Synthesis of a Lewis b hexasaccharide thioglycoside donor and its use towards an extended mucin core Tn heptasaccharide structure and a photoreactive biotinylated serine linked hexasaccharide

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List of supplementary data contents

Experimental Section

General methods

The ^{1}H / ^{13}C NMR spectra (δ in ppm, relative to TMS in $CDCl_3$ and relative to solvent peak in CD_2Cl_2) were recorded with Varian spectrometers (400/100 MHz, 500/125 MHz or 600/150 MHz) at 25 °C. Assignments were aided by ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments. HRMS spectra were recorded on a micromass LCT instrument from Waters. Optical rotations were measured on a Perkin Elmer polarimeter with a Na lamp (589 nm) at 20 °C and are not corrected. TLC was carried out on precoated 60 F254 silica gel alumina plates (Merck) using UV-light, H_2SO_4 (10% in ethanol) and/or ninhydrin-solution (ninhydrin/CH_3COOH/ethanol [0.3:3:100 w/v/v]. Flash chromatography was performed on silica gel (Apollo scientific, pore size 60 Å, particle size 40-63 µm) or *via* pre-packed columns (Biotage AB, particle size 50 µm) on a Biotage SP4 system. Size exclusion chromatography was performed using Biogel P2 (Biorad, < 45 µm bead size, 100-1800 MW) with H_2O-*n*-butanol (99:1) as eluent.

(2,6-di-O-Benzyl-3-O-(2-naphthylmethyl)-β-D-galactopyranosyl)-(1→4)-2,3:5,6-di-O-isopropylidene-β-D-glucose dimethyl acetal (3) A mixture of **2**[23,24] (23.7 g, 36.5 mmol) and dibutyltin oxide (12.3 g, 49.3 mmol) were refluxed in toluene (1.0 L) for 2 h using a Dean-Stark apparatus for continuous azeotrophic distillation of water. Tetrabutylammonium bromide (15.9 g, 49.3 mmol) and 2-(bromomethyl)naphthalene (8.88 g, 40.2 mmol) were added and the reaction mixture was refluxed for another 2 h. EtOAc (400 mL) was added and the mixture washed with H_2O (300 mL), 10% aq KF (3 x 250 mL) and saturated aq NaCl (250 mL) respectively. The organic layer was dried over $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (toluene-EtOAc, 4:1 to 7:2, v/v) gave **3** (23.3 g, 81%) as a colourless solid. R_f 0.67 (toluene-EtOAc 1:1); $[\alpha]_D^{20}$ +6.4 (*c* 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 4H, Ar), 7.49 – 7.26 (m, 13H, Ar), 4.93 (d, J_{gem} = 11.1 Hz, 1H, C*H*$_2$Ph), 4.89 – 4.82 (m, 2H, C*H*$_2$NAP), 4.72 (d, J_{gem} = 11.1 Hz, 1H, C*H*$_2$Ph), 4.69 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1^{I}), 4.59 – 4.50 (m, 3H, C*H*$_2$Ph, H-2^{II}), 4.33 (d, $J_{1,2}$ = 6.3 Hz, 1H, H-1^{II}), 4.31 – 4.27 (m, 1H, H-5^{I}), 4.15 (dd, J_{gem} = 8.6 Hz, $J_{5,6a}$ = 6.2 Hz, 1H, H-6a^{I}), 4.11 – 4.05 (m, 2H, H-4^{II}, H-3^{II}), 4.04 – 4.01 (m, 1H, H-4^{I}), 3.96 (dd, J_{gem} = 8.6 Hz, $J_{5,6b}$ = 6.3 Hz, 1H, H-6b^{I}), 3.75 (dd, *J* = 9.5 Hz, *J* = 7.0 Hz, 1H, H-6a^{II}), 3.68 – 3.60 (m, 2H, H-2^{I}, H-6b^{II}), 3.56 – 3.51 (m, 2H, H-5^{II}, H-3^{I}), 3.32 (2 x s, 6H, OC*H*$_3$), 2.52 (d, *J* = 1.8 Hz, 1H, OH^{II}), 1.42, 1.40, 1.39 and 1.32 (s, 12H, CC*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.0, 135.3, 133.3, 133.0, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 126.6, 126.1, 126.0 and 125.8 (Ar), 110.3 and 108.5 (*C*CH$_3$), 105.2 (C-1^{II}), 103.2 (C-1^{I}), 80.8 (C-3^{I}), 79.5 (C-2^{I}), 77.9 C-3^{II}), 77.6 (C-5^{I}), 75.4 (*C*H$_2$Ph), 74.9 (C-2^{II}), 74.4 (C-4^{I}), 73.7 (*C*H$_2$Ph), 72.8 (C-5^{II}), 72.4 (*C*H$_2$NAP), 68.6 (C-6^{II}), 66.6 (C-4^{II}), 65.6 (C-6^{I}), 55.5 and 52.8 (*C*H$_3$O), 27.6, 26.8, 26.7, 25.4 (C*C*H$_3$); ES-HRMS calcd for $C_{45}H_{56}O_{12}$ $[Na]^+$ 811.3669 found 811.3648.

(2,4,6-tri-O-Benzyl-3-O-(2-naphthylmethyl)-β-D-galactopyranosyl)-(1→4)-2,3:5,6-di-O-isopropylidene-β-D-glucose dimethyl acetal (4) NaH (2.29 g, 57.5 mmol) was added portion-wise to an ice-cold solution of **3** (22.6 g, 28.6 mmol) in DMF (200 mL) and the mixture was stirred for 10 min. Benzyl bromide (6.81 mL, 57.3 mmol) was added and the mixture stirred for 3 h while allowing to warm to room temperature. After completion of the reaction, the mixture was cooled to 5 °C, MeOH (10 mL) was added carefully, and the resulting solution stirred for further 10 min. H_2O (700 mL) was added and the mixture extracted with EtOAc (1300 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using a gradient elution (toluene-EtOAc) to afford **4** (22.5 g, 89%) as a colourless solid. R_f 0.55 (toluene-EtOAc 4:1); $[\alpha]_D^{20}$ +19.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H, Ar), 7.78 – 7.74 (m, 2H, Ar), 7.71 – 7.67 (m, 1H, Ar), 7.47 – 7.39 (m, 3H, Ar), 7.38 – 7.34 (m, 2H, Ar), 7.33 – 7.22 (m, 13H, Ar), 4.99 (d, J_{gem} = 11.8 Hz, 1H, C*H*$_2$Ph), 4.92 (d, J_{gem} = 11.1 Hz, 1H, C*H*$_2$Ph), 4.89 – 4.83 (m, 2H, C*H*$_2$NAP), 4.75 (d, J_{gem} = 11.1 Hz, 1H, C*H*$_2$Ph), 4.67 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1^{II}), 4.61 (d, J_{gem} = 11.8 Hz, 1H, C*H*$_2$Ph), 4.56 (dd, $J_{2,3}$ = 7.4 Hz, $J_{1,2}$ = 6.5 Hz, 1H, H-2^{I}), 4.43 – 4.36 (m, 2H, C*H*$_2$Ph), 4.33 (d, $J_{1,2}$ = 6.5 Hz, 1H, H-1^{I}), 4.28 (m, 1H, H-5^{I}), 4.16 (dd, *J* = 8.7, *J* = 6.0 Hz, 1H, H-6a^{I}), 4.05 (dd, $J_{2,3}$ = 7.4 Hz, $J_{3,4}$ = 1.0 Hz, 1H, H-3^{I}), 4.01 – 3.98 (m, 1H, H-4^{I}), 3.98 – 3.94 (m, 2H, H-4^{II}, H-6b^{I}), 3.81 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 7.6 Hz, 1H, H-2^{II}), 3.61 – 3.52 (m, 3H, H-6a^{II}, H-5^{II}, H-3^{II}), 3.48 (dd, *J* = 8.0, *J* = 4.4 Hz, 1H, H-6b^{II}), 3.29 and 3.27 (s, 6H, OC*H*$_3$), 1.44, 1.41, 1.39 and 1.32 (s, 12H, CC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 139.0, 138.0, 136.2, 133.5, 133.1, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 126.3, 126.2, 126.0 and 125.8 (Ar), 110.3 and 108.7 (*C*CH$_3$), 105.3 (C-1^{I}), 103.5 (C-1^{II}), 82.4 (C-5^{II}), 80.3 (C-2^{II}), 78.2 (C-3^{I}), 77.7 (C-5^{I}), 75.5 (*C*H$_2$Ph), 74.7 (*C*H$_2$Ph), 74.6 (C-2^{I}), 74.4 (C-4^{I}), 74.0 (C-4^{II}), 73.7 (*C*H$_2$Ph), 73.2 (C-3^{II}), 73.1 (*C*H$_2$NAP), 68.3 (C-6^{II}), 66.0 (C-6^{I}), 55.5 and 52.4 (O*C*H$_3$), 27.7, 26.9, 26.8 and 25.7 (C*C*H$_3$); ES-HRMS calcd for $C_{52}H_{62}O_{12}$ $[Na]^+$ 901.4139, found 901.4107.

(2,4,6-tri-O-Benzyl-3-O-(2-naphthylmethyl)-β-D-galactopyranosyl)-(1→4)-1,2,3,6-tetra-O-acetyl-D-glucopyranose (5) A mixture of compound **4** (22.5 g, 25.6 mmol) in 80% acetic acid (500 mL) was stirred at 70 °C for 20 h. After completion of the reaction the solvent was removed by co-evaporation (2 x 100 mL). The residue was dissolved in acetic anhydride (100 mL) before being added to a refluxing solution of sodium acetate (12.0 g, 146 mmol) in acetic anhydride (100 mL), and the resulting mixture was refluxed for 30 min. Progress of the reaction was continuously monitored by TLC and after completion the reaction mixture was allowed to cool before being poured into ice-water (500 mL). The mixture was extracted with CH_2Cl_2 (500 mL) and the organic layer washed with water (2 x 500 mL) and then carefully washed with saturated aq Na_2CO_3 until the gas development had ceased. The organic layer was dried over $MgSO_4$, filtered and concentrated. Flash chromatography (toluene-EtOAc) afforded **5** (19.5 g, 83%, α/β 1:3) as a colourless foam. R_f 0.61 (toluene-EtOAc 2:1); β-anomer (assigned from mixture) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.68 (m, 4H, Ar), 7.48 – 7.38 (m, 3H, Ar), 7.36 – 7.23 (m, 15H, Ar), 5.67 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1^I), 5.21 (m, 1H, H-3^I), 5.06 – 5.01 (m, 1H, H-2^I), 4.97 (d, J_{gem} = 11.5 Hz, 1H, CH_2Ph), 4.88 – 4.74 (m, 4H, CH_2NAP, CH_2Ph), 4.56 (d, J_{gem} = 11.5 Hz, 1H, CH_2Ph), 4.47 – 4.36 (m, 3H, CH_2Ph, H-6a^I), 4.25 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1^{II}), 4.18 (dd, J_{gem} = 12.1 Hz, $J_{5,6b}$ = 5.3 Hz, 1H, H-6b^I), 3.92 – 3.89 (m, 1H, H-4^{II}), 3.85 – 3.79 (m, 1H, H-4^I), 3.72 (dd, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 7.6 Hz, 1H, H-2^{II}), 3.66 (ddd, J = 9.9 Hz, J = 5.3 Hz, J = 2.0 Hz, 1H, H-5^I), 3.60 – 3.45 (m, 4H, H-6a,b^{II}, H-3^{II}, H-5^{II}), 2.08, 2.02, 1.97 and 1.88 (4 s, 12H, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 170.4, 169.7 and 169.1 (COCH$_3$), 139.0, 138.8, 138.0, 136.0, 133.5, 133.2, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 126.4, 126.3, 126.1 and 125.8 (Ar), 103.1 (C-1^{II}), 92.0 (C-1^I), 82.4 (C-3^{II}), 80.0 (C-2^{II}), 75.6 (CH_2Ph), 74.8 (CH_2Ph), 74.4 (2C, C-4^I, C-5^I), 73.9 (C-4^{II}), 73.7 (2C, CH_2Ph, C-5^{II}), 73.2 (CH_2NAP), 72.8 (C-3^I), 70.6 (C-2^I), 68.6 (C-6^{II}), 62.2 (C-6^I), 21.1, 21.0, 20.9 and 20.8 (COCH$_3$); ES-HRMS calcd for $C_{52}H_{56}O_{15}$ $[Na]^+$ 943.3517, found 943.3470.

Ethyl (2,4,6-tri-O-benzyl-3-O-(2-naphtylmethyl)-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (6) EtSH (0.375 mL, 5.07 mmol) was added to an ice-cooled solution of **5** (1.15g, 1.27 mmol) in dry DCE (30 mL). The mixture was stirred for 15 min before BF_3OEt_2 (0.482 mL, 3.80 mmol) was added dropwise. The mixture was stirred at 0 °C for 90 min during which time the reaction was monitored by TLC. When no further progress of the reaction was observed the reaction was quenched with Et_3N (0.400 mL), diluted with CH_2Cl_2 (50 mL) and subsequently washed with saturated aq $NaHCO_3$, 1 M aq HCl, saturated aq $NaHCO_3$ and water (50 mL each). The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by flash chromatography on silica gel (toluene-EtOAc 7:1 to 3:1) to obtain **6** (0.637 g, 54%) as a colourless solid and recovered starting material (0.376 g, 33%). R_f 0.44 (toluene-EtOAc 4:1); $[\alpha]_D^{20}$ +23.2 (*c* 1.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.68 (m, 4H, Ar), 7.48 – 7.43 (m, 2H, Ar), 7.42 – 7.39 (m, 1H, Ar), 7.36 – 7.22 (m, 15H, Ar), 5.20 – 5.14 (m, 1H, H-3^I), 5.00 – 4.91 (m, 2H, CH_2Ph, H-2^I), 4.88 – 4.74 (m, 4H, CH_2NAP, CH_2Ph), 4.56 (d, J_{gem} = 11.5 Hz, 1H, CH_2Ph), 4.43 (m, 4H, H-1^I, CH_2Ph, H-6a^I), 4.25 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1^{II}), 4.16 (dd, J_{gem} = 12.0, $J_{5,6b}$ = 5.7 Hz, 1H, H-6b^I), 3.92 – 3.88 (m, 1H, H-4^{II}), 3.79 – 3.69 (m, 2H, H-4^I, H-2^{II}), 3.59 – 3.45 (m, 5H, H-6a,b^{II}, H-5^I, H-3^{II}, H-5^{II}), 2.72 – 2.58 (m, 2H, CH_2CH$_3$), 2.04, 1.97 and 1.88 (s, 9H, COCH_3), 1.24 (t, J_{CH2CH3} = 7.4 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.5 and 169.9 (COCH$_3$), 139.0, 138.9, 138.0, 136.1, 133.5, 133.2, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 126.4, 126.3, 126.1 and 125.8 (Ar), 103.2 (C-1^{II}), 83.6 (C-1^I), 82.4 (C-3^{II}), 80.0 (C-2^{II}), 77.6 (C-5^I), 75.6 (CH_2NAP), 74.9 (C-4^I), 74.8 (CH_2Ph), 74.0 (C-3^I), 73.9 (C-4^{II}), 73.7 (CH_2Ph), 73.6 (C-5^{II}), 73.2 (CH_2Ph), 70.3 (C-2^I), 68.6 (C-6^{II}), 62.8 (C-6^I), 24.4 (CH_2CH$_3$), 21.0 (3C, COCH$_3$), 15.15 (CH$_2$CH_3); ES-HRMS calcd for $C_{52}H_{58}O_{13}S$ $[Na]^+$ 945.3496, found 945.3476.

Ethyl (2,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside. (7) DDQ (0.686 g, 3.02 mmol) was added to a solution of **6** (930 mg, 1.01 mmol) in CH_2Cl_2 (20 mL) and isobutanol (5 mL) and the mixture stirred for 4 h. The solvent was then evaporated and the residue dissolved in CH_2Cl_2 (50 mL), before being washed with saturated aq $NaHCO_3$ (3 x 40 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated under reduced pressure and the residue purified by flash chromatography on silica gel (toluene-EtOAc, 4:1 to 2:1, v/v) to afford **7** (0.623 g, 79%) as a colourless solid. R_f 0.32 (toluene-EtOAc 2:1); $[\alpha]_D^{20}$ - 9.8° (*c* 0.63 $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 15H, Ar), 5.21 – 5.17 (m, 1H, H-3^I), 4.98 – 4.93 (m, 1H, H-2^I), 4.81 – 4.74 (m, 2H, CH_2Ph), 4.66 (d, J_{gem} = 11.6 Hz, 1H, CH_2aPh), 4.56 (d, J_{gem} = 11.6 Hz, 1H, CH_2bPh), 4.51 – 4.41 (m, 4H, CH_2Ph, H-1^I, H-6a^I), 4.23 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1^{II}), 4.16 (dd, J_{gem} = 12.0 Hz, $J_{5,6b}$ = 5.5 Hz, 1H, H-6b^I), 3.86 – 3.83 (m, 1H, H-4^{II}), 3.83 – 3.77 (m, 1H, H-4^I), 3.62 – 3.52 (m, 5H, H-6a,b^{II}, H-5^{II}, H-3^{II}, H-5^I), 3.43 (dd, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 7.6 Hz, 1H, H-2^{II}), 2.73 – 2.58 (m, 2H, CH_2CH$_3$), 2.12 (d, J = 5.5 Hz, 1H, OH^{II}), 2.05, 2.00 and 1.90 (s, 9H, COCH_3), 1.25 (t, J_{CH2CH3} = 7.4 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.5 and 169.8 (CH$_3$$C$O), 138.7, 138.6, 137.9, 128.7, 128.6, 128.1, 128.0 and 127.9 (Ar), 102.9 (C-1^{II}), 83.6 (C-1^I), 80.3 (C-2^{II}), 77.4 (C-5^I (from HSQC)) 75.9 (C-4^{II}), 75.2

(2C, *C*H_2Ph), 74.8 (C-4^{I}), 74.2 and 73.9 (2C) (C-3^{II}, C-3^{I}, C-5^{II}), 73.7 *C*H_2Ph, 70.3 (C-2^{I}), 68.6 (C-6^{II}), 62.8 C-6^{I}), 24.5 (*C*H_2CH$_3$), 21.0 (3C, CO*C*H$_3$), 15.1 (CH$_2$*C*H$_3$); ES-HRMS calcd for $C_{41}H_{50}O_{13}S$ $[Na]^+$ 805.2870, found 805.2873.

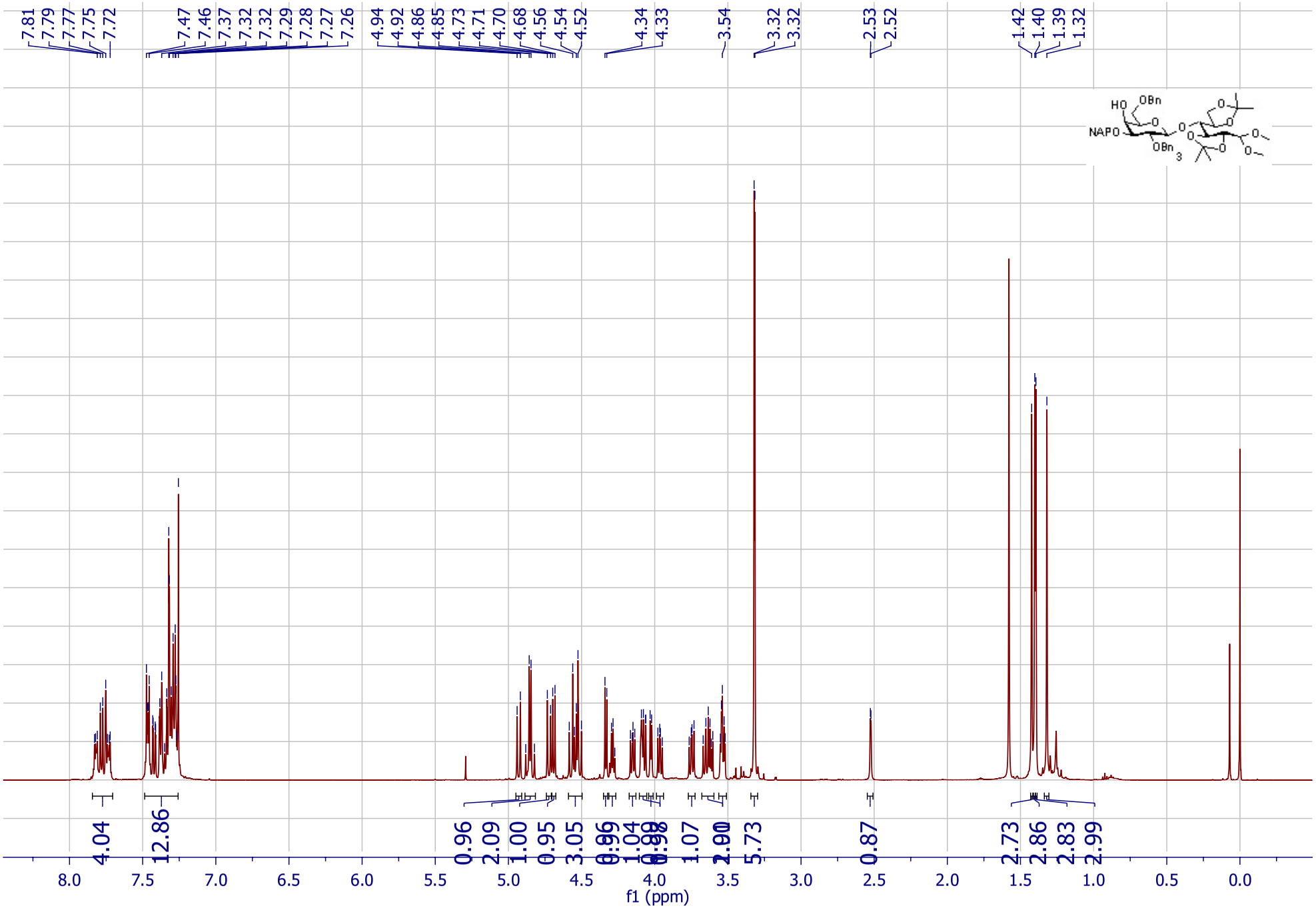
4,6-O-Benzylidene-3-O-p-methoxybenzyl-2-deoxy-2-phthalamido-β-D-glucopyranosyl trichloroacetimidate (9) NIS (7.56 g, 33.6 mmol) was added to a solution of **8**[27,28](9.44 g, 16.8 mmol) in CH_3CN-H_2O 10:1 (220 mL) and the mixture stirred for 1 h. After completion of the reaction EtOAc (200 mL) was added, the solution washed with saturated aq $NaHCO_3$ (2 x 50 mL) and the combined aqueous layers extracted with EtOAc (2 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and the material was dried overnight. The crude material was dissolved in DCE (50 mL), the mixture cooled to 0 °C and trichloroacetonitrile (20.2 mL, 0.202 mol) and DBU (1.01 mL, 6.72 mmol) were added subsequently. The mixture was stirred for 30 min and then directly applied on a silica gel column (toluene with 0.1% Et_3N to toluene-EtOAc 6:1 with 0.1% Et_3N, v/v) to afford **9** (10.2 g, 92%) as a colourless solid. R_f 0.59 (toluene-EtOAc 4:1); $[\alpha]_D^{20}$ +72.1° (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H, NH), 7.75 – 7.65 (m, 4H, Ar), 7.56 – 7.51 (m, 2H, Ar), 7.43 – 7.35 (m, 3H, Ar), 6.95 – 6.90 (m, 2H, Ar), 6.49 (d, $J_{1,2}$ = 8.7 Hz, 1H, H-1), 6.41 – 6.36 (m, 2H, Ar), 5.64 (s, 1H, C*H*-Ph), 4.74 (d, J_{gem} = 12.3 Hz, 1H, CH_2*a*C$_6$H$_4$OCH$_3$), 4.54 (dd, *J* = 10.3 Hz, *J* = 8.5 Hz, 1H, H-3), 4.51 – 4.43 (m, 3H, H-6a, H-2, CH_2*b*C$_6$H$_4$OCH$_3$), 3.93 – 3.82 (m, 3H, H-6b, H-4, H-5), 3.62 (s, 3H. C$_6$H$_4$OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4 (N*C*O(Phth)), 160.9, 158.9, 137.2, 133.9, 131.4, 130.0, 129.7, 129.1, 128.3, 126.1, 123.3 and 113.4 (Ar), 101.5 (*C*H-Ph), 94.4 (C-1), 82.7 (C-4), 74.0 (C-3), 73.8 (*C*H_2C$_6$H$_4$OCH$_3$), 68.6 (C-6), 67.0 (C-5), 54.9 (C$_6$H$_4$O*C*H$_3$), 54.8 (C-2); ES-HRMS calcd for $C_{31}H_{27}N_2O_8Cl_3$ $[Na]^+$ 683.0731 found 683.0741

Ethyl 3,4,6-tri-O-benzyl-2-O-chloroacetyl-1-thio-β-D-galactopyranoside (14) To a solution of **13**[34] (1.100 g, 2.050 mmol) in 50 mL dry MeOH, sodium methoxide (1M, in MeOH) was added until pH = 13 was reached and the mixture stirred for 72 h. Upon completion of reaction the mixture was neutralized with Dowex 50 W+ ion exchange resin, filtered, concentrated, and dried *in vacuo* to afford the respective deacetylated intermediate (1.004 g, 99%) as a colourless oil. Chloroacetyl chloride (0.181 mL, 2.26 mmol) was added to an ice-cooled solution of the crude (560 mg, 1.13 mmol) in CH_2Cl_2-pyridine 14:1 (28.3 mL) which was stirred for 30 min while allowing to warm to room temperature. After completion of the reaction, the mixture was diluted with CH_2Cl_2 (25 mL) and washed with saturated aq $NaHCO_3$ (50 mL), H_2O (50 mL) and saturated aq $CuSO_4$ (50 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The crude material was purified by flash chromatography (toluene-EtOAc) to afford **14** (0.575 g, 89%) as a colourless solid. R_f 0.39 (toluene-EtOAc 20:1); $[\alpha]_D^{20}$ +6° (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 15H, Ar), 5.47 – 5.40 (m, 1H, H-2), 4.93 (d, J_{gem} = 11.6 Hz, 1H, CH_2-Ph), 4.67 (d, J_{gem} = 12.2 Hz, 1H, CH_2-Ph), 4.58 (d, J_{gem} = 11.6 Hz, 1H, CH_2-Ph), 4.51 (d, J_{gem} = 12.2 Hz, 1H, CH_2-Ph), 4.48 – 4.40 (m, 2H, CH_2-Ph), 4.35 (d, $J_{1,2}$ = 9.9 Hz, 1H, H-1), 4.03 – 3.88 (m, 3H, H-4, COCH_2Cl), 3.62 – 3.60 (m, 3H, H-5, H-6a,b), 3.57 (dd, *J* = 9.6, *J* = 2.8 Hz, 1H, H-3), 2.77 – 2.59 (m, 2H, SCH_2CH$_3$), 1.22 (t, J_{CH2CH3} = 7.5 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (*C*OCH$_2$Cl), 138.4, 137.8, 137.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.6 and 127.5 (Ar), 83.2 (C-1), 81.2 (C-3), 77.5 (C-5), 74.5 (*C*H$_2$-Ph), 73.6 (*C*H$_2$-Ph), 72.9 (C-4), 72.1 (*C*H$_2$-Ph), 71.5 (C-2), 68.4 (C-6), 40.9 (CO*C*H$_2$Cl), 23.5 (S*C*H$_2$CH$_3$), 14.8 (SCH$_2$*C*H$_3$); ES-HRMS calcd for $C_{31}H_{35}O_6SCl$ $[Na]^+$ 593.1741 found 593.1755.

3,4,6-Tri-O-benzyl-2-O-chloroacetyl-D-galactopyranosyl trichloroacetimidate (15) *N*-bromosuccinimide (1.86 g, 10.4 mmol) was added to a solution of **14** (2.98 g, 5.22 mmol) in CH_3CN-H_2O (10:1, 110 mL) and the mixture stirred for 30 min. The mixture was then diluted with CH_2Cl_2 (100 mL) and washed with saturated aq Na_2SO_3 (100 mL) and saturated aq $NaHCO_3$, respectively. The organic layer was dried over $MgSO_4$, filtered, concentrated under reduced pressure and the crude purified on silica gel (toluene-EtOAc) and directly used for the next step without further characterisation. Trichloroacetonitrile (4.22 mL, 42.1 mmol) and DBU (0.254 mL, 1.68 mmol) were subsequently added to an ice-cold solution of the obtained material (2.16 g) in DCE (15 mL) under a N_2-atmosphere and the mixture was stirred for 30 min. The solution was directly applied on a column with silica gel (Eluent: toluene-EtOAc 30:1 to 20:1 + 0.1 % Et_3N), which gave **15** (1.67 g, 47%) as pure α- anomer and a mixture of α and β anomers (0.169 g, 5%) over two steps. α-anomer: R_f 0.51 (toluene-EtOAc 10:1); $[\alpha]_D^{20}$ +62.9° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H, N*H*), 7.39 – 7.13 (m, 15H, Ar), 6.54 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 5.57 (dd, $J_{2,3}$ = 10.4, $J_{1,2}$ = 3.5 Hz, 1H, H-2), 4.96 (d, J_{gem}= 11.3 Hz, 1H, CH_2-Ph), 4.73 (d, J_{gem} = 12.1 Hz, 1H, CH_2-Ph), 4.61 (m, 2H, CH_2-Ph), 4.50 – 4.40 (m, 2H, CH_2-Ph), 4.20 – 4.15 (m, 1H, H-5), 4.14 – 4.10 (m, 1H, H-4), 4.06 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 2.7 Hz, 1H, H-3), 3.91 (s, 2H, COCH_2Cl), 3.66 (dd, J_{gem} = 9.2, $J_{5,6a}$ = 7.8 Hz, 1H, H-6a), 3.58 (dd, J_{gem} = 9.2, $J_{5,6b}$ = 5.5 Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (*C*OCH$_2$Cl), 160.9 (O*C*(CCl$_3$)NH), 138.1, 137.7, 128.5, 128.3, 128.2, 127.9 and 127.8 (Ar), 94.2 (C-1), 91.4

(OC(*C*Cl_3)NH) 75.6 (C-3), 75.0 (*C*H_2Ph), 73.8 (C-4), 73.6 and 72.5 (*C*H_2Ph), 72.4 (C-5), 71.7 (C-2), 68.0 (C-6), 40.5 (CO*C*H_2Cl); ES-HRMS calcd for $C_{31}H_{31}NO_7Cl_4$ $[Na]^+$ 692.0752 found 692.0771.

