Supplementary Information

For

Enzymatic modular synthesis and microarray assay of poly-*N*-acetyllactosamine derivatives

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Table of Contents

I. Supplementary Figures

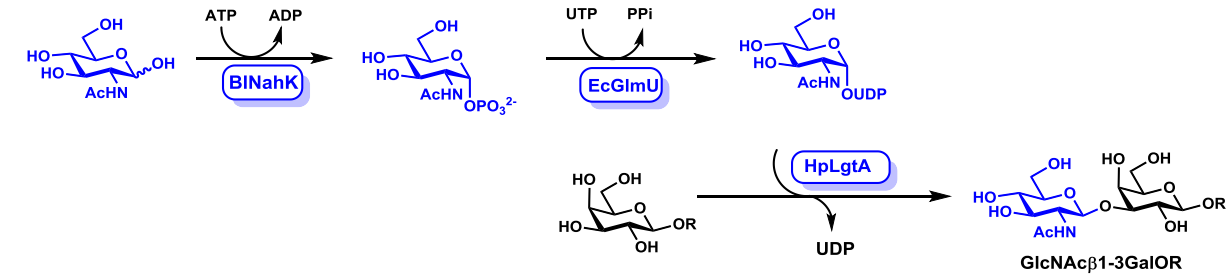


Fig. S1 Enzyme Module 1 (EM1) for β1-3-N-acetylglucosaminylation

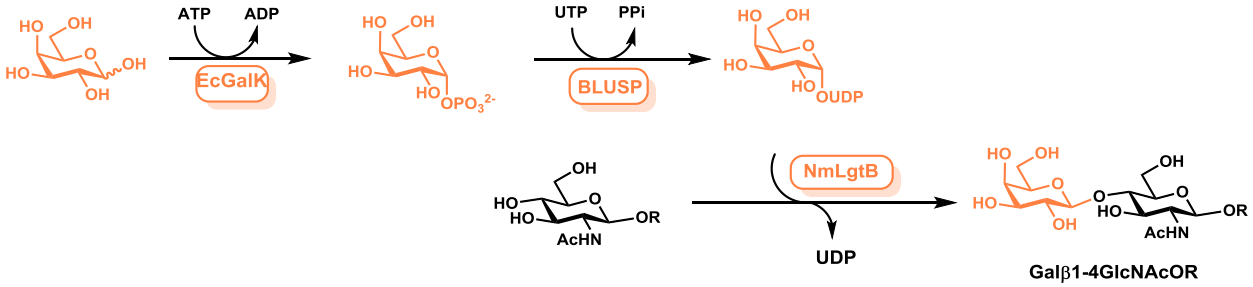


Fig. S2 Enzyme Module 2 (EM2) for β1-4-galactosylation

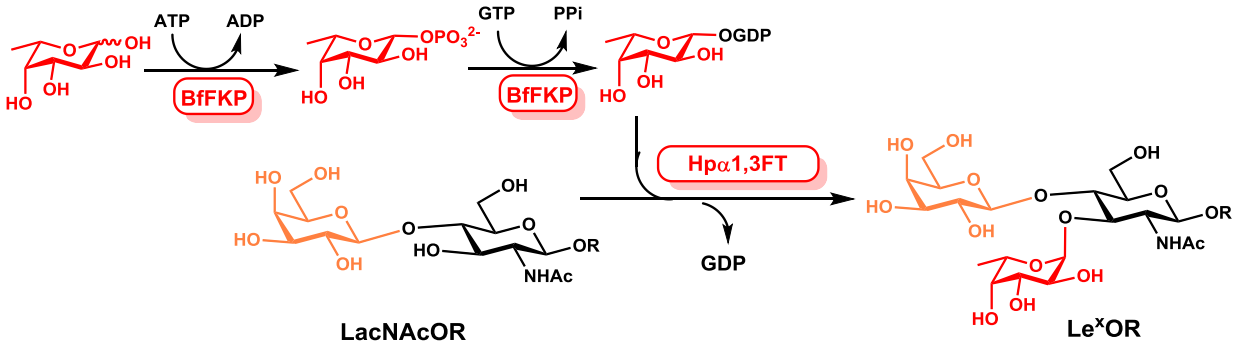


Fig. S3 Enzyme Module 3 (EM3) for α1-3-fucosylation

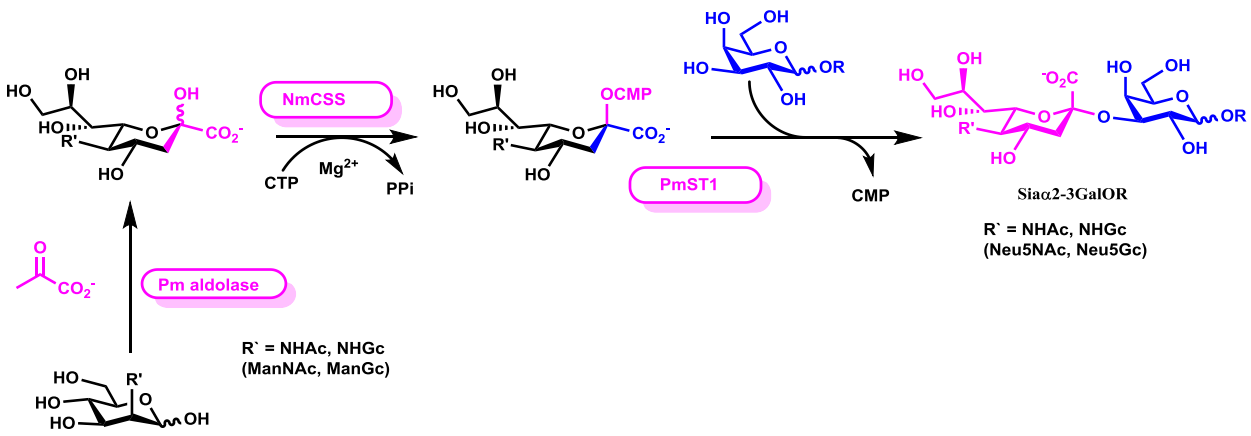


Fig. S4 Enzyme Module 4 (EM4) for α2-3-sialylation

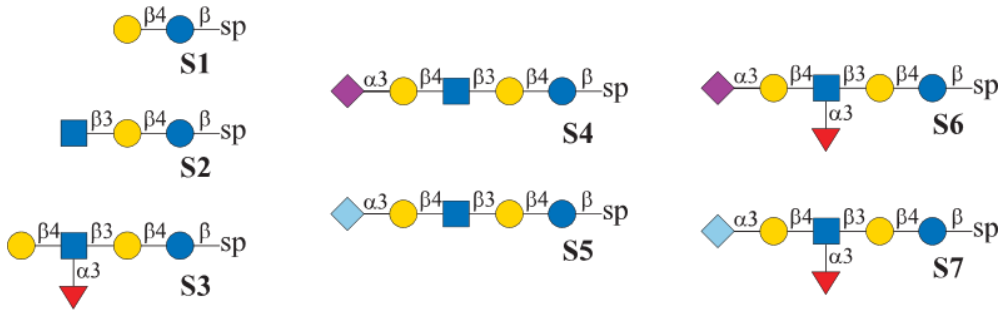


Fig. S5 Structure of compounds **S1**–**S7**

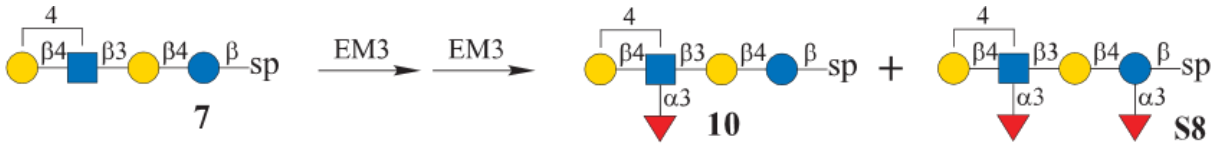


Fig. S6 Synthesis of **10** and **S8** with EM3

Compound **10** was prepared according to general procedure of α1-3-fucosylation with EM3. The acceptor **7** was only partially fucosylated in the first round, the partially fucosylated compounds was purified and another round of fucosylation with EM3 was performed. The partially fucosylated **S8** (11 mg, 9 %) was also obtained along with major product **10** after two rounds fucosylation with EM3.

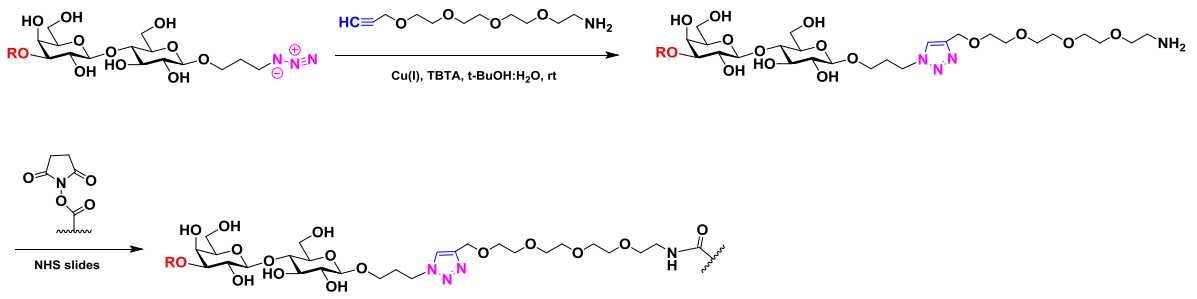
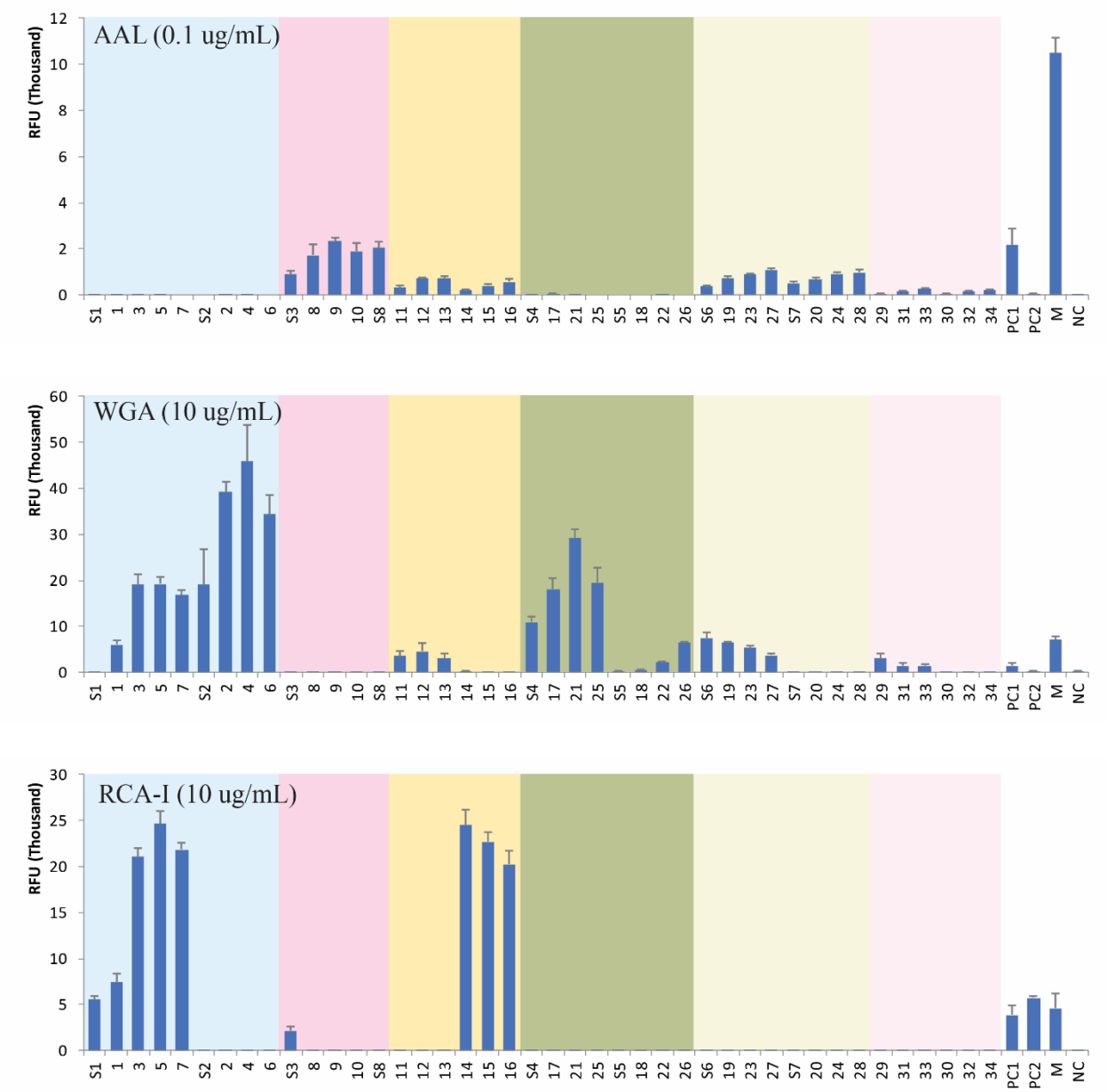
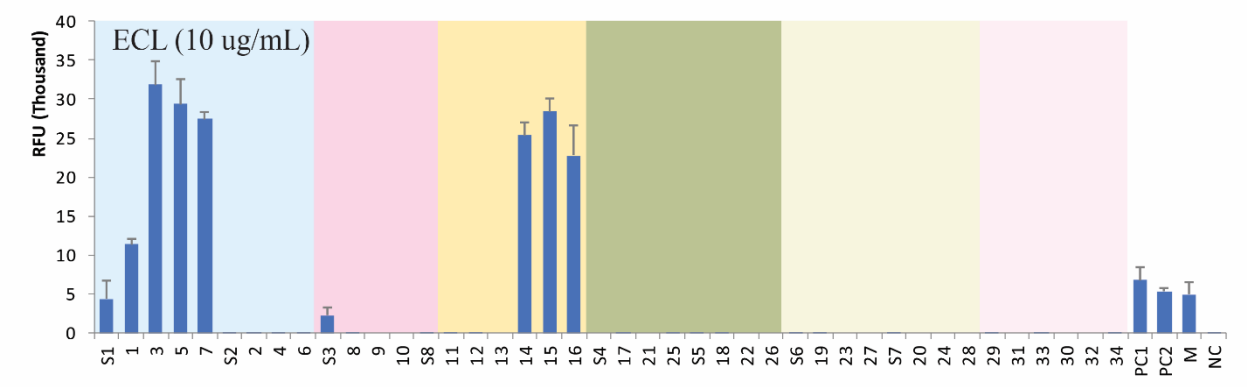
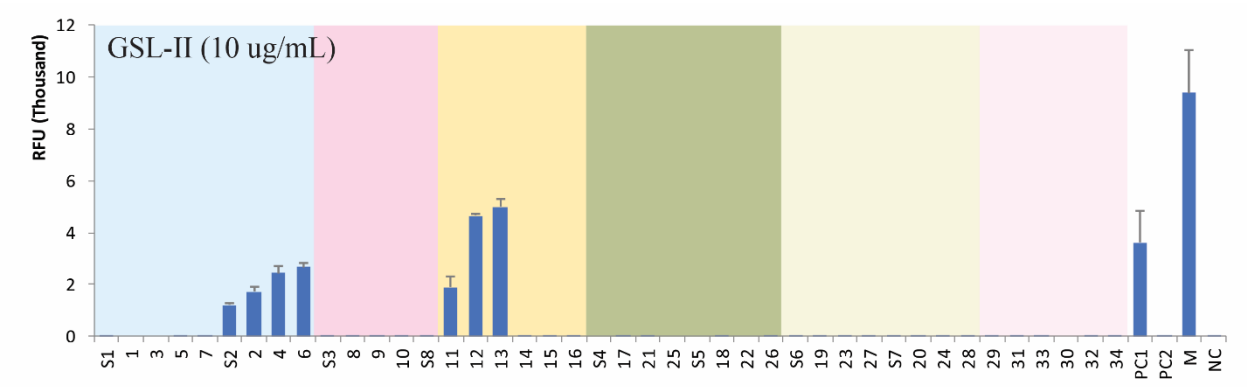
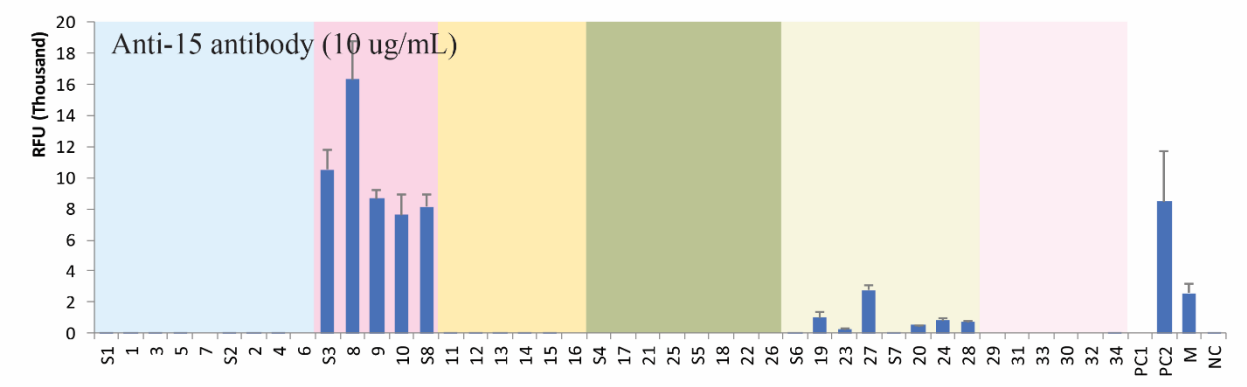


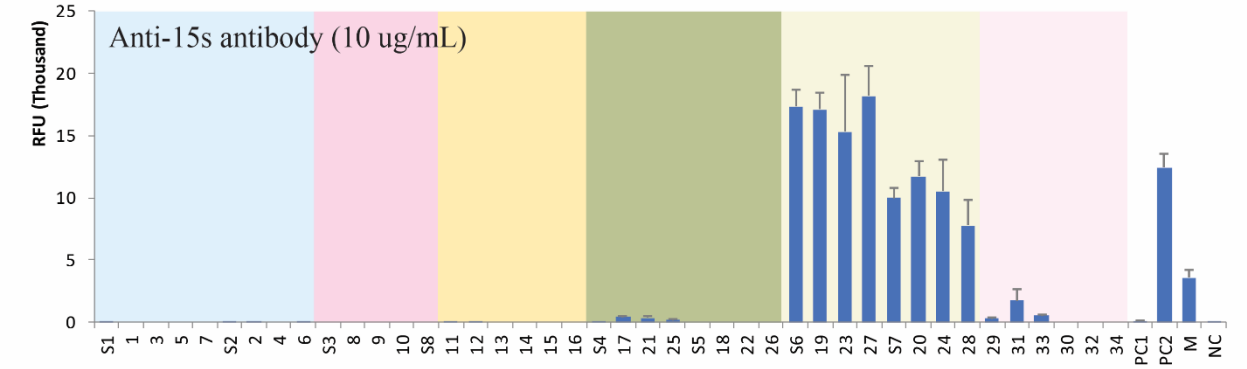
Fig. S7 preparation of -NH_2 glycans for glycan array




ECL (10 ug/mL)
RFU (Thousand)
0 5 10 15 20 25 30 35 40
S1 1 3 5 7 S2 2 4 6 S3 8 9 10 S8 11 12 13 14 15 16 S4 17 21 25 S5 18 22 26 S6 19 23 27 S7 20 24 28 29 31 33 30 32 34 PC1 PC2 M NC


GSL-II (10 ug/mL)
RFU (Thousand)
0 2 4 6 8 10 12
S1 1 3 5 7 S2 2 4 6 S3 8 9 10 S8 11 12 13 14 15 16 S4 17 21 25 S5 18 22 26 S6 19 23 27 S7 20 24 28 29 31 33 30 32 34 PC1 PC2 M NC


Anti-15 antibody (10 ug/mL)
RFU (Thousand)
0 2 4 6 8 10 12 14 16 18 20
S1 1 3 5 7 S2 2 4 6 S3 8 9 10 S8 11 12 13 14 15 16 S4 17 21 25 S5 18 22 26 S6 19 23 27 S7 20 24 28 29 31 33 30 32 34 PC1 PC2 M NC


Anti-15s antibody (10 ug/mL)
RFU (Thousand)
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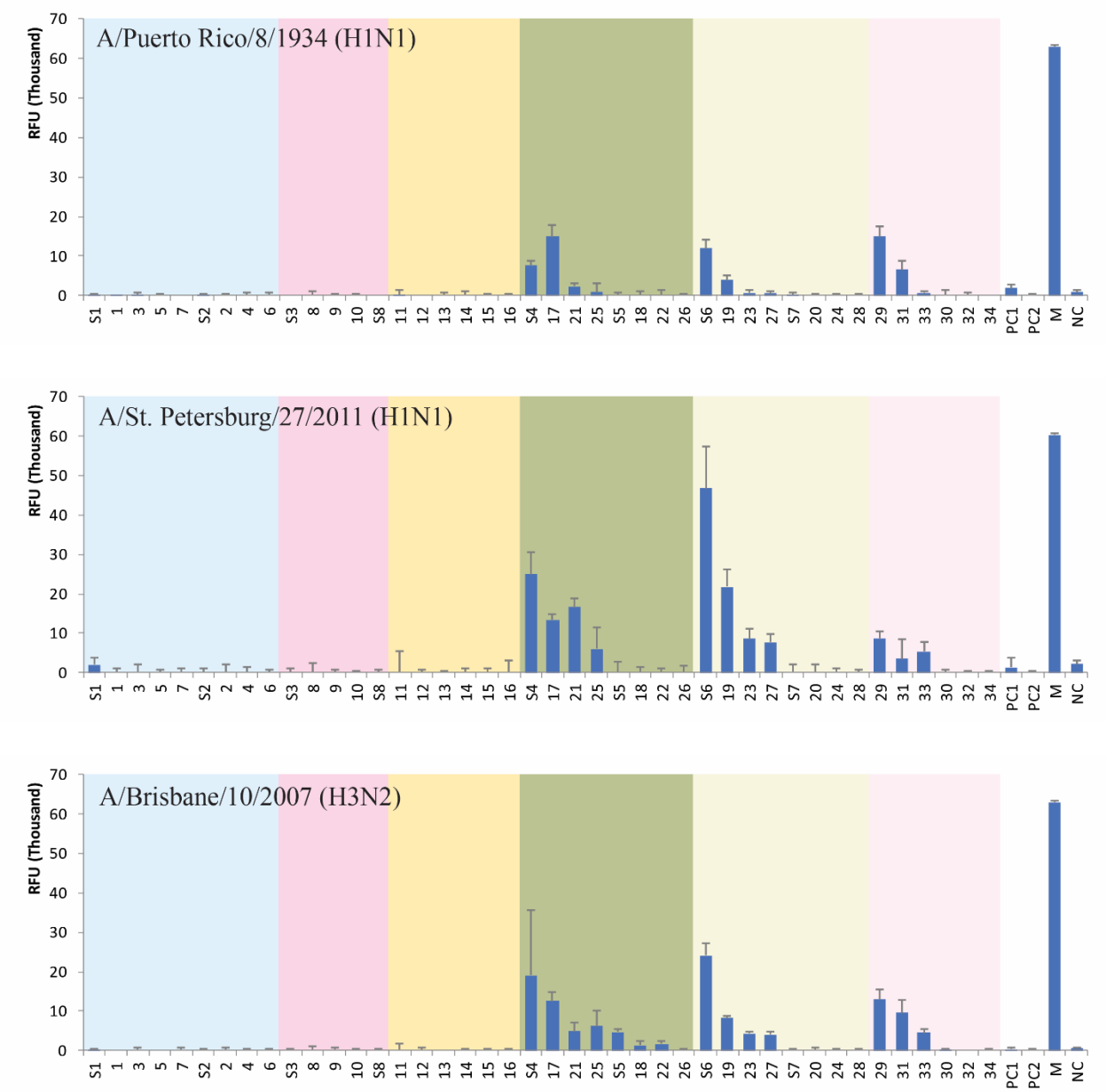
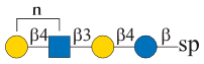
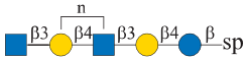
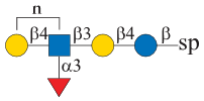
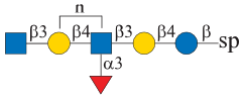
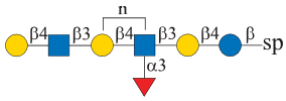
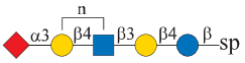
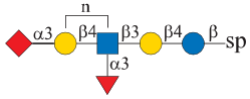
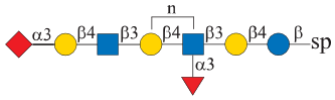


Fig. S8 Binding specificities of glycans with glycan binding proteins

The x-axis shows glycans, and the y-axis shows relative fluorescence readout by Cy5-streptavidin (1 µg/mL). PC1 = biotinylated PEG amine (0.01 mg/mL); PC2 = human IgG (0.1 mg/mL), M = Cy3-conjugated anti-Human IgG (0.01 mg/mL) + Alexs647-conjugated anti-Human IgG (0.01 mg/mL); NC = printing buffer.

Table S1 Glycan structures present on glycan array

Glycan symbol structure	n	Poly-LacNAc	Neu5Ac	Neu5Gc
	0	**S1**		
	1	**1**		
	2	**3**		
	3	**5**		
	4	**7**		
	0	**S2**		
	1	**2**		
	2	**4**		
	3	**6**		
	1	**S3**		
	2	**8**		
	3	**9**		
	4	**10**		
	1	**11**		
	2	**12**		
	3	**13**		
	1	**14**		
	2	**15**		
	3	**16**		
	1		**S4**	**S5**
	2		**17**	**18**
	3		**21**	**22**
	4		**25**	**26**
	1		**S6**	**S7**
	2		**19**	**20**
	3		**23**	**24**
	4		**27**	**28**
	1		**29**	**30**
	2		**31**	**32**
	3		**33**	**34**

II. General Experiment Information

All chemicals were obtained from commercial suppliers and used without further purification unless noted. NahK-GlmU[1], a fusion enzyme from *Bifidobacterium longum N*-acetylhexosamine-1-kinase (NahK) and *Escherichia coli N*-acetylglucosamine uridylyltransferase (GlmU), *Helicobacter pylori* β1−3-*N*-acetylglucosaminyltransferase (HpLgtA)[2], recombinant *Escherichia coli* K-12 galactokinase (EcGalK), *Bifidobacterium longum* UDP-sugar pyrophosphorylase (BLUSP) [3], *Neisseria meningitides* β1−4-galactosyltransferase (NmLgtB)[4], *Pasteurella multocida* aldolase (Pm aldolase)[5], *Neisseria* meningitidis CMP-sialic acid synthetase (NmCSS)[5], *Pasteurella multocida* multifunctional α2−3-sialyltransferase 1 M144D mutant (PmST1 M144D)[6], *Bacteroides fragilis* bifunctional L-fucokinase/GDP-fucose pyrophosphorylase (BfFKP) [7], and *Helicobacter pylori* α1−3-fucosyltransferase (Hpα1,3FT)[8, 9] were expressed and purified as described previously. All enzymatic reactions were monitored by thin layer chromatography (TLC), which was performed on silica gel plates 60 F_{254} (Merck, Billerica MA). Plates were visualized by treatment with 5% sulfuric acid in ethanol or *p*-anisaldehyde sugar stain followed by heating. Gel filtration chromatography was performed using a column (100×2.5 cm) packed with BioGel P-2 Fine resins (Bio-Rad, Hercules, CA). Ion exchange chromatography was performed using a colum (30×5 cm) packed with DEAE–Sepharose (Sigma). ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on Bruker AVANCE-600 spectrometer or Agilent VNMRS-600 spectrometer at 25 °C. NMR spectra were calibrated using solvent signals (^{1}H: δ 4.79 for D_2O). High resolution electrospray ionization (ESI) mass spectra were obtained at the National Glycoengineering Research Center and Drug Testing and Analysis Center at Shandong University.

General procedure of β1−3-*N*-acetylglucosaminylation with Enzyme Module 1:

As shown in Fig. S1, acceptor (GalOR, 1.0 equiv.), *N*-acetylglucosamine (GlcNAc, 1.5 equiv.), adenosine 5'-triphosphate (ATP, 1.5 equiv.) and uridine 5'-triphosphate (UTP, 1.5 equiv.) were dissolved in water in a 50 mL centrifuge tube containing Tris-HCl buffer (100 mmol, pH 8.0) and $MgCl_2$ (20 mmol). After the addition of appropriate amount of NahK-GlmU and HpLgtA, the reaction mixture was incubated at 37 °C with agitation at 140 rpm in an isotherm incubator overnight. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc = 4:2:1:0.2, *v/v* or *t*-BuOH/MeOH/H_2O/HOAc = 2:2:1:1, *v/v* or *t*-BuOH/MeOH/H_2O/NH_4OH= 2:2:1:1, *v/v*) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 °C for 30 min. The mixture was then centrifuged, and the precipitates were removed. The supernatant containing the product was concentrated, purified by DEAE column (gradient eluted with 0.5 M NaCl) and BioGel P-2 column (eluted with H_2O) to provide the purified product.

General procedure of β1-4-galactosylation with Enzyme Module 2:

As shown in Fig S2, acceptor (GlcNAcOR, 1.0 equiv.), galactose (Gal, 1.5 equiv.) ATP (1.5 equiv.) and UTP (1.5 equiv.) were dissolved in water in a 50 mL centrifuge tube containing Tris-HCl buffer (100 mmol, pH 7.5) and $MgCl_2$ (20 mmol). After the addition of appropriate amount of EcGalK, BLUSP, and NmLgtB, the reaction mixture was incubated at 37 °C with agitation at 140 rpm in an isotherm incubator for 6-12 h. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc = 4:2:1:0.2, *v/v* or *t*-BuOH/MeOH/H2O/HOAc = 2:2:1:1, *v/v* or *t*-BuOH/MeOH/H_2O/NH_4OH = 2:2:1:1, *v/v*) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 °C for 30 min. The mixture was then centrifuged, and the precipitates were removed. The supernatant containing the product was concentrated, purified by DEAE column (gradient eluted with 0.5 M NaCl) and BioGel P-2 column (eluted with H_2O) to provide purified product.

General procedure of α1-3-fucosylation with Enzyme Module 3:

As shown in Fig S3, acceptor (LacNAcOR or GlcNAc-LacNAcOR, 1.0 equiv.), based on the number (n) of fucose residues on desirable product, L-fucose (Fuc, 1.5 × n equiv.), ATP (1.5 × n equiv.), guanosine 5'-triphosphate (GTP, 1.5 × n equiv.) were dissolved in Tris-HCl buffer (100 mmol, pH 7.5) containing $MgCl_2$ (20 mmol) and appropriate amounts of BfFKP and Hpα1,3FT. The reaction mixture was incubated at 37 °C with agitation at 140 rpm in an isotherm incubator for 6-12h. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc = 4:2:1:0.2, *v/v* or *t*-BuOH/MeOH/H_2O/HOAc = 2:2:1:1, *v/v* or *t*-BuOH/MeOH/H2O/NH_4OH = 2:2:1:1, *v/v*) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 °C for 30 min. The mixture was then centrifuged, and the precipitates were removed. The supernatant containing the product was concentrated, purified successively by DEAE column (gradient eluted with 0.5 M NaCl) and BioGel P-2 column (eluted with H_2O) to provide purified product.

General procedure of α2-3-sialylation with Enzyme Module 4:

Acceptor (LacNAcOR or α1–3-fucosylated LacNAcOR, 1.0 equiv.), a sialic acid precursor (ManNAc or ManNGc, 1.5 equiv.), sodium pyruvate (5.0 equiv.), and cytidine 5'-triphosphate (CTP, 1.5 equiv.) were dissolved in Tris-HCl buffer (100 mmol, pH 8.5) containing $MgCl_2$ (20 mmol) and appropriate amounts of Pm aldolase, NmCSS, and PmST1 M144D. The reaction mixture was incubated at 37 °C with agitation at 140 rpm in an isotherm incubator incubator for 30 min. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc = 4:2:1:0.2, *v/v* or *t*-BuOH/MeOH/H_2O/HOAc = 2:2:1:1, *v/v* or *t*-BuOH/MeOH/H_2O/NH_4OH = 2:2:1:1, *v/v*) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 °C for 30 min. The mixture was then centrifuged, and the precipitates were removed. The supernatant containing the product was concentrated, purified by DEAE column (gradient eluted with 0.5 M NaCl) and BioGel P-2 column (eluted with H_2O) to provide purified product.

III. Glycan microarray

3.1 Methods for glycans preparation

The synthesized 3-azidopropyl glycans (10 mg) and triethylene glycol 2-aminoethyl propargyl ether (H_2N-PEG4-ALK, 1.0 equiv., Sigma) were added to a stirred solution of $CuSO_4$ (0.2 equiv.), sodium ascorbate (0.5 equiv.), and *tris*-benzyltriazolylmethyl amine (TBTA, 0.2 equiv.) in *tert*-butyl alcohol/water (2.0 mL, 2:1, *v/v*). The reaction mixture was stirred at room temperature. Upon completion (about 1 h), the solvent was removed under reduced pressure and the residue was purified by Bio-Gel P2 gel filtration chromatography. All the resulted glycans were quantitated using HPLC before the slide printing.

3.2 Methods for microarray printing Glycans linked with amine group were prepared at a concentration of 100 μM in the printing buffer (150 mM phosphate, pH 8.5), and printed on multivalent NHS-derivatized microscope-glass slides (Z Biotech, LLC), each for 500 pL in replicates of six. Non-contact printing was performed at room temperature with a humidity of 60% by a sciFLEXARRAYER S3 spotter (Scienion) with PDC 80 Piezo Dispense Capillary, and 8 subarrays were printed on each slide. After overnight dehumidification under room temperature, the slides were washed with MilliQ water and subsequently blocked with 50 mM ethanolamine in 100 mM Tris buffer (pH 9.0) for 2 hours. The blocked slides were then washed with MilliQ water twice, dried, and stored desiccated at -20 °C until use. Print buffer was printed as a negative control (NC). In addition, biotinylated PEG amine (0.01mg/mL) (PC1), Human IgG (0.1 mg/mL) (PC2) were printed in six replicates with print buffer to serve as a positive control. A marker containing anti-human IgG conjugate with Cy3 (0.01 mg/mL) and anti-human IgG conjugate with Alexa 647 (0.01 mg/mL) was also printed in the replicates of six as marker (M).

3.3 Method for microarray assay

Microarray slides were rehydrated by ethanolamine buffer (50 mM ethanolamine in 50 mM sodium borate, pH 9.2) and washed with Milli-Q water. The slides were blocked for 30 min in TSMTB buffer (20 mM Tris-HCl, 150 mM NaCl, 0.2 mM $CaCl_2$, and 0.2 mM $MgCl_2$, 0.05% Tween, 1% BSA). Then, properly diluted lectins, antibodies and viral hemagglutinin (HA) proteins (see following) were incubated with each subarray for 1 hour. Subsequently, the unbounded glycan-binding proteins were washed with TSMT buffer (20 mM Tris-HCl, 150 mM NaCl, 0.2 mM $CaCl_2$, and 0.2 mM $MgCl_2$, 0.05% Tween) and TSM buffer (20 mM Tris-HCl, 150 mM NaCl, 0.2 mM $CaCl_2$, and 0.2 mM $MgCl_2$). The corresponding secondary antibodies were then added and incubated for 1 hour and washed as described aboved. Then the developed glycan microarray slides were scanned with a microarray scanner (GenePix 4000B) at wavelength 635 with 600 PMT Gain and 100% power. The collected data was analyzed with GenePix Pro.

Biotinylated plant lectins, including *Lotus tetragonolobus* lectin (LTL, 10 μg/mL), *Aleuria aurantia* lectin (0.1 μg/mL), *Maackia amurensis* lectin I (MAL-I, 10 μg/mL), Wheat germ agglutinin (WGA, 10 μg/mL), *Griffonia (Bandeiraea) simplicifolia* lectin II (GSL II, BSL II, 10 μg/mL), *Ricinus Communis* lectin I (RCA-I, 10 μg/mL), *Erythrina cristagalli* Lectin (ECL, 10 μg/mL) were applied and detected by Cy5-streptavidin (1 μg/mL). Anti-CD15 antibody (10 μg/mL), anti-CD15s antibody (10 μg/mL) and anti-CD65s antibody (10 μg/mL) were also tested and the primary antibodies were bound by goat anti-mouse IgG-Alexa Fluor 647 conjugate (5 μg/mL). Recombinant human E-Selectin/CD62E Fc chimera protein (20 ug/ml) was incubated with array and goat anti-human IgG Fc fragment secondary antibody (5 μg/mL) was used for detection. Influenza virus, A/Puerto Rico/8/1934 (H1N1), A/St. Petersburg/27/2011 (H1N1), A/Brisbane/10/2007 (H3N2), A/gyrfalcon/Washington/41088-6/2014 (H5N8) and A/Anhui/1/2013 (H7N9) were assayed with microarray and Penta·His-Alexa Fluor 647 conjugate (25 μg/mL) was used to bound with the primary HA proteins.

IV. Reference

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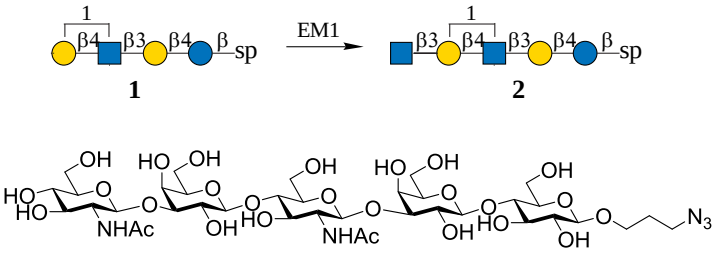
9. S. W. Lin, T. M. Yuan, J. R. Li and C. H. Lin, *Biochemistry*, 2006, **45**, 8108-8116.

V. Experimental Detail

GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (2)

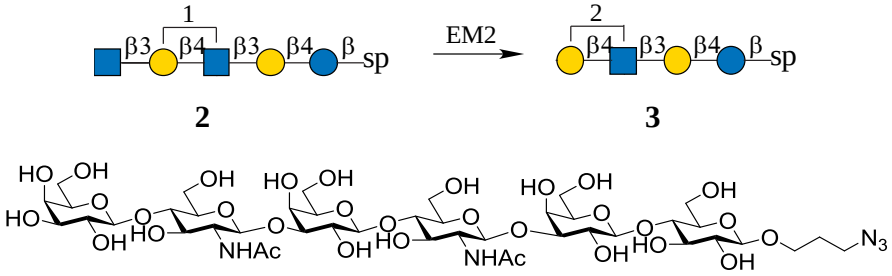
3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **2** was prepared according to general procedure of β1-3-*N*-acetylglucosaminylation with EM1. After lyophilization, **2** was obtained as white solid (684 mg, 91%). ^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 3.0 Hz, 2H), 4.00-3.87 (m, 4H), 3.82 (dd, *J* = 4.2, 12 Hz, 1H), 3.80-3.40 (m, 26H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.90 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.89, 174.84, 102.90, 102.85, 102.82, 102.70, 102.08, 81.99, 81.95, 78.31, 78.14, 75.62, 74.83, 74.73, 74.51, 74.32, 73.52, 72.76, 72.12, 69.96, 69.92, 69.65, 68.29, 67.32, 60.93, 60.45, 60.03, 59.82, 55.62, 55.11, 47.84, 28.21, 22.17; HRMS (ESI) *m/z* calculated for $C_{37}H_{63}N_5O_{26}Na$ $[M+Na]^+$ 1016.3659, found 1016.3692.

Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (3)

3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

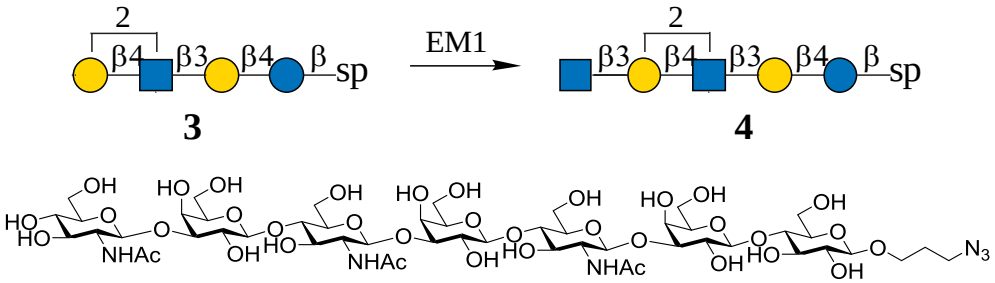


Compound **3** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **3** was obtained as white solid (540 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 4.65 (d, *J* = 7.8 Hz, 2H), 4.45 (d, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 6.6 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.11 (s, 2H), 3.98-3.48 (m, 35H), 3.42 (t, *J* = 6.6 Hz, 2H), 3.27 (t, *J* = 8.4 Hz, 1H), 1.99 (s, 6H), 1.87 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.77, 102.81, 102.75, 102.72, 102.65, 102.63, 101.98, 81.94, 81.90, 78.17, 77.97, 75.22, 74.74, 74.64, 74.41, 74.22, 72.65, 72.36, 72.04, 70.83, 69.82, 68.41, 68.20, 67.23, 60.91, 60.83, 59.90, 59.70, 55.05,

55.01, 47.73, 28.10, 22.04; HRMS (ESI) *m/z* calculated for $C_{43}H_{73}N_5O_{31}Na$ $[M+Na]^+$ 1178.4187, found 1178.4216.

GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (4)

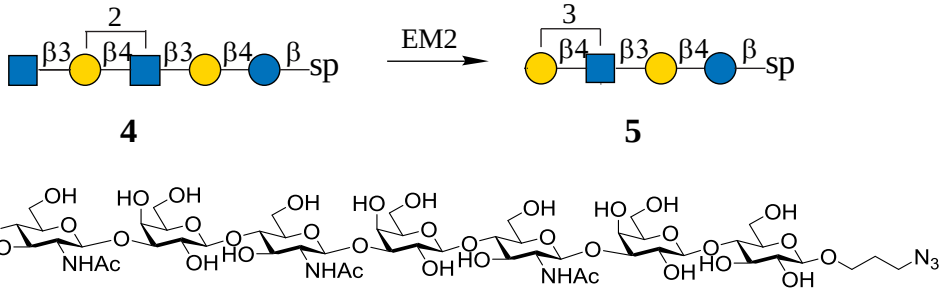
3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **4** was prepared according to general procedure of β1-3-*N*-acetylglucosaminylation with EM1. After lyophilization, **4** was obtained as white solid (488 mg, 90%). ^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 9.0 Hz, 2H), 4.66 (d, *J* = 10.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 2H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.14 (s, 3H), 4.00–3.43 (m, 42H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 9H), 1.89 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.84, 174.79, 102.83, 102.77, 102.65, 102.00, 81.95, 81.93, 81.88, 78.22, 78.03, 75.55, 74.76, 74.66, 74.44, 74.25, 73.45, 72.68, 72.06, 69.89, 69.85, 69.57, 68.22, 67.26, 60.85, 60.36, 59.94, 59.74, 55.55 , 55.04, 47.76, 28.13, 22.07; HRMS (ESI) *m/z* calcd for $C_{51}H_{86}N_6O_{36}Na$ $[M+Na]^+$ 1381.4981, found 1381.4961.

Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (5)

3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

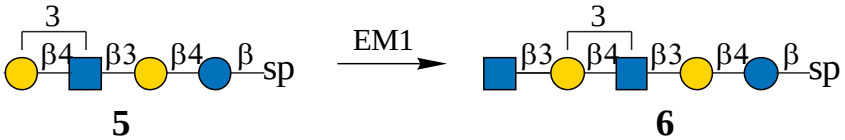


Compound **5** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **5** was obtained as white solid (404 mg, 90%). ^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 8.4 Hz, 3H), 4.47 (d, *J* = 6.6 Hz, 1H), 4.46 (d, *J* = 6.6 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 2H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.14 (d, *J* = 3.0 Hz, 3H), 4.00–3.51 (m, 46H), 3.44 (t, *J* = 6.6 Hz,

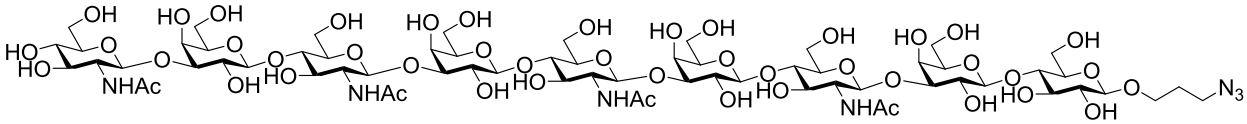
2H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 9H), 1.89 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.79, 102.83, 102.77, 102.75, 102.65, 102.00, 81.95, 81.93, 78.22, 78.02, 75.24, 74.76, 74.66, 74.43, 74.24, 72.68, 72.39, 72.06, 70.85, 69.85, 68.44, 68.21, 67.26, 60.92, 60.85, 59.94, 59.73, 55.08, 55.04, 47.75, 28.12, 22.07; HRMS (ESI) *m/z* calcd for $C_{57}H_{100}N_7O_{41}$ $[M+NH_4]^+$ 1538.5955, found 1538.5966.

GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (6)

3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



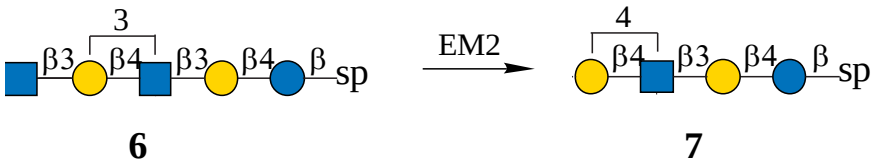
5 **6**



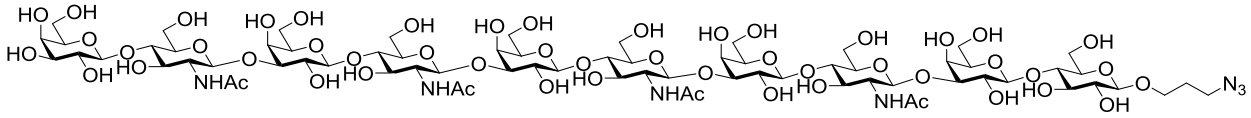
Compound **6** was prepared according to general procedure of β1-3-*N*-acetylglucosaminylation with EM1. After lyophilization, **6** was obtained as white solid (331 mg, 91%). ^{1}H NMR (600 MHz, D_2O) δ 4.71 (d, *J* =8.4 Hz, 3H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.50 (d, *J* = 8.4 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 3H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 1.8 Hz, 4H), 4.03–3.56 (m, 51H), 3.40 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 9.0 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 9H), 1.92 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.87, 174.82, 174.67, 166.30, 141.51, 102.84, 102.78, 102.66, 102.55, 102.01, 94.42, 94.38, 88.34, 88.24, 83.13, 83.07, 81.96, 81.94, 81.88, 78.23, 78.03, 75.55, 74.79, 74.77, 74.67, 74.44, 74.25, 73.68, 73.45, 72.89, 72.69, 72.07, 71.81, 70.84, 69.90, 69.86, 69.57, 69.53, 69.38, 69.21, 69.00, 68.22, 67.27, 64.86, 64.82, 60.90, 60.86, 60.36, 60.20, 59.94, 59.73, 57.32, 55.55, 55.05, 53.59, 53.54, 47.76, 28.13, 22.07, 22.06, 21.96; HRMS (ESI) *m/z* calcd for $C_{65}H_{113}N_8O_{46}$ $[M+NH_4]^+$ 1741.6749, found 1741.6766.

Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (7)

3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



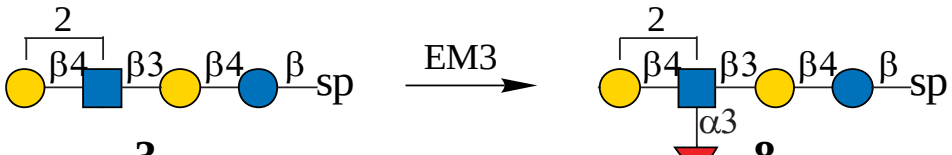
6 **7**



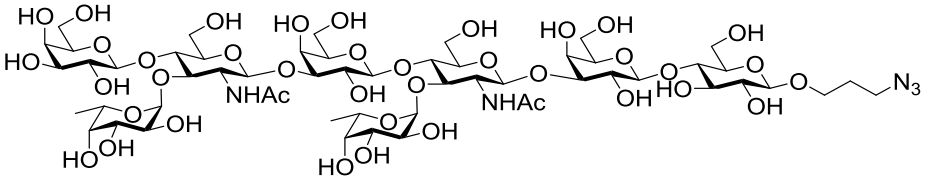
Compound **7** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **7** was obtained as white solid (202 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 4.71 (d, *J* = 8.4 Hz, 4H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 10.2 Hz, 3H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 2.4 Hz, 4H), 4.03–3.54 (m, 57H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 8.4 Hz, 1H), 2.04 (s,12H),1.92 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.82, 102.86, 102.84, 102.78, 102.76, 102.67, 102.01, 81.97, 78.22, 78.03, 75.25, 74.77, 74.67, 74.44, 74.25, 72.69, 72.40, 72.07, 70.86, 69.86, 68.44, 68.23, 68.21, 67.27, 60.93, 60.86, 59.74, 55.04, 47.76, 28.12, 22.07; HRMS (ESI) *m/z* calcd for $C_{71}H_{124}N_8O_{51}$ $[M+H+NH_4]^{2+}$ 952.3678, found 952.3688.

Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (8)

3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



3 **8**

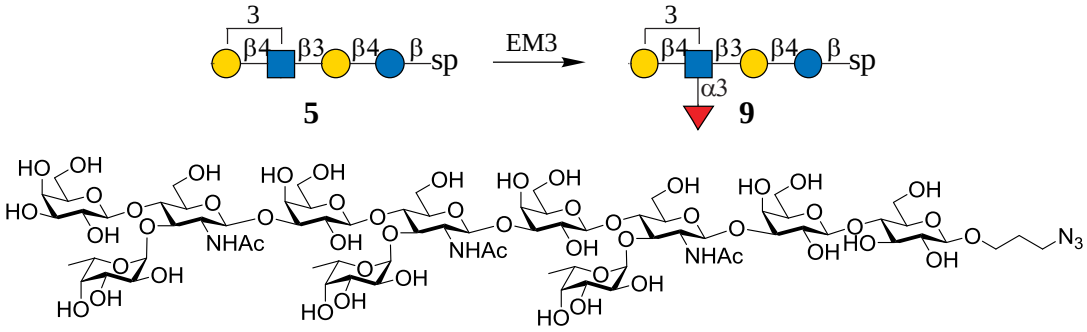


Compound **8** was prepared according to general procedure of α1-3-fucosylation with EM3. After lyophilization, **8** was obtained as white solid (114 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 4.2 Hz, 1H), 4.72 (d, *J* = 5.4 Hz, 1H), 4.70 (d, *J* = 8.4 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.44 (t, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 3.0 Hz, 1H), 4.10 (d, *J* = 3.0 Hz, 1H), 4.02-3.48 (m, 43H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.02 (s, 3H), 2.02 (s, 3H), 1.91 (p, *J* = 6.6 Hz, 2H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.69, 174.63, 102.92, 102.50,102.47, 102.09, 101.72, 101.71, 98.68, 98.57, 82.04, 81.59, 78.31, 75.07, 75.04, 74.89, 74.84, 74.74, 74.42, 74.33, 73.00, 72.77,

72.74, 72.45, 71.89, 71.83, 71.03, 70.50, 69.93, 69.17, 69.15, 68.33, 68.28, 68.21, 67.68, 67.62, 67.35, 66.66, 61.49, 61.44, 60.93, 60.04, 59.61, 59.42, 55.93, 47.85, 28.21, 22.23, 15.30, 15.26; HRMS (ESI) *m/z* calculated for $C_{55}H_{93}N_5O_{39}Na$ $[M+Na]^+$ 1470.5345, found 1470.5320.

Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (9)

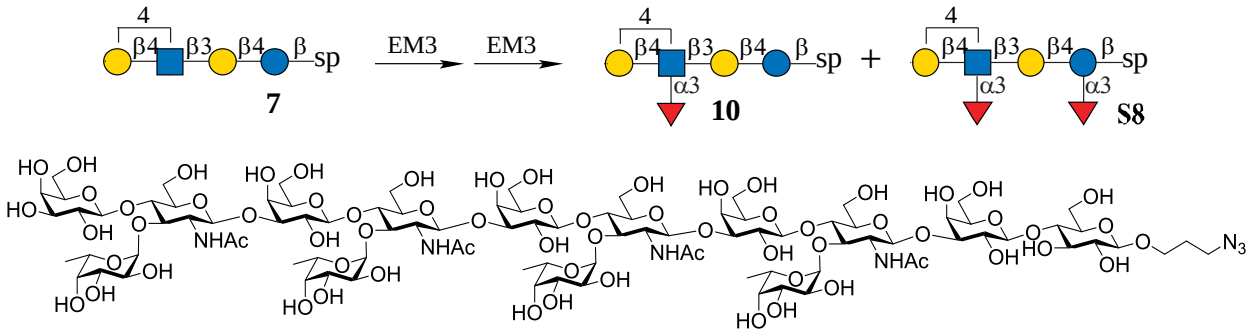
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **9** was prepared according to general procedure of α1-3-fucosylation with EM3. After lyophilization, **9** was obtained as white solid (111 mg, 88%). ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 3.6 Hz, 2H), 4.71 (d, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 7.8 Hz, 2H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), 4.42 (d, *J* = 8.4 Hz, 2H), 4.43 (t, *J* = 7.8 Hz, 1H), 4.15 (s, 1H), 4.10 (s, 2H), 4.01–3.48 (m, 58H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 9H), 1.91 (p, *J* = 6.6 Hz, 2H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 174.62, 174.56, 102.84, 102.41, 102.01, 101.65, 101.62, 98.60, 98.50, 81.96, 81.51, 78.22, 75.00, 74.97, 74.82, 74.76, 74.66, 74.34, 74.26, 72.92, 72.69, 72.66, 72.64, 72.37, 71.95, 71.81, 71.76, 70.95, 70.43, 69.86, 69.09, 69.07, 68.26, 68.21, 68.14, 67.60, 67.54, 67.27, 66.59, 62.37, 61.42, 61.37, 60.85, 59.95, 59.53, 55.85, 47.76, 28.13, 22.14, 15.21, 15.17. HRMS (ESI) *m/z* calcd for $C_{75}H_{126}N_6O_{53}Na$ $[M+Na]^+$ 1981.7246, found 1981.7326.

Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (10)

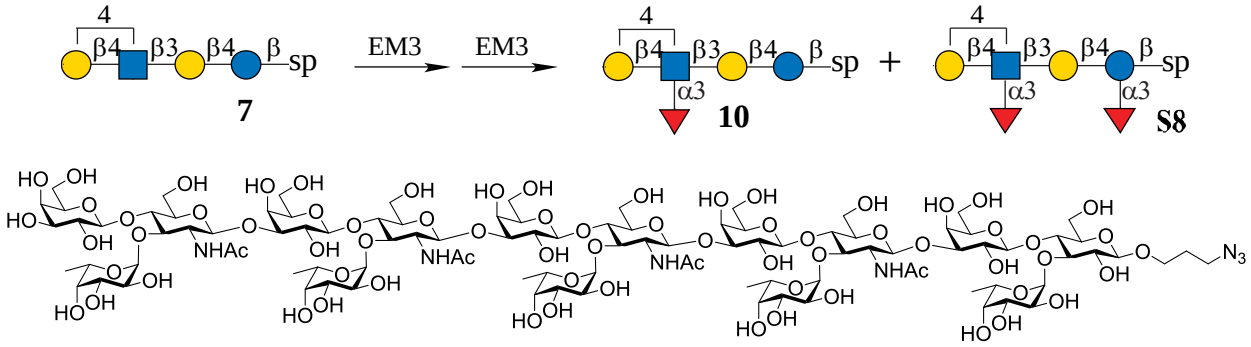
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **10** was prepared according to general procedure of α1-3-fucosylation with EM3. Due to acceptor **7** was only partially fucosylated in the first time, the partially fucosylated compounds was purified and another round of reaction was performed with EM3. After lyophilization, **10** was obtained as white solid (101 mg, 82%). ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.2 Hz, 1H), 5.11 (t, *J* = 3.6 Hz, 2H), 5.10 (t, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 5.4 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 3H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.43 (d, *J* = 7.8 Hz, 3H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.14 (d, *J* = 3.0 Hz, 1H), 4.08 (d, *J* = 2.4 Hz, 3H), 4.00–3.47 (m, 73H), 3.45 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 2.00 (s, 6H),1.92 (p, *J* = 6.6 Hz, 2H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 9H); ^{13}C NMR (150 MHz, D_2O) δ 174.71, 174.66, 102.95, 102.49, 102.12, 101.74, 98.70, 98.59, 82.07, 81.61, 78.36, 75.08, 74.87, 74.77, 74.44, 73.04, 72.79, 72.50, 71.88, 71.07, 70.54, 69.97, 69.20, 68.31, 68.24, 67.66, 67.38, 66.69, 61.47, 60.97, 60.09, 59.66, 55.96, 47.89, 28.25, 22.27, 15.30. HRMS (ESI) *m/z* calcd for $C_{95}H_{159}N_7O_{67}Na_2$ $[M+2Na]^{2+}$ 1258.4561, found 1258.4461.

Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcβProN$_3$ (S8)

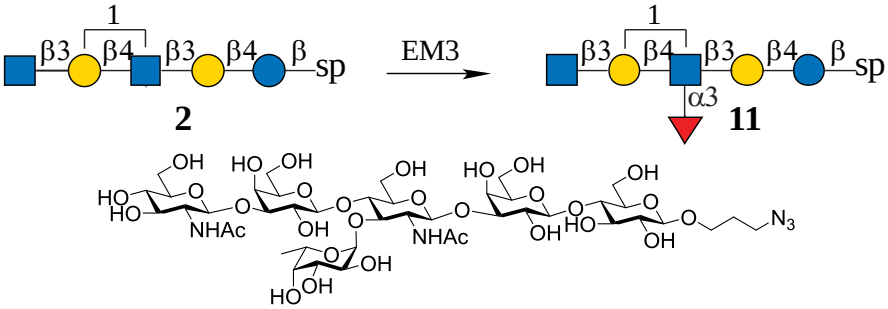
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)- [α-L-fucopyranosyl-(1→3)]-β-D-glucopyranoside



Compound **S8** was prepared according to general procedure of α1-3 fucosylation with EM3. Due to acceptor **7** was only partially fucosylated in the first time, the partially fucosylated compounds was purified and another round of reaction was performed with EM3. After lyophilization, **S8** was obtained as white solid (11 mg, 9%). ^{1}H NMR (600 MHz, D_2O) δ 5.44 (d, *J* = 3.9 Hz, 1H), δ 5.14 (d, *J* = 4.0 Hz, 1H), 5.12 (t, *J* = 4.0 Hz, 3H), 4.71 (d, *J* = 8.4 Hz, 3H), 4.48 (d, *J* = 6.7 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 7H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.10 (s, 4H), 4.02–3.50 (m, 96H), 3.51 (t, *J* = 8.7 Hz, 2H), 3.47 (t, *J* = 6.7 Hz, 1H), 2.02 (s, 12H), 1.92 (p, *J* = 6.5 Hz, 2H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 12H); ^{13}C NMR (151 MHz, D_2O) δ 174.65, 171.00, 102.47, 102.23, 101.72, 98.68, 98.45, 81.60, 76.93, 75.30, 75.06, 74.90, 74.75, 74.44, 73.03, 72.75, 72.48, 72.39, 71.89, 71.05, 70.65, 70.53, 69.19, 68.35, 68.23, 68.00, 67.65, 67.41, 66.68, 66.48, 61.46, 59.64, 55.95, 47.86, 28.22, 22.25, 15.32, 15.28, 15.21. HRMS (ESI) *m/z* calcd for $C_{101}H_{169}N_7O_{71}Na_2$ $[M+2Na]^{2+}$ 1331.4812, found 1331.4756.

GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (11)

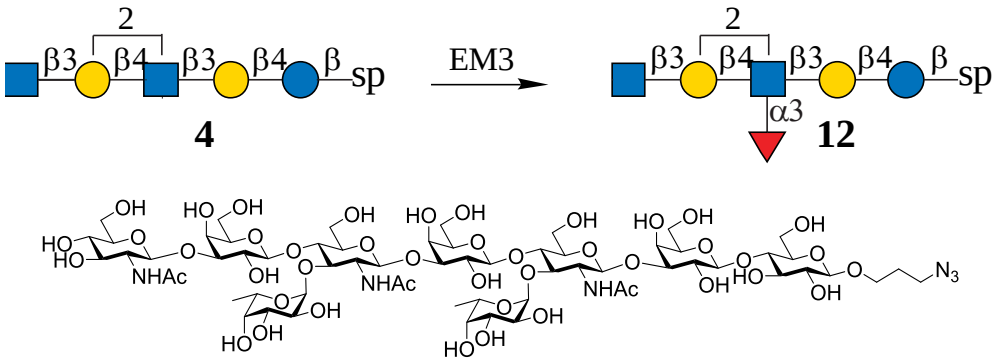
3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **11** was prepared according to general procedure of α1-3-fucosylation with EM3. After lyophilization, **11** was obtained as white solid (110 mg, 96%). ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.42 (t, *J* = 7.8 Hz, 2H), 4.14 (d, *J* = 3.0 Hz, 1H), 4.08 (d, *J* = 3.0 Hz, 1H), 4.00–3.41 (m, 33H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.30 (t, *J* = 8.4 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.14 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.87, 174.68, 102.90, 102.76, 102.49, 102.08, 101.69, 98.67, 82.03, 81.47, 78.30, 75.59, 75.06, 74.83, 74.73, 74.41, 74.32, 73.44, 72.76, 71.83, 70.53, 69.93, 69.67, 69.14, 68.27, 68.23, 67.61, 67.33, 66.65, 61.43, 60.93, 60.44, 60.03, 59.60, 55.60, 47.84, 28.21, 22.24, 22.15, 15.26; HRMS (ESI) *m/z* calculated for $C_{43}H_{73}N_5O_{30}Na$ $[M+Na]^{+}$ 1162.4238, found 1162.4245.

GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (12)

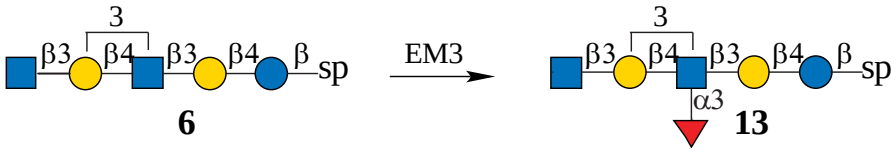
3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

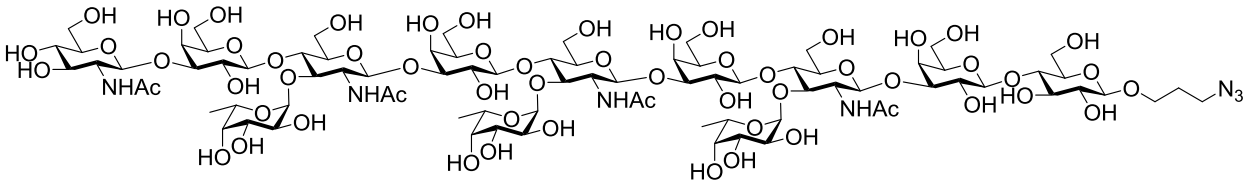


Compound **12** was prepared according to general procedure of α1-3-fucosylation with EM3. After lyophilization, **12** was obtained as white solid (74 mg, 89%). ^{1}H NMR (600 MHz, D_2O) δ 5.09 (t, *J* = 3.6 Hz, 2H), 4.68 (t, *J* = 7.2 Hz, 2H), 4.65 (d, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.41 (t, *J* = 7.8 Hz, 3H), 4.13 (s, 1H), 4.07 (s, 2H), 3.99–3.43 (m, 48H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.28 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.89 (p, *J* = 6.6 Hz, 2H), 1.124 (d, *J* = 6.0 Hz, 3H), 1.119 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.80, 174.60, 174.56, 102.83, 102.69, 102.43, 102.37, 102.00, 101.62, 101.60, 98.59, 81.97, 81.48, 81.40, 78.22, 75.51, 74.98, 74.94, 74.76, 74.66, 74.34, 74.25, 73.38, 72.69, 72.65, 71.76, 70.46, 70.43, 69.86, 69.59, 69.07, 68.20, 68.17, 68.14, 67.54, 67.27, 66.58, 61.37, 60.86, 60.36, 59.95, 59.53, 55.85, 55.53, 47.77, 28.14, 22.17, 22.16, 22.08, 15.20; HRMS (ESI) *m/z* calcd for $C_{63}H_{106}N_6O_{44}Na_2$ $[M+2Na]^{2+}$ 848.3019, found 848.3022.

GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN_3 (13)

3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

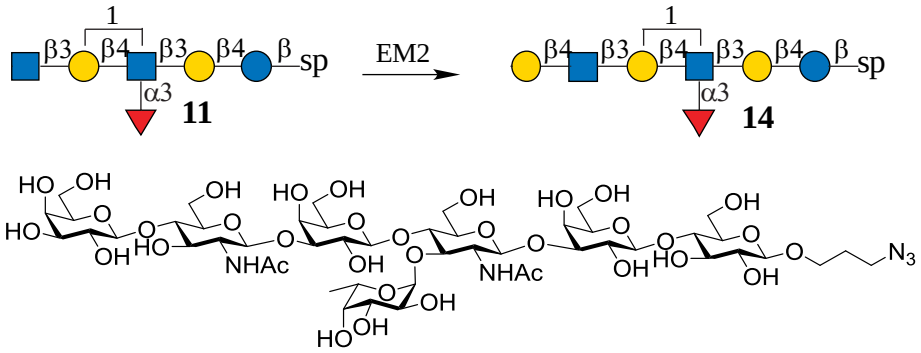




Compound **13** was prepared according to general procedure of α1-3-fucosylation with EM3. After lyophilization, **13** was obtained as white solid (58 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.2 Hz, 2H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 5.4 Hz, 1H), 4.68 (d, *J* = 8.4 Hz, 2H), 4.66 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 3H), 4.42 (t, *J* = 7.8 Hz, 1H), 4.14 (d, *J* =3.0 Hz, 1H), 4.08 (d, *J* =2.4 Hz, 3H), 4.00–3.47 (m, 63H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.01 (s, 3H), 2.01 (s, 3H), 2.00 (s, 6H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.14 (t, *J* = 6.0 Hz, 3H), 1.13 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 174.76, 174.57, 174.52, 102.80, 102.68, 102.40, 102.36, 101.97, 101.57, 98.57, 81.92, 81.45, 81.38, 78.15, 75.47, 74.94, 74.90, 74.72, 74.62, 74.30, 74.21, 73.34, 72.64, 72.59, 71.71, 70.39, 69.81, 69.53, 69.02, 68.14, 68.11, 67.49, 67.22, 66.55, 61.34, 60.82, 60.30, 59.90, 59.48, 55.81, 55.48, 47.72, 28.10, 22.10, 22.02, 15.15; HRMS (ESI) *m/z* calcd for $C_{83}H_{139}N_7O_{58}Na_2$ $[M+2Na]^{2+}$ 1103.8969, found 1103.8957.

Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (14)

3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

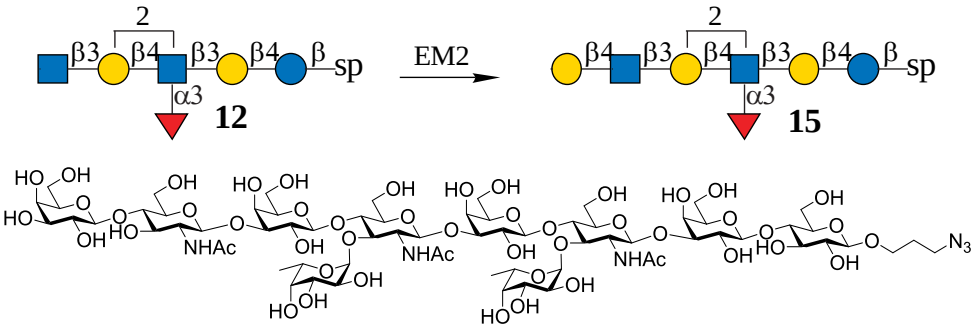


Compound **14** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **14** was obtained as white solid (93 mg, 94%). ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.2 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 4.14 (d, *J* = 3.0 Hz, 1H), 4.09 (d, *J* = 3.0 Hz, 1H), 4.01–3.49 (m, 39H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.30 (t, *J* = 8.4 Hz, 1H), 2.02 (s, 3H), 2.02 (s, 3H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.14 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.82, 174.68, 102.91, 102.84, 102.65, 102.49, 102.08, 101.70, 98.67, 82.04, 81.57, 78.31, 78.16, 75.32, 75.06, 74.83, 74.73, 74.49, 74.41, 74.33, 72.77, 72.48, 72.08, 71.84, 70.94, 70.48, 69.93, 69.15, 68.52, 68.27, 68.21, 67.61, 67.33, 66.65, 61.43, 61.01, 60.93, 60.91, 60.04, 59.83, 55.13, 47.85,

28.21, 22.25, 22.17, 15.27; HRMS (ESI) *m/z* calculated for $C_{49}H_{83}N_5O_{35}Na$ $[M+Na]^+$ 1324.4766, found 1324.4783.

Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (15)

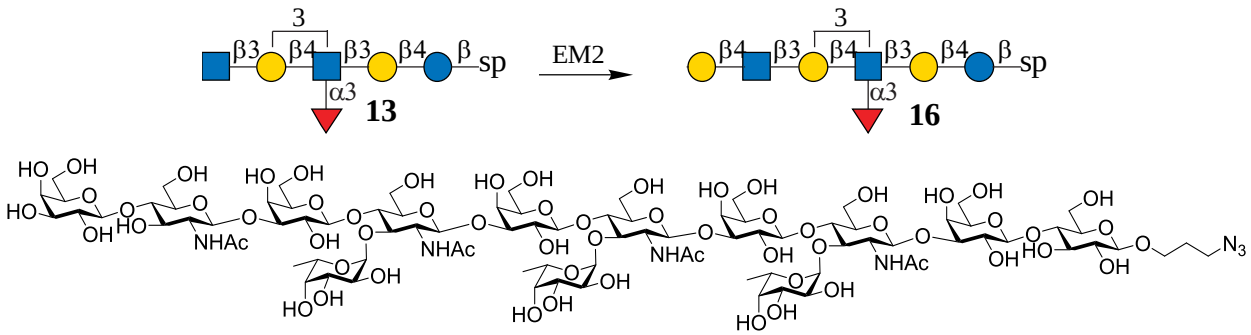
3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **15** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **15** was obtained as white solid (56 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ 5.08 (t, *J* = 3.6 Hz, 2H), 4.67 (d, *J* = 7.2 Hz, 1H), 4.66 (d, *J* = 7.8 Hz, 2H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 6.6 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 3.0 Hz, 1H), 4.09 (s, 2H), 4.00–3.45 (m, 54H), 3.43 (t, *J* = 6.6 Hz, 2H), 3.28 (t, *J* = 8.4 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.88 (p, *J* = 6.6 Hz, 2H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.73, 174.59, 174.54, 102.82, 102.74, 102.59, 102.42, 102.37, 101.99, 101.61, 101.60, 98.59, 81.94, 81.50, 81.49, 78.20, 78.04, 75.23, 74.98, 74.94, 74.74, 74.65, 74.40, 74.33, 74.24, 72.67, 72.64, 72.38, 72.00, 71.74, 70.85, 70.41, 70.38, 69.84, 69.05, 68.43, 68.19, 68.14, 68.13, 67.52, 67.25, 66.57, 61.35, 60.92, 60.85, 59.94, 59.73, 59.51, 55.84, 55.05, 47.75, 28.13, 22.14, 22.13, 22.06, 15.18, 15.17; HRMS (ESI) *m/z* calcd for $C_{69}H_{116}N_6O_{49}Na_2$ $[M+2Na]^{2+}$ 929.3283, found 929.3298.

Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (16)

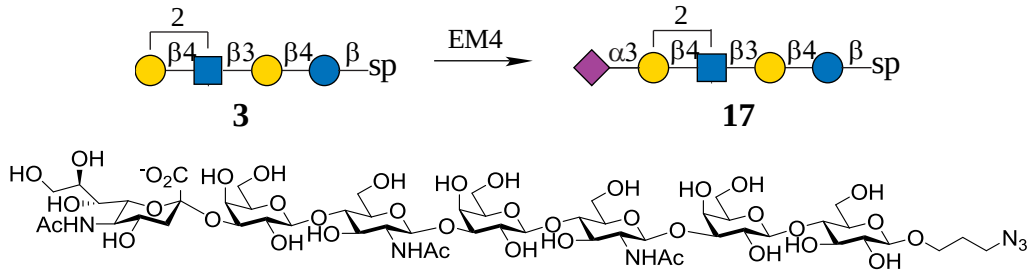
3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **16** was prepared according to general procedure of β1-4-galactosylation with EM2. After lyophilization, **16** was obtained as white solid (30 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 5.08 (t, *J* = 3.6 Hz, 2H), 5.08 (t, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 7.8 Hz, 4H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 7.2 Hz, 3H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 3.0 Hz, 1H), 4.06 (s, 3H), 3.98–3.45 (m, 69H), 3.43 (t, *J* = 6.6 Hz, 2H), 3.27 (t, *J* = 8.4 Hz, 1H), 1.99 (s, 3H), 1.99 (s, 3H), 1.98 (s, 6H), 1.88 (p, *J* = 6.6 Hz, 2H), 1.12 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 6H);^{13}C NMR (150 MHz, D_2O) δ 174.72, 174.58, 174.53, 102.81, 102.73, 102.57, 102.40, 102.36, 101.98, 101.59, 98.57, 81.93, 81.47, 78.19, 78.04, 75.22, 74.96, 74.93, 74.73, 74.64, 74.39, 74.31, 74.23, 72.66, 72.63, 72.38, 71.99, 71.73, 70.84, 70.40, 69.83, 69.04, 68.42, 68.18, 68.12, 67.51, 67.24, 66.56, 61.34, 60.92, 60.84, 59.93, 59.72, 59.50, 55.83, 55.04, 47.75, 28.12, 22.13, 22.06, 15.17; HRMS (ESI) *m/z* calcd for $C_{89}H_{149}N_7O_{63}Na_2$ $[M+2Na]^{2+}$ 1184.9233, found 1185.4266.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (17)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

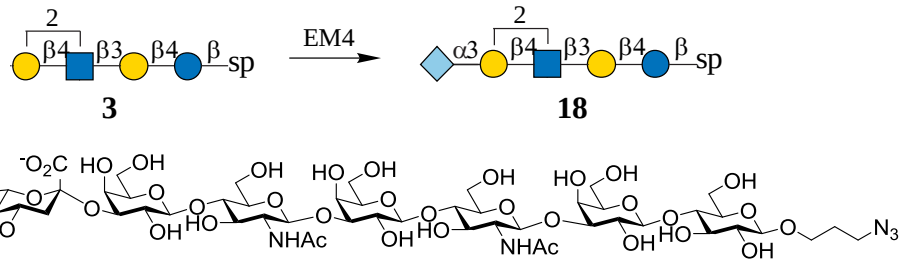


Compound **17** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **17** was obtained as white solid (88 mg, 94%). ^{1}H NMR (600 MHz, D_2O) δ 4.70 (d, *J* = 8.4 Hz, 1H), 4.70 (d, *J* = 7.8 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.16 (t, *J* = 3.0 Hz, 2H), 4.12 (dd, *J* = 3.0,10.2 Hz, 1H), 4.02-3.56 (m, 42H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.76 (dd, *J* = 4.2,12 Hz, 1H), 2.04 (s, 9H), 1.92 (p, *J* = 6.6 Hz, 2H), 1.80 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 174.99, 174.88, 174.87, 173.85, 102.92, 102.85, 102.78, 102.73, 102.52, 102.09, 99.78, 82.05, 82.01, 78.32, 78.13, 77.95, 75.46, 75.15, 74.86, 74.85, 74.74, 74.52, 74.33, 72.86, 72.76, 72.14,

72.11, 71.74, 69.94, 69.35, 68.31, 68.30, 68.28, 68.05, 67.34, 62.55, 61.02, 60.95, 60.93, 60.03, 59.80, 55.16, 55.11, 51.66, 47.85, 28.21, 22.16, 22.02; HRMS (ESI) *m/z* calculated for $C_{54}H_{89}N_6O_{39}^-$[M-H]$^-$ 1445.5171, found 1445.5084.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (18)

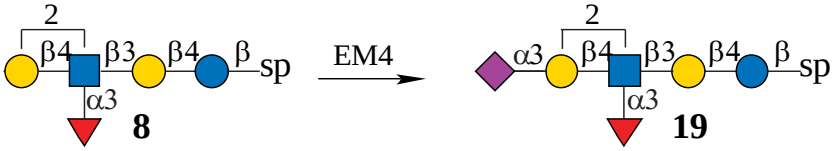
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

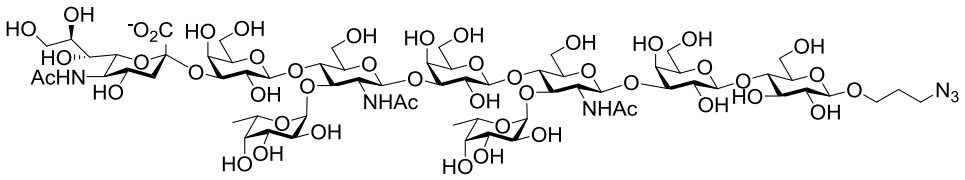


Compound **18** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **18** was obtained as white solid (87 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ 4.70 (d, *J* = 8.4 Hz, 2H), 4.56 (d, *J* = 8.4 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.16 (t, *J* = 3.0 Hz, 2H), 4.13 (dd, *J* = 3.0,6.0 Hz, 1H), 4.12 (s, 2H), 4.02-3.57 (m, 42H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 4.2,12 Hz, 1H), 2.03 (s, 6H), 1.91 (p, *J* = 6.6 Hz, 2H), 1.82 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 175.76, 174.87, 173.88, 102.92, 102.86, 102.79, 102.73, 102.53, 102.09, 99.81, 82.06, 82.02, 78.32, 78.14, 77.96, 75.46, 75.16, 74.87, 74.85, 74.75, 74.53, 74.34, 72.77, 72.59, 72.14, 72.11, 71.81, 69.94, 69.37, 68.31, 68.29, 68.06, 67.99, 67.45, 67.34, 62.53, 61.03, 60.96, 60.93, 60.03, 59.82, 55.16, 55.12, 51.37, 47.85, 28.22, 22.17; HRMS (ESI) *m/z* calcd for $C_{54}H_{89}N_6O_{40}^-$[M-H]$^-$ 1461.5120, found 1461.5156.

Neu5Acα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (19)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

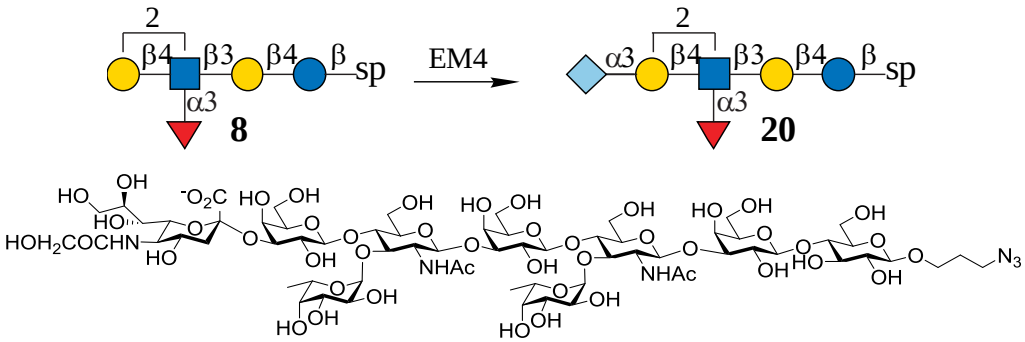




Compound **19** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **19** was obtained as white solid (32 mg, 61%). ^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.2 Hz, 1H), 5.06 (d, *J* = 3.6 Hz, 1H), 4.65 (t, J = 8.4 Hz, 2H), 4.48 (d, J = 7.8 Hz, 1H), 4.44 (d, J = 7.8 Hz, 1H), 4.39 (t, J = 7.8 Hz, 2H), 4.11 (d, J = 3.0 Hz, 1H), 4.05 (d, J = 3.0 Hz, 1H), 4.04 (dd, J = 3.0, 9.6 Hz, 1H), 3.97-3.43 (m, 50H), 3.41 (t, J = 6.6 Hz, 2H), 3.26 (t, J = 8.4 Hz, 1H), 2.71 (dd, J = 4.2,12.6 Hz, 1H),1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H),1.86 (p, J = 6.6 Hz, 2H), 1.75 (t, J = 12.6 Hz, 1H); 1.12 (d, *J* = 6.6 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.95, 174.66, 174.59, 173.83, 102.87, 102.48, 102.04, 101.66, 101.46, 99.57, 98.66, 98.51, 82.00, 81.56, 78.20, 75.57, 75.01, 74.90, 74.85, 74.80, 74.70, 74.57, 74.39, 74.28, 72.90, 72.83, 72.71, 72.65, 71.83, 71.79, 70.45, 69.89, 69.19, 69.09, 68.24, 68.18, 68.01, 67.62, 67.56, 67.29, 67.23, 66.63, 66.59, 62.50, 61.44, 60.90, 59.96, 59.54, 59.42, 55.88, 51.61, 47.78, 46.56, 39.70, 28.16, 22.17, 21.97, 15.21; HRMS (ESI) *m/z* calculated for $C_{66}H_{109}N_6O_{47}$- $[M-2H]^{2-}$ 868.3128, found 868.3142.

Neu5Gcα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (20)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

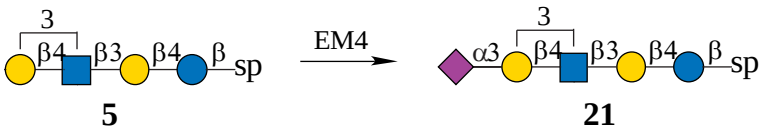


Compound **20** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **20** was obtained as white solid (20 mg, 56%). ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 2.4 Hz, 1H), 4.71 (t, J = 7.8 Hz, 2H), 4.54 (d, J = 7.2 Hz, 1H), 4.49 (d, J = 7.8 Hz, 1H), 4.44 (t, J = 6.6 Hz, 2H), 4.16 (s, 1H), 4.12 (s, 2H), 4.10 (s, 2H), 4.01–3.50 (m, 50H), 3.46 (t, J = 6.6 Hz, 2H), 3.31 (t, J = 7.2 Hz, 1H), 2.78 (dd, J = 3.0, 12 Hz, 1H), 2.02 (s, 6H), 1.92 (p, J = 6.6 Hz, 2H), 1.82 (t, J = 12.0 Hz, 1H); 1.17 (d, *J* = 6.0 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 175.79, 174.70, 174.62, 173.75, 102.94, 102.51, 102.09, 101.71,

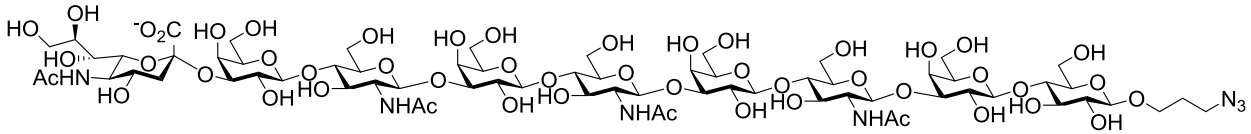
101.51, 99.56, 98.69, 98.54, 82.06, 81.63, 78.35, 78.30, 75.67, 75.11, 74.97, 74.87, 74.75, 74.63, 74.44, 74.33, 73.03, 72.77, 72.63, 71.84, 70.51, 69.95, 69.28, 69.15, 68.29, 68.22, 67.98, 67.69, 67.62, 67.34, 67.27, 66.64, 62.59, 62.56, 61.48, 60.95, 60.03, 59.61, 59.49, 55.94, 51.37, 47.84, 39.78, 28.21, 22.23, 15.27; HRMS (ESI) *m/z* calculated for $C_{66}H_{109}N_6O_{48}$- $[M-H]^-$ 1753.6278, found 1753.6188.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (21)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



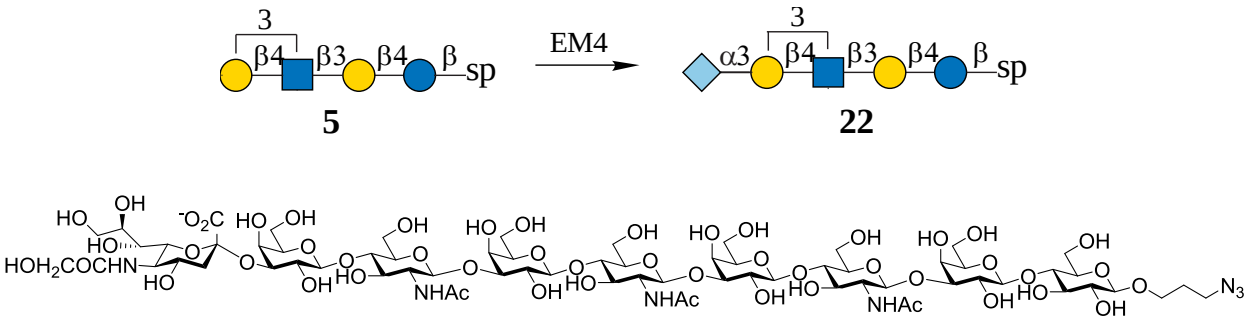
5 **21**



Compound **21** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **21** was obtained as white solid (111 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 4.71 (d, *J* = 8.4 Hz, 3H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 2H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.17 (t, *J* = 3.0 Hz, 3H), 4.12 (dd, *J* = 3.0, 9.6 Hz, 1H), 4.03–3.57 (m, 53H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 8.4 Hz, 1H), 2.77 (dd, *J* = 4.2,12 Hz, 1H), 2.04 (s, 12H), 1.92 (p, *J* = 6.6 Hz, 2H), 1.81 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 175.02, 174.89, 173.86, 171.02, 102.94, 102.88, 102.79, 102.74, 102.55, 102.11, 99.81, 82.06, 82.04, 78.36, 78.17, 78.00, 75.49, 75.17, 74.87, 74.77, 74.55, 74.36, 72.89, 72.79, 72.16, 72.14, 71.77, 69.96, 69.38, 68.33, 68.09, 67.48, 67.37, 62.59, 61.04, 60.95, 60.06, 59.85, 55.18, 55.15, 51.69, 47.87, 39.64, 28.23, 22.19, 22.05; HRMS (ESI) *m/z* calcd for $C_{68}H_{111}N_7O_{49}^{2-}$ $[M-2H]^{2-}$ 904.8182, found 904.8197.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (22)

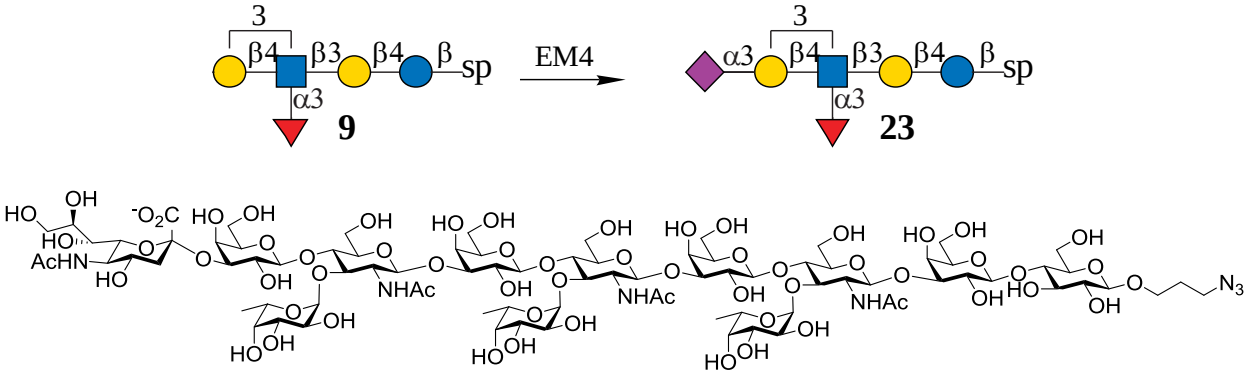
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **22** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **22** was obtained as white solid (111 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 4.70 (d, *J* = 8.4 Hz, 3H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 2H), 4.43 (d, *J* = 7.8 Hz, 1H), 4.16 (t, *J* = 3.6 Hz, 3H), 4.13 (dd, *J* =3.0, 7.8 Hz, 1H), 4.12 (s, 2H), 4.02–3.57 (m, 53H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 4.2,12.0 Hz, 1H), 2.03 (s, 9H), 1.91 (p, *J* = 6.6 Hz, 2H), 1.82 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 175.65, 174.74, 173.79, 102.83, 102.77, 102.70, 102.65, 102.45, 102.00, 99.71, 81.95, 78.22, 78.02, 77.87, 75.36, 75.07, 74.77, 74.66, 74.43, 74.25, 72.70, 72.50, 72.05, 71.72, 69.86, 69.28, 68.22, 67.98, 67.91, 67.38, 67.25, 62.46, 60.96, 60.90, 59.96, 59.74, 55.04, 51.30, 47.78, 39.59, 28.16, 22.14; HRMS (ESI) *m/z* calcd for $C_{68}H_{111}N_7O_{50}^{2-}$ [M-2H]$^{2-}$ 912.8173, found 912.8213.

Neu5Acα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (23)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

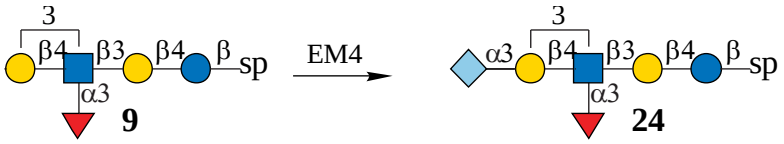


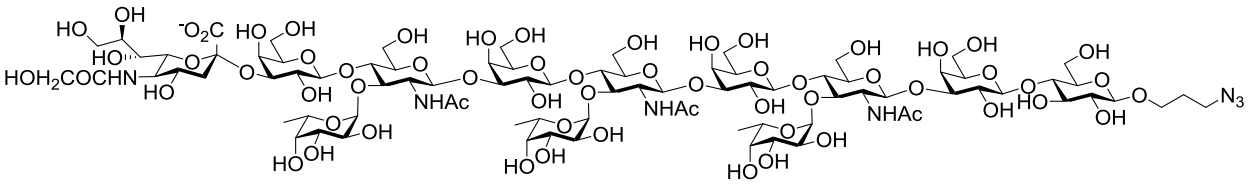
Compound **23** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **23** was obtained as white solid (25 mg, 55%). ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 7.8 Hz, 1H), 4.68 (d, *J* =6.0 Hz, 1H), 4.68 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H),

4.43 (d, *J* = 6.6 Hz, 2H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.14 (d, *J* = 2.4 Hz, 1H), 4.08-4.06 (m, 3H), 4.00–3.47 (m, 65H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* =8.4 Hz, 1H), 2.75 (dd, *J* = 4.8,12.6 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 6H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.78 (t, *J* = 12 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 174.93, 174.65, 174.60, 173.83, 170.98, 102.85, 102.48, 102.44, 102.31, 102.03, 101.65, 101.63, 101.44, 99.55, 98.65, 98.51, 81.99, 81.55, 81.50, 78.17, 75.55, 75.00, 74.95, 74.88, 74.84, 74.78, 74.69, 74.56, 74.37, 74.26, 72.88, 72.82, 72.70, 72.63, 72.61, 71.78, 70.45, 69.88, 69.18, 69.07, 68.23, 68.18, 68.00, 67.61, 67.54, 67.28, 66.61, 62.49, 61.92, 61.43, 61.28, 60.89, 60.50, 59.94, 59.71, 59.52, 58.41, 55.86, 51.61, 47.77, 39.70, 28.15, 22.16, 21.97, 15.21; HRMS (ESI) *m/z* calcd for $C_{86}H_{141}N_7O_{61}^{2-}$ $[M-2H]^{2-}$ 1123.9076, found 1123.9018.

Neu5Gcα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN_3 (24)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



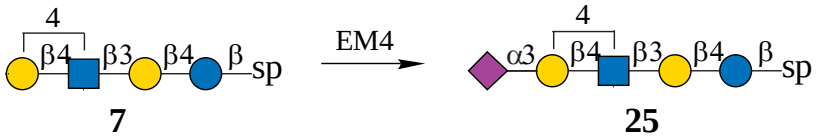


Compound **24** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **24** was obtained as white solid (25 mg, 55%). ^{1}H NMR (600 MHz, D_2O) δ δ 5.11 (d, *J* = 4.2 Hz, 1H), 5.10 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 4.2 Hz, 1H), 4.69 (t, *J* = 7.2 Hz, 1H), 4.68 (t, *J* = 6.0 Hz, 2H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.43 (d, *J* = 6.6 Hz, 2H), 4.41 (d, *J* =7.2Hz,1H), 4.14 (d, *J* =2.4Hz,1H), 4.10 (s, 2H), 4.08 (s, 3H), 4.00–3.47 (m, 65H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 9.0 Hz, 1H), 2.76 (dd, *J* = 4.2,12.6 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 6H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.79 (t, *J* = 12 Hz, 1H), 1.15 (d, *J* = 6.6Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 6H);^{13}C NMR (150 MHz, D_2O) δ 175.79, 174.70, 174.65, 173.89, 170.57, 102.93, 102.50, 102.10, 101.72, 101.55, 99.67, 98.67, 98.54, 82.06, 81.63, 81.60, 78.33, 75.66, 75.08, 75.06, 74.99, 74.89, 74.85, 74.75, 74.64, 74.43, 74.36, 73.02, 72.79, 72.63, 71.91, 71.86, 70.53, 69.96, 69.27, 69.17, 68.29, 68.23, 68.03, 67.70, 67.64, 67.36, 66.66, 62.57, 61.47, 60.97, 60.95, 60.06, 59.63,

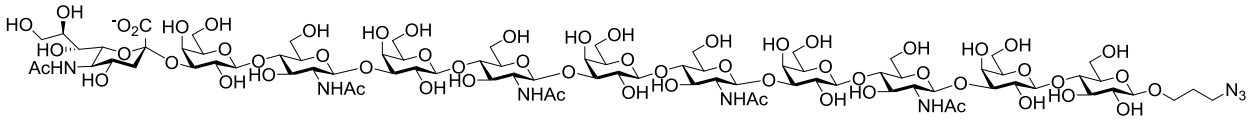
59.53, 55.95, 51.40, 47.87, 39.84, 28.22, 22.24, 15.27; HRMS (ESI) *m/z* calcd for $C_{86}H_{142}N_7O_{62}^-$ $[M-H]^-$ 2264.8179, found 2264.8193.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (25)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



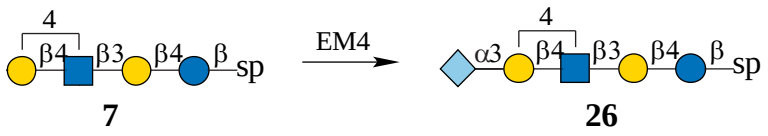
7 **25**

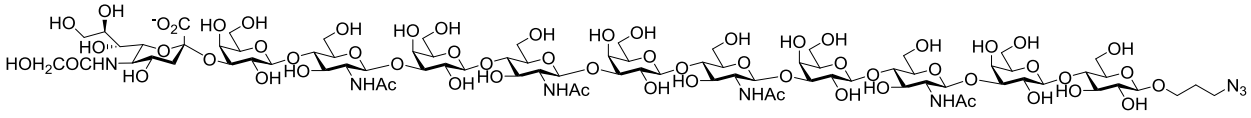


Compound **25** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **25** was obtained as white solid (53 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ δ 4.68 (d, *J* = 7.8 Hz, 4H), 4.54 (d, *J* = 7.2 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 3H), 4.42 (d, *J* = 8.4 Hz, 1H), 4.14 (s, 4H), 4.10 (d, *J* = 9.6 Hz, 1H), 4.00–3.52 (m, 64H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.74 (dd, *J* = 3.6,12 Hz, 1H), 2.02 (s, 15H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.78 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 174.89, 174.78, 173.76, 102.84, 102.78, 102.71, 102.66, 102.44, 102.01, 99.70, 81.95, 81.94, 78.23, 78.04, 77.87, 75.38, 75.07, 74.77, 74.67, 74.44, 74.25, 72.78, 72.69, 72.06, 71.66, 69.86, 69.28, 68.23, 67.98, 67.38, 67.26, 62.48, 60.94, 60.86, 59.95, 59.73, 55.08, 55.04, 51.59, 47.77, 39.54, 28.14, 22.10, 21.96; HRMS (ESI) *m/z* calcd for $C_{82}H_{134}N_8O_{60}^{2-}$ $[M-2H]^{2-}$ 1087.3869, found 1087.3848.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (26)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

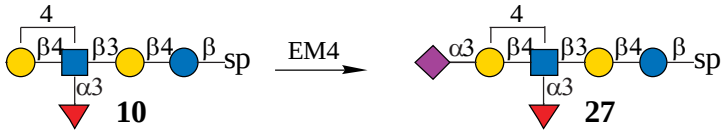


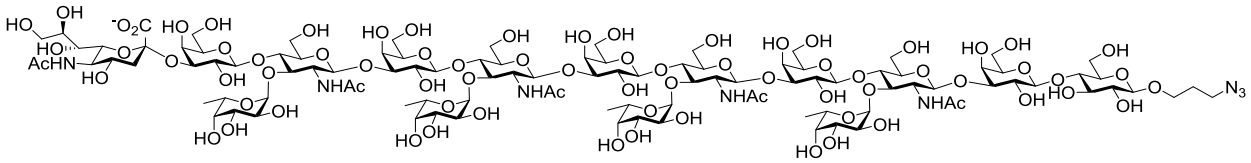


Compound **26** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **26** was obtained as white solid (51 mg, 89%). ^{1}H NMR (600 MHz, D_2O) δ 4.67 (d, *J* = 7.8 Hz, 4H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 3H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.13 (s, 4H), 4.10 (d, *J* = 9.6 Hz, 1H), 4.09 (s, 2H), 3.99–3.54 (m, 64H), 3.43 (t, *J* = 6.6 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 1H), 2.75 (dd, *J* = 3.6,12 Hz, 1H), 2.00 (s, 12H), 1.89 (p, *J* = 6.6 Hz, 2H), 1.79 (t, *J* = 12 Hz, 1H); ^{13}C NMR (150 MHz, D_2O) δ 175.66, 174.78, 173.79, 102.82, 102.76, 102.70, 102.65, 102.42, 102.00, 99.70, 81.95, 81.92, 78.21, 78.01, 77.85, 75.36, 75.07, 74.76, 74.66, 74.43, 74.24, 72.68, 72.49, 72.05, 71.71, 69.85, 69.28, 68.21, 67.98, 67.89, 67.35, 67.25, 62.42, 60.94, 60.86, 59.93, 59.72, 59.20, 55.06, 55.03, 51.27, 47.75, 39.58, 28.13, 22.07. HRMS (ESI) *m/z* calcd for $C_{82}H_{134}N_8O_{60}^{2-}$ $[M-2H]^{2-}$ 1095.3882, found 1095.3869.

Neu5Acα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (27)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



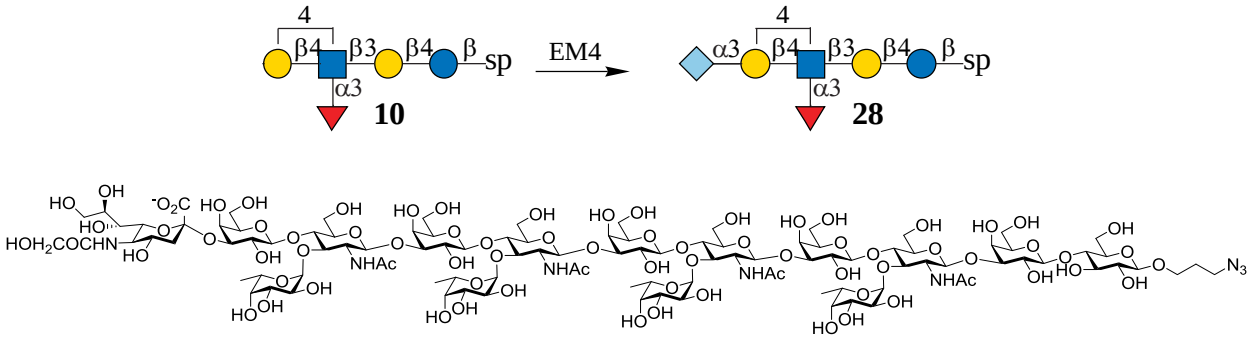


Compound **27** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **27** was obtained as white solid (31 mg, 56%). ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 3.6 Hz, 4H), 4.72 (t, *J* = 6.6 Hz, 3H), 4.54 (d, *J* = 7.2 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 2H), 4.46 (d, *J* = 6.6 Hz, 3H), 4.44 (d, *J* = 7.2 Hz, 1H), 4.16 (d, *J* = 2.4 Hz, 1H), 4.11-4.09 (m, 4H), 4.03–

3.50 (m, 80H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 3.6,12.0 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 1.93 (p, *J* = 6.0 Hz, 2H),1.81 (t, *J* = 12 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 175.03, 174.71, 174.66, 174.44, 173.86, 102.94, 102.50, 102.11, 101.71, 101.54, 99.65, 98.68, 98.55, 82.05, 81.60, 78.33, 75.66, 75.06, 74.85, 74.75, 74.43, 74.35, 73.02, 72.91, 72.77, 71.85, 70.67, 70.52, 69.95, 69.40, 69.26, 69.17, 68.29, 68.23, 68.10, 67.75, 67.64, 67.36, 66.67, 63.26, 62.60, 61.46, 60.95, 60.06, 59.64, 55.95, 53.52, 51.69, 47.87, 41.35, 28.23, 22.24, 22.04, 21.89, 15.27; HRMS (ESI) *m/z* calcd for $C_{106}H_{174}N_8O_{75}^{2-}$ $[M-2H]^{2-}$ 1379.5027, found 1379.9945.

Neu5Gcα2-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (28)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

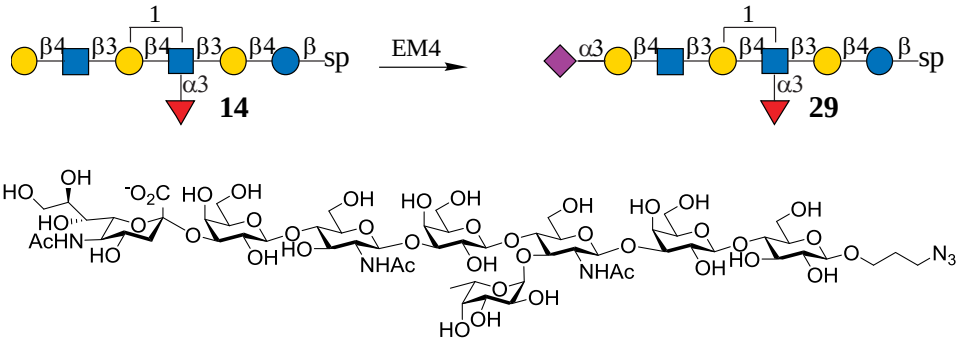


Compound **28** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **28** was obtained as white solid (27 mg, 49%). ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.2 Hz, 1H), 5.10 (d, *J* = 3.6 Hz, 2H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.68 (d, *J* = 6.6 Hz, 3H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 3H), 4.41 (d, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 2.4 Hz, 1H), 4.11 (s, 2H), 4.08 (s, 4H), 4.00–3.47 (m, 80H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.39 (t, *J* = 8.4 Hz, 1H), 2.76 (dd, *J* = 4.2, 12.6 Hz, 1H), 2.00 (s, 3H), 2.00 (s, 9H), 1.90 (p, *J* = 6.6 Hz, 2H),1.79 (t, *J* = 12 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 9H); ^{13}C NMR (150 MHz, D_2O) δ 175.80, 174.71, 174.66, 173.90, 102.94, 102.51, 102.47, 102.11, 101.71, 101.55, 99.68, 98.68, 98.55, 82.06, 81.65, 81.61, 78.34, 75.67, 75.10, 75.06, 75.00, 74.91, 74.86, 74.76, 74.66, 74.44, 74.36, 73.03, 72.79, 72.75, 72.64, 71.91, 71.86, 70.53, 69.96, 69.28, 69.18, 68.30, 68.23, 68.04, 67.72, 67.65, 67.37, 67.31, 66.68, 62.57, 61.49, 61.45, 60.98,

60.95, 60.07, 59.64, 59.32, 55.96, 51.40, 47.88, 39.85, 28.23, 22.24, 15.27; HRMS (ESI) *m/z* calcd for $C_{106}H_{174}N_8O_{76}^{2-}$ $[M-2H]^{2-}$ 1387.5001, found 1388.0043.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (29)

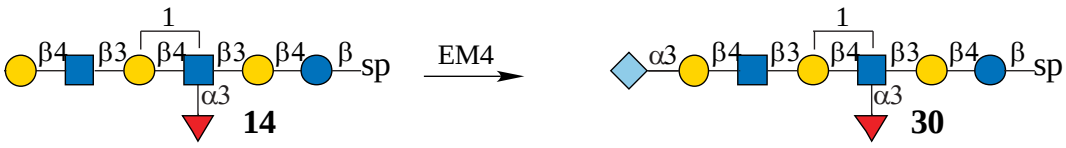
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

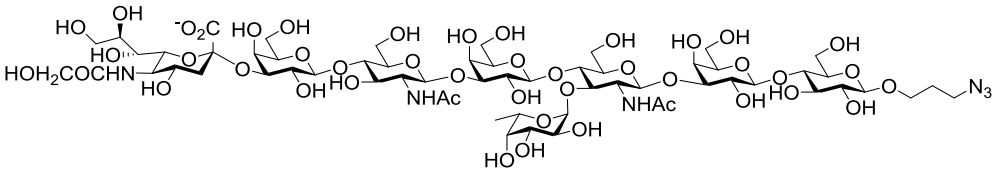


Compound **29** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **29** was obtained as white solid (57 mg, 93%). ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.44 (t, *J* = 7.8 Hz, 2H), 4.15 (d, *J* = 3.0 Hz, 1H), 4.12 (dd, *J* = 3.0, 9.6 Hz, 1H), 4.10 (d, *J* = 3.6 Hz, 1H), 4.02–3.50 (m, 46H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 9.0 Hz, 1H), 2.76 (dd, *J* = 4.2,12.6 Hz, 1H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (p, *J* = 6.6 Hz, 2H), 1.80 (t, *J* = 12.6 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.99, 174.82, 174.69, 173.85, 102.92, 102.71, 102.52, 102.09, 101.70, 99.78, 98.68, 82.04, 81.61, 78.31, 77.98, 75.46, 75.15, 75.08, 74.84, 74.74, 74.50, 74.43, 74.33, 72.86, 72.76, 72.06, 71.83, 71.74, 71.68, 70.47, 69.94, 69.36, 69.14, 68.32, 68.27, 68.22, 68.05, 67.62, 67.45, 67.34, 66.67, 62.55, 61.46, 61.01, 60.93, 60.03, 59.80, 59.60, 55.94, 55.13, 51.65, 47.84, 39.61, 28.21, 22.22, 22.14, 22.02, 15.26; HRMS (ESI) *m/z* calculated for $C_{60}H_{99}N_6O_{43}^-$ $[M-H]^-$ 1591.5750, found 1591.5427.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (30)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside

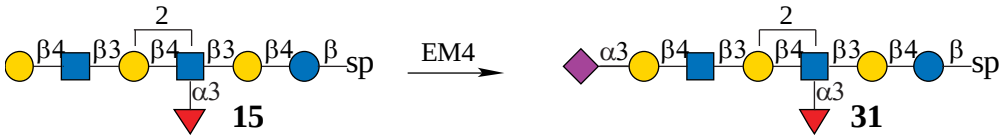


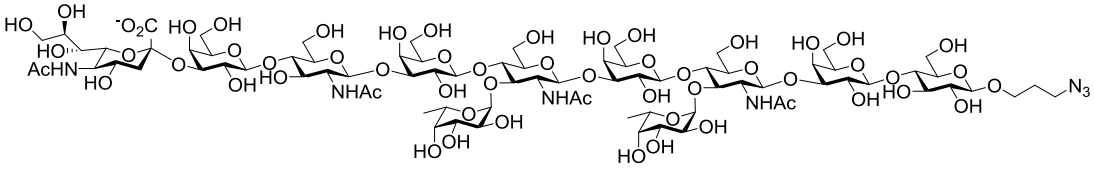


Compound **30** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **30** was obtained as white solid (57 mg, 92%). ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 9.6 Hz, 1H), 4.70 (d, *J* = 8.4 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 4.44 (t, *J* = 7.8 Hz, 2H), 4.16 (d, *J* = 3.0 Hz, 1H), 4.13 (dd, *J* = 3.6, 8.4Hz, 1H), 4.12 (s, 2H), 4.10 (d, *J* = 3.0 Hz, 1H), 4.02–3.57 (m, 45H), 3.52 (t, *J* = 8.4 Hz, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 4.8,12.6 Hz, 1H), 2.03 (s, 3H), 2.03 (s, 3H), 1.92 (p, *J* = 6.6 Hz, 2H), 1.82 (t, *J* = 12 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (150 MHz, D_2O) δ 175.66, 174.73, 174.59, 173.79, 102.83, 102.62, 102.43, 102.00, 101.61, 99.70, 98.60, 81.95, 81.51, 78.20, 77.88, 75.36, 75.06, 74.99, 74.75, 74.66, 74.41, 74.35, 74.24, 72.68, 72.65, 72.49, 71.97, 71.71, 70.39, 69.85, 69.28, 69.05, 68.19, 68.14, 67.98, 67.89, 67.53, 67.35, 67.25, 66.58, 62.43, 61.37, 60.94, 60.87, 59.94, 59.71, 59.51, 55.85, 55.05, 51.27, 47.76, 39.59, 28.13, 22.15, 22.07, 15.19; HRMS (ESI) *m/z* calculated for $C_{60}H_{99}N_6O_{44}^-$ $[M-H]^-$ 1607.5699, found 1607.5357.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (31)

3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



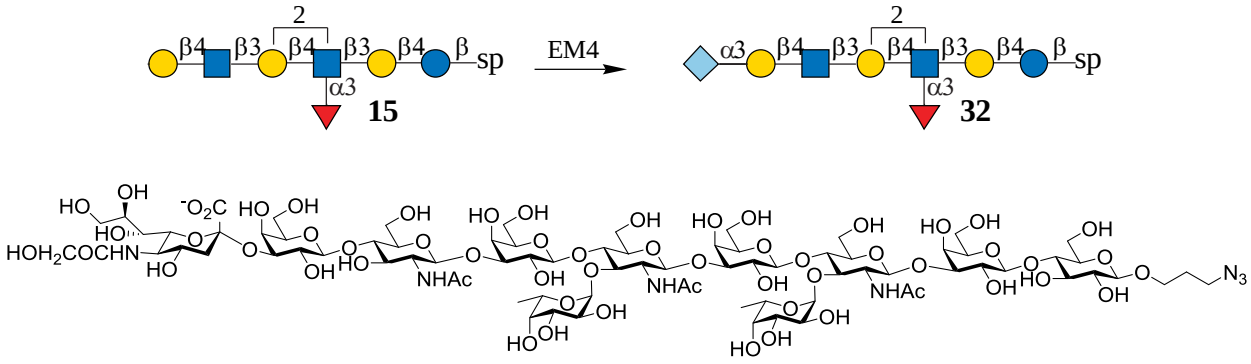


Compound **31** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **31** was obtained as white solid (22 mg, 86%). ^{1}H NMR (600 MHz, D_2O) δ 5.13 (t, *J* = 3.6 Hz, 2H), 4.71 (t, *J* = 8.4 Hz, 3H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 6.0 Hz, 2H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 2.4 Hz, 1H), 4.13 (dd, *J* = 3.0,10.2 Hz, 1H), 2.01 (s, 2H), 4.03–3.50 (m, 61H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 8.4 Hz, 1H), 2.77 (dd,

J = 5.6,12.6 Hz, 1H), 2.04 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 1.93 (p, *J* = 6.6 Hz, 2H), 1.81 (t, *J* = 12.0 Hz, 1H), 1.16 (d, *J* =6.0 Hz, 3H), 1.16 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 174.92, 174.79, 174.65, 173.83, 102.86, 102.70, 102.44, 102.03, 101.65, 99.70, 98.65, 81.98, 81.52, 78.18, 77.83, 75.38, 75.09, 74.99, 74.78, 74.68, 74.42, 74.38, 74.26, 72.79, 72.70, 72.63, 71.99, 71.76, 71.69, 70.42, 69.87, 69.30, 69.07, 68.28, 68.18, 67.97, 67.54, 67.37, 67.28, 66.61, 62.47, 61.42, 60.97, 60.88, 59.93, 59.70, 59.51, 55.86, 55.06, 51.58, 47.76, 39.53, 28.14, 22.14, 22.06, 21.95, 15.19; HRMS (ESI) *m/z* calcd for $C_{80}H_{132}N_7O_{57}^-$ [M-H]$^-$ 2102.7651, found 2102.7645.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (32)

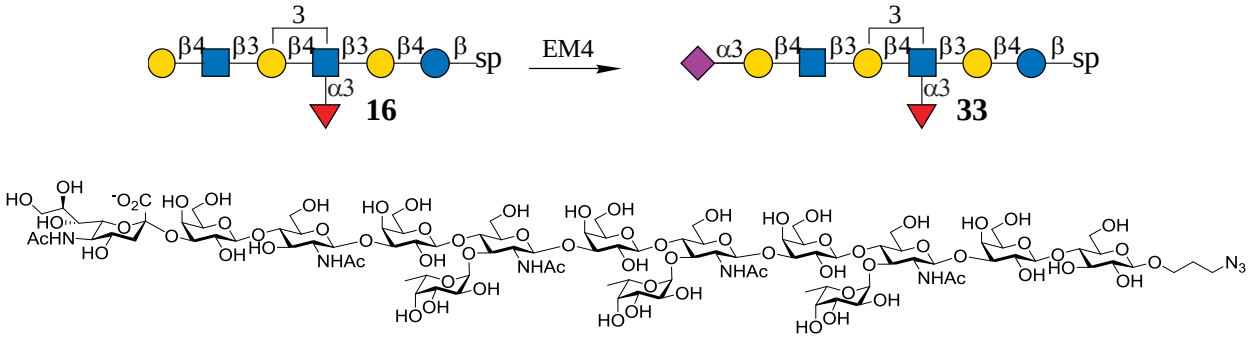
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **32** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **32** was obtained as white solid (22 mg, 85%). ^{1}H NMR (600 MHz, D_2O) δ 5.07 (t, *J* = 3.6 Hz, 2H), 4.66 (t, *J* = 10.2 Hz, 1H), 4.65 (t, *J* = 7.8 Hz, 1H), 4.64 (t, *J* = 8.4 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.39 (d, *J* = 6.6 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H), 4.11 (d, *J* = 3.0 Hz, 1H), 4.08 (dd, *J* = 3.0,12.0 Hz, 1H),4.07 (s, 2H), 4.05 (s, 2H), 3.97–3.44 (m, 61 H), 3.41 (t, *J* = 6.6 Hz, 2H), 3.26 (t, *J* = 8.4 Hz, 1H), 2.73 (dd, *J* = 4.8,12.6 Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.86 (p, *J* = 6.6 Hz, 2H), 1.77 (t, *J* = 12 Hz, 1H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.096 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, D_2O) δ 175.71, 174.78, 174.65, 174.60, 173.85, 102.86, 102.69, 102.48, 102.45, 102.03, 101.65, 101.63, 99.72, 98.65, 98.64, 81.98, 81.52, 78.19, 77.86, 75.38, 75.10, 75.01, 74.97, 74.78, 74.69, 74.43, 74.38, 74.27, 72.70, 72.65, 72.52, 72.00, 71.97, 71.76, 71.75, 70.45, 70.42, 69.88, 69.31, 69.08, 68.23, 68.18, 68.02, 67.91, 67.55, 67.37, 67.28, 66.62, 62.44, 62.38, 61.42, 61.41, 60.97, 60.88, 59.95, 59.72, 59.52, 55.87, 55.07, 51.29, 47.77, 39.61, 28.15, 22.15, 22.15, 22.07, 15.21, 15.20; HRMS (ESI) *m/z* calcd for $C_{80}H_{132}N_7O_{58}^-$ [M-H]$^-$ 2118.7600, found 2118.7592.

