Supporting Information for

Enzyme-Sialylation-Controlled Chemical Sulfation of Glycan Epitopes for Decoding the Binding of Siglec Ligands

Shengzhou Ma[1,2,3†], Pengfei Zhang[1,2†], Jinfeng Ye[4†], Yinping Tian[1,2], Xiao Tian[5], Jaesoo Jung[6], Matthew S Macauley[6,7], Jiabin Zhang[1,3,5*], Peng Wu[4*], Liuqing Wen[1,2,3*]

[1]Carbohydrate-Based Drug Research Center, [2]State Key Laboratory of Chemical Biology, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai, 201203, China.

[3]University of Chinese Academy of Sciences, Beijing, 100049, China.

[4]Department of Molecular Medicine, The Scripps Research Institute, La Jolla, CA, 92037, USA.

[5]Zhongshan Institute for Drug Discovery, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Zhongshan, Guangdong, 528400, China.

[6]Department of Chemistry, [7]Department of Medical Microbiology and Immunology, University of Alberta, Edmonton, Alberta T6G 2E1, Canada.

†These authors contributed equally to this work

*Corresponding Author: Email: jiabinzhang@simm.ac.cn (Jiabin Zhang); Email: pengwu@scripps.edu (Peng Wu); Email: lwen@simm.ac.cn (Liuqing Wen).

Table of Contents

1. Figures

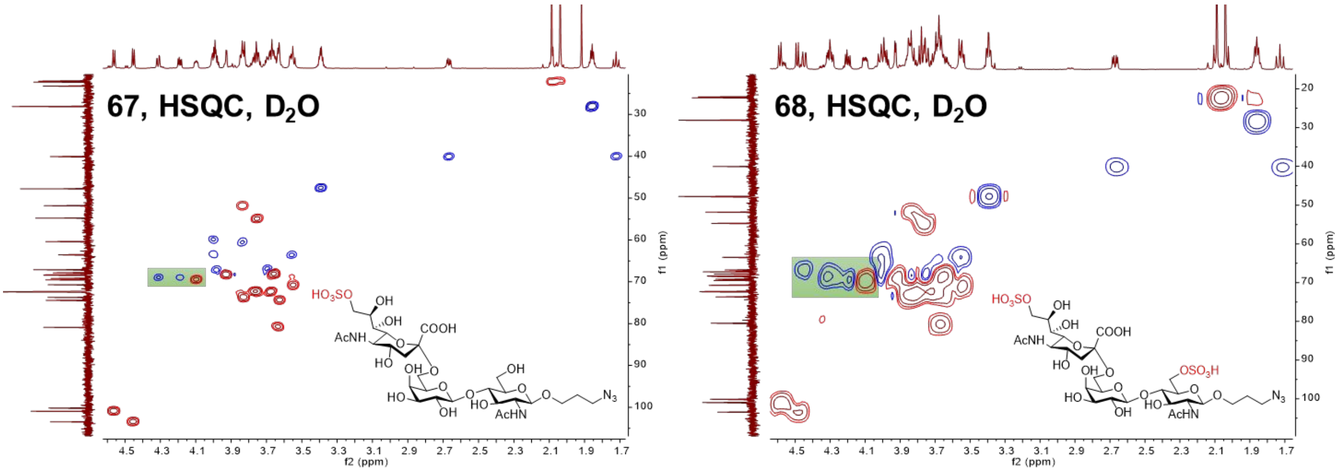


Figure S1 Structure determination of **67** (left) and **68** (right) via HSQC. H-8, H-9a, and H-9b signals of Neu5Ac were marked by a green rectangle on the left picture. A significant downfield shift corresponding to protons of -CH_2OH as new signals occurred at 4.45 ppm and 4.35 ppm compared with compound **67** revealed that the 6-OH of GlcNAc residue of compound **78** was sulfated. The HRMS data of both compounds were collected. For **67**: ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2358. For **78**: ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{25}S_2$, $[M-H]^-$: 916.1929, found 916.1925.

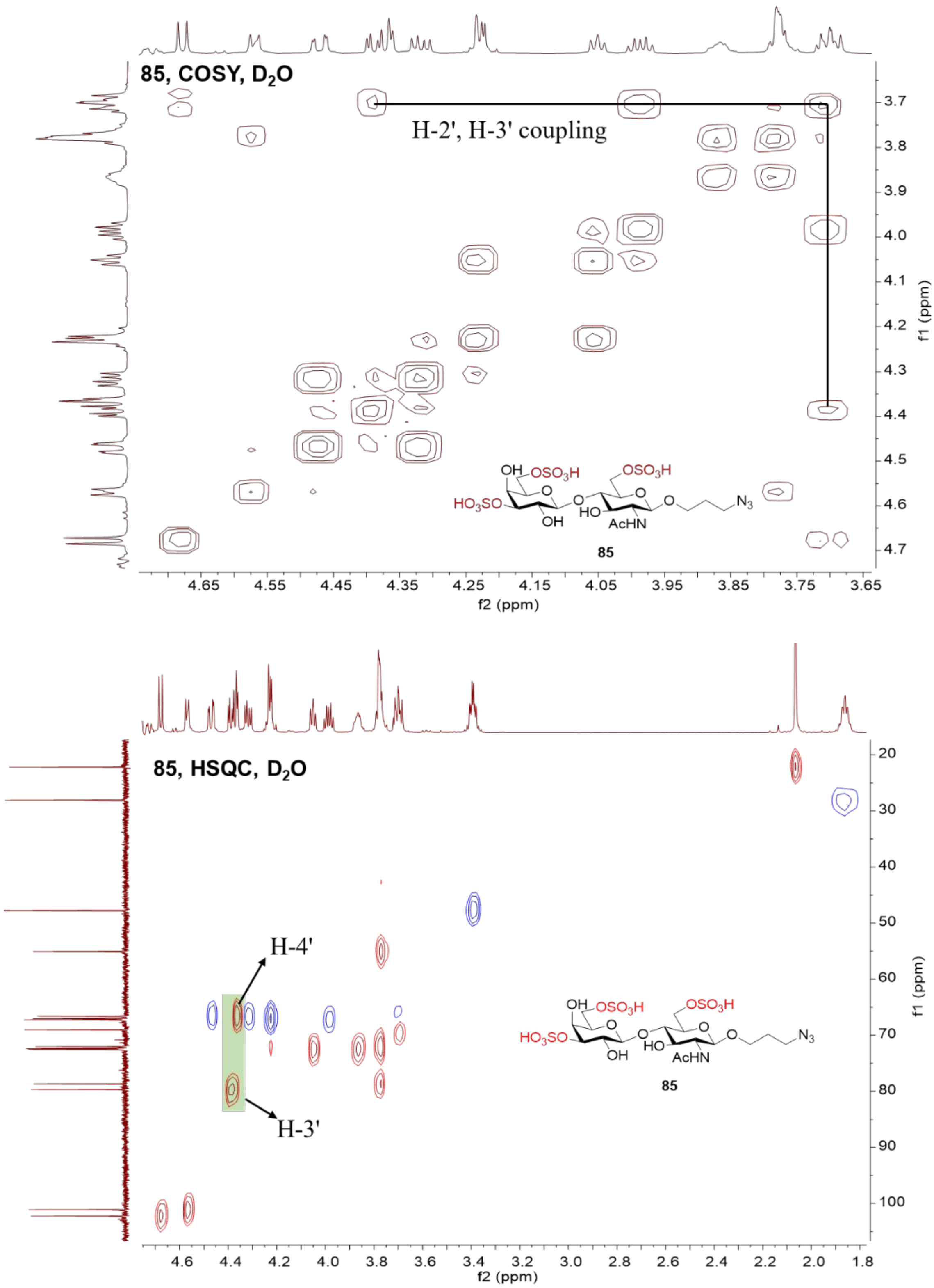


Figure S2 Structure determination of **85** via HSQC. The chemical shift of H-3' was a downfield move to 4.4 ppm, illustrating that electron-withdrawing group -SO$_3$H occurred on the 3'-OH position of Gal residue of **85**. The sulfation of the 3'-OH of Gal has also affected the chemical shift of neighboring H-4' to the downfield shift.

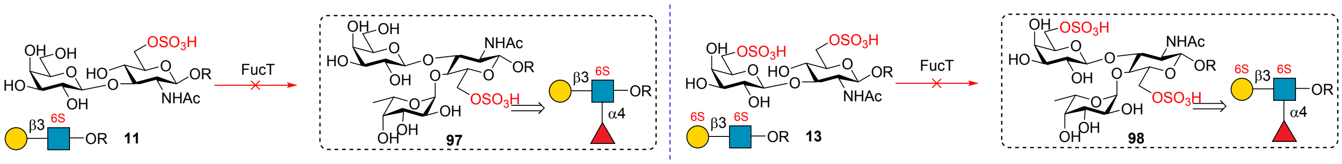


Figure S3 The attempt to synthesize **97** and **98** from **11** and **13** using FucTs is unsuccessful as the FucTs cannot accept **11** or **13** as substrate.

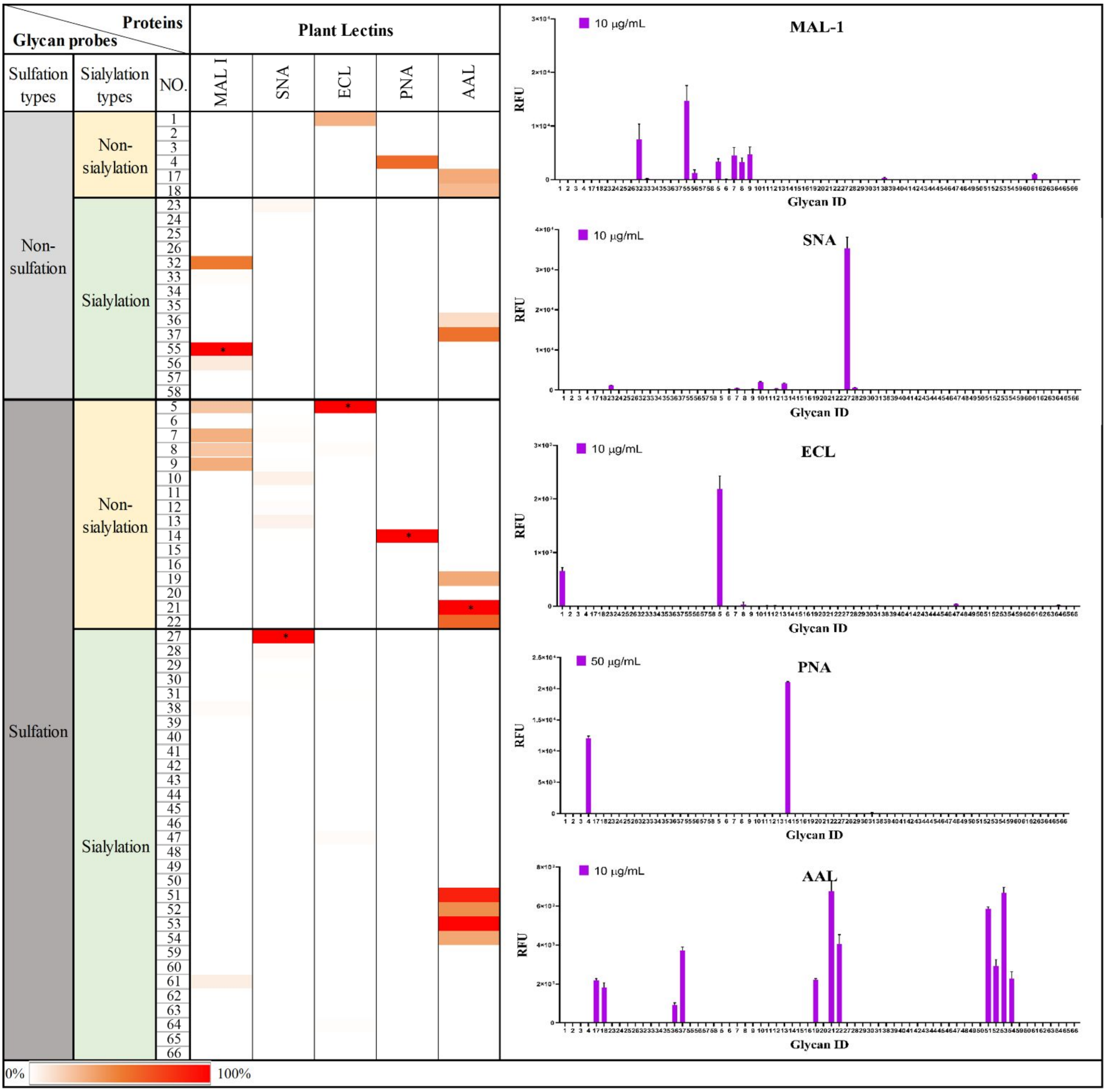
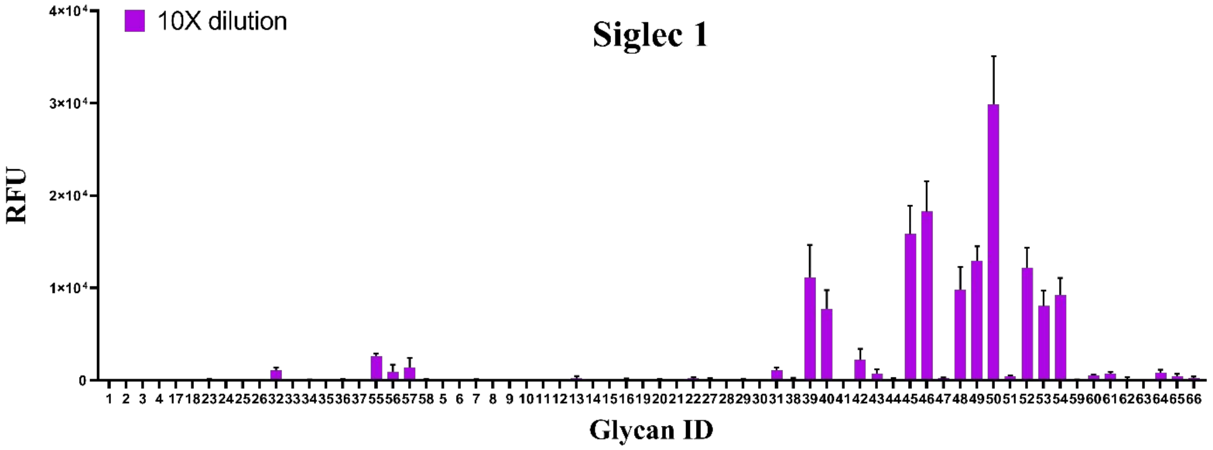
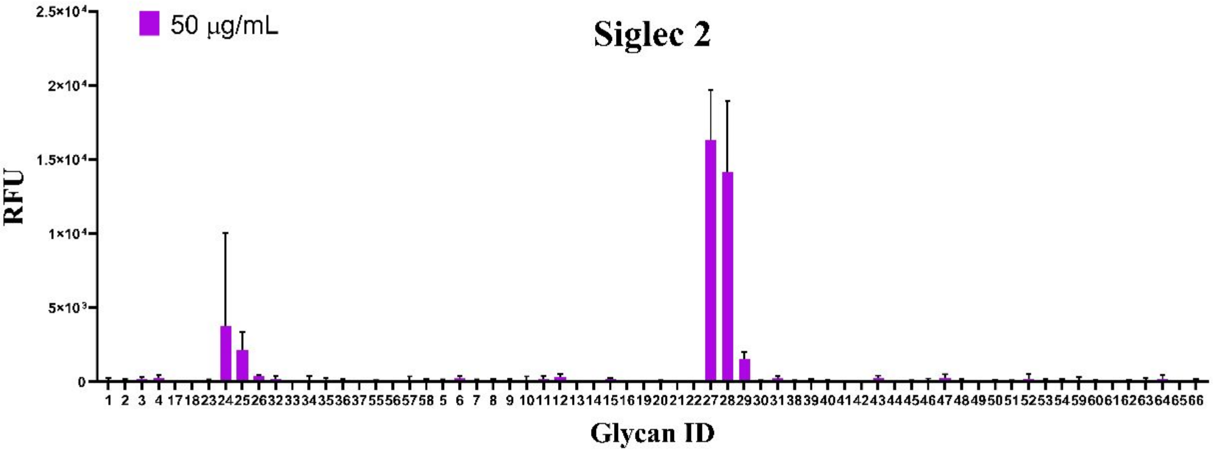
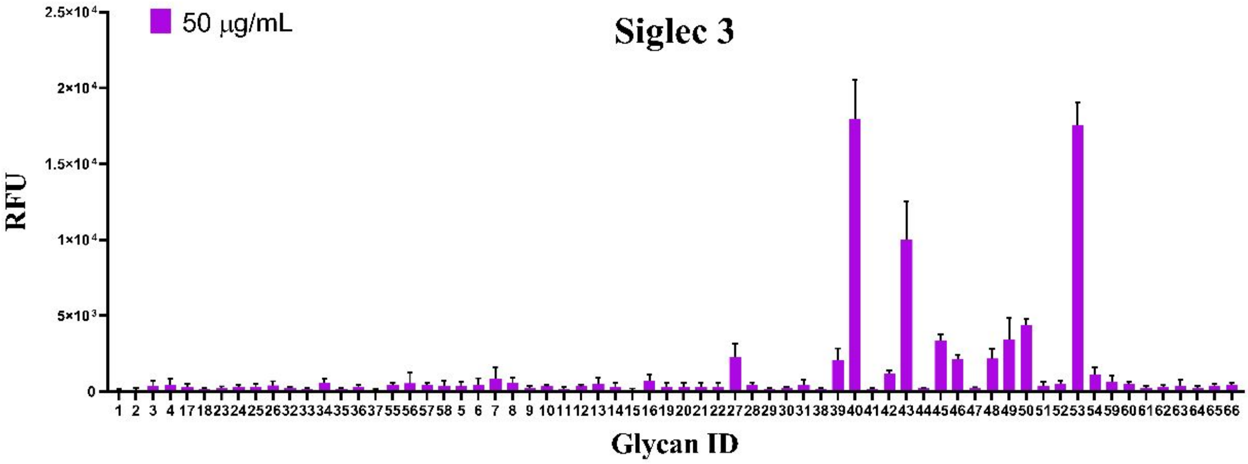
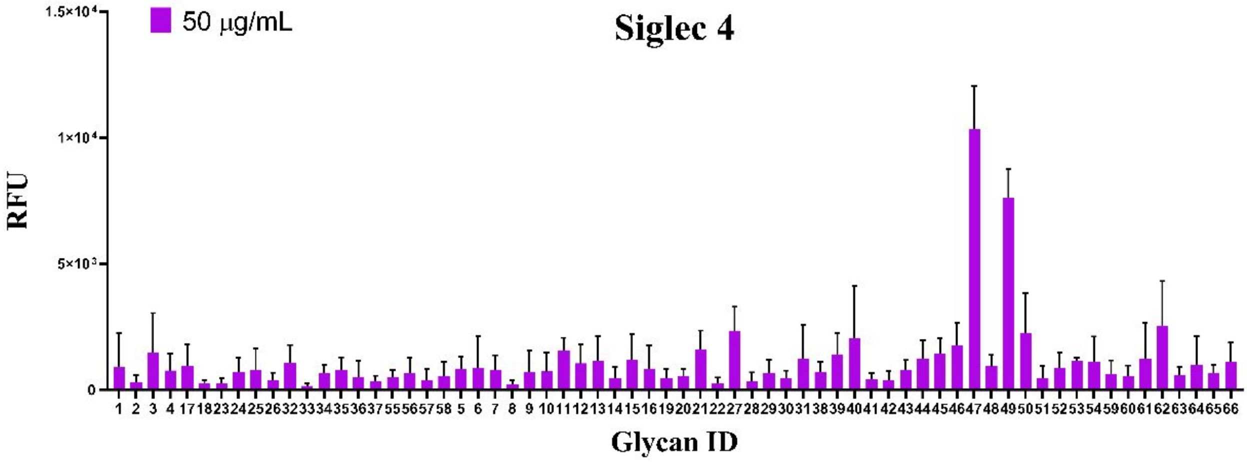


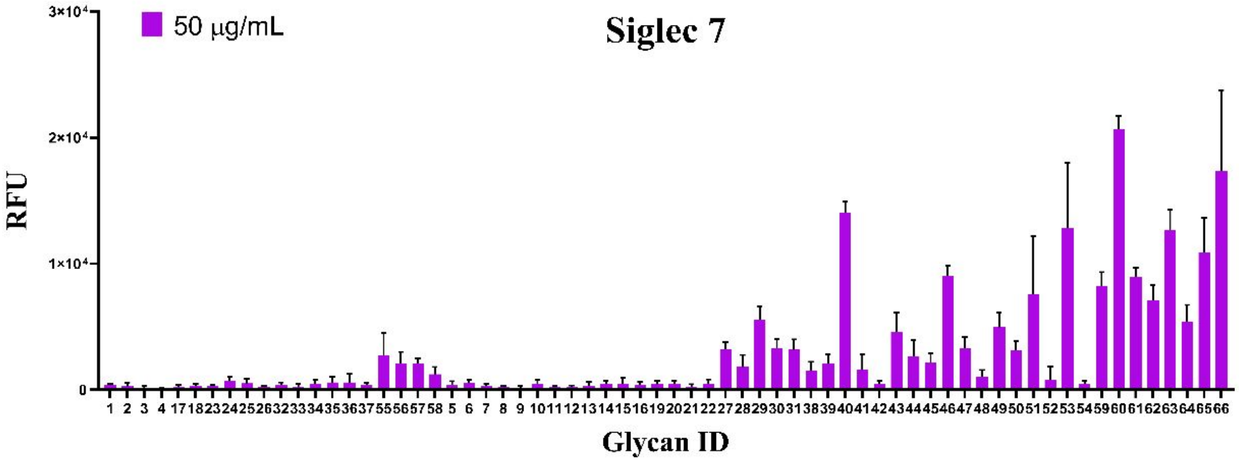
Figure S4 Glycan microarray binding profiles of plant lectins (MAL I, SNA, ECL, PNA, and AAL). Appropriate protein concentrations were applied to screen the microarray. Histogram charts showing fluorescence intensities of binding of 5 plant lectins. Error bars represent the SD of the four values. *The highest relative fluorescence unit of the ligand is defined as 100%.

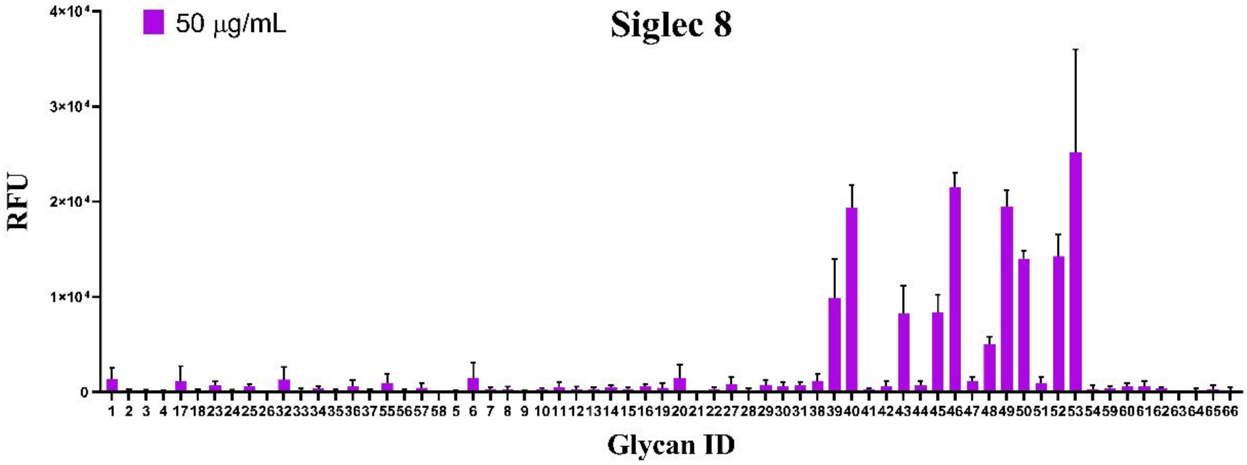

10X dilution
Siglec 1
RFU
4×10⁴
3×10⁴
2×10⁴
1×10⁴
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

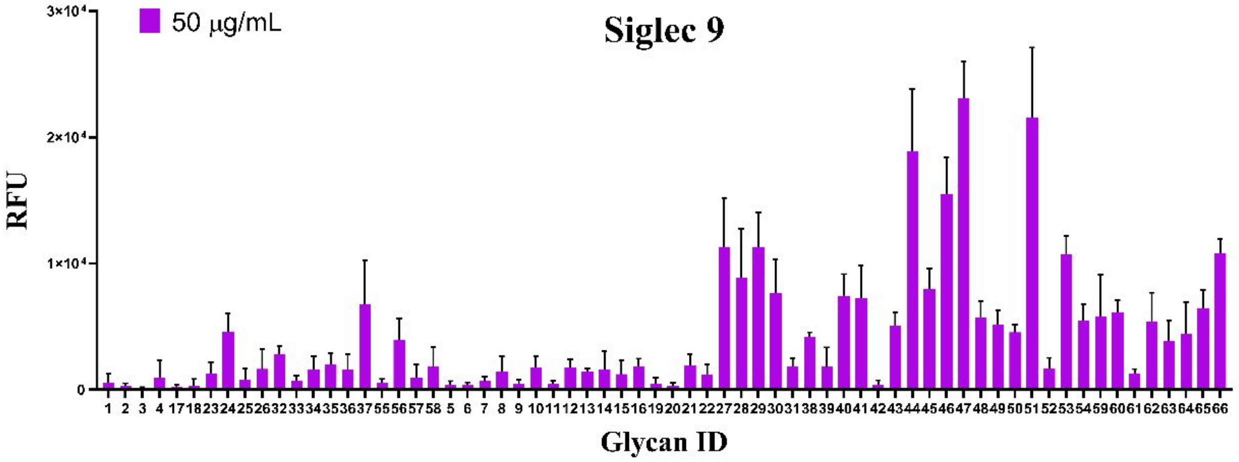

50 μg/mL
Siglec 2
RFU
2.5×10⁴
2×10⁴
1.5×10⁴
1×10⁴
5×10³
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

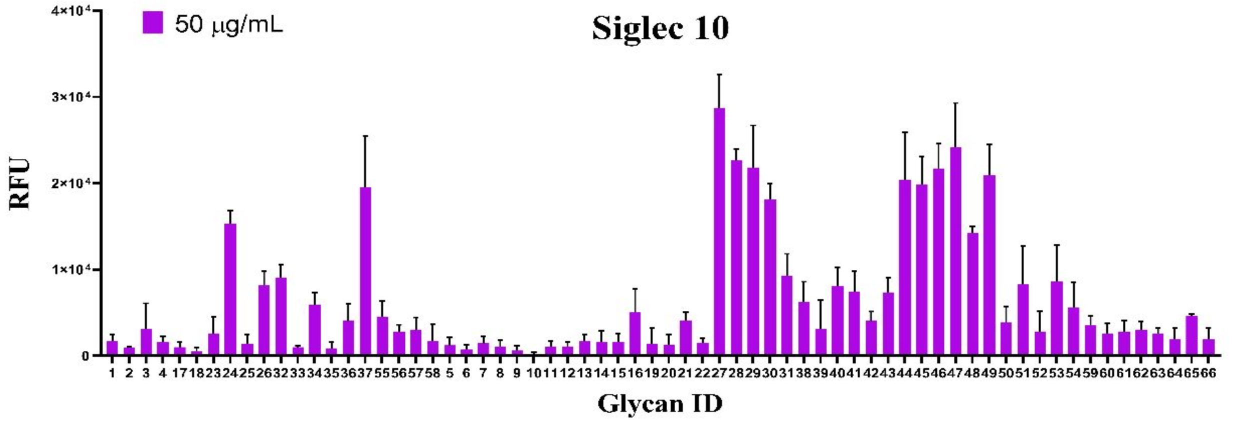

50 μg/mL
Siglec 3
RFU
2.5×10⁴
2×10⁴
1.5×10⁴
1×10⁴
5×10³
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

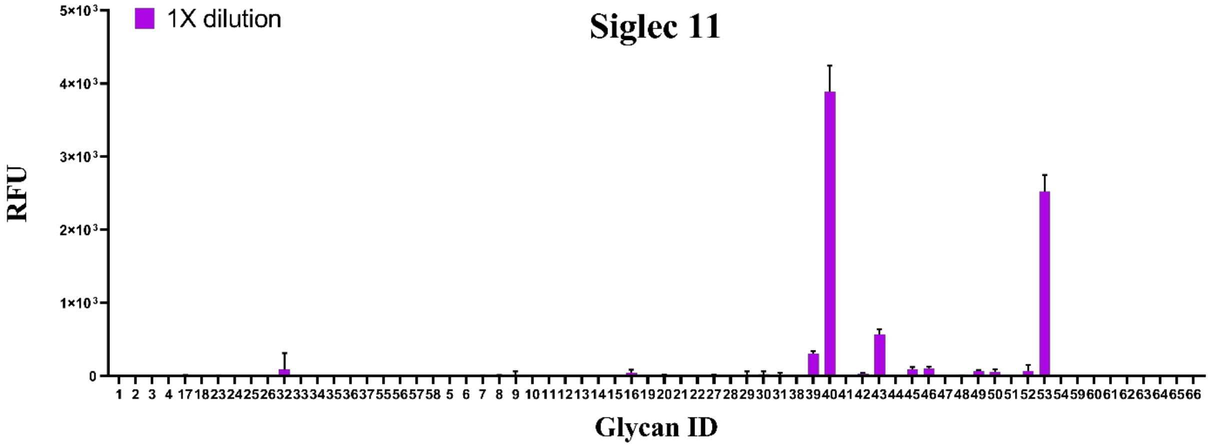

50 μg/mL
Siglec 4
RFU
1.5×10⁴
1×10⁴
5×10³
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID


50 µg/mL
Siglec 7
RFU
3×10⁴
2×10⁴
1×10⁴
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

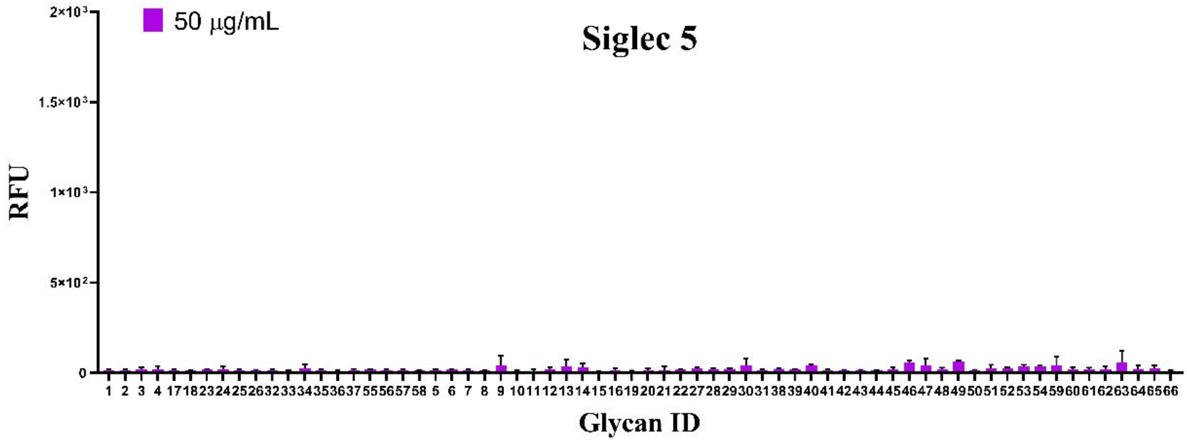

50 µg/mL
Siglec 8
RFU
4×10⁴
3×10⁴
2×10⁴
1×10⁴
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID


50 µg/mL
Siglec 9
RFU
3×10⁴
2×10⁴
1×10⁴
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

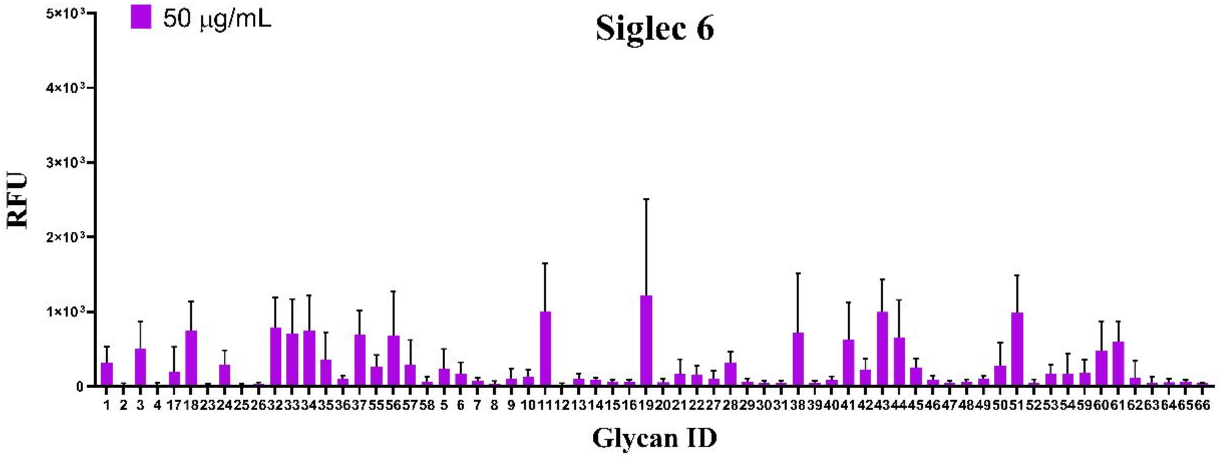

50 µg/mL
Siglec 10
RFU
4×10⁴
3×10⁴
2×10⁴
1×10⁴
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID



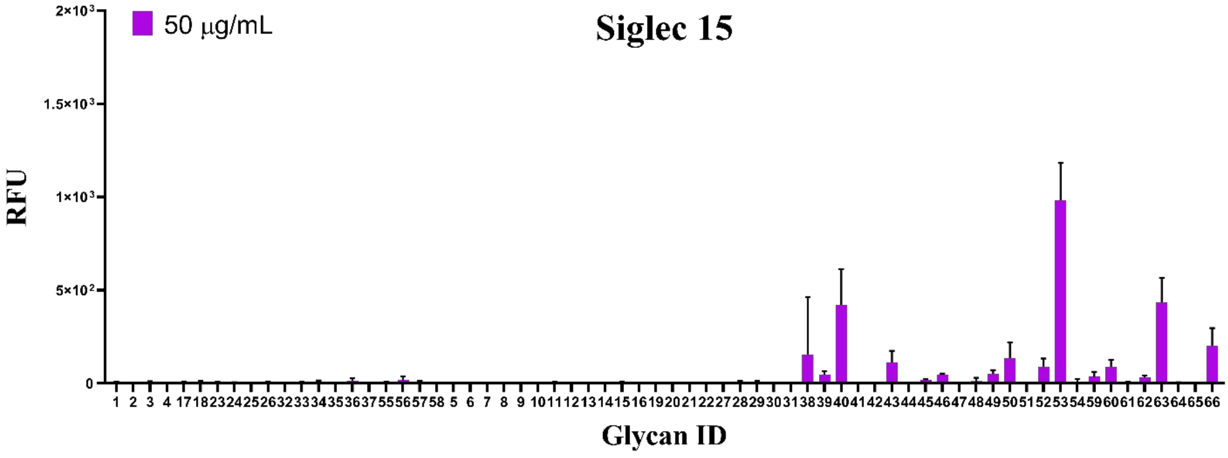
1X dilution
Siglec 11
RFU
5×10³
4×10³
3×10³
2×10³
1×10³
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID



50 μg/mL
Siglec 5
RFU
2×10³
1.5×10³
1×10³
5×10²
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID



50 μg/mL
Siglec 6
RFU
5×10³
4×10³
3×10³
2×10³
1×10³
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID



50 μg/mL
Siglec 15
RFU
2×10³
1.5×10³
1×10³
5×10²
0
1 2 3 4 17 18 23 24 25 26 32 33 34 35 36 37 55 56 57 58 5 6 7 8 9 10 11 12 13 14 15 16 19 20 21 22 27 28 29 30 31 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 59 60 61 62 63 64 65 66
Glycan ID

Figure S5 The histogram charts of the binding of Siglecs in humans. 50 μg/mL protein (Commercial source) concentrations were applied to screen the microarray. Lab-expressed Siglec-1 and -11 were used for screening after diluting ten folds (10X dilution) and one fold (1X dilution) individually. Siglec -1, -2, -3, -4, -7, -8, -9 -10, and -11 presented strong binding affinities with corresponding glycan ligands. Silgec -5, -6, and -15 displayed weak binding with glycans in the library. Error bars represent the SD of the four values. *The highest relative fluorescence unit of the ligand is defined as 100%. These histogram chart results corresponded to the main text's heat map of Fig. 8.

2. Materials and methods

Chemicals and solvents were purchased from Sigma-Aldrich unless otherwise stated and directly used without further purification. Chemical reactions were performed according to standard protocols, and enzymatic reactions were performed in aqueous buffers at an appropriate pH for each enzyme. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates (Merck, MA) using p-anisaldehyde sugar stain and orcinol stain. Unless otherwise noted, all nuclear magnetic resonance (NMR) spectra were acquired on Bruker NMR spectrometer (500 MHz, 600 MHz, or 800 MHz) operating at 25 ℃. Samples were dissolved in 99.96% D_2O, and chemical shifts were referenced to residual HDO signal at 4.79 ppm. Compounds **78**, **80**, **82** and **84** were dissolved in 99.8% CD_3OD to perform the same analysis. Data were collected using standard pulse programs. High-resolution electrospray ionization (ESI) mass spectra were obtained using LC-MS (Thermo HPLC-Orbitrap Elite). Ion-exchange chromatography was performed using a glass column (2.5 cm × 20 cm) packed with anion-exchange resin (Cytiva). Size exclusion chromatography was performed using a glass column (2.5 cm × 80 cm) packed with Bio-Gel P-2 fine resins (Bio-Rad, CA).

NHS-activated glass slides were purchased from Schott Inc. The printer and scanner for the glycan microarray were provided by Shanghai Wayen Biotech. Sugar nucleotides used in this work were prepared as reported previously.[1-3] Biotinylated plant lectins *Maackia amurensis* Lectin I (MAL I), *Sambucus nigra* Lectin (SNA), *Erythrina cristagalli* Lectin (ECL), *Peanut* agglutinin (PNA), and Aleuria Aurantia Lectin (AAL) were purchased from Vector Labs. Human Siglec -2, -3, -4, -5, -6, -7, -8, -9, -10 and -15 proteins (Fc-tag) were purchased from Acro Biosystems. Human Siglic-1, and -11 containing Fc-tag were designed as reported previously [4] and expressed using the HEK293 expression system in our lab. Biotinylated goat anti-Human IgG Fc Antibody and Streptavidin-AlexaFluor® 647 conjugate were purchased from Thermo Fisher Scientific.

CMP-Sialic acid synthetase from *Neisseria meningitides* (NmCSS),[5] α2,6-sialyltransferase from *Photobacterium damsela* (Pd2,6ST),[6] Mutant α2,6-sialyltransferase from *Photobacterium damsela* (M2,6ST),[7] α2,3-sialyltransferase from *Bibersteinia trehalosi* (BtST),[8] α2,3-sialyltransferase from *Photobacterium phosphoreum* (PPST),[9] α2,3/8-sialyltransferase from *Campylobacter jejuni* (CST II),[10] sialidase from *Streptococcus penumoniae*[11] and α1,3/4-fucosyltransferases from *Helicobacter pylori* (NCTC 11369 and UA948),[12] were prepared as reported previously.[13-16] In detail, *E. coli* BL21 (DE3) cells harboring recombinant vector pET-28a were cultured in two liters of Luria−Bertani (LB) medium containing 50 μg/ml kanamycin in a rotary shaker at 37°C, 200 rpm. 0.2 mM of IPTG was added until OD was 0.8, and then protein expression was allowed to proceed at 16 °C overnight. The cells were harvested by centrifugation at 7000 rpm for 10 min. The cell precipitation was re-suspended in lysis buffer (50 mM Tris-HCl buffer, 300 mM NaCl, 10 mM imidazole; pH 7.5). Cells were disrupted by a microfluidizer and the lysate was centrifuged at 12,000 g for 10 minutes to remove the cell debris. The His-tagged proteins were purified by using a Ni-NTA agarose column. Before purification, the column was equilibrated with the lysis buffer (50 mM Tris-HCl, 300 mM NaCl, 10 mM imidazole; pH 7.5). The column was washed with 2 column volumes of the lysis buffer and eluted with elution buffer (50 mM Tris-HCl, 300 mM NaCl, 300 mM imidazole; pH 7.5). Protein concentration was determined by the BCA Protein Assay Kit.

3. Experimental procedures

General procedure for the installation of α2, 6-Neu5Ac using One-pot multi-enzymes (OPMEs) strategies. Acceptor (1.0 eq), Neu5Ac (1.5 eq), and CTP (2 eq) were dissolved at a final acceptor concentration of 20 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 20 mM $MgCl_2$. Appropriate amounts of NmCSS and sialyltransferase (Pd2,6ST or M2,6ST) were successively added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing the product were collected and concentrated to give products. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing products were collected and loaded into the P-2 column again to remove the sodium chloride to afford products.

General procedure for the installation of α2, 6-9-N_3-Neu5Ac using One-pot multi-enzymes (OPMEs) strategies. Acceptor (1.0 eq), 9-N_3-Neu5Ac[44] (1.5 eq) and CTP (2 eq), were dissolved at a final acceptor concentration of 20 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 20 mM $MgCl_2$. Appropriate amounts of NmCSS and sialyltransferase (Pd2,6ST or M2,6ST) were successively added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing products were collected and concentrated to give products. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.

General procedure for the sulfation of substrates and hydrolyzation of α2, 6-9-N_3-Neu5Ac by NanA. Substrate (1 eq) was dissolved in a mixed solution of DMF and TEA (9:1, *V: V*). SO_3/Py (8 eq) was then added under the ice bath. The reaction was stirred for 15 min at 0 ℃ and then continued to stir at r.t. for 1-2 h to achieve complete conversion. Monitoring reaction by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction after complete conversion. After purification by size-exclusion and ion-exchange column, the sulfated product was directly concentrated and dissolved at a final concentration of 10 mM in NaOAc buffer (50 mM, pH = 6.5), to solution add NanA (0.1 mg/mmol substrate) and incubated overnight at 37°C. Monitoring reaction by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column again to remove the sodium chloride to afford the product.

General procedure for the installation of TBDMS groups and hydrolyzation of 9-TBS-O-Neu5Ac by NanA. Substrate (1 eq) was dissolved in pyridine, and TBDMSCl (10 eq) was added to the above solution with an ice bath. The reaction was stirred for 15 min at 0℃ and then continued to stir at r.t. for 1-2 h to drive it to completion. TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*) monitors reaction. After the reaction finished, Et_3N was dropped into the reaction, and methanol was added to quench the reaction. The resulting solution was concentrated and diluted with water, washed with diethyl ether (×2), and the aqueous phase was concentrated to yield a crude product. The crudes were subsequently dissolved at a final concentration of 10 mM in NaOAc buffer (50 mM, pH = 6.5), added NanA (0.1 mg/mmol substrate), and incubated overnight at 37°C. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. Resulted solution was centrifuged, and the supernatant was concentrated and purified by reverse phase (C18) column chromatography (Phase A: 10 mM ammonium bicarbonate aqueous buffer; Phase B: Acetonitrile. 50%-70% of phase B gradient elution) to afford the product.

General procedure for the sulfation of substrates and removal of TBDMS group. Substrate (1 eq) was dissolved in a mixed solution of DMF and TEA (1:1, *V: V*). SO_3/Py (4 eq) was then added under an ice bath. The reaction was stirred for 15 min at 0 ℃ and then continued to stir at 40 ℃ for 3-4 h to achieve complete conversion. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction after complete conversion. Subsequently, the mixed solution was directly concentrated and dissolved in water with 10 mg/mL of final concentration. The pH was adjusted to 3.0 using 1 M AcOH aqueous, and the resulting solution was stirred for 30 min at r.t. to perform the deprotection of the TBDMS group. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Once the reaction was finished, the pH of the mixture solution was neutralized utilizing 1 M NaOH aqueous to 7, and then the final solution was concentrated and purified by size-exclusion (P-2 gel) column utilizing DI water as eluent. The fractions containing products were collected and concentrated to give products. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column again to remove the sodium chloride to afford the sulfated product. Note: The detailed synthetic protocols of compounds **6**, **9**, **12**, **15**, **20**, and **22** were described in the individual glycan synthetic section to ensure the production of the fewest C-3 OH sulfated by-products.

General procedure for the installation of α2, 3-9-N_3-Neu5Ac using One-pot multi-enzymes (OPMEs)

strategies. Acceptor (1.0 eq), 9-N_3-Neu5Ac (1.5 eq), and CTP (2 eq) were dissolved at a final acceptor concentration of 20 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 20 mM $MgCl_2$. Appropriate amounts of NmCSS and sialyltransferase (BtST or PPST) were successively added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing products were collected and concentrated to give products. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.

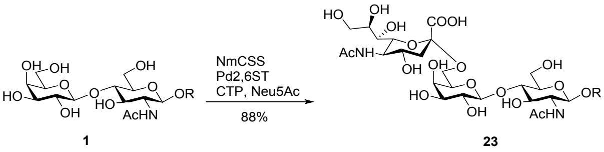
General procedure for the di-sulfation of substrates and hydrolyzation of α2, 3-9-N_3-Neu5Ac by NanA. Substrate (1 eq) was dissolved in a mixed solution of DMF and Py (1:1, *V: V*). SO_3/Py (15 eq) was then added under the ice bath. The reaction was stirred for 1h at 0 ℃ to achieve complete conversion. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, v/v). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction after complete conversion. Subsequently, the mixed solution was directly concentrated and dissolved at a final concentration of 10 mM in NaOAc buffer (50 mM, pH = 6.5), to solution add NanA (0.1 mg/mmol substrate) and incubated overnight at 37°C. Monitoring reaction by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing products were collected and concentrated to give products. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.

General procedure for the synthesis of fucosylated glycan backbones. Acceptor (1 eq) GDP-Fuc (1.5 eq) were dissolved at a final acceptor concentration of 10 mM in a tris-HCl buffer (100 mM, pH 7.5) containing 10 mM $MgCl_2$. Appropriate amounts of FucT were added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing the product were collected and concentrated to give the product. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product. For the purification of compounds **94** and **99** that containing the TBDMS group, The resulting solution was centrifuged and the supernatant was concentrated and purified by reverse phase (C18) column chromatography (Phase A: 10 mM ammonium bicarbonate aqueous buffer; Phase B: Acetonitrile. 50%-70% of phase B gradient elution) to afford the product. (**Notes:** Glycan **6**, **7**, **11**, **12**, and **13** were also performed using the fucosylated procedure, but the reactions failed.)

General procedure for the α2, 6-sialylation of sulfated glycan backbones. Acceptor (1 eq) and CMP-Neu5Ac (1.5 eq) were dissolved at a final acceptor concentration of 10 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 5 mM $MgCl_2$. Appropriate amounts of sialyltransferase (Pd2,6ST) were added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing the product were collected and concentrated to give the product. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.

General procedure for the α2, 3-sialylation of glycan backbones. Acceptor (1 eq) and CMP-Neu5Ac (1.5 eq) were dissolved at a final acceptor concentration of 10 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 5 mM $MgCl_2$. Appropriate amounts of sialyltransferase (BtST or PPST) were added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing the product were collected and concentrated to give the product. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.

General procedure for the installation of α2, 8-Neu5Ac using CST Ⅱ. Acceptor (1 eq) and CMP-Neu5Ac (1.5 eq) were dissolved at a final acceptor concentration of 10 mM in a tris-HCl buffer (100 mM, pH 8.5) containing 5 mM $MgCl_2$. Appropriate amounts of sialyltransferase (CST Ⅱ) were added to the reaction solution. The reaction mixture was incubated at 37°C and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, *v/v*). Once the reaction finished, the reaction was quenched by adding an equal volume of cold ethanol. The solution was centrifuged, and the supernatant was concentrated and purified using a size-exclusion (P-2 gel) column utilizing DI water as an eluent. The fractions containing the product were collected and concentrated to give the product. If needed, further purification was performed by ion-exchange column by gradient elution using sodium chloride solution (0-500 mM). The fractions containing the product were collected and loaded into the P-2 column to remove the sodium chloride to afford the product.



Synthesis of 23

23 was prepared from **1**[17] using sialyltransferase Pd2,6ST according to the general procedure in the methods and was the white solid after lyophilization (1.4 g, yield 88%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{48}N_5O_{19}$, $[M-H]^-$: 758.2938, found 758.2935.

^1H NMR (600 MHz, D_2O): δ (ppm)

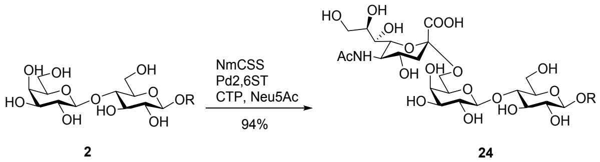
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 (d, J = 8.3 Hz, 1H)	3.75	N/R	3.64	3.63	4.00, 3.84	-	-	-	2.08 (s, 3H) or 2.04 (s, 3H)
Gal	4.45 (d, J = 8.0 Hz, 1H)	3.55	N/R	3.93 (dd, J = 3.4, 1.0 Hz, 1H)	3.83	3.99, 356	-	-	-	-
Neu5Ac	-	-	2.68 (dd, J = 12.4, 4.7 Hz, 1H), 1.72 (t, J = 12.2 Hz, 1H)	3.67	3.81	3.77	N/R	3.89	3.88, 3.65	2.08 (s, 3H) or 2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.93	54.86	N/R	80.73	74.45	60.35	-	-	-	22.26 or 22.01
Gal	103.47	70.72	N/R	N/R	73.67	63.32	-	-	-	-
Neu5Ac	173.51	100.14	40.07	N/R	51.87	N/R	N/R	71.69	62.63	22.26 or 22.01

Linker	**1**	**2**	**3**
H	3.44 – 3.35 (m, 2H)	1.89 – 1.81 (m, 2H)	3.99, 370
C	47.77	28.10	67.10

N/R: not reported.



Synthesis of 24

24 was prepared from **2**[18] using sialyltransferase Pd2,6ST according to the general procedure in the methods and was the white solid after lyophilization (790 mg, yield 94%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{19}$, $[M-H]^-$: 715.2527, found 715.253.

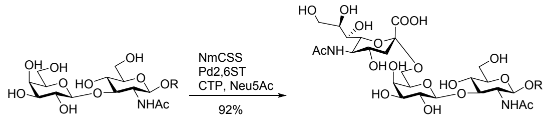
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.50 (d, *J* = 8.1 Hz, 1H)	3.35 (t, *J* = 8.6 Hz, 1H)	3.67	3.63	3.62	3.98, 3.81	-	-	-	-
Gal	4.44 (d, *J* = 7.9 Hz, 1H)	3.57 – 3.51 (m, 1H)	3.66	3.95 (d, *J* = 3.4 Hz, 1H)	3.82	3.98, 3.61	-	-	-	-
Neu5Ac	-	-	2.72 (dd, *J* = 12.3, 4.7 Hz, 1H), 1.75 (t, *J* = 12.2 Hz, 1H)	3.66	3.87	3.73 (dd, *J* = 10.5, 1.7 Hz, 1H)	3.57 (dd, *J* = 9.3, 1.8 Hz, 1H)	3.89	3.89, 3.65	2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.91	72.63	74.52	79.52	74.55	60.16				
Gal	103.11	70.69	72.43	68.28	73.60	63.47				
Neu5Ac	17339	100.20	40.01	68.28	51.69	72.27	68.42	71.70	62.54	21.96

Linker	**1**	**2**	**3**
H	3.48 (t, *J* = 6.7 Hz, 2H)	1.97 – 1.89 (m, 2H)	4.01, 3.78
C	47.79	28.14	67.24



3

25

Synthesis of 25

25 was synthesized from **3**[19] using sialyltransferase Pd2,6ST according to the general procedure in the methods and white solid after lyophilization (985 mg, yield 92%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{19}$, $[M-H]^-$: 756.2792, found 756.2795.

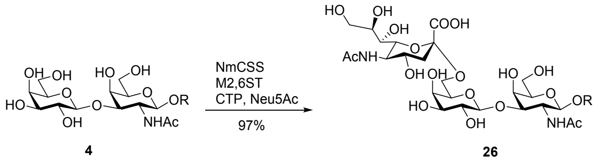
^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 (d, *J* = 8.4 Hz, 1H)	3.84	3.75	3.54	3.53	4.00, 3.80	-	-	-	2.03 (s, 6H)
Gal	4.38 (d, *J* = 7.8 Hz, 1H)	3.53	3.65	3.93	3.73	3.98, 3.59	-	-	-	-
Neu5Ac	-	-	2.70 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.71 (t, *J* = 12.2 Hz, 1H)	3.66	3.83	3.81	3.58	3.89	3.89, 3.65	2.03 (s, 6H)

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	100.91	54.32	84.06	68.42	75.48	60.89	-	-	-	22.21 or 22.06
Gal	103.94	70.52	72.40	68.25	72.47	63.52	-	-	-	-
Neu5Ac	173.37	100.05	40.09	68.45	51.80	73.59	68.92	71.77	62.65	22.21 or 22.06

Linker	**1**	**2**	**3**
H	3.38 (td, J = 6.6, 1.6 Hz, 2H)	1.90 – 1.81 (m, 2H)	4.00, 3.71
C	47.80	28.10	67.16



Synthesis of 26

26 was synthesized from **4**[19] using sialyltransferase M2,6ST according to the general procedure in the methods and white solid after lyophilization (474 mg, 97%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{19}$, [M-H]$^-$: 756.2792, found 756.2792.

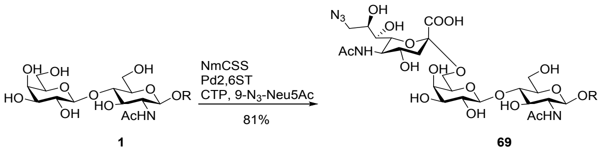
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GalNAc	4.51 (d, J = 8.5 Hz, 1H)	4.02	3.89	4.20	3.73	3.82	**-**	**-**	**-**	2.04
Gal	4.44 (d, J = 7.8 Hz, 1H)	3.53	3.62	3.92	3.77	3.91, 3.65	-	-	-	-
Neu5Ac	-	-	2.75 (dd, J = 12.4, 4.5 Hz), 1.69 (t, J = 12.2 Hz)	3.69	3.83	3.72	3.60	3.89	3.90, 3.65	2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GalNAc	101.41	51.22	79.93	67.96	74.85	61.14	-	-	-	22.22
Gal	104.71	70.46	72.58	68.22	73.15	63.39	-	-	-	-
Neu5Ac	173.41	100.41	40.16	68.47	51.84	72.34	68.17	71.74	62.60	22.00

Linker	**1**	**2**	**3**
H	3.39	1.86	4.00, 3.70
C	47.78	28.10	67.00



Synthesis of 69

1 was treated following the general procedure in the methods to install 9-N_3-Neu5Ac giving **69** as the white solid after lyophilization (1.3 g, yield 81%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, $[M-H]^-$: 781.2857, found 781.2859.

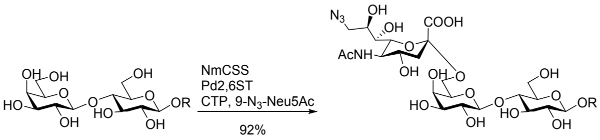
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.54 (d, *J* = 7.8 Hz, 1H)	3.72	3.74	3.61	3.59	3.97, 3.81	-	-	-	2.05 or 2.01
Gal	4.43 (d, *J* = 7.9 Hz, 1H)	3.52	3.72	3.91	3.82	3.97, 3.52	-	-	-	-
Neu5Ac	-	-	2.64 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.69 (t, *J* = 12.2 Hz, 1H)	3.63	3.79	3.72	3.54	4.01	3.65, 3.48	2.05 or 2.01

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.91	54.85	72.34	80.73	74.44	60.32	-	-	-	22.26 or 22.01
Gal	103.47	70.68	72.38	68.32	73.66	63.32	-	-	-	-
Neu5Ac	173.51	100.16	40.08	68.17	51.85	72.38	69.00	70.23	53.09	22.26 or 22.01

Linker	**1**	**2**	**3**
H	3.36	1.83	3.96, 3.66
C	47.75	28.09	67.08



2 **71**

Synthesis of 71

2 was treated following the general procedure in the methods to install 9-N_3-Neu5Ac giving **71** as the white solid after lyophilization (320 mg, yield 92%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{44}N_7O_{18}$, $[M+H]^+$: 742.2737, found 742.2742.

^1H NMR (600 MHz, D_2O): δ (ppm)

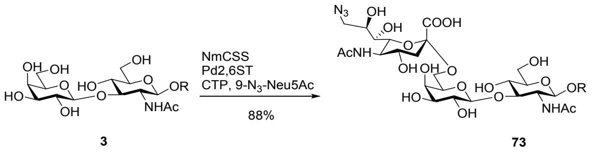
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.48 (d, *J* = 8.0 Hz, 1H)	3.33 (t, *J* = 8.5 Hz, 1H)	3.65	3.60	3.58	3.96, 3.79	-	-	-	-
Gal	4.41 (d, *J* = 7.9 Hz, 1H)	3.52	3.64	3.92	3.79	3.95, 3.58	-	-	-	-
Neu5Ac	-	-	2.69 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.72 (t, *J* = 12.2 Hz, 1H)	3.64	3.84 (t, *J* = 10.1 Hz, 1H)	3.74	3.55	4.01	3.68, 3.49	2.02 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**

Glc	101.96	72.67	74.56	79.57	74.60	60.20	-	-	-	-
Gal	103.15	70.72	72.67	68.45	73.66	63.55	-	-	-	-
Neu5Ac	173.45	100.29	40.07	68.31	51.73	72.28	68.97	70.30	53.06	22.02

Linker	**1**	**2**	**3**
H	3.45 (t, *J* = 6.7 Hz, 2H)	1.90 (p, *J* = 6.7 Hz, 2H)	3.98, 3.75
C	47.82	28.19	67.28



Synthesis of 73

3 was treated following the general procedure in the methods to install 9-N_3-Neu5Ac giving **73** as the white solid after lyophilization (738 mg, yield 88%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, $[M-H]^-$: 781.2857, found 781.2858.

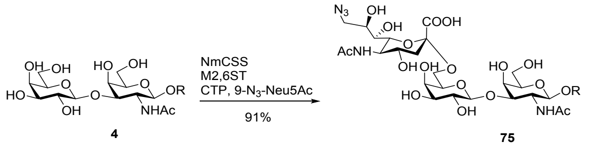
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.55 (d, *J* = 8.5 Hz, 1H)	3.80	3.73	3.50	3.49	3.97, 3.77	-	-	-	2.06 – 1.97 (m, 6H)
Gal	4.36 (d, *J* = 7.8 Hz, 1H)	3.50	3.62	3.89 (d, *J* = 3.5 Hz, 1H)	3.79	3.95, 3.54	-	-	-	-
Neu5Ac	-	-	2.68 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.67 (t, *J* = 12.2 Hz, 1H)	3.64	3.81	3.74	3.55	4.01	3.65, 3.48	2.06 – 1.97 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	103.88	54.26	84.02	69.02	75.43	60.83	-	-	-	22.17 or 22.03
Gal	100.86	70.45	72.21	68.40	73.57	63.48	-	-	-	-
Neu5Ac	173.45	100.09	40.12	68.22	51.76	72.34	68.87	70.29	53.07	22.17 or 22.03

Linker	**1**	**2**	**3**
H	3.40 – 3.34 (m, 2H)	1.83 (p, *J* = 6.4 Hz, 2H)	3.97, 3.67
C	47.75	28.05	67.11



Synthesis of 75

4 was treated following the general procedure in the methods to install 9-N_3-Neu5Ac giving **75** as the white solid after lyophilization (307 mg, 91%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, [M-

H]$^-$: 781.2857, found 781.2854.

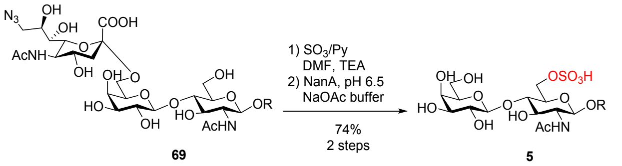
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.50 (d, *J* = 8.6 Hz, 1H)	4.01	3.88	4.19	3.72	3.82	**-**	**-**	**-**	2.05, 2.04
Gal	4.44 (d, *J* = 7.8 Hz, 1H)	3.52	3.62	3.93	3.72	3.91, 3.65	-	-	-	-
Neu5Ac	-	-	2.73 (dd, *J* = 12.4, 4.7 Hz), 1.65 (t, *J* = 12.1 Hz)	3.68	3.82	3.72	3.60	4.01	3.69, 3.50	2.05, 2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.41	51.23	79.91	67.96	74.86	61.15	-	-	-	22.21
Gal	104.67	70.44	72.38	68.21	73.13	63.37	-	-	-	-
Neu5Ac	173.39	100.42	40.17	68.45	51.83	72.34	68.83	70.30	53.06	22.00

Linker	**1**	**2**	**3**
H	3.40	1.86	3.99, 3.69
C	47.78	28.09	66.99



Synthesis of 5

69 was treated via the general procedure in the methods to provide **5** as the white solid after lyophilization (104 mg, yield 74% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{31}N_4O_{14}S$, [M+H]$^+$: 547.1552, found 547.1552.

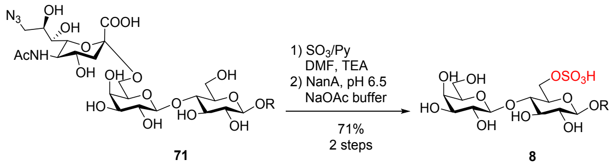
^{1}H NMR (800 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.54	3.73	3.70	3.77	3.79	4.38, 4.32	**-**	**-**	**-**	2.03
Gal	4.52	3.52 (dd, *J* = 10.0, 7.9 Hz, 1H)	3.67	3.92	3.71	3.74	**-**	**-**	**-**	**-**

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.15	55.06	72.26	77.36	72.50	66.25	**-**	**-**	**-**	22.14
Gal	102.49	70.96	72.45	68.58	75.32	61.02	**-**	**-**	**-**	**-**

Linker	**1**	**2**	**3**
H	3.36	1.83	3.95, 3.68
C	47.76	28.07	67.26



Synthesis of 8

71 was treated via the general procedure in the methods to provide **8** as the white solid after lyophilization (47 mg, yield 71% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{15}H_{26}N_3O_{14}S$, $[M-H]^-$: 504.1141, found 504.1144.

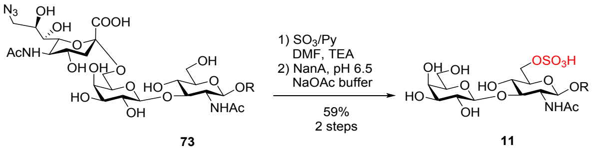
^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.52	3.34 (dd, *J* = 9.4, 8.0 Hz, 1H)	3.65	3.74	3.82	4.40 (dd, *J* = 11.1, 2.1 Hz, 1H), 4.31 (dd, *J* = 11.1, 4.2 Hz, 1H)	-	-	-	-
Gal	4.52	3.54 (dd, *J* = 9.9, 7.9 Hz, 1H)	3.68	3.93 (d, *J* = 3.4 Hz, 1H)	3.74	3.78 (2H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
Glc	102.07	72.56	75.18	77.05	72.37	66.09	-	-	-	-
Gal	102.37	70.82	72.33	68.46	74.08	60.88	-	-	-	-

Linker	**1**	**2**	**3**
H	3.49 – 3.43 (m, 2H)	1.96 – 1.88 (m, 2H)	4.04 – 3.96 (m, 1H), 3.78
C	47.72	28.10	67.38



Synthesis of 11

73 was treated via the general procedure in the methods to provide **11** as the white solid after lyophilization (41 mg, yield 59% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{14}S$, $[M-H]^-$: 545.1406, found 545.1406.

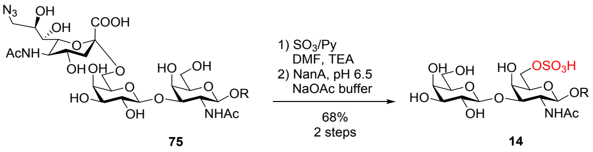
^{1}H NMR (800 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.58 (d, *J* = 8.3 Hz, 1H)	3.87 – 3.84 (m, 1H)	3.81	3.60 (dd, *J* = 10.0, 8.5 Hz, 1H)	3.72	4.38 (dd, *J* = 11.3, 2.1 Hz, 1H), 4.24 (dd, *J* = 11.2, 5.6 Hz, 1H)	-	-	-	2.05 (s, 3H)
Gal	4.45 (d, *J* = 7.8 Hz, 1H)	3.53 (dd, *J* = 10.0, 7.8 Hz, 1H)	3.65 (dd, *J* = 9.9, 3.4 Hz, 1H)	3.92 (d, *J* = 3.4 Hz, 1H)	3.71	3.79, 3.75	-	-	-	-

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	103.49	54.55	81.99	68.43	73.26	67.10	-	-	-	22.21
Gal	100.960	70.66	72.48	68.55	75.27	61.01	-	-	-	-

Linker	**1**	**2**	**3**
H	3.42 – 3.36 (m, 2H)	1.90 – 1.81 (m, 2H)	3.99 (dt, *J* = 10.9, 5.6 Hz, 1H), 3.70
C	47.79	28.10	67.30



Synthesis of 14

75 was treated via the general procedure in the methods to provide **14** as the white solid after lyophilization (62 mg, 68% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{14}S$, $[M-H]^-$: 545.1406, found 545.1409.

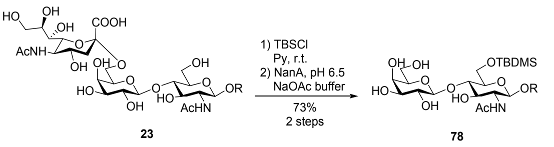
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GalNAc	4.54 (d, *J* = 8.5 Hz, 1H)	4.04	3.92	4.26	3.97	3.22	-	-	-	2.05
Gal	4.46 (d, *J* = 7.8 Hz, 1H)	3.55 (dd, *J* = 10.1, 7.6 Hz, 1H)	3.64	3.93	3.69	3.77	-	-	-	-

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GalNAc	101.35	51.16	79.70	67.71	72.37	67.19	-	-	-	22.19
Gal	104.85	70.57	72.47	68.57	74.94	60.94	-	-	-	-

Linker	**1**	**2**	**3**
H	3.40	1.87	3.98, 3.73
C	47.80	28.12	67.19



Synthesis of 78

23 was treated via the general procedure in the methods to provide **78** as the white solid after lyophilization (280 mg, yield 73% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{43}N_4O_{11}Si$, $[M-H]^-$: 579.2703, found 579.2705.

^1H NMR (600 MHz, CD_3OD): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.39 (d, *J* = 8.4 Hz, 1H)	3.72	3.65 – 3.61 (m, 1H)	3.70	3.39	4.04 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.99 (dd, *J* = 11.6, 1.8 Hz, 1H)	-	-	-	1.99 (s, 3H)

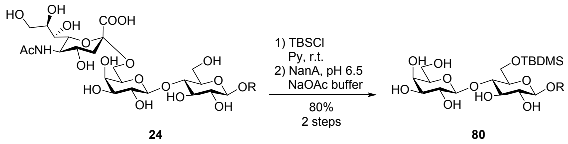
Gal	4.44 (d, *J* = 7.7 Hz, 1H)	3.53	3.45 (dd, *J* = 9.7, 3.3 Hz, 1H)	3.82 (dd, *J* = 3.3, 1.0 Hz, 1H)	3.52	3.77, 3.67	-	-	-	-

^{13}C NMR (151 MHz, CD$_3$OD): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.35	55.31	72.74	77.90	75.40	61.50	-	-	-	21.61
Gal	103,26	71.23	73.56	68.99	75.92	61.23	-	-	-	-

Linker	**1**	**2**	**3**
H	3.39 (2H)	1.87 – 1.75 (m, 2H)	3.92 (ddd, *J* = 9.9, 6.1, 5.1 Hz, 1H), 3.59 – 3.56 (m, 1H)
C	47.36	28.79	65.66

TBS Group	**1′**	**2′**	**3′**
H	0.94 (s, 9H)	-	0.13 (d, *J* = 8.4 Hz, 6H)
C	25.11	17.85	-6.15, -6.43



Synthesis of 80

24 was treated via the general procedure in the methods to provide **80** as the white solid after lyophilization (507 mg, yield 80% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{21}H_{41}N_3NaO_{11}Si$, $[M+Na]^+$: 562.2403, found 562.2403.

^{1}H NMR (600 MHz, CD$_3$OD): δ (ppm)

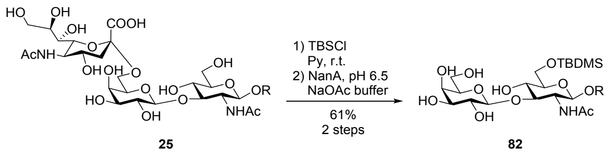
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.26 (d, *J* = 7.8 Hz, 1H)	3.23 (dd, *J* = 9.3, 7.8 Hz, 1H)	3.51	3.64	3.39 – 3.36 (m, 1H)	4.03 – 3.95 (m, 2H)	-	-	-	-
Gal	4.40 (d, *J* = 7.7 Hz, 1H)	3.52	3.44	3.81 (dd, *J* = 3.4, 1.0 Hz, 1H)	3.51	3.80 – 3.75 (m, 1H), 3.70 – 3.66 (m, 1H)	-	-	-	-

^{13}C NMR (151 MHz, CD$_3$OD): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	104.19	74.89	76.31	78.97	76.65	62.88	-	-	-	-
Gal	104.64	72.57	74.78	70.30	77.17	62.53	-	-	-	-

Linker	**1**	**2**	**3**
H	3.44 (2H)	1.91 – 1.84 (m, 2H)	3.95 – 3.90 (m, 1H), 3.64
C	49.43	30.29	67.53

TBS group	**1′**	**2′**	**3′**
H	0.92 (s, 9H)	-	0.11 (s, 3H), 0.10 (s, 3H)
C	26.47	19.22	-4.79, -5.07



Synthesis of 82

25 was treated via the general procedure in the methods to provide **82** as the white solid after lyophilization (186 mg, yield 61% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{43}N_4O_{11}Si$, $[M-H]^-$: 579.2703, found 579.2702.

^1H NMR (600 MHz, CD_3OD): δ (ppm)

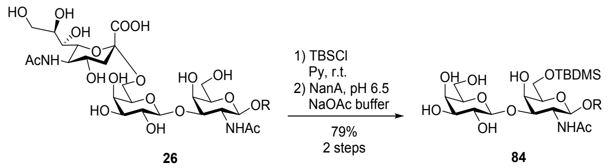
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.46 (d, *J* = 8.3 Hz, 1H)	3.73	3.69	3.47	3.31	3.99 (dd, *J* = 11.3, 1.9 Hz, 1H), 3.85 (dd, *J* = 11.4, 5.1 Hz, 1H)	-	-	-	1.99 (s, 3H)
Gal	4.29 (d, *J* = 7.6 Hz, 1H)	3.55	3.47	3.82 (dd, *J* = 3.4, 1.0 Hz, 1H)	3.57	3.77, 3.71	-	-	-	-

^{13}C NMR (151 MHz, CD_3OD): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	102.43	56.28	84.89	70.25	77.75	63.90	-	-	-	23.21
Gal	105.62	72.39	74.68	70.18	77.14	62.53	-	-	-	-

Linker	**1**	**2**	**3**
H	3.42 – 3.37 (m, 2H)	1.88 – 1.77 (m, 2H)	3.96 – 3.90 (m, 1H), 3.59
C	48.89	30.16	67.24

TBS group	**1′**	**2′**	**3′**
H	0.93 (s, 9H)	-	0.11 (s, 3H), 0.11 (s, 3H)
C	26.44	19.32	-4.98, -5.09



Synthesis of 84

26 was treated via the general procedure in the methods to provide **84** as the white solid after lyophilization (88 mg, 79%). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{43}N_4O_{11}Si$, $[M-H]^-$: 579.2703, found 579.2702.

^1H NMR (600 MHz, CD_3OD): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.43 (d, *J* = 8.5 Hz, 1H)	3.99	3.76	4.09	3.53	3.82	**-**	**-**	**-**	1.95
Gal	4.31 (d, *J* = 7.6 Hz, 1H)	3.53	3.43	3.82	3.50	3.69	-	-	-	-

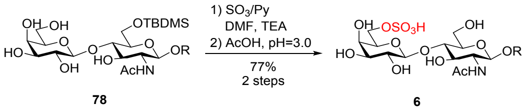
^{13}C NMR (201 MHz, CD_3OD): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**

GalNAc	101.47	51.75	80.02	67.85	74.97	62.10	-	-	-	172.86, 21.82
Gal	105.26	71.11	73.18	68.60	75.11	60.86	-	-	-	-

Linker	**1**	**2**	**3**
H	3.37	1.82	3.90, 3.56
C	47.83	28.76	65.69

TBS Group	**1′**	**2′**	**3′**
H	0.9	-	0.09
C	24.98	17.77	-6.57, -6.63



Synthesis of 6

78 was treated according to the general procedure in the methods to give **6** as the white solid after lyophilization (363 mg, yield 77% for 2 steps). In detail, **78** (500 mg, 0.86 mmol) was dissolved in a mixed solution of 3 mL DMF and 3 mL TEA. SO_3/Py (548 mg, 3.45 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 °C and then stirred at 40 °C for 4 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **6**. ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{14}S$, $[M-H]^-$: 545.1406, found 545.1405.

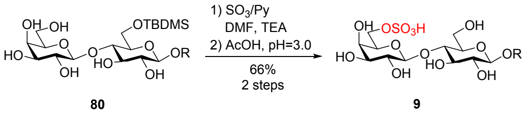
^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57	3.78	3.77	3.73	3.66	4.03, 3.88	-	-	-	2.09 (s, 3H)
Gal	4.55	3.58	3.73	4.03	4.01	4.28 – 4.22 (m, 2H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.10	55.16	72.15	79.17	74.69	60.24	-	-	-	22.20
Gal	102.80	70.81	72.33	68.25	72.81	67.13	-	-	-	-

Linker	**1**	**2**	**3**
H	3.47 – 3.37 (m, 2H)	1.94 – 1.83 (m, 2H)	4.00, 3.72
C	47.79	28.10	67.19



Synthesis of 9

80 was treated according to the general procedure in the methods to give **9** as the white solid after lyophilization (123 mg, yield 66% for 2 steps). In detail, **80** (200 mg, 0.37 mmol) was dissolved in a mixed solution of 2 mL DMF and 2 mL TEA. SO_3/Py (236 mg, 1.48 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 °C and then stirred at 40 °C for 3 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **9**. ESI-Q-TOF-HRMS m/z calculated for $C_{15}H_{26}N_3O_{14}S$, $[M-H]^-$: 504.1141, found 504.1141.

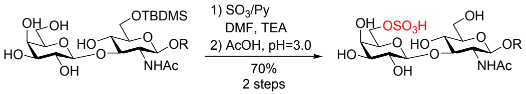
^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.48	3.37 – 3.31 (m, 1H)	3.66	3.62	3.62	4.00, 3.81	-	-	-	-
Gal	4.48	3.56 (dd, *J* = 9.9, 7.9 Hz, 1H)	3.69	3.98	3.99	4.24 – 4.18 (m, 2H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.90	72.73	74.23	79.28	74.56	60.10	-	-	-	-
Gal	102.94	70.62	72.19	68.12	72.62	67.16	-	-	-	-

Linker	**1**	**2**	**3**
H	3.49 – 3.43 (m, 2H)	1.96 – 1.87 (m, 2H)	4.01, 3.76
C	47.74	28.10	67.21



82 12

Synthesis of 12

82 was treated according to the general procedure in the methods to give **12** as the white solid after lyophilization (53 mg, yield 70% for 2 steps). In detail, **82** (80 mg, 0.14 mmol) was dissolved in a mixed solution of 0.5 mL DMF and 0.5 mL TEA. SO_3/Py (89 mg, 0.56 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 °C and then stirred at 40 °C for 3 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **12**. ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{14}S$, $[M-H]^-$: 545.1406, found 545.1404.

^1H NMR (500 MHz, D_2O): δ (ppm)

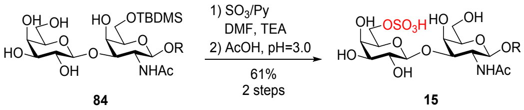
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.56 (d, *J* = 8.4 Hz, 1H)	3.84 (dd, *J* = 10.4, 8.4 Hz, 1H)	3.78	3.51	3.49	3.92, 3.76	-	-	-	2.04 (s, 3H)
Gal	4.45 (d, *J* = 7.8 Hz, 1H)	3.53	3.65	3.96	3.96	4.26 – 4.15 (m, 2H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	103.59	54.45	82.89	68.26	75.30	60.66	-	-	-	22.18

Gal	100.91	70.48	72.26	68.73	72.77	67.37	-	-	-	-

Linker	**1**	**2**	**3**
H	3.44 – 3.32 (m, 2H)	1.90 – 1.80 (m, 2H)	3.99, 3.67
C	47.76	28.07	67.14



Synthesis of 15

84 was treated according to the general procedure in the methods to give **15** as the white solid after lyophilization (20 mg, 61% for 2 steps). In detail, **84** (35 mg, 0.06 mmol) was dissolved in a mixed solution of 0.5 mL DMF and 0.5 mL TEA. SO_3/Py (38 mg, 0.24 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 ℃ and then stirred at 40 ℃ for 3 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **15**. ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{14}S$, $[M-H]^-$: 545.1406, found 545.1406.

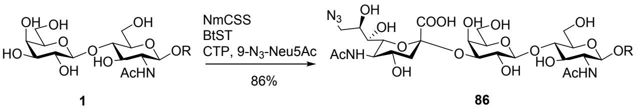
^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.50 (d, *J* = 8.5 Hz, 1H)	4.02	3.86	4.24	3.72	3.80	-	-	-	2.05
Gal	4.46 (d, *J* = 7.8 Hz, 1H)	3.54 (dd, *J* = 9.9, 7.9 Hz, 1H)	3.65	3.96	3.90	4.19	-	-	-	2.05

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.38	51.15	80.04	68.03	74.92	61.18	-	-	-	22.19
Gal	104.66	70.42	72.32	68.32	72.52	67.47	-	-	-	-

Linker	**1**	**2**	**3**
H	3.40	1.87	4.01, 3.70
C	47.78	28.09	66.99



Synthesis of 86

86 was synthesized using sialyltransferase BtST via the general procedure in the methods and white solid after lyophilization (289mg, 86%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, $[M-H]^-$: 781.2857, found 781.2856.

^1H NMR (600 MHz, D_2O): δ (ppm)

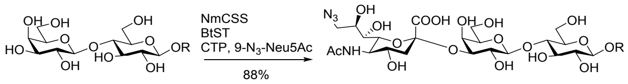
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**

GlcNAc	4.51	3.72	3.69	3.71	3.57	3.99, 3.83	-	-	-	2.03 or 2.02
Gal	4.53	3.56	4.09	3.93	3.67	3.72	-	-	-	-
Neu5Ac			2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.76	3.67	3.84	3.72	3.58	4.01	3.67, 3.48	2.03 or 2.02

^{13}C NMR (151 MHz, D$_2$O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.12	55.06	72.33	78.26	74.76	60.05	-	-	-	22.15
Gal	102.55	69.37	75.51	67.39	75.14	61.00	-	-	-	-
Neu5Ac	173.80	99.78	39.67	68.32	51.65	72.67	68.72	70.35	53.04	22.15

Linker	**1**	**2**	**3**
H	3.36	1.83	3.98, 3.65
C	47.75	28.09	67.11



Synthesis of 88

88 was synthesized using sialyltransferase BtST via the general procedure in the methods and white solid after lyophilization (460 mg, 88%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{42}N_7O_{18}$, [M-H]$^-$: 740.2592, found 740.2592.

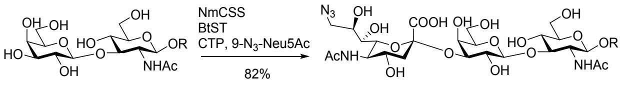
^{1}H NMR (600 MHz, D$_2$O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.50 (d, *J* = 8.0 Hz, 1H)	3.33 (dd, *J* = 9.1, 7.9 Hz, 1H)	3.65	3.67	3.61	4.02, 3.83	-	-	-	-
Gal	4.53 (d, *J* = 7.9 Hz, 1H)	3.58	4.11 (dd, *J* = 9.9, 3.2 Hz, 1H)	3.96 (d, *J* = 3.2 Hz, 1H)	3.71	3.75 (2H)	-	-	-	-
Neu5Ac	-	-	2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.80 (t, *J* = 12.1 Hz, 1H)	3.69	3.87	3.66	3.60	4.03	3.70, 3.52 – 3.49 (m, 1H)	2.05 (s, 3H)

^{13}C NMR (151 MHz, D$_2$O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	102.01	72.57	74.23	78.14	74.67	59.98	-	-	-	-
Gal	102.53	69.24	75.42	67.24	75.04	60.89	-	-	-	-
Neu5Ac	173.70	99.68	39.58	68.20	51.55	72.68	68.64	70.25	52.94	21.92

Linker	**1**	**2**	**3**
H	3.47 (t, *J* = 6.7 Hz, 2H)	1.93 (p, *J* = 6.5 Hz, 2H)	4.00, 3.78
C	47.75	28.10	67.28



3 90

Synthesis of 90

90 was synthesized using sialyltransferase BtST via the general procedure in the methods and white solid after lyophilization (277mg, 82%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, $[M-H]^-$: 781.2857, found 781.2856.

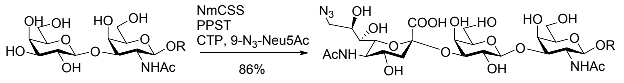
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 (d, J = 8.3 Hz, 1H)	3.82	3.79	3.53	3.50	3.94, 3.77	-	-	-	2.06 (s, 3H) or 2.04 (s, 3H)
Gal	4.50 (d, J = 7.8 Hz, 1H)	3.54	4.08 (dd, J = 9.8, 3.2 Hz, 1H)	3.93	3.68	3.74 (2H)	-	-	-	-
Neu5Ac	-	-	2.76 (dd, J = 12.5, 4.6 Hz, 1H), 1.79 (t, J = 12.2 Hz, 1H)	3.67	3.85	3.66	3.61 (dd, J = 9.0, 2.0 Hz, 1H)	3.99	3.67, 3.52	2.06 (s, 3H) or 2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.89	54.47	83.40	68.75	75.39	60.75	-	-	-	22.29 or 22.05
Gal	103.38	69.11	75.65	67.15	75.07	61.02	-	-	-	-
Neu5Ac	173.82	99.63	39.82	68.37	51.64	72.60	68.75	70.57	53.05	22.29 or 22.05

Linker	**1**	**2**	**3**
H	3.39 (td, J = 6.6, 2.3 Hz, 2H)	1.89 – 1.83 (m, 2H)	3.98, 3.71
C	47.79	28.10	67.15



4 92

Synthesis of 92

92 was synthesized using sialyltransferase PPST via the general procedure in the methods and white solid after lyophilization (145 mg, 86%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{45}N_8O_{18}$, $[M-H]^-$: 781.2857, found 781.2858.

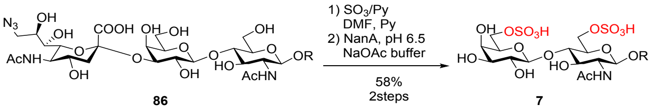
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.52	4.02	3.89	4.18	3.72	3.79, 3.73	**-**	**-**	**-**	2.05 or 2.04
Gal	4.51	3.56	4.07	3.94	3.64	3.79, 3.73	-	-	-	-
Neu5Ac	-	-	2.77 (dd, J = 12.5, 4.7 Hz), 1.79 (t, J = 12.2 Hz)	3.69	3.85	3.71	3.60	4.00	3.69, 3.51	2.05 or 2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GalNAc	101.36	51.17	79.94	67.85	74.73	60.93	-	-	-	22.28
Gal	104.53	69.01	75.57	67.27	74.73	60.97	-	-	-	-
Neu5Ac	173.87	99.66	39.77	68.36	51.63	72.57	68.74	70.51	53.02	22.04

Linker	1	2	3
H	3.40	1.86	3.98, 3.71
C	47.79	28.10	66.99



Synthesis of 7

7 was prepared via the general procedure in the methods and was the white solid after lyophilization (46mg, 58%). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{17}S_2$, $[M-H]^-$: 625.0975, found 625.0977.

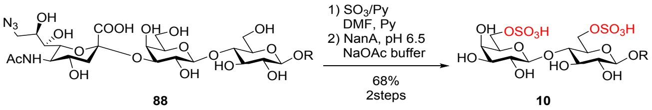
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.57	3.75	3.75	3.76	3.84	4.44, 4.33	-	-	-	2.06
Gal	4.57	3.55 (dd, *J* = 10.0, 7.8 Hz, 1H)	3.70	3.97	3.99	4.21	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	101.31	55.06	72.10	78.61	72.50	66.51	-	-	-	22.17
Gal	102.70	70.80	72.26	68.22	72.71	67.04	-	-	-	-

Linker	1	2	3
H	3.39	1.86	3.97, 3.70
C	47.77	28.09	67.24



Synthesis of 10

10 was prepared via the general procedure in the methods and was the white solid after lyophilization (27mg, 68%). ESI-Q-TOF-HRMS m/z calculated for $C_{15}H_{27}N_3O_{17}S_2$, $[M-H]^-$: 584.0723, found 584.0709.

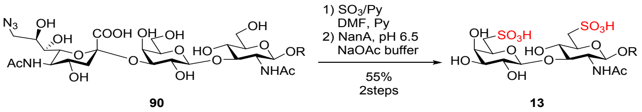
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
Glc	4.54	3.40 – 3.34 (m, 1H)	3.68	3.79	3.88 – 3.83 (m, 1H)	4.46 – 4.40 (m, 1H), 4.34 – 4.27 (m, 1H)	-	-	-	-
Gal	4.54	3.59 – 3.54 (m, 1H)	3.72	4.01	4.01	4.26 – 4.20 (m, 2H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
Glc	101.96	72.47	74.15	78.67	72.32	66.34	-	-	-	-
Gal	102.82	70.62	72.13	68.10	72.63	67.00	-	-	-	-

Linker	**1**	**2**	**3**
H	3.51 – 3.45 (m, 2H)	1.96 – 1.90 (m, 2H)	4.01, 3.82 – 3.76 (m, 1H)
C	47.73	28.11	67.38



Synthesis of 13

13 was prepared via the general procedure in the methods and was the white solid after lyophilization (44mg, 55%). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{17}S_2$, $[M-H]^-$: 625.0975, found 625.0983.

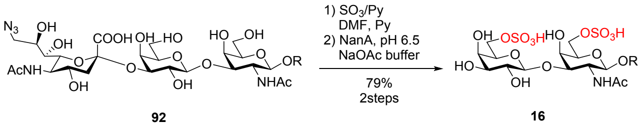
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.58 (d, *J* = 8.3 Hz, 1H)	3.87	3.83	3.63 – 3.58 (m, 1H)	3.74	4.41 – 4.37 (m, 1H), 4.26	-	-	-	2.06 (s, 3H)
Gal	4.47 (d, *J* = 7.8 Hz, 1H)	3.57 – 3.53 (m, 1H)	3.68	3.99	3.97	4.23 (2H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	103.47	54.53	82.03	68.24	73.21	67.08	-	-	-	22.23
Gal	100.97	70.52	72.28	68.25	72.69	67.17	-	-	-	-

Linker	**1**	**2**	**3**
H	3.44 – 3.36 (m, 2H)	1.91 – 1.83 (m, 2H)	4.02, 3.71
C	47.81	28.10	67.32



Synthesis of 16

16 was prepared via the general procedure in the methods and was the white solid after lyophilization (44 mg, 79% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{17}H_{29}N_4O_{17}S_2$, $[M-H]^-$: 625.0975, found 625.0978.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

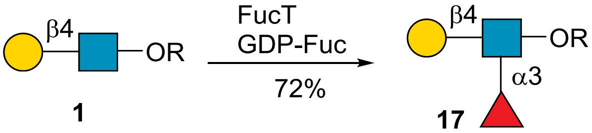
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GalNAc	4.52 (d, *J* = 8.6 Hz)	4.05	3.90	4.24	3.93	4.25	-	-	-	2.05
Gal	4.49 (d, *J* = 7.8 Hz)	3.56	3.66	3.99	3.96	4.20	-	-	-	-

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc

GalNAc	101.31	51.12	79.56	67.89	72.43	67.21	-	-	-	22.23
Gal	104.61	70.44	72.31	68.20	72.63	67.89	-	-	-	-

Linker	**1**	**2**	**3**
H	3.40	1.87	3.98, 3.73
C	47.82	28.12	67.06



Synthesis of 17

17 was synthesized using FucT as described in the methods. White solid after lyophilization (88 mg, yield 72%). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{15}$, $[M-H]^-$: 611.2417, found 611.2417.

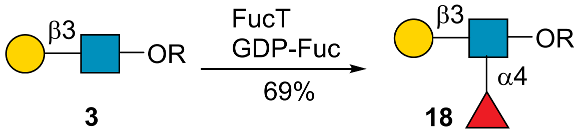
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.55 (d, *J* = 8.1 Hz, 1H)	3.90	3.87	3.92	3.60	4.02, 3.85	-	-	-	2.05 (s, 3H)
Gal	4.46 (d, *J* = 7.8 Hz, 1H)	3.50 (dd, *J* = 9.9, 7.8 Hz, 1H)	3.66	3.90	3.60	3.73	-	-	-	-
Fuc	5.12 (d, *J* = 4.0 Hz, 1H)	3.70	3.90	3.80 (d, *J* = 3.3 Hz, 1H)	4.84 (q, *J* = 6.6 Hz, 1H)	1.18 (d, *J* = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.95	55.81	74.90	73.36	75.33	59.76	-	-	-	22.22
Gal	101.82	71.03	72.45	68.33	74.90	61.48	-	-	-	-
Fuc	98.63	67.69	69.19	71.90	66.70	15.29	-	-	-	-

Linker	**1**	**2**	**3**
H	3.38 (q, *J* = 6.1 Hz, 2H)	1.89 – 1.81 (m, 2H)	3.98, 368
C	47.75	28.10	67.19



Synthesis of 18

18 was synthesized using FucT as described in the methods. White solid after lyophilization (272 mg, yield 69%). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{15}$, $[M-H]^-$: 611.2417, found 611.2415.

^{1}H NMR (500 MHz, D_2O): δ (ppm)

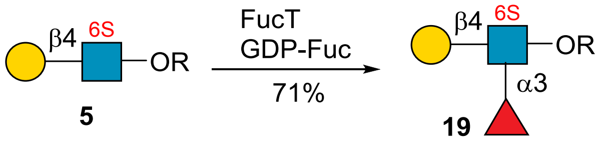
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.53 (d, *J* = 8.5 Hz,	3.88	4.07 (t, *J* = 9.7 Hz,	3.72	N/R	3.98, 3.86	-	-	-	2.05 (s, 3H)

	1H)		1H)							
Gal	4.49 (d, *J* = 7.7 Hz, 1H)	3.48 (dd, *J* = 9.8, 7.7 Hz, 1H)	3.62	3.88	N/R	3.73	-	-	-	-
Fuc	5.02 (d, *J* = 4.0 Hz, 1H)	3.80	N/R	N/R	4.87 (q, *J* = 6.7 Hz, 1H)	1.18 (d, *J* = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.01	55.74	76.05	72.40	N/R	59.67	-	-	-	22.25
Gal	102.86	70.45	72.8	68.33	N/R	61.64	-	-	-	-
Fuc	98.05	67.75	N/R	N/R	66.83	15.34	-	-	-	-

Linker	**1**	**2**	**3**
H	3.43 – 3.32 (m, 2H)	1.91 – 1.80 (m, 1H)	3.97, 3.67
C	47.75	28.10	67.17



Synthesis of 19

19 was synthesized using FucT as described in the methods. White solid after lyophilization (27 mg, yield 71%). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{18}S$, $[M-H]^-$: 691.1986, found 691.1987.

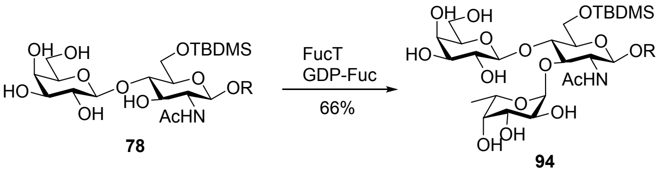
^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.58 (d, *J* = 7.8 Hz, 1H)	3.90	3.88	4.00	3.81	4.42 – 4.34 (m, 2H)	-	-	-	2.04 (s, 3H)
Gal	4.55 (d, *J* = 7.8 Hz, 1H)	3.53 – 3.46 (m, 1H)	3.66	3.91	3.61	3.73	-	-	-	-
Fuc	5.12 (d, *J* = 4.1 Hz, 1H)	3.68	3.90	3.80	4.84	1.18 (d, *J* = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.94	55.69	74.95	72.95 or 72.77	72.95 or 72.77	65.95	-	-	-	22.21
Gal	101.51	70.98	72.42	68.42	74.78	61.44	-	-	-	-
Fuc	98.59	67.76	69.19	71.90	66.72	15.30	-	-	-	-

Linker	**1**	**2**	**3**
H	3.42 – 3.33 (m, 2H)	1.89 – 1.79 (m, 2H)	3.97, 3.67
C	47.77	28.10	67.26



Synthesis of 94

94 was synthesized using FucT as described in the methods. White solid after lyophilization (83 mg, yield 66%). ESI-Q-TOF-HRMS m/z calculated for $C_{29}H_{53}N_4O_{15}Si$, $[M-H]^-$: 725.3282, found 725.3285.

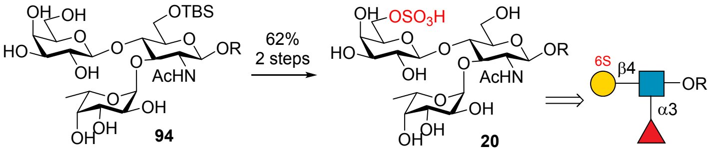
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.53 (d, *J* = 8.2 Hz, 1H)	3.92	3.87	3.95	3.57	4.13 (dd, *J* = 11.9, 2.1 Hz, 1H), 3.96	-	-	-	2.04 (s, 3H)
Gal	4.49 (d, *J* = 7.8 Hz, 1H)	3.51 (dd, *J* = 9.9, 7.8 Hz, 1H)	3.64	3.91	3.57	3.73 (2H)	-	-	-	-
Fuc	5.11 (d, *J* = 4.0 Hz, 1H)	3.71	3.91	3.82 – 3.78 (m, 1H)	4.84 (q, *J* = 6.8 Hz, 1H)	1.18 (d, *J* = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.77	55.72	75.01	73.42	75.61	61.60	-	-	-	22.17
Gal	101.73	70.84	72.45	68.33	75.07	61.48	-	-	-	-
Fuc	98.59	67.64	69.15	71.84	66.67	15.26	-	-	-	-

Linker	**1**	**2**	**3**
H	3.43 – 3.34 (m, 2H)	1.91 – 1.80 (m, 2H)	3.95, 3.67
C	47.76	28.10	66.95



Synthesis of 20

94 was treated according to the general procedure in the methods to give **20** as the white solid after lyophilization (26 mg, yield 62% for 2 steps). In detail, **94** (44 mg, 0.06 mmol) was dissolved in a mixed solution of 0.5 mL DMF and 0.5 mL TEA. SO_3/Py (39 mg, 0.24 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 °C and then continued to stir at 40 °C for 3 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **20**.

ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{18}S$, $[M-H]^-$: 691.1986, found 691.1986.

^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.55 (d, *J* = 7.8 Hz, 1H)	2.88	3.86	3.94	3.63 – 3.58 (m, 1H)	4.01, 3.86	-	-	-	2.05 (s, 3H)
Gal	4.48 (d, *J* = 7.9 Hz,	3.52 (dd, *J* = 9.9, 7.8	3.68	3.96	N/R	4.20 – 4.11 (m,	-	-	-	-

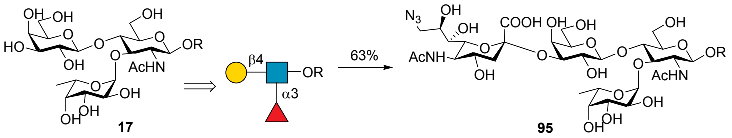
	1H)	Hz, 1H)				2H)				
Fuc	5.11 (d, *J* = 4.0 Hz, 1H)	3.66	3.90	3.81 (d, *J* = 3.3 Hz, 1H)	4.84	1.19 (d, *J* = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.93	55.84	75.09	73.73	75.37	59.86	-	-	-	22.22
Gal	101.77	70.92		67.85 or 67.80	N/R	66.94	-	-	-	-
Fuc	98.57	67.85 or 67.80	69.13	N/R	66.69	15.32	-	-	-	-

Linker	**1**	**2**	**3**
H	3.43 – 3.34 (m, 2H)	1.90 – 1.81 (m, 2H)	3.96, 3.66
C	47.75	28.10	67.13

N/R: not reported.



Synthesis of 95

95 was synthesized using sialyltransferase PPST via the general procedure in the methods and white solid after lyophilization (191mg, 63%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{55}N_8O_{22}$, $[M-H]^-$: 927.3436, found 927.3432.

^1H NMR (600 MHz, D_2O): δ (ppm)

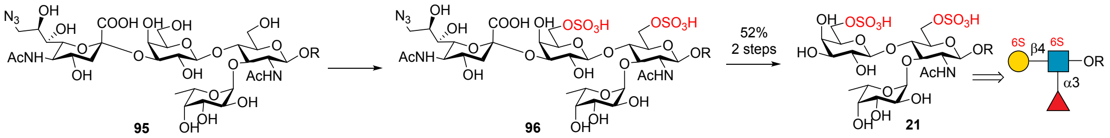
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.52	3.90	3.85	3.95	3.58	4.02, 3.89	-	-	-	2.04 (s, 6H)
Gal	4.51	3.53	4.07	3.92	N/R	3.69	-	-	-	-
Fuc	5.11 (d, *J* = 4.0 Hz, 1H)	3.67	3.90	3.78 (d, *J* = 3.9 Hz, 1H)	4.82	1.17 (d, *J* = 6.6 Hz, 2H)	-	-	-	-
Neu5Ac	-	-	2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 178	3.67	3.86	N/R	N/R	4.03	3.69, 3.50	2.04 (s, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.96	55.80	N/R	73.31	N/R	59.68	-	-	-	22.21 or 22.03
Gal	101.58	N/R	75.71	67.23	N/R	61.46	-	-	-	-
Fuc	98.58	N/R	N/R	71.88	66.67	15.25	-	-	-	-
Neu5Ac	173.82	99.65	39.85	N/R	51.67	N/R	N/R	70.46	53.09	22.21 or 22.03

Linker	**1**	**2**	**3**
H	3.43 – 3.32 (m, 2H)	1.85 (q, *J* = 6.3 Hz, 2H)	3.97, 3.68
C	47.75	28.10	67.17

N/R: not reported.



Synthesis of 21

21 was prepared via the general procedure in the methods and was the white solid after lyophilization (22mg, 52% for 2 steps). ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{21}S_2$, $[M-H]^-$: 771.1554, found 771.1552.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

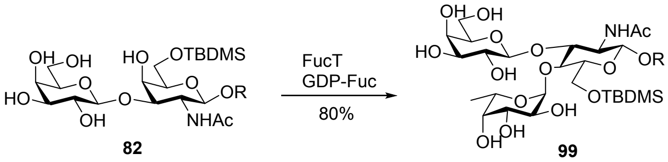
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.56 (d, *J* = 7.9 Hz, 1H)	3.87	3.87	3.86	3.80	4.41 – 4.34 (m, 2H)	-	-	-	2.02 (s, 3H)
Gal	4.53 (d, *J* = 7.8 Hz, 1H)	3.49 (dd, *J* = 9.9, 7.8 Hz, 1H)	3.67	3.95	N/R	4.18 – 4.10 (m, 2H)	-	-	-	-
Fuc	5.08 (d, *J* = 4.0 Hz, 1H)	3.63	3.88	3.79	4.81	1.16 (d, *J* = 6.7 Hz, 2H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.92	55.69	74.99	73.42	73.06	66.07	-	-	-	22.21
Gal	101.70	70.84	N/R	67.87	N/R	66.78	-	-	-	-
Fuc	98.66	67.87	69.11	N/R	66.70	15.33	-	-	-	-

Linker	**1**	**2**	**3**
H	3.41 – 3.30 (m, 2H)	1.83 (qp, *J* = 7.9, 2.1 Hz, 2H)	3.95, 3.65
C	47.76	28.10	67.23

N/R: not reported.



Synthesis of 99

99 was synthesized using FucT as described in the methods. White solid after lyophilization (80 mg, yield 80%). ESI-Q-TOF-HRMS m/z calculated for $C_{29}H_{53}N_4O_{15}Si$, $[M-H]^-$: 725.3282, found 725.3283.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.51 (d, *J* = 8.6 Hz, 1H)	3.87	4.06 (t, *J* = 9.7 Hz, 1H)	3.66	N/R	4.15 (dd, *J* = 11.8, 2.2 Hz, 1H), 3.94	-	-	-	2.05 (s, 3H)
Gal	4.49 (d, *J* = 7.7 Hz, 1H)	3.49 (dd, *J* = 9.9, 7.7 Hz, 1H)	N/R	3.87	N/R	3.75 – 3.72 (m, 2H)	-	-	-	-

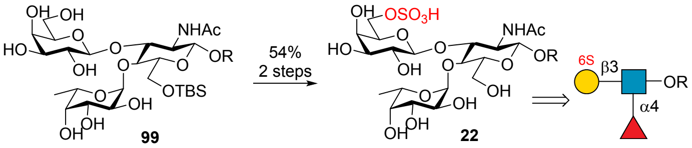
Fuc	5.02 (d, J = 4.0 Hz, 1H)	3.79	3.87	N/R	4.87 (q, J = 6.6 Hz, 1H)	1.18 (d, J = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	102.81	55.74	76.09	73.33	N/R	61.82	-	-	-	22.22
Gal	100.95	70.39	N/R	68.32	N/R	61.67	-	-	-	-
Fuc	98.38	67.65	N/R	N/R	66.83	15.35	-	-	-	-

Linker	**1**	**2**	**3**
H	3.39 (td, J = 6.5, 2.9 Hz, 2H)	1.90 – 1.81 (m, 2H)	3.96, 3.68
C	28.10	47.78	67.06

N/R: not reported.



Synthesis of 22

99 was treated according to the general procedure in the methods to give **22** as the white solid after lyophilization (37 mg, yield 54% for 2 steps). In detail, **99** (72 mg, 0.10 mmol) was dissolved in a mixed solution of 0.5 mL DMF and 0.5 mL TEA. SO_3/Py (63 mg, 0.40 mmol) was then added under an ice bath. The reaction was stirred for 15 min at 0 °C and then continued to stir at 40 °C for 3 h. Monitoring reaction by TLC (EtOAc/MeOH/H_2O, 10:3:2, *v/v*). Methanol and saturated $NaHCO_3$ aqueous were poured into the reaction mixture to quench the reaction. Subsequently, the reaction crude was treated according to the general procedure in the methods to deprotect the TBDMS group to give **22**. ESI-Q-TOF-HRMS m/z calculated for $C_{23}H_{39}N_4O_{18}S$, $[M-H]^-$: 691.1986, found 691.1986.

^1H NMR (600 MHz, D_2O): δ (ppm)

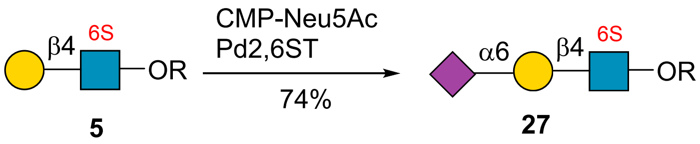
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.48	3.89	4.07 – 4.02 (m, 1H)	3.69	3.55	3.98, 3.86	-	-	-	2.03 (s, 3H)
Gal	4.49	3.47 (dd, J = 9.8, 7.8 Hz, 1H)	3.63	3.92	3.91	4.19 – 4.14 (m, 1H), 4.14 – 4.10 (m, 1H)	-	-	-	-
Fuc	4.99 (d, J = 4.0 Hz, 1H)	3.75 (dd, J = 10.5, 4.0 Hz, 1H)	N/R	N/R	4.90 – 4.83 (m, 1H)	1.16 (d, J = 6.6 Hz, 3H)	-	-	-	-

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.63	55.22	75.82	72.14	74.90	59.16	-	-	-	21.80
Gal	102,31	69.87	71.59	67.48	68.56	67.07	-	-	-	-
Fuc	97.68	67.48	N/R	N/R	66.35	14.93	-	-	-	-

Linker	1	2	3
H	3.41 – 3.31 (m, 2H)	1.85 – 1.79 (m, 2H)	3.95, 3.66
C	47.31	27.66	66.74

N/R: not reported.



Synthesis of 27

27 was synthesized using Pd2,6ST as described in the methods. White solid after lyophilization (23 mg, yield 74%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2362.

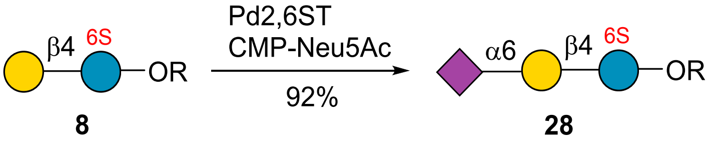
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.59 (d, *J* = 7.8 Hz, 1H)	3.76	3.79	3.69	3.85	4.46, 4.30	-	-	-	2.08 or 2.04
Gal	4.50 (d, *J* = 7.9 Hz, 1H)	3.54	3.69	3.94	3.85	4.01, 3.54	-	-	-	-
Neu5Ac	-	-	2.67 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.72 (t, *J* = 12.2 Hz, 1H)	3.67	3.81	3.76	3.56	3.91	3.90, 3.66	2.08 or 2.04

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	100.96	54.78	72.32	80.34	72.52	66.77	-	-	-	22.27 or 22.00
Gal	103.42	70.74	72.37	68.35	73.62	63.26	-	-	-	-
Neu5Ac	173.51	100.12	40.07	68.21	51.87	72.37	68.39	71.66	62.63	22.27 or 22.00

Linker	1	2	3
H	3.40	1.87	3.99, 3.72
C	47.78	28.10	67.24



Synthesis of 28

28 was synthesized using Pd2,6ST as described in the methods. White solid after lyophilization (22 mg, yield 92%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{22}S$, $[M-H]^-$: 795.2095, found 795.2098.

^1H NMR (600 MHz, D_2O): δ (ppm)

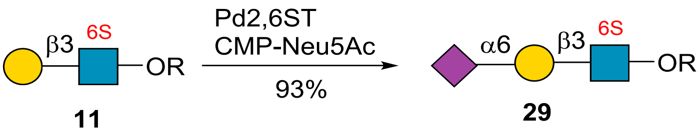
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.58 (d, *J* = 8.4 Hz,	3.87	3.81	3.57	3.74	4.41, 4.24 (dd, *J* = 11.3, 5.9	-	-	-	2.08 – 2.01 (m, 6H)

	1H)					Hz, 1H)				
Gal	4.41	3.52 (dd, *J* = 10.0, 7.8 Hz, 1H)	3.65	3.93	3.74	3.95, 3.63	-	-	-	-
Neu5Ac	-	-	2.73 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.71 (t, *J* = 12.2 Hz, 1H)	3.69	3.82	3.79	3.58	3.89	3.89, 3.65	2.08 – 2.01 (m, 6H)

^{13}C NMR (151 MHz, D$_2$O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.94	54.40	82.75	68.16	72.56	67.27	-	-	-	22.22 or 22.01
Gal	103.72	70.54	72.36	68.45	73.25	63.38	-	-	-	-
Neu5Ac	173.47	100.37	40.19	68.28	51.95	73.44	68.67	71.73	62.62	22.22 or 22.01

Linker	**1**	**2**	**3**
H	3.43 – 3.35 (m, 2H)	1.91 – 1.81 (m, 2H)	3.99, 3.72
C	47.80	28.10	67.30



Synthesis of 29

29 was synthesized using Pd2,6ST as described in the methods. White solid after lyophilization (14 mg, yield 93%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, [M-H]$^-$: 836.2361, found 836.2365.

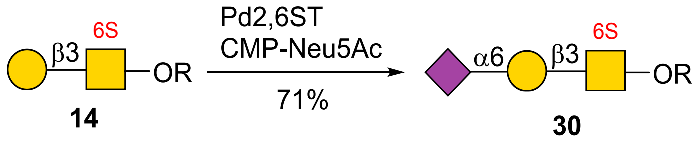
^{1}H NMR (600 MHz, D$_2$O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.58 (d, *J* = 8.4 Hz, 1H)	3.87	3.81	3.57	3.74	4.41, 4.24 (dd, *J* = 11.3, 5.9 Hz, 1H)	-	-	-	2.08 – 2.01 (m, 6H)
Gal	4.41	3.52 (dd, *J* = 10.0, 7.8 Hz, 1H)	3.65	3.93	3.74	3.95, 3.63	-	-	-	-
Neu5Ac	-	-	2.73 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.71 (t, *J* = 12.2 Hz, 1H)	3.69	3.82	3.79	3.58	3.89	3.89, 3.65	2.08 – 2.01 (m, 6H)

^{13}C NMR (151 MHz, D$_2$O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.94	54.40	82.75	68.16	72.56	67.27	-	-	-	22.22 or 22.01
Gal	103.72	70.54	72.36	68.45	73.25	63.38	-	-	-	-
Neu5Ac	173.47	100.37	40.19	68.28	51.95	73.44	68.67	71.73	62.62	22.22 or 22.01

Linker	**1**	**2**	**3**
H	3.43 – 3.35 (m, 2H)	1.91 – 1.81 (m, 2H)	3.99, 3.72



Synthesis of 30

30 was synthesized using Pd2,6ST as described in the methods. White solid after lyophilization (10.7 mg, 71%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2361.

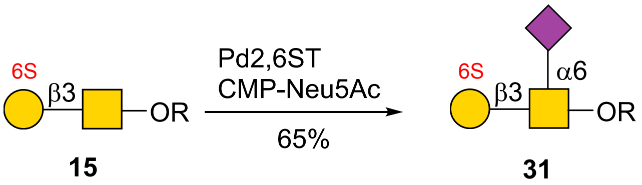
^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.51 (d, *J* = 8.5 Hz)	4.03	3.92	4.21	3.96	4.25	-	-	-	2.04
Gal	4.45 (d, *J* = 7.8 Hz)	3.51	3.62	3.94	3.73	3.90, 3.66	-	-	-	-
Neu5Ac	-	-	2.75 (dd, *J* = 12.5, 4.7 Hz), 1.69 (t, *J* = 12.1 Hz)	3.69	3.83	3.73	3.60	3.89	3.90, 3.66	2.04

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.29	51.14	79.26	67.74	72.60	67.71	-	-	-	22.18
Gal	104.52	70.41	72.53	N/R	73.07	63.17	-	-	-	-
Neu5Ac	173.38	100.47	40.14	N/R	51.82	72.26	N/R	71.66	62.55	21.94

Linker	**1**	**2**	**3**
H	3.40	1.86	3.98, 3.73
C	47.75	28.06	67.12



Synthesis of 31

31 was synthesized using Pd2,6ST as described in the methods. White solid after lyophilization (20 mg, 65%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2360.

^{1}H NMR (500 MHz, D_2O): δ (ppm)

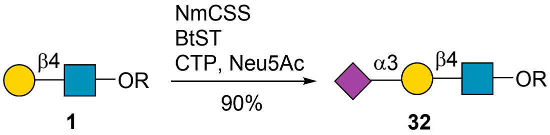
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.48	4.01	3.88	4.17	3.75	3.98	-	-	-	2.04
Gal	4.47	3.53	3.64	3.96	3.80	4.18	-	-	-	-
Neu5Ac	-	-	2.75 (dd, *J* = 12.4, 4.6 Hz), 1.74 (t, *J* = 12.2 Hz)	3.68	3.83	3.72	3.58	3.90	3.89, 3.65	2.04

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.43	51.22	79.32	68.24	73.26	63.69	-	-	-	22.22 or

										22.01
Gal	104.57	70.43	72.27	68.24	72.58	67.27	-	-	-	-
Neu5Ac	173.41	100.37	40.07	68.16 or 68.06	51.83	72.39	68.16 or 68.06	71.60	62.62	22.22 or 22.01

Linker	**1**	**2**	**3**
H	3.39	1.86	3.99, 3.70
C	47.77	28.14	66.94



Synthesis of 32

32 was synthesized using BtST as described in the methods. White solid after lyophilization (730 mg, yield 90%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{19}$, $[M-H]^-$: 756.2792, found 756.2792.

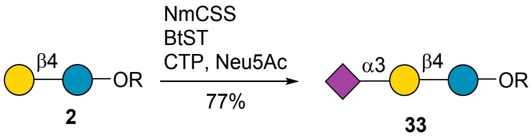
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.53 (d, *J* = 7.8 Hz, 1H)	3.75	3.70	3.74	3.60	4.01, 3.87	-	-	-	2.05 or 2.04
Gal	4.55 (d, *J* = 8.0 Hz, 1H)	3.58	4.12	3.98	3.69	3.74	-	-	-	-
Neu5Ac	-	-	2.76 (dd, *J* = 12.4, 4.2 Hz, 1H), 1.82	3.69	3.85	3.75	3.59	3.90	3.65	2.05 or 2.04

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.12	55.06	72.31	78.29	74.72	60.01	-	-	-	22.14
Gal	102.54	69.36	75.44	67.45	75.13	60.99	-	-	-	-
Neu5Ac	173.68	99.70	39.55	68.07	51.65	72.88	68.27	71.68	62.58	22.14

Linker	**1**	**2**	**3**
H	3.38	1.85	3.99, 3.69
C	47.75	28.08	67.11



Synthesis of 33

33 was synthesized using BtST as described in the methods. White solid after lyophilization (130 mg, yield 77%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{19}$, $[M-H]^-$: 715.2527, found 715.2524.

^{1}H NMR (800 MHz, D_2O): δ (ppm)

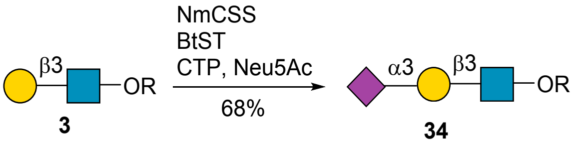
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.49 (d,	3.34 –	3.64	3.66	3.60	4.00,	-	-	-	-

	J = 8.1 Hz, 1H)	3.29 (m, 1H)				3.83				
Gal	4.54 (d, *J* = 7.9 Hz, 1H)	3.58	4.12 (dd, *J* = 9.9, 3.1 Hz, 1H)	3.96 (d, *J* = 3.1 Hz, 1H)	3.72	3.74 (2H)	-	-	-	-
Neu5Ac			2.76 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.81 (t, *J* = 12.2 Hz, 1H)	3.69	3.84	3.64	3.60	3.89	3.87, 3.64	2.04 (s, 3H)

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	102.01	72.75	74.22	78.13	74.65	59.93	-	-	-	-
Gal	102.52	69.24	75.36	67.24	75.04	60.90	-	-	-	-
Neu5Ac	173.72	99.65	39.50	68.22	51.55	72.68	67.97	71.63	62.45	21.90

Linker	**1**	**2**	**3**
H	3.47 (t, *J* = 6.7 Hz, 2H)	1.94 – 1.89 (m, 2H)	4.00, 3.77
C	47.75	28.10	67.33



Synthesis of 34

34 was synthesized using BtST as described in the methods. White solid after lyophilization (110 mg, yield 68%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{19}$, $[M-H]^-$: 756.2792, found 756.2794.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

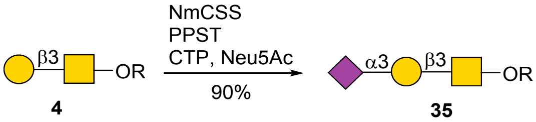
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 (d, *J* = 8.3 Hz, 1H)	3.82	3.79	3.55	3.51 – 3.47 (m, 1H)	3.94, 3.76	-	-	-	2.10 – 2.00 (m, 6H)
Gal	4.51 (d, *J* = 7.8 Hz, 1H)	3.55	4.09 (dd, *J* = 9.8, 3.2 Hz, 1H)	3.95	3.69	3.75	-	-	-	-
Neu5Ac	-	-	2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.79 (t, *J* = 12.1 Hz, 1H)	3.55	3.84	3.65	3.61	3.88	3.85, 3.65	2.10 – 2.00 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.91	54.44	82.52	68.04	75.09	60.74	-	-	-	22.31 or 22.04
Gal	103.45	69.08	75.62	67.25	75.39	61.01	-	-	-	-
Neu5Ac	173.90	99.65	39.77	69.39	51.66	72.80	68.74	71.84	62.45	22.31 or 22.04

Linker	**1**	**2**	**3**
H	3.39 (td, *J* = 6.6, 2.4 Hz, 2H)	1.90 – 1.82 (m, 2H)	3.99 (dt, *J* = 10.9, 5.6 Hz, 1H), 3.71

C	47.79	28.10	67.15



Synthesis of 35

35 was synthesized using BtST as described in the methods. White solid after lyophilization (145 mg, 90%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{19}$, $[M-H]^-$: 756.2792, found 756.2795.

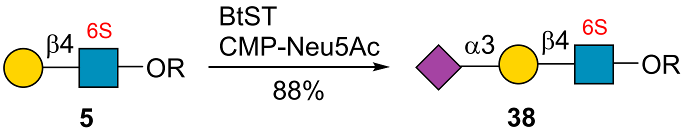
^1H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.53	4.03	3.88	4.19	3.72	3.74	-	-	-	2.05 or 2.04
Gal	4.54	3.56	4.09	3.95	3.65	3.74	-	-	-	-
Neu5Ac	-	-	2.76 (dd, J = 12.4, 4.2 Hz), 1.79 (t, J = 12.1 Hz)	3.65	3.86	3.74	3.62	3.89	3.86, 3.66	2.05 or 2.04

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.39	51.14	80.02	67.84	74.75	60.93	-	-	-	22.29
Gal	104.57	68.98	75.54	67.34	74.72	60.97	-	-	-	-
Neu5Ac	173.91	99.66	39.71	68.03	51.65	72.77	68.37	71.80	62.46	22.03

Linker	**1**	**2**	**3**
H	3.40	1.87	3.99, 3.72
C	47.78	28.10	66.99



Synthesis of 38

38 was synthesized using BtST as described in the methods. White solid after lyophilization (68 mg, yield 88%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2363.

^1H NMR (600 MHz, D_2O): δ (ppm)

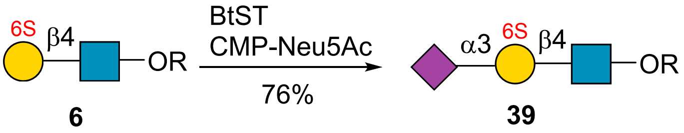
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.55 (d, J = 8.2 Hz, 1H)	3.75	3.70	3.79	3.79	4.39, 4.31	-	-	-	2.03 or 2.01
Gal	4.62 (d, J = 7.8 Hz, 1H)	3.56	4.12	3.95	3.70	3.72	-	-	-	-
Neu5Ac	-	-	2.75 (dd, J = 12.4, 4.7 Hz, 1H), 1.80	3.68	3.83	3.70	3.58	3.90	3.87, 3.64	2.03 or 2.01

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.17	55.05	72.20	77.16	72.50	66.25	-	-	-	22.15

Gal	102.09	69.44	75.30	67.45	75.05	61.02	-	-	-	-
Neu5Ac	173.95	99.72	39.56	68.04	51.68	72.81	68.43	71.47	62.49	22.03

Linker	**1**	**2**	**3**
H	3.36	1.83	3.96, 3.67
C	47.76	28.08	67.24



Synthesis of 39

39 was synthesized using BtST as described in the methods. White solid after lyophilization (35 mg, yield 76%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2360.

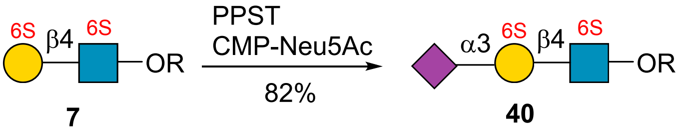
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.53 (d, *J* = 7.4 Hz, 1H)	3.75	3.74	3.72	3.64	4.02, 3.86	-	-	-	2.06 or 2.04
Gal	4.61 (d, *J* = 7.9 Hz, 1H)	3.60	4.14	4.02	3.98	4.19	-	-	-	-
Neu5Ac	-	-	2.77 (dd, *J* = 12.4, 4.2 Hz, 1H), 1.82	3.71	3.87	3.75	3.60	3.91	3.89, 3.66	2.06 or 2.04

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.12	55.13	72.03	79.13	74.68	60.26	-	-	-	22.16
Gal	102.36	69.25	75.20	67.35	72.69	67.40	-	-	-	-
Neu5Ac	173.80	99.94	39.49	68.08	51.64	72.87	68.37	71.69	62.56	22.16

Linker	**1**	**2**	**3**
H	3.39	1.85	3.98, 3.67
C	47.75	28.08	67.08



Synthesis of 40

40 was synthesized using PPST as described in the methods. White solid after lyophilization (18 mg, yield 82%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{25}S_2$, $[M-H]^-$: 916.1929, found 916.1929.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

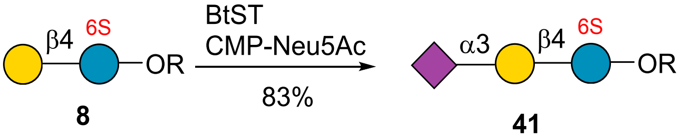
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.56	3.75	3.77	3.77	3.85	4.46,4.32	-	-	-	2.06 or 2.05

Gal	4.64 (d, *J* = 7.9 Hz, 1H)	3.47	4.16	4.04	3.98	4.20	-	-	-	-
Neu5Ac	-	-	2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.81	3.68	3.88	3.71	3.60	3.93	3.91, 3.66	2.06 or 2.05

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.15	55.07	72.00	78.63	72.52	66.63	-	-	-	22.17
Gal	102.28	69.31	75.06	67.32	72.56	67.31	-	-	-	-
Neu5Ac	173.91	99.91	39.45	68.10	51.66	72.82	68.50	71.53	62.52	22.05

Linker	**1**	**2**	**3**
H	3.39	1.85	3.97, 3.67
C	47.78	28.09	67.24



Synthesis of 41

41 was synthesized using BtST as described in the methods. White solid after lyophilization (20 mg, yield 83%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{22}S$, $[M-H]^-$: 795.2095, found 795.2094.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

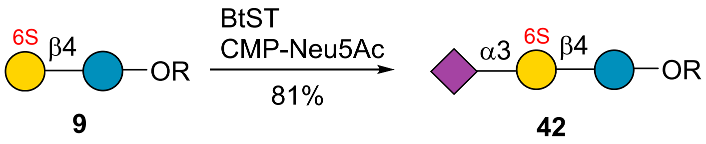
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.51 (d, *J* = 8.0 Hz, 1H)	3.34 (dd, *J* = 9.5, 8.0 Hz, 1H)	3.66	3.76	3.82	4.40 (dd, *J* = 11.1, 2.1 Hz, 1H), 4.32 (dd, *J* = 11.0, 4.4 Hz, 1H)	-	-	-	-
Gal	4.61 (d, *J* = 7.9 Hz, 1H)	3.56 (dd, *J* = 9.9, 7.9 Hz, 1H)	4.13 (dd, *J* = 9.9, 3.2 Hz, 1H)	3.97	3.72	3.75 (2H)	-	-	-	-
Neu5Ac	-	-	2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.82 (t, *J* = 12.1 Hz, 1H)	3.69	3.86	3.64	3.61 (dd, *J* = 9.1, 1.8 Hz, 1H)	3.95 – 3.91 (m, 1H)	3.90, 3.66	2.04 (s, 3H)

^{13}C NMR (150 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	102.00	72.70	74.06	76.87	72.37	66.06	-	-	-	-
Gal	102.07	69.30	75.19	67.37	74.90	60.88	-	-	-	-
Neu5Ac	173.72	99.52	39.40	68.27	51.54	72.56	67.92	71.28	62.38	21.89

Linker	**1**	**2**	**3**

H	3.49 – 3.44 (m, 2H)	1.95 – 1.89 (m, 2H)	4.00, 3.78
C	47.73	28.10	67.31



Synthesis of 42

42 was synthesized using BtST as described in the methods. White solid after lyophilization (26 mg, yield 81%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{22}S$, $[M-H]^-$: 795.2095, found 795.2090.

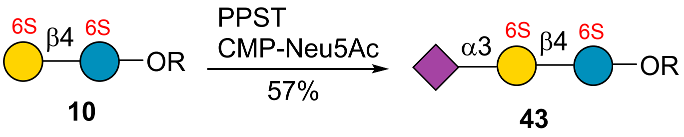
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.51 (d, *J* = 8.0 Hz, 1H)	3.37 – 3.32 (m, 1H)	3.66	3.65	3.63	4.00, 3.83	-	-	-	-
Gal	4.57 (d, *J* = 7.9 Hz, 1H)	3.60	4.15 (dd, *J* = 9.9, 3.1 Hz, 1H)	4.03	3.99	4.24 – 4.18 (m, 2H)	-	-	-	-
Neu5Ac	-	-	2.77 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.82 (t, *J* = 12.1 Hz, 1H)	3.71	3.87	3.65	3.61	3.90	3.90, 3.66	2.05 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.90	72.61	72.19	79.35	74.53	60.13	-	-	-	-
Gal	102.65	69.07	75.06	67.20	72.75	67.36	-	-	-	-
Neu5Ac	173.72	99.83	39.37	68.26	51.54	72.61	67.97	71.58	62.45	21.91

Linker	**1**	**2**	**3**
H	3.47 (t, *J* = 6.7 Hz, 2H)	1.96 – 1.89 (m, 2H)	3.99, 3.78 (dt, *J* = 10.3, 6.2 Hz, 1H)
C	47.74	28.10	67.23



Synthesis of 43

43 was synthesized using PPST as described in the methods. White solid after lyophilization (17 mg, yield 57%). ESI-Q-TOF-HRMS m/z calculated for $C_{26}H_{43}N_4O_{25}S_2$, $[M-H]^-$: 875.1663, found 875.1661.

^{1}H NMR (500 MHz, D_2O): δ (ppm)

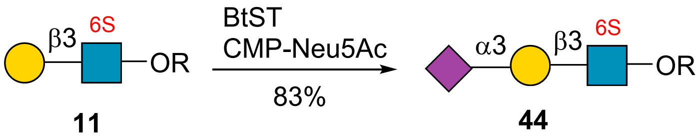
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.51 (d, *J* = 8.0 Hz, 1H)	3.35 (dd, *J* = 9.1, 8.0 Hz, 1H)	3.67	3.70	3.83	4.43 (dd, *J* = 11.2, 2.1 Hz, 1H), 4.29 (dd, *J* = 11.2,	-	-	-	-

						5.2 Hz, 1H)				
Gal	4.61 (d, *J* = 7.9 Hz, 1H)	3.57	4.16 (dd, *J* = 10.0, 3.2 Hz, 1H)	4.03	3.98	4.19 (2H)	-	-	-	-
Neu5Ac			2.75 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.82 (t, *J* = 12.1 Hz, 1H)	3.70	3.85	3.64	3.59	3.91	3.88, 3.64	2.03 (s, 3H)

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.94	72.69	74.09	78.67	72.31	66.39	-	-	-	-
Gal	102.47	69.11	74.90	67.18	72.47	67.37	-	-	-	-
Neu5Ac	173.64	99.68	39.27	68.31	51.52	72.44	67.95	71.32	62.39	21.90

Linker	**1**	**2**	**3**
H	3.47 (t, *J* = 6.7 Hz, 2H)	1.96 – 1.87 (m, 2H)	3.98, 3.82 – 3.74 (m, 1H)
C	47.72	28.10	67.20



Synthesis of 44

44 was synthesized using BtST as described in the methods. White solid after lyophilization (12.5 mg, yield 83%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, $[M-H]^-$: 836.2361, found 836.2364.

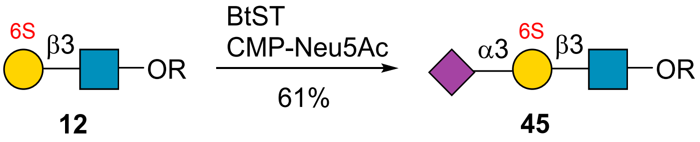
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.59 (d, *J* = 8.3 Hz, 1H)	3.84	3.81	3.61	3.73	4.38 (dd, *J* = 11.3, 2.2 Hz, 1H), 4.23 (dd, *J* = 11.3, 5.7 Hz, 1H)	-	-	-	2.05 – 2.03 (m, 6H)
Gal	4.51 (d, *J* = 7.8 Hz, 1H)	3.54	4.10 (dd, *J* = 9.8, 3.2 Hz, 1H)	3.94	3.68	3.73 (2H)	-	-	-	-
Neu5Ac	-	-	2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.83 – 1.77 (m, 1H)	3.71	3.86	3.65	3.60	3.88	3.86, 3.65	2.05 – 2.03 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.41	53.92	81.68	67.53	72.29	66.78	-	-	-	21.78, 21.52
Gal	102.96	68.57	75.08	67.53	74.55	60.49	-	-	-	-
Neu5Ac	173.17	99.00	39.17	68.00	51.12	72.77	67.80	71.23	61.96	21.78, 21.52

Linker	1	2	3
H	3.43 – 3.35 (m, 2H)	1.90 – 1.83 (m, 2H)	3.99, 3.70
C	47.28	27.59	66.78



Synthesis of 45

45 was synthesized using BtST as described in the methods. White solid after lyophilization (14 mg, yield 61%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, [M-H]$^-$: 836.2361, found 836.2362.

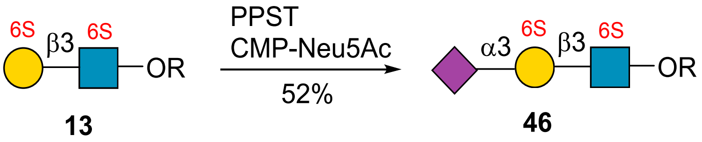
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.56 (d, *J* = 8.5 Hz, 1H)	3.84	3.77	3.54	3.50	3.93, 3.78	-	-	-	2.05 (s, 3H) or 2.04 (s, 3H)
Gal	4.52 (d, *J* = 7.9 Hz, 1H)	3.54	4.12 (dd, *J* = 9.8, 3.2 Hz, 1H)	4.00	3.95	4.23 – 4.15 (m, 2H)	-	-	-	-
Neu5Ac	-	-	2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.80 (t, *J* = 12.1 Hz, 1H)	3.69	3.86	3.64	3.60	3.88	3.86, 3.65	2.05 (s, 3H) or 2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	100.89	51.64	83.22	68.40	75.36	60.69	-	-	-	22.27 or 22.02
Gal	103.55	68.93	75.34	67.20	72.70	67.62	-	-	-	-
Neu5Ac	173.82	99.77	39.63	68.93	54.31	72.79	68.03	71.77	62.46	22.27 or 22.02

Linker	1	2	3
H	3.44 – 3.34 (m, 2H)	1.89 – 1.83 (m, 2H)	3.96, 3.70
C	47.78	28.08	67.13



Synthesis of 46

46 was synthesized using PPST as described in the methods. White solid after lyophilization (15 mg, yield 52%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{25}S_2$, [M-H]$^-$: 916.1929, found 916.193.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.58 (d, *J* = 8.3 Hz,	3.85	3.81	3.60	3.73	4.39 (dd, *J* = 11.2, 2.1 Hz, 1H), 4.24 (dd,	-	-	-	2.09 – 1.99 (m, 6H)

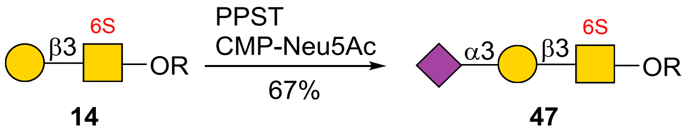
	1H)					J = 11.3, 5.8 Hz, 1H)				
Gal	4.53 (d, J = 7.8 Hz, 1H)	3.56	4.12 (dd, J = 9.8, 3.2 Hz, 1H)	4.00	3.94	4.22 – 4.16 (m, 2H)	-	-	-	-
Neu5Ac	-	-	2.77 (dd, J = 12.4, 4.6 Hz, 1H), 1.81 (t, J = 12.1 Hz, 1H)	3.69	3.87	3.65	3.60	3.88	3.85, 3.65	2.09 – 1.99 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.92	54.39	82.31	68.04	73.23	67.14	-	-	-	22.31 or 22.04
Gal	103.44	68.95	75.36	67.14	N/R	67.42	-	-	-	-
Neu5Ac	173.83	99.74	39.67	68.54	51.62	72.62	68.41	71.78	62.45	22.31 or 22.04

Linker	**1**	**2**	**3**
H	3.43 – 3.35 (m, 2H)	1.90 – 1.84 (m, 2H)	3.98, 3.70
C	47.80	28.10	67.30

N/R: not reported.



Synthesis of 47

47 was synthesized using PPST as described in the methods. White solid after lyophilization (10 mg, 67%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, [M-H]$^-$: 836.2361, found 836.2361.

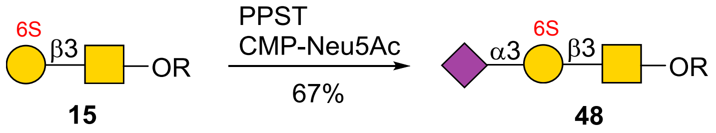
^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.53	4.03	3.90	4.24	3.95	4.22	**-**	**-**	**-**	2.04/2.04
Gal	4.53	3.56	4.08	3.94	3.65	3.73	-	-	-	-
Neu5Ac	-	-	2.76 (dd, J = 12.5, 4.7 Hz), 1.80 (t, J = 12.1 Hz)	3.68	3.85	3.70	3.62	3.89	3.86, 3.65	2.04/2.04

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.34	51.01	79.87	67.59	72.38	67.33	-	-	-	22.26
Gal	104.62	68.96	75.52	67.28	74.71	60.91	-	-	-	-
Neu5Ac	173.90	99.64	39.69	68.02	51.62	72.74	68.38	71.77	62.43	22.00

Linker	**1**	**2**	**3**
H	3.40	1.86	3.99, 3.71
C	47.78	28.10	67.14



Synthesis of 48

48 was synthesized using PPST as described in the methods. White solid after lyophilization (15 mg, 67%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{22}S$, [M-H]$^-$: 836.2361, found 836.2362.

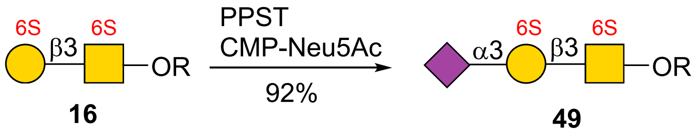
^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.50	4.02	3.85	4.23	3.71	3.80	**-**	**-**	**-**	2.04 or 2.03
Gal	4.53	3.58	4.10	3.98	3.88	4.16	-	-	-	-
Neu5Ac	-	-	2.76, 1.80	3.68	3.85	3.73	3.62	3.89	3.86, 3.64	2.04 or 2.03

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.41	51.02	80.20	67.90	74.93	61.21	-	-	-	22.22, 22.01
Gal	104.35	68.85	75.35	67.71	72.41	67.33	-	-	-	-
Neu5Ac	173.85	99.78	39.59	68.03	51.62	72.77	68.40	71.73	62.47	22.22, 22.01

Linker	**1**	**2**	**3**
H	3.39	1.86	3.99, 3.70
C	47.78	28.09	66.96



Synthesis of 49

49 was synthesized using PPST as described in the methods. White solid after lyophilization (12 mg, 92%). ESI-Q-TOF-HRMS m/z calculated for $C_{28}H_{46}N_5O_{25}S_2$, [M-H]$^-$: 916.1929, found 916.1927.

^{1}H NMR (800 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.52 (d, J = 8.5 Hz)	4.04	3.90	4.24	3.96	4.24	**-**	**-**	**-**	2.05 or 2.04
Gal	4.56 (d, J = 7.9 Hz)	3.57	4.10	3.99	3.90	4.18	-	-	-	-
Neu5Ac	-	-	2.76 (dd, J = 12.5, 4.7 Hz), 1.81 (t, J = 12.1 Hz)	3.69	3.85	3.65	3.62	3.89	3.86, 3.65	2.05 or 2.04

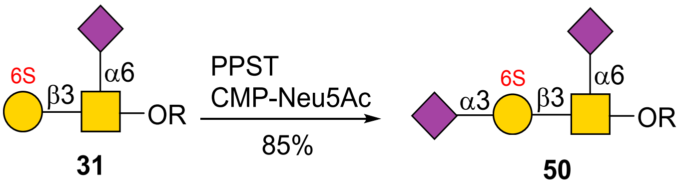
^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.33	51.00	79.70	67.83	72.36	N/R	-	-	-	22.30
Gal	104.31	68.87	75.35	N/R	72.68	N/R	-	-	-	-
Neu5Ac	173.88	99.81	39.62	N/R	51.64	72.26	N/R	71.76	62.48	22.05

Linker	**1**	**2**	**3**
H	3.40	1.86	3.99, 3.73

C	47.83	28.13	N/R

N/R: not reported.



31 **50**

Synthesis of 50

50 was synthesized using PPST as described in the methods. White solid after lyophilization (11.5 mg, 85%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{30}S$, $[M-H]^-$: 1127.3315, found 1127.331.

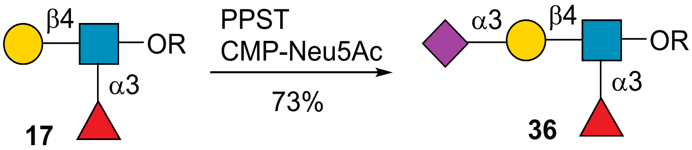
^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.48 (d, *J* = 8.5 Hz)	4.03	3.88	4.18	3.75	3.98	**-**	**-**	**-**	2.04
Gal	4.54 (d, *J* = 7.9 Hz)	3.57	4.09	4.00	3.80	4.16	-	-	-	-
Neu5Ac	-	-	2.74, 1.73	3.69	3.84	3.72	3.58	3.89	3.87, 3.65	2.04
Neu5Ac′	-	-	2.76, 1.80	3.68	3.83	3.72	3.58	3.90	3.87, 3.65	2.04

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.45	51.08	79.42	68.26	73.28	63.74	-	-	-	22.29 or 22.02 or 22.01
Gal	104.25	68.82	75.31	67.16	72.77	67.26	-	-	-	-
Neu5Ac	173.40	100.38	40.05	68.04 or 67.95	51.82	72.57	68.41	71.74	62.63	22.29 or 22.02 or 22.01
Neu5Ac′	173.83	99.75	39.63	68.04 or 67.95	51.62	72.32	68.26	71.58	62.45	22.29 or 22.02 or 22.01

Linker	**1**	**2**	**3**
H	3.39	1.86	3.98, 3.71
C	47.77	28.14	67.24



17 **36**

Synthesis of 36

36 was synthesized using PPST as described in the methods. White solid after lyophilization (32 mg, 73%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{23}$, $[M-H]^-$: 902.3372, found 902.3376.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

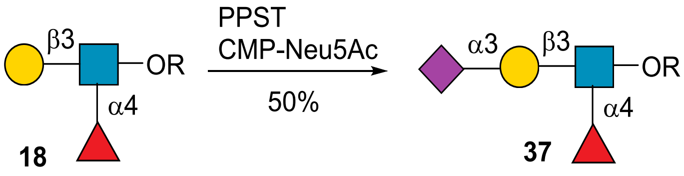
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.51	2.89	3.83	3.92	3.56	3.98, 386	-	-	-	2.03 – 1.98 (m, 6H)
Gal	4.51	3.51 (dd, *J* = 9.8, 7.8 Hz, 1H)	4.07 (dd, *J* = 9.8, 3.2 Hz, 1H)	3.91	N/R	3.67 (2H)	-	-	-	-
Fuc	5.09 (d, *J* = 4.0 Hz, 1H)	3.67	3.90	3.76 (d, *J* = 3.3 Hz, 1H)	4.80	1.15 (d, *J* = 6.6 Hz, 3H)	-	-	-	-
Neu5Ac	-	-	2.75 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.78	3.66	3.81	N/R	N/R	3.87	3.84, 3.62	2.03 – 1.98 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.98	55.80	N/R	N/R	N/R	59.62	-	-	-	22.21 or 22.02
Gal	101.59	N/R	75.62	N/R	N/R	61.48	-	-	-	-
Fuc	98.60	N/R	N/R	71.85	66.67	15.26	-	-	-	-
Neu5Ac	173.88	99.64	39.76	N/R	51.67	N/R	N/R	N/R	62.57	22.21 or 22.02

Linker	**1**	**2**	**3**
H	3.40 – 3.30 (m, 2H)	1.82 (2H)	3.95, 3.67
C	47.74	28.10	67.18

N/R: not reported.



Synthesis of 37

37 was synthesized using PPST as described in the methods. White solid after lyophilization (37 mg, yield 50%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{23}$, $[M-H]^-$: 902.3372, found 902.3369.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 – 4.52 (m, 2H)	3.89	4.08	3.73	3.55	3.98, 3.86	-	-	-	2.06 (s, 3H) or 2.04 (s, 3H)
Gal	4.57 – 4.52 (m, 2H)	3.52	4.06	3.92	N/R	3.70 (2H)	-	-	-	-
Fuc	5.01 (d, *J* = 4.0 Hz,	3.80	3.88	N/R	4.88 (q, *J* = 6.9 Hz,	1.18 (d, *J* = 6.6 Hz, 2H)	-	-	-	-

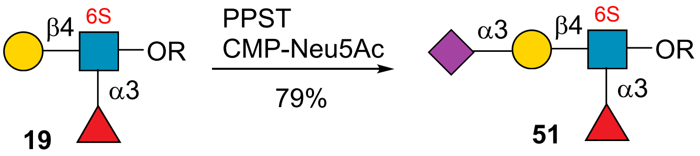
	1H)				0H)					
Neu5Ac	-	-	2.78 (dd, J = 12.4, 4.6 Hz, 1H), 1.78 (t, J = 12.2 Hz, 1H)	3.68	3.85	N/R	N/R	N/R	3.82, 3.67	2.06 (s, 3H) or 2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.96	55.70	76.03	72.32	75.44	59.69	-	-	-	22.39 or 22.02
Gal	102.78	68.76	75.59	66.82	N/R	61.64	-	-	-	-
Fuc	98.04	68.40	N/R	71.84	66.82	15.31	-	-	-	-
Neu5Ac	173.92	99.36	39.99	69.08	51.65	N/R	N/R	N/R	62.28	22.39 or 22.02

Linker	**1**	**2**	**3**
H	3.39 (td, J = 6.5, 4.0 Hz, 2H)	1.90 – 1.81 (m, 2H)	3.97, 3.68
C	47.76	28.10	67.17

N/R: not reported.



19 **51**

Synthesis of 51

51 was synthesized using PPST as described in the methods. White solid after lyophilization (11 mg, yield 79%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{26}S$, $[M-H]^-$: 982.294, found 982.2937.

^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.57 (d, J = 8.0 Hz, 1H)	3.91	3.87	4.02 (t, J = 9.2 Hz, 1H)	3.81	4.43 – 4.33 (m, 2H)	-	-	-	2.07 – 2.01 (m, 6H)
Gal	4.62 (d, J = 7.9 Hz, 1H)	3.51 (dd, J = 9.9, 7.8 Hz, 1H)	4.10 (dd, J = 9.9, 3.2 Hz, 1H)	3.96	N/R	3.69 (2H)	-	-	-	-
Fuc	5.11 (d, J = 4.0 Hz, 1H)	3.67	N/R	3.77	4.81	1.17 (d, J = 6.6 Hz, 3H)	-	-	-	-
Neu5Ac	-	-	2.75 (dd, J = 12.4, 4.7 Hz, 1H), 1.80	3.69	3.86	N/R	N/R	3.91	3.90, 3.66	2.07 – 2.01 (m, 6H)

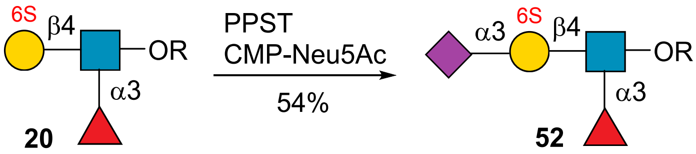
^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.96	55.68	74.69	72.86	N/R	65.87	-	-	-	22.21 or 22.04
Gal	101.16	69.39	75.39	N/R	N/R	61.47	-	-	-	-
Fuc	98.55			N/R	66.70	15.28	-	-	-	-

Neu5Ac	174.05	99.56	39.70	N/R	51.73	N/R	N/R	71.34	62.52	22.21 or 22.04

Linker	**1**	**2**	**3**
H	3.43 – 3.32 (m, 2H)	184 (2H)	3.96, 3.68
C	47.77	28.10	67.26

N/R: not reported.



Synthesis of 52

52 was synthesized using PPST as described in the methods. White solid after lyophilization (15 mg, yield 54%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{26}S$, $[M-H]^-$: 982.294, found 982.2943.

^1H NMR (600 MHz, D_2O): δ (ppm)

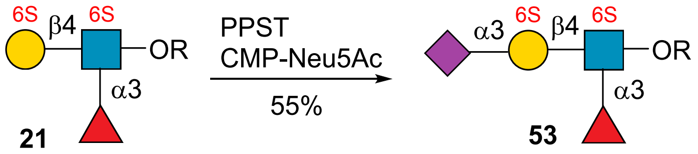
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.54	3.90	3.88	3.96	3.61	4.04 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.90	-	-	-	2.05 – 2.02 (m, 6H)
Gal	4.55	3.55 (dd, *J* = 9.8, 7.9 Hz, 1H)	4.12	3.99	N/R	4.13 (2H)	-	-	-	-
Fuc	5.11 (d, *J* = 4.0 Hz, 1H)	3.65	3.91	3.81	4.82	1.18 (d, *J* = 6.7 Hz, 3H)	-	-	-	-
Neu5Ac	-	-	2.78 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.81	3.70	3.87	N/R	N/R	N/R	3.89, 3.65	2.05 – 2.02 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.66	56.52	75.74	74.46	76.01	60.45	-	-	-	22.91 or 22.71
Gal	102.22	69.84	76.13	N/R	N/R	N/R	-	-	-	-
Fuc	99.24	N/R	N/R	73.62	67.35	16.00	-	-	-	-
Neu5Ac	174.45	100.44	40.42	N/R	52.35	N/R	N/R	N/R	63.29	22.91 or 22.71

Linker	**1**	**2**	**3**
H	3.43 – 3.34 (m, 2H)	1.85	3.97, 3.69
C	48.44	28.79	

N/R: not reported.



Synthesis of 53

53 was synthesized using PPST as described in the methods. White solid after lyophilization (7.7mg, 55%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{29}S_2$, $[M-H]^-$: 1062.2508, found 1062.2508.

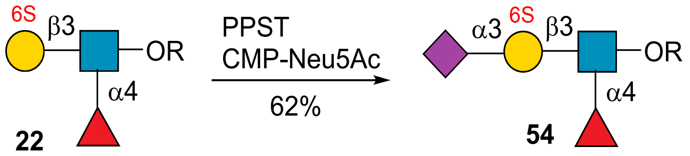
^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.55 (d, *J* = 8.0 Hz, 1H)	3.88	3.86	4.00	3.82	4.37	-	-	-	2.02 – 1.99 (m, 6H)
Gal	4.60 (d, *J* = 7.8 Hz, 1H)	3.51 (dd, *J* = 9.9, 7.9 Hz, 1H)	4.11	4.00	3.81	4.11	-	-	-	-
Fuc	5.08 (d, *J* = 4.0 Hz, 1H)	3.63	3.89	3.70	4.71	1.15 (d, *J* = 6.7 Hz, 3H)	-	-	-	-
Neu5Ac	-	-	2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.80	3.67	3.85	3.76	3.58	3.89	3.87, 3.63	2.02 – 1.99 (m, 6H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.94	55.67	74.92	73.31	72.99	66.00	-	-	-	22.20
Gal	101.26	69.29	75.14	66.85	72.02	67.03	-	-	-	-
Fuc	98.60	69.07	67.88	71.99	66.68	15.32	-	-	-	-
Neu5Ac	173.53	99.41	39.57	68.06	51.67	72.90	68.29	71.16	62.61	22.03

Linker	**1**	**2**	**3**
H	3.39 – 3.30 (m, 2H)	1.82	3.94, 3.65
C	47.75	28.09	67.20



Synthesis of 54

54 was synthesized using PPST as described in the methods. White solid after lyophilization (13 mg, yield 62%). ESI-Q-TOF-HRMS m/z calculated for $C_{34}H_{56}N_5O_{26}S$, $[M-H]^-$: 982.2940, found 982.2939.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.52 (d, *J* = 8.6	3.91	4.08	3.70	N/R	3.98, 3.86	-	-	-	2.06 (s, 3H) or 2.04 (s,

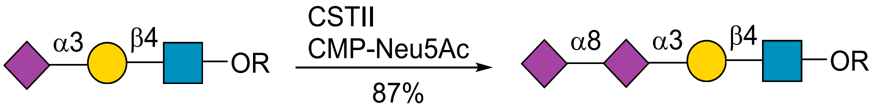
	Hz, 1H)									3H)
Gal	4.57 (d, J = 7.7 Hz, 1H)	3.52 (dd, J = 9.8, 7.8 Hz, 1H)	4.07	3.96	N/R	4.17 (dd, J = 10.6, 4.2 Hz, 1H), 4.10	-	-	-	-
Fuc	5.00 (d, J = 4.0 Hz, 1H)	3.76	N/R	N/R	4.89 (q, J = 6.8 Hz, 1H)	1.18 (d, J = 6.6 Hz, 3H)	-	-	-	-
Neu5Ac	-	-	2.78 (dd, J = 12.4, 4.6 Hz, 1H), 1.78 (t, J = 12.2 Hz, 1H)	3.69	3.85	N/R	N/R	N/R	3.85, 3.66	2.06 (s, 3H) or 2.04 (s, 3H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.04	55.59	76.24	72.54	N/R	59.64	-	-	-	22.40 or 22.03
Gal	102.58	68.67	N/R	66.71	N/R	67.77	-	-	-	-
Fuc	98.12	68.41	N/R	N/R	66.78	15.36	-	-	-	-
Neu5Ac	173.81	99.48	39.92	N/R	51.63	N/R	N/R	N/R	62.31	22.40 or 22.03

Linker	**1**	**2**	**3**
H	3.44 – 3.34 (m, 2H)	1.88 – 1.81 (m, 2H)	3.97, 3.68
C	47.77	28.10	67.19

N/R: not reported.



32 **55**

Synthesis of 55

55 was synthesized as described in the methods. White solid after lyophilization (2.4 mg, 87%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{27}$, $[M-H]^-$: 1047.3747, found 1047.3747.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.53	3.73	N/R	3.75	N/R	4.02, 3.88	-	-	-	2.10 – 2.02 (m, 9H)
Gal	4,56	3.57	4.10 (dd, J = 10.0, 3.1 Hz, 1H)	3.98	N/R	3.75 (2H)	-	-	-	-
Neu5Ac	-	-	2.69 (dd, J = 12.3, 4.4 Hz, 1H), 1.75 (t, J = 12.1 Hz, 1H)	3.62	3.84	N/R	N/R	4.15	4.22, 3.77	2.10 – 2.02 (m, 9H)
Neu5Ac′	-	-	2.79 (dd, J = 12.5,	3.68	3.84	N/R	N/R	3.92	3.89,	2.10 –

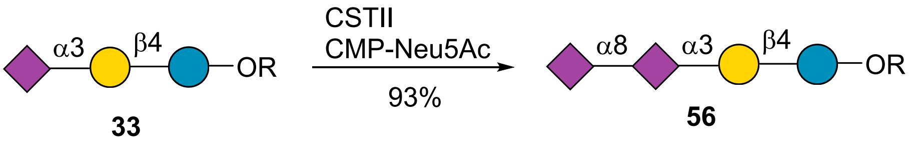
			4.6 Hz, 1H), 1.75 (t, $J = 12.1$ Hz, 1H)						366	2.02 (m, 9H)

^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.16	55.14	N/R	78.04	N/R	59.98	-	-	-	22.32 or 22.17 or 22.04
Gal	102.55	69.31	75.46	N/R	N/R	61.10	-	-	-	-
Neu5Ac	173.51 or 173.36	100.22	39.66	N/R	52.28	N/R	N/R	78.19	61.56	22.32 or 22.17 or 22.04
Neu5Ac′	173.51 or 173.36	100.51	40.49	N/R	51.75	N/R	N/R	71.75	62.57	22.32 or 22.17 or 22.04

Linker	**1**	**2**	**3**
H	3.44 – 3.34 (m, 2H)	1.89 – 1.81 (m, 2H)	3.99, 3.68
C	47.78	28.10	67.13

N/R: not reported.



Synthesis of 56

56 was synthesized as described in the methods. White solid after lyophilization (2.6 mg, 93%). ESI-Q-TOF-HRMS m/z calculated for $C_{37}H_{60}N_5O_{27}$, $[M-H]^-$: 1006.3481, found 1006.3485.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.50 (d, J = 8.0 Hz, 1H)	3.35 – 3.30 (m, 1H)	3.65	3.69	3.61	4.01, 3.86	-	-	-	-
Gal	4.53 (d, J = 7.8 Hz, 1H)	3.58	4.10 (dd, J = 9.9, 3.2 Hz, 1H)	3.97	3.73	3.75	-	-	-	-
Neu5Ac	-	-	2.69 (dd, J = 12.5, 4.5 Hz, 1H), 1.79 – 1.72 (m, 2H)	3.62	3.83	N/R	N/R	4.16 – 4.13 (m, 1H)	4.19 (dd, J = 12.3, 3.6 Hz, 1H), 3.77	2.08 (s, 3H) or 2.04 (s, 3H)
Neu5Ac′	-	-	2.79 (dd, J = 12.4, 4.7 Hz, 1H), 1.79 – 1.72 (m, 2H)	3.68	3.83	3.68	3.61	3.91	3.89, 3.65	2.08 (s, 3H) or 2.04 (s, 3H)

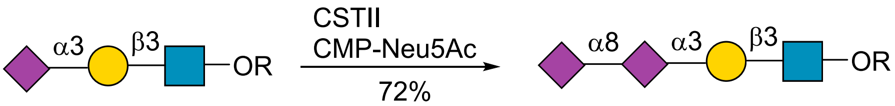
^{13}C NMR (151 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	102.01	72.71	74.15	77.90	74.68	59.86	-	-	-	-
Gal	102.54	69.15	75.32	67.22	75.08	60.96	-	-	-	-

Neu5Ac	173.37 or 173.22	100.06	39.56	67.80	52.14	N/R	N/R	78.08	61.43	22.18 or 21.90
Neu5Ac′	173.37 or 173.22	100.38	40.36	67.80	51.61	72.52	68.36	71.61	62.43	22.18 or 21.90

Linker	**1**	**2**	**3**
H	3.50 – 3.44 (m, 2H)	1.92 (p, *J* = 7.2 Hz, 2H)	4.01, 3.78
C	47.75	28.10	67.33

N/R: not reported.



34 **57**

Synthesis of 57

57 was synthesized as described in the methods. White solid after lyophilization (2 mg, 72%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{27}$, $[M-H]^-$: 1047.3747, found 1047.3749.

^1H NMR (500 MHz, D_2O): δ (ppm)

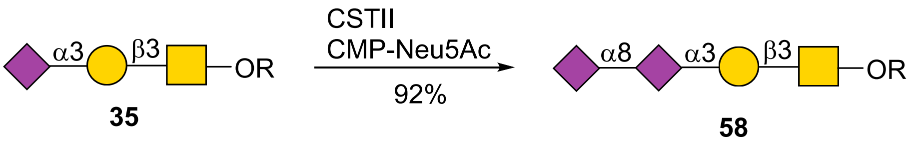
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GlcNAc	4.56 (d, *J* = 8.2 Hz, 1H)	3.82	3.79	3.54	3.49	3.93, 3.76	-	-	-	2.10 – 2.01 (m, 9H)
Gal	4.49 (d, *J* = 7.8 Hz, 1H)	3.53	4.09 (dd, *J* = 9.9, 3.1 Hz, 1H)	3.95	3.72	3.73	-	-	-	-
Neu5Ac	-	-	2.69 (dd, *J* = 12.3, 4.4 Hz, 1H), 1.77 – 1.69 (m, 1H)	3.59	3.82	N/R	N/R	4.17 – 4.12 (m, 1H)	4.20 (dd, *J* = 12.1, 3.8 Hz, 1H), 3.94	2.10 – 2.01 (m, 9H)
Neu5Ac′	-	-	2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.77 – 1.69 (m, 1H)	3.67	3.82	N/R	N/R	3.91	3.88, 3.66	2.10 – 2.01 (m, 9H)

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	100.96	54.39	82.74	68.46	75.37	60.74	-	-	-	22.37 or 22.31 or 22.04
Gal	103.60	68.78	75.38	67.61	75.06	60.05	-	-	-	-
Neu5Ac	173.38 or 173.63	99.93	39.83	N/R	52.24	N/R	N/R	78.57	61.61	22.37 or 22.31 or 22.04
Neu5Ac′	173.38 or 173.63	100.46	41.52	N/R	51.77	N/R	N/R	71.73	62.58	22.37 or 22.31 or 22.04

Linker	**1**	**2**	**3**
H	3.95 – 3.86 (m, 2H)	2.42 – 2.34 (m, 2H)	4.52, 4.21
C	47.79	28.11	67.18

N/R: not reported.



Synthesis of 58

58 was synthesized as described in the methods. White solid after lyophilization (19.2 mg, 92%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{27}$, $[M-H]^-$: 1047.3747, found 1047.3750.

^1H NMR (500 MHz, D_2O): δ (ppm)

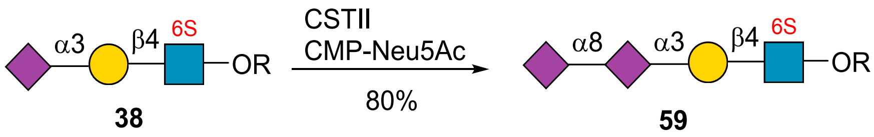
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.51	4.02	3.88	4.17	3.70	3.79 or 3.72	-	-	-	2.07 or 2.06 or 2.04
Gal	4.52	3.55	4.07	3.93	3.63	3.79 or 3.72	-	-	-	-
Neu5Ac	-	-	2.70 (dd, J = 12.3, 4.4 Hz), 1.73	3.61	3.82	N/R	N/R	4.15	4.20	2.07 or 2.06 or 2.04
Neu5Ac′	-	-	2.79 (dd, J = 12.3, 4.7 Hz), 1.73	3.69	3.82	3.70	3.61	3.90	3.89, 3.66	2.07 or 2.06 or 2.04

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.45	51.09	80.13	67.87	74.76	60.94	-	-	-	22.35 or 22.30 or 22.02
Gal	104.77	68.95	75.29	67.20	74.73	61.03	-	-	-	-
Neu5Ac	173.59 or 173.34	99.93	39.78	68.10 or 67.90	51.74	N/R	N/R	78.48	61.59	22.35 or 22.30 or 22.02
Neu5Ac′	173.59 or 173.34	100.45	40.50	68.10 or 67.90	52.21	72.64	68.43	71.70	62.55	22.35 or 22.30 or 22.02

Linker	**1**	**2**	**3**
H	3.40	1.86	3.98, 3.72
C	47.78	28.10	67.01

N/R: not reported.