2-Azidoethyl 3-O-benzoyl-2-deoxy-2-acetamido-α-D-galactopyranoside (21) To a solution of **20**[37] (1 g, 3.45 mmol) in DMF (20 mL) was subsequently added benzaldehyde dimethylacetal (1.03 mL, 6.89 mmol) and *p*-TsOH x H_2O (0.066 g, 0.345 mmol) and the mixture stirred at room temperature overnight. The reaction was then quenched with Et_3N (0.14 mL), concentrated and co-evaporated with toluene (2 x 10 mL) and the residue dried *in-vacuo*. The crude product was dissolved in pyridine (10 mL), benzoyl chloride (0.600 mL, 5.17 mmol) added and the mixture stirred for 30 min. The mixture was concentrated, dissolved in CH_2Cl_2 (50 mL) and the solution subsequently washed with $NaHCO_3$ (50 mL), H_2O (20 mL) and saturated aq $CuSO_4$. The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated. Flash chromatography afforded a colourless foam (0.813 g). This compound (0.800 g) was dissolved in 80% AcOH (50 mL) and stirred at 85 °C overnight. The mixture was then concentrated and co-evaporated with toluene (2 x 10 mL) and the residue purified by flash chromatography (CH_2Cl_2-MeOH) to give **21** (0.270 g) and recovered fully protected starting material (0.320 g) which corresponds to 34% yield of **21** over 3 steps. R_f 0.34 (CH_2Cl_2-MeOH 9:1); $[\alpha]_D^{20}$ 116.5° (*c* 1.00, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 8.06 – 8.01 (m, 2H, Ar), 7.63 – 7.57 (m, 1H, Ar), 7.49 – 7.44 (m, 2H, Ar), 5.24 (dd, $J_{2,3}$ = 11.4 Hz, $J_{3,4}$ = 3.0 Hz, 1H, H-3), 4.98 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.86 – 4.80 (m, 1H, H-2), 4.28 – 4.25 (m, 1H, H-4), 4.03 – 3.92 (m, 2H, H-5, CH_2*a*-CH_2-N_3), 3.78 – 3.66 (m, 3H, H-6a,b, CH_2*b*-CH_2-N_3), 3.55 – 3.50 (m, 2H, CH_2-CH_2-N_3), 1.88 (s, 3H, NHCOCH_3); ^{13}C NMR (100 MHz, CD_3OD) δ 173.7 (NH*C*OCH_3), 167.9 (*C*OPh), 134.5, 131.4, 131.0 and 129.7 (Ar), 99.5 (C-1), 73.8 (C-3), 72.8 (C-5), 68.2 (*C*H_2-CH_2-N_3), 68.0 (C-4), 62.7 (C-6), 51.9 (CH_2-*C*H_2-N_3), 22.8 (NHCO*C*H_3); ES-HRMS calcd for $C_{17}H_{22}N_4O_7$ $[Na]^+$ 417.1386 found 417.1404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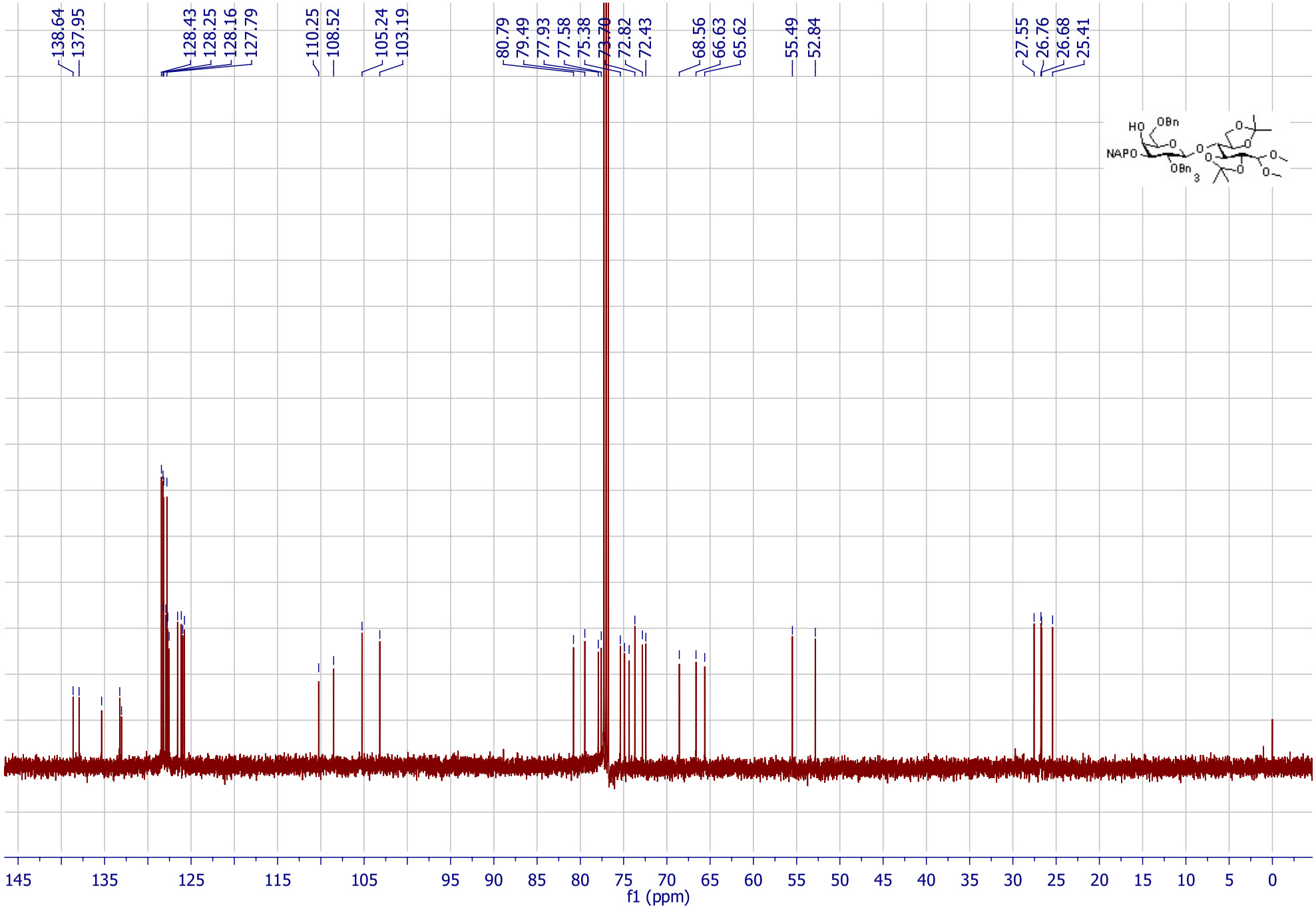
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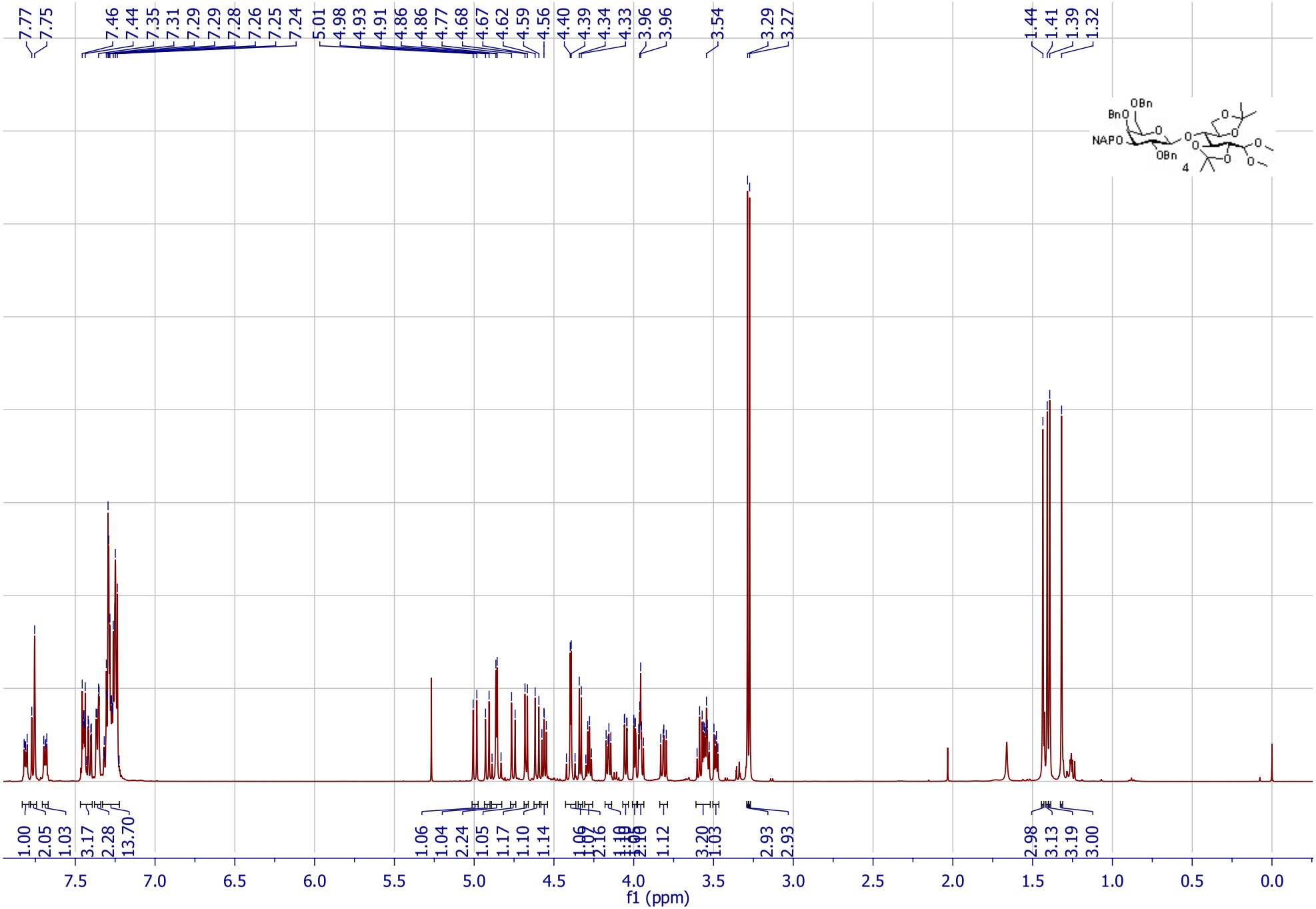
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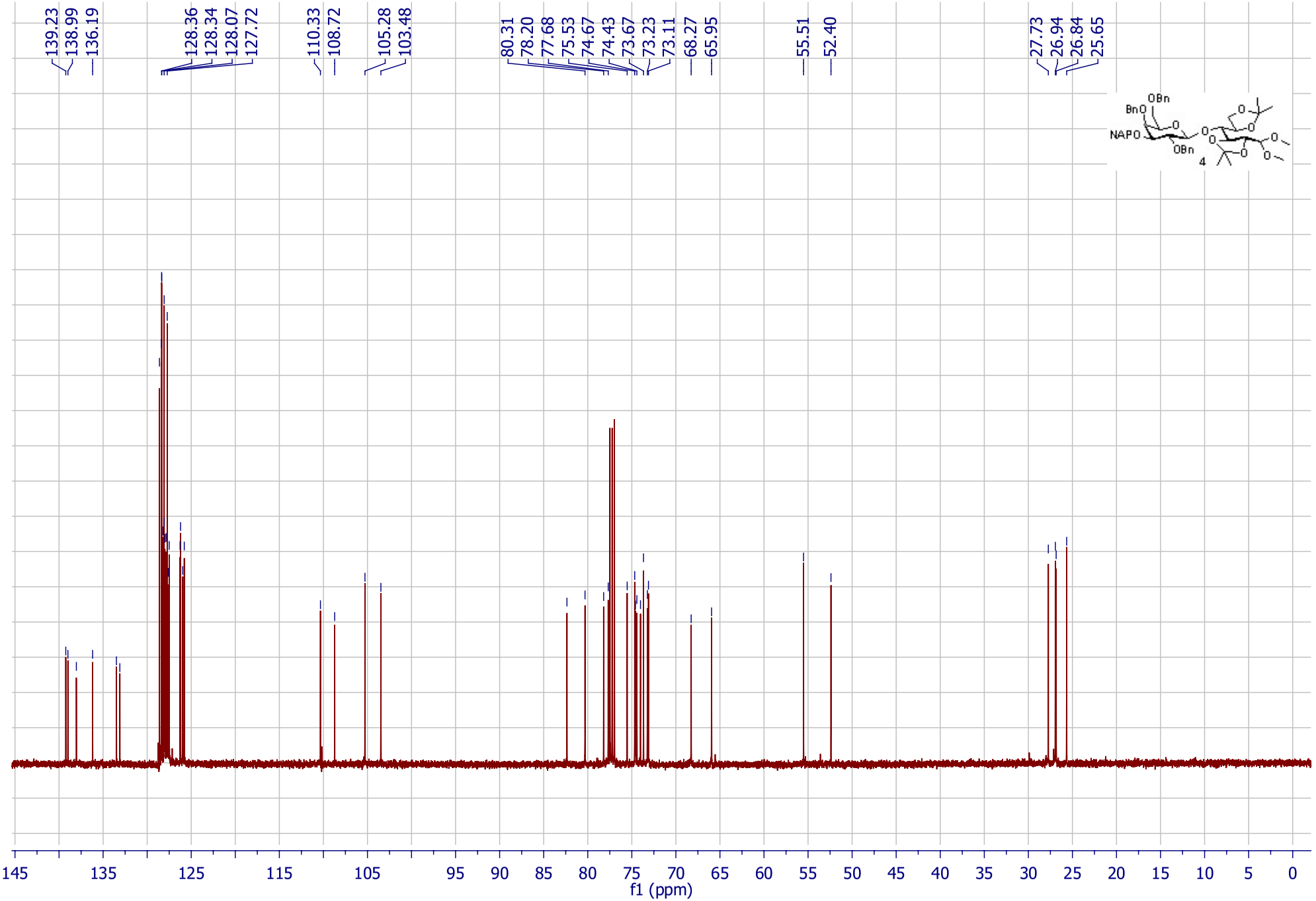
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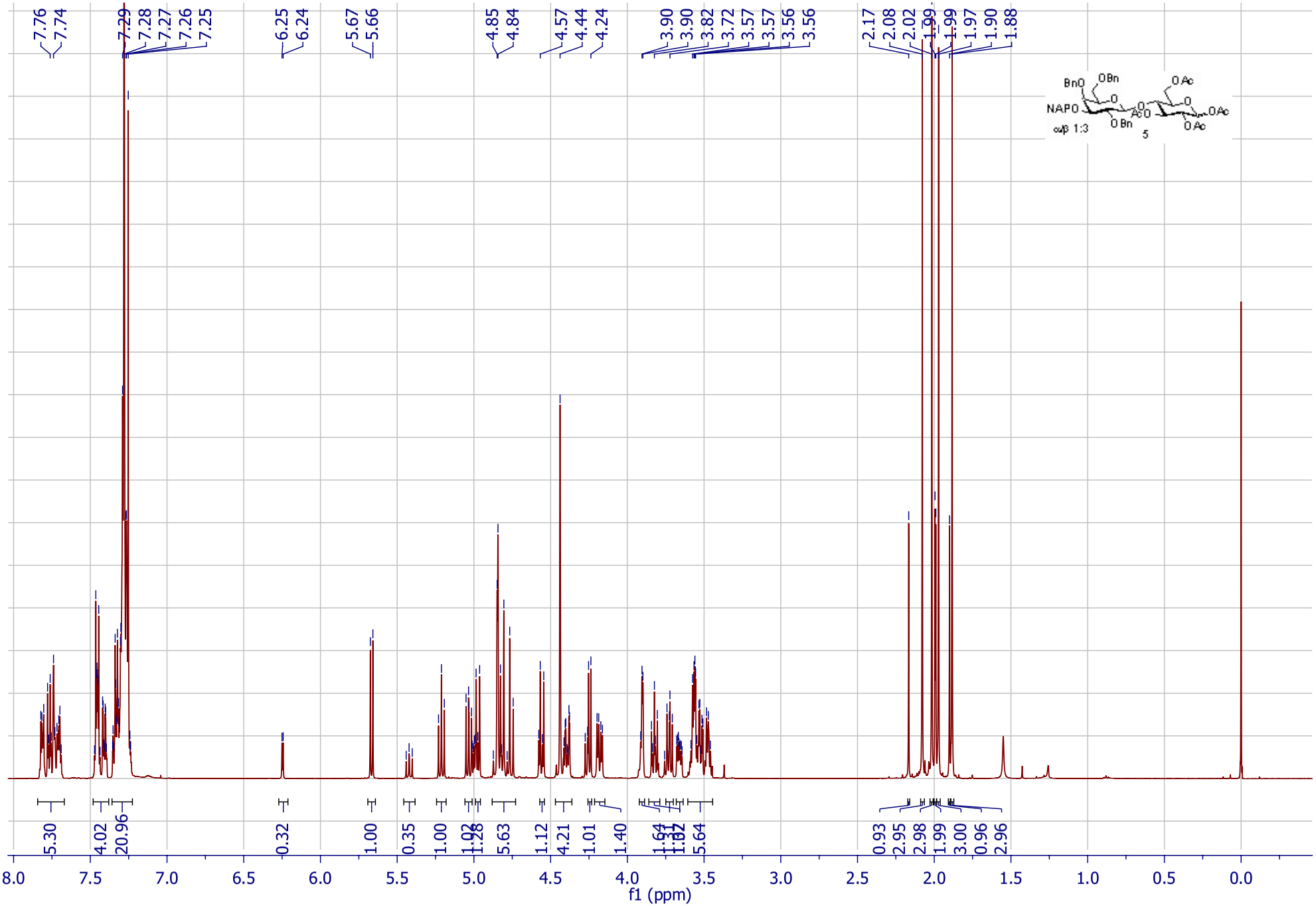
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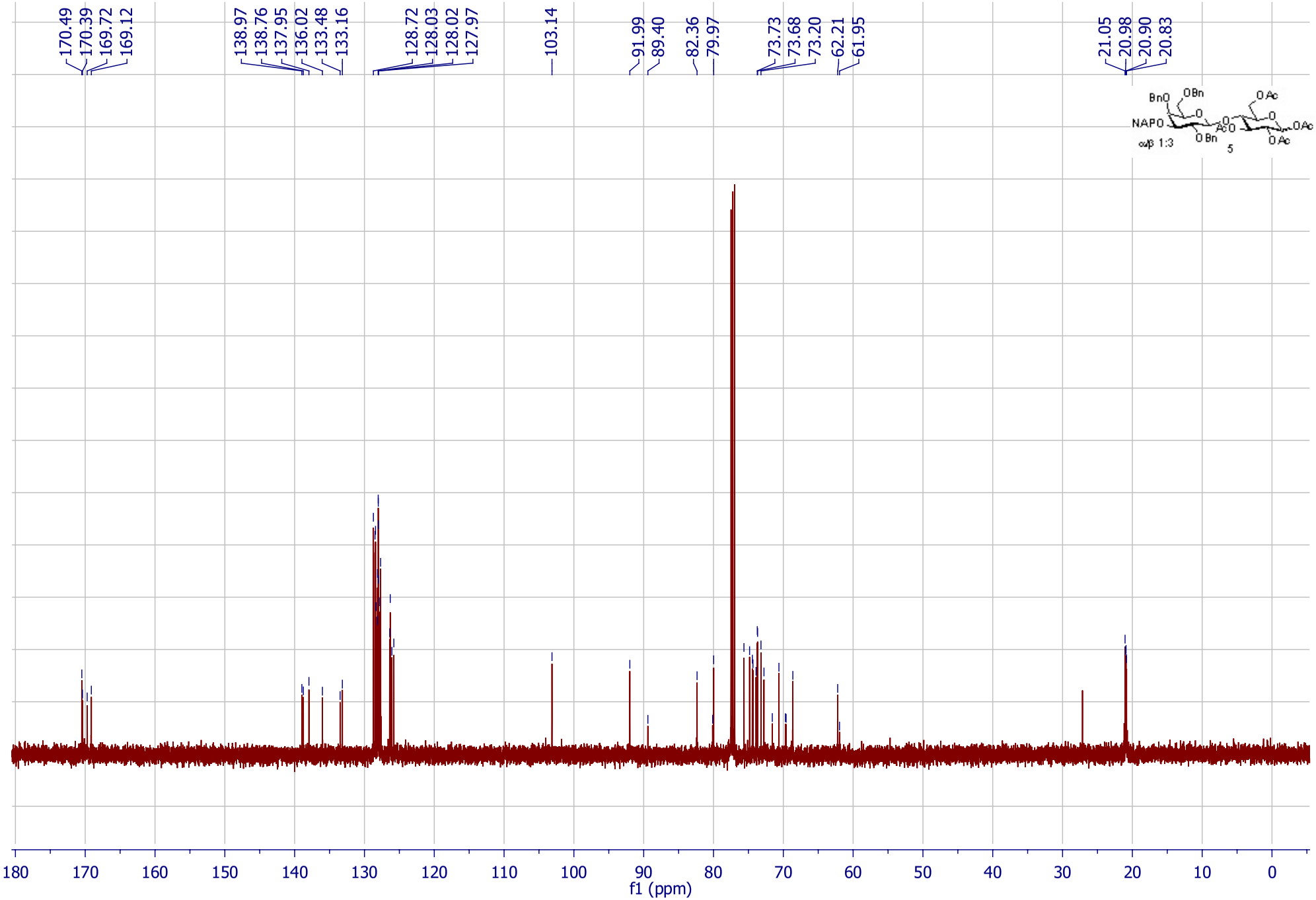
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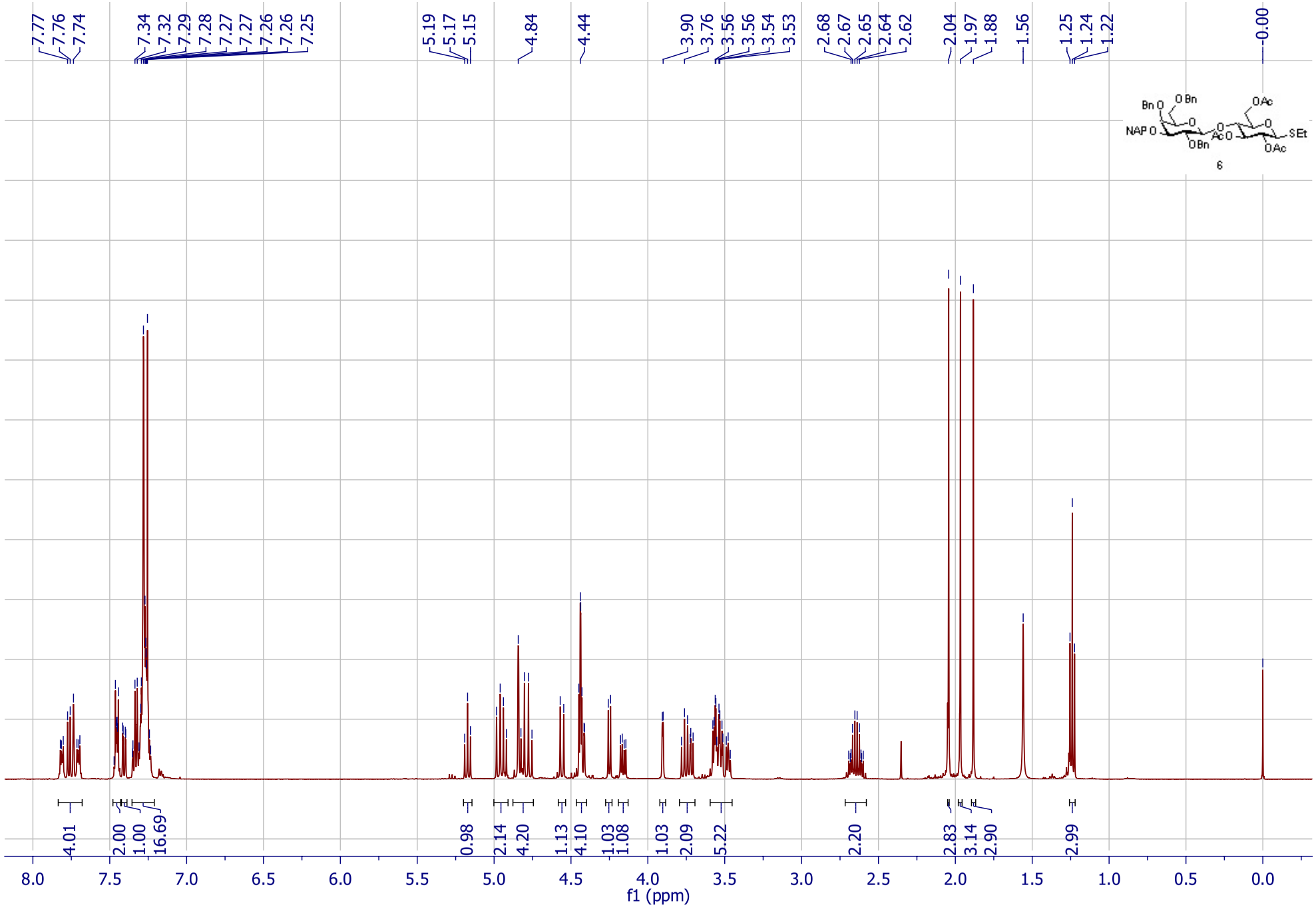
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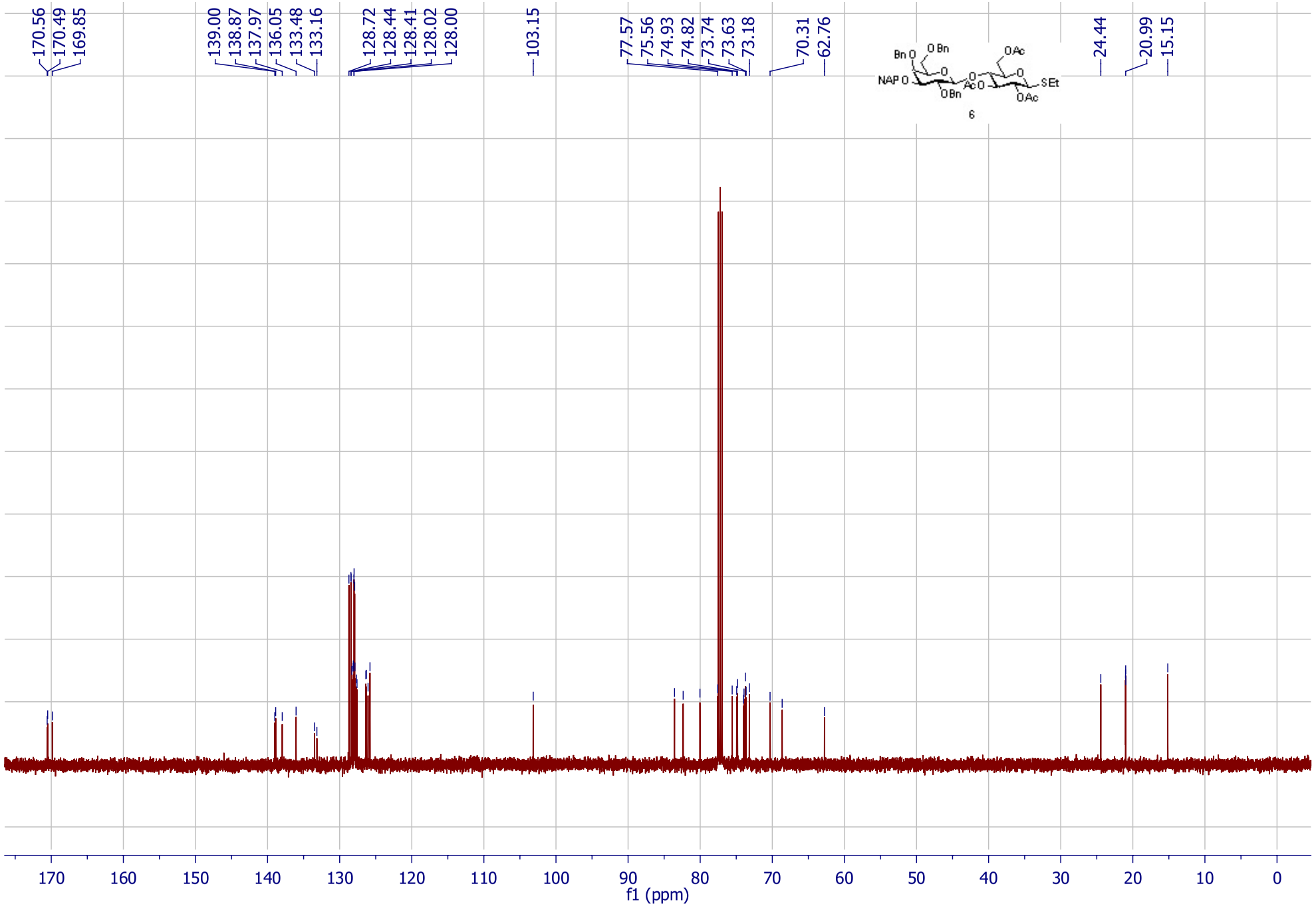
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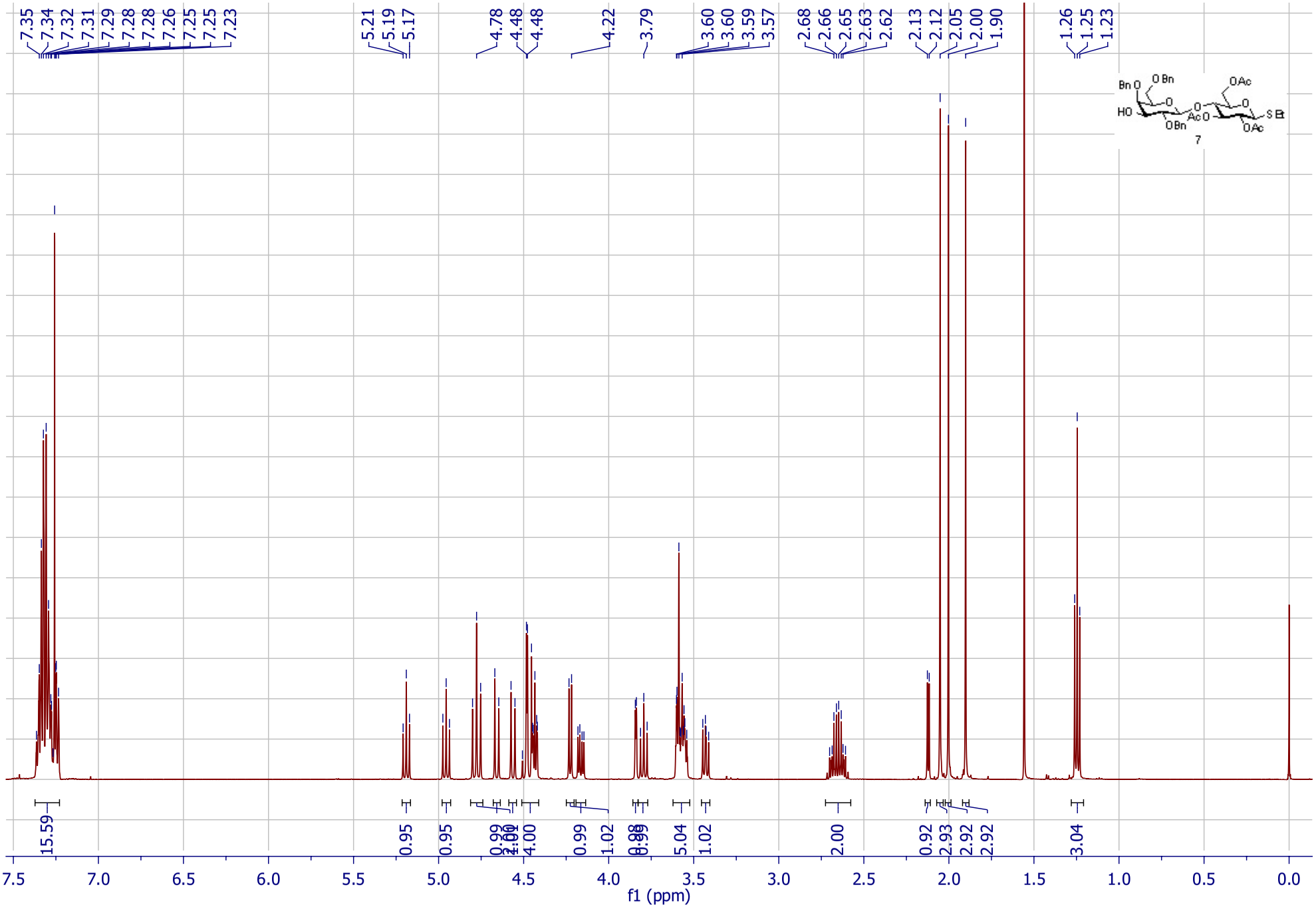
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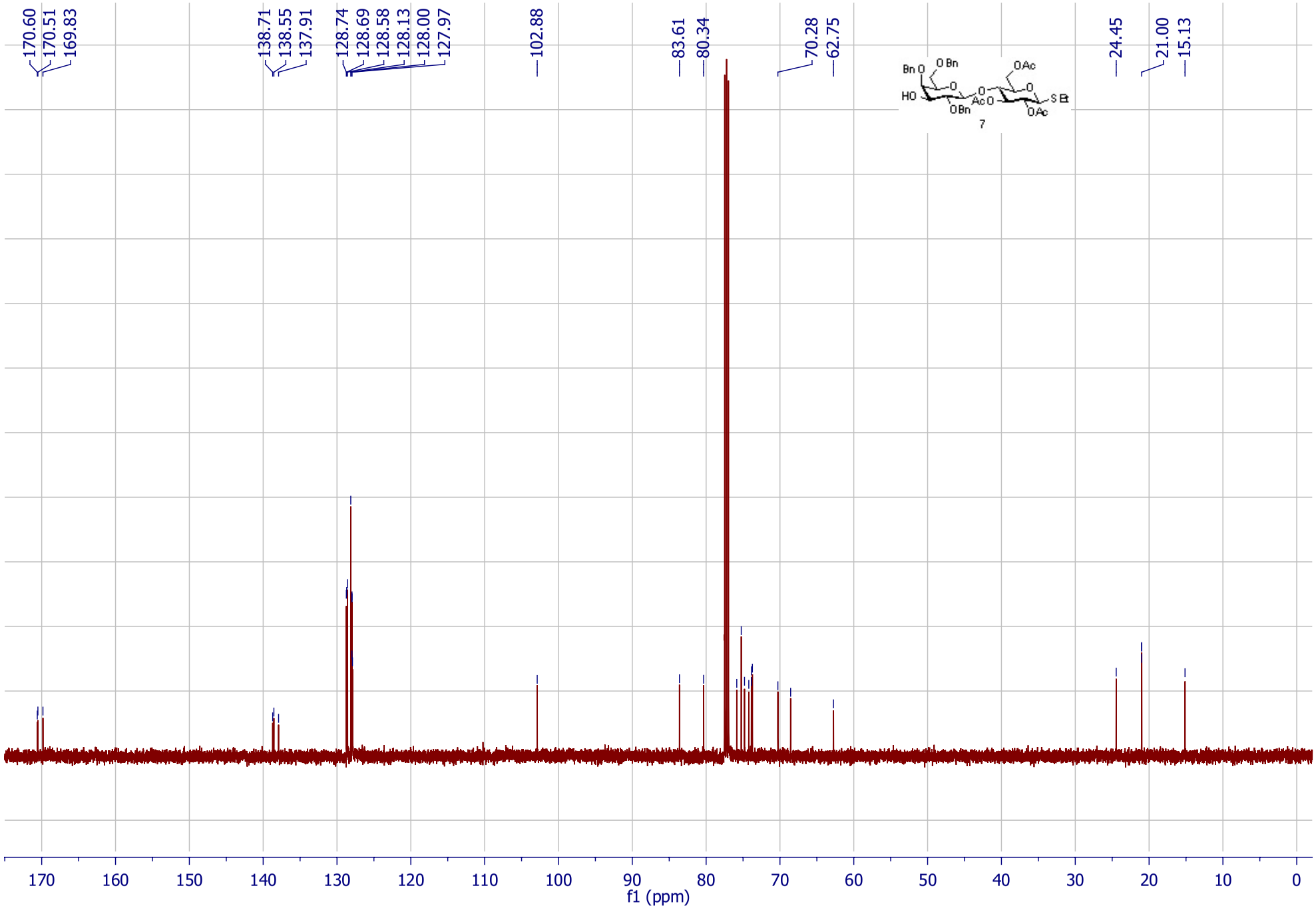
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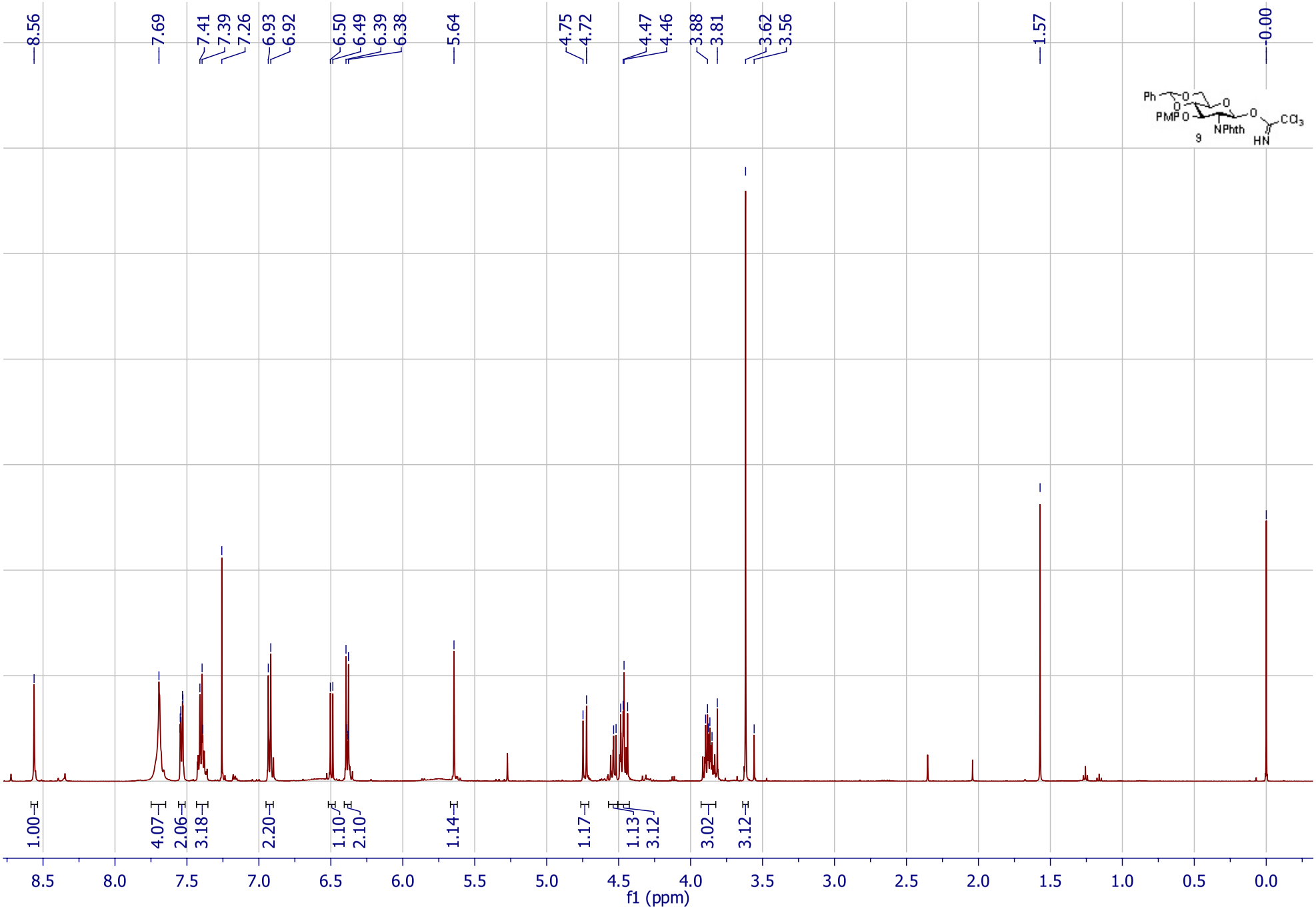
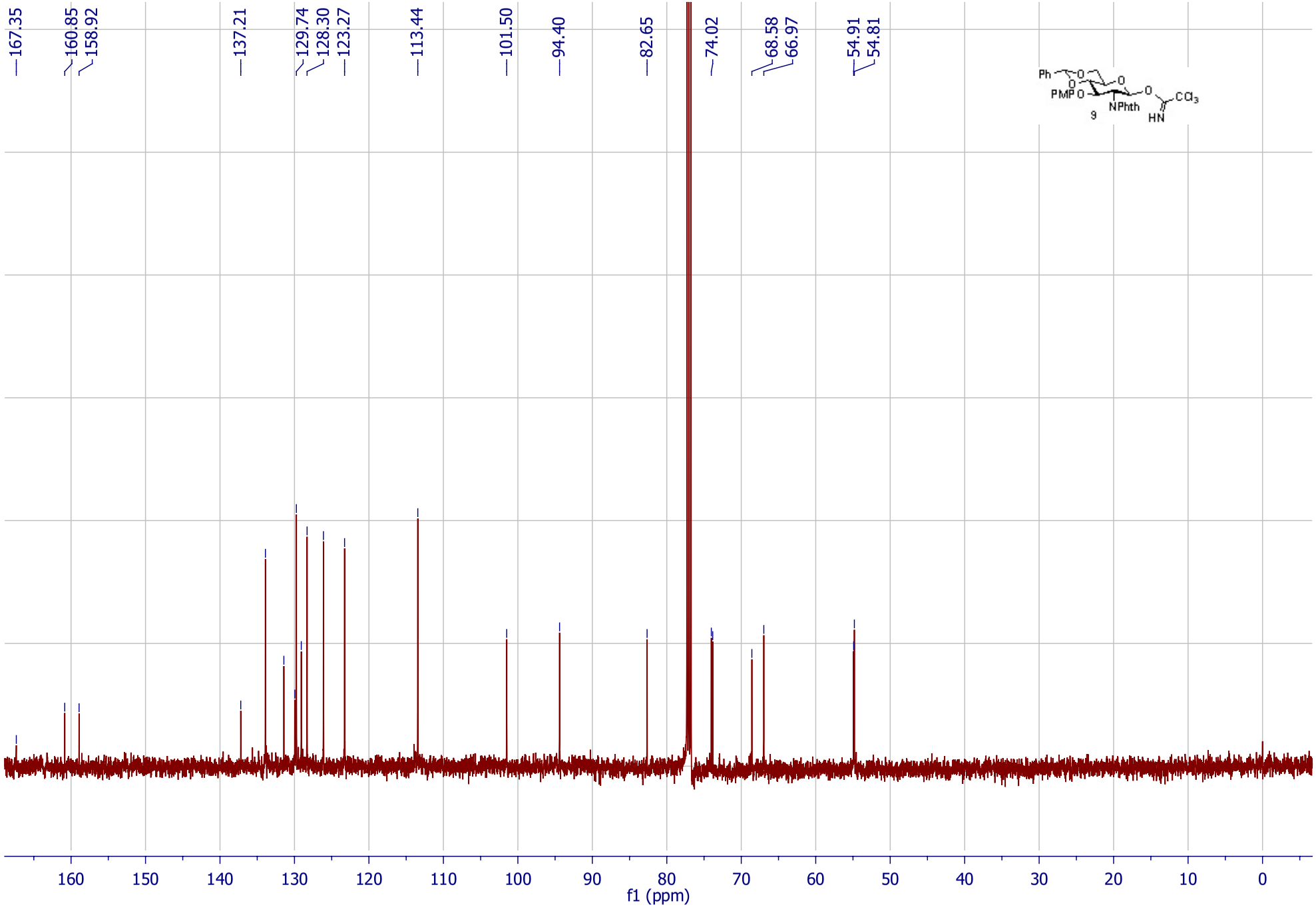
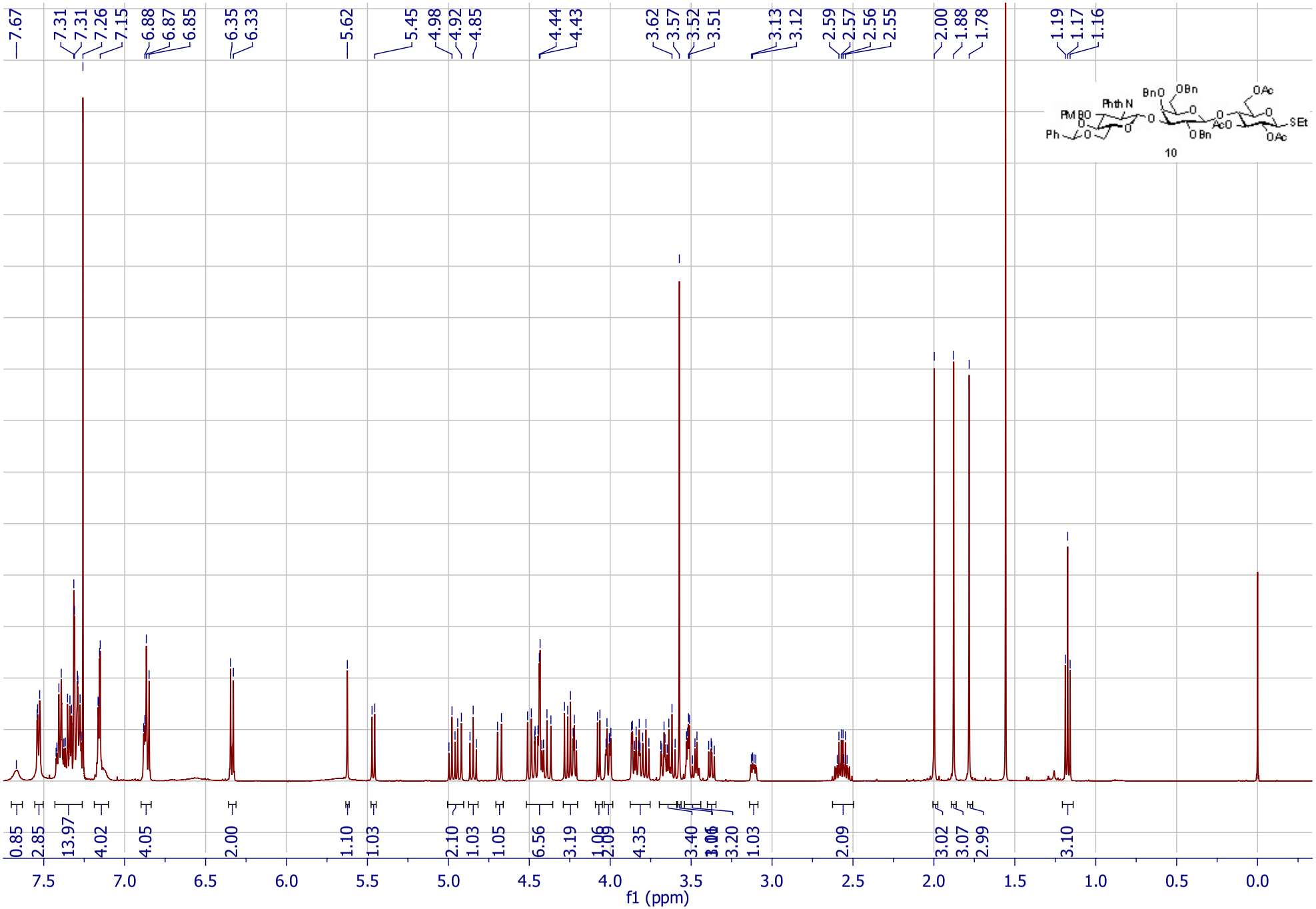
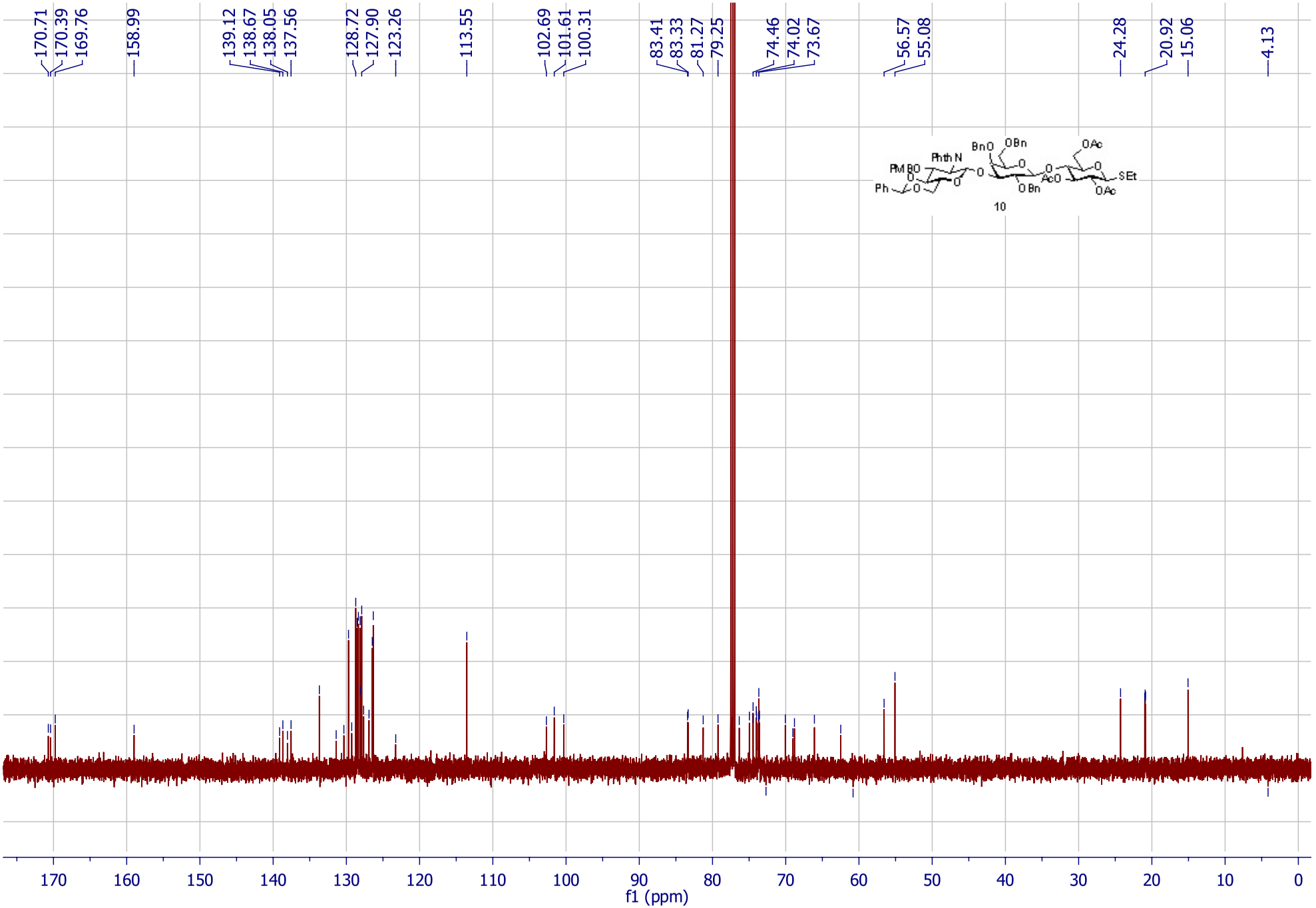
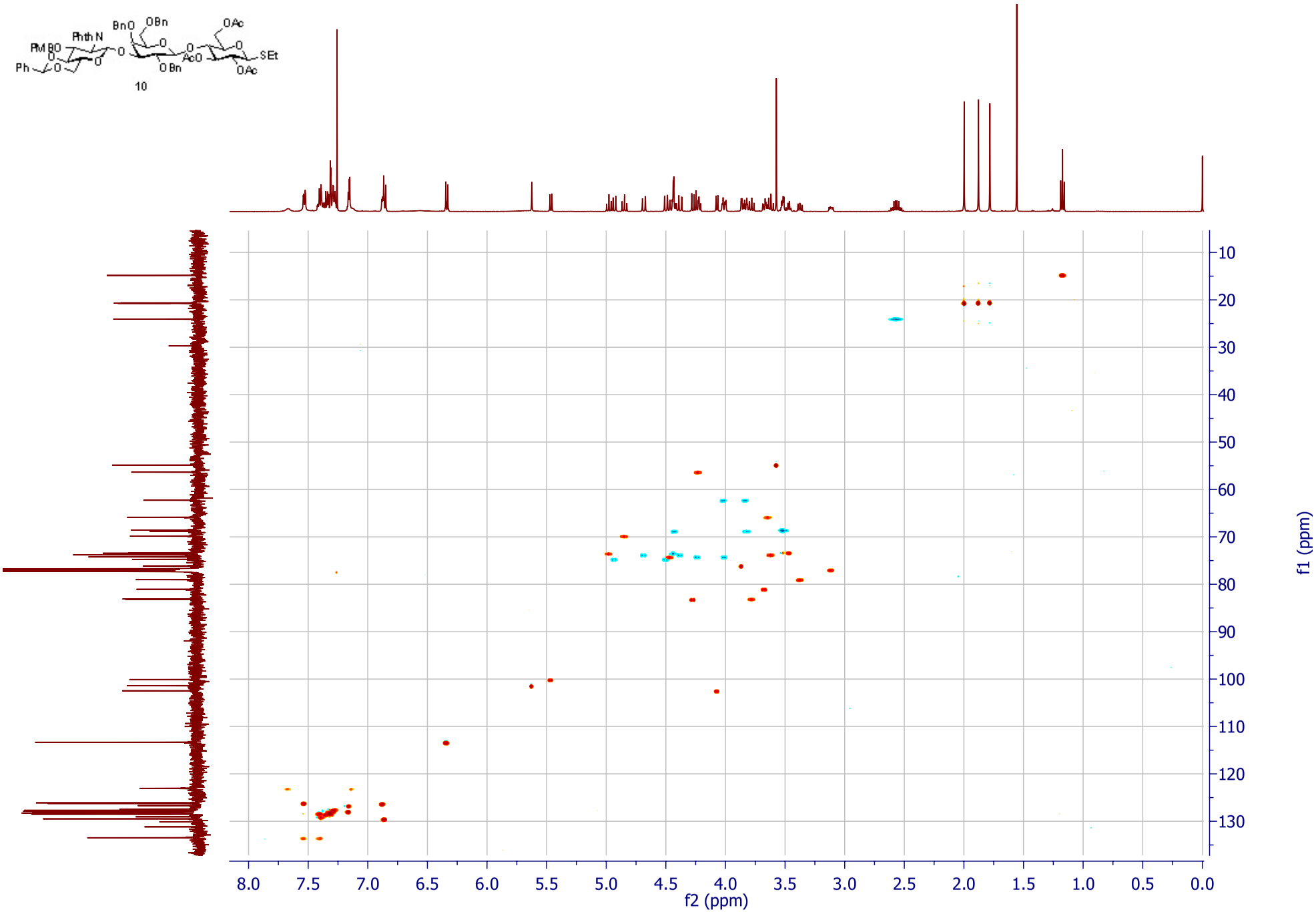
f1 (ppm)

