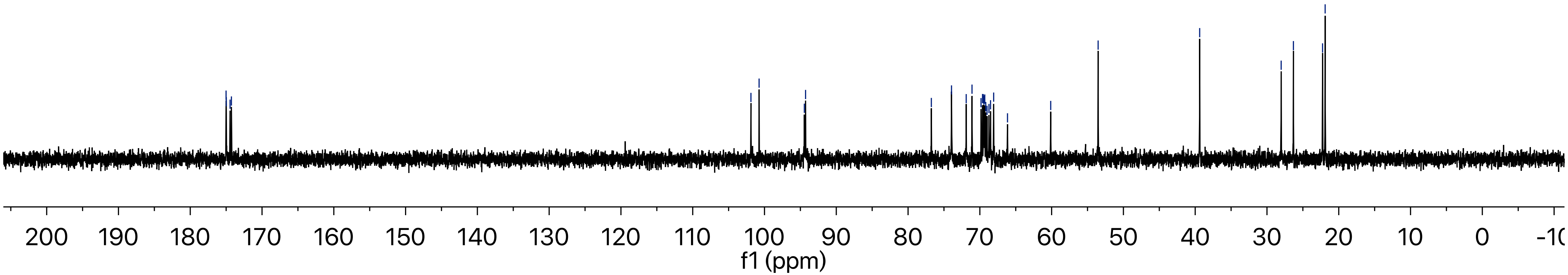



WL-2-167-D-NAc-B-NAc-6SO3-H-TC.1.1.1r
5.07 5.06 4.88 4.87 4.77 4.76 4.73 4.42 4.41 4.24 4.15 4.14 3.98 3.95 3.88 3.87 3.84 3.83 3.83 3.82 3.82 3.81 3.80 3.72 3.72 3.72 3.68 3.67 3.66 3.65 3.65 3.64 3.64 3.62 3.61 3.59 3.56 3.52 3.51 3.50 3.49 3.37 2.90 2.88 2.86
1.93 1.91 1.91 1.57 1.57 1.55 1.55 1.37 1.35
OSO3Na
NaO2C
AcHN
O(CH2)5NH2
9
2.03 0.96 1.12 0.98 0.94 0.93 0.93 2.96 0.98 3.28 7.82 2.73 1.00 2.00 5.85 4.47 2.07
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 -0.5 -1.0
f1 (ppm)

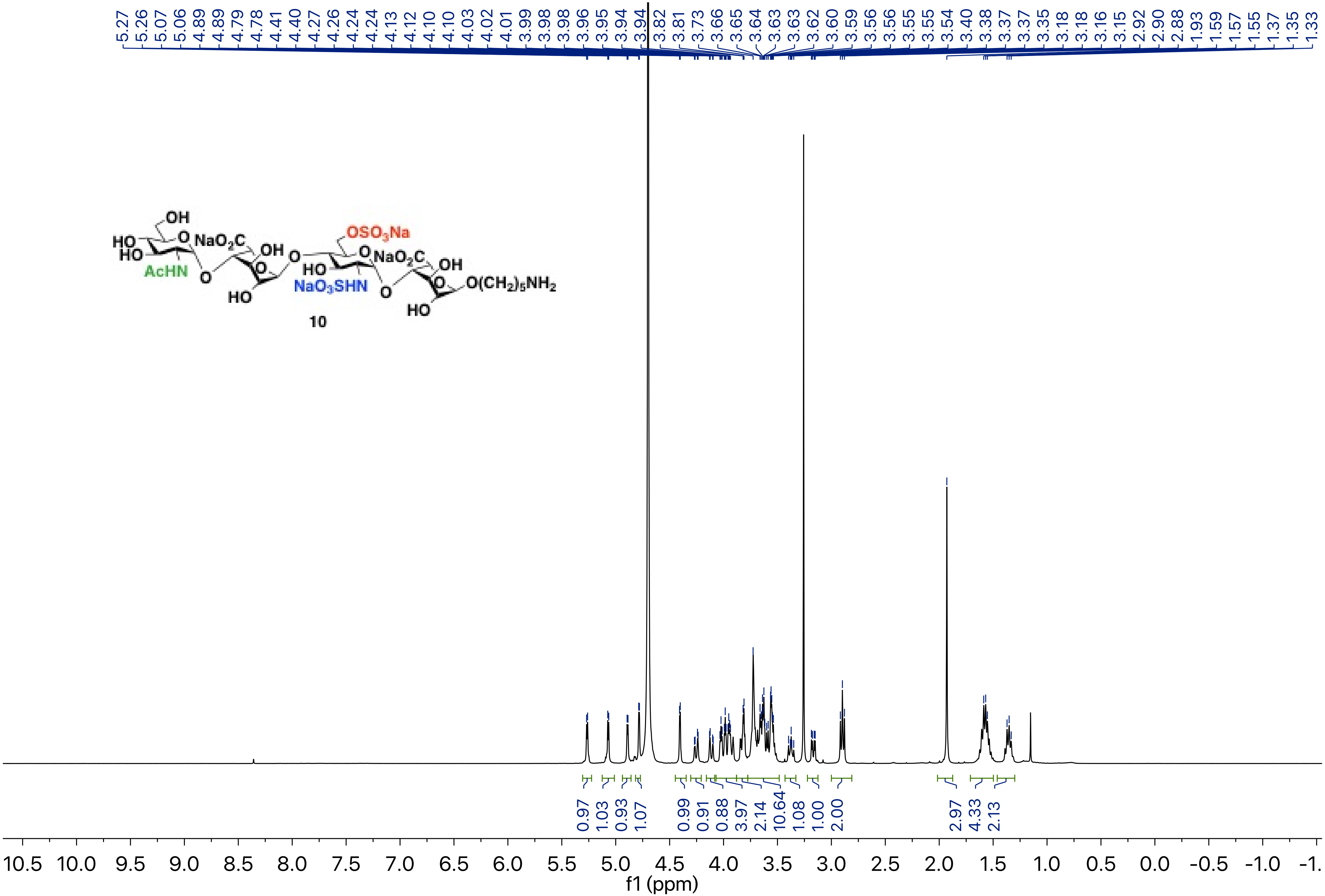
WL-2-167-D-NAc-B-NAc-6SO3-C-TC.1.1.1r



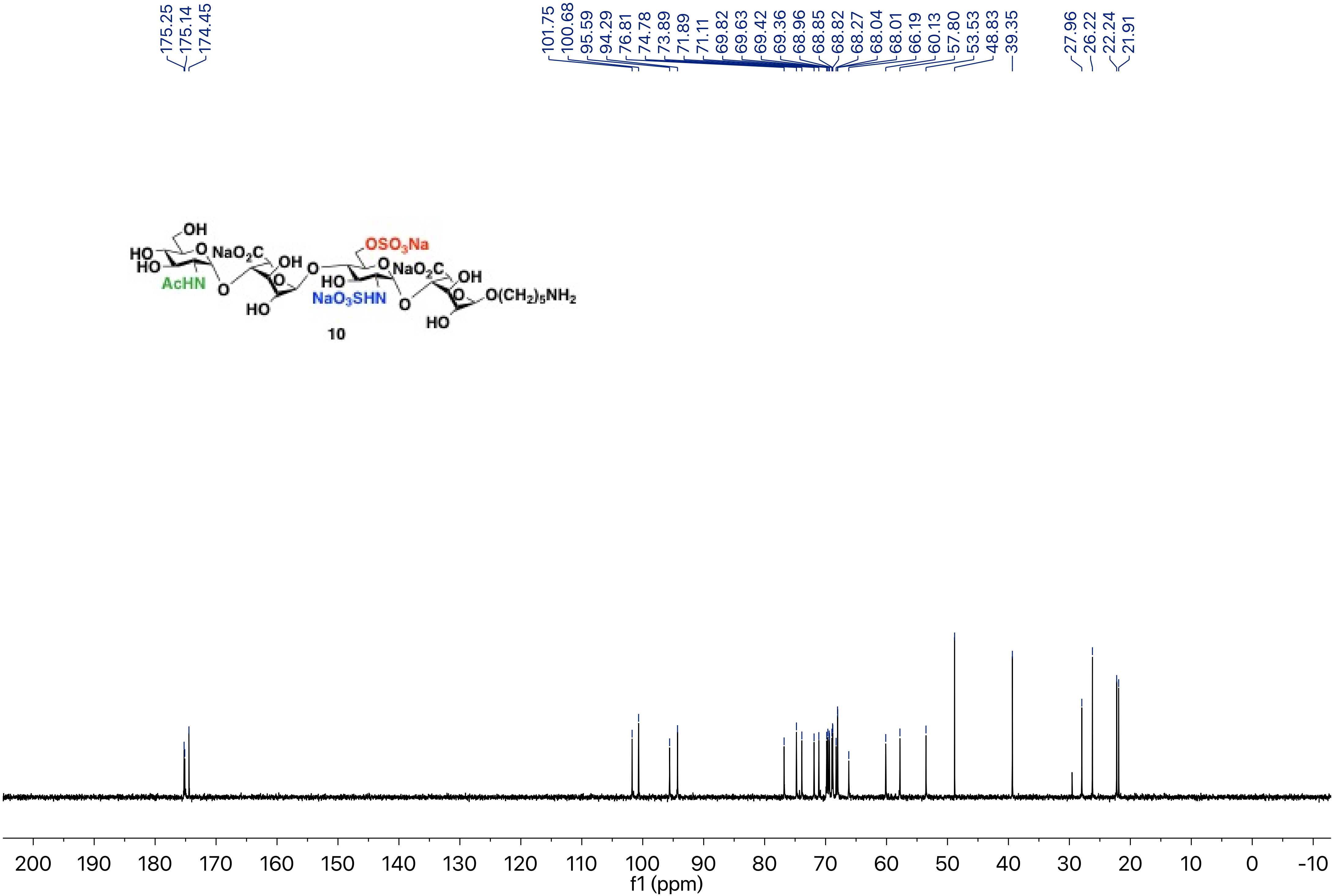
9



WL-2-168-D-NAc-B-NS-6S-H-TC.1.1.1r

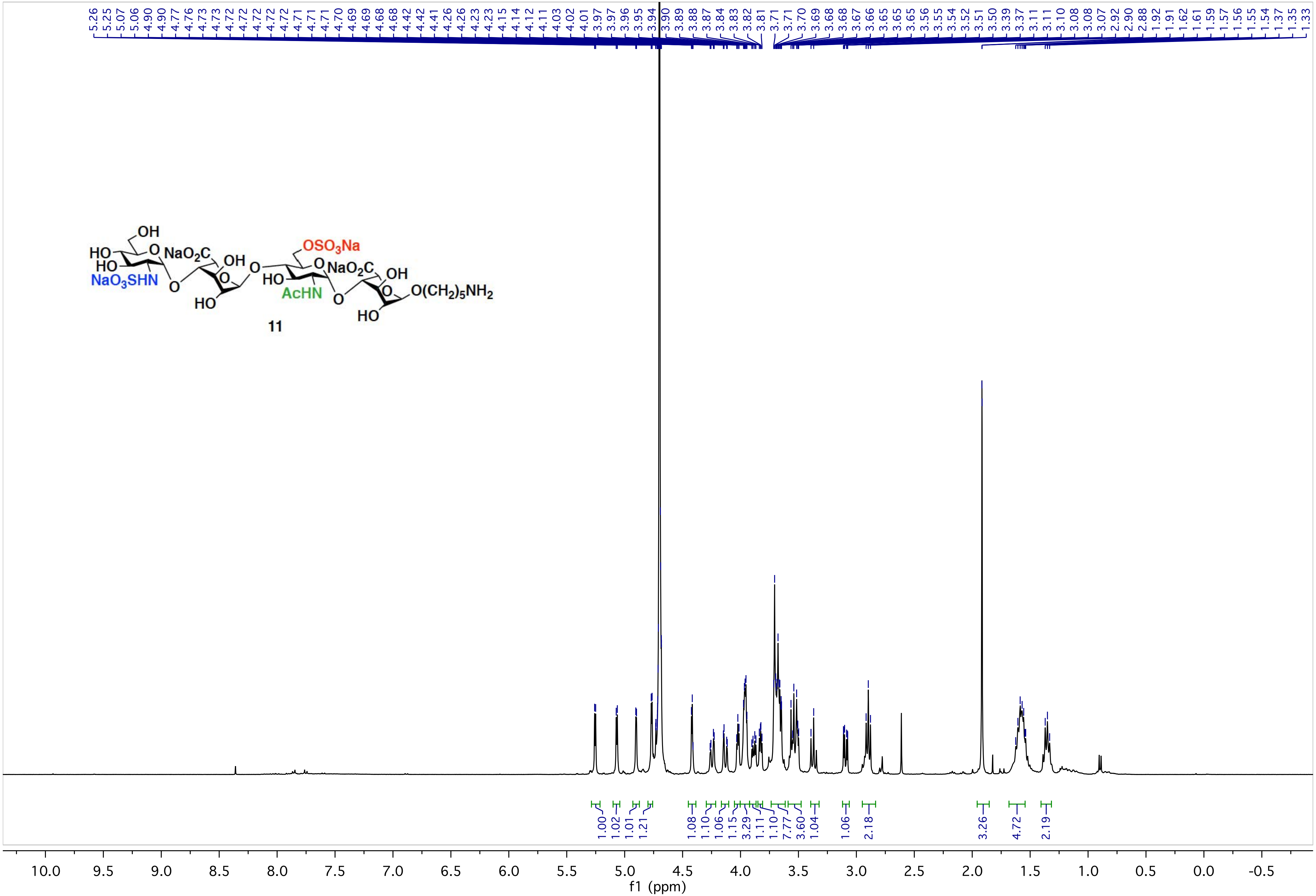


WL-2-168-D-NAc-B-NS-6S-C-TC.1.1.1r

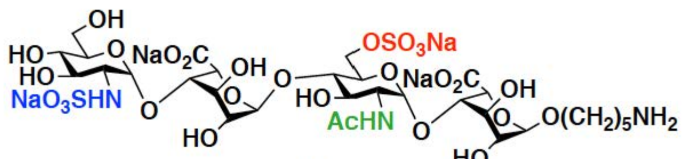


10

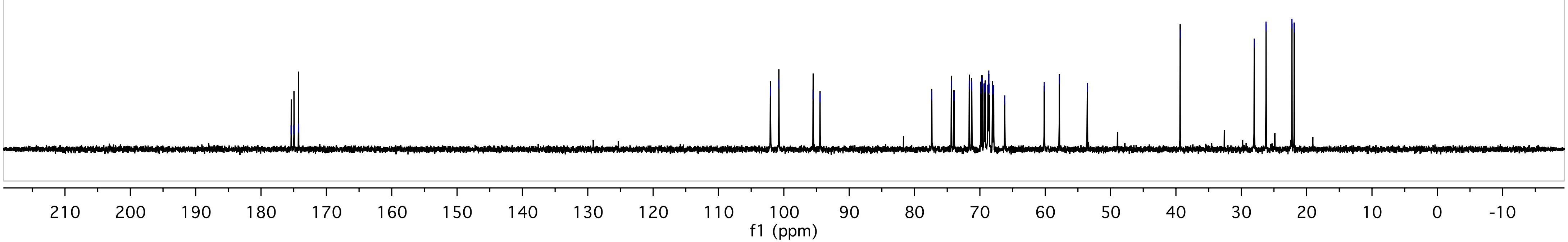
BSH-01-68.1.fid —



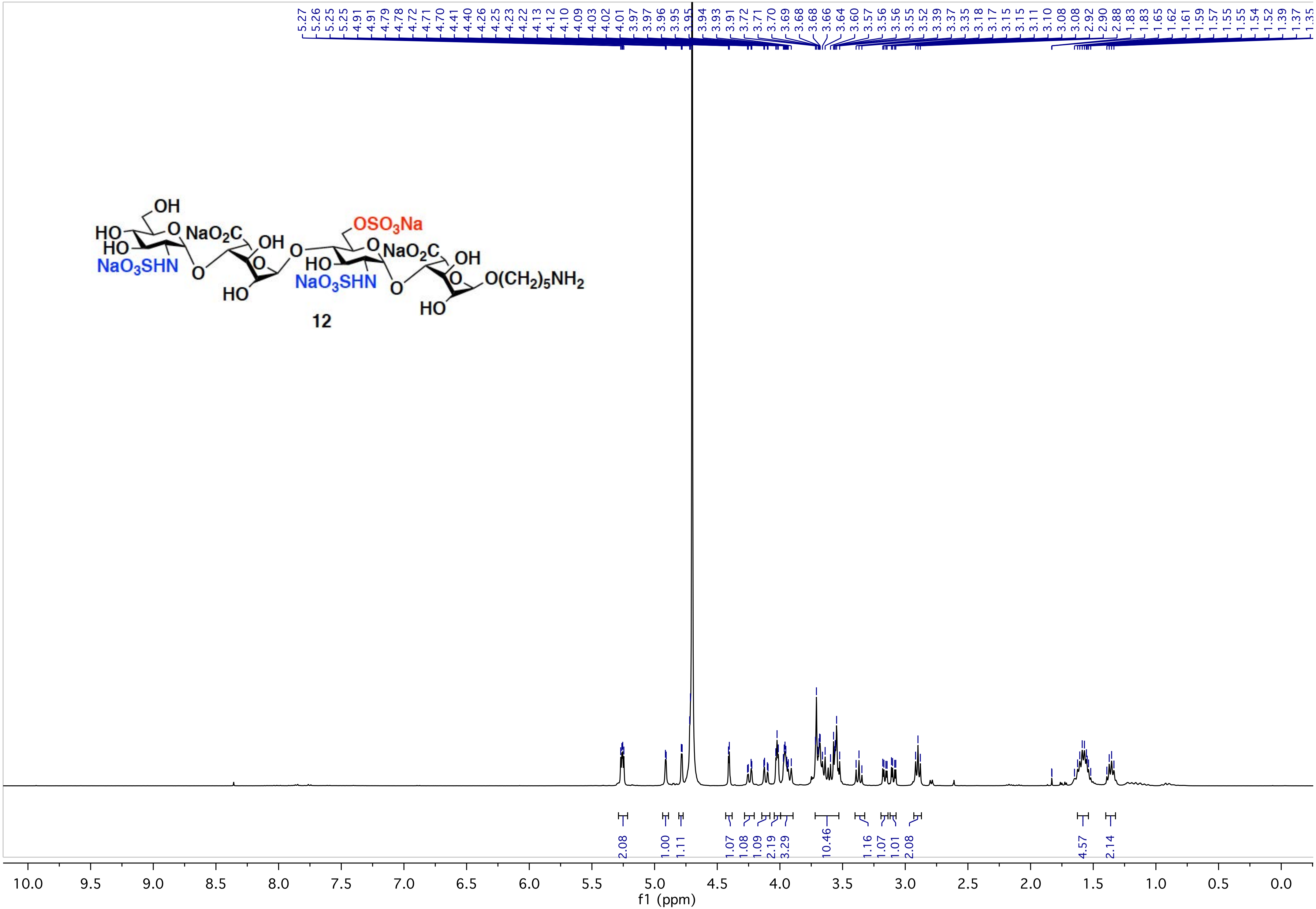
BSH-01-68.2.fid —



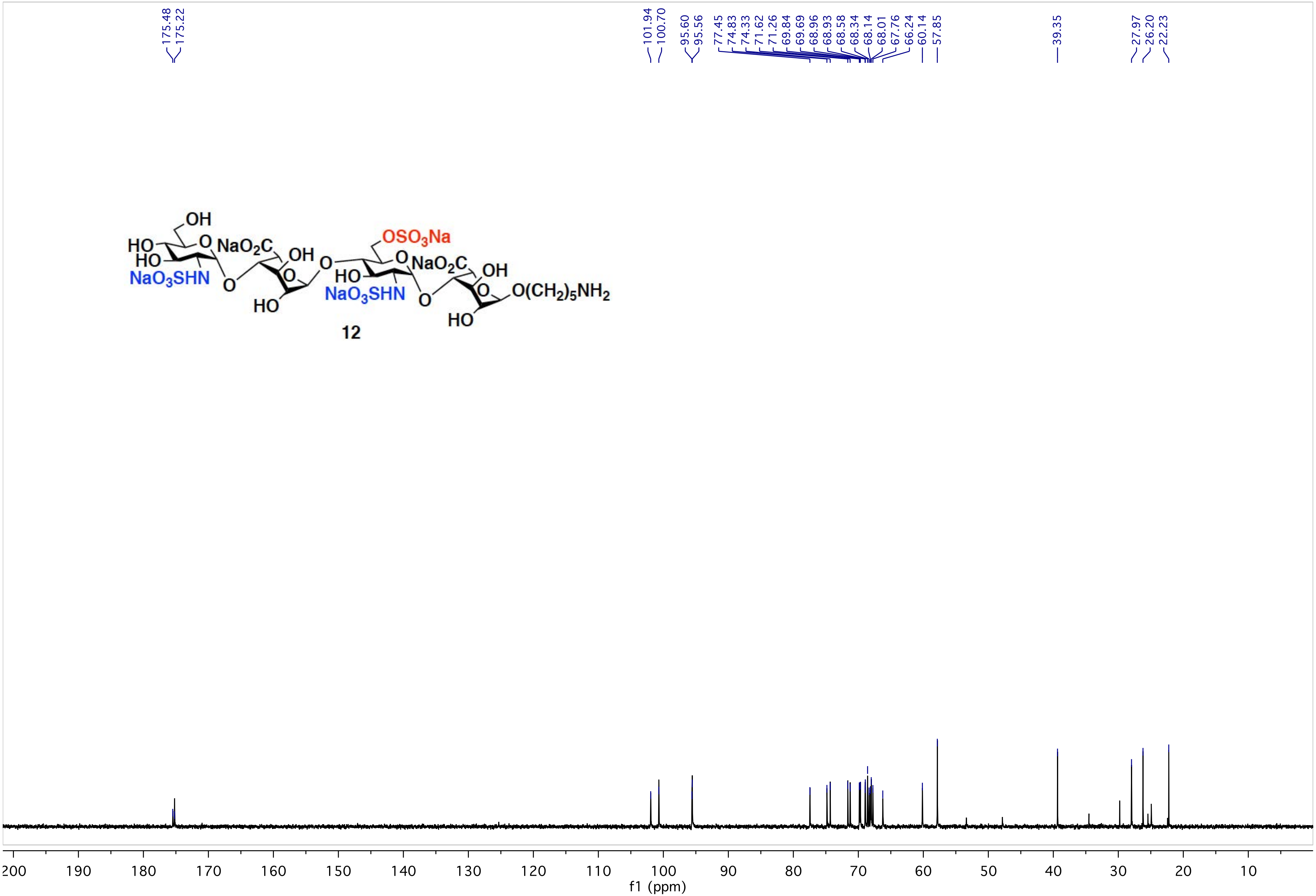
11

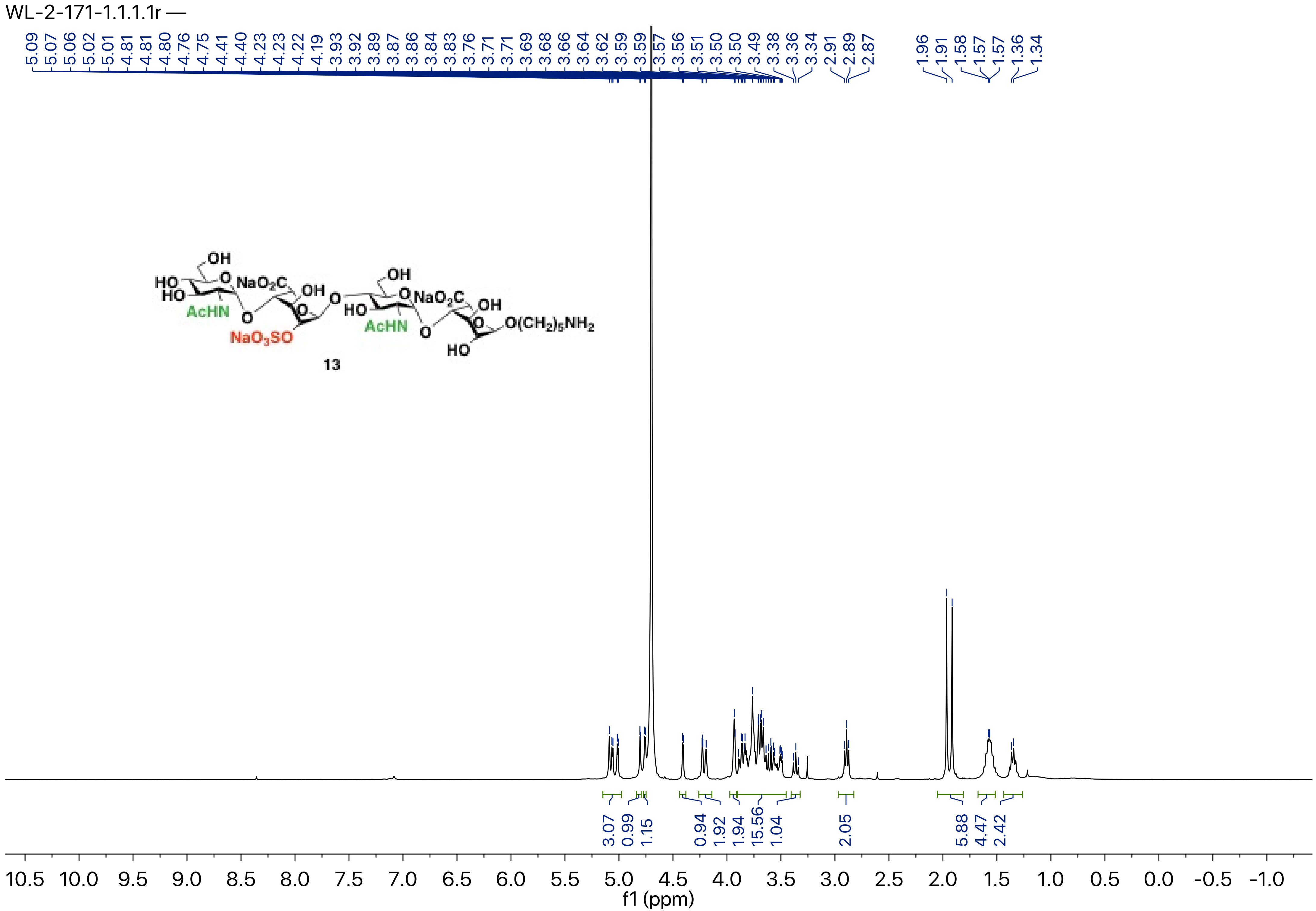


BSH-01-64.1.fid —

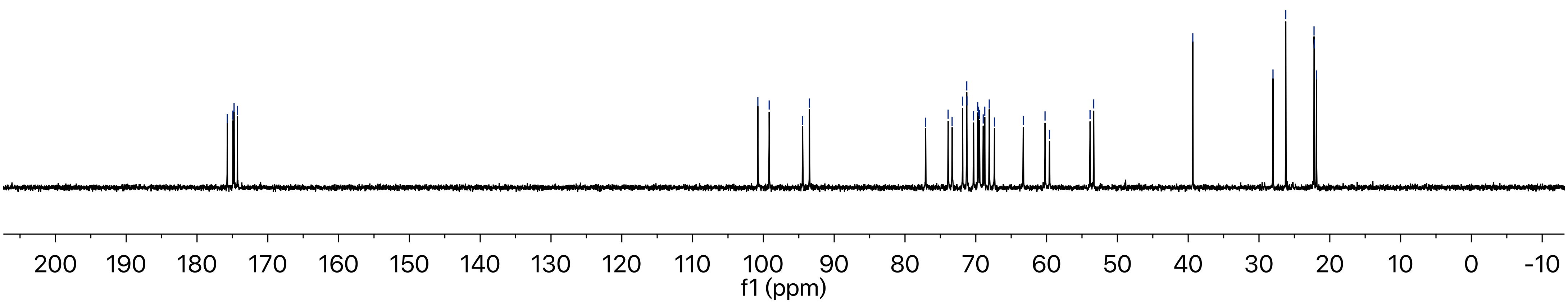


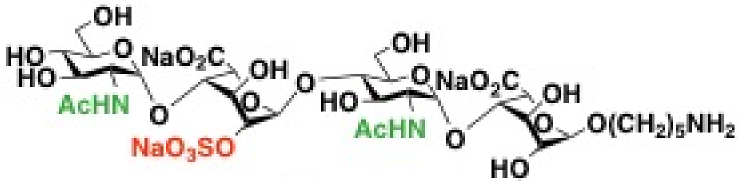
BSH-01-64.3.fid —




WL-2-171-1.1.1.1r
5.09 5.07 5.06 5.02 5.01 4.81 4.81 4.80 4.76 4.75 4.41 4.40 4.23 4.23 4.22 4.19 3.93 3.92 3.89 3.87 3.86 3.84 3.83 3.76 3.71 3.71 3.69 3.68 3.66 3.64 3.62 3.59 3.59 3.57 3.56 3.51 3.50 3.50 3.49 3.38 3.36 3.34 2.91 2.89 2.87 1.96 1.91 1.58 1.57 1.57 1.36 1.34
NaO2C
NaO3SO
AcHN
O(CH2)5NH2
13
3.07 0.99 1.15 0.94 1.92 1.94 15.56 1.04 2.05 5.88 4.47 2.42
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 -0.5 -1.0
f1 (ppm)

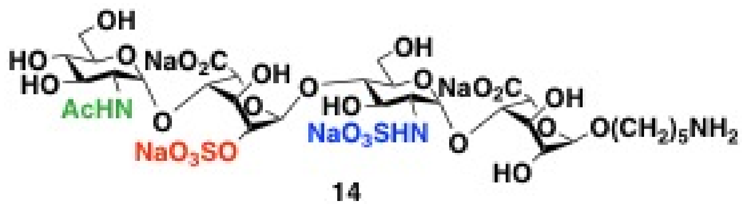
WL-2-171-D-NAc-C-2S-B-NAc-C-TC.1.1.1r



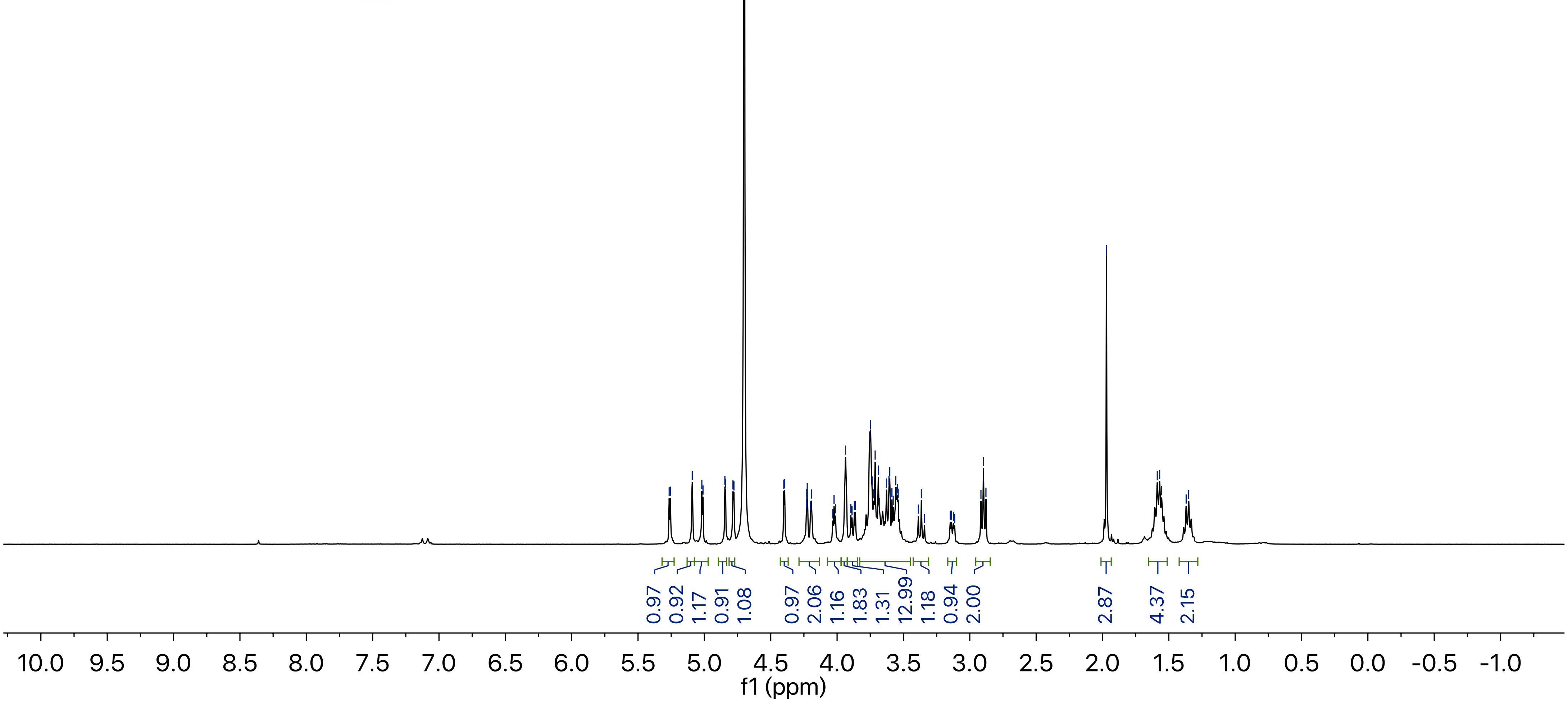


13

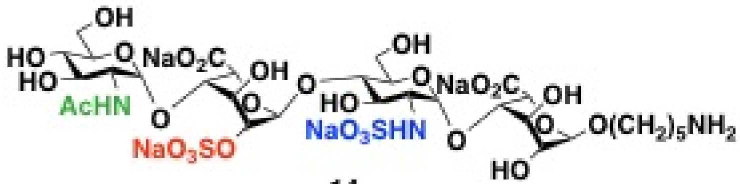
WL-2-172-D-NAc-C-2S-B-NS-H-TC.2.1.1r —



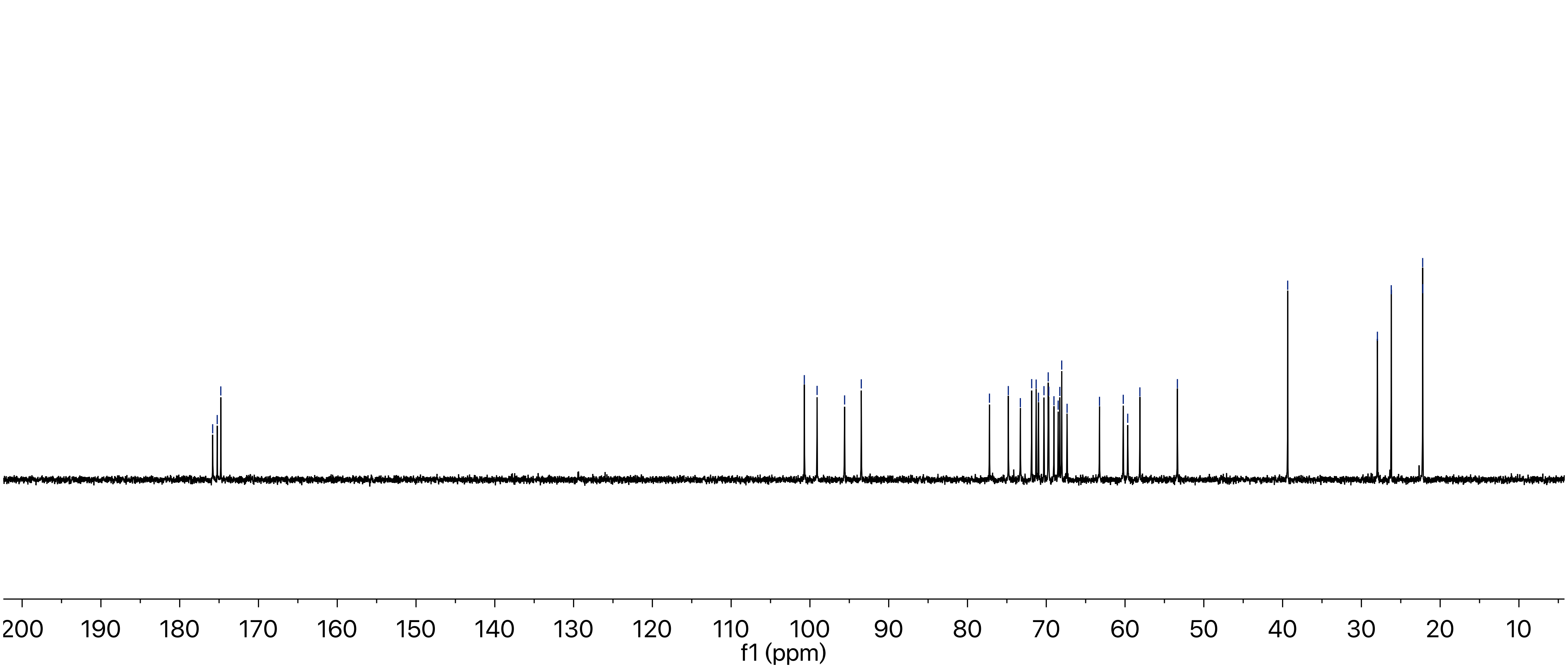
14



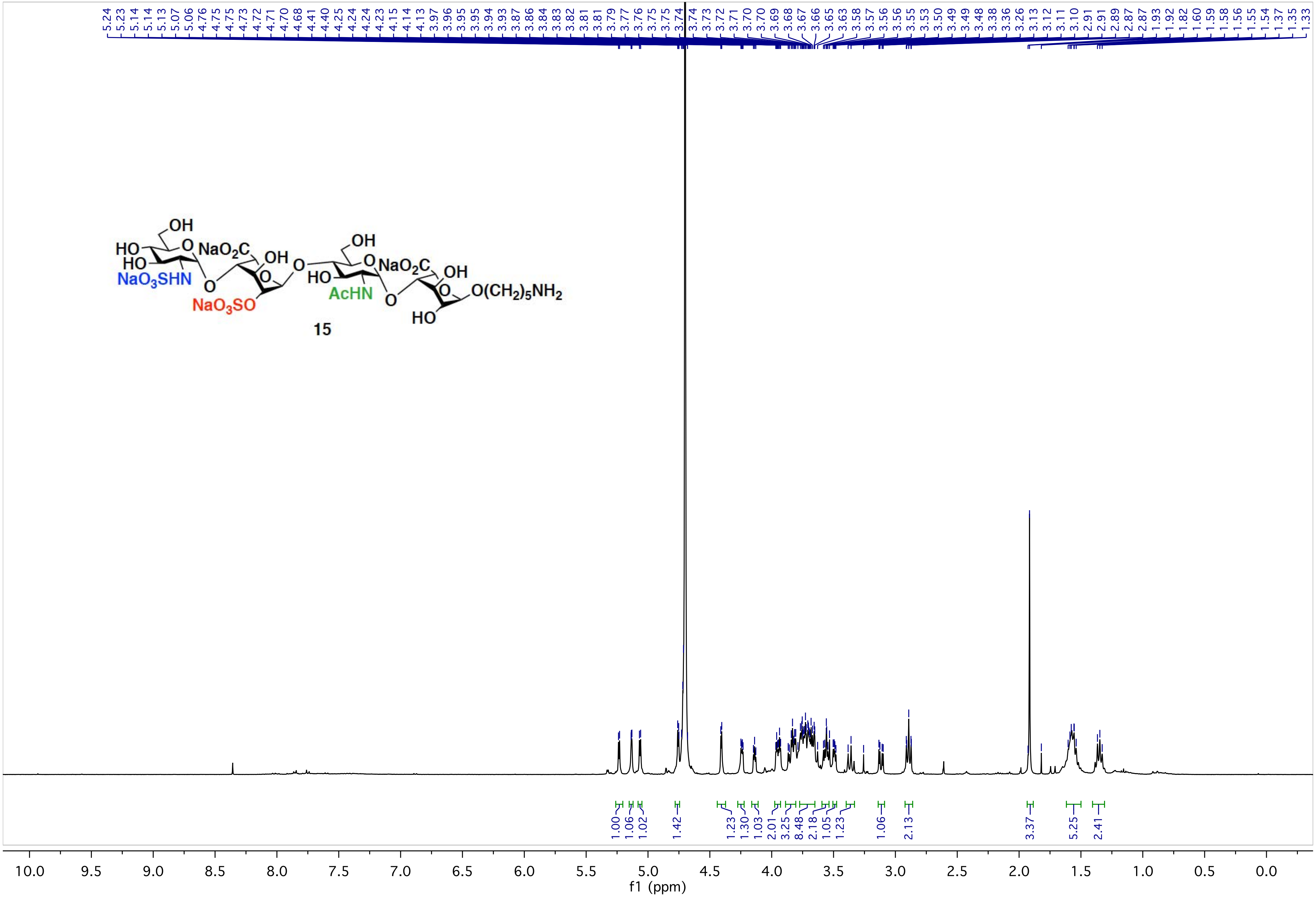
WL-2-172-D-NAc-C-2S-B-NS-C-TC.1.1.1r



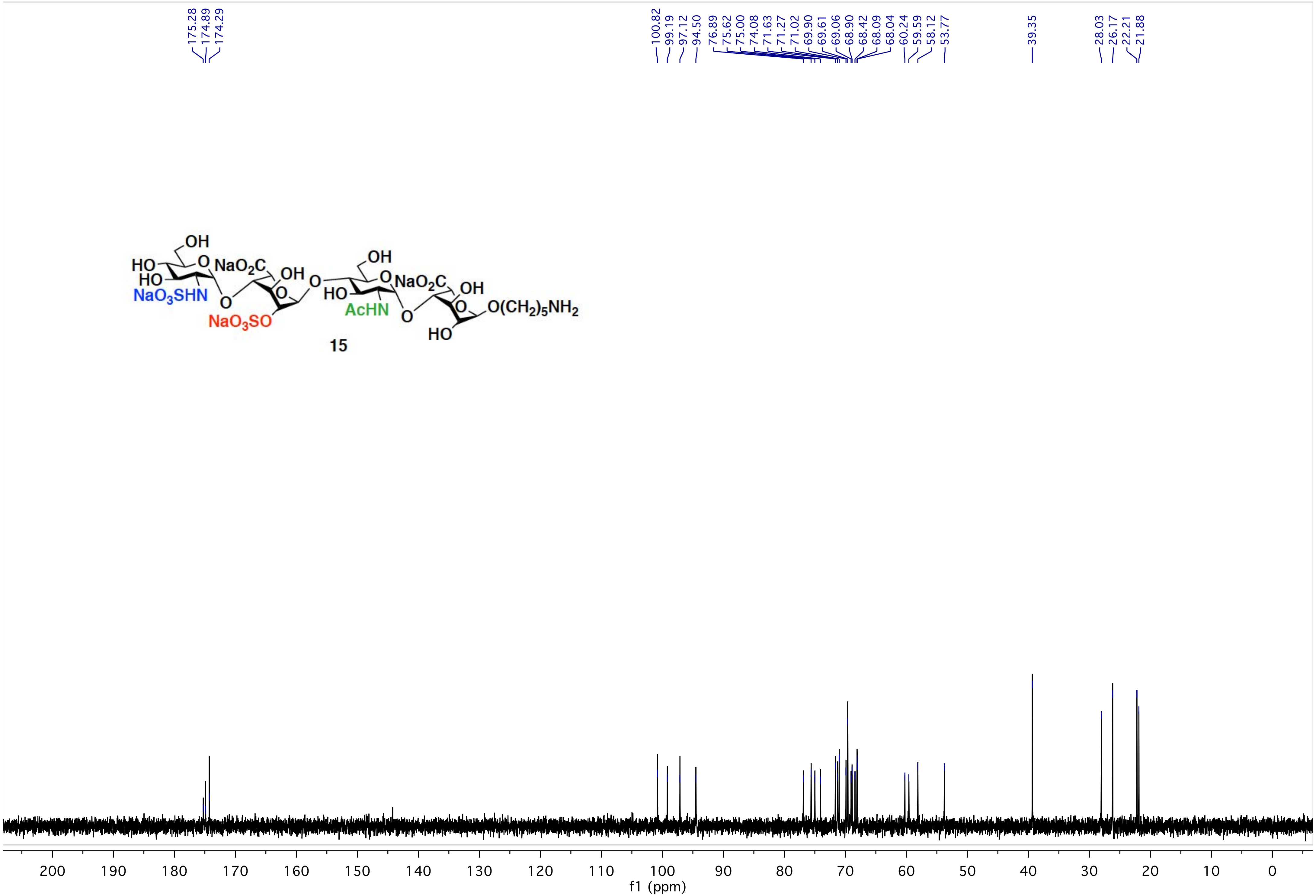
14



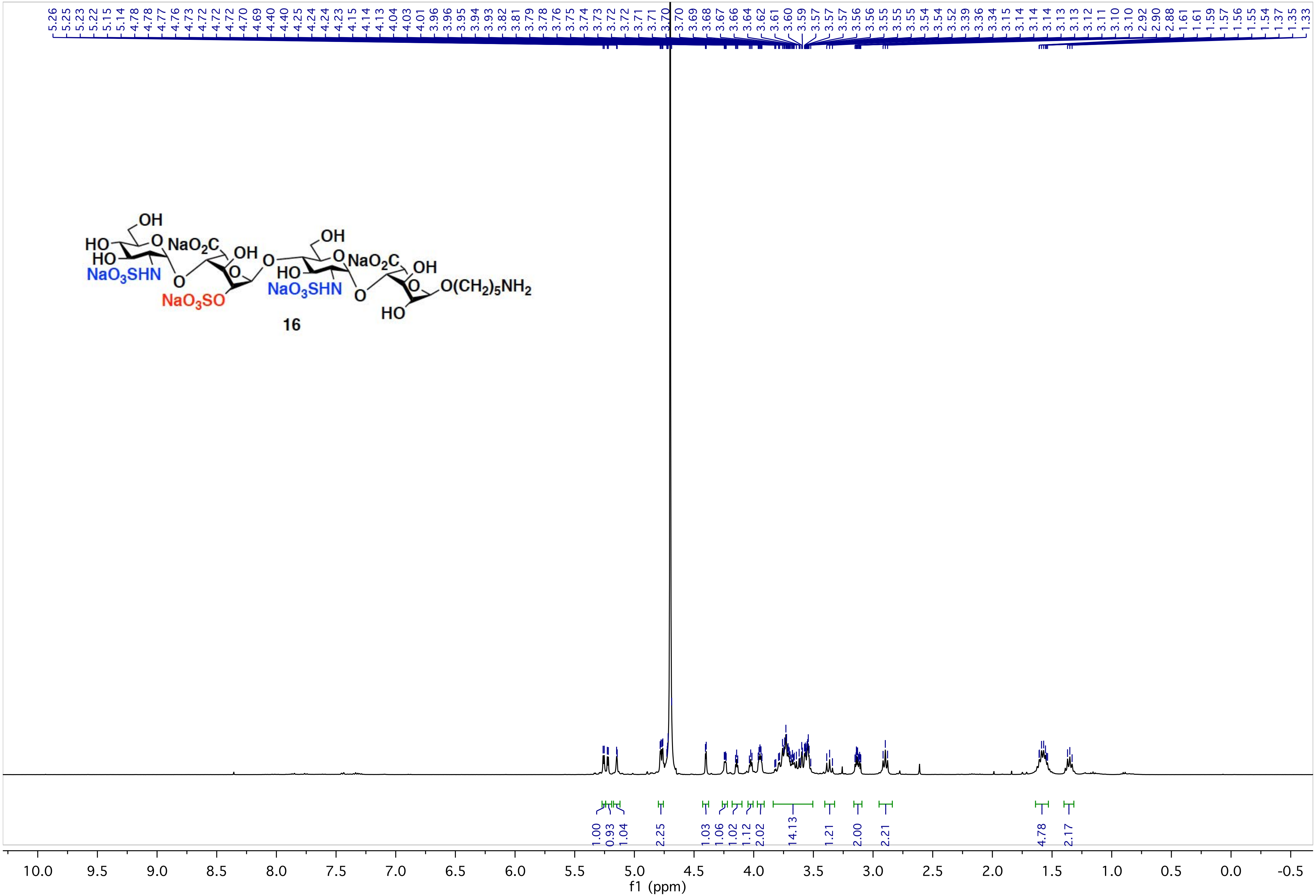
BSH-01-104.1.fid —



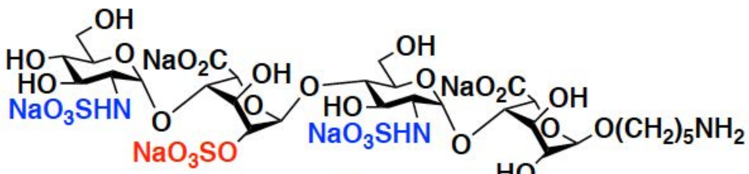
BSH-01-104.6.fid —



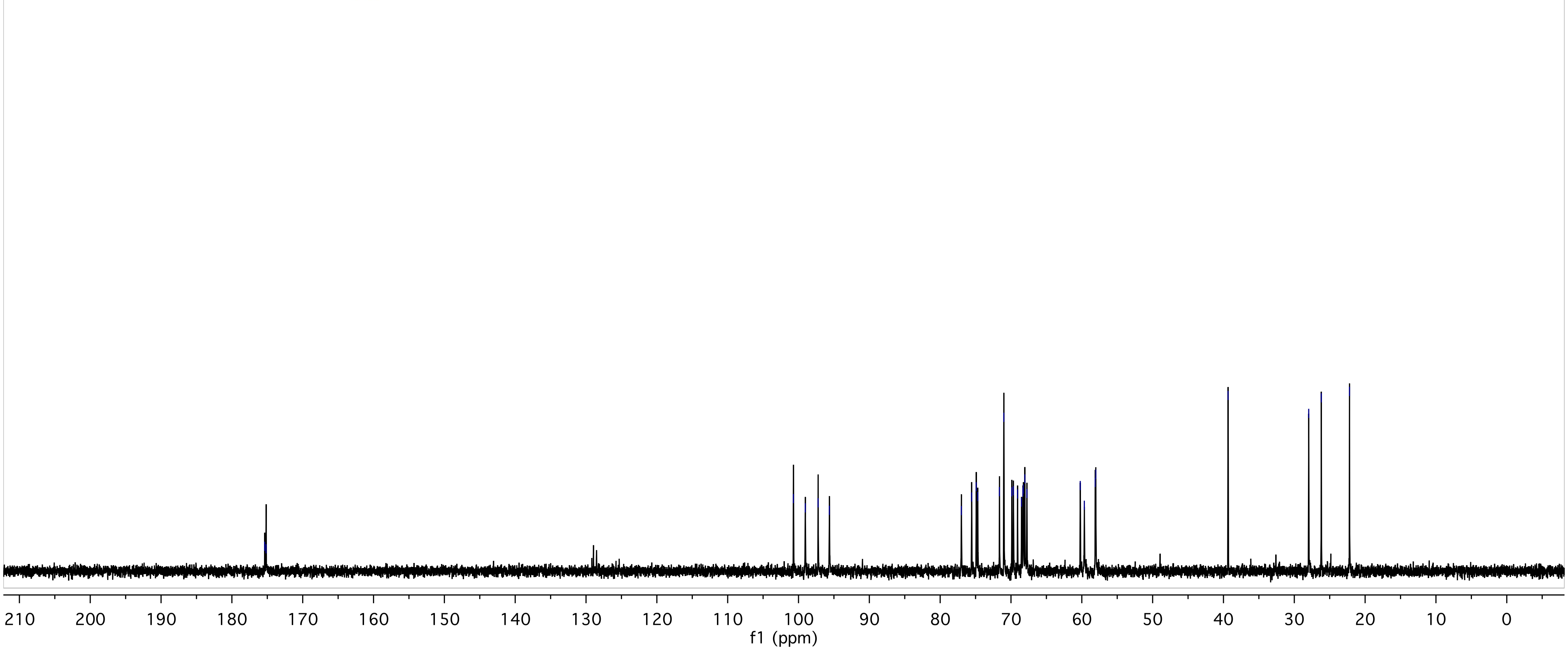
BSH-01-102-repurified.1.fid —

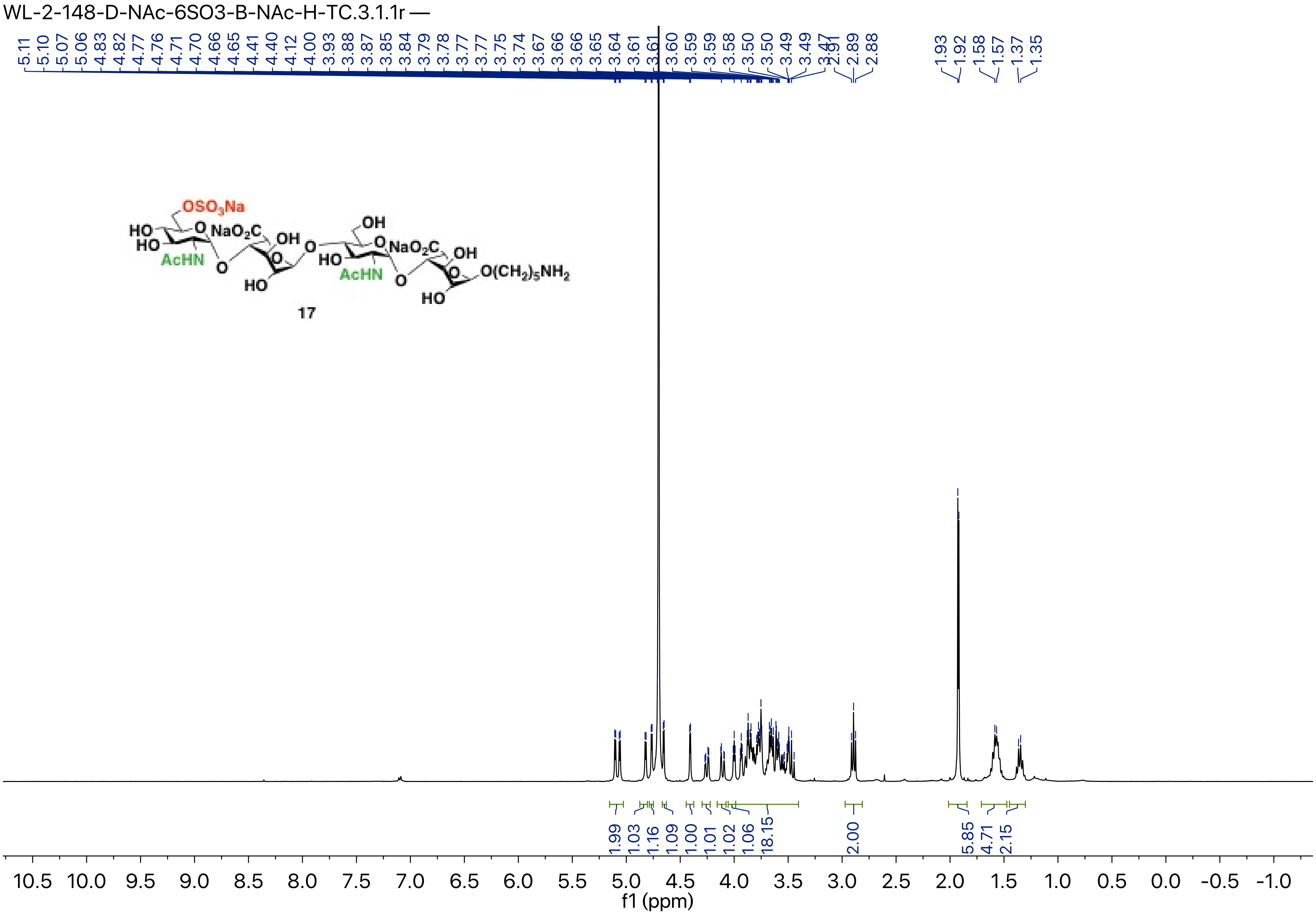


BSH-01-102-repurified.2.fid —



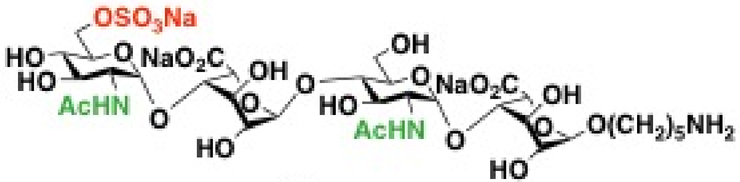
16



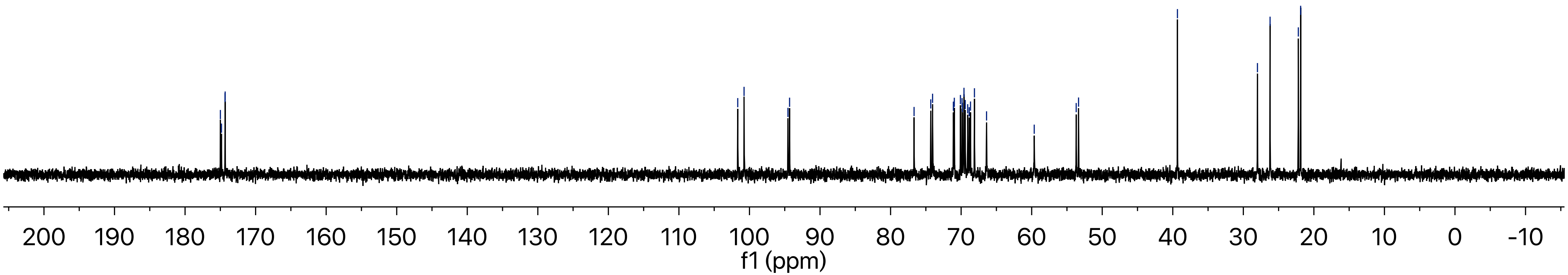

WL-2-148-D-NAc-6SO3-B-NAc-H-TC.3.1.1r
5.11 5.10 5.07 5.06 4.83 4.82 4.77 4.76 4.71 4.70 4.66 4.65 4.41 4.40 4.12 4.00 3.93 3.88 3.87 3.85 3.84 3.79 3.78 3.77 3.77 3.75 3.74 3.67 3.66 3.66 3.65 3.64 3.61 3.61 3.60 3.59 3.59 3.58 3.50 3.50 3.49 3.49 3.47 2.91 2.89 2.88 1.93 1.92 1.58 1.57 1.37 1.35
OSO3Na
HO
HO
AcHN
NaO2C
OH
HO
OH
HO
AcHN
NaO2C
OH
O(CH2)5NH2
HO
17
1.99 1.03 1.16 1.09 1.00 1.01 1.02 1.06 18.15 2.00 5.85 4.71 2.15
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 -0.5 -1.0
f1 (ppm)

WL-2-148-D-NAc-6SO3-B-NAc-C-TC.2.1.1r

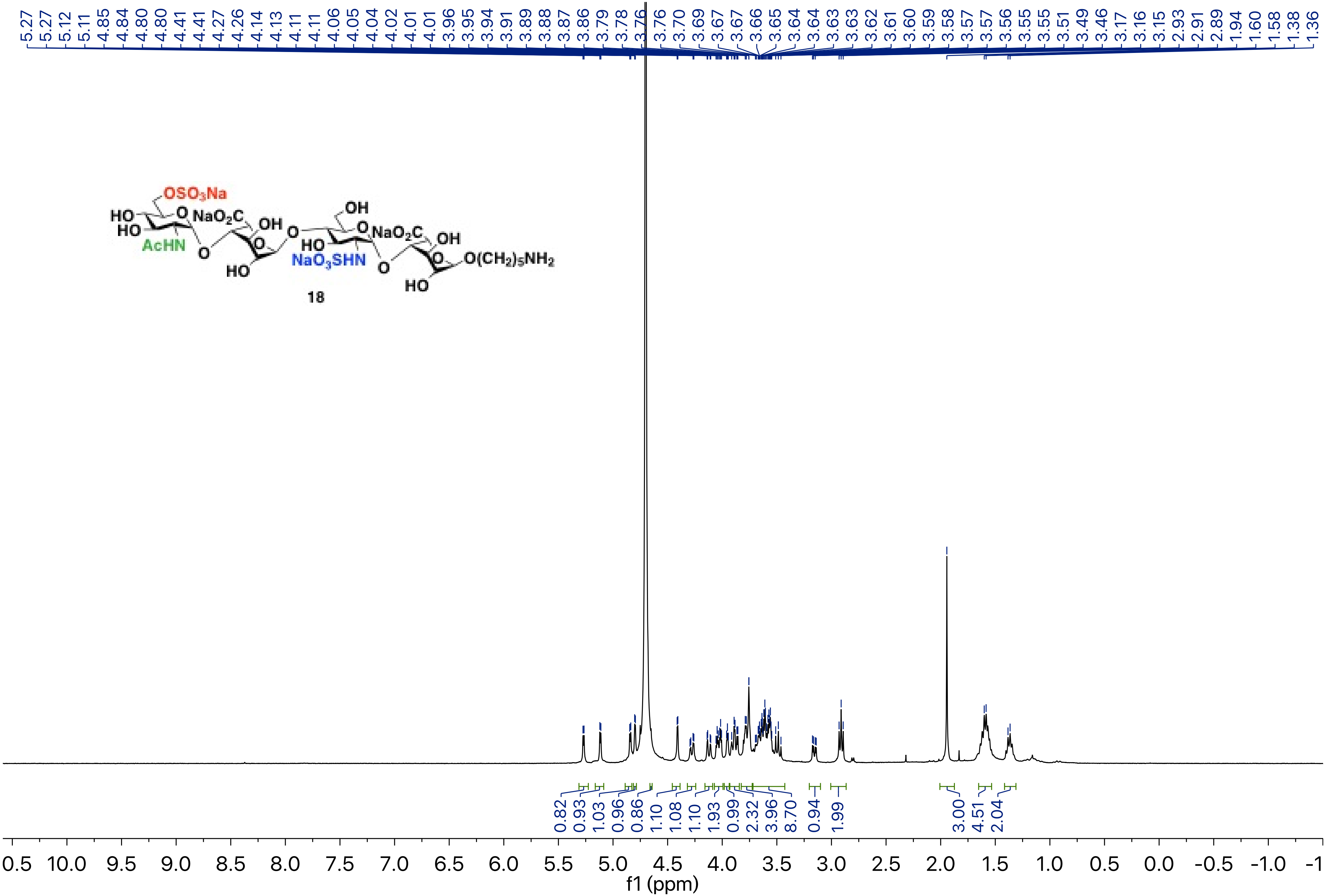
174.99
174.84
174.34
174.31
101.66
100.77
94.55
94.32
76.67
74.30
74.05
71.10
70.97
70.10
69.87
69.81
69.59
69.42
69.07
68.86
68.67
68.11
66.40
59.64
53.69
53.35
39.34
28.00
26.21
22.20
21.88



17

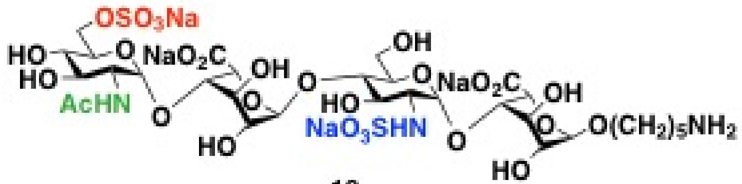


WL-2-062-F-Pd-D-6-OS3-NAc-B-2-NSO3-H.1.1.1r —

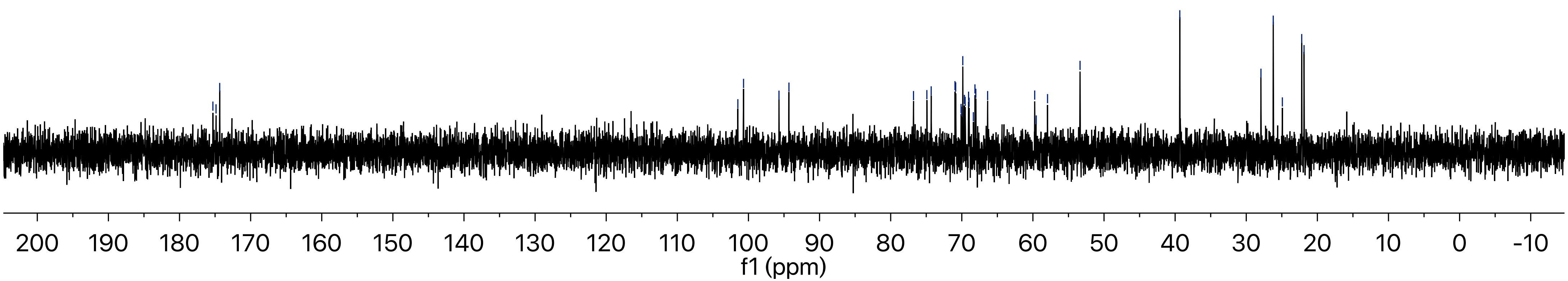


WL-2-062-F-Pd-D-6-SO3-NAc-B-NSO3.1.1.1r

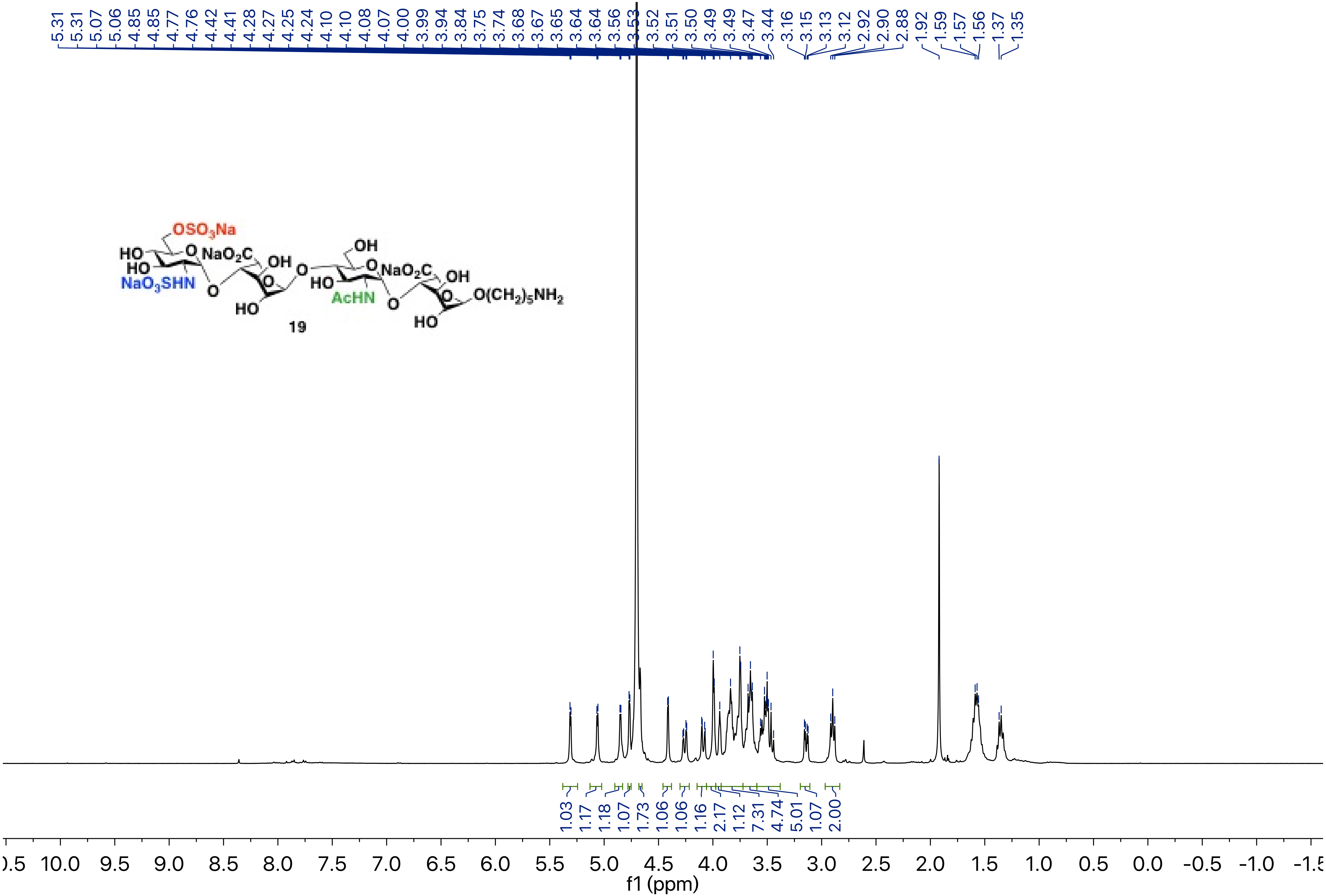
175.31 174.86 174.35 101.49 100.69 95.71 94.31 76.79 74.91 74.30 70.96 70.86 70.10 70.04 69.86 69.63 69.53 69.05 68.97 68.38 68.15 68.03 66.37 59.75 59.53 57.94 53.37 39.35 27.93 26.21 24.92 22.20 21.87



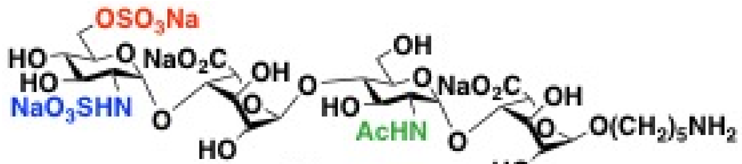
18



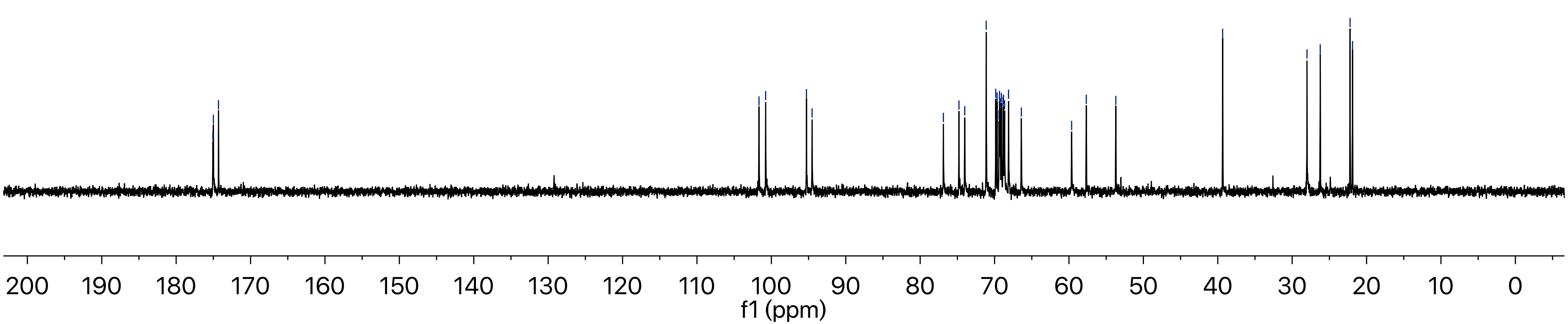
WL-2-248-D-6S-NS-B-NAc-Prod-H-TC.1.1.1r —



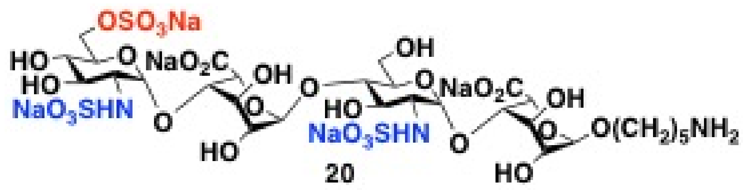
WL-2-248-D-6S-NS-B-NAc-Prod-C-TC.1.1.1r



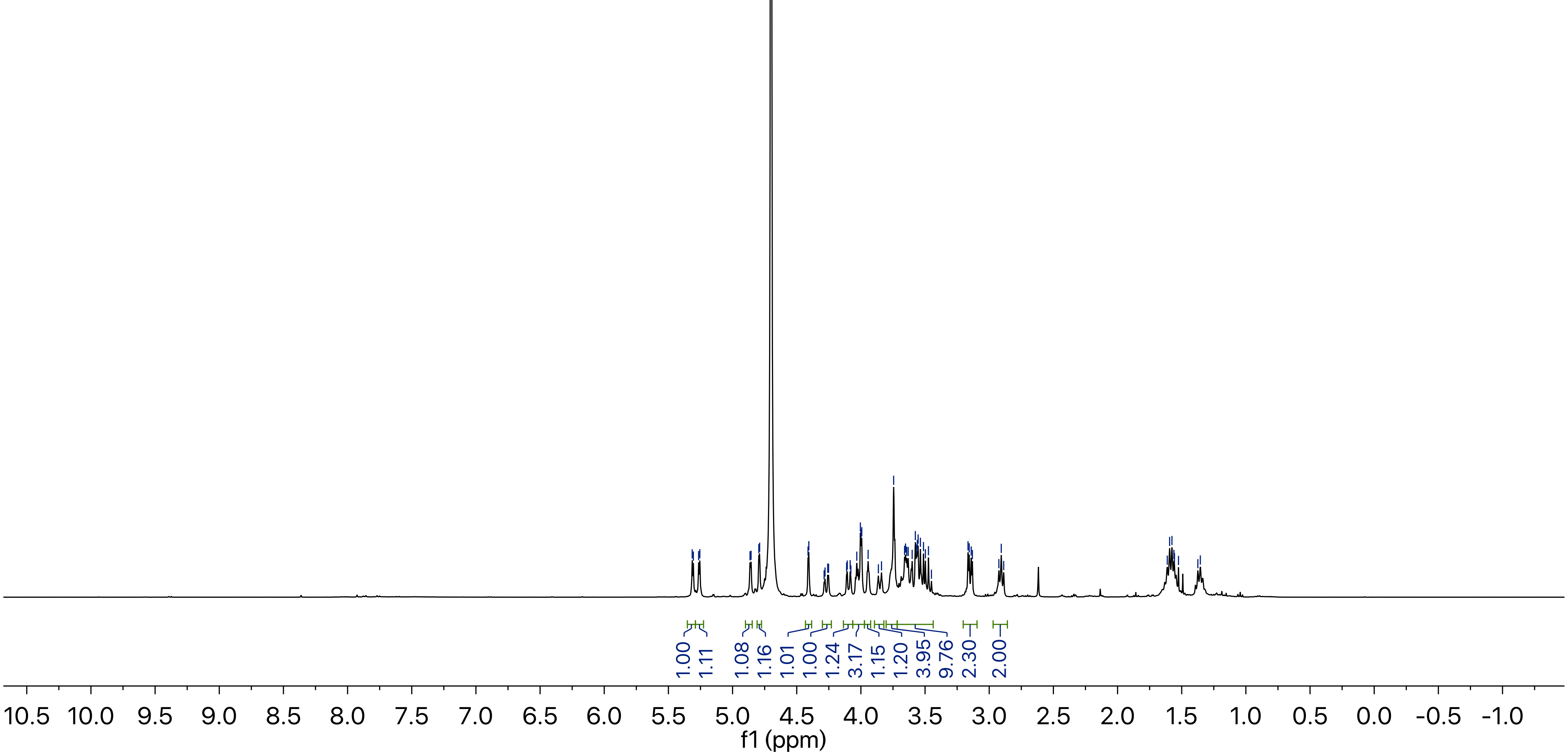
19



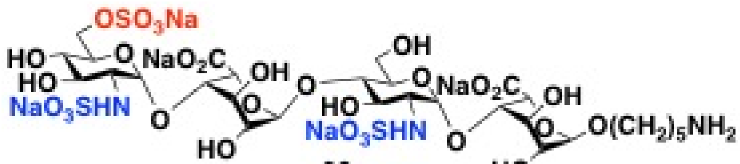
WL-2-245-D-6S-NS-B-NS-prod-H-TC.1.1.1r —



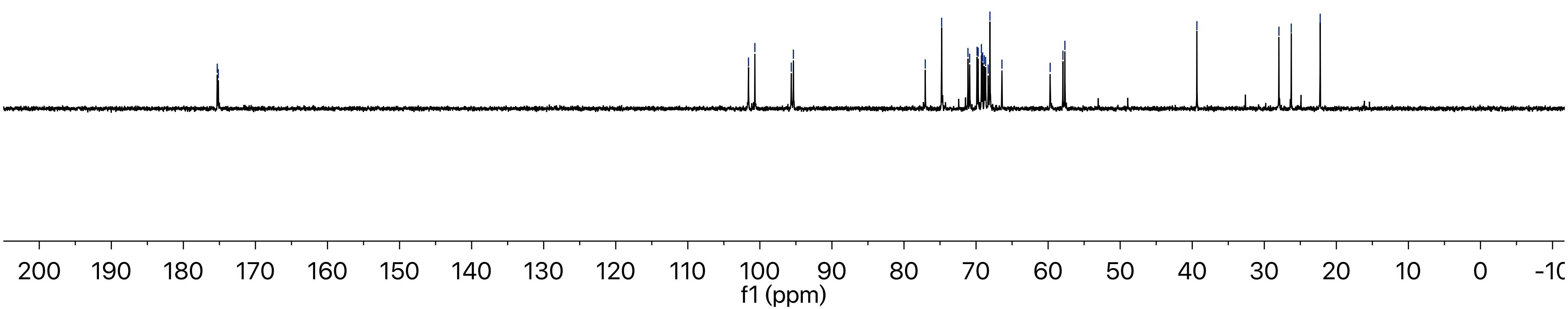
20



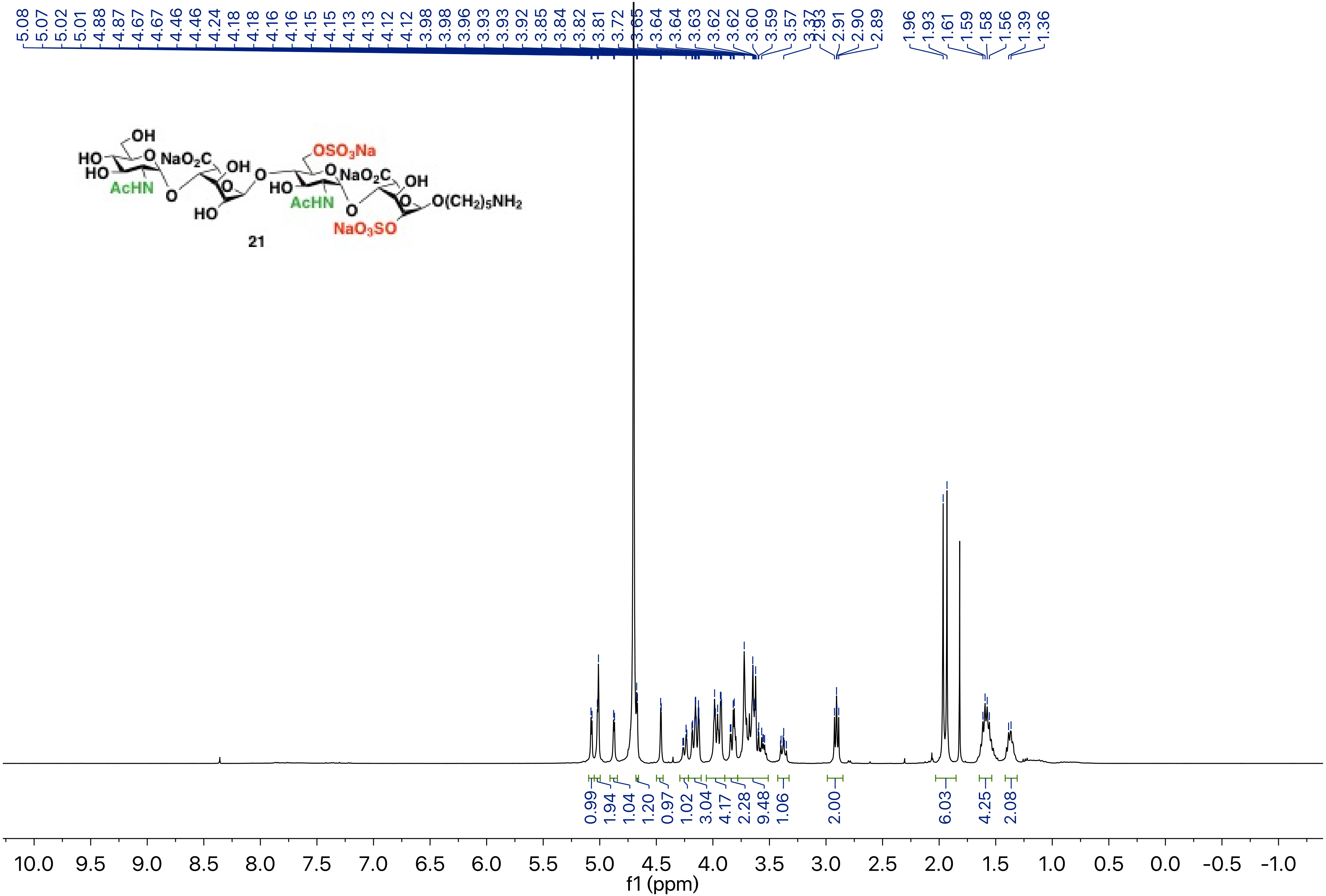
WL-2-245-D-6S-NS-B-NS-Prod-C-TC.1.1.1r



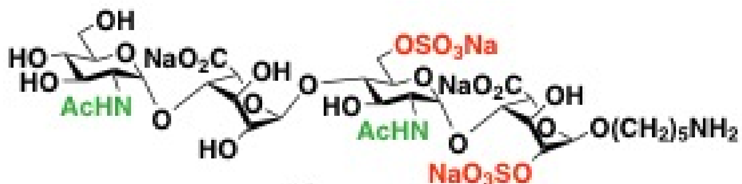
20



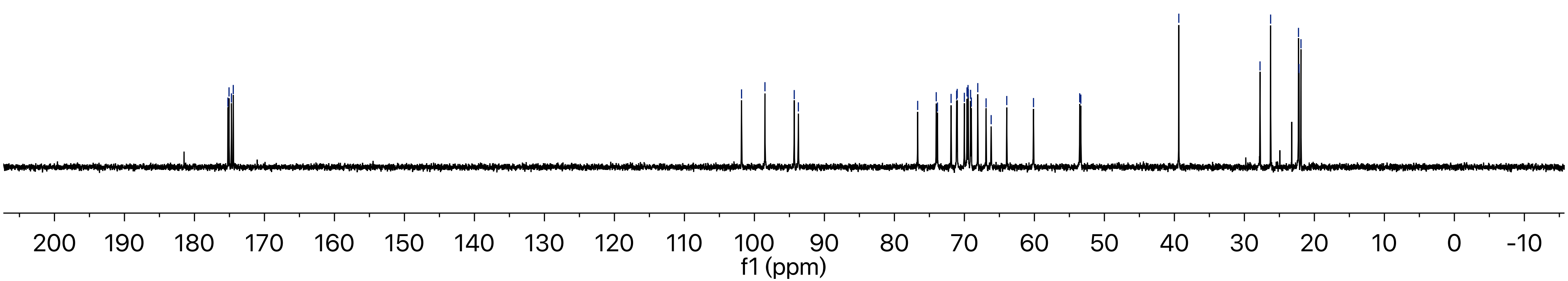
WL-2-261-run2.1.1.1r —



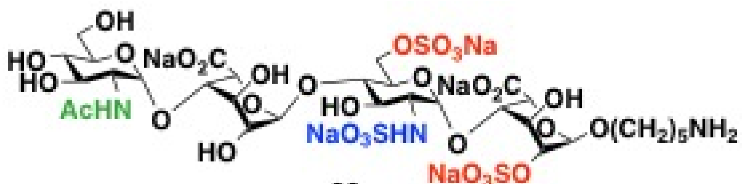
WL-2-261-run2-D-NAc-B-NAc-6S-A-2S-C-TC.8.1.1r



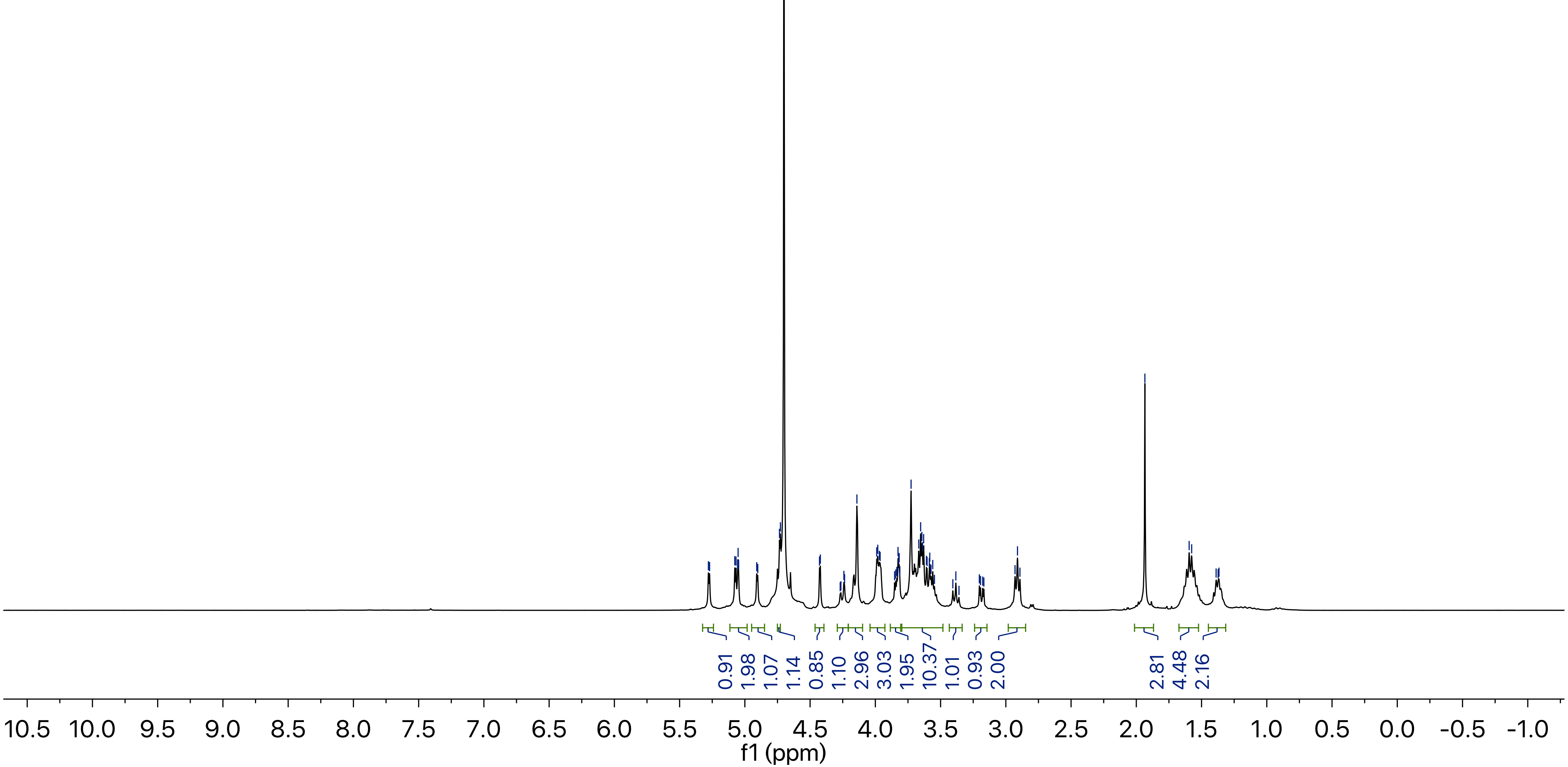
21



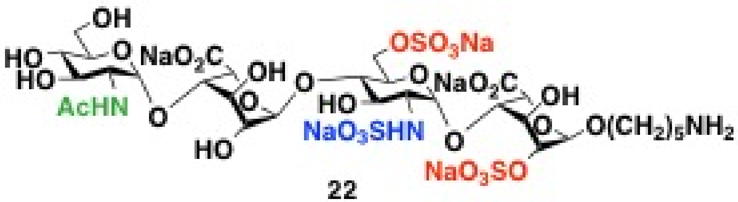
WL-2-267-D-NAc-B-NS-6S-A-2S-H-TC.7.1.1r



22



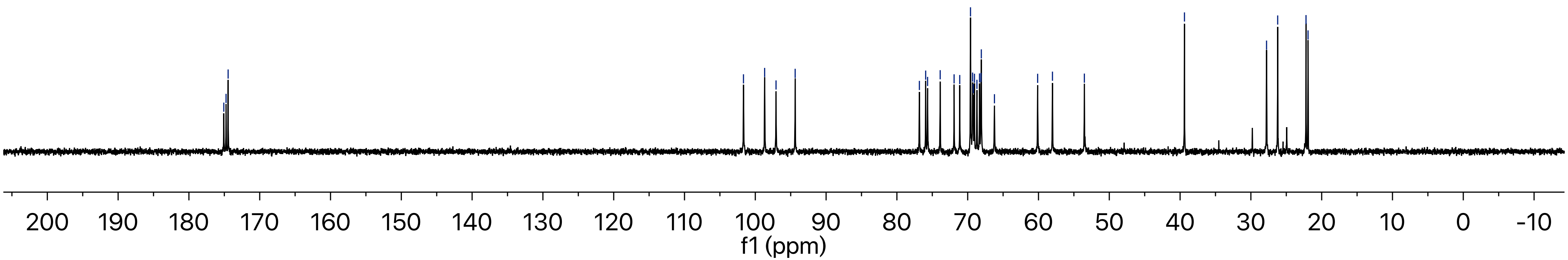
WL-2-267-D-NAc-B-NS-6S-A-2S-C-TC.1.1.1r —



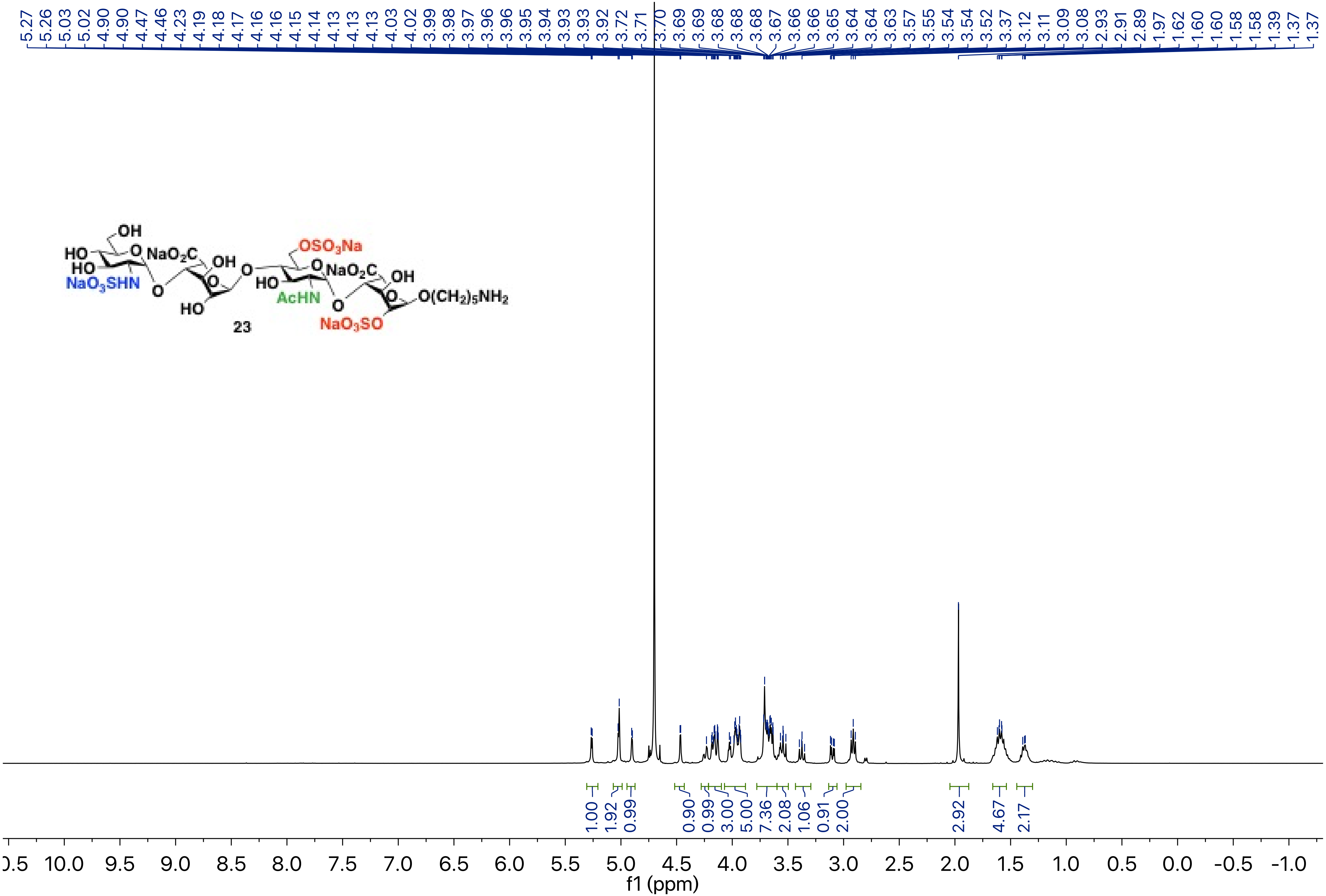
22

175.07
174.75
174.46

101.67
98.68
97.07
94.37
76.82
75.94
75.66
73.89
71.92
71.12
69.60
69.31
69.22
69.05
68.70
68.33
68.12
68.08
66.22
60.12
58.03
53.52
39.38
27.79
26.21
22.21
21.93

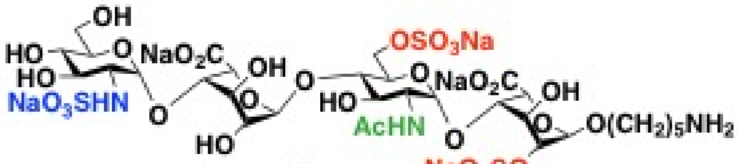


WL-2-286-D-NS-B-BAc-6S-A-2S-H-TC.6.1.1r —

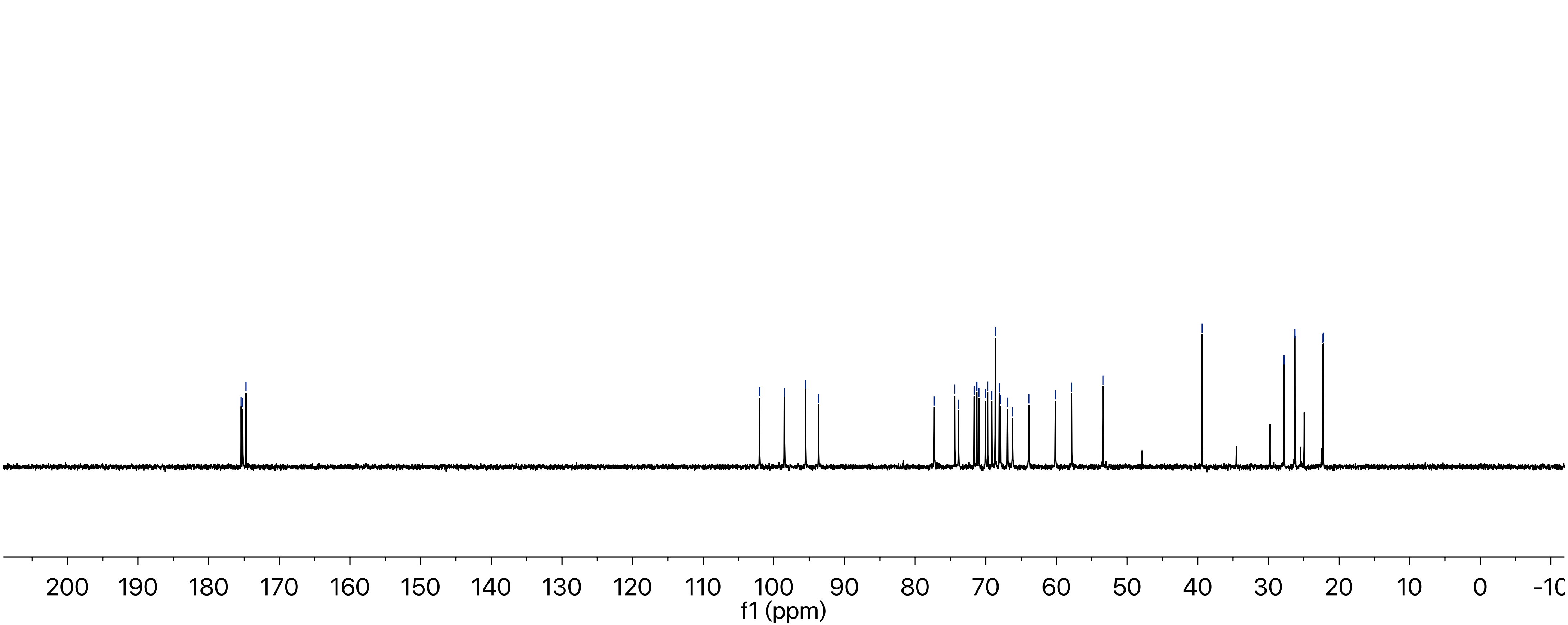


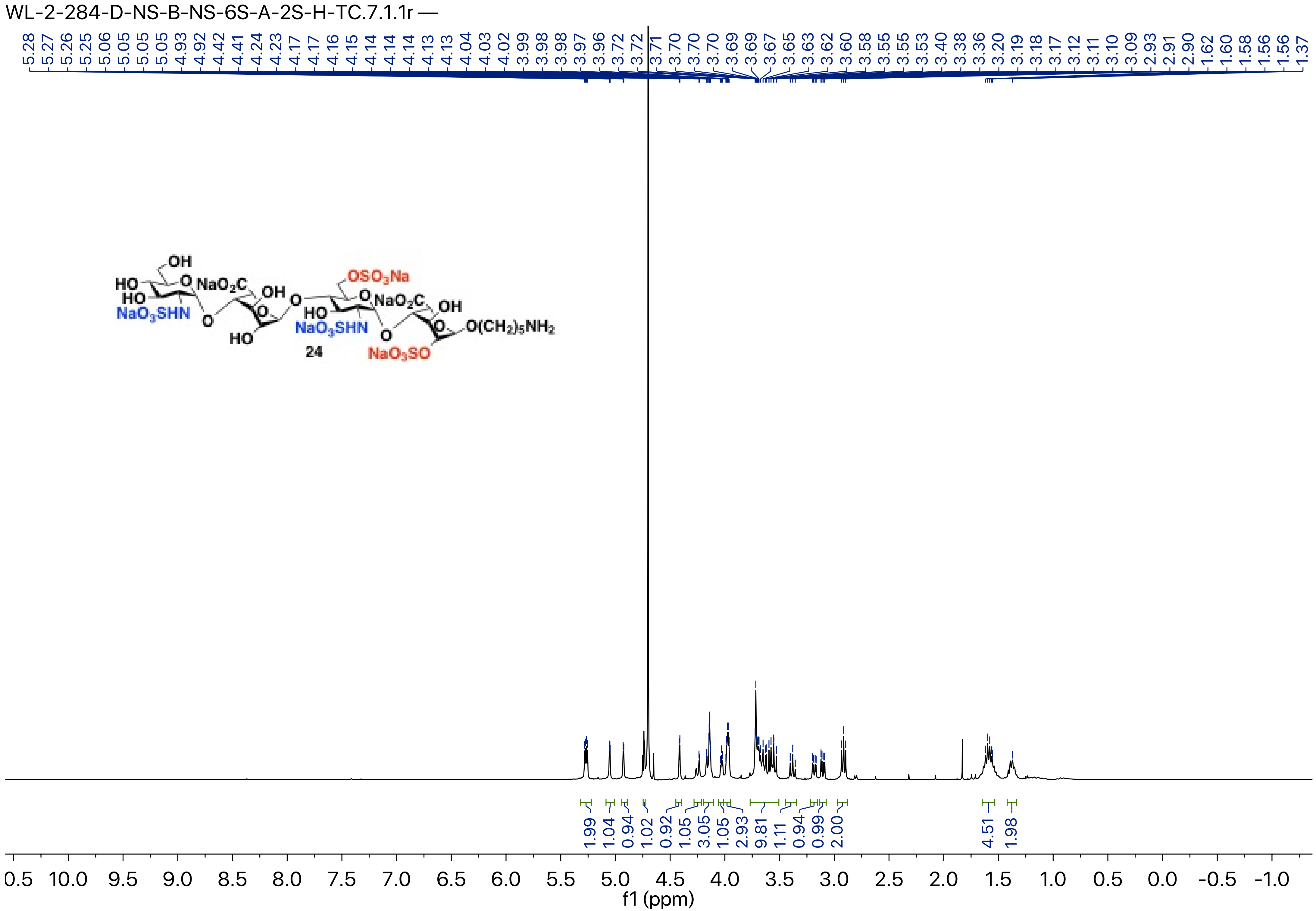
23

WL-2-286-D-NS-B-BAc-6S-A-2S-C-TC.1.1.1r —

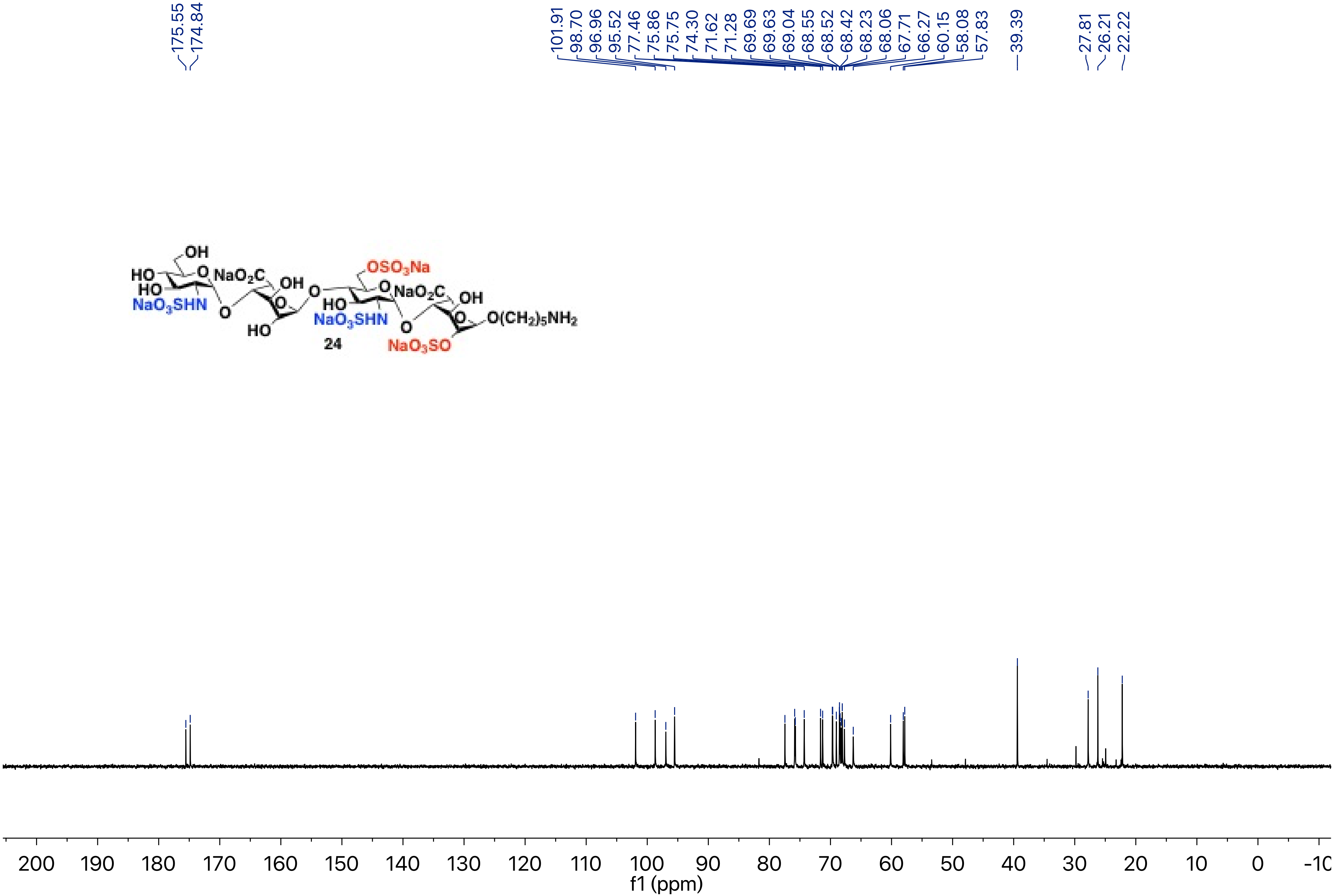


23

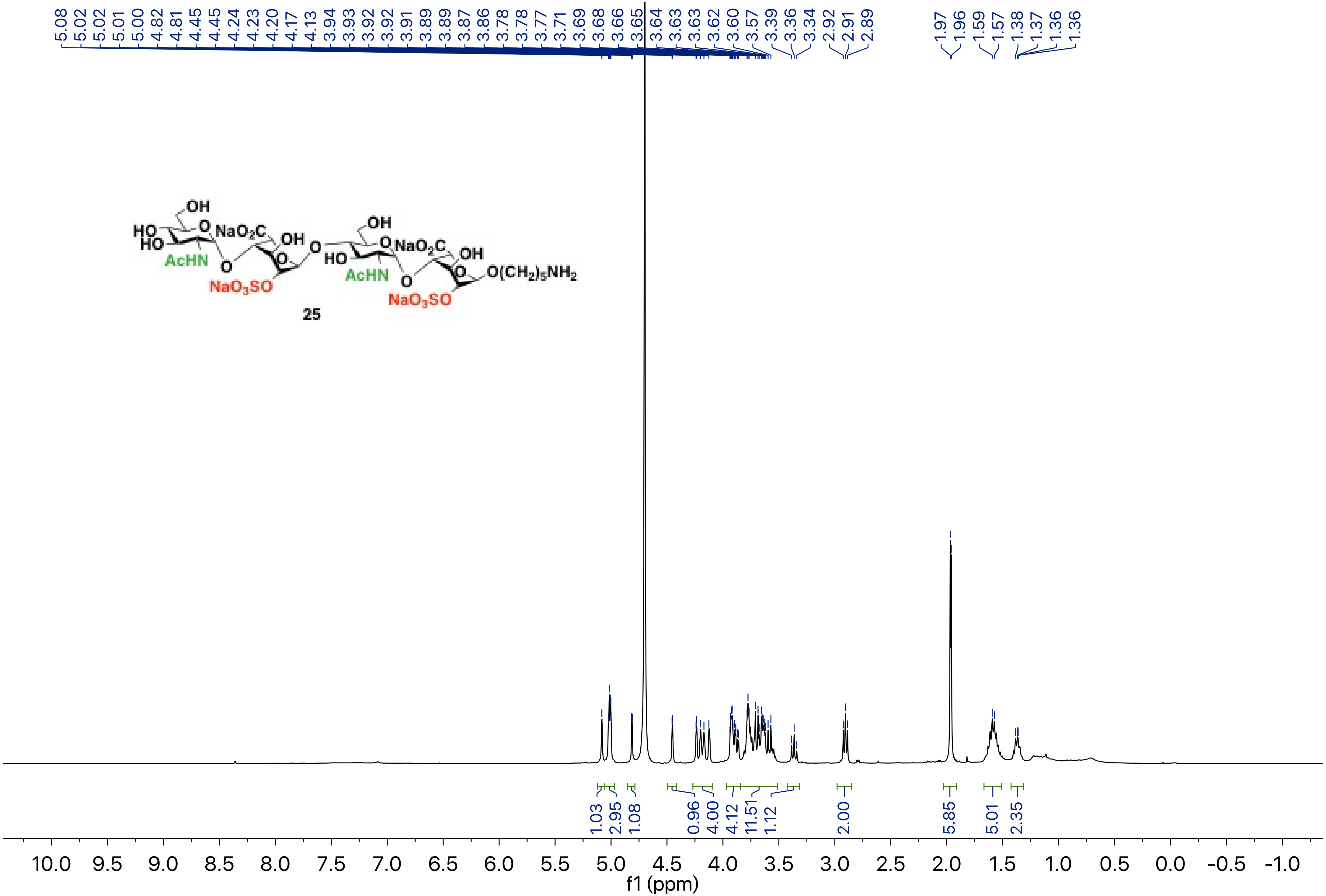



WL-2-284-D-NS-B-NS-6S-A-2S-H-TC.7.1.1r
5.28 5.27 5.26 5.25 5.06 5.05 5.05 5.05 4.93 4.92 4.42 4.41 4.24 4.23 4.17 4.17 4.16 4.15 4.14 4.14 4.14 4.13 4.13 4.04 4.03 4.02 3.99 3.98 3.98 3.97 3.96 3.72 3.72 3.71 3.70 3.70 3.70 3.69 3.69 3.67 3.65 3.63 3.62 3.60 3.58 3.55 3.55 3.53 3.40 3.38 3.36 3.20 3.19 3.18 3.17 3.12 3.11 3.10 3.09 2.93 2.91 2.90 1.62 1.60 1.58 1.56 1.56 1.37
OH
HO
HO
NaO3SHN
O
NaO2C
OH
O
HO
OSO3Na
NaO2C
OH
HO
NaO3SHN
NaO3SO
O(CH2)5NH2
24
1.99 1.04 0.94 1.02 0.92 1.05 3.05 1.05 2.93 9.81 1.11 0.94 0.99 2.00 4.51 1.98
0.5 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 -0.5 -1.0
f1 (ppm)

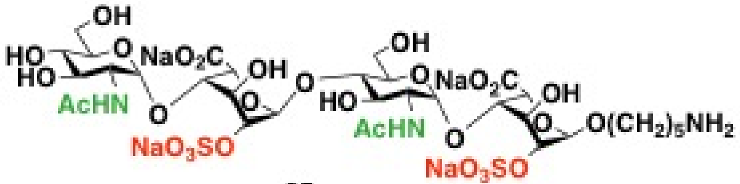
WL-2-284-D-NS-B-NS-6S-A-2S-C-TC.1.1.1r —



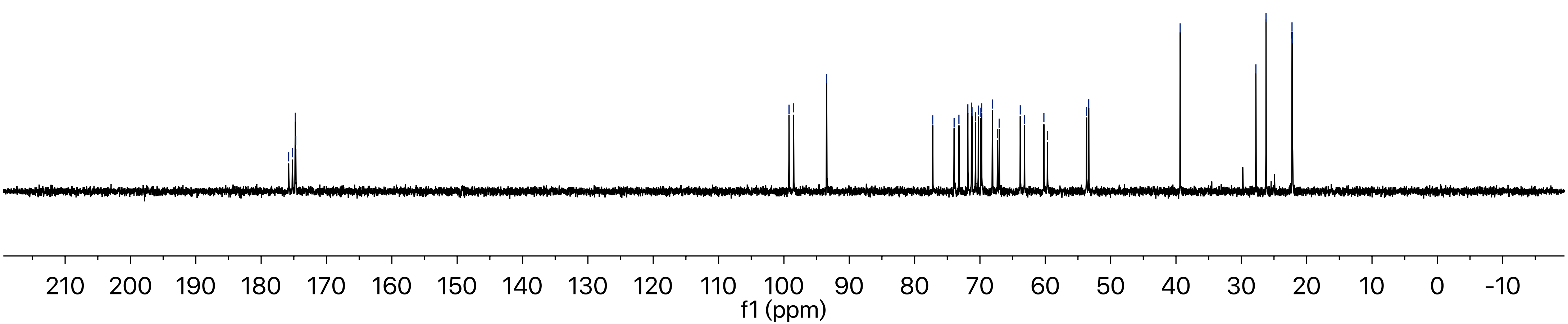
WL-2-137-D-NAc-C-2SO3-B-NAc-A-2SO3-H.1.1.1r



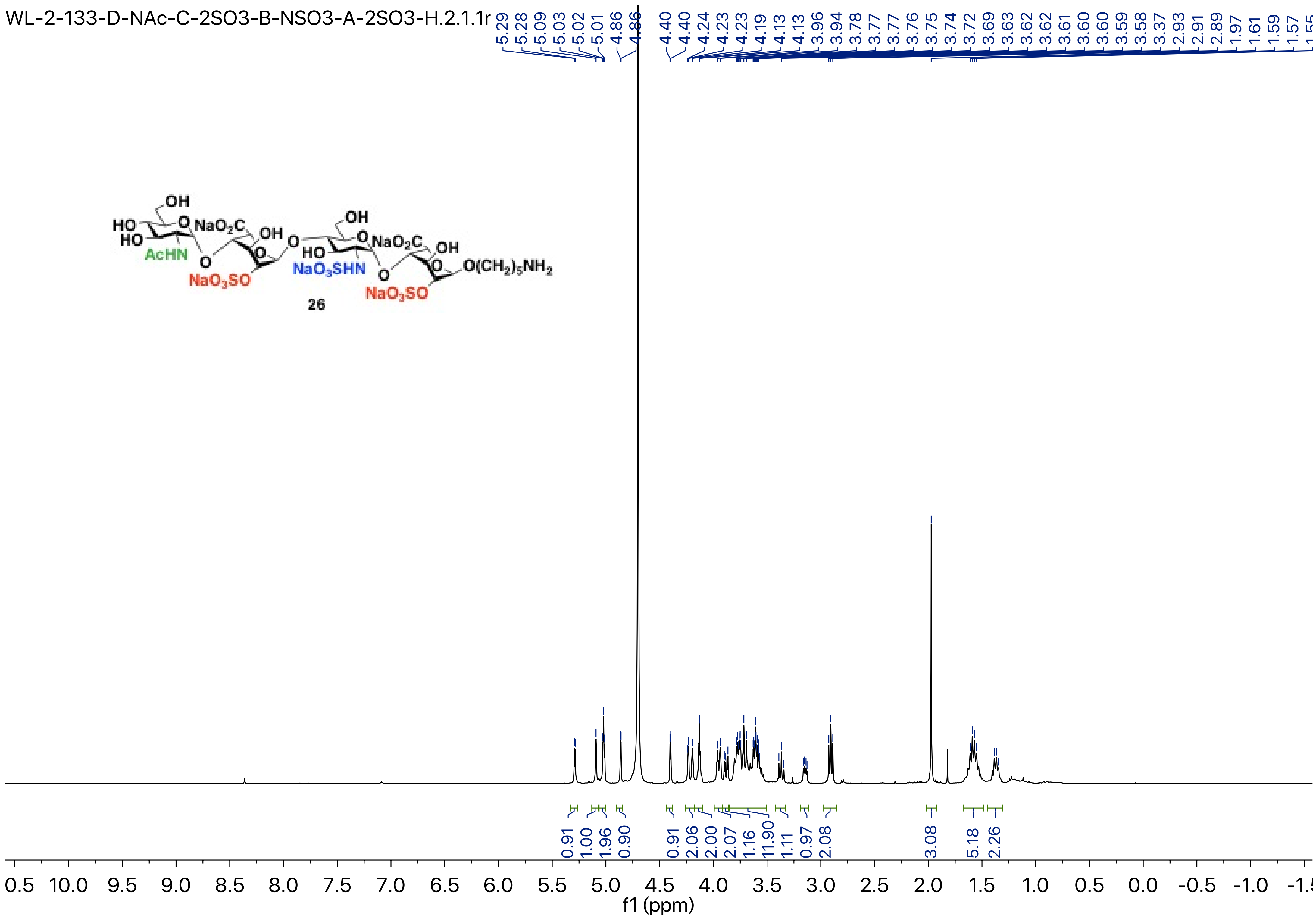
WL-2-137-D-NAc-C-2SO3-B-NAc-A-2SO3-C.1.1.1r



25

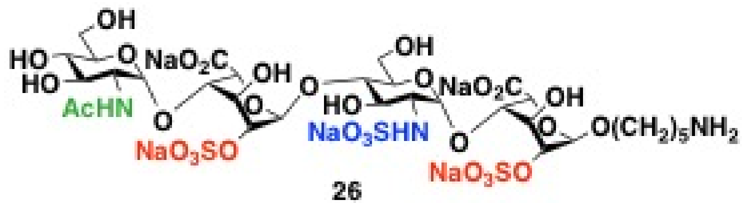


WL-2-133-D-NAc-C-2SO3-B-NSO3-A-2SO3-H.2.1.1r

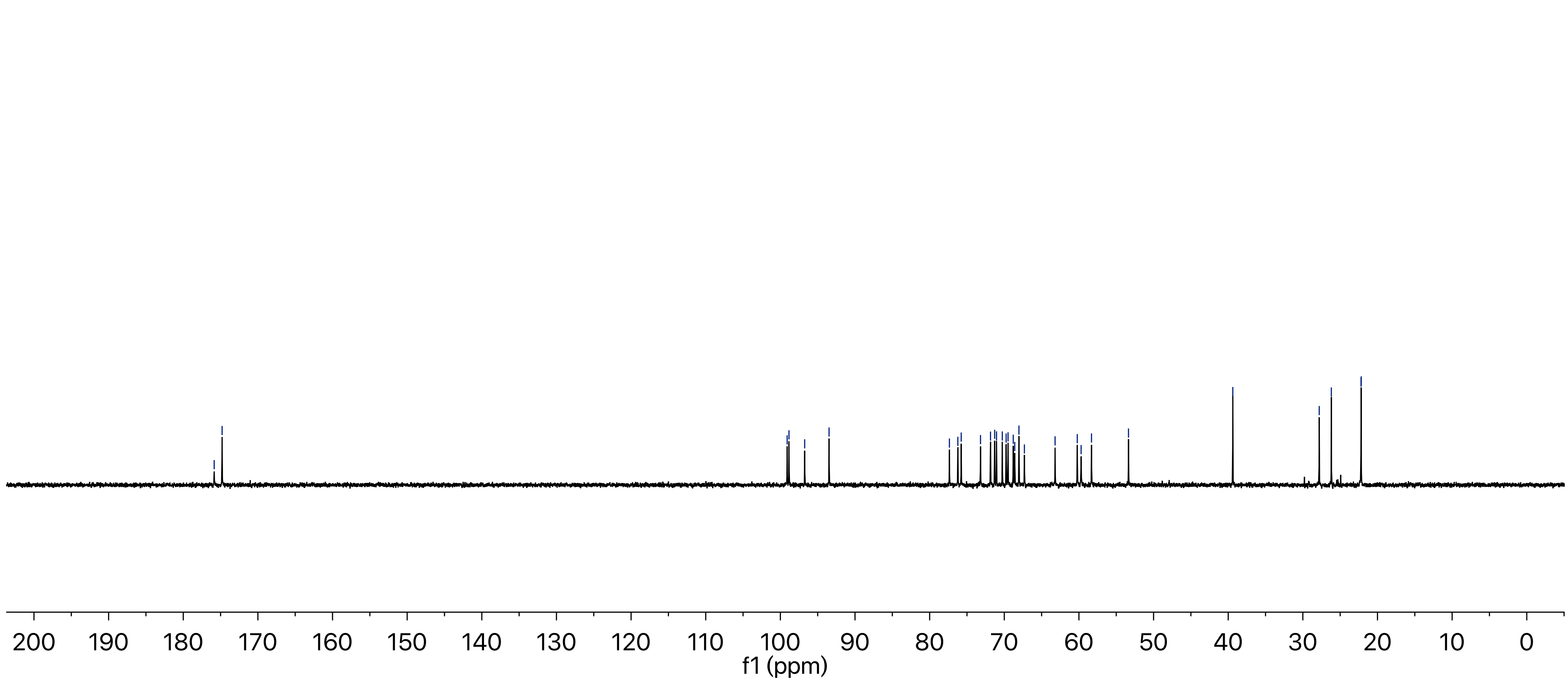


26

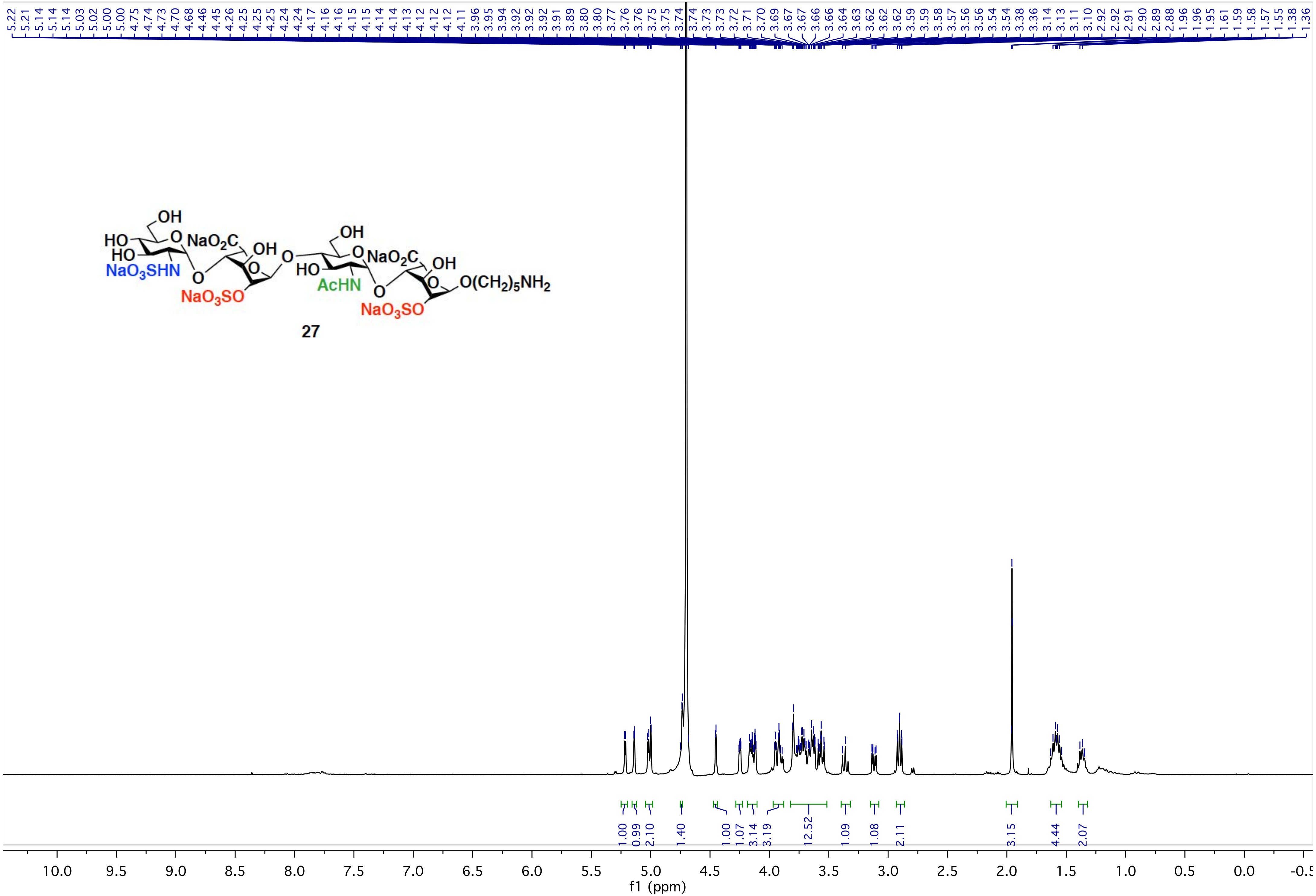
WL-2-133-D-NAc-C-2SO3-B-NSO3-A-2SO3-C.1.1.1r



26

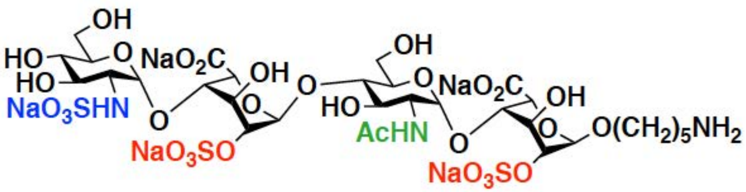


BSH-02-50.1.fid —

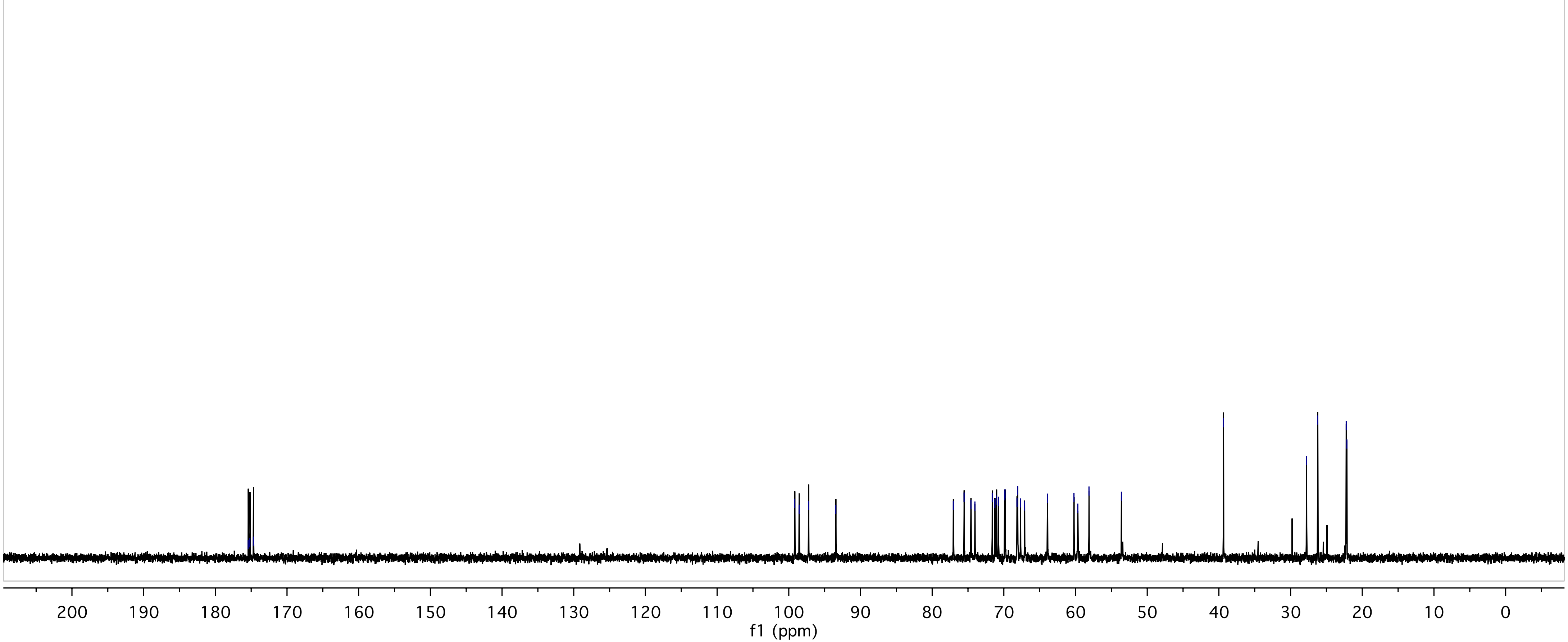


27

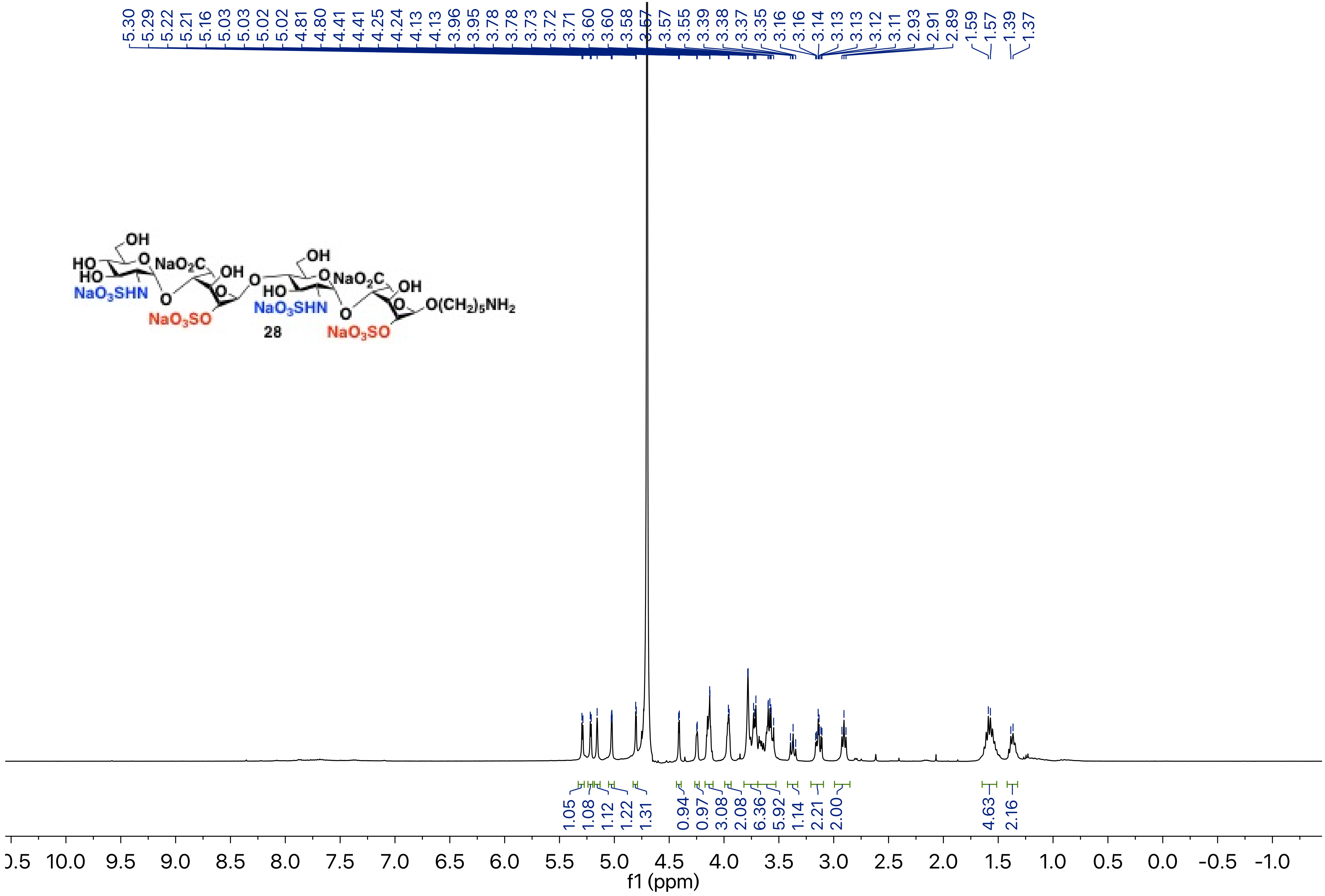
BSH-02-50.2.fid —



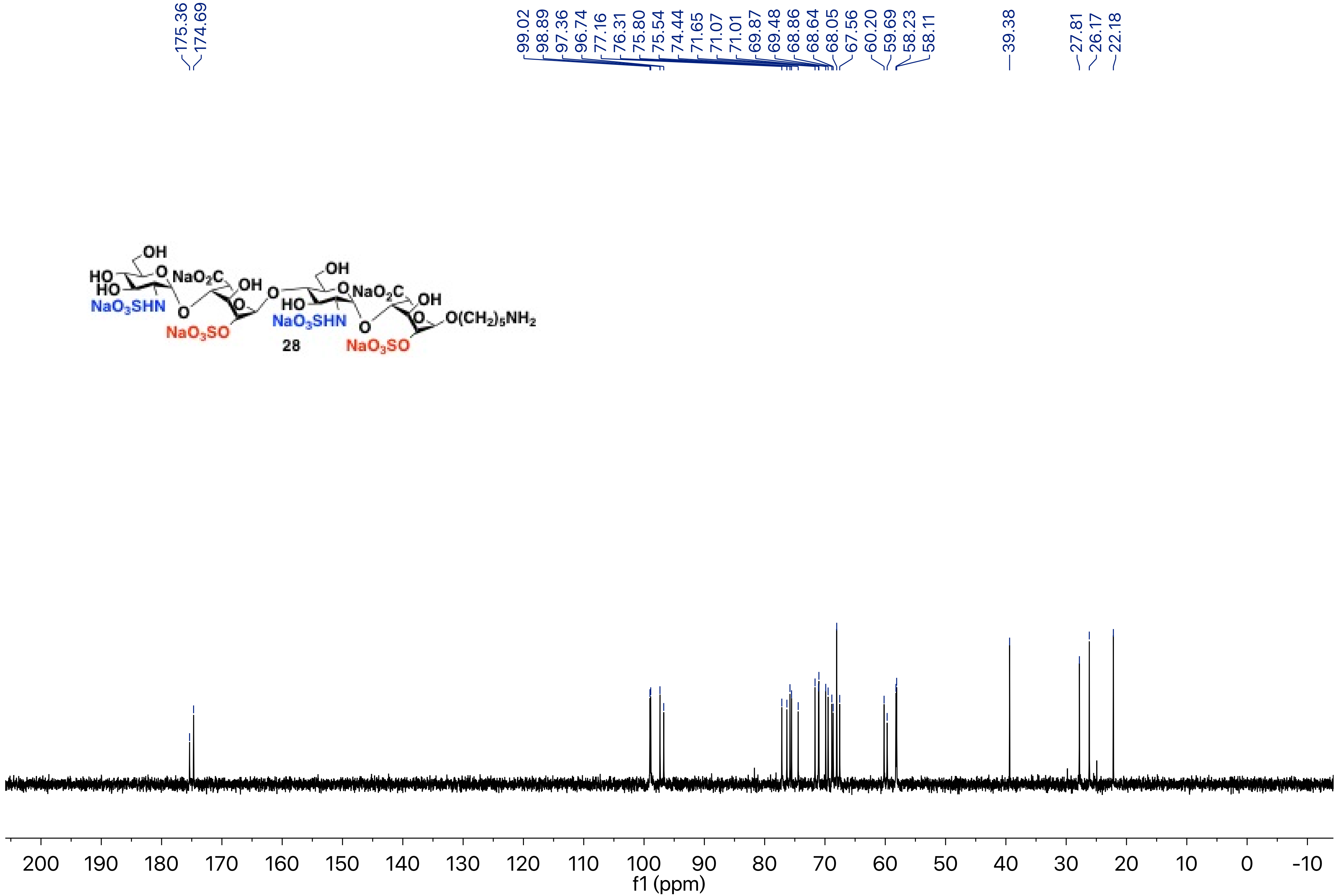
27



WL-2-317-D-NS-C-2S-B-NS-A-2S-H-TC.1.1.1r —

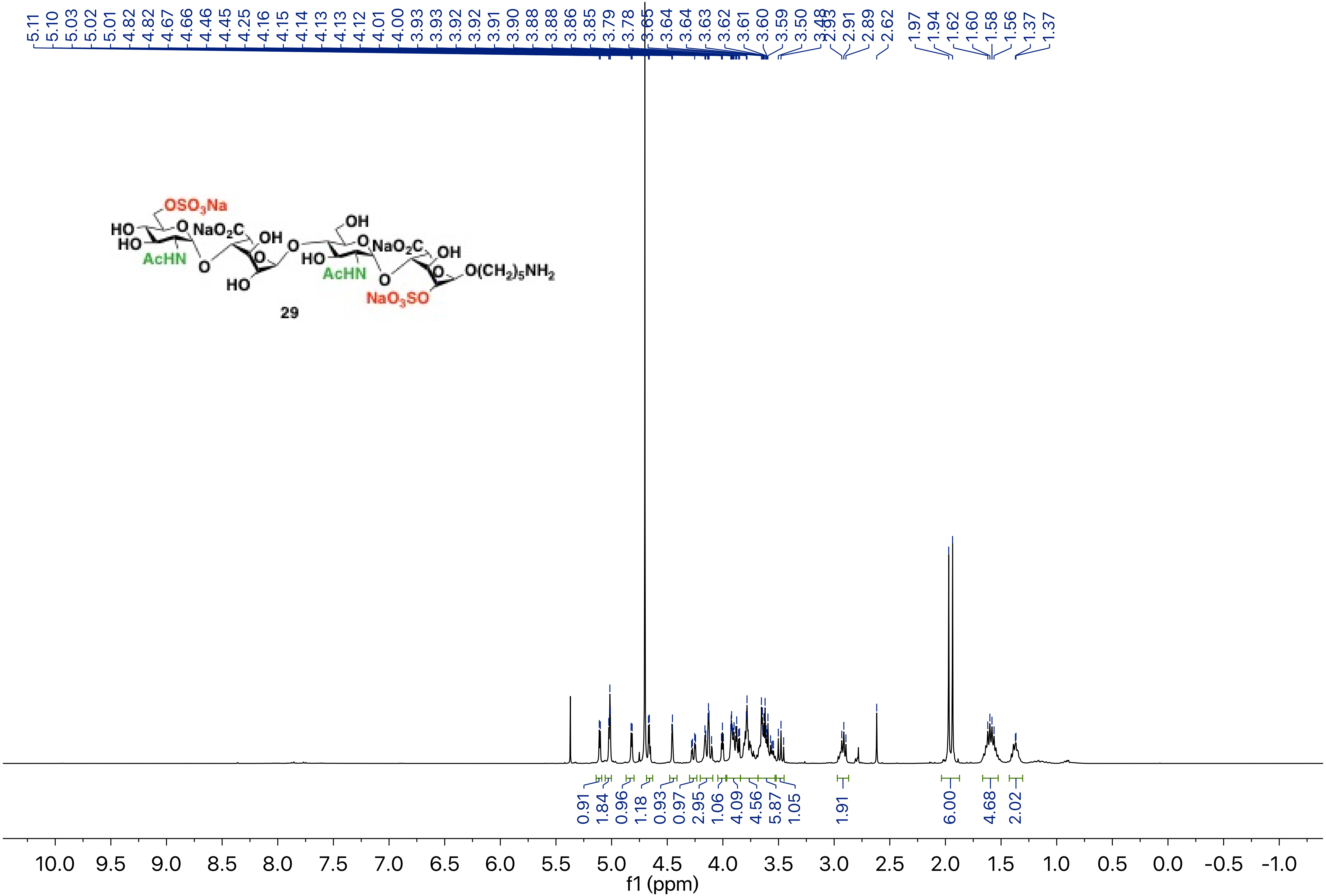


WL-2-317-D-NS-C-2S-B-NS-A-2S-C-TC.12.1.1r

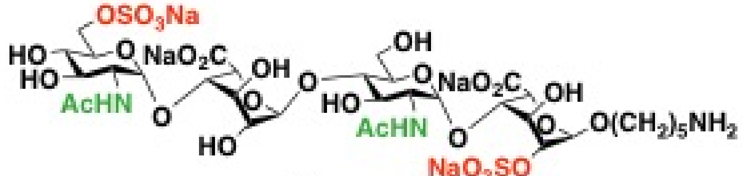


28

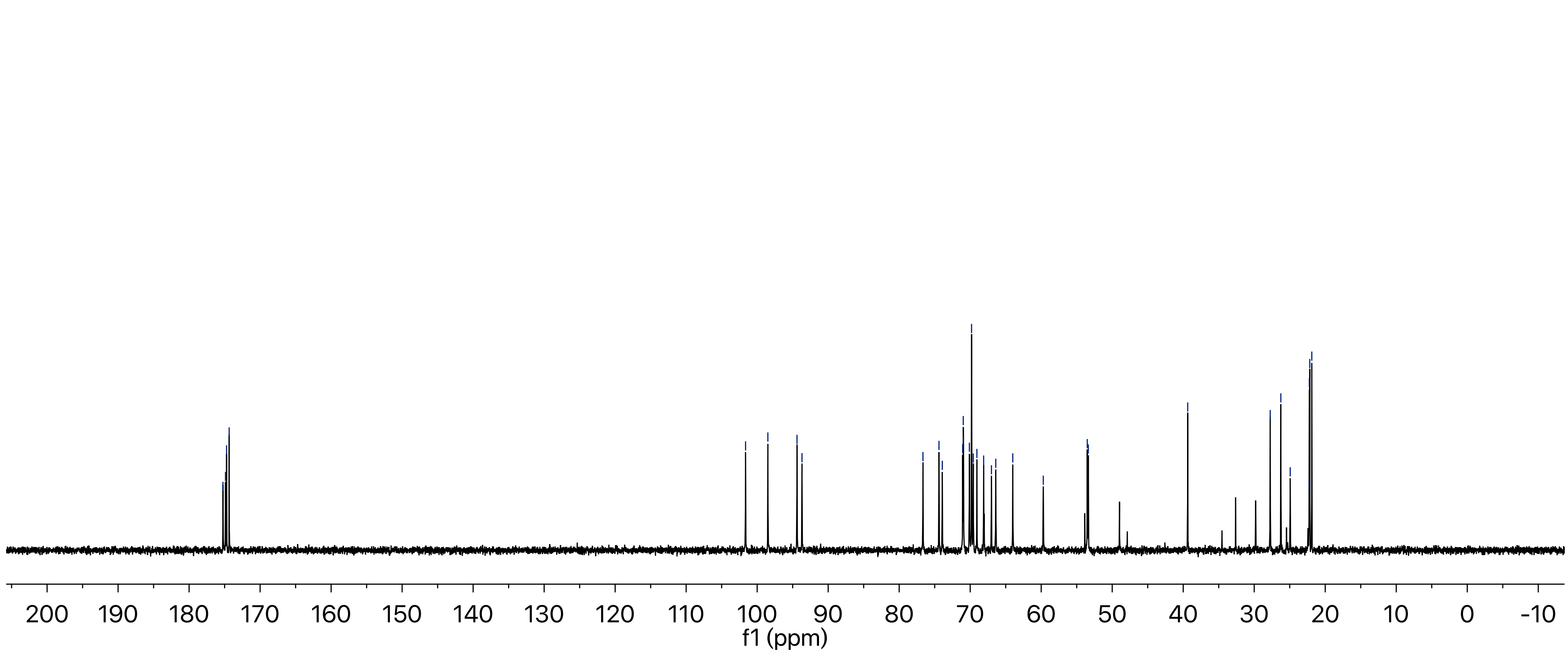
WL-2-265-D-NAc-6S-B-NAc-A-2S-H-TC.9.1.1r —