Synthesis of 59

59 was synthesized as described in the methods. White solid after lyophilization (2.2 mg, 80%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{30}S$, $[M-H]^-$: 1127.3315, found 1127.3315.

^1H NMR (600 MHz, D_2O): δ (ppm)

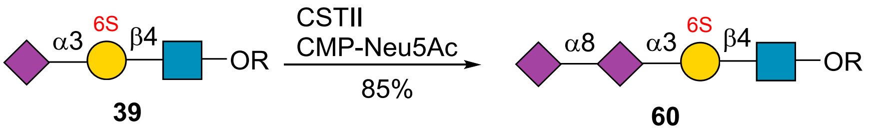
	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.56 (d, *J* = 7.9 Hz, 1H)	3.77	N/R	3.81	N/R	4.47 (dd, *J* = 11.1, 2.0 Hz, 1H), 4.29 (dd, *J* = 11.4, 5.1 Hz, 1H)	-	-	-	2.12 – 1.99 (m, 9H)
Gal	4.62 (d, *J* = 7.8 Hz, 1H)	3.57	4.11	4.02	N/R	3.76 (2H)	-	-	-	-
Neu5Ac	-	-	2.70 – 2.62 (m, 1H), 1.81	3.66	3.84	N/R	N/R	4.16	4.14, 3.76	2.12 – 1.99 (m, 9H)
Neu5Ac′	-	-	2.78 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.75	3.68	3.84	N/R	N/R	3.92	3.91, 3.66	2.12 – 1.99 (m, 9H)

^{13}C NMR (150 MHz, D_2O): δ (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	NHAc
GlcNAc	191.13	55.03	N/R	77.32	N/R	66.63	-	-	-	22.30 or 22.17 or 22.04
Gal	101.96	68.21	75.22	67.77	N/R	61.07	-	-	-	-
Neu5Ac	173.68 or 173.45	100.38	39.02	N/R	52.23	N/R	N/R	78.08	61.75	22.30 or 22.17 or 22.04
Neu5Ac′	173.68 or 173.45	100.68	40.48	N/R	51.73	N/R	N/R	71.72	62.57	22.30 or 22.17 or 22.04

Linker	**1**	**2**	**3**
H	3.39 (td, *J* = 6.7, 3.2 Hz, 2H)	1.86 (2H)	3.99, 3.68
C	47.79	28.10	67.26

N/R: not reported.



Synthesis of 60

60 was synthesized as described in the methods. White solid after lyophilization (2.3 mg, 85%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{30}S$, $[M-H]^-$: 1127.3315, found 1127.3312.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	H2	H3	H4	H5	H6	H7	H8	H9	NHAc
GlcNAc	4.51 (d, *J* = 7.6 Hz, 1H)	3.72	4.10	3.71		3.97, 3.84	-	-	-	2.07 – 2.00 (m, 9H)
Gal	4.57 (d, *J* = 7.9 Hz, 1H)	3.55	4.10 (dd, *J* = 9.9, 3.2 Hz, 1H)	4.00	3.95	4.17	-	-	-	-
Neu5Ac	-	-	2.66 (dd, *J* = 12.3, 4.4 Hz,	3.59	3.81	N/R	N/R	4.13	4.15, 3.73	2.07 – 2.00 (m,

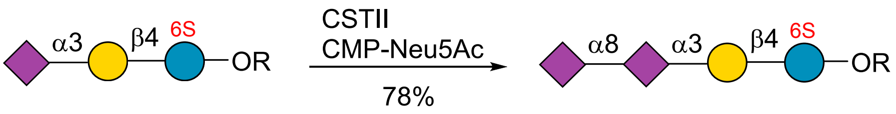
			1H), 1.73							9H)
Neu5Ac′	-	-	2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.73	3.65	3.81	N/R	N/R	3.89	3.83, 3.62	2.07 – 2.00 (m, 9H)

^{13}C NMR (151 MHz, D$_2$O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GlcNAc	101.15	55.19	N/R	78.88	N/R	60.20	-	-	-	22.33 or 22.19 or 22.05
Gal	102.36	67.47	75.24	N/R	N/R	N/R	-	-	-	-
Neu5Ac	173.41	100.35	39.61	N/R	52.24	N/R	N/R	78.19	61.60	22.33 or 22.19 or 22.05
Neu5Ac′	173.41	100.44	40.48	N/R	51.74	N/R	N/R	71.75	62.55	22.33 or 22.19 or 22.05

Linker	**1**	**2**	**3**
H	3.41 – 3.31 (m, 2H)	1.83 (p, *J* = 6.4 Hz, 2H)	3.96, 3.66
C	47.77	28.10	67.12

N/R: not reported.



41 **61**

Synthesis of 61

61 was synthesized as described in the methods. White solid after lyophilization (2.1 mg, 78%). ESI-Q-TOF-HRMS m/z calculated for $C_{37}H_{60}N_5O_{30}S$, [M-H]$^-$: 1086.3049, found 1086.3049.

^{1}H NMR (500 MHz, D$_2$O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.51 (d, *J* = 8.0 Hz, 1H)	3.34 (dd, *J* = 9.4, 8.0 Hz, 1H)	3.67	3.75	3.83	4.45 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.26 (dd, *J* = 11.2, 5.2 Hz, 1H)	-	-	-	-
Gal	4.59 (d, *J* = 7.9 Hz, 1H)	3.56	4.10	4.01	3.73	3.75	-	-	-	-
Neu5Ac	-	-	2.64 (dd, *J* = 12.4, 4.5 Hz, 1H), 1.80 (t, *J* = 12.3 Hz, 1H)	3.64	3.82	N/R	N/R	3.91	4.14, 3.75	2.07 (s, 3H) or 2.03 (s, 3H)
Neu5Ac′	-	-	2.77 (dd, *J* = 12.3, 4.8 Hz, 1H),	3.66	3.82	3.64	3.61	4.15	3.89, 3.65	2.07 (s, 3H) or 2.03 (s,

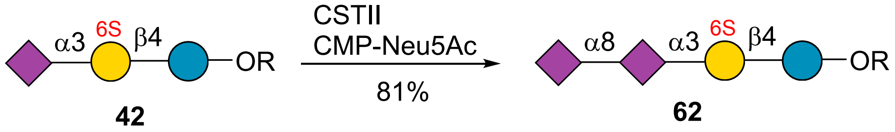
			1.74 (t, J = 12.2 Hz, 1H)							3H)

^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.87	72.54	74.05	77.03	72.39	66.45	-	-	-	-
Gal	102.00	69.38	75.07	67.61	74.82	60.93	-	-	-	-
Neu5Ac	173.54 or 173.32	100.19	38.84	68.06	52.08	N/R	N/R	78.00	61.60	22.14 or 21.88
Neu5Ac′	173.54 or 173.32	100.55	40.34	68.06	51.58	72.44	68.39	71.55	62.41	22.14 or 21.88

Linker	**1**	**2**	**3**
H	3.46 (t, J = 6.7 Hz, 2H)	1.92 (p, J = 6.5 Hz, 2H)	3.98, 3.78
C	47.73	28.10	67.37

N/R: not reported.



Synthesis of 62

62 was synthesized as described in the methods. White solid after lyophilization (2.2 mg, 81%). ESI-Q-TOF-HRMS m/z calculated for $C_{37}H_{60}N_5O_{30}S$, $[M-H]^-$: 1086.3049, found 1086.3049.

^{1}H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.50 (d, J = 8.0 Hz, 1H)	3.37 – 3.30 (m, 1H)	3.66	3.66	3.62	4.01, 3.94	-	-	-	-
Gal	4.56 (d, J = 8.0 Hz, 1H)	3.58	4.12	4.03	3.98	4.20 (2H)	-	-	-	-
Neu5Ac	-	-	2.68 (dd, J = 12.3, 4.4 Hz, 1H), 1.79 – 1.71 (m, 1H)	3.62	3.83	N/R	N/R	4.15	4.17, 3.84	2.08 (s, 3H) or 2.04 (s, 3H)
Neu5Ac′	-	-	2.78 (dd, J = 12.3, 4.6 Hz, 1H), 1.79 – 1.71 (m, 1H)	3.66	3.83	3.66	N/R	3.91	3.89, 3.65	2.08 (s, 3H) or 2.04 (s, 3H)

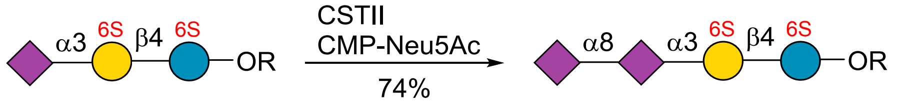
^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.9	72.65	74.13	79.18	74.57	60.10	-	-	-	-
Gal	102.67	69.01	75.09	67.20	72.65	67.42	-	-	-	-

Neu5Ac	173.29	100.23	39.47	67.84	52.14	N/R	N/R	78.04	61.48	22.19 or 21.91
Neu5Ac′	173.29	100.32	40.36	68.02	51.61	72.50	N/R	71.61	62.43	22.19 or 21.91

Linker	**1**	**2**	**3**
H	3.47 (t, J = 6.7 Hz, 2H)	1.92 (p, J = 6.5 Hz, 2H)	3.99, 3.77
C	47.75	28.10	67.20

N/R: not reported.



43 **63**

Synthesis of 63

63 was synthesized as described in the methods. White solid after lyophilization (2 mg, 74%). ESI-Q-TOF-HRMS m/z calculated for $C_{37}H_{60}N_5O_{33}S_2$, $[M-H]^-$: 1166.2617, found 1166.2614.

^1H NMR (500 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
Glc	4.51 (d, J = 8.0 Hz, 1H)	3.39 – 3.32 (m, 1H)	3.69	3.68	3.85	4.47 (dd, J = 11.2, 2.0 Hz, 1H), 4.24 (dd, J = 11.3, 5.9 Hz, 2H)	-	-	-	-
Gal	4.59 (d, J = 7.9 Hz, 1H)	3.57	4.12	4.05	4.00	4.20 (2H)	-	-	-	-
Neu5Ac	-	-	2.65 (dd, J = 12.3, 4.5 Hz, 1H), 1.75 (t, J = 12.1 Hz, 1H)	3.64	3.82	N/R	N/R	4.15	4.14, 3.77	2.07 (s, 3H) or 2.03 (s, 2H)
Neu5Ac′	-	-	2.77 (dd, J = 12.4, 4.6 Hz, 1H), 1.75 (t, J = 12.1 Hz, 1H)	3.66	3.82	3.61	3.58	3.91	3.89, 3.65	2.07 (s, 3H) or 2.03 (s, 2H)

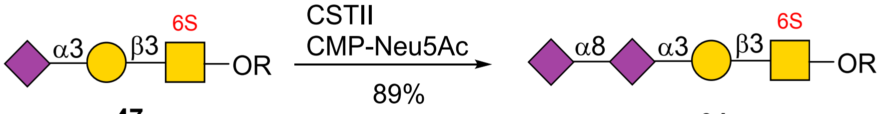
^{13}C NMR (126 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
Glc	101.87	72.44	74.07	78.84	72.36	66.74	-	-	-	-
Gal	102.30	69.16	74.82	67.37	72.48	67.46	-	-	-	-
Neu5Ac	173.43 or 173.32	100.18	38.83	N/R	52.05	N/R	N/R	77.98	61.65	22.15 or 21.89
Neu5Ac′	173.43 or 173.32	100.63	40.35	N/R	51.58	72.44	N/R	71.56	62.41	22.15 or 21.89

Linker	**1**	**2**	**3**

H	3.46 (t, $J = 6.8$ Hz, 2H)	1.92 (p, $J = 6.5$ Hz, 2H)	3.98, 3.78
C	47.74	28.10	67.42

N/R: not reported.



47 **64**

Synthesis of 64

64 was synthesized as described in the methods. White solid after lyophilization (12 mg, 89%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{30}S$, $[M-H]^-$: 1127.3315, found 1127.3317.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

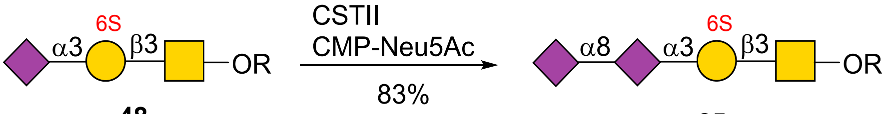
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.53	4.03	3.90	4.23	3.94	4.20	-	-	-	2.08 or 2.06 or 2.04
Gal	4.52	3.55	4.08	N/R	3.66		-	-	-	-
Neu5Ac	-	-	2.69 (dd, J = 12.4, 4.6 Hz, 1H), 1.73	3.60	3.83	N/R	N/R	4.16	4.20	2.08 or 2.06 or 2.04
Neu5Ac′	-	-	2.79 (dd, J = 12.3, 4.4 Hz, 1H), 1.73	3.67	3.83	N/R	3.62	3.90	3.89, 3.67	2.08 or 2.06 or 2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.41	51.00	79.95	67.68	72.42	67.34	-	-	-	22.34 or 22.29 or 22.01
Gal	104.84	68.95	75.30	67.22	74.72	60.99	-	-	-	-
Neu5Ac	173.61 or 173.35	99.95	39.76	68.10 or 67.94	51.74	N/R	N/R	78.49	61.59	22.34 or 22.29 or 22.01
Neu5Ac′	173.61, 173.35	100.42	40.50	68.10 or 67.94	52.22	72.63	68.45	71.69	62.54	22.34 or 22.29 or 22.01

Linker	**1**	**2**	**3**
H	3.40	1.86	4.00, 3.72
C	47.80	28.12	67.17

N/R: not reported.



48 **65**

Synthesis of 65

65 was synthesized as described in the methods. White solid after lyophilization (11.2 mg, 83%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{30}S$, $[M-H]^-$: 1127.3315, found 1127.3316.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

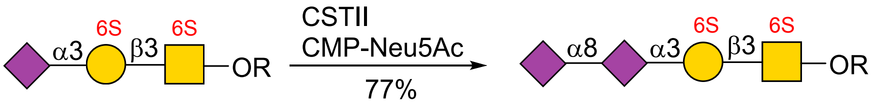
	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.51	4.04	3.85	4.23	3.72	3.74	-	-	-	2.07 or 2.06 or 2.04
Gal	4.54	3.57	4.10	3.99	3.90	4.19	-	-	-	-
Neu5Ac	-	-	2.69, 1.74	3.62	3.83	N/R	N/R	4.17	N/R	2.07 or 2.06 or 2.04
Neu5Ac′	-	-	2.78, 1.74	3.69	3.83	3.70	3.66	3.91	3.90, 3.66	2.07 or 2.06 or 2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.49	50.98	80.32	67.81	74.94	61.24	-	-	-	22.31 or 22.29 or 22.01
Gal	104.53	68.82	75.18	67.22	72.44	67.93	-	-	-	-
Neu5Ac	173.49 or 173.36	100.05	39.72	68.11, 67.93	51.73	N/R	N/R	78.42	61.59	22.31 or 22.29 or 22.01
Neu5Ac′	173.49 or 173.36	100.38	40.48	68.11, 67.93	52.22	72.61	68.47	71.68	62.52	22.31 or 22.29 or 22.01

Linker	**1**	**2**	**3**
H	3.39	1.87	4.00, 3.72
C	47.78	28.10	66.98

N/R: not reported.



49 **66**

Synthesis of 66

66 was synthesized as described in the methods. White solid after lyophilization (20 mg, 77%). ESI-Q-TOF-HRMS m/z calculated for $C_{39}H_{63}N_6O_{33}S_2$, $[M-H]^-$: 1207.2883, found 1207.2885.

^{1}H NMR (600 MHz, D_2O): δ (ppm)

	H1	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**	**H9**	**NHAc**
GalNAc	4.51	4.04	3.90	4.23	3.98	4.22	-	-	-	2.08 or 2.07 or 2.04
Gal	4.54	3.56	4.09	N/R	3.90	4.18	-	-	-	-
Neu5Ac	-	-	2.69, 1.75	3.62	3.83	N/R	N/R	4.16	4.20, 3.71	2.08 or 2.07 or 2.04
Neu5Ac′	-	-	2.78, 1.75	3.68	3.83	N/R	3.61	3.90	3.91, 3.66	2.08 or 2.07 or 2.04

^{13}C NMR (201 MHz, D_2O): δ (ppm)

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**NHAc**
GalNAc	101.37	50.96	79.77	67.88	72.36	67.18	-	-	-	22.34 or 22.30 or 22.02
Gal	104.48	68.84	75.15	N/R	72.68	67.47	-	-	-	-
Neu5Ac	173.51 or 173.39	100.09	39.69	67.96	51.73	N/R	N/R	78.43	61.60	22.34 or 22.30 or 22.02
Neu5Ac′	173.51 or 173.39	100.37	40.48	N/R	52.22	72.61	N/R	71.69	62.53	22.34 or 22.30 or 22.02

Linker	**1**	**2**	**3**
H	3.40	1.87	4.00, 3.73
C	47.82	28.12	67.13

N/R: not reported.

4. Microarray Studies

4.1 General procedure for Hydrogenolysis Mediated reduction of glycan terminal azide group.

Glycan substrate (0.5 mg) was dissolved in 300 µL DI water, and palladium hydroxide on carbon slurry (0.3 mg, 20% wt suspended in water solution) was added to the above solution. The reaction was vigorously stirred under an atmosphere of hydrogen and monitored by TLC until no starting material could be detected (2h). Subsequently, the reaction was filtered through a syringe filter (0.2 microns) to remove the catalyst, and the filtrate was lyophilized to give amine-linked glycan products as a white fluffy solid.

4.2 Glycan microarray printing

66 amine-linked glycans were printed using a Scienion sciFLEXARRAYER S1 non-contact microarray printer equipped with a Scienion PDC80 nozzle (Scienion Inc) on the surface of N-hydroxy succinimide (NHS)-activated glass slides (NEXTERION® Slide H, Schott Inc) to form glycan microarray. Glycans were dissolved in sodium phosphate buffer (250 mM, pH 8.5) at a concentration of 100 µM and printed in replicates of 4 (spot volume of ~400 pL, at 20 °C and 50% humidity). Each slide contained 14 subarrays (2x7), and 1 subarray displayed 288 spots (18 x16). Slides were incubated overnight in a saturated NaCl chamber (providing a 75% relative humidity environment) after printing and were blocked with 5 mM ethanolamine in Tris-HCl buffer (pH 9, 50 mM) for 1 h at 50 °C and rinsed with DI water.

4.3 Screening of proteins

Sub-arrays were incubated with the protein of interest at the indicated concentrations in TSM binding buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween, 1% BSA) for 0.5-1h at r.t. followed by washing. Wash steps involved 2 successive washes with TSM wash buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween-20) - TSM buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$) - deionized H_2O. All incubation and wash steps were performed at RT.

Plant lectins:

Working solutions at specific concentrations of biotinylated plant lectins were freshly prepared by diluting an appropriate amount of stock solution in a TSM binding buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween, 1% BSA). The above working solution (100 µL) was carefully added to the subarray and was allowed to incubate for 1h in the dark, followed by a washing procedure. Then, the subarrays were incubated with 100 µL Streptavidin-AlexaFluor® 647 (5 µg/mL) in TSM binding buffer for 0.5 h in the dark. After incubation, the slide was performed using a washing procedure and kept in the dark before analysis.

Fc-tagged Siglecs:

Streptavidin-AlexaFluor® 647 (5 µg/mL) was pre-complexed with biotinylated anti-IgG Fc (5 µg/mL) in a 1:1 molar ratio in 100 µL TMS binding buffer and was incubated on ice for 15 min as the pre-mixed solution for further use. Working solutions of Fc-tagged Siglecs at specific concentrations were freshly prepared by diluting an appropriate amount of stock solution in a TSM binding buffer. The above working solution (100 µL) was carefully added to the subarray and was allowed to incubate for 1h in the dark, followed by the washing procedure. Then, the subarrays were incubated with 100 µL pre-mixed solution above for 1 h in the dark. After incubation, the slide was performed using a washing procedure and kept in the dark before analysis.

Screened arrays were dried by centrifugation and immediately scanned for fluorescence on a GenePix 4000 B microarray scanner (Molecular Devices). The detection gain was adjusted to avoid saturation of the signal. The data were processed with GenePix Pro 7 software and further analyzed using Microsoft Excel macro. The mean fluorescent intensities (corrected for mean background) and standard deviations (SD) were calculated (n = 4). Data were fitted using Prism software Version 8.3.0 (GraphPad Software, Inc). Bar graphs represent the mean ± SD for each compound.

4.4 MIRAGE compliant Glycan Microarray Document

Supplementary Glycan Microarray Document according to MIRAGE Guidelines (doi:10.3762/mirage.3)

	Description
1. Sample: Glycan Binding Sample	
Description of Sample	The human Siglecs, Plant lectins used in this work are described in SI section 2. Materials and methods
Sample modifications	Not relevant.
Assay protocol	The incubation protocol was included in SI section 4.3 Screening of proteins.
2. Glycan Library	
Glycan description for defined glycans	66 synthetic glycans are listed in Fig. 1.
Glycan description for undefined glycans	Not relevant.
Glycan modifications	The synthesis of glycans was described in SI section 3. Experimental procedures.
3. Printing Surface; e.g., Microarray Slide	
Description of surface	Covalent arrays were prepared in this work. The details are included in SI section 4.2 Glycan microarray printing.
Manufacturer	The details are included in SI section 4.2 Glycan microarray printing.
Custom preparation of surface	Not relevant.
covalent Immobilization	The details are included in SI section 4.2 Glycan microarray printing.
4. Arrayer (Printer)	
Description of Arrayer	The details are included in SI section 4.2 Glycan microarray printing.
Dispensing mechanism	Non-contact liquid delivery with PDC nozzle.
Glycan deposition	The details are included in SI section 4.2 Glycan microarray printing.

Printing conditions	The details are included in SI section 4.2 Glycan microarray printing.
5. Glycan Microarray with "Map"	
Array layout	The array layout of array was described in SI section 4.2 Glycan microarray printing.
Glycan identification and quality control	The structure of glycans was confirmed via NMR and HRMS as described in SI section 3. Experimental procedures. The quality control of the arrayed glycans was performed using plant lectins as shown in SI section Fig. S6.
6. Detector and Data Processing	
Scanning hardware	GenePix 4000B (Molecular Devices, Berkshire, UK)
Scanner settings	The details are included in SI section 4.3 Screening of proteins.
Image analysis software	The details are included in SI section 4.3 Screening of proteins.
Data processing	The details are included in SI section 4.3 Screening of proteins.
7. Glycan Microarray Data Presentation	
Data presentation	Siglecs binding results are presented as heat map (Fig. 8) in the main text and corresponding histogram charts in SI section (Fig. S5). Plant lectins binding results are displayed in SI section by the histogram charts and heat map (Fig. S6).
8. Interpretation and Conclusion from Microarray Data	
Data interpretation	No software or algorithms were used to interpret processed data.
Conclusions	Different glycan has different preferences for different proteins.

5. References

1. Zheng, Y.; Zhang, J.; Meisner, J., et al., Cofactor-Driven Cascade Reactions Enable the Efficient Preparation of Sugar Nucleotides. *Angew Chem Int Ed Engl* **2022,** *61* (20), e202115696.

2. Wei, F.; Yuan, R.; Wen, Q., et al., Systematic Enzymatic Synthesis of dTDP-Activated Sugar Nucleotides. *Angew Chem Int Ed Engl* **2023,** *62* (20), e202217894.

3. Wang, S.; Zhang, J.; Wei, F., et al., Facile Synthesis of Sugar Nucleotides from Common Sugars by the Cascade Conversion Strategy. *J Am Chem Soc* **2022,** *144* (22), 9980-9989.

4. Rodrigues, E.; Jung, J.; Park, H., et al., A versatile soluble siglec scaffold for sensitive and quantitative detection of glycan ligands. *Nat Commun* **2020,** *11* (1), 5091.

5. Li, Y. H.; Yu, H.; Cao, H. Z., et al., Pasteurella multocida CMP-sialic acid synthetase and mutants of Neisseria meningitidis CMP-sialic acid synthetase with improved substrate promiscuity. *Appl Microbiol Biot* **2012,** *93* (6), 2411-2423.

6. Yu, H.; Huang, S.; Chokhawala, H., et al., Highly Efficient Chemoenzymatic Synthesis of Naturally Occurring and Non-Natural α-2,6-Linked Sialosides: A P. damsela α-2,6-Sialyltransferase with Extremely Flexible Donor–Substrate Specificity. *Angew Chem Int Ed Engl* **2006,** *45* (24), 3938-3944.

7 Xu, Y.; Fan, Y.; Ye, J., et al., Successfully Engineering a Bacterial Sialyltransferase for Regioselective α2,6-sialylation. *ACS Catal* **2018,** *8* (8), 7222-7227.

8. Talafová, K.; Hrabárová, E.; Nahálka, J., A semi-multifunctional sialyltransferase from Bibersteinia trehalosi and its comparison to the Pasteurella multocida ST1 mutants. *J Biotechnol* **2015,** *216*, 116-124.

9. Mertsch, A.; He, N.; Yi, D., et al., An alpha2,3-Sialyltransferase from Photobacterium phosphoreum with Broad Substrate Scope: Controlling Hydrolytic Activity by Directed Evolution. *Chemistry* **2020,** *26* (50), 11614-11624.

10. Schwardt, O.; Visekruna, T.; Zenhäusern, G., et al., Cloning, Expression, and Preparative Application of a Mutated, Bifunctional α(2→3/8)-Sialyltransferase from Campylobacter jejuni. *J Carbohydr Chem* **2007,** *25* (7), 543-556.

11. Xu, G.; Kiefel, M. J.; Wilson, J. C., et al., Three Streptococcus pneumoniae sialidases: three different products. *J Am Chem Soc* **2011,** *133* (6), 1718-21.

12. Rasko, D. A.; Wang, G.; Palcic, M. M., et al., Cloning and Characterization of the α(1,3/4) Fucosyltransferase of Helicobacter pylori. *J Biol Chem* **2000,** *275* (7), 4988-4994.

13. Luo, Y. W.; Wang, Y. Q.; Tian, Y. P., et al., "Two Birds One Stone" Strategy for the Site-Specific Analysis of Core Fucosylation and GlcNAcylation. *J Am Chem Soc* **2023,** *145* (29), 15879-15887.

14. Tian, Y. P.; Wang, Y. Q.; Yin, H. B., et al., A Sensitive and Reversible Labeling Strategy Enables Global Mapping of the Core-Fucosylated Glycoproteome on Cell Surfaces. *Angew Chem Int Ed Engl* **2022,** *61* (49).

15. Wei, F.; Zang, L.; Zhang, P.; Zhang, J.; Wen, L., Concise chemoenzymatic synthesis of N-glycans. *Chem* **2024**. doi.org/10.1016/j.chempr.2024.05.006.

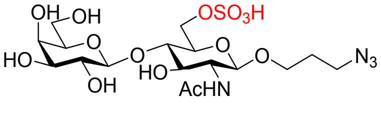
16. Wen, L. Q.; Zheng, Y.; Jiang, K., et al., Two-Step Chemoenzymatic Detection of Acetylneuraminic Acid-α(2-3)-Galactose Glycans. *J Am Chem Soc* **2016,** *138* (36), 11473-11476.

17. Ye, J. F.; Xia, H.; Sun, N., et al., Reprogramming the enzymatic assembly line for site-specific fucosylation. *Nat Catal* **2019,** *2* (6), 514-522.

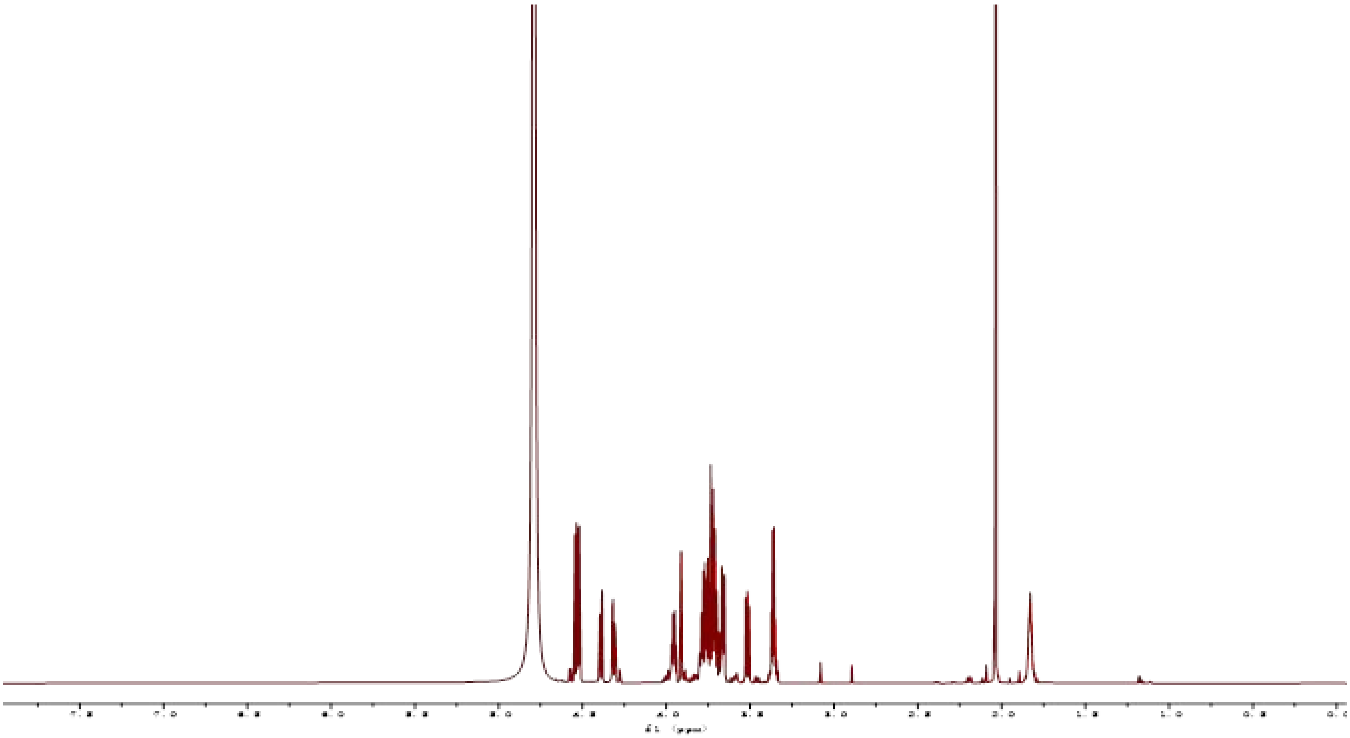
18. Yu, H.; Chokhawala, H.; Karpel, R., et al., A multifunctional sialyltransferase:: A powerful tool for the synthesis of sialoside libraries. *J Am Chem Soc* **2005,** *127* (50), 17618-17619.

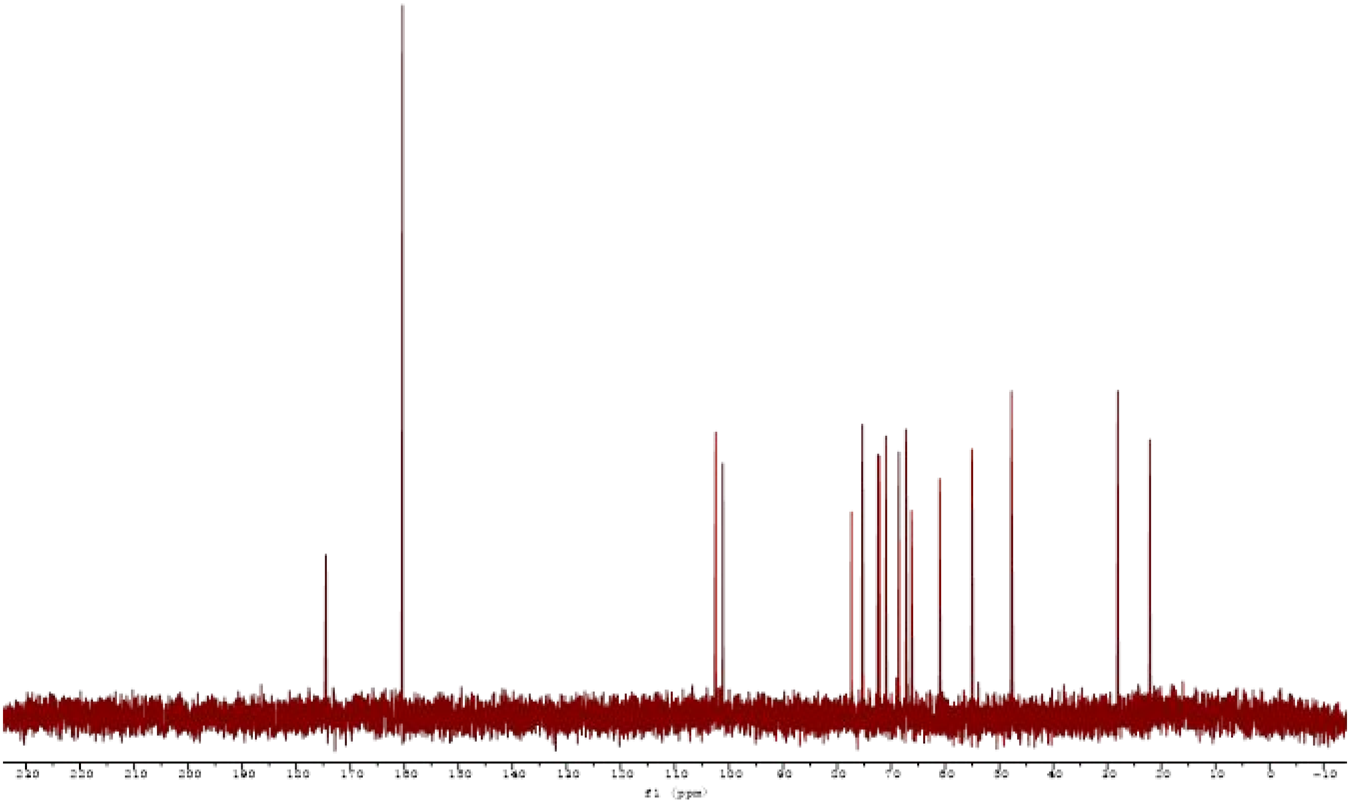
19. Yu, H.; Thon, V.; Lau, K., et al., Highly efficient chemoenzymatic synthesis of beta1-3-linked galactosides. *Chem Commun* **2010,** *46* (40), 7507-9.

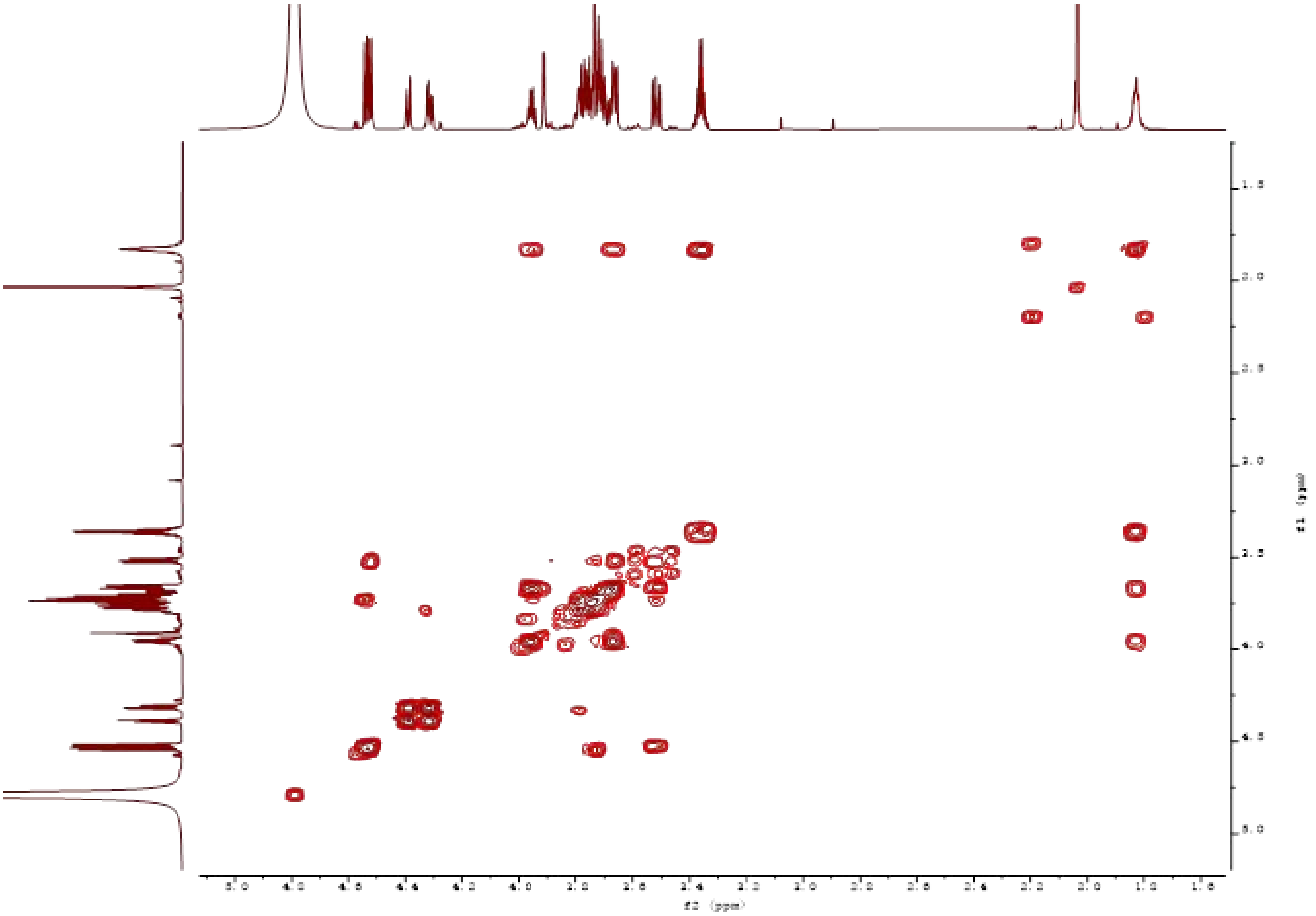
6. NMR spectra

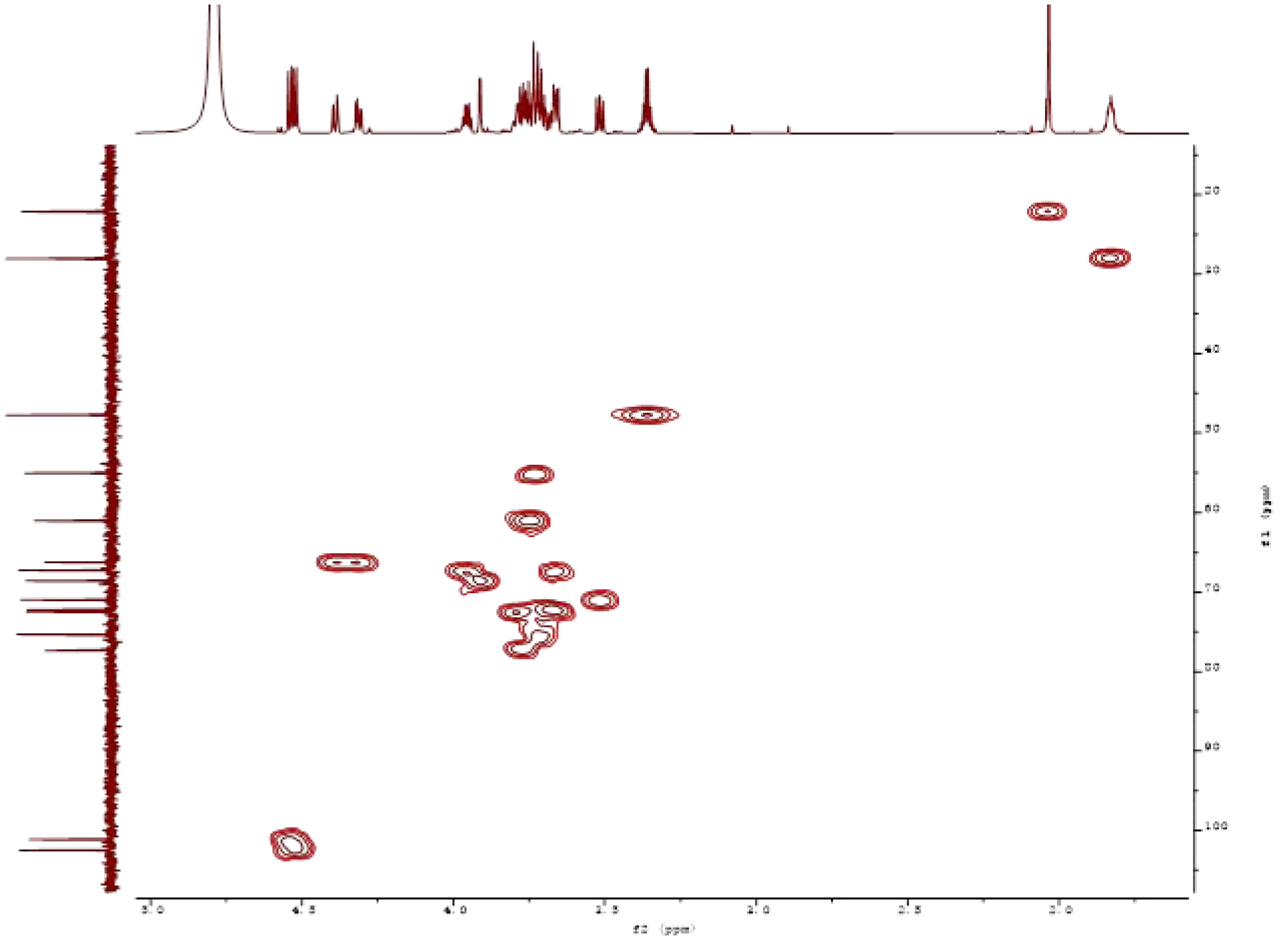


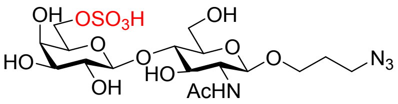
5



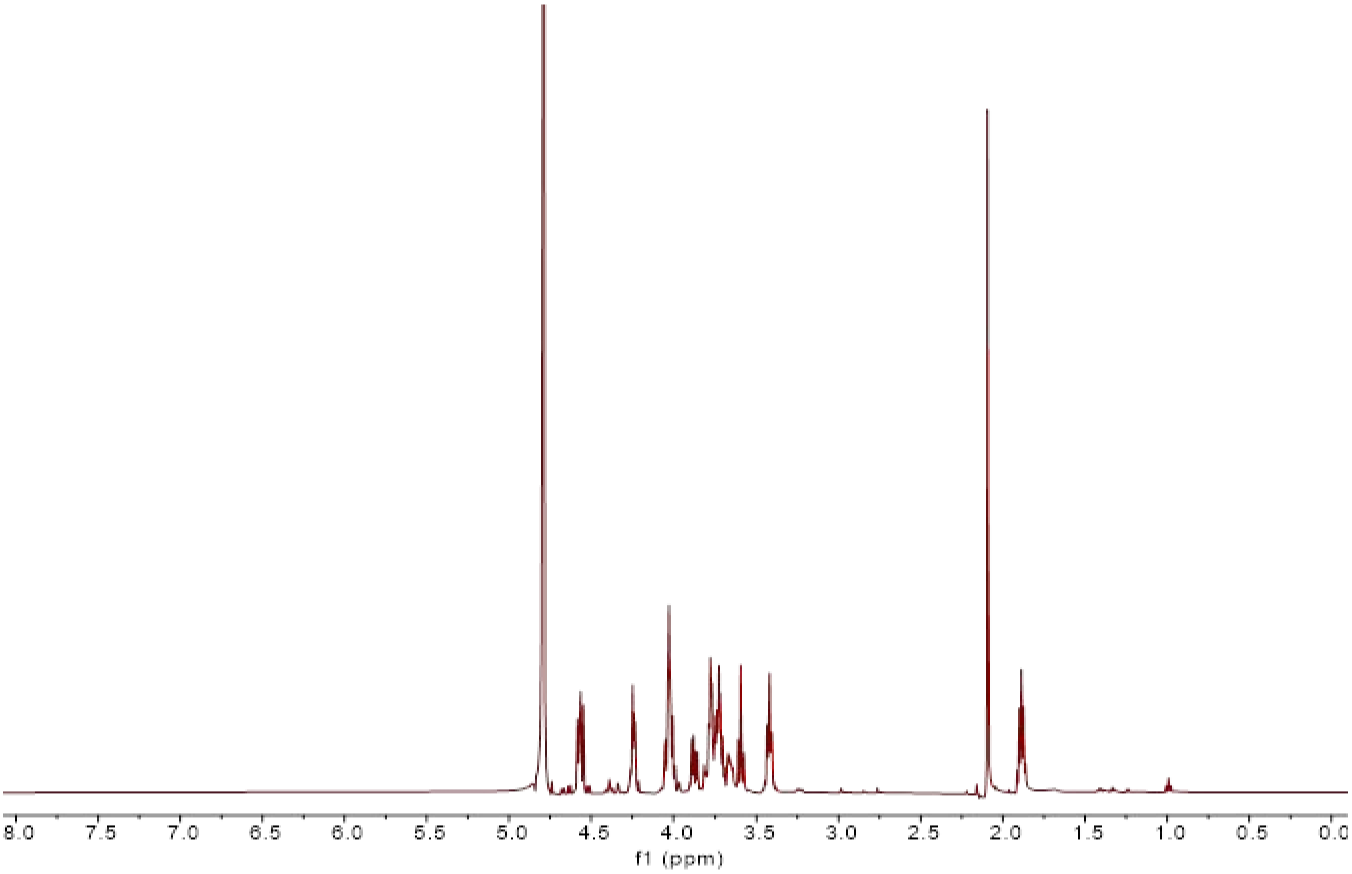


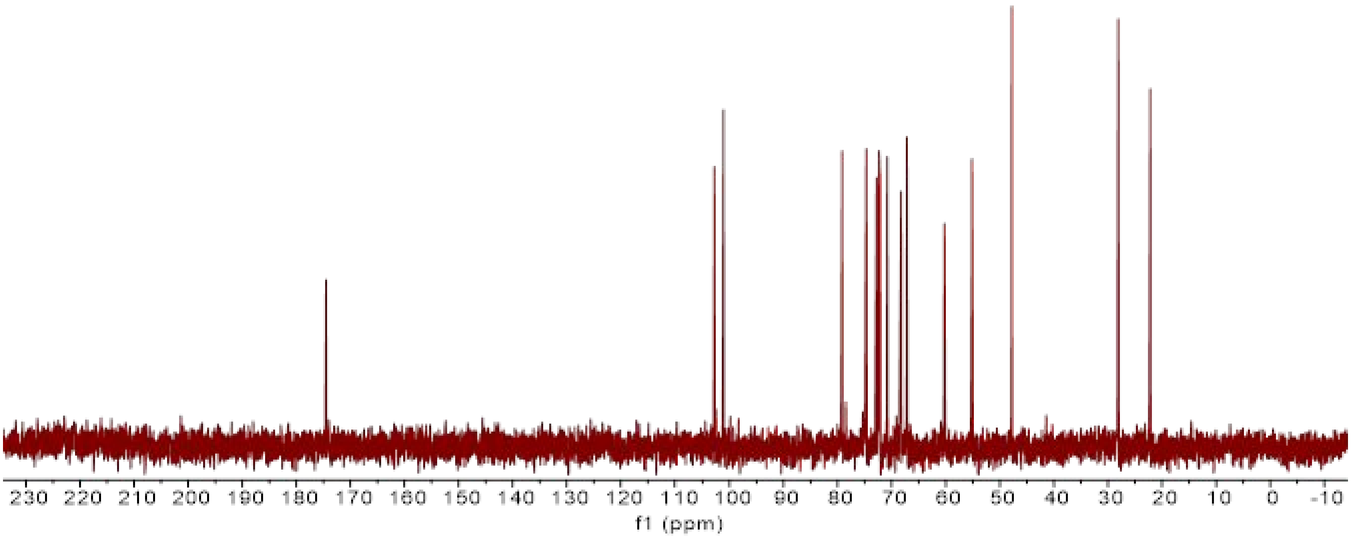

f2 (ppm)
f1 (ppm)

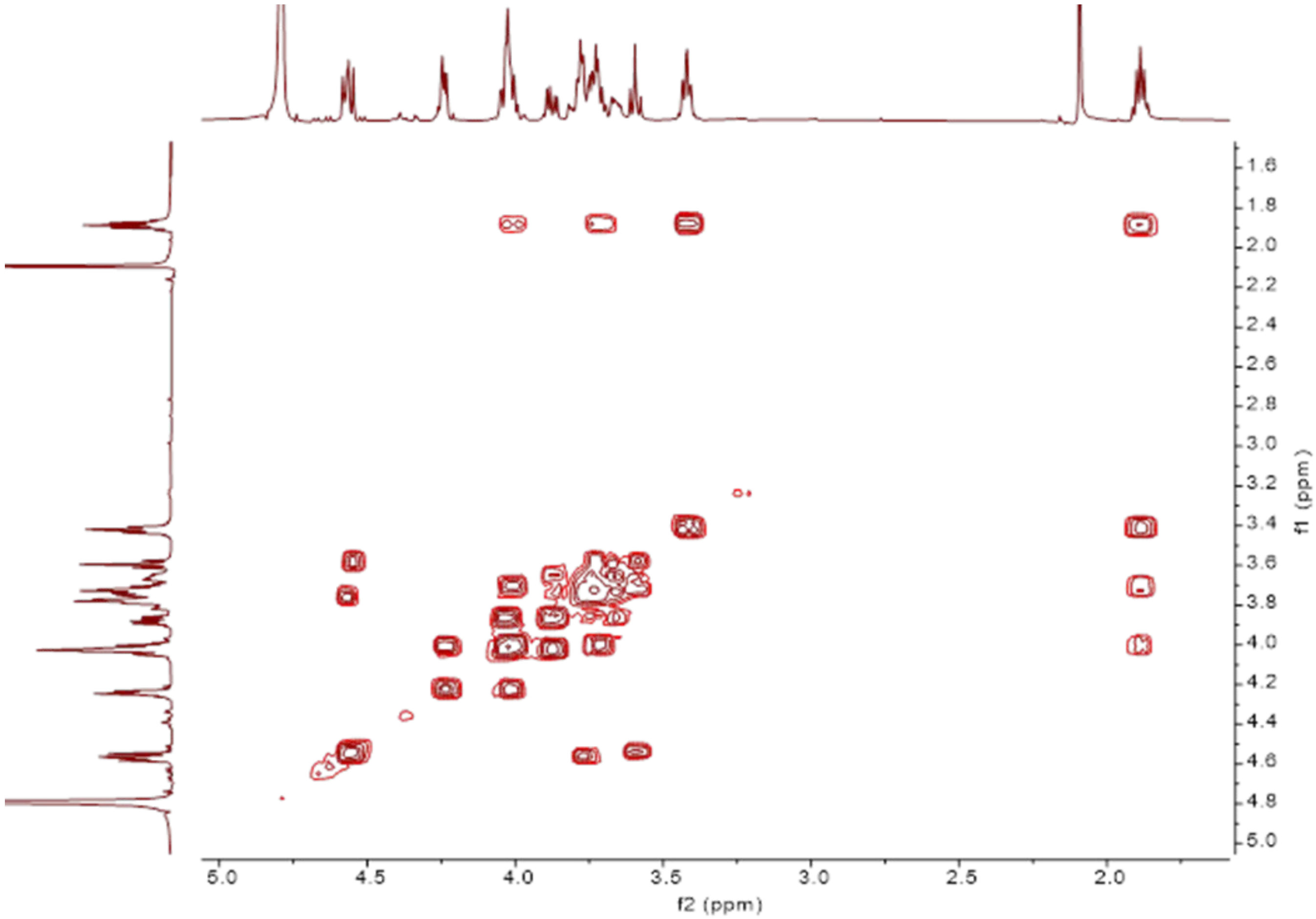

f2 (ppm)
f1 (ppm)

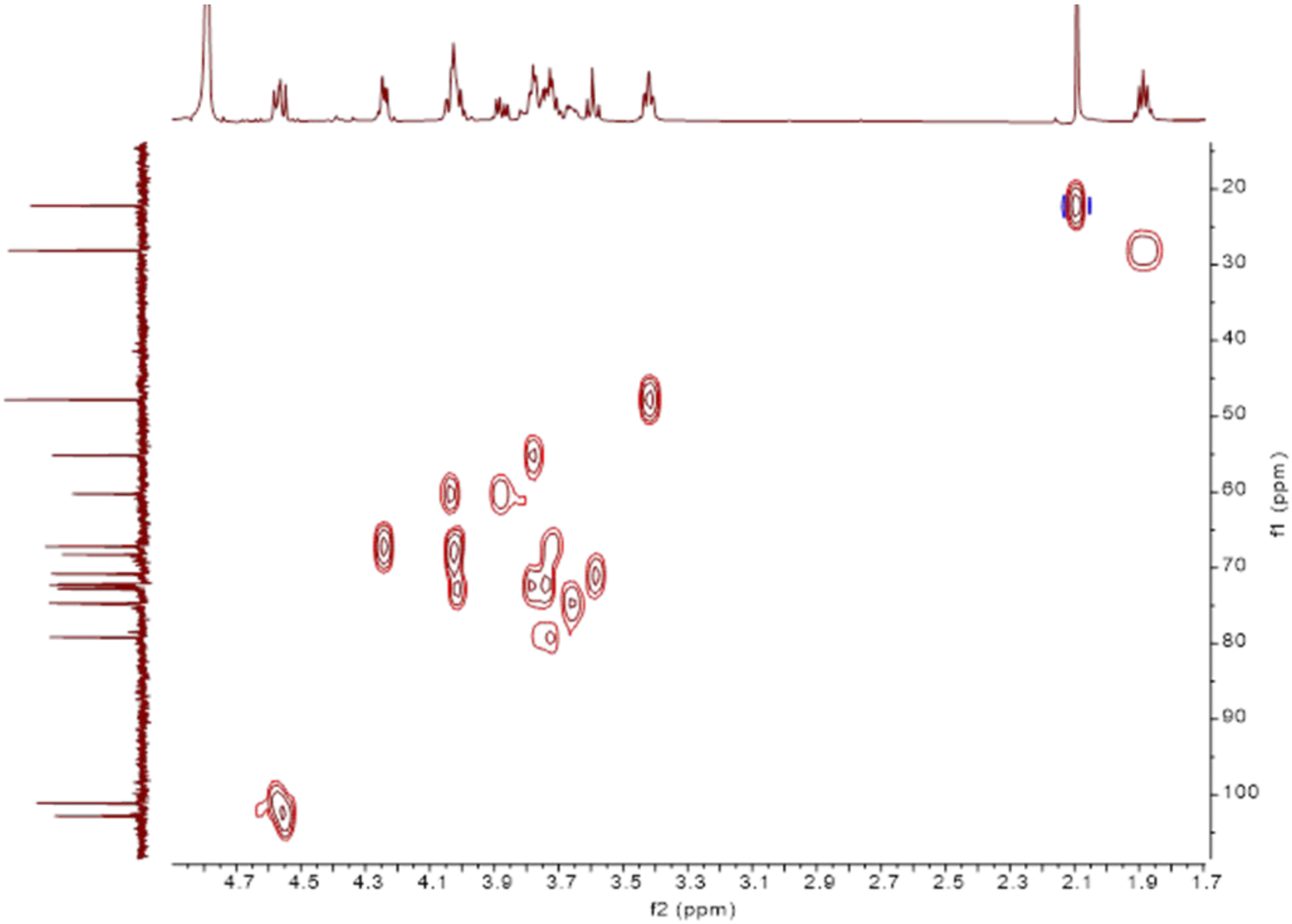

OH
OSO$_3$H
O
HO
OH
O
OH
O
HO
AcHN
O
N$_3$

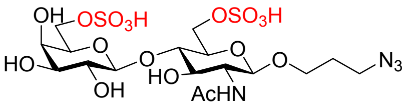
6


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

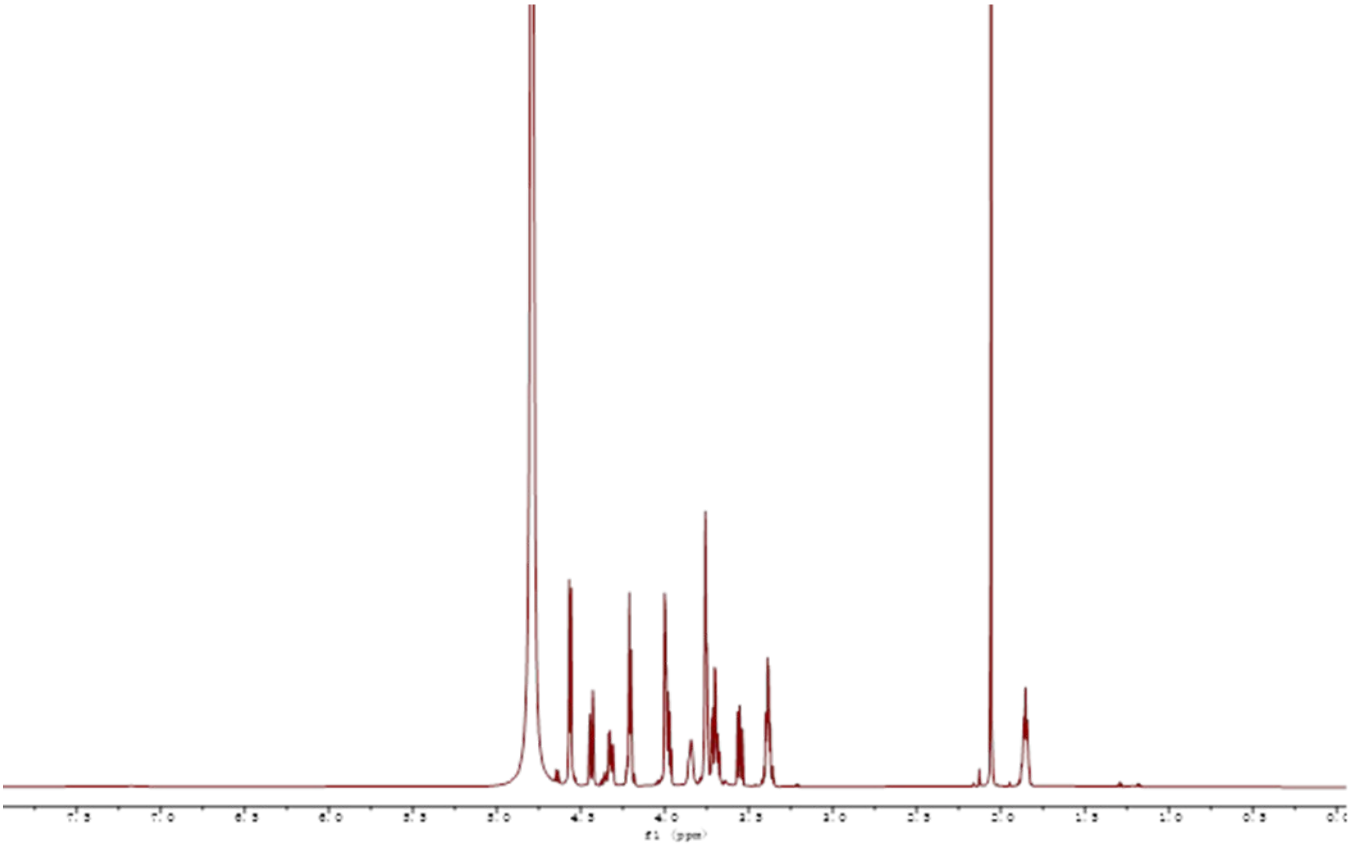

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

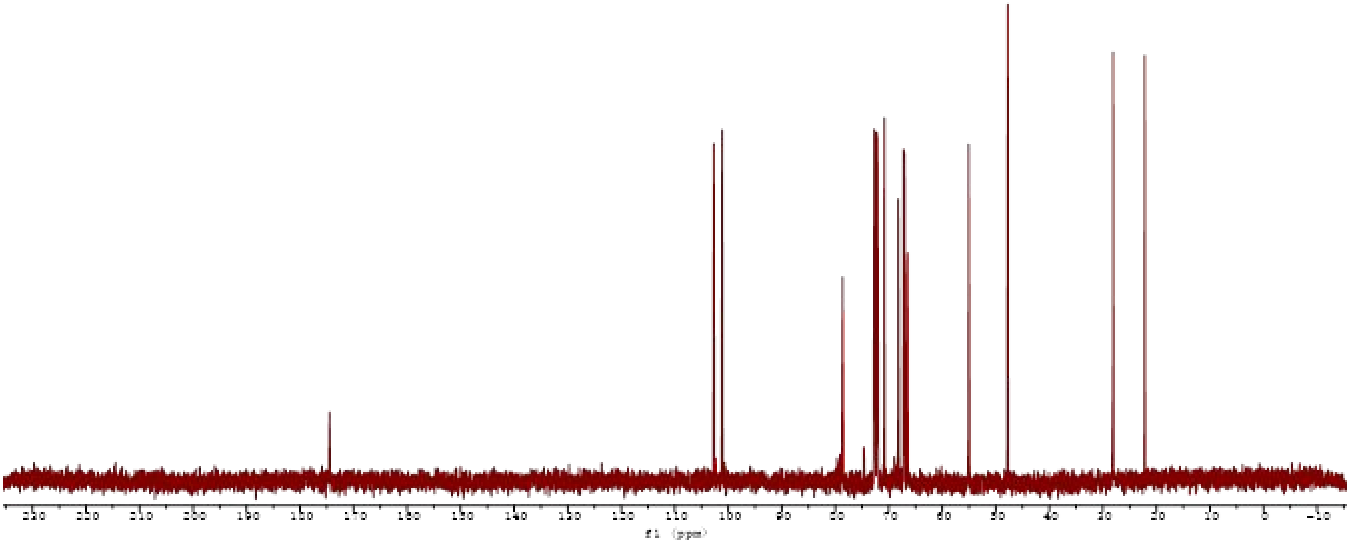

1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

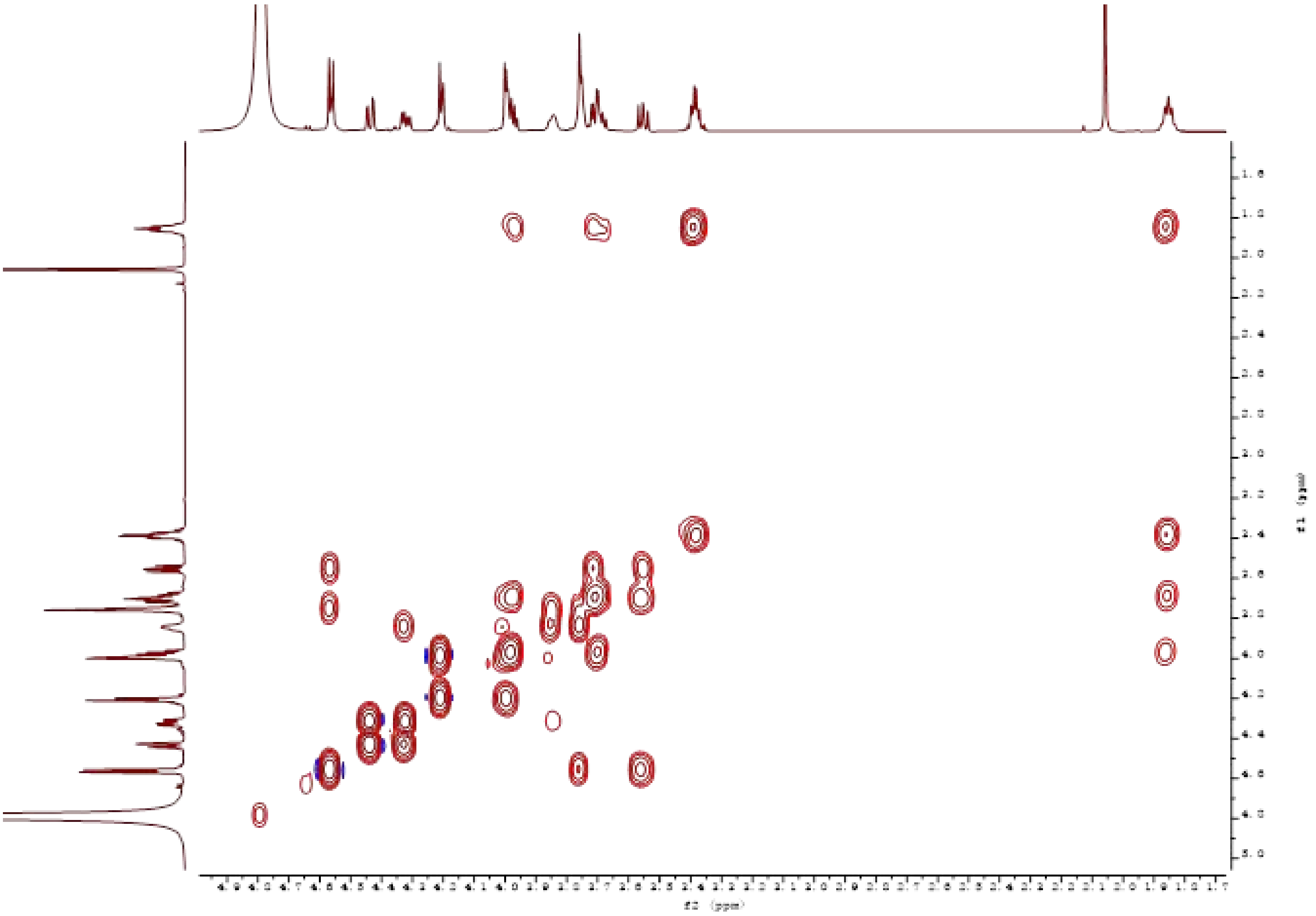

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)

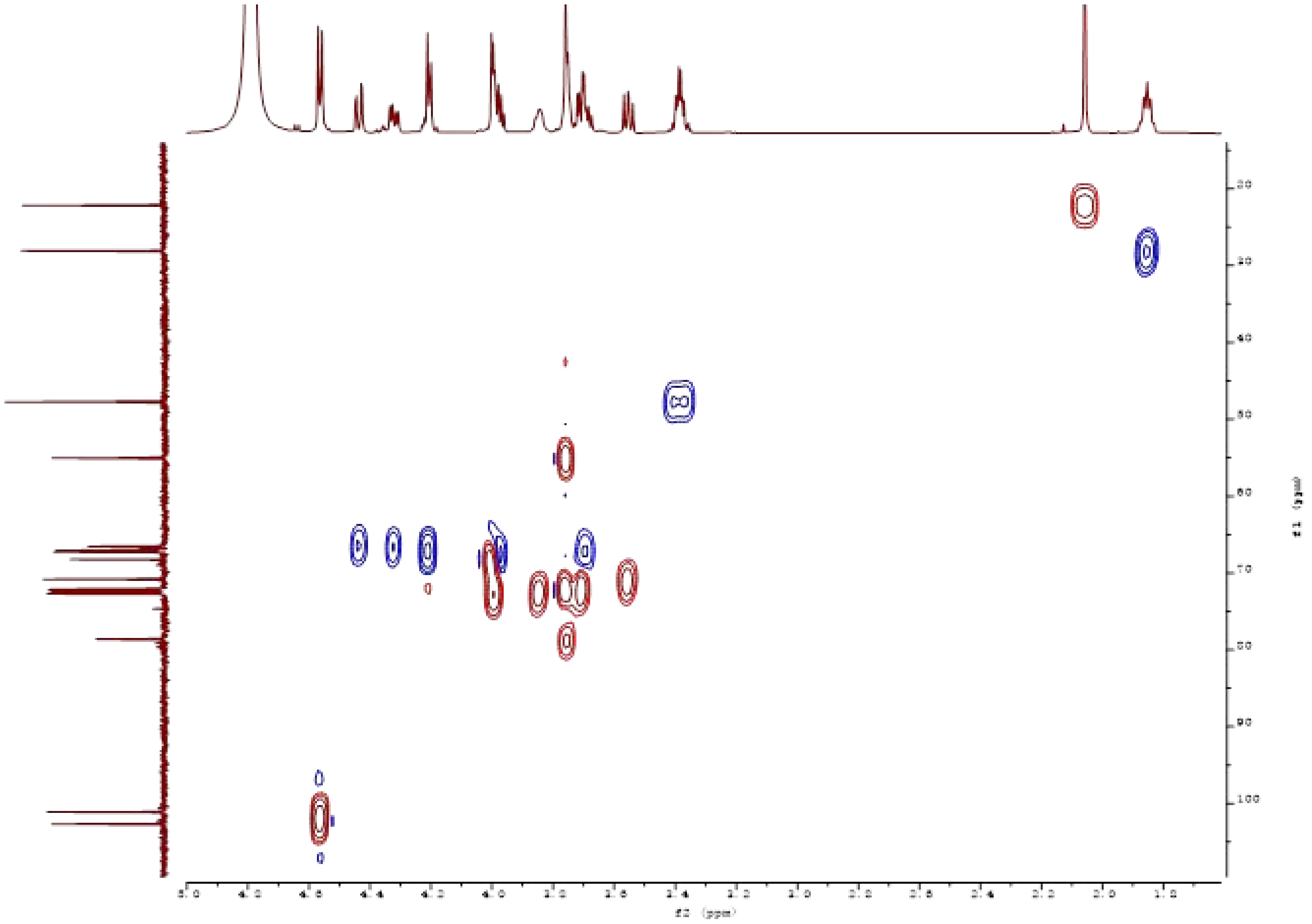

OH
OSO3H
OSO3H
HO
O
O
O
HO
O
OH
AcHN
N3

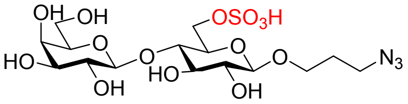
7


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

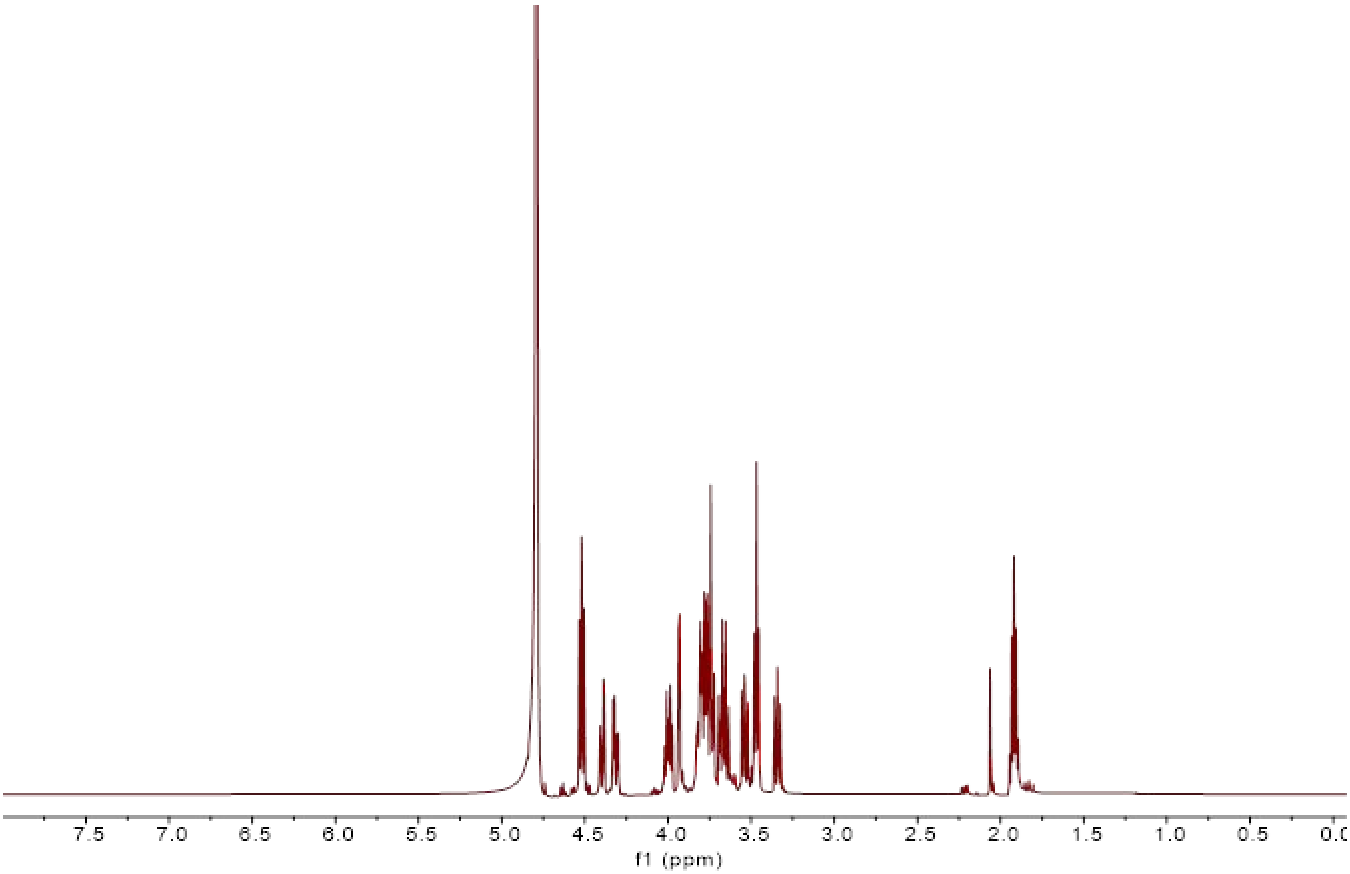

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

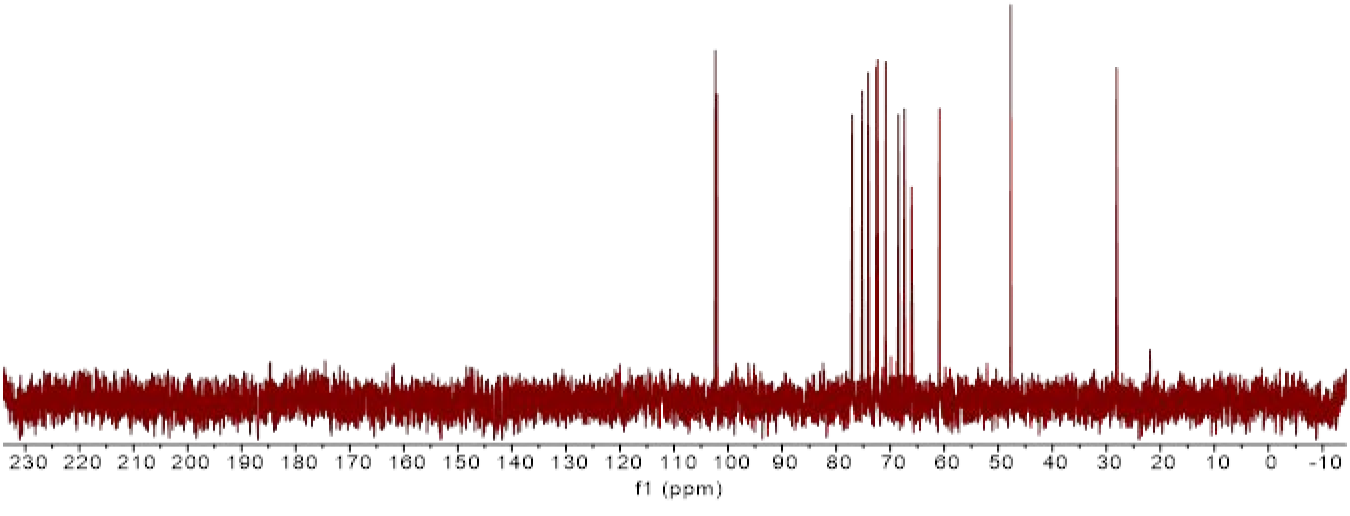

f2 (ppm)
f1 (ppm)

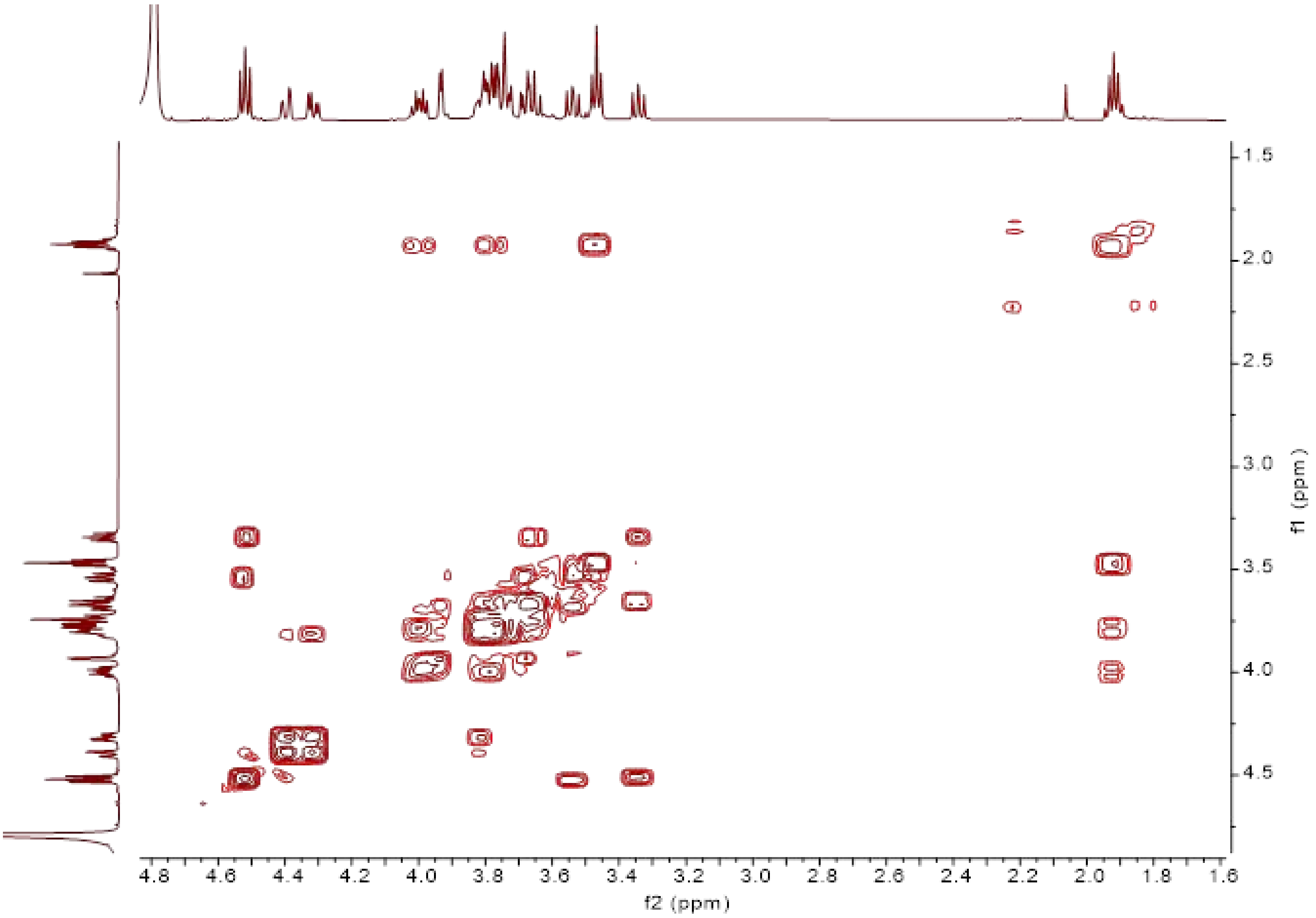

f2 (ppm)
f1 (ppm)

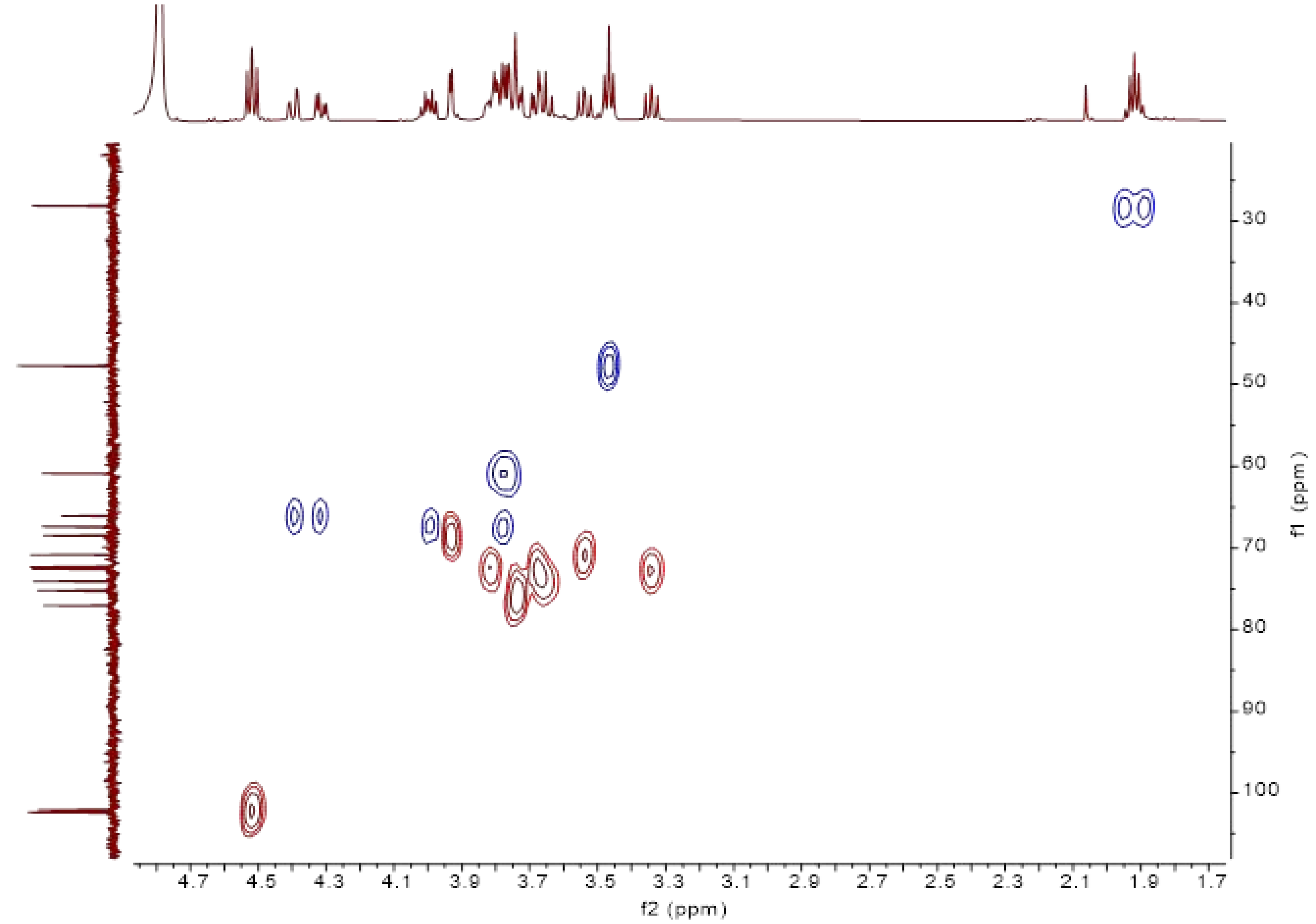

OH
OH
OSO3H
HO
O
O
O
O
HO
OH
OH
N3

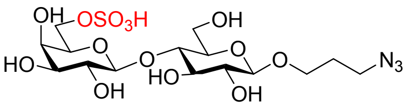
8


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)

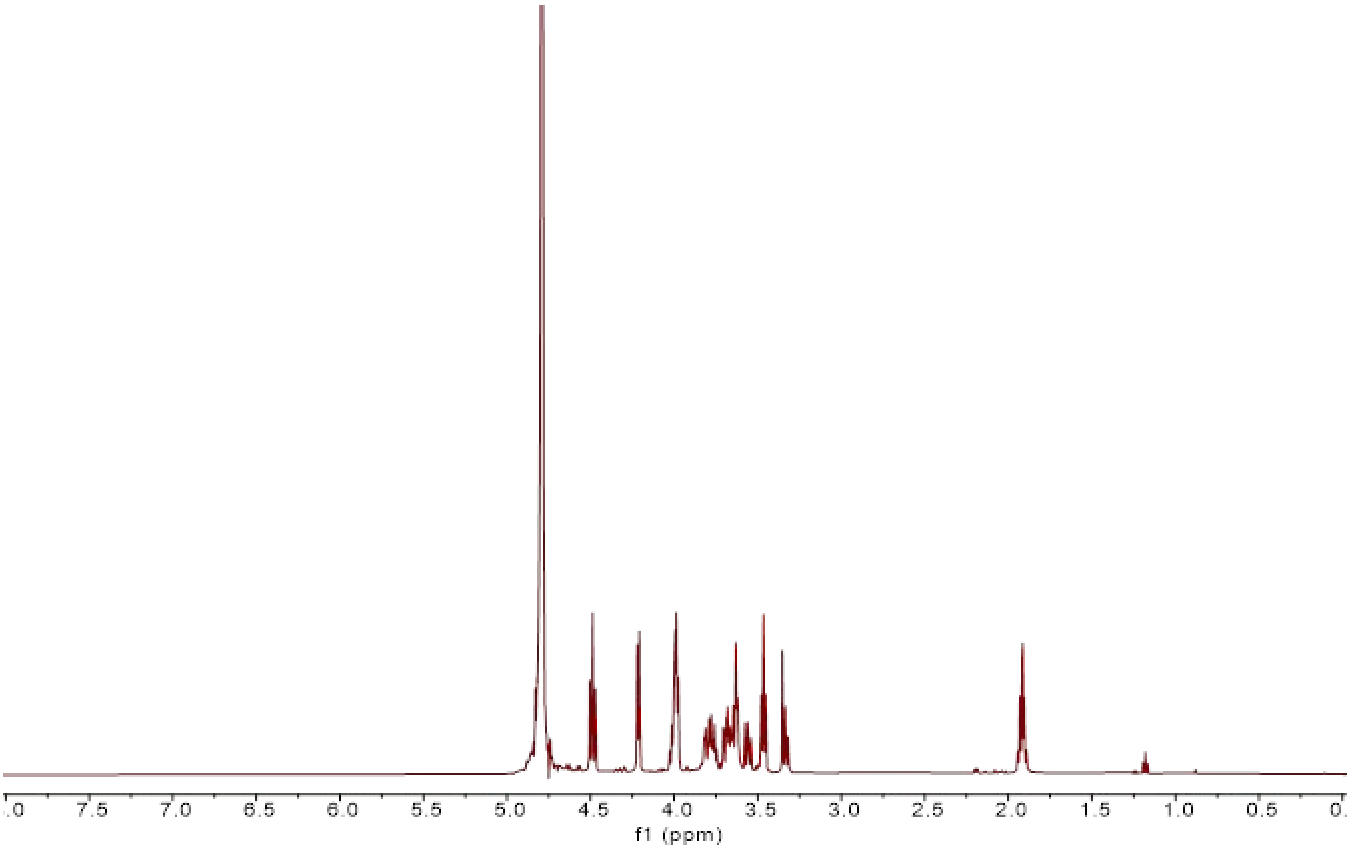

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

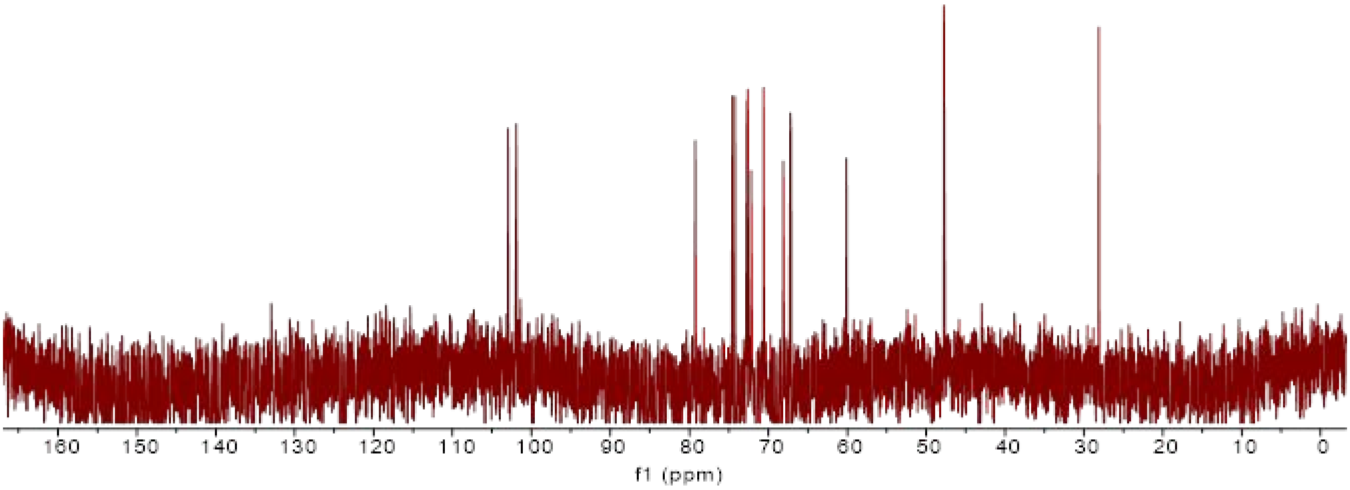

1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

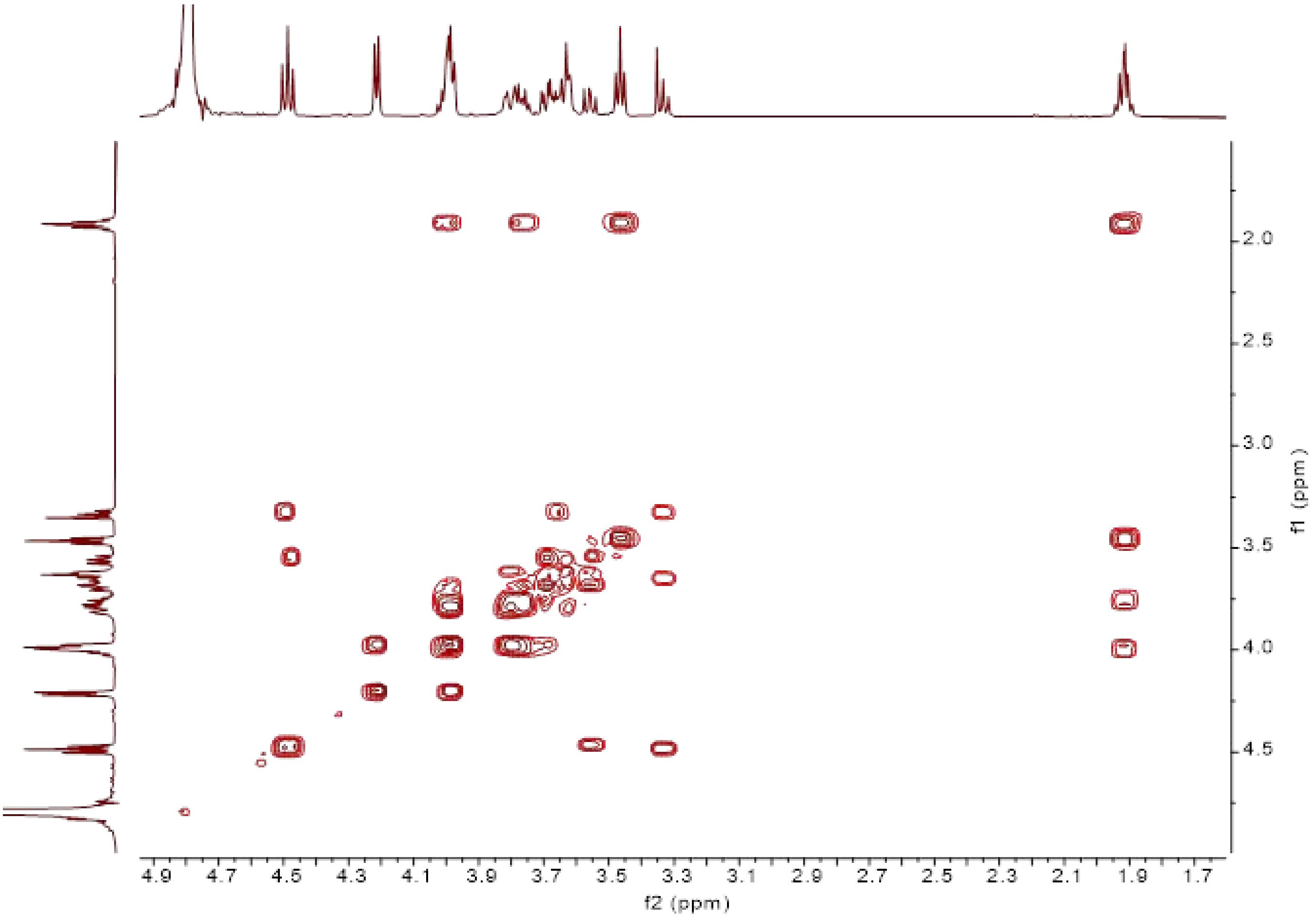

30
40
50
60
70
80
90
100
f1 (ppm)
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)

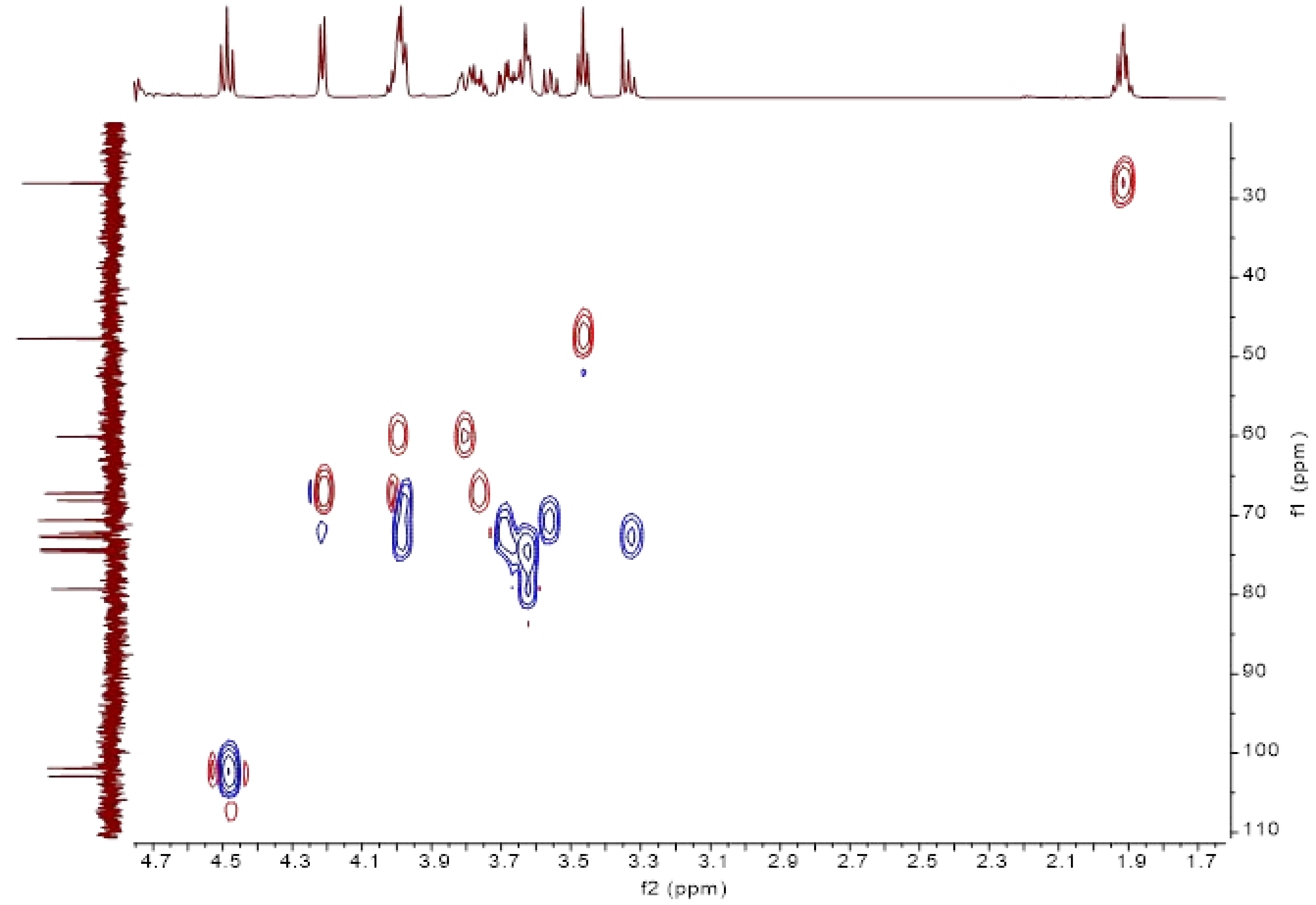

OH
OSO$_3$H
OH
HO
O
O
OH
HO
O
O
OH
N$_3$

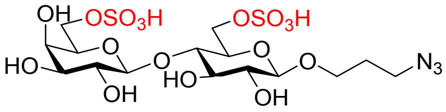
9


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


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

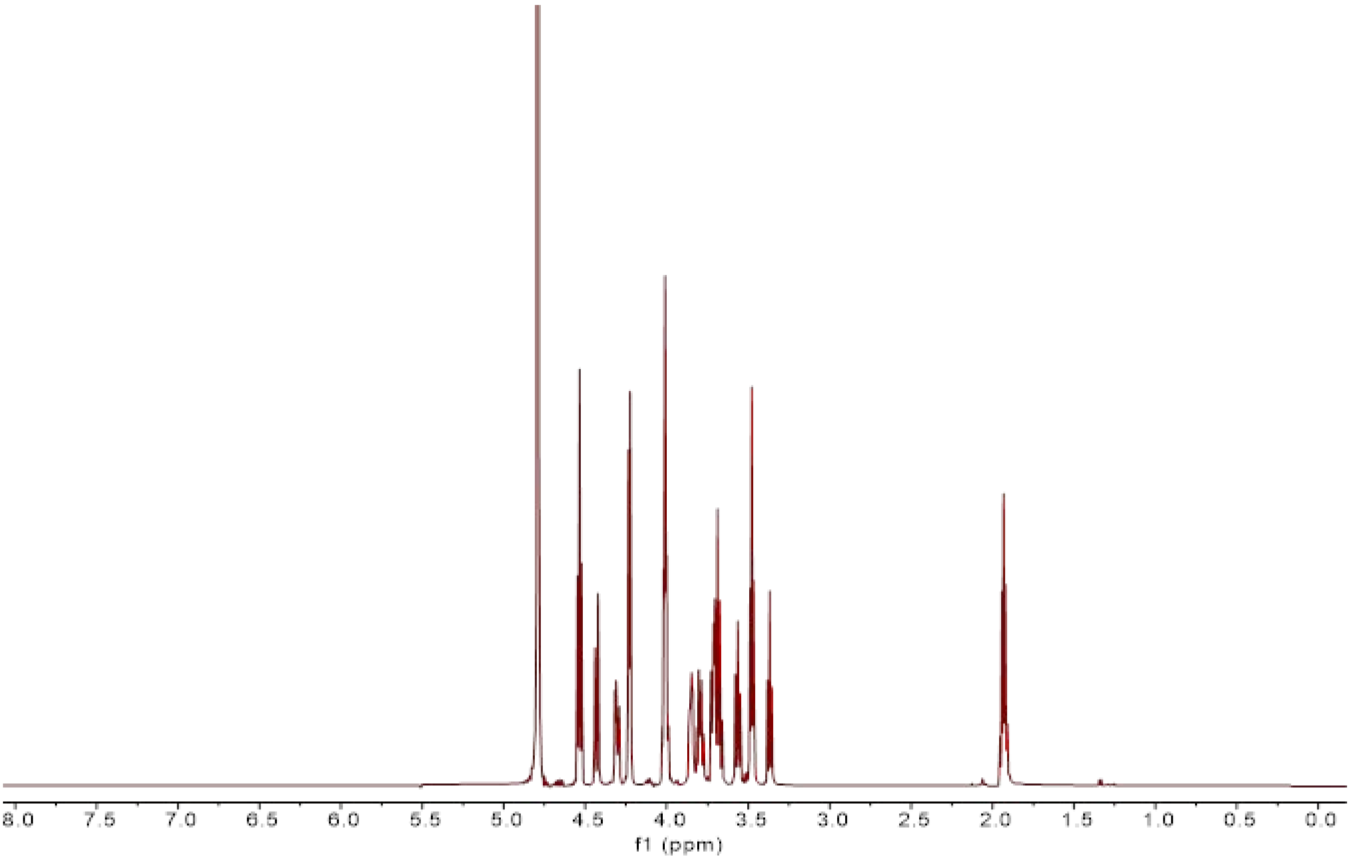

f1 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)


f1 (ppm)
30
40
50
60
70
80
90
100
110
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)

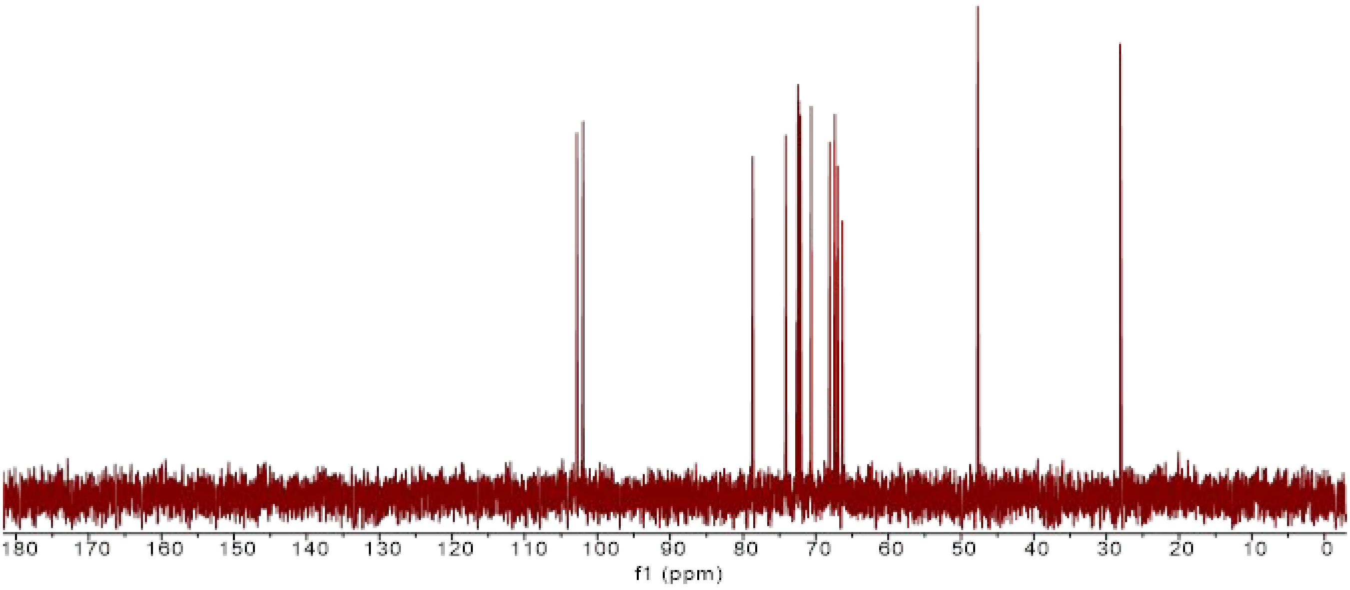


OH
OSO_3H
O
HO
OH
O
HO
OSO_3H
O
OH
O
N_3

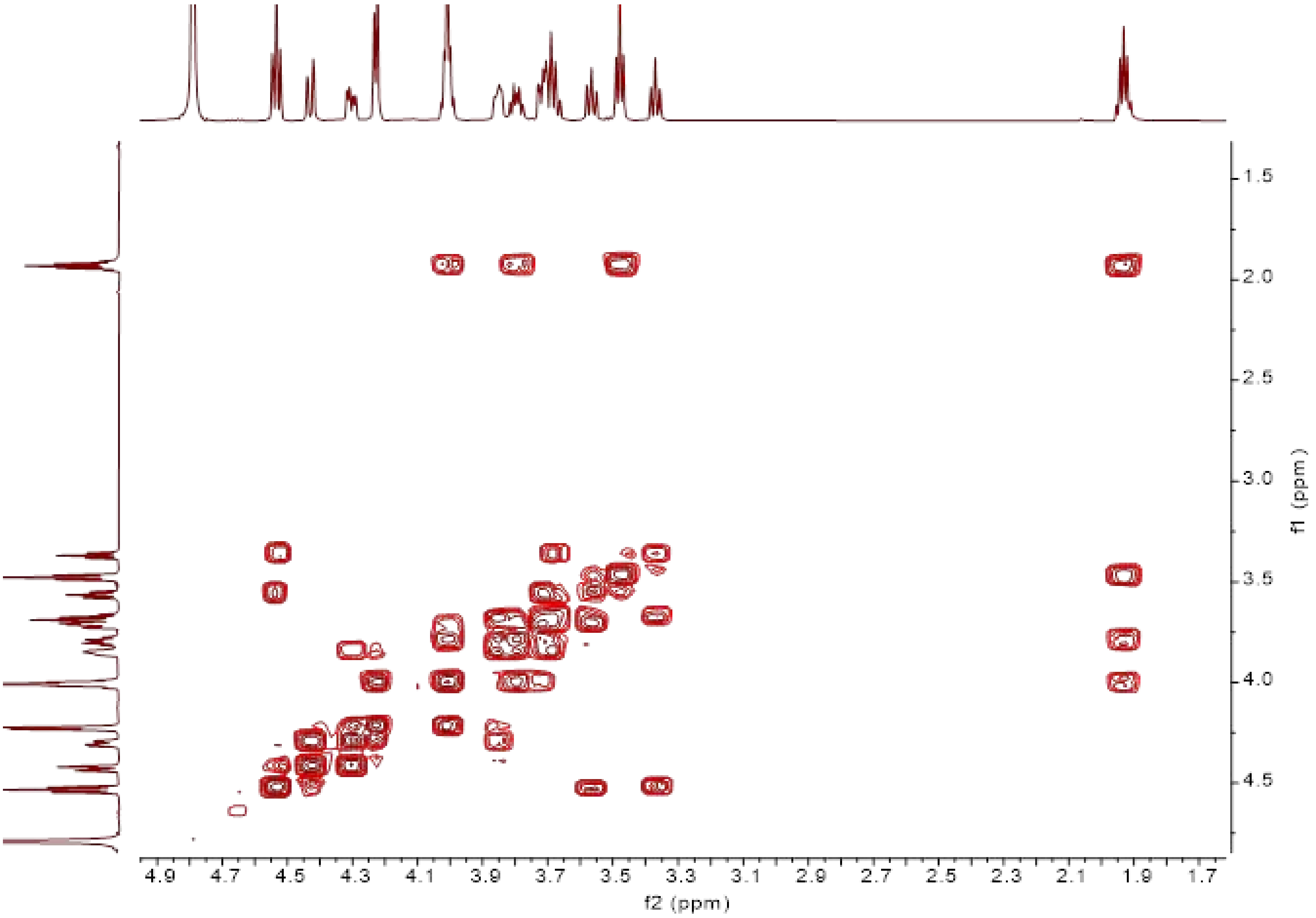
10



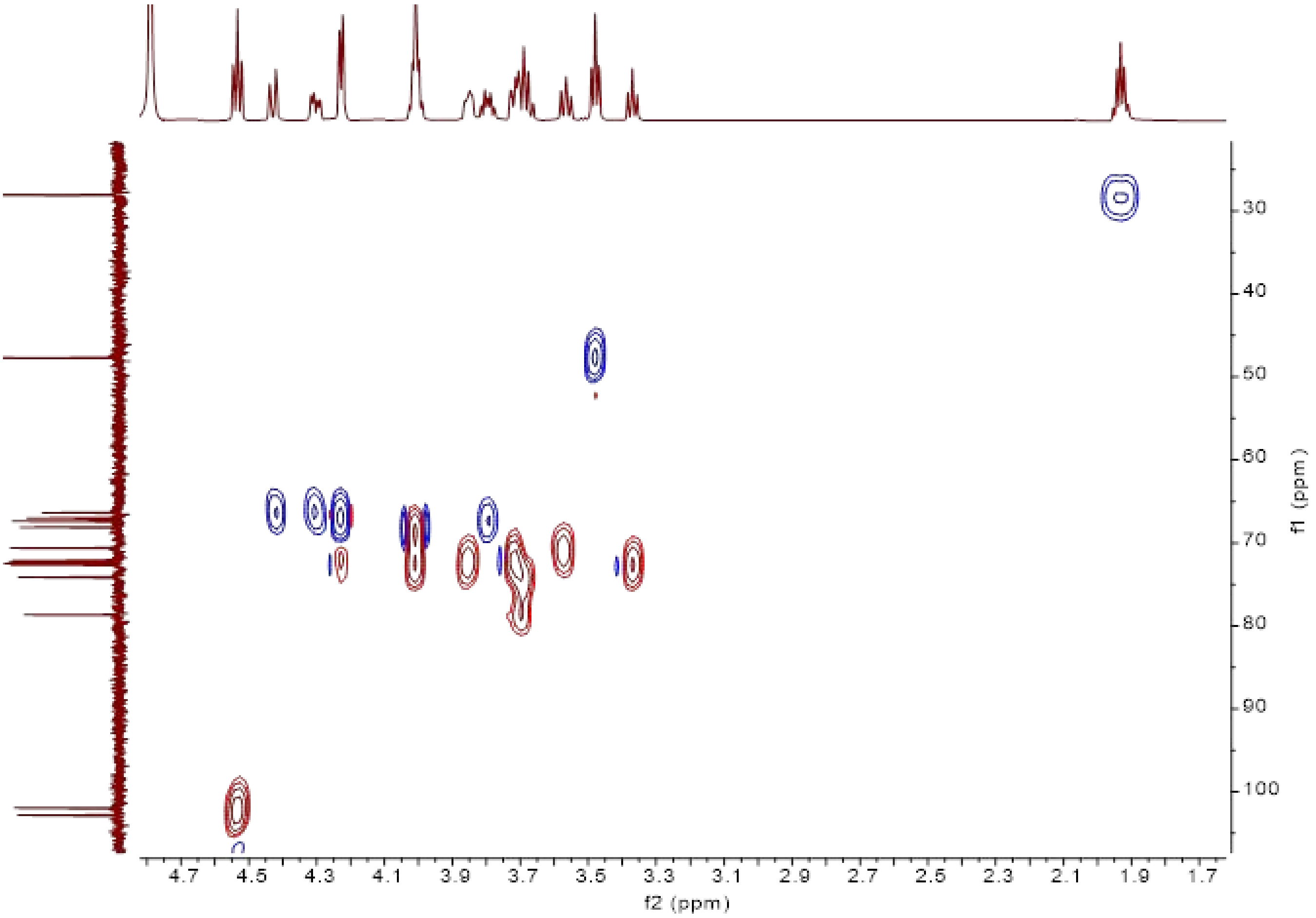
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



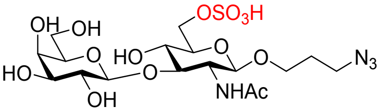
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



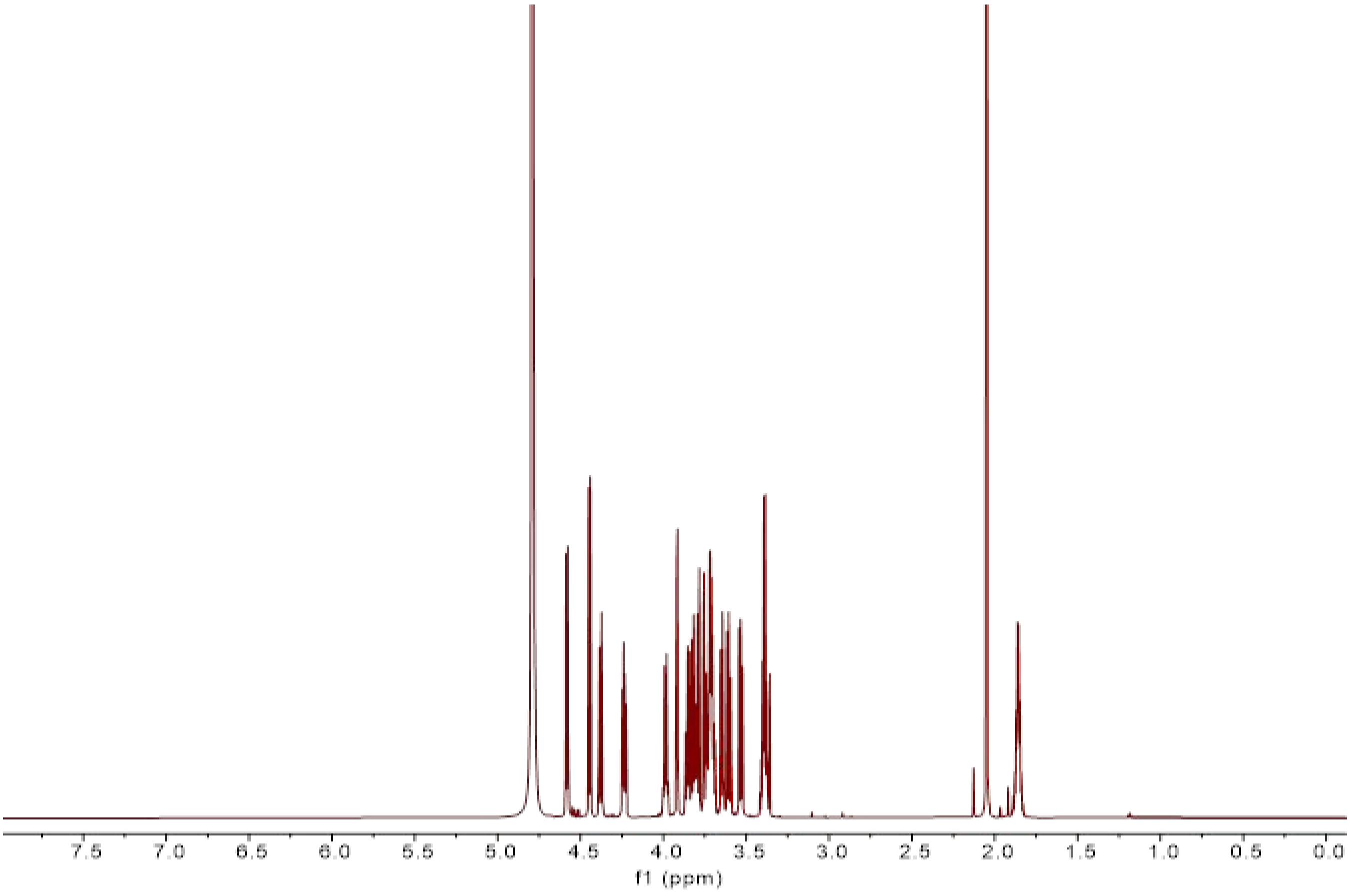
f2 (ppm)
f1 (ppm)
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
2.0
2.5
3.0
3.5
4.0
4.5

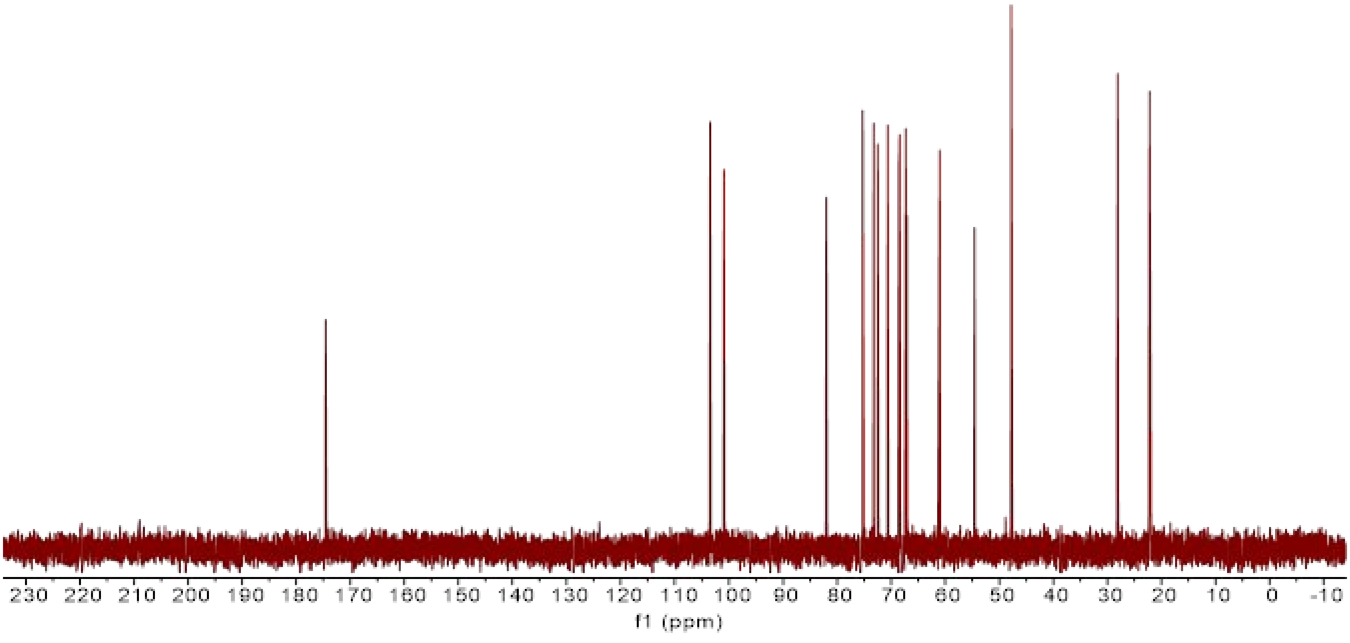


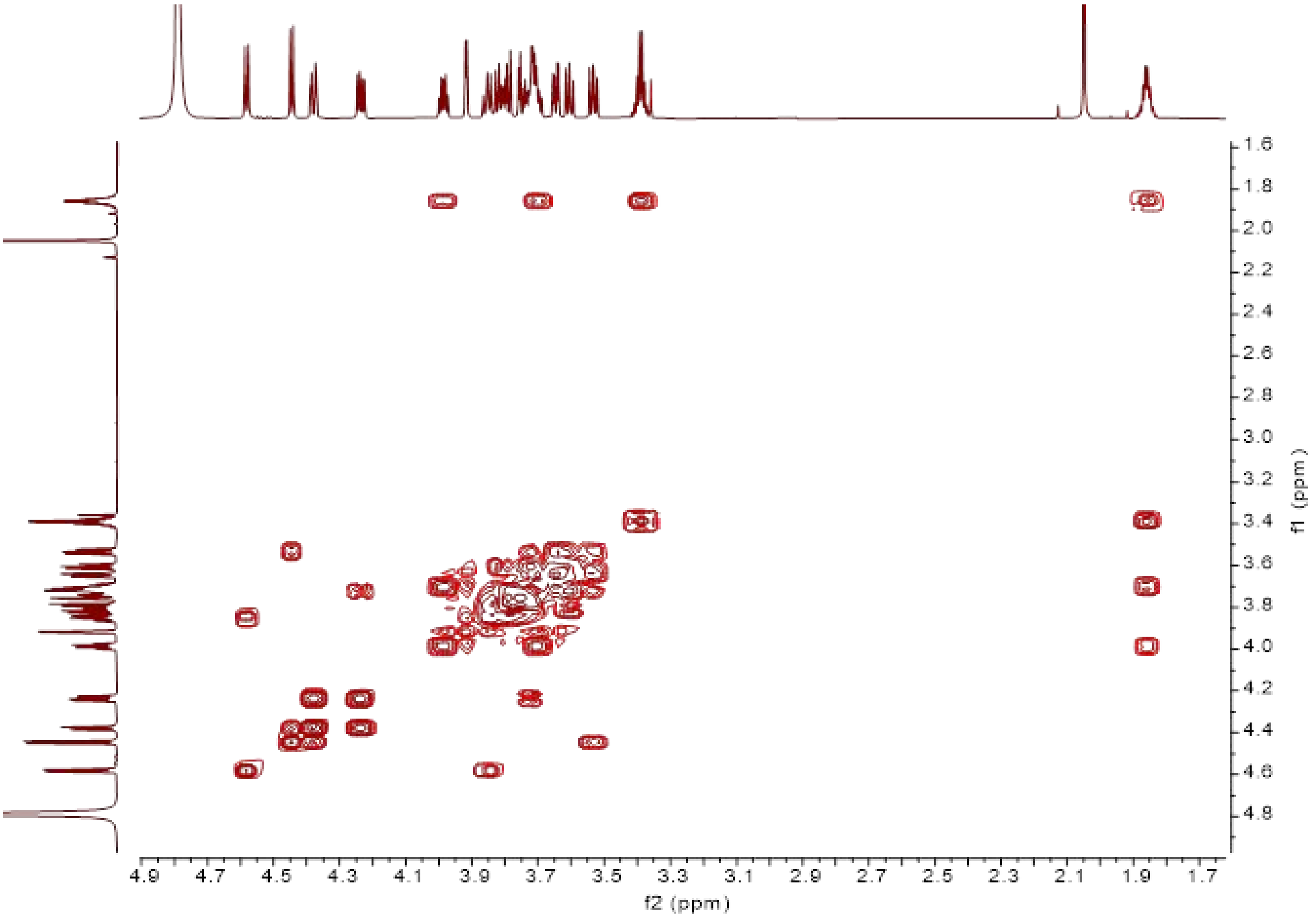
f2 (ppm)
f1 (ppm)
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
30
40
50
60
70
80
90
100

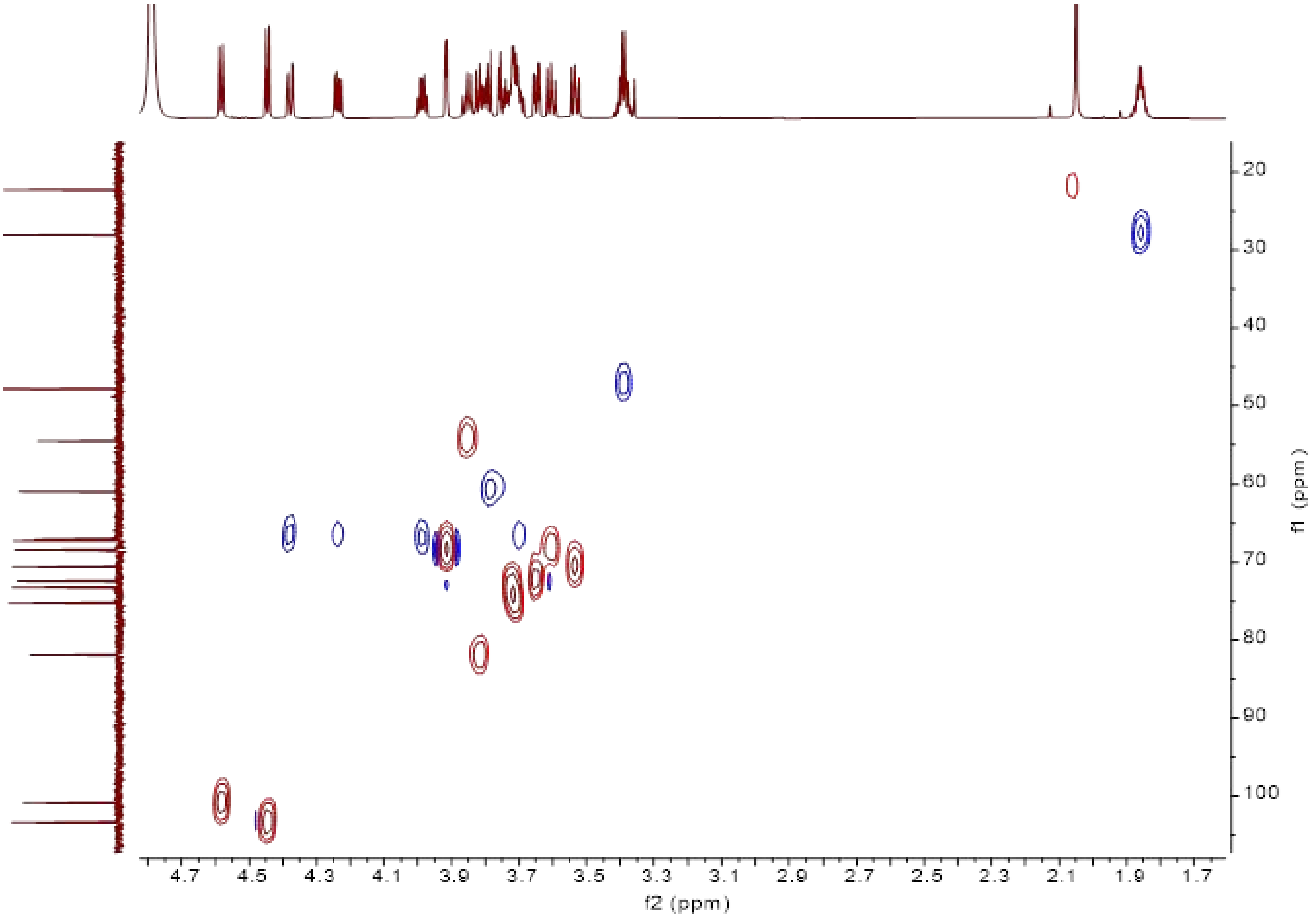

OH
OH
OSO3H
O
HO
O
O
N3
HO
O
OH
NHAc

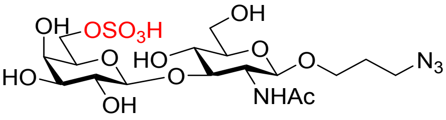
11


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)

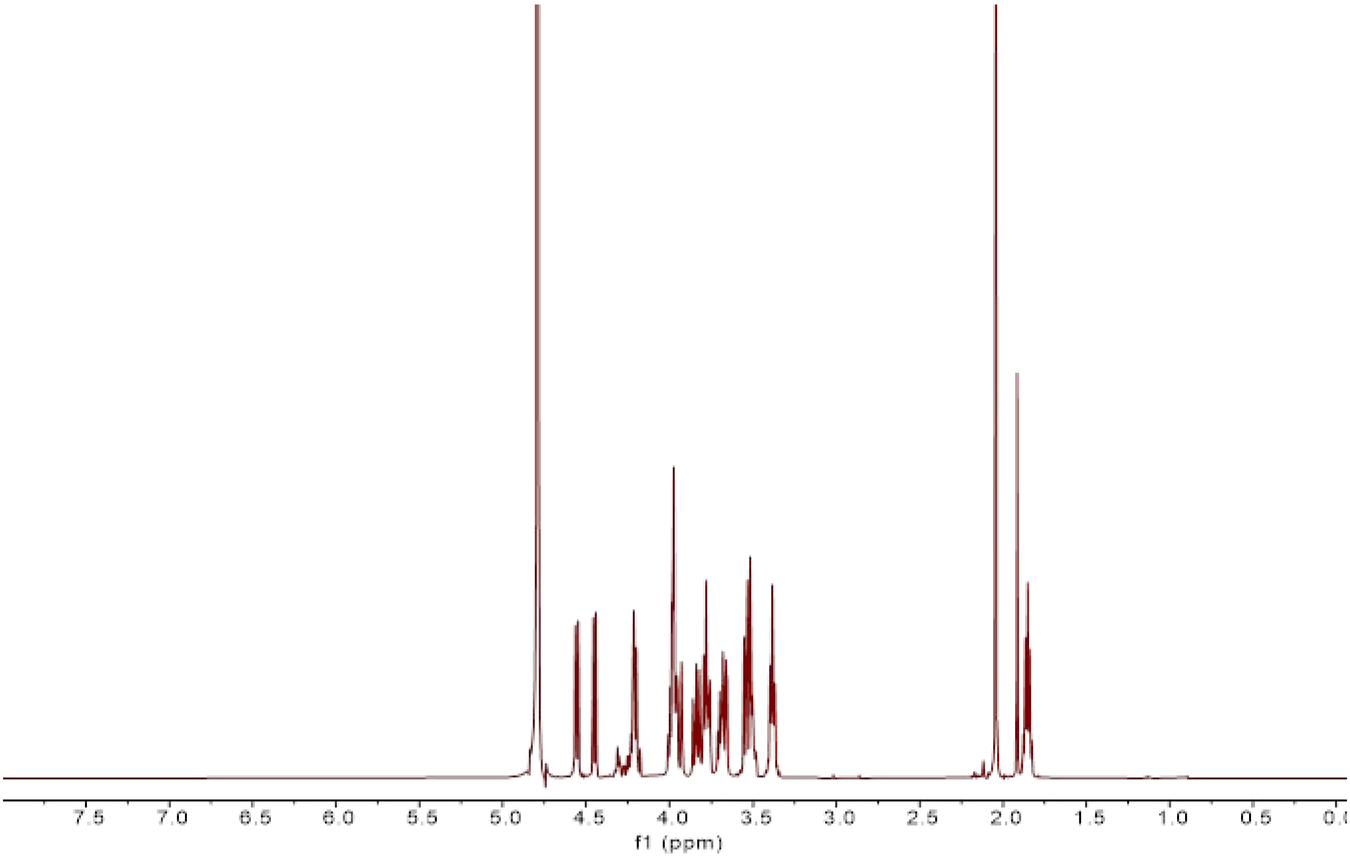

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

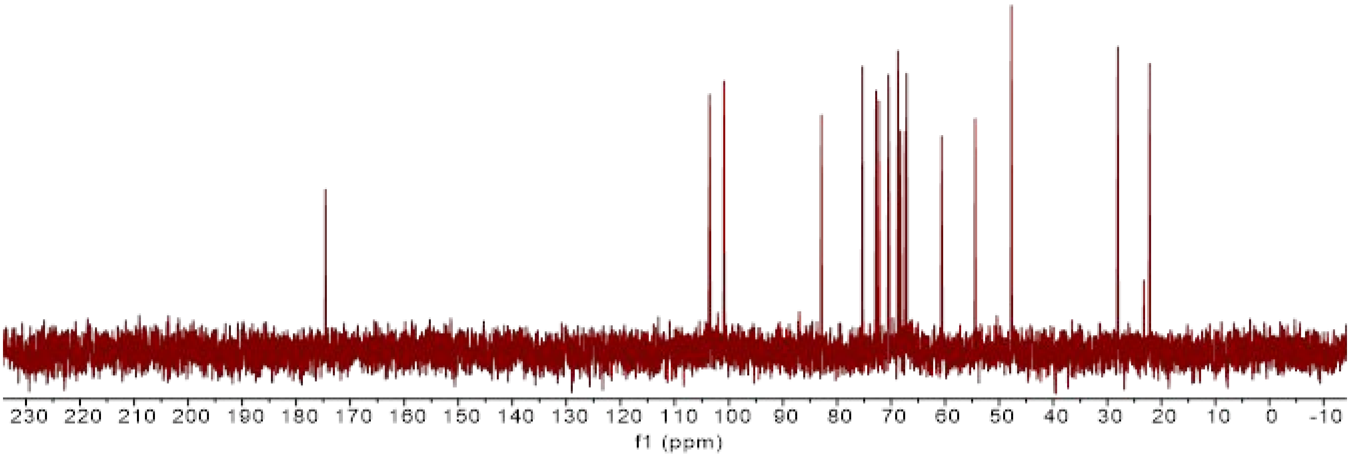

f1 (ppm)
f2 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7

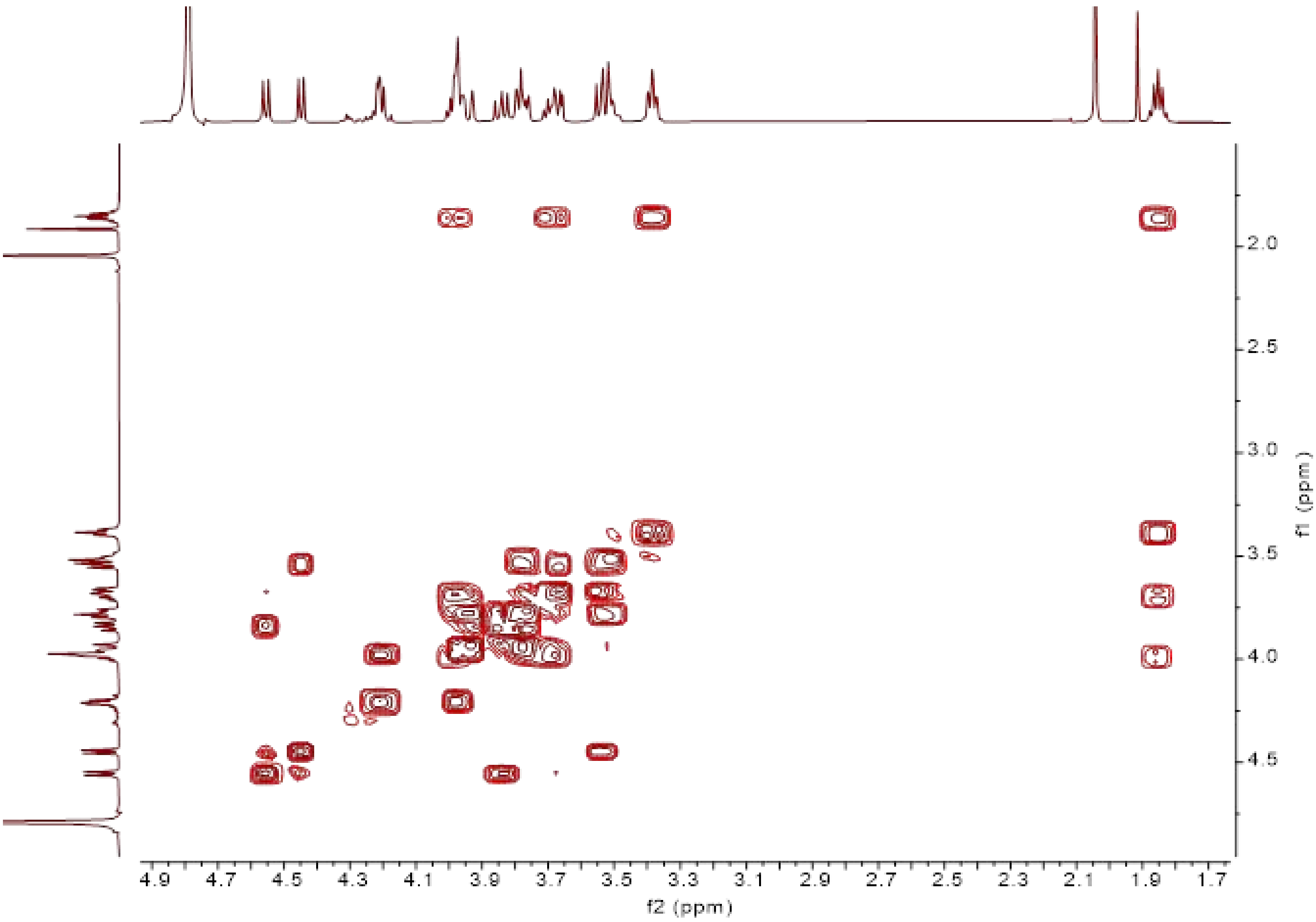

f1 (ppm)
f2 (ppm)
20
30
40
50
60
70
80
90
100
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7

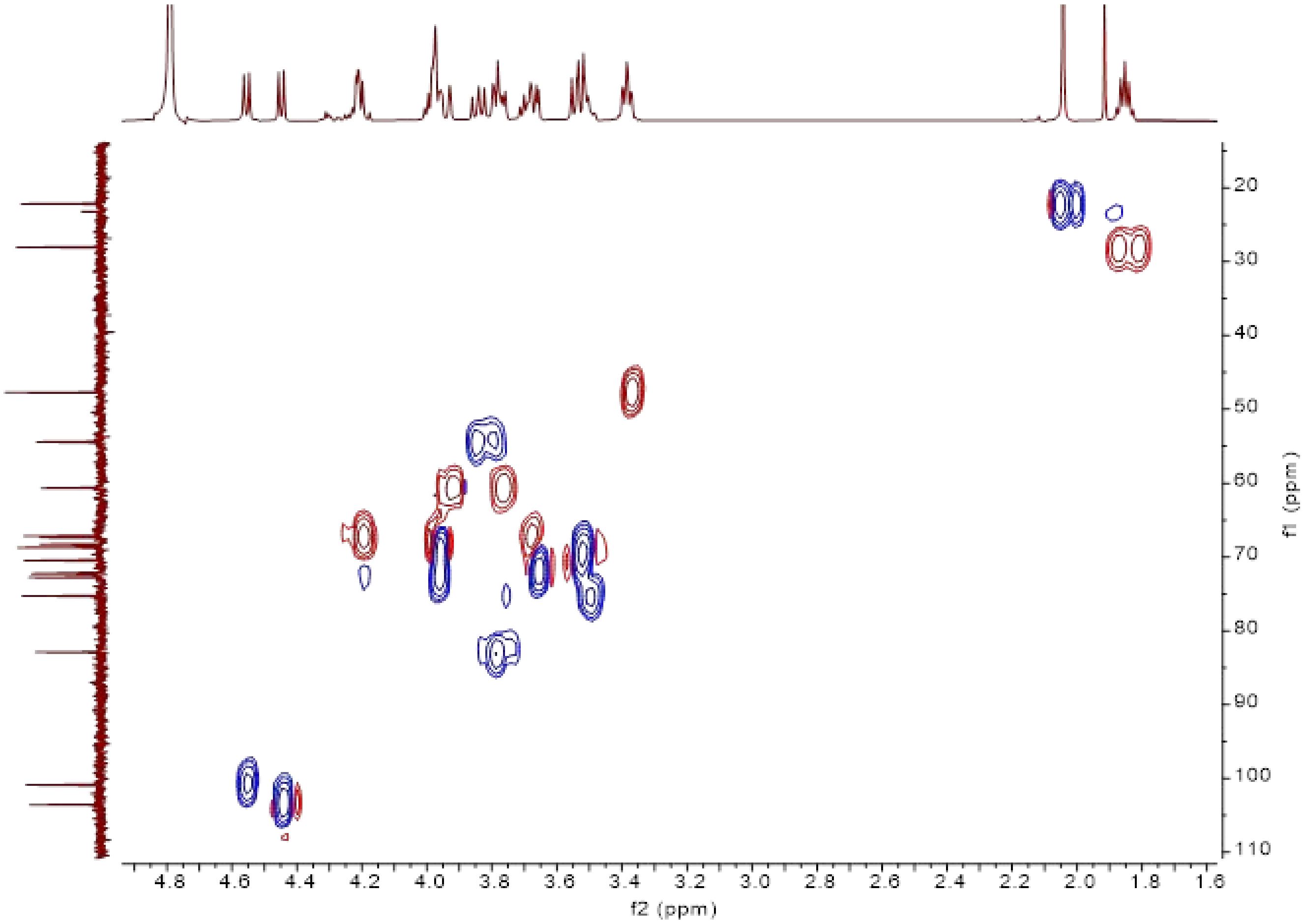

OH
OSO$_3$H
OH
HO
O
HO
O
O
N$_3$
HO
OH
NHAc

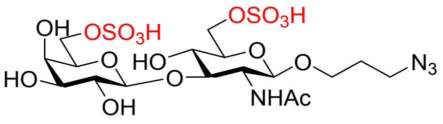
12


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)

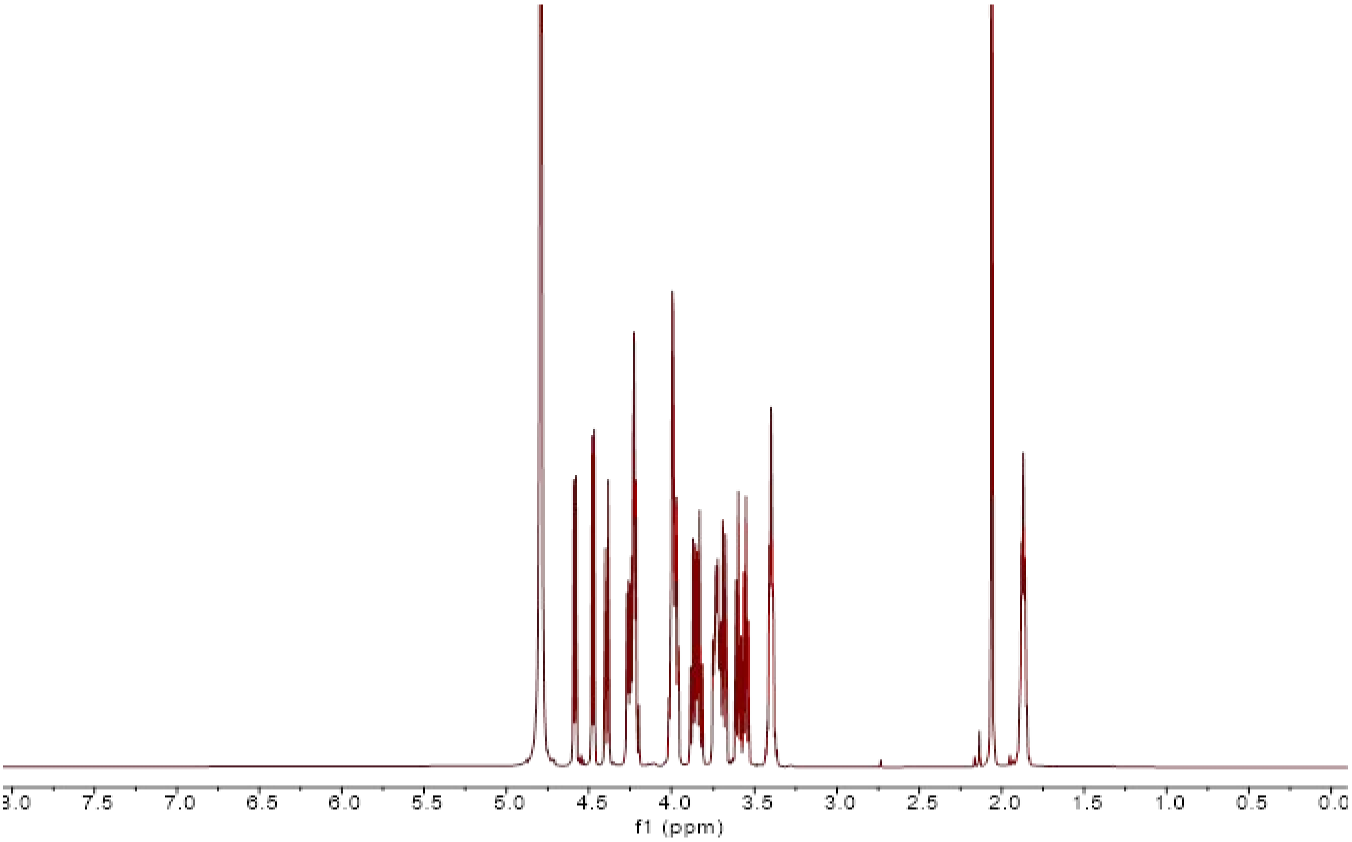

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

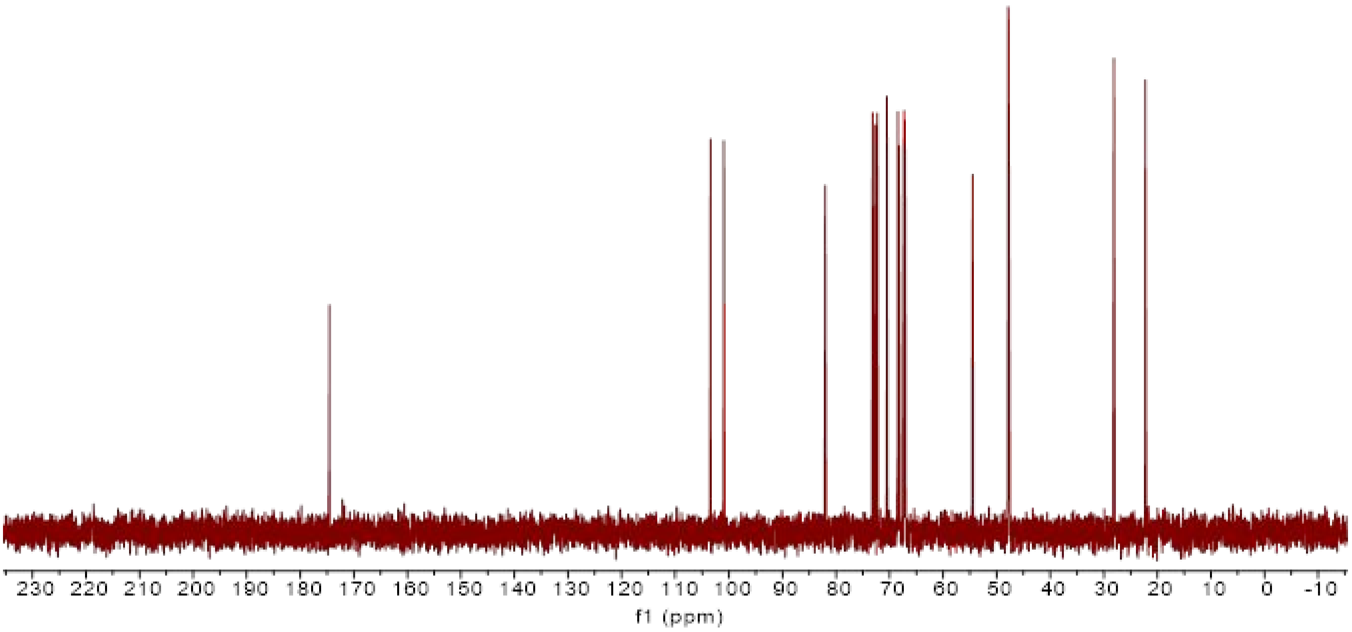

2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)

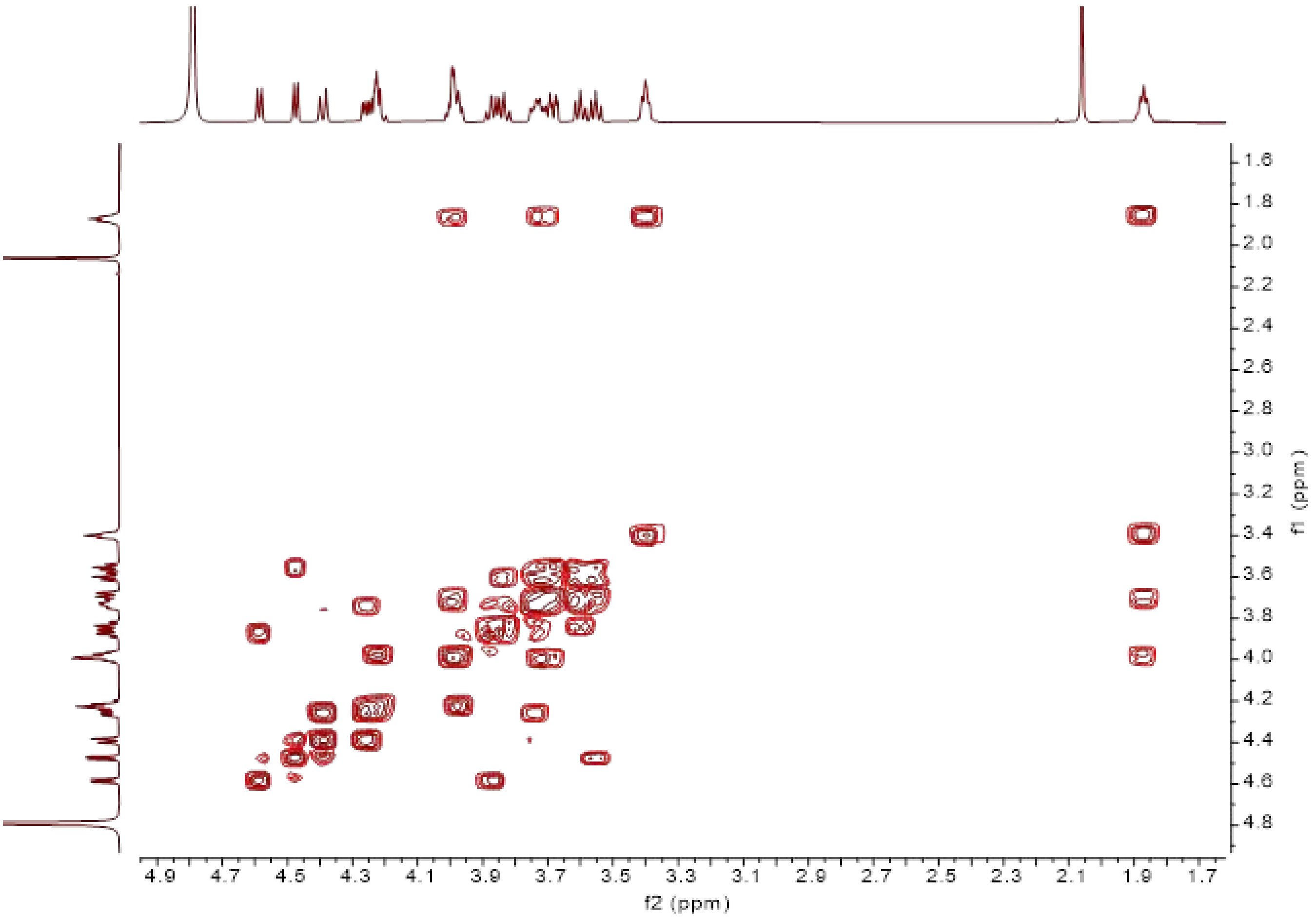

20
30
40
50
60
70
80
90
100
110
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

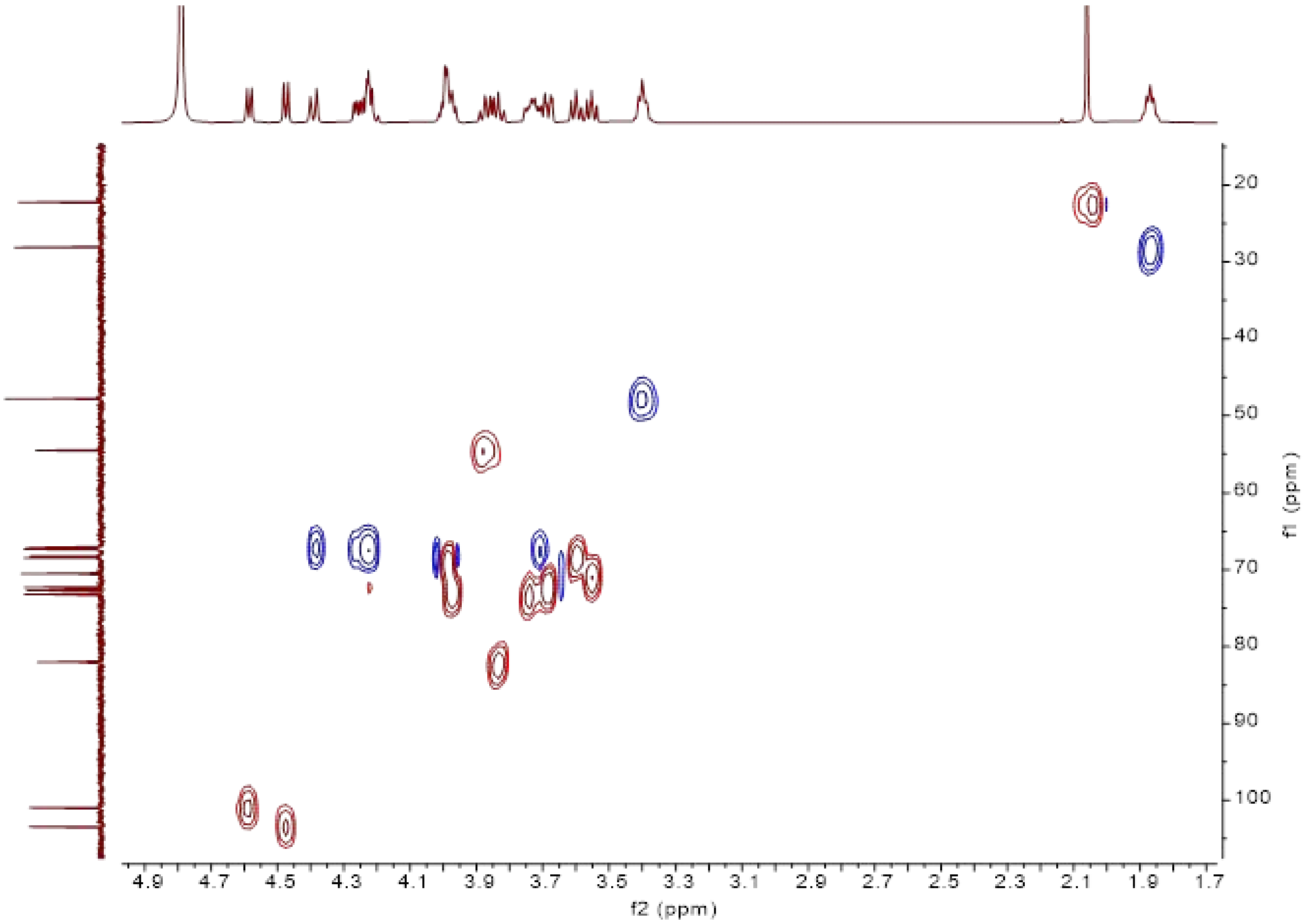


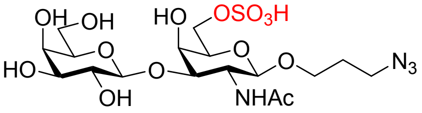
13


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

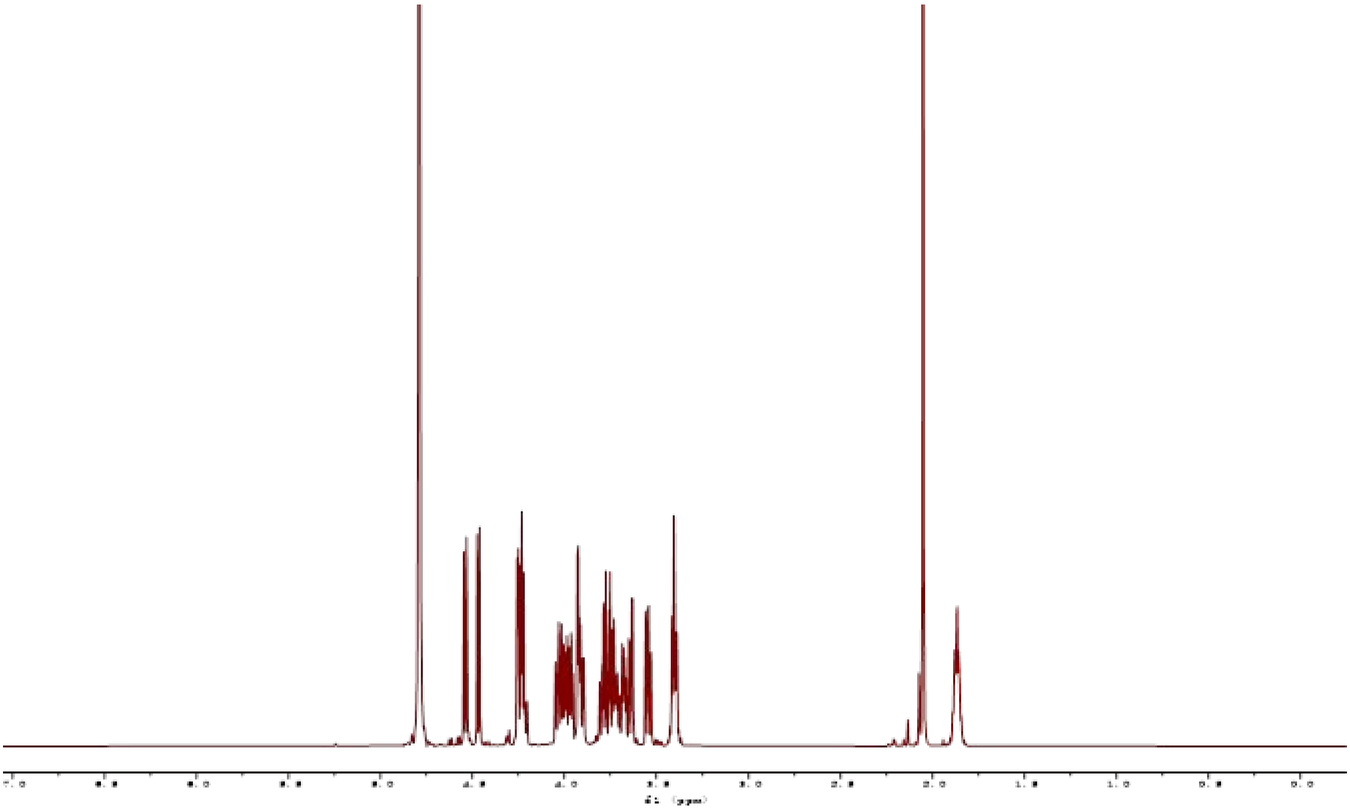

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

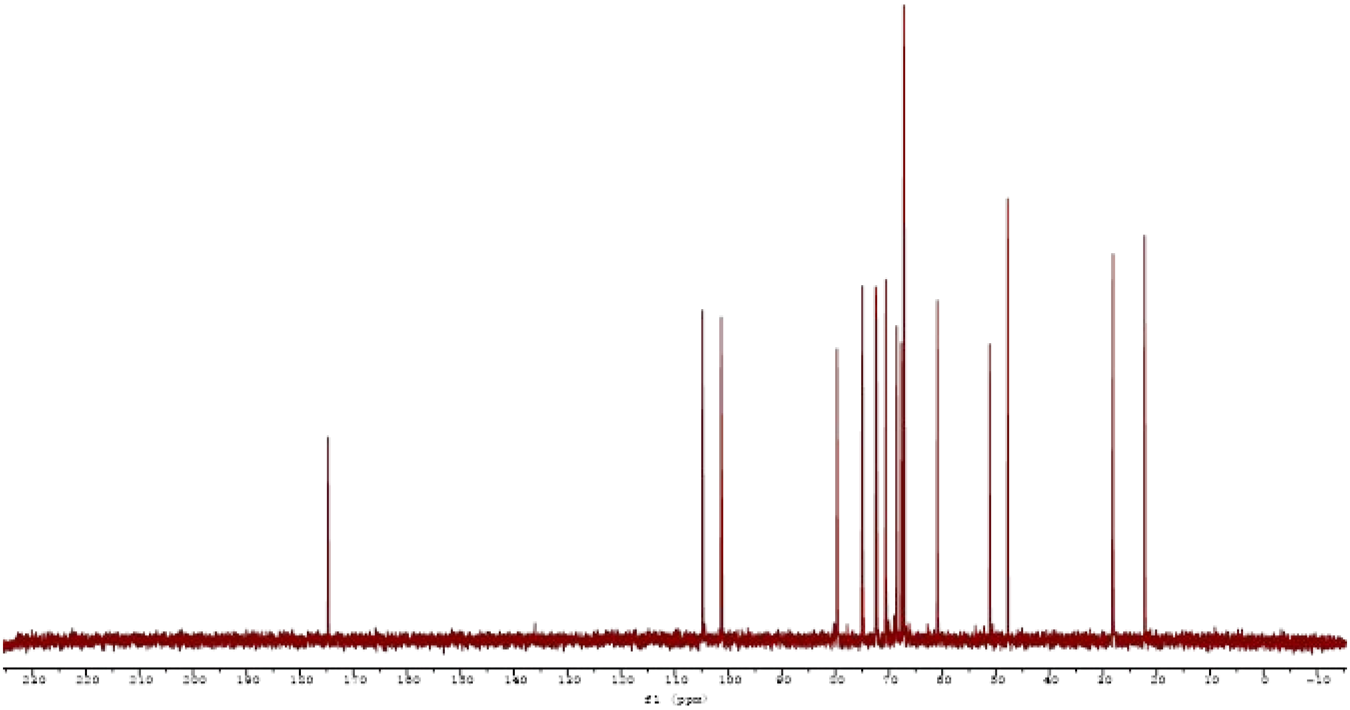

f2 (ppm)
f1 (ppm)
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8

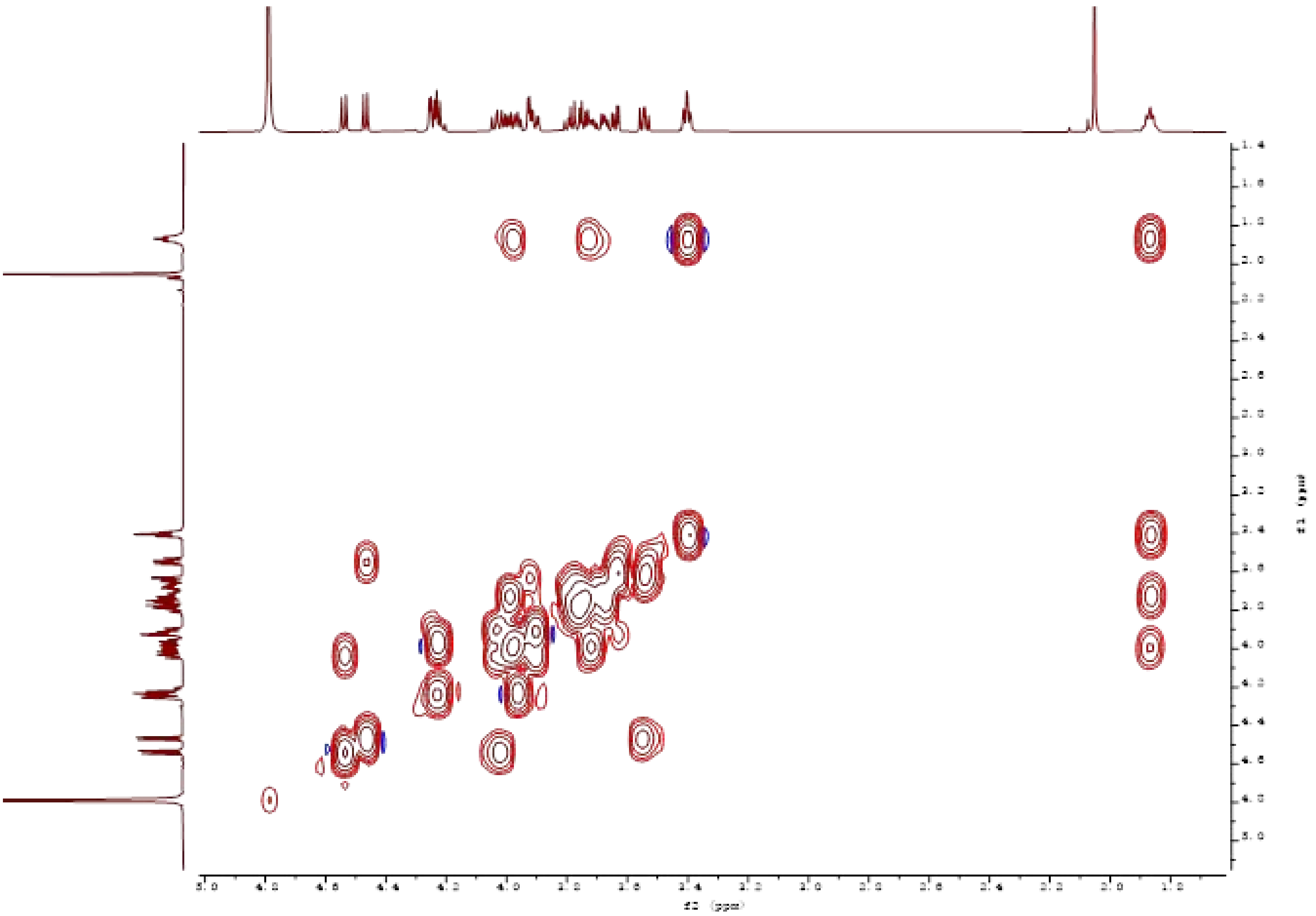

f2 (ppm)
f1 (ppm)
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
20
30
40
50
60
70
80
90
100