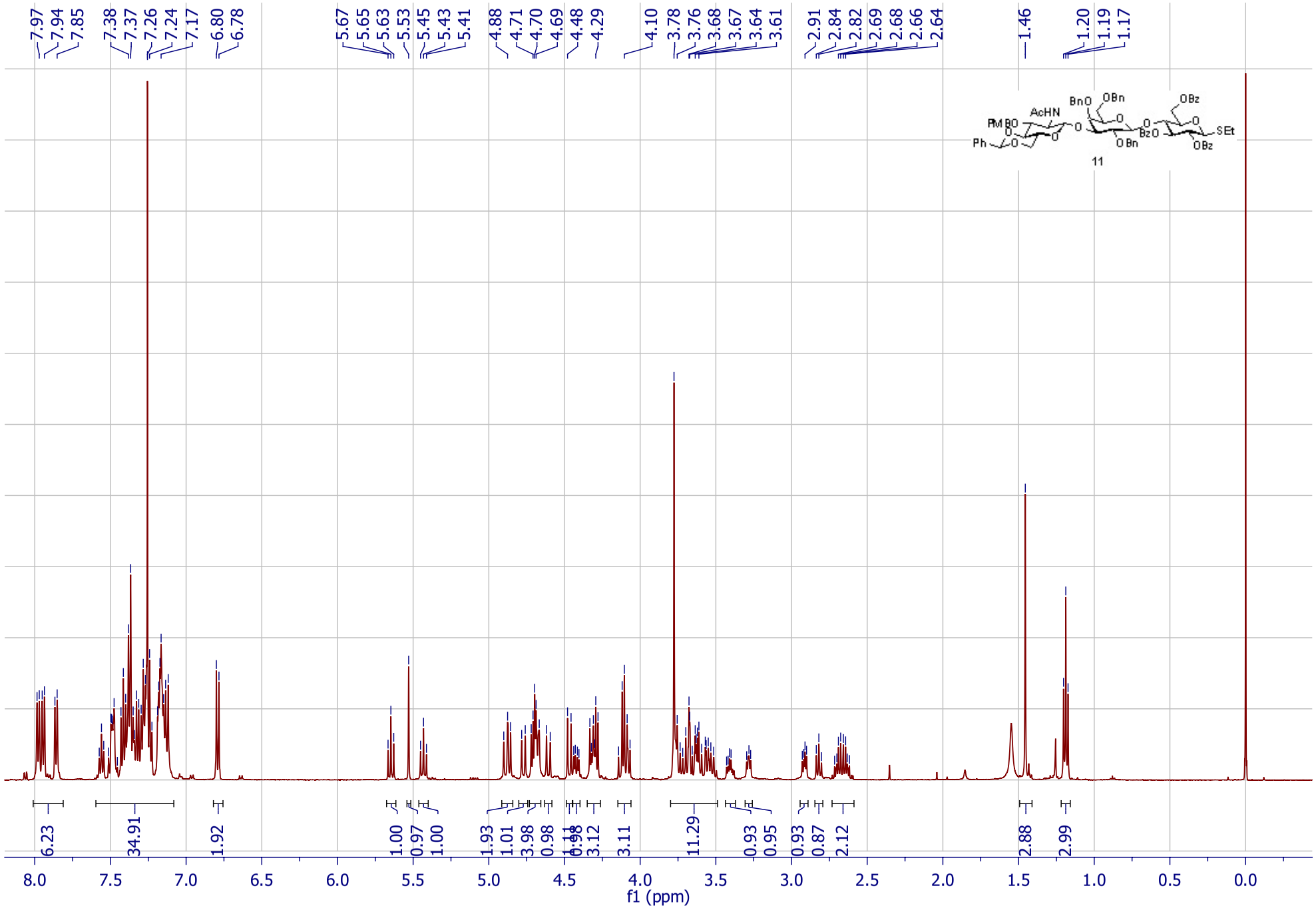

8.56
7.69
7.41
7.39
7.26
6.93
6.92
6.50
6.49
6.39
6.38
5.64
4.75
4.72
4.47
4.46
3.88
3.81
3.62
3.56
1.57
0.00
Ph
PMP
O
NPhth
HN
CCl3
9
1.00
4.07
2.06
3.18
2.20
1.10
2.10
1.14
1.17
1.13
3.12
3.02
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