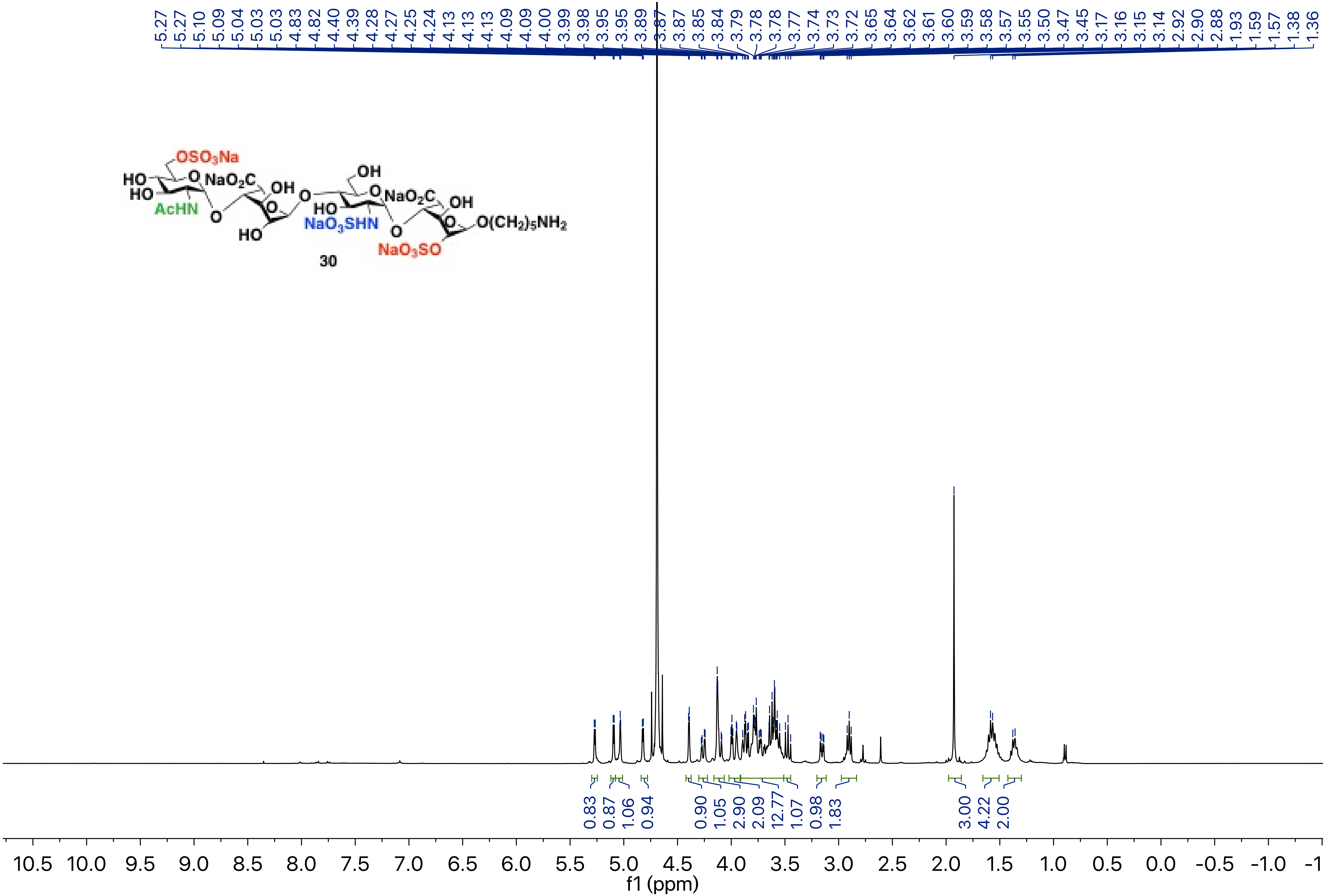
WL-2-265-D-NAc-6S-B-NAc-A-2S-C-TC.1.1.1r



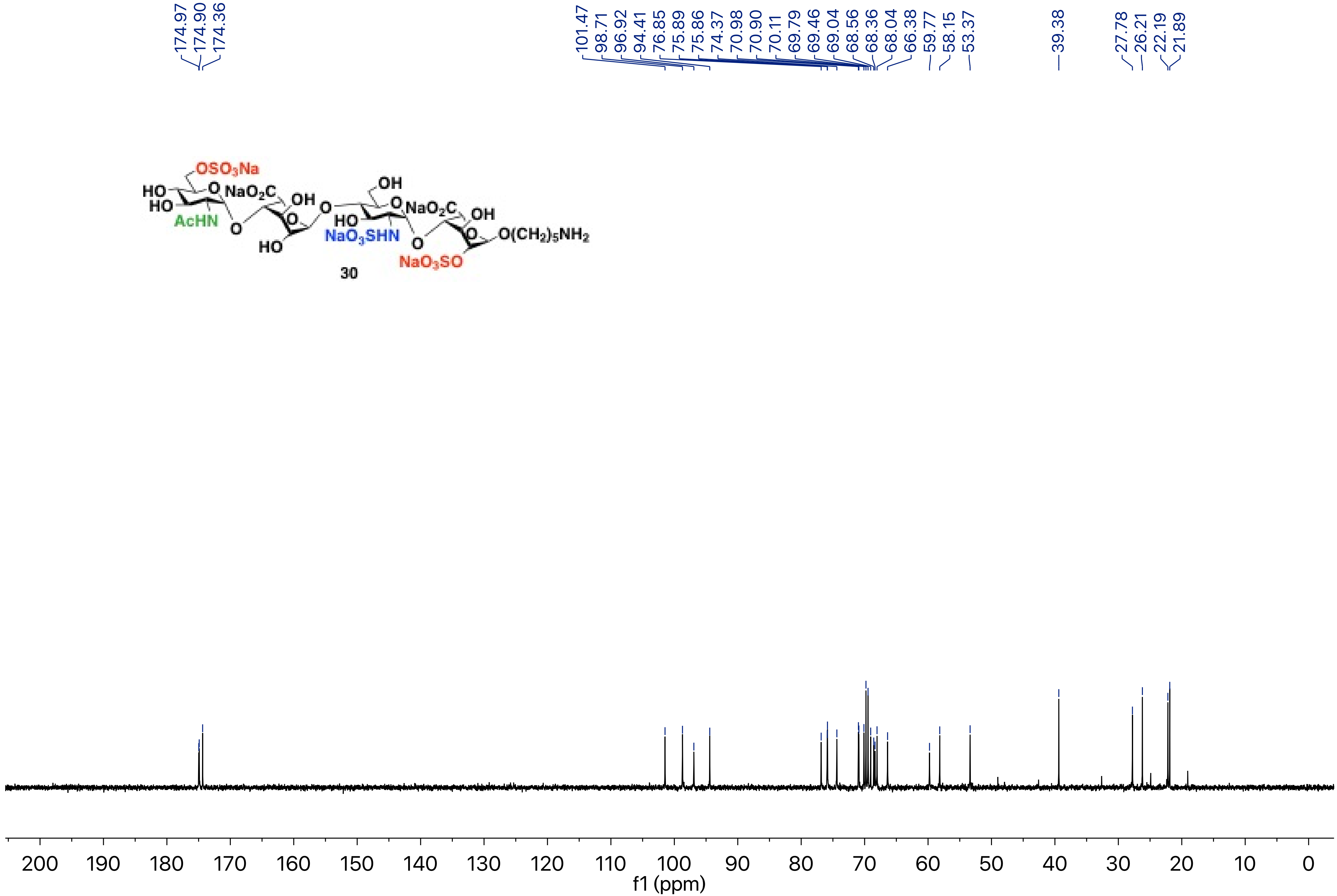
29



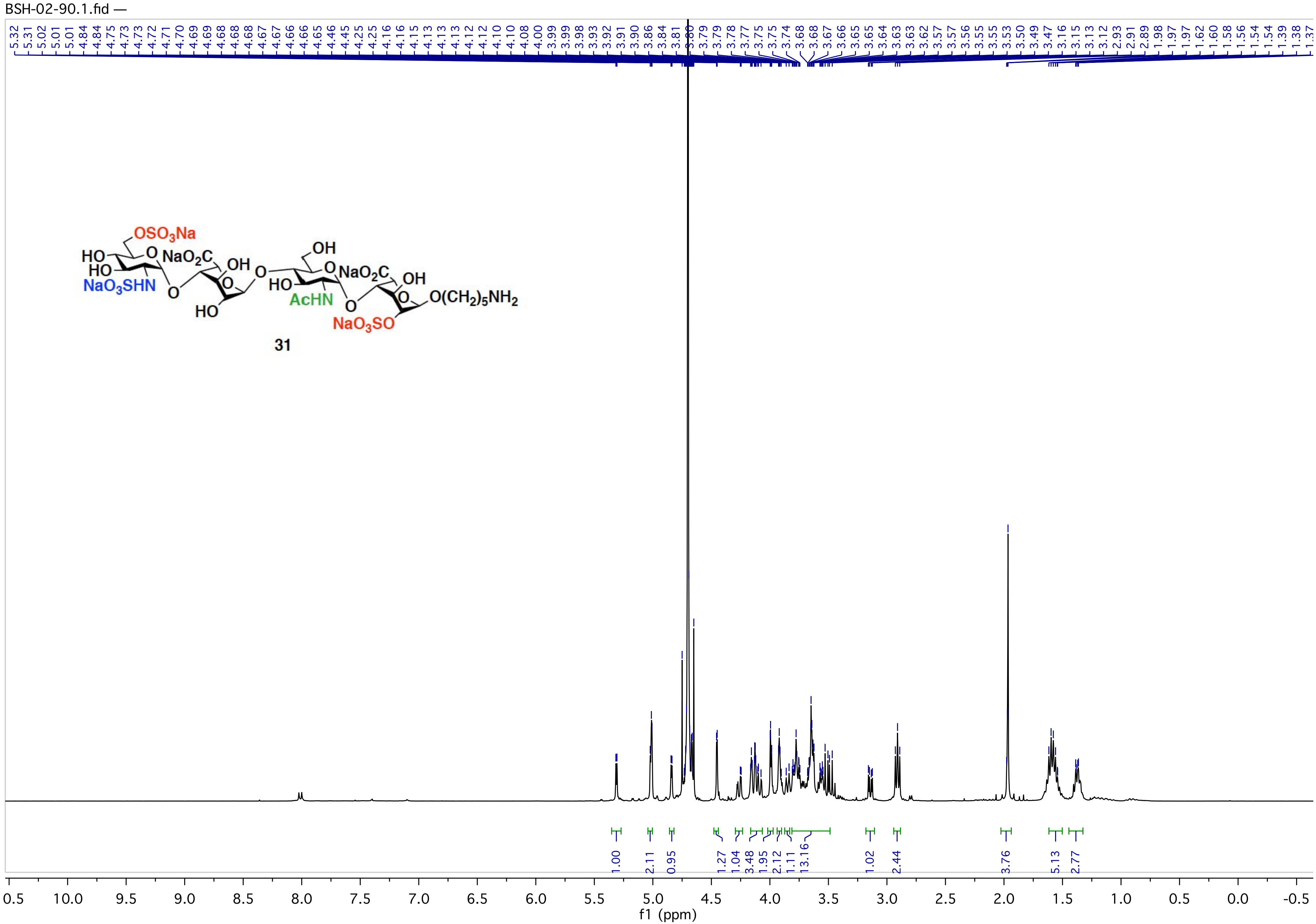
WL-2-259-D-NAc-6S-B-NS-A-2S-H-TC.7.1.1r



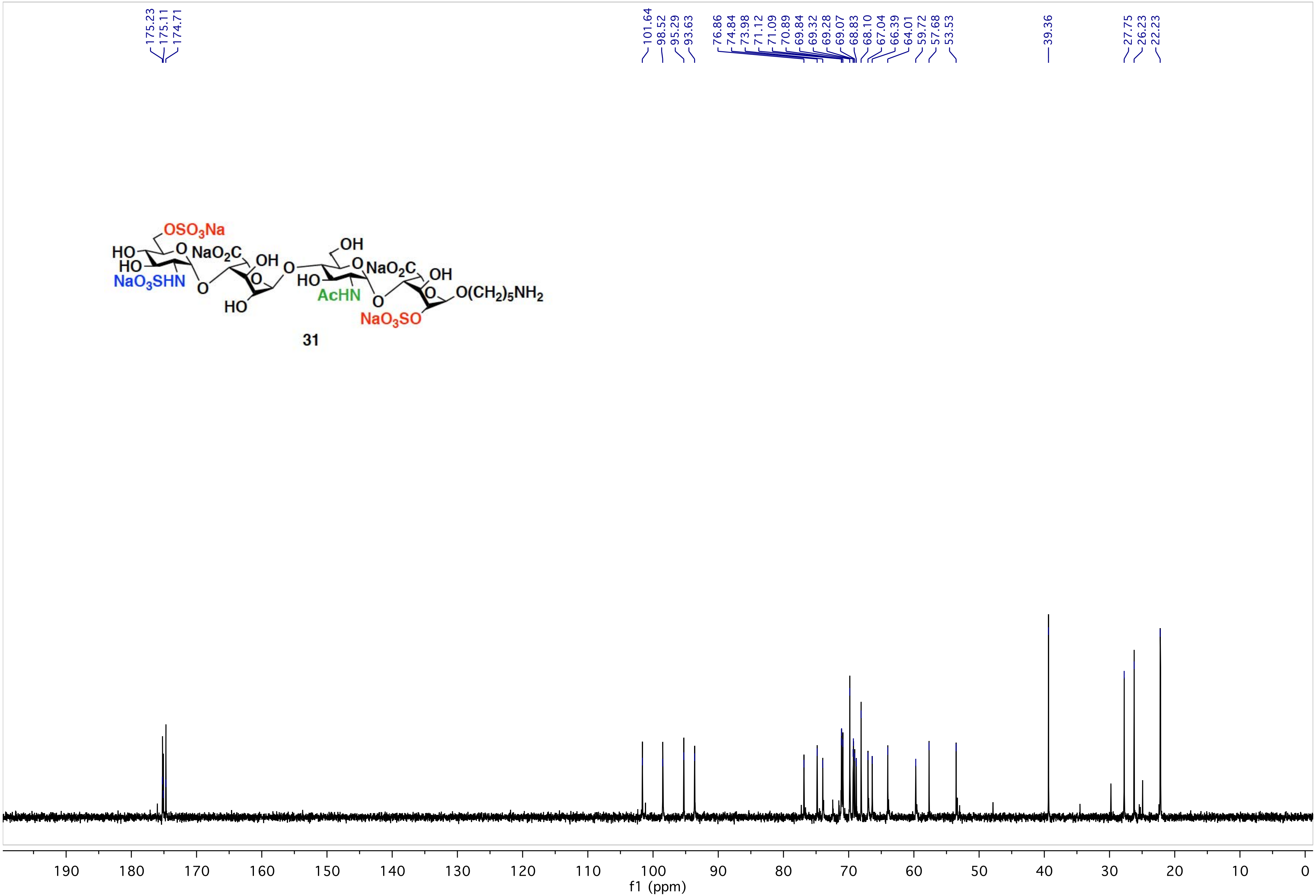
WL-2-259-D-NAc-6S-B-NS-A-2S-C-TC.1.1.1r —



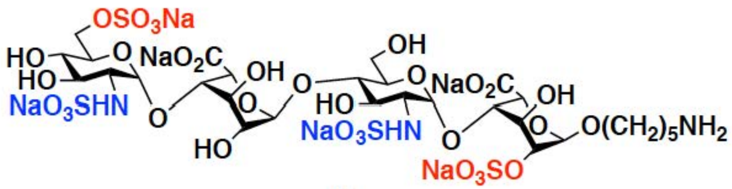
30


BSH-02-90.1.fid —
5.32 5.31 5.02 5.01 5.01 4.84 4.84 4.75 4.73 4.73 4.72 4.71 4.70 4.69 4.69 4.68 4.68 4.68 4.67 4.67 4.66 4.66 4.65 4.46 4.45 4.25 4.25 4.16 4.16 4.15 4.13 4.13 4.13 4.12 4.12 4.10 4.10 4.08 4.00 3.99 3.99 3.98 3.93 3.92 3.91 3.90 3.86 3.84 3.81 3.80 3.79 3.79 3.78 3.77 3.75 3.75 3.74 3.68 3.68 3.67 3.66 3.65 3.65 3.64 3.63 3.63 3.62 3.57 3.57 3.56 3.55 3.55 3.53 3.50 3.49 3.47 3.16 3.15 3.13 3.12 2.93 2.91 2.89 1.98 1.97 1.97 1.62 1.60 1.58 1.56 1.54 1.54 1.39 1.38 1.37
OSO3Na
HO
HO
NaO3SHN
O
NaO2C
OH
O
HO
OH
HO
AcHN
NaO2C
OH
O(CH2)5NH2
NaO3SO
31
1.00
2.11
0.95
1.27
1.04
3.48
1.95
2.12
1.11
13.16
1.02
2.44
3.76
5.13
2.77
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 -0.5
f1 (ppm)

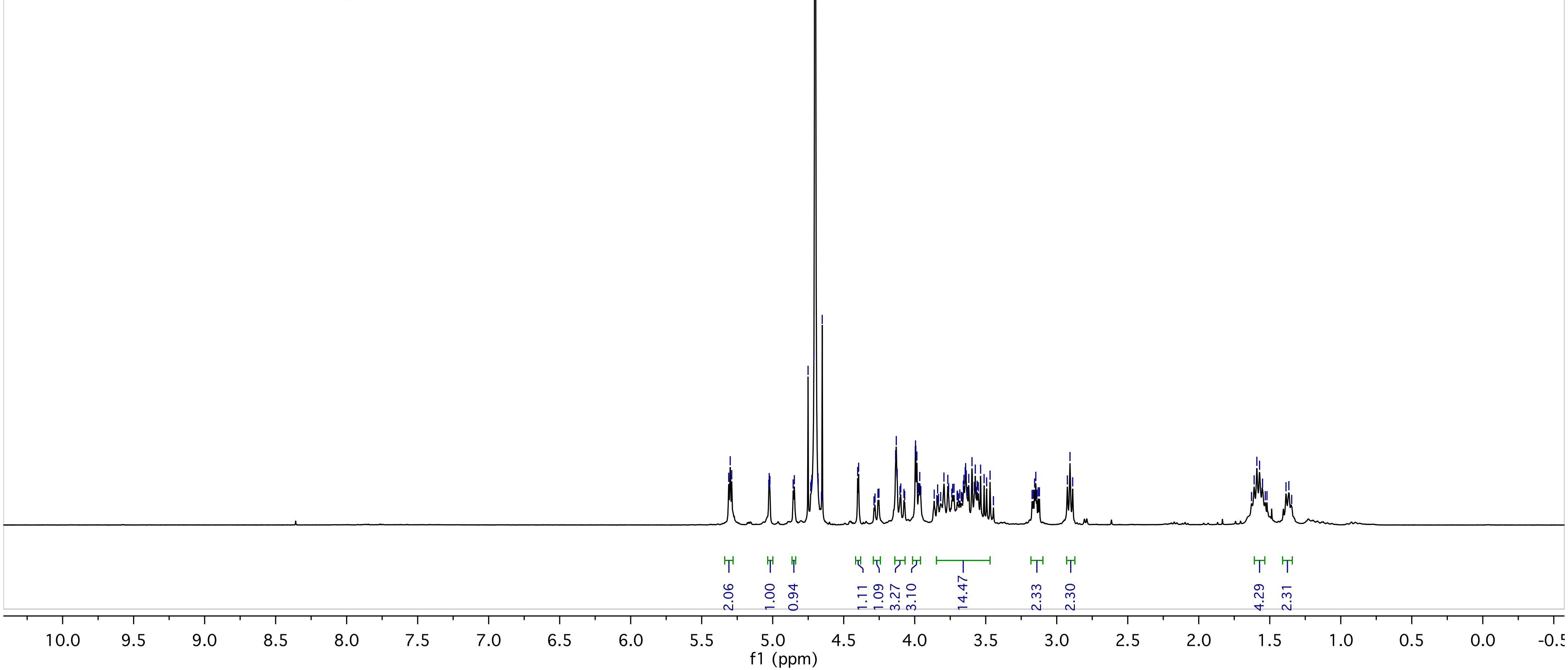
BSH-02-90.2.fid —



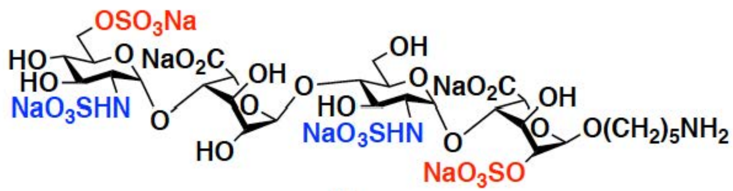
BSH-02-88.1.fid —



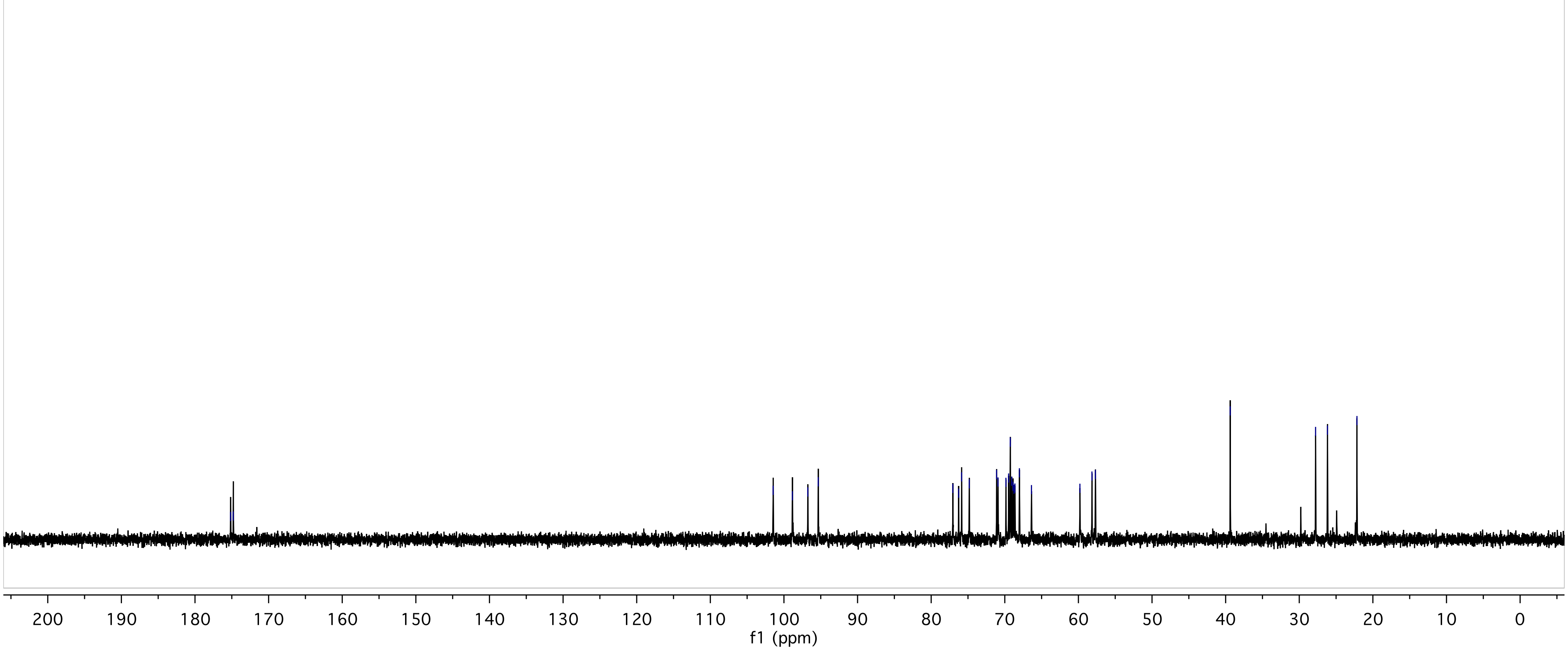
32



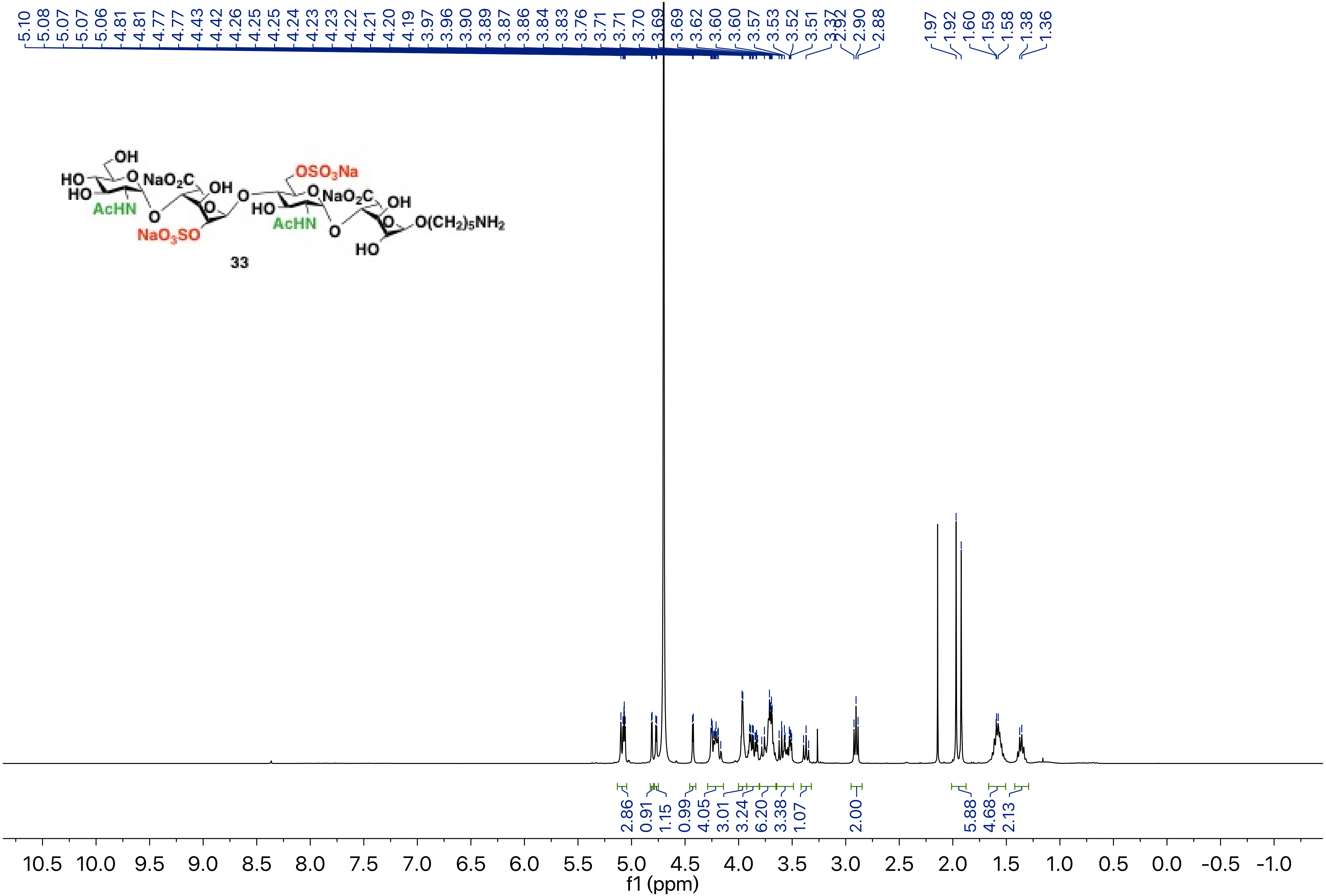
BSH-02-88.2.fid —



32



WL-2-184-D-NAc-C-2S-B-NAc-6S-A-2S-H-TC.7.1.1r —



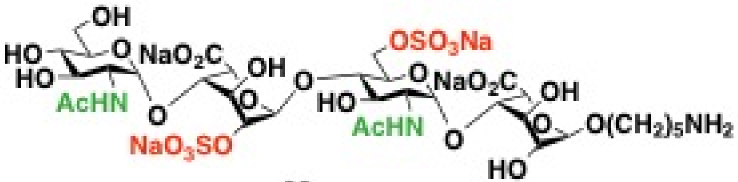
WL-2-184-D-NAc-C-2S-B-NAc-6S-A-2S-C-TC.1.1.1r —

175.46
174.92
174.79
174.31

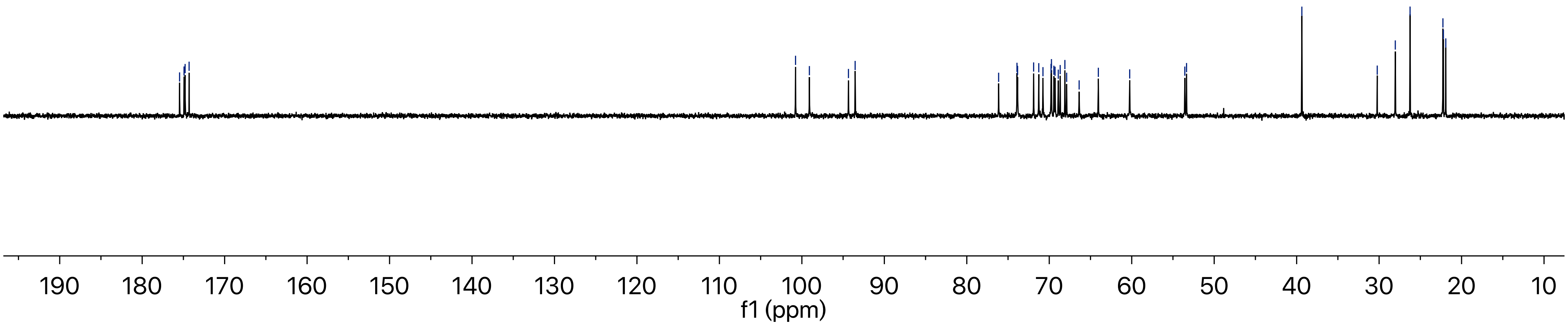
100.77
99.09
94.35
93.54
76.14
73.92
73.84
71.89
71.27
70.76
69.78
69.73
69.44
69.30
68.91
68.67
68.11
67.89
66.38
64.05
60.25
53.56
53.35

39.37

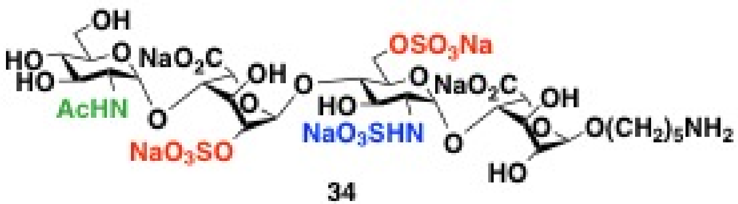
30.23
28.04
26.25
22.26
22.20
21.91



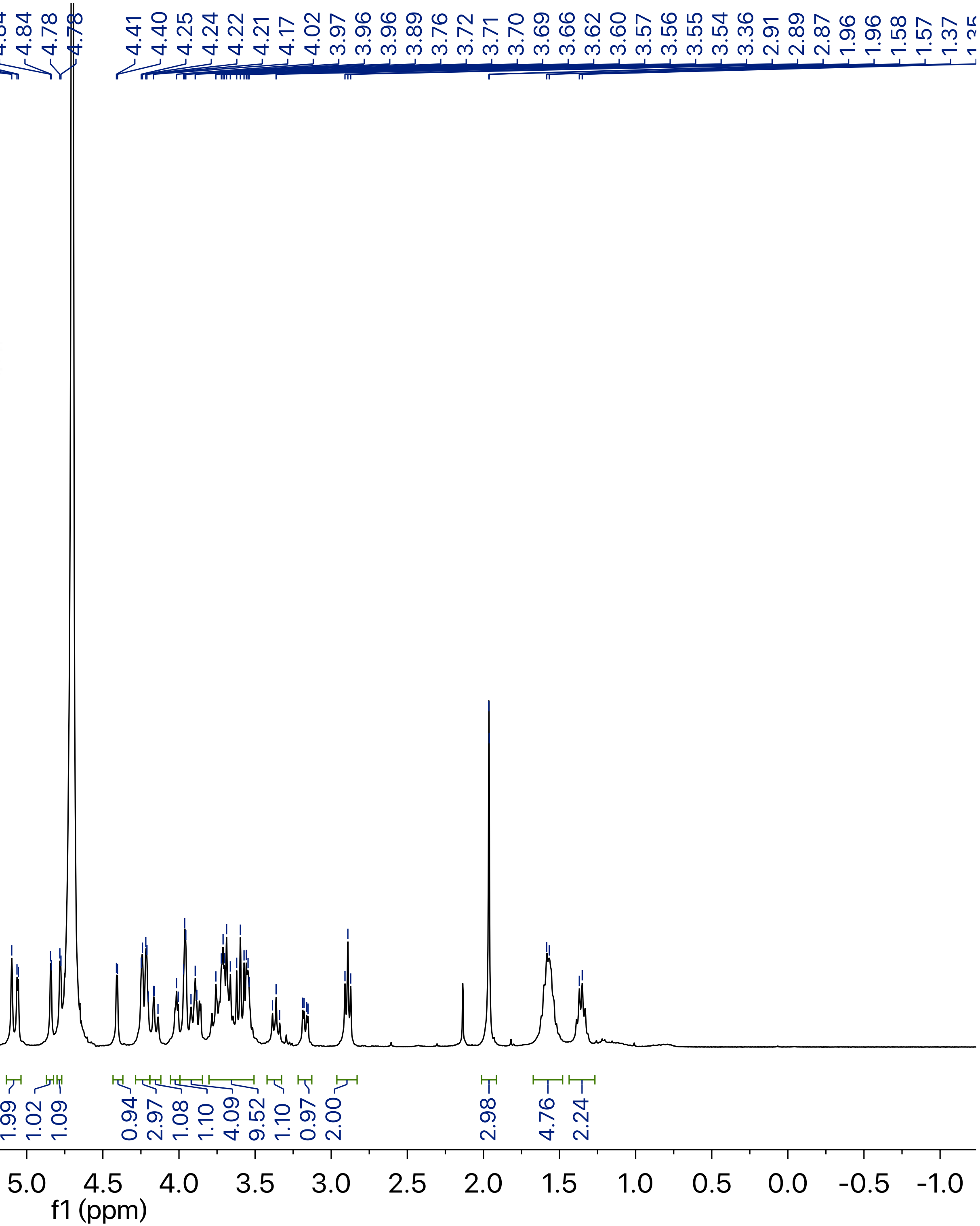
33



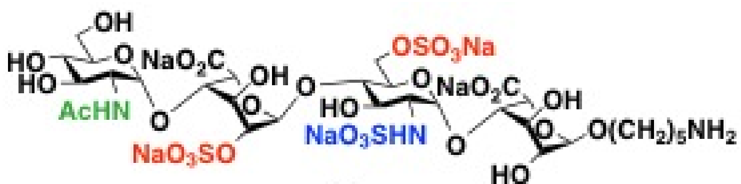
WL-2-185-D-NAc-C-2S-B-NS-6S-H-TC.7.1.1r



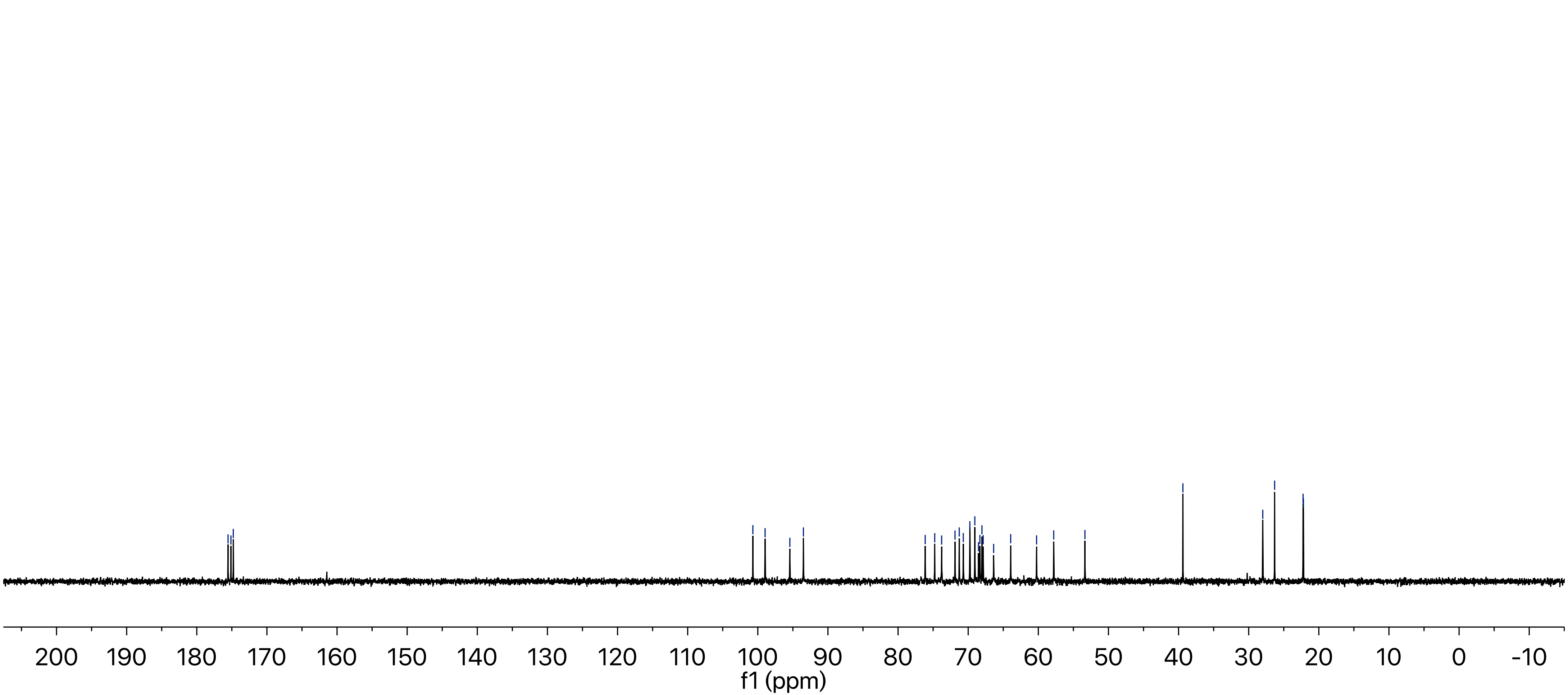
34



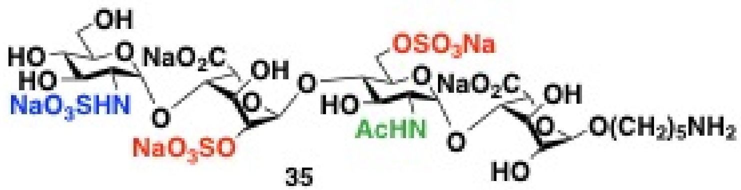
WL-2-185-D-NAc-C-2S-B-NS-6S-C-TC.1.1.1r



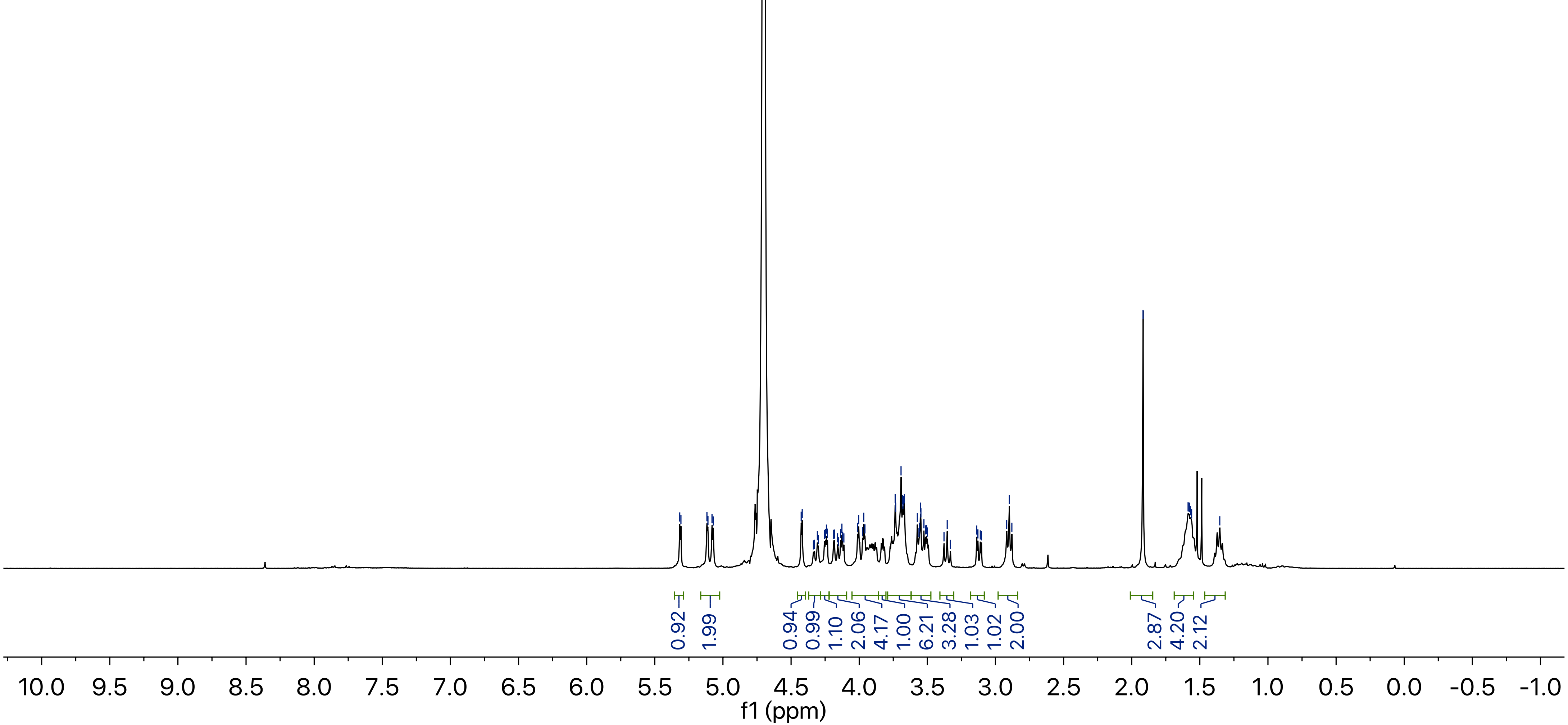
34



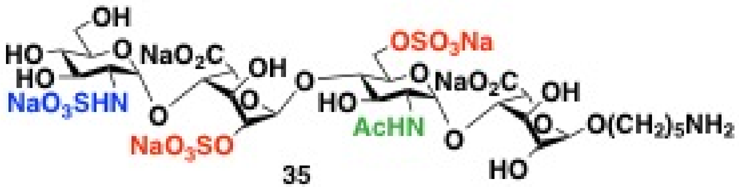
WL-2-228-D-NS-C-2S-B-6S-NAc-proc-H-TC.8.1.1r —



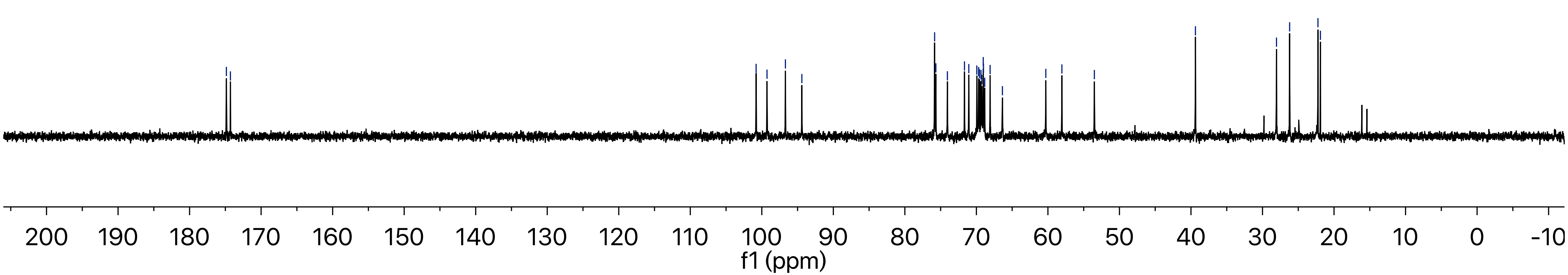
35

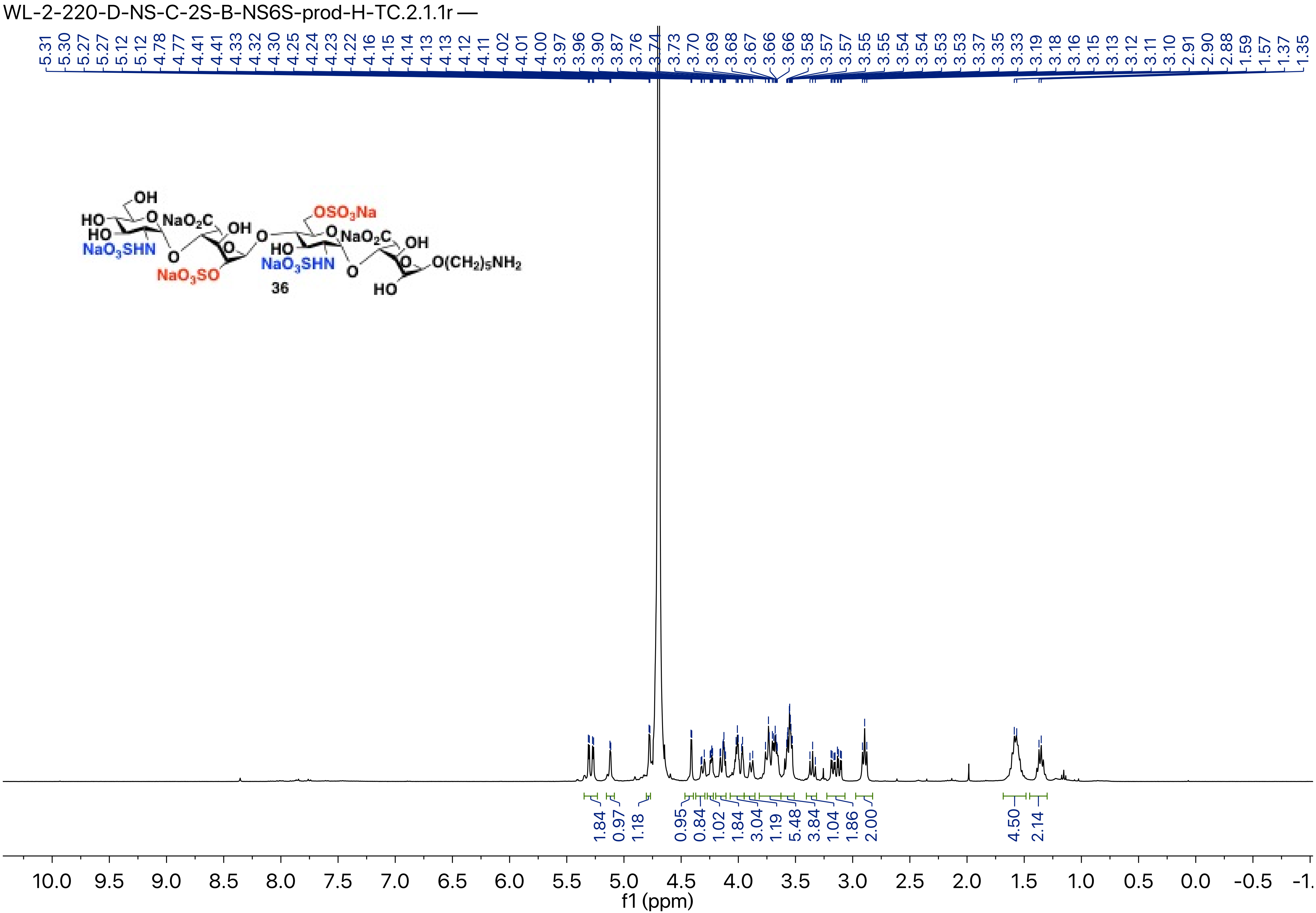


WL-2-228-D-NS-C-2S-B-6S-NAc-proc-C-TC.2.1.1r

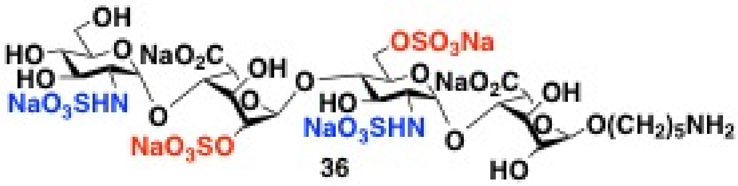


35

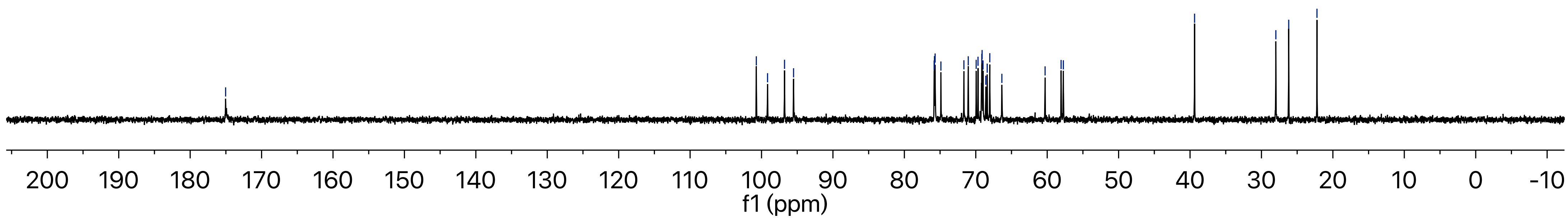


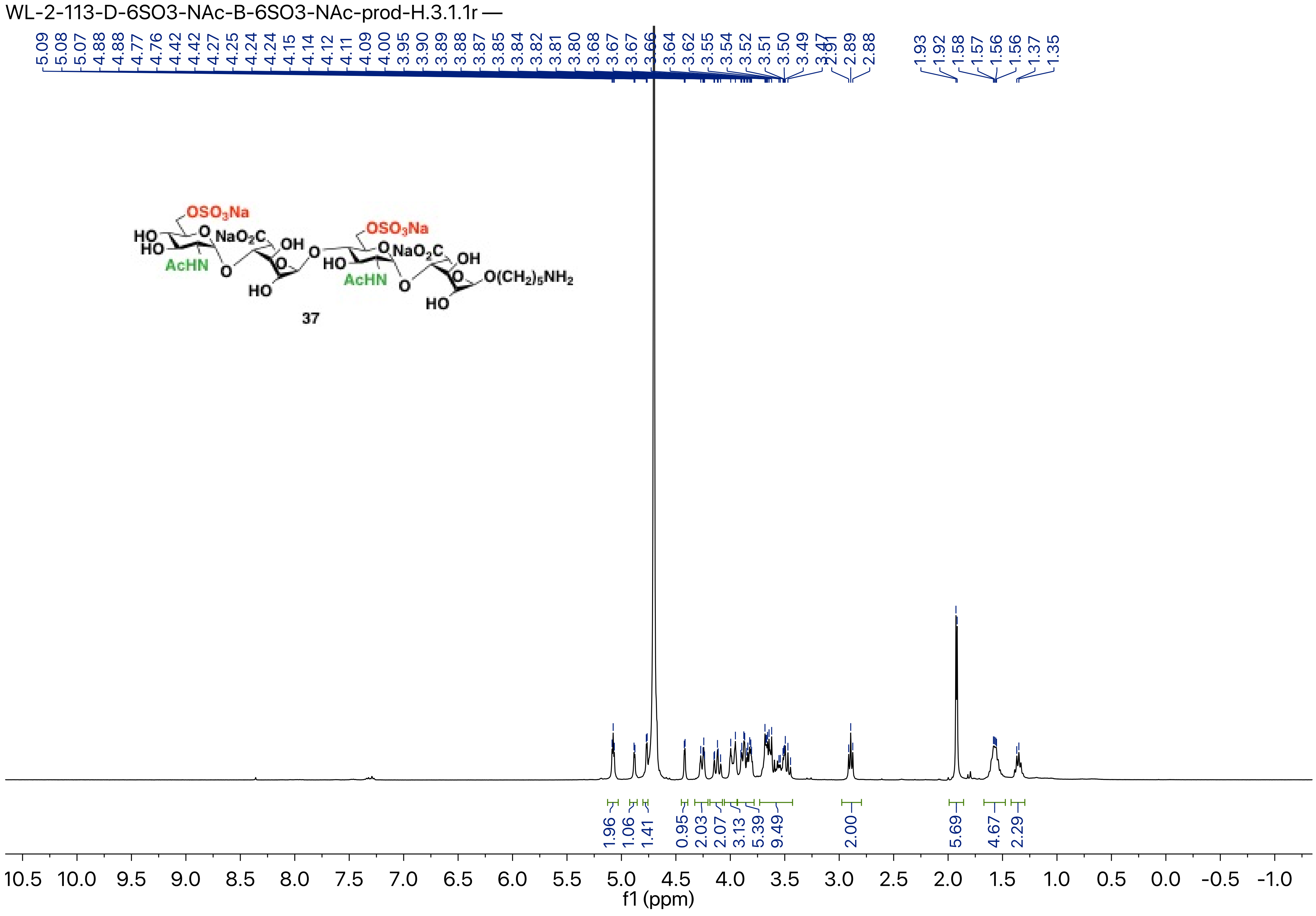

WL-2-220-D-NS-C-2S-B-NS6S-prod-H-TC.2.1.1r
5.31 5.30 5.27 5.27 5.12 5.12 4.78 4.77 4.41 4.41 4.33 4.32 4.30 4.25 4.24 4.23 4.22 4.16 4.15 4.14 4.13 4.13 4.12 4.11 4.02 4.01 4.00 3.97 3.96 3.90 3.87 3.76 3.74 3.73 3.70 3.69 3.68 3.67 3.66 3.66 3.58 3.57 3.57 3.55 3.55 3.54 3.54 3.53 3.53 3.37 3.35 3.33 3.19 3.18 3.16 3.15 3.13 3.12 3.11 3.10 2.91 2.90 2.88 1.59 1.57 1.37 1.35
HO
HO
OH
O
NaO3SHN
NaO2C
OH
O
NaO3SO
OSO3Na
HO
NaO3SHN
NaO2C
OH
O(CH2)5NH2
HO
36
1.84 0.97 1.18 0.95 0.84 1.02 1.84 3.04 1.19 5.48 3.84 1.04 1.86 2.00 4.50 2.14
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 -0.5 -1.
f1 (ppm)

WL-2-220-D-NS-C-2S-B-NS6S-prod-C-TC.1.1.1r

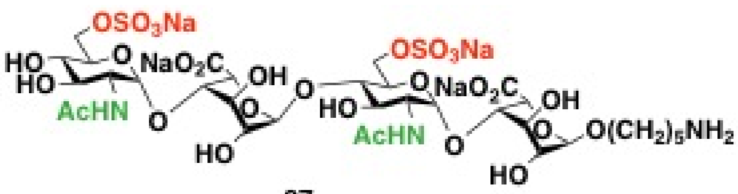


36

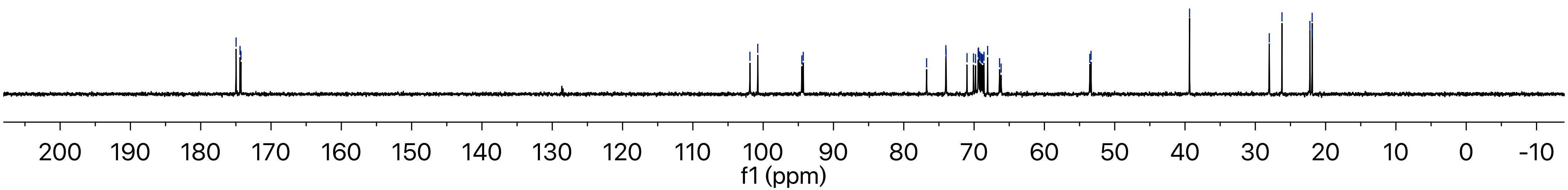



WL-2-113-D-6SO3-NAc-B-6SO3-NAc-prod-H.3.1.1r
5.09 5.08 5.07 4.88 4.88 4.77 4.76 4.42 4.42 4.27 4.25 4.24 4.24 4.15 4.14 4.12 4.11 4.09 4.00 3.95 3.90 3.89 3.88 3.87 3.85 3.84 3.82 3.81 3.80 3.68 3.67 3.67 3.66 3.64 3.62 3.55 3.54 3.52 3.51 3.50 3.49 3.47 2.91 2.89 2.88 1.93 1.92 1.58 1.57 1.56 1.56 1.37 1.35
OSO3Na
NaO2C
OH
HO
AcHN
O(CH2)5NH2
37
1.96 1.06 1.41 0.95 2.03 2.07 3.13 5.39 9.49 2.00 5.69 4.67 2.29
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 -0.5 -1.0
f1 (ppm)

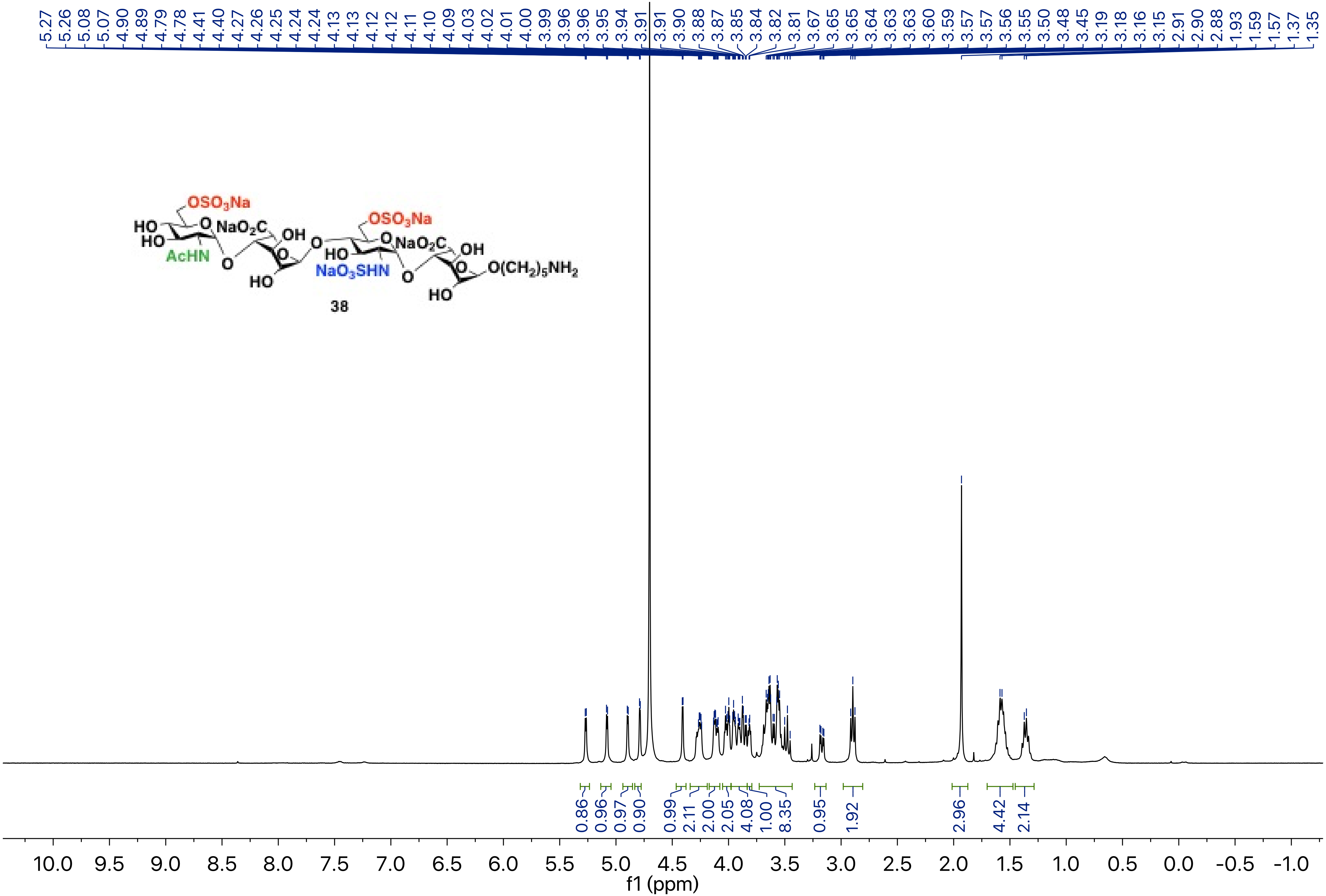
WL-2-113-D-6SO3-NAc-B-6SO3-NAc-final-C.1.1.1r —



37

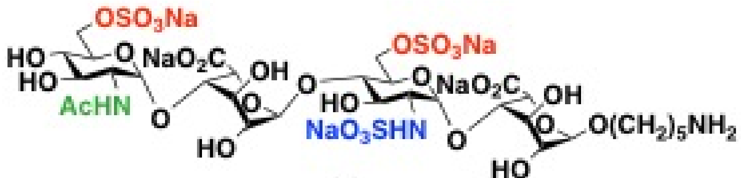


WL-2-112-D-6SO3-NAc-B-6SO3-NSO3-prod-HMBC.4.1.1r —

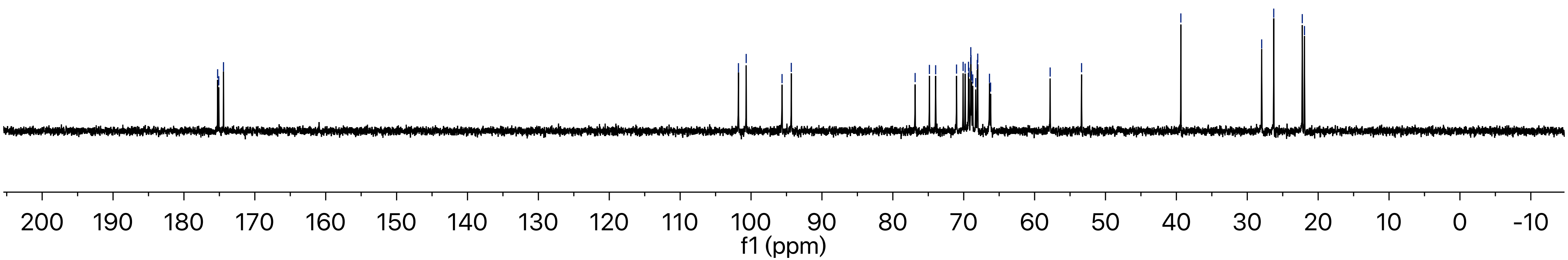


38

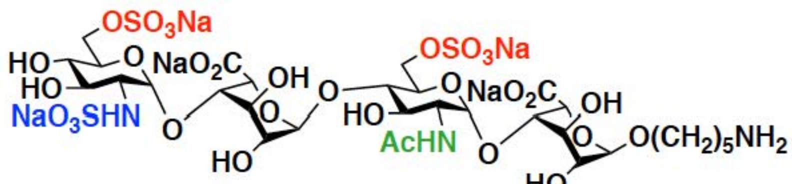
WL-2-112-D-6SO3-NAc-B-6SO3-NSO3-prod-C.1.1.1r



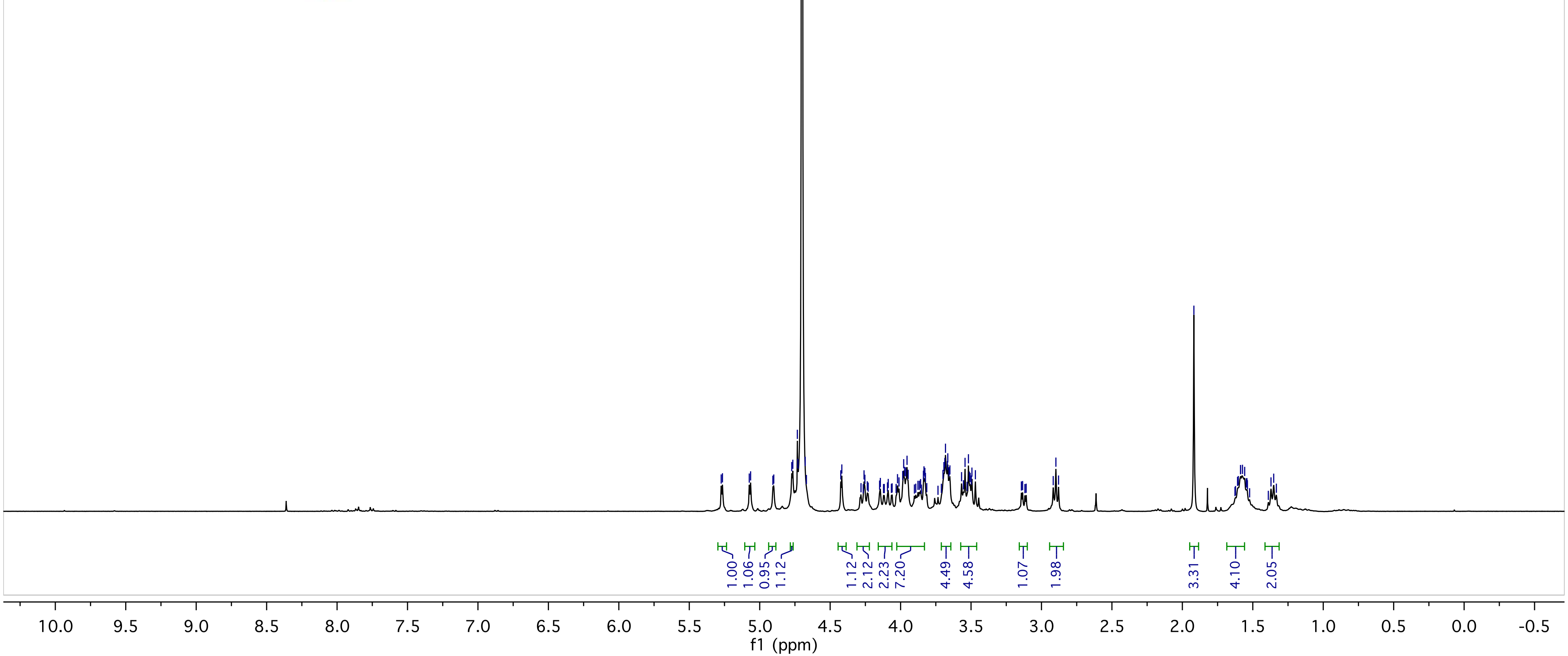
38



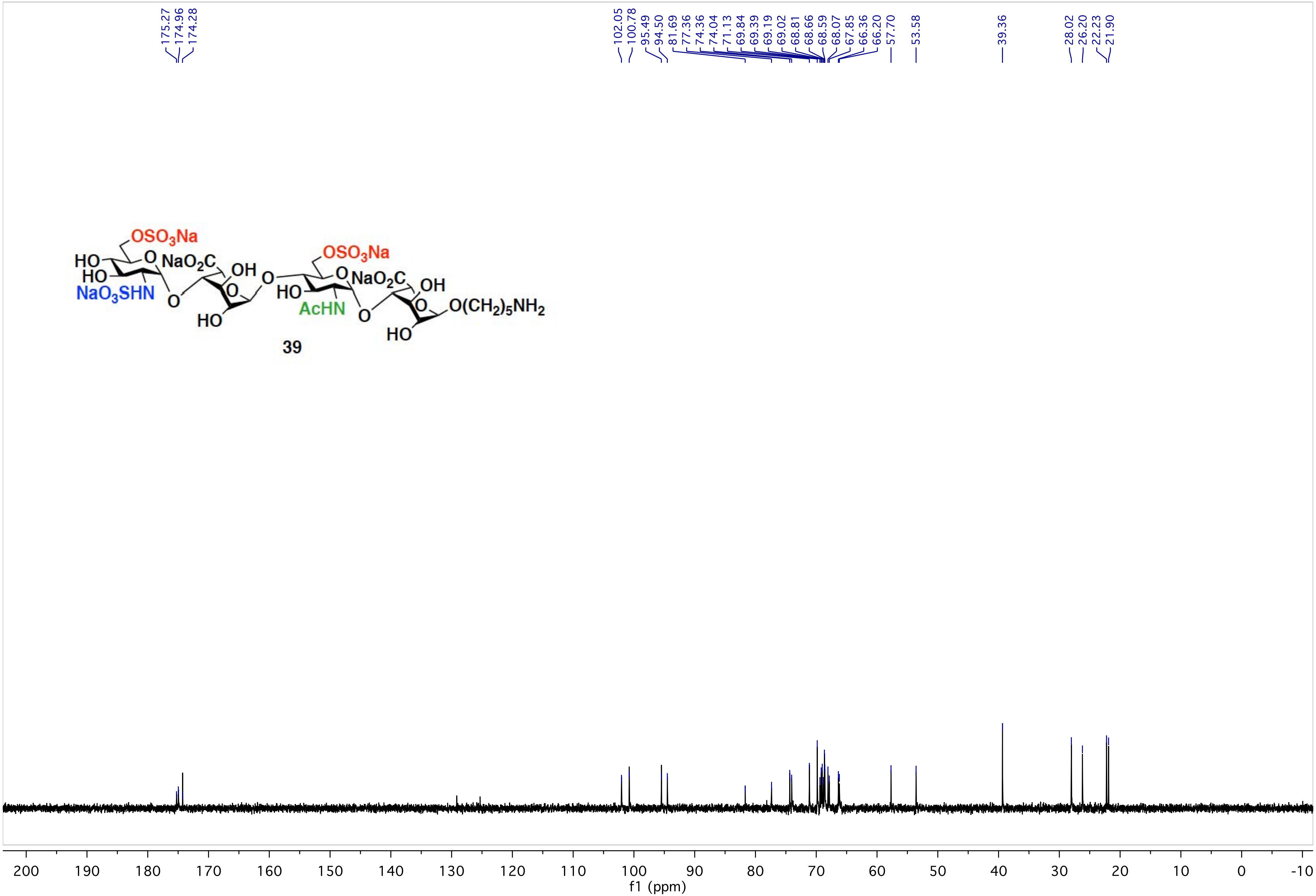
BSH-01-66.1.fid —



39

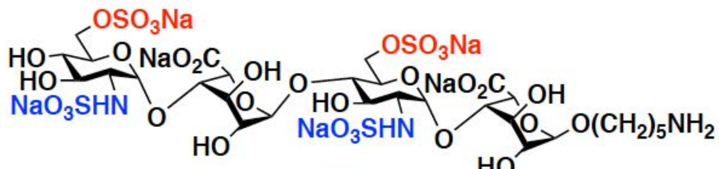


BSH-01-66.2.fid —

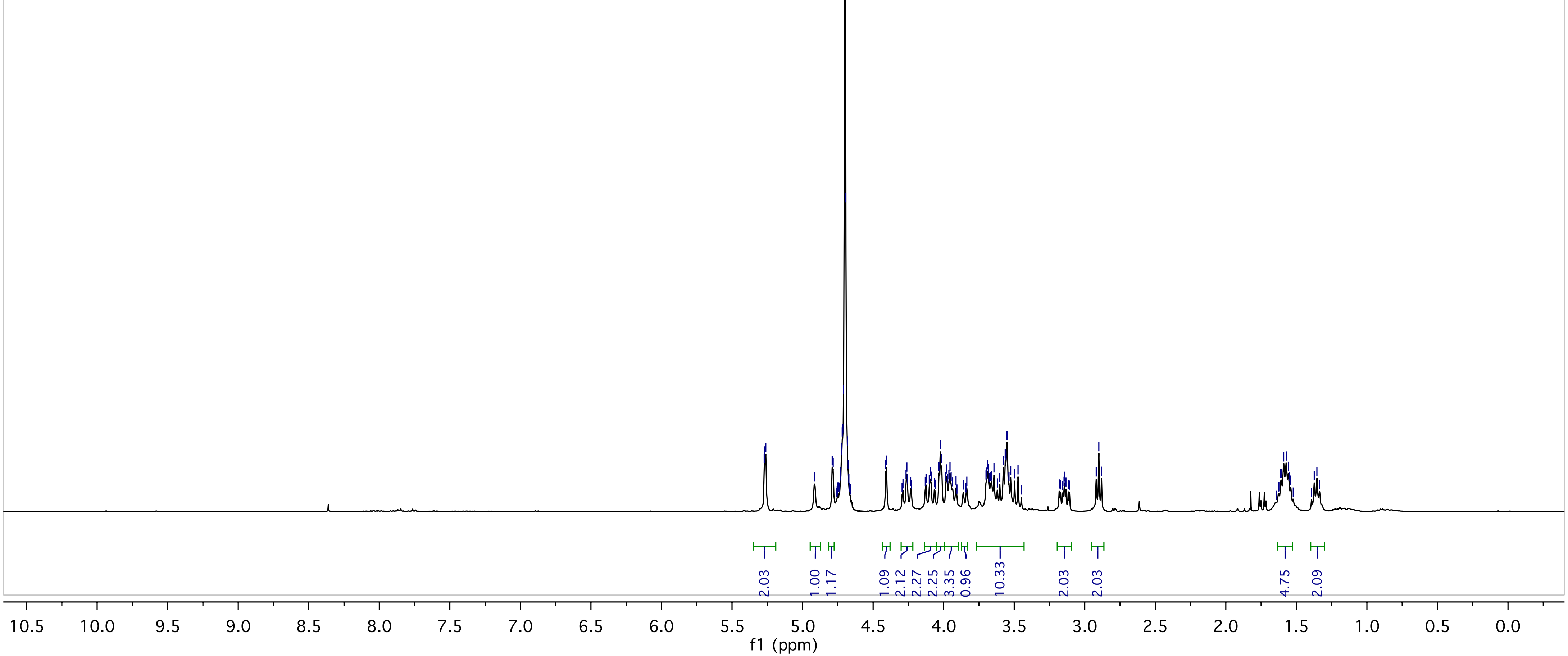


39

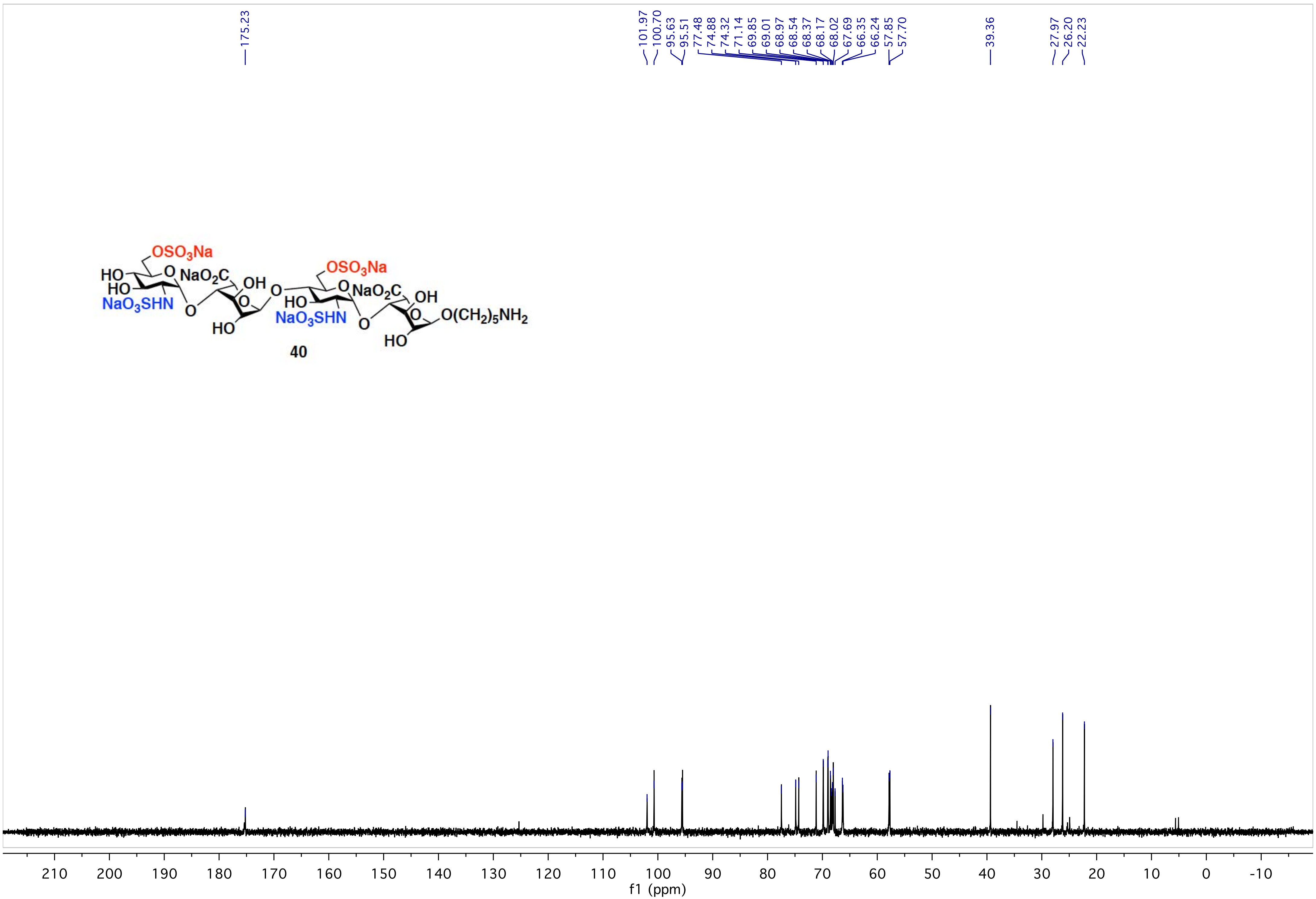
BSH-01-62.1.fid —



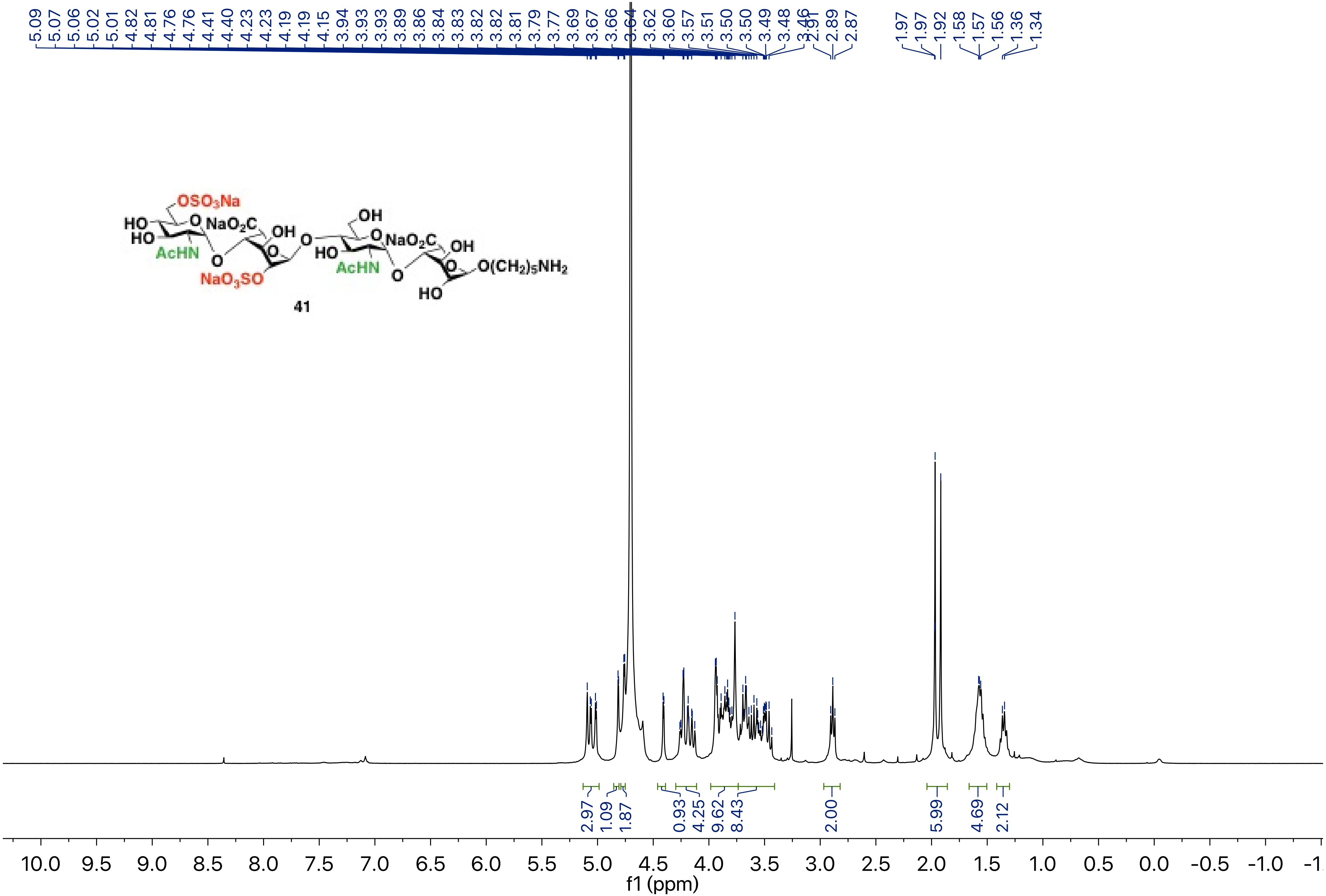
40



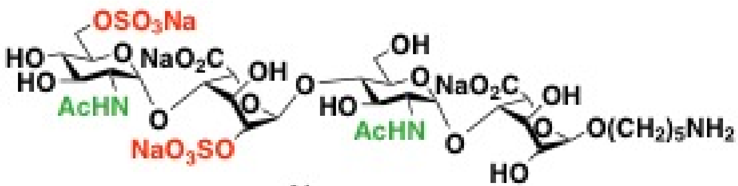
BSH-01-62.2.fid —



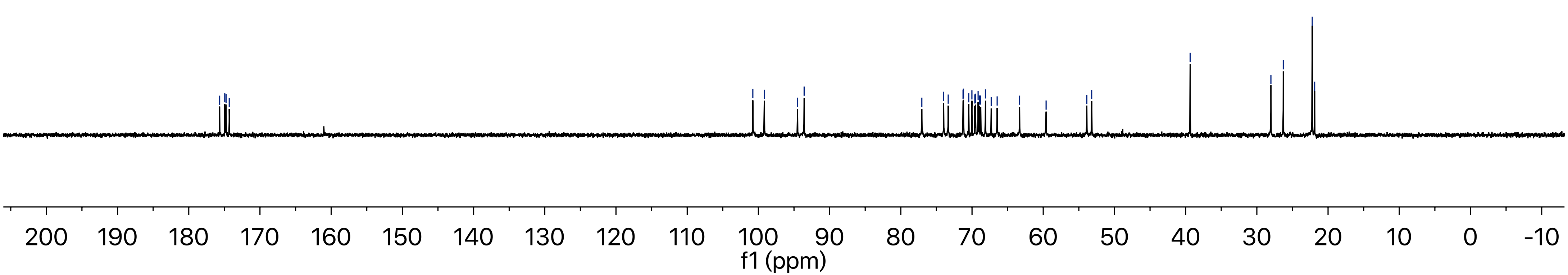
WL-2-181-D-NAc-6S-C-2S-B-NAc-H-TC.2.1.1r



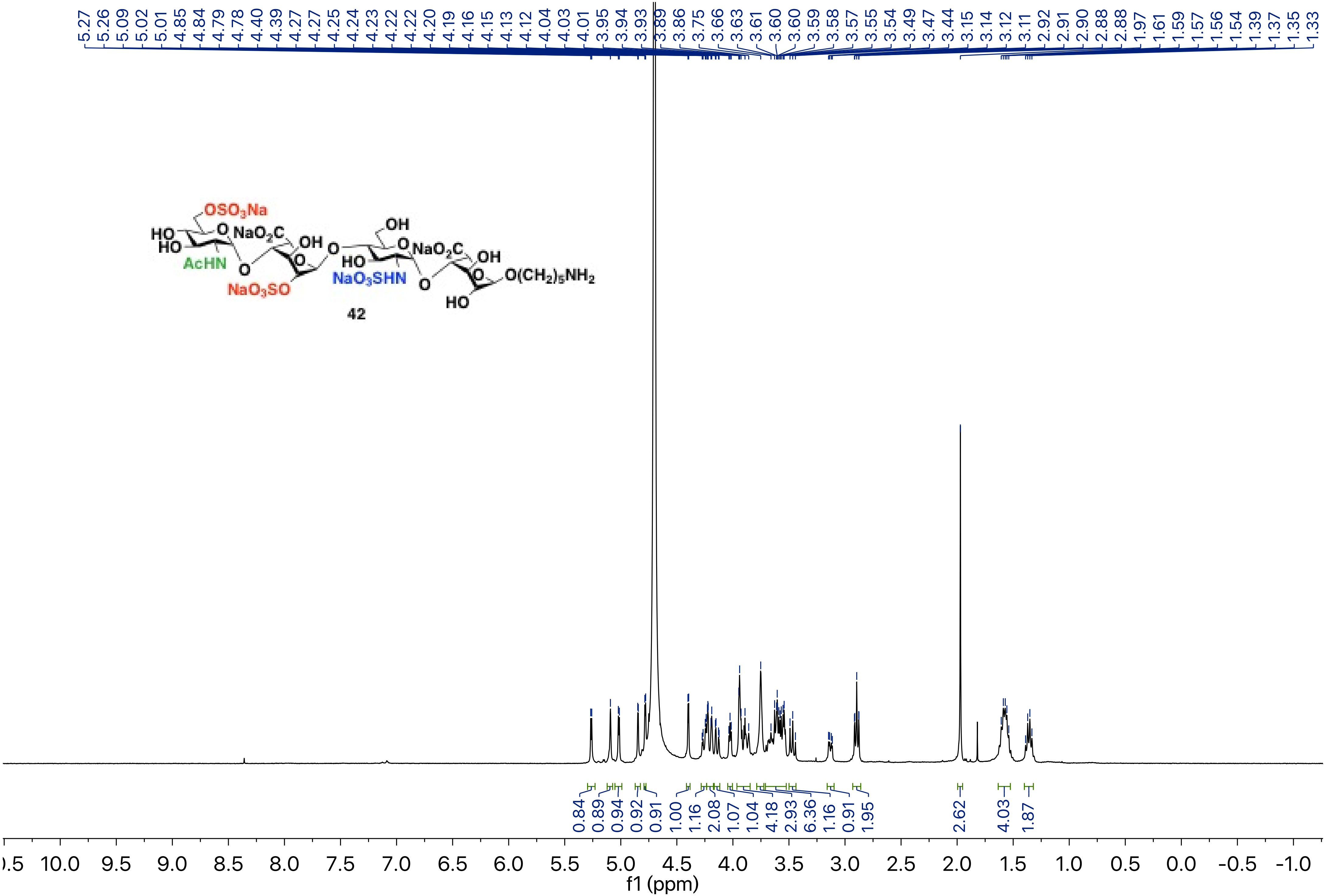
WL-2-181-D-NAc-6S-C-2S-B-NAc-C-TC.1.1.1r —



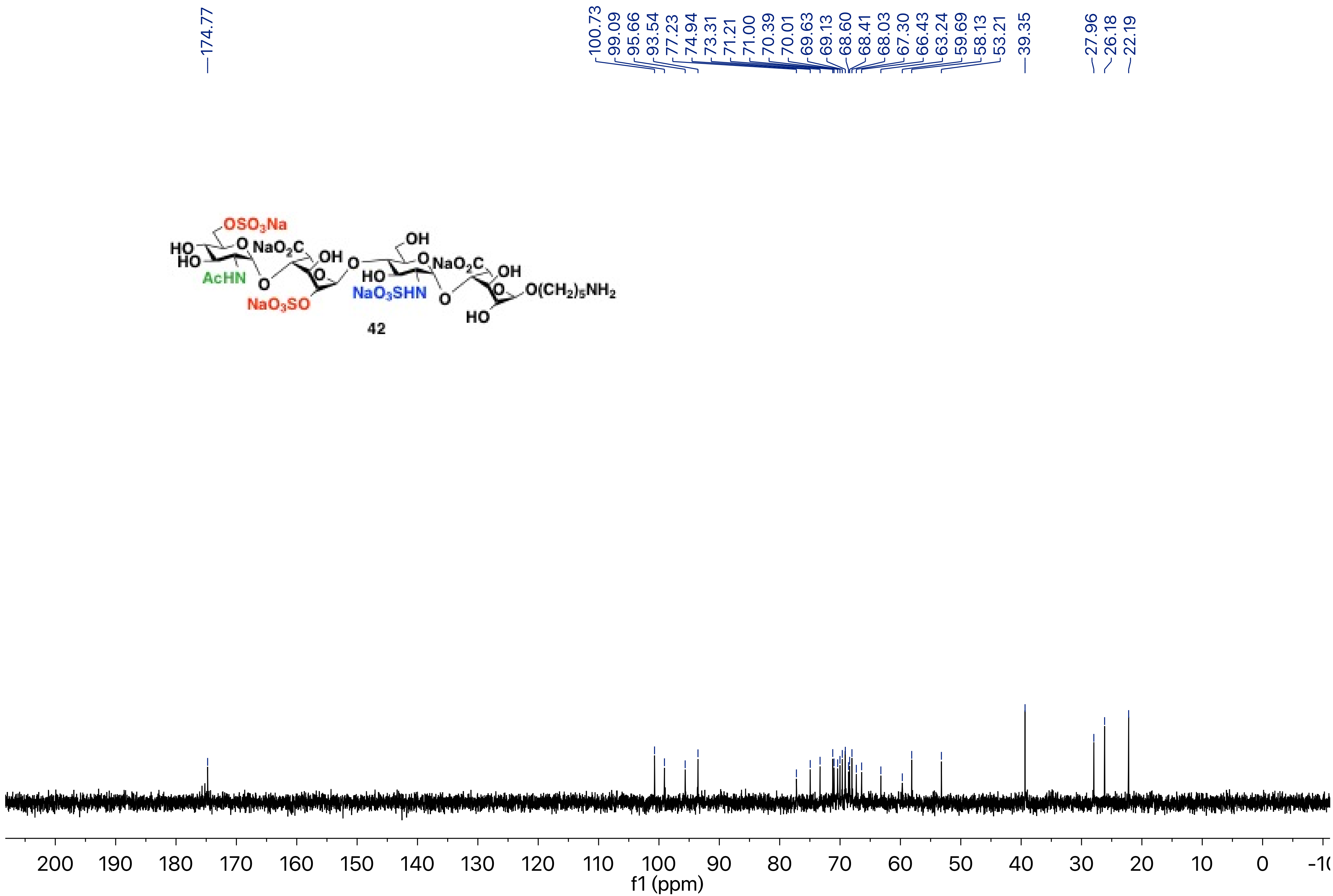
41



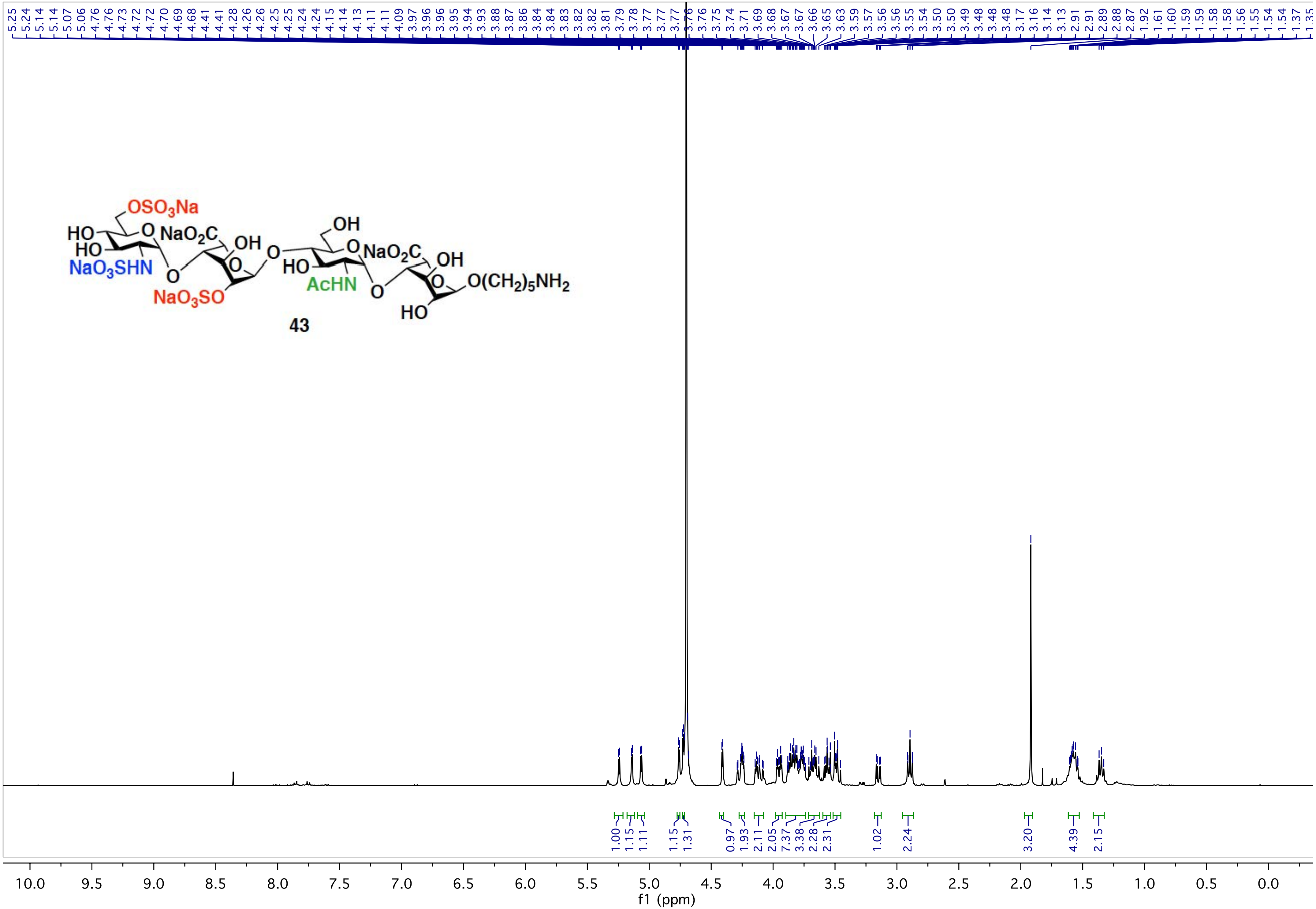
WL-2-073-D-6OSO3-NAc-C-2OSO3-B-NSO3-H.2.1.1r



WL-2-073-D-6OSO3-NAc-C-2OSO3-B-NSO3-C.1.1.1r

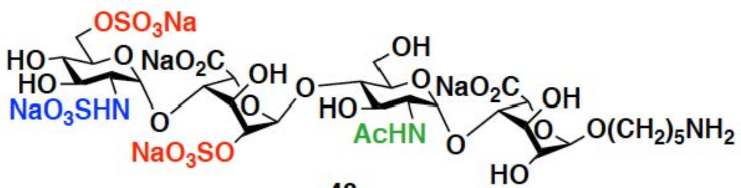


BSH-02-02.1.fid —

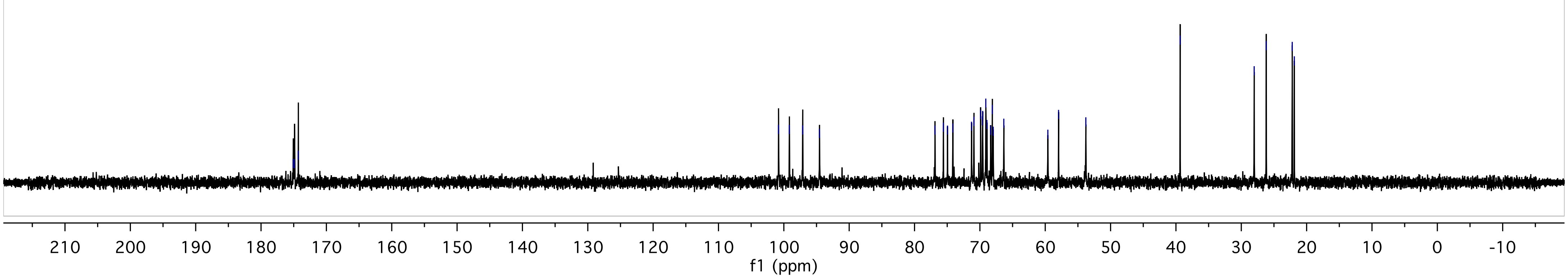


43

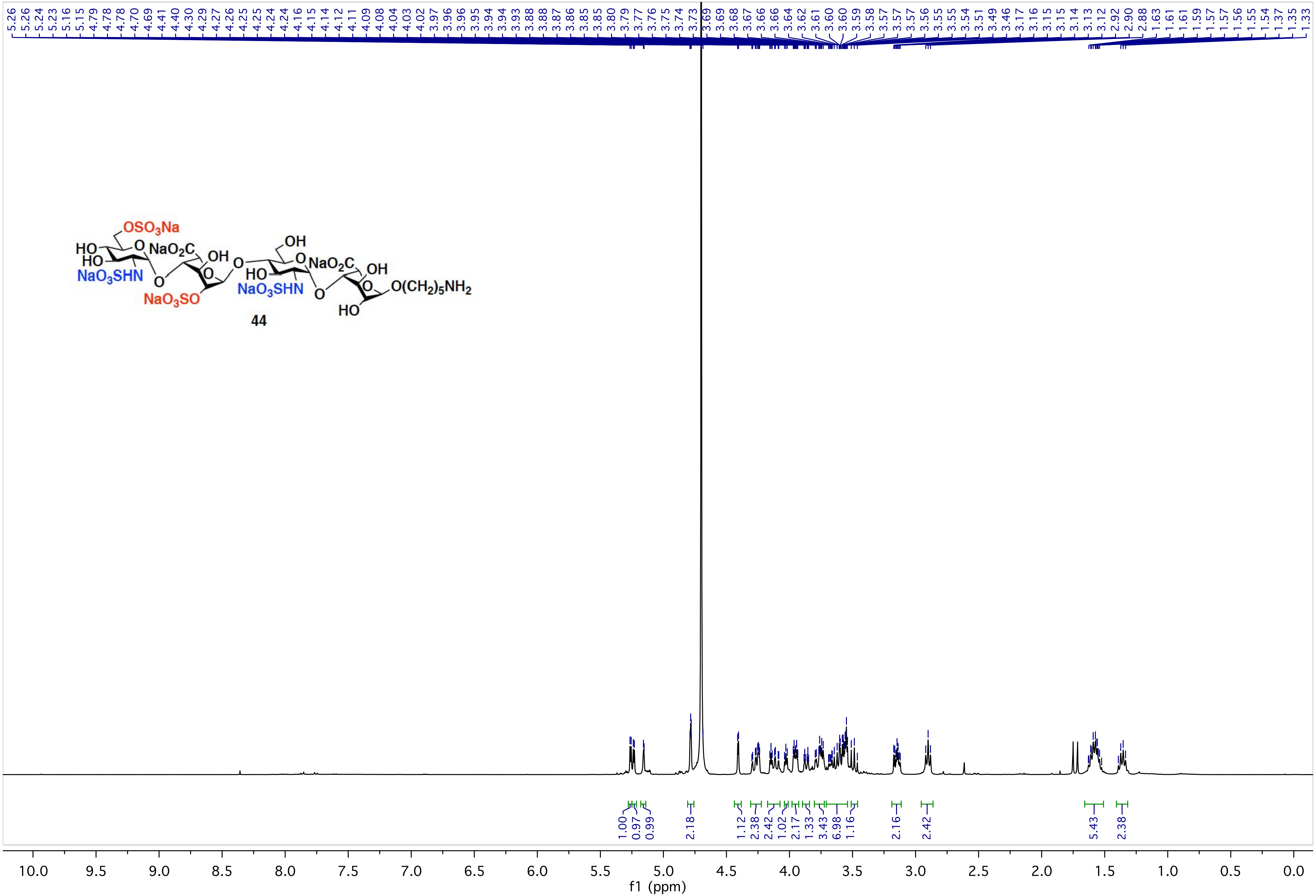
BSH-02-02.2.fid —



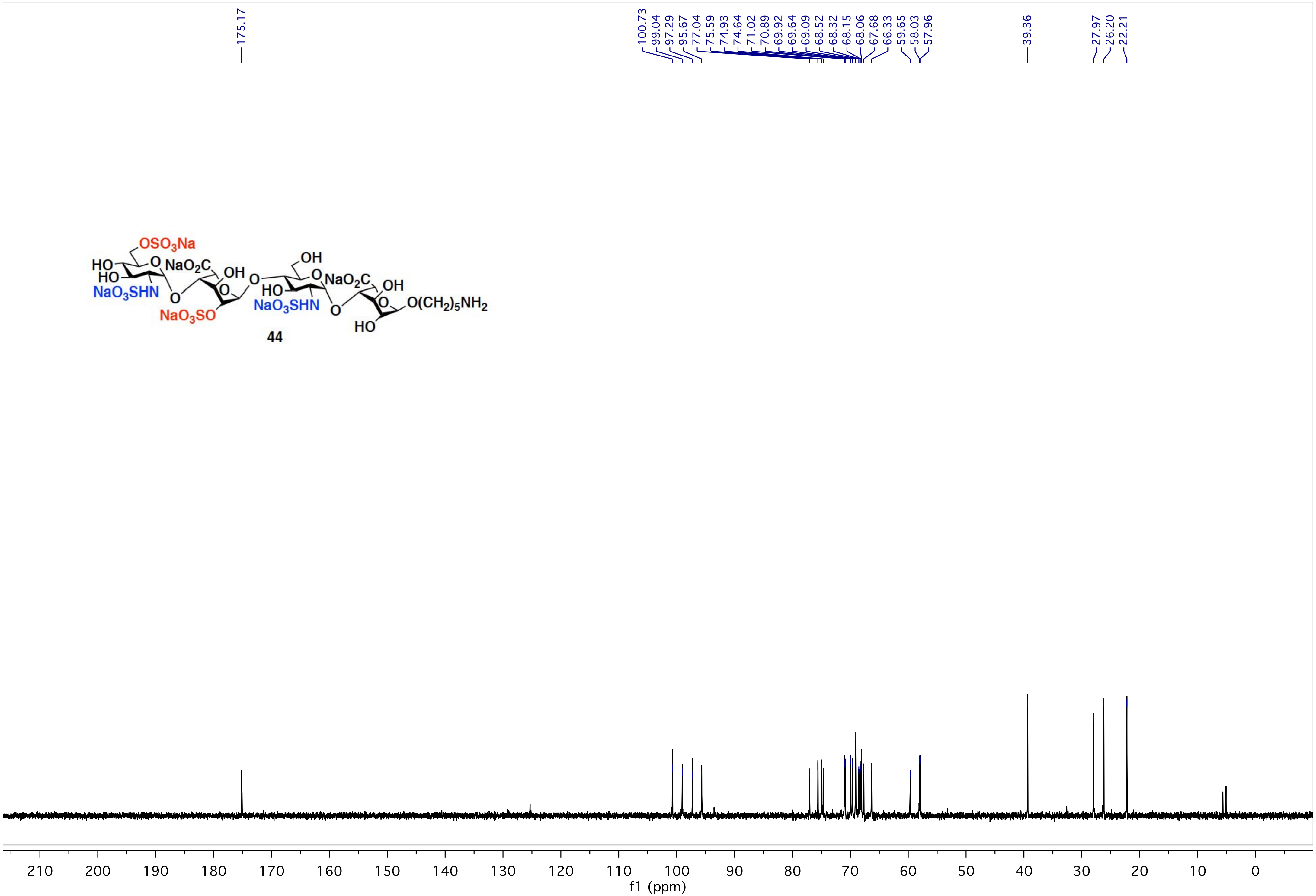
43



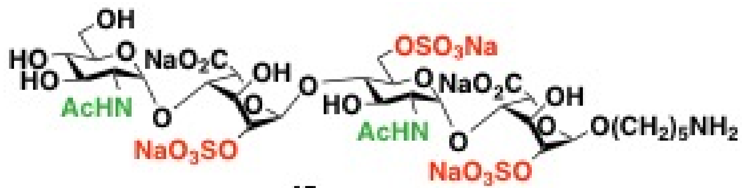
BSH-01-114.1.fid —



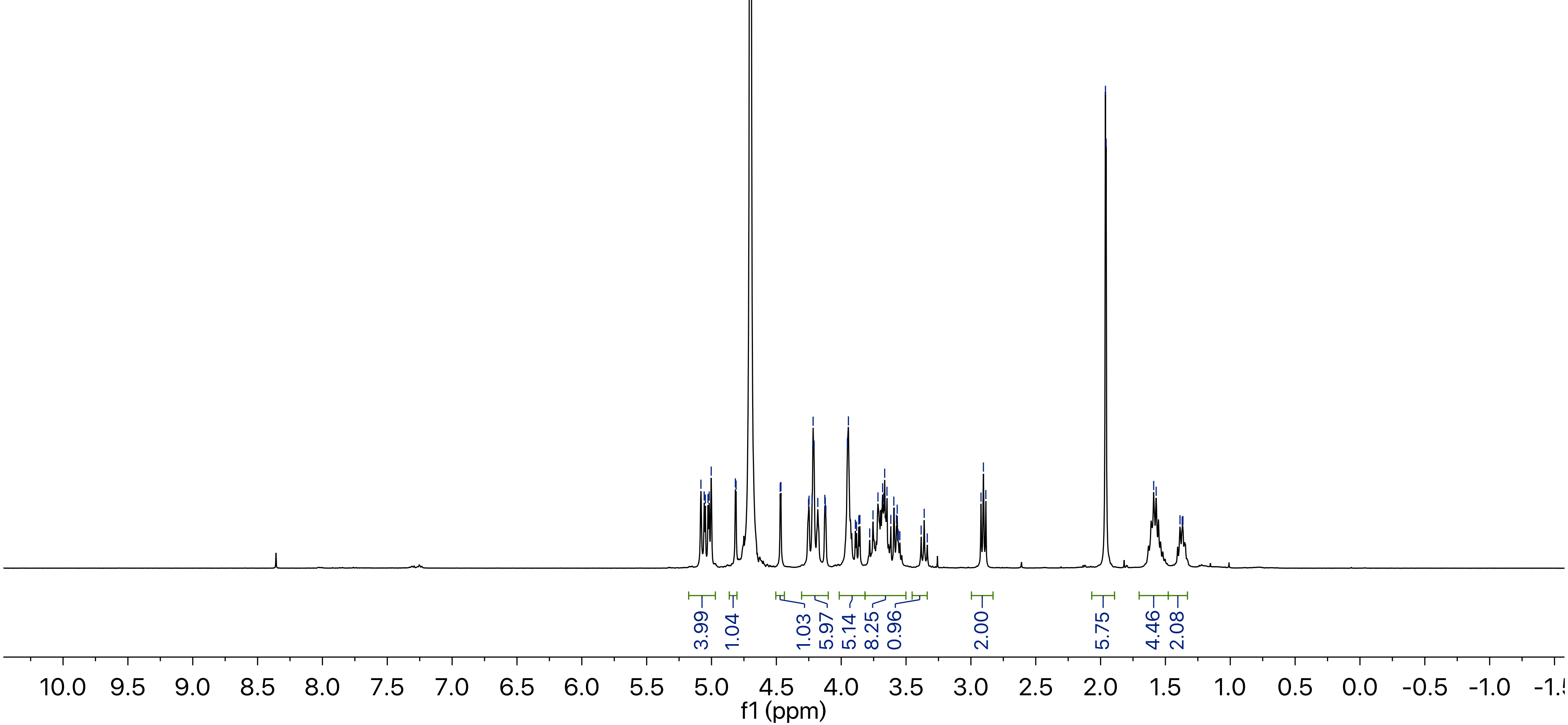
BSH-01-114.2.fid —



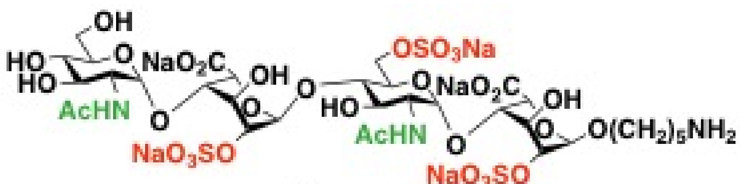
WL-2-198-D-NAc-C-2S-B-NAc-6S-A-2S-H-TC.1.fid —



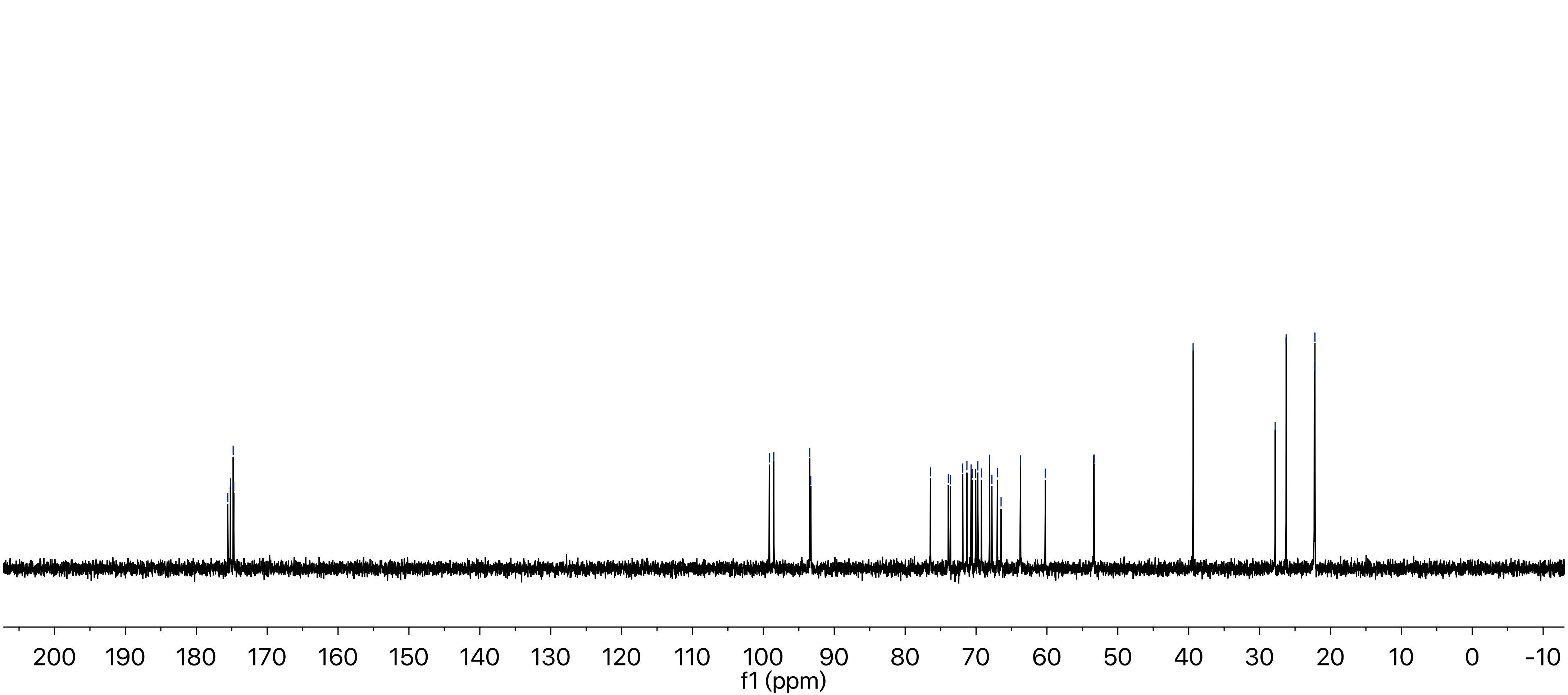
45



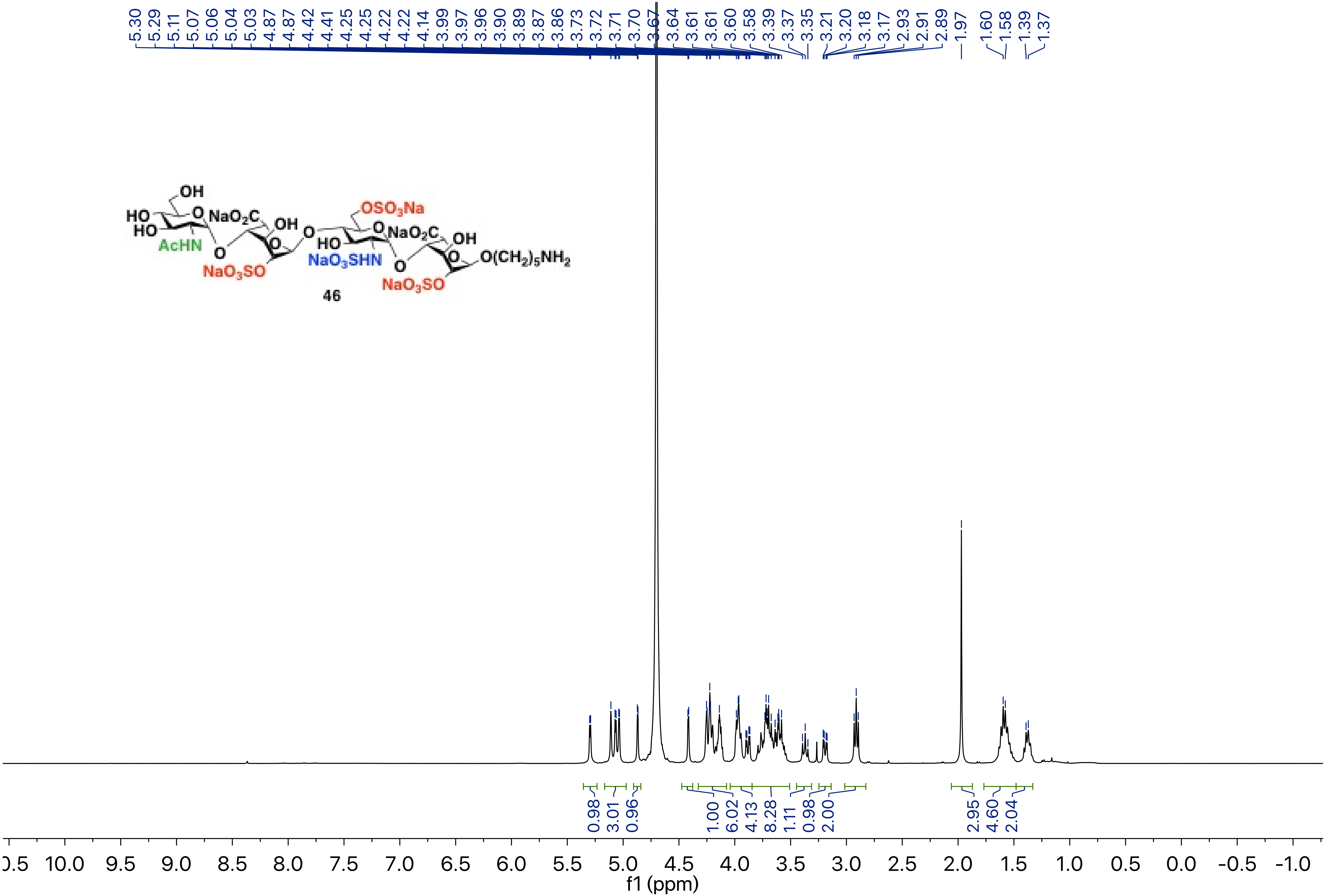
WL-2-198-D-NAc-C-2S-B-NAc-6S-A-2S-C-TC.1.1.1r



45

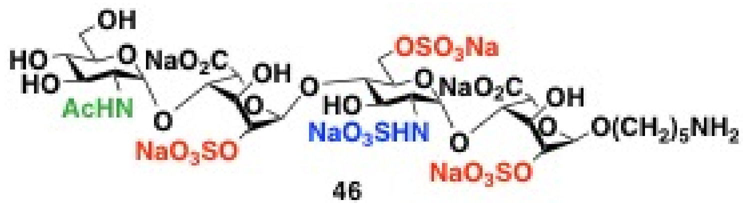


WL-2-199-D-NAc-C-2S-B-NS-6S-A-2S-H-TC-2.1.1.1r

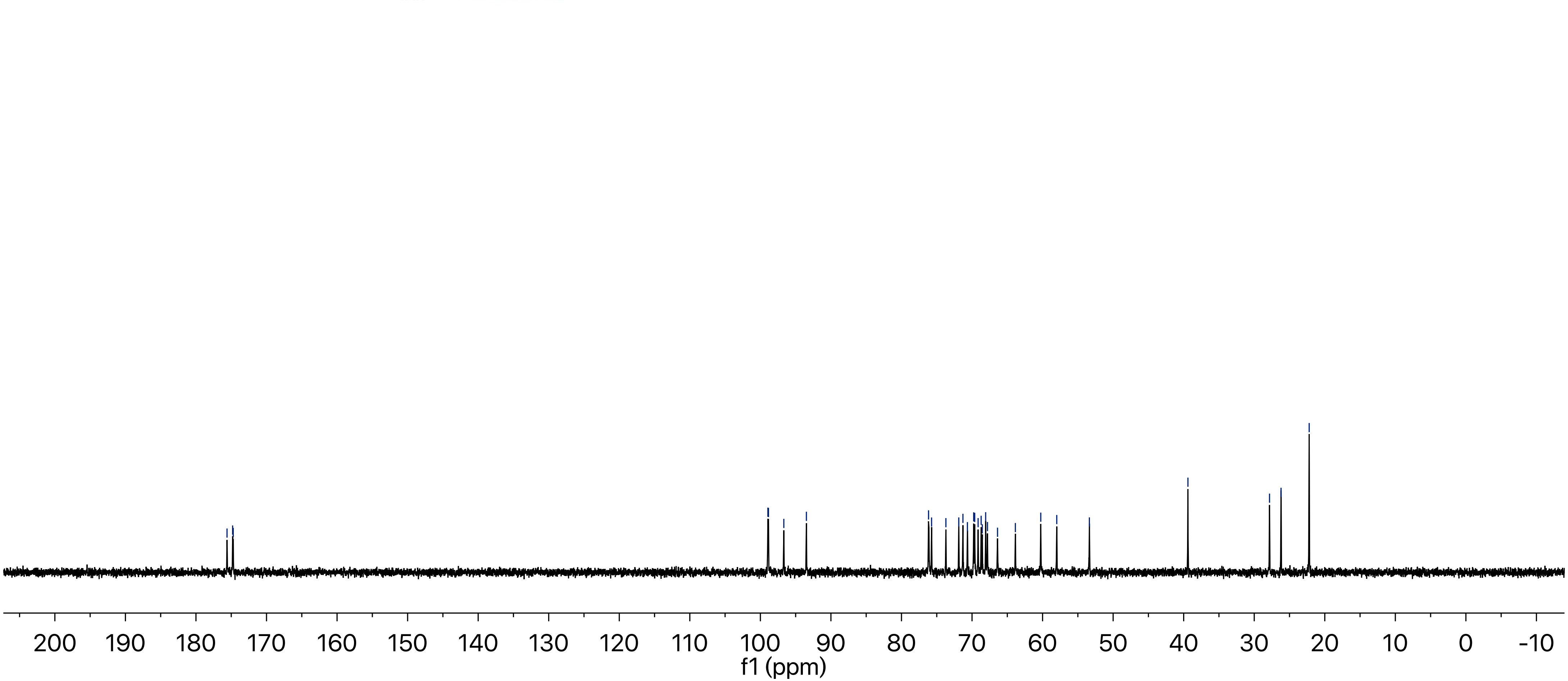


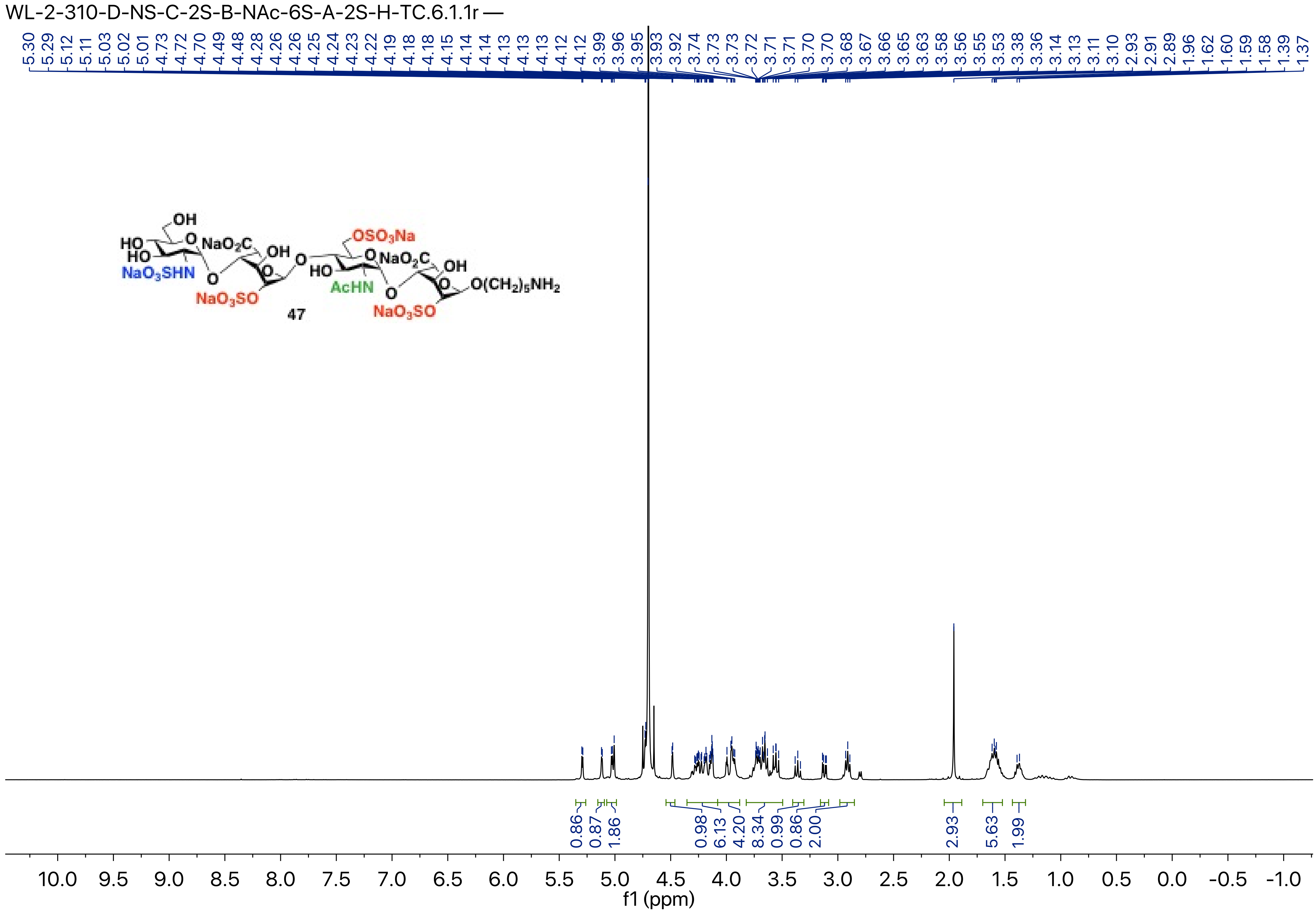
46

WL-2-199-D-NAc-C-2S-B-NS-6S-A-2S-C-TC.8.1.1r

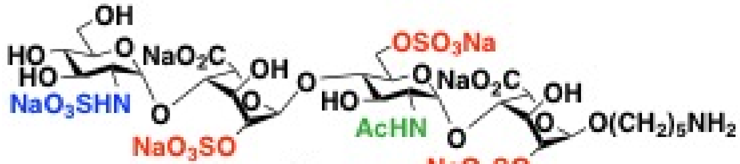


46

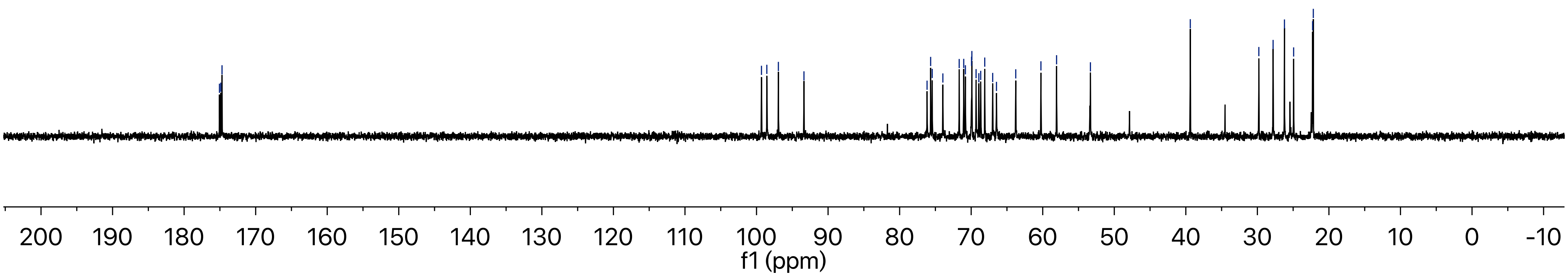


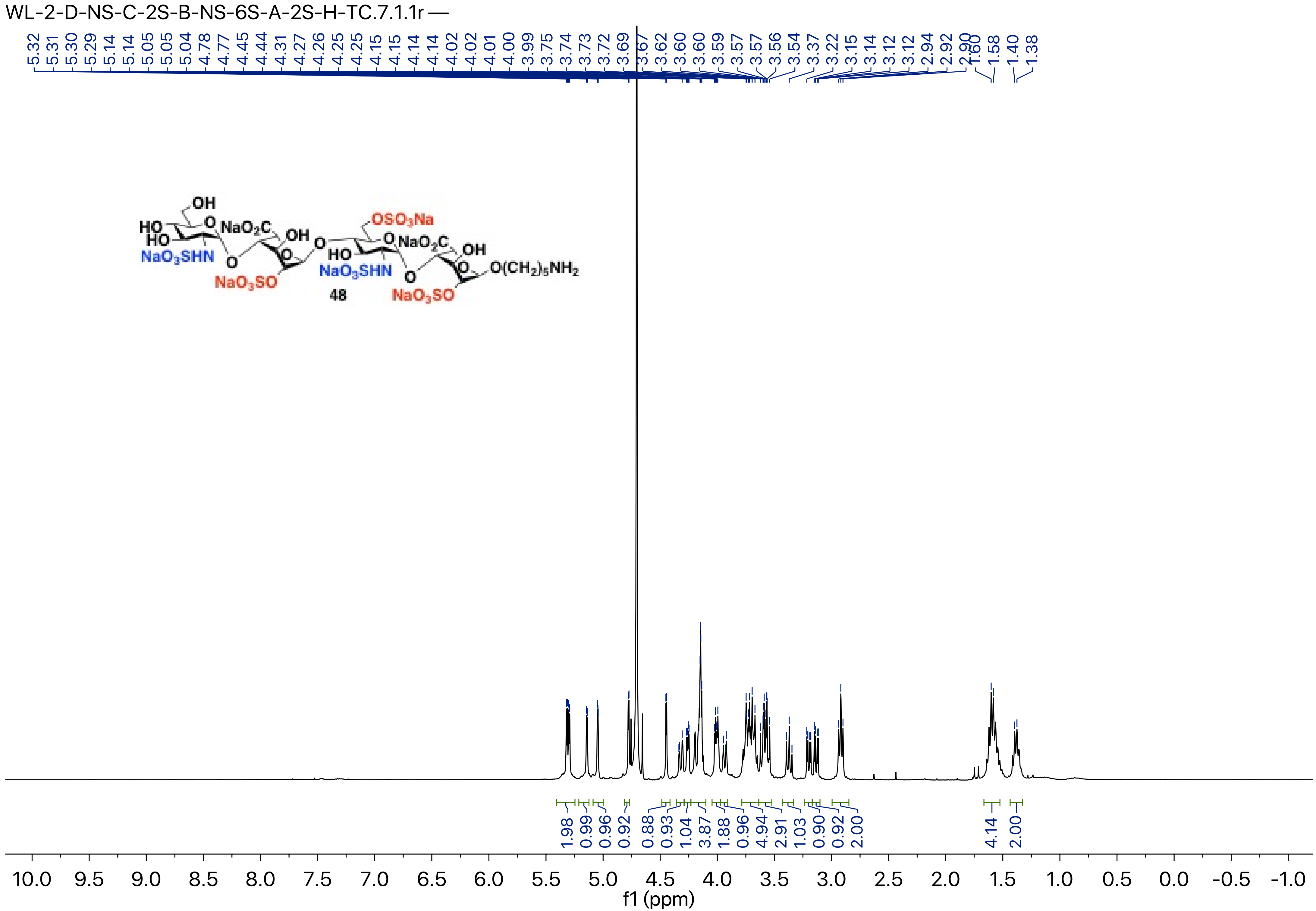

WL-2-310-D-NS-C-2S-B-NAc-6S-A-2S-H-TC.6.1.1r
5.30 5.29 5.12 5.11 5.03 5.02 5.01 4.73 4.72 4.70 4.49 4.48 4.28 4.26 4.26 4.25 4.24 4.23 4.22 4.19 4.18 4.18 4.15 4.14 4.14 4.13 4.13 4.13 4.12 4.12 3.99 3.96 3.95 3.93 3.92 3.74 3.73 3.73 3.72 3.71 3.71 3.70 3.70 3.68 3.67 3.66 3.65 3.63 3.58 3.56 3.55 3.53 3.38 3.36 3.14 3.13 3.11 3.10 2.93 2.91 2.89 1.96 1.62 1.60 1.59 1.58 1.39 1.37
HO
HO
OH
O
NaO2C
NaO3SHN
O
OH
NaO3SO
O
OSO3Na
HO
AcHN
NaO2C
OH
O
NaO3SO
O(CH2)5NH2
47
0.86 0.87 1.86 0.98 6.13 4.20 8.34 0.99 0.86 2.00 2.93 5.63 1.99
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 -0.5 -1.0
f1 (ppm)

