Supporting Information

Reagent controlled stereoselective synthesis of α-glucans

Liming Wang, Herman S. Overkleeft, Gijsbert A. van der Marel, Jeroen D. C. Codée*

Leiden institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands

Table of Contents

General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon atmosphere. DCM used in the glycosylation reactions was dried with flamed4Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Flash column chromatography was performed on silica gel (40-63µm). ^1H and ^{13}C spectra were recorded on a Bruker AV 400 and Bruker AV 500 in $CDCl_3$ or D_2O. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^1H NMR in $CDCl_3$) or the residual signal of the deuterated solvent. Coupling constants (*J*) are given in Hz. All ^{13}C spectra are proton decoupled. NMR peak assignments were made using COSY and HSQC experiments, where applicable Clean TOCSY, HMBC and GATED experiments were used to further elucidate the structure. The anomeric product ratios were analyzed through integration of proton NMR signals and HPLC. HPLC analysis was performed over chiralpak AD column (0.46cmΦ×25cm) and eluted with hexane/isopropanol (95/5) mixture at a 1 mL/min flow rate and UV 254nm detector. Column chromatography was carried out using silica gel (0.040-0.063 mm). Size-exclusion chromatography was carried out using Sephadex LH-20.

Standard procedure for glycosylation of secondary alcohols with thiodonors (2a-5a) (procedure A)

The donor (1.0 eq, co-evaporated with toluene) was dissolved in dry DCM (see experimental description below for concentrations) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (16 eq) was added to the solution. The solution was cooled to 0℃, after which NIS (1.0 eq) and TMSOTf (1.0 eq) were added. After 1 h, the pre-activation was complete as indicated by TLC-analysis. Then acceptor (0.7 eq, see experimental description below for concentrations) was added to the solution. The reaction was stirred at 0 ^oC until TLC-analysis showed complete conversion of the acceptor. The reaction mixture was diluted and the reaction was quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by size exclusion (eluent (50/50) MeOH/DCM and silica gel column chromatography (See experimental description below for eluent system).

Standard procedure for glycosylation of secondary alcohols with imidate donors (2b-5b) (procedure B)

The donor (1.0 eq, co-evaporated with toluene) was dissolved in dry DCM (see experimental description below for concentrations) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (16 eq) was added to the solution. The solution was cooled to -78 ^oC, after which TfOH (1.0 eq) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor (0.7 eq, see experimental description below for concentrations) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 ^oC until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The products were purified by size exclusion (eluent

(50/50) MeOH/DCM and silica gel column chromatography (See experimental description below for eluent system).

Standard procedure for the glycosylation of primary alcohols (procedure C)

A mixture of donor (1.0 eq), acceptor (0.7 eq) was co-evaporated with toluene three times and together with $Ph_3P=O$ (6 eq) dissolved in dry DCM (see experimental description below for concentrations) and stirred over fresh flame-dried molecular sieves 3A under nitrogen. Then TMSI (1.0 eq) was added slowly in the mixture. The reaction was stirred at room temperature until TLC-analysis indicated the reaction to be complete. The solution was diluted and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by size exclusion (eluent (50/50) MeOH/DCM and silica gel column chromatography (See experimental description below for eluent system).

General procedure for deprotection of the Nap protecting group (general procedure D)

The starting material (1.0 eq) was dissolved in CH_2Cl_2 (DCM):H_2O (10:1, 0.1 M). DDQ (1.1 eq) was added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (± 2h). Then the mixture was diluted with DCM and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (See experimental description below for eluent system).

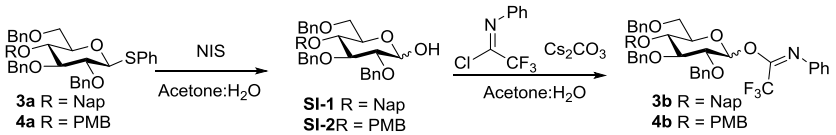
General procedure for deprotection of the PMB protecting group (general procedure E)

The starting material (1.0 eq) and triethylsilane (1.0 eq) were dissolved in DCM:HFIP (hexafluoro-*iso*-propanol) (1:1, 0.1 M). Then 0.2M HCl in HFIP (0.1 eq) was added to the mixture. The reaction was stirred until TLC-analysis indicated complete consumption of the starting material (± 30 min.). Then the mixture was diluted with DCM and the reaction quenched with saturated Na_2CO_3. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (See experimental description below for eluent system).

Experimental Procedures and Characterization Data of Products

For the synthesis procedure and data of known compounds **2a** [S1], **2b** [S2,10], **3a** [S3], **4a** [S4], **6** [S5,6], **7** [S5,7], **8** [S5,8], **9** [S10], **11** [S10], **12** [S10], **22** [S5,9], **23** [S10] see references.

Scheme S1. Preparation of **3b** and **4b**.



N-phenyl trifluoroacetimidate glucose donor 3b

Compound **3a** (8.0 g, 11.7 mmol) was dissolved in acetone:H_2O (10:1, 120 mL). N-Iodosuccinimide (NIS) (5.27 g, 23.4 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$, then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography (PE:EA = 2:1). Compound **SI-1** (6.37 g, 92% yield) was obtained as a white solid. Next, compound **SI-1** (6.37 g, 10.8 mmol) was dissolved in acetone:H_2O (10:1, 110 mL). Cs_2CO_3 (5.27 g, 16.2 mmol) and 2,2,2-trifluoro-N-phenylacetimidoyl chloride (2.62 ml, 16.2 mmol) were added to the solution respectively. The reaction stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (PE:EA = 50:1-20:1). Compound **3b** (7.89 g, 96% yield, mixture of α and β, PE:EA = 10:1, R*f* = 0.45-0.55) was obtained as yellow syrup.

^{1}H-NMR ($CDCl_3$, 500 MHz, 60℃) δ 7.77-6.72(m, aromatic *H*), 6.46 (bs, 1 H, H-1α), 5.61 (bs, 1 H, H-1β), 5.00-4.71 (m, CH*H*), 4.58-4.43 (m, CH*H*), 4.06 (t, J = 9.0 Hz, 1 H, H-α), 3.99 (bd, 1 H, H-α), 3.80-3.68 (m), 3.42 (bs, 1 H). ^{13}C-APT ($CDCl_3$, 125 MHz, 60℃) δ 143.93, 143.73, 143.42, 138.94, 138.72, 138.32, 138.22, 138.14, 138.12, 135.91, 135.82, 133.57, 133.54, 133.28, 133.26 (aromatic *C*), 129.42, 128.81, 128.58, 128.55, 128.49, 128.46, 128.21, 128.17, 128.06, 128.05, 127.98, 127.94, 127.90, 127.80, 127.94, 127.90, 127.80, 127.74, 127.71, 127.68, 126.72, 126.70, 126.42, 126.17, 126.06, 126.00, 124.44, 124.30, 120.75, 119.66, 119.59 (aromatic *C*H), 116.50 (q, *C*F_3), 97.65 (C-1β), 93.95 (C-1α), 84.76 (β), 81.77 (α), 81.25 (β), 79.73 (α), 77.61 (β), 77.34 (α), 76.06 (β), 75.79, 75.60, 75.32, 75.07, 75.05, 73.72, 73.64, 73.57 (α), 73.52, 68.69 (C-6α and β). HR-MS: Calculated for $C_{43}H_{42}F_3O_7N$ [M-[O(C=NPh)CF3]+OH+Na]$^+$: 593.2510, found:593.2516.

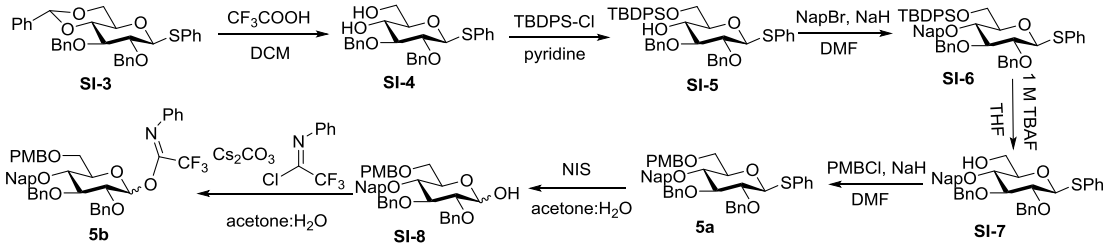
N-phenyl trifluoroacetimidate glucose donor 4b

Compound **4a** (10 g, 15.1 mmol) was dissolved in acetone:H_2O (10:1, 150 mL). N-Iodosuccinimide (NIS) (6.79 g, 30.2 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$, then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography (PE:EA = 2:1). Compound **SI-2** (7.40 g, 86% yield) was obtained as a white solid. Next, compound **SI-2** (7.40 g, 10.8 mmol) was dissolved in acetone:H_2O (10:1, 110 mL). Cs_2CO_3 (6.34 g, 19.4 mmol) and 2,2,2-trifluoro-N-phenylacetimidoyl chloride (3.15 ml, 19.4 mmol) were added to the solution respectively. The reaction stirred overnight, then quenched

with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (PE:EA = 50:1-20:1). Compound **4b** (9.14 g, 95% yield, mixture of α and β, PE:EA = 10:1, R*f* = 0.34) was obtained as yellow syrup.

^{1}H-NMR ($CDCl_3$, 500 MHz, 60℃) δ 7.79-6.70 (m, aromatic*H*), 6.44 (bs, 1 H, H-1α), 5.57 (bs, 1 H, H-1β), 4.97-4.70 (m, CH*H*), 4.60-4.47 (m, CH*H*), 4.01 (t, J = 9.5 Hz, 1 H, H-α), 3.94 (bd, 1 H, H-α), 3.75-3.61 (m), 3.36 (bs, 1 H). ^{13}C-APT ($CDCl_3$, 125 MHz, 60℃) δ 159.66, 143.94, 143.73, 139.00, 138.78, 138.38, 138.28, 138.14, 130.67, 130.57 (aromatic *C*), 129.68, 129.64, 129.46, 128.80, 128.57, 128.54, 128.51, 128.48, 128.46, 128.18, 127.96, 127.92, 127.80, 127.78, 127.74, 127.70, 127.66, 126.46, 124.43, 124.27, 120.78, 119.65, 119.58 (aromatic *C*H), 116.48 (q, *C*F_3), 114.12, 114.10 (aromatic *C*H), 97.64 (C-1β), 93.91 (C-1α), 84.78, 81.78, 81.25, 79.70, 77.32, 77.07, 76.07, 75.75, 75.58, 75.06, 74.95, 74.70, 73.72, 73.64, 73.56, 73.52, 68.71 (C-6), 68.69 (C-6), 55.39 (O*C*H_3), 55.38 (O*C*H_3). HR-MS: Calculated for $C_{46}H_{42}F_3O_6N$ [M-[O(C=NPh)CF3]+OH+Na]$^+$: 613.2561, found: 613.2562.

Scheme S2. Preparation of **5b**.



CF_3COOH was added to the solution of **SI-3** (16.9 g, 31.2 mmol) in wet DCM (160 mL). After TLC-analysis showed complete consumption of the starting material, the reaction was quenched with Et_3N. Then the mixture was diluted with DCM, washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product **SI-4** (10.6 g, 75% yield) was purified by column chromatography (PE:EA = 2:1). Compound **SI-4** (10.6 g, 23.4 mmol) was dissolved in pyridine (60 mL). TBDPS-Cl (6.08 ml, 23.4 mmol) was added to the solution. After TLC-analysis showed complete consumption of the starting material, the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with DCM, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo*, purified by column chromatography (PE:EA = 20:1). Compound **SI-5** (12.9 g, 80% yield) was obtained as colorless solid. The compound **SI-5** (12.9 g, 18.7 mmol) was dissolved in DMF (75 mL). Sodium hydride (1.34g, 56 mmol) and NapBr (5.37 g, 24.3 mmol) were added to the mixture at 0 ^oC under N_2. The reaction was stirred at room temperature until TLC-analysis showed complete consumption of the starting material. The mixture was poured in cold water, diluted with Et_2O, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The compound **SI-6** (14.4 g, 93% yield) was obtained as yellow syrup. Compound **SI-6** (14.4g, 17.3 mmol) was treated with 1M TBAF in THF (52.0 ml, 52.0 mmol). After TLC-analysis showed complete consumption of the starting material, the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with DCM, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound **SI-7** was dissolved in DMF (70 mL). Sodium hydride (1.25 g, 52 mmol) and PMBCl (3.52 ml, 26.0 mmol) were added to the mixture at 0 ^oC under N_2. The reaction was stirred at room

temperature until TLC-analysis showed complete consumption of the starting material. The mixture was poured in cold water, diluted with Et_2O, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound was crystallization from EtOH. Compound **5a** (9.70g, 78% yield over two steps, PE:EA = 4:1, R*f* = 0.63, melting point 90.4-91 ^oC) was obtained as a white solid.

$[\alpha]_D^{20}$ +0.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 744, 818, 1029, 1066, 1084, 1125, 1247, 1363, 1512, 1612, 2860, 2920. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.78-7.71 (m, 3 H, aromatic *H*), 7.602-7.57 (m, 3 H, aromatic *H*), 7.45-7.38 (m, 4 H, aromatic *H*), 7.33-7.20 (m, 14 H, aromatic *H*), 6.84-6.79 (m, 2 H, aromatic *H*), 4.96-4.84 (m, 4 H, 4 C*H*H), 4.75-4.67 (m, 3 H, H-1, 2 CH*H*), 4.54 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.42 (d, *J* = 11.6 Hz, 1 H, C*H*H), 3.77-3.69 (m, 7 H), 3.56-3.51 (m, 2 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 159.18, 138.49, 138.08, 135.60, 133.98, 133.26, 132.99 (aromatic *C*), 131.88 (aromatic *C*H), 130.29 (aromatic *C*), 129.43, 128.94, 128.58, 128.47, 128.45, 128.25, 128.15, 127.95, 127.89, 127.78, 127.70, 127.69, 127.43, 126.61, 126.11, 125.96, 125.93, 113.91, 113.76 (aromatic *C*H), 87.54 (C-1), 86.79, 80.91, 79.12, 77.79, 75.82, 75.44, 75.04, 73.08, 68.61, 64.83 (C-6), 55.19 (O*C*H_3). HR-MS: Calculated for $C_{45}H_{44}O_6S$ $[M+Na]^+$: 735.2751, found: 735.2760.

Compound **5a** (9.63g, 13.5 mmol) was dissolved in acetone:H_2O (10:1, 135 mL). NIS (6.08 g, 27.0 mmol) was added in a portion. The reaction was stirred at room temperature for 2 hours, after which the solution was diluted with DCM and the reaction quenched with saturated $Na_2S_2O_3$. Then the organic layer was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacu*o. The crude product was purified by column chromatography (PE:EA = 3:1). Compound **SI-8** (7.30 g, 87% yield) was obtained as white solid. Then compound **SI-8** (7.30 g, 11.7 mmol) was dissolved in acetone:H_2O (10:1, 120 mL). Cs_2CO_3 (5.75g, 17.6 mmol) and 2,2,2-trifluoro-N-phenylacetimidoyl chloride (2.86 mL, 17.6 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo.* The product was purified by column chromatography (PE:EA = 50:1-20:1). Compound **5b** (8.50 g, 91% yield, mixture of α and β, PE:EA = 10:1, R*f* = 0.25-0.36) was obtained as yellow syrup.

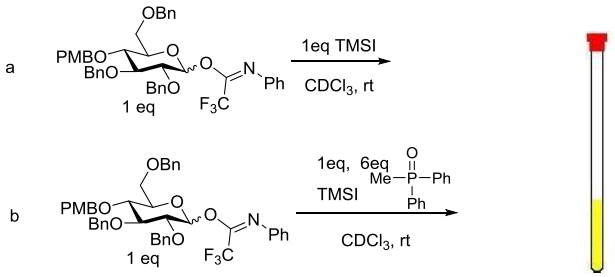
^{1}H-NMR ($CDCl_3$, 500 MHz, 60 ℃) δ 7.78-6.72 (m, aromatic *H*), 6.46 (bs, 1 H, H-1α), 5.60 (bs, 1 H, H-1β), 4.98-4.37 (m, CH*H*), 4.05 (t, J = 9.5 Hz, 1 H, H-α), 3.97 (bd, 1 H, H-α), 3.78-3.64 (m), 3.40 (bs, 1 H). ^{13}C-APT ($CDCl_3$, 125 MHz, 60℃)δ 159.63, 159.59, 143.95, 143.75, 143.44, 138.97, 138.74, 138.15, 138.13, 135.95, 135.86, 133.58, 133.55, 133.28, 133.27, 130.41, 130.29 (aromatic *C*), 129.62, 129.56, 129.46, 128.81, 128.59, 128.55, 128.48, 128.46, 128.19, 128.08, 128.07, 127.98, 127.95, 127.80, 127.76, 127.71, 127.67, 126.66, 126.45, 126.16, 126.04, 125.99, 124.44, 124.30, 120.75, 119.68, 119.60 (aromatic *C*H), 116.50 (q, *C*F_3), 114.10, 114.08 (aromatic *C*H), 97.65 (C-1β), 93.97 (C-1α), 84.78, 81.78, 81.26, 79.71, 77.62, 77.34, 76.06, 75.79, 75.61, 75.30, 75.07, 75.05, 73.54, 73.52, 73.33, 73.27, 68.25 (C-6), 68.22 (C-6), 55.31 (O*C*H_3). HR-MS: Calculated for $C_{47}H_{44}F_3O_7N$ $[M-[O(C=NPh)CF3]+OH+Na]^+$: 643.2666, found: 643.2676.

Activation of donor 4b using TMSI with or without $Ph_2MeP=O$.

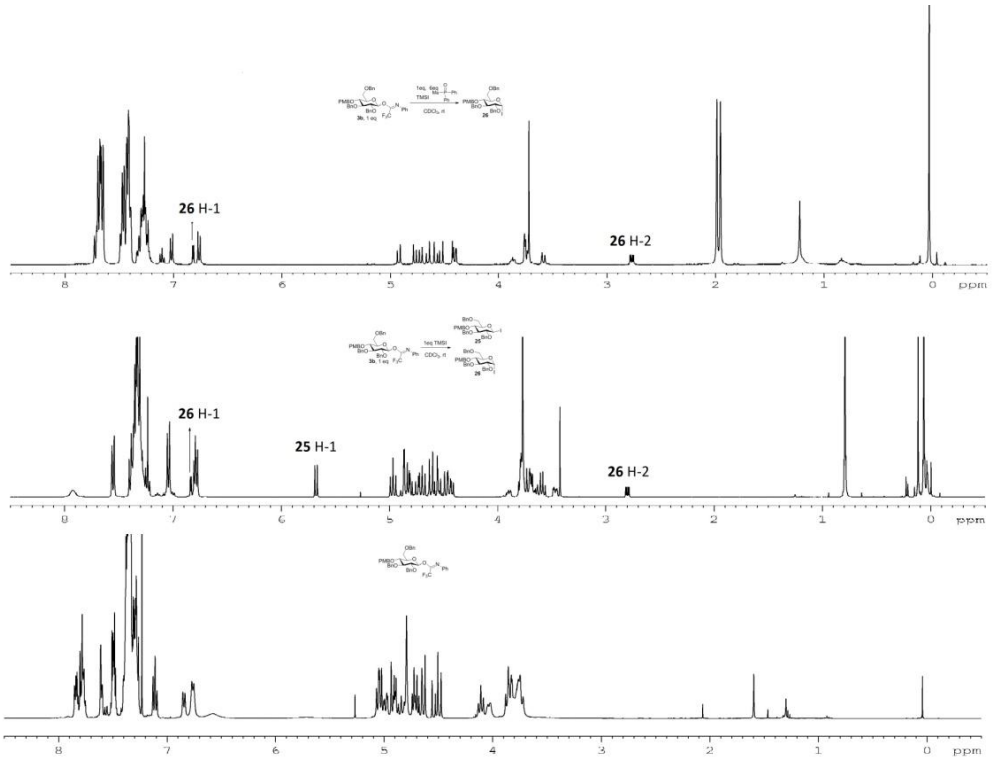
TMSI (10 μL, 0.07 mmol) was added to a solution of donor **4b** (51 mg, 0.07 mmol), with or without

$Ph_2MeP{=}O$ (91 mg, 0.42 mmol) in $CDCl_3$ (0.6 mL) in a normal NMR tube under N_2 at room temperature. Spectra were recorded every 10 min.

Figure S1. Activation study of donor **4b** using NMR (for full NMR spectra: see below)



The following NMR spectra were obtained (from bottom to top): Starting donor; Activation with TMSI (after 5 min); Activation with TMSI and $Ph_2MeP{=}O$ (after 55 min)



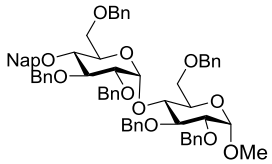
Synthesis of diglucoside **9** using NIS/TMSOTf

The donor **2a** (102 mg, 0.16 mmol) and acceptor **6** (50 mg, 0.11 mmol) were co-evaporated with toluene 3 times, then dissolved in dry DCM (2 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A. The solution was cooled to 0 ^{o}C, after which NIS (36 mg, 0.16 mmol) and TMSOTf (29 µL, 0.16 mmol) were added. The reaction was stirred at 0 ^{o}C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with saturated $Na_2S_2O_3$, then the organic layer was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by size exclusion (DCM:MeOH = 1:1). Compound **9** (91mg, 86% yield, α:β= 2:1, PE:EA = 4:1, R*f* = 0.32) was obtained as a colorless syrup.

Synthesis of diglucoside **9** using NIS/TMSOTf + DMF

The donor **2a** (102 mg, 0.16 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (202 μL, 2.56 mmol) was added to the solution. The solution was cooled to 0 ^{o}C, after which NIS (36 mg, 0.16 mmol) and TMSOTf (29 μL, 0.16 mmol) were added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **6** (50 mg, 0.11 mmol, dissolved in a little DCM and washed 2 times with DCM (totally 1 mL) was added to the solution. The reaction was stirred at 0 ^{o}C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with saturated $Na_2S_2O_3$, then the organic layer was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by size exclusion (DCM:MeOH = 1:1). Compound **9** (88 mg, 83% yield, α:β> 50:1) was obtained as a colorless syrup.

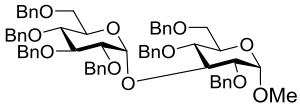
Synthesis of diglucoside **10**



The reaction was carried out according to the standard procedure B at -78 - 0 ^{o}C. The donor **3b** (1.34g, 1.96 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (20 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (2.47 mL, 31.4 mmol) was added to the solution. The solution was cooled to -78 ^{o}C, after which TfOH (173μL, 1.96 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **6** (608mg, 1.31 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 6 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 ^{o}C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **10** (1113mg, 82% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.48) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +34.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 735, 820, 857, 910, 1028, 1045, 1093, 1156, 1207, 1261, 1273, 1363, 1453, 1496, 2860, 3030.^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.81-7.79 (m, 1 H, aromatic *H*), 7.74-7.70 (m, 2 H, aromatic *H*), 7.50 (bs, 1 H, aromatic *H*), 7.47-7.43 (m, 2 H, aromatic *H*), 7.30-7.18 (m, 31 H, aromatic *H*), 5.73 (d, *J* = 3.6Hz, 1 H, H-1b), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.91 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.81 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.70 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.63-4.49(m, 8 H, 7 C*H*H, H-1a), 4.23 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.13-4.05 (m, 2 H, H-3a, H-4a), 3.94 (t, *J* = 9.2 Hz, 1 H, H-3b), 3.87-3.82 (m, 2 H, H-5a, H-6a_a), 3.73-3.59 (m, 4 H, H-5a, H-4b, H-2a, H-6a_b), 3.54-3.50 (m, 2H, H-2b, H-6b_a), 3.40-3.37 (m, 4 H, H-6b_b). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.01, 138.88, 138.22, 138.05, 137.96, 136.00, 139.29, 132.99 (aromatic *C*), 128.54, 128.45, 128.41, 128.35, 128.32, 128.31, 128.20, 128.04, 127.96, 127.88, 127.82, 127.78, 127.74, 127.69, 127.61, 127.46, 127.29, 127.21, 126.86, 126.61, 126.15, 126.10, 125.93 (aromatic *C*H), 97.86 (C-1a), 96.72 (C-1b), 82.19 (C-3b), 82.15 (C-3a), 80.28 (C-2a), 79.52 (C-2b), 77.65 (C-4b), 75.66, 75.11, 74.54, 73.54, 73.49, 73.35, 73.20 (7 *C*H_2), 72.17 (C-4a), 71.03 (C-5a), 69.57 (C-5b),

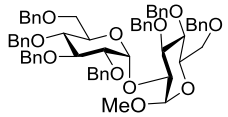
69.05 (C-6a), 68.12 (C-6b), 55.25 (OCH_3). HR-MS: Calculated for $C_{66}H_{68}O_{11}$ $[M+Na]^+$: 1059.4654 found: 1059.4681.

Synthesis of diglucoside **11**



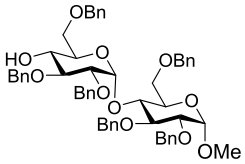
The reaction was carried out according to the standard procedure B at -78 - 0 °C. The donor **2b** (106 g, 0.15 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (188 μL, 2.39 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (13 μL, 0.15 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **7** (46 mg, 0.10 mmol, dissolved in a little DCM and washed 2 times with DCM, totally 1 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **11** (83 mg, 85% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.32) was obtained as a colorless syrup.

Synthesis of diglucoside **12**



The reaction was carried out according to the standard procedure B at -78 - 0 °C. The donor **2b** (106 g, 0.15 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (188 μL, 2.39 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (13 μL, 0.15 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **7** (46 mg, 0.10 mmol, dissolved in a little DCM and washed 2 times with DCM, totally 1 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **12** (88 mg, 90% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.22) was obtained as a colorless syrup.

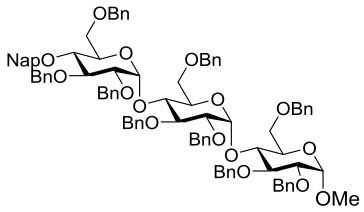
Synthesis of diglucoside **13**



The reaction was carried out according to the general procedure D, using **12** (750mg, 0.73 mmol, 0.1 M in DCM:H_2O) and DDQ (180 mg, 0.80 mmol). The product was purified by silica gel column chromatography (PE:EA = 6:1). Compound **13** (510mg, 78% yield, PE:EA = 4:1, R*f* = 0.20) was

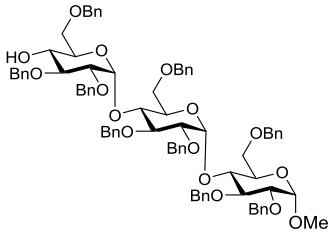
obtained as a colorless syrup. $[\alpha]_D^{20}$ +38.4 (c=1, $CHCl_3$), IR (neat, cm^{-1}) ν 696, 735, 764, 910, 1027, 1046, 1093, 1153, 1208, 1456, 2867, 2923. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.34-7.17 (m, 30 H, aromatic *H*), 5.71 (d, *J* = 3.6Hz, 1 H, H-1b), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.90 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.71 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.69 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.61 (d, *J* = 3.6Hz, 1 H, H-1a), 4.59-4.47(m, 6 H, 6 C*H*H), 4.43 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.32 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.12-4.03 (m, 2 H, H-3a, H-4a), 3.88-3.83 (m, 2 H), 3.77-3.58 (m, 5 H), 3.54-3.51 (m, 2H), 3.46-3.42 (m, 2 H), 3.38 (s, 3 H, OCH_3). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ138.97, 138.81, 138.25, 137.97, 137.94, 137.90 (aromatic *C*), 128.51, 128.48, 128.38, 128.36, 128.30, 128.25, 128.13, 127.99, 127.90, 127.76, 127.69, 127.43, 127.36, 127.16, 126.75 (aromatic *C*H), 97.77 (C-1a), 96.58 (C-1b), 82.09 (C-3a), 81.30 (C-3b), 80.21 (C-2a), 79.02 (C-2b), 75.35, 74.43, 73.56, 73.38, 73.19, 73.12 (6 *C*H_2), 72.27 (C-4a), 71.48 (C-4b), 70.57 (C-5a), 69.77 (C-5b), 69.56 (C-6a), 69.03 (C-6b), 55.21 (OCH_3). HR-MS: Calculated for $C_{55}H_{60}O_{11}$ [M+Na^+]: 919.4028; found: 919.4058.

Synthesis of triglucoside **14**



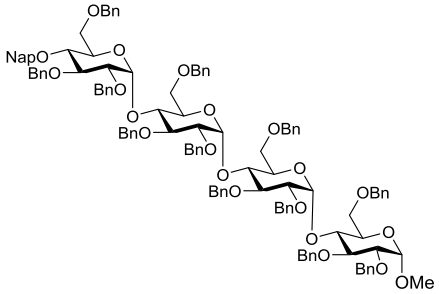
The reaction was carried out according to the standard procedure B. The donor **3b** (1.04g, 1.53 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (10 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (1.90 mL, 24.4 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (134 μL, 1.52 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **13** (680 mg, 0.76 mmol) dissolved in a little DCM and washed 3 times with DCM (totally 5 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **14** (906mg, 81% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.42) was obtained as a colorless syrup.$[\alpha]_D^{20}$ +49.4(c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 749, 764, 1028, 1043, 1094, 1154, 1275, 2870, 3030.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81-7.78 (m, 1 H, aromatic *H*), 7.74-7.68 (m, 2 H, aromatic *H*), 7.50 (bs, 1 H, aromatic *H*), 7.47-7.43 (m, 2 H, aromatic *H*), 7.30-7.09 (m, 46 H, aromatic *H*), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.59 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.04 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.93 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.91 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.85-4.68 (m, 5 H, 5 C*H*H), 4.60-4.40 (m, 12 H), 4.24 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.11-4.02 (m, 4 H), 3.95-3.83 (m, 4 H), 3.74-3.50 (m, 9 H), 3.40-3.37 (m, 4 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.12, 138.95, 138.89, 138.42, 138.30, 138.12, 138.01, 137.85, 136.06, 133.31, 133.00 (aromatic *C*), 128.55, 128.42, 128.38, 128.36, 128.34, 128.31, 128.29, 128.19, 128.05, 127.97, 127.96, 127.78, 127.76, 127.7, 127.64, 127.62, 127.60, 127.55, 127.46, 127.22, 127.13, 126.89, 126.71, 126.59, 126.15, 126.12, 125.94 (aromatic *C*H), 97.90 (C-1a), 96.83 (C-1b), 96.37 (C-1c), 82.23, 82.01, 81.83 (3 C-3), 80.09, 79.71, 79.67 (3 C-2), 77.66 (C-4), 75.55, 75.11, 74.57, 74.15, 73.57, 73.48, 73.32, 73.12, 73.08 (*C*H_2), 73.03, 72.47 (2 C-4), 71.03, 70.83, 69.65 (3 C-5), 68.98, 68.87, 68.16 (3 C-6), 55.31 (OCH_3). HR-MS: Calculated for $C_{93}H_{96}O_{16}$ [M+Na^+]: 1491.6591; found: 1491.6603.

Synthesis of triglucoside **15**



The reaction was carried out according to the general procedure D, using **14** (800mg, 0.54 mmol, 0.1 M in DCM:H_2O) and DDQ (136 mg, 0.60 mmol). The product was purified by silica gel column chromatography (PE:EA = 6:1). Compound **15** (564mg, 78% yield, PE:EA = 4:1, R*f* = 0.20) was obtained as a colorless syrup. $[\alpha]_D^{20}$+41.0(c=1, $CHCl_3$). IR (neat, cm^{-1}) ν696, 735, 1028, 1042, 1077, 1081, 1094, 1125, 1132, 1154, 1364, 1453, 2854, 2930. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.28-7.06 (m, 45 H, aromatic *H*), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.60 (d, *J* = 3.2 Hz, 1 H, H-1c), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.96 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.85-4.62 (m, 2 H, 2 C*H*H), 4.77-4.39 (m, 13 H), 4.33 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.13-4.03 (m, 5 H), 3.91-3.85 (m, 3 H), 3.77-3.52 (m, 9 H), 3.47-3.42 (m, 2 H) 3.38 (s, 3 H, OC*H*$_3$). ^{13}C-APT ($CDCl_3$, 125 MHz,) δ 139.19, 138.97, 138.95, 138.51, 138.24, 138.21, 138.17, 137.05, 137.88 (aromatic *C*), 128.56, 128.55, 128.48, 128.39, 128.35, 128.32, 128.05, 127.99, 127.85, 127.79, 127.78, 127.75, 127.70, 127.67, 127.60, 127.54, 127.48, 127.23, 127.17, 127.92, 126.72(aromatic *C*H), 97.95, 96.64, 96.37 (3 C-1), 82.01, 81.83, 81.47, 80.13, 79.74, 79.25, 75.32, 74.58, 74.08, 73.70, 73.49, 73.35, 73.27, 73.08, 72.94, 72.39, 7169, 70.88, 70.53, 69.95, 69.73, 69.03, 68.93, 55.33 (O*C*H_3). HR-MS: Calculated for $C_{82}H_{88}O_{16}$ [M+Na^+]: 1351.5965; found: 1351.6018.

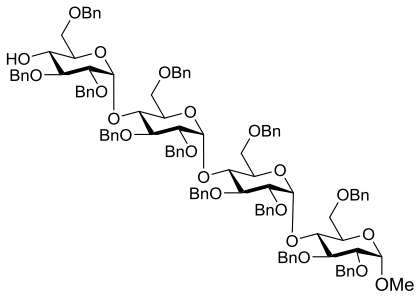
Synthesis of tetraglucoside **16**



The reaction was carried out according to the standard procedure B. The donor **3b** (620 mg, 0.91 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (5 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (1.13 mL, 14.5 mmol) was added to the solution. The solution was cooled to -78 ^{o}C, after which TfOH (80 μL, 0.91 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **15** (680 mg, 0.76 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 ^{o}C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **16** (661mg, 82% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.33) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +64.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 735, 1028, 1040, 1095, 1155, 1208,

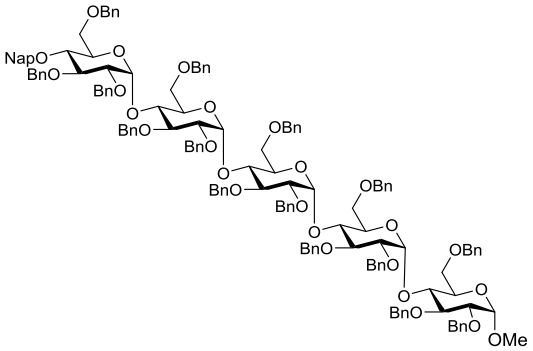
1275, 1456, 2865, 3031, 3064.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81-7.78 (m, 1 H, aromatic *H*), 7.74-7.68 (m, 2 H, aromatic *H*), 7.51 (bs, 1 H, aromatic *H*), 7.46-7.42 (m, 2 H, aromatic *H*), 7.30-7.09 (m, 61 H, aromatic *H*), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.60 (m, 2 H, H-1c, H-1d), 5.04 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.94-4.69 (m, 9 H, 9 C*H*H), 4.61 (d, *J* = 3.6 Hz, 1 H, H-1b), 4.60-4.37 (m, 15 H), 4.23 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.14-4.01 (m, 6 H), 3.96 (t, *J* = 9.2 Hz, 1 H), 3.90-3.85 (m, 4 H), 3.79-3.71 (m, 4 H), 3.66-3.50 (m, 8 H), 3.40-3.37 (m, 4 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.09, 138.97, 138.93, 138.87, 138.42, 138.23, 138.14, 138.12, 138.09, 138.02, 137.96, 137.87, 136.02, 133.28, 132.97 (aromatic *C*), 128.49, 128.37, 128.27, 128.25, 128.22, 128.20, 128.14, 128.00, 127.98, 127.91, 127.73, 127.71, 127.66, 127.62, 127.58, 127.54, 127.48, 127.40, 127.16, 127.10, 127.02, 126.87, 126.73, 126.58, 126.12, 126.07, 125.90 (aromatic *C*H), 97.87 (C-1a), 96.94 (C-1b), 96.45, 96.32 (2 C-1), 82.19, 81.97, 81.85, 81.59 (4 C-3), 80.04, 79.79, 79.57, 79.42 (4 C-2), 77.67 (C-4), 75.52, 75.09, 74.56, 74.11, 74.05, 73.52, 73.41, 73.35, 73.31, 73.25 (CH_2), 73.18, 73.14 (2 C-4), 73.06, 73.02, 72.87 (CH_2), 72.53 (C-4), 70.99, 70.88, 70.81, 69.66 (4 C-5), 68.90, 68.84, 68.78, 68.15 (4 C-6), 55.26 (OCH_3). HR-MS: Calculated for $C_{120}H_{124}O_{21}$ [M+H$^+$]: 1901.8708; found: 1901.8695.

Synthesis of tetraglucoside **17**



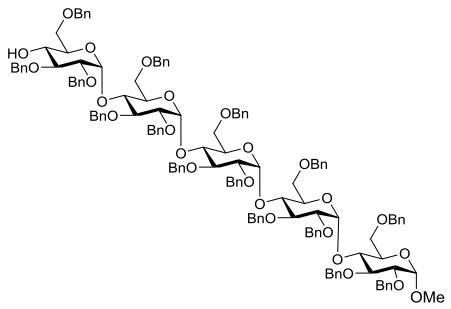
The reaction was carried out according to the general procedure D, using **16** (590 mg, 0.31 mmol, 0.05 M in DCM:H_2O) and DDQ (80 mg, 0.35 mmol). The product was purified by silica gel column chromatography (PE:EA = 5:1). Compound **17** (460 mg, 84% yield, PE:EA = 4:1, R*f* = 0.18) was obtained as a colorless syrup. $[\alpha]_D^{20}$+59.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 695, 733, 747, 764, 910, 1027, 1039, 1094, 1152, 1207, 1260, 1456, 2855, 3923, 3031.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.29-7.10 (m, 60 H, aromatic *H*), 5.70 (d, *J* = 3.2 Hz, 1 H, H-1b), 5.61 (bd, 2 H, H-1c, H-1d), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.94-4.78 (m, 5 H, 5 C*H*H), 4.73-4.37 (m, 18 H), 4.31 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.14-4.01 (m, 6 H), 3.90-3.86 (m, 4 H), 3.78-3.39 (m, 17 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.19, 139.05, 138.98, 138.95, 138.54, 138.34, 138.24, 138.20, 138.12, 138.07, 138.04, 137.97 (aromatic *C*), 128.57, 128.55, 128.48, 128.40, 128.35, 128.33, 128.29, 128.05, 127.99, 127.85, 127.83, 127.79, 127.77, 127.75, 127.72, 127.70, 127.67, 127.61, 127.59, 127.52, 127.47, 127.23, 127.17, 127.12, 126.97, 126.92, 126.81, 126.73, 126.64 (aromatic *C*H), 97.97, 96.79, 96.56, 96.34 (4 C-1), 82.03, 81.91, 81.63, 81.50 (4 C-3), 80.14, 79.86, 79.50, 79.17 (4 C-2), 75.36, 74.65, 74.15, 73.69, 73.50, 73.45 (C-4), 73.41, 73.38, 73.33 , 73.27 (C-4), 72.93, 72.90, 72.40, 71.72 (C-4), 70.95, 70.91, 70.50 (3 C-5), 69.95 (C-6), 69.77 (C-5), 68.97, 68.88 (3 C-6), 55.35 (OCH_3). HR-MS: Calculated for $C_{109}H_{116}O_{21}$ [M+Na$^+$]: 1783.7901; found: 1783.7969.

Synthesis of pentaglucoside **18**



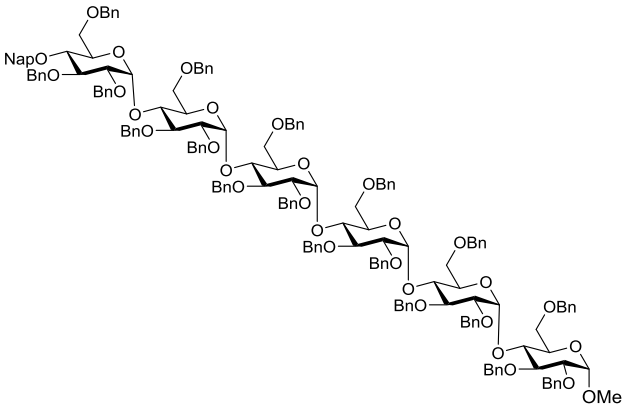
The reaction was carried out according to the standard procedure B. The donor **3b** (380 mg, 0.56 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (2 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (700 µL, 8.90 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (49 µL, 0.55 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **15** (680 mg, 0.76 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **18** (410mg, 80% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.26) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +92.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) v695, 734, 820, 857, 910, 1027, 1037, 1094, 1154, 1207, 1363, 1453, 2862, 2927, 3031. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81-7.79 (m, 1 H, aromatic *H*), 7.74-7.69 (m, 2 H, aromatic *H*), 7.50 (bs, 1 H, aromatic *H*), 7.46-7.44 (m, 2 H, aromatic *H*), 7.29-7.04 (m, 76 H, aromatic *H*), 5.72 (bs, 1 H, H-1), 5.63 (bs, 1 H, H-1) , 5.59 (bs, 2 H, 2 H-1), 5.04 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.93-4.70 (m, 11 H, 11 C*H*H), 4.60-4.37 (m, 20 H), 4.22 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.11-3.47 (m, 29 H), 3.38-3.35 (m, 4 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.14, 139.00, 138.95, 138.89, 138.44, 138.28, 138.27, 138.14, 138.08, 137.99, 137.94, 137.90, 136.06, 133.30, 133.00 (aromatic *C*), 128.52, 128.40, 128.33, 128.21, 128.17, 128.02, 128.00, 127.94, 127.81, 127.77, 127.74, 127.71. 127.65, 127.59, 127.53, 127.50, 127.42, 127.18, 127.13, 127.05, 126.91, 126.77, 126.66, 126.59, 126.57, 126.15, 126.10, 125.93 (aromatic *C*H), 97.91 (C-1a), 97.01, 96.52, 96.46, 96.34 (4 C-1), 82.24, 81.98, 81.89, 81.68 (5 C-3), 80.05, 79.75, 79.57, 79.49 (5 C-2), 77.69 (C-4), 75.54, 75.12, 74.60, 74.12, 74.06, 73.55, 73.45, 73.41, 73.33, 73.29 (*C*H_2), 73.17 (2 C-4), 73.06 (*C*H_2), 72.95 (C-4), 72.91, 72.85 (*C*H_2), 72.50 (C-4), 71.02, 70.90, 70.85, 69.69 (5 C-5), 68.92, 68.86, 68.80, 68.73, 68.16 (5 C-6), 55.29 (O*C*H_3). MALDI-TOF: Calculated for $C_{147}H_{152}O_{26}$ [M+H^+]: 2356.0; found: 2357.9.

Synthesis of pentaglucoside **19**



The reaction was carried out according to the general procedure D, using **18** (590 mg, 0.25 mmol, 0.05 M in DCM:H_2O) and DDQ (63 mg, 0.28 mmol). The product was purified by silica gel column chromatography (PE:EA = 5:1). Compound **19** (415mg, 81% yield, PE:EA = 4:1, R*f* = 0.16) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +73.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν695, 733, 746, 763, 937, 1027, 1037, 1092, 1153, 1207, 1275, 1363, 1454, 2860, 2920, 3030, 3064. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.31-7.02 (450m, 75 H, aromatic *H*), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1), 5.60 (bd, 2 H, 2 H-1), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.95-4.36 (m, 29 H), 4.30 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.13-3.98 (m, 8 H), 3.91-3.86 (m, 5 H), 3.80-3.50 (m, 15 H), 3.45-3.37 (m, 5 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.56, 139.19, 139.03, 138.99, 138.95, 138.92, 138.50, 138.33, 138.20, 138.17, 138.11, 138.10, 138.00, 137.94 (aromatic *C*), 128.63, 128.53, 128.52, 128.45, 128.37, 128.31, 128.29, 128.27, 128.25, 128.22, 128.01, 127.96, 127.84, 127.80, 127.76, 127.30, 127.70, 127.69, 127.62, 127.55, 127.48, 127.44, 127.20, 127.15, 127.07, 126.94, 126.80, 126.69, 126.57 (aromatic *C*H), 97.95 (C-1a), 96.81, 96.55, 96.41, 96.36 (4 C-1), 81.99, 81.90, 81.68, 81.66, 81.50 (5 C-3), 80.10, 79.77, 79.58, 79.53, 79.13, 75.32, 74.62, 74.12, 74.04, 73.98, 73.66, 73.51, 73.46, 73.41, 73.37, 73.33, 73.22, 73.08, 73.02, 72.93, 72.91, 72.82, 72.35, 71.71, 70.93, 70.91, 70.46, 69.92, 69.74, 68.91, 68.77, 55.31 (O*C*H_3). MALDI-TOF: Calculated for $C_{136}H_{144}O_{26}$ [M+Na^+]: 2216.0; found: 2220.0.