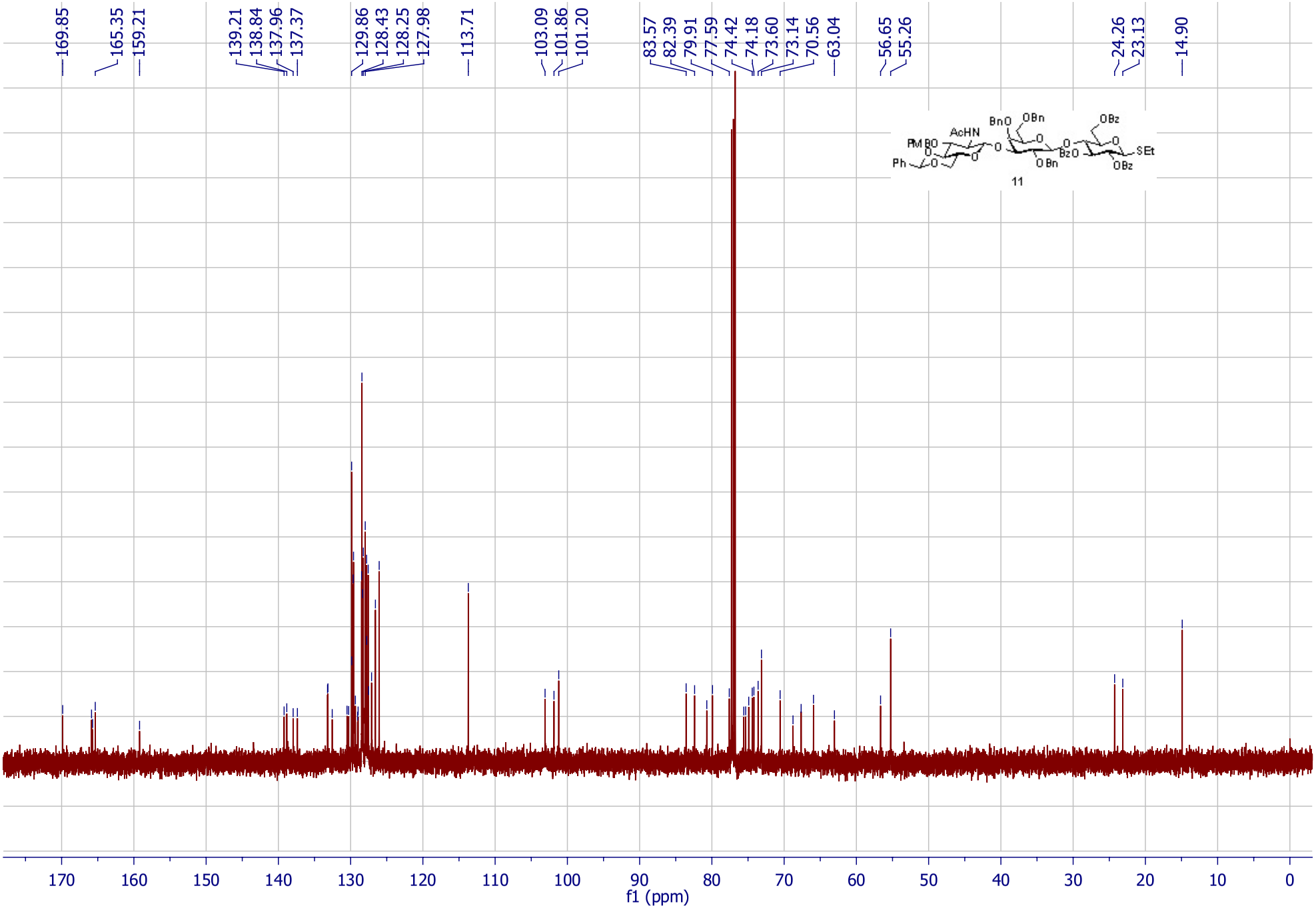

167.35
160.85
158.92
137.21
129.74
128.30
123.27
113.44
101.50
94.40
82.65
74.02
68.58
66.97
54.91
54.81
Ph
O
O
PMPO
O
O
CCl3
NPhth
HN
9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

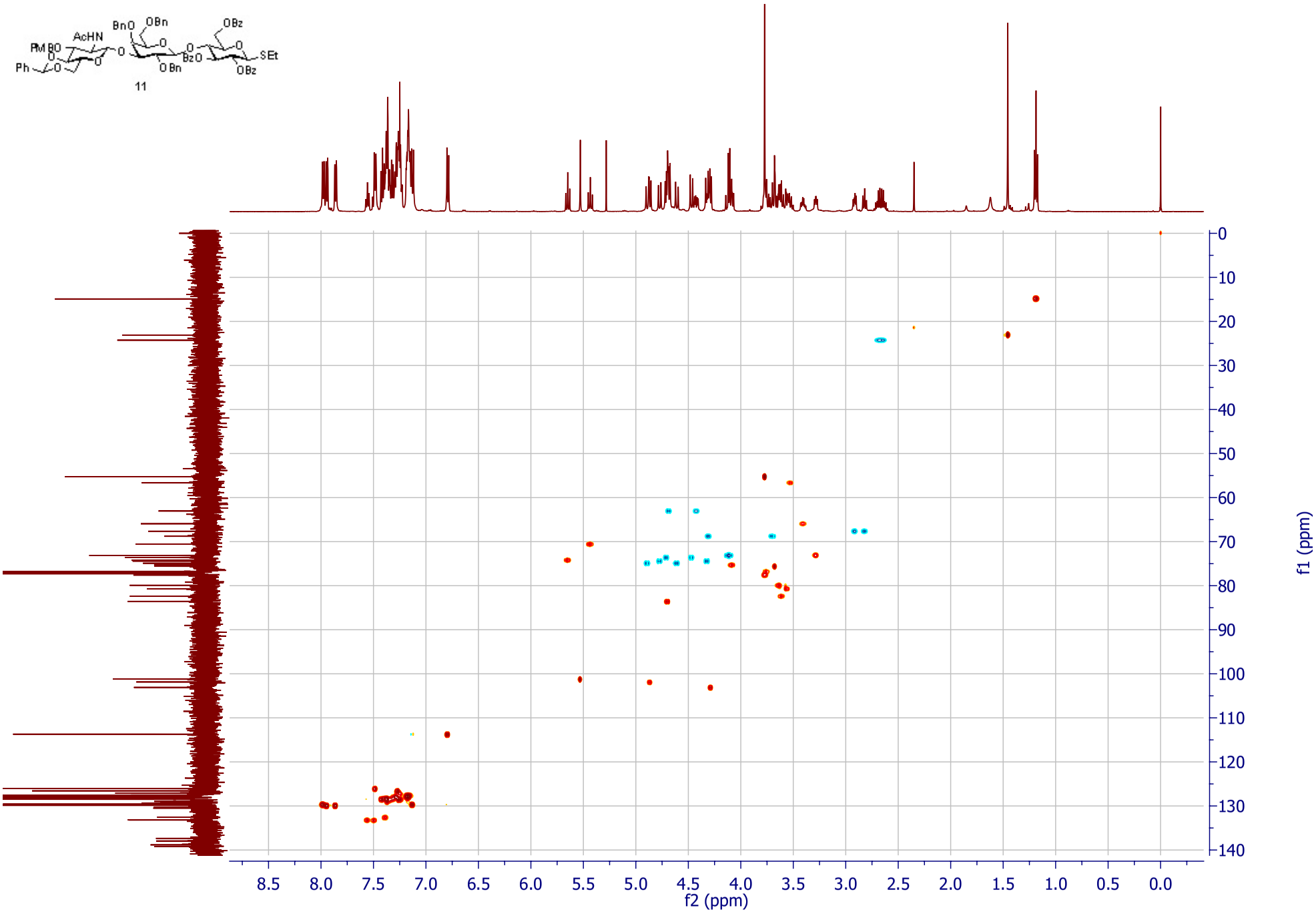

7.67
7.31
7.31
7.26
7.15
6.88
6.87
6.85
6.35
6.33
5.62
5.45
4.98
4.92
4.85
4.44
4.43
3.62
3.57
3.52
3.51
3.13
3.12
2.59
2.57
2.56
2.55
2.00
1.88
1.78
1.19
1.17
1.16
PhthN
BnO
OBn
OAc
PMBO
AcO
SEt
Ph
OBn
OAc
10
0.85
2.85
13.97
4.02
4.05
2.00
1.10
1.03
2.10
1.03
1.05
6.56
3.19
1.06
2.09
4.35
3.40
3.20
1.03
2.09
3.02
3.07
2.99
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

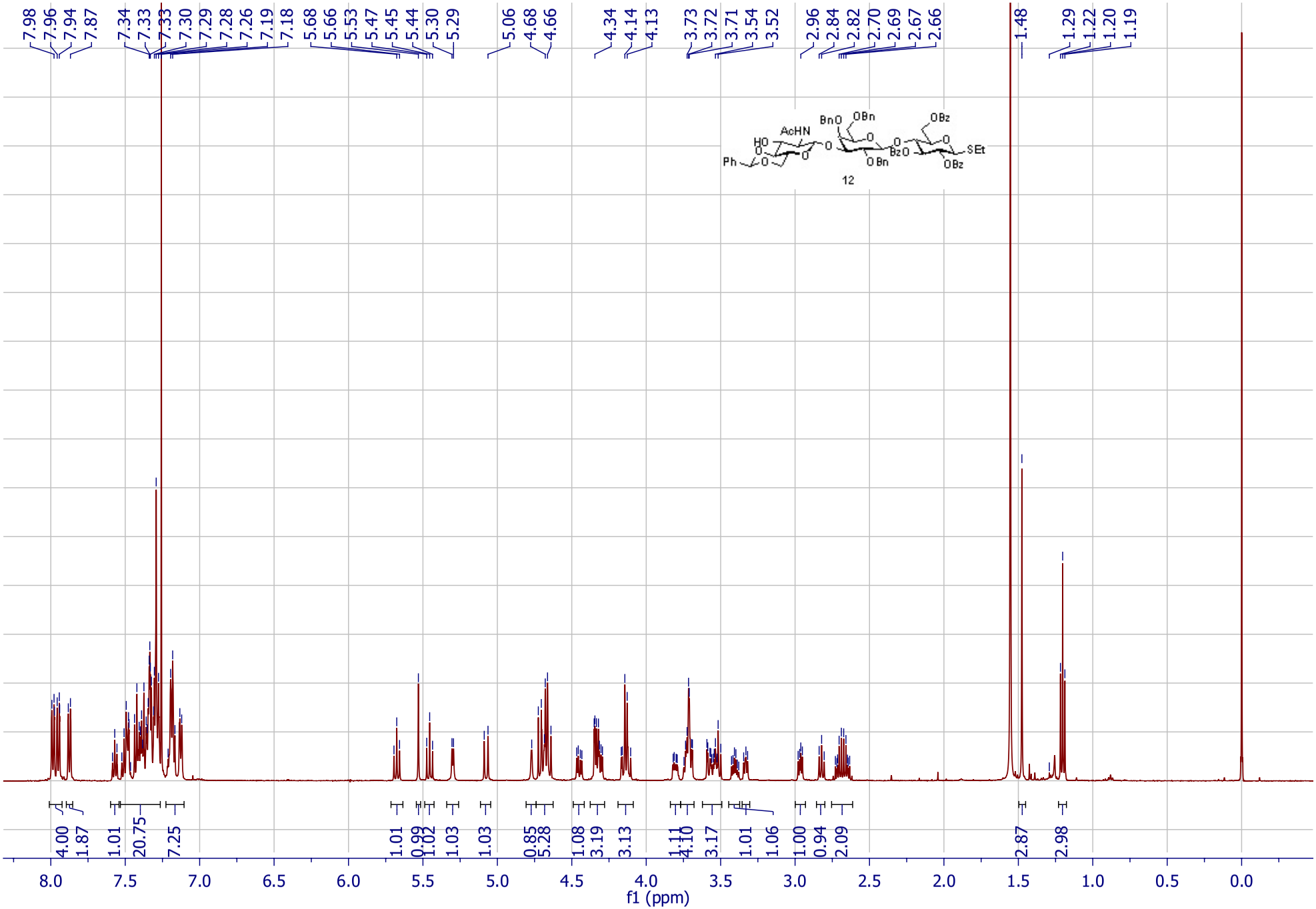

170.71
170.39
169.76
158.99
139.12
138.67
138.05
137.56
128.72
127.90
123.26
113.55
102.69
101.61
100.31
83.41
83.33
81.27
79.25
74.46
74.02
73.67
56.57
55.08
24.28
20.92
15.06
4.13
BnO
OBn
OAc
PhthN
PMBO
AcO
SEt
Ph
OBn
OAc
10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

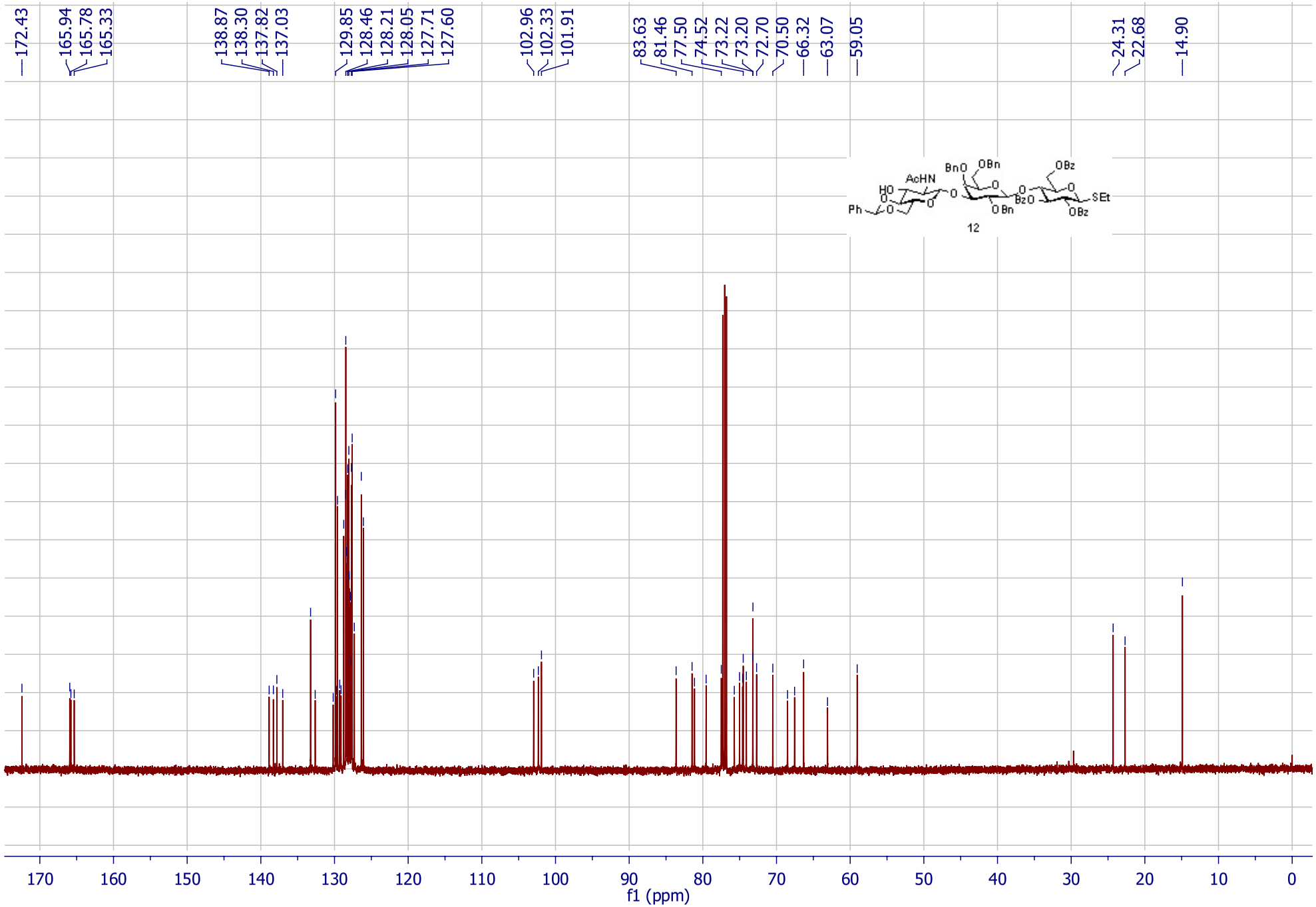

BnO
OBn
OAc
PhthN
PMBO
O
AcO
SEt
Ph
OBn
OAc
10
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
10
20
30
40
50
60
70
80
90
100
110
120
130

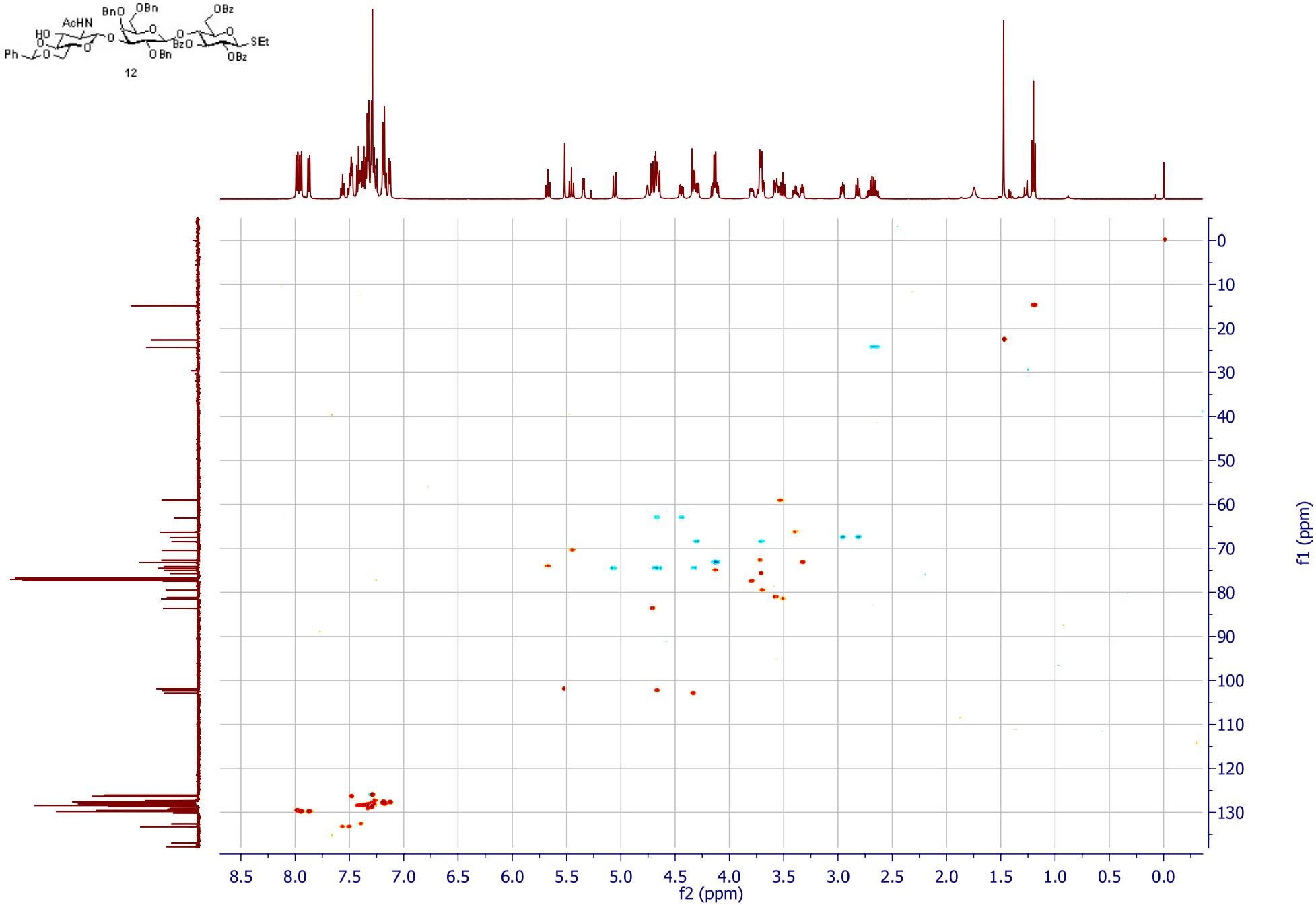

7.97
7.94
7.85
7.38
7.37
7.26
7.24
7.17
6.80
6.78
5.67
5.65
5.63
5.53
5.45
5.43
5.41
4.88
4.71
4.70
4.69
4.48
4.29
4.10
3.78
3.76
3.68
3.67
3.64
3.61
2.91
2.84
2.82
2.69
2.68
2.66
2.64
1.46
1.20
1.19
1.17
AcHN
BnO
OBn
PMBO
Ph
BzO
OBz
SEt
11
6.23
34.91
1.92
1.00
0.97
1.00
1.93
1.01
3.98
0.98
1.11
0.98
3.12
3.11
11.29
0.93
0.95
0.93
0.87
2.12
2.88
2.99
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)

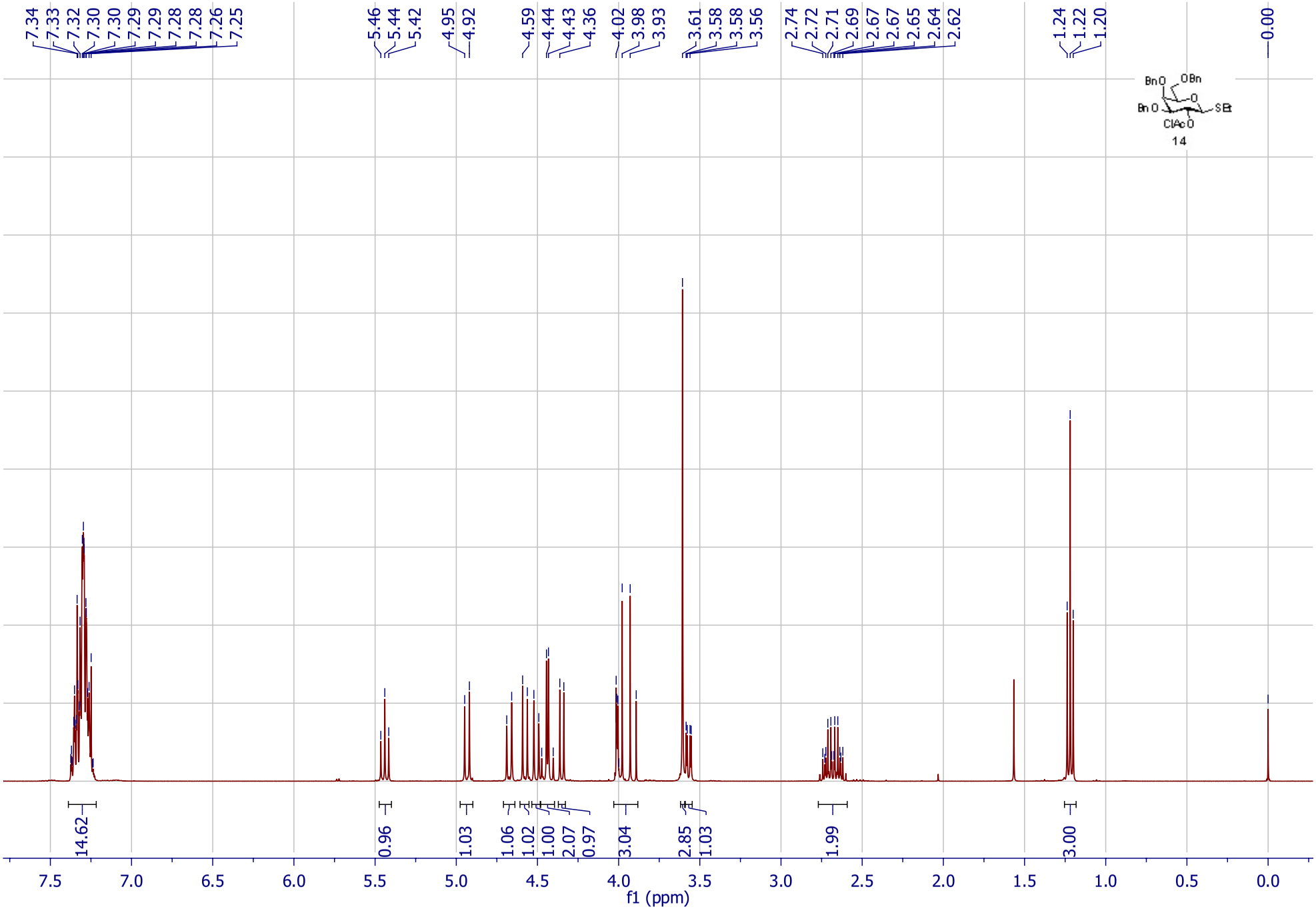

169.85
165.35
159.21
139.21
138.84
137.96
137.37
129.86
128.43
128.25
127.98
113.71
103.09
101.86
101.20
83.57
82.39
79.91
77.59
74.42
74.18
73.60
73.14
70.56
63.04
56.65
55.26
24.26
23.13
14.90
AcHN
BnO
OBn
OBz
PMBO
Ph
BzO
SEt
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

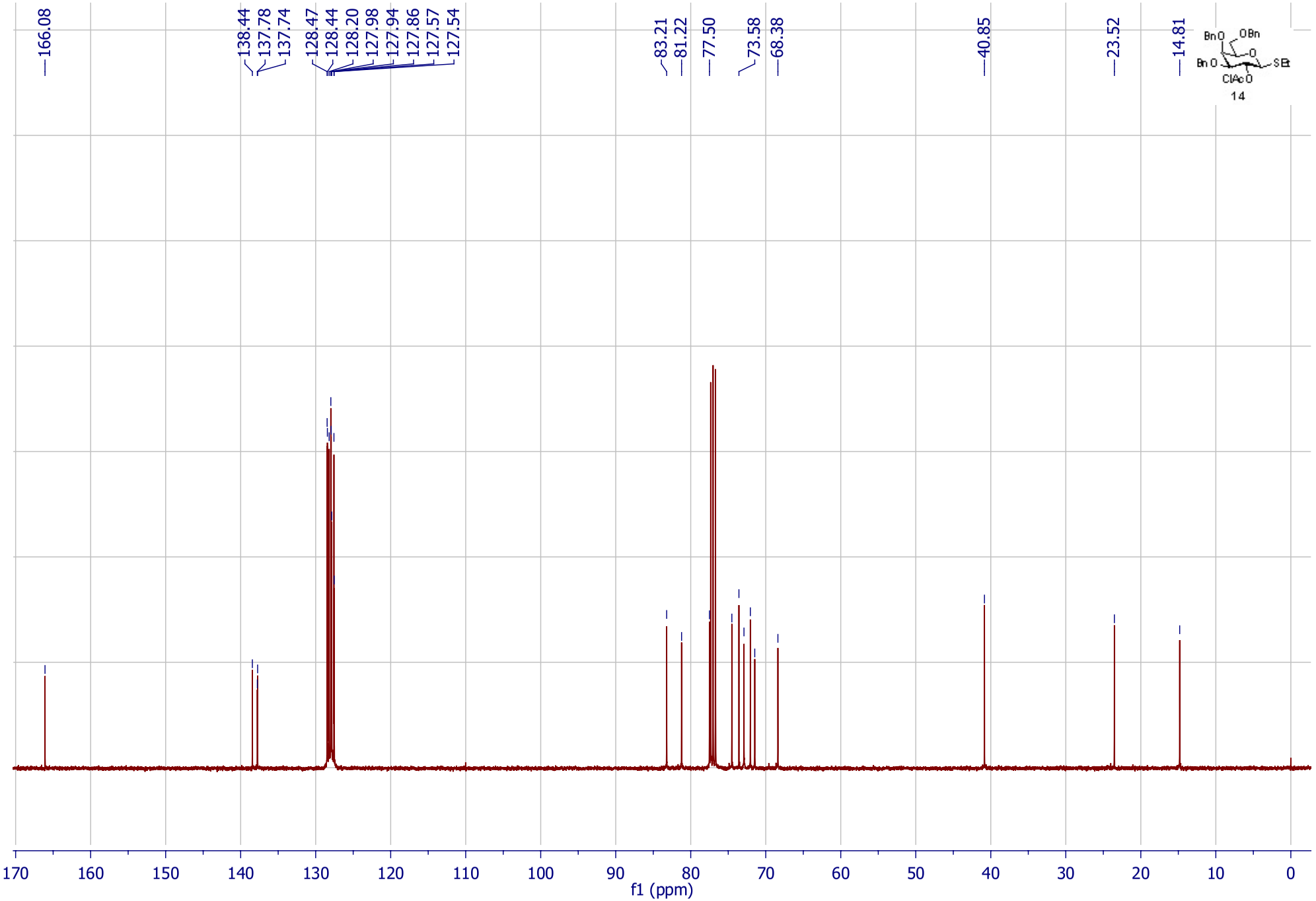

AcHN
BnO
OBn
OBz
PMBO
Ph
O
SEt
BzO
OBn
OBz
11
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