WL-2-310-D-NS-C-2S-B-NAc-6S-A-2S-C-TC.1.1.1r

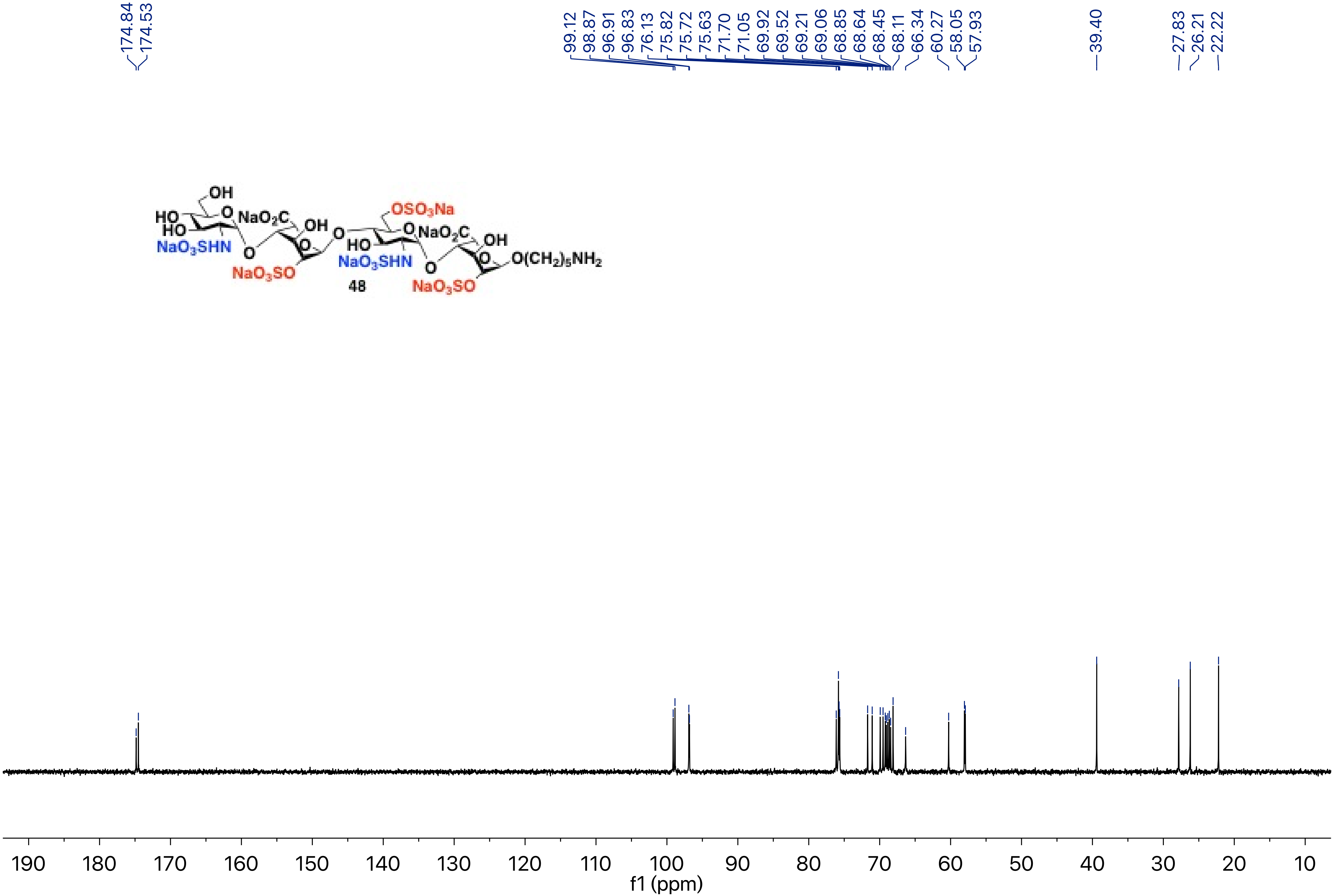


47

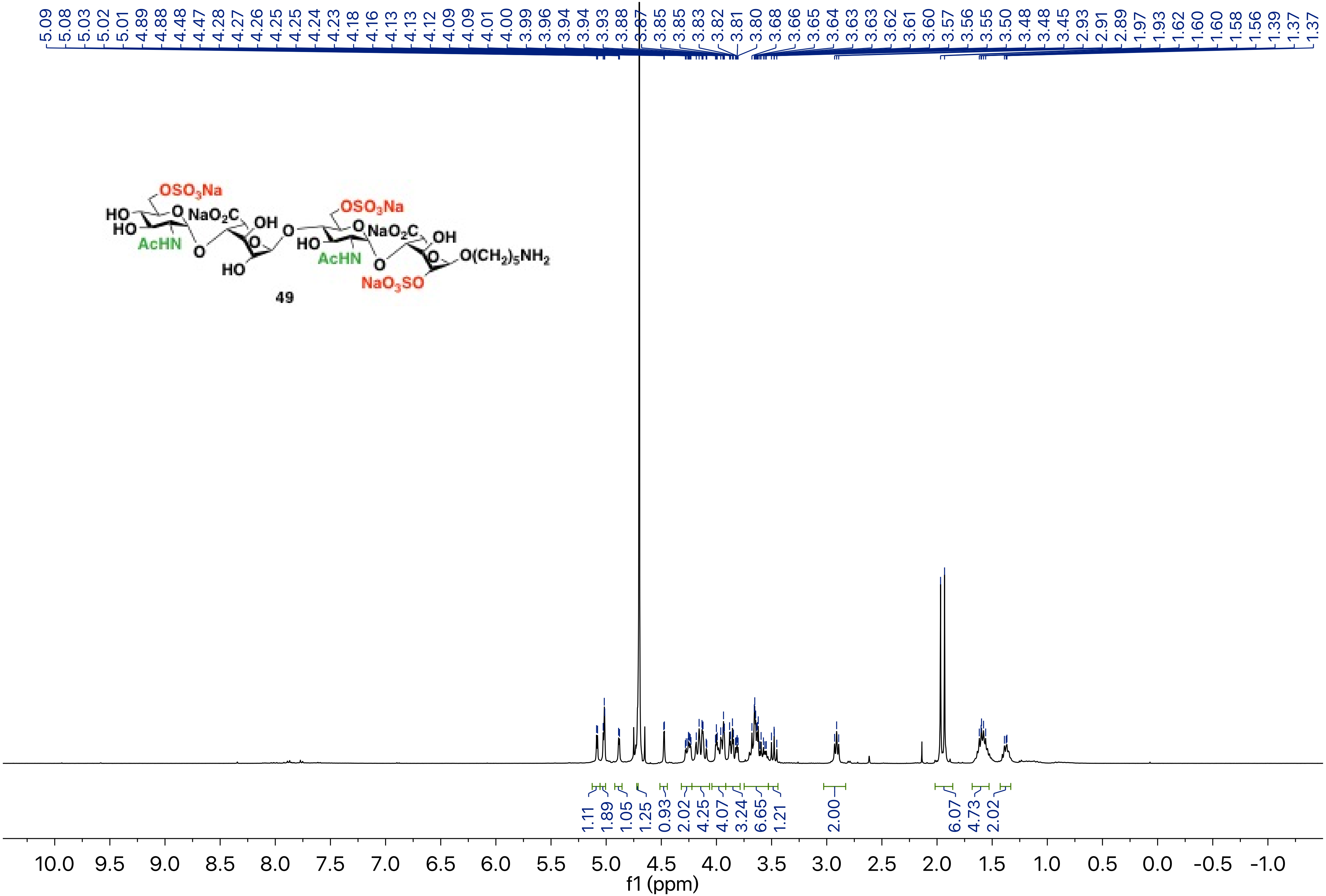



WL-2-D-NS-C-2S-B-NS-6S-A-2S-H-TC.7.1.1r
5.32 5.31 5.30 5.29 5.14 5.14 5.05 5.05 5.04 4.78 4.77 4.45 4.44 4.31 4.27 4.26 4.25 4.25 4.15 4.15 4.14 4.14 4.02 4.02 4.01 4.00 3.99 3.75 3.74 3.73 3.72 3.69 3.67 3.62 3.60 3.60 3.59 3.57 3.57 3.56 3.54 3.37 3.22 3.15 3.14 3.12 3.12 2.94 2.92 2.90 1.60 1.58 1.40 1.38
48
1.98 0.99 0.96 0.92 0.88 0.93 1.04 3.87 1.88 0.96 4.94 2.91 1.03 0.90 0.92 2.00 4.14 2.00
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 -0.5 -1.0
f1 (ppm)

WL-2-D-NS-C-2S-B-NS-6S-A-2S-C-TC.1.1.1r —

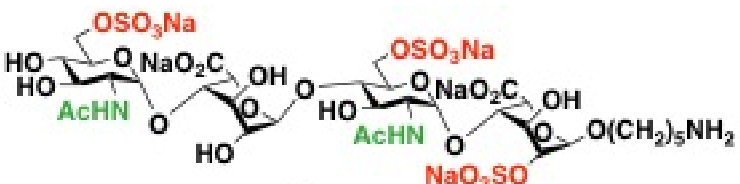


WL-2-263-run2-D-NAc-6S-B-NAc-6S-A-2S-TC-H.7.1.1r —

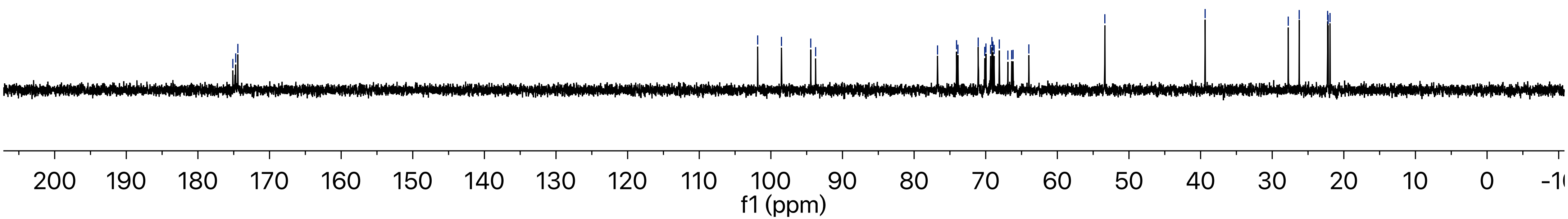


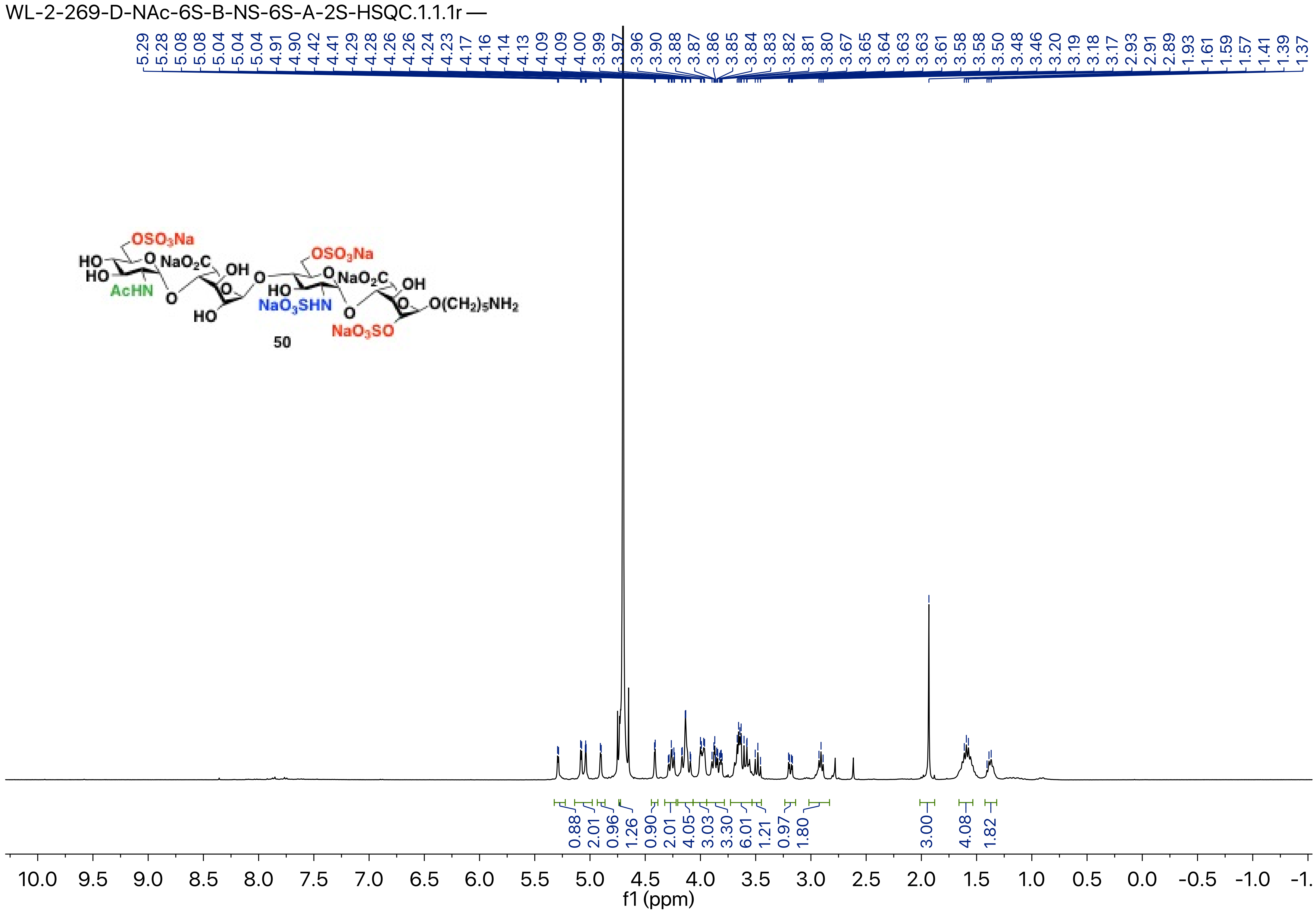
49

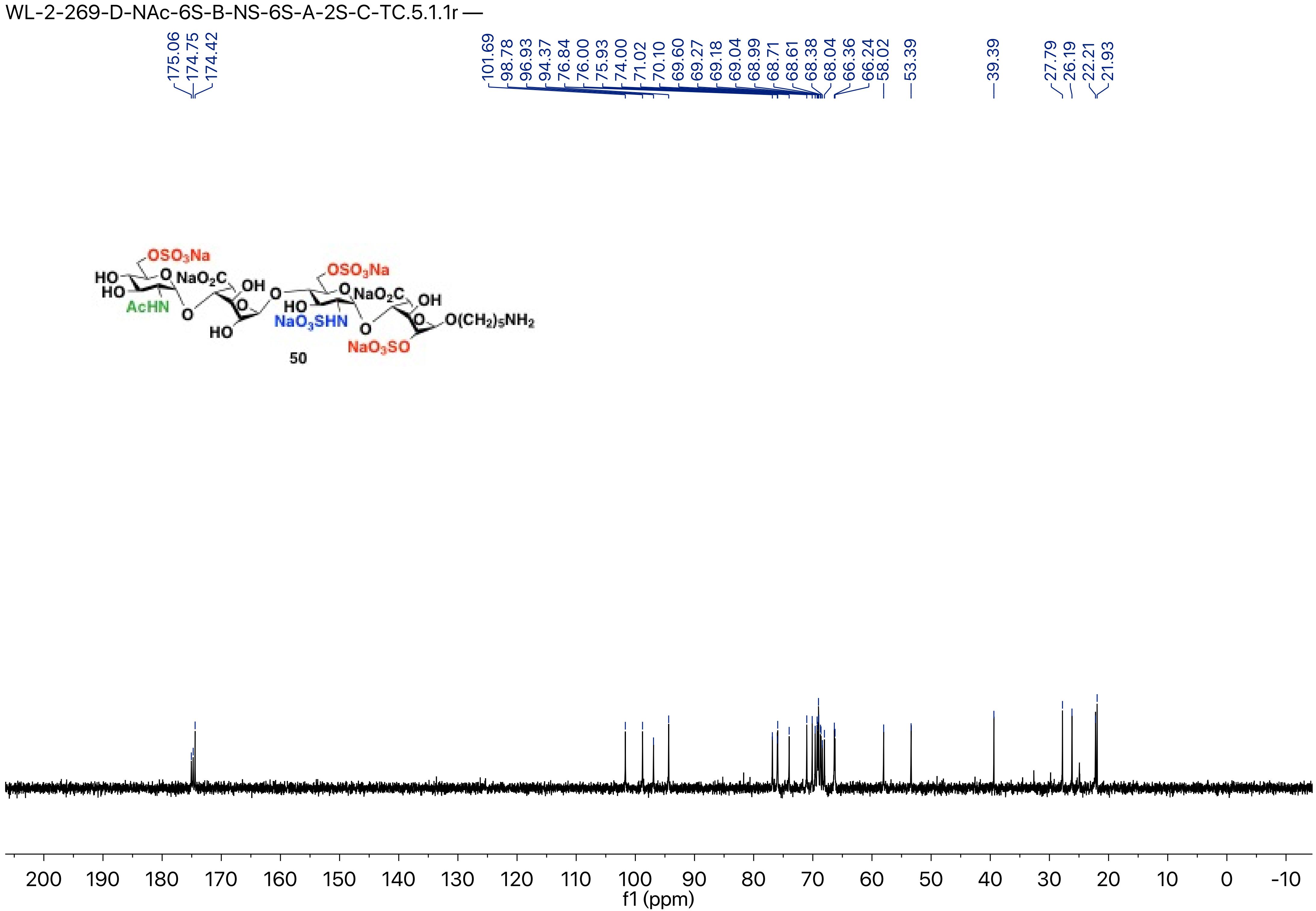
WL-2-263-run2-D-NAc-6S-B-NAc-6S-A-2S-TC-C.1.1.1r —



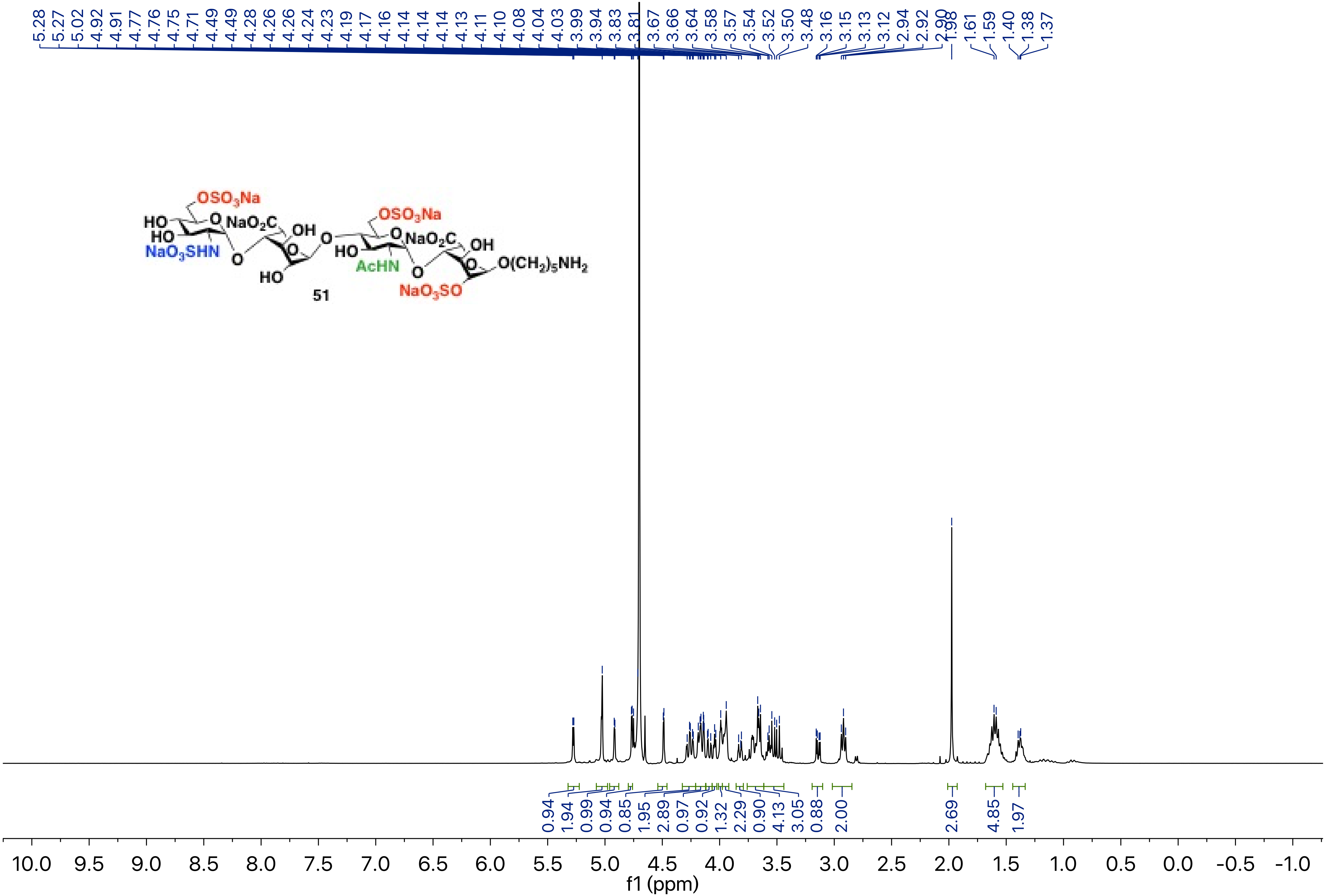
49



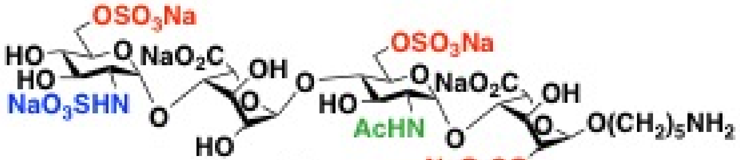

WL-2-269-D-NAc-6S-B-NS-6S-A-2S-HSQC.1.1.1r
5.29 5.28 5.08 5.08 5.04 5.04 5.04 4.91 4.90 4.42 4.41 4.29 4.28 4.26 4.26 4.24 4.23 4.17 4.16 4.14 4.13 4.09 4.09 4.00 3.99 3.97 3.96 3.90 3.88 3.87 3.86 3.85 3.84 3.83 3.82 3.81 3.80 3.67 3.65 3.64 3.63 3.63 3.61 3.58 3.58 3.50 3.48 3.46 3.20 3.19 3.18 3.17 2.93 2.91 2.89 1.93 1.61 1.59 1.57 1.41 1.39 1.37
50
0.88 2.01 0.96 1.26 0.90 2.01 4.05 3.03 3.30 6.01 1.21 0.97 1.80 3.00 4.08 1.82
f1 (ppm)


WL-2-269-D-NAc-6S-B-NS-6S-A-2S-C-TC.5.1.1r
175.06
174.75
174.42
101.69
98.78
96.93
94.37
76.84
76.00
75.93
74.00
71.02
70.10
69.60
69.27
69.18
69.04
68.99
68.71
68.61
68.38
68.04
66.36
66.24
58.02
53.39
39.39
27.79
26.19
22.21
21.93
50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

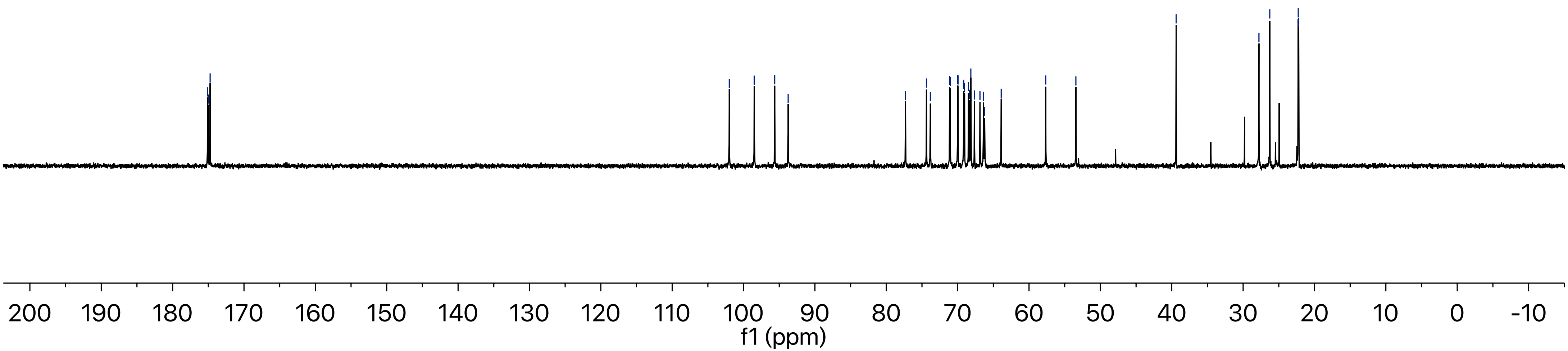
WL-2-290-D-6S-NS-B-6S-NAc-A-2S-H-TC.7.1.1r —

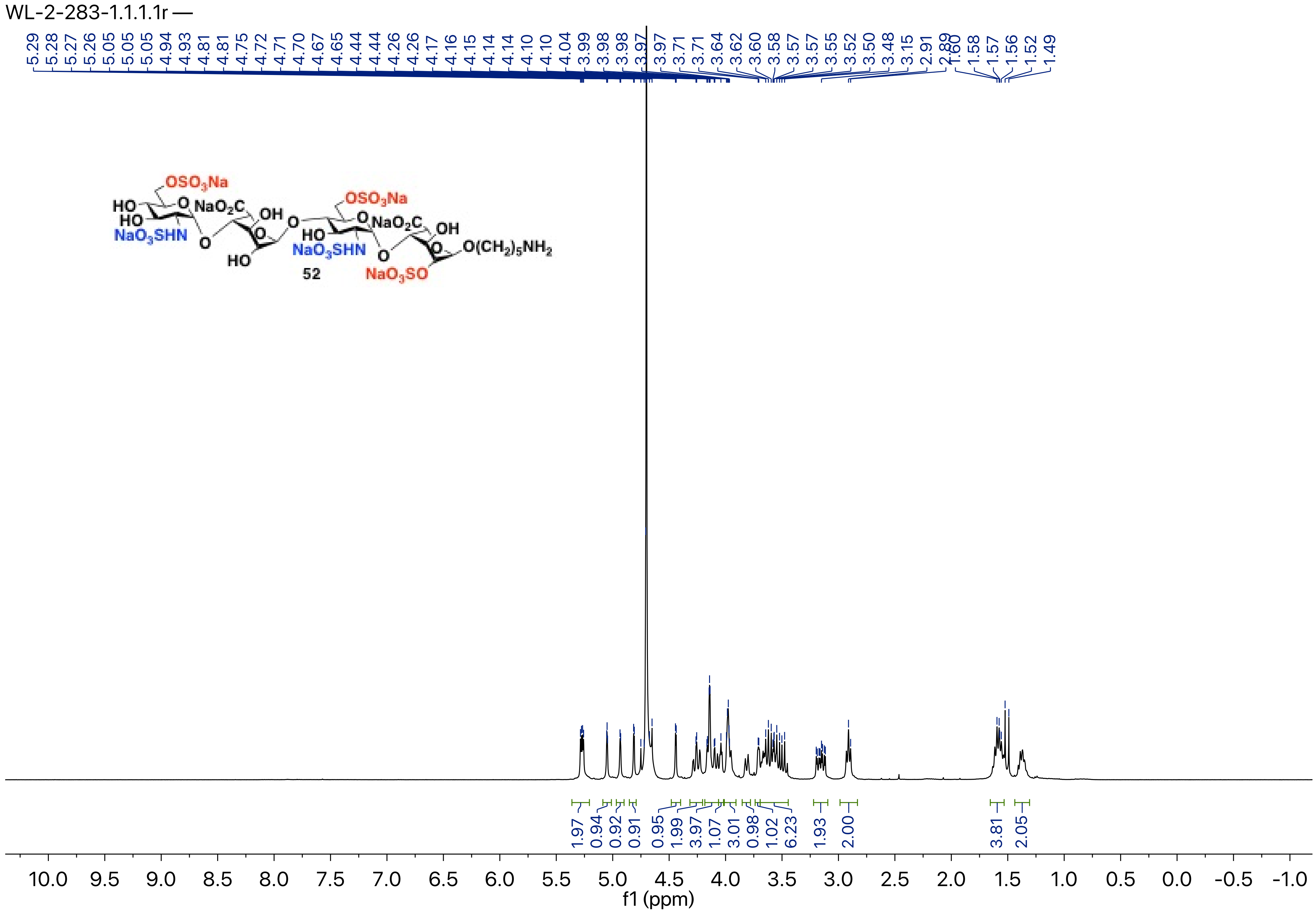


WL-2-290-D-6S-NS-B-6S-NAc-A-2S-C-TC.1.1.1r

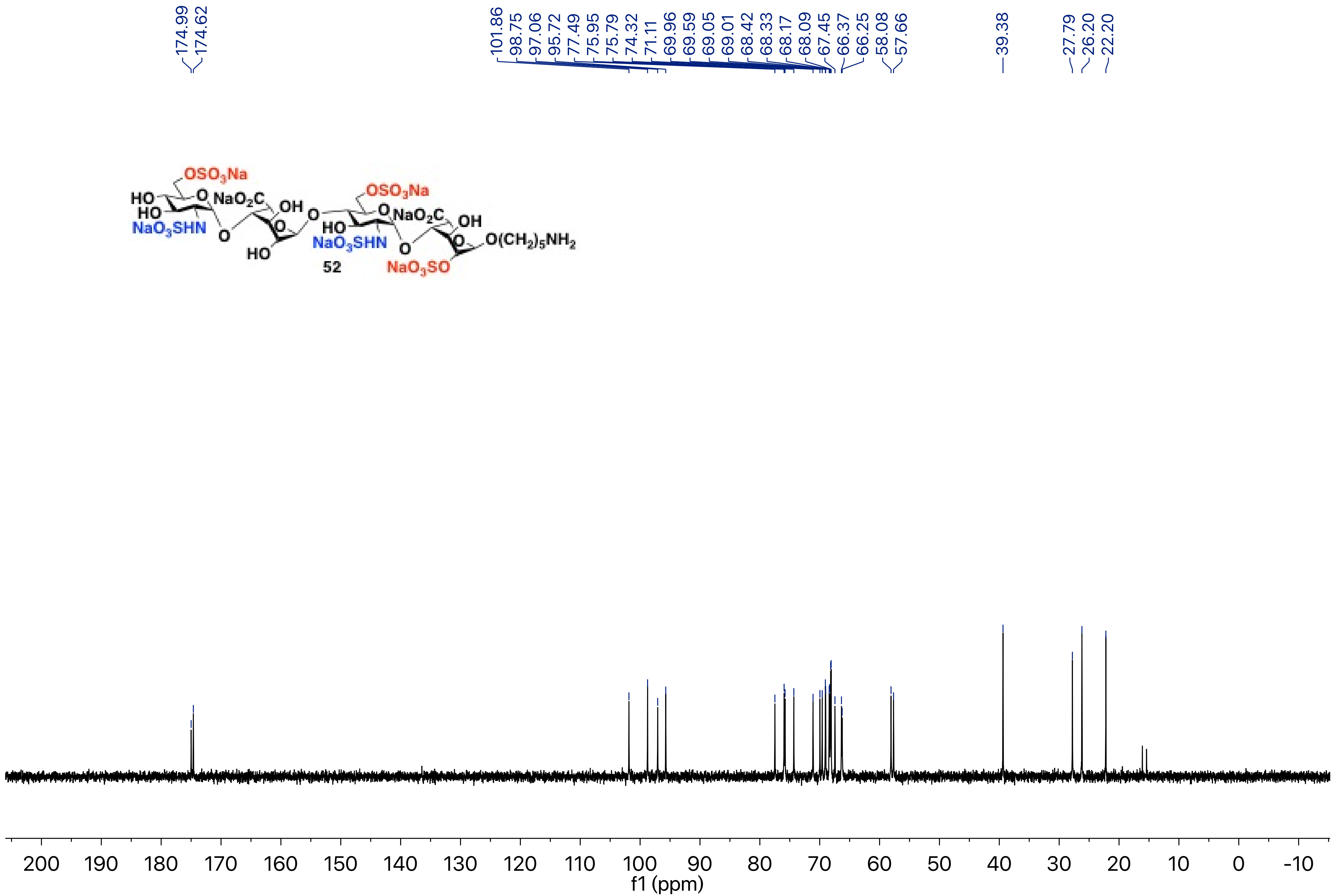


51

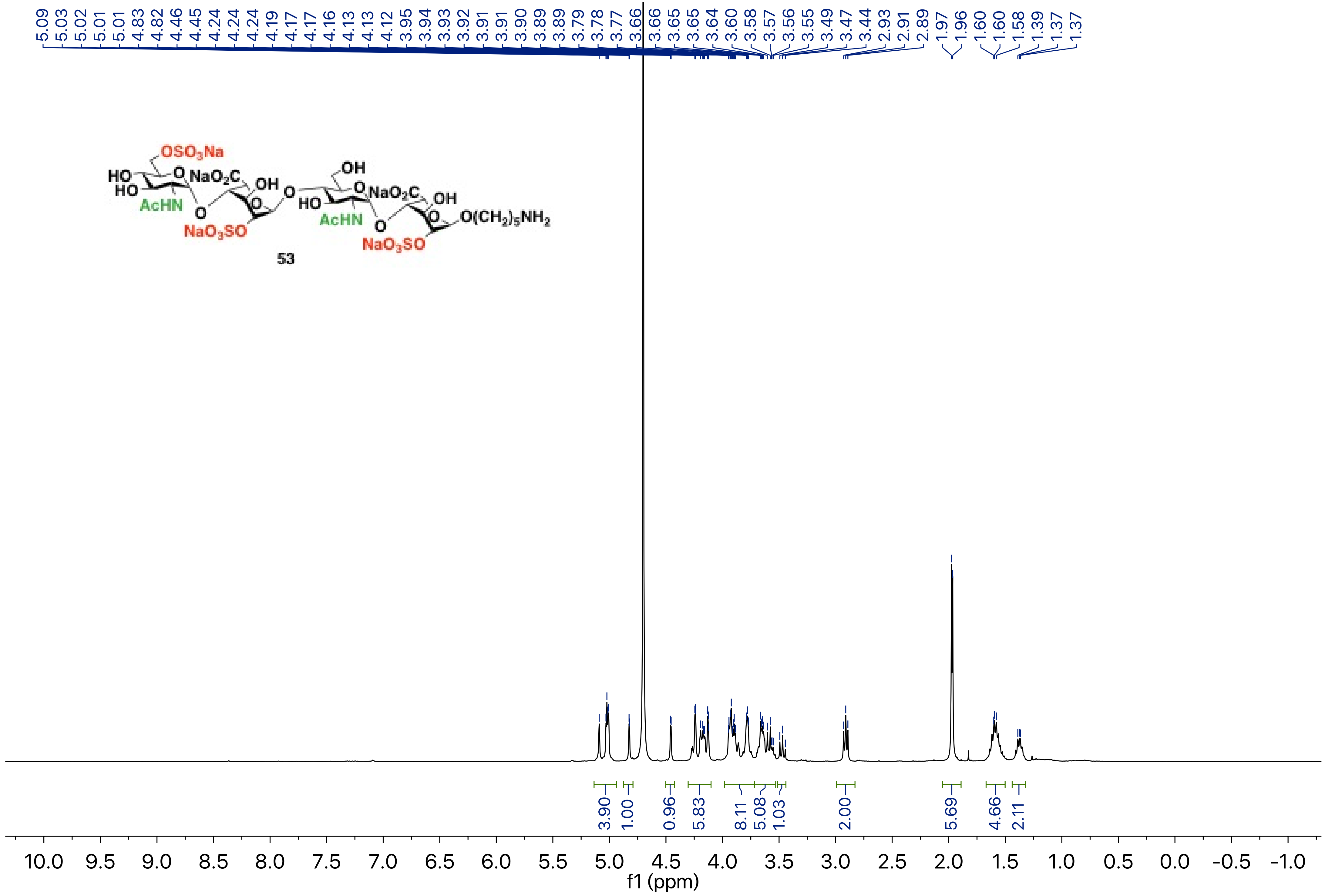



WL-2-283-1.1.1.1r
5.29 5.28 5.27 5.26 5.05 5.05 5.05 4.94 4.93 4.81 4.81 4.75 4.72 4.71 4.70 4.67 4.65 4.44 4.44 4.26 4.26 4.17 4.16 4.15 4.14 4.14 4.10 4.10 4.04 3.99 3.98 3.98 3.97 3.97 3.71 3.71 3.64 3.62 3.60 3.58 3.57 3.57 3.55 3.52 3.50 3.48 3.15 2.91 2.89 1.60 1.58 1.57 1.56 1.52 1.49
OSO3Na
HO
HO
NaO3SHN
NaO2C
OH
HO
52
NaO3SO
O(CH2)5NH2
1.97 0.94 0.92 0.91 0.95 1.99 3.97 1.07 3.01 0.98 1.02 6.23 1.93 2.00 3.81 2.05
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 -0.5 -1.0
f1 (ppm)

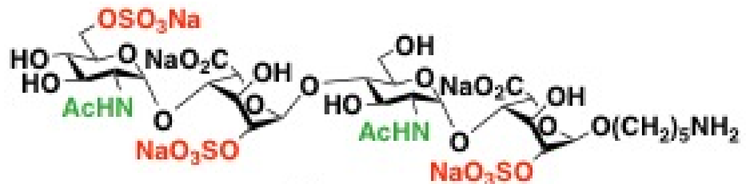
WL-2-283-D-NS-6S-B-NS-6S-A-2S-C-TC.1.1.1r



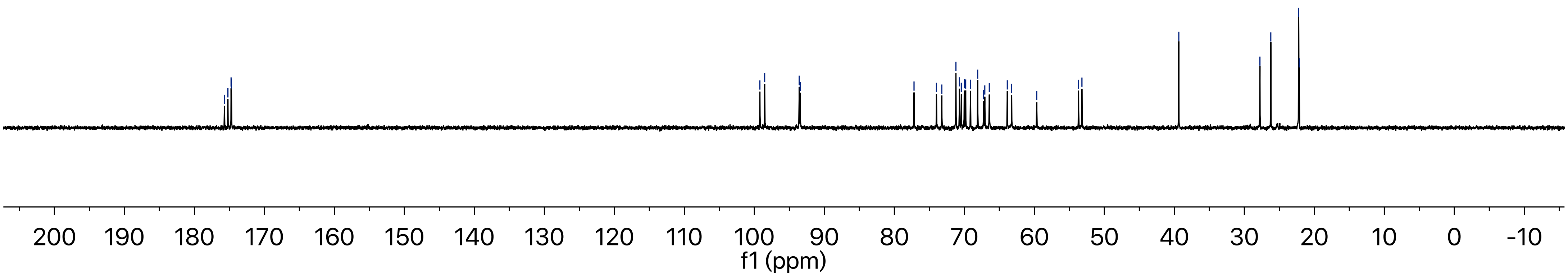
WL-2-156-D-NAc-6SO3-C-2SO3-B-NAc-A-2SO3-H-TC.2.1.1r



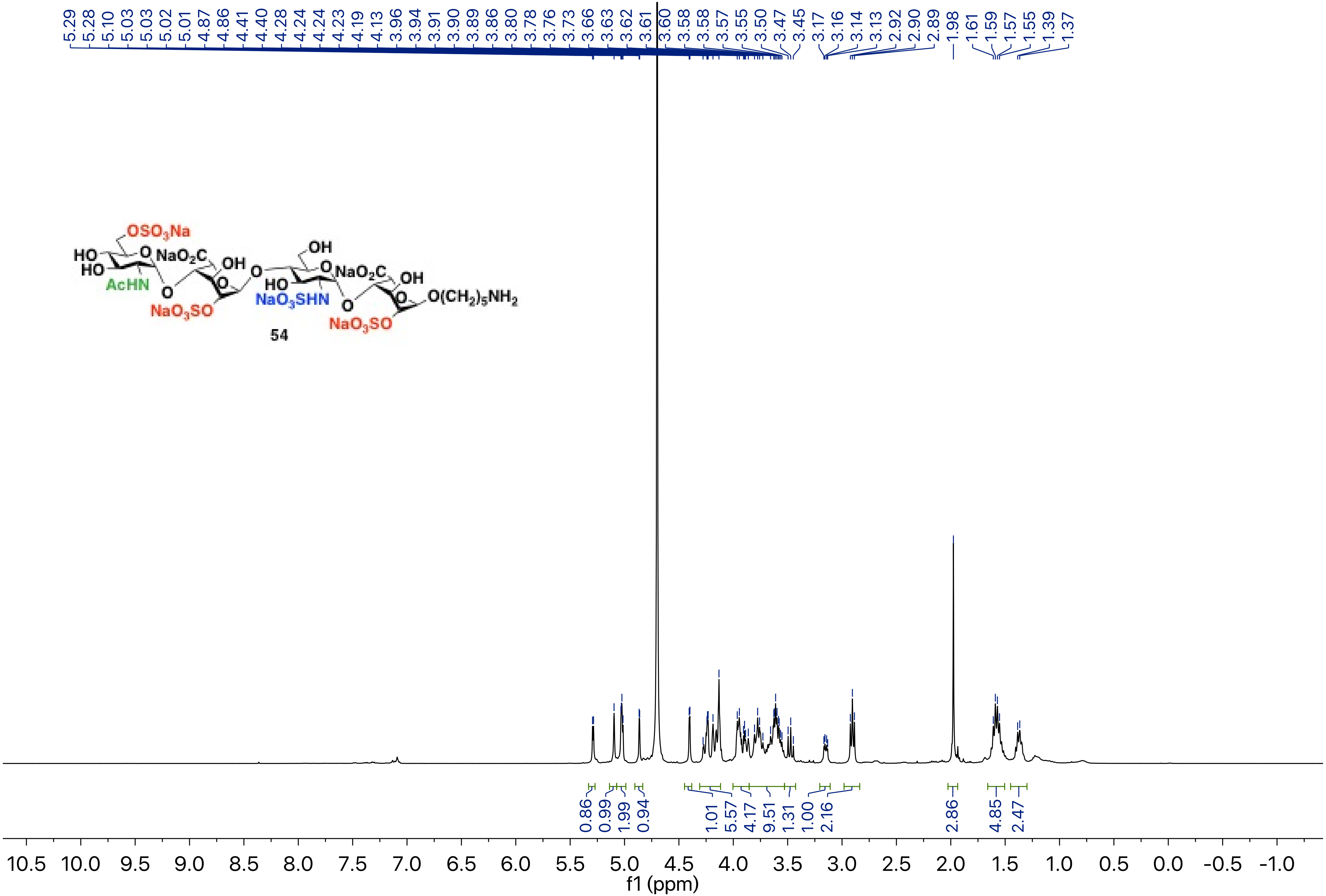
WL-2-156-D-NAc-6SO3-C-2SO3-B-NAc-A-2SO3-C-TC.1.1.1r



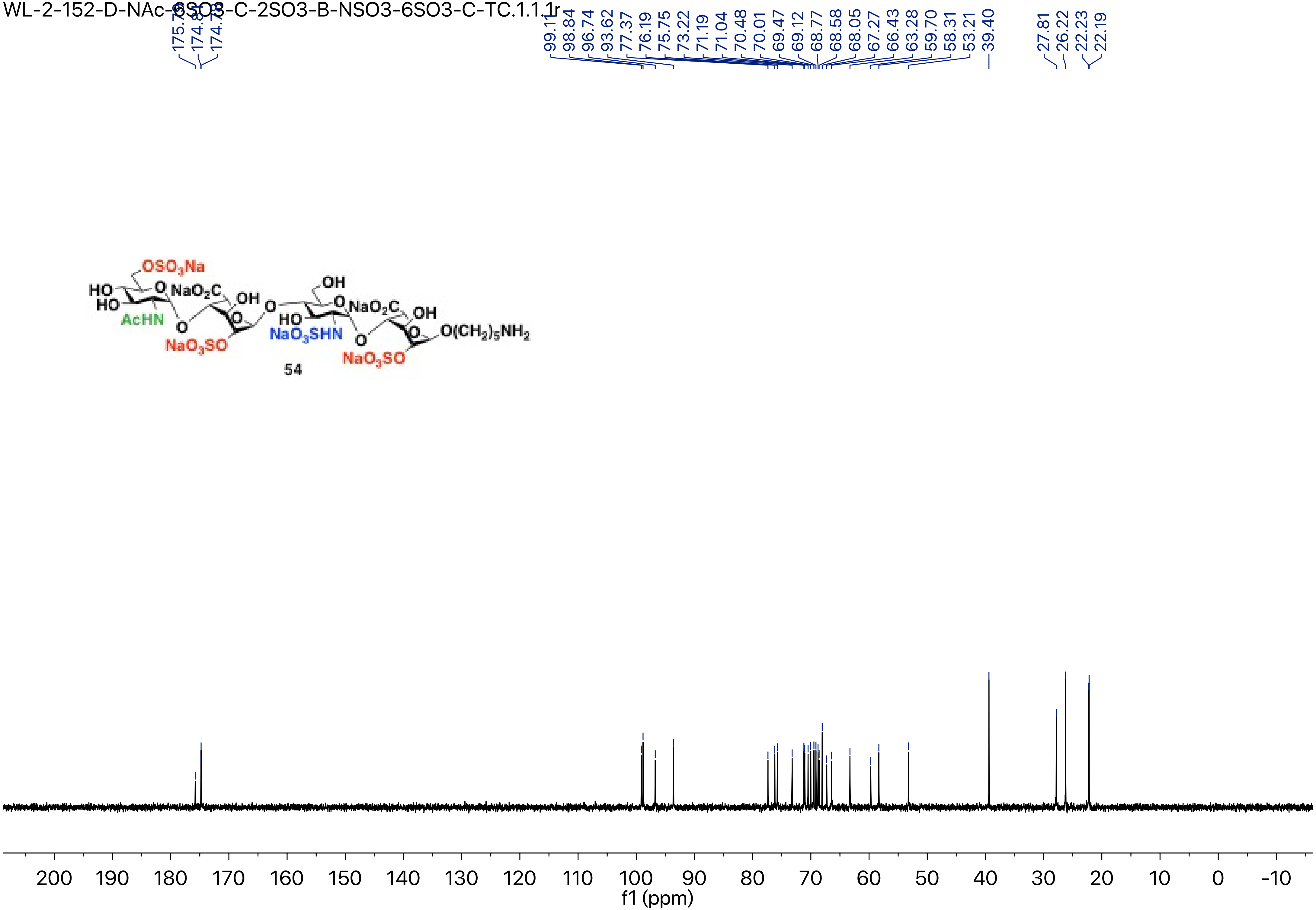
53



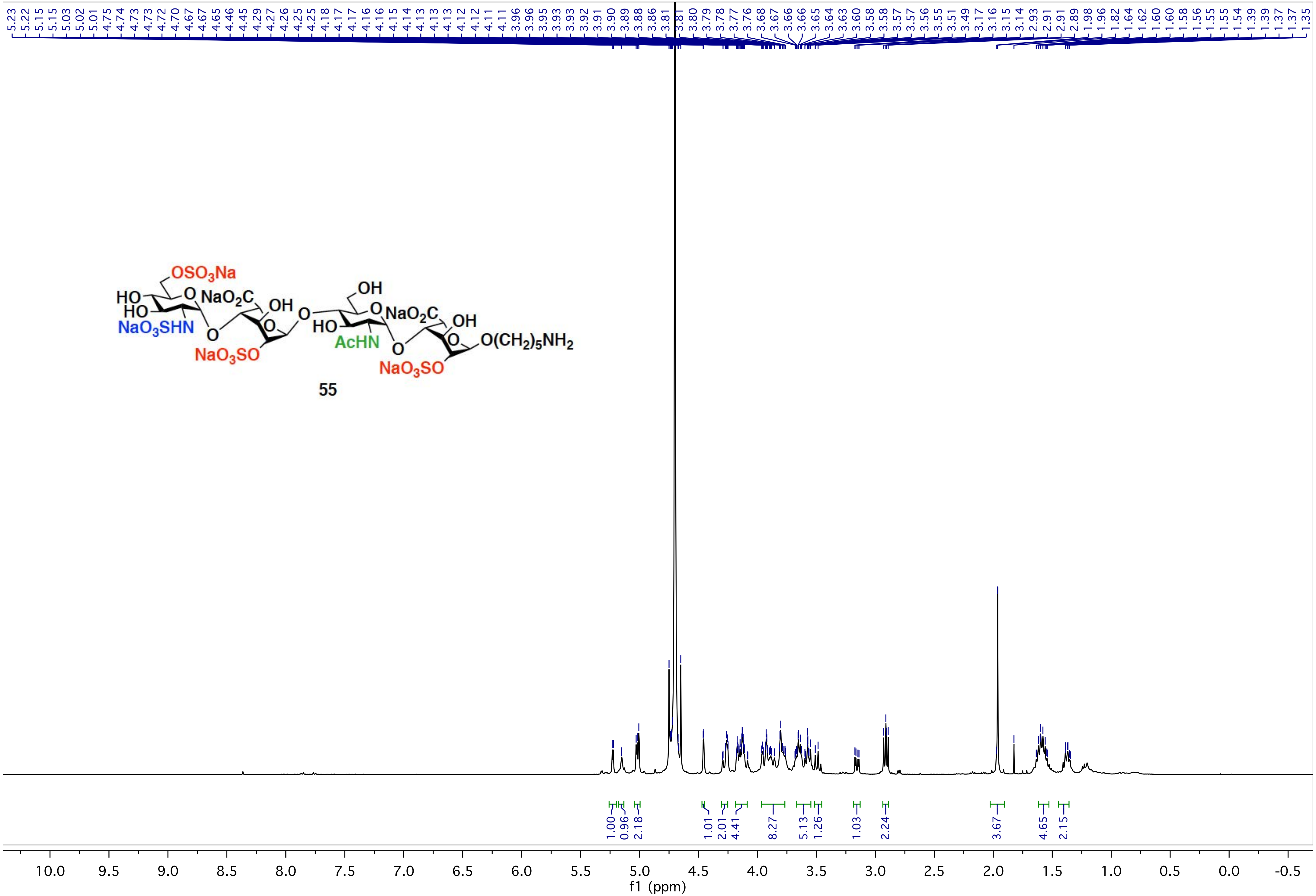
c-6SO3-C-2SO3-B-NSO3-6SO3-H-TC.2.1.1r



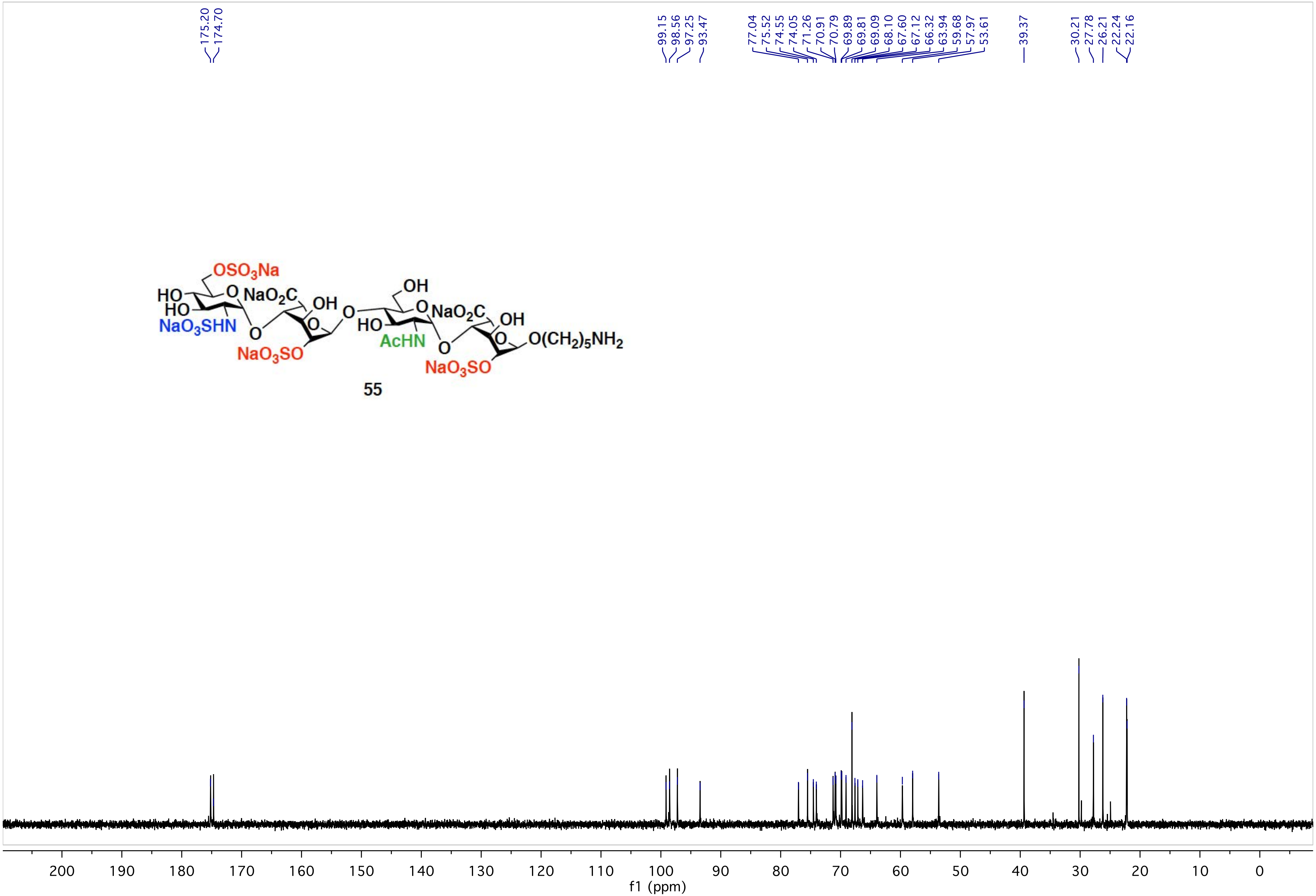
WL-2-152-D-NAc-6SO3-C-2SO3-B-NSO3-6SO3-C-TC.1.1.1r



BSH-02-72-pure.1.fid —

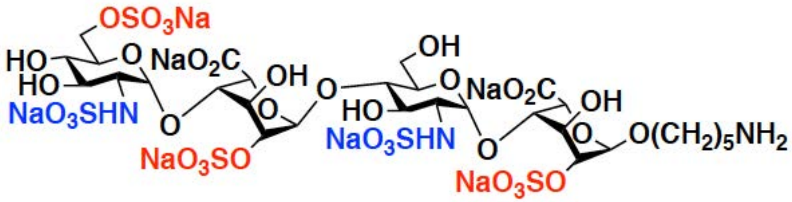


BSH-02-72.5.fid —

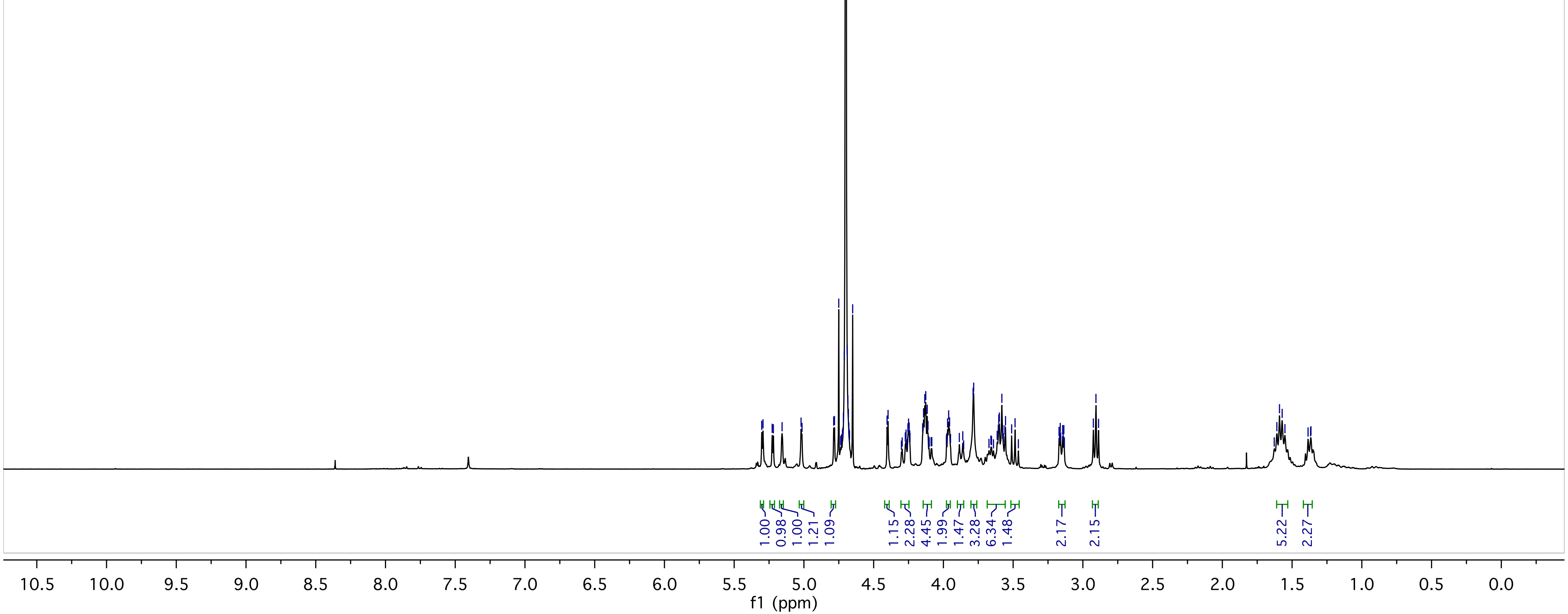


55

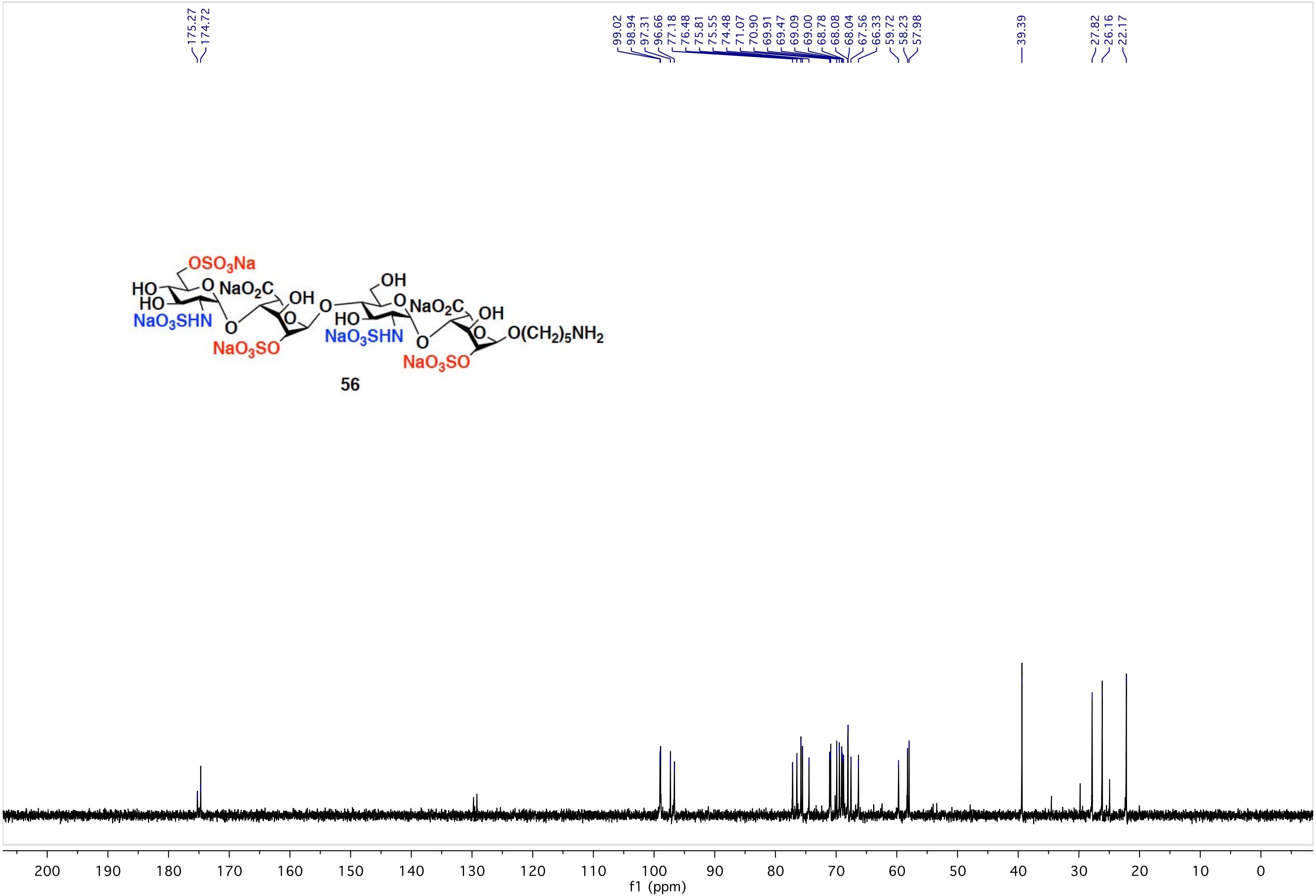
BSh-02-70-pure.1.fid —



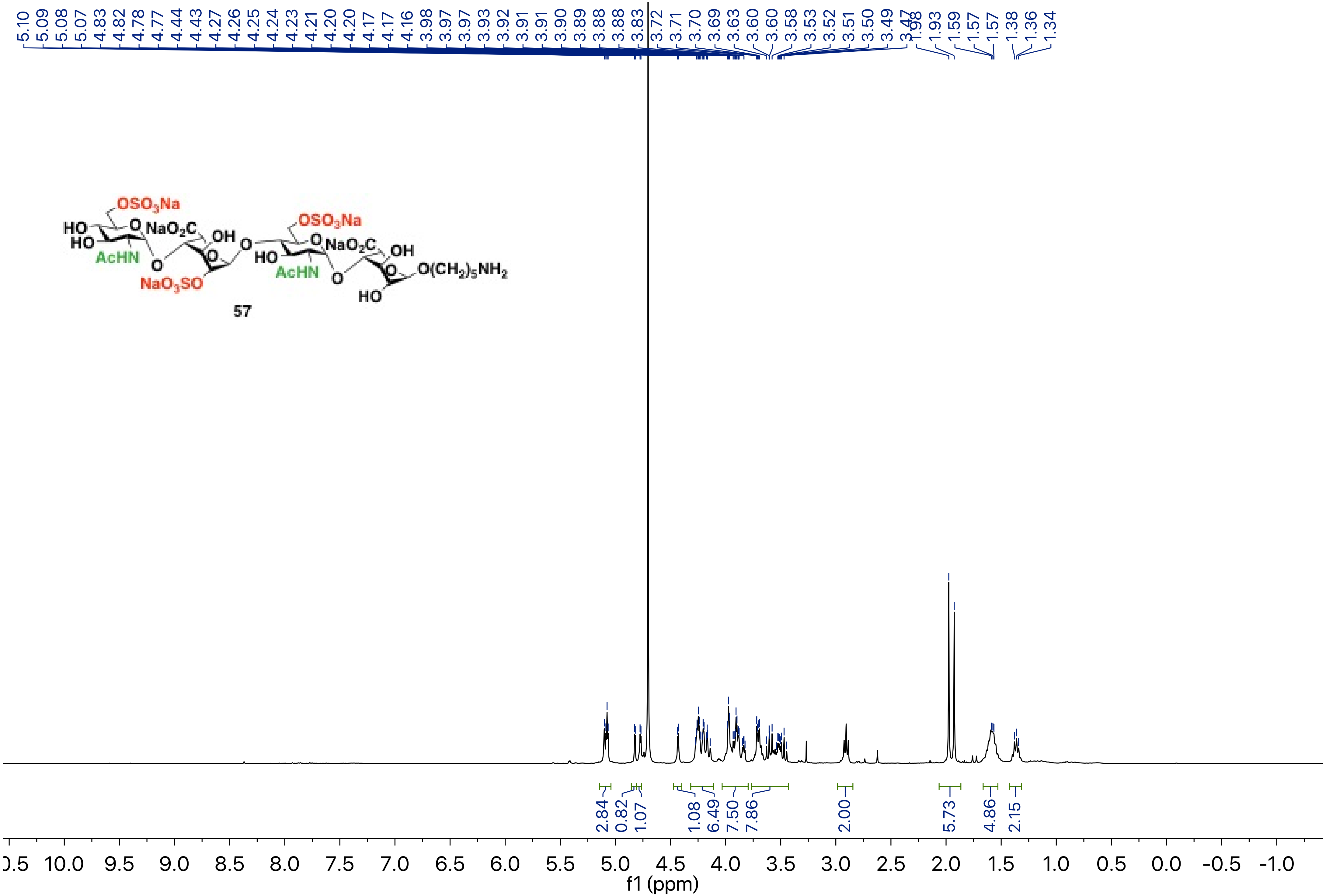
56



BSH-02-70-13C.1.fid —

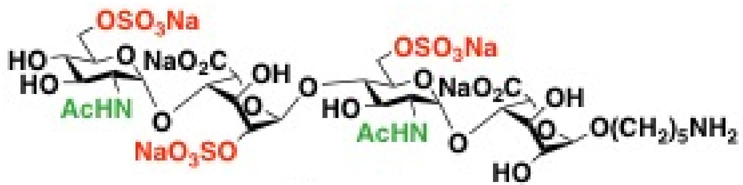


WL-2-230-D-6S-NAc-C-2S-B-6S-NAc-prod-H-TC.1.1.1r

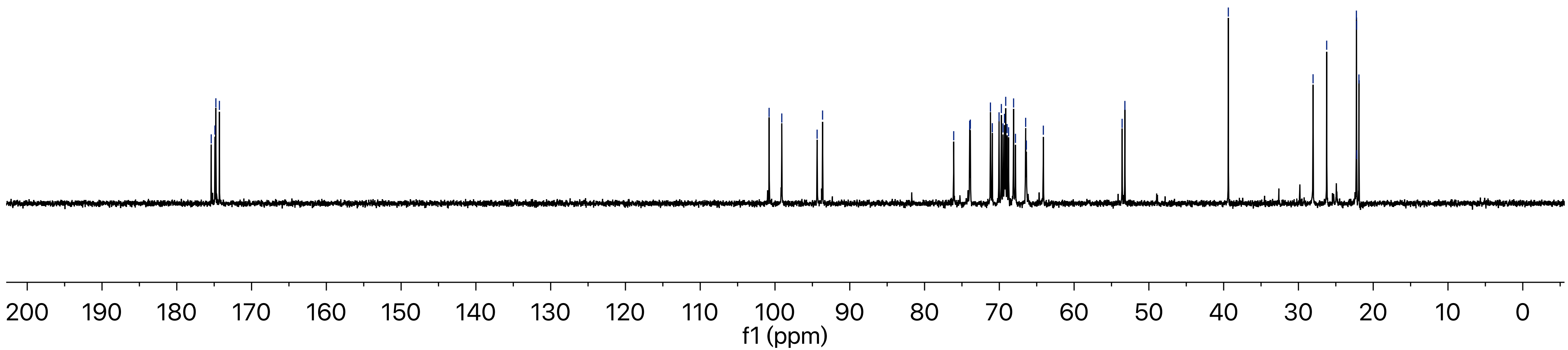


57

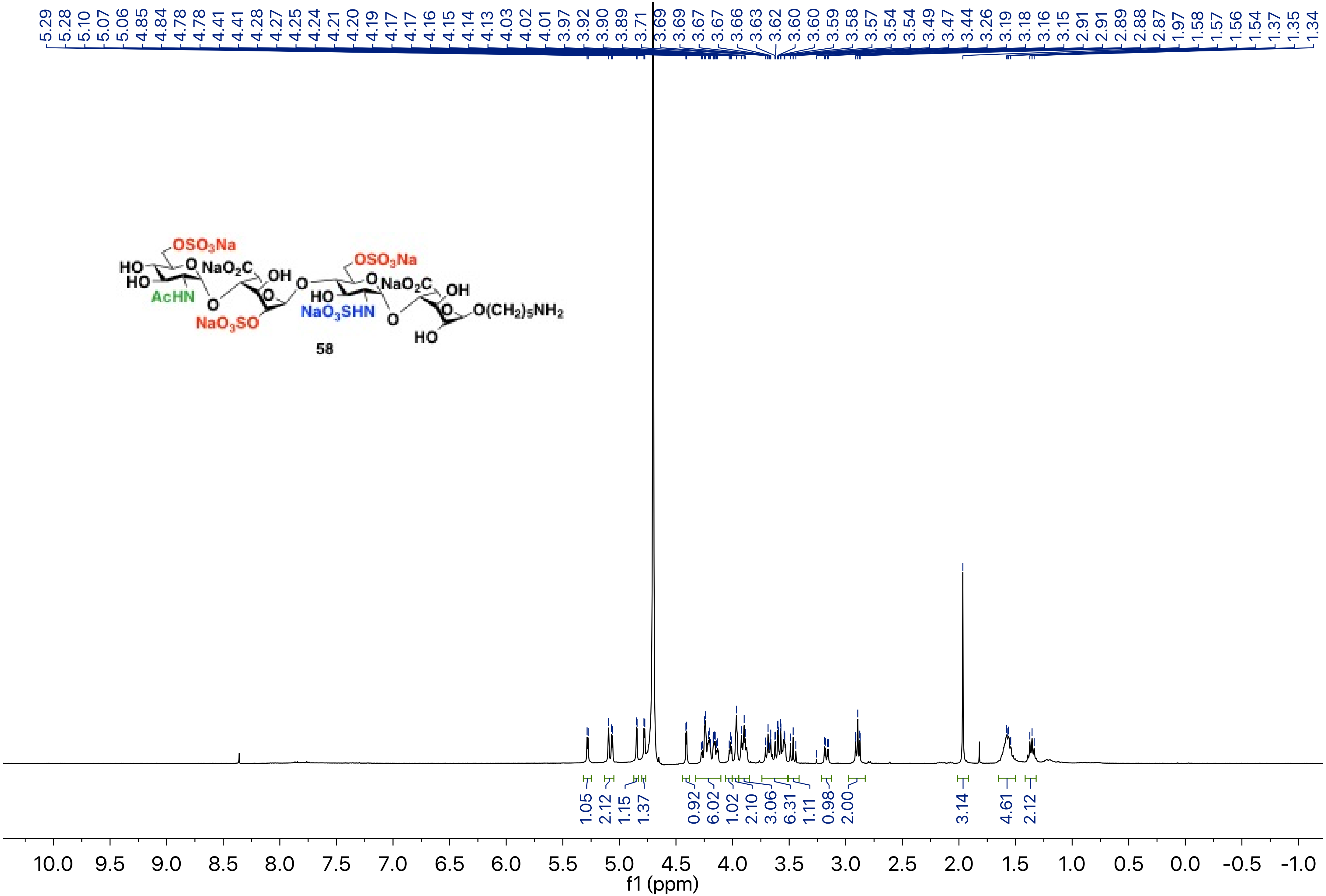
WL-2-D-6S-NAc-C-2S-B-6S-NAc-prod-C-TC.1.1.1r



57

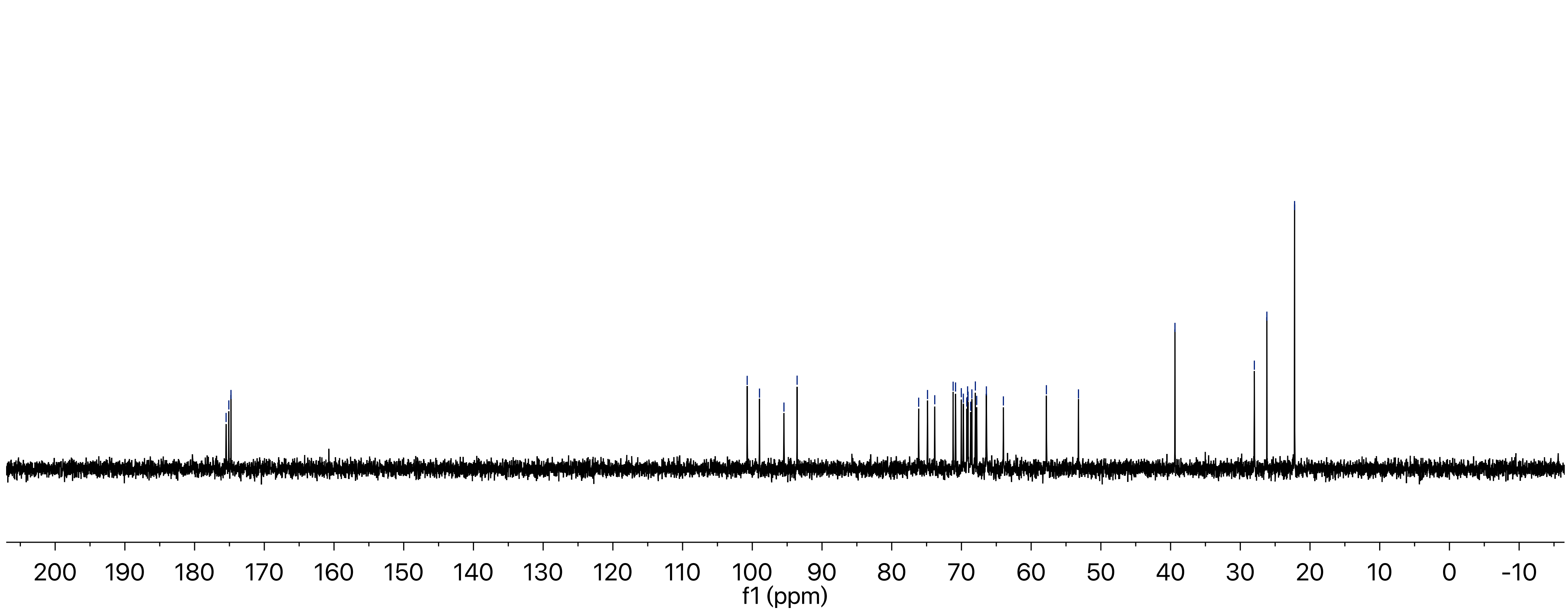


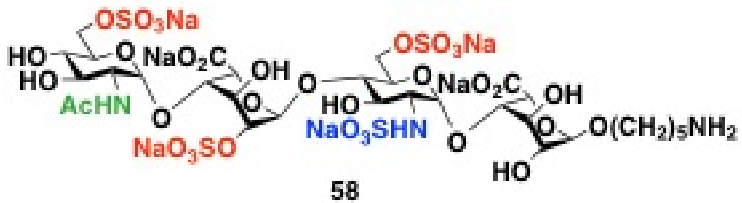
WL-2-092-Run2-D-NAc-6S-C2S-B-NS6S-H-TC.1.1.1r —



58

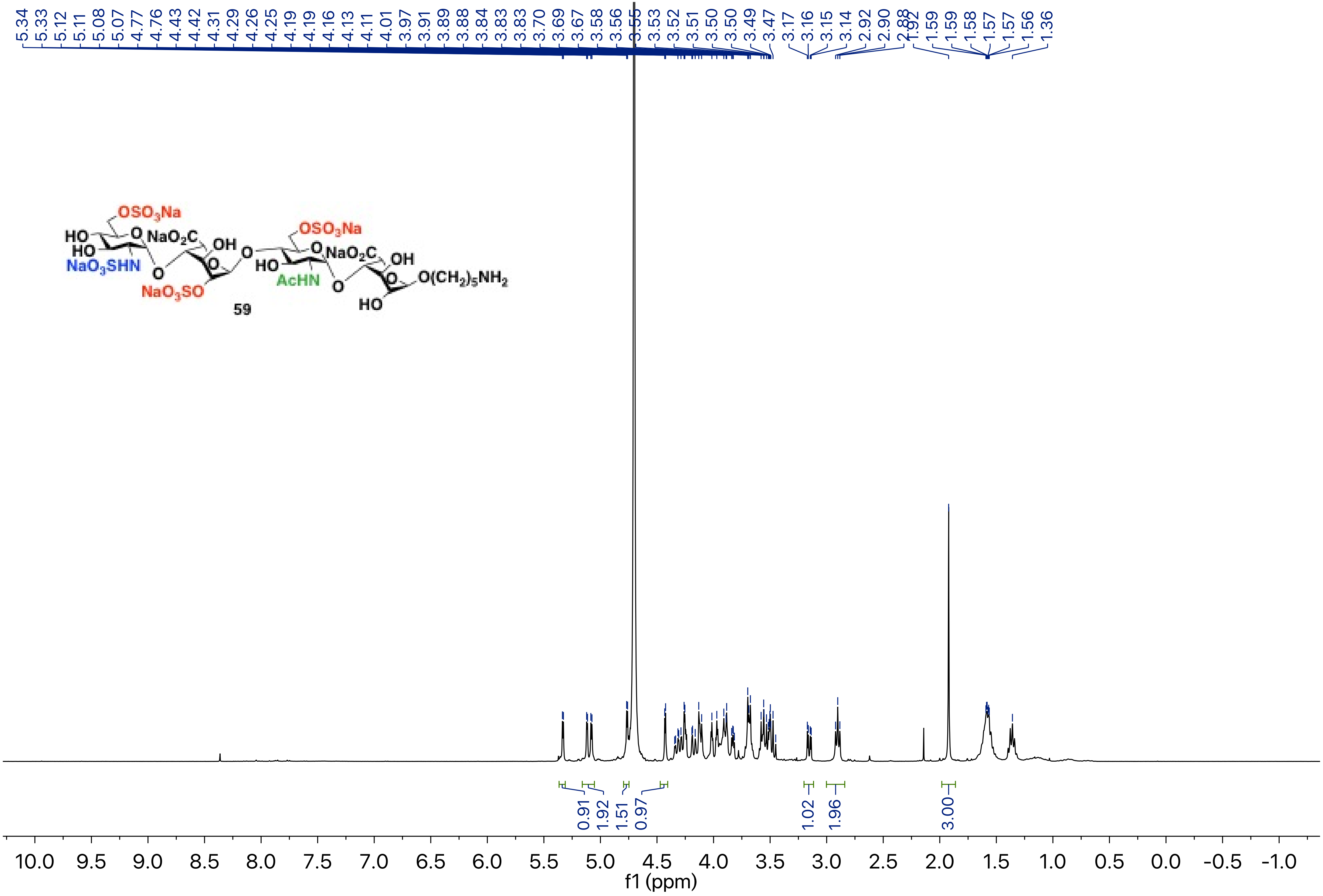
WL-2-092-Run2-D-NAc-6S-C2S-B-NS6S-C-TC.7.1.1r



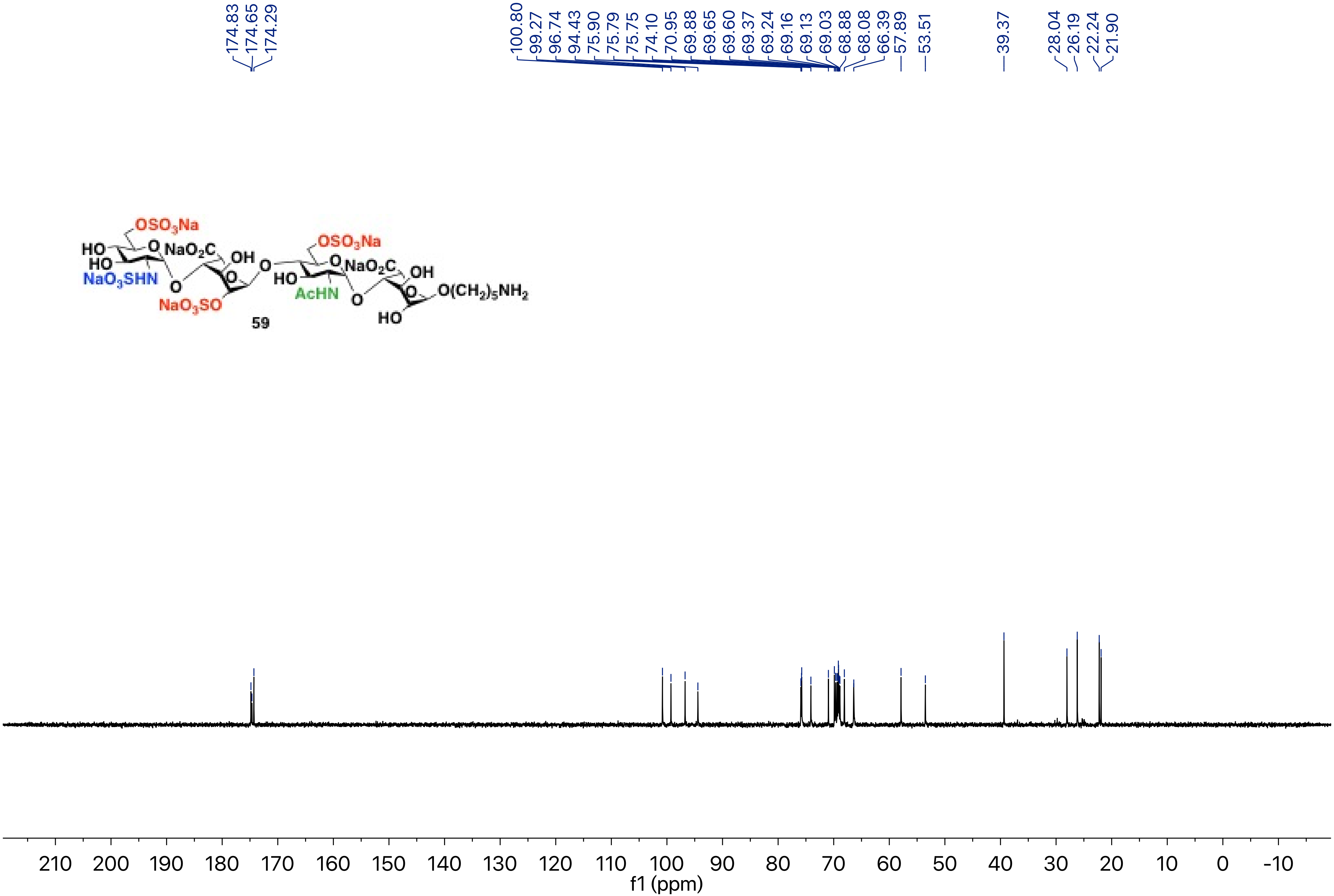


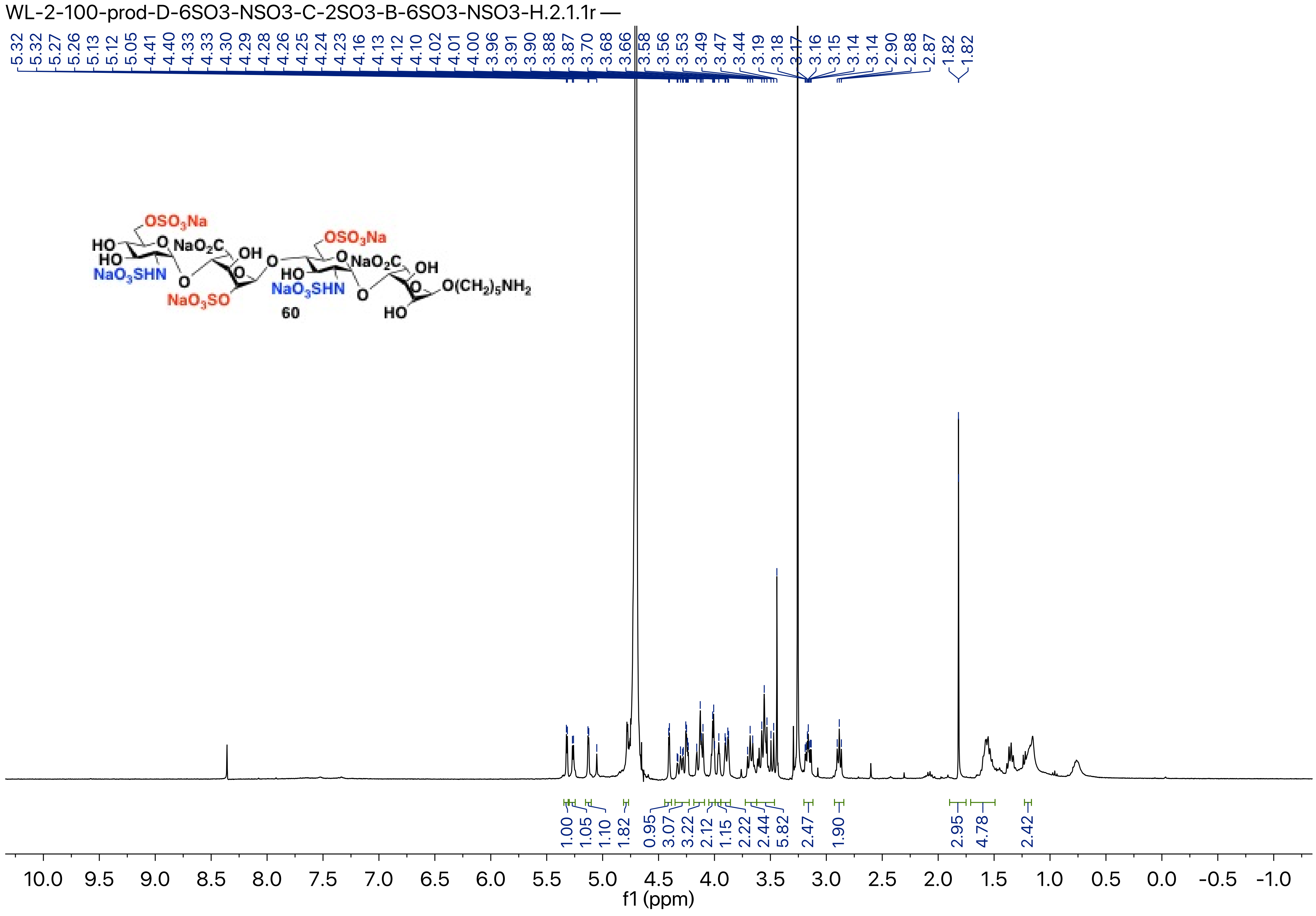
58

WL-2-226-D-6S-NS-C-2S-B-6S-NAc-Prod-H-TC.8.1.1r —

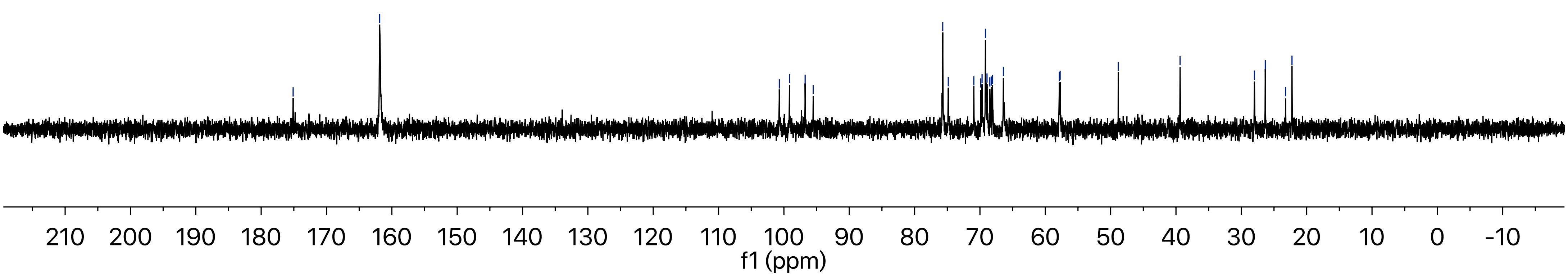


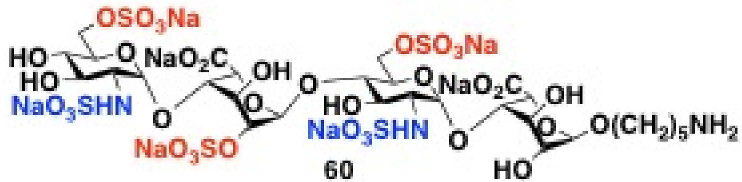
WL-2-226-D-6S-NS-C-2S-B-6S-NAc-Prod-C-TC.7.1.1r —




WL-2-100-prod-D-6SO3-NSO3-C-2SO3-B-6SO3-NSO3-H.2.1.1r
5.32 5.32 5.27 5.26 5.13 5.12 5.05 4.41 4.40 4.33 4.33 4.30 4.29 4.28 4.26 4.25 4.24 4.23 4.16 4.13 4.12 4.10 4.02 4.01 4.00 3.96 3.91 3.90 3.88 3.87 3.70 3.68 3.66 3.58 3.56 3.53 3.49 3.47 3.44 3.19 3.18 3.17 3.16 3.15 3.14 3.14 2.90 2.88 2.87 1.82 1.82
OSO3Na
HO
HO
NaO3SHN
NaO2C
OH
NaO3SO
OSO3Na
HO
NaO3SHN
NaO2C
OH
O(CH2)5NH2
HO
60
1.00 1.05 1.10 1.82 0.95 3.07 3.22 2.12 1.15 2.22 2.44 5.82 2.47 1.90 2.95 4.78 2.42
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 -0.5 -1.0
f1 (ppm)

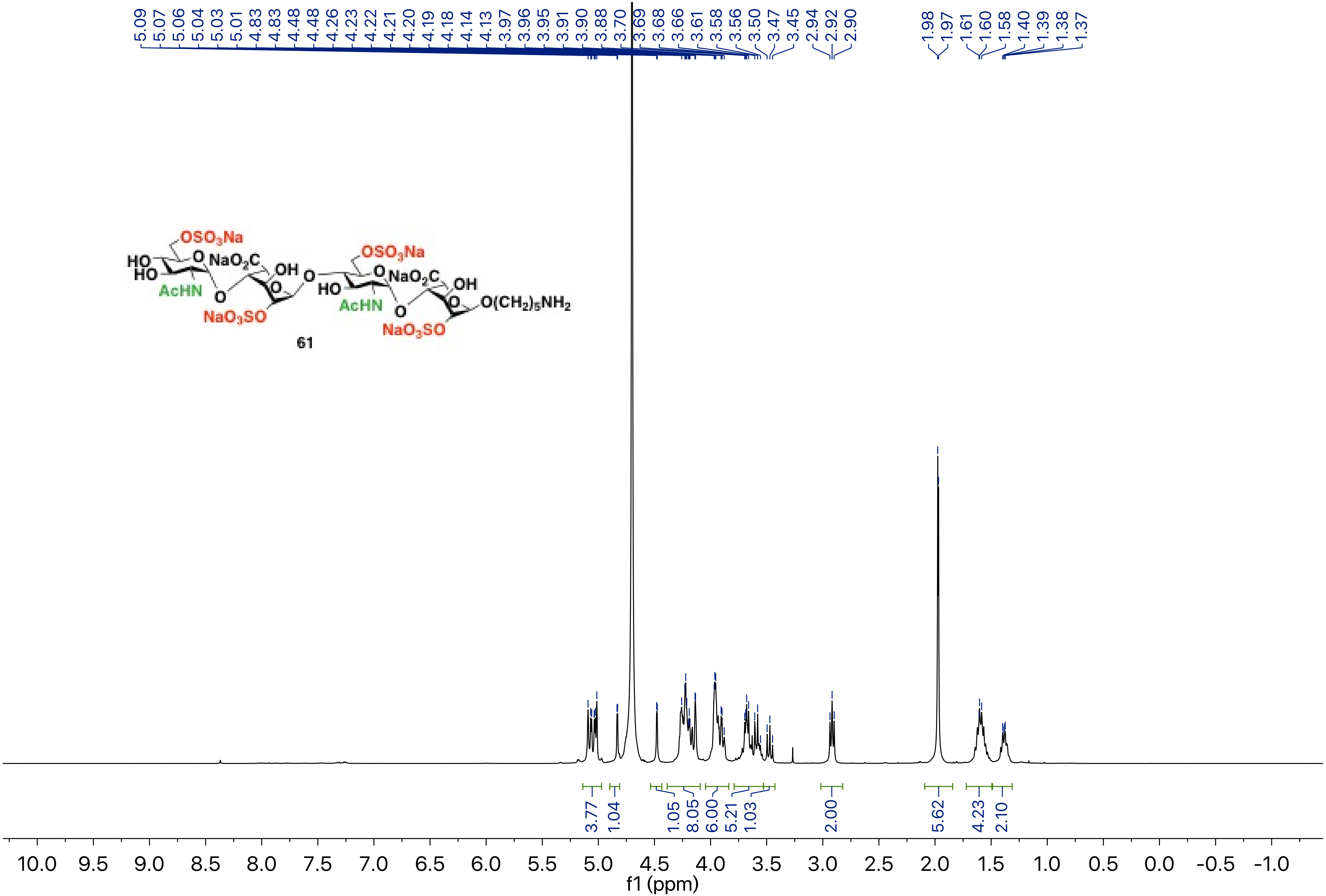
WL-2-100-D-6SO3-NSO3-C-2SO3-B-6SO3-NSO3-C.1.1.1r



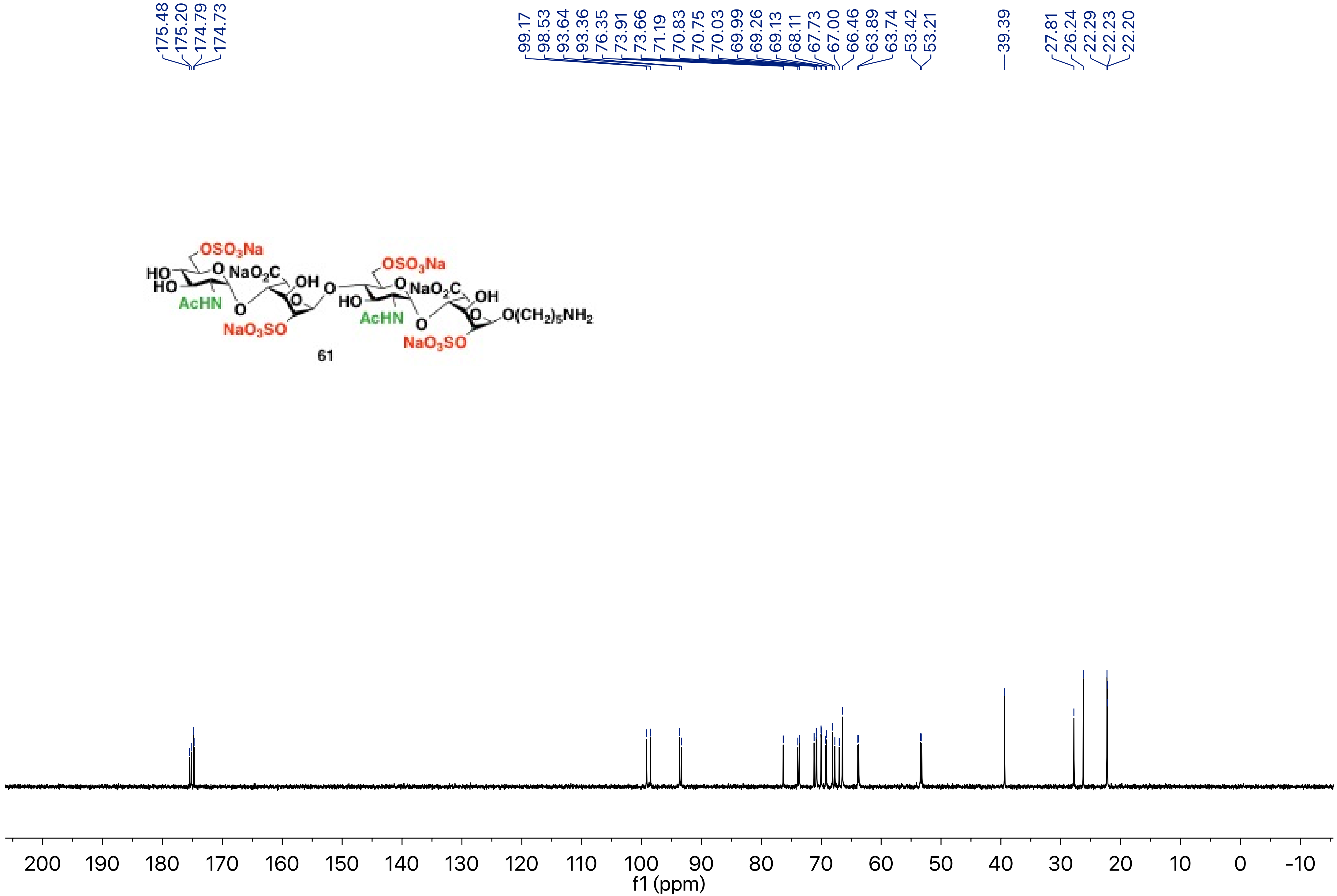


60

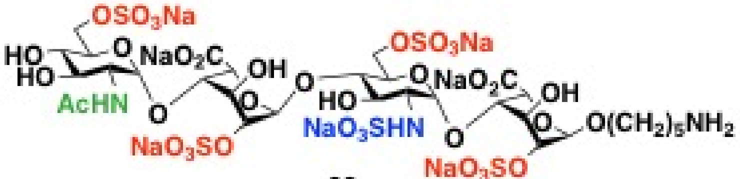
WL-2-196-D-NAc-6S-C-2S-B-NAc-6S-A-2S-H-TC.1.1.1r —



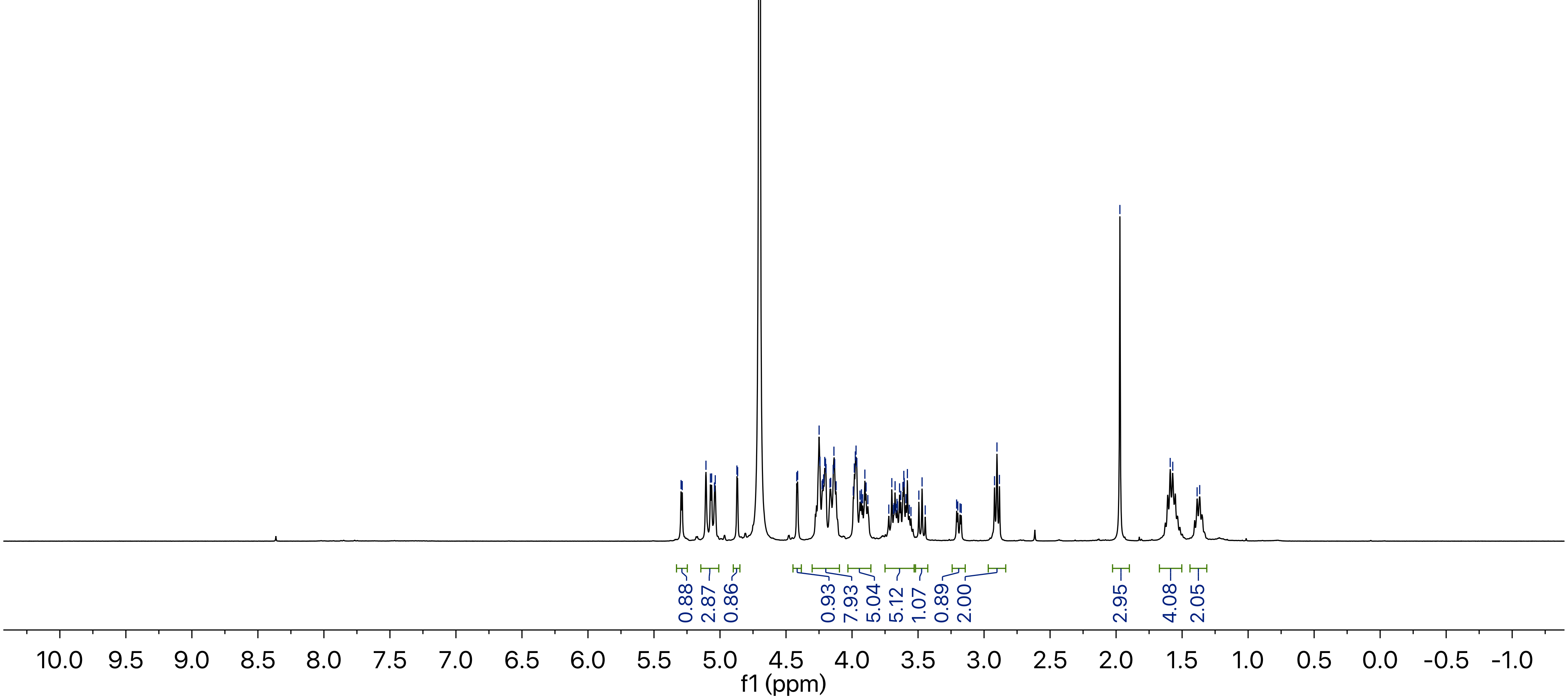
WL-2-196-D-NAc-6S-C-2S-B-NAc-6S-A-2S-C-TC.7.1.1r



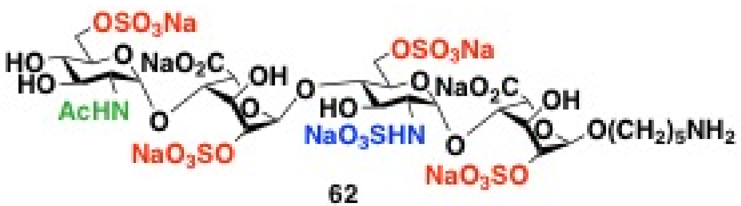
WL-2-197-D-NAc-6S-C-2S-B-NS-6S-A-2S-H-TC.1.1.1r —



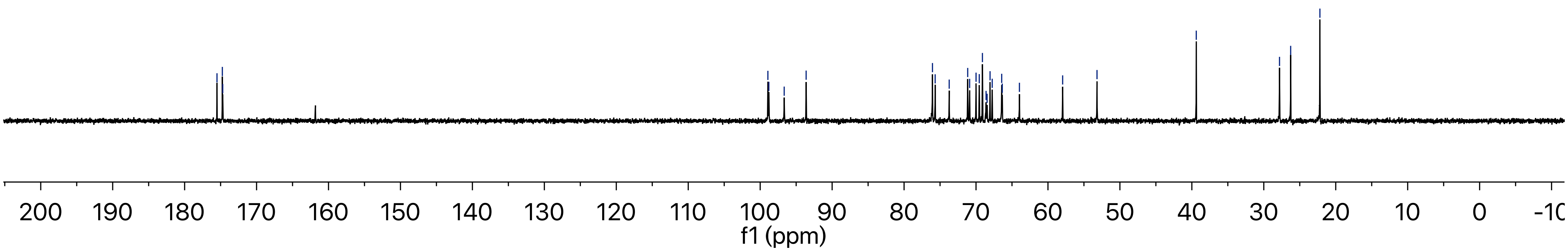
62



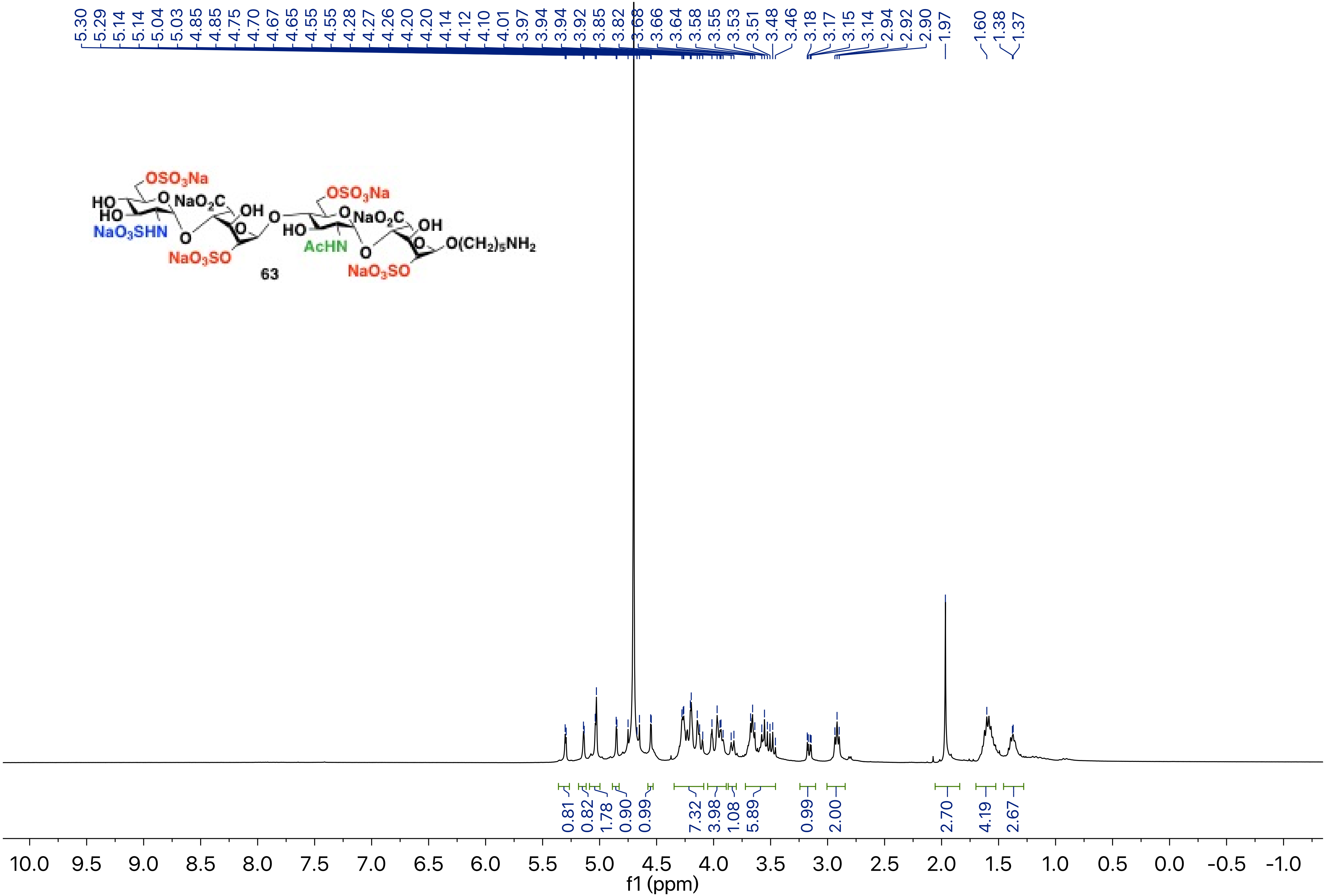
WL-2-197-D-NAc-6S-C-2S-B-NS-6S-A-2S-C-TC.7.1.1r



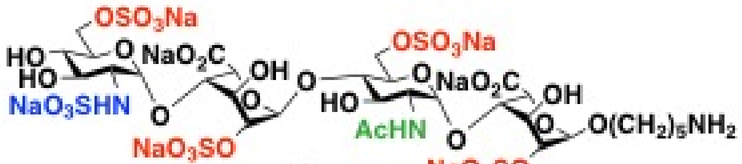
62



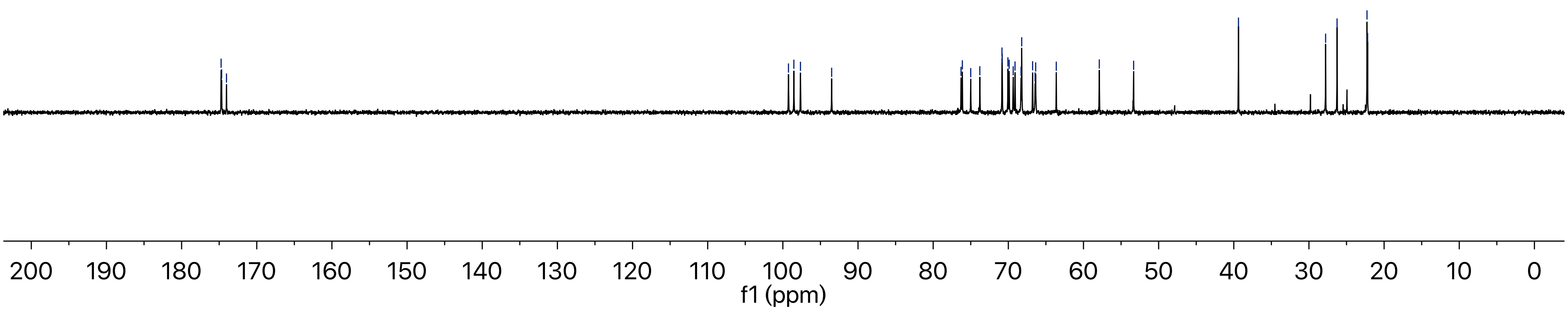
WL-2-314-D-NS-6S-C-2S-B-NAc-6S-A-2S-H-TC.8.1.1r

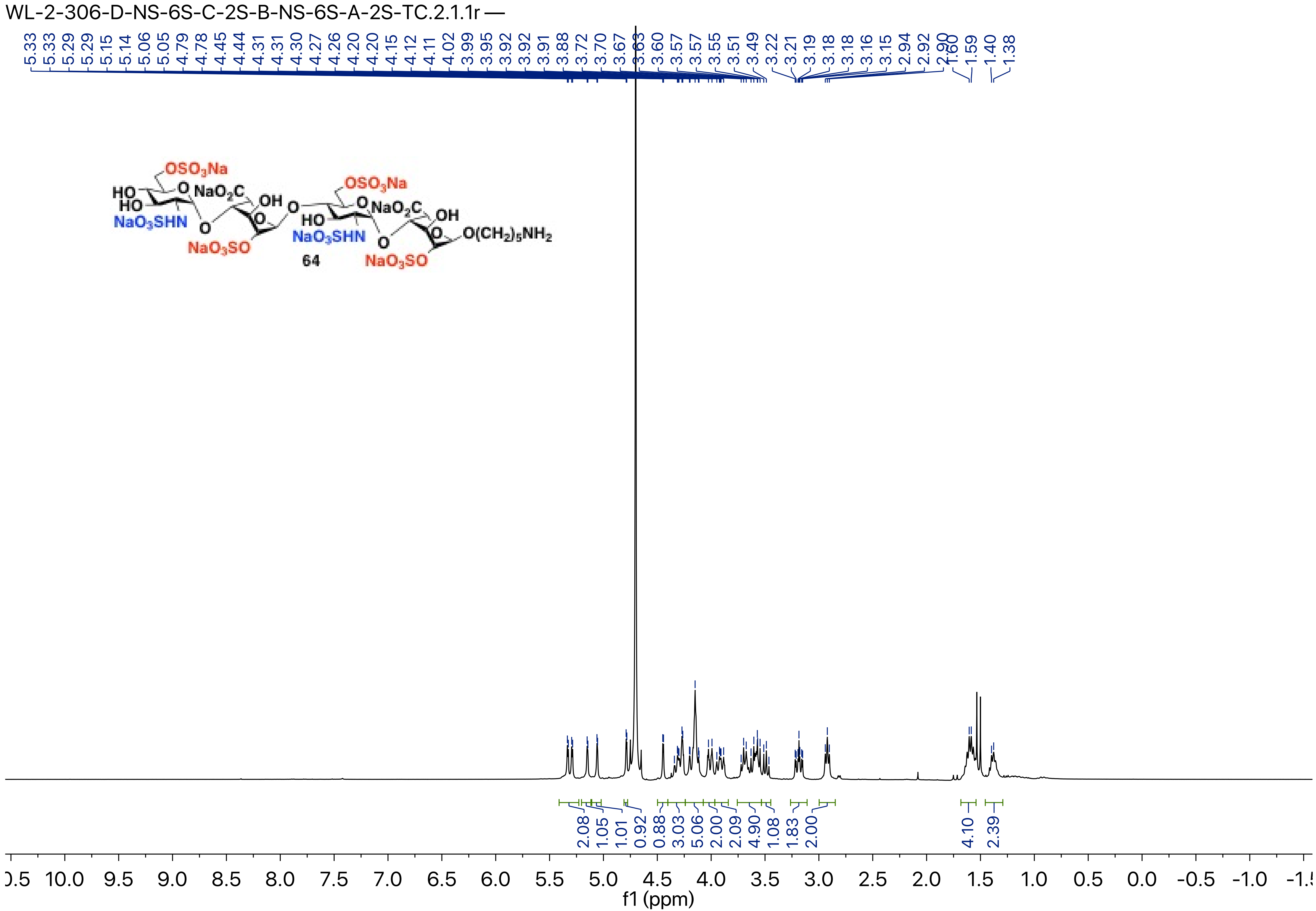


WL-2-314-D-NS-6S-C-2S-B-NAc-6S-A-2S-C-TC.7.1.1r

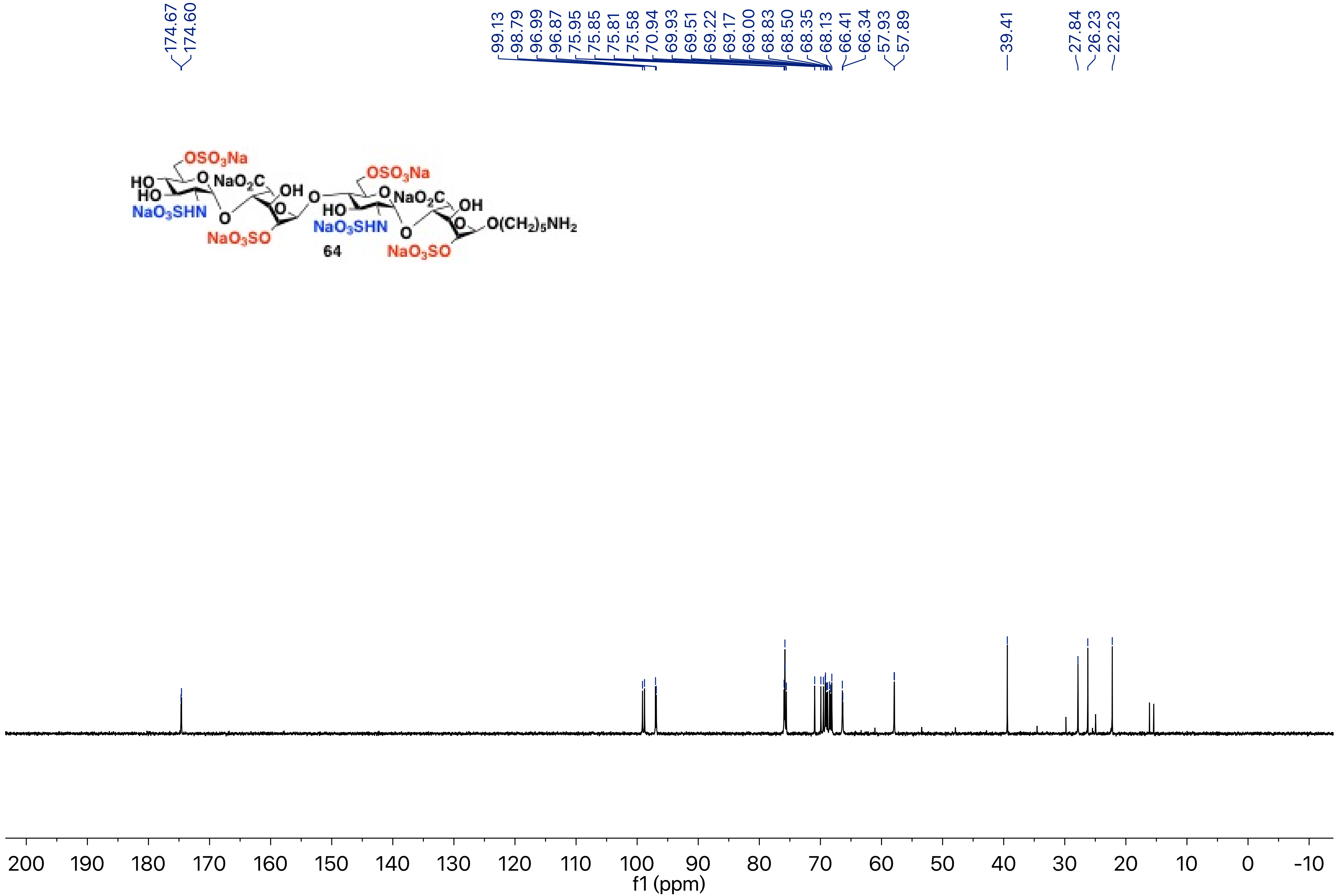


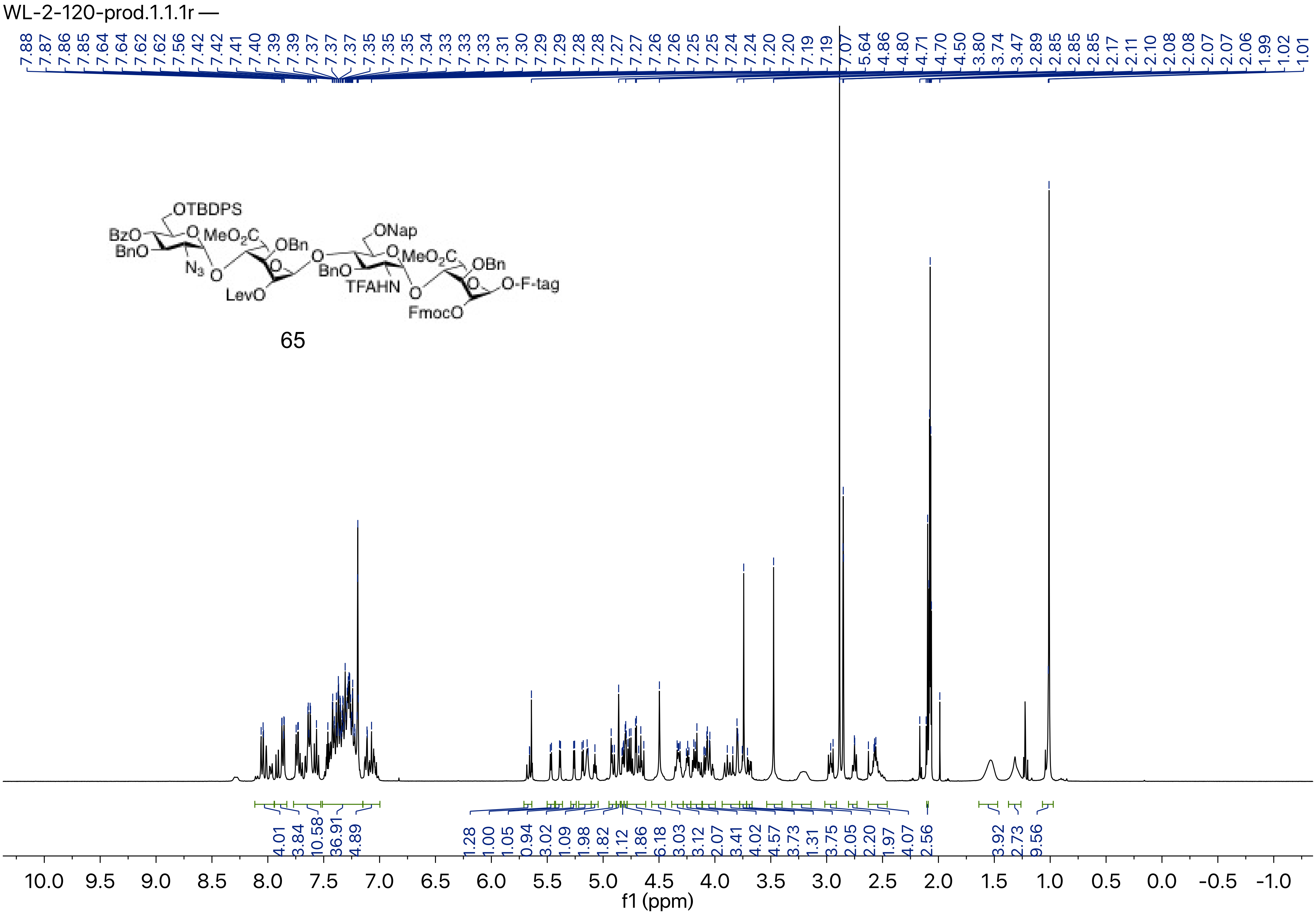
63




WL-2-306-D-NS-6S-C-2S-B-NS-6S-A-2S-TC.2.1.1r
5.33 5.33 5.29 5.29 5.15 5.14 5.06 5.05 4.79 4.78 4.45 4.44 4.31 4.31 4.30 4.27 4.26 4.20 4.20 4.15 4.12 4.11 4.02 3.99 3.95 3.92 3.92 3.91 3.88 3.72 3.70 3.67 3.63 3.60 3.57 3.57 3.55 3.51 3.49 3.22 3.21 3.19 3.18 3.18 3.16 3.15 2.94 2.92 2.90 1.60 1.59 1.40 1.38
OSO3Na
NaO2C
OH
HO
NaO3SHN
NaO3SO
O(CH2)5NH2
64
2.08 1.05 1.01 0.92 0.88 3.03 5.06 2.00 2.09 4.90 1.08 1.83 2.00 4.10 2.39
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 -0.5 -1.0 -1.5
f1 (ppm)

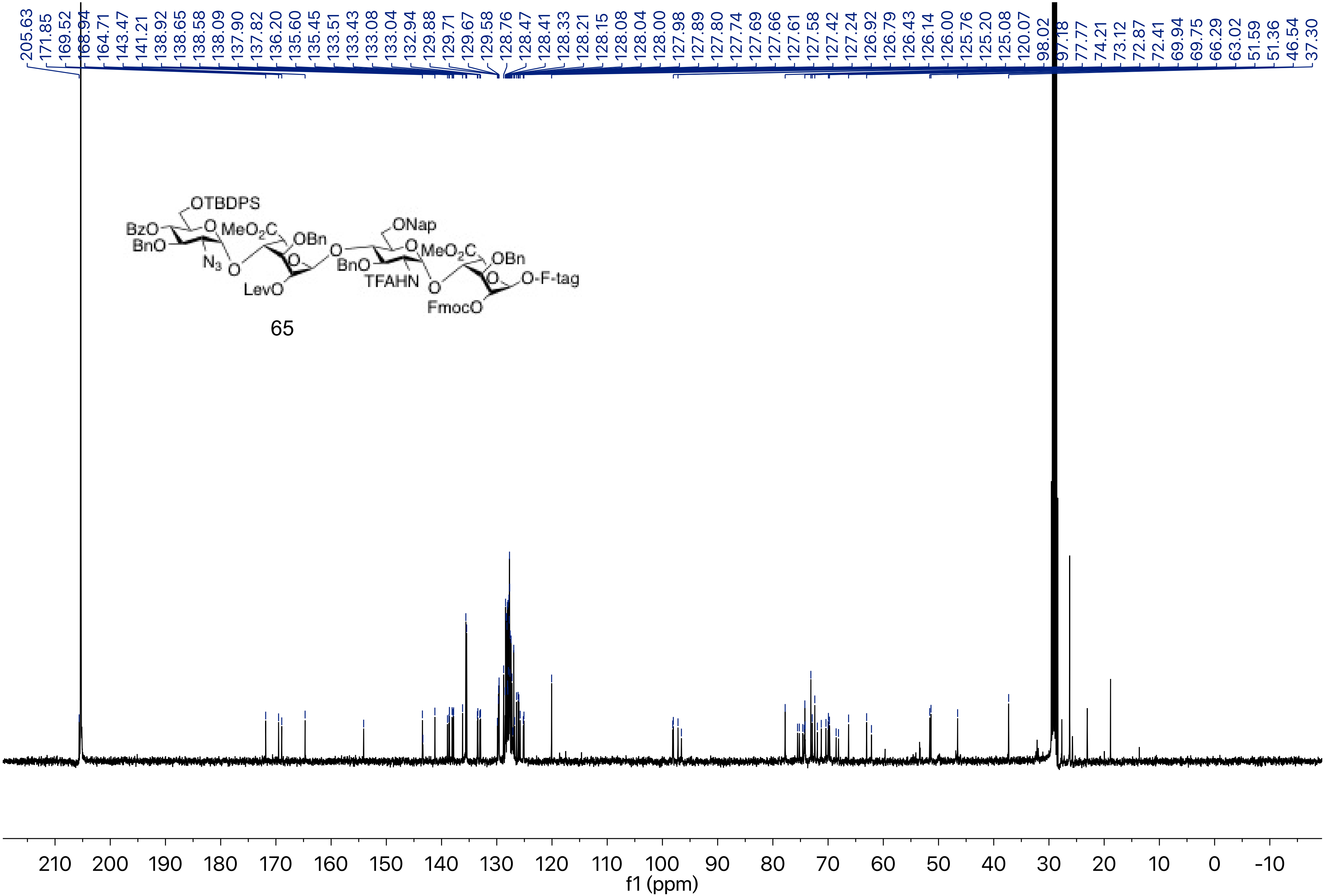
WL-2-306-D-NS-6S-C-2S-B-NS-6S-A-2S-TC.1.1.1r

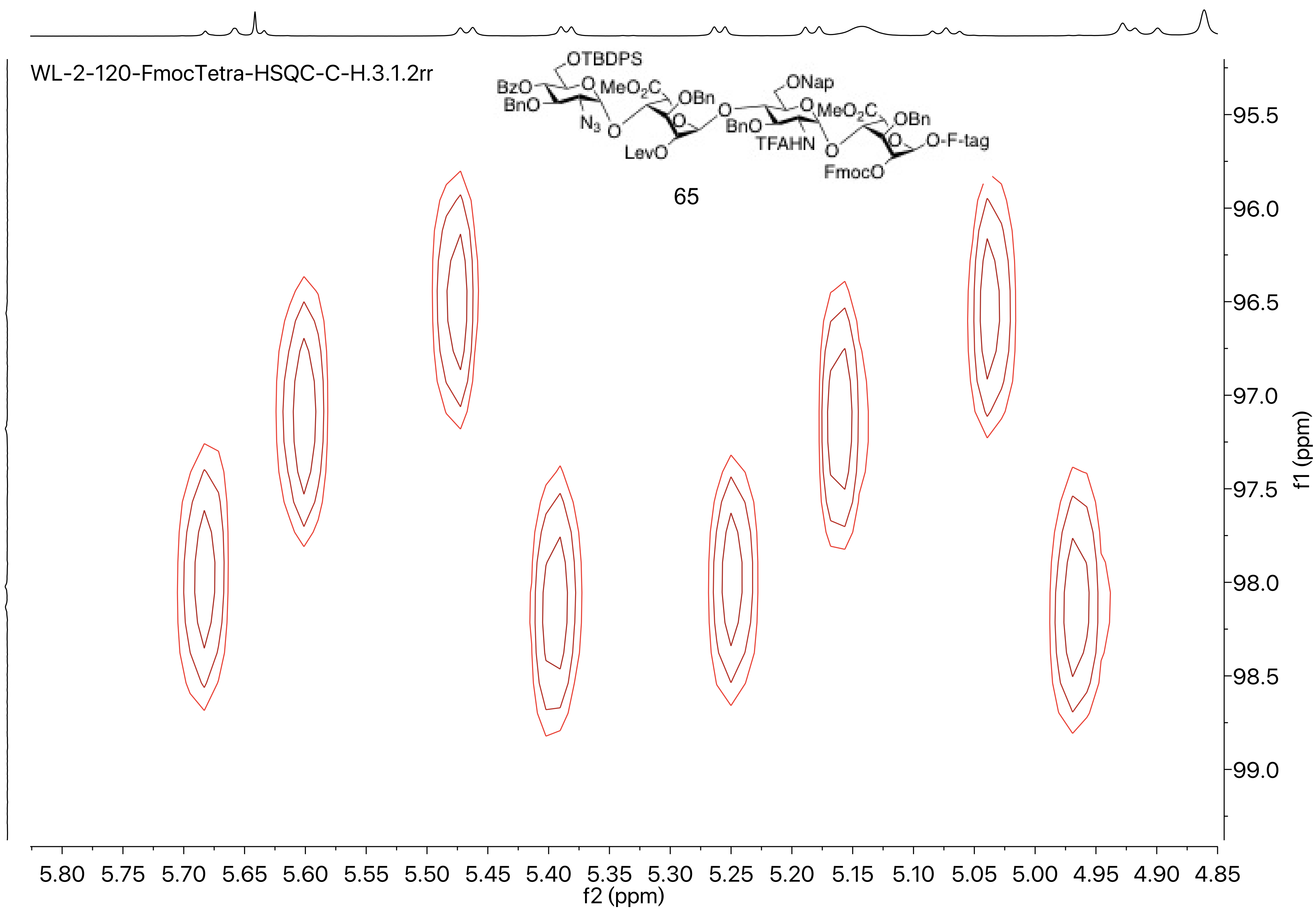



WL-2-120-prod.1.1.1r —
7.88 7.87 7.86 7.85 7.64 7.64 7.62 7.62 7.56 7.42 7.42 7.41 7.40 7.39 7.39 7.37 7.37 7.37 7.35 7.35 7.35 7.34 7.33 7.33 7.33 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.20 7.20 7.19 7.19 7.07 5.64 4.86 4.80 4.71 4.70 4.50 3.80 3.74 3.47 2.89 2.85 2.85 2.85 2.17 2.11 2.10 2.08 2.08 2.07 2.07 2.06 1.99 1.02 1.01
OTBDPS
BzO
BnO
O
MeO2C
OBn
N3
O
LevO
O
ONap
BnO
O
MeO2C
OBn
TFAHN
O
O-F-tag
FmocO
4.01 3.84 10.58 36.91 4.89
1.28 1.00 1.05 0.94 3.02 1.09 1.98 1.82 1.12 1.86 6.18 3.03 3.12 2.07 3.41 4.02 4.57 3.73 1.31 3.75 2.05 2.20 1.97 4.07 2.56
3.92 2.73 9.56
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 -0.5 -1.0
f1 (ppm)