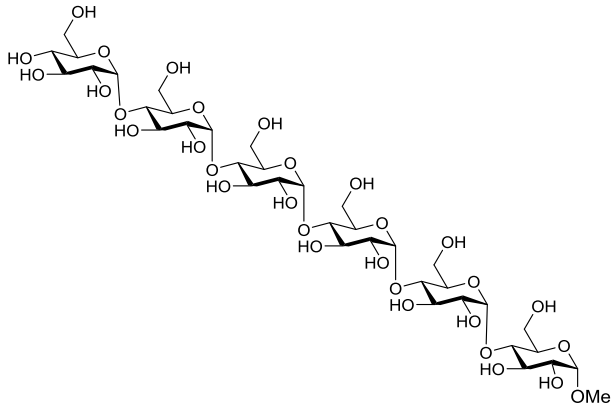
Synthesis of hexaglucoside **20**



The reaction was carried out according to the standard procedure B. The donor **3b** (95 mg, 0.14 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (175 μL, 2.25 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (12 μL, 0.14 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **15** (680 mg, 0.76 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **20** (104mg, 81% yield, α:β> 20:1, PE:EA = 4:1, R*f* = 0.21) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +72.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν696, 738, 749, 764, 1028, 1039, 1095, 1154, 1208, 1261, 1456, 2859, 2922, 3031. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82-7.79 (m, 1 H, aromatic *H*), 7.74-7.67 (m, 2 H, aromatic *H*), 7.50 (bs, 1 H, aromatic *H*), 7.47-7.43 (m, 2 H, aromatic *H*), 7.29-7.02 (m, 91 H, aromatic *H*), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1), 5.64 (d, *J* = 3.2 Hz, 1 H, H-1) , 5.61 (bt, 2 H, 2 H-1), 5.58 (d, *J* = 3.6 Hz, 1 H, H-1), 5.04 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.93-4.69 (m, 13

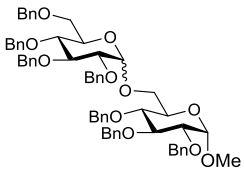
H, 11 C*H*H), 4.61-4.34 (m, 24 H), 4.21 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.13-3.46 (m, 35 H), 3.38-3.35 (m, 4 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.16, 138.98, 138.96, 138.91, 138.46, 138.30, 138.27, 138.16, 138.07, 138.00, 137.95, 137.92, 136.08, 133.32, 133.01 (aromatic *C*), 128.54, 128.41, 128.23, 128.19, 128.02, 127.97, 127.83, 127.80, 127.76, 127.73, 127.60, 127.58, 127.54, 127.50, 127.43, 127.21, 127.15, 127.06, 126.94, 126.79, 126.67, 126.64, 126.60, 126.58, 126.17, 126.11, 125.94 (aromatic *C*H), 97.93 (C-1a), 97.02, 96.55, 96.47, 96.34 (5 C-1), 82.25, 82.00, 81.92, 81.77, 81.73, 81.65 (6 C-3), 80.07, 79.77, 79.65, 79.58, 79.50, 77.71, 75.55, 75.13, 74.63, 74.07, 73.98, 73.56, 73.47, 73.37, 73.34, 73.30, 73.08, 72.99, 72.91, 72.63, 72.48, 71.02, 70.91, 70.85, 69.71, 68.88 (C-6), 68.72 (C-6), 68.18 (C-6), 55.31 (O*C*H$_3$). MALDI-TOF: Calculated for $C_{174}H_{180}O_{31}$ [M+Na$^+$]: 2788.2; found: 2790.1.

Synthesis of hexaglucoside **21**



Compound **20** (31 mg, 0.011 mmol) was dissolved in THF/H_2O/*tert*-BuOH (4 ml/4 ml/1.6 ml) before a catalytic amount of $Pd(OH)_2$/C was added. The reaction mixture was stirred for 3 days under a H_2 atmosphere (3.5 bar), filtered and concentrated *in vacuo*. A white powder was obtained, which was purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O) to provide **21** (9mg, 80%).^{1}H-NMR ($CDCl_3$, 400 MHz) δ5.37-5.36 (m, 5 H, 5 H-1), 4.77 (d, *J* = 4.0 Hz, 1 H, H-1a), 3.94-3.53 (m, 35 H), 3.41-3.35 (m, 4 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 96.68, 96.53, 99.40, 99.07 (6 C-1), 76.71, 76.64, 76.55, 73.50, 73.29, 72.81, 72.66, 71.68, 71.50, 71.12, 71.01, 70.00, 69.26, 60.41 (C-6), 60.34 (C-6), 55.04 (O*C*H$_3$). HR-MS: Calculated for $C_{37}H_{64}O_{31}$ [M+Na$^+$]: 1027.3324; found: 1027.3348.

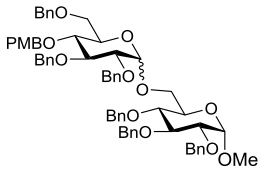
Synthesis of diglucoside **23** using NIS/TMSOTf+DMF



The donor **2a** (102 mg, 0.16 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (202 μL, 2.56 mmol) was added to the solution. The solution was cooled to 0 ^{o}C, after which NIS (36 mg, 0.16 mmol) and TMSOTf (29 μL, 0.16 mmol) were added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **22** (50 mg, 0.11 mmol, dissolved in a little DCM and washed 2 times with DCM (totally 1 mL) was added to the solution. The reaction was

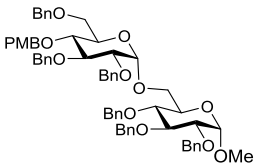
stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with saturated $Na_2S_2O_3$, then the organic layer was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by size exclusion (DCM:MeOH = 1:1). Compound **23** (88 mg, 83% yield, α:β = 2.7:1, PE:EA = 4:1, R*f* = 0.32) was obtained as a colorless syrup.

Synthesis of diglucoside **24** (α:β = 3:1)



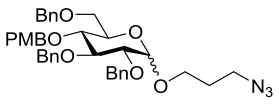
The donor **4b** (123 mg, 0.16 mmol) and acceptor **22** (70 mg, 0.15 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (2 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (50 μL, 0.64 mmol) was added to the solution. Then TMSOTf (10 μL, 0.05 mmol) was added. The reaction was stirred at rt until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **24** (144 mg, 94% yield, α:β = 3:1) was obtained as a white solid.

Synthesis of diglucoside **24**



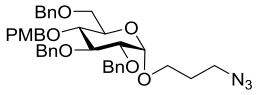
The reaction was carried out according to the standard procedure C, using **4b** (90 mg, 0.15 mmol), **22** (40 mg, 0.09 mmol, 0.1 M in DCM), $Ph_3P{=}O$ (143 mg, 0.51 mmol) and TMSI (19 μL, 0.12 mmol). The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **24** (79 mg, 90% yield, α:β = 25:1, PE:EA = 4:1, R*f* = 0.34, melting point 117.5-118.6 °C) was obtained as a white solid. IR (neat, cm^{-1}) v696, 737, 747, 821, 1028, 1052, 1072, 1084, 1137, 1159, 1249, 1363, 1456, 1515, 1855, 2924, 3030.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.33-7.22 (m, 30 H, aromatic *H*), 7.04-7.01 (m, 2 H, aromatic *H*), 6.79-6.76 (m, 2 H, aromatic *H*), 4.99-4.89 (m, 4 H, 3 C*H*H, H-1), 4.82-4.54 (m, 10 H, 10 C*H*H), 4.43-4.37 (m, 2 H, C*H*H, H-1), 4.00-3.92 (m, 2 H), 3.84-3.52 (m, 12 H), 3.43 (dd, J_1 = 3.6 Hz, J_2= 9.6 Hz, 1 H), 3.34 (s, 3 H). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 159.22, 138.98, 138.93, 138.55, 138.27, 138.10, 130.72 (aromatic *C*), 129.54, 128.51, 128.46, 128.25, 128.11, 128.07, 128.00, 127.95, 127.87, 127.74, 127.72, 127.67, 127.59, 113.78 (aromatic *C*H), 98.04 (C-1), 97.35 (C-1), 82.22, 81.80, 80.22, 80.07, 77.85, 77.42, 75.81, 75.57, 75.08, 74.68, 73.49, 73.48, 72.45, 70.47, 70.35, 68.56, 66.10, 55.35, 55.25. HR-MS: Calculated for$C_{63}H_{68}O_{12}$[M+Na^+]: 1039.4603; found: 1039.4642.

Synthesis of glucoside **27** (α:β = 1:1)



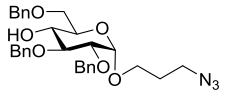
The donor **4b** (123 mg, 0.16 mmol) and 3-aminopropanol (30 μL, 0.32 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (2 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A. Then TMSOTf (5 μL, 0.03 mmol) was added. The reaction was quenched with Et_3N after 3 h, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (PE:EA = 10:1). Compound **27** (53 mg, 49% yield, α:β = 1:1) was obtained as a colorless syrup.

Synthesis of glucoside **27**



The reaction was carried out according to the standard procedure C, using **4b** (1.95 g, 2.63mmol, 0.1 M in DCM), 3-aminopropanol (369 μL, 3.94mmol), $Ph_3P{=}O$ (4.39 g, 15.8 mmol) and TMSI (413 μL, 2.89 mmol). The product was purified by silica gel column chromatography (PE:EA = 10:1). Compound **27** (1530 mg, 91% yield, α:β = 11:1, PE:EA = 4:1, R*f* = 0.48) was obtained as a colorless syrup. An analytical sample of the pure α-anomer was obtained by careful silica gel column chromatography (PE:EA = 10:1). $[\alpha]_D^{20}$ +24.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν697, 749, 764, 823, 1014, 1028, 1040, 1071, 1158, 1249, 1257, 1456, 2096, 2867, 2910, 2923, 3031. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.33-7.22 (m, 15 H, aromatic *H*), 7.03 (d, *J* = 8.6 Hz, 2 H, aromatic *H*), 6.78 (d, *J* = 8.6 Hz, 2 H, aromatic *H*), 4.98 (d, *J* = 11.0 Hz, 1 H, C*H*H), 4.83 (d, *J* = 11.0 Hz, 1 H, CH*H*), 4.79-4.72 (m, 3 H, 2 C*H*H, H-1), 4.63 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.61 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.47 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.39 (d, *J* = 12.0 Hz, 1 H, C*H*H), 3.94 (t, $J_1 = J_2$ = 9.2 Hz, 1 H, H-3), 3.76 (s, 3 H, CH_3), 3.74-3.68 (m, 3H, H-5, H-6a, H-1°a), 3.64-3.59 (m, 2H, H-6b, H-4), 3.55 (dd, J_1 = 3.6 Hz, J_2 = 9. 6Hz, 1 H, H-2), 3.48-3.33 (m, 3 H, H-1°b, H-3°), 1.95-1.77 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 159.33, 138.96, 138.32, 137.99, 130.39 (5 aromatic *C*), 129.73, 128.55, 128.48, 128.46, 128.09, 128.01, 127.99, 127.94, 127.79, 127.66, 113.86 (19 aromatic *C*H), 97.30 (C-1), 82.12 (C-3), 80.13 (C-2), 77.41 (C-4), 75.74, 74.85, 73.55, 73.38 (4 Ph*C*H2), 70.41 (C-5), 68.49 (C-6), 64.79 (C-1°), 55.33 (O*C*H_3), 48.38 (C-3°), 28.93 (C-2°). HR-MS: Calculated for $C_{38}H_{43}O_7N_3$[M+Na^+]: 676.2993; found: 676.3008.

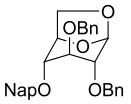
Synthesis of glucoside **28**



The reaction was carried out according to the general procedure E, using **27** (1605 mg, 2.51 mmol, 0.1 M in DCM:HFIP), triethylsilane (400 μL, 2.52 mmol) and 0.2M HCl/HFIP (1.3 ml, 0.26 mmol). The product was purified by silica gel column chromatography (PE:EA = 6:1). Compound **28** (1138 mg, 85% yield, PE:EA = 2:1, R*f* = 0.49) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +30.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν697, 749, 764, 1000, 1028, 1053, 1080, 1152, 1261, 1275, 1456, 2096, 2874, 2916, 3032. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.33-7.21 (m, 15 H, aromatic *H*), 4.99 (d, *J* = 11.4 Hz, 1 H, C*H*H), 4.76-4.71 (m, 3 H, 2 C*H*H, H-1), 4.61 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.58 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.52 (d, *J* = 12.0 Hz, 1 H, C*H*H), 3.81-3.66 (m, 5 H, H-6, H-5, H-1°a), 3.60 (dt, J_1 = 2.2 Hz, J_2 = 9.2 Hz, 1 H, H-4), 3.52 (dd, J_1 = 3.6 Hz, J_2 = 9. 6Hz, 1 H, H-2), 3.47-3.33 (m, 3 H, H-1°b, H-3°), 2.46 (d, J = 2.2 Hz, 1 H, OH), 1.94-1.82 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ138.85, 138.18, 138.02 (3 aromatic

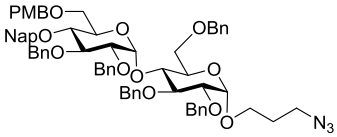
C), 128.59, 128.52, 128.04, 128.02, 127.98, 127.94, 127.84, 127.68, 127.64 (15 aromatic *C*H), 97.21 (C-1), 82.42 (C-3), 79.80 (C-2), 75.39, 73.59, 73.07 (3 Ph*C*H2), 70.77 (C-4), 70.20 (C-5), 69.49 (C-6), 64.78 (C-1°), 48.35 (C-3°), 28.86 (C-2°). HR-MS: Calculated for $C_{30}H_{35}O_6N_3$ [M+Na^+]: 556.2418; found: 556.2771.

Characterization of anhydroglucose **29**



Compound **29** was obtained in the glycosylation reaction of **5b** and **28** as a side product. Compound **29** was obtained as a colorless syrup. $[\alpha]_D^{20}$-21.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 819, 857, 898, 925, 953, 1027, 1071, 1089, 1173, 1197, 1315, 1337, 1454, 1718, 2858, 2895, 2922, 2956, 3060. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.85-7.78 (m, 3 H, aromatic *H*), 7.74 (s, 1 H, aromatic *H*), 7.51-7.46 (m, 3 H, aromatic *H*), 7.33-7.27 (m, 8 H, aromatic *H*), 7.20-7.17 (m, 2 H, aromatic *H*), 5.47 (s, 1 H, H-1), 4.47 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.71 (d, *J* = 12.4 Hz, 1 H, CH*H*), 4.62 (d, *J* = 5.4 Hz, 1 H, H-5), 4.58 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.54 (d, *J* = 12.4 Hz, 1 H, CH*H*), 4.42 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.37 (d, *J* = 12.4 Hz, 1 H, CH*H*), 3.89 (dd, J_1 = 0.8 Hz, J_2 = 7.2 Hz, 1 H, H-6a), 3.62 (dd, J_1 = 5.4 Hz, J_2 = 7.2Hz, 1 H, H-6b), 3.61 (bs, 1 H, H-3), 3.36 (bd, 2 H, H-4, H-2),. ^{13}C-APT ($CDCl_3$, 100 MHz,) δ137.93, 135.47, 133.27, 133.16 (aromatic *C*), 128.56, 128.55, 128.45, 128.09, 127.98, 127.96, 127.94, 127.83, 127.71, 126.78, 126.35, 126.15, 125.92 (aromatic *C*H), 100.69 (C-1), 76.71 (C-4), 76.06 (C-3), 776.04 (C-2), 74.51 (C-5), 72.08, 71.90, 71.47 (3 CH_2), 65.469 (C-6). HR-MS: Calculated for $C_{31}H_{30}O_5$ [M+Na^+]: 505.1985; found: 505.1999.

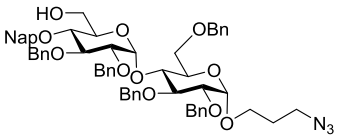
Synthesis of diglucoside **30**



The reaction was carried out according to the standard procedure B. The donor **5b** (2.60 g, 3.28 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (35 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (2.80 mL, 35.5 mmol) was added to the solution. The solution was cooled to -78 °C, after which TMSOTf (600 µL, 3.35 mmol) was added. After 60 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **28** (1.19 g, 2.23 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 10 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **30** (2.05 g, 81% yield, α:β> 20:1, Toluene (Tol):EA = 12:1, R*f* = 0.55) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +44.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν697, 750, 764, 1014, 1029, 1038, 1093, 1156, 1261, 2096, 2868, 2925.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81-7.78 (m, 1 H, aromatic *H*), 7.73-7.68 (m, 2 H, aromatic *H*), 7.47-7.42 (m, 3 H, aromatic *H*), 7.29-7.10 (m, 28 H, aromatic *H*), 6.76-6.72 (m, 2 H, aromatic *H*), 5.73 (d, *J* = 3.6Hz, 1 H, H-1b), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.92 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.88 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.83 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.81 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.74 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.67 (d, *J* = 12.0 Hz, 1 H, C*H*H),

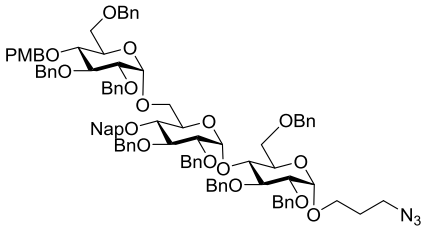
4.61-4.46 (m, 7 H, 7 C*H*H), 4.16 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.11-4.05 (m, 2 H, H-3a, H-4a), 3.93 (t, *J* = 8.8 Hz, 1 H, H-3b), 3.86-3.82 (m, 2 H, H-5a, H-6a$_a$), 3.76-3.61 (m, 8H, H-5b, H-4b, H-2a, H-1°$_a$, H-6a$_b$, OCH$_3$), 3.55-3.49 (m, 2H, H-2b, H-6b$_a$), 3.48-3.34 (m, 4 H, H-1°$_b$, H-6b$_b$, H-3°), 1.92-1.85 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 159.25, 139.02, 138.89, 138.23, 138.11, 137.98, 135.99, 133.26, 132.96 (aromatic *C*), 129.91 (aromatic *C*H), 129.88 (aromatic *C*), 128.52, 128.40, 128.36, 128.32, 128.29, 128.15, 128.00, 127.94, 127.93, 127.87, 127.80, 127.68, 127.55, 127.44, 127.27, 127.17, 126.79, 126.47, 126.04, 125.88, 113.72 (aromatic *C*H), 96.88 (C-1a), 96.84 (C-1b), 82.09 (C-3b), 81.97 (C-3a), 80.48 (C-2a), 79.42 (C-2b), 77.63 (C-4b), 75.59, 75.03, 74.36, 73.30, 73.25, 73.18, 73.07 (7 *C*H$_2$), 72.34 (C-4a), 71.01 (C-5b), 69.84 (C-5a), 69.02 (C-6a), 67.52 (C-6b), 64.86 (C-1°), 55.12 (O*C*H$_3$), 48.36 (C-3°), 28.90 (C-2°). HR-MS: Calculated for $C_{69}H_{73}O_{12}N_3$[M+Na$^+$]: 1158.5086; found: 1158.5112.

Synthesis of diglucoside **31**



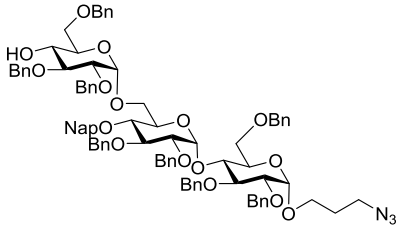
The reaction was carried out according to the general procedure E, using **30** (1.78 g, 1.57 mmol, 0.1 M in DCM:HFIP), triethylsilane (250 μL, 1.57 mmol) and 0.2M HCl/HFIP (0.8 ml, 0.16mmol). The product was purified by silica gel column chromatography (Tol:EA = 20:1). Compound **31** (1.36 g, 85% yield, Tol:EA = 12:1, R*f* = 0.21) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +30.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) v696, 735, 748, 818, 1027, 1047, 1072, 1089, 1155, 1208, 1261, 1275, 1355, 1363, 1456, 2096, 2862, 2871, 2918, 2924, 3031.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82-7.74 (m, 3 H, aromatic *H*), 7.68 (bs, 1 H, aromatic *H*), 7.48-7.43 (m, 2 H, aromatic *H*), 7.39 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1 H, aromatic *H*), 7.30-7.19 (m, 25 H, aromatic *H*), 5.63 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.04 (d, *J* = 11.2 Hz, 1 H, C*H*H), 5.00 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.93 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.82 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.80 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.77 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.74 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.68 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.61-4.50 (m, 5 H, 5 C*H*H), 4.09-4.04 (m, 2 H, H-3a, H-4a), 3.96 (t, *J* = 8.8 Hz, 1 H, H-3b), 3.86-3.82 (bd, 2 H, H-5a, H-6a$_a$), 3.76-3.51 (m, 7H, H-6b, H-5b, H-4b, H-6a$_b$, H-2a, H-1°$_a$), 3.48-3.37 (m, 4 H, H-2b, H-1°$_b$, H-3°), 1.93-1.87 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.01, 138.79, 138.10, 137.99, 137.95, 135.77, 133.32, 133.07 (aromatic *C*), 128.58, 128.48, 128.47, 128.40, 128.38, 128.28, 128.19, 128.08, 128.01, 127.94, 127.86, 127.83, 127.80, 127.67, 126.85, 126.71, 126.23, 126.12, 126.07 (aromatic *C*H), 96.90 (C-1a), 96.53 (C-1b), 82.00 (C-3a), 81.85 (C-3b), 80.41 (C-2a), 79.60 (C-2b), 77.59 (C-4b), 75.64, 75.31, 74.40, 73.50, 73.35 (6 *C*H$_2$), 72.31 (C-4a), 71.71 (C-5b), 69.91 (C-5a), 68.70 (C-6a), 64.94 (C-1°), 64.68 (C-6b), 48.41 (C-3°), 28.93 (C-2°). HR-MS: Calculated for $C_{62}H_{67}O_{11}N_3$ [M+Na$^+$]: 1038.4511; found: 1038.4543.

Synthesis of triglucoside **32**



The reaction was carried out according to the standard procedure C, using **4b** (1.80 g, 2.43 mmol), **31** (1.28 g, 1.26 mmol, 0.1 M in DCM), Ph_3P=O (4.00g, 14.4 mmol) and TMSI (382 µL, 2.67 mmol). The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **32** (1.34 g, 68% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.52) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +58.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν697, 749, 764, 820, 1028, 1051, 1073, 1084, 1156, 1208, 1251, 1261, 1275, 1465, 2096, 2868, 2923, 3031.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.78-7.68 (m, 4 H, aromatic *H*), 7.46-7.37 (m, 3 H, aromatic *H*), 7.32-7.10 (m, 40 H, aromatic *H*), 7.01 (bd, 2 H, aromatic *H*), 6.75-6.72 (m, 2 H, aromatic *H*), 5.63 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.07 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.03 (d, *J* = 12.0 Hz, 1 H, C*H*H), 5.02 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.93 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.88 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.80-4.72 (m, 6 H, H-1a, 5 C*H*H), 4.65-4.46 (m, 7 H, 7 C*H*H), 4.41-4.34 (m, 4 H, 4 C*H*H), 4.07-4.03 (m, 2 H, H-4a, H-3a), 3.96-3.56 (m, 17 H), 3.53 (dd, J_1 = 3.2 Hz, J_2 = 9.6 Hz, 1 H, H-2c), 3.48-3.37 (m, 4 H, H-6c, H-3°), 3.26 (dd, J_1 = 3.6 Hz, J_2 = 9.6 Hz, 1 H, H-2b), 1.91-1.85 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 159.20, 134.14, 139.03, 138.96, 138.54, 138.17, 138.13, 138.11, 138.03, 136.20, 133.36, 133.01, 130.77 (aromatic *C*), 129.62, 128.57, 128.45, 128.39, 128.36, 128.33, 128.22, 128.15, 128.05, 128.04, 127.80, 127.75, 127.70, 127.55, 127.50, 127.47, 127.38, 127.21, 126.61, 126.53, 126.15, 126.08, 125.87, 113.76 (aromatic *C*H), 97.20 (C-1c), 96.90 (C-1a), 96.29 (C-1b), 82.12 (C-3a), 81.98 (C-3b), 81.81 (C-3c), 80.38 (C-2a), 80.21 (C-2c), 80.00 (C-2b), 77.65 (C-4b), 77.31 (C-4c), 75.58, 75.50, 75.22, 74.77, 74.09, 73.54, 73.34, 73.29 (*C*H_2), 71.94 (C-4a), 71.84 (*C*H_2), 71.70 (C-5b), 70.27 (C-5c), 69.79 (C-5a), 69.14 (C-6a), 68.39 (C-6c), 65.24 (C-6b), 64.91 (C-1°), 55.33 (O*C*H_3), 48.41 (C-3°), 28.93 (C-2°).HR-MS: Calculated for $C_{62}H_{67}O_{11}N_3$ [M+Na^+]: 1591.7162; found: 1591.6997.

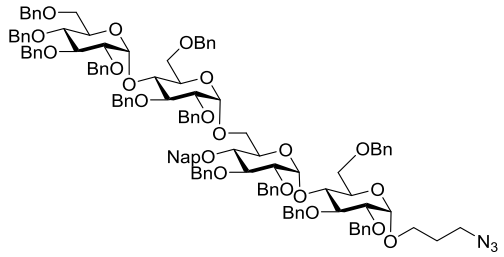
Synthesis of triglucoside **33**



The reaction was carried out according to the general procedure E, using **30** (1.90 g, 1.21 mmol, 0.1 M in DCM:HFIP), triethylsilane (302 µL, 1.90 mmol) and 0.2M HCl/HFIP (0.95 ml, 0.19 mmol). The product was purified by silica gel column chromatography (Tol:EA = 25:1). Compound **33** (1456mg, 83% yield, Tol:EA = 12:1, R*f* = 0.33) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +47.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν696, 737, 749, 764, 820, 857, 911, 1027, 1051, 1081, 1091, 1141, 1155, 1208, 1261, 1275, 2097, 2867, 2923.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82-7.70 (m, 4 H, aromatic *H*), 7.49-7.39 (m, 3 H, aromatic *H*), 7.31-7.12 (m, 40 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.06-5.03 (m, 3 H, H-1c, 2 C*H*H), 4.94 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.89 (d, *J* = 10.8 Hz, 1 H, C*H*H),

4.81-4.35 (m, 15 H, H-1a, 14 C*H*H), 4.09-4.03 (m, 2 H, H-4a, H-3a), 3.93-3.32 (m, 19 H), 3.26 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1 H, H-2b), 1.91-1.85 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.04, 138.92, 138.42, 134.14, 138.09, 137.99, 136.15, 133.35, 133.02 (aromatic *C*), 128.55, 128.45, 128.40, 128.36, 128.32, 128.20, 128.17, 128.10, 128.05, 128.01, 127.82, 127.79, 127.69, 127.58, 127.53, 127.46, 127.38, 127.32, 127.23, 126.65, 126.59, 126.14, 125.93 (aromatic *C*H), 97.17 (C-1c), 96.85 (C-1a), 96.16 (C-1b), 82.15 (C-3a), 81.99 (C-3b), 80.86 (C-3c), 80.39 (C-2a), 80.01 (C-2b), 79.76 (C-2c), 77.71 (C-4b), 77.48, 77.16, 76.84, 75.52, 75.17, 74.12, 73.58, 73.33, 73.28 (*C*H_2), 71.69 (C-4a), 71.65 (C-5b), 71.58 (*C*H_2), 70.62 (C-5c), 70.70 (C-4c), 69.75 (C-5a), 69.36 (C-6a), 69.07 (C-6c), 65.34 (C-6b), 64.90 (C-1°), 48.38 (C-3°), 28.90 (C-2°). HR-MS: Calculated for $C_{62}H_{67}O_{11}N_3$ [M+H$^+$]: 1448.6629; found: 1448.6653.

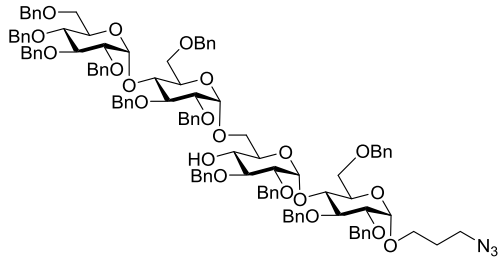
Synthesis of tetraglucose **34**



The reaction was carried out according to the standard procedure B. The donor **2b** (1.05 g, 1.47 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (10 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (1.86 mL, 23.6 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (130 µL, 1.47 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **33** (1.07 g, 0.74 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 5 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **34** (1.18 g, 81% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.57) was obtained as a colorless syrup.$[\alpha]_D^{20}$ +60.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) v696, 734, 749, 764, 819, 856, 909, 1027, 1047, 1072, 1091, 1155, 1207, 1261, 1275, 1363, 1456, 2090, 2095, 2863, 2923, 3031. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.78-7.73 (m, 4 H, aromatic *H*), 7.48-7.37 (m, 3 H, aromatic *H*), 7.28-7.03 (m, 60 H, aromatic *H*), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1d), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.20 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.08-5.00 (m ,3 H, 3 C*H*H), 4.90-4.29 (m, 23 H, H-1a, 22 C*H*H), 4.22 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.11-4.03 (m, 4 H, H-5b, H-4c, H-3a, H-3c), 3.95-3.31 (m, 23 H), 3.23 (dd, J_1 = 3.6 Hz, J_2 = 9.2 Hz, 1 H, H-2b), 1.91-1.85 (m, 2 H, H-2°).^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.05, 139.04, 139.02, 138.85, 138.64, 138.38, 138.21, 138.07 138.04, 138.01, 137.98, 136.24, 133.38, 133.05 (aromatic *C*), 128.57, 128.41, 128.35, 128.32, 128.31, 128.26, 128.21, 128.12, 128.06, 128.03, 127.93, 127.80, 127.76, 127.68, 127.63, 127.50, 127.46, 127.34, 127.24, 127.06, 126.93, 126.75, 126.54, 126.35, 126.08. 125.85 (aromatic *C*H), 96.90 (C-1a), 96.71 (2 C, C-1c and 1d), 96.18 (C-1b), 82.15 (2 C, C-3a and 3d), 81.88 (C-3b), 81.71 (C-3c), 80.38 (C-2a), 80.22 (C-2c), 79.98 (C-2b), 79.38 (C-2d), 77.65 (2 C, C-4b and 4d), 75.51, 75.41, 75.27, 74.99, 74.07, 74.01, 73.49, 73.43, 73.34, 73.23, 72.96 (*C*H_2), 72.06 (C-4a), 71.97 (C-4c), 71.54 (*C*H_2), 71.40 (C-5b), 70.91 (C-5d), 69.83 (C-5c), 69.70 (C-5a), 68.95 (2 C, C-6a and 6c), 68.15 (C-6d), 64.90 (C-1°), 64.55 (C-6b), 48.36 (C-3°), 28.90 (C-2°). HR-MS:

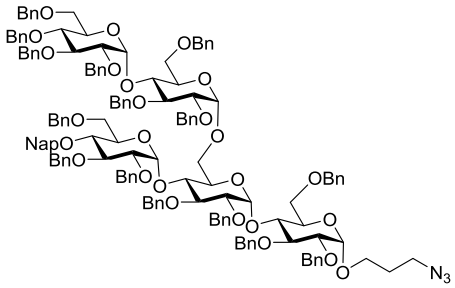
Calculated for $C_{122}H_{127}O_{21}N_3$ [M+H$^+$]: 1970.9035; found: 1970.9066.

Synthesis of tetraglucoside **35**



The reaction was carried out according to the general procedure D, using **34** (1.20 g, 0.61 mmol, 0.05 M in DCM:H_2O) and DDQ (152 mg, 0.67 mmol). The product was purified by silica gel column chromatography (Tol:EA = 25:1). Compound **35** (928mg, 84% yield, Tol:EA = 12:1, R*f* = 0.28) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +64.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν695, 733, 747, 764, 911, 1026, 1044, 1092, 1155, 1208, 1261, 1275, 1355, 1363, 1456, 2095, 2868, 2926, 3031, 3064.^{1}H-NMR ($CDCl_3$, 400MHz) δ7.43-7.09 (m, 60 H, aromatic *H*), 5.70 (d, *J* = 3.6 Hz, 1 H, H-1d), 5.67 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.04 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.99 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.89-4.39 (m, 23 H, H-1a, H-1c, 21 C*H*H), 4.25 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.11-3.97 (m, 4 H, H-4a, H-4c, H-3a, H-3c), 3.88-3.33 (m, 24 H), 1.93-1.86 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.09, 138.98, 138.86, 138.62, 138.19, 138.10, 138.06, 138.00, 137.97 (aromatic *C*), 128.77, 128.57, 128.51, 128.44, 128.43, 128.37, 128.35, 128.29, 128.20, 128.15, 128.05, 127.92, 127.90, 127.84, 127.79, 127.74, 127.70, 127.66, 127.64, 127.60, 127.54, 127.44, 127.23, 127.12, 126.75, 126.69 (aromatic *C*H), 97.53 (C-1a), 96.90 (C-1c), 96.82 (C-1d), 96.52 (C-1b), 82.06 (C-3d and 3c), 81.96 (C-3a), 81.37 (C-3b), 80.44 (C-2c), 80.04 (C-2a), 79.40 (C-2d), 79.26 (C-2b), 77.69 (C-4d), 75.63, 75.53, 75.02, 74.22, 73.54, 73.32, 73.27, 72.57 (*C*H$_2$), 72.03 (C-4a), 71.92 (C-4c), 71.72 (C-4b), 71.06 (C-5b), 70.94 (C-5d), 69.84 (C-5c and 5a), 68.92 (C-6a), 68.83 (C-6c), 68.17 (C-6d), 67.73 (C-6b), 64.90 (C-1°), 48.40 (C-3°), 28.93 (C-2°). HR-MS: Calculated for $C_{111}H_{119}O_{21}N_3$ [M+H$^+$]: 1830.8409; found: 1830.8458.

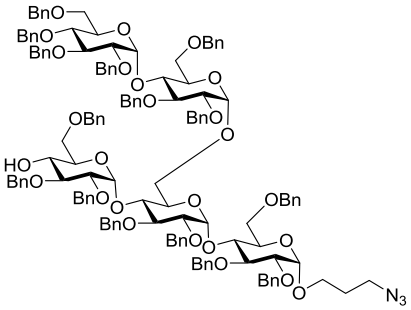
Synthesis of pentaglucoside **36**



The reaction was carried out according to the standard procedure B. The donor **3b** (1.20 g, 1.57 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (6 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (1.98 mL, 25.1 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (139 µL, 1.57 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **35** (860 mg, 0.47 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with

Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **36** (1.04 g, 91% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.64) was obtained as a colorless syrup.$[\alpha]_D^{20}$ +60.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν696, 749, 765, 1297, 1275, 2094, 2868, 2925, 3012. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.69-7.62 (m, 3 H, aromatic *H*), 7.51 (s, 1 H, aromatic *H*), 7.39-7.36 (m, 2 H, aromatic *H*), 7.28-7.02 (m, 74 H, aromatic *H*), 6.97-6.95 (m, 2 H, aromatic *H*), 5.72-5.71 (bt, 2 H, H-1d, H-1e), 5.54 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.35 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.96-3.56 (m, 59H), 3.47-3.30 (m, 6H), 3.20 (dd, J_1 = 3.6 Hz, J_2 = 9.6 Hz, 1 H, H-2b), 1.91-1.85 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.12, 138.98, 138.89, 138.87, 138.72, 138.51, 138.25, 138.18, 138.16, 138.11, 138.07, 138.04, 137.72, 135.91, 133.29, 133.01 (aromatic *C*), 128.58, 128.43, 128.36, 128.34, 128.32, 128.27, 128.20, 128.18, 128.15, 128.12, 128.06, 127.98, 127.94, 127.90, 127.77, 127.72, 127.68, 127.65, 127.56, 127.47, 127.43, 127.31, 127.24, 127.04, 126.94, 126.79, 126.75, 126.61, 126.24, 126.05, 125.88 (aromatic *C*H), 97.14 (C-1a), 96.95 (C-1e), 96.63 (C-1d), 96.51 (C-1c), 95.80 (C-1b), 82.13 (C-3a), 81.98 (2 C, C-3d, C-3e), 81.78 (C-3c), 81.08 (C-3b), 80.34 (C-2a), 80.20 (2 C, C-2c, C-2d), 79.46 (C-2b), 79.25 (C-2e), 77.69 (C-4d), 77.57 (C-4e), 75.49, 75.24, 75.01, 74.43 (CH_2), 74.24 (C-4b), 74.12, 73.68, 73.49, 73.35, 73.24, 73.11, 72.89 (CH_2), 72.38 (C-4a), 72.24 (C-5e), 72.11 (C-5b), 71.76 (CH_2), 71.60 (C-4c), 70.99 (C-5d), 69.90 (C-5c), 69.80 (C-5a), 68.98 (C-6e), 68.80 (2 C, C-6a, C-6c), 68.20 (C-6d), 64.91 (C-1°), 64.30 (C-6b), 48.38 (C-3°), 28.91 (C-2°). MALDI-TOF: Calculated for $C_{149}H_{155}O_{26}N_3$ $[M+H^+]$: 2403.1; found: 2397.7.

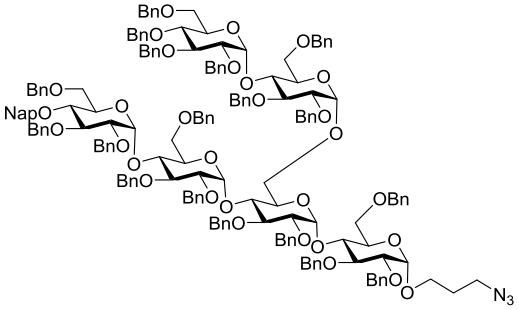
Synthesis of pentaglucoside **37**



The reaction was carried out according to the general procedure D, using **36** (1.10 g, 0.46 mmol, 0.05 M in DCM:H_2O) and DDQ (125 mg, 0.55 mmol). The product was purified by silica gel column chromatography (Tol:EA = 20:1). Compound **37** (777mg, 75% yield, Tol:EA = 12:1 =, R*f* = 0.36) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +79.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν697, 749, 764, 1028, 1045, 1098, 1155, 1261, 1275, 2098, 2855, 2923, 3031.^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.28-6.98 (m, 75 H, aromatic *H*), 5.74(d, *J* = 3.2 Hz, 1 H, H-1d), 5.63 (d, *J* = 3.2 Hz, 1 H, H-1e), 5.56 (d, *J* = 3.2 Hz, 1 H, H-1b), 5.32 (d, *J* = 3.2 Hz, 1 H, H-1c), 5.06 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.93-3.36 (m, 63H), 3.21 (dd, J_1 = 3.2 Hz, J_2 = 9.6 Hz, 1 H, H-2b), 1.92-1.86 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 12 MHz,) δ139.02, 138.96, 138.92, 138.82, 138.55, 138.43, 138.34, 138.21, 138.17, 138.08, 138.03, 137.96, 137.59 (aromatic *C*), 128.53, 128.38, 128.28, 128.15, 128.08, 128.03, 127.88, 127.84, 127.76, 127.70, 127.68, 127.57, 127.45, 127.42, 127.38, 127.31, 127.20, 127.09, 127.02, 126.93, 126.79, 126.55 (aromatic *C*H), 96.90 (C-1a), 96.87 (C-1e), 96.55 (C-1c), 95.72 (C-1d), 95.68 (C-1b), 82.15 (C-3a), 82.00 (C-3e), 81.59 (C-3c), 81.41 (C-3d), 81.26 (C-3b), 80.14 (C-2a), 80.09 (C-2c), 79.74 (C-2b), 79.60 (C-2d), 79.31 (C-2e), 77.65 (C-4d), 75.50, 75.21, 74.92, 74.20, 74.08, 73.89, 73.76, 73.44, 73.29, 73.20, 73.07, 73.02, 72.96, 72.74, 72.64, 71.84, 71.79, 71.47 (CH_2), 71.44 (C-4b), 71.84 (2 C, C-4e, C-4a),

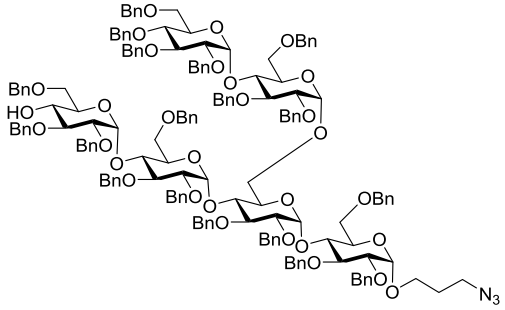
71.79 (2 C, C-5b, C-5d), 71.47 (CH_2), 71.44 (C-4c), 70.98 (C-4c), 70.85 (C-5e), 69.83 (C-5c), 69.76 (C-6), 69.70 (C-5a), 68.91, 68.60, 68.21 (3 C-6), 64.86 (C-1°), 64.20 (C-6b), 48.31 (C-3°), 28.87 (C-2°). MALDI-TOF: Calculated for $C_{138}H_{147}O_{26}N_3$ [M+H$^+$]: 2263.0; found: 2259.9.

Synthesis of hexasaccharide **38**



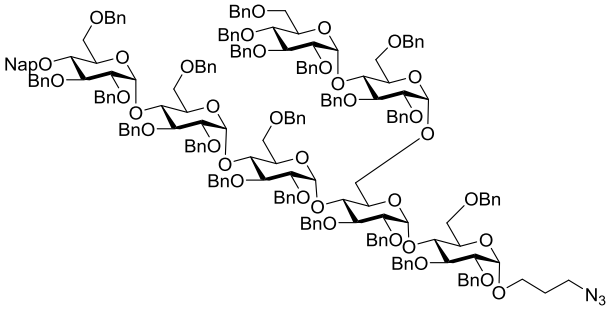
The reaction was carried out according to the standard procedure B. The donor **3b** (860 mg, 1.13 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (3 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (1.30 mL, 16.5 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (100 µL, 1.13 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **37** (620 mg, 0.27 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **38** (717mg, 93% yield, α:β> 20:1, Tol:EA = 12:1 =, R*f* = 0.64) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +62.6 (c=1, $CHCl_3$).IR (neat, cm^{-1}) ν696, 749, 764, 1028, 1042, 1094, 1144, 1155, 1208, 1261, 1275, 1456, 2096, 2860, 2923, 3031.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80-7.77 (m, 1 H, aromatic *H*), 7.71-7.67 (m, 2 H, aromatic *H*), 7.46-7.42 (m, 3 H, aromatic *H*), 7.34-6.92 (m, 91 H, aromatic *H*), 5.78 (d, *J* = 3.6 Hz, 1 H, H-1d), 5.74 (d, *J* = 3.6 Hz, 1 H, H-1e), 5.58 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.48 (d, *J* = 3.6 Hz, 1 H, H-1f), 5.33 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.14 (d, *J* = 10.8 Hz, 1 H, C*H*H), 5.04 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.91-3.30 (m, 75 H), 3.25 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1 H, H-2b), 1.90-1.84 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.37, 139.25, 139.00, 138.89, 138.78, 138.53, 138.40, 138.26, 138.23, 138.11, 138.08, 137.98, 137.93, 136.10, 133.35, 133.05 (aromatic *C*), 129.17, 128.59, 128.05, 127.71, 127.68, 127.41, 127.23, 127.04, 126.96, 126.75, 126.72, 126.58, 126.25, 126.11, 125.95, 125.43 (aromatic *C*H),96.99 (C-1a, 1e, 1f), 96.84 (C-1d), 96.70 (C-1c), 96.28 (C-1b), 82.29, 82.16, 82.00, 81.87, 81.56 (5 C-3), 80.62 (C-2), 80.48 (C-3), 80.42, 80.35. 79.52, 79.25, 78.88 (5 C-2), 78.49, 77.78 (2 C-4), 75.58, 75.34, 75.17, 74.98, 74.30, 74.01, 73.58, 73.55, 73.44, 73.35, 73.29, 73.07 (CH_2), 72.90 (C-4), 72.81 (C-5), 72.64, 72.16 (CH_2), 72.02, 71.85 (2 C-4), 71.28, 71.08, 71.00, 70.04, 70.00 (5 C-5), 69.28, 69.11, 69.00, 68.26, 68.16 (5 C-6), 64.94 (C-1°), 64.83 (C-6b), 48.44 (C-3°), 28.95 (C-2°). MALDI-TOF: Calculated for $C_{176}H_{183}O_{31}N_3$ [M+H$^+$]: 2835.3; found: 2833.2.

Synthesis of hexaglucoside **39**



The reaction was carried out according to the general procedure D, using **38** (700 g, 0.25 mmol, 0.05 M in DCM:H_2O) and DDQ (67 mg, 0.30 mmol). The product was purified by silica gel column chromatography (PE:EA = 20:1). Compound **39** (440 mg, 66% yield, Tol:EA = 12:1, R*f* = 0.38) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +67.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 732, 734, 1016, 1028, 1050, 1094, 1152, 1363, 1453, 2093, 2872, 2927. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.30-6.93 (m, 90 H, aromatic *H*), 5.78 (d, *J* = 3.6 Hz, 1 H, H-1d), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1e), 5.58 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.53 (d, *J* = 3.2 Hz, 1 H, H-1f), 5.36 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.09 (d, *J* = 11.2 Hz, 1 H, C*H*H), 5.05 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.91-3.31 (m, 75 H), 3.25 (dd, J_1 = 3.6 Hz, J_2 = 9.6 Hz, 1 H, H-2b), 1.92-1.86 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.28, 139.19, 138.92, 138.86, 138.70, 138.49, 138.42, 138.17, 138.04, 137.95, 137.82 (aromatic *C*), 128.59, 128.51, 128.23, 128.18, 128.06, 128.01, 127.93, 127.86, 127.84, 127.82, 127.75, 127.59, 127.50, 127.45, 127.40, 127.34, 127.24, 127.04, 126.97, 126.69, 126.60, 126.55 (aromatic *C*H), 97.06 (C-1e), 96.96 (C-1a), 96.75 (C-1f), 96.64 (C-1c, 1d), 96.19 (C-1b), 82.09, 82.00, 81.83, 81.65, 81.58, 80.59 (6 C-3), 80.52, 80.36, 80.29, 79.13, 78.89 (6 C-2), 77.69 (2 C-4), 75.55, 75.29, 75.15, 74.99, 74.27, 74.02, 73.93, 73.60, 73.51, 73.37, 73.32, 73.25, 73.06, 72.98, 72.79, 72.65, 72.05, 71.91, 71.68, 71.57, 71.22, 70.59, 70.51, 69.98, 69.93, 69.69, 69.14, 68.96, 68.16, 64.92 (C-1°), 64.63 (C-6b), 48.41 (C-3°), 28.93 (C-2°). MALDI-TOF: Calculated for $C_{165}H_{175}O_{31}N_3$ [M+H$^+$]: 695.2; found: 2692.7.