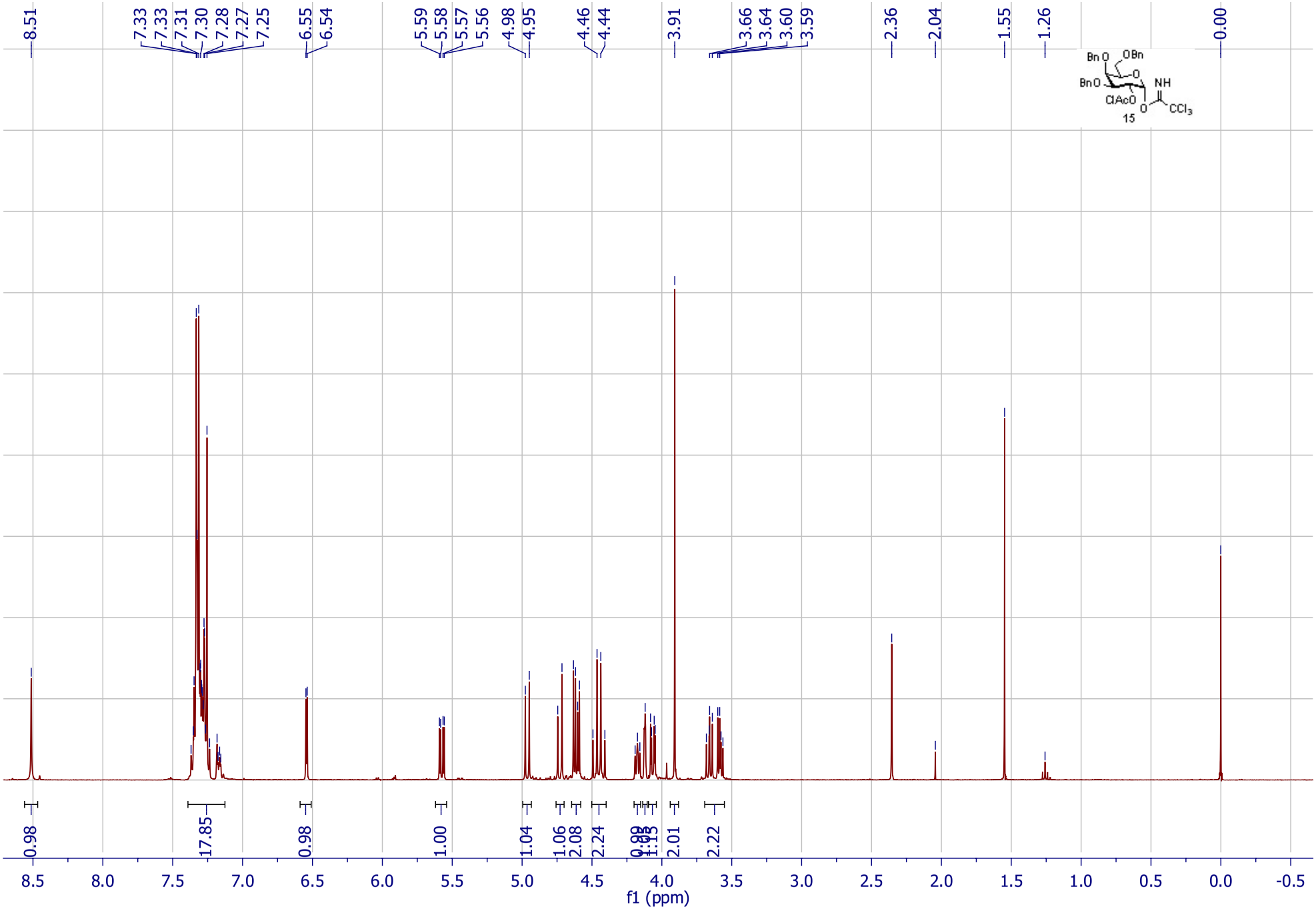

7.98
7.96
7.94
7.87
7.34
7.33
7.33
7.30
7.29
7.28
7.26
7.19
7.18
5.68
5.66
5.53
5.47
5.45
5.44
5.30
5.29
5.06
4.68
4.66
4.34
4.14
4.13
3.73
3.72
3.71
3.54
3.52
2.96
2.84
2.82
2.70
2.69
2.67
2.66
1.48
1.29
1.22
1.20
1.19
AcHN
BnO
OBn
OBz
HO
Ph
BzO
SEt
12
4.00
1.87
1.01
20.75
7.25
1.01
0.99
1.02
1.03
1.03
0.85
5.28
1.08
3.19
3.13
1.11
4.10
3.17
1.01
1.06
1.00
0.94
2.09
2.87
2.98
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)

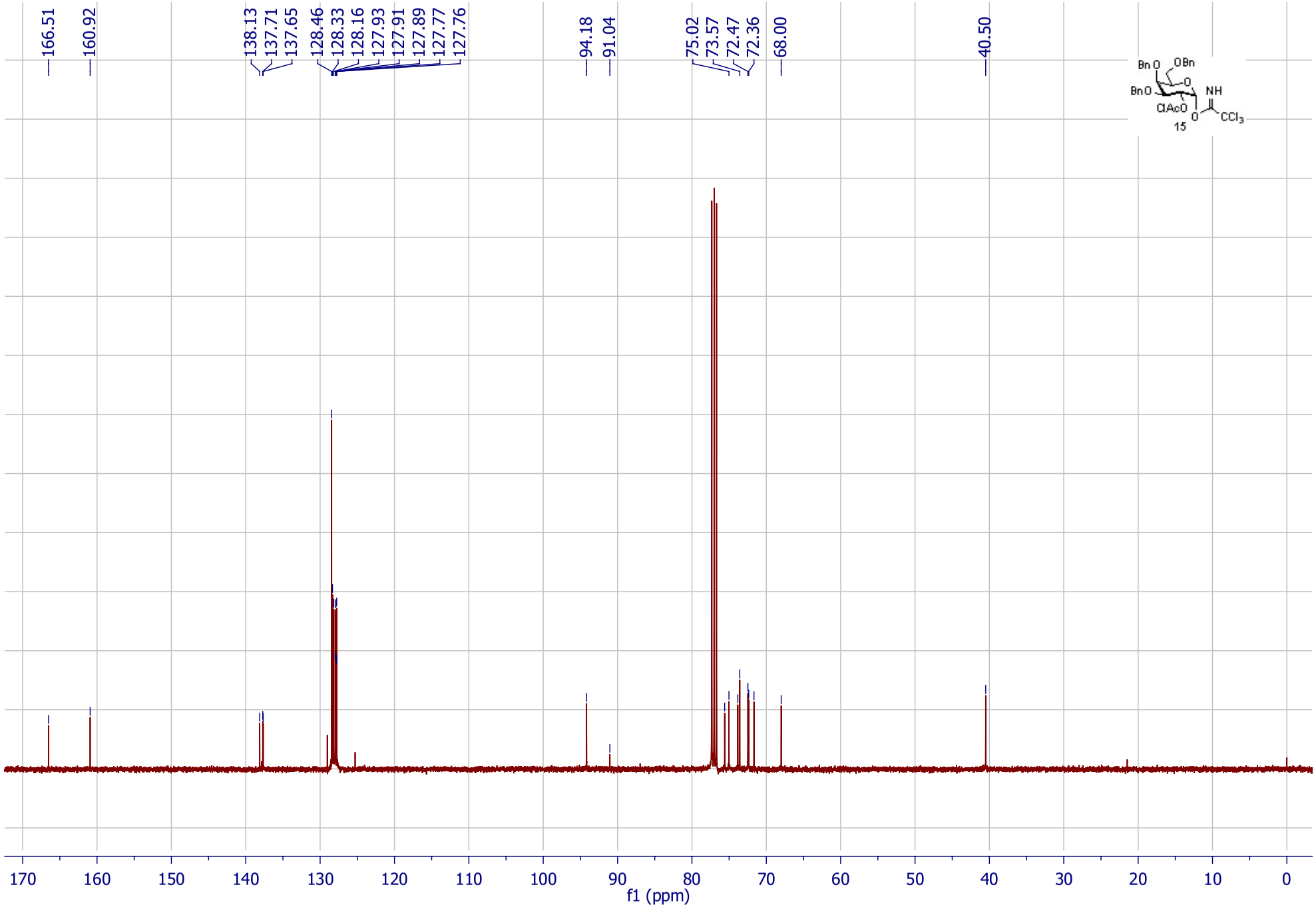

172.43
165.94
165.78
165.33
138.87
138.30
137.82
137.03
129.85
128.46
128.21
128.05
127.71
127.60
102.96
102.33
101.91
83.63
81.46
77.50
74.52
73.22
73.20
72.70
70.50
66.32
63.07
59.05
24.31
22.68
14.90
AcHN
BnO
OBn
OBz
HO
Ph
BzO
SEt
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

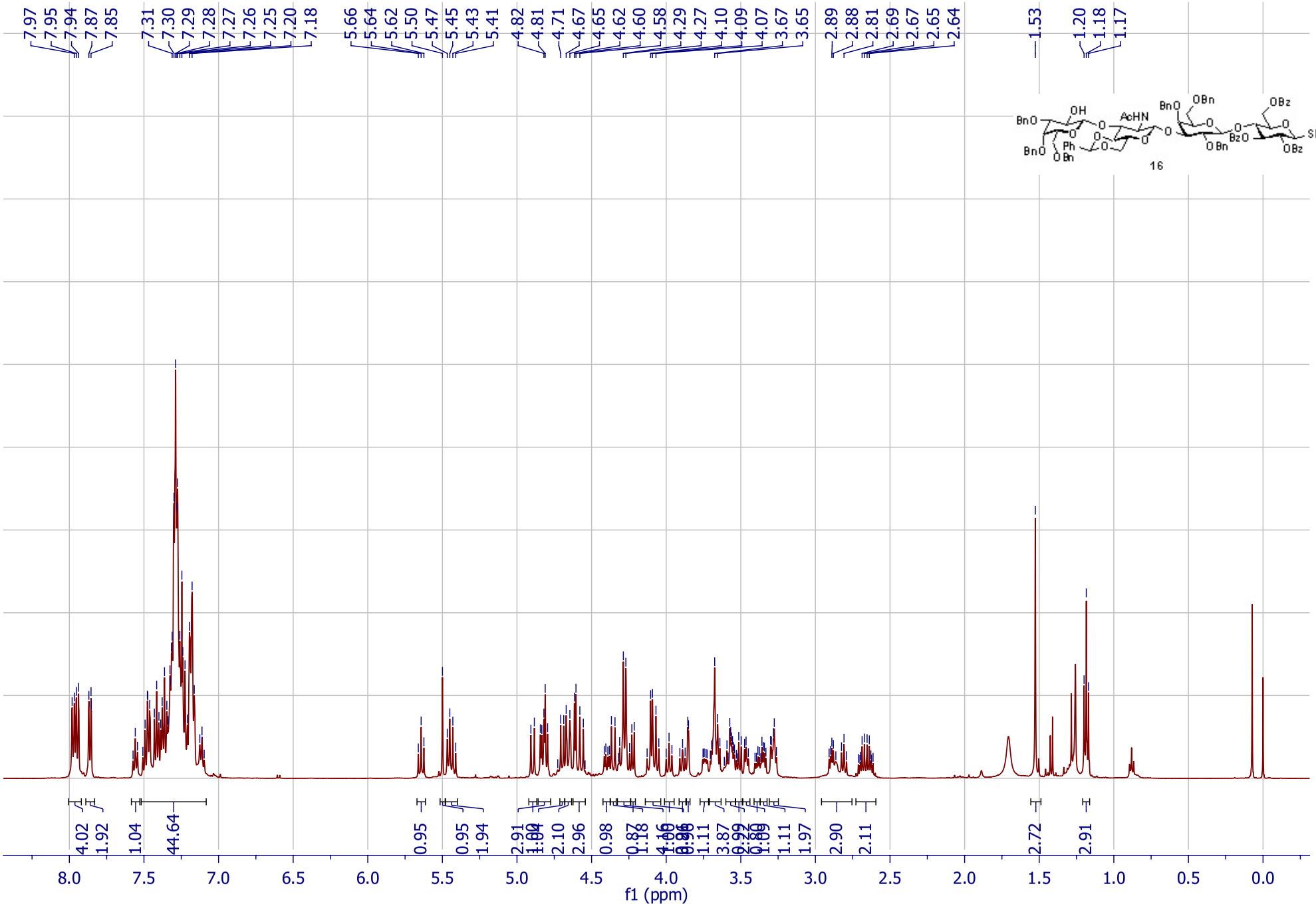

AcHN
HO
BnO
OBn
OBz
Ph
O
SEt
BzO
OBn
OBz
12
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130

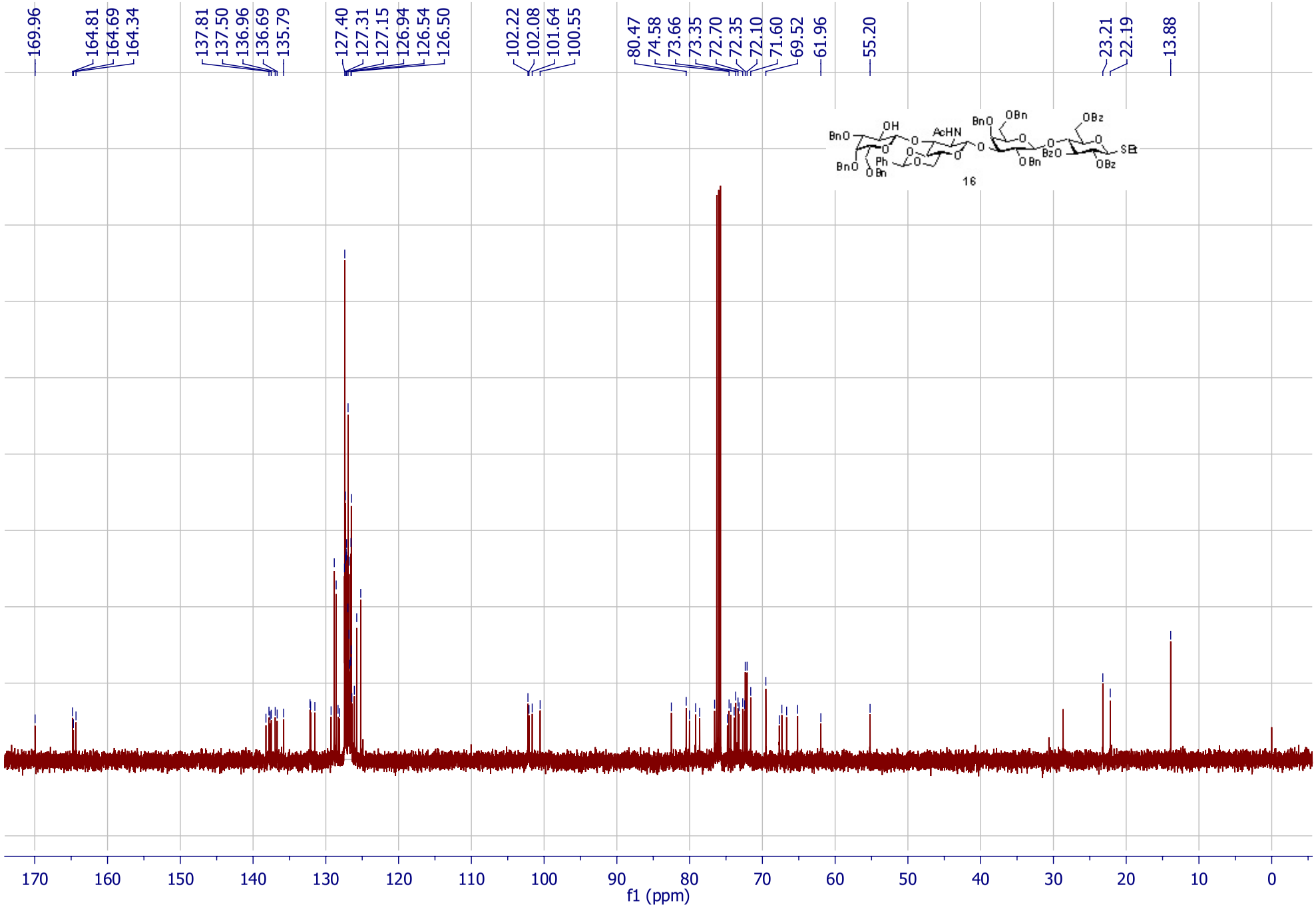

7.34
7.33
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.25
5.46
5.44
5.42
4.95
4.92
4.59
4.44
4.43
4.36
4.02
3.98
3.93
3.61
3.58
3.58
3.56
2.74
2.72
2.71
2.69
2.67
2.67
2.65
2.64
2.62
1.24
1.22
1.20
0.00
BnO
OBn
O
BnO
SEt
ClAcO
14
14.62
0.96
1.03
1.06
1.02
1.00
2.07
0.97
3.04
2.85
1.03
1.99
3.00
7.5
7.0
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)

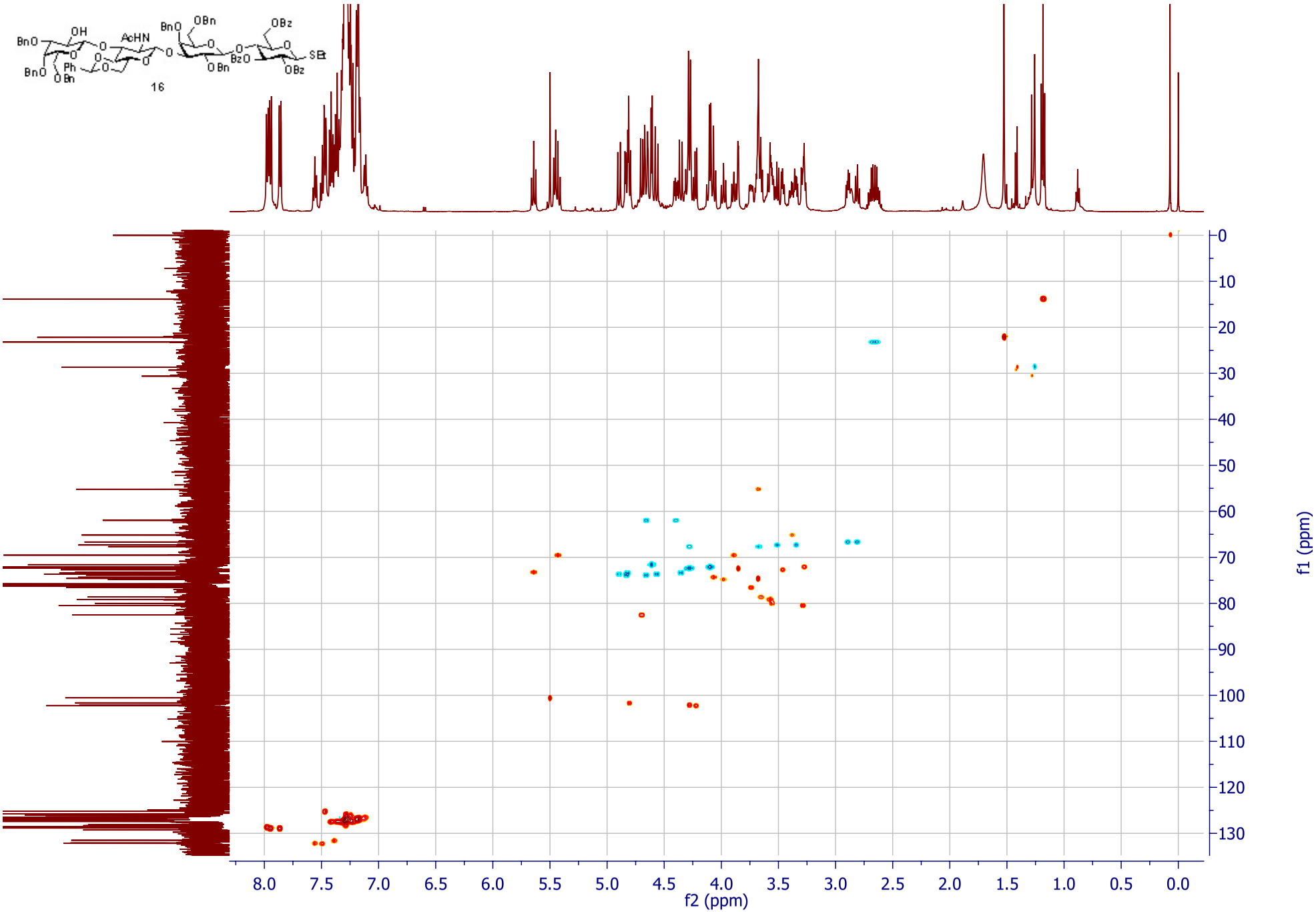

166.08
138.44
137.78
137.74
128.47
128.44
128.20
127.98
127.94
127.86
127.57
127.54
83.21
81.22
77.50
73.58
68.38
40.85
23.52
14.81
BnO
OBn
O
BnO
SEt
ClAcO
14
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

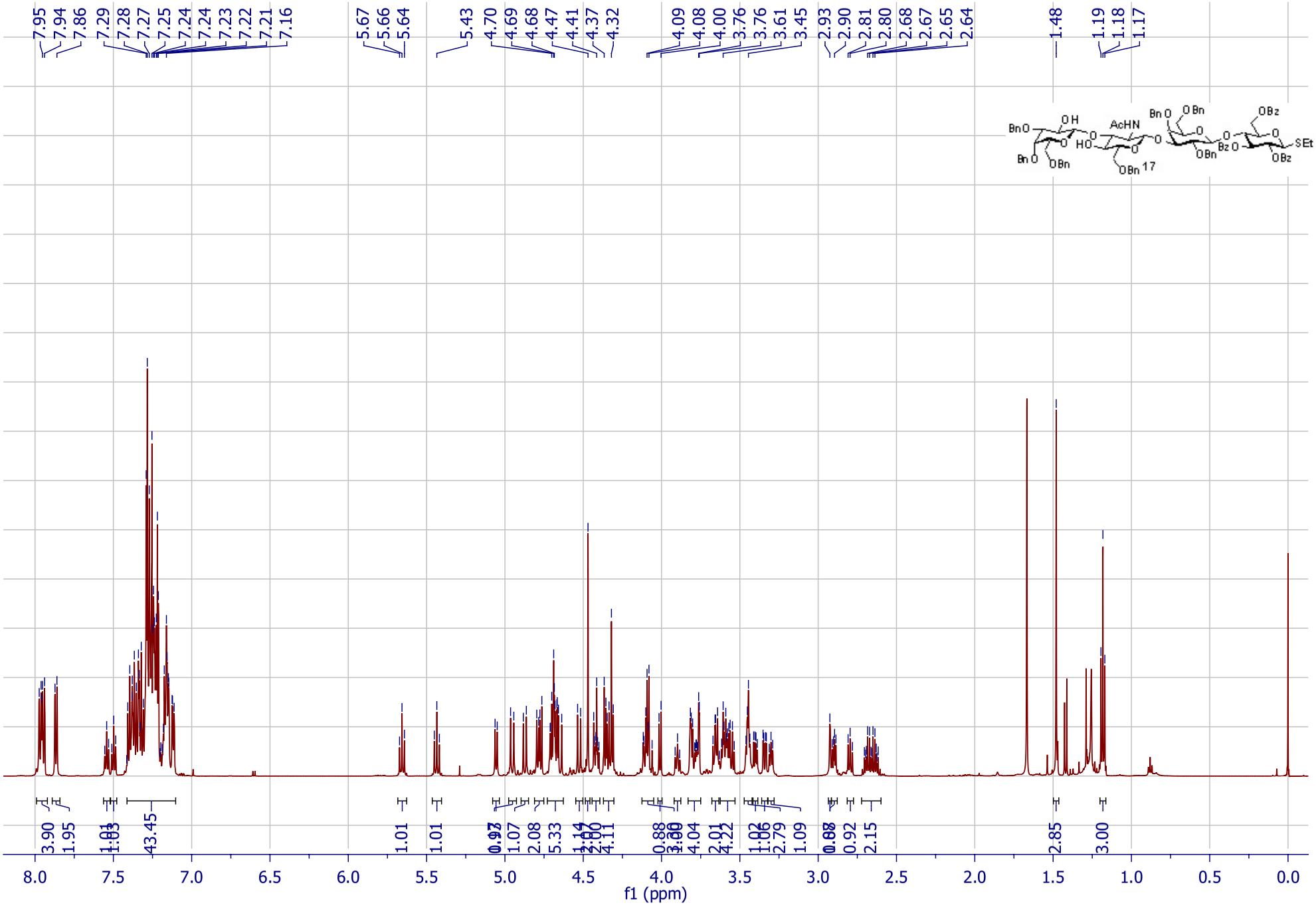

8.51
7.33
7.33
7.31
7.30
7.28
7.27
7.25
6.55
6.54
5.59
5.58
5.57
5.56
4.98
4.95
4.46
4.44
3.91
3.66
3.64
3.60
3.59
2.36
2.04
1.55
1.26
0.00
Bn O
OBn
O
Bn O
NH
ClAcO
O
CCl3
15
0.98
17.85
0.98
1.00
1.04
1.06
2.08
2.24
2.01
2.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

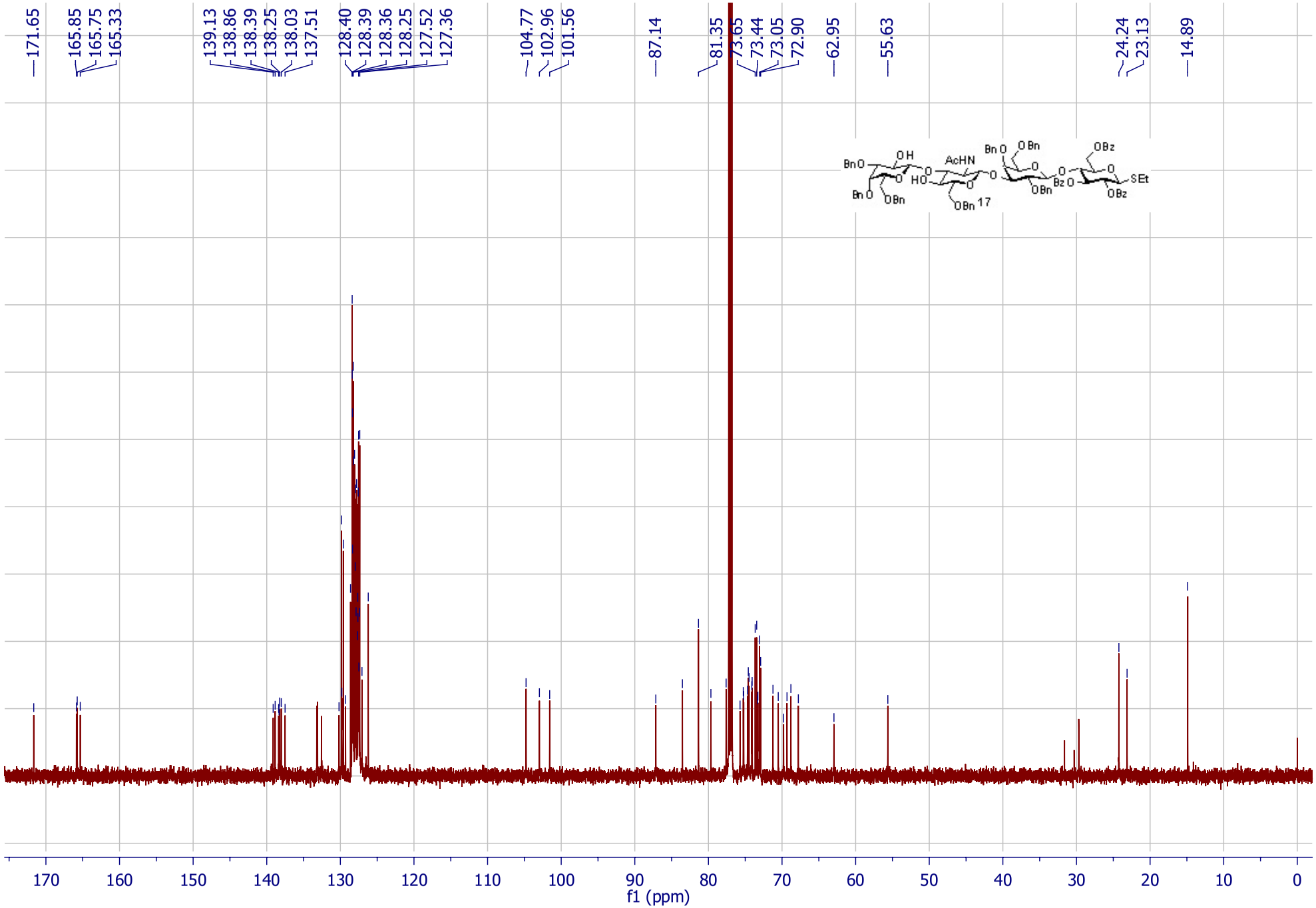

166.51
160.92
138.13
137.71
137.65
128.46
128.33
128.16
127.93
127.91
127.89
127.77
127.76
94.18
91.04
75.02
73.57
72.47
72.36
68.00
40.50
BnO
OBn
O
BnO
NH
ClAcO
O
CCl3
15
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