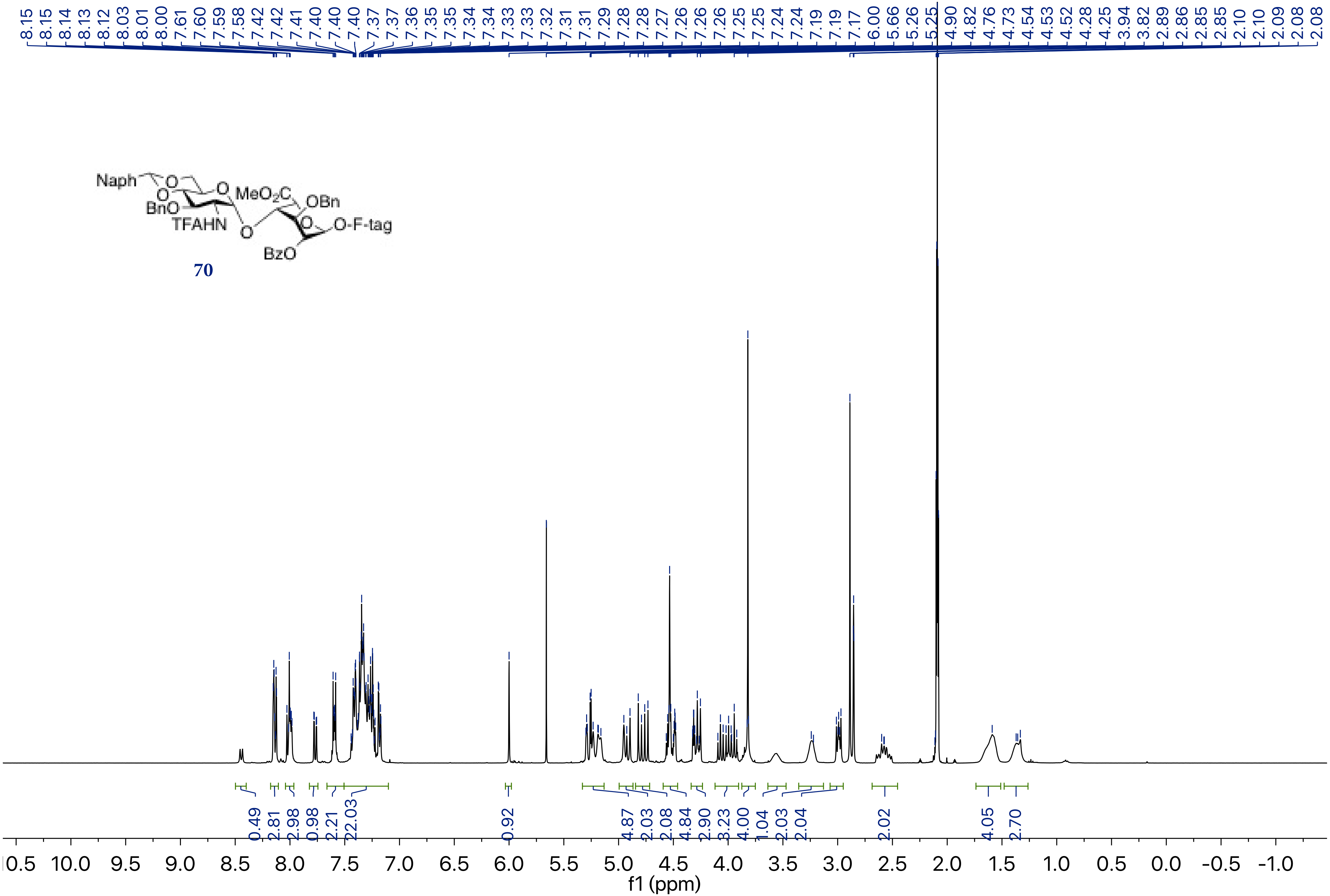
65

WL-2-120-FmocTetra-C.1.1.1r —

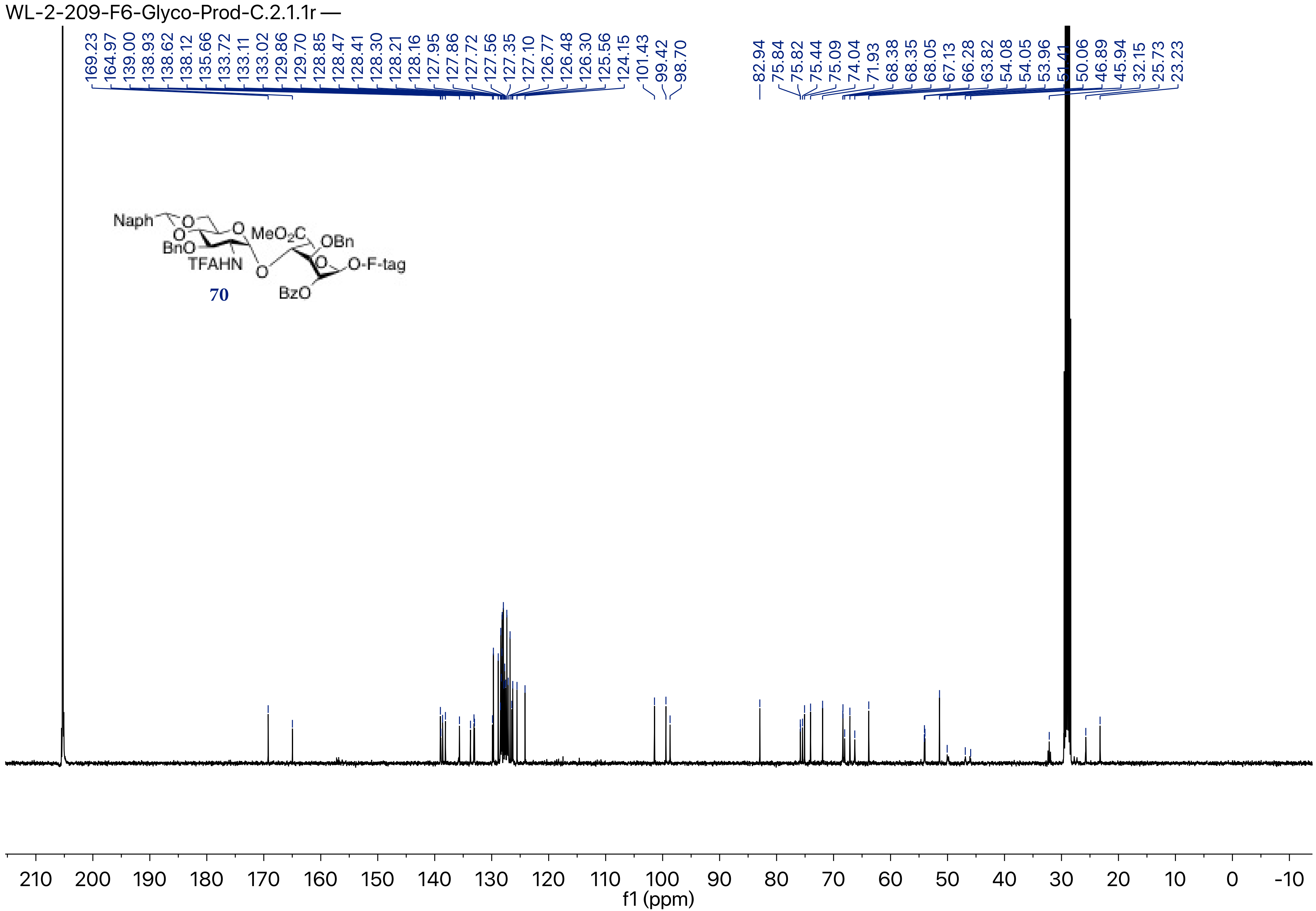


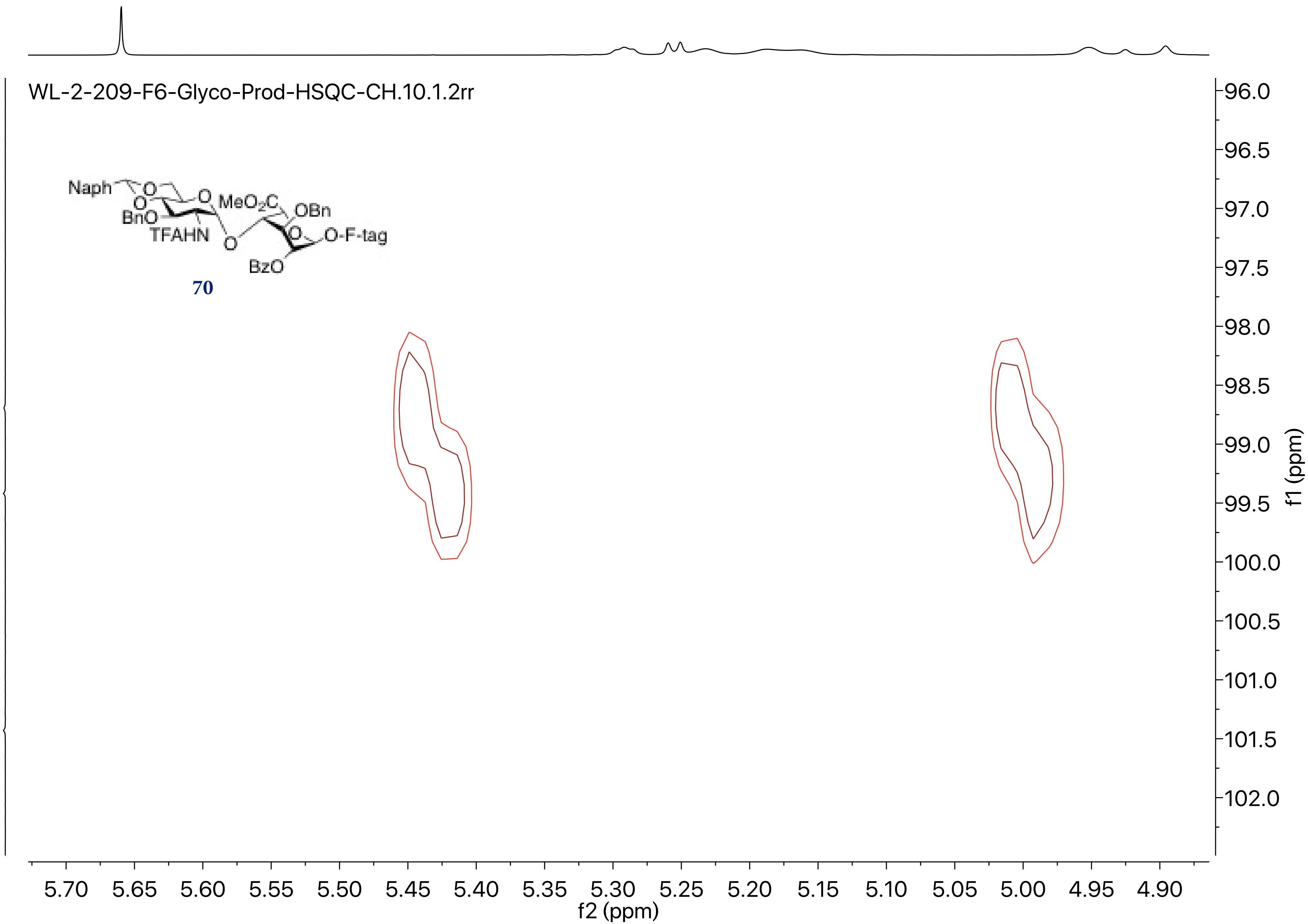

WL-2-120-FmocTetra-HSQC-C-H.3.1.2rr
OTBDPS
BzO
BnO
O
MeO2C
N3
O
OBn
O
LevO
O
ONap
O
BnO
TFAHN
MeO2C
O
OBn
O
O-F-tag
FmocO
65
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
f1 (ppm)
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
5.40
5.35
5.30
5.25
5.20
5.15
5.10
5.05
5.00
4.95
4.90
4.85
f2 (ppm)

WL-2-209-F6-Glyco-Prod-H.3.1.1r —

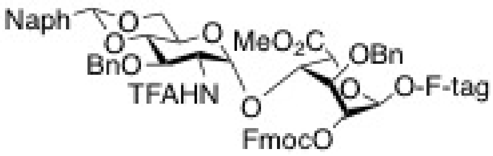


70

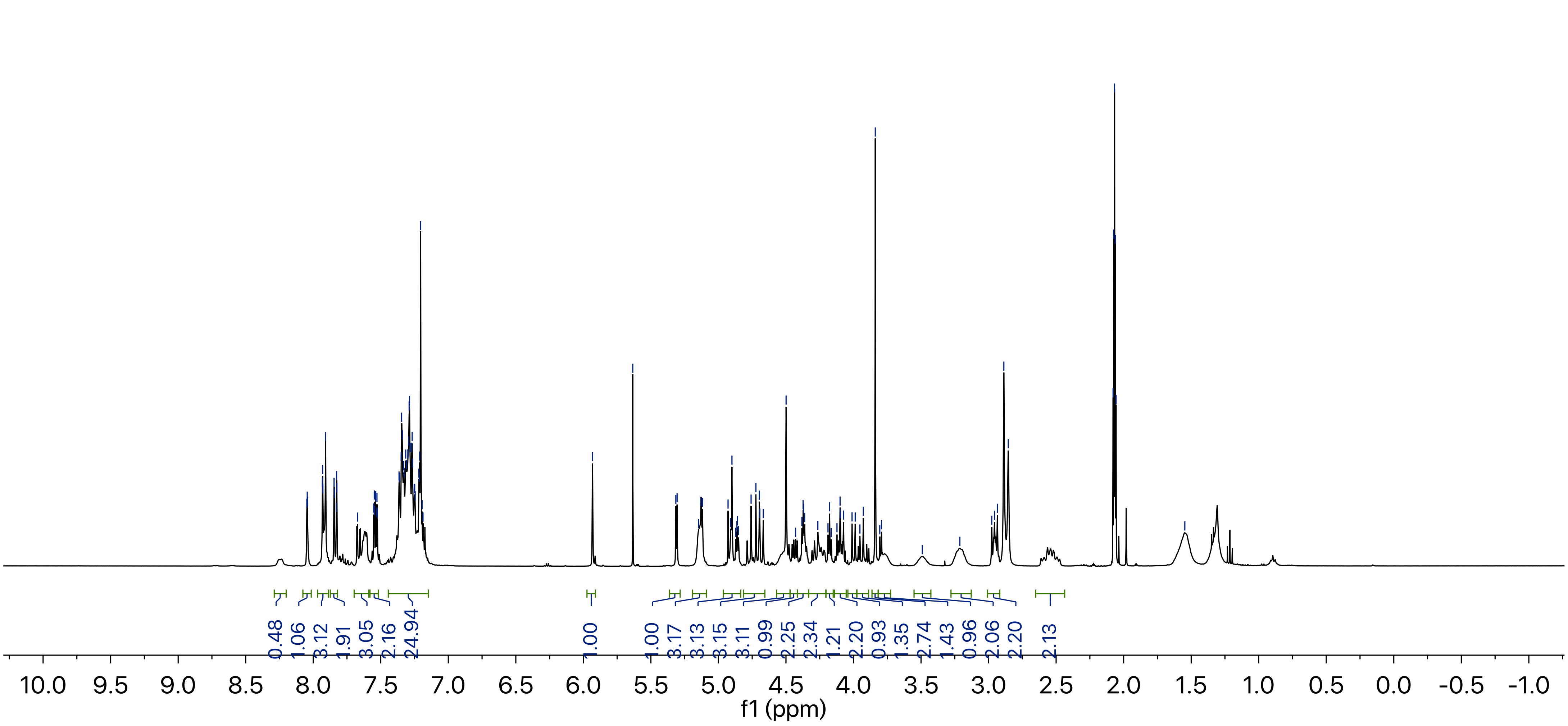

WL-2-209-F6-Glyco-Prod-C.2.1.1r
169.23
164.97
139.00
138.93
138.62
138.12
135.66
133.72
133.11
133.02
129.86
129.70
128.85
128.47
128.41
128.30
128.21
128.16
127.95
127.86
127.72
127.56
127.35
127.10
126.77
126.48
126.30
125.56
124.15
101.43
99.42
98.70
82.94
75.84
75.82
75.44
75.09
74.04
71.93
68.38
68.35
68.05
67.13
66.28
63.82
54.08
54.05
53.96
51.41
50.06
46.89
45.94
32.15
25.73
23.23
Naph
O
O
BnO
TFAHN
O
MeO2C
OBn
O
O-F-tag
BzO
70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

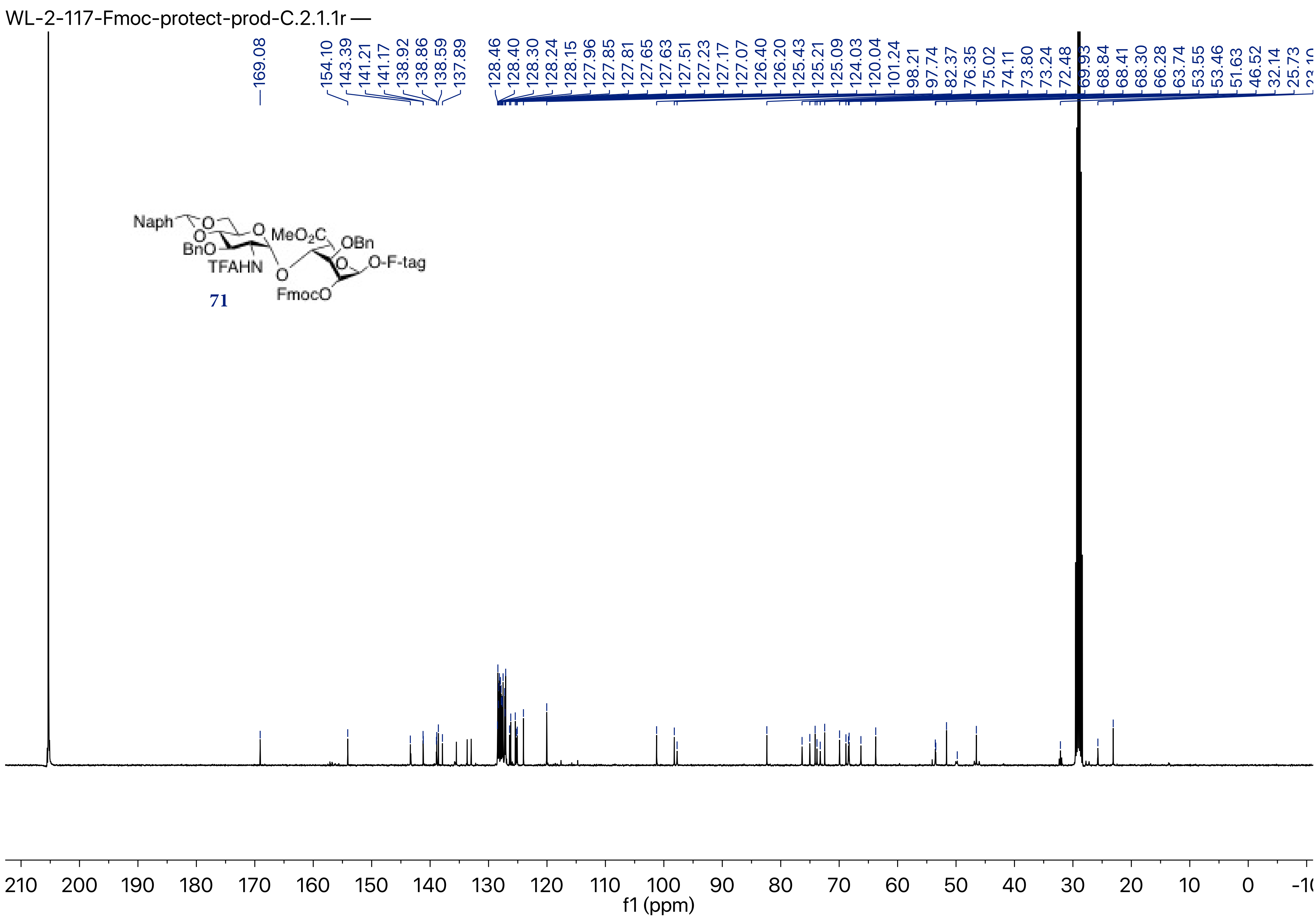

WL-2-209-F6-Glyco-Prod-HSQC-CH.10.1.2rr
Naph
O
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
70
5.70 5.65 5.60 5.55 5.50 5.45 5.40 5.35 5.30 5.25 5.20 5.15 5.10 5.05 5.00 4.95 4.90
f2 (ppm)
96.0 96.5 97.0 97.5 98.0 98.5 99.0 99.5 100.0 100.5 101.0 101.5 102.0
f1 (ppm)

WL-2-117-Fmoc-protect-prod-H.3.1.1r

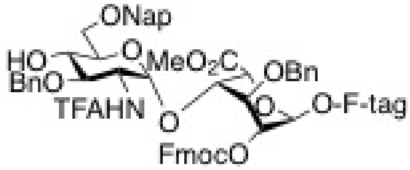


71

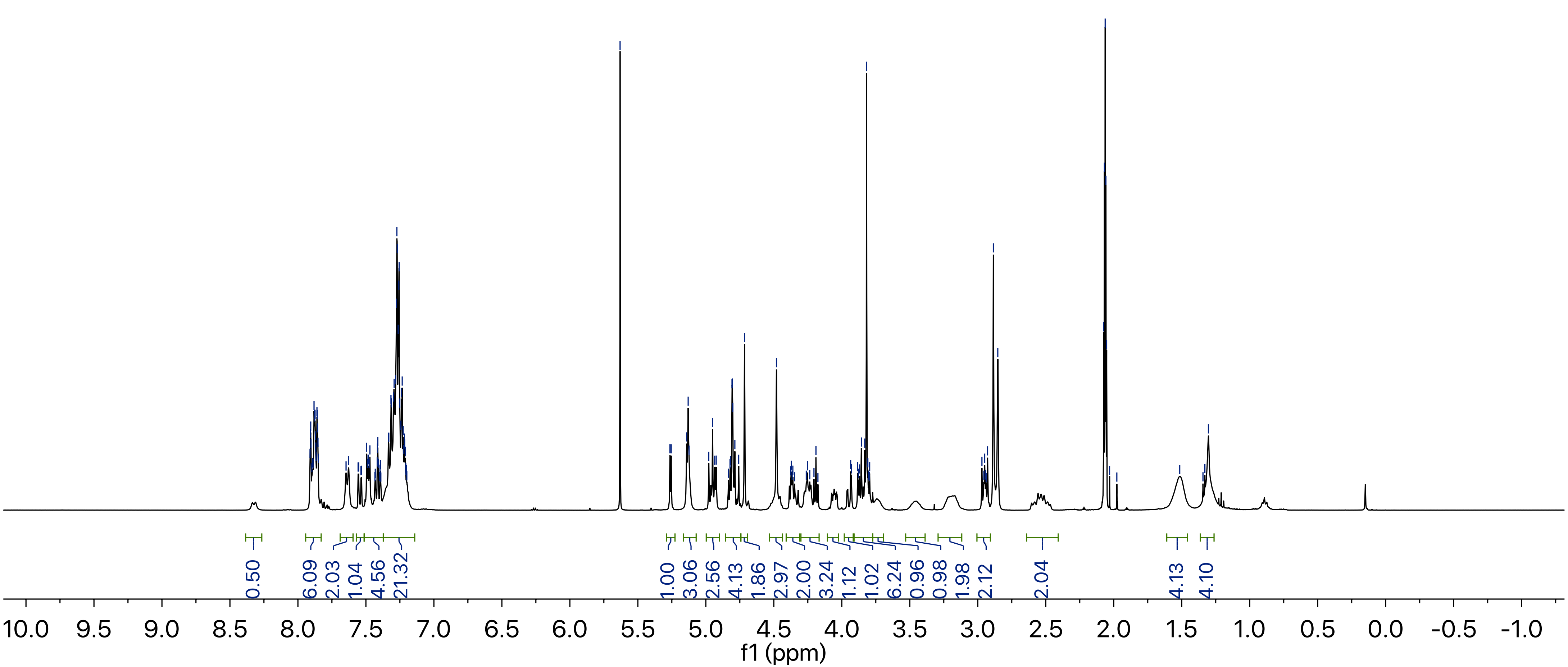



WL-2-117-Fmoc-protect-prod-C.2.1.1r
169.08
154.10
143.39
141.21
141.17
138.92
138.86
138.59
137.89
128.46
128.40
128.30
128.24
128.15
127.96
127.85
127.81
127.65
127.63
127.51
127.23
127.17
127.07
126.40
126.20
125.43
125.21
125.09
124.03
120.04
101.24
98.21
97.74
82.37
76.35
75.02
74.11
73.80
73.24
72.48
69.93
68.84
68.41
68.30
66.28
63.74
53.55
53.46
51.63
46.52
32.14
25.73
Naph
O
BnO
TFAHN
MeO2C
OBn
O-F-tag
FmocO
71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

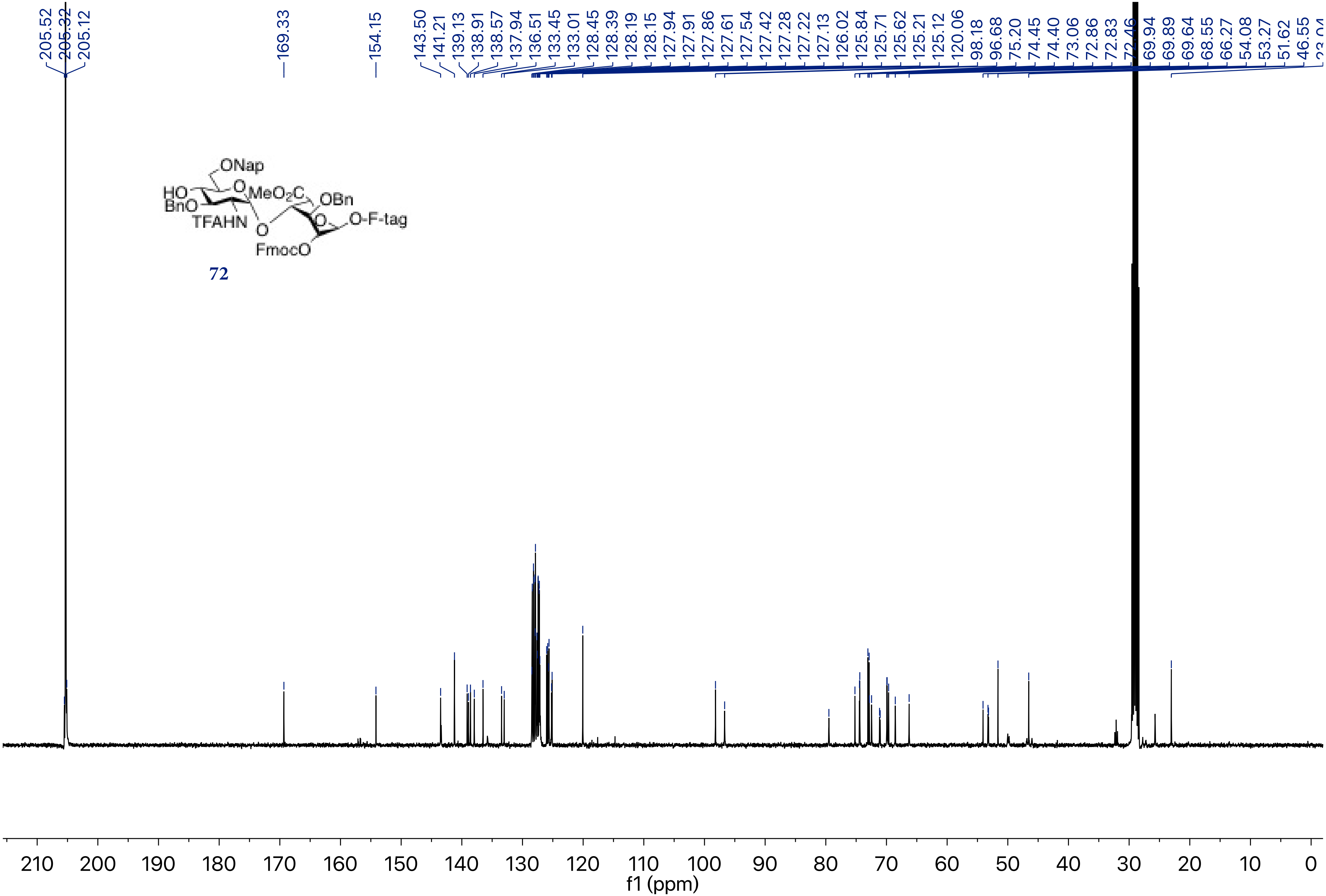
WL-2-118-Fmoc-Acceptor-H.3.1.1r —



72

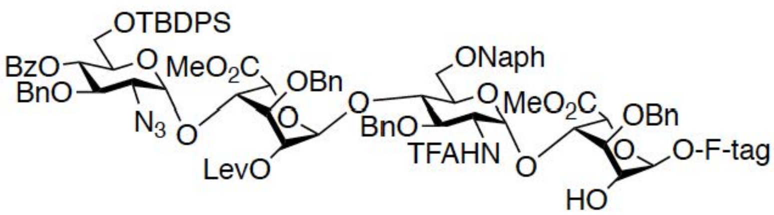


WL-2-118-Fmoc-Acceptor-C.2.1.1r —

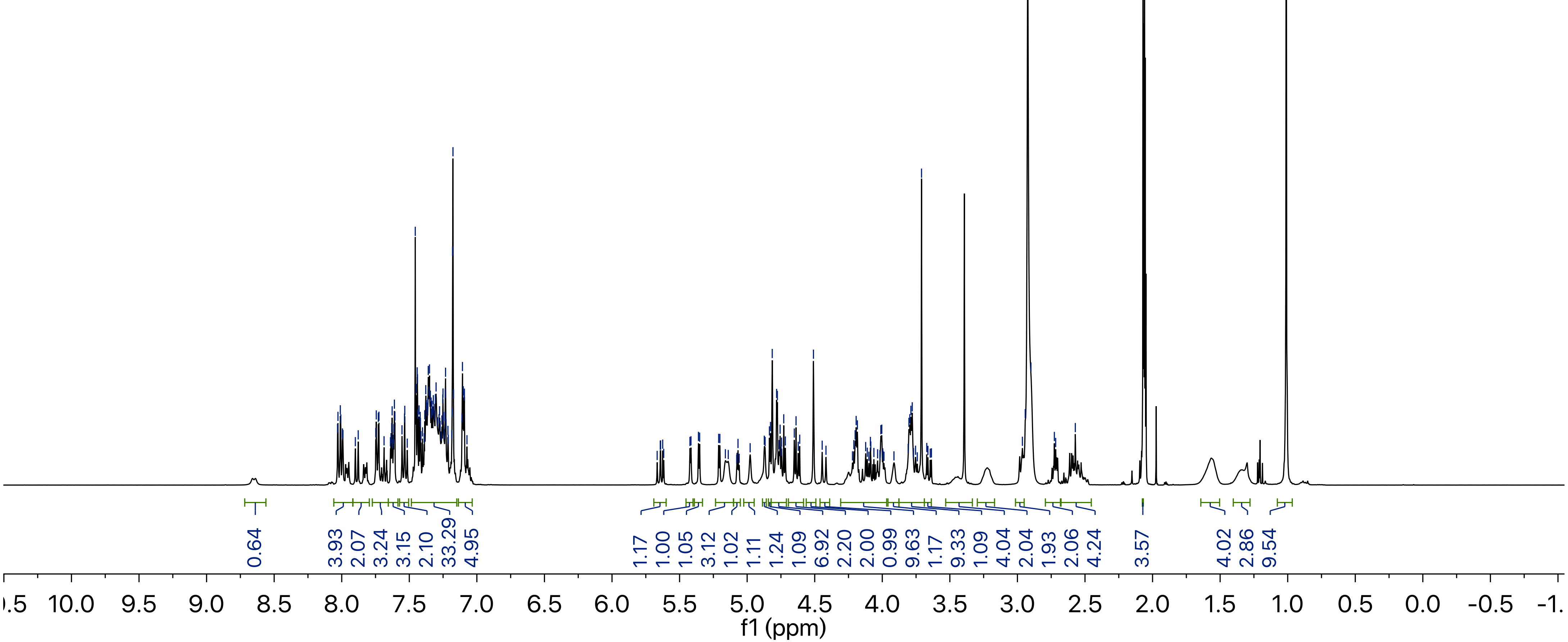


72

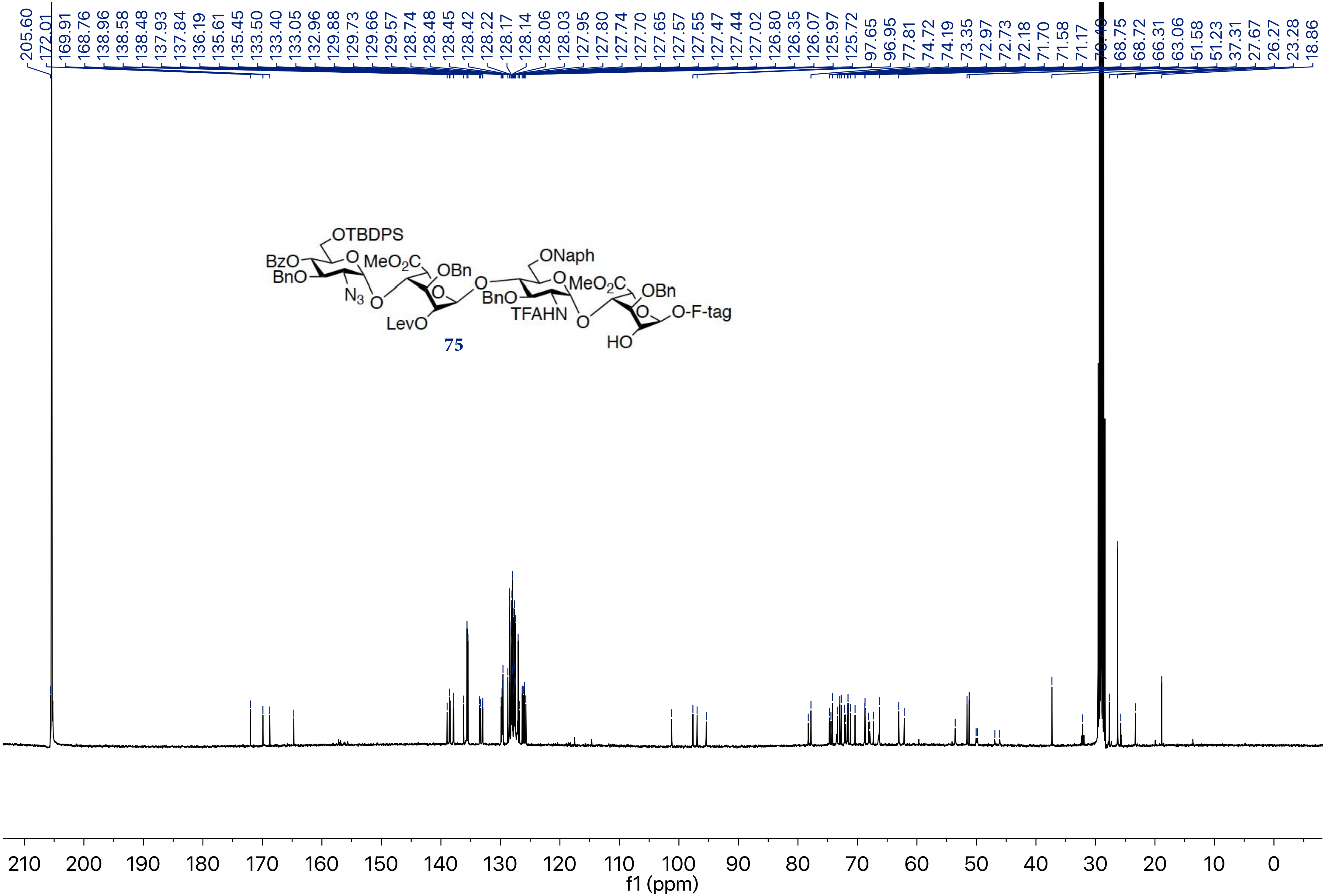
WL-2-121.1.1.1r



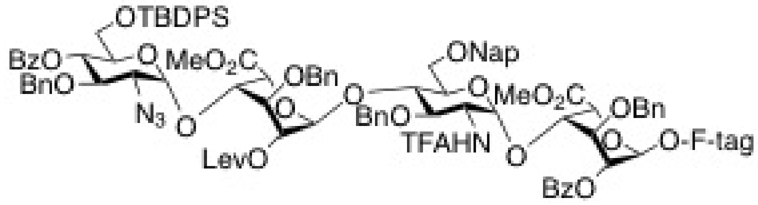
75



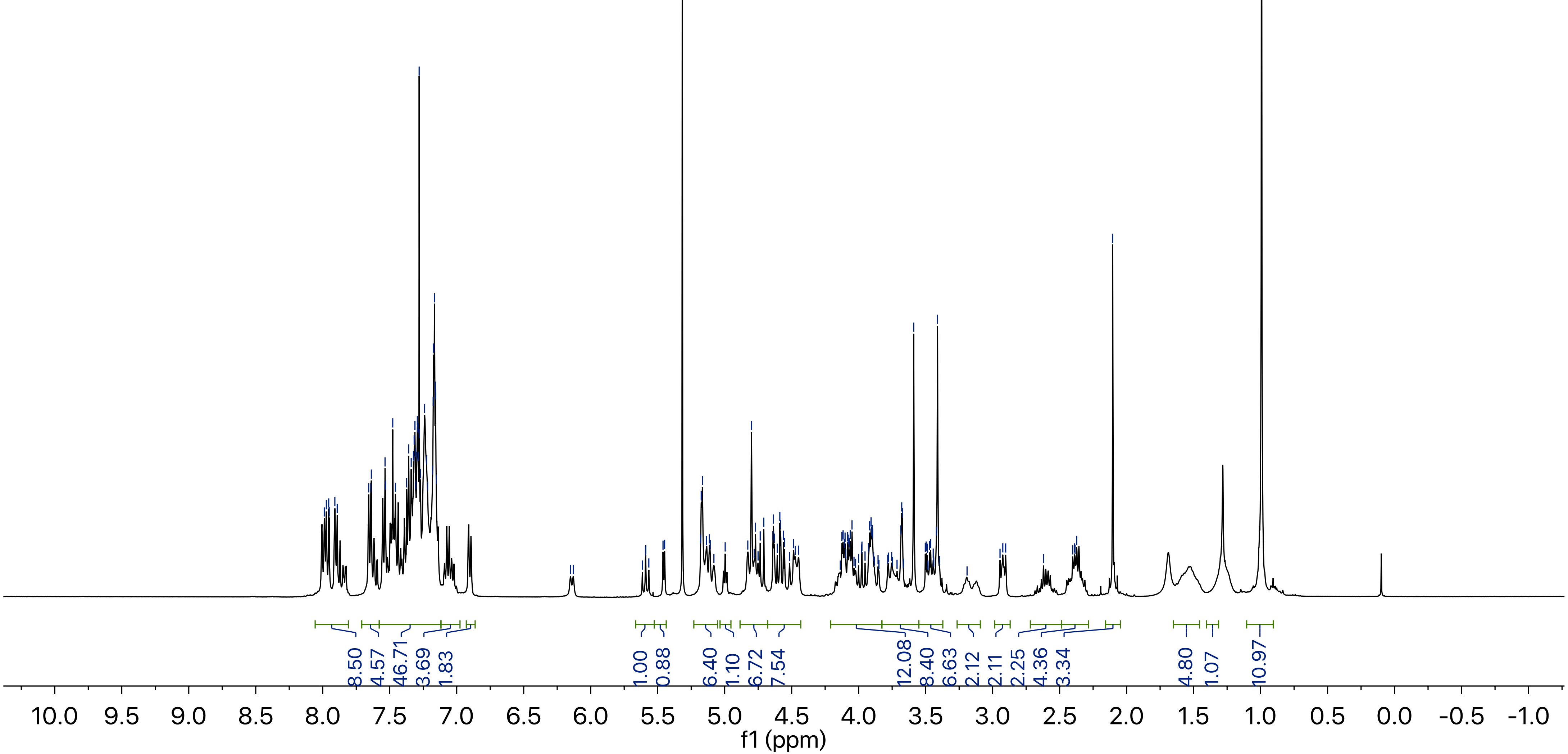
WL-2-121.2.1.1r —


205.60
172.01
169.91
168.76
138.96
138.58
138.48
137.93
137.84
136.19
135.61
135.45
133.50
133.40
133.05
132.96
129.88
129.73
129.66
129.57
128.74
128.48
128.45
128.42
128.22
128.17
128.14
128.06
128.03
127.95
127.80
127.74
127.70
127.65
127.57
127.55
127.47
127.44
127.02
126.80
126.35
126.07
125.97
125.72
97.65
96.95
77.81
74.72
74.19
73.35
72.97
72.73
72.18
71.70
71.58
71.17
70.40
68.75
68.72
66.31
63.06
51.58
51.23
37.31
27.67
26.27
23.28
18.86
OTBDPS
BzO
BnO
N_3
MeO_2C
OBn
LevO
ONaph
BnO
TFAHN
MeO_2C
OBn
O-F-tag
HO
75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

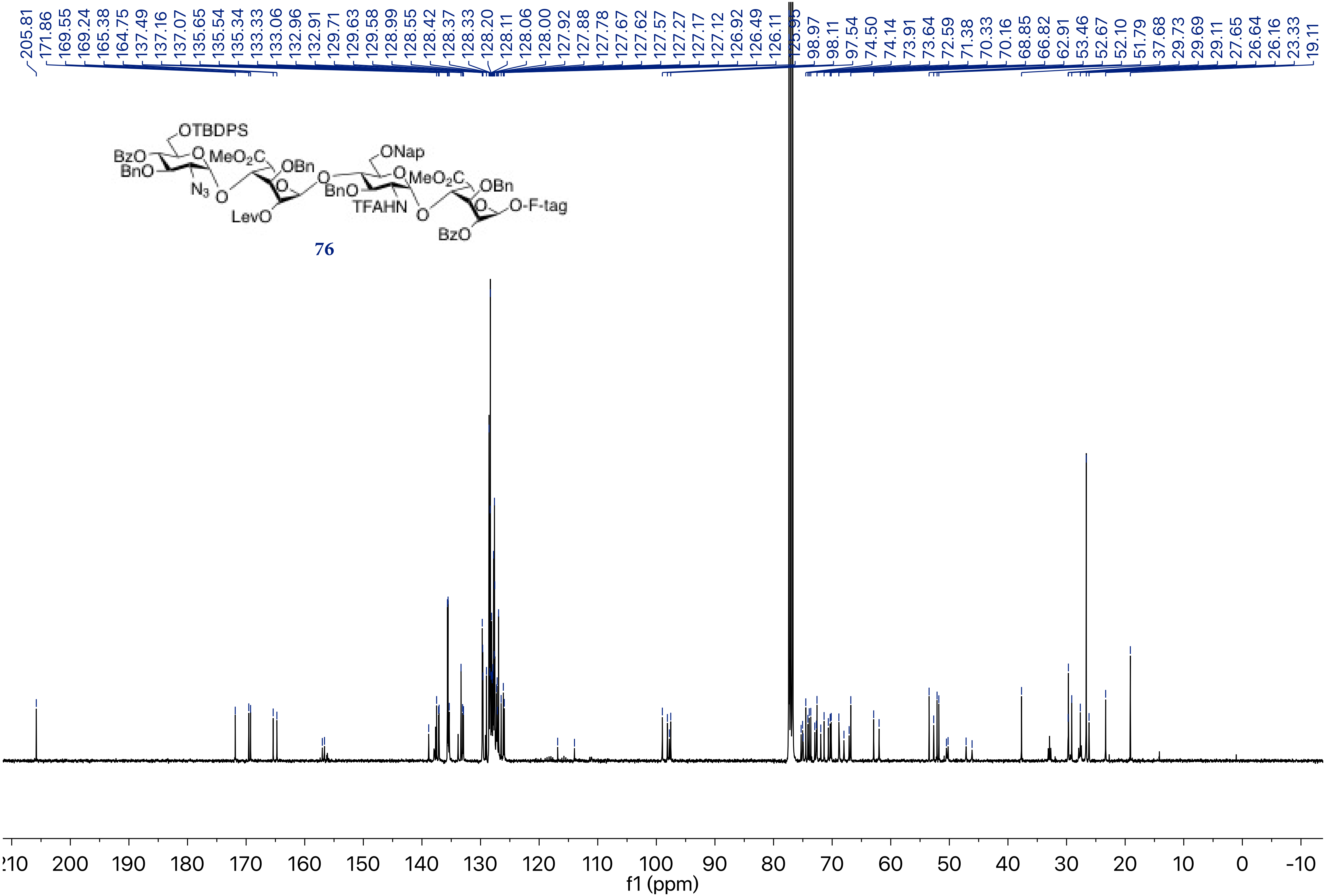
WL-2-055-Tetra-H.3.1.1r —

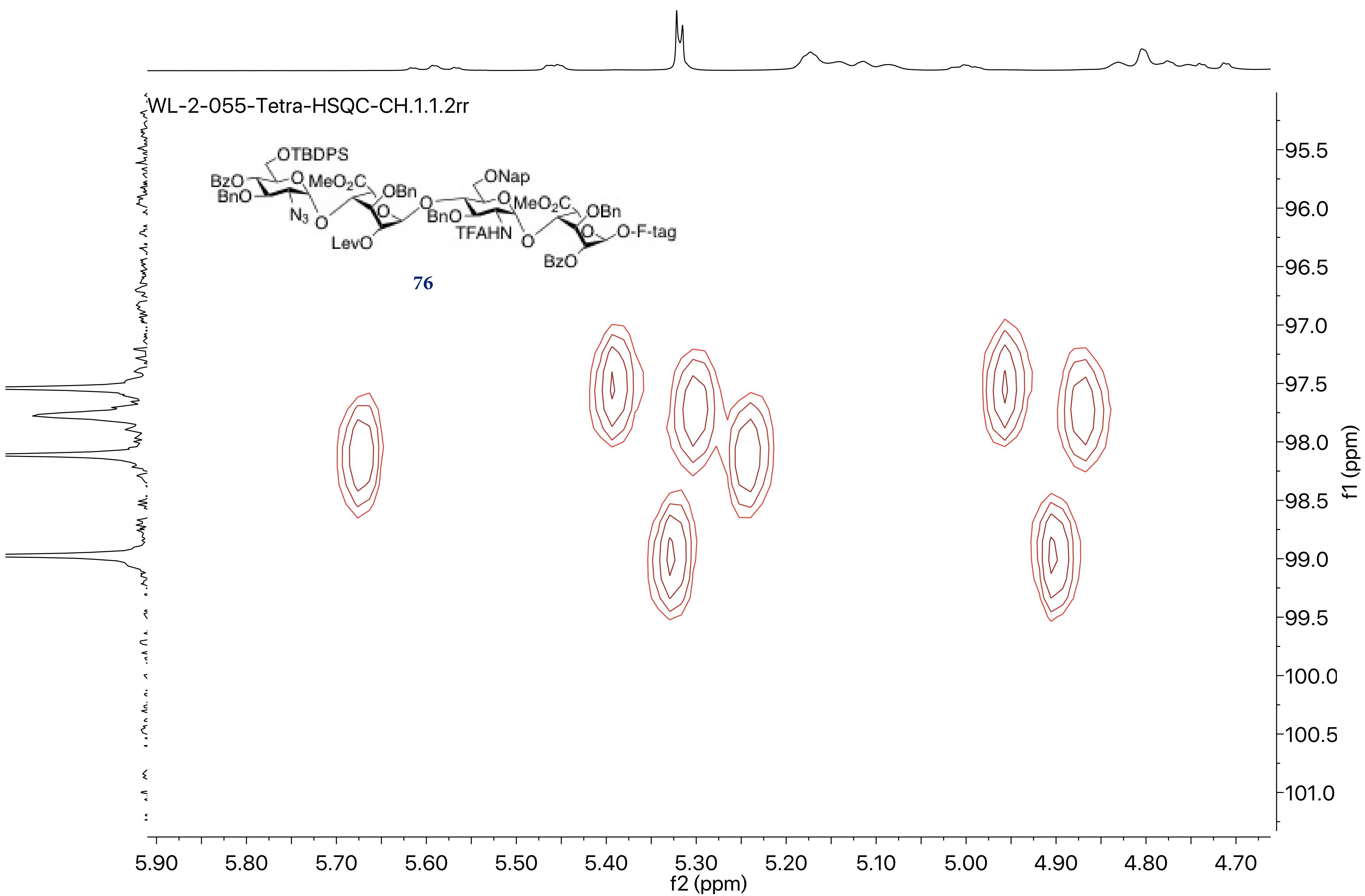


76

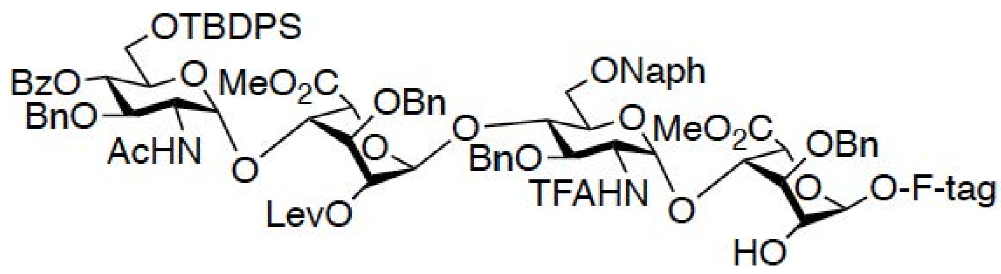


WL-2-055-Tetra-C.1.1.1r —

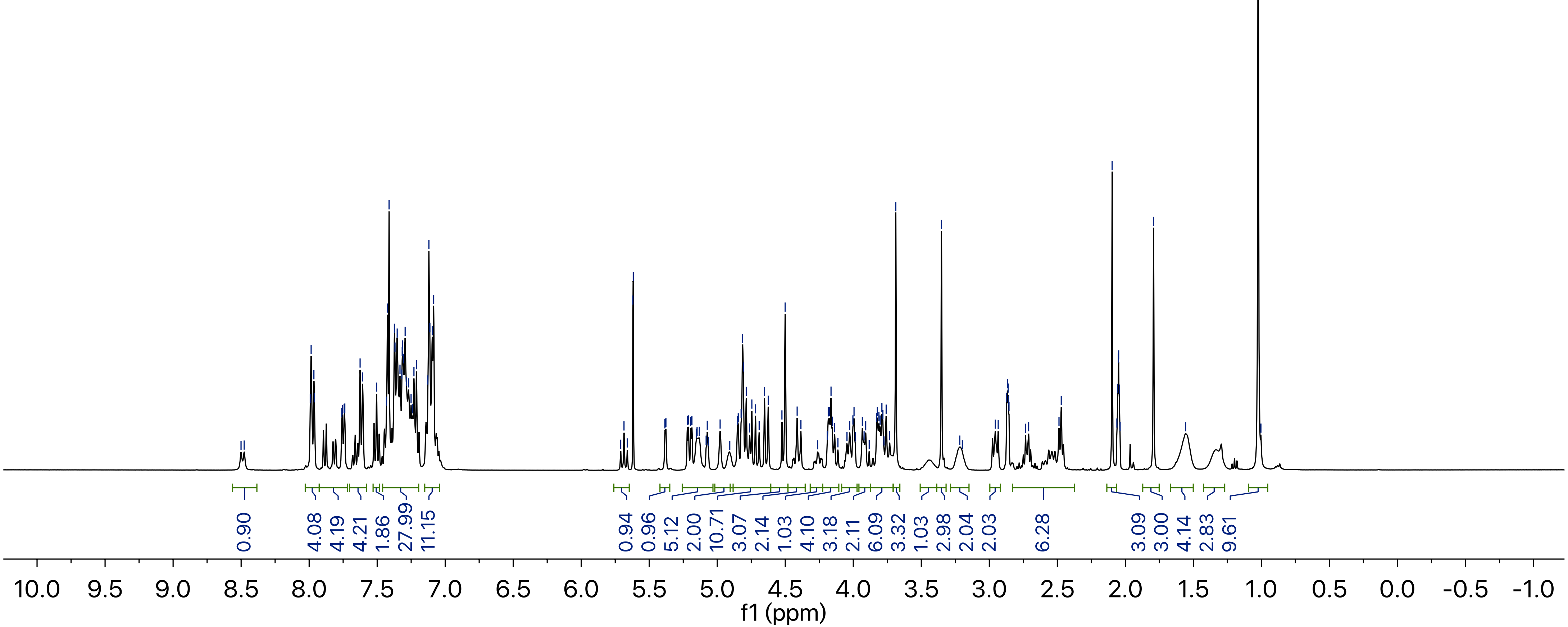



WL-2-055-Tetra-HSQC-CH.1.1.2rr
OTBDPS
BzO
BnO
N3
MeO2C
OBn
LevO
ONap
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
76
5.90
5.80
5.70
5.60
5.50
5.40
5.30
5.20
5.10
5.00
4.90
4.80
4.70
f2 (ppm)
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
100.5
101.0
f1 (ppm)

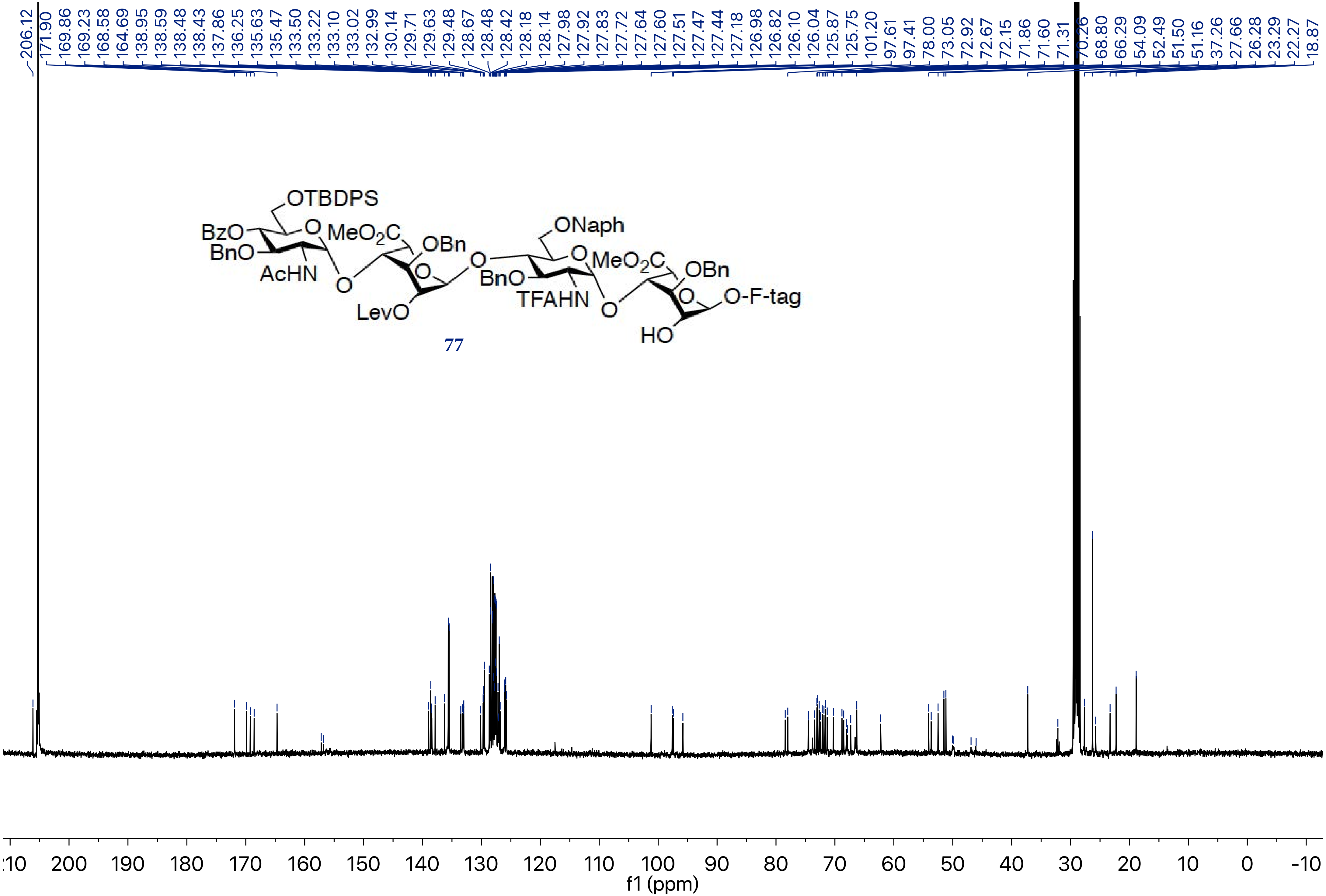
WL-2-122-D-N-Acetylation-H.6.1.1r

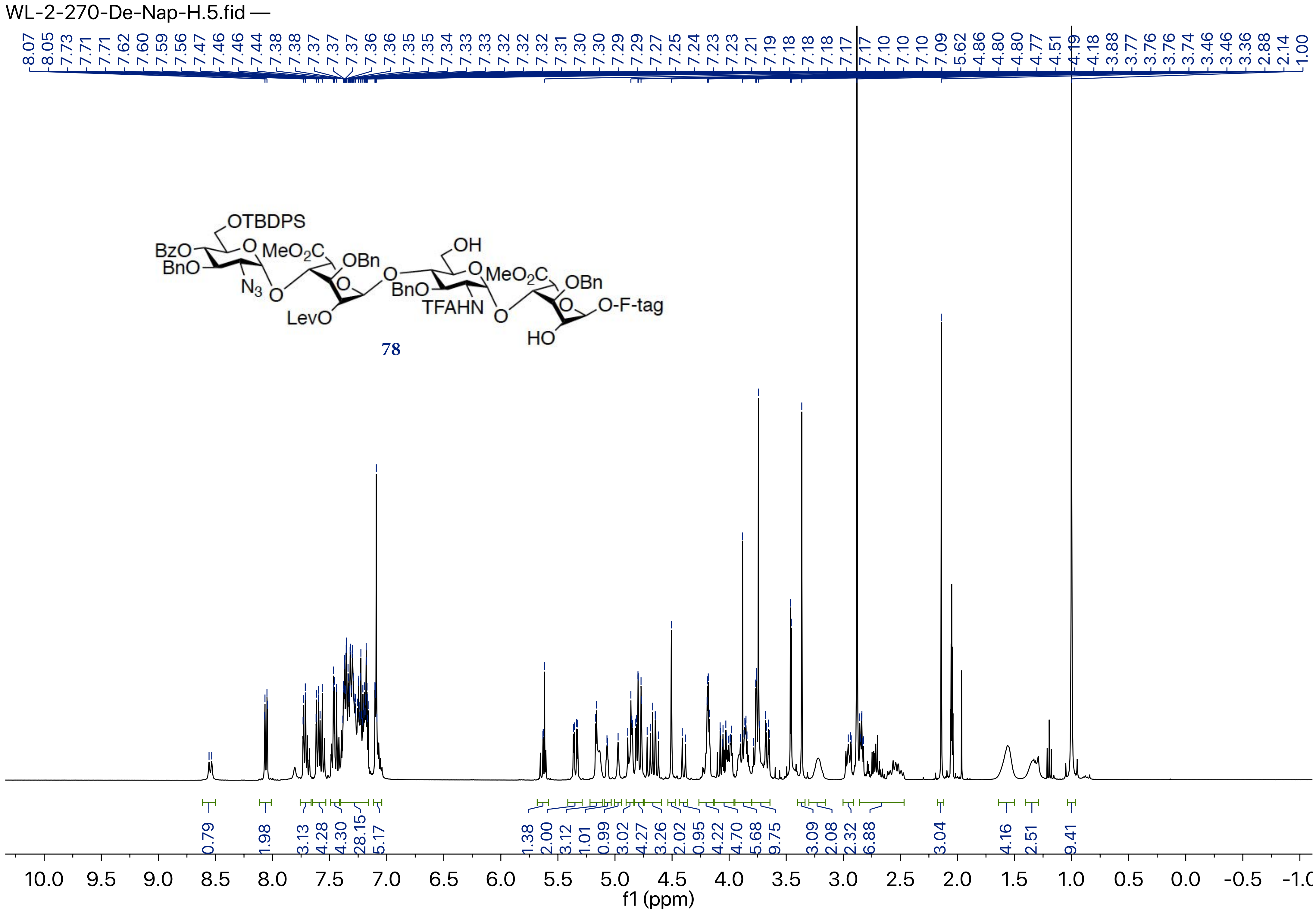


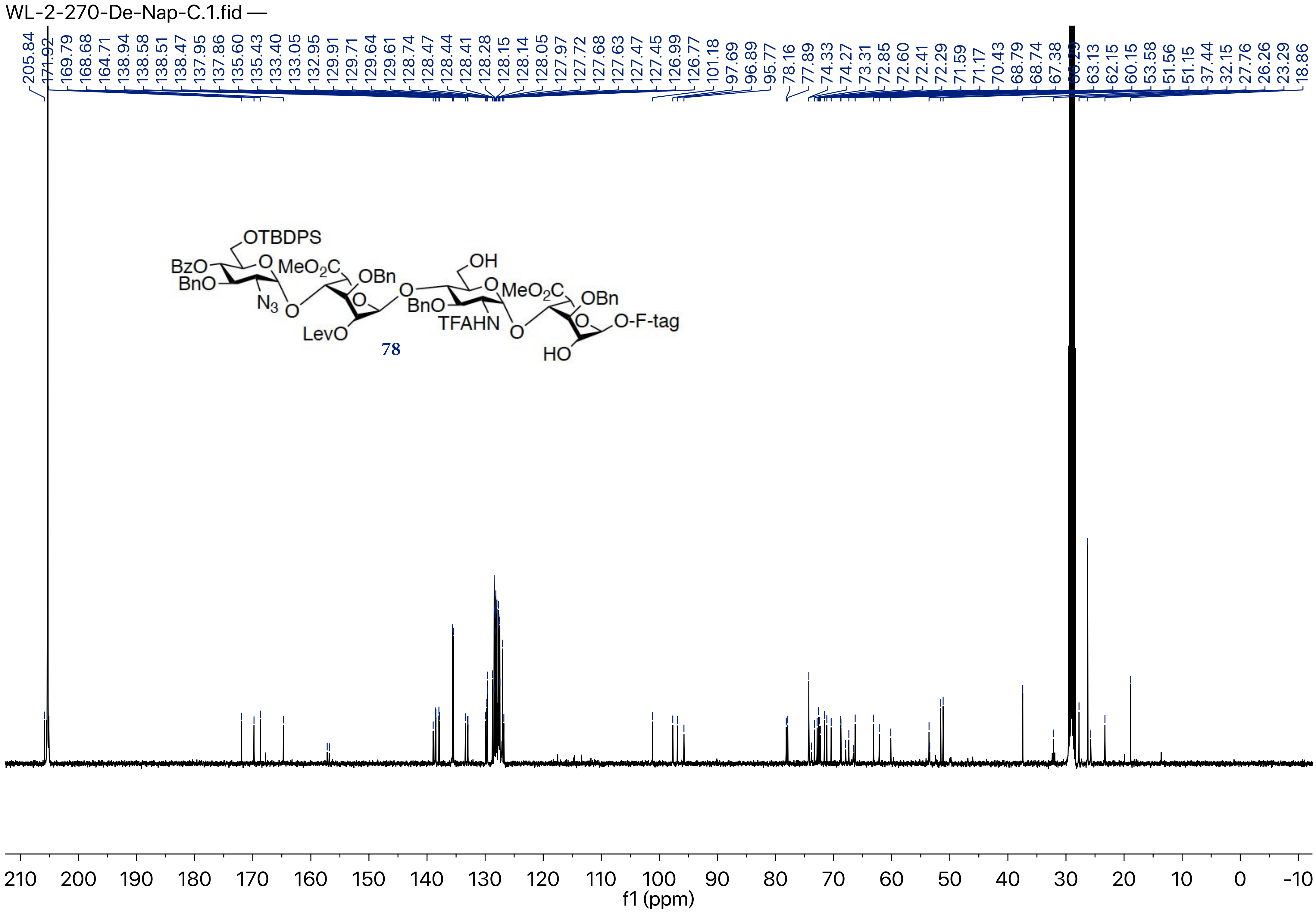
77



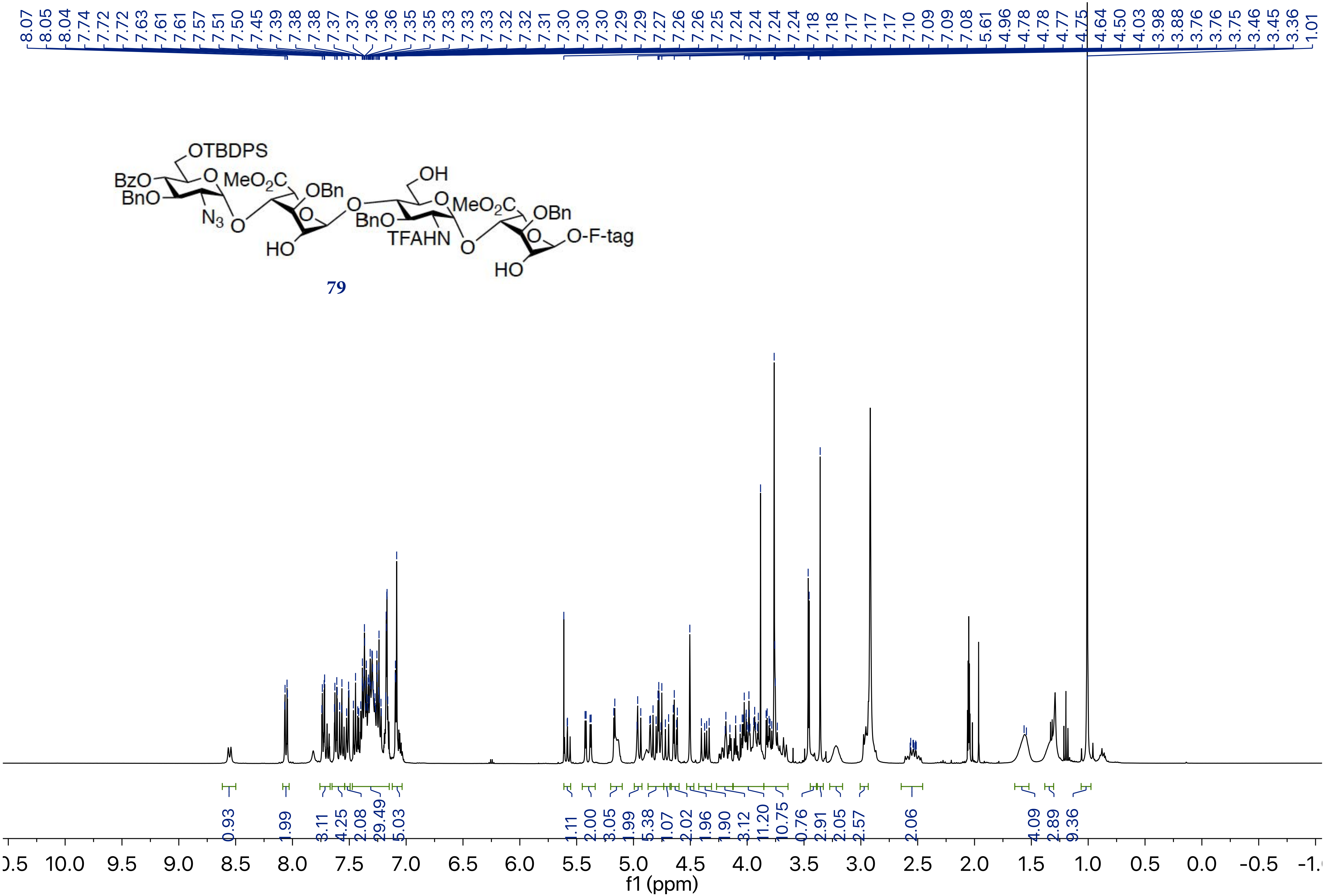
WL-2-122-D-N-Acetylation-C.1.1.1r




WL-2-270-De-Nap-H.5.fid —
8.07 8.05 7.73 7.71 7.71 7.62 7.60 7.59 7.56 7.47 7.46 7.46 7.44 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.27 7.25 7.24 7.23 7.23 7.21 7.19 7.18 7.18 7.18 7.17 7.17 7.10 7.10 7.10 7.09 5.62 4.86 4.80 4.80 4.77 4.51 4.19 4.18 3.88 3.77 3.76 3.76 3.74 3.46 3.46 3.36 2.88 2.14 1.00
OTBDPS
BzO
BnO
N_3
O
MeO_2C
OBn
LevO
BnO
OH
TFAHN
OBn
O-F-tag
HO
78
0.79
1.98
3.13
4.28
4.30
28.15
5.17
1.38
2.00
3.12
1.01
0.99
3.02
4.27
3.26
2.02
0.95
4.22
4.70
5.68
9.75
3.09
2.08
2.32
6.88
3.04
4.16
2.51
9.41
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 -0.5 -1.0
f1 (ppm)

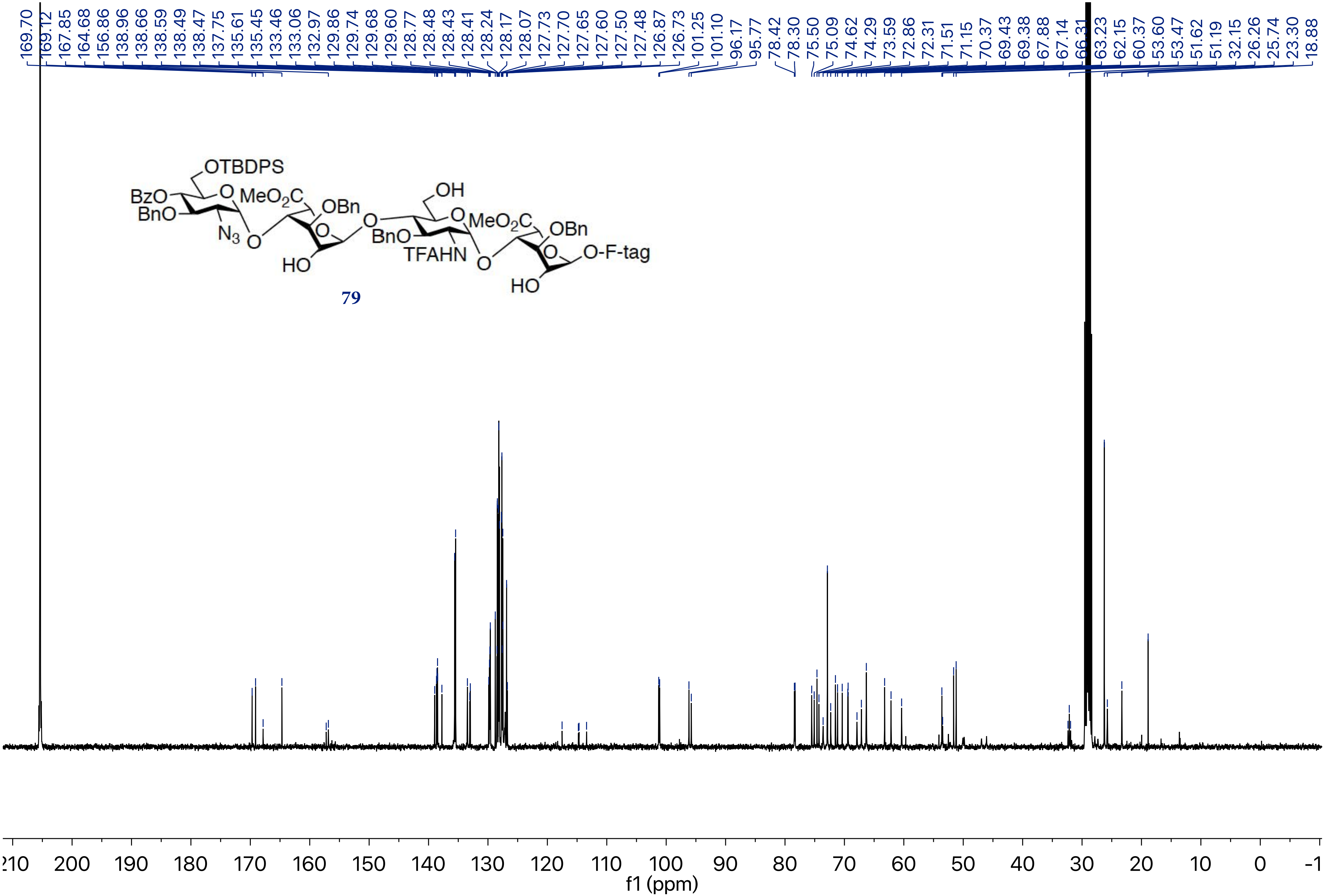

WL-2-270-De-Nap-C.1.fid —
205.84
171.92
169.79
168.68
164.71
138.94
138.58
138.51
138.47
137.95
137.86
135.60
135.43
133.40
133.05
132.95
129.91
129.71
129.64
129.61
128.74
128.47
128.44
128.41
128.28
128.15
128.14
128.05
127.97
127.72
127.68
127.63
127.47
127.45
126.99
126.77
101.18
97.69
96.89
95.77
78.16
77.89
74.33
74.27
73.31
72.85
72.60
72.41
72.29
71.59
71.17
70.43
68.79
68.74
67.38
63.13
62.15
60.15
53.58
51.56
51.15
37.44
32.15
27.76
26.26
23.29
18.86
OTBDPS
BzO
BnO
N_3
MeO_2C
OBn
LevO
OH
BnO
TFAHN
MeO_2C
OBn
O-F-tag
HO
78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

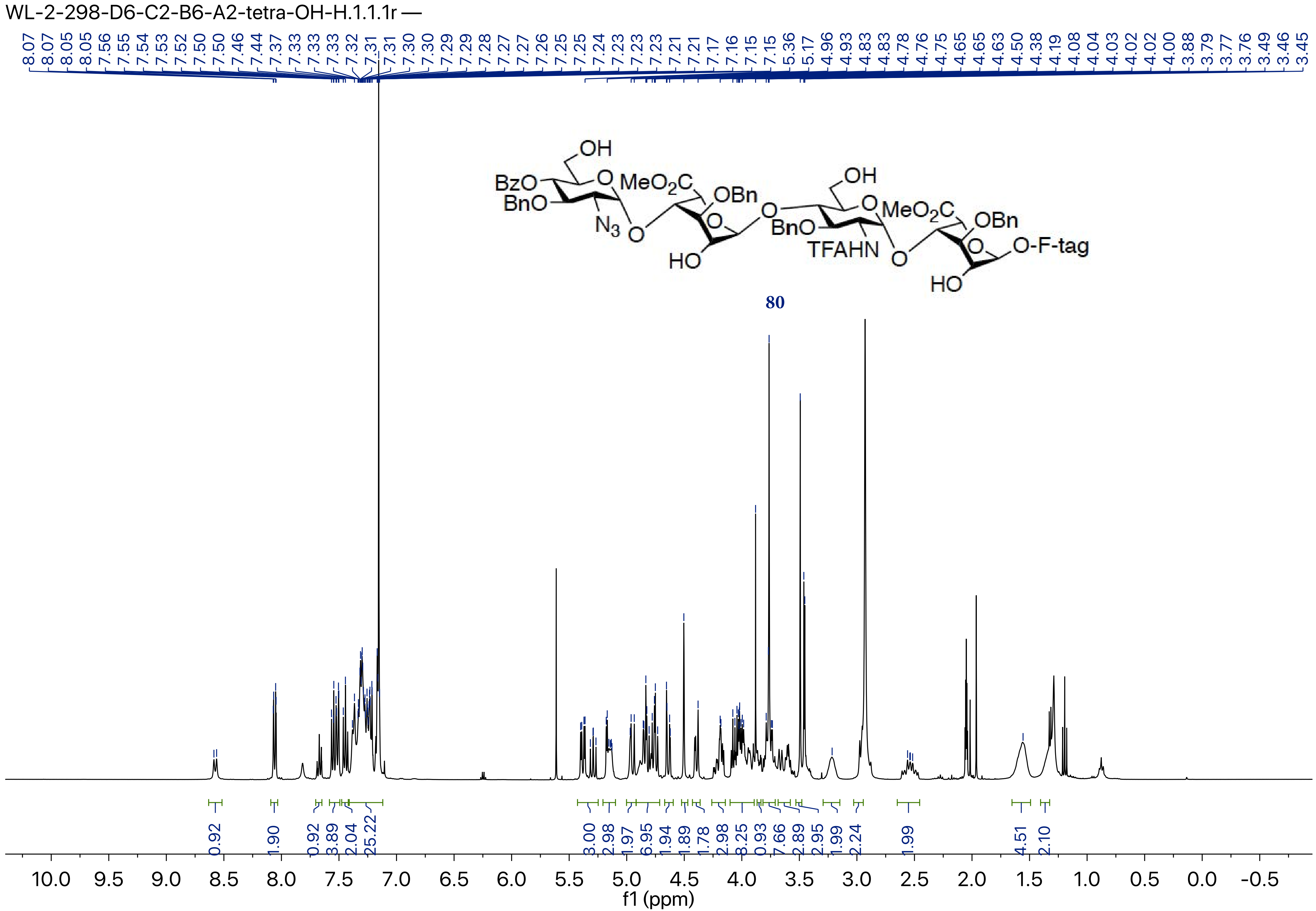
WL-2-295-De-Lev-H.6.1.1r —



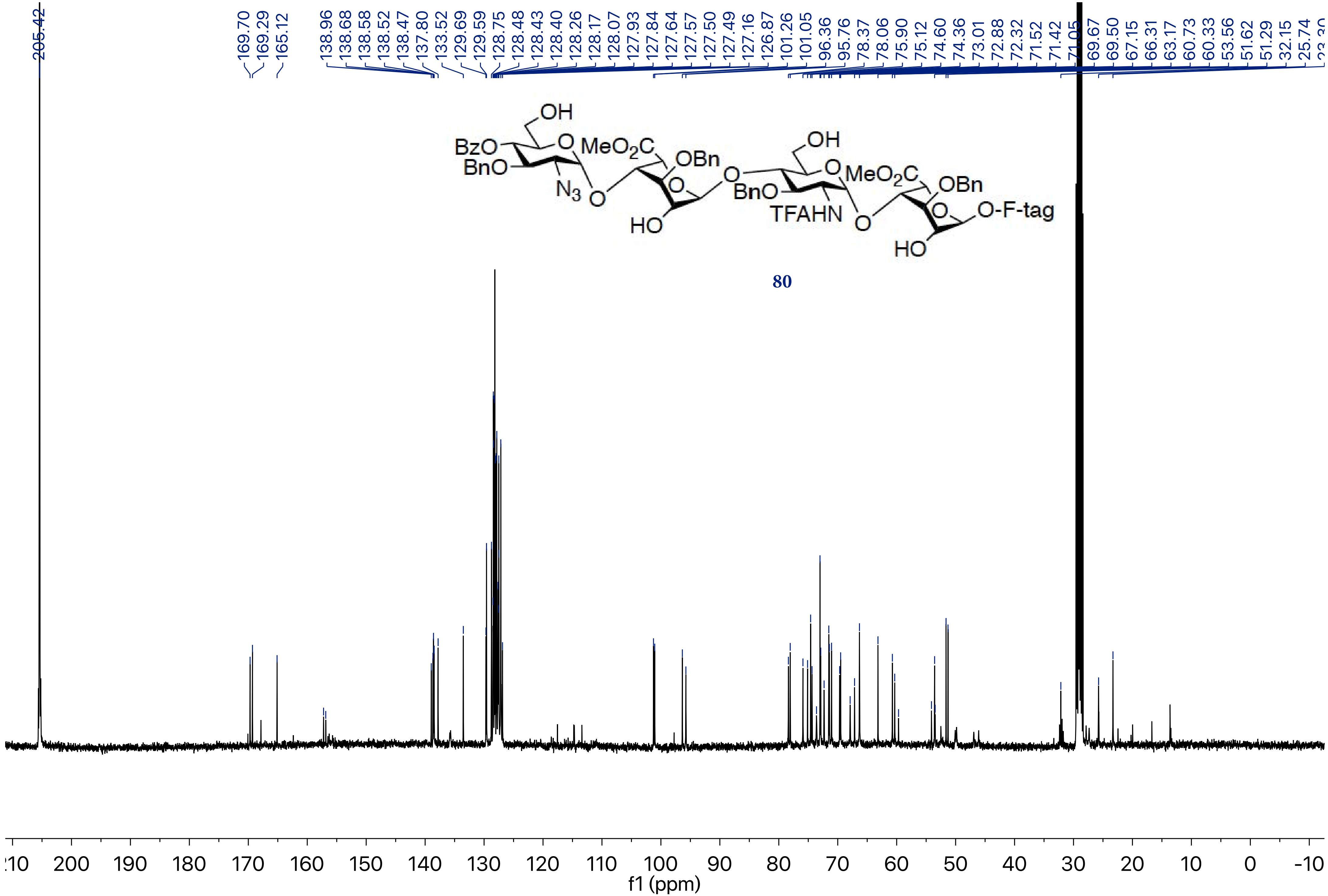
79

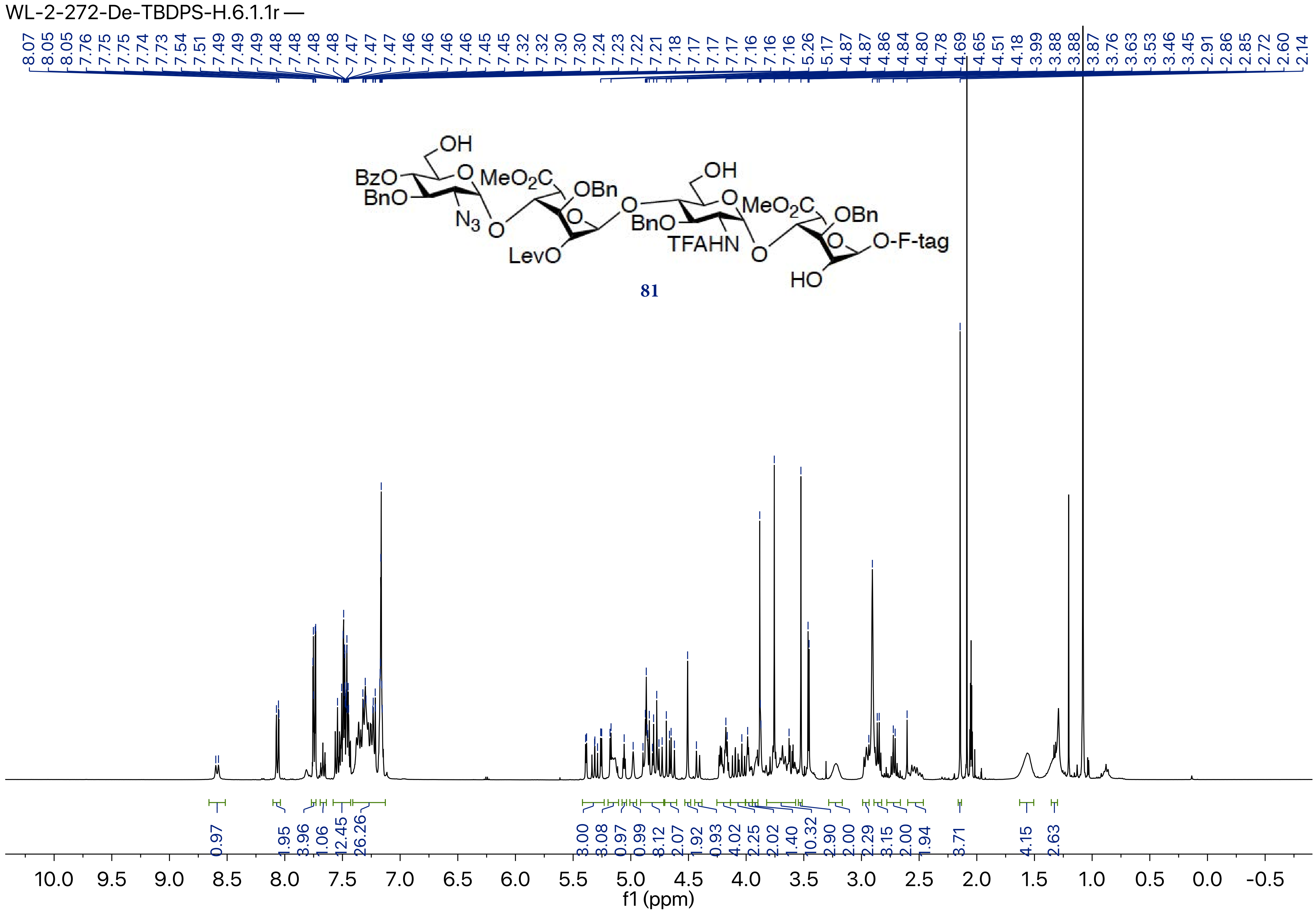
WL-2-295-De-Lev-C.1.1.1r



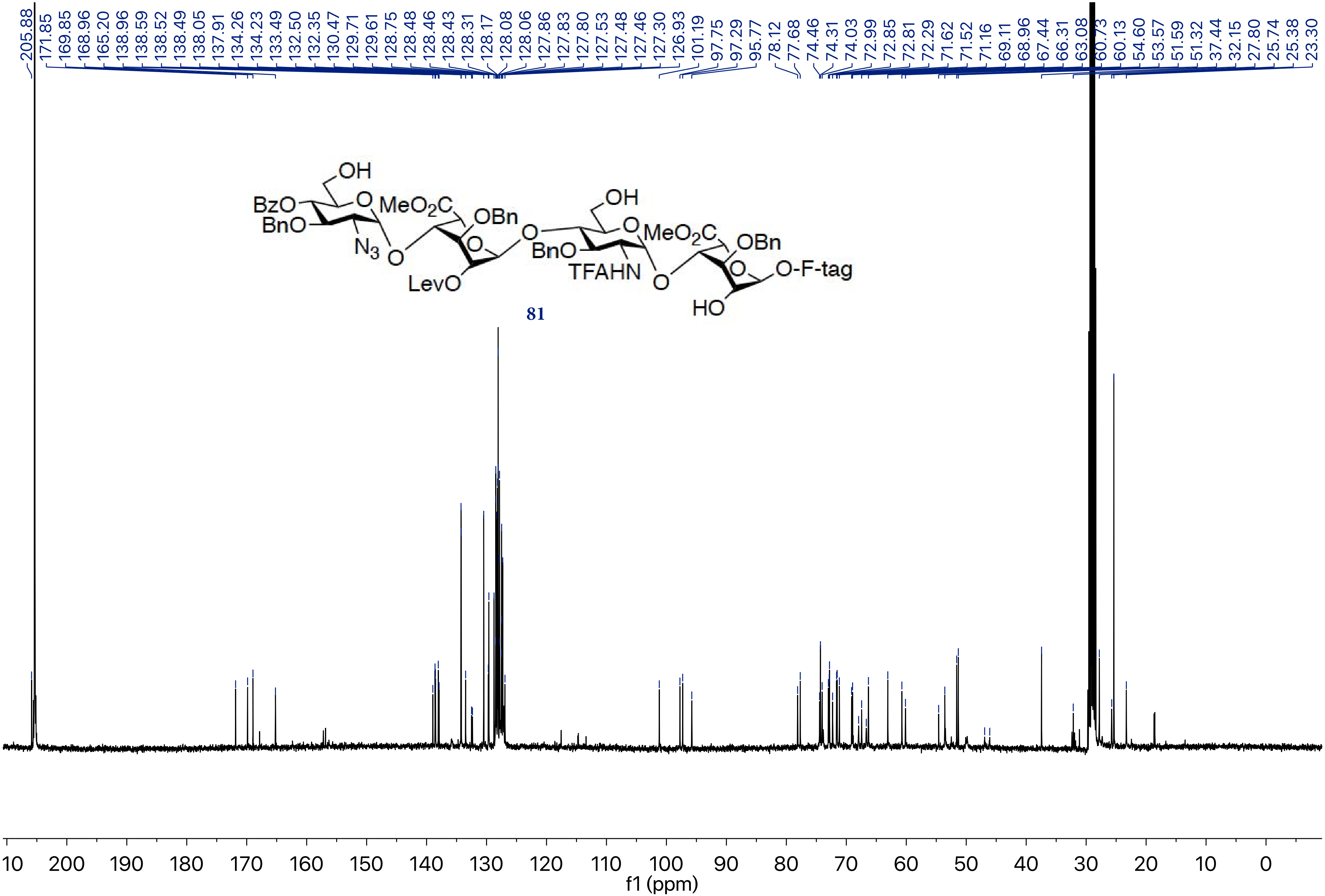

WL-2-298-D6-C2-B6-A2-tetra-OH-H.1.1.1r
8.07 8.07 8.05 8.05 7.56 7.55 7.54 7.53 7.52 7.50 7.50 7.46 7.44 7.37 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.23 7.21 7.21 7.17 7.16 7.15 7.15 5.36 5.17 4.96 4.93 4.83 4.83 4.78 4.76 4.75 4.65 4.65 4.63 4.50 4.38 4.19 4.08 4.04 4.03 4.02 4.02 4.00 3.88 3.79 3.77 3.76 3.49 3.46 3.45
BzO
BnO
OH
O
N3
MeO2C
OBn
HO
BnO
TFAHN
MeO2C
OBn
O-F-tag
HO
0.92 1.90 0.92 3.89 2.04 25.22 3.00 2.98 1.97 6.95 1.94 1.89 1.78 2.98 8.25 0.93 7.66 2.89 2.95 1.99 2.24 1.99 4.51 2.10
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 -0.5
f1 (ppm)

80


WL-2-298-D6-C2-B6-A2-tetra-OH-C.6.1.1r
205.42
169.70
169.29
165.12
138.96
138.68
138.58
138.52
138.47
137.80
133.52
129.69
129.59
128.75
128.48
128.43
128.40
128.26
128.17
128.07
127.93
127.84
127.64
127.57
127.50
127.49
127.16
126.87
101.26
101.05
96.36
95.76
78.37
78.06
75.90
75.12
74.60
74.36
73.01
72.88
72.32
71.52
71.42
71.05
69.67
69.50
67.15
66.31
63.17
60.73
60.33
53.56
51.62
51.29
32.15
25.74
BzO
BnO
OH
O
N3
MeO2C
OBn
HO
TFAHN
O-F-tag
80
f1 (ppm)

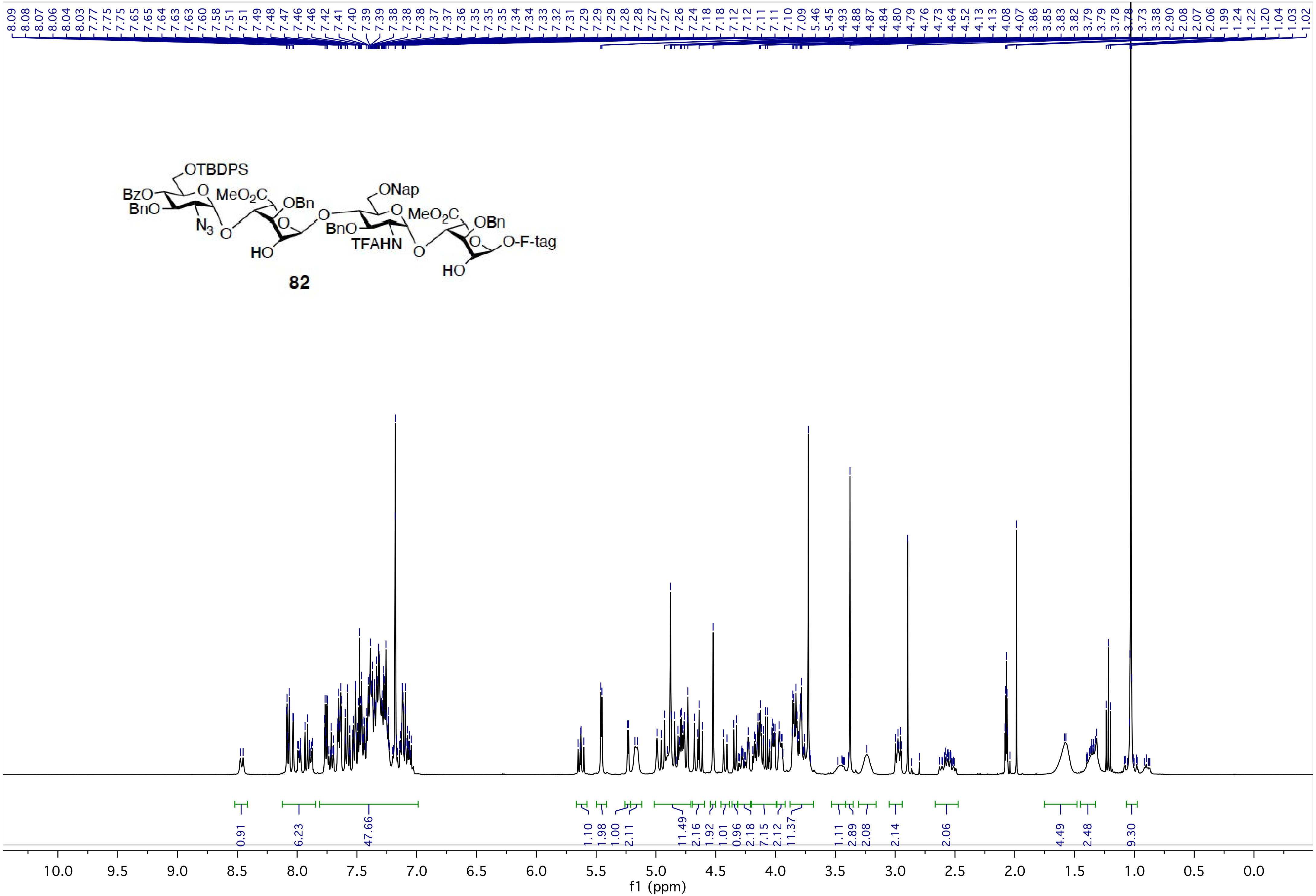

WL-2-272-De-TBDPS-H.6.1.1r
8.07 8.05 8.05 7.76 7.75 7.75 7.74 7.73 7.54 7.51 7.49 7.49 7.49 7.48 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.32 7.32 7.30 7.30 7.24 7.23 7.22 7.21 7.18 7.17 7.17 7.17 7.16 7.16 7.16 5.26 5.17 4.87 4.87 4.86 4.84 4.80 4.78 4.69 4.65 4.51 4.18 3.99 3.88 3.88 3.87 3.76 3.63 3.53 3.46 3.45 2.91 2.86 2.85 2.72 2.60 2.14
BzO
BnO
OH
N3
MeO2C
OBn
LevO
BnO
TFAHN
OH
MeO2C
OBn
O-F-tag
HO
81
0.97 1.95 3.96 1.06 12.45 26.26 3.00 3.08 0.97 0.99 8.12 2.07 1.92 0.93 4.02 2.25 2.02 1.40 10.32 2.90 2.00 2.29 3.15 2.00 1.94 3.71 4.15 2.63
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 -0.5
f1 (ppm)

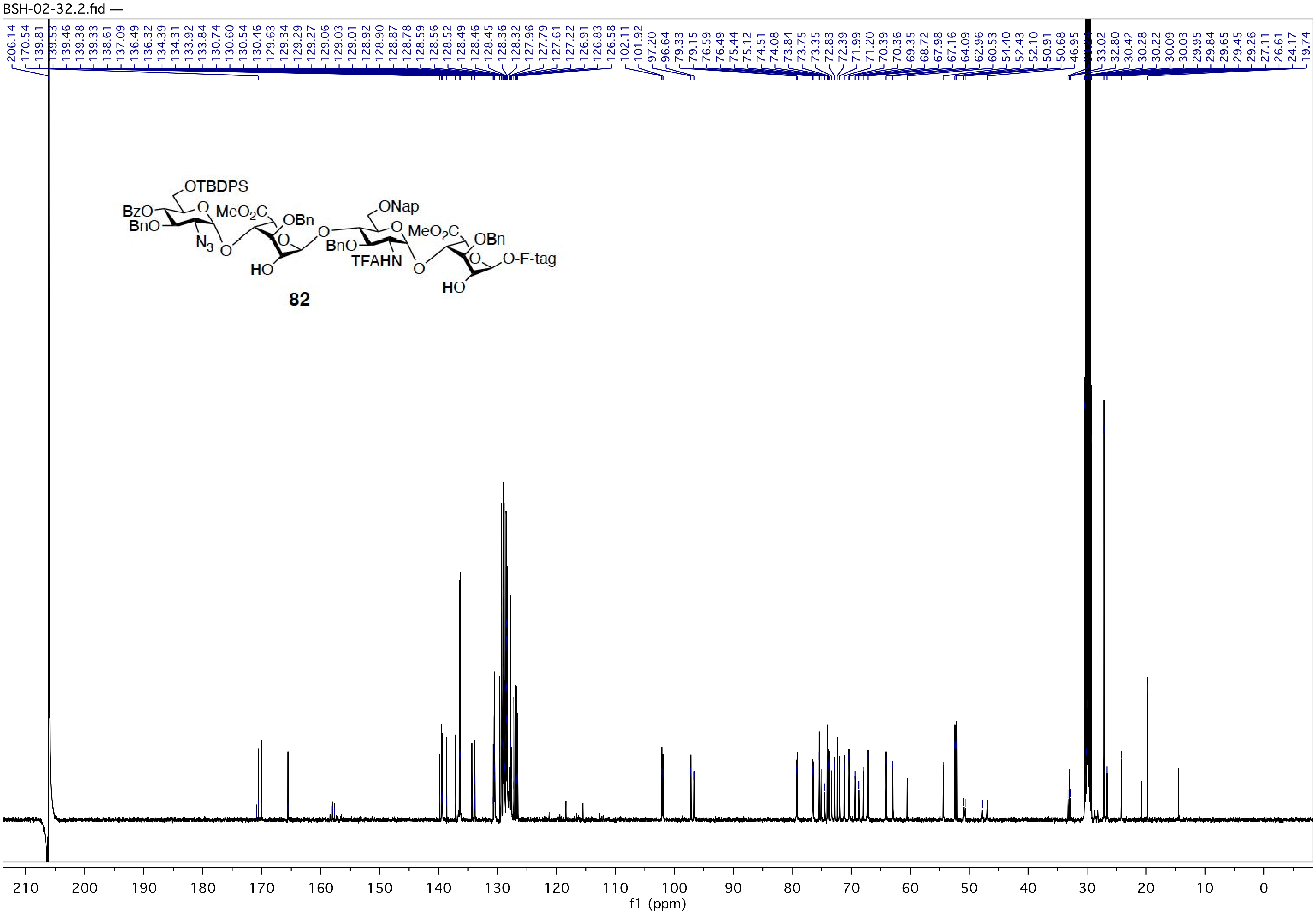
WL-2-272-De-TBDPS-C.1.1.1r



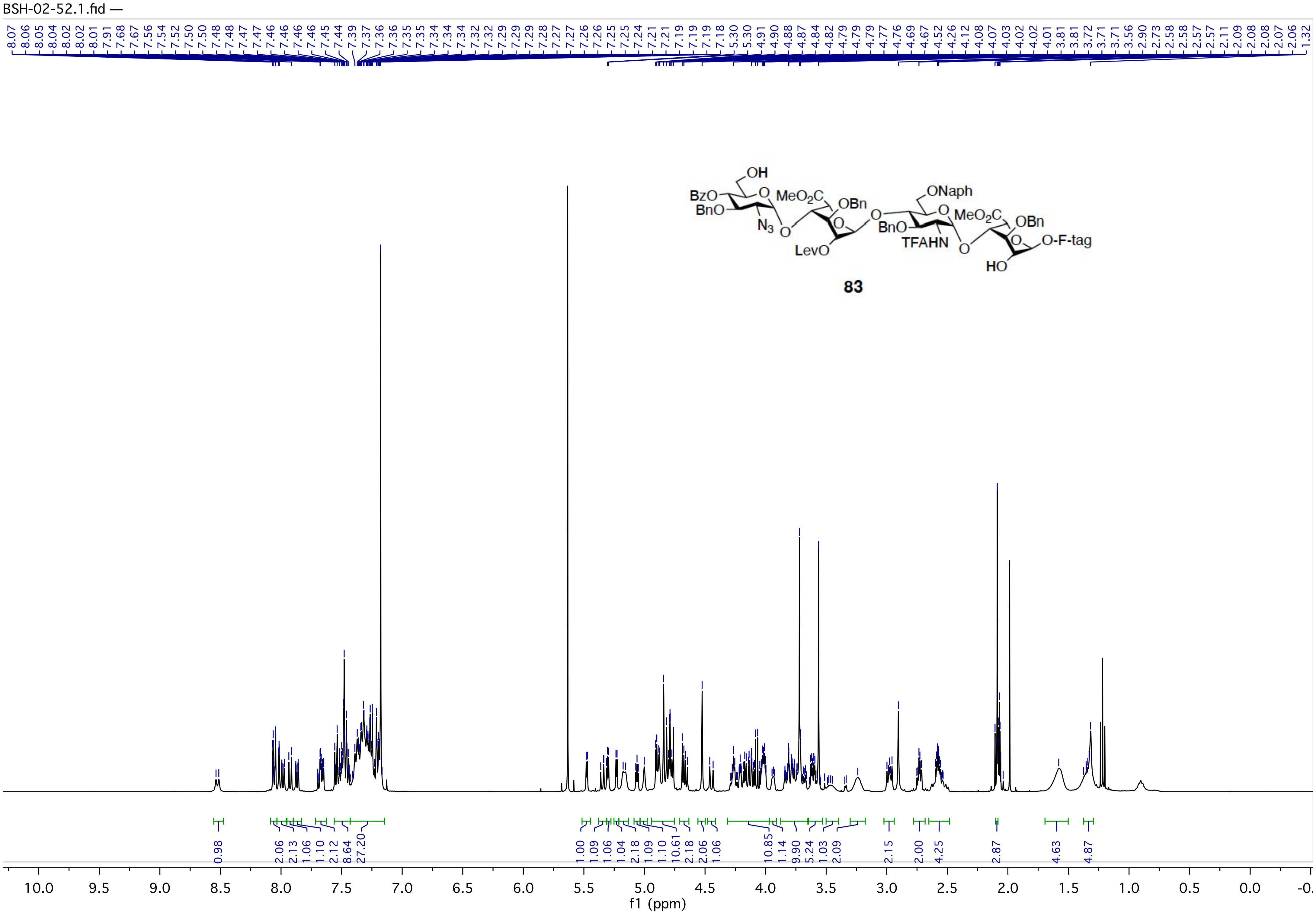
81

BSH-02-32.1.fid —

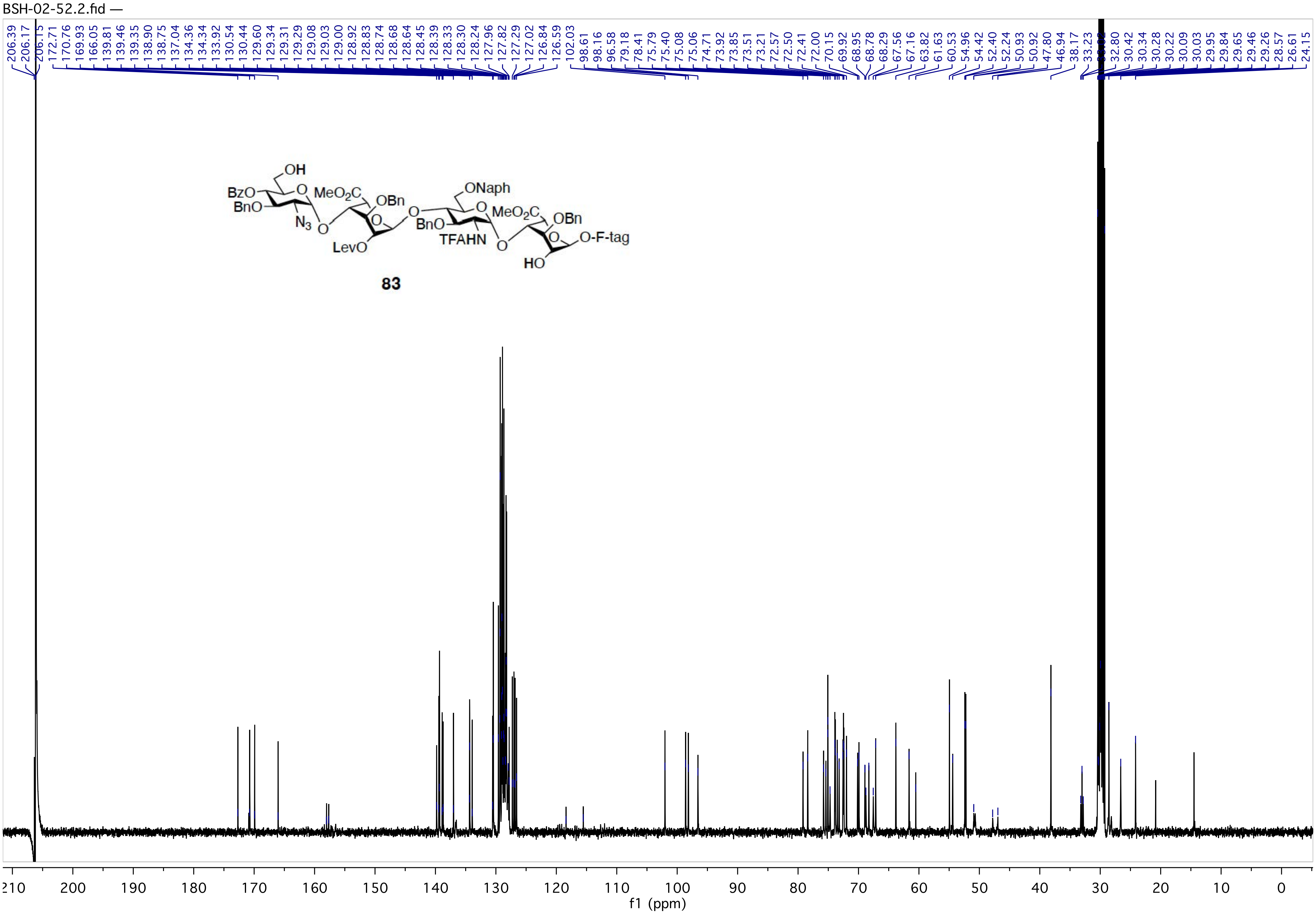



BSH-02-32.2.fid —
206.14
170.54
139.81
139.53
139.46
139.38
139.33
138.61
137.09
136.49
136.32
134.39
134.31
133.92
133.84
130.74
130.60
130.54
130.46
129.63
129.34
129.29
129.27
129.06
129.03
129.01
128.92
128.90
128.87
128.78
128.59
128.56
128.52
128.49
128.46
128.45
128.36
128.32
127.96
127.79
127.61
127.22
126.91
126.83
126.58
102.11
101.92
97.20
96.64
79.33
79.15
76.59
76.49
75.44
75.12
74.51
74.08
73.84
73.75
73.35
72.83
72.39
71.99
71.20
70.39
70.36
69.35
68.72
67.98
67.16
64.09
62.96
60.53
54.40
52.43
52.10
50.91
50.68
46.95
33.02
32.80
30.42
30.28
30.22
30.09
30.03
29.95
29.84
29.65
29.45
29.26
27.11
26.61
24.17
19.74
OTBDPS
BzO
BnO
O
N3
O
MeO2C
OBn
O
HO
O
ONap
BnO
O
TFAHN
O
MeO2C
OBn
O
O-F-tag
HO
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

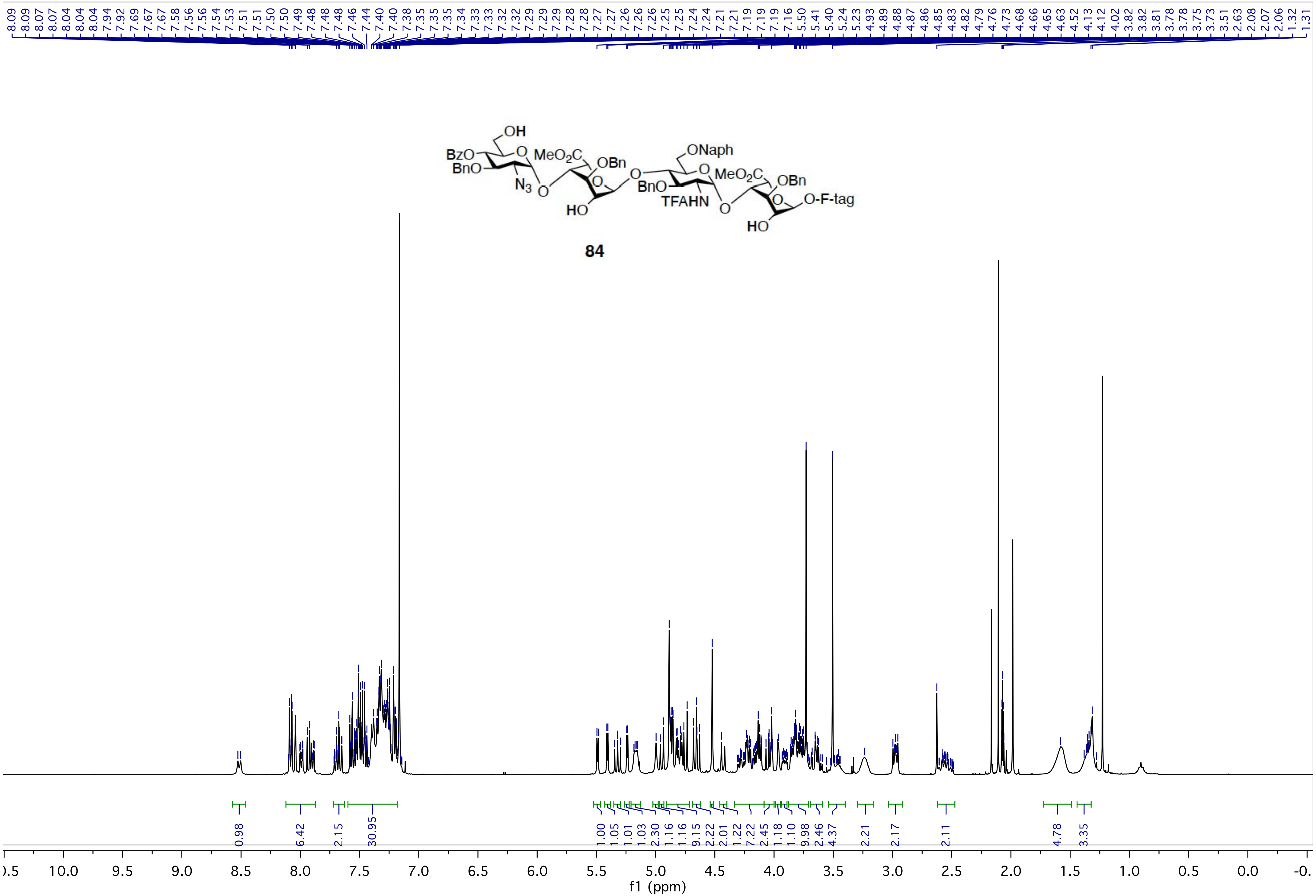
82

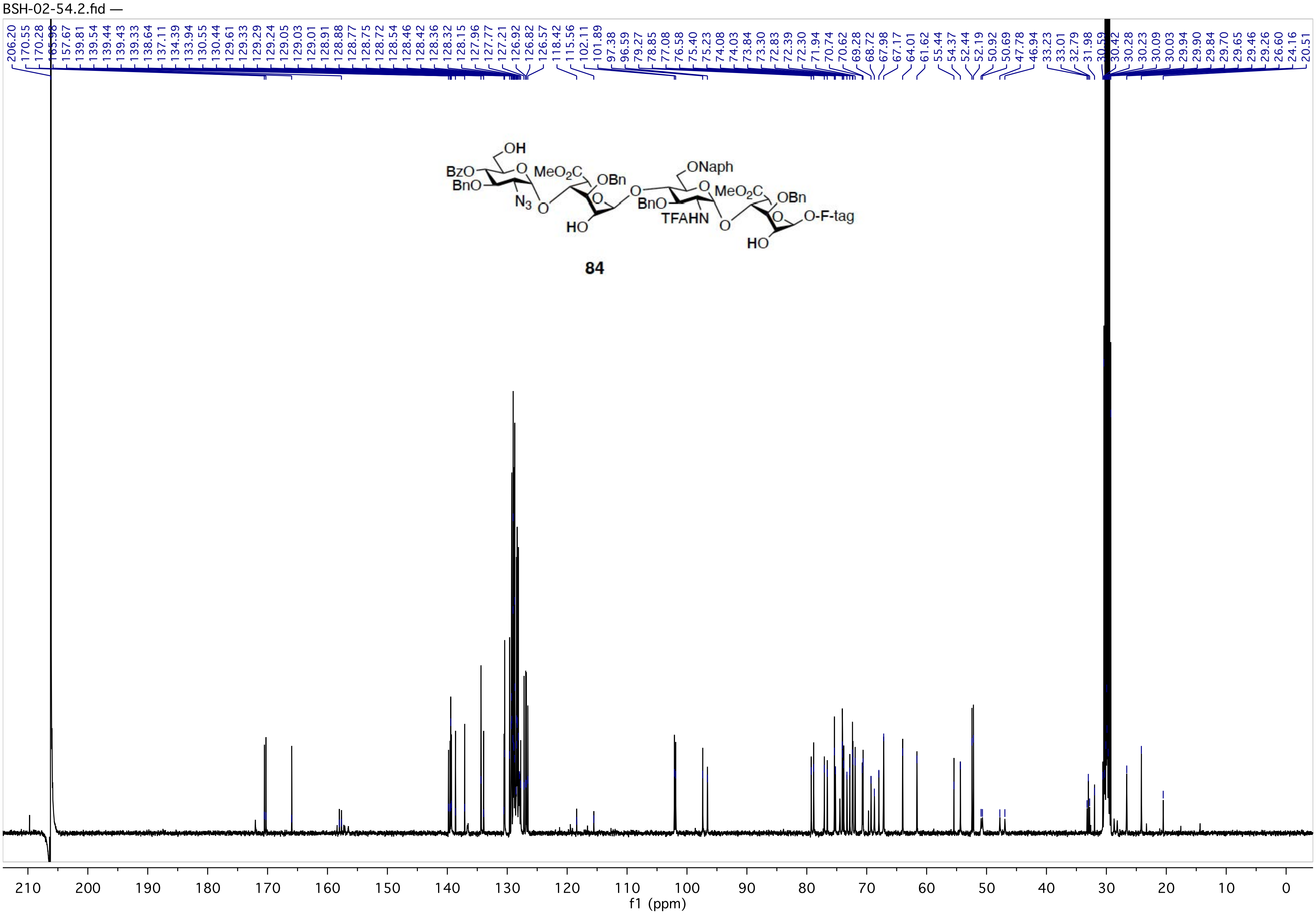


BSH-02-52.1.fid —
8.07 8.06 8.05 8.04 8.02 8.02 8.01 7.91 7.68 7.67 7.56 7.54 7.52 7.50 7.50 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.44 7.39 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.32 7.32 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.21 7.21 7.19 7.19 7.19 7.18 5.30 5.30 4.91 4.90 4.88 4.87 4.84 4.82 4.79 4.79 4.77 4.76 4.69 4.67 4.52 4.26 4.12 4.08 4.07 4.03 4.02 4.02 4.01 3.81 3.81 3.72 3.71 3.71 3.56 2.90 2.73 2.58 2.58 2.57 2.57 2.11 2.09 2.08 2.07 2.06 1.32
BzO BnO OH O N3 O MeO2C OBn O LevO O BnO ONaph O TFAHN O MeO2C OBn O O-F-tag HO
83
0.98 2.06 2.13 1.06 1.10 2.12 8.64 27.20 1.00 1.09 1.06 1.04 2.18 1.09 1.10 10.61 2.18 2.06 1.06 10.85 1.14 9.90 5.24 1.03 2.09 2.15 2.00 4.25 2.87 4.63 4.87
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 -0.
f1 (ppm)

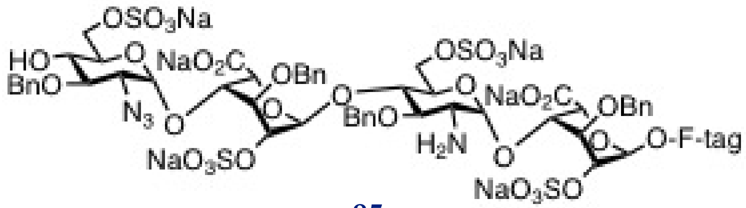

BSH-02-52.2.fid —
206.39
206.17
206.15
172.71
170.76
169.93
166.05
139.81
139.46
139.35
138.90
138.75
137.04
134.36
134.34
133.92
130.54
130.44
129.60
129.34
129.31
129.29
129.08
129.03
129.00
128.92
128.83
128.74
128.68
128.64
128.45
128.39
128.33
128.30
128.24
127.96
127.82
127.29
127.02
126.84
126.59
102.03
98.61
98.16
96.58
79.18
78.41
75.79
75.40
75.08
75.06
74.71
73.92
73.85
73.51
73.21
72.57
72.50
72.41
72.00
70.15
69.92
68.95
68.78
68.29
67.56
67.16
63.82
61.63
60.53
54.96
54.42
52.40
52.24
50.93
50.92
47.80
46.94
38.17
33.23
32.80
30.42
30.34
30.28
30.22
30.09
30.03
29.95
29.84
29.65
29.46
29.26
28.57
26.61
24.15
OH
BzO
BnO
N3
O
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
HO
83
f1 (ppm)

BSH-02-54.1.fid —

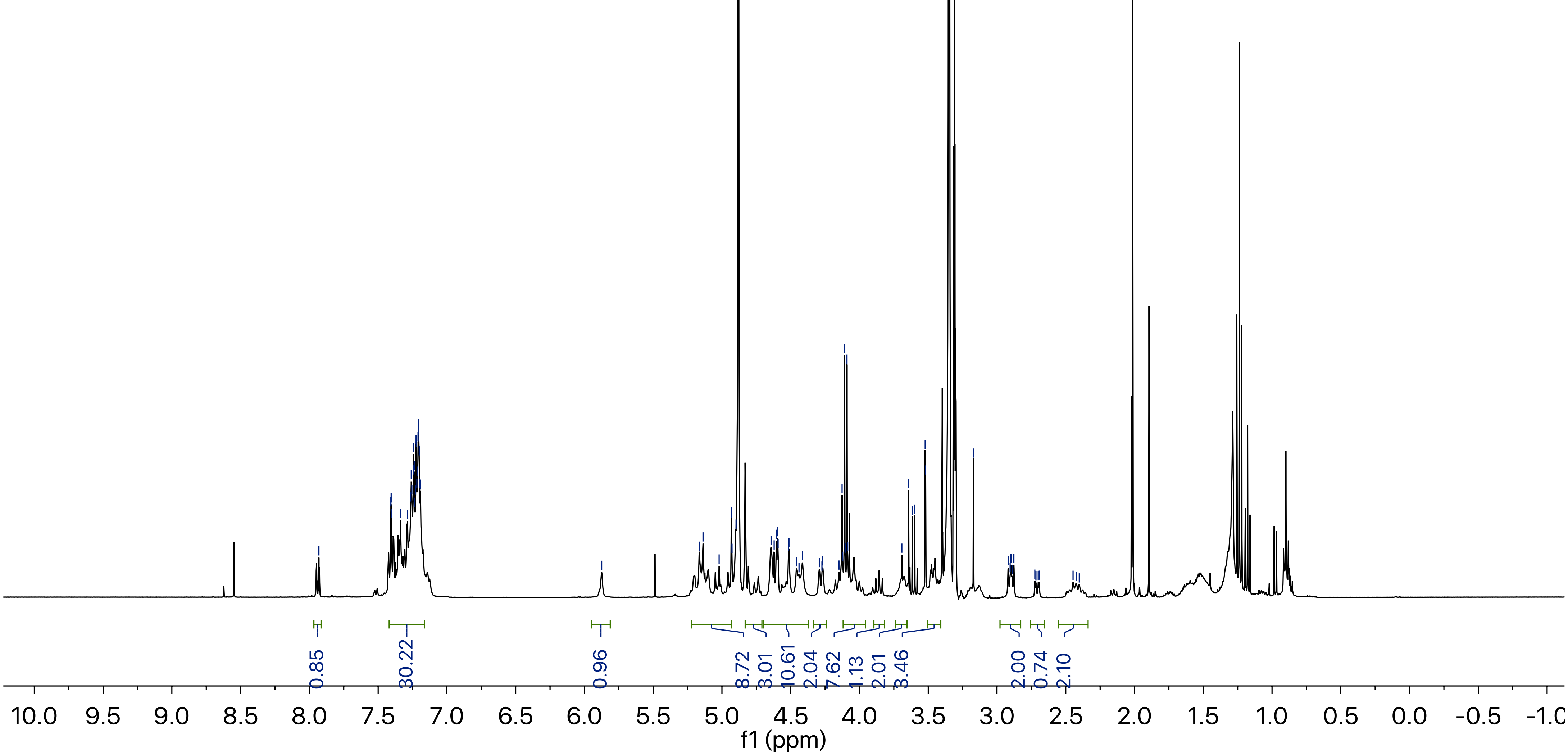



BSH-02-54.2.fid —
206.20
170.55
170.28
165.98
157.67
139.81
139.54
139.44
139.43
139.33
138.64
137.11
134.39
133.94
130.55
130.44
129.61
129.33
129.29
129.24
129.05
129.03
129.01
128.91
128.88
128.77
128.75
128.72
128.54
128.46
128.42
128.36
128.32
128.15
127.96
127.77
127.21
126.92
126.82
126.57
118.42
115.56
102.11
101.89
97.38
96.59
79.27
78.85
77.08
76.58
75.40
75.23
74.08
74.03
73.84
73.30
72.83
72.39
72.30
71.94
70.74
70.62
69.28
68.72
67.98
67.17
64.01
61.62
55.44
54.37
52.44
52.19
50.92
50.69
47.78
46.94
33.23
33.01
32.79
31.98
30.59
30.42
30.28
30.23
30.09
30.03
29.94
29.90
29.84
29.70
29.65
29.46
29.26
26.60
24.16
20.51
OH
BzO
BnO
O
MeO2C
OBn
N3
O
HO
O
ONaph
BnO
O
MeO2C
OBn
TFAHN
O
O-F-tag
HO
84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

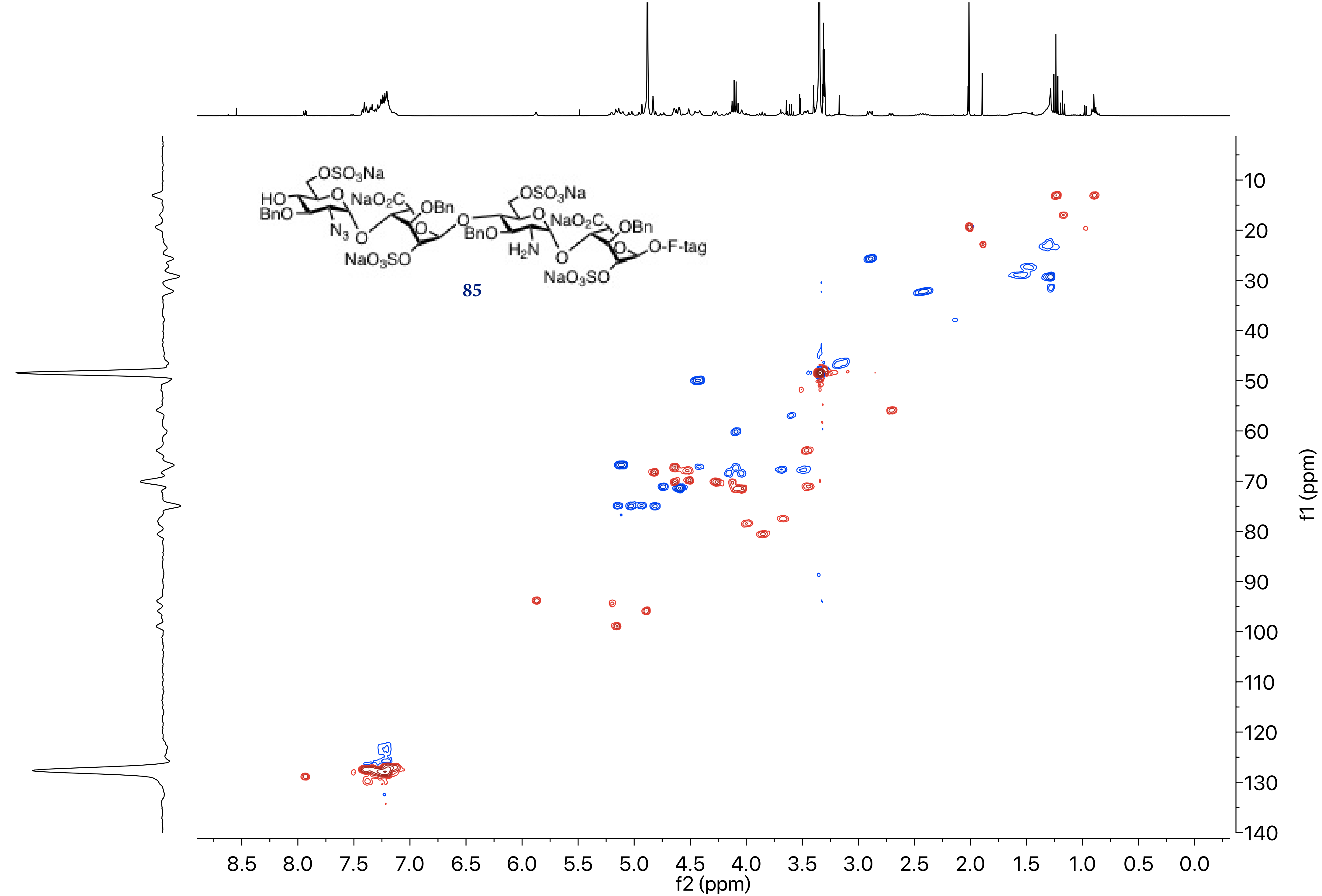
WL-2-300-D6S-C2S-B6S-A2S-LiOH.1.1.1r —



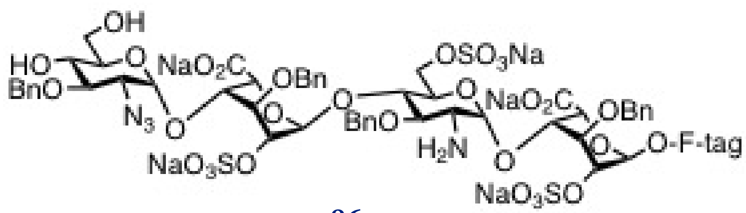
85



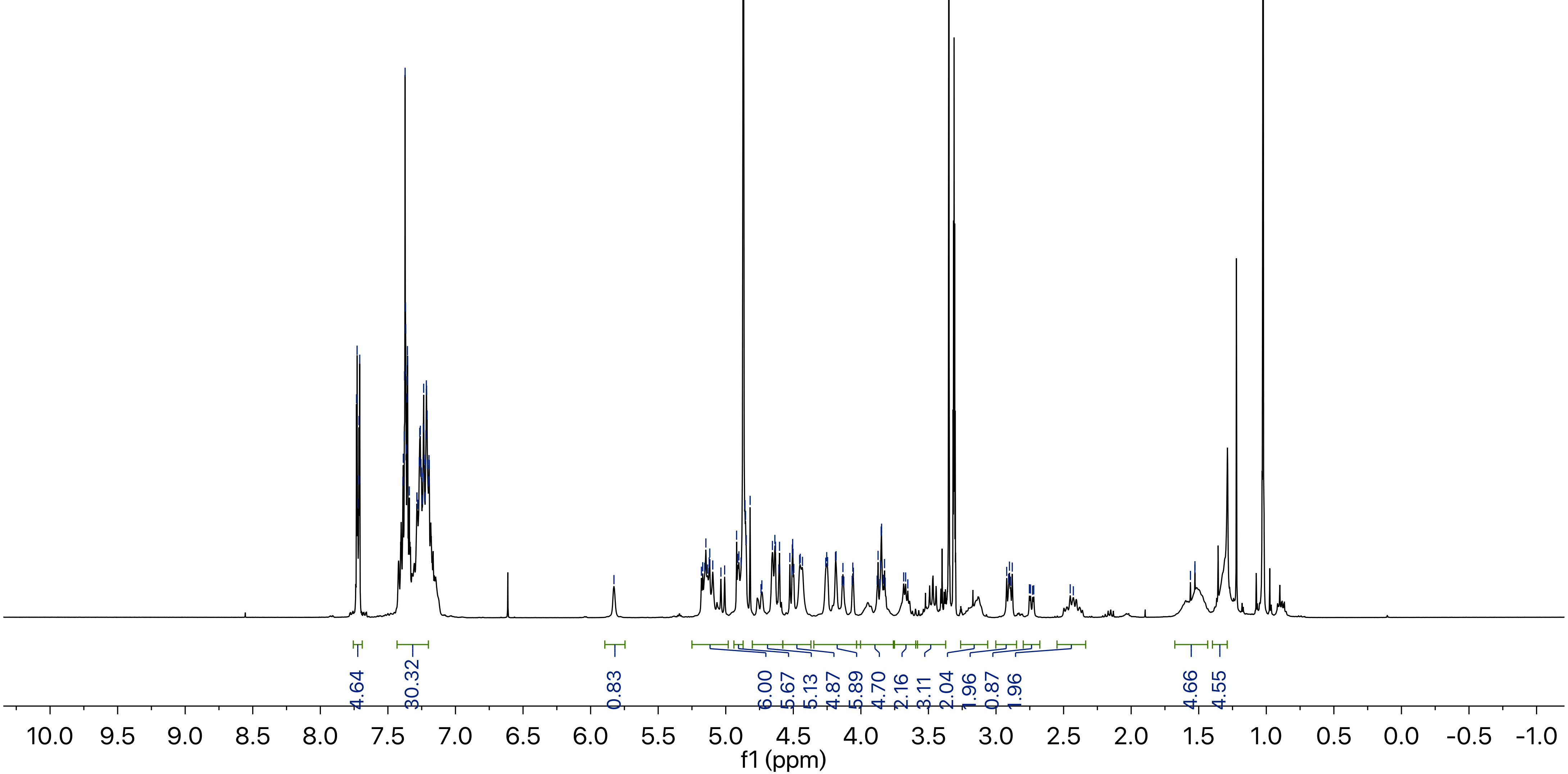
WL-2-300-D6S-C2S-B6S-A2S-LiOH.3.1.2rr —



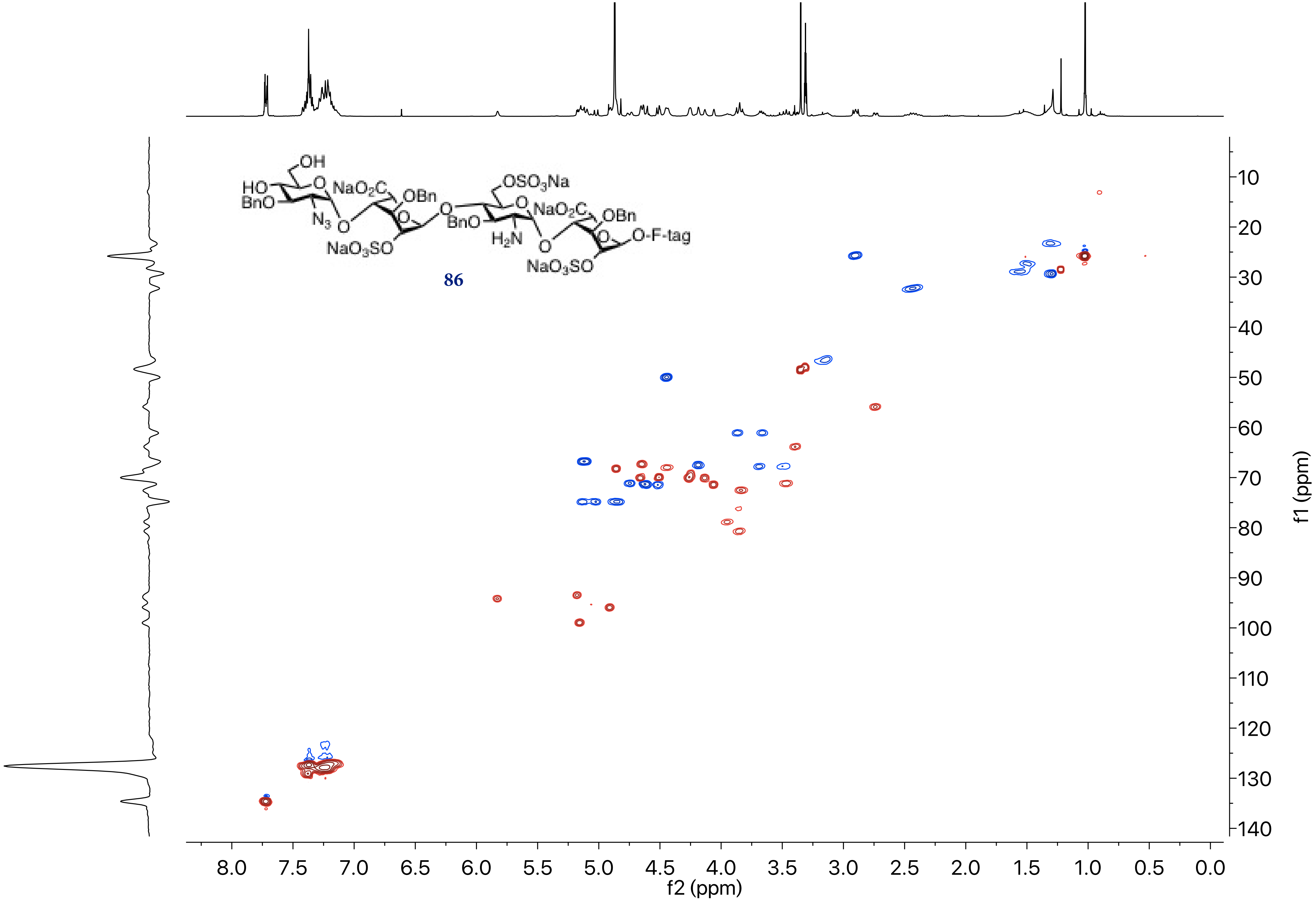
WL-2-297-C2S-B6S-A2S-LiOH-2.1.1.1r —

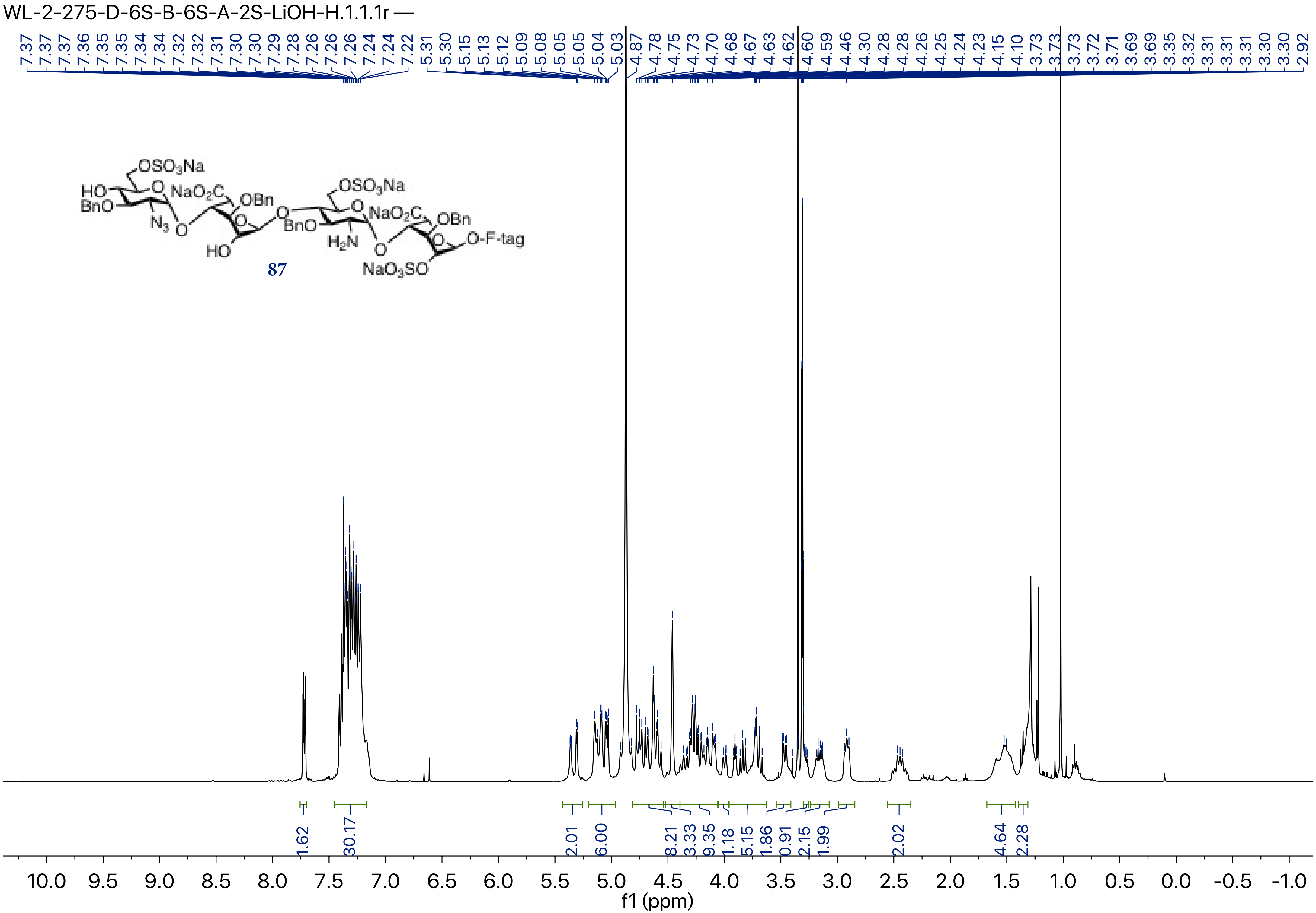


86

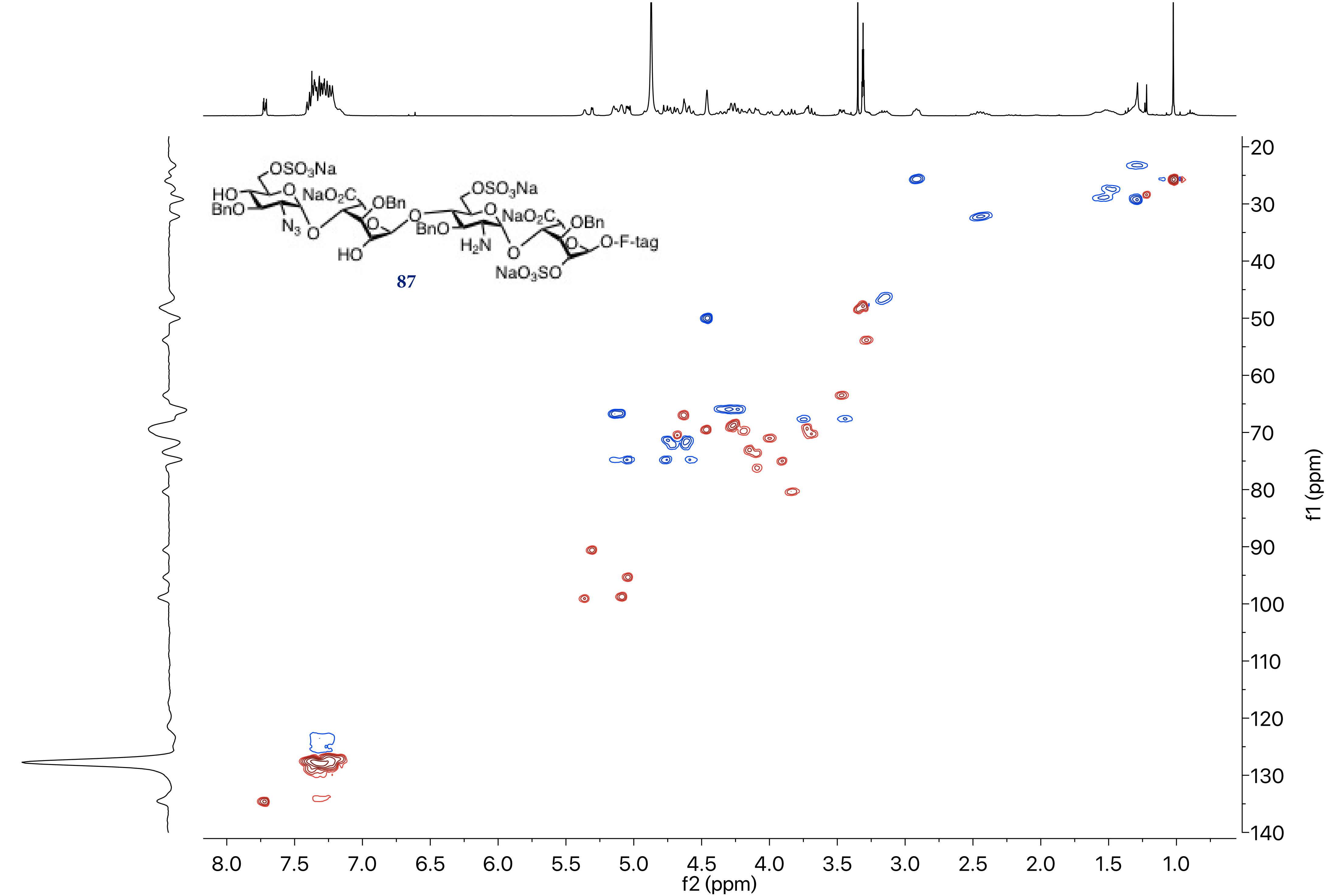


WL-2-297-C2S-B6S-A2S-LiOH-2.3.1.2rr —

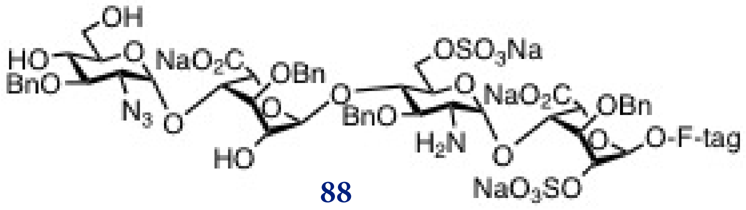



WL-2-275-D-6S-B-6S-A-2S-LiOH-H.1.1.1r
7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.26 7.26 7.26 7.24 7.24 7.22 5.31 5.30 5.15 5.13 5.12 5.09 5.08 5.05 5.05 5.04 5.03 4.87 4.78 4.75 4.73 4.70 4.68 4.67 4.63 4.62 4.60 4.59 4.46 4.30 4.28 4.28 4.26 4.25 4.24 4.23 4.15 4.10 3.73 3.73 3.73 3.72 3.71 3.69 3.69 3.35 3.32 3.31 3.31 3.31 3.30 3.30 2.92
OSO3Na
HO
BnO
N3
NaO2C
OBn
HO
BnO
H2N
NaO2C
OBn
O-F-tag
NaO3SO
87
1.62
30.17
2.01
6.00
8.21
3.33
9.35
1.18
5.15
1.86
0.91
2.15
1.99
2.02
4.64
2.28
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 -0.5 -1.0
f1 (ppm)