Neu5Acα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (33)

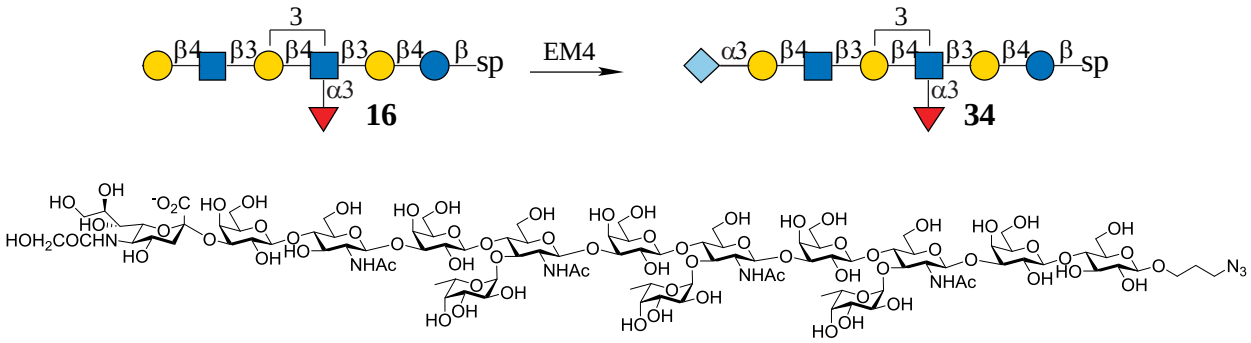
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **33** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **33** was obtained as white solid (21 mg, 86%). ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 3.6 Hz, 2H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 1H), 4.68 (d, *J* = 7.8 Hz, 2H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.54 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 3H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.14 (d, *J* = 3.0 Hz, 1H), 4.10 (dd, *J* = 3.0,10.2 Hz, 1H), 4.08 (s, 3H), 4.00–3.47 (m, 76H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 8.4 Hz, 1H), 2.74 (dd, *J* = 4.8,12.6 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 2.00 (s, 6H),1.90 (p, *J* = 6.6 Hz, 2H),1.78 (t, *J* = 12.0 Hz, 1H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 6H);^{13}C NMR (150 MHz, D_2O) δ 175.03, 174.86, 174.72, 174.66, 173.84, 102.95, 102.72, 102.55, 102.48, 102.12, 101.72, 99.81, 98.69, 82.06, 81.62, 80.52, 78.34, 78.04, 76.94, 75.50, 75.31, 75.17, 75.07, 74.86, 74.77, 74.53, 74.45, 74.36, 74.24, 73.70, 72.90, 72.78, 72.56, 72.42, 72.09, 71.87, 71.76, 71.71, 70.53, 69.97, 69.39, 69.18, 68.33, 68.24, 68.09, 67.66, 67.48, 67.38, 66.69, 66.49, 62.62, 62.49, 61.47, 61.04, 60.95, 60.07, 59.84, 59.64, 55.97, 55.16, 51.88, 51.69, 47.88, 40.07, 39.64, 28.24, 22.25, 22.17, 22.05, 15.28; HRMS (ESI) *m/z* calcd for $C_{100}H_{165}N_8O_{71}^-$ [M-H]$^-$ 1306.4735, found 1306.9730.

Neu5Gcα2-3Galβ1-4GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4(Fucα1-3)GlcNAcβ1-3Galβ1-4GlcβProN$_3$ (34)

3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-galacto-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside



Compound **34** was prepared according to general procedure of α2-3-sialylation with EM4. After lyophilization, **34** was obtained as white solid (22 mg, 85%).^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.2 Hz, 2H), 5.07 (d, *J* = 3.6 Hz, 1H), 4.67 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 7.2 Hz, 2H), 4.65 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 8.4 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 3H), 4.39 (d, *J* = 8.4 Hz, 1H), 4.11 (d, *J* = 3.0 Hz, 1H), 4.09 (dd, J = 1.8, 10.8 Hz, 1H), 4.08 (s, 2H), 4.06 (s, 3H), 3.98–3.45 (m, 76H), 3.42 (t, *J* = 6.6 Hz, 2H), 3.27 (t, *J* = 9.0 Hz, 1H), 2.74 (dd, J = 4.8, 12.6 Hz, 1H), 1.99 (s, 3H), 1.98 (s, 3H), 1.97 (s, 6H), 1.87 (p, J = 6.6 Hz, 2H),1.78 (t, J = 12.6 Hz, 1H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 6H);^{13}C NMR (150 MHz, D_2O) δ 175.79, 174.85, 174.72, 174.67, 173.90, 102.95, 102.73, 102.56, 102.53, 102.48, 102.12, 101.72, 99.83, 98.69, 82.07, 81.62, 78.35, 78.05, 75.49, 75.19, 75.07, 74.87, 74.77, 74.53, 74.45, 74.37, 72.79, 72.78, 72.62, 72.10, 71.86, 71.84, 70.53, 69.97, 69.40, 69.18, 68.25, 68.10, 68.03, 67.66, 67.47, 67.38, 66.69, 62.56, 61.47, 61.05, 60.99, 60.96, 60.08, 59.85, 59.65, 55.97, 55.17, 51.39, 47.88, 39.71, 28.24, 22.25, 22.18, 15.28; HRMS (ESI) *m/z* calcd for $C_{100}H_{164}N_8O_{72}^{2-}$ $[M-2H]^{2-}$ 1314.4712, found 1314.9692.

VI. Microarray Data

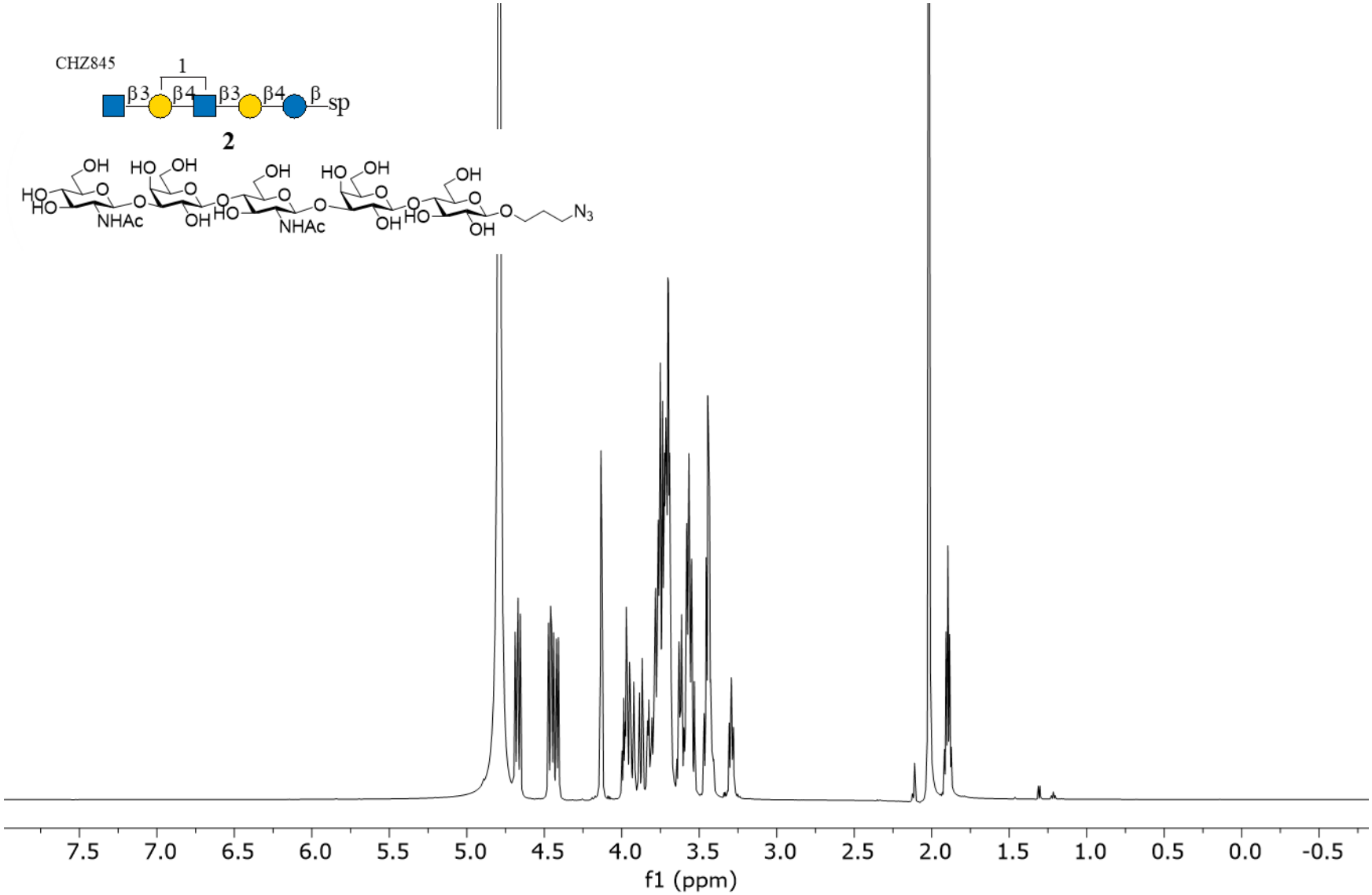
Glycan NO#	MAL I		LTL		E selectin		anti-CD65s		H5N8		H7N9		AAL		WGA	
	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV
S1	618	560	1	1	0	2	0	1	188	293	23	326	3	7	77	35
1	1769	632	0	1	0	3	2	2	0	90	0	216	1	1	5968	882
3	5287	508	0	2	0	3	0	2	0	76	0	180	1	2	19147	2071
5	6934	640	0	2	0	10	0	4	0	503	0	378	0	2	19216	1449
7	5365	822	0	3	0	3	4	7	0	179	0	393	0	2	16853	1075
S2	22	33	0	1	0	2	0	3	0	67	0	247	0	1	19037	7812
2	204	251	0	2	0	4	13	19	0	54	0	254	1	2	39211	2297
4	38	66	0	2	0	4	11	22	0	242	0	386	2	1	45832	7952
6	170	319	0	3	0	3	19	26	0	170	0	90	0	2	34243	4223
S3	29	47	2535	444	0	1	0	2	0	89	0	217	882	149	20	43
8	2	3	18337	4151	0	4	13	19	0	464	0	429	1716	506	3	86
9	208	247	19247	1745	0	9	0	2	0	513	0	408	2325	167	83	60
10	0	1	15710	2128	0	5	2	2	0	81	0	485	1898	343	109	25
S8	8	23	12522	2192	0	4	1	2	0	170	0	322	2039	260	92	60
11	25	32	3	4	0	3	4	2	0	480	0	438	322	86	3528	1166
12	131	202	12	17	0	6	4	13	0	165	0	409	732	56	4631	1716
13	4	16	16	7	0	3	7	10	0	127	0	402	727	75	3049	1114
14	2500	955	1	2	0	3	1	1	0	279	0	152	187	41	159	81
15	3885	145	9	9	0	3	1	3	0	134	0	411	410	78	71	77
16	3382	528	6	3	0	5	0	3	0	257	0	410	573	148	93	72
S4	2722	466	0	1	0	1	0	2	19613	7736	8139	2463	1	2	10970	1242
17	6293	888	0	1	0	5	0	2	17959	3692	7736	2250	23	43	18082	2465
21	8907	1247	0	6	0	10	1	2	10928	6934	4461	1246	1	1	29204	1934
25	7217	1485	0	2	0	7	0	2	5179	610	6988	4579	0	1	19327	3335
S5	5647	1085	0	2	0	2	0	2	1301	214	0	178	0	1	180	299
18	7575	1199	0	3	0	5	0	1	824	188	0	481	0	1	441	115

22	9589	1397	0	3	0	7	1	2	1103	301	0	320	0	2	2144	346
26	13202	1902	0	2	0	4	0	1	0	156	0	208	0	1	6601	156
S6	0	3	6	2	2364	276	1	3	26732	3201	11564	1623	371	65	7289	1279
19	15	29	420	153	3700	151	3	8	10531	942	8591	5147	721	73	6534	230
23	108	277	930	221	3345	365	0	4	8020	1150	4793	1098	879	43	5363	539
27	147	207	1665	284	2466	315	0	1	3575	644	1535	1324	1059	84	3731	244
S7	96	32	165	59	3556	249	0	3	37	245	0	134	507	100	54	34
20	1	7	339	109	4336	360	1	3	0	229	0	196	673	115	35	64
24	80	96	1426	210	4859	575	0	2	0	412	0	218	932	56	24	66
28	0	2	1374	158	3462	226	0	4	0	200	0	460	989	96	95	44
29	6110	752	0	3	0	6	2816	402	14362	4173	10785	2299	46	14	2957	1231
31	6507	470	0	2	0	6	1439	300	9178	3911	8283	2718	150	37	1469	630
33	10413	1177	0	2	0	1	2024	436	7284	1015	4176	1027	263	14	1405	253
30	6775	579	0	2	0	5	948	224	456	316	0	447	61	6	74	38
32	11143	2216	0	1	0	9	490	125	0	83	0	157	179	16	97	18
34	9867	1112	0	2	0	5	553	106	0	110	0	470	213	27	142	33
PC1	1620	1469	3034	980	3	7	1	1	317	313	758	514	2148	731	1452	569
PC2	15	14	93	12	8205	577	11512	1679	0	113	0	285	47	3	205	37
M	5688	436	4642	1826	5900	586	4888	724	64200	128	64249	157	10472	657	6964	985
NC	0	2	0	1	3	5	1	3	0	305	26	182	1	2	305	34

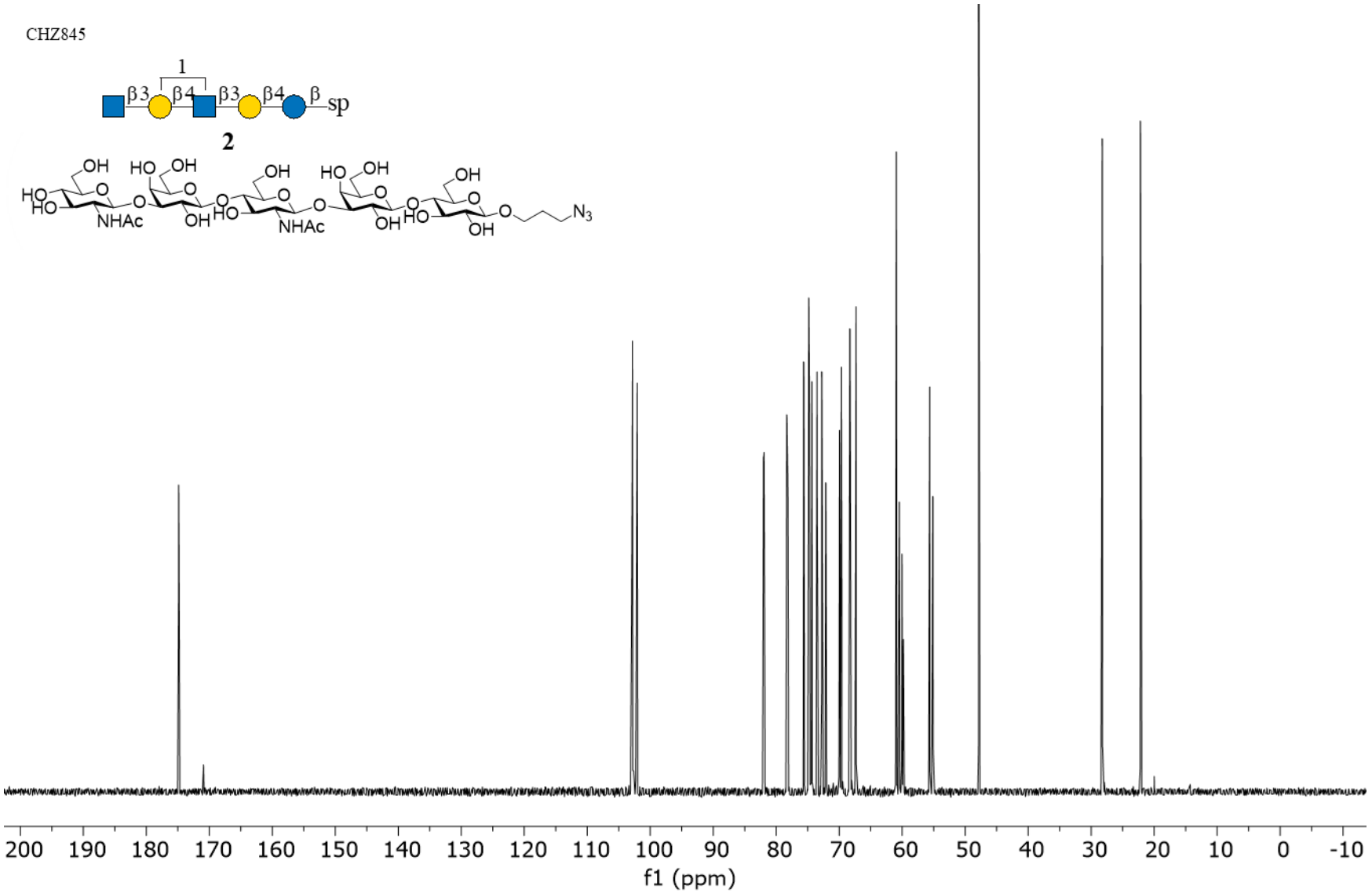
Glycan NO#	RCA-I		ECL		GSII		anti-CD15s		anti-CD15		1934 (H1N1)		2011 (H1N1)		H3N2	
	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV	Median	STEDV
S1	5501	394	4374	2408	1	2	2	3	2	3	225	271	2031	1750	61	245
1	7426	968	11380	791	0	2	0	2	2	2	58	137	0	936	0	167
3	21044	1005	31825	3055	0	1	0	2	7	14	71	531	0	2202	0	644
5	24633	1435	29362	3159	2	1	0	2	0	2	0	248	0	662	0	197
7	21793	834	27425	959	1	3	0	8	0	7	0	190	0	1039	0	666
S2	1	1	1	2	1205	97	1	2	4	2	125	144	0	988	0	275
2	2	1	2	4	1717	215	3	3	7	18	0	307	0	2029	0	635
4	4	3	2	2	2453	233	0	2	15	14	0	799	0	1293	0	278
6	4	2	2	4	2667	171	19	44	0	6	0	618	0	898	0	433
S3	2136	413	2338	873	1	1	0	2	10508	1290	0	92	0	1032	0	303
8	3	1	4	3	3	3	0	2	16303	2446	0	1184	0	2462	0	1033
9	2	1	0	2	1	3	0	3	8675	500	0	527	0	833	0	761
10	2	1	0	2	1	3	0	2	7594	1360	0	380	0	479	0	572
S8	2	2	0	2	3	3	0	3	8151	812	0	64	0	720	0	339
11	3	2	1	2	1886	421	0	2	2	3	54	1400	0	5418	0	1599
12	3	2	4	2	4641	100	2	15	3	2	0	188	0	818	0	739
13	2	1	0	1	4999	299	0	2	6	5	0	655	0	282	0	229
14	24486	1677	25366	1691	8	16	0	3	3	5	0	1169	0	922	0	354
15	22677	1096	28461	1586	3	2	0	3	8	10	0	332	0	1056	0	432
16	20228	1502	22732	3854	4	4	0	3	0	3	0	424	0	2962	0	447
S4	0	1	0	2	0	2	37	26	0	3	7752	967	24872	5712	19091	16509
17	2	2	0	2	1	3	447	96	0	2	14888	2779	13409	1274	12597	2298
21	1	2	0	1	2	2	381	77	0	3	2349	664	16534	2289	4869	2141
25	4	1	1	6	0	2	176	106	0	1	885	2042	5940	5504	6165	3961
S5	1	1	1	2	0	3	0	2	0	4	0	837	0	2628	4671	930
18	2	1	1	2	2	2	0	4	0	2	0	1216	0	1477	1313	1082
22	2	2	0	1	0	2	0	4	0	2	0	1478	0	955	1744	521
26	2	1	0	6	1	2	0	3	0	12	0	559	0	1666	0	472

S6	2	1	3	3	4	3	17337	1359	12	19	11897	2114	46779	10614	24048	3152
19	0	1	1	3	1	3	17124	1324	1001	369	3902	1295	21728	4631	8125	654
23	3	1	0	2	2	2	15328	4580	302	39	623	752	8453	2606	4375	426
27	2	2	0	4	2	2	18174	2457	2779	325	485	635	7616	2326	3994	702
S7	2	2	1	2	1	2	9996	805	1	2	137	492	0	2148	0	252
20	1	1	0	2	1	2	11702	1206	511	26	0	310	0	1930	0	608
24	2	2	0	3	2	4	10542	2534	833	120	0	453	0	934	0	332
28	3	1	0	3	0	4	7801	2019	719	83	0	326	0	601	0	309
29	0	2	0	3	2	3	332	82	0	3	14824	2645	8679	1638	12855	2713
31	4	2	0	2	0	3	1730	950	0	2	6589	2352	3575	4920	9487	3184
33	3	2	2	3	1	3	594	59	0	9	603	581	5394	2389	4576	701
30	1	1	0	3	0	3	0	4	0	4	0	1348	0	685	90	388
32	3	1	0	3	2	2	0	2	0	8	0	754	0	484	0	120
34	3	1	1	3	0	2	0	6	1	15	0	229	0	561	0	321
PC1	3845	1126	6805	1674	3605	1219	31	74	0	4	1760	961	1316	2300	313	289
PC2	5728	234	5366	335	26	4	12462	1088	8457	3214	0	565	0	328	0	373
M	4606	1651	4950	1617	9385	1679	3568	704	2559	588	62966	323	60204	375	63029	336
NC	4	0	1	2	1	2	3	2	12	12	782	484	2171	949	551	289

VII. ^{1}H and ^{13}C NMR spectra



^{1}H NMR of 2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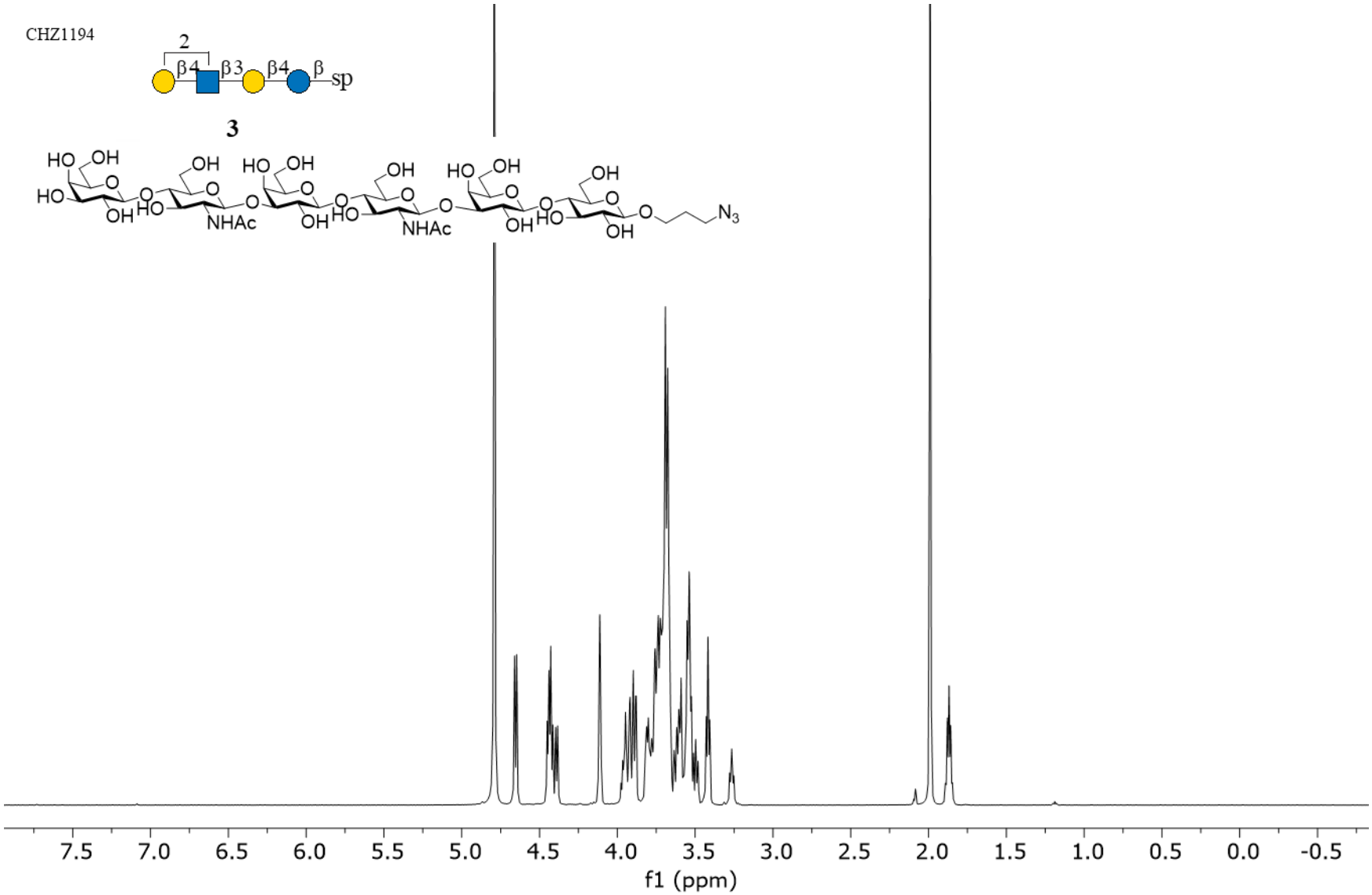
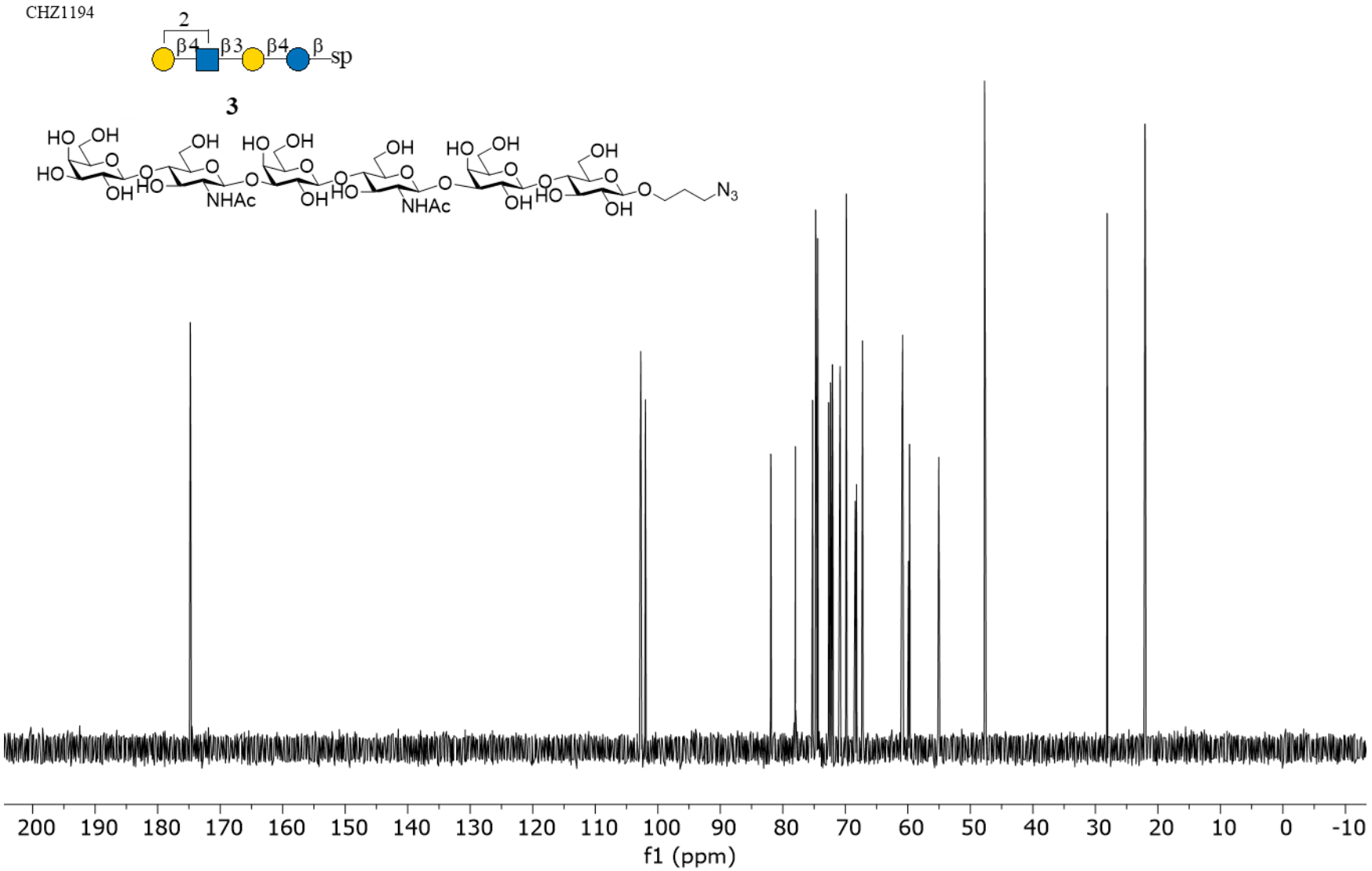
1
β3
β4
β3
β4
β
sp
2
OH
HO
NHAc
OH
HO
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

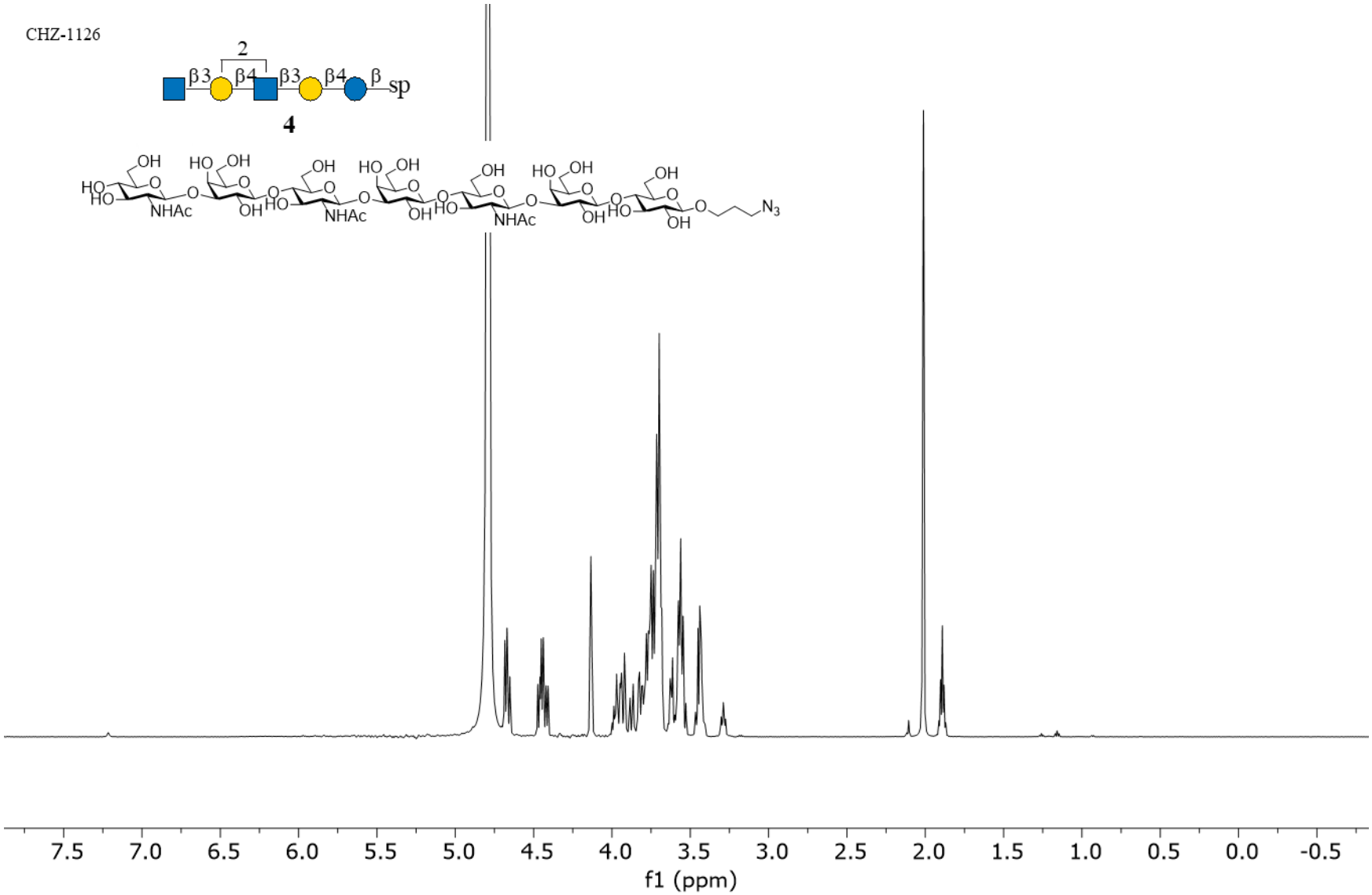
^{13}C NMR of 2


CHZ1194
2
β4
β3
β4
β
sp
3
HO
OH
O
NHAc
N3
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)

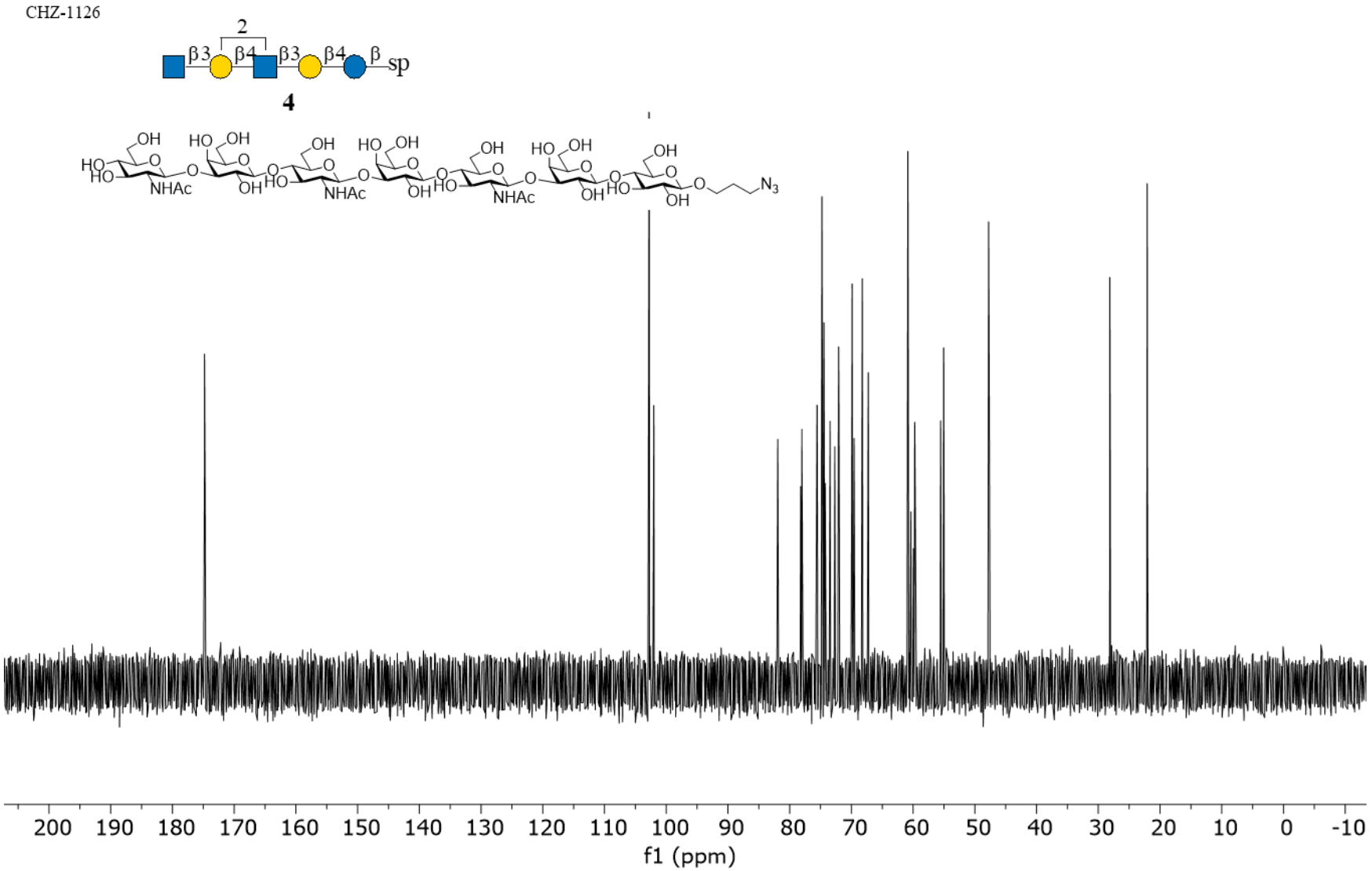
^{1}H NMR of 3


CHZ1194
2
β4
β3
β4
β
sp
3
HO
OH
O
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

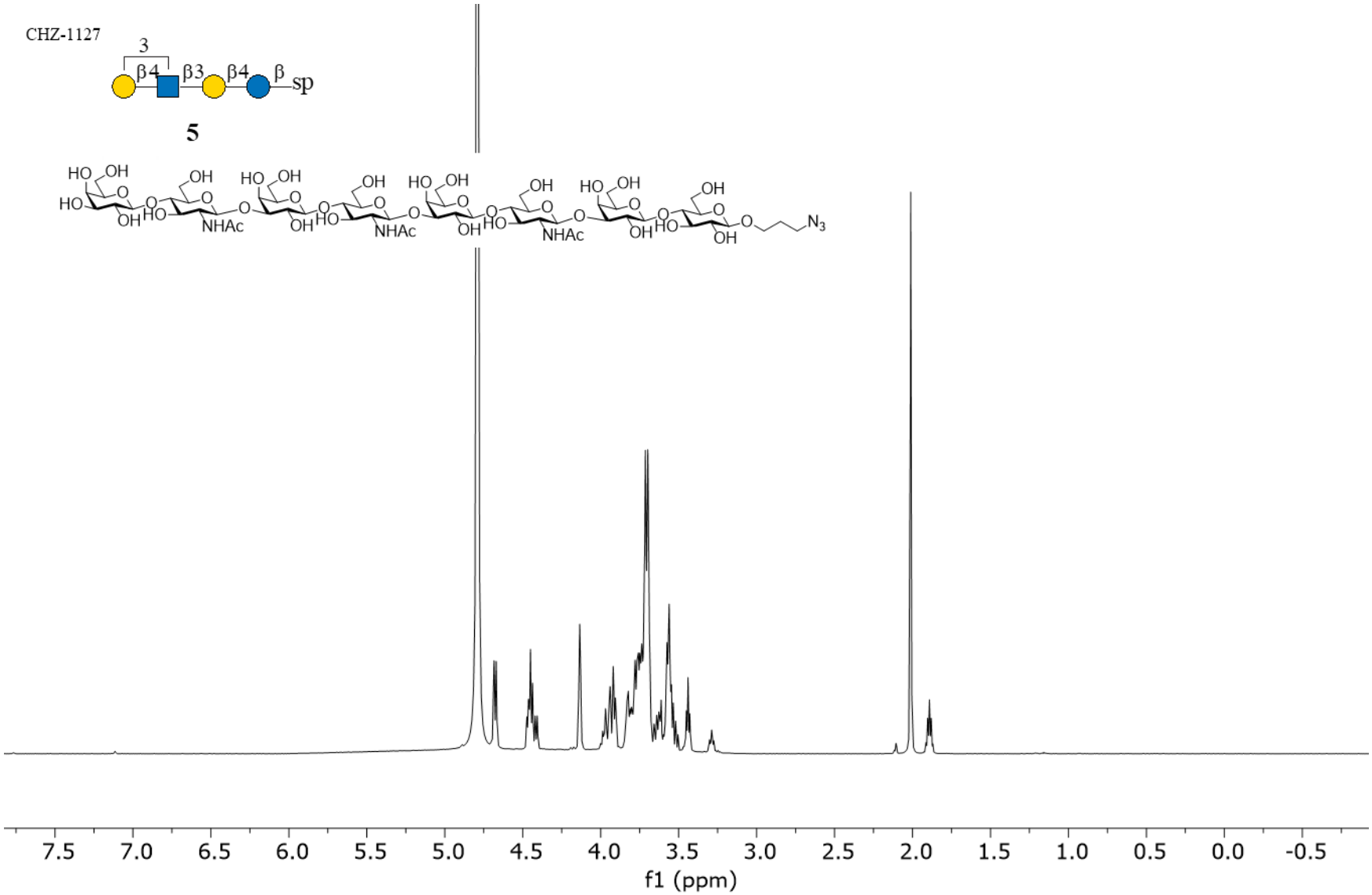
^{13}C NMR of 3


CHZ-1126
2
β3
β4
β3
β4
β
sp
4
OH
HO
NHAc
N3
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)

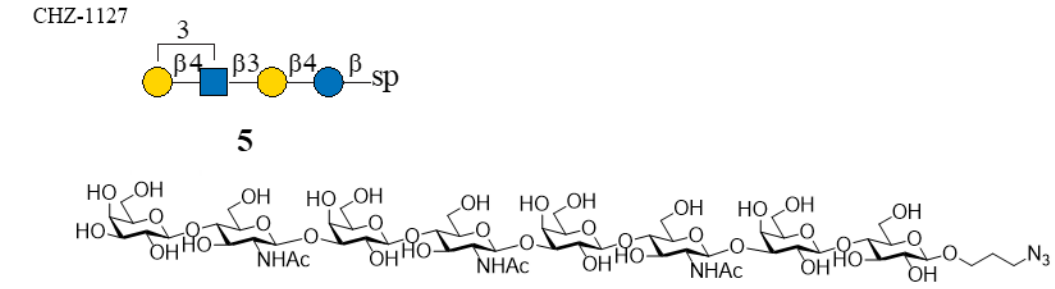
^{1}H NMR of 4


CHZ-1126
2
β3 β4 β3 β4 β sp
4
OH HO OH HO OH HO OH HO OH
NHAc NHAc NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

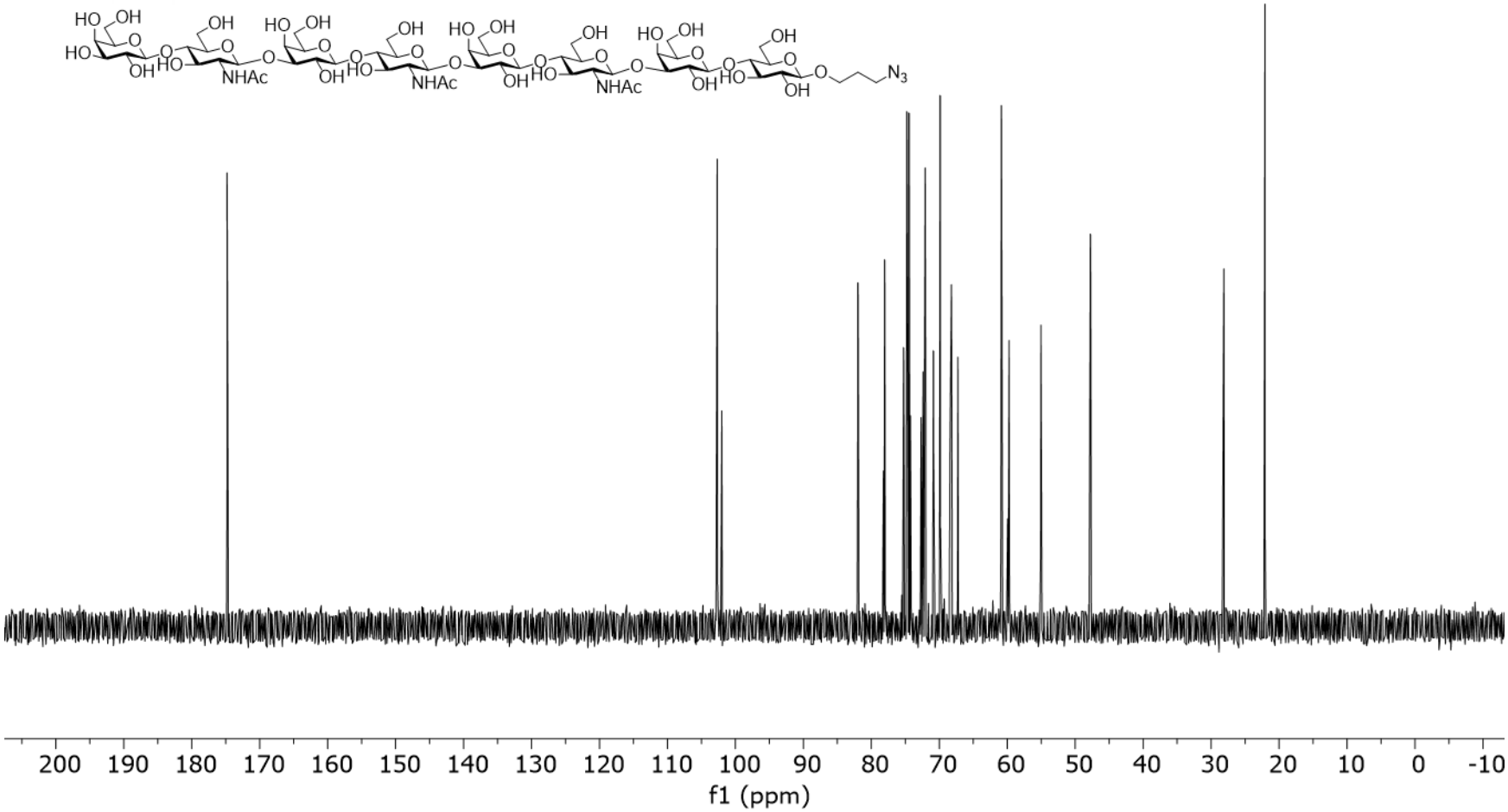
^{13}C NMR of 4


CHZ-1127
3
β4
β3
β4
β
sp
5
HO
OH
O
NHAc
N3
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)

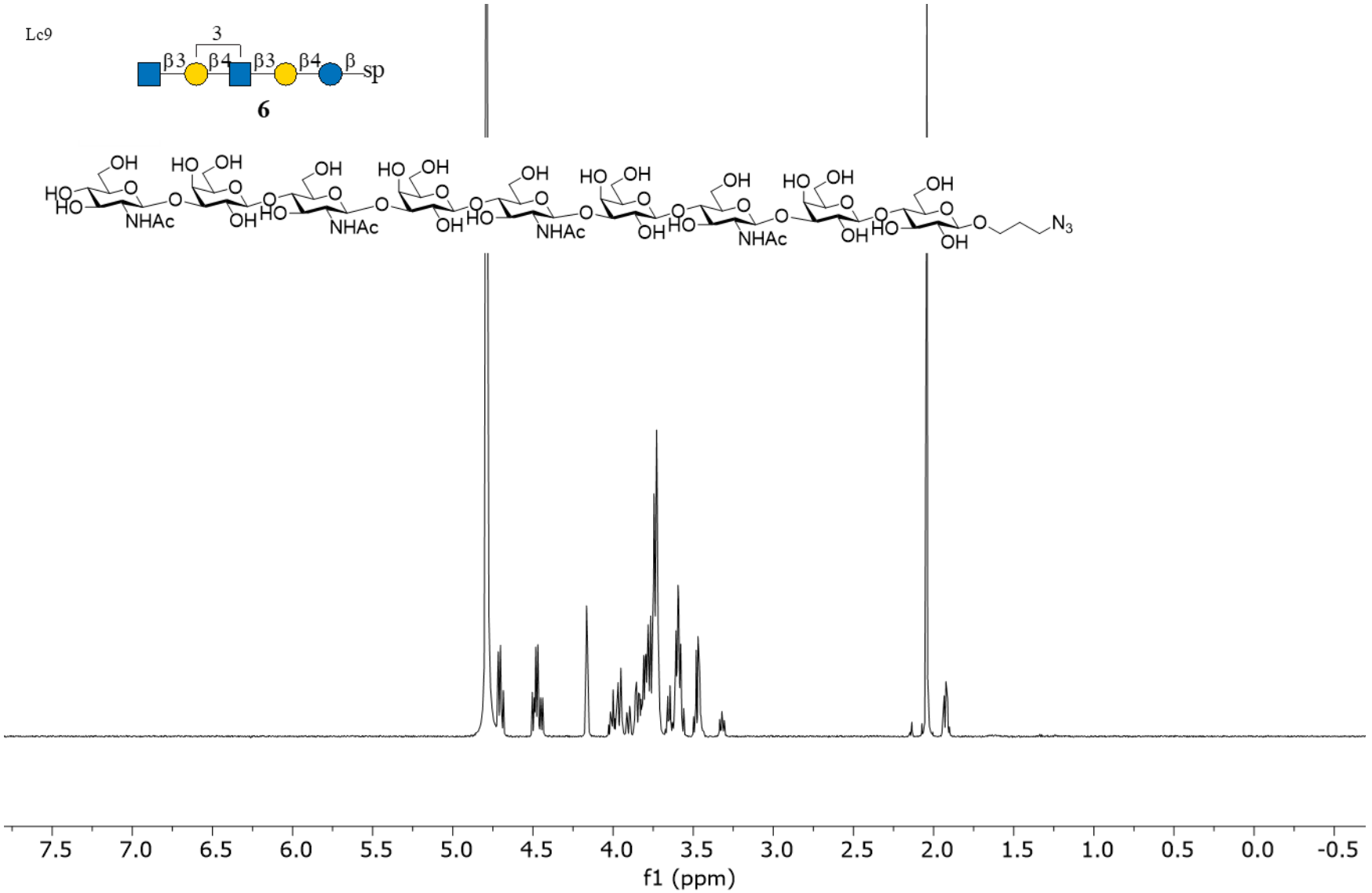
^{1}H NMR of 5


CHZ-1127
3
β4
β3
β4
β
sp

5

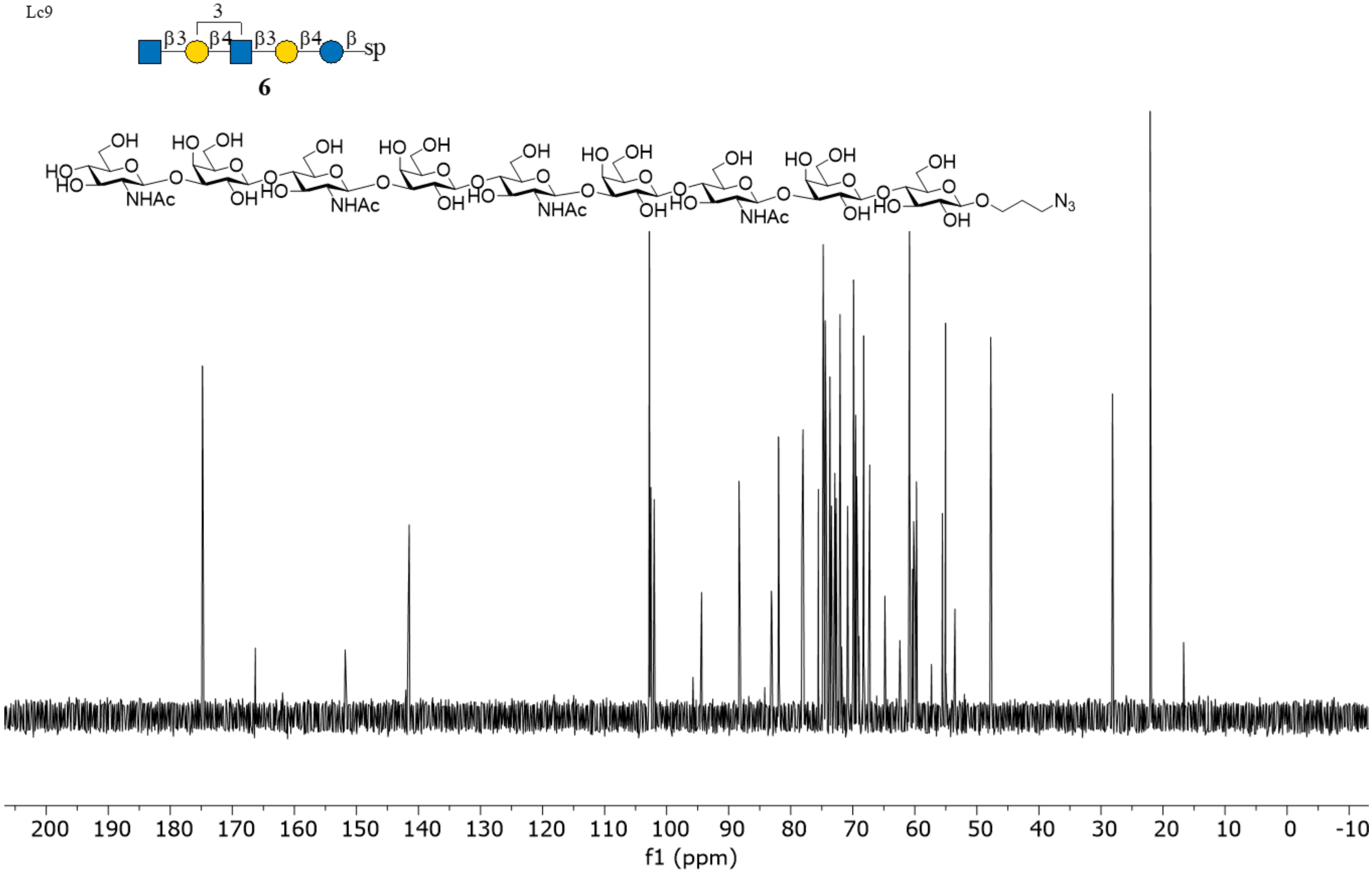

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{13}C NMR of 5

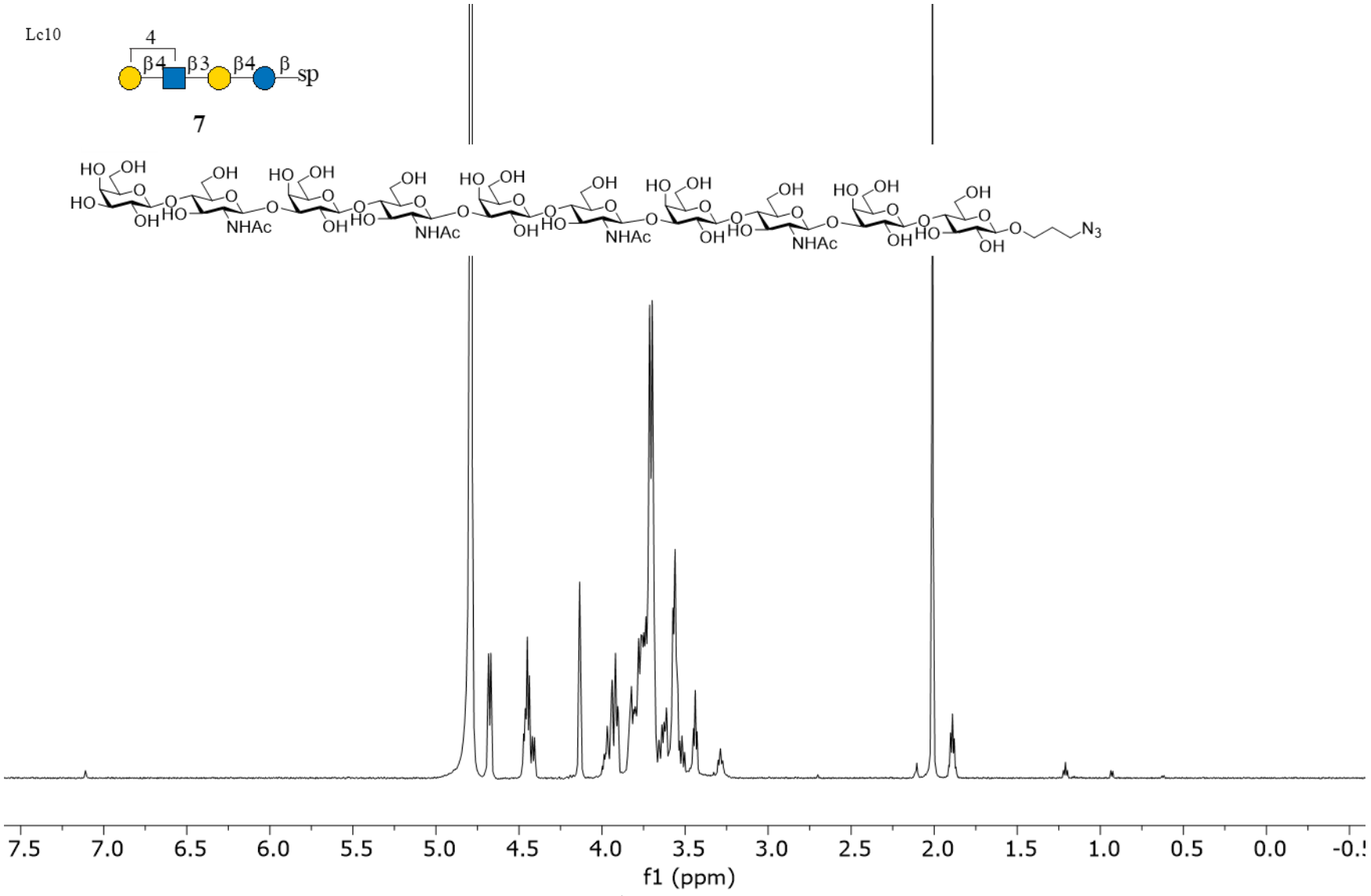

Lc9
3
β3 β4 β3 β4 β sp
6
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{1}H NMR of 6