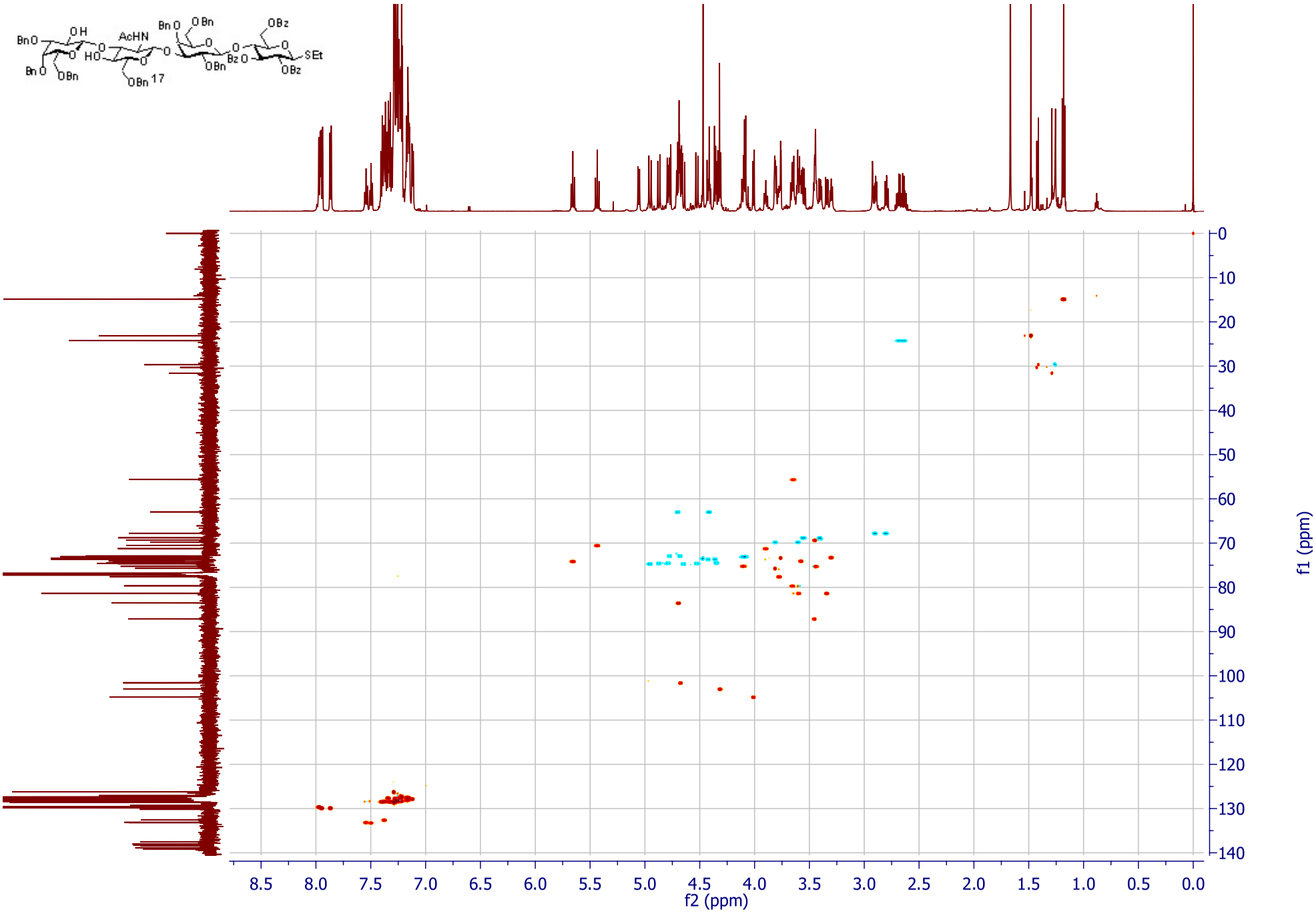

7.97
7.95
7.94
7.87
7.85
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.20
7.18
5.66
5.64
5.62
5.50
5.47
5.45
5.43
5.41
4.82
4.81
4.71
4.67
4.65
4.62
4.60
4.58
4.29
4.27
4.10
4.09
4.07
3.67
3.65
2.89
2.88
2.81
2.69
2.67
2.65
2.64
1.53
1.20
1.18
1.17
BnO
OH
AcHN
BnO
OBn
OBz
BnO
Ph
OBn
OBn
BzO
OBn
OBz
SE
16
4.02
1.92
1.04
44.64
0.95
0.95
1.94
2.91
2.10
2.96
0.98
0.87
1.18
1.11
3.87
1.11
1.97
2.90
2.11
2.72
2.91
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)

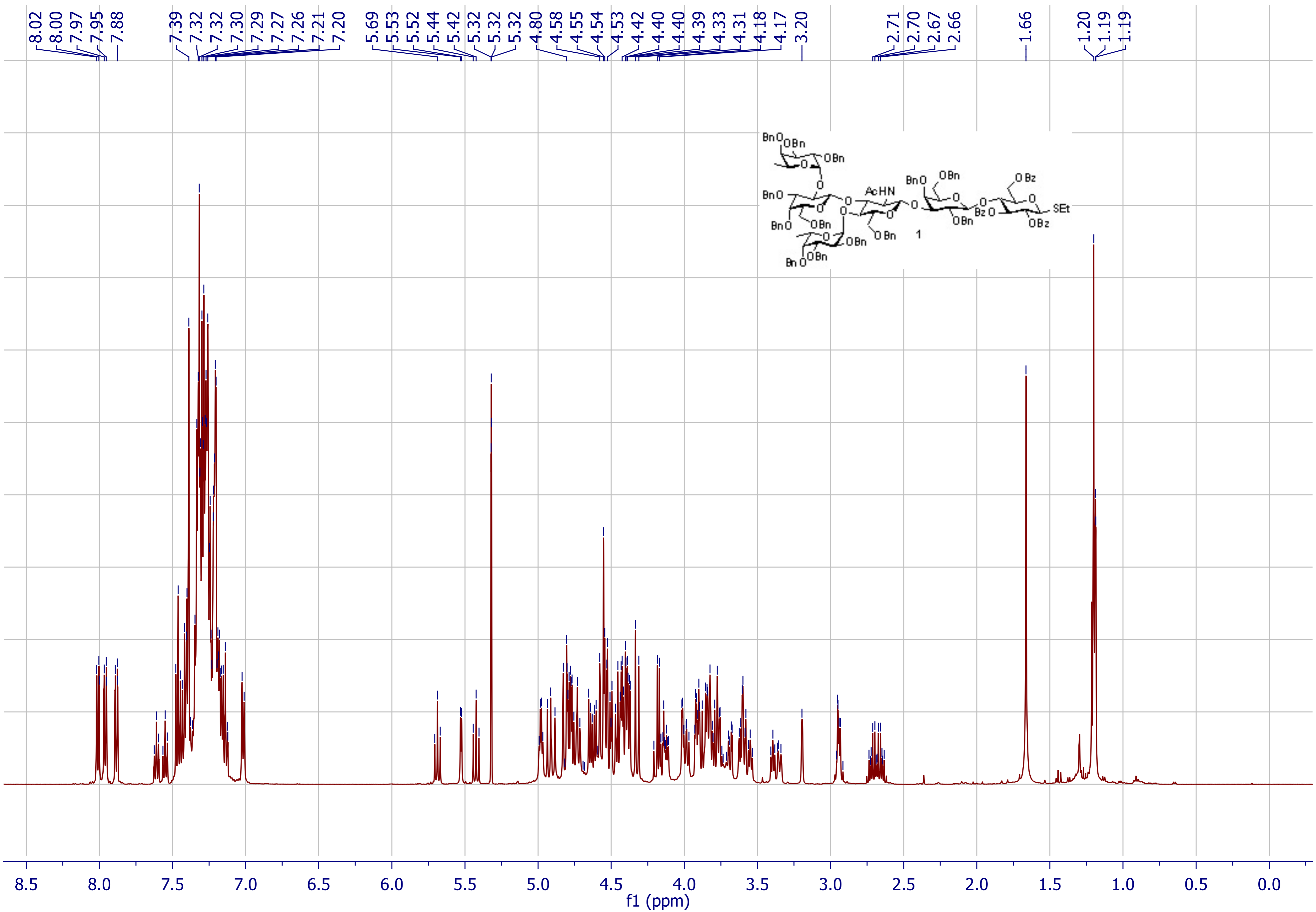

169.96
164.81
164.69
164.34
137.81
137.50
136.96
136.69
135.79
127.40
127.31
127.15
126.94
126.54
126.50
102.22
102.08
101.64
100.55
80.47
74.58
73.66
73.35
72.70
72.35
72.10
71.60
69.52
61.96
55.20
23.21
22.19
13.88
16
f1 (ppm)

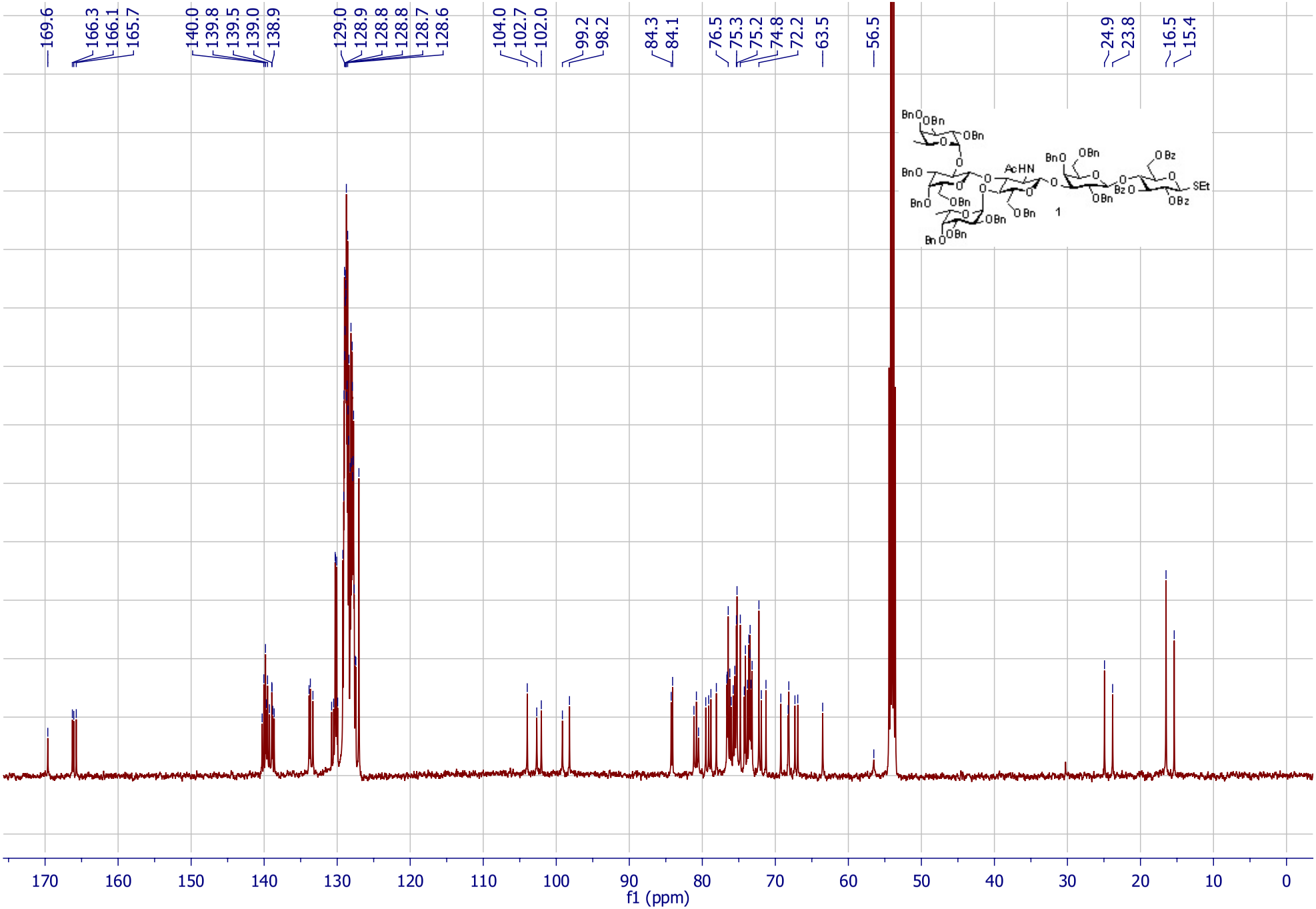

BnO
OH
AcHN
BnO
OBn
OBz
BnO
Ph
OBn
OBn
BzO
SEt
OBz
16
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130

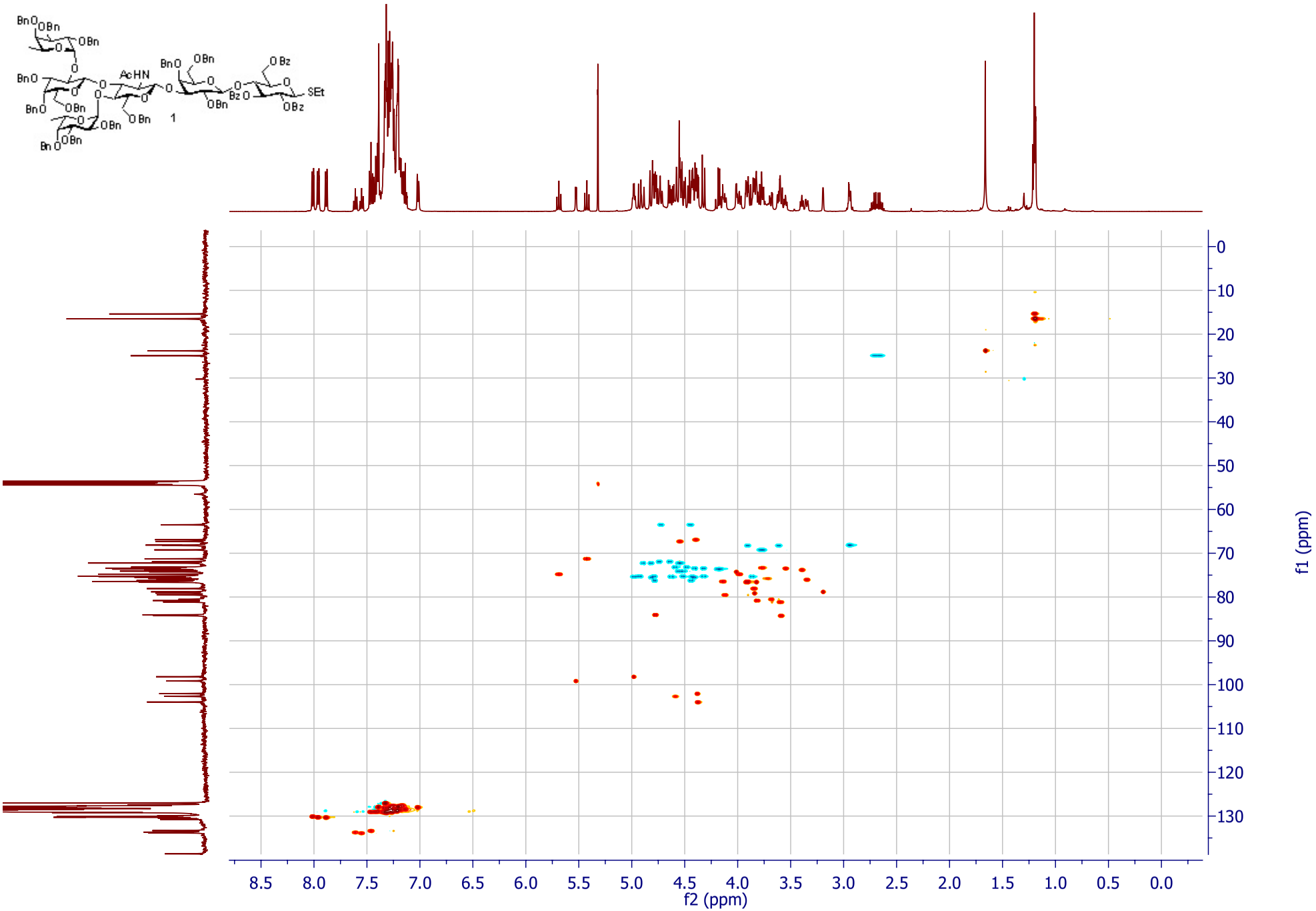

7.95
7.94
7.86
7.29
7.28
7.27
7.25
7.24
7.24
7.23
7.22
7.21
7.16
5.67
5.66
5.64
5.43
4.70
4.69
4.68
4.47
4.41
4.37
4.32
4.09
4.08
4.00
3.76
3.76
3.61
3.45
2.93
2.90
2.81
2.80
2.68
2.67
2.65
2.64
1.48
1.19
1.18
1.17
3.90
1.95
1.03
1.03
43.45
1.01
1.01
0.97
0.97
1.07
2.08
5.33
1.14
2.00
4.11
0.88
3.00
3.00
4.04
2.01
4.22
1.02
1.06
2.79
1.09
0.87
0.87
0.92
2.15
2.85
3.00
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)

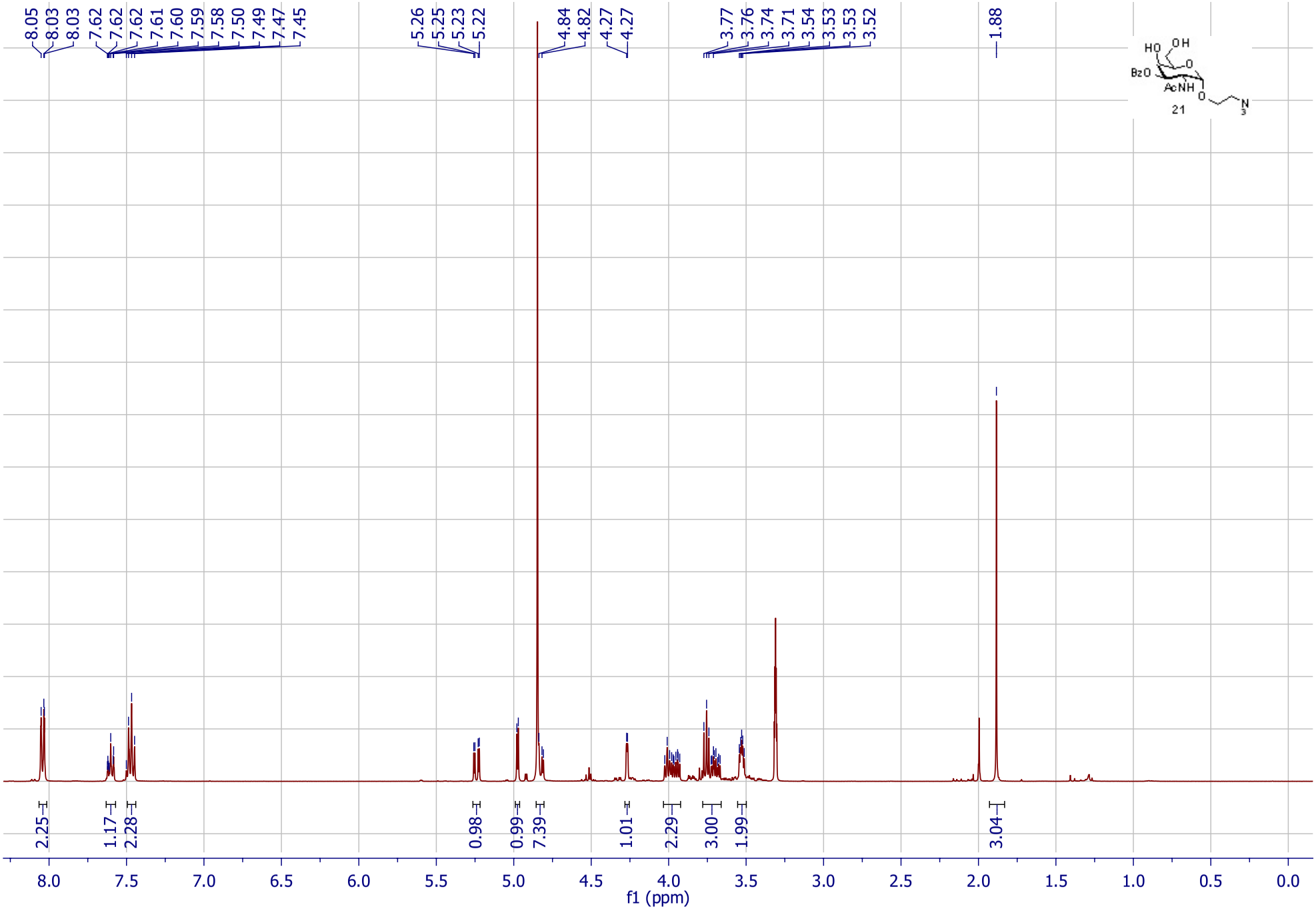

171.65
165.85
165.75
165.33
139.13
138.86
138.39
138.25
138.03
137.51
128.40
128.39
128.36
128.25
127.52
127.36
104.77
102.96
101.56
87.14
81.35
73.65
73.44
73.05
72.90
62.95
55.63
24.24
23.13
14.89
BnO
OH
AcHN
HO
OBn
OBn
OBn
17
BnO
OBn
OBn
OBz
OBz
SEt
OBz
f1 (ppm)

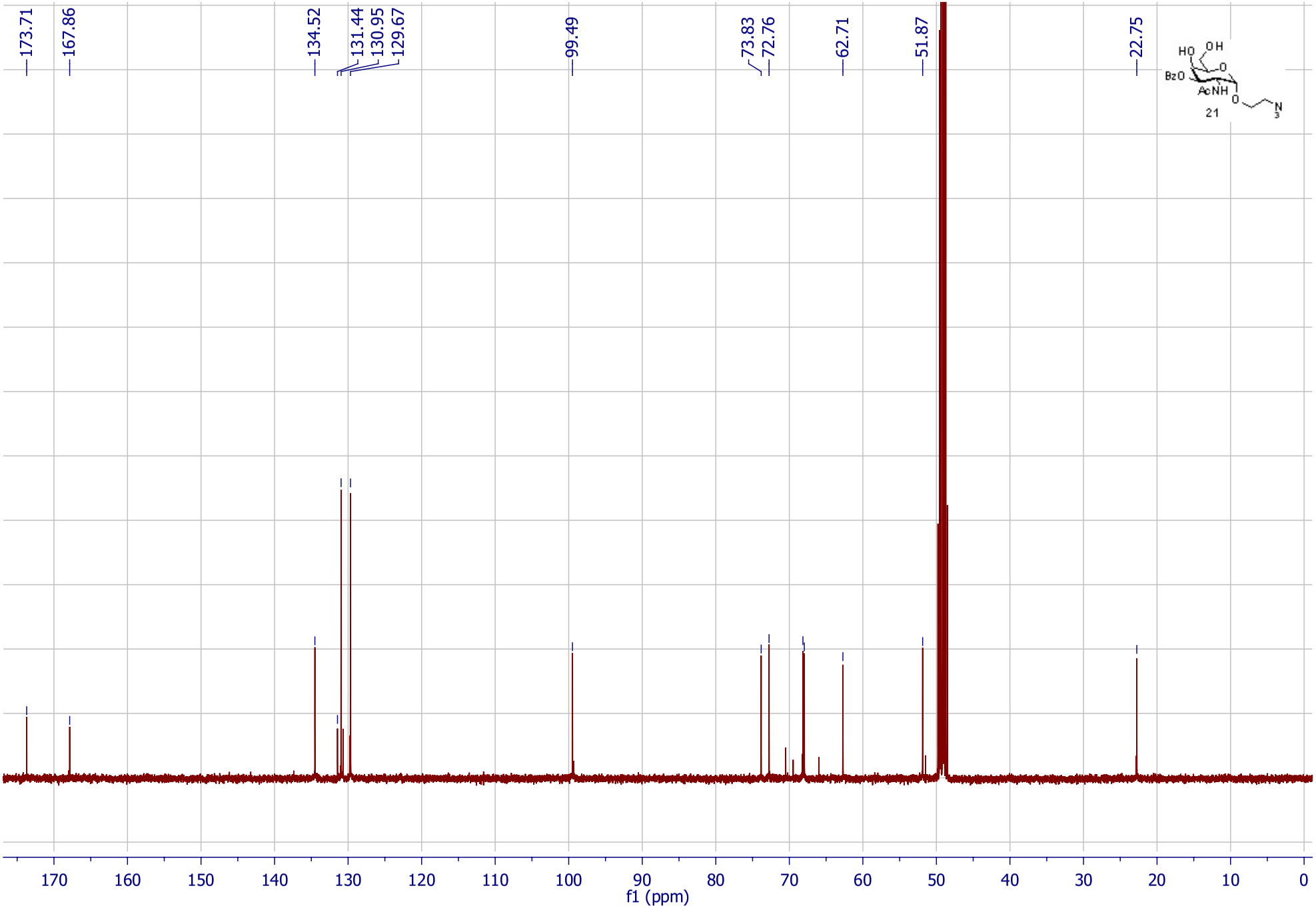

BnO
OH
AcHN
HO
Bn O
OBn
OBn
17
Bn O
OBn
OBn
Bz O
OBz
OBz
SEt
f2 (ppm)
f1 (ppm)

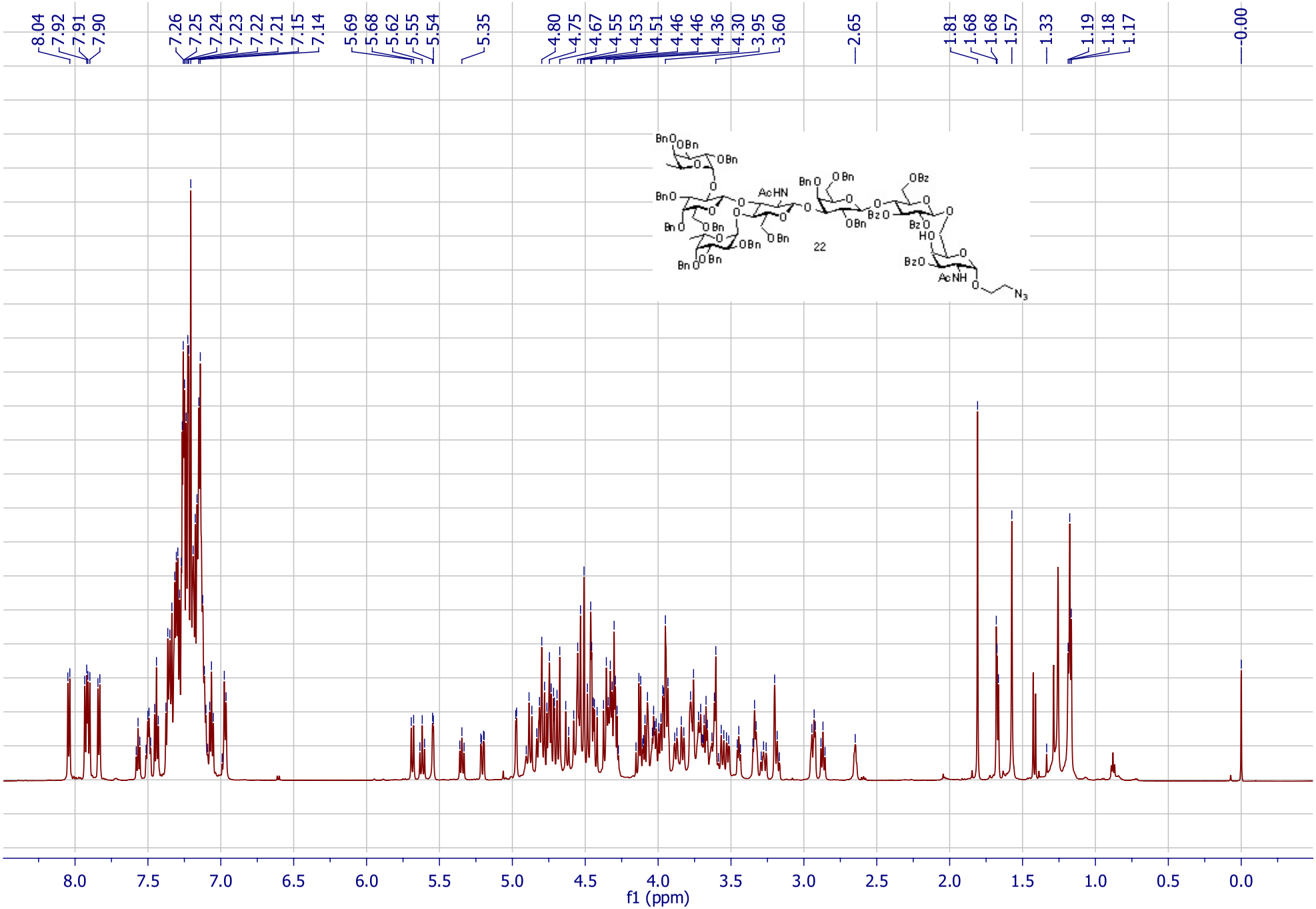

8.02
8.00
7.97
7.95
7.88
7.39
7.32
7.32
7.30
7.29
7.27
7.26
7.21
7.20
5.69
5.53
5.52
5.44
5.42
5.32
5.32
5.32
4.80
4.58
4.55
4.54
4.53
4.42
4.40
4.40
4.39
4.33
4.31
4.18
4.17
3.20
2.71
2.70
2.67
2.66
1.66
1.20
1.19
1.19
BnO
OBn
AcHN
OBz
BzO
SEt
1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