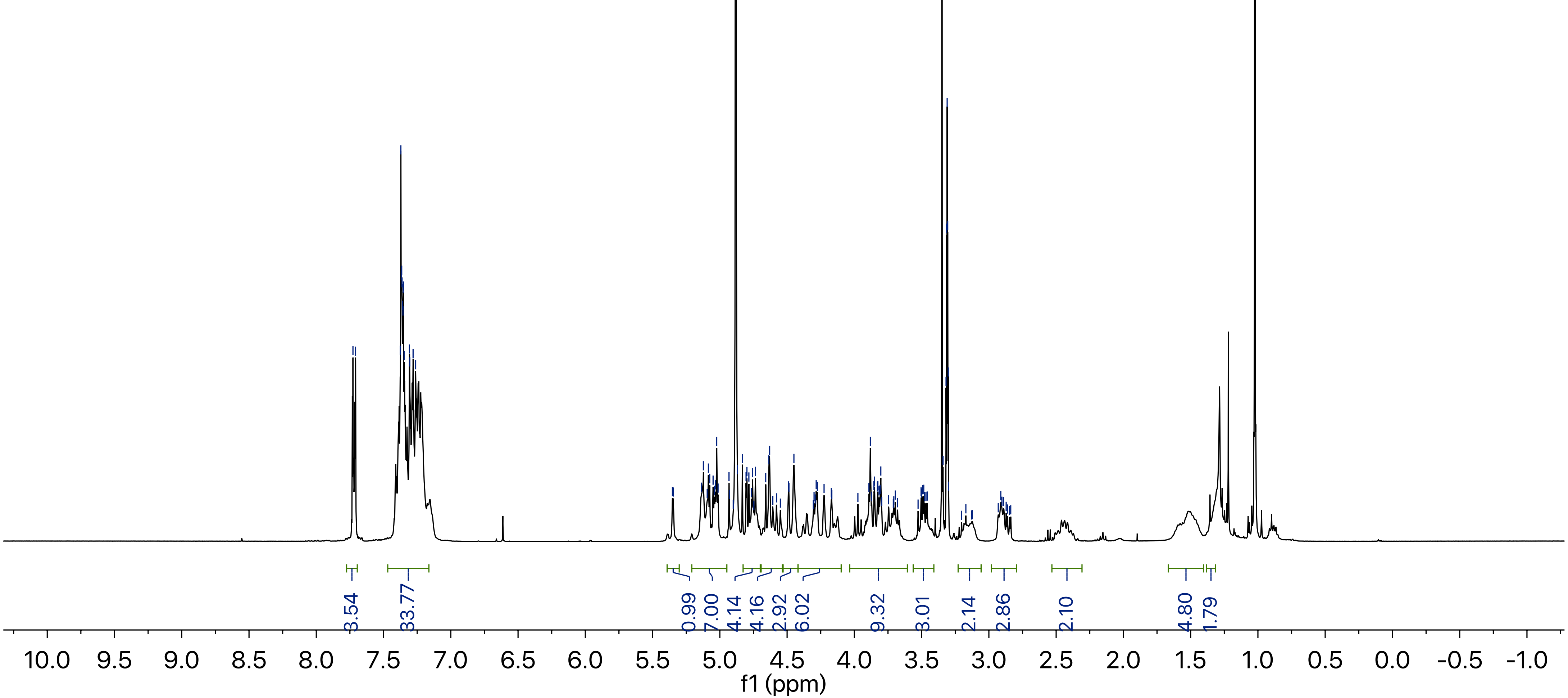
WL-2-275-D-6S-B-6S-A-2S-LiOH-H.2.1.2rr —



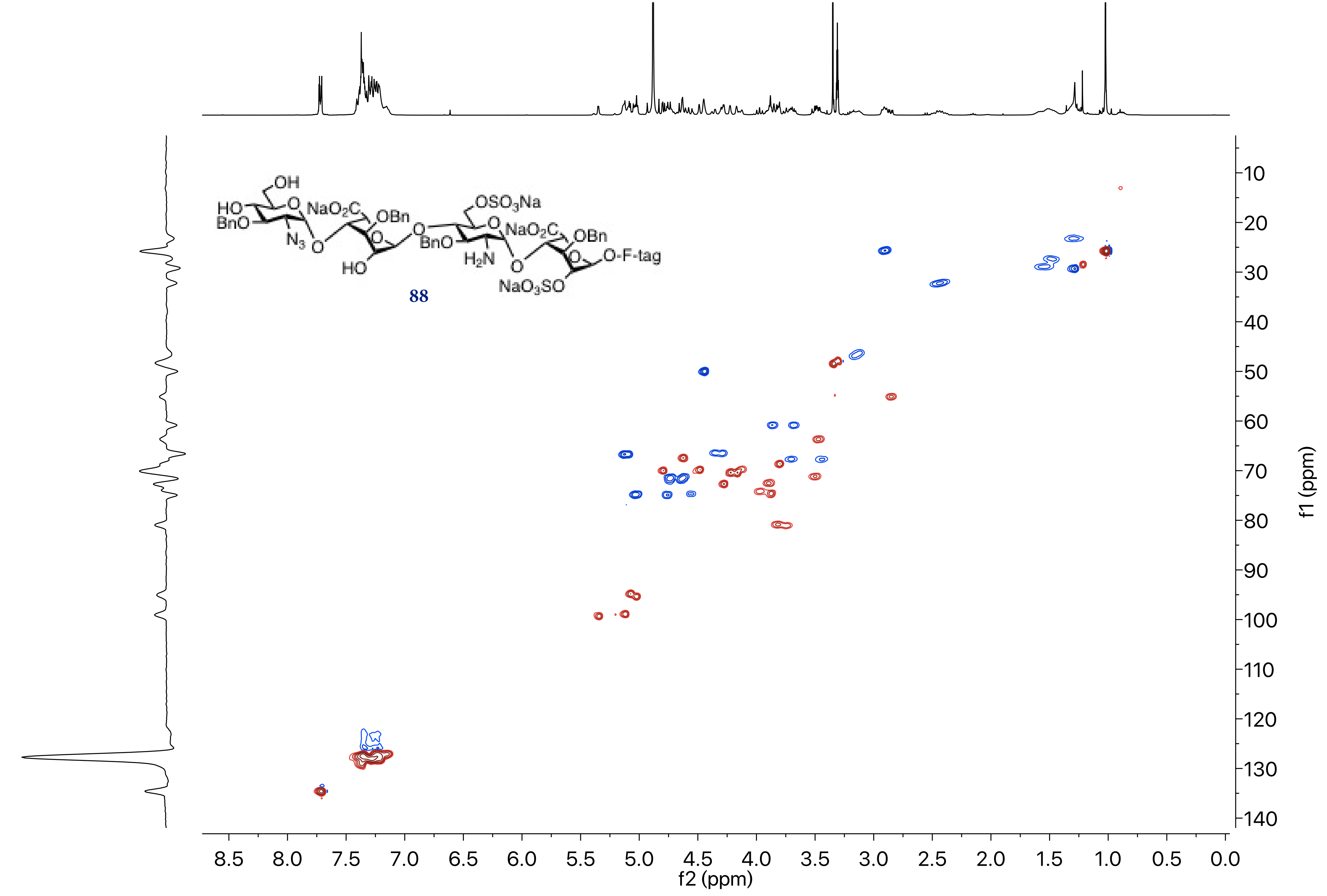
WL-2-276-B-6S-A-2S-LiOH-H.1.1.1r

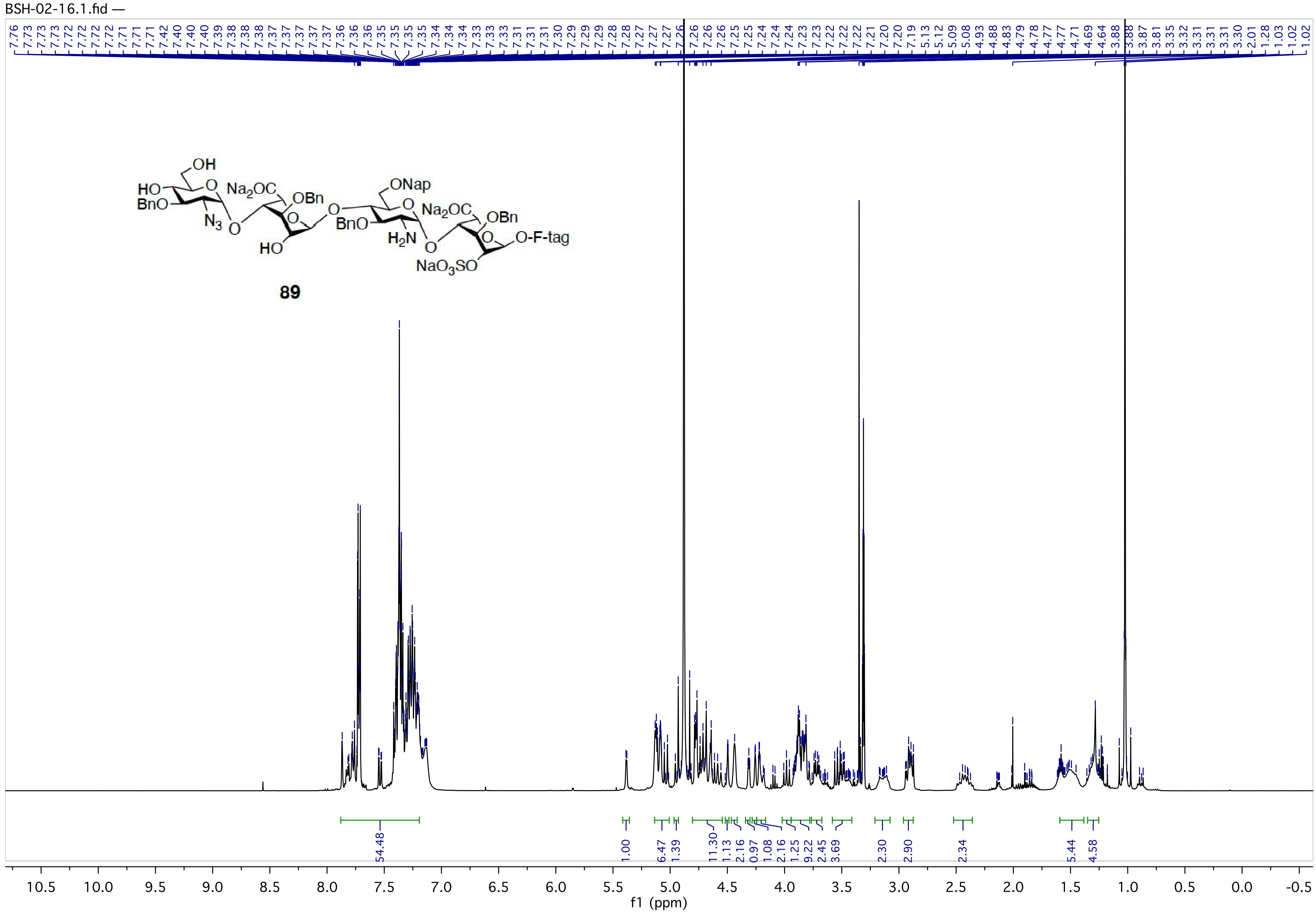


88



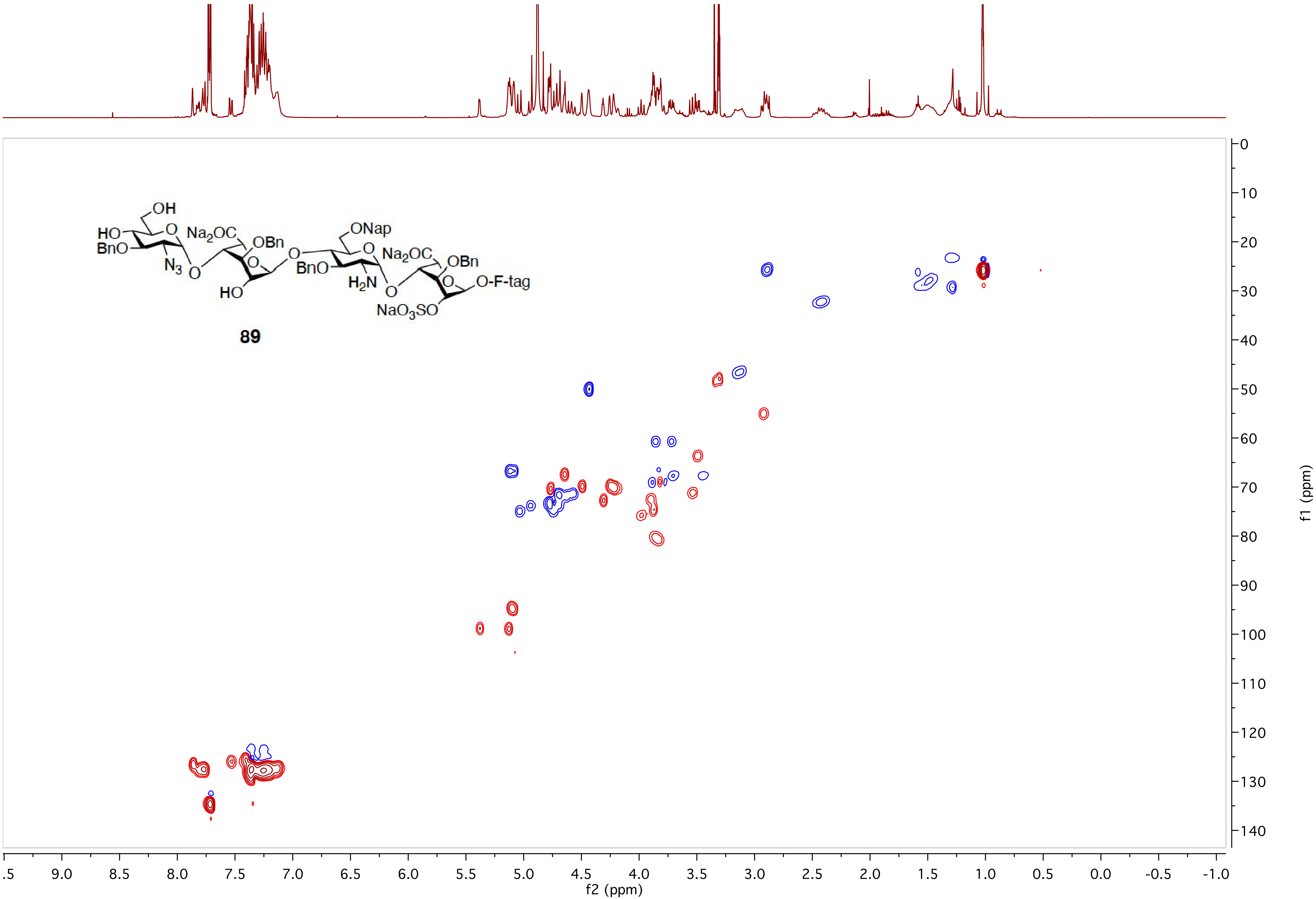
WL-2-276-B-6S-A-2S-LiOH-HSQC.4.1.2rr —





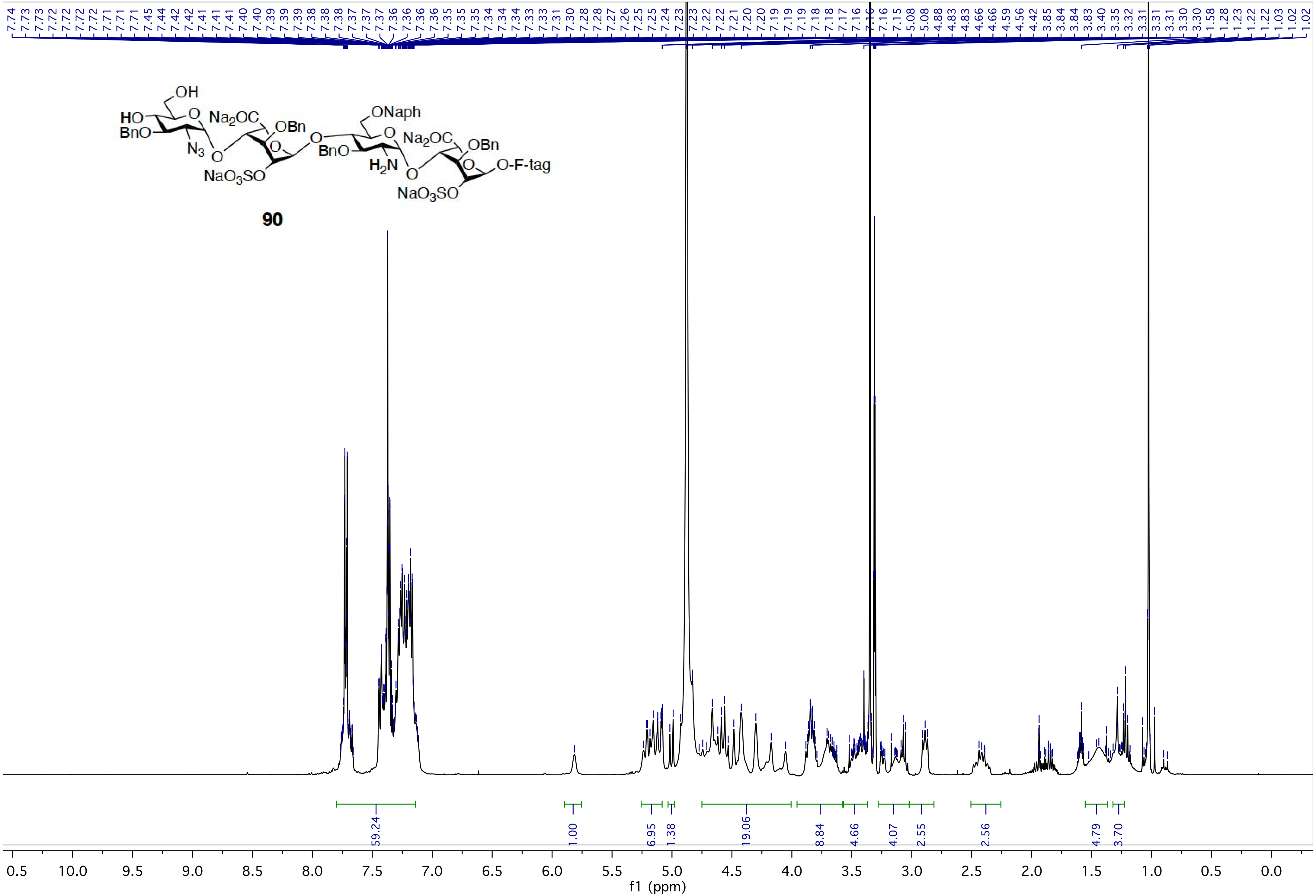
BSH-02-16.1.fid —
7.76 7.73 7.73 7.72 7.72 7.72 7.72 7.71 7.71 7.71 7.42 7.40 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.20 7.20 7.19 5.13 5.12 5.09 5.08 4.93 4.88 4.83 4.79 4.78 4.77 4.77 4.71 4.69 4.64 3.88 3.88 3.87 3.81 3.35 3.32 3.31 3.31 3.31 3.30 2.01 1.28 1.03 1.02 1.02
HO
BnO
OH
O
N3
O
Na2OC
OBn
O
HO
O
ONap
BnO
O
H2N
O
Na2OC
OBn
O
O-F-tag
NaO3SO
89
54.48
1.00
6.47
1.39
11.30
1.13
2.16
0.97
1.08
2.16
1.25
9.22
2.45
3.69
2.30
2.90
2.34
5.44
4.58
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 -0.5
f1 (ppm)

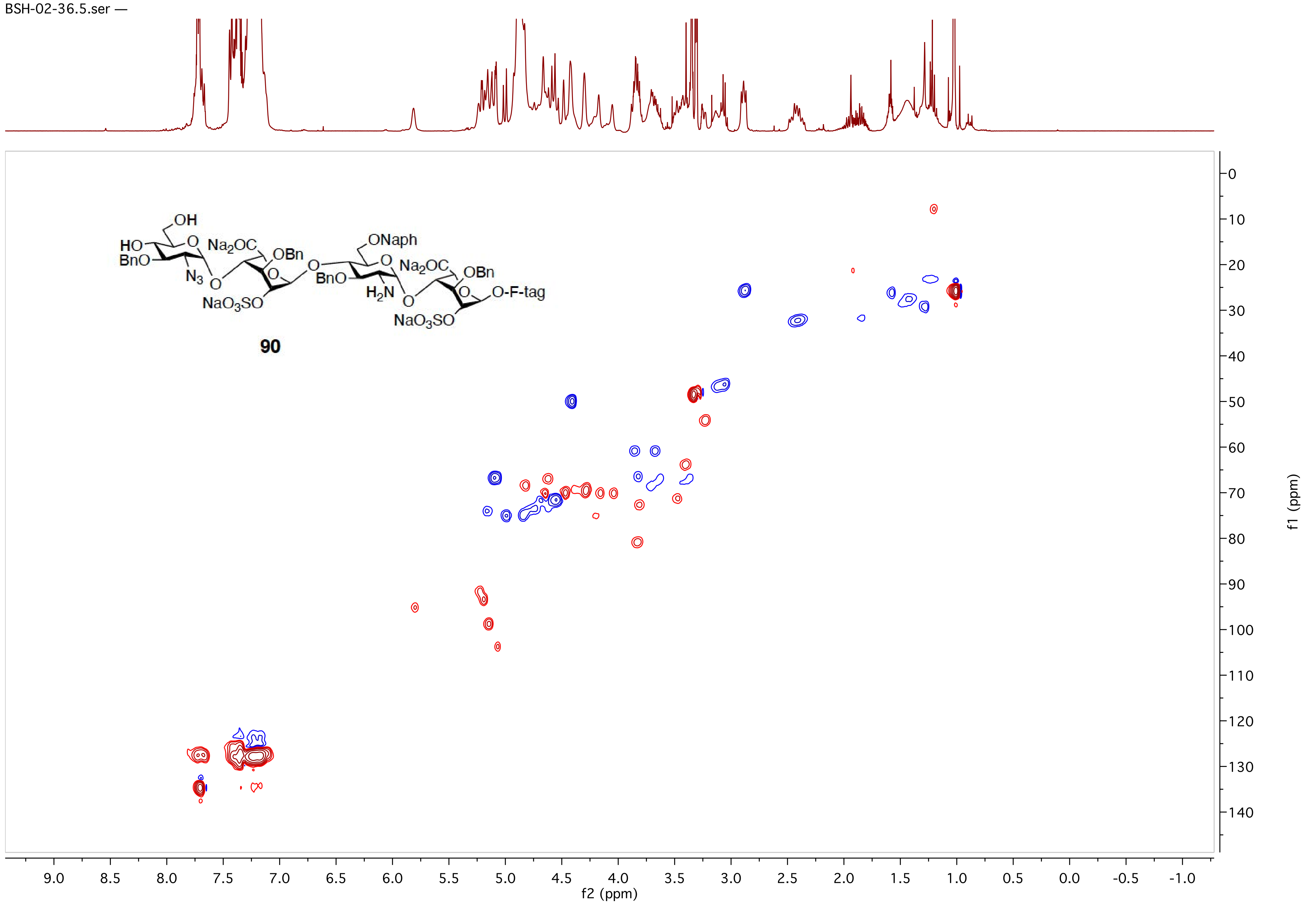
BSH-02-16.4.ser —

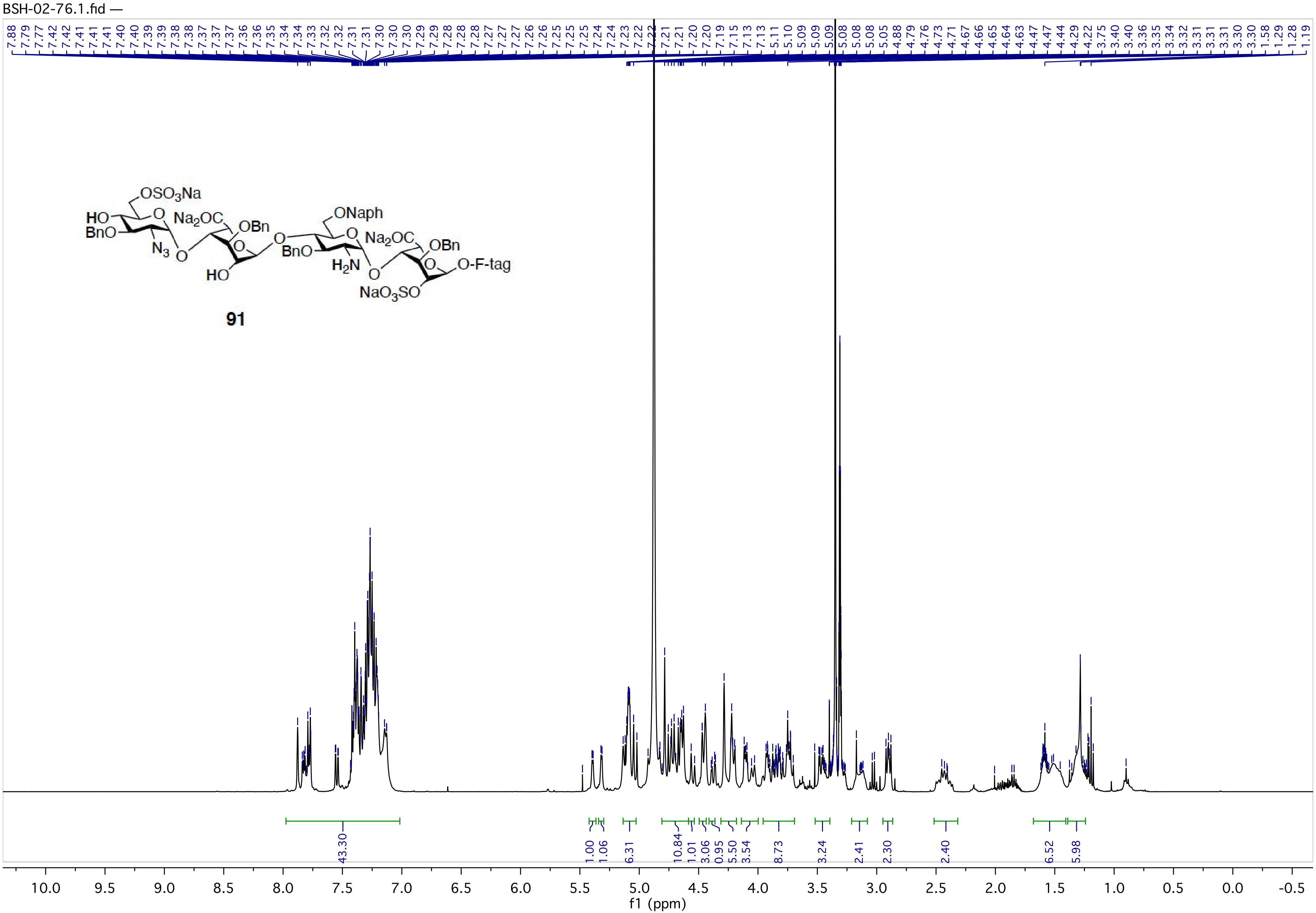


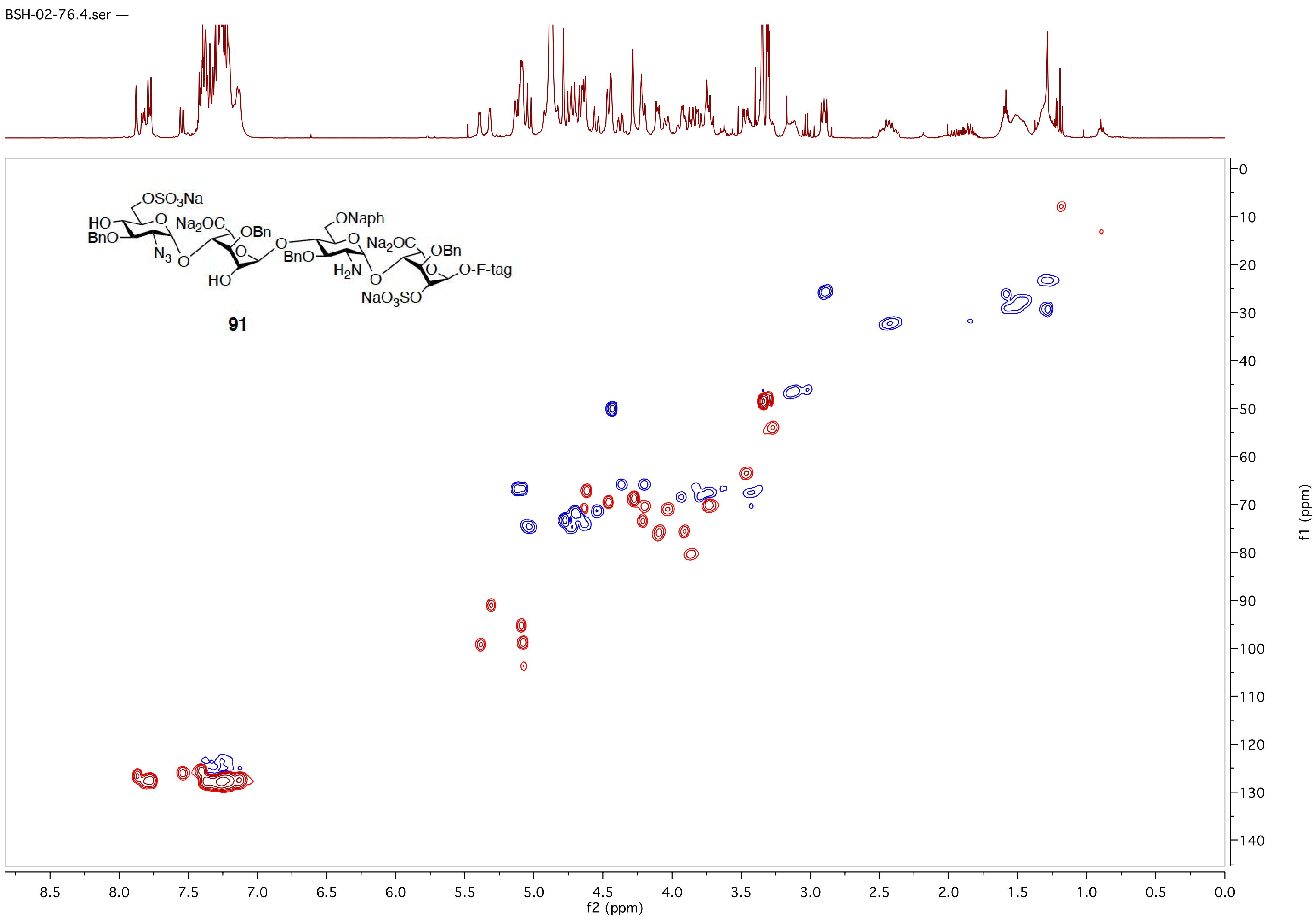
89

BSH-02-36.1.fid —



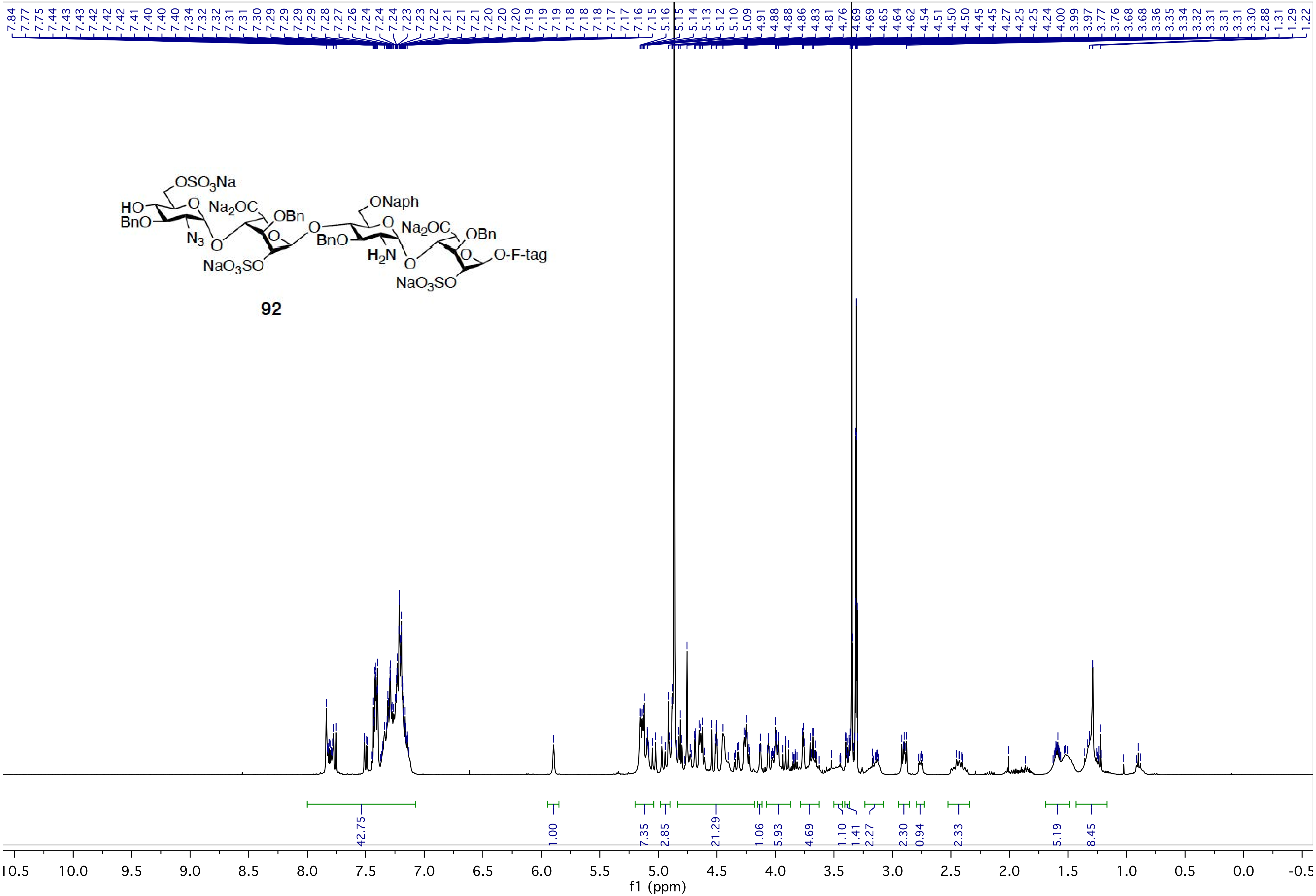

BSH-02-36.5.ser —
HO
BnO
OH
O
N3
O
Na2OC
OBn
O
NaO3SO
O
BnO
ONaph
O
H2N
O
Na2OC
OBn
O
O-F-tag
NaO3SO
90
f2 (ppm)
f1 (ppm)


BSH-02-76.1.fid —
7.88 7.79 7.77 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.15 7.13 7.13 5.11 5.10 5.09 5.09 5.09 5.08 5.08 5.08 5.05 4.88 4.79 4.76 4.73 4.71 4.67 4.66 4.65 4.64 4.63 4.47 4.47 4.44 4.29 4.22 3.75 3.40 3.40 3.36 3.35 3.34 3.32 3.31 3.31 3.31 3.30 3.30 1.58 1.29 1.28 1.19
OSO3Na
HO
BnO
N3
O
Na2OC
OBn
HO
BnO
ONaph
H2N
Na2OC
OBn
O-F-tag
NaO3SO
91
43.30
1.00
1.06
6.31
10.84
1.01
3.06
0.95
5.50
3.54
8.73
3.24
2.41
2.30
2.40
6.52
5.98
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 -0.5
f1 (ppm)

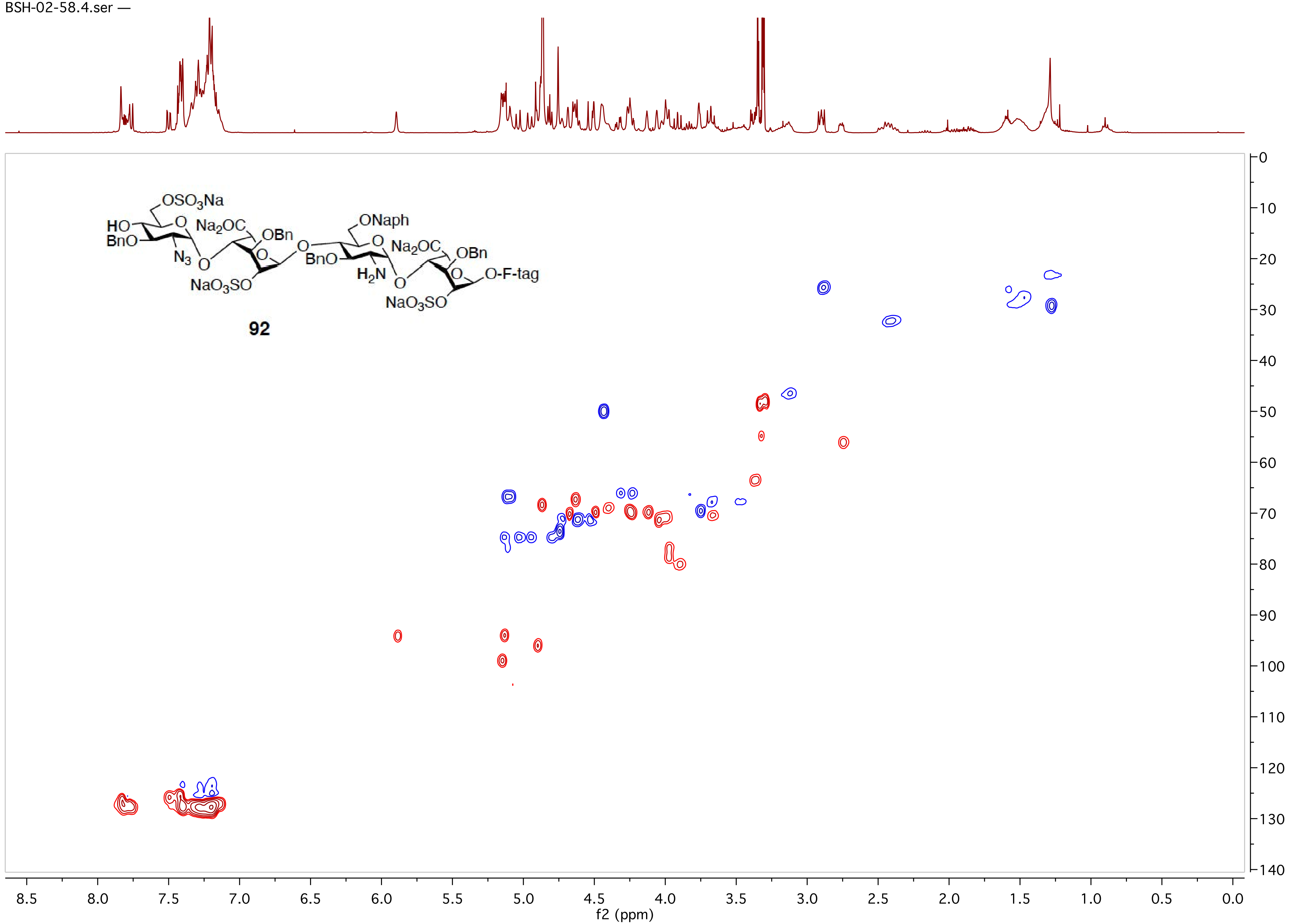


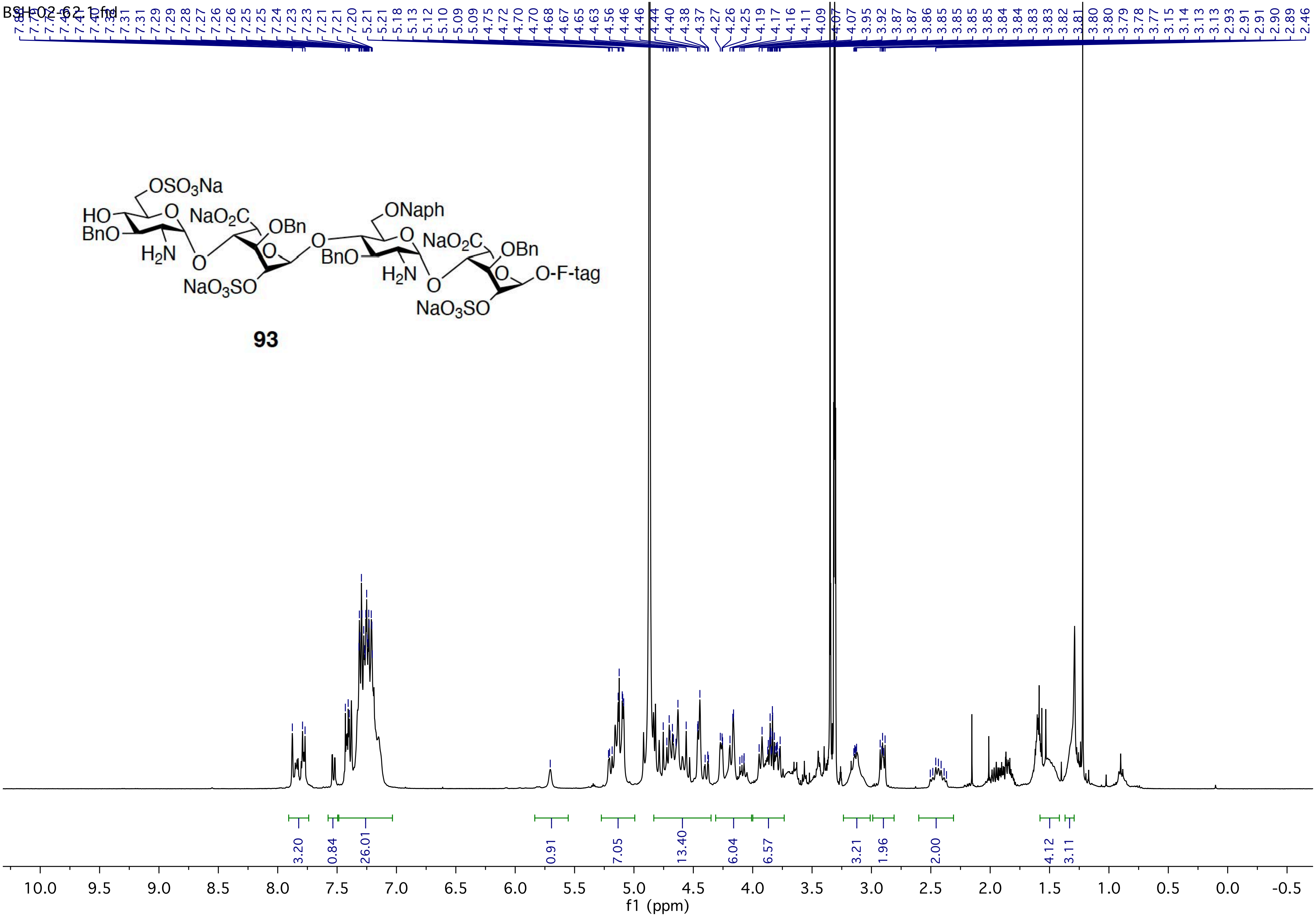
BSH-02-76.4.ser —
OSO3Na
HO
BnO
O
N3
Na2OC
OBn
HO
ONaph
BnO
H2N
Na2OC
OBn
O-F-tag
NaO3SO
91
f2 (ppm)
f1 (ppm)

BSH-02-58.1.fid —

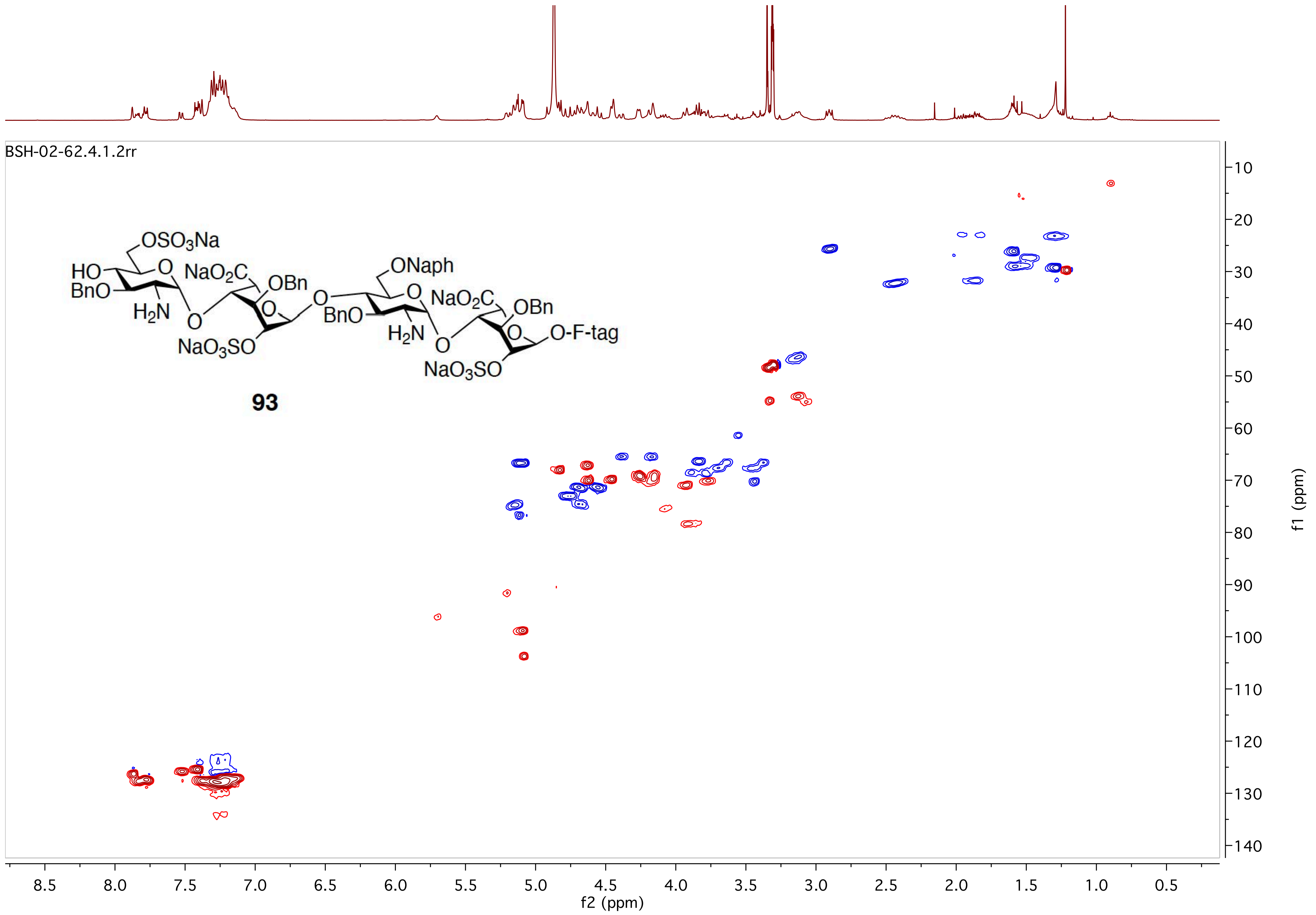


BSH-02-58.4.ser —

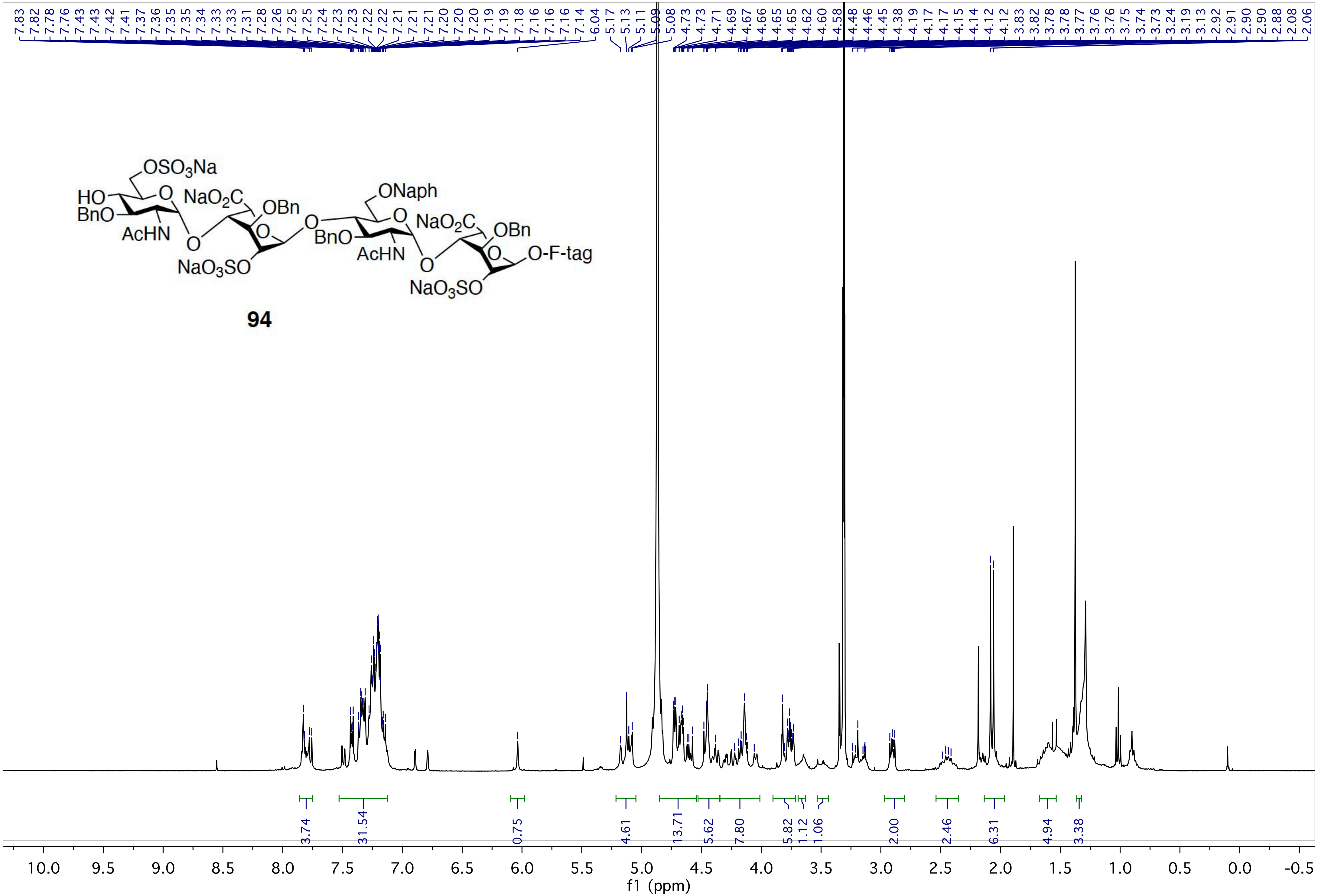



BSH-02-62_1.fid
OSO3Na
HO
BnO
H2N
NaO2C
OBn
NaO3SO
ONaph
BnO
H2N
NaO2C
OBn
O-F-tag
NaO3SO
3.20
0.84
26.01
0.91
7.05
13.40
6.04
6.57
3.21
1.96
2.00
4.12
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

93

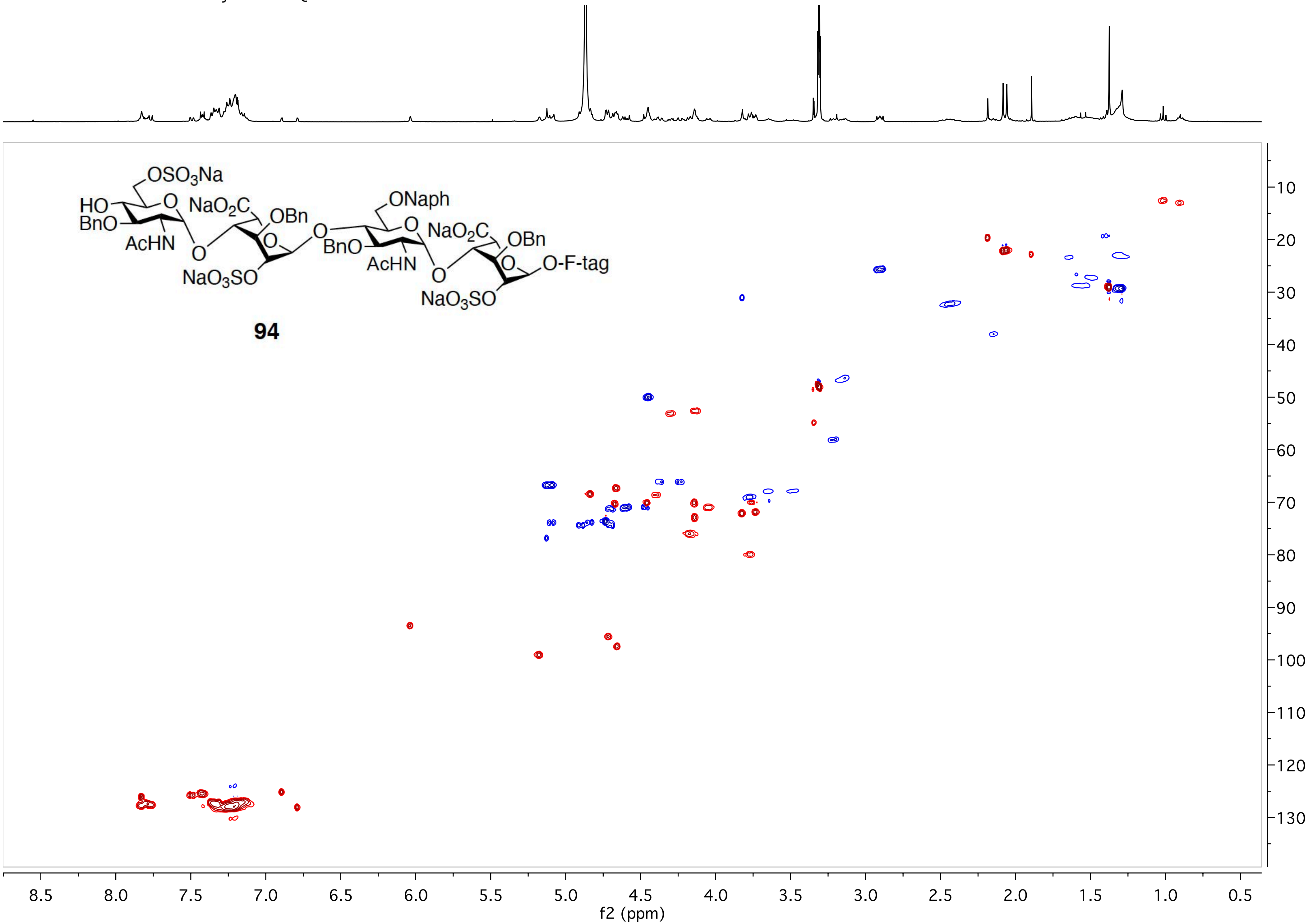

BSH-02-62.4.1.2rr
OSO3Na
HO
BnO
O
H2N
O
NaO2C
OBn
O
NaO3SO
O
BnO
ONaph
O
H2N
O
NaO2C
OBn
O
O-F-tag
NaO3SO
93
f1 (ppm)
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

WL-2-D6S-C2S-A2S-Di-N-acetylation-H.4.1.1r —



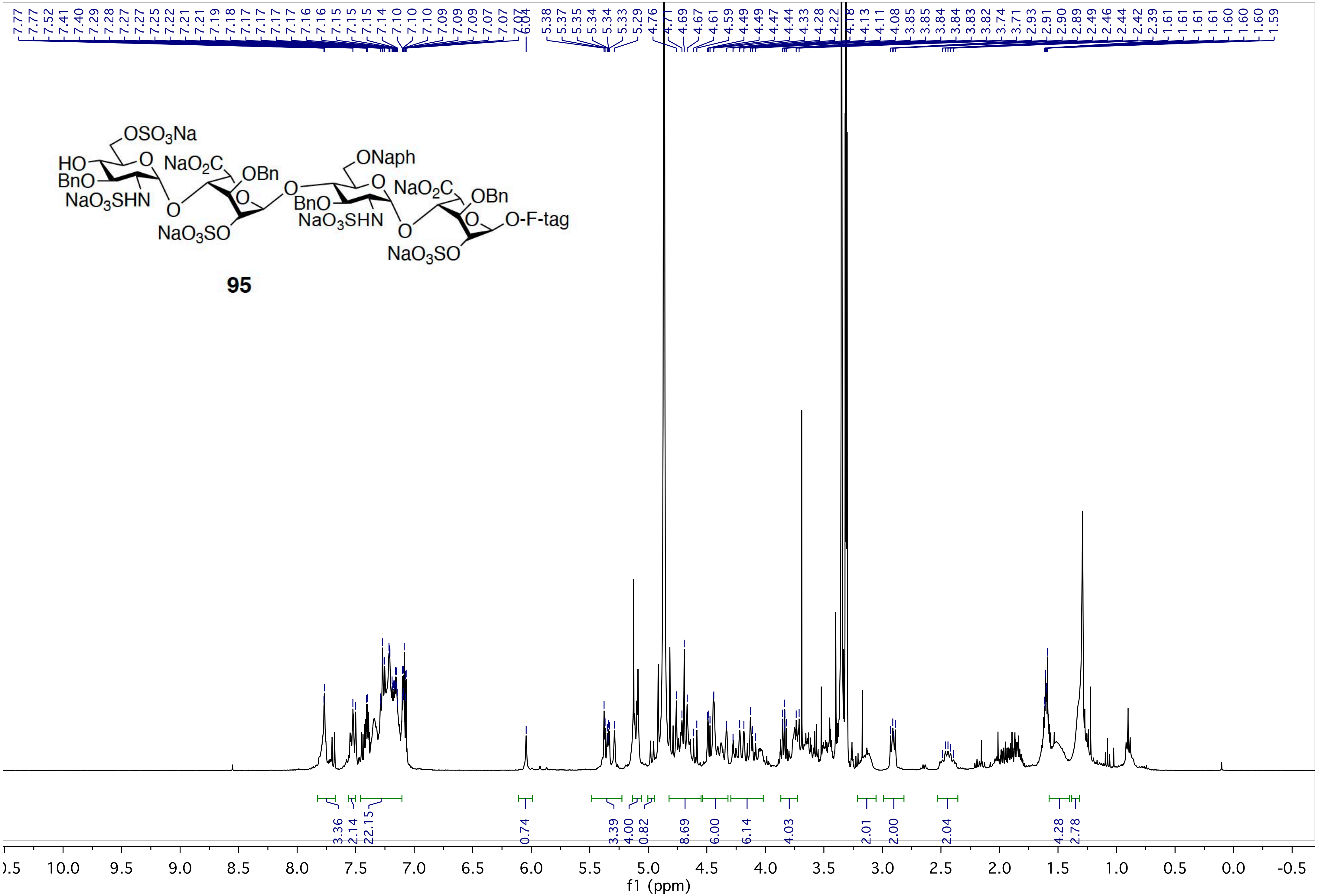
94

WL-2-D6S-C2S-A2S-Di-N-acetylation-HSQC.5.1.2rr —

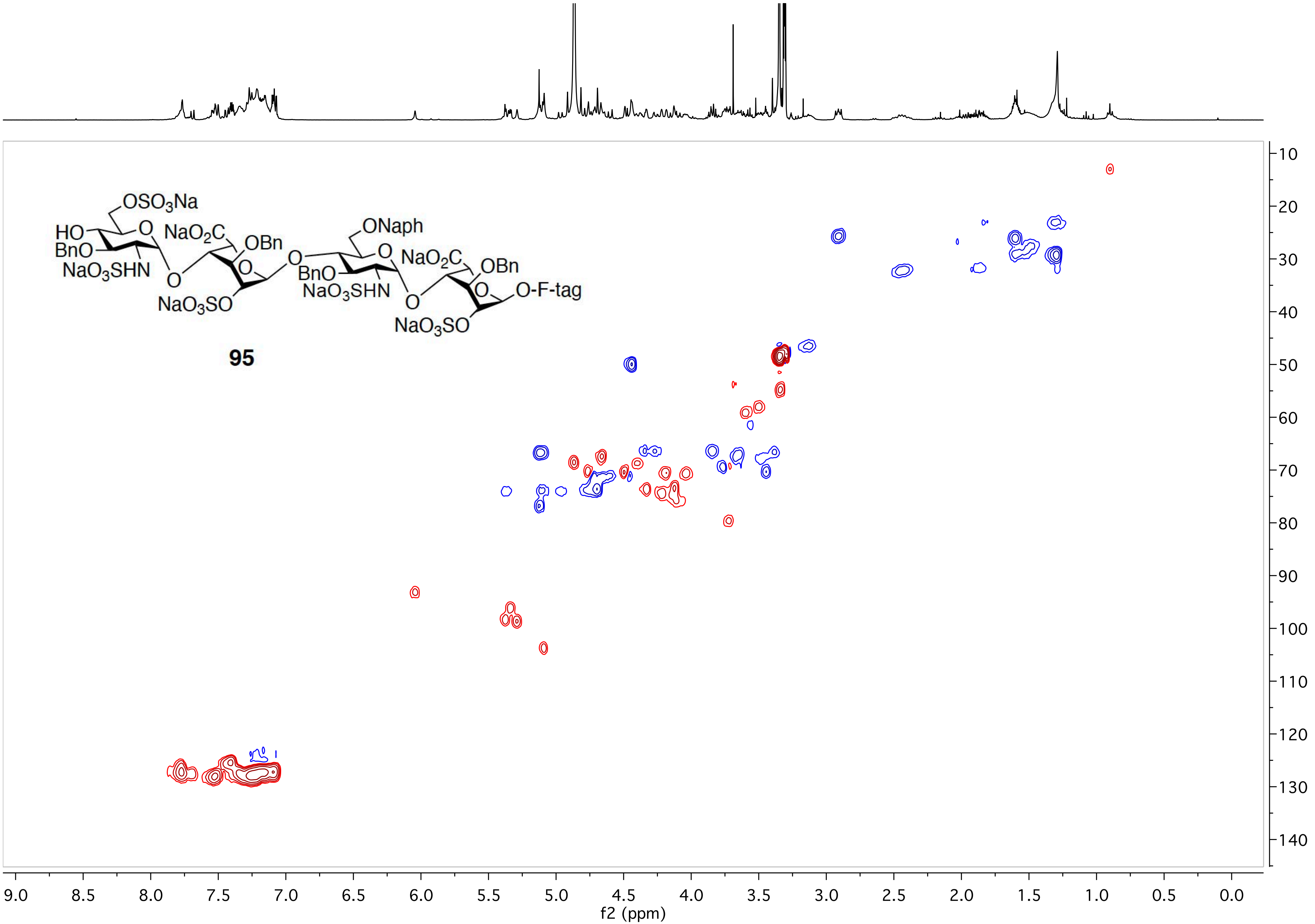


94

BSH-02-66.1.fid —

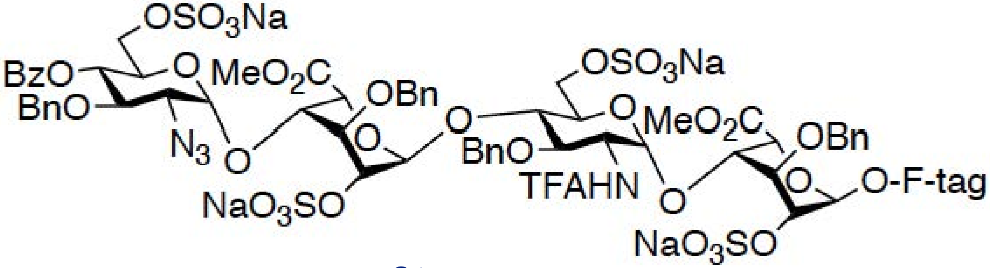


BSH-02-66.4.ser —

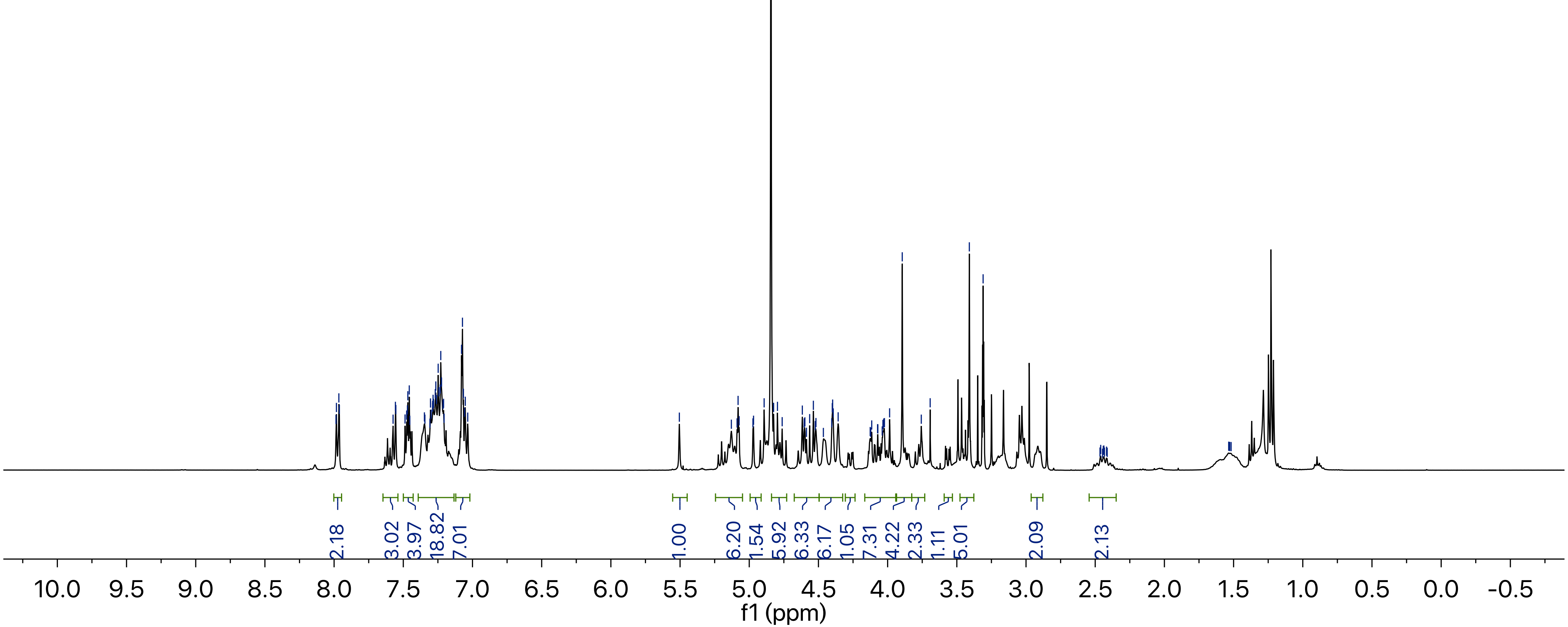


95

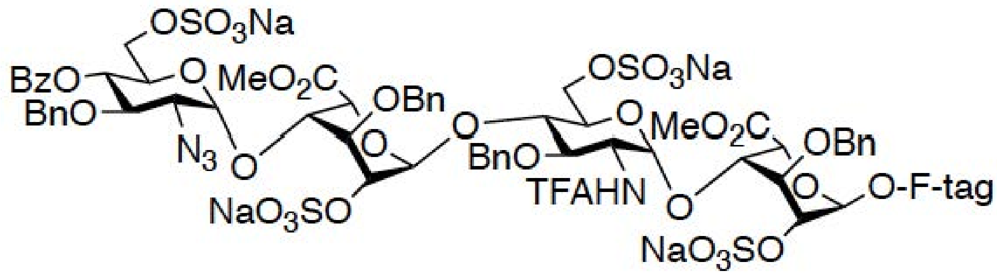
WL-2-299-D6-C2-B6-A2-Tetra-O-Sulfation-H.1.1.1r —



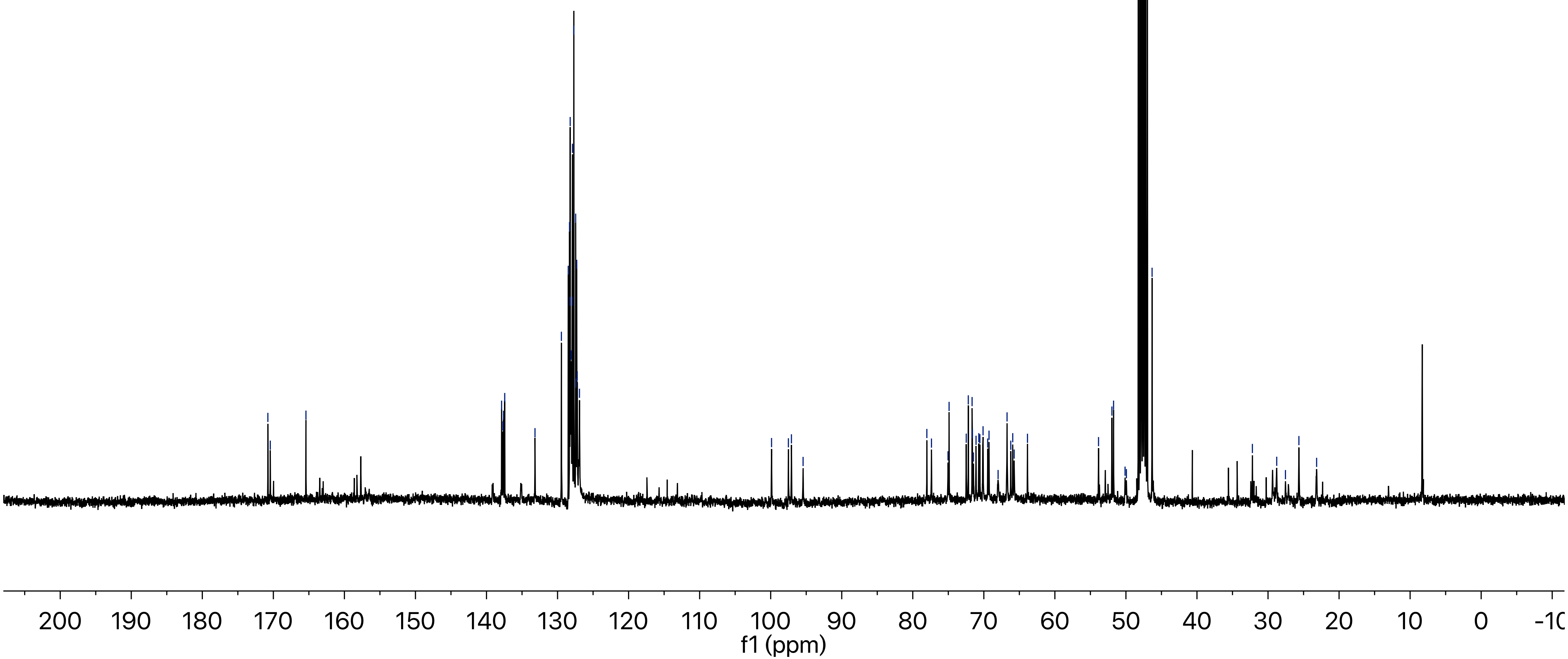
S1



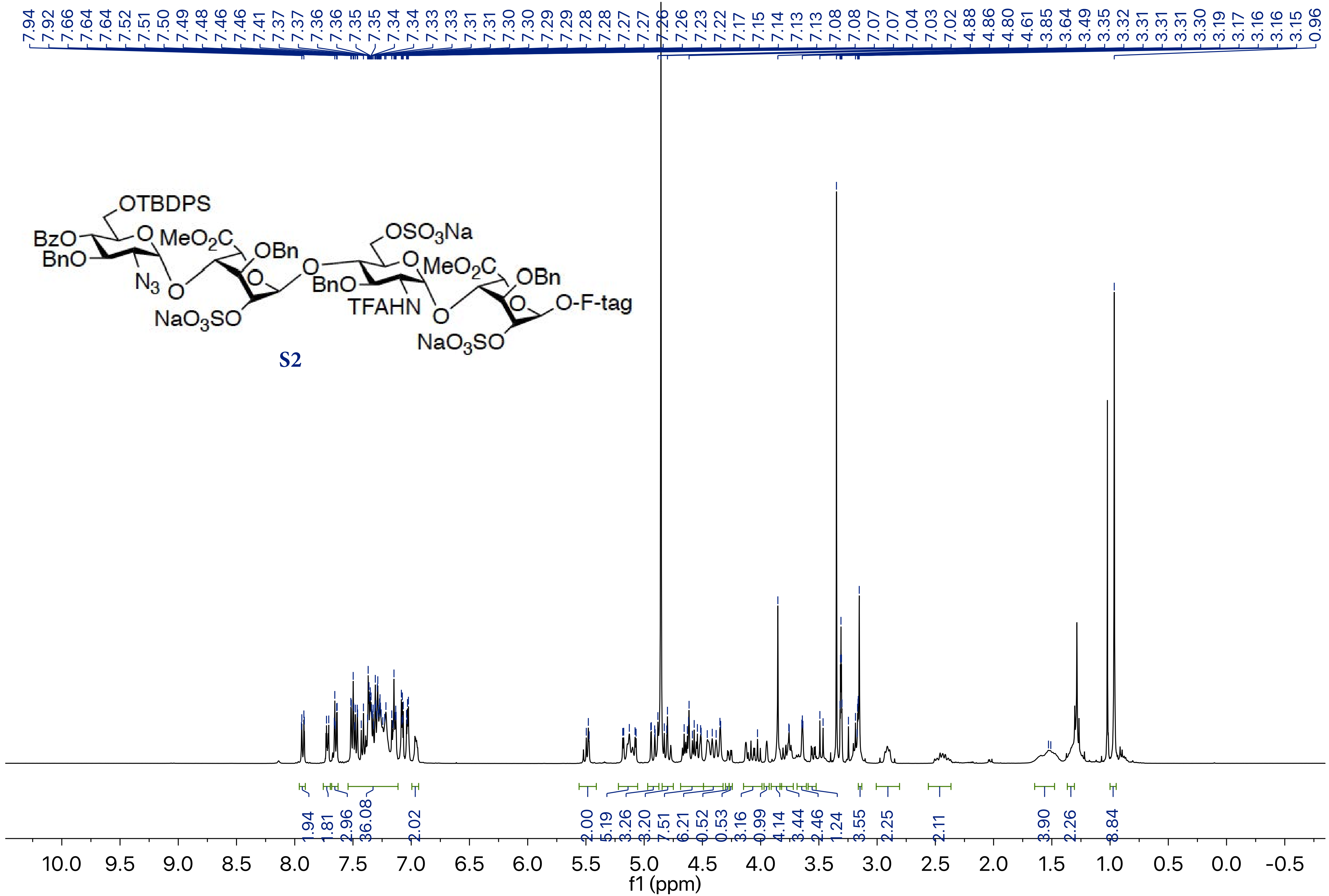
WL-2-299-D6-C2-B6-A2-Tetra-O-Sulfation-H.3.1.1r —



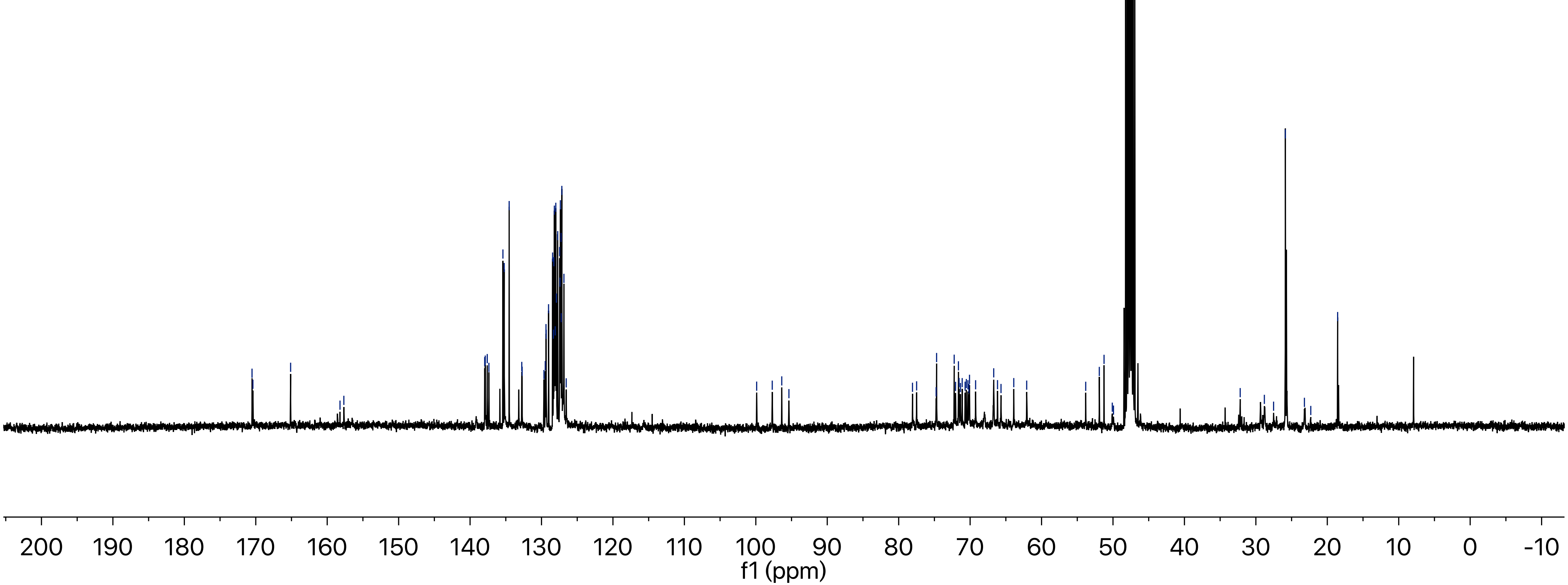
S1

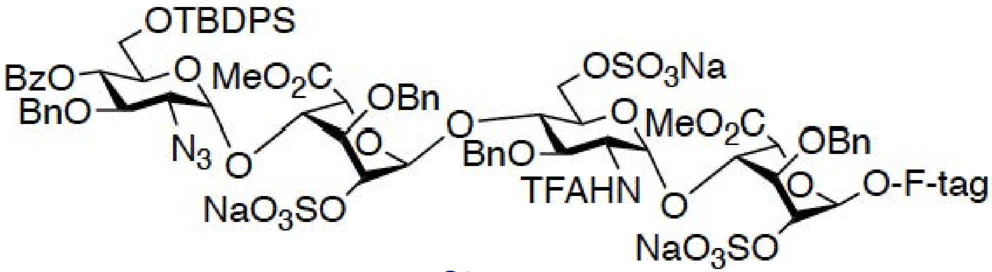


WL-2-296-C2-B6-A2-tri-O-sulfation-H.6.1.1r



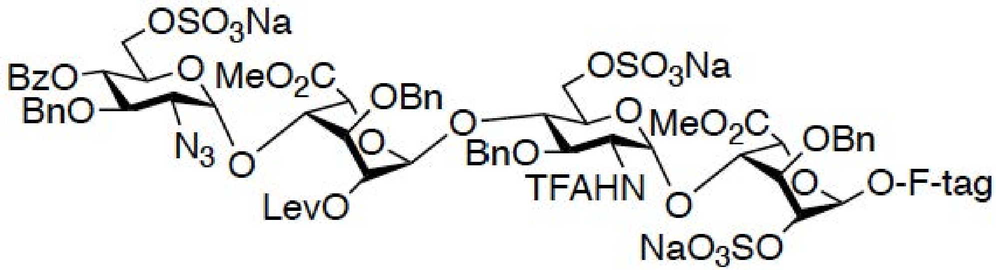
WL-2-296-C2-B6-A2-tri-O-sulfation-C.2.1.1r —



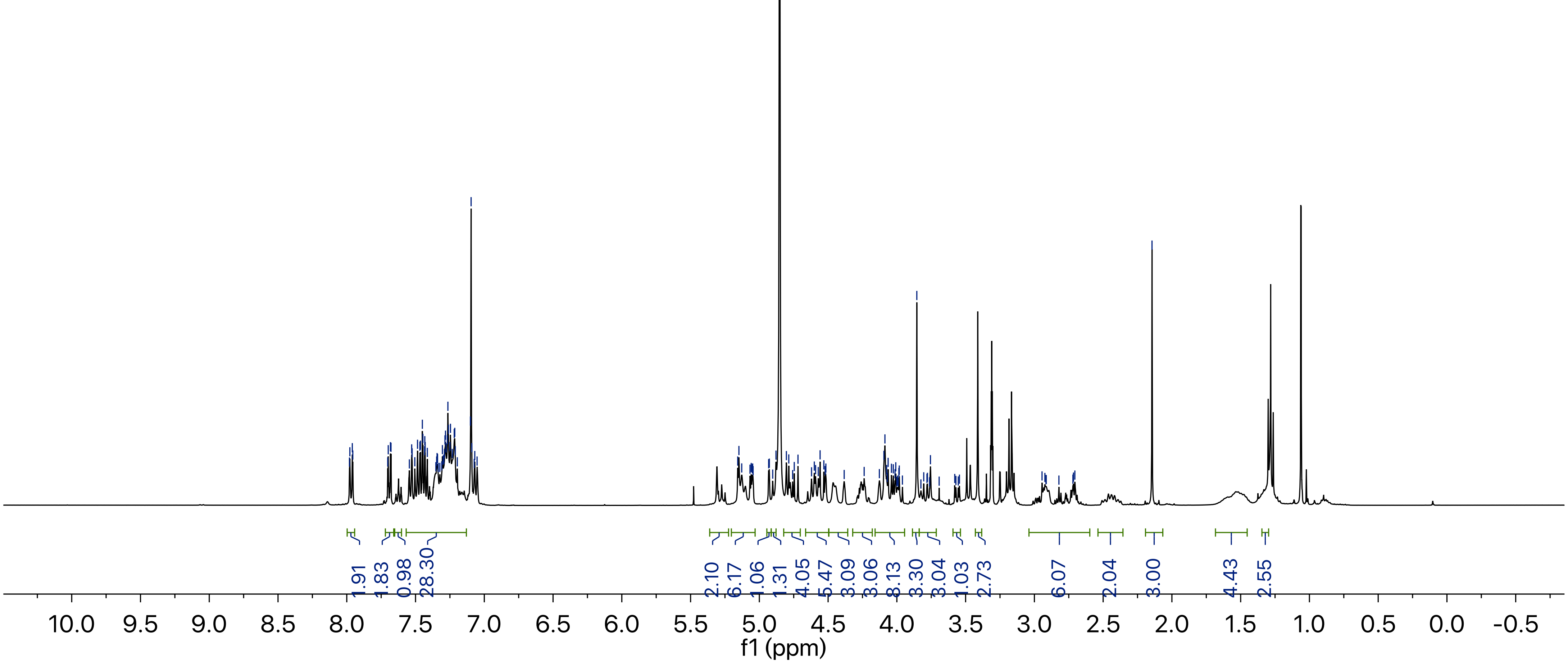


S2

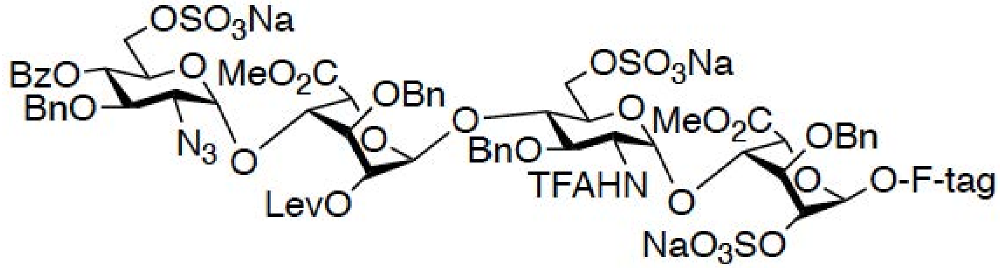
WL-2-273-D6-B6-A2-tri-O-sulfation-H.6.1.1r —



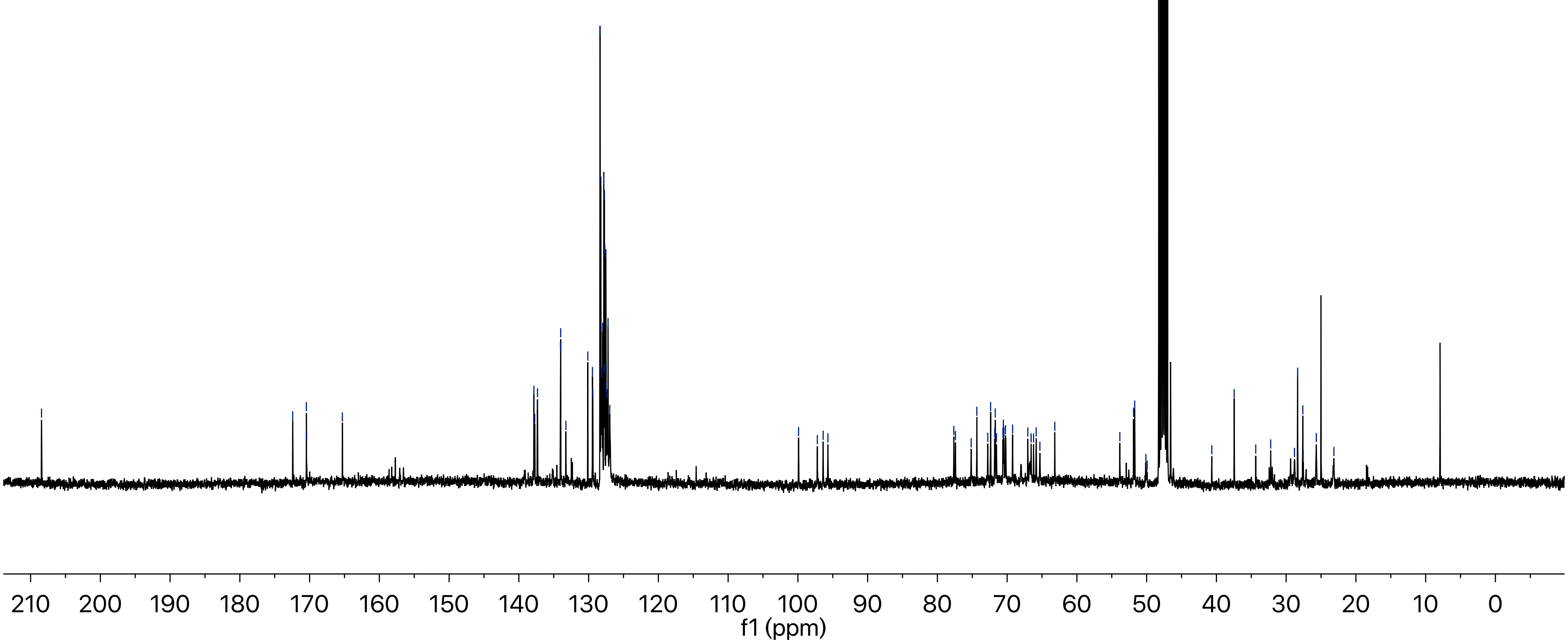
S3



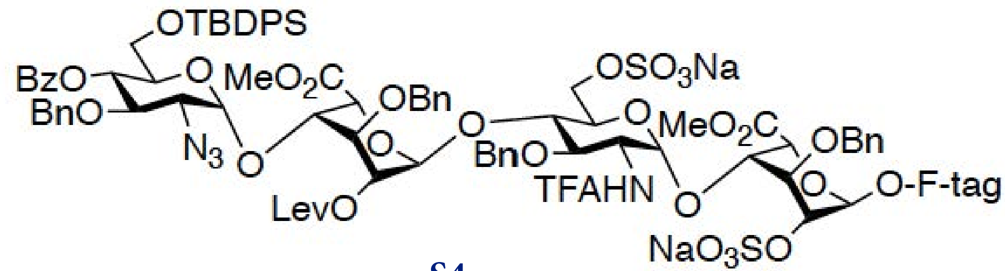
WL-2-273-D6-B6-A2-tri-O-sulfation-C.1.1.1r —



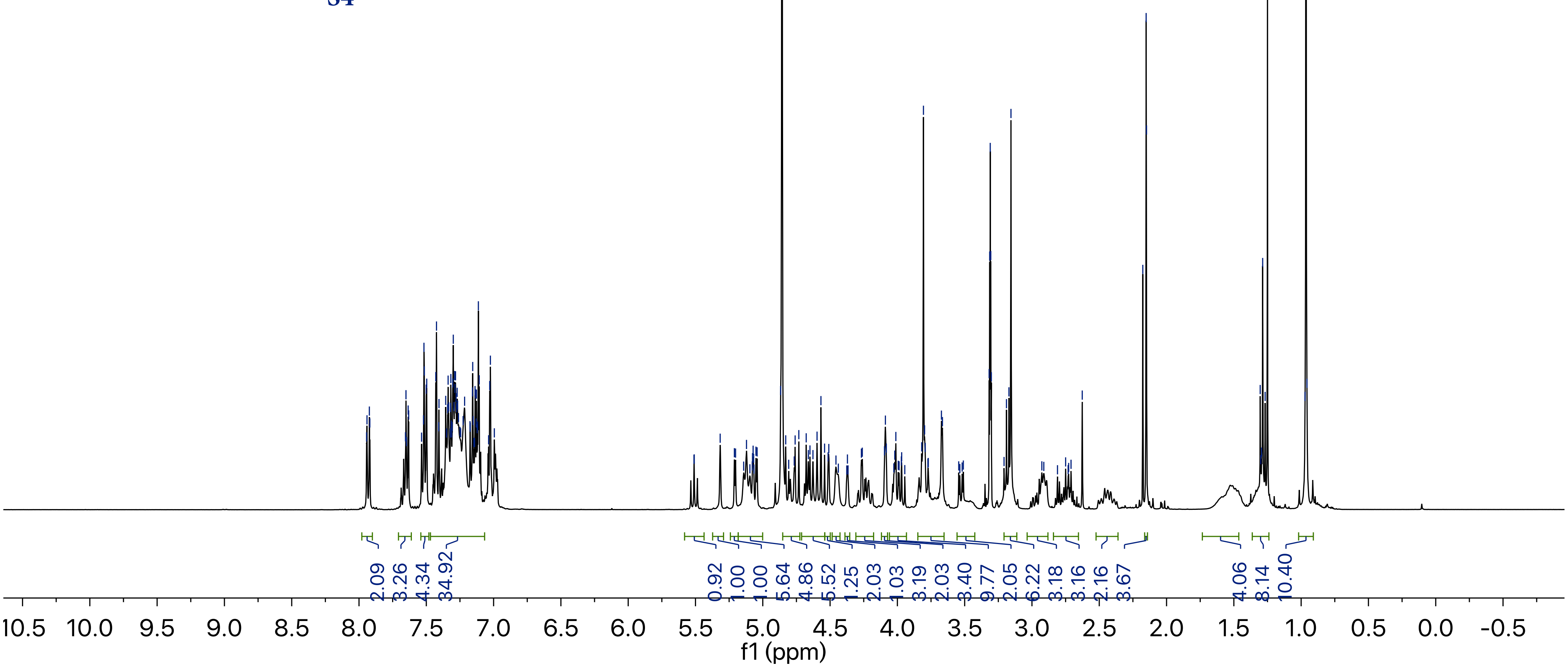
S3



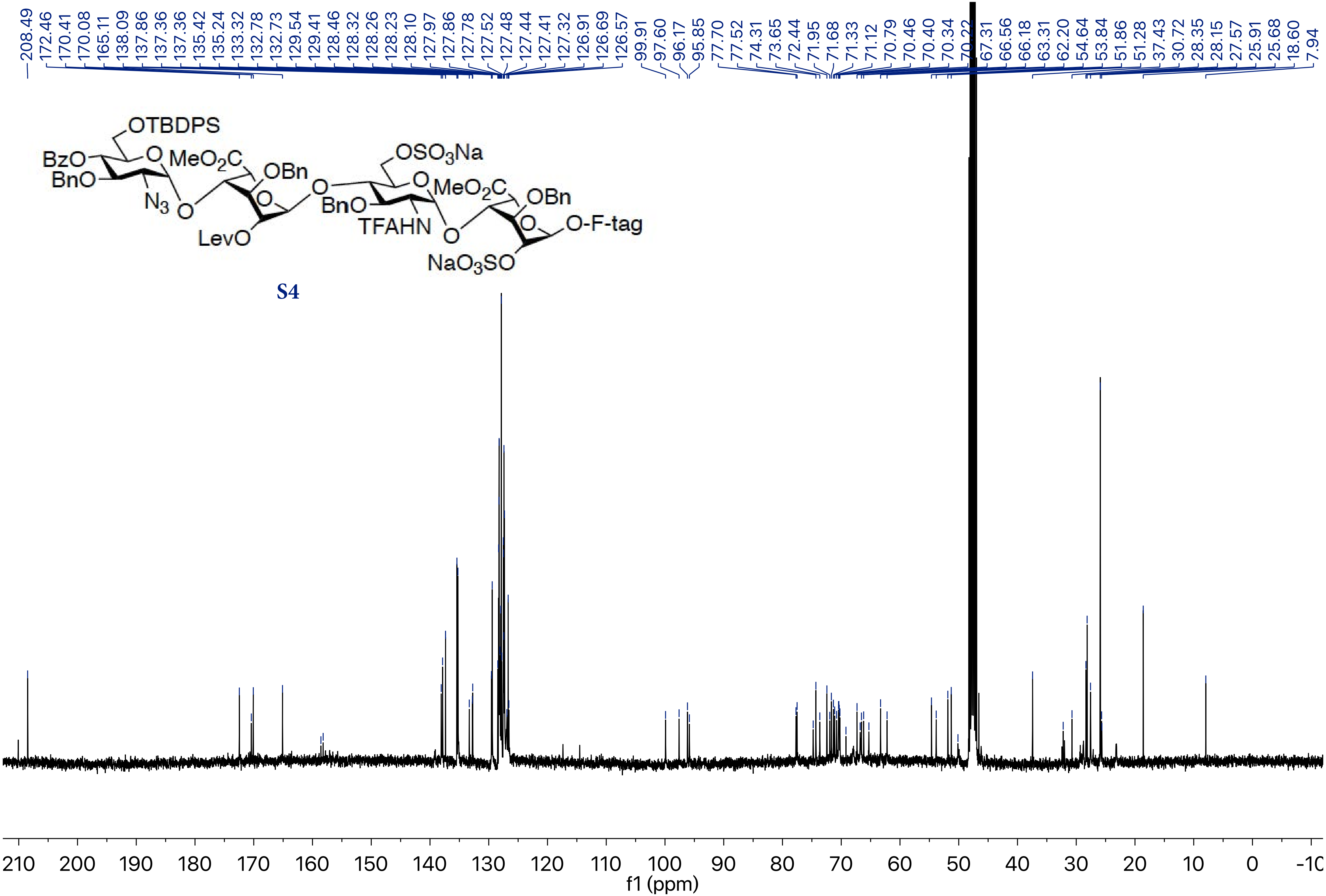
WL-2-271-B6-A2-Di-sulfation-H.6.fid —



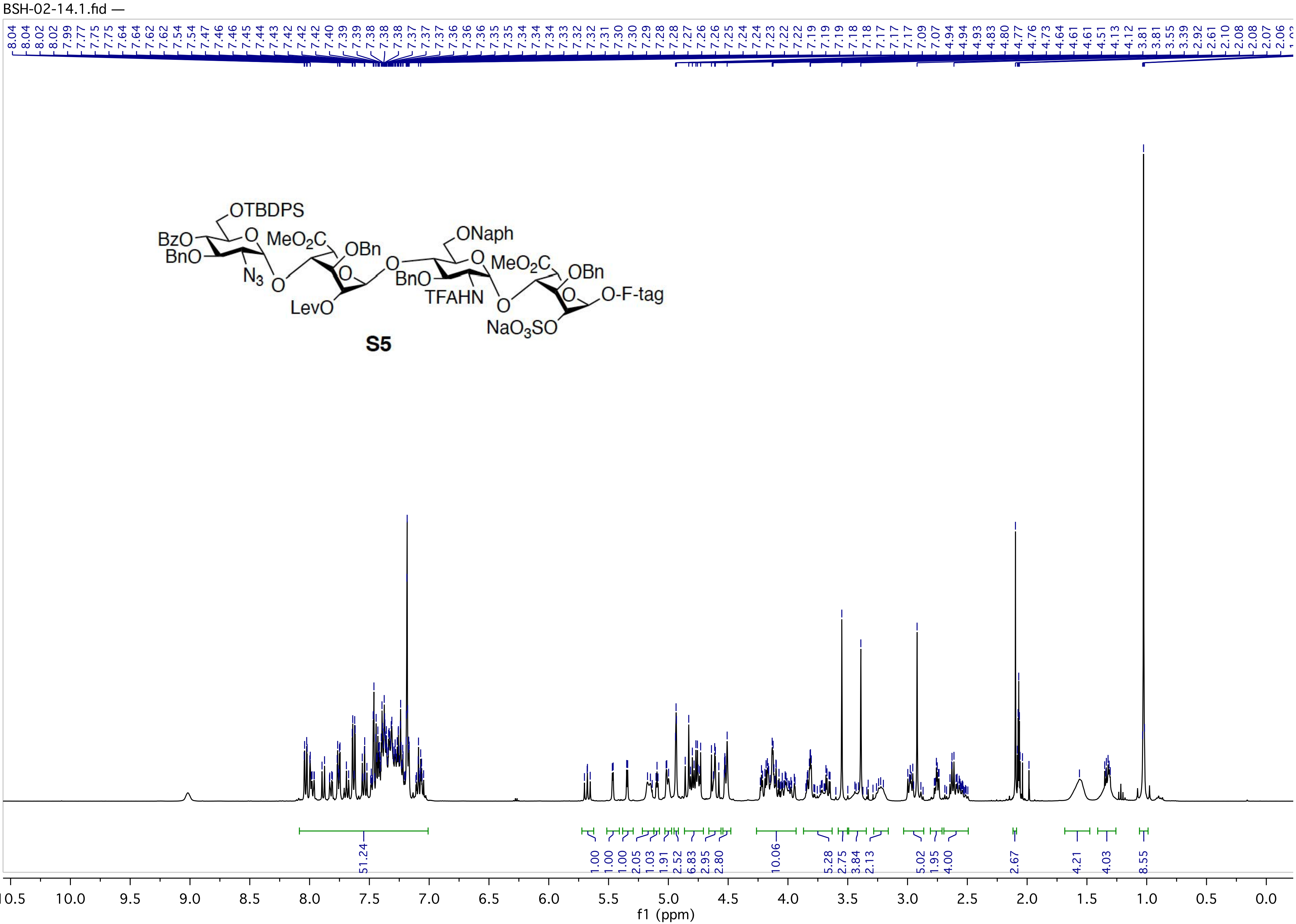
S4



WL-2-271-B6-A2-Di-sulfation-C.1.1.1r

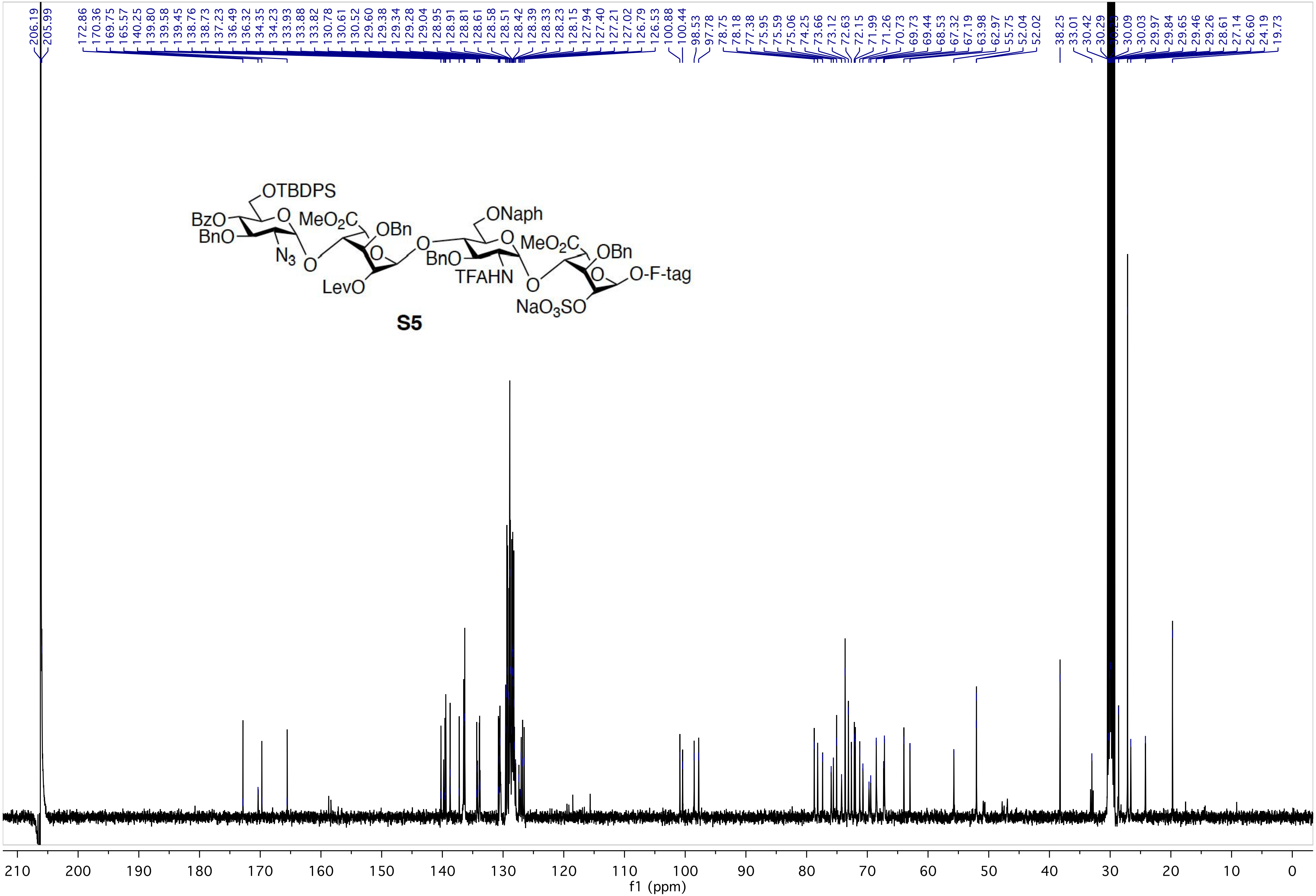


S4

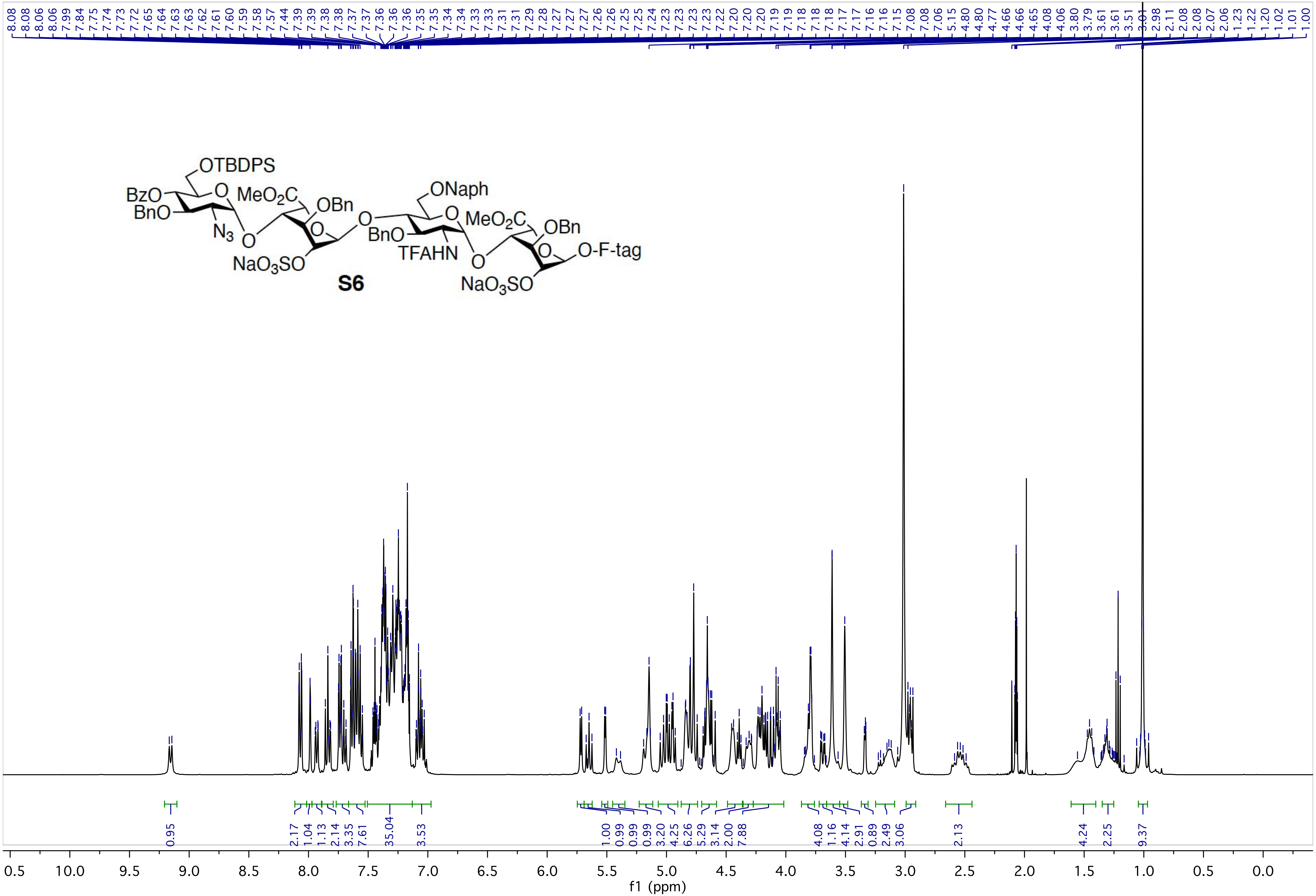

BSH-02-14.1.fid —
8.04 8.04 8.02 8.02 7.99 7.77 7.75 7.75 7.64 7.64 7.62 7.62 7.54 7.54 7.47 7.46 7.46 7.45 7.44 7.43 7.42 7.42 7.42 7.40 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.09 7.07 4.94 4.94 4.93 4.83 4.80 4.77 4.76 4.73 4.64 4.61 4.61 4.51 4.13 4.12 3.81 3.81 3.55 3.39 2.92 2.61 2.10 2.08 2.08 2.07 2.06
OTBDPS
BzO
BnO
O
N3
MeO2C
OBn
O
LevO
O
ONaph
BnO
O
TFAHN
MeO2C
OBn
O
O-F-tag
NaO3SO
S5
51.24
1.00
1.00
1.00
2.05
1.03
1.91
2.52
6.83
2.95
2.80
10.06
5.28
2.75
3.84
2.13
5.02
1.95
4.00
2.67
4.21
4.03
8.55
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)

BSH-02-14.2.fid —

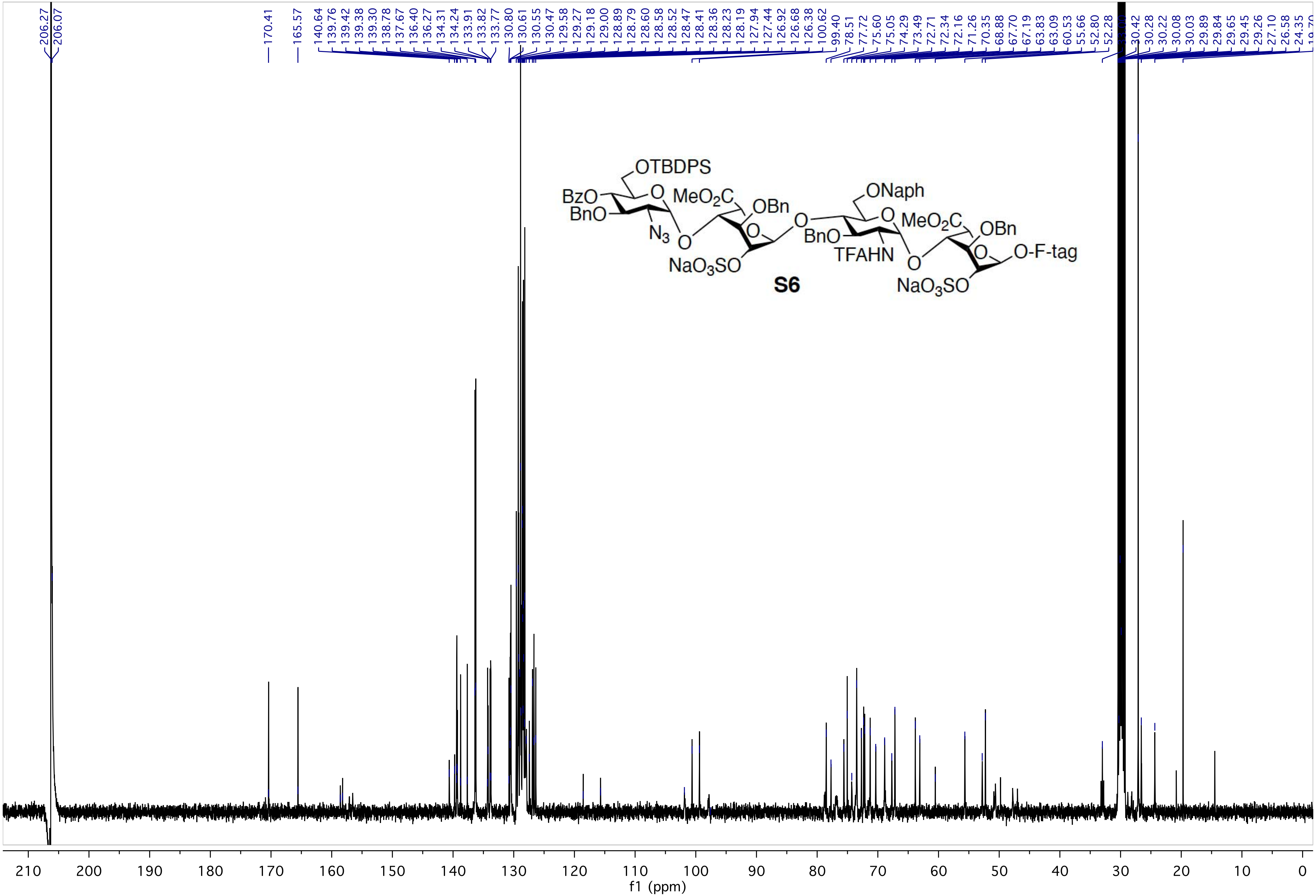
S5



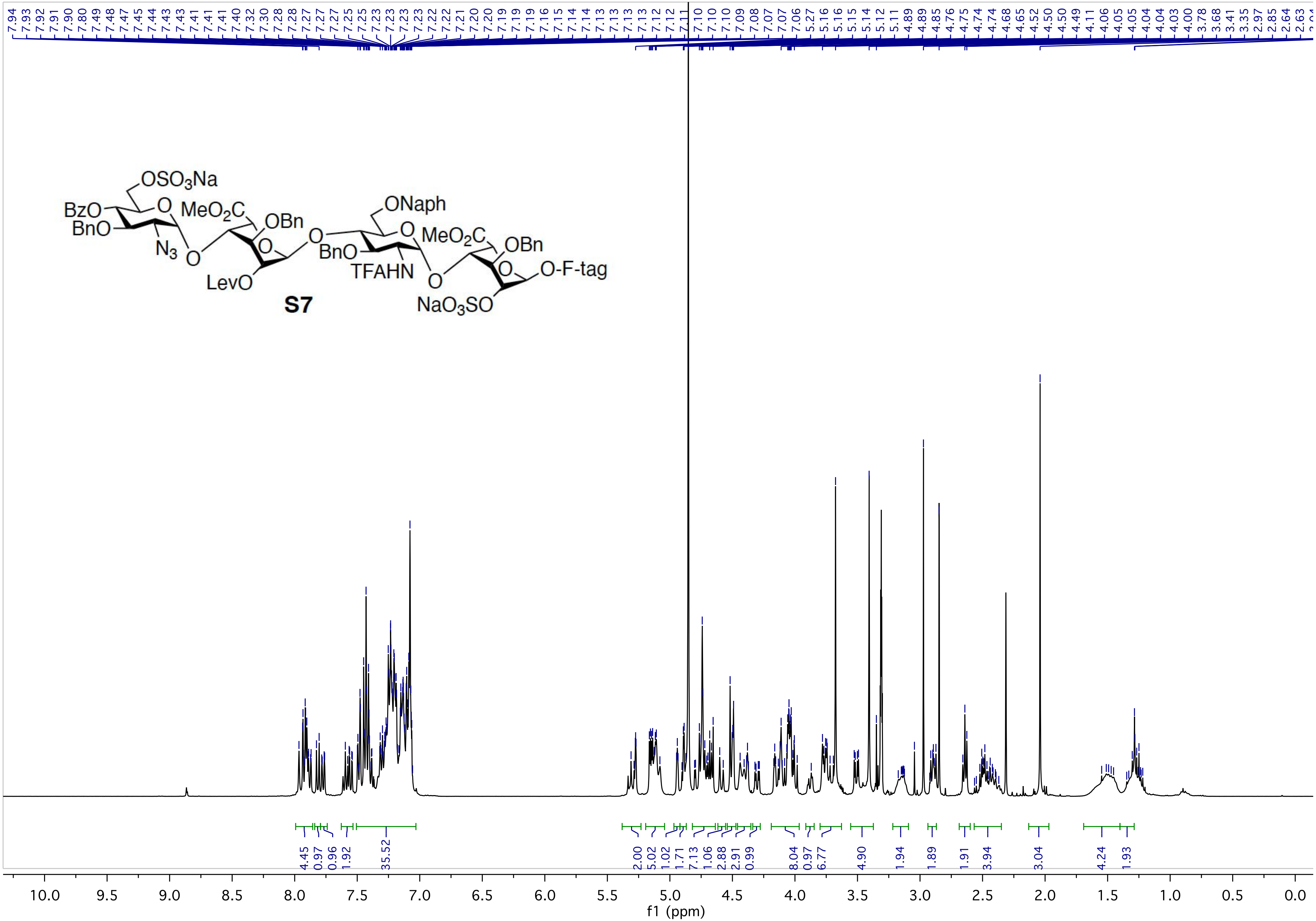
BSH-02-34.1.fid —



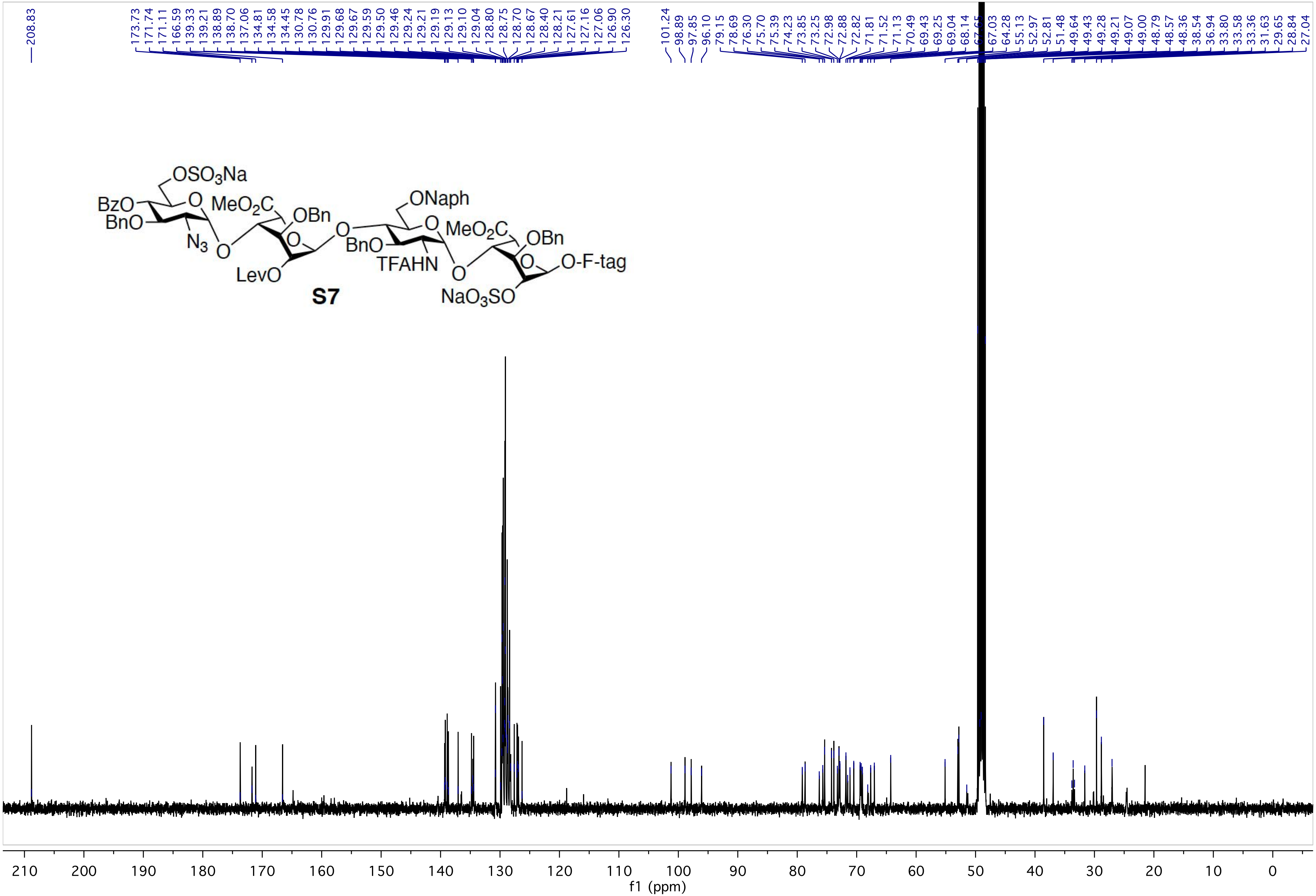
BSH-02-34.2.fid —



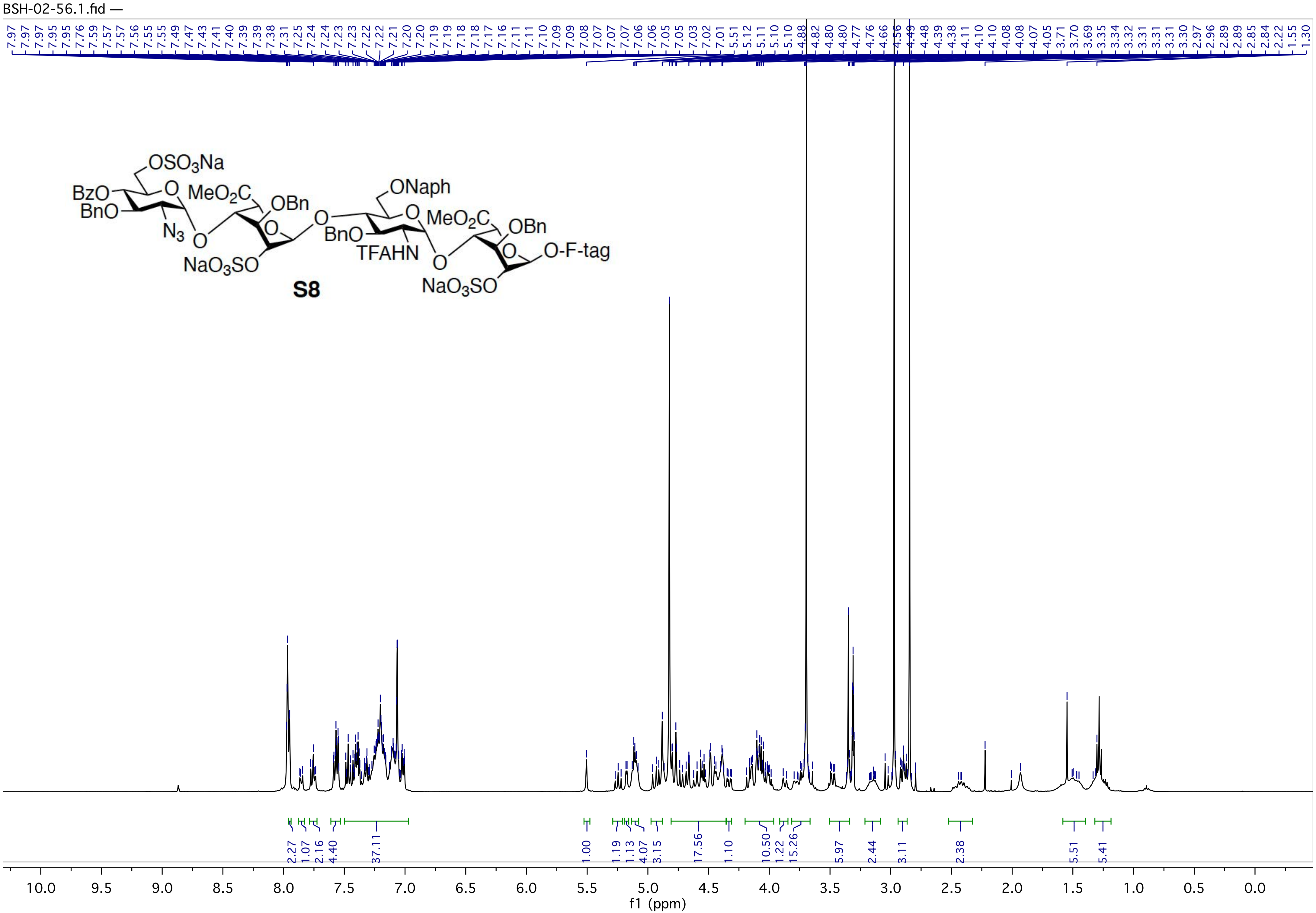
BSH-02-74-pure.1.fid —



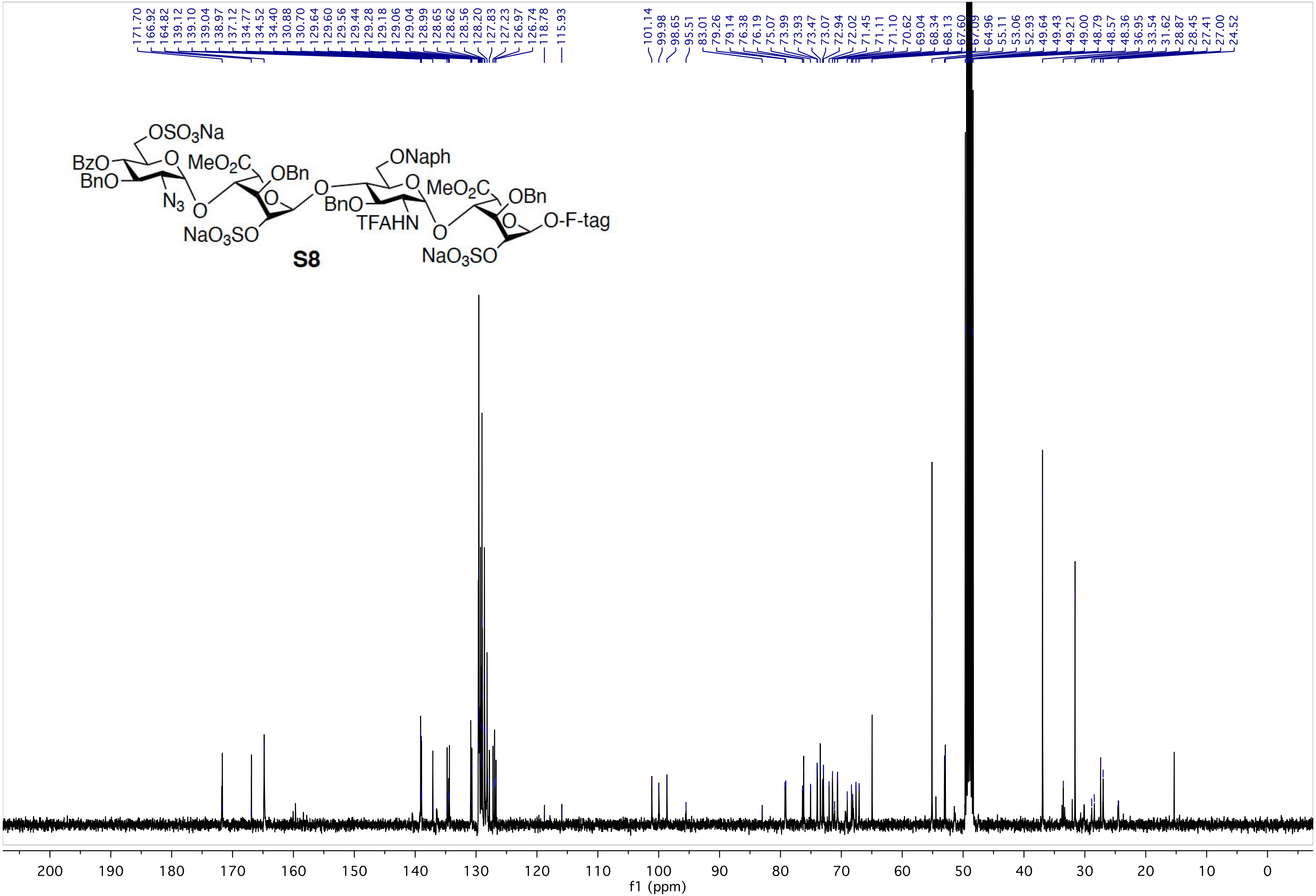
BSH-02-74-pure.2.fid —

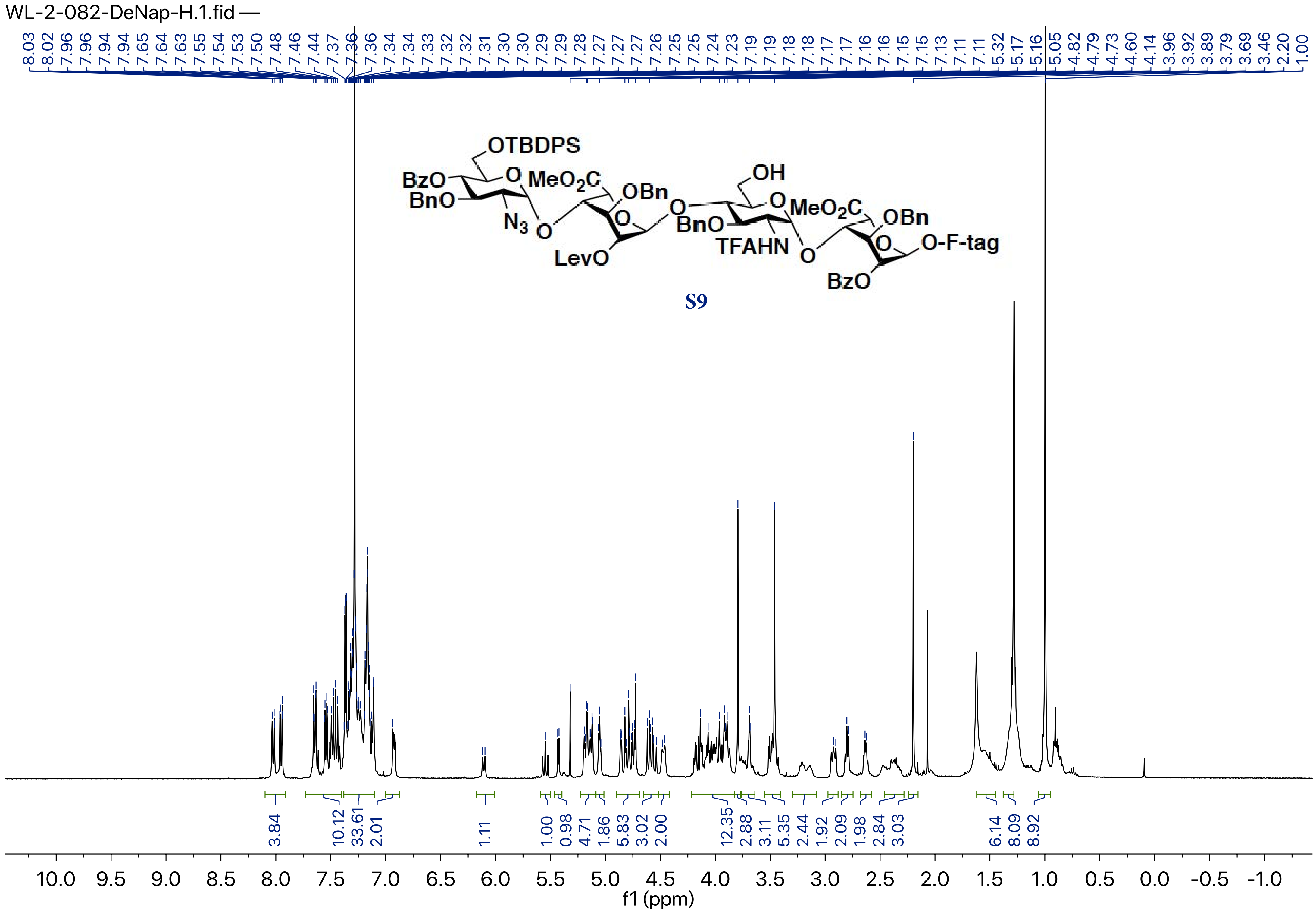


S7

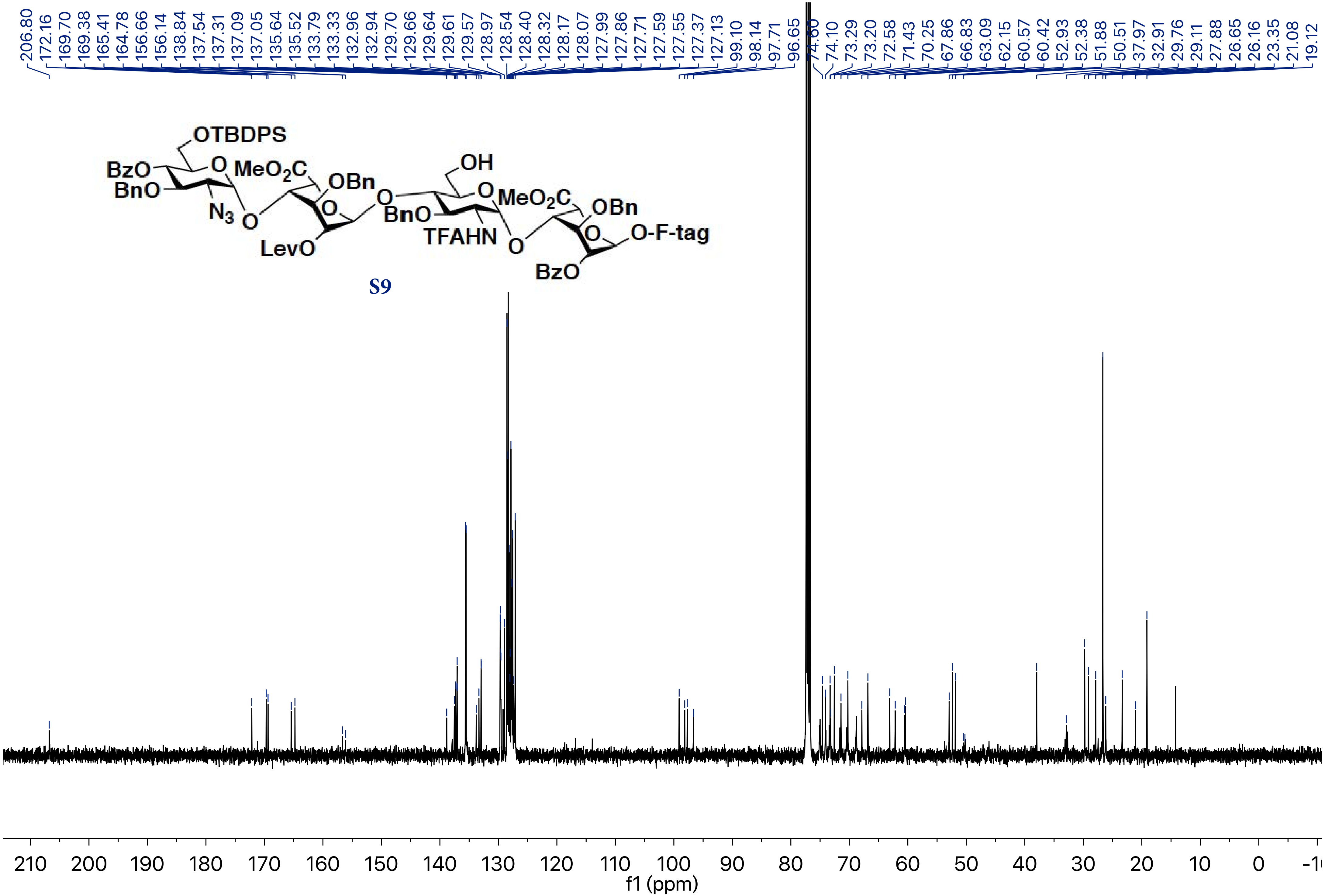

BSH-02-56.1.fid —
7.97 7.97 7.95 7.95 7.76 7.59 7.57 7.57 7.56 7.55 7.55 7.49 7.47 7.43 7.41 7.40 7.39 7.39 7.38 7.31 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.11 7.11 7.10 7.09 7.09 7.08 7.07 7.07 7.07 7.06 7.06 7.05 7.05 7.03 7.02 7.01 5.51 5.12 5.11 5.10 5.10 4.88 4.82 4.80 4.80 4.77 4.76 4.66 4.56 4.49 4.48 4.39 4.38 4.11 4.10 4.10 4.08 4.08 4.07 4.05 3.71 3.70 3.69 3.35 3.34 3.32 3.31 3.31 3.31 3.30 2.97 2.96 2.89 2.89 2.85 2.84 2.22 1.55 1.30
S8
2.27 1.07 2.16 4.40 37.11 1.00 1.19 1.13 4.07 3.15 17.56 1.10 10.50 1.22 15.26 5.97 2.44 3.11 2.38 5.51 5.41
f1 (ppm)