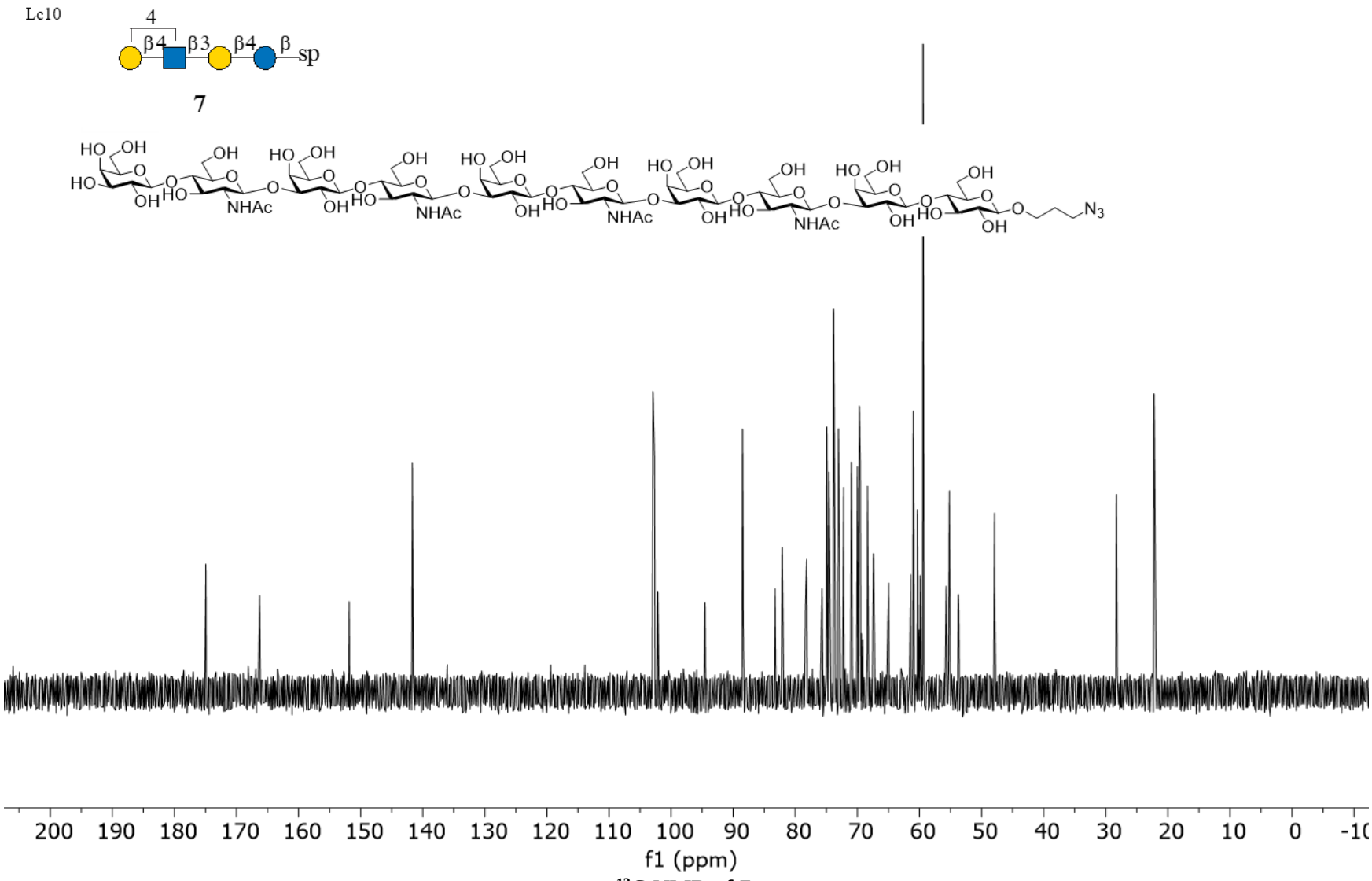
Lc9



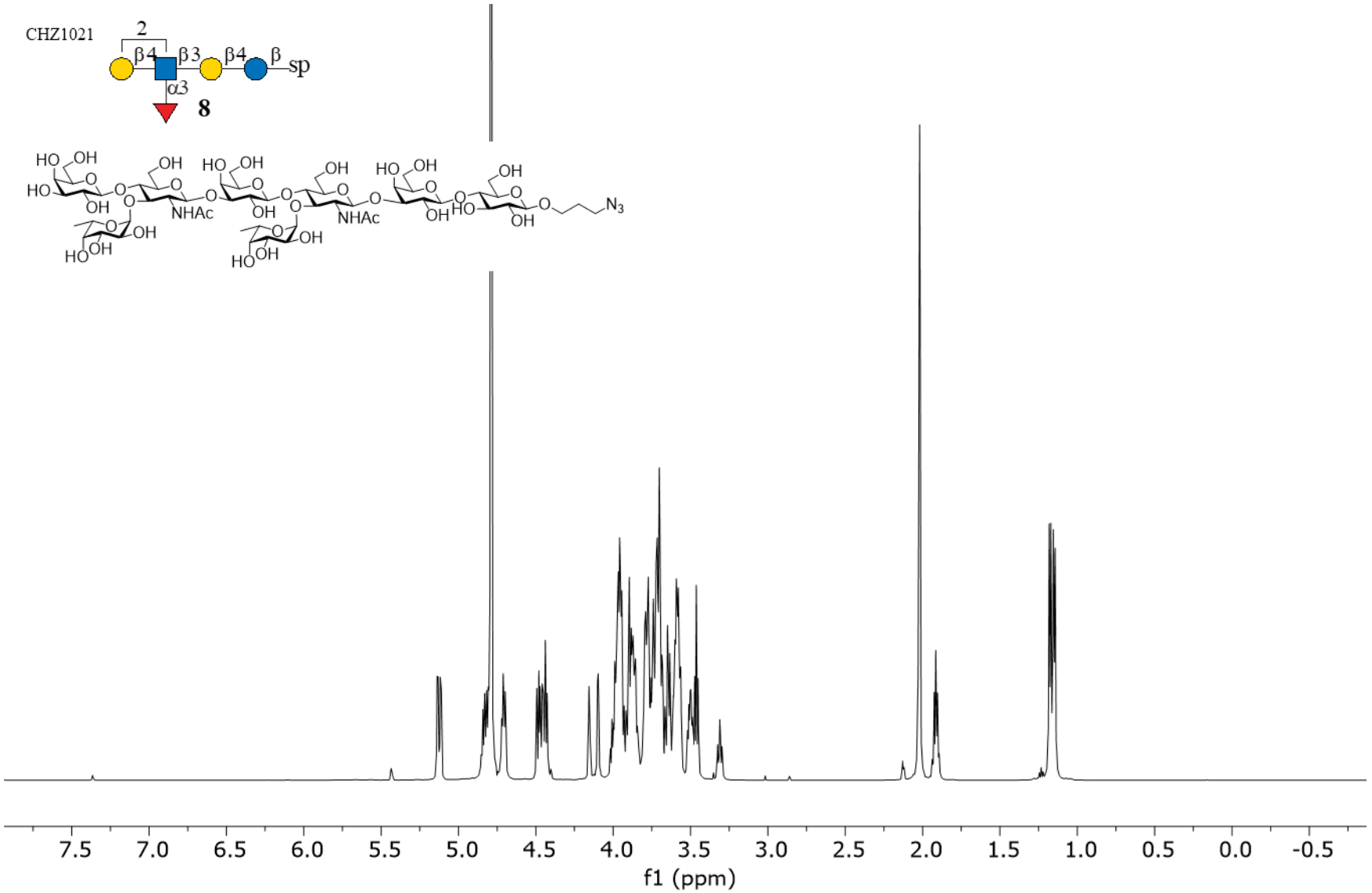
^{13}C NMR of 6


Lc10
4
β4 β3 β4 β sp
7
HO OH
OH
HO
O
NHAc
N3
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)

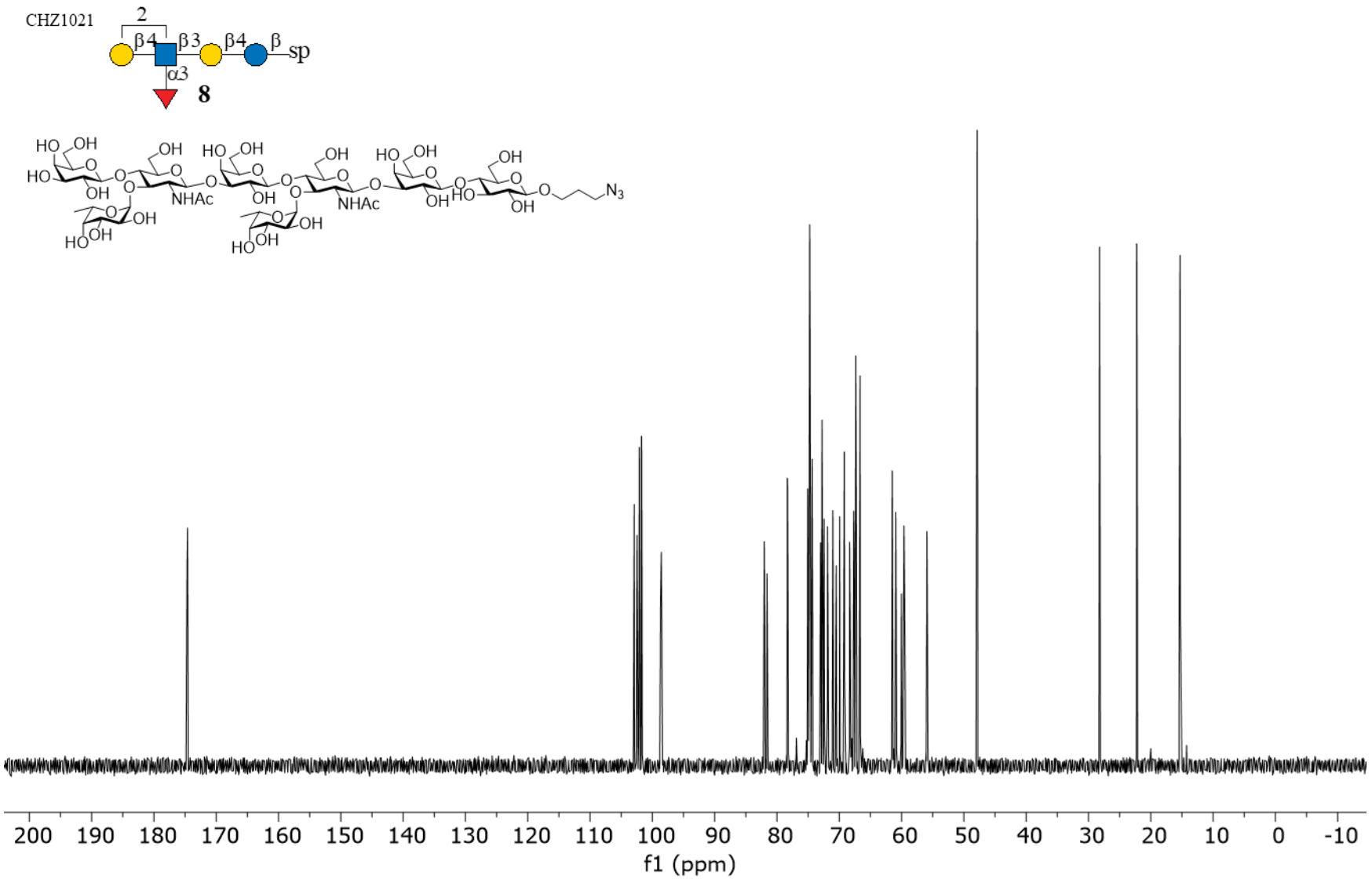
^{1}H NMR of 7


Lc10
4
β4 β3 β4 β sp
7
HO OH
OH
HO
O
NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

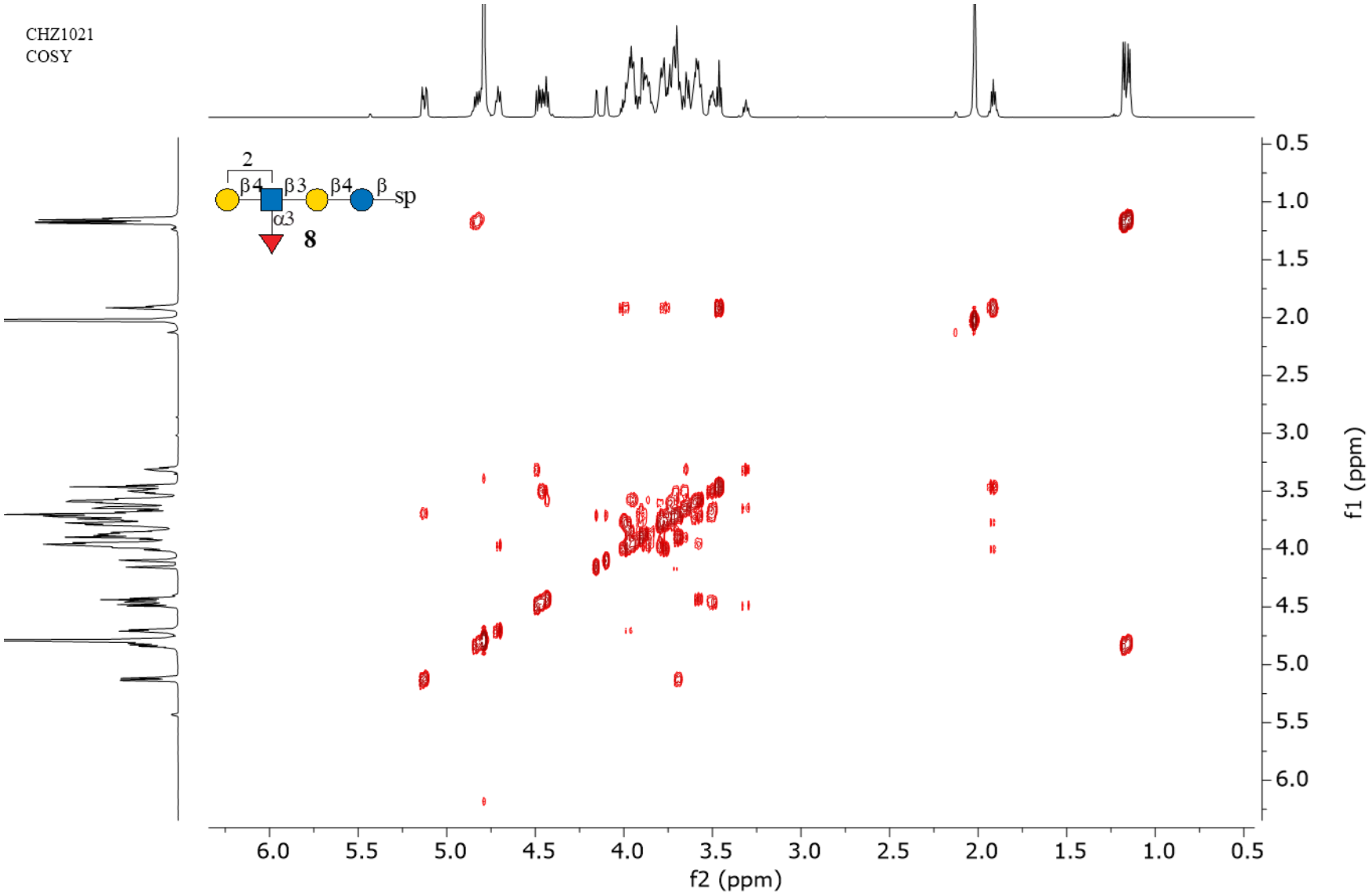
^{13}C NMR of 7


CHZ1021
2
β4
β3
β4
β
sp
α3
8
HO
OH
O
NHAc
N3
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)

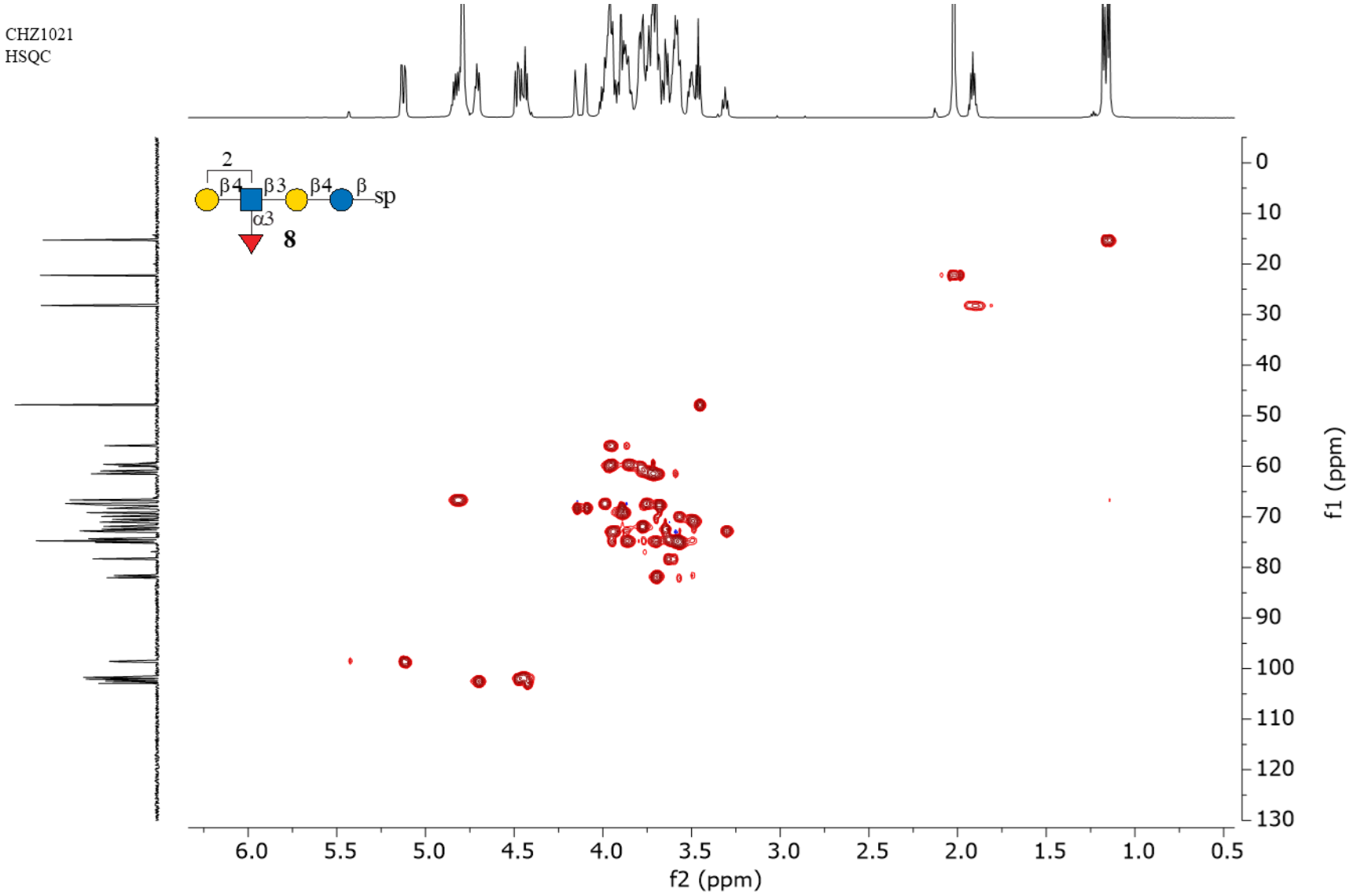
^{1}H NMR of 8


CHZ1021
2
β4
β3
β4
β
sp
α3
8
HO
OH
O
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

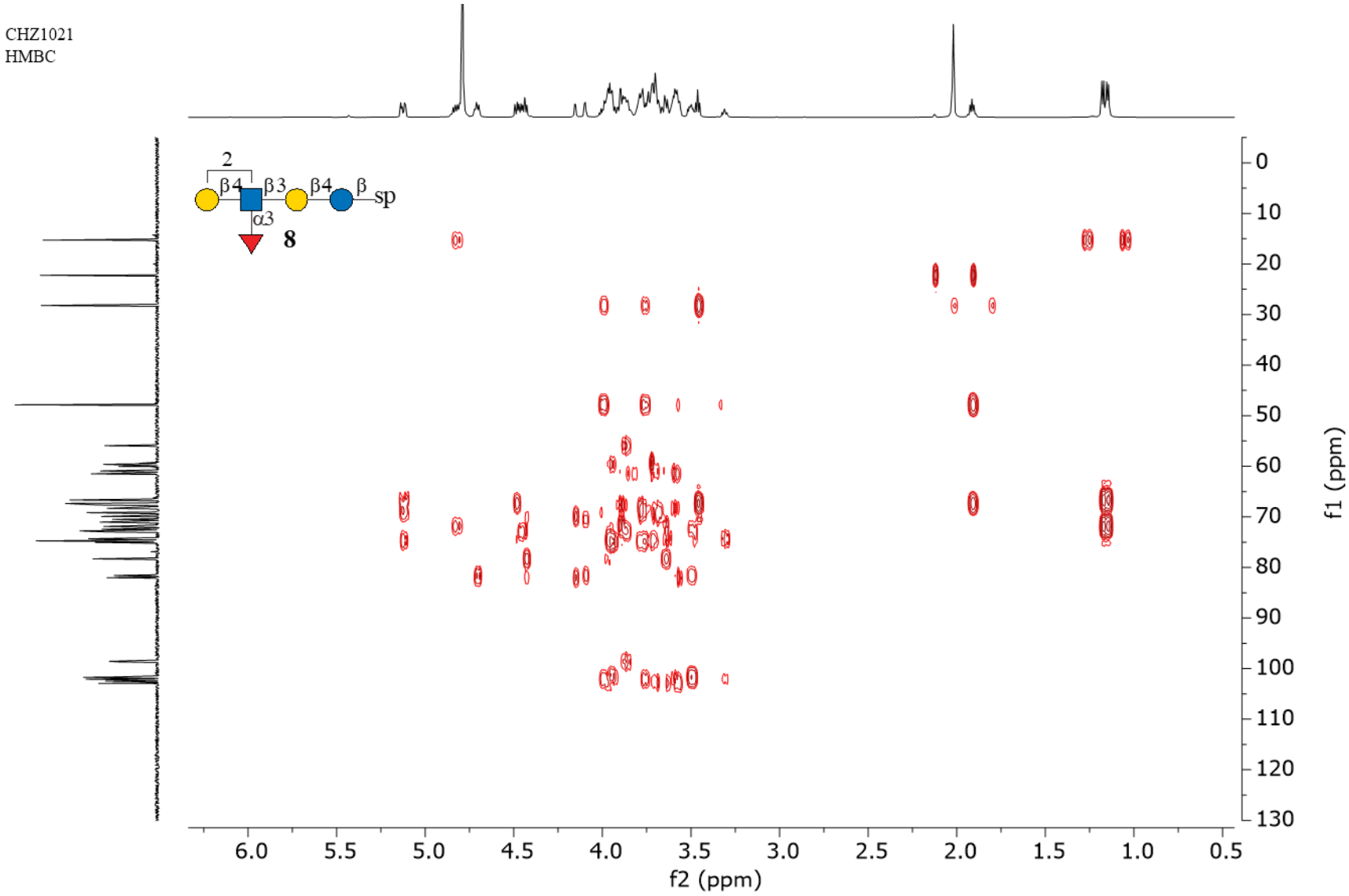
^{13}C NMR of 8



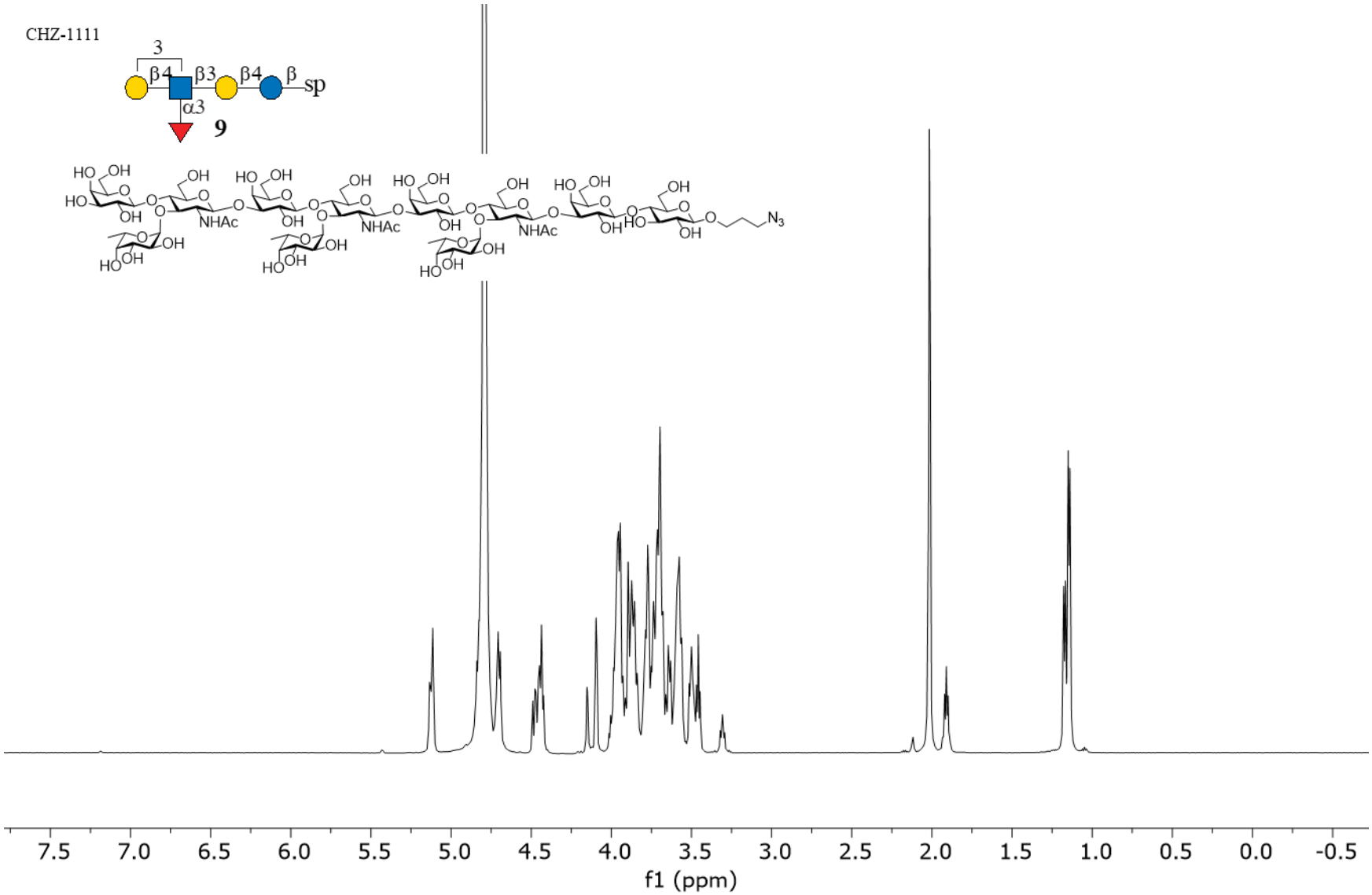
COSY NMR of 8



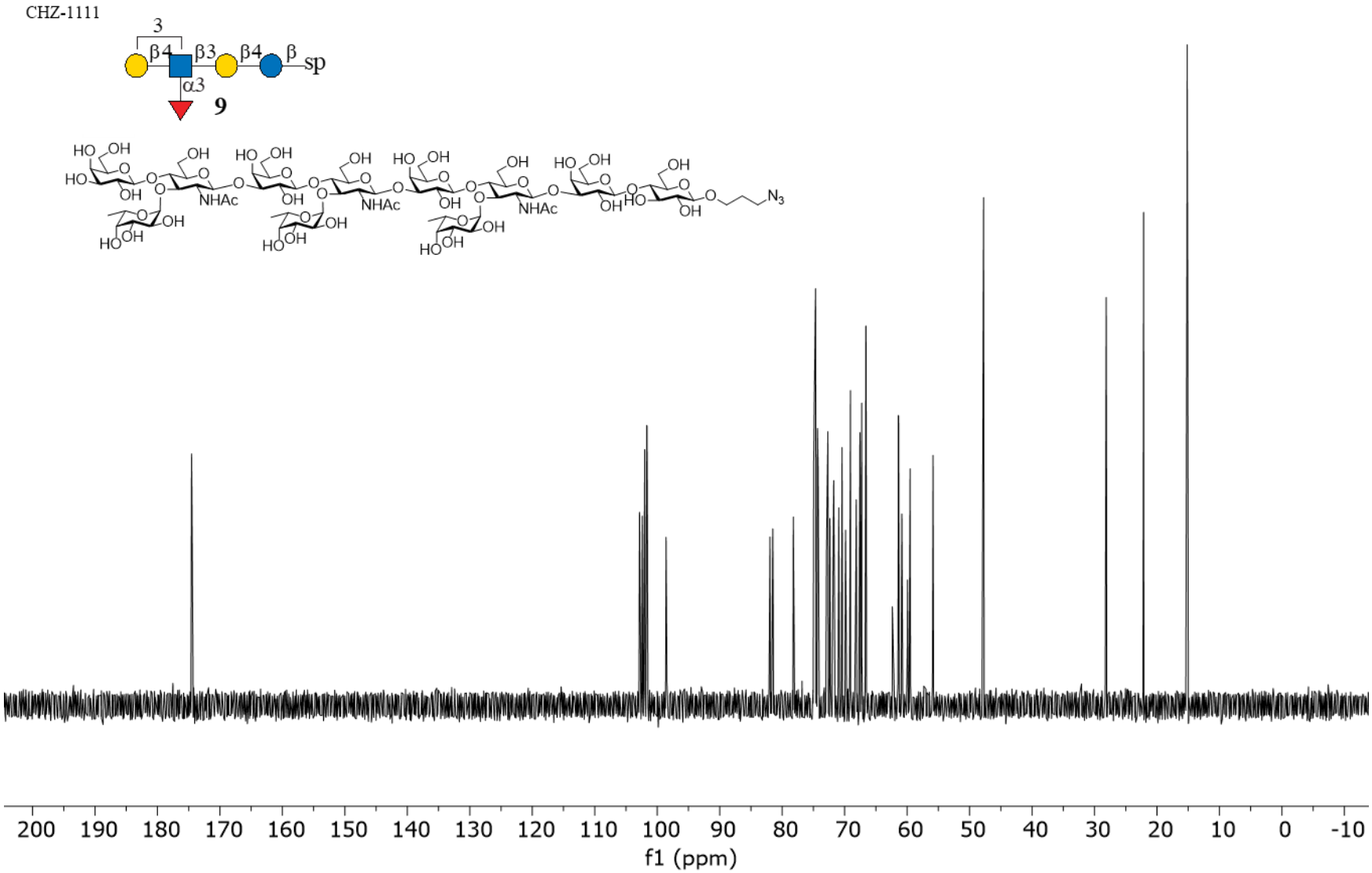
HSQC NMR of 8



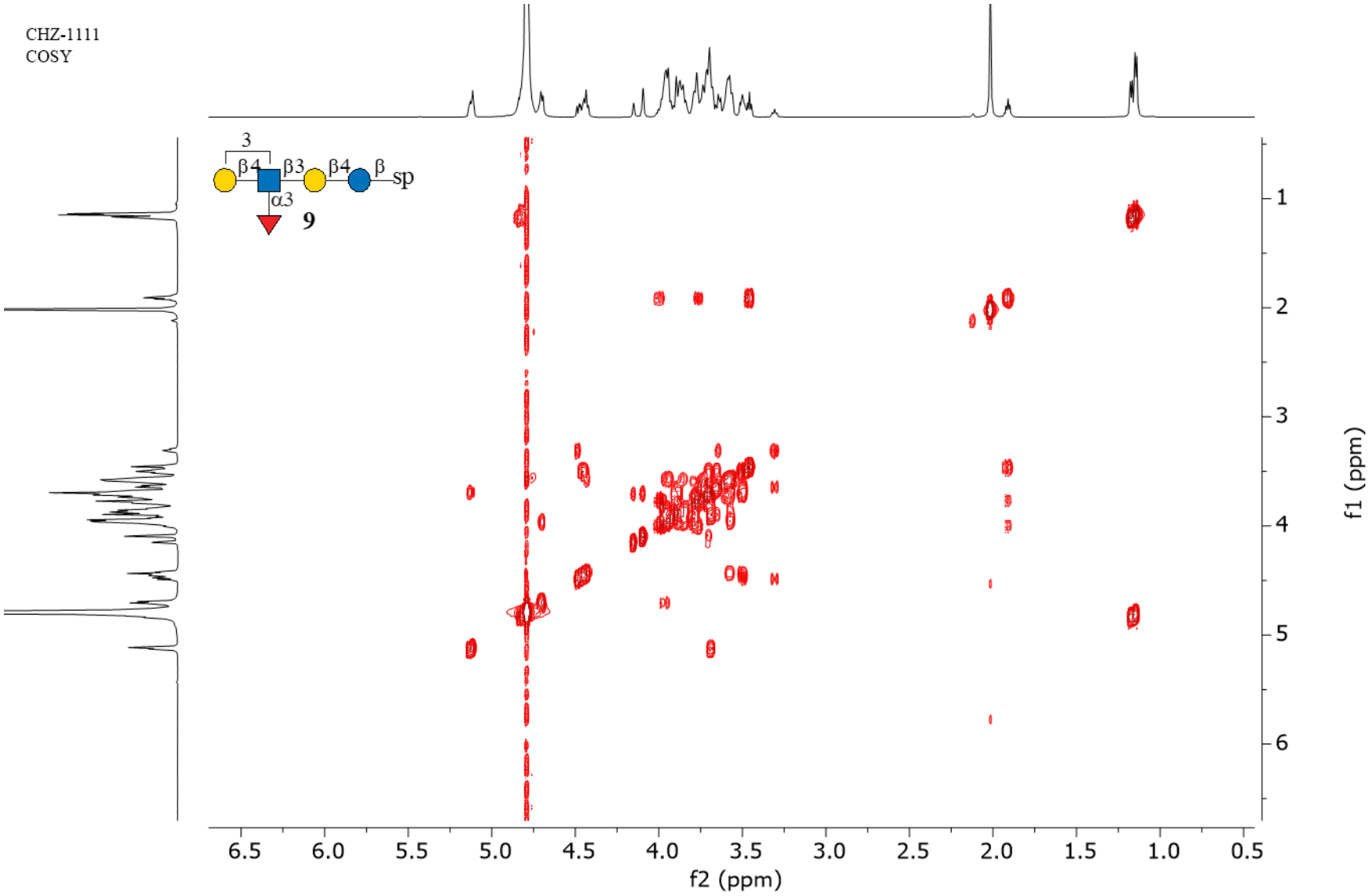
HMBC NMR of 8


CHZ-1111
3
β4
β3
β4
β
sp
α3
9
HO
OH
NHAc
N3
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)

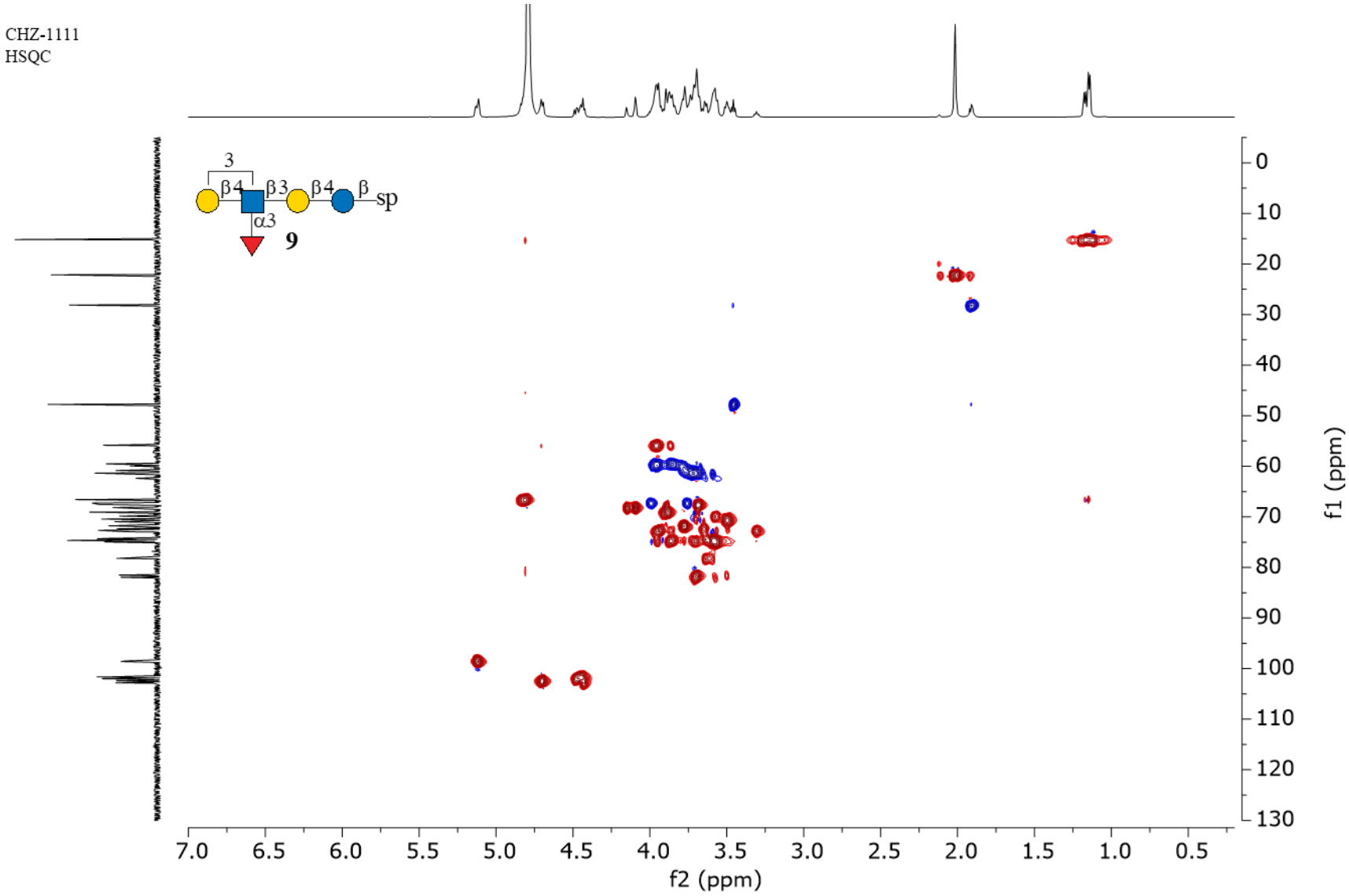
^{1}H NMR of 9


CHZ-1111
3
β4
β3
β4
β
sp
α3
9
HO
OH
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

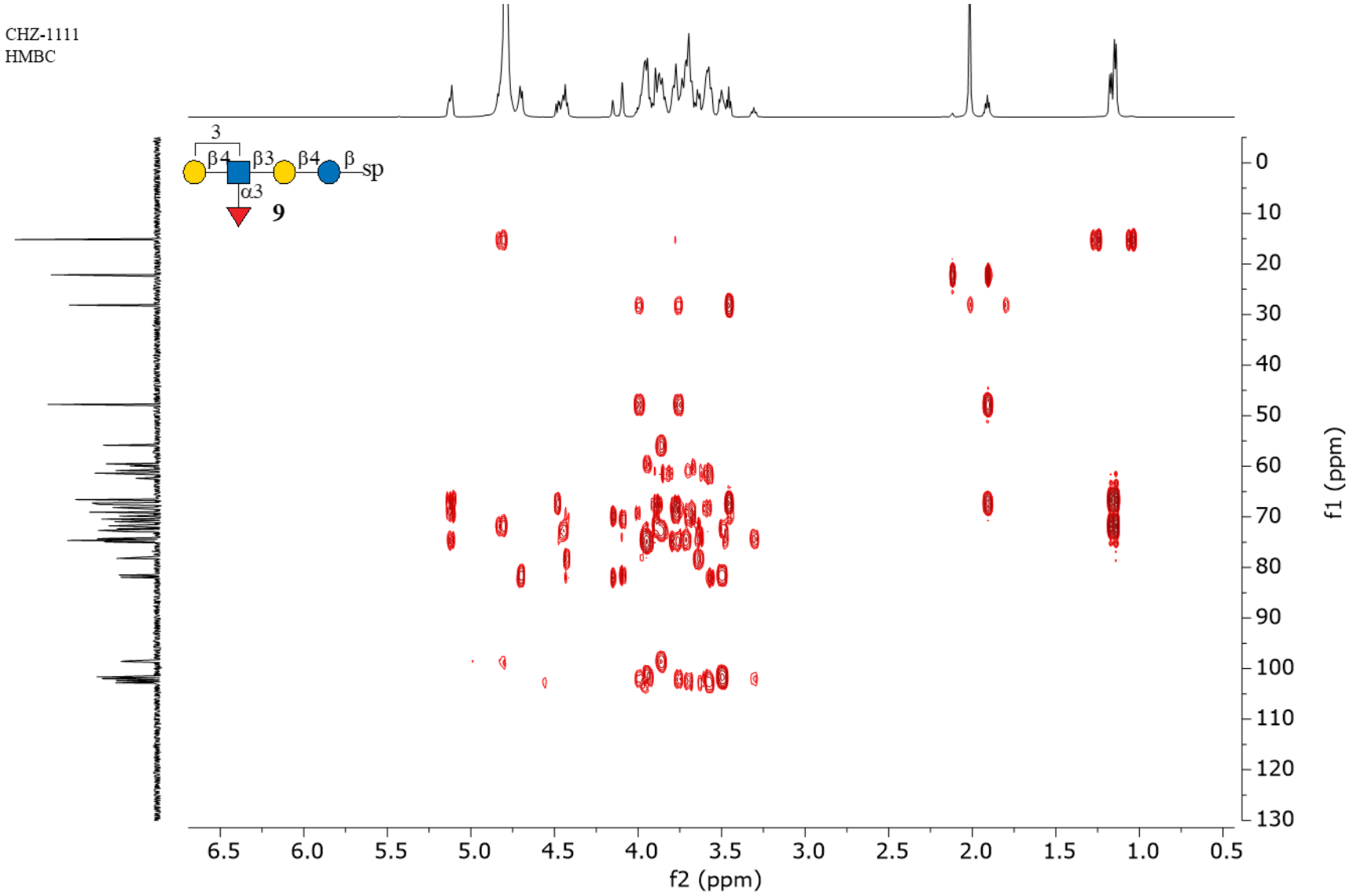
^{13}C NMR of 9


CHZ-1111
COSY
3
β4
β3
β4
β
sp
α3
9
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
f1 (ppm)

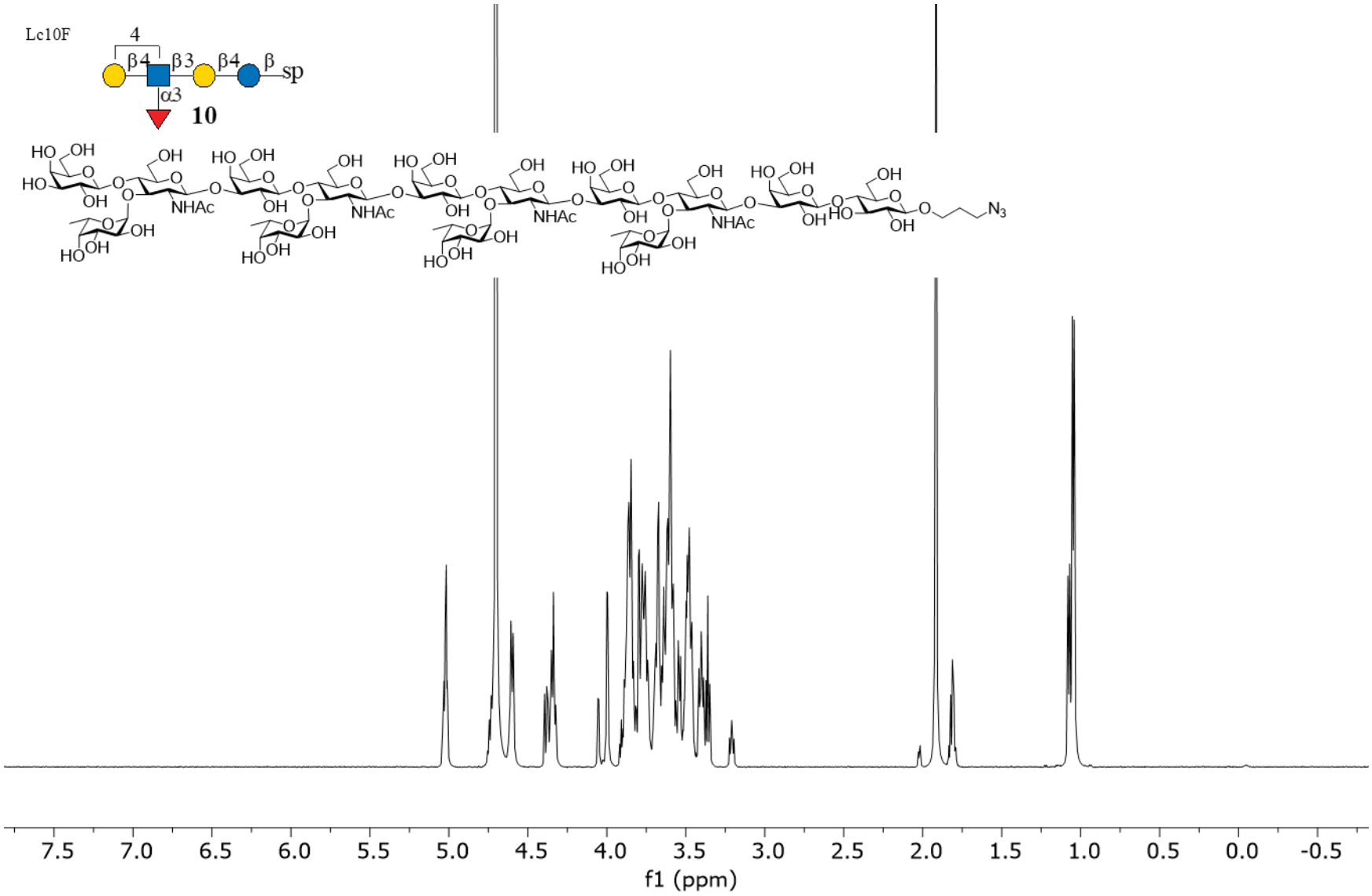
COSY NMR of 9



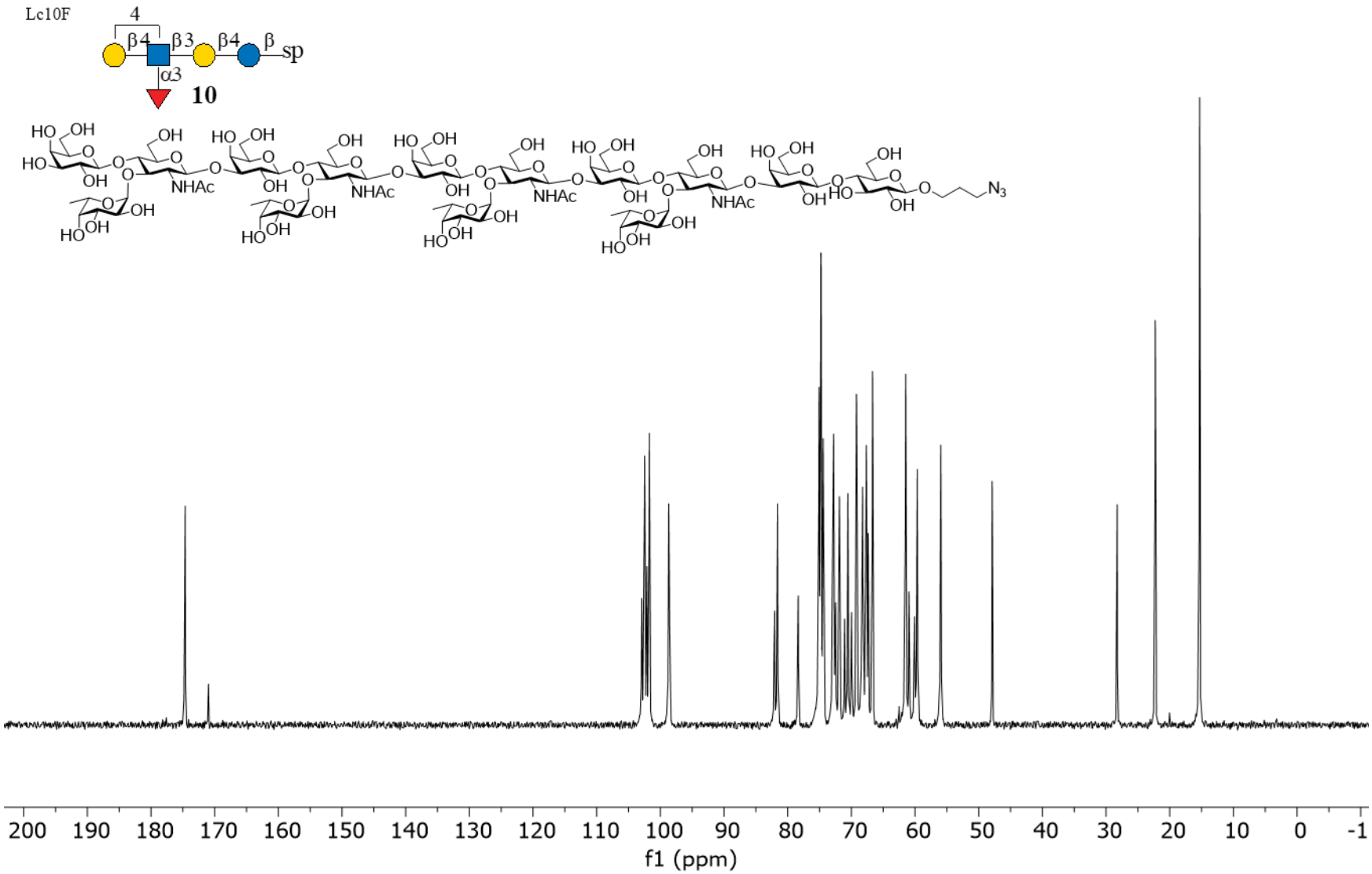
HSQC NMR of 9



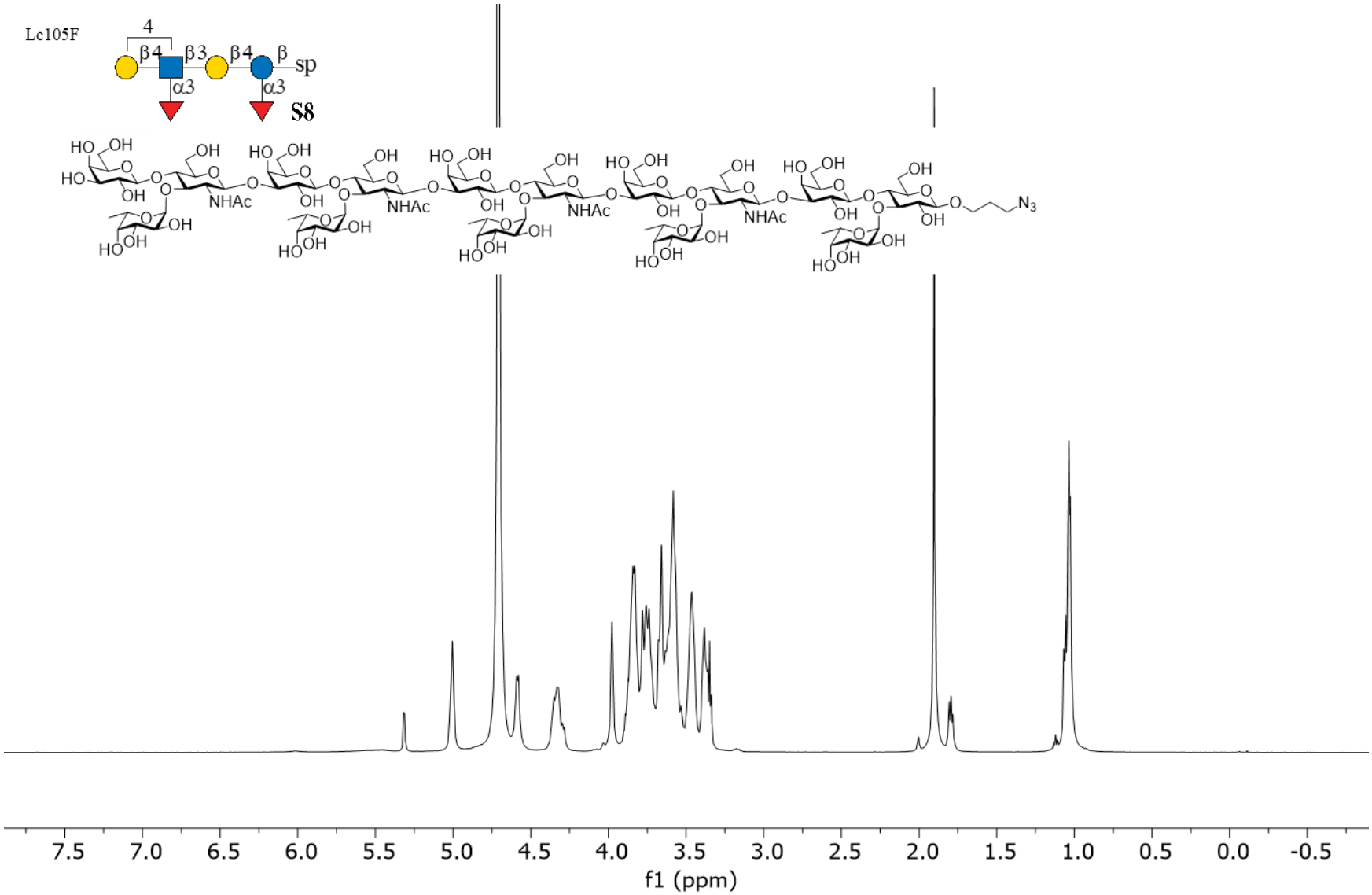
HMBC NMR of 9


Lc10F
4
β4
β3
β4
β
sp
α3
10
NHAc
N3
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)