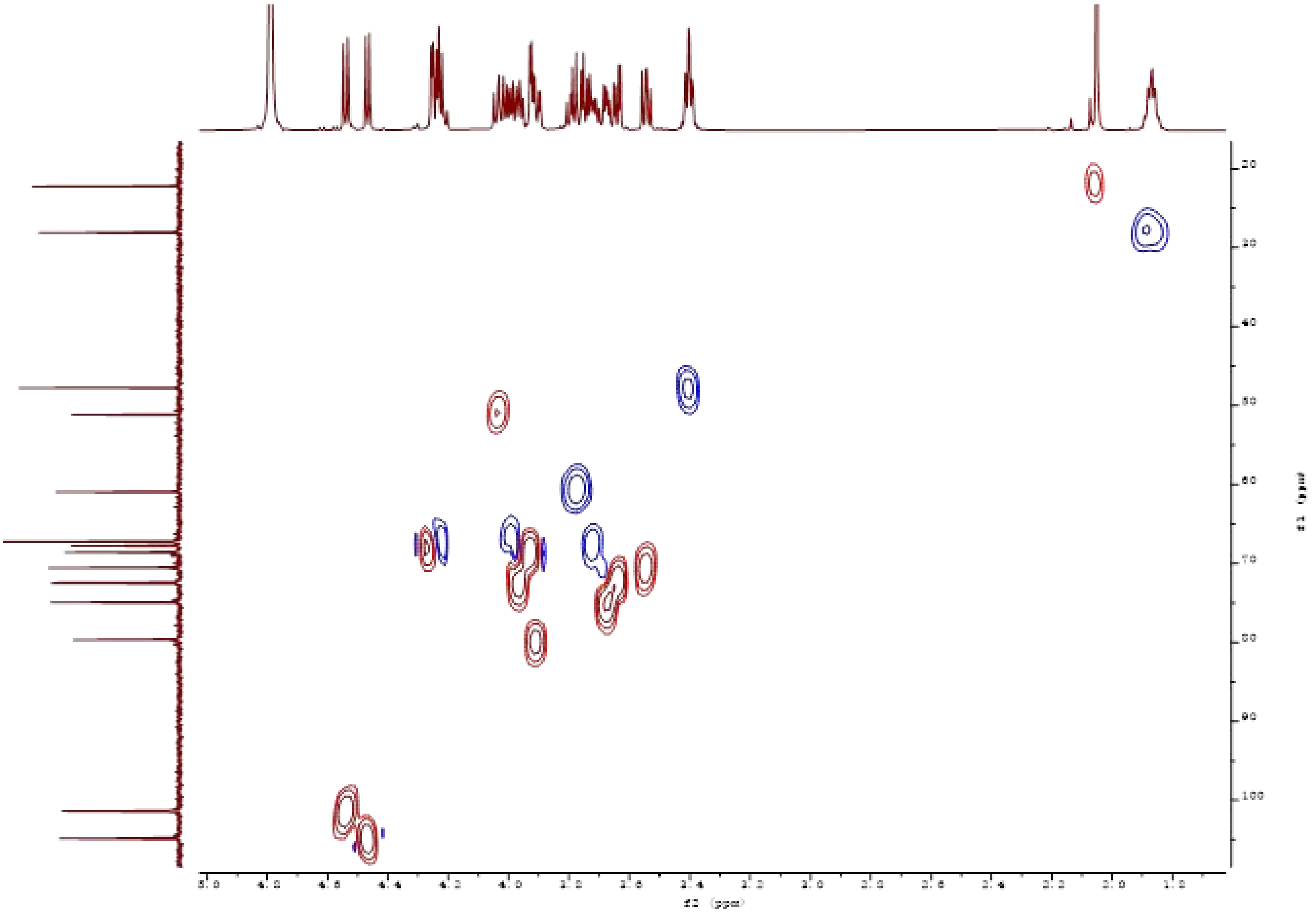

OH
OH
HO
OSO3H
O
HO
O
O
O
N3
OH
NHAc

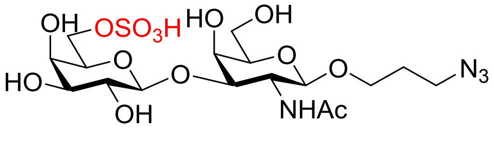
14


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)

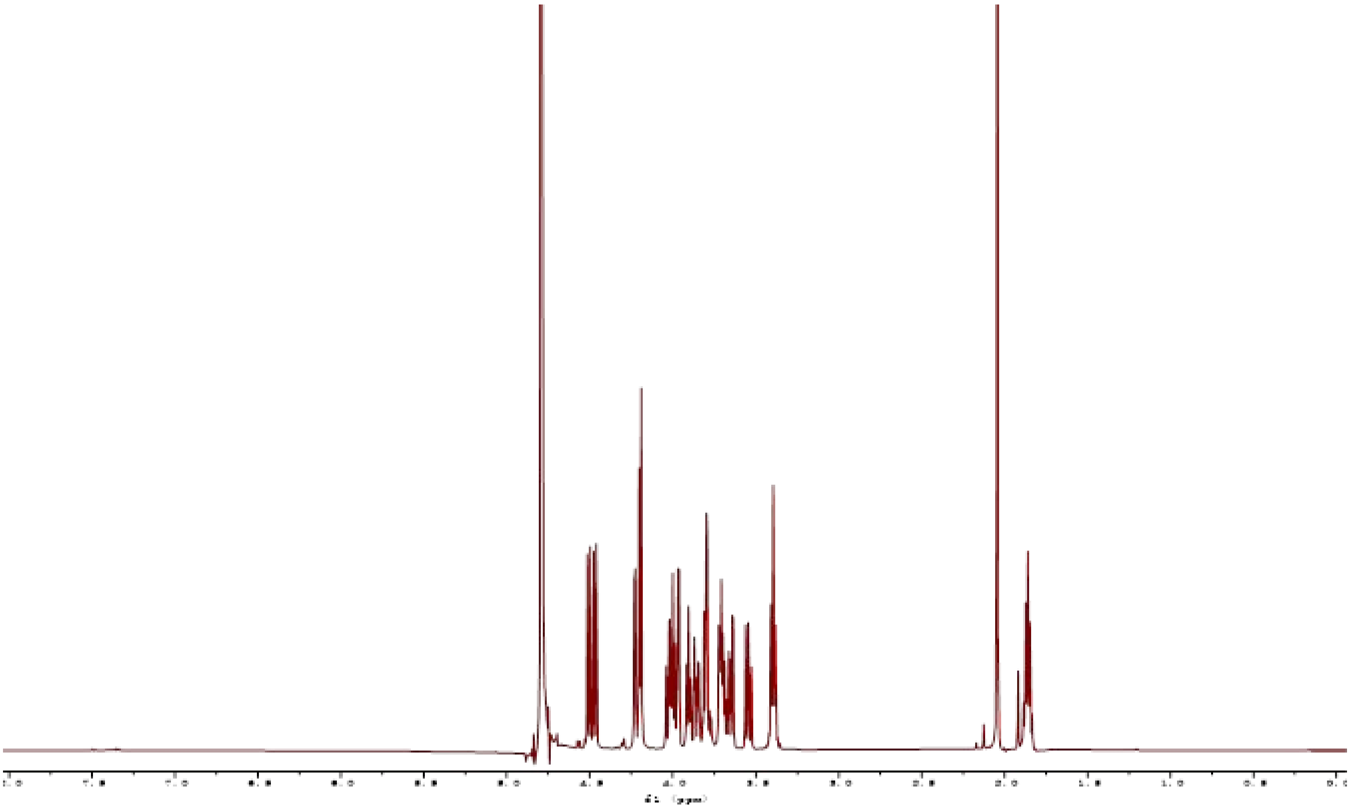

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

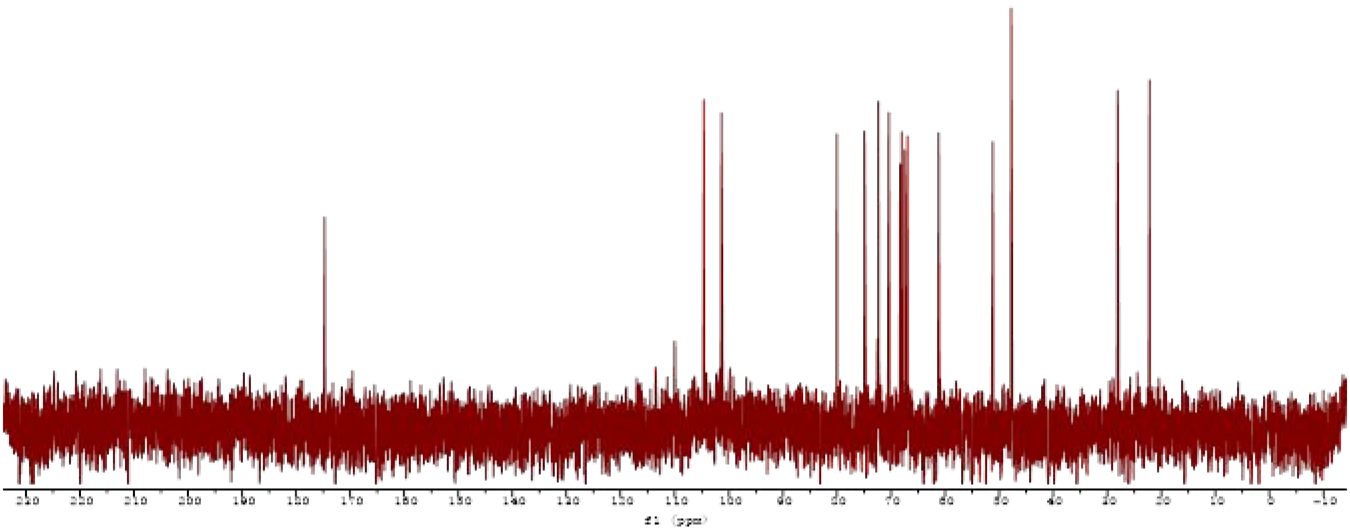

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)

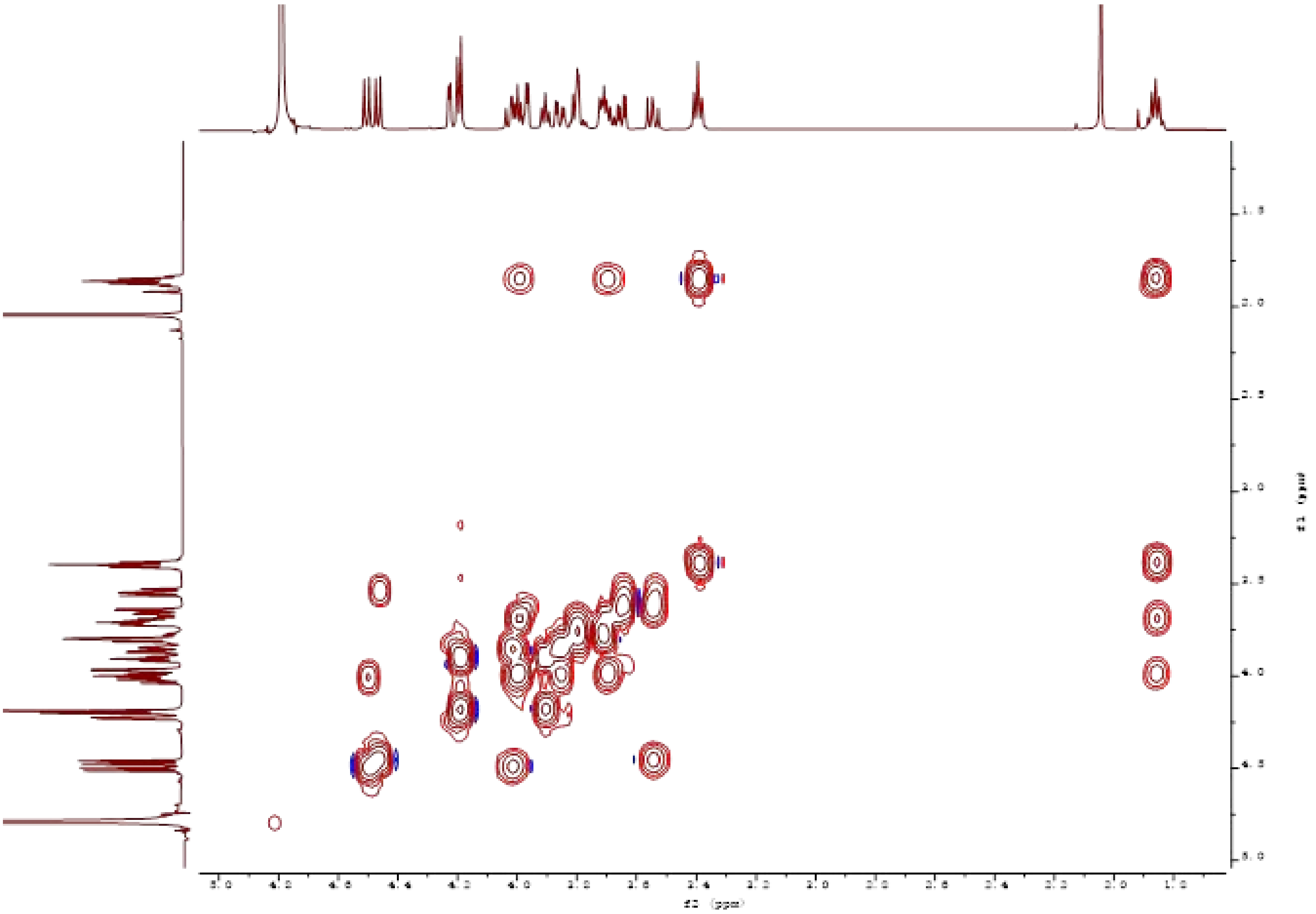

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

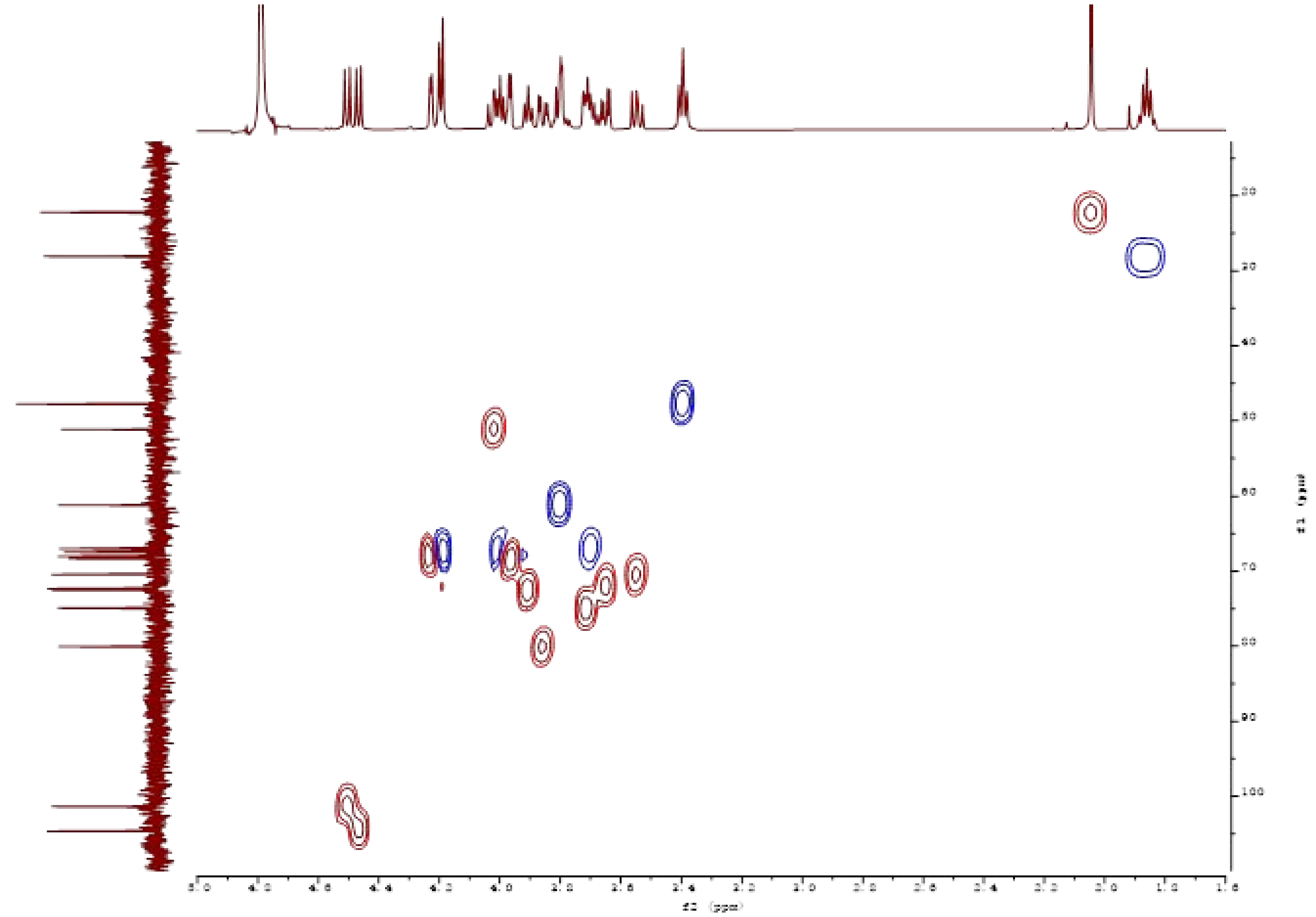

OH
OSO3H
HO
OH
O
HO
O
O
O
OH
NHAc
N3

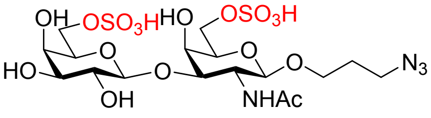
15


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


230
220
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)

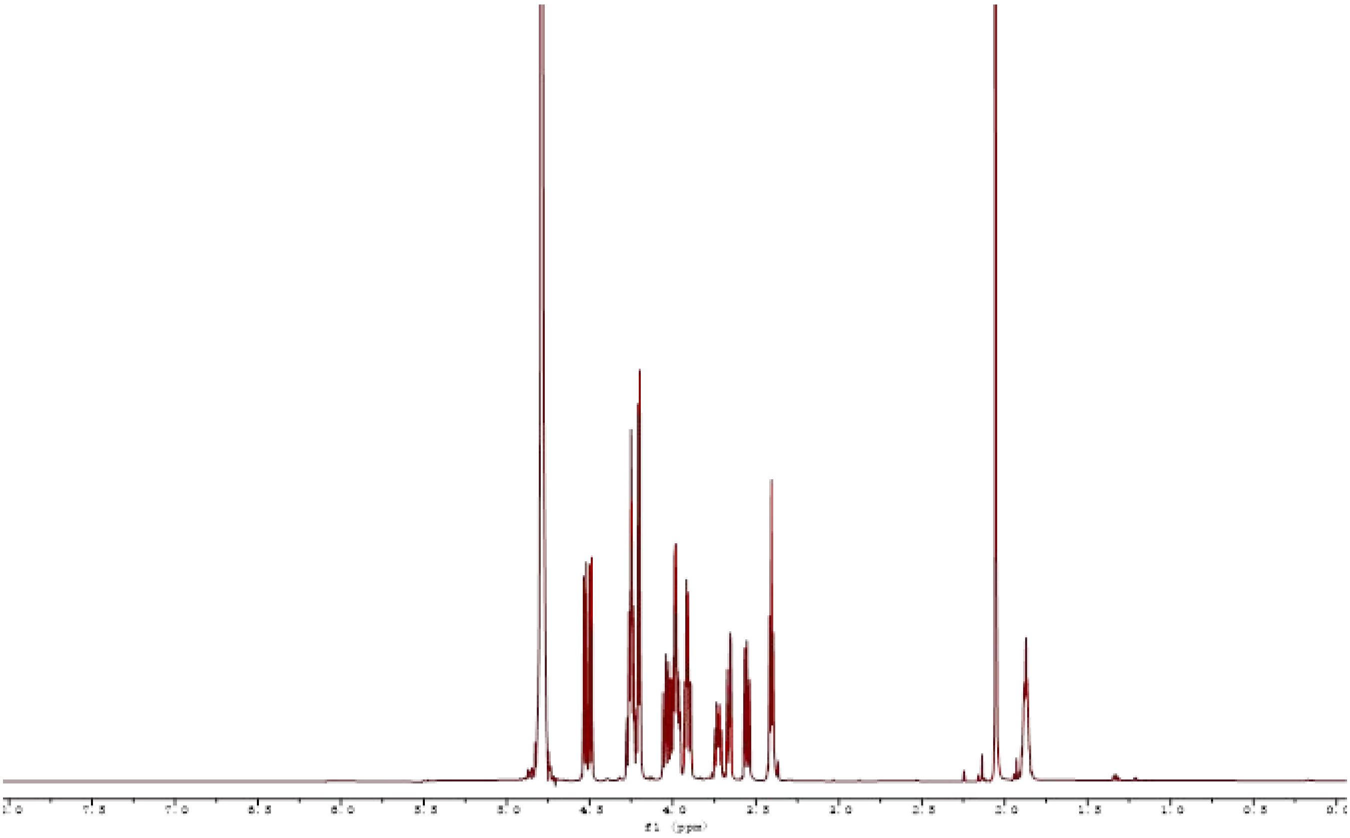

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

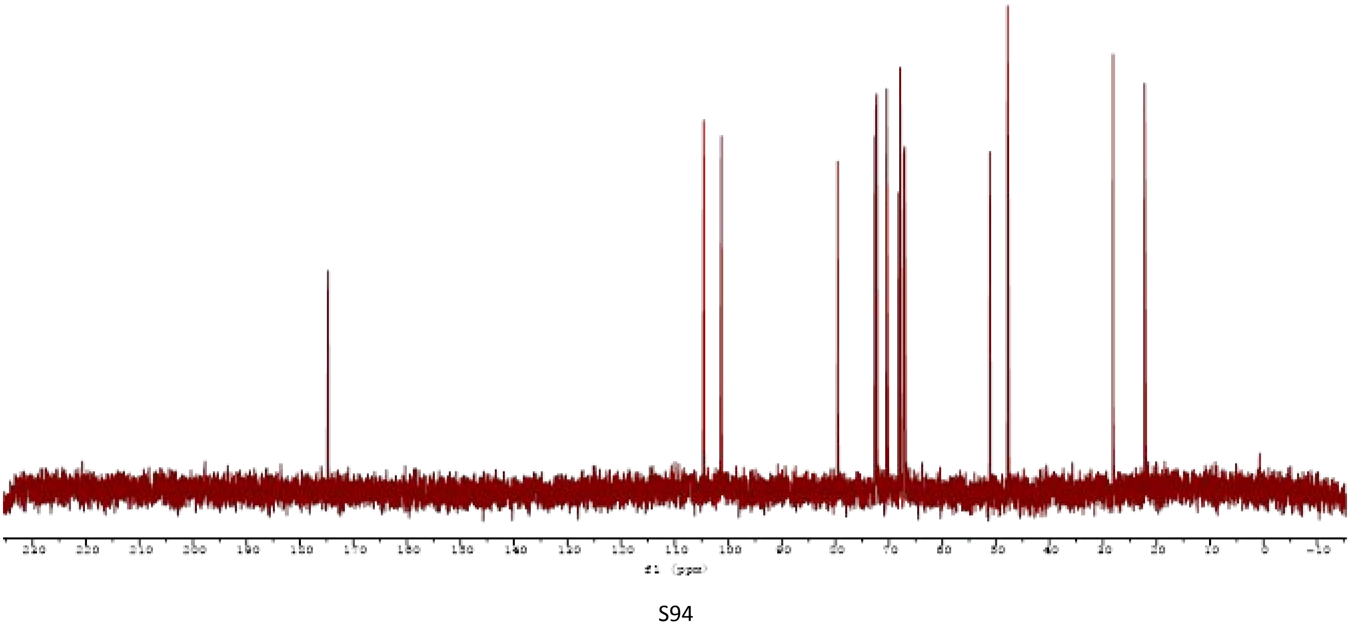


OH
OSO3H
HO
OSO3H
HO
O
O
O
O
N3
OH
NHAc

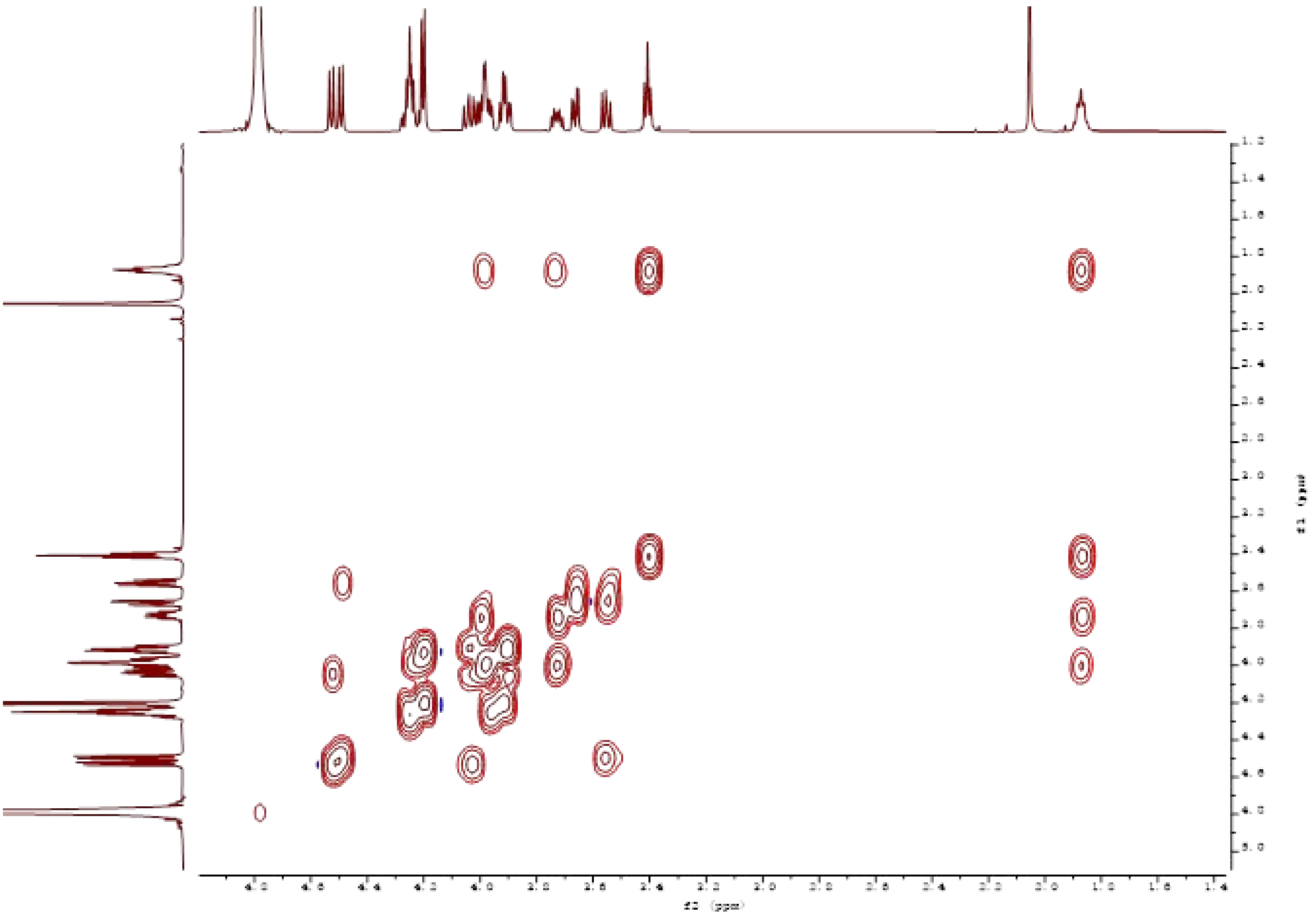
16

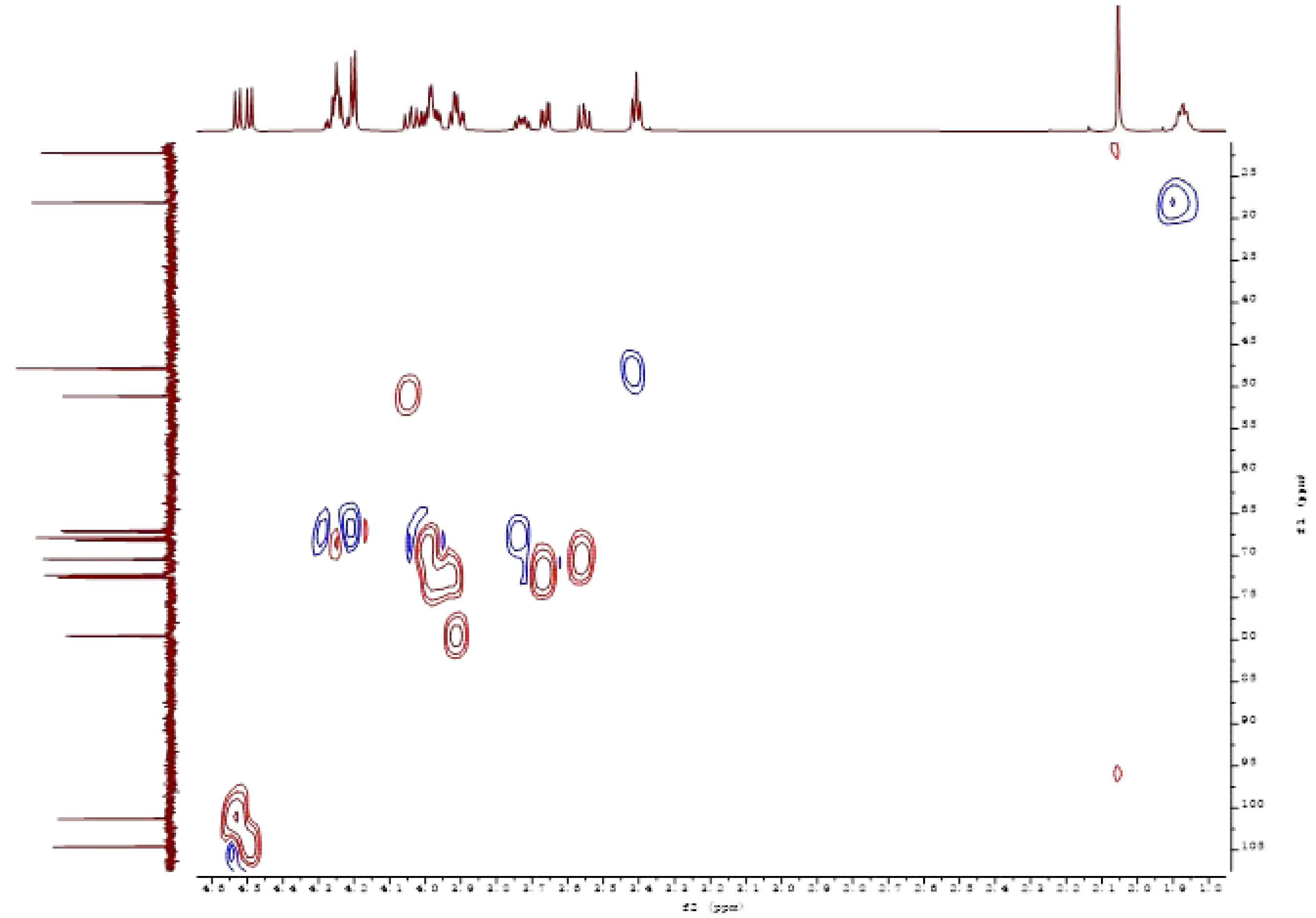


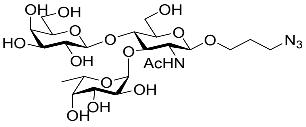
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



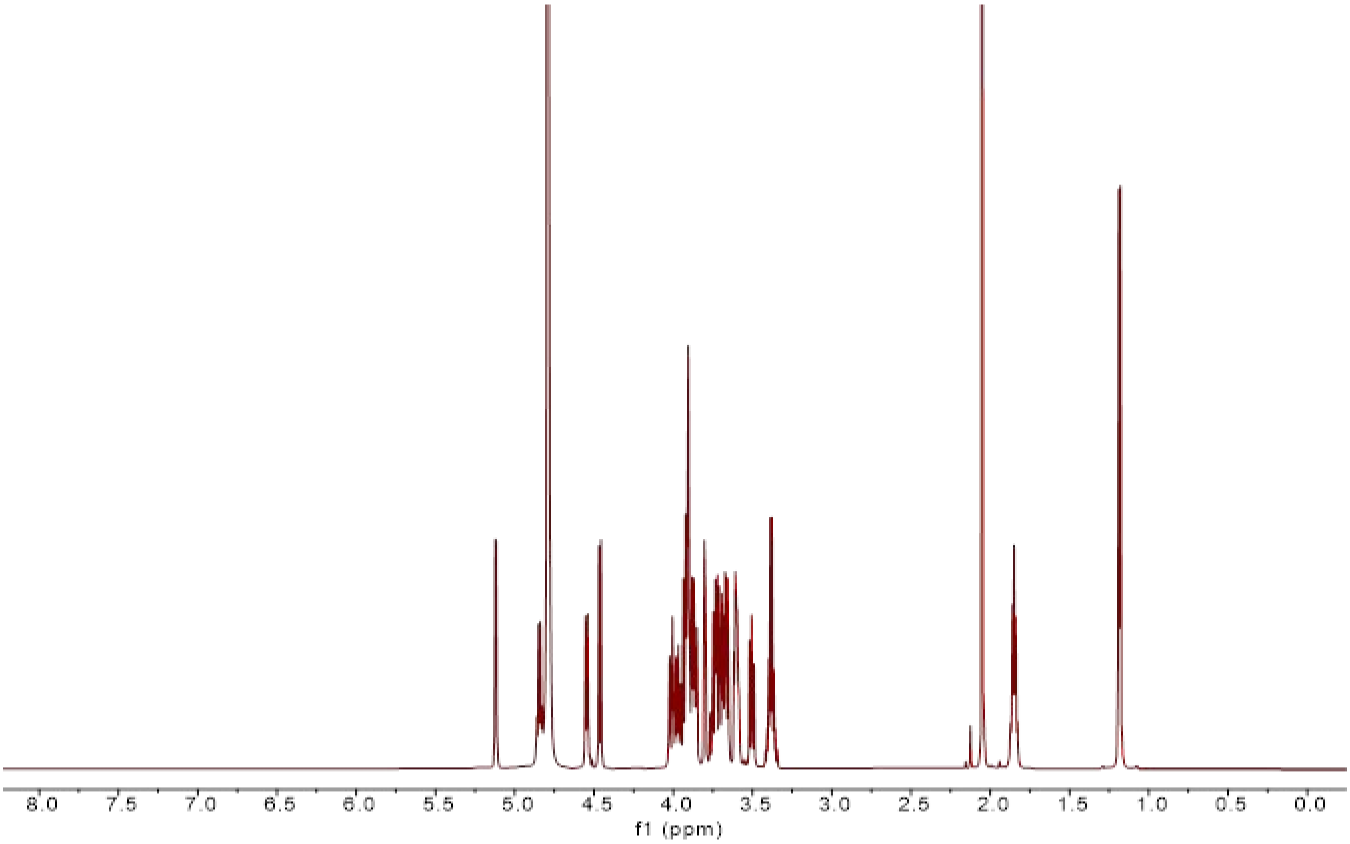
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

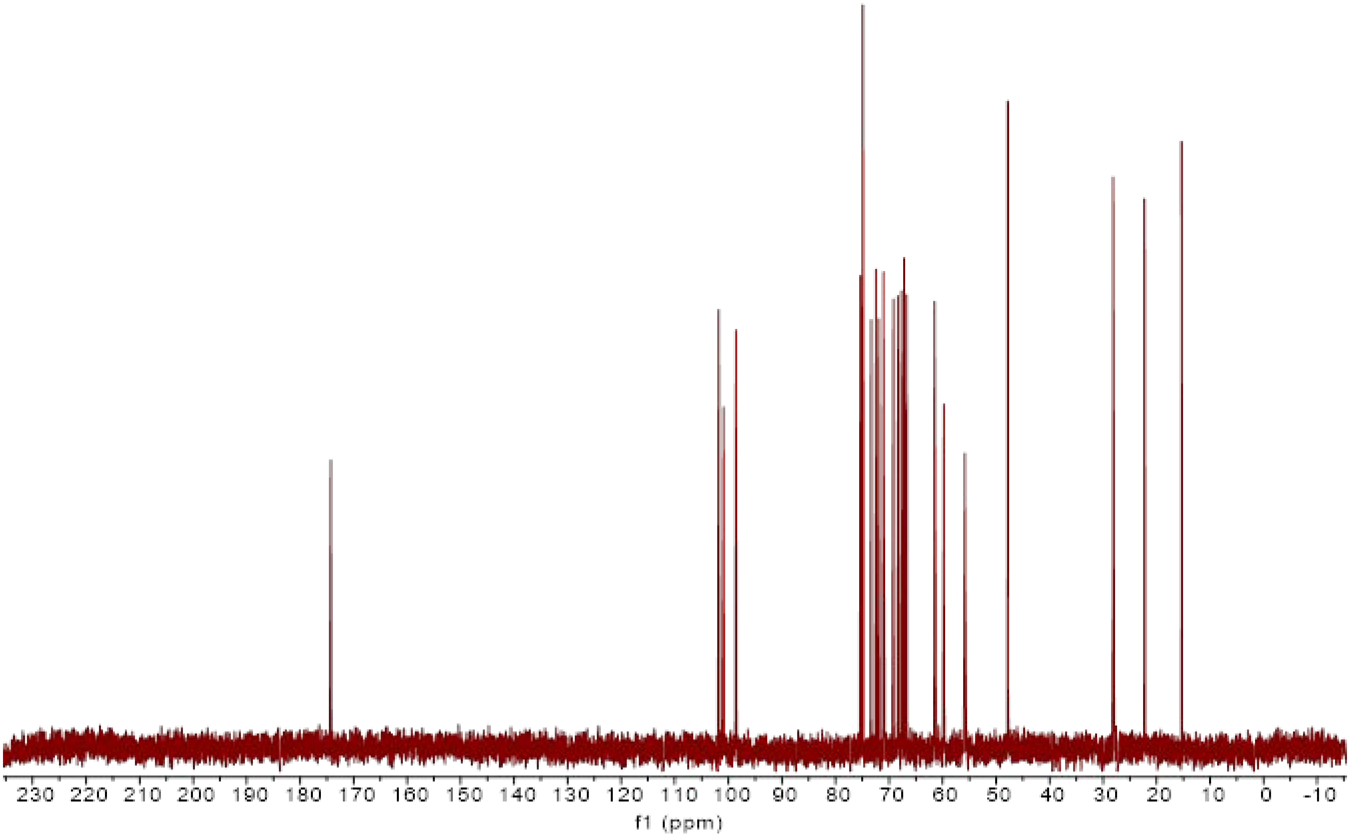

f1 (ppm)
f2 (ppm)

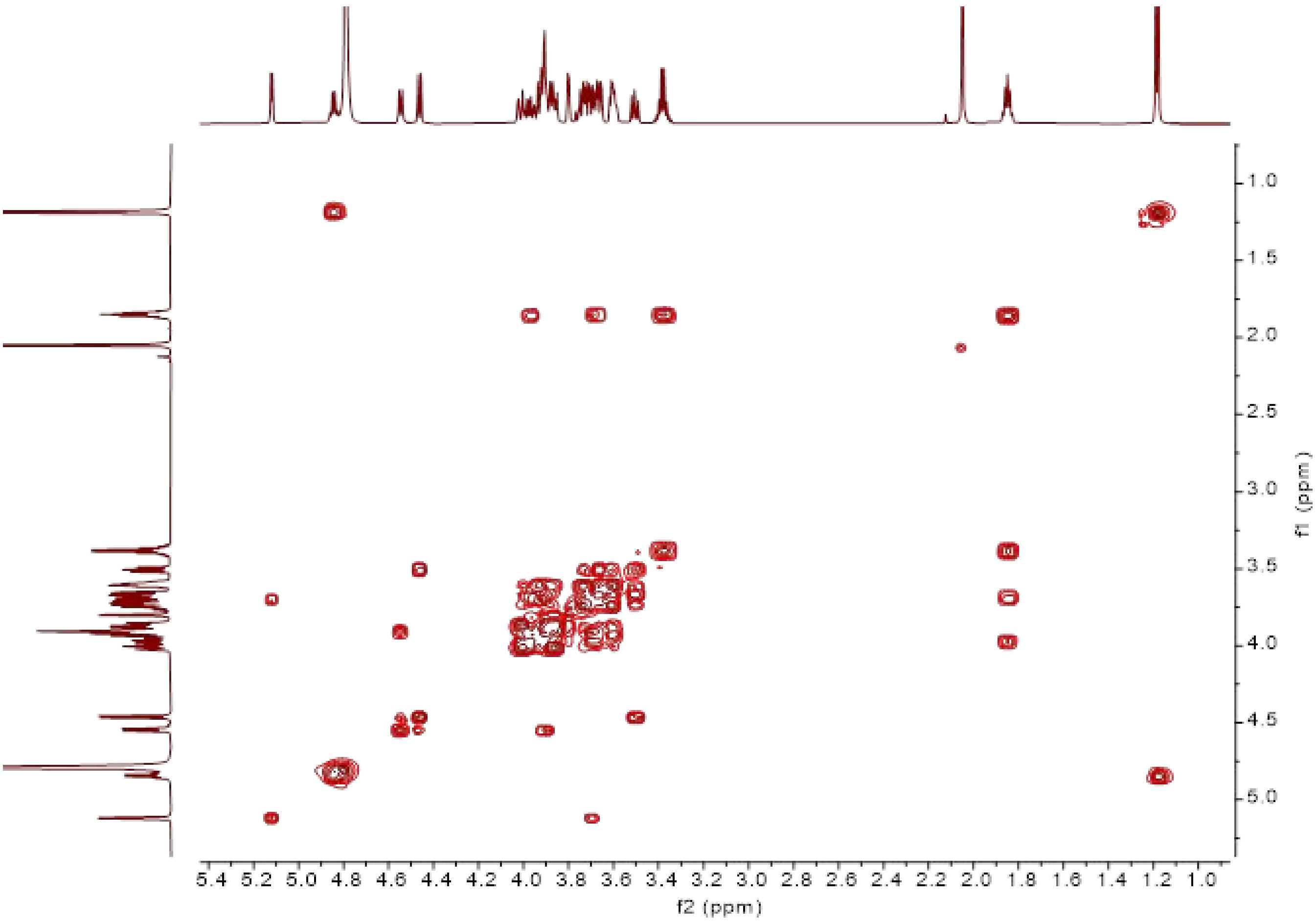

f1 (ppm)
f2 (ppm)

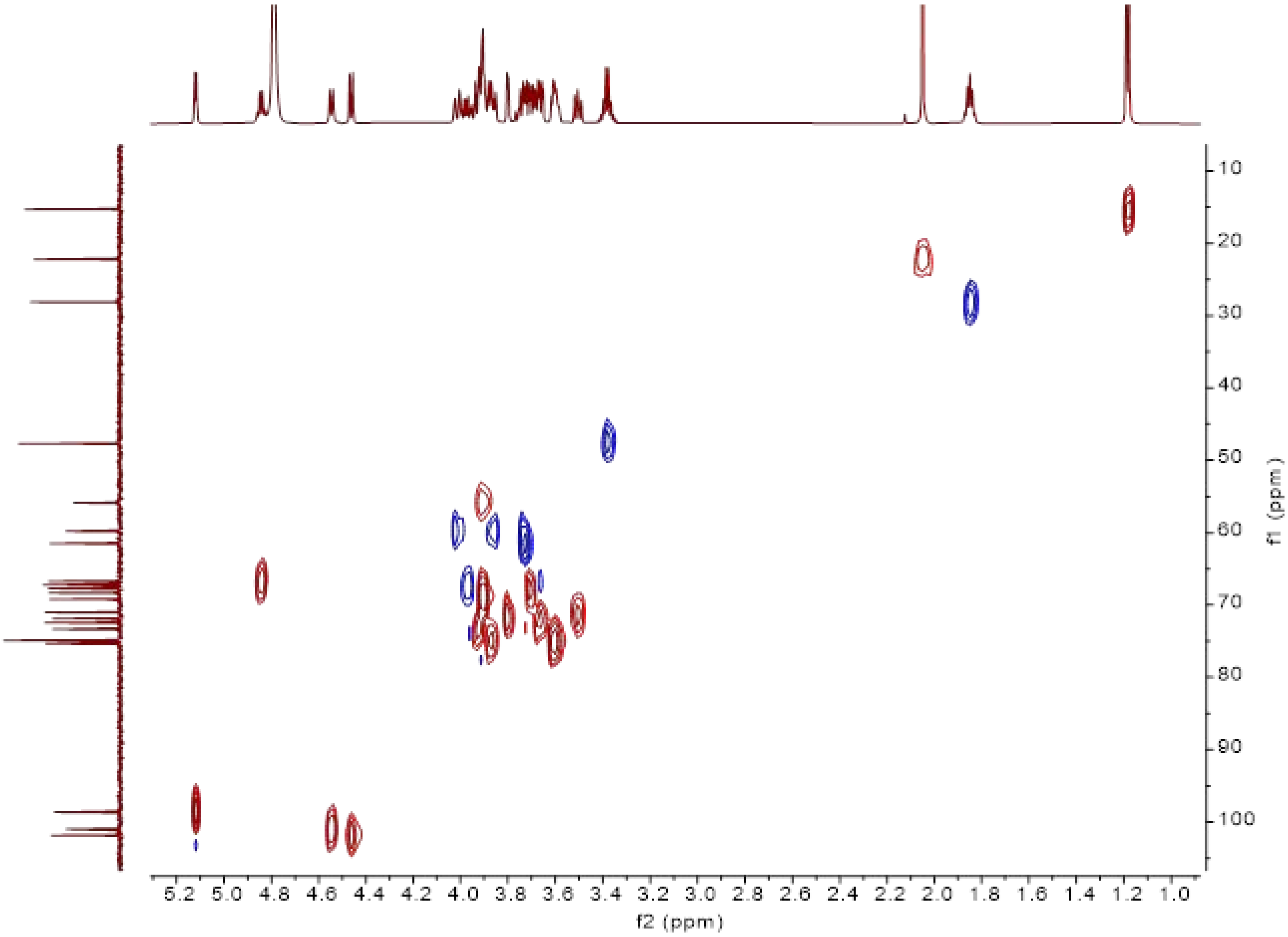


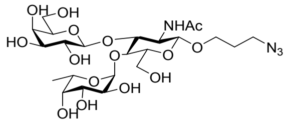
17


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

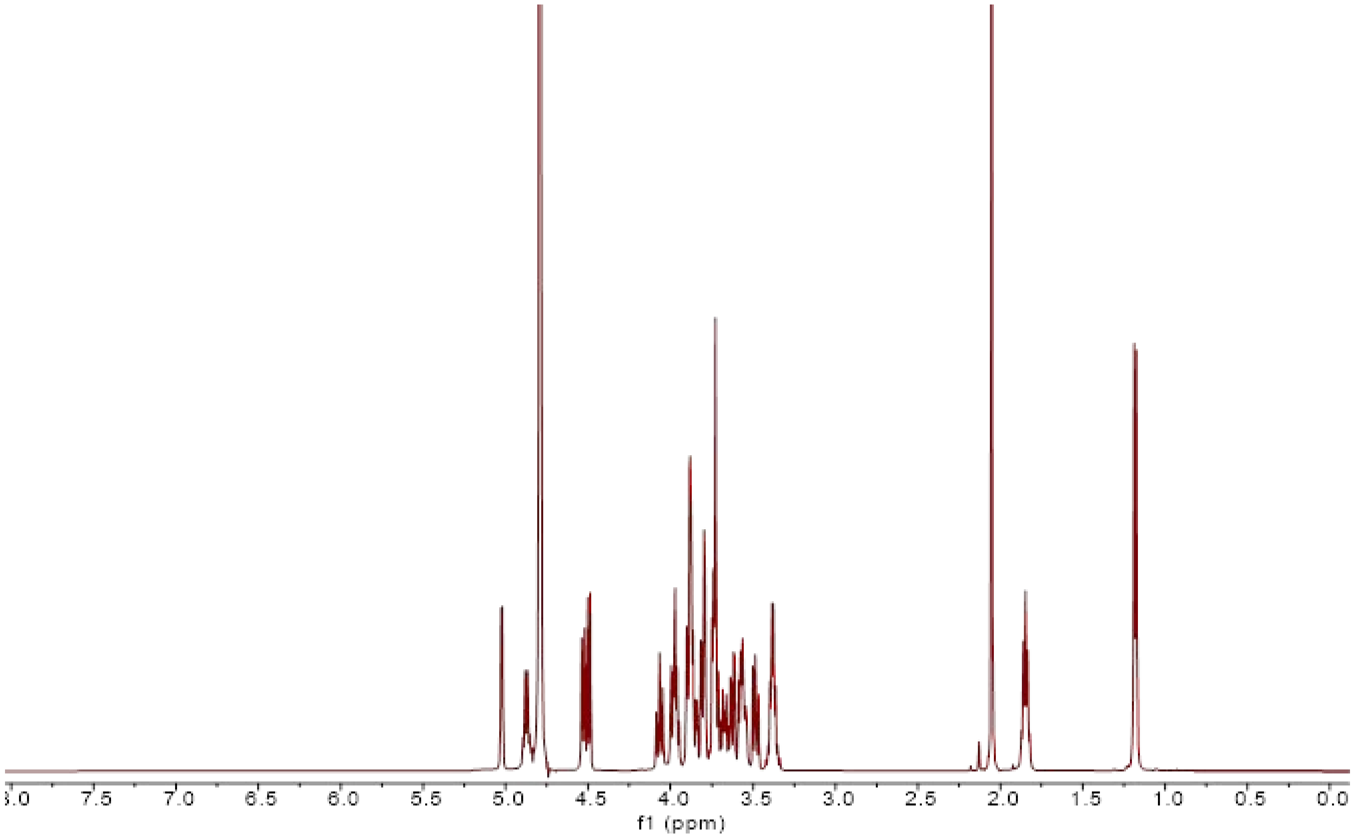

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

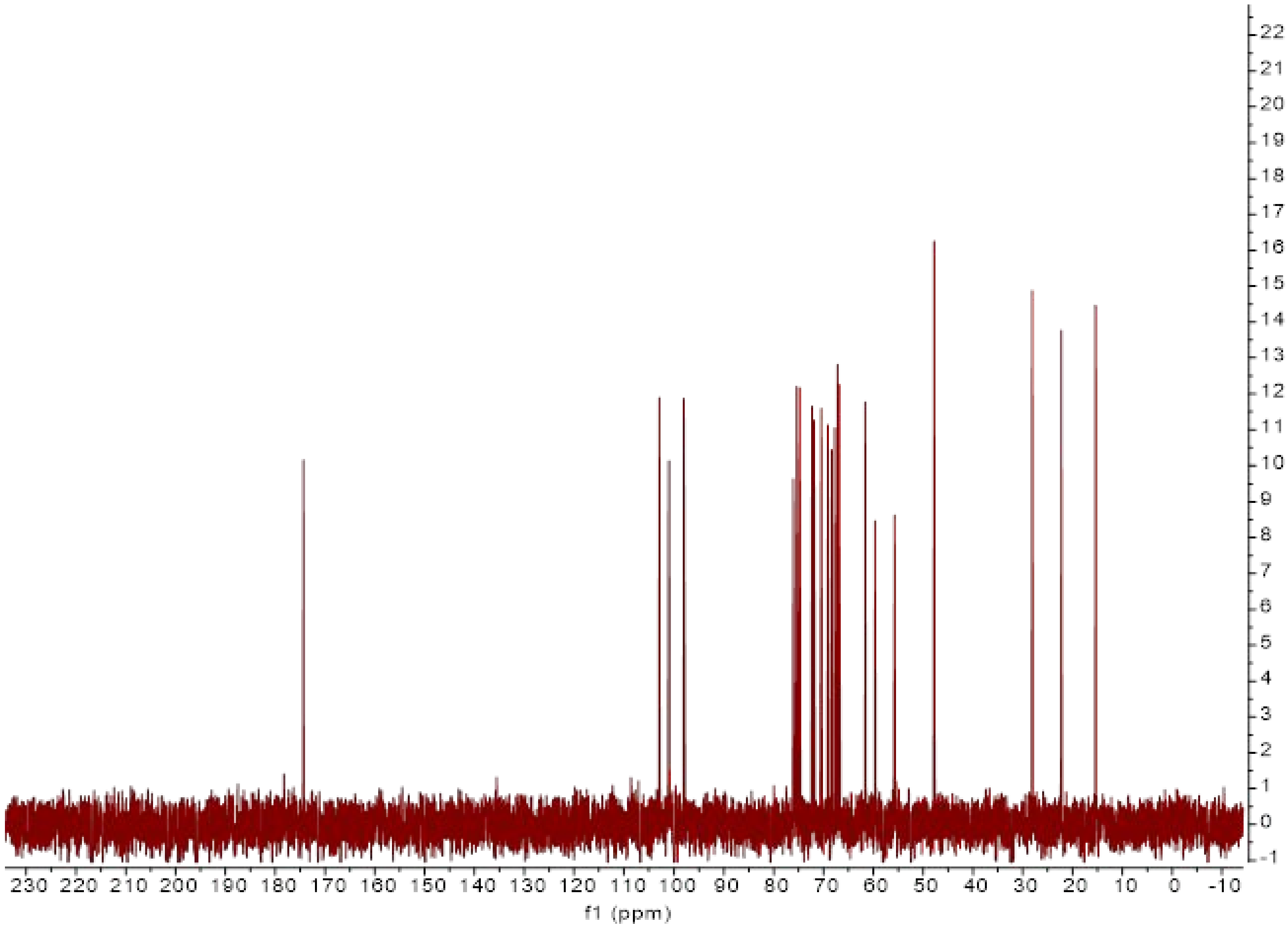

5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

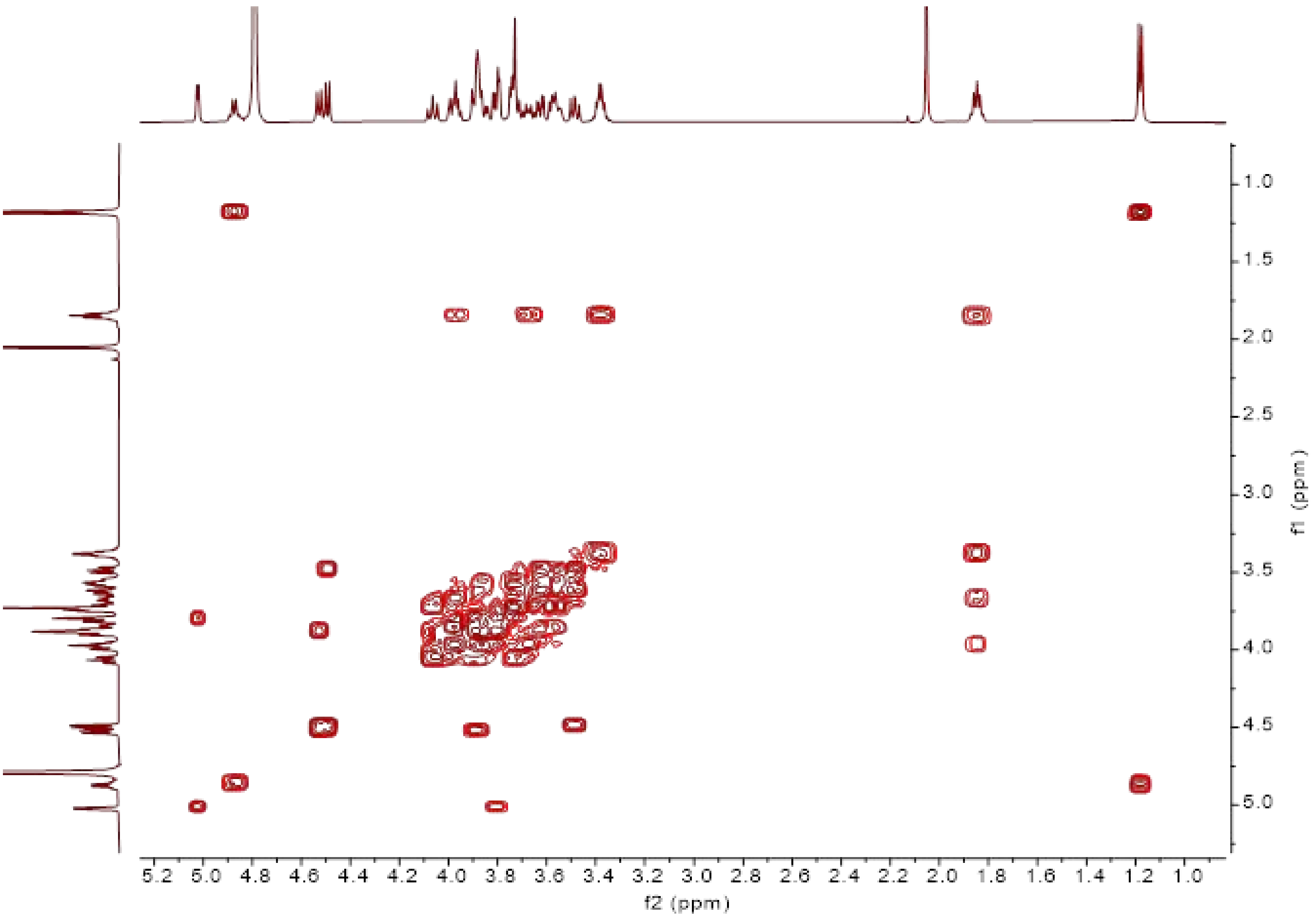

5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
10 20 30 40 50 60 70 80 90 100
f1 (ppm)

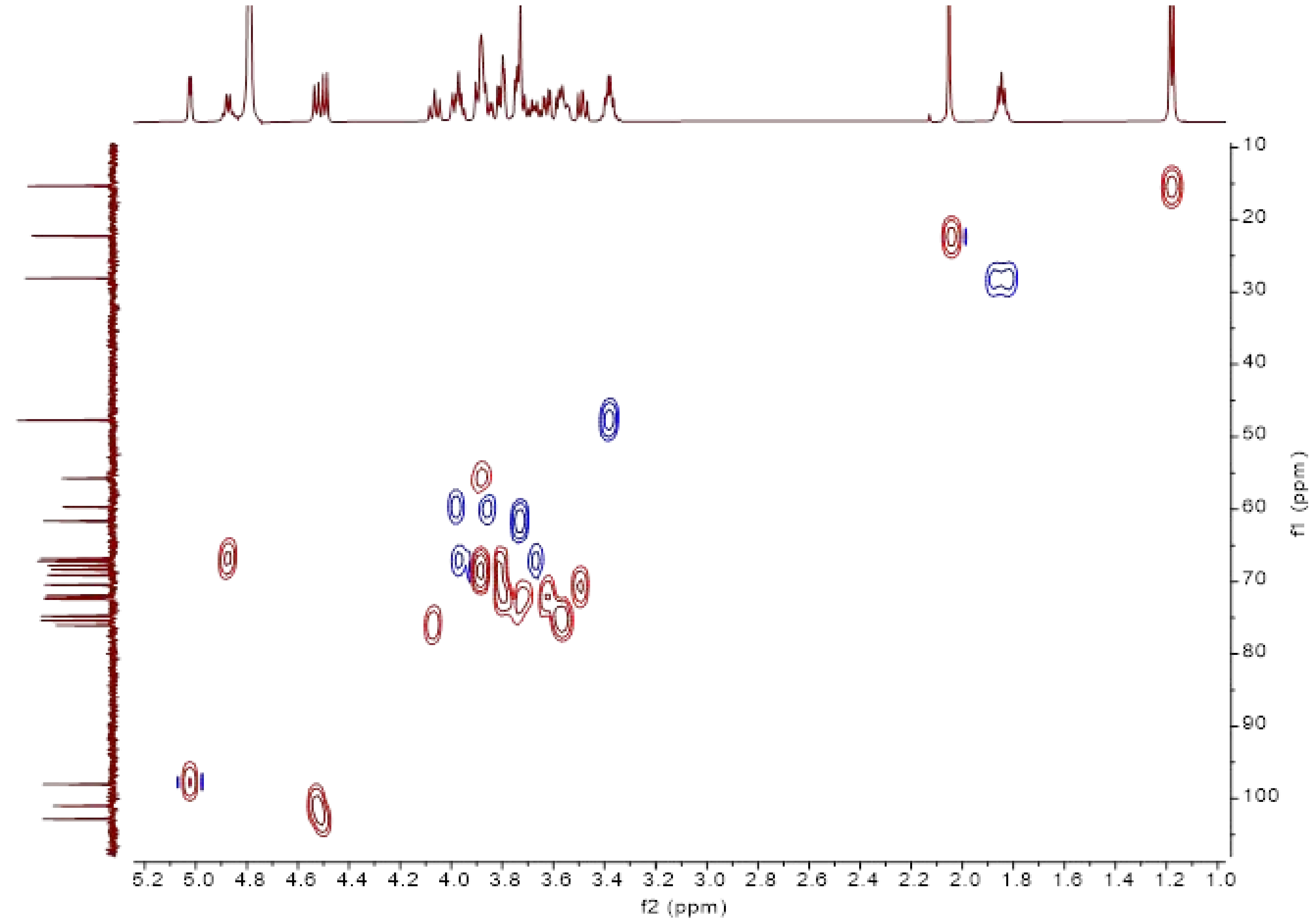

OH
OH
NHAc
HO
O
O
O
N3
OH
O
O
OH
OH
OH
OH

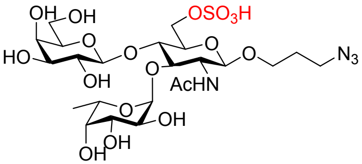
18


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

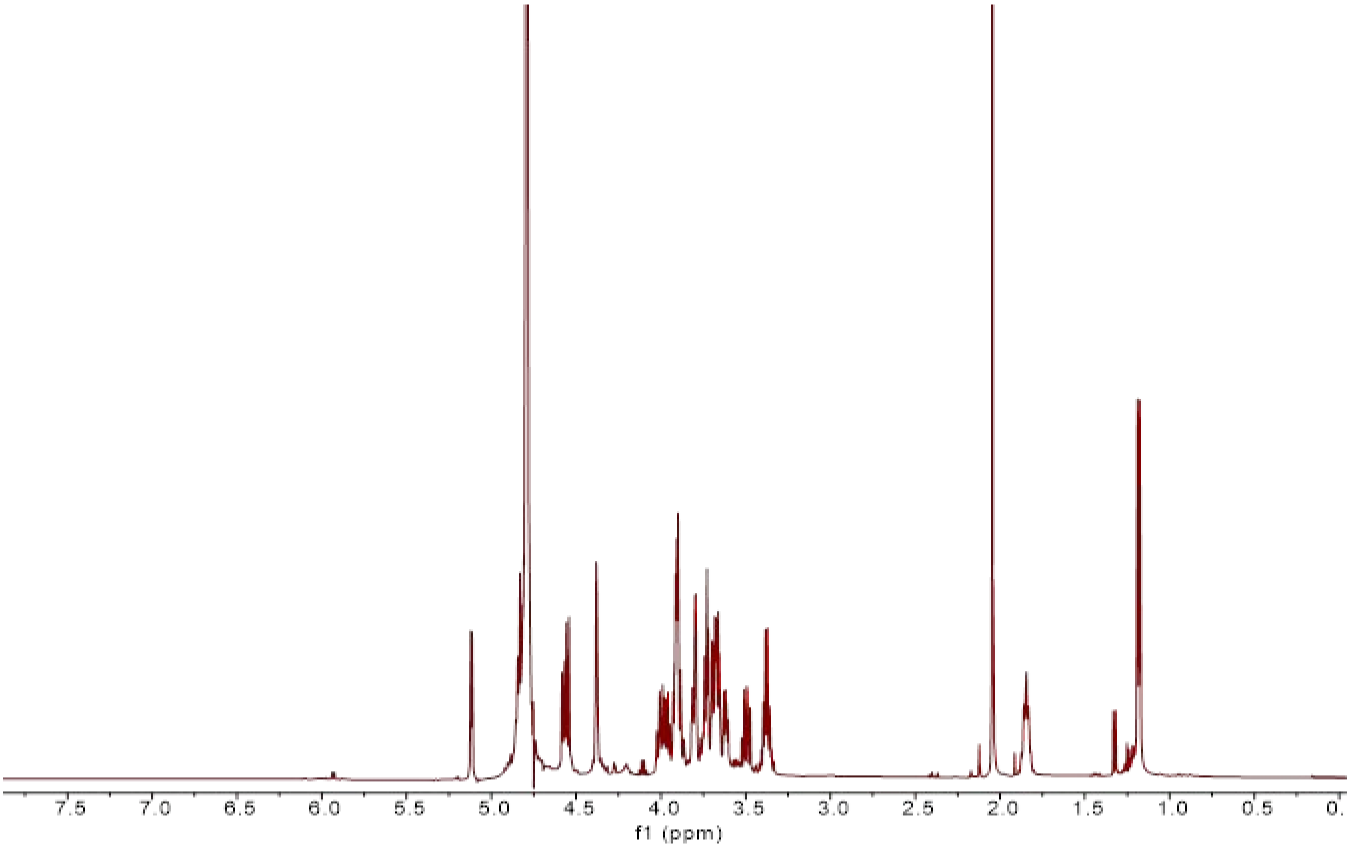

22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

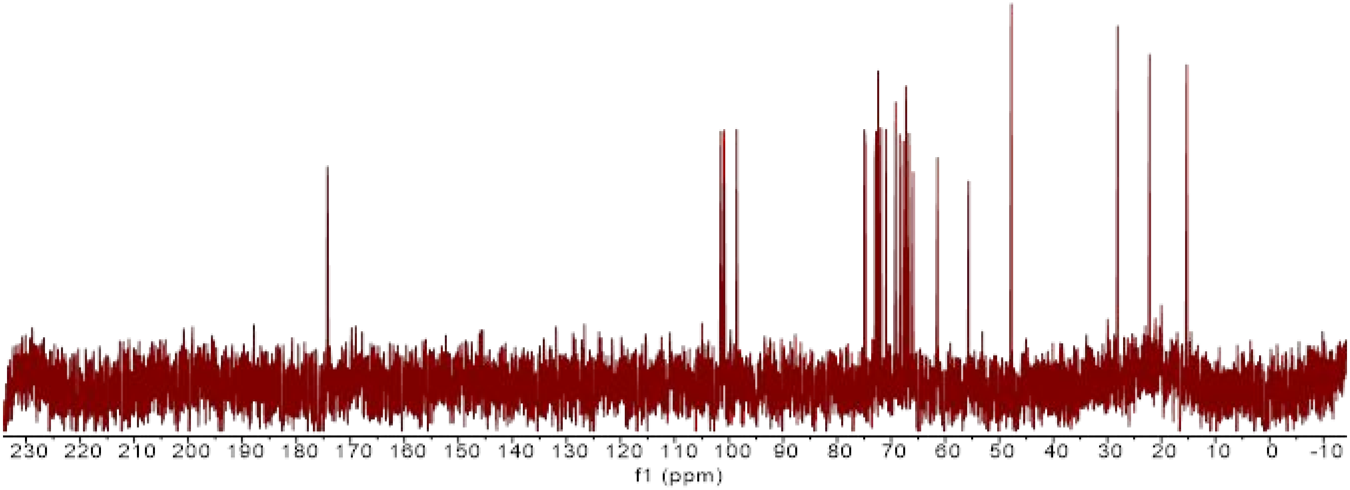

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

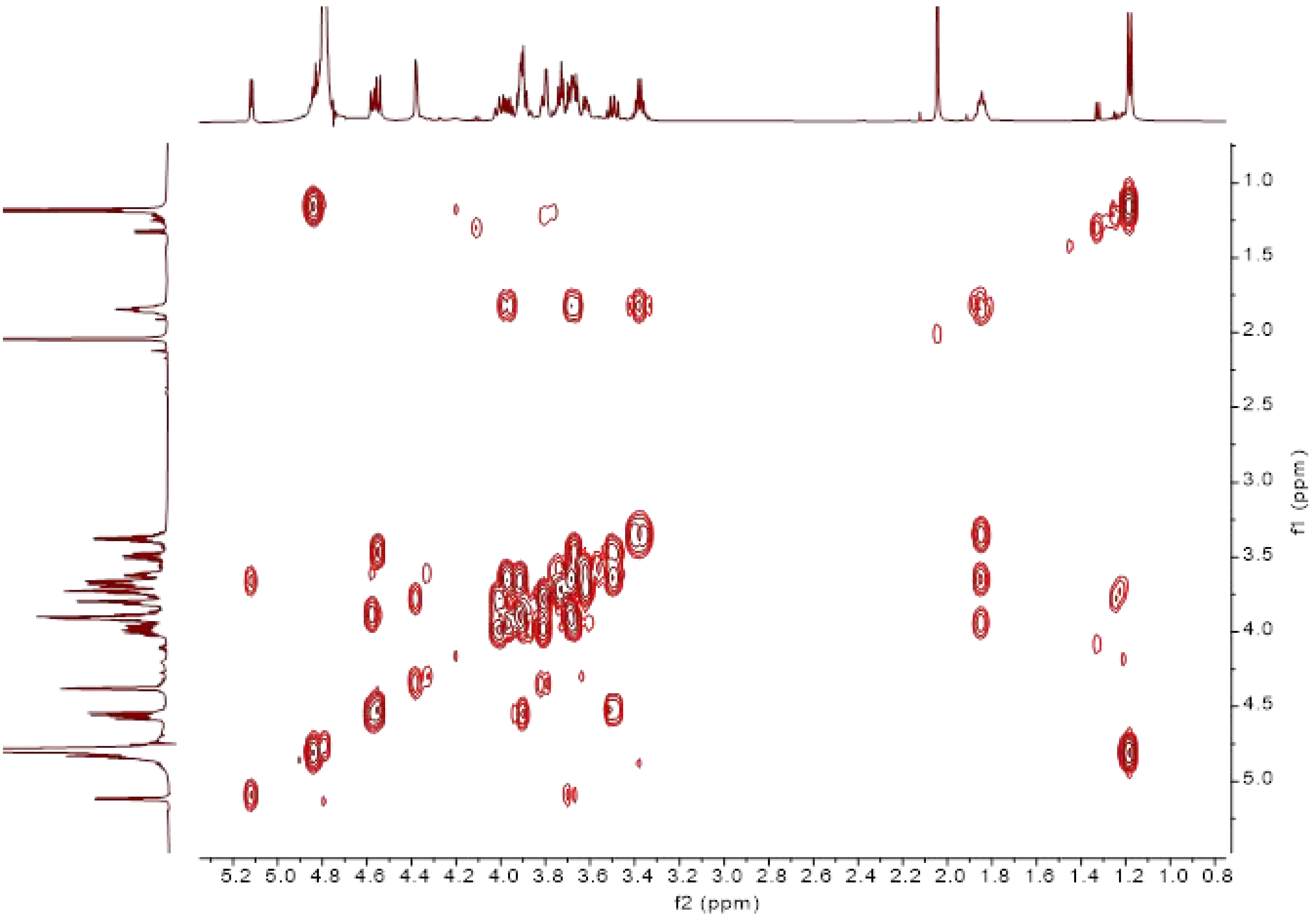

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)

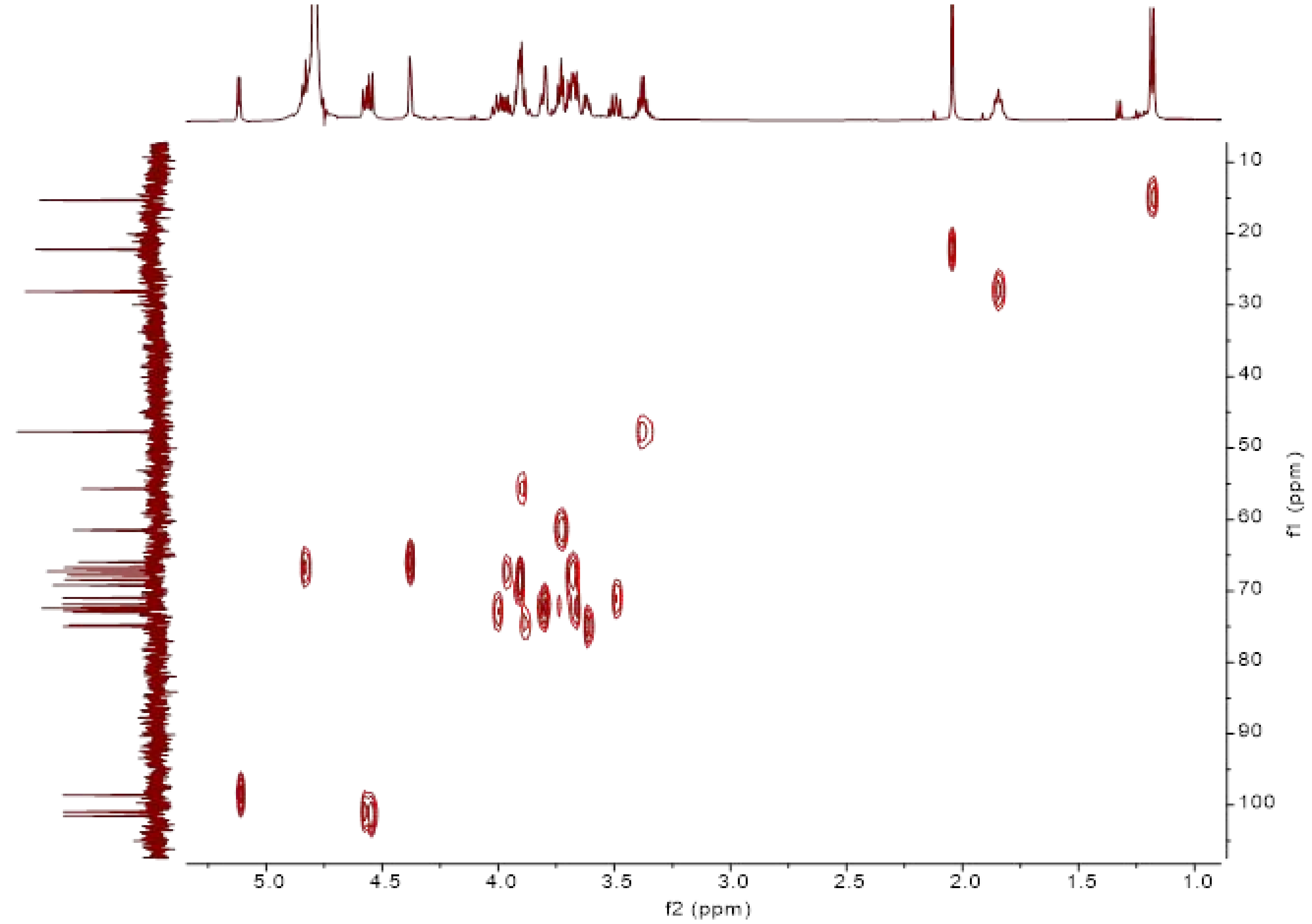

OH
OH
OSO3H
O
O
O
O
HO
N3
OH
AcHN
O
O
OH
OH
OH

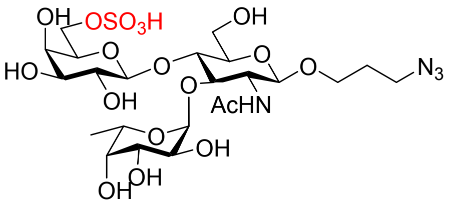
19


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.
f1 (ppm)

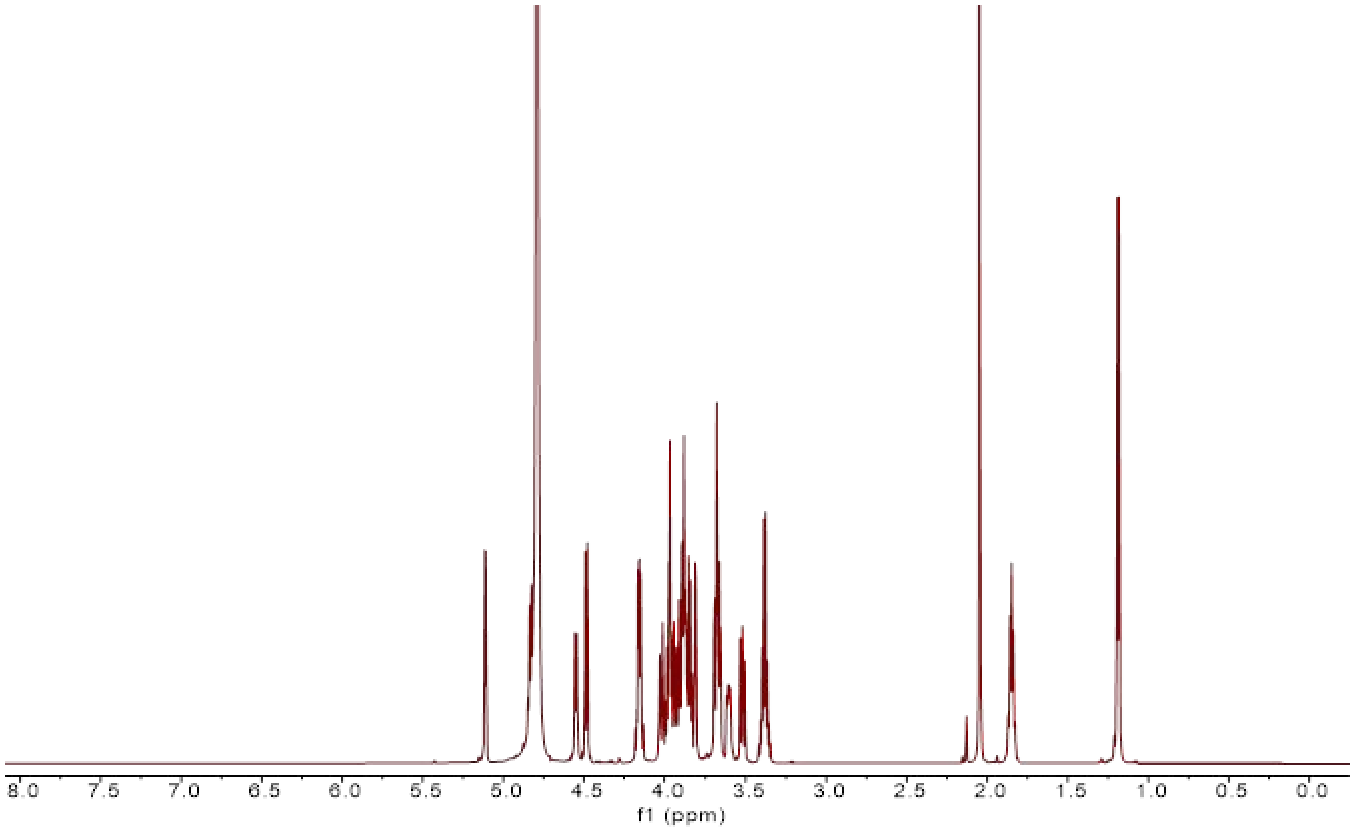

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

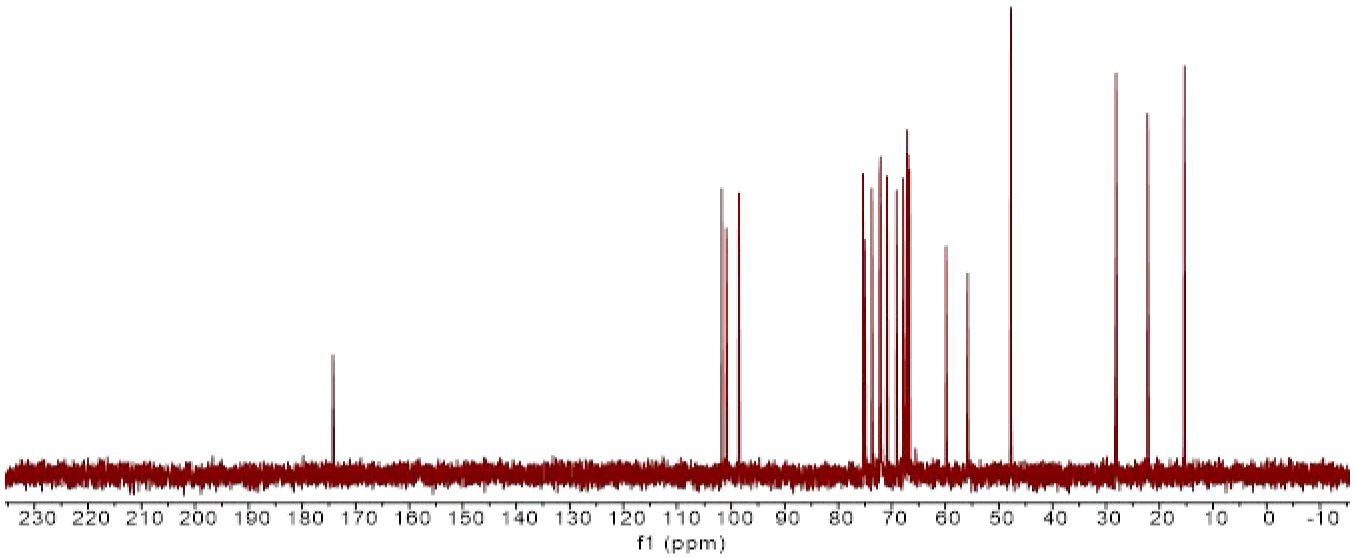

1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)

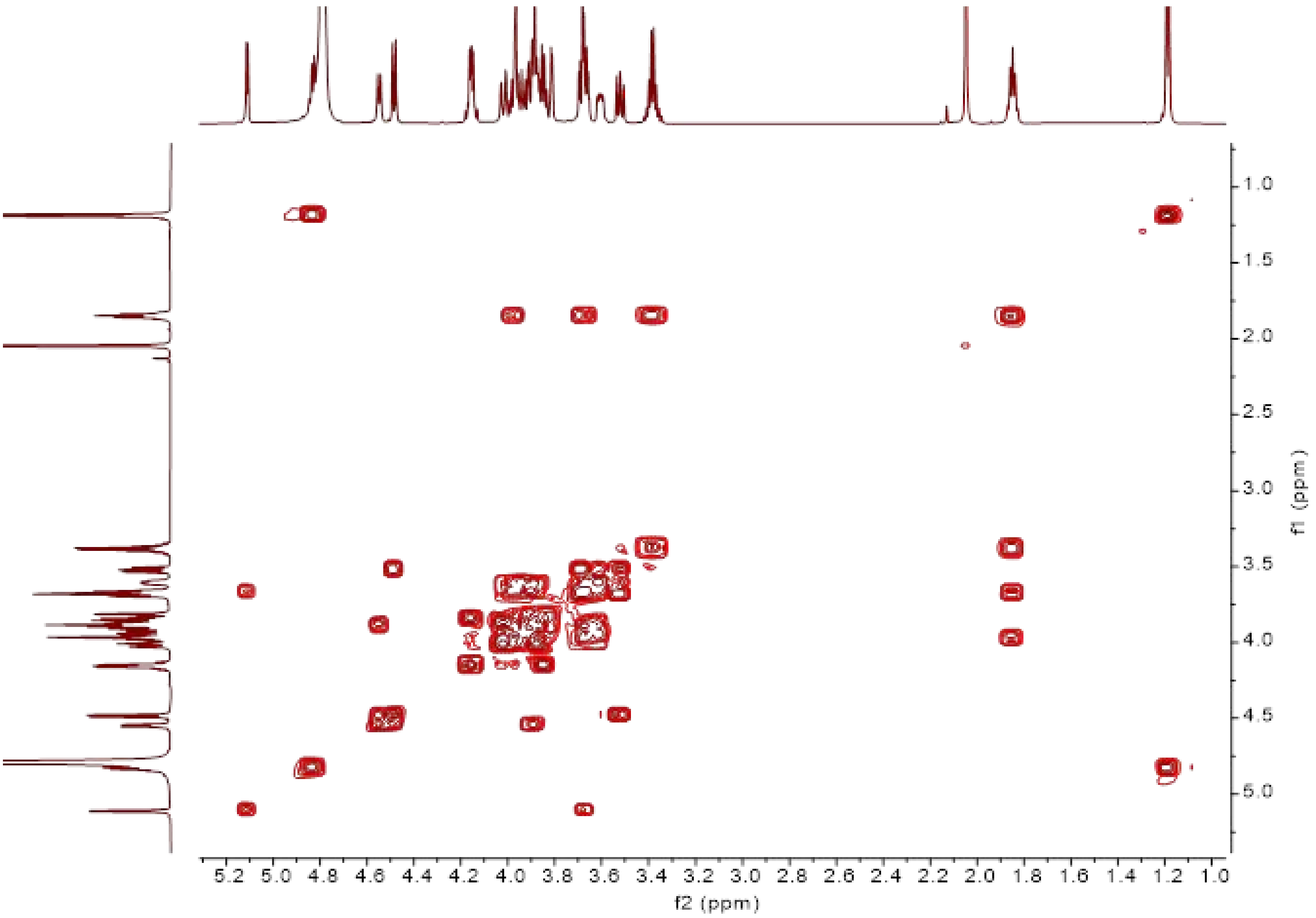

10
20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)

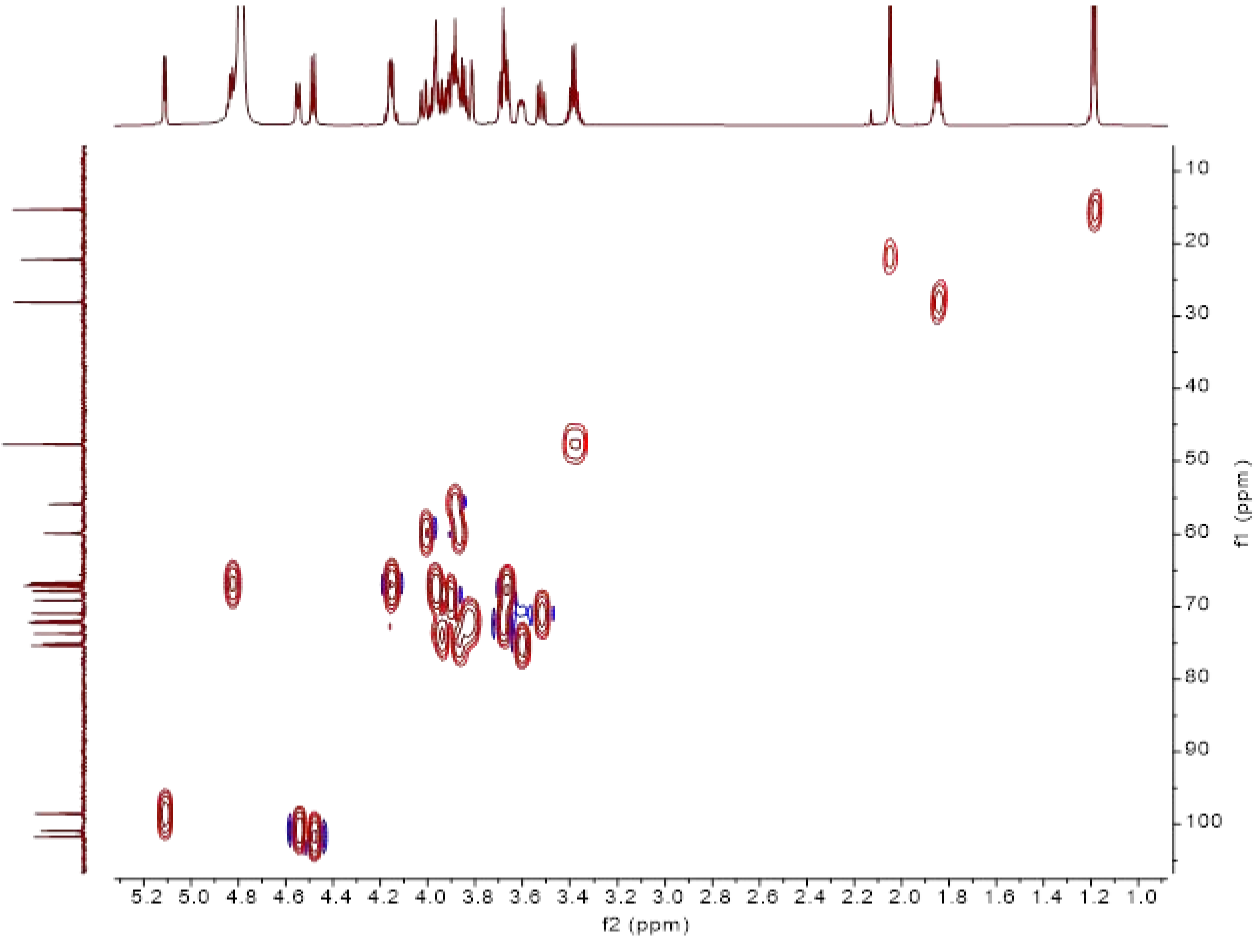

OH
OSO3H
OH
HO
O
O
O
O
N3
OH
AcHN
O
O
OH
OH
OH

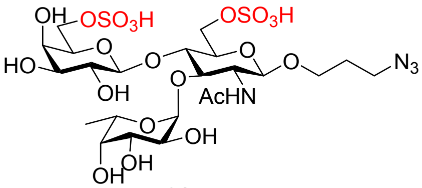
20


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

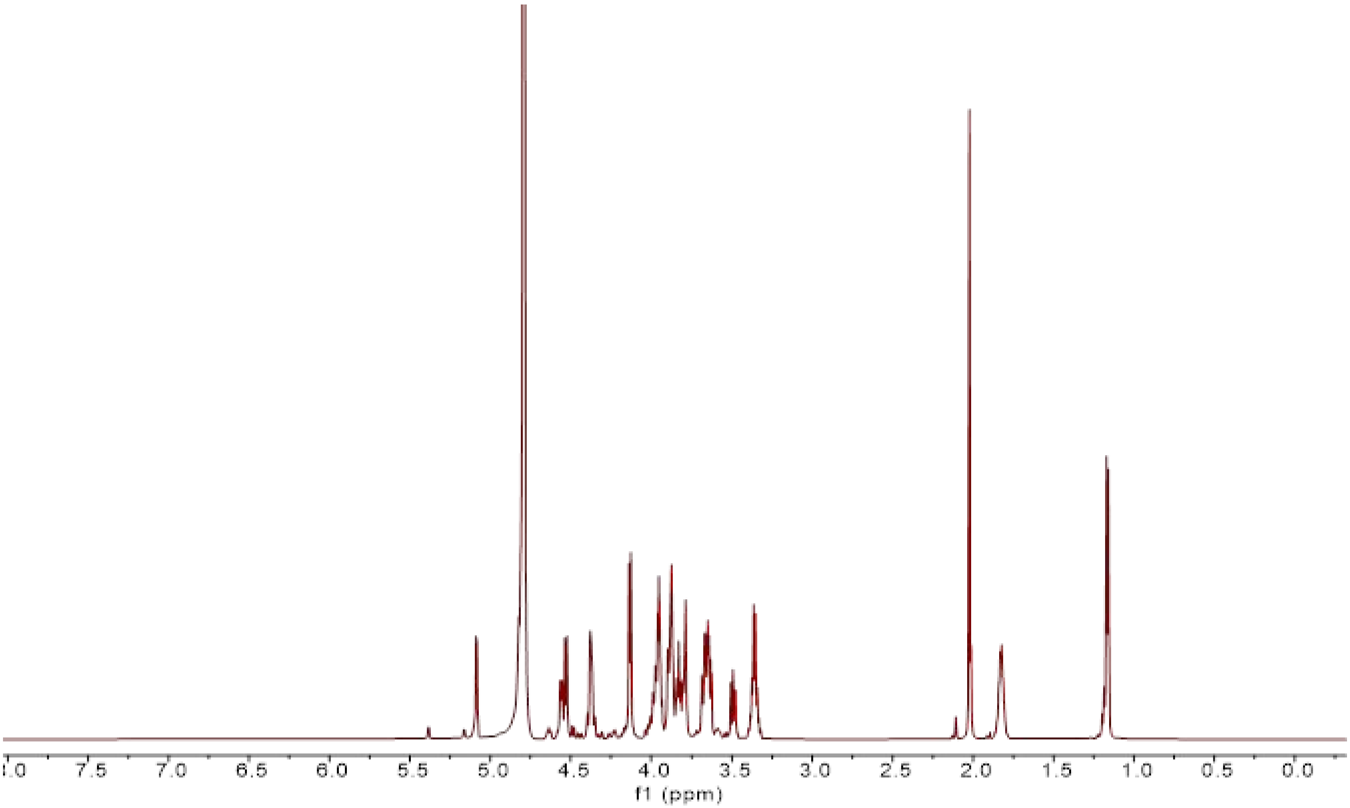

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

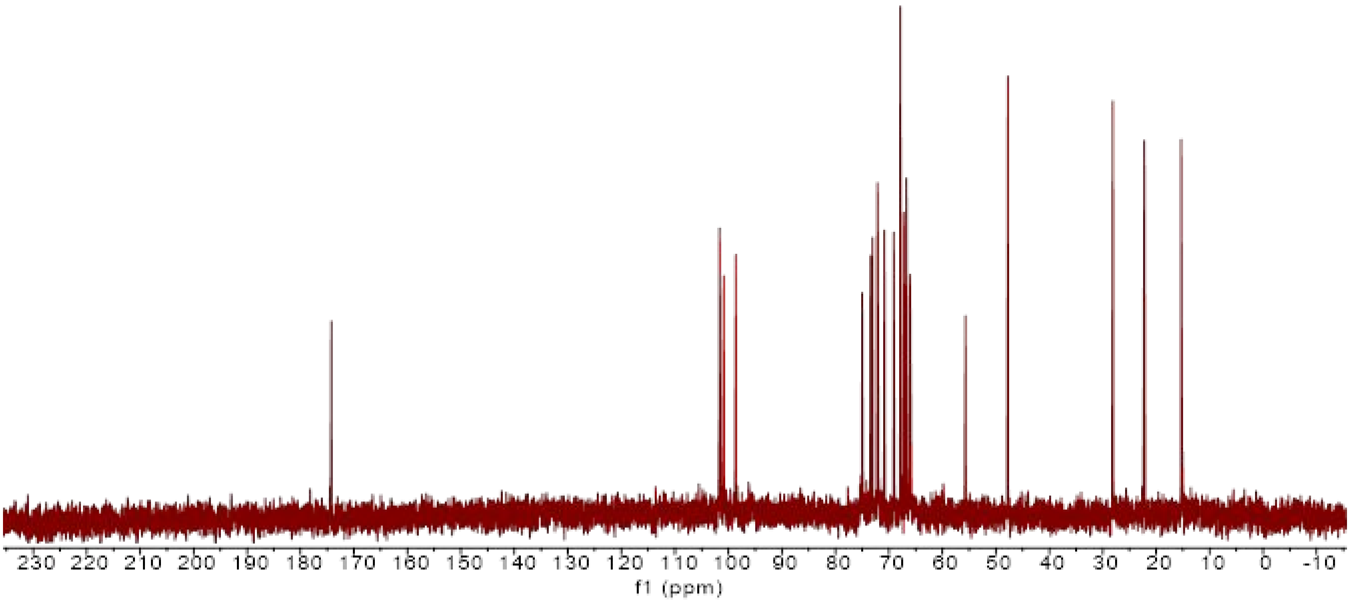

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

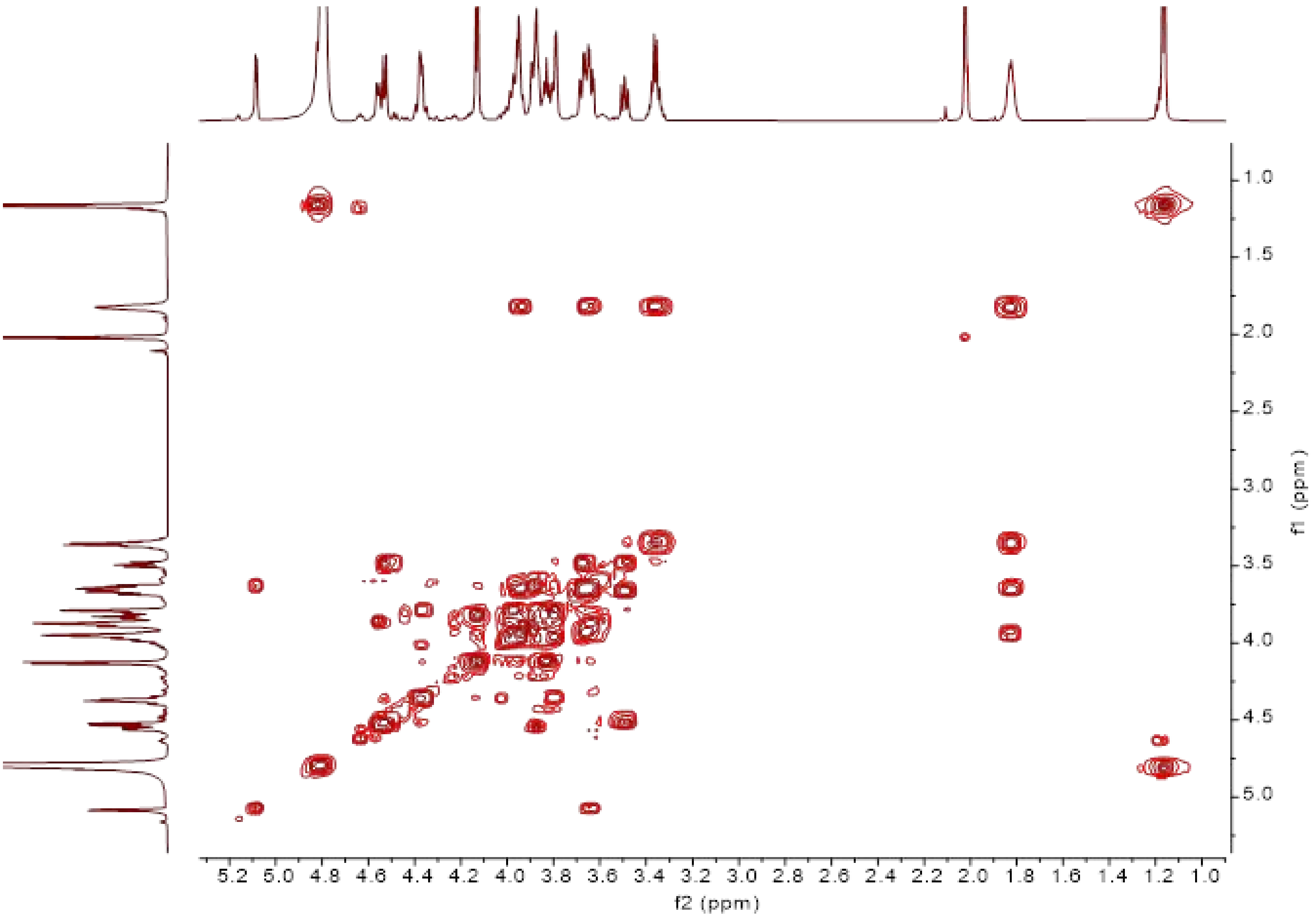

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)


OH
OSO3H
OSO3H
HO
O
O
O
O
N3
OH
AcHN
O
O
OH
OH
OH

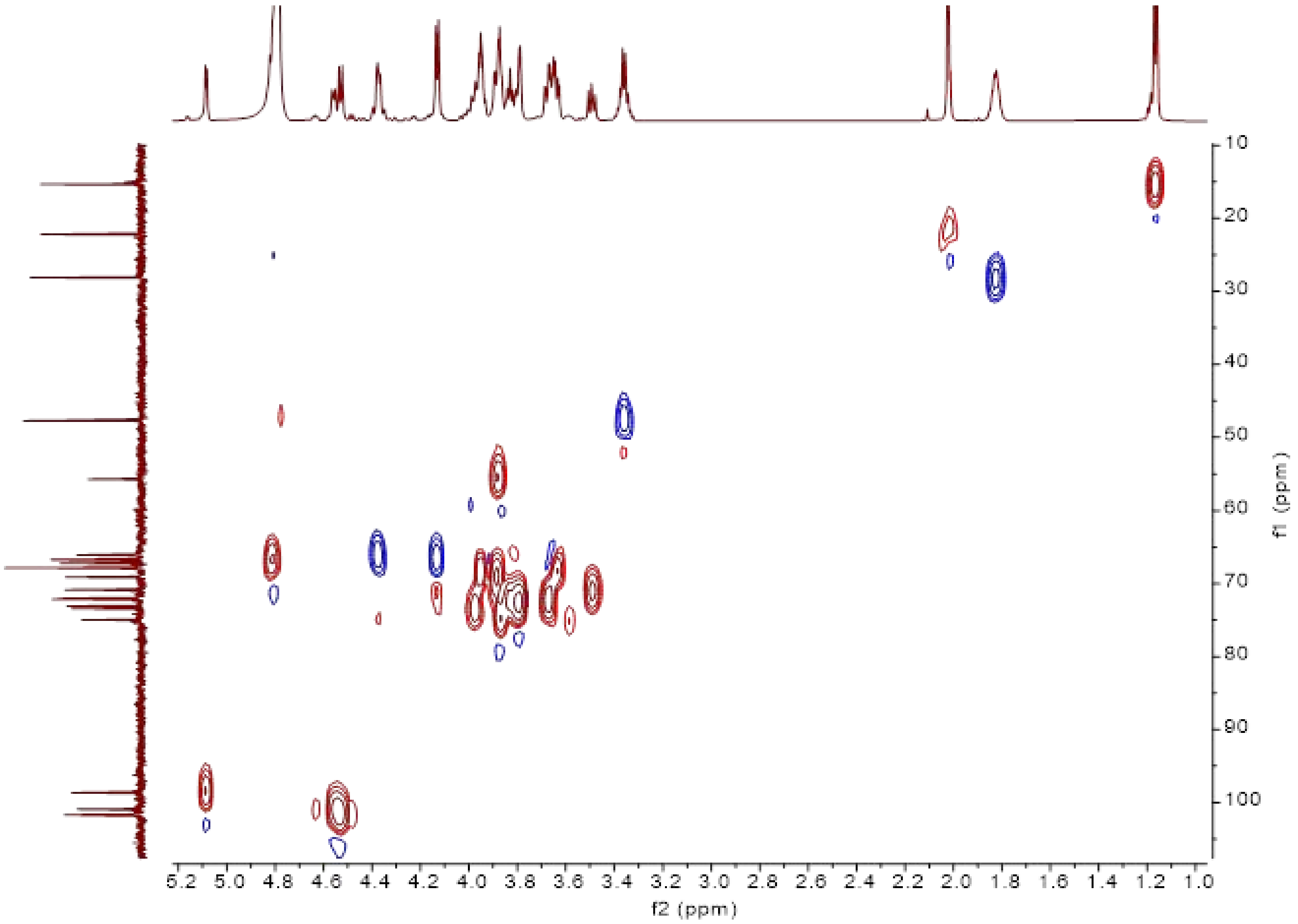
21


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

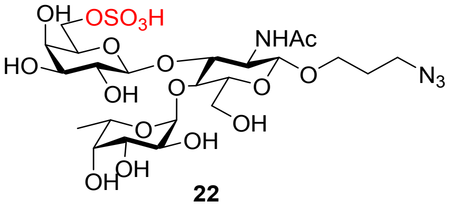

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



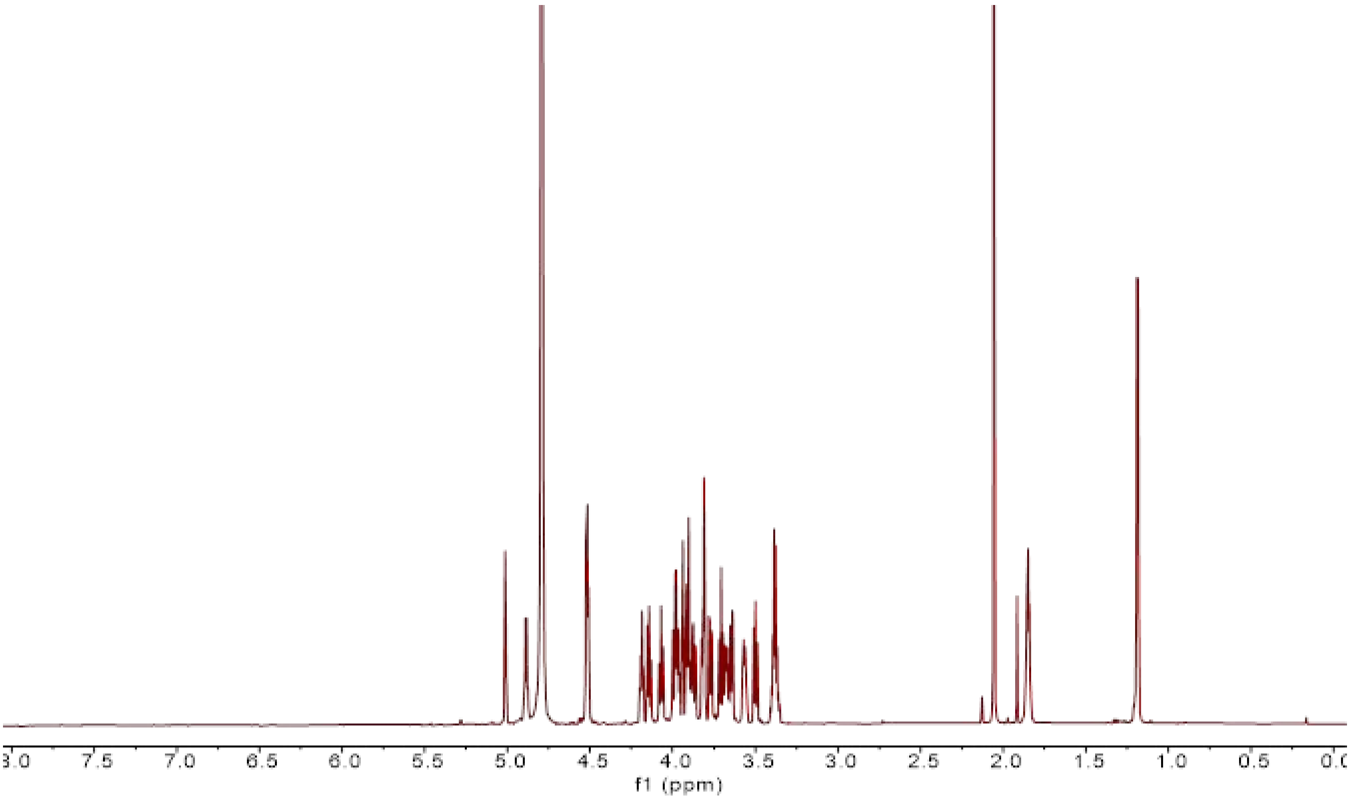
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

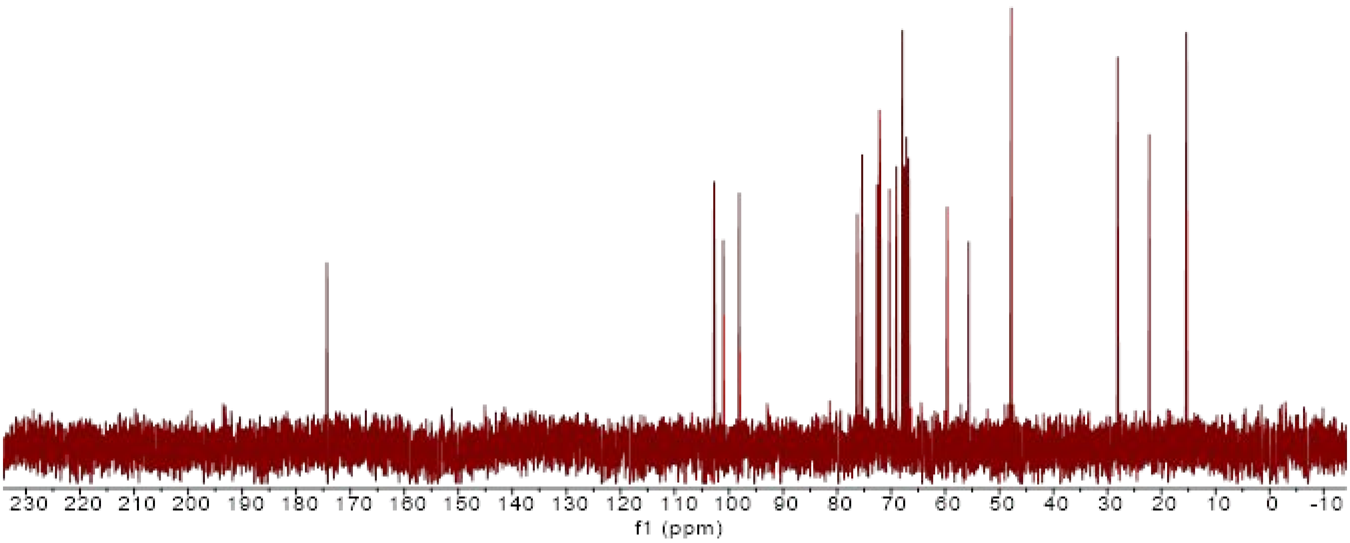


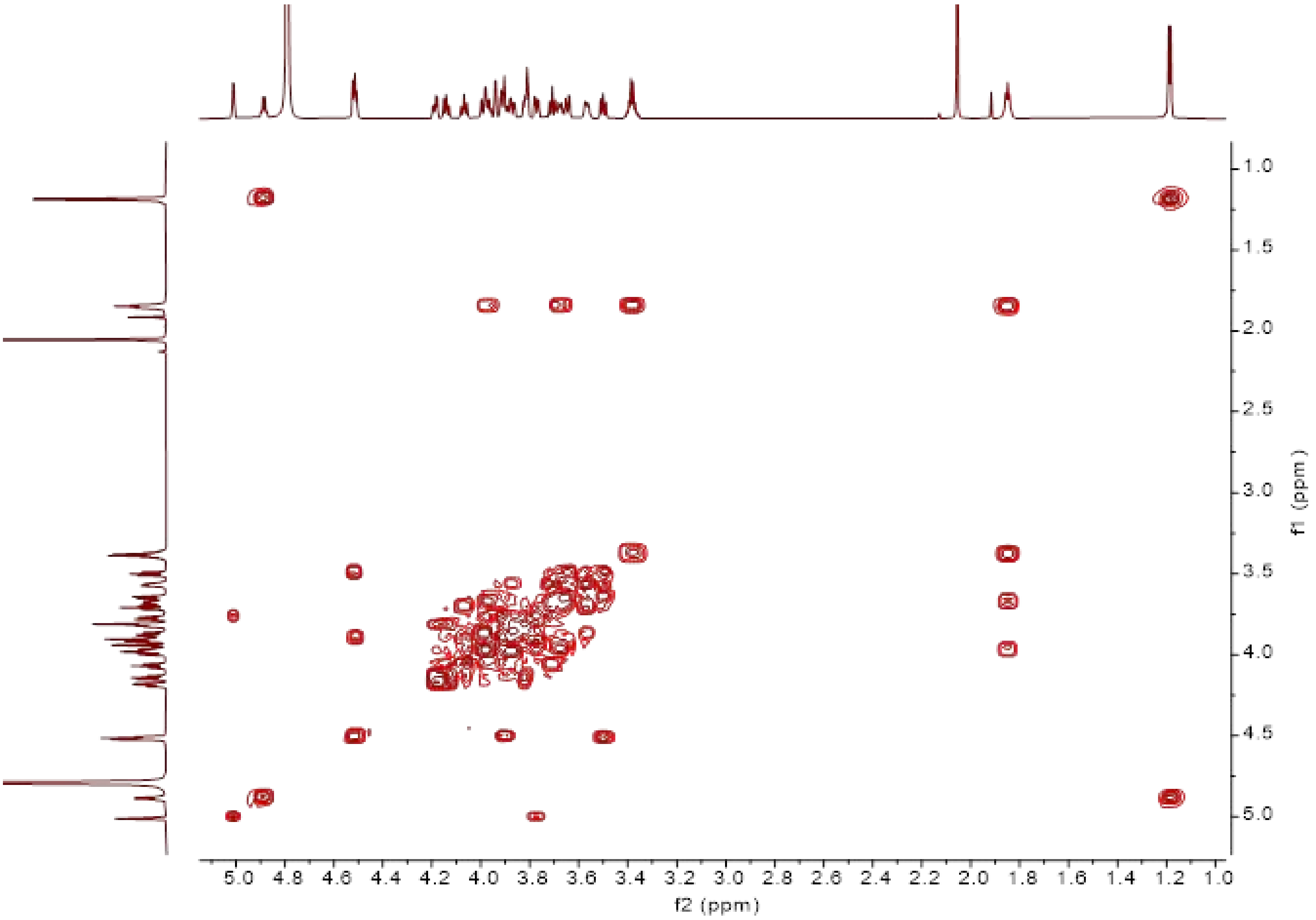
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
10 20 30 40 50 60 70 80 90 100
f1 (ppm)

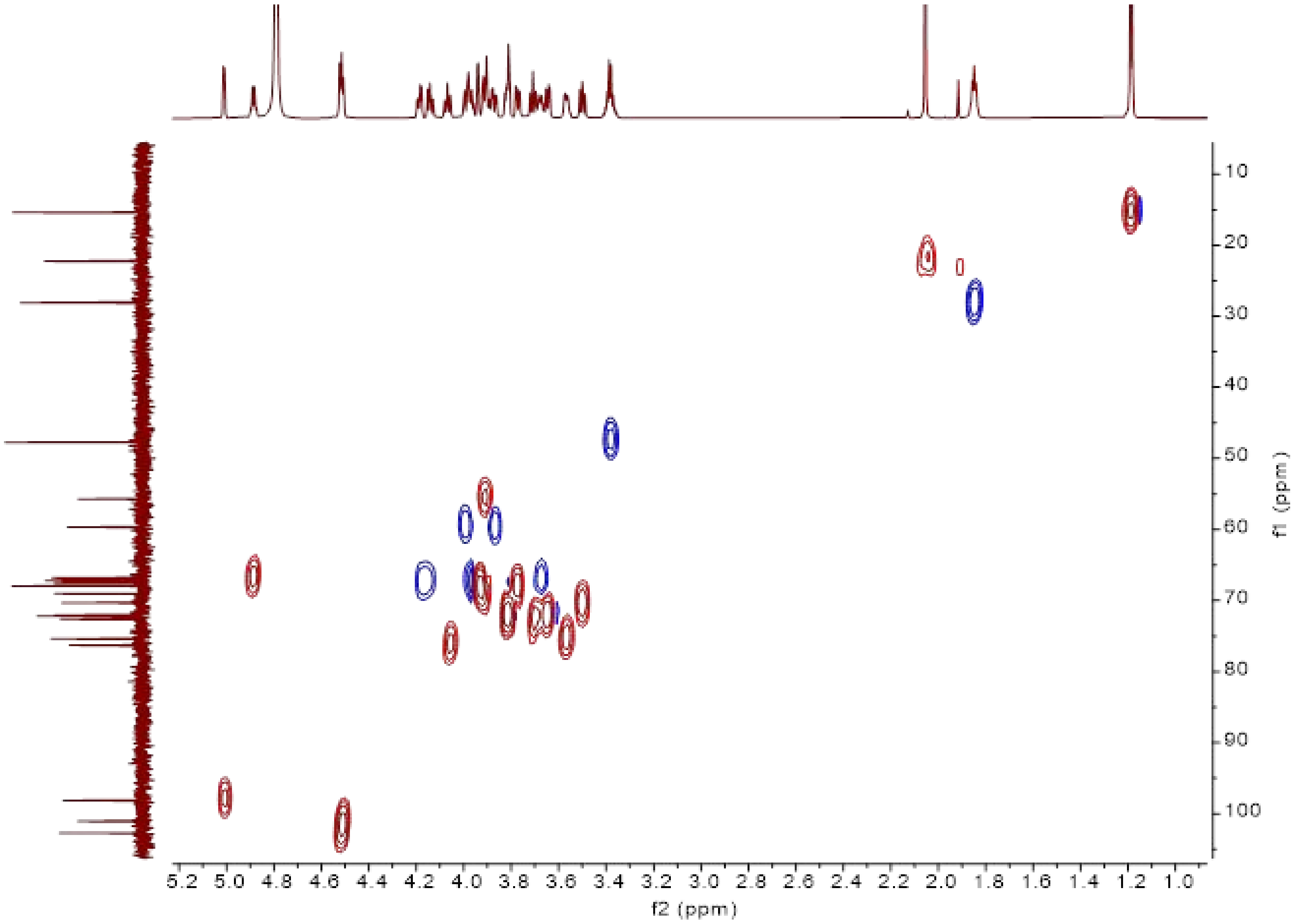

OH
OSO3H
NHAc
HO
O
OH
O
O
O
N3
OH
OH
OH
OH

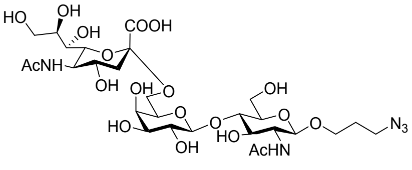
22


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

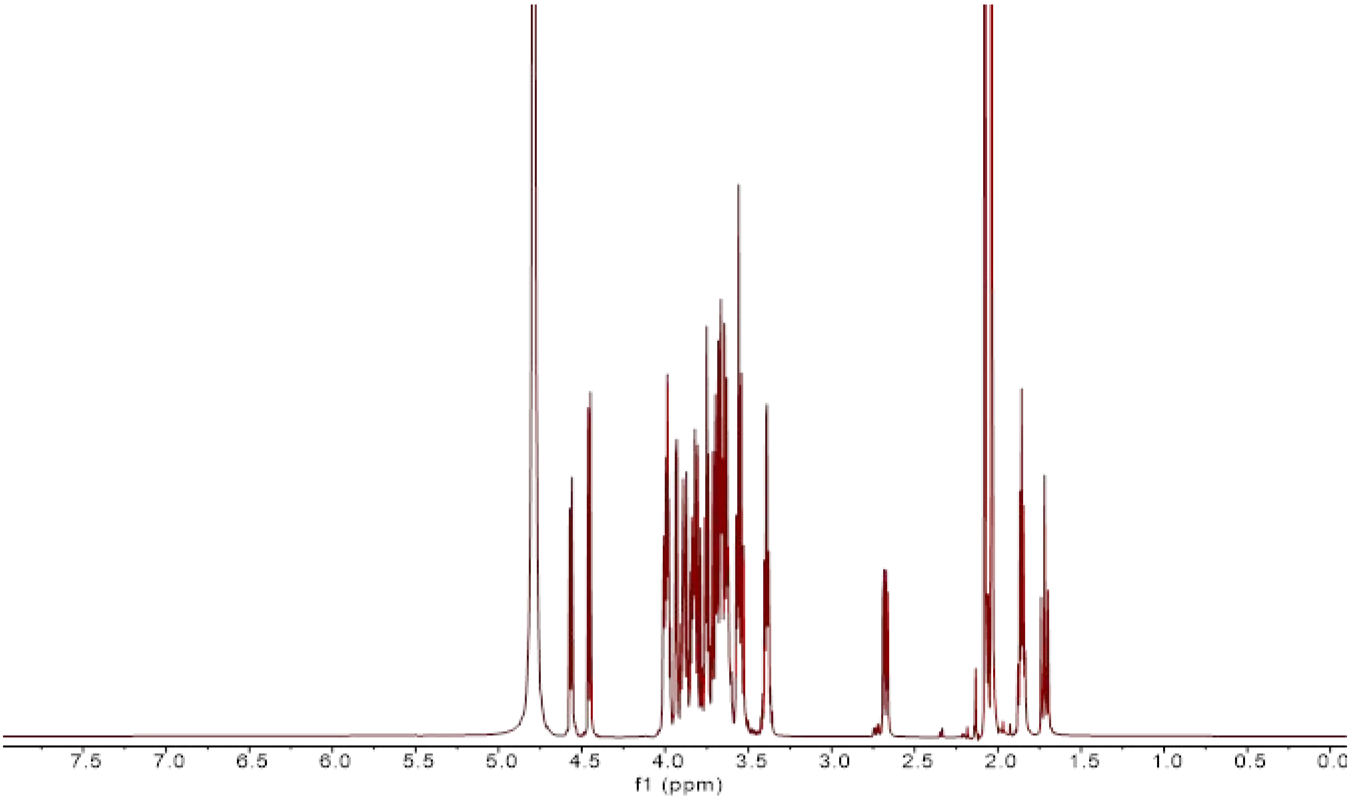

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

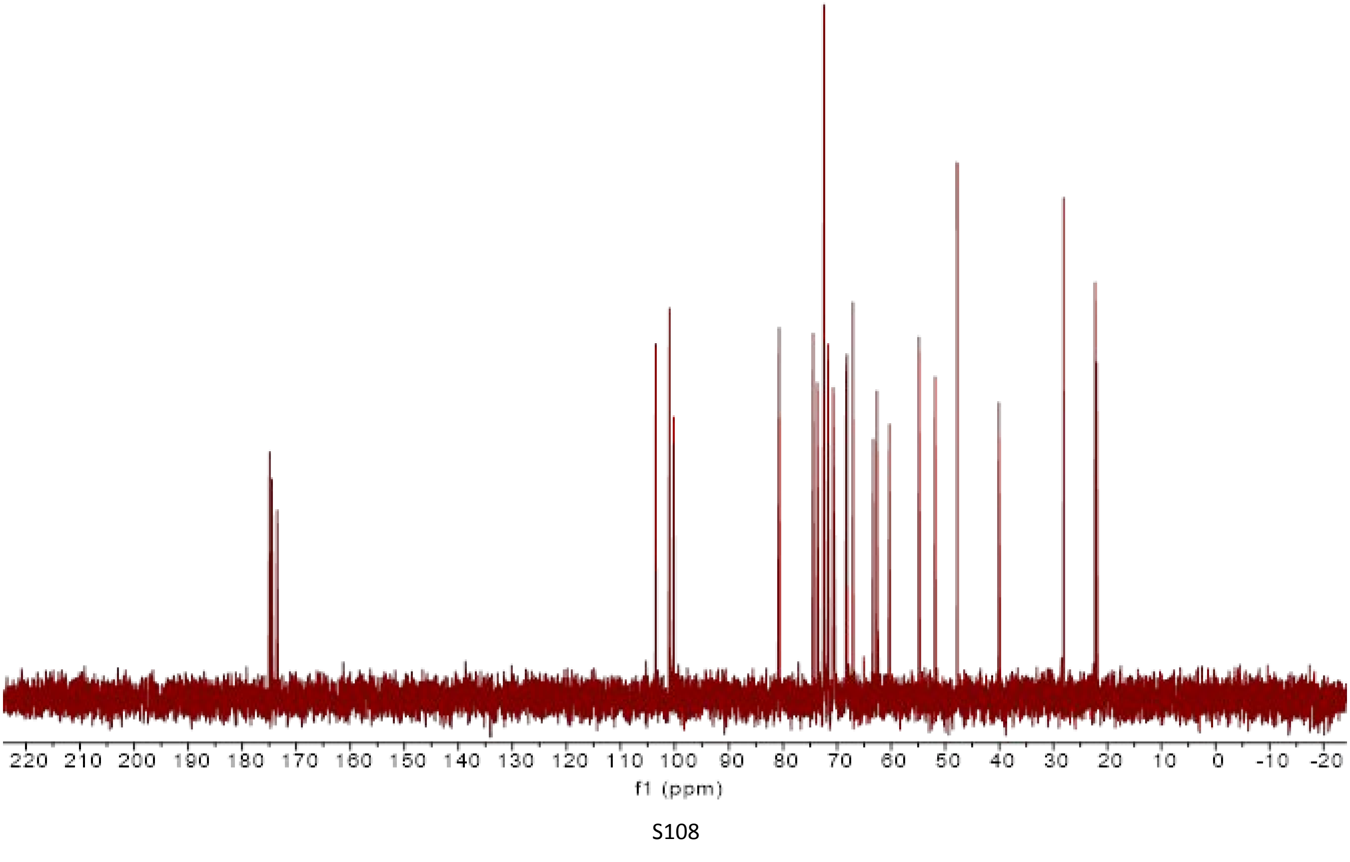

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)



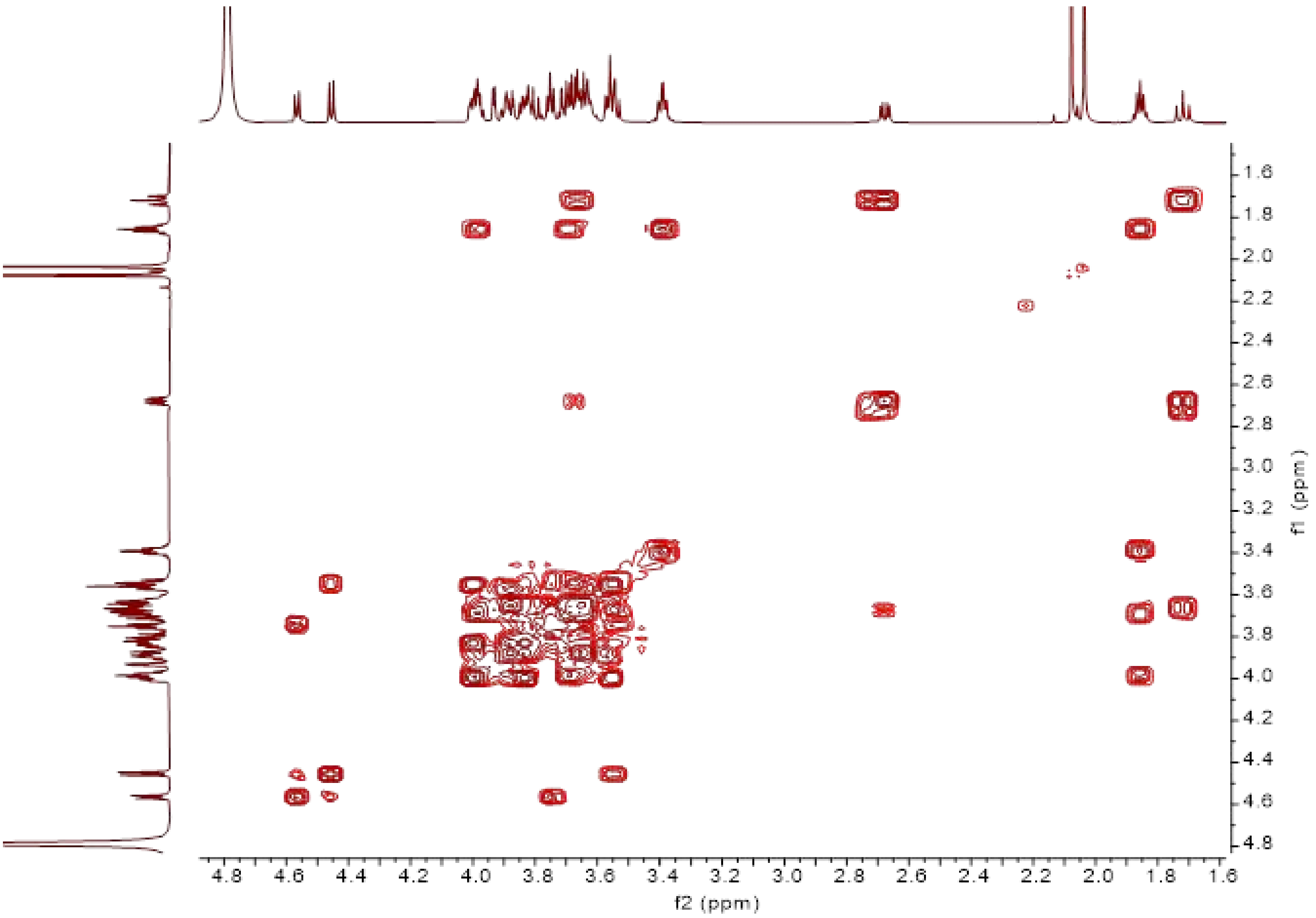
23

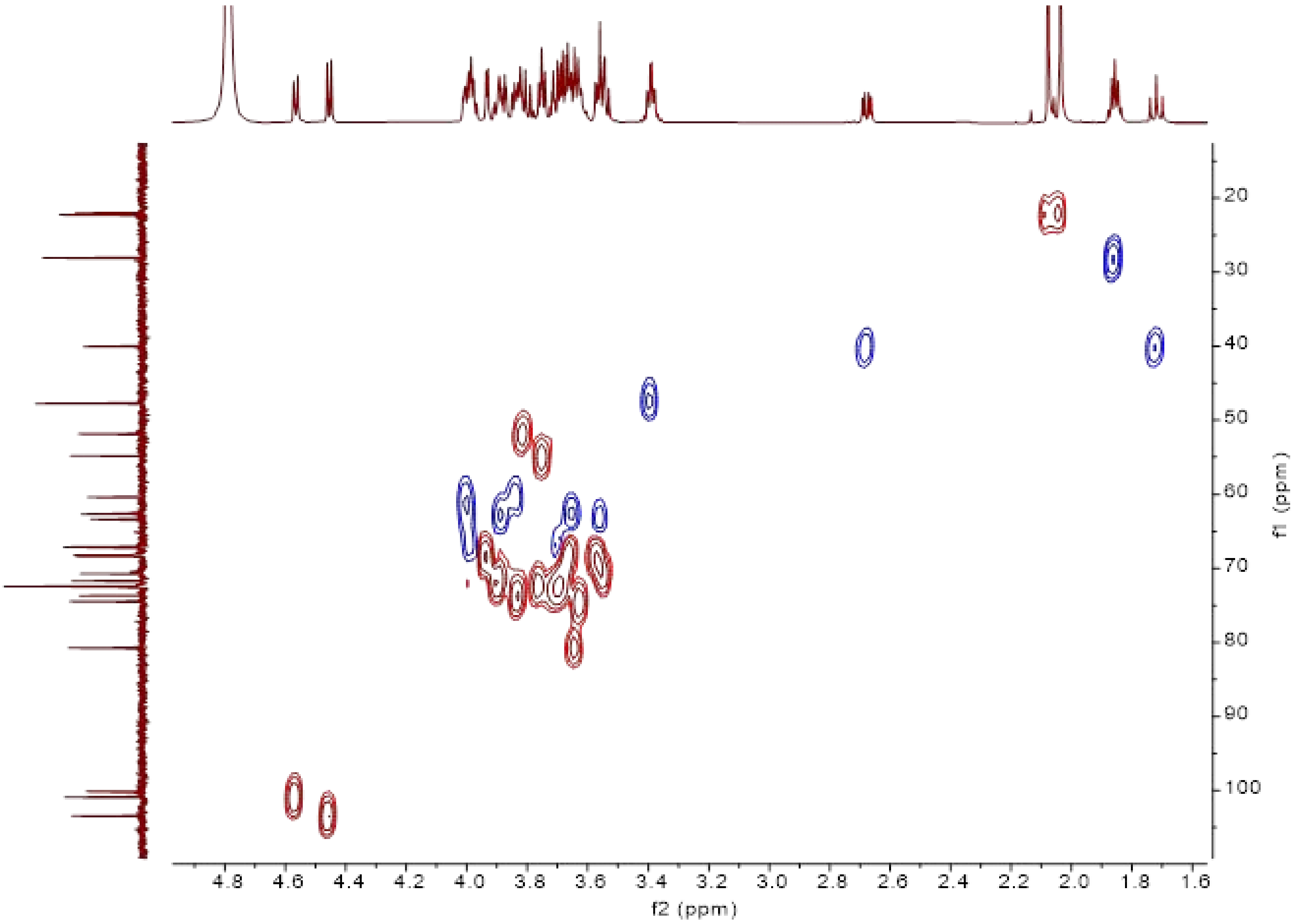


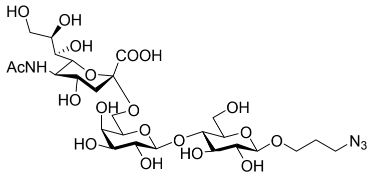
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



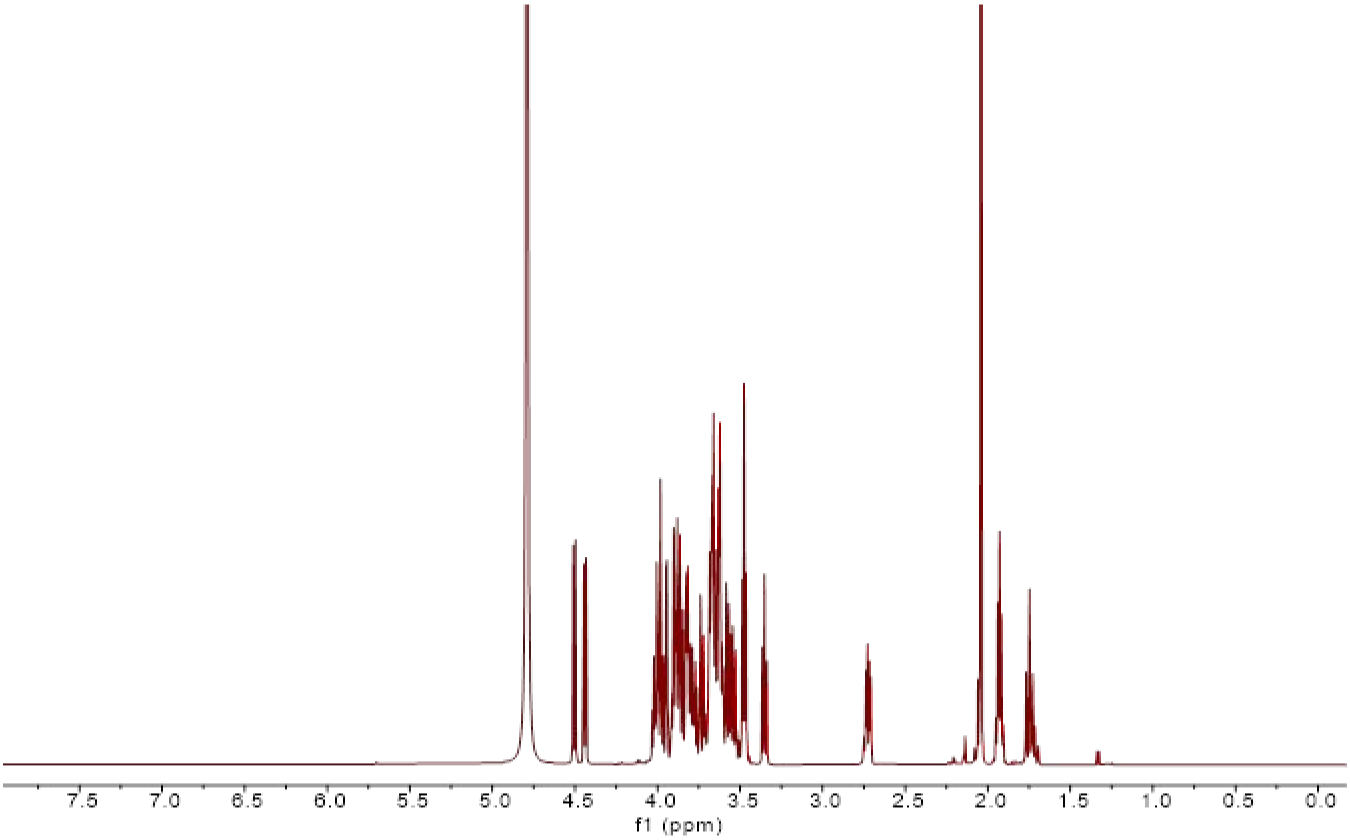
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

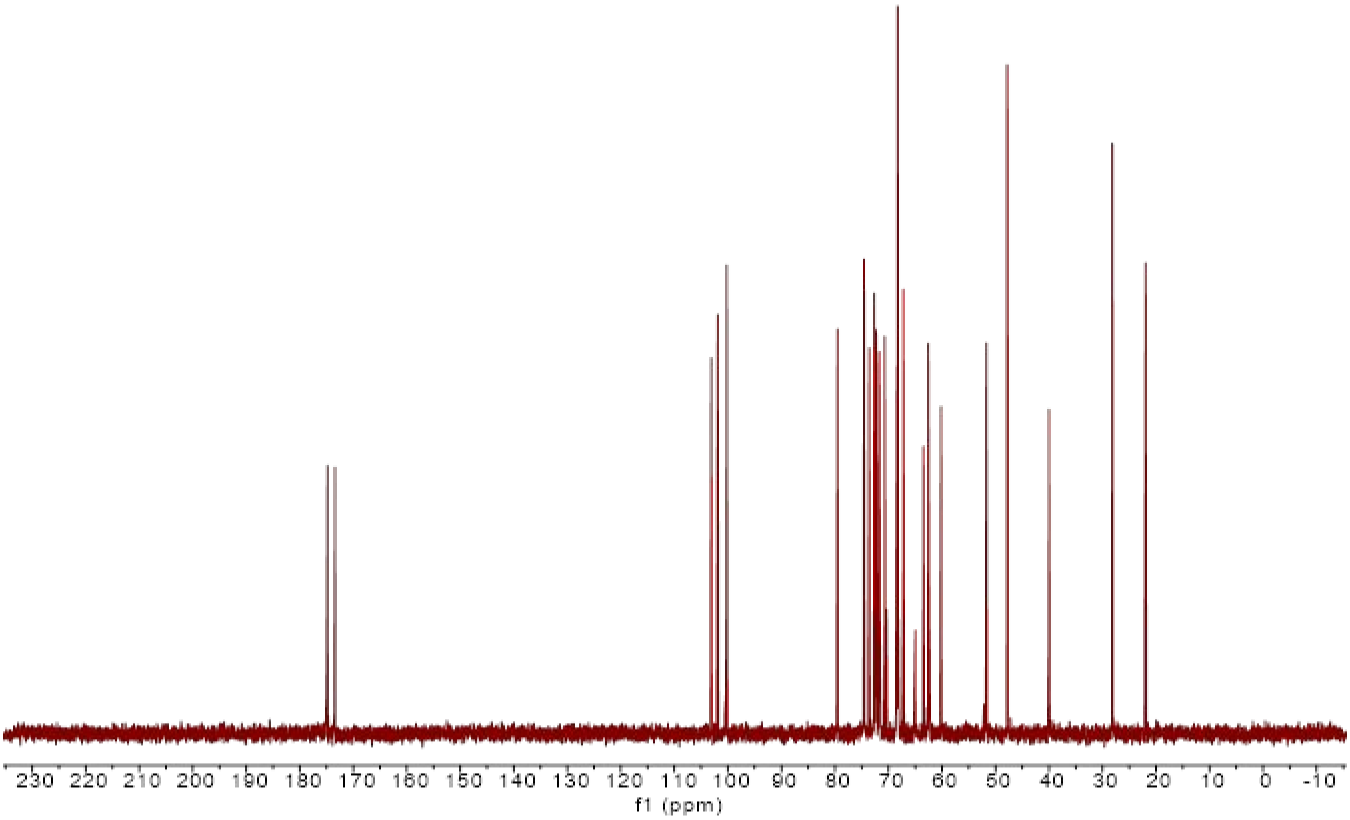

f1 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f2 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

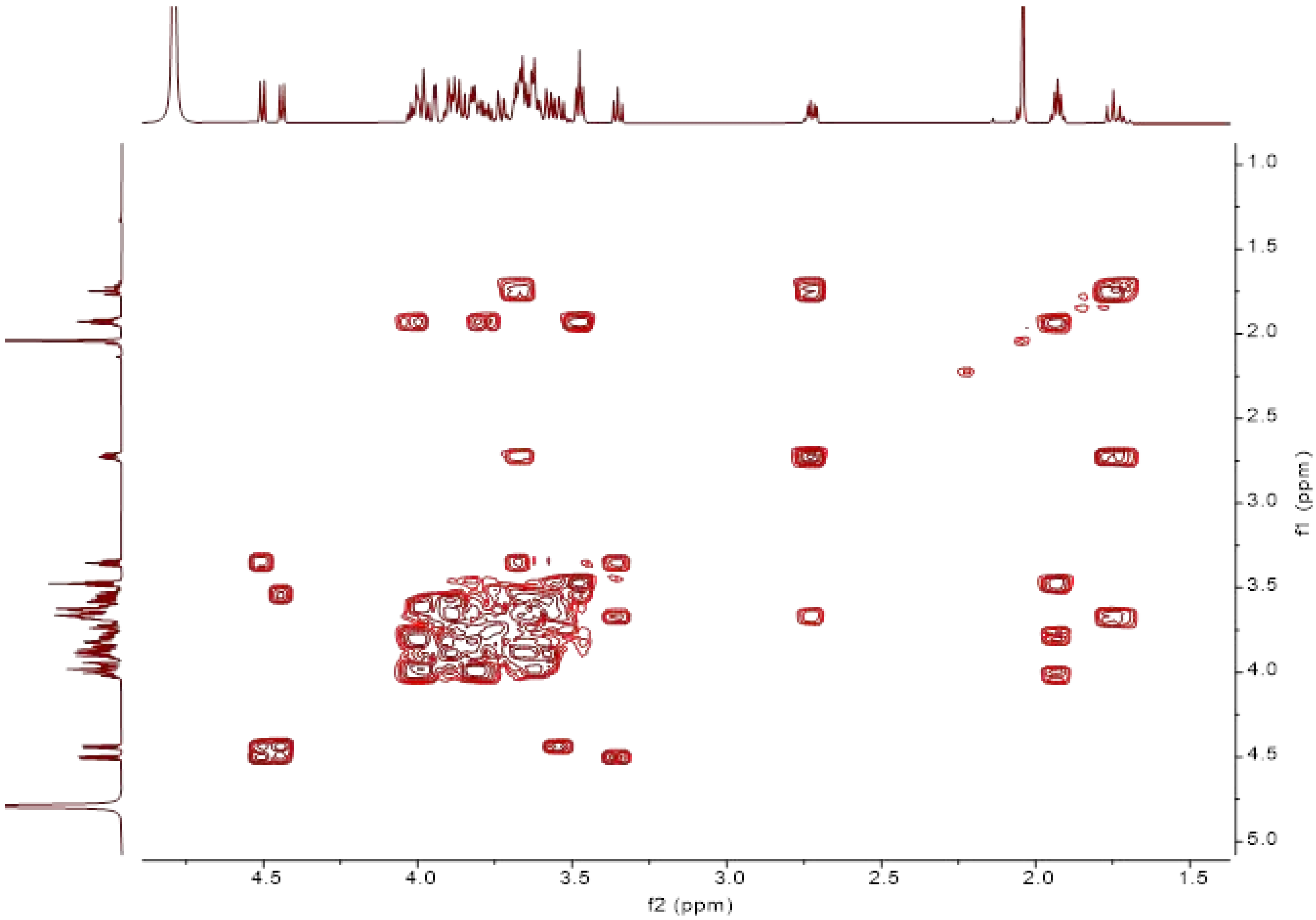

f1 (ppm)
20
30
40
50
60
70
80
90
100
f2 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

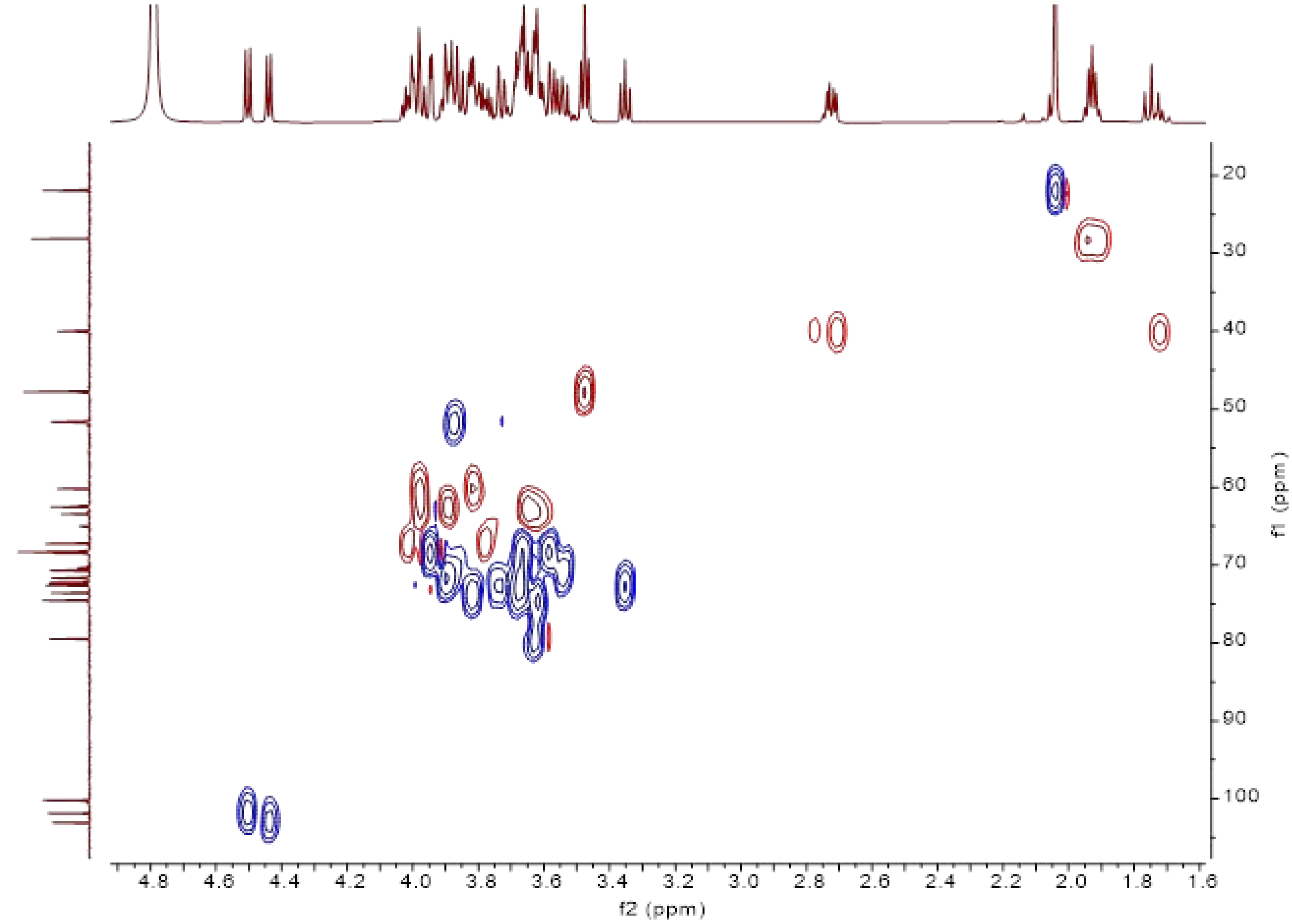

HO
OH
OH
COOH
AcNH
O
HO
OH
O
O
HO
OH
O
OH
O
O
HO
OH
N3

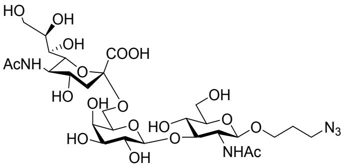
24


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
f1 (ppm)