BSH-02-56.2.fid —

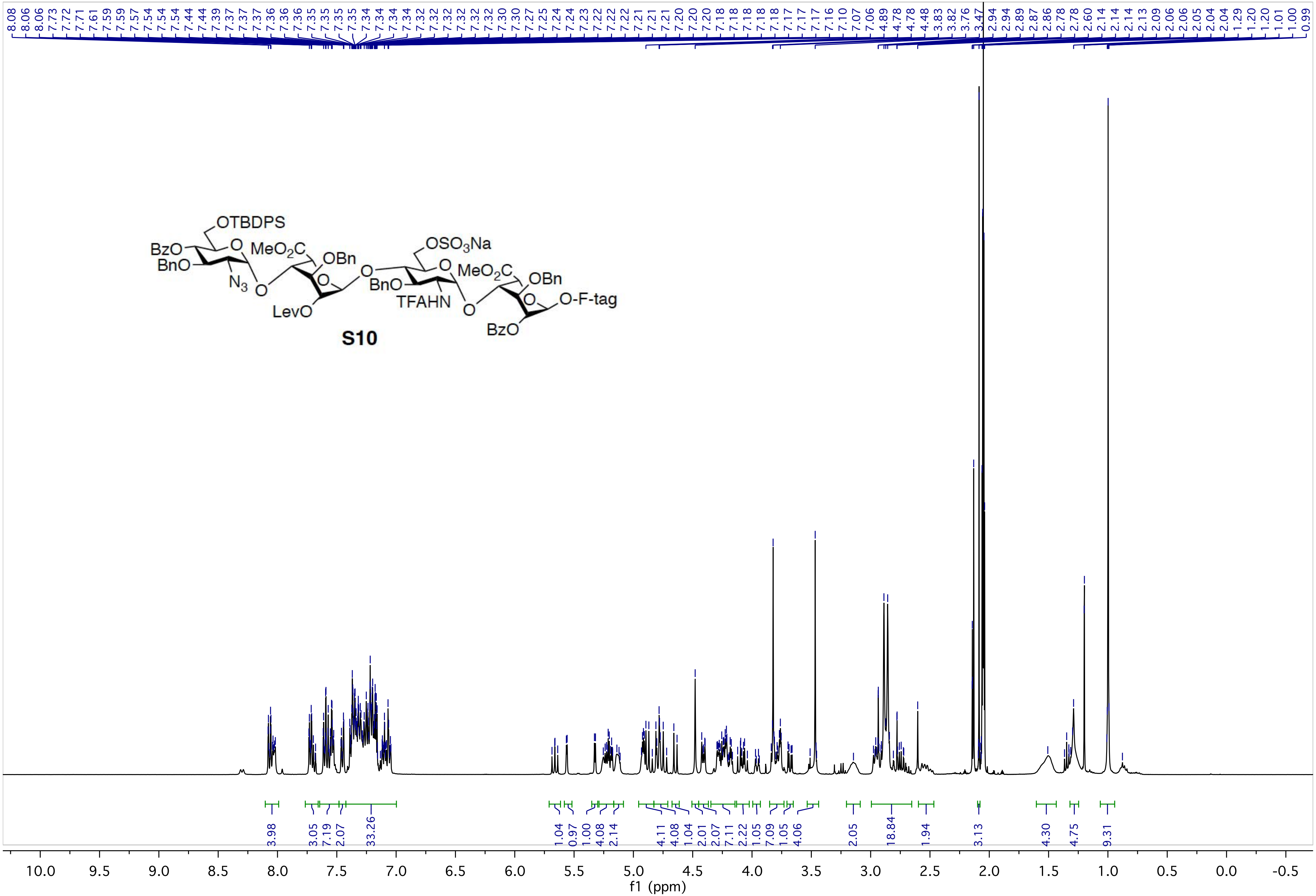



WL-2-082-DeNap-H.1.fid —
8.03 8.02 7.96 7.96 7.94 7.94 7.65 7.64 7.63 7.55 7.54 7.53 7.50 7.48 7.46 7.44 7.37 7.36 7.36 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.13 7.11 7.11 5.32 5.17 5.16 5.05 4.82 4.79 4.73 4.60 4.14 3.96 3.92 3.89 3.79 3.69 3.46 2.20 1.00
OTBDPS
BzO
BnO
O
N_3
O
MeO_2C
OBn
O
LevO
O
OH
BnO
O
TFAHN
O
MeO_2C
OBn
O
O-F-tag
BzO
S9
3.84 10.12 33.61 2.01 1.11 1.00 0.98 4.71 1.86 5.83 3.02 2.00 12.35 2.88 3.11 5.35 2.44 1.92 2.09 1.98 2.84 3.03 6.14 8.09 8.92
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 -0.5 -1.0
f1 (ppm)

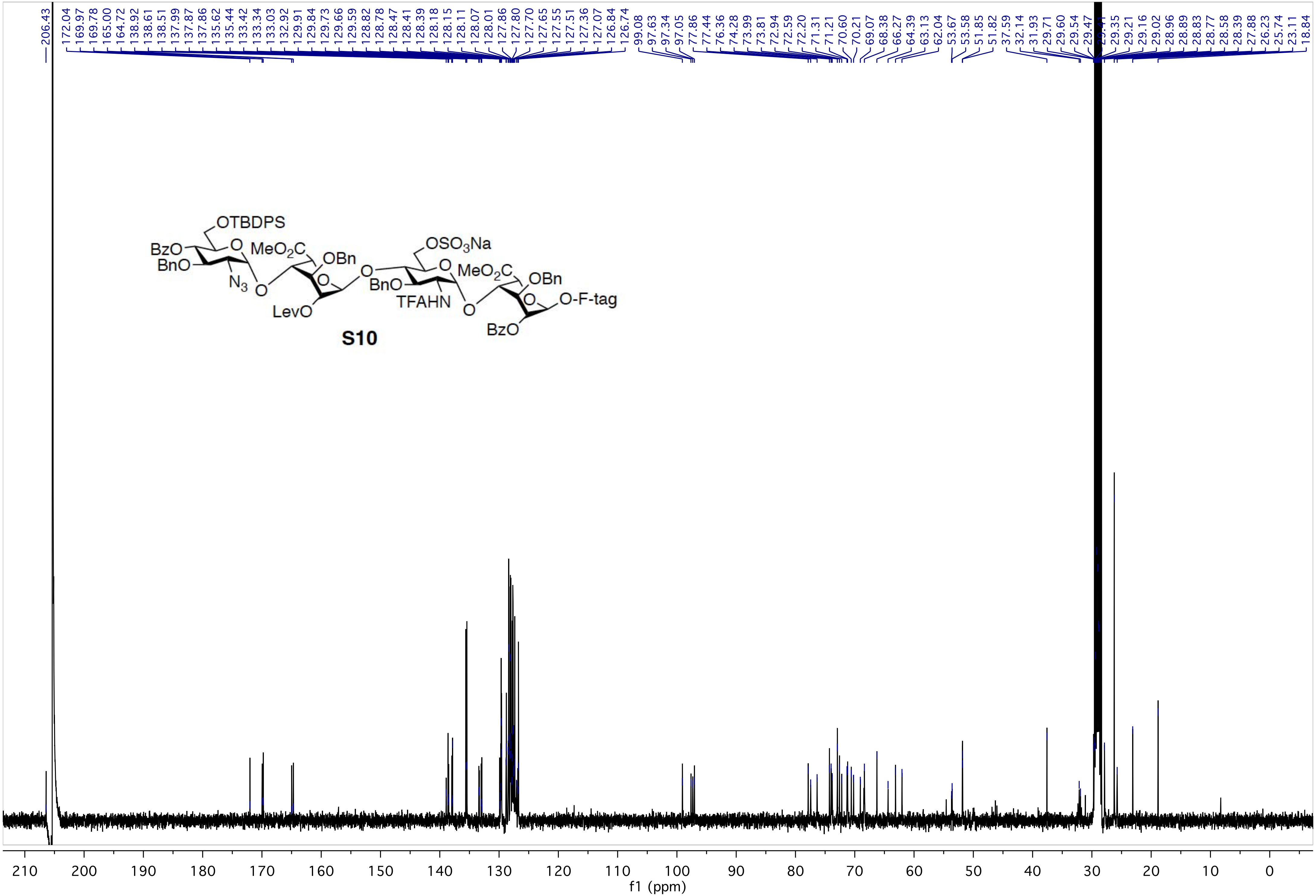
WL-2-082-De-Nap-C-prod.2.fid —



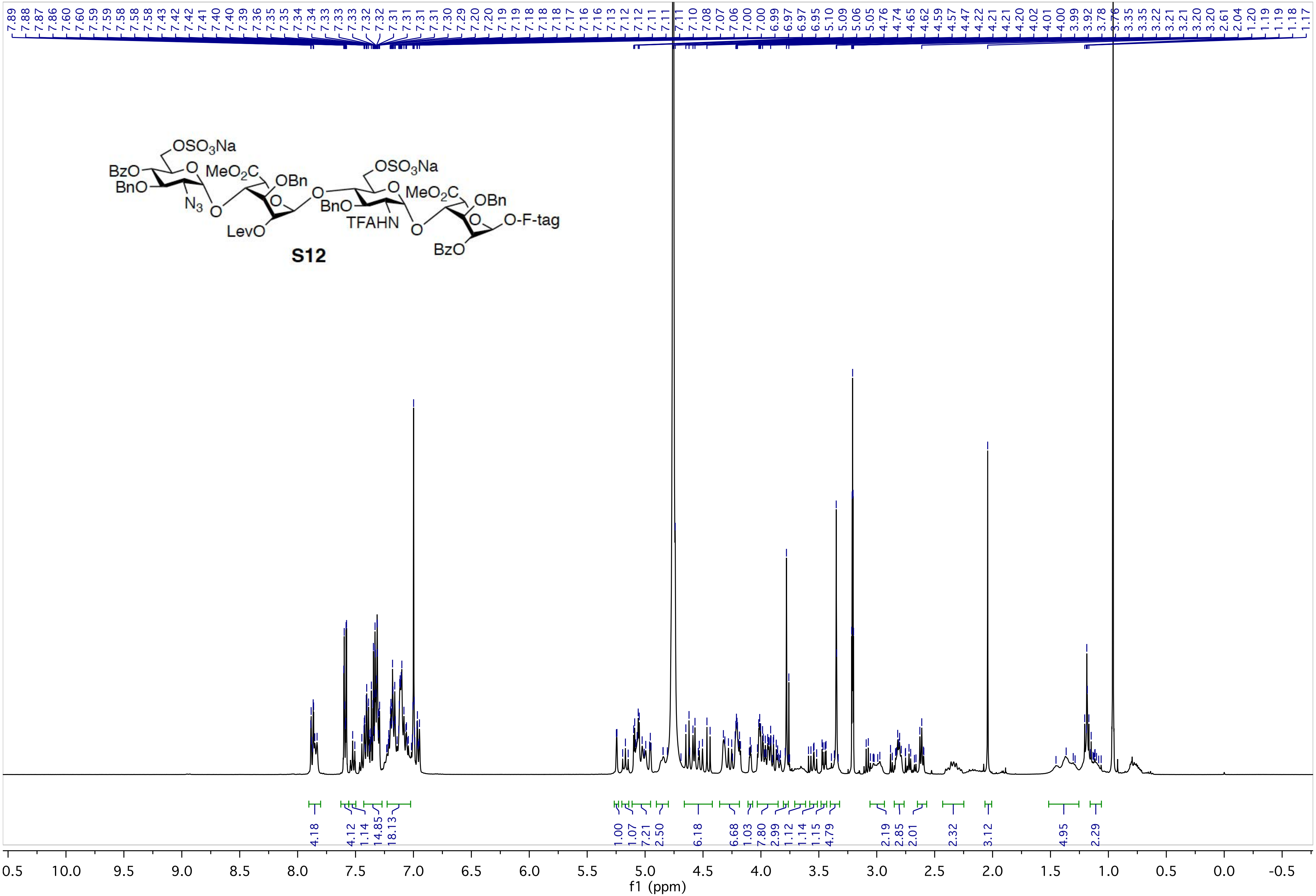
BSH-01-24.1.fid —



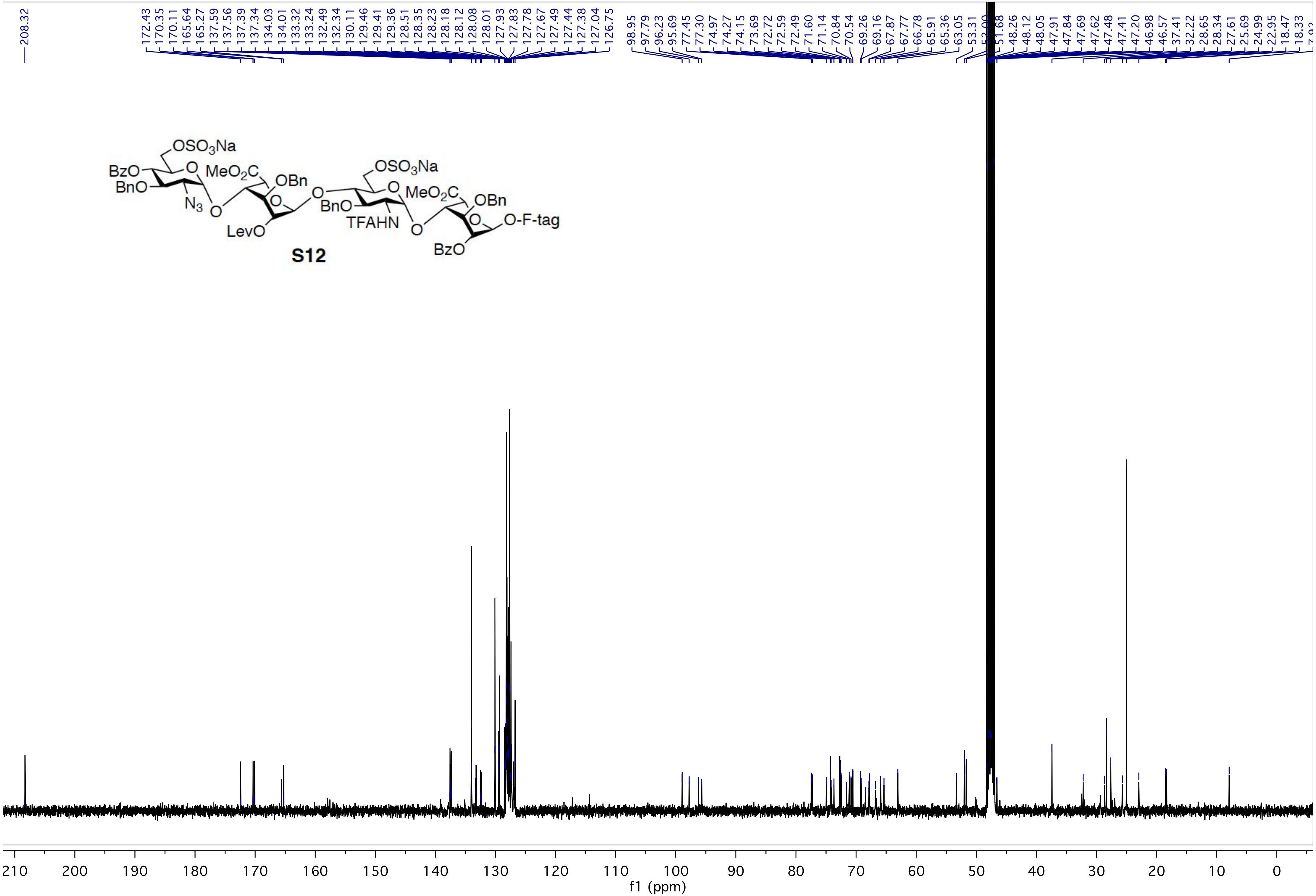
BSH-01-24.2.fid —



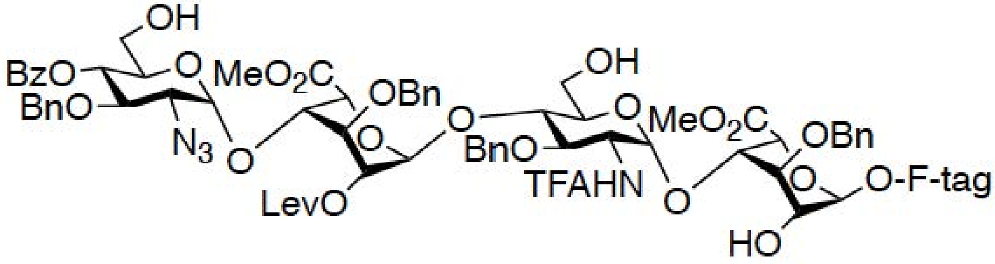
BSH-01-30.1.fid —



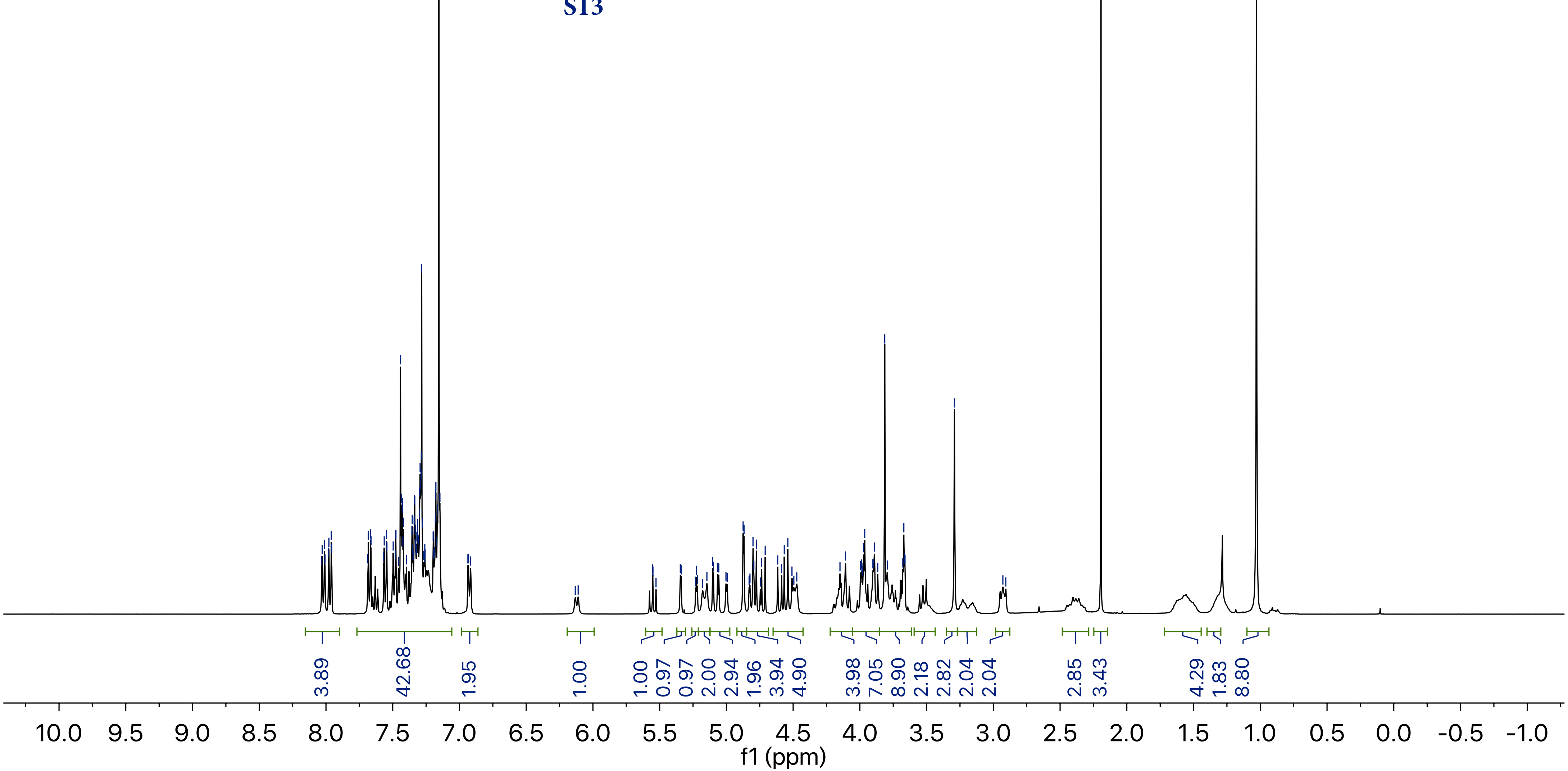
BSH-01-30.2.fid —



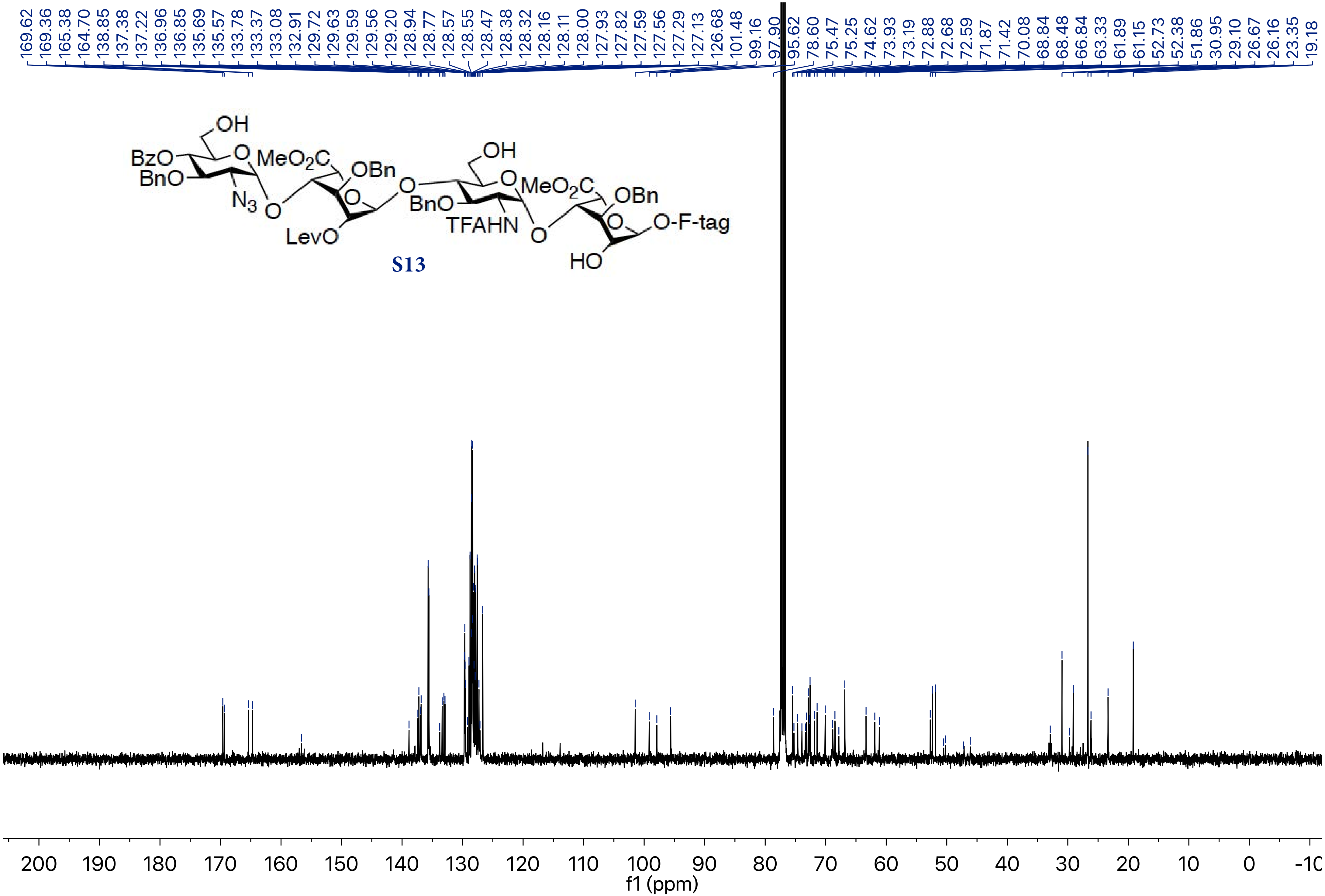
WL-2-083-De-Nap-De-Lev-H.1.fid —



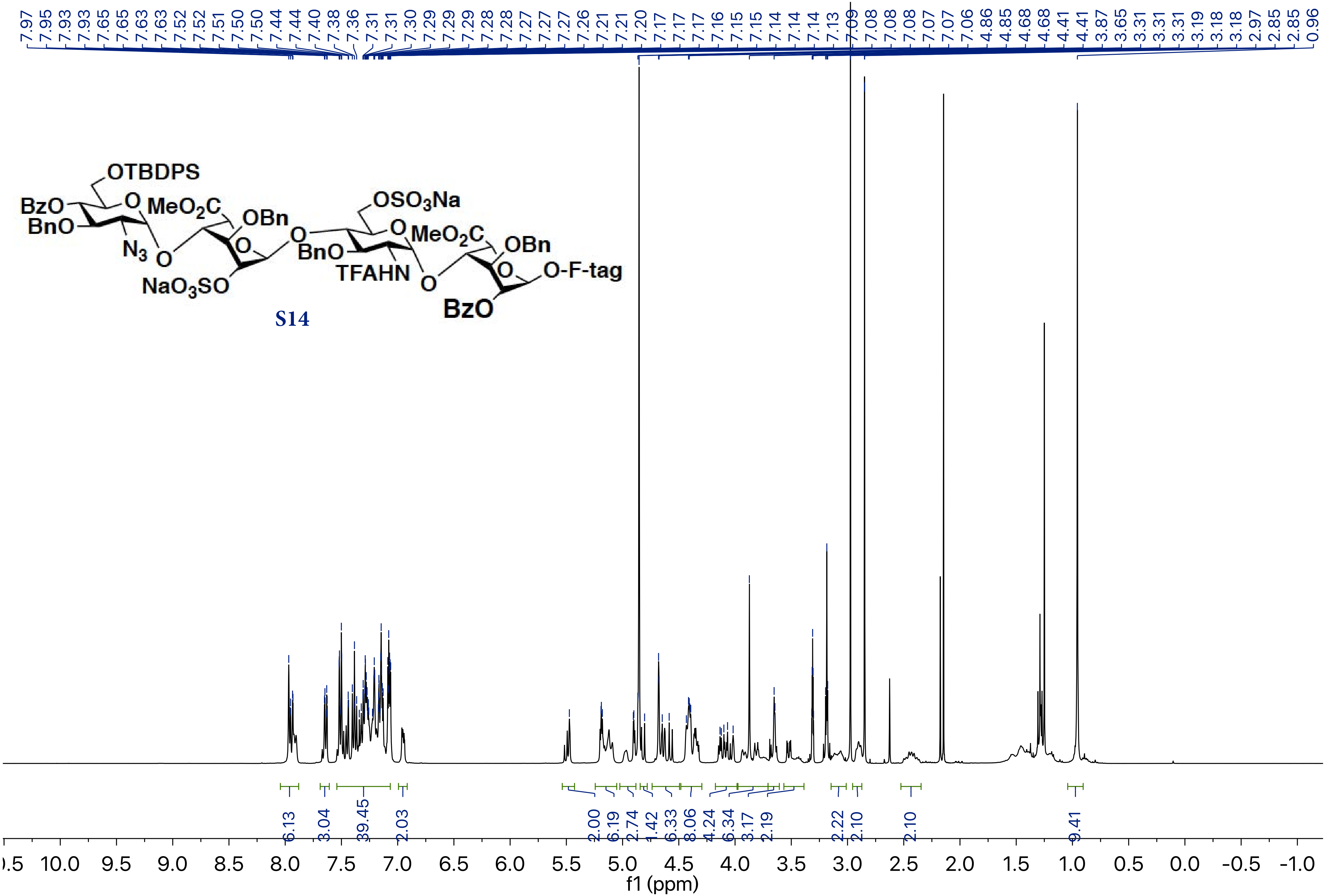
S13

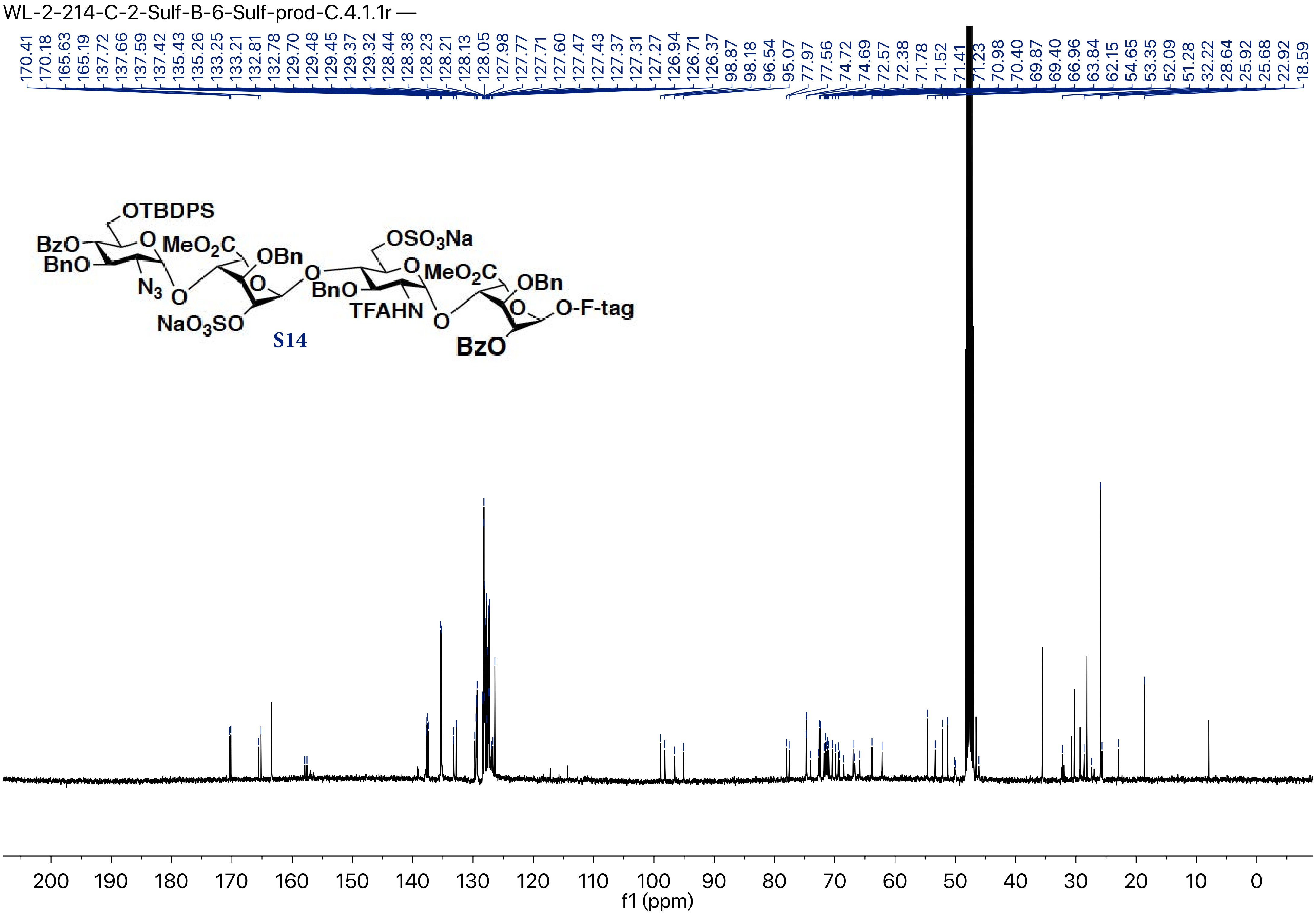


WL-2-083-De-Nap-De-Lev-C.1.1.1r —

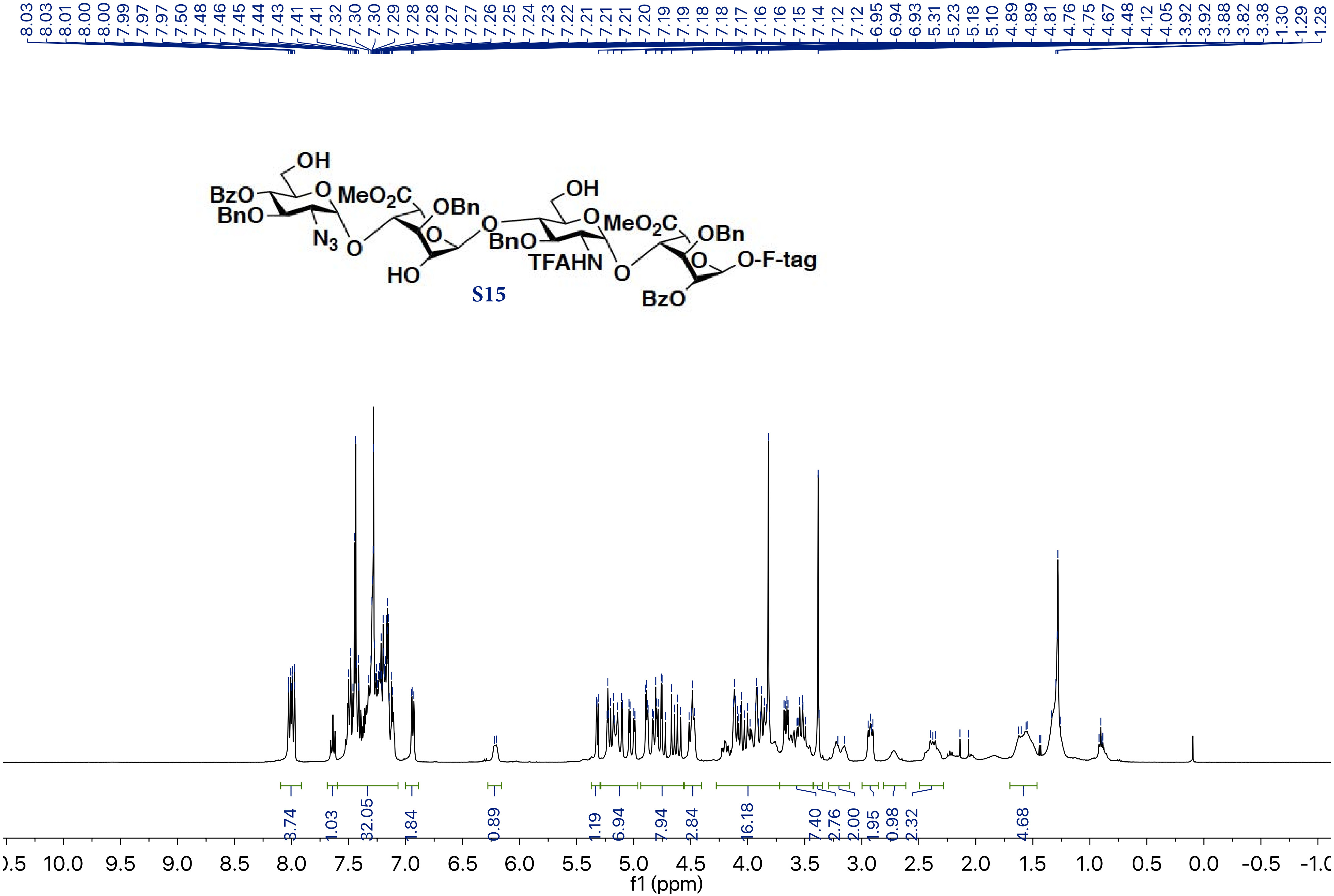


WL-2-214-C-2-Sulf-B-6-Sulf-prod-H.3.1.1r —

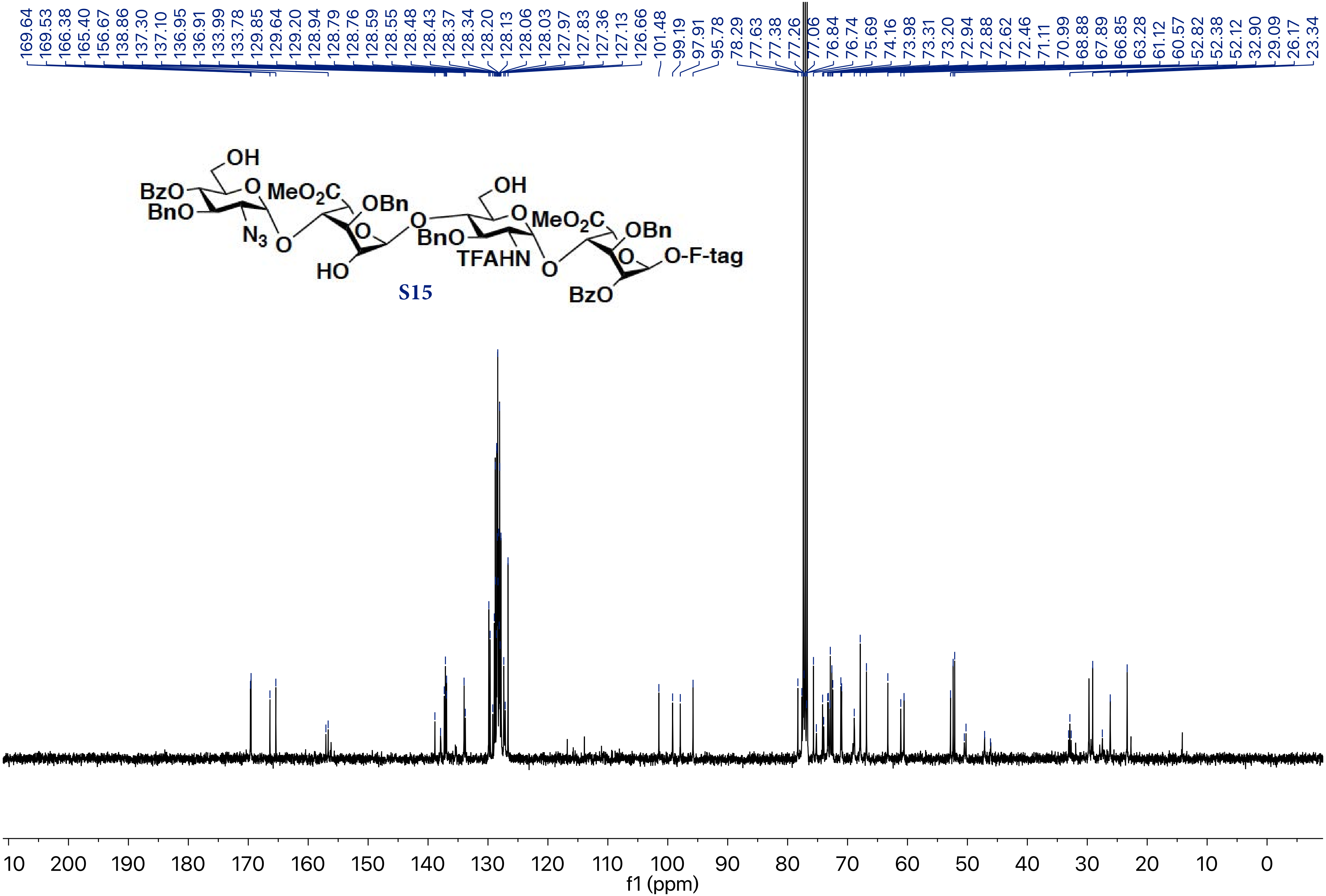



WL-2-214-C-2-Sulf-B-6-Sulf-prod-C.4.1.1r —
S14
170.41 170.18 165.63 165.19 137.72 137.66 137.59 137.42 135.43 135.26 133.25 133.21 132.81 132.78 129.70 129.48 129.45 129.37 129.32 128.44 128.38 128.23 128.21 128.13 128.05 127.98 127.77 127.71 127.60 127.47 127.43 127.37 127.31 127.27 126.94 126.71 126.37 98.87 98.18 96.54 95.07 77.97 77.56 74.72 74.69 72.57 72.38 71.78 71.52 71.41 71.23 70.98 70.40 69.87 69.40 66.96 63.84 62.15 54.65 53.35 52.09 51.28 32.22 28.64 25.92 25.68 22.92 18.59
f1 (ppm)

WL-2-085-DeNap-DeLev-DeTBDPS-Prod-H.3.1.1r —

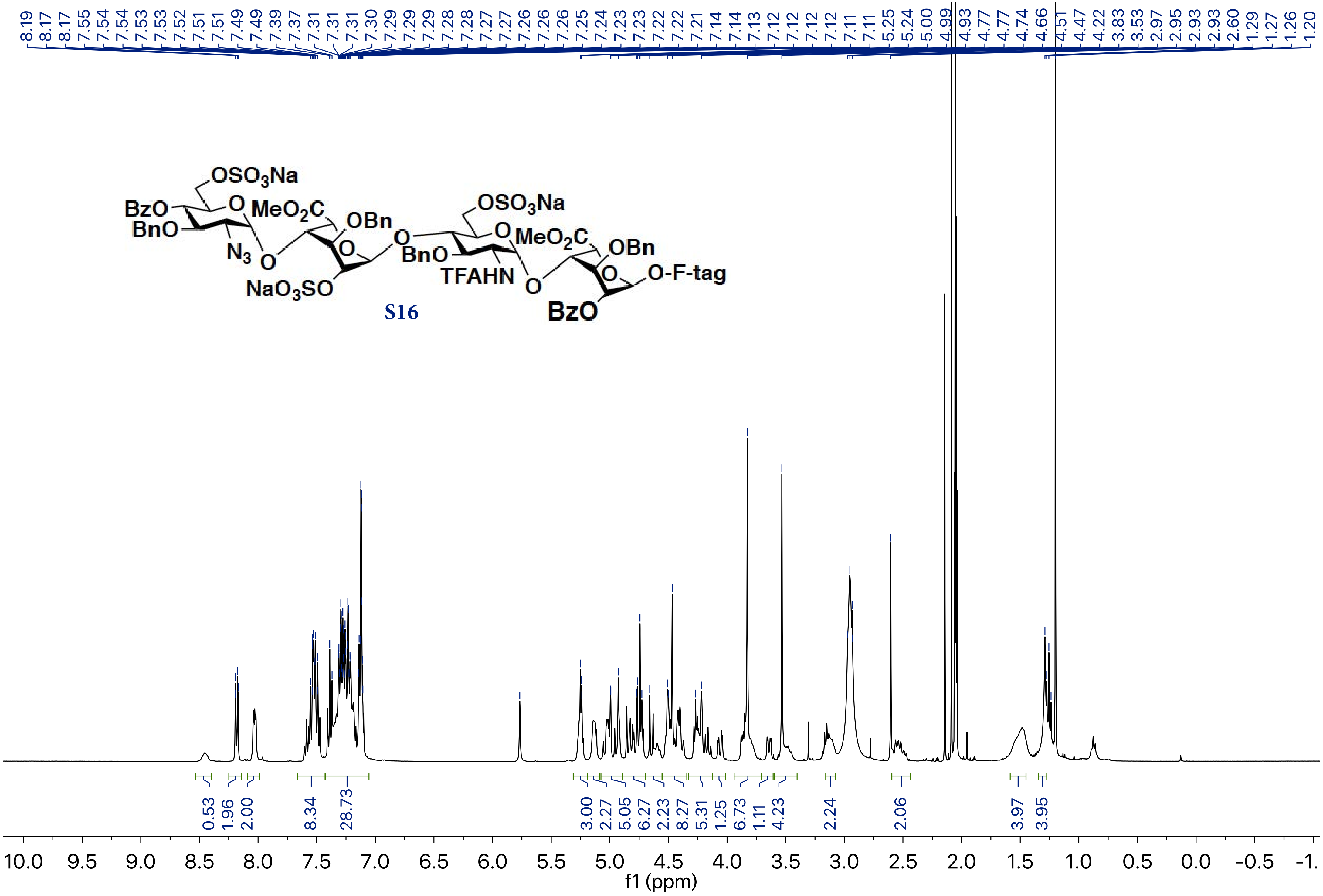


WL-2-085-DeNap-DeLev-DeTBDPS-Prod-C.4.1.1r —



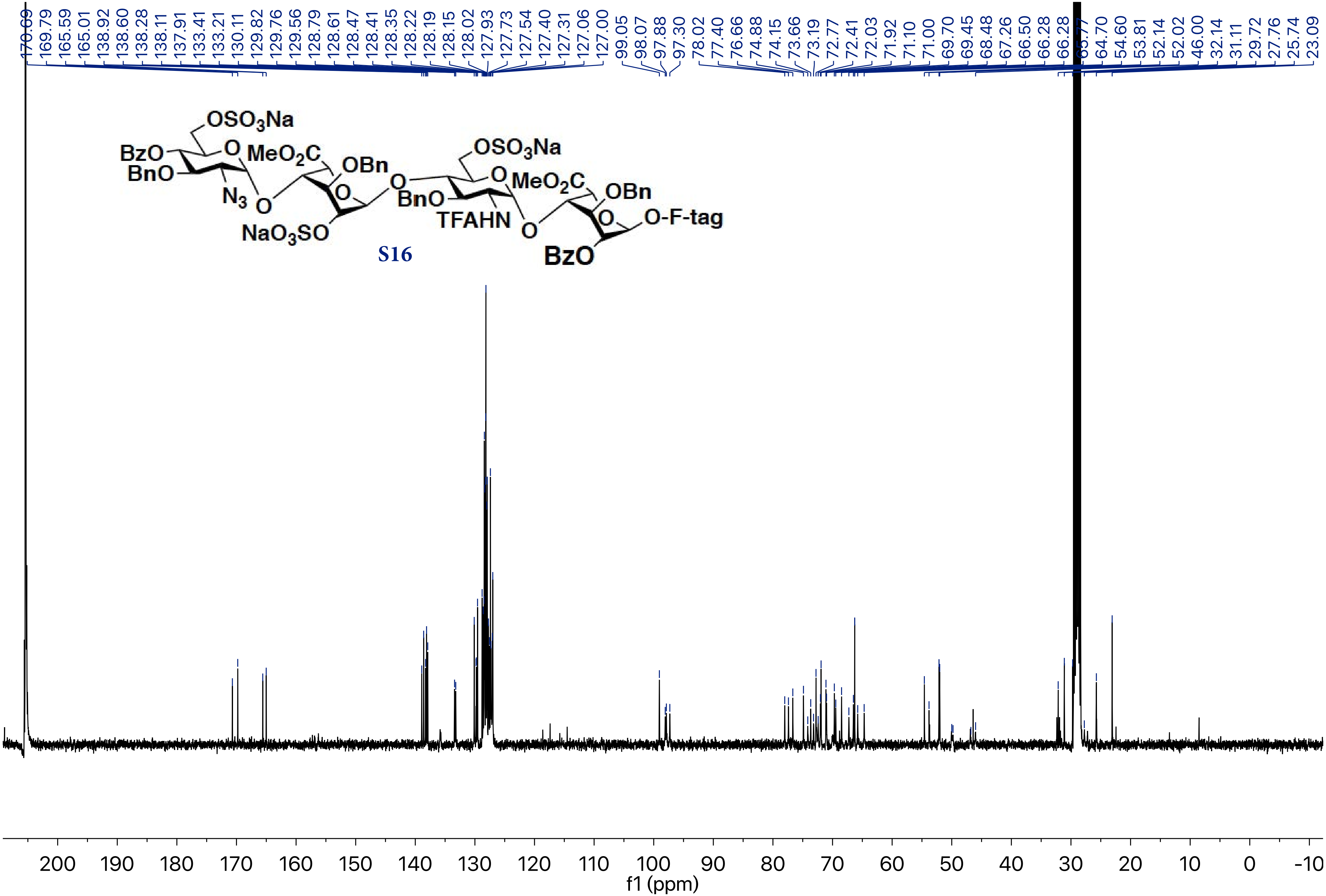
S15

WL-2-086-prod-D6SO3-C2SO3-B6SO3-H.4.1.1r —

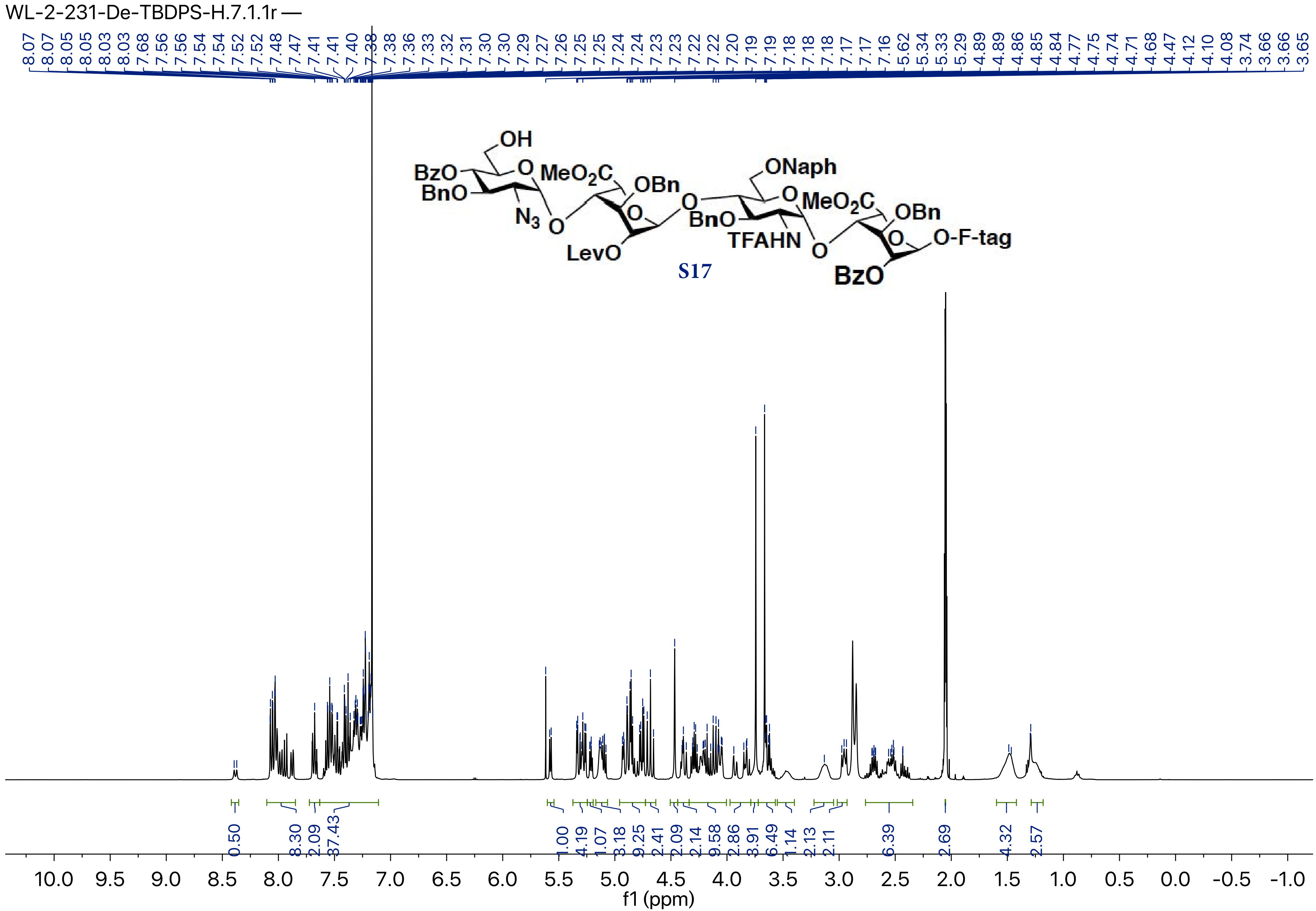


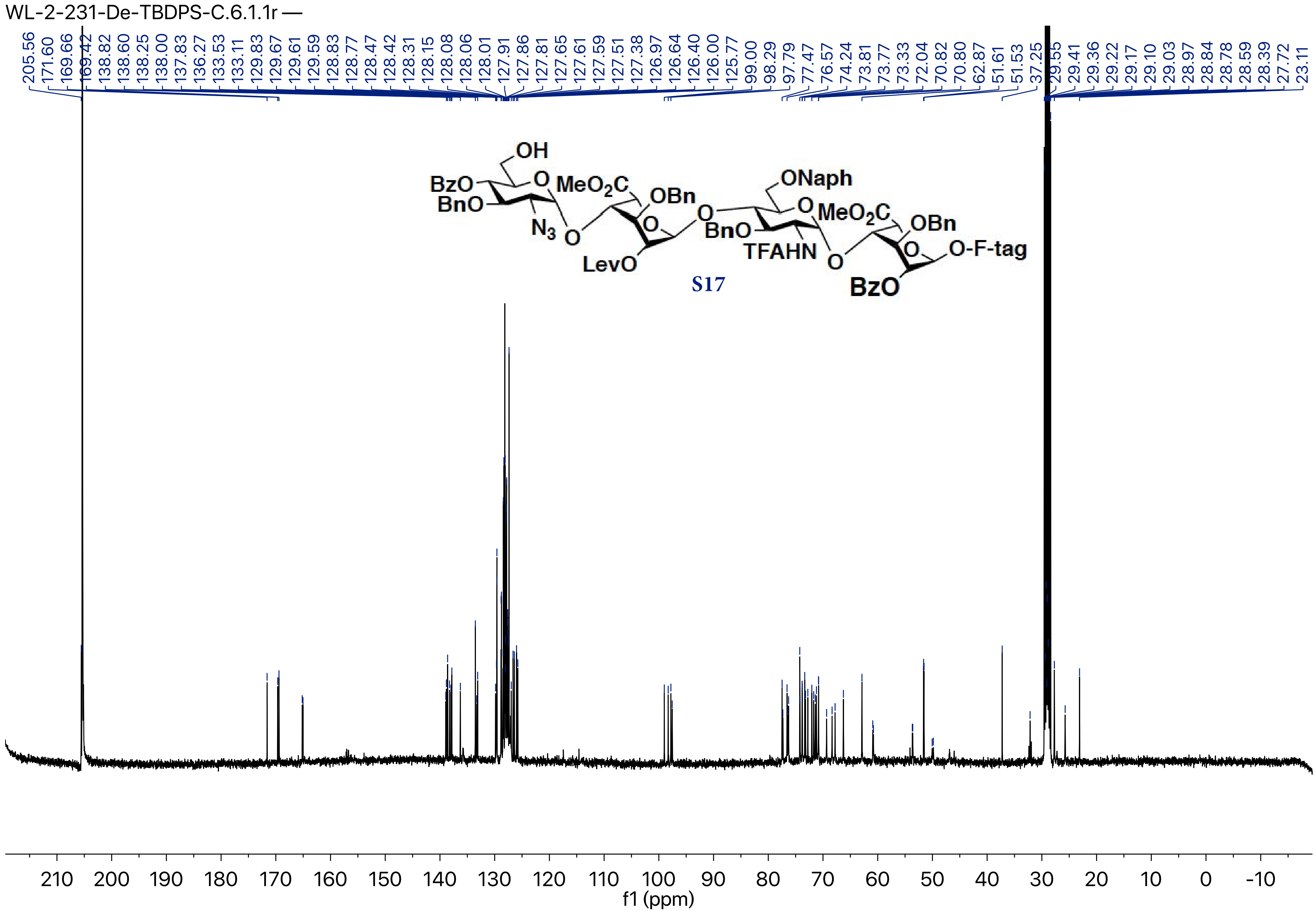
S16

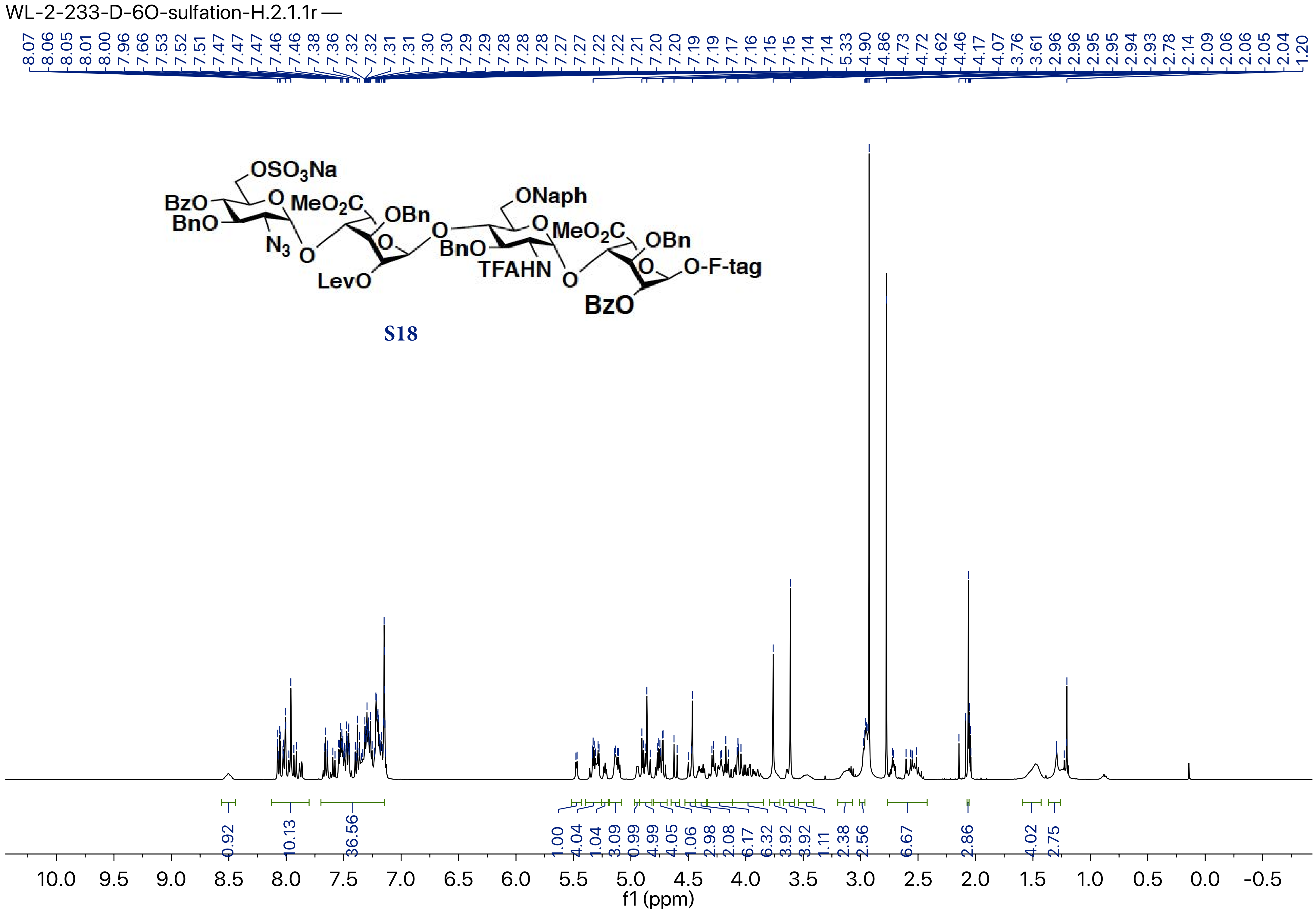
WL-2-086-prod-D6SO3-C2SO3-B6SO3-C.3.1.1r



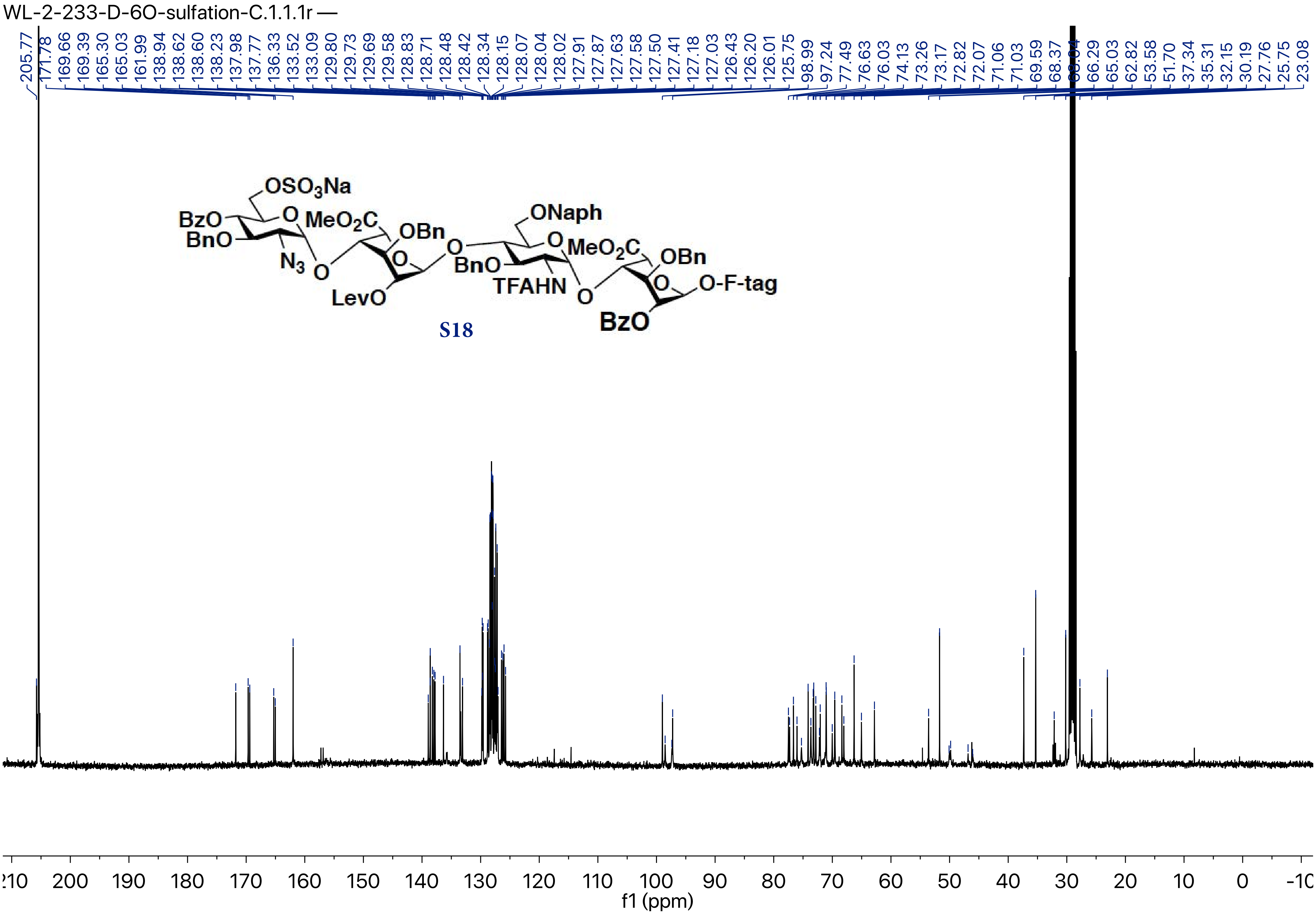
S16


WL-2-231-De-TBDPS-H.7.1.1r
8.07 8.07 8.05 8.05 8.03 8.03 7.68 7.56 7.56 7.54 7.54 7.52 7.52 7.48 7.47 7.41 7.41 7.40 7.38 7.38 7.36 7.33 7.32 7.31 7.30 7.30 7.29 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.16 5.62 5.34 5.33 5.29 4.89 4.89 4.86 4.85 4.84 4.77 4.75 4.74 4.71 4.68 4.47 4.12 4.10 4.08 3.74 3.66 3.66 3.65
OH
BzO
BnO
O
N3
MeO2C
OBn
O
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
S17
0.50 8.30 2.09 37.43 1.00 4.19 1.07 3.18 9.25 2.41 2.09 2.14 9.58 2.86 3.91 6.49 1.14 2.13 2.11 6.39 2.69 4.32 2.57
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 -0.5 -1.0
f1 (ppm)


WL-2-231-De-TBDPS-C.6.1.1r
205.56
171.60
169.66
169.42
138.82
138.60
138.25
138.00
137.83
136.27
133.53
133.11
129.83
129.67
129.61
129.59
128.83
128.77
128.47
128.42
128.31
128.15
128.08
128.06
128.01
127.91
127.86
127.81
127.65
127.61
127.59
127.51
127.38
126.97
126.64
126.40
126.00
125.77
99.00
98.29
97.79
77.47
76.57
74.24
73.81
73.77
73.33
72.04
70.82
70.80
62.87
51.61
51.53
37.25
29.55
29.41
29.36
29.22
29.17
29.10
29.03
28.97
28.84
28.78
28.59
28.39
27.72
23.11
OH
BzO
BnO
O
N_3
MeO_2C
OBn
LevO
ONaph
BnO
TFAHN
OBn
O-F-tag
BzO
S17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

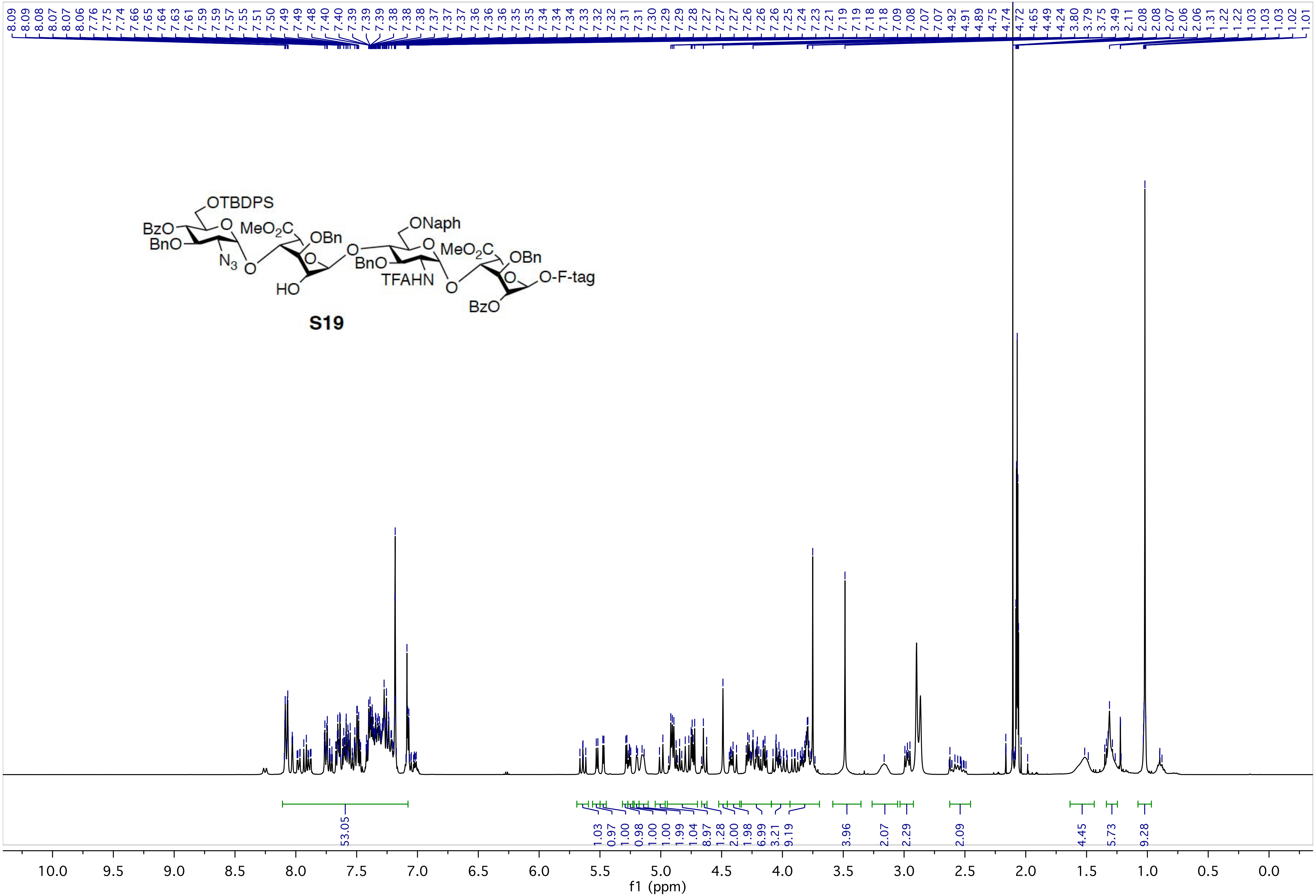

WL-2-233-D-6O-sulfation-H.2.1.1r
8.07 8.06 8.05 8.01 8.00 7.96 7.66 7.53 7.52 7.51 7.47 7.47 7.47 7.46 7.46 7.38 7.36 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.17 7.16 7.15 7.15 7.14 7.14 5.33 4.90 4.86 4.73 4.72 4.62 4.46 4.17 4.07 3.76 3.61 2.96 2.96 2.95 2.95 2.94 2.93 2.78 2.14 2.09 2.06 2.06 2.05 2.04 1.20
OSO3Na
BzO
BnO
N3
O
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
0.92 10.13 36.56 1.00 4.04 1.04 3.09 0.99 4.99 4.05 1.06 2.98 2.08 6.17 6.32 3.92 3.92 1.11 2.38 2.56 6.67 2.86 4.02 2.75
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 -0.5
f1 (ppm)

S18

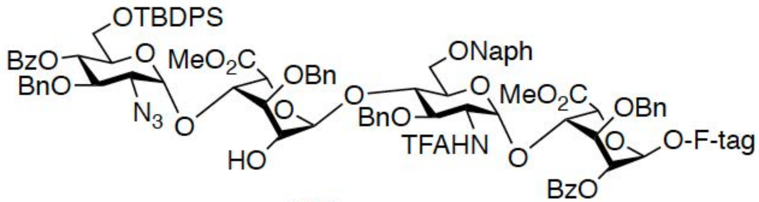

WL-2-233-D-6O-sulfation-C.1.1.1r
205.77
171.78
169.66
169.39
165.30
165.03
161.99
138.94
138.62
138.60
138.23
137.98
137.77
136.33
133.52
133.09
129.80
129.73
129.69
129.58
128.83
128.71
128.48
128.42
128.34
128.15
128.07
128.04
128.02
127.91
127.87
127.63
127.58
127.50
127.41
127.18
127.03
126.43
126.20
126.01
125.75
98.99
97.24
77.49
76.63
76.03
74.13
73.26
73.17
72.82
72.07
71.06
71.03
69.59
68.37
66.29
65.03
62.82
53.58
51.70
37.34
35.31
32.15
30.19
27.76
25.75
23.08
OSO3Na
BzO
BnO
O
N3
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
OBn
O-F-tag
BzO
f1 (ppm)

S18

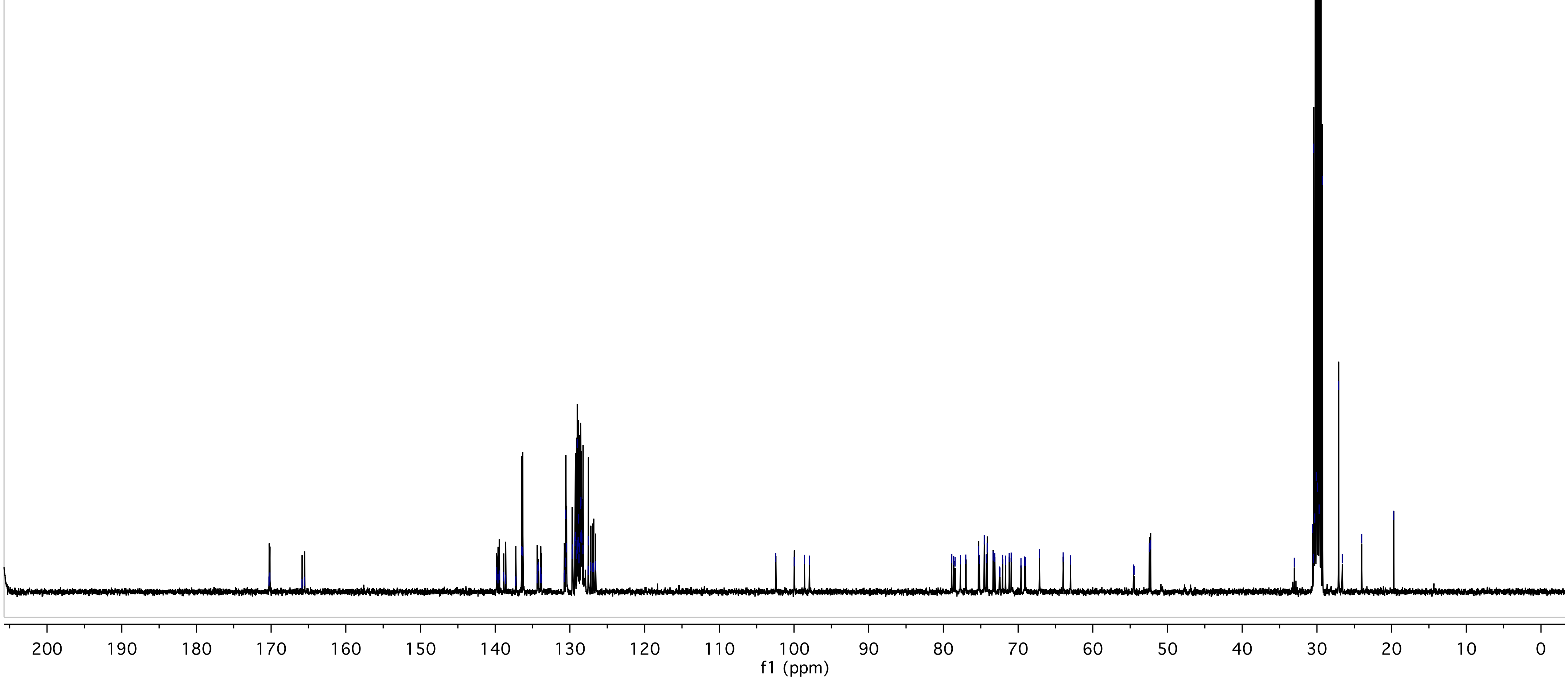
BSH-01-74.1.fid —



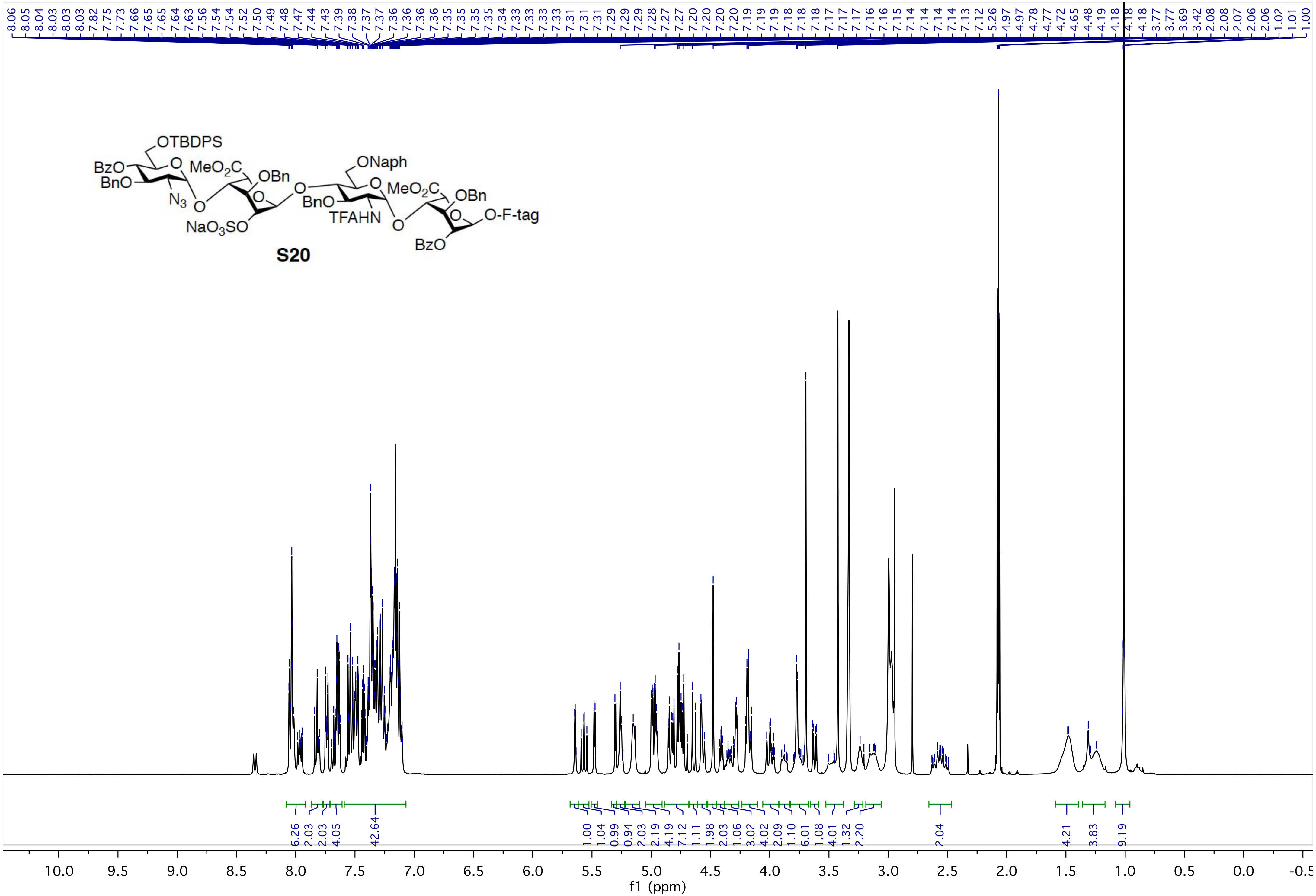
BSH-01-74.7.fid —



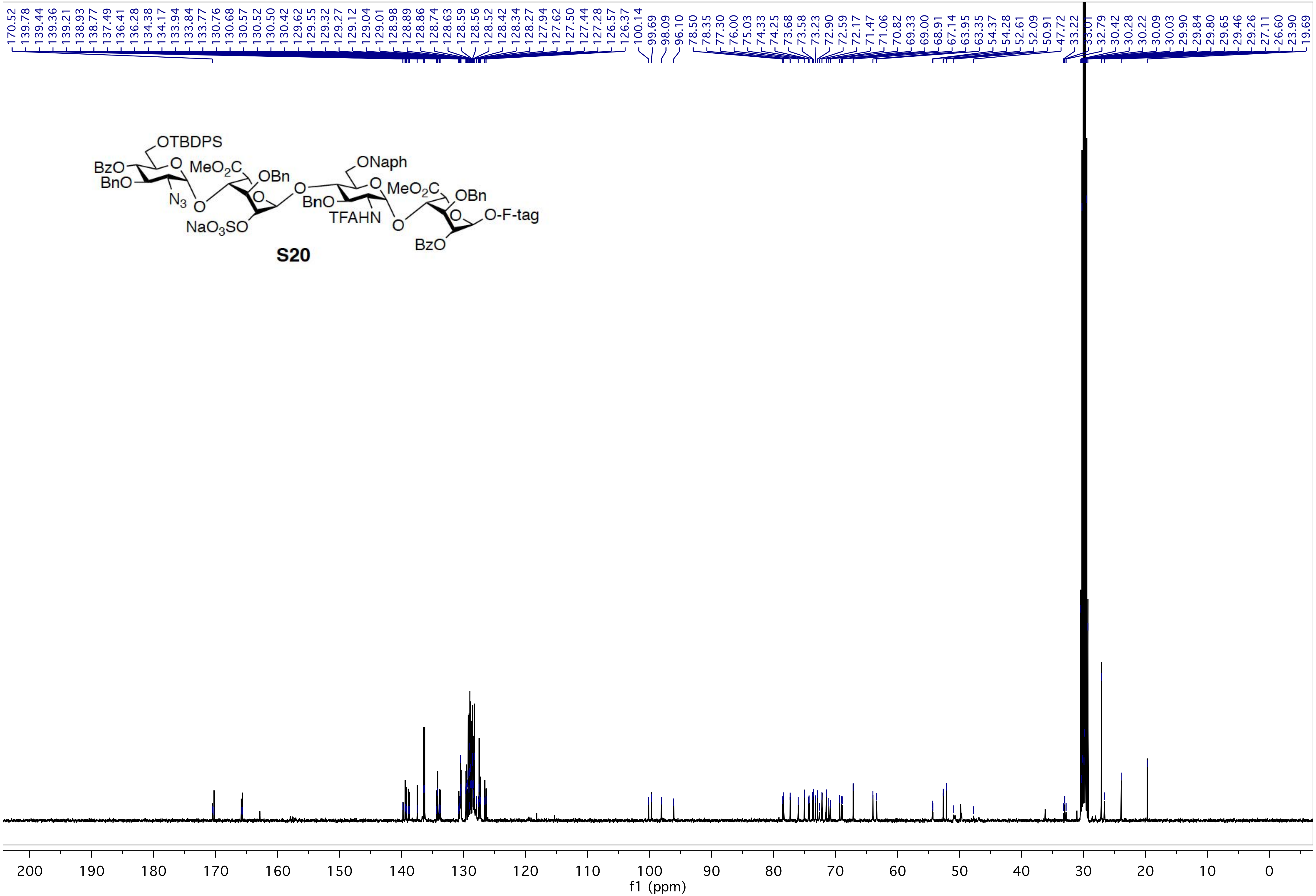
S19



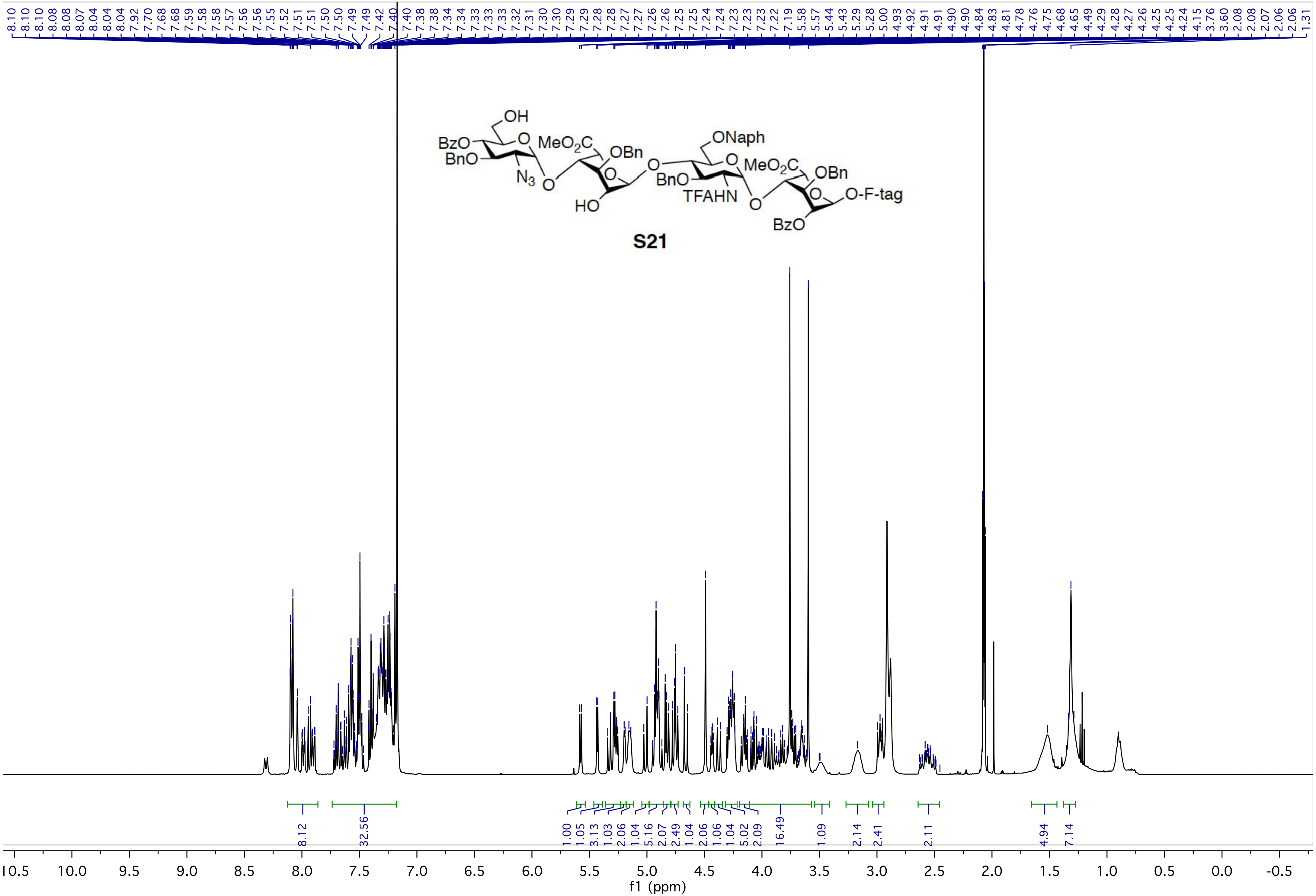
BSH-01-76.1.fid —



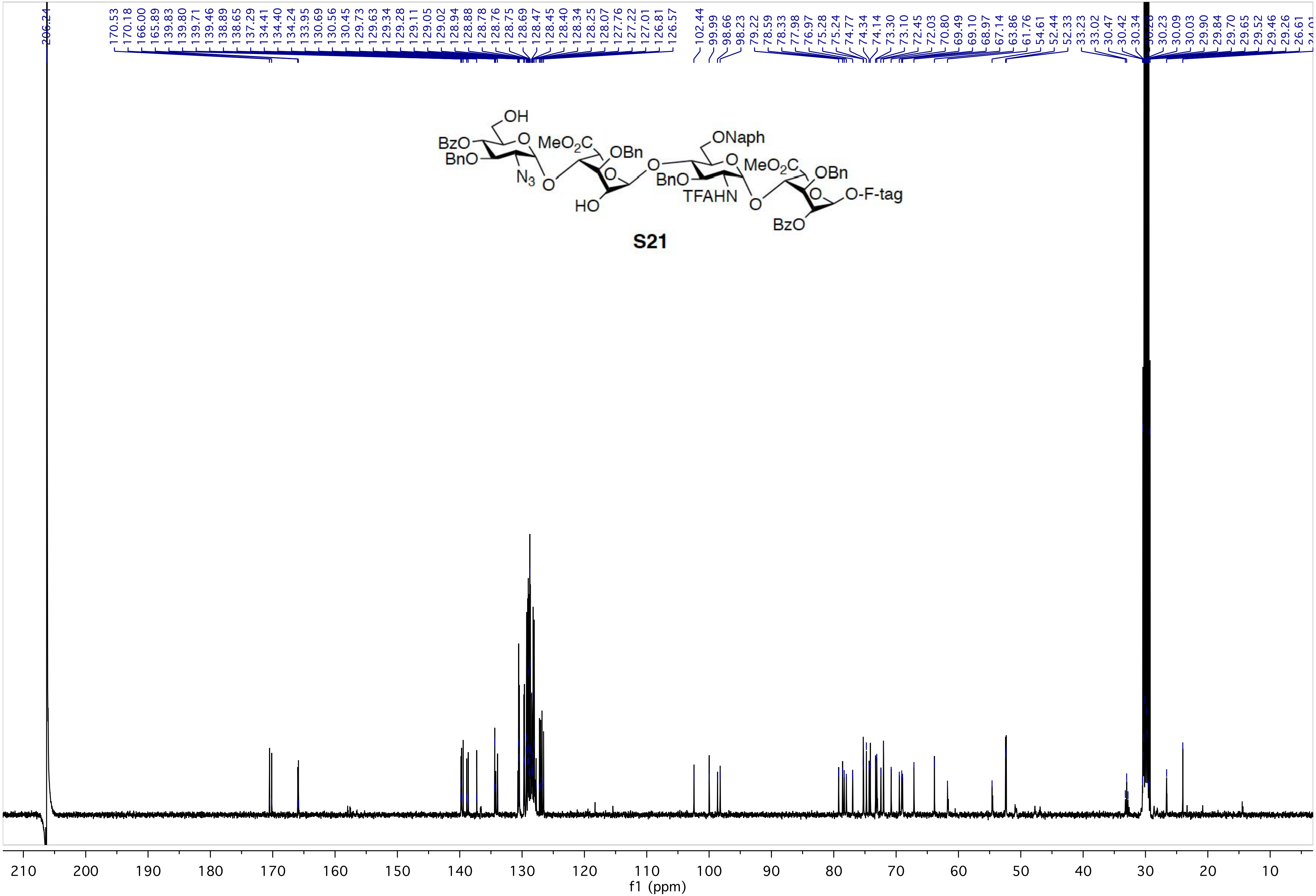
BSH-01-76.2.fid —



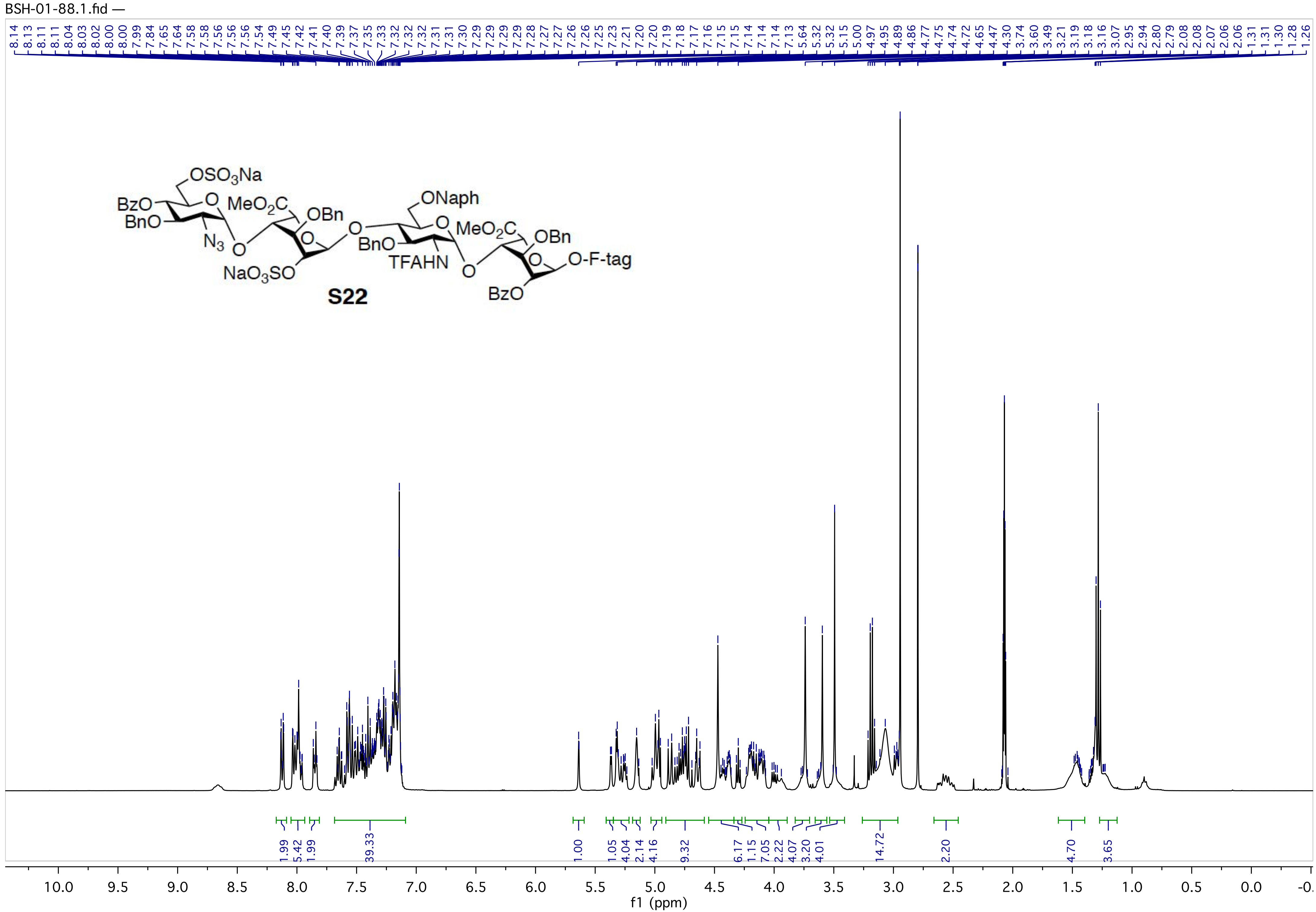
BSH-01-84.1.fid —



BSH-01-84.2.fid —

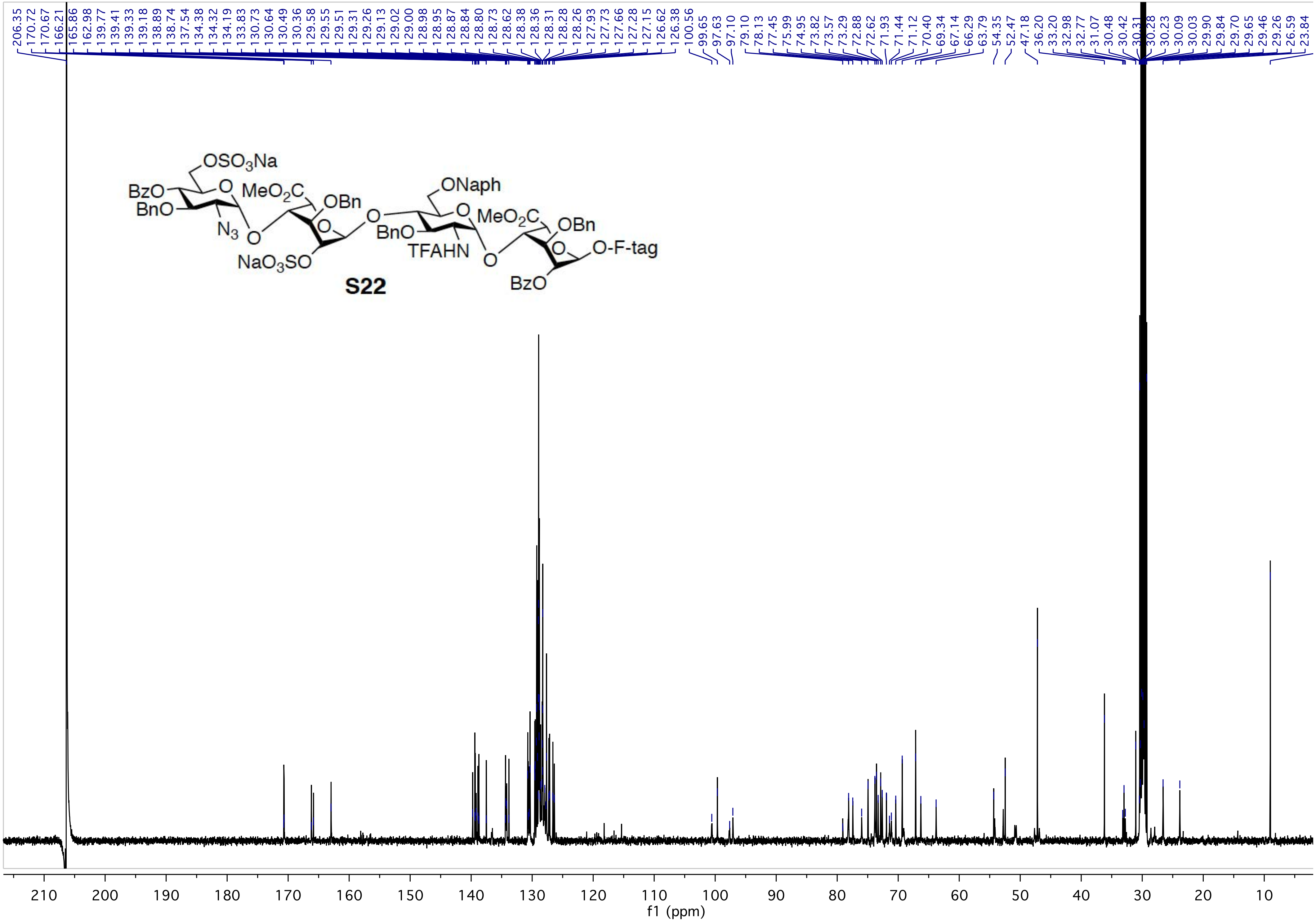


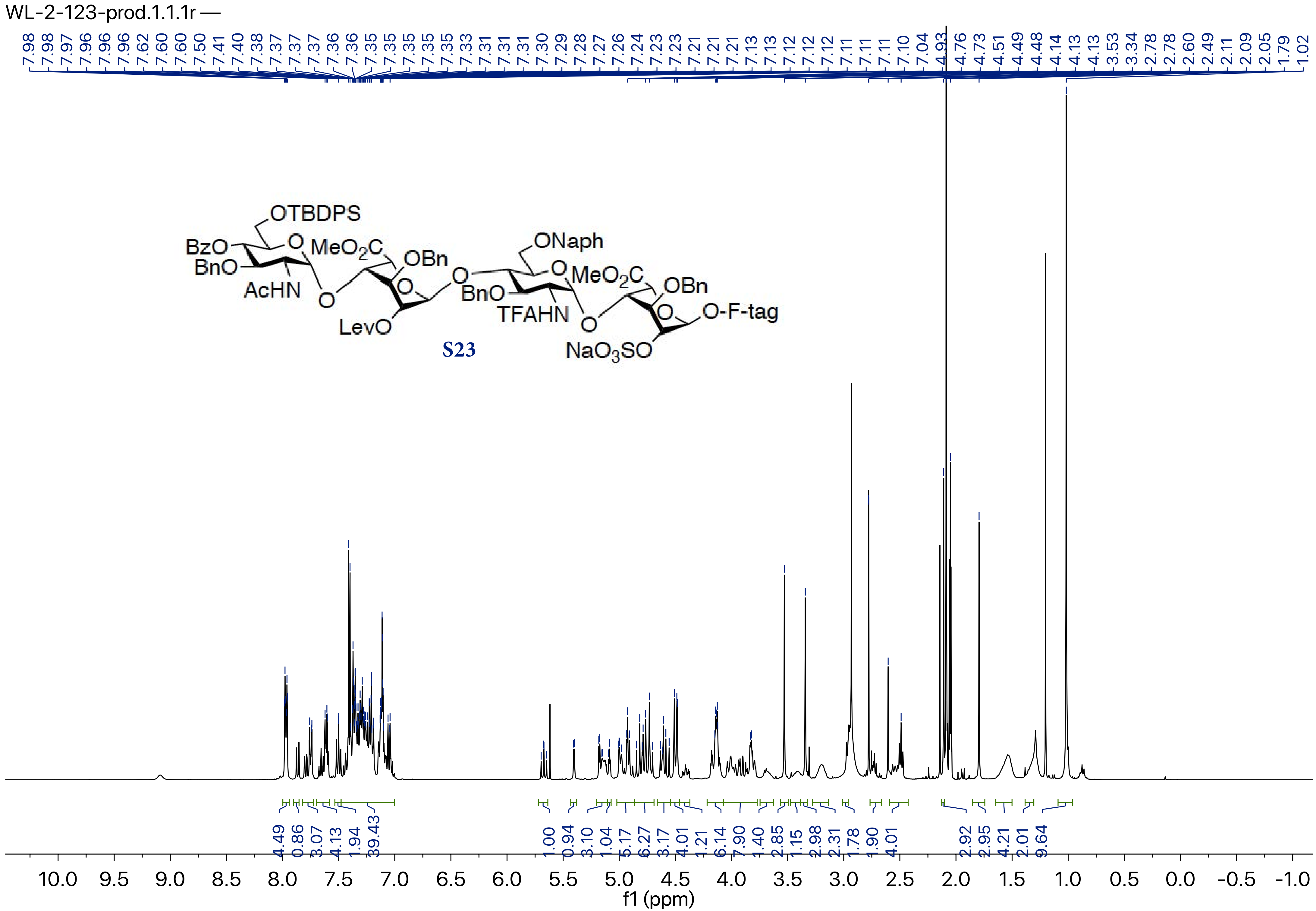
S21

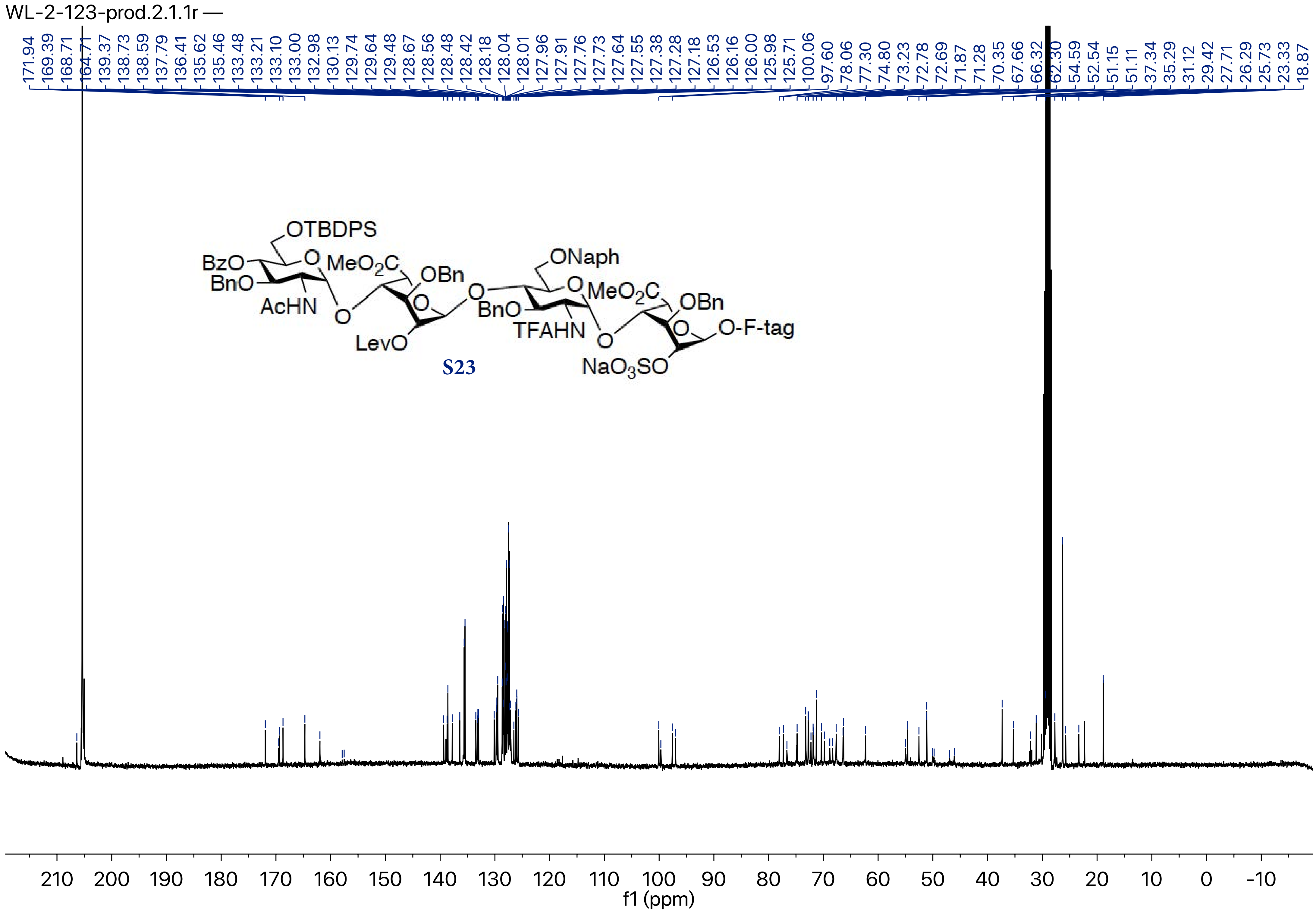

BSH-01-88.1.fid —
8.14 8.13 8.11 8.11 8.04 8.03 8.02 8.00 8.00 7.99 7.84 7.65 7.64 7.58 7.58 7.56 7.56 7.56 7.54 7.49 7.45 7.42 7.41 7.40 7.39 7.37 7.35 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.23 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.14 7.13 5.64 5.32 5.32 5.15 5.00 4.97 4.95 4.89 4.86 4.77 4.75 4.74 4.72 4.65 4.47 4.30 3.74 3.60 3.49 3.21 3.19 3.18 3.16 3.07 2.95 2.94 2.80 2.79 2.08 2.08 2.07 2.06 2.06 1.31 1.31 1.30 1.28 1.26
OSO3Na
BzO
BnO
N3
O
MeO2C
OBn
NaO3SO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
1.99 5.42 1.99 39.33 1.00 1.05 4.04 2.14 4.16 9.32 6.17 1.15 7.05 2.22 4.07 3.20 4.01 14.72 2.20 4.70 3.65
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 -0.
f1 (ppm)

S22

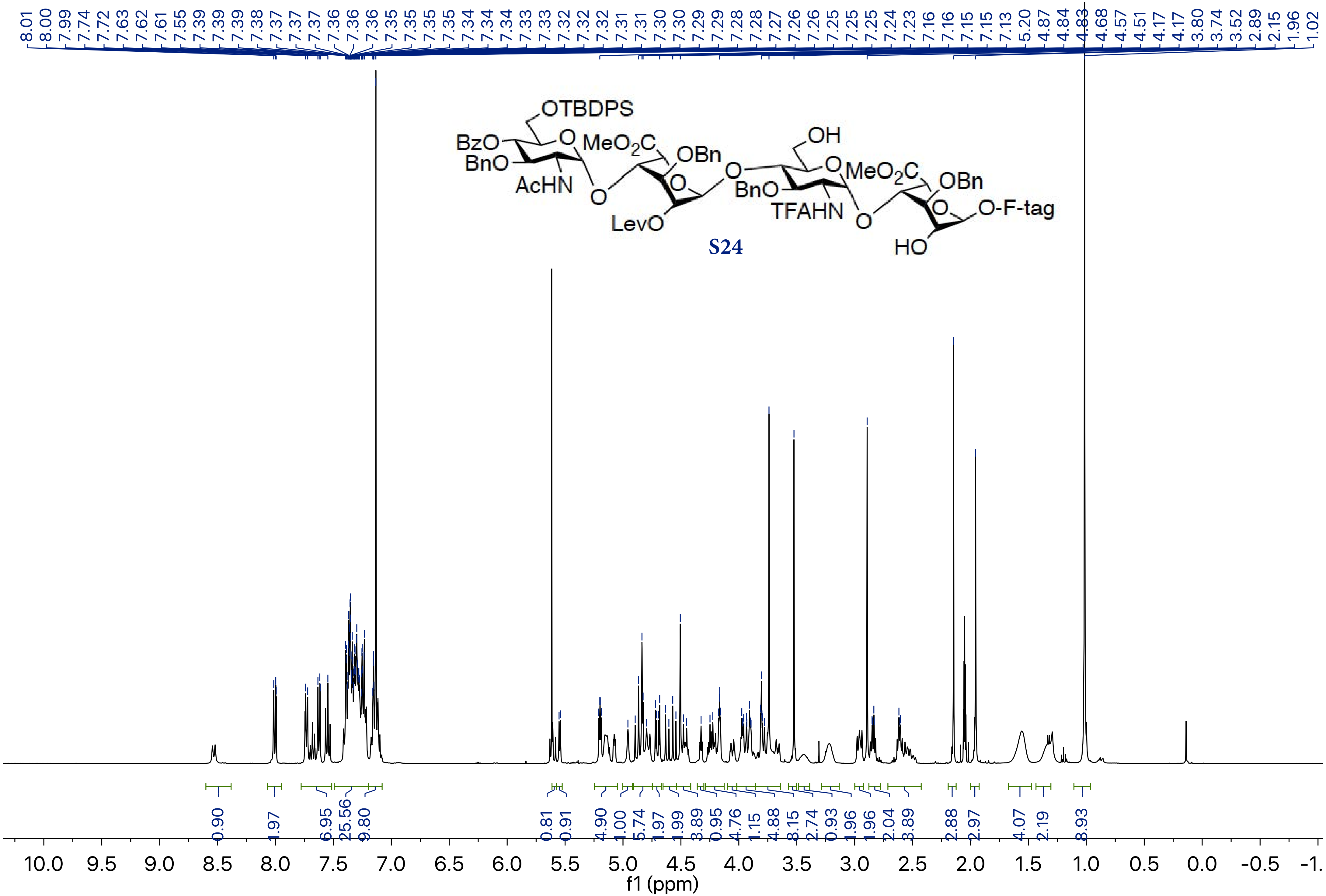
BSH-01-88.2.fid —

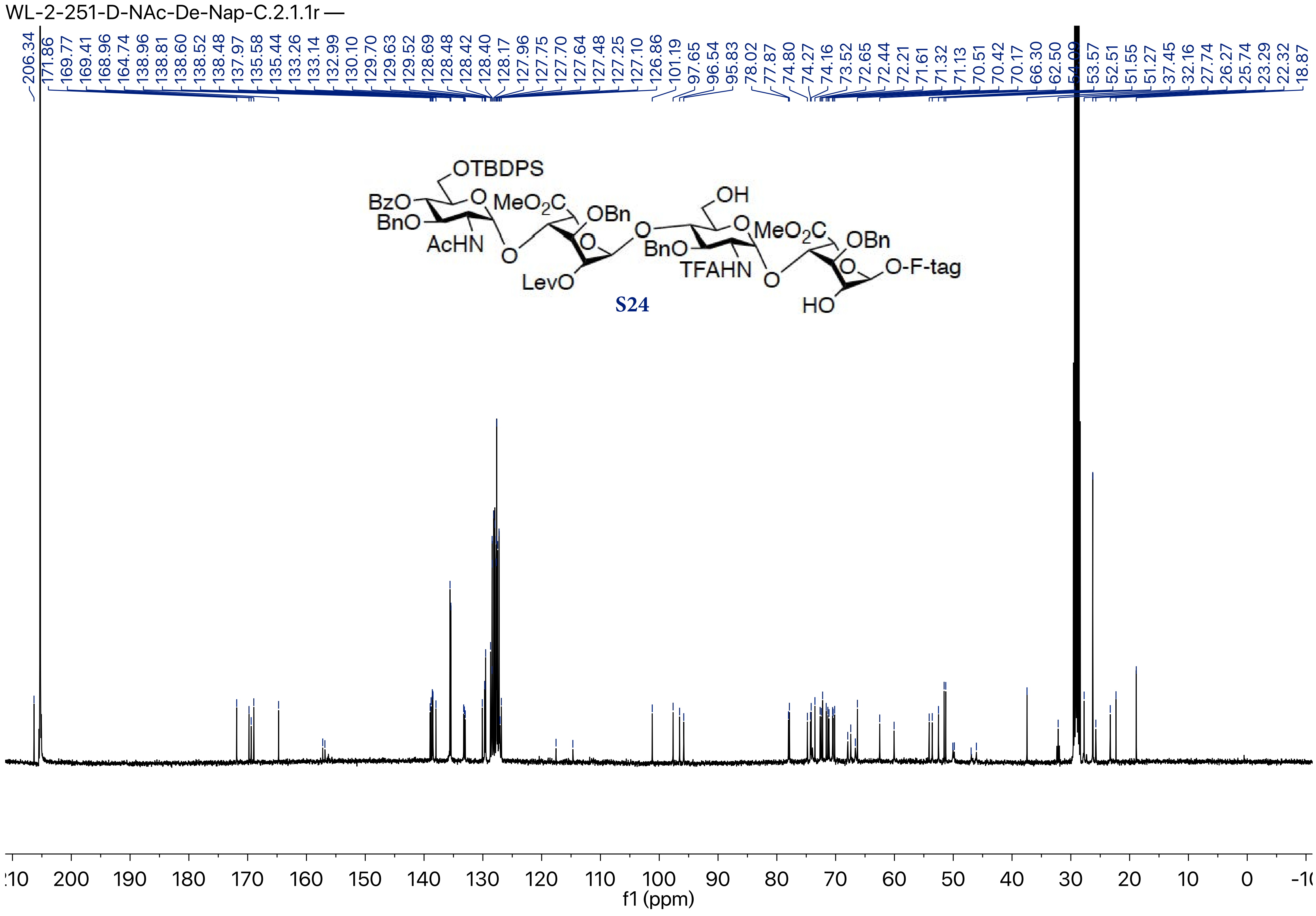



WL-2-123-prod.1.1.1r —
7.98 7.98 7.97 7.96 7.96 7.96 7.62 7.60 7.60 7.50 7.41 7.40 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.35 7.35 7.33 7.31 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.24 7.23 7.23 7.21 7.21 7.21 7.13 7.13 7.12 7.12 7.12 7.11 7.11 7.11 7.10 7.04 4.93 4.76 4.73 4.51 4.49 4.48 4.14 4.13 4.13 3.53 3.34 2.78 2.78 2.60 2.49 2.11 2.09 2.05 1.79 1.02
OTBDPS
BzO
BnO
AcHN
O
MeO2C
OBn
LevO
O
BnO
ONaph
TFAHN
MeO2C
OBn
O-F-tag
NaO3SO
S23
4.49 0.86 3.07 4.13 1.94 39.43 1.00 0.94 3.10 1.04 5.17 6.27 3.17 4.01 1.21 6.14 7.90 1.40 2.85 1.15 2.98 2.31 1.78 1.90 4.01 2.92 2.95 4.21 2.01 9.64
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 -0.5 -1.0
f1 (ppm)

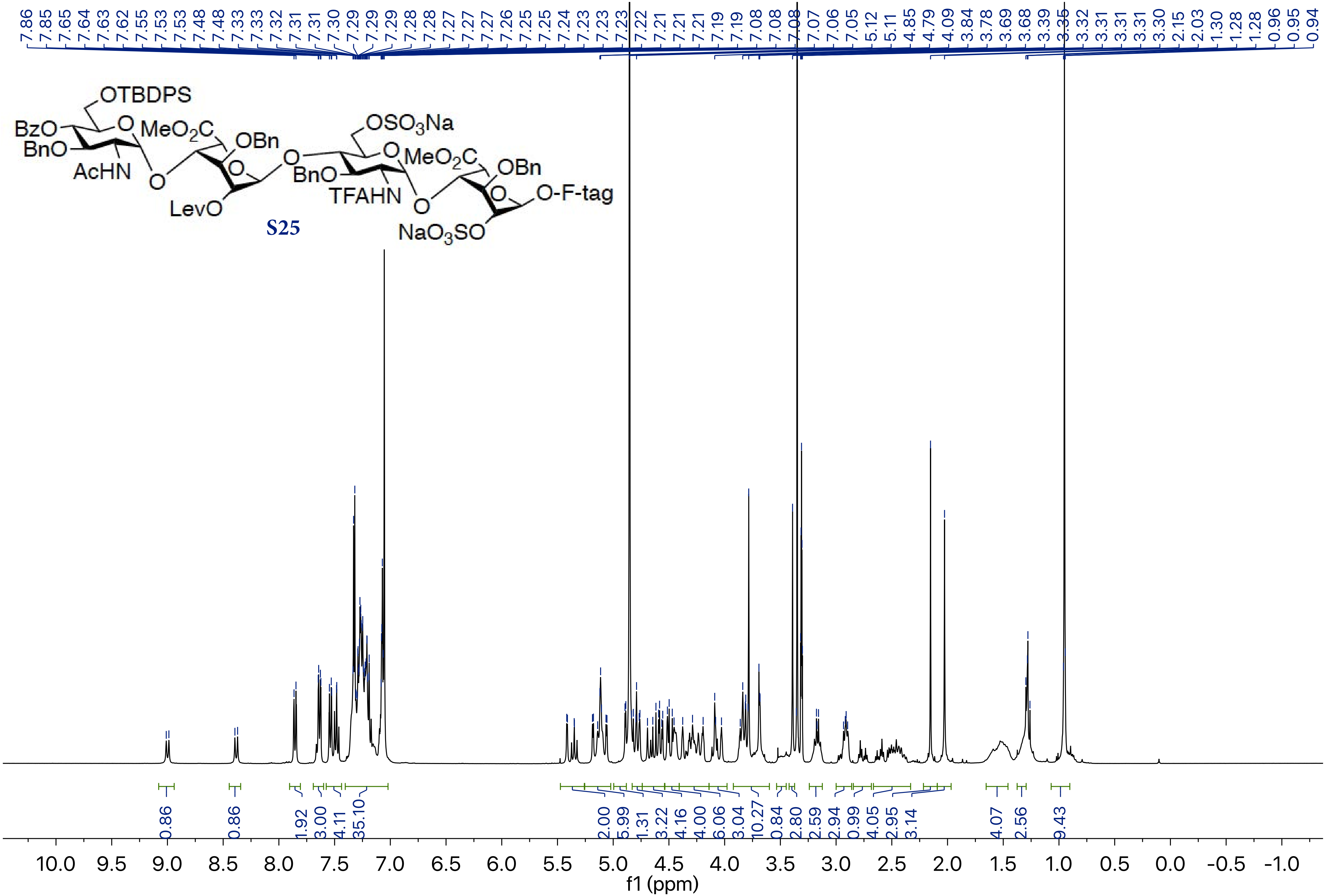

WL-2-123-prod.2.1.1r
171.94
169.39
168.71
164.71
139.37
138.73
138.59
137.79
136.41
135.62
135.46
133.48
133.21
133.10
133.00
132.98
130.13
129.74
129.64
129.48
128.67
128.56
128.48
128.42
128.18
128.04
128.01
127.96
127.91
127.76
127.73
127.64
127.55
127.38
127.28
127.18
126.53
126.16
126.00
125.98
125.71
100.06
97.60
78.06
77.30
74.80
73.23
72.78
72.69
71.87
71.28
70.35
67.66
66.32
62.30
54.59
52.54
51.15
51.11
37.34
35.29
31.12
29.42
27.71
26.29
25.73
23.33
18.87
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
NaO3SO
S23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

WL-2-251-D-NAc-De-Nap-H.1.1.1r —



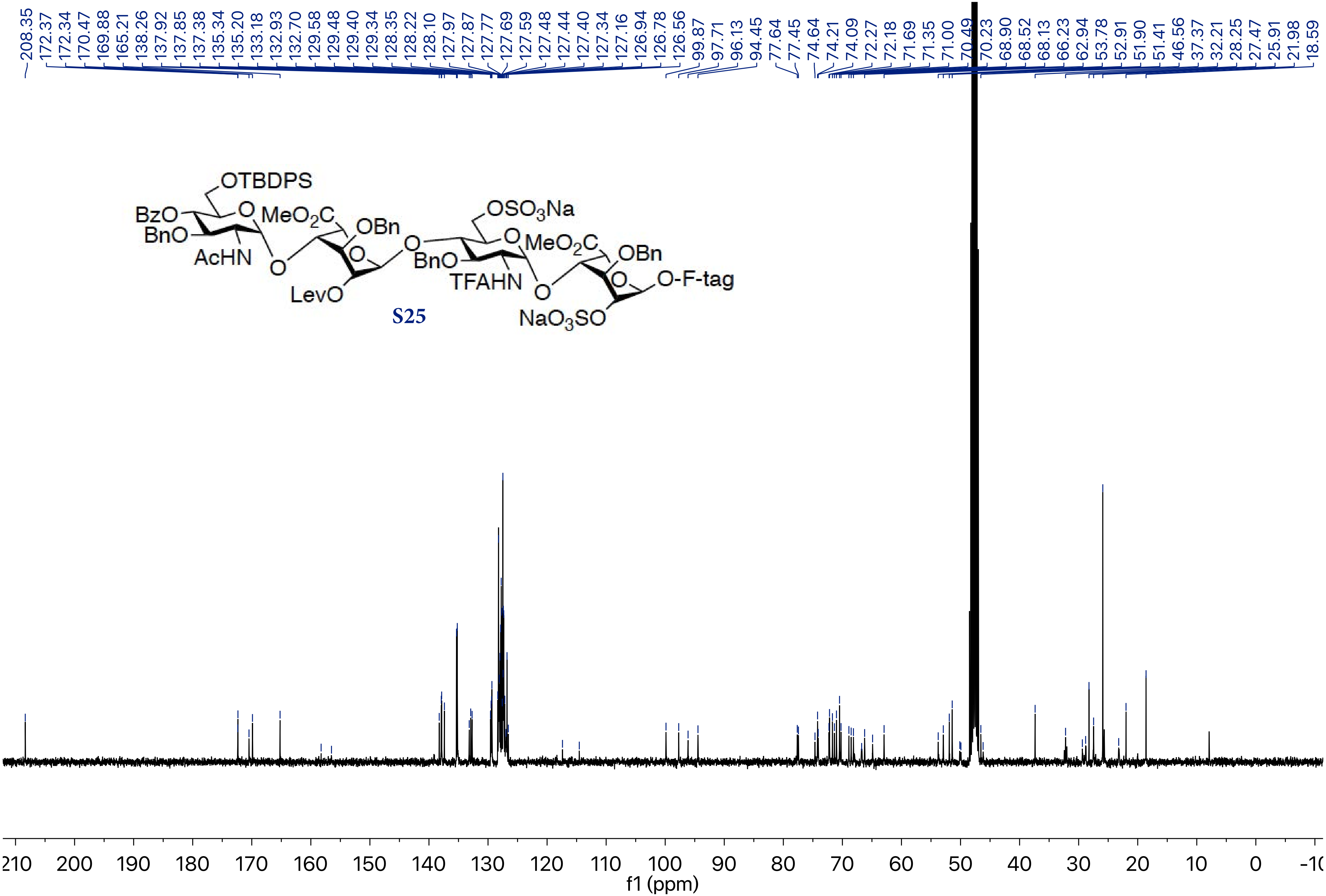

WL-2-251-D-NAc-De-Nap-C.2.1.1r
206.34
171.86
169.77
169.41
168.96
164.74
138.96
138.81
138.60
138.52
138.48
137.97
135.58
135.44
133.26
133.14
132.99
130.10
129.70
129.63
129.52
128.69
128.48
128.42
128.40
128.17
127.96
127.75
127.70
127.64
127.48
127.25
127.10
126.86
101.19
97.65
96.54
95.83
78.02
77.87
74.80
74.27
74.16
73.52
72.65
72.44
72.21
71.61
71.32
71.13
70.51
70.42
70.17
66.30
62.50
54.09
53.57
52.51
51.55
51.27
37.45
32.16
27.74
26.27
25.74
23.29
22.32
18.87
OTBDPS
BzO
BnO
AcHN
O
MeO2C
OBn
LevO
OH
BnO
TFAHN
OBn
O-F-tag
HO
f1 (ppm)
S24

WL-2-253-run2-D-NAc-B6-A2-Di-O-sulfation-H.1.1.1r —



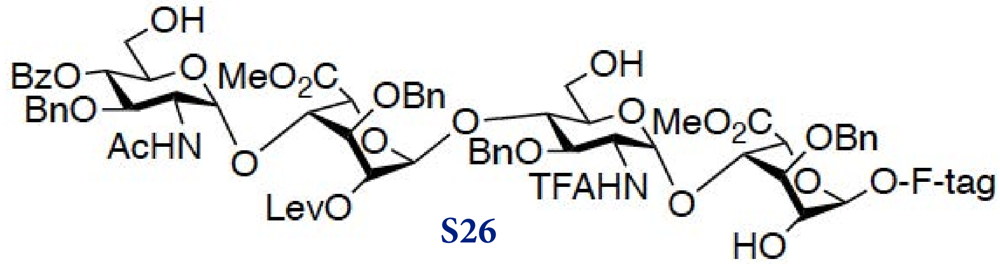
S25

WL-2-253-run2-D-NAc-B6-A2-Di-O-sulfation-C.2.1.1r

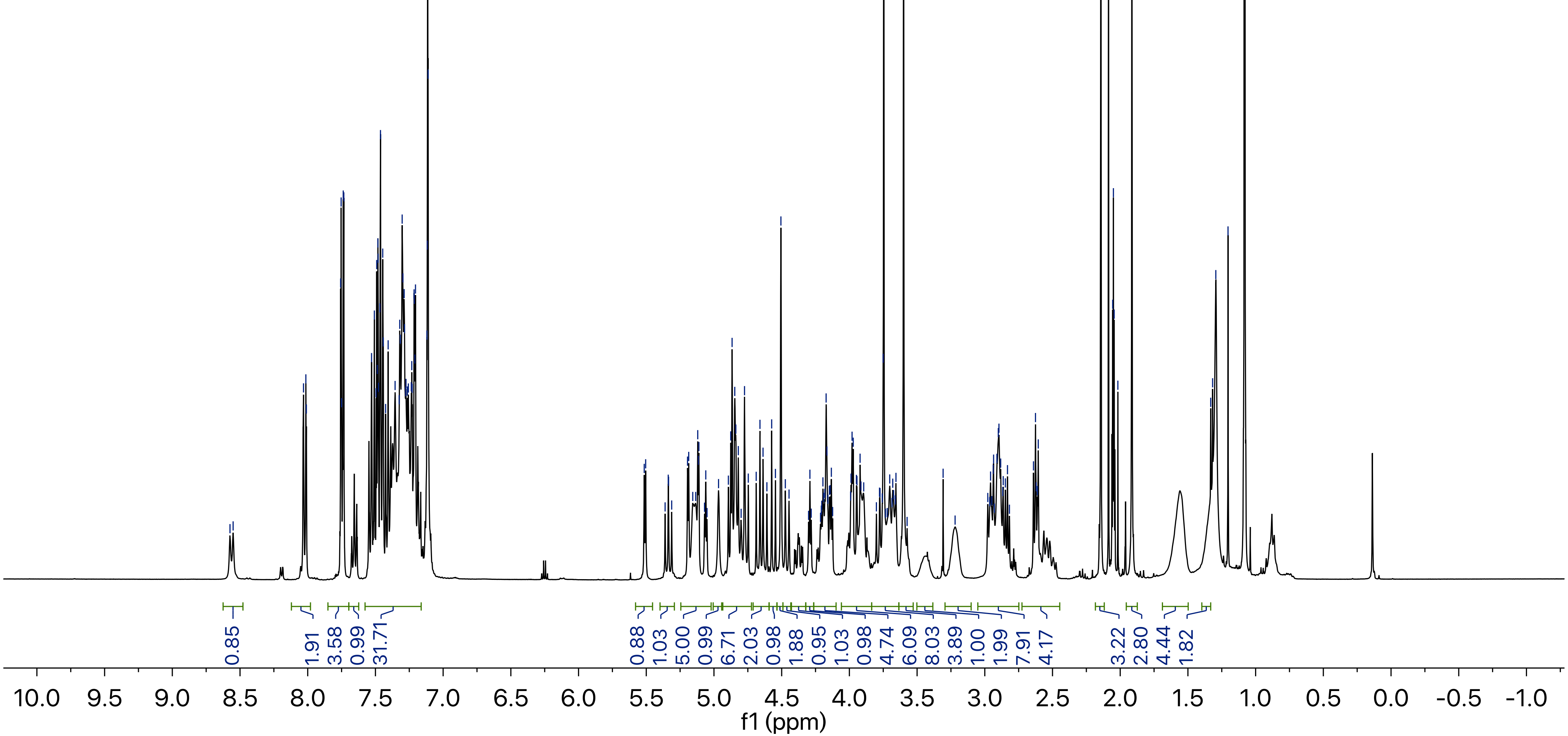


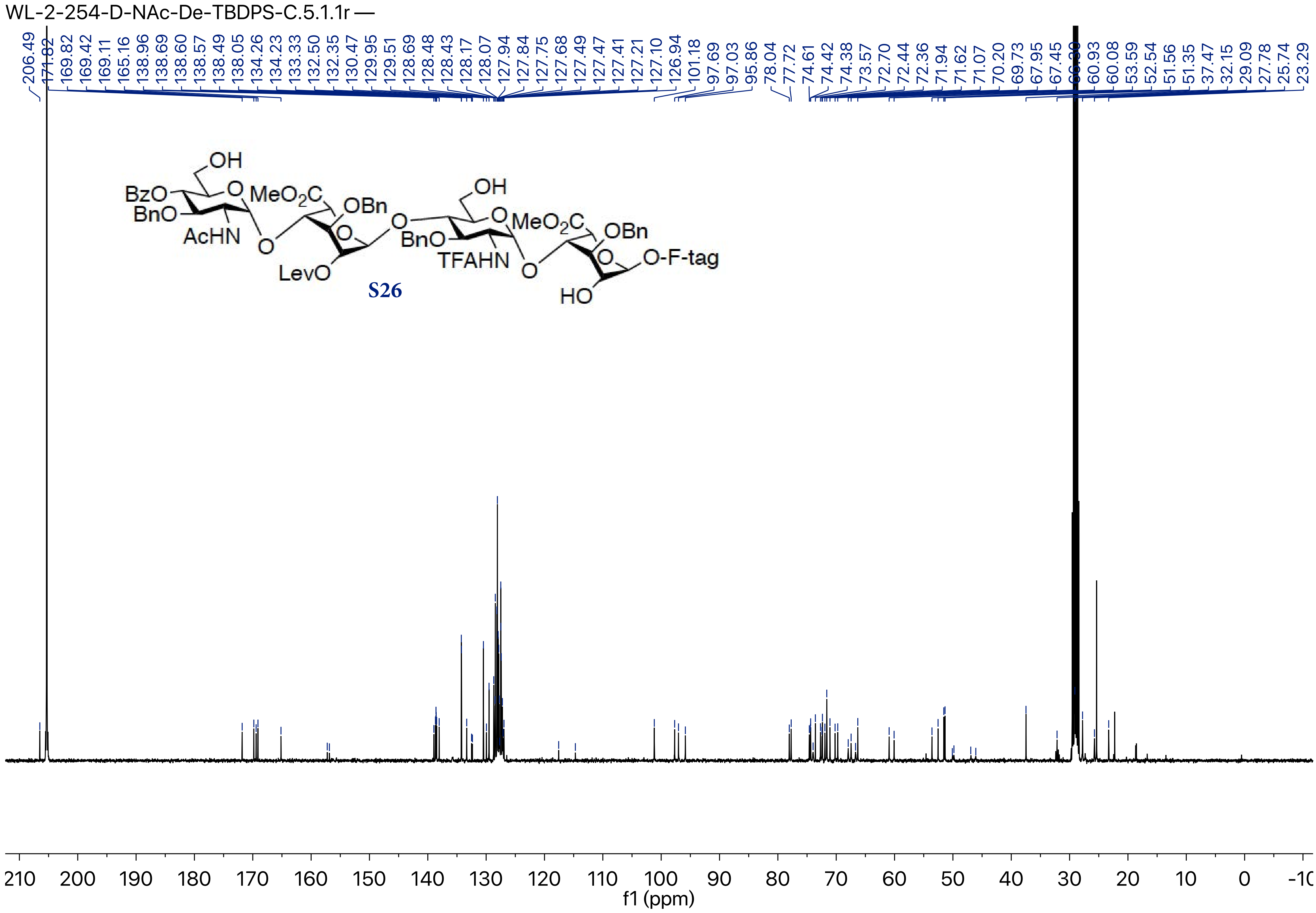
S25

WL-2-254-D-NAc-De-TBDPS-H.1.1.1r —



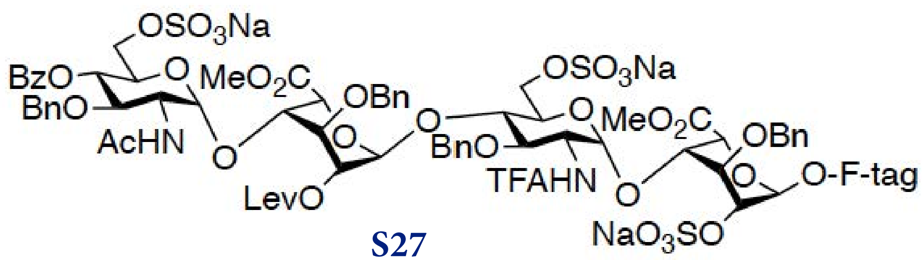
S26



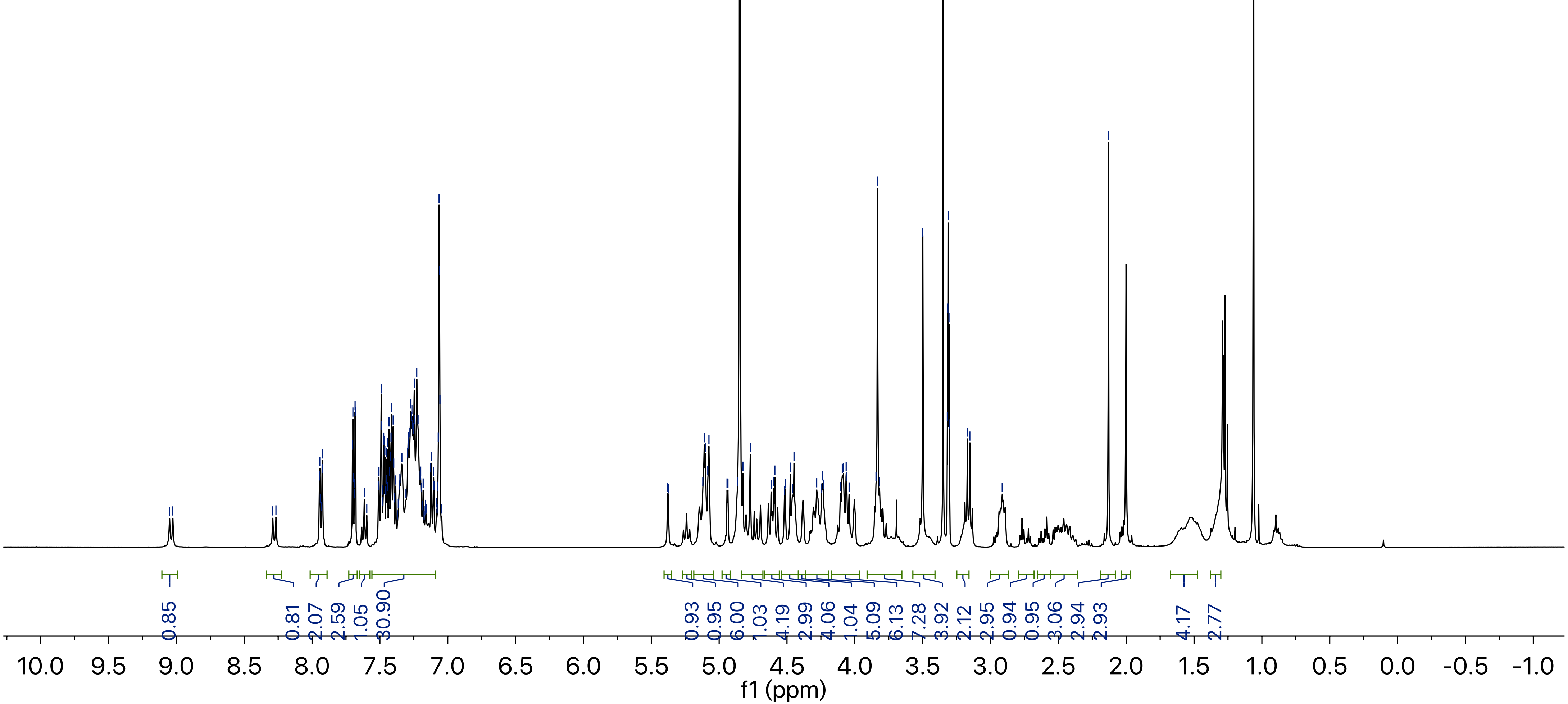

WL-2-254-D-NAc-De-TBDPS-C.5.1.1r —
206.49
171.82
169.82
169.42
169.11
165.16
138.96
138.69
138.60
138.57
138.49
138.05
134.26
134.23
133.33
132.50
132.35
130.47
129.95
129.51
128.69
128.48
128.43
128.17
128.07
127.94
127.84
127.75
127.68
127.49
127.47
127.41
127.21
127.10
126.94
101.18
97.69
97.03
95.86
78.04
77.72
74.61
74.42
74.38
73.57
72.70
72.44
72.36
71.94
71.62
71.07
70.20
69.73
67.95
67.45
66.30
60.93
60.08
53.59
52.54
51.56
51.35
37.47
32.15
29.09
27.78
25.74
23.29
OH
BzO
BnO
O
MeO2C
OBn
AcHN
O
LevO
O
OH
BnO
O
MeO2C
OBn
TFAHN
O
O
O-F-tag
HO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S26