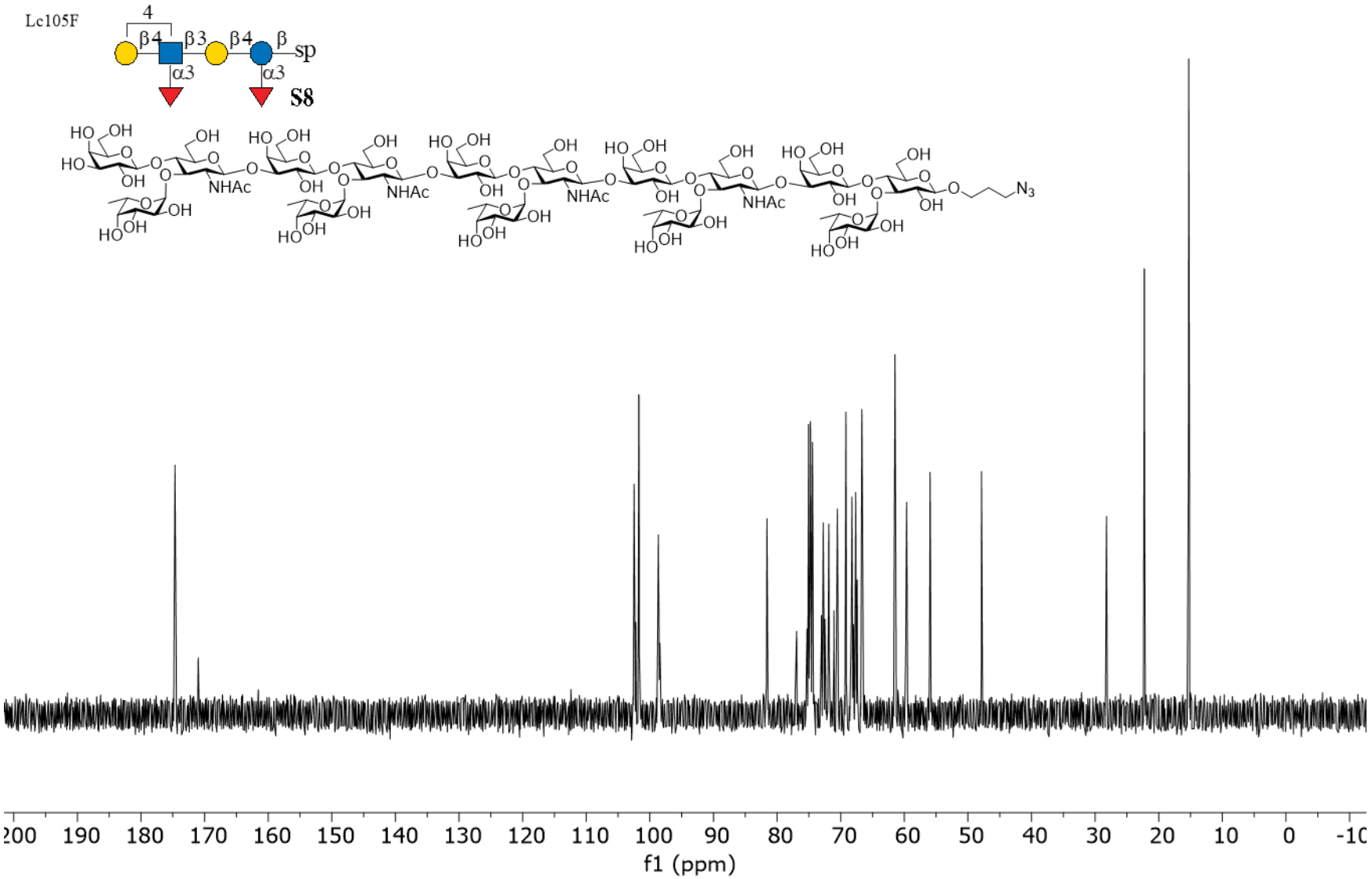
^{1}H NMR of 10


Lc10F
4
β4
β3
β4
β
sp
α3
10
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

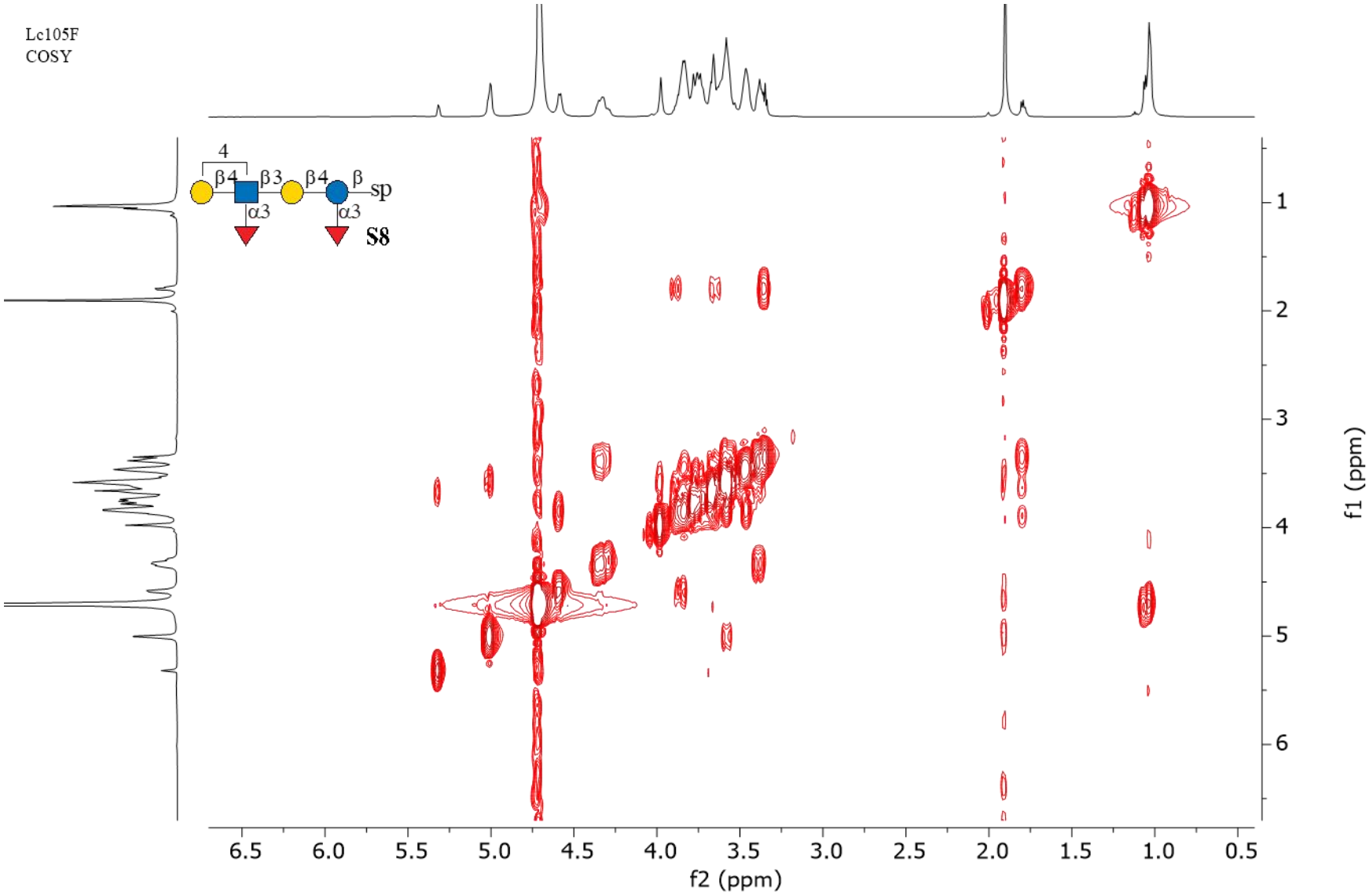
^{13}C NMR of 10


Lc105F
4
β4
β3
β4
β
sp
α3
α3
S8
NHAc
N3
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)

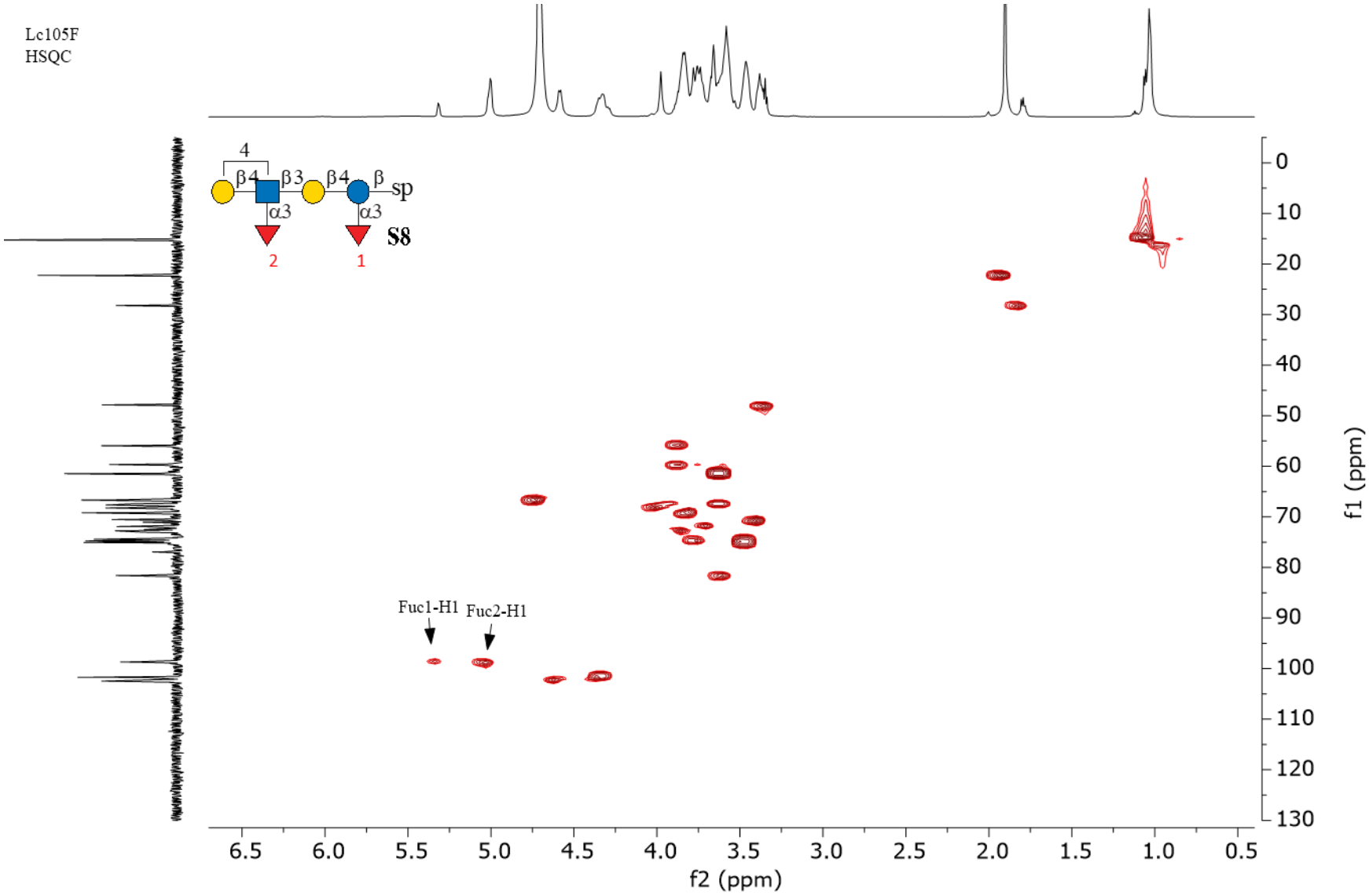
^{1}H NMR of S8


Lc105F
4
β4
β3
β4
β
sp
α3
α3
S8
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

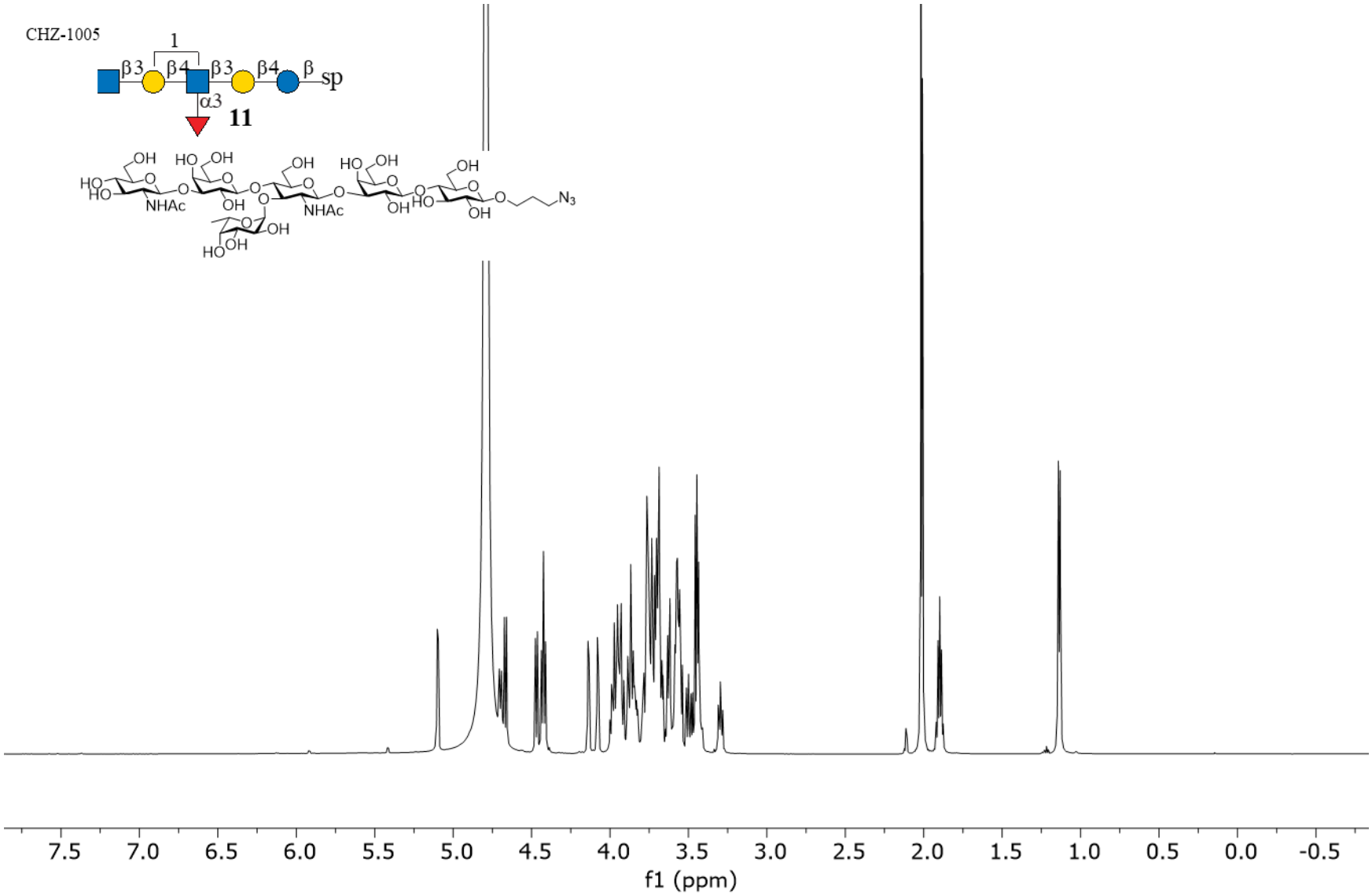
^{13}C NMR of S8



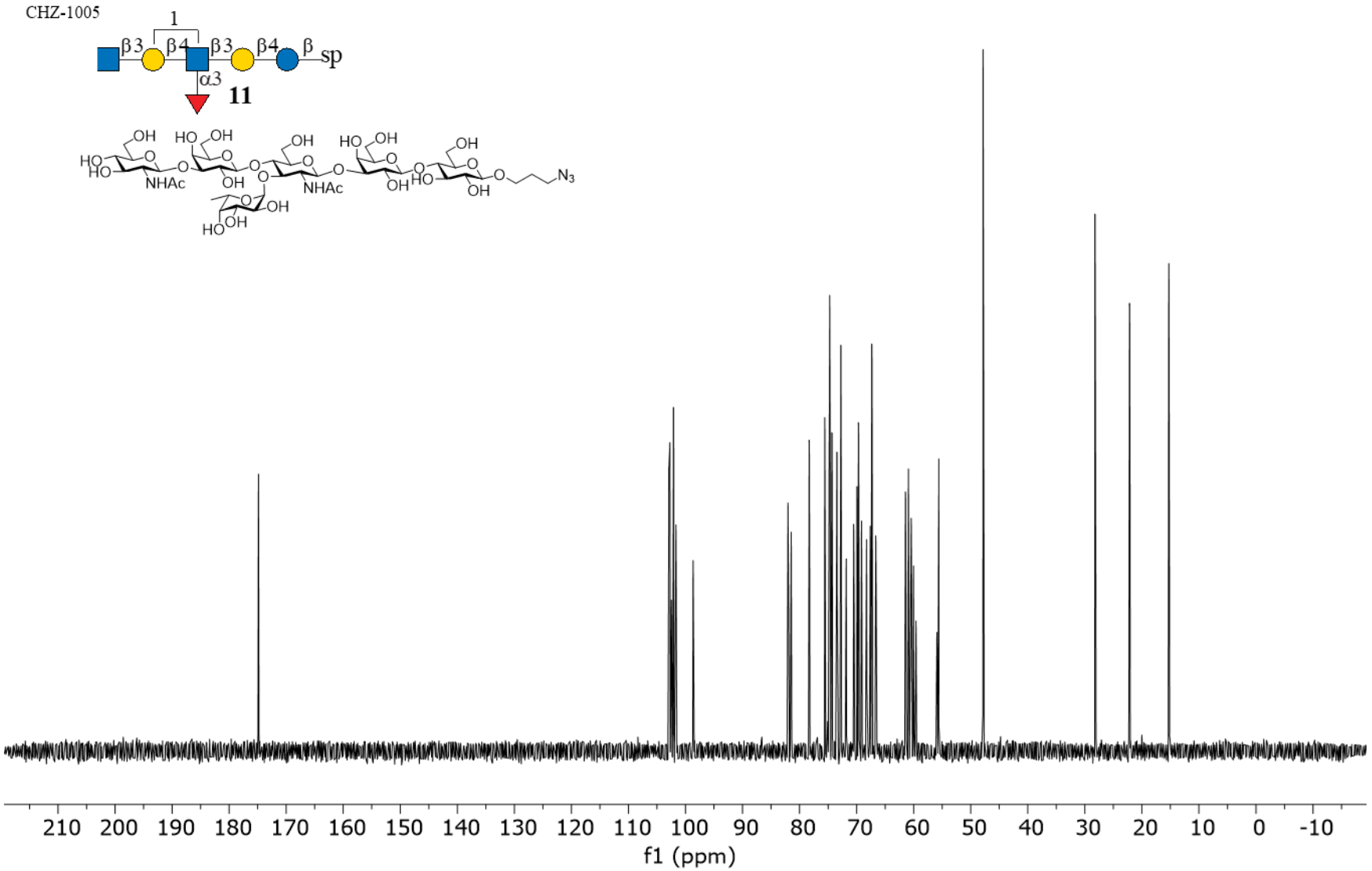
COSY NMR of S8



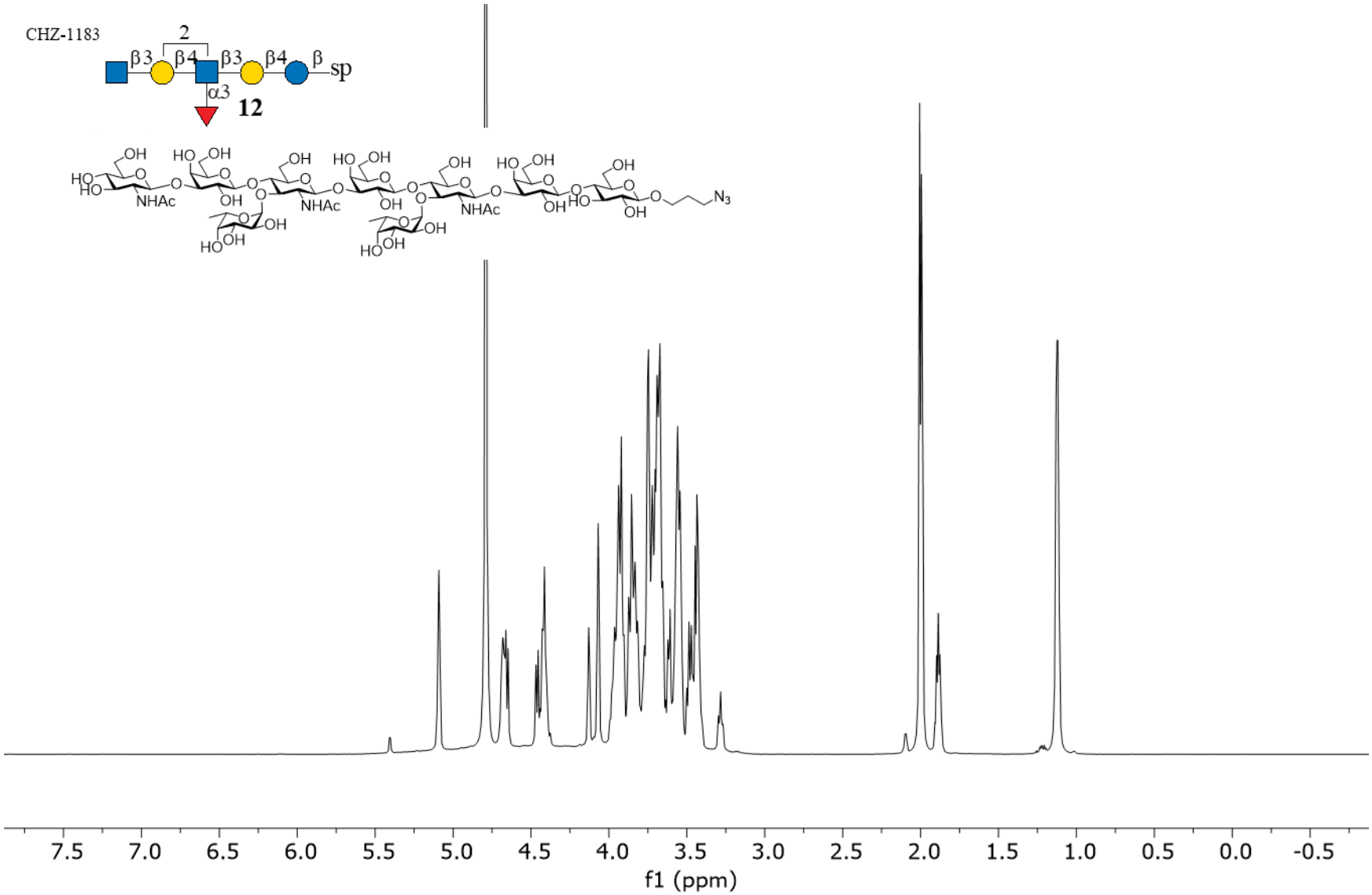
HSQC NMR of S8


CHZ-1005
1
β3
β4
β3
β4
β
sp
α3
11
OH
HO
NHAc
N3
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)

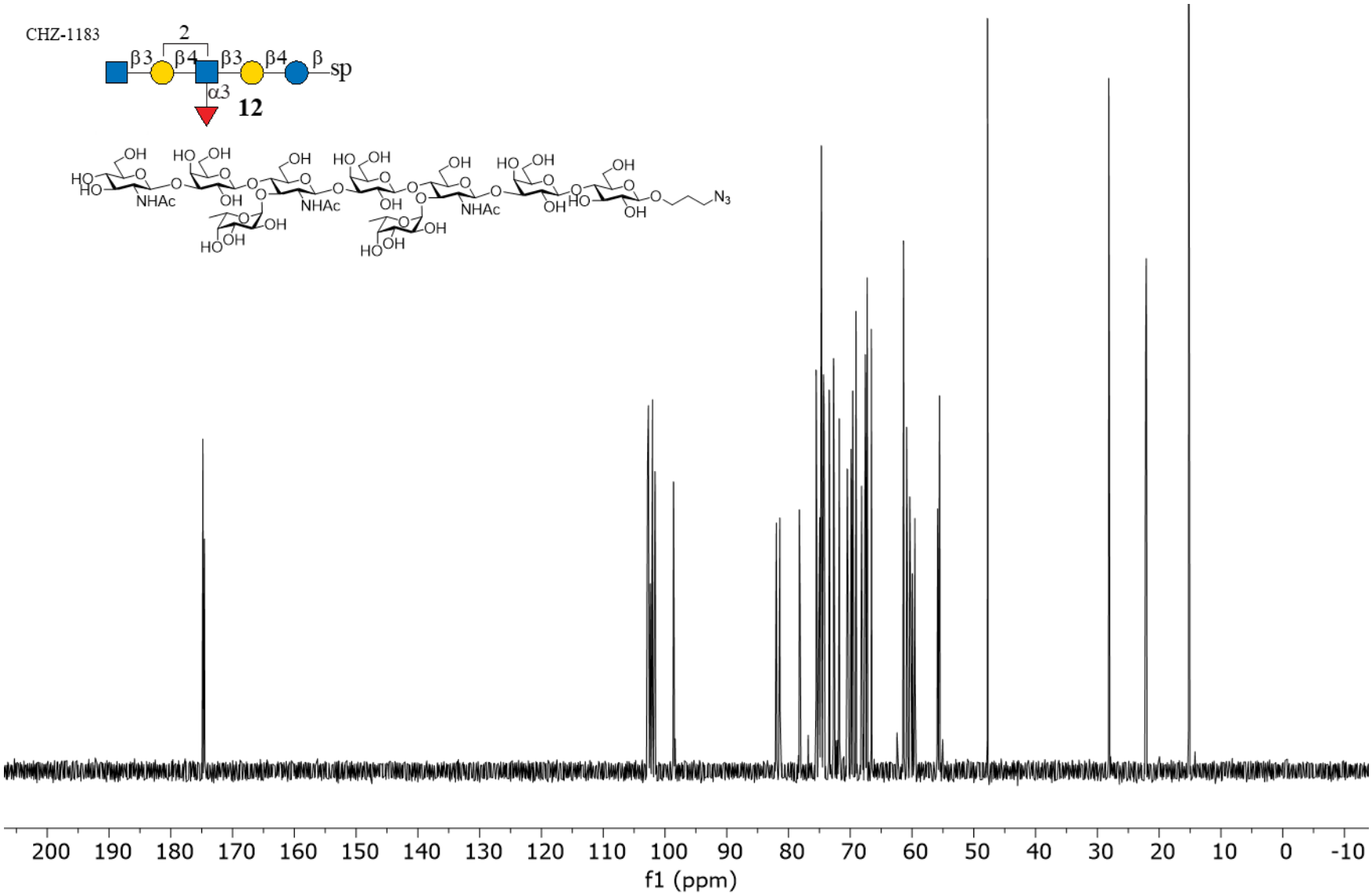
^{1}H NMR of 11


CHZ-1005
1
β3
β4
β3
β4
β
sp
α3
11
OH
HO
NHAc
N3
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)

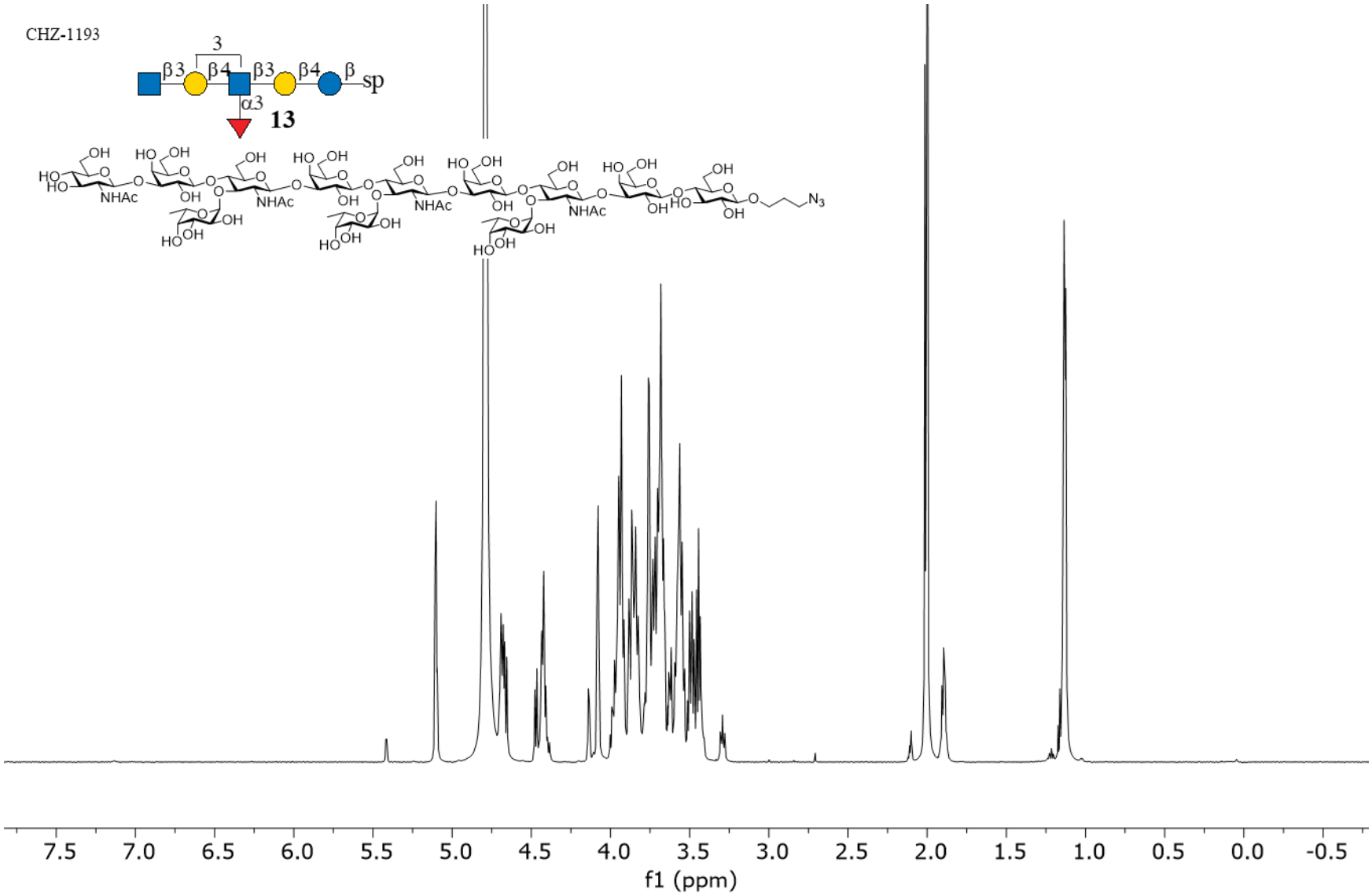
^{13}C NMR of 11


CHZ-1183
2
β3
β4
β3
β4
β
sp
α3
12
NHAc
NHAc
NHAc
N3
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)

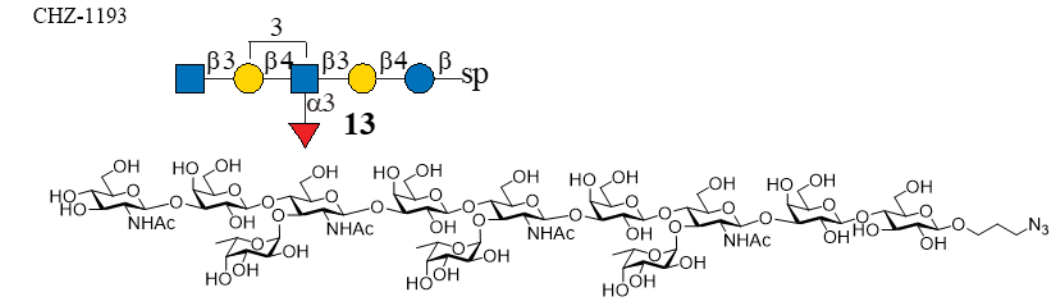
^{1}H NMR of 12

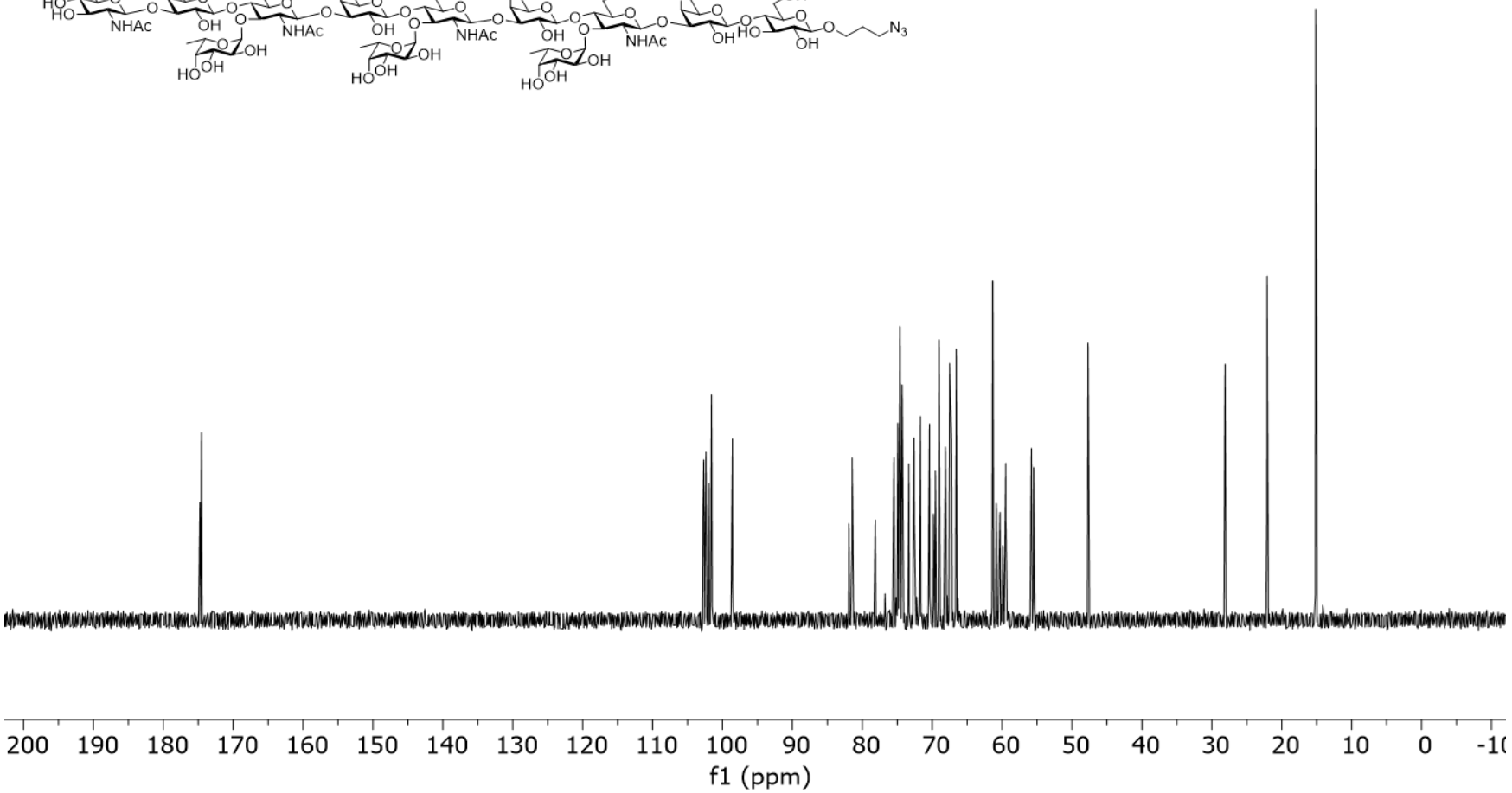

CHZ-1183
2
β3
β4
β3
β4
β
sp
α3
12
NHAc
NHAc
NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{13}C NMR of 12

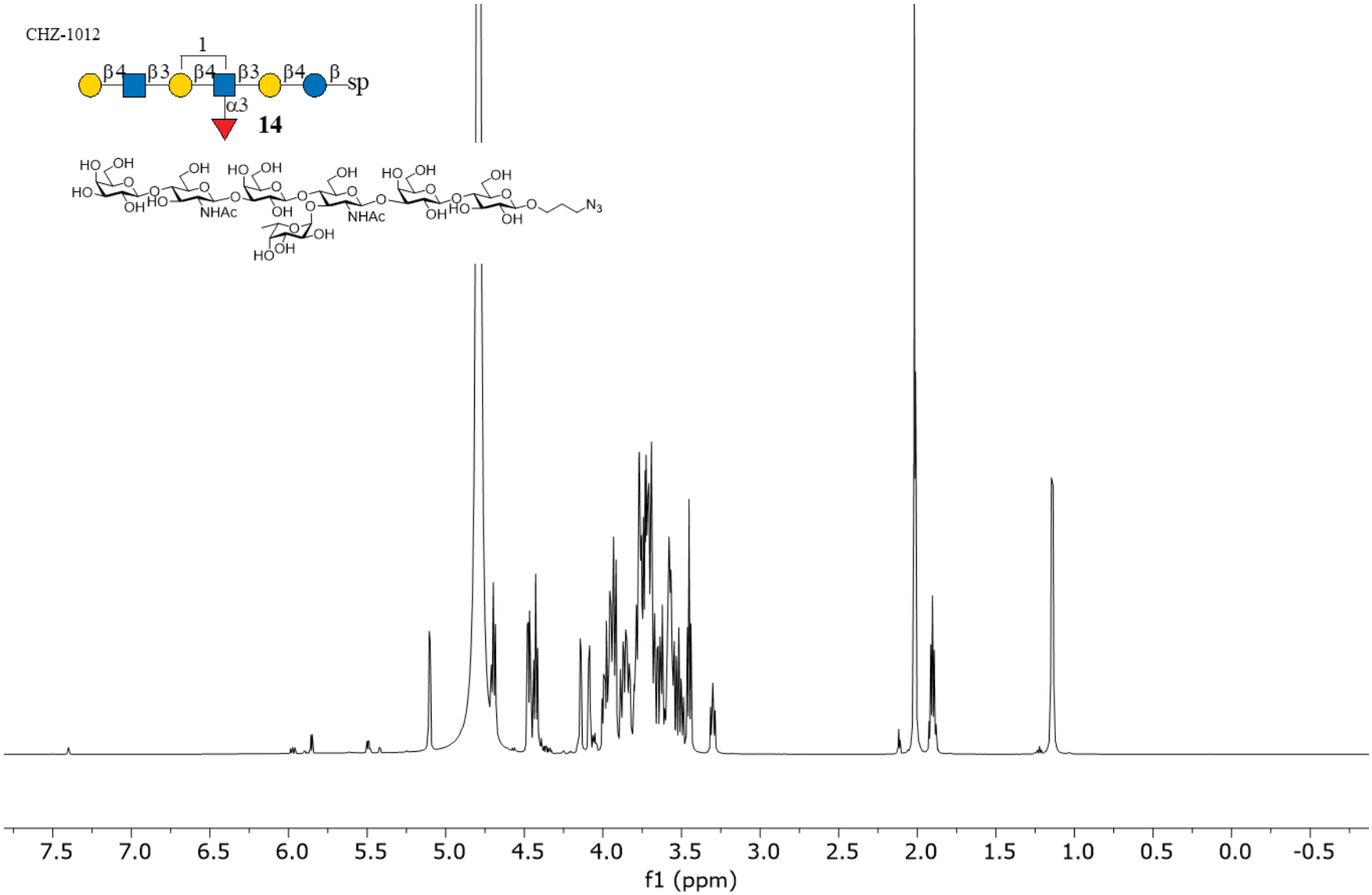

CHZ-1193
3
β3 β4 β3 β4 β sp
α3
13
NHAc
N3
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{1}H NMR of 13

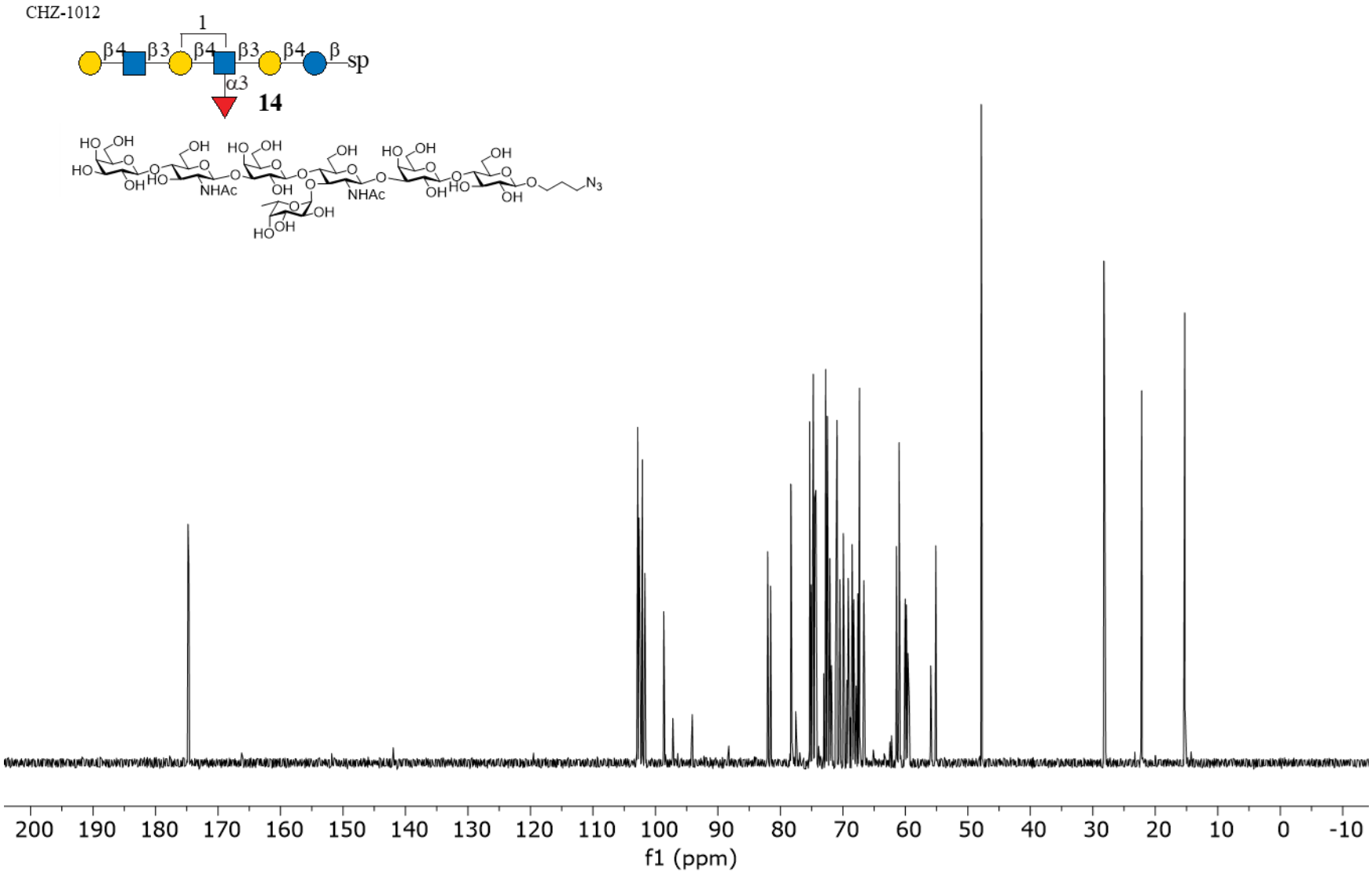

CHZ-1193
3
β3
β4
β3
β4
β
sp
α3
13
NHAc
N3


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

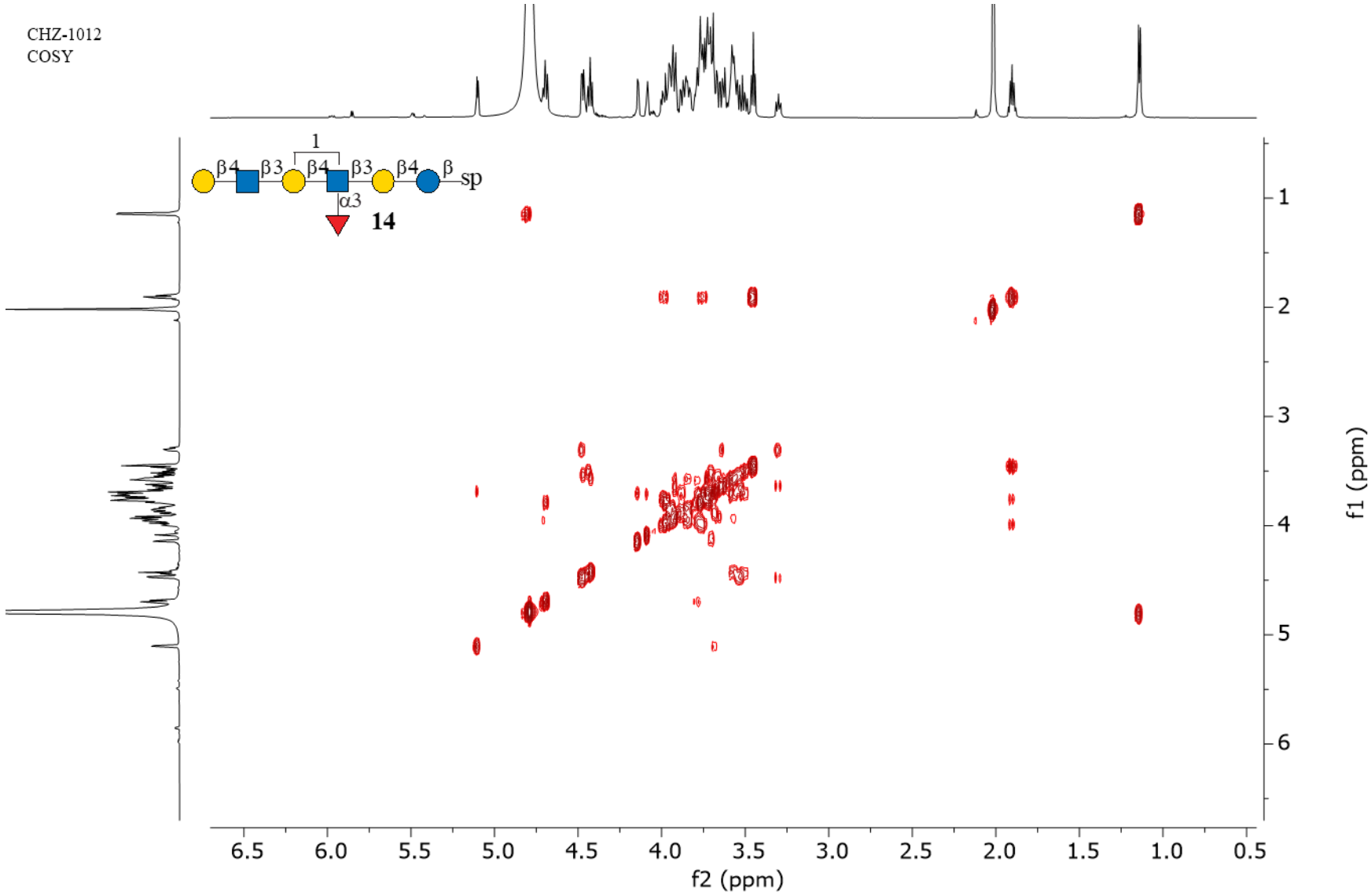
^{13}C NMR of 13


CHZ-1012
1
β4 β3 β4 β3 β4 β sp
α3
14
HO OH
HO
OH
O
NHAc
N3
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)

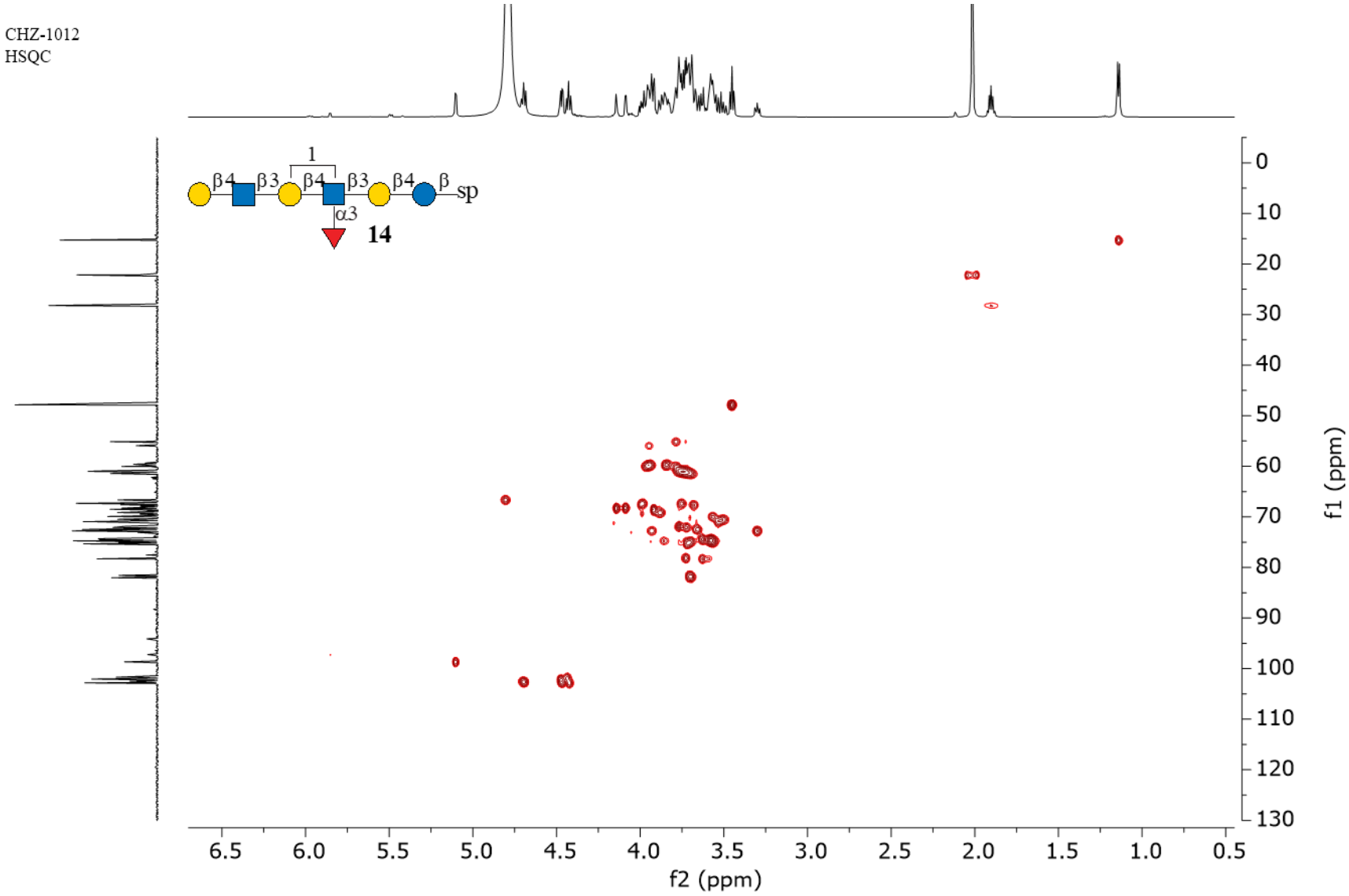
^{1}H NMR of 14


CHZ-1012
1
β4 β3 β4 β3 β4 β sp
α3
14
HO OH
HO
OH
NHAc
NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