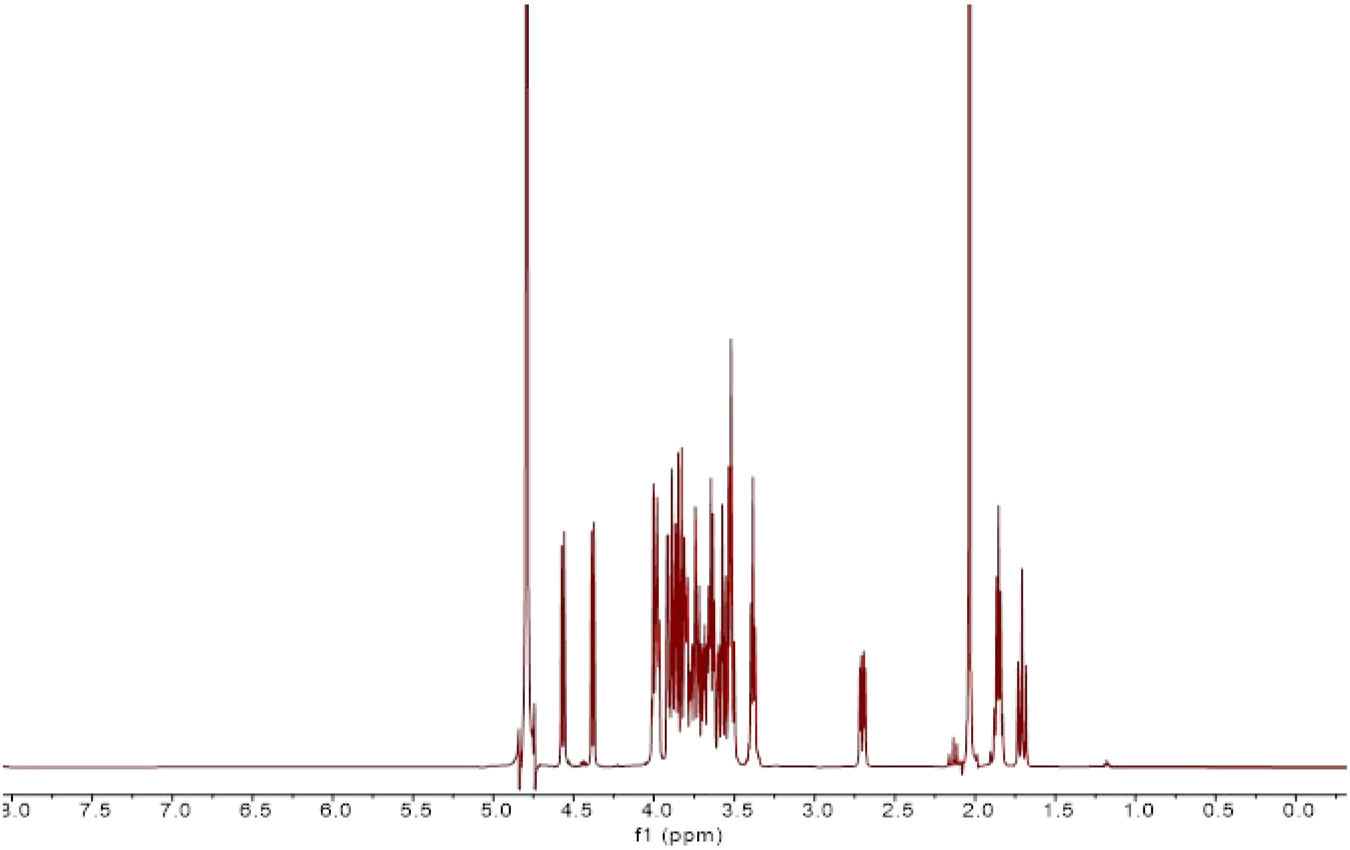

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

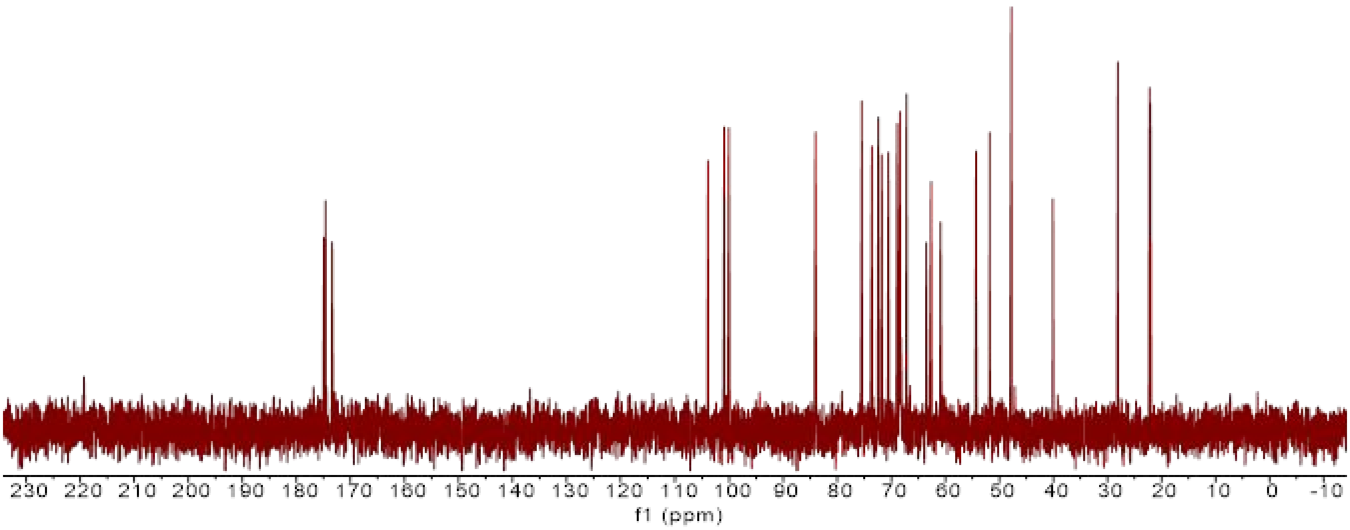

1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

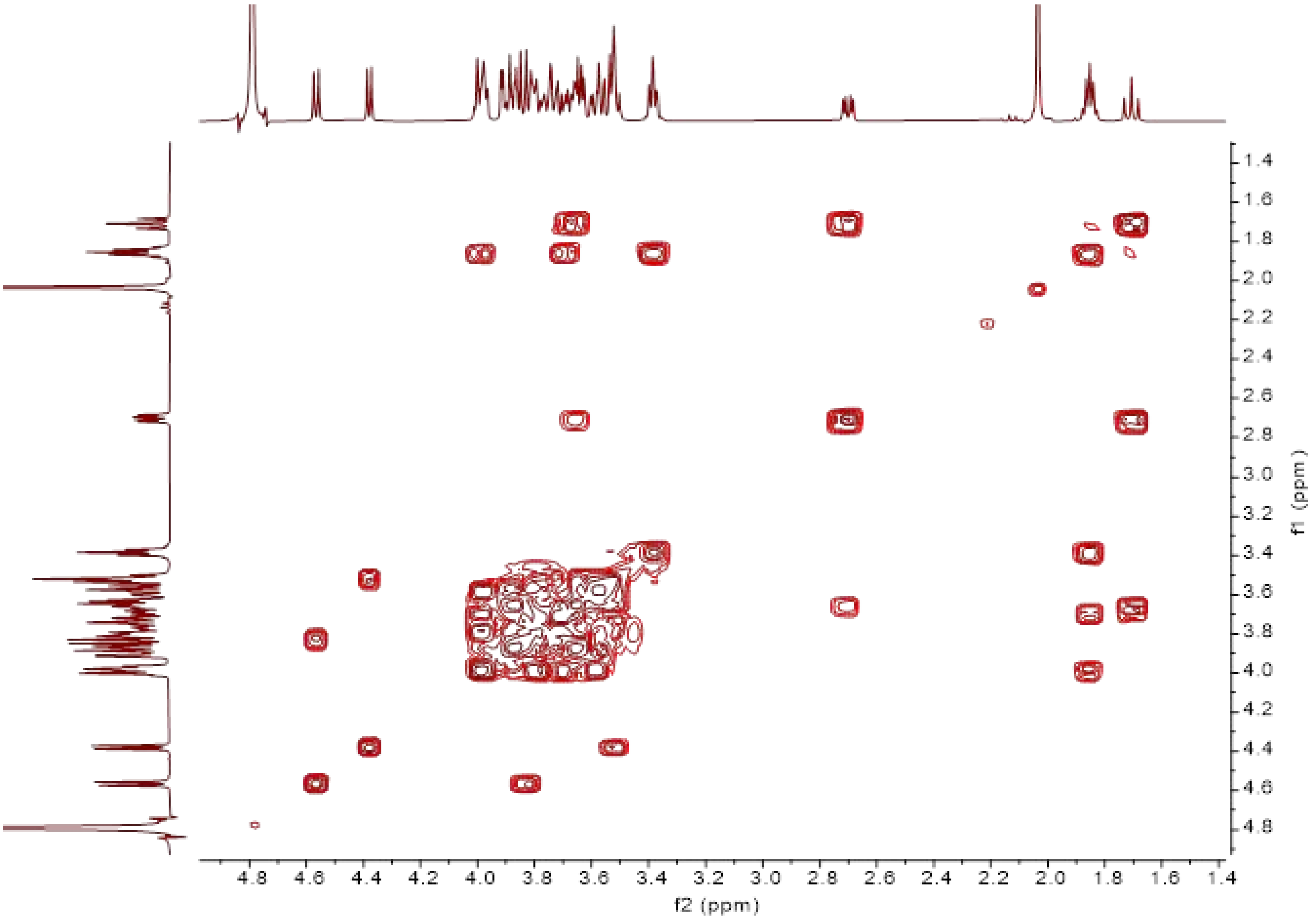

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

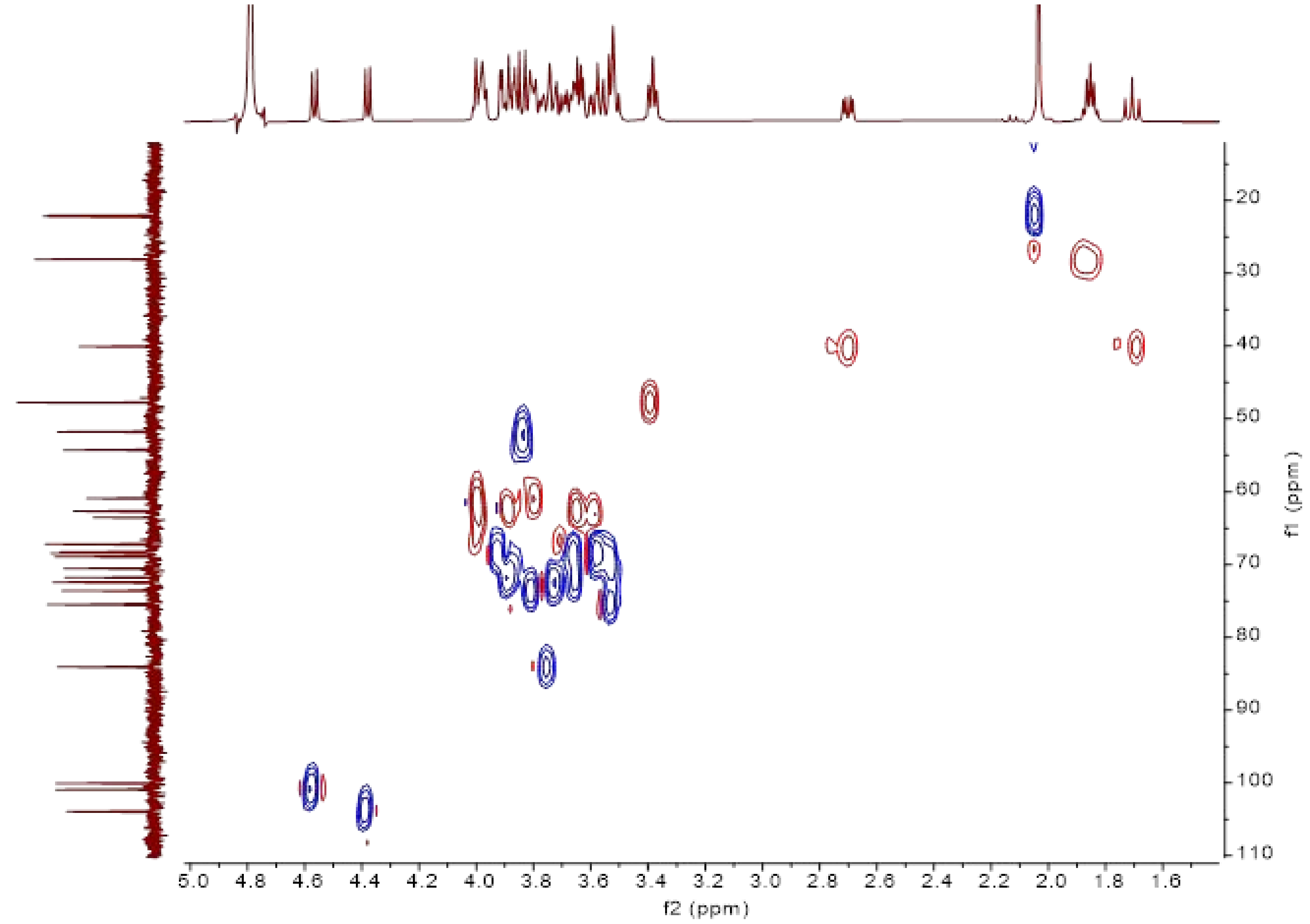

HO
OH
OH
COOH
AcNH
O
HO
OH
O
O
HO
OH
HO
O
O
O
N3
HO
OH
NHAc

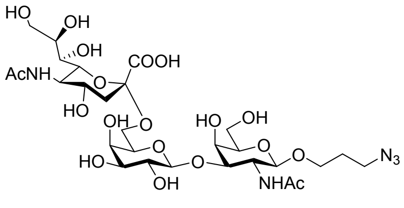
25


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

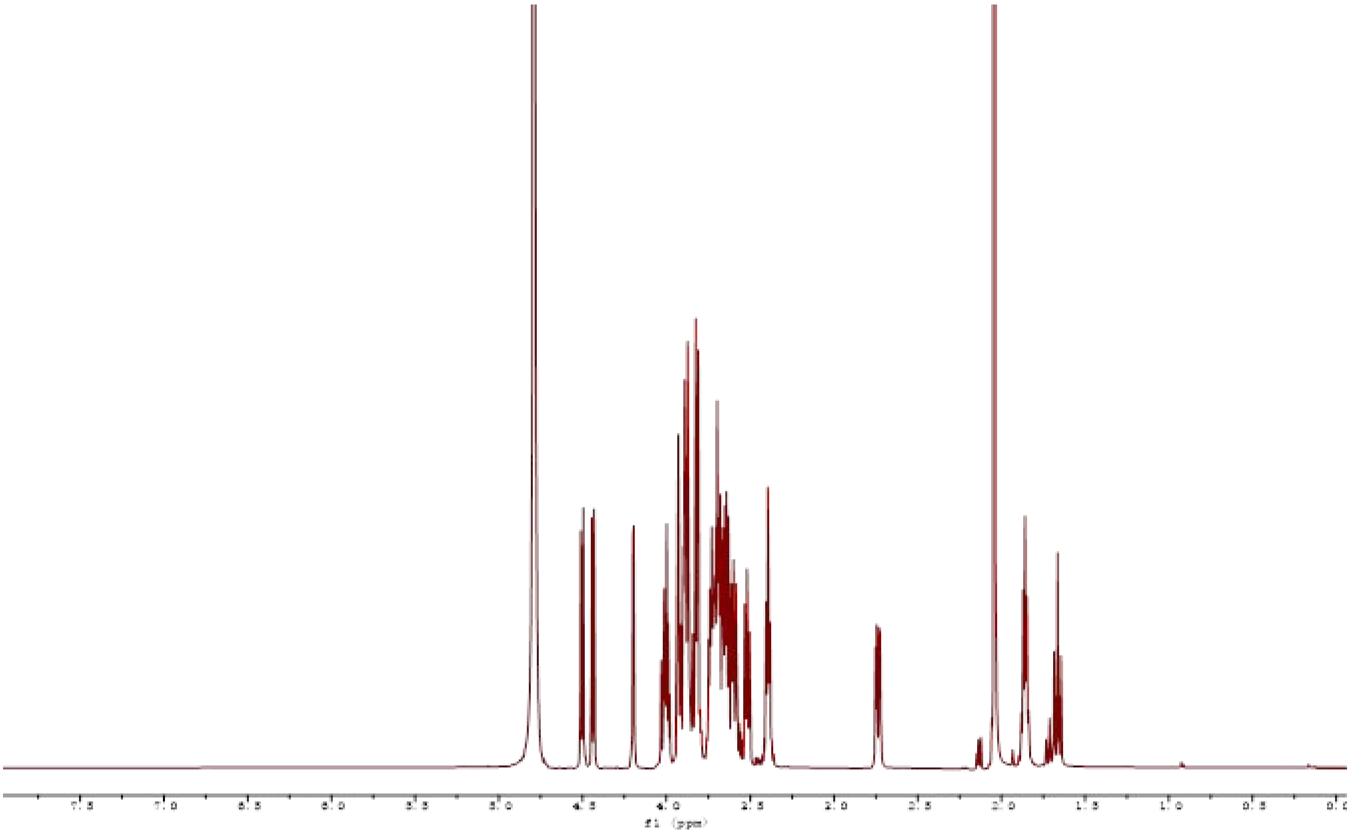

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

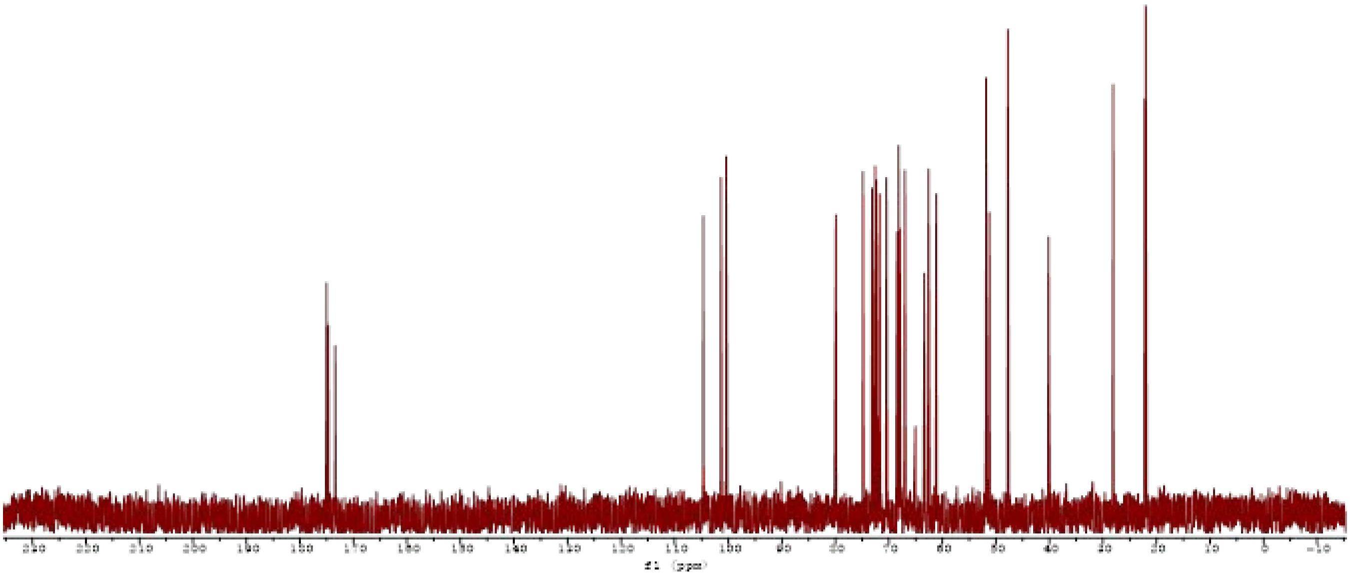

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
f1 (ppm)

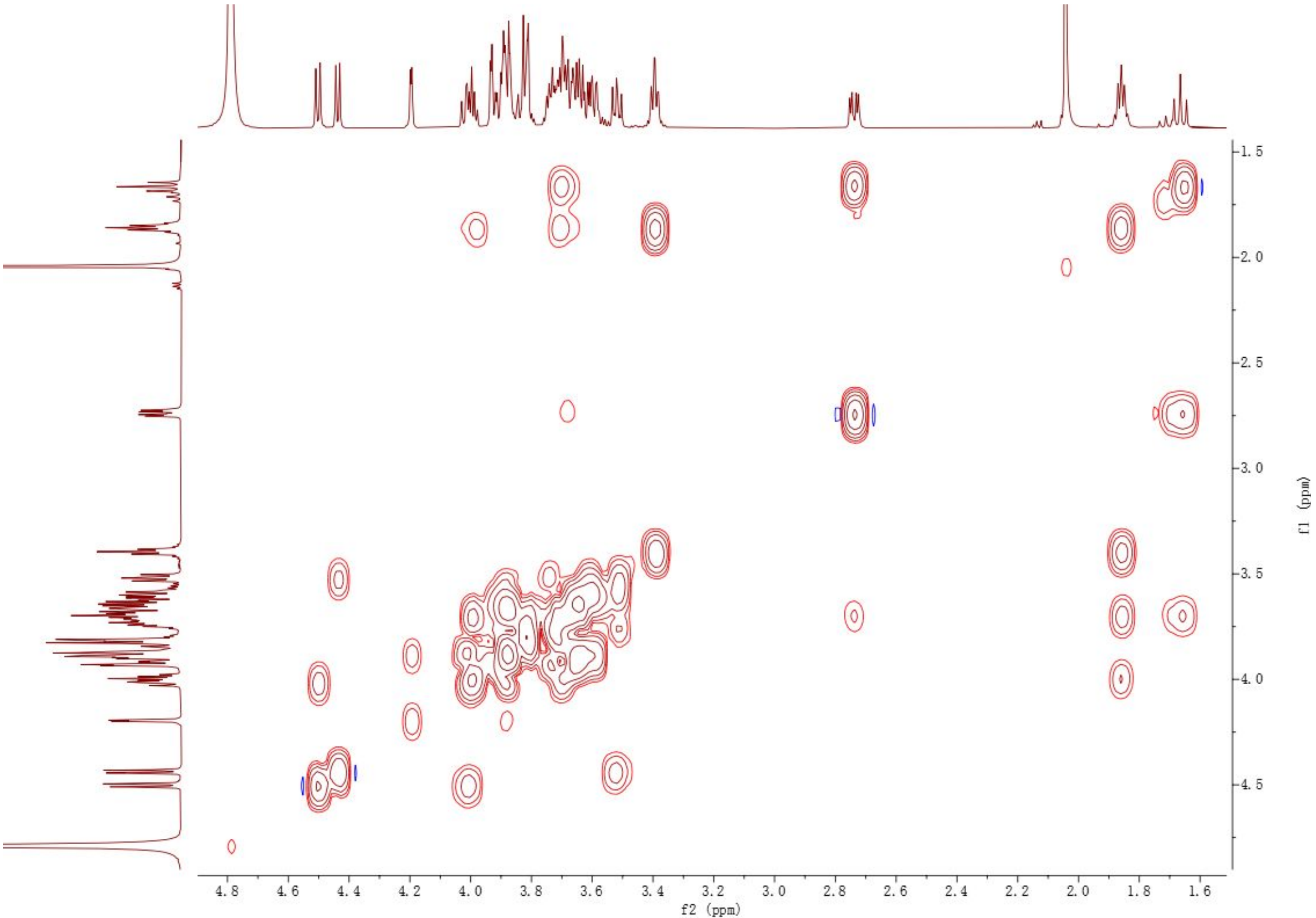

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)


HO
OH
OH
COOH
AcNH
O
HO
OH
O
HO
OH
O
O
HO
O
O
N3
OH
NHAc

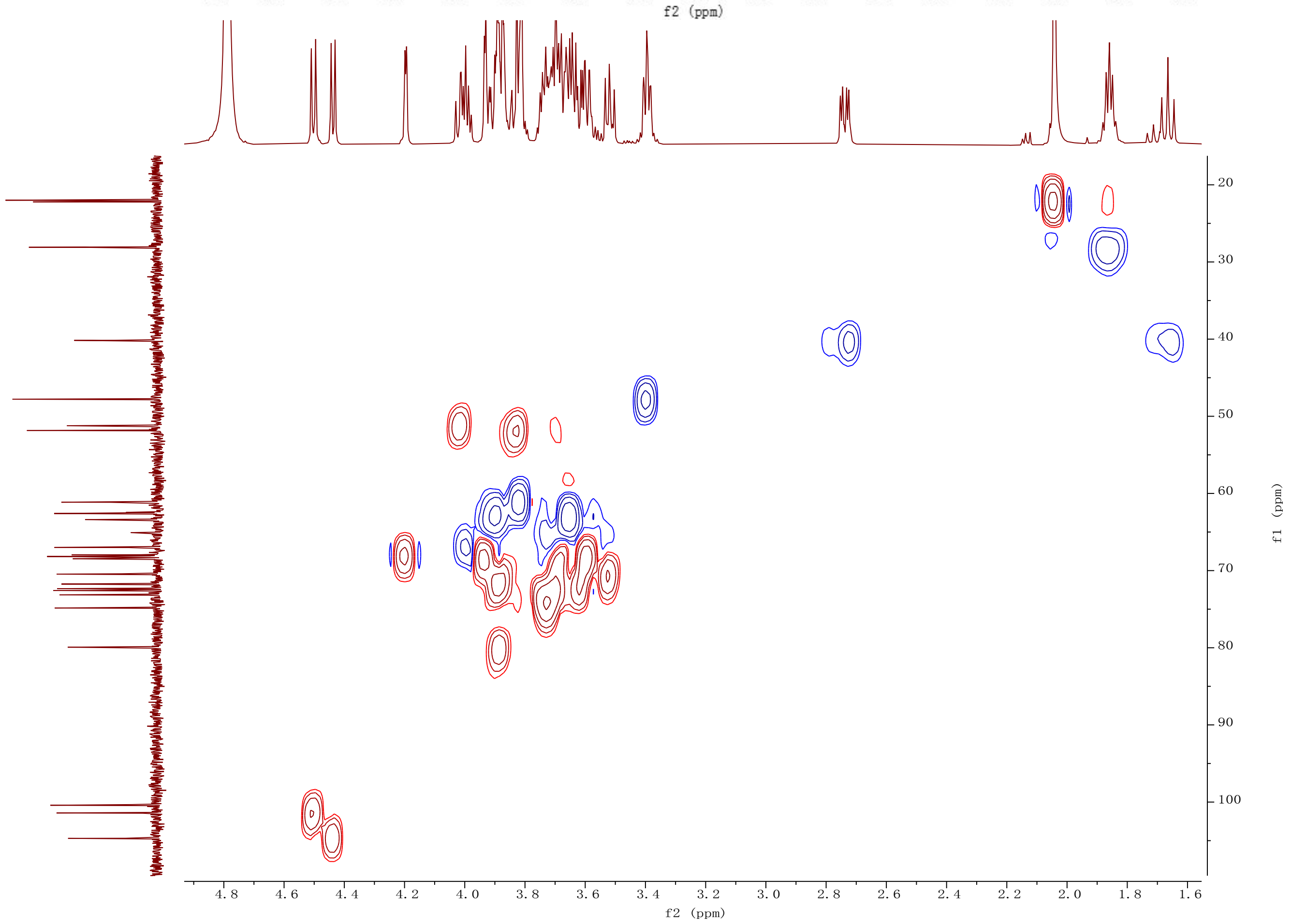
26


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
f1 (ppm)

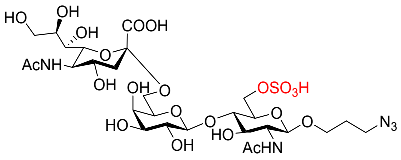

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



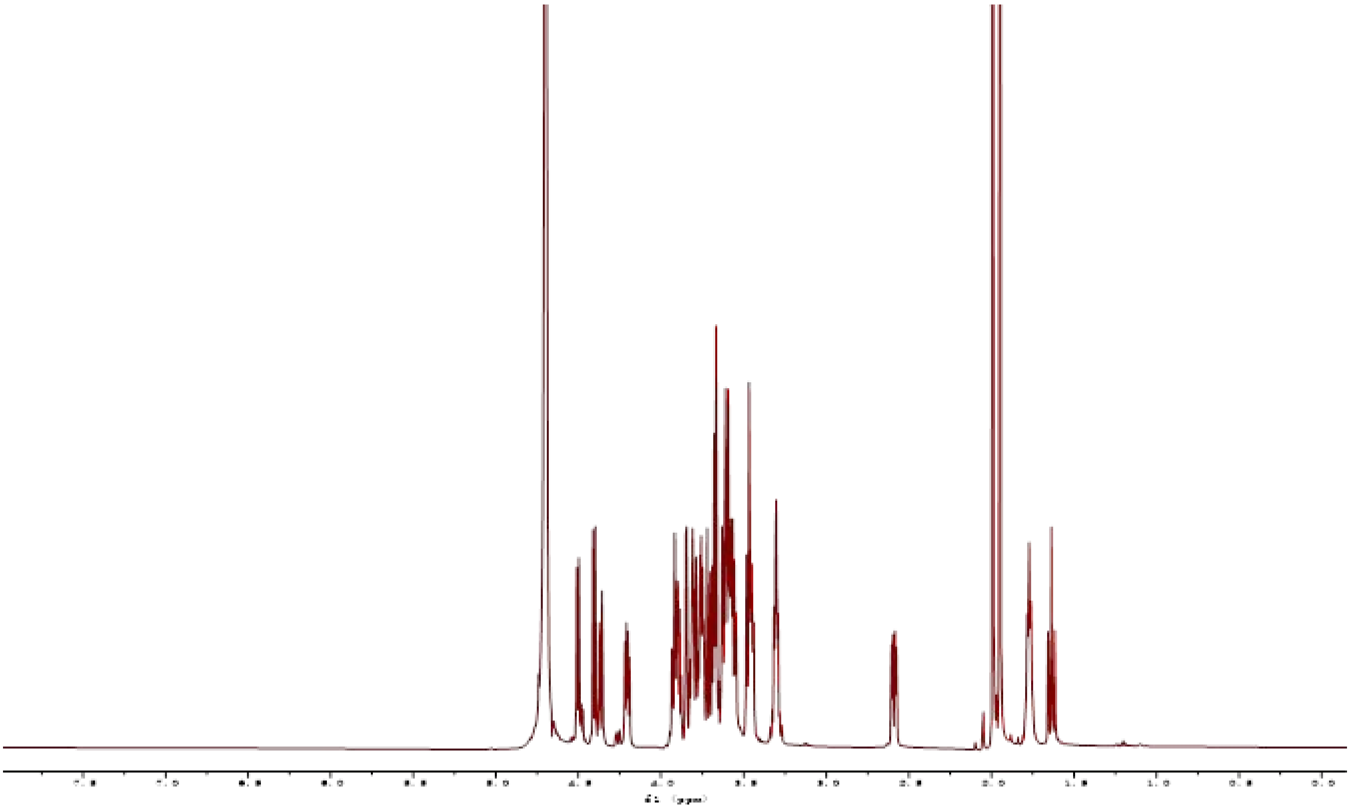
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

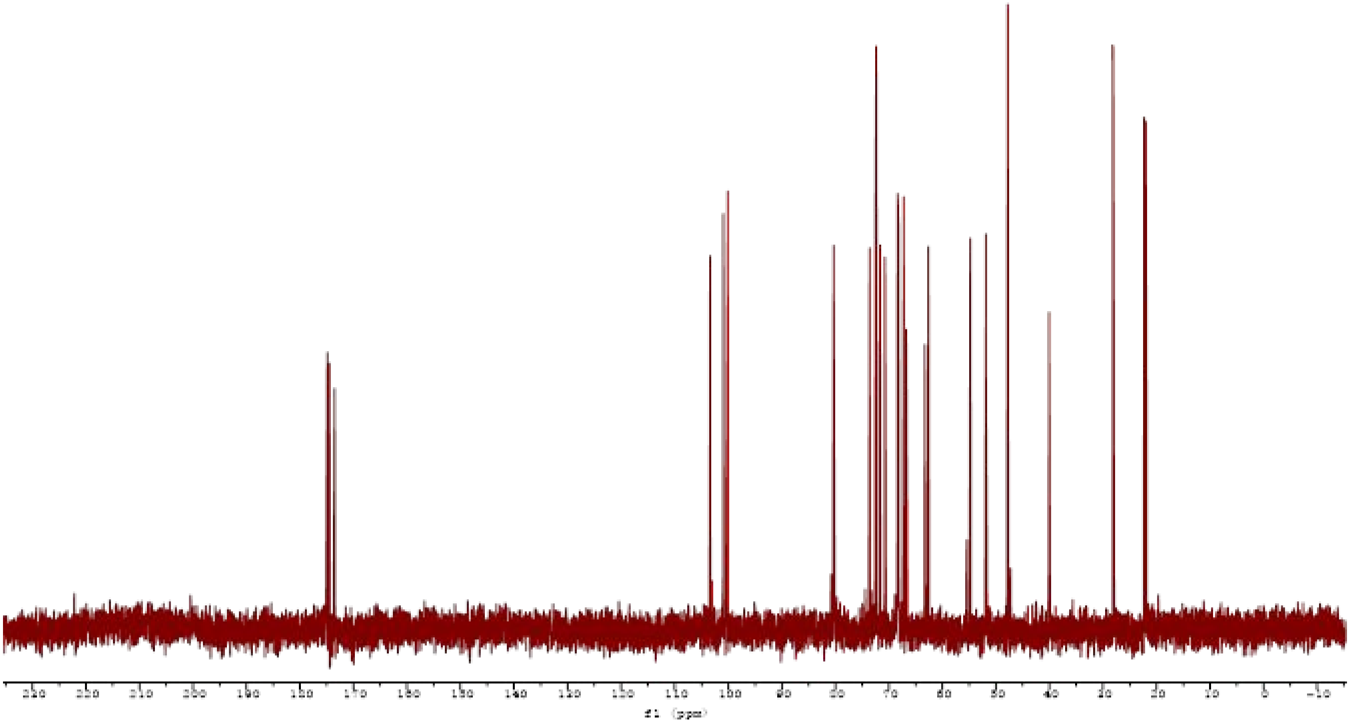


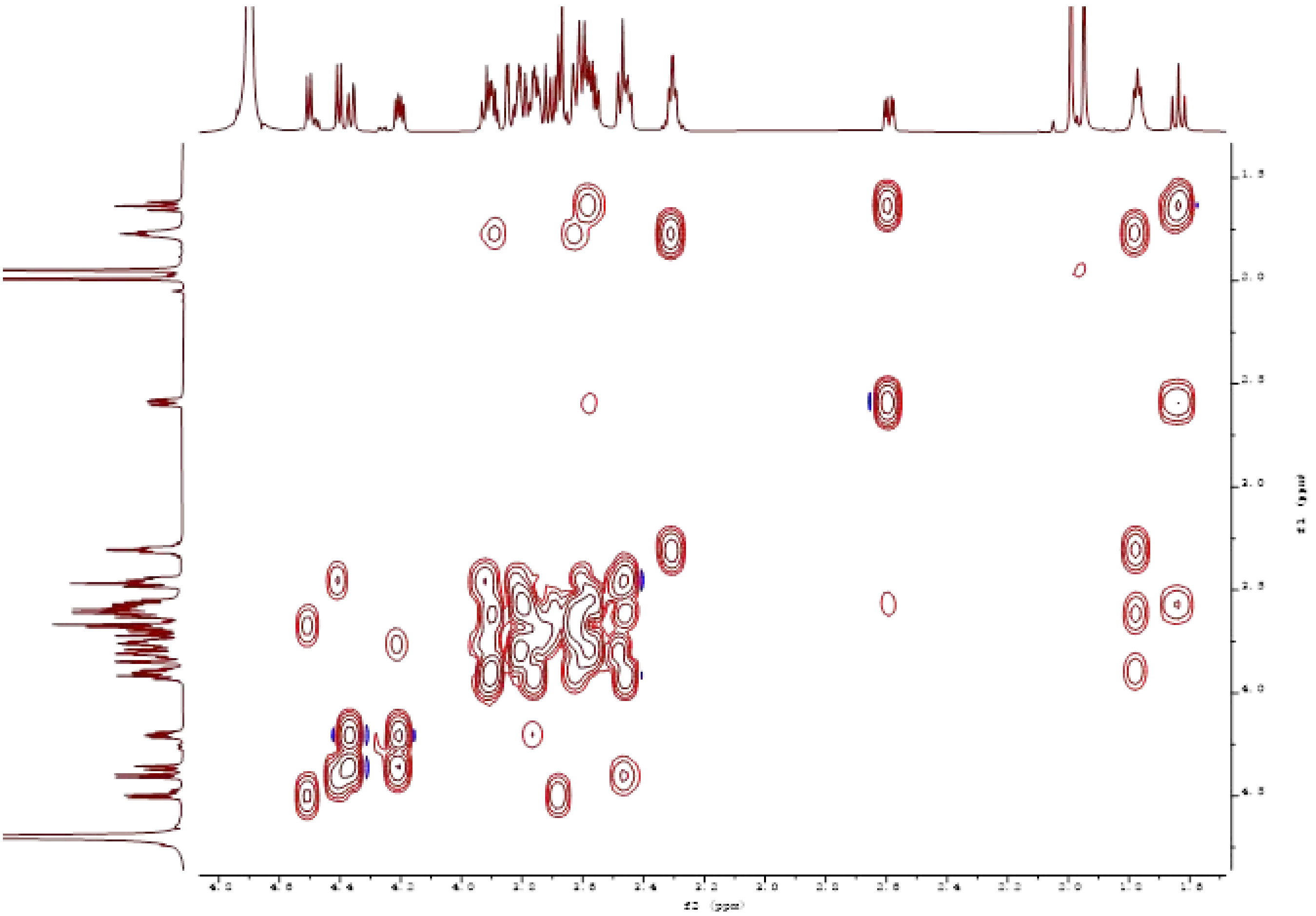
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

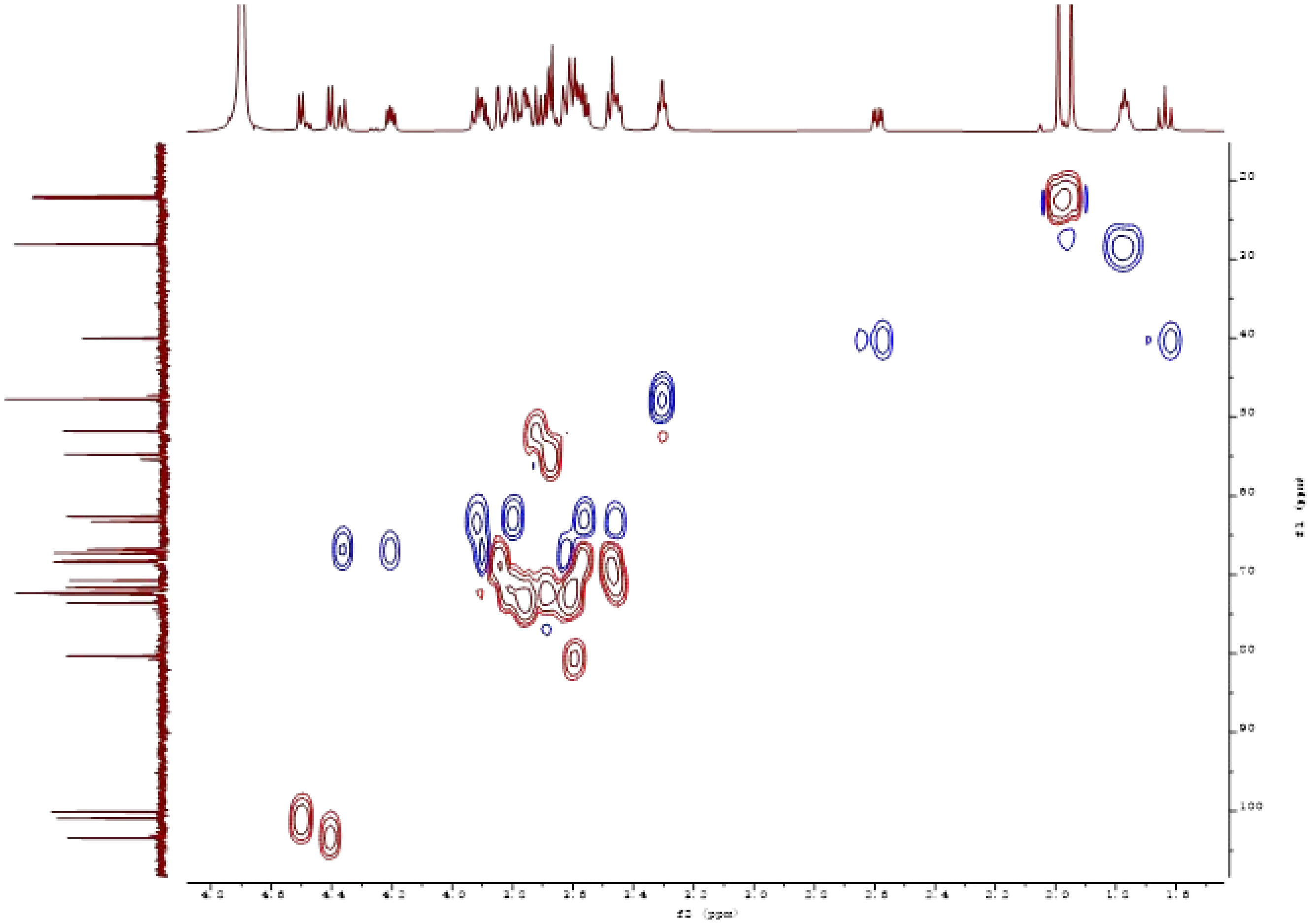

HO
OH
OH
COOH
AcNH
O
OH
OH
O
OSO$_3$H
HO
O
O
O
O
N$_3$
OH
HO
AcHN

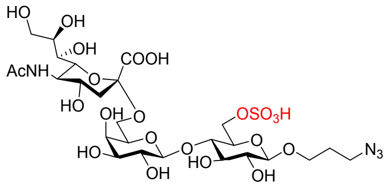
27


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)

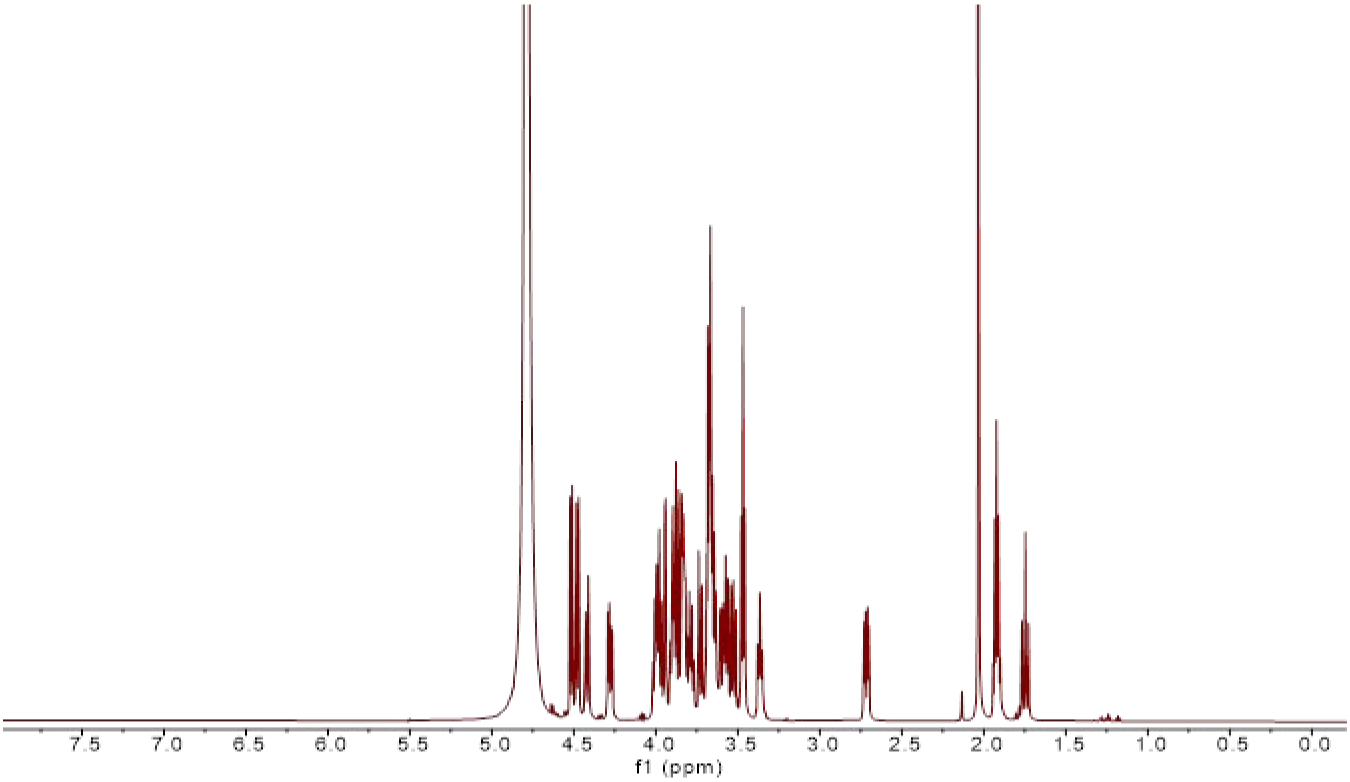

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

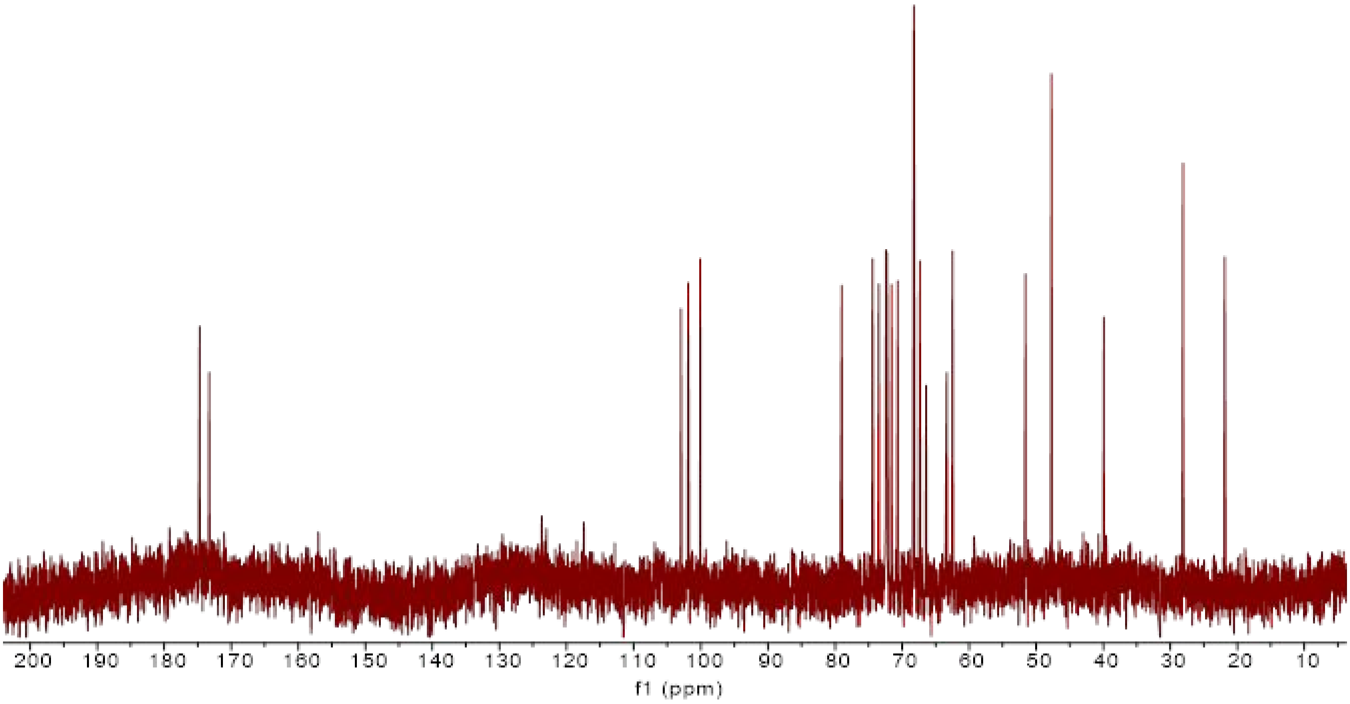

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

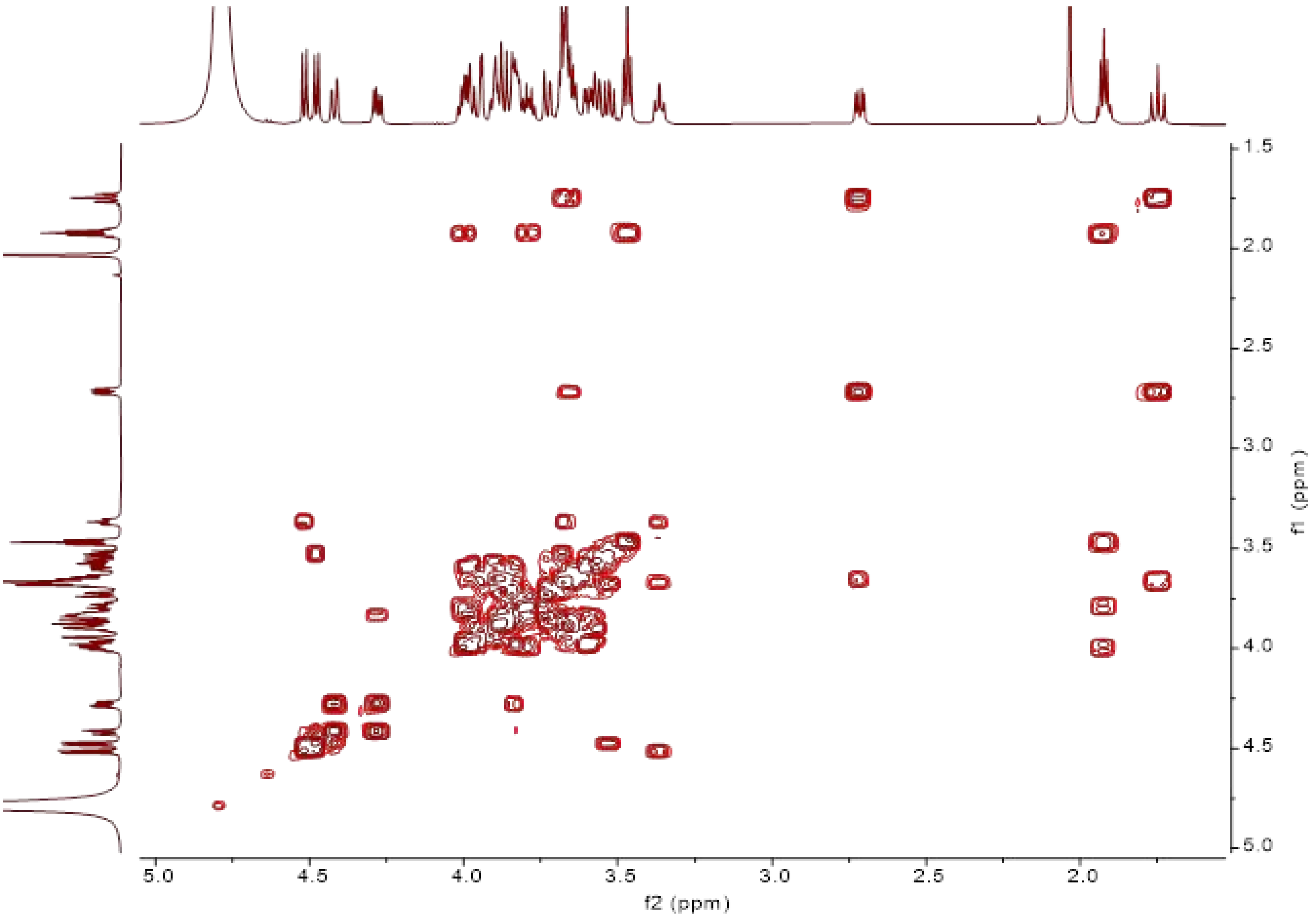

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

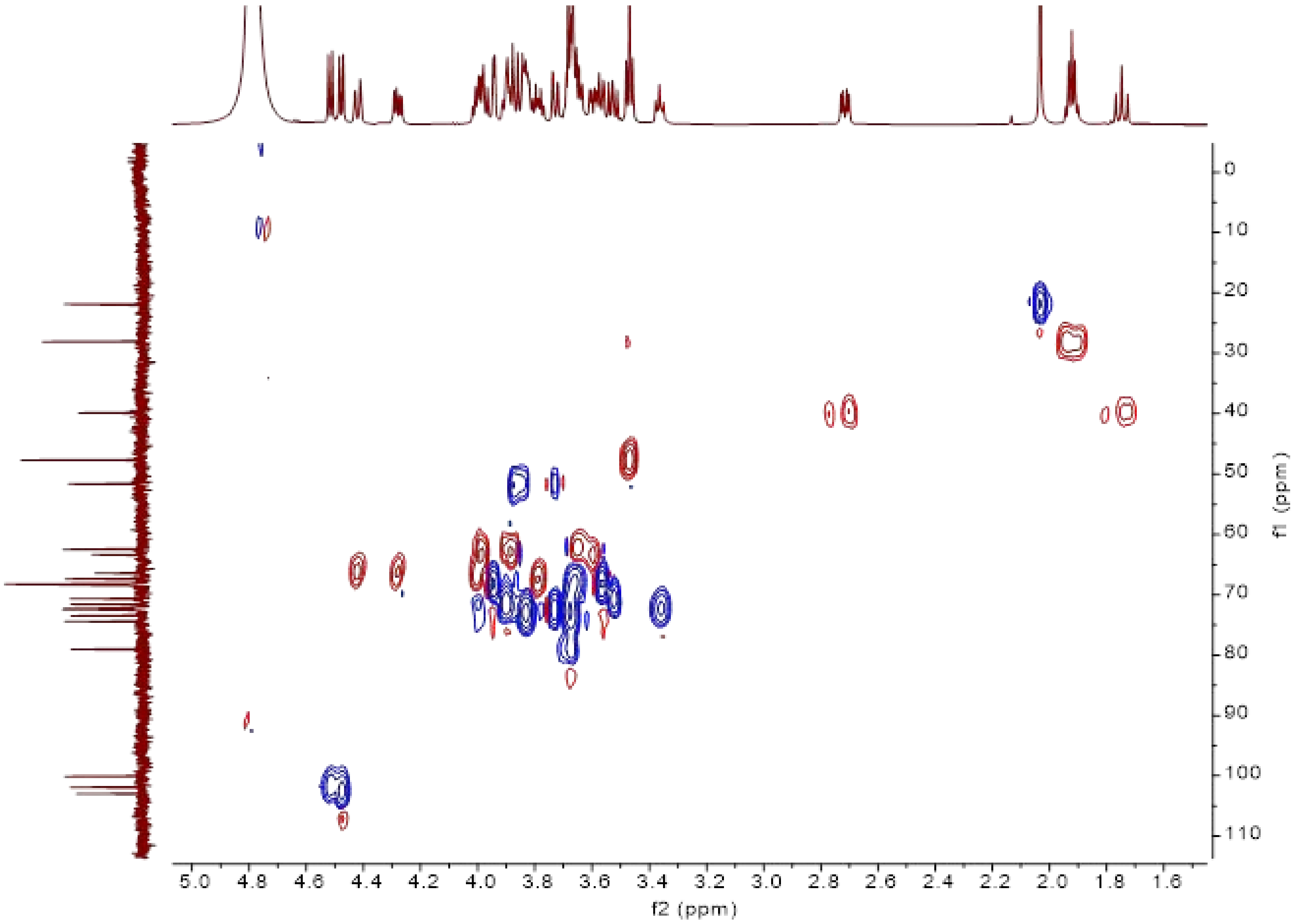

HO
OH
OH
AcNH
COOH
O
HO
OH
O
OSO3H
HO
O
O
HO
O
O
N3
OH
OH

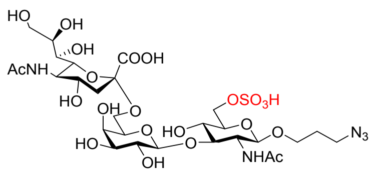
28


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
f1 (ppm)

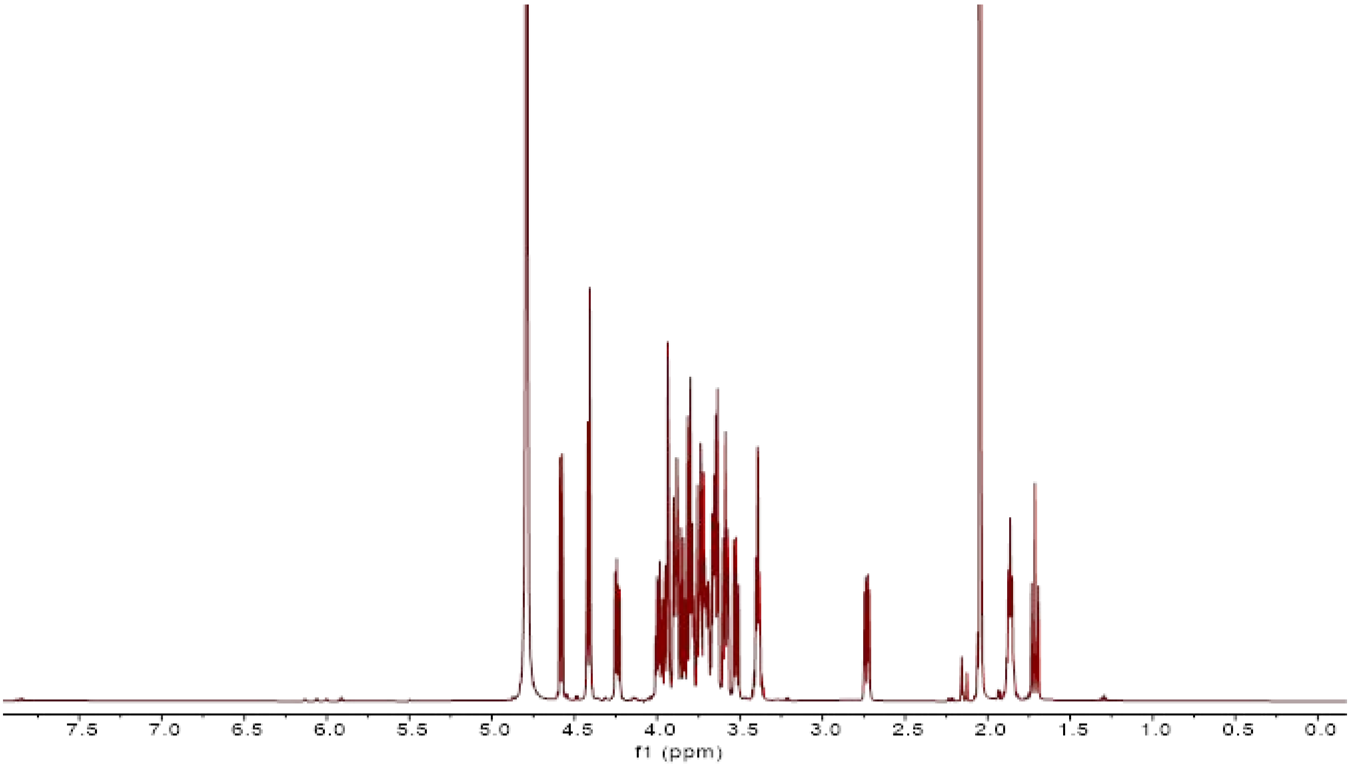

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

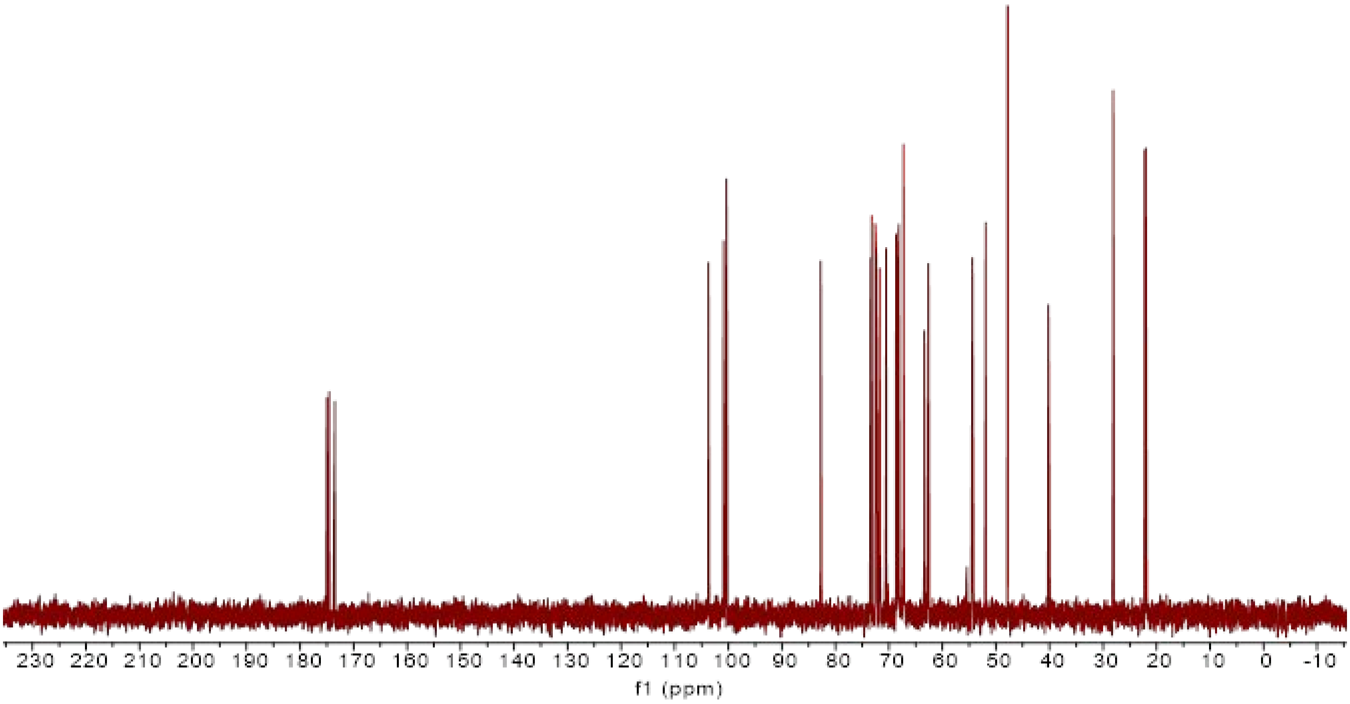

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

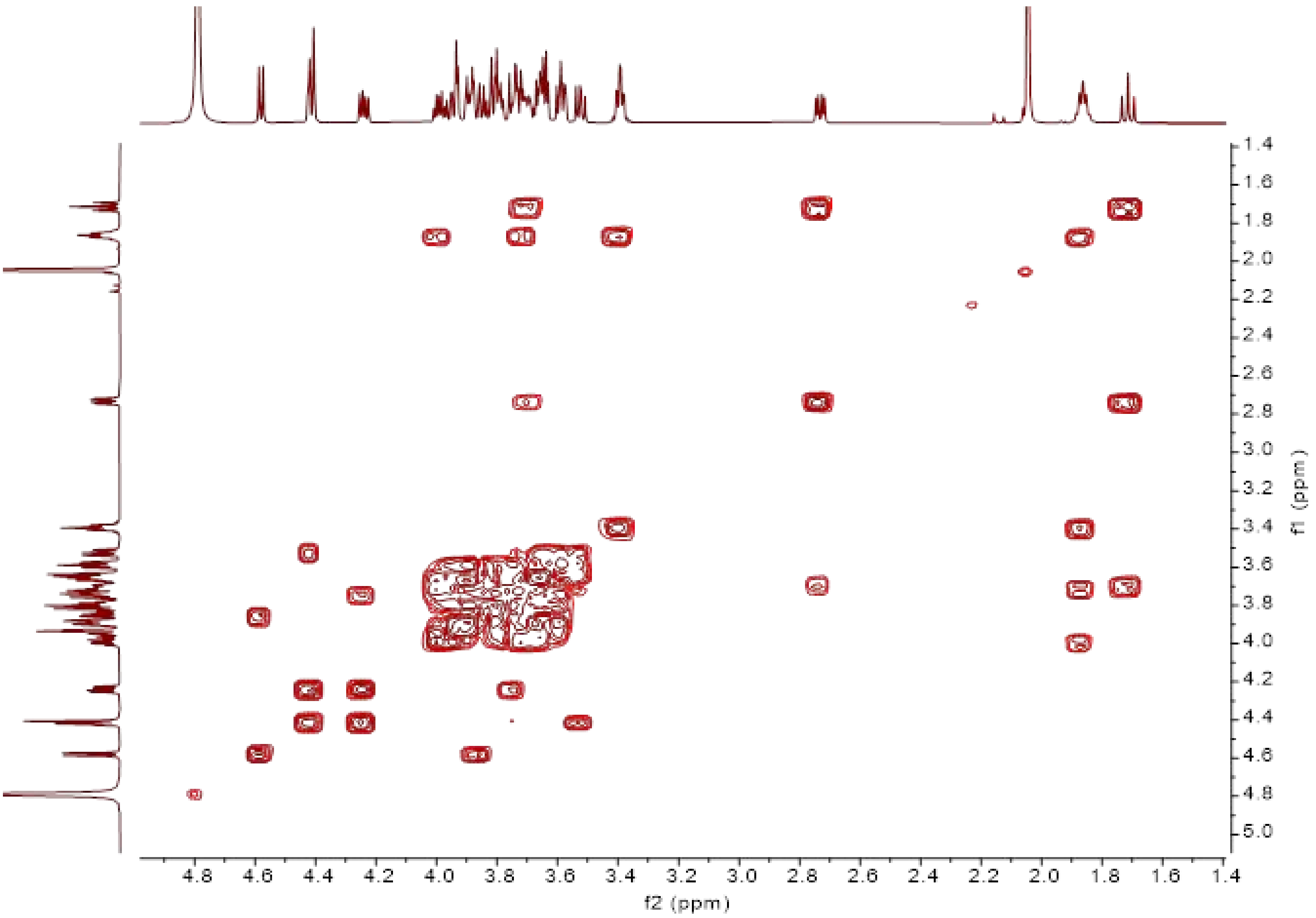

0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

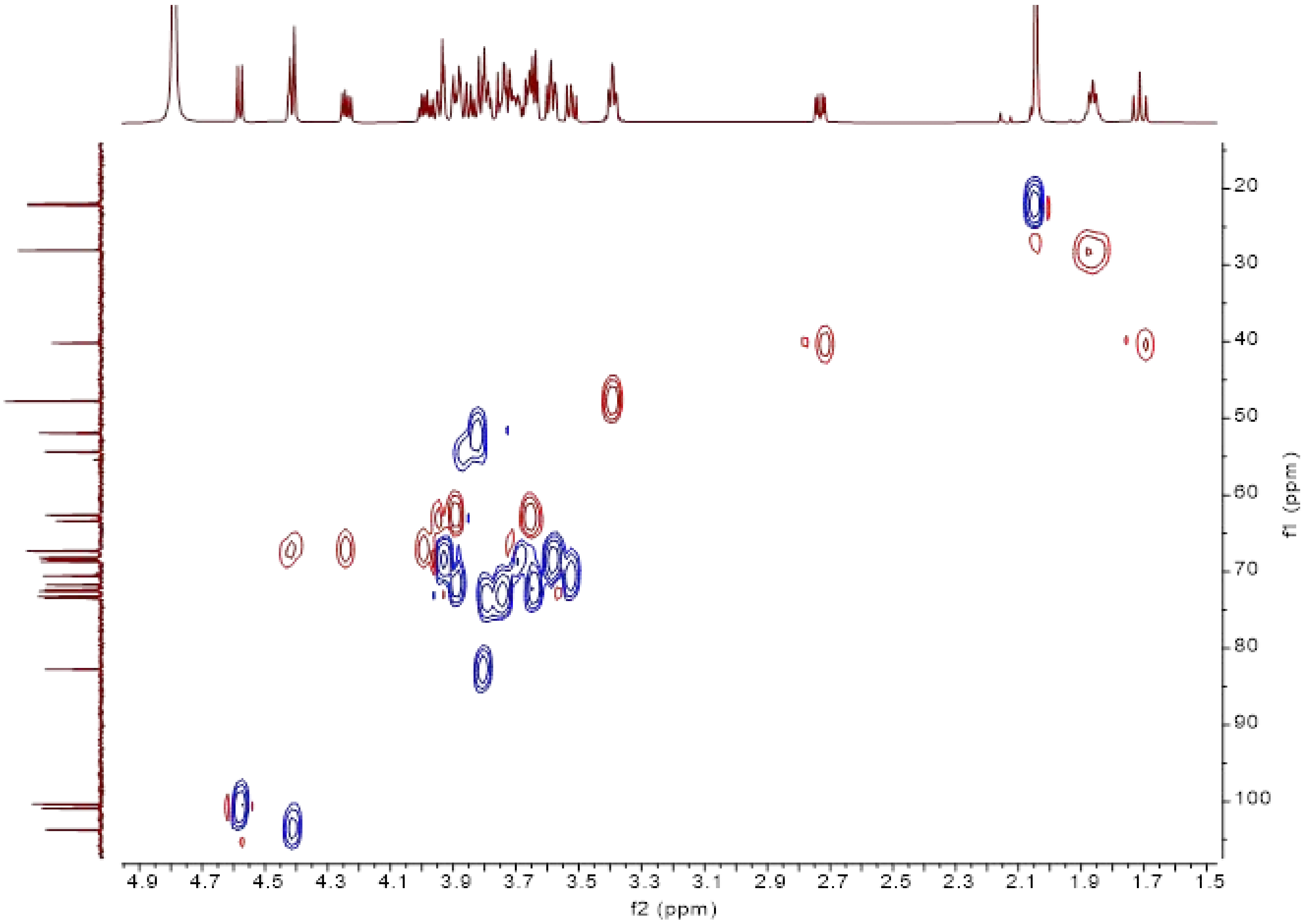

HO
OH
OH
AcNH
O
COOH
HO
O
OH
O
OSO3H
HO
O
O
N3
HO
OH
NHAc

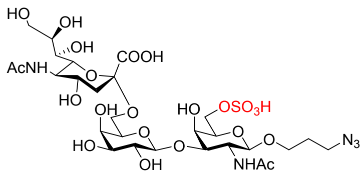
29


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)

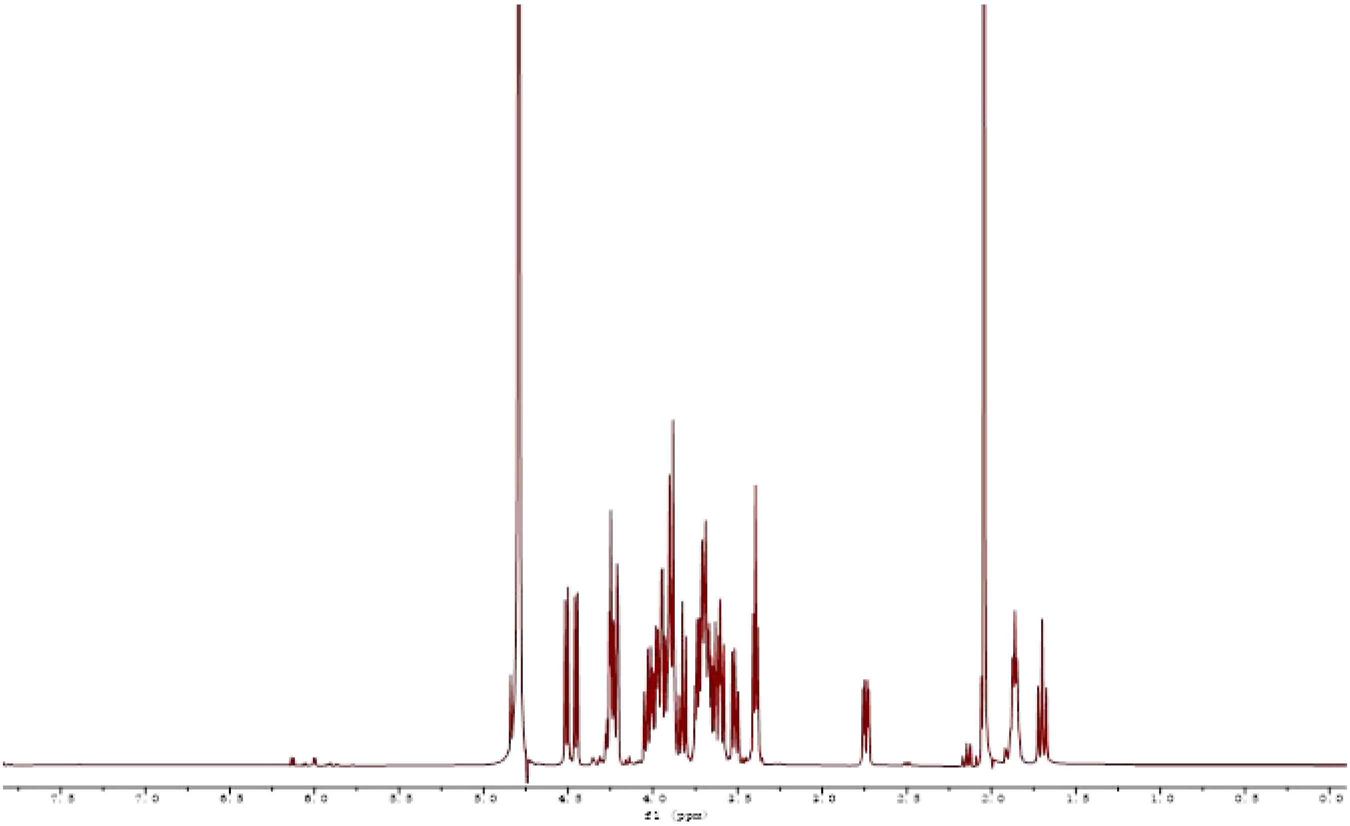

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

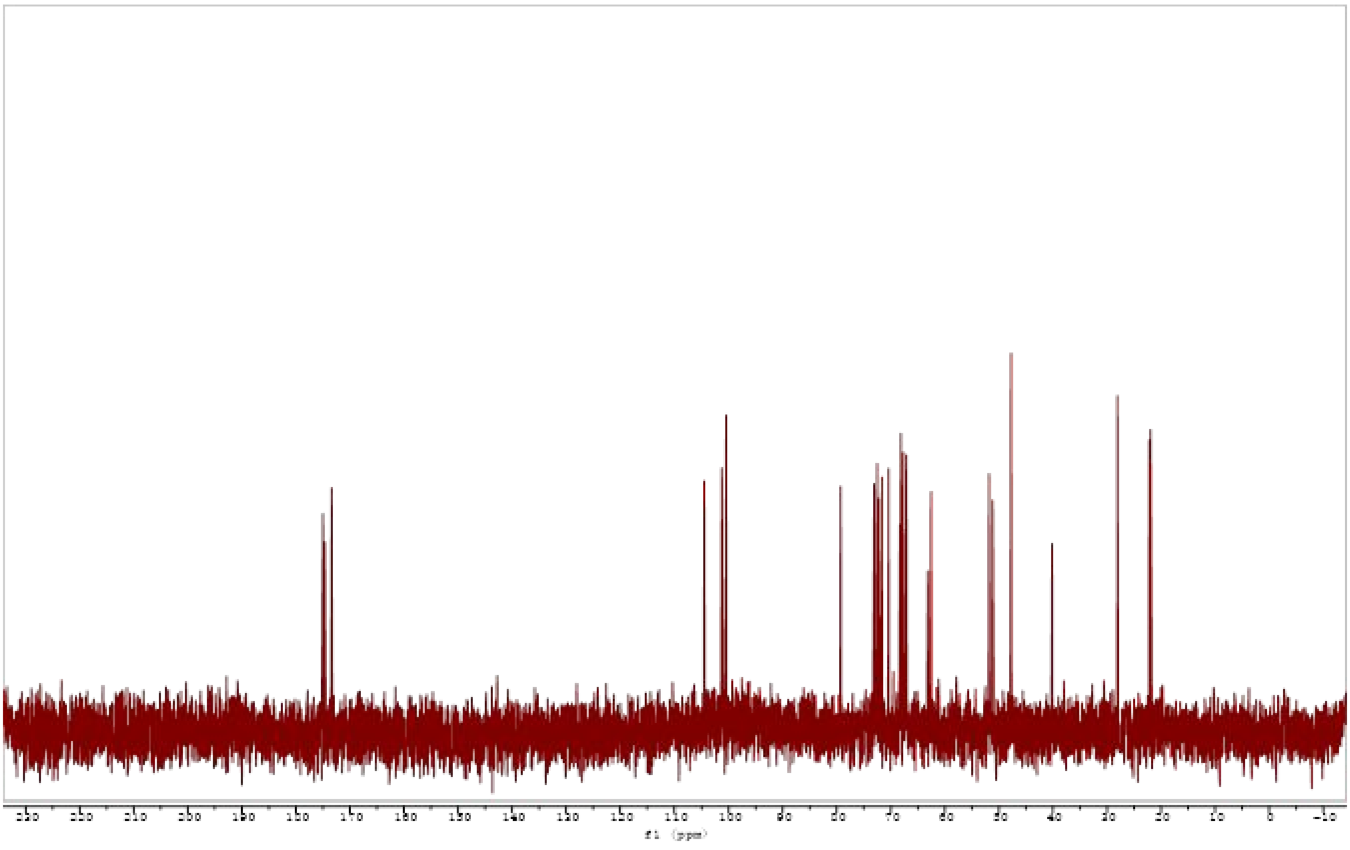

f2 (ppm)
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
5.0

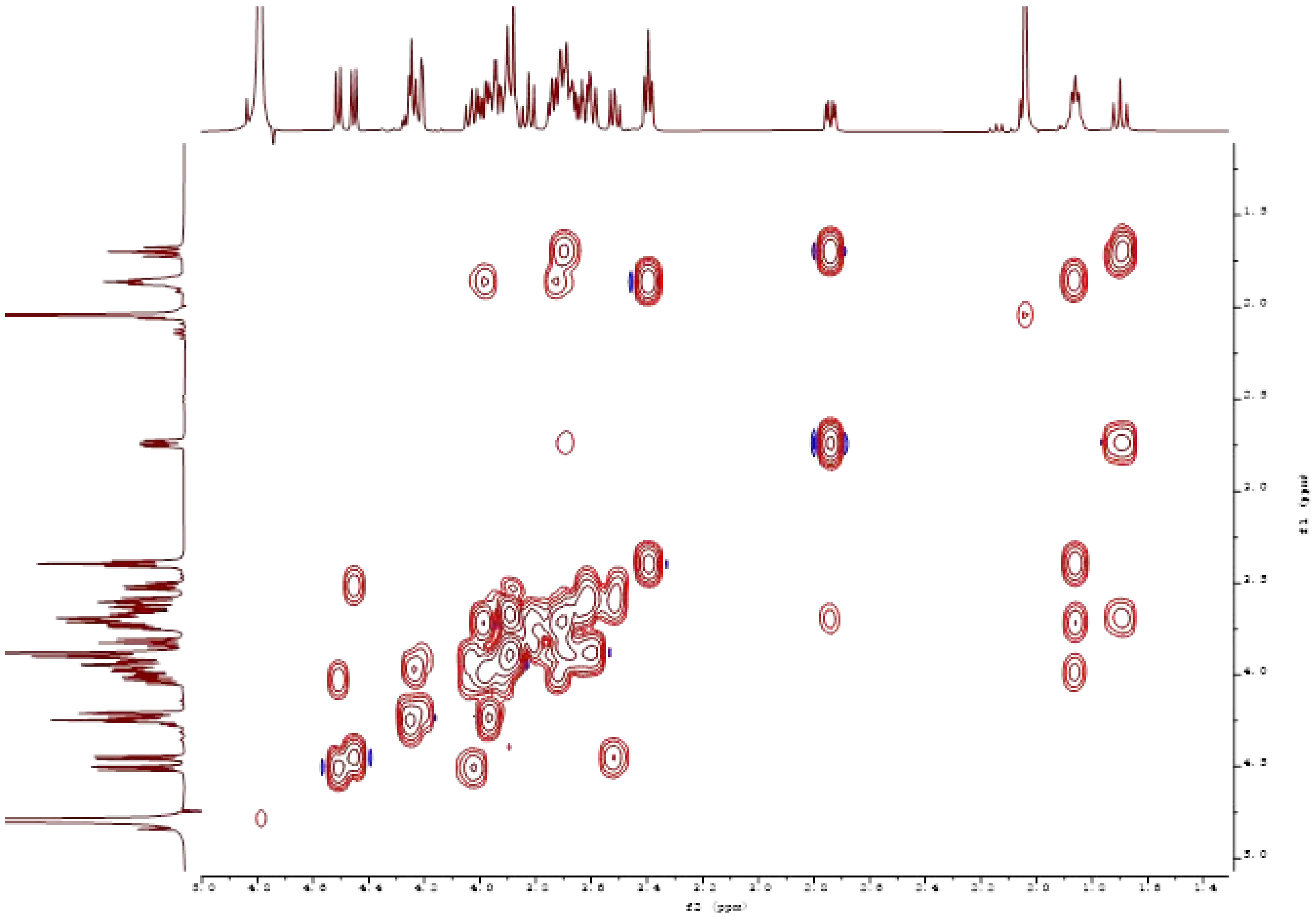

f2 (ppm)
f1 (ppm)
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
20
30
40
50
60
70
80
90
100


HO
OH
OH
AcNH
COOH
O
HO
OH
O
HO
OSO3H
O
HO
O
O
O
N3
OH
NHAc

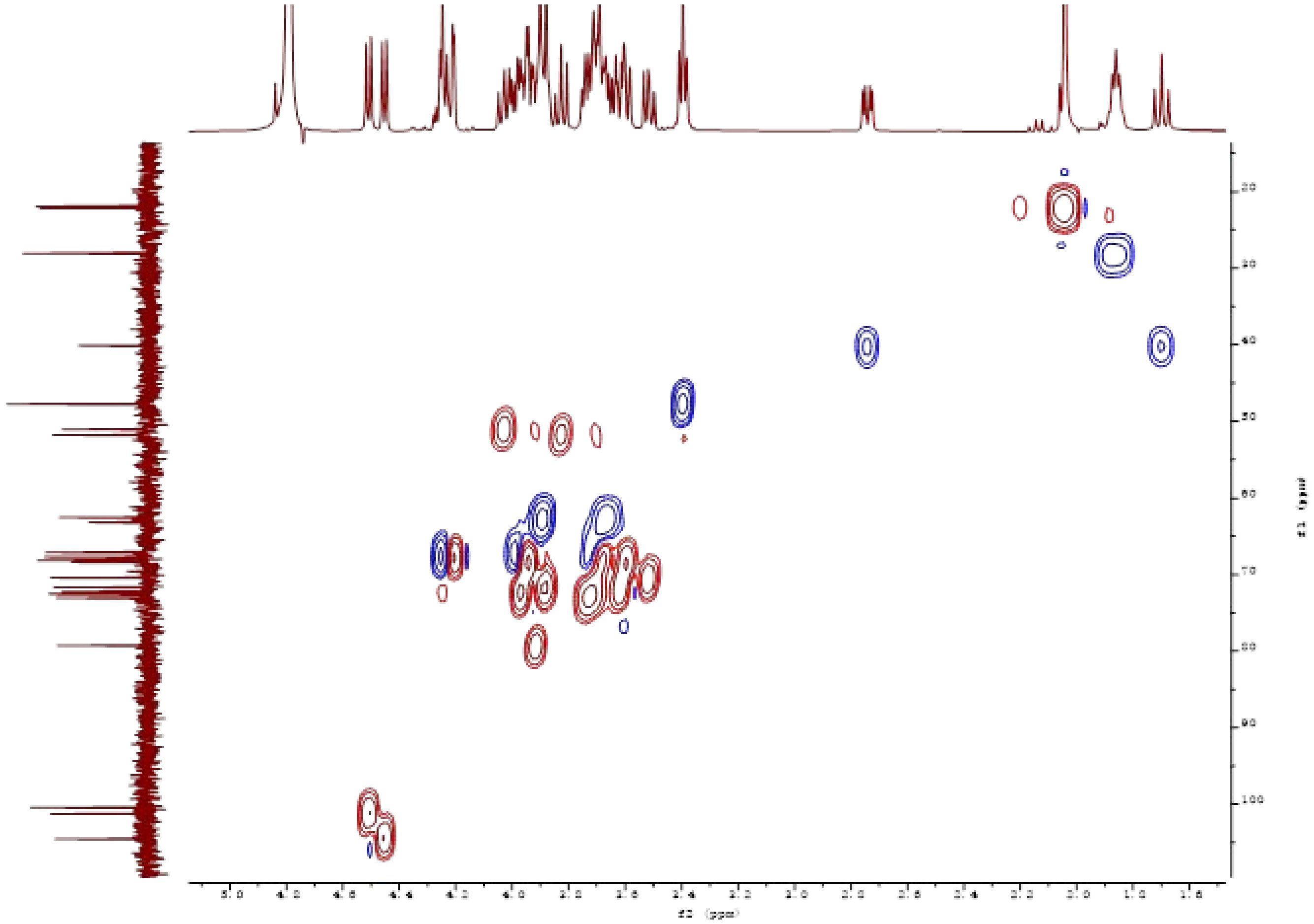
30


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

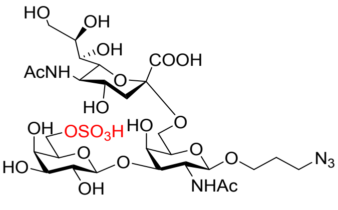

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



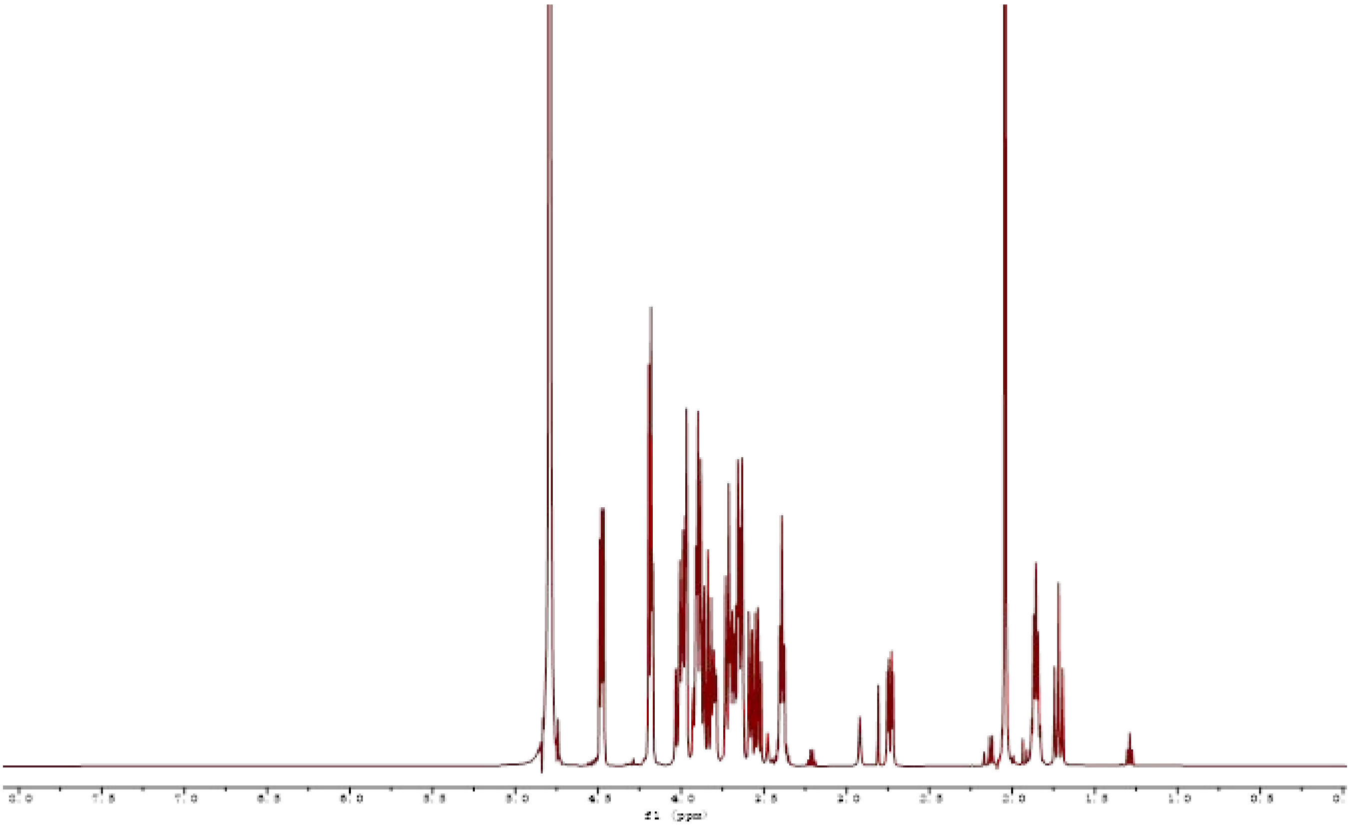
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

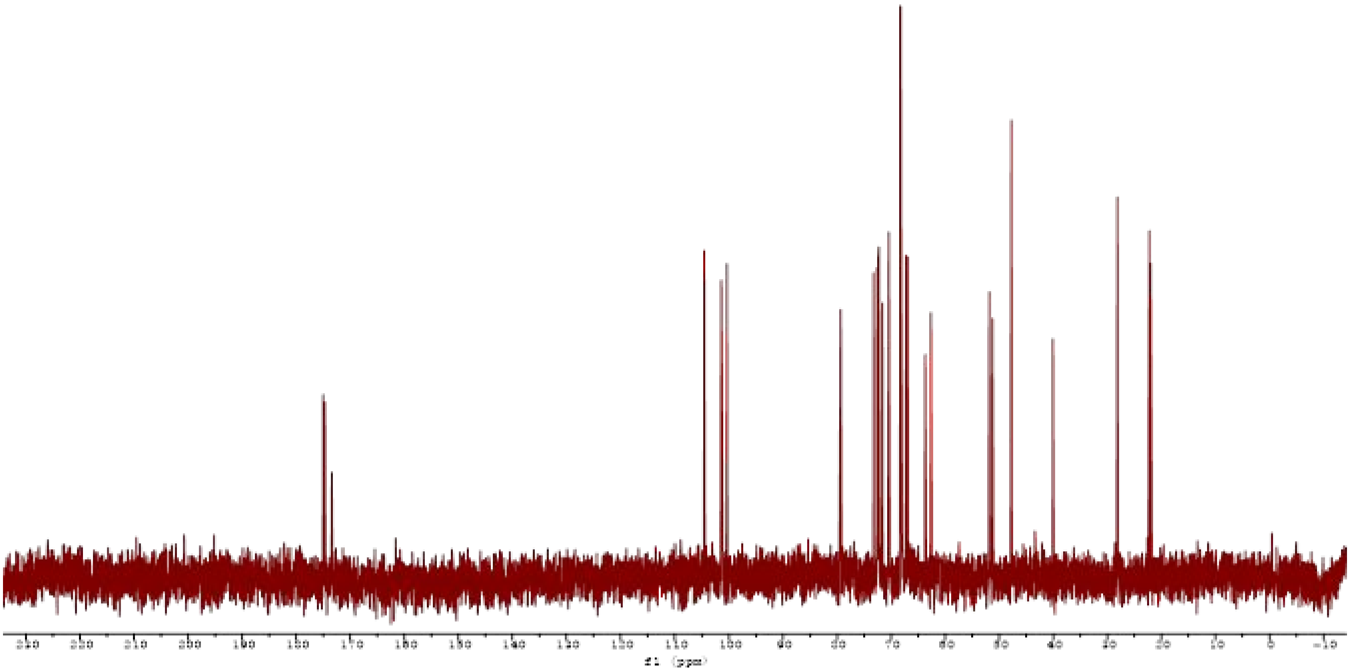


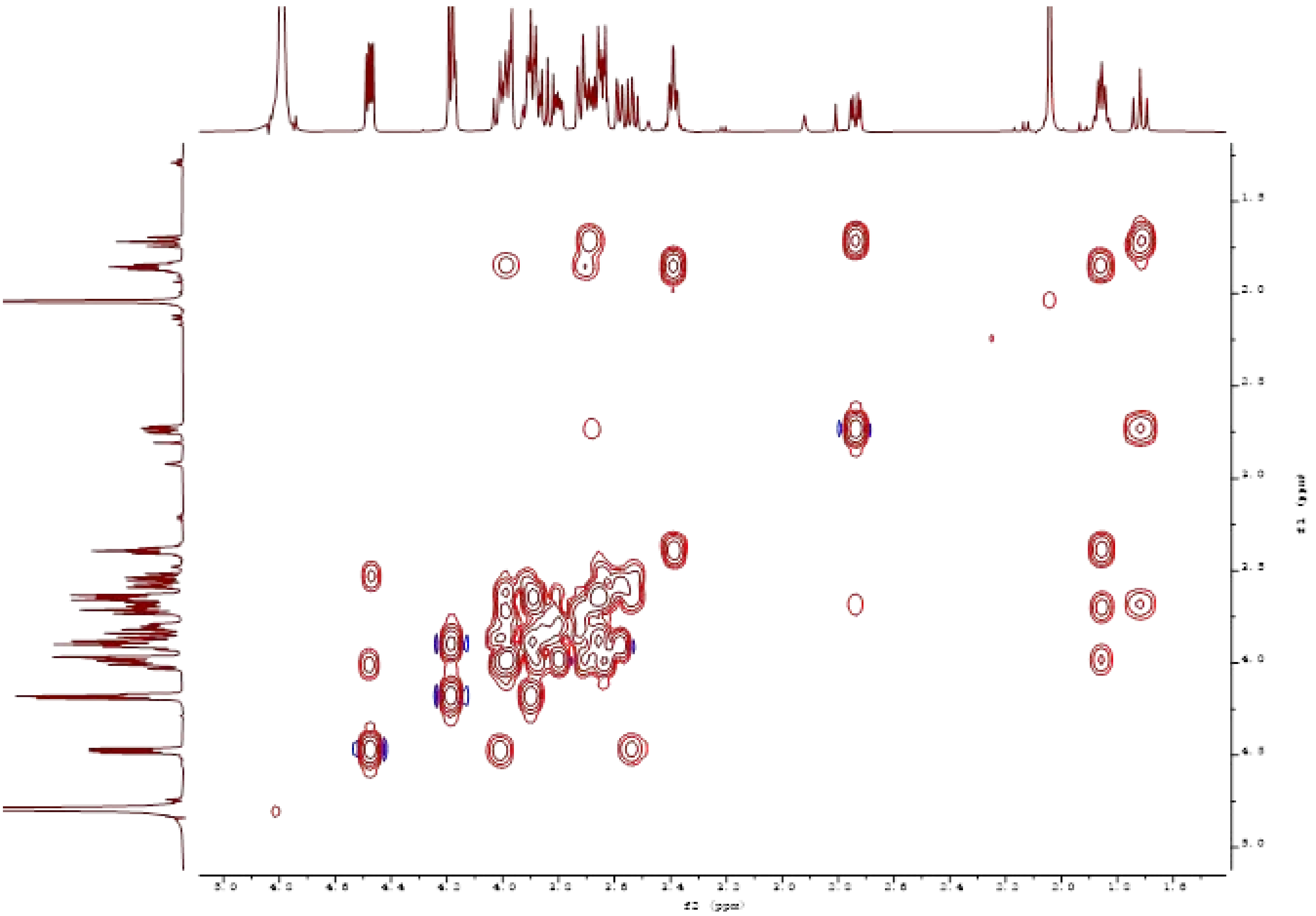
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

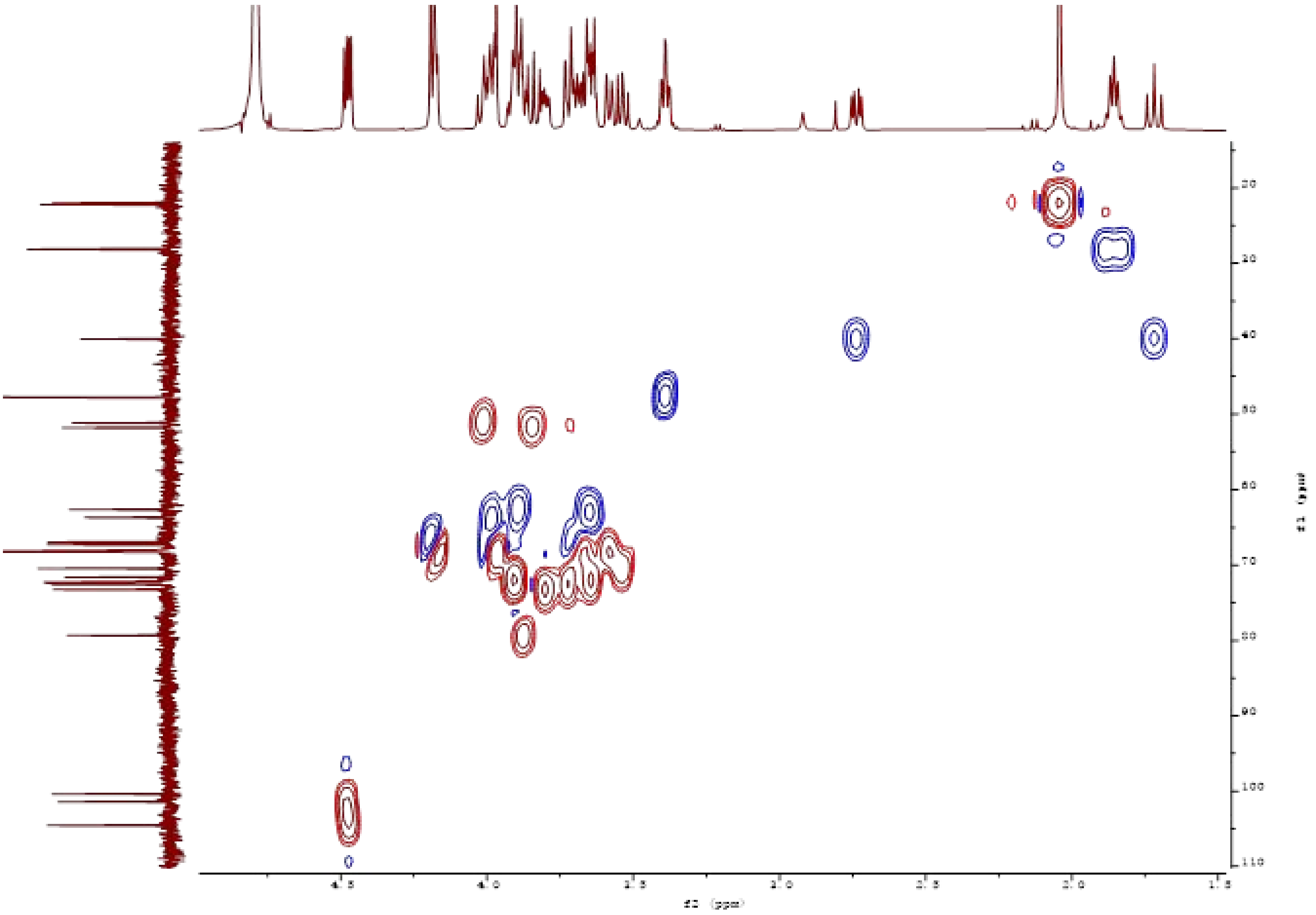

HO
OH
OH
COOH
AcNH
O
HO
O
OH
OSO$_3$H
HO
O
HO
O
O
O
N$_3$
OH
NHAc

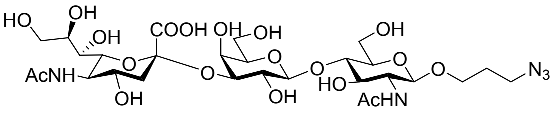
31


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

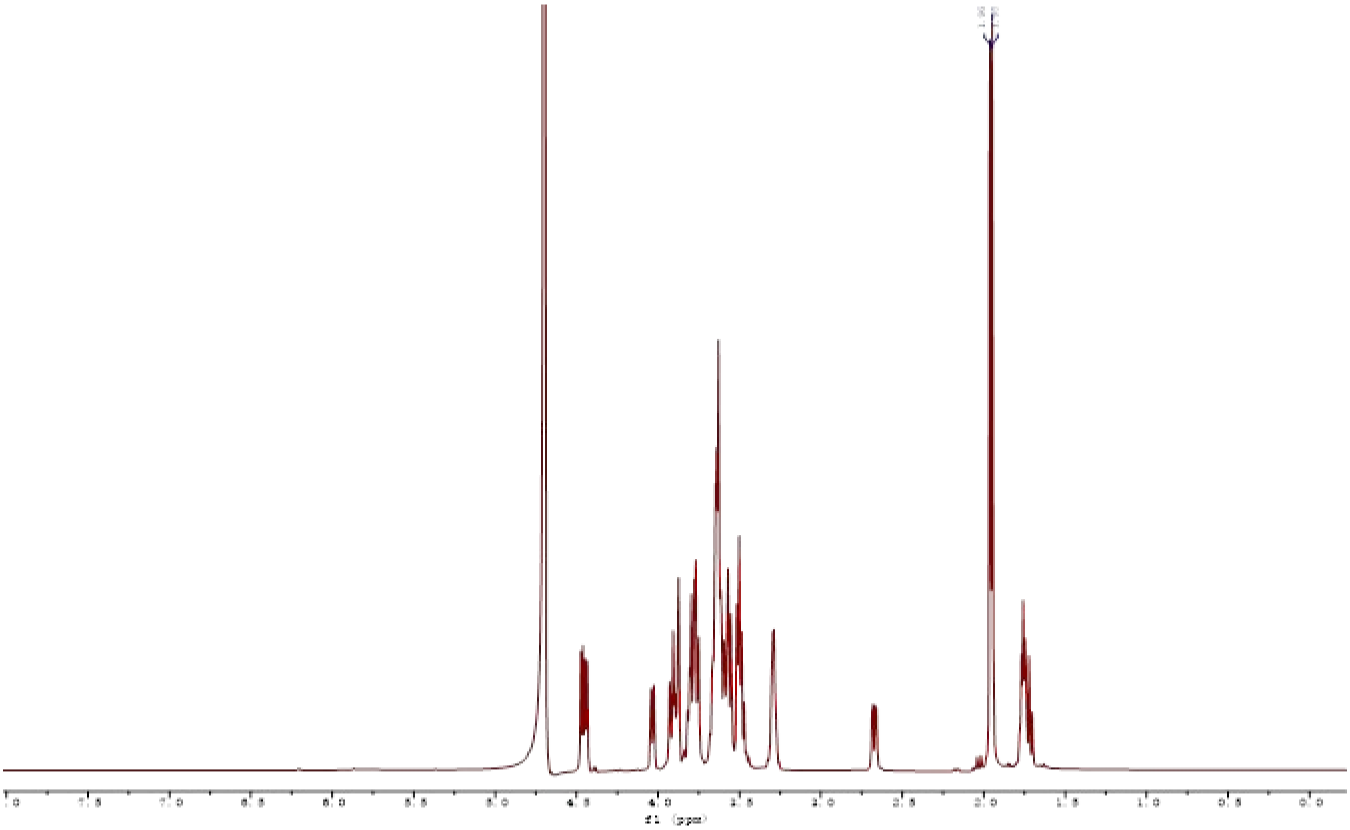

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

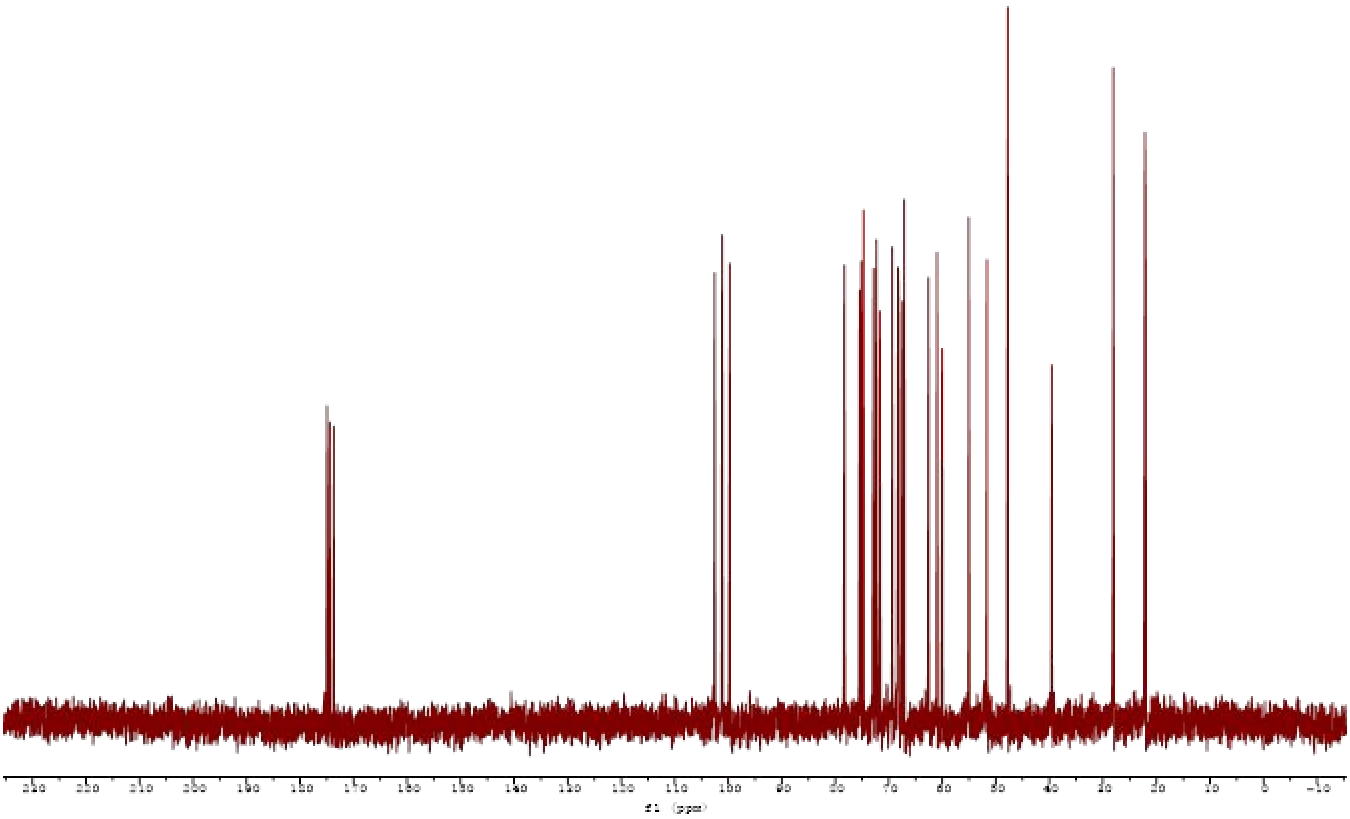

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

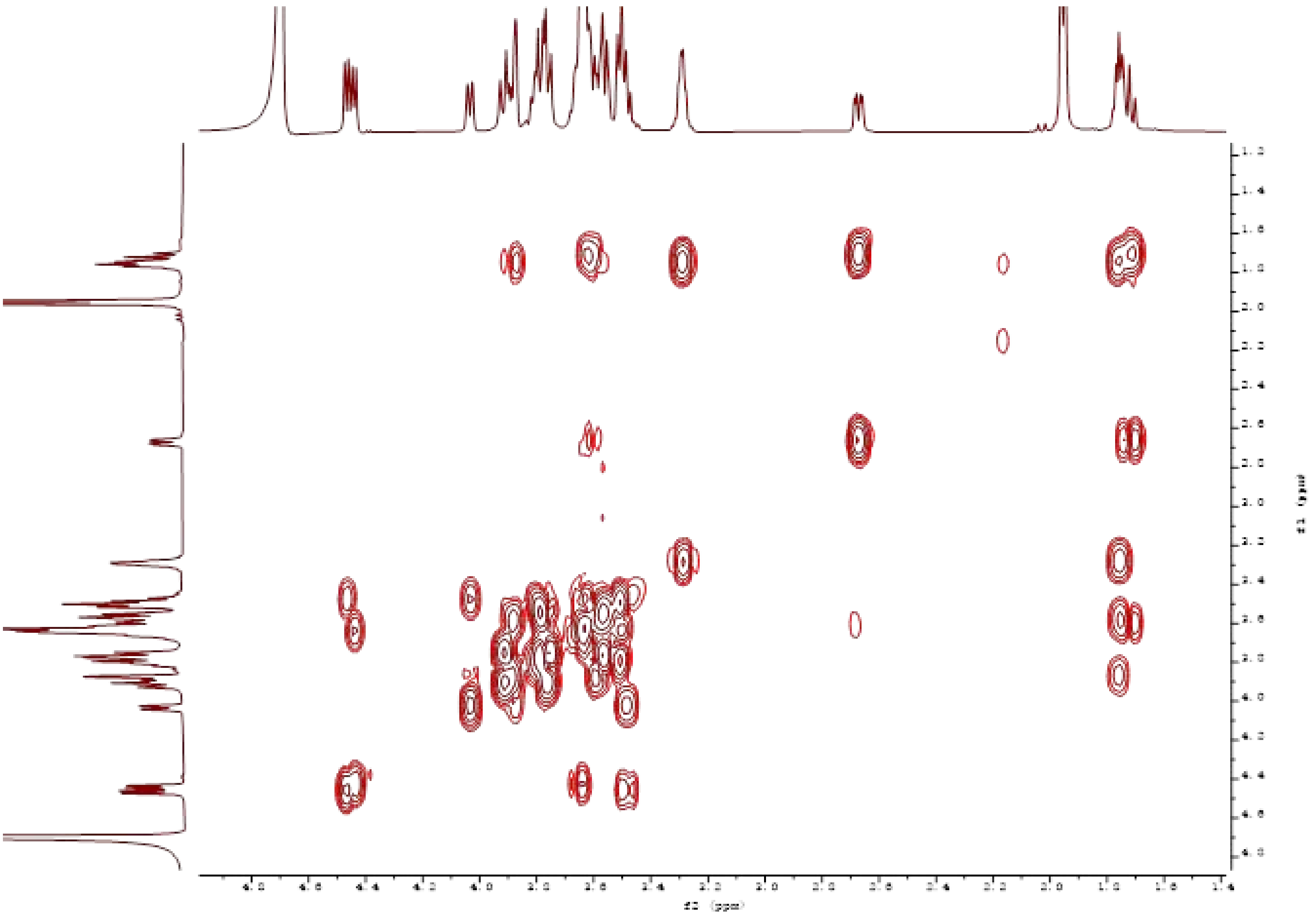

4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

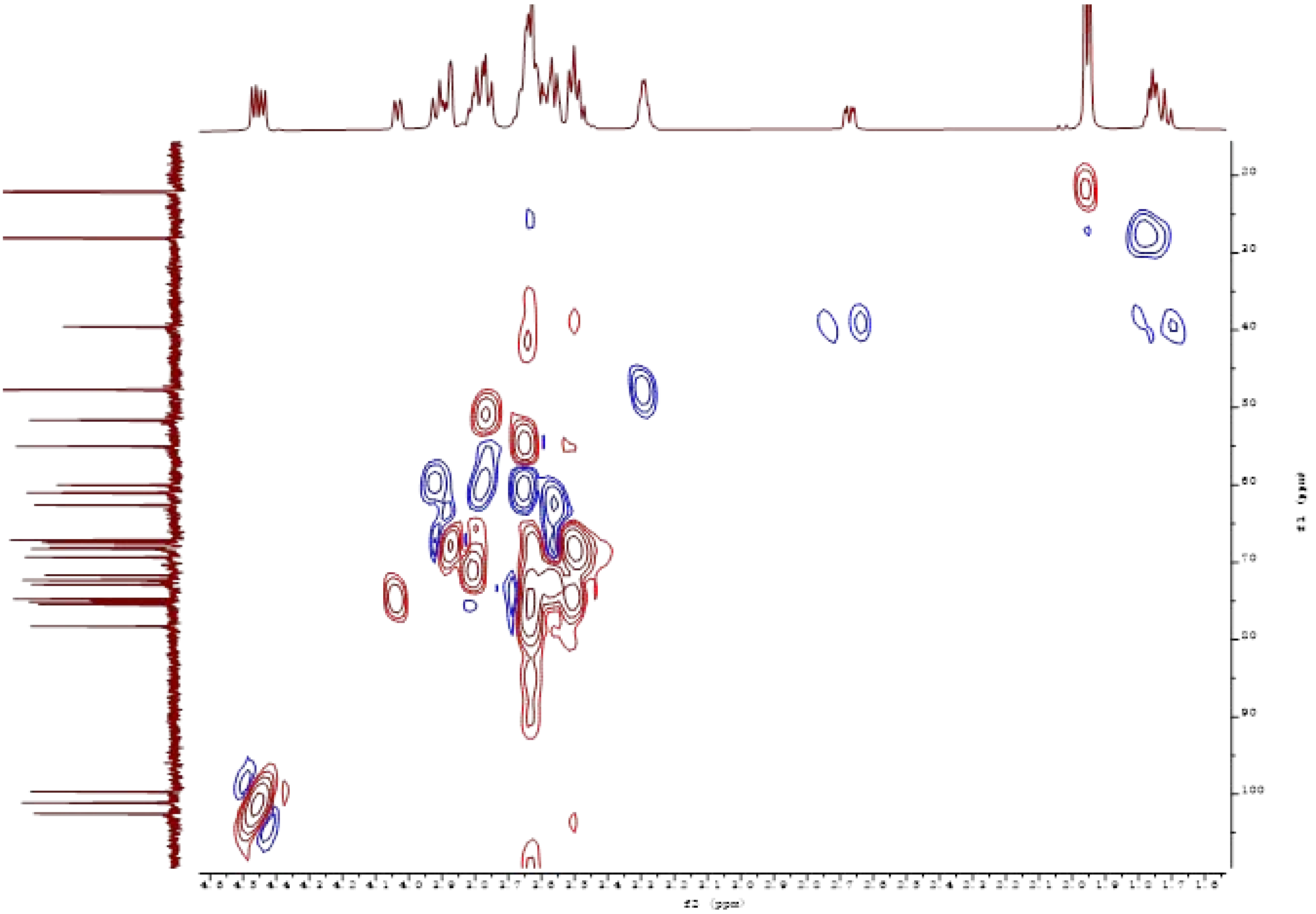


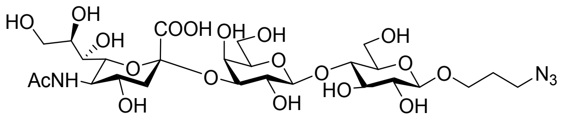
32



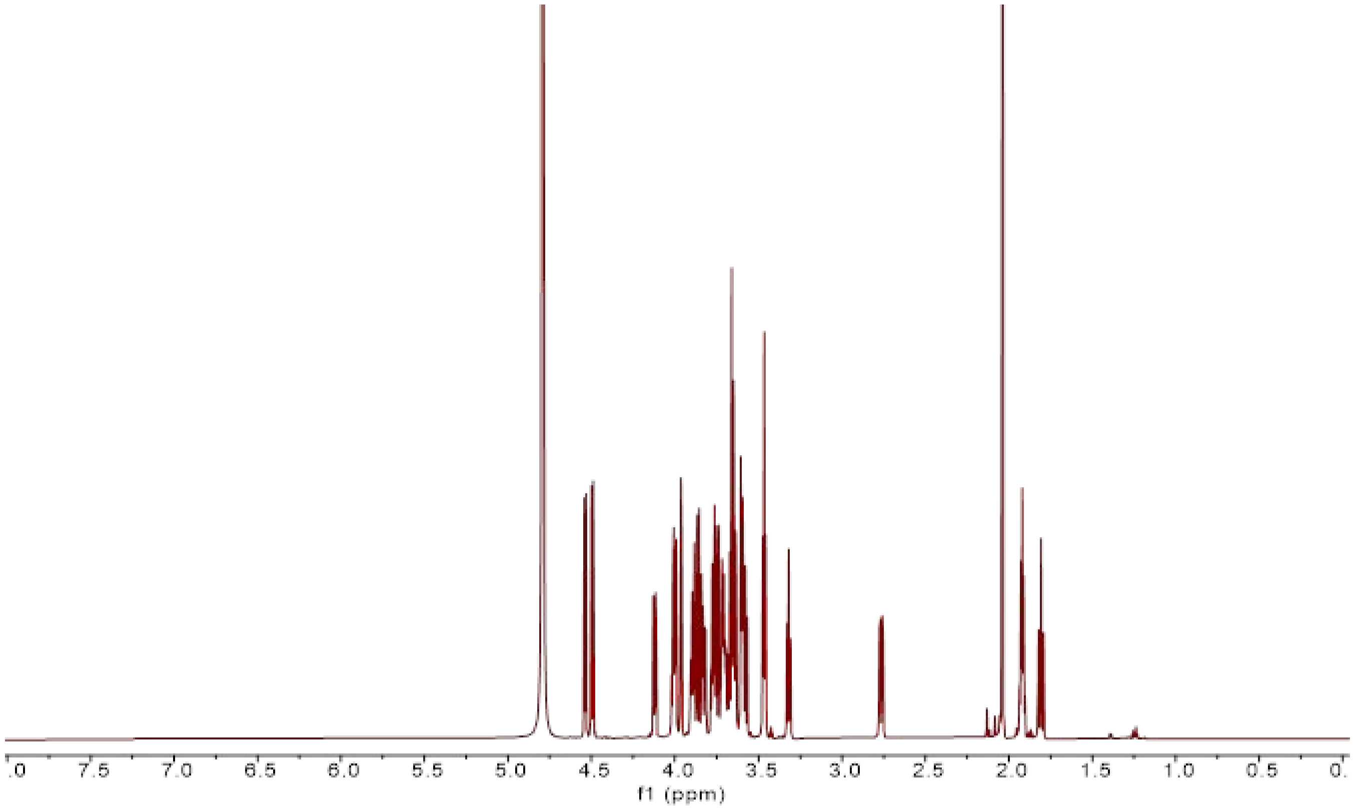


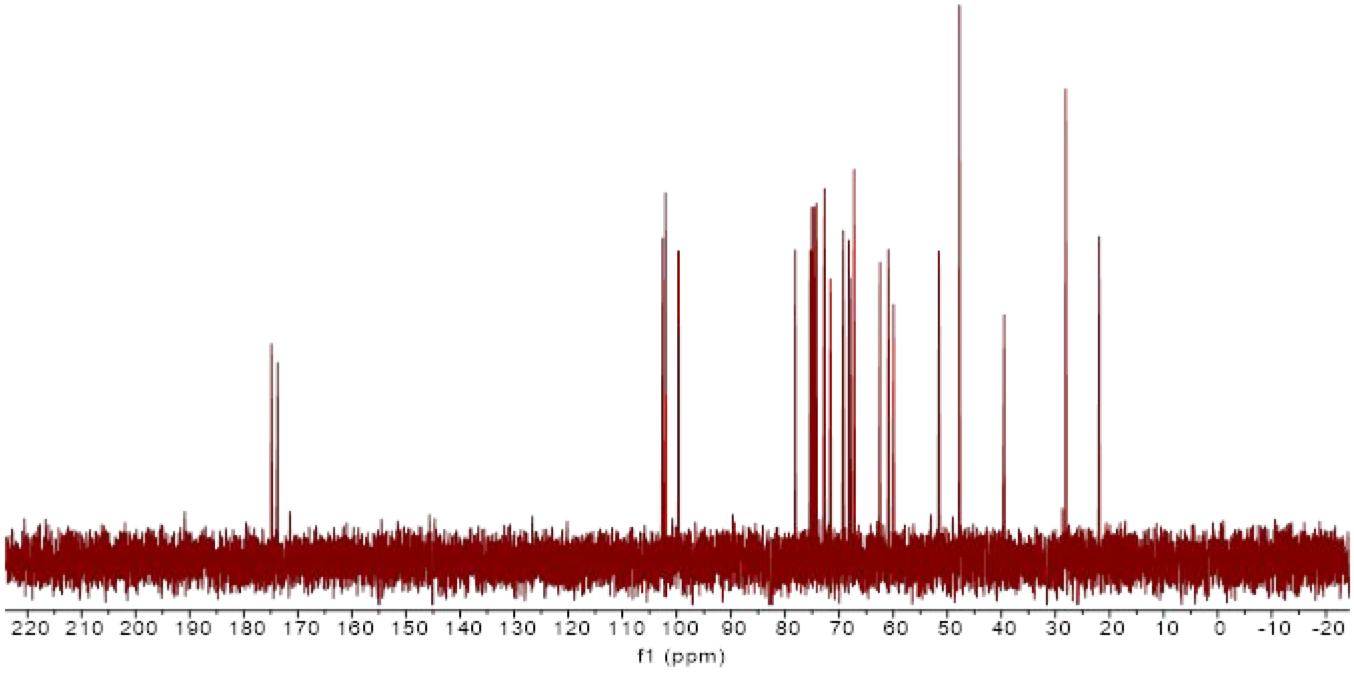

f2 (ppm)
f1 (ppm)

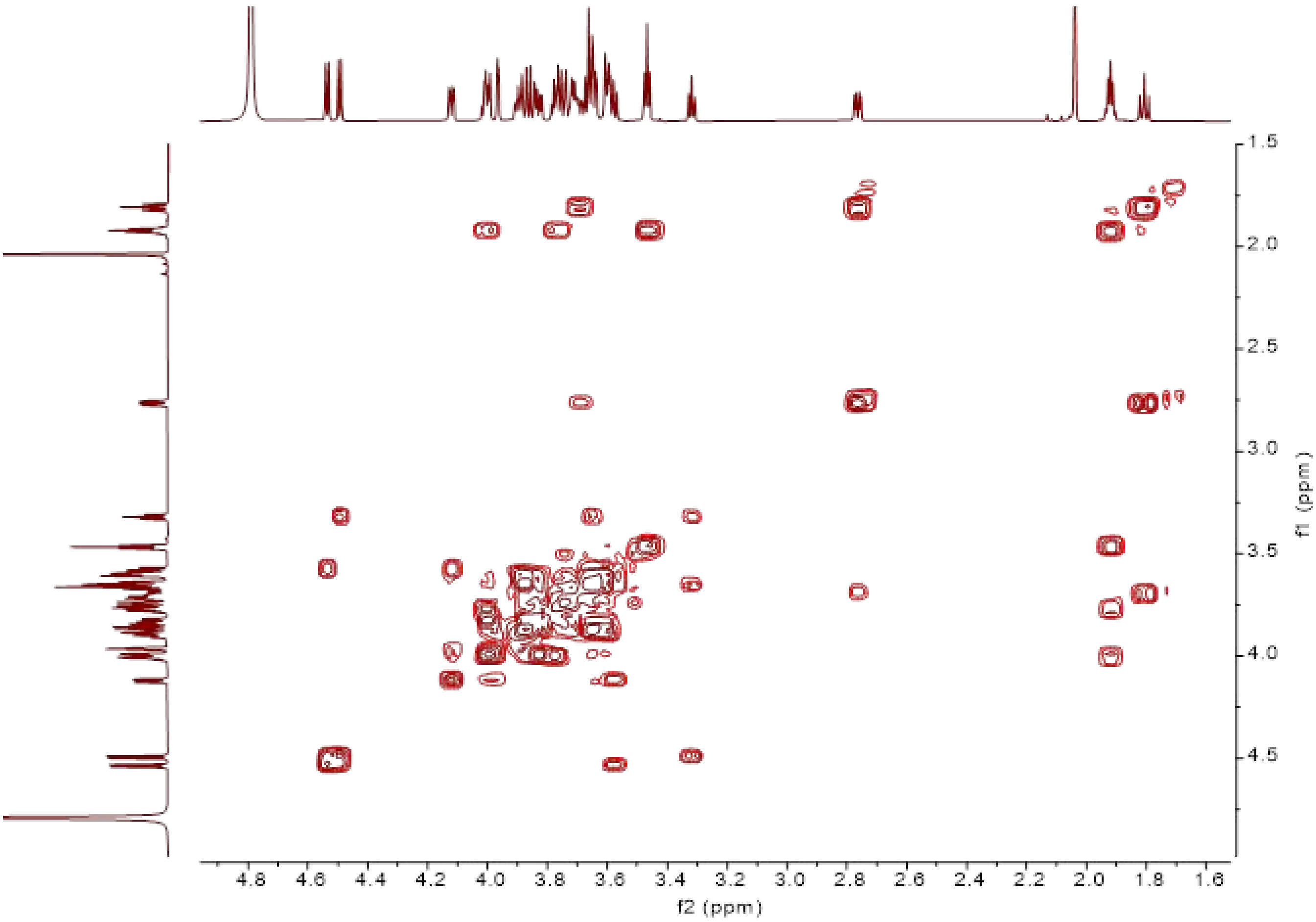

f2 (ppm)
f1 (ppm)

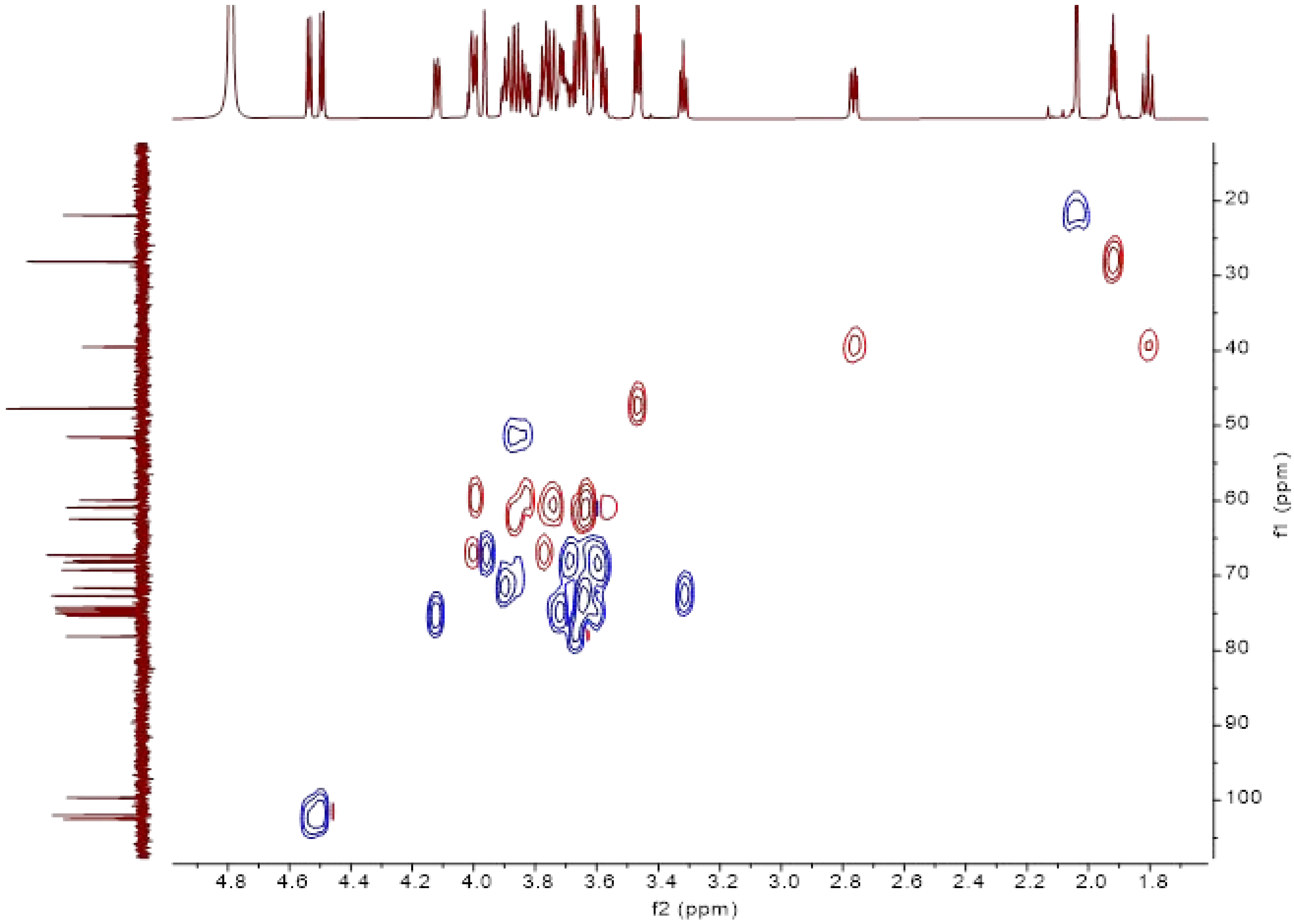

HO
OH
OH
COOH
OH
OH
OH
AcNH
O
O
O
O
O
O
OH
OH
HO
OH
N3

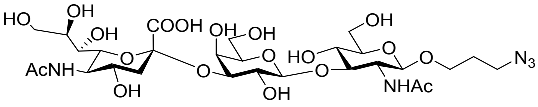
33


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

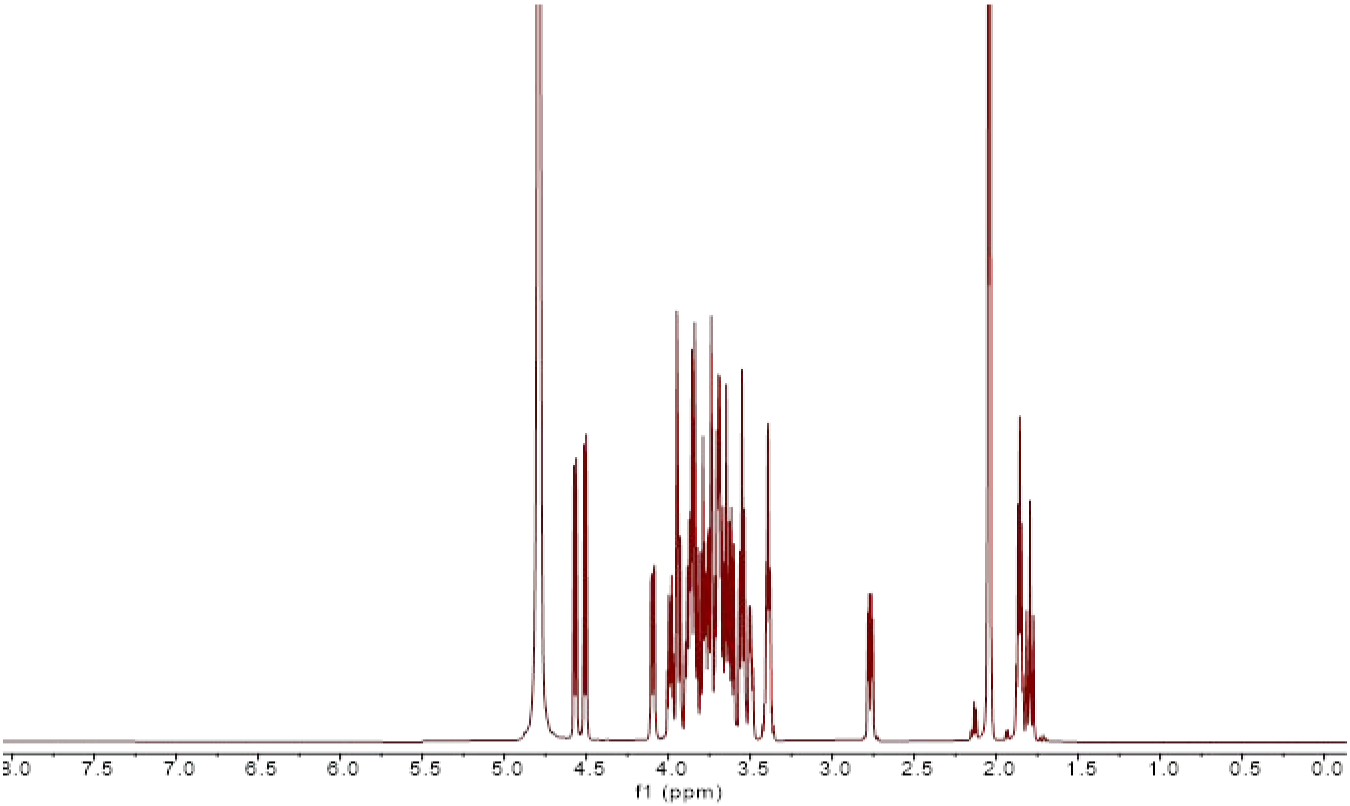

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

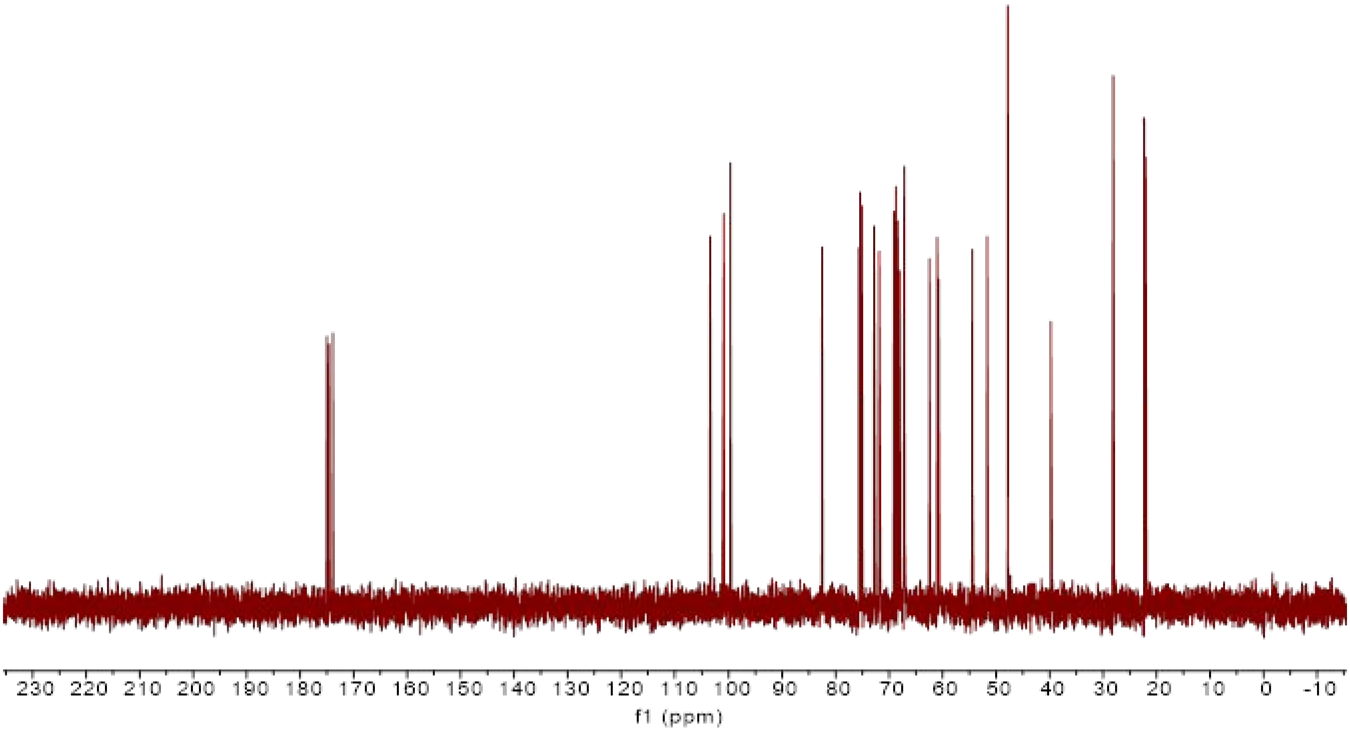

1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f2 (ppm)

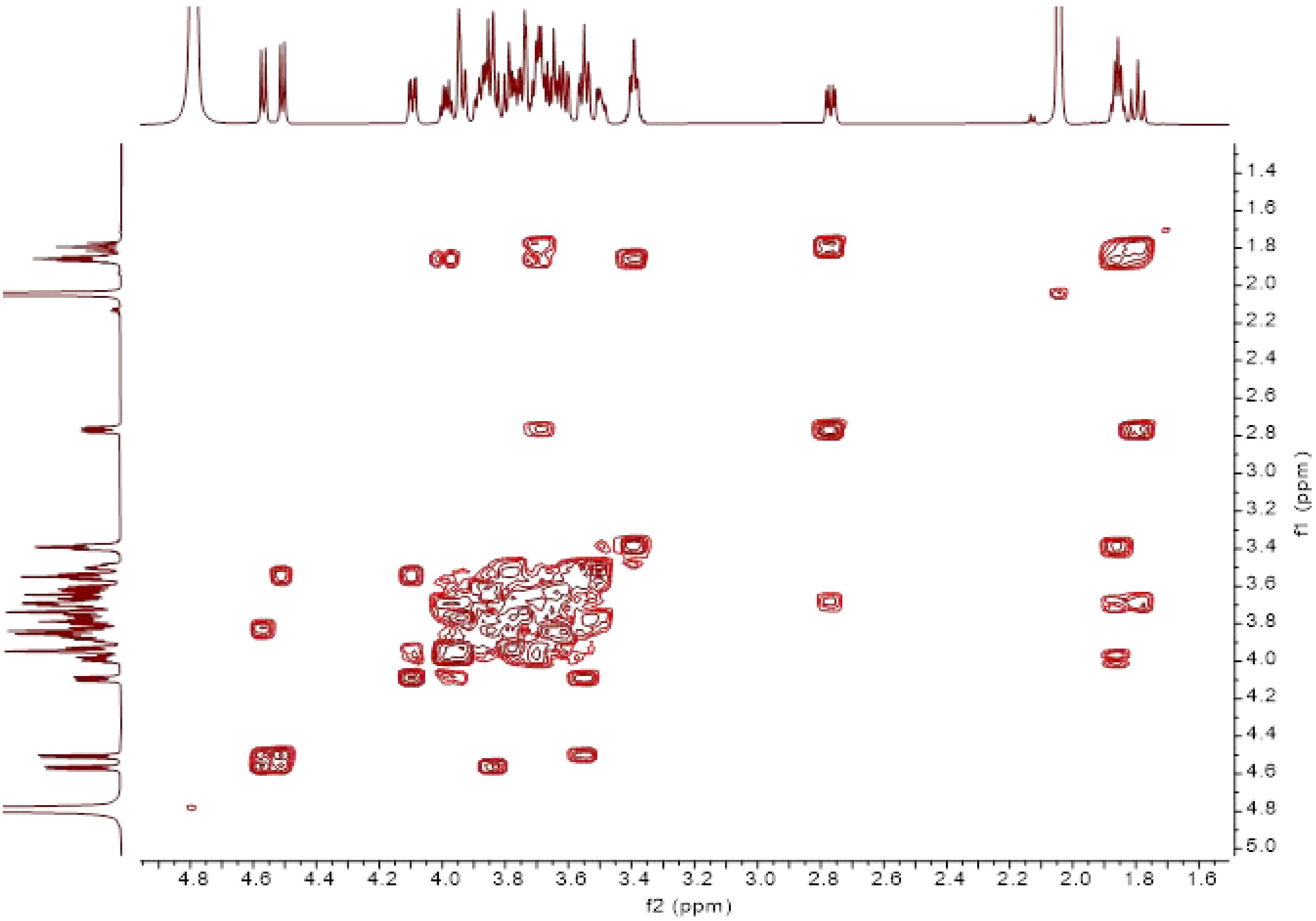

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f2 (ppm)

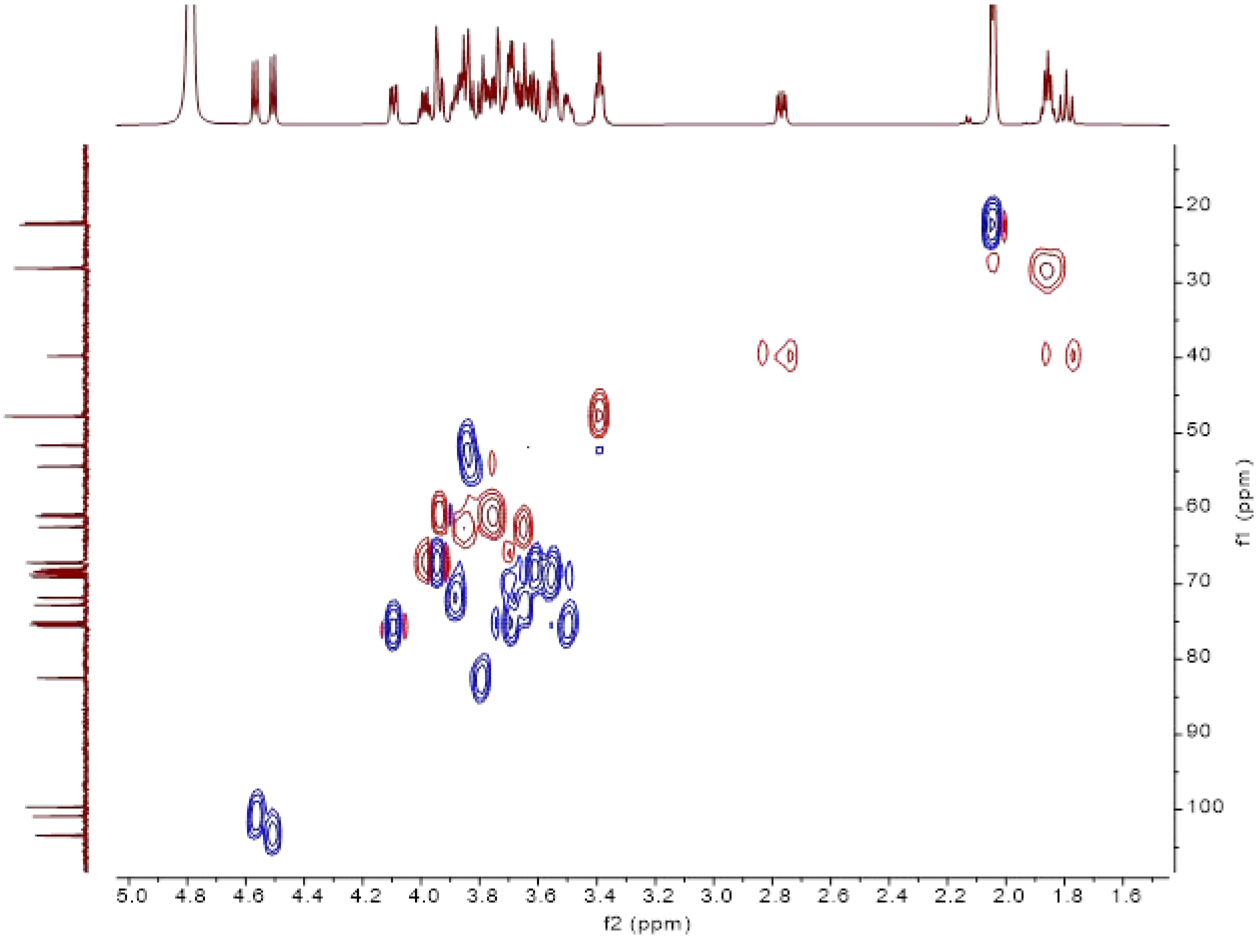

HO
OH
OH
COOH
OH
OH
OH
AcNH
O
O
O
HO
O
O
O
N3
OH
OH
NHAc

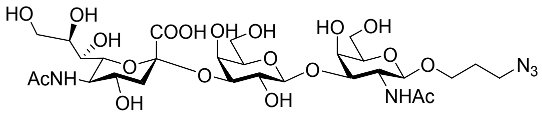
34


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)

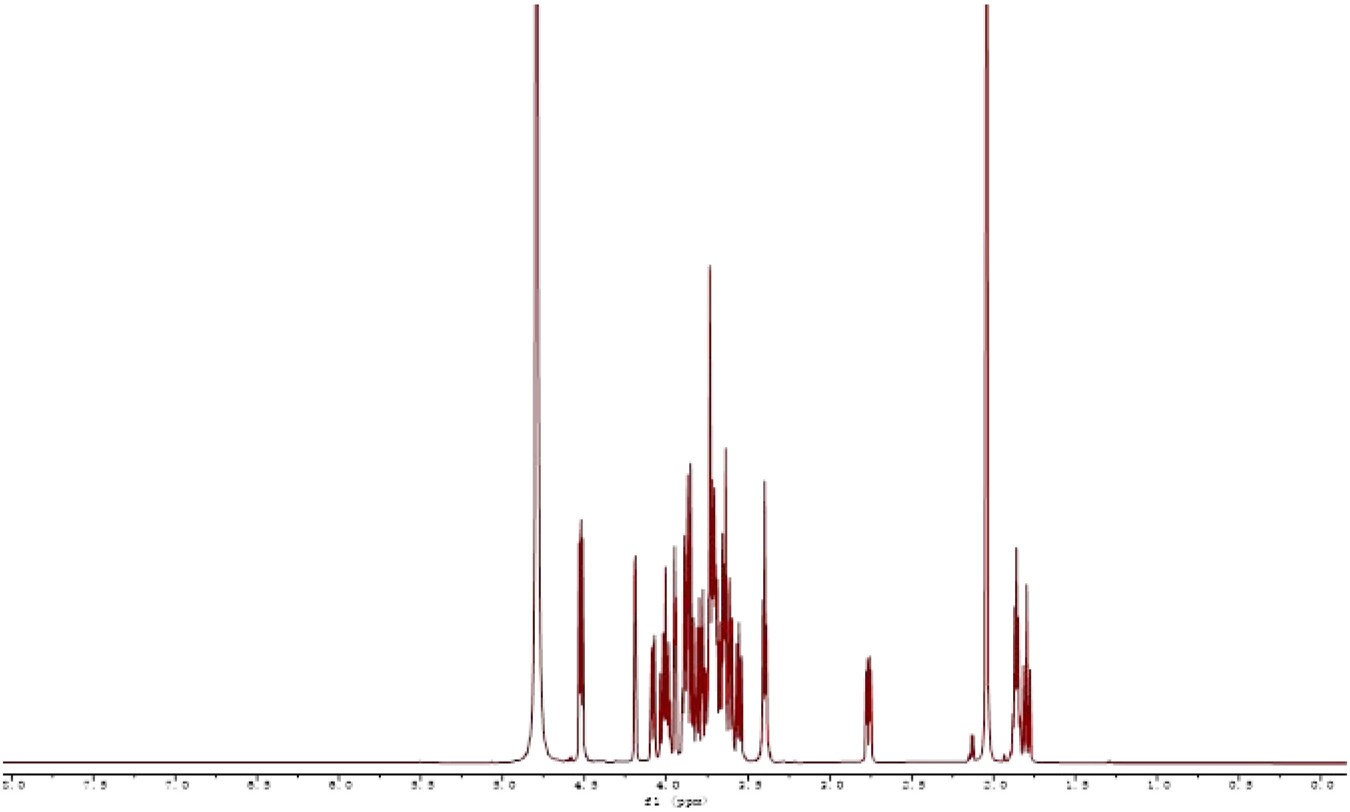

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

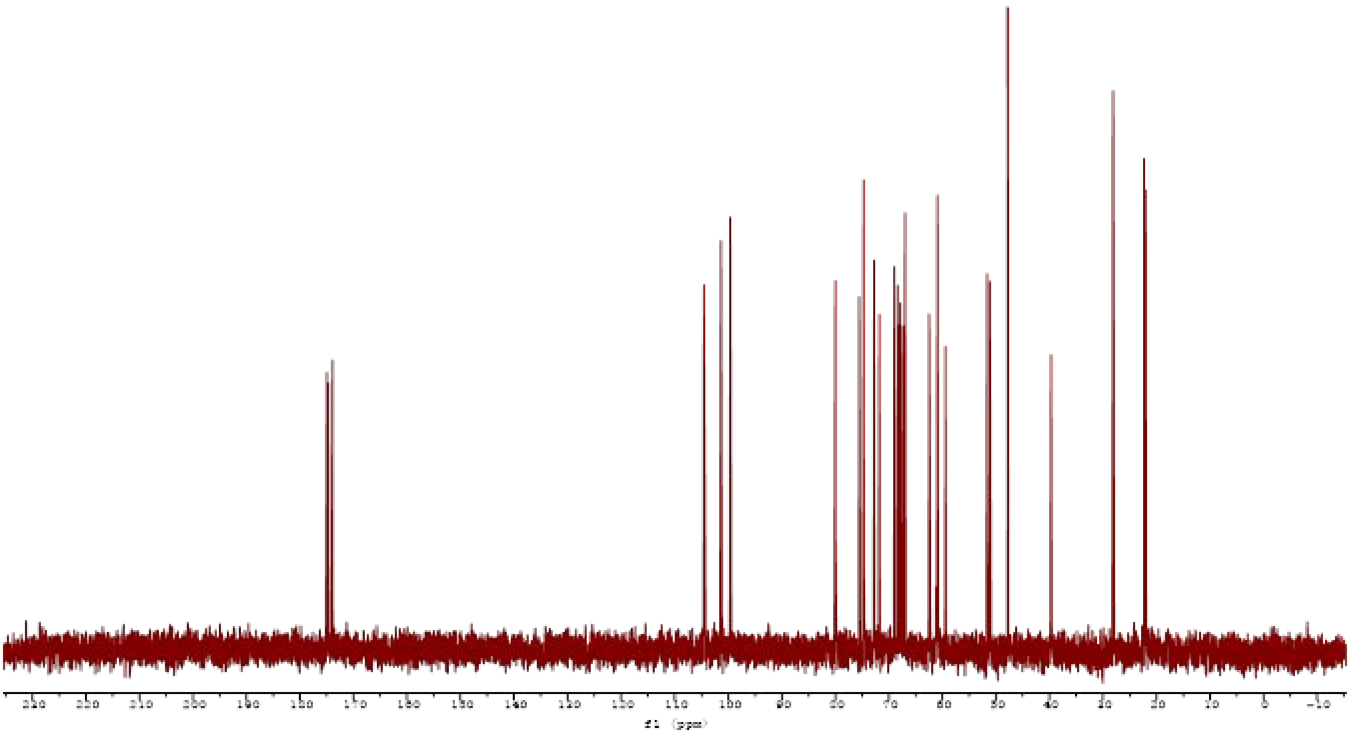

1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

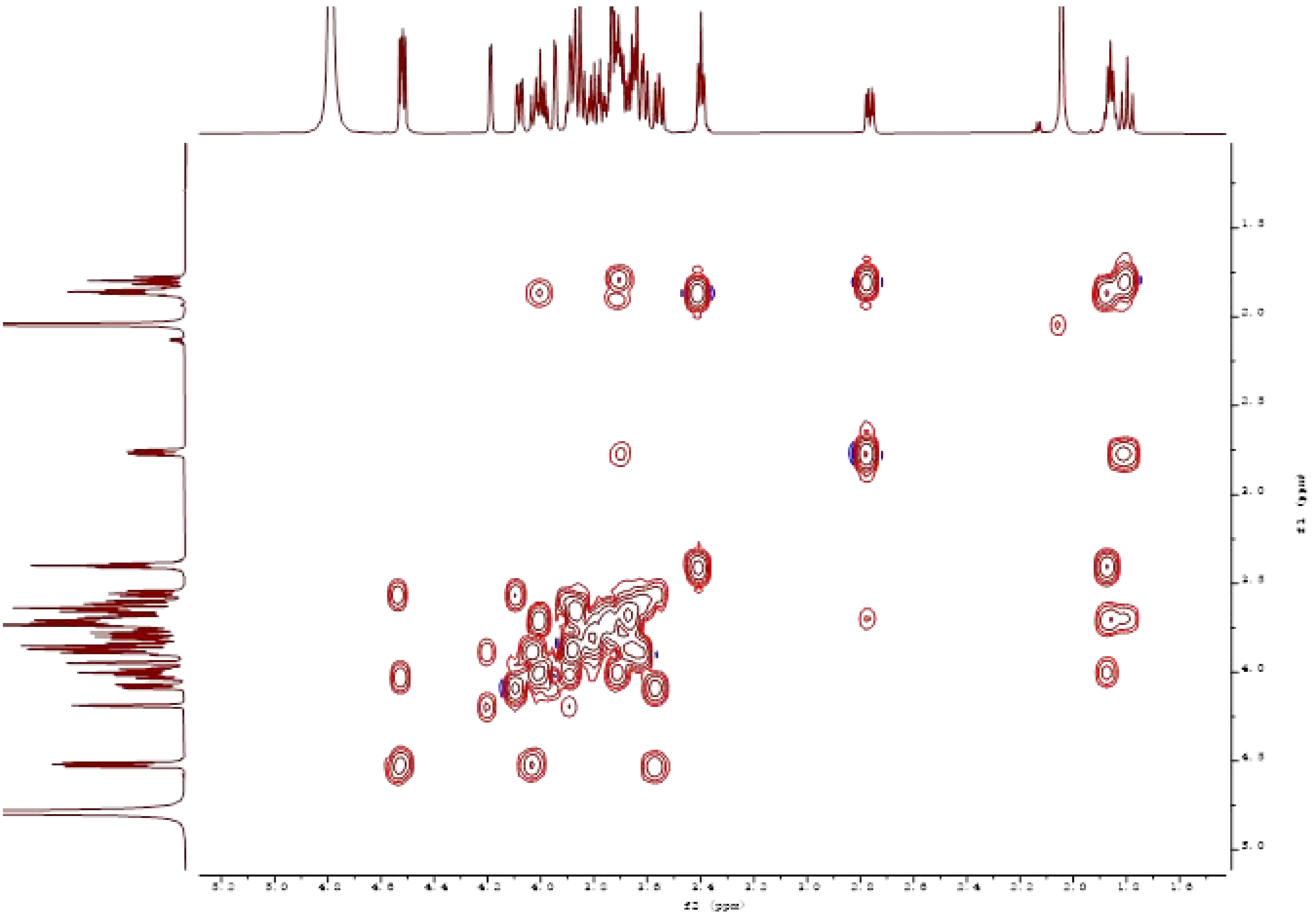

20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

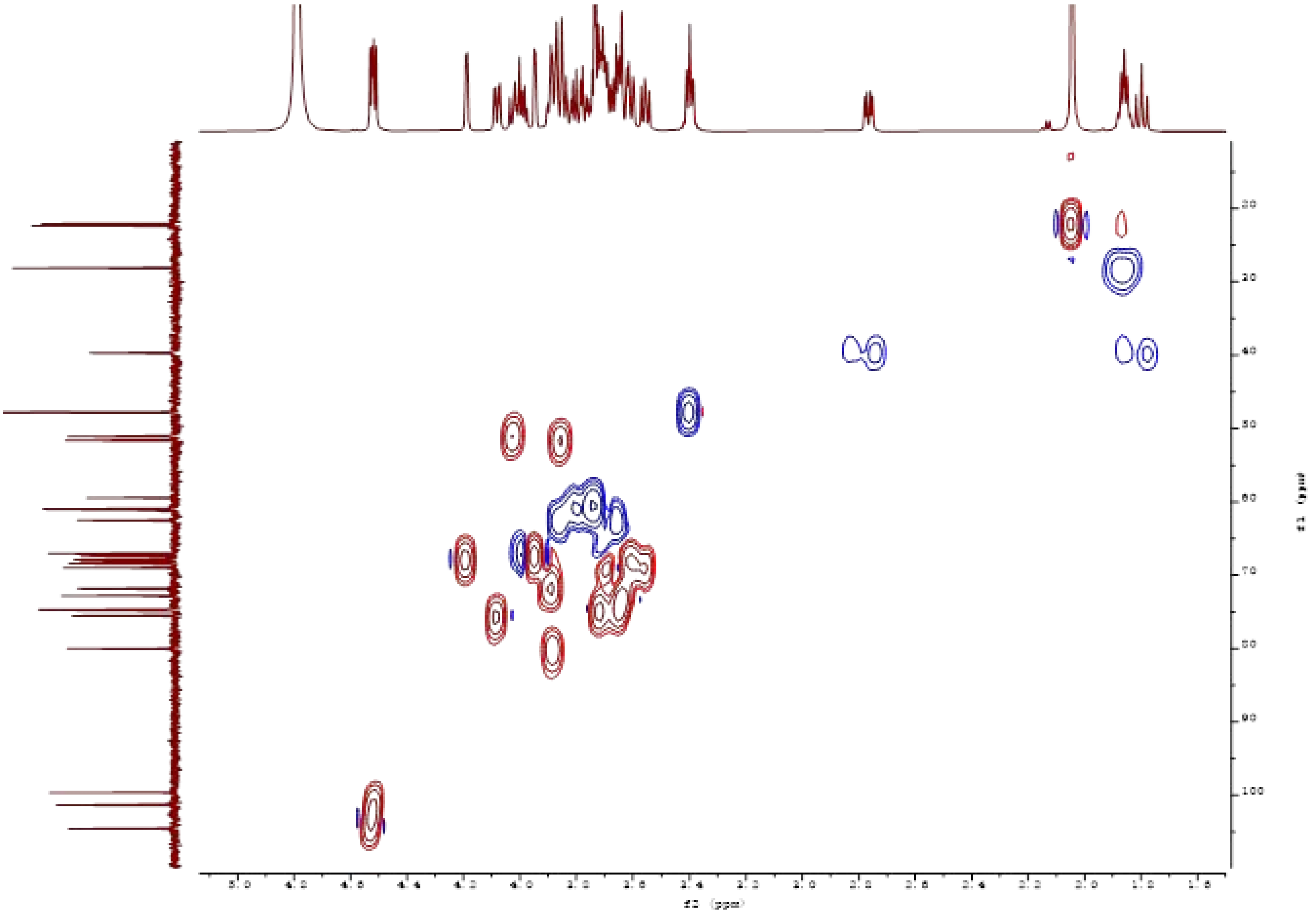

HO
OH
OH
COOH
OH
OH
HO
OH
AcNH
O
O
O
O
O
OH
OH
NHAc
N_3

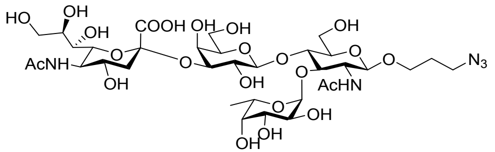
35


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

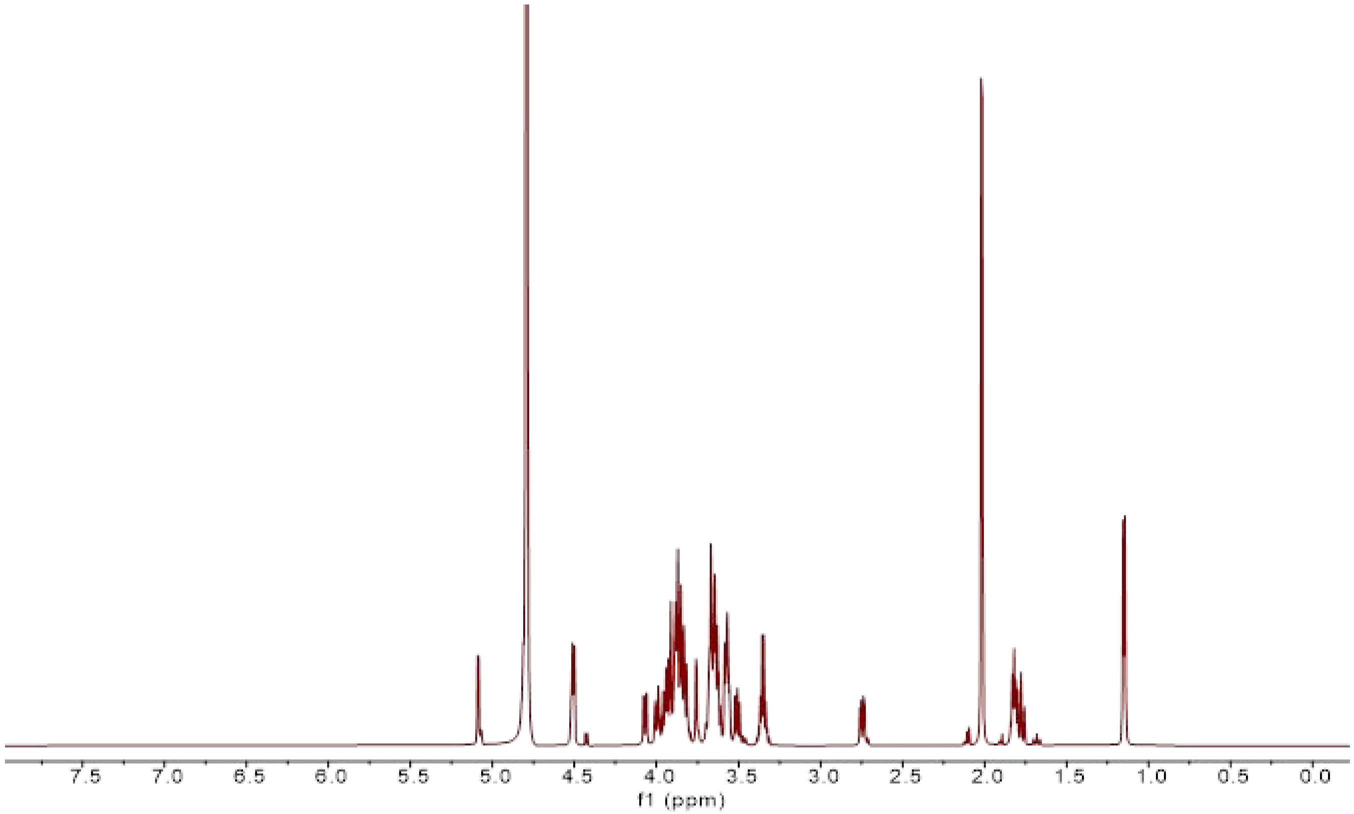

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

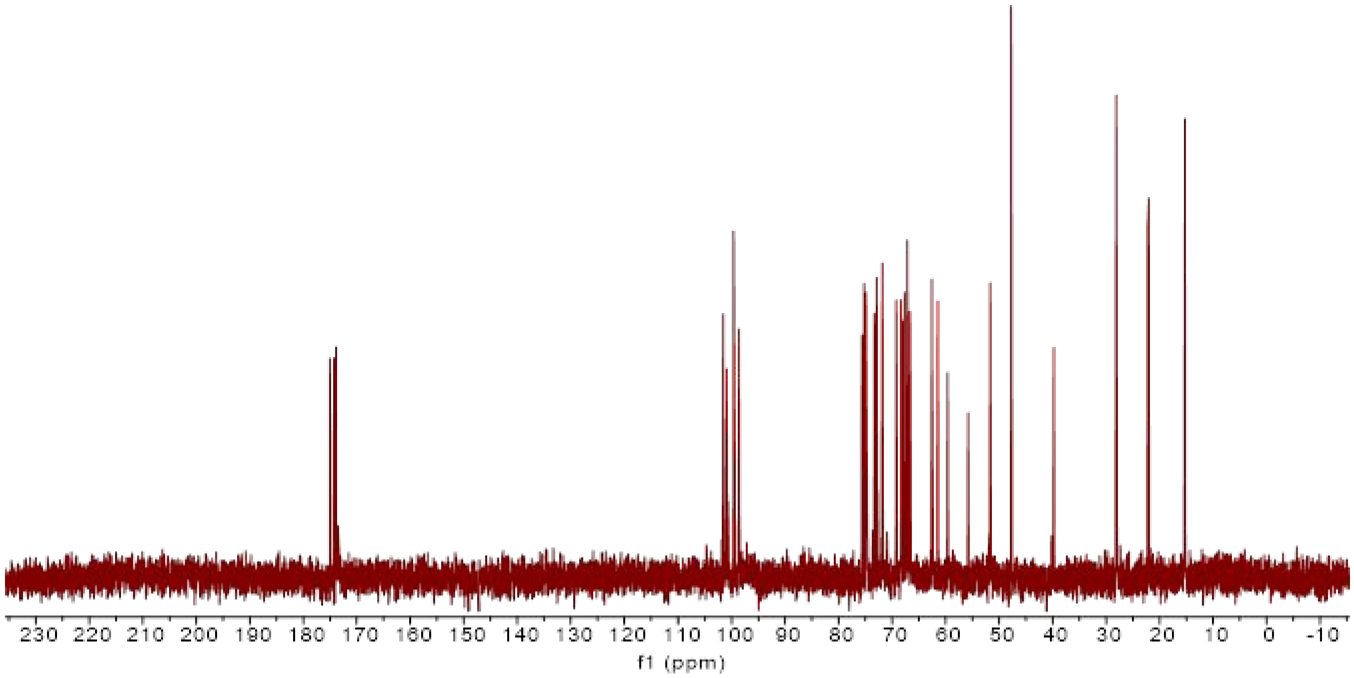

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

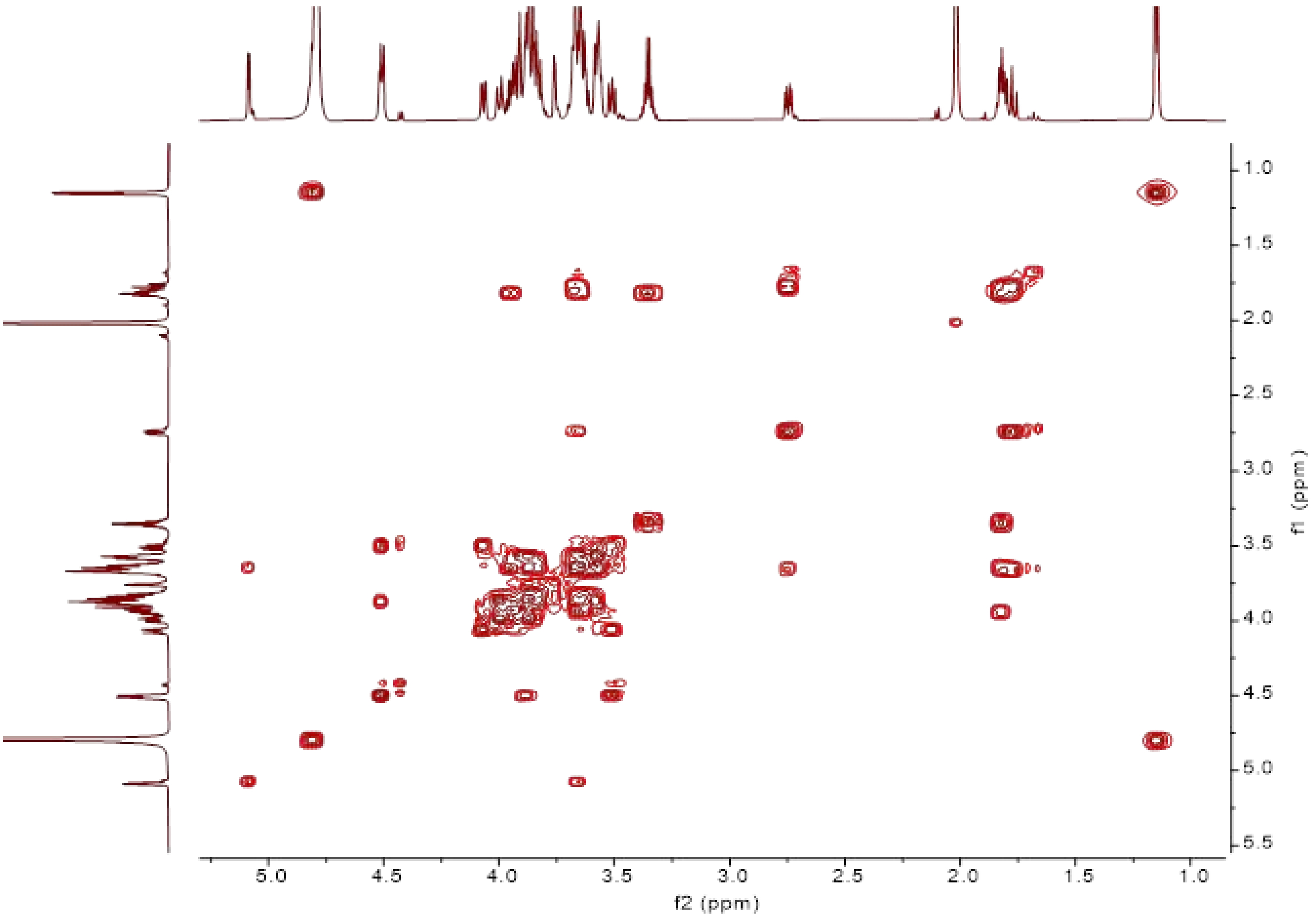

20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

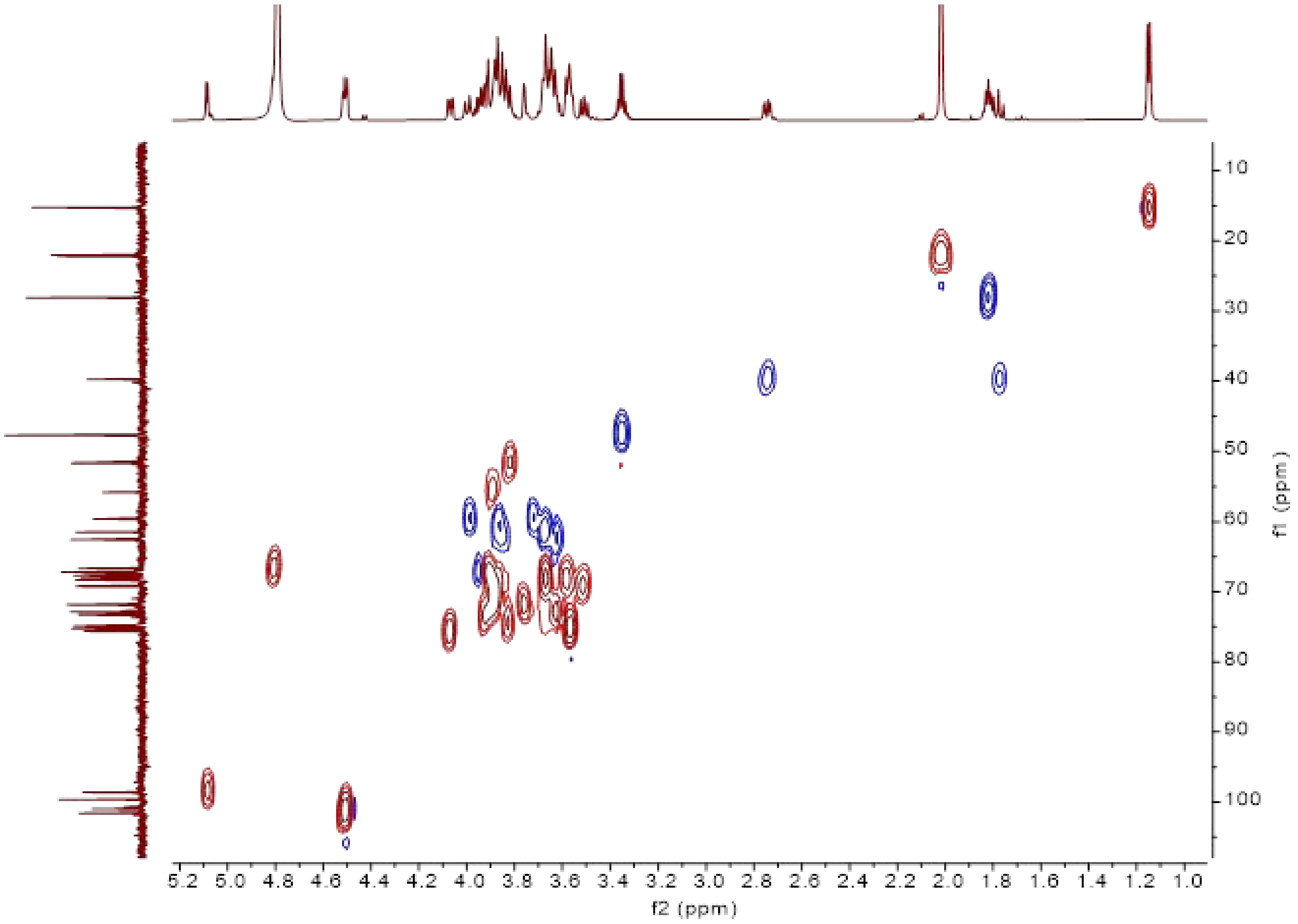

HO
OH
OH
COOH
OH
OH
OH
AcNH
O
OH
O
OH
O
O
AcHN
O
N3
O
OH
OH
OH
O

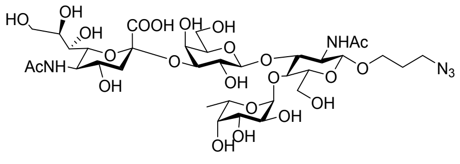
36


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)