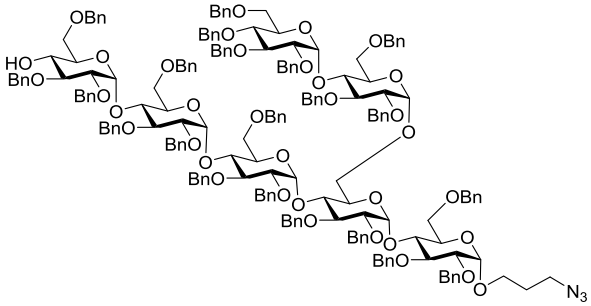
Synthesis of heptaglucoside **40**



The reaction was carried out according to the standard procedure B. The donor **3b** (550 mg, 0.72 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (900 μL, 11.4 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (63 μL, 0.71 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **39** (360 mg, 0.13 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with

Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **40** (397 mg, 91% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.67) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +67.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 733, 1027, 1035, 1078, 1082, 1093, 1132, 1141, 1145, 1155, 1361, 1453, 1496, 2098, 2864, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80-7.78 (m, 1 H, aromatic *H*), 7.73-7.68 (m, 2 H, aromatic *H*), 7.50 (s, 1 H, aromatic *H*), 7.46-7.40 (m, 2 H, aromatic *H*), 7.28-6.88 (m, 106 H, aromatic *H*), 5.75 (d, *J* = 3.2 Hz, 1 H, H-1), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1), 5.69 (d, *J* = 3.2 Hz, 1 H, H-1), 5.61 (d, *J* = 3.2 Hz, 1 H, H-1b), 5.49 (d, *J* = 2.8 Hz, 1 H, H-1), 5.34 (d, *J* = 3.2 Hz, 1 H, H-1c), 5.22 (d, *J* = 10.8 Hz, 1 H, C*H*H), 5.07 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.97-3.32 (m, 88 H), 3.25 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1 H, H-2b), 1.90-1.84 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.25, 139.13, 138.97, 138.89, 138.84, 138.78, 138.65, 138.45, 138.17, 138.12, 138.10, 138.08, 138.03, 137.95, 137.82, 137.78, 137.63, 136.03, 133.25, 132.93 (aromatic *C*), 128.51, 128.35, 128.30, 128.25, 128.21, 128.18, 128.12, 128.03, 127.97, 127.96, 127.89, 127.85, 127.82, 127.79, 127.67, 127.60, 127.54, 127.51, 127.47. 127.36, 127.26, 127.17, 127.03, 126.98, 126.88, 126.83, 126.66, 126.63, 126.53, 126.38, 126.10, 126.04, 125.87 (aromatic *C*H), 97.04, 96.89, 96.85, 96.77, 96.64, 96.25, 96.15 (7 C-1), 82.18, 82.07, 81.93, 81.84, 81.77, 81.26, 80.63, 80.34, 80.26, 80.20, 79.58, 79.52, 79.21, 78.79, 78.64, 77.64, 77.36, 75.55, 75.46, 75.05, 74.92, 74.22, 74.02, 73.93, 73.86, 73.48, 73.45, 73.40, 73.30, 73.24, 73.04, 72.97, 72.53, 72.46, 72.26, 72.19, 72.00, 71.84, 71.14, 70.92, 70.80, 69.90, 68.99, 68.85, 68.71, 68.08, 64.81 (C-1°), 64.69 (C-6b), 48.29 (C-3°), 28.83 (C-2°). MALDI-TOF: Calculated for $C_{203}H_{211}O_{36}N_3$ [M^+]: 3266.5; found: 3266.2.

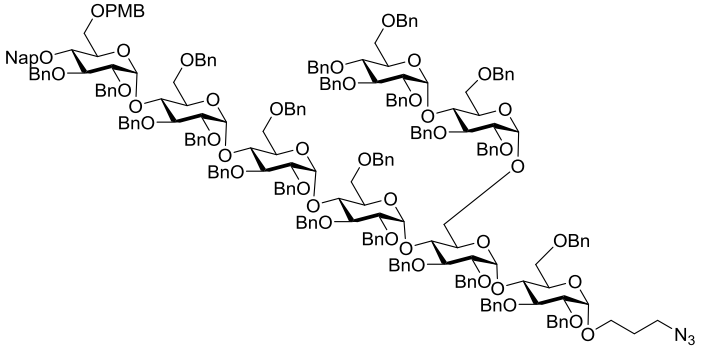
Synthesis of heptaglucoside **41**



The reaction was carried out according to the general procedure D, using **40** (260 g, 0.080mmol, 0.05 M in DCM:H_2O) and DDQ (20 mg, 0.09 mmol). The product was purified by silica gel column chromatography (Tol:EA = 20:1). Compound **41** (175mg, 70% yield, Tol:EA = 12:1, R*f* = 0.40) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +70.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 695, 731, 1026, 1036, 1092, 1135, 1152, 1207, 1363, 1453, 1496, 2098, 2857, 2923.^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.29-6.89 (m, 105 H, aromatic *H*), 5.73 (d, *J* = 3.0 Hz, 1 H, H-1), 5.67 (bd, 2 H, H-1), 5.59 (d, *J* = 3.0 Hz, 1 H, H-1b), 5.48 (bs, 1 H, H-1), 5.32 (bs, 1 H, H-1c), 5.19 (d, *J* = 11.0 Hz, 1 H, C*H*H), 5.04 (d, *J* = 11.5 Hz, 1 H, C*H*H), 4.93 (d, *J* = 11.5 Hz, 1 H, C*H*H), 4.88-3.32 (m, 86 H), 3.27 (bd, 1 H, H-2b), 2.52 (s, 1 H, O*H*), 1.89-1.88 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 125 MHz,) δ 139.34, 139.24, 139.08, 139.00, 138.97, 138.95, 138.89, 138.78, 138.56, 138.52, 138.24, 138.22, 138.20, 138.16, 138.11, 138.07, 138.03, 137.93, 137.88, 137.72 (aromatic *C*), 128.60, 128.53, 128.46, 128.44, 128.39, 128.37, 128.34, 128.29, 128.26, 128.19, 128.12, 128.05, 127.98, 127.93, 127.90, 127.86, 127.81, 127.78, 127.71, 127.64, 127.60, 127.55, 127.52, 127.46, 127.38, 127.37, 127.24, 127.14, 127.04, 126.97, 126.91, 126.74, 126.61, 126.49 (aromatic *C*H), 97.12 (C-1), 97.00 (C-1), 96.85 (C-1), 96.76 (2 C-1),

96.38 (C-1), 96.21 (C-1),82.16, 81.99, 81.88, 81.50, 81.34, 80.68, 80.43, 80.38, 80.30, 79.66, 79.35, 79.13, 78.79, 77.77, 75.63, 75.58, 75.00, 74.32, 74.02, 73.92, 73.67, 73.56, 73.47, 73.39, 73.35, 73.33, 73.12, 73.03, 73.00, 72.87, 72.75, 72.64, 72.43, 72.29, 72.11, 71.99, 71.70, 71.24, 71.03, 70.90, 70.45, 70.04, 70.01, 69.90 (C-6), 69.13 (C-6), 69.02 (C-6), 68.98 (C-6), 68.78 (C-6), 68.25 (C-6), 64.94 (C-1°), 64.81 (C-6b), 48.43 (C-3°), 28.96 (C-2°). MALDI-TOF: Calculated for $C_{192}H_{203}O_{36}N_3$ [M^+]: 3126.4; found: 3126.1.

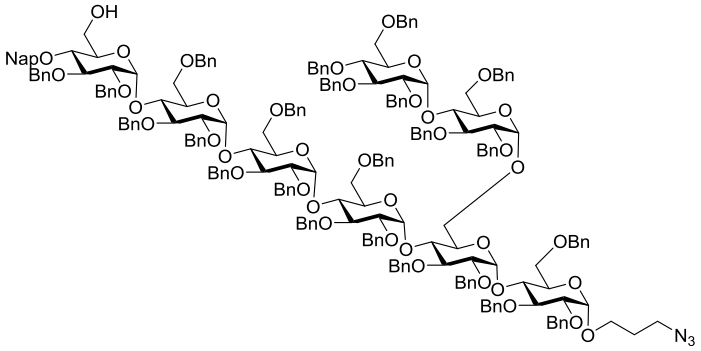
Synthesis of octaglucoside **42**



The reaction was carried out according to the standard procedure B. The donor **5b** (285 mg, 0.36 mmol, co-evaporated with toluene 3 times) was dissolved in dry DCM (1 mL) under nitrogen and stirred over fresh flame-dried molecular sieves 3A, after which DMF (455 μL, 5.78 mmol) was added to the solution. The solution was cooled to -78 °C, after which TfOH (31 μL, 0.35 mmol) was added. After 30 min, the pre-activation was complete as indicated by TLC-analysis. Acceptor **15** (680 mg, 0.76 mmol, dissolved in a little DCM and washed 3 times with DCM, totally 3 mL) was added to the solution and the mixture was placed in an ice bath. The reaction was stirred at 0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **42** (135 mg, 80% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.64) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +69.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) v697, 734, 1028, 1035, 1074, 1077, 1082, 1093, 1095, 1154, 1363, 2093, 2863, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80-7.78 (m, 1 H, aromatic *H*), 7.72-7.68 (m, 2 H, aromatic *H*), 7.45-7.42 (m, 3 H, aromatic *H*), 7.30-6.86 (m, 118 H, aromatic *H*), 6.73-6.71 (m, 2 H, aromatic *H*), 5.75-5.71 (m, 3H, 3 H-1), 5.71 (bt, 2 H, 2 H-1), 5.46 (d, *J* = 3.2 Hz, 1 H, H-1), 5.33 (d, *J* = 3.2 Hz, 1 H, H-1), 5.21 (d, *J* = 10.8 Hz, 1 H, C*H*H), 5.05 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.92-3.24 (m, 104 H), 1.90-1.83 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 125 MHz,) δ 159.29, 139.33, 139.23, 139.04, 139.01, 138.98, 138.85, 138.56, 138.32, 138.21, 138.12, 138.09, 138.06, 138.01, 137.89, 137.86, 137.74, 136.17, 133.34, 133.02, 130.01 (aromatic *C*), 129.95, 128.60, 128.42, 128.39, 128.36, 128.34, 128.30, 128.26, 128.20, 128.12, 128.06, 128.00, 127.97, 127.94, 127.90, 127.88, 127.84, 127.74, 127.70, 127.65, 127.59, 127.56, 127.54, 127.47, 127.42, 127.36, 127.25, 127.14, 127.05, 126.96, 126.90, 126.75, 126.72, 126.69, 126.61, 126.49, 126.46, 126.11, 125.92, 113.78 (aromatic *C*H), 97.07 (C-1), 96.99 (2 C-1), 96.73 (2 C-1), 96.34 (2 C-1), 96.16 (C-1), 82.27, 82.17, 82.01, 81.97, 81.88, 81.74, 81.38, 80.87, 80.40, 80.28, 79.82, 79.56, 79.43, 79.32, 78.87, 78.73, 77.76, 77.70, 75.64, 75.54, 75.08, 75.02, 74.30, 74.01, 73.88, 73.56, 73.44, 73.40, 73.35, 73.31, 73.14, 73.09, 73.03, 72.84, 72.75, 72.64, 72.52, 72.23, 72.11, 71.99, 71.79, 71.25, 71.00, 70.93, 70.02, 69.98, 69.12, 69.02, 68.94, 68.61, 68.22, 67.62, 64.91 (C-1°), 64.76 (C-6b), 55.21 (O*C*H$_3$), 48.41 (C-3°), 28.94 (C-2°). MALDI-TOF: Calculated for $C_{231}H_{241}O_{42}N_3$ [M^+]: 3728.7;

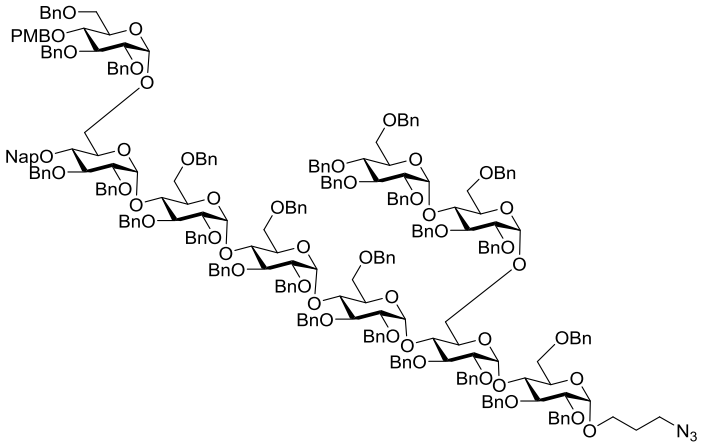
found: 3728.9.

Synthesis of octaglucoside **43**



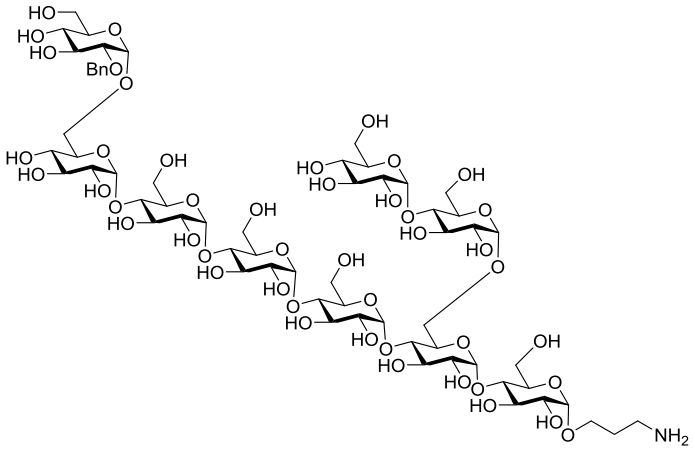
The reaction was carried out according to the general procedure E atrt about 1 h, using **42** (70 mg, 0.019 mmol, 0.01 M in DCM:HFIP),triethylsilane (3 μL, 0.018 mmol) and 0.1M HCl/HFIP (20 μL, 0.19 mmol). The product was purified by silica gel column chromatography (Tol:EA = 20:1). Compound **43** (60 mg, 88% yield, Tol:EA = 12:1, R*f* = 0.29) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +79.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 735, 1027, 1039, 1042, 1078, 1094, 1138, 1155, 1363, 1454, 2097, 2858, 2927. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81-7.72 (m, 3 H, aromatic *H*), 7.67 (s, 1 H, aromatic *H*), 7.46-7.38 (m, 3 H, aromatic *H*), 7.30-6.86 (m, 115 H, aromatic *H*), 5.75 (d, *J* = 3.6 Hz, 1 H, H-1), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1), 5.65 (d, *J* = 3.6 Hz, 1 H, H-1), 5.61 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.56 (d, *J* = 3.6 Hz, 1 H, H-1), 5.48 (d, *J* = 3.2 Hz, 1 H, H-1), 5.34 (d, *J* = 3.2 Hz, 1 H, H-1c), 5.22 (d, *J* = 11.6 Hz, 1 H, C*H*H), 5.06 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.99 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.94 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.90-3.31 (m, 97 H), 3.27 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1 H, H-2b), 1.90-1.84 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz,) δ 139.29, 139.18, 138.98, 138.94, 138.80, 138.77, 138.72, 138.52, 138.26, 138.17, 138.13, 138.08, 138.03, 138.00, 137.93, 137.94, 137.81, 137.66, 135.80, 133.32, 133.07 (aromatic *C*), 128.59, 128.45, 128.42, 128.37, 138.31, 128.26, 128.20, 128.10, 128.06, 128.00, 127.94, 127.89, 127.87, 127.85, 127.80, 127.75, 127.71, 127.64, 127.62, 127.54, 127.46, 127.32, 127.24, 127.16, 127.11, 127.04, 126.95, 126.83, 126.71, 126.68, 126.64, 126.61, 126.41, 126.23, 126.11, 126.06 (aromatic *C*H), 97.07 (C-1), 96.97 (C-1), 96.68 (3 C-1), 96.29 (C-1), 96.17 (C-1), 96.10 (C-1), 82.15, 82.02, 81.96, 81.847, 81.36, 80.88, 80.36, 80.23, 79.61, 79.47, 79.26, 78.83, 78.66, 77.72, 77.65, 75.64, 75.53, 75.32, 75.01, 74.28, 74.10, 74.01, 73.88, 73.63, 73.53, 73.44, 73.39, 73.32, 73.27, 73.15, 73.06, 72.82, 72.41, 72.07, 71.87, 71.66, 71.21, 70.97, 70.86, 70.82, 69.96, 69.07, 68.89, 68.52, 68.37, 68.14, 64.88 (C-1°), 64.67 (C-6b), 61.73 (C-6), 48.38 (C-3°), 28.92 (C-2°). MALDI-TOF: Calculated for $C_{223}H_{233}O_{41}N_3$ [M+H$^+$]: 3609.6; found: 3604.8.

Synthesis of nonaglucoside **44**



The reaction was carried out according to the standard procedure C, using **4b** (100 mg, 0.13 mmol), 4**3** (40 mg, 0.011 mmol, 0.005 M in DCM), $Ph_3P{=}O$ (225 mg, 0.81 mmol) and TMSI (30 µL, 0.21 mmol). The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **44** (31 mg, 67% yield, α:β> 20:1, Tol:EA = 12:1, R*f* = 0.65) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +86.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 734, 1008, 1028, 1049, 1084, 1091, 1154, 1362, 2097, 2858, 2924. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.75 (bd, 1 H, aromatic *H*), 7.70 (bd, 1 H, aromatic *H*), 7.67-7.64 (m, 3 H, aromatic *H*), 7.43-7.36 (m, 3 H, aromatic *H*), 7.29-6.87 (31mg, 132 H, aromatic *H*), 6.76-6.73 (m, 2 H, aromatic *H*), 5.74 (d, *J* = 3.5 Hz, 1 H, H-1), 5.71 (d, *J* = 3.5 Hz, 1 H, H-1), 5.65 (d, *J* = 3.5 Hz, 1 H, H-1), 5.61 (d, *J* = 3.5 Hz, 1 H, H-1), 5.60 (d, *J* = 3.5 Hz, 1 H, H-1), 5.47 (d, *J* = 3.5 Hz, 1 H, H-1), 5.32 (d, *J* = 3.5 Hz, 1 H, H-1), 5.20 (d, *J* = 11.0 Hz, 1 H, C*H*H), 5.09 (d, *J* = 3.5 Hz, 1 H, H-1), 5.02 (bt, 2 H, C*H*H), 4.92-3.31 (m, 113 H), 3.27 (dd, J_1 = 3.5 Hz, J_2 = 9.0 Hz, 1 H, H-2), 3.23-3.20 (m, 1 H, H-2), 1.89-1.84 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 125 MHz,) δ 159.24, 139.34, 139.24, 139.09, 139.05, 139.01, 138.87, 138.78, 138.58, 138.39, 138.32, 138.28, 138.24, 138.21, 138.19, 138.14, 138.12, 138.08, 137.96, 137.91, 137.87, 137.77, 136.42, 133.41, 133.04, 130.86 (aromatic *C*), 129.65, 128.60, 128.46, 128.44, 128.40, 128.34, 128.30, 128.21, 128.19, 128.12, 128.06, 128.04, 127.99, 127.97, 127.95, 127.90, 127.88, 127.80, 127.76, 127.74, 127.72, 127.69, 127.65, 127.61, 127.57, 127.54, 127.47, 127.42, 127.37, 127.35, 127.25, 127.15, 127.09, 127.05, 126.97, 126.91, 126.76, 126.74, 126.72, 126.48, 126.38, 126.19, 126.07, 125.84, 113.81 (aromatic *C*H), 97.25 (C-1), 97.08 (C-1), 97.00 (C-1), 96.76 (2 C-1), 96.33 (2 C-1), 96.20 (2 C-1), 82.14, 82.01, 81.89, 81.74, 81.38, 80.86, 80.42, 80.30, 80.25, 80.16, 79.78, 79.43, 79.36, 78.88, 78.76, 77.79, 77.54, 77.34, 75.64, 75.54, 75.35, 75.19, 75.02, 74.77, 74.31, 73.99, 73.88, 73.68, 73.57, 73.44, 73.38, 73.33, 73.15, 73.10, 72.83, 72.71, 72.66, 72.61, 72.13, 72.05, 71.84, 71.71, 71.27, 71.03, 70.91, 70.78, 70.35, 70.04, 70.01, 69.15, 69.02, 68.97, 68.85, 68.62, 68.45, 68.26, 65.05, 64.92 (C-1°), 64.79 (C-6), 55.38 (O*C*H_3), 48.42 (C-3°), 28.96 (C-2°). MALDI-TOF: Calculated for $C_{258}H_{269}O_{47}N_3$ [M+H^+]: 4161.8; found: 4161.7.

Synthesis of nonaglucoside **1.**



Compound **40** (20 mg, 0.0048 mmol) was dissolved in THF/H_2O/*tert*-BuOH (4 ml/4 ml/1.6 ml) before a catalytic amount of $Pd(OH)_2$/C was added. The reaction mixture was stirred for 3 days under a H_2 atmosphere (3.5 bar), filtered and concentrated *in vacuo*. A white powder **1** was obtained, which was purified by gel filtration (HW-40, 0.15M NH4OAc in H_2O) to yield **1** (4.7 mg, 61%).^{1}H-NMR ($CDCl_3$, 500 MHz) δ 5.40-5.38 (m, 3 H, 3 H-1), 5.35 (bt, 2 H, 2 H-1), 5.32 (d, *J* = 4.0 Hz, 1 H, H-1), 4.96-4.93 (m, 3 H, 3 H-1), 4.02-3.54 (m, 53 H), 3.49 (t, *J* = 9.5 Hz, 1 H), 3.44-3.39 (m, 2 H), 3.20-3.10 (m, 2 H), 2.02-1.97 (m, 2 H). ^{13}C-APT ($CDCl_3$, 125 MHz,) δ 100.03, 99.94, 99.83, 99.63, 99.56, 98.60, 98.11 (9 C-1), 78.86, 77.94, 77.57, 77.16, 76.78, 73.44, 73.02, 72.98, 72.79, 71.87, 71.83, 71.69, 71.53, 71.38, 71.31, 70.90, 70.57, 71.42, 70.23, 69.54, 69.41, 69.33, 67.55, 65.93, 60.79, 60.54, 60.49, 60.44, 37.85, 26.60. HR-MS: Calculated for $C_{57}H_{99}O_{46}N$ [M+H$^+$]: 1534.5511; found: 1534.5779.

References

(S1)Heuckendorff, M.; Poulsen, L. T.; Jensen, H. H. *J. Org. Chem*2016, *81*, 4988.

(S2) Yu, H. Tao, *Tetrahedron Lett.*2001, *42*, 2405-2407.

(S3) Herczeg, M.; Mező, E.; Eszenyi, D.; Antus, S.; Borbás, A. *Tetrahedron*2014, *70*, 2919.

(S4) Herczeg, M.; Mező, E.; Lázár, L.; Fekete, A.; Kövér, K. E.; Antus, S.; Borbás, A. *Tetrahedron*2013, *69*, 3149.

(S5) Ranade, S. C.; Kaeothip, S.; Demchenko, A. V. *Org. Lett.* 2010, *12*, 5628-5631.

(S6) Garegg, P. J.; Hultberg, H. *Carbohydr. Res.*1981, 93, C10-C11.

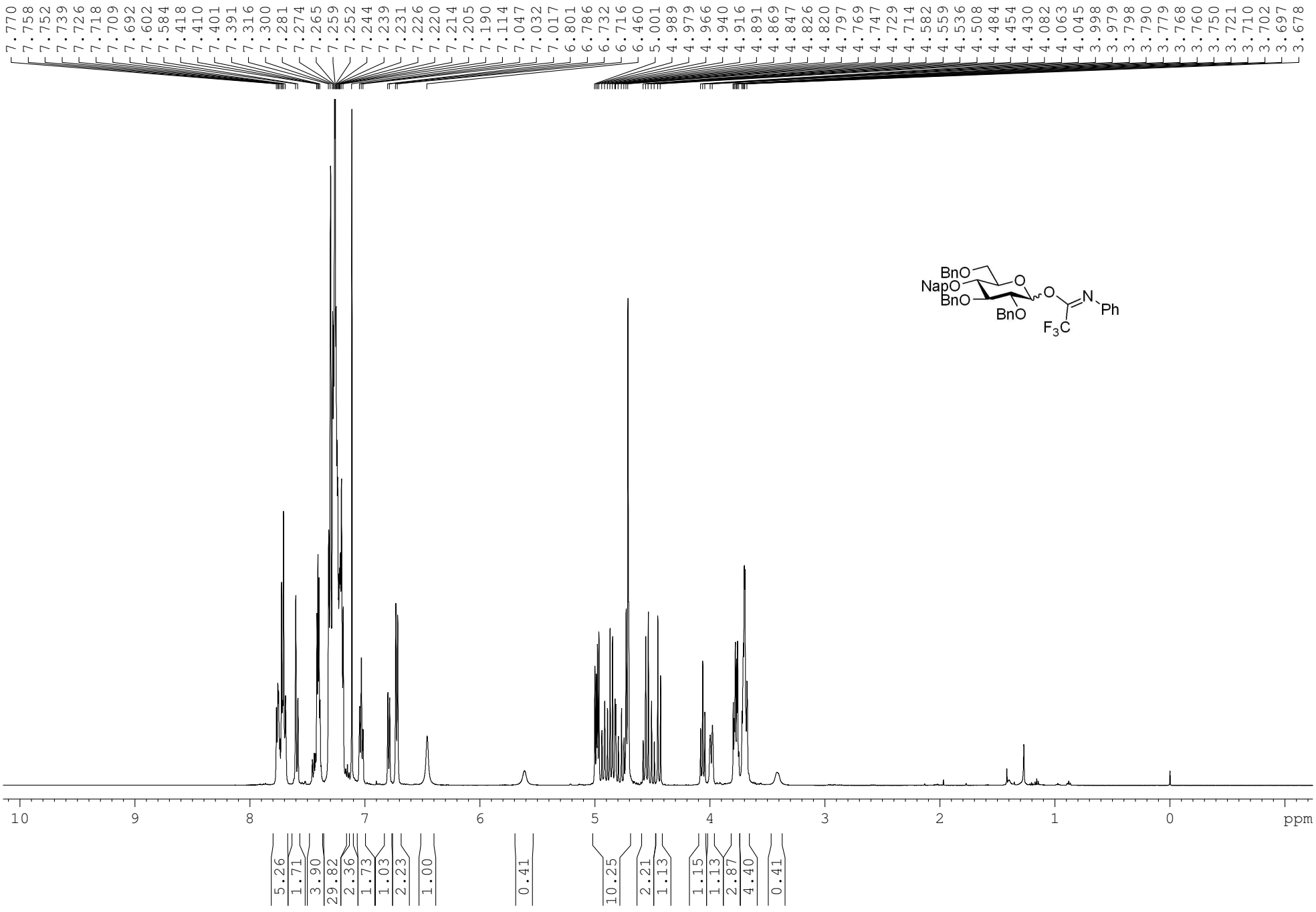
(S7) Koto, S.; Takebe, Y.; Zen, S. *Bull. Chem. Soc. Jpn.*1972, 45, 291-293.

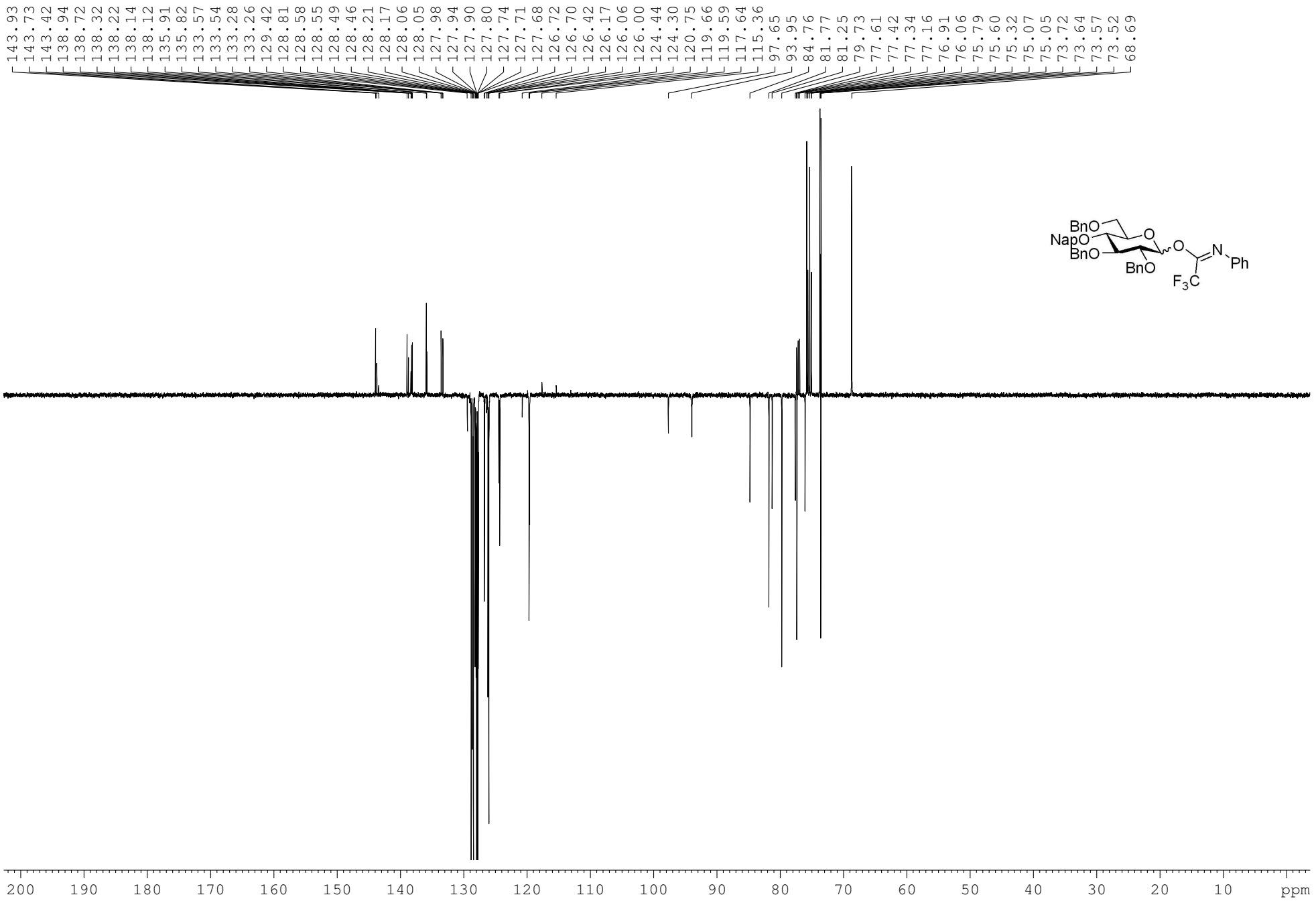
(S8) Sollogoub, M.; Das, S. K.; Mallet, J.-M.; Sinay, P. *C. R.Acad. Sci. Ser. 2*1999, 2, 441- 448.

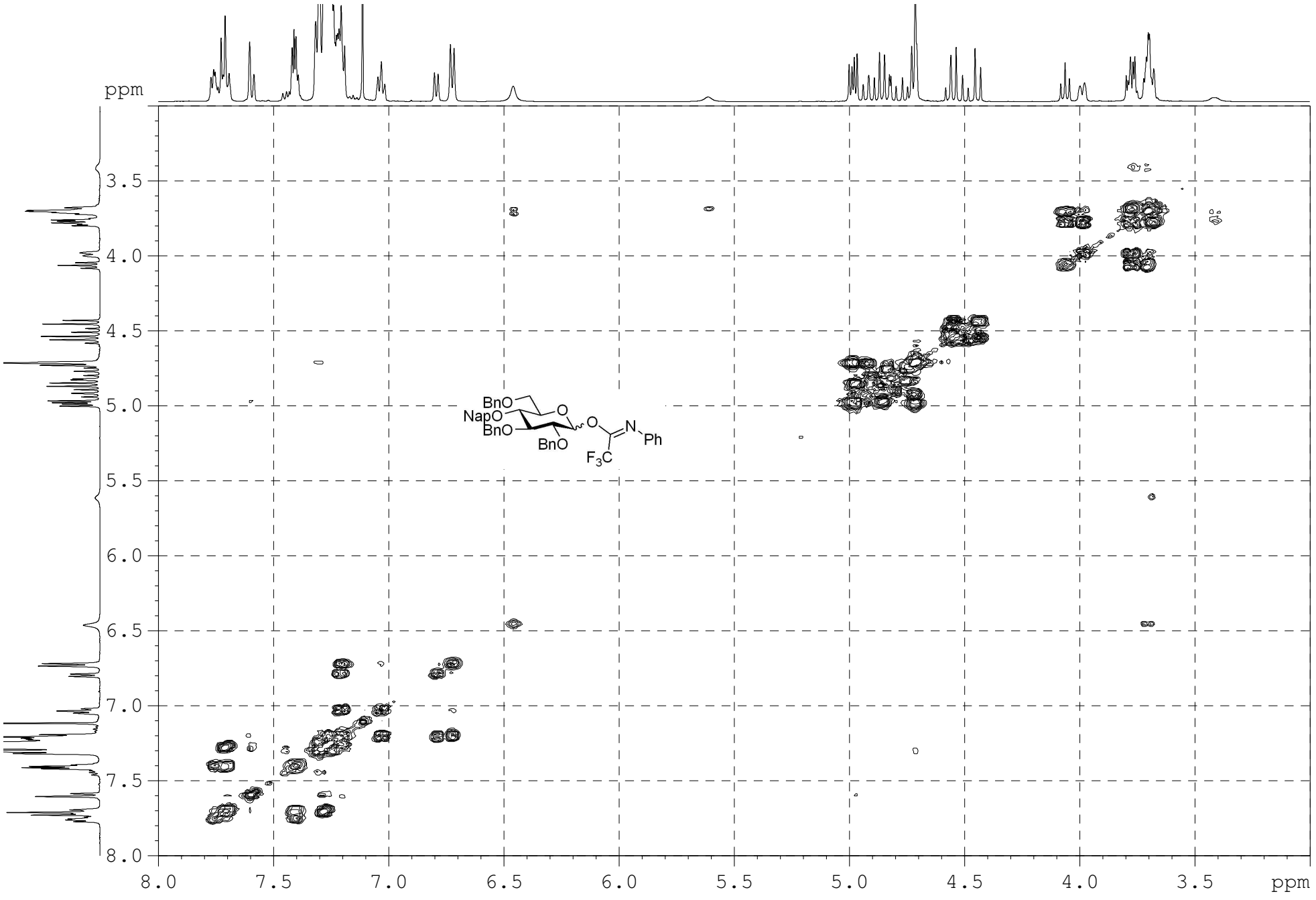
(S9) Kuester, J. M.; Dyong, I. *Justus Liebigs Ann. Chem.*1975, 2179-2189.

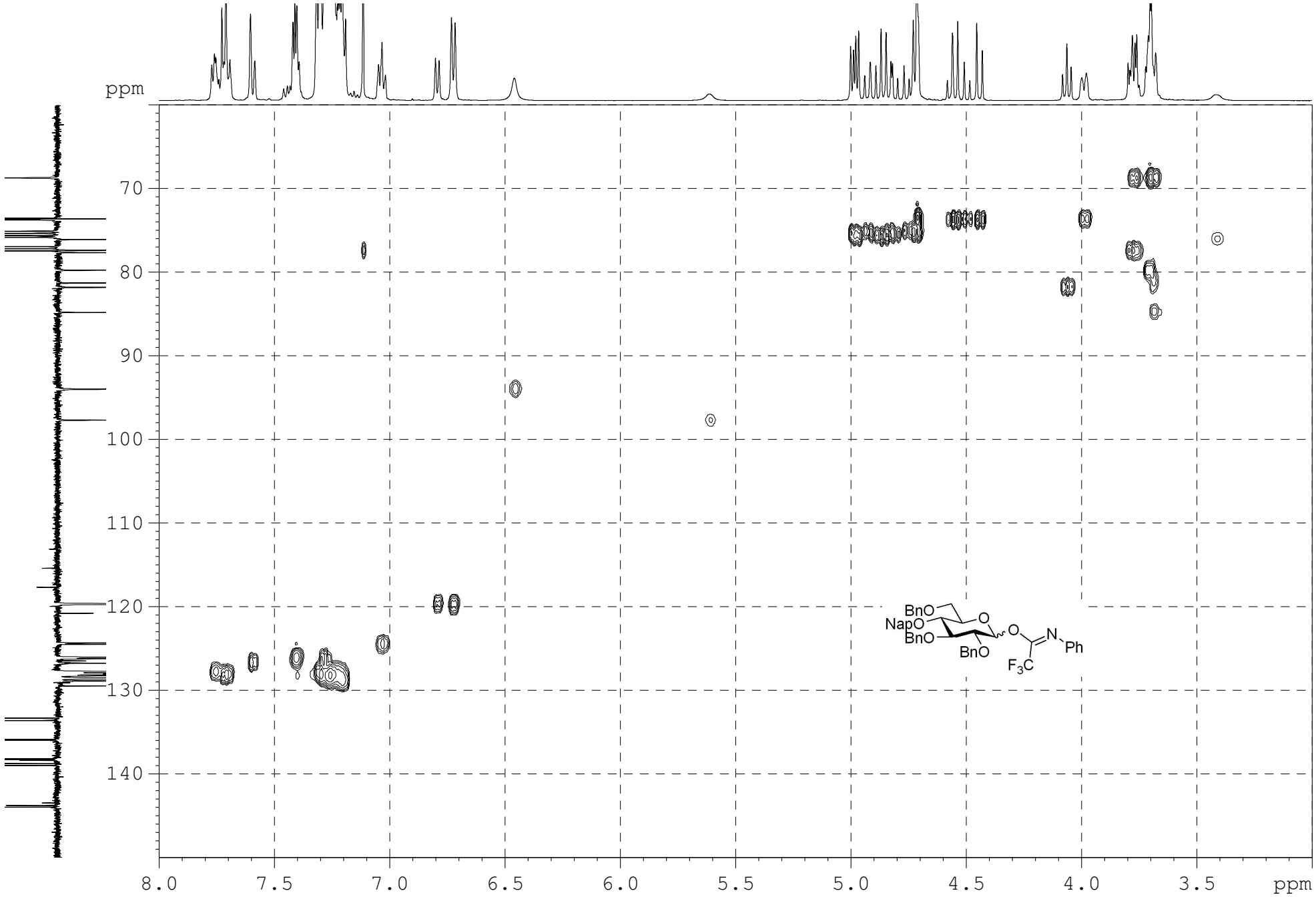
(S10) Nigudkar, S. S.; Stine, K. J.; Demchenko, A. V.*J. Am. Chem. Soc.*2014, *136*, 921

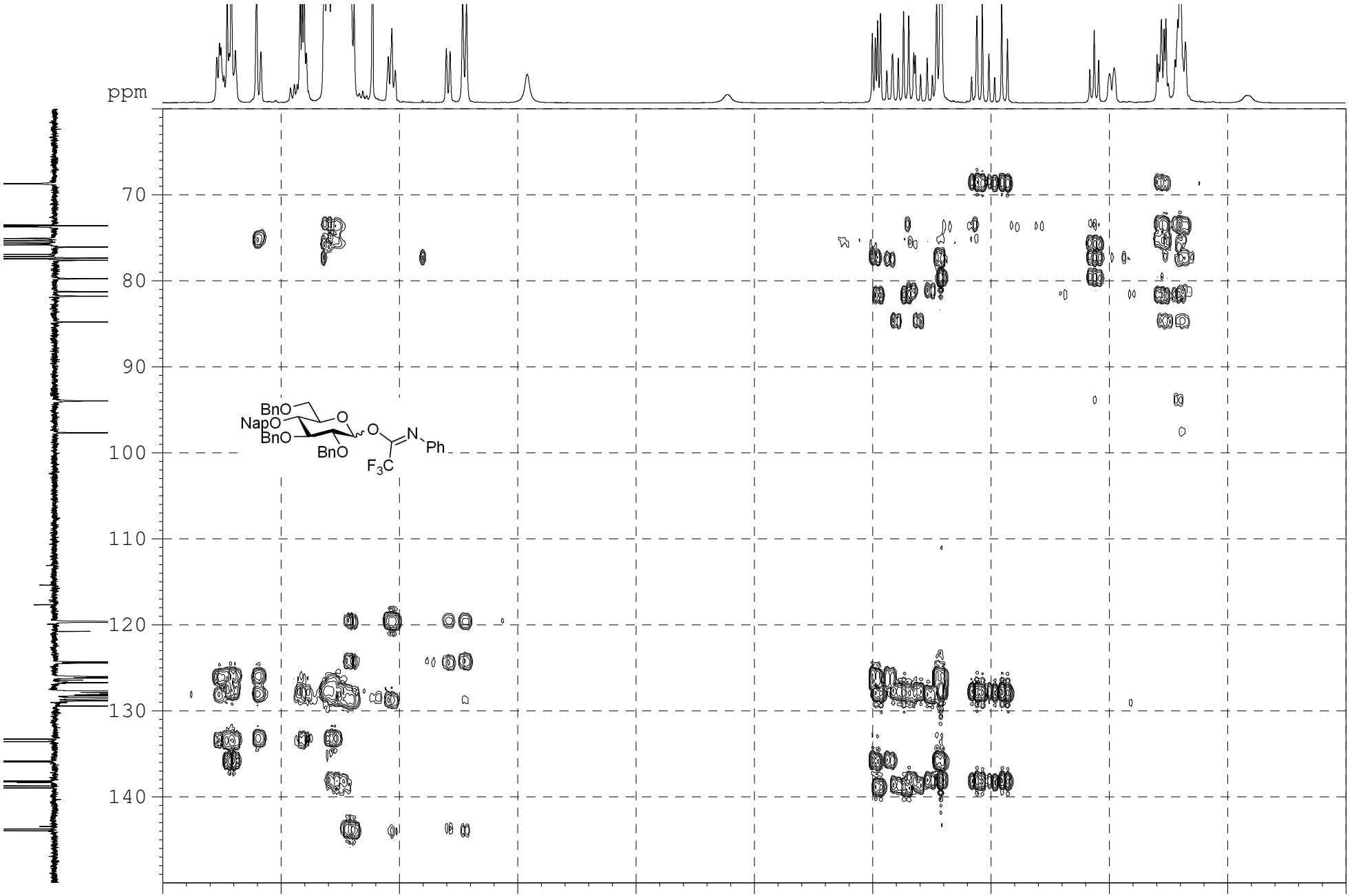
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **3b**



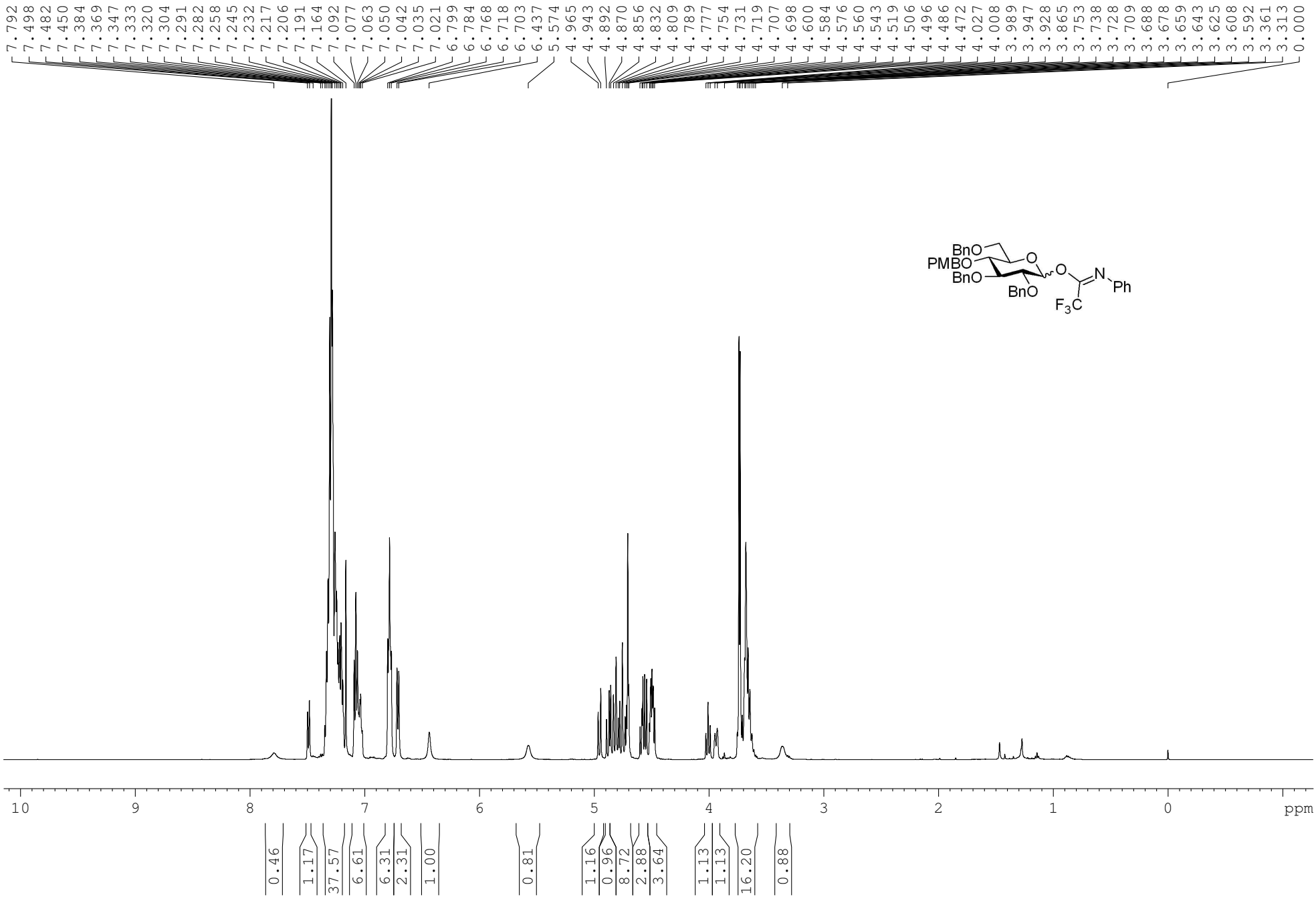

143.93
143.73
143.42
138.94
138.72
138.32
138.22
138.14
138.12
135.91
135.82
133.57
133.54
133.28
133.26
129.42
128.81
128.58
128.55
128.49
128.46
128.21
128.17
128.06
128.05
127.98
127.94
127.90
127.80
127.74
127.71
127.68
126.72
126.70
126.42
126.17
126.06
126.00
124.44
124.30
120.75
119.66
119.59
117.64
115.36
97.65
93.95
84.76
81.77
81.25
79.73
77.61
77.42
77.34
77.16
76.91
76.06
75.79
75.60
75.32
75.07
75.05
73.72
73.64
73.57
73.52
68.69
BnO
NapO
BnO
BnO
O
O
N
Ph
F3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