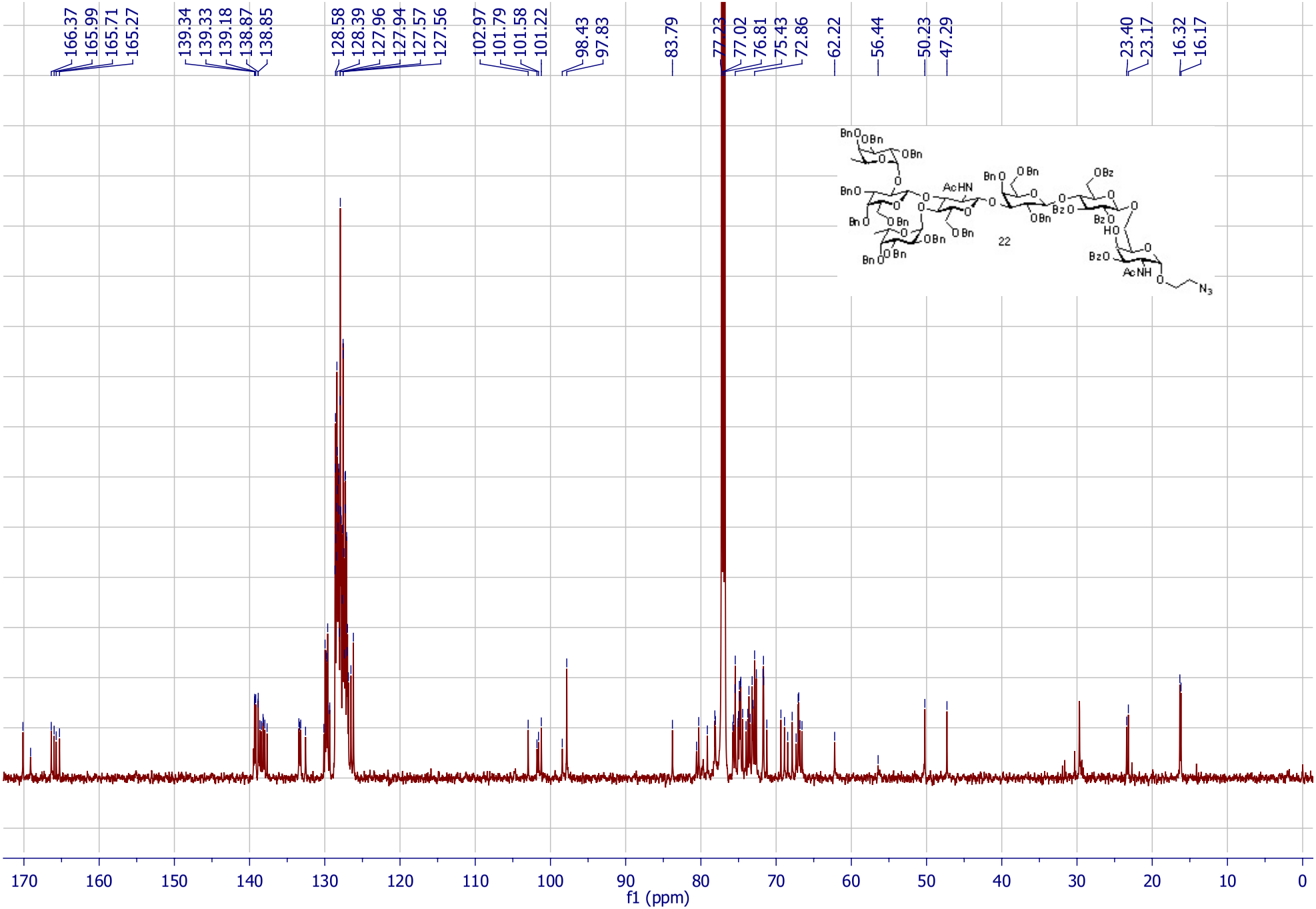

169.6
166.3
166.1
165.7
140.0
139.8
139.5
139.0
138.9
129.0
128.9
128.8
128.8
128.7
128.6
104.0
102.7
102.0
99.2
98.2
84.3
84.1
76.5
75.3
75.2
74.8
72.2
63.5
56.5
24.9
23.8
16.5
15.4
BnO
OBn
AcHN
OBz
SEt
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

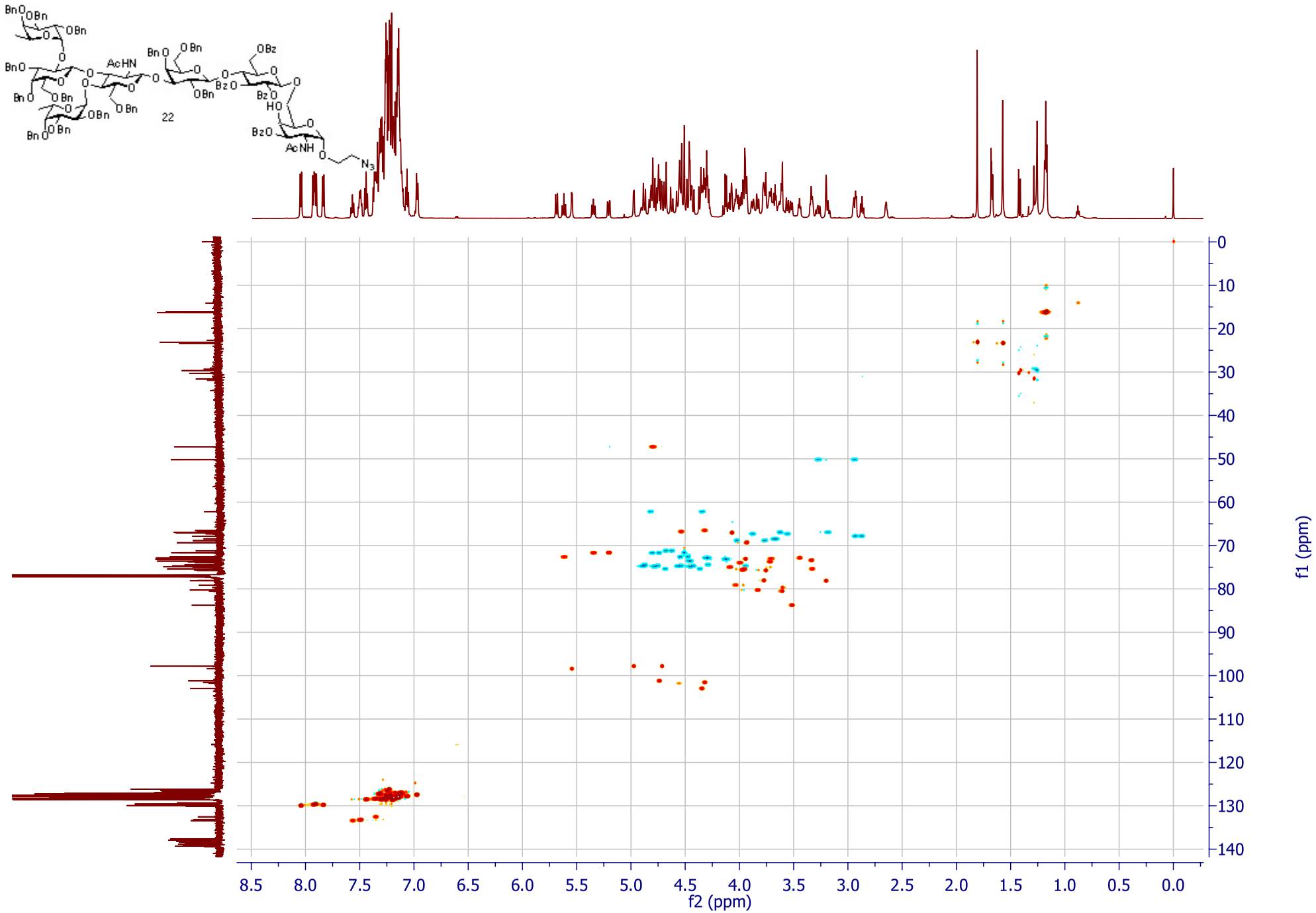

BnO
OBn
AcHN
OBz
SEt
1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)

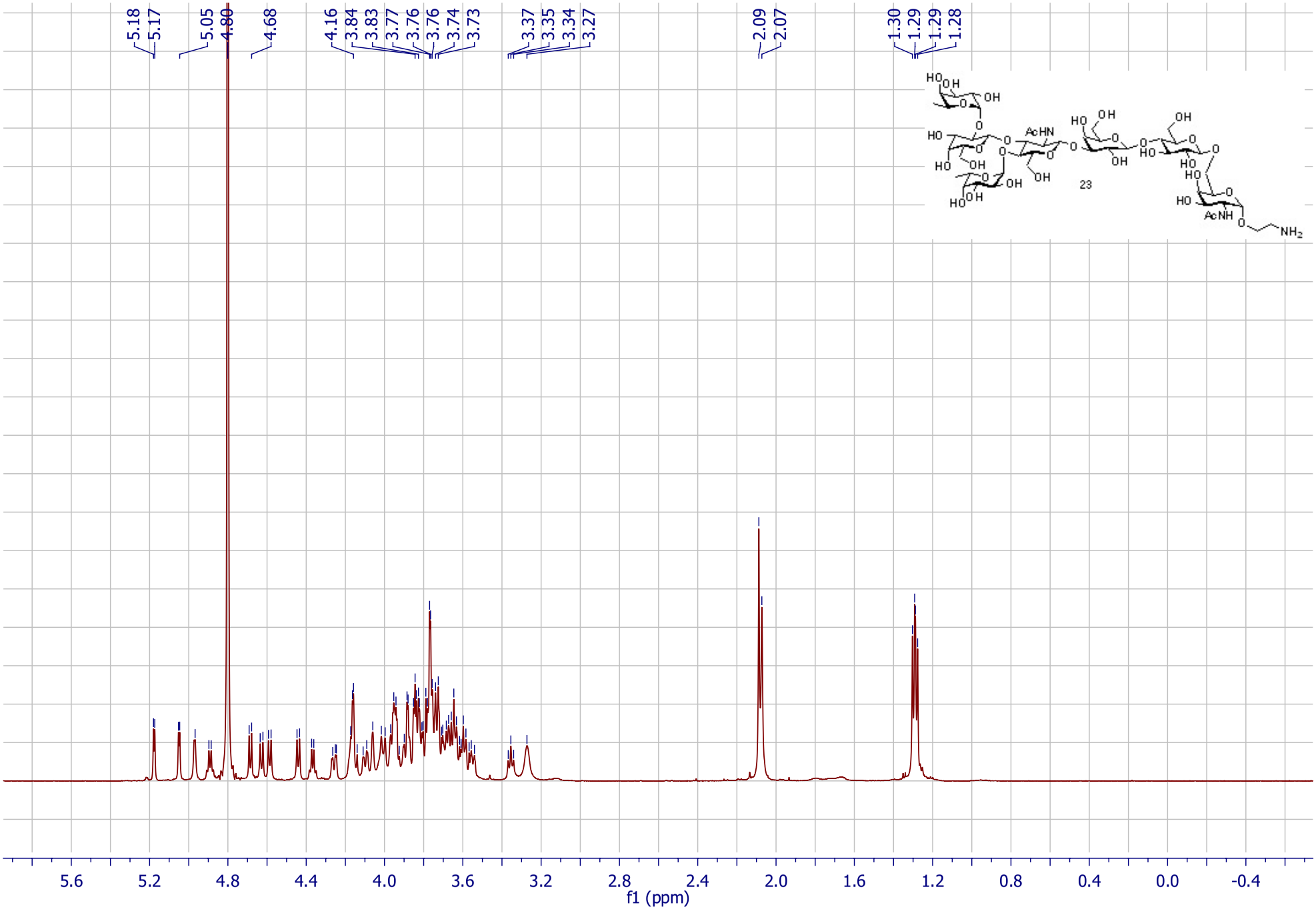

8.05
8.03
8.03
7.62
7.62
7.62
7.61
7.60
7.59
7.58
7.50
7.49
7.47
7.45
5.26
5.25
5.23
5.22
4.84
4.82
4.27
4.27
3.77
3.76
3.74
3.71
3.54
3.53
3.53
3.52
1.88
HO
OH
O
BzO
AcNH
O
N
3
21
2.25
1.17
2.28
0.98
0.99
7.39
1.01
2.29
3.00
1.99
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

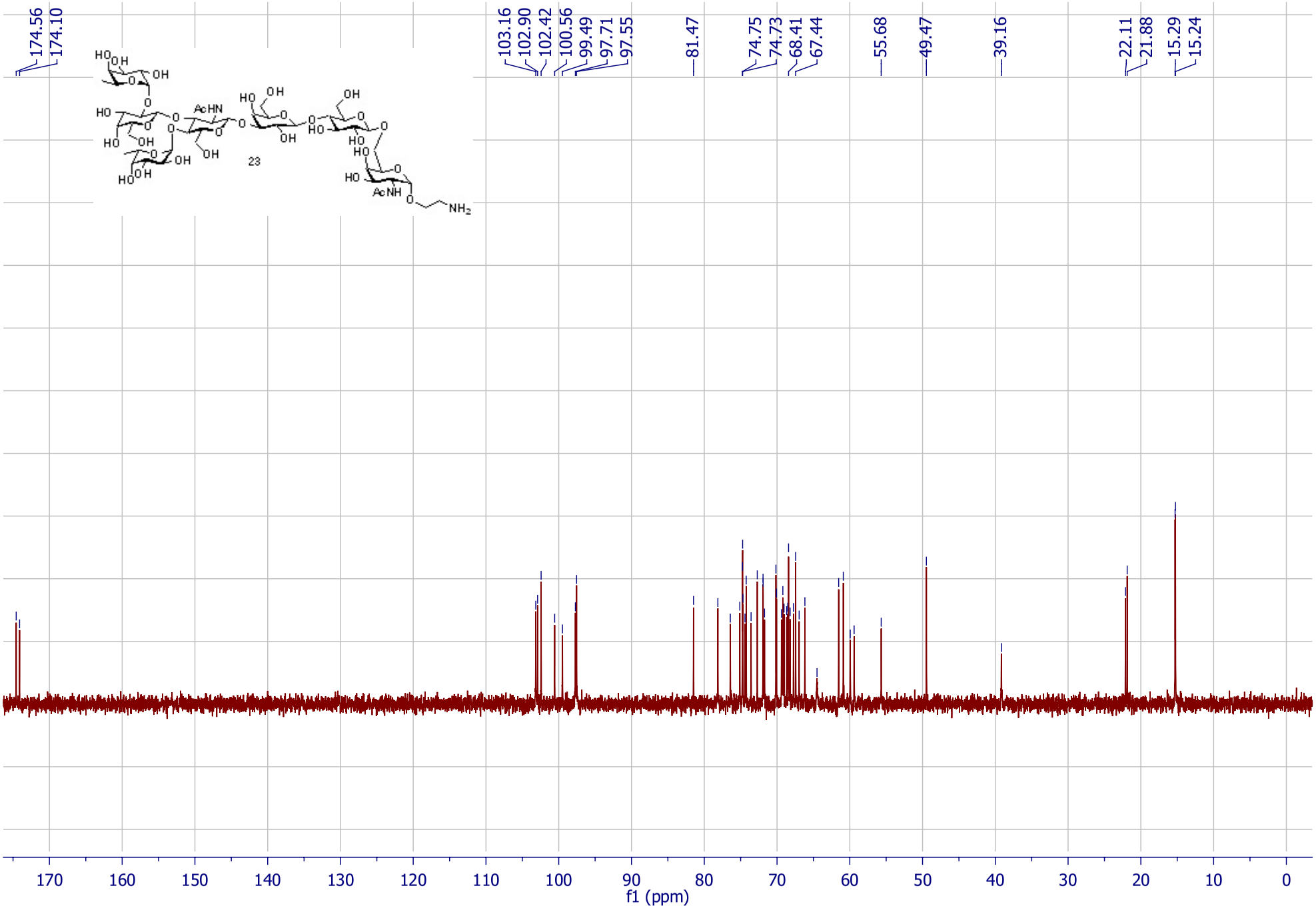

173.71
167.86
134.52
131.44
130.95
129.67
99.49
73.83
72.76
62.71
51.87
22.75
HO
OH
O
BzO
AcNH
O
N3
21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

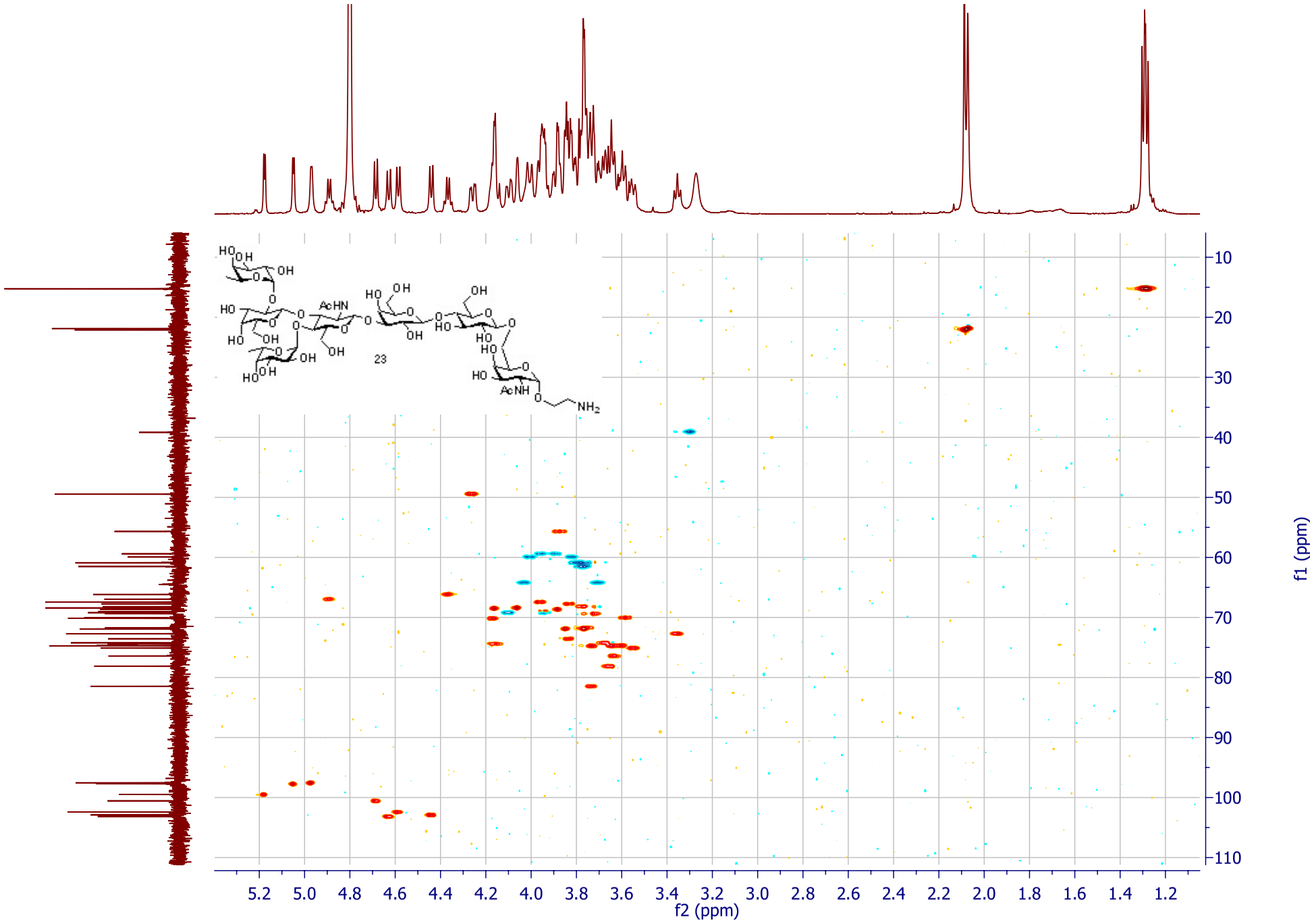

8.04
7.92
7.91
7.90
7.26
7.25
7.24
7.23
7.22
7.21
7.15
7.14
5.69
5.68
5.62
5.55
5.54
5.35
4.80
4.75
4.67
4.55
4.53
4.51
4.46
4.46
4.36
4.30
3.95
3.60
2.65
1.81
1.68
1.68
1.57
1.33
1.19
1.18
1.17
0.00
22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

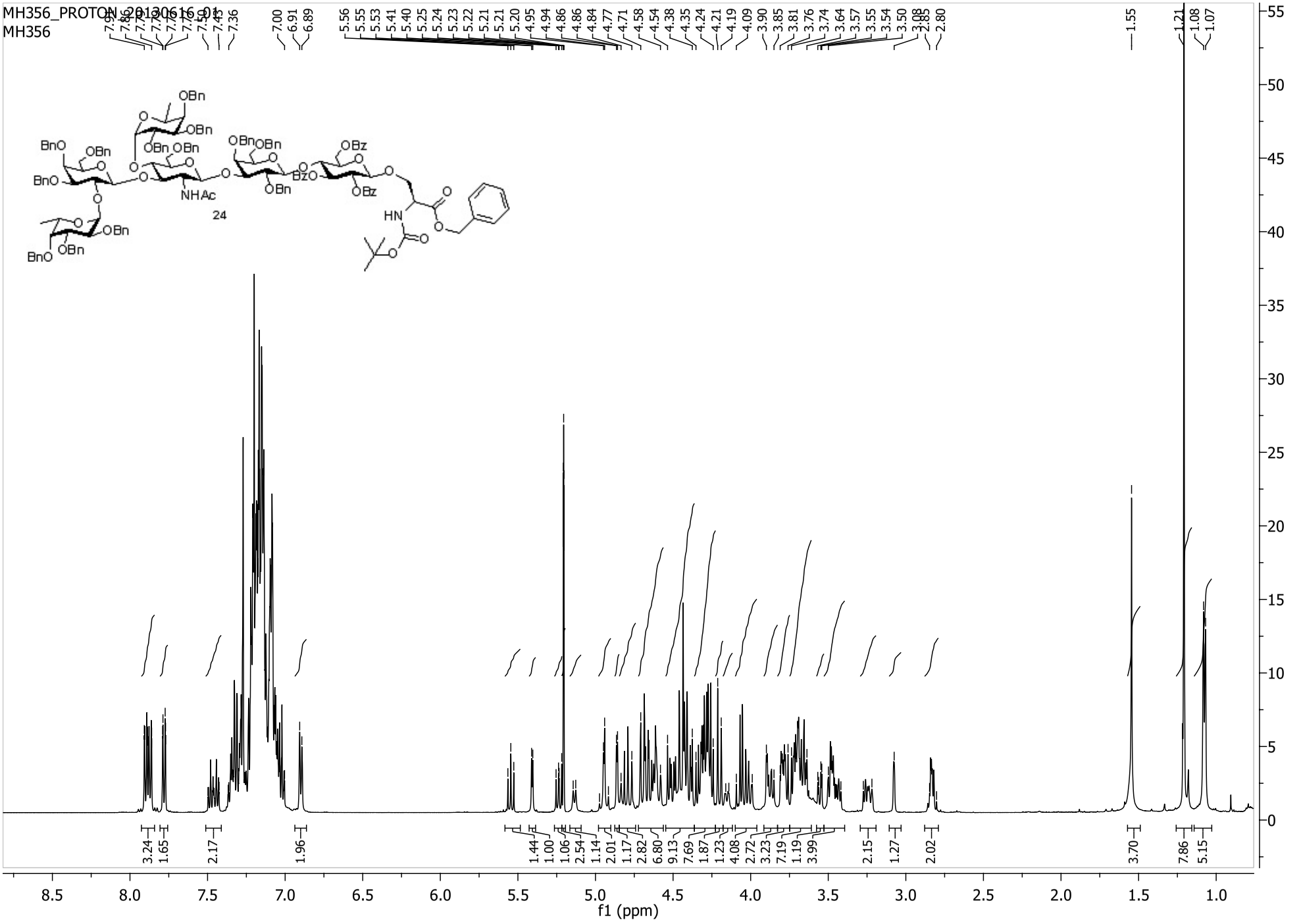

166.37
165.99
165.71
165.27
139.34
139.33
139.18
138.87
138.85
128.58
128.39
127.96
127.94
127.57
127.56
102.97
101.79
101.58
101.22
98.43
97.83
83.79
77.23
77.02
76.81
75.43
72.86
62.22
56.44
50.23
47.29
23.40
23.17
16.32
16.17
22
f1 (ppm)

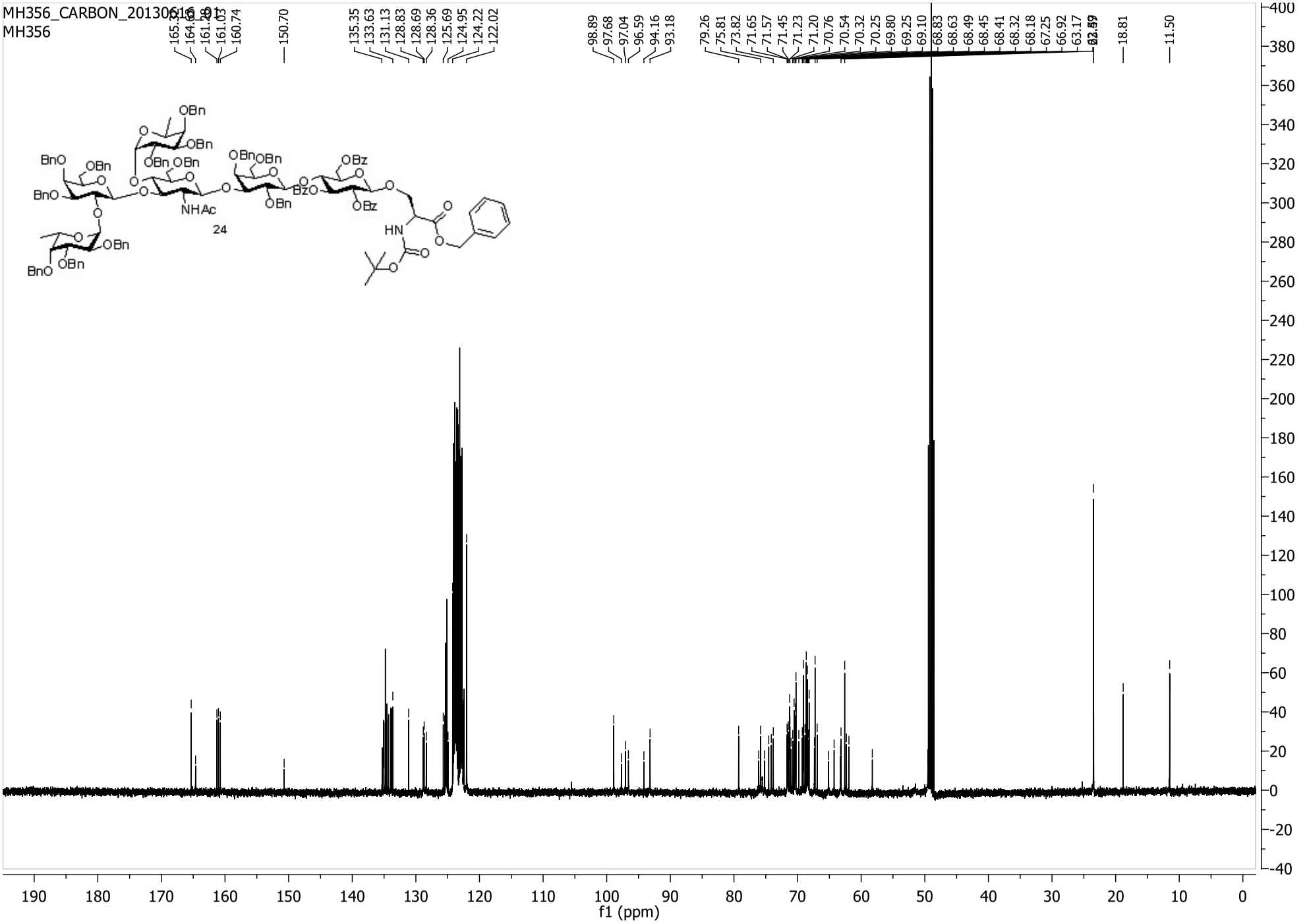

22
f2 (ppm)
f1 (ppm)

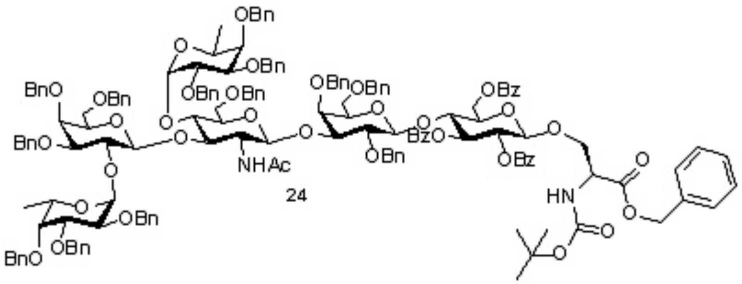

5.18
5.17
5.05
4.80
4.68
4.16
3.84
3.83
3.77
3.76
3.76
3.74
3.73
3.37
3.35
3.34
3.27
2.09
2.07
1.30
1.29
1.29
1.28
23
f1 (ppm)


174.56
174.10
103.16
102.90
102.42
100.56
99.49
97.71
97.55
81.47
74.75
74.73
68.41
67.44
55.68
49.47
39.16
22.11
21.88
15.29
15.24
23
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