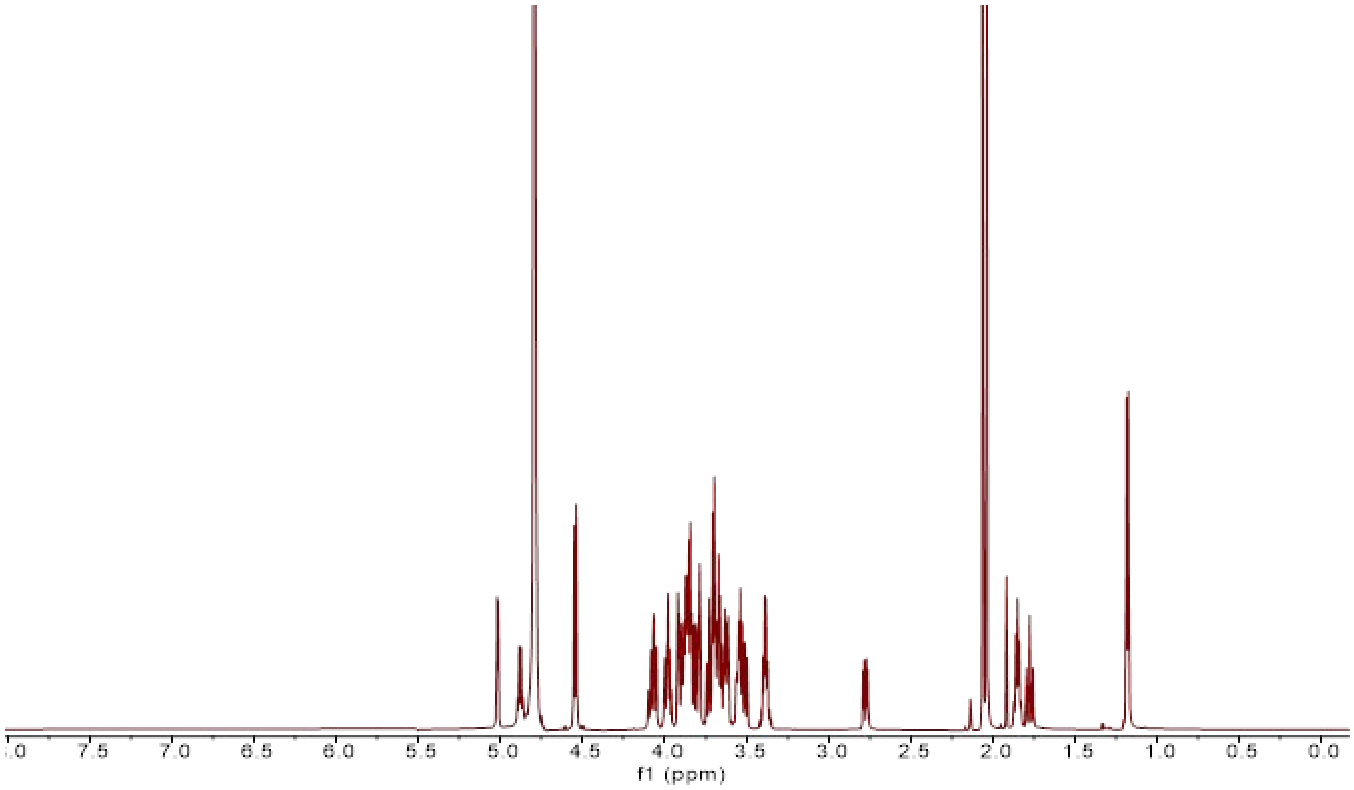

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

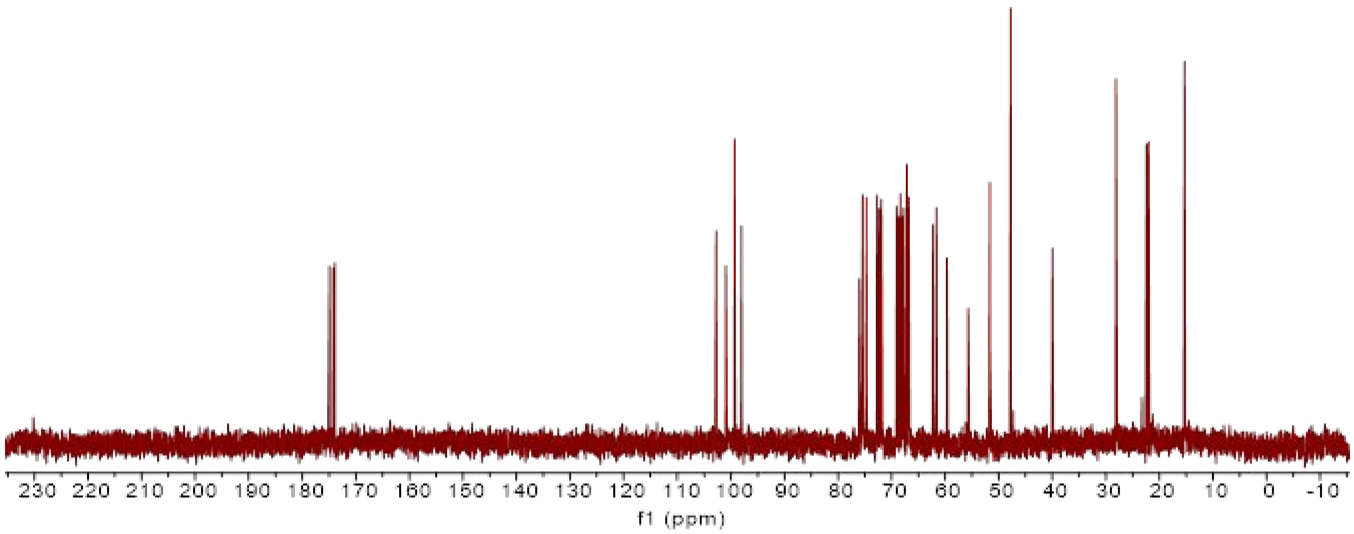

1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

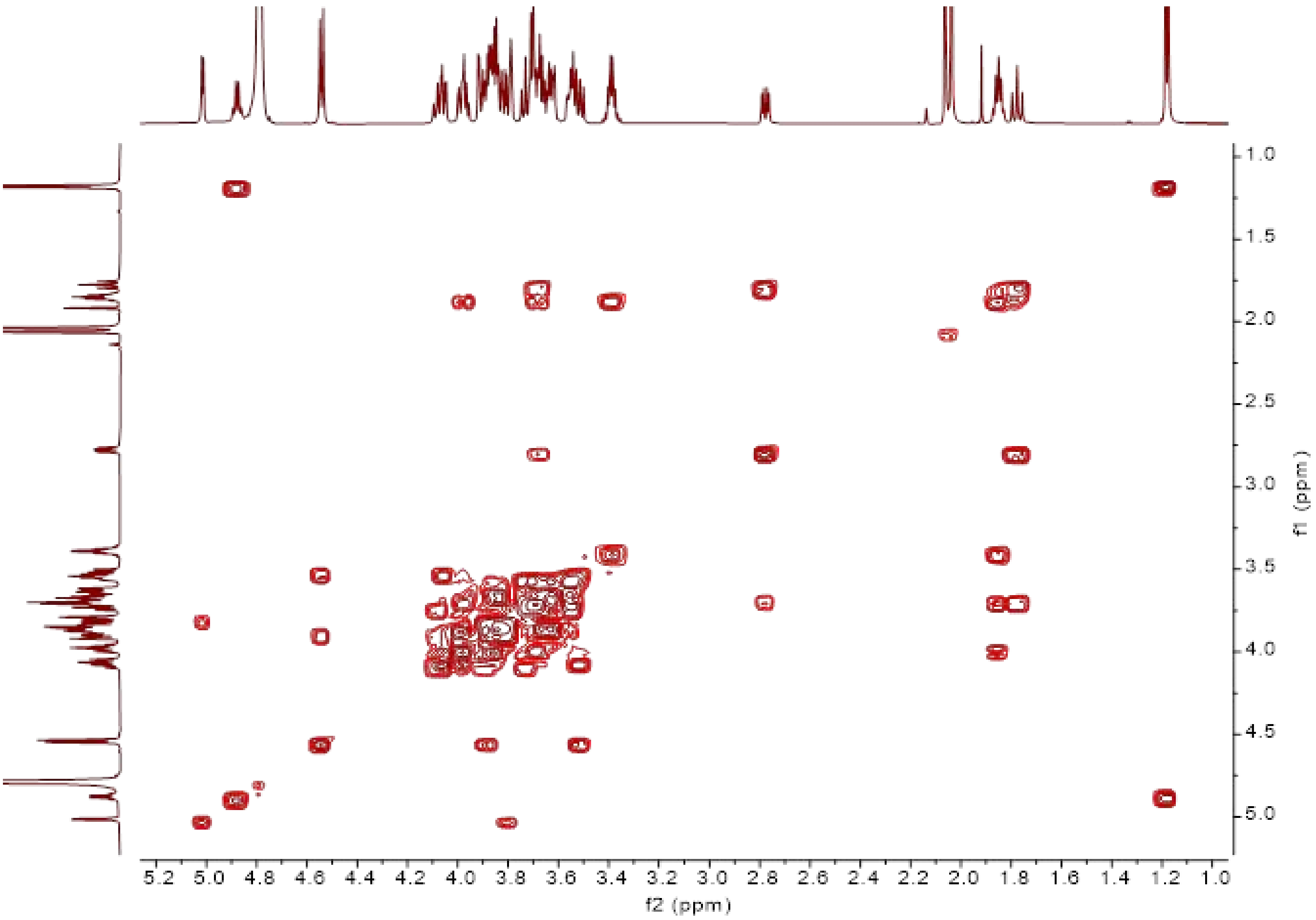

10
20
30
40
50
60
70
80
90
100
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)

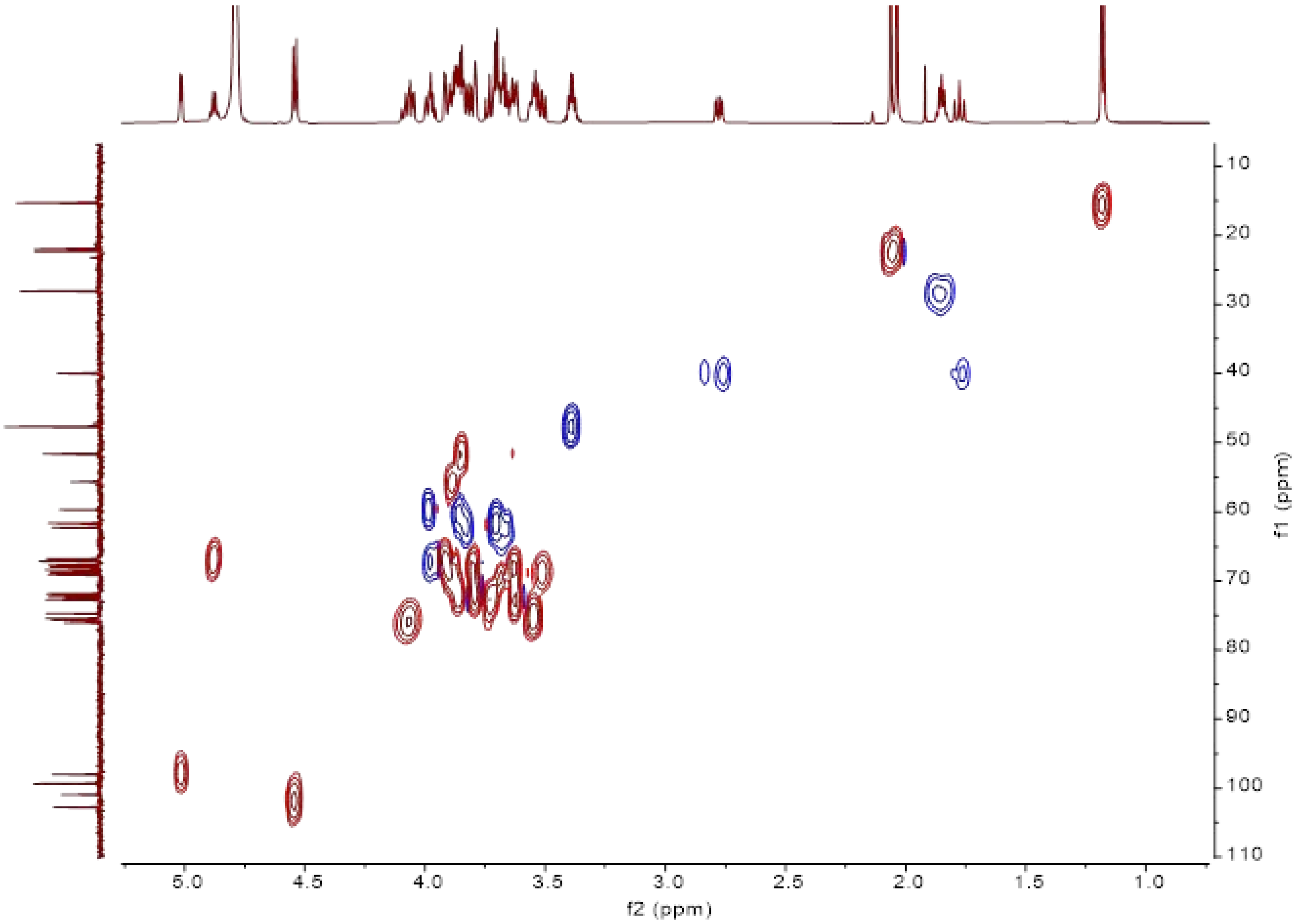

HO
OH
OH
COOH
OH
OH
NHAc
AcNH
O
O
O
O
O
N3
OH
OH
O
O
OH
OH
OH
OH

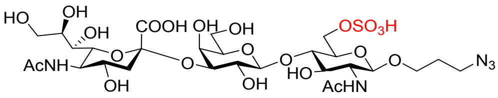
37


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

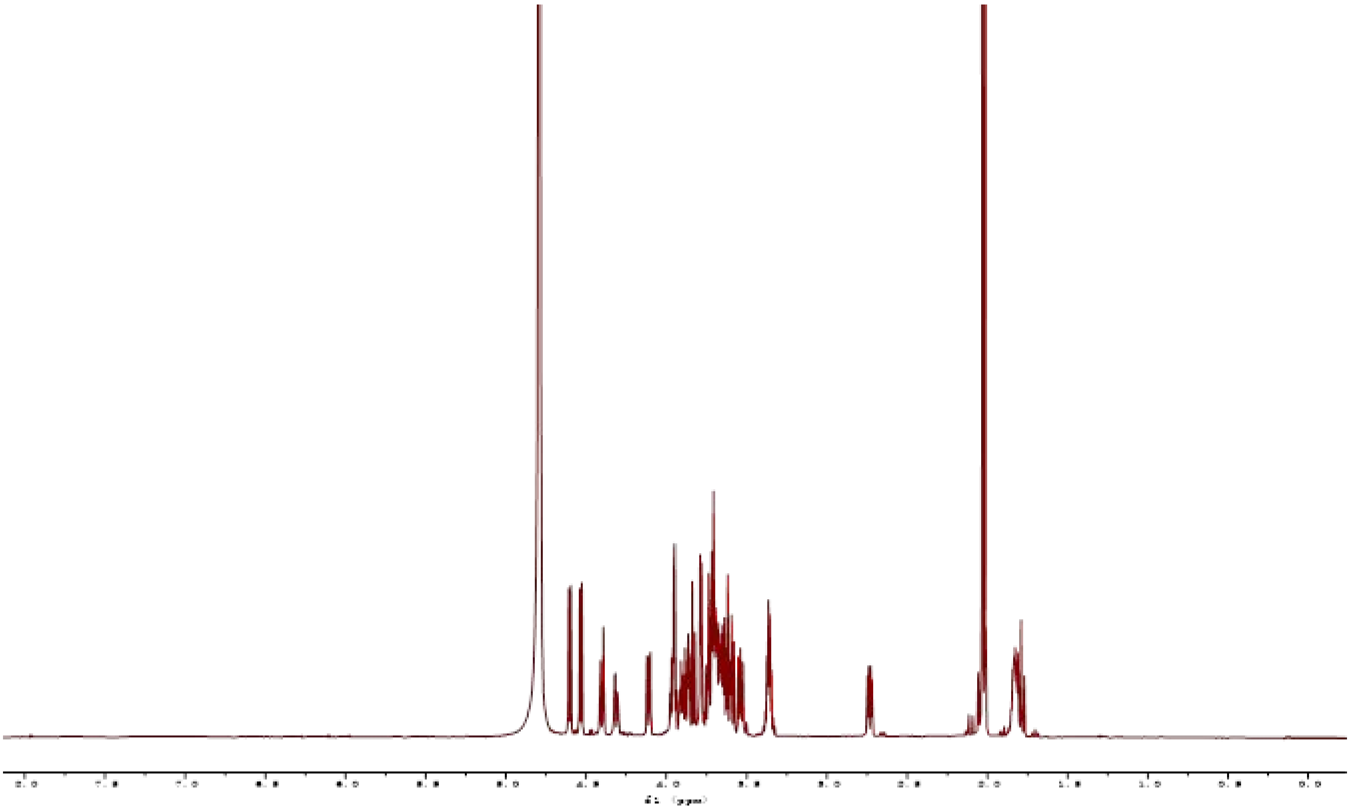

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

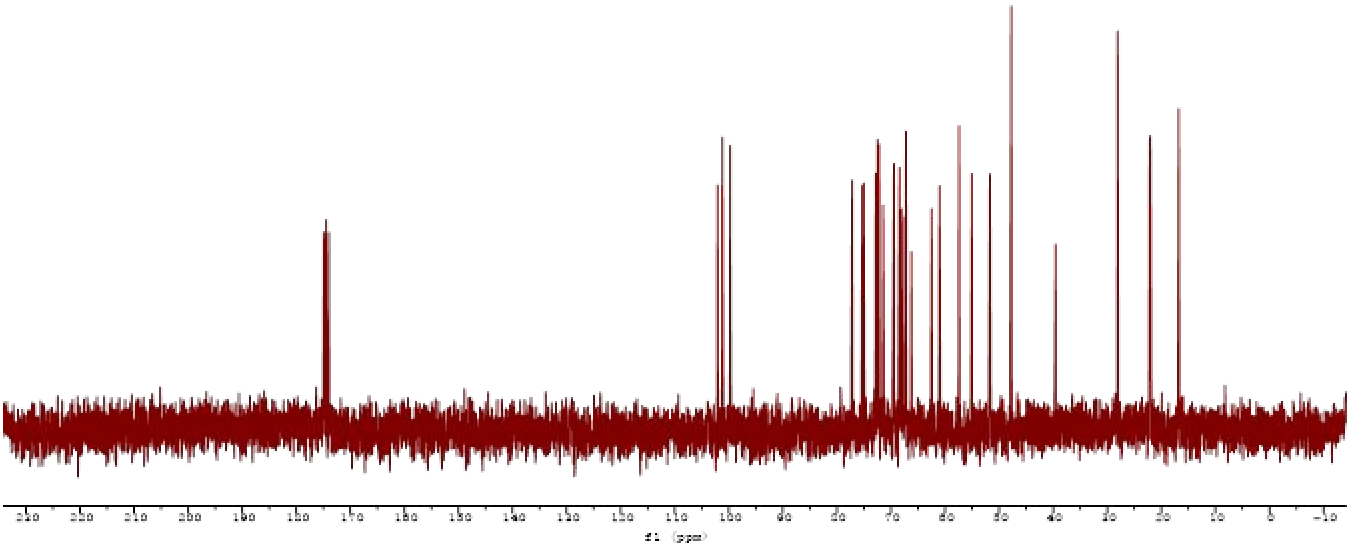

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

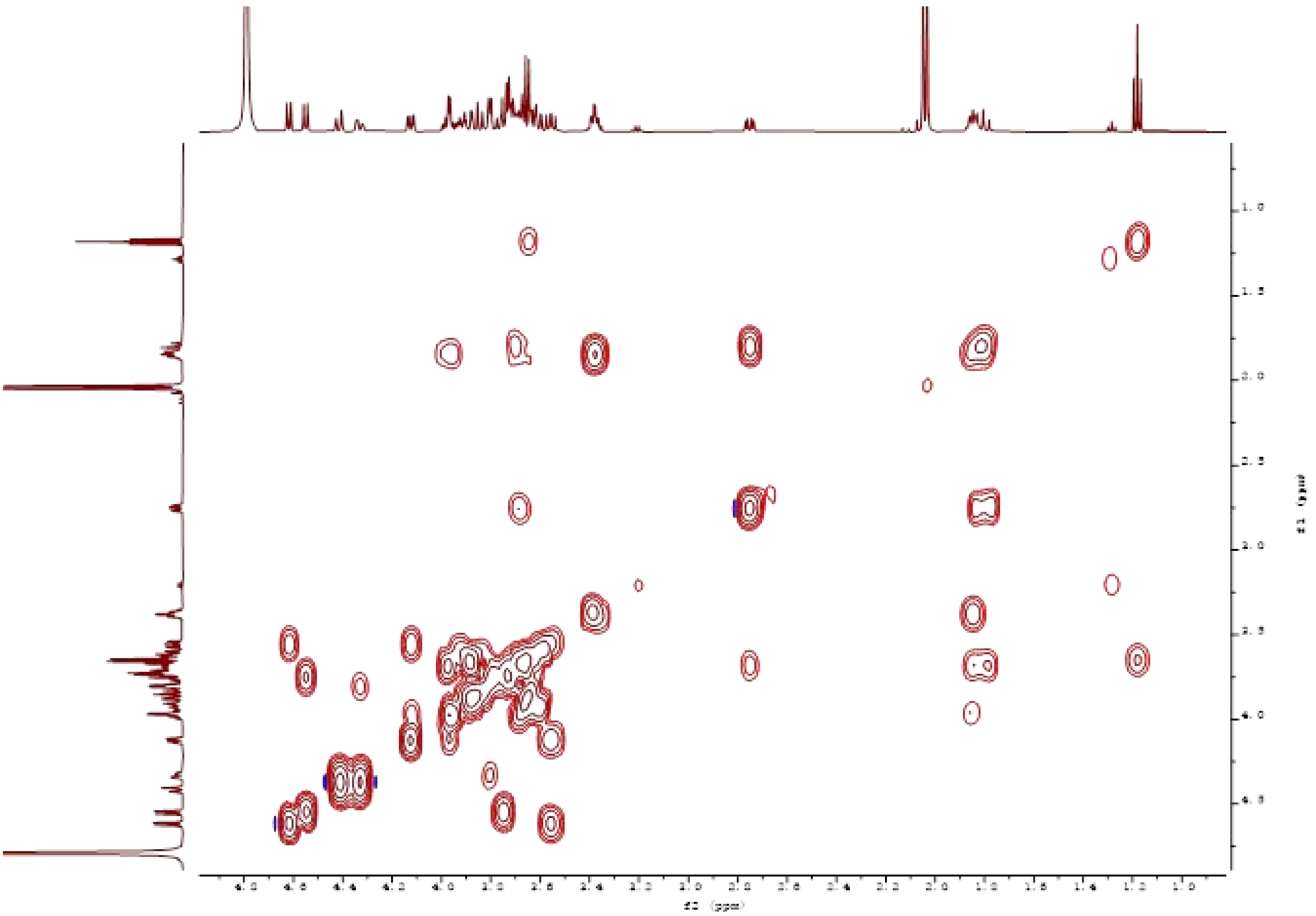

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

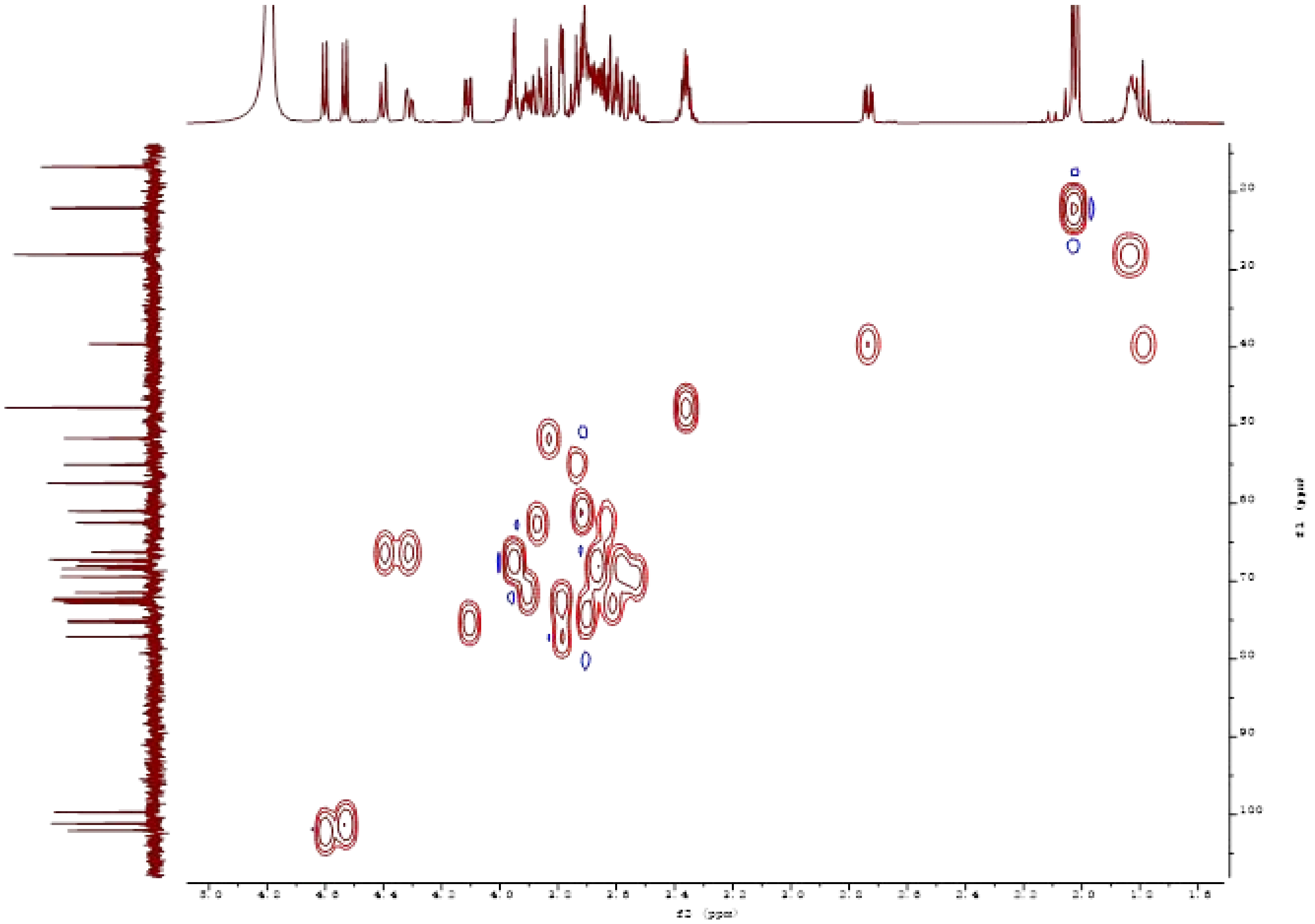

HO
OH
OH
AcNH
O
OH
COOH
O
OH
OH
O
OH
O
OSO3H
O
HO
AcHN
O
N3

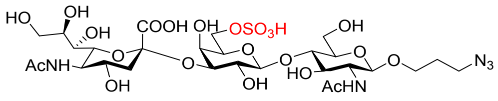
38


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

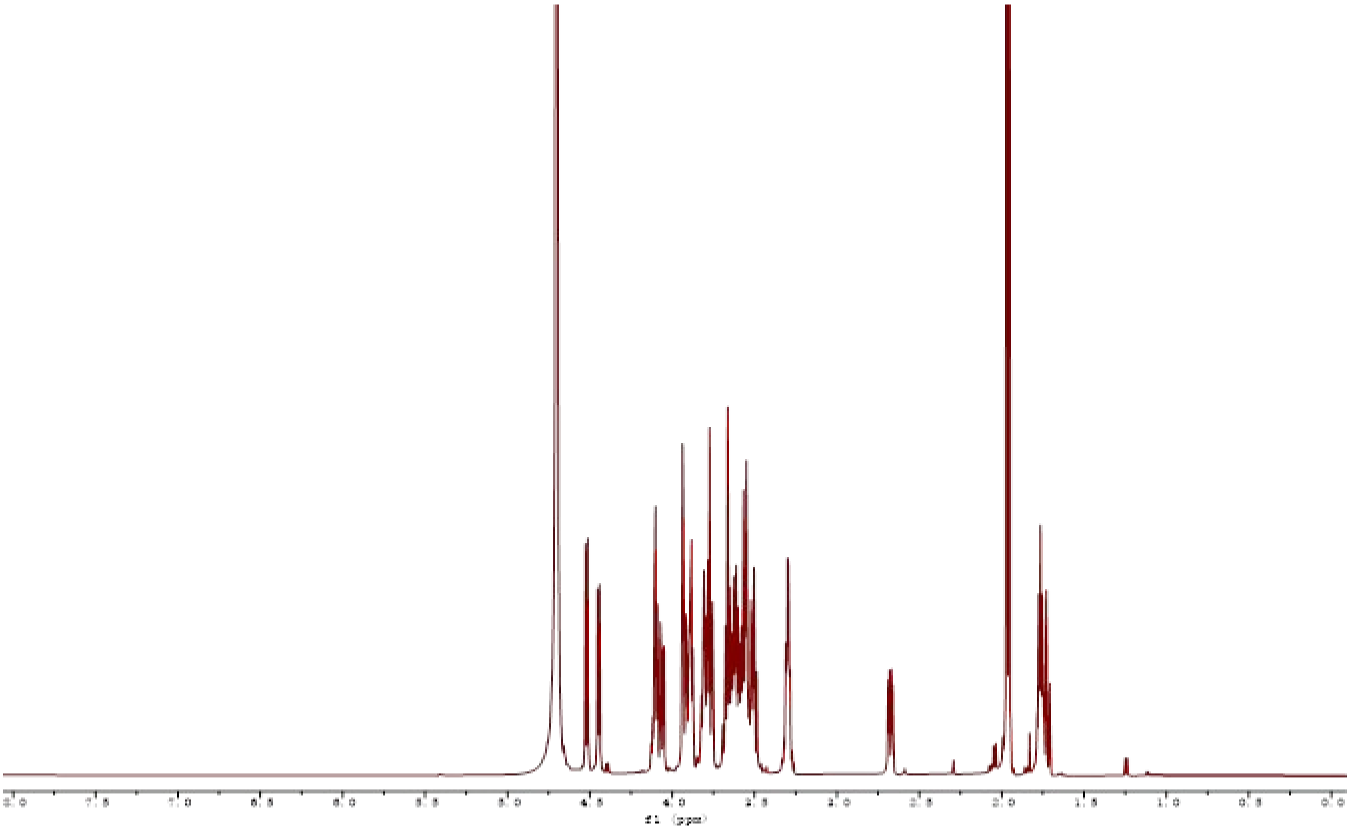

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

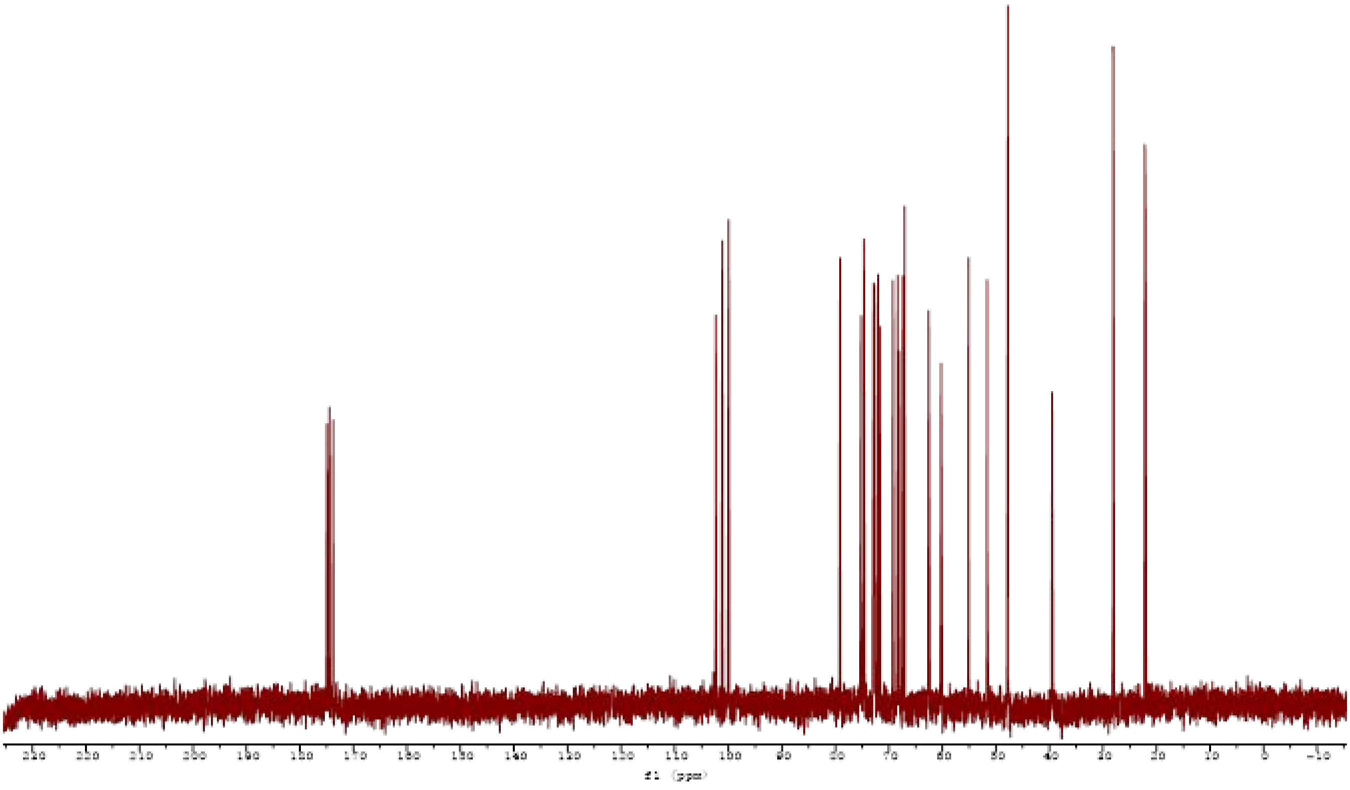

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

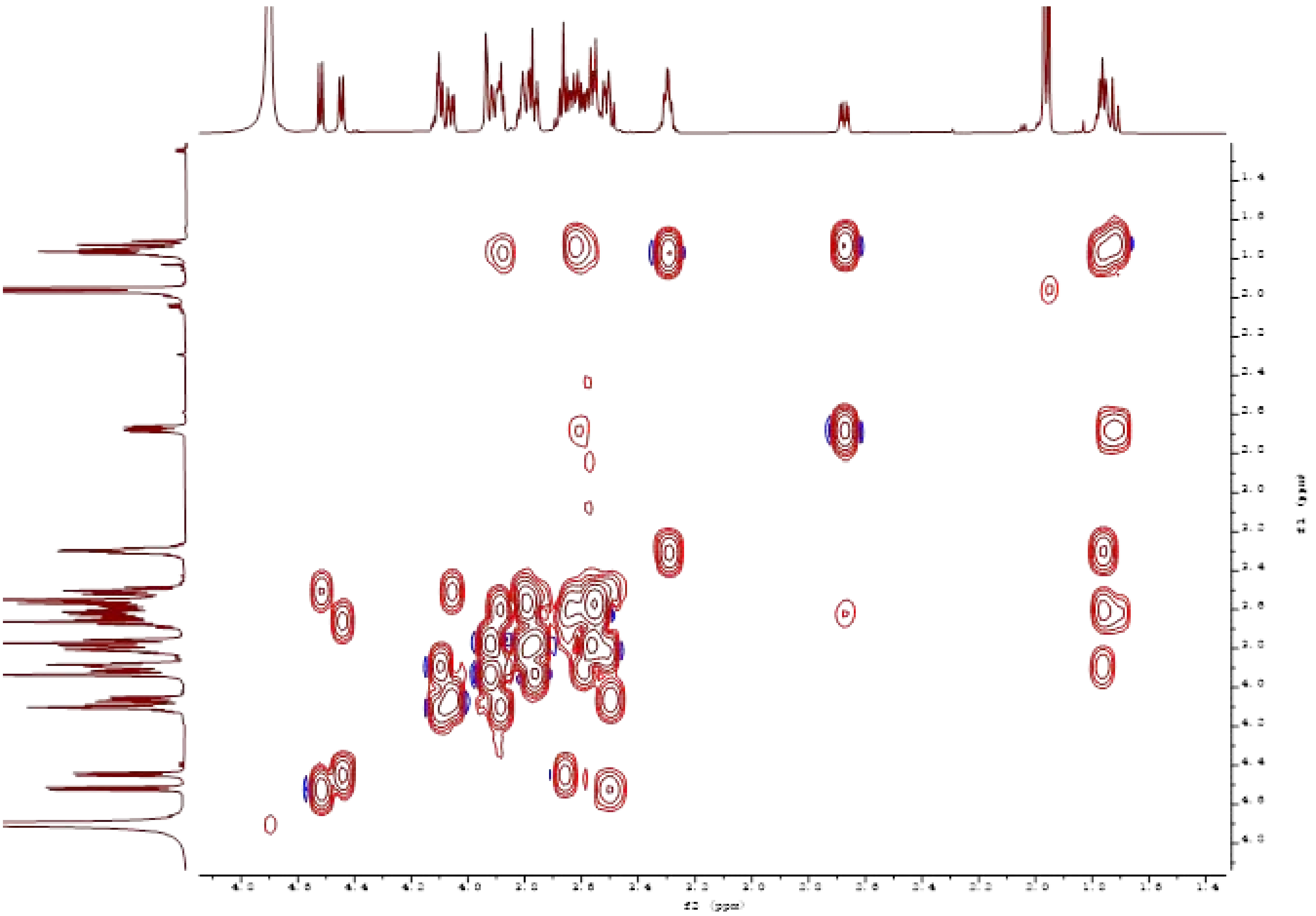

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

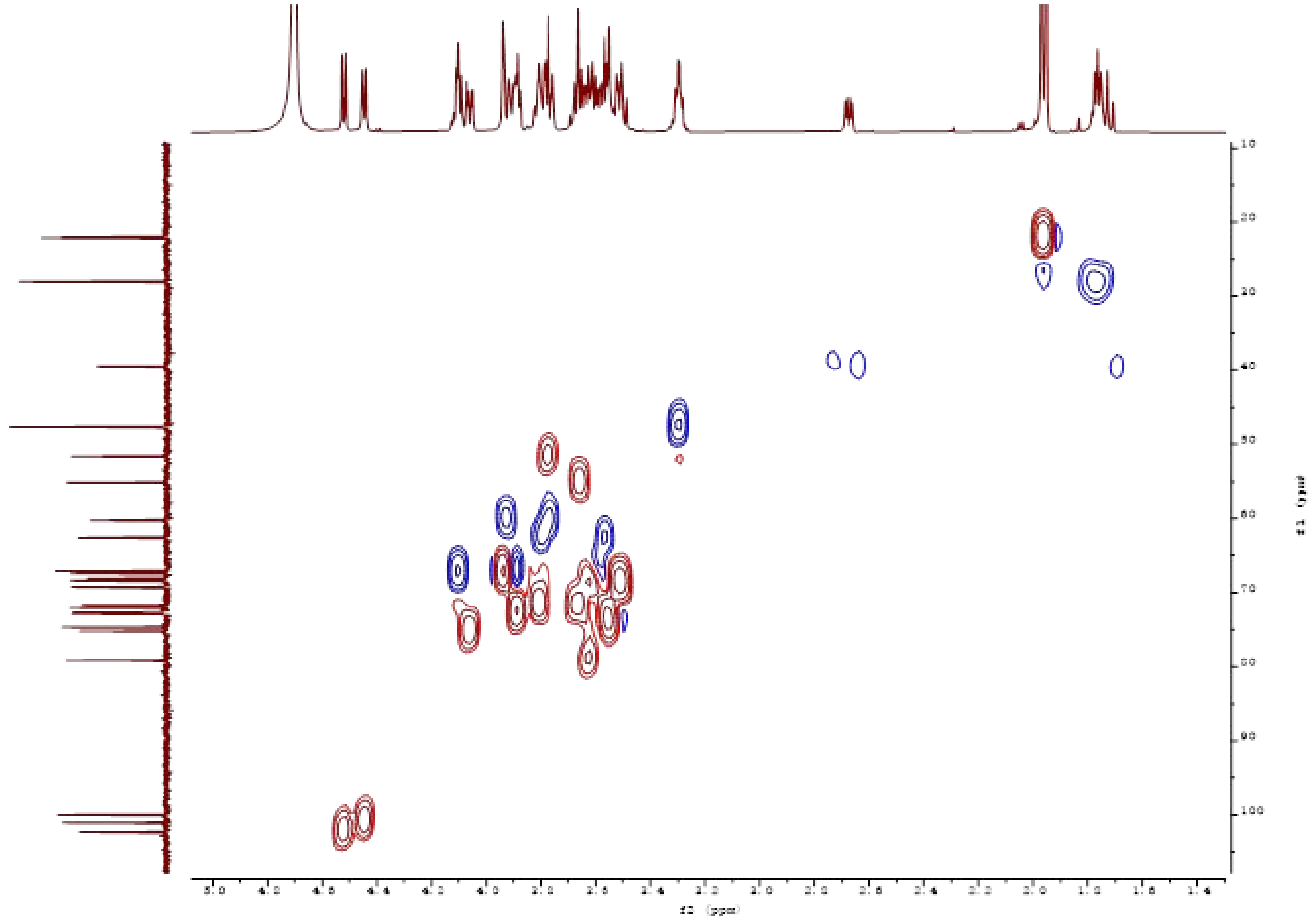

HO
OH
OH
COOH
OH
OSO$_3$H
OH
AcNH
O
O
OH
O
O
OH
O
HO
AcHN
O
N$_3$

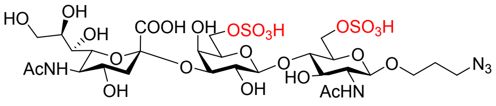
39


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


230
220
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)

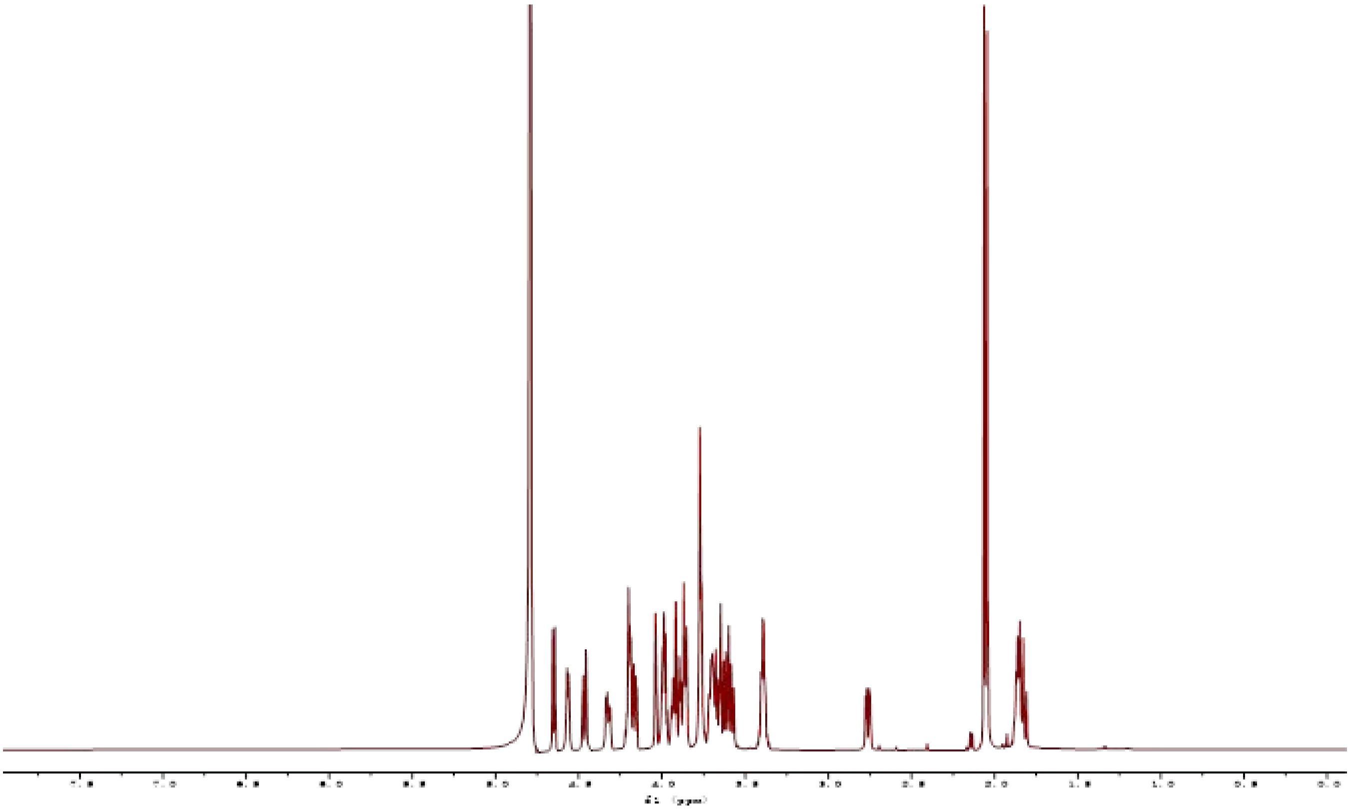

f2 (ppm)
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4


f2 (ppm)
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
10
20
30
40
50
60
70
80
90
100

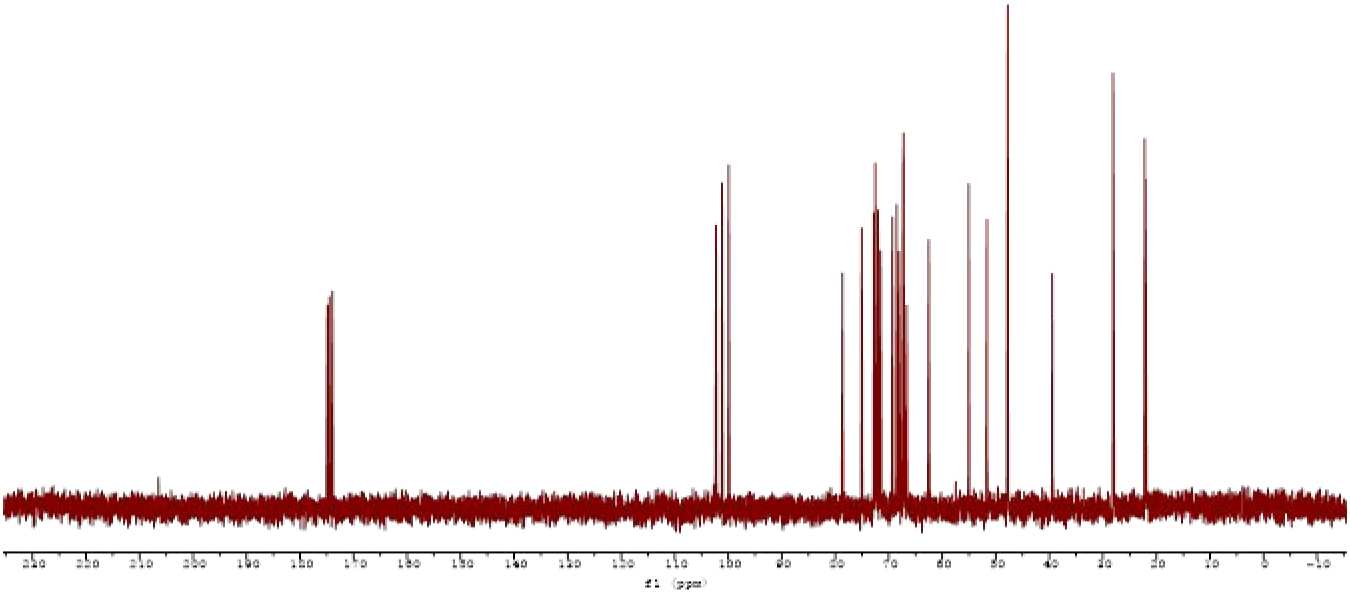


HO
OH
OH
COOH
OH
OSO3H
OSO3H
O
O
O
O
O
O
AcNH
OH
OH
HO
AcHN
N3

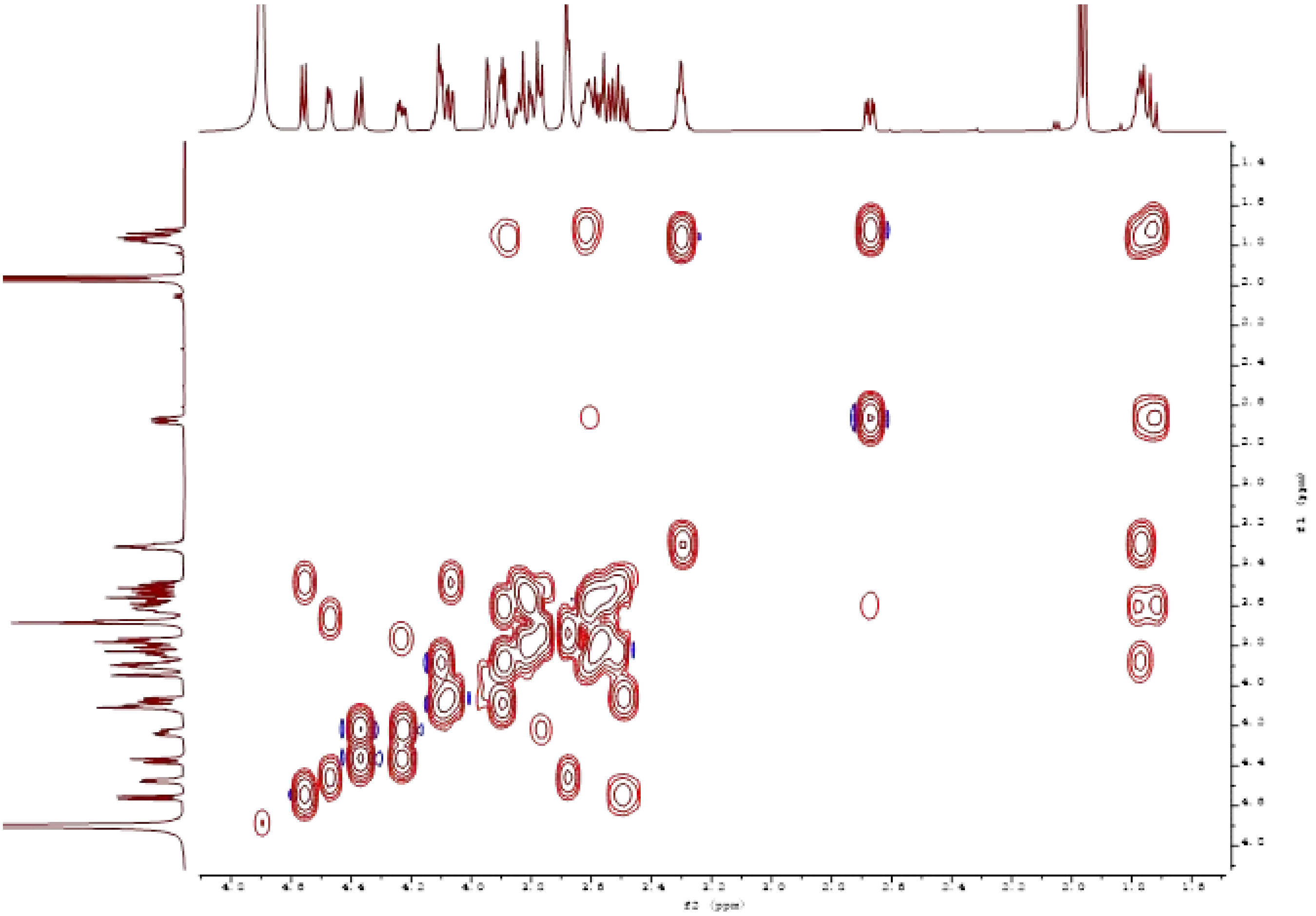
40

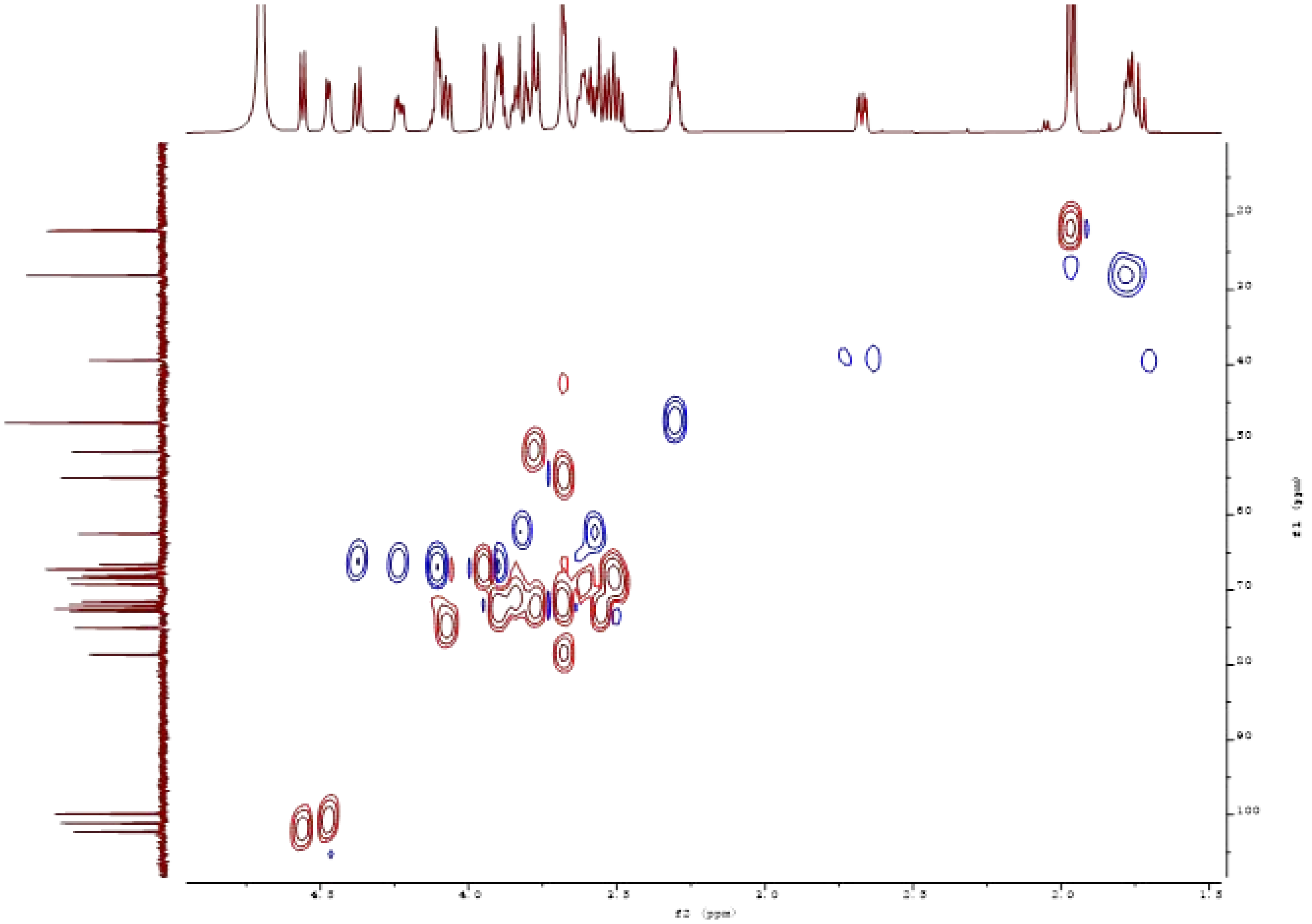


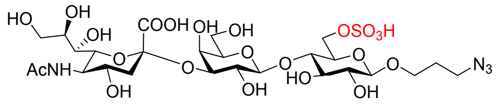
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



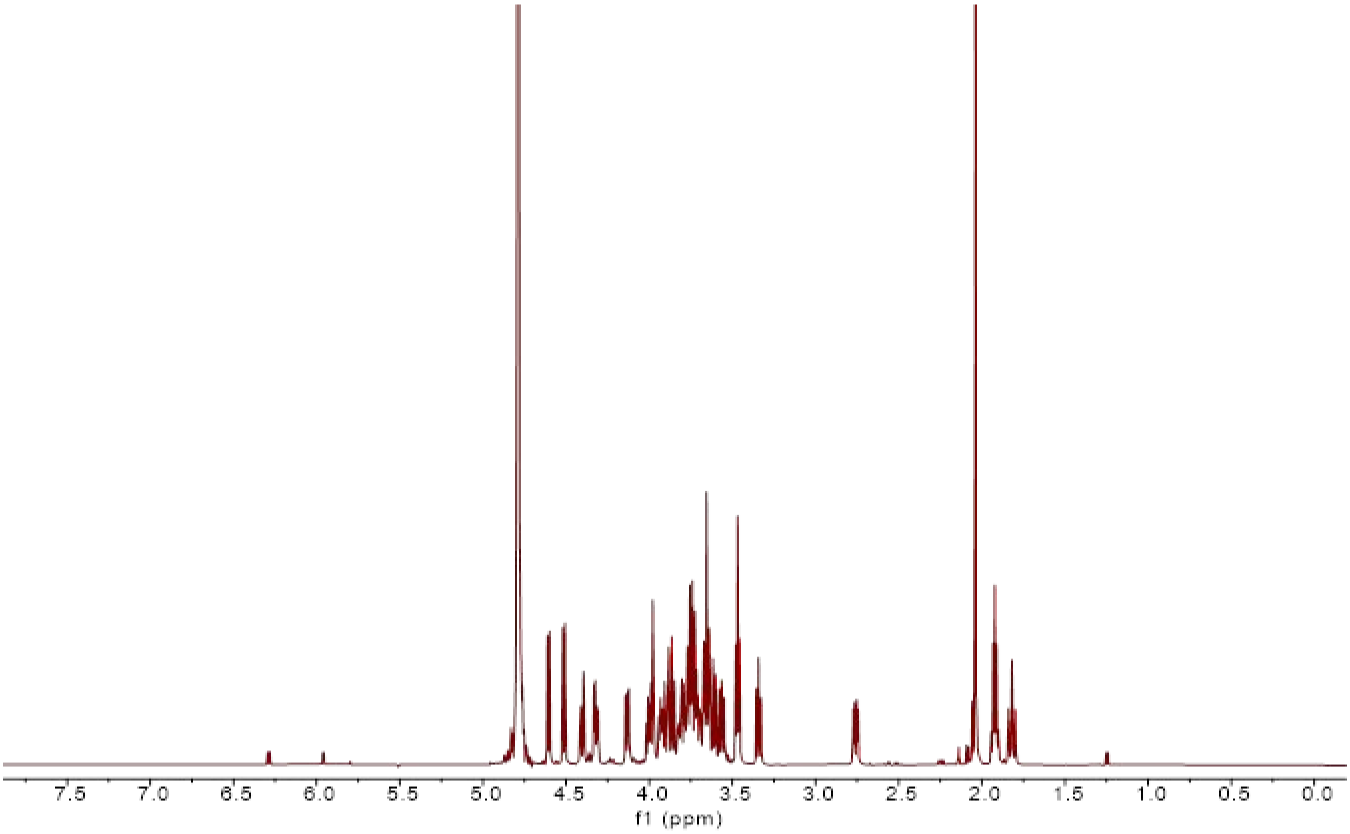
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

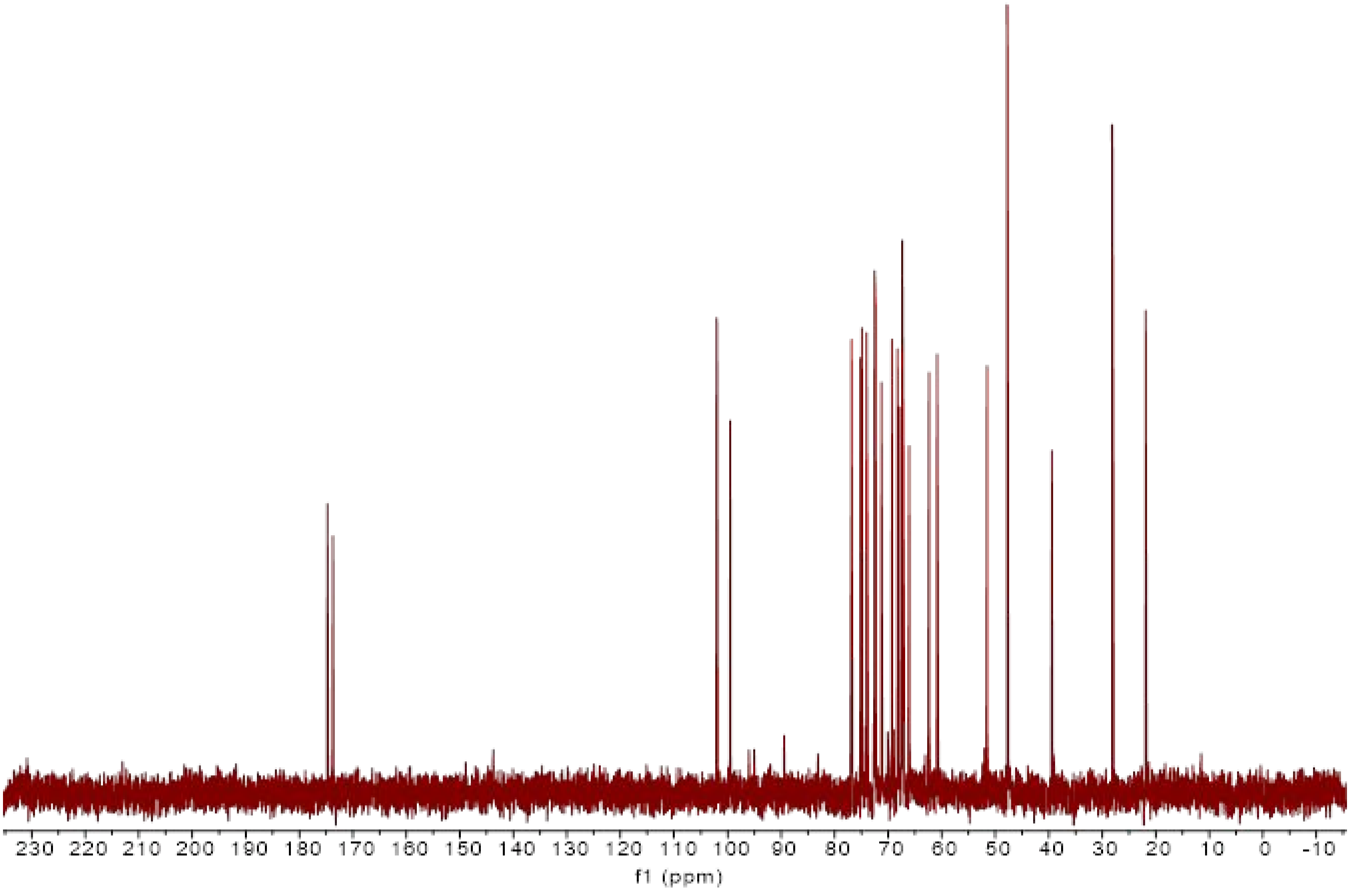

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

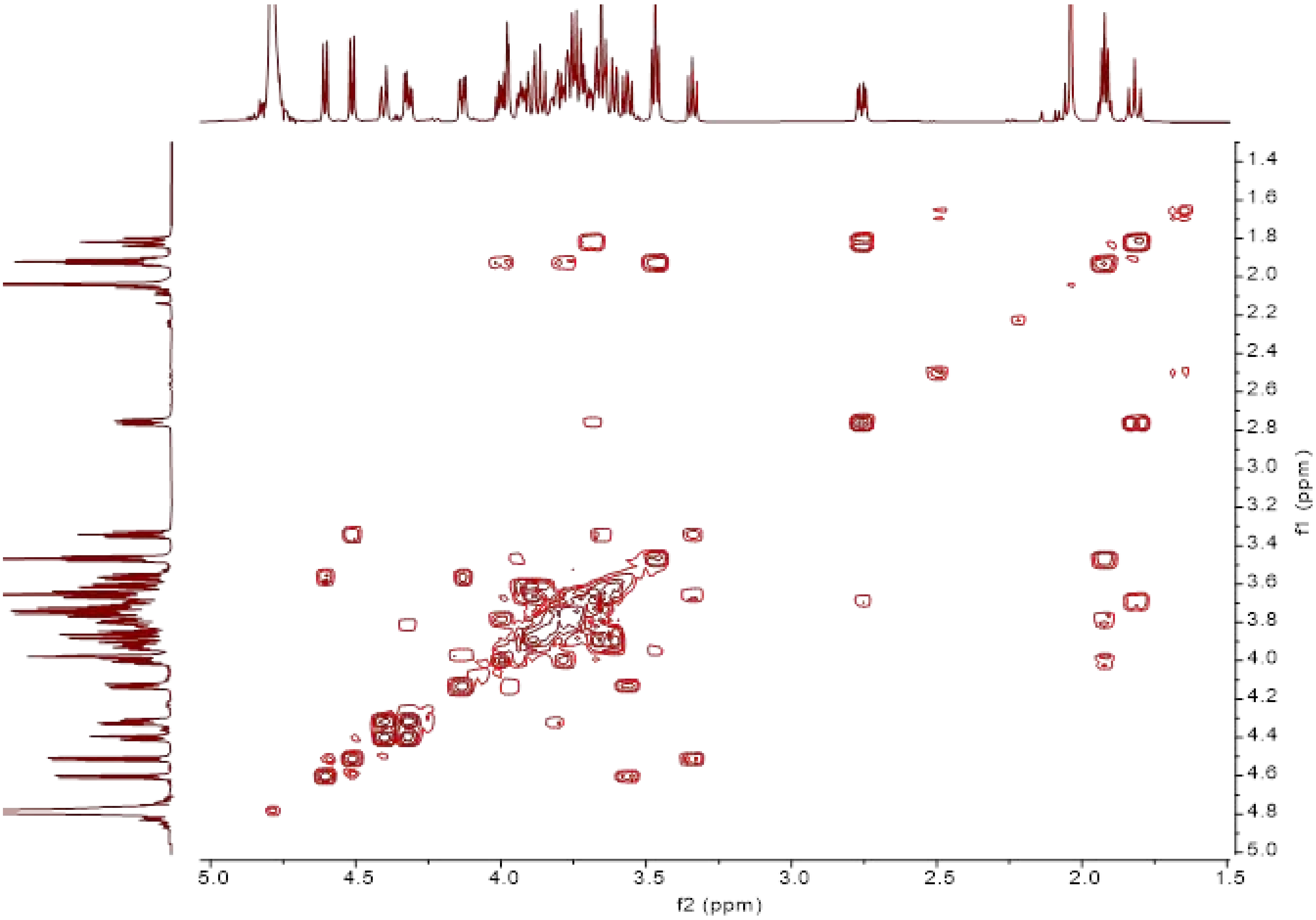

4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

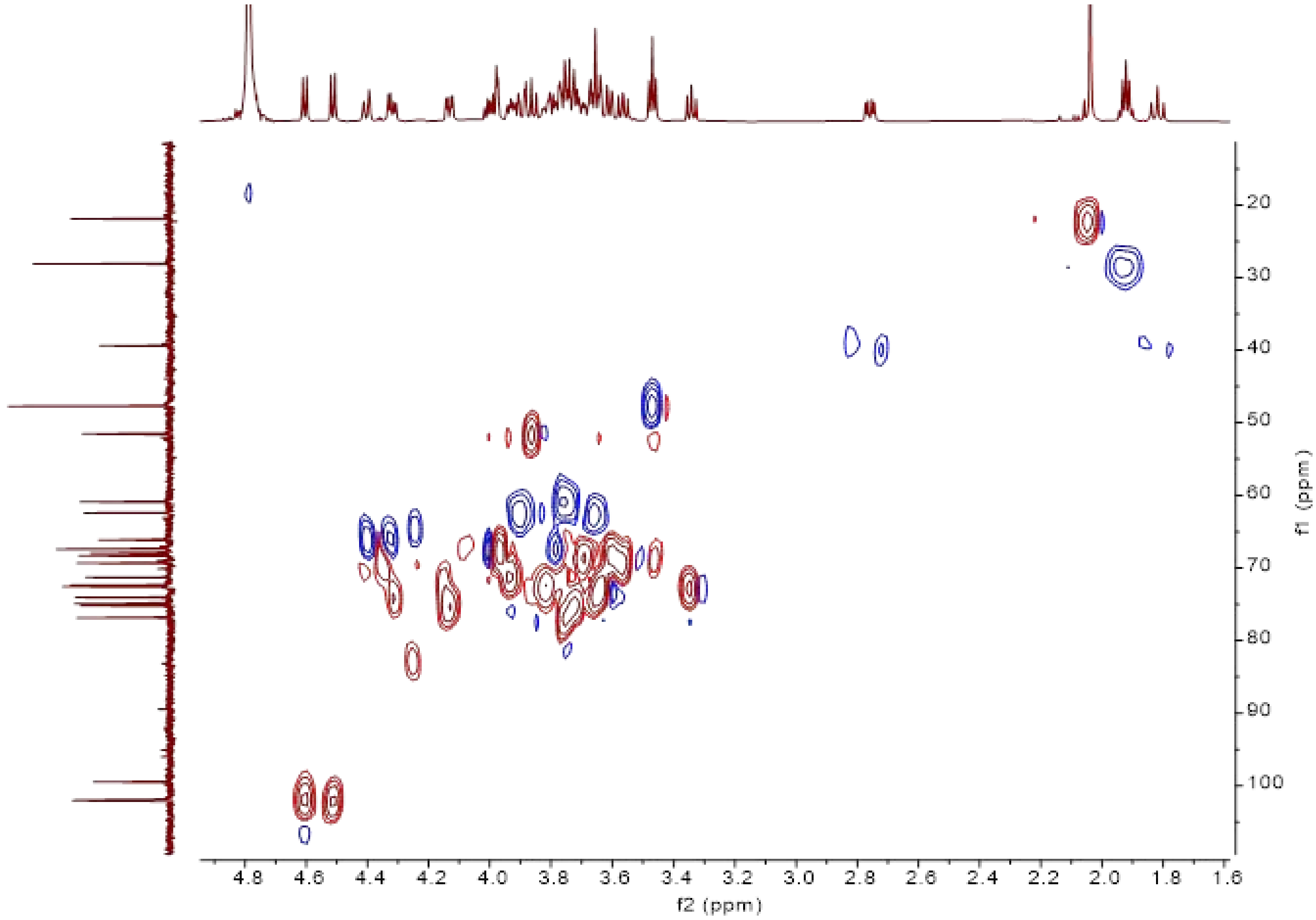

HO
OH
OH
COOH
OH
OH
OSO3H
AcNH
O
O
O
O
O
HO
OH
OH
OH
N3

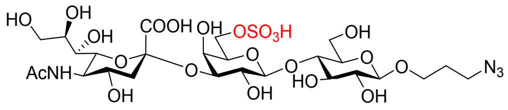
41


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)

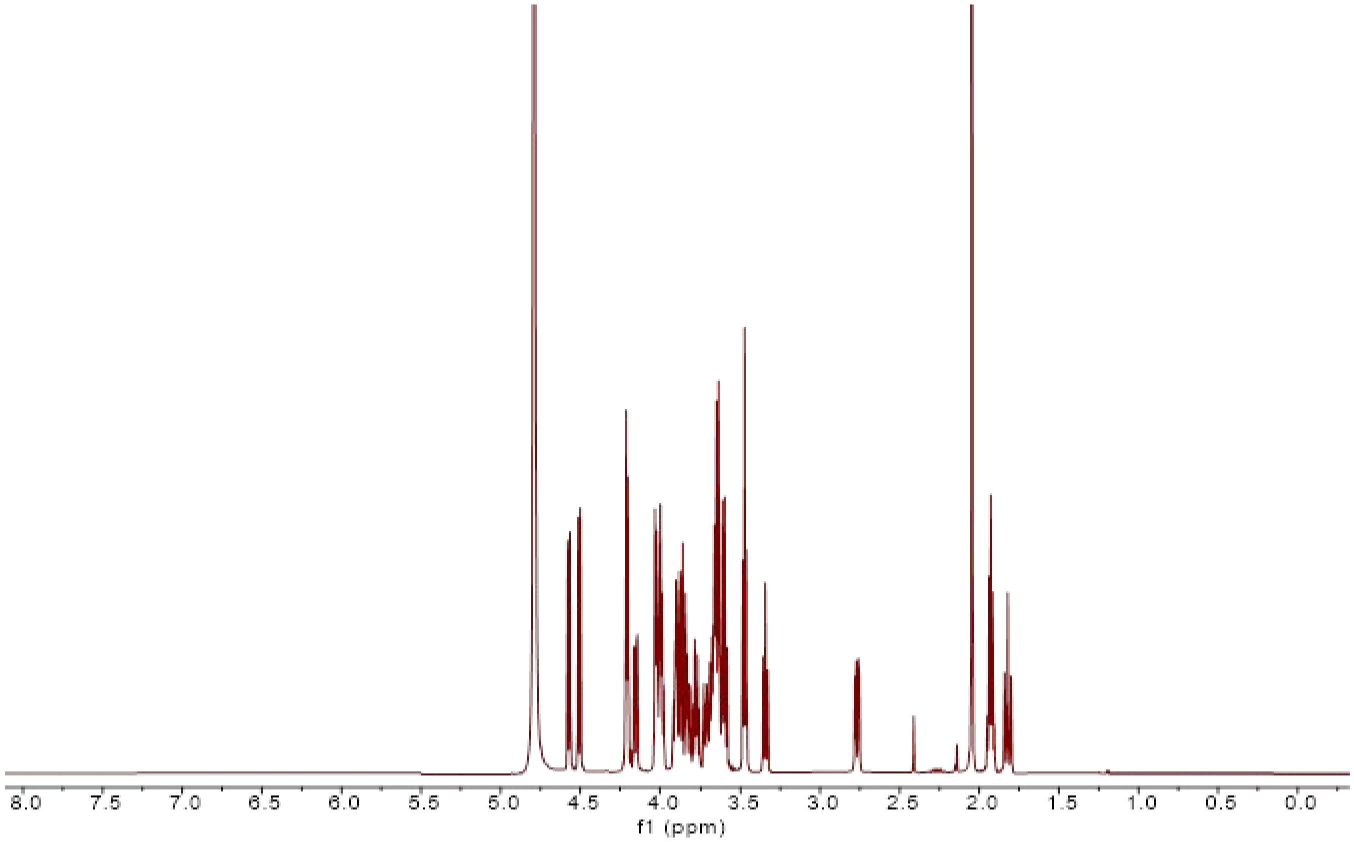

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

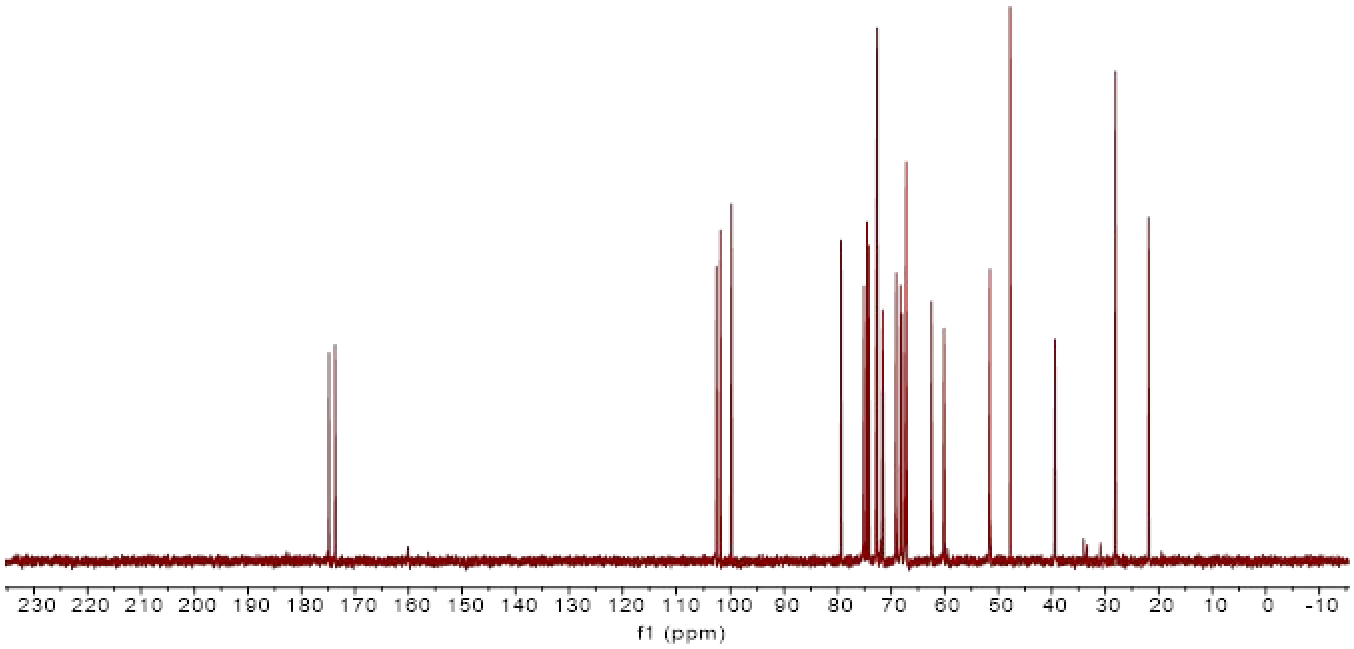

1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

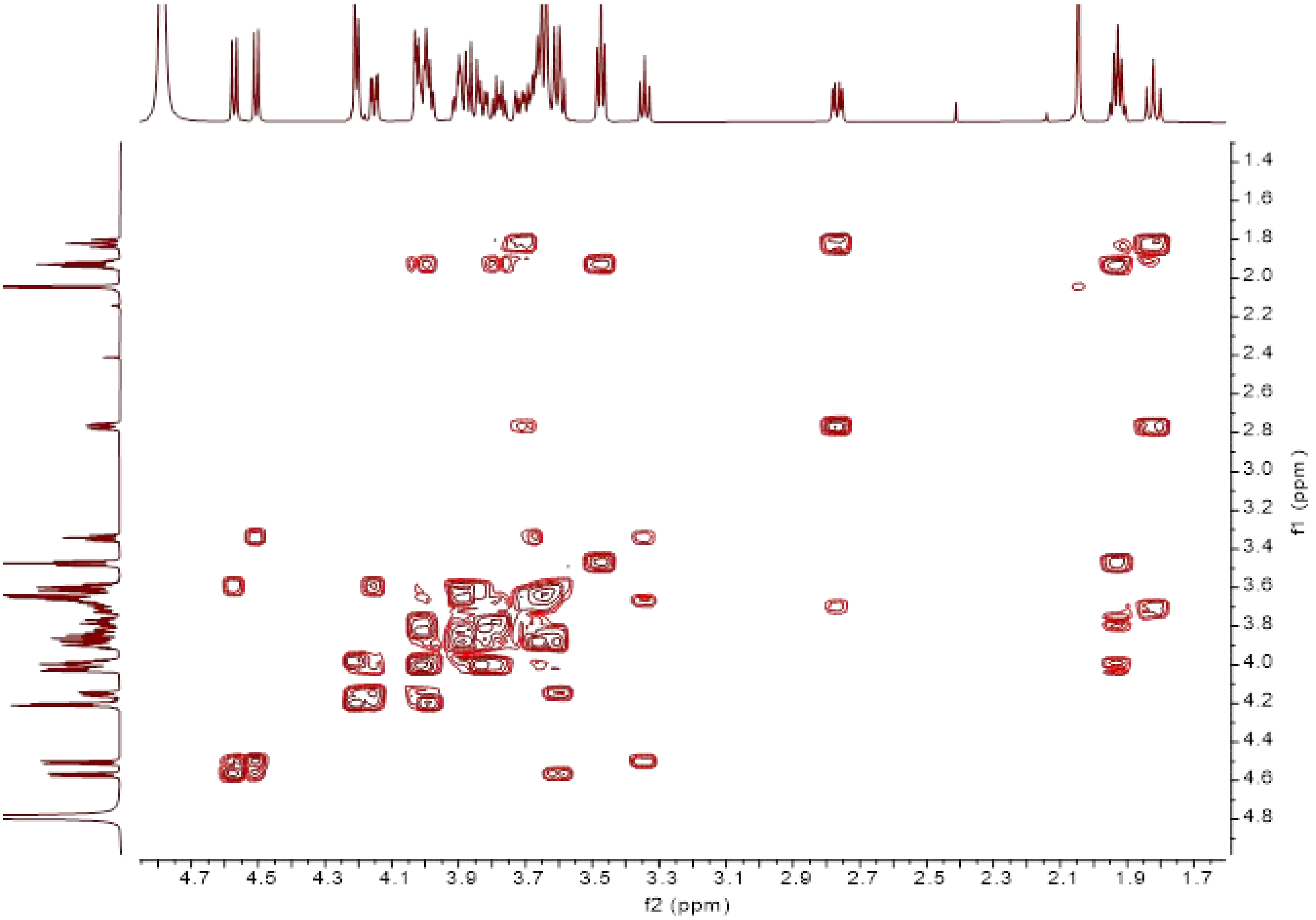

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)


HO
OH
OH
COOH
OH
OSO3H
OH
AcNH
O
OH
O
O
OH
O
HO
O
OH
O
N3

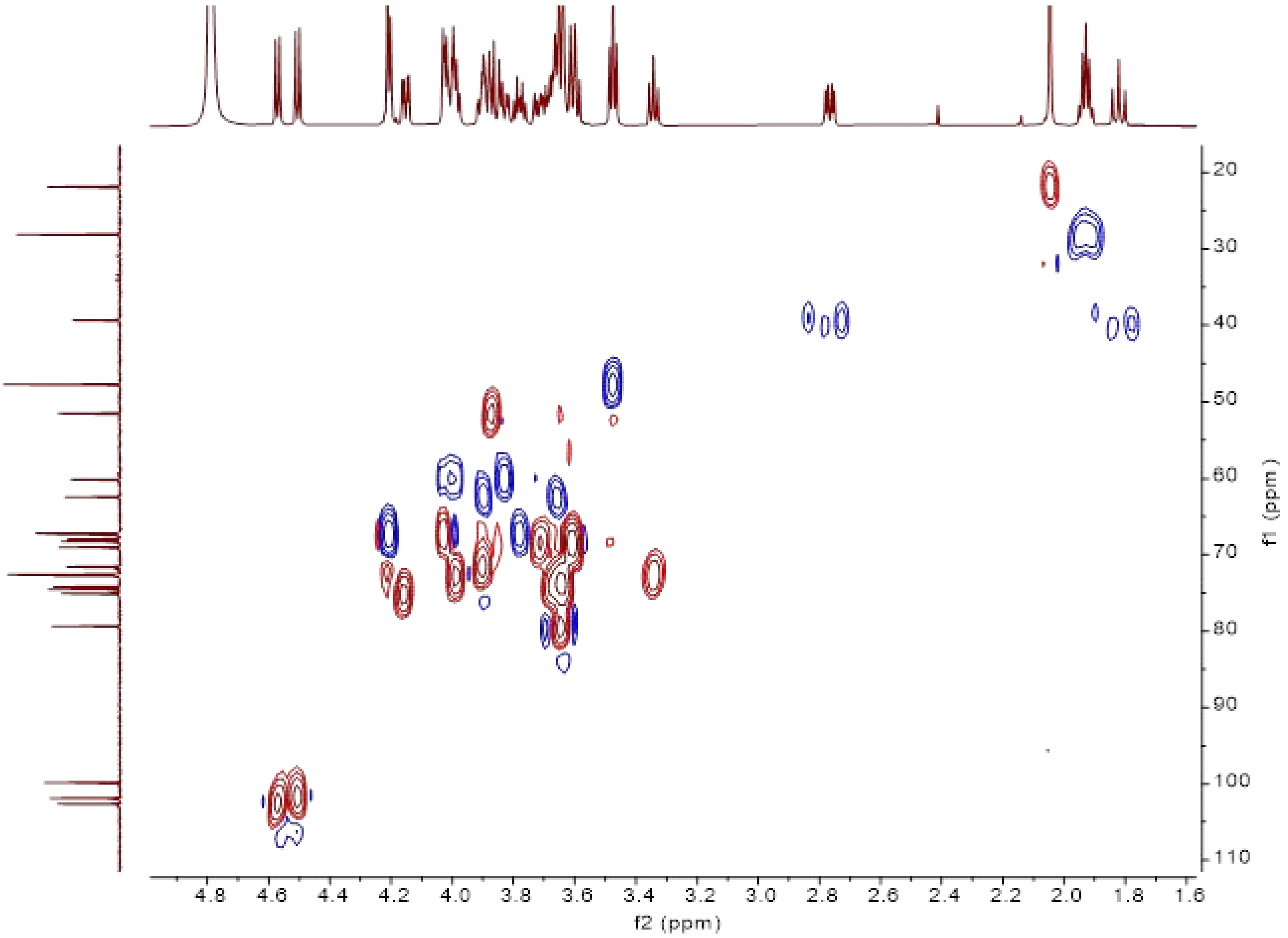
42


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

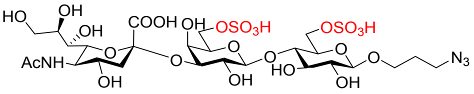

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



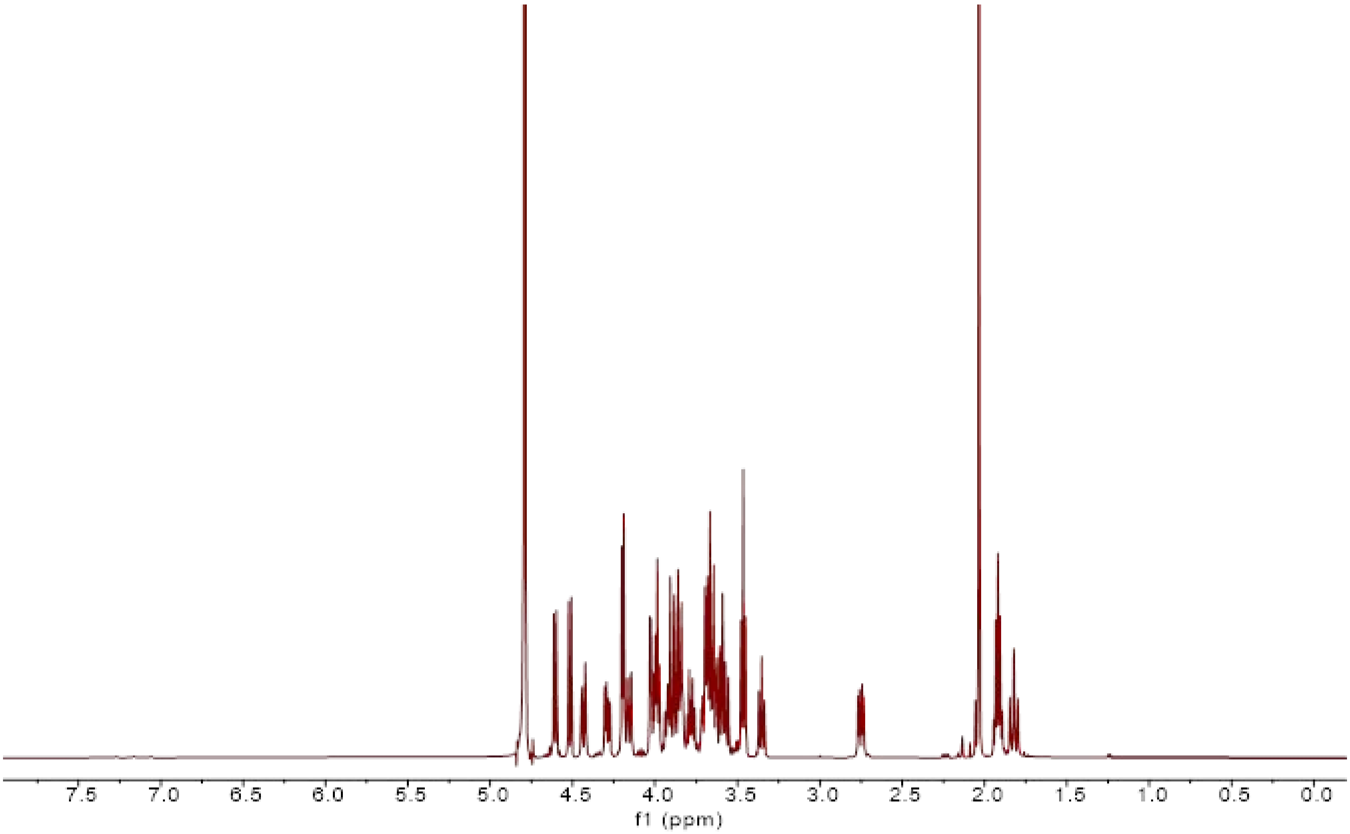
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

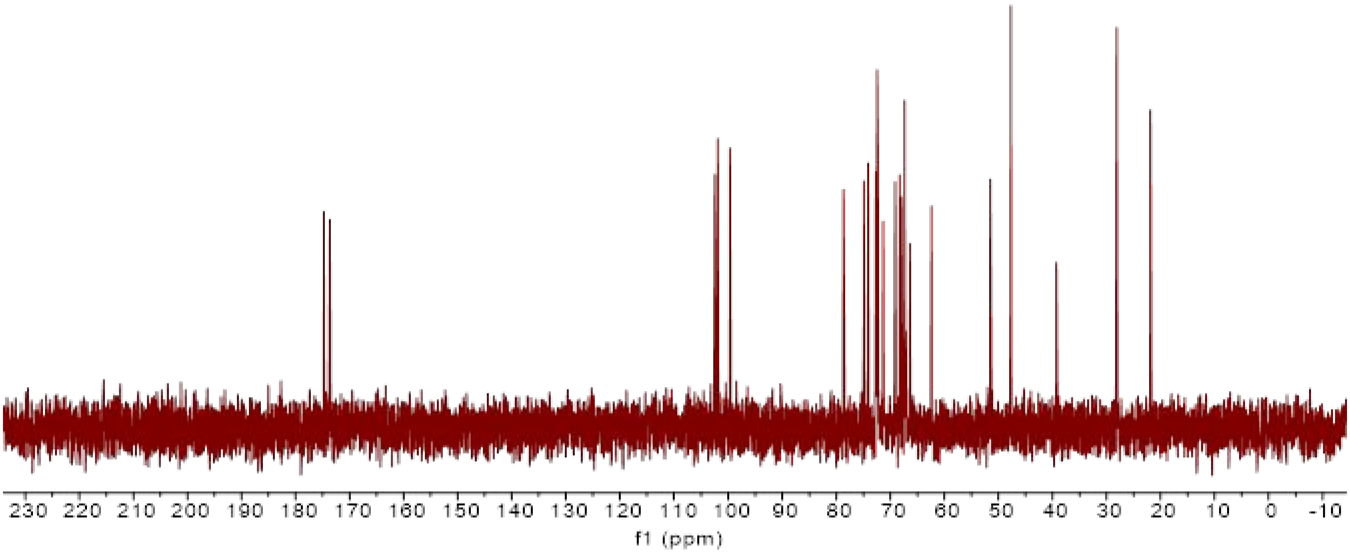


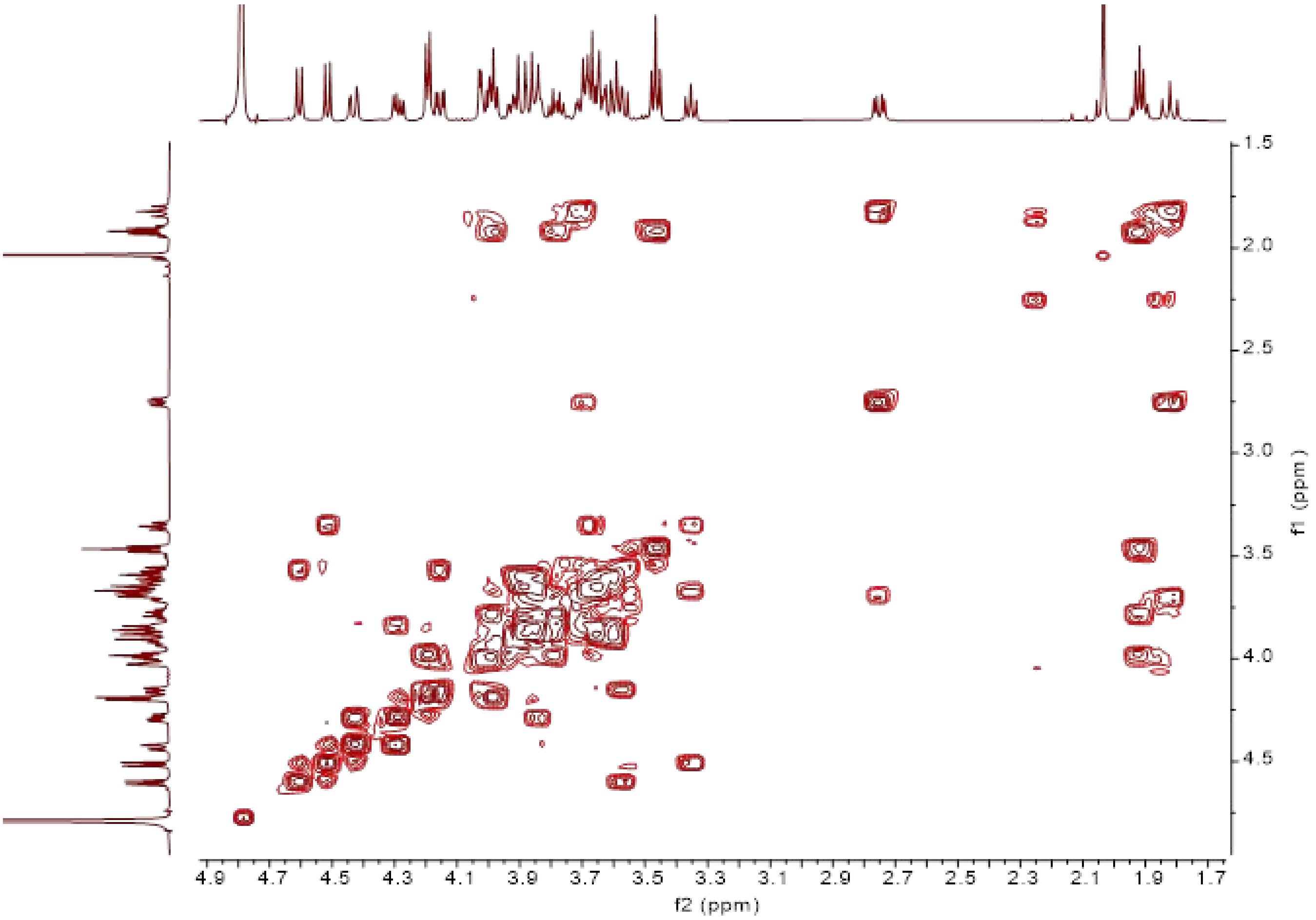
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

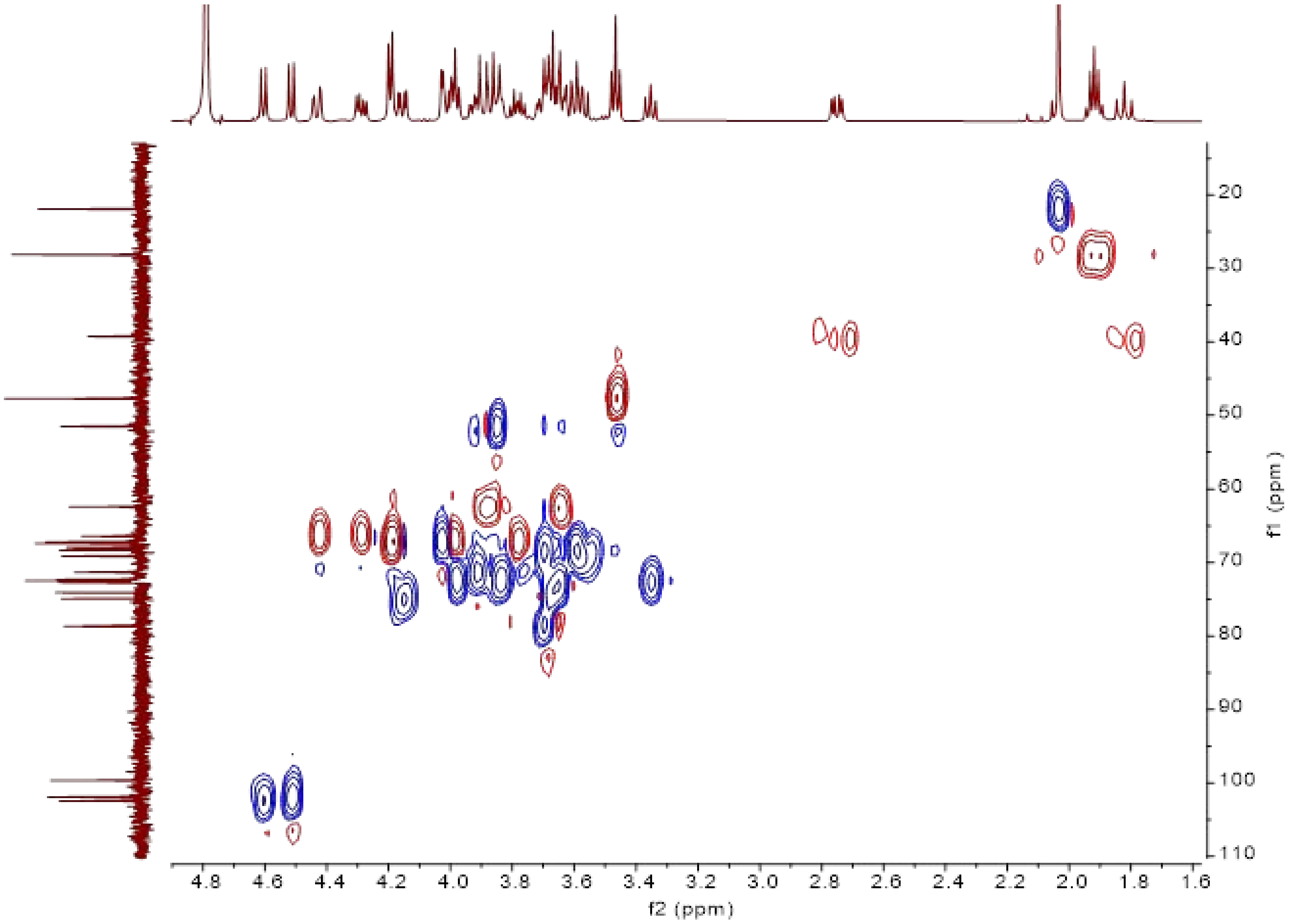


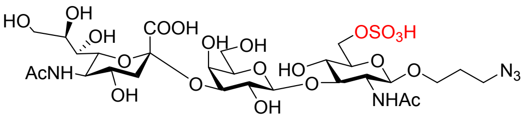
43


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)

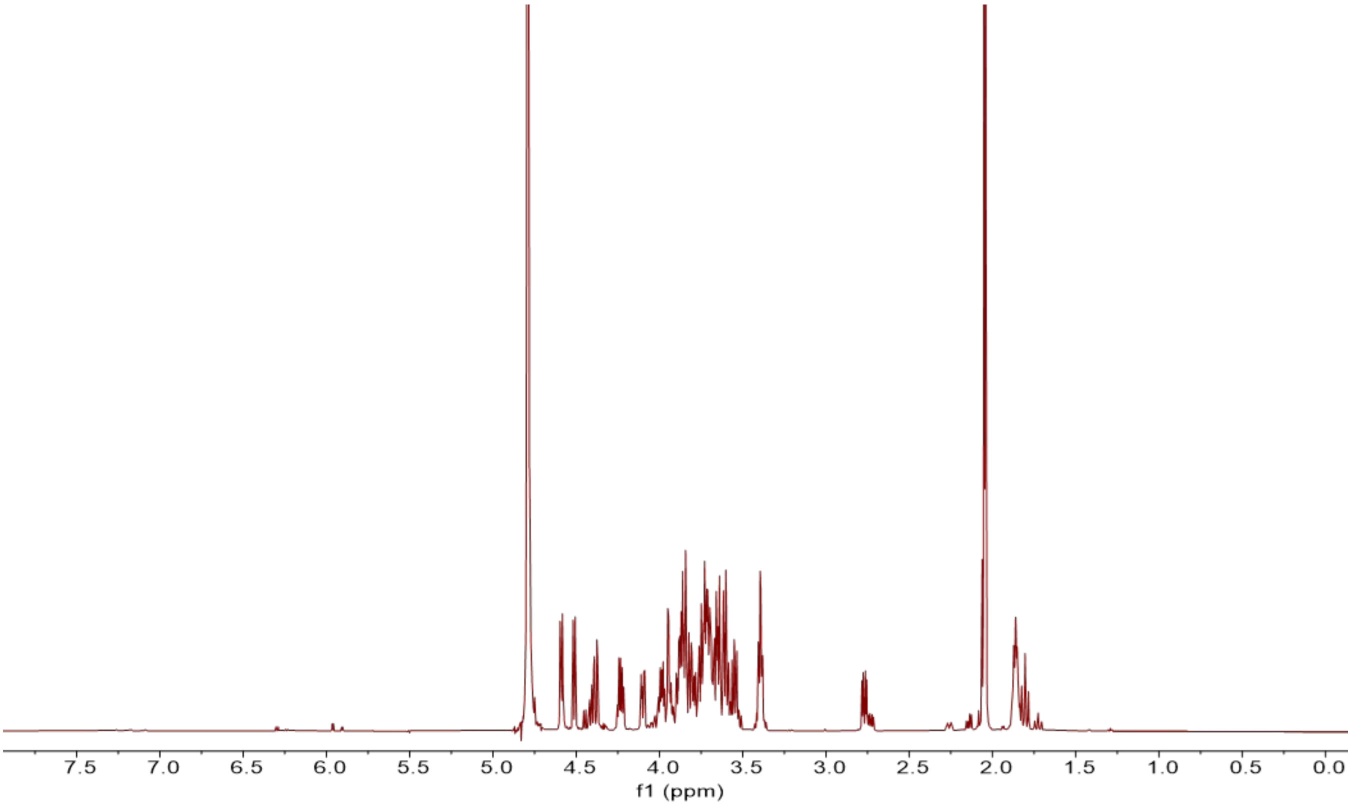

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

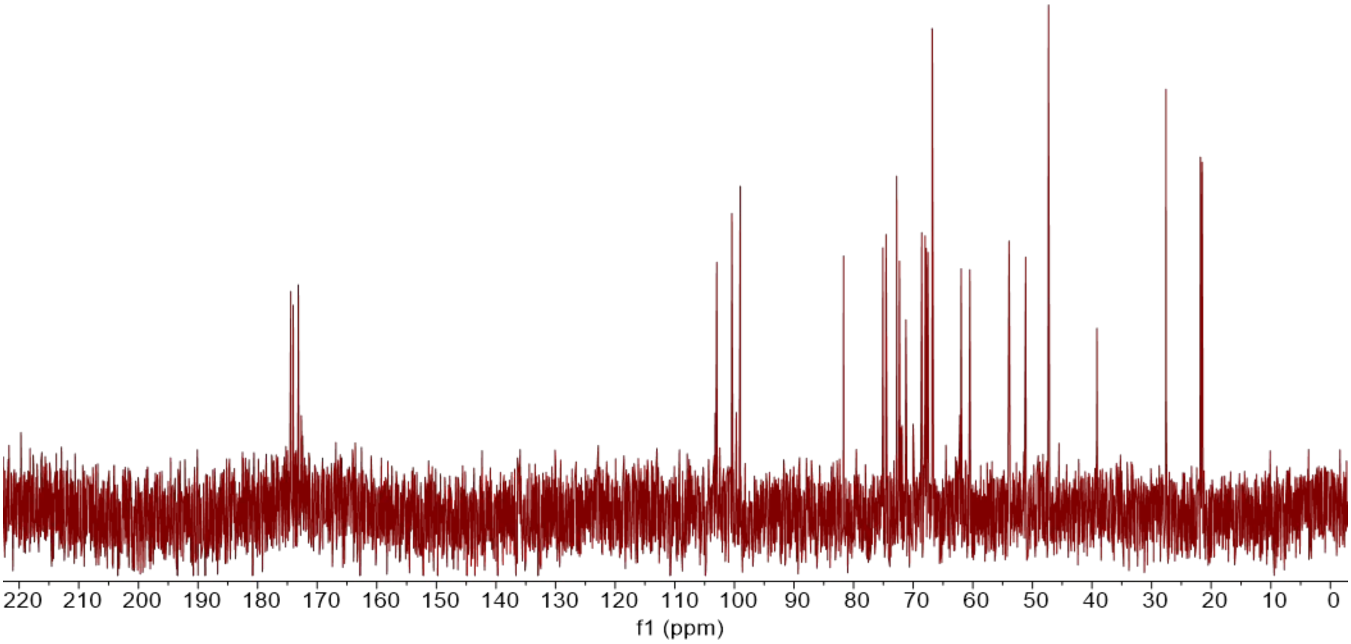

4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

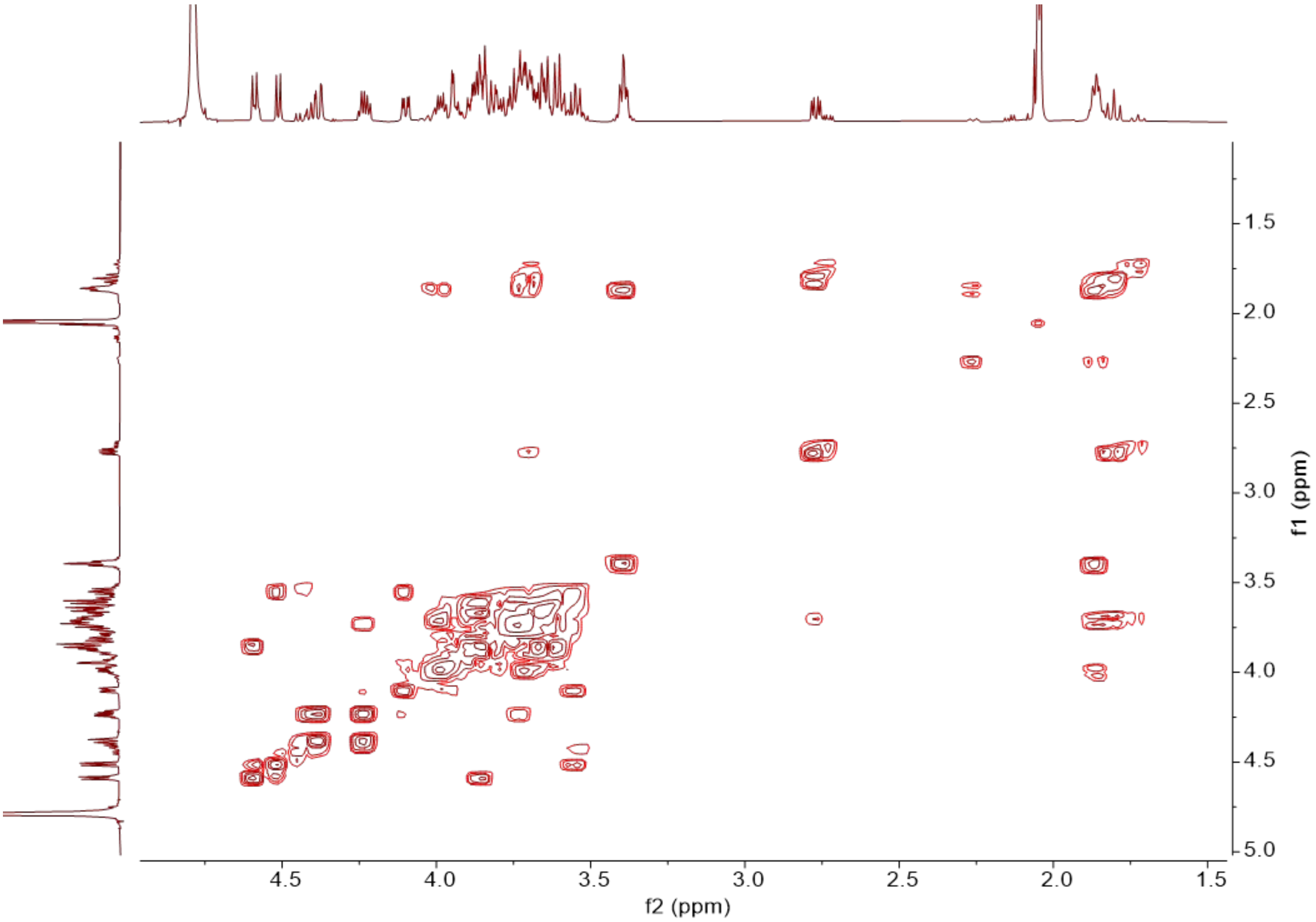

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

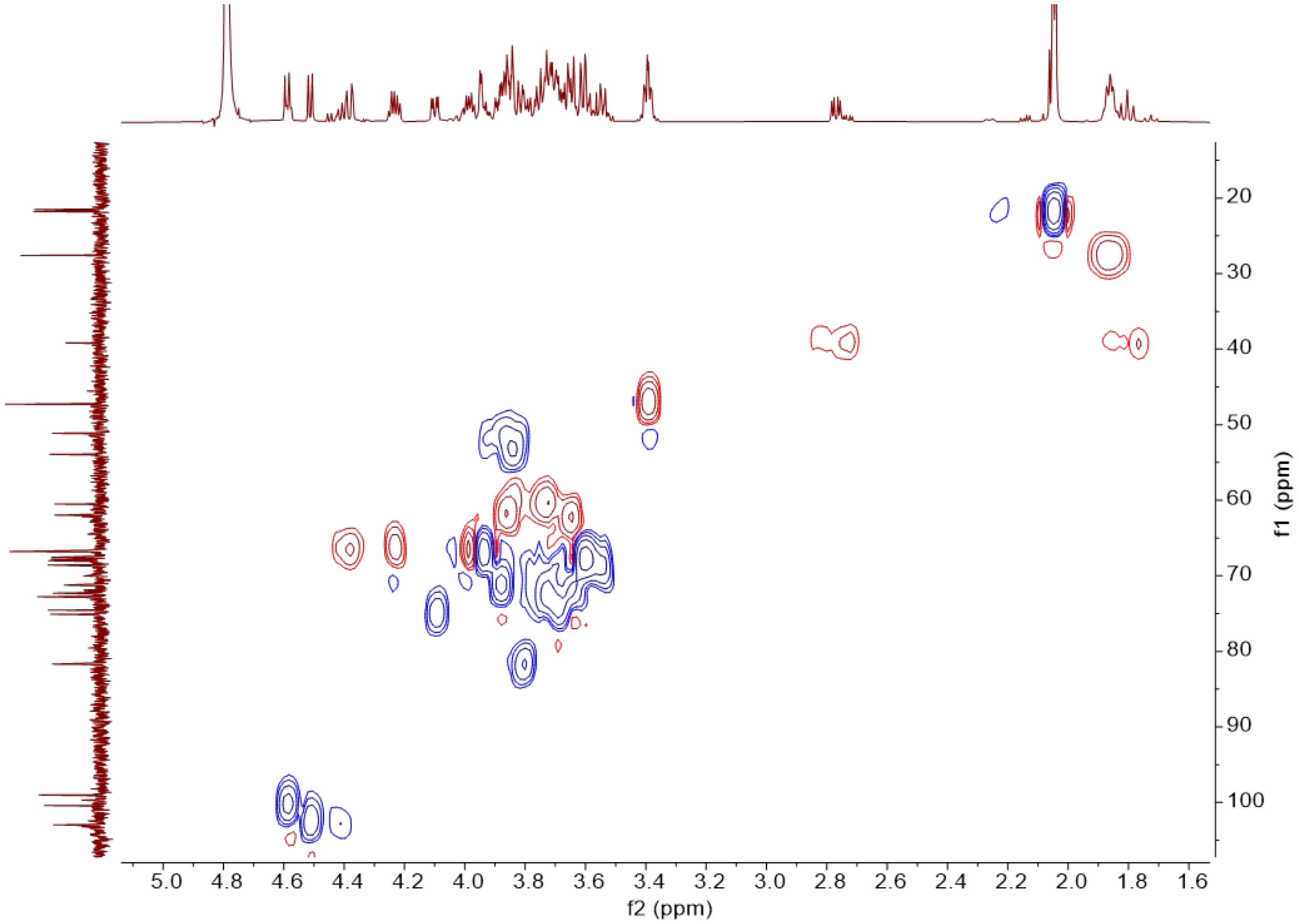

HO
OH
OH
COOH
OH
OH
OSO3H
AcNH
O
O
O
HO
O
O
O
N3
OH
OH
NHAc

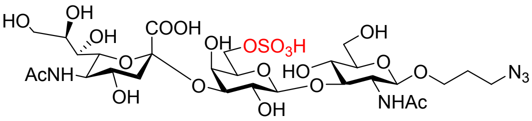
44


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)

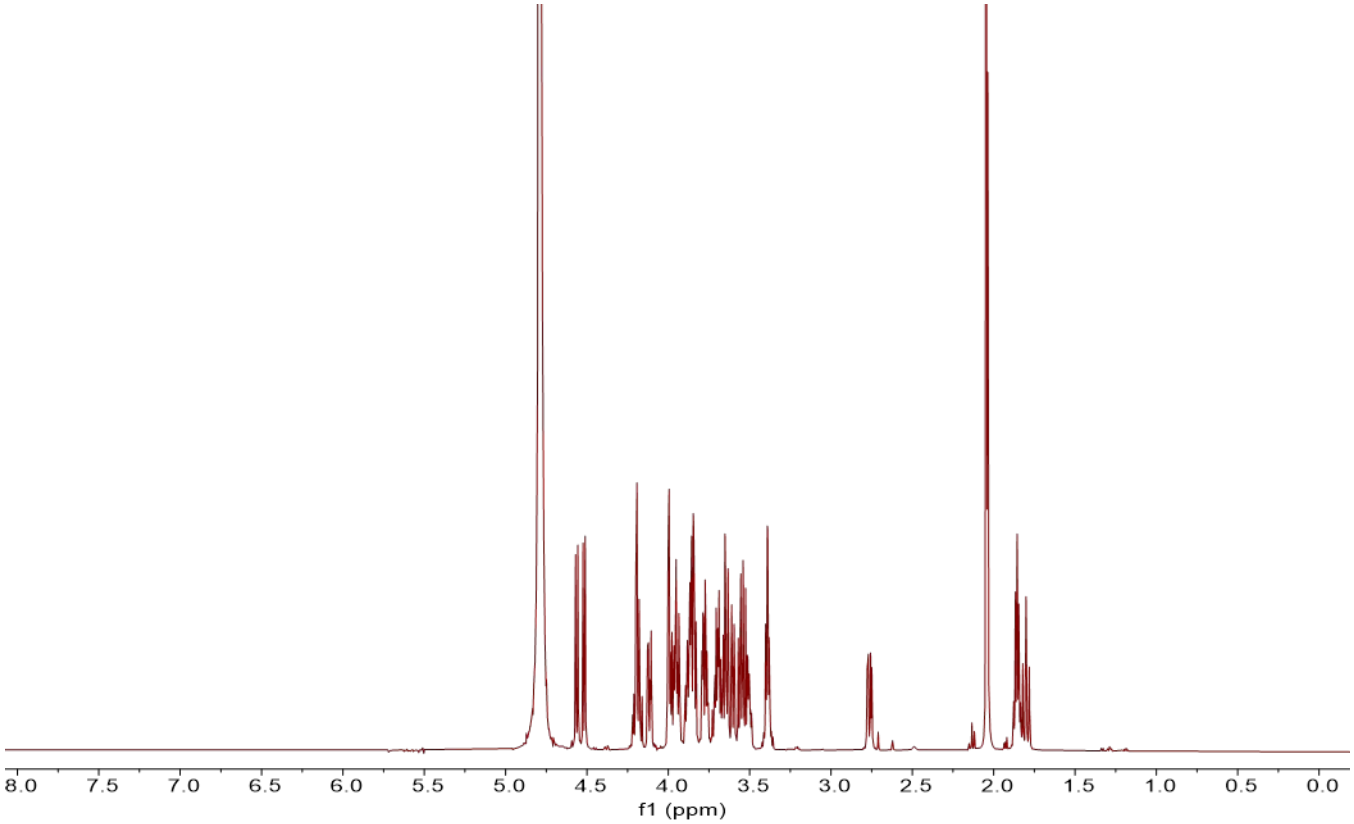

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

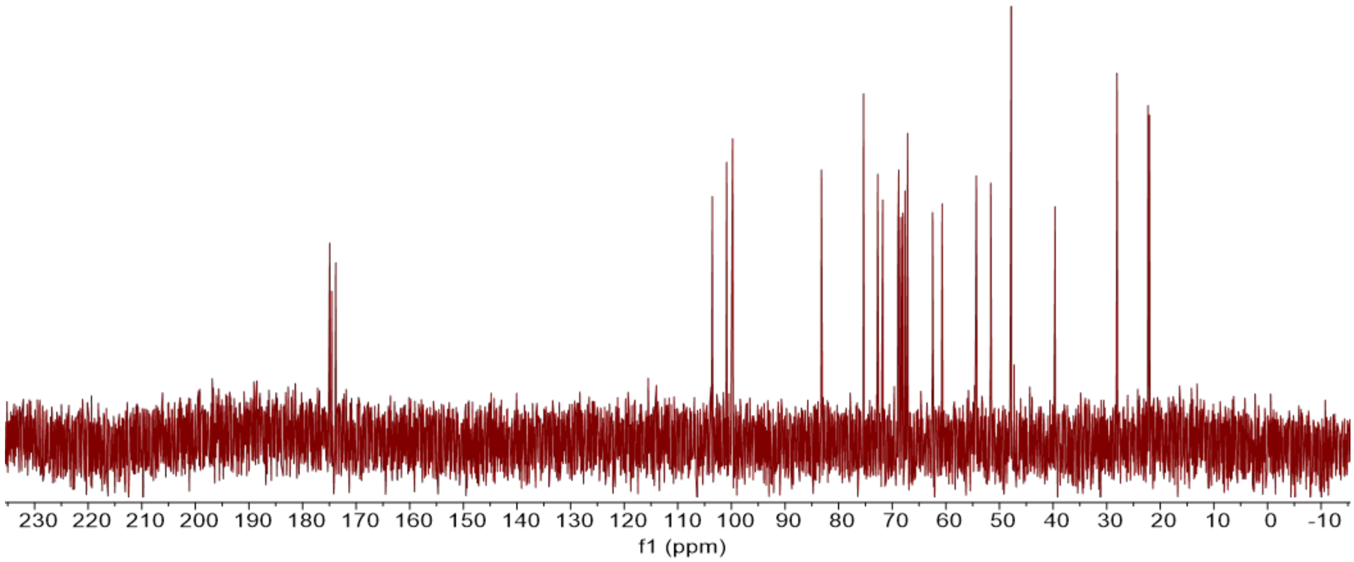

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

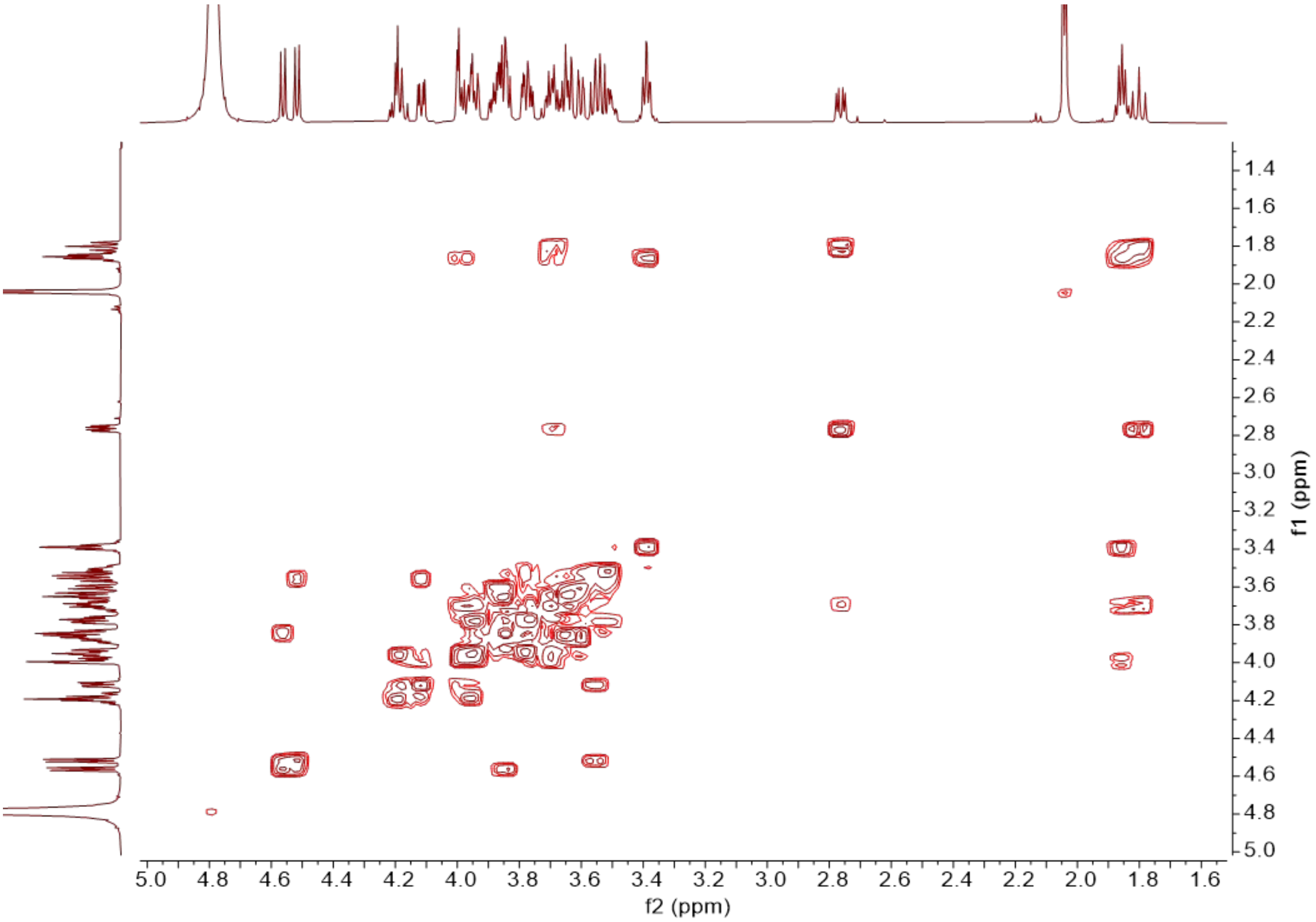

20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)


HO
OH
OH
COOH
AcNH
O
OH
O
OH
OSO3H
O
OH
HO
O
OH
O
O
NHAc
N3

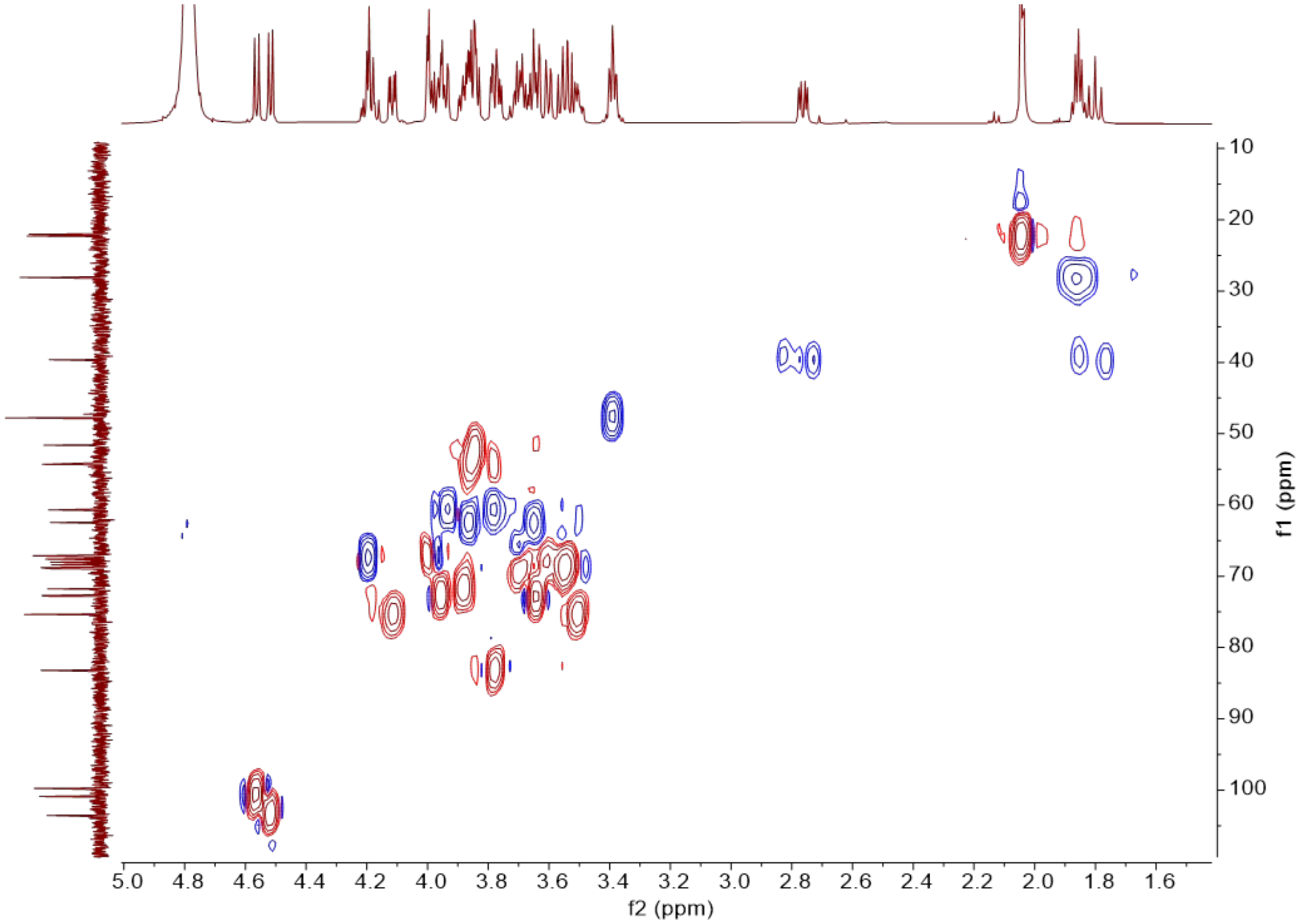
45


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

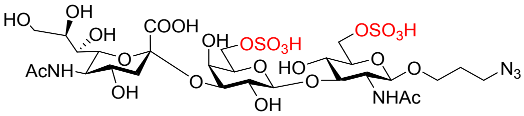

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



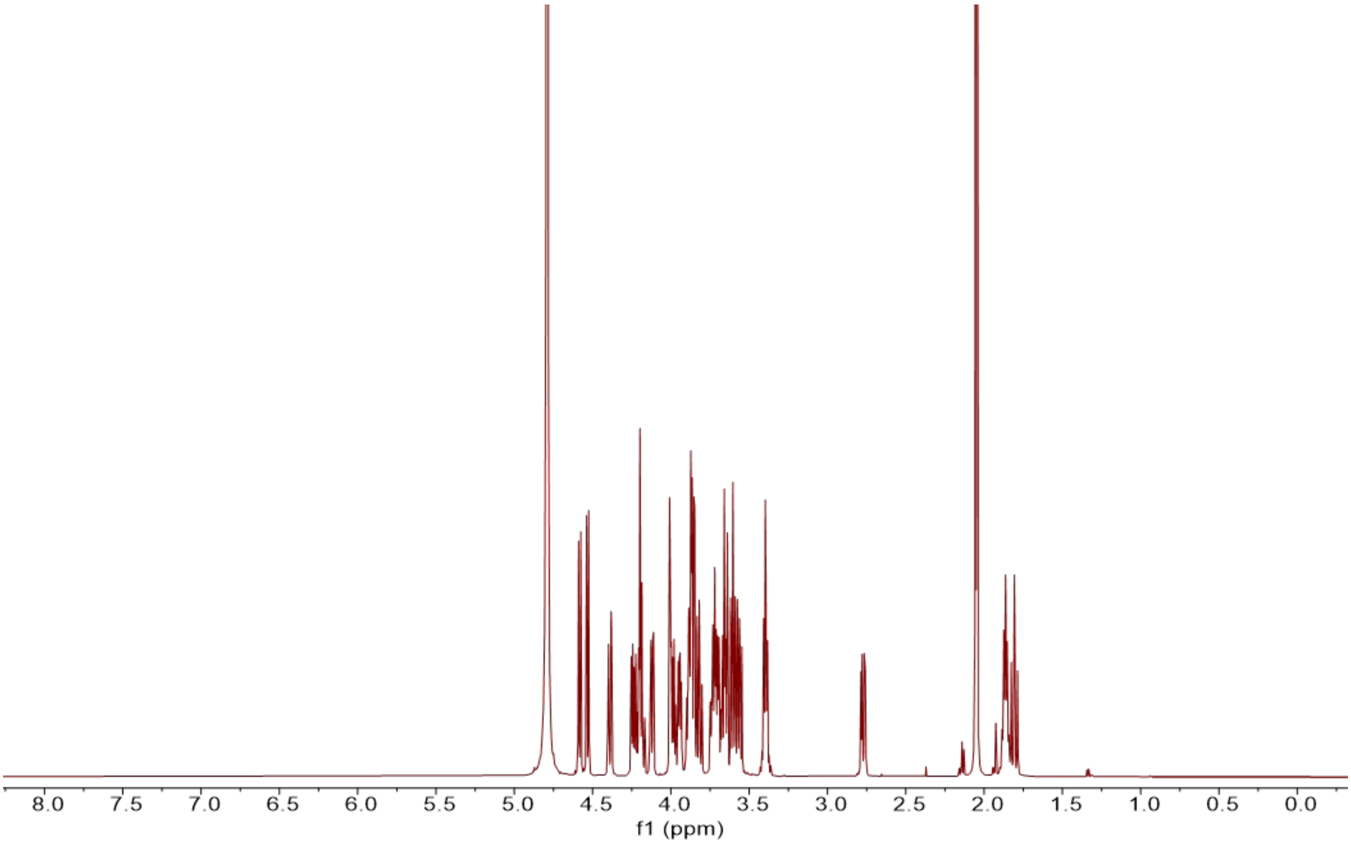
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

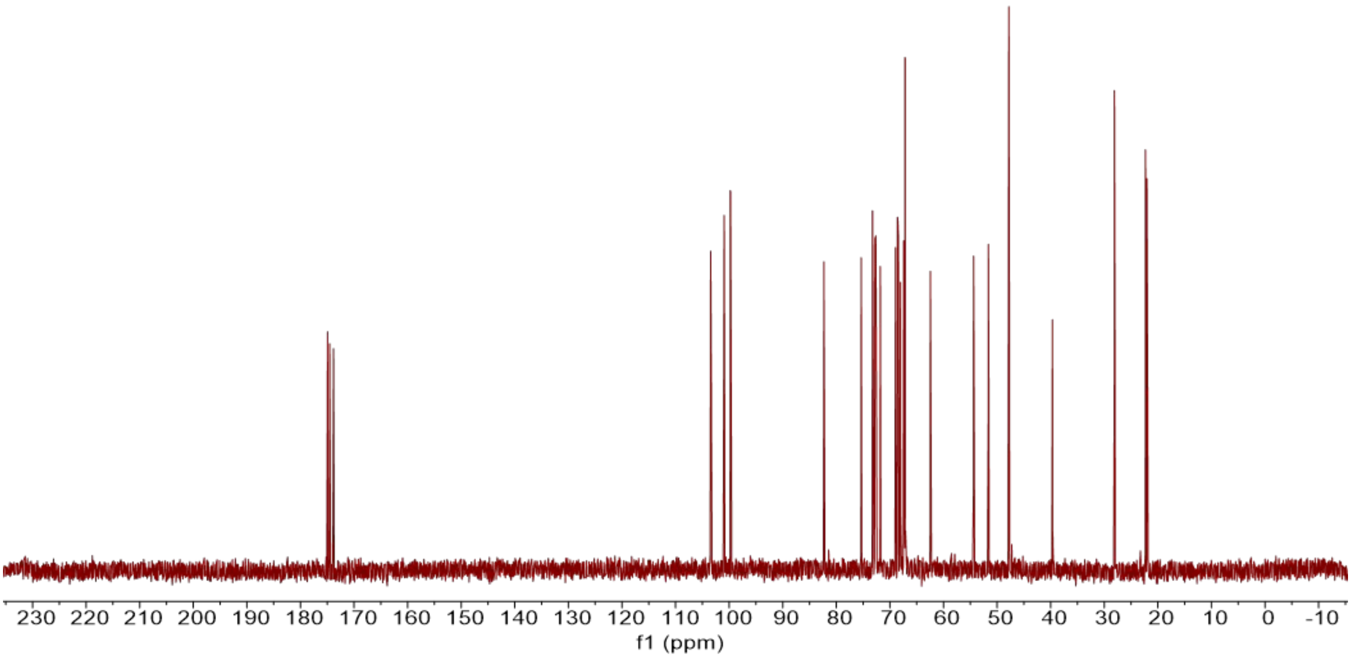


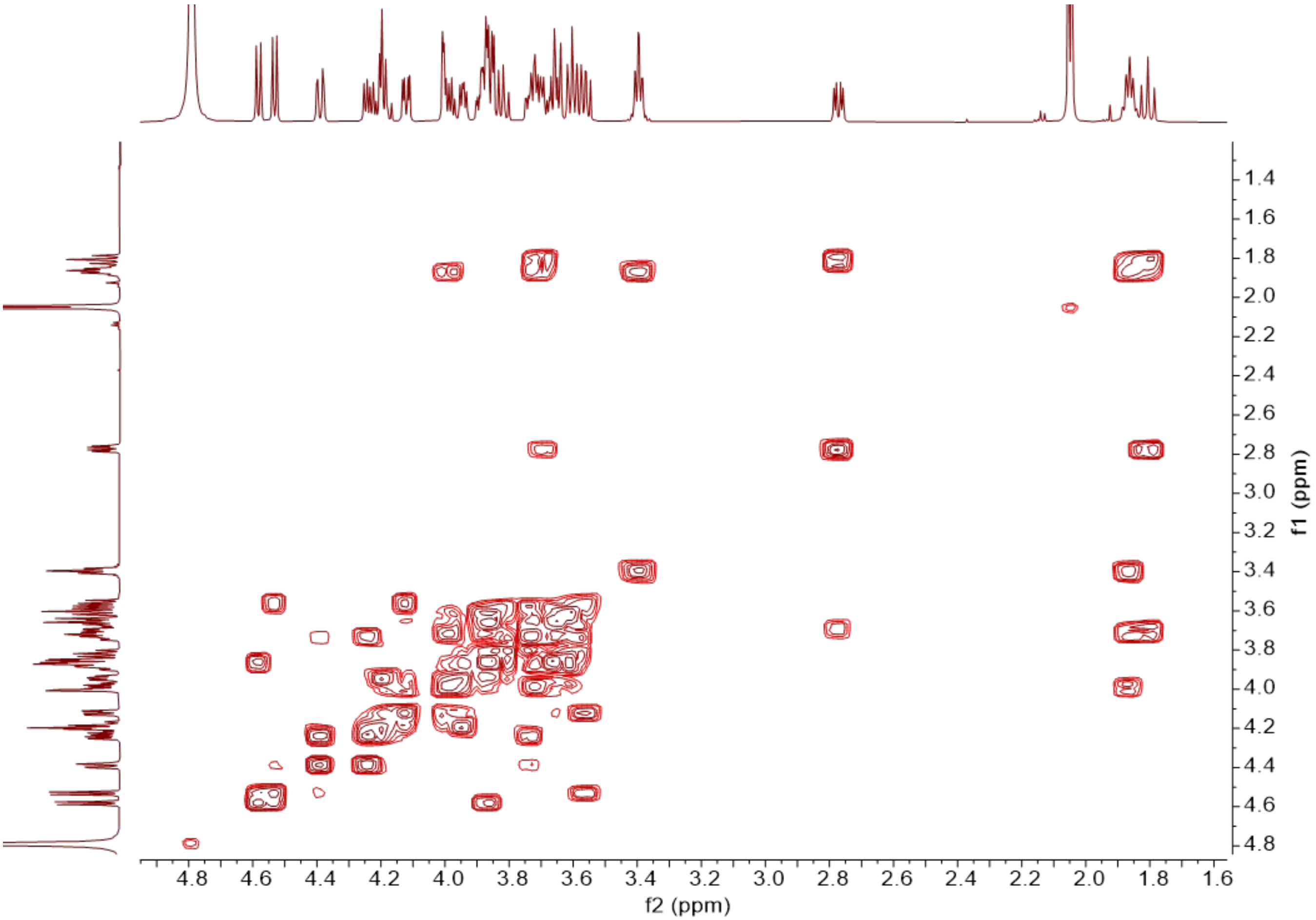
10
20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

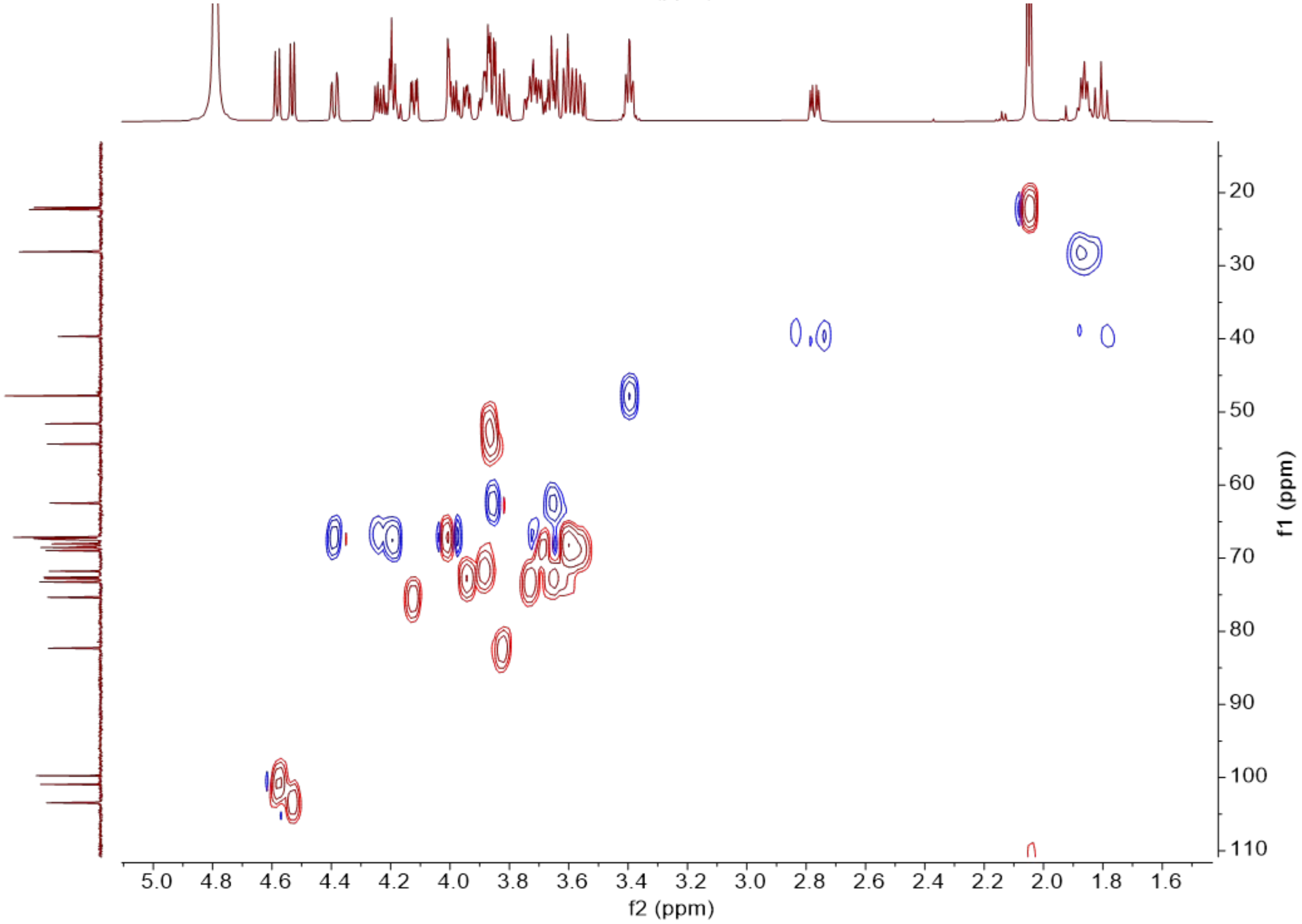

HO
OH
OH
COOH
AcNH
OH
O
OH
OSO3H
O
OH
O
HO
OSO3H
O
NHAc
O
N3

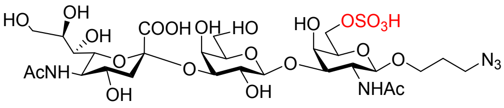
46


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

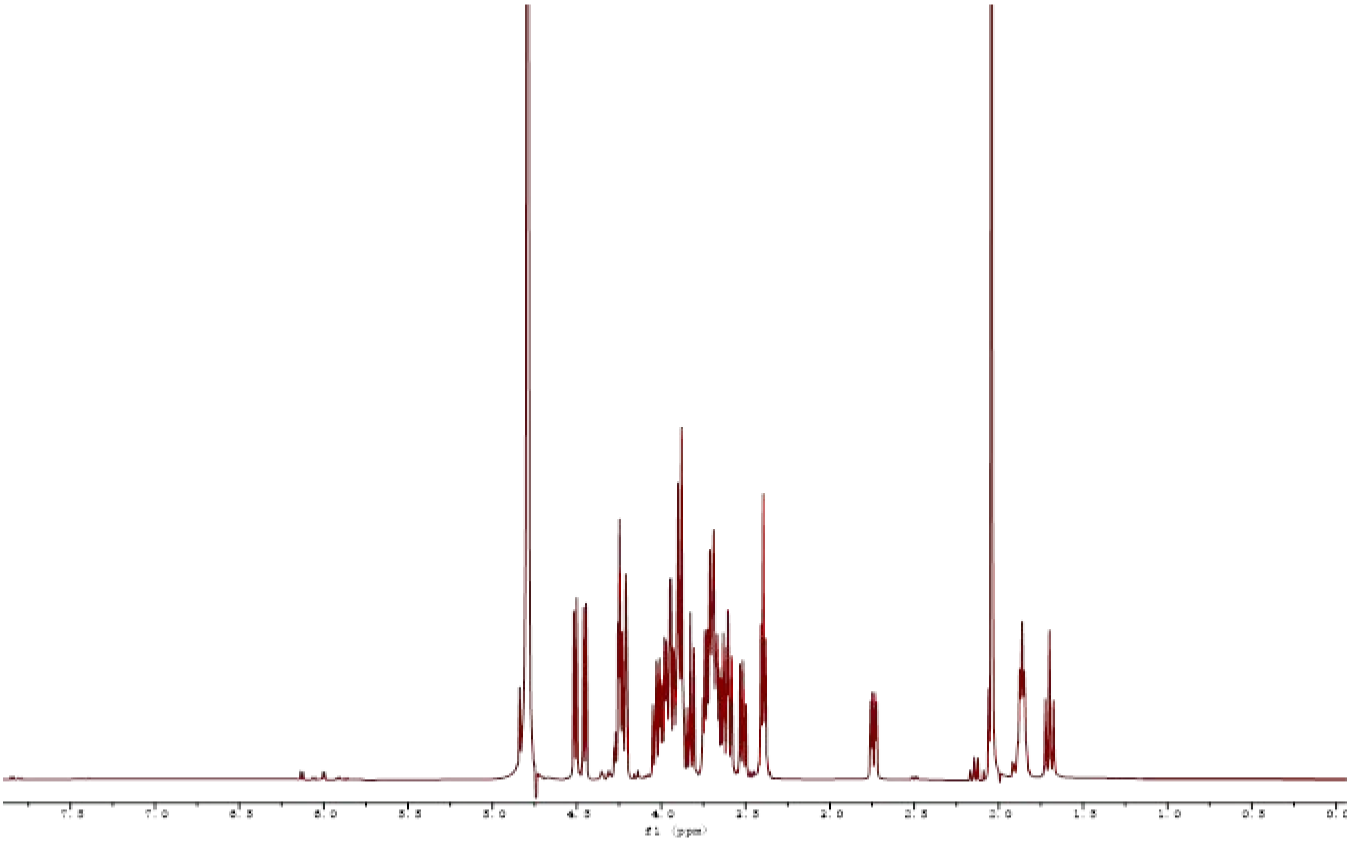

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

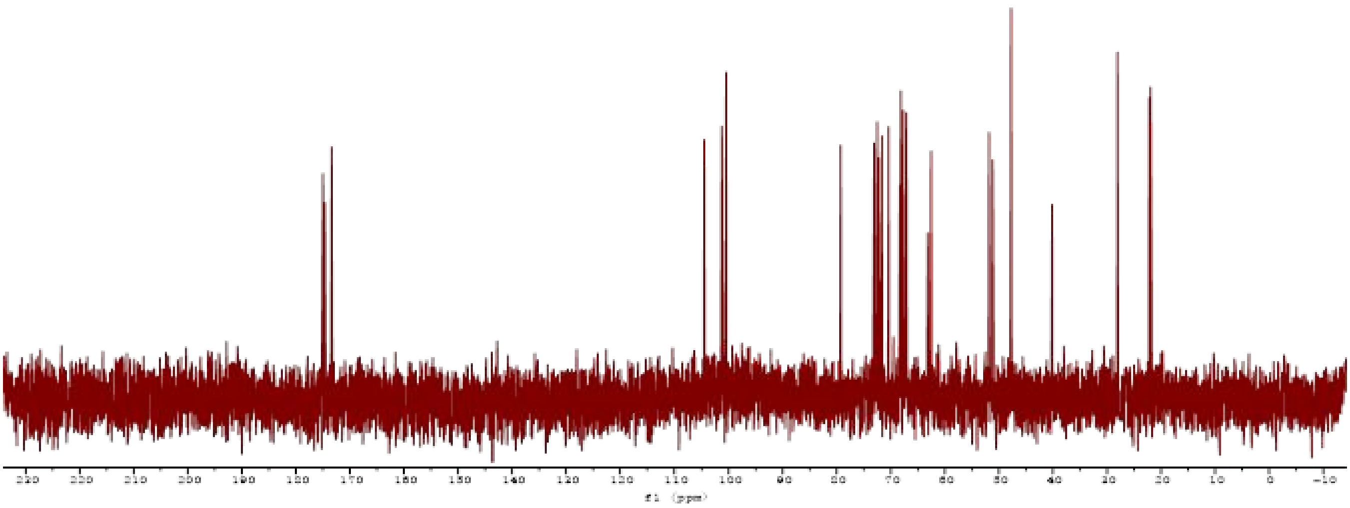

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

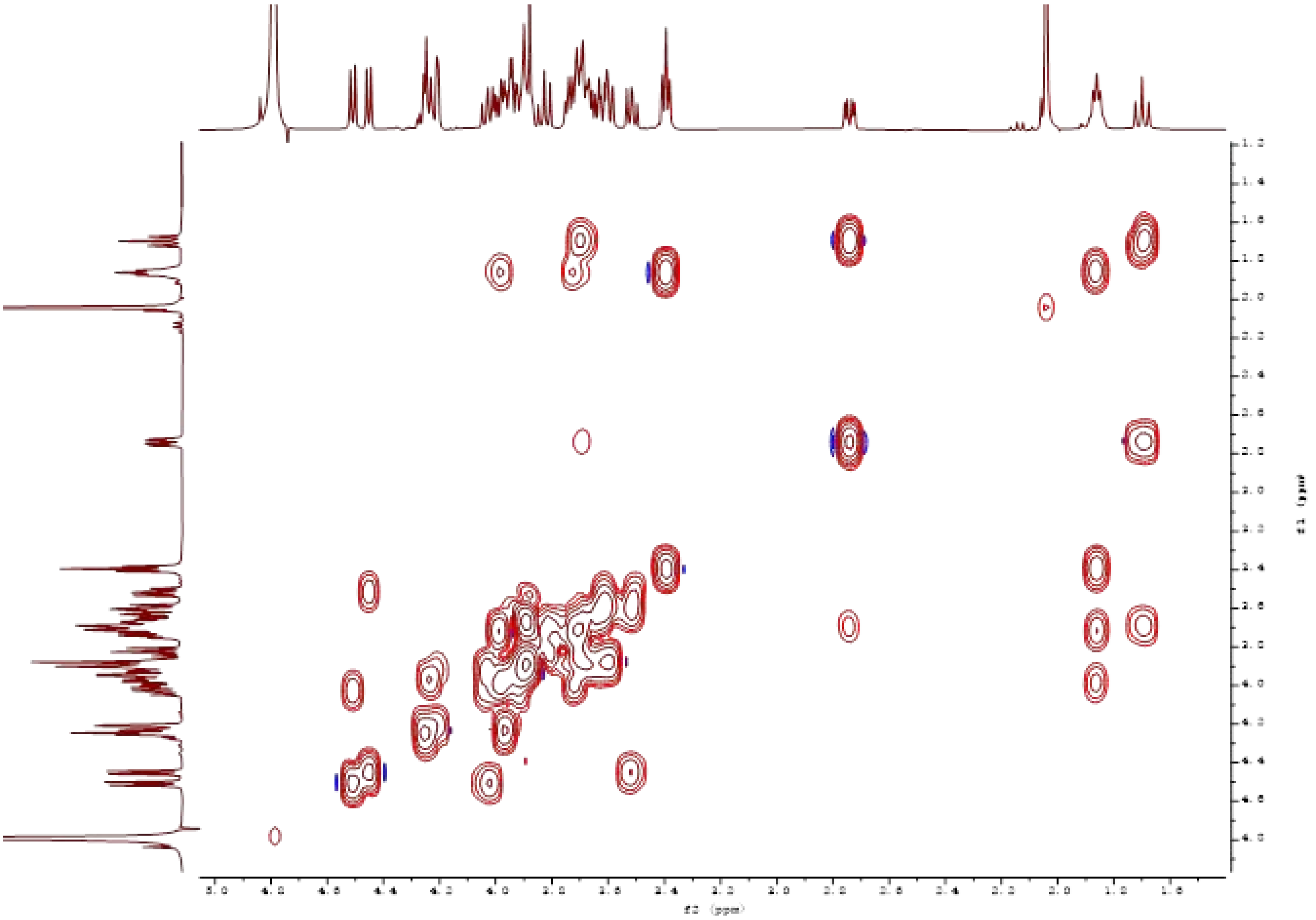

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)


HO
OH
OH
COOH
OH
HO
HO
OSO3H
AcNH
O
O
O
O
O
O
OH
OH
NHAc
N3

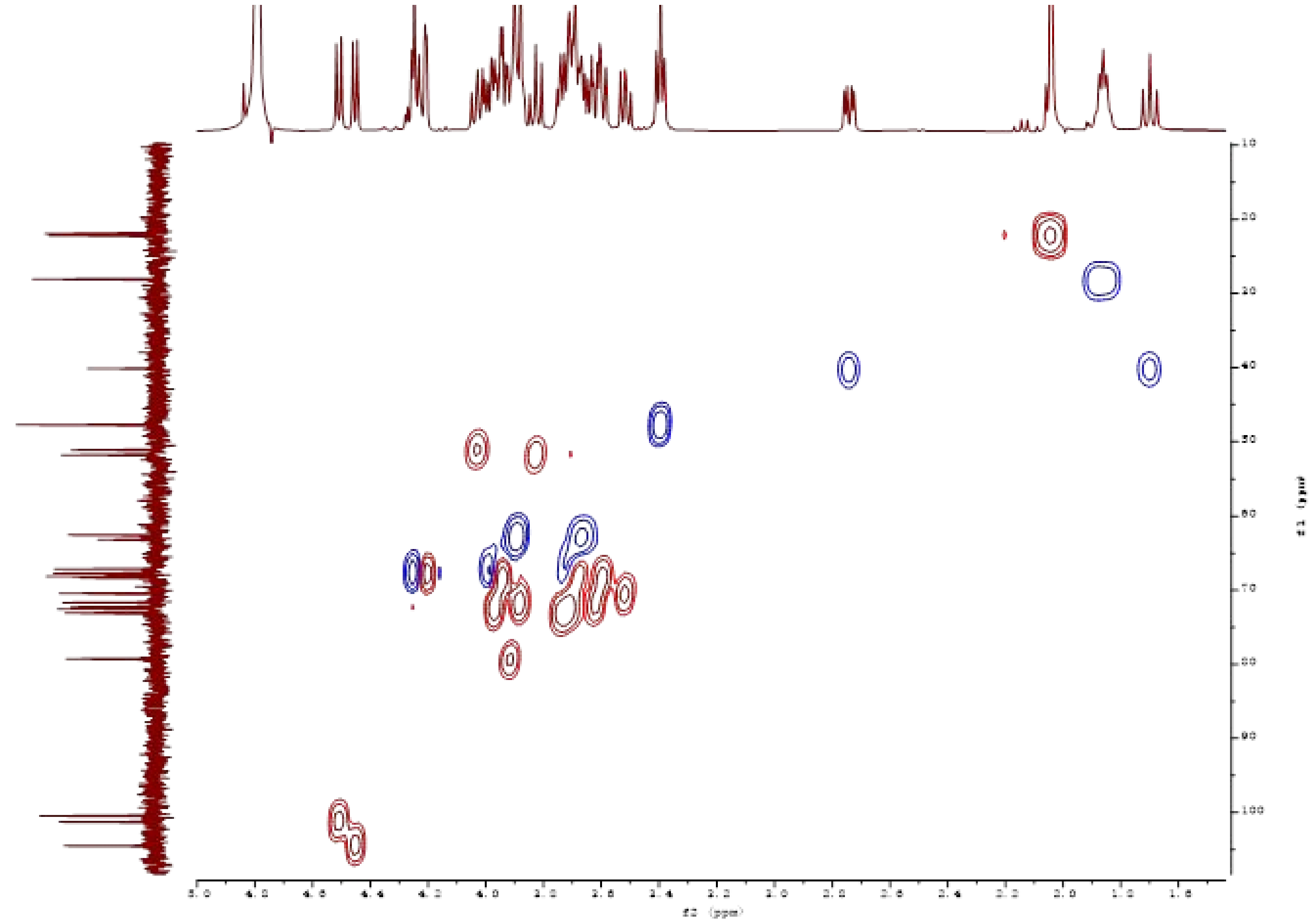
47


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)