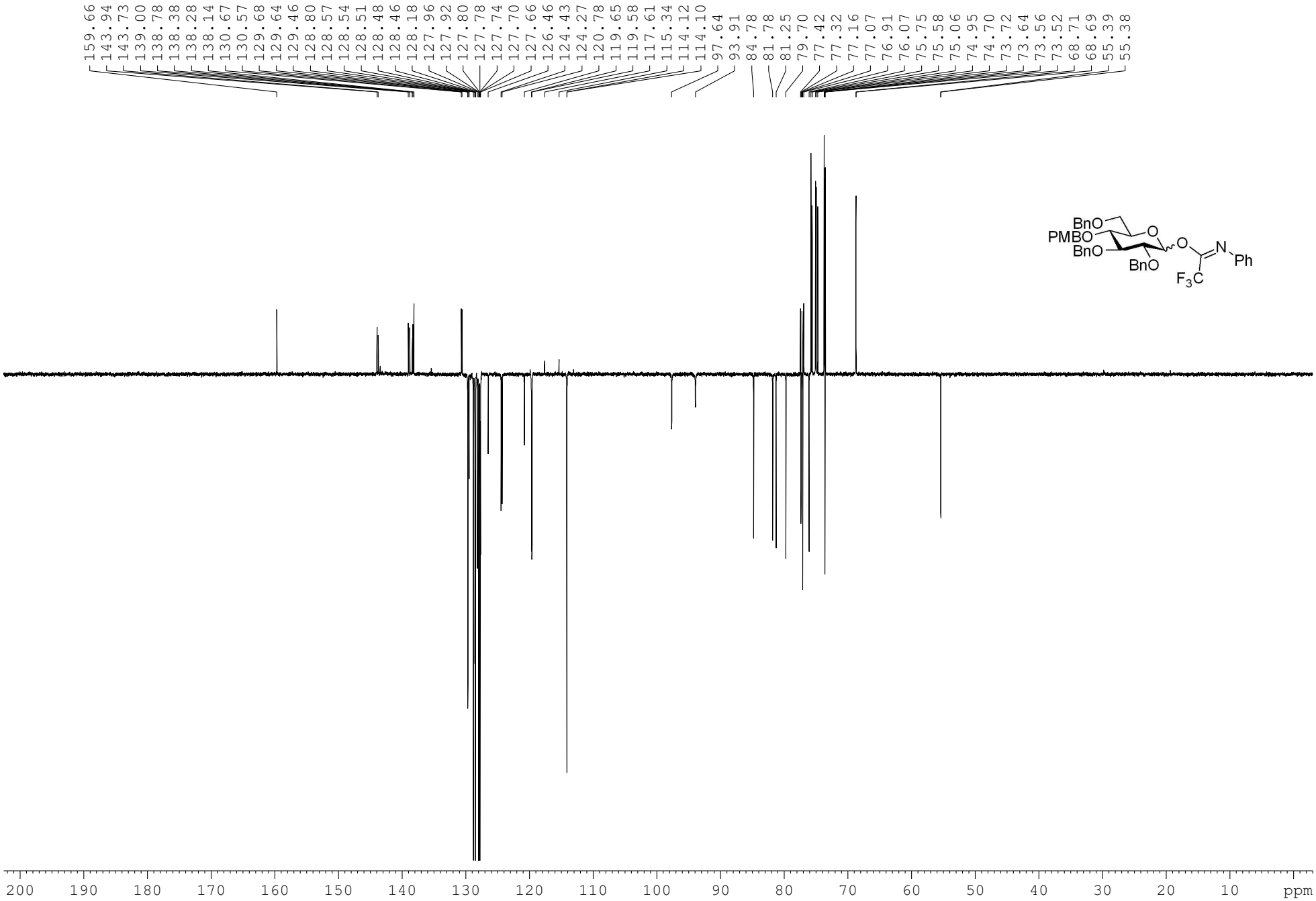

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
BnO
NapO
BnO
BnO
O
O
N
Ph
F3C

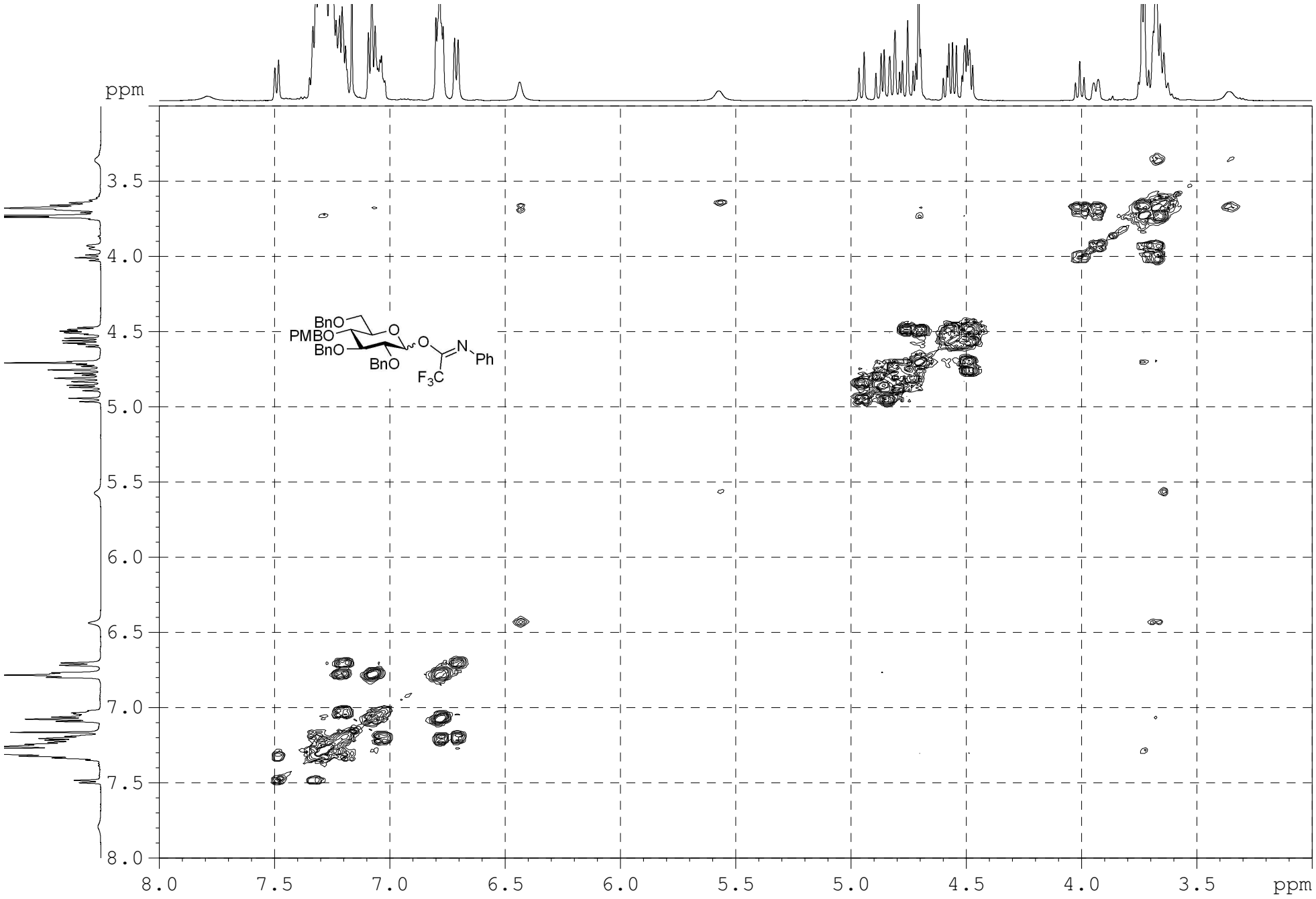

ppm
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
NapO
BnO
O
BnO
O
N
Ph
F3C

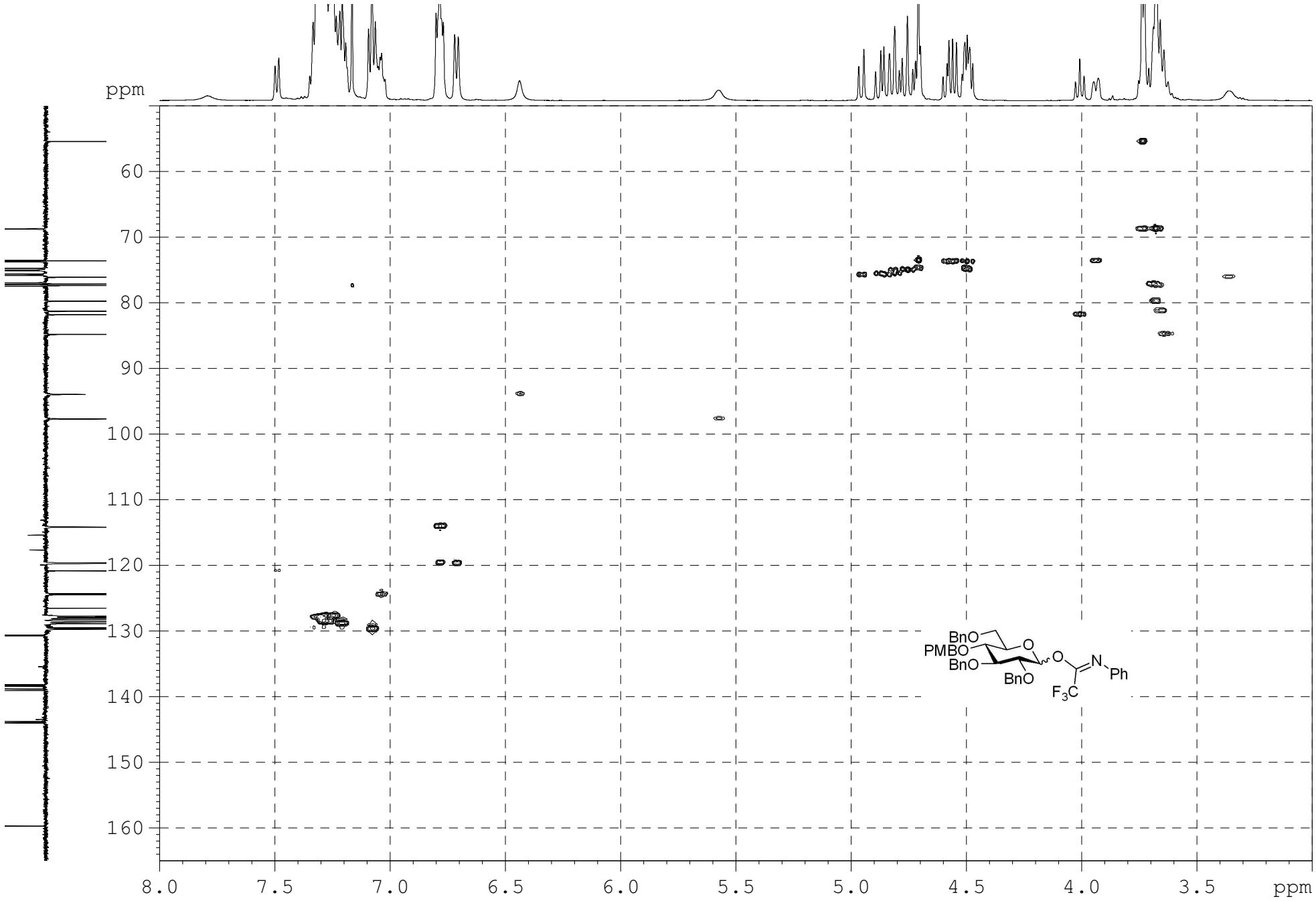

ppm
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
NapO
BnO
BnO
O
O
N
Ph
F3C

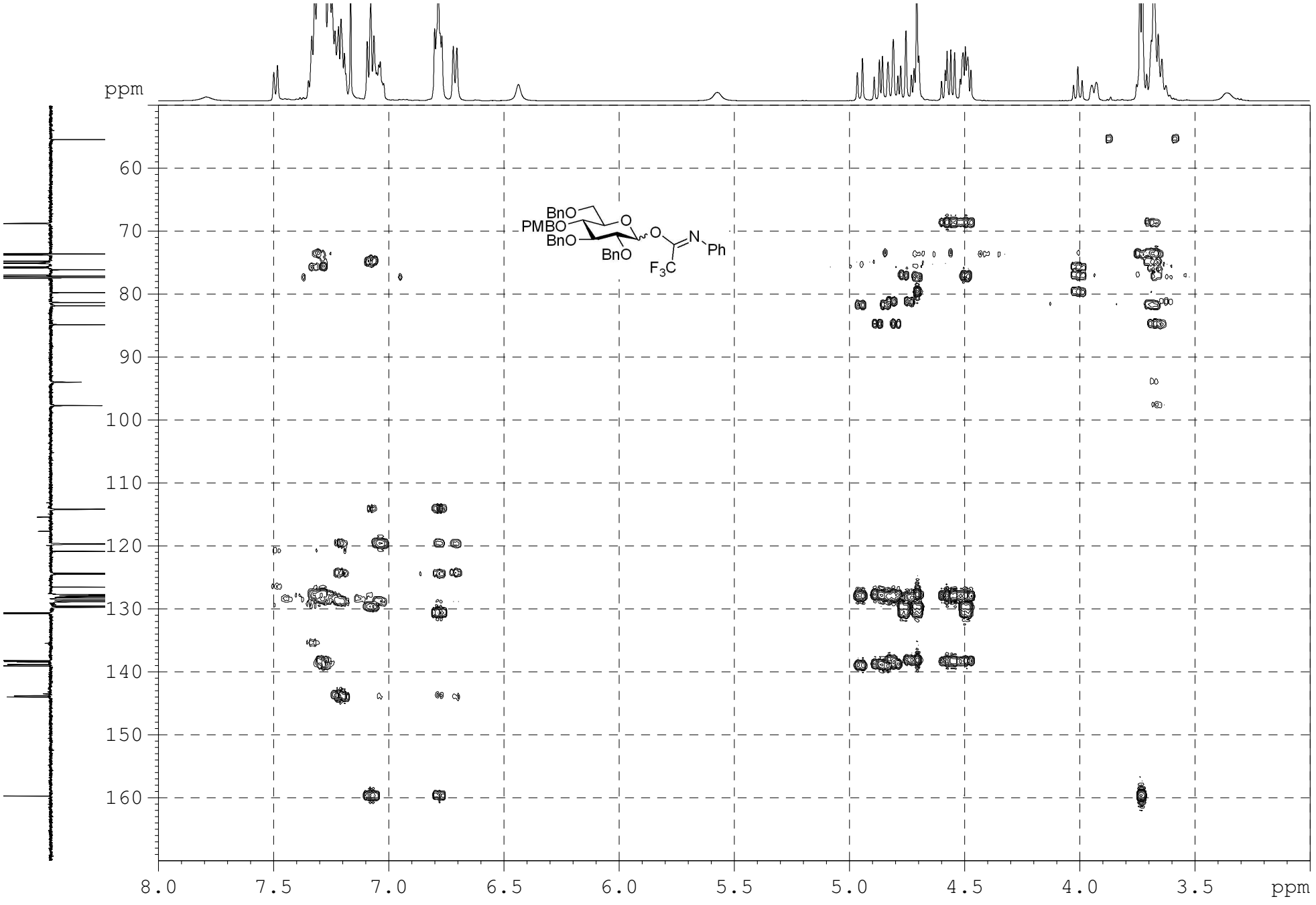
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **4b**



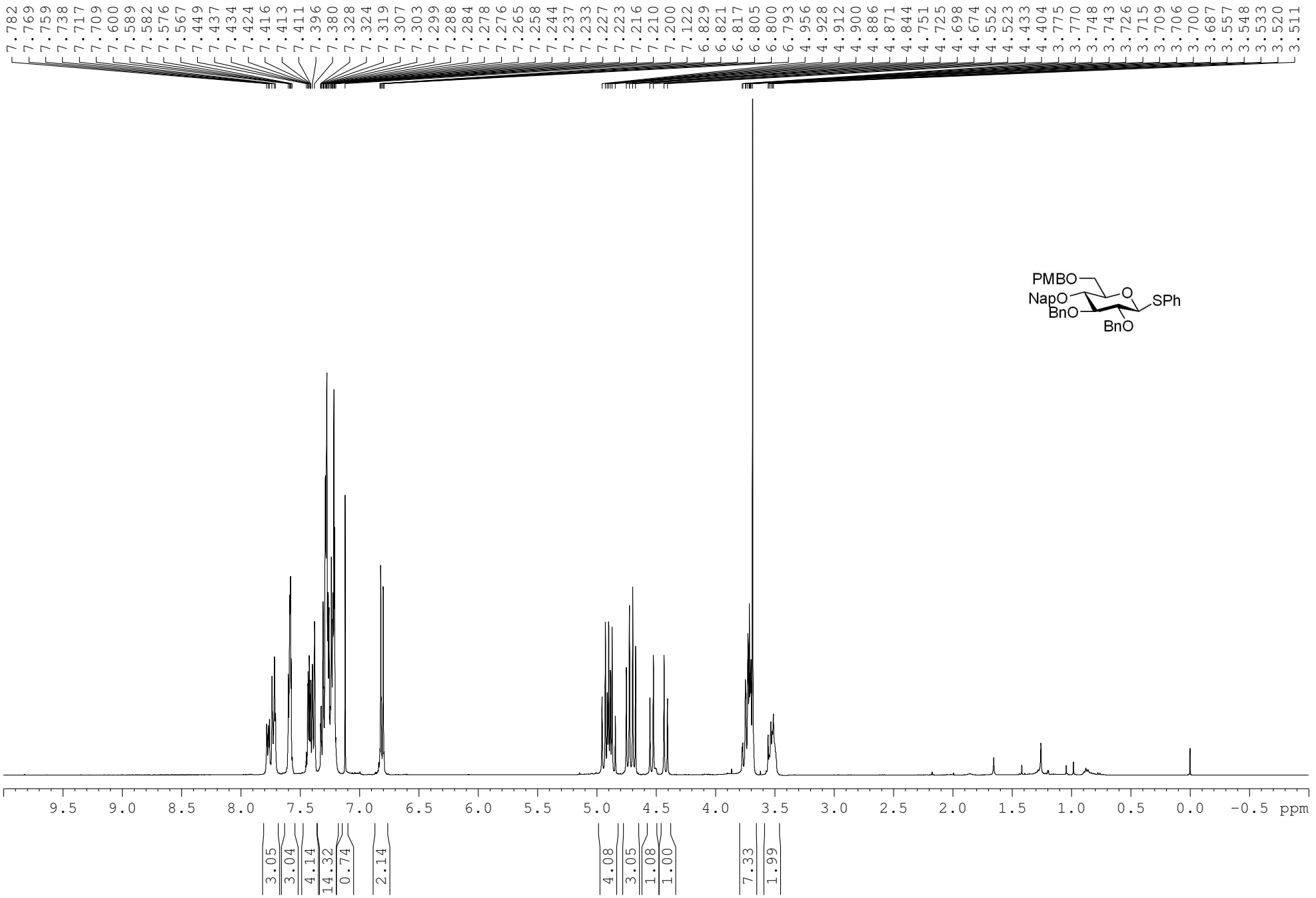

159.66
143.94
143.73
139.00
138.78
138.38
138.28
138.14
130.67
130.57
129.68
129.64
129.46
128.80
128.57
128.54
128.51
128.48
128.46
128.18
127.96
127.92
127.80
127.78
127.74
127.70
127.66
126.46
124.43
124.27
120.78
119.65
119.58
117.61
115.34
114.12
114.10
97.64
93.91
84.78
81.78
81.25
79.70
77.42
77.32
77.16
77.07
76.91
76.07
75.75
75.58
75.06
74.95
74.70
73.72
73.64
73.56
73.52
68.71
68.69
55.39
55.38
BnO
PMBO
BnO
BnO
O
O
N
Ph
F3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

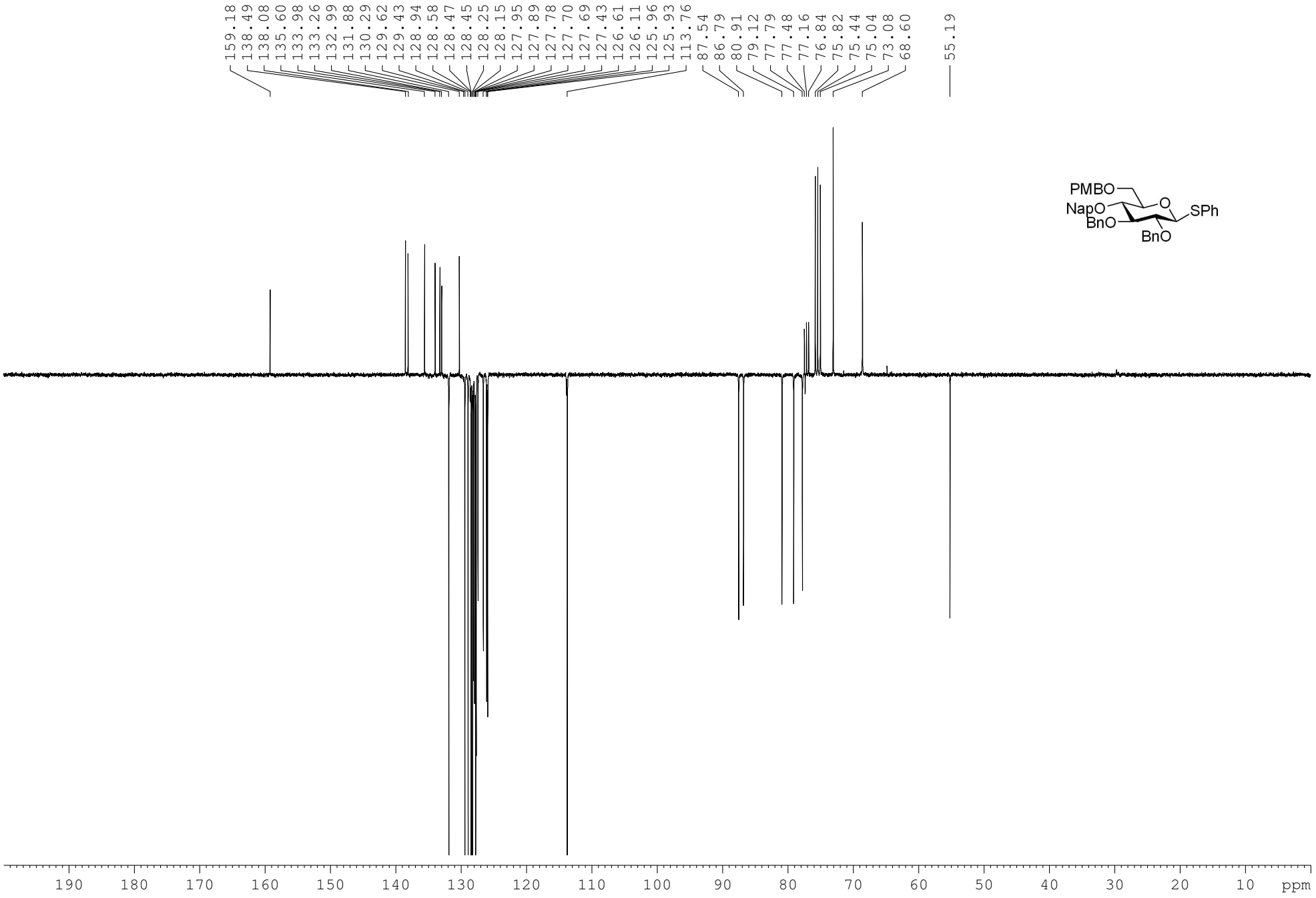

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
PMBO
BnO
O
BnO
O
N
Ph
F3C

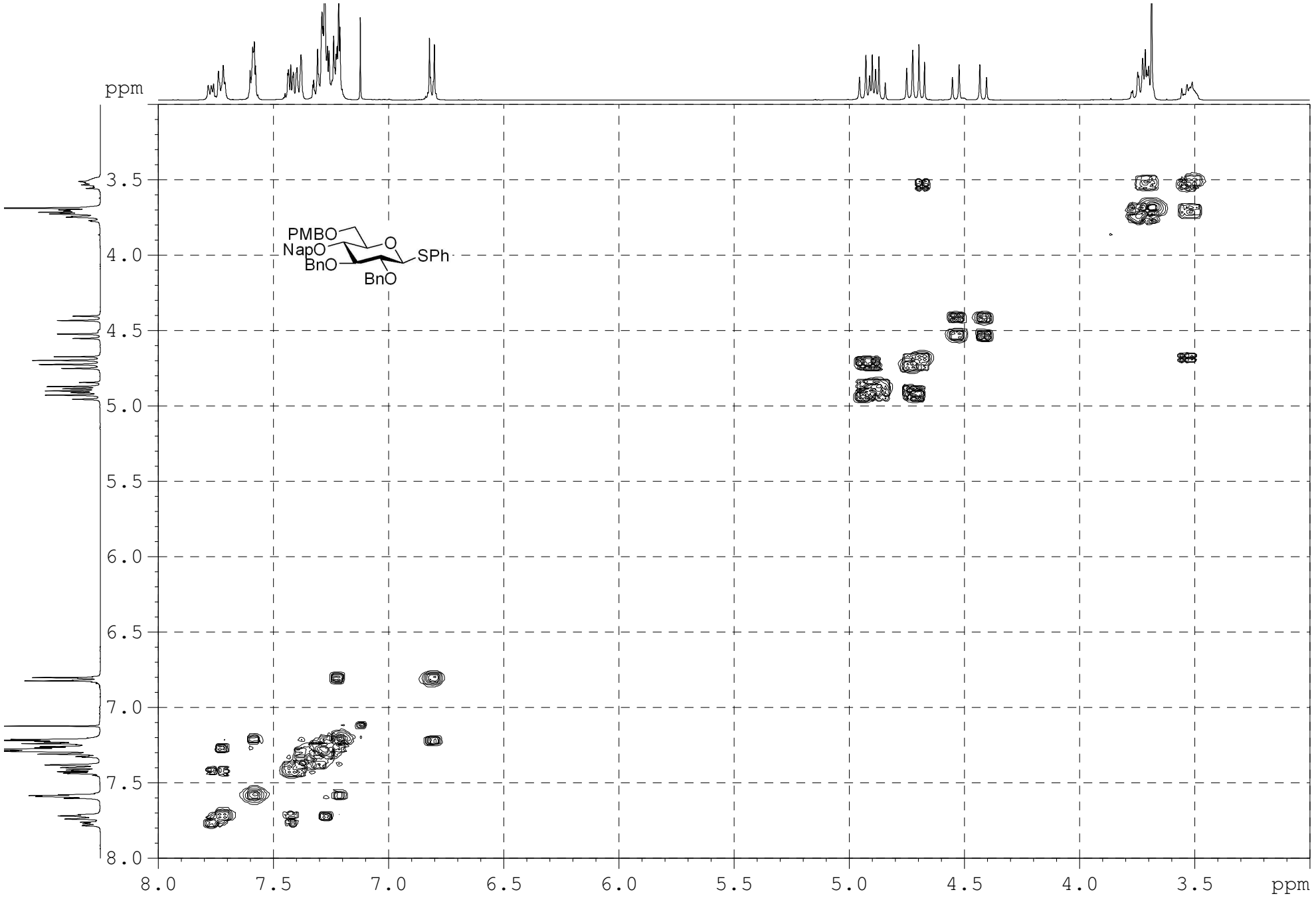

ppm
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
PMBO
BnO
O
BnO
O
N
Ph
F3C

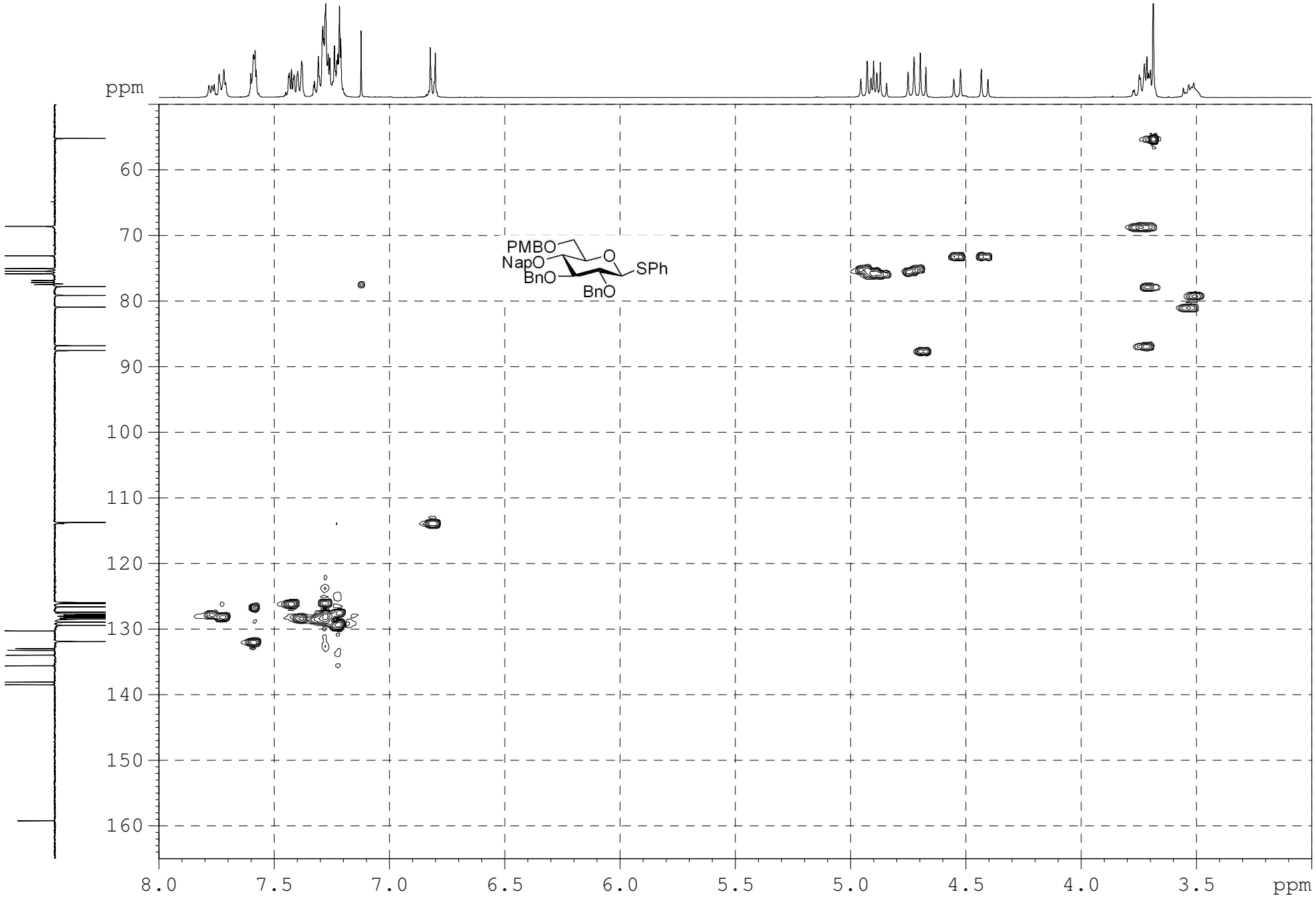

ppm
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
PMBO
BnO
O
BnO
O
N
Ph
F3C

^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC of **5a**

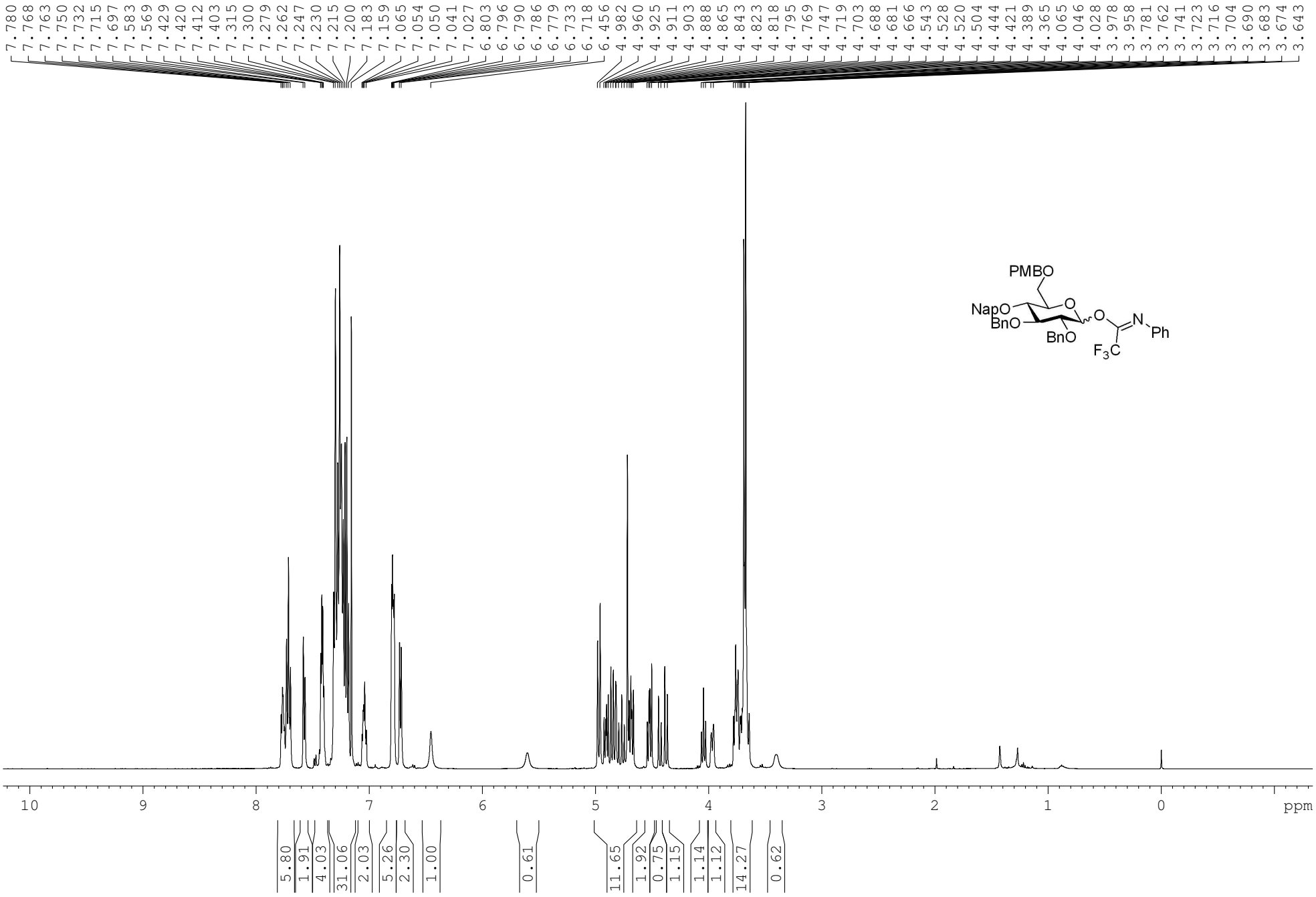


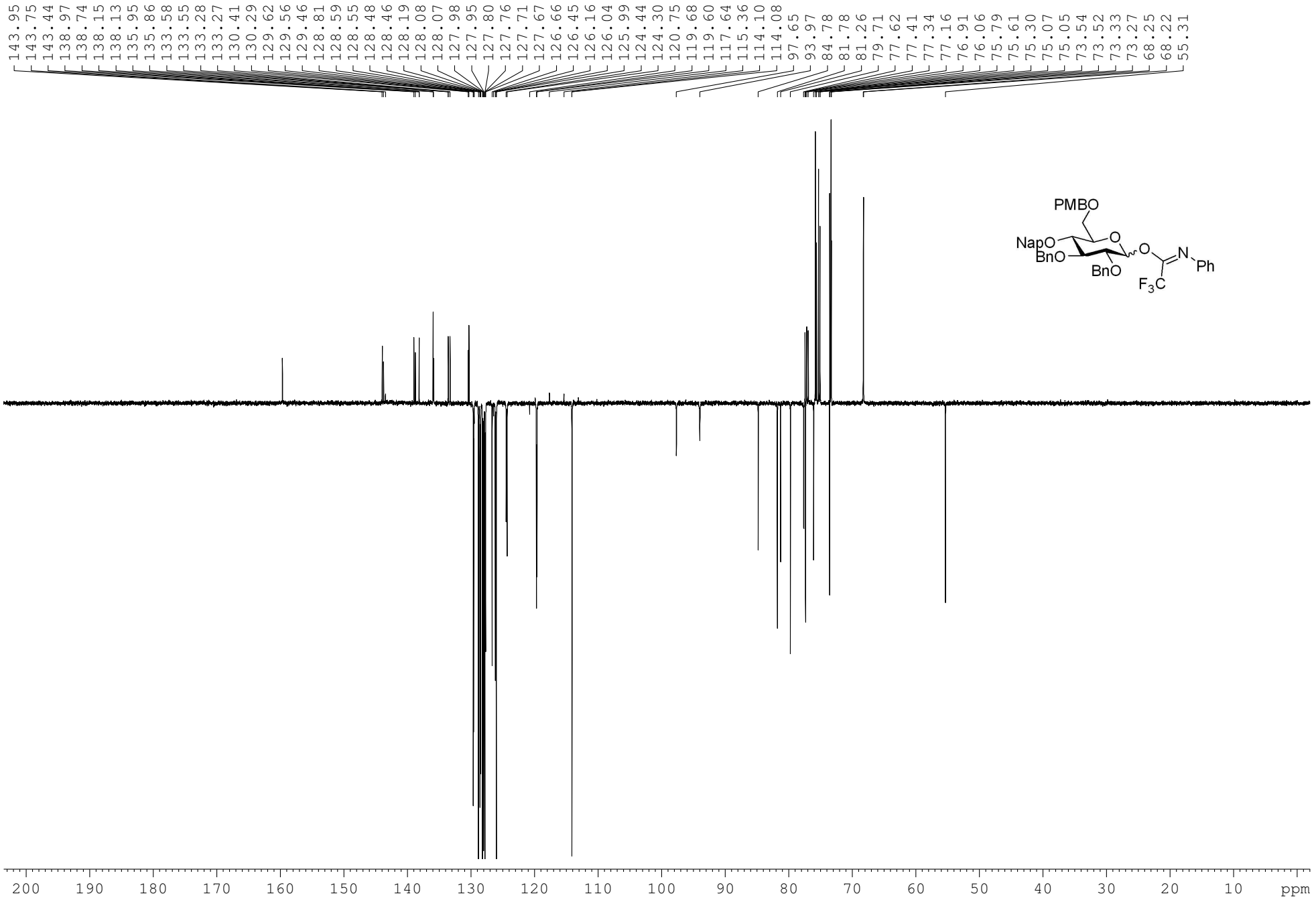

159.18
138.49
138.08
135.60
133.98
133.26
132.99
131.88
130.29
129.62
129.43
128.94
128.58
128.47
128.45
128.25
128.15
127.95
127.89
127.78
127.70
127.69
127.43
126.61
126.11
125.96
125.93
113.76
87.54
86.79
80.91
79.12
77.79
77.48
77.16
76.84
75.82
75.44
75.04
73.08
68.60
55.19
PMBO
NapO
BnO
O
SPh
BnO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

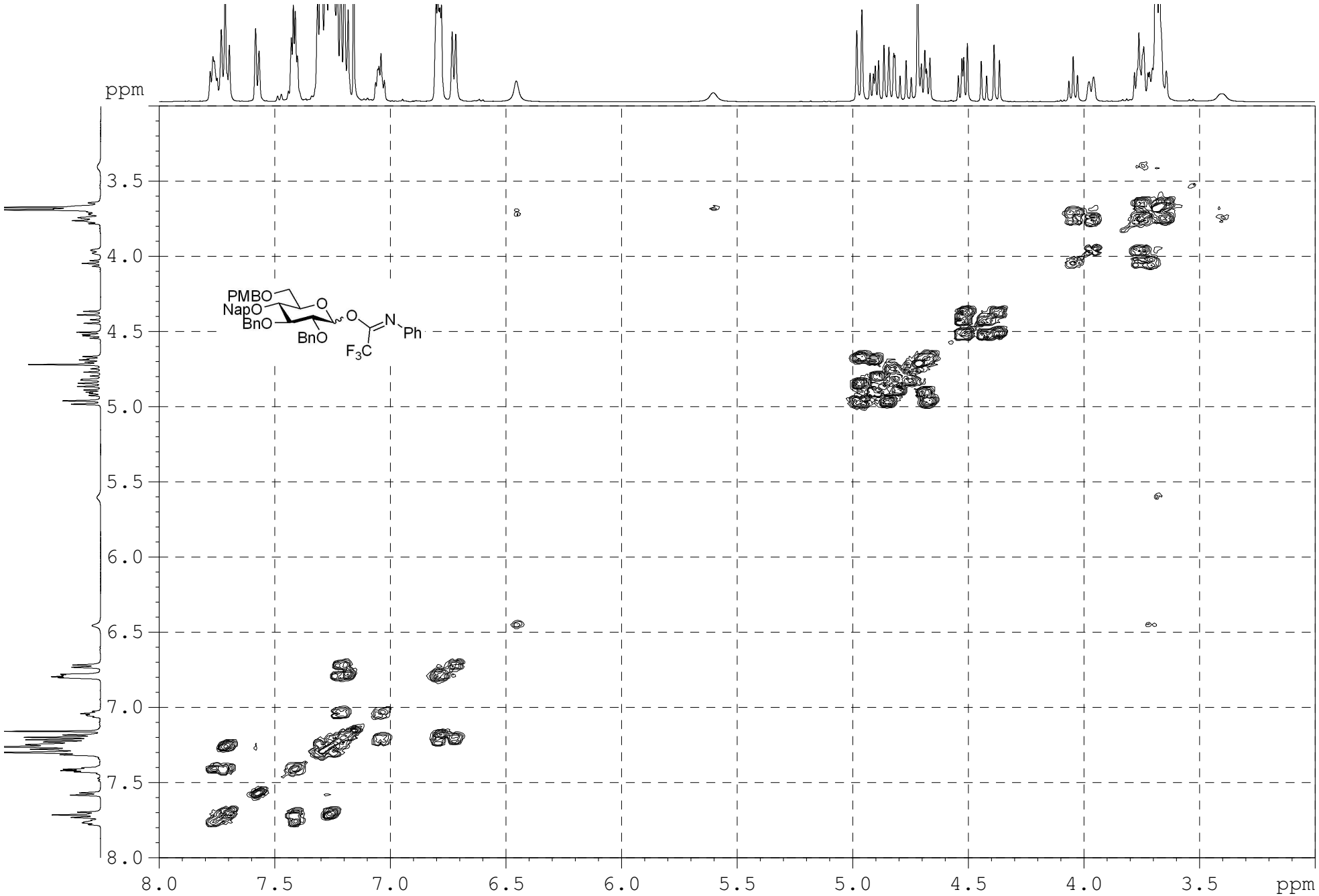

ppm
PMBO
NapO
BnO
O
SPh
BnO
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

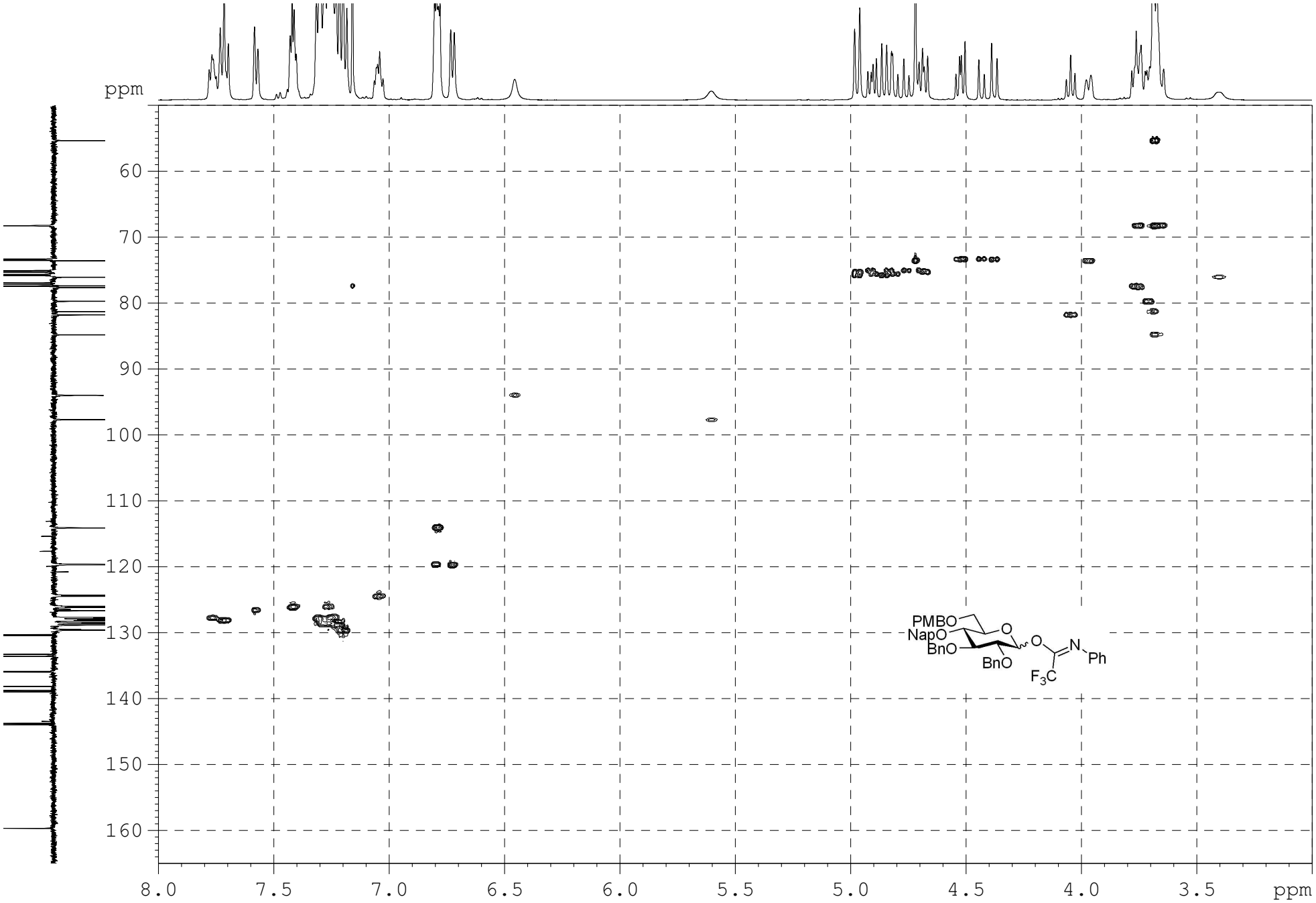

ppm
PMBO
NapO
BnO
O
SPh
BnO
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