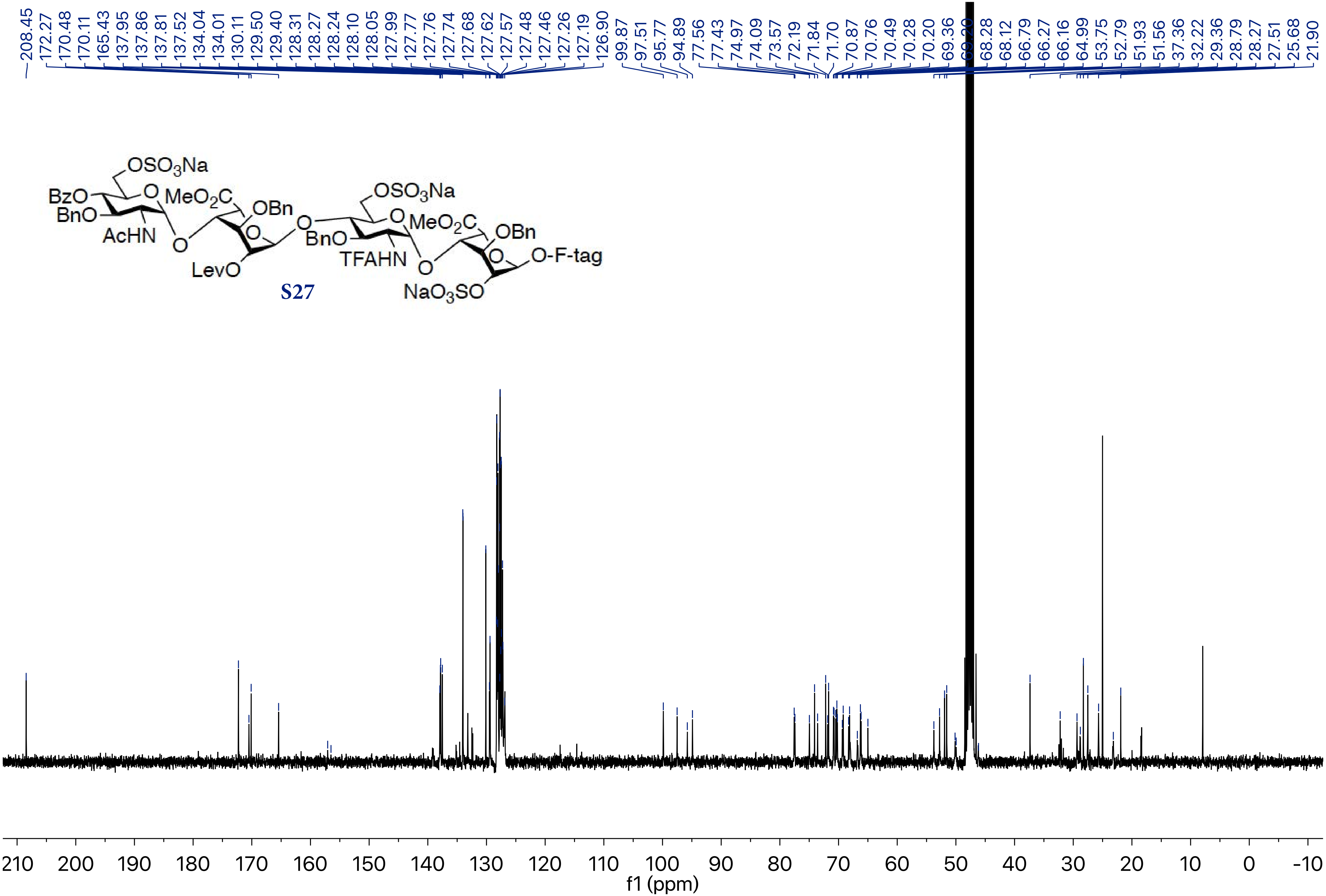
WL-2-255-D-NAc-D6-B6-A2-Tri-O-Sulfation-H.1.1.1r —



S27

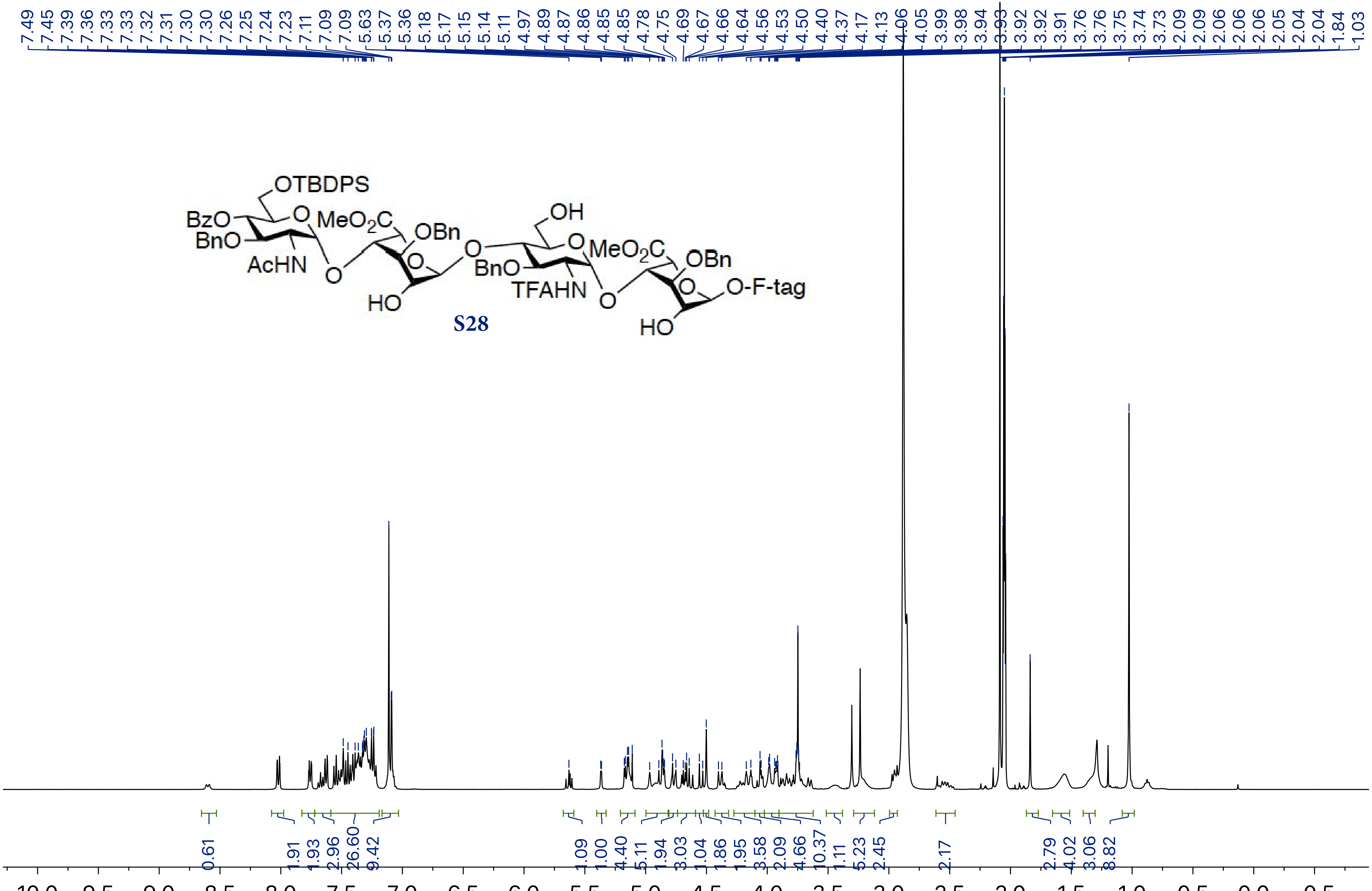


WL-2-255-D-NAc-D6-B6-A2-Tri-O-Sulfation-C.5.1.1r



S27

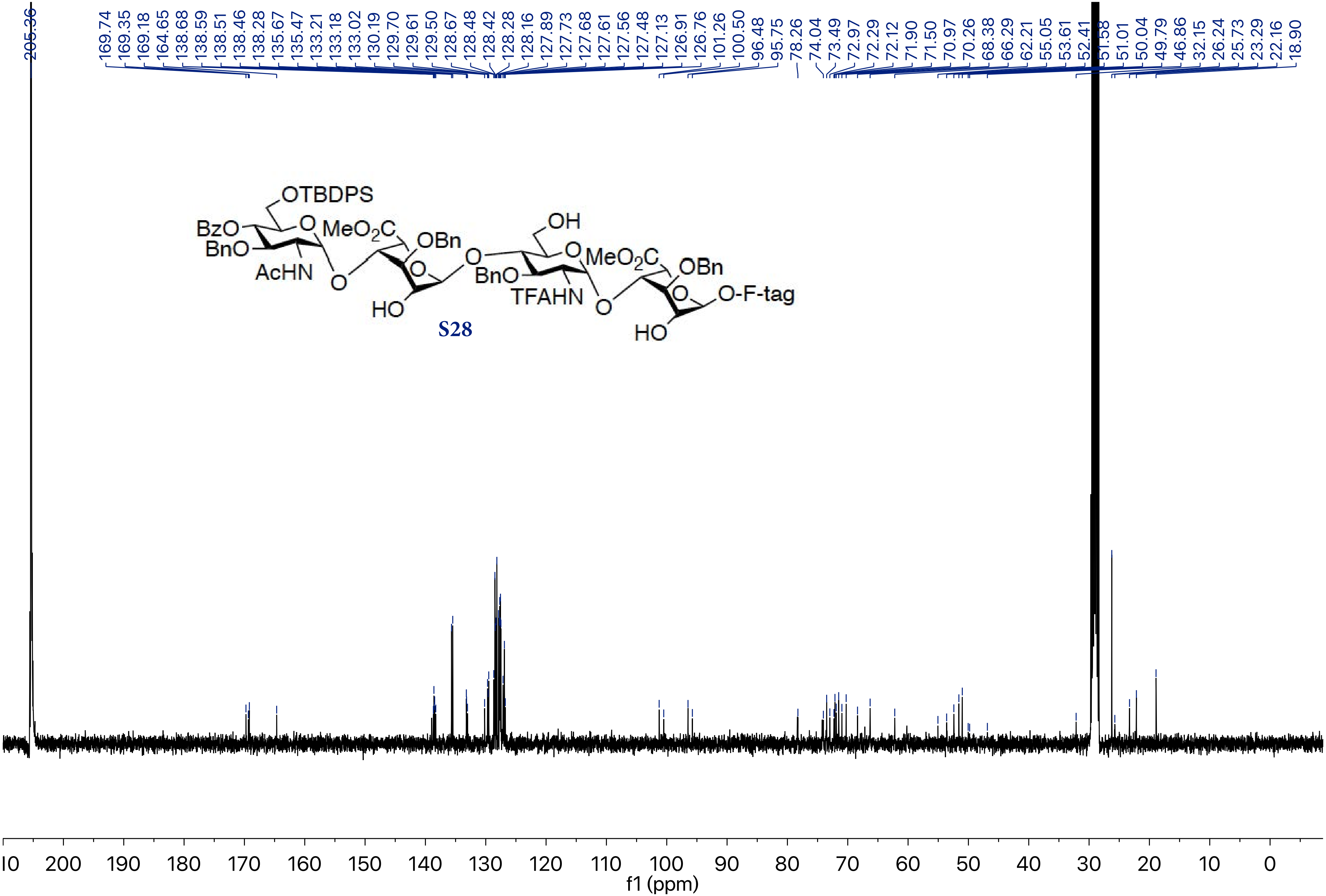
WL-2-138-De-Nap-H.3.1.1r



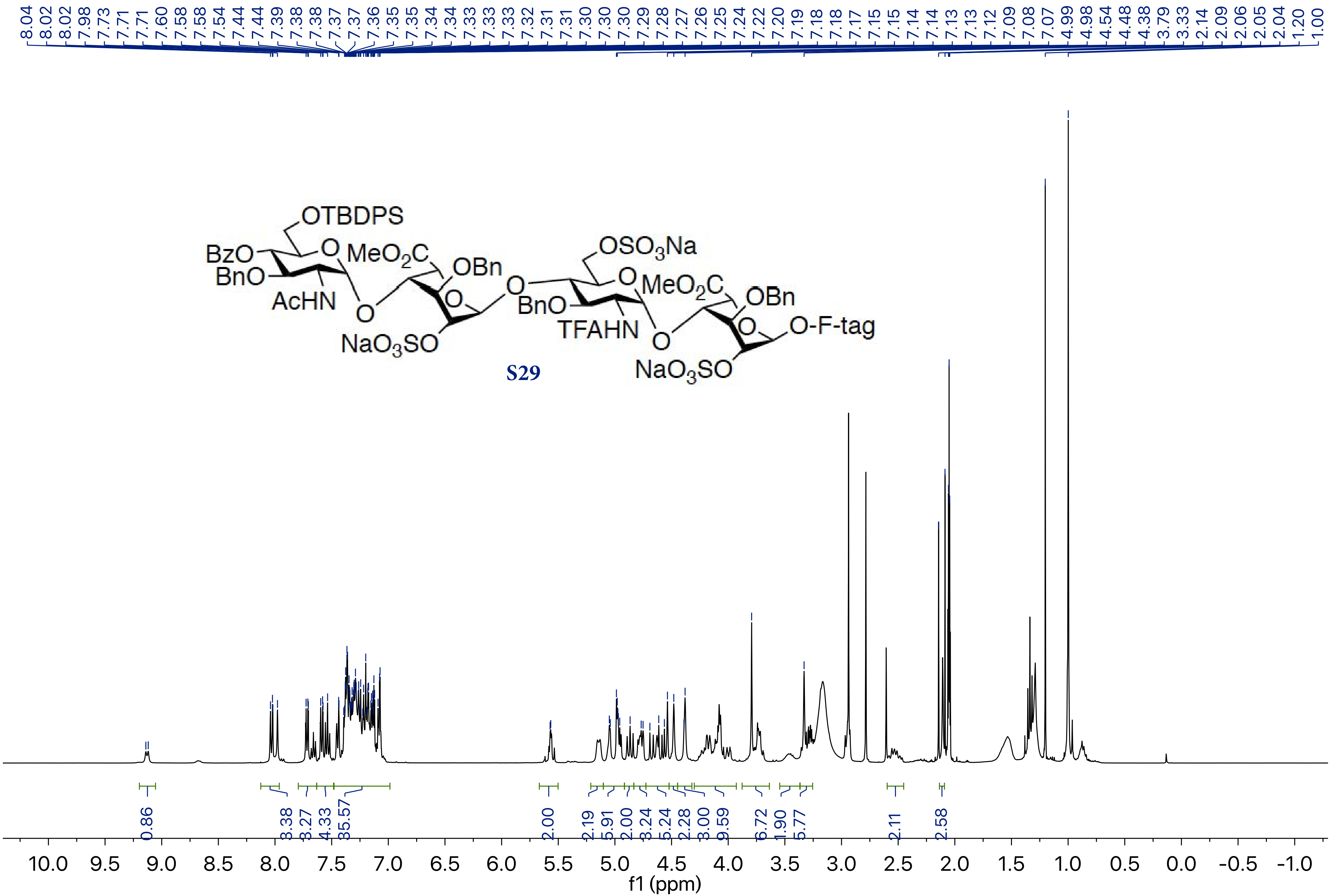
S28

f1 (ppm)

WL-2-138-De-Nap-C.2.1.1r —

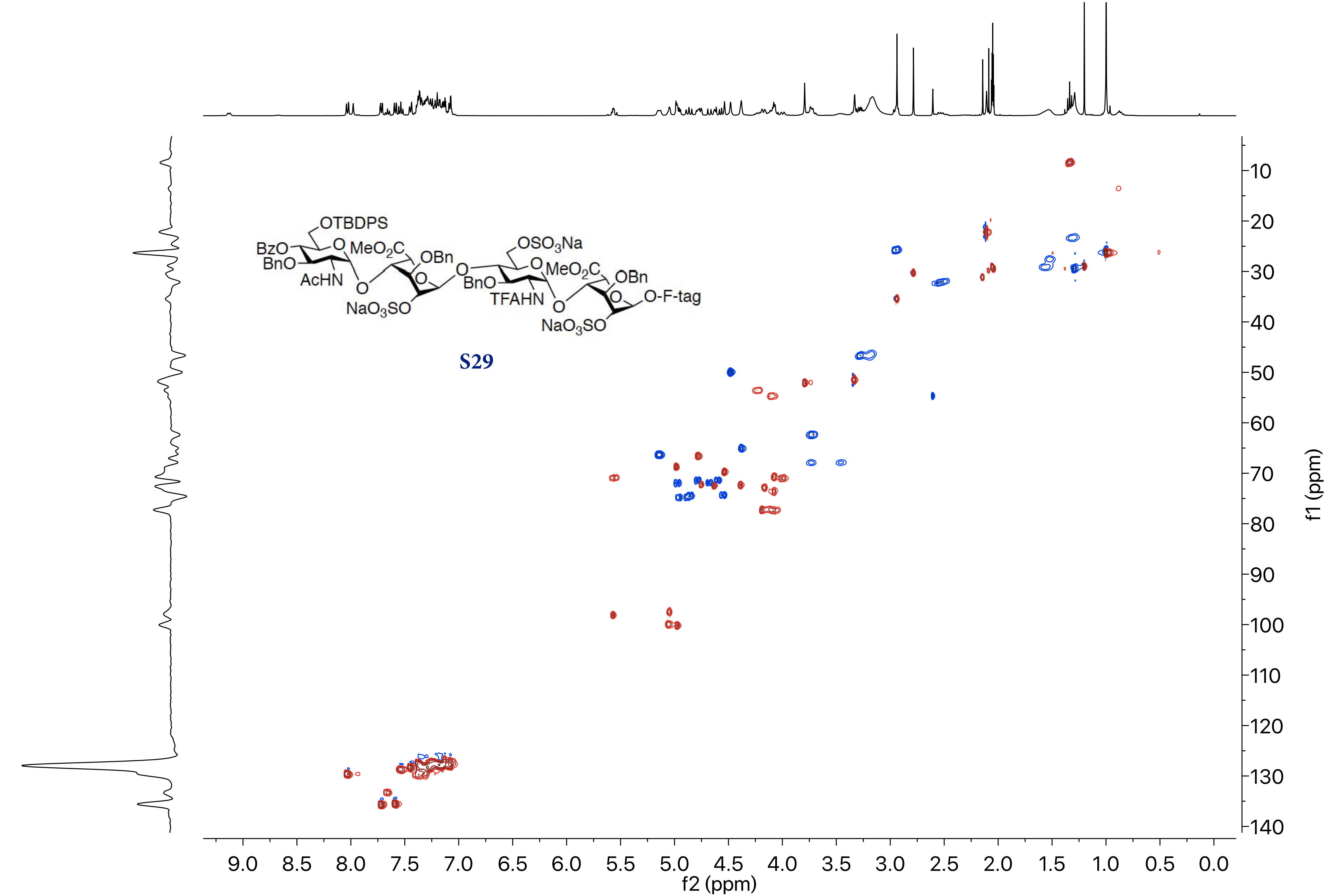


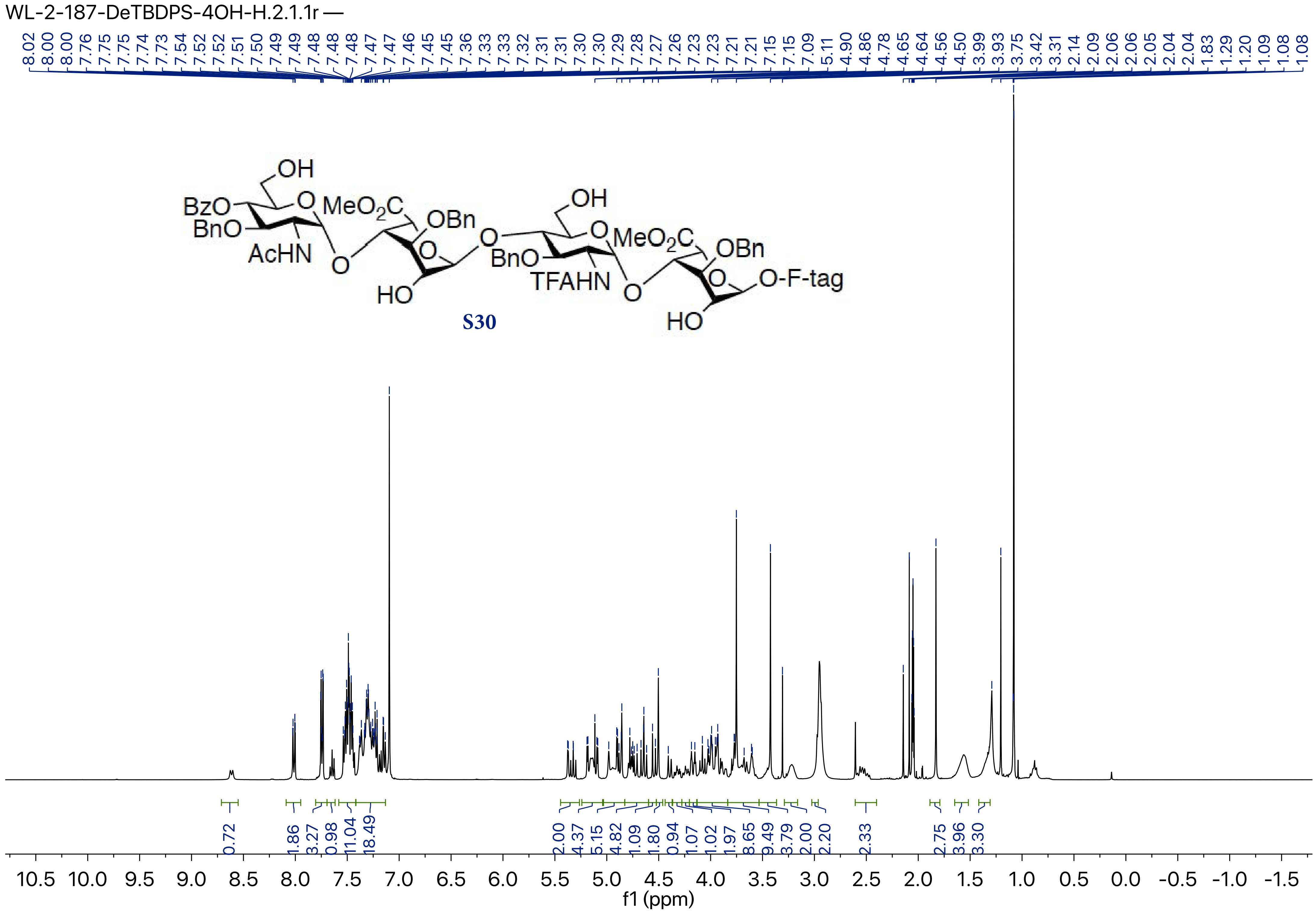
WL-2-186-C2-B6-A2-tri-sulfation.1.1.1r

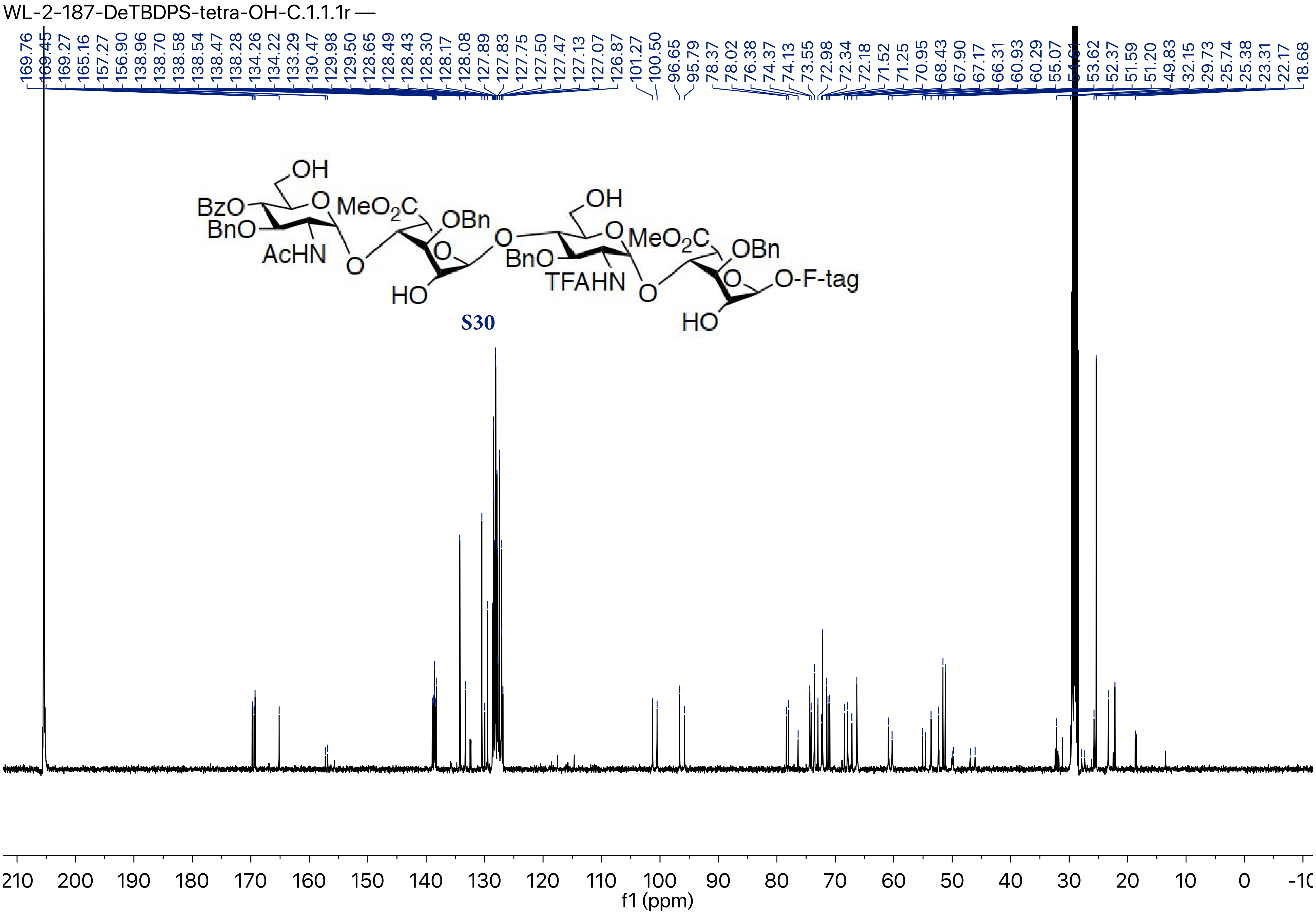


S29

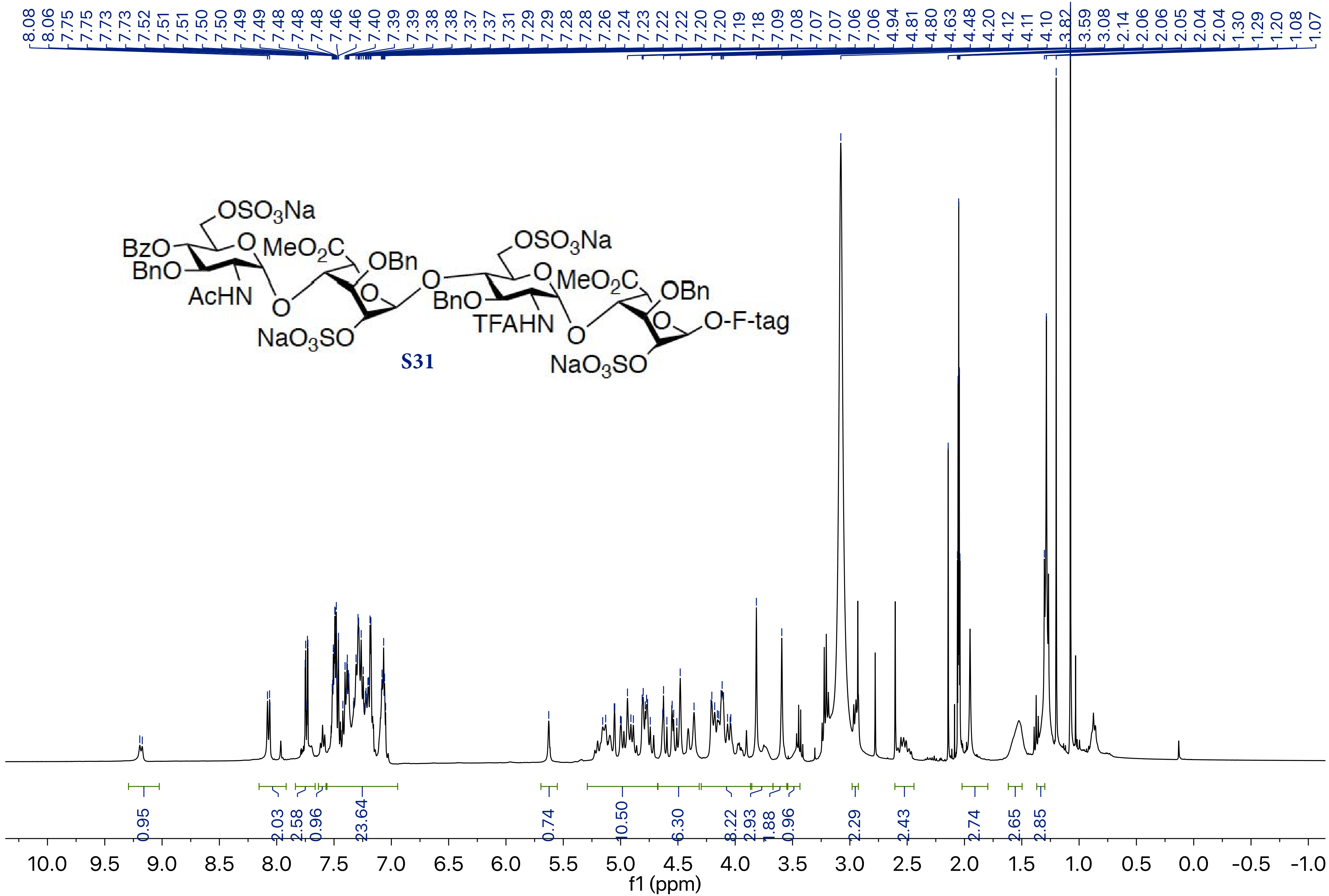
WL-2-186-C2-B6-A2-tri-sulfation.2.1.2rr




WL-2-187-DeTBDPS-4OH-H.2.1.1r
8.02 8.00 8.00 7.76 7.75 7.75 7.74 7.73 7.54 7.52 7.52 7.51 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.36 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.26 7.23 7.23 7.21 7.21 7.15 7.15 7.09 5.11 4.90 4.86 4.78 4.65 4.64 4.56 4.50 3.99 3.93 3.75 3.42 3.31 2.14 2.09 2.06 2.06 2.05 2.04 2.04 1.83 1.29 1.20 1.09 1.08 1.08
BzO
BnO
AcHN
OH
O
MeO2C
OBn
HO
BnO
TFAHN
O-F-tag
S30
0.72 1.86 3.27 0.98 11.04 18.49 2.00 4.37 5.15 4.82 1.09 1.80 0.94 1.07 1.02 1.97 8.65 9.49 3.79 2.00 2.20 2.33 2.75 3.96 3.30
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 -0.5 -1.0 -1.5
f1 (ppm)

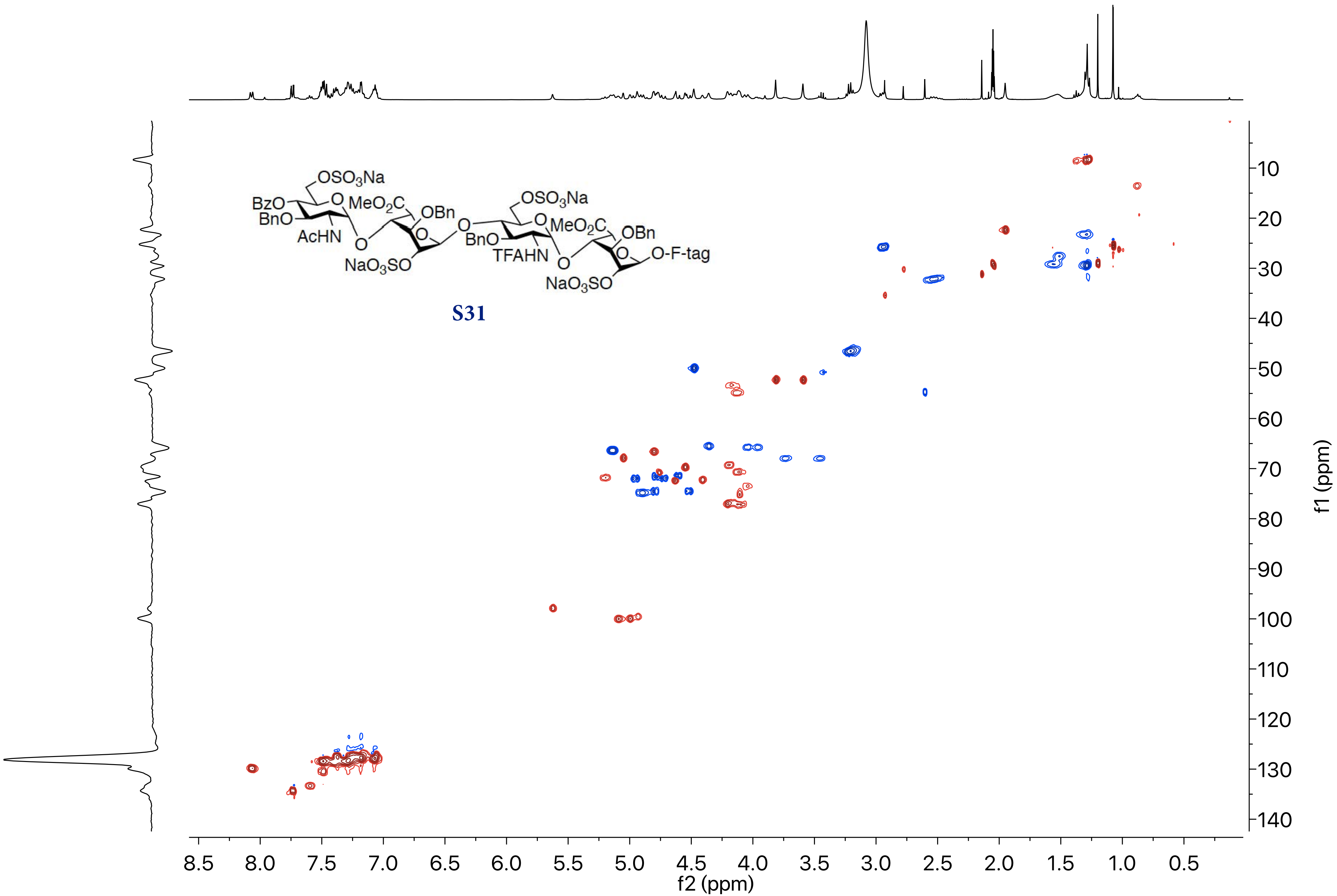

WL-2-187-DeTBDPS-tetra-OH-C.1.1.1r
169.76
169.45
169.27
165.16
157.27
156.90
138.96
138.70
138.58
138.54
138.47
138.28
134.26
134.22
133.29
130.47
129.98
129.50
128.65
128.49
128.43
128.30
128.17
128.08
127.89
127.83
127.75
127.50
127.47
127.13
127.07
126.87
101.27
100.50
96.65
95.79
78.37
78.02
76.38
74.37
74.13
73.55
72.98
72.34
72.18
71.52
71.25
70.95
68.43
67.90
67.17
66.31
60.93
60.29
55.07
54.61
53.62
52.37
51.59
51.20
49.83
32.15
29.73
25.74
25.38
23.31
22.17
18.68
OH
BzO
BnO
O
AcHN
O
MeO_2C
OBn
O
HO
O
OH
BnO
O
TFAHN
O
MeO_2C
OBn
O
O-F-tag
HO
S30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-189-Tetra-O-sulfation.1.1.1r —

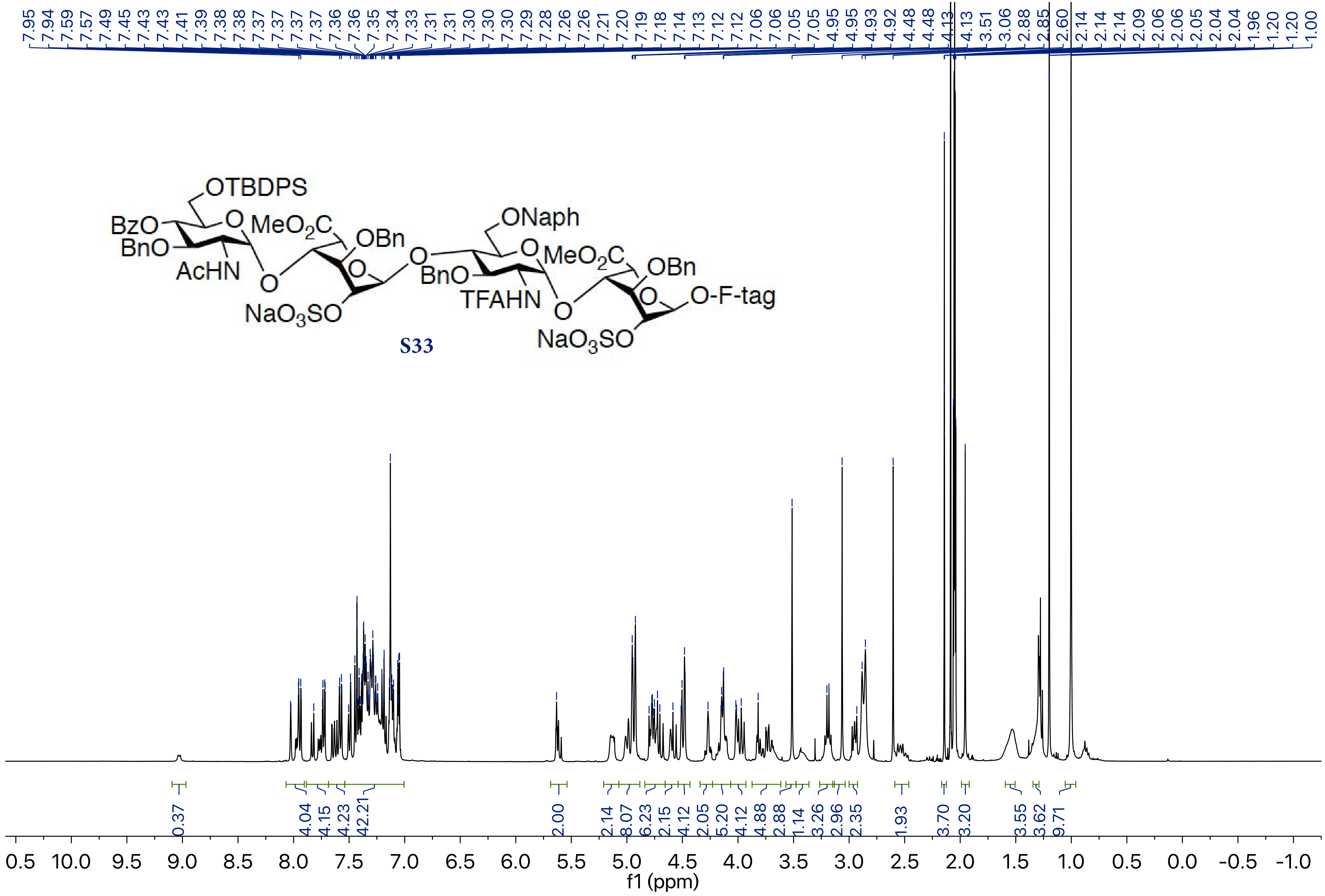


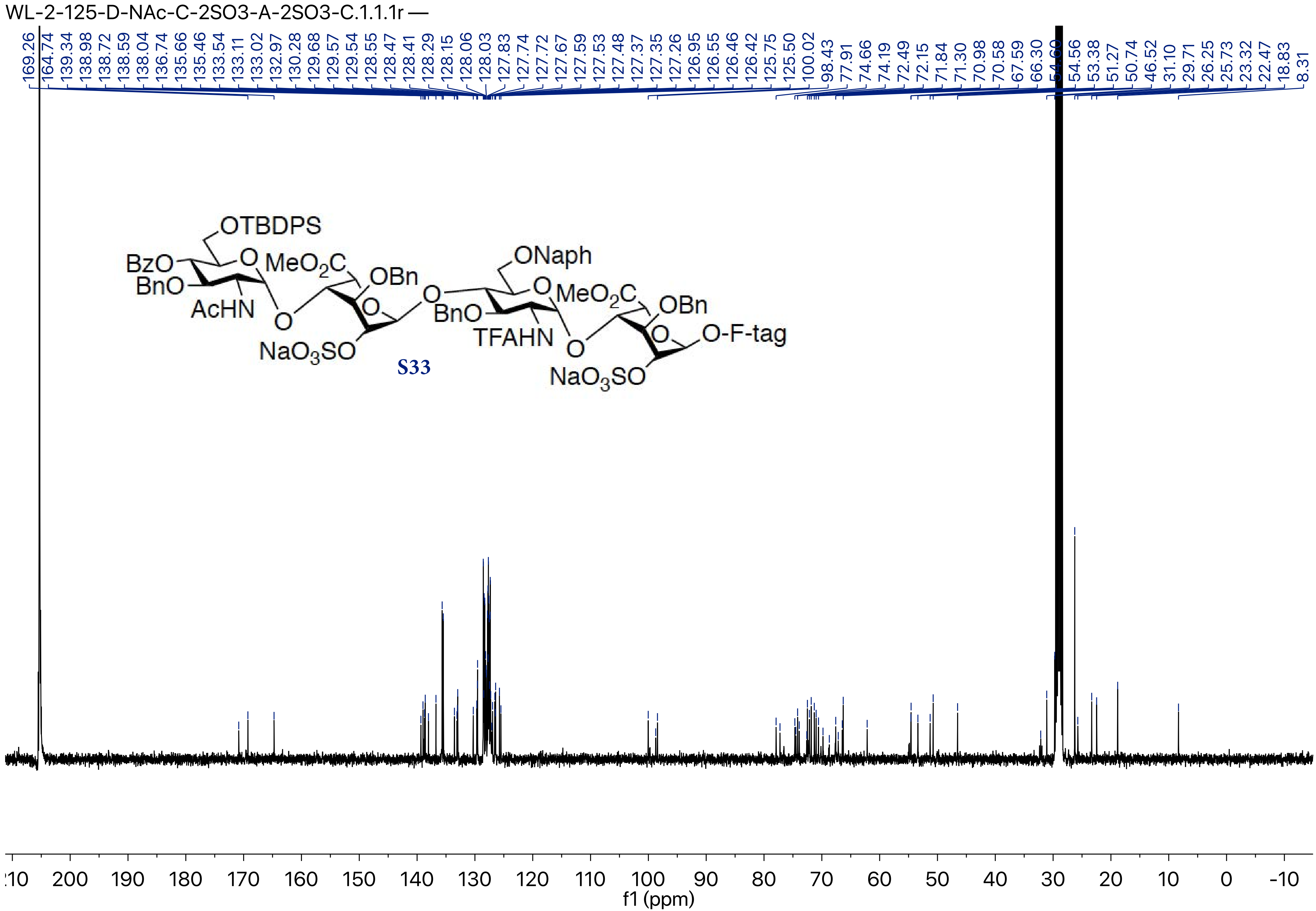
S31

WL-2-189-Tetra-O-sulfation.2.1.2rr —

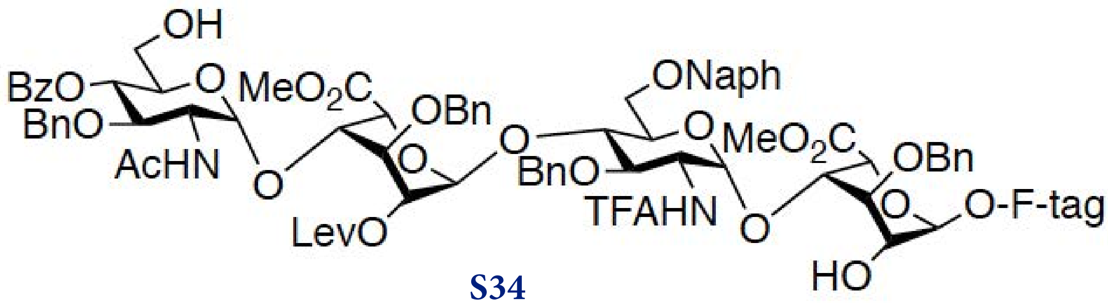


WL-2-125-D-NAc-C-2SO3-A-2SO3-COSY.2.1.1r

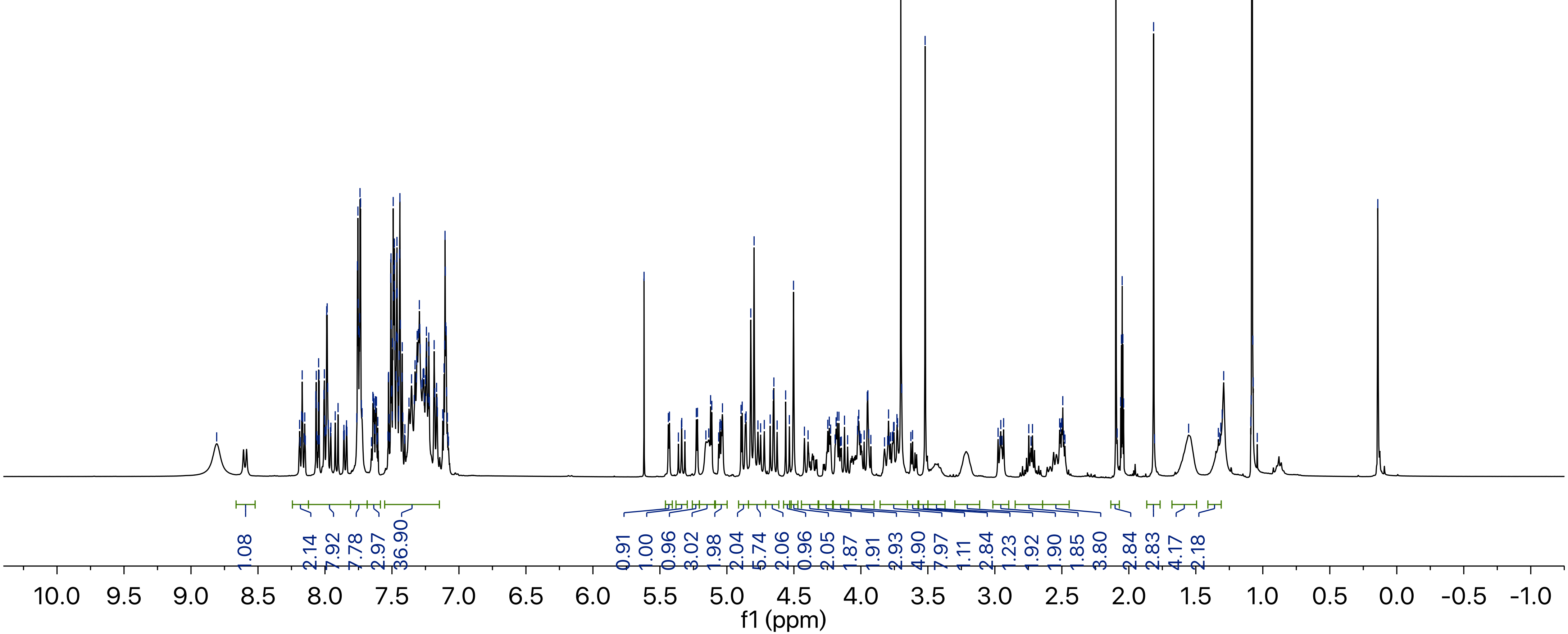


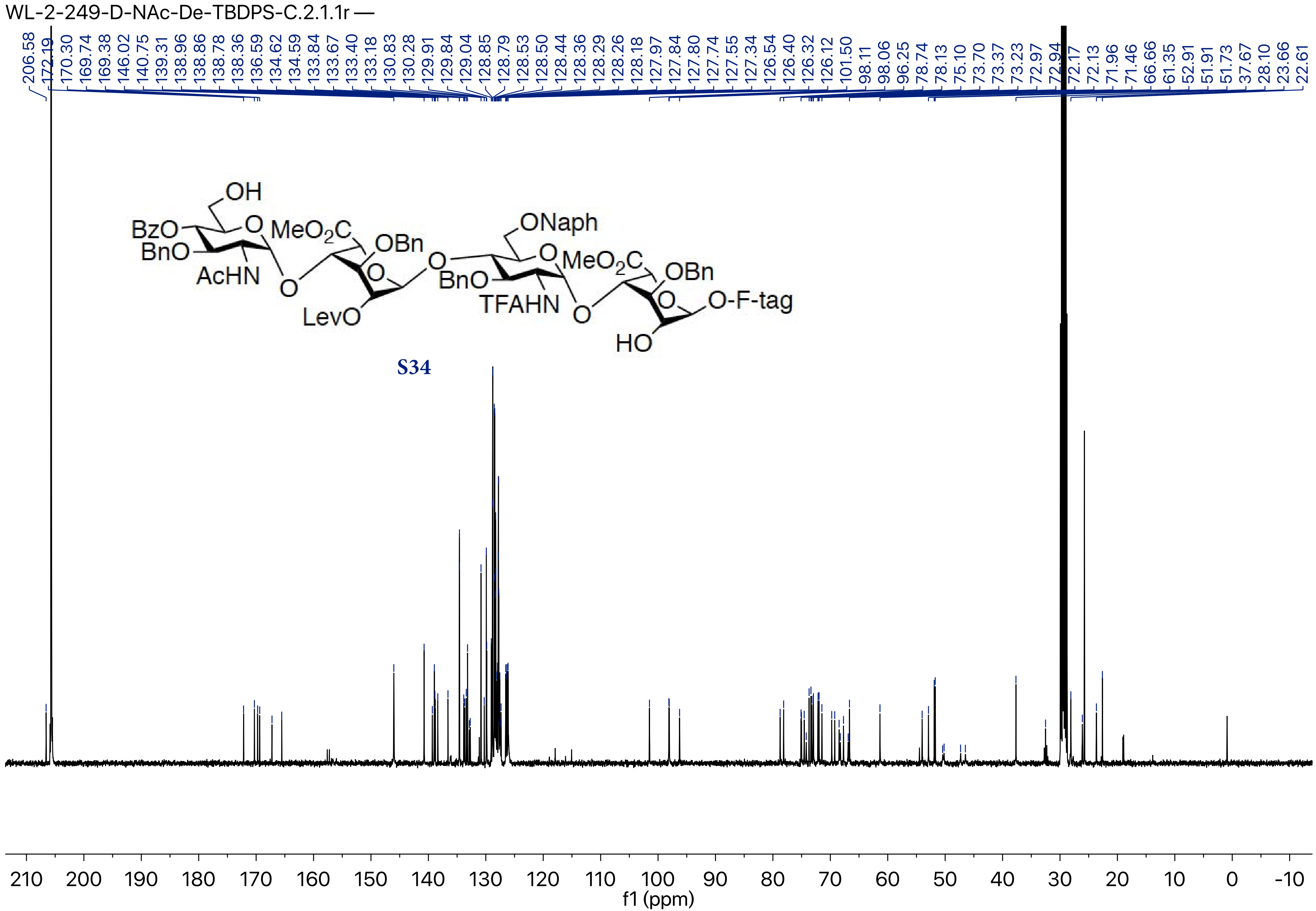

WL-2-125-D-NAc-C-2SO3-A-2SO3-C.1.1.1r
169.26 164.74 139.34 138.98 138.72 138.59 138.04 136.74 135.66 135.46 133.54 133.11 133.02 132.97 130.28 129.68 129.57 129.54 128.55 128.47 128.41 128.29 128.15 128.06 128.03 127.83 127.74 127.72 127.67 127.59 127.53 127.48 127.37 127.35 127.26 126.95 126.55 126.46 126.42 125.75 125.50 100.02 98.43 77.91 74.66 74.19 72.49 72.15 71.84 71.30 70.98 70.58 67.59 66.30 54.60 54.56 53.38 51.27 50.74 46.52 31.10 29.71 26.25 25.73 23.32 22.47 18.83 8.31
OTBDPS
BzO
BnO
AcHN
O
MeO2C
OBn
NaO3SO
S33
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
NaO3SO
f1 (ppm)

WL-2-249-D-NAc-De-TBDPS-H.1.1.1r —

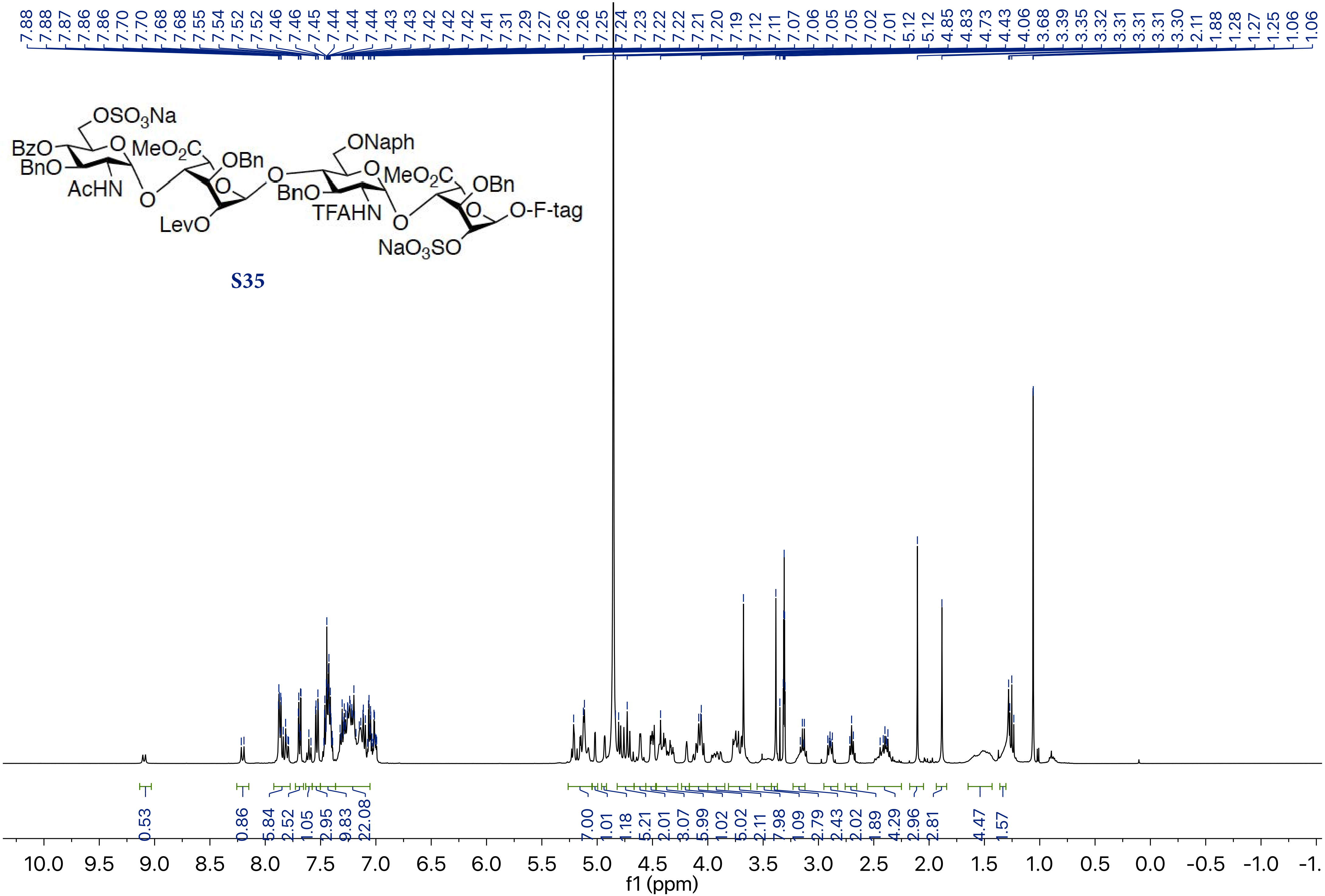


S34

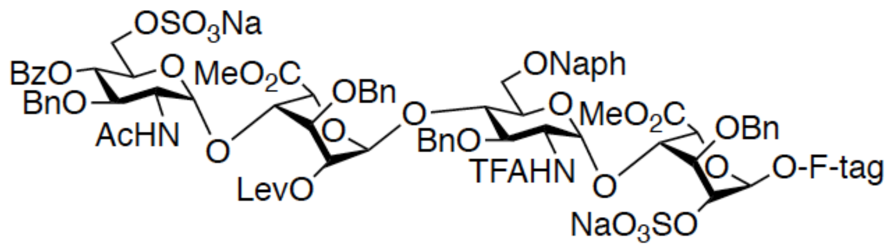



WL-2-249-D-NAc-De-TBDPS-C.2.1.1r
206.58
172.19
170.30
169.74
169.38
146.02
140.75
139.31
138.96
138.86
138.78
138.36
136.59
134.62
134.59
133.84
133.67
133.40
133.18
130.83
130.28
129.91
129.84
129.04
128.85
128.79
128.53
128.50
128.44
128.36
128.29
128.26
128.18
127.97
127.84
127.80
127.74
127.55
127.34
126.54
126.40
126.32
126.12
101.50
98.11
98.06
96.25
78.74
78.13
75.10
73.70
73.37
73.23
72.97
72.94
72.17
72.13
71.96
71.46
66.66
61.35
52.91
51.91
51.73
37.67
28.10
23.66
22.61
OH
BzO
BnO
O
AcHN
MeO2C
OBn
O
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
HO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

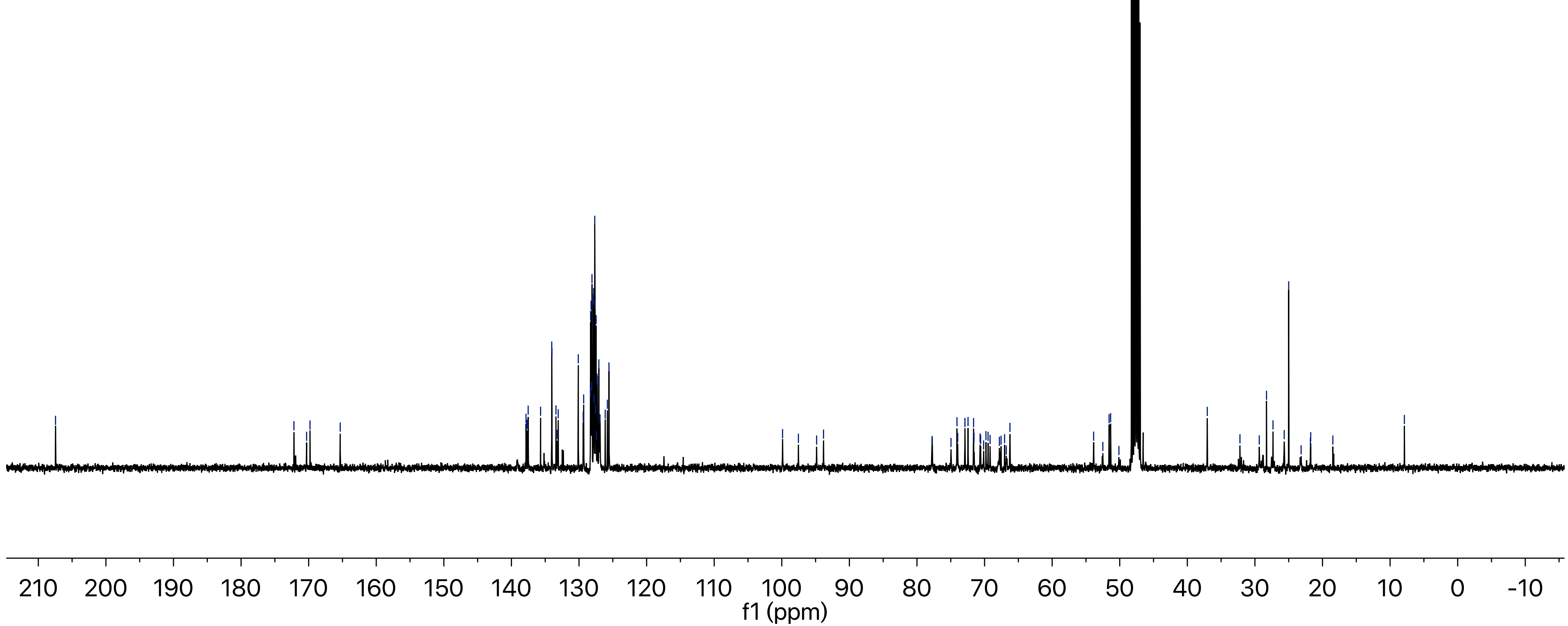
S34


WL-2-250-run2-D-NAc-D6-A2-disulfation-H.1.1.1r
7.88 7.88 7.87 7.86 7.86 7.70 7.70 7.68 7.68 7.55 7.54 7.52 7.52 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.31 7.29 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.12 7.11 7.07 7.06 7.05 7.05 7.02 7.01 5.12 5.12 4.85 4.83 4.73 4.43 4.06 3.68 3.39 3.35 3.32 3.31 3.31 3.31 3.30 2.11 1.88 1.28 1.27 1.25 1.06 1.06
OSO3Na
BzO
BnO
AcHN
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
NaO3SO
0.53 0.86 5.84 2.52 1.05 2.95 9.83 22.08 7.00 1.01 1.18 5.21 2.01 3.07 5.99 1.02 5.02 2.11 7.98 1.09 2.79 2.43 2.02 1.89 4.29 2.96 2.81 4.47 1.57
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 -0.5 -1.0 -1.
f1 (ppm)

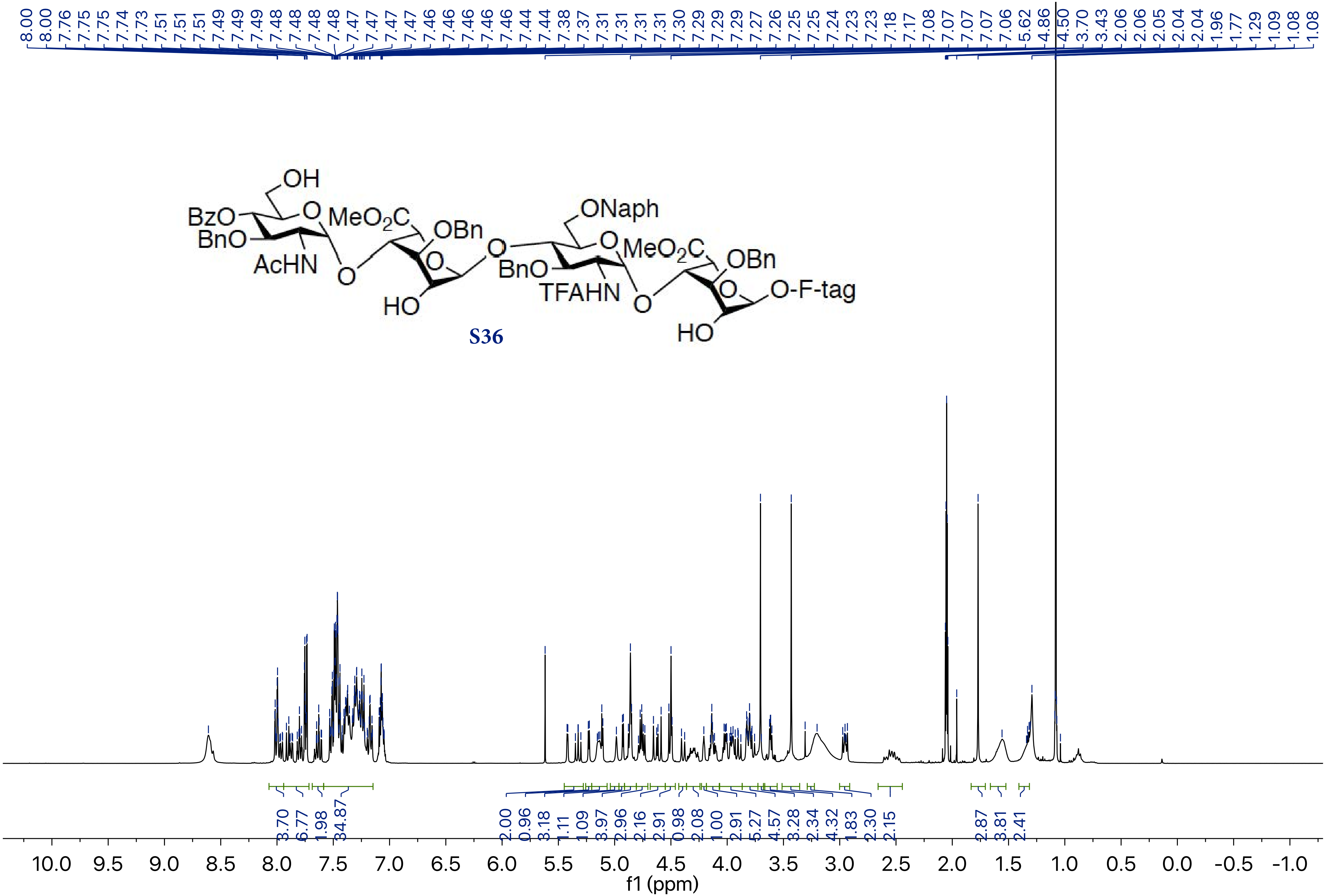
S35


OSO3Na
BzO
BnO
AcHN
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
MeO2C
OBn
O-F-tag
NaO3SO

S35

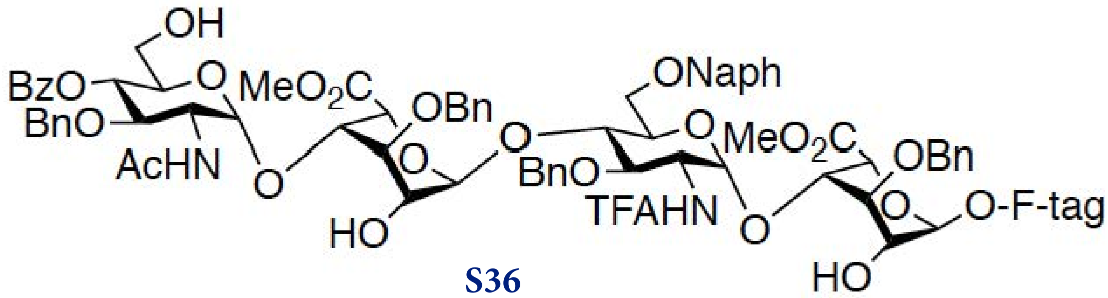

WL-2-250-run2-D-NAc-D6-A2-disulfation-C-2.1.1.1r
207.45
172.18
170.31
169.80
165.33
137.84
137.75
137.61
137.52
135.69
134.04
134.01
133.41
133.21
133.08
130.11
129.38
129.31
128.31
128.29
128.22
128.12
128.08
127.88
127.84
127.77
127.67
127.62
127.56
127.47
127.44
127.33
127.28
127.07
126.89
126.13
125.81
125.57
99.88
97.54
94.85
93.83
74.08
73.97
72.90
72.44
71.62
71.56
70.67
70.58
69.79
69.48
69.18
67.04
66.24
53.86
51.57
51.35
37.05
32.21
29.36
28.29
27.32
25.67
25.00
21.74
18.47
7.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

WL-2-139-DeTBDPS.1.fid —

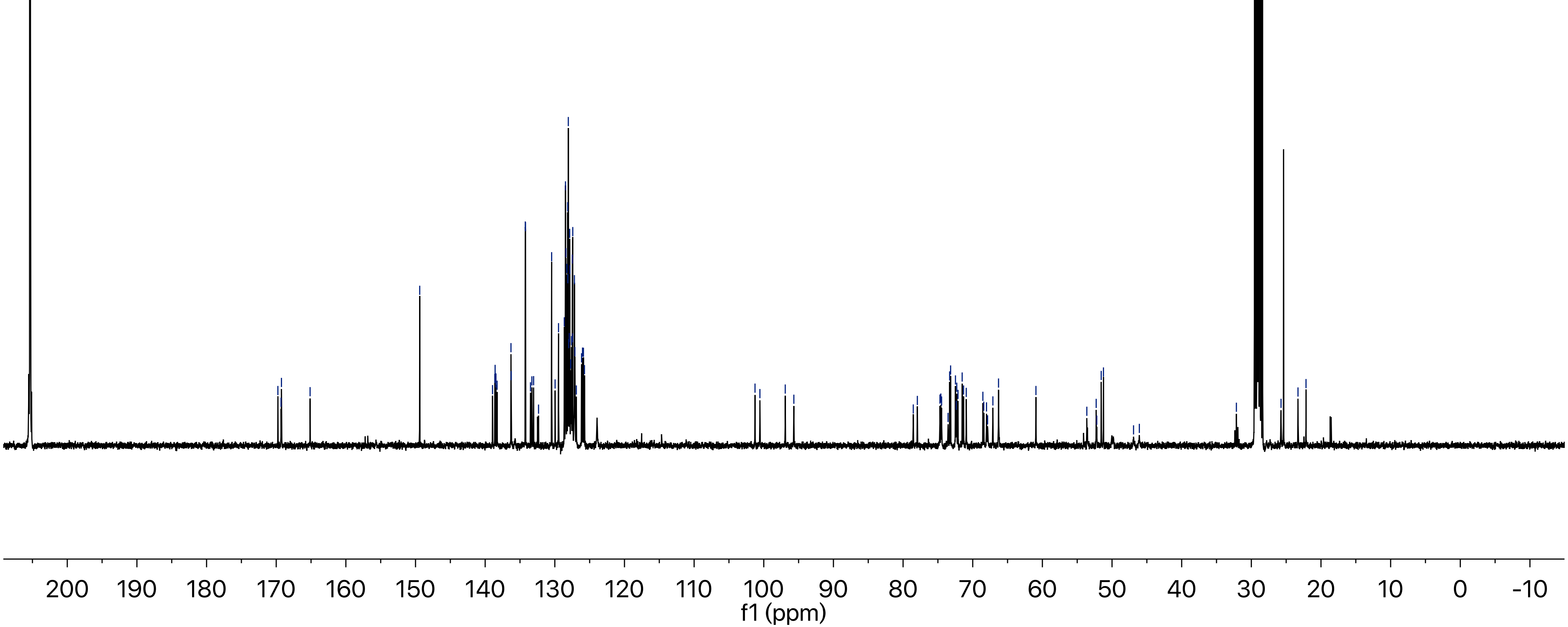


S36

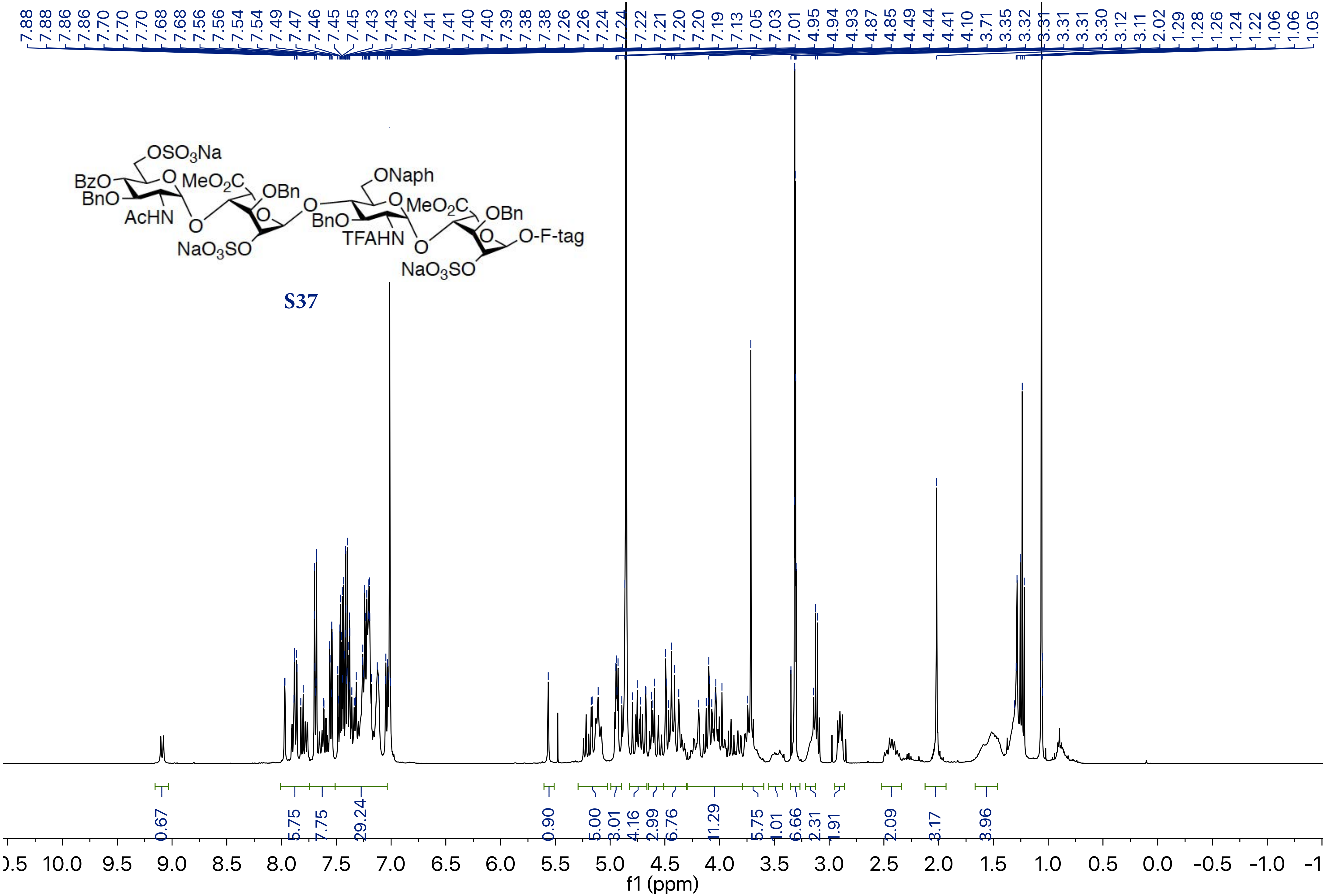
WL-2-139-DeTBDPS.2.fid —



S36

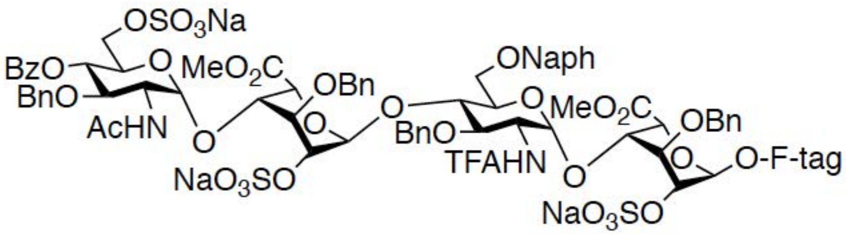


WL-2-141-6-2-2-trisulfation-H.3.1.1r —

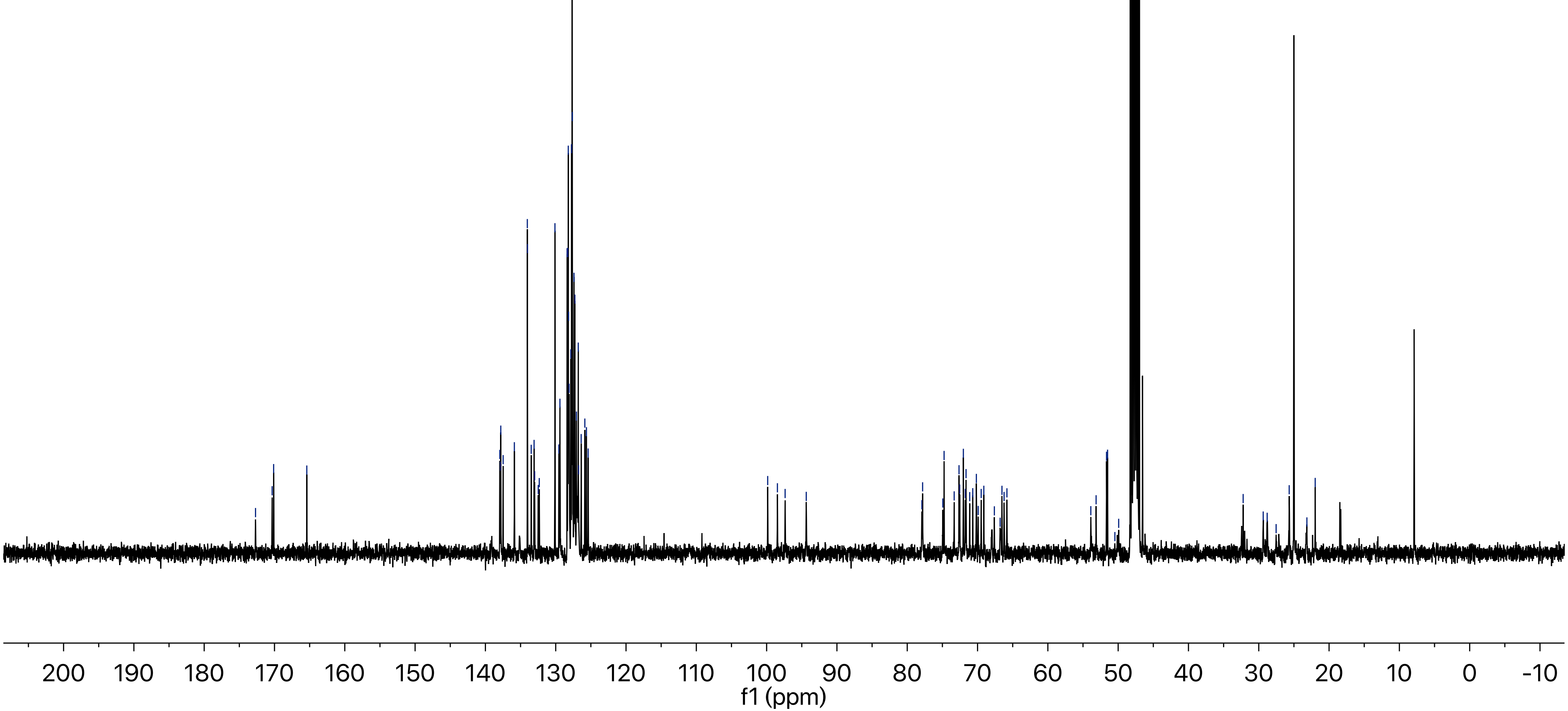


S37

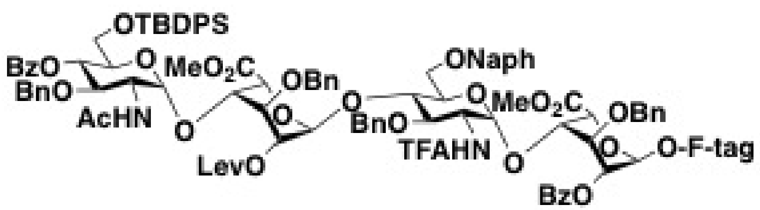
WL-2-141-6-2-2-trisulfation-C.4.1.1r



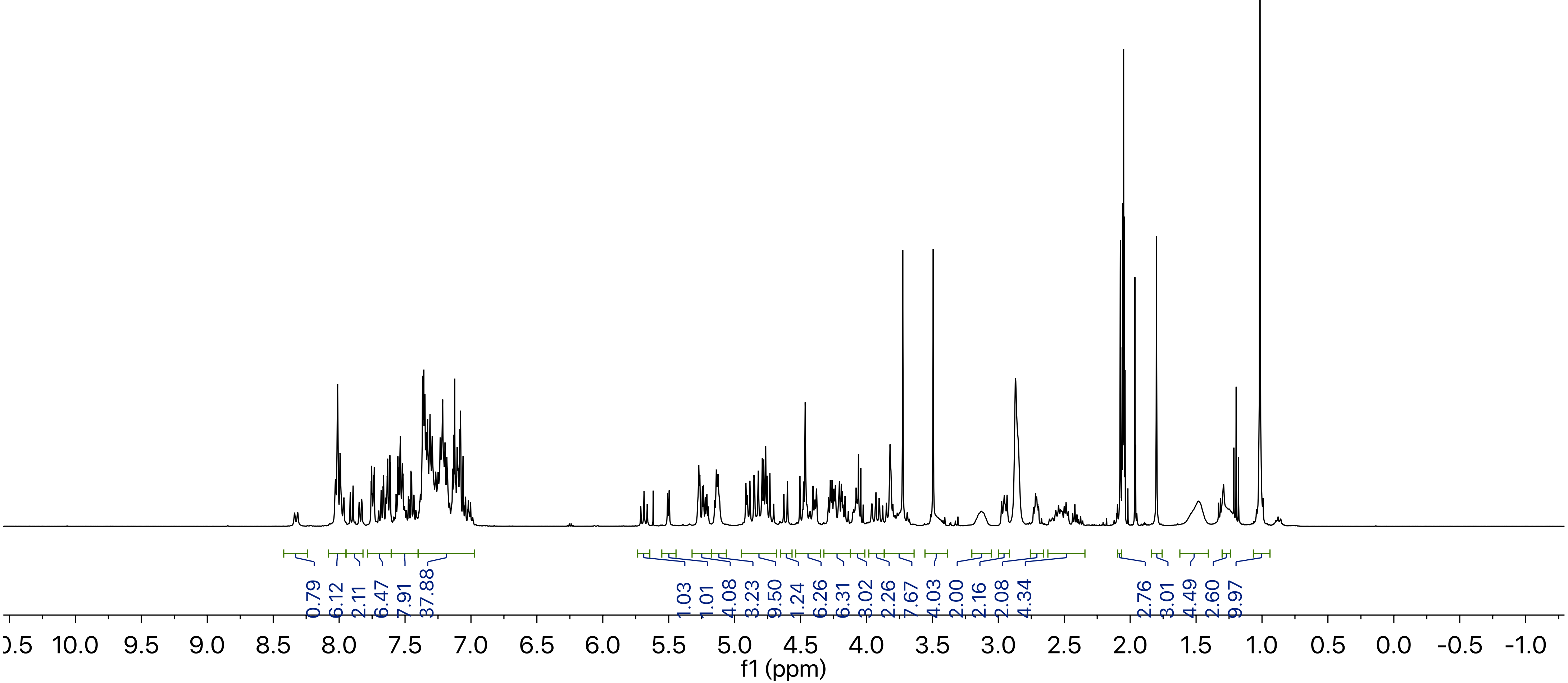
S37

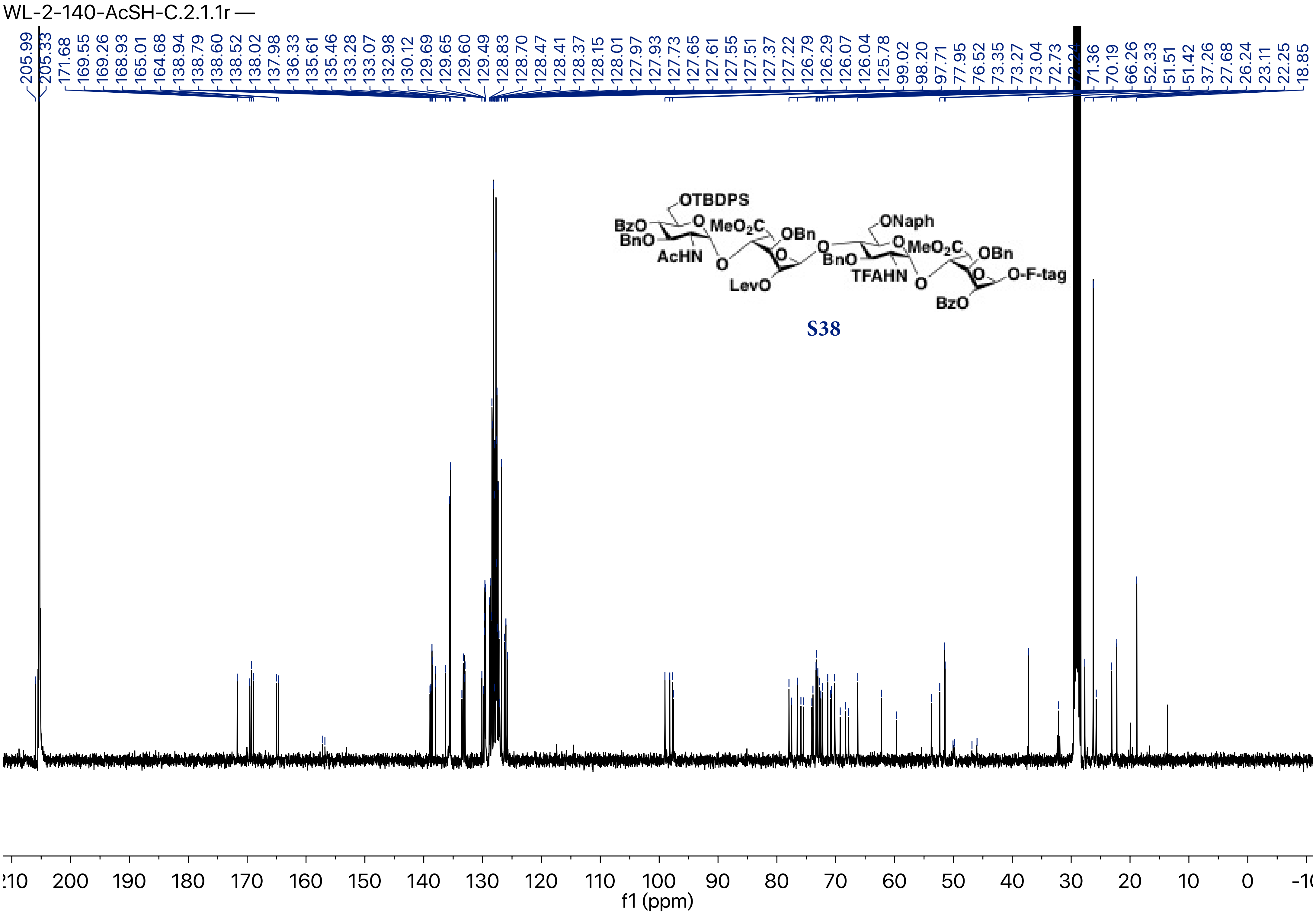


WL-2-140-AcSH-H.1.1.1r —



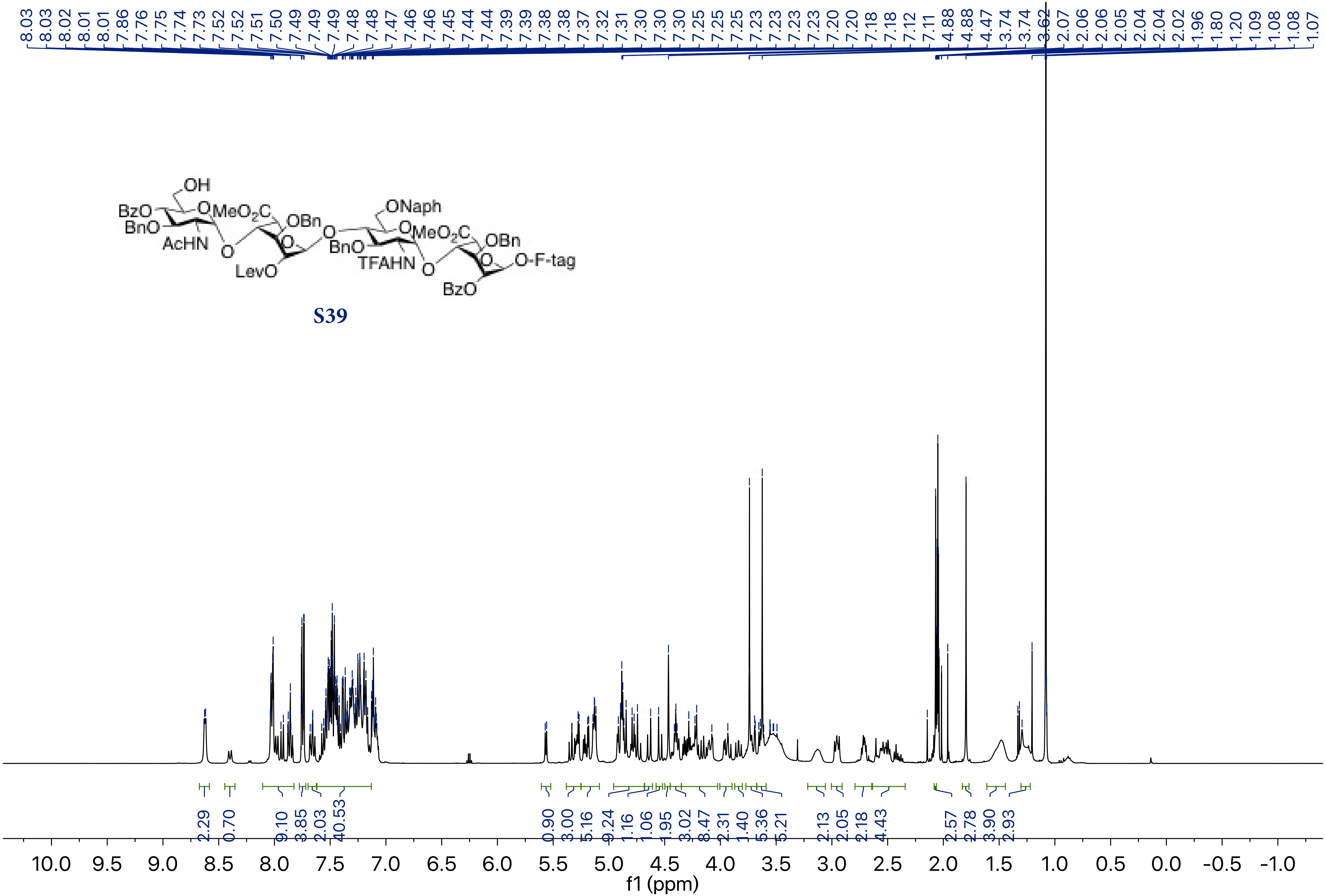
S38

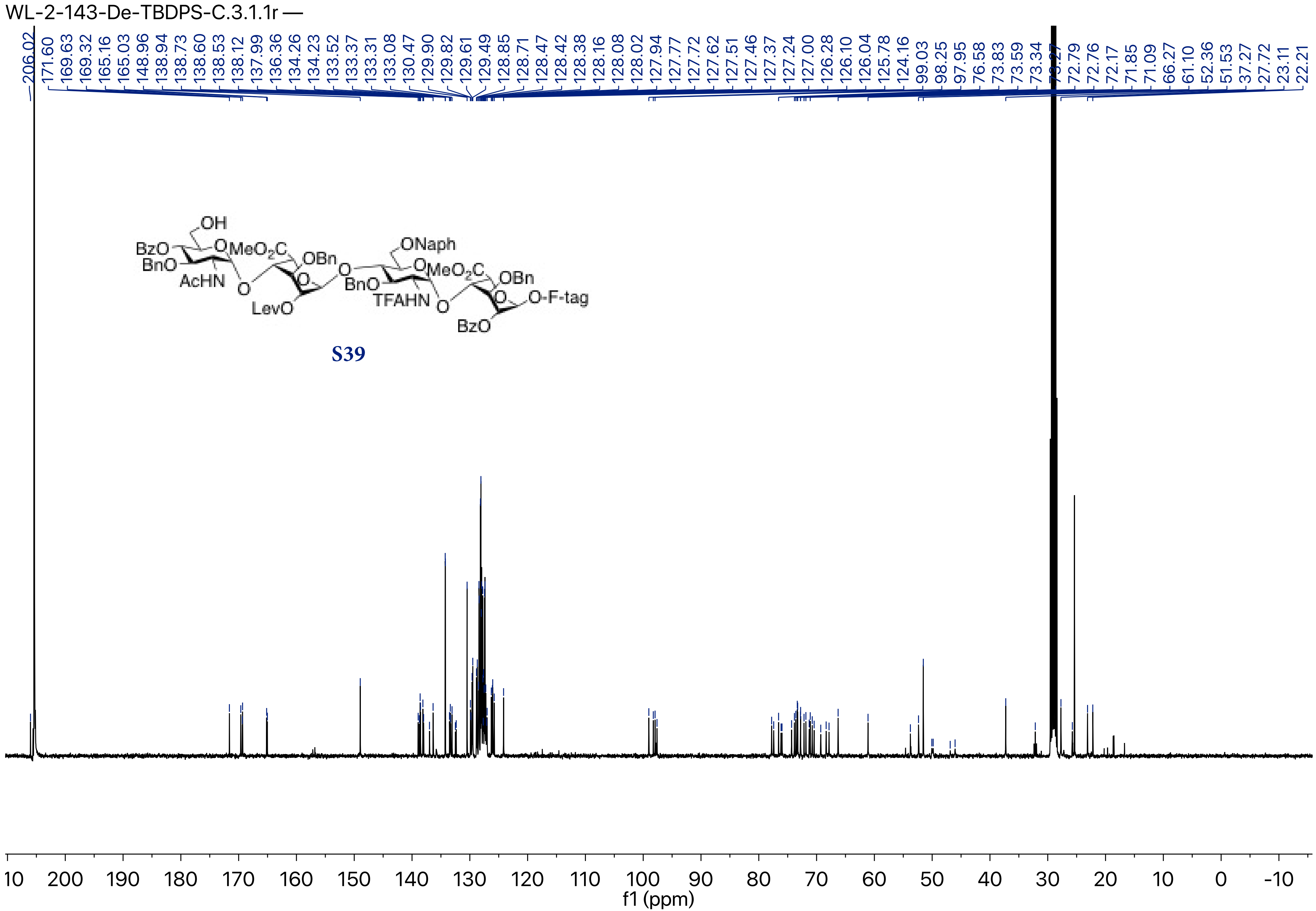



WL-2-140-AcSH-C.2.1.1r
205.99
205.33
171.68
169.55
169.26
168.93
165.01
164.68
138.94
138.79
138.60
138.52
138.02
137.98
136.33
135.61
135.46
133.28
133.07
132.98
130.12
129.69
129.65
129.60
129.49
128.83
128.70
128.47
128.41
128.37
128.15
128.01
127.97
127.93
127.73
127.65
127.61
127.55
127.51
127.37
127.22
126.79
126.29
126.07
126.04
125.78
99.02
98.20
97.71
77.95
76.52
73.35
73.27
73.04
72.73
72.24
71.36
70.19
66.26
52.33
51.51
51.42
37.26
27.68
26.24
23.11
22.25
18.85
OTBDPS
BzO
BnO
AcHN
O
MeO2C
OBn
LevO
ONaph
BnO
TFAHN
OBn
O-F-tag
BzO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

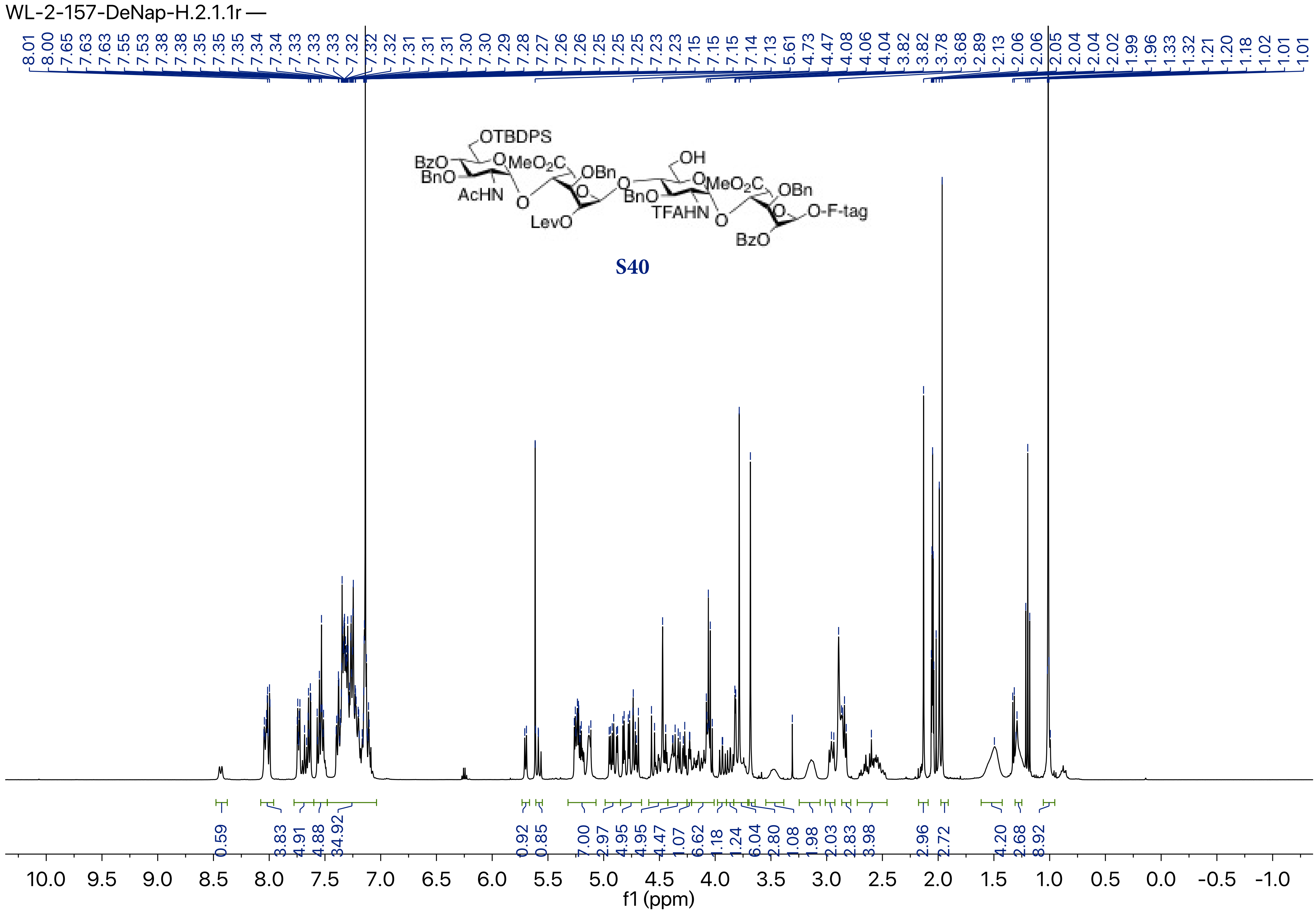
S38

WL-2-143-De-TBDPS-H.2.1.1r —

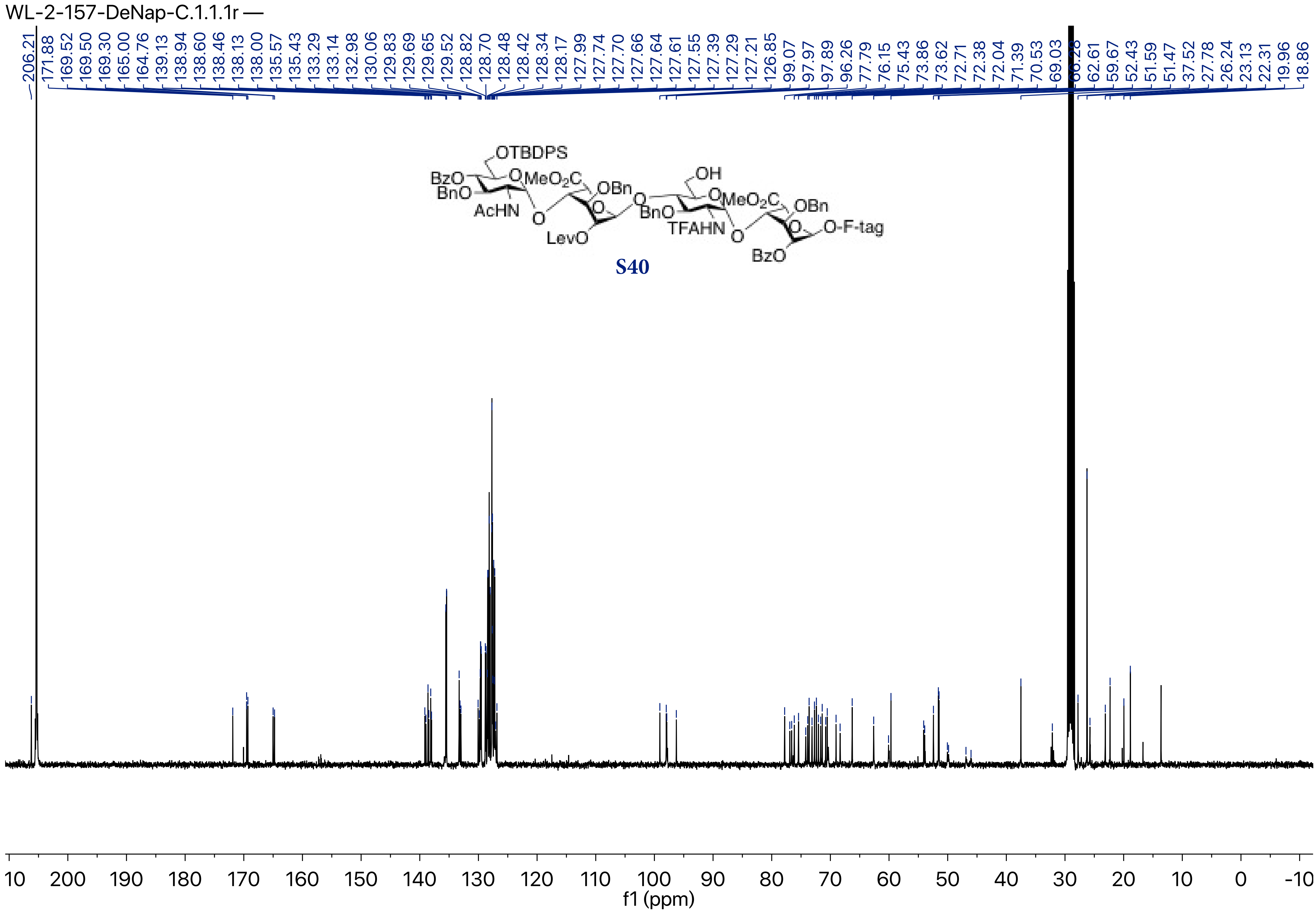



WL-2-143-De-TBDPS-C.3.1.1r
206.02
171.60
169.63
169.32
165.16
165.03
148.96
138.94
138.73
138.60
138.53
138.12
137.99
136.36
134.26
134.23
133.52
133.37
133.31
133.08
130.47
129.90
129.82
129.61
129.49
128.85
128.71
128.47
128.42
128.38
128.16
128.08
128.02
127.94
127.77
127.72
127.62
127.51
127.46
127.37
127.24
127.00
126.28
126.10
126.04
125.78
124.16
99.03
98.25
97.95
76.58
73.83
73.59
73.34
72.79
72.76
72.17
71.85
71.09
66.27
61.10
52.36
51.53
37.27
27.72
23.11
22.21
OH
BzO
BnO
OMeO2C
AcHN
O
OBn
LevO
ONaph
BnO
TFAHN
OMeO2C
OBn
O-F-tag
BzO
f1 (ppm)

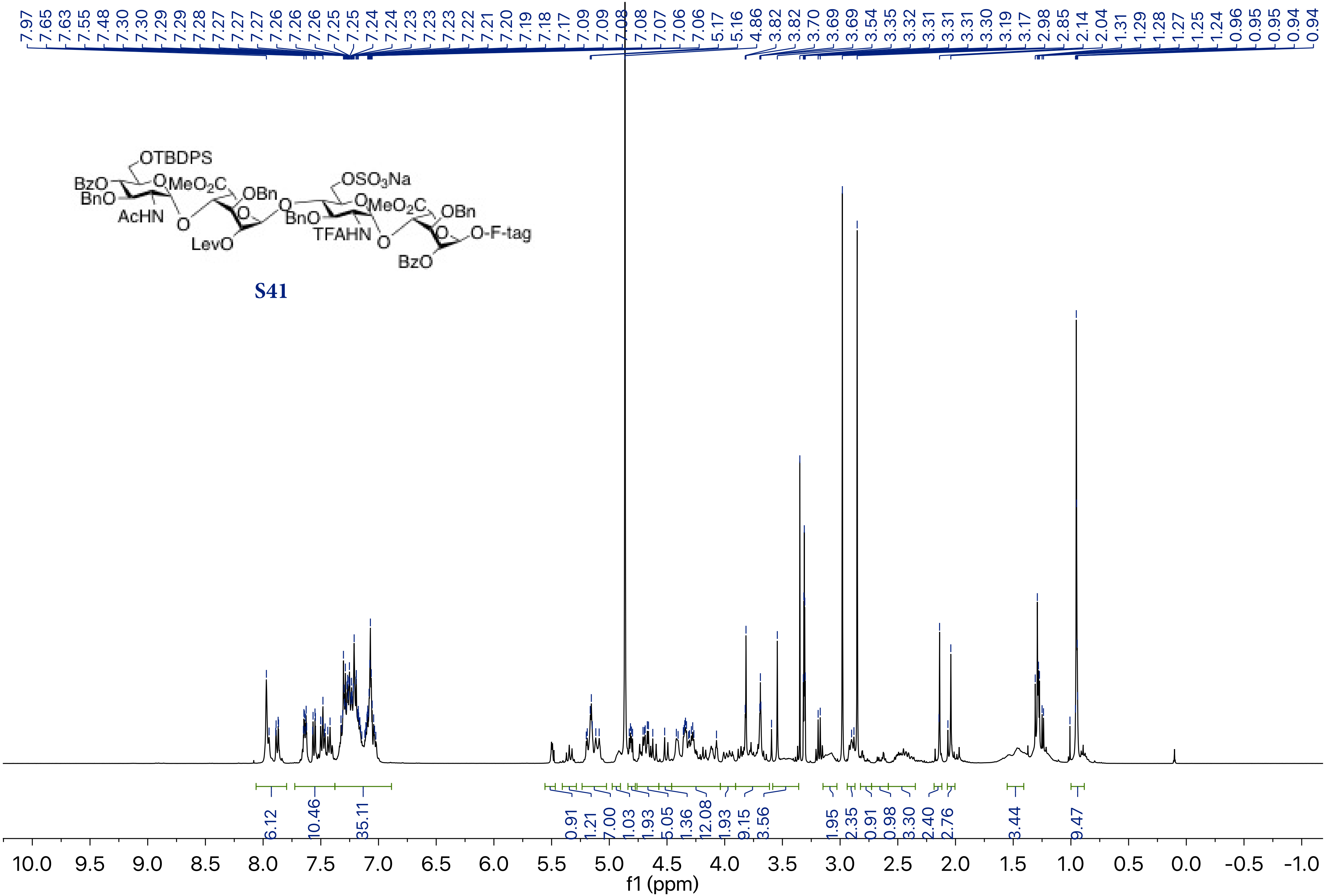
S39


WL-2-157-DeNap-H.2.1.1r
8.01
8.00
7.65
7.63
7.63
7.55
7.53
7.38
7.38
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.25
7.25
7.23
7.23
7.15
7.15
7.15
7.14
7.13
5.61
4.73
4.47
4.08
4.06
4.04
3.82
3.82
3.78
3.68
2.89
2.13
2.06
2.06
2.05
2.04
2.04
2.02
1.99
1.96
1.33
1.32
1.21
1.20
1.18
1.02
1.01
1.01
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
LevO
OH
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
0.59
3.83
4.91
4.88
34.92
0.92
0.85
7.00
2.97
4.95
4.95
4.47
1.07
6.62
1.18
1.24
6.04
2.80
1.08
1.98
2.03
2.83
3.98
2.96
2.72
4.20
2.68
8.92
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
-0.5
-1.0
f1 (ppm)

S40

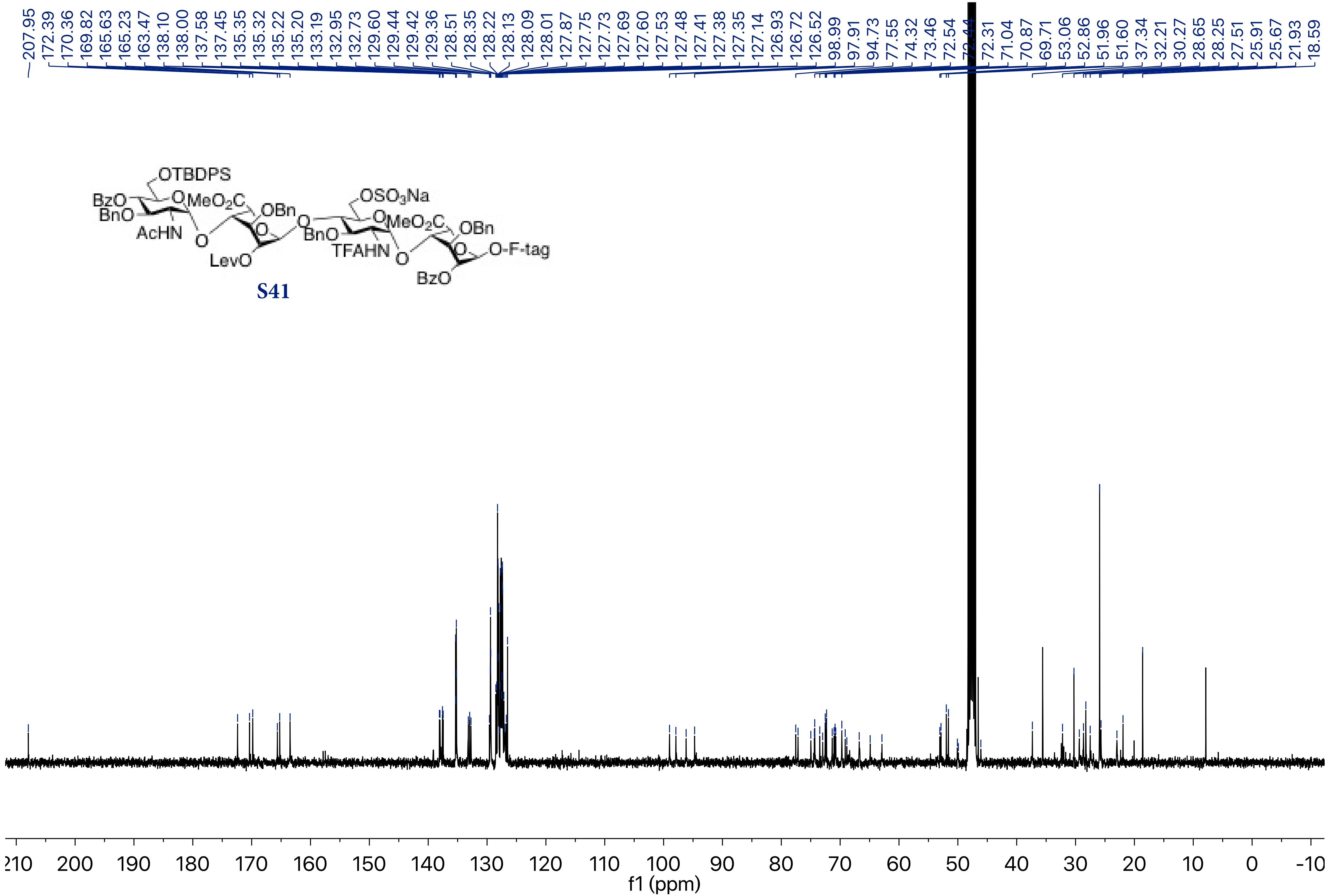

WL-2-157-DeNap-C.1.1.1r
206.21
171.88
169.52
169.50
169.30
165.00
164.76
139.13
138.94
138.60
138.46
138.13
138.00
135.57
135.43
133.29
133.14
132.98
130.06
129.83
129.69
129.65
129.52
128.82
128.70
128.48
128.42
128.34
128.17
127.99
127.74
127.70
127.66
127.64
127.61
127.55
127.39
127.29
127.21
126.85
99.07
97.97
97.89
96.26
77.79
76.15
75.43
73.86
73.62
72.71
72.38
72.04
71.39
70.53
69.03
66.28
62.61
59.67
52.43
51.59
51.47
37.52
27.78
26.24
23.13
22.31
19.96
18.86
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
LevO
OH
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
S40
f1 (ppm)

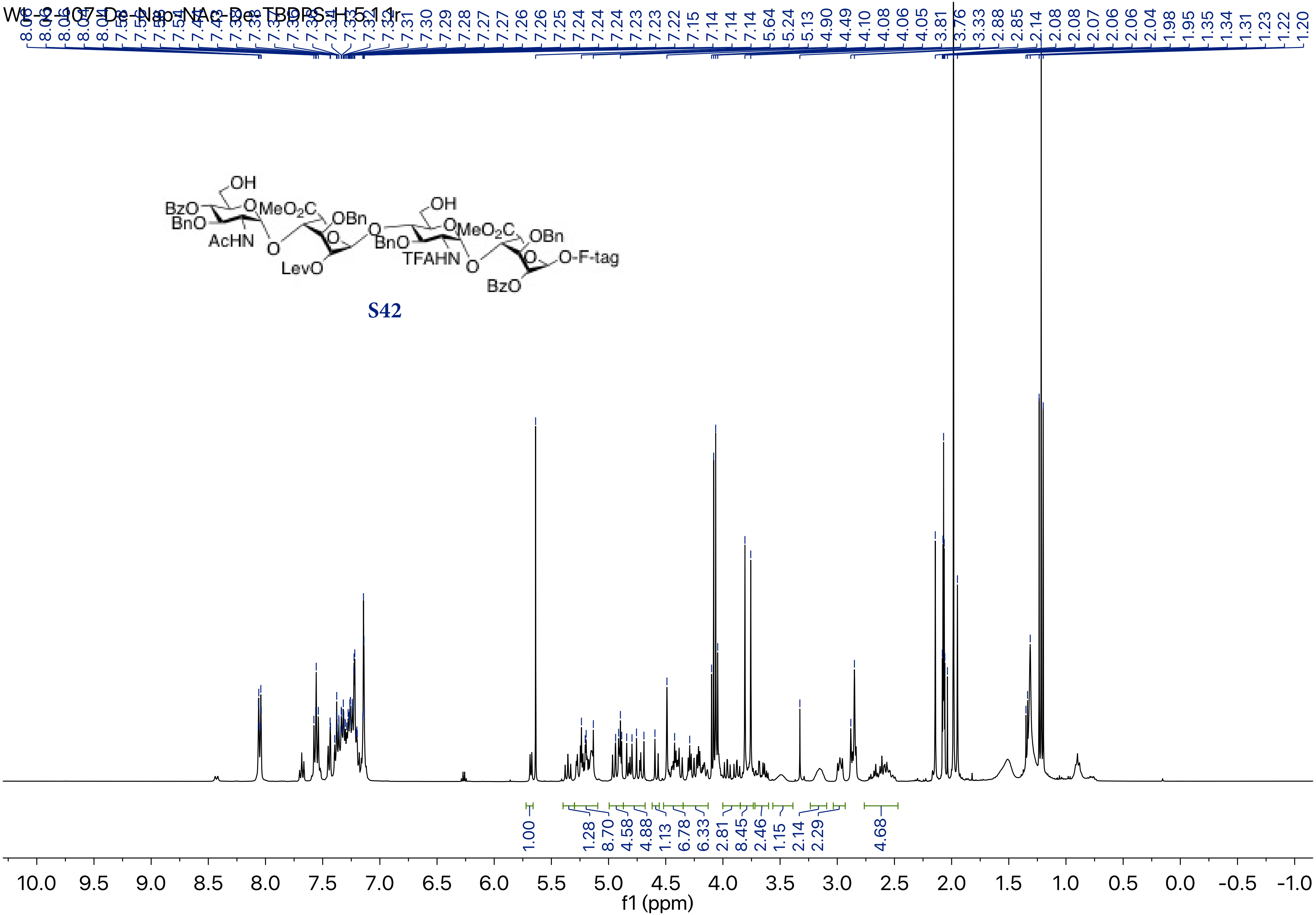
WL-2-158-B-6-sulfation-H.4.1.1r —

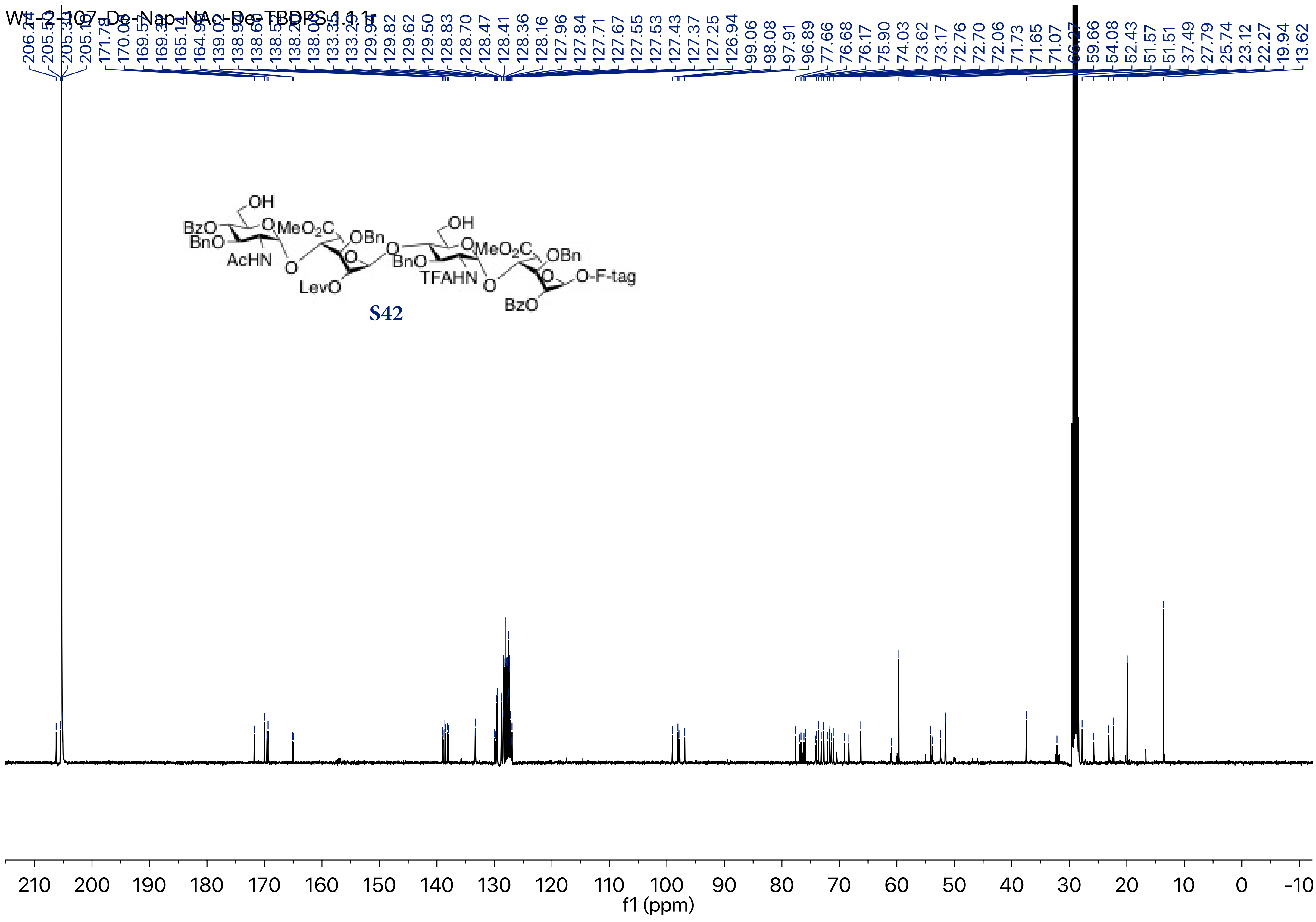


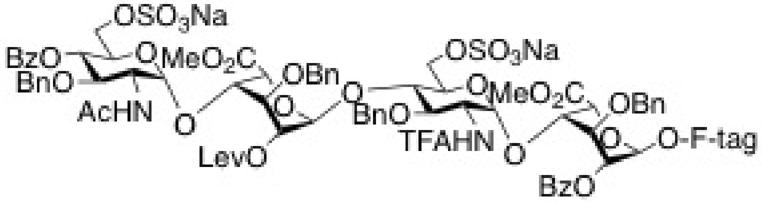
S41

WL-2-158-B-6-sulfation-C.2.1.1r —

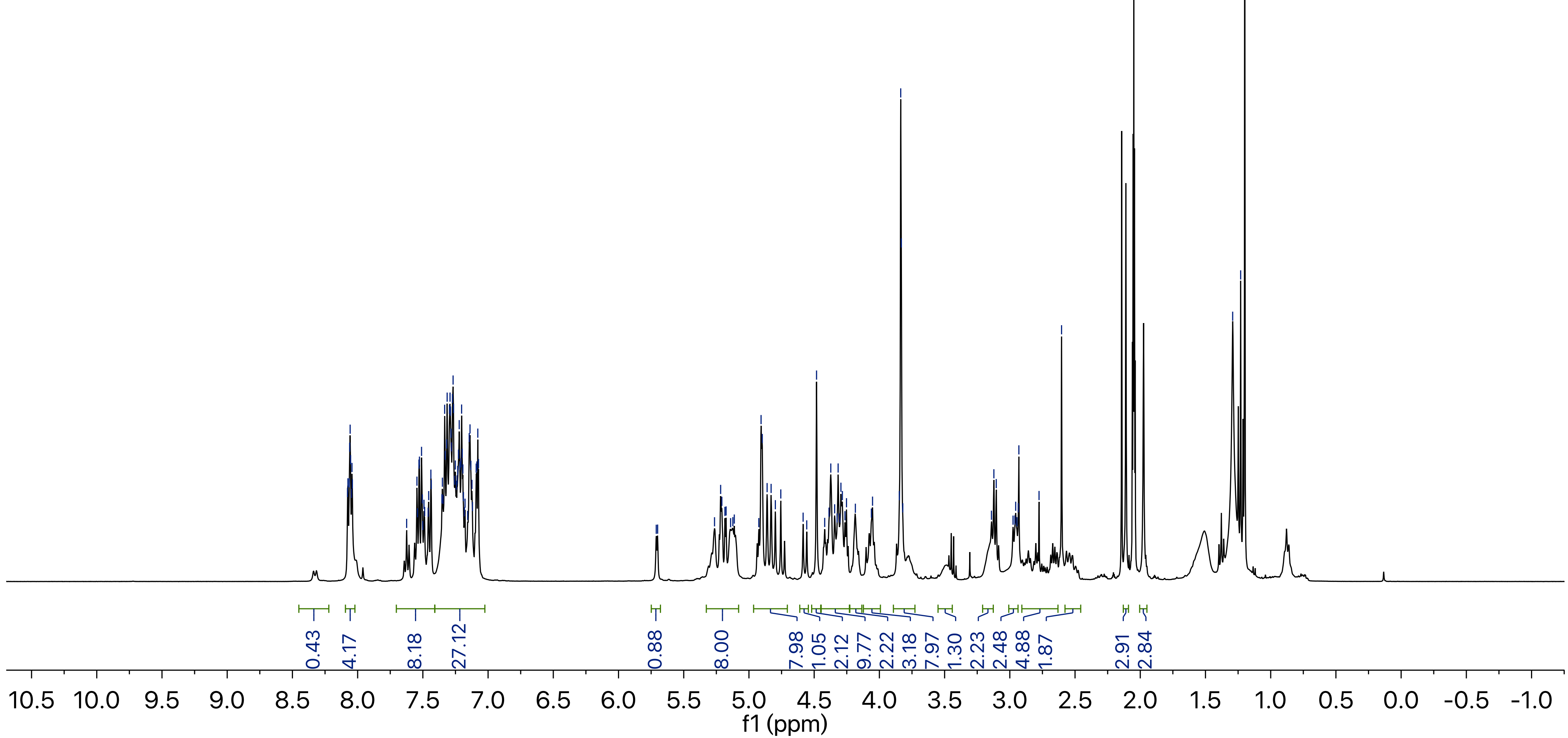



Wl-2-107-De-Nap-NAc-De-TBDPS-H-5-1-1r
8.05 8.05 8.04 8.04 8.03 7.55 7.55 7.54 7.54 7.44 7.43 7.38 7.38 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.15 7.14 7.14 7.14 5.64 5.24 5.13 4.90 4.49 4.10 4.08 4.06 4.05 3.81 3.76 3.33 2.88 2.85 2.14 2.08 2.08 2.07 2.06 2.06 2.04 1.98 1.95 1.35 1.34 1.31 1.23 1.22 1.20
OH
BzO
BnO
AcHN
O
MeO_2C
OBn
LevO
OH
BnO
TFAHN
MeO_2C
OBn
O-F-tag
BzO
S42
1.00
1.28
8.70
4.58
4.88
1.13
6.78
6.33
2.81
8.45
2.46
1.15
2.14
2.29
4.68
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 -0.5 -1.0
f1 (ppm)

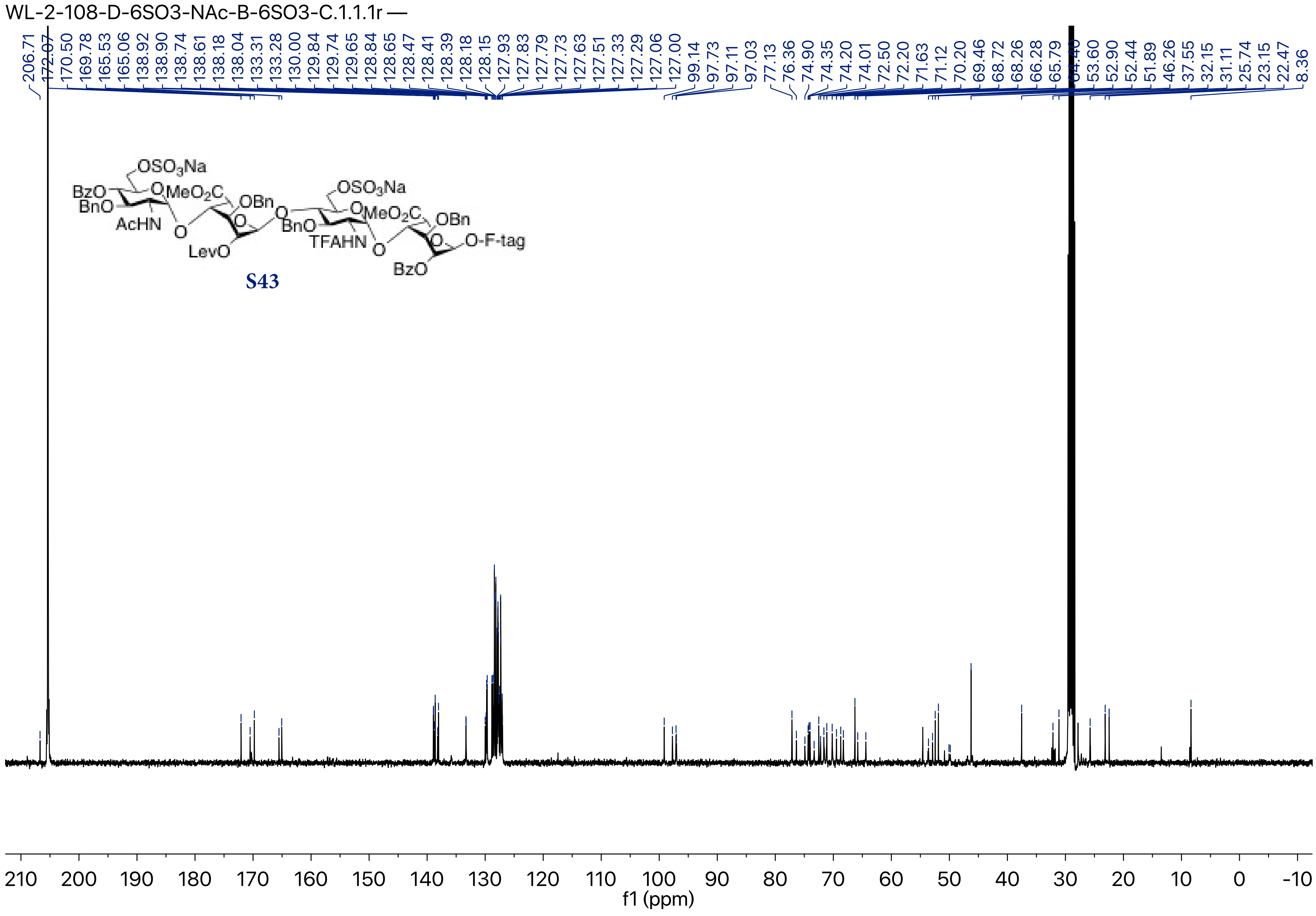

Wt-2-107_De-Nap-NAc-De-TBDPS.1.1.1r
206.2
205.5
205.3
205.1
171.78
170.0
169.5
169.3
165.14
164.9
139.0
138.9
138.6
138.5
138.2
138.0
133.35
133.2
129.9
129.82
129.62
129.50
128.83
128.70
128.47
128.41
128.36
128.16
127.96
127.84
127.71
127.67
127.55
127.53
127.43
127.37
127.25
126.94
99.06
98.08
97.91
96.89
77.66
76.68
76.17
75.90
74.03
73.62
73.17
72.76
72.70
72.06
71.73
71.65
71.07
66.27
59.66
54.08
52.43
51.57
51.51
37.49
27.79
25.74
23.12
22.27
19.94
13.62
BzO
BnO
OH
OMeO2C
OBn
AcHN
O
LevO
BnO
OH
OMeO2C
OBn
TFAHN
O
O-F-tag
BzO
S42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

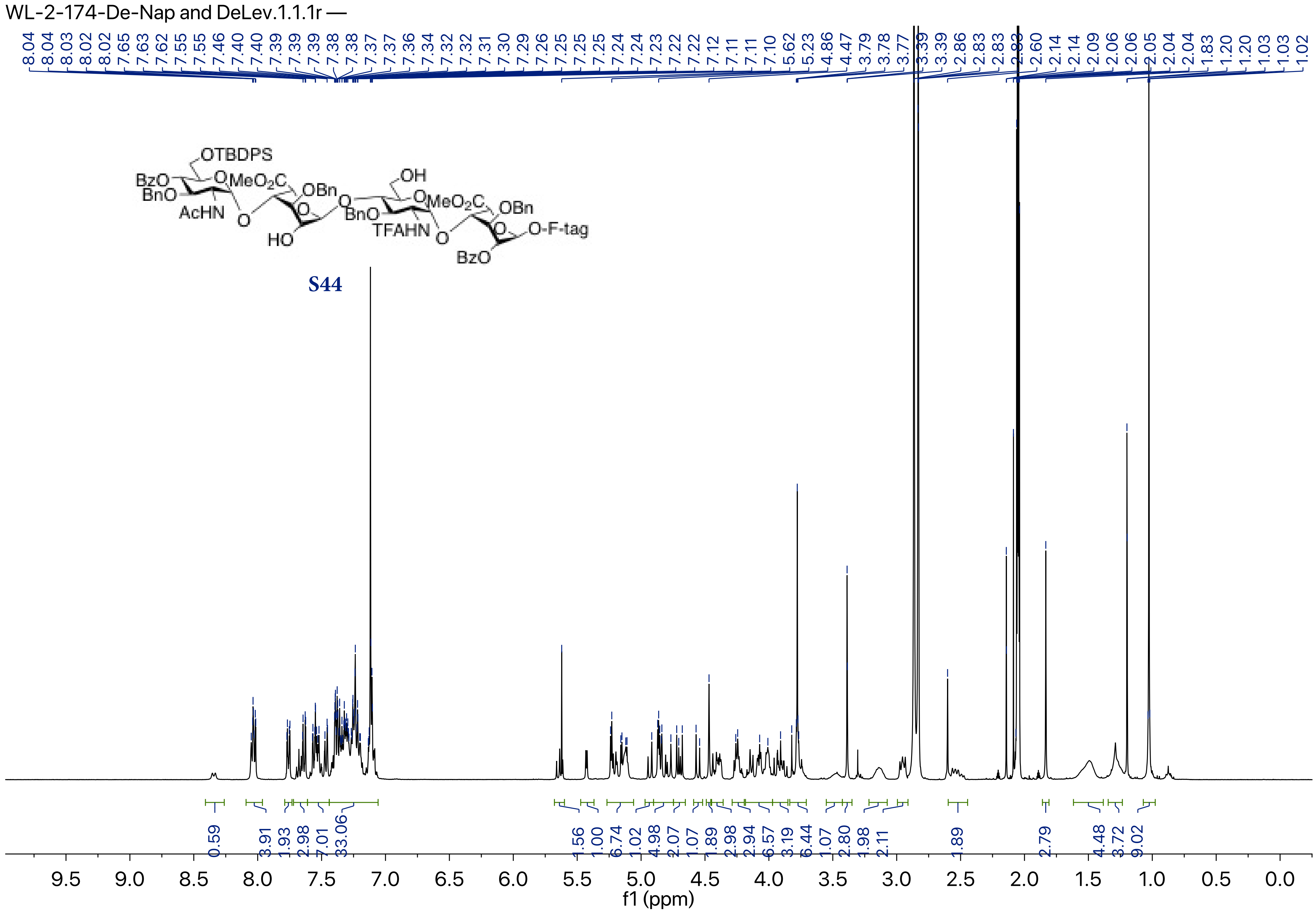


S43

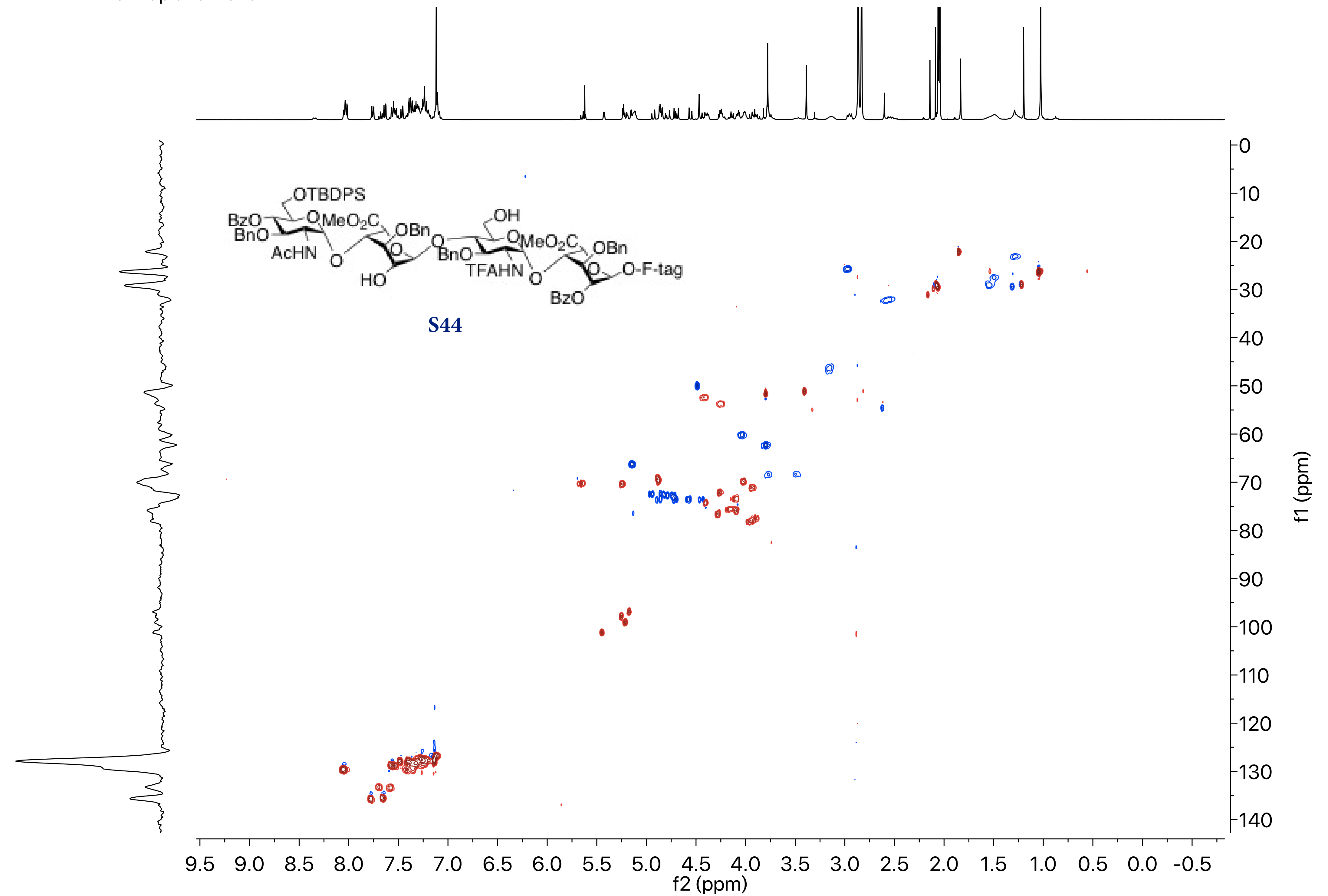


WL-2-108-1.1.1.1r
8.08 8.07 8.07 8.06 8.06 8.05 8.05 8.04 8.04 7.55 7.53 7.53 7.51 7.44 7.44 7.35 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.14 7.14 7.13 7.12 7.09 7.09 7.08 7.07 5.22 4.91 4.90 4.86 4.83 4.76 4.48 4.37 4.32 4.29 3.84 3.83 3.12 3.10 2.93 2.78 2.60 1.29 1.23 1.20
0.43 4.17 8.18 27.12 0.88 8.00 7.98 1.05 2.12 9.77 2.22 3.18 7.97 1.30 2.23 2.48 4.88 1.87 2.91 2.84
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 -0.5 -1.0
f1 (ppm)