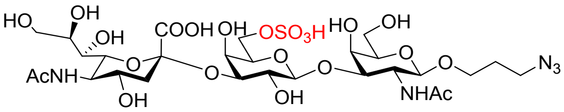

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



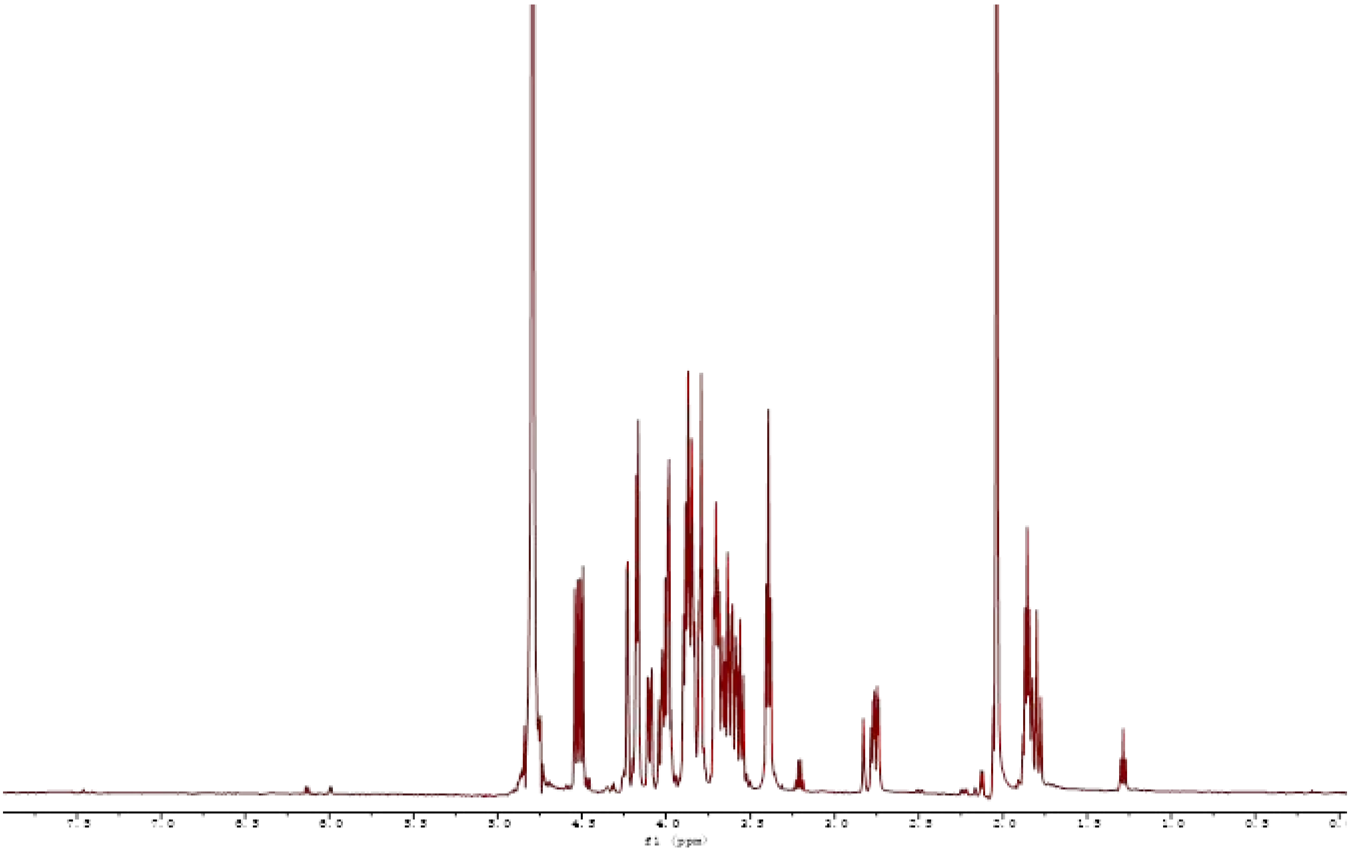
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

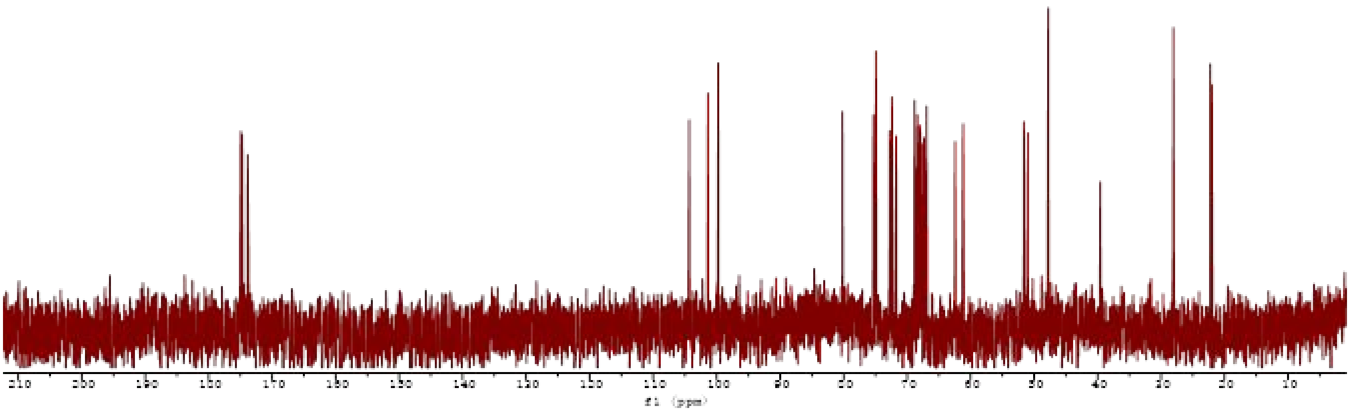


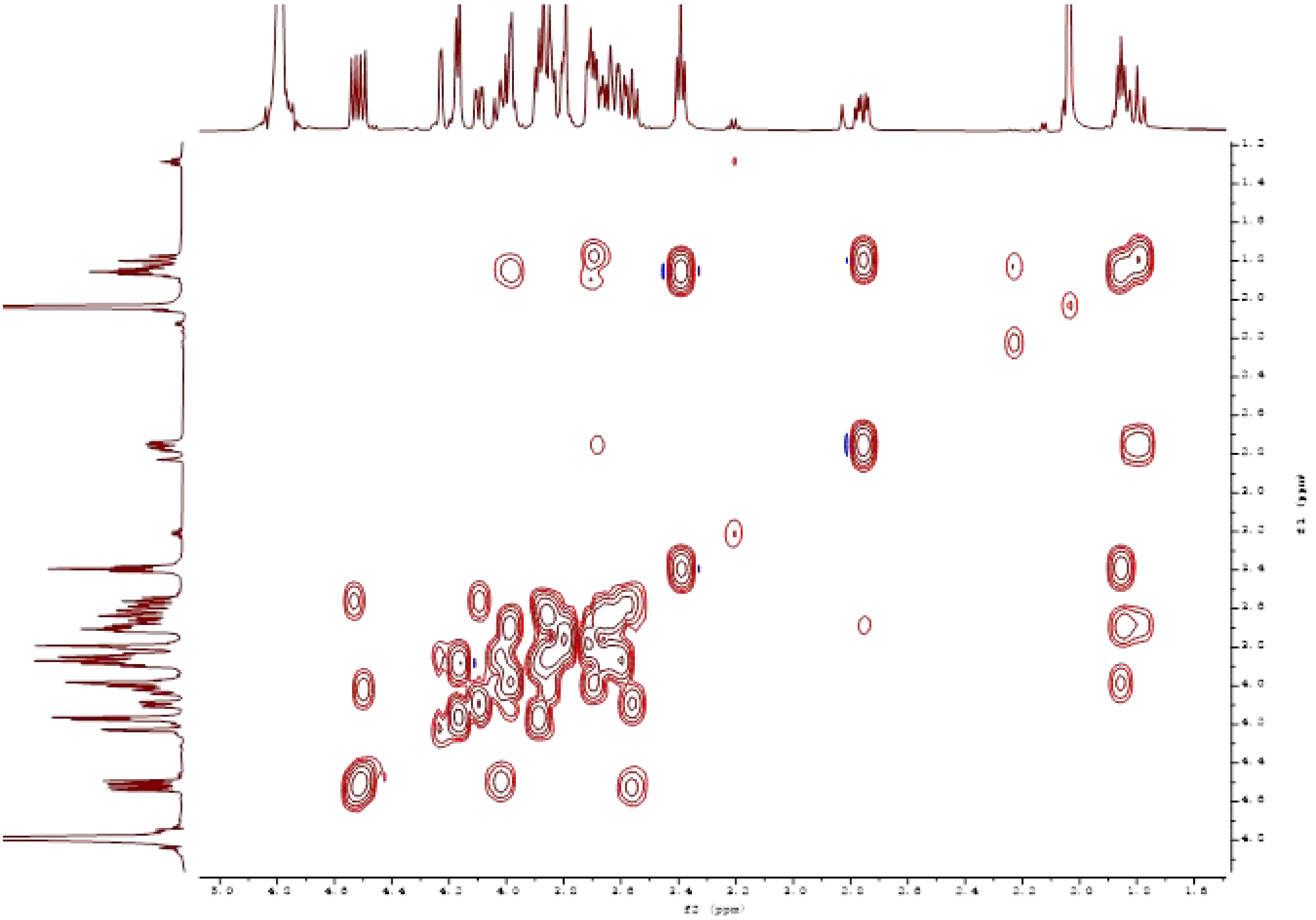
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)

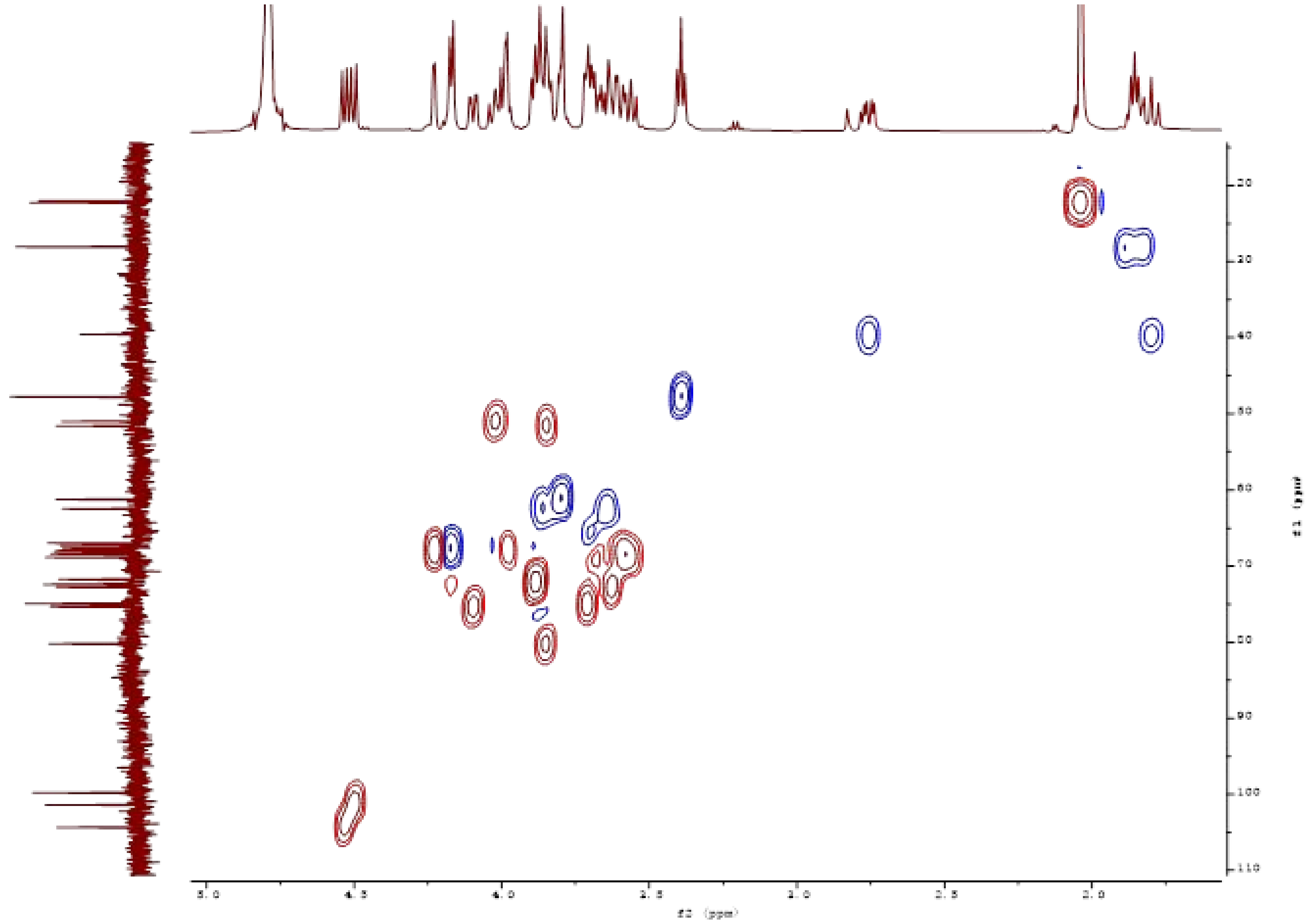

HO
OH
OH
COOH
OH
OSO3H
HO
OH
AcNH
O
O
O
O
O
O
OH
OH
NHAc
N3

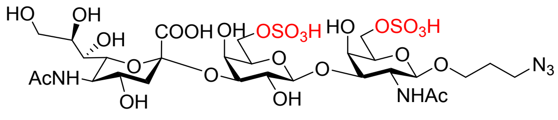
48


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)

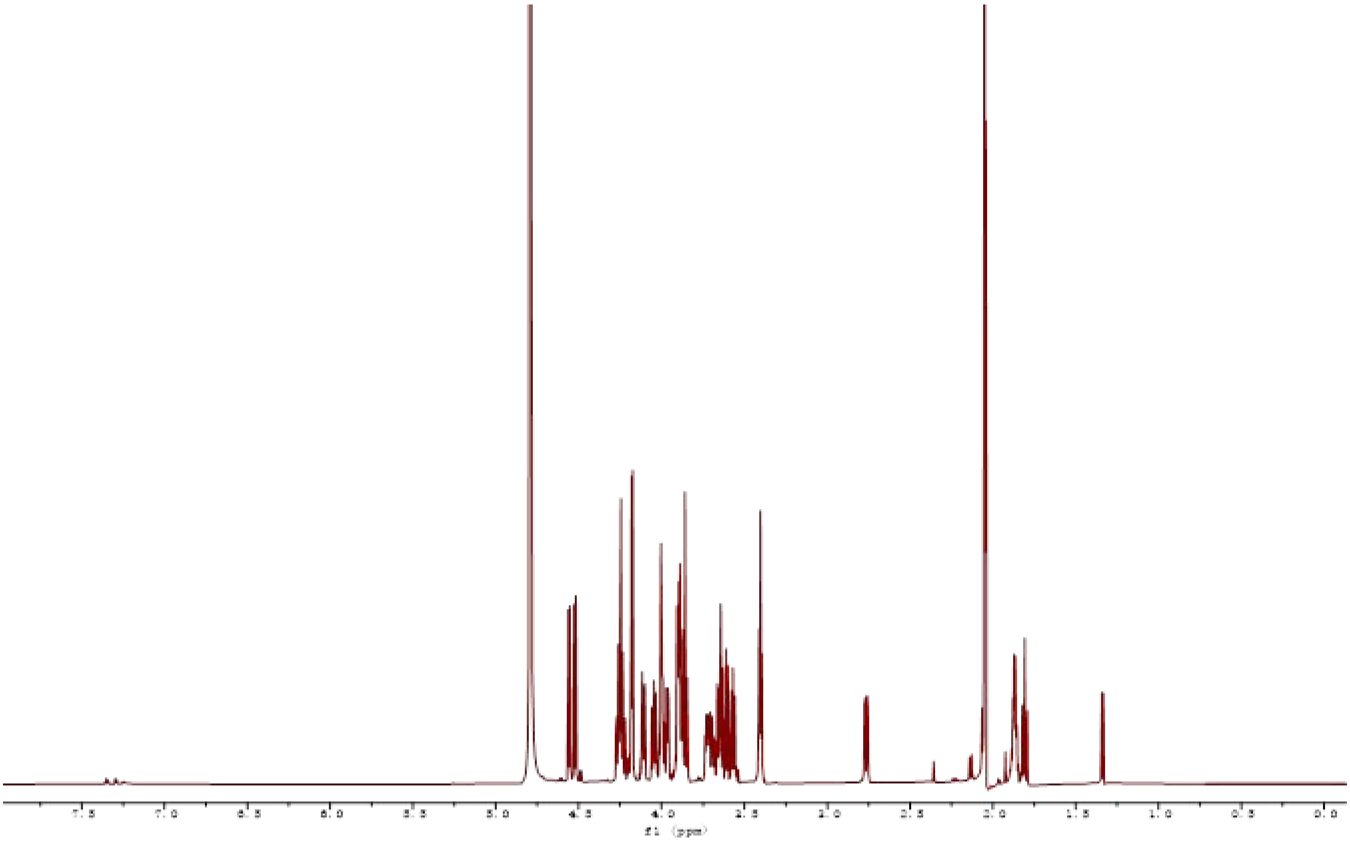

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

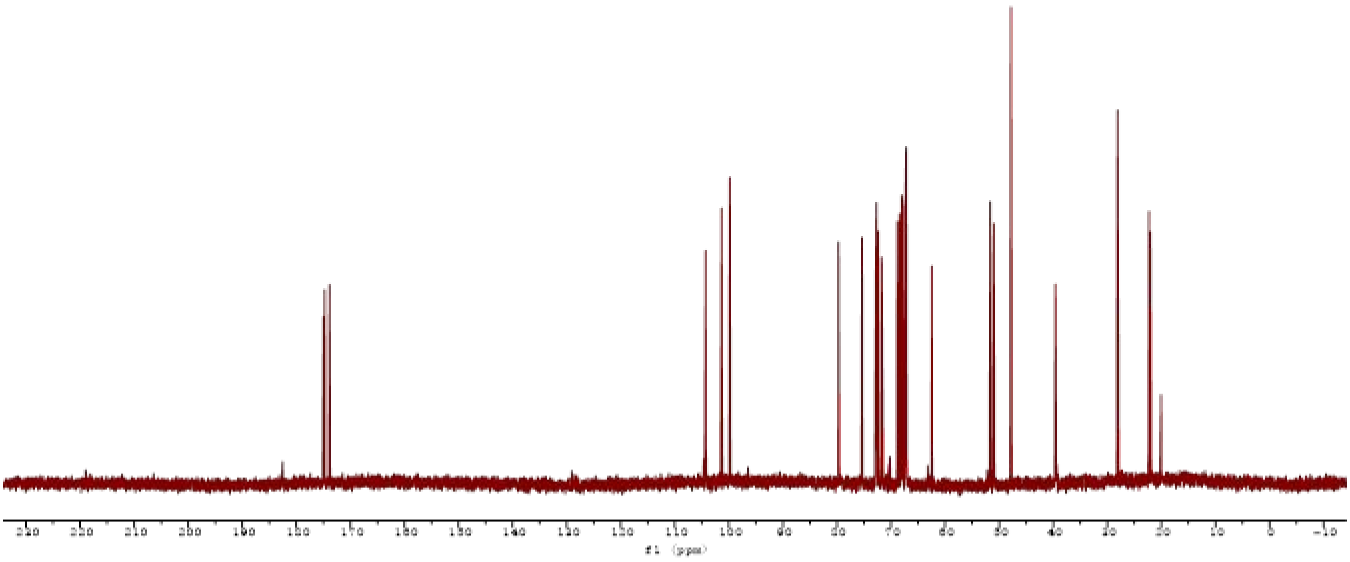

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

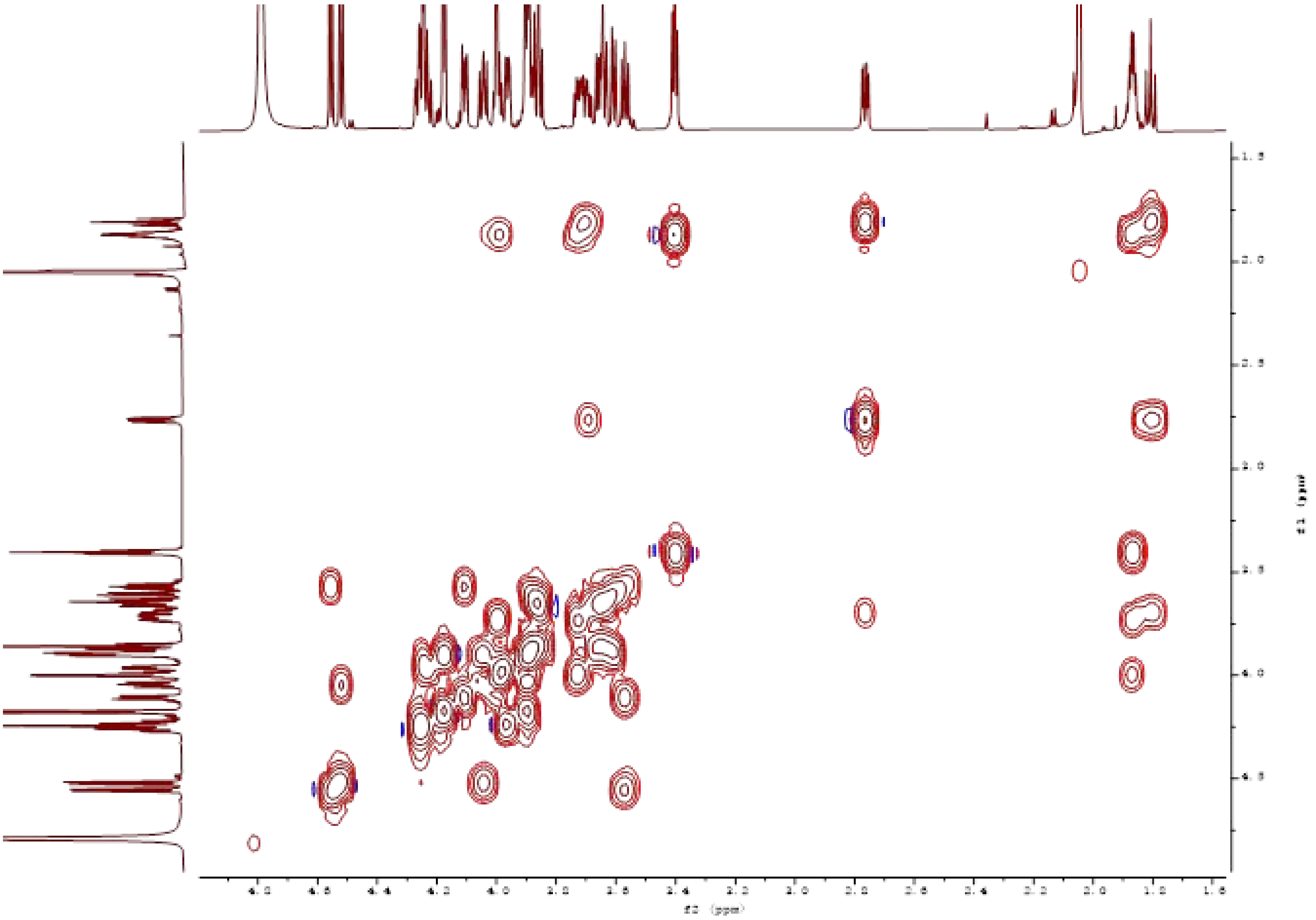

5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

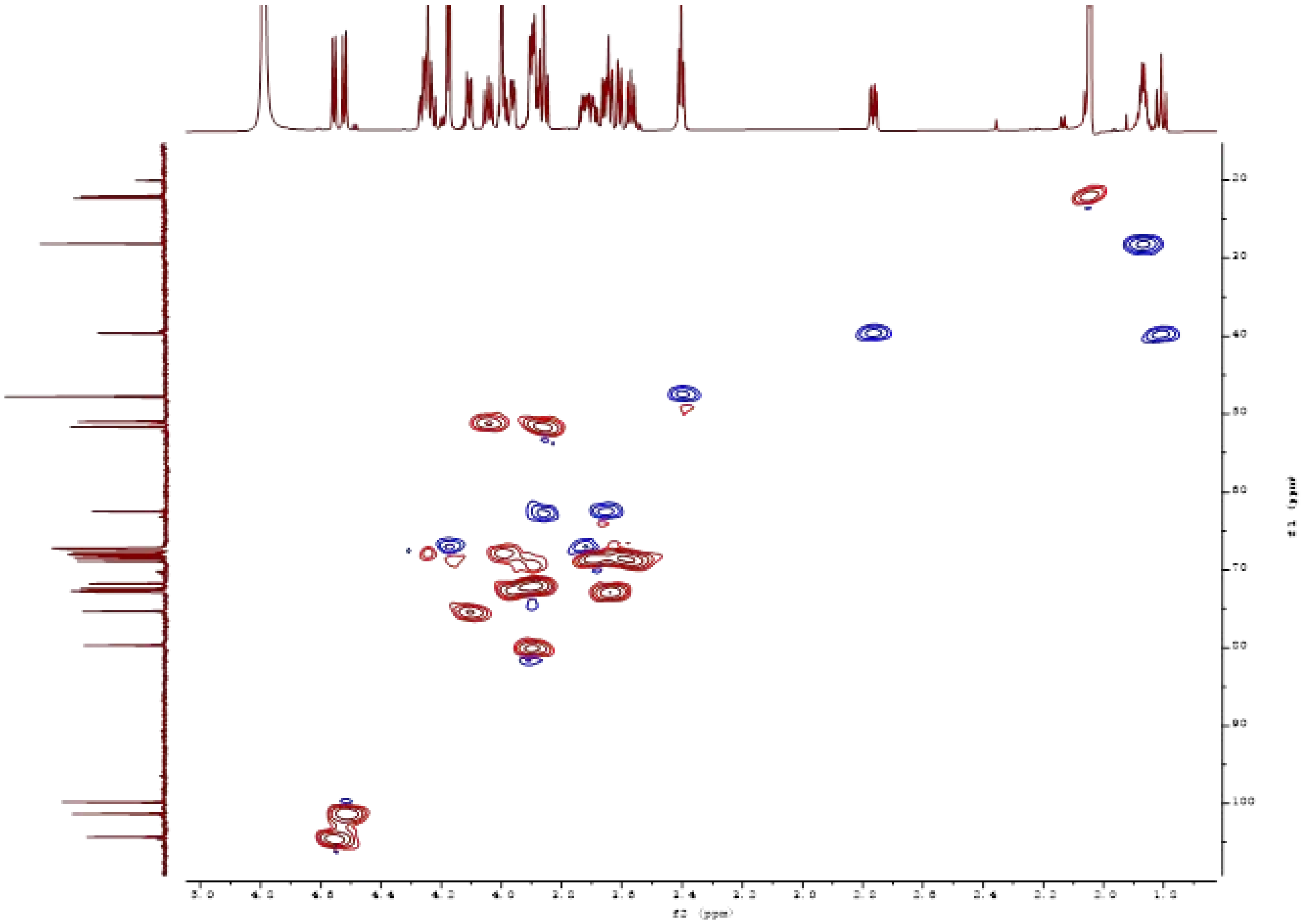

HO
OH
OH
COOH
OH
OSO3H
HO
OSO3H
AcNH
O
O
O
O
O
O
N3
OH
OH
NHAc

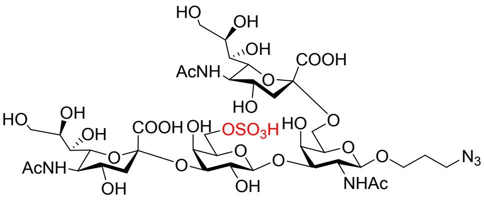
49


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)

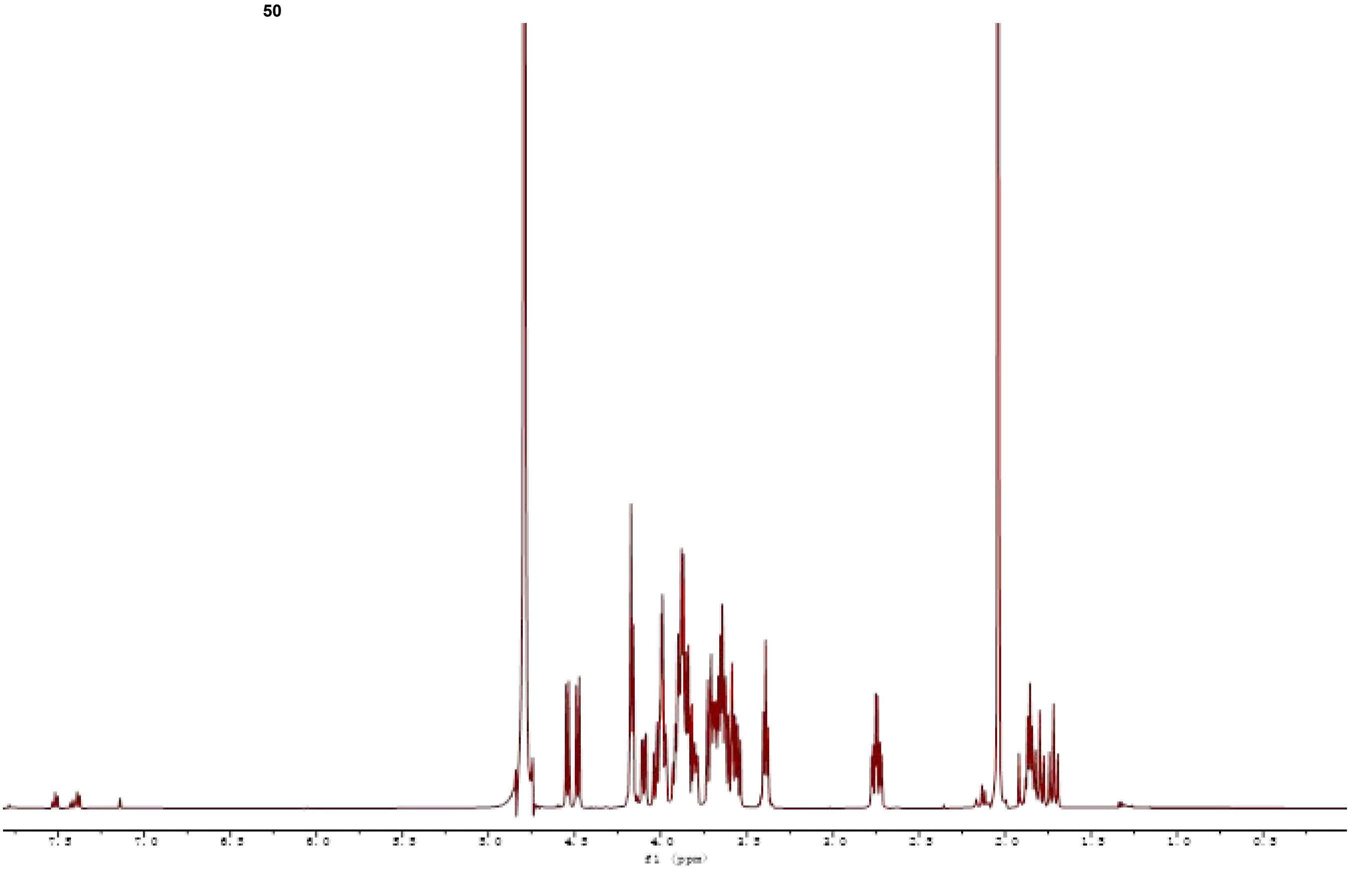

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

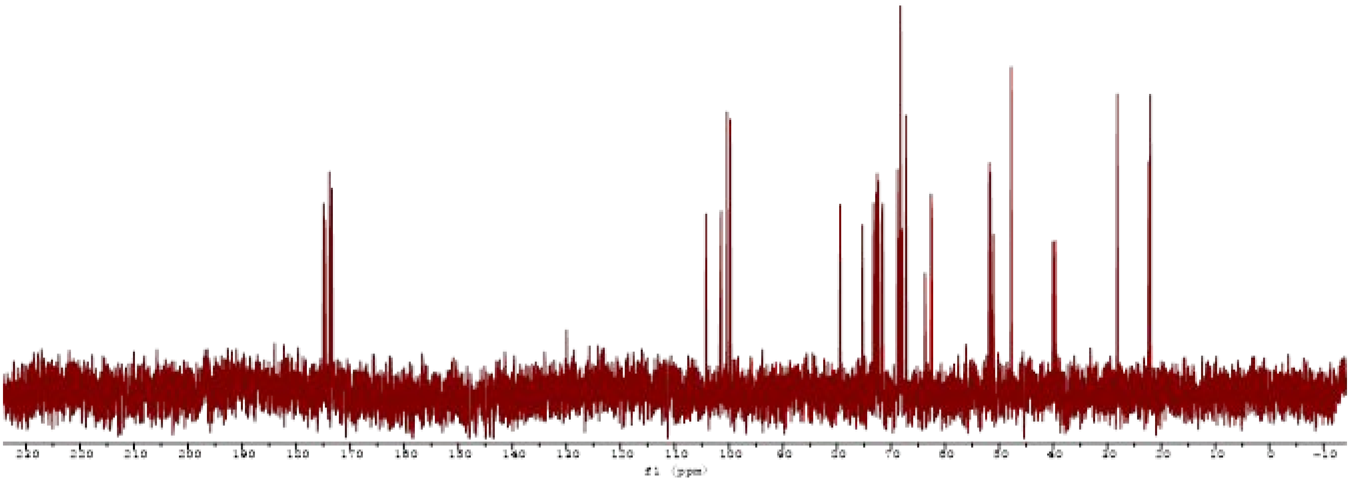

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

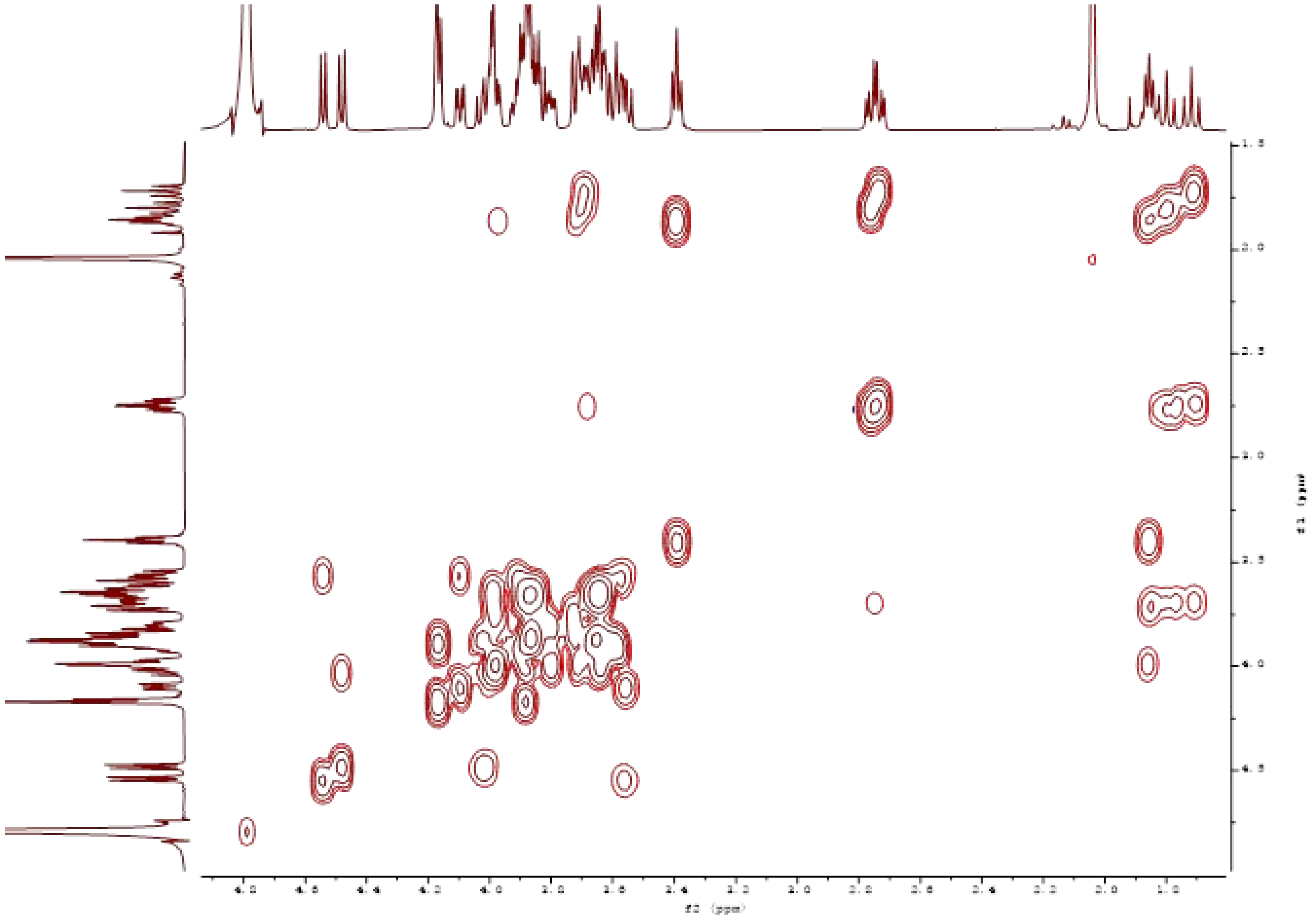

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)


HO
OH
OH
COOH
AcNH
O
HO
O
HO
OH
OH
COOH
OH
OSO3H
HO
O
O
O
O
O
N3
AcNH
OH
OH
NHAc

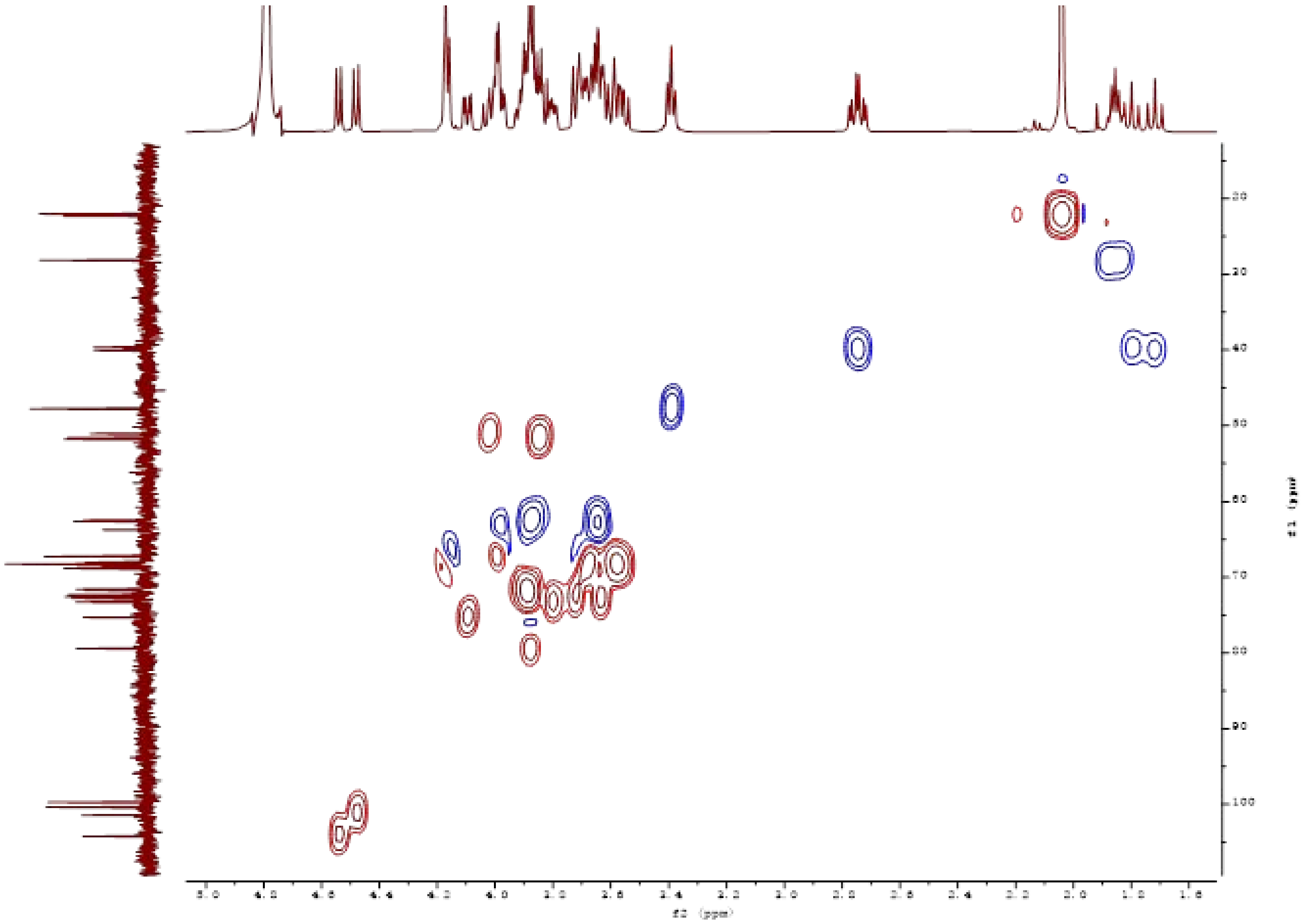
50


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

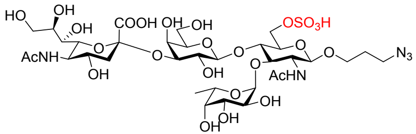

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



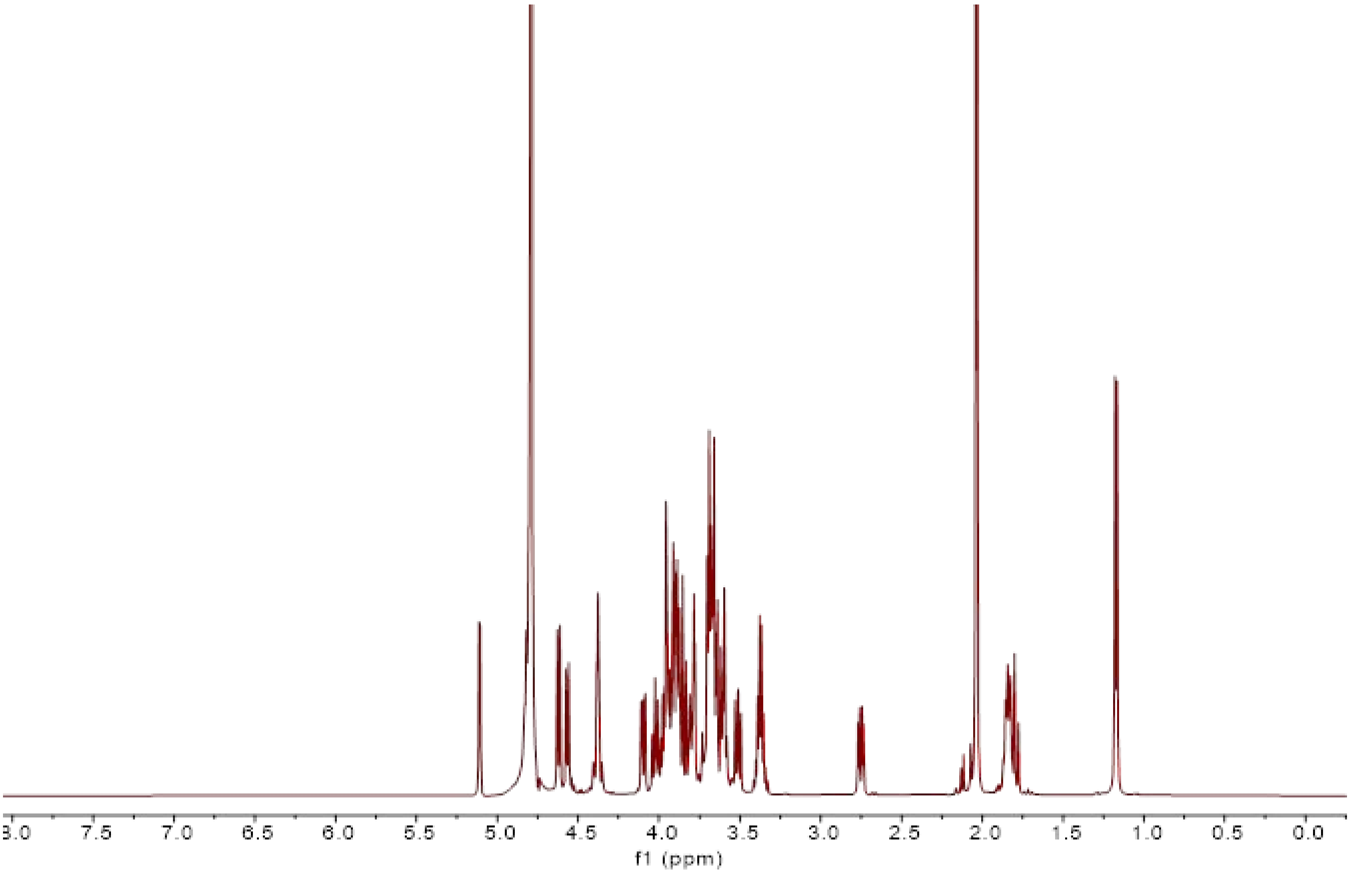
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

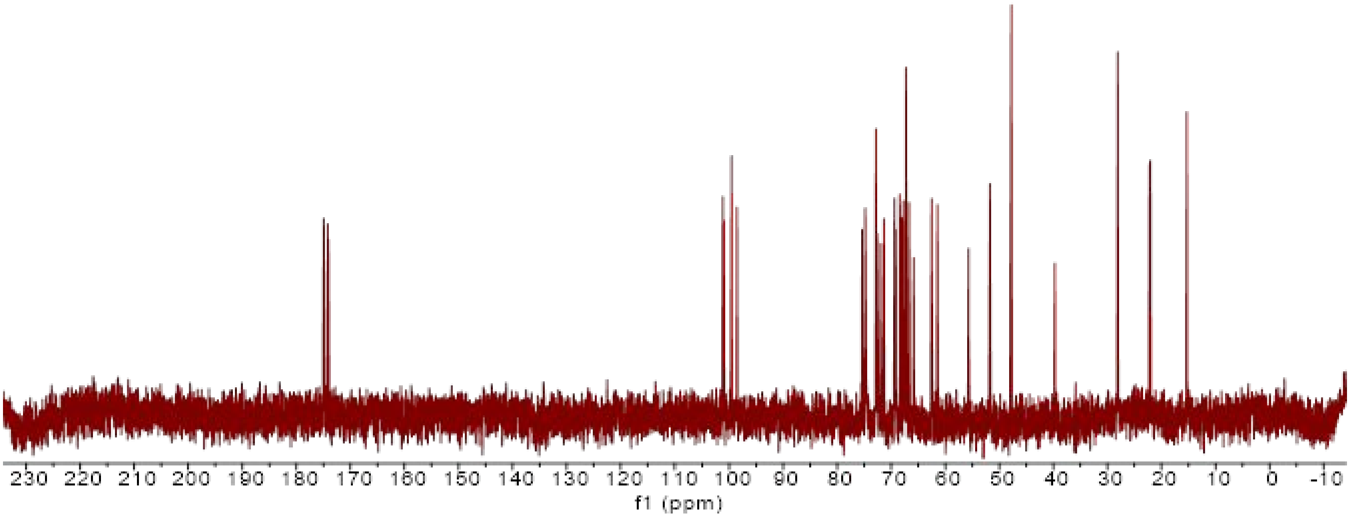


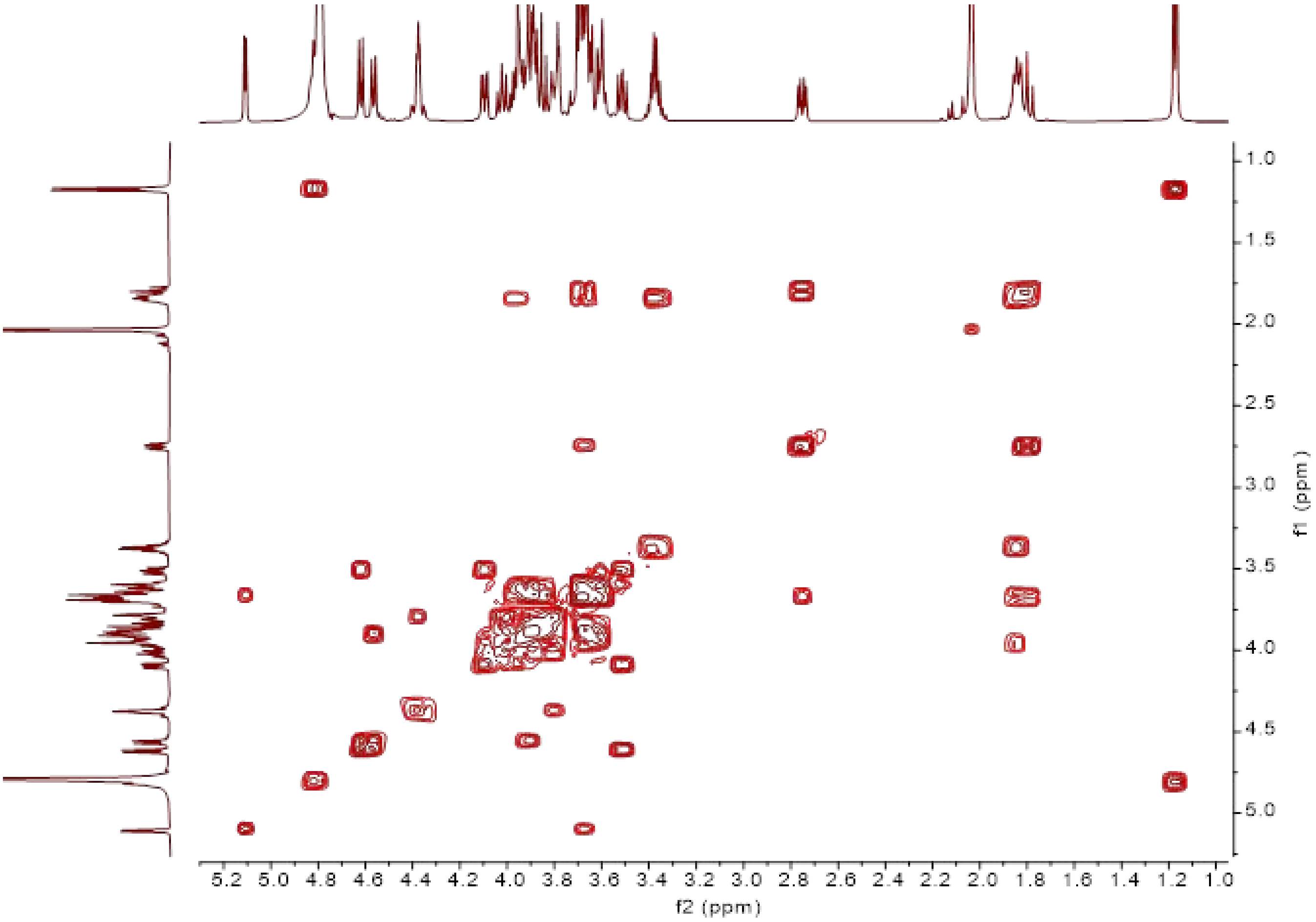
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

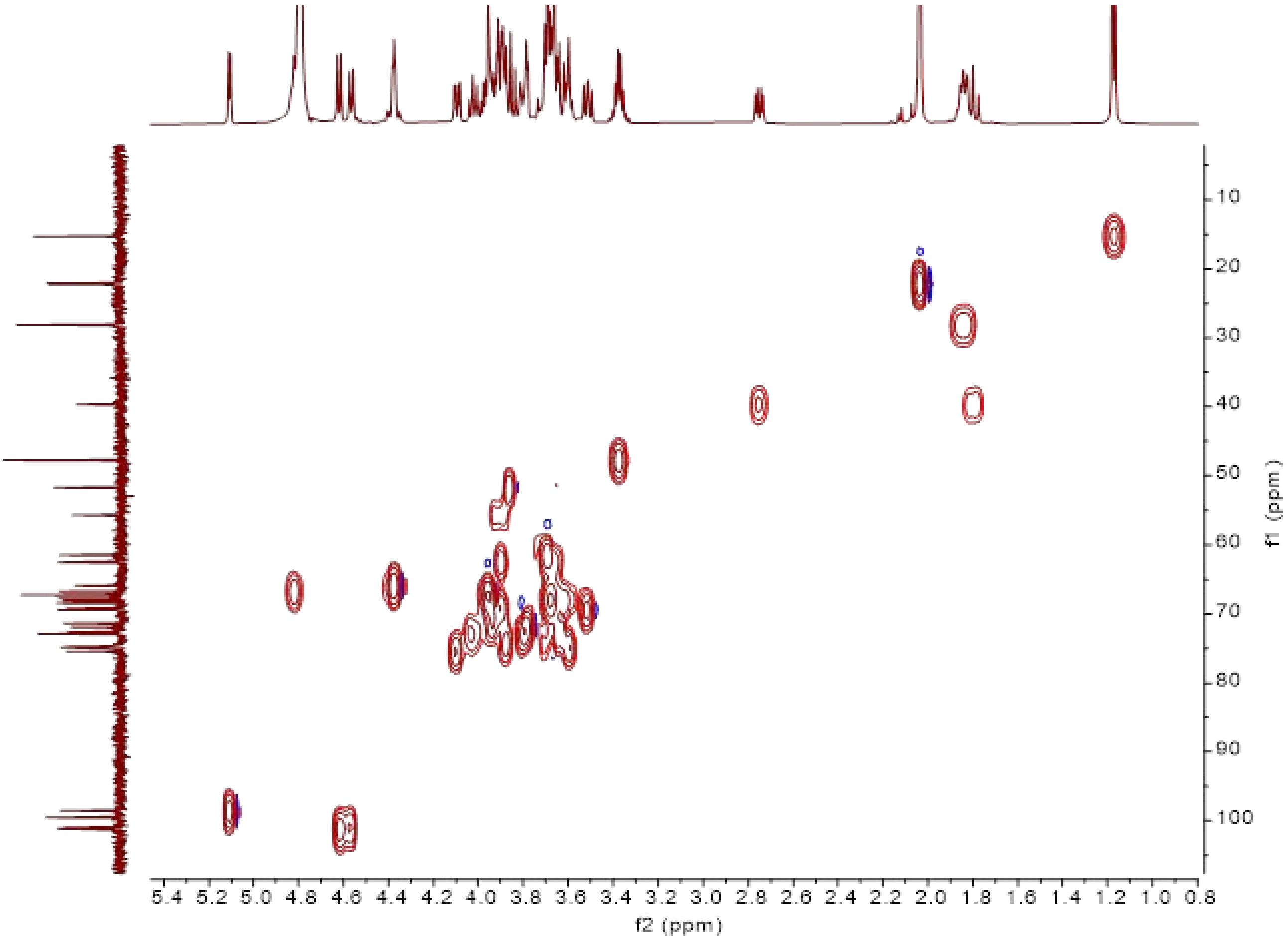

HO
OH
OH
COOH
OH
OH
OSO3H
AcNH
OH
OH
AcHN
N3
OH
OH
OH

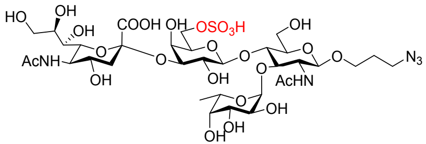
51


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

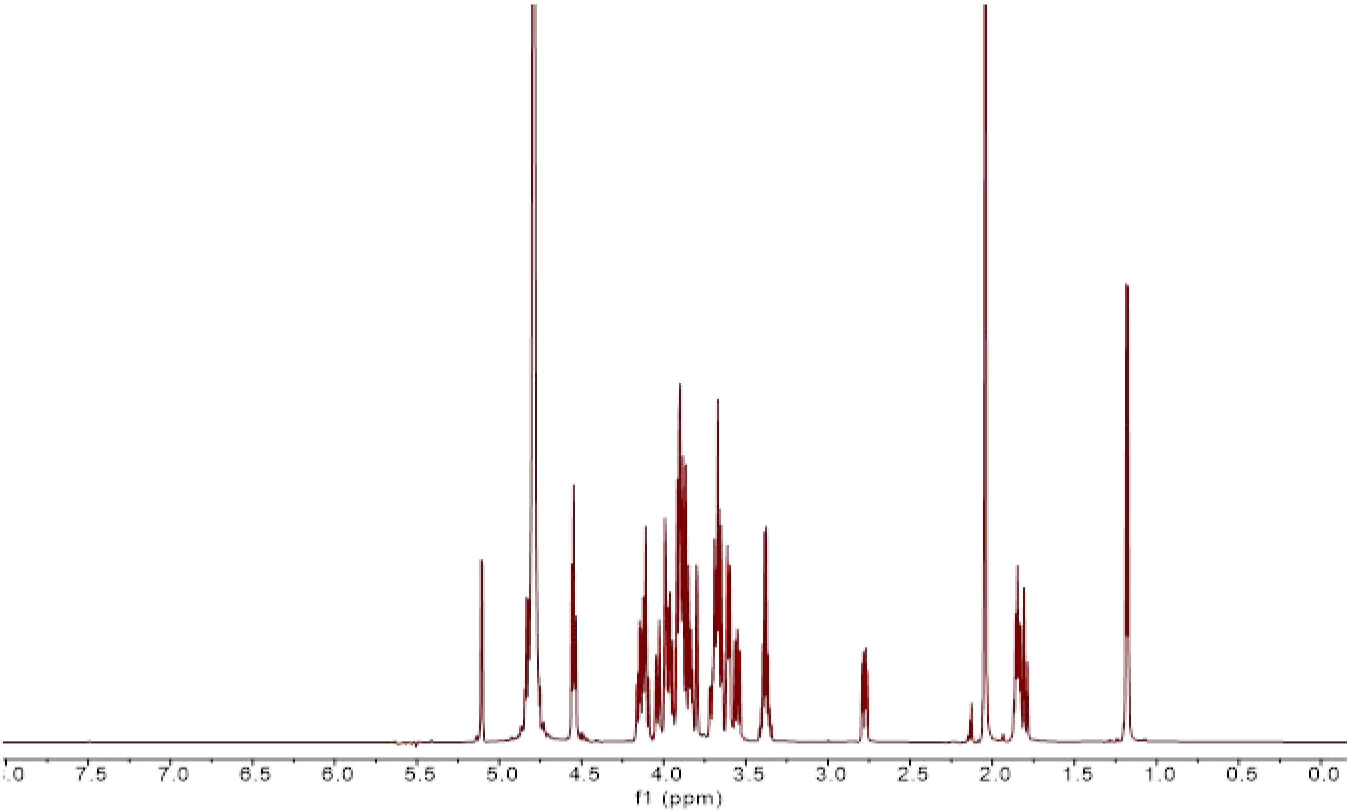

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

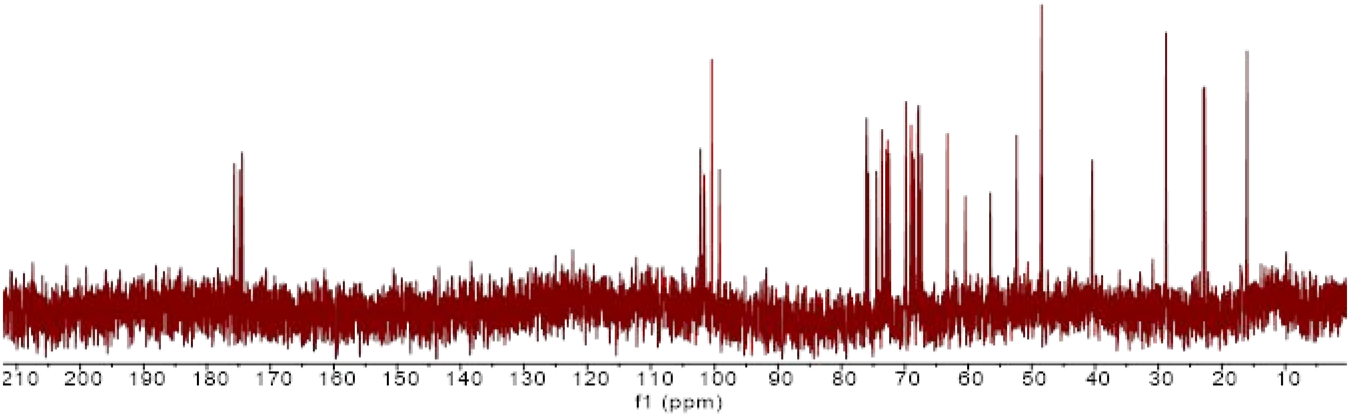

5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

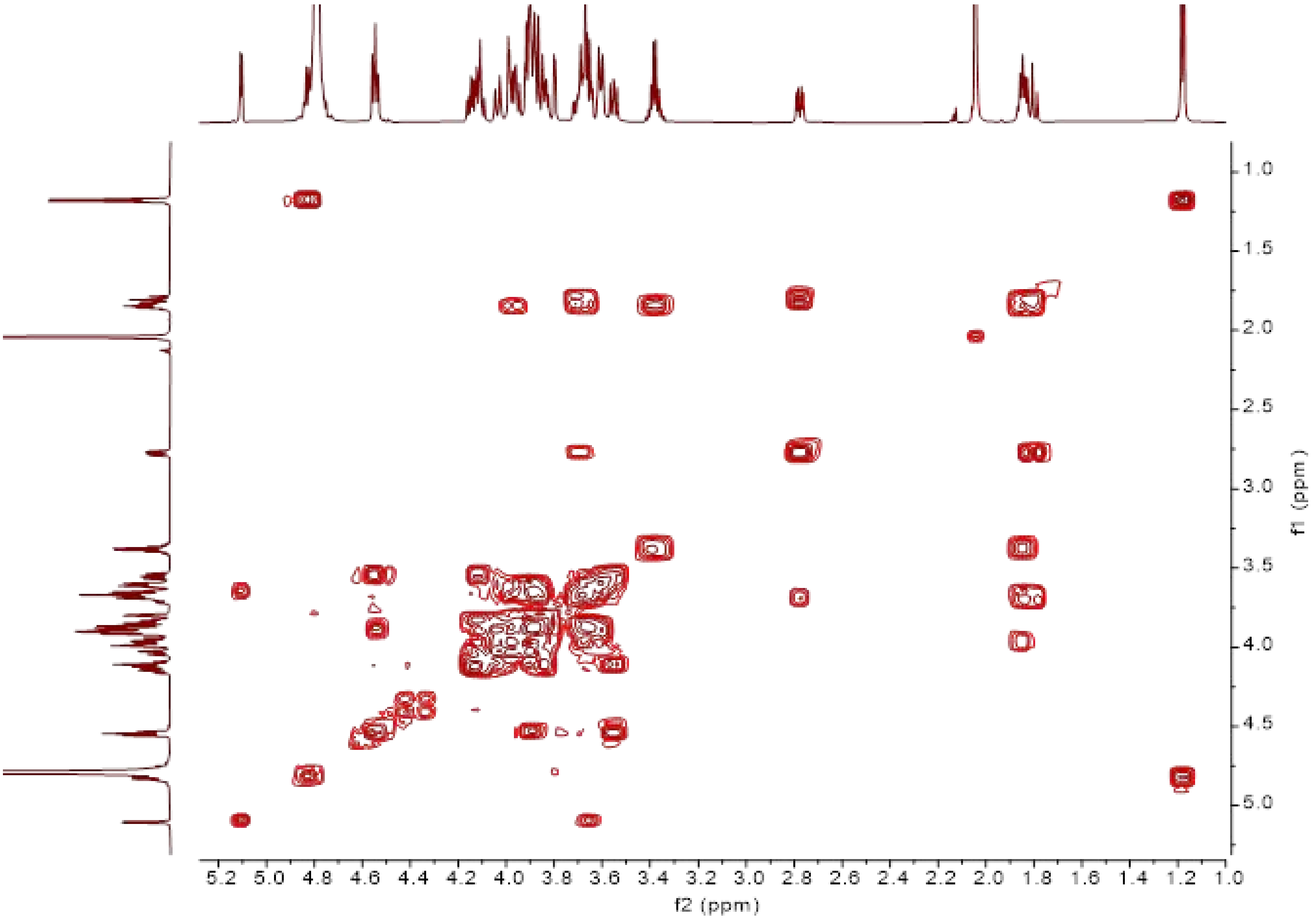

5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)
10 20 30 40 50 60 70 80 90 100
f1 (ppm)

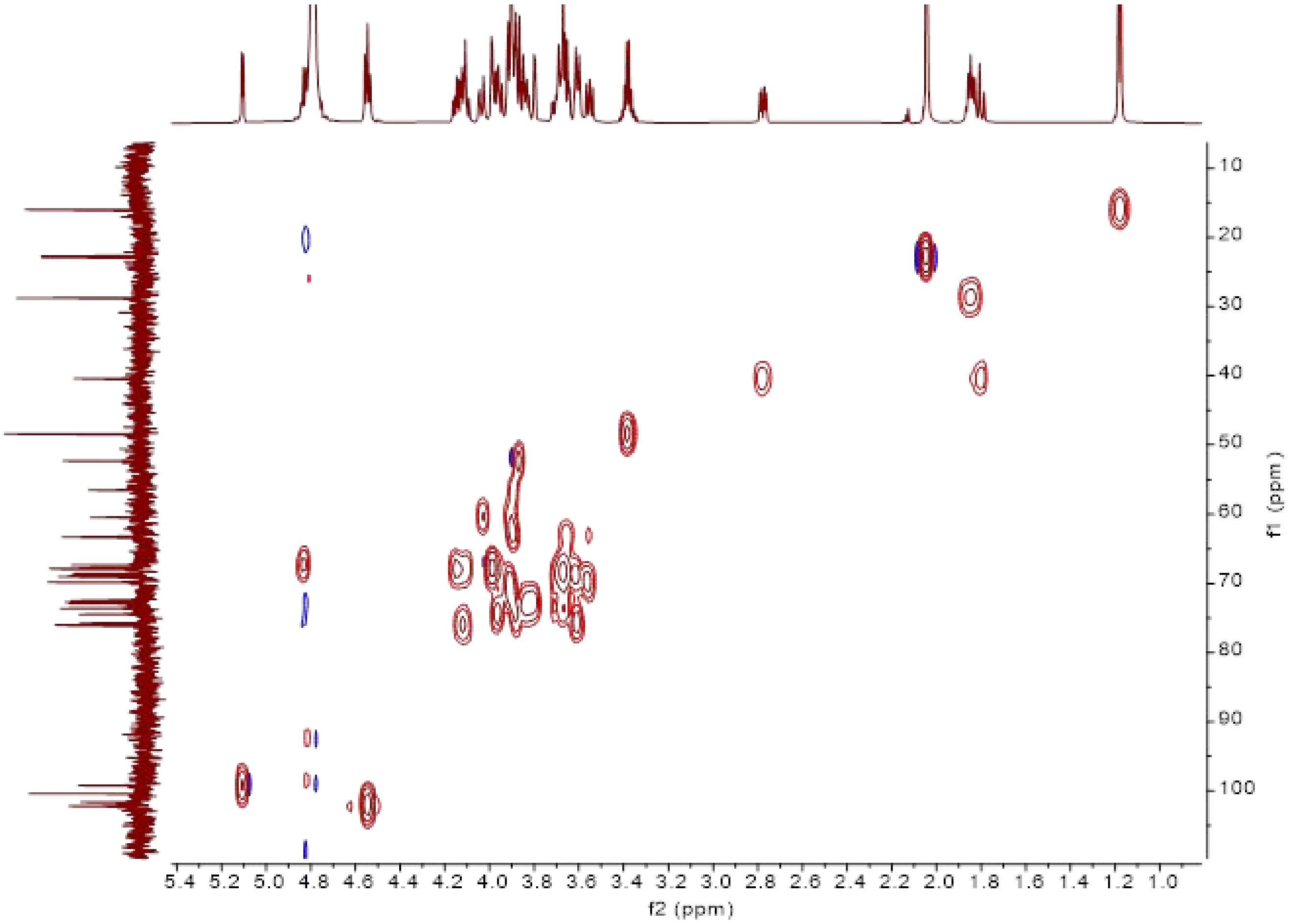

HO
OH
OH
COOH
OH
OSO3H
OH
AcNH
O
OH
O
O
OH
O
AcHN
O
N3
O
O
OH
OH
OH

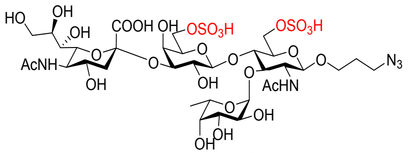
52


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

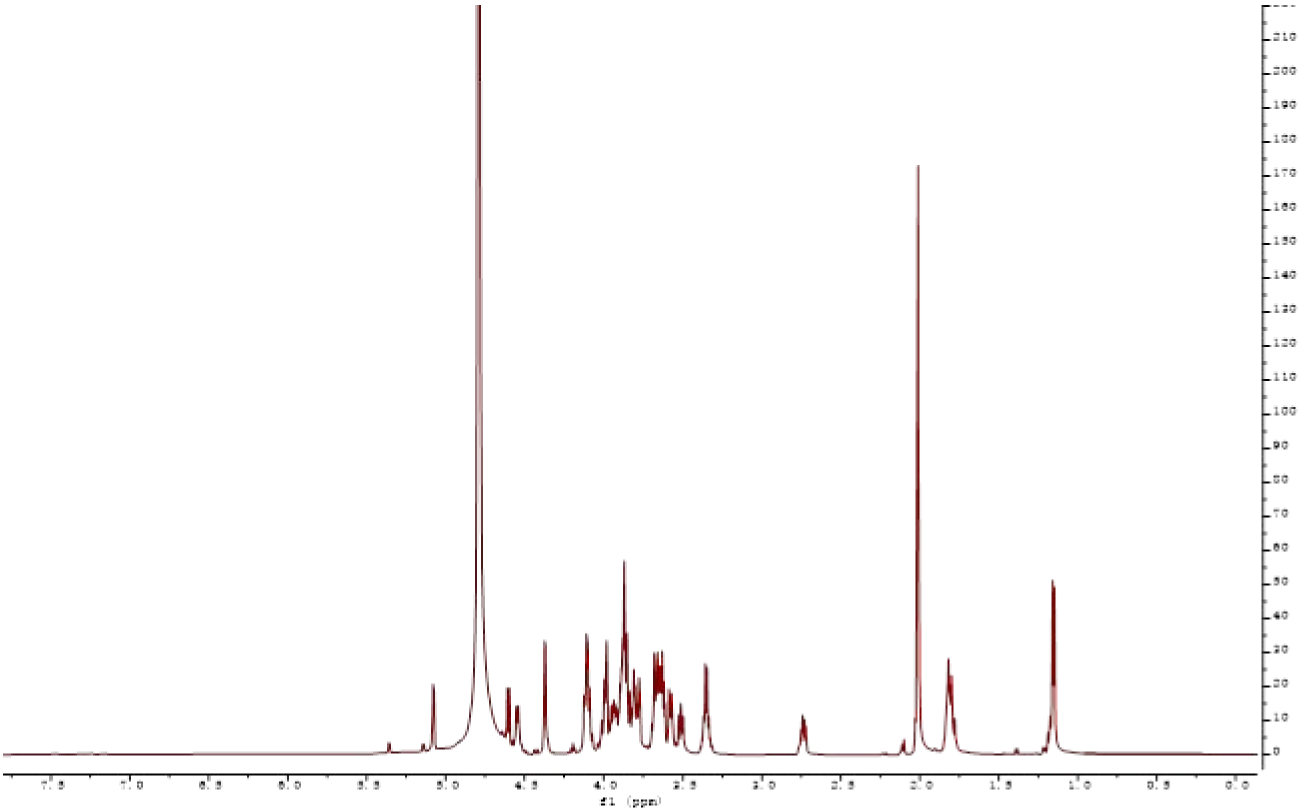

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

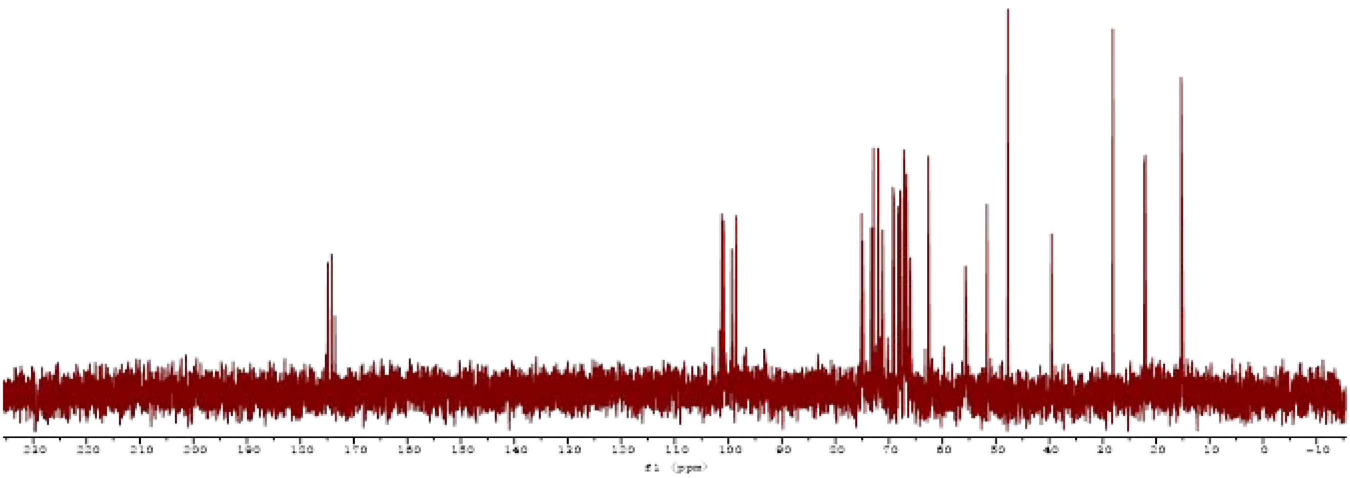

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

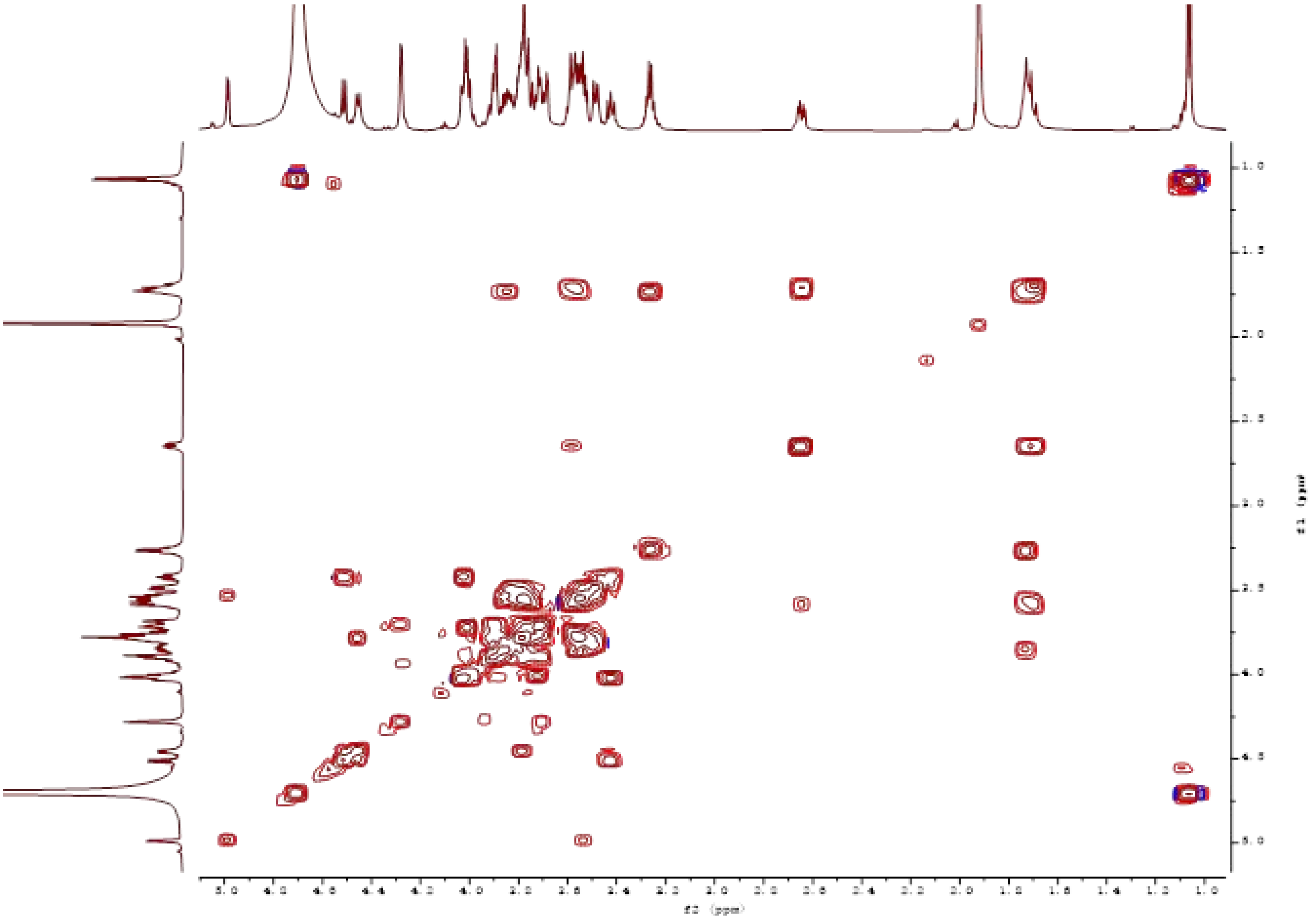

5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)

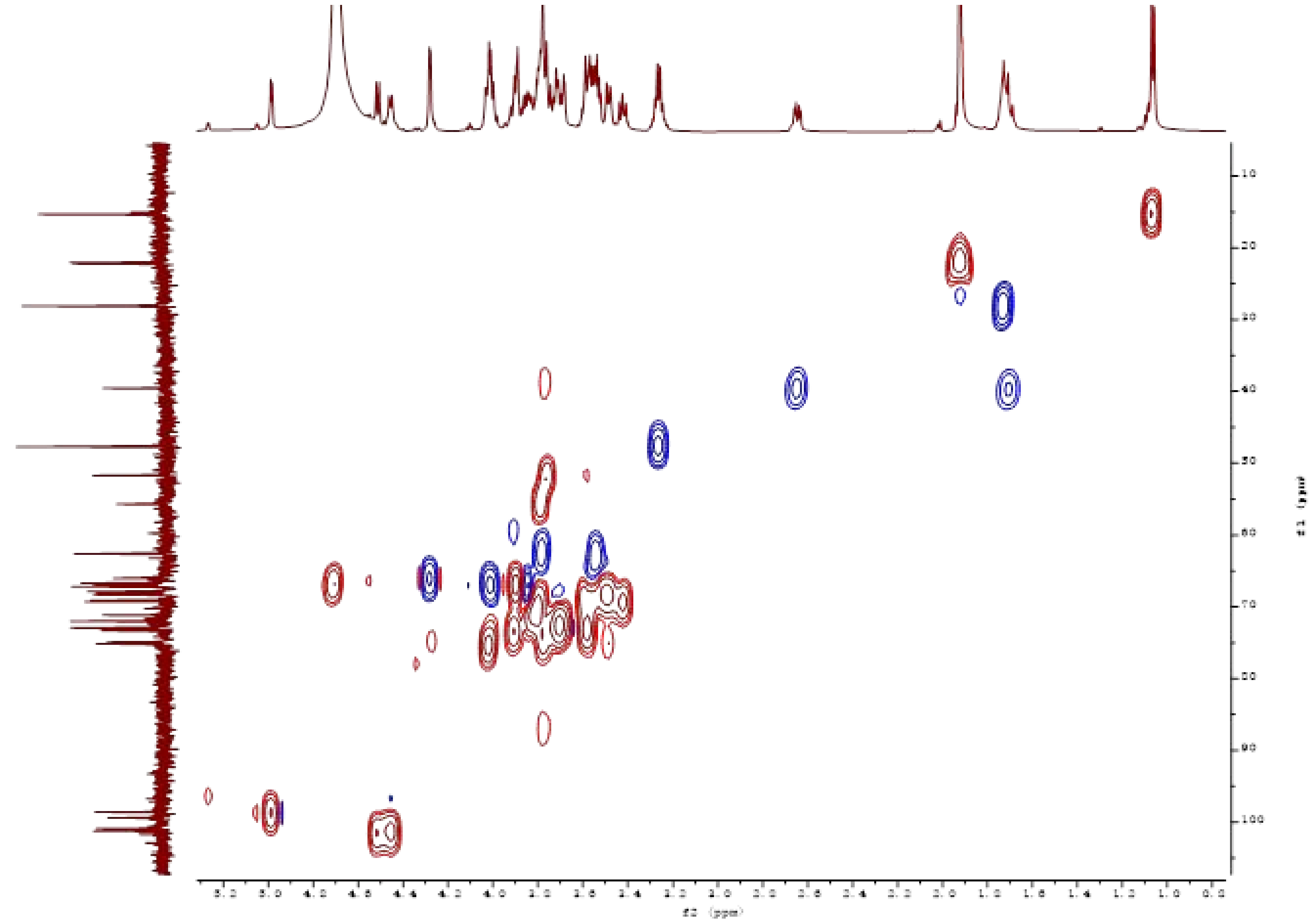

HO
OH
OH
COOH
OH
OSO3H
OSO3H
AcNH
O
OH
O
O
OH
O
N3
AcHN
O
OH
OH
OH

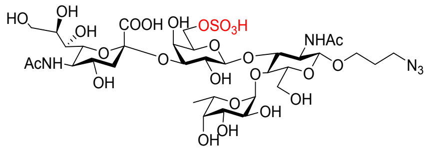
53


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)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

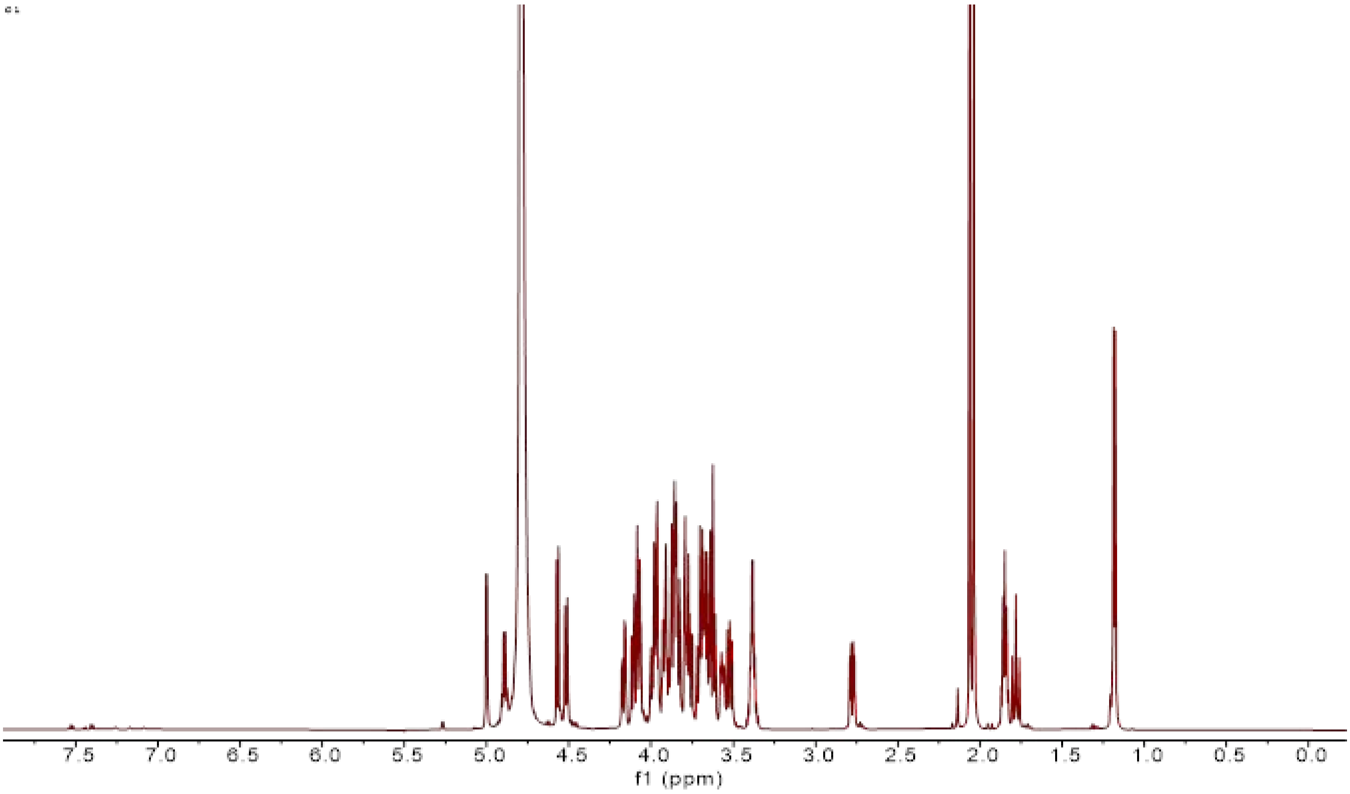

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

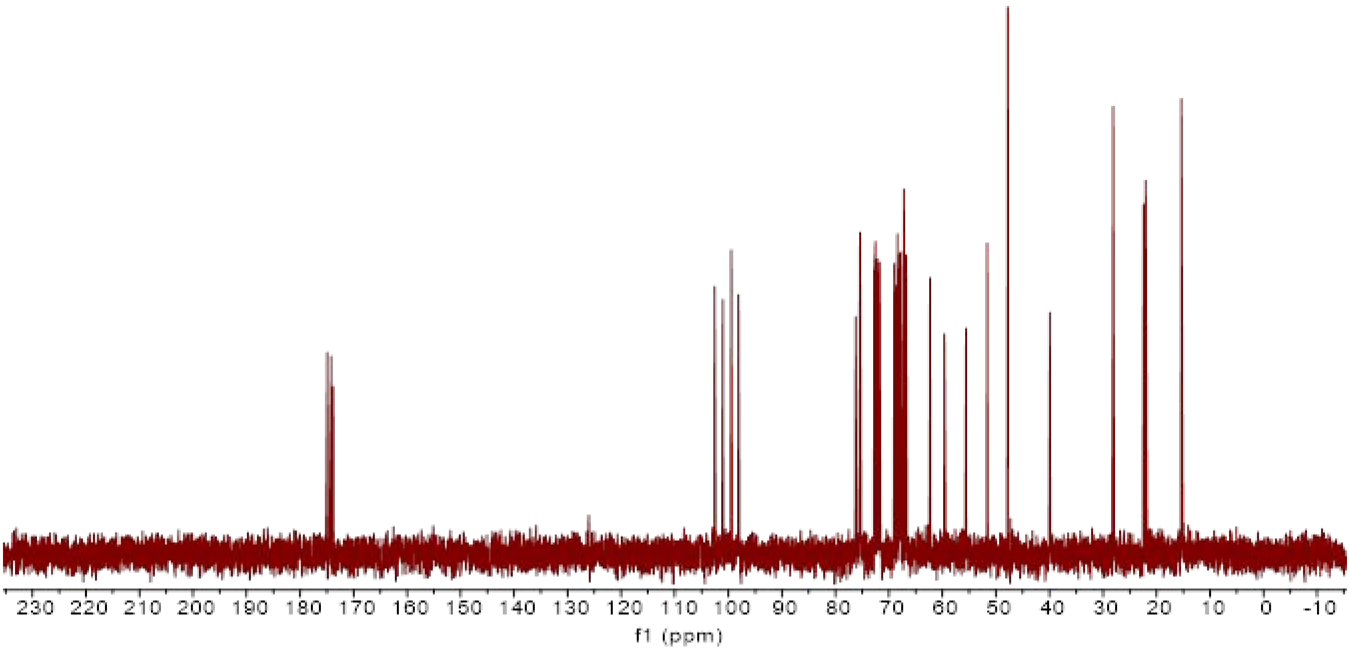

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

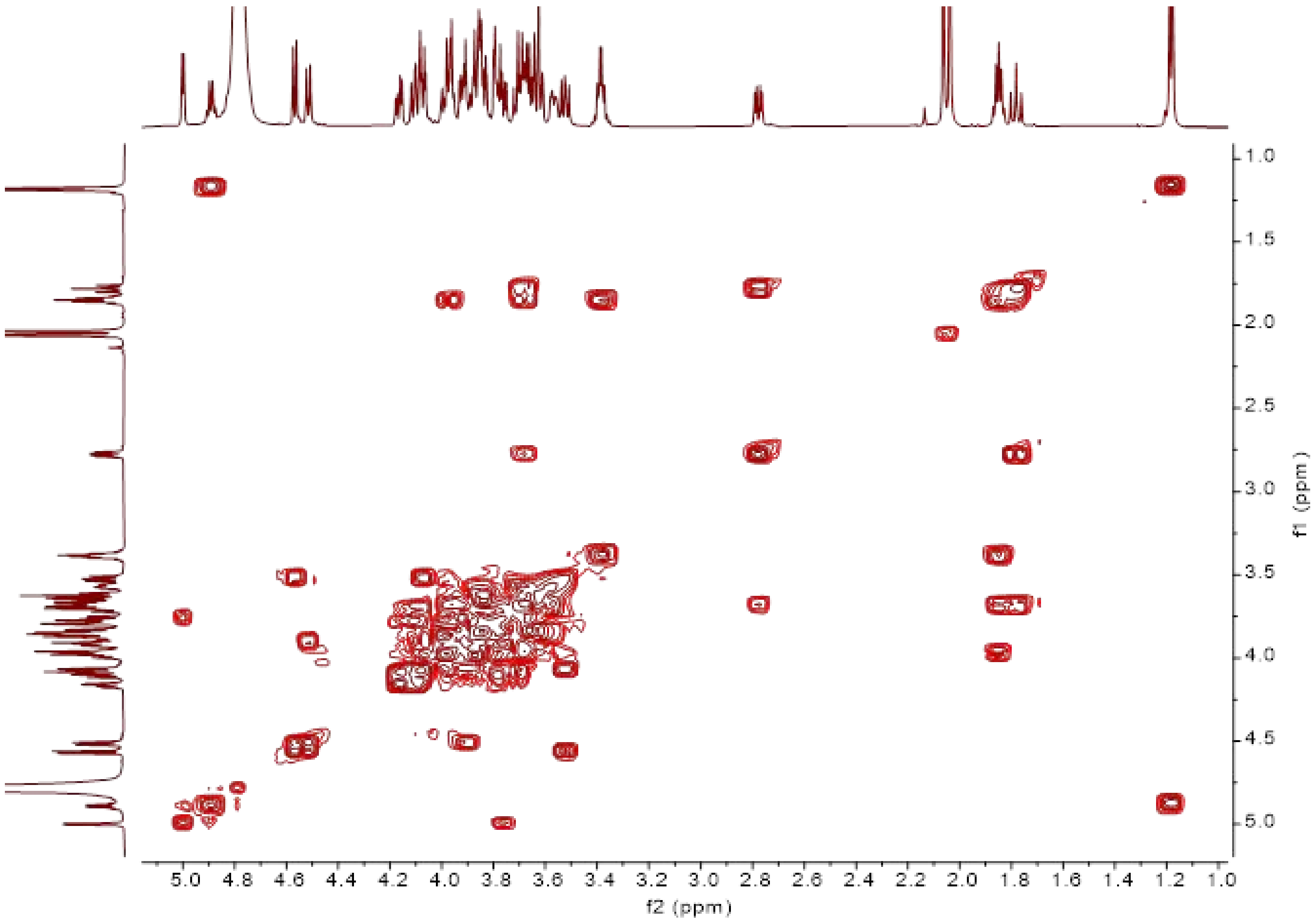

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)


HO
OH
OH
COOH
OH
OSO3H
NHAc
AcNH
O
O
O
O
OH
OH
O
O
N3
OH
O
OH
OH
OH

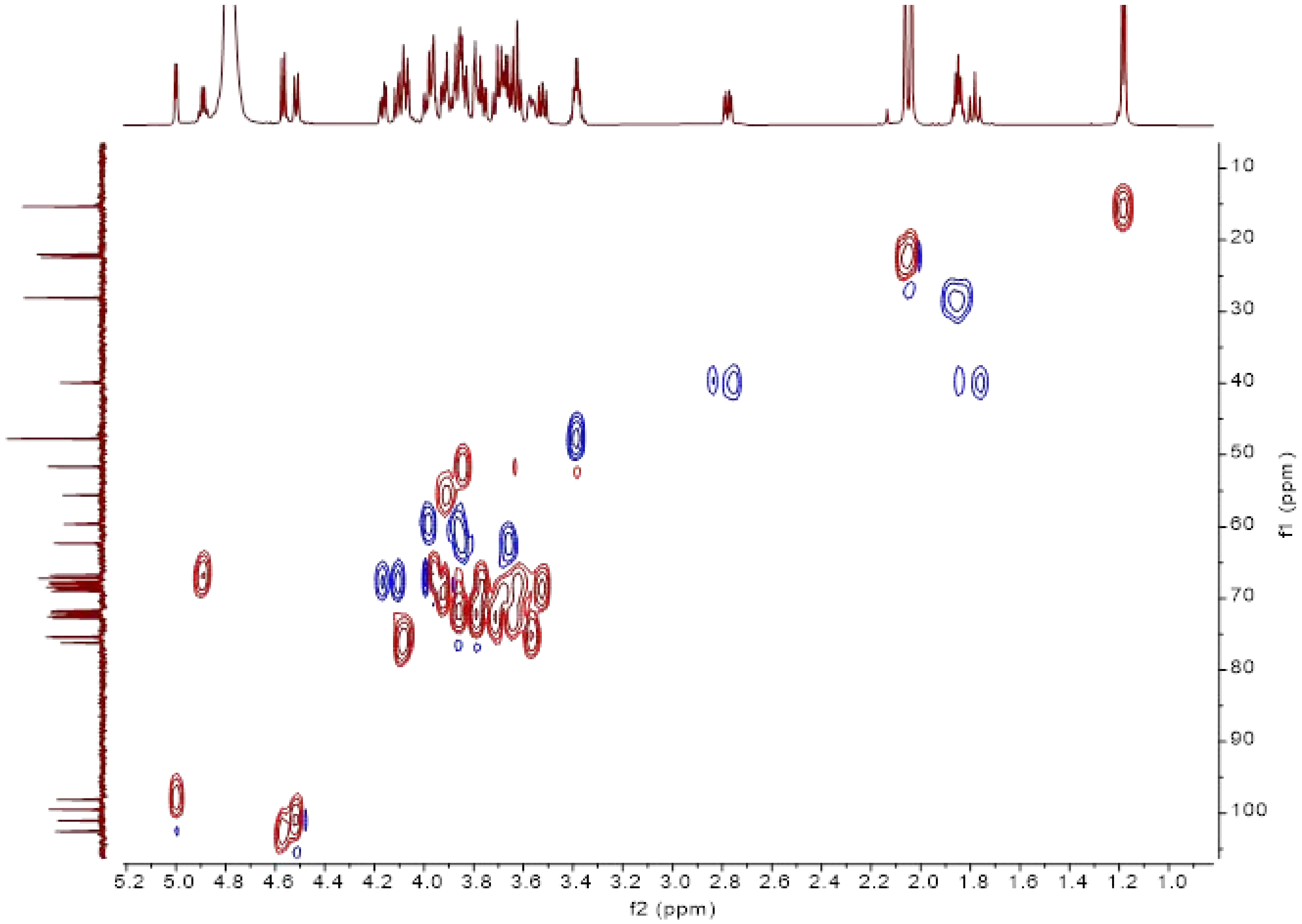
54


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)

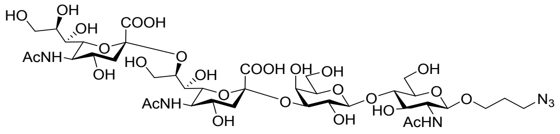

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



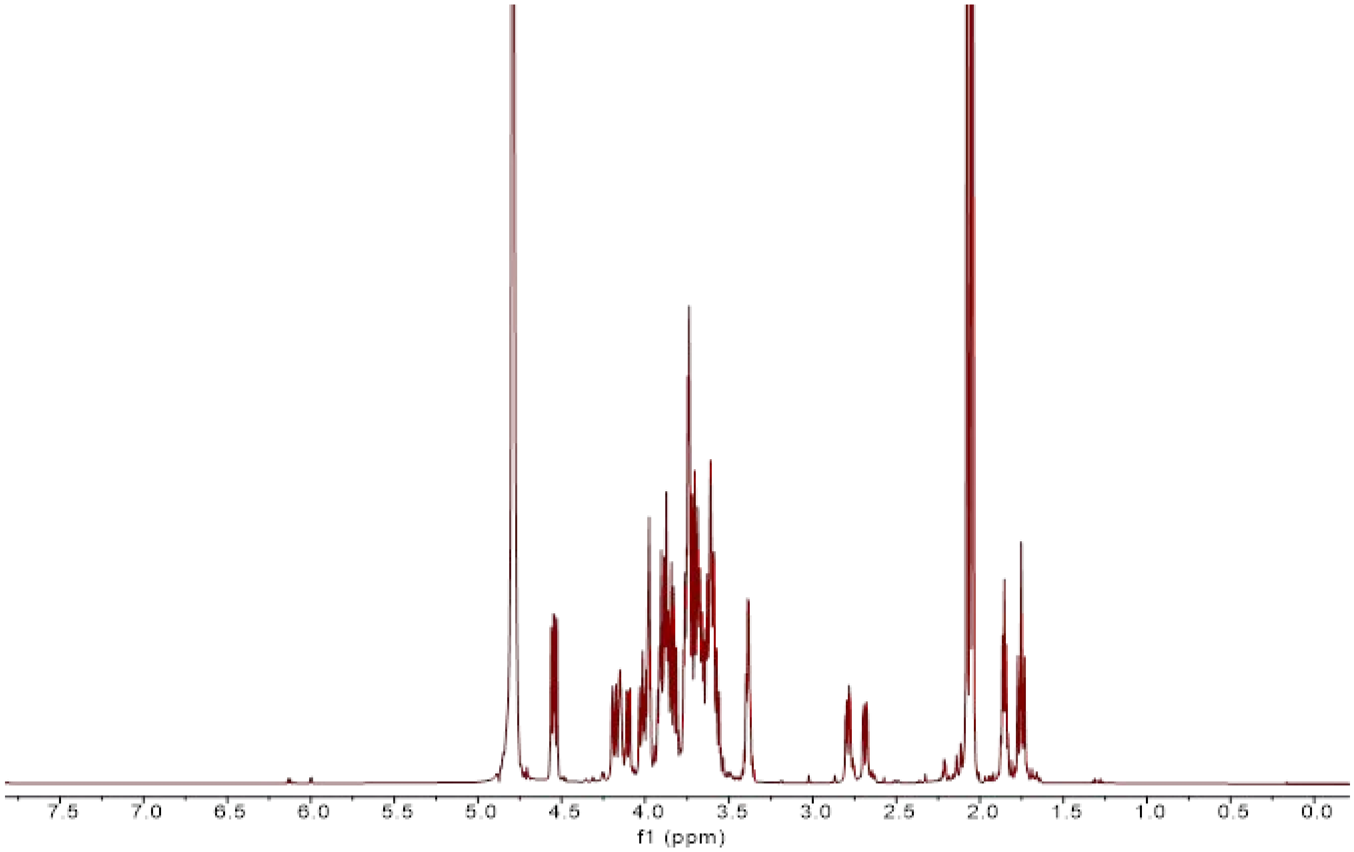
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)

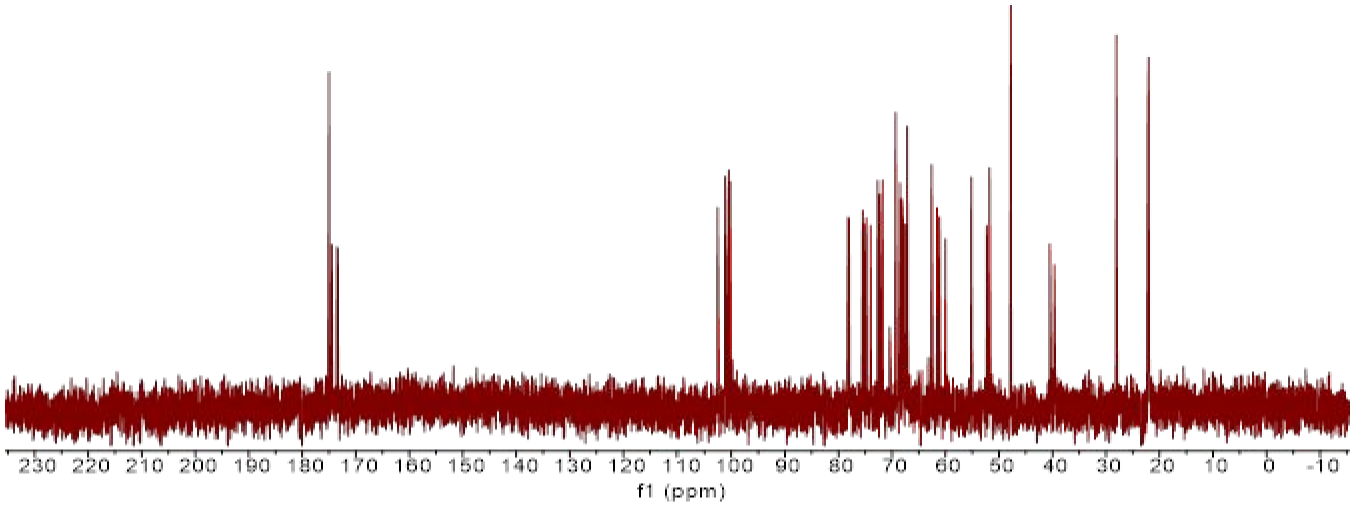


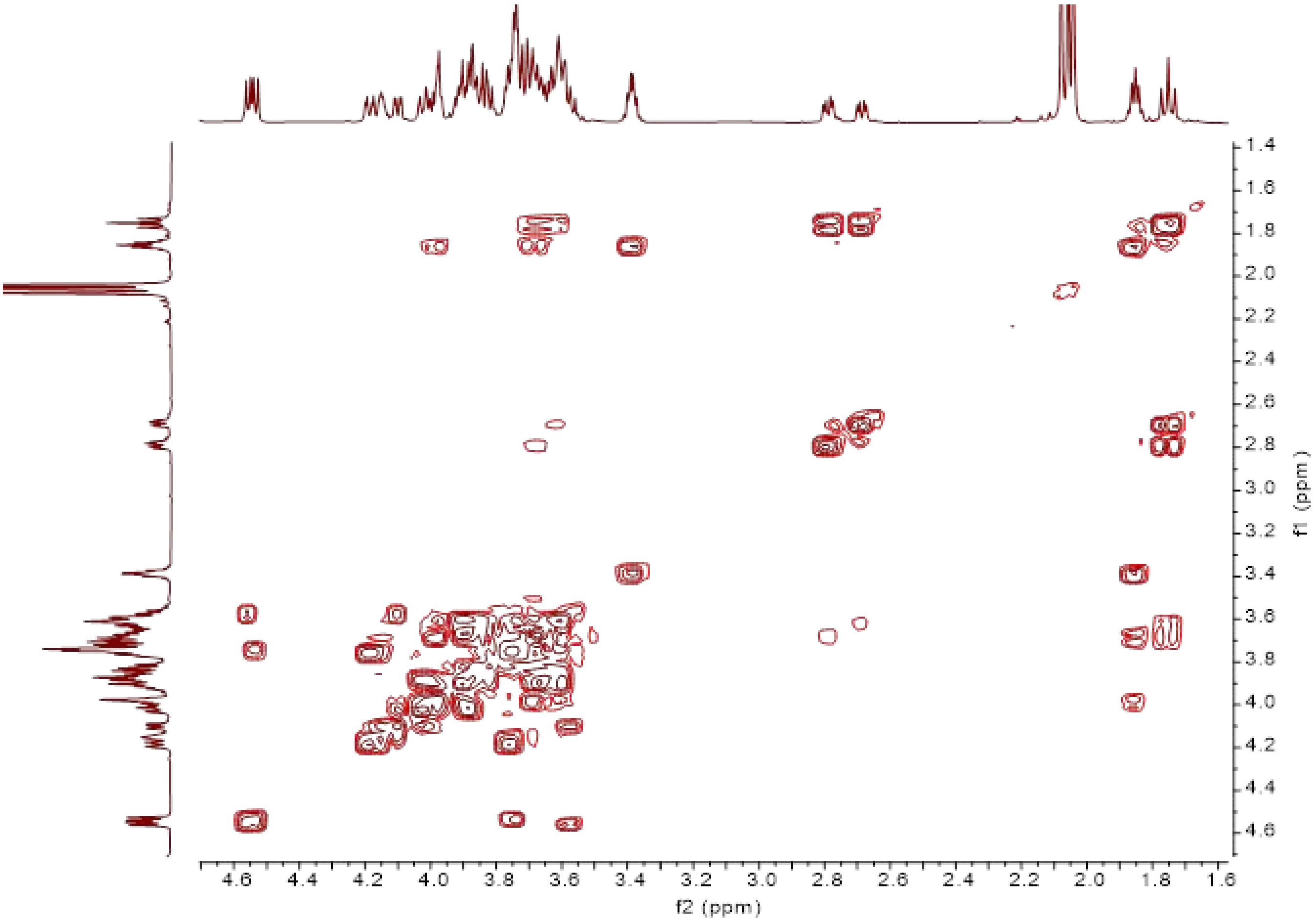
10
20
30
40
50
60
70
80
90
100
f1 (ppm)
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f2 (ppm)

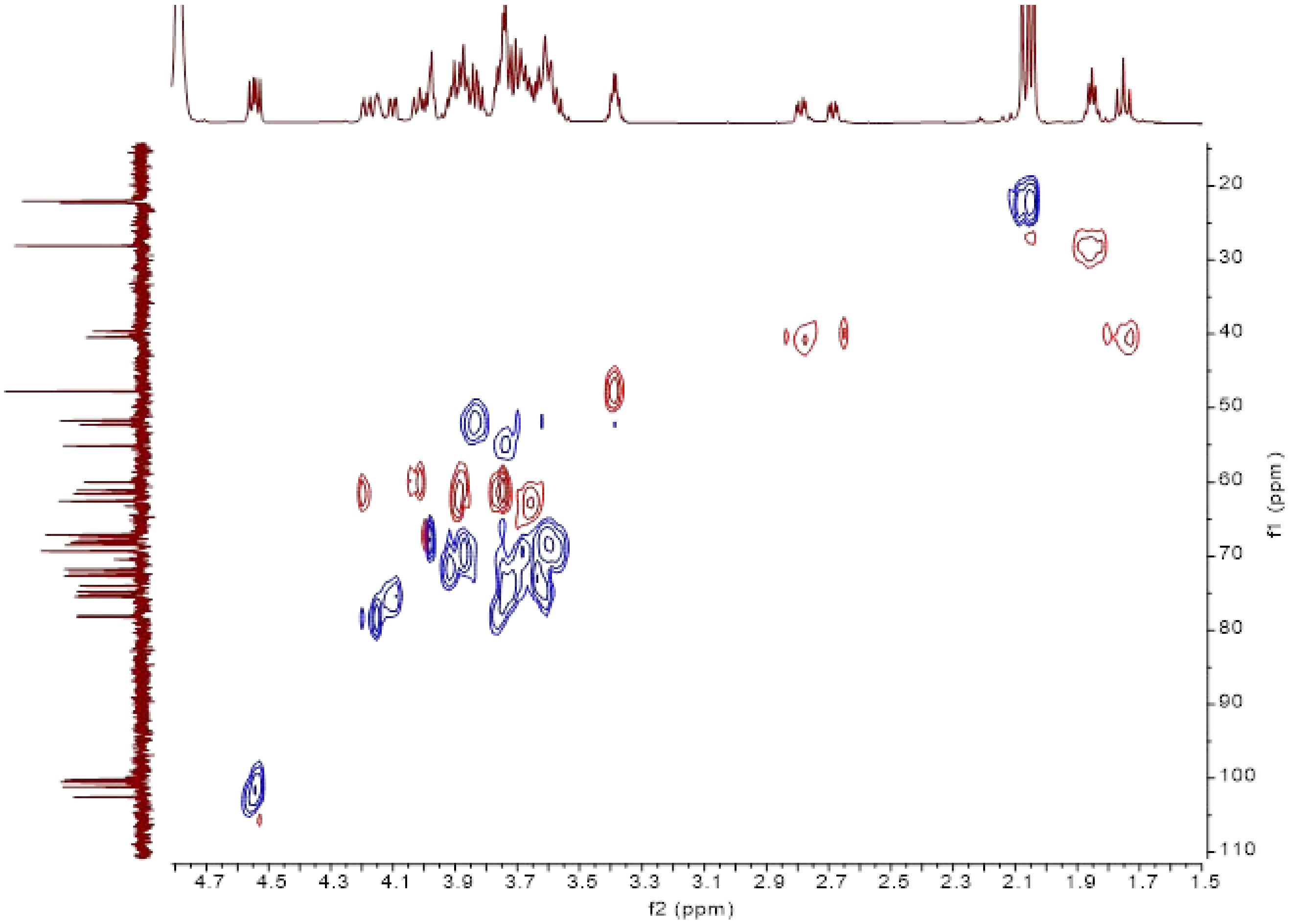

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
OH
AcNH
O
O
OH
O
OH
O
HO
AcHN
O
N_3

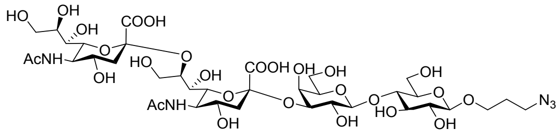
55


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)

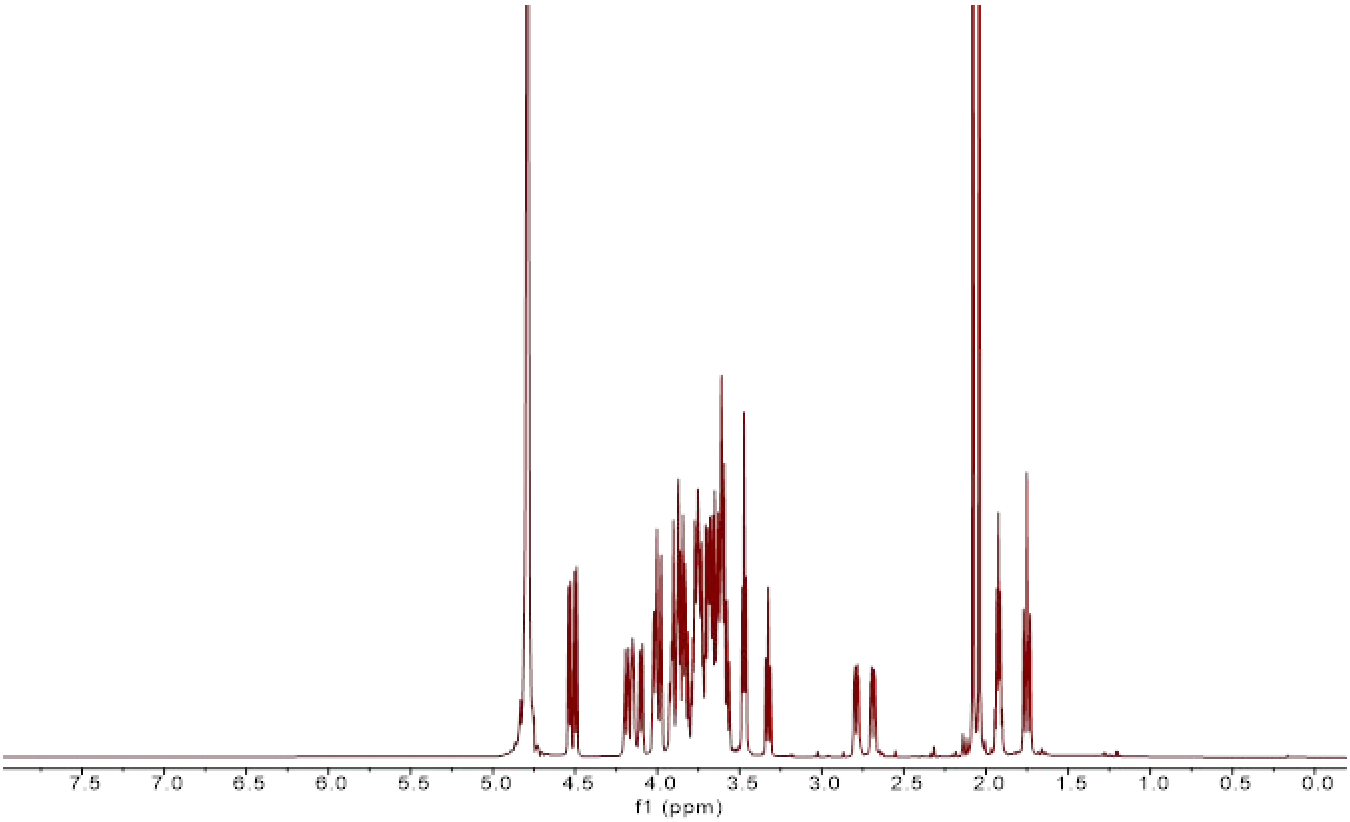

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

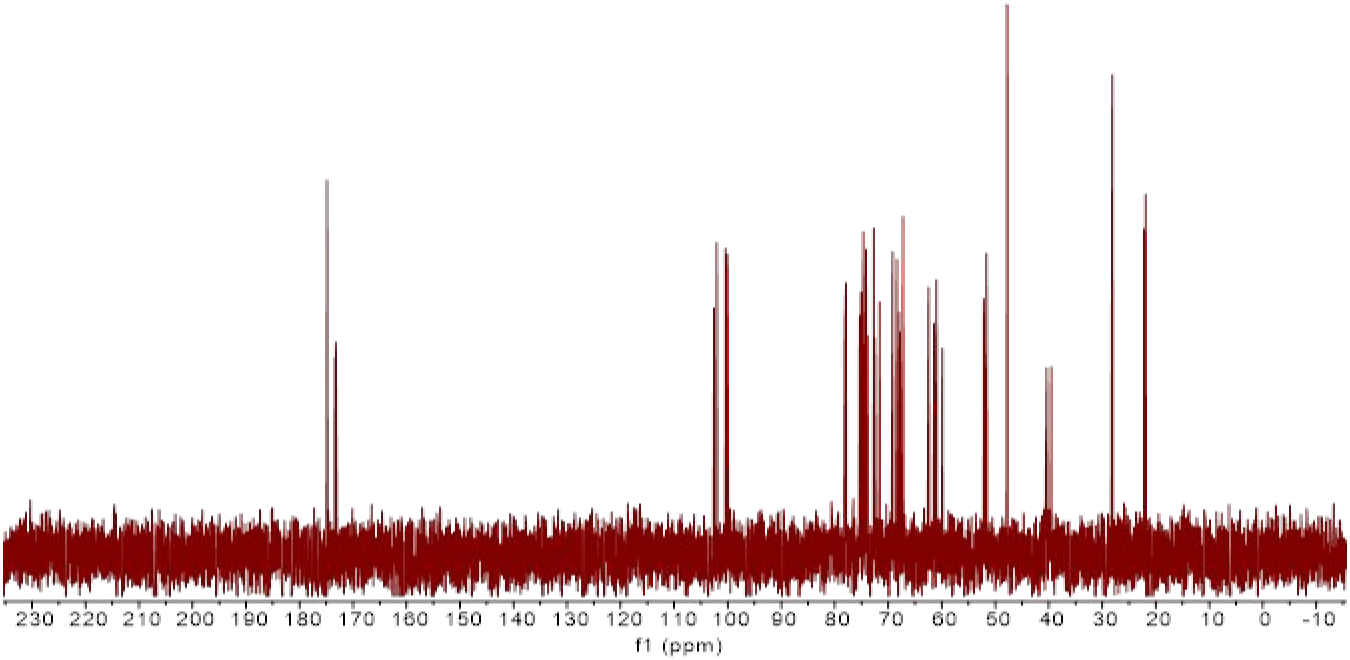

4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
f1 (ppm)

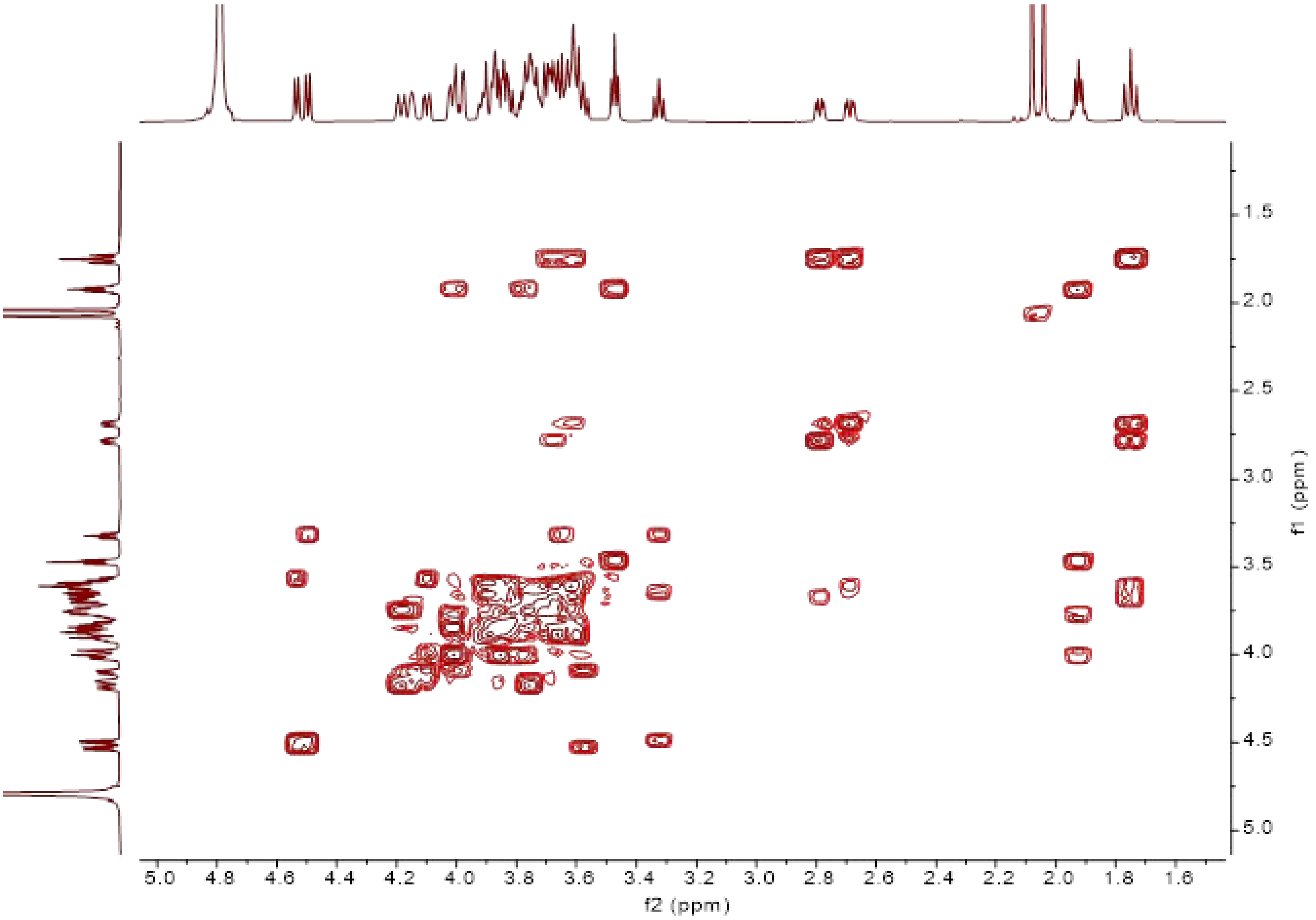

4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

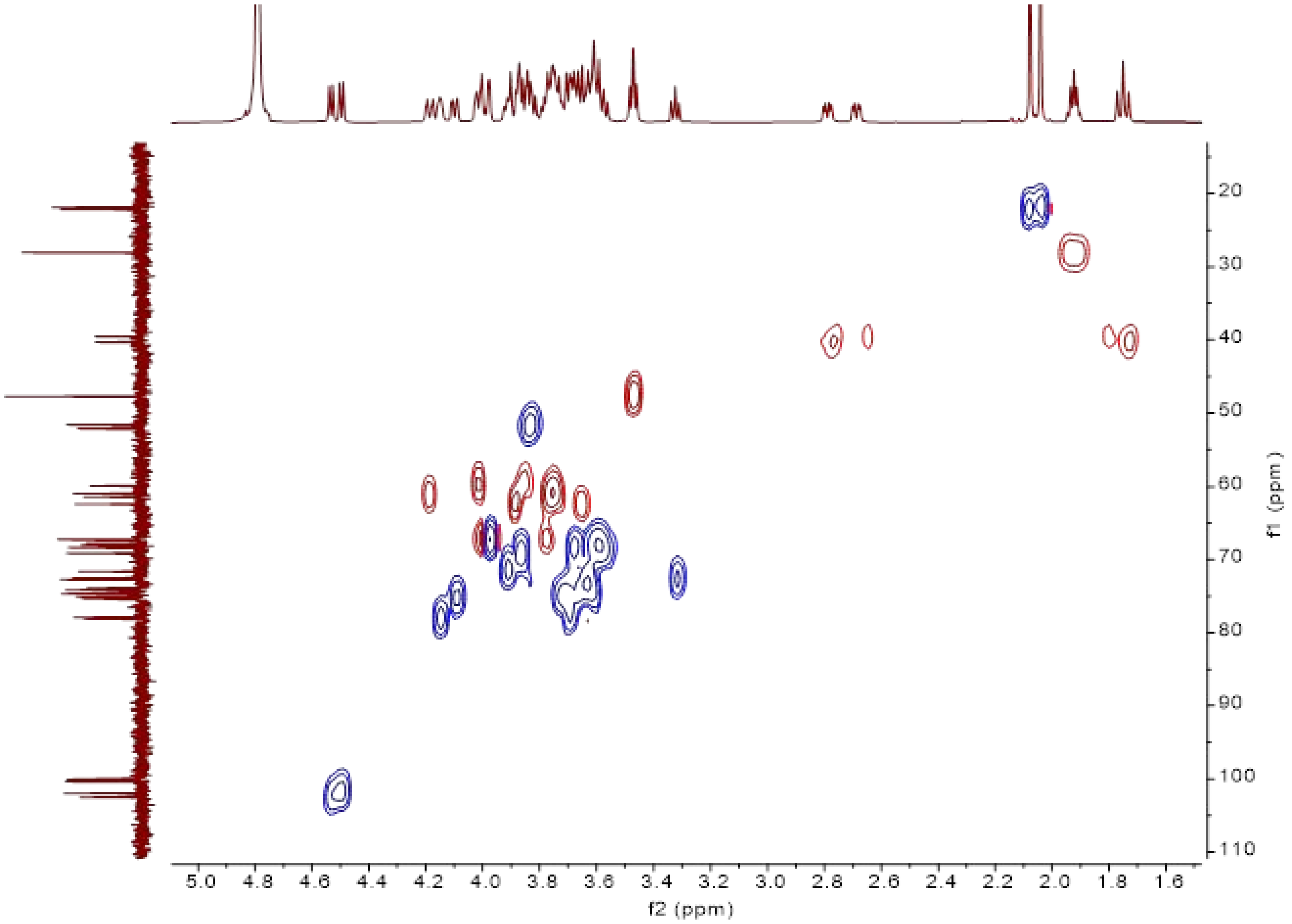

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
OH
AcNH
O
O
O
O
HO
O
OH
OH
O
N3

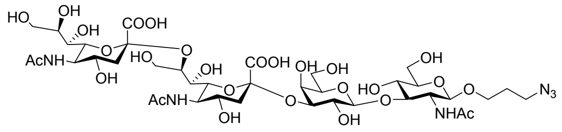
56


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)

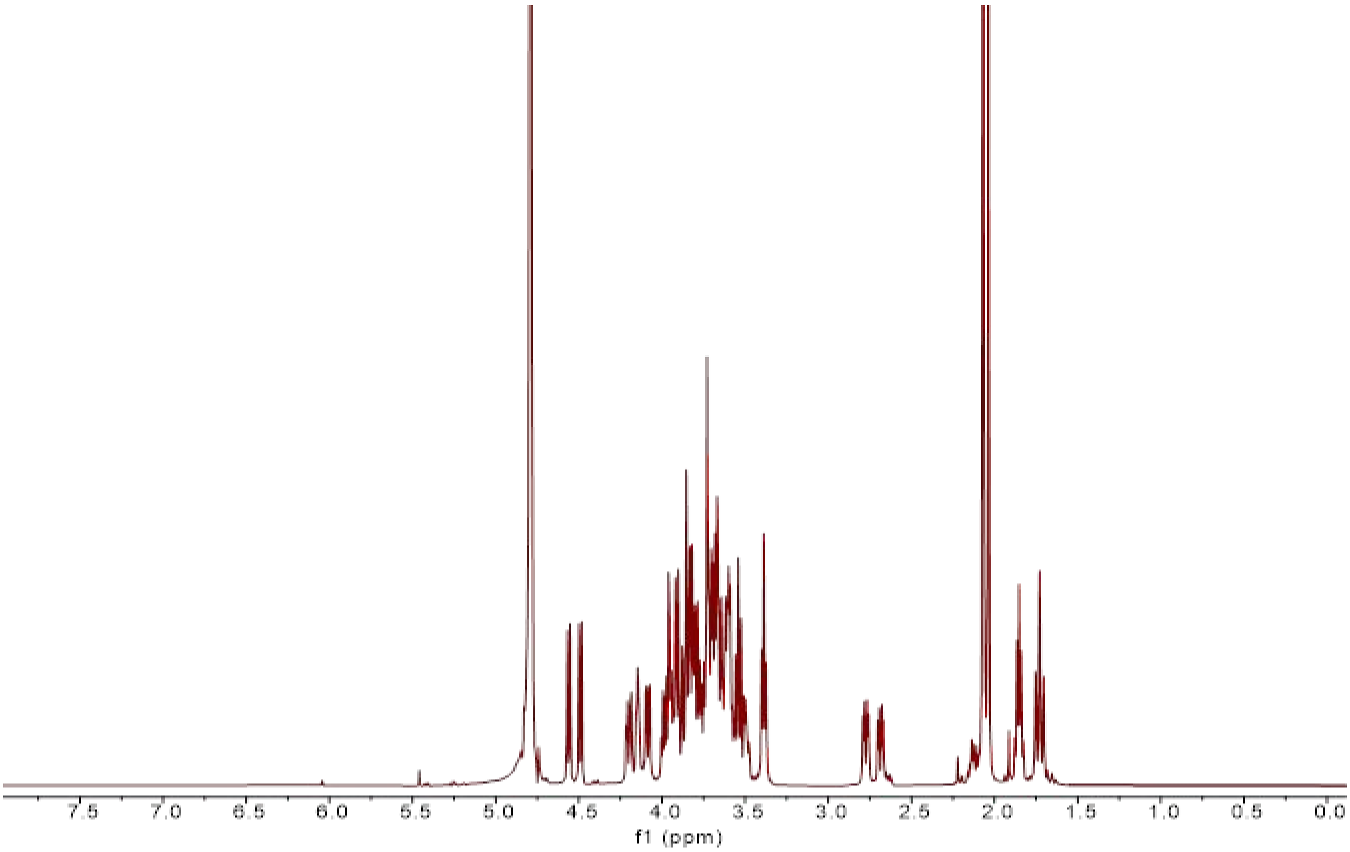

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

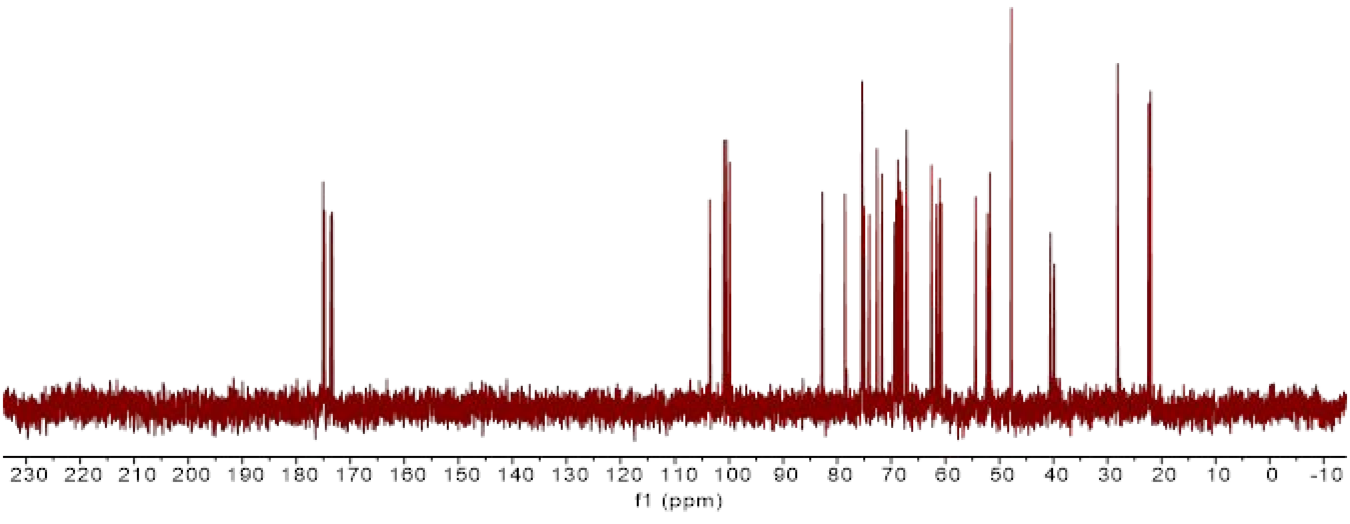

f2 (ppm)
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

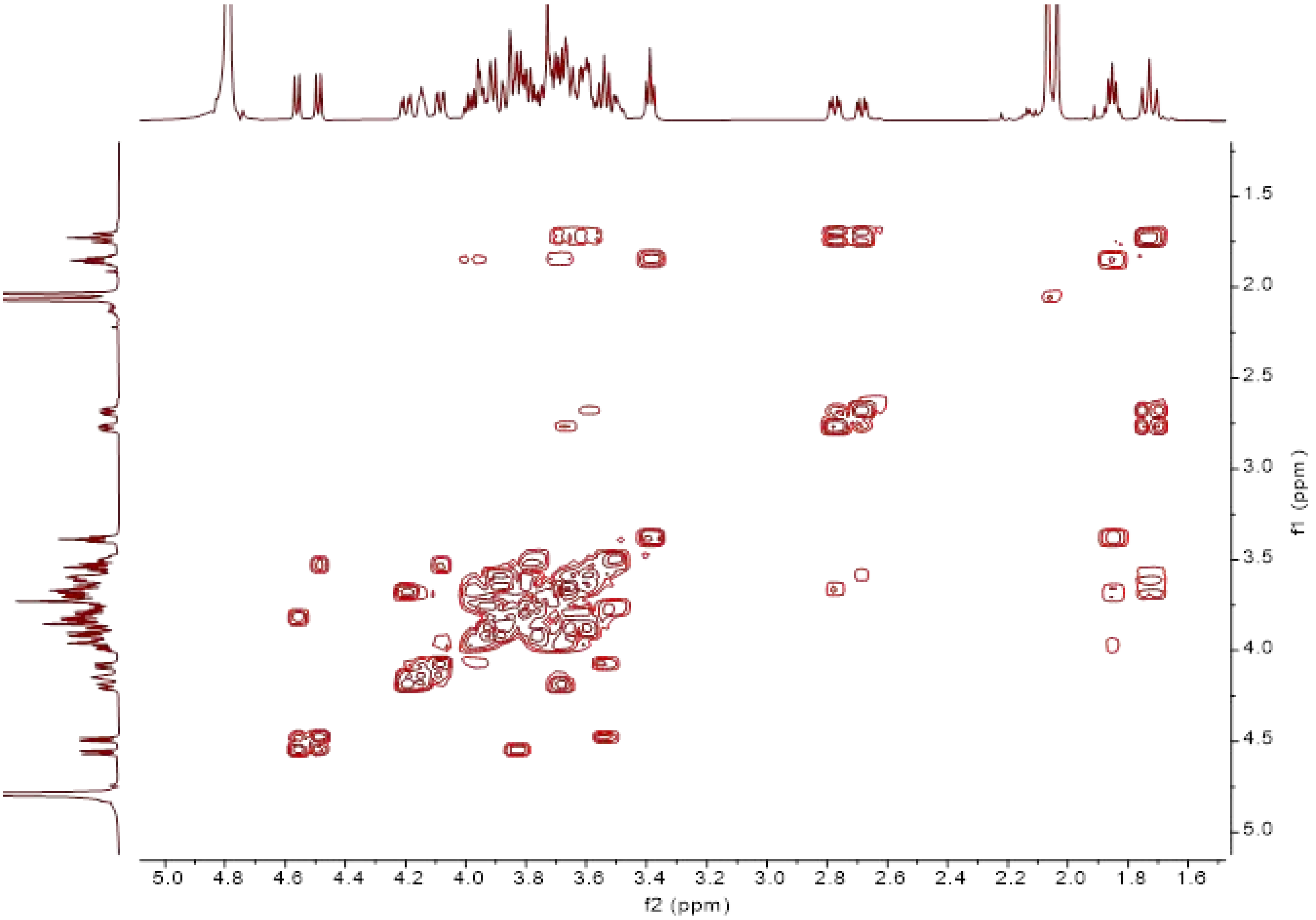

f2 (ppm)
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
20
30
40
50
60
70
80
90
100
110

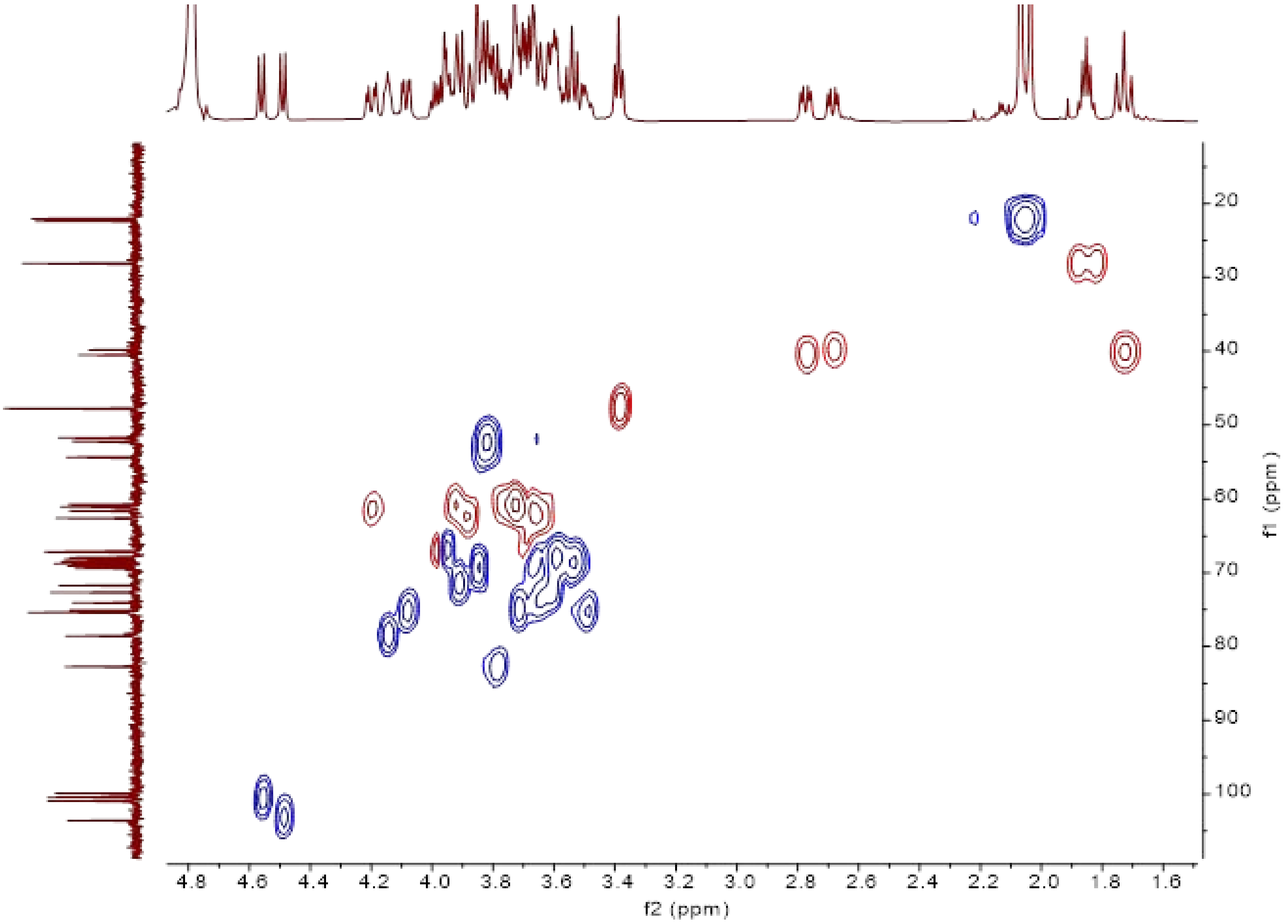

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
O
AcNH
O
OH
HO
O
OH
OH
O
NHAc
O
N3

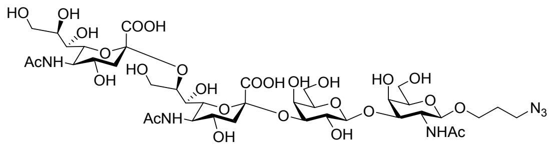
57


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)

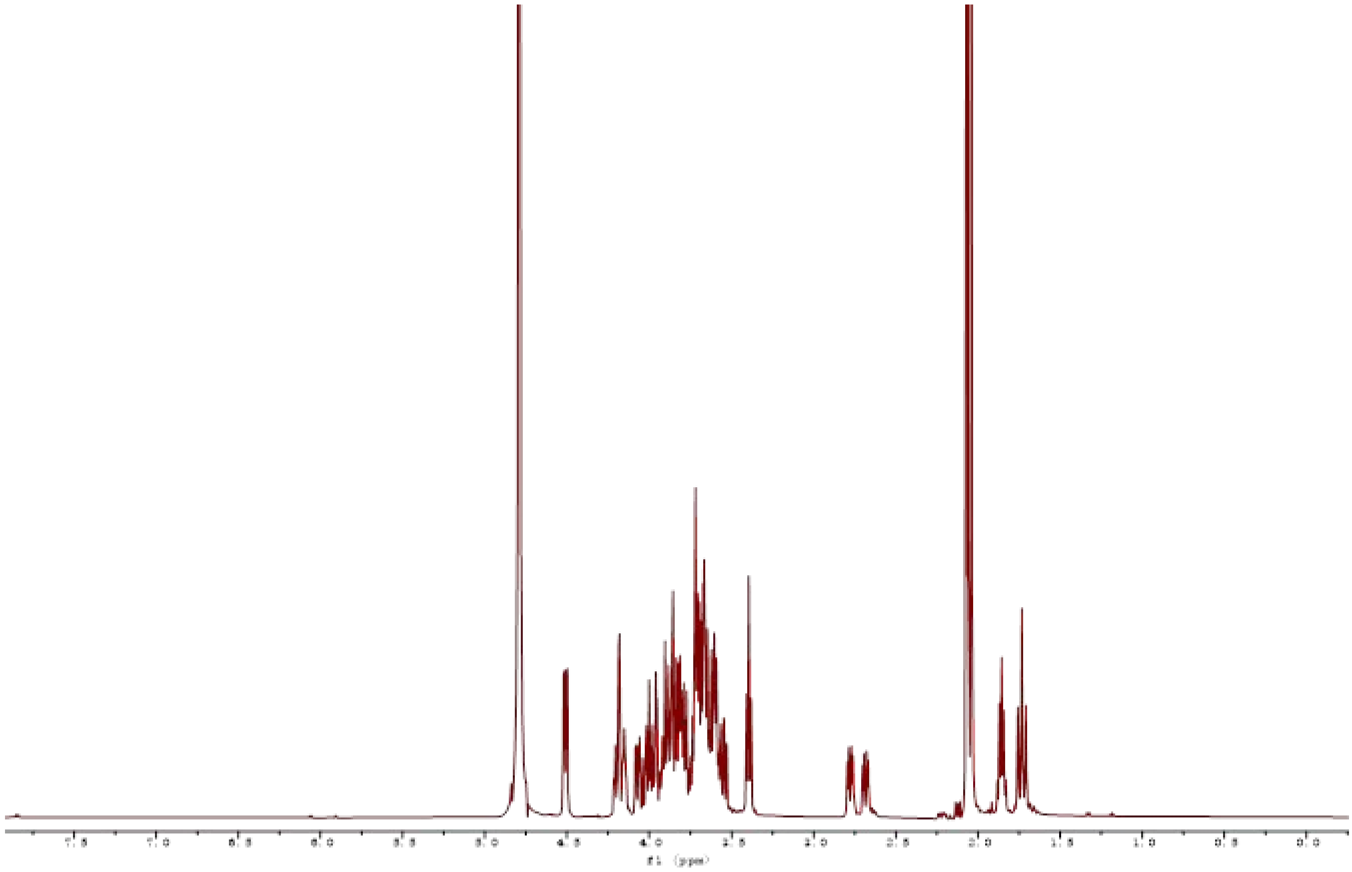

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

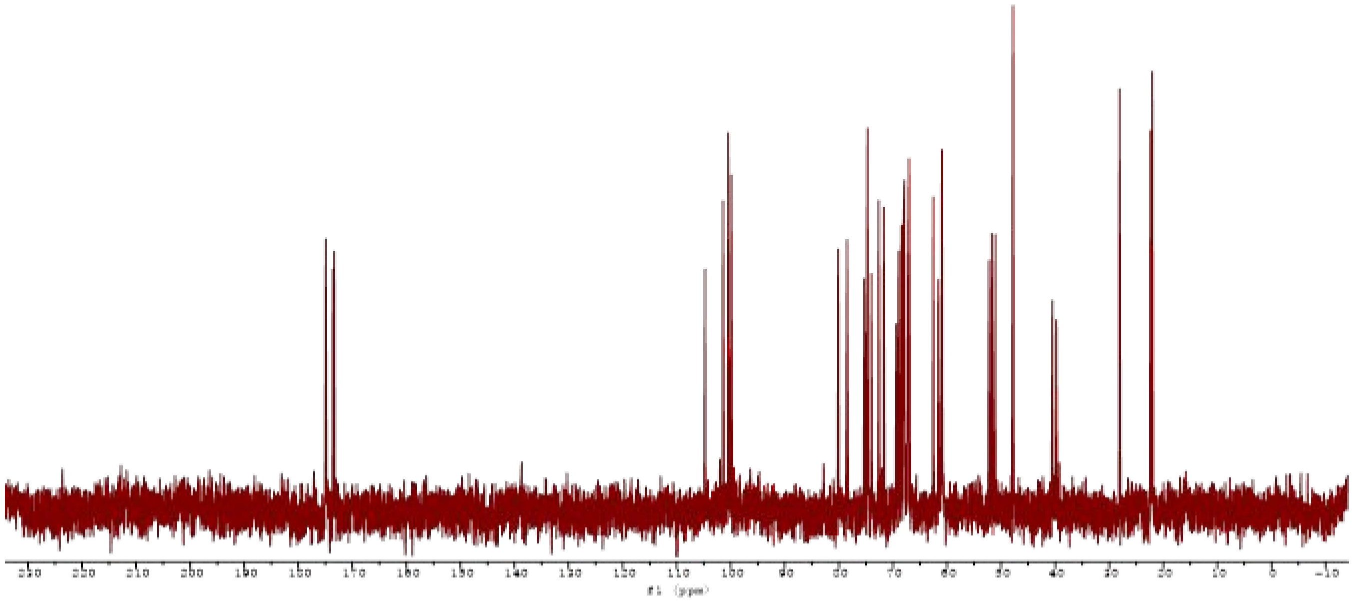

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

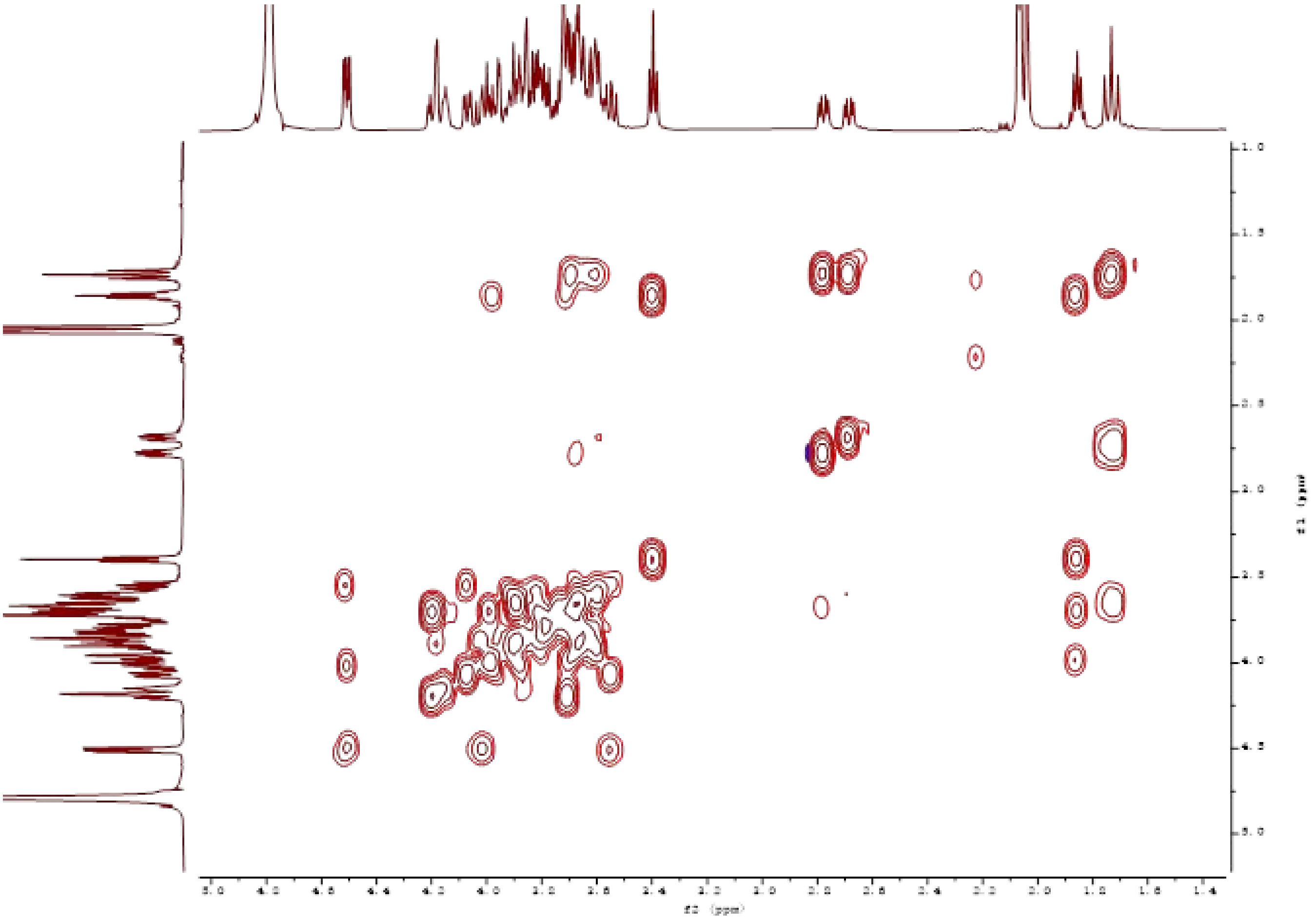

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)

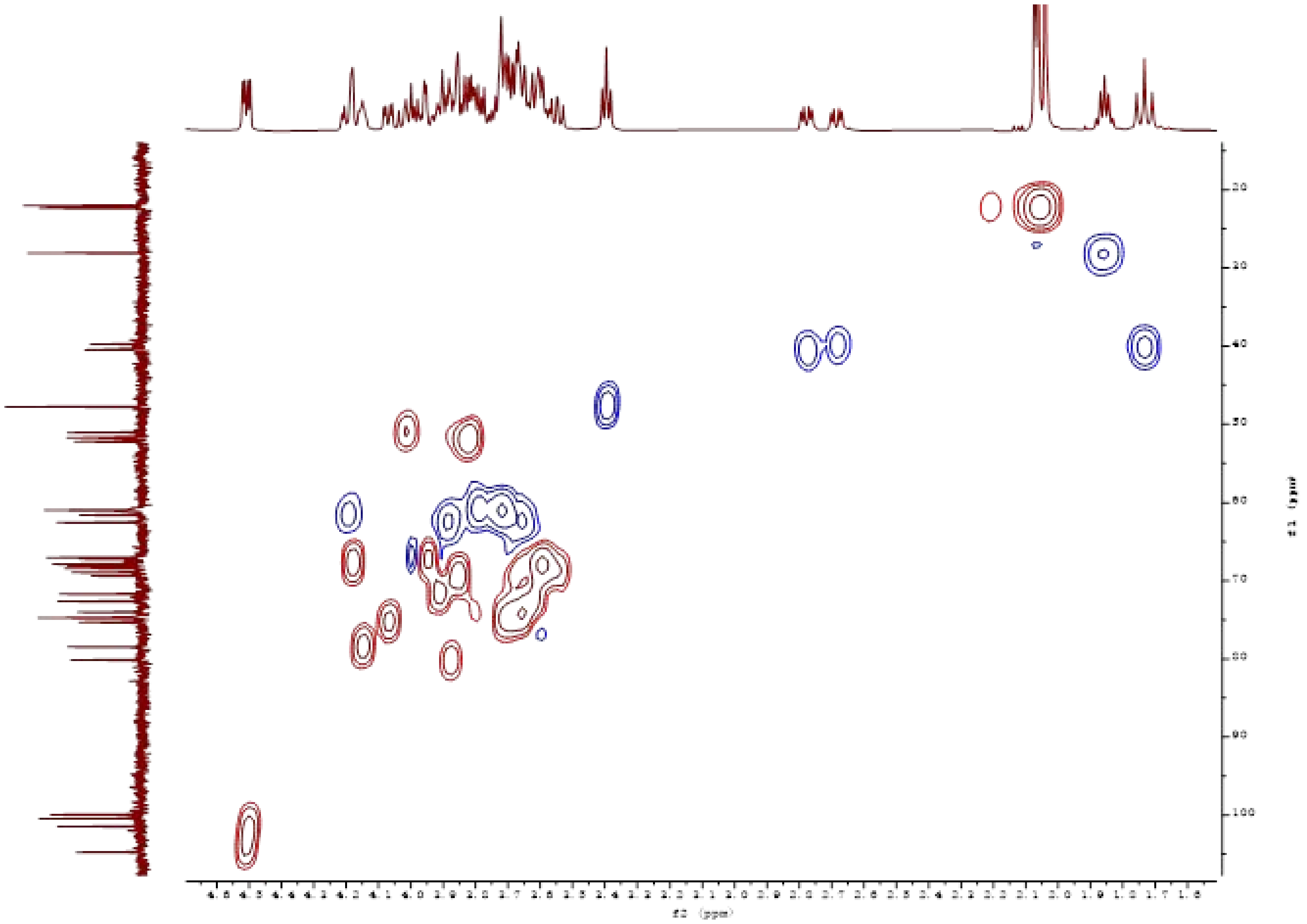

HO
OH
OH
COOH
AcNH
O
O
OH
HO
OH
COOH
OH
OH
HO
OH
AcNH
O
O
O
O
O
O
N3
OH
OH
NHAc

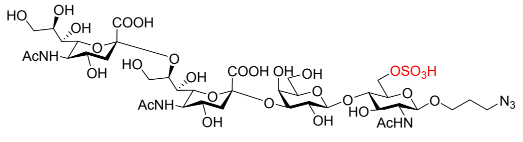
58


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)

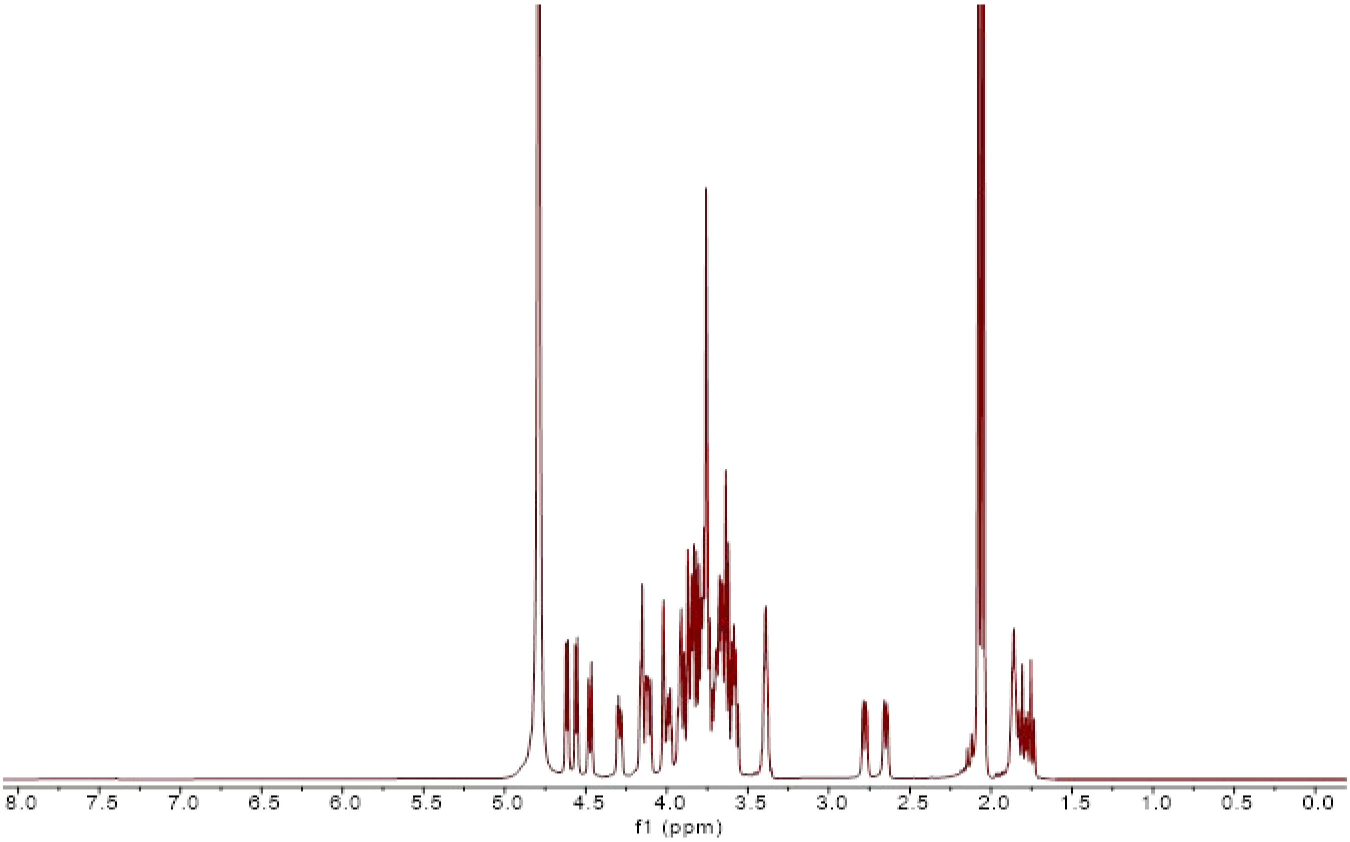

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

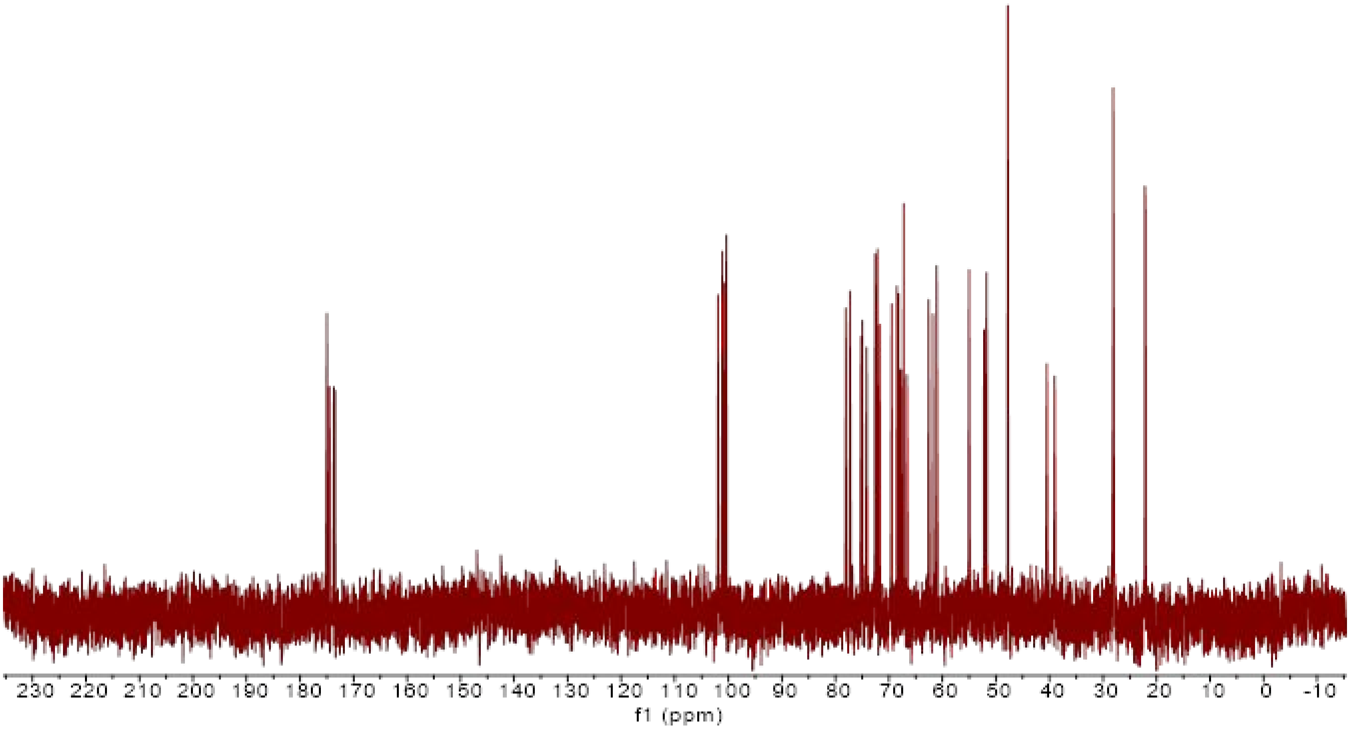

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

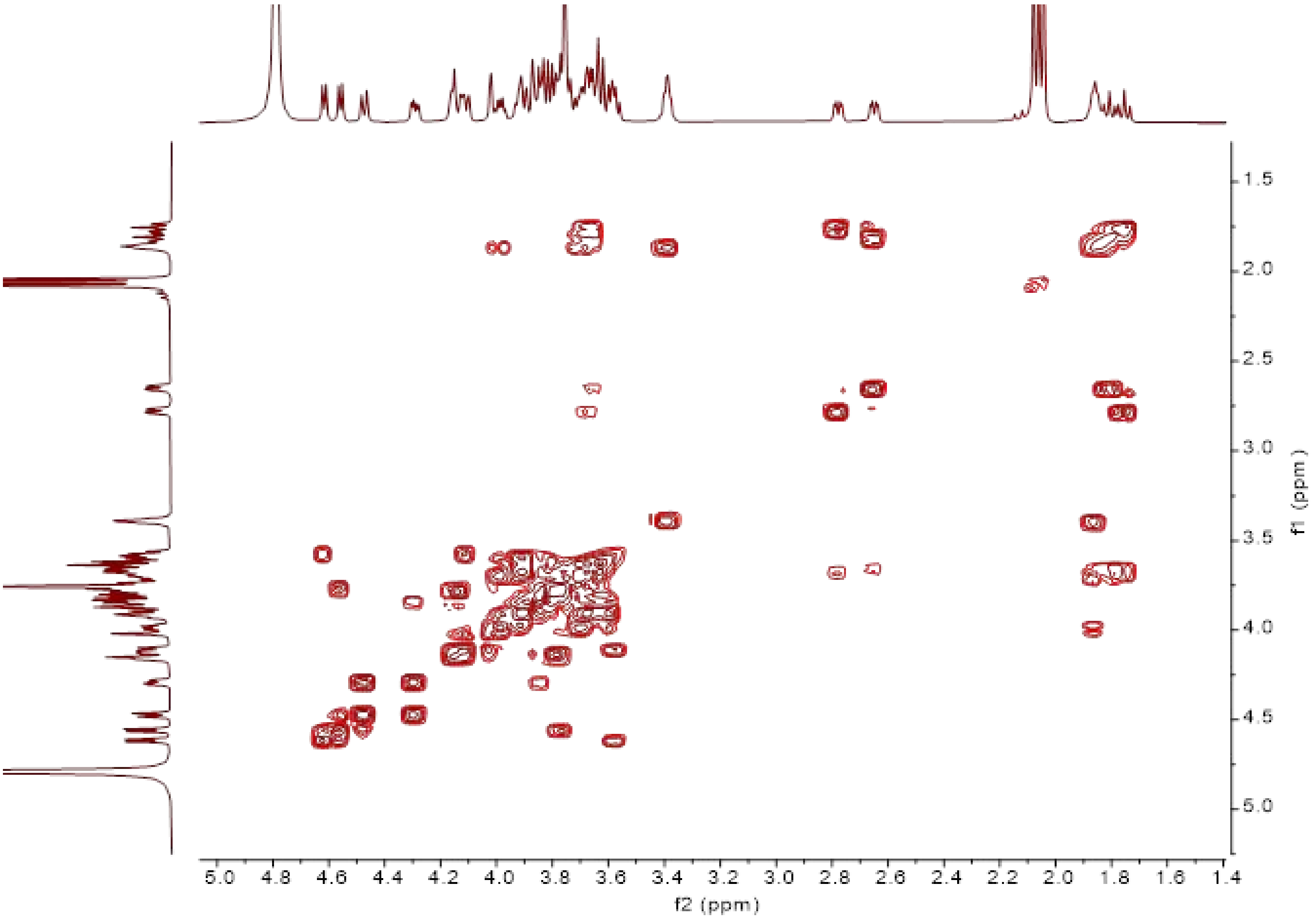

4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

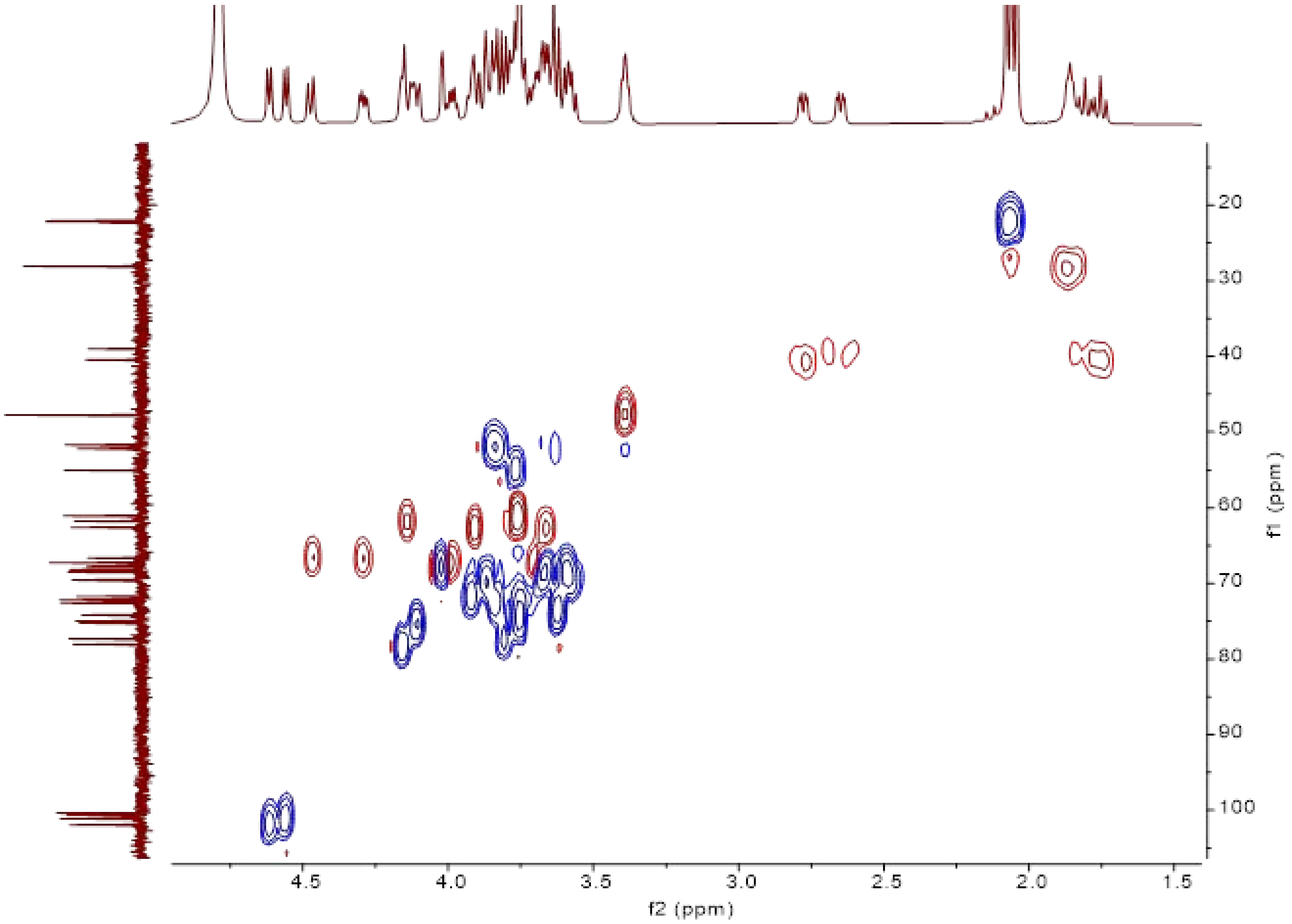

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
OSO3H
AcNH
O
O
O
O
O
N3
OH
OH
HO
AcHN