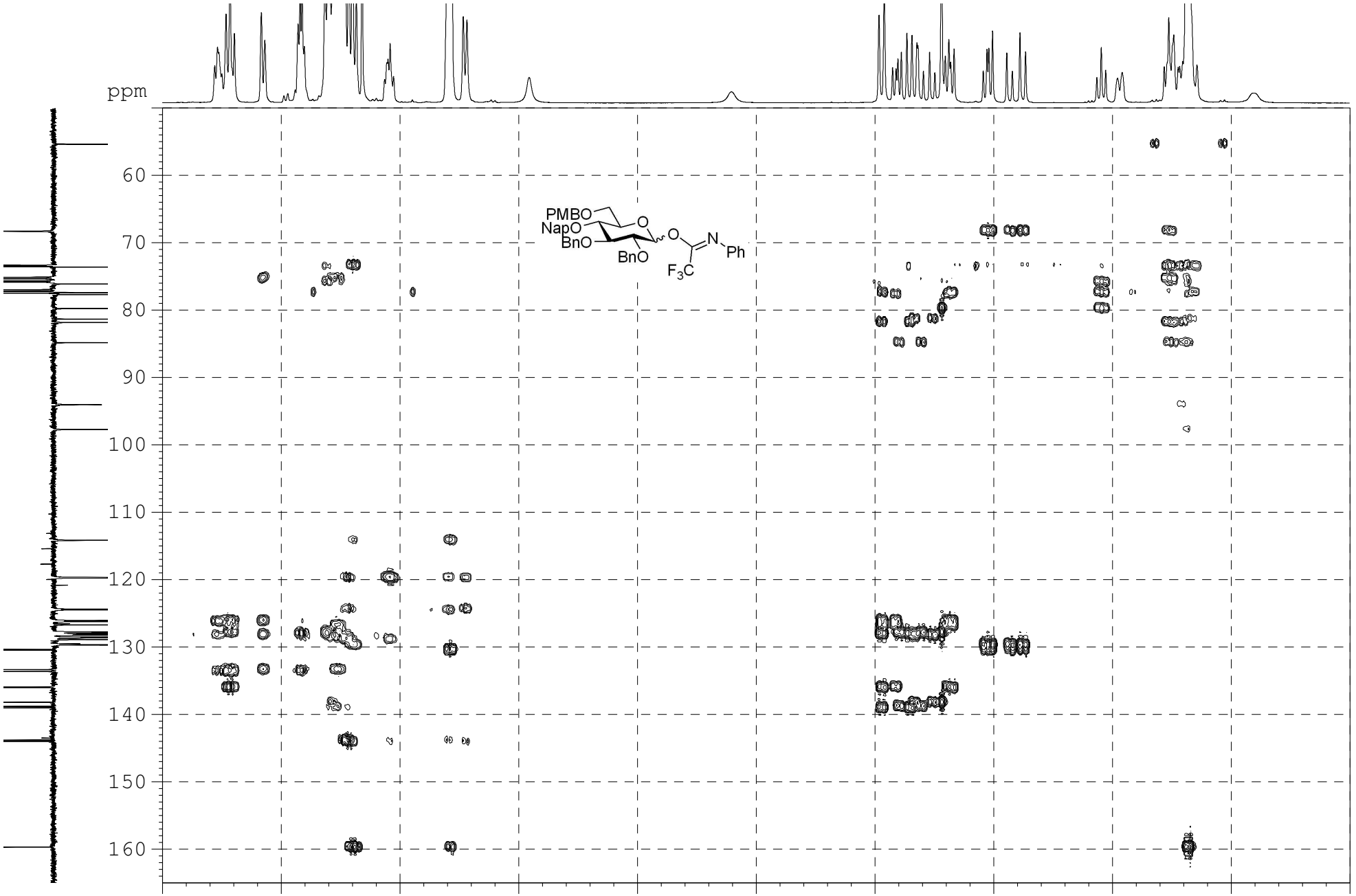
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **5b**



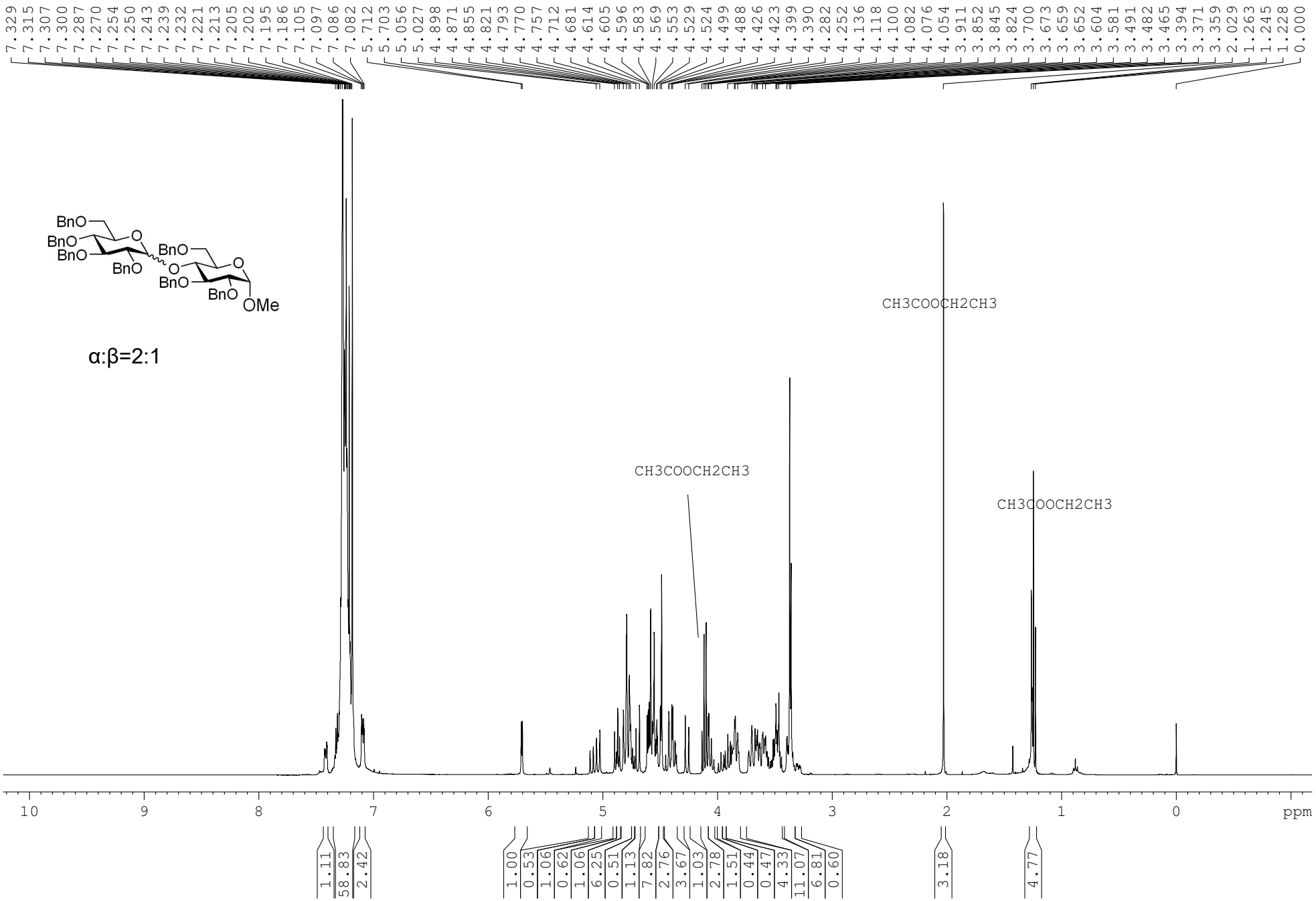

143.95
143.75
143.44
138.97
138.74
138.15
138.13
135.95
135.86
133.58
133.55
133.28
133.27
130.41
130.29
129.62
129.56
129.46
128.81
128.59
128.55
128.48
128.46
128.19
128.08
128.07
127.98
127.95
127.80
127.76
127.71
127.67
126.66
126.45
126.16
126.04
125.99
124.44
124.30
120.75
119.68
119.60
117.64
115.36
114.10
114.08
97.65
93.97
84.78
81.78
81.26
79.71
77.62
77.41
77.34
77.16
76.91
76.06
75.79
75.61
75.30
75.07
75.05
73.54
73.52
73.33
73.27
68.25
68.22
55.31
PMBO
NapO
BnO
BnO
O
O
N
Ph
F3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
PMBO
NapO
BnO
BnO
O
O
N
Ph
F3C
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


ppm
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
PMBO
NapO
BnO
BnO
O
O
N
Ph
F3C


ppm
PMBO
NapO
BnO
BnO
O
O
N
Ph
F3C
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

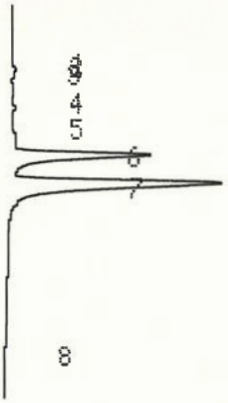
^{1}H-NMR of **9**


7.329
7.315
7.307
7.300
7.287
7.270
7.254
7.250
7.243
7.239
7.232
7.221
7.213
7.205
7.202
7.195
7.186
7.105
7.097
7.086
7.082
5.712
5.703
5.056
5.027
4.898
4.871
4.855
4.821
4.793
4.770
4.757
4.712
4.681
4.614
4.605
4.596
4.583
4.569
4.553
4.529
4.524
4.499
4.488
4.426
4.423
4.399
4.390
4.282
4.252
4.136
4.118
4.100
4.082
4.076
4.054
3.911
3.852
3.845
3.824
3.700
3.673
3.659
3.652
3.604
3.581
3.491
3.482
3.465
3.394
3.371
3.359
2.029
1.263
1.245
1.228
0.000
BnO
BnO
BnO
O
BnO
BnO
O
BnO
BnO
O
OMe
α:β=2:1
CH3COOCH2CH3
CH3COOCH2CH3
CH3COOCH2CH3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.11
58.83
2.42
1.00
0.53
1.06
0.62
1.06
6.25
0.51
1.13
7.82
2.76
3.67
1.03
2.78
1.51
0.44
0.47
4.33
11.07
6.81
0.60
3.18
4.77

ANALYSIS PARAMETER FILE 0

WIDTH	5	SLOPE	7500
DRIFT	0	MIN.AREA	20000
T.DBL	0	STOP.TM	45
ATTEN	8	SPEED	2.5
METHOD$	2241	FORMAT$	0
SPL.WT	100	IS.WT	1

Chiral pak IA
Eluent Hex / IPA
UV 254 nm 95 / 5
1 ml/min



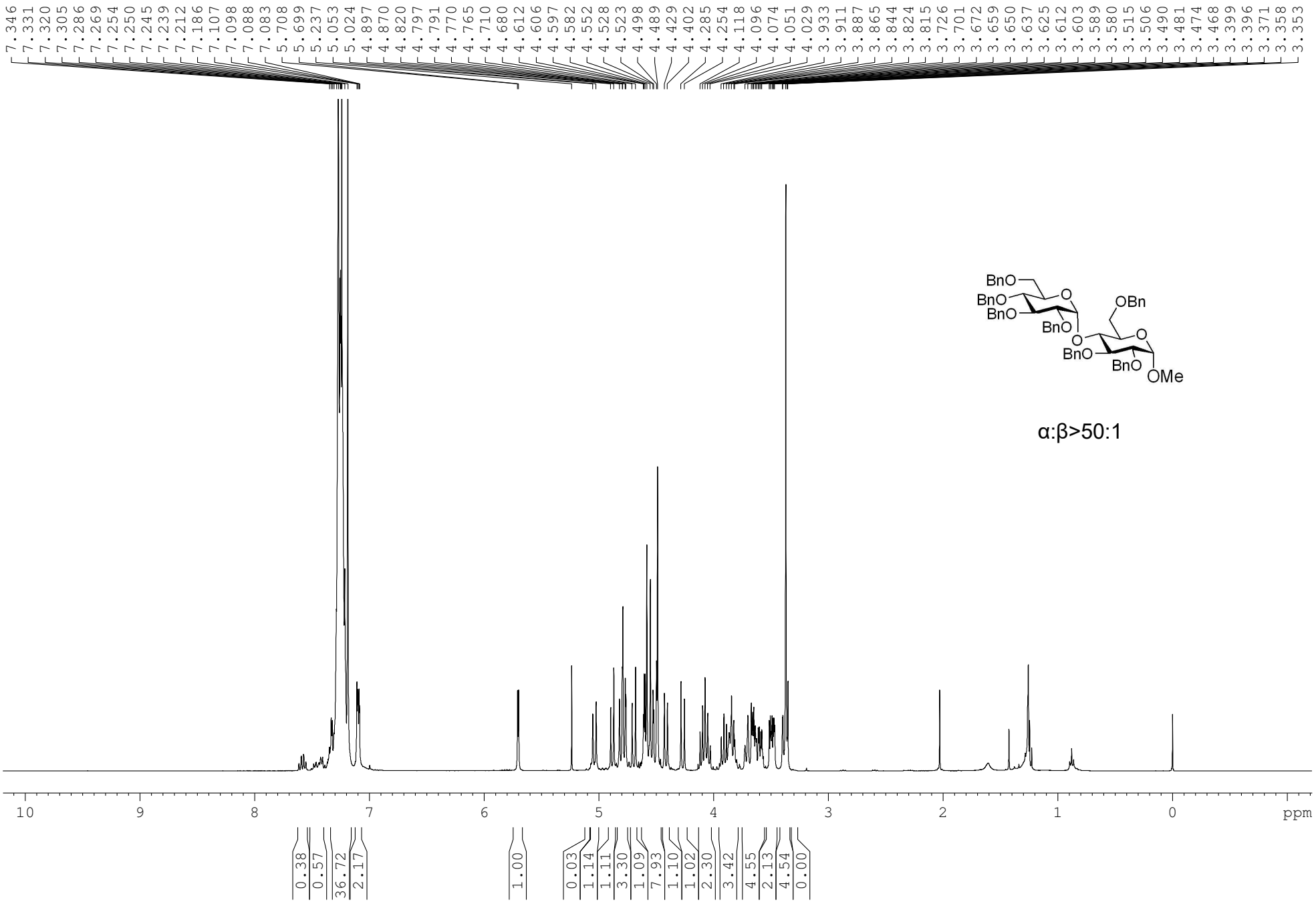
CHROMATOGRAM 1 MEMORIZED

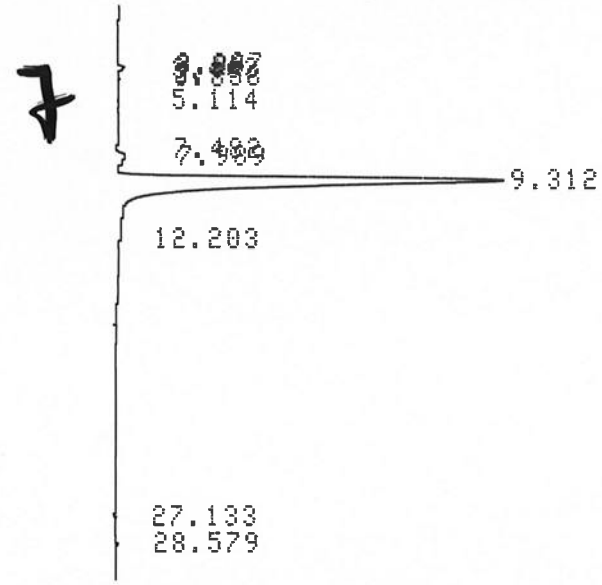
C-R5A CHROMATOPAC

CHANNEL NO	1	FILE	0
SAMPLE NO	0	METHOD	2241
REPORT NO	28		

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.285	10559			0.3959	
		1270hi				
2	3.466	808	V		0.0303	
		343hi				
3	3.688	5029			0.1885	
		423hi				
4	5.367	20494			0.7683	
		1660hi				
5	6.748	4115			0.1543	
		439hi				
6	7.954	895145			33.5582	
		34474hi				
7	9.443	1719131			64.4486	
		52613hi				
8	18.226	12164			0.456	
		452hi				
	TOTAL	2667444			100	

^{1}H-NMR of **9**


7.346
7.331
7.320
7.305
7.286
7.269
7.254
7.250
7.245
7.239
7.212
7.186
7.107
7.098
7.088
7.083
5.708
5.699
5.237
5.053
5.024
4.897
4.870
4.820
4.797
4.791
4.770
4.765
4.710
4.680
4.612
4.606
4.597
4.582
4.552
4.528
4.523
4.498
4.489
4.429
4.402
4.285
4.254
4.118
4.096
4.074
4.051
4.029
3.933
3.911
3.887
3.865
3.844
3.824
3.815
3.726
3.701
3.672
3.659
3.650
3.637
3.625
3.612
3.603
3.589
3.580
3.515
3.506
3.490
3.481
3.474
3.468
3.399
3.396
3.371
3.358
3.353
BnO
BnO
BnO
BnO
O
OBn
O
BnO
O
BnO
BnO
OMe
α:β>50:1
10
9
8
7
6
5
4
3
2
1
0
ppm
0.38
0.57
36.72
2.17
1.00
0.03
1.14
1.11
3.30
1.09
7.93
1.10
1.02
2.30
3.42
4.55
2.13
4.54
0.00



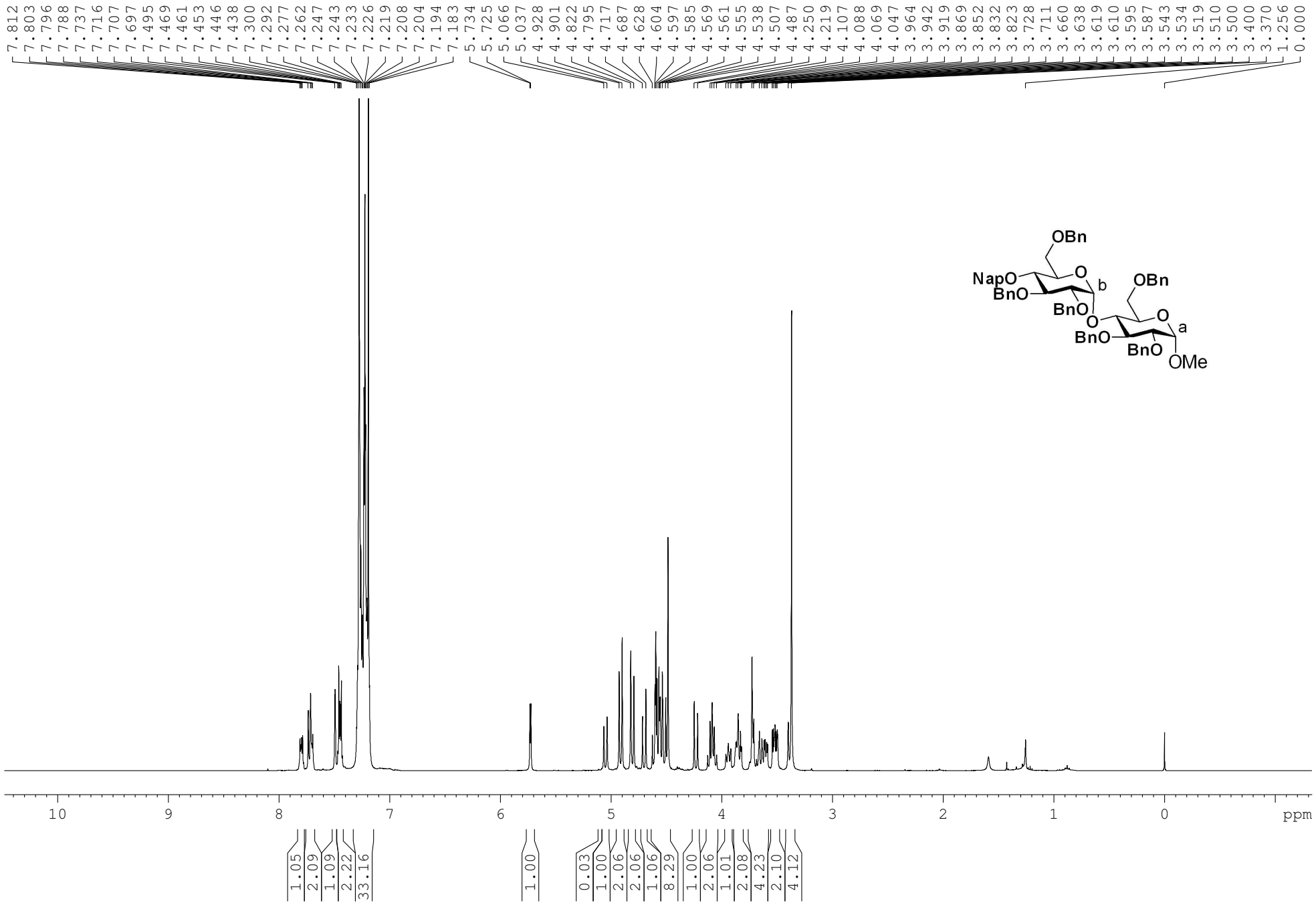
CHROMATOGRAM 1 MEMORIZED

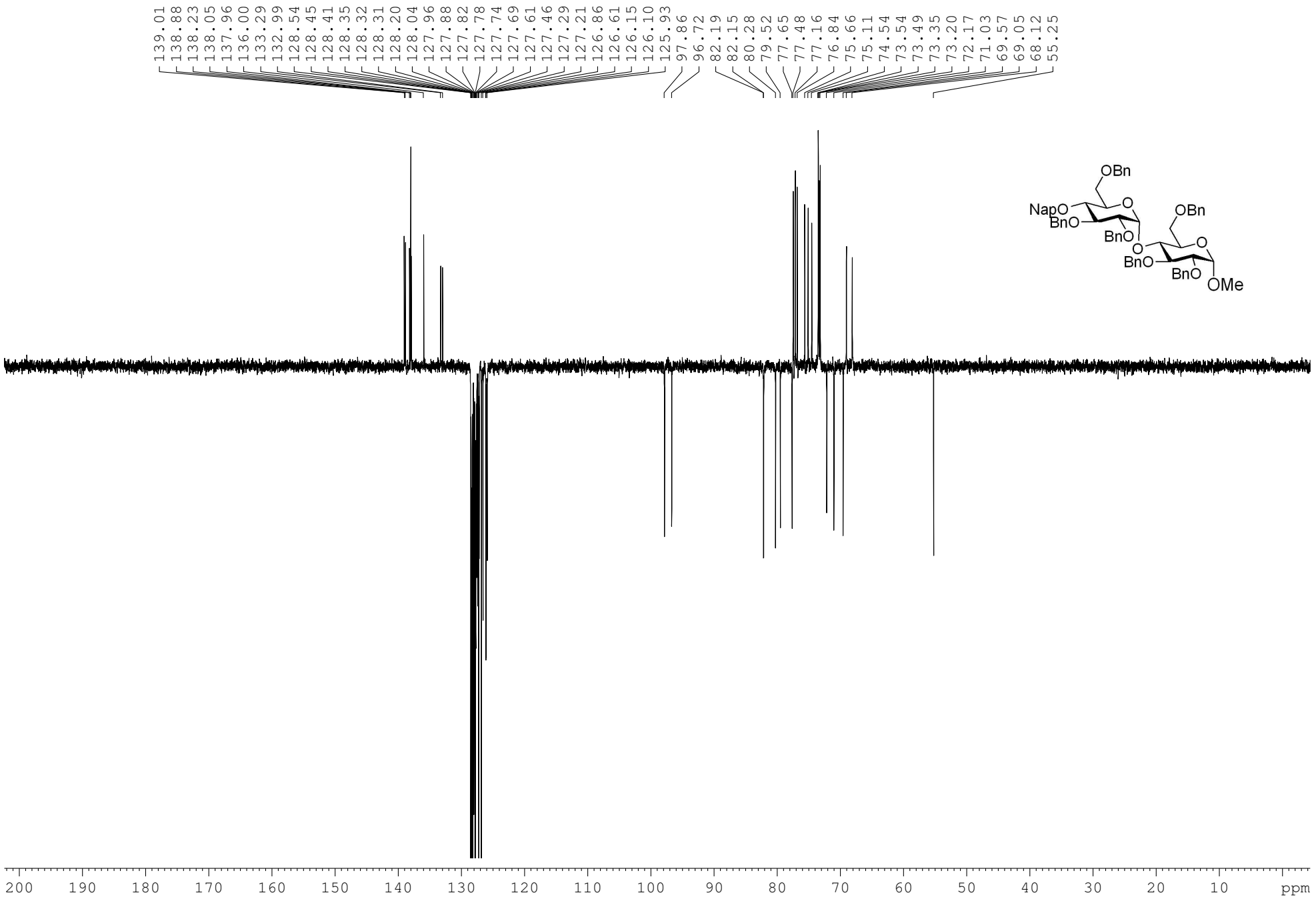
C-R5A CHROMATOPAC

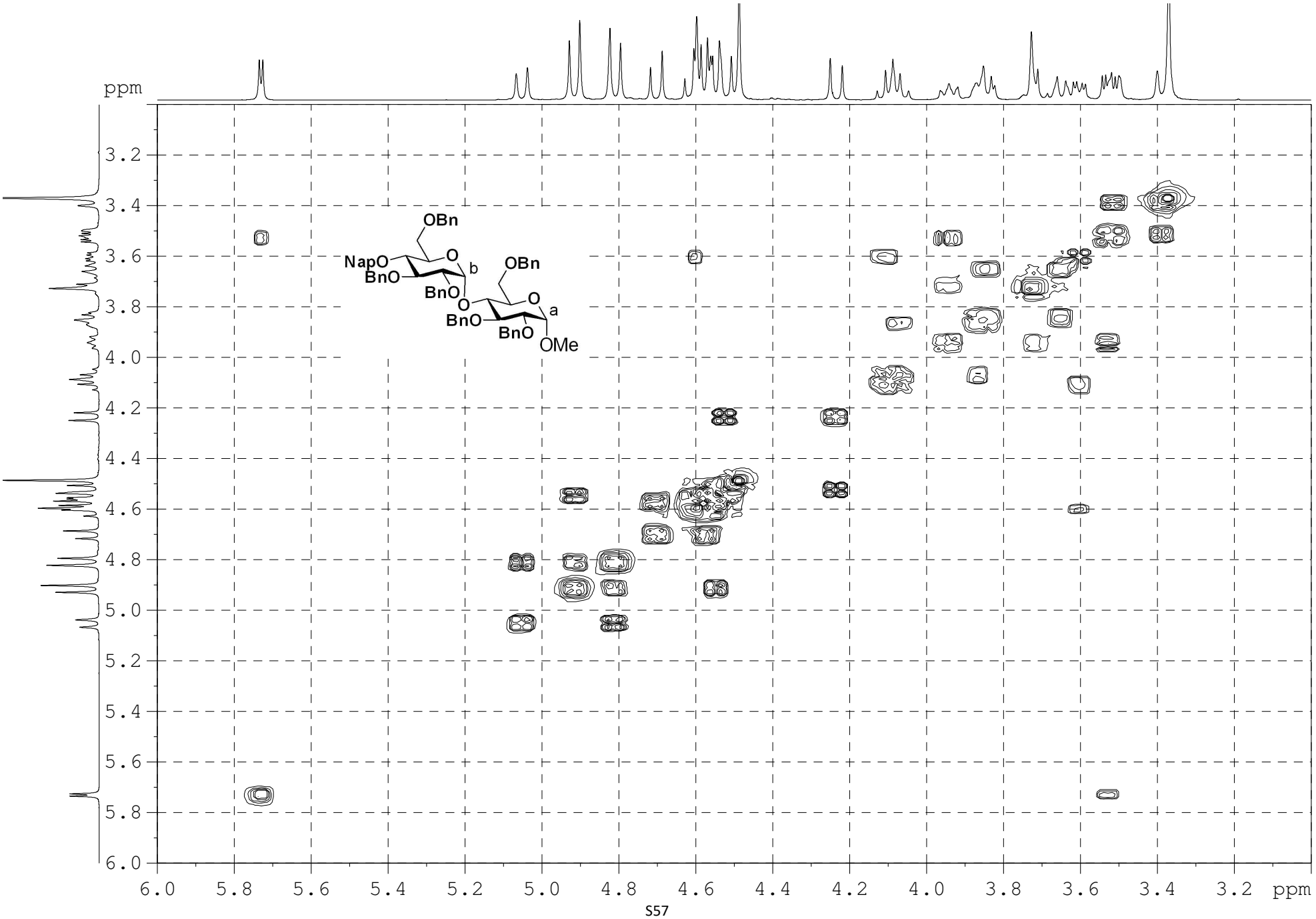
CHANNEL NO	1	FILE	0
SAMPLE NO	0	METHOD	2041
REPORT NO	38		

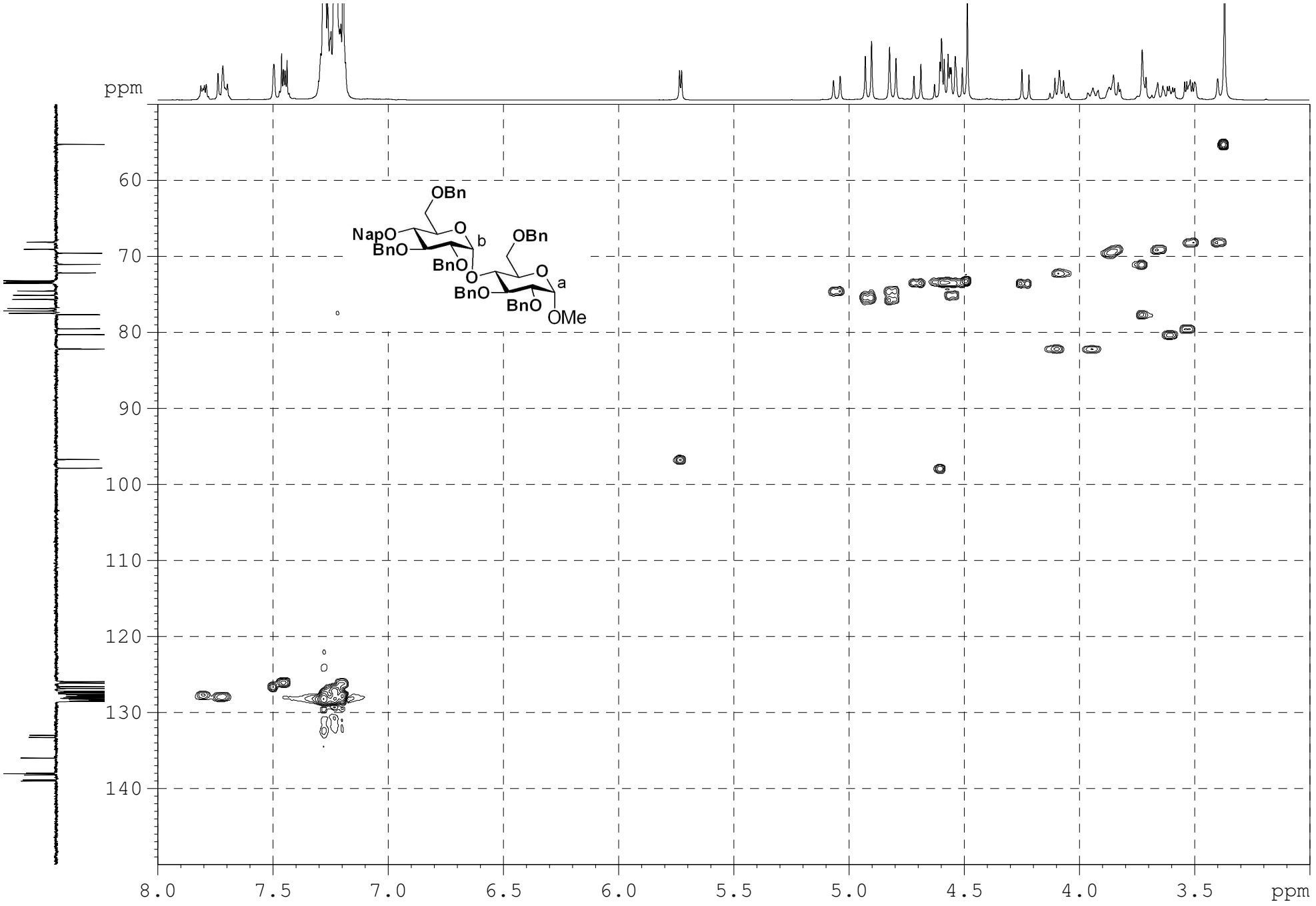
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.26	22080	V		0.6756	
		2212hi				
2	7.989	40699			1.2453	
		2093hi				
3	9.312	3205479			98.0791	
		96667hi				
		---			---	
	TOTAL	3268258			100	

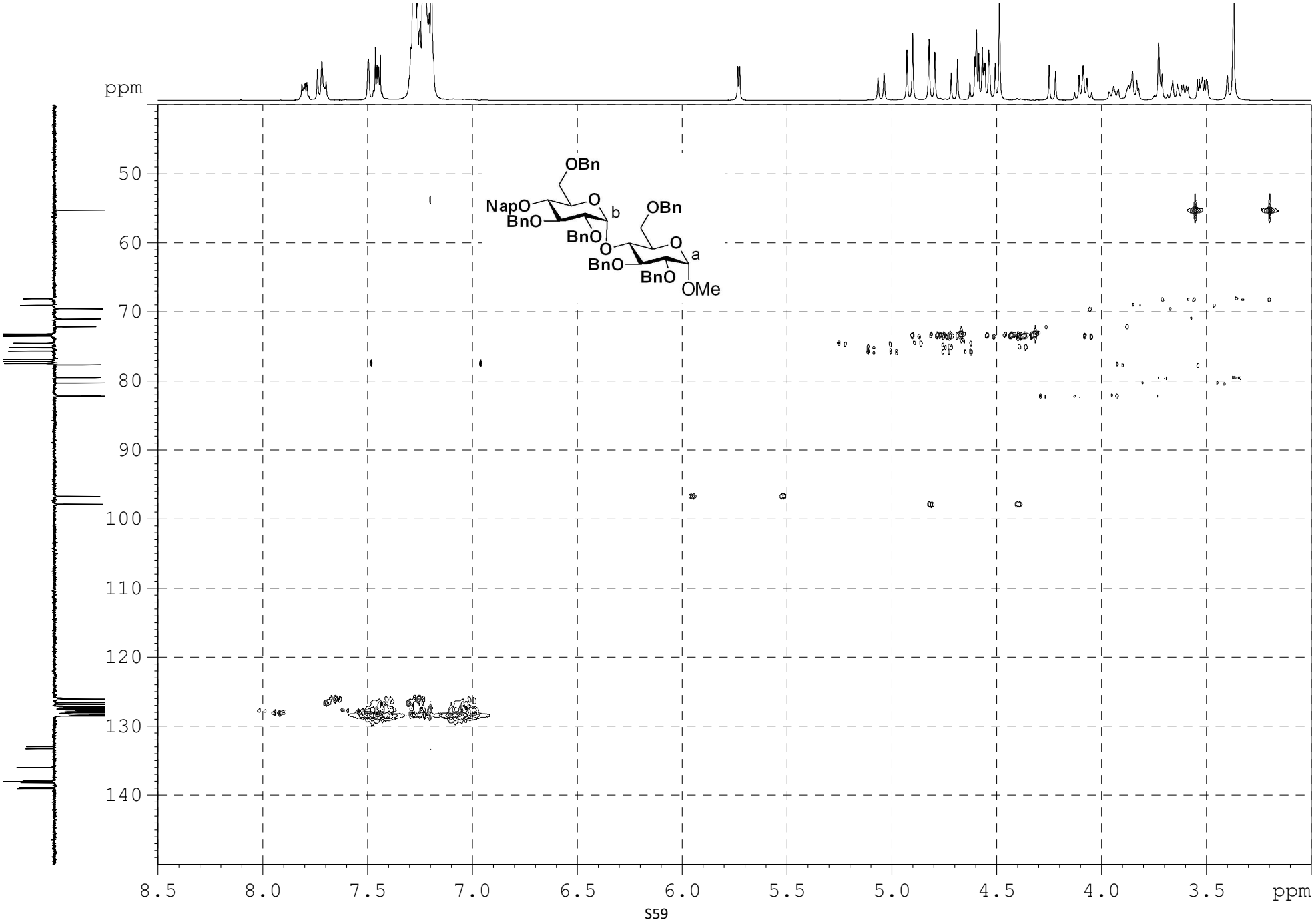
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **10**



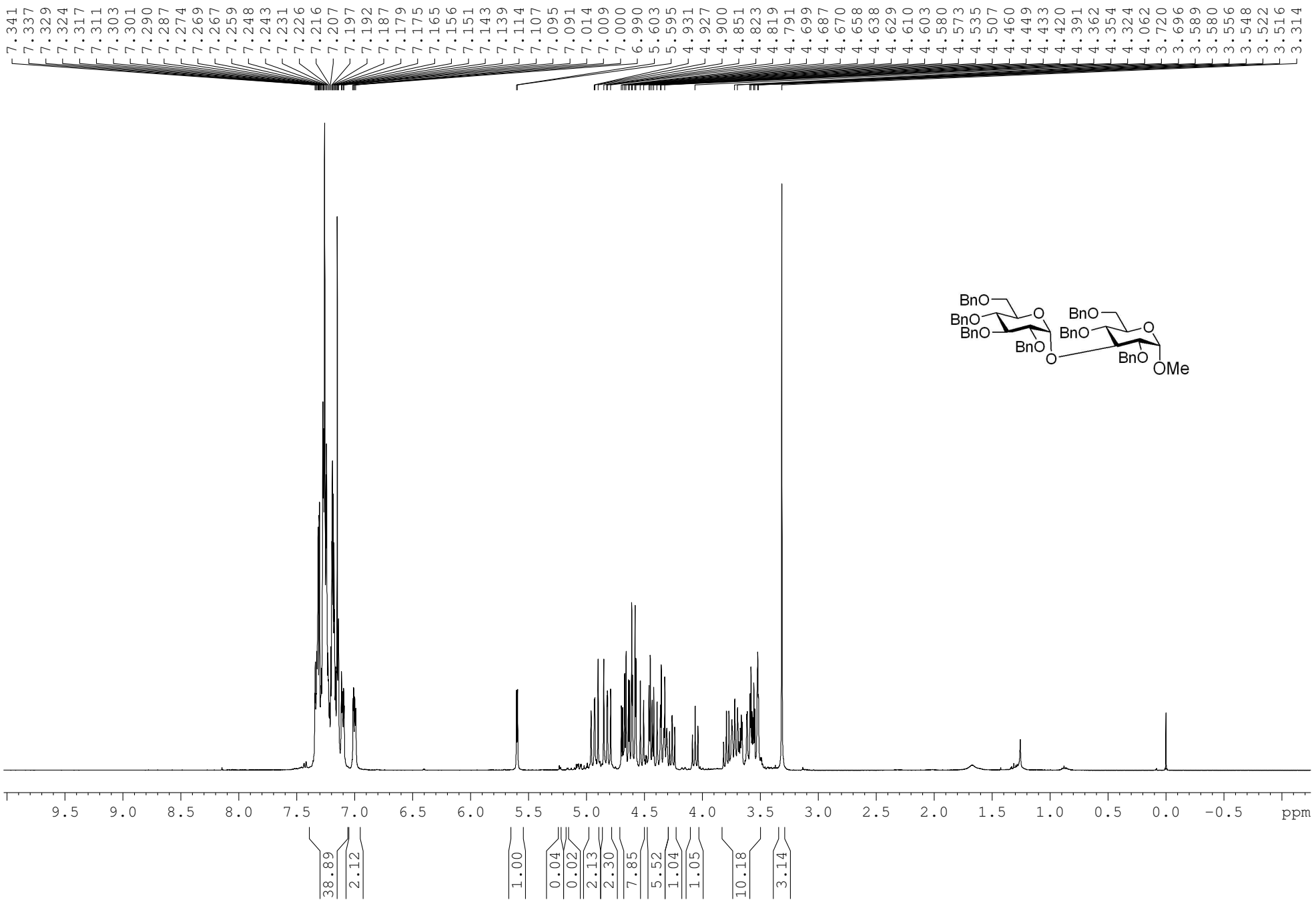

139.01
138.88
138.23
138.05
137.96
136.00
133.29
132.99
128.54
128.45
128.41
128.35
128.32
128.31
128.20
128.04
127.96
127.88
127.82
127.78
127.74
127.69
127.61
127.46
127.29
127.21
126.86
126.61
126.15
126.10
125.93
97.86
96.72
82.19
82.15
80.28
79.52
77.65
77.48
77.16
76.84
75.66
75.11
74.54
73.54
73.49
73.35
73.20
72.17
71.03
69.57
69.05
68.12
55.25
OBn
NapO
BnO
O
BnO
OBn
O
BnO
BnO
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
OBn
NapO
BnO
O
b
BnO
O
OBn
O
a
BnO
BnO
OMe

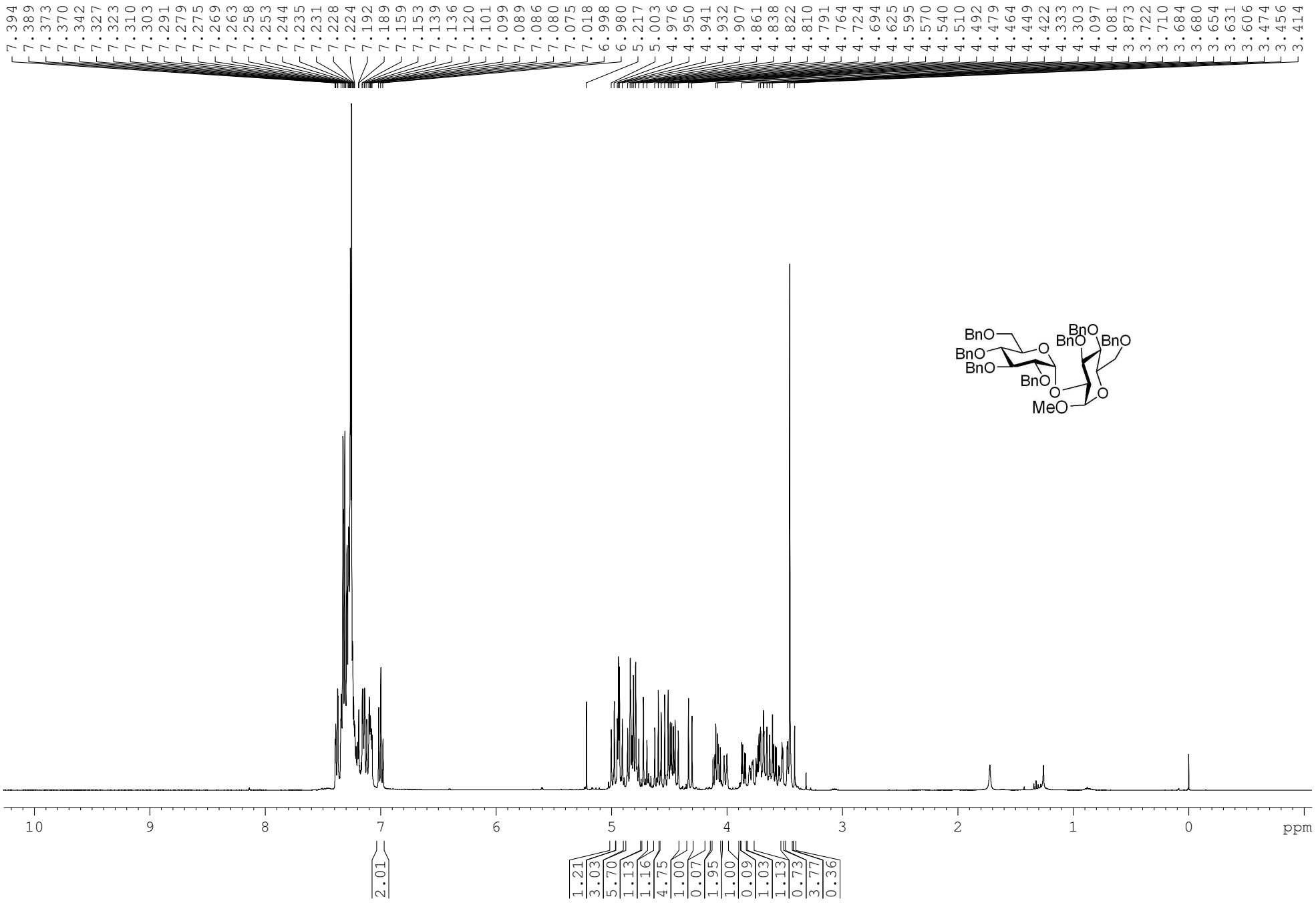

ppm
60
70
80
90
100
110
120
130
140
OBn
NapO
BnO
O
b
OBn
BnO
O
O
a
BnO
BnO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


ppm
OBn
NapO
BnO
O
b
OBn
BnO
O
O
a
BnO
BnO
OMe
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