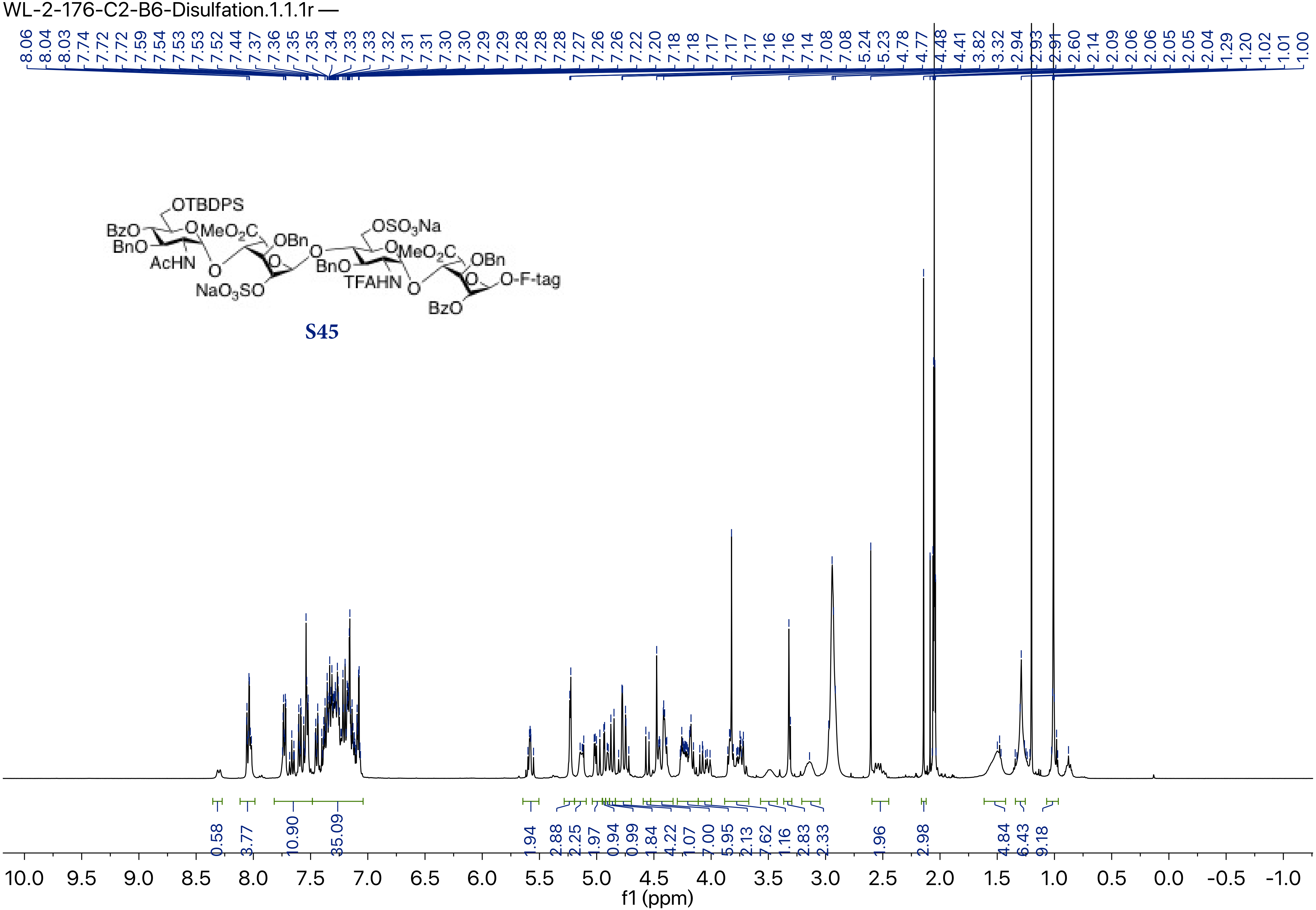

WL-2-108-D-6SO3-NAc-B-6SO3-C.1.1.1r
206.71
172.07
170.50
169.78
165.53
165.06
138.92
138.90
138.74
138.61
138.18
138.04
133.31
133.28
130.00
129.84
129.74
129.65
128.84
128.65
128.47
128.41
128.39
128.18
128.15
127.93
127.83
127.79
127.73
127.63
127.51
127.33
127.29
127.06
127.00
99.14
97.73
97.11
97.03
77.13
76.36
74.90
74.35
74.20
74.01
72.50
72.20
71.63
71.12
70.20
69.46
68.72
68.26
66.28
65.79
64.40
53.60
52.90
52.44
51.89
46.26
37.55
32.15
31.11
25.74
23.15
22.47
8.36
OSO3Na
BzO
BnO
OMeO2C
OBn
AcHN
O
LevO
OSO3Na
BnO
OMeO2C
OBn
TFAHN
O
O-F-tag
BzO
S43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


WL-2-174-De-Nap and DeLev.1.1.1r —
8.04 8.04 8.03 8.02 8.02 7.65 7.63 7.62 7.55 7.55 7.46 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.34 7.32 7.32 7.31 7.30 7.29 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.12 7.11 7.11 7.10 5.62 5.23 4.86 4.47 3.79 3.78 3.77 3.39 3.39 2.86 2.83 2.83 2.82 2.60 2.14 2.14 2.09 2.06 2.06 2.05 2.04 2.04 1.83 1.20 1.20 1.03 1.03 1.02
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
HO
OH
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
S44
0.59 3.91 1.93 2.98 7.01 33.06 1.56 1.00 6.74 1.02 4.98 2.07 1.07 1.89 2.98 2.94 6.57 3.19 6.44 1.07 2.80 1.98 2.11 1.89 2.79 4.48 3.72 9.02
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)

WL-2-174-De-Nap and DeLev.2.1.2rr —

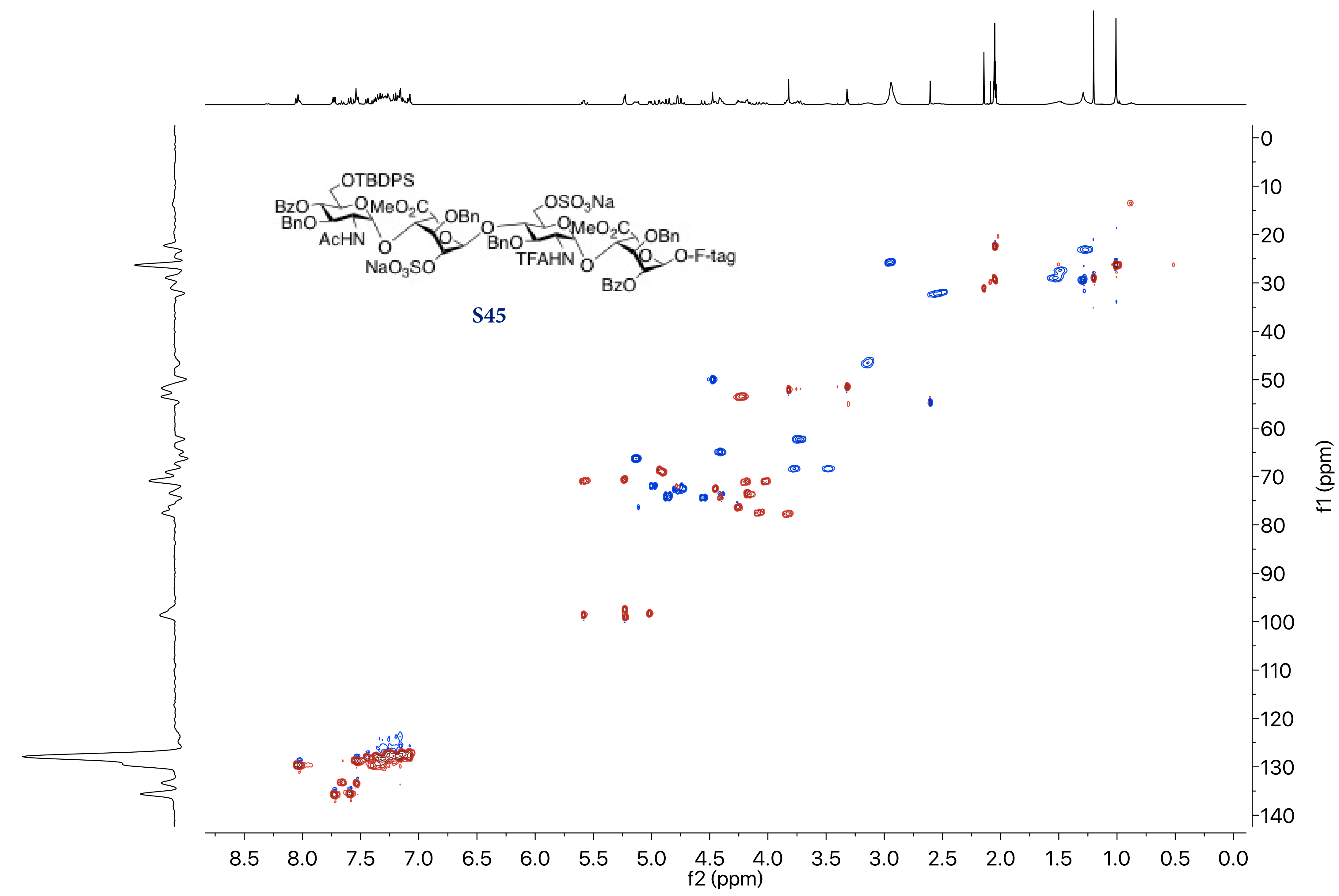


S44

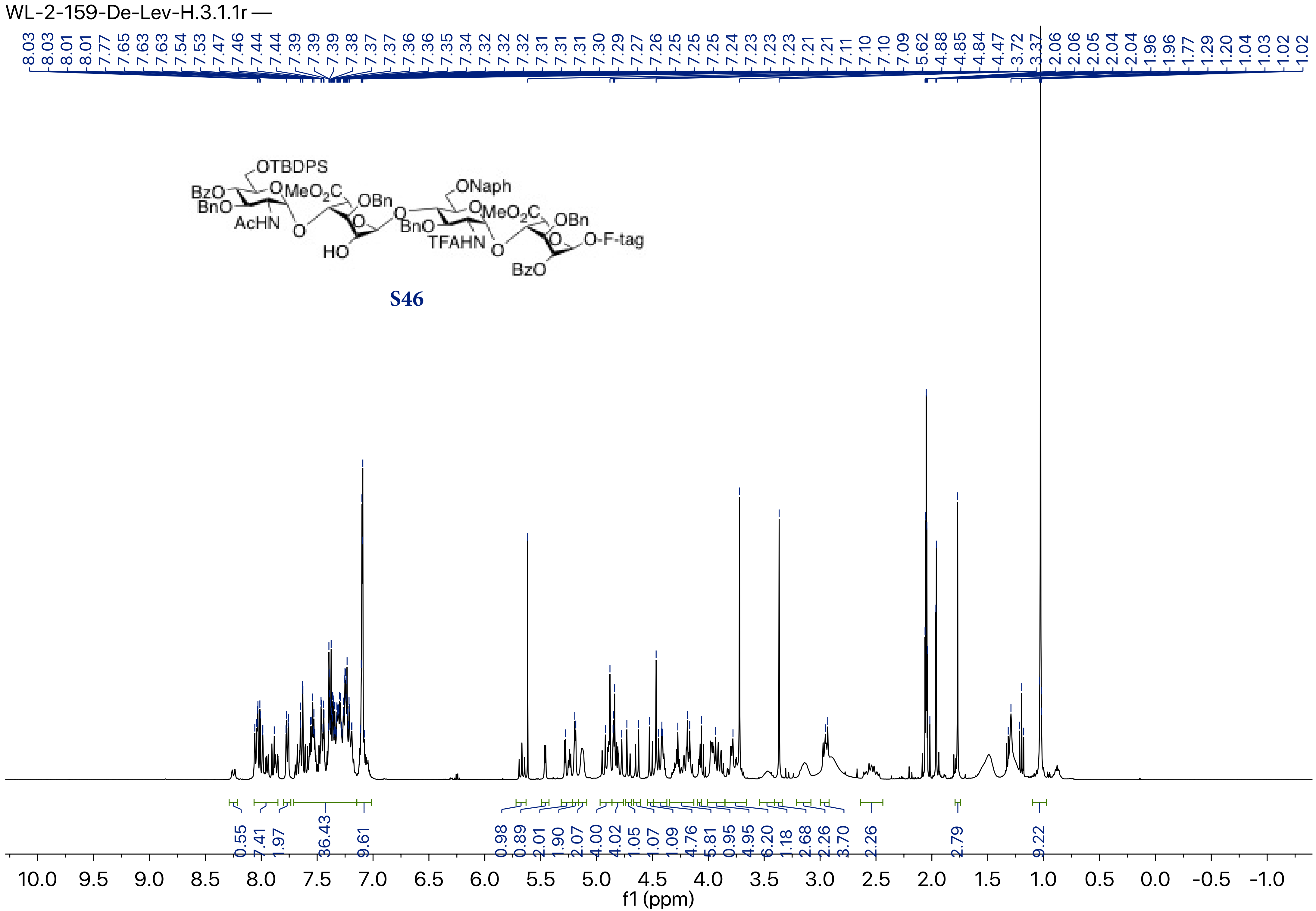

WL-2-176-C2-B6-Disulfation.1.1.1r
8.06 8.04 8.03 7.74 7.72 7.72 7.59 7.54 7.53 7.53 7.52 7.44 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.26 7.26 7.22 7.20 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.14 7.08 7.08 5.24 5.23 4.78 4.77 4.48 4.41 3.82 3.32 2.94 2.93 2.91 2.60 2.14 2.09 2.06 2.06 2.05 2.05 2.04 1.29 1.20 1.02 1.01 1.00
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
NaO3SO
OSO3Na
BnO
TFAHN
MeO2C
OBn
O-F-tag
BzO
0.58
3.77
10.90
35.09
1.94
2.88
2.25
1.97
0.94
0.99
1.84
4.22
1.07
7.00
5.95
2.13
7.62
1.16
2.83
2.33
1.96
2.98
4.84
6.43
9.18
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 -0.5 -1.0
f1 (ppm)

S45

WL-2-176-C2-B6-Disulfation.2.1.2rr —

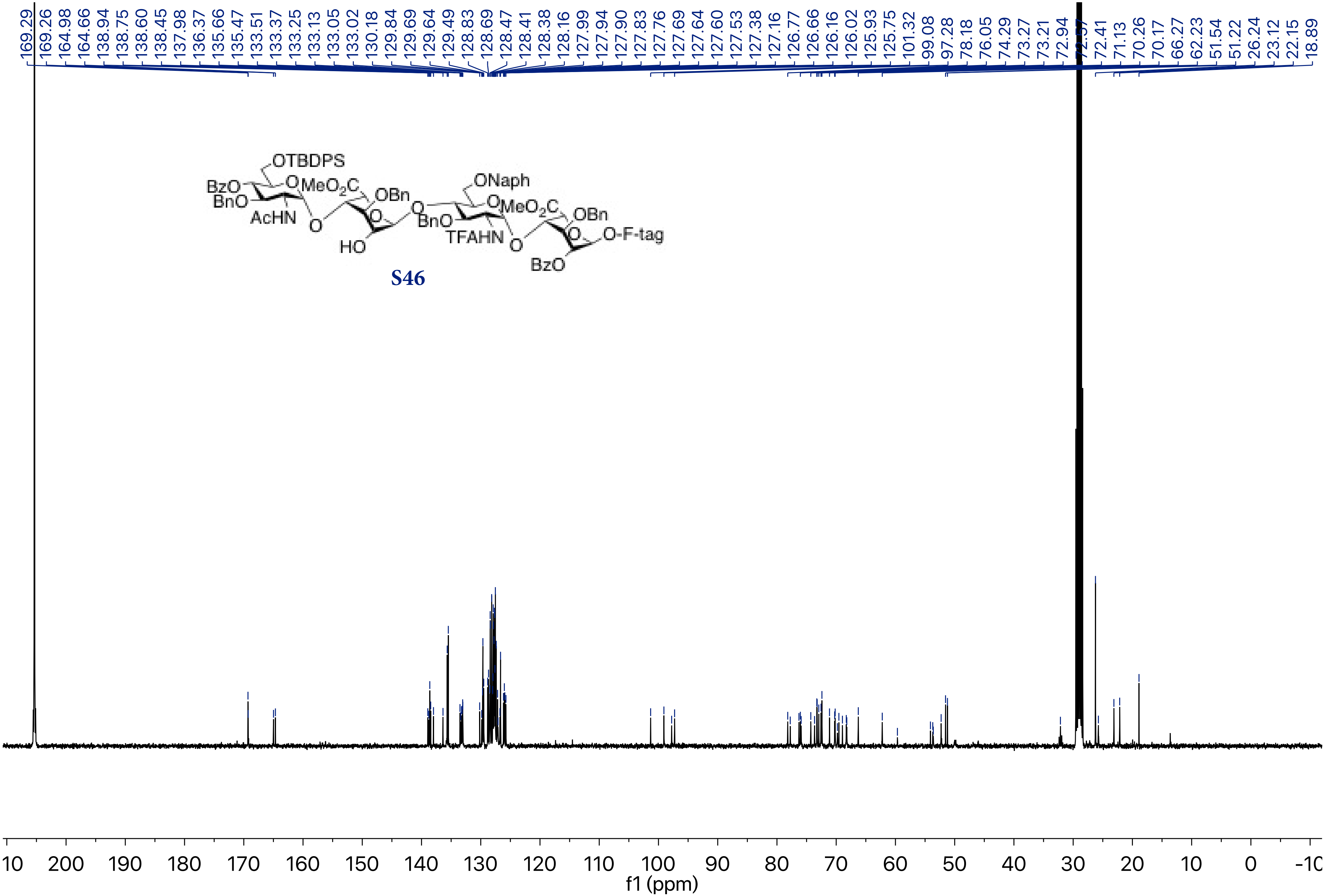


S45

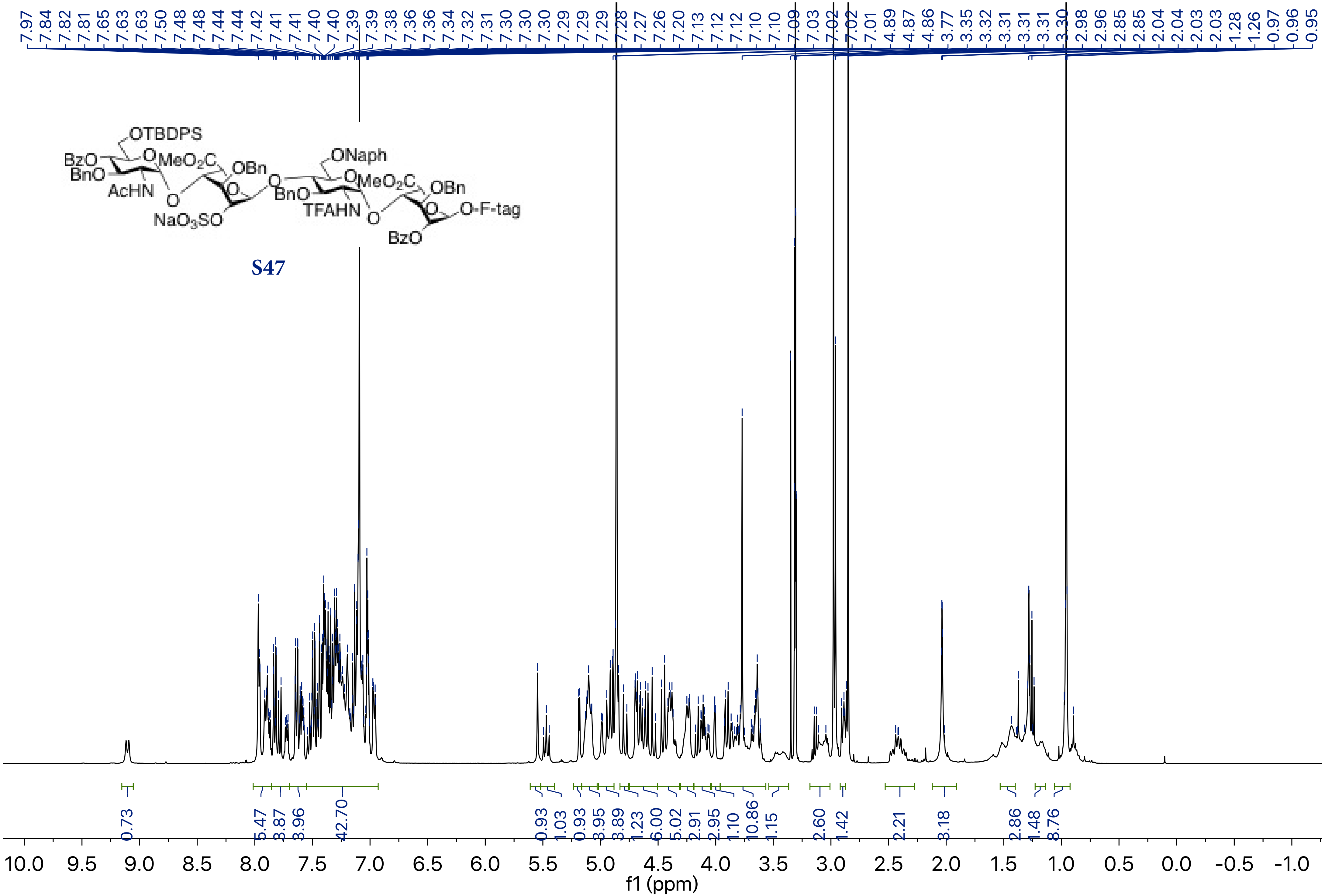

WL-2-159-De-Lev-H.3.1.1r
8.03 8.03 8.01 8.01 7.77 7.65 7.63 7.63 7.54 7.53 7.47 7.46 7.44 7.44 7.39 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.27 7.26 7.25 7.25 7.25 7.24 7.23 7.23 7.23 7.21 7.21 7.11 7.10 7.10 7.09 5.62 4.88 4.85 4.84 4.47 3.72 3.37 2.06 2.06 2.05 2.04 2.04 1.96 1.96 1.77 1.29 1.20 1.04 1.03 1.02 1.02
OTBDPS
BzO
BnO
AcHN
MeO2C
OBn
HO
BnO
ONaph
TFAHN
OBn
O-F-tag
BzO
0.55 7.41 1.97 36.43 9.61 0.98 0.89 2.01 1.90 2.07 4.00 4.02 1.05 1.07 1.09 4.76 5.81 0.95 4.95 6.20 1.18 2.68 2.26 3.70 2.26 2.79 9.22
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 -0.5 -1.0
f1 (ppm)

S46

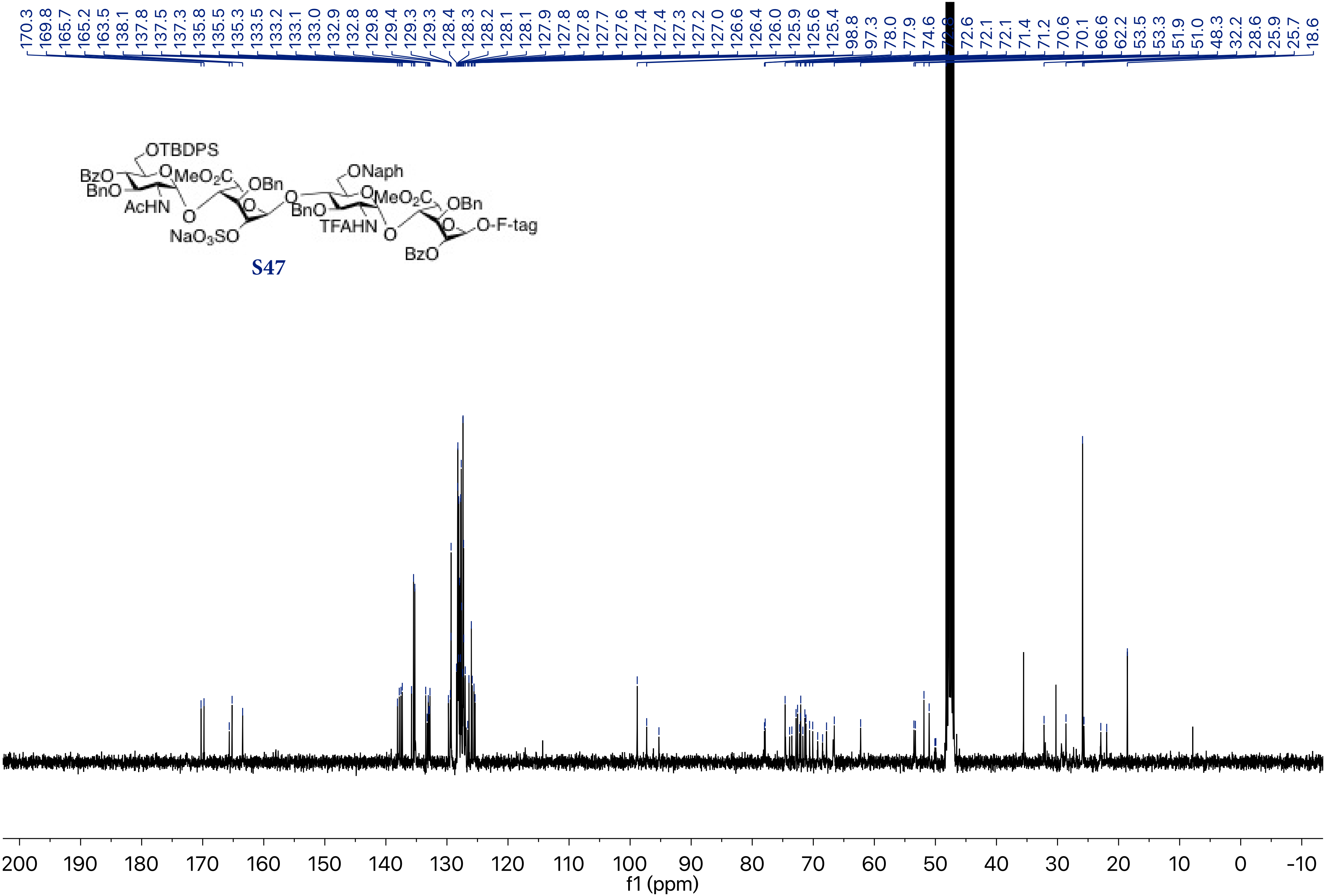
WL-2-159-De-Lev-C.2.1.1r —



WL-2-160-C-2Sulfation-H.6.1.1r

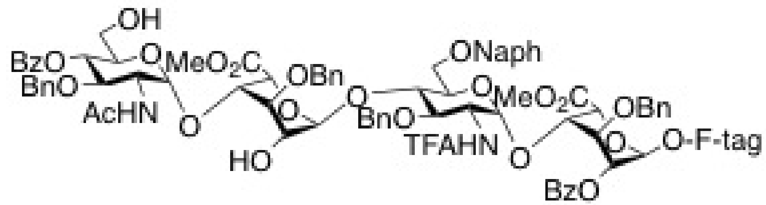


WL-2-160-C-2Sulfation-C.5.1.1r —

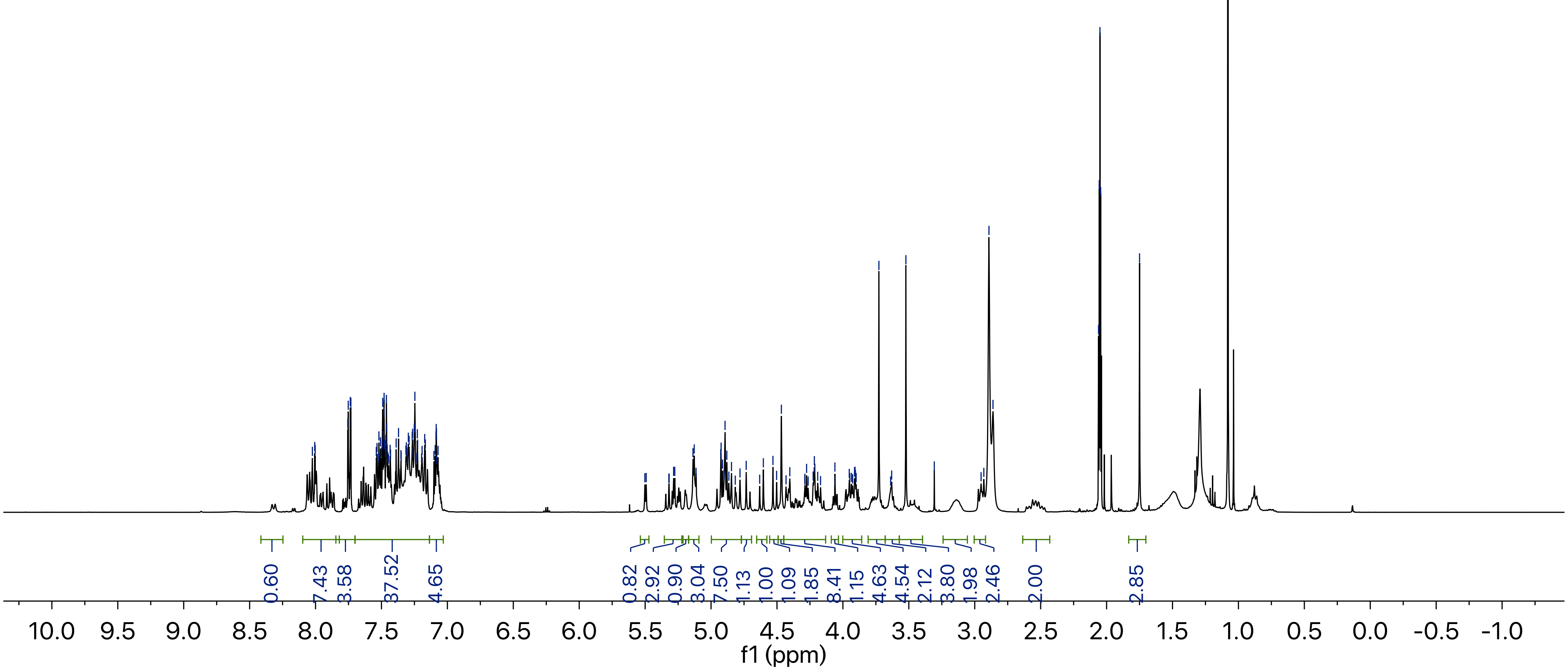


S47

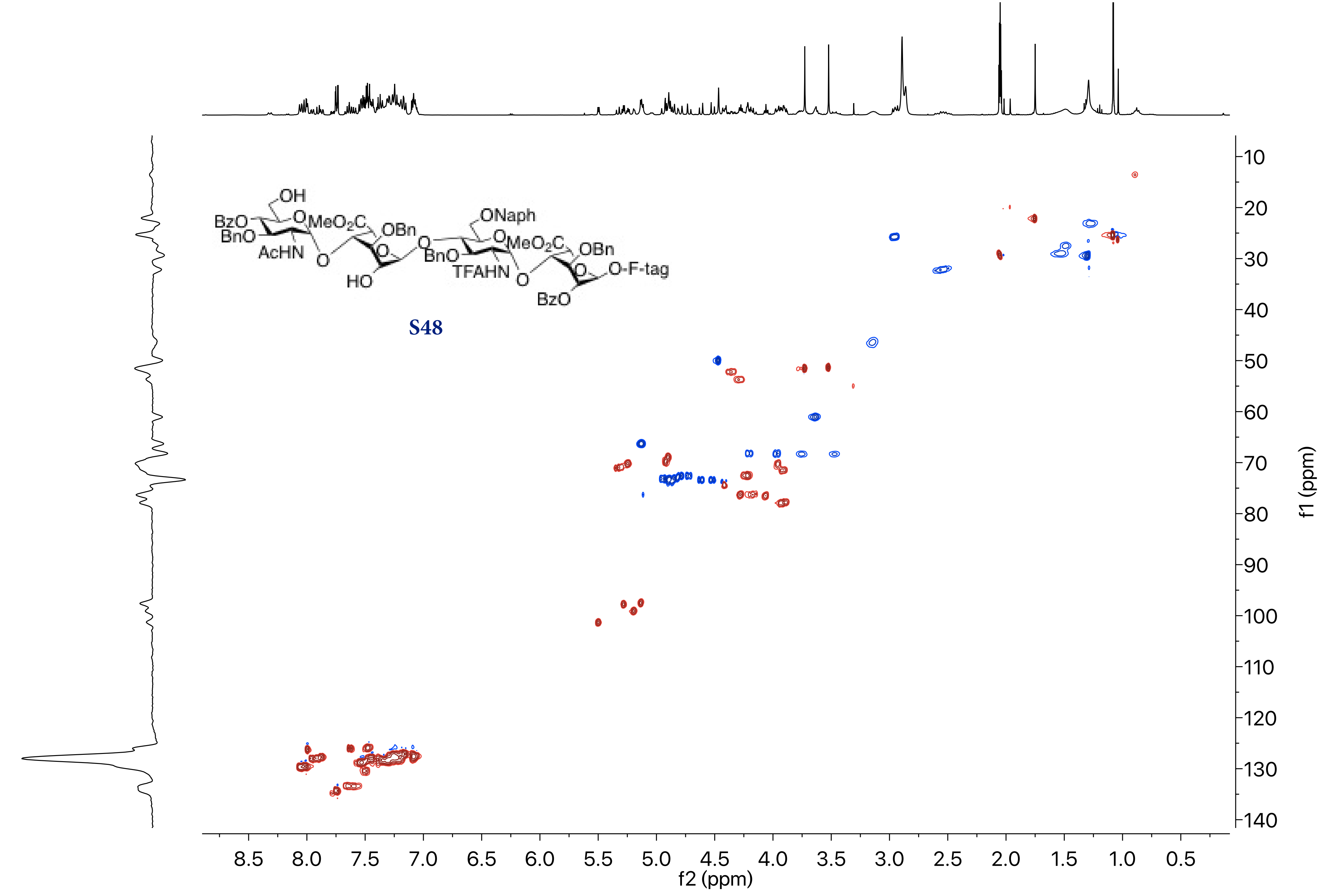
WL-2-173-De-TBDPS-H.2.1.1r



S48

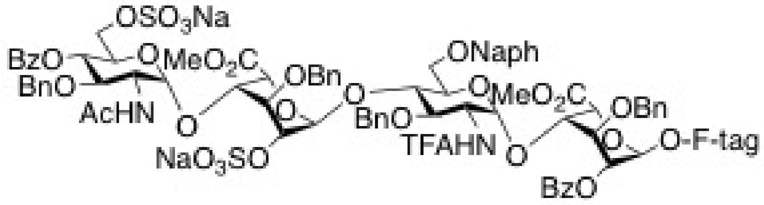


WL-2-173-De-TBDPS-HSQC.3.1.2rr

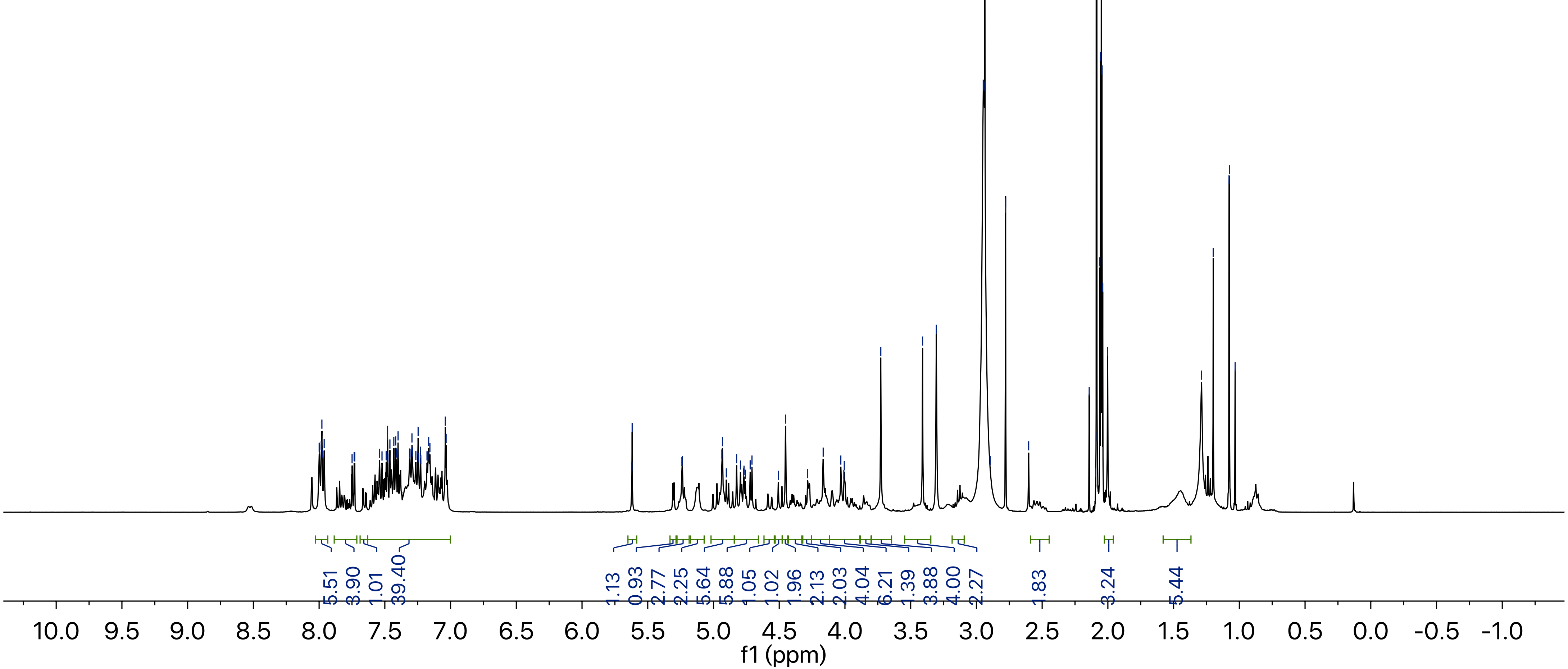


S48

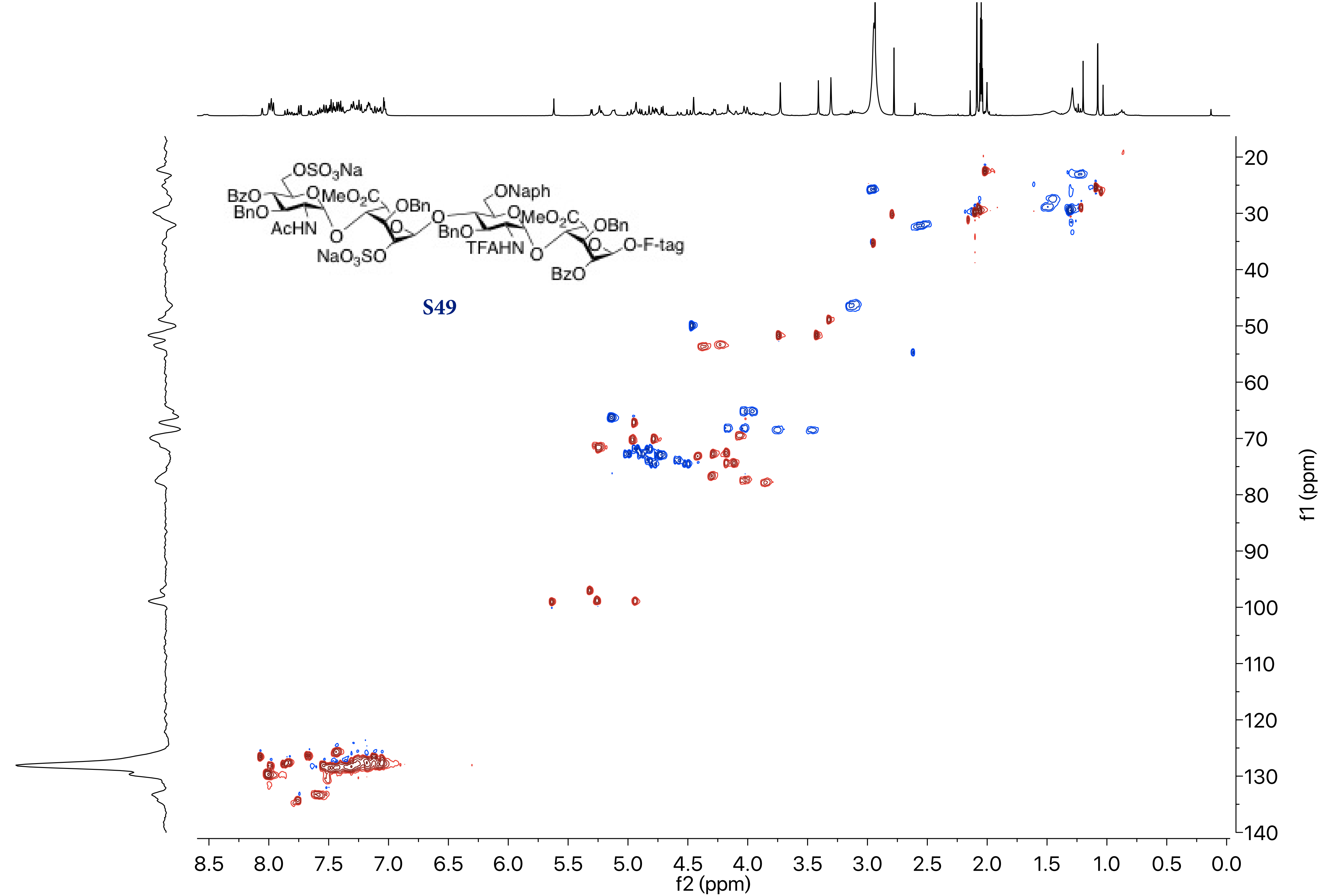
WL-2-175-6-2-Osulfation.1.1.1r —



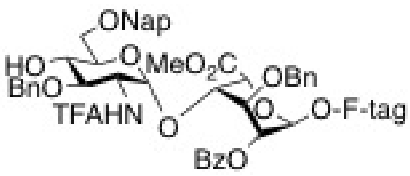
S49



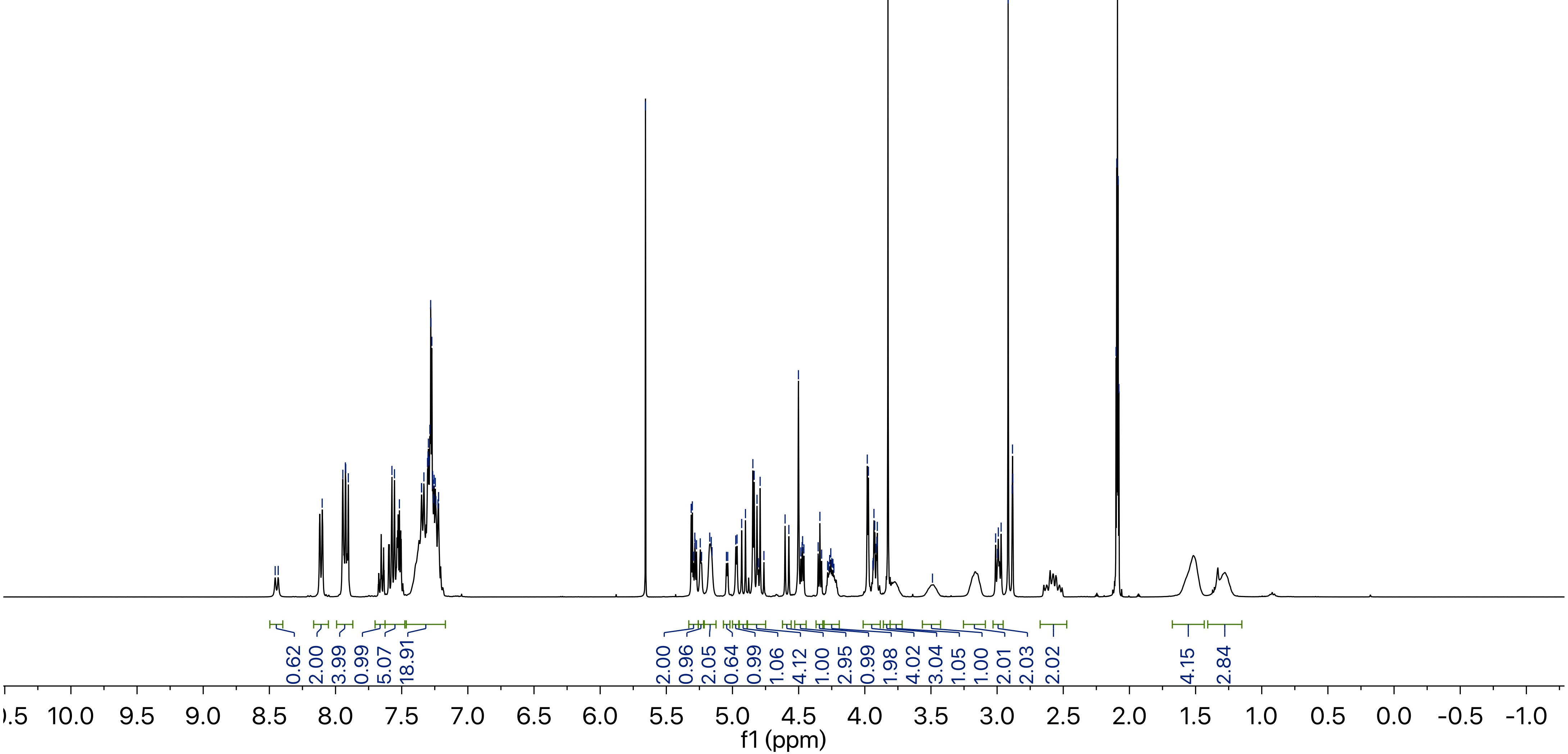
WL-2-175-6-2-Osulfation.2.1.2rr —



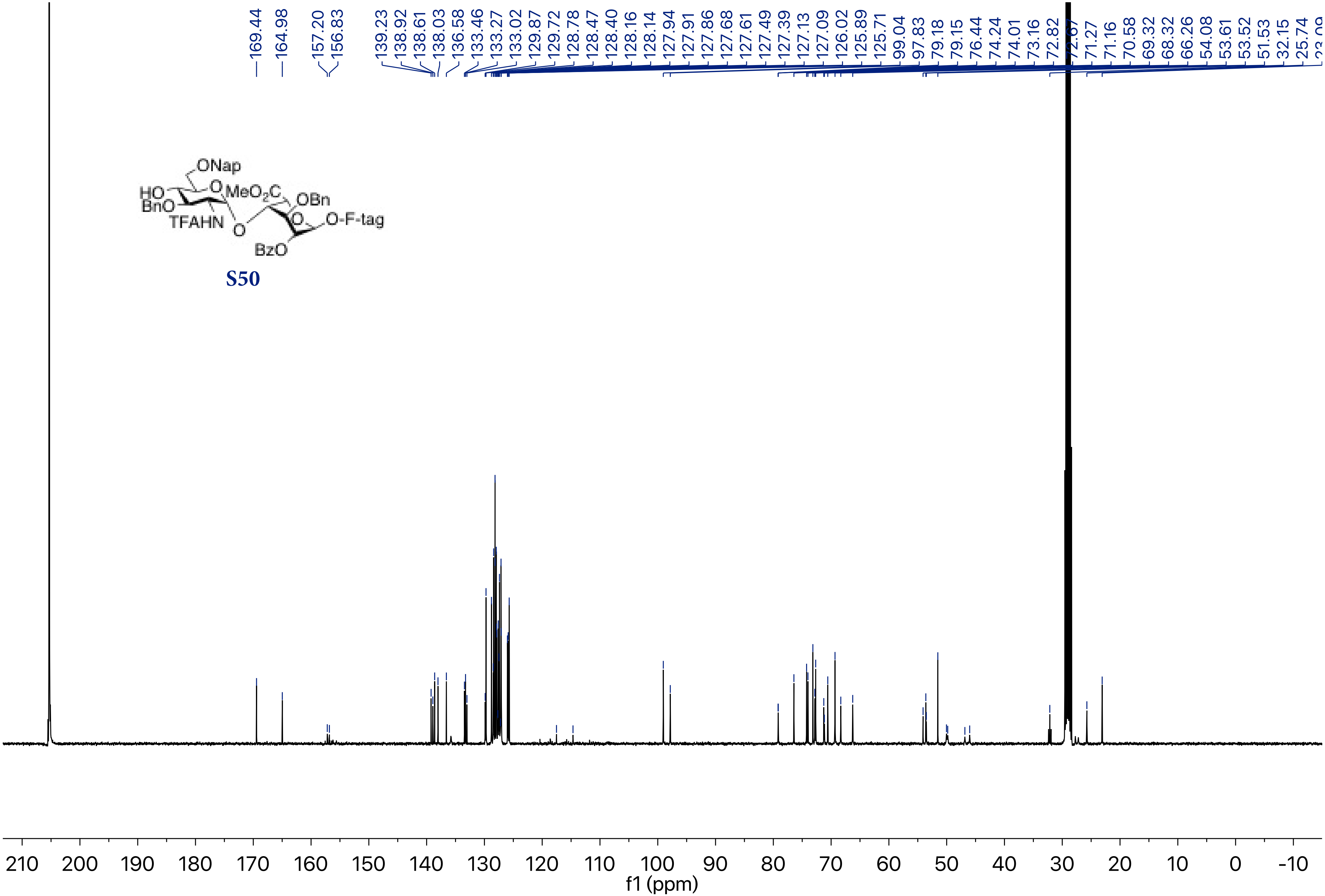
WL-2-210-Bz-Acceptor-Prod-H.3.1.1r



S50

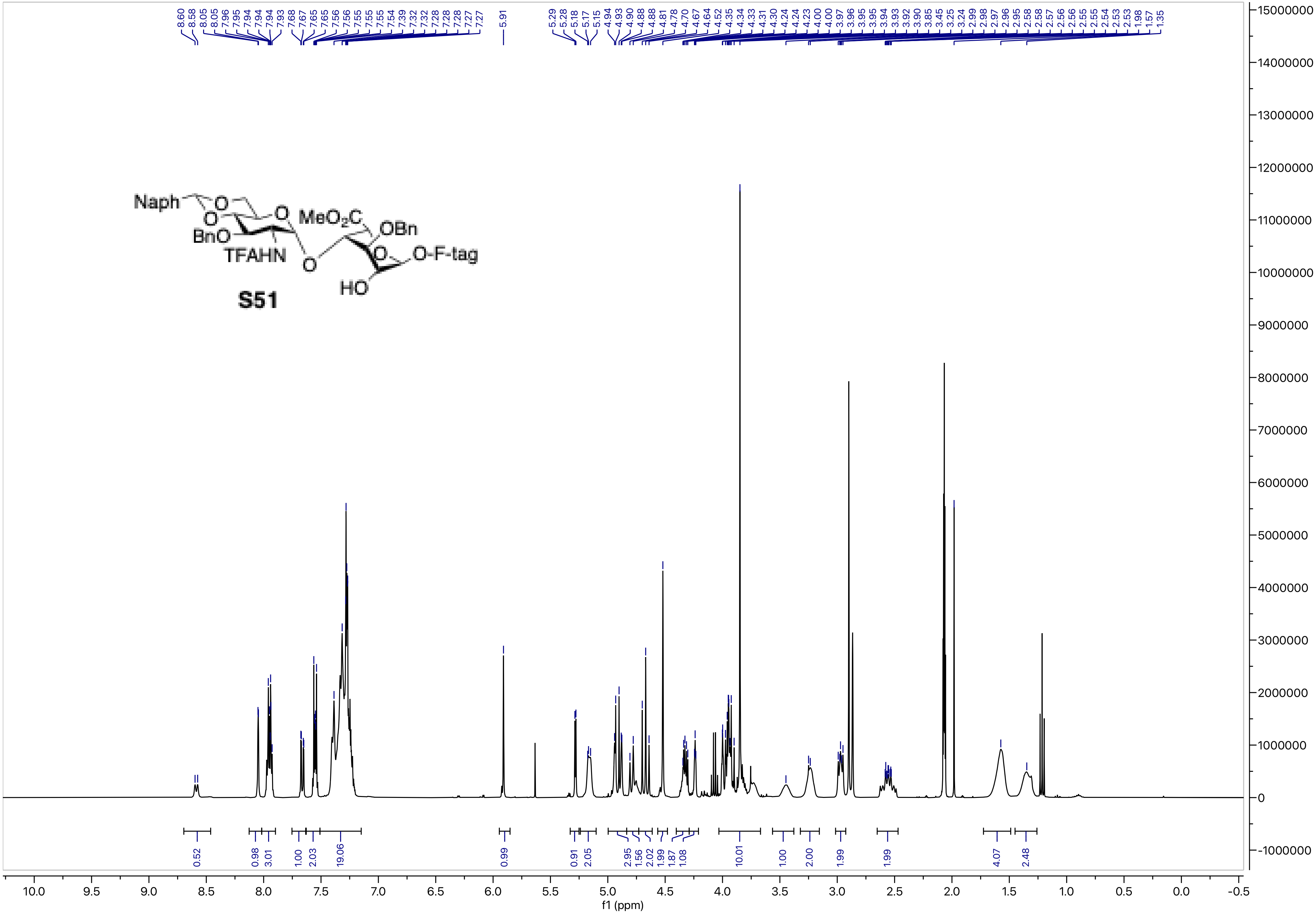


WL-2-210-Bz-Acceptor-Prod-C.2.1.1r



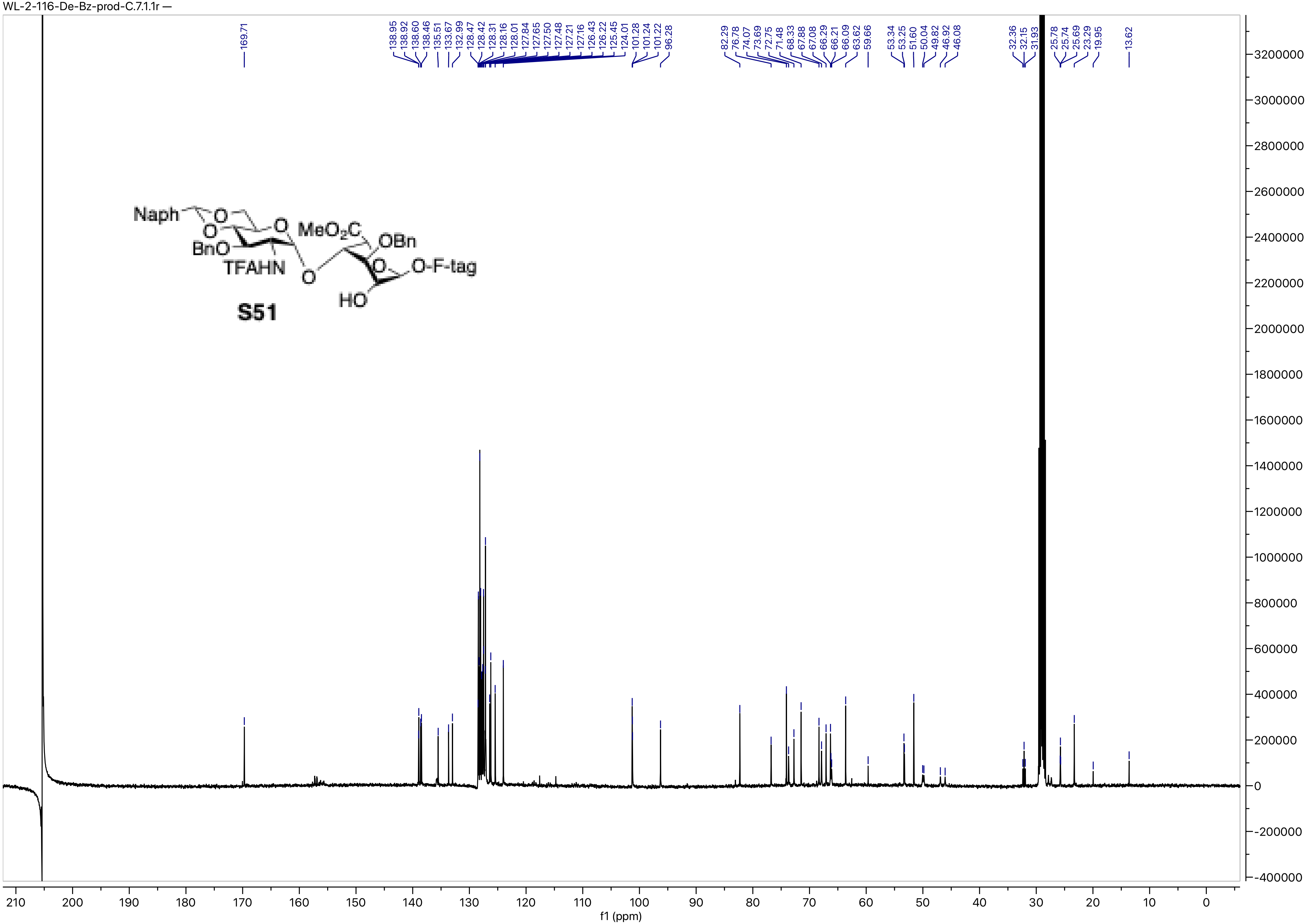
S50

WL-2-116-De-Bz-prod-H.9.1.1r —

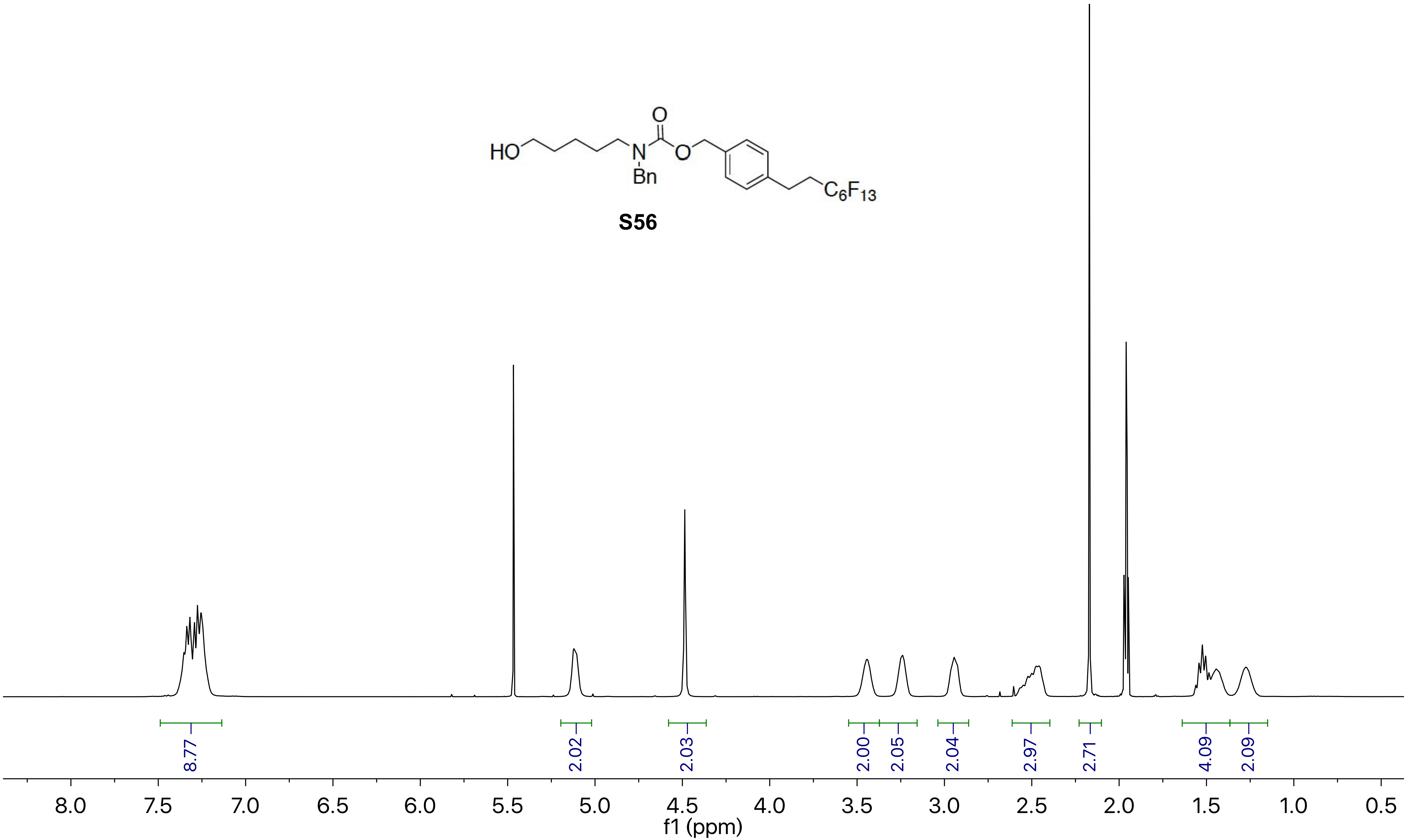


S51

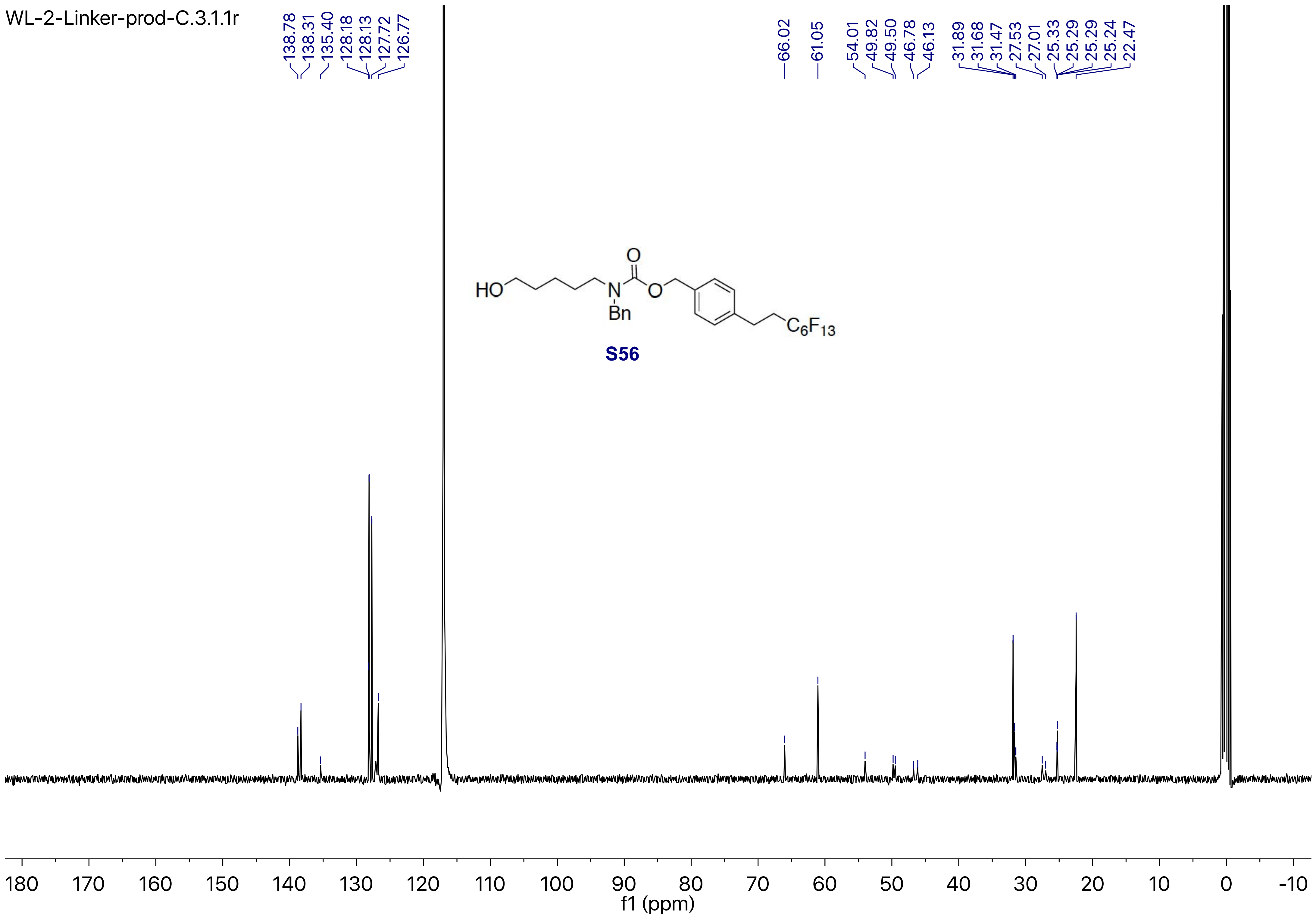
WL-2-116-De-Bz-prod-C.7.1.1r —

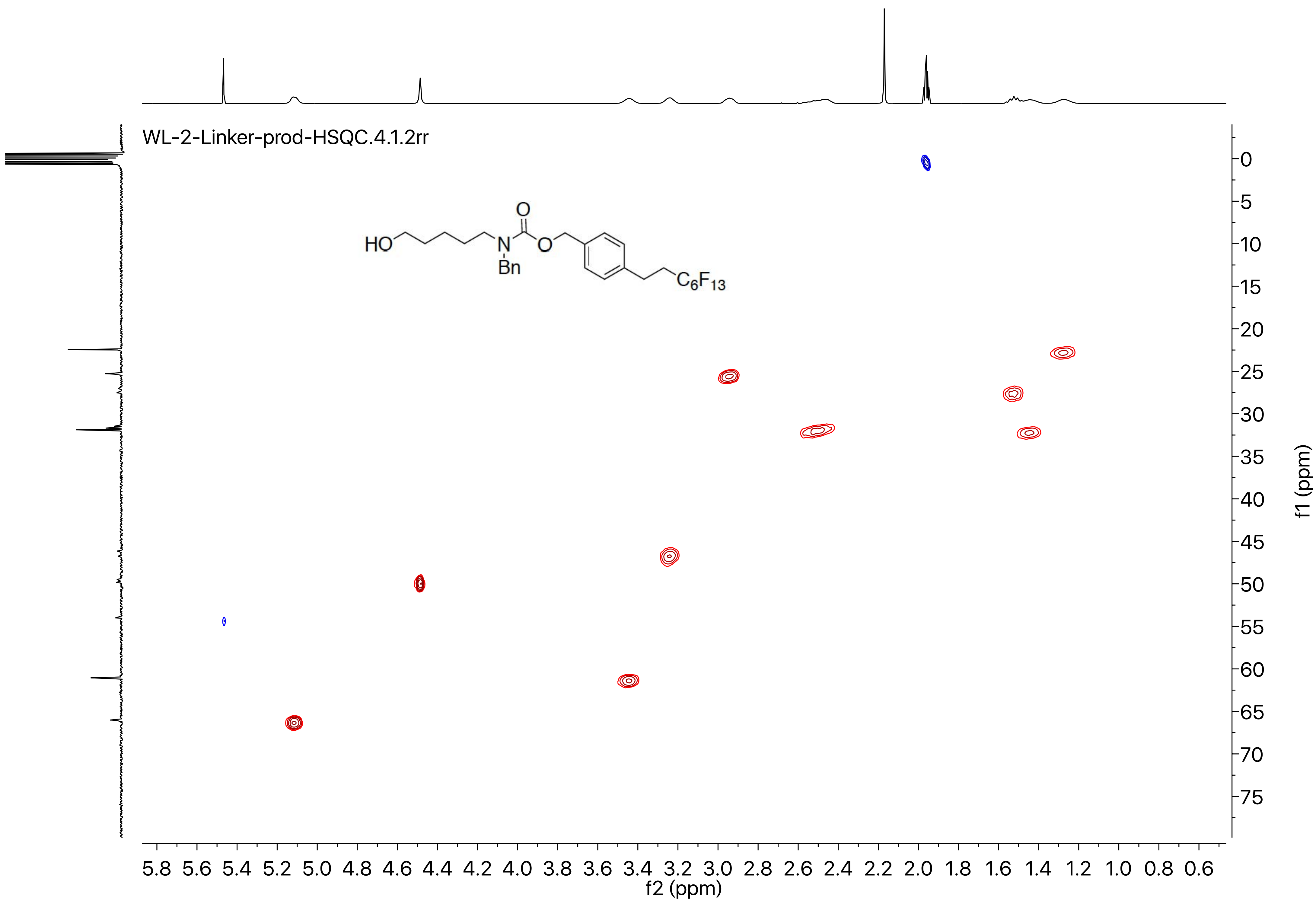


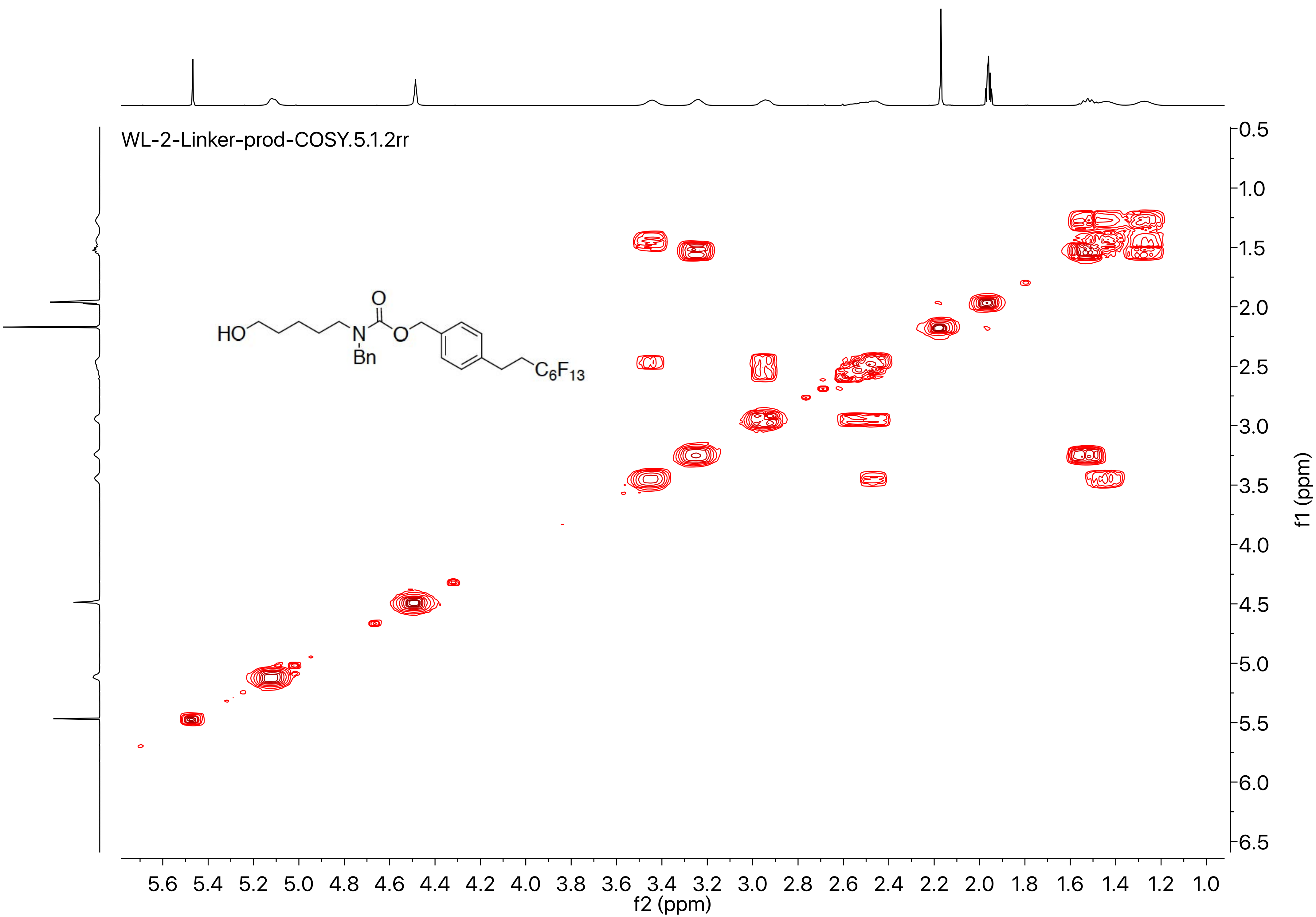
WL-2-Linker-prod-H.2.1.1r



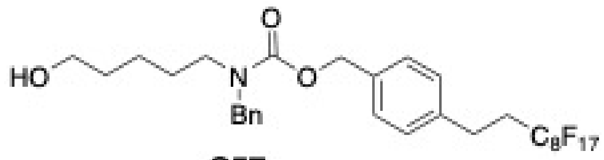
S56

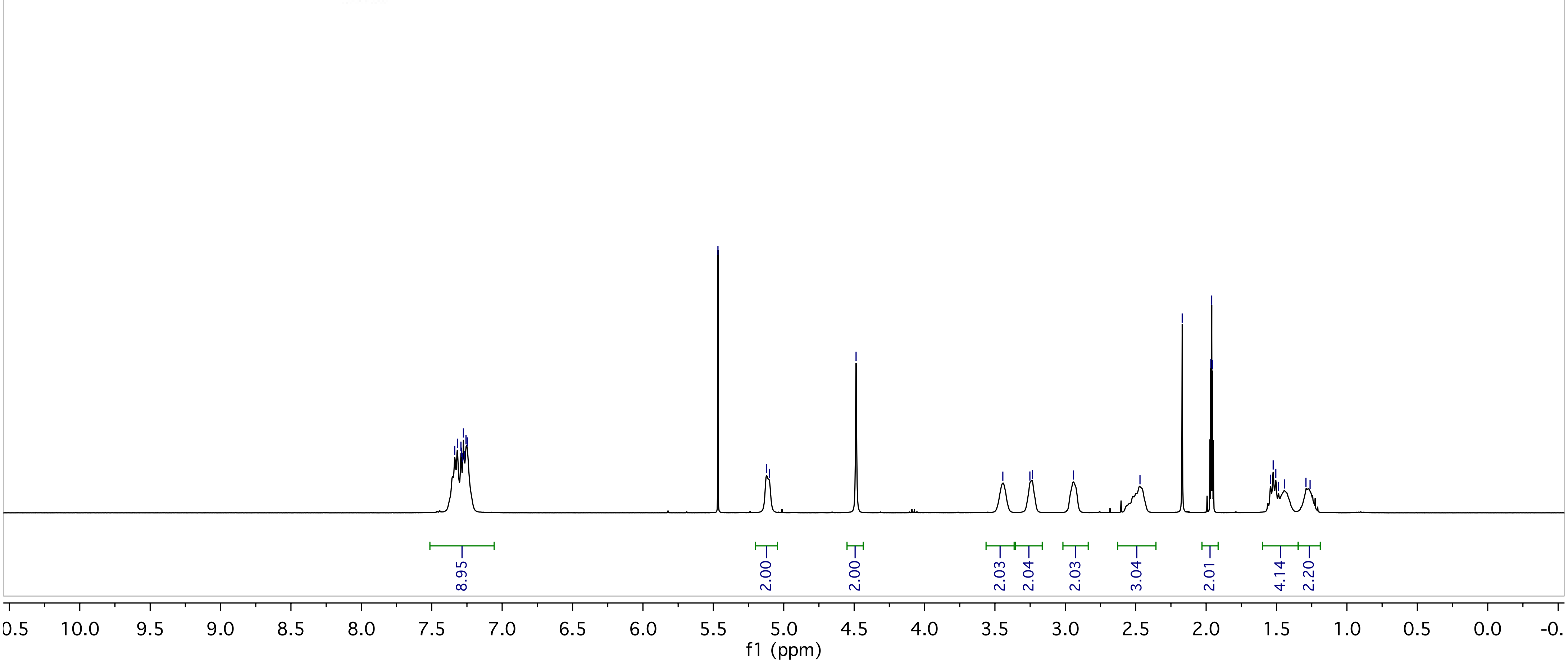

WL-2-Linker-prod-C.3.1.1r
138.78
138.31
135.40
128.18
128.13
127.72
126.77
66.02
61.05
54.01
49.82
49.50
46.78
46.13
31.89
31.68
31.47
27.53
27.01
25.33
25.29
25.29
25.24
22.47
HO
N
Bn
O
O
C_6F_{13}
S56
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


WL-2-Linker-prod-HSQC.4.1.2rr
HO
N
Bn
O
O
C_6F_{13}
f2 (ppm)
f1 (ppm)

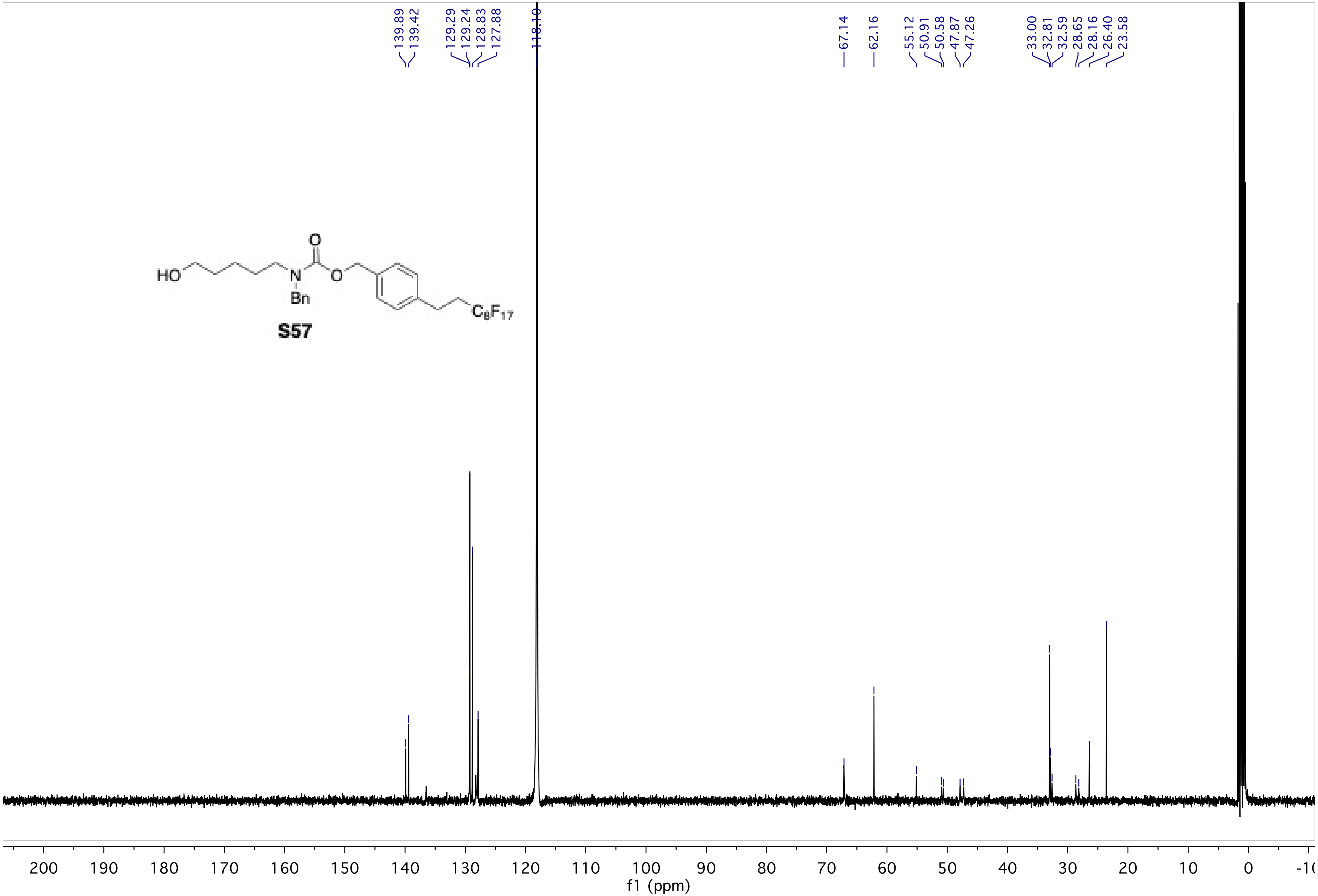

WL-2-Linker-prod-COSY.5.1.2rr
HO
N
Bn
O
O
C6F13
f2 (ppm)
f1 (ppm)

WL-2-063-F8-Linker-H.1.1.1r —





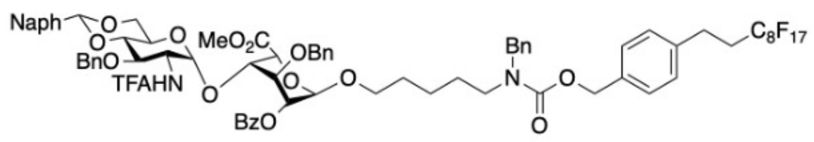
WL-2-063-F8-Linker-C.1.1.1r —



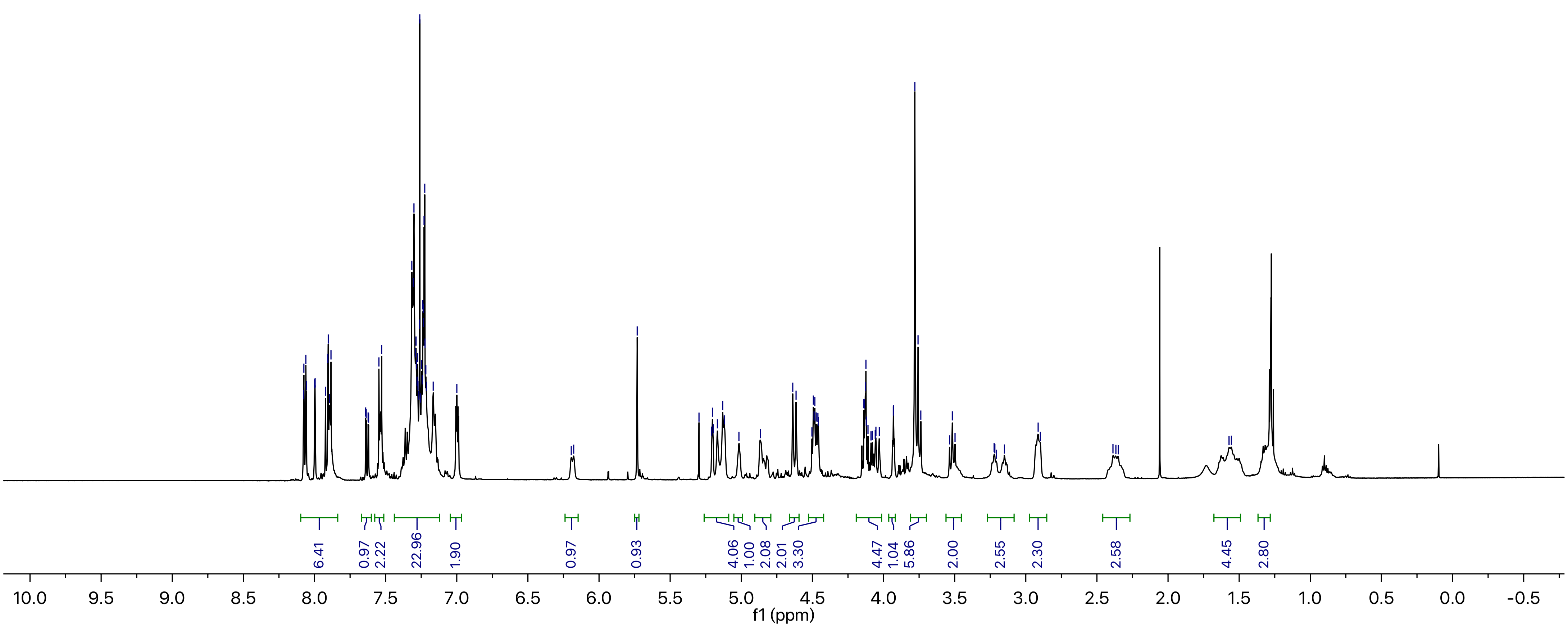
S57

PROTON01
WL-2-064-prod

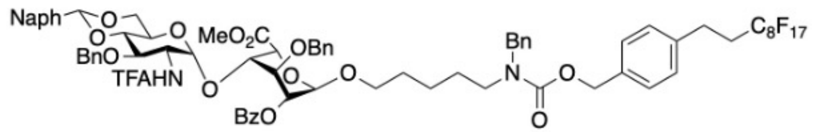
8.08 8.07 8.06 8.06 8.00 8.00 7.92 7.91 7.90 7.89 7.88 7.64 7.64 7.62 7.62 7.55 7.53 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.17 7.00 5.73 5.30 5.21 5.20 5.20 5.17 5.13 5.12 5.02 4.87 4.64 4.61 4.50 4.49 4.49 4.48 4.47 4.46 4.46 4.14 4.13 4.13 4.12 4.12 4.11 4.09 4.08 4.06 4.05 4.03 3.93 3.93 3.78 3.76 3.74 3.54 3.52 3.50 3.22 2.91 2.90 1.57 1.55



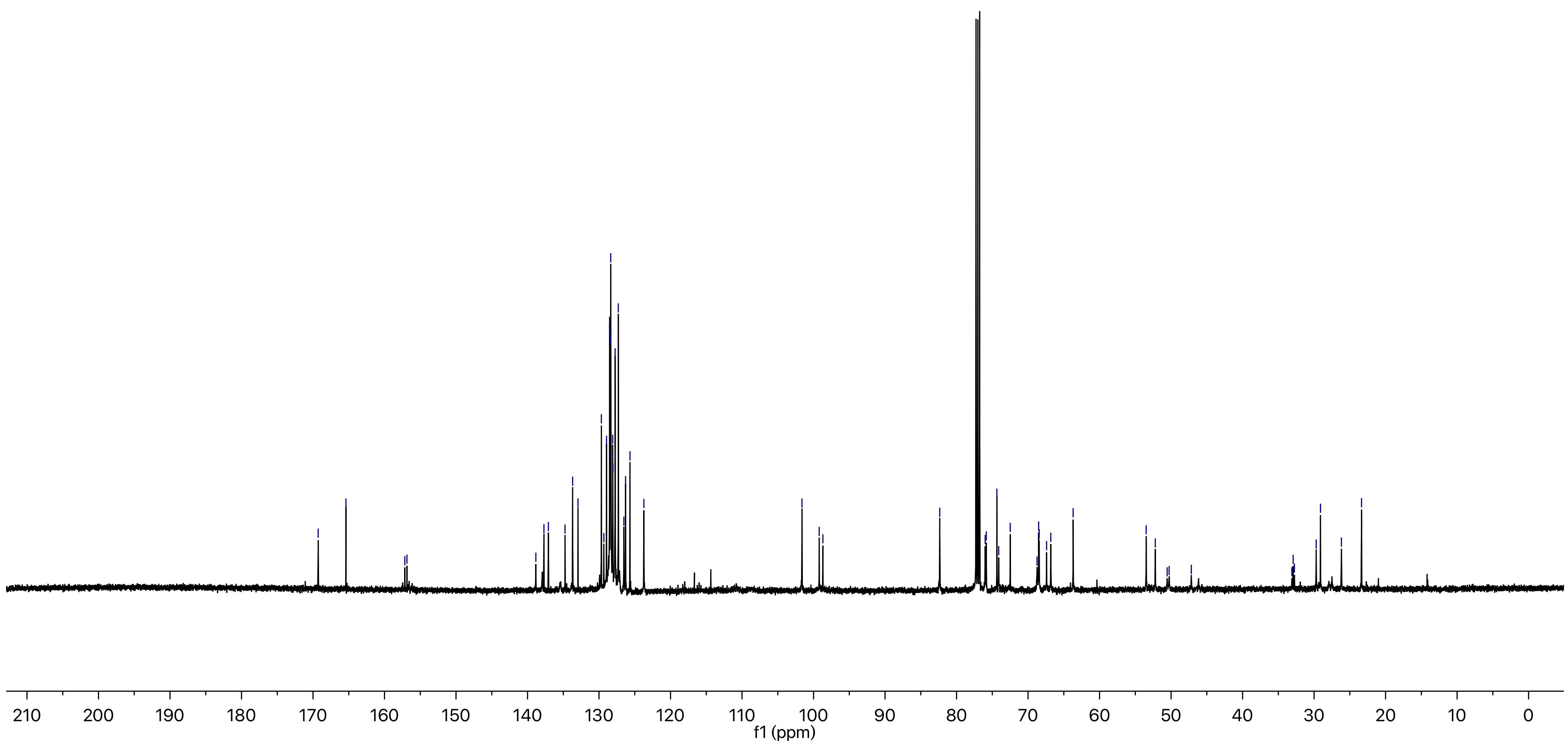
S58

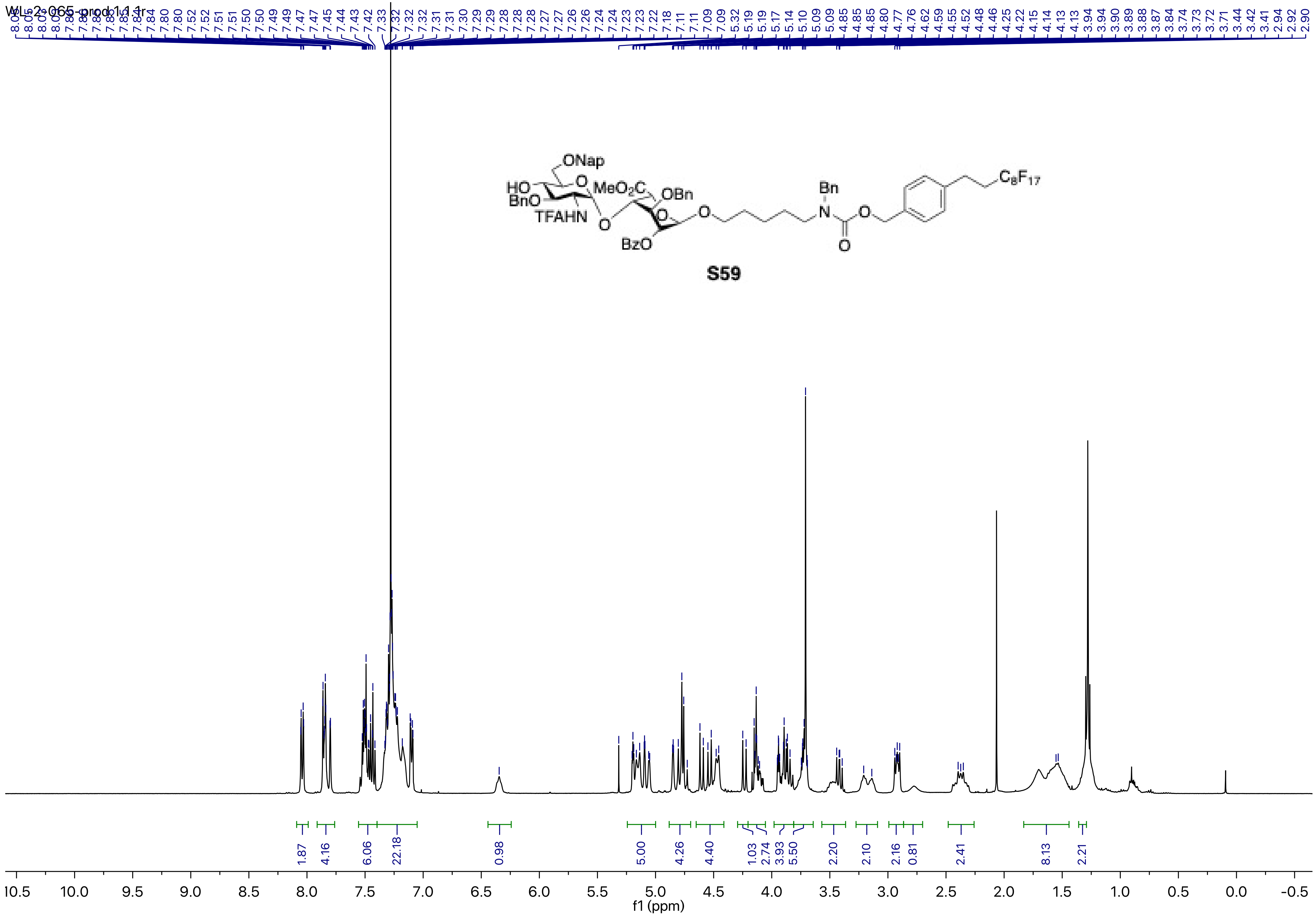


CARBON01
WL-2-064-prod

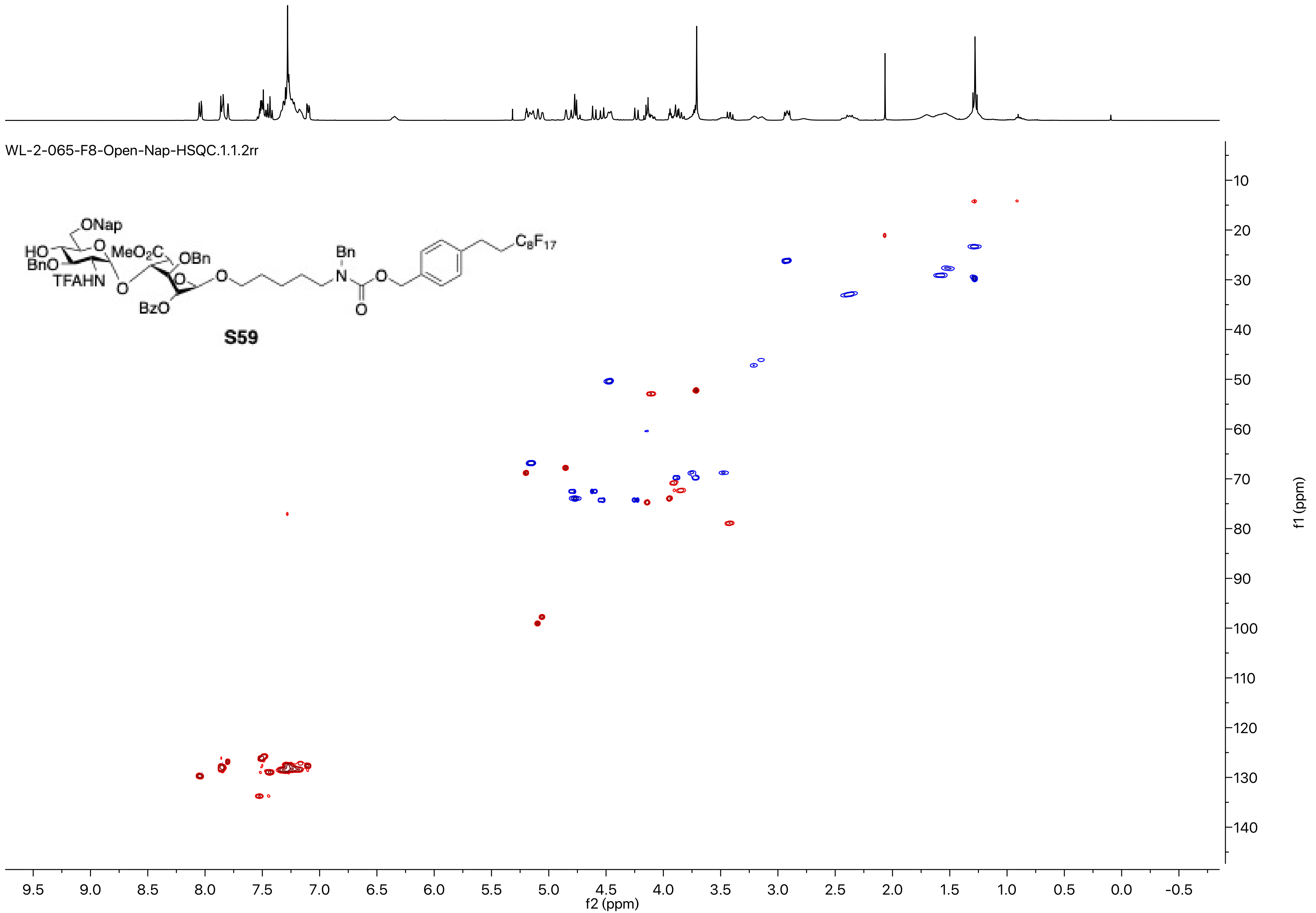


S58

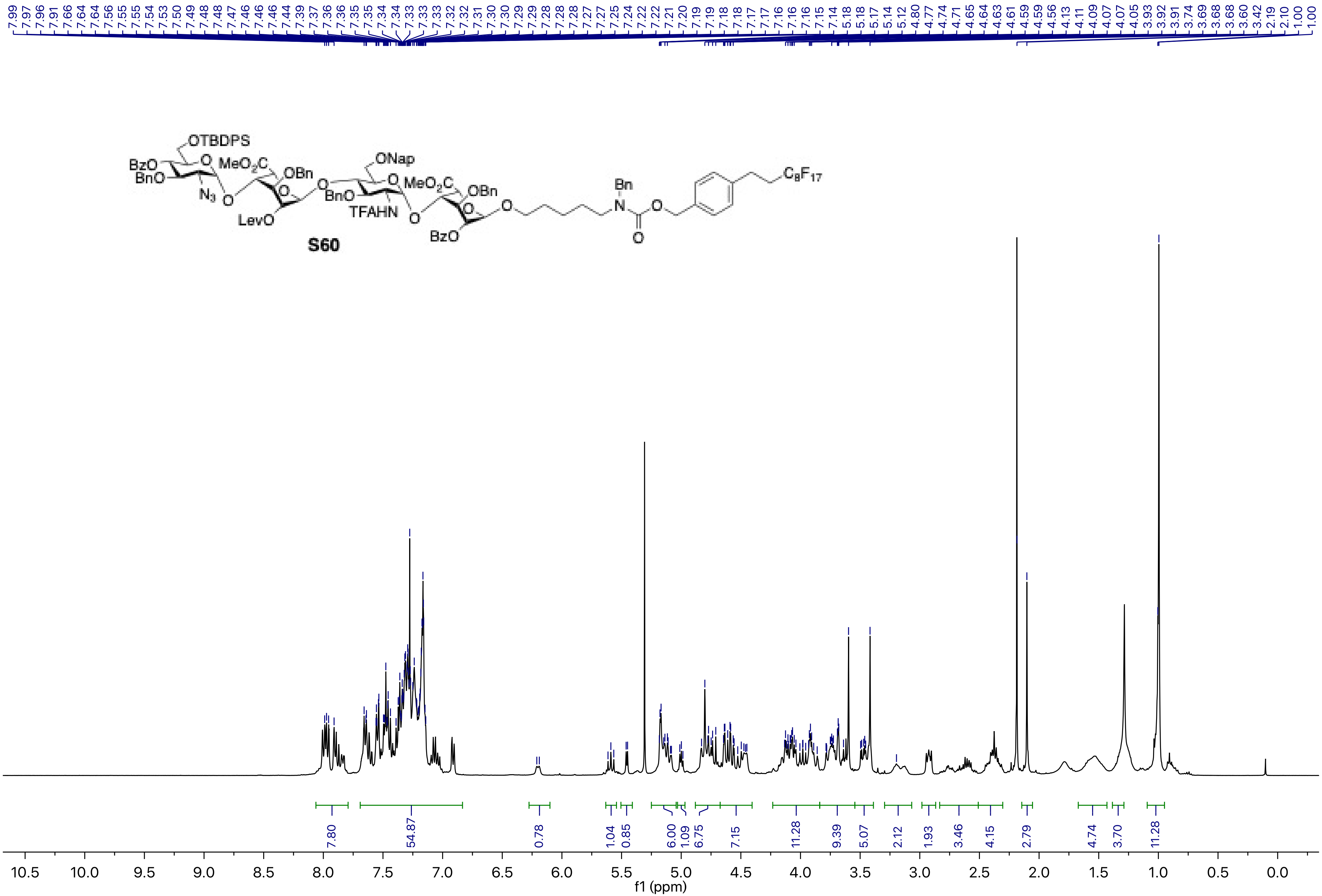




WL-2-065-prod.1.1.1r
7.84 7.80 7.80 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.47 7.47 7.45 7.44 7.43 7.42 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.23 7.23 7.22 7.18 7.11 7.11 7.09 7.09 5.32 5.19 5.19 5.17 5.14 5.10 5.09 5.09 4.85 4.85 4.85 4.80 4.77 4.76 4.62 4.59 4.55 4.52 4.48 4.46 4.25 4.22 4.15 4.14 4.13 4.13 3.94 3.94 3.90 3.89 3.88 3.87 3.84 3.74 3.73 3.72 3.71 3.44 3.42 3.41 2.94 2.92 2.90
ONap
HO
BnO
TFAHN
MeO2C
OBn
BzO
Bn
N
O
C8F17
S59
1.87 4.16 6.06 22.18 0.98 5.00 4.26 4.40 1.03 2.74 3.93 5.50 2.20 2.10 2.16 0.81 2.41 8.13 2.21
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 -0.5
f1 (ppm)

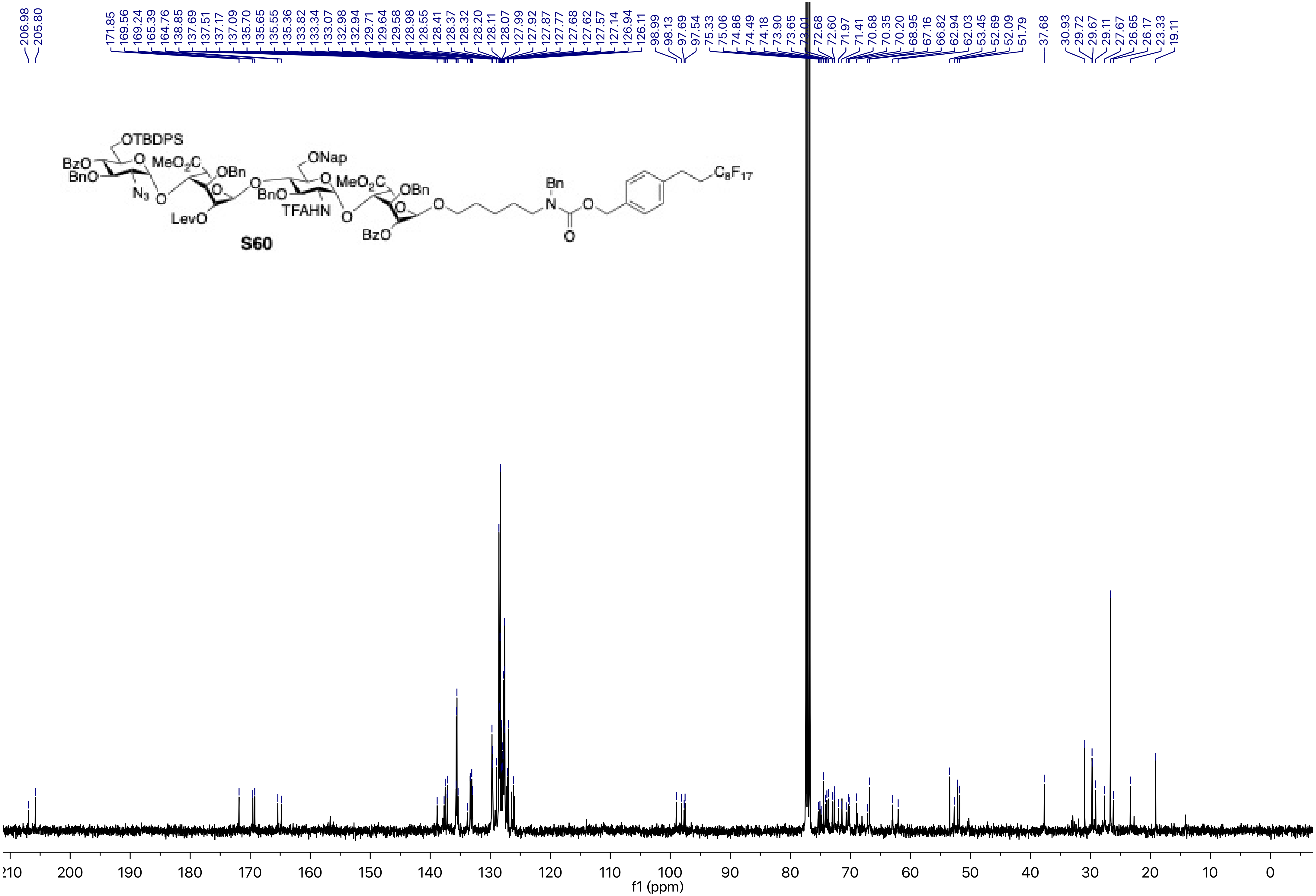

WL-2-065-F8-Open-Nap-HSQC.1.1.2rr
S59
f2 (ppm)
f1 (ppm)

WL-2-066-F8-Tetra-H.1.fid —

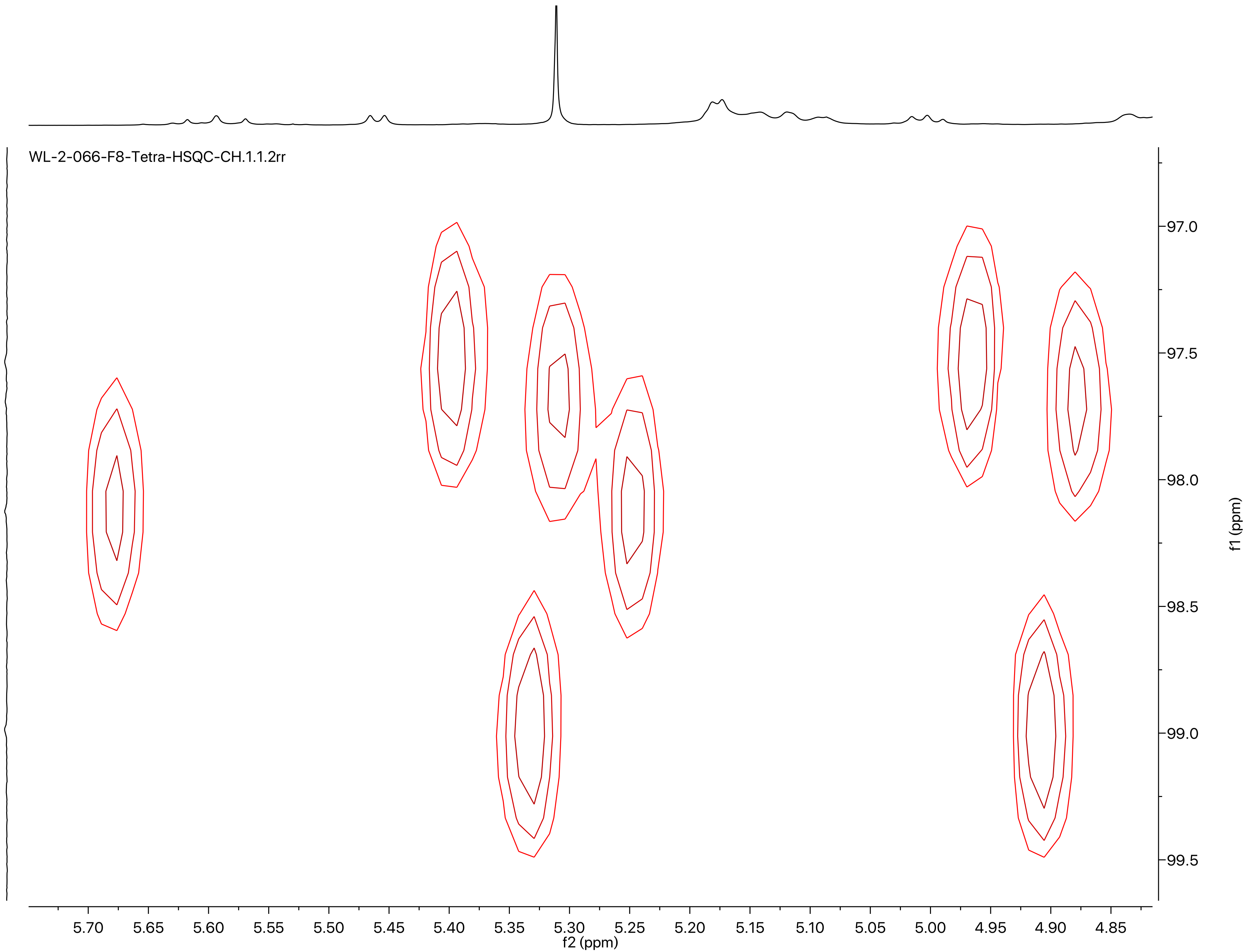


S60

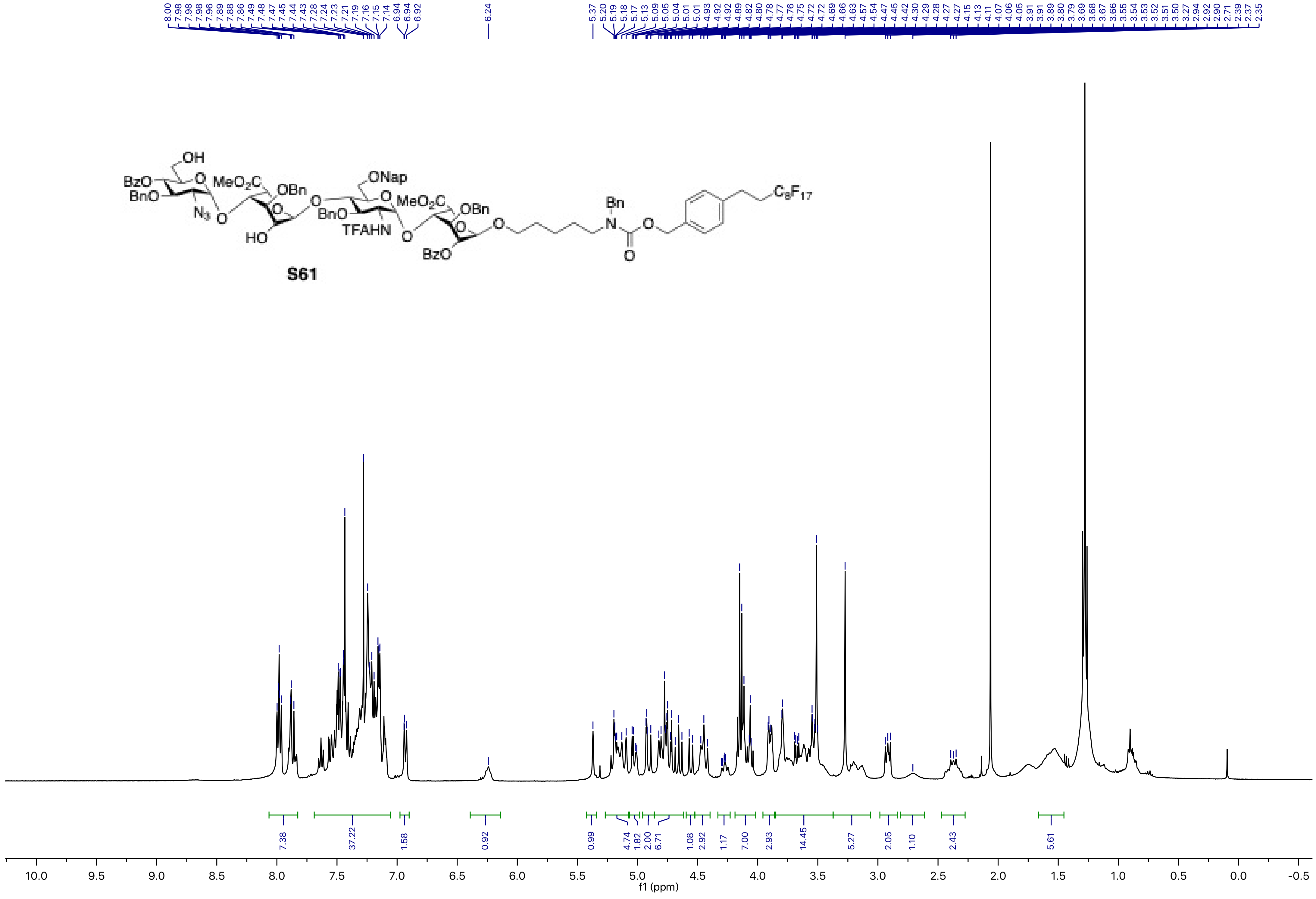
WL-2-066-F8-Tetra-C.1.1.1r



S60

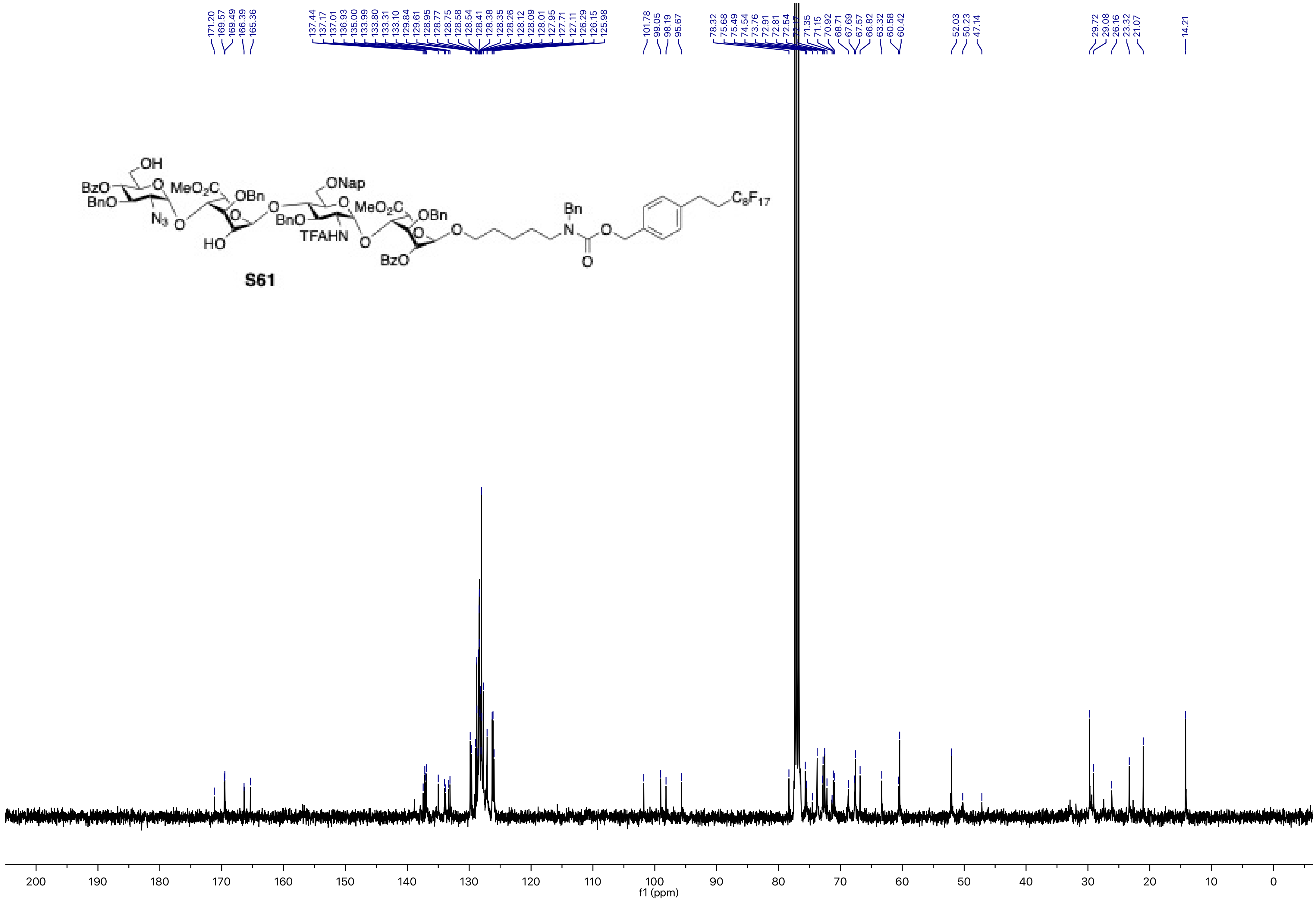

WL-2-066-F8-Tetra-HSQC-CH.1.1.2rr
f2 (ppm)
f1 (ppm)
5.70
5.65
5.60
5.55
5.50
5.45
5.40
5.35
5.30
5.25
5.20
5.15
5.10
5.05
5.00
4.95
4.90
4.85
97.0
97.5
98.0
98.5
99.0
99.5

WL-2-068-De-Lev-De-TBDPS-H.1.1.1r —



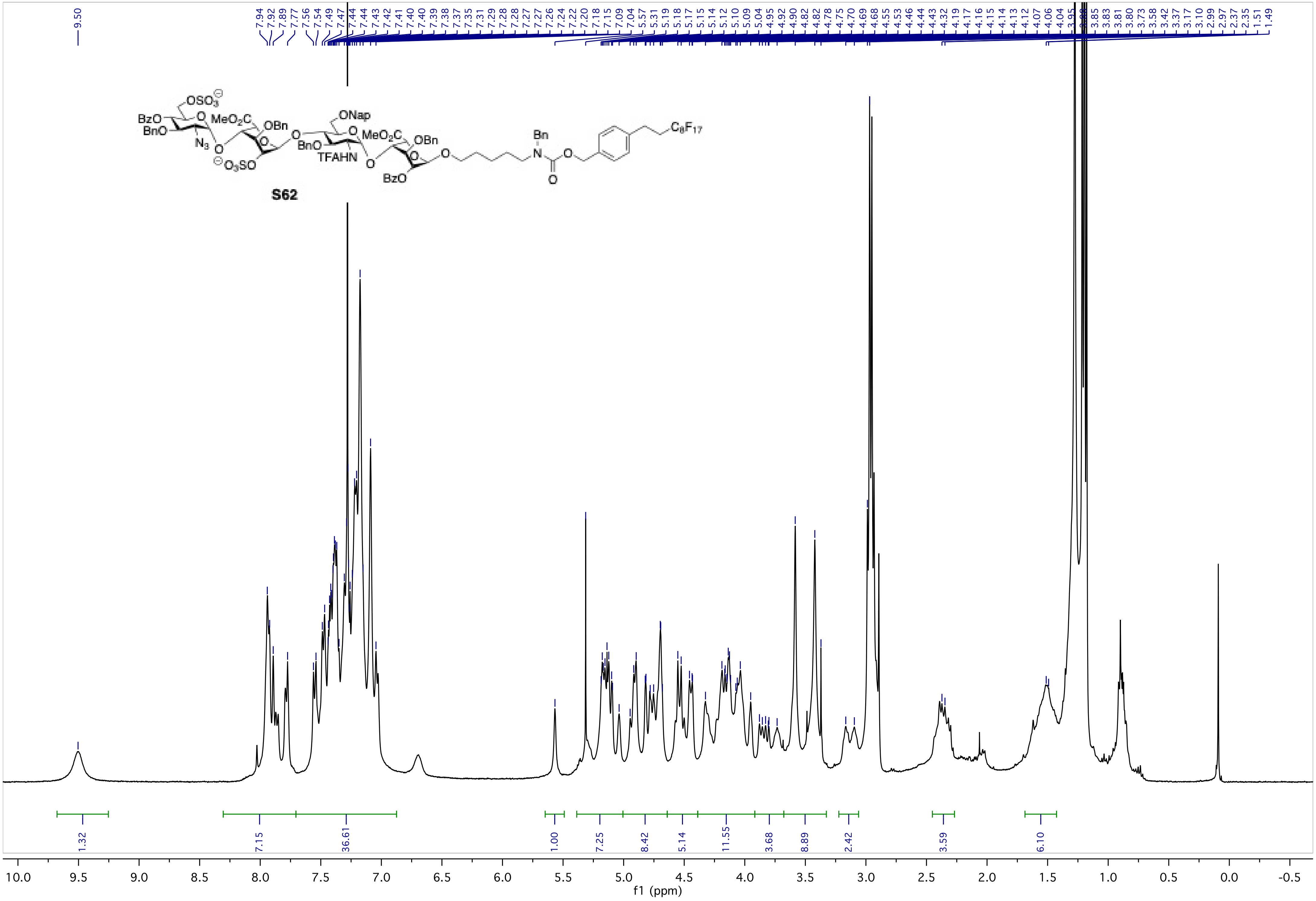
S61

WL-2-068-F8-DeLev-DeTBDPS-C.1.1.1r —

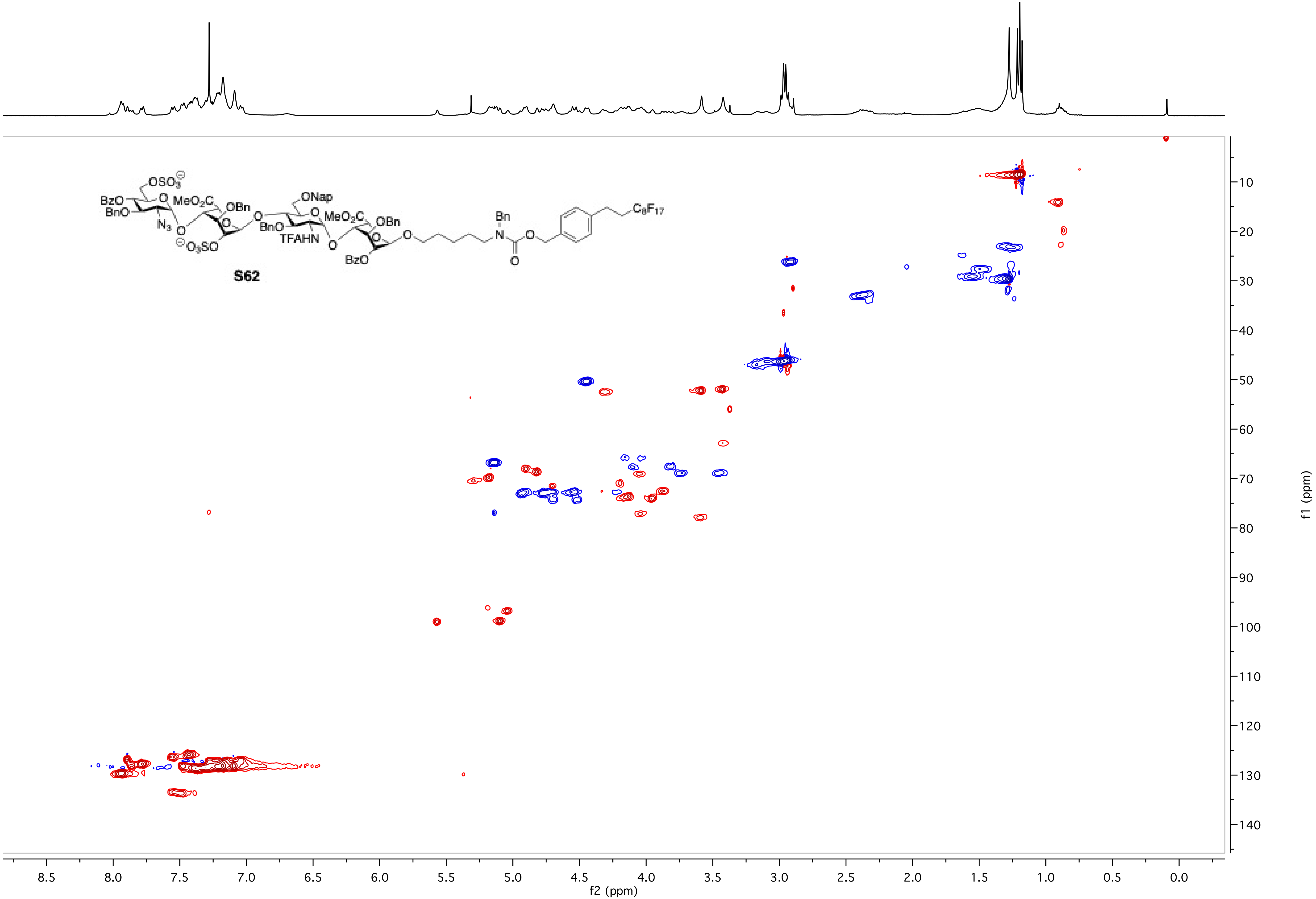


S61

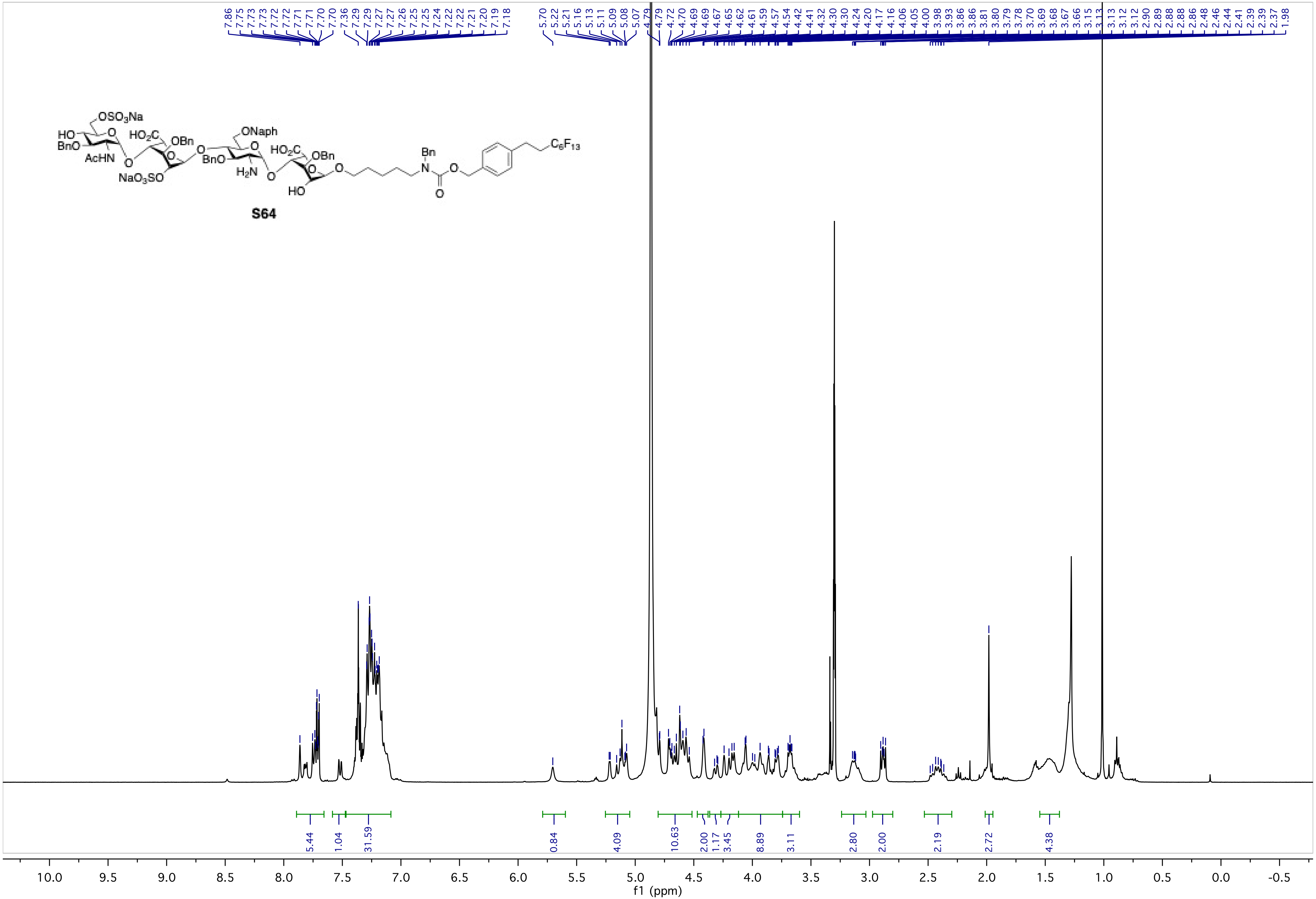
WL-2-069-F8-D-6-SO3-2-SO3-H.3.1.1r



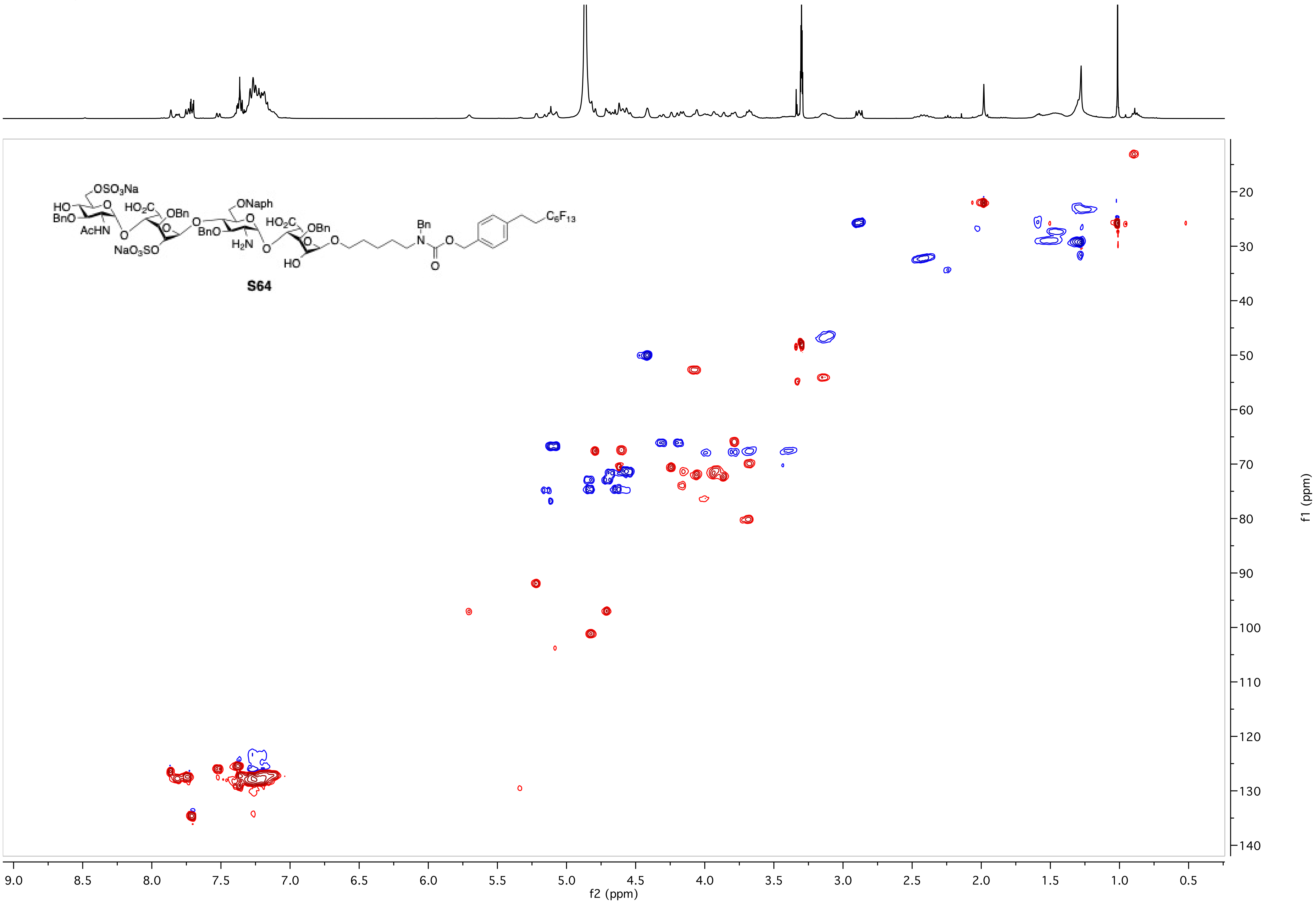
WL-2-069-F8-D-6-SO3-2-SO3-HSQC.2.1.2rr —



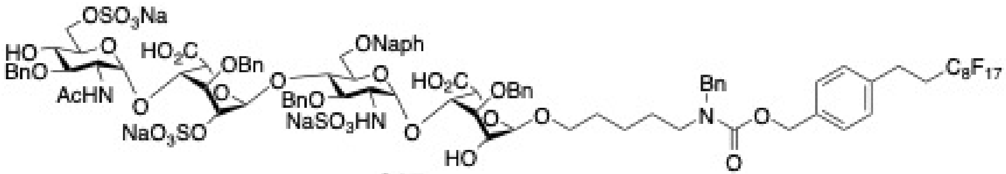
WL-2-177-LiOH.1.1.1r —



WL-2-177-LiOH.2.1.2rr —



WL-2-072-F8-NSO3-crude.1.fid —



S67