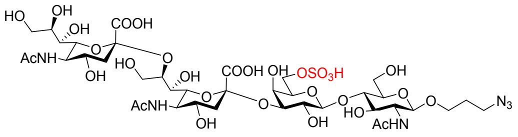
59


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

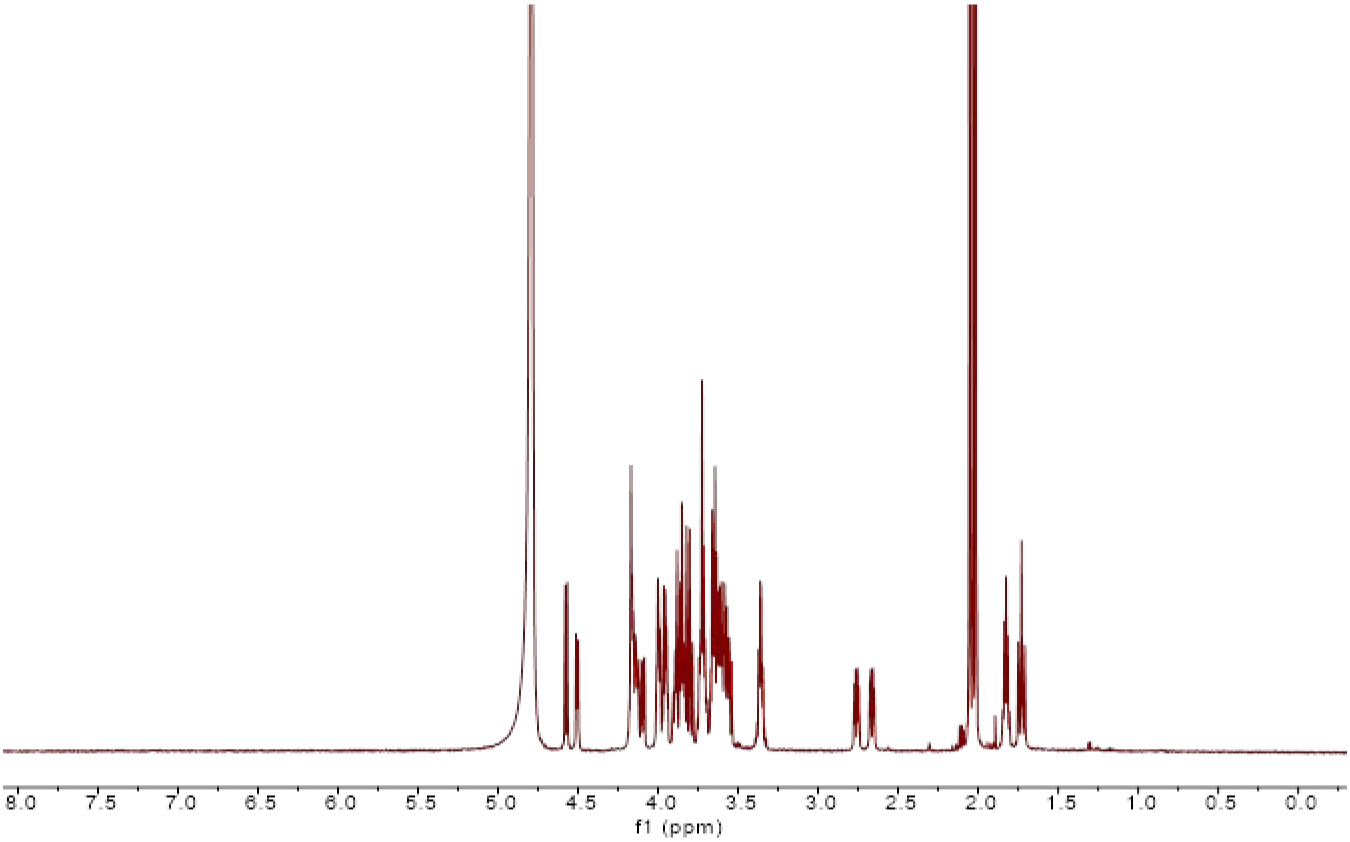

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

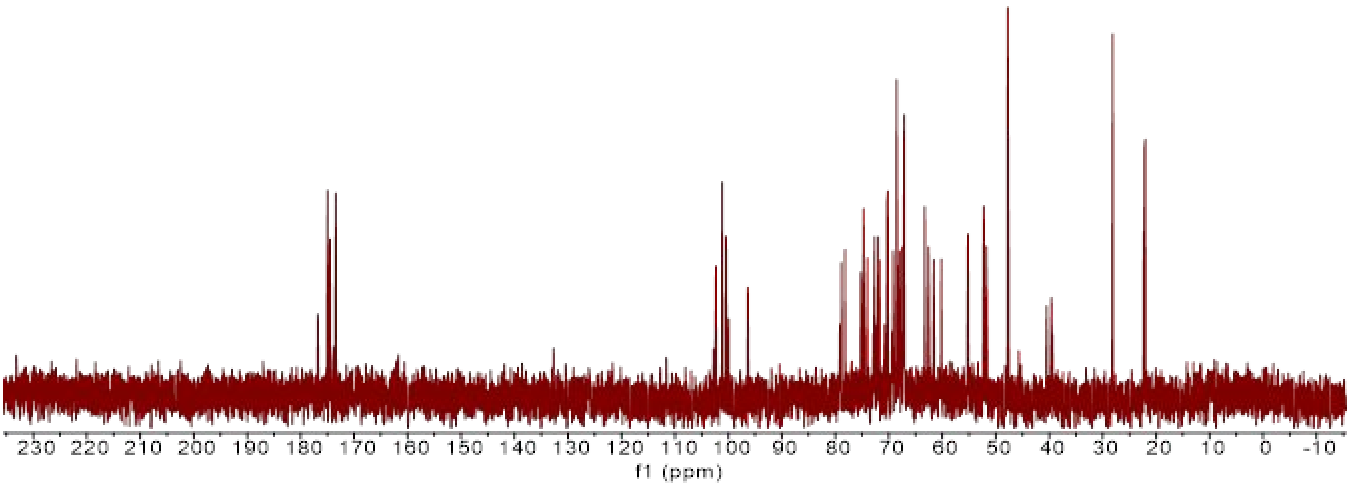

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

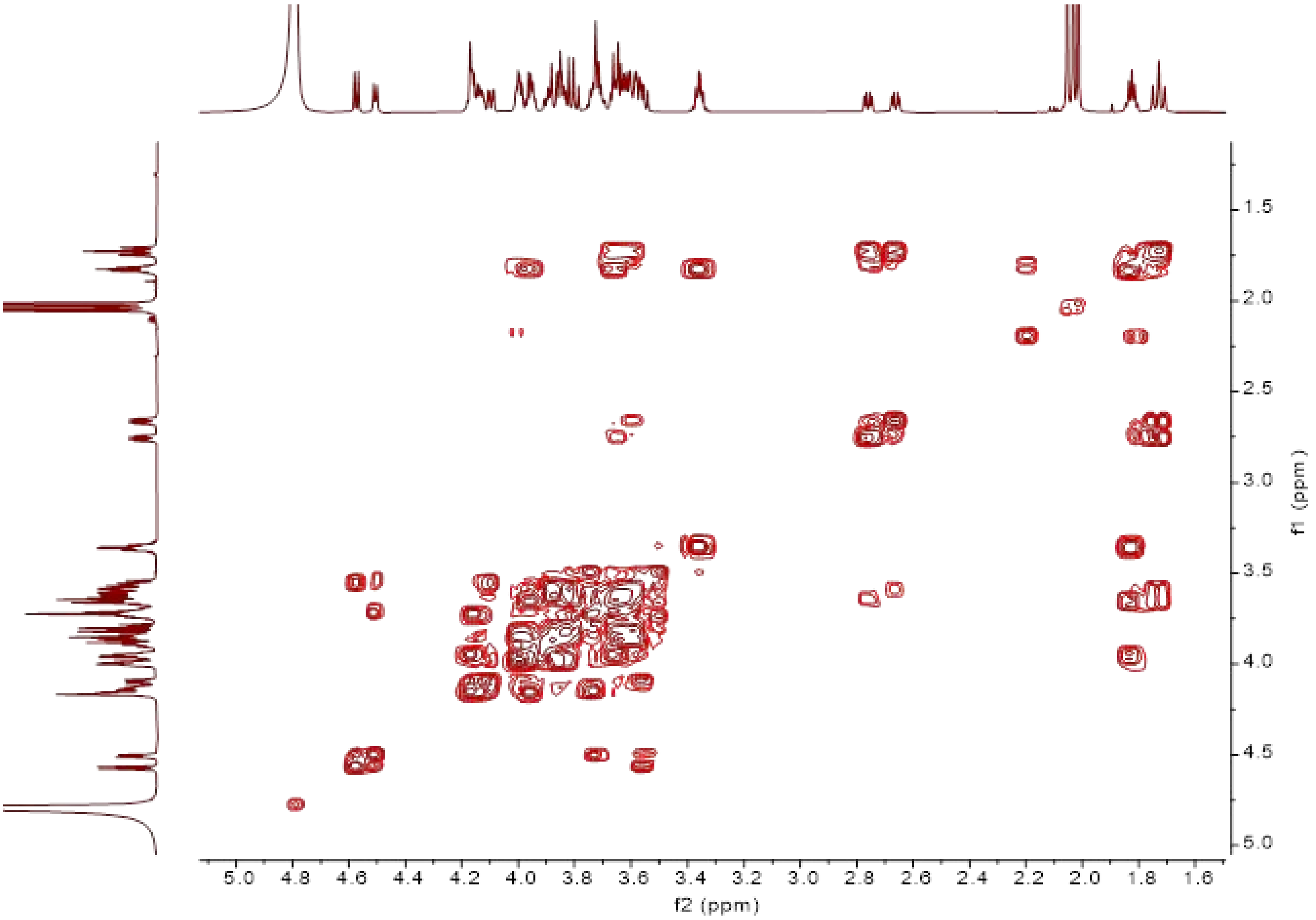

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

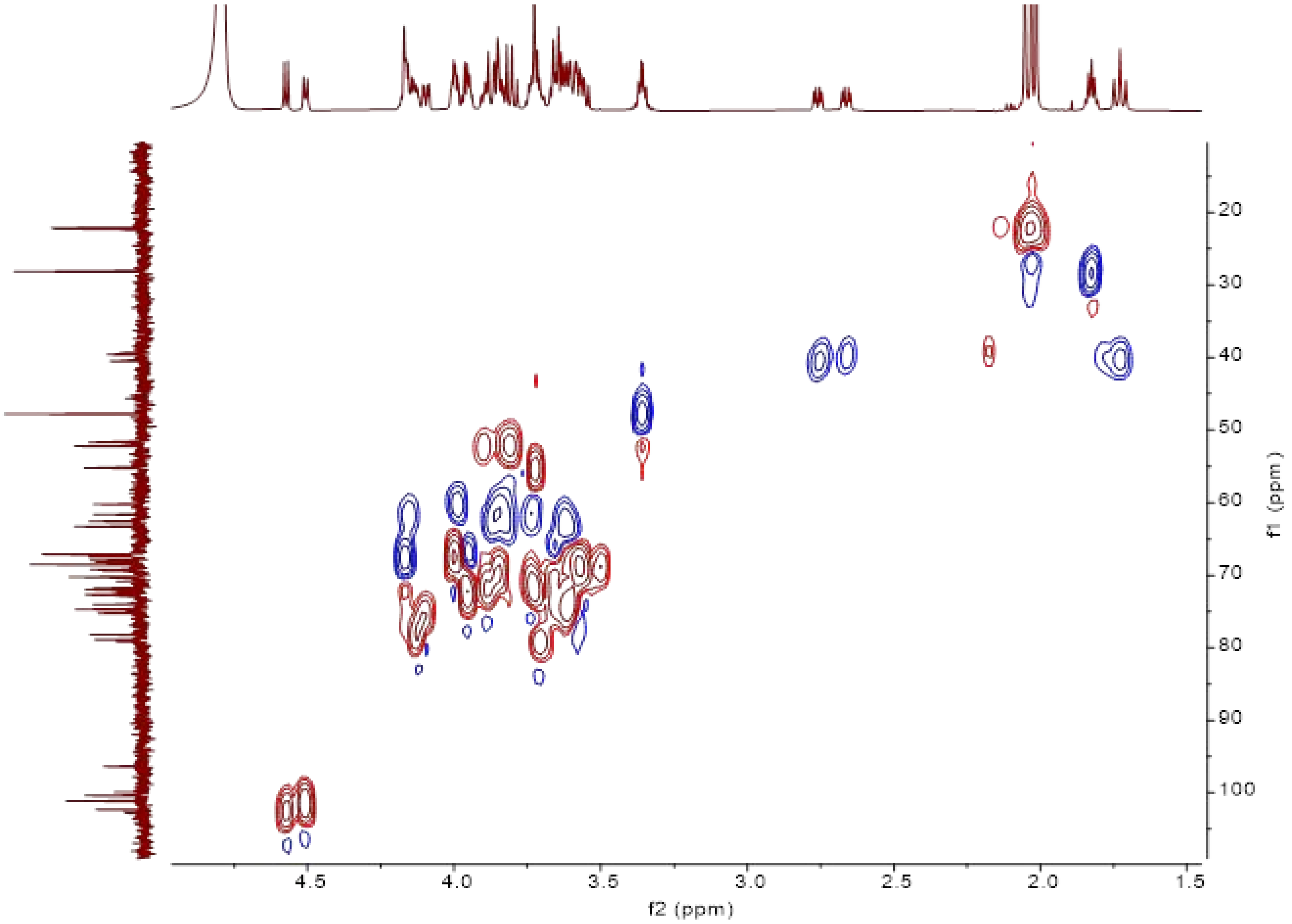

HO
OH
OH
COOH
AcNH
OH
HO
OH
COOH
OH
OSO$_3$H
OH
AcNH
OH
OH
HO
AcHN
N$_3$

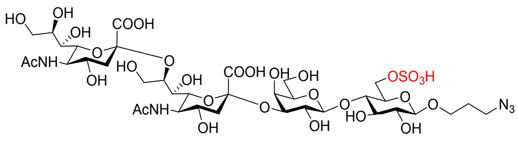
60


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

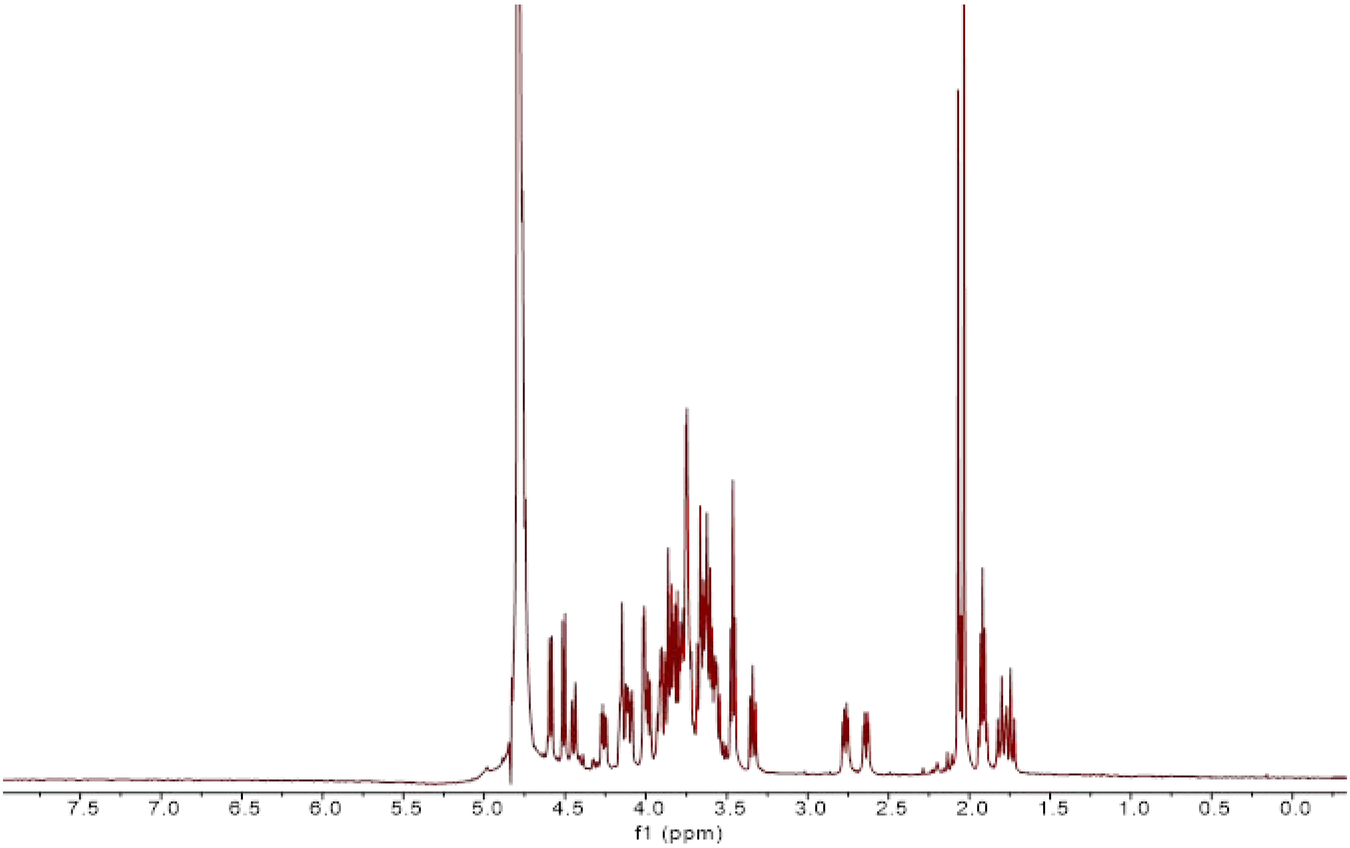

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

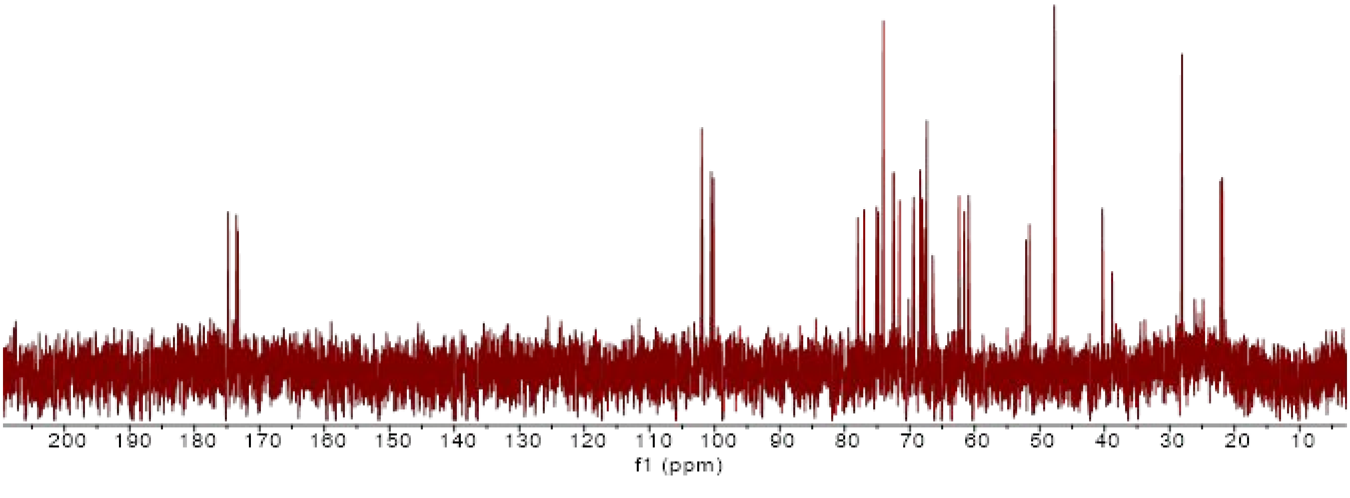

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f2 (ppm)

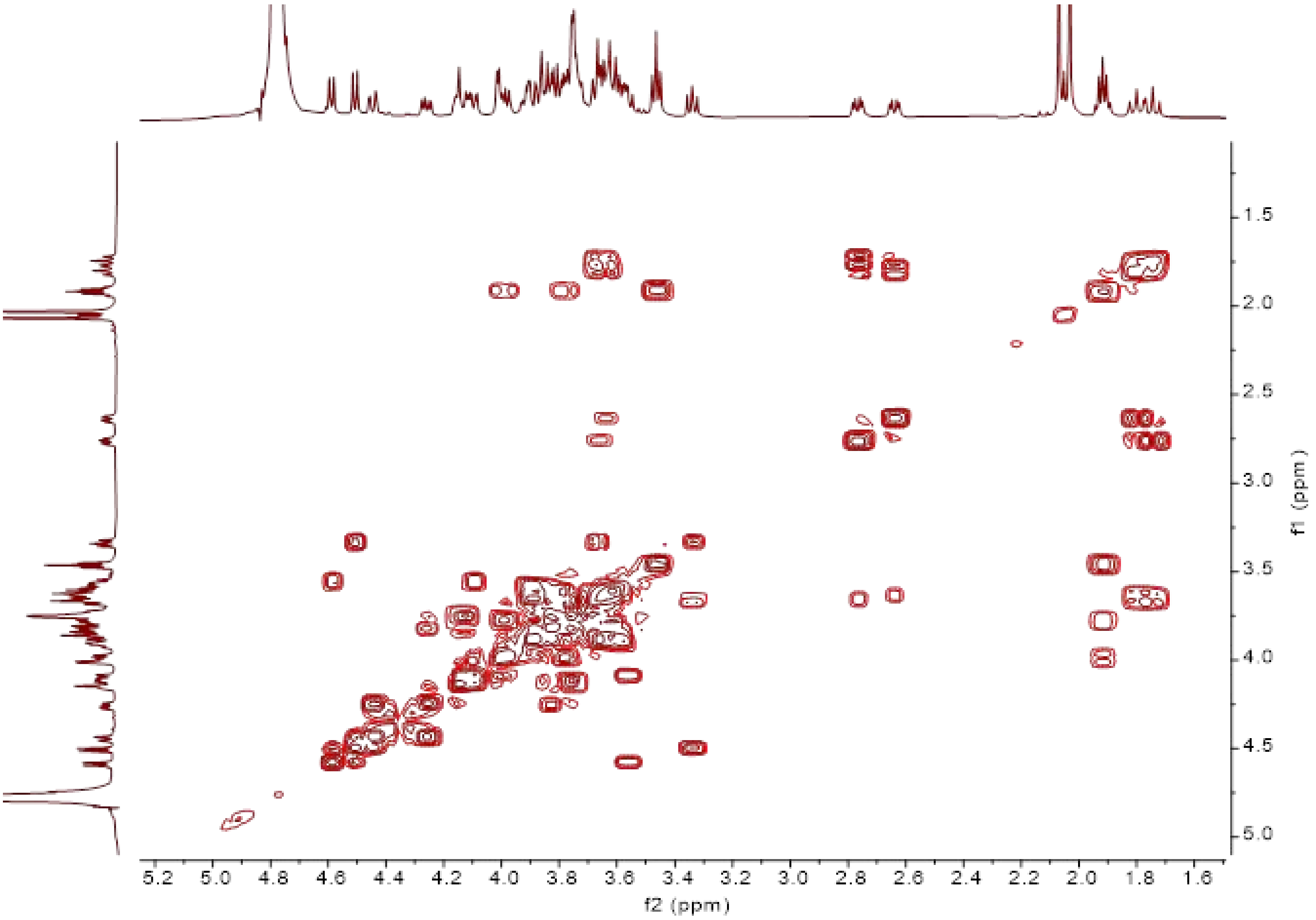

20
30
40
50
60
70
80
90
100
f1 (ppm)
4.5 4.0 3.5 3.0 2.5 2.0 1.5
f2 (ppm)

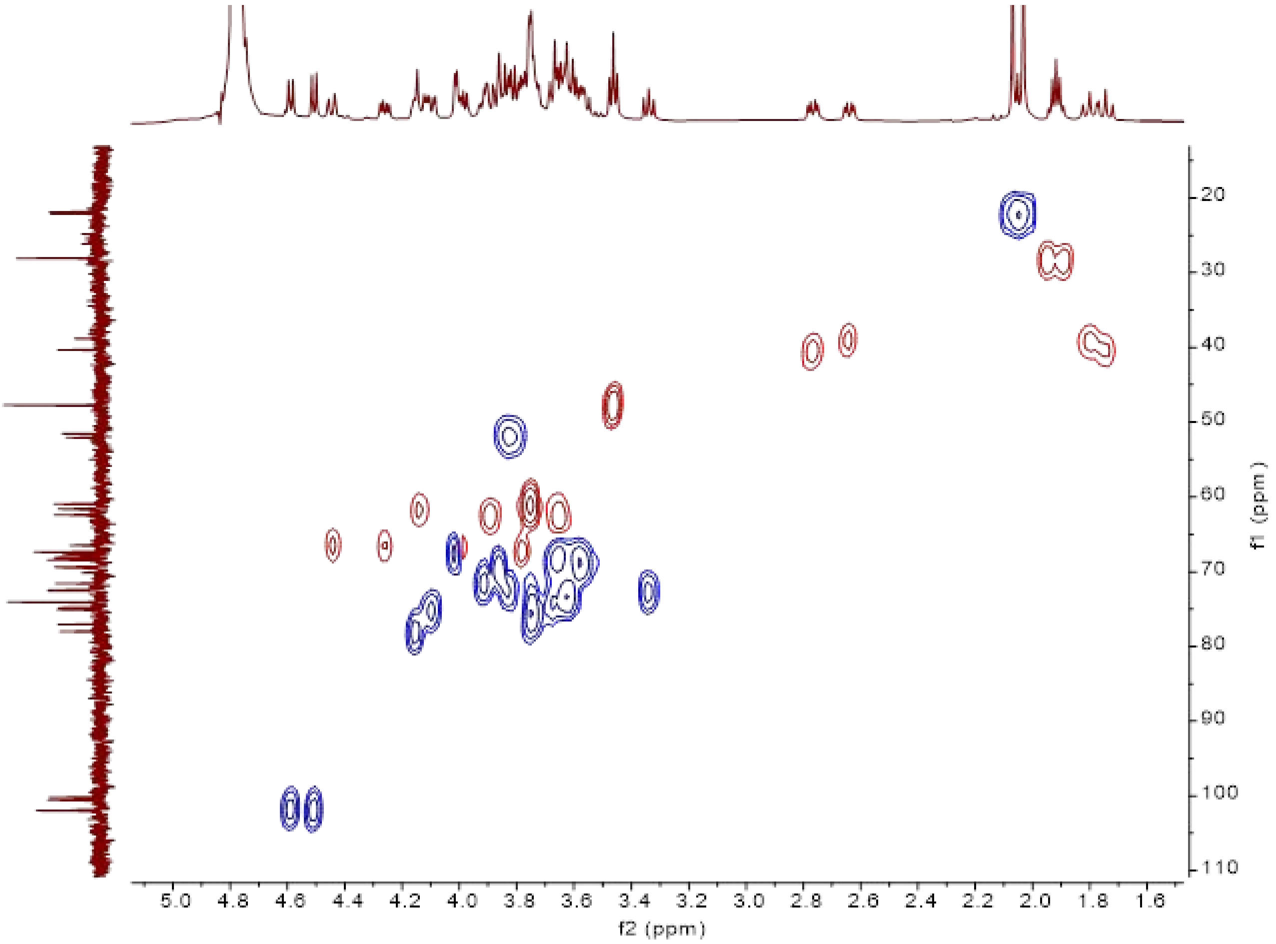

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
AcNH
O
OH
O
O
OSO$_3$H
O
HO
OH
OH
O
N$_3$

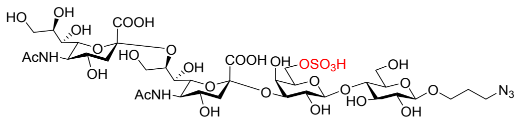
61


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)

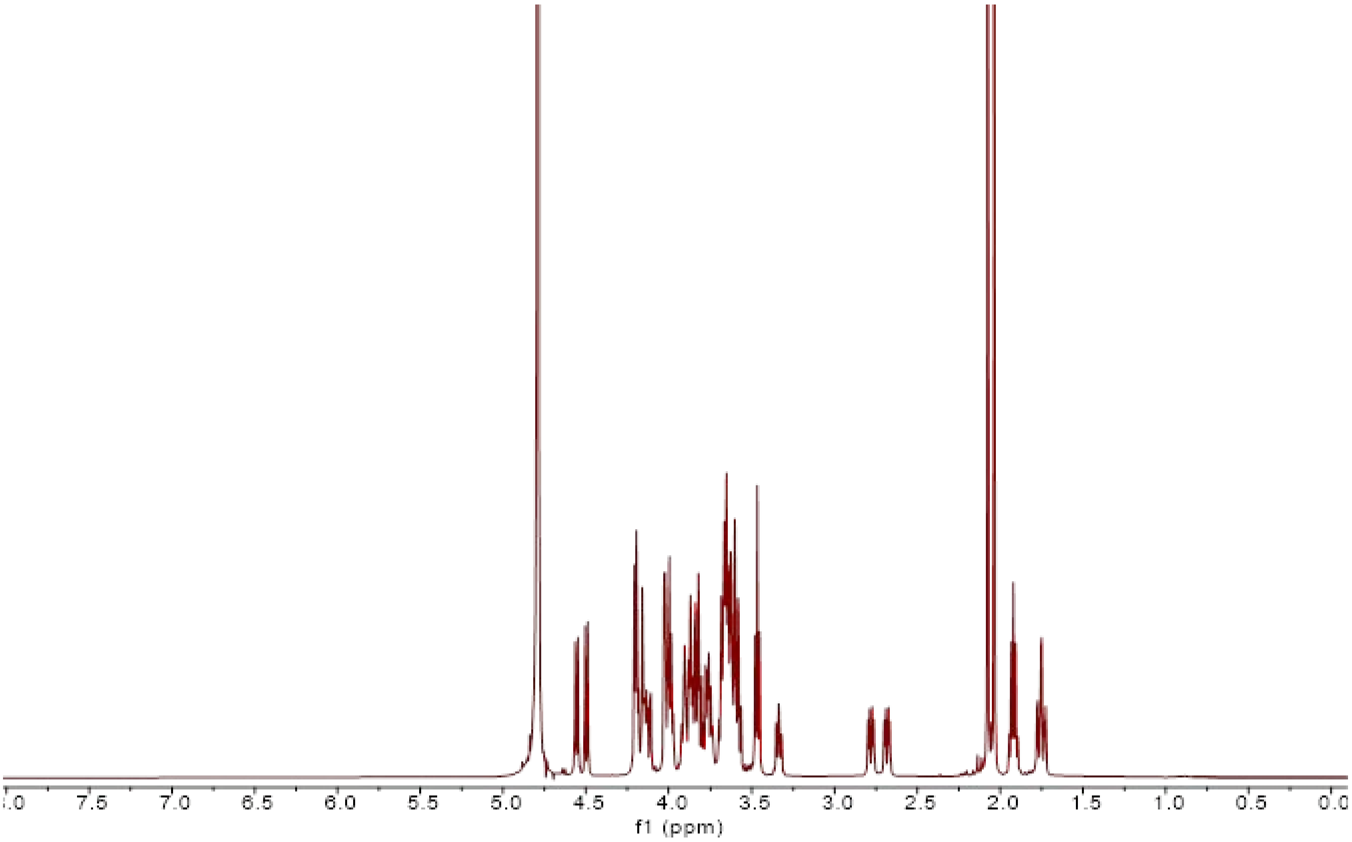

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

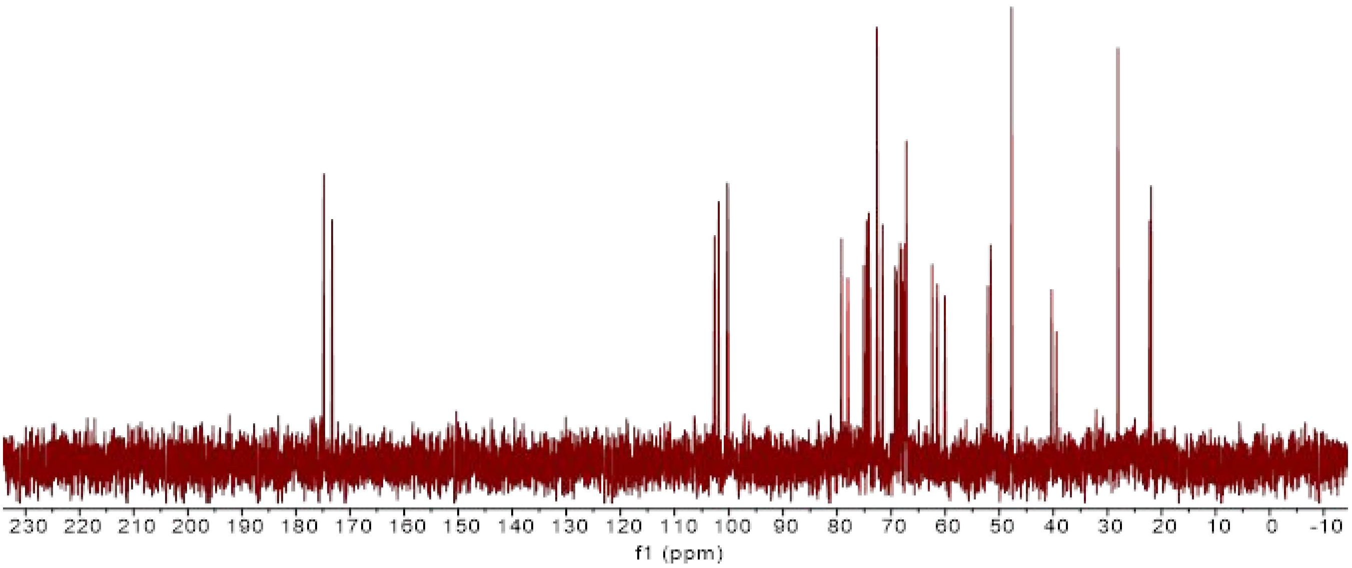

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

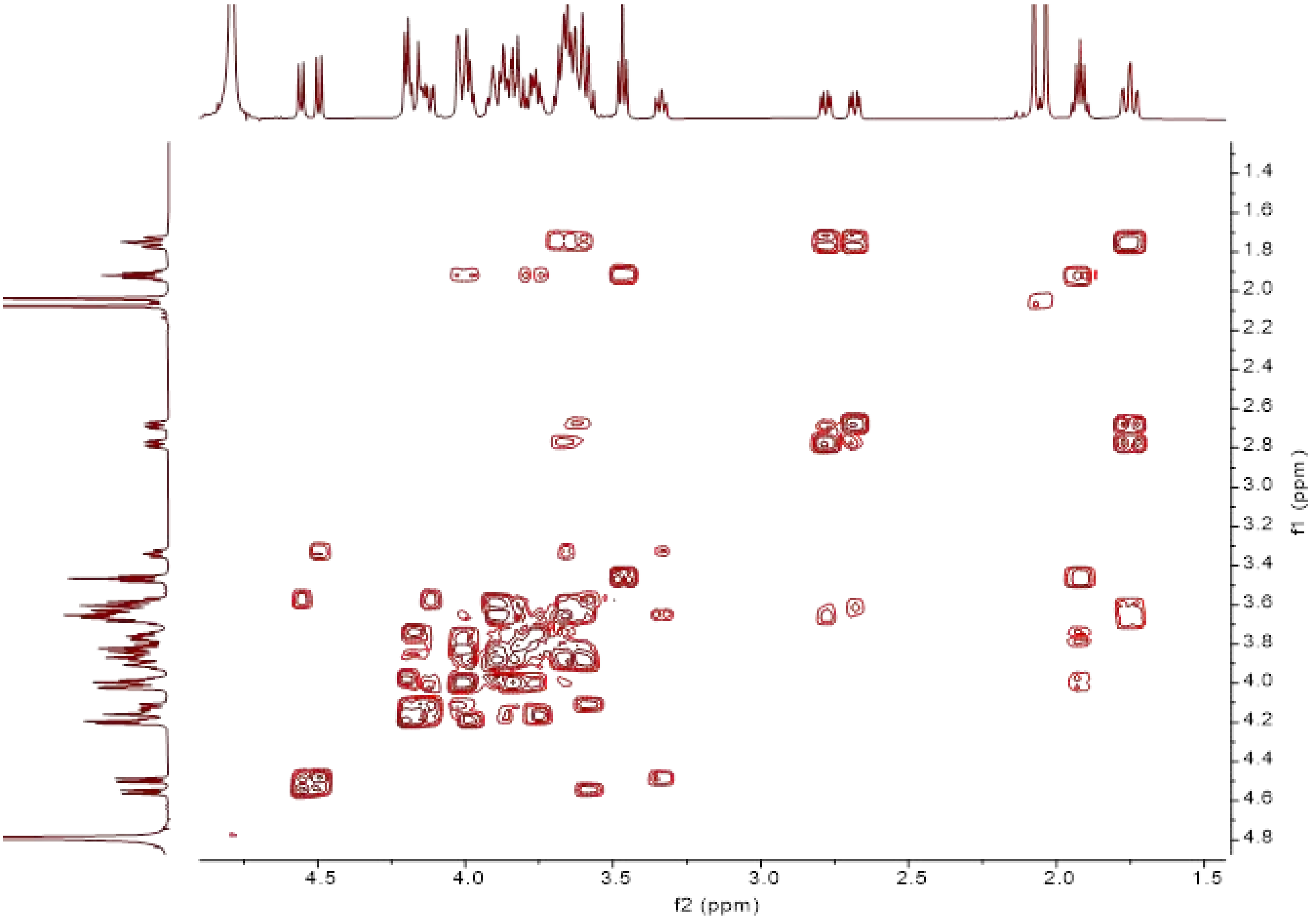

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

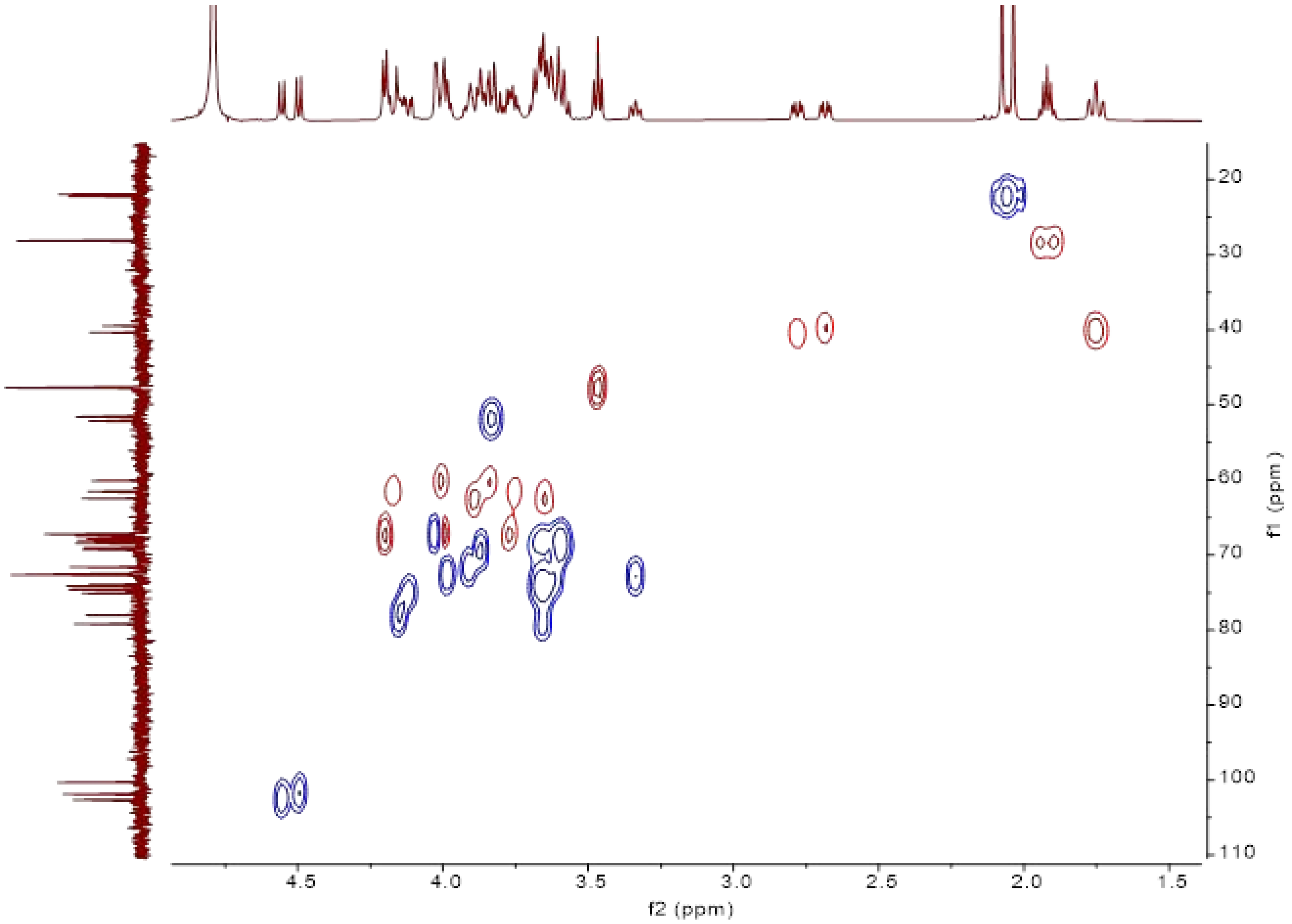

HO
OH
OH
COOH
O
AcNH
OH
HO
OH
COOH
OH
OSO$_3$H
OH
AcNH
OH
O
O
OH
HO
O
OH
O
N$_3$

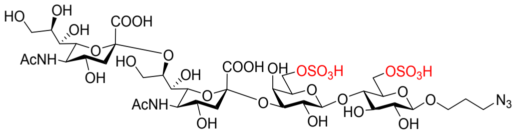
62


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

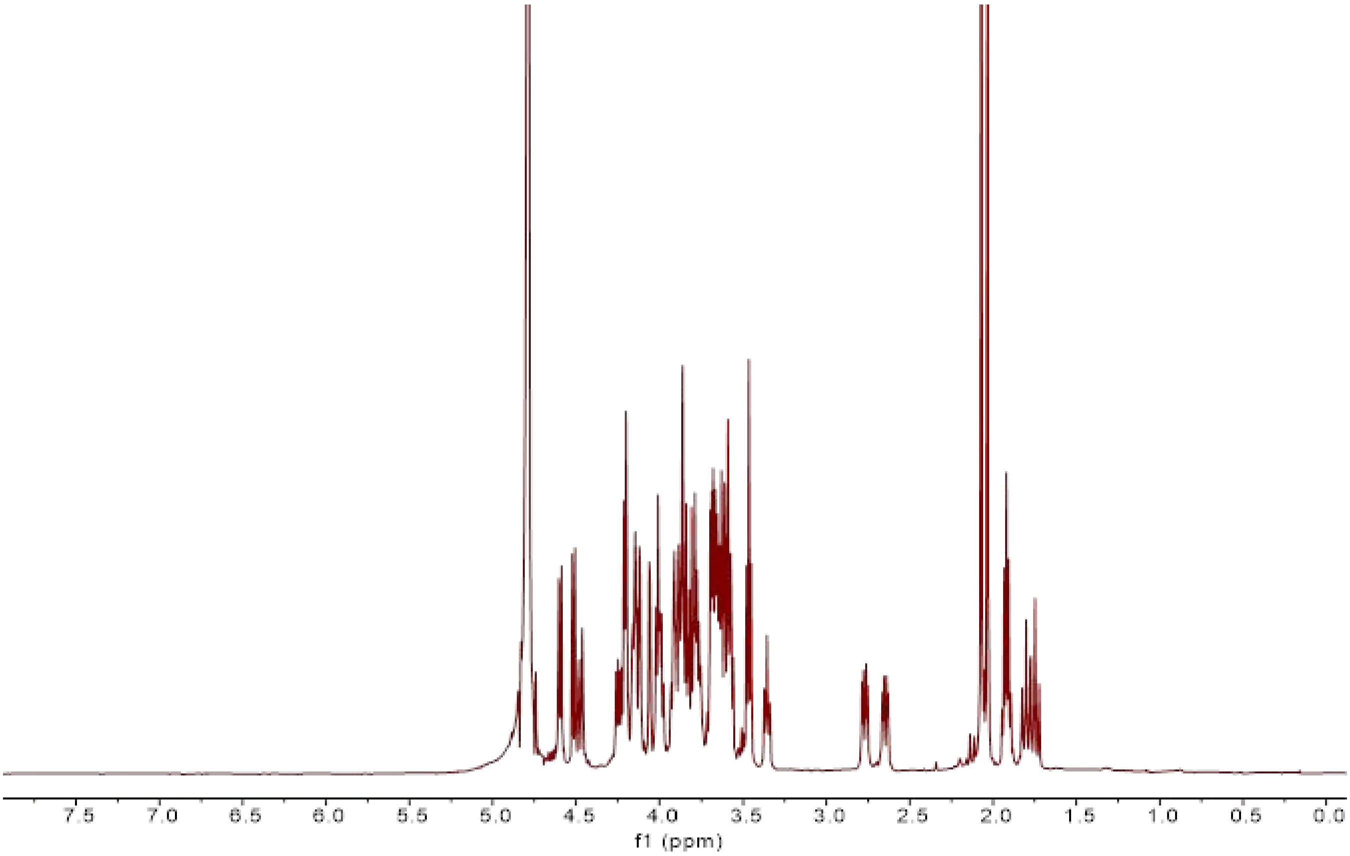

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

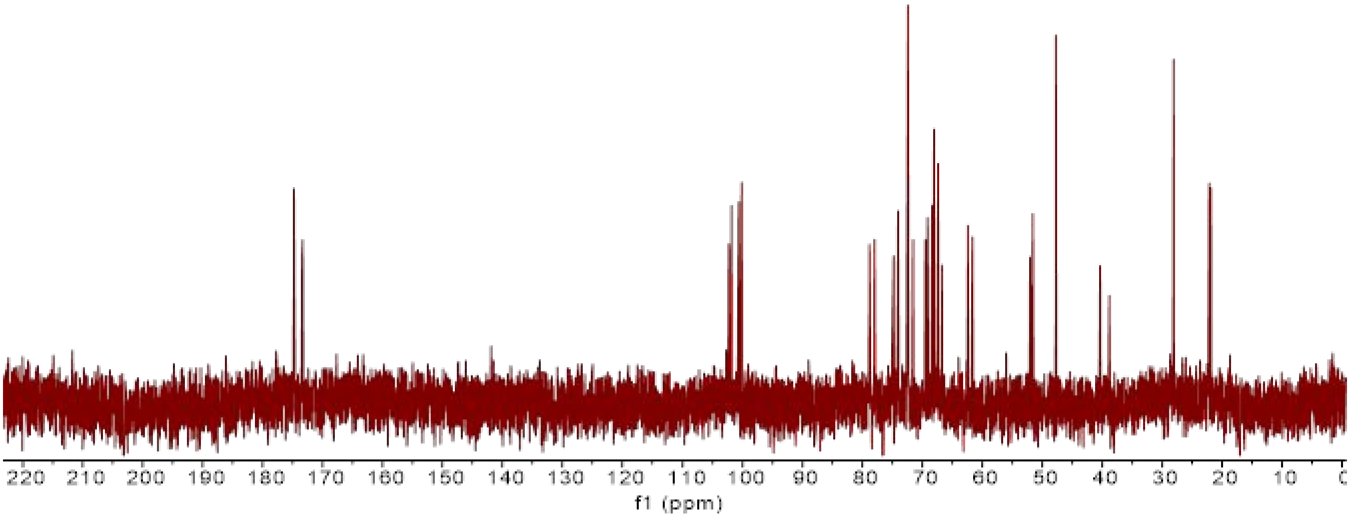

1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

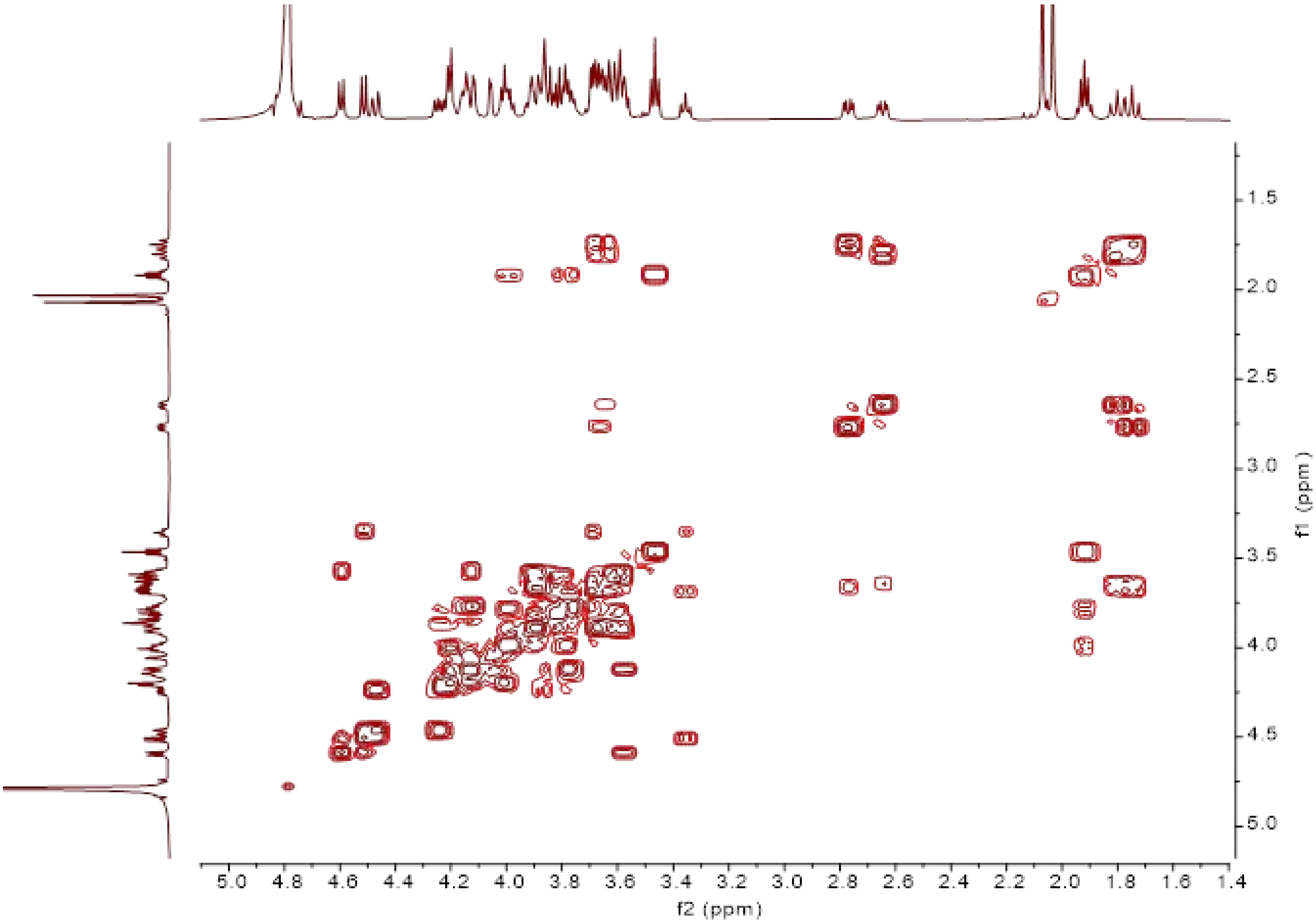

20
30
40
50
60
70
80
90
100
110
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

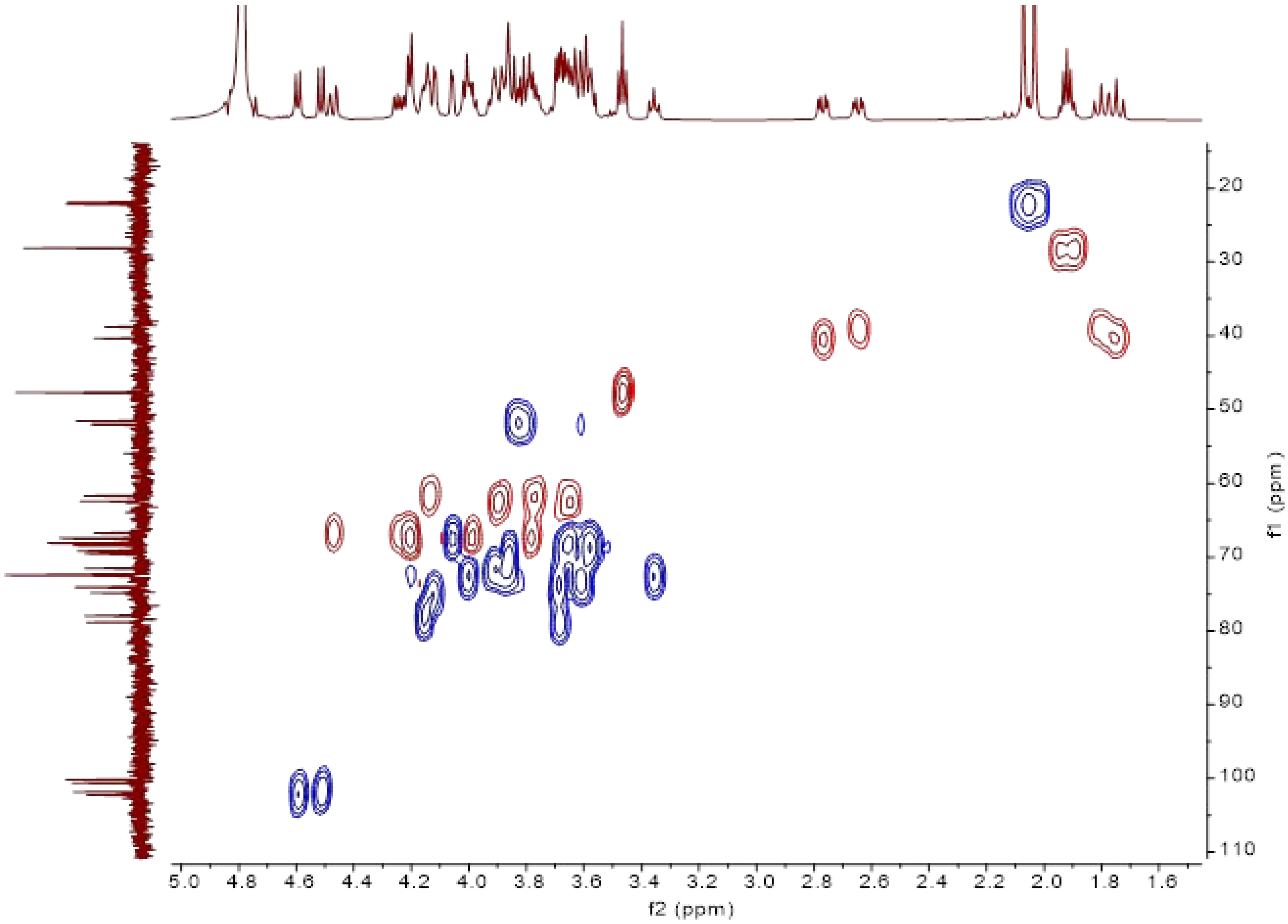

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OSO3H
OSO3H
AcNH
O
O
O
O
O
HO
O
N3
OH
OH
OH

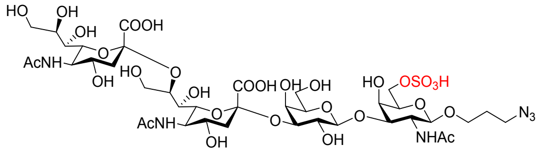
63


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)

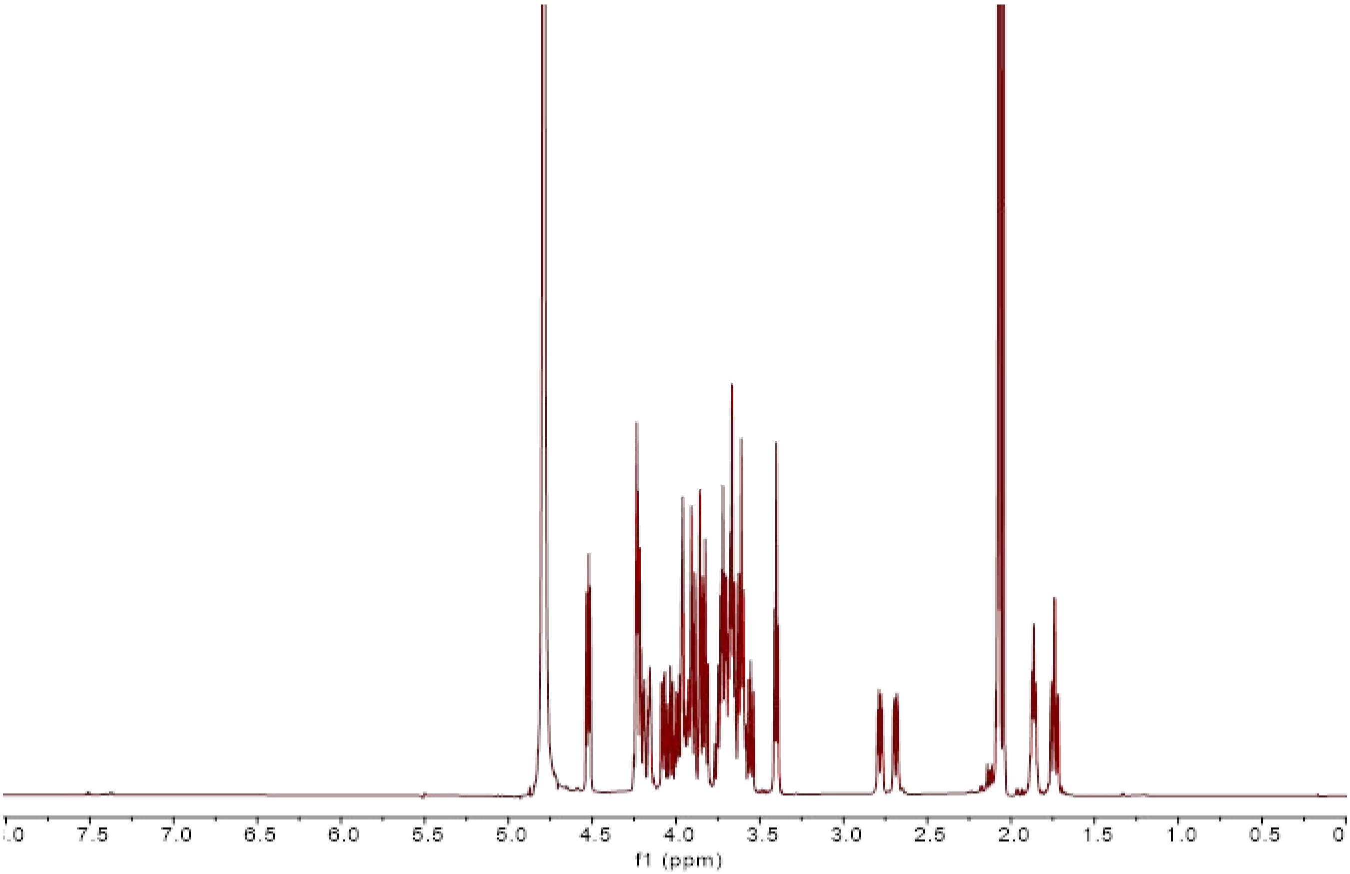

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

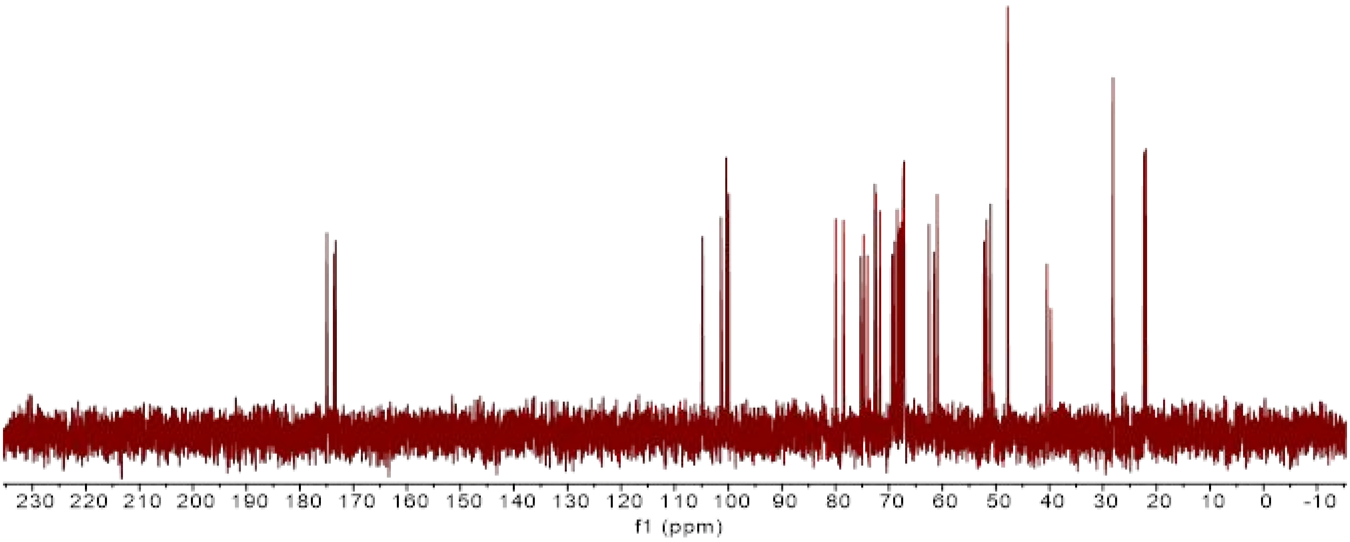

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

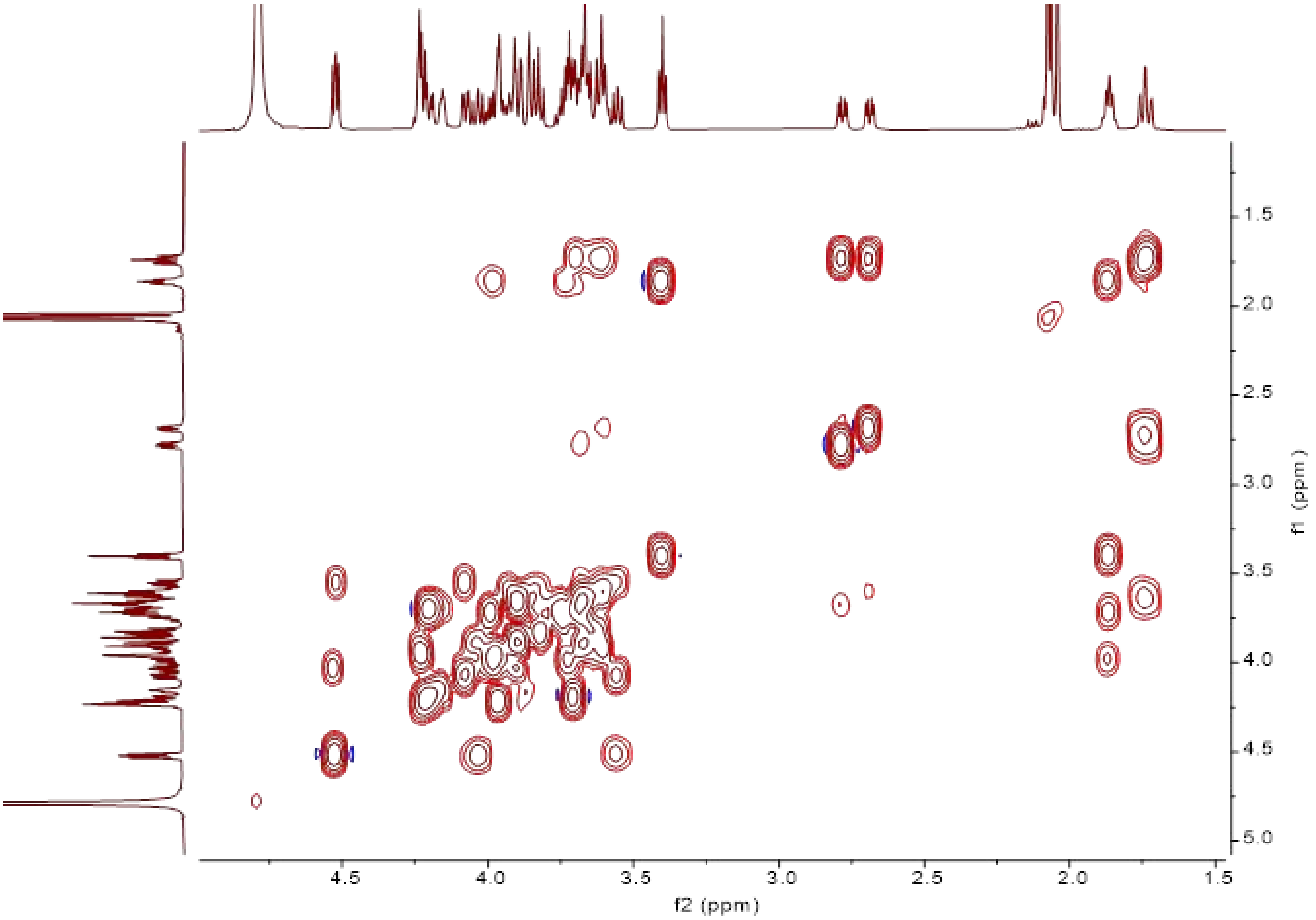

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

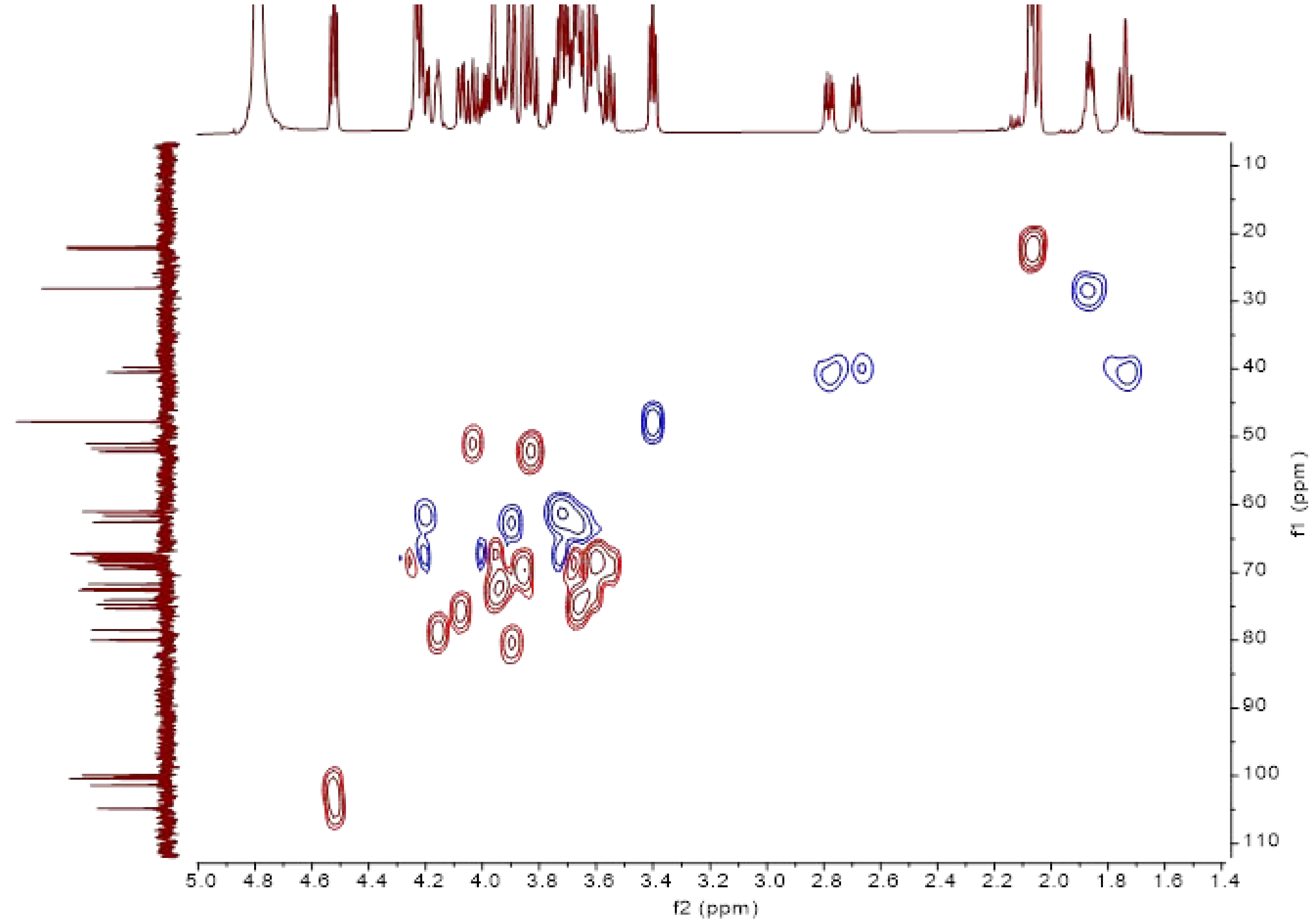

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OH
HO
OSO3H
AcNH
O
O
O
O
O
OH
OH
NHAc
N3

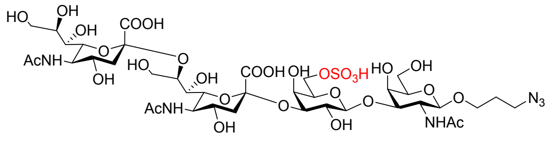
64


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
f1 (ppm)

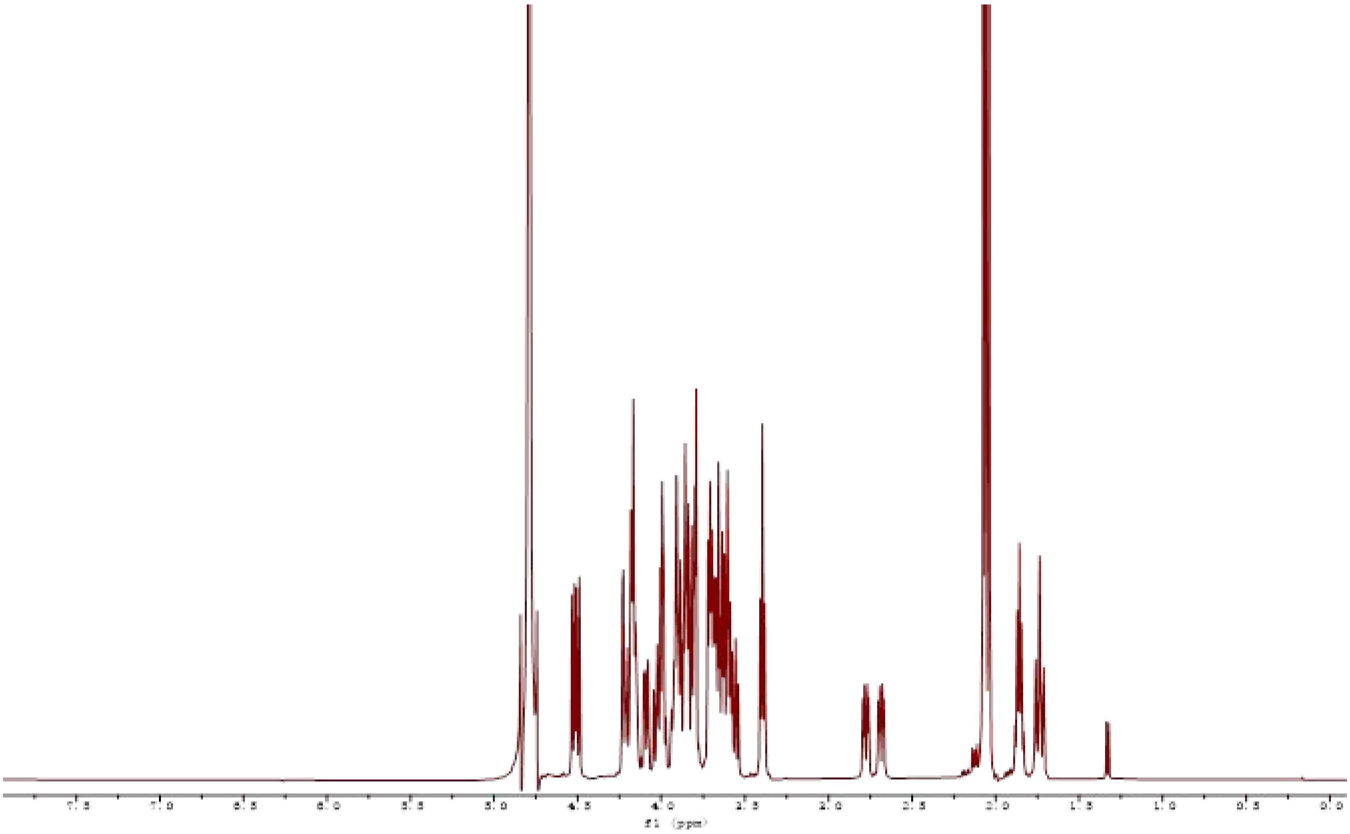

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

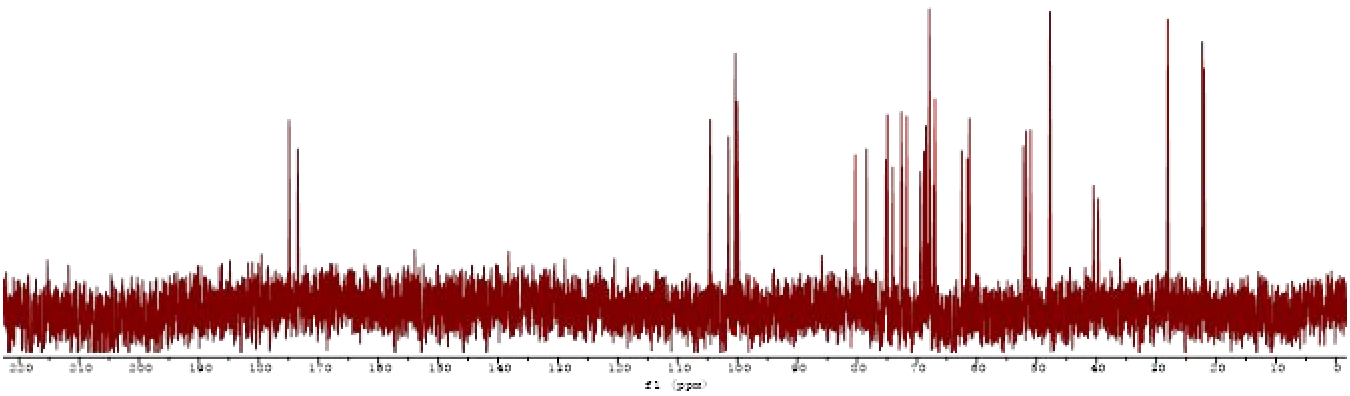

4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

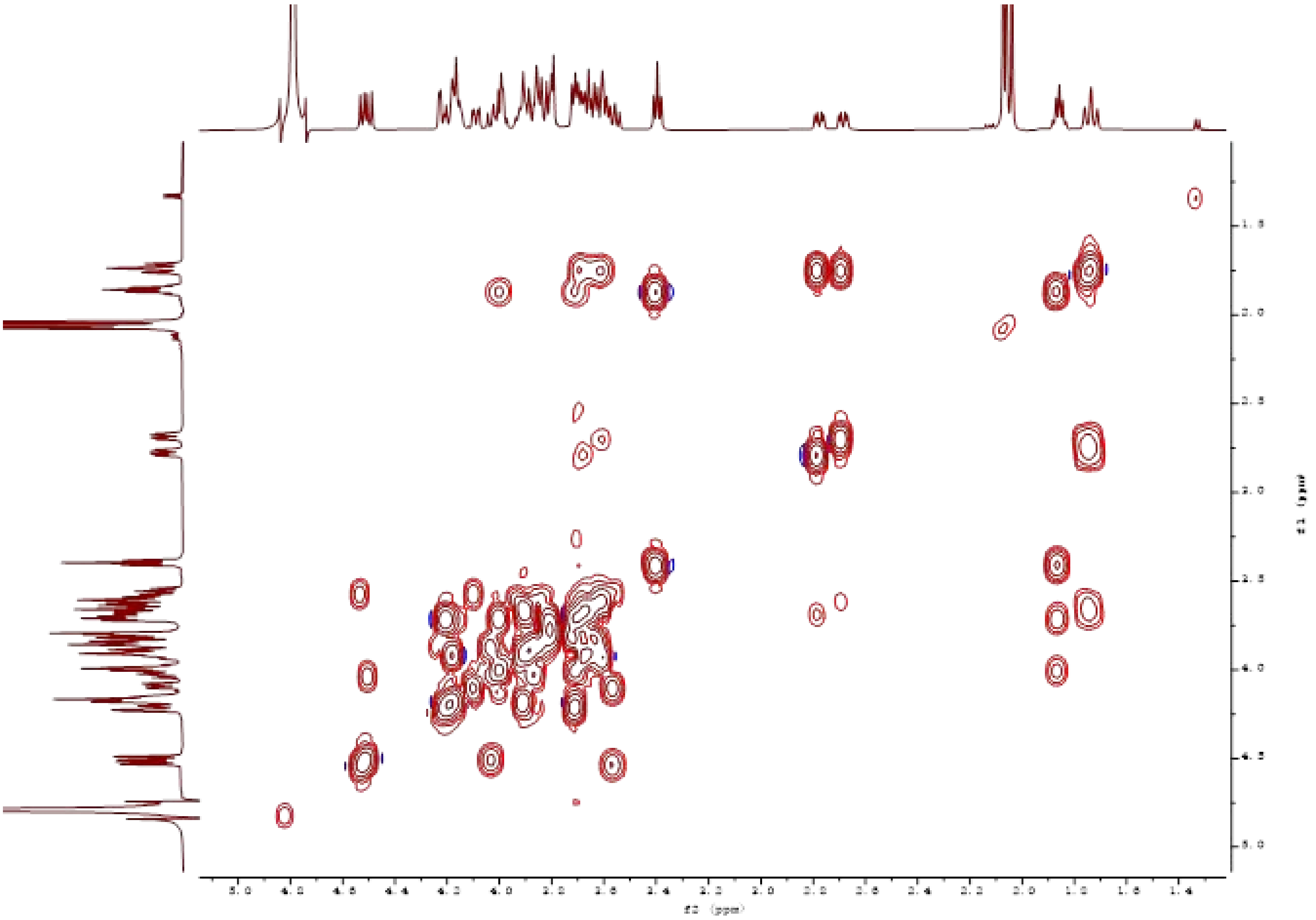

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

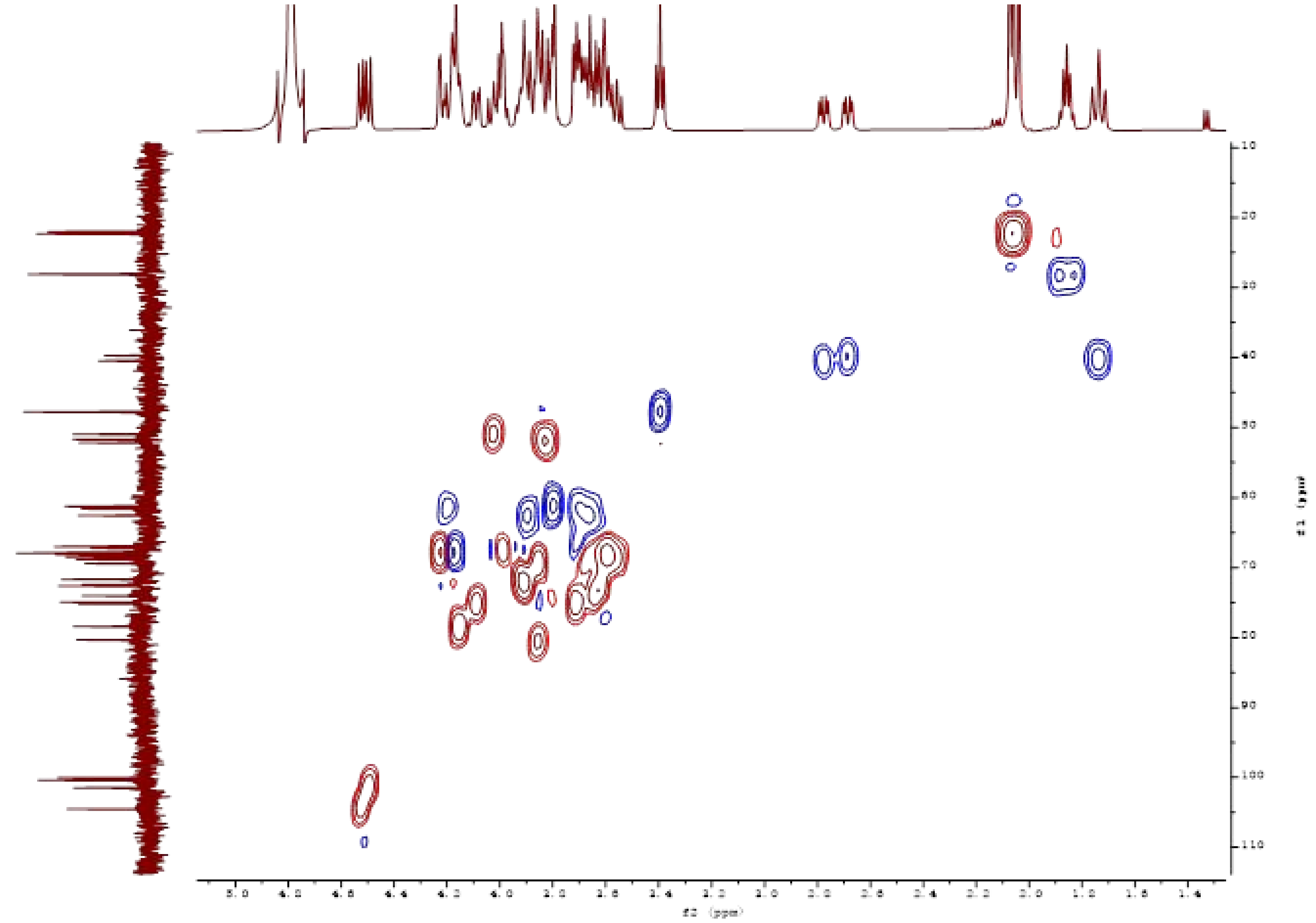

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OSO3H
HO
OH
AcNH
O
O
O
O
O
O
N3
OH
OH
NHAc

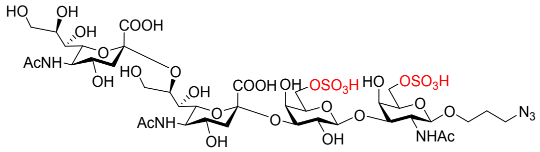
65


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)

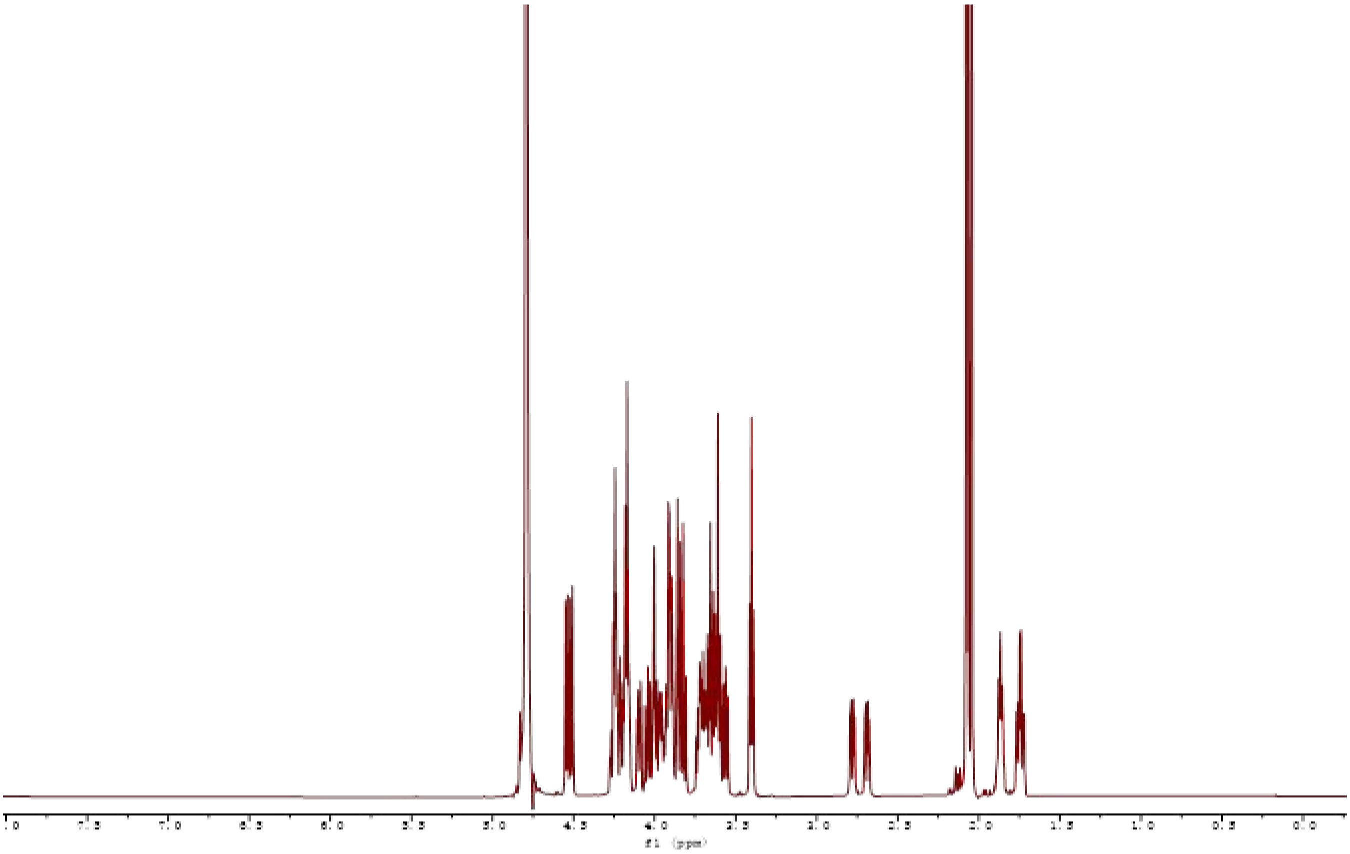

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

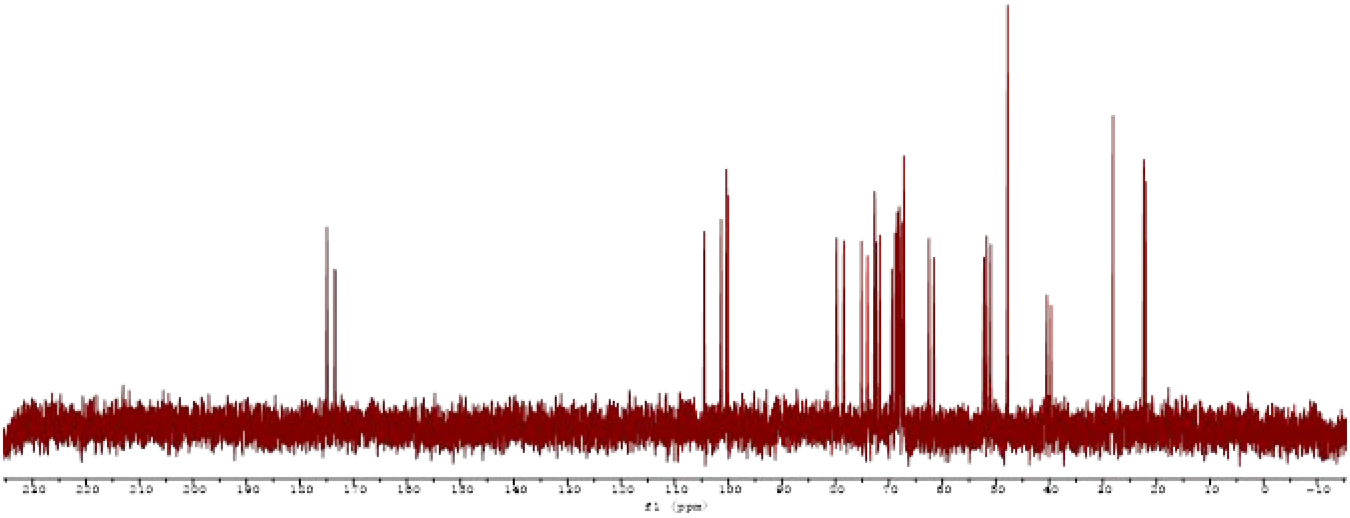

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

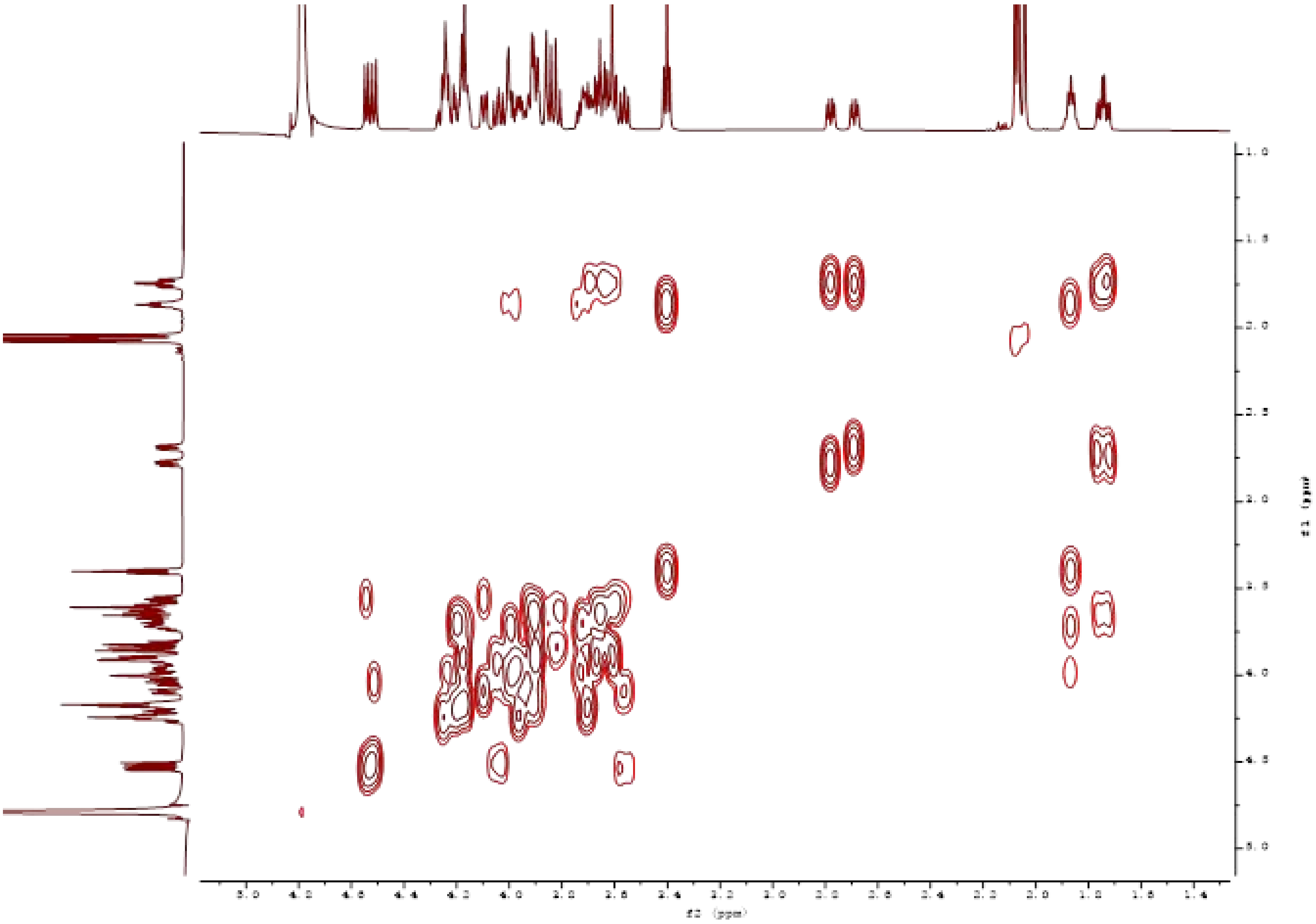

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

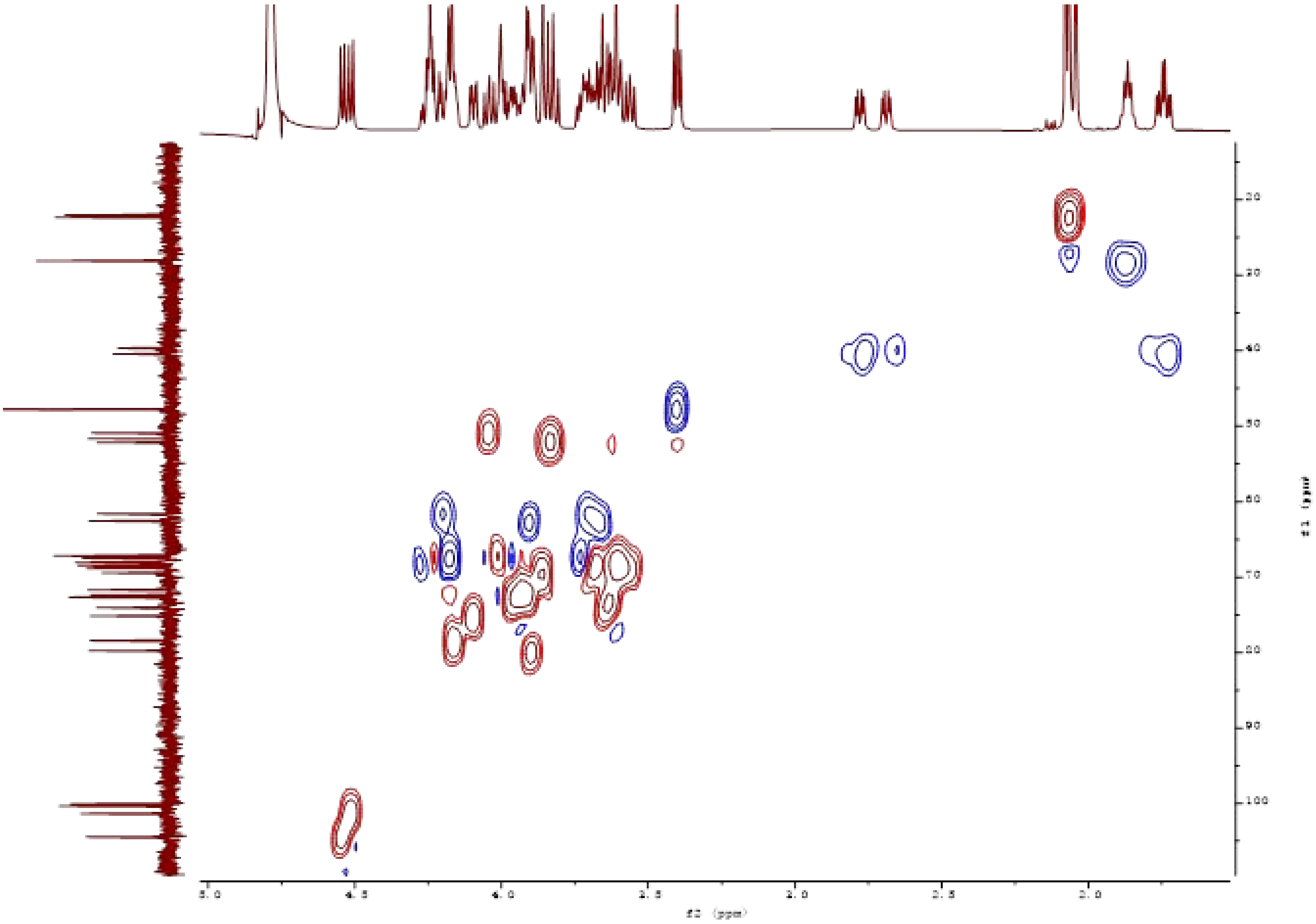

HO
OH
OH
COOH
AcNH
O
OH
HO
O
OH
COOH
OH
OSO3H
HO
OSO3H
AcNH
O
O
O
OH
O
O
NHAc
O
N3
OH

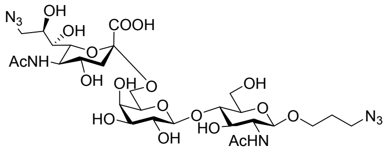
66


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

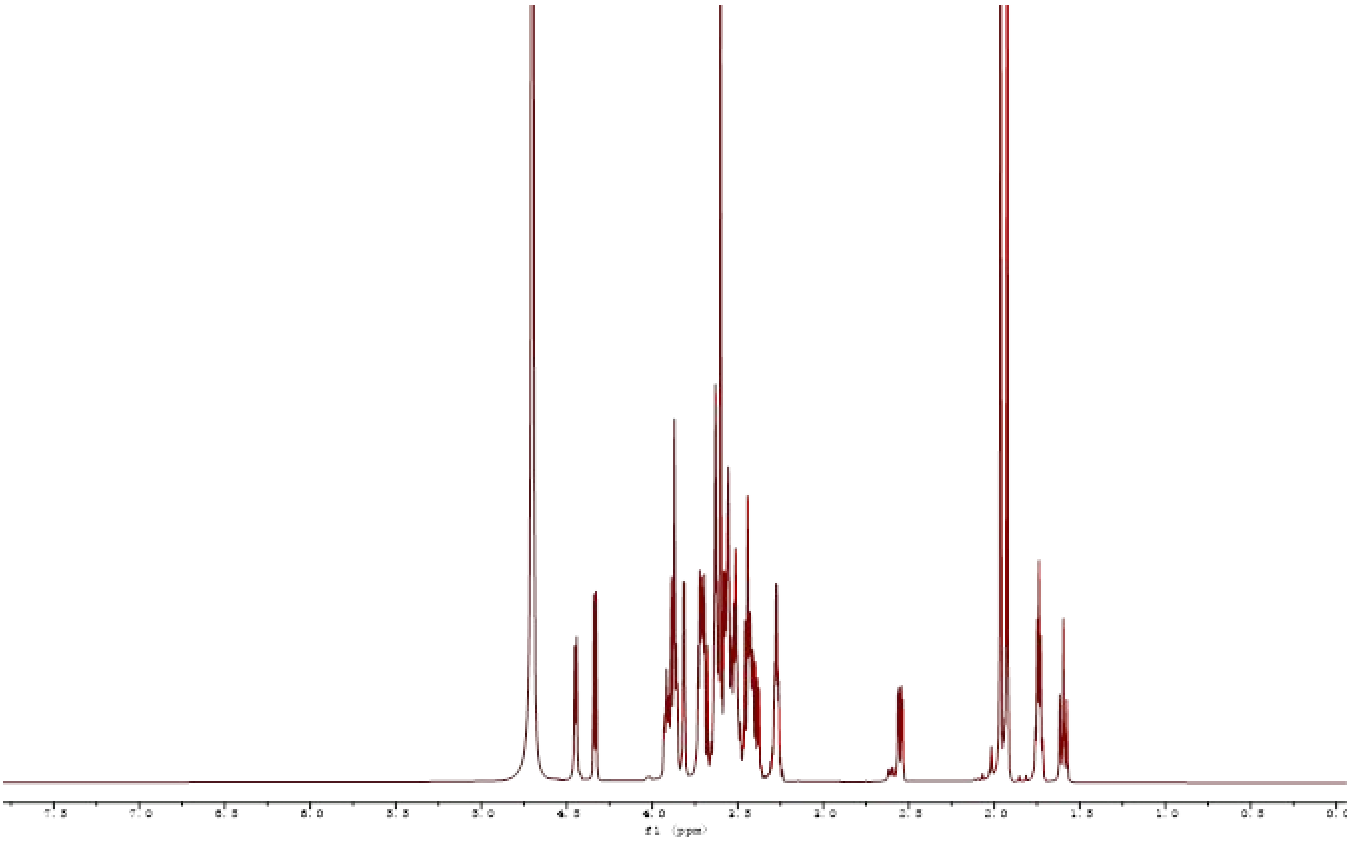

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

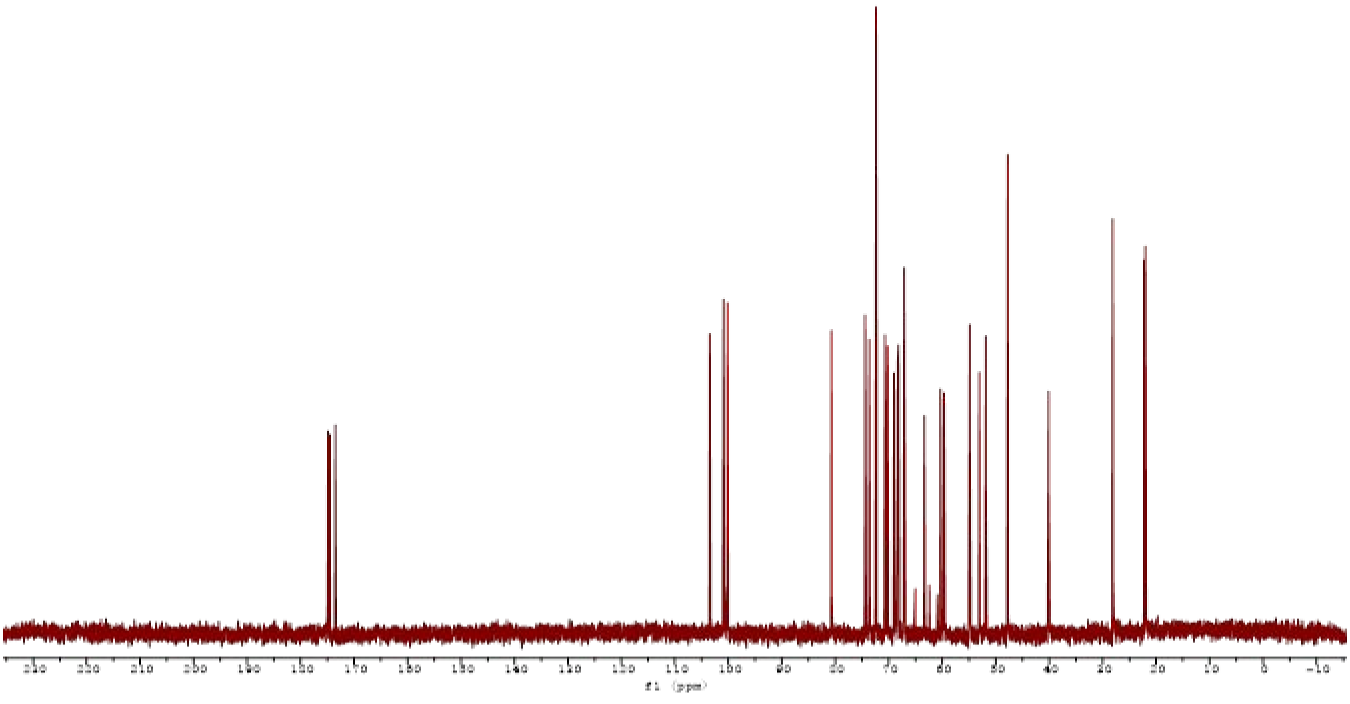

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

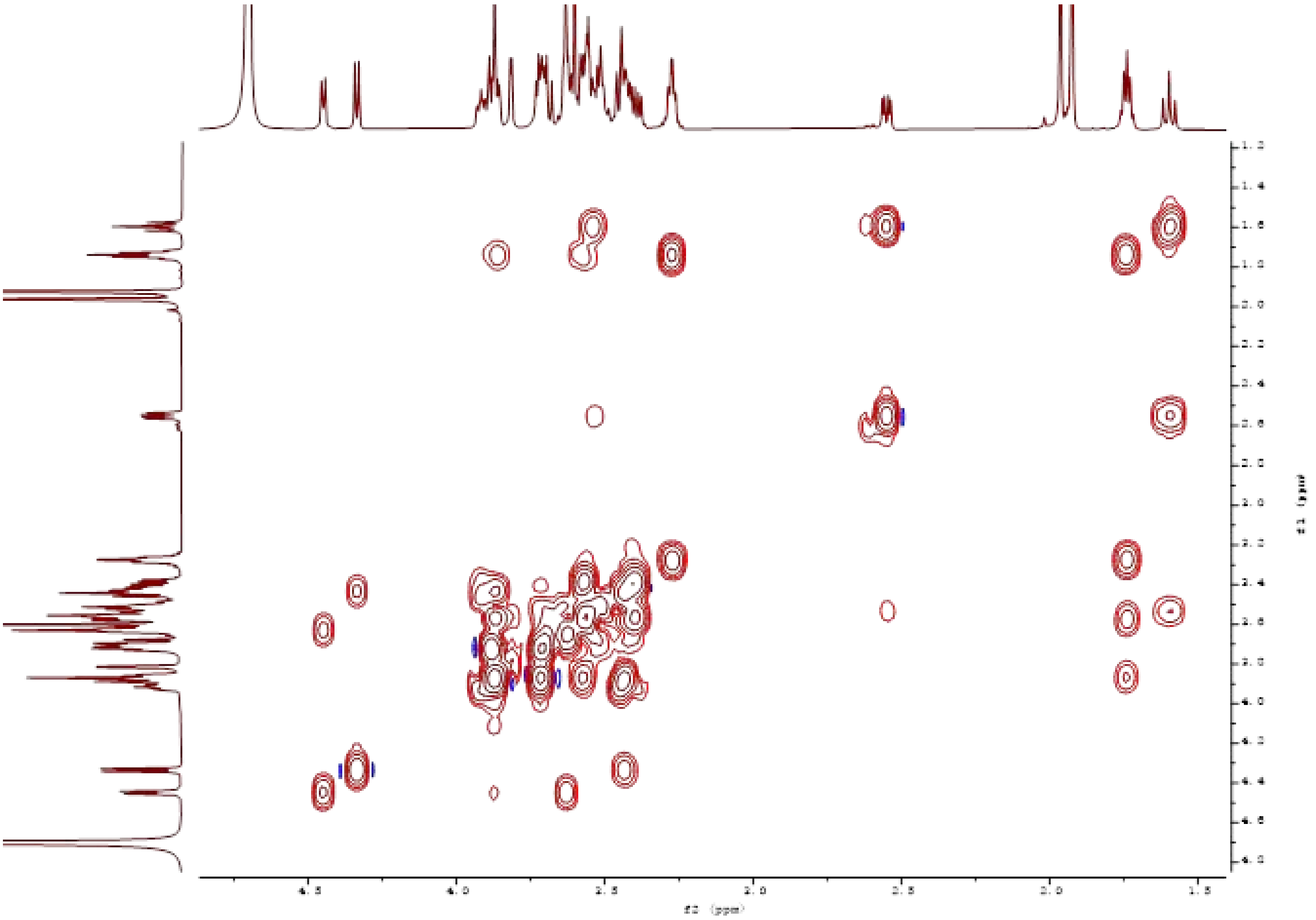

5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

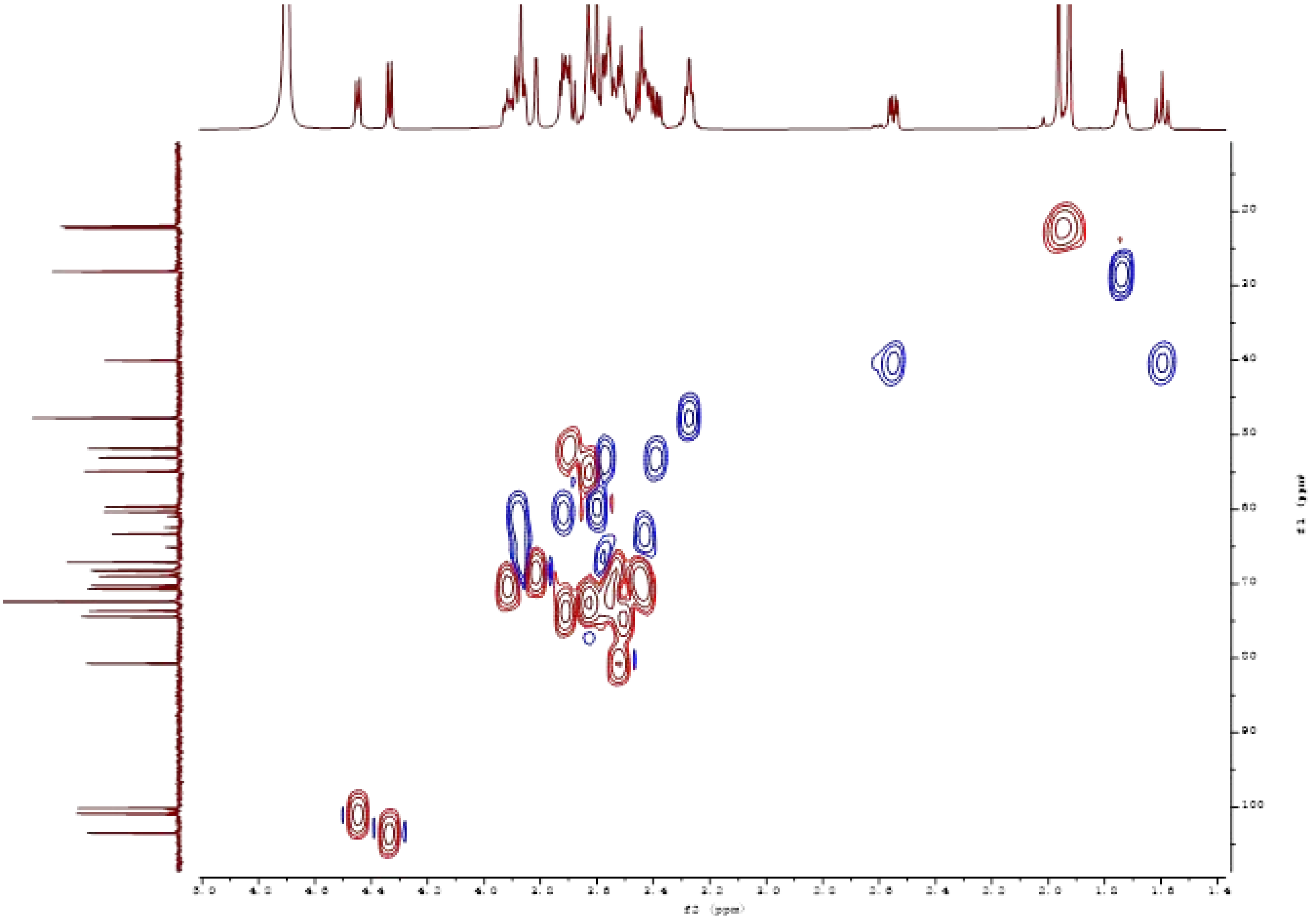

N3
OH
OH
COOH
AcNH
O
OH
OH
O
OH
HO
O
OH
O
HO
AcHN
O
O
N3

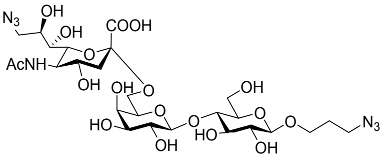
69


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)

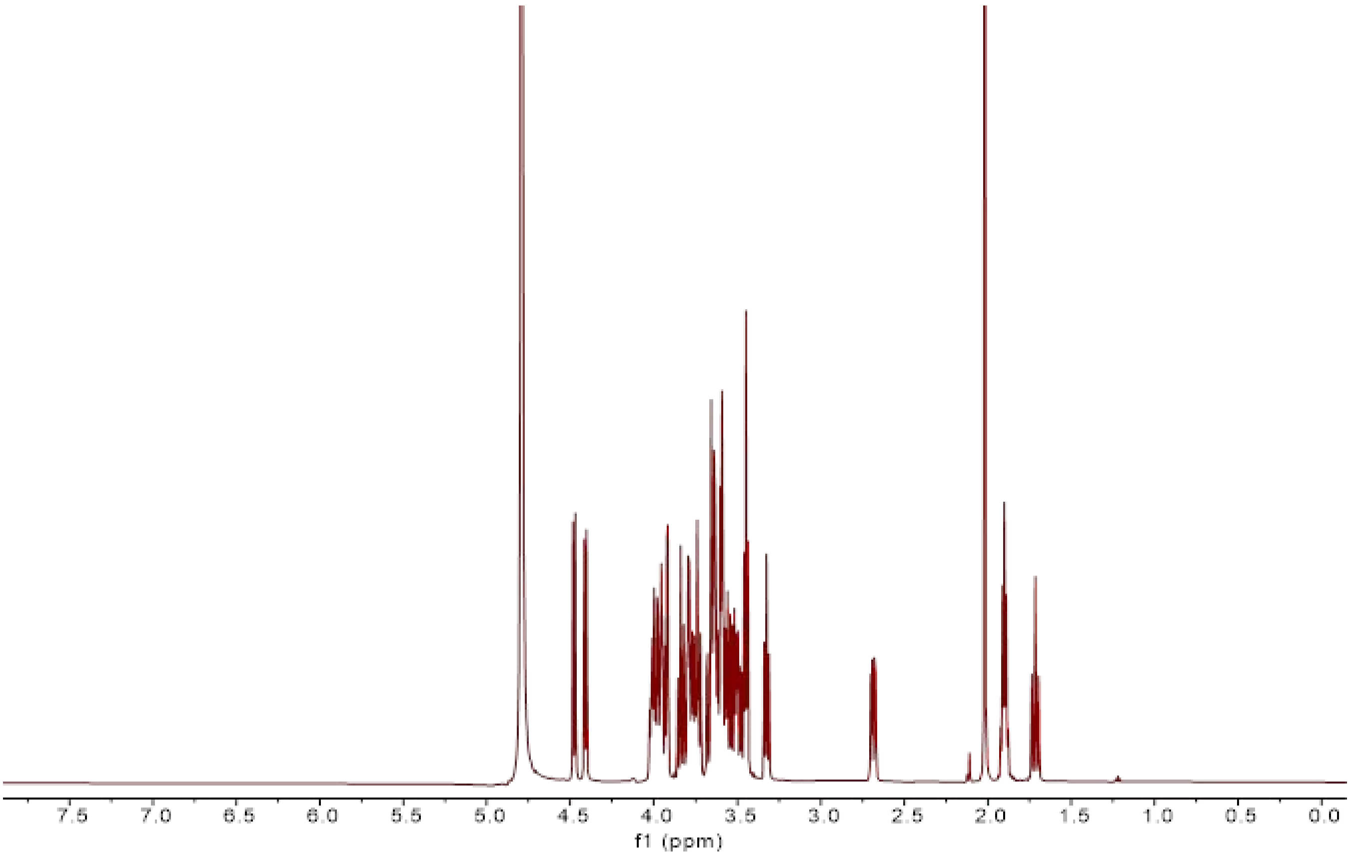

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

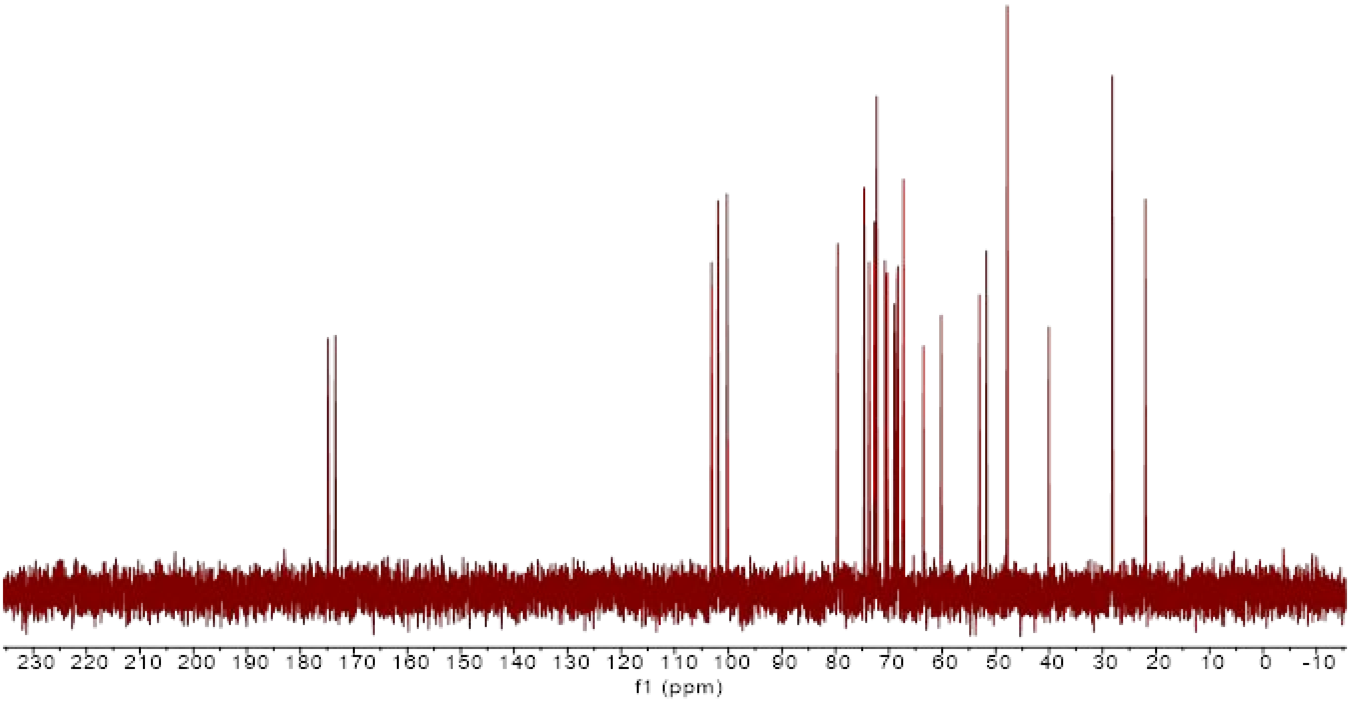

f2 (ppm)
f1 (ppm)

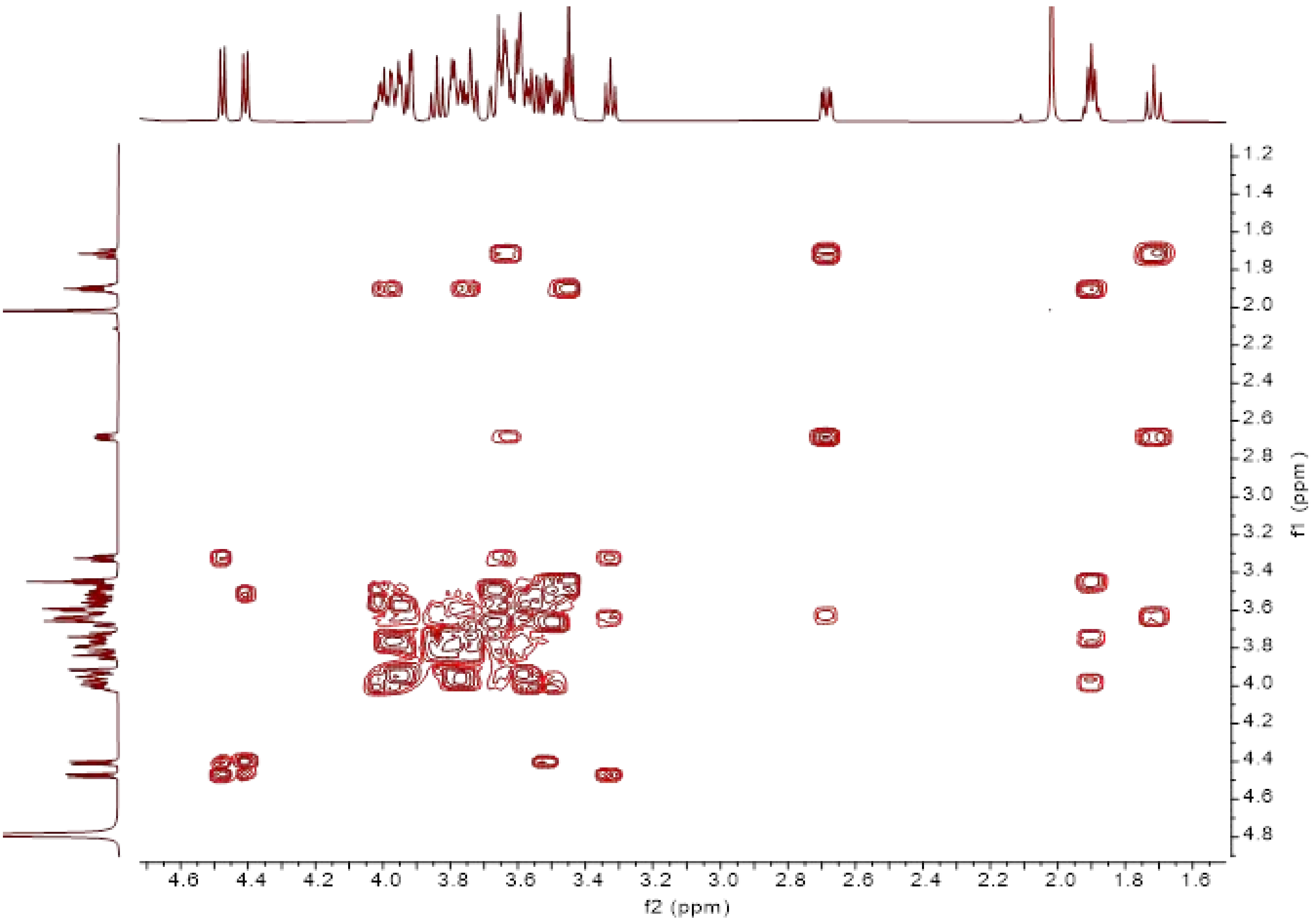

f2 (ppm)
f1 (ppm)

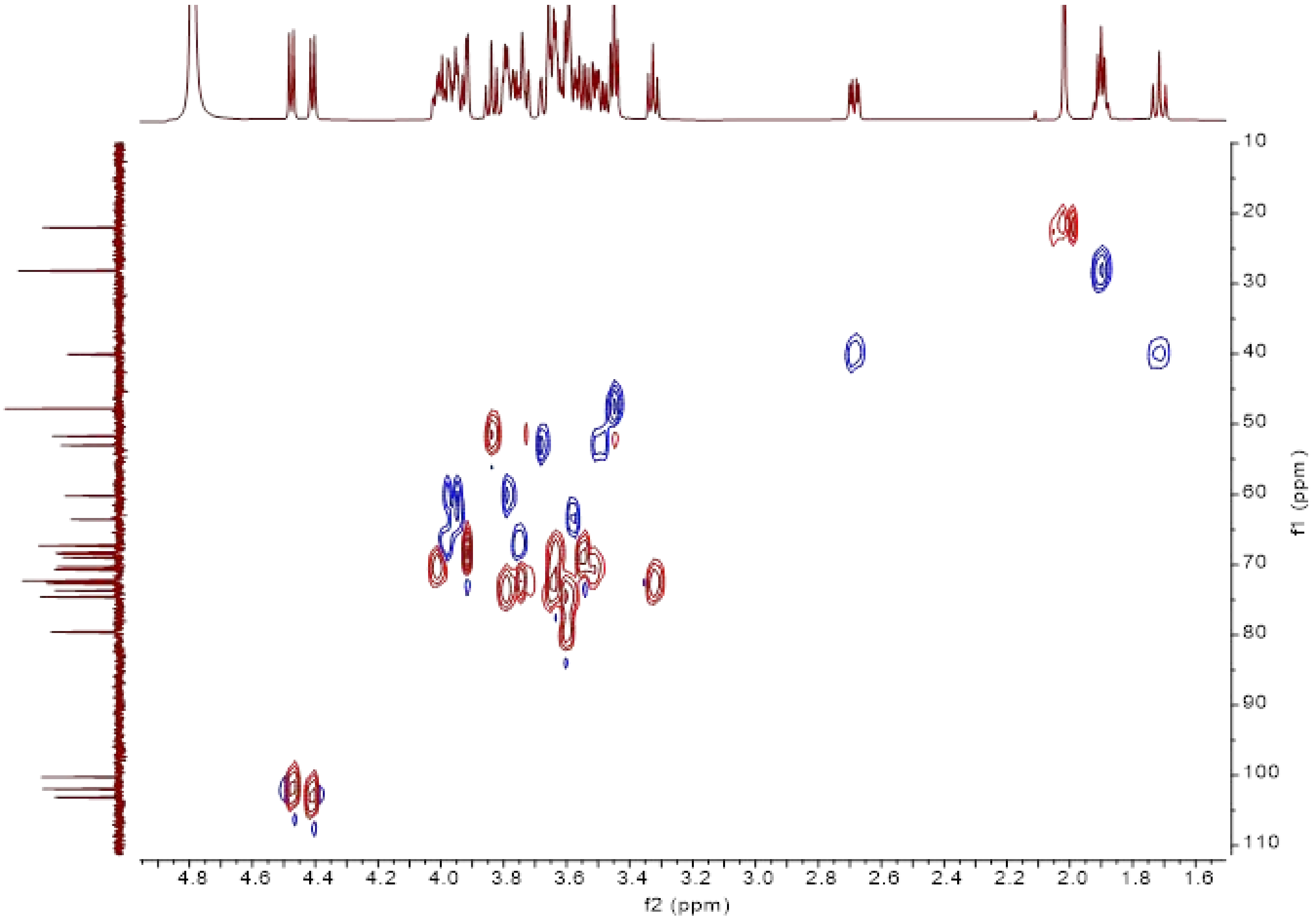

N3
OH
OH
COOH
AcNH
O
OH
OH
O
OH
HO
O
OH
O
HO
O
OH
O
N3

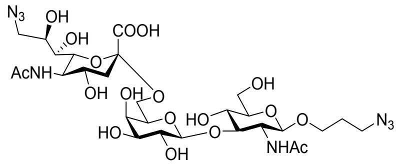
71


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)

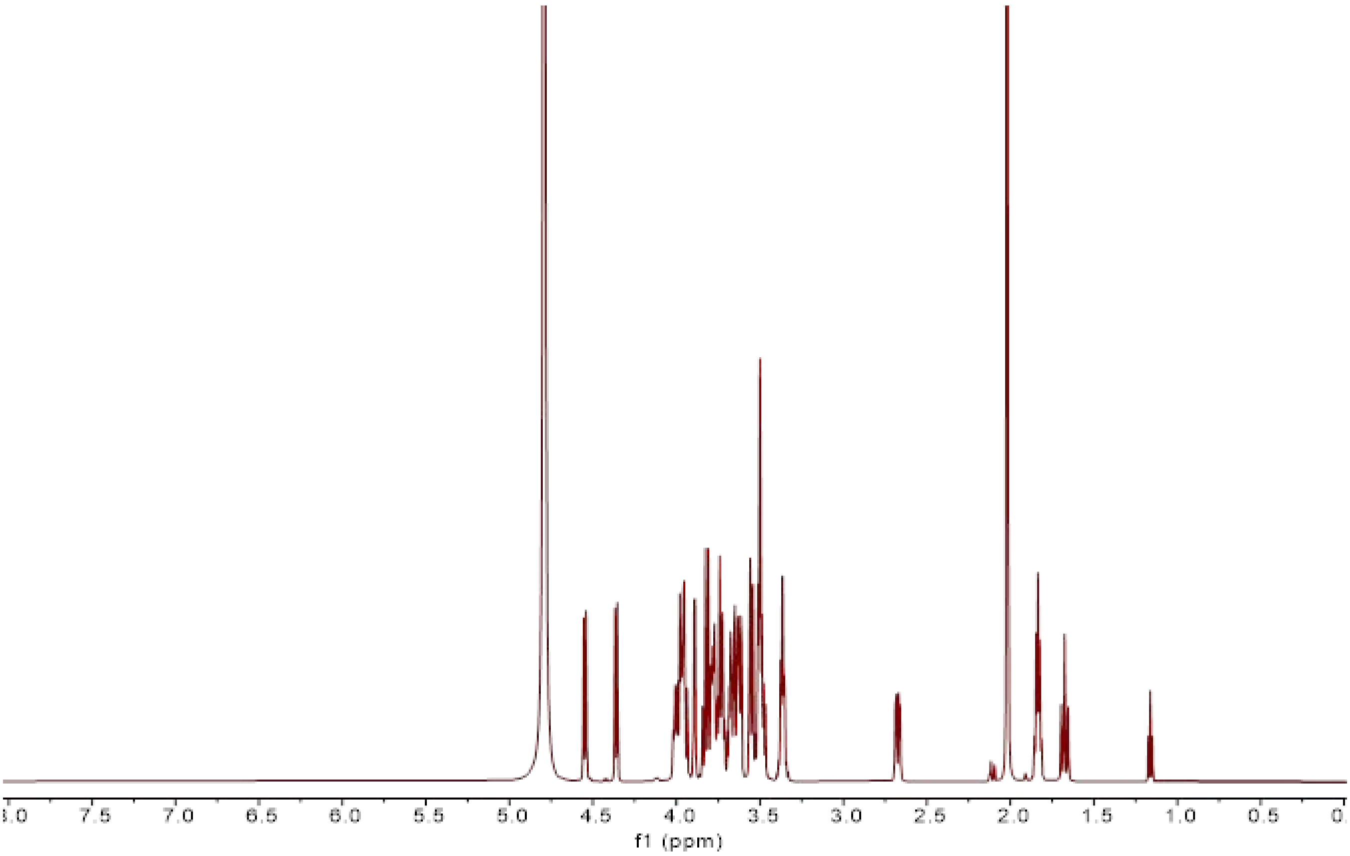

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

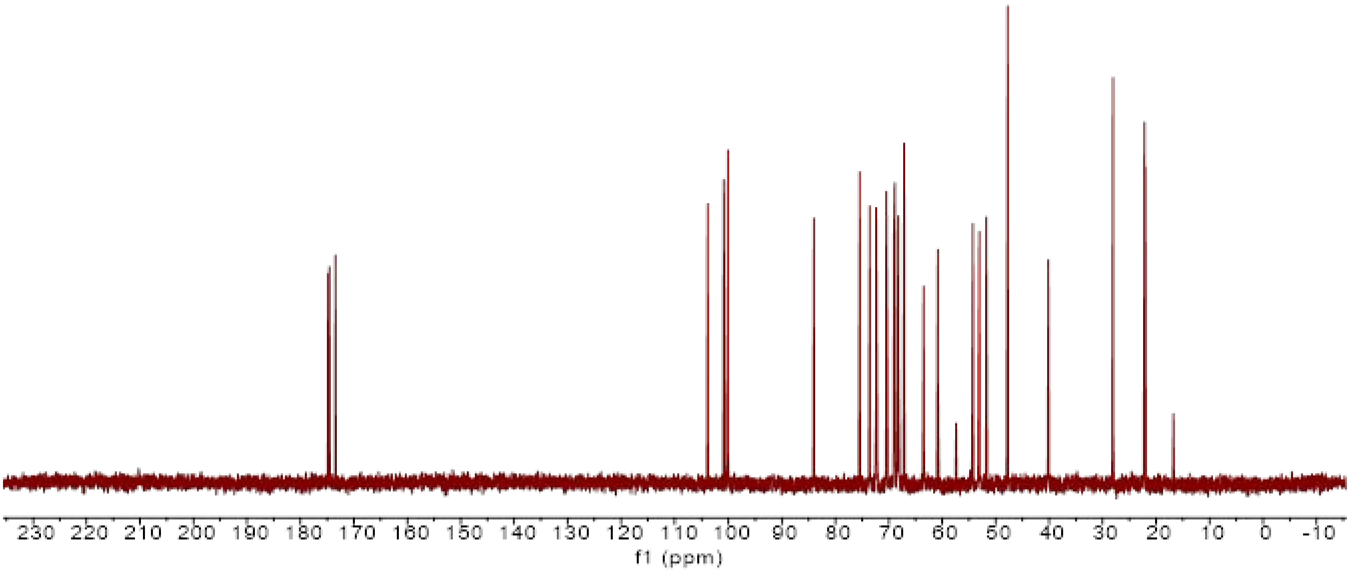

4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

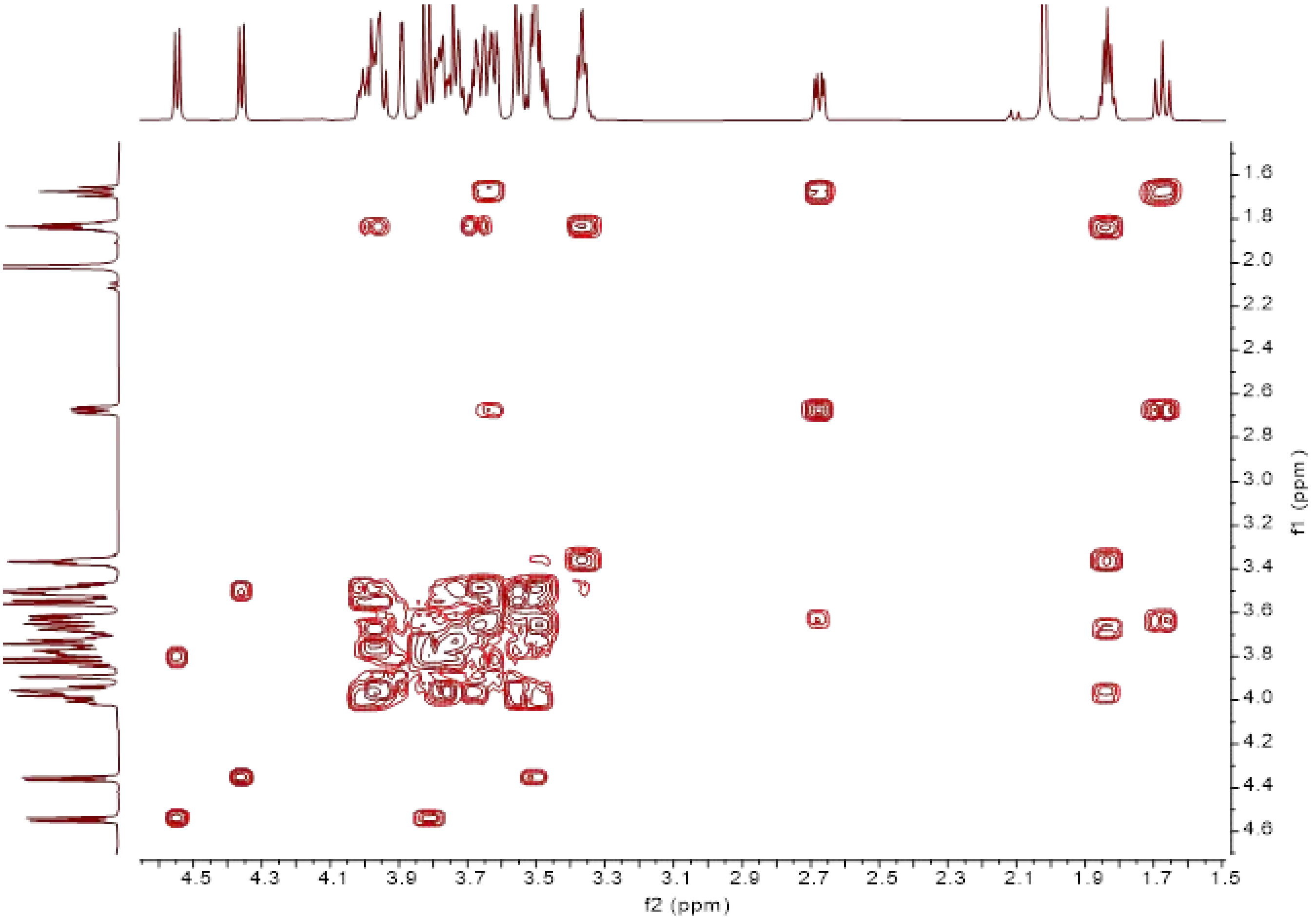

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

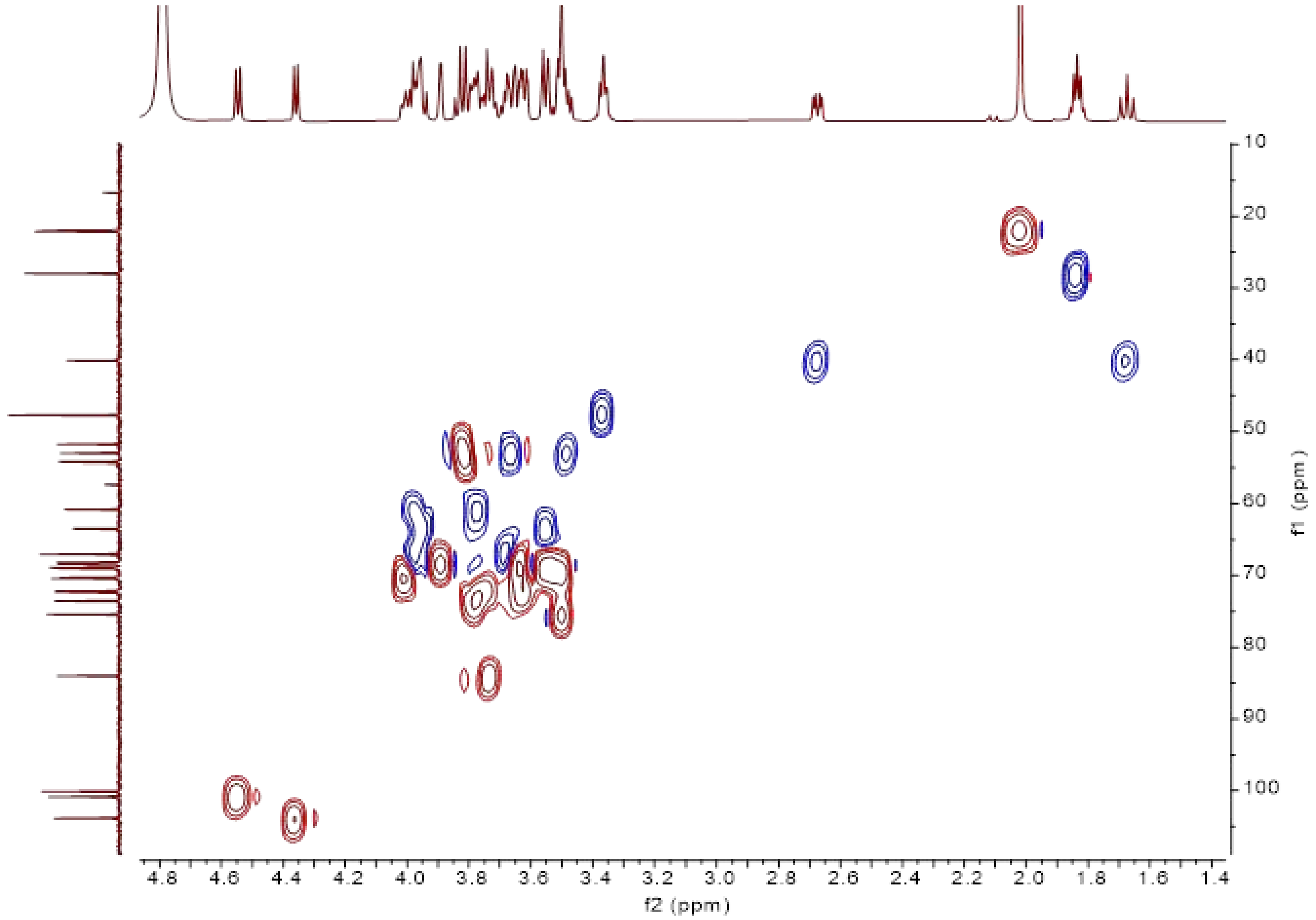

N3
OH
OH
COOH
AcNH
O
OH
OH
O
OH
O
HO
HO
O
OH
O
NHAc
O
N3
OH

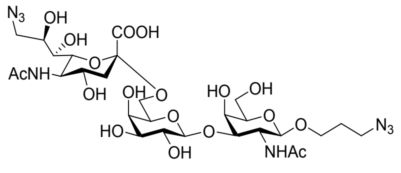
73


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

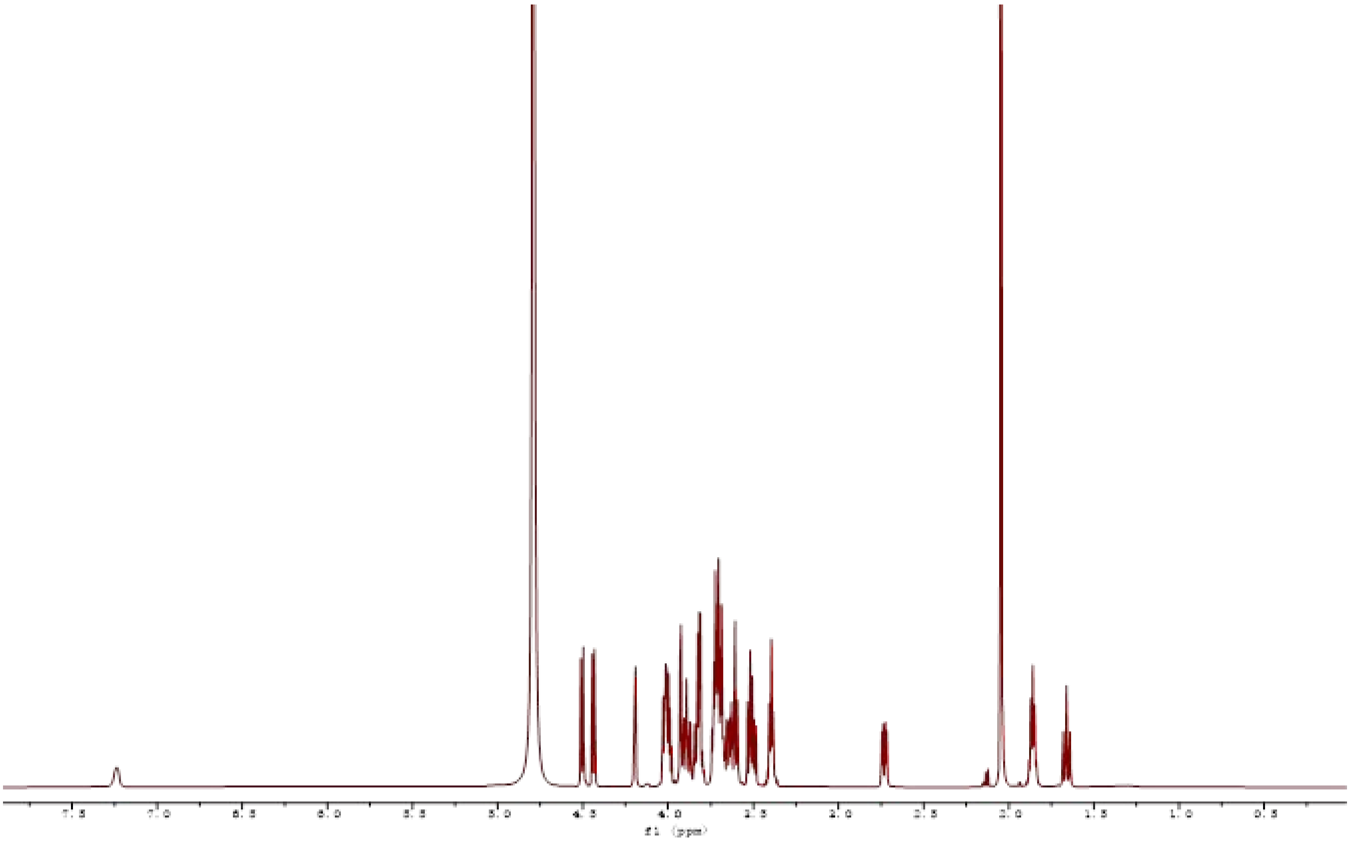

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

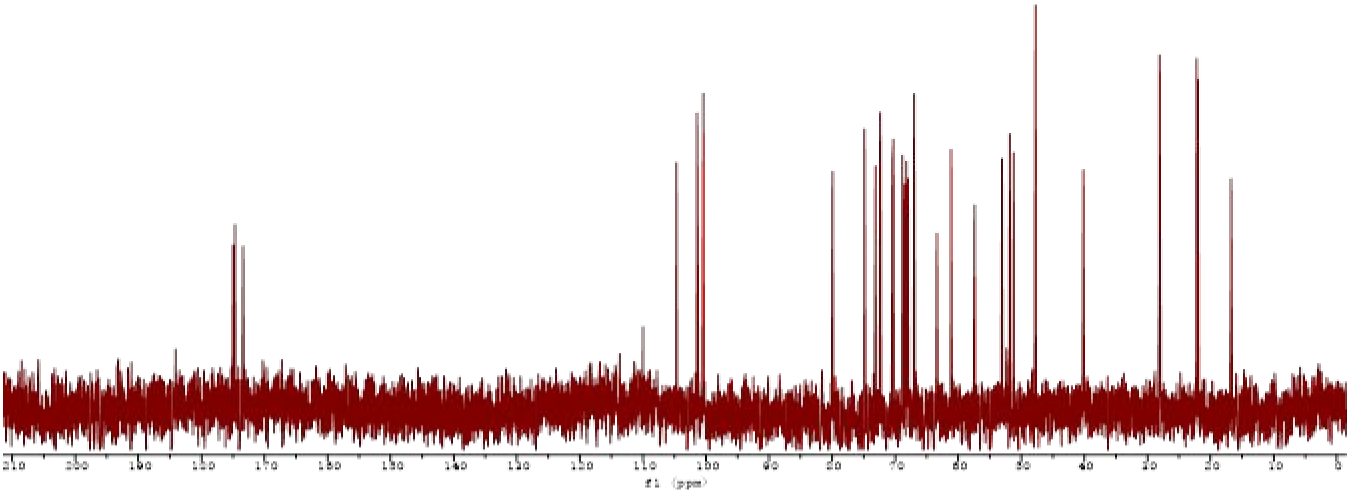

1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
f1 (ppm)
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
f2 (ppm)