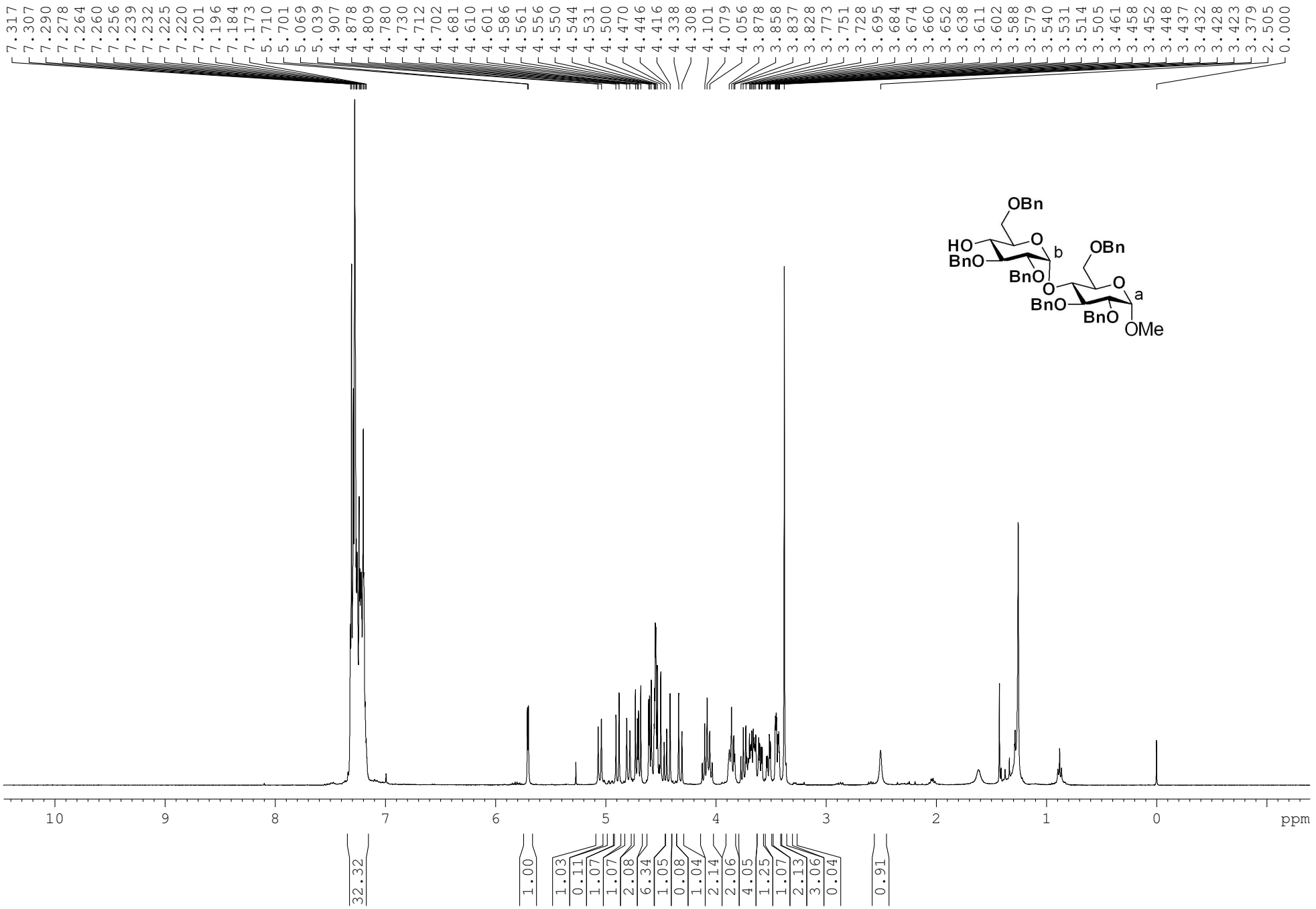
^{1}H-NMR of **11**

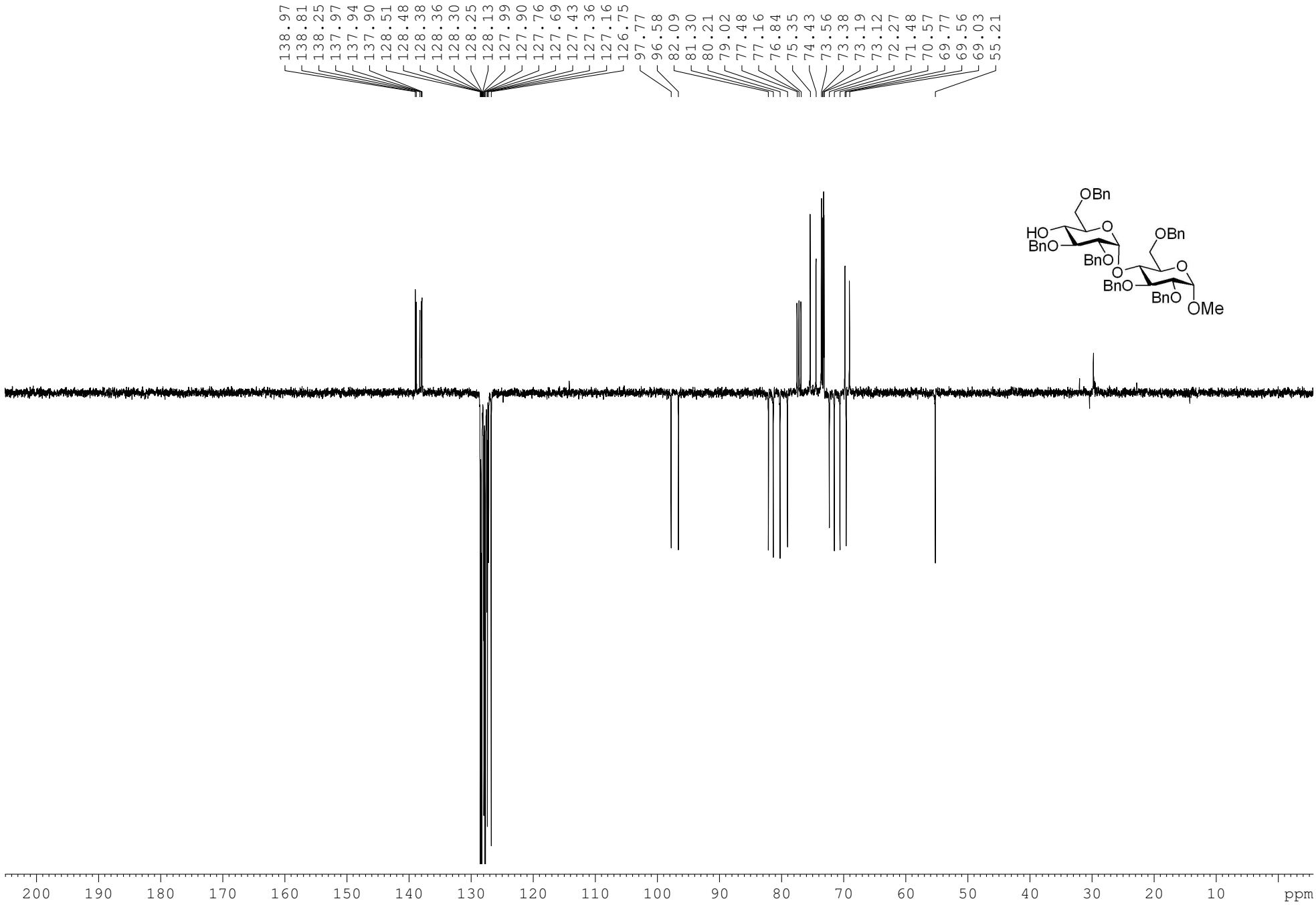

7.341
7.337
7.329
7.324
7.317
7.311
7.303
7.301
7.290
7.287
7.274
7.269
7.267
7.259
7.248
7.243
7.231
7.226
7.216
7.207
7.197
7.192
7.187
7.179
7.175
7.165
7.156
7.151
7.143
7.139
7.114
7.107
7.095
7.091
7.014
7.009
7.000
6.990
5.603
5.595
4.931
4.927
4.900
4.851
4.823
4.819
4.791
4.699
4.687
4.670
4.658
4.638
4.629
4.610
4.603
4.580
4.573
4.535
4.507
4.460
4.449
4.433
4.420
4.391
4.362
4.354
4.324
4.062
3.720
3.696
3.589
3.580
3.556
3.548
3.522
3.516
3.314
BnO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
BnO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
38.89
2.12
1.00
0.04
0.02
2.13
2.30
7.85
5.52
1.04
1.05
10.18
3.14

^{1}H-NMR of **12**

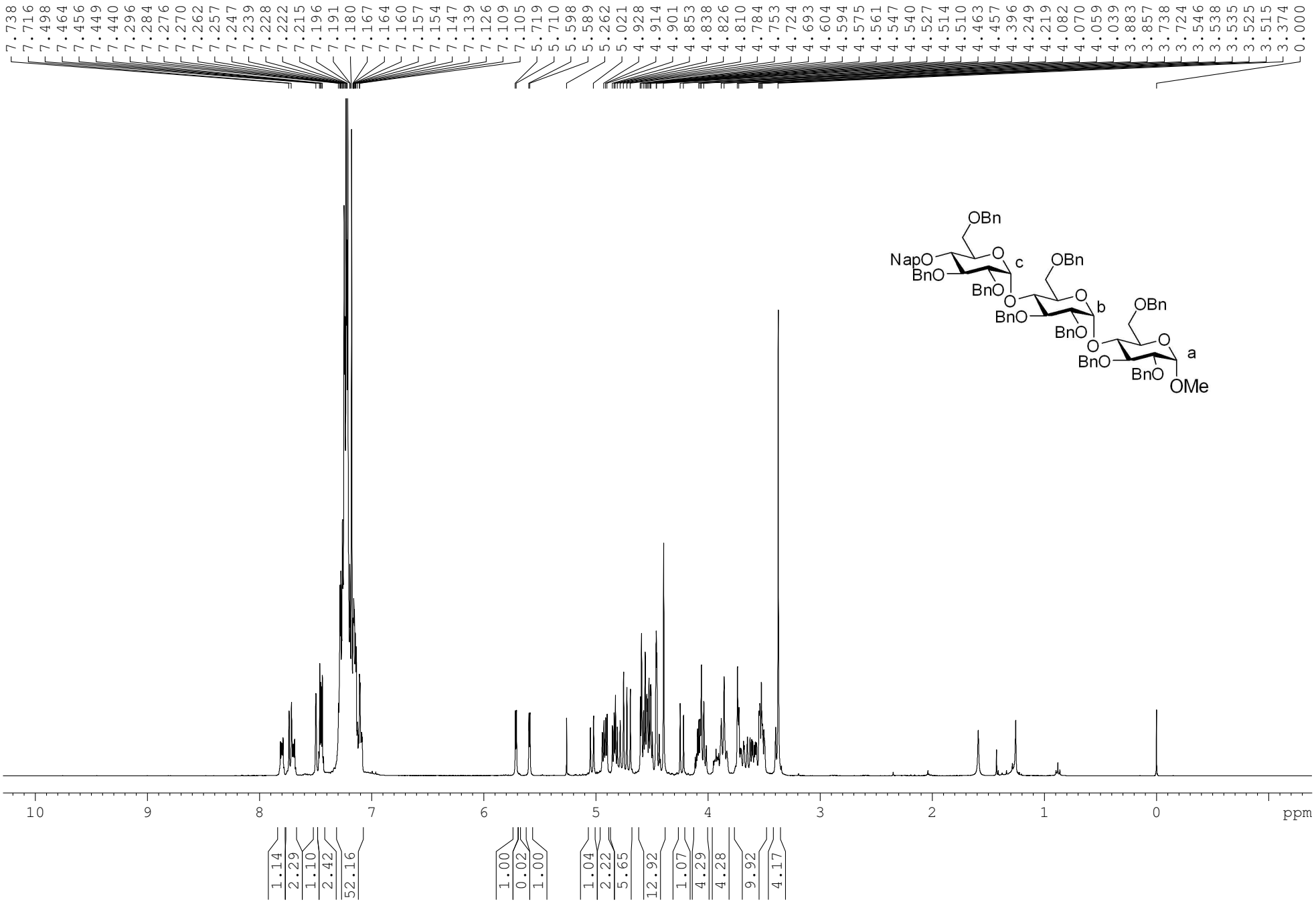

7.394
7.389
7.373
7.370
7.342
7.327
7.323
7.310
7.303
7.291
7.279
7.275
7.269
7.263
7.258
7.253
7.244
7.235
7.231
7.228
7.224
7.192
7.189
7.159
7.153
7.139
7.136
7.120
7.101
7.099
7.089
7.086
7.080
7.075
7.018
6.998
6.980
5.217
5.003
4.976
4.950
4.941
4.932
4.907
4.861
4.838
4.822
4.810
4.791
4.764
4.724
4.694
4.625
4.595
4.570
4.540
4.510
4.492
4.479
4.464
4.449
4.422
4.333
4.303
4.097
4.081
3.873
3.722
3.710
3.684
3.680
3.654
3.631
3.606
3.474
3.456
3.414
BnO
BnO
BnO
BnO
O
BnO
BnO
BnO
O
O
MeO
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.21
3.03
5.70
1.13
1.16
4.75
1.00
0.07
1.95
1.00
0.09
1.03
1.13
0.73
3.77
0.36

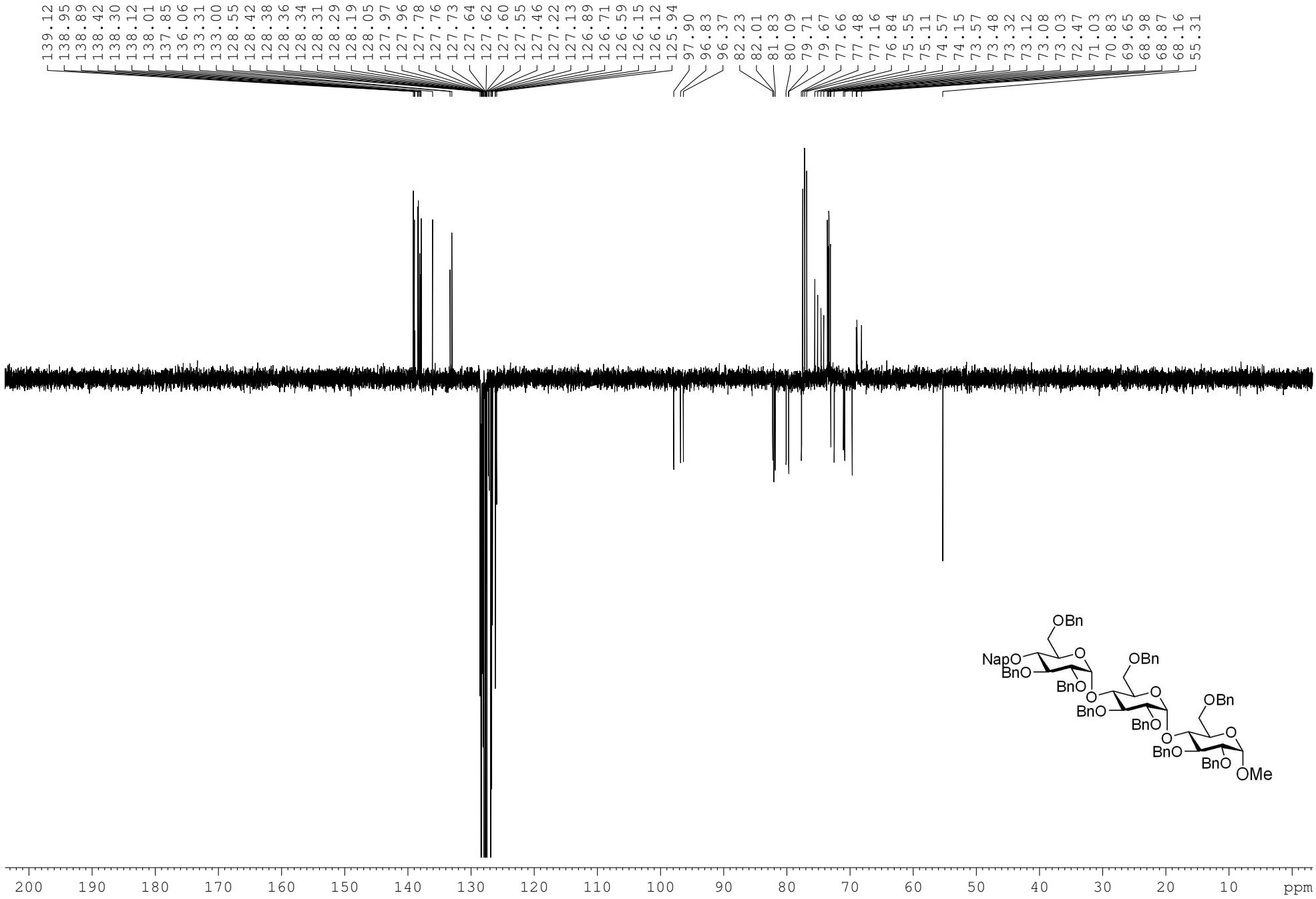
^{1}H-NMR, ^{13}C-APT of **13**

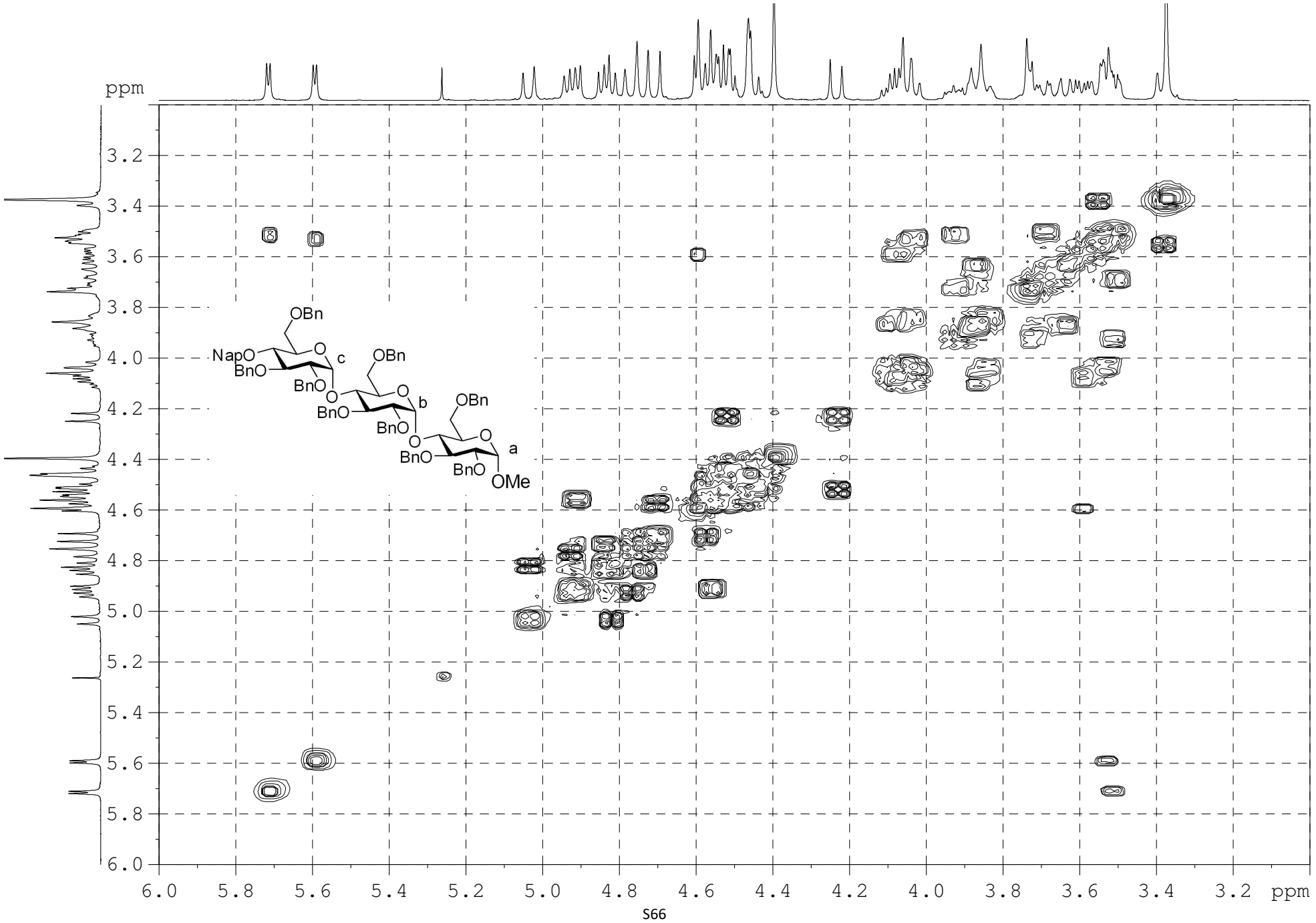


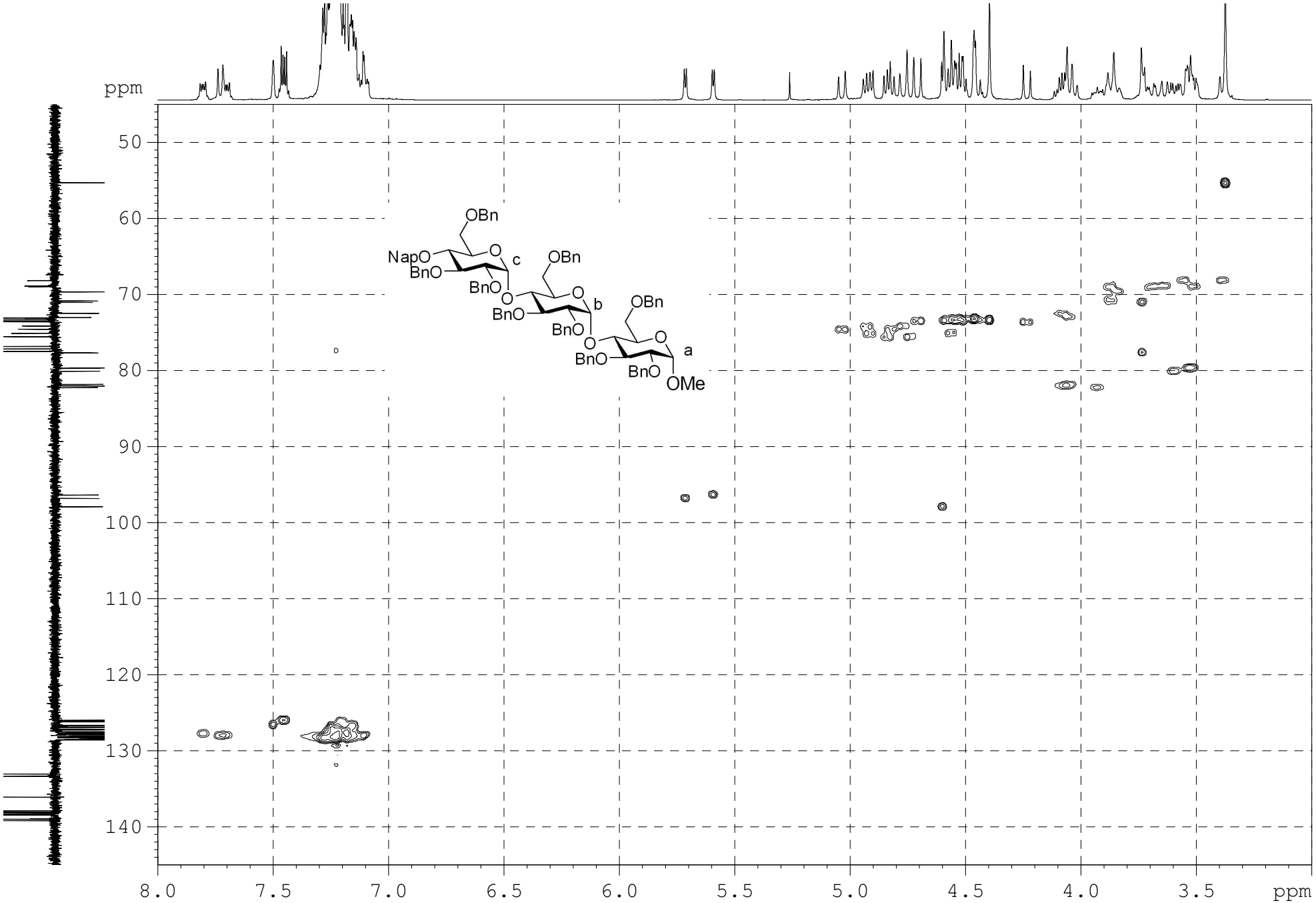

138.97
138.81
138.25
137.97
137.94
137.90
128.51
128.48
128.38
128.36
128.30
128.25
128.13
127.99
127.90
127.76
127.69
127.43
127.36
127.16
126.75
97.77
96.58
82.09
81.30
80.21
79.02
77.48
77.16
76.84
75.35
74.43
73.56
73.38
73.19
73.12
72.27
71.48
70.57
69.77
69.56
69.03
55.21
OBn
HO
BnO
O
OBn
BnO
O
O
BnO
BnO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

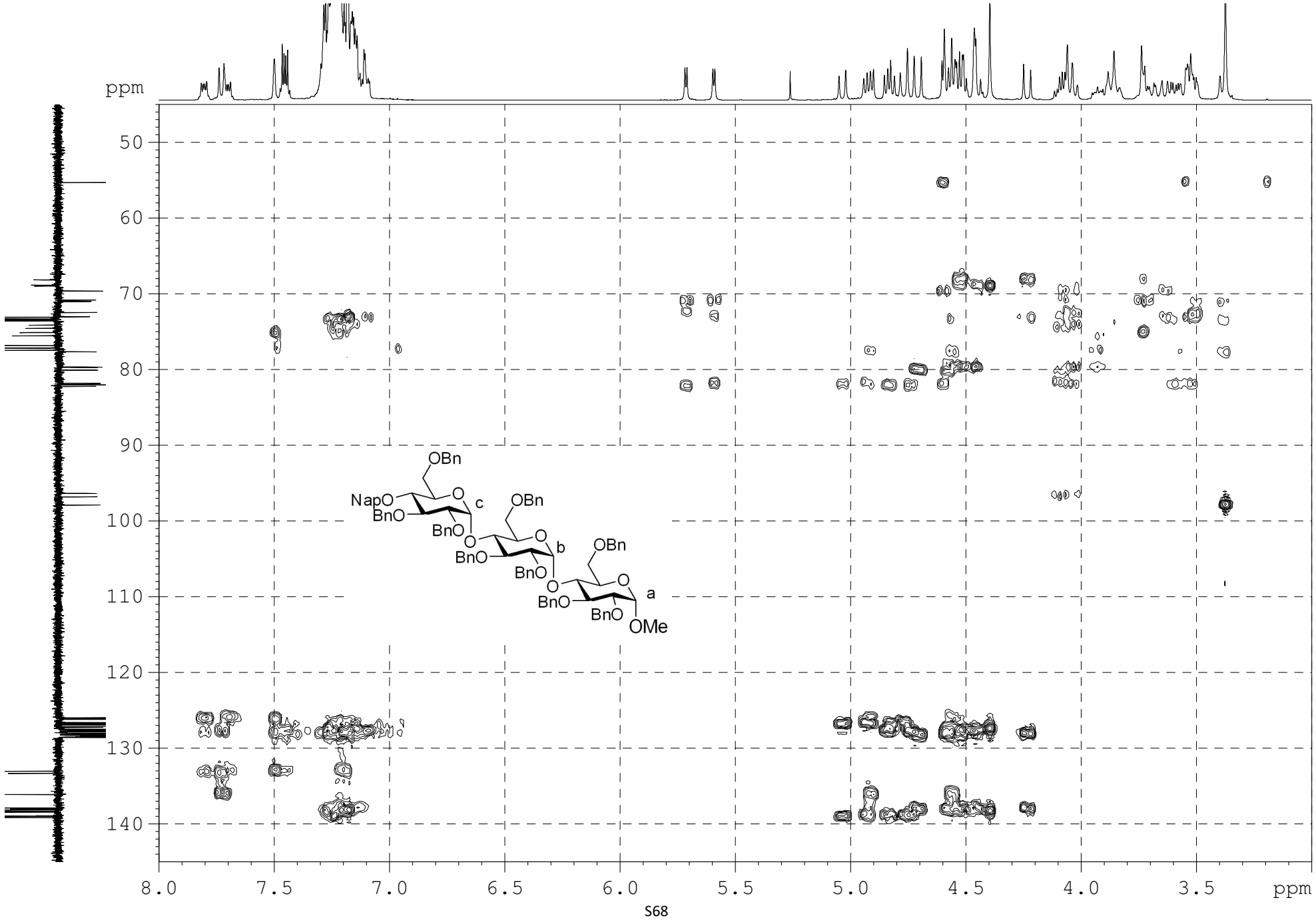
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **14**

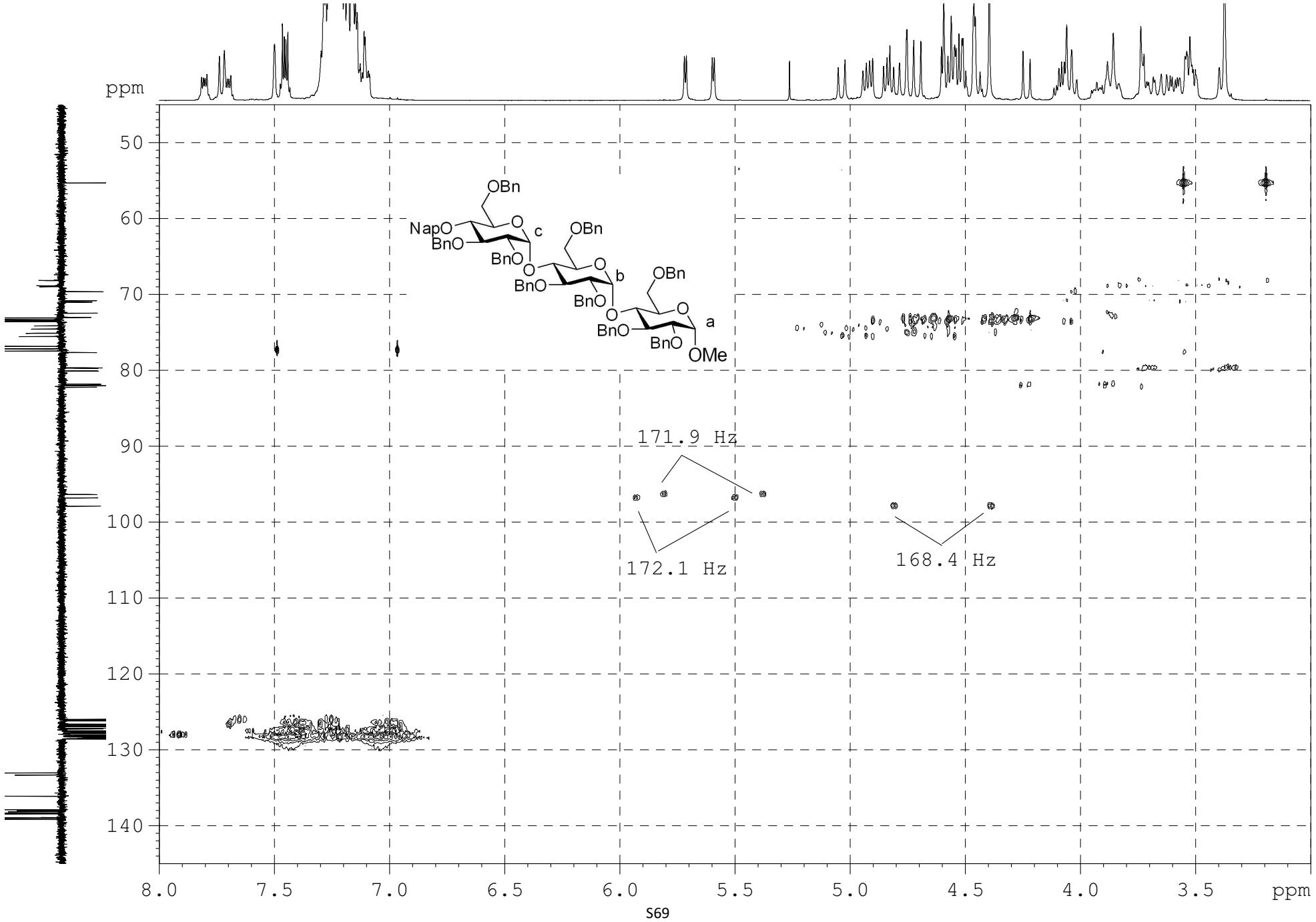



139.12
138.95
138.89
138.42
138.30
138.12
138.01
137.85
136.06
133.31
133.00
128.55
128.42
128.38
128.36
128.34
128.31
128.29
128.19
128.05
127.97
127.96
127.78
127.76
127.73
127.64
127.62
127.60
127.55
127.46
127.22
127.13
126.89
126.71
126.59
126.15
126.12
125.94
97.90
96.83
96.37
82.23
82.01
81.83
80.09
79.71
79.67
77.66
77.48
77.16
76.84
75.55
75.11
74.57
74.15
73.57
73.48
73.32
73.12
73.08
73.03
72.47
71.03
70.83
69.65
68.98
68.87
68.16
55.31
OBn
NapO
BnO
BnO
O
OBn
O
BnO
BnO
O
OBn
O
BnO
BnO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

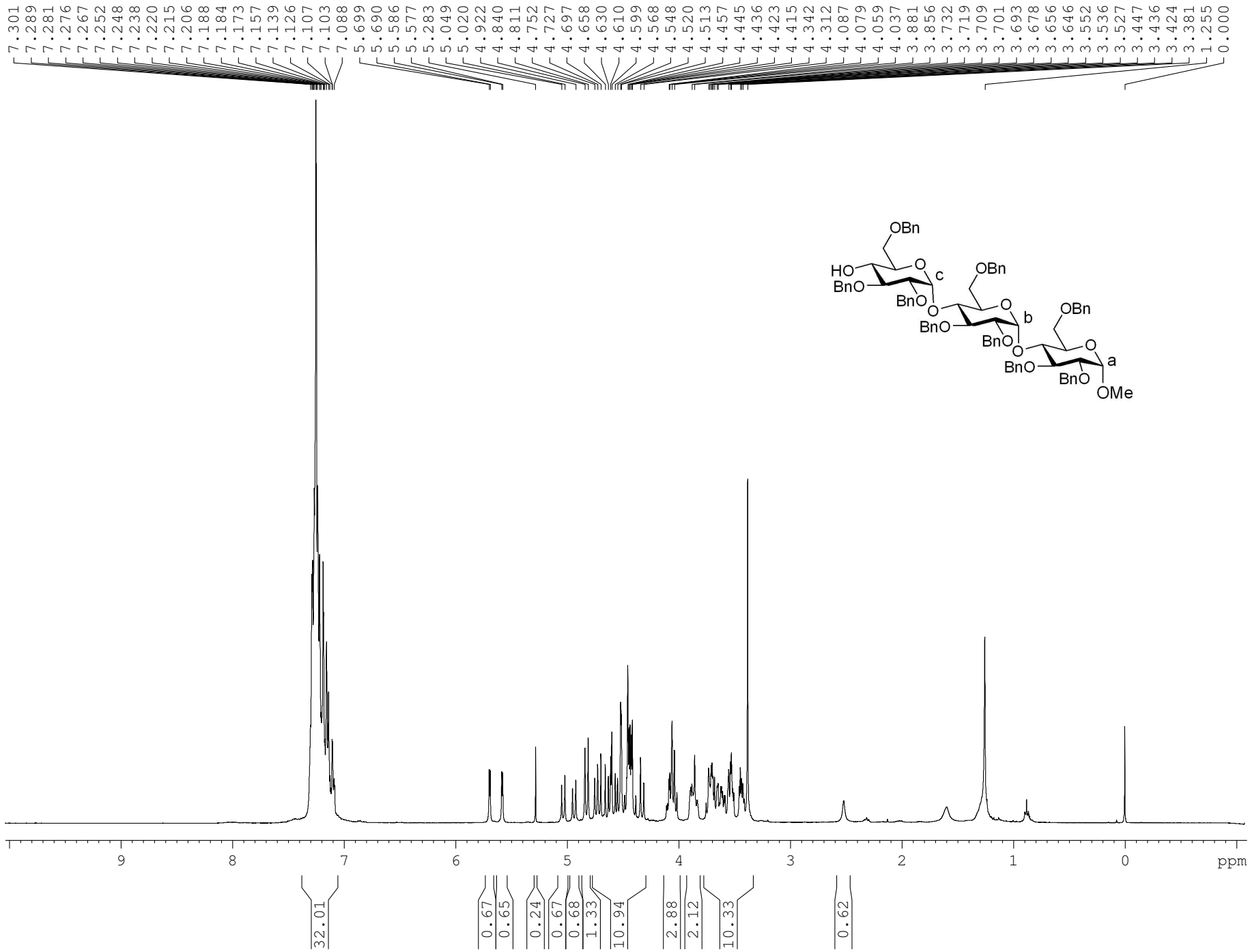

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
OBn
NapO
BnO
O
c
OBn
BnO
O
b
OBn
BnO
BnO
O
a
BnO
BnO
OMe

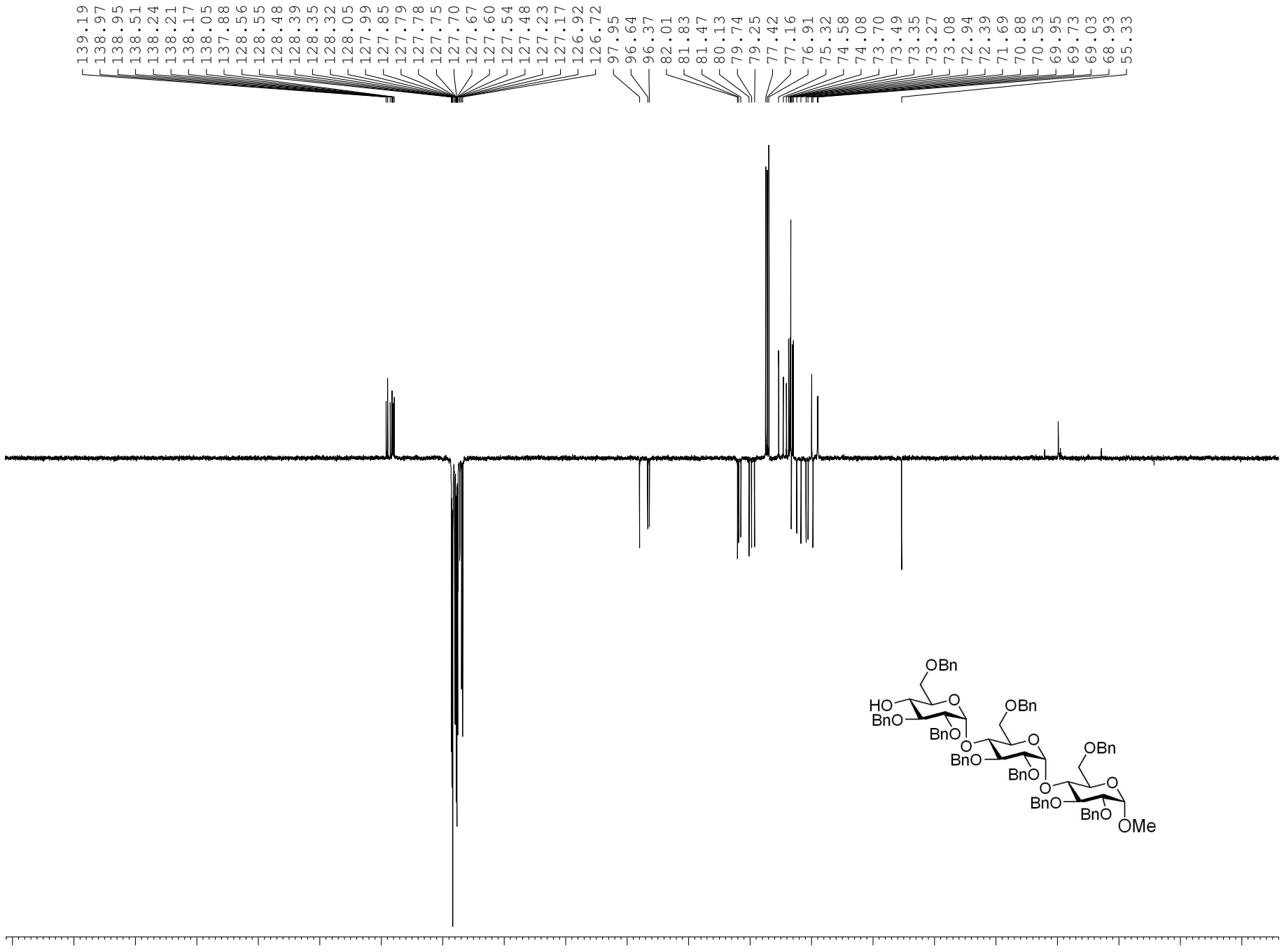

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
O
c
OBn
BnO
O
O
b
OBn
BnO
BnO
O
O
a
BnO
BnO
OMe


ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
O
c
OBn
BnO
O
O
b
BnO
OBn
BnO
O
O
a
BnO
BnO
OMe

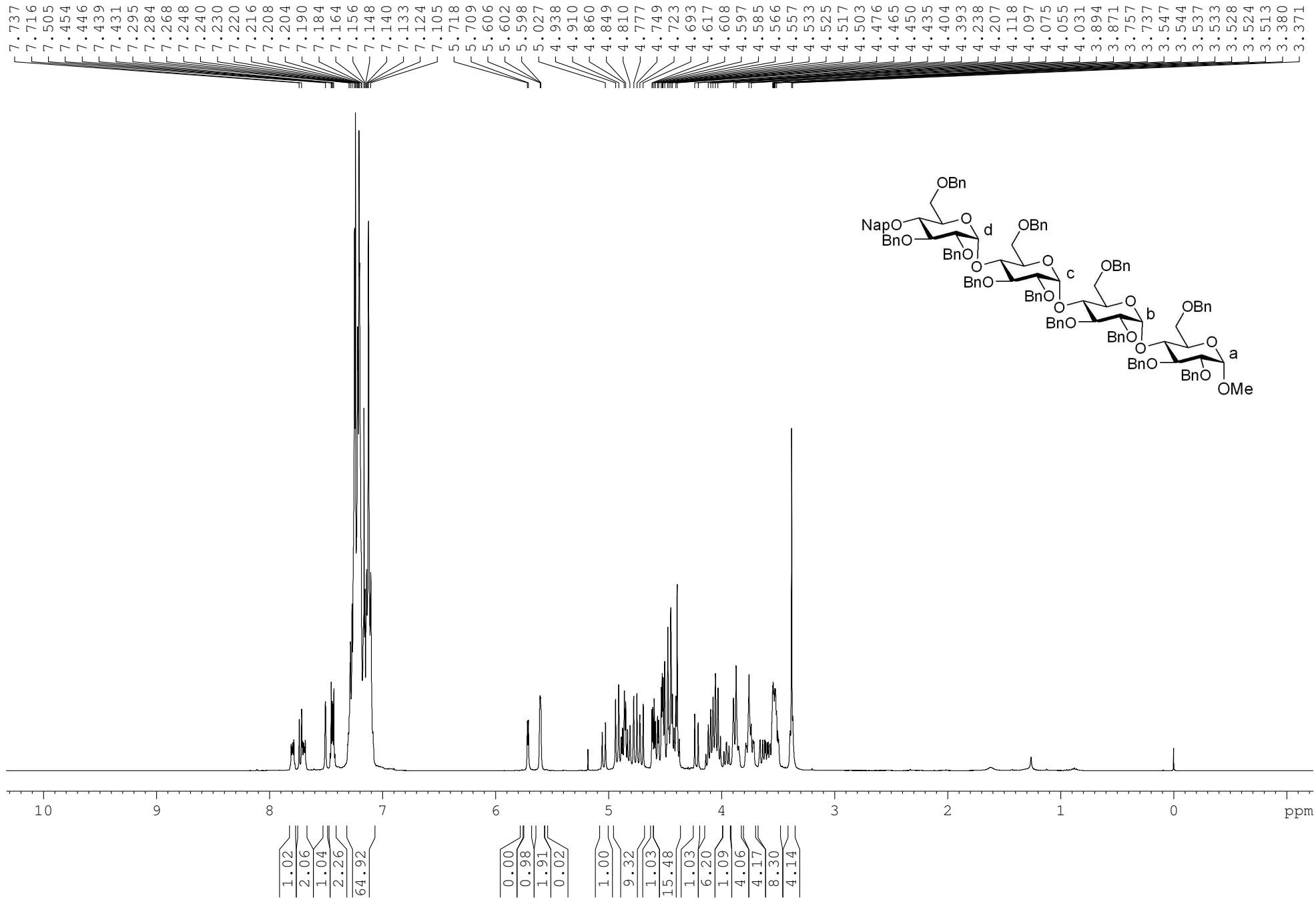

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
BnO
O
c
OBn
O
b
BnO
BnO
OBn
O
a
BnO
BnO
OMe
171.9 Hz
172.1 Hz
168.4 Hz