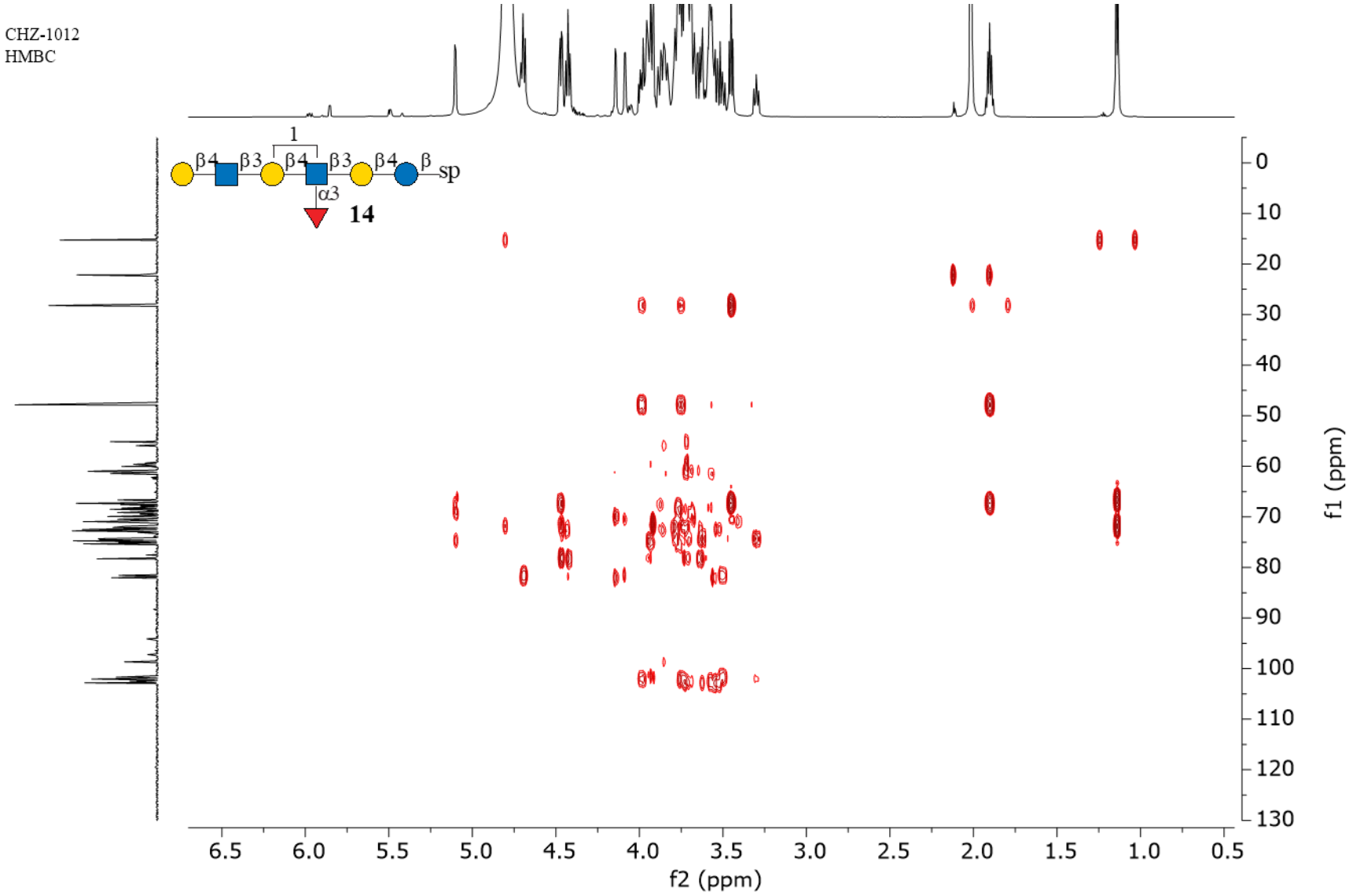
^{13}C NMR of 14



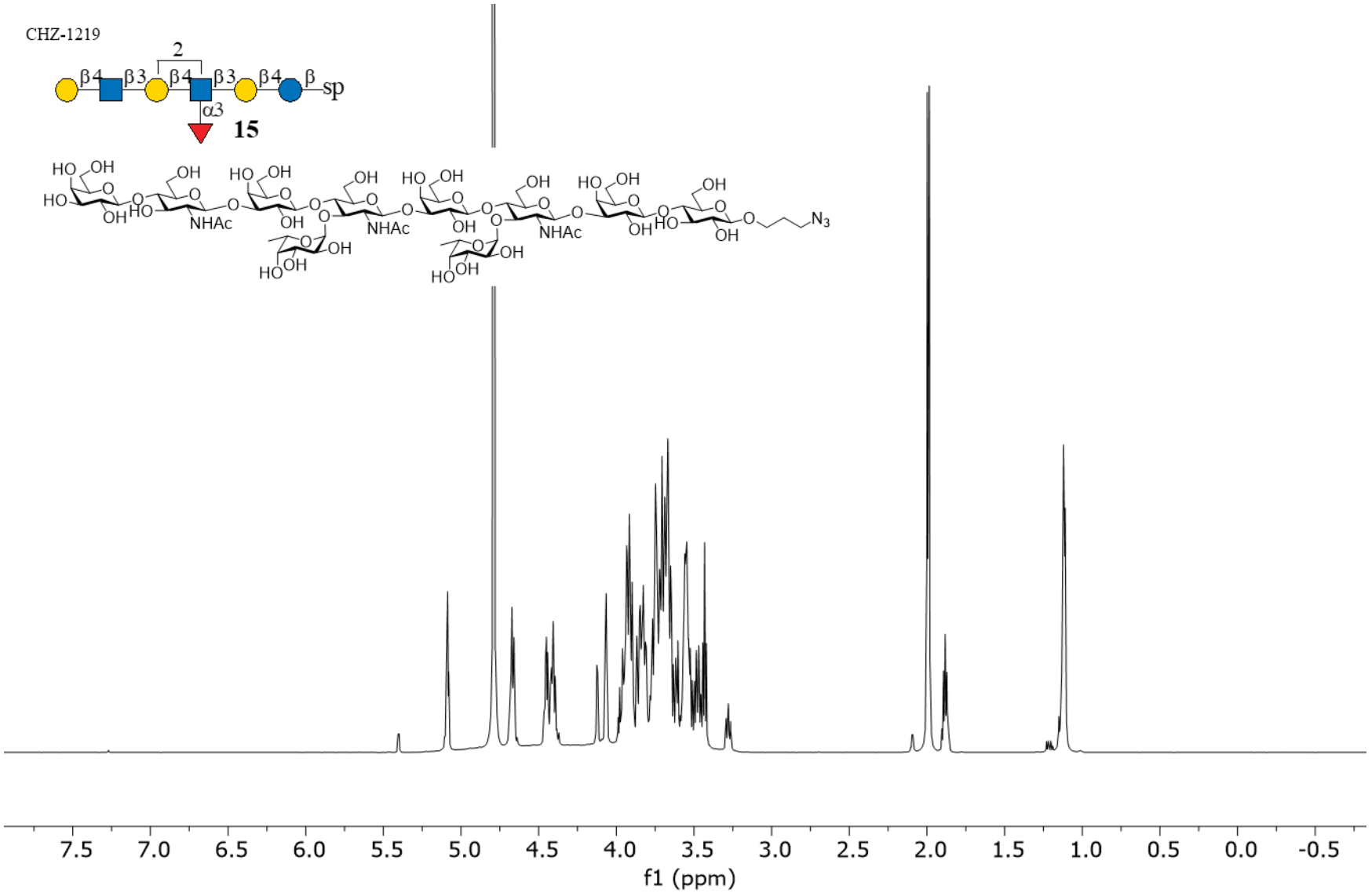
COSY NMR of 14



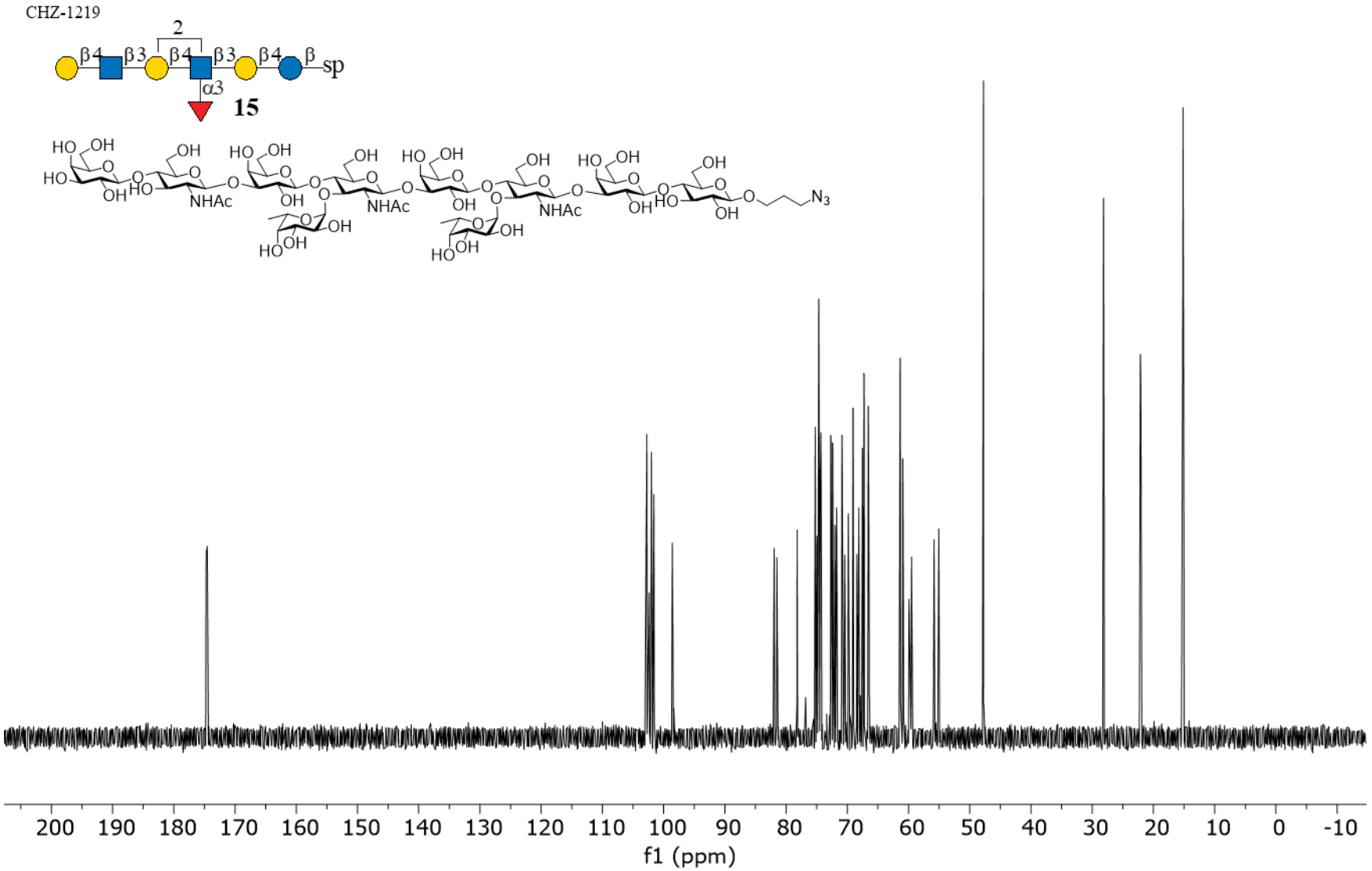
HSQC NMR of 14



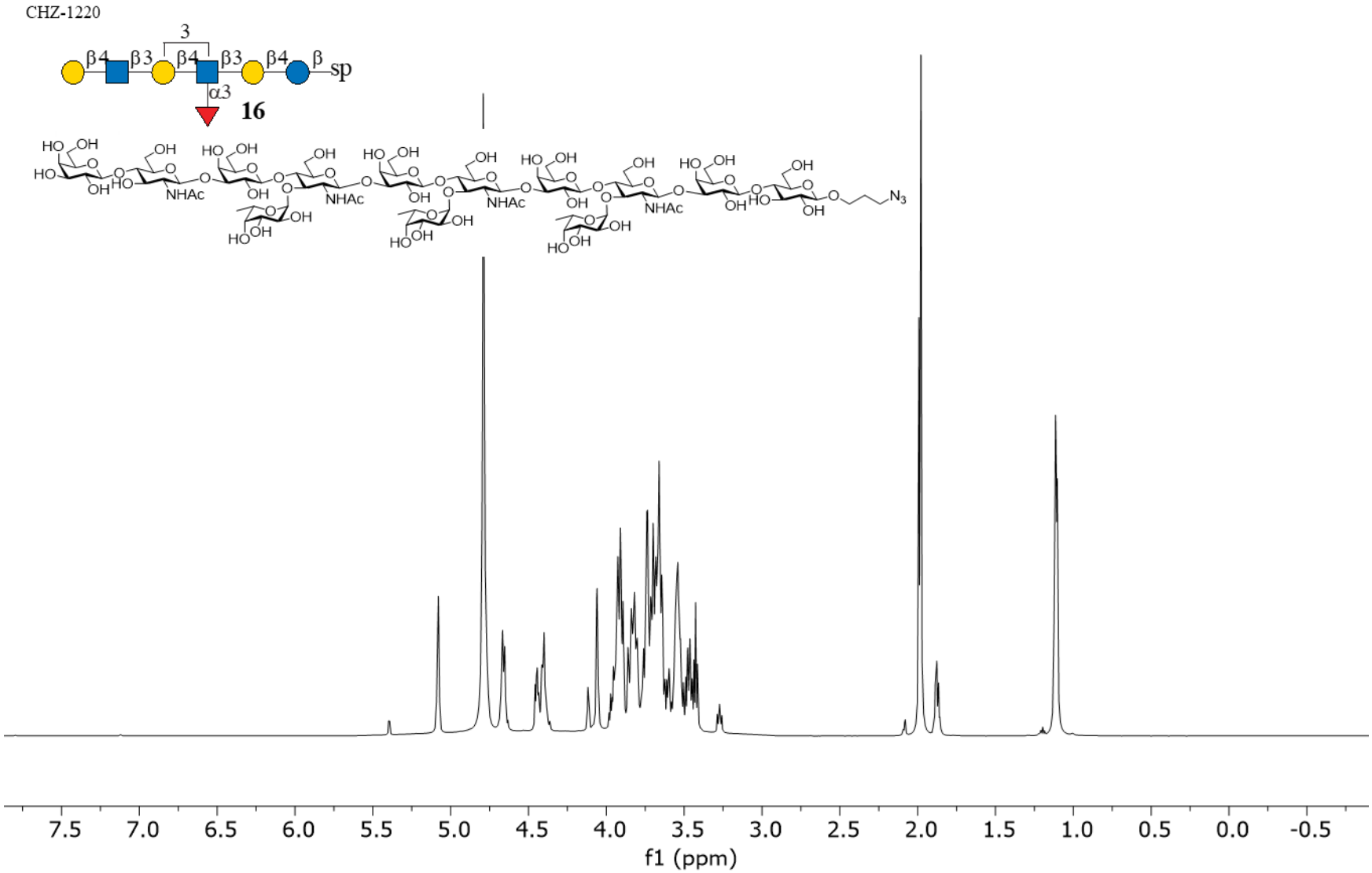
HMBC NMR of 14


CHZ-1219
2
β4 β3 β4 β3 β4 β sp
α3
15
HO OH
O
OH
HO
NHAc
N3
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)

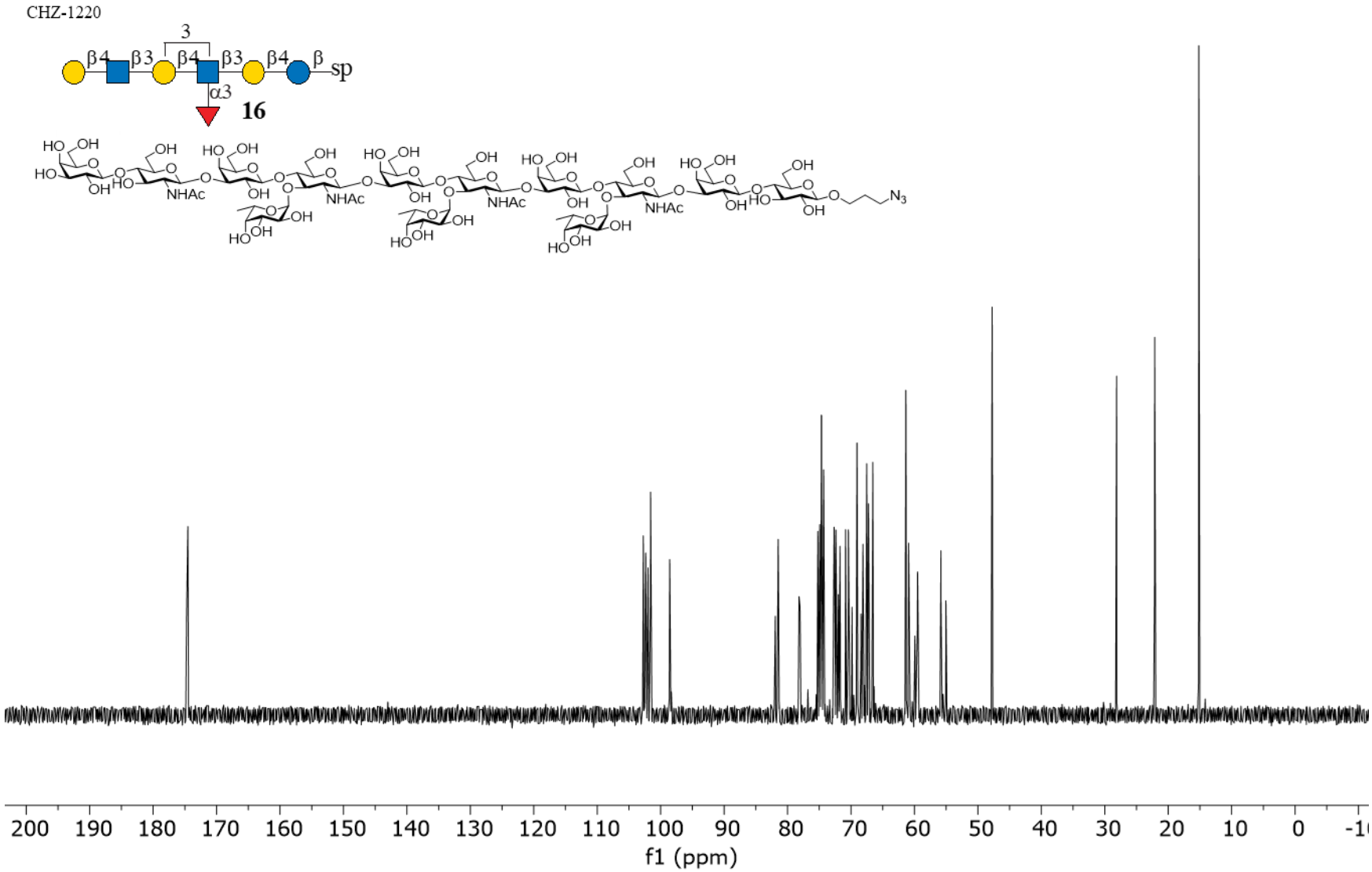
^{1}H NMR of 15


CHZ-1219
2
β4 β3 β4 β3 β4 β sp
α3
15
HO OH
O
NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

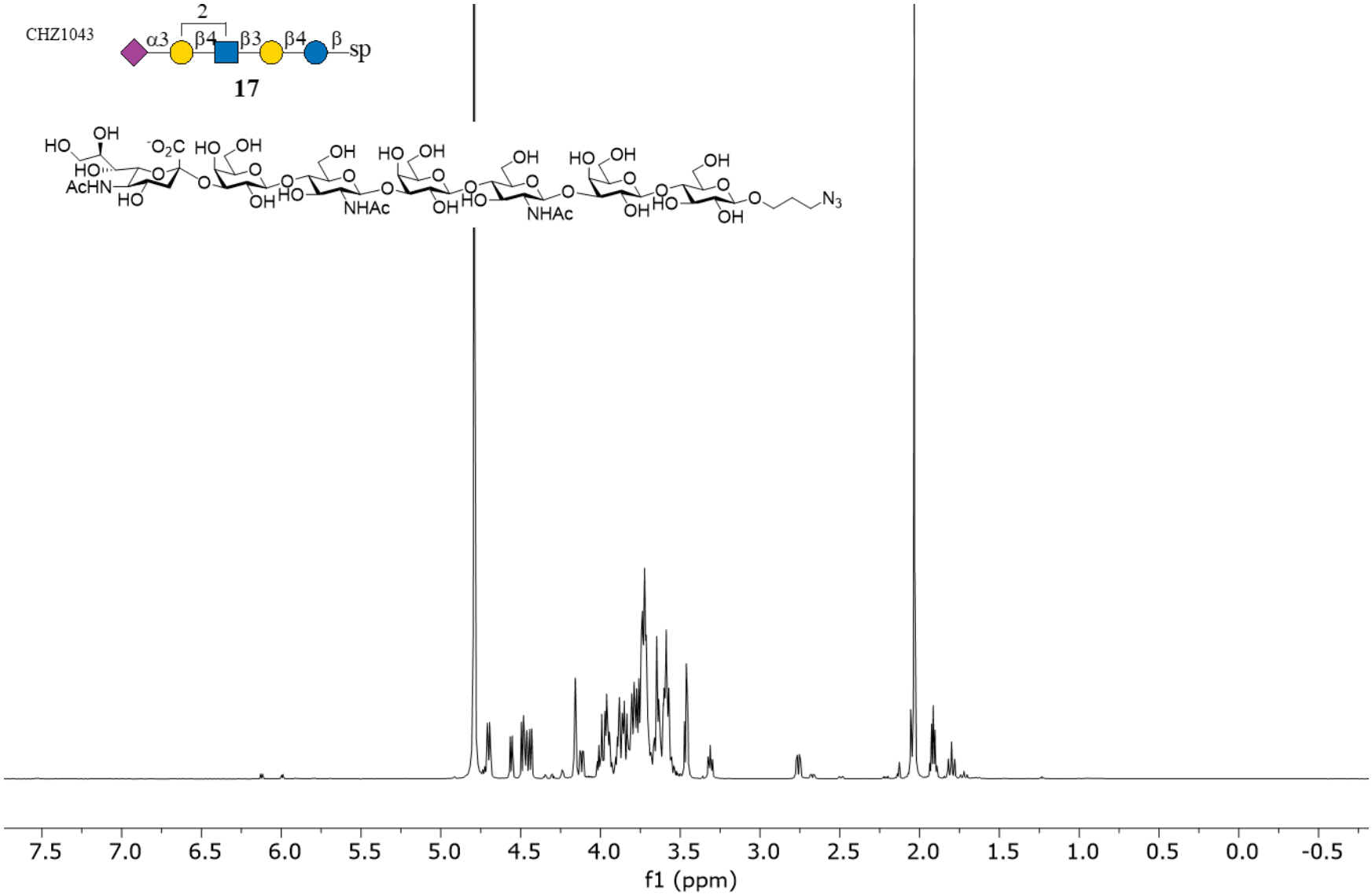
^{13}C NMR of 15


CHZ-1220
3
β4 β3 β4 β3 β4 β sp
α3
16
NHAc
N3
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)

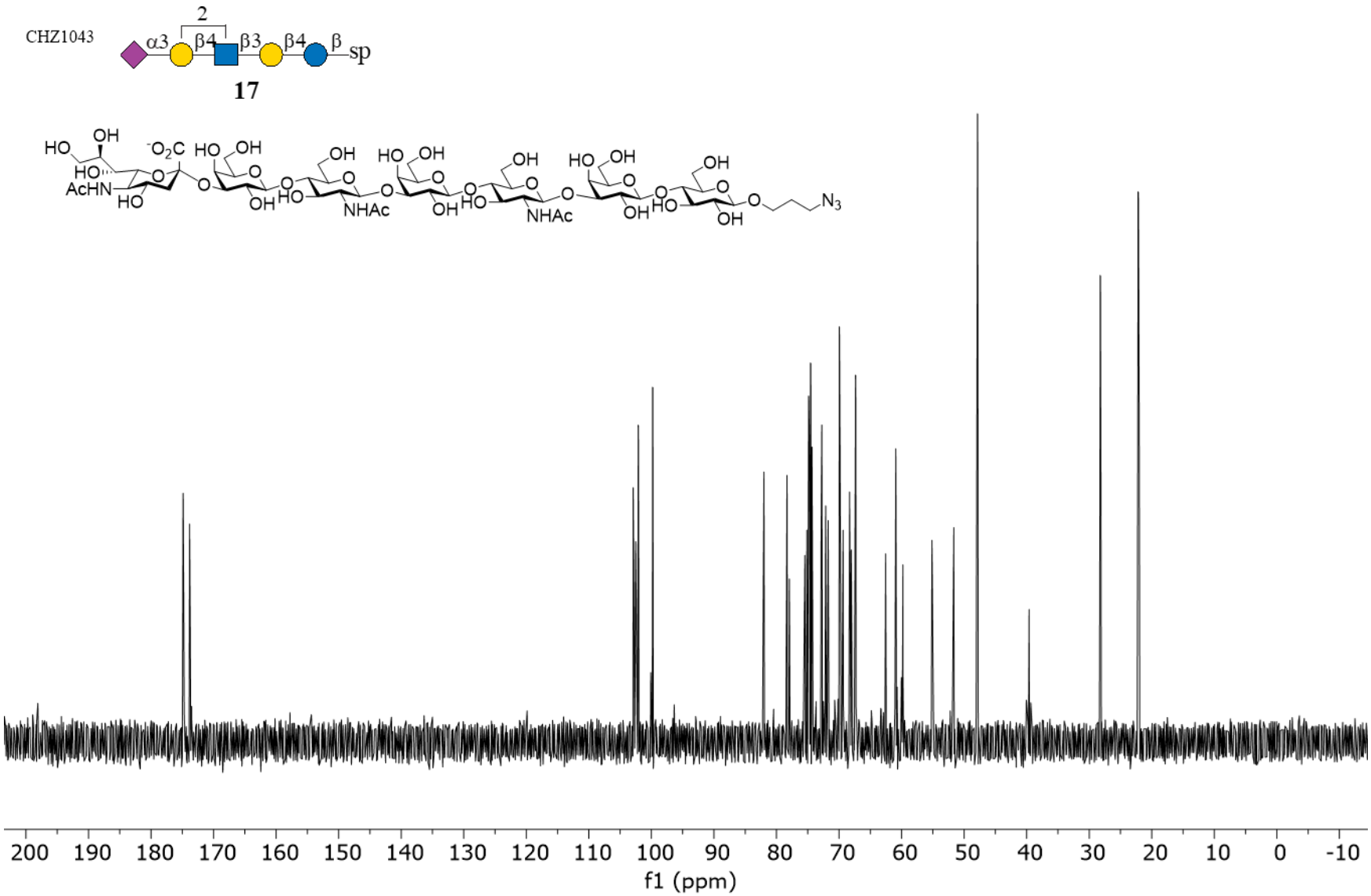
^{1}H NMR of 16


CHZ-1220
3
β4 β3 β4 β3 β4 β sp
α3
16
NHAc
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

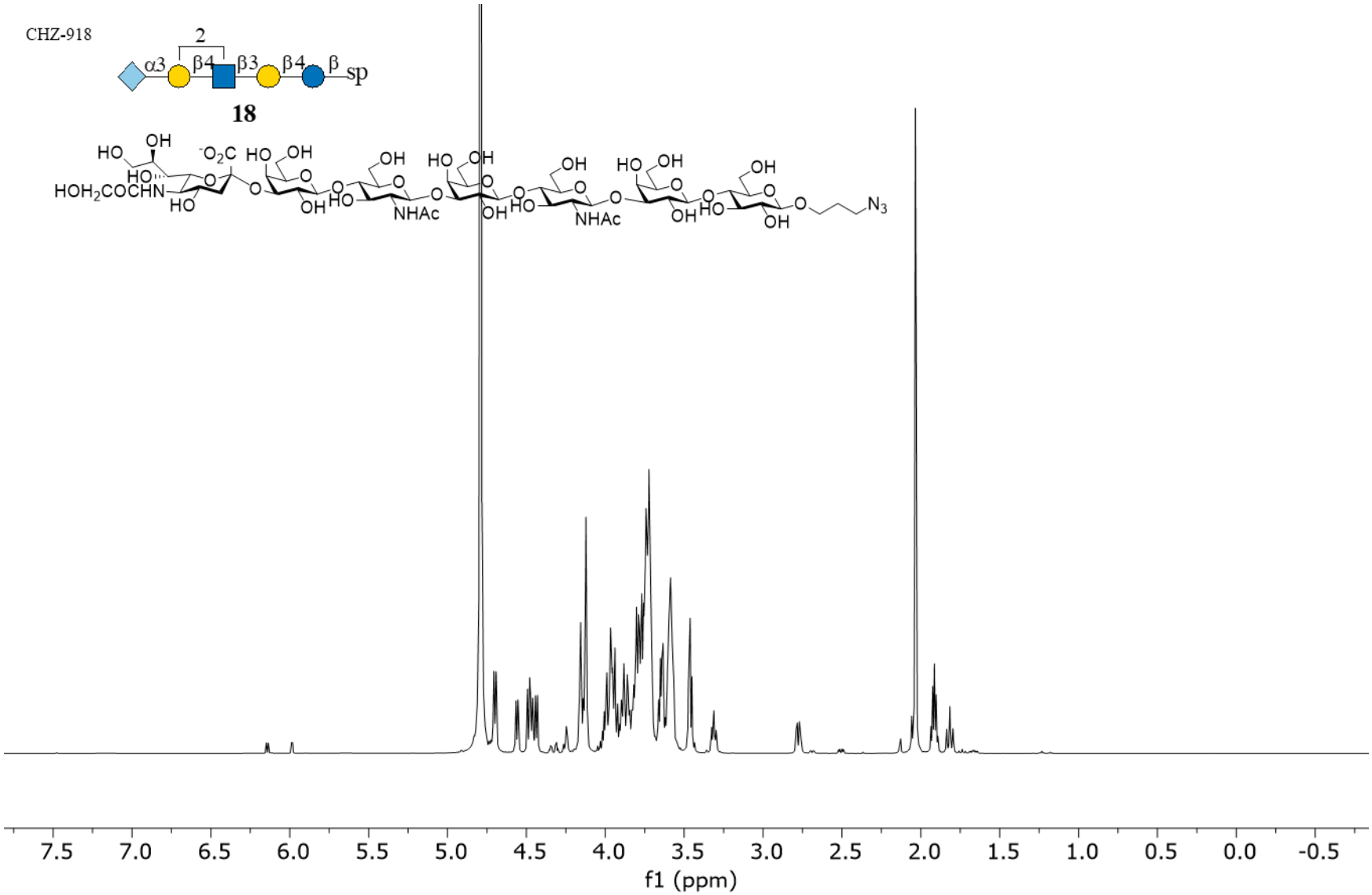
^{13}C NMR of 16


CHZ1043
2
α3
β4
β3
β4
β
sp
17
HO
OH
HO
AcHN
HO
$^{-}O_2C$
HO
OH
O
O
OH
HO
OH
O
O
NHAc
HO
OH
O
O
OH
HO
OH
O
O
NHAc
HO
OH
O
O
OH
HO
OH
O
O
OH
O
N_3
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)

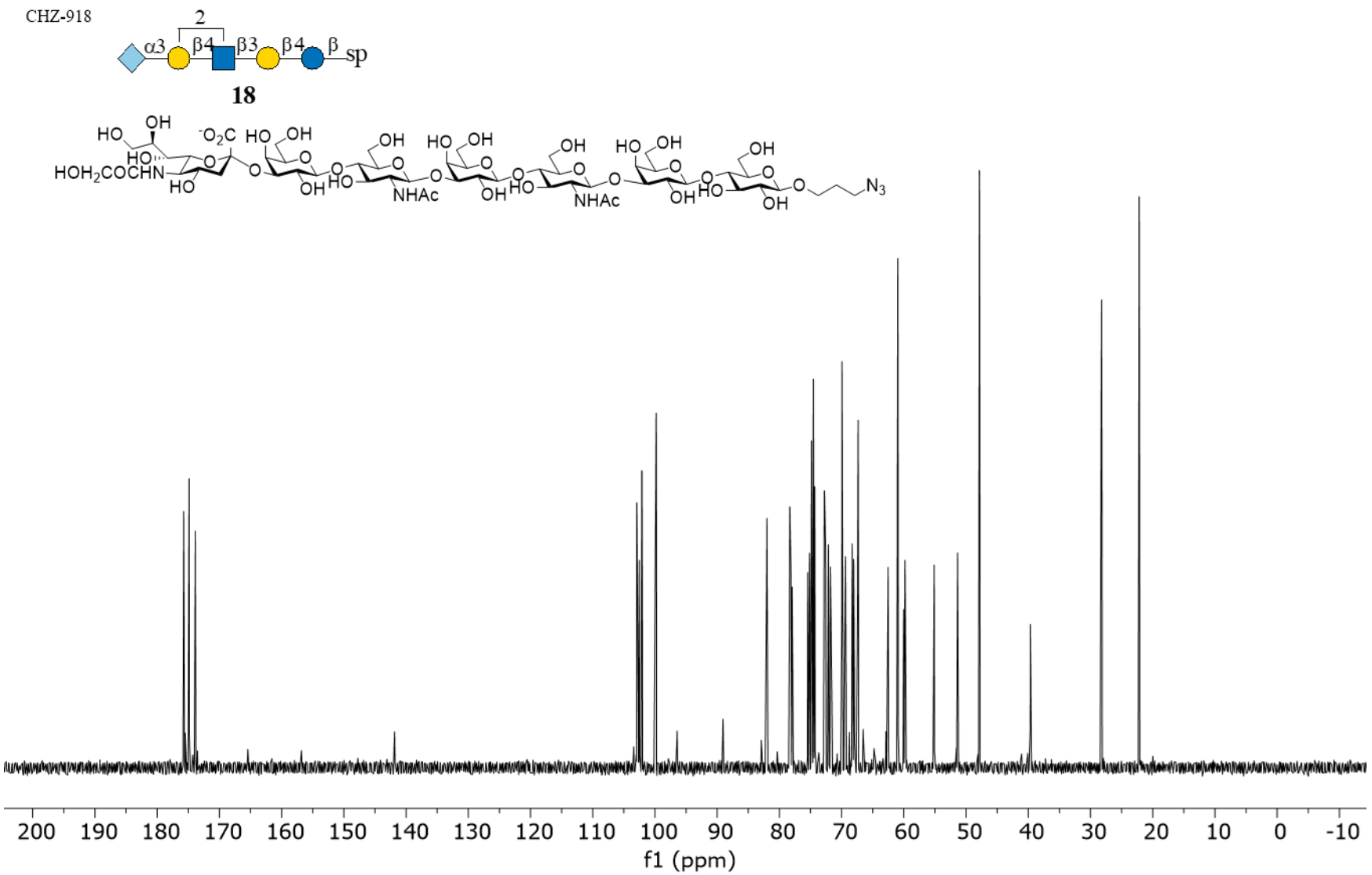
^{1}H NMR of 17


CHZ1043
2
α3
β4
β3
β4
β
sp
17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

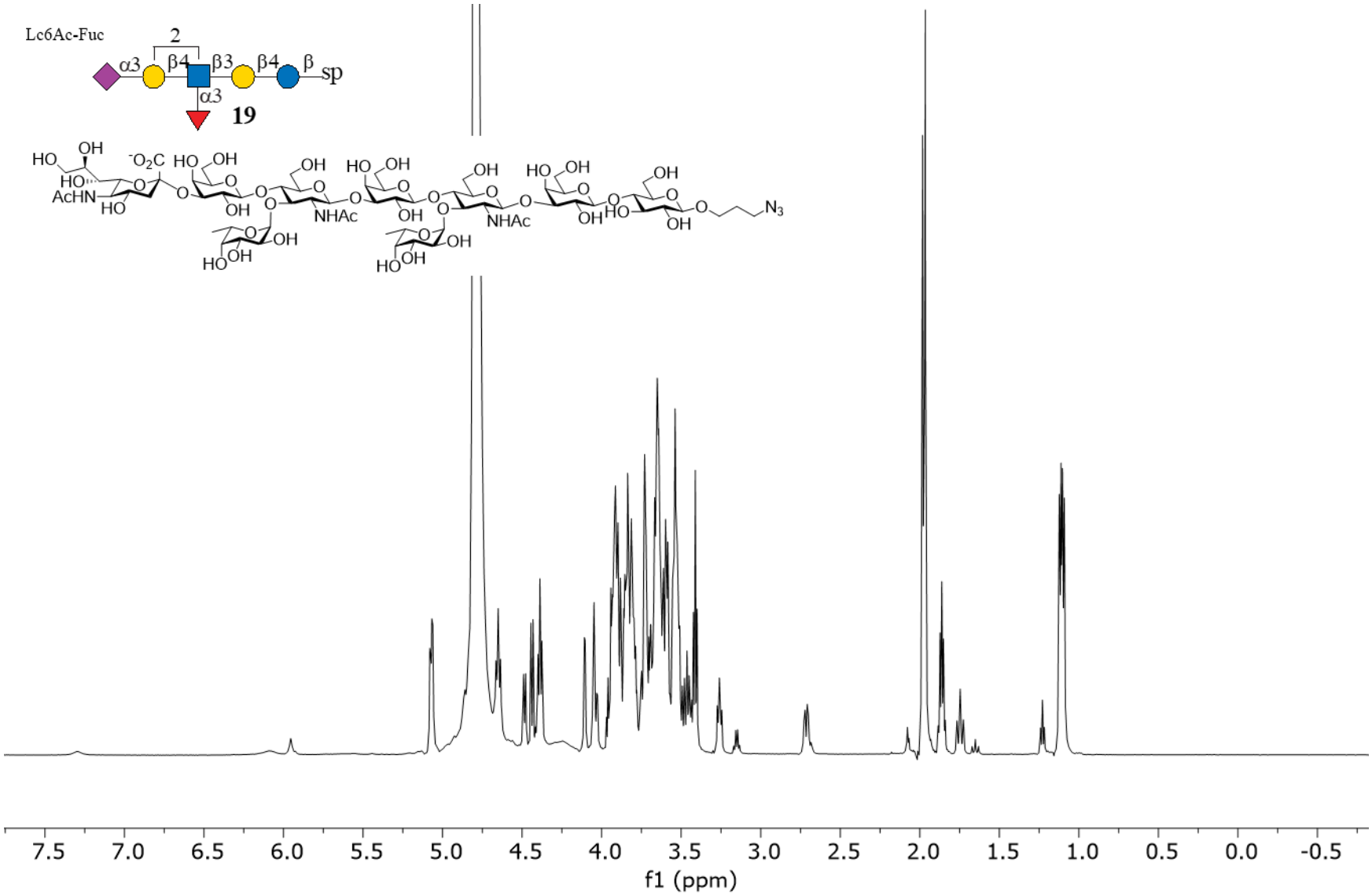
^{13}C NMR of 17


CHZ-918
2
α3
β4
β3
β4
β
sp
18
HO
OH
HO
HOH2COCHN
HO
O
-O2C
HO
OH
O
OH
HO
O
NHAc
HO
OH
O
OH
HO
O
NHAc
HO
OH
O
OH
HO
O
O
N3
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)

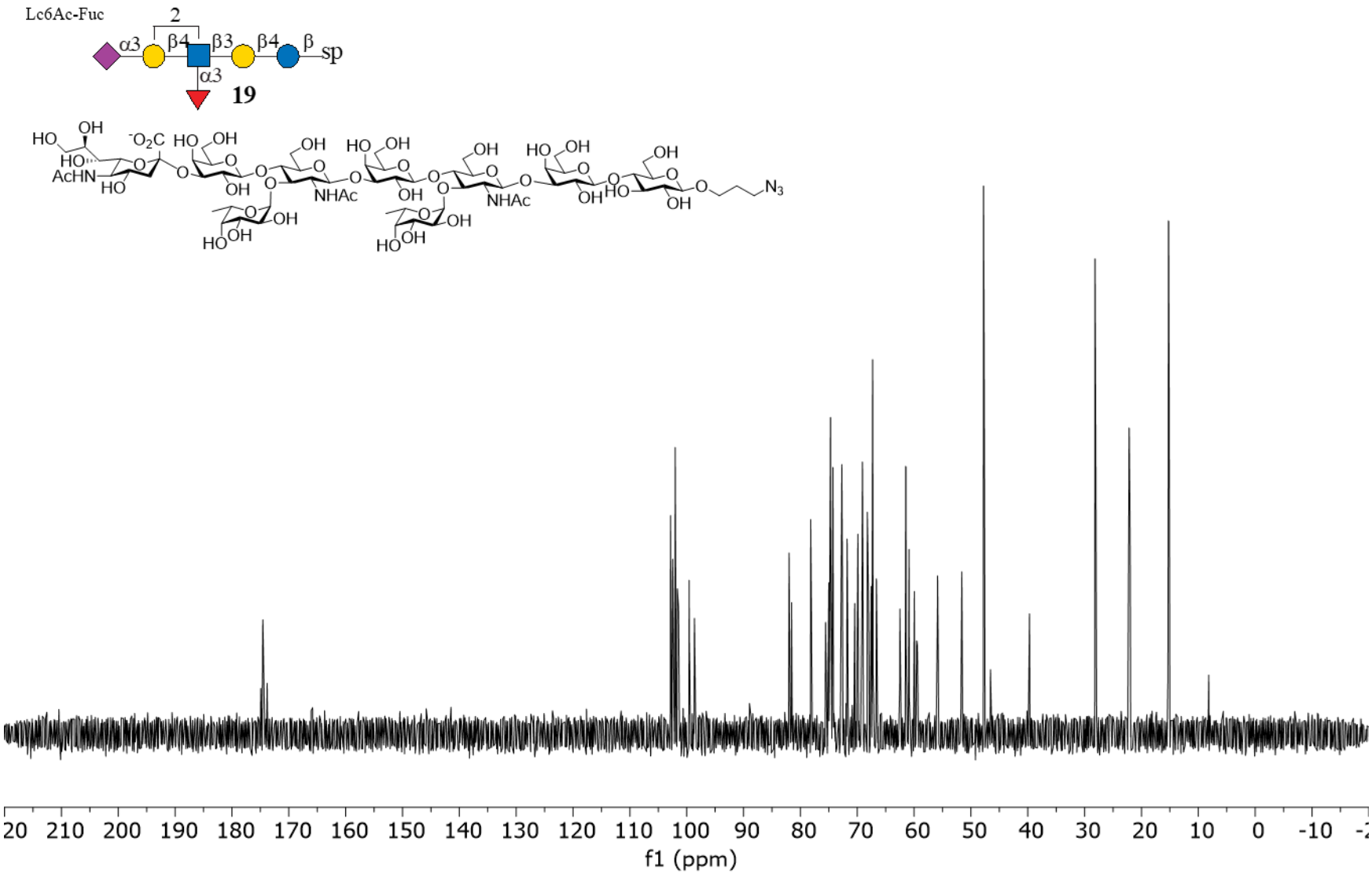
^{1}H NMR of 18


CHZ-918
2
α3
β4
β3
β4
β
sp
18
HO
OH
HO
HOH2COCHN
HO
-O2C
HO
OH
O
OH
HO
O
NHAc
HO
OH
O
OH
HO
O
NHAc
HO
OH
O
OH
HO
O
OH
O
N3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

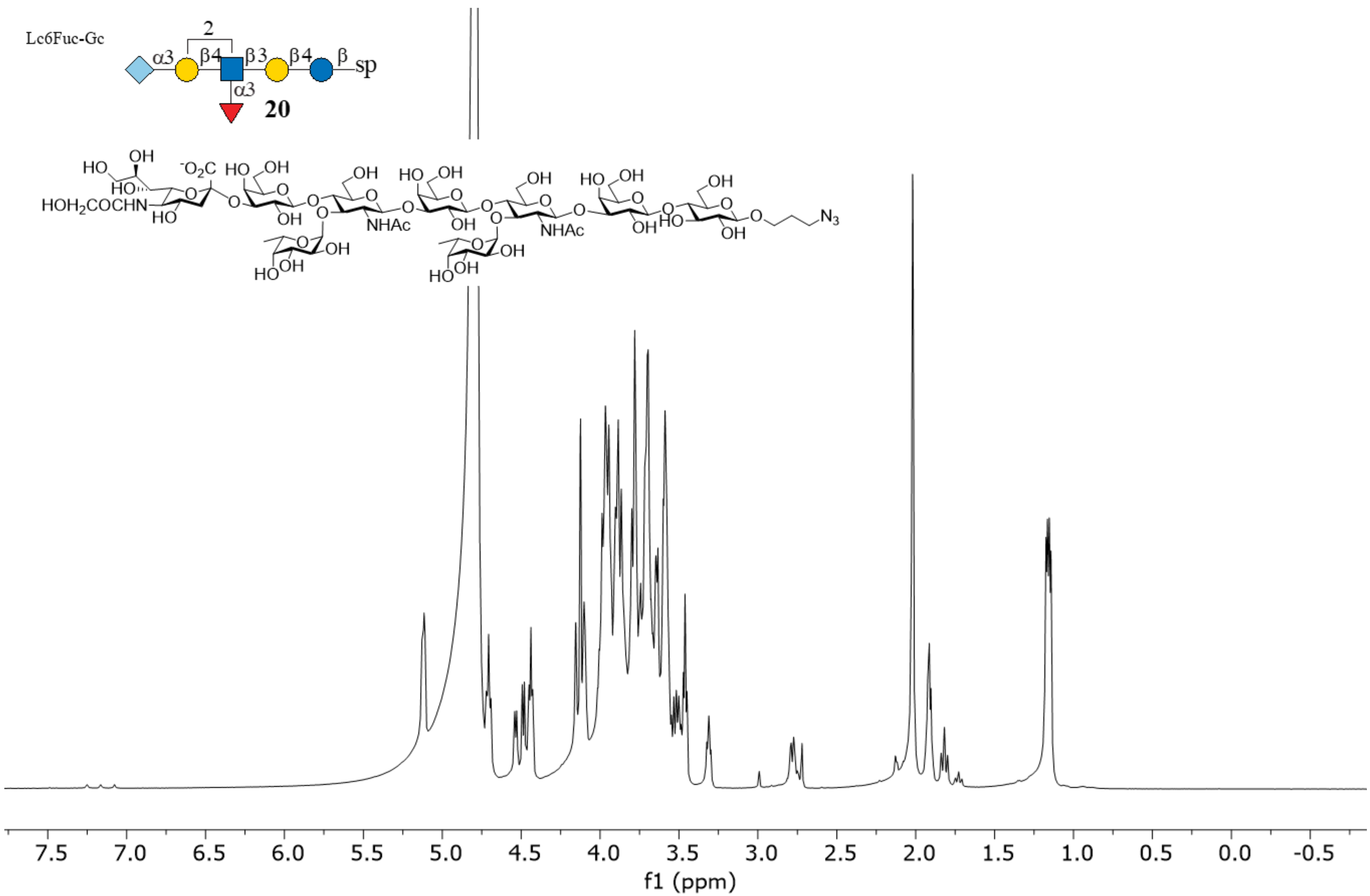
^{13}C NMR of 18


Lc6Ac-Fuc
2
α3
β4
β3
β4
β
sp
α3
19
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)

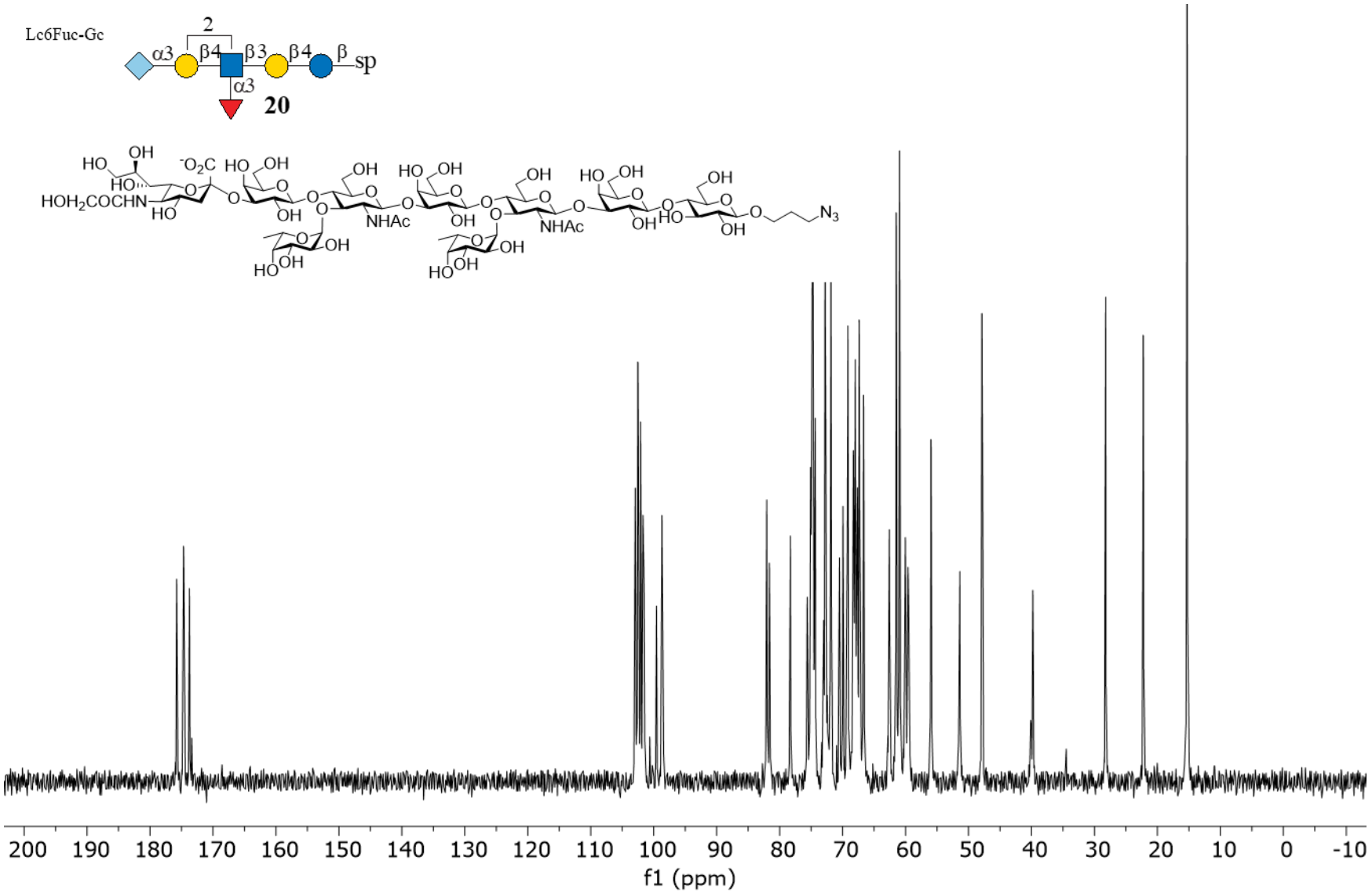
^{1}H NMR of 19



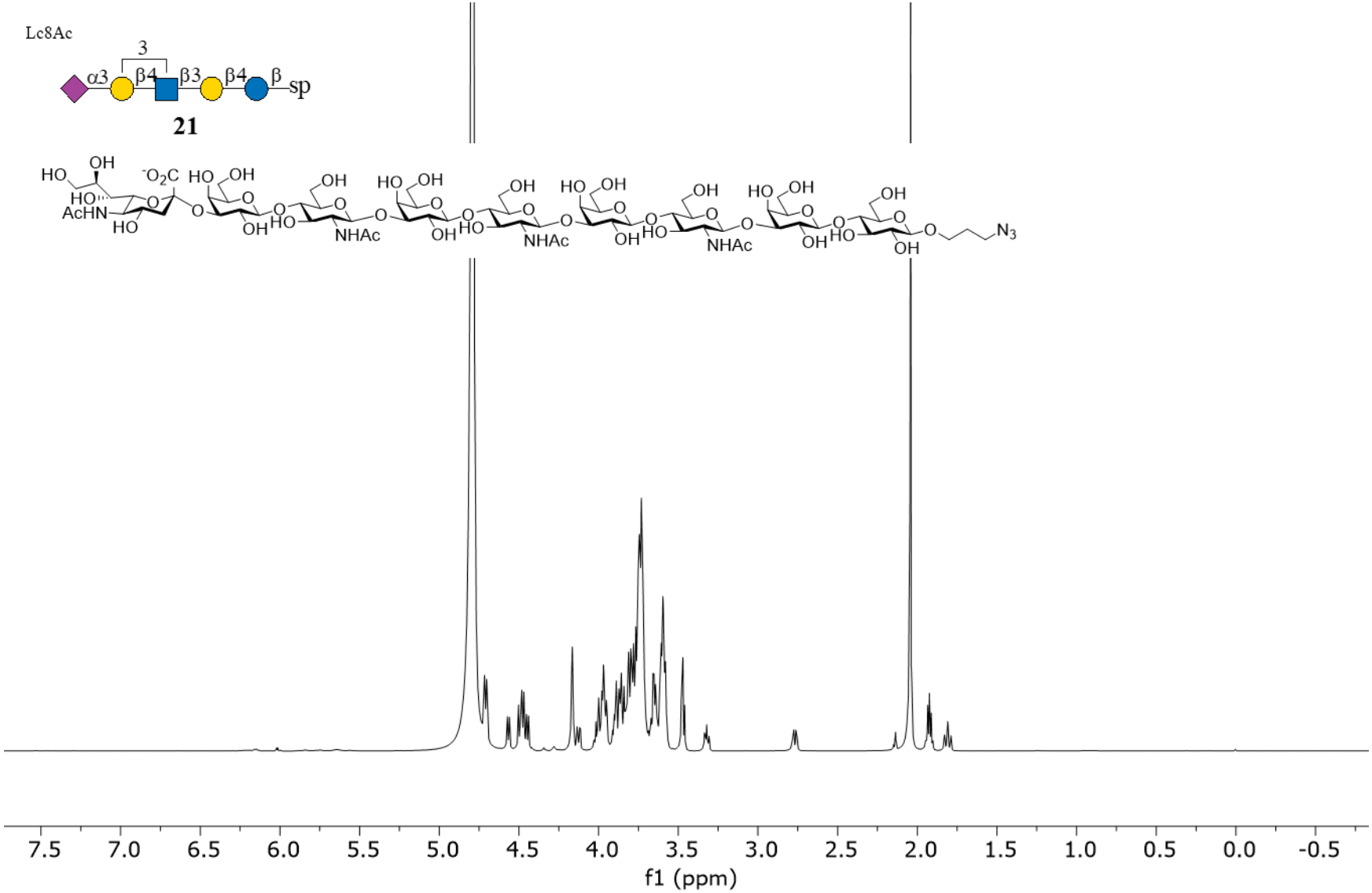
^{13}C NMR of 19



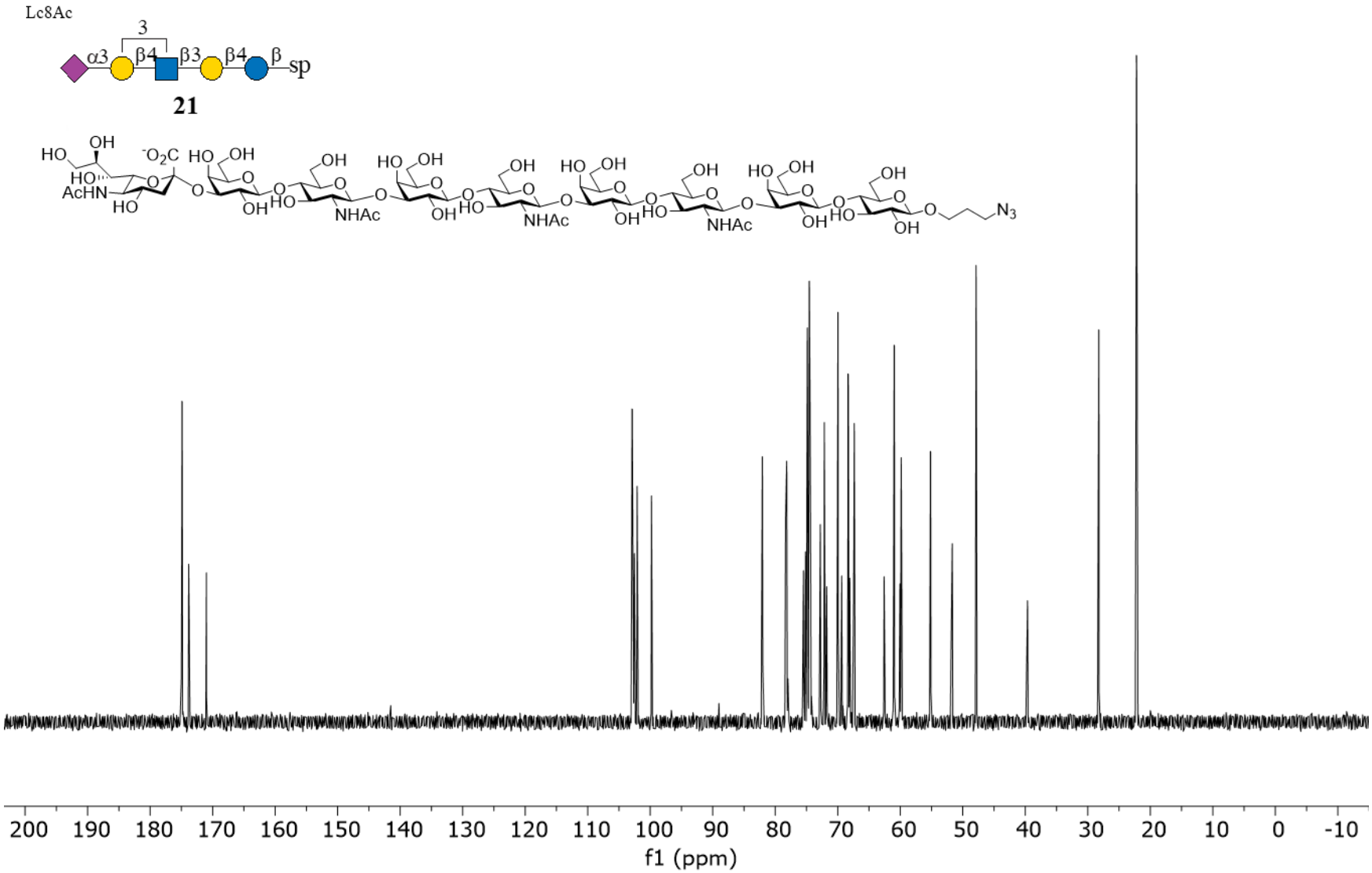
¹H NMR of 20


Lc6Fuc-Gc
2
α3
β4
β3
β4
β
sp
α3
20
HO
OH
HO
HOH2COCHN
HO
-O2C
HO
OH
O
O
OH
O
NHAc
HO
OH
O
O
OH
O
NHAc
HO
OH
O
O
OH
HO
OH
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

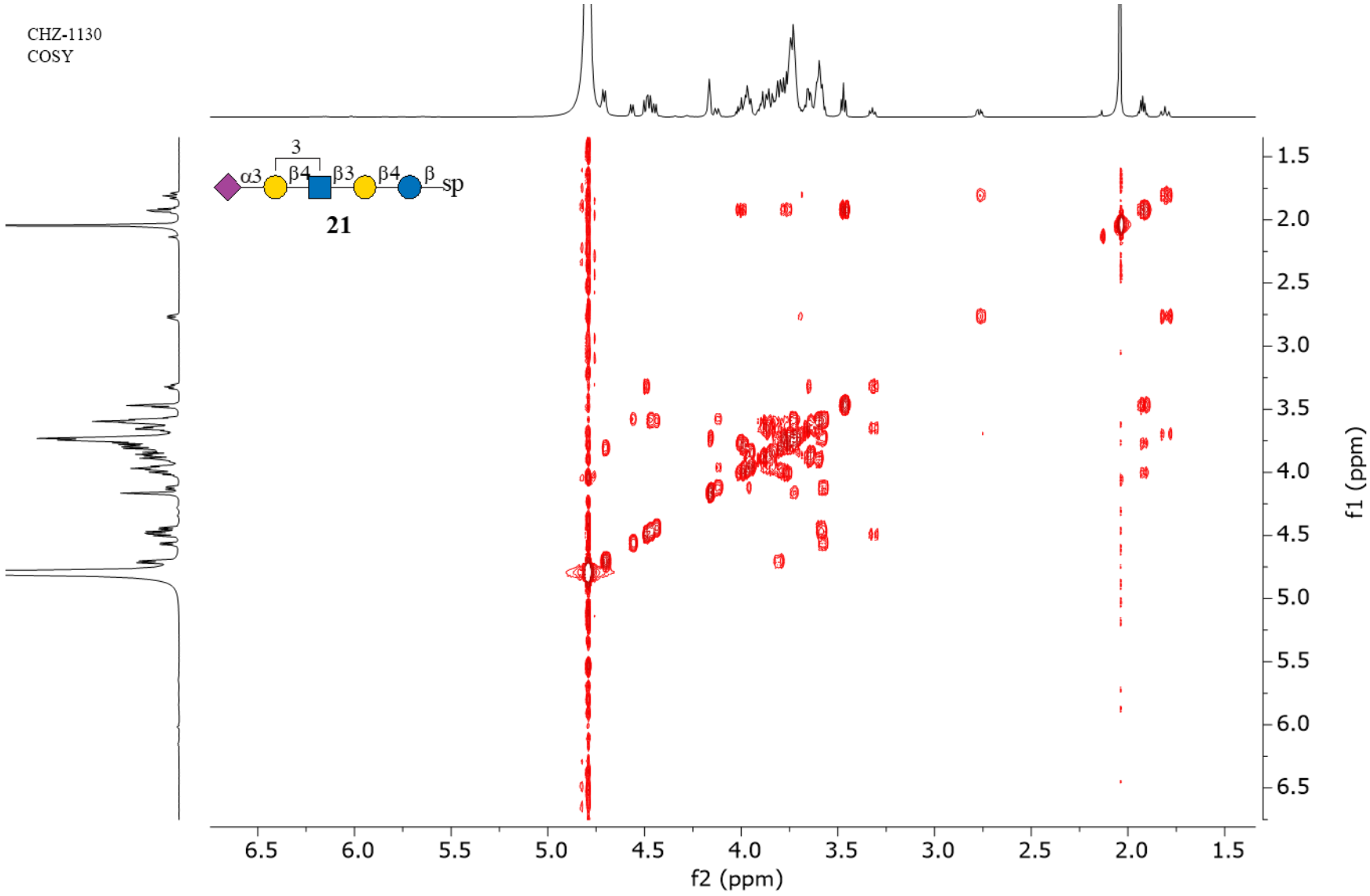
^{13}C NMR of 20


Lc8Ac
3
α3
β4
β3
β4
β
sp
21
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)