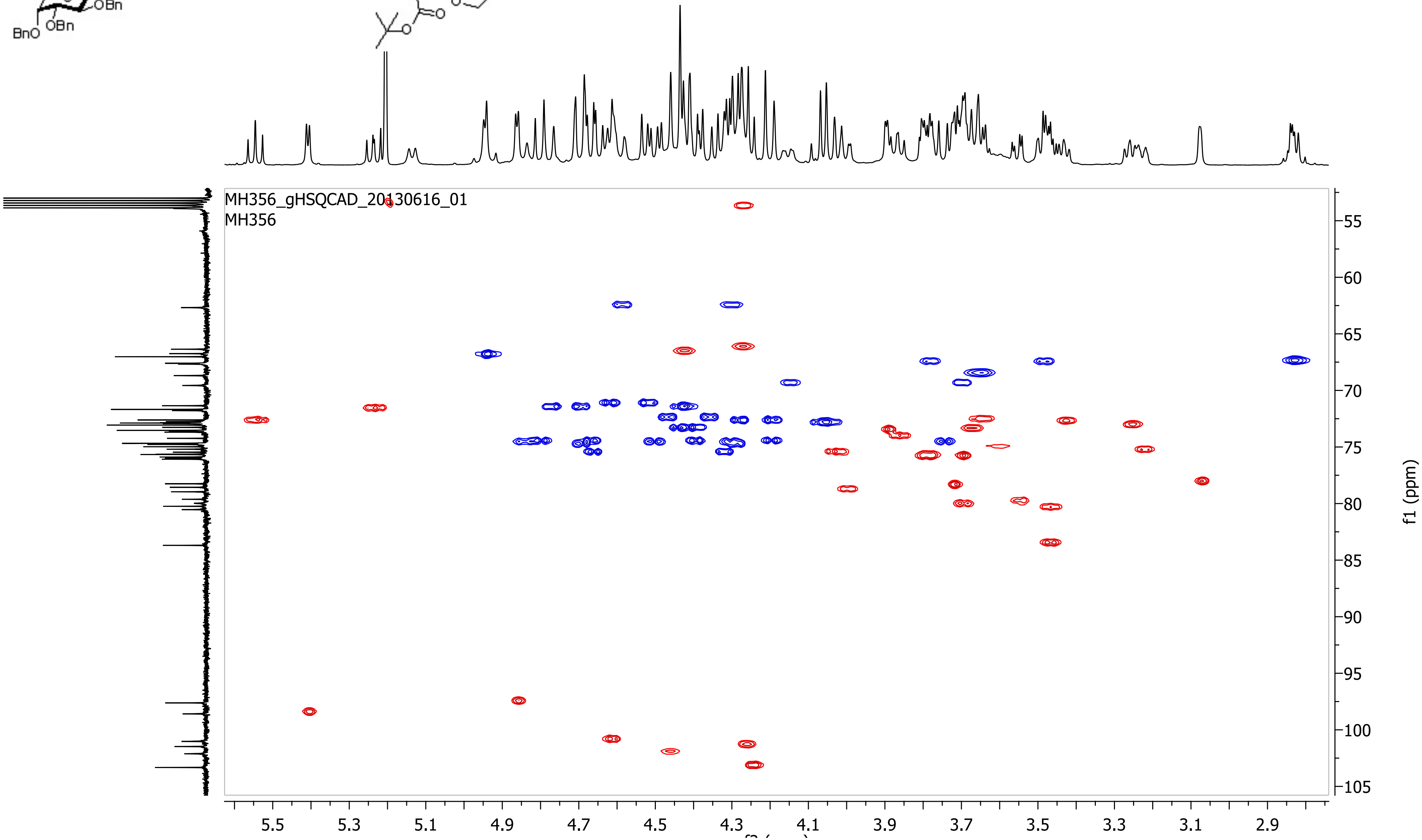

23
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
10
20
30
40
50
60
70
80
90
100
110

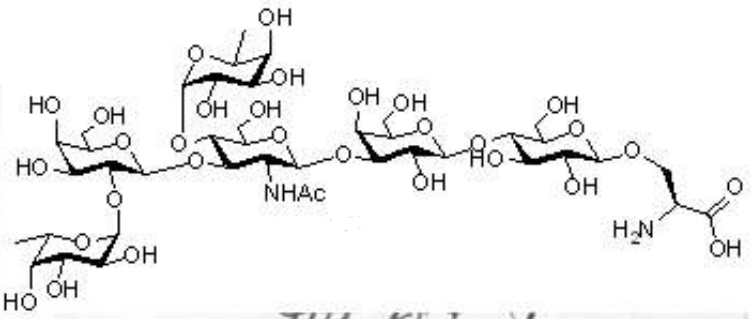

MH356_PROTON_20130616_01
MH356
24
f1 (ppm)


MH356_CARBON_20130616-01
MH356
165.31
164.24
161.41
161.03
160.74
150.70
135.35
133.63
131.13
128.83
128.69
128.36
125.69
124.95
124.22
122.02
98.89
97.68
97.04
96.59
94.16
93.18
79.26
75.81
73.82
71.65
71.57
71.45
71.23
71.20
70.76
70.54
70.32
70.25
69.80
69.25
69.10
68.83
68.63
68.49
68.45
68.41
68.32
68.18
67.25
66.92
63.17
18.81
11.50
24
f1 (ppm)


BnO
OBn
BnO
OBn
OBn
OBn
OBn
OBn
NHAc
OBn
OBn
OBn
BzO
OBz
OBz
HN
BnO
OBn

24


MH356_gHSQCAD_20130616_01
MH356
f1 (ppm)
55
60
65
70
75
80
85
90
95
100
105
5.5
5.3
5.1
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9



Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 1000.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

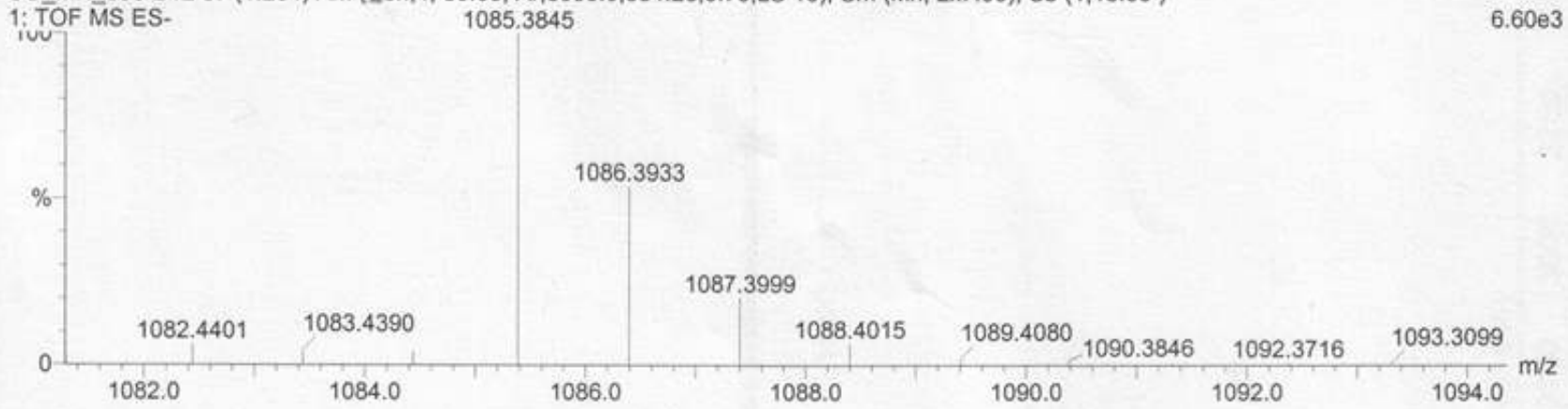
TM 856_2

Monoisotopic Mass, Odd and Even Electron Ions

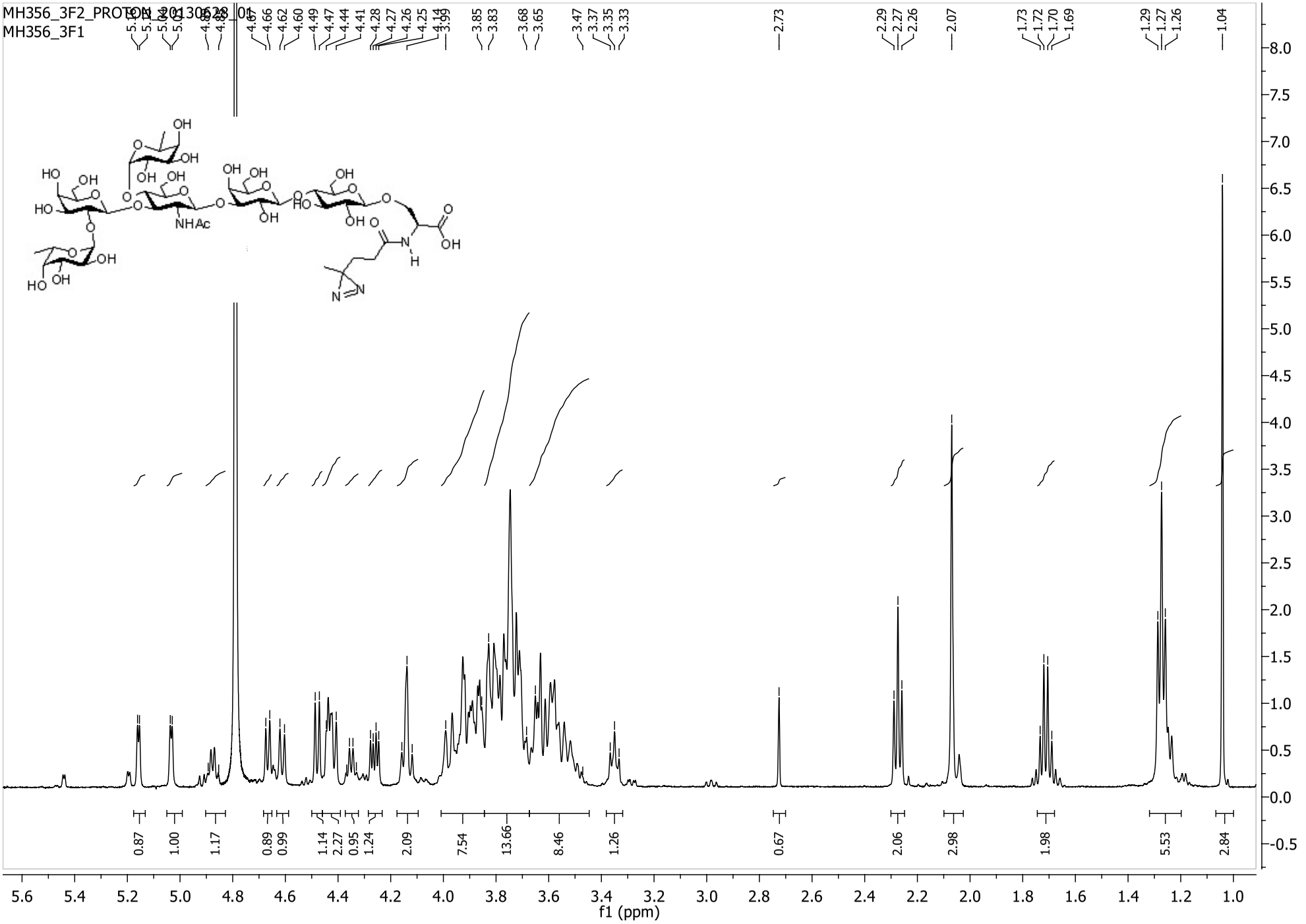
96 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

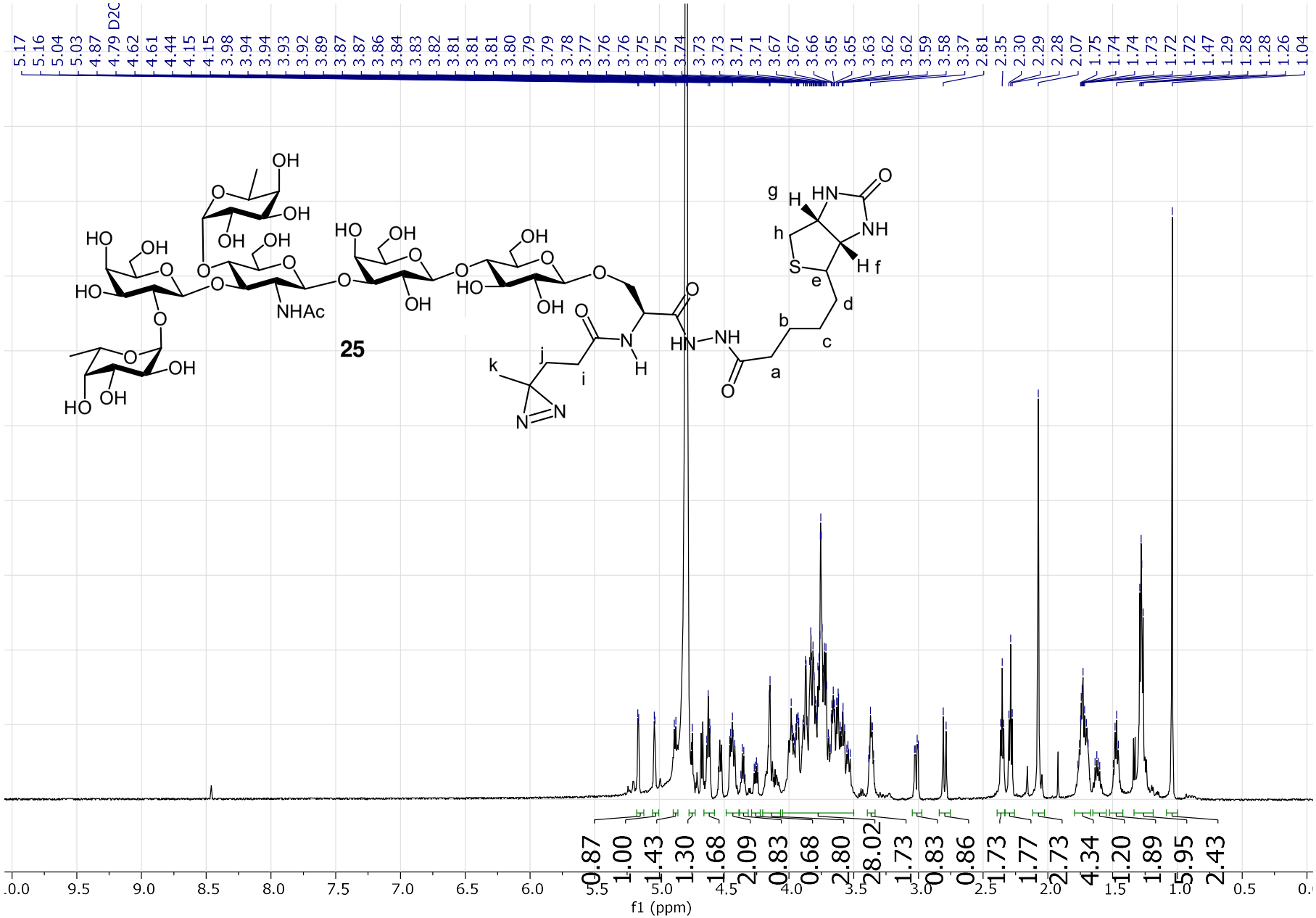
SO_MH_356-2-r2 37 (1.204) AM (Cen,4, 80.00, Ar,5000.0,554.26,0.70,LS 10); Sm (Mn, 2x7.00); Sb (1,15.00)

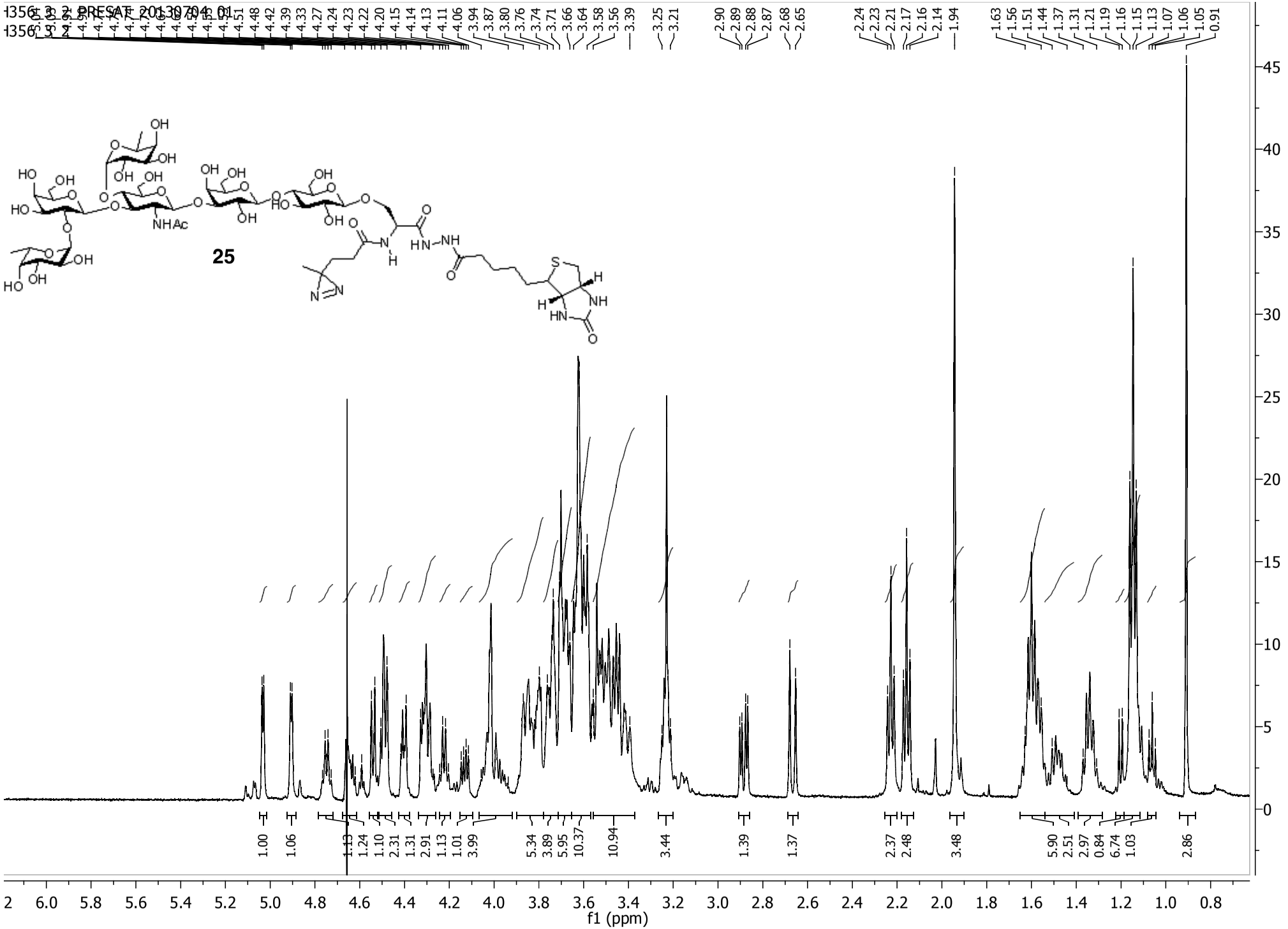
1: TOF MS ES-

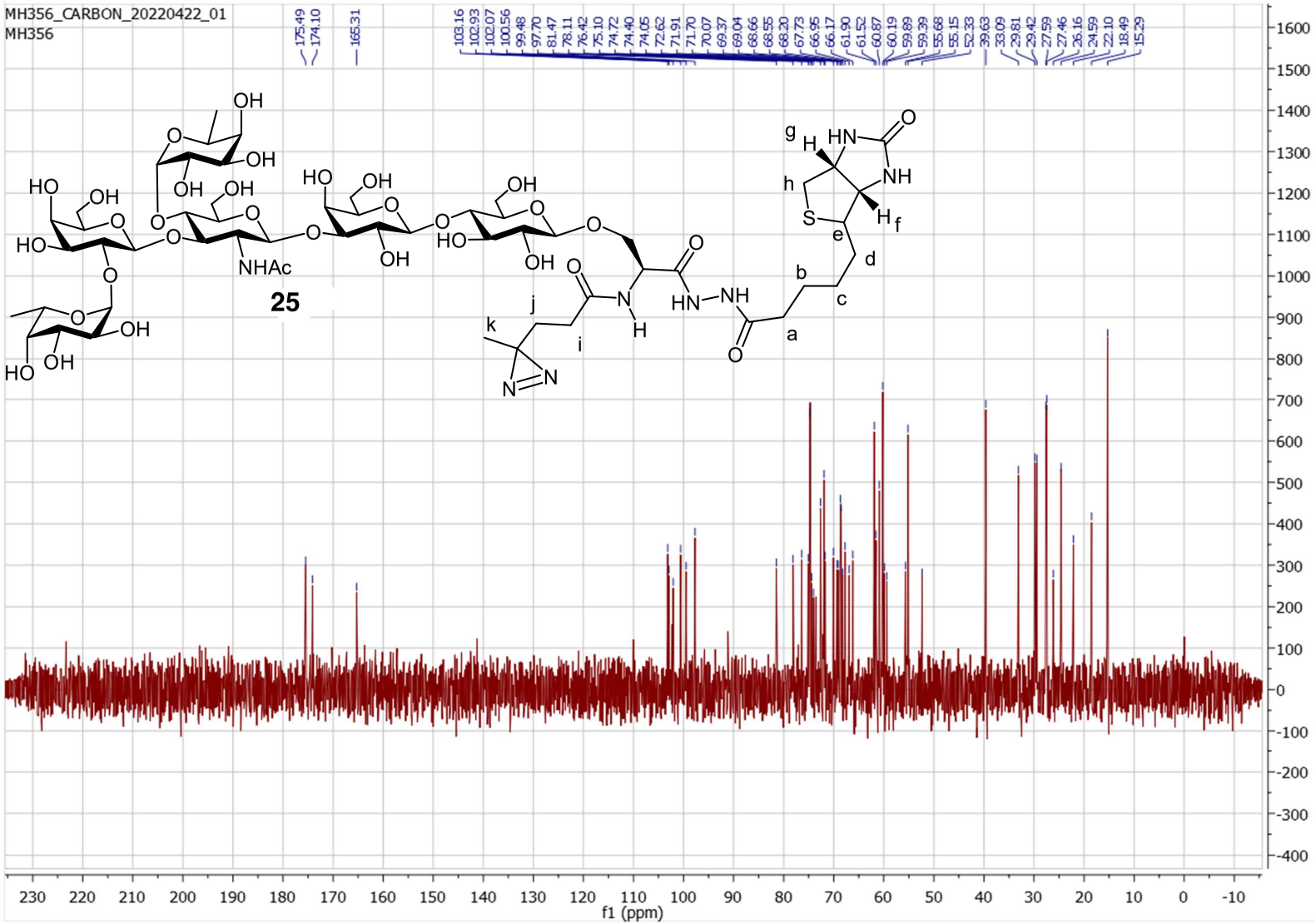


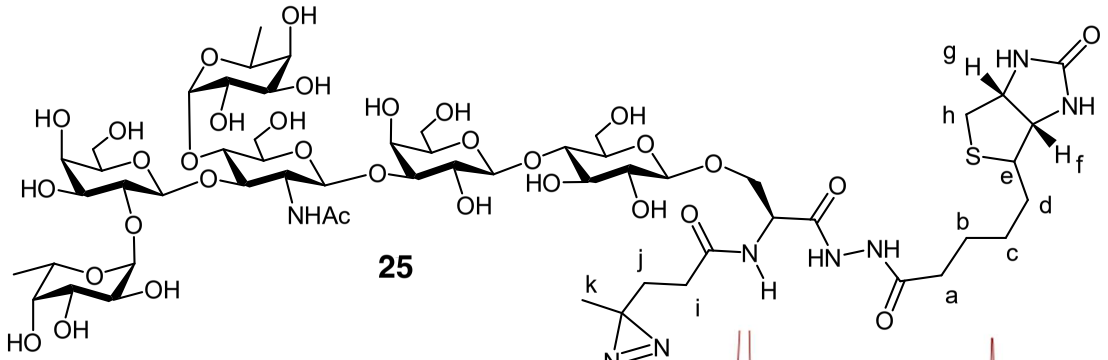
Minimum:				-1.5		
Maximum:		200.0	20.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1085.3845	1085.3884	-3.9	-3.6	8.5	1	C41 H69 N2 O31


MH356_3F2_PROTON_1_20130628_01
MH356_3F1
5.19
5.18
5.04
5.03
4.68
4.67
4.66
4.62
4.60
4.49
4.47
4.44
4.41
4.28
4.27
4.26
4.25
4.14
3.99
3.85
3.83
3.68
3.65
3.47
3.37
3.35
3.33
2.73
2.29
2.27
2.26
2.07
1.73
1.72
1.70
1.69
1.29
1.27
1.26
1.04
NHAc
0.87
1.00
1.17
0.89
0.99
1.14
2.27
0.95
1.24
2.09
7.54
13.66
8.46
1.26
0.67
2.06
2.98
1.98
5.53
2.84
f1 (ppm)

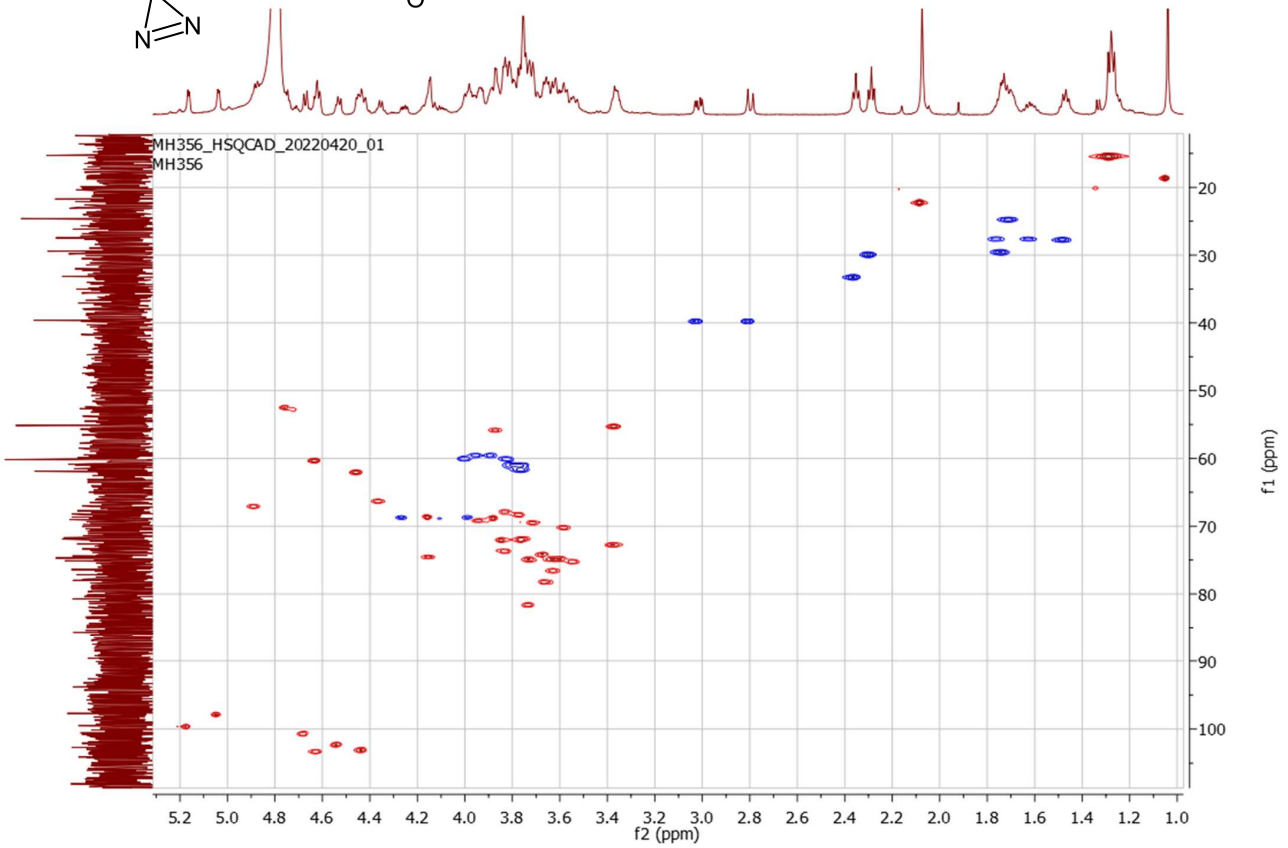

5.17 5.16 5.04 5.03 4.87 4.79 D2O 4.62 4.61 4.44 4.15 4.15 3.98 3.94 3.94 3.93 3.92 3.89 3.87 3.87 3.86 3.84 3.83 3.82 3.81 3.81 3.81 3.80 3.79 3.79 3.78 3.77 3.76 3.76 3.75 3.75 3.74 3.73 3.73 3.71 3.67 3.67 3.66 3.65 3.65 3.63 3.62 3.62 3.59 3.58 3.37 2.81 2.35 2.30 2.29 2.28 2.07 1.75 1.74 1.74 1.73 1.72 1.72 1.47 1.29 1.28 1.28 1.26 1.04
25
0.87 1.00 1.43 1.30 1.68 2.09 0.83 0.68 2.80 28.02 1.73 0.83 0.86 1.73 1.77 2.73 4.34 1.20 1.89 5.95 2.43
f1 (ppm)


25
f1 (ppm)


MH356_CARBON_20220422_01
MH356
175.49
174.10
165.31
103.16
102.93
102.07
100.56
99.48
97.70
81.47
78.11
76.42
75.10
74.72
74.40
74.05
72.62
71.91
71.70
70.07
69.37
69.04
68.66
68.55
68.20
67.73
66.95
66.17
61.90
61.52
60.87
60.19
59.89
59.39
55.68
55.15
52.33
39.63
33.09
29.81
29.42
27.59
27.46
26.16
24.59
22.10
18.49
15.29
25
NHAc
HO
OH
O
HN
NH
N
H
S
a
b
c
d
e
f
g
h
i
j
k
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
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)


OH
HO
NHAc
O
N
H
HN
NH
S
a
b
c
d
e
f
g
h
i
j
k

25


MH356_HSQCAD_20220420_01
MH356
f2 (ppm)
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
20
30
40
50
60
70
80
90
100