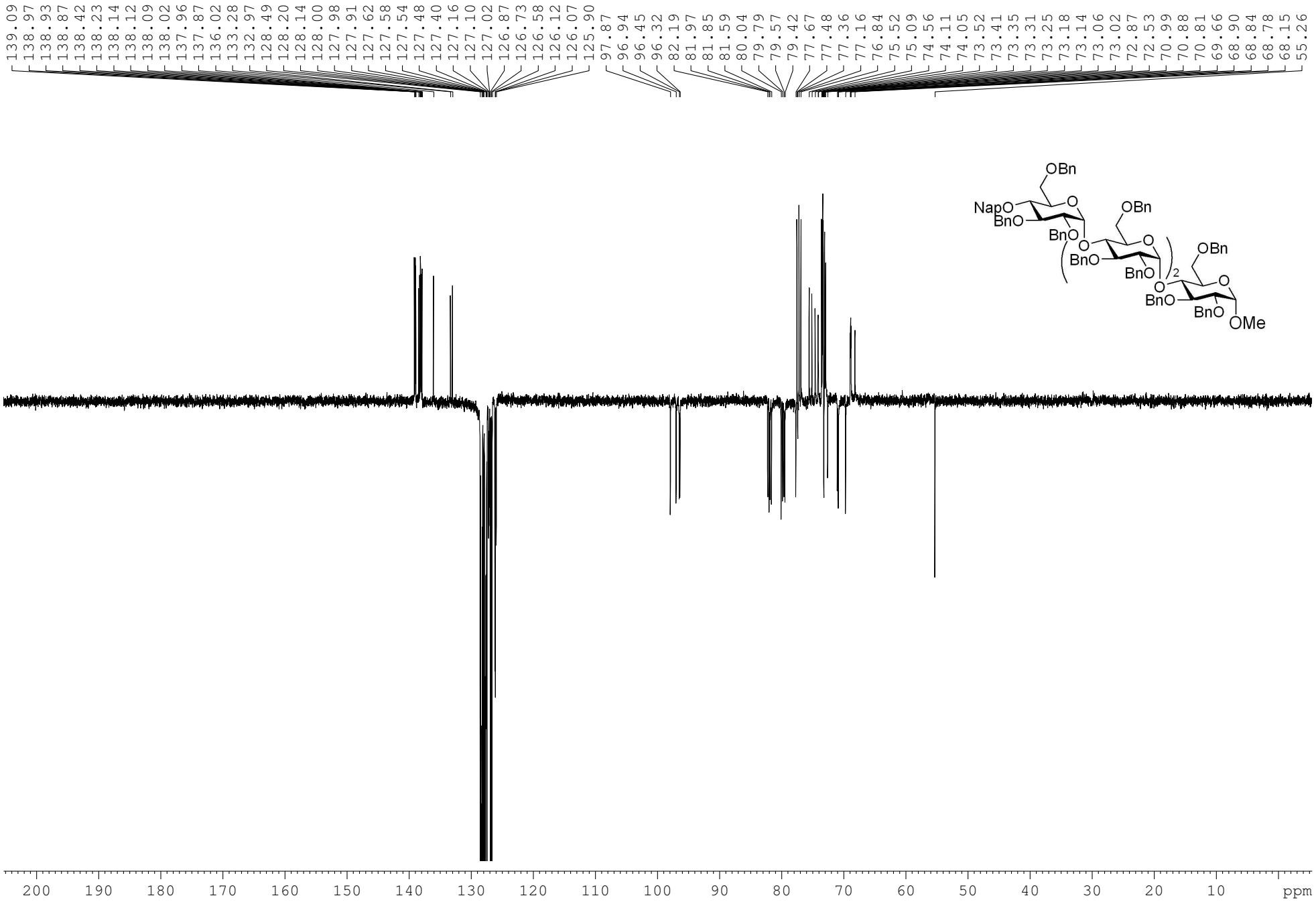
^{1}H-NMR, ^{13}C-APT of **15**

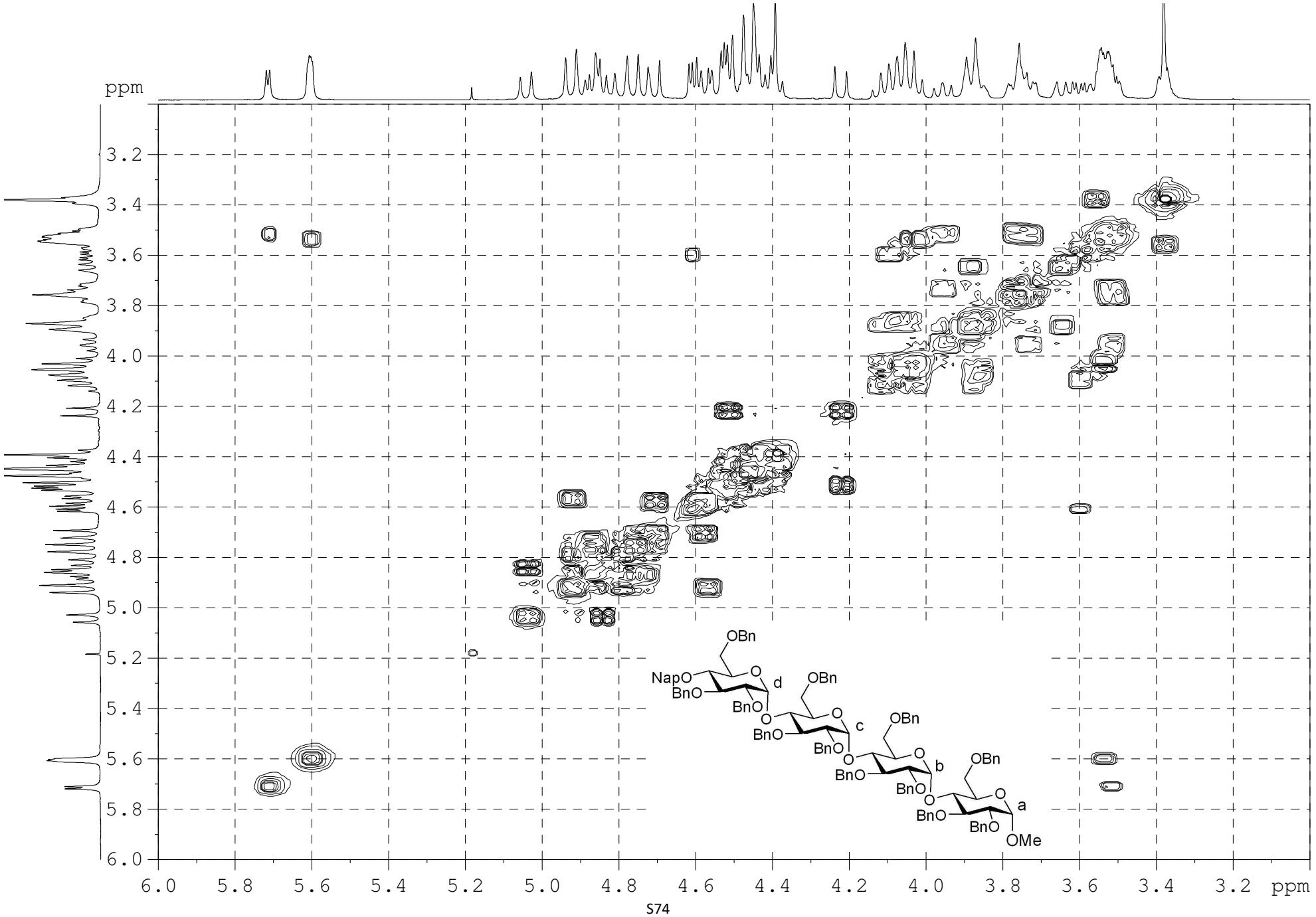


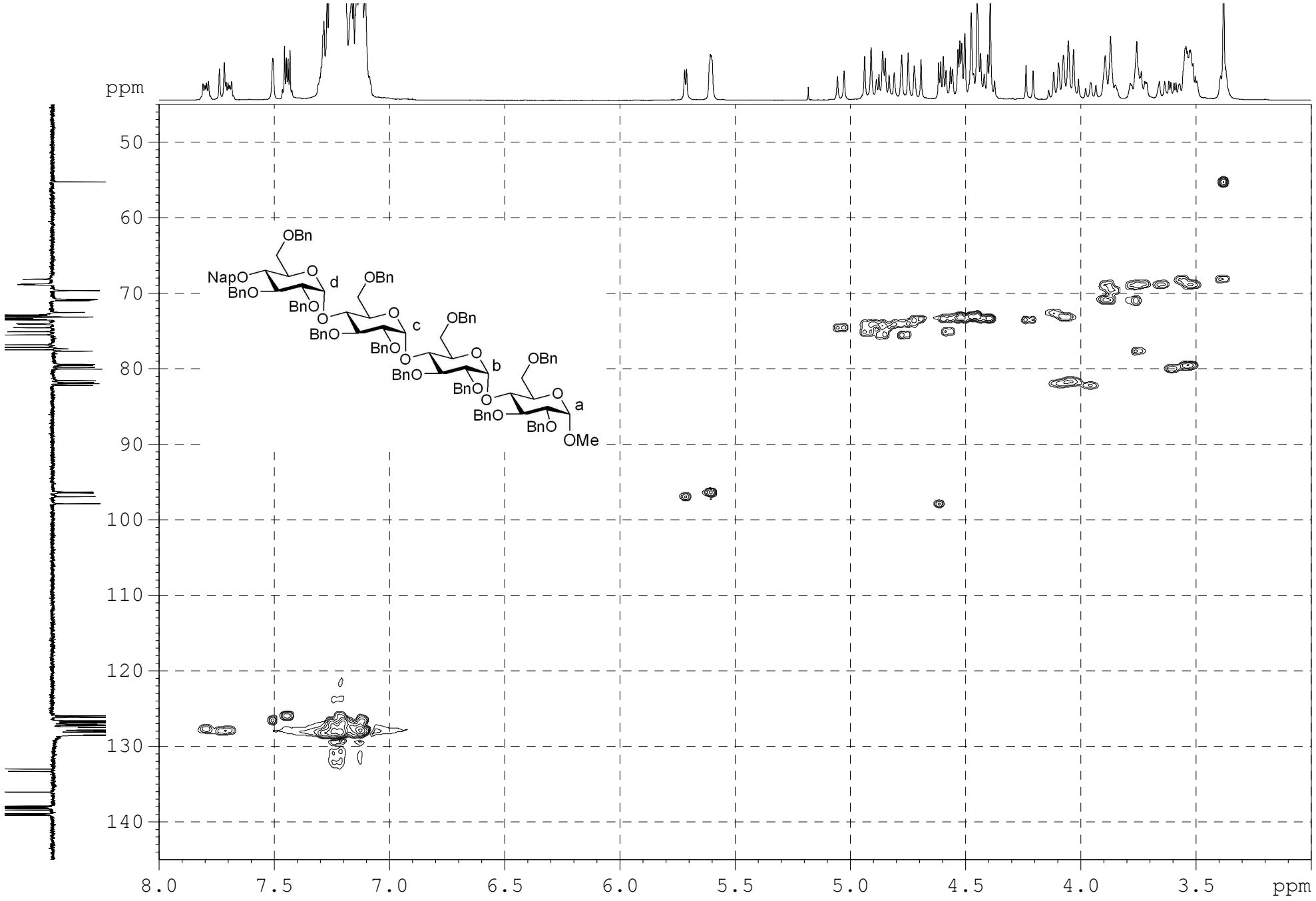

139.19
138.97
138.95
138.51
138.24
138.21
138.17
138.05
137.88
128.56
128.55
128.48
128.39
128.35
128.32
128.05
127.99
127.85
127.79
127.78
127.75
127.70
127.67
127.60
127.54
127.48
127.23
127.17
126.92
126.72
97.95
96.64
96.37
82.01
81.83
81.47
80.13
79.74
79.25
77.42
77.16
76.91
75.32
74.58
74.08
73.70
73.49
73.35
73.27
73.08
72.94
72.39
71.69
70.88
70.53
69.95
69.73
69.03
68.93
55.33
OBn
HO
BnO
O
OBn
BnO
O
OBn
BnO
O
OBn
BnO
O
BnO
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

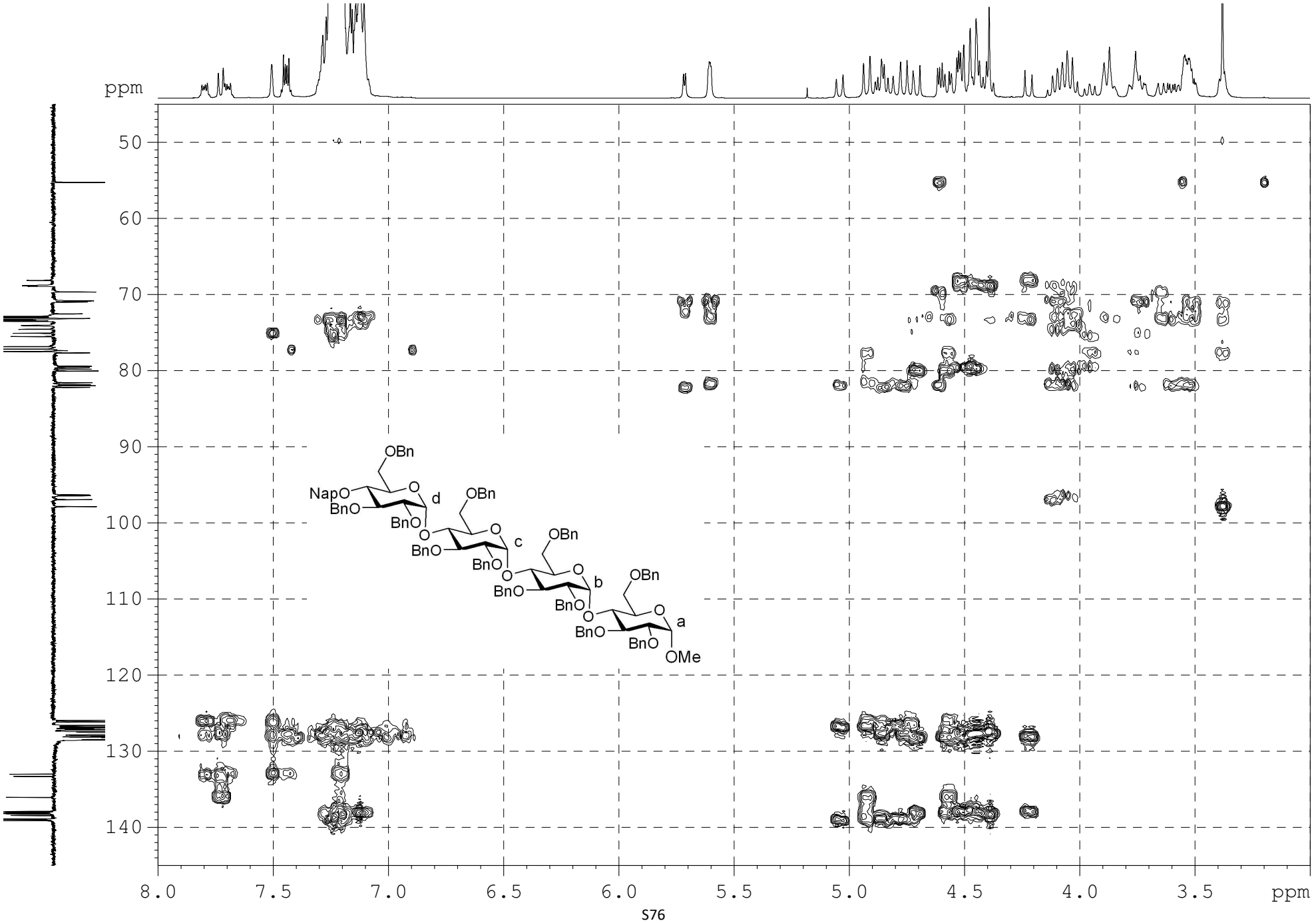
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **16**

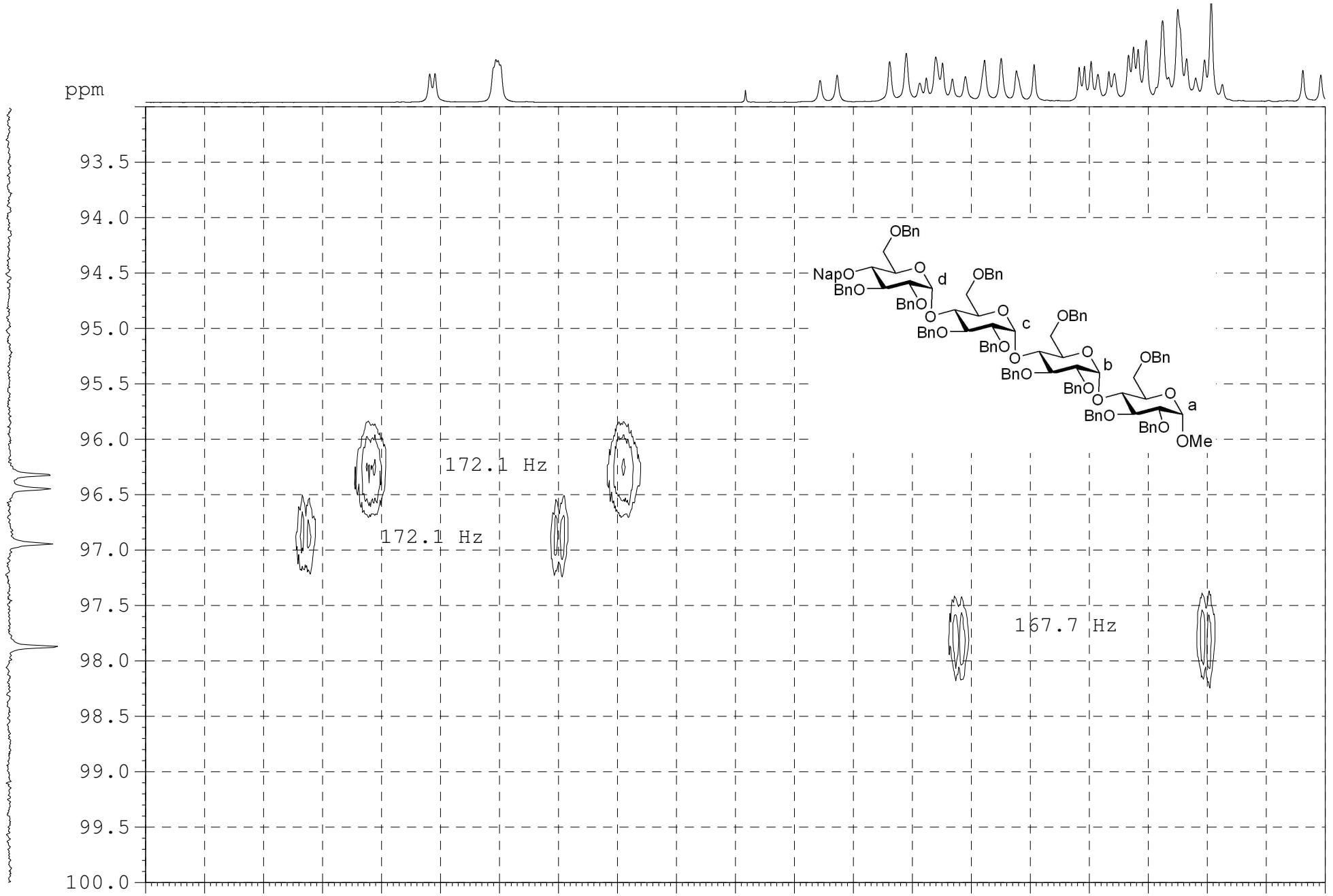



139.09
138.97
138.93
138.87
138.42
138.23
138.14
138.12
138.09
138.02
137.96
137.87
136.02
133.28
132.97
128.49
128.20
128.14
128.00
127.98
127.91
127.62
127.58
127.54
127.48
127.40
127.16
127.10
127.02
126.87
126.73
126.58
126.12
126.07
125.90
97.87
96.94
96.45
96.32
82.19
81.97
81.85
81.59
80.04
79.79
79.57
79.42
77.67
77.48
77.36
77.16
76.84
75.52
75.09
74.56
74.11
74.05
73.52
73.41
73.35
73.31
73.25
73.18
73.14
73.06
73.02
72.87
72.53
70.99
70.88
70.81
69.66
68.90
68.84
68.78
68.15
55.26
OBn
NapO
BnO
BnO
O
OBn
O
BnO
BnO
2
OBn
O
O
BnO
BnO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

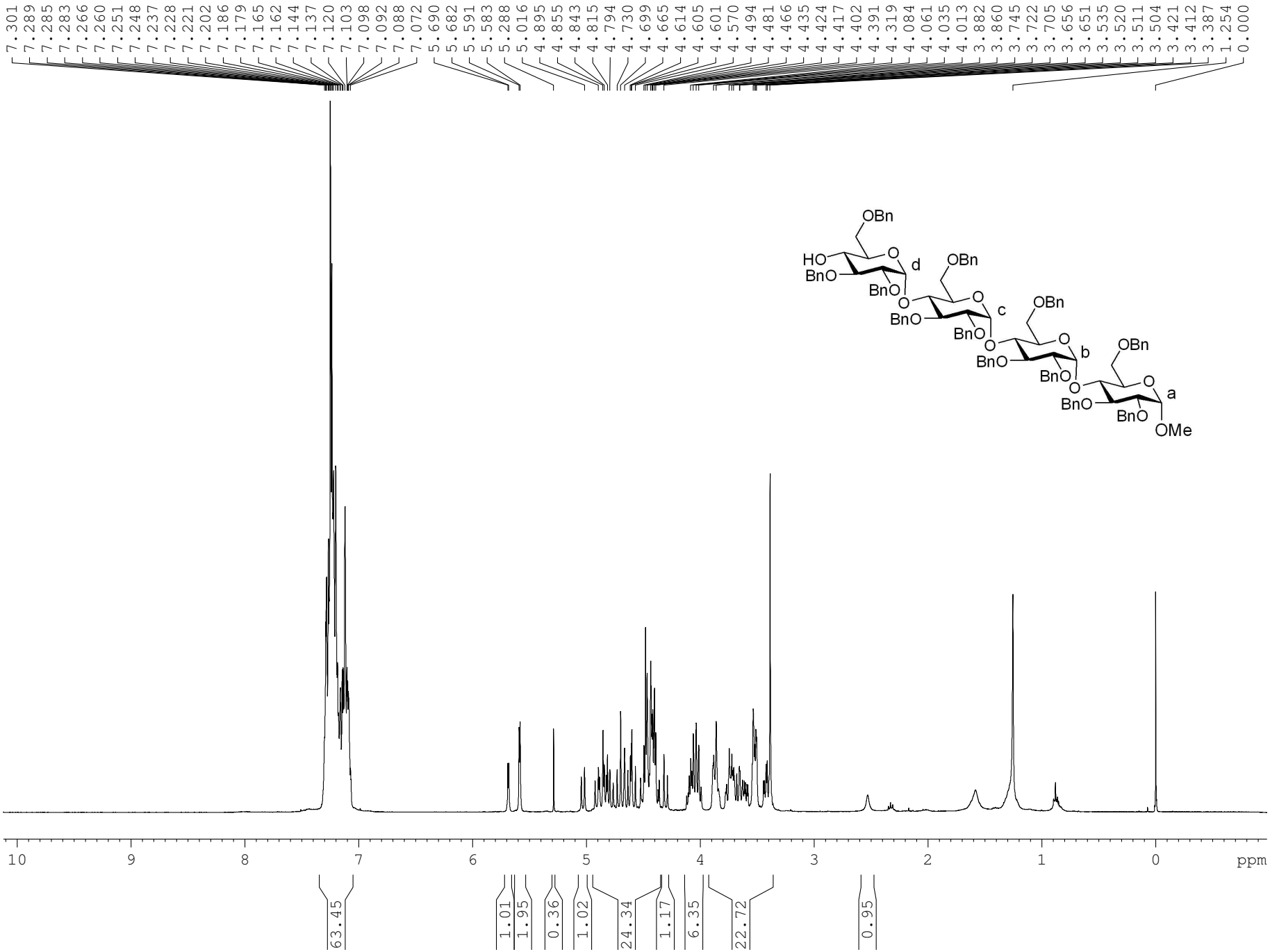

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm
OBn
NapO
BnO
O
d
c
b
a
OMe

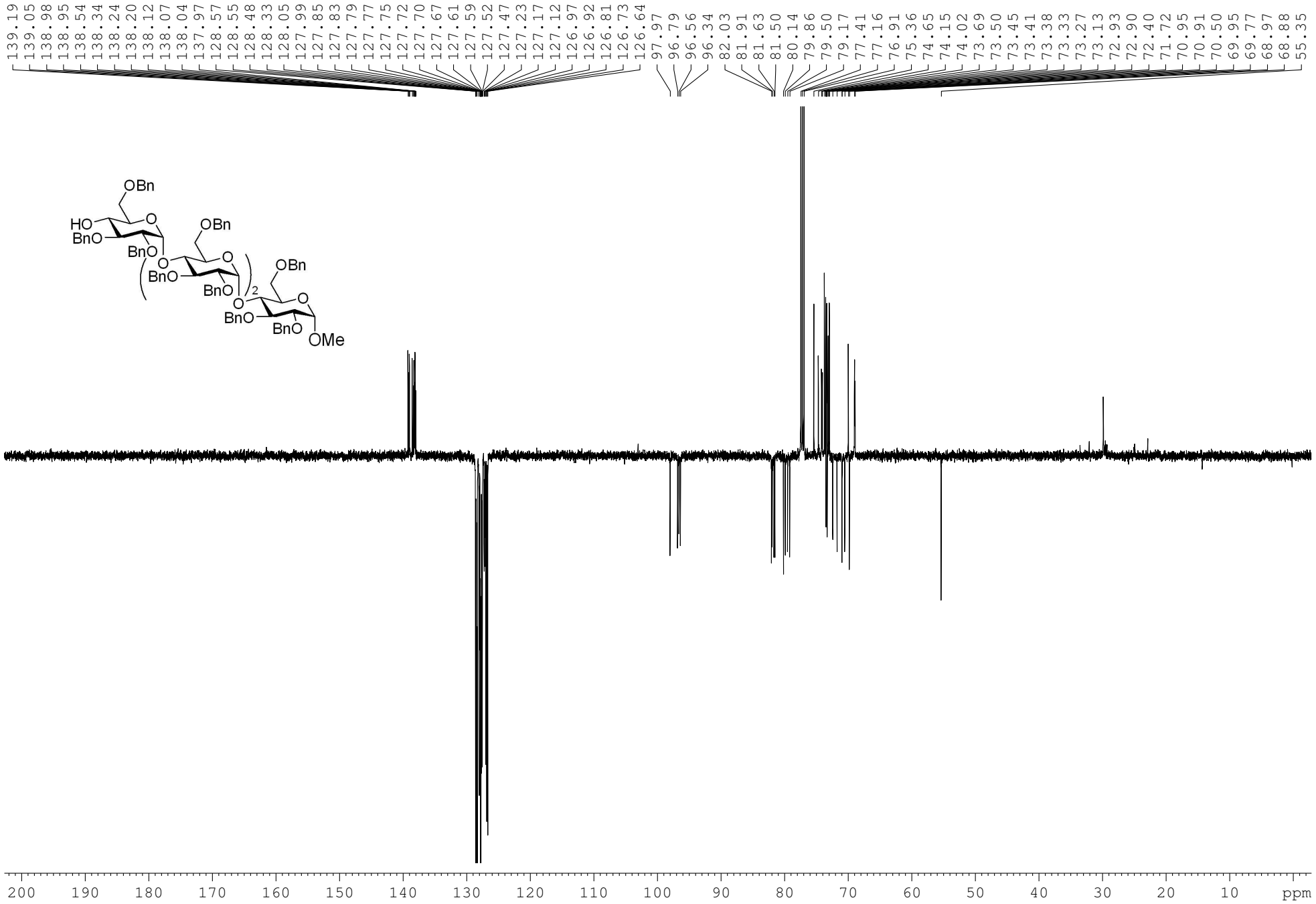

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
d
c
b
a
OMe


ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
d
c
b
a
OMe

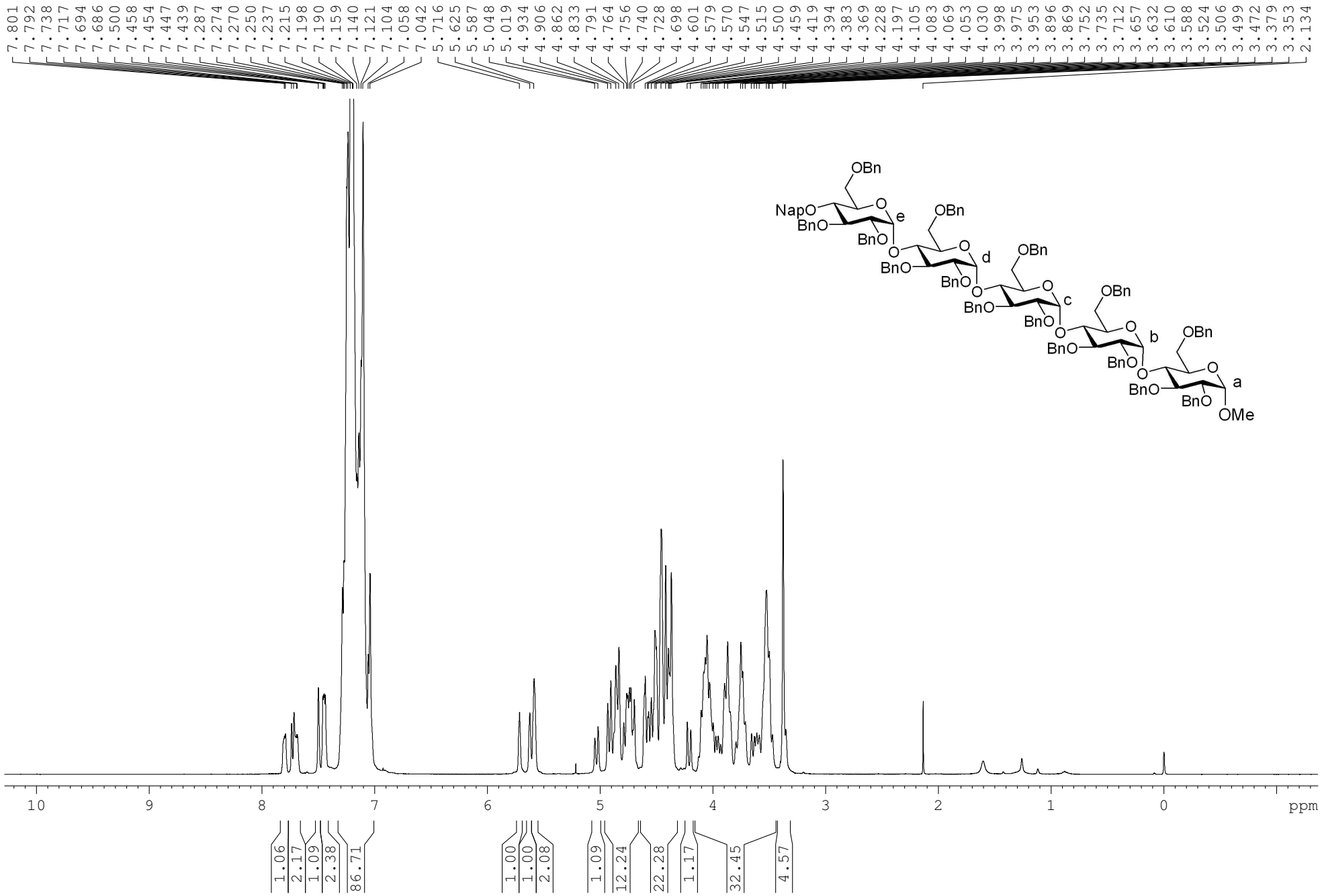

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
172.1 Hz
172.1 Hz
167.7 Hz
OBn
NapO
BnO
O
d
c
b
a
OMe
6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
ppm

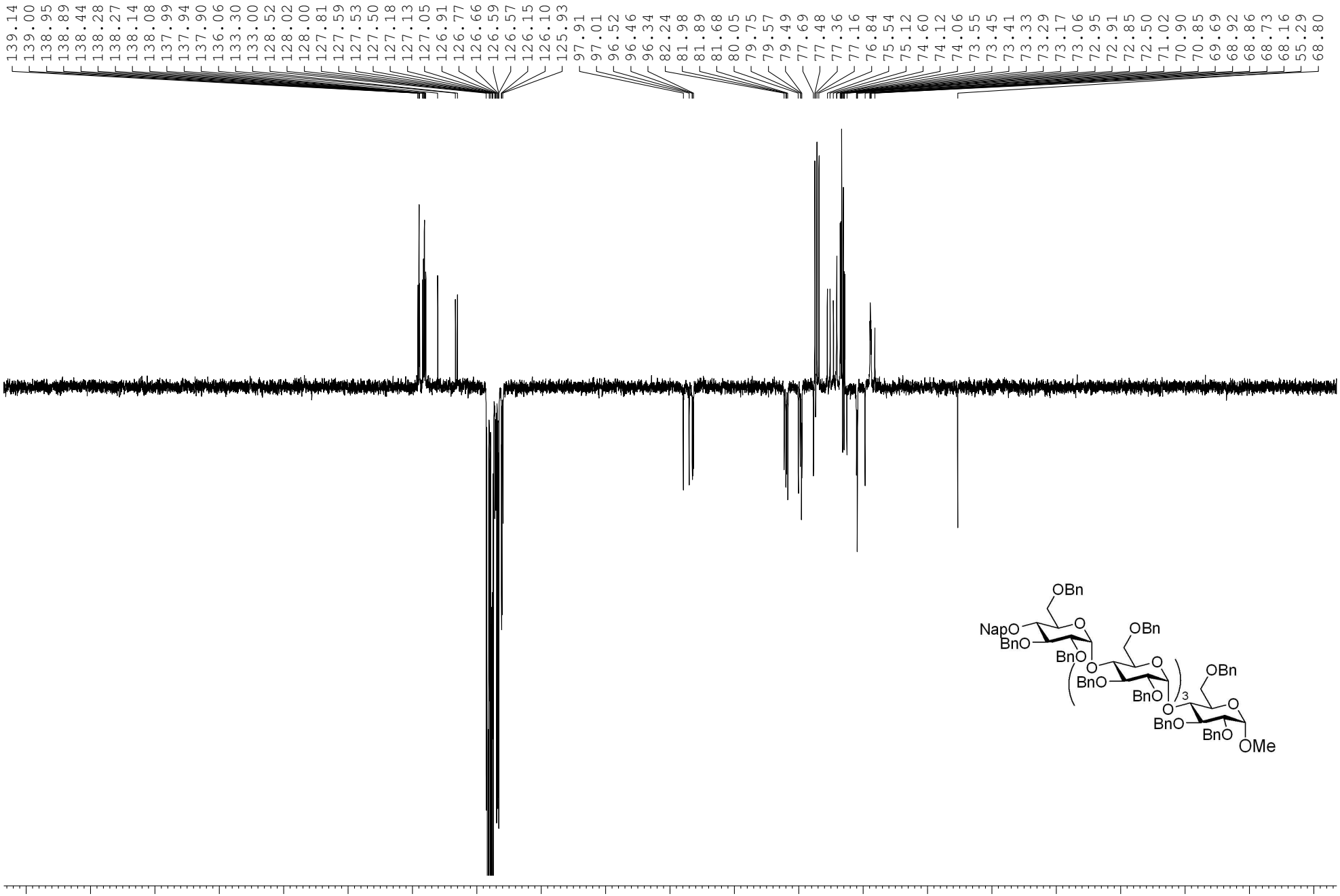
^{1}H-NMR, ^{13}C-APT of **17**

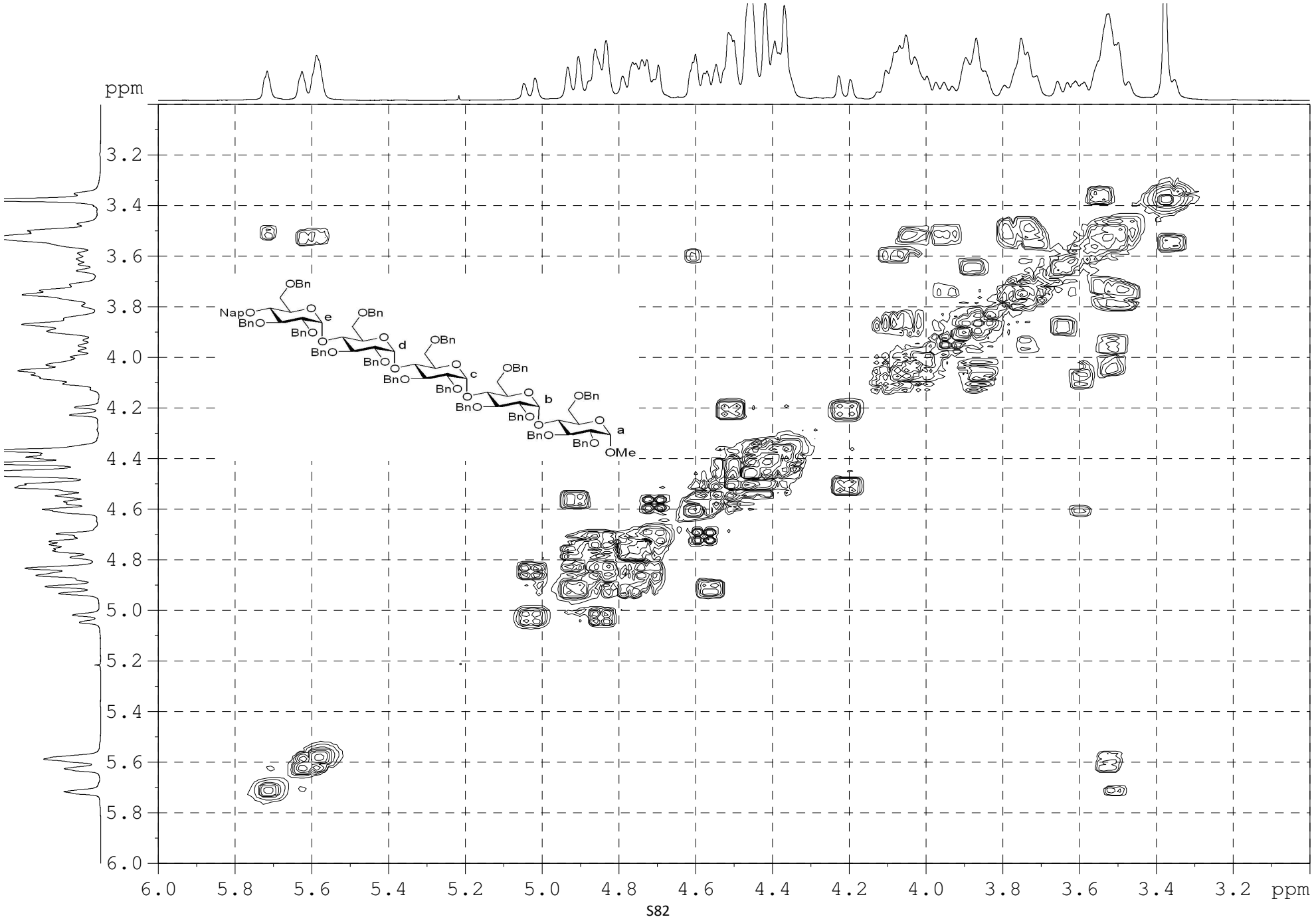


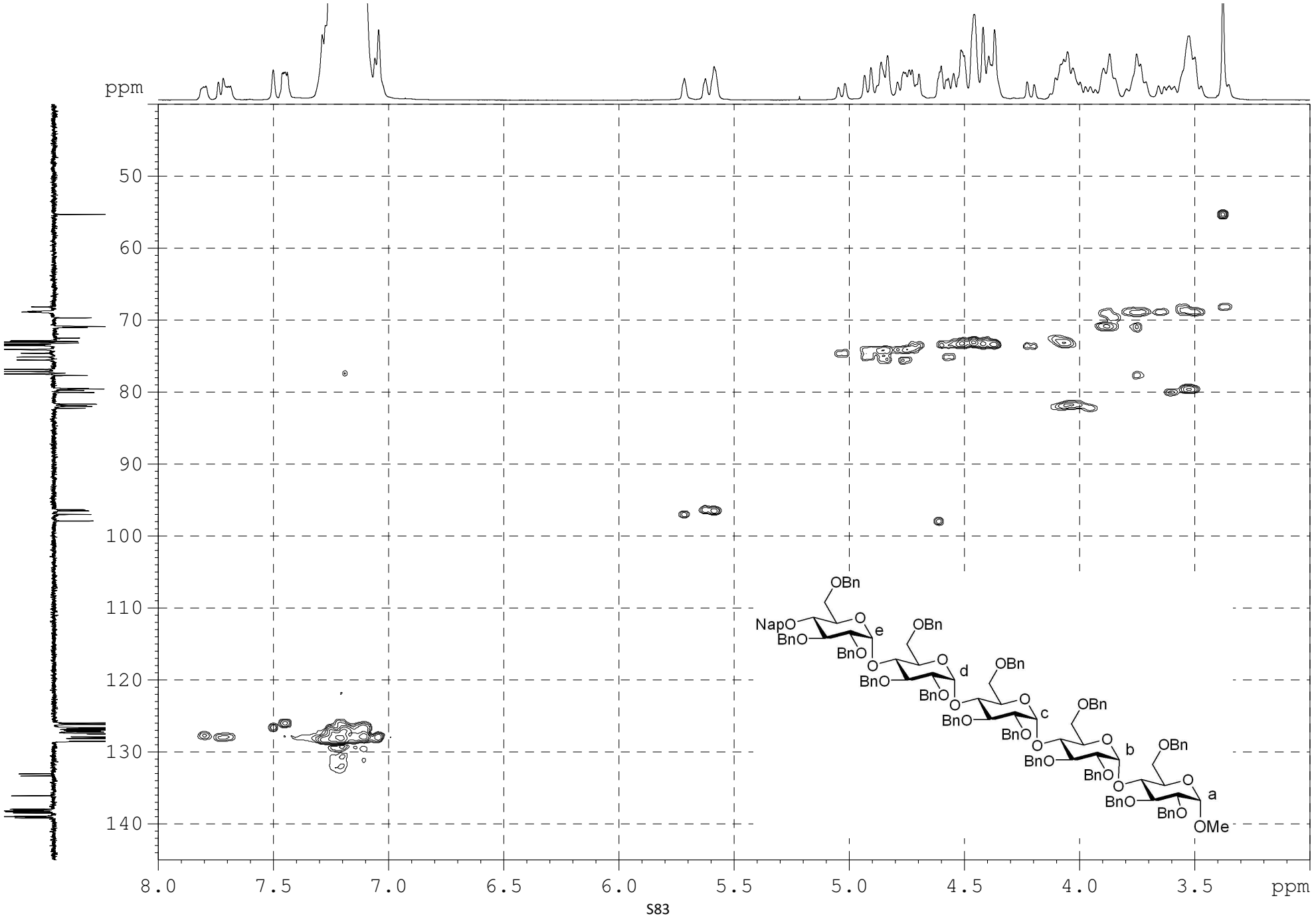

139.19
139.05
138.98
138.95
138.54
138.34
138.24
138.20
138.12
138.07
138.04
137.97
128.57
128.55
128.48
128.33
128.05
127.99
127.85
127.83
127.79
127.77
127.75
127.72
127.70
127.67
127.61
127.59
127.52
127.47
127.23
127.17
127.12
126.97
126.92
126.81
126.73
126.64
97.97
96.79
96.56
96.34
82.03
81.91
81.63
81.50
80.14
79.86
79.50
79.17
77.41
77.16
76.91
75.36
74.65
74.15
74.02
73.69
73.50
73.45
73.41
73.38
73.33
73.27
73.13
72.93
72.90
72.40
71.72
70.95
70.91
70.50
69.95
69.77
68.97
68.88
55.35
OBn
HO
BnO
O
OBn
BnO
O
OBn
BnO
BnO
O
2
O
BnO
BnO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

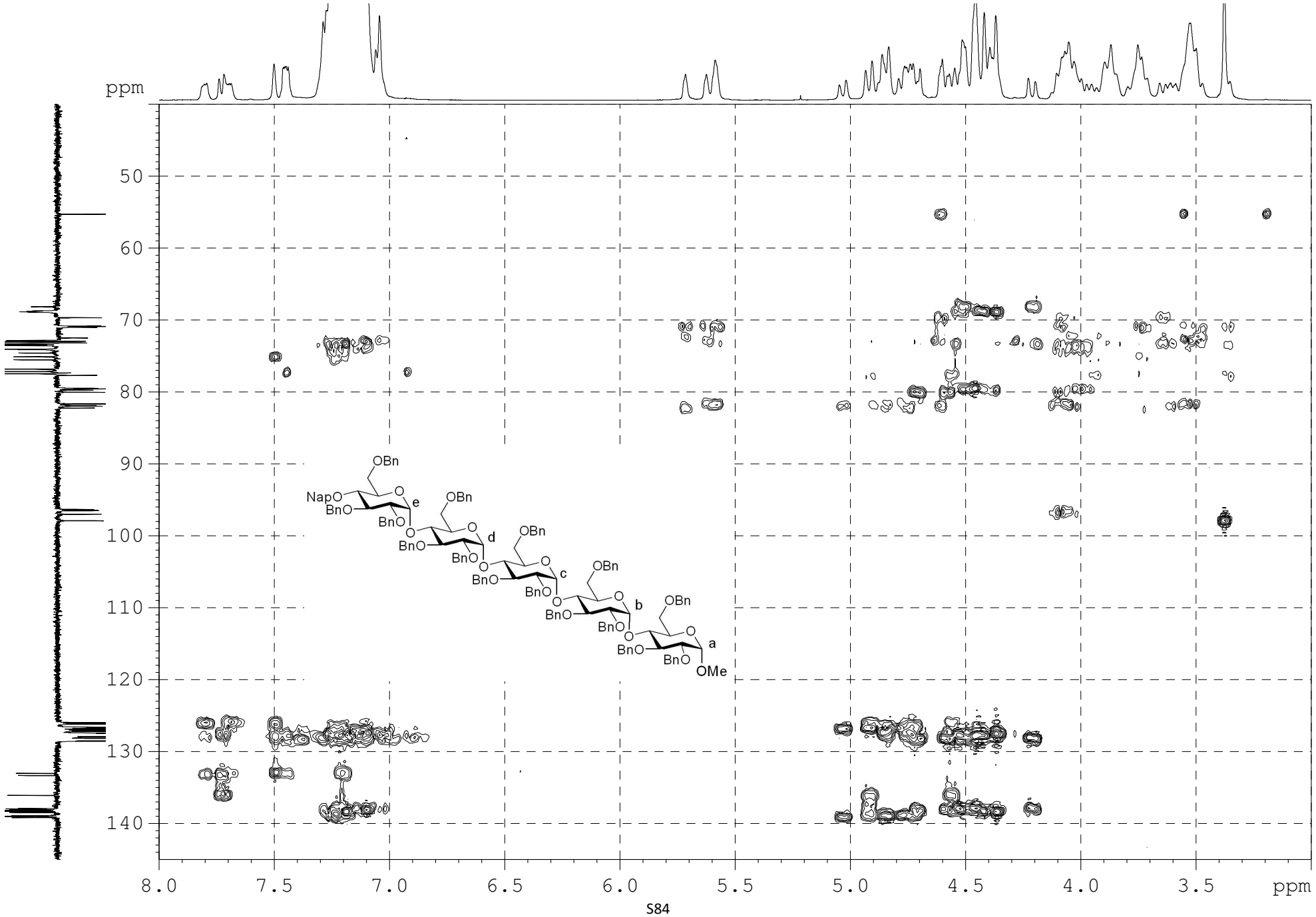
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **18**