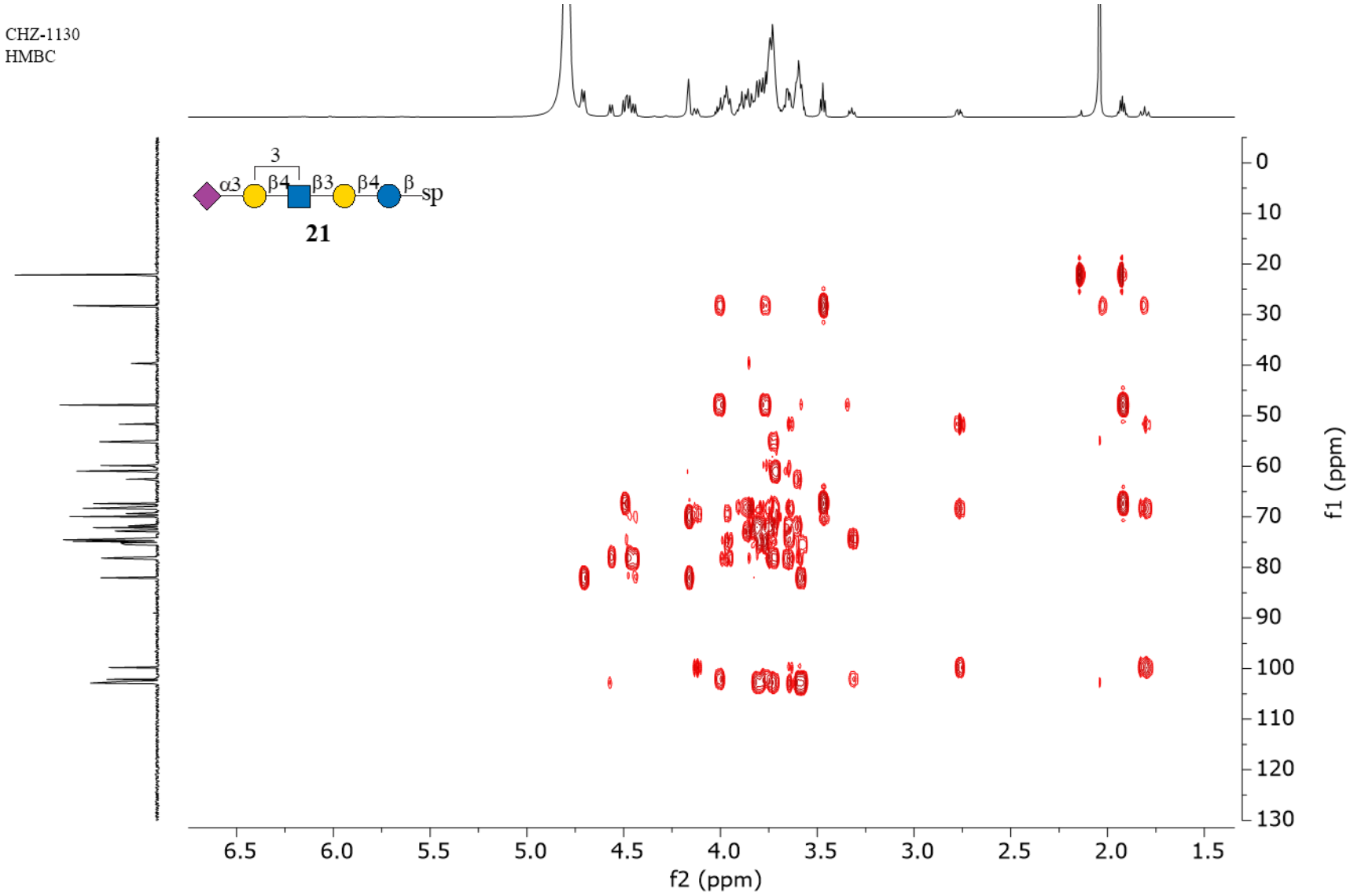
1H NMR of 21


Lc8Ac
3
α3
β4
β3
β4
β
sp
21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

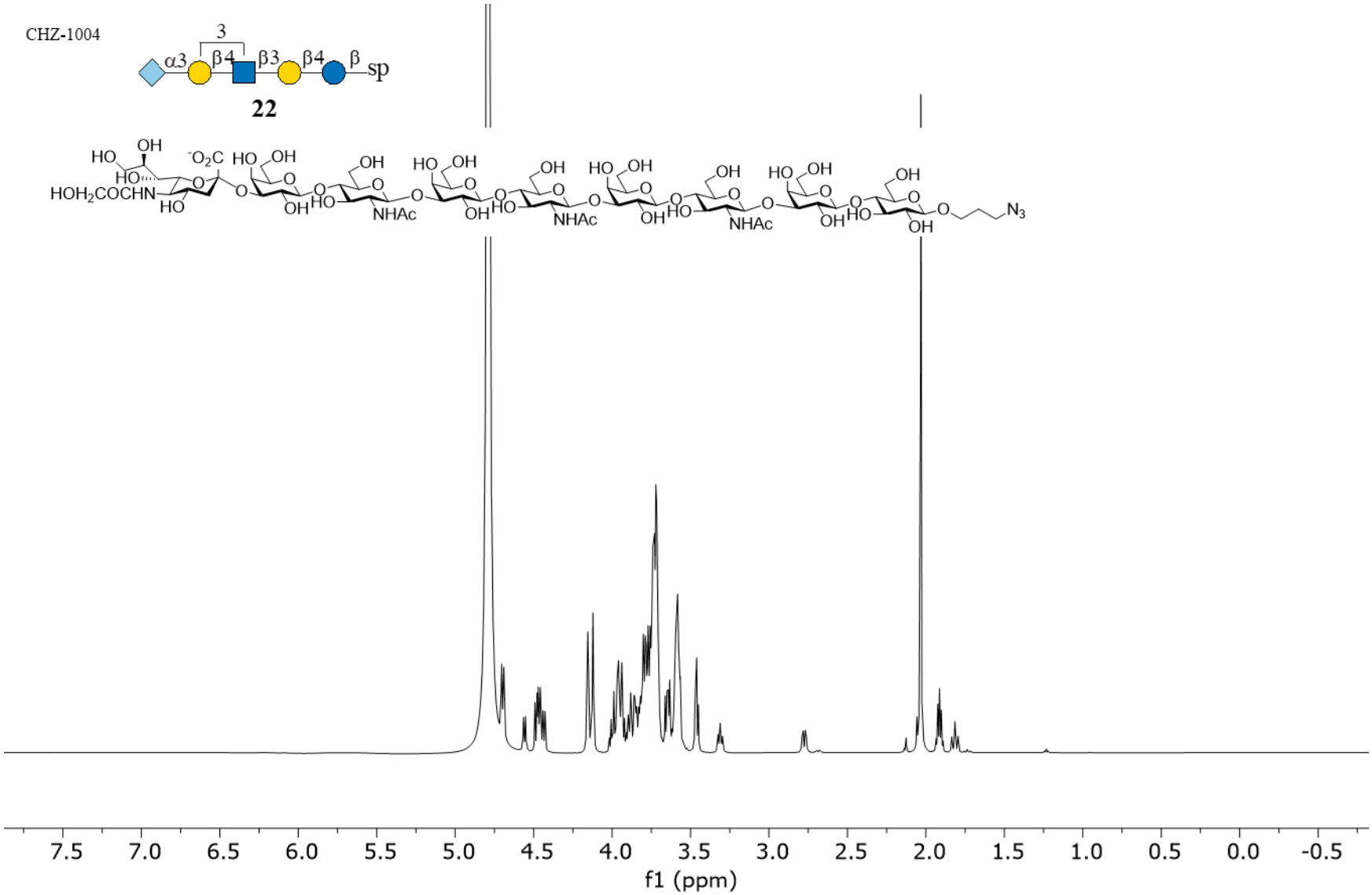
^{13}C NMR of 21



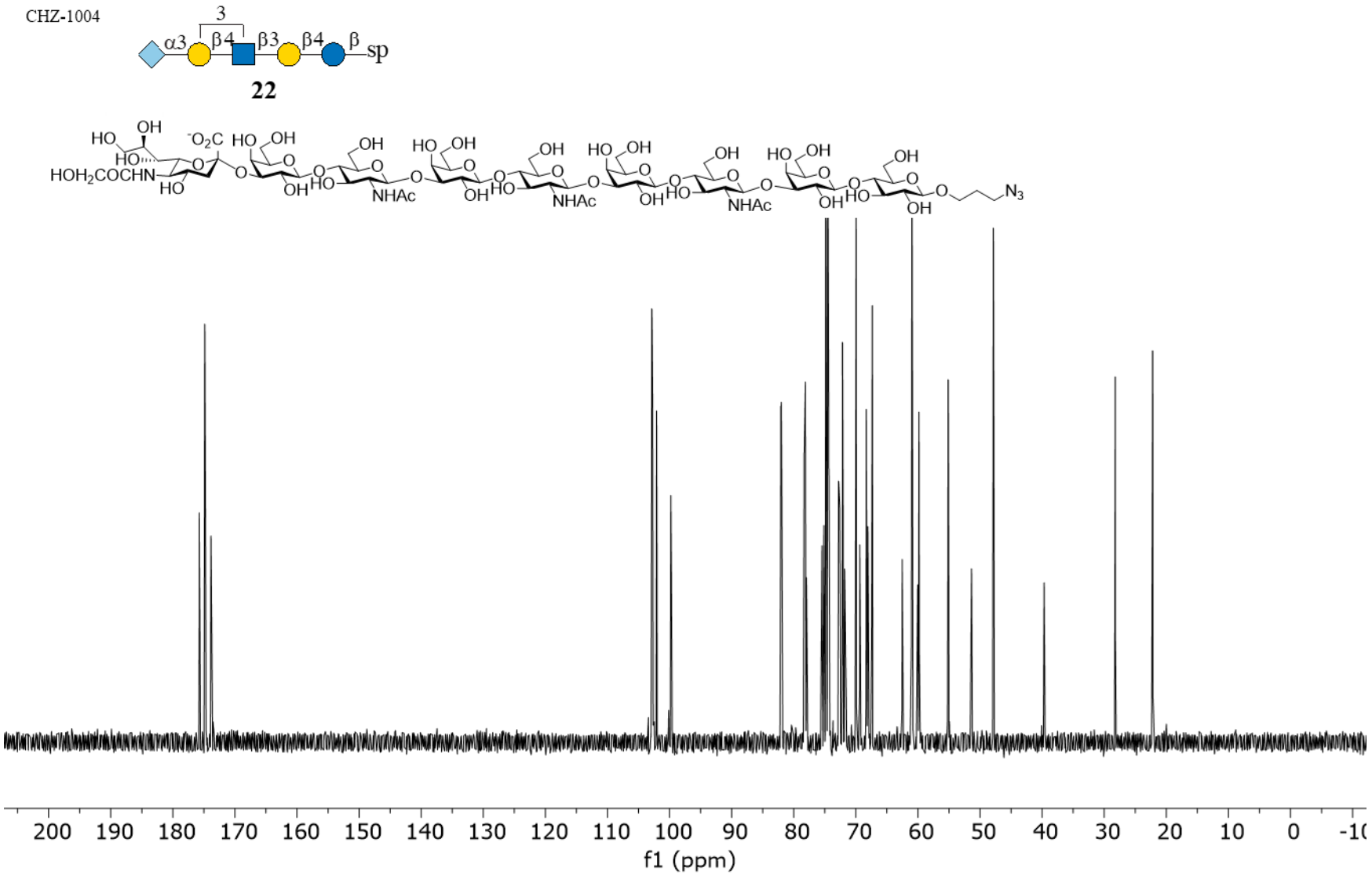
COSY NMR of 21



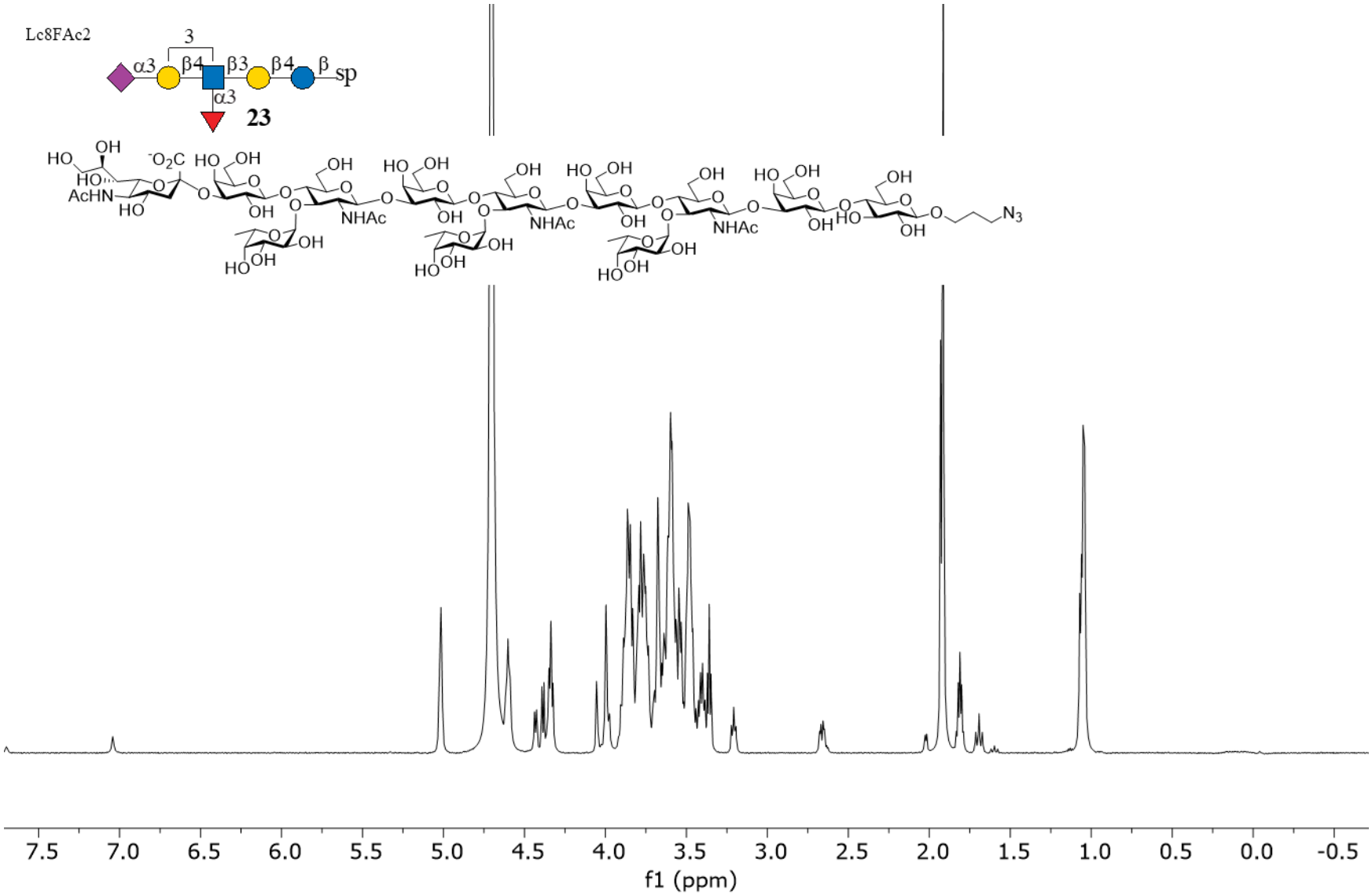
HMBC NMR of 21


CHZ-1004
3
α3
β4
β3
β4
β
sp
22
HO
OH
HO
HOH2COCHN
HO
-O2C
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
O
N3
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)

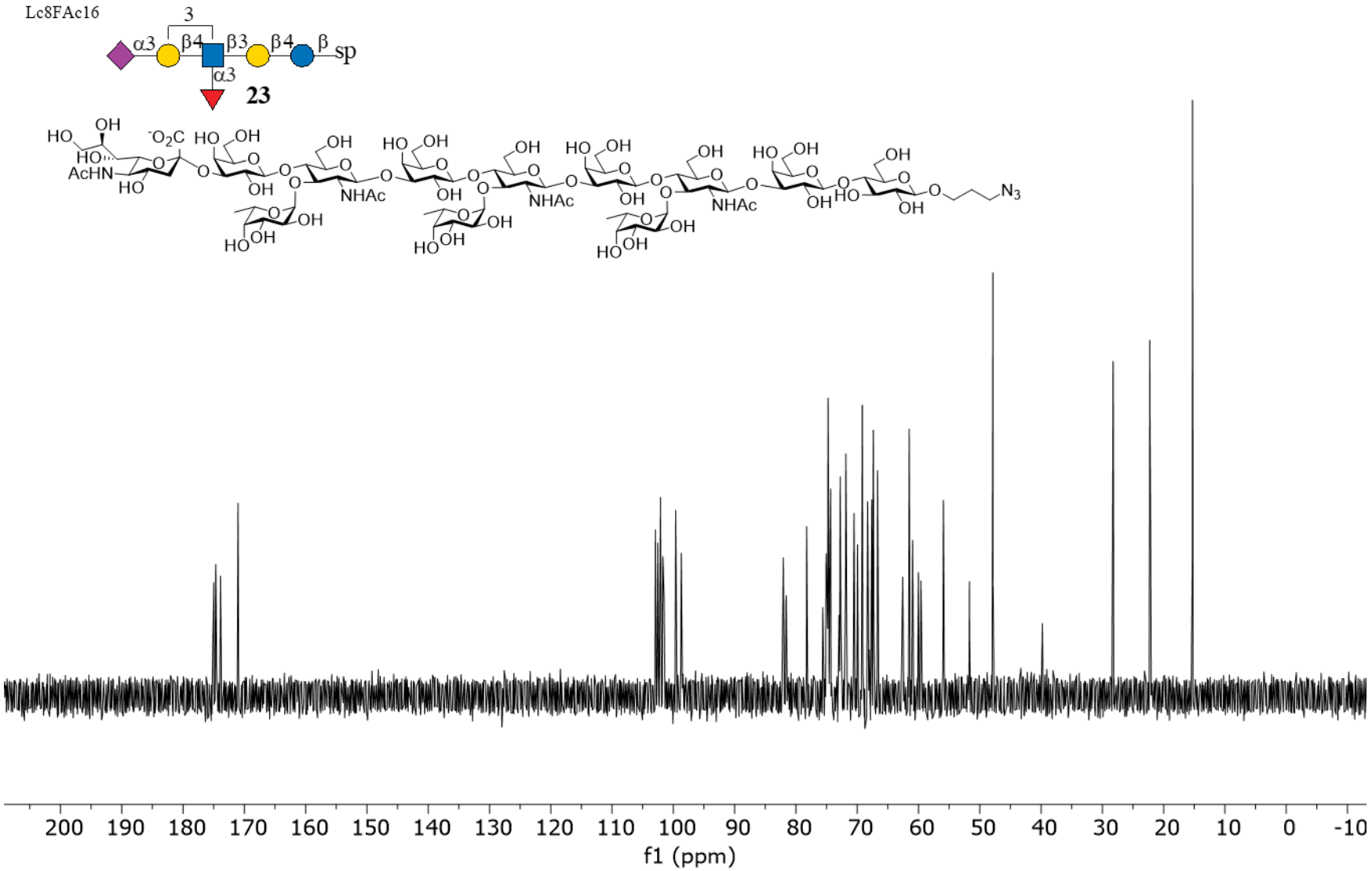
^{1}H NMR of 22


CHZ-1004
3
α3
β4
β3
β4
β
sp
22
HO
OH
HO
HOH2COCHN
HO
-O2C
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
NHAc
HO
OH
O
O
HO
OH
O
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

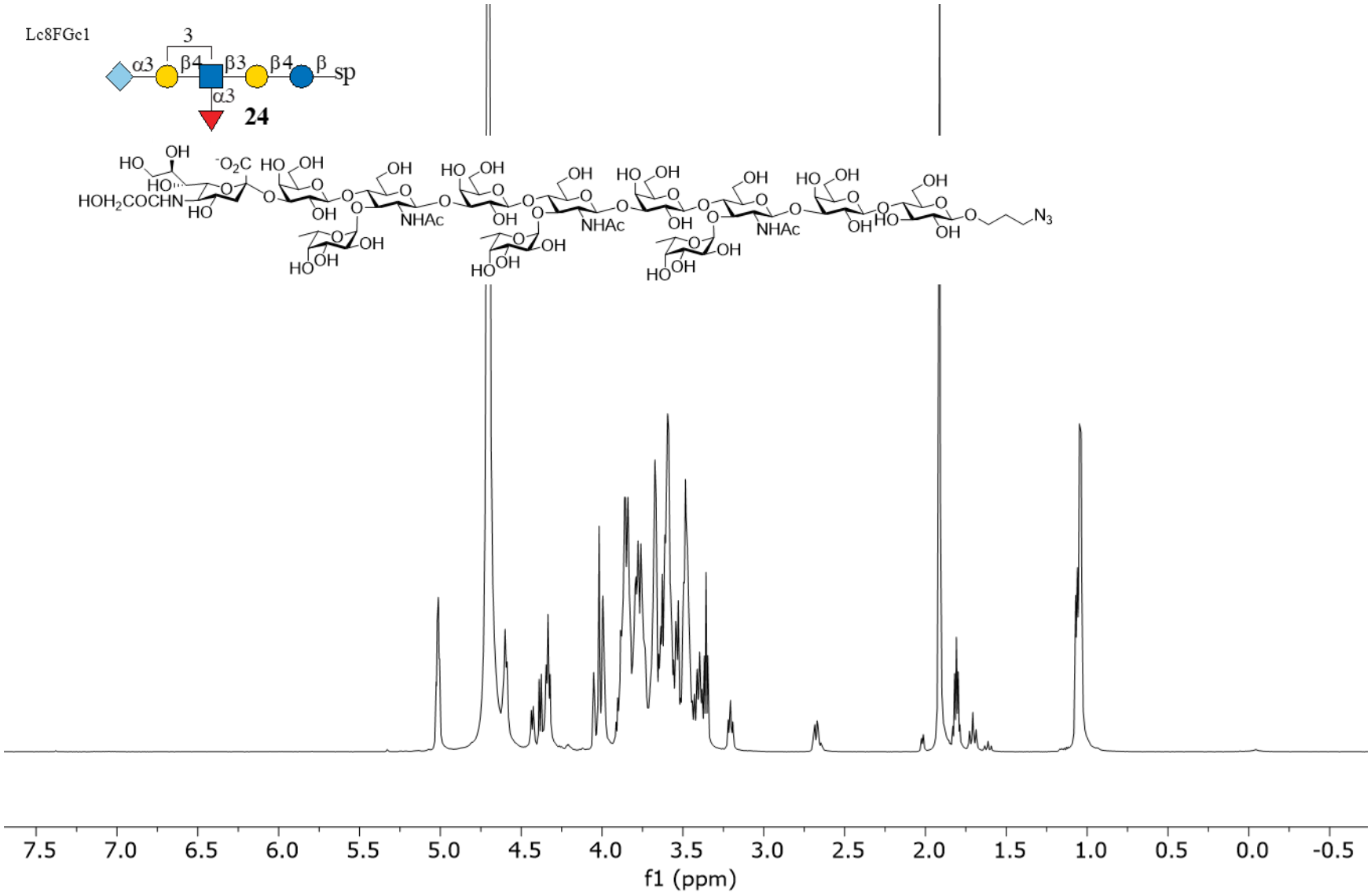
^{13}C NMR of 22


Lc8FAc2
3
α3
β4
β3
β4
β
sp
α3
23
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)

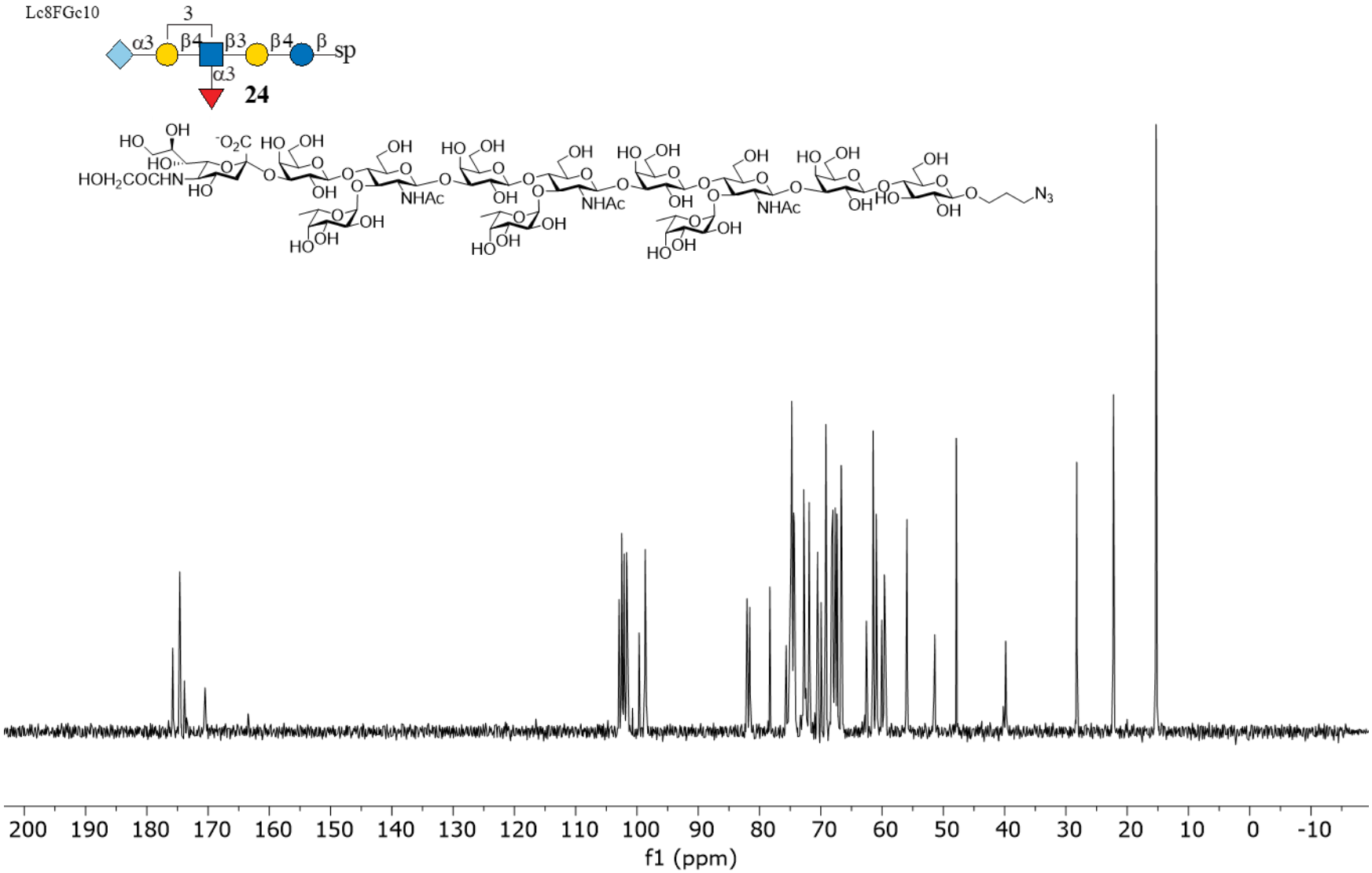
^{1}H NMR of 23


Lc8FAc16
3
α3
β4
β3
β4
β
sp
α3
23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

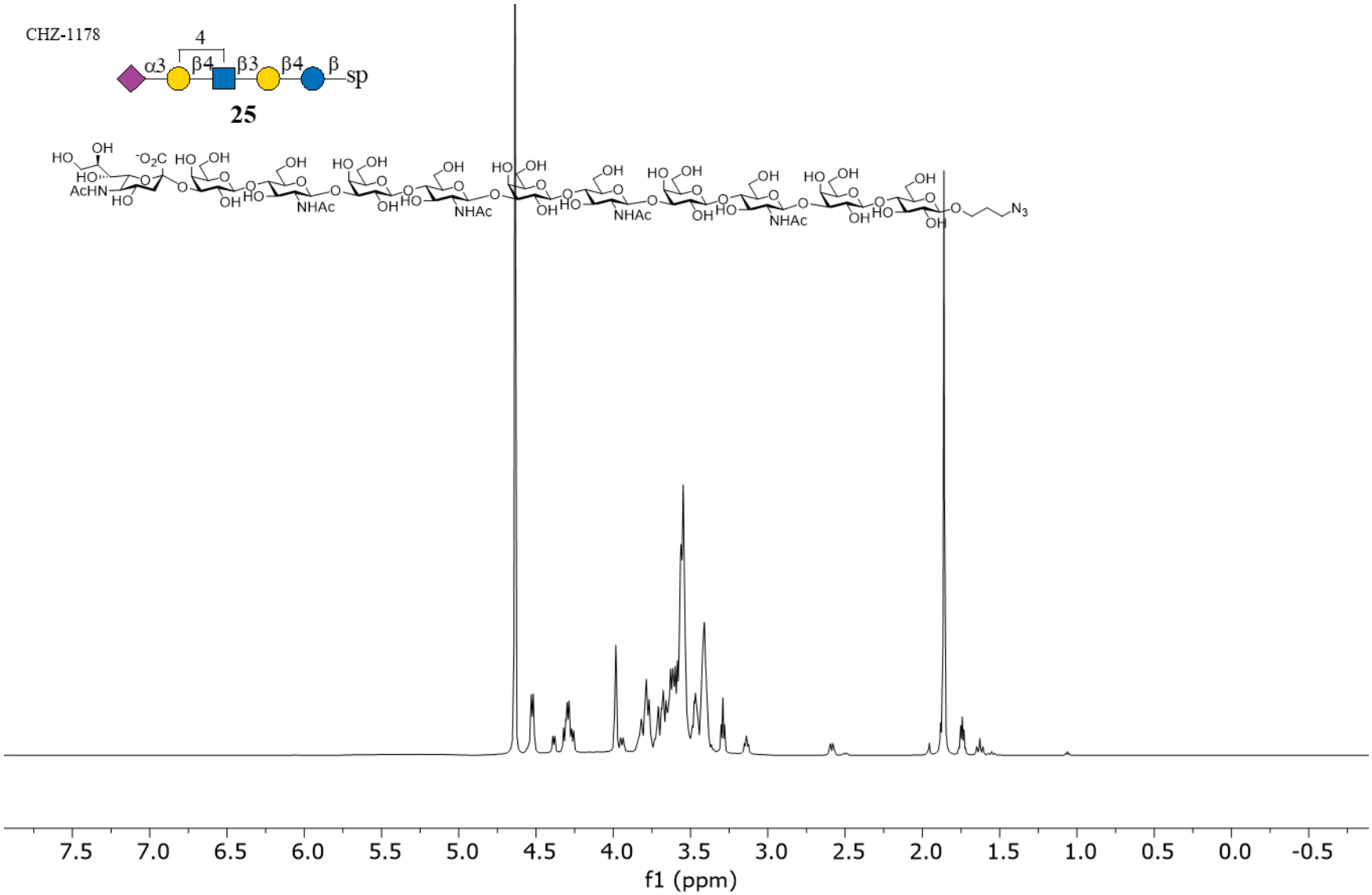
^{13}C NMR of 23


Lc8FGc1
3
α3
β4
β3
β4
β
sp
α3
24
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)

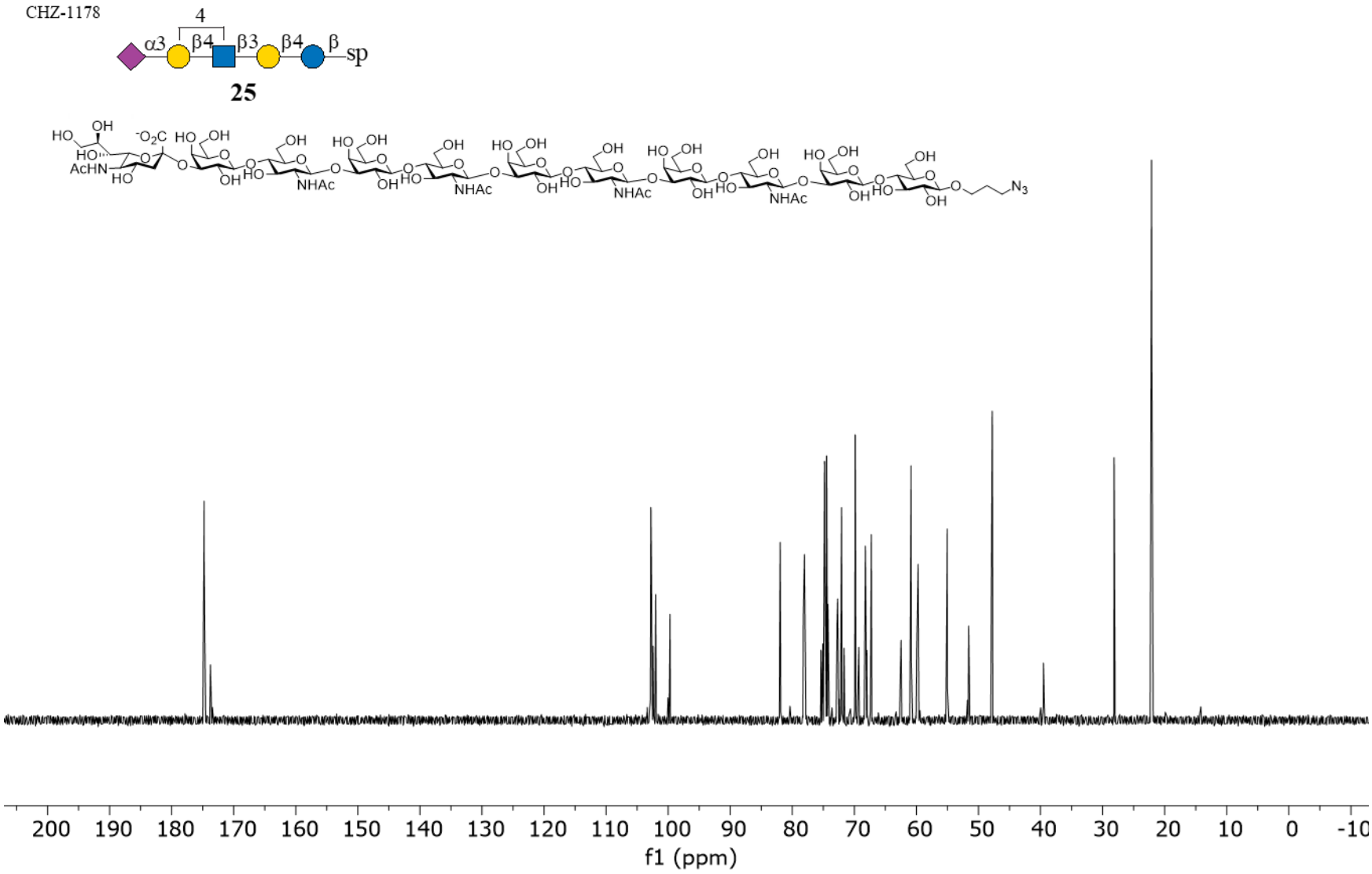
^{1}H NMR of 24


Lc8FGc10
3
α3
β4
β3
β4
β
sp
α3
24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

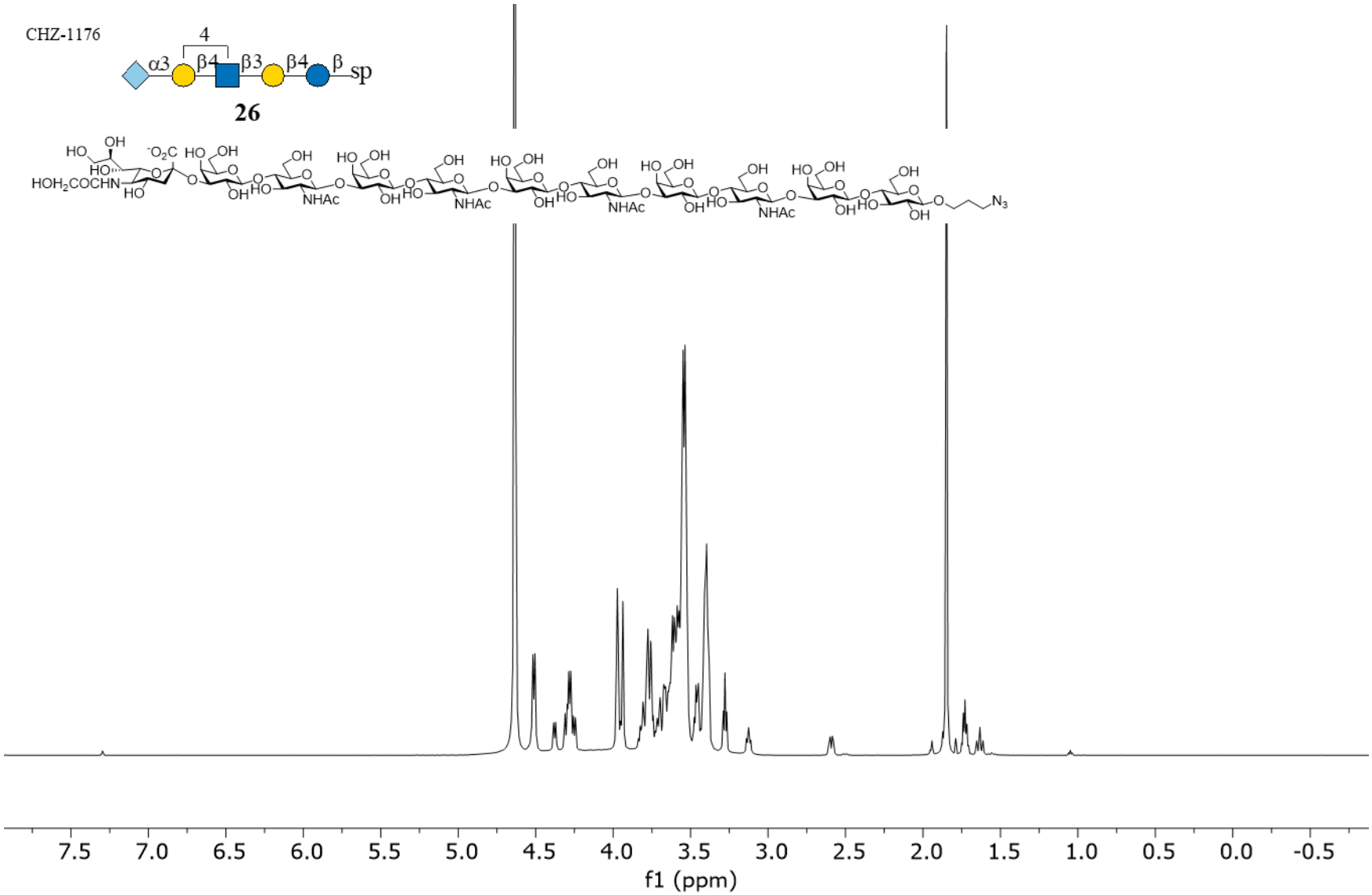
^{13}C NMR of 24


CHZ-1178
4
α3
β4
β3
β4
β
sp
25
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)

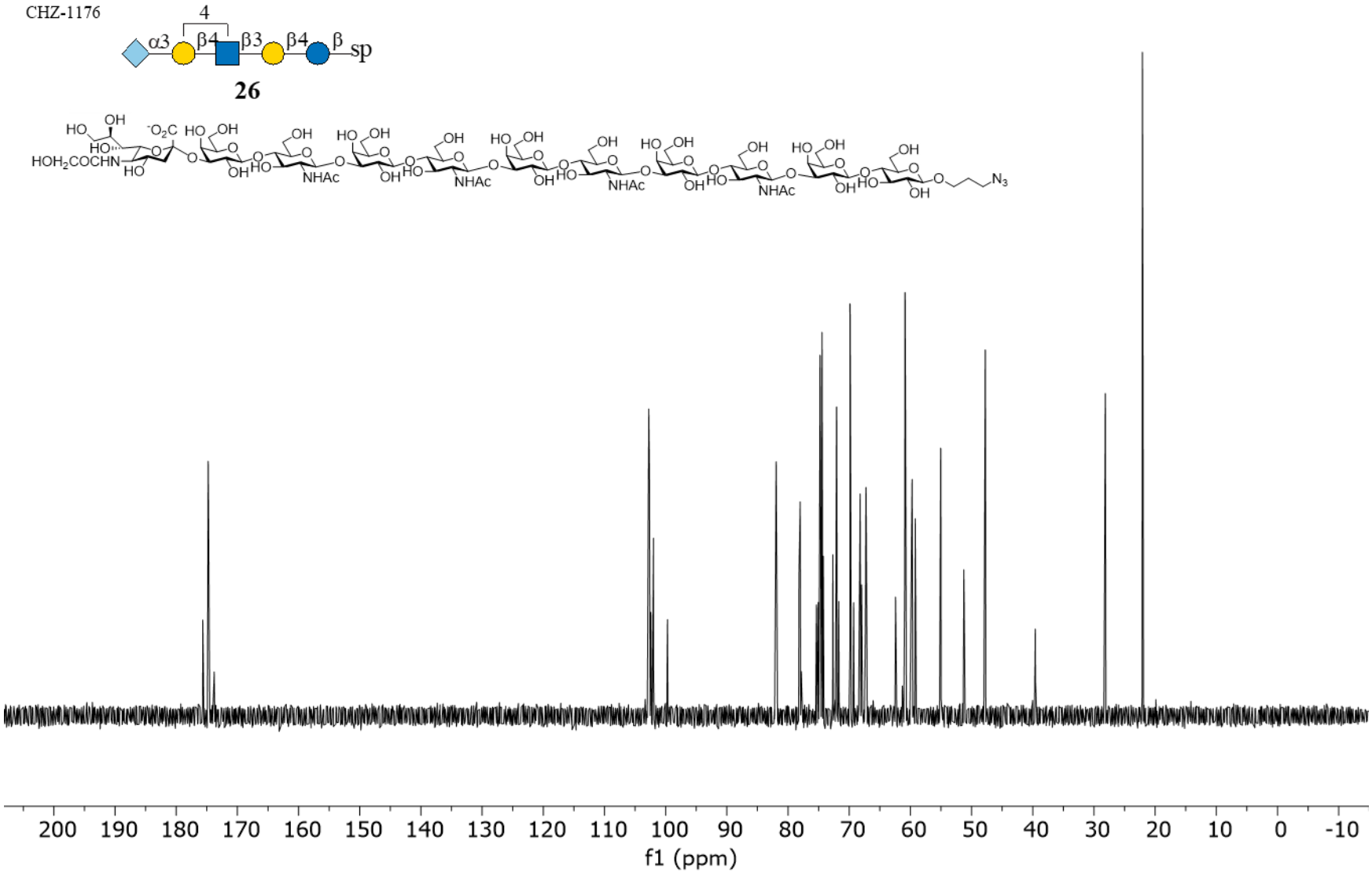
^{1}H NMR of 25


CHZ-1178
4
α3
β4
β3
β4
β
sp
25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

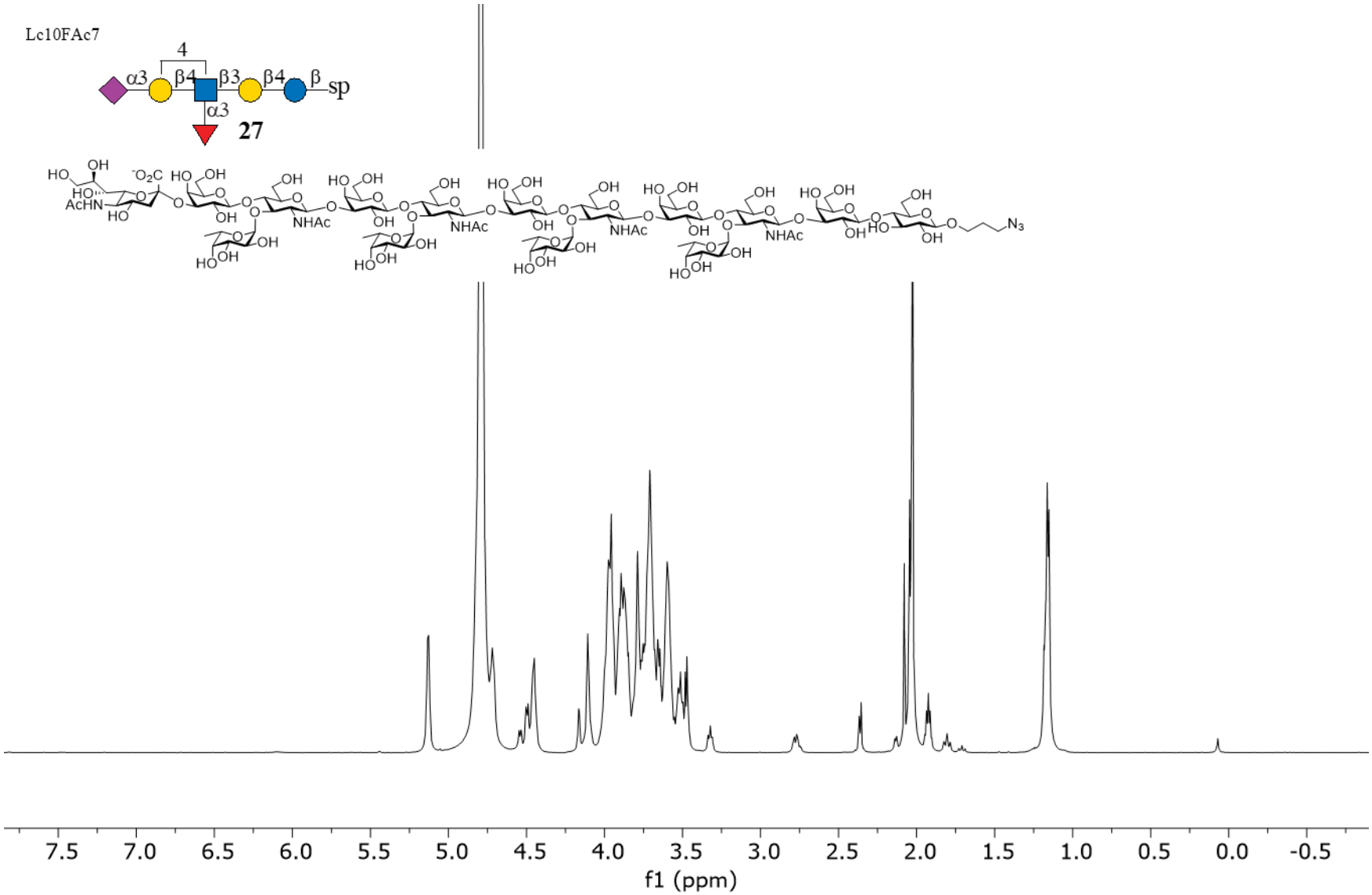
^{13}C NMR of 25


CHZ-1176
4
α3
β4
β3
β4
β
sp
26
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)

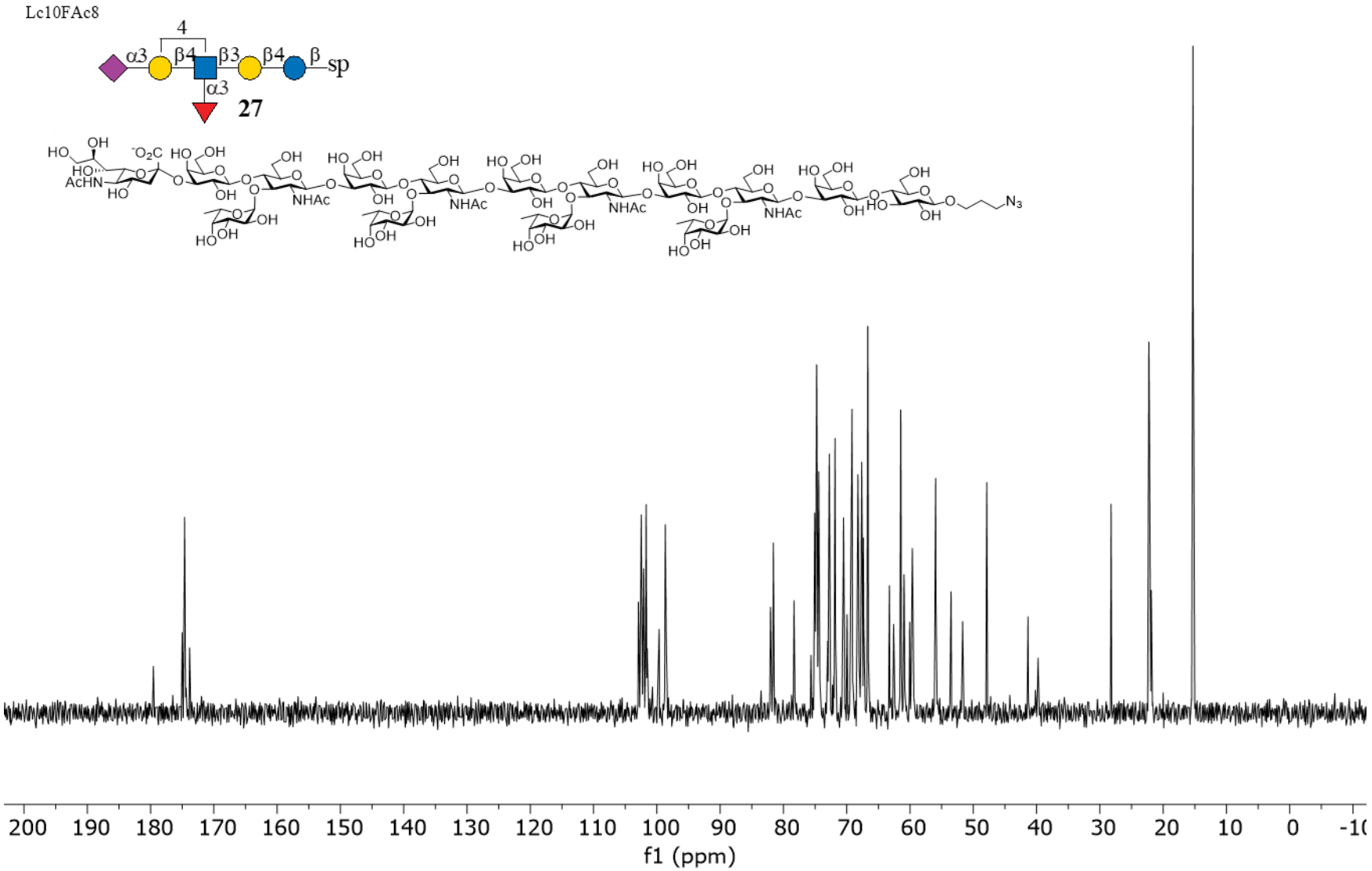
^{1}H NMR of 26


CHZ-1176
4
α3
β4
β3
β4
β
sp
26
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

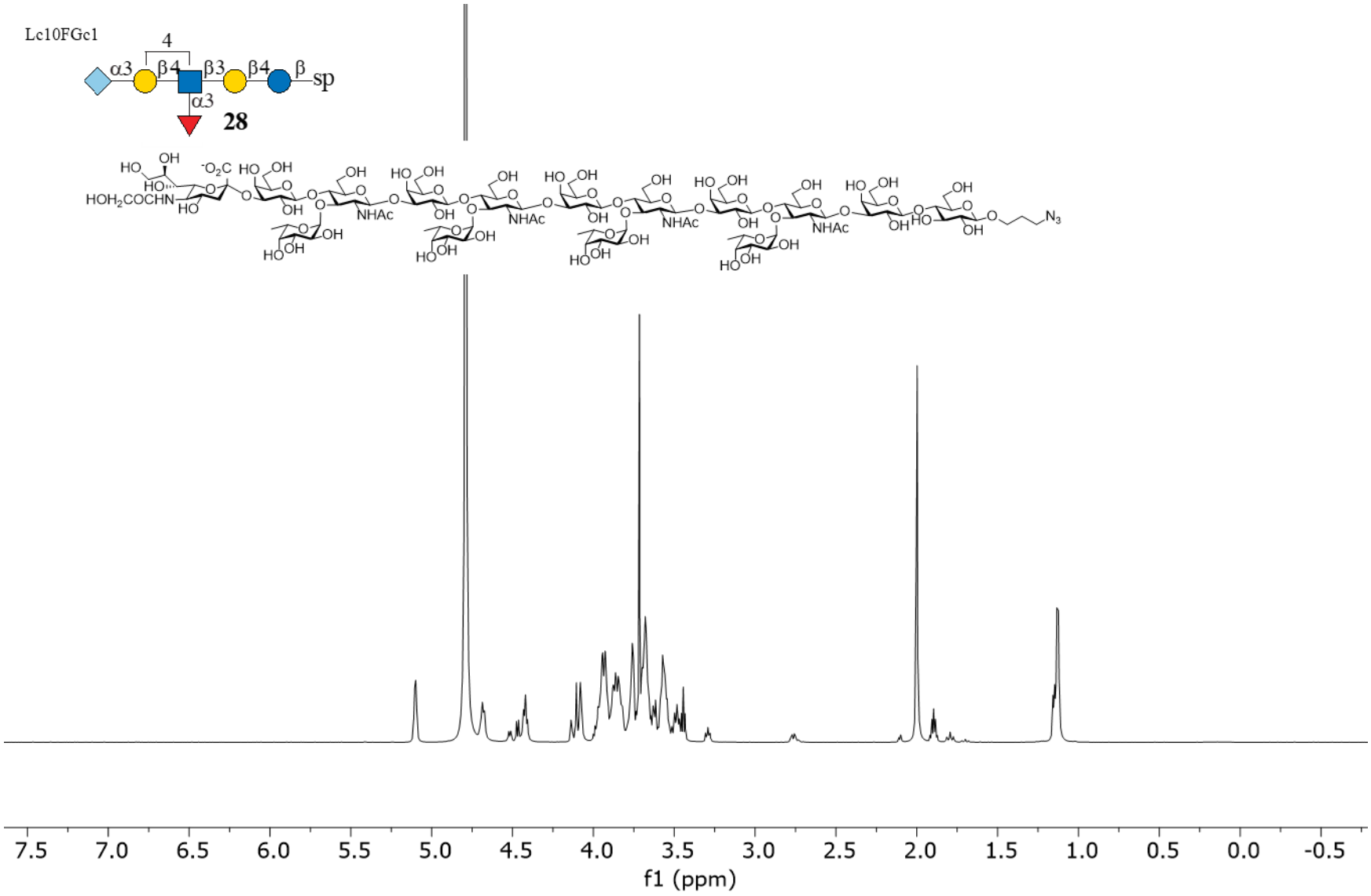
^{13}C NMR of 26



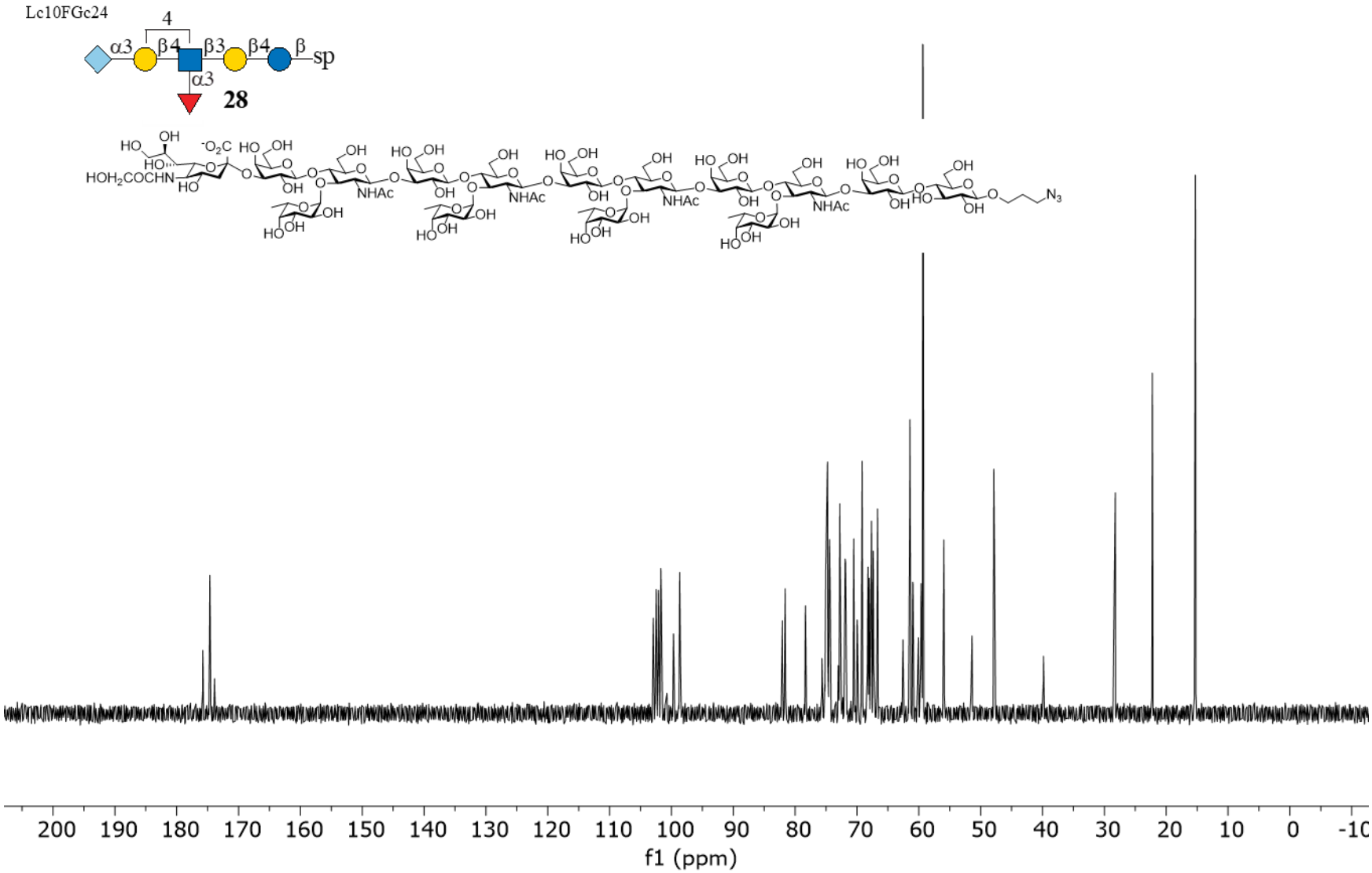
^{1}H NMR of 27


Lc10FAc8
4
α3
β4
β3
β4
β
sp
α3
27
NHAc
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