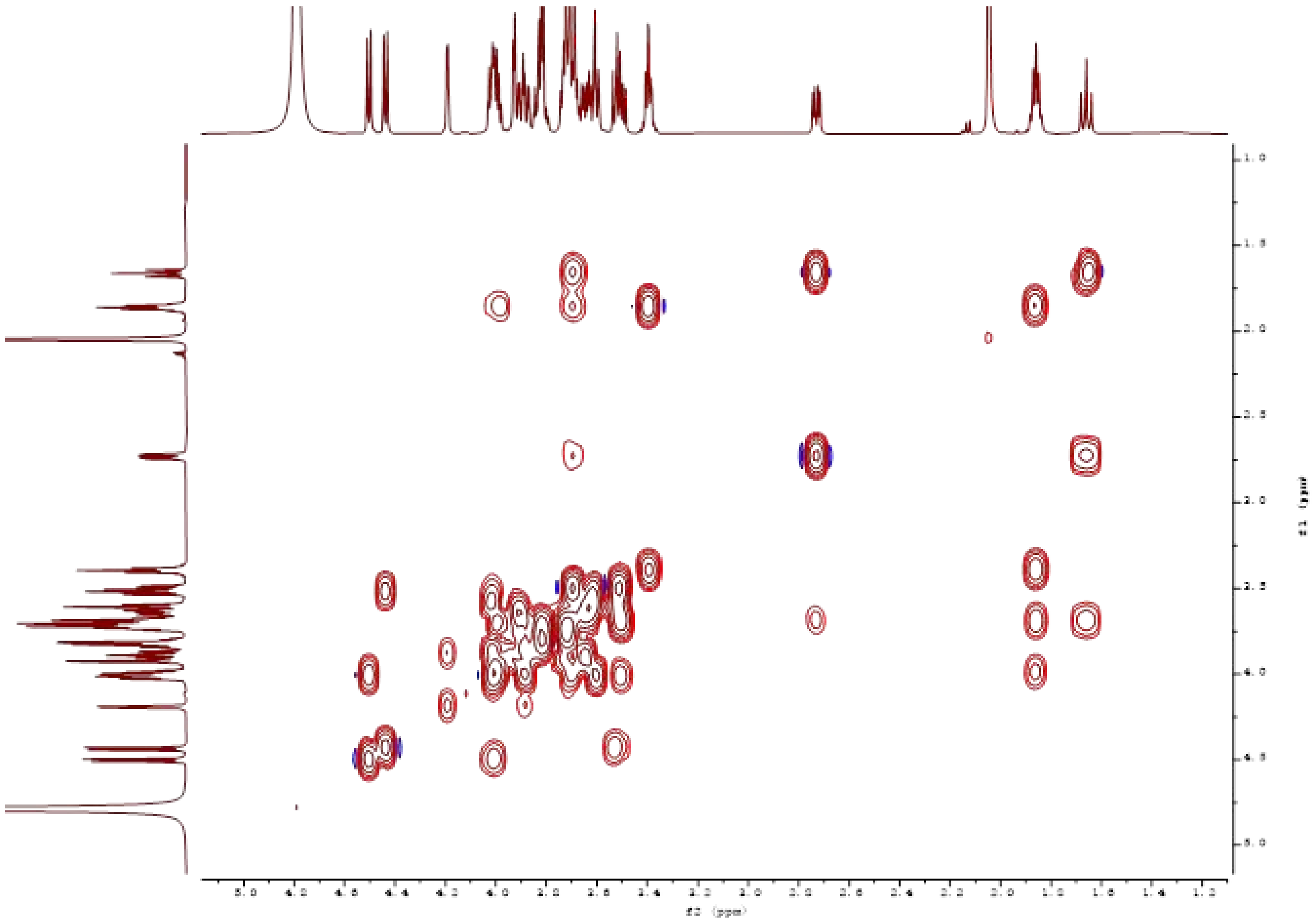

10
20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

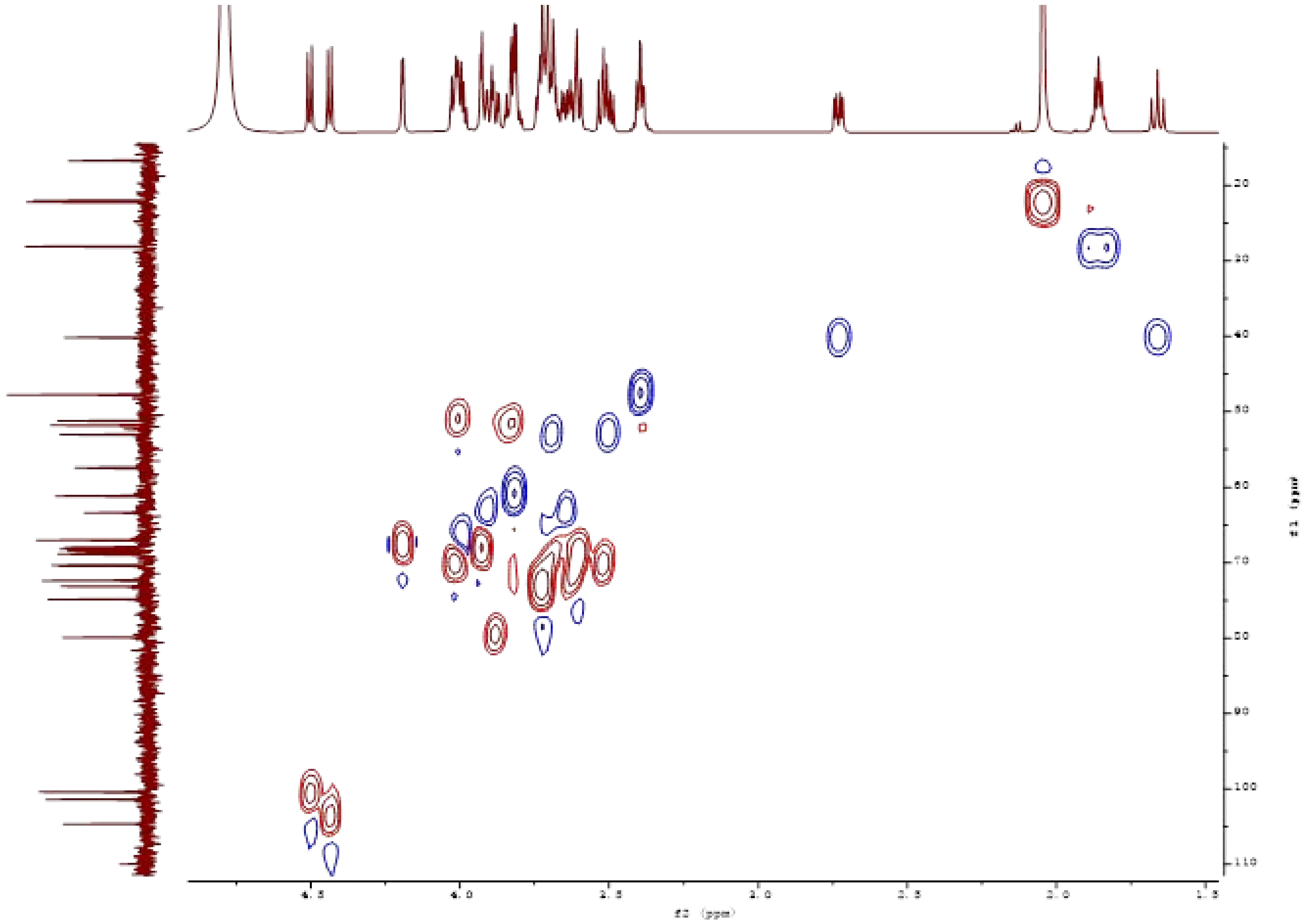

N3
OH
OH
COOH
AcNH
O
OH
OH
O
HO
OH
O
HO
O
O
OH
O
N3
NHAc

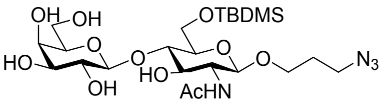
75


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

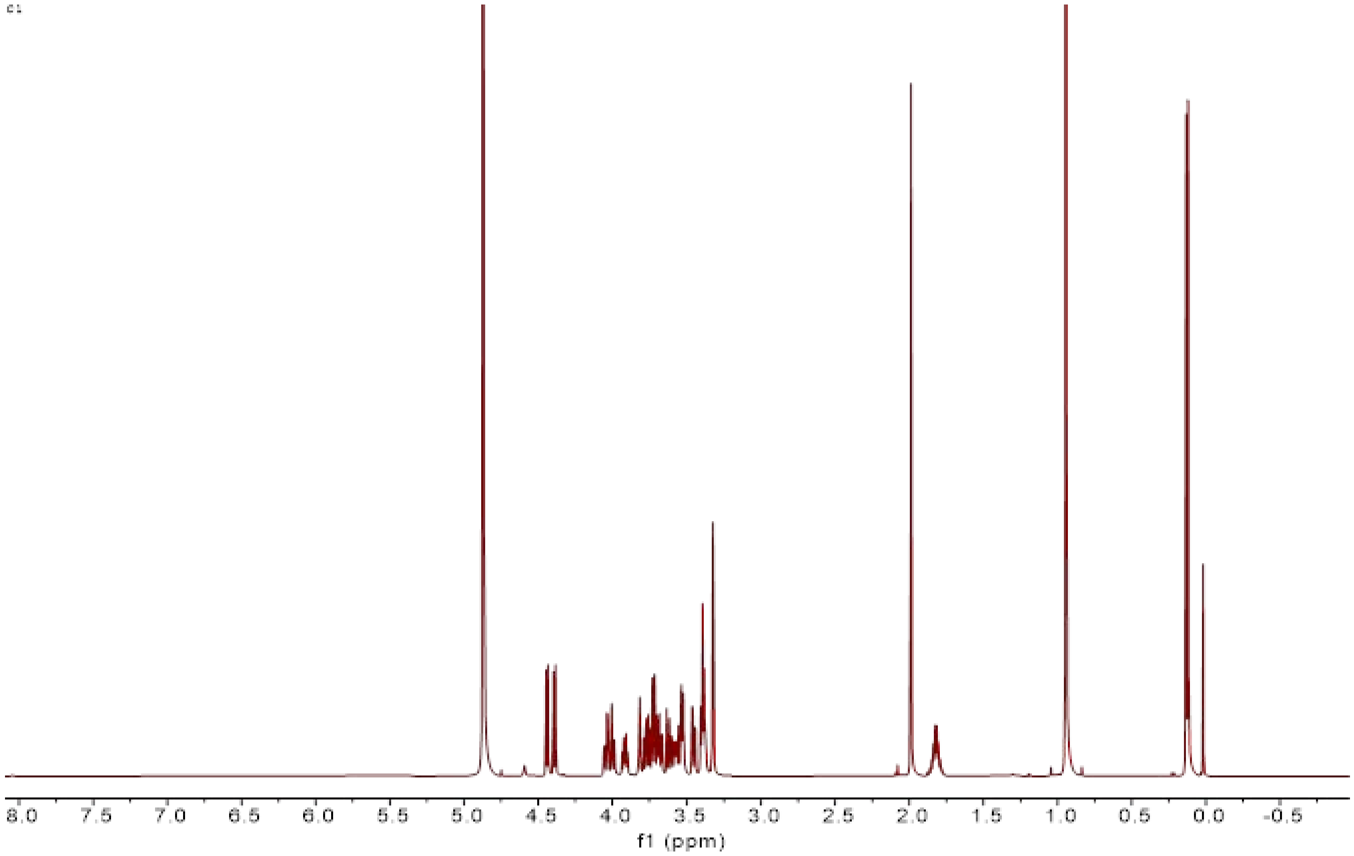

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

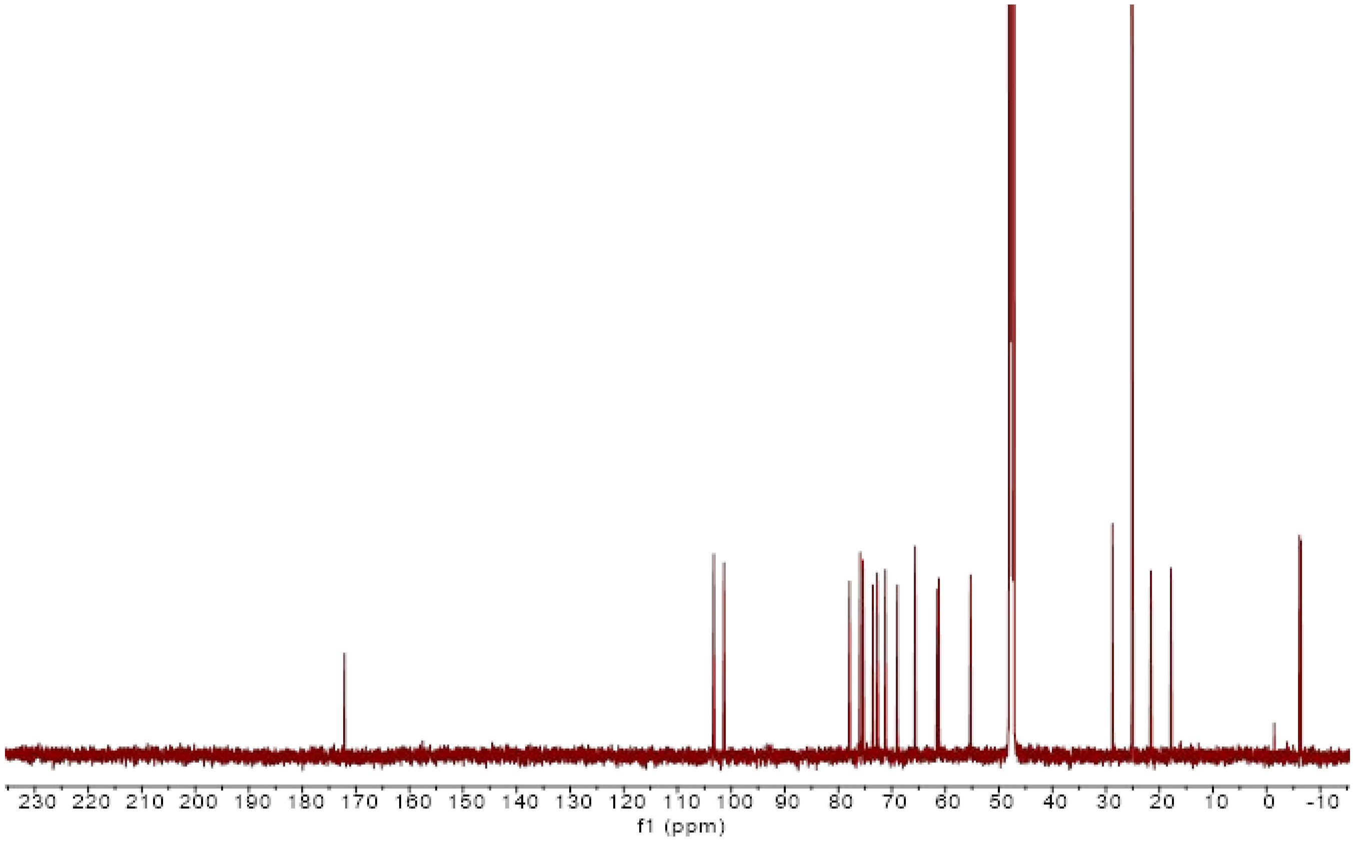

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

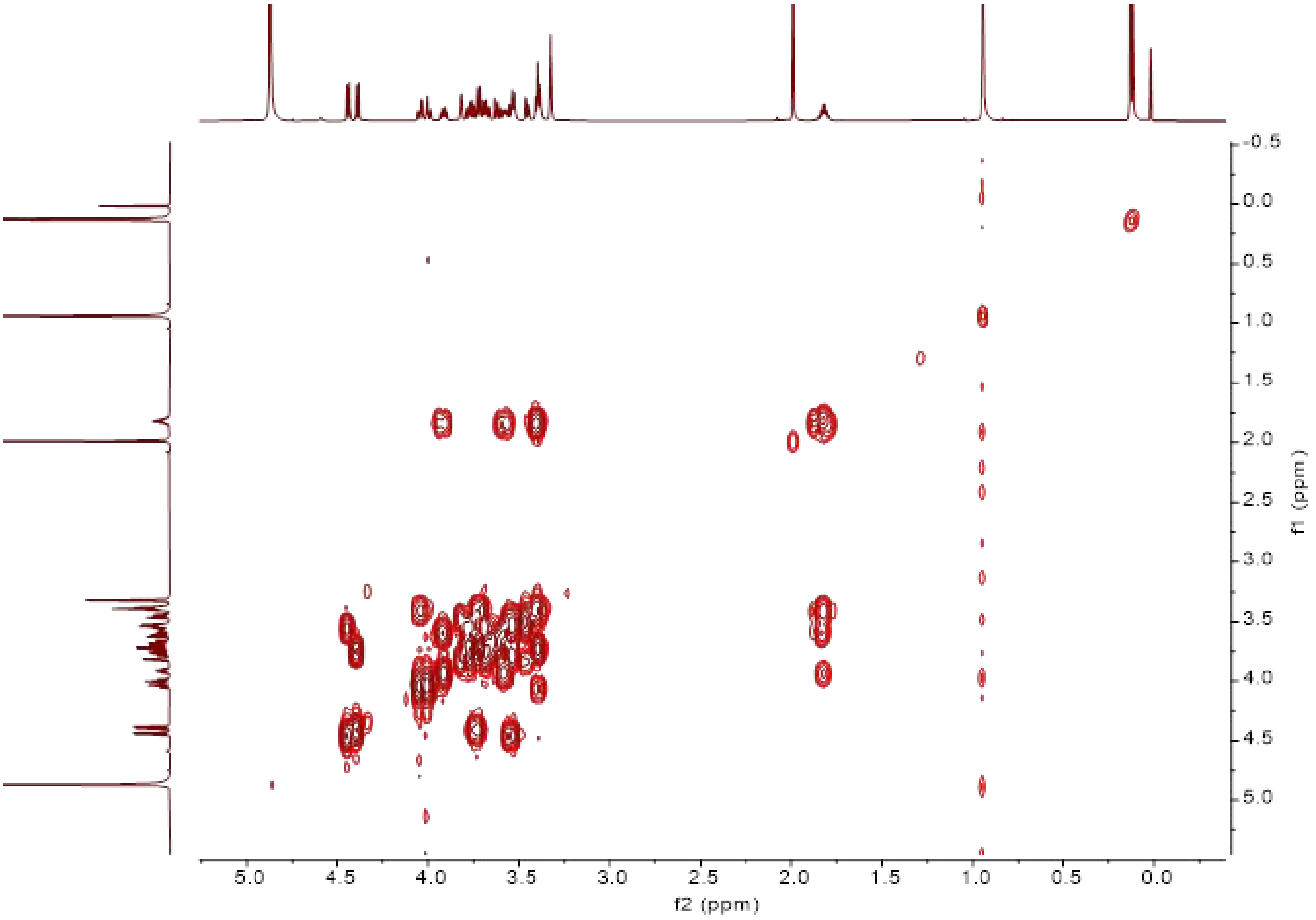

4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

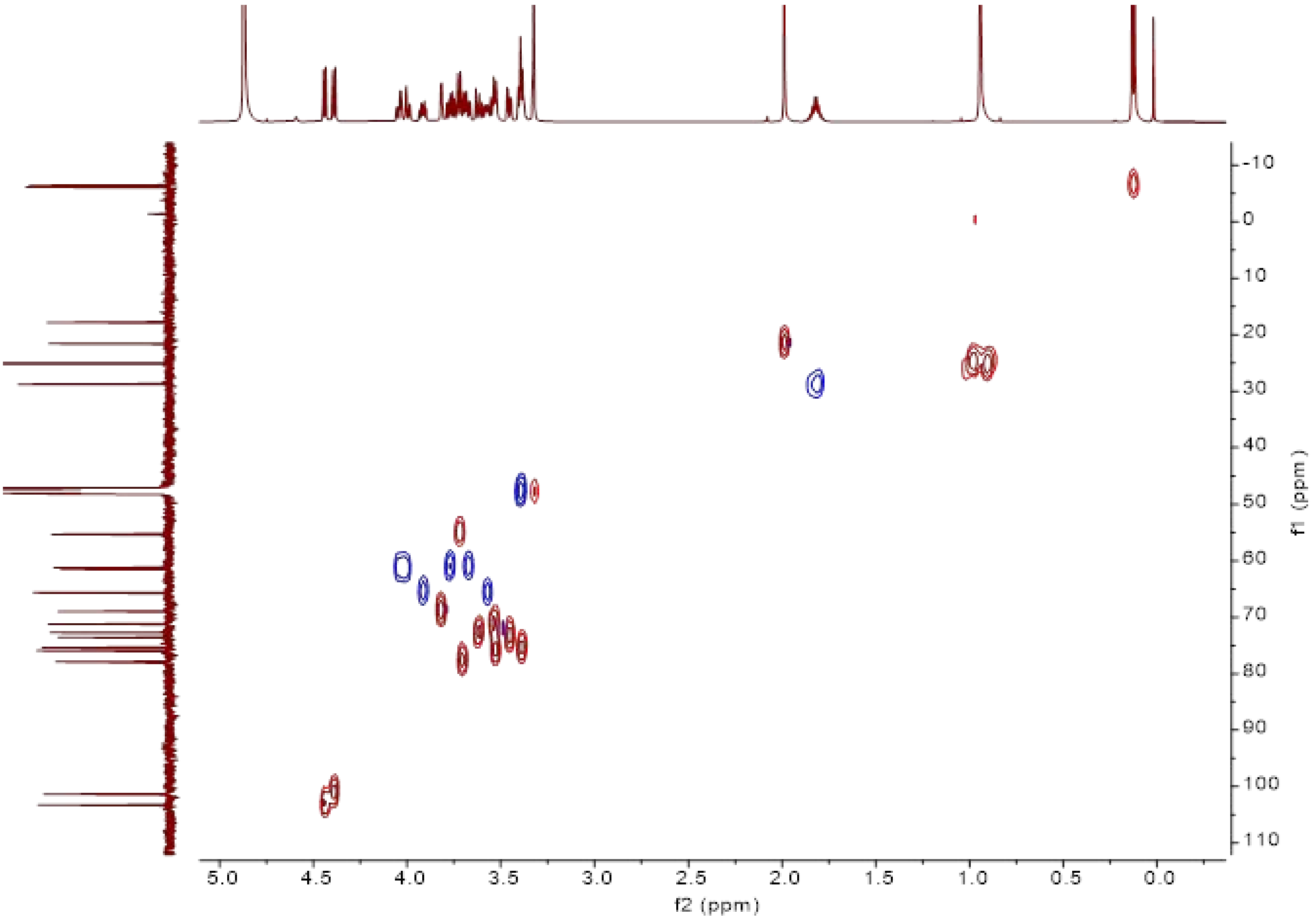

OH
OH
OTBDMS
O
O
HO
O
O
N3
OH
HO
AcHN

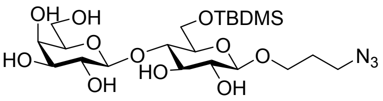
78


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


230
220
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)

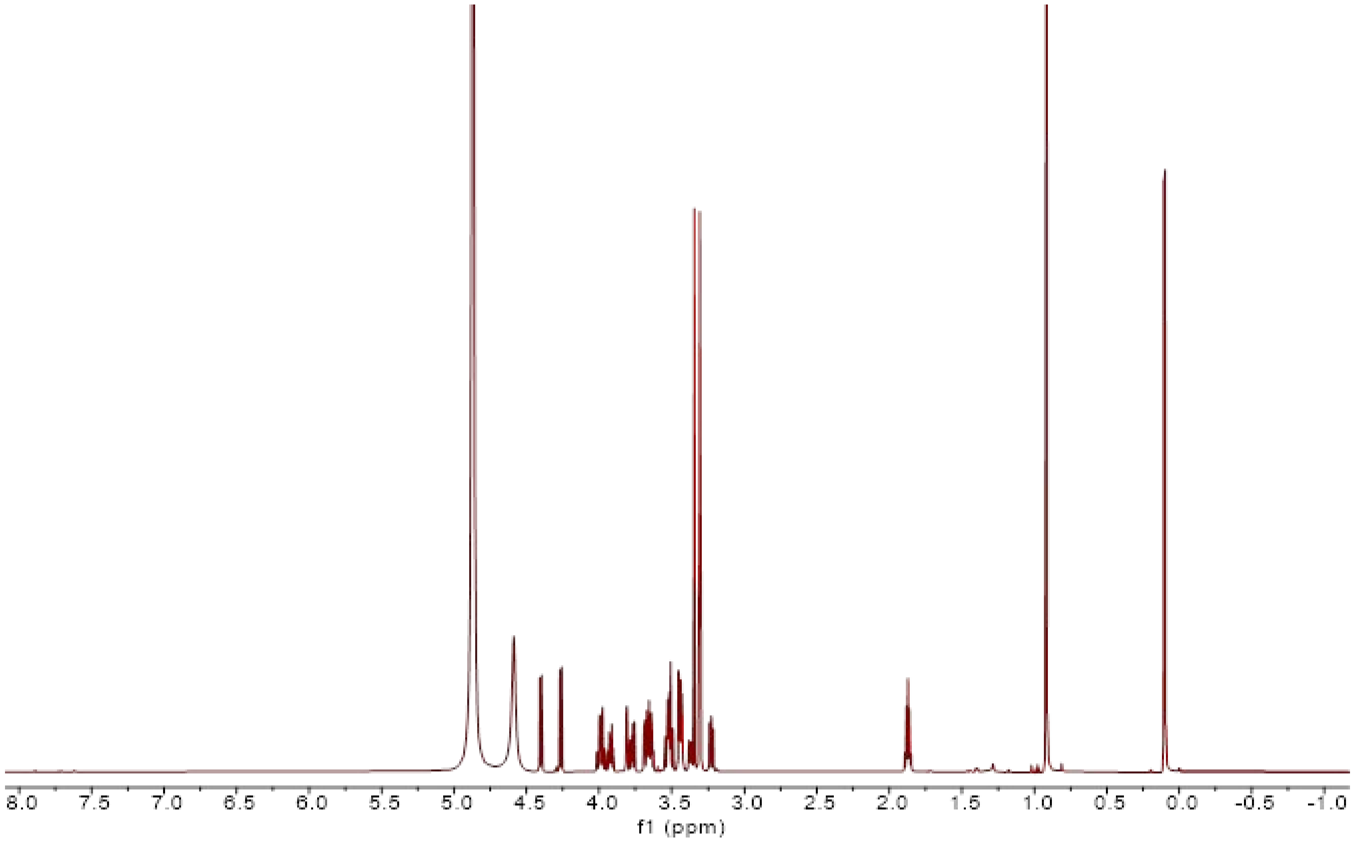

f2 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0


f2 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110

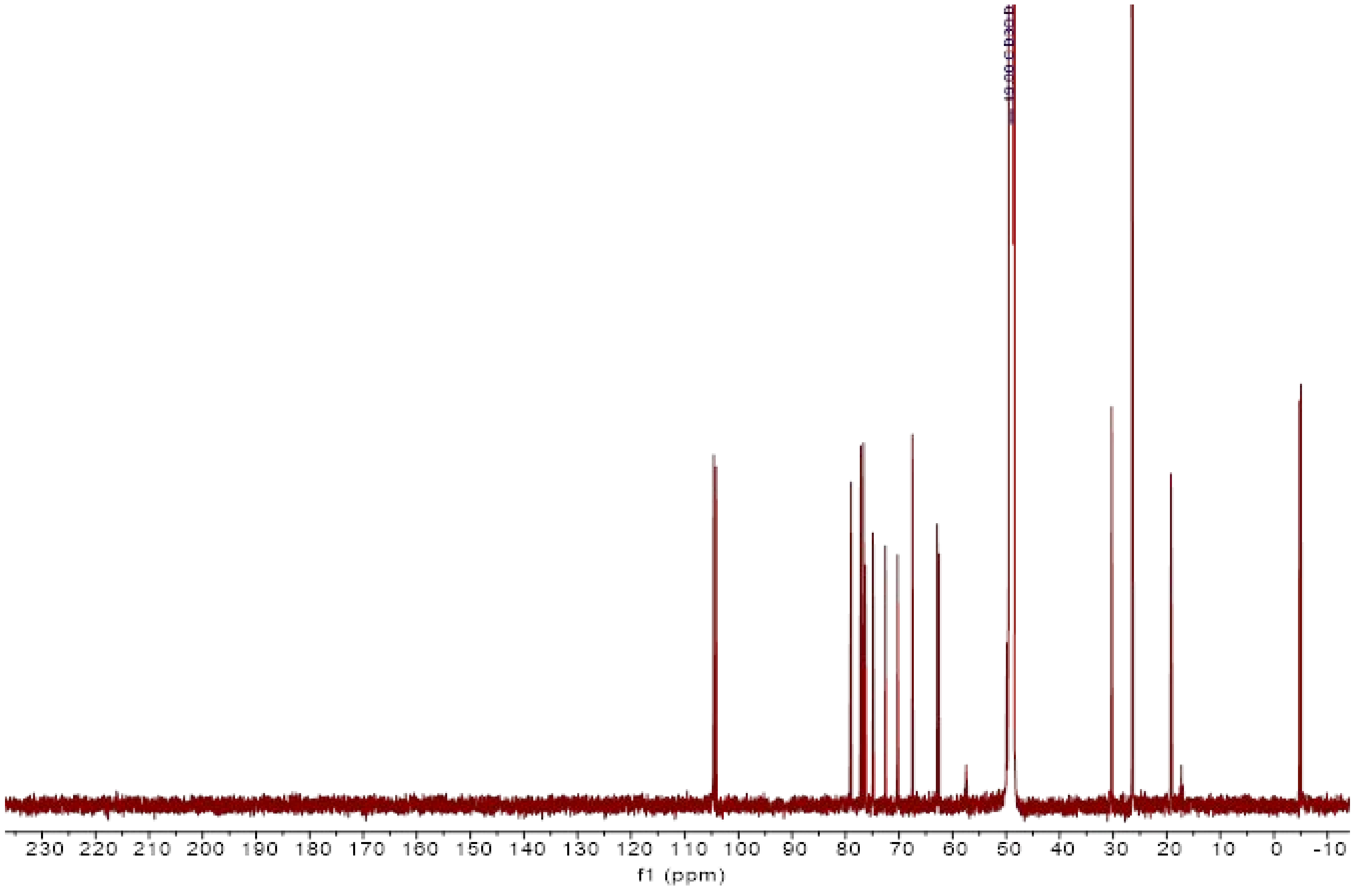


OH
OH
OTBDMS
O
O
HO
O
HO
OH
O
OH
N3

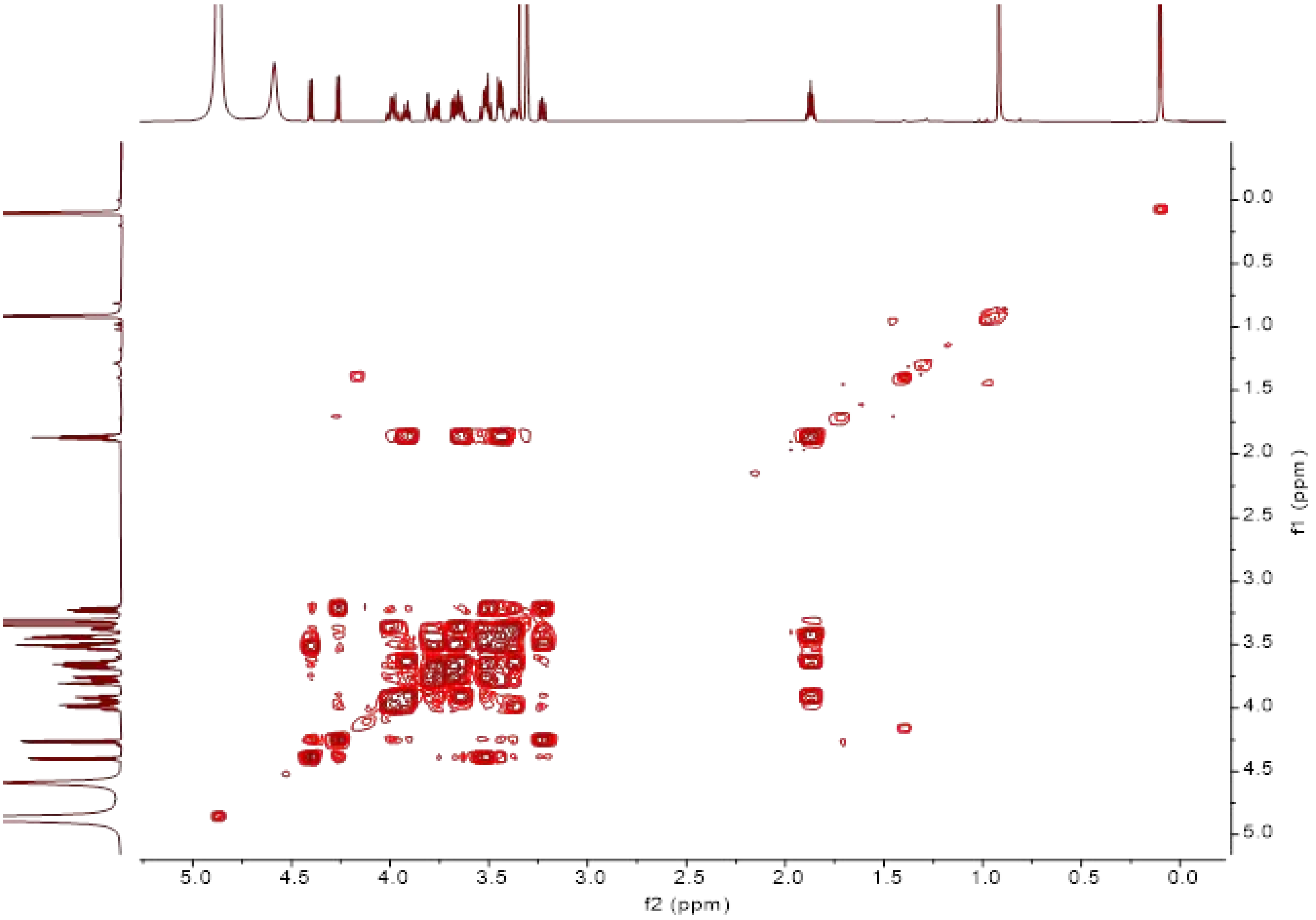
80



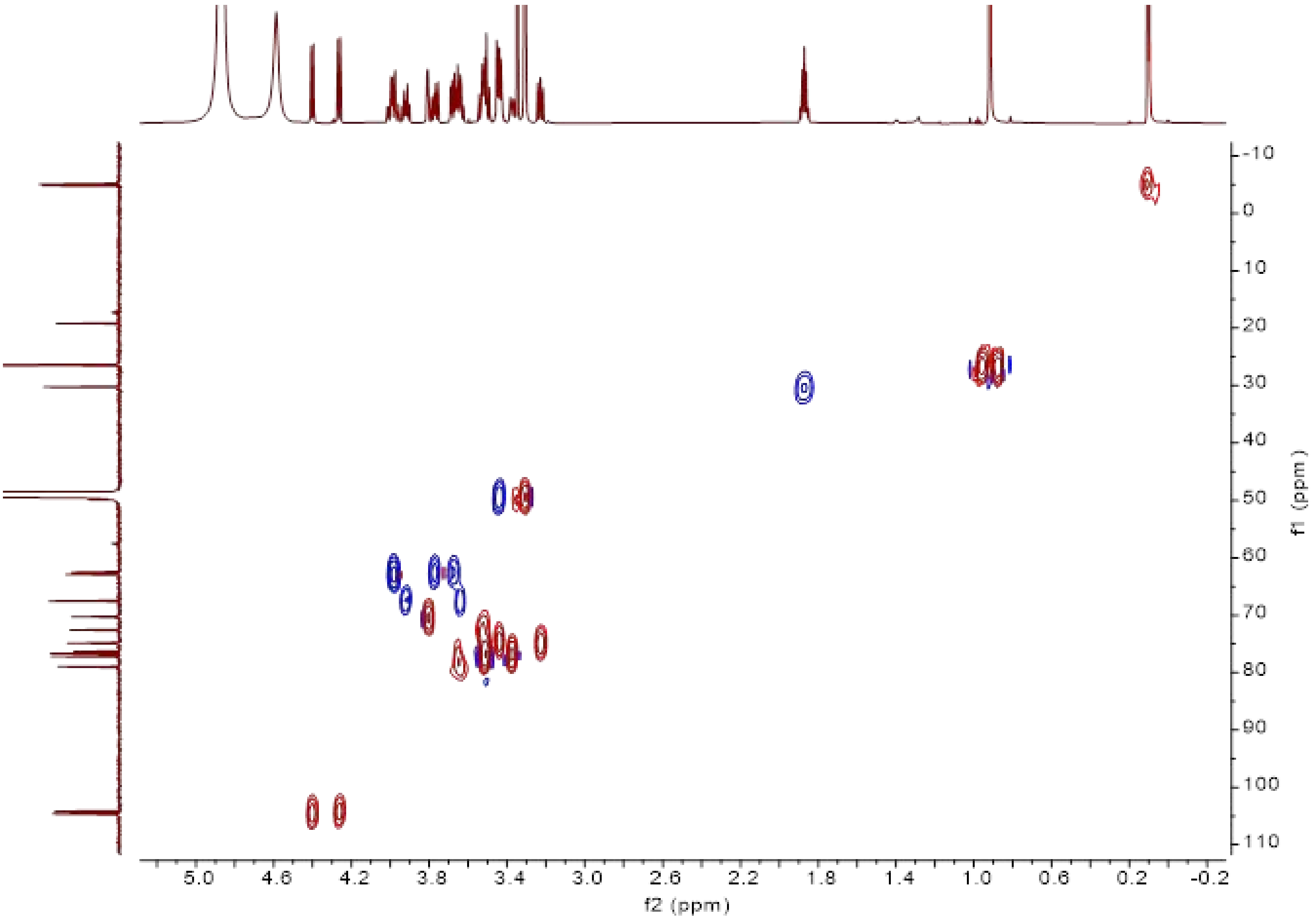
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



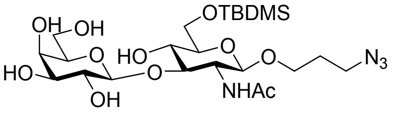
49.00 CD3OD
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



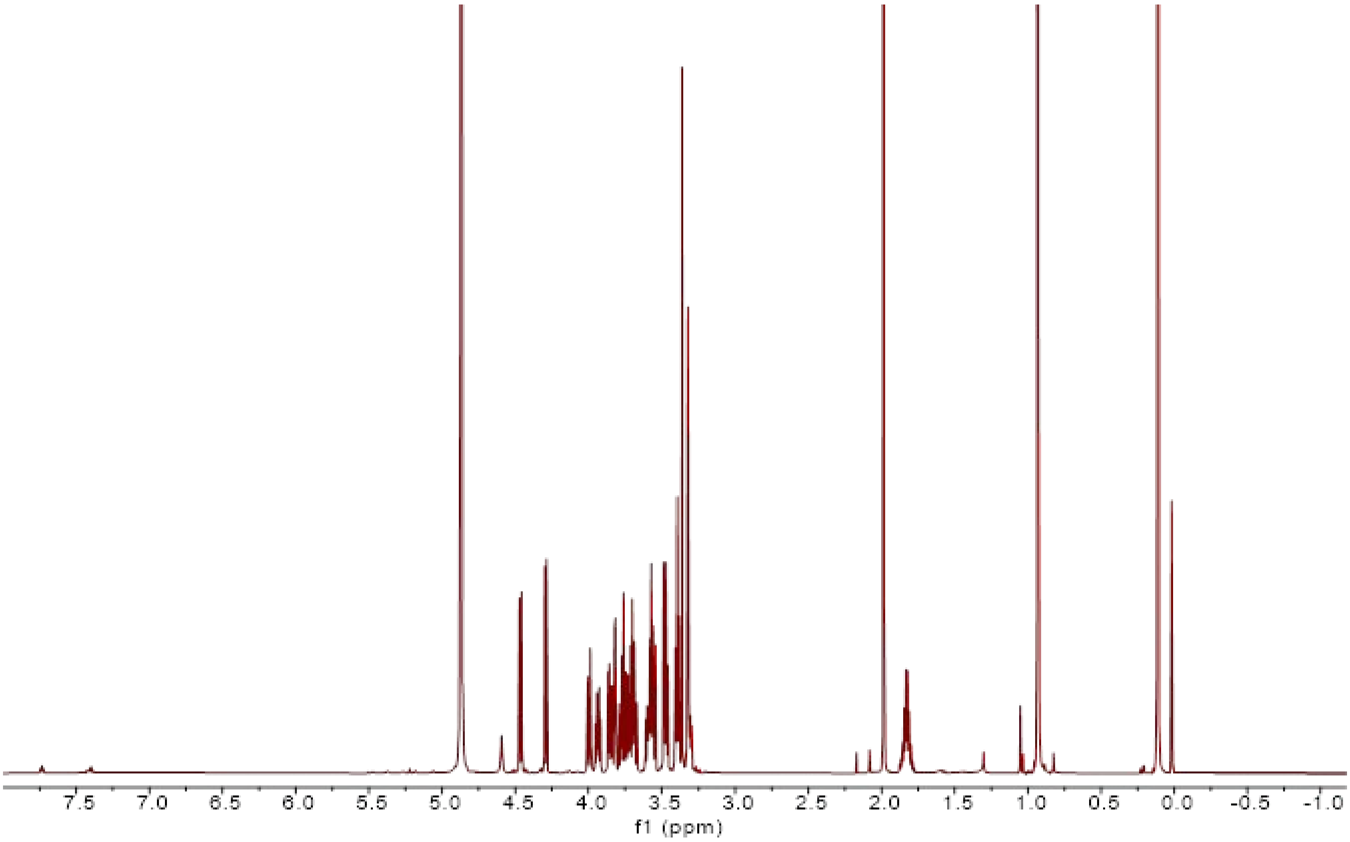
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

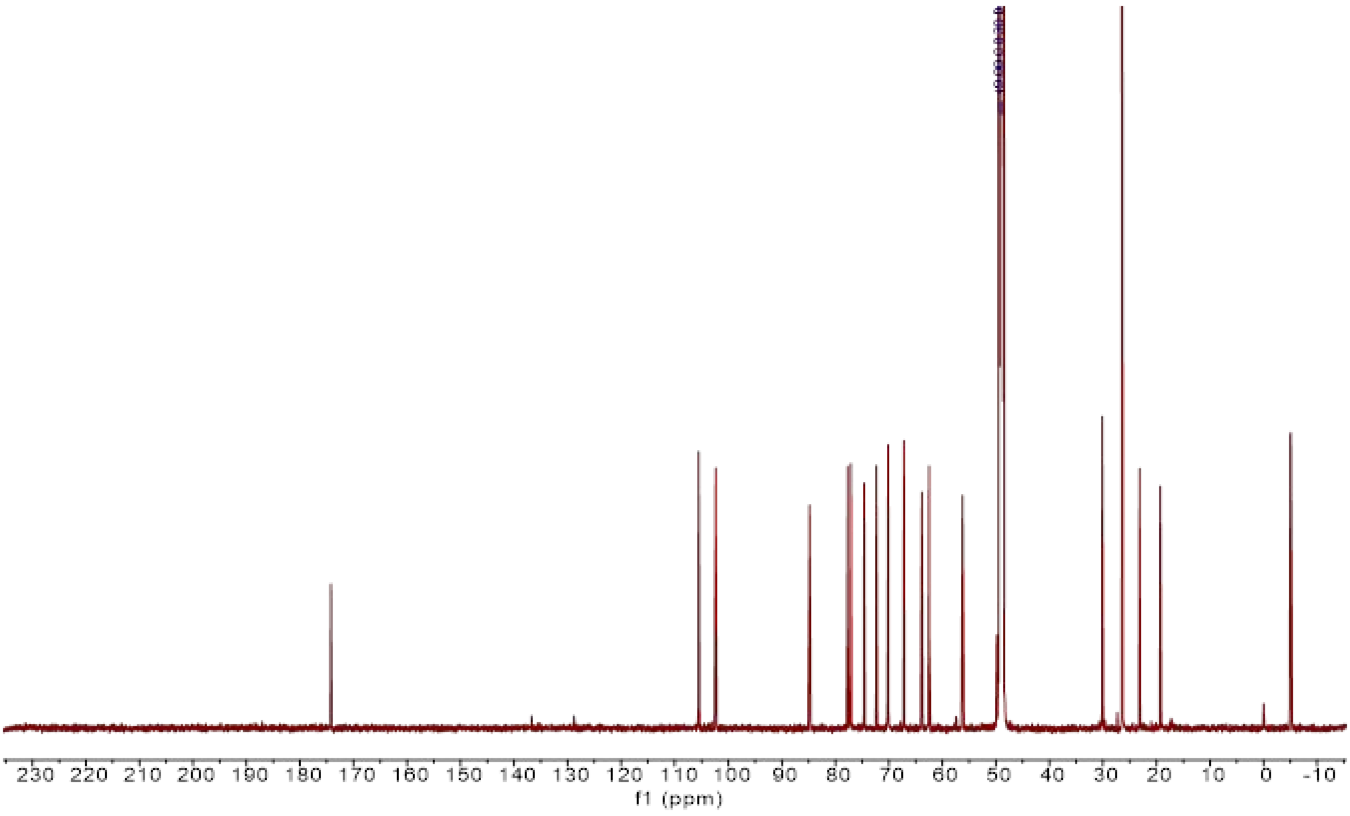


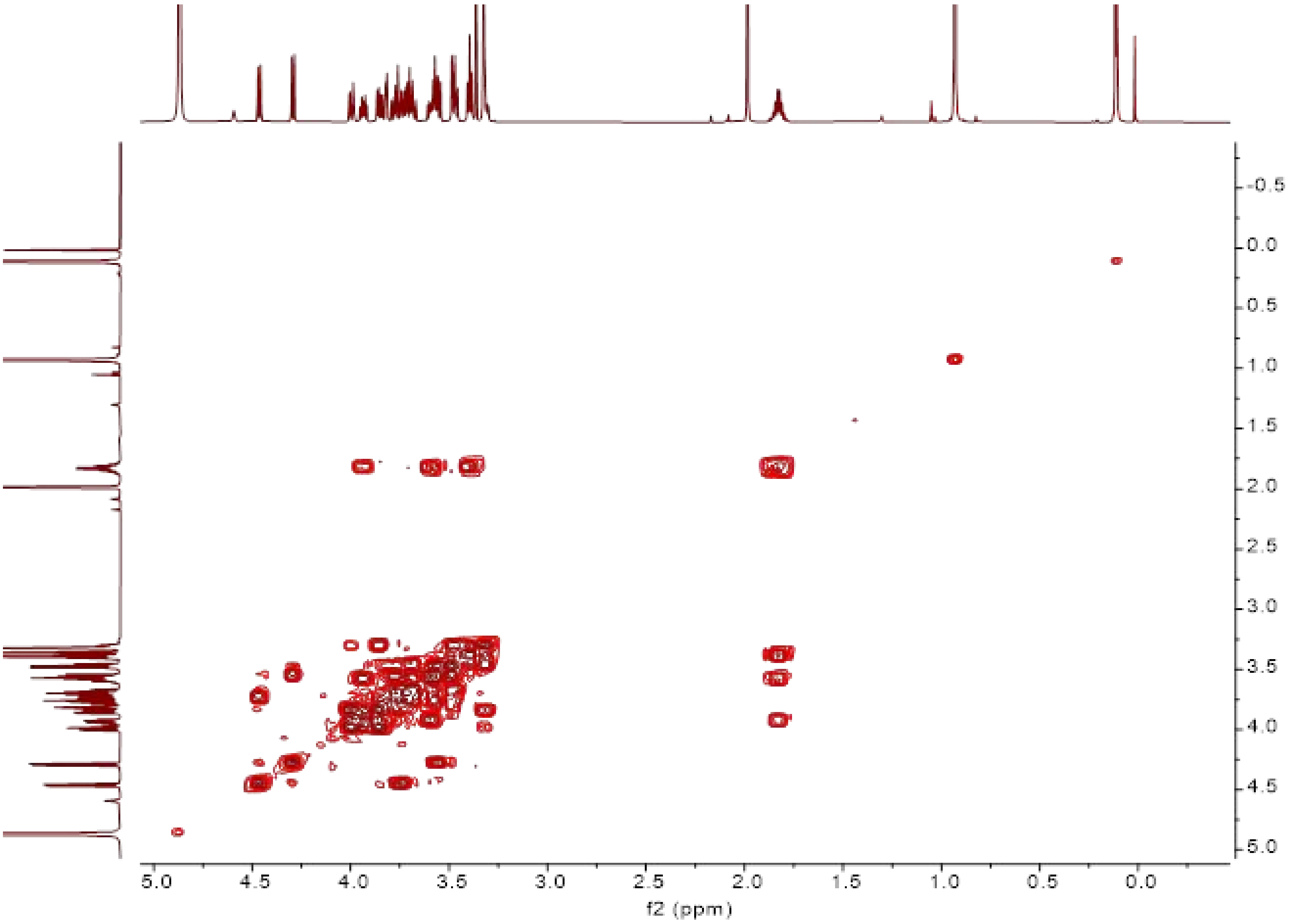
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

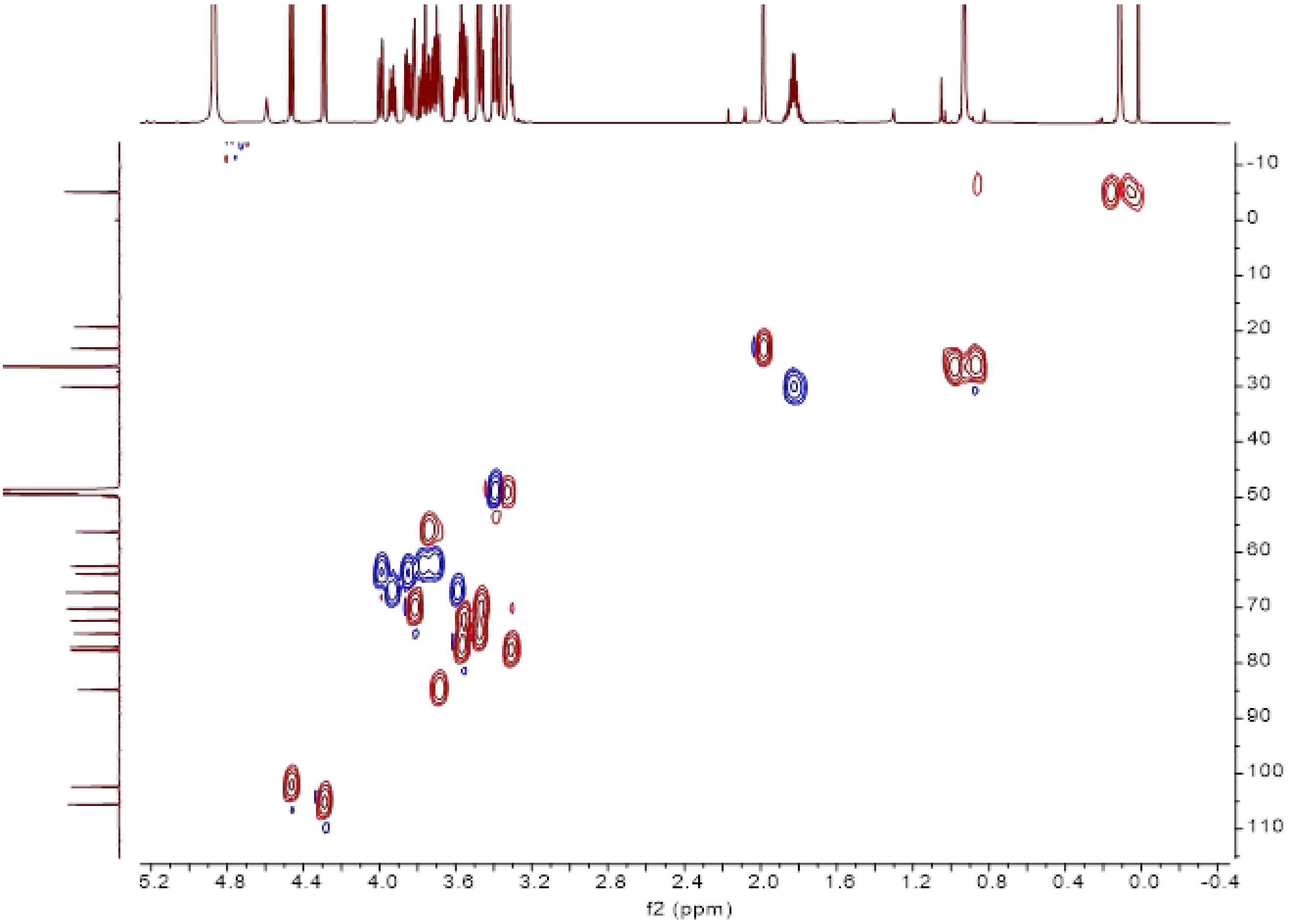

OH
OH
OTBDMS
O
HO
O
O
HO
N3
O
OH
NHAc

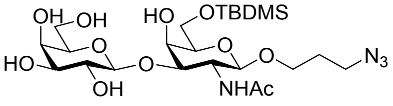
82


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

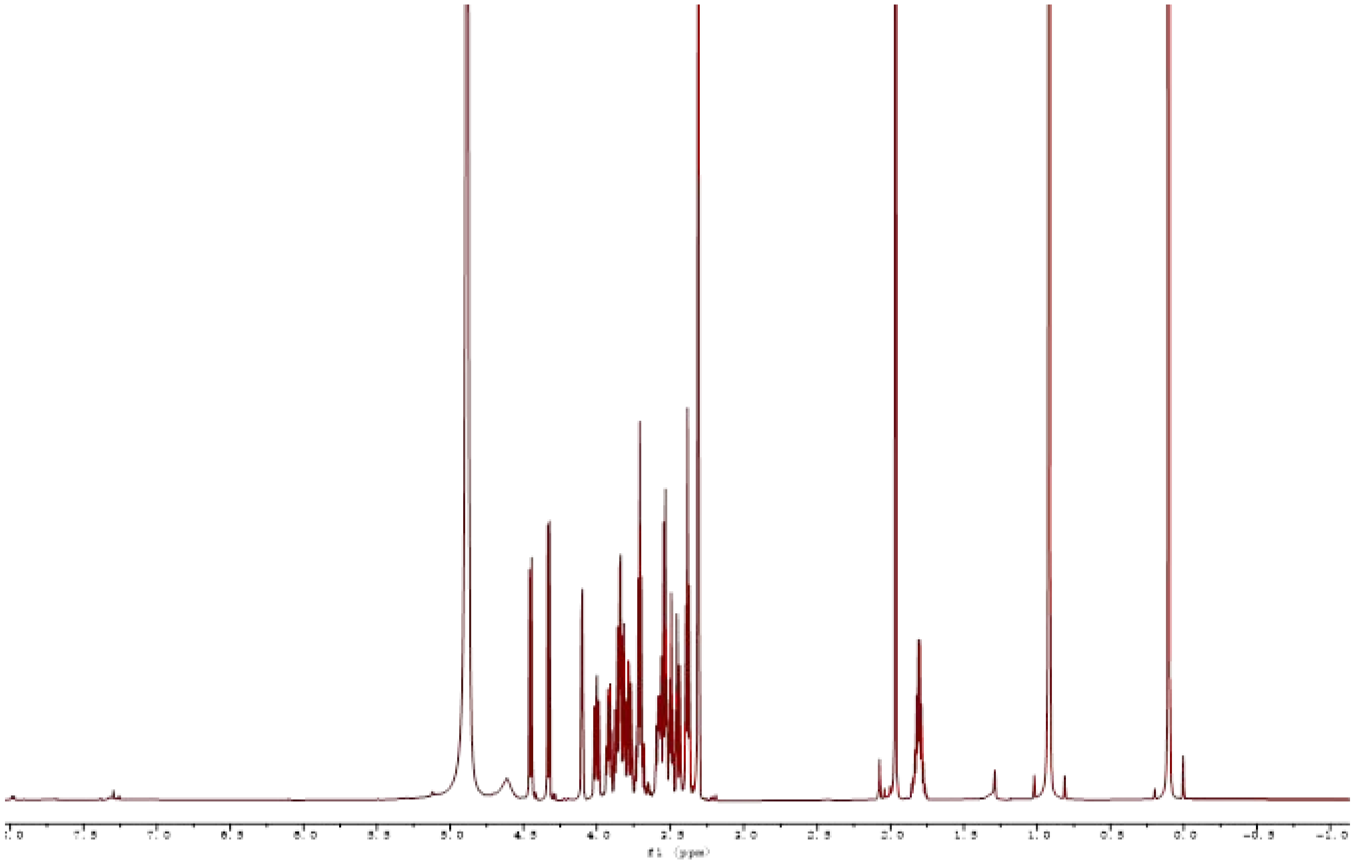

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

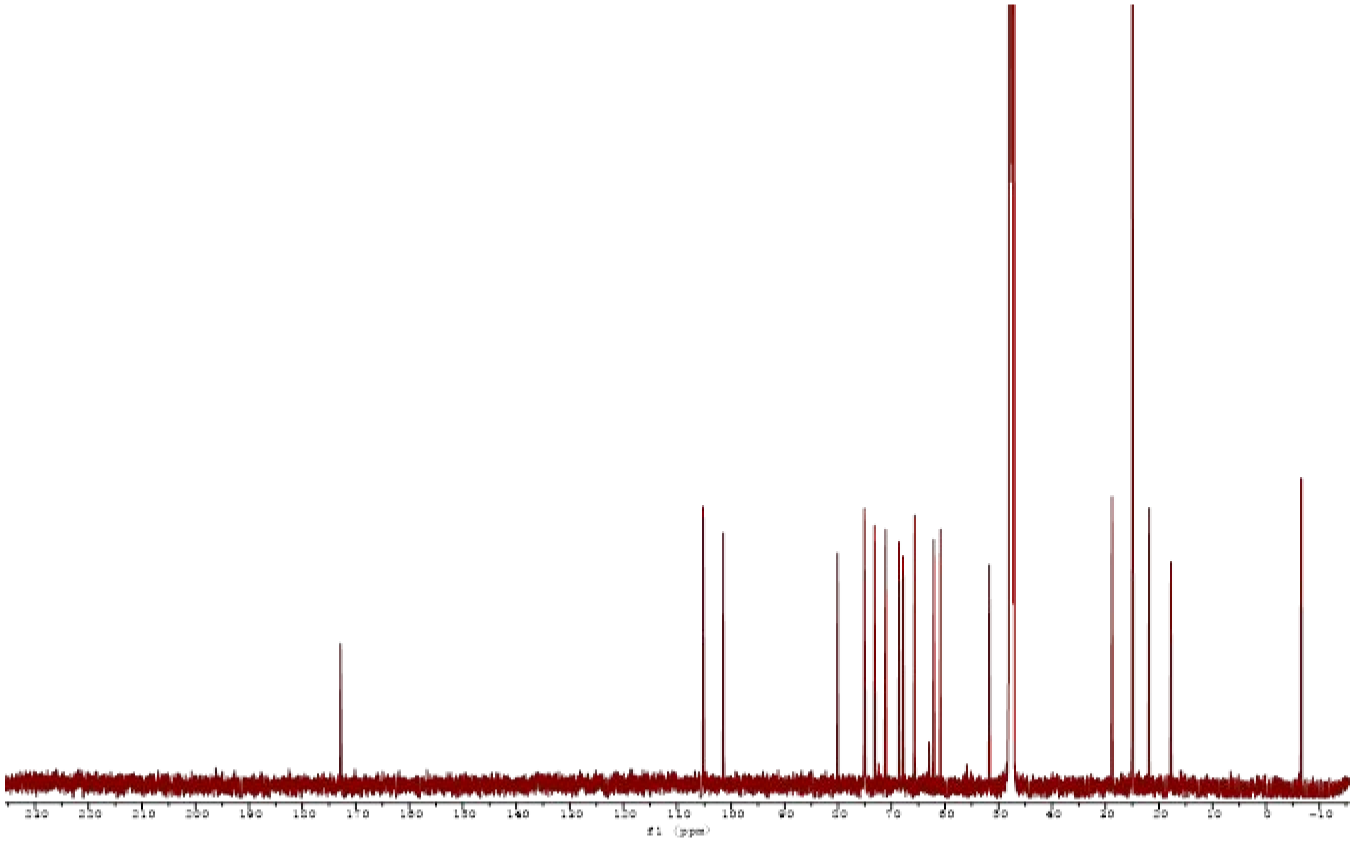

-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

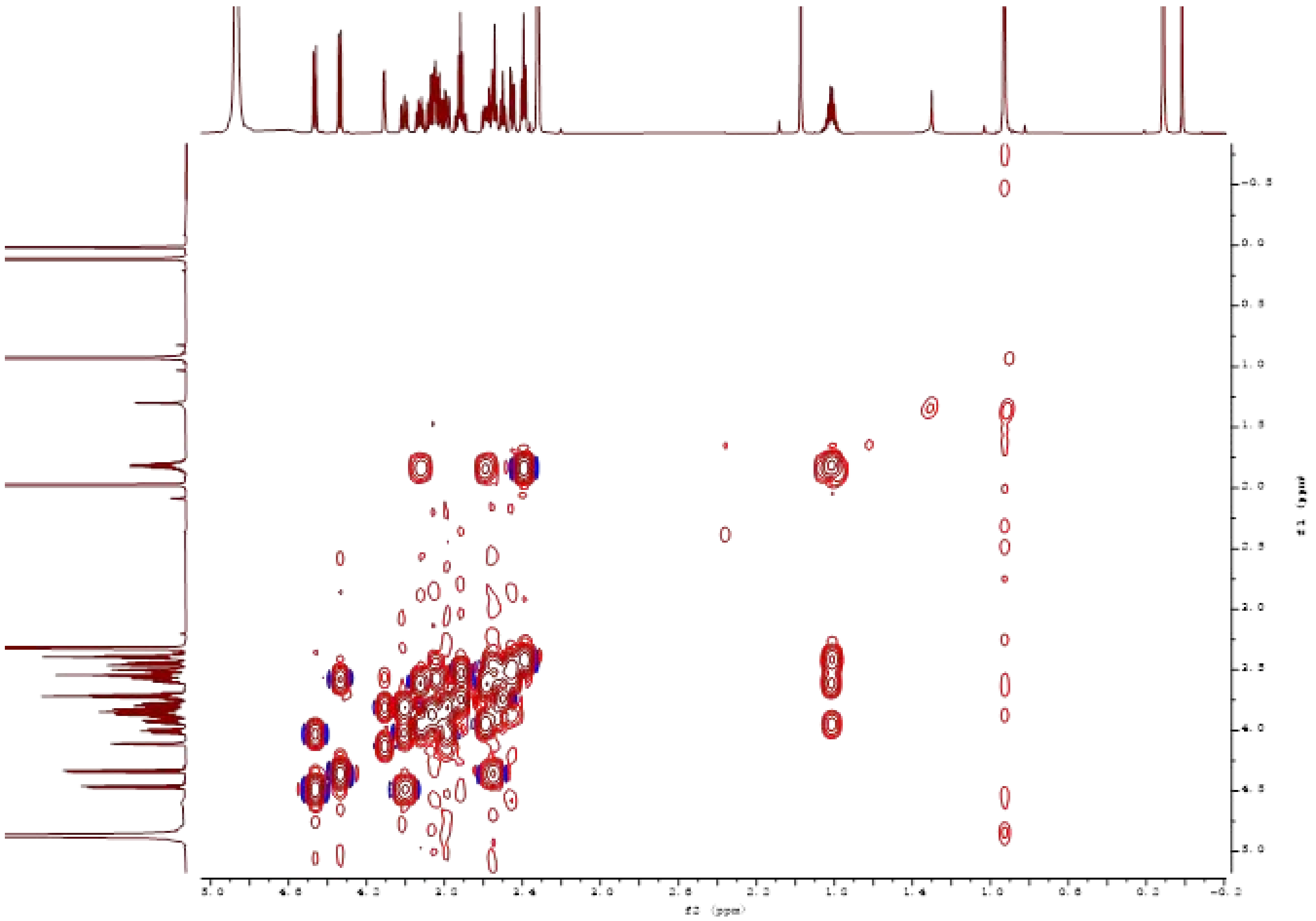

-10
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
f2 (ppm)

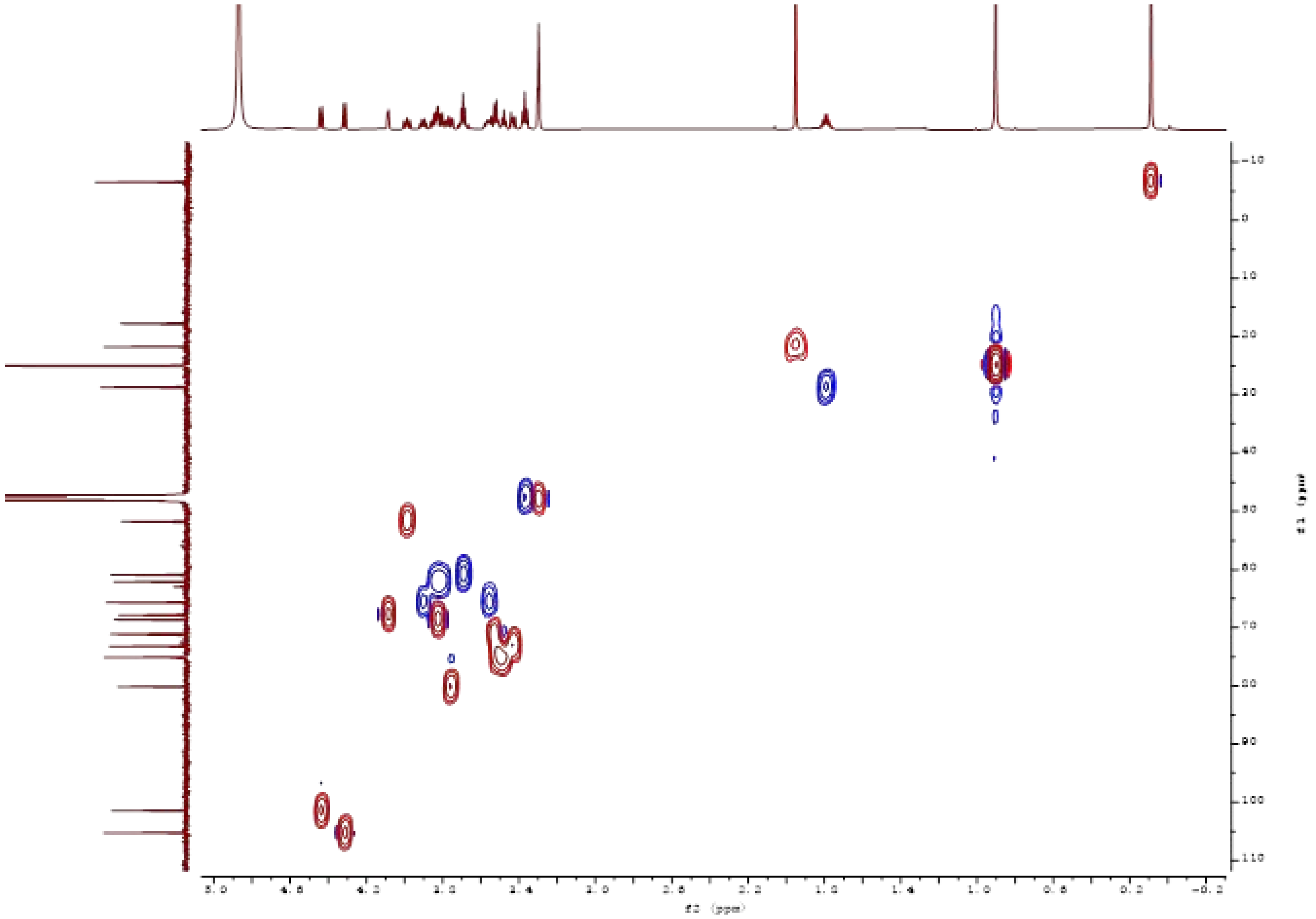

OH
OH
HO
OTBDMS
O
O
HO
O
O
N3
OH
NHAc

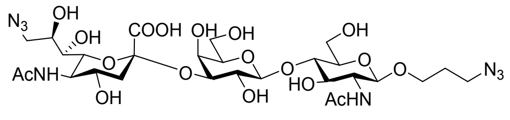
84


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

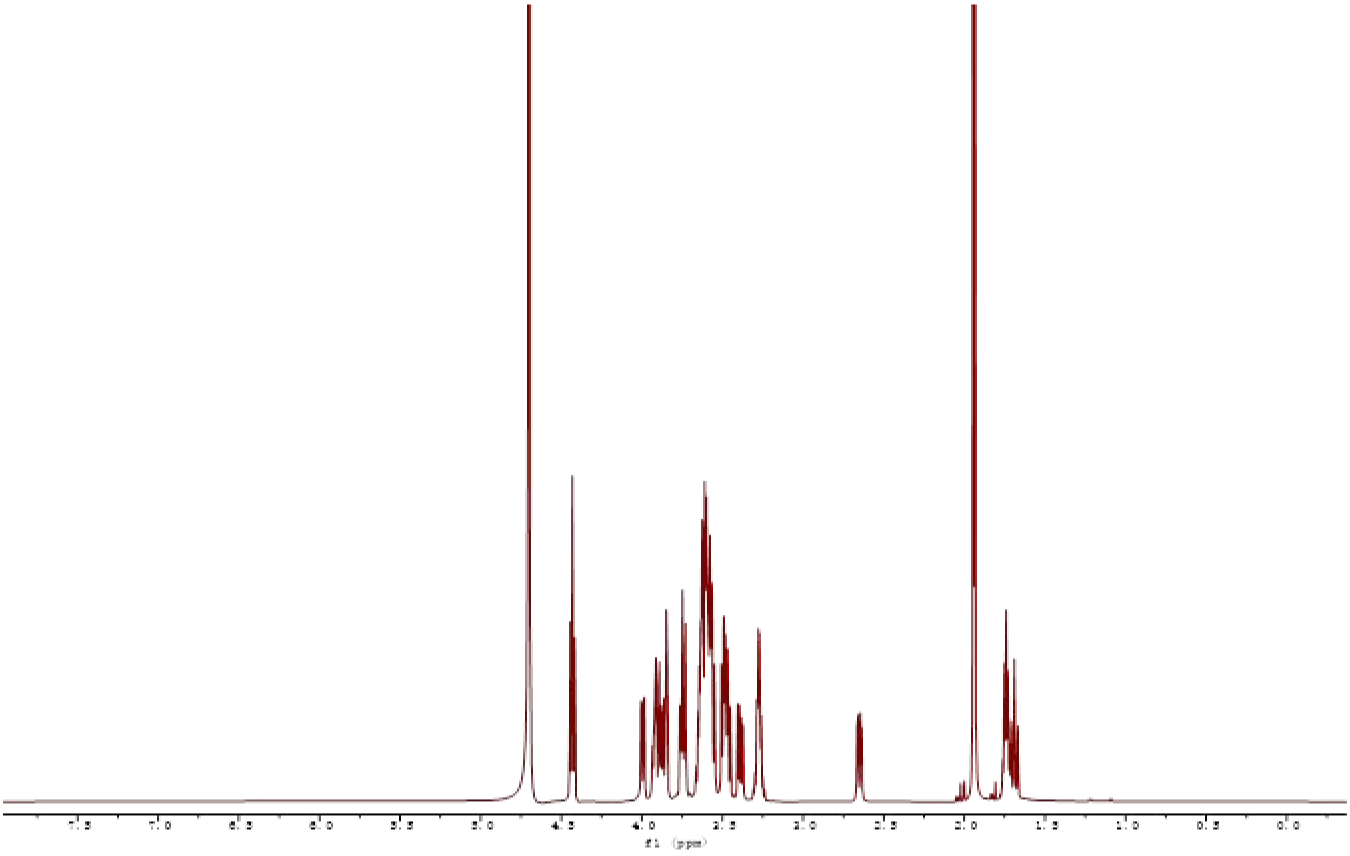

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

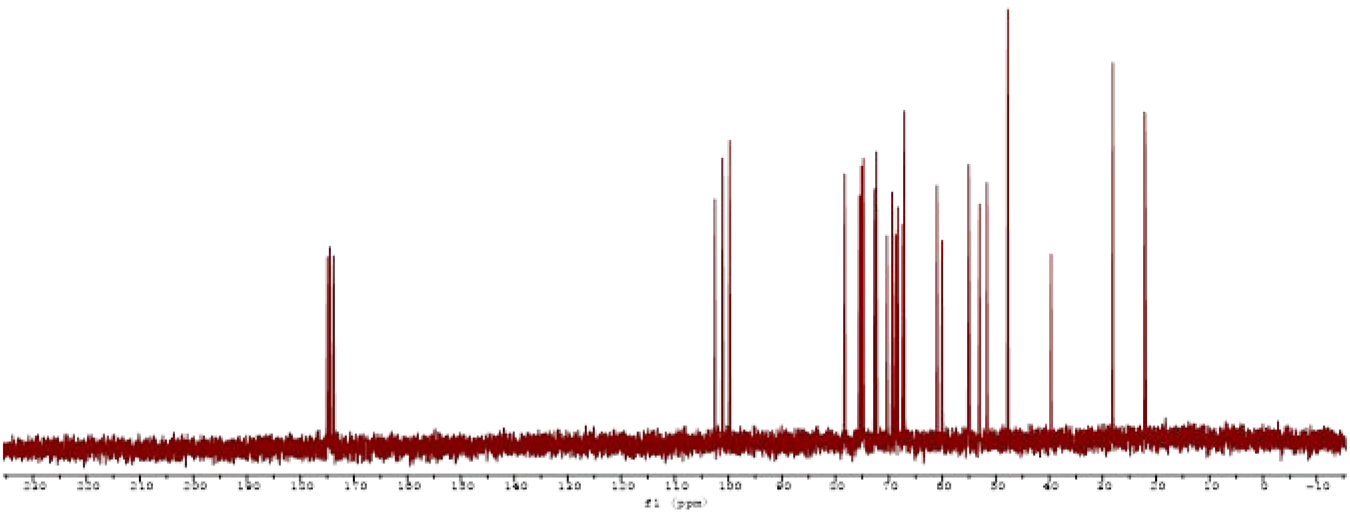

5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
f2 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

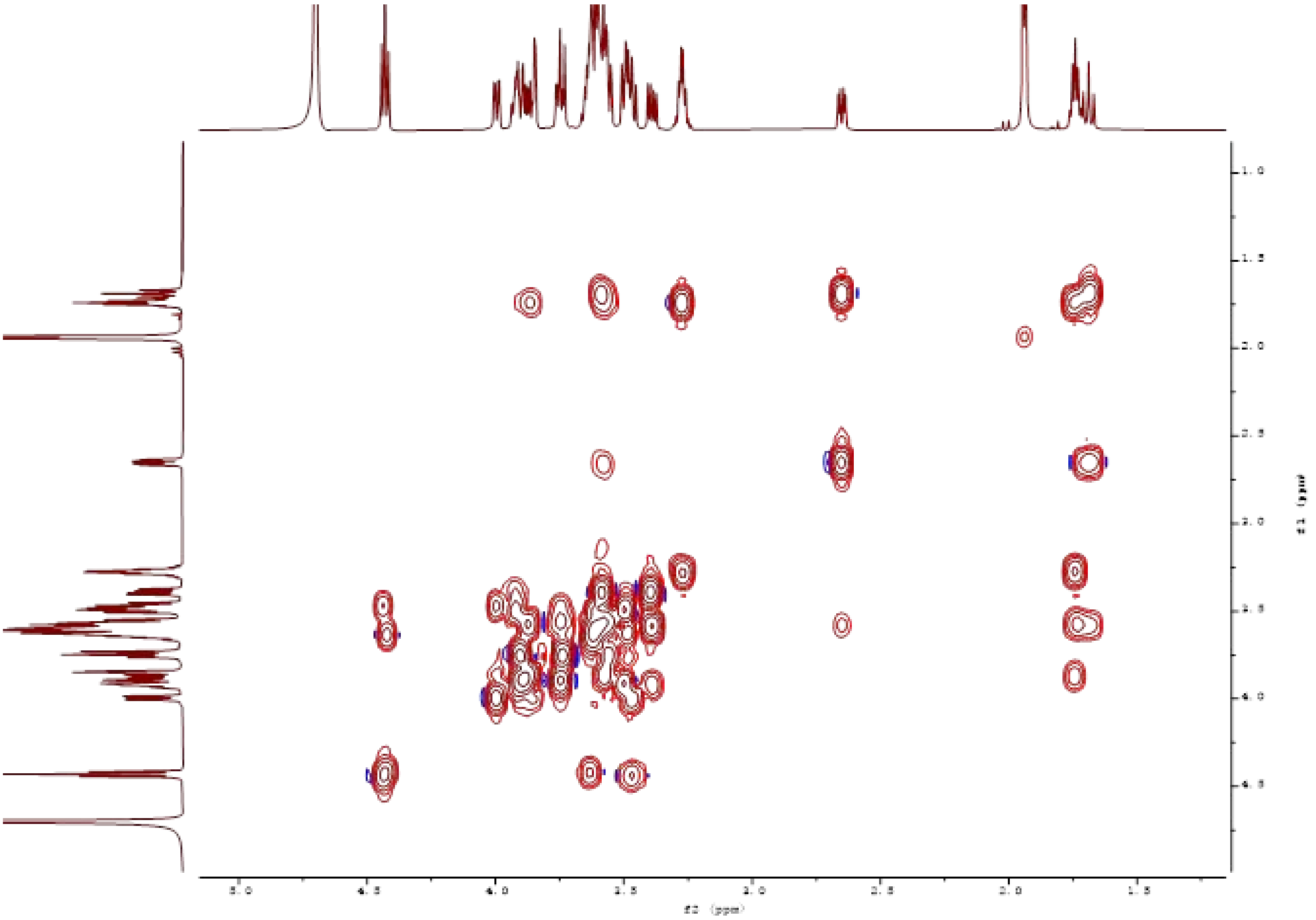

5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

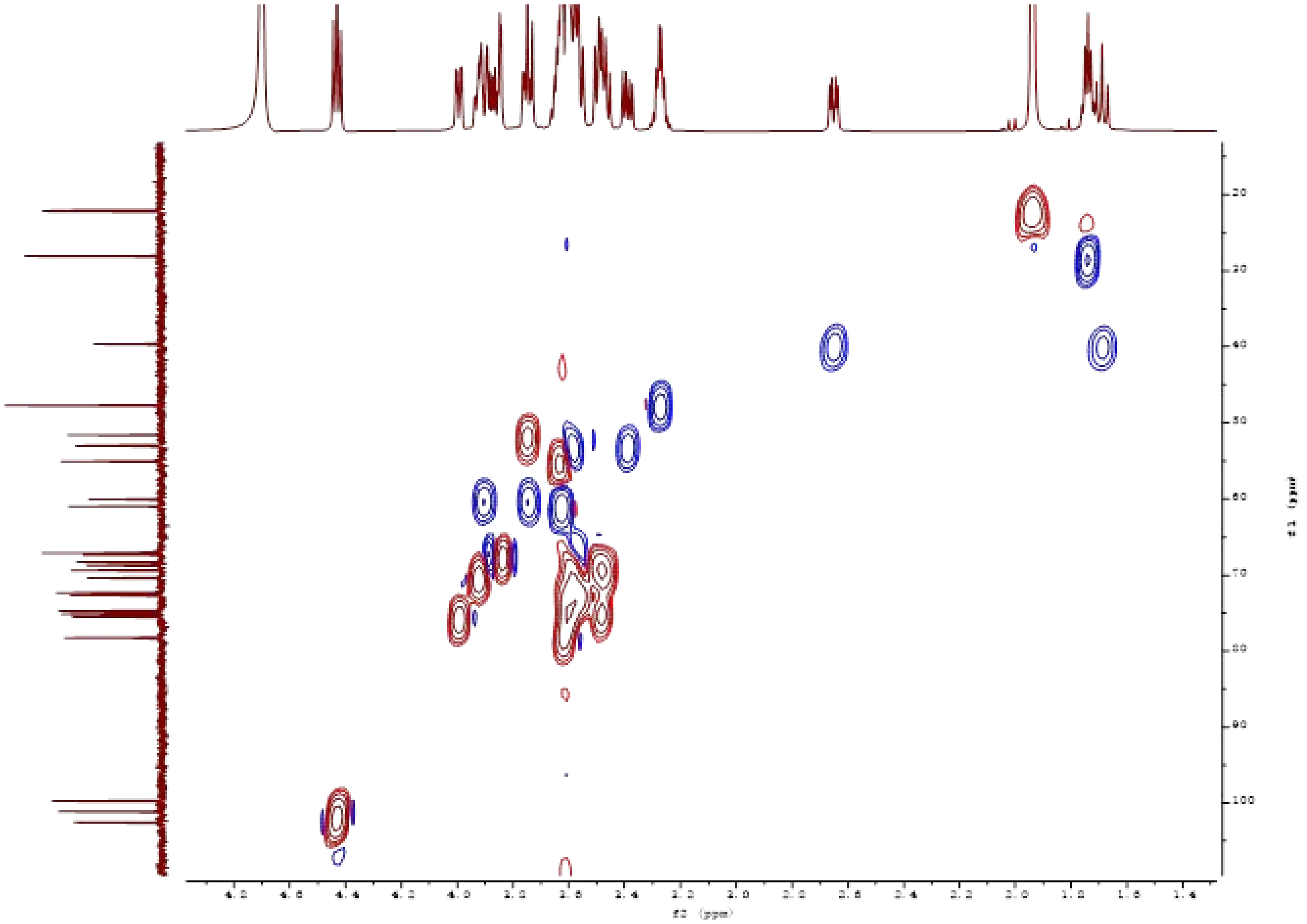

N3
OH
OH
COOH
OH
OH
OH
AcNH
O
O
O
O
O
O
OH
OH
HO
AcHN
N3

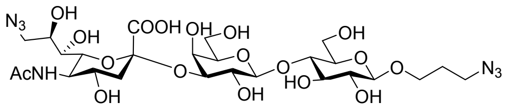
86


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)

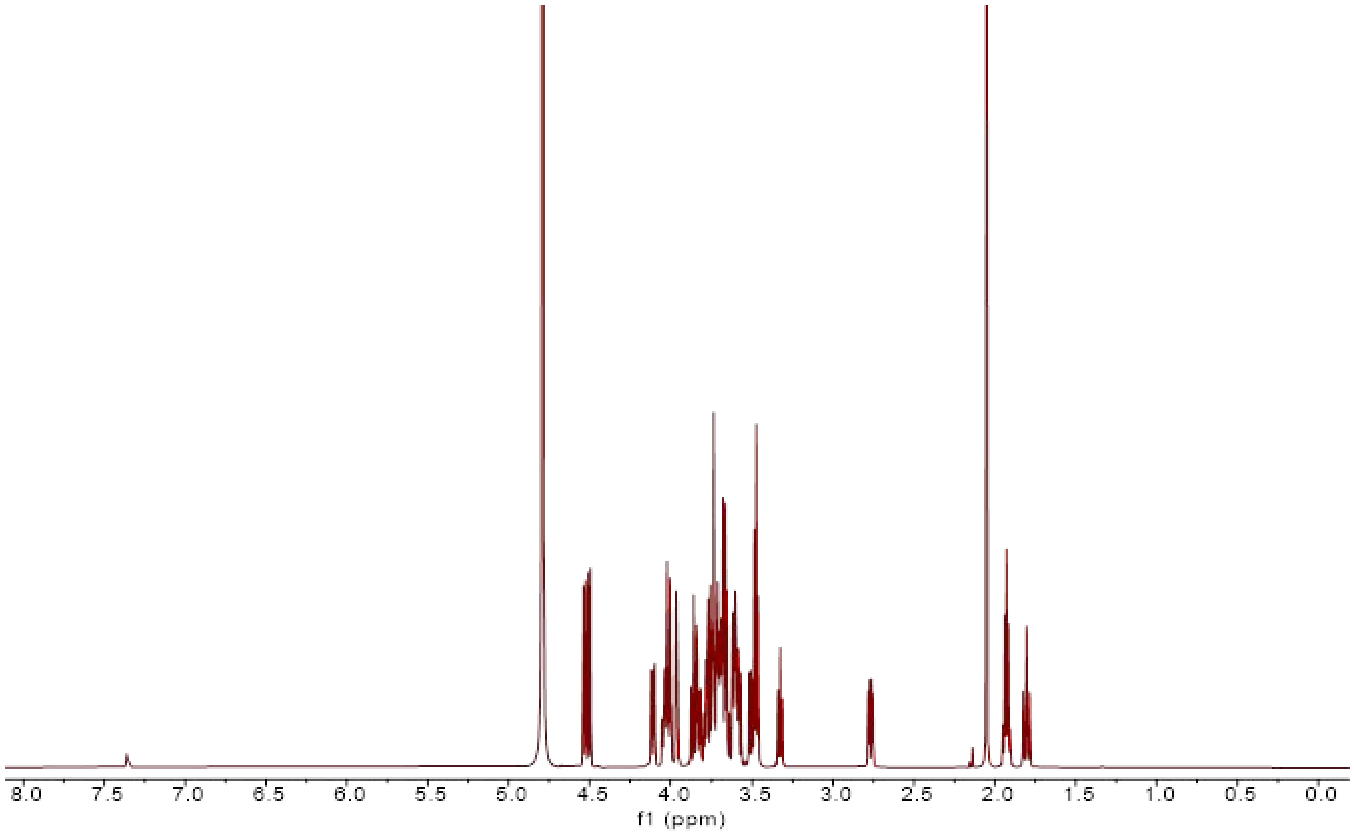

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

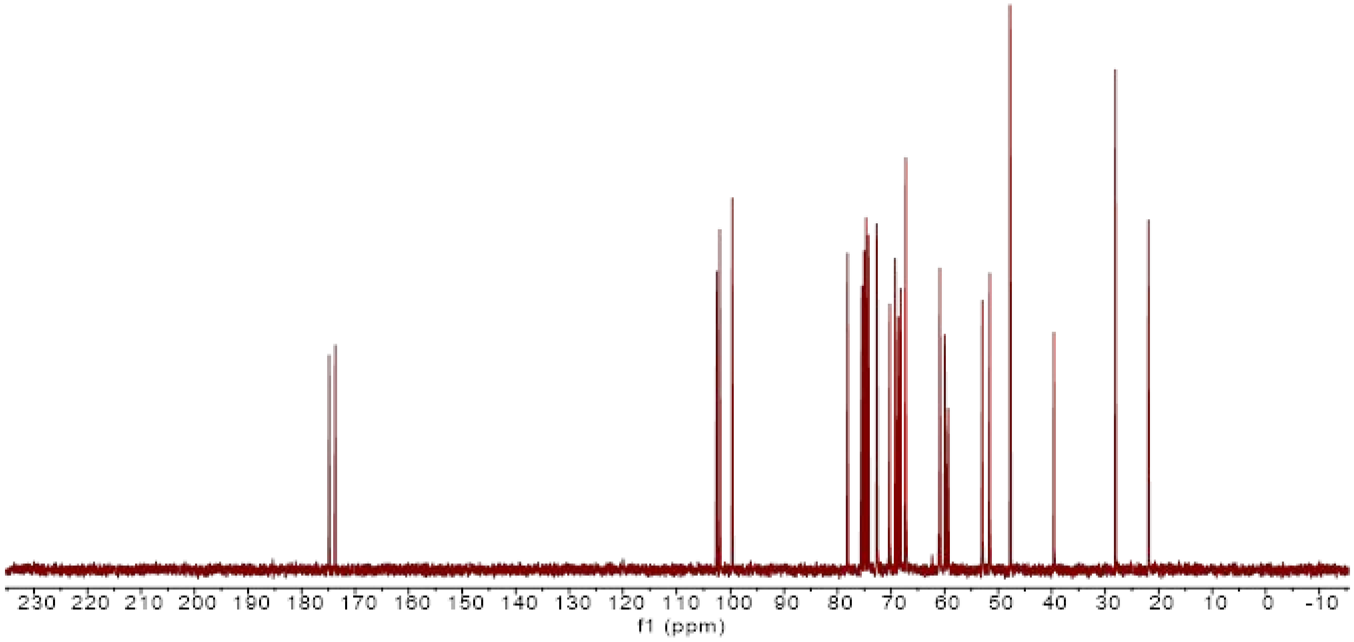

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

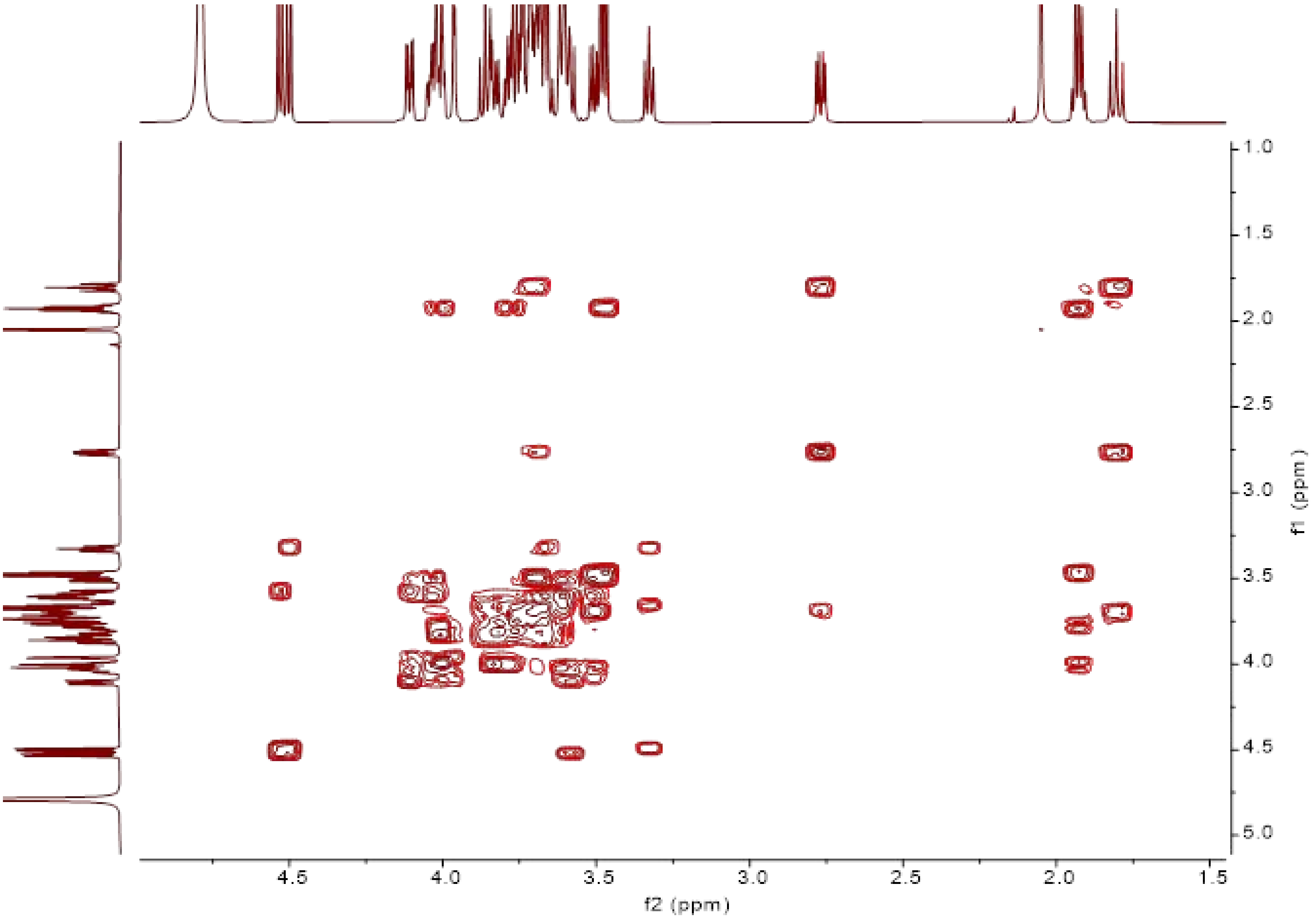

4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

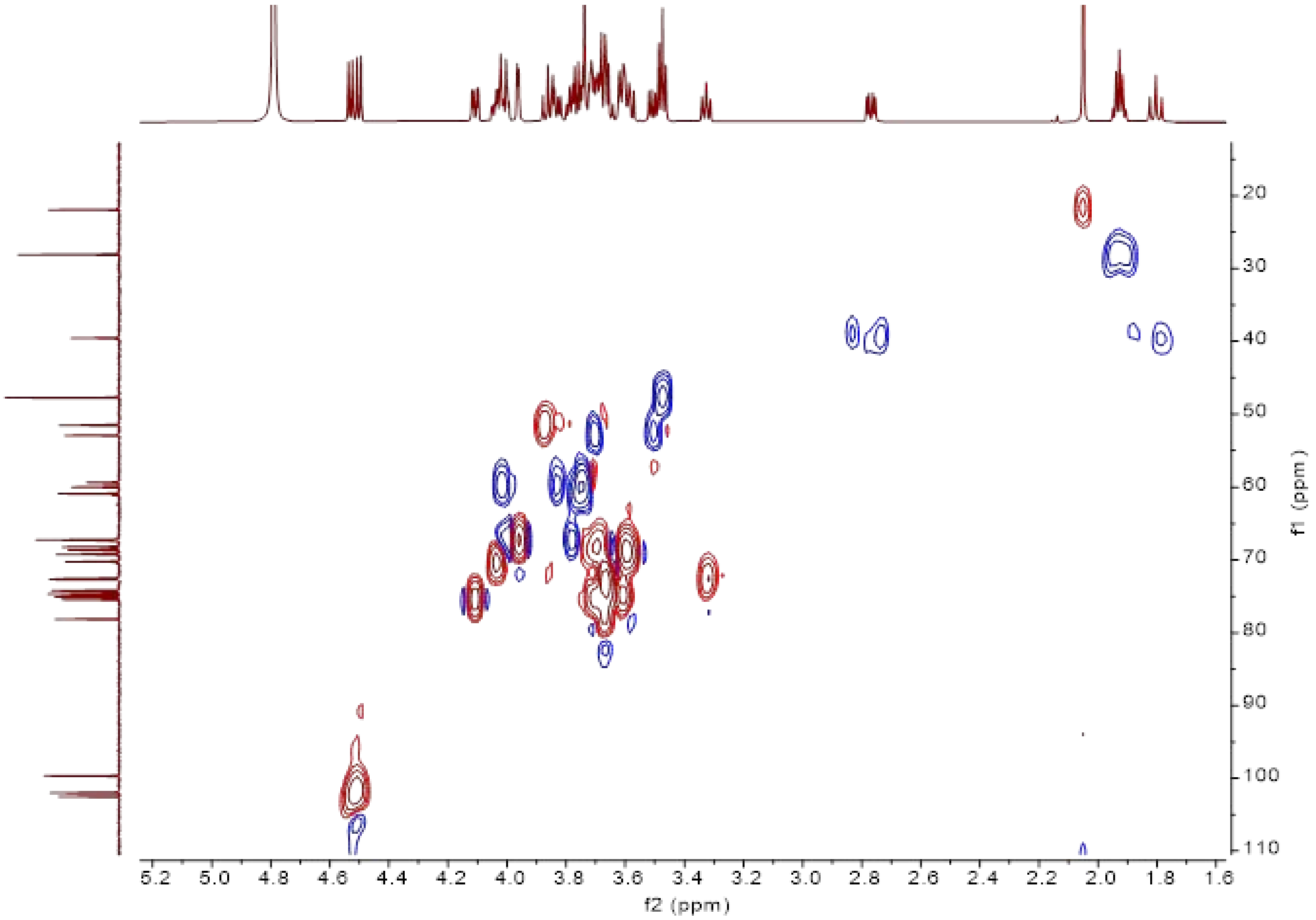

N3
OH
OH
COOH
OH
OH
O
AcNH
OH
O
OH
O
OH
HO
O
OH
O
N3

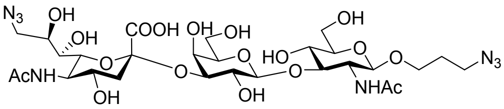
88


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

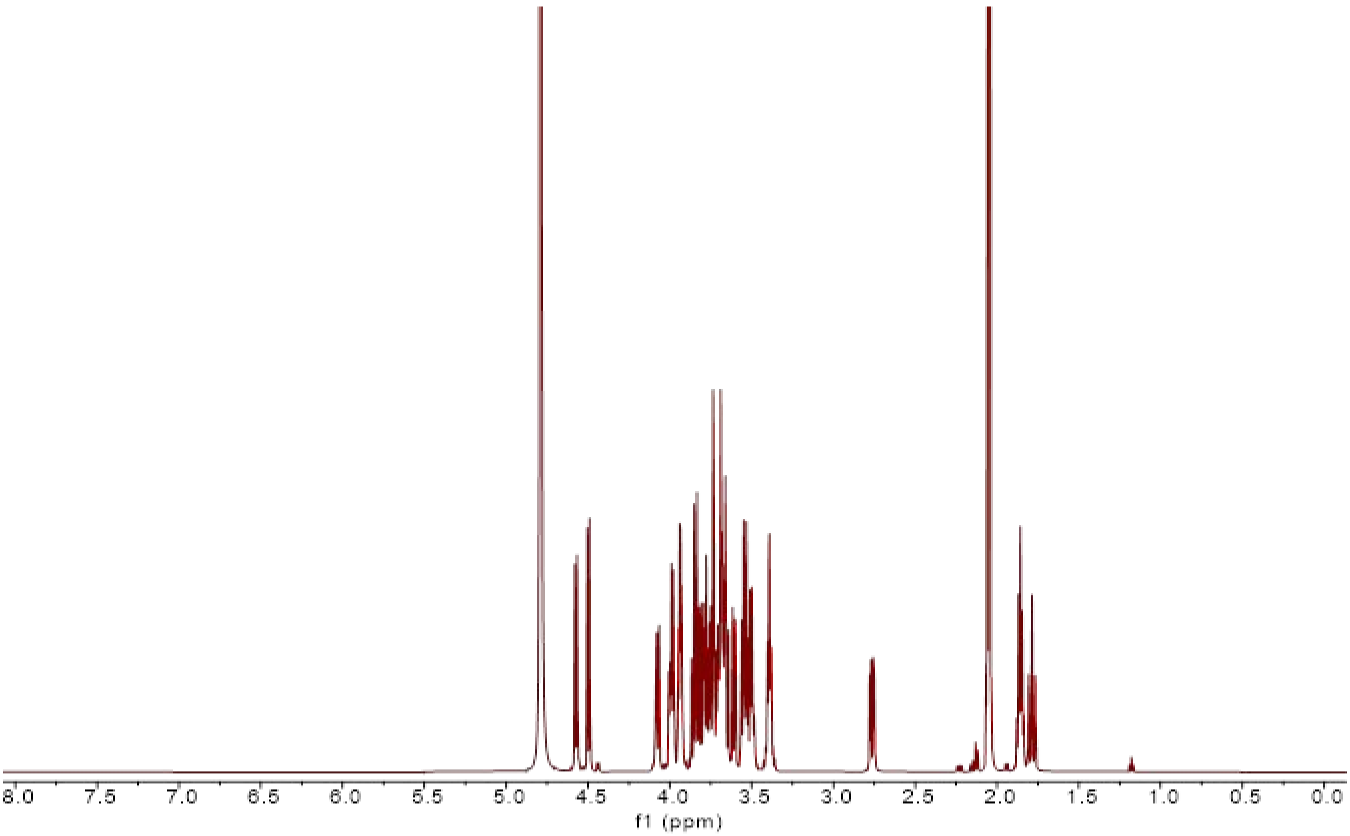

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

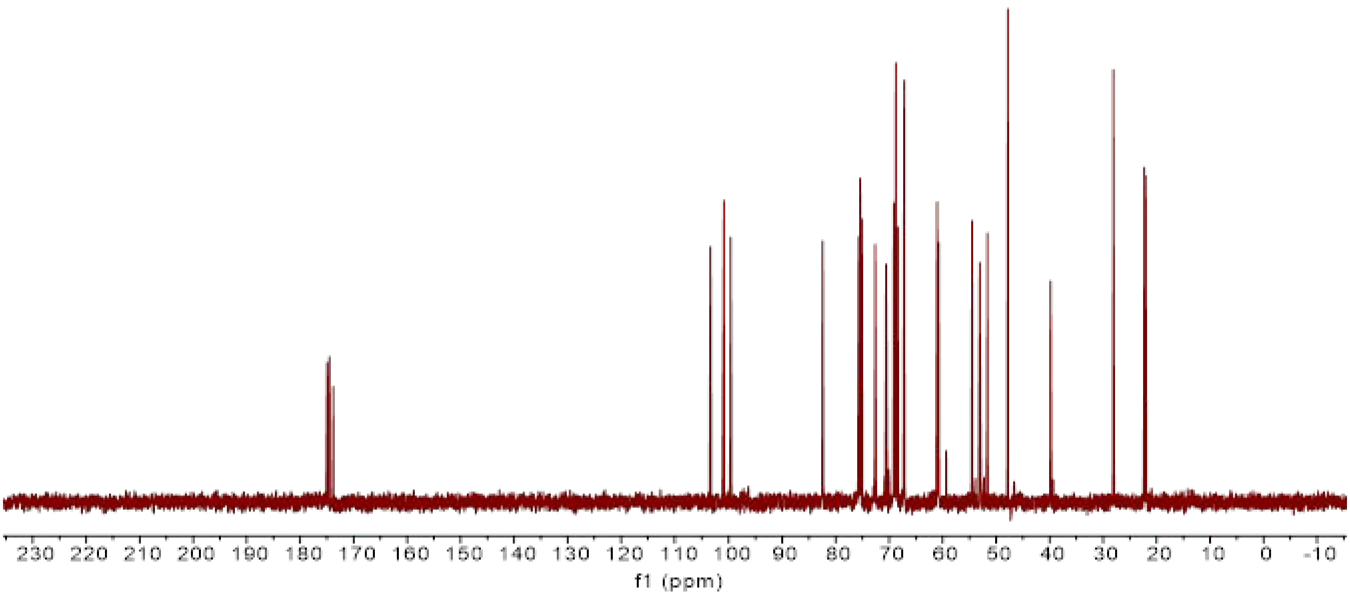

4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

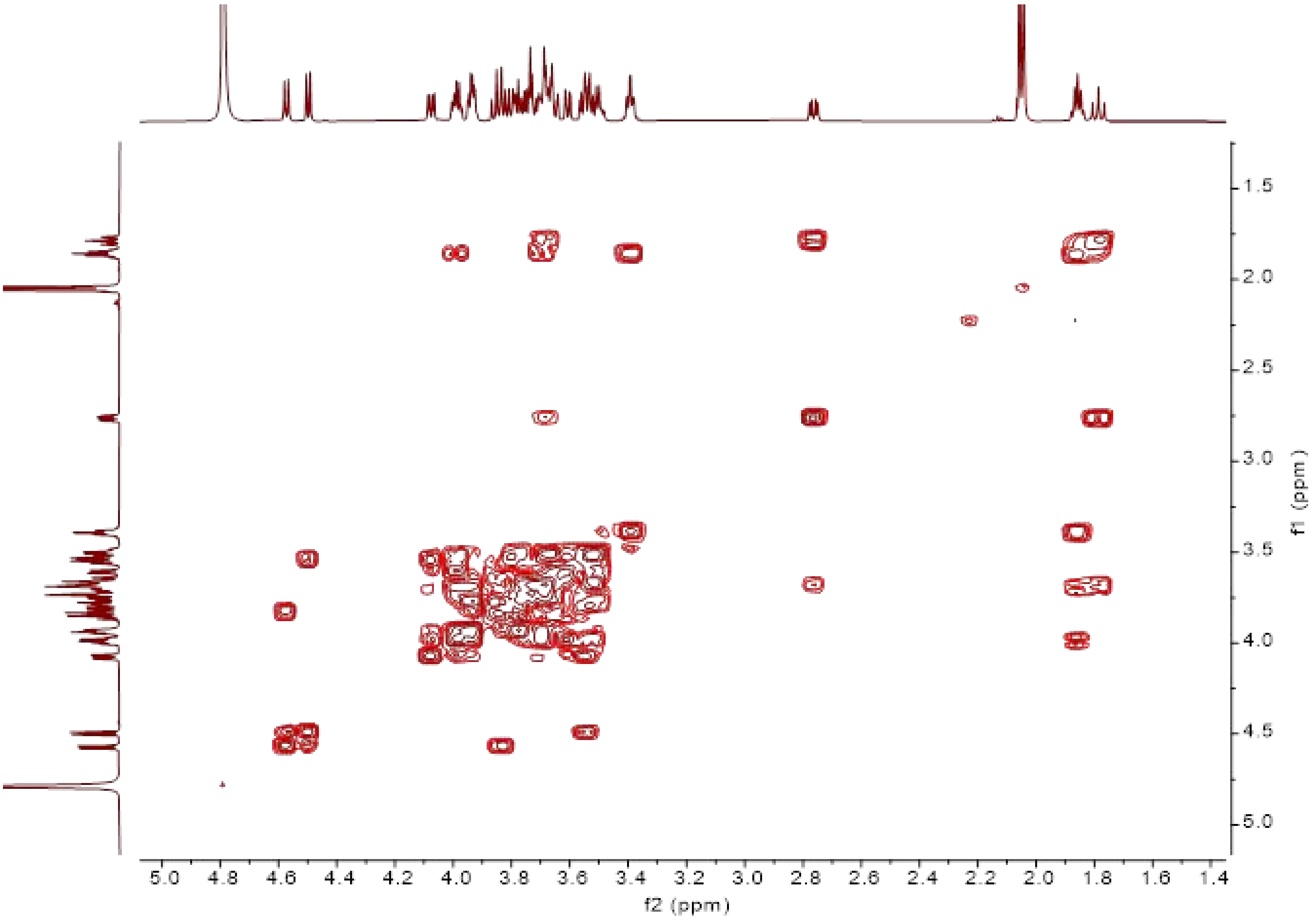

5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

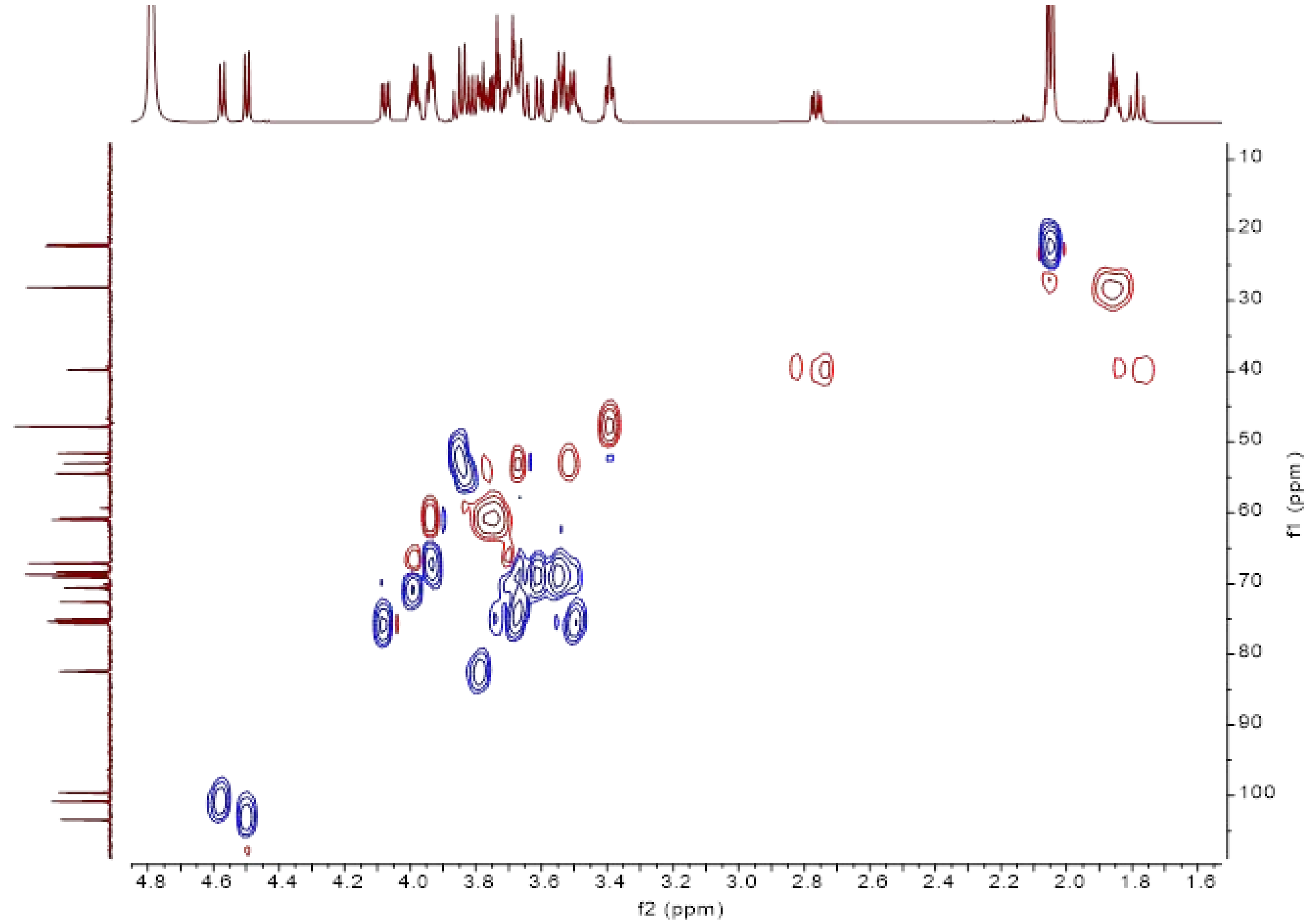

N3
OH
OH
COOH
OH
OH
OH
HO
O
O
O
O
O
O
N3
AcNH
OH
OH
NHAc

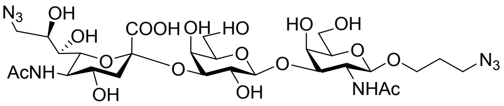
90


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

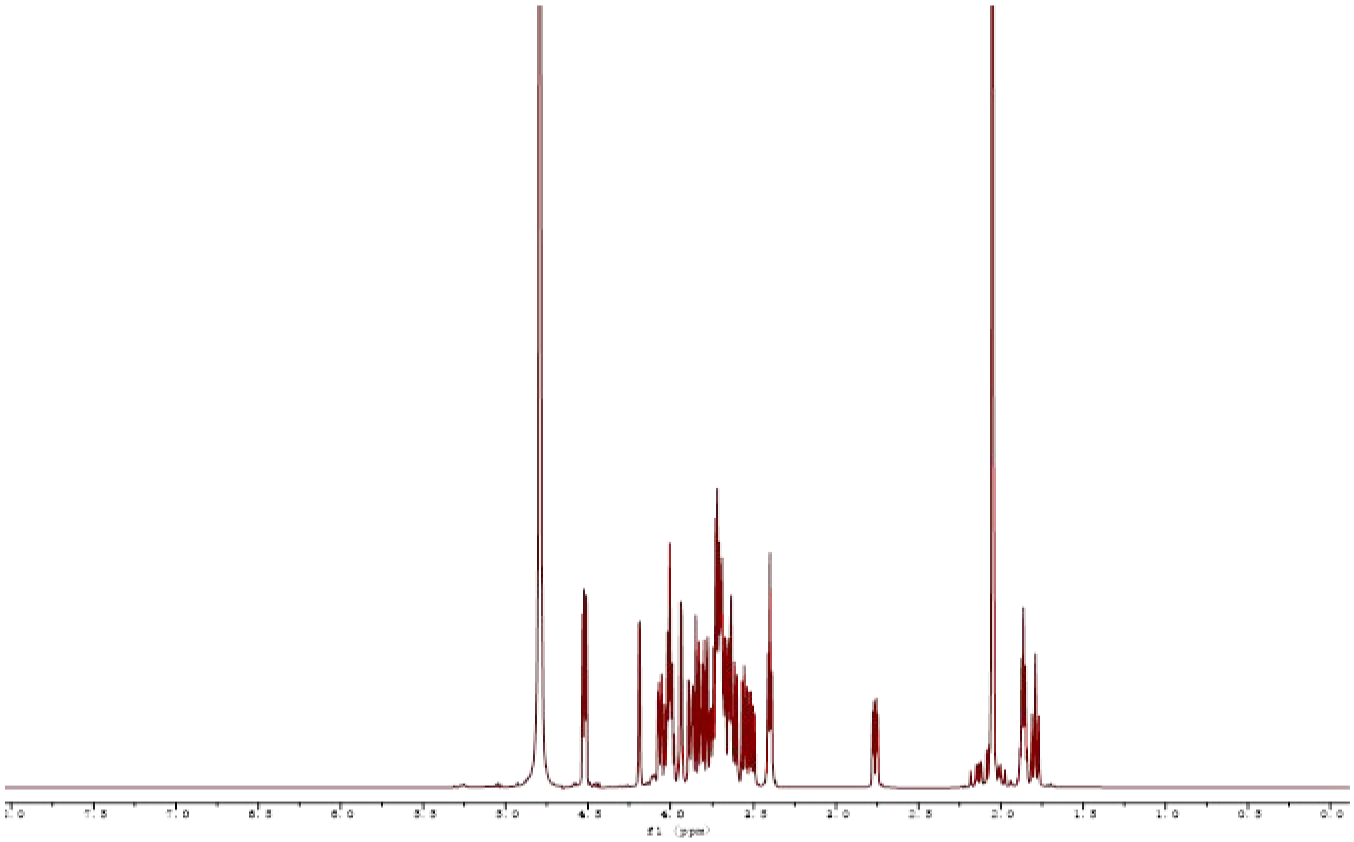

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

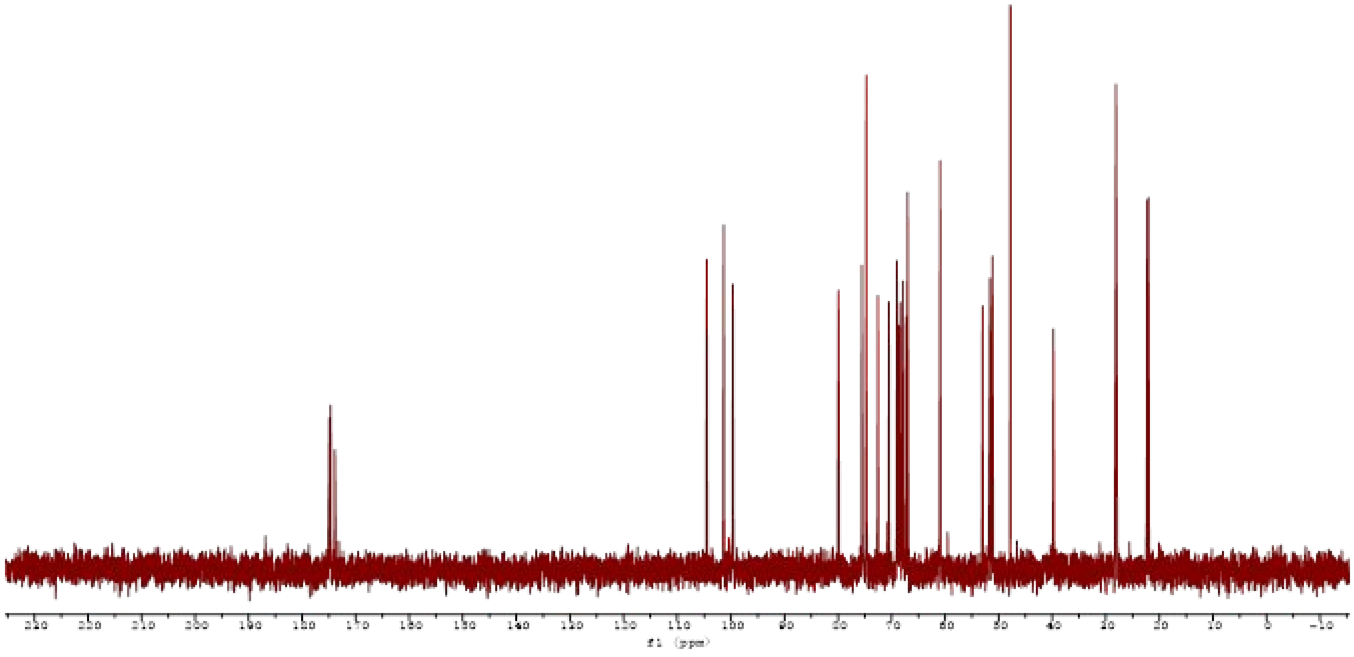

1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f2 (ppm)

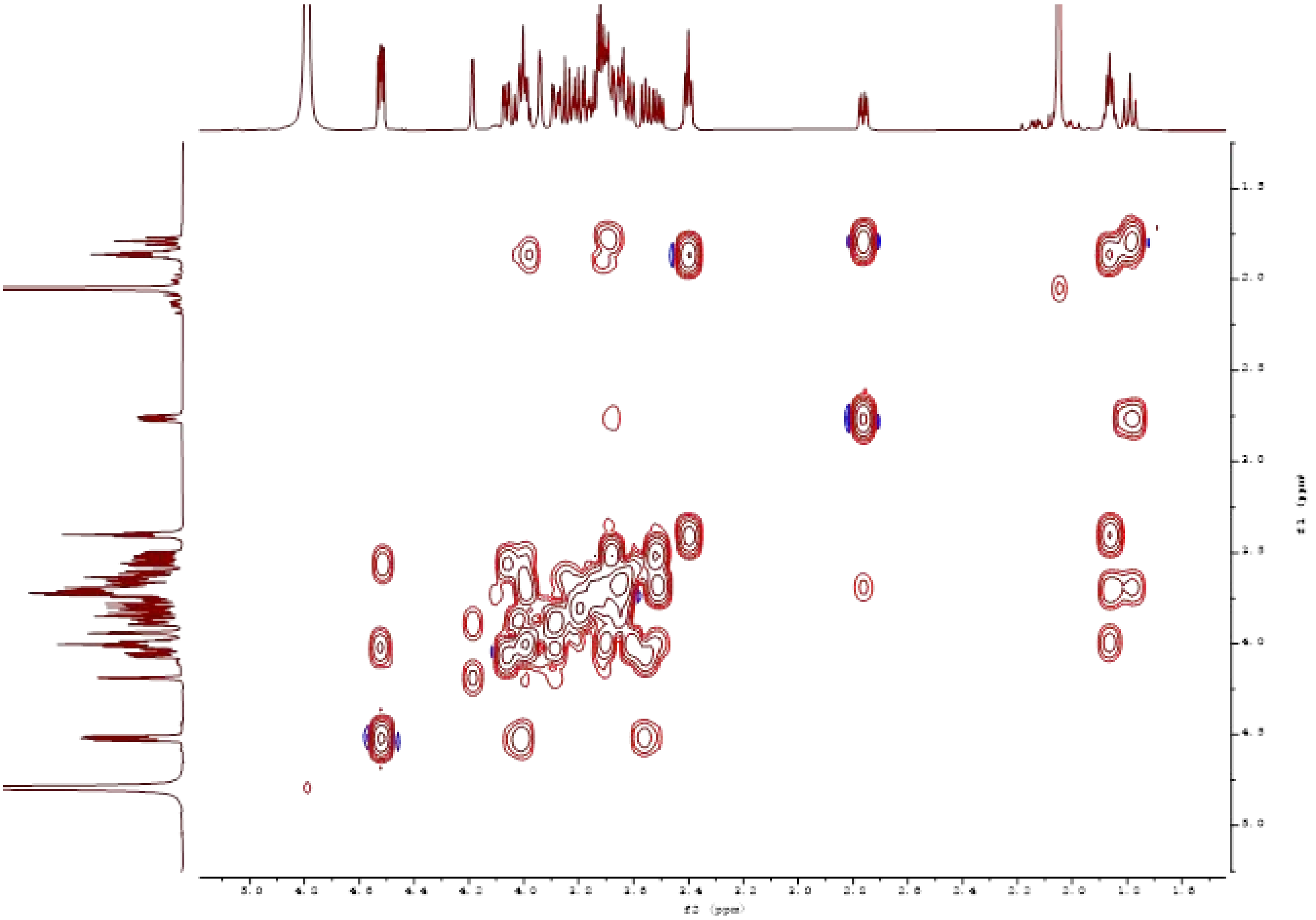

10
20
30
40
50
60
70
80
90
100
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f2 (ppm)

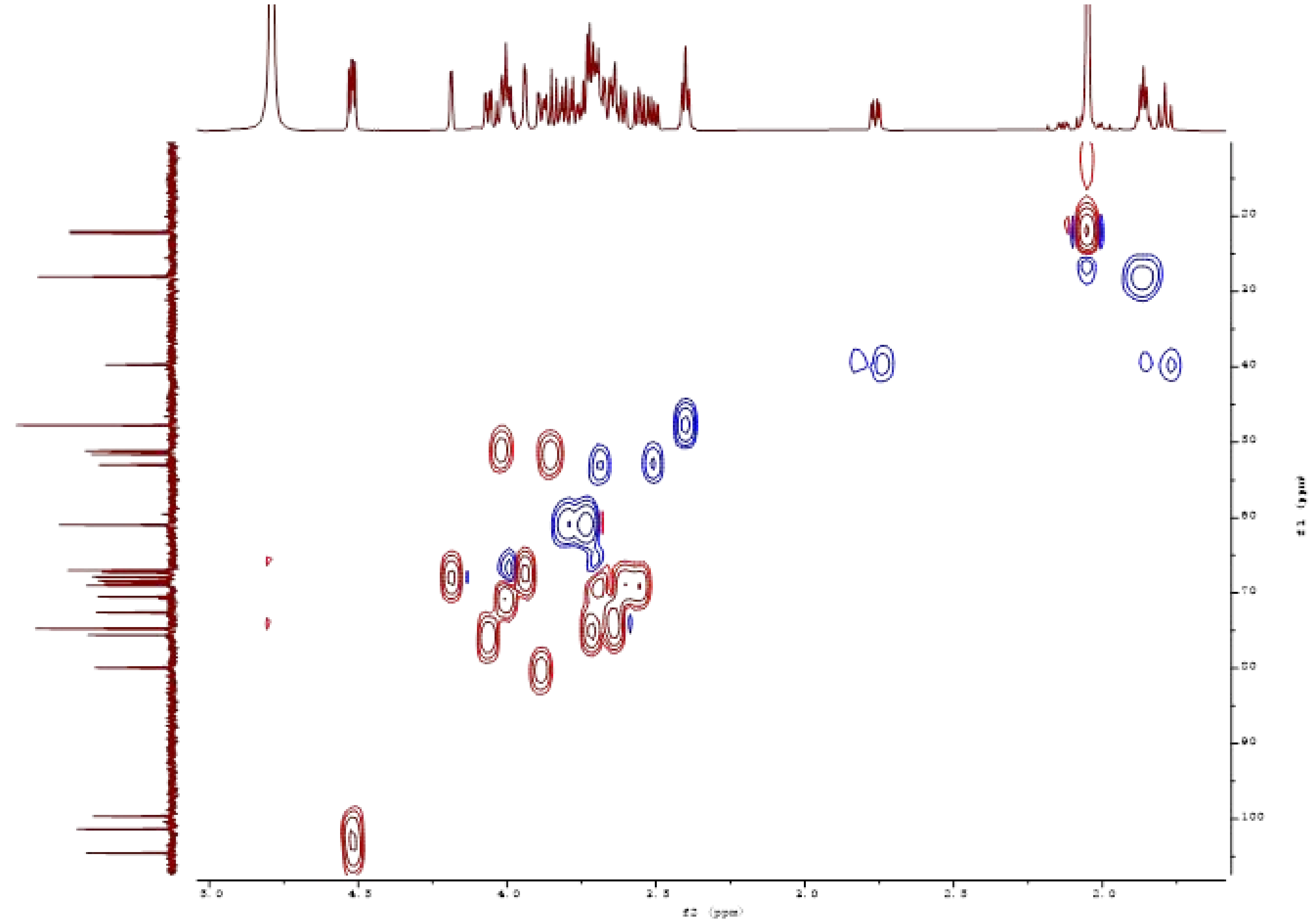

N3
OH
OH
COOH
OH
HO
HO
OH
AcNH
O
O
O
O
O
N3
OH
OH
NHAc

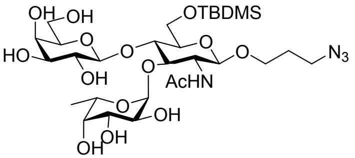
92


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

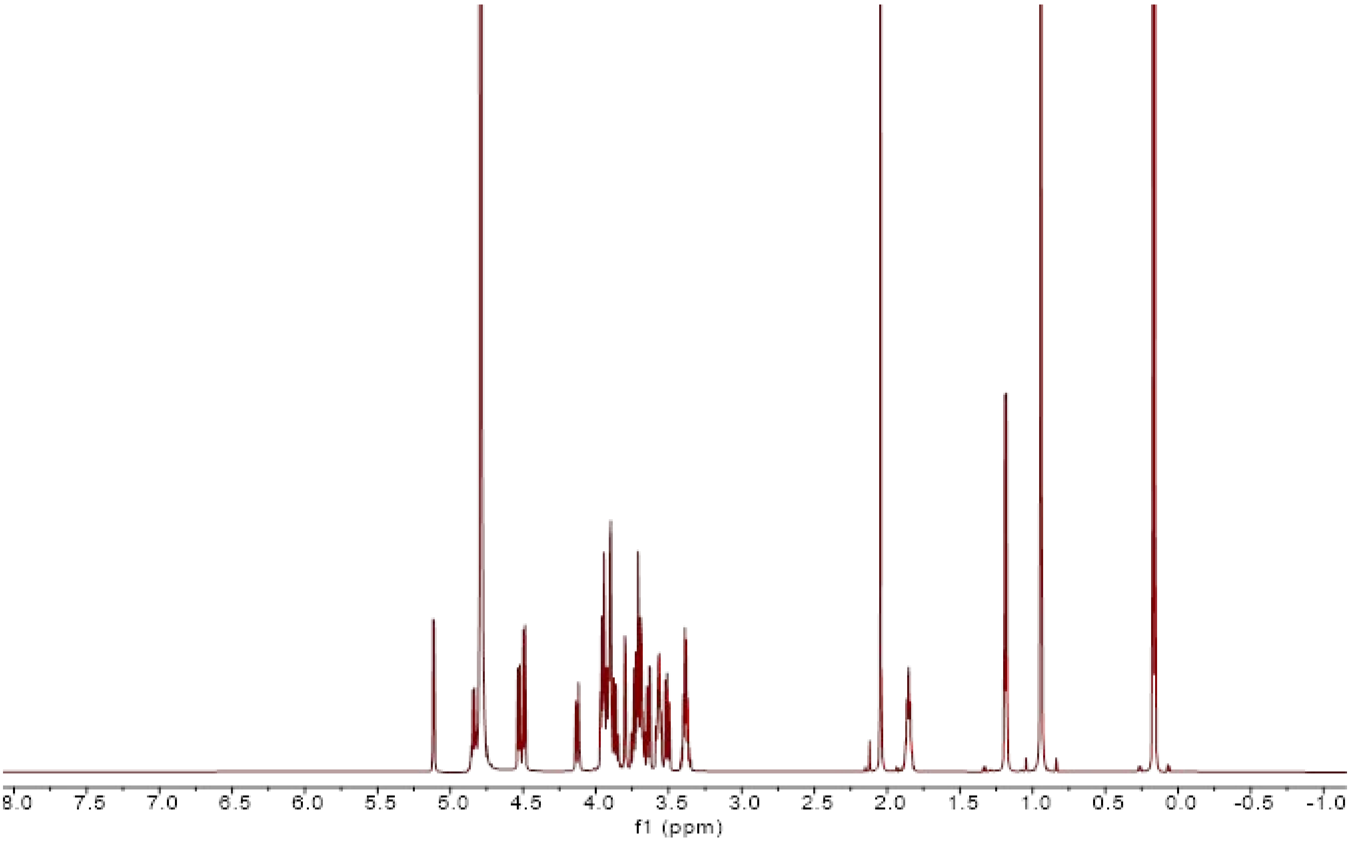

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

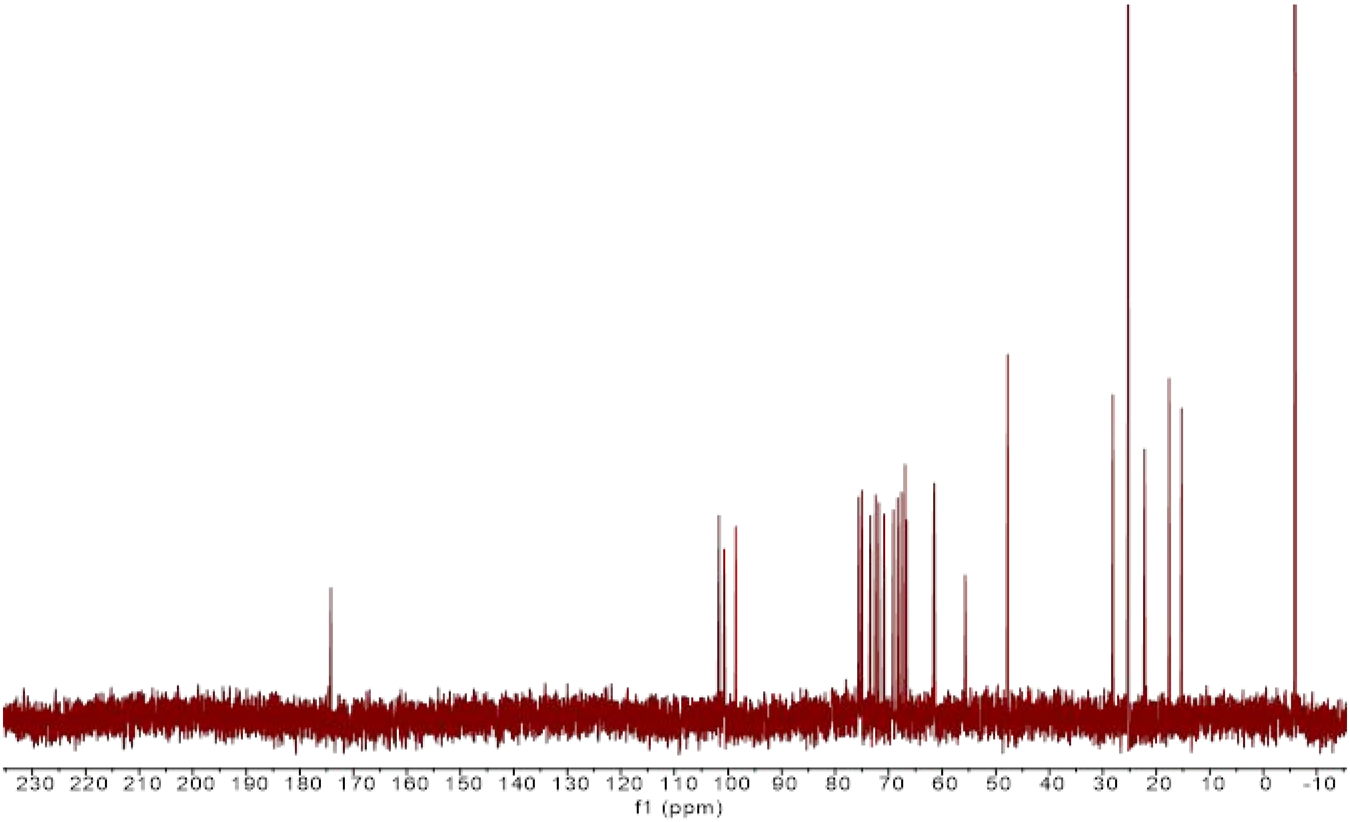

5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

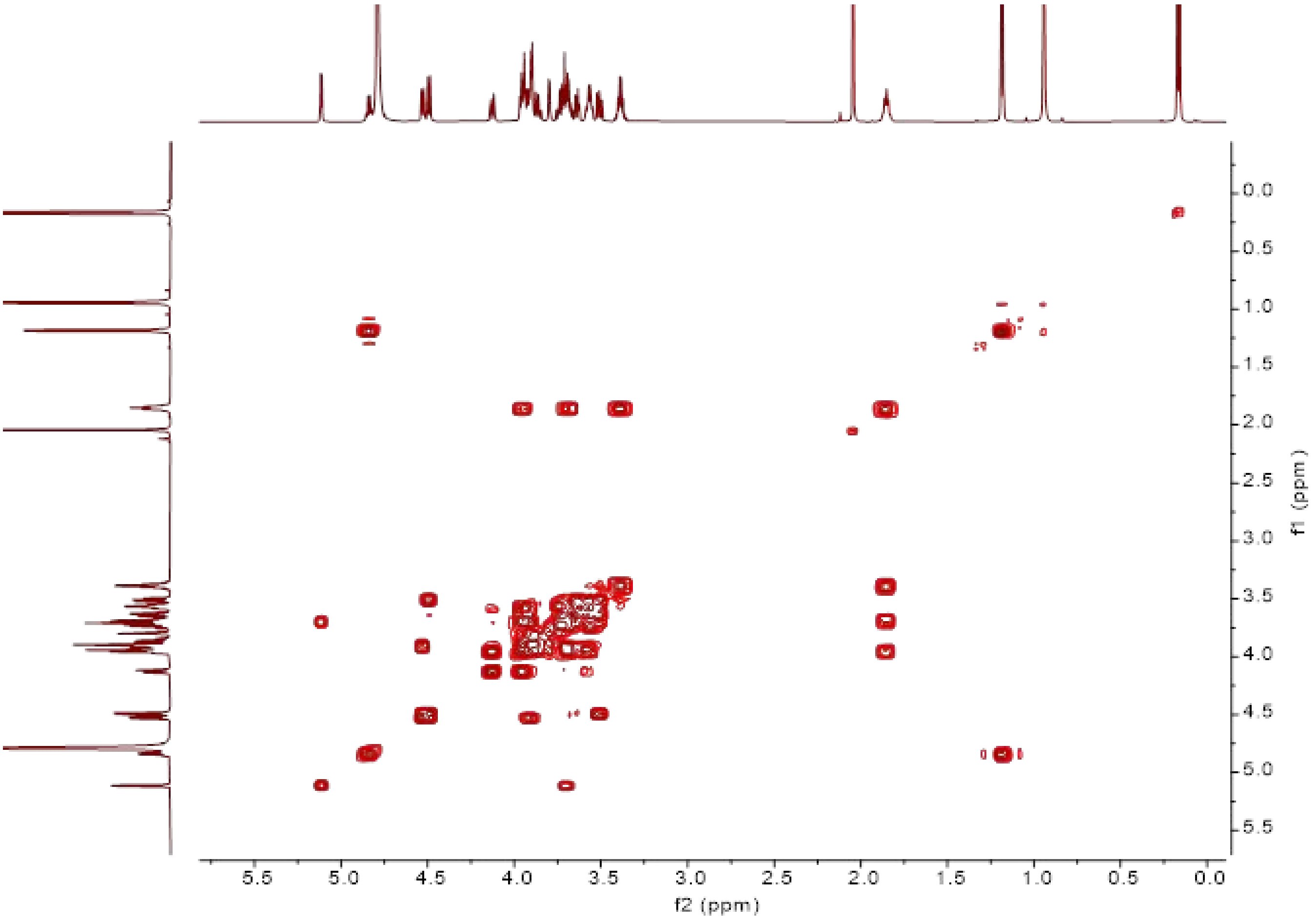

5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
f1 (ppm)

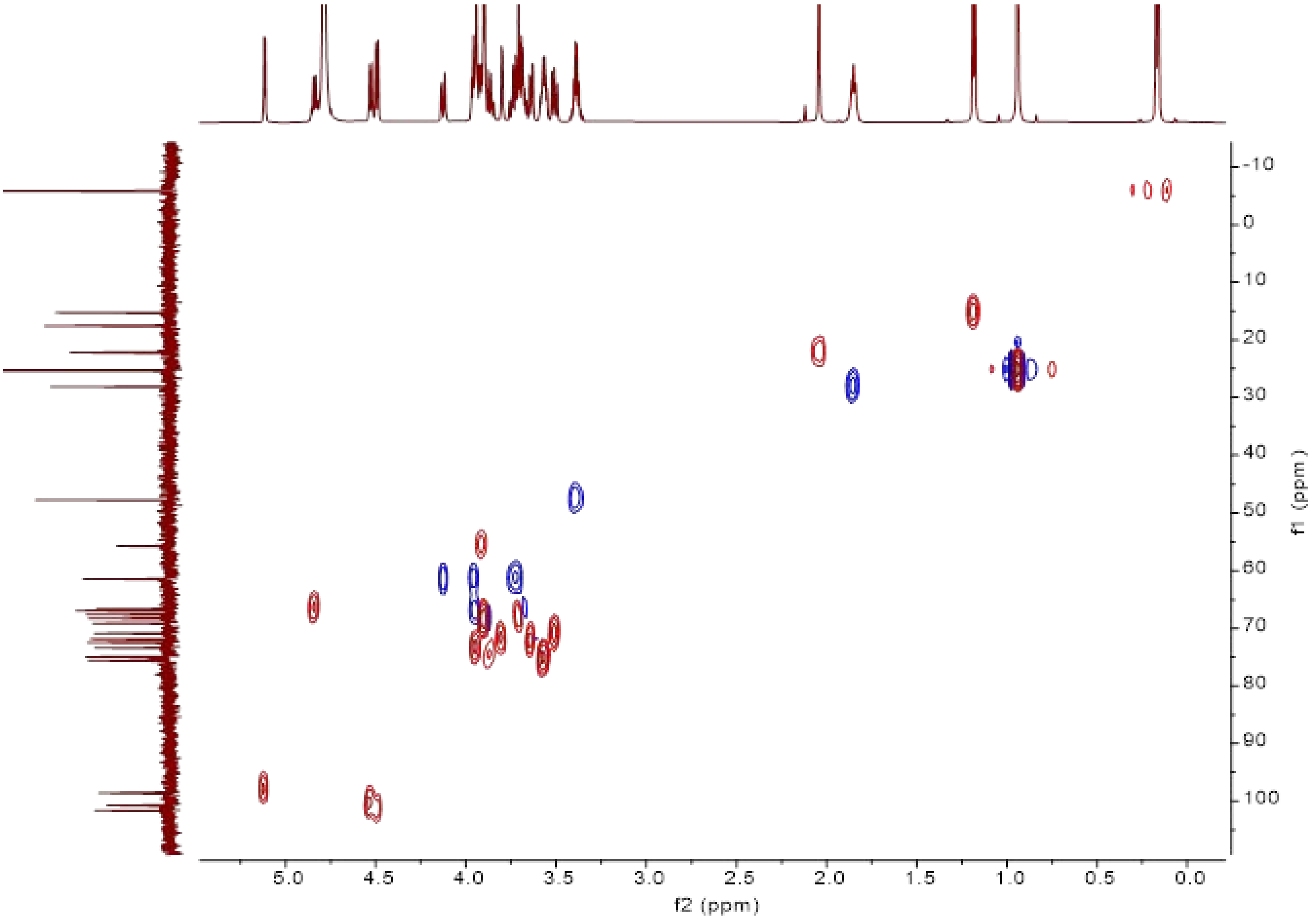

OH
OH
OTBDMS
O
O
HO
O
O
N3
OH
O
AcHN
O
OH
OH
OH

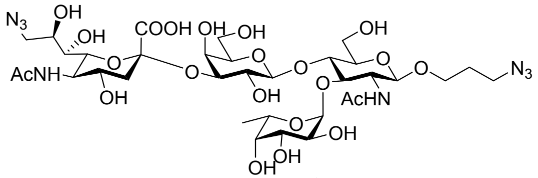
94


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

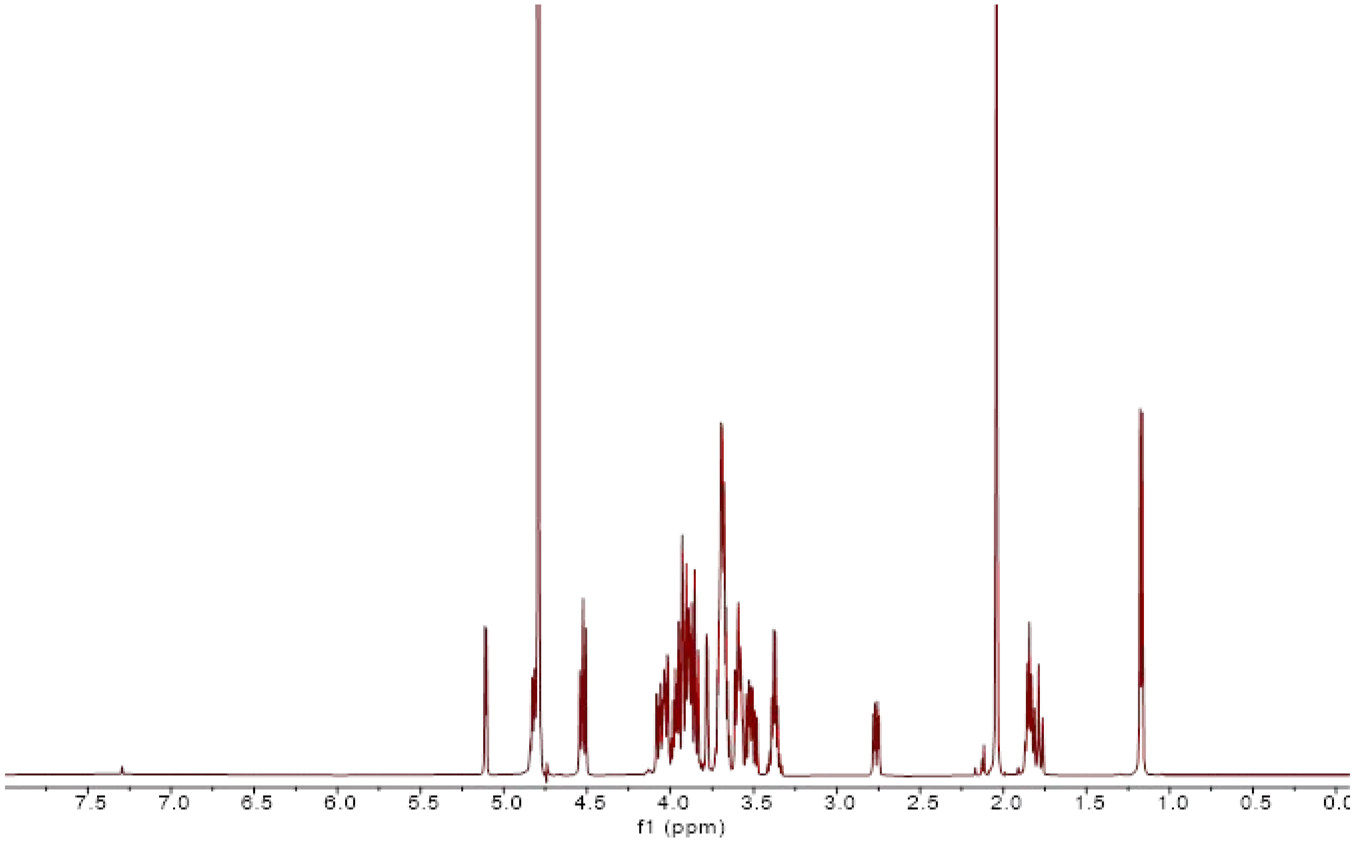

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

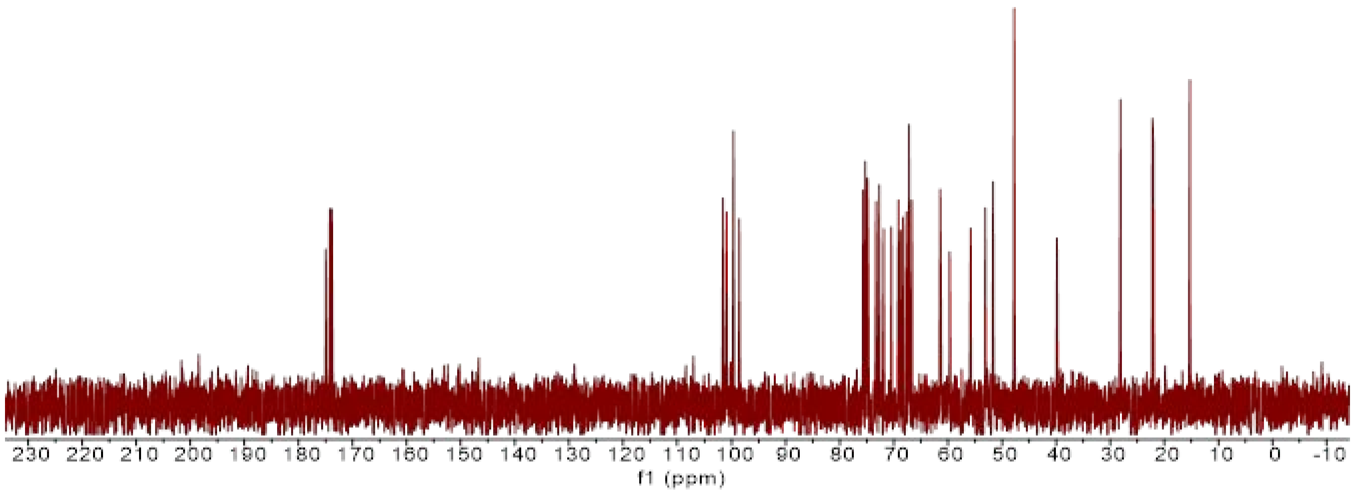

0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

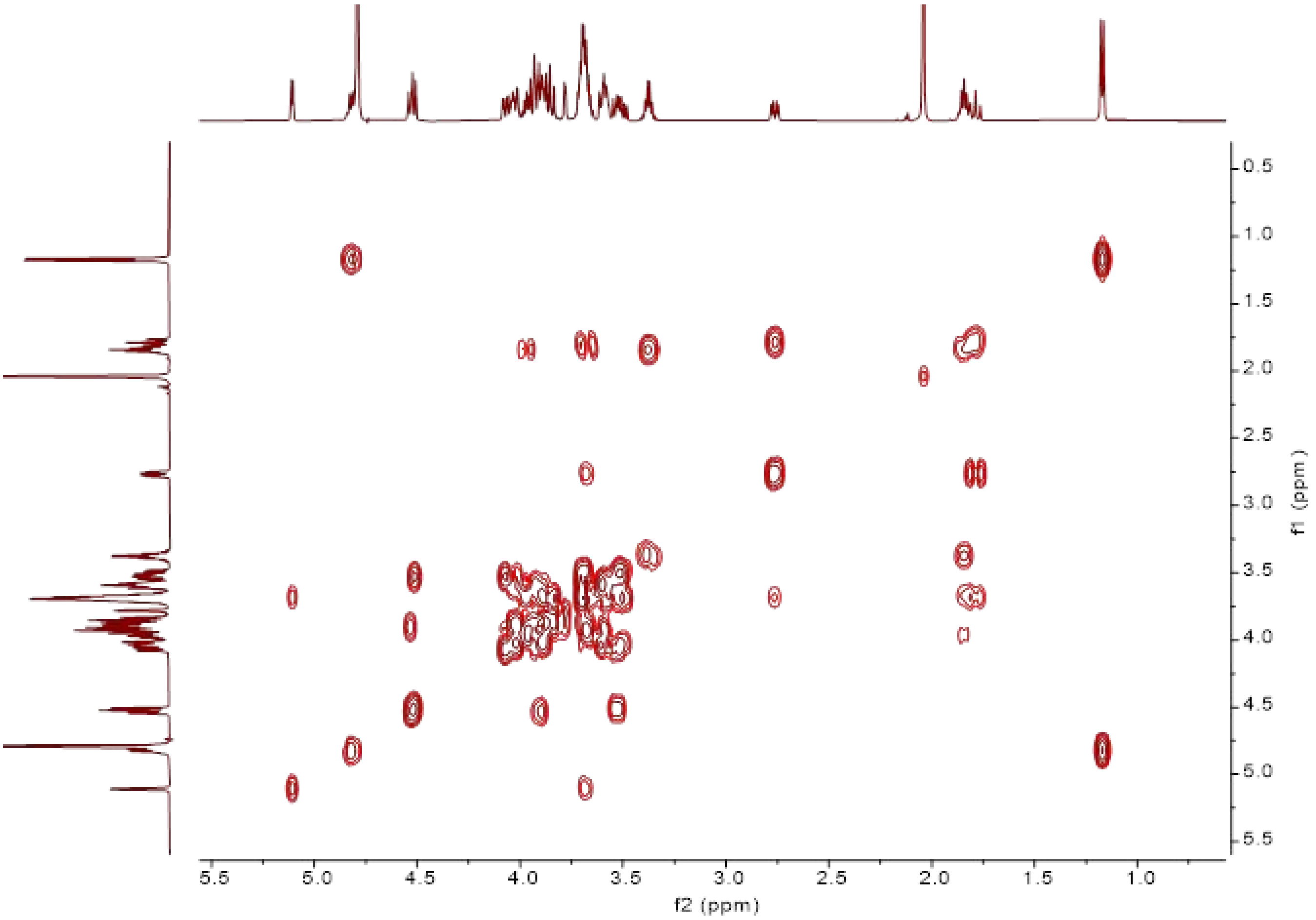

-10
0
10
20
30
40
50
60
70
80
90
100
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

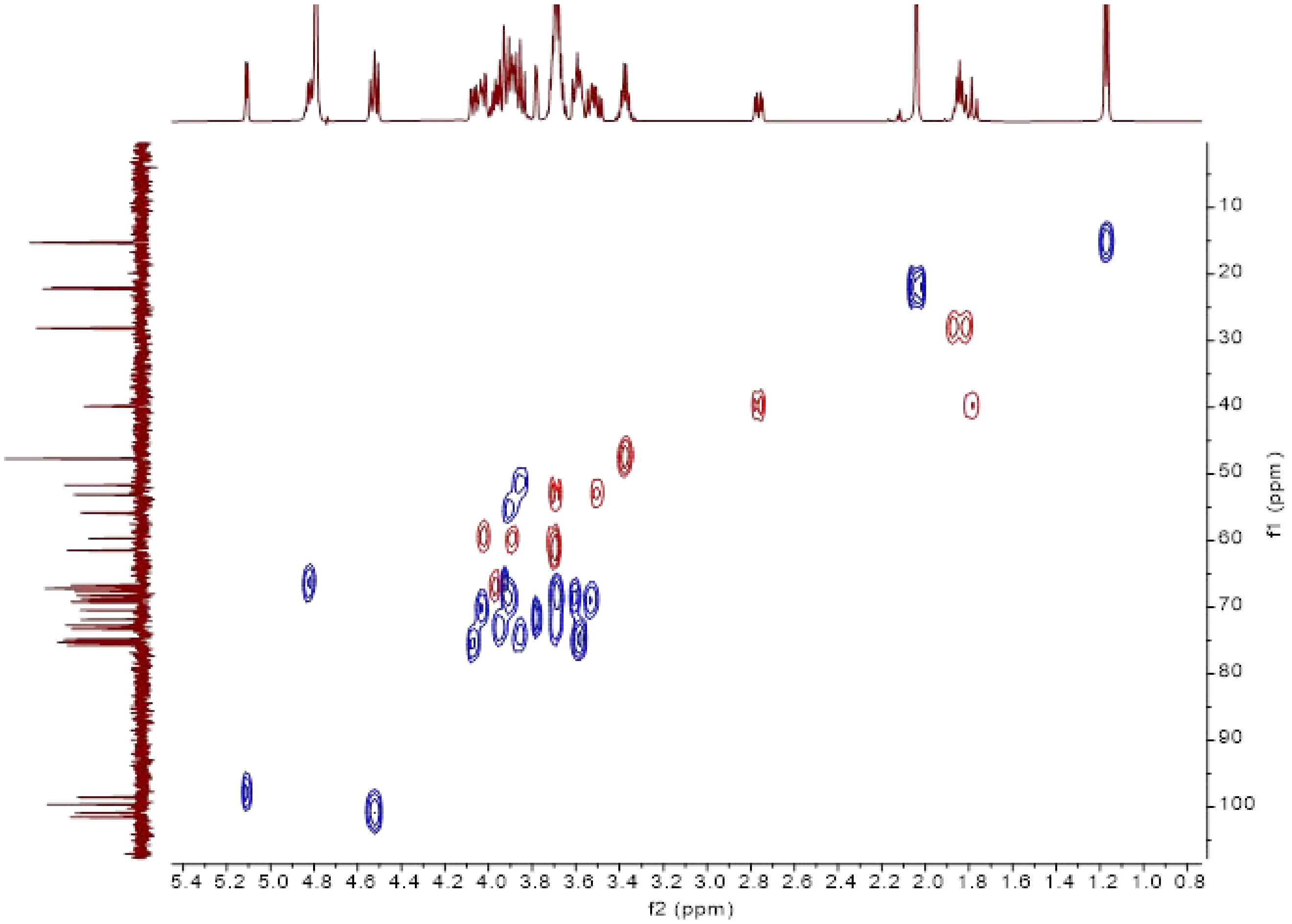


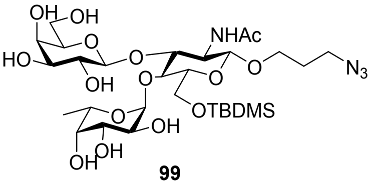
95


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)

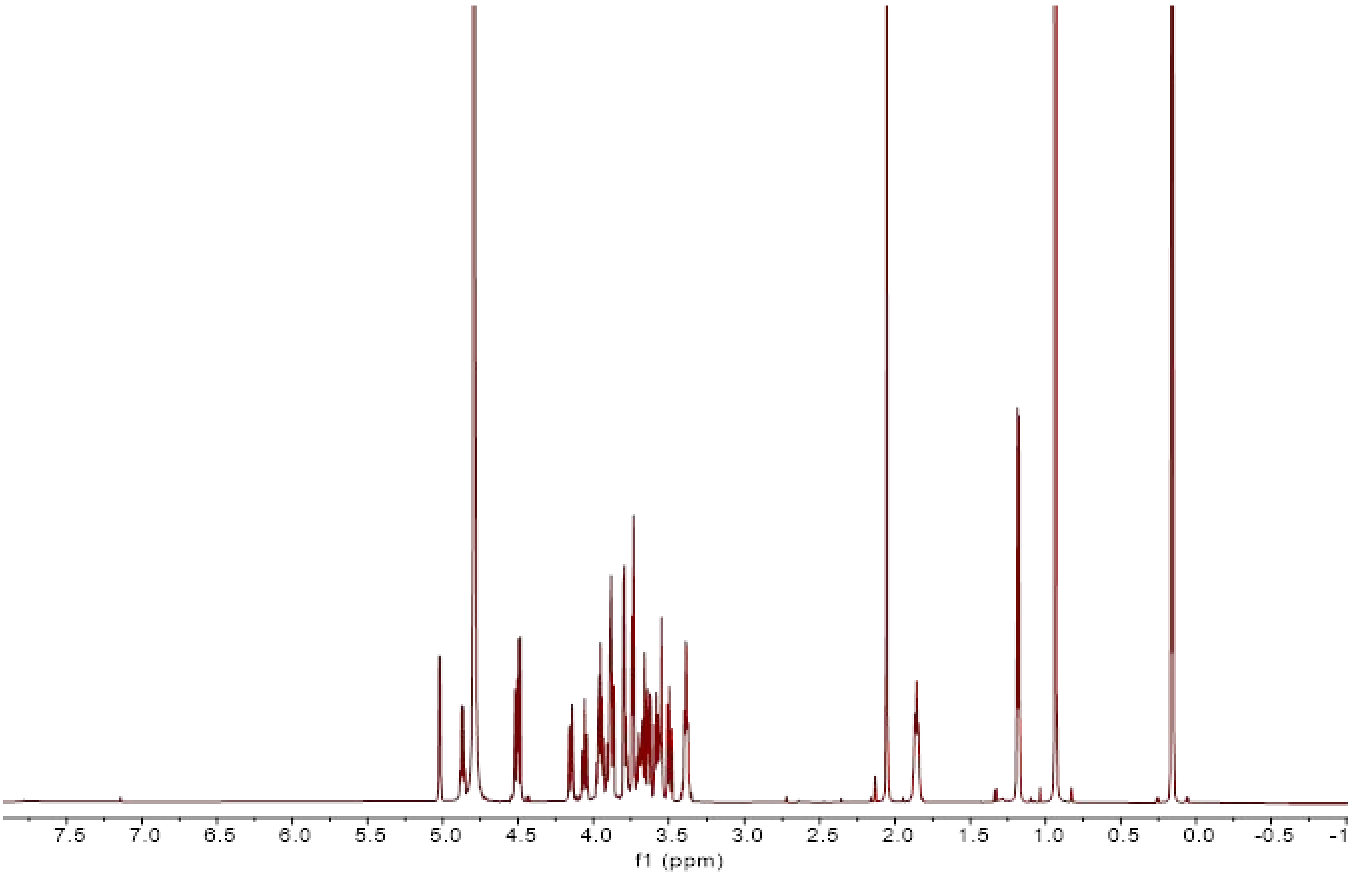

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

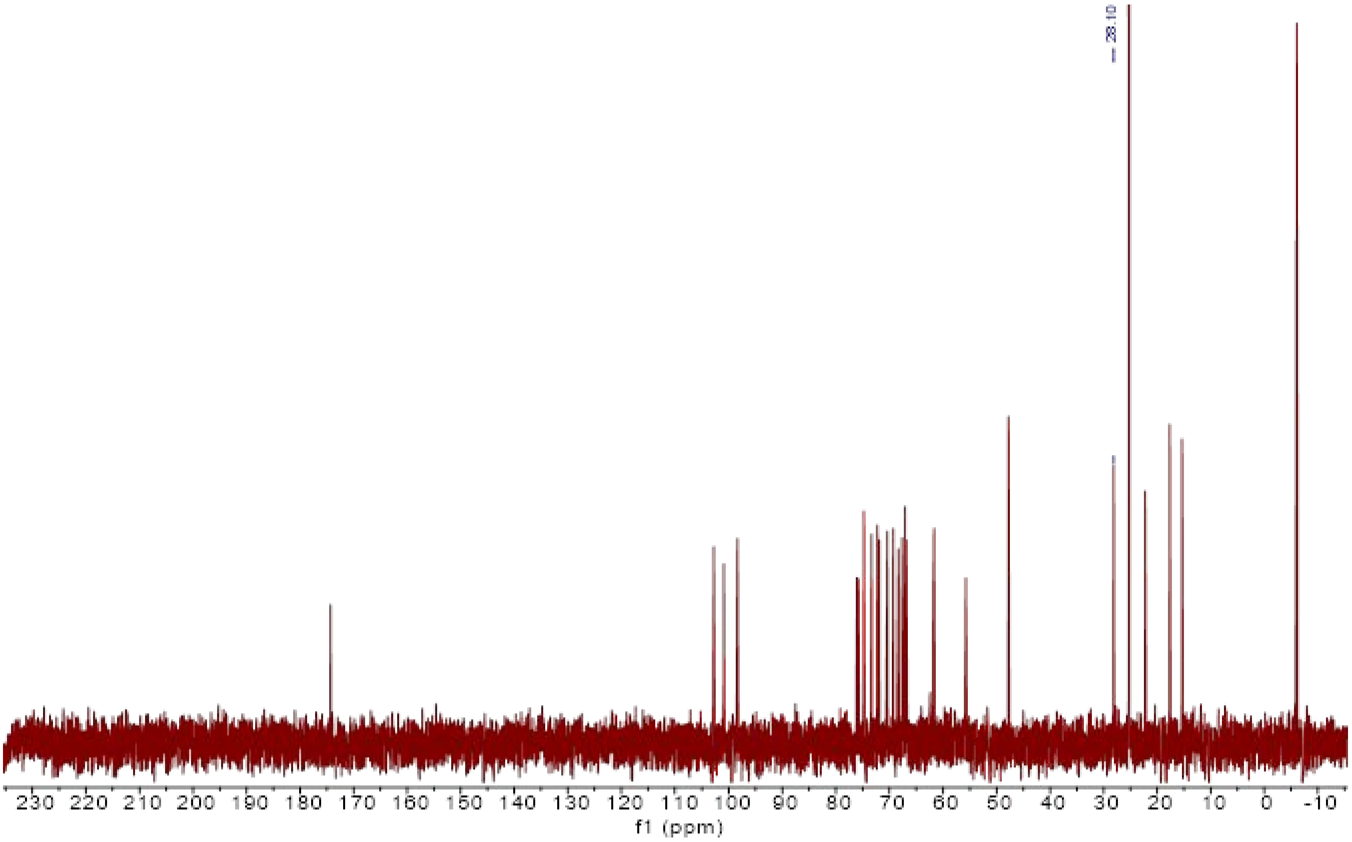

f2 (ppm)
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

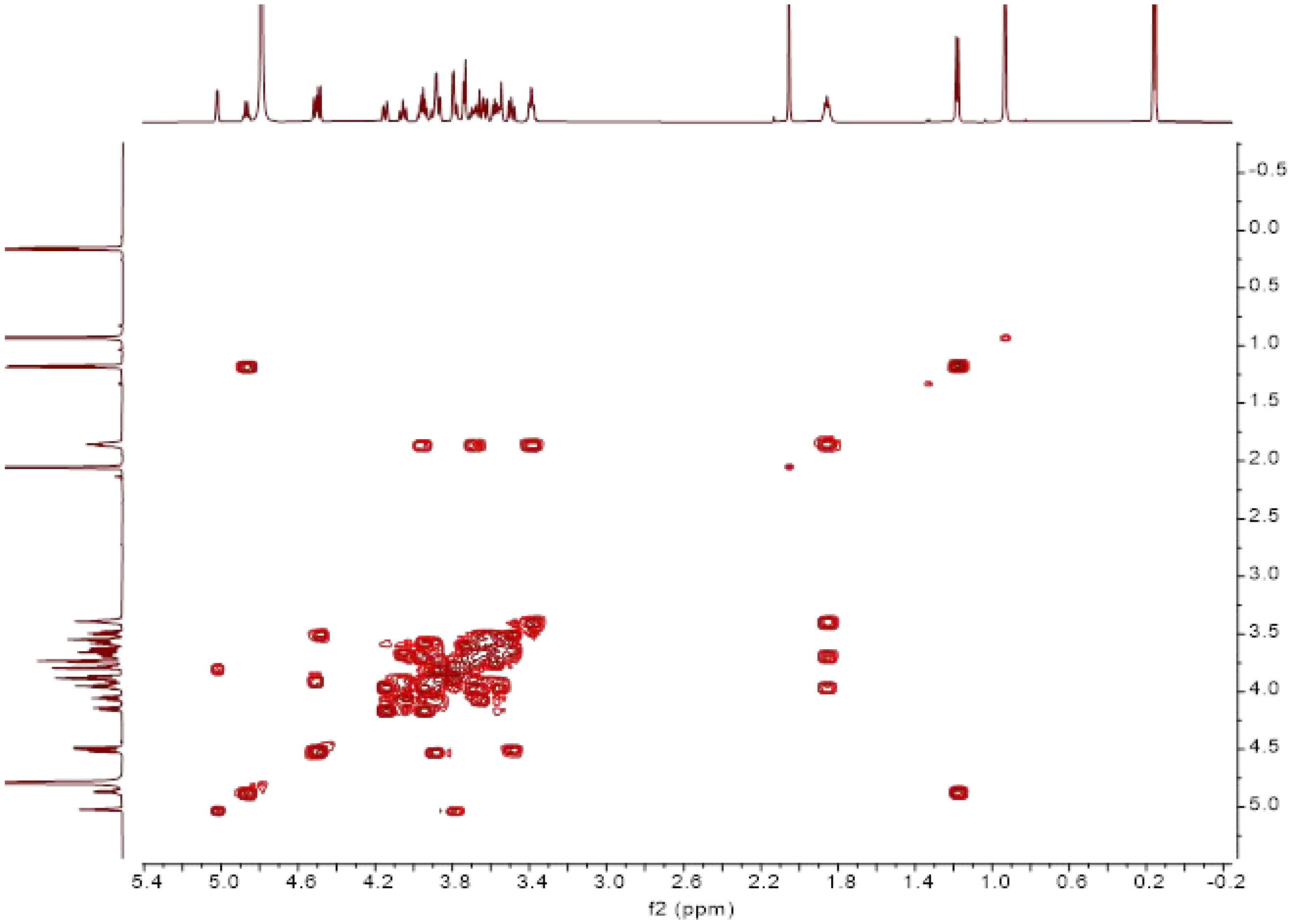

f2 (ppm)
f1 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
10
20
30
40
50
60
70
80
90
100

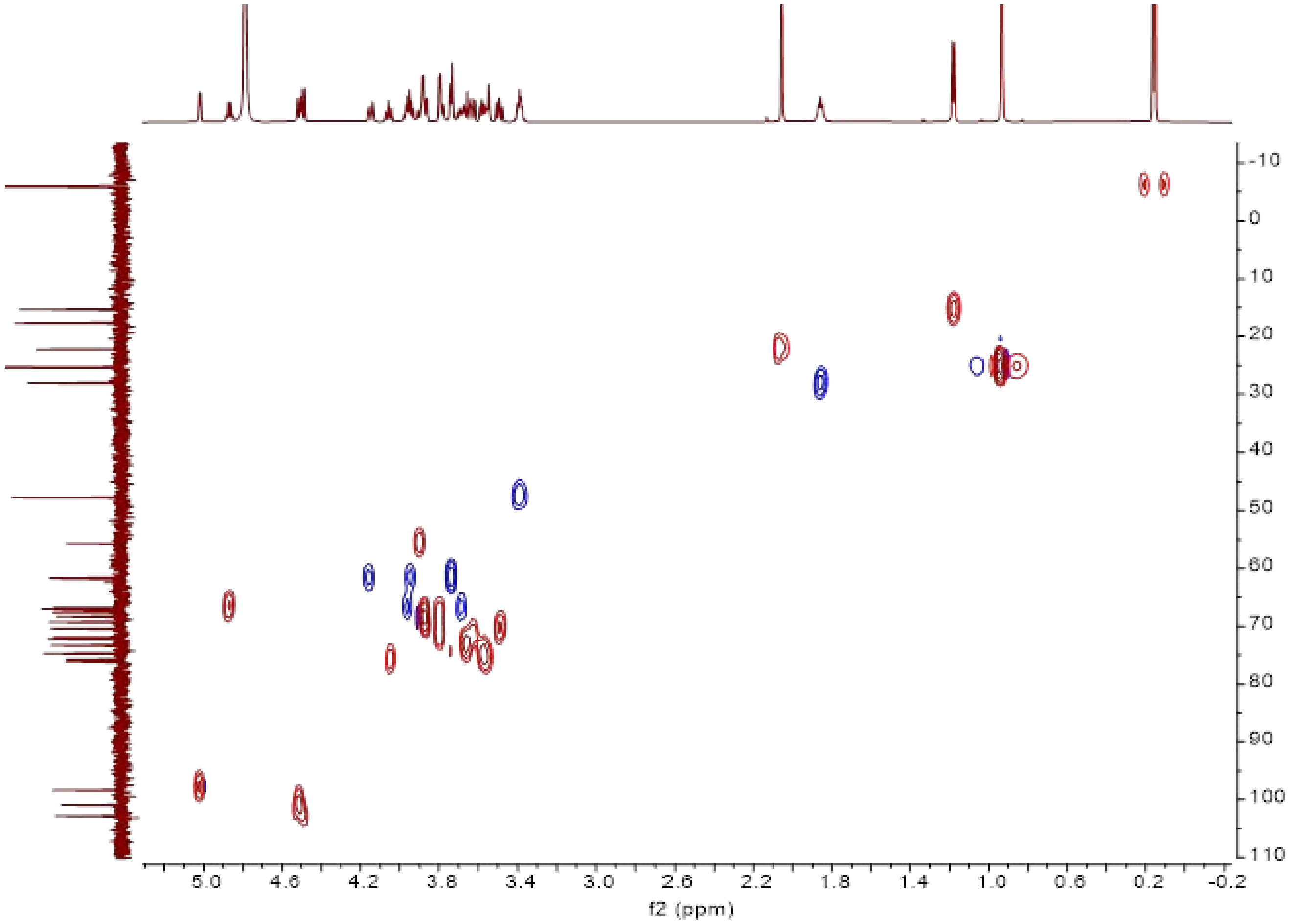

OH
OH
NHAc
HO
O
O
O
O
O
N3
OH
OTBDMS
O
OH
OH
OH

99


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


28.10
230
220
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)


5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
f2 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)