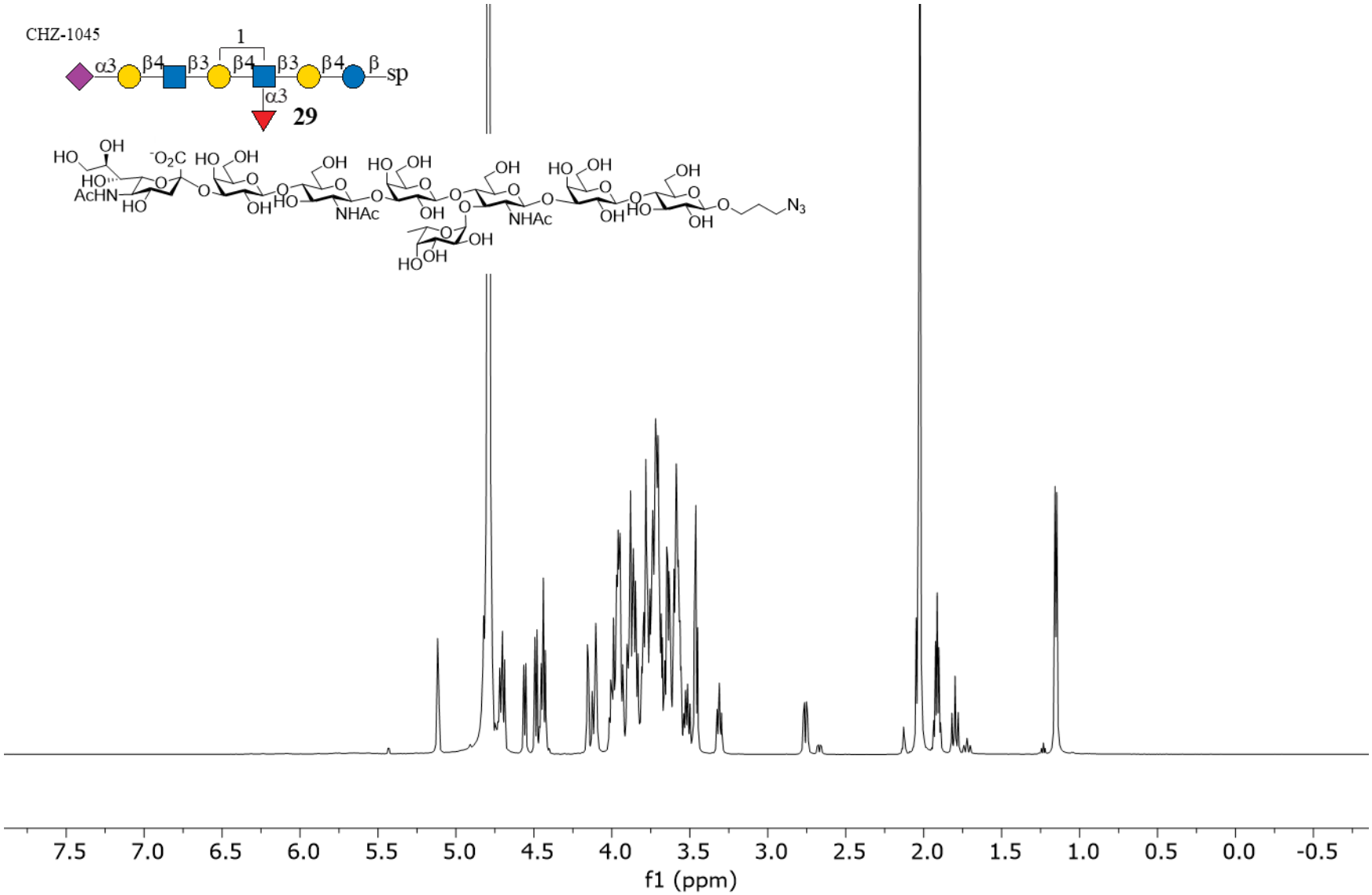
^{13}C NMR of 27


Lc10FGc1
4
α3
β4
β3
β4
β
sp
α3
28
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)

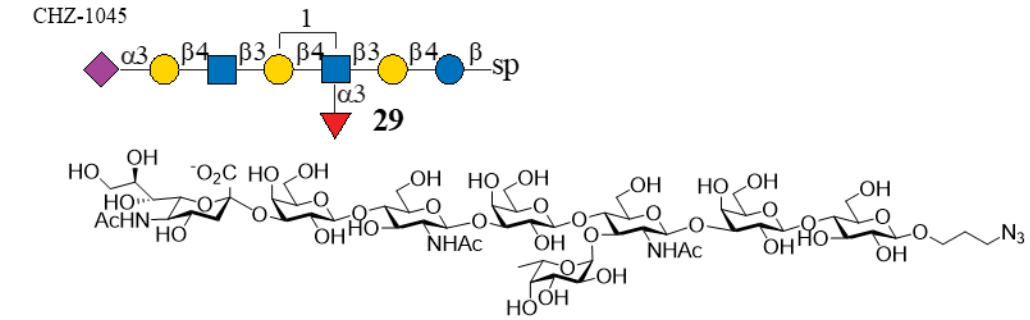
^{1}H NMR of 28


Lc10FGc24
4
α3
β4
β3
β4
β
sp
α3
28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

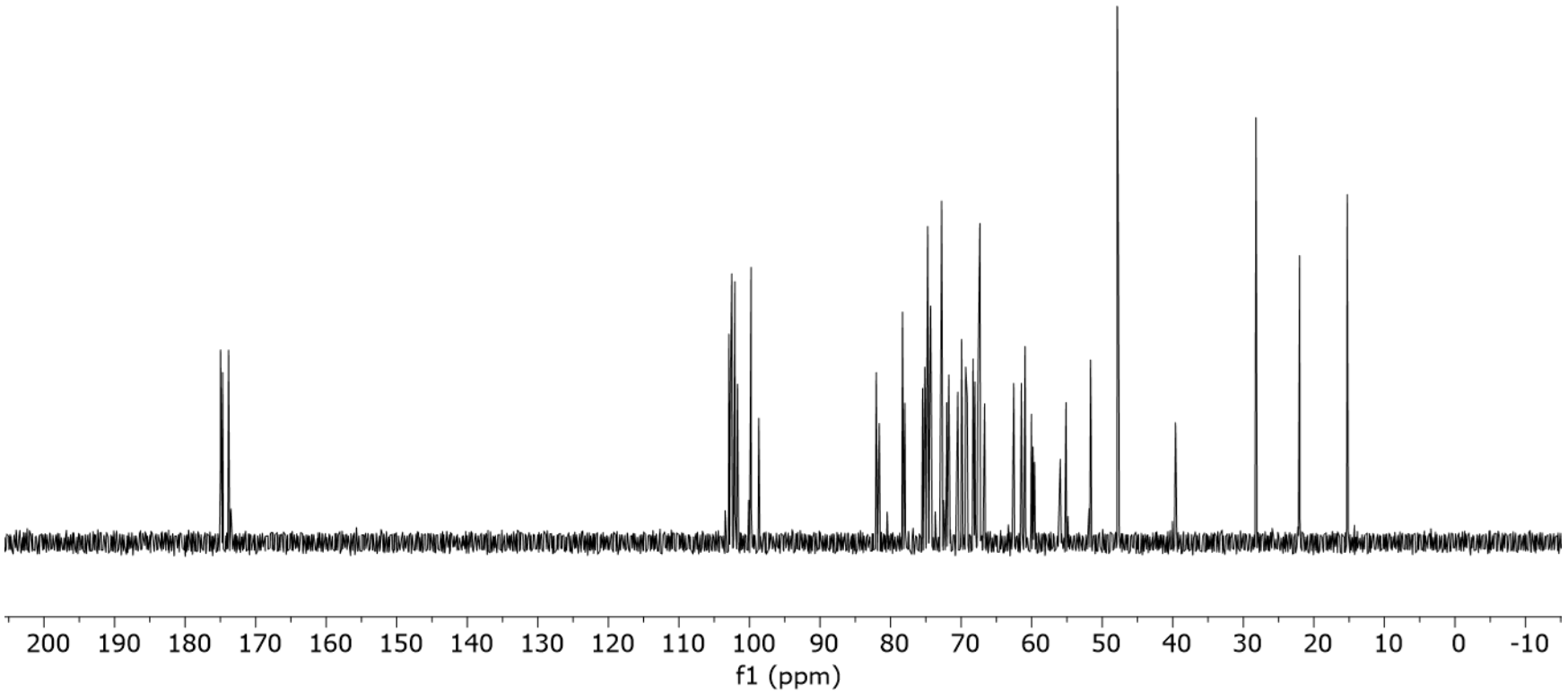
^{13}C NMR of 28


CHZ-1045
1
α3
β4
β3
β4
β3
β4
β
sp
α3
29
HO
OH
HO
AcHN
HO
$^{-}O_2C$
HO
OH
O
OH
HO
NHAc
OH
HO
OH
O
OH
HO
NHAc
OH
HO
OH
O
OH
HO
OH
O
N_3
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)

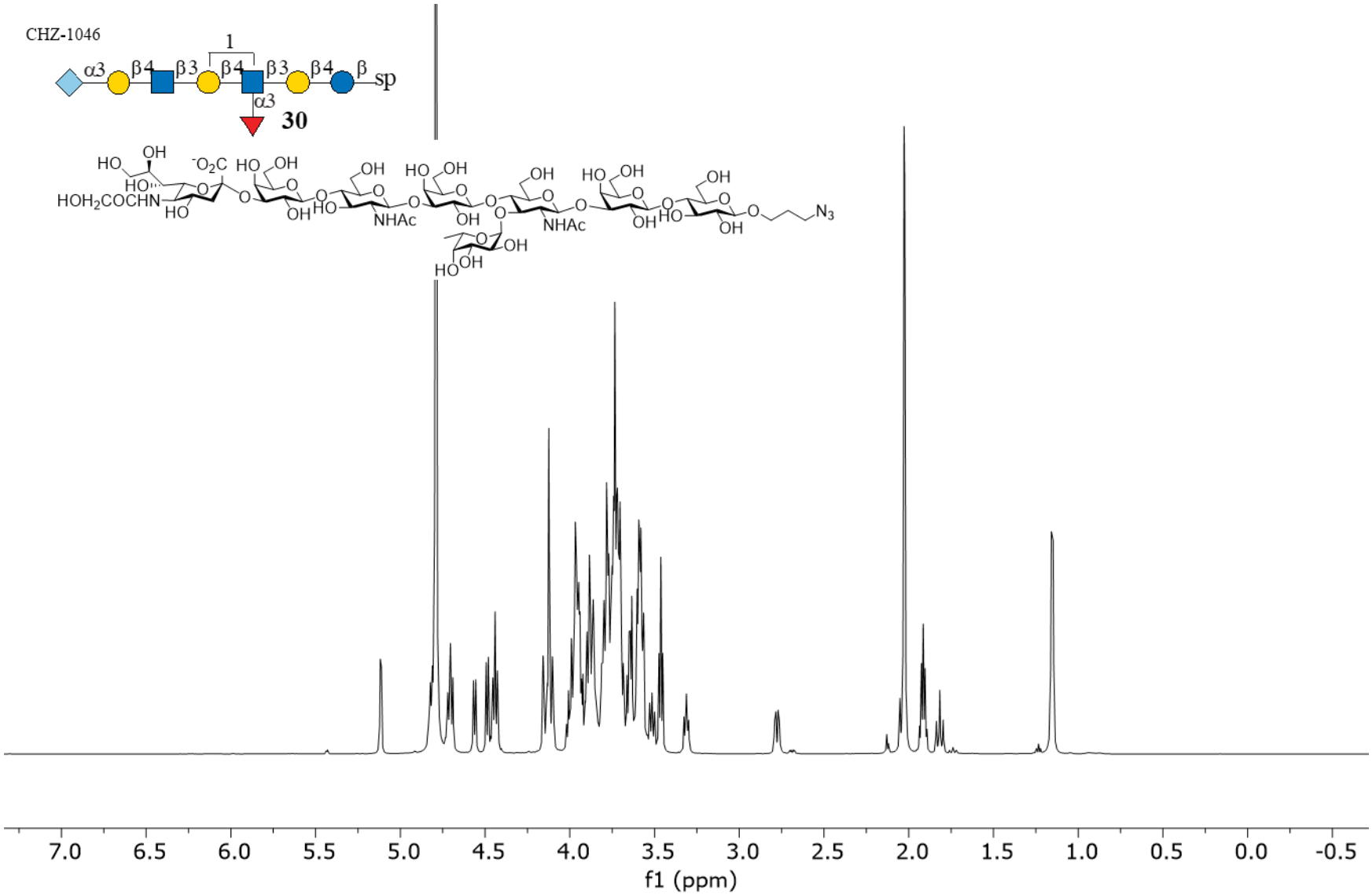
^{1}H NMR of 29



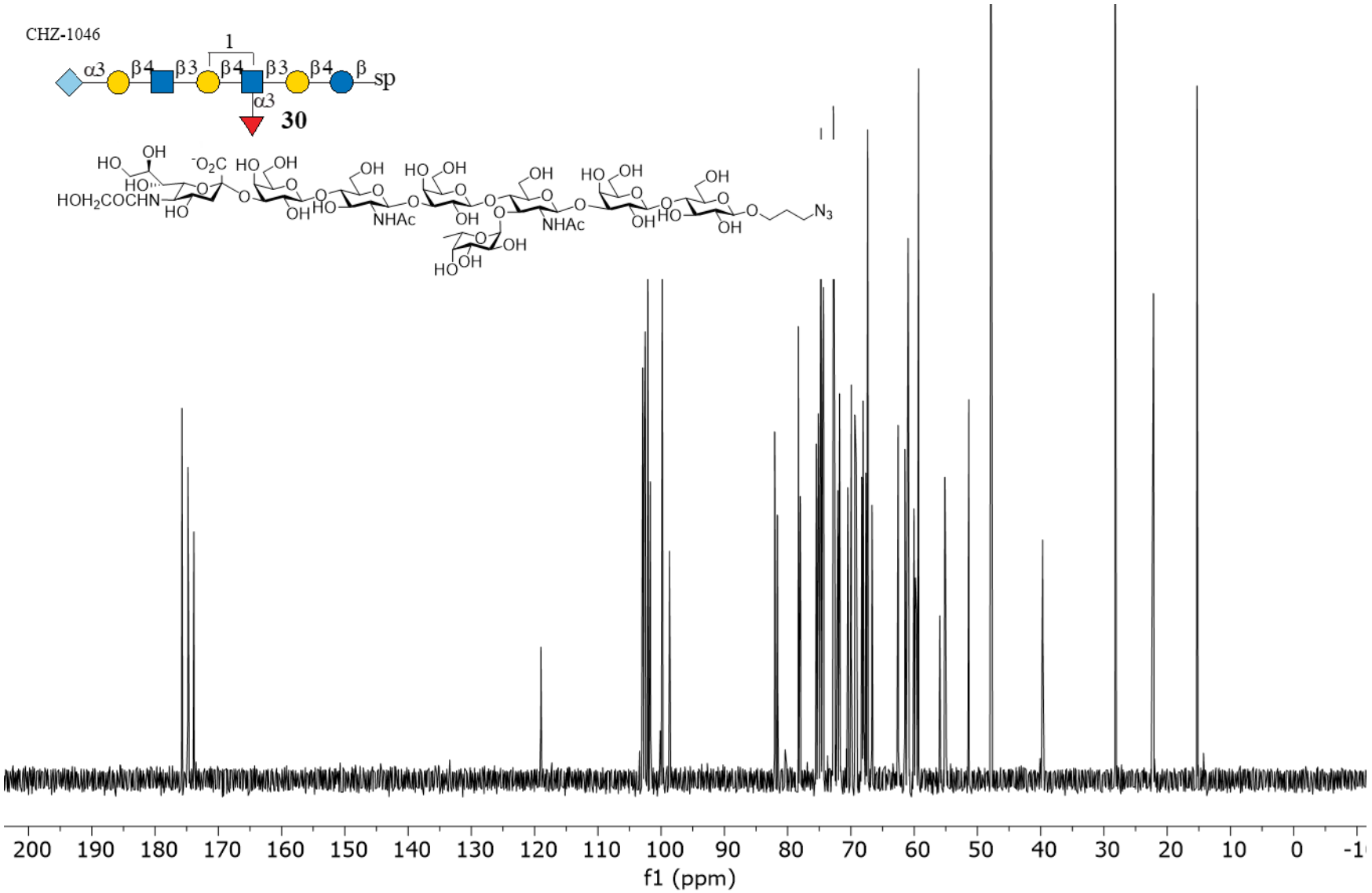
29



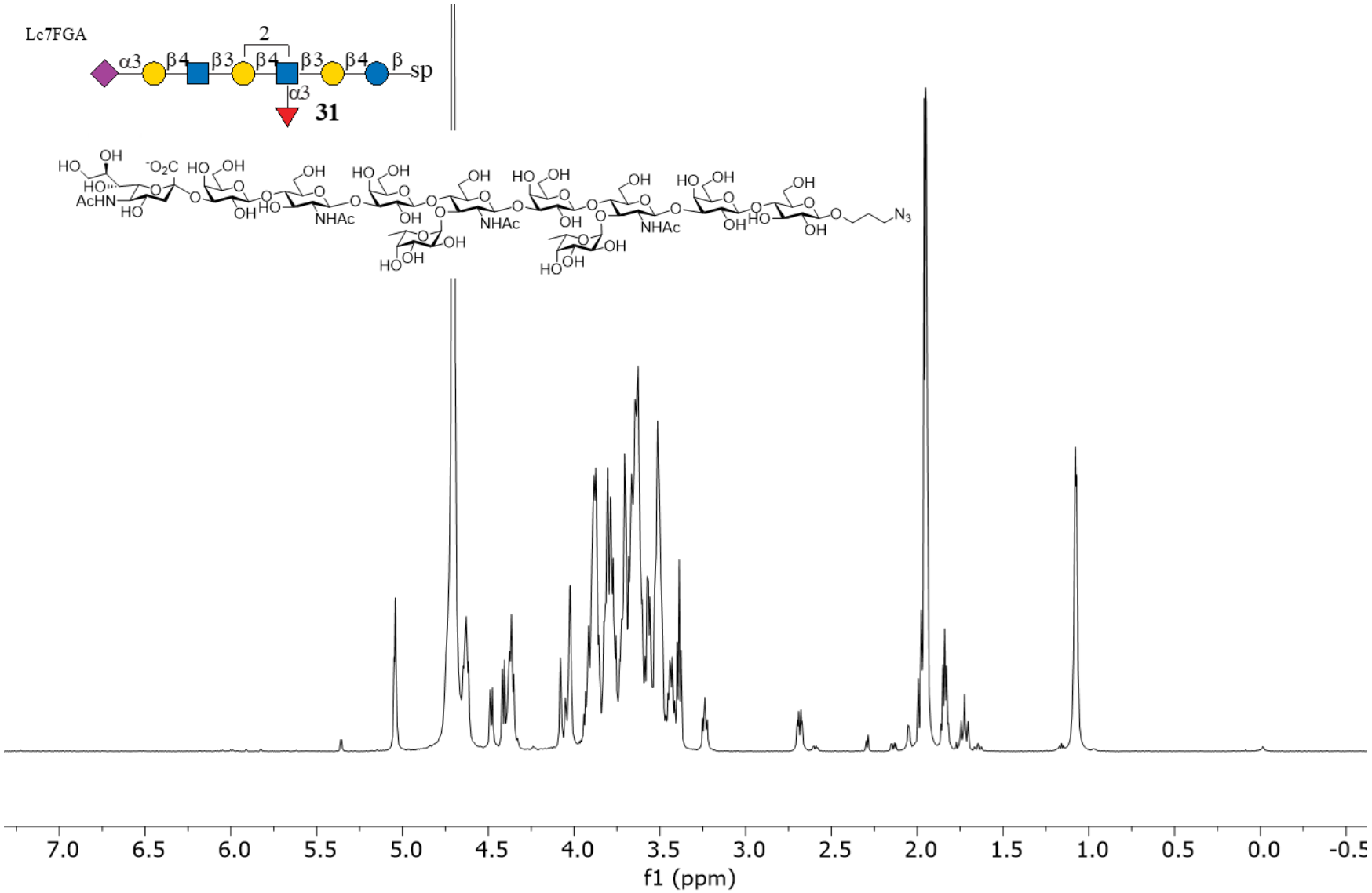
^{13}C NMR of 29


CHZ-1046
1
α3 β4 β3 β4 β3 β4 β sp
α3
30
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)

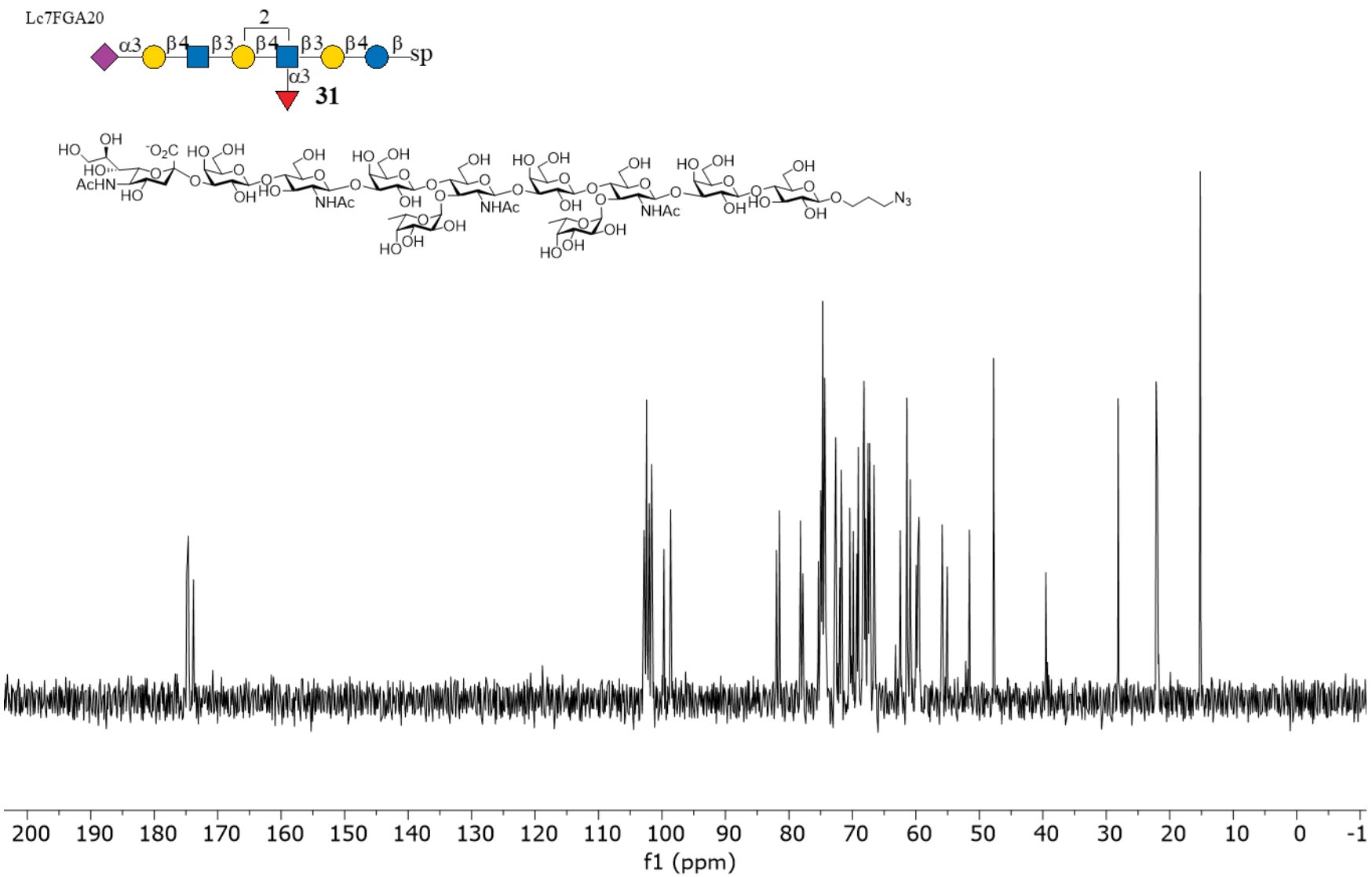
^{1}H NMR of 30


CHZ-1046
α3 β4 β3 β4 β3 β4 β sp
1
α3
30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

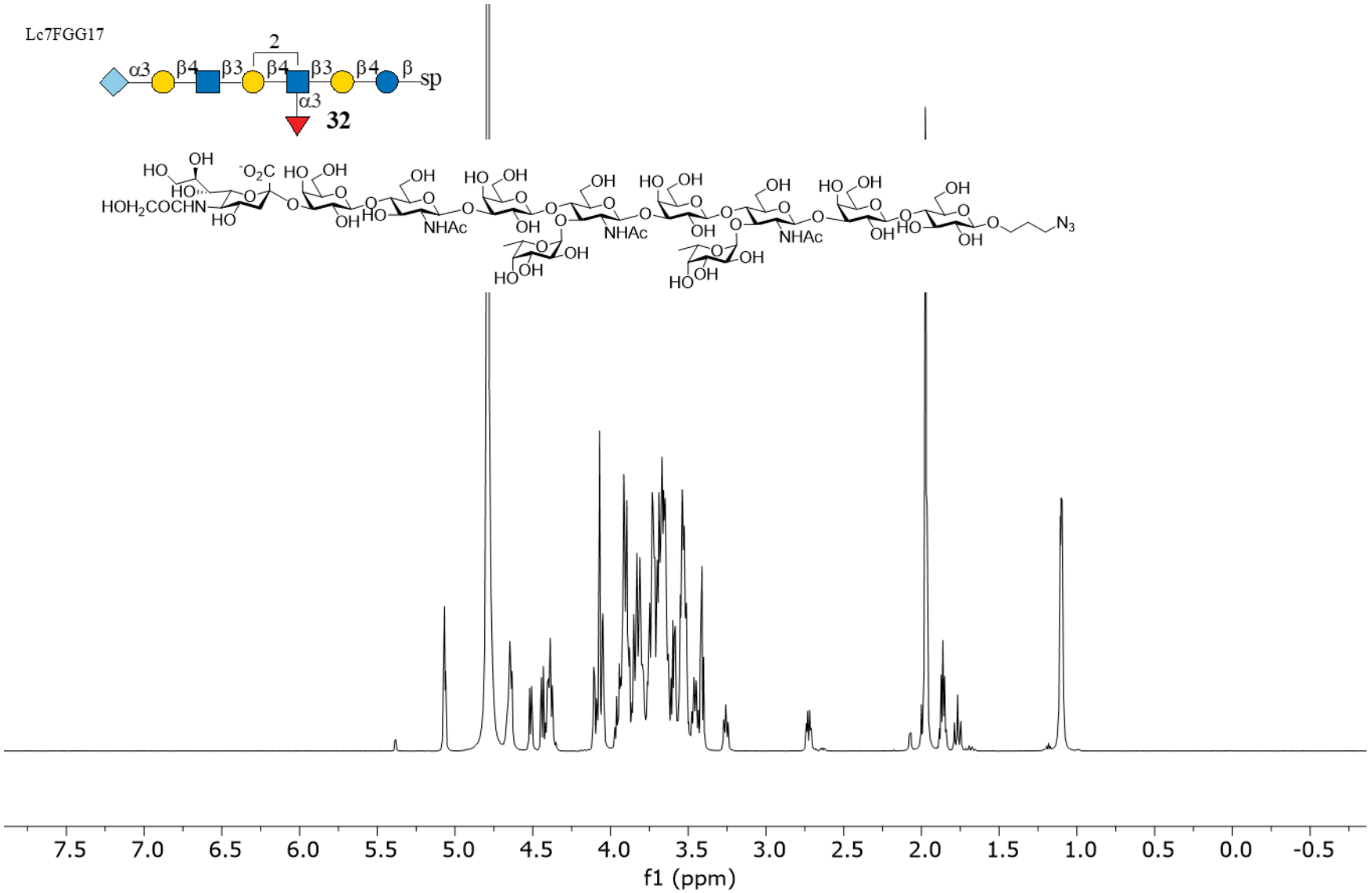
^{13}C NMR of 30


Lc7FGA
α3 β4 β3 β4 β3 β4 β sp
2
α3
31
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)

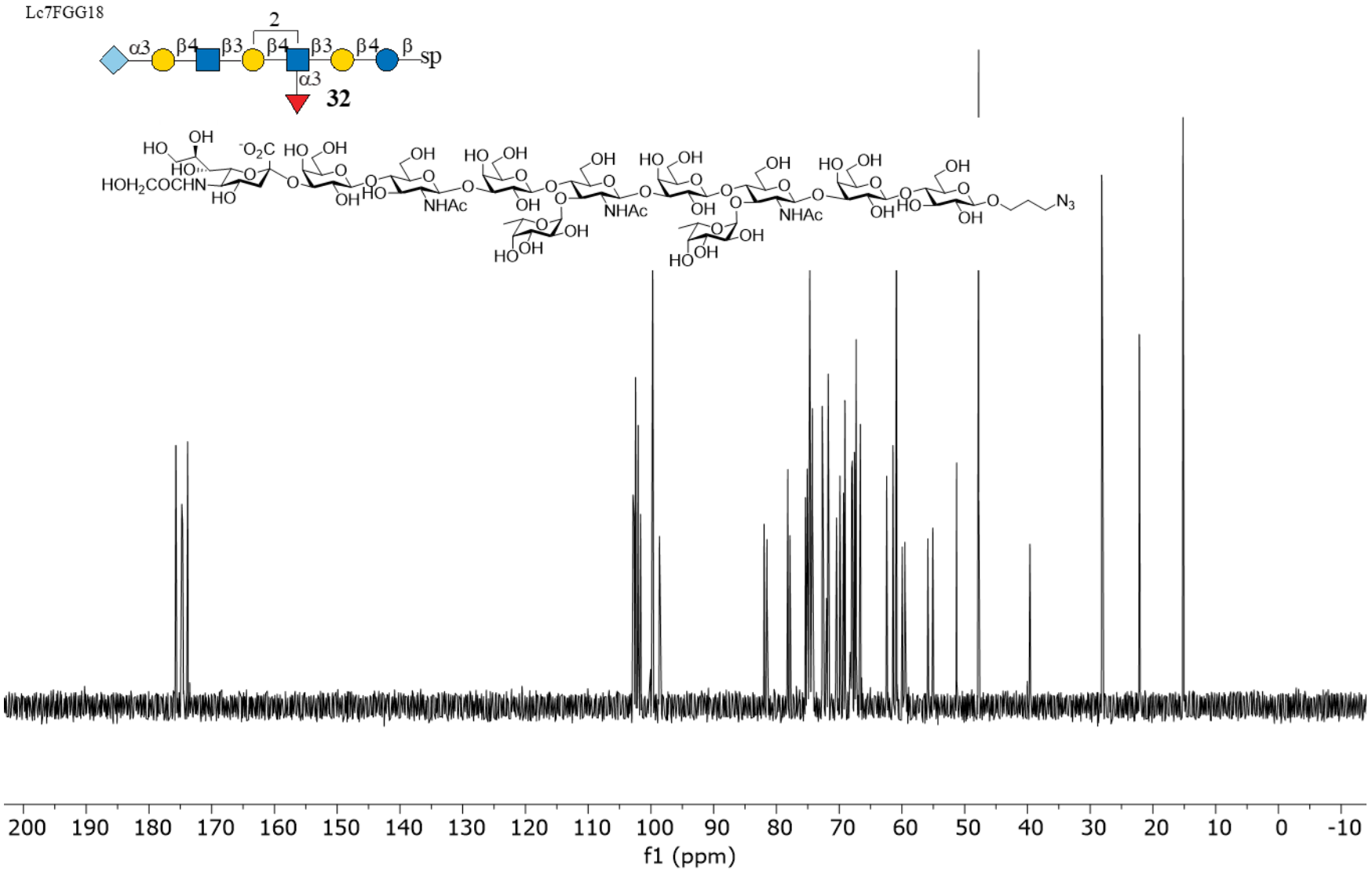
^{1}H NMR of 31


Lc7FGA20
2
α3 β4 β3 β4 β3 β4 β sp
α3
31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

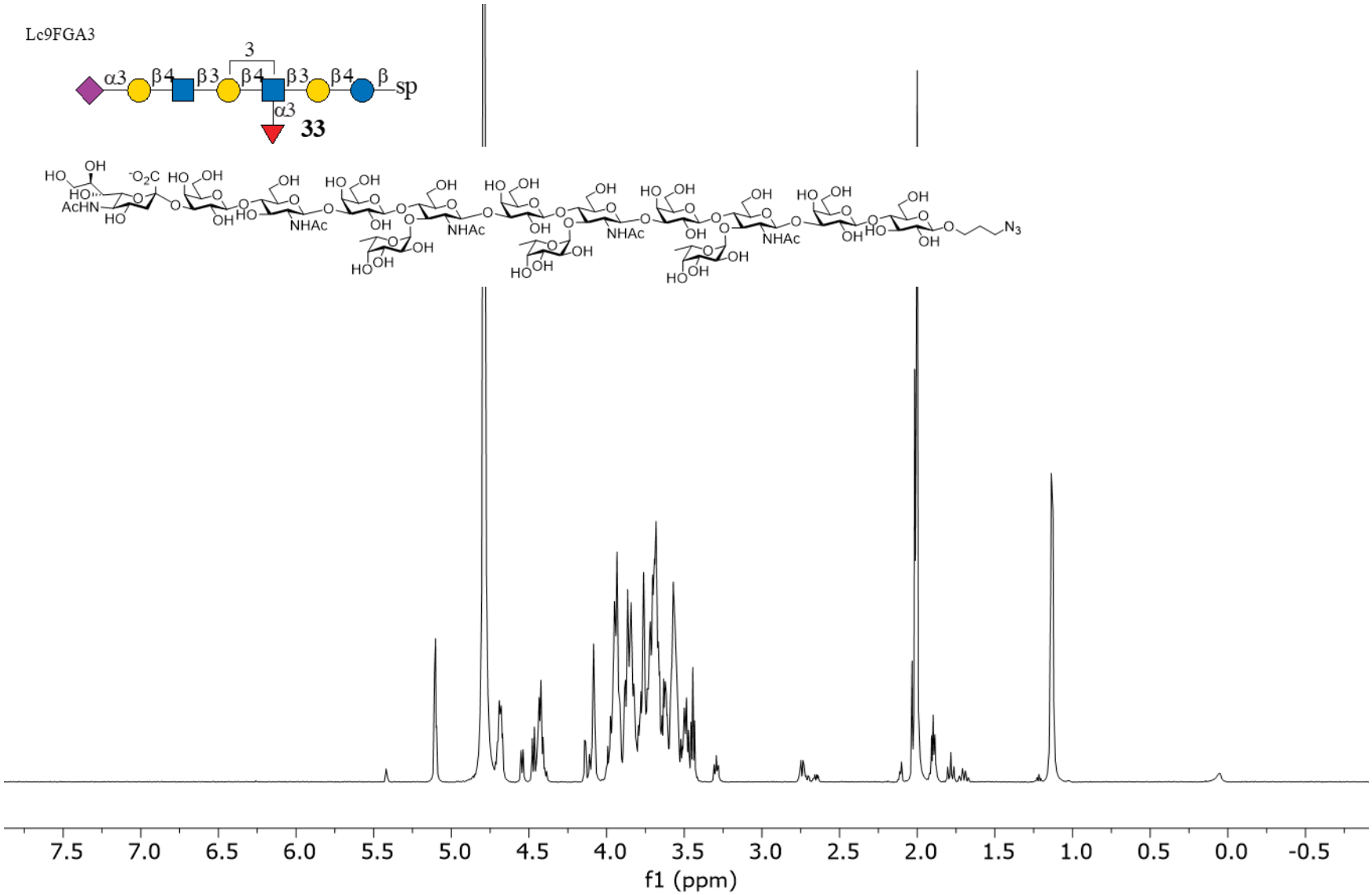
^{13}C NMR of 31


Lc7FGG17
2
α3
β4
β3
β4
β3
β4
β
sp
α3
32
HO
OH
HO
HOH2COCHN
HO
-O2C
HO
OH
O
O
OH
HO
NHAc
OH
HO
OH
O
O
OH
HO
NHAc
OH
HO
OH
O
O
OH
HO
NHAc
OH
HO
OH
O
O
OH
HO
N3
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)

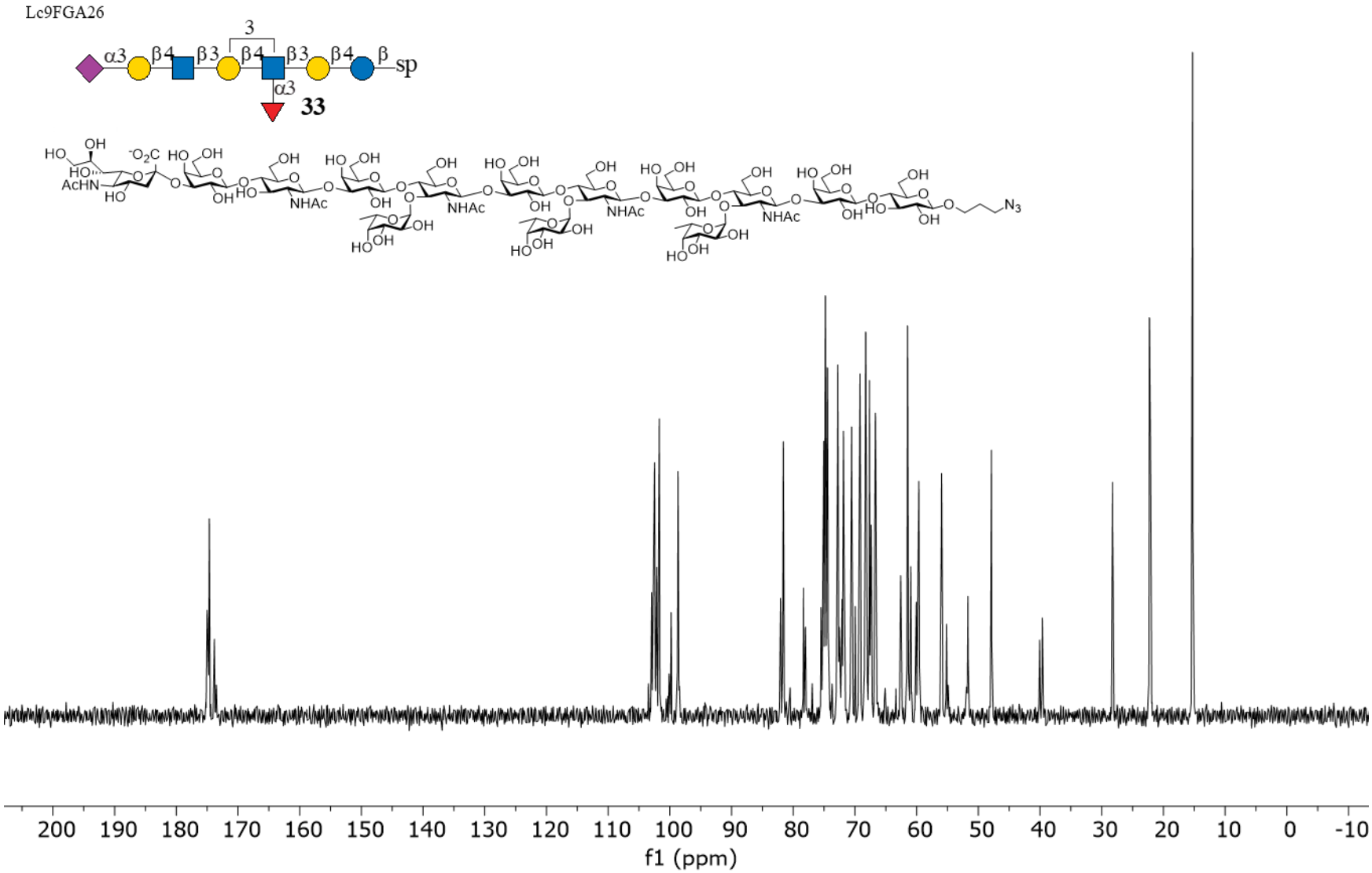
^{1}H NMR of 32


Lc7FGG18
2
α3 β4 β3 β4 β3 β4 β sp
α3
32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

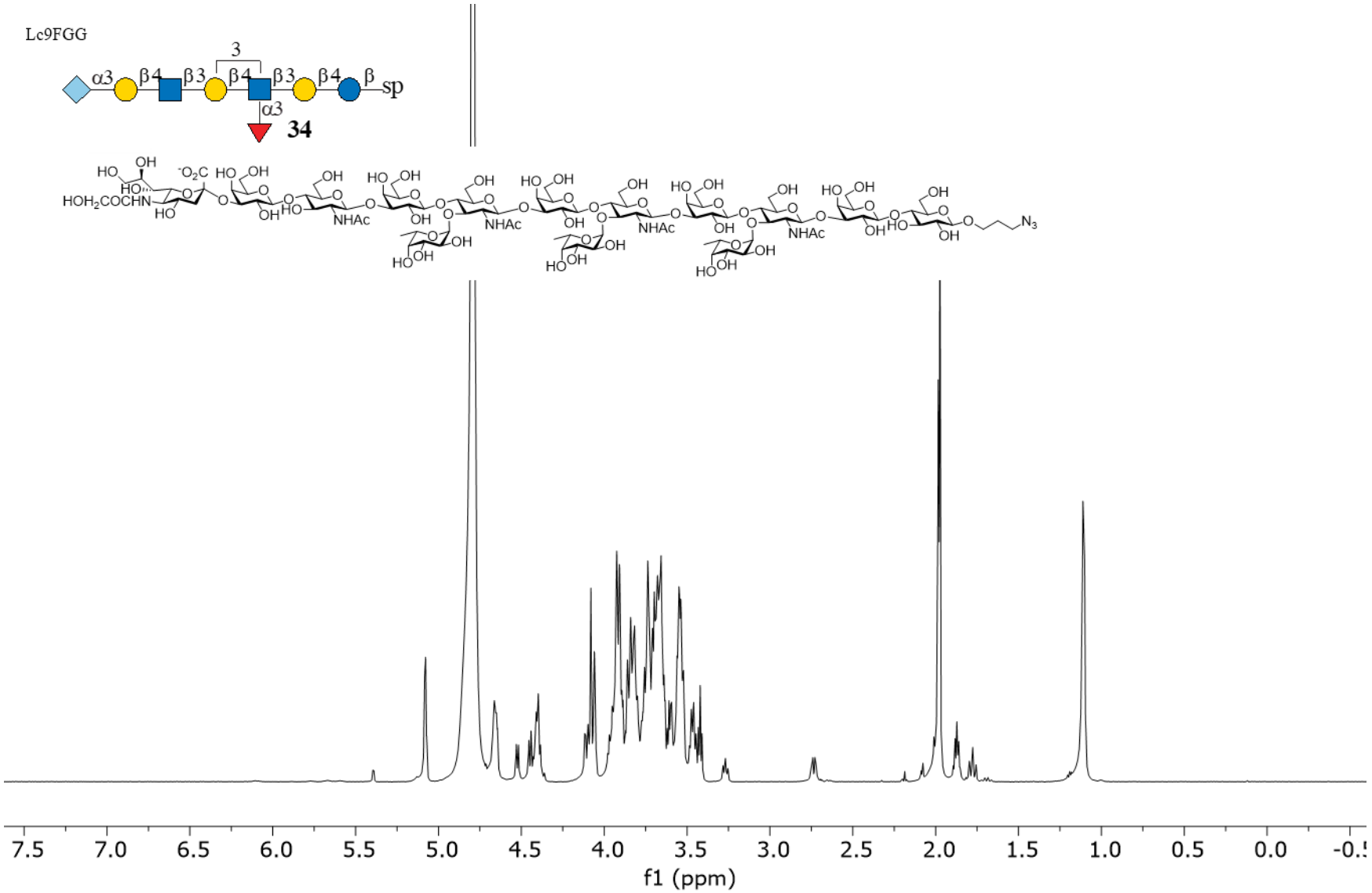
^{13}C NMR of 32


Lc9FGA3
3
α3 β4 β3 β4 β3 β4 β sp
α3
33
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)

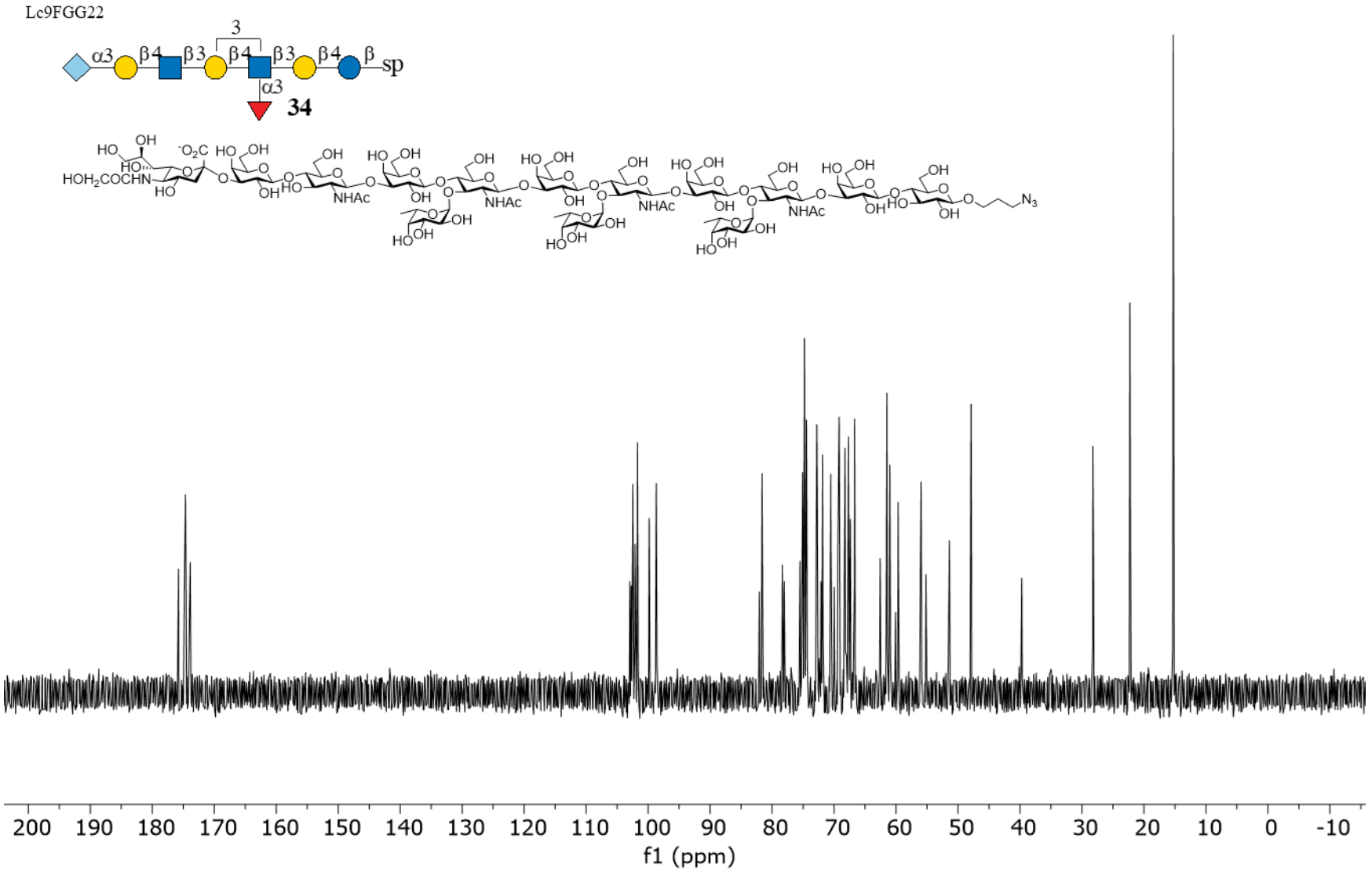
^{1}H NMR of 33


Lc9FGA26
3
α3 β4 β3 β4 β3 β4 β sp
α3
33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

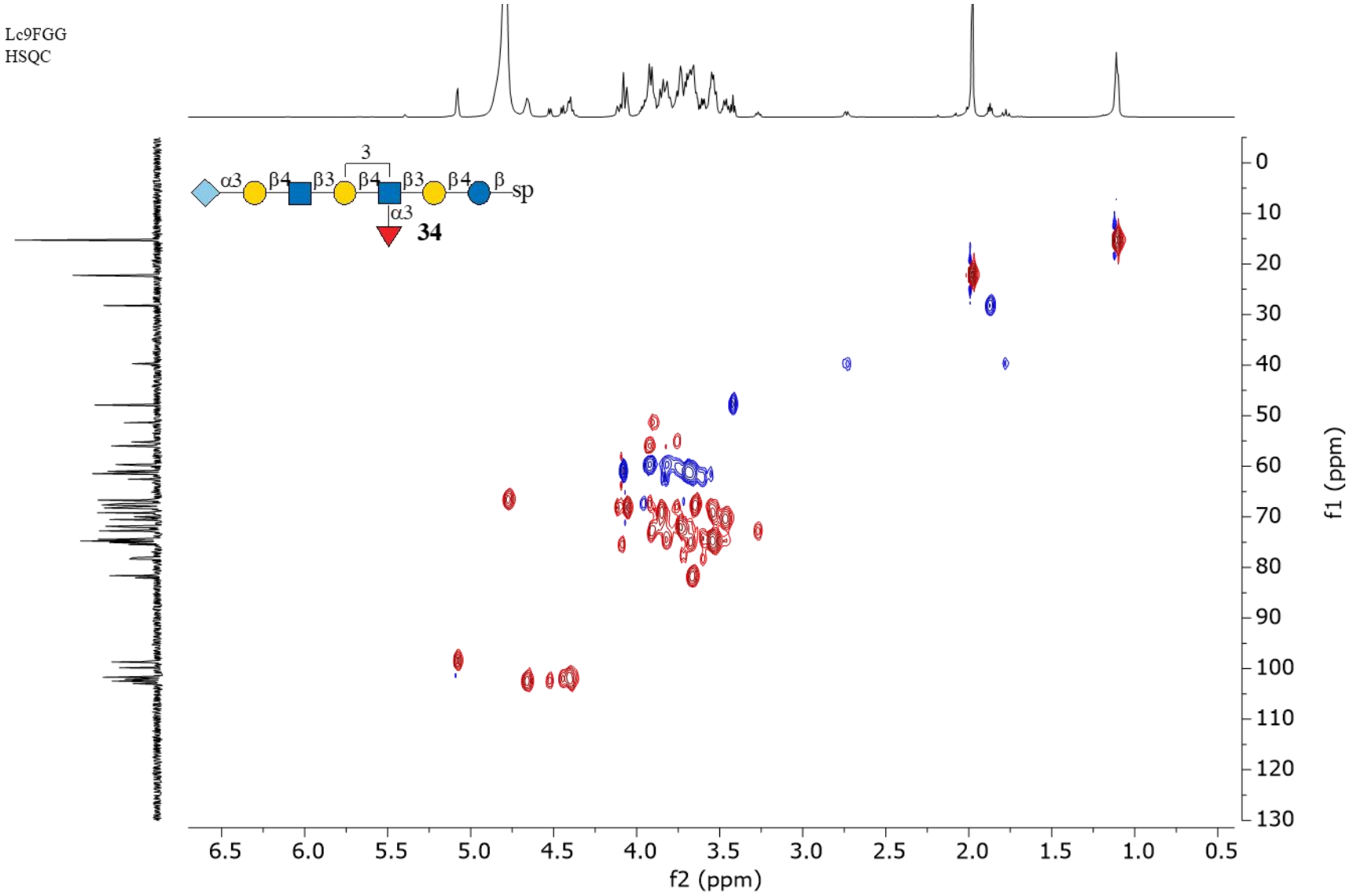
^{13}C NMR of 33


Lc9FGG
α3 β4 β3 β4 β3 β4 β sp
3
α3
34
HO OH
HO
HOH2COCHN
-O2C
NHAc
OH
HO
N3
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)

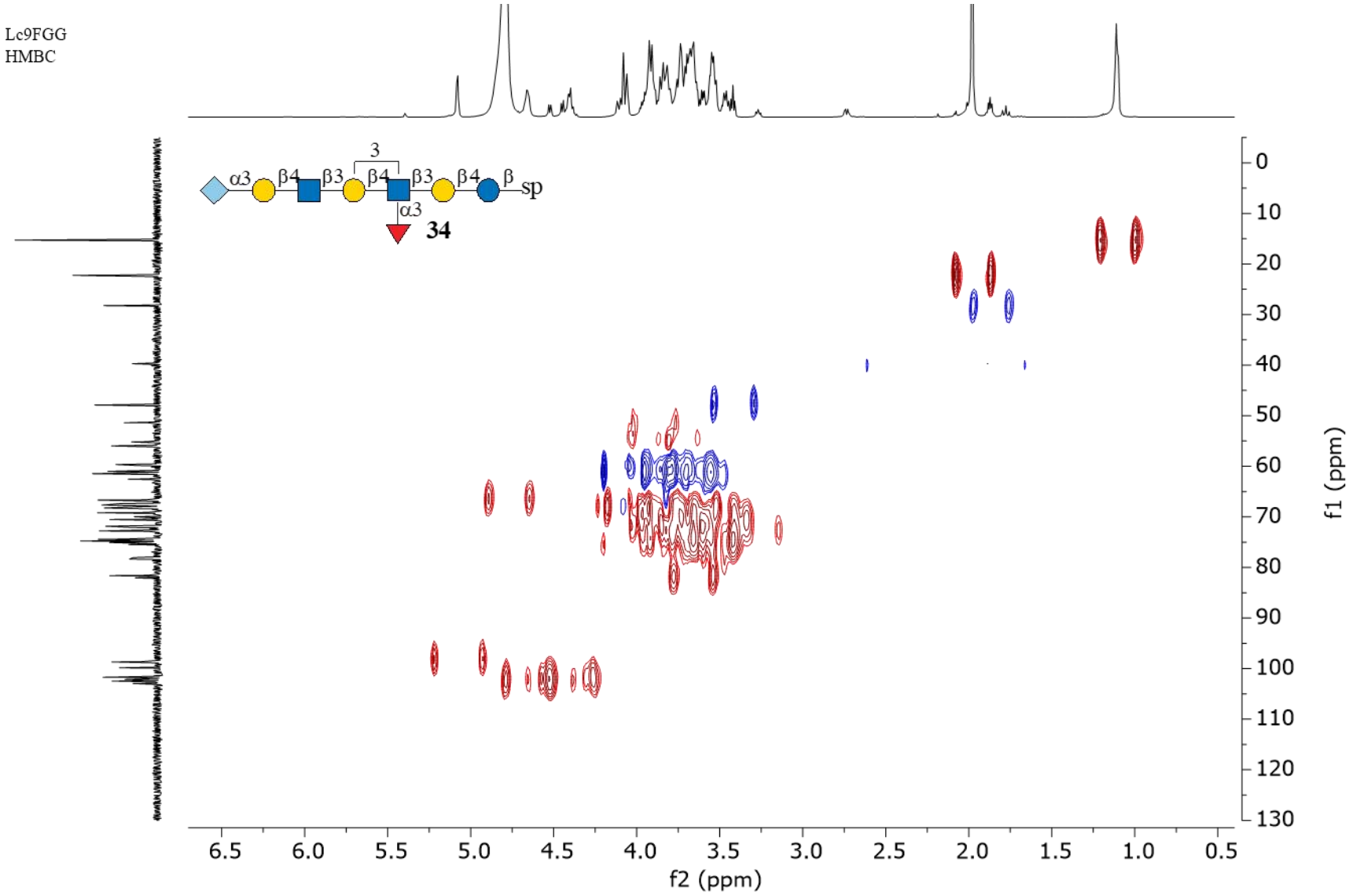
^{1}H NMR of 34


Lc9FGG22
3
α3 β4 β3 β4 β3 β4 β sp
α3
34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{13}C NMR of 34



HSQC NMR of 34



HMBC NMR of 34