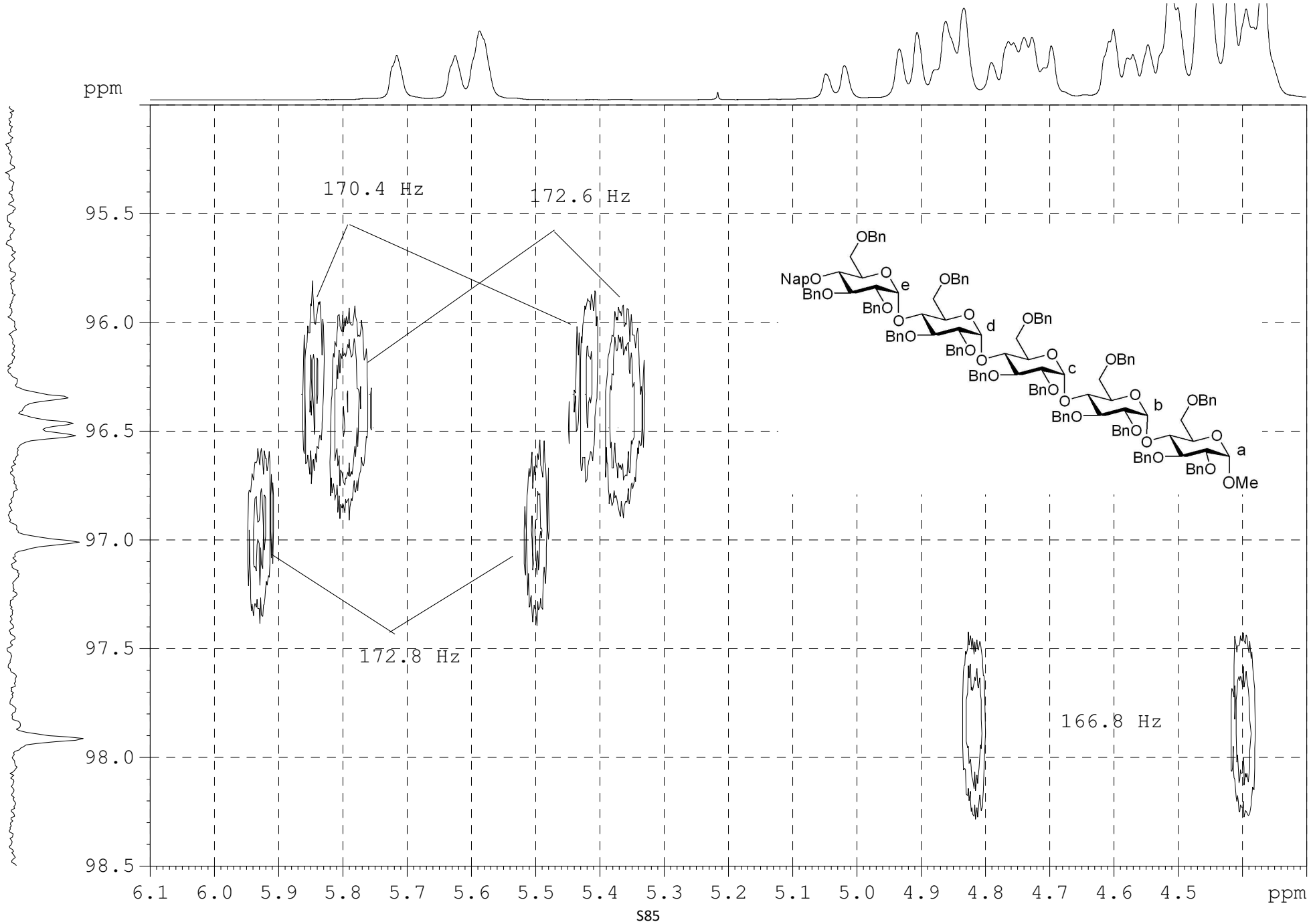



139.14
139.00
138.95
138.89
138.44
138.28
138.27
138.14
138.08
137.99
137.94
137.90
136.06
133.30
133.00
128.52
128.02
128.00
127.81
127.59
127.53
127.50
127.18
127.13
127.05
126.91
126.77
126.66
126.59
126.57
126.15
126.10
125.93
97.91
97.01
96.52
96.46
96.34
82.24
81.98
81.89
81.68
80.05
79.75
79.57
79.49
77.69
77.48
77.36
77.16
76.84
75.54
75.12
74.60
74.12
74.06
73.55
73.45
73.41
73.33
73.29
73.17
73.06
72.95
72.91
72.85
72.50
71.02
70.90
70.85
69.69
68.92
68.86
68.73
68.16
55.29
68.80
OBn
NapO
BnO
BnO
O
O
OBn
BnO
BnO
3
O
OBn
O
BnO
BnO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

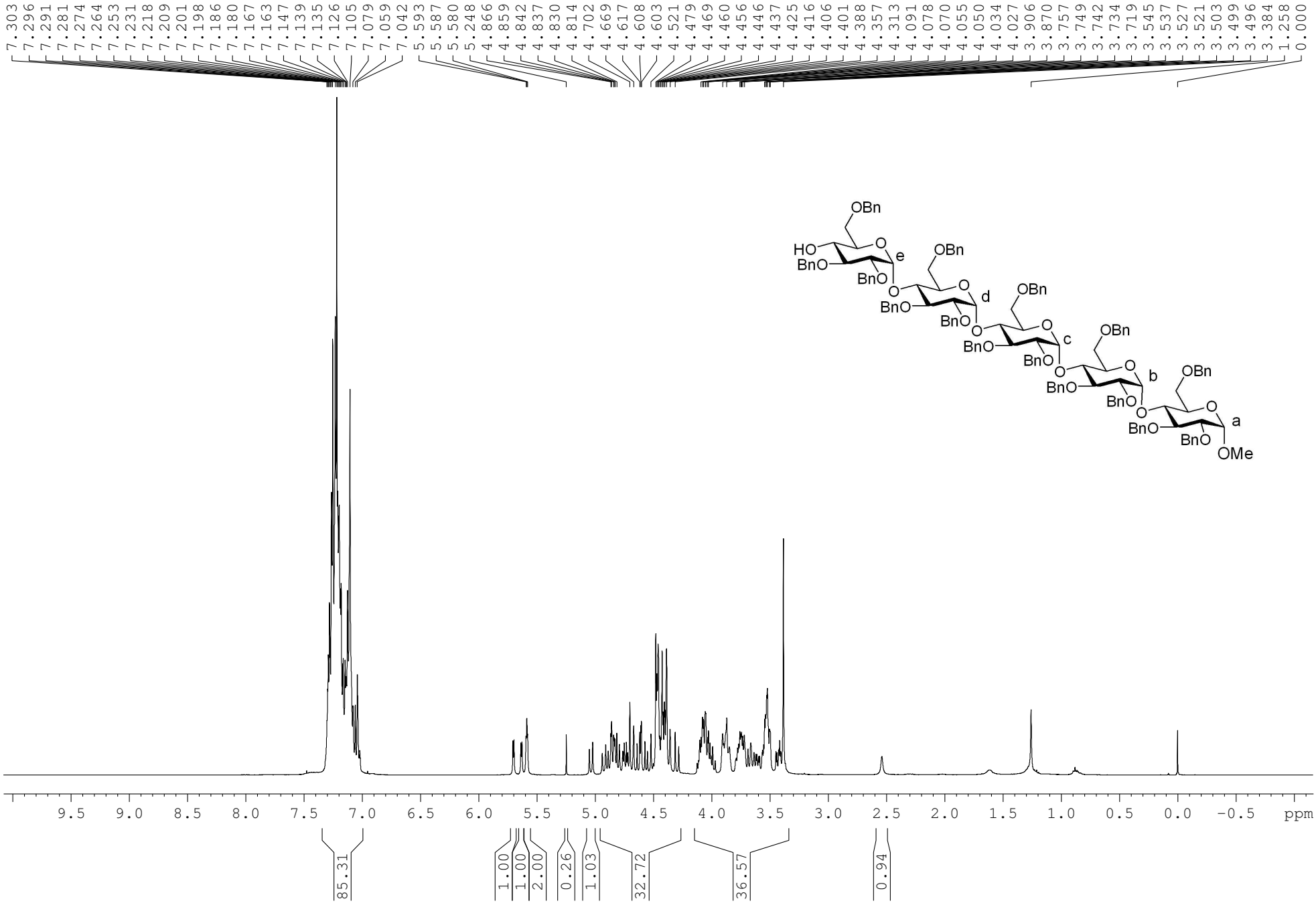

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
OBn
NapO
BnO
OMe
a
b
c
d
e

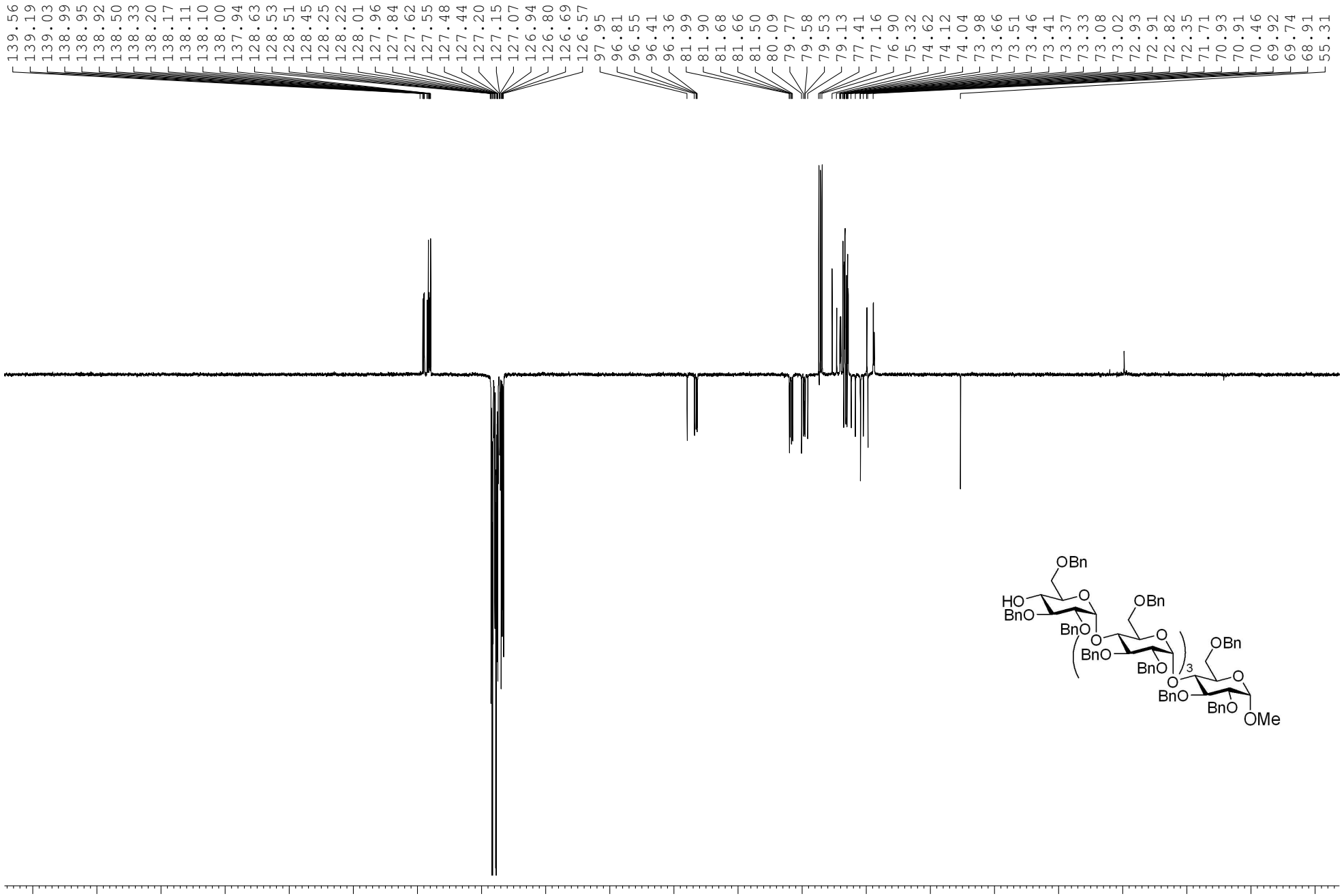

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
O
e
d
c
b
a
OMe


ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
e
d
c
b
a
OMe

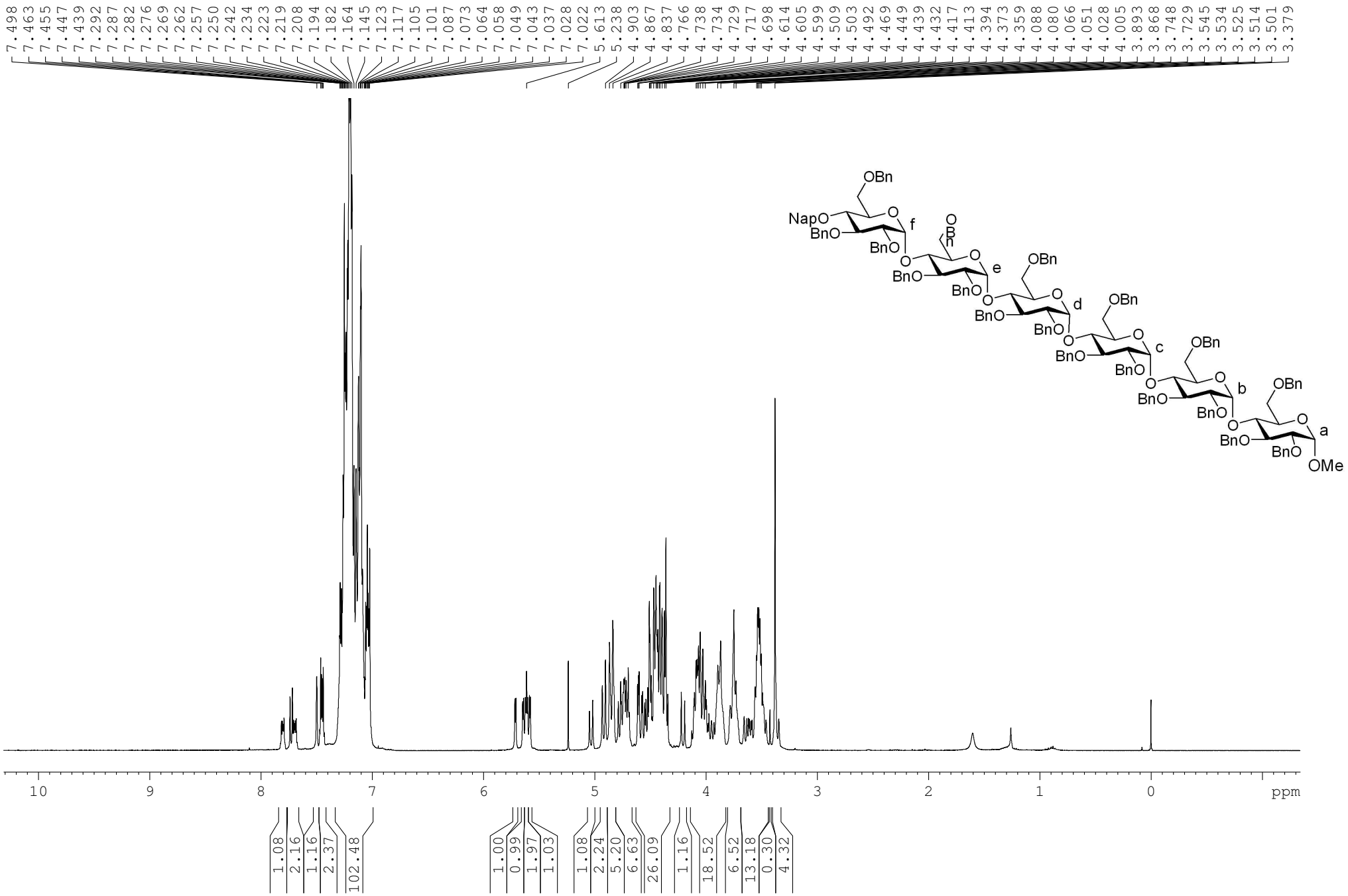

ppm
170.4 Hz
172.6 Hz
172.8 Hz
166.8 Hz
95.5
96.0
96.5
97.0
97.5
98.0
98.5
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
ppm
OBn
NapO
BnO
O
e
d
c
b
a
OMe

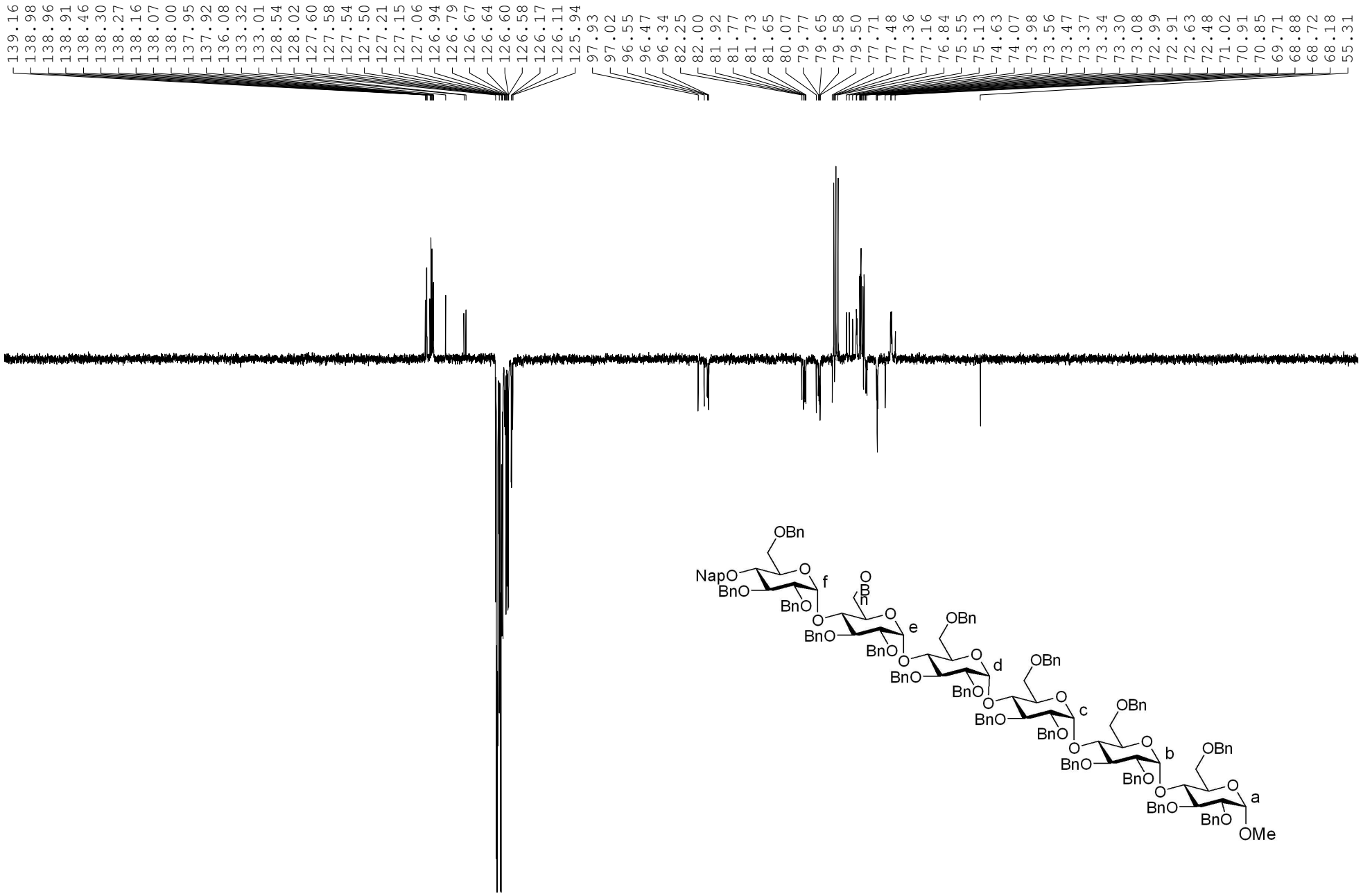
^{1}H-NMR, ^{13}C-APT of **19**

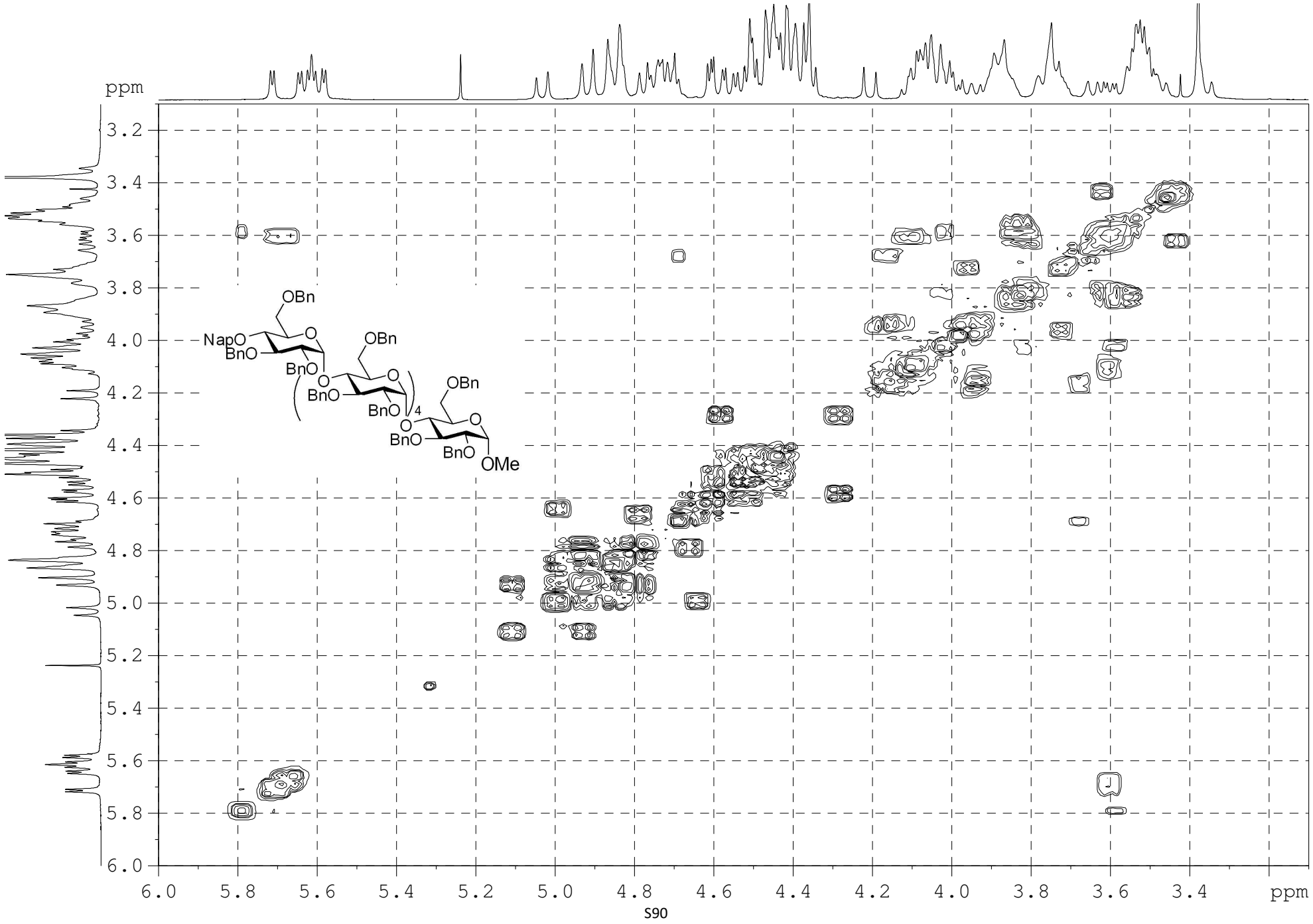


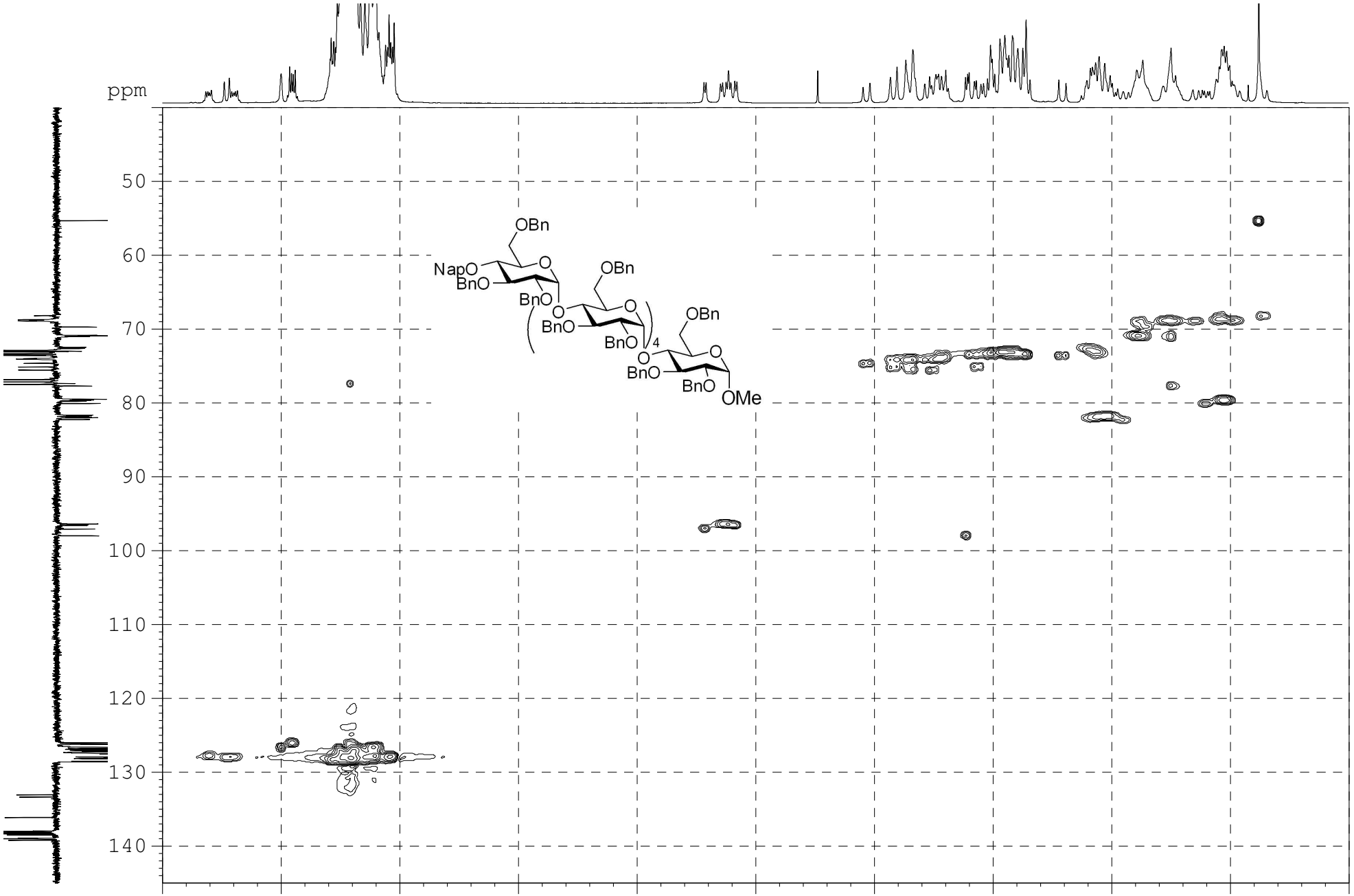

139.56
139.19
139.03
138.99
138.95
138.92
138.50
138.33
138.20
138.17
138.11
138.10
138.00
137.94
128.63
128.53
128.51
128.45
128.25
128.22
128.01
127.96
127.84
127.62
127.55
127.48
127.44
127.20
127.15
127.07
126.94
126.80
126.69
126.57
97.95
96.81
96.55
96.41
96.36
81.99
81.90
81.68
81.66
81.50
80.09
79.77
79.58
79.53
79.13
77.41
77.16
76.90
75.32
74.62
74.12
74.04
73.98
73.66
73.51
73.46
73.41
73.37
73.33
73.08
73.02
72.93
72.91
72.82
72.35
71.71
70.93
70.91
70.46
69.92
69.74
68.91
55.31
OBn
HO
BnO
O
BnO
OBn
O
BnO
BnO
3
OBn
O
BnO
BnO
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

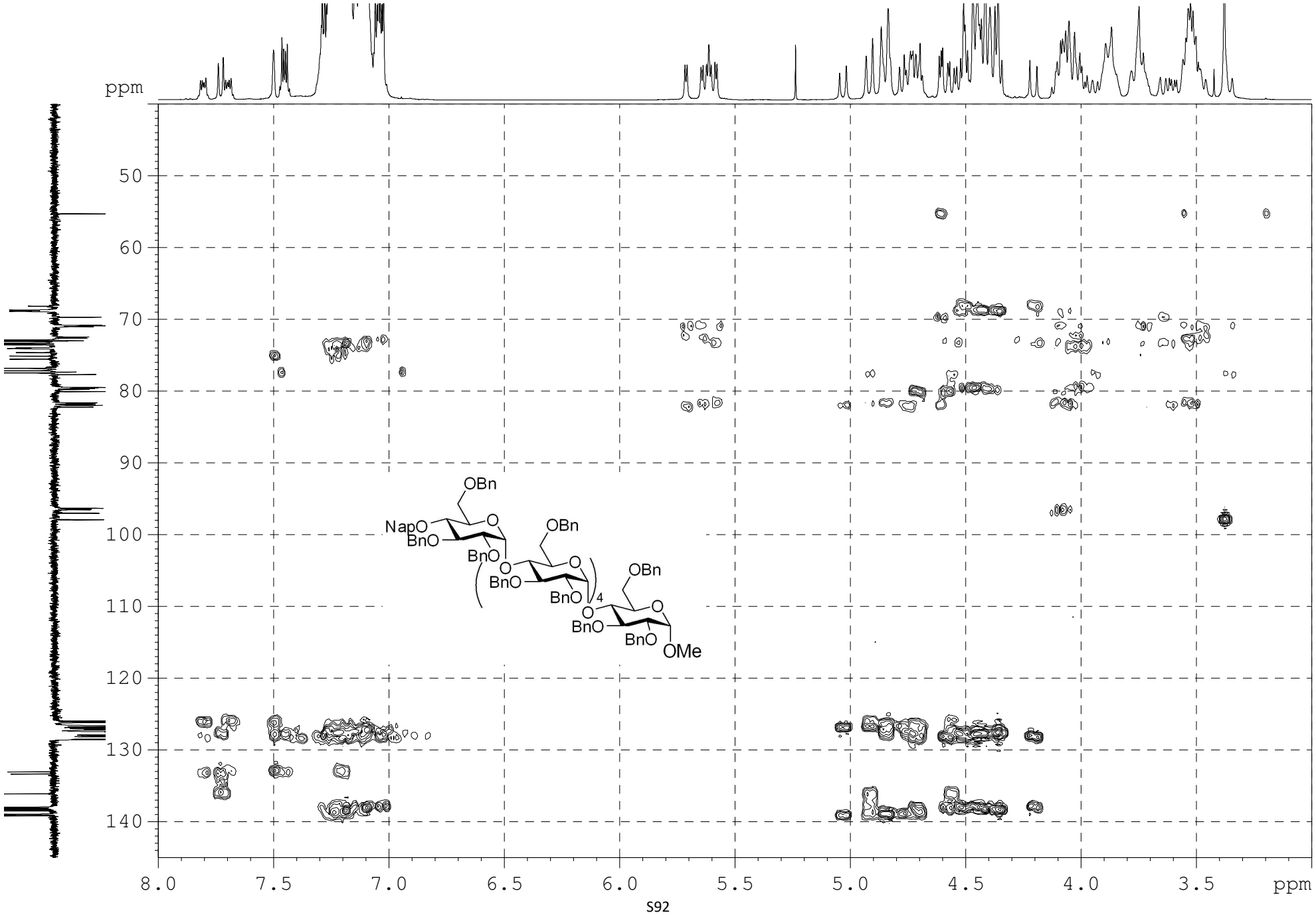
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **20**

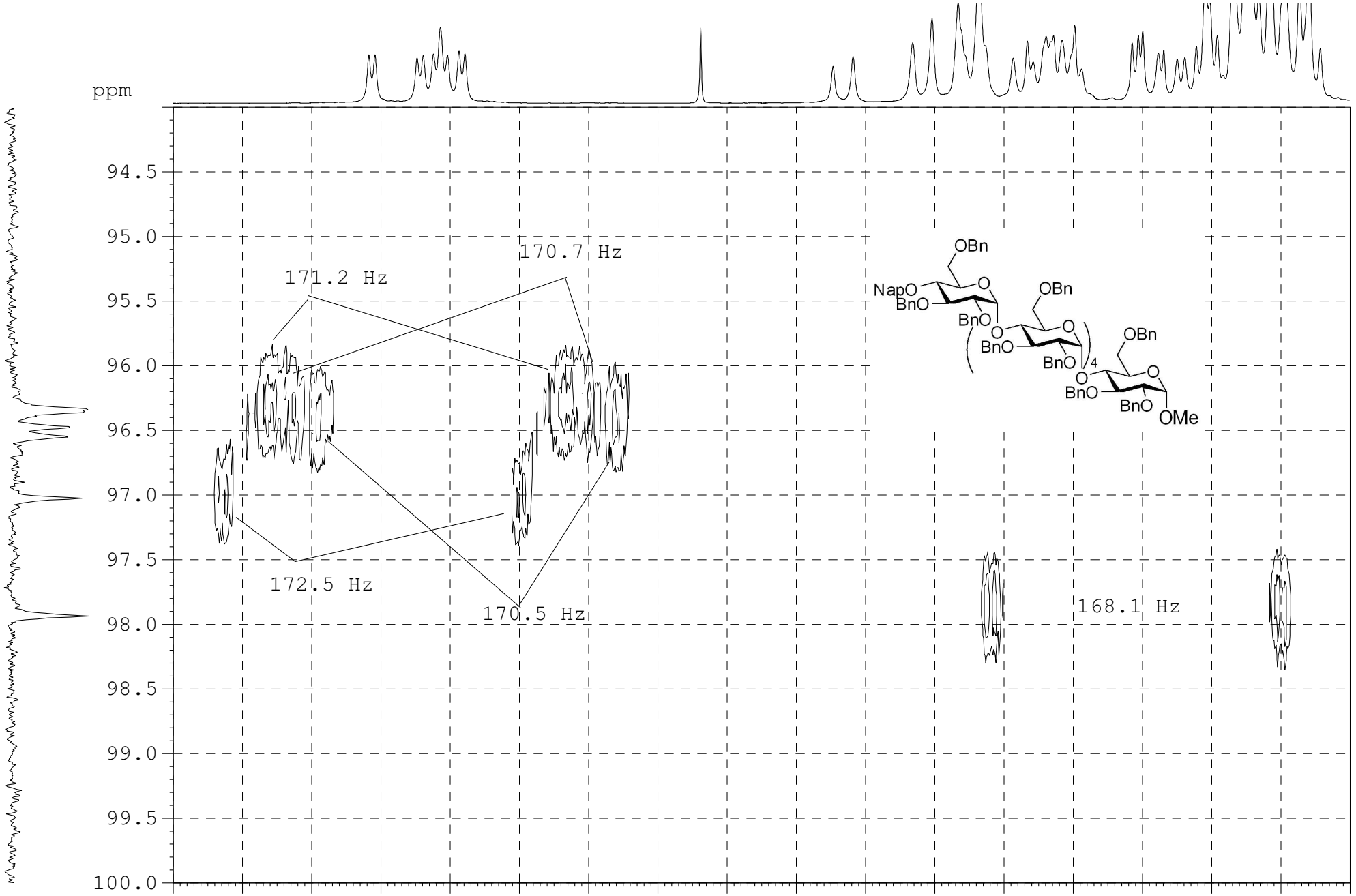



139.16
138.98
138.96
138.91
138.46
138.30
138.27
138.16
138.07
138.00
137.95
137.92
136.08
133.32
133.01
128.54
128.02
127.60
127.58
127.54
127.50
127.21
127.15
127.06
126.94
126.79
126.67
126.64
126.60
126.58
126.17
126.11
125.94
97.93
97.02
96.55
96.47
96.34
82.25
82.00
81.92
81.77
81.73
81.65
80.07
79.77
79.65
79.58
79.50
77.71
77.48
77.36
77.16
76.84
75.55
75.13
74.63
74.07
73.98
73.56
73.47
73.37
73.34
73.30
73.08
72.99
72.91
72.63
72.48
71.02
70.91
70.85
69.71
68.88
68.72
68.18
55.31
OBn
NapO
BnO
BnO
O
f
O
B
n
O
BnO
BnO
O
e
OBn
O
BnO
O
d
OBn
BnO
O
BnO
O
c
OBn
BnO
O
b
OBn
BnO
O
BnO
BnO
O
a
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

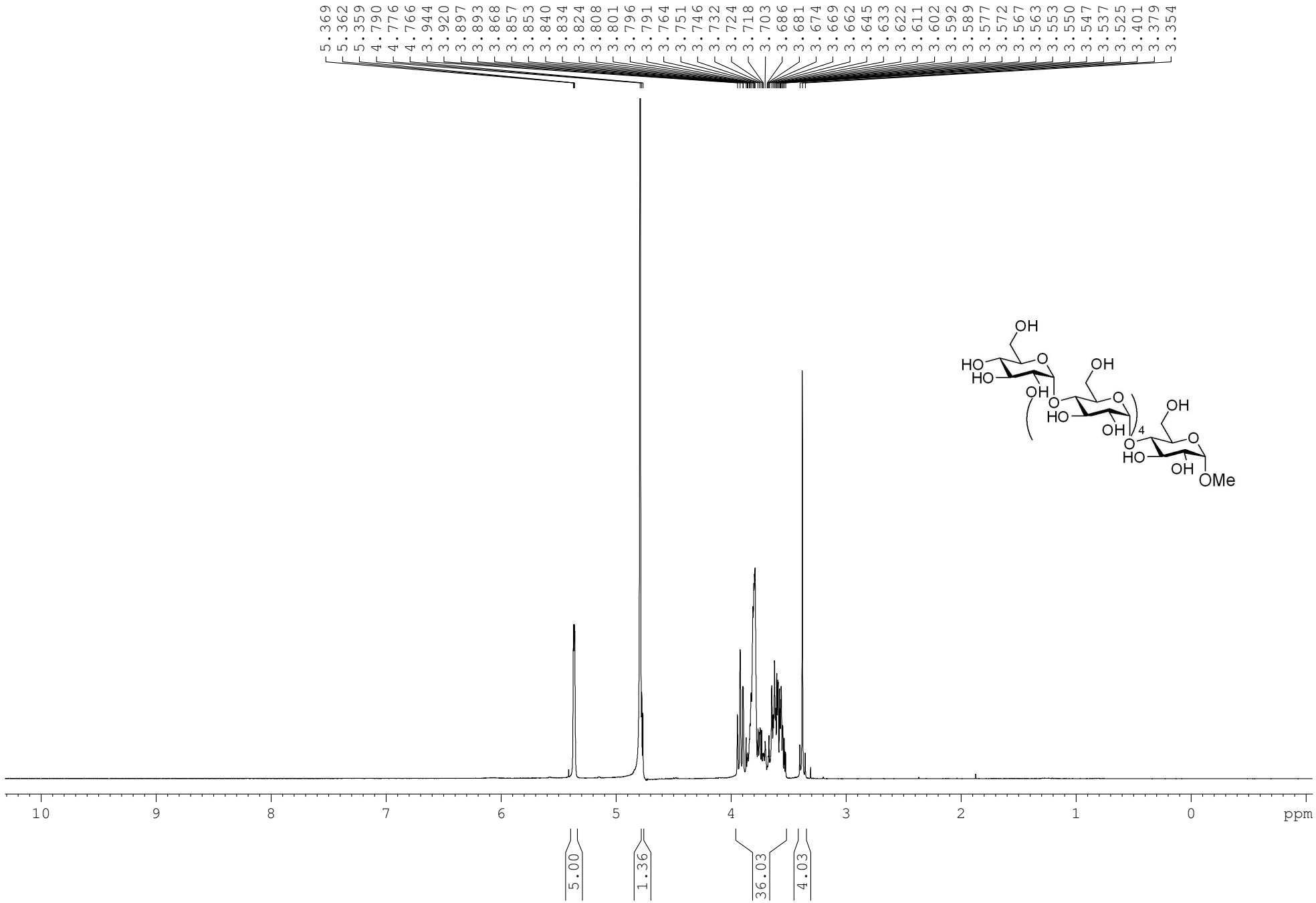

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
OBn
NapO
BnO
O
BnO
OBn
O
BnO
BnO
4
O
OBn
O
BnO
BnO
OMe

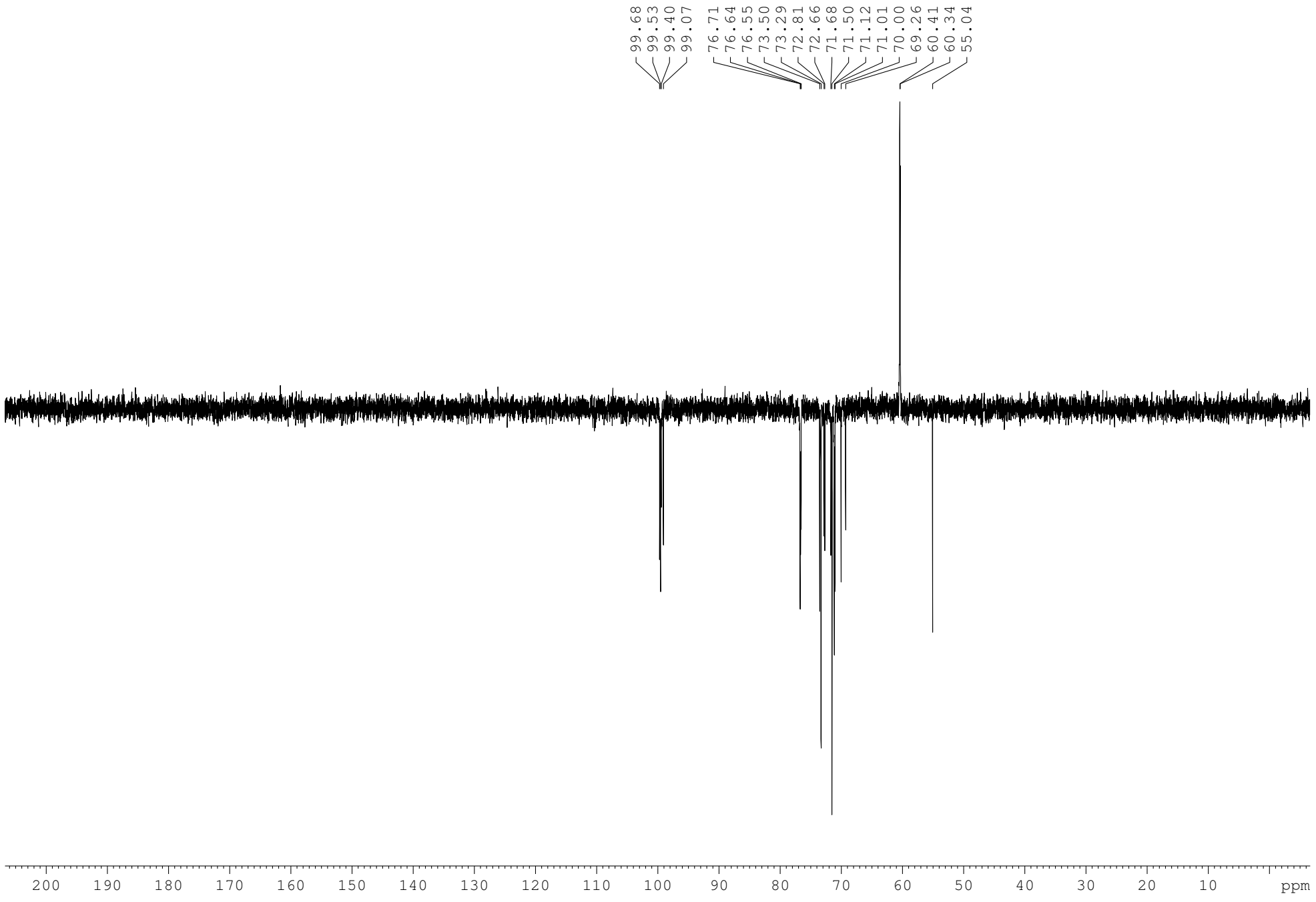

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
O
BnO
OBn
O
BnO
BnO
4
OBn
O
BnO
BnO
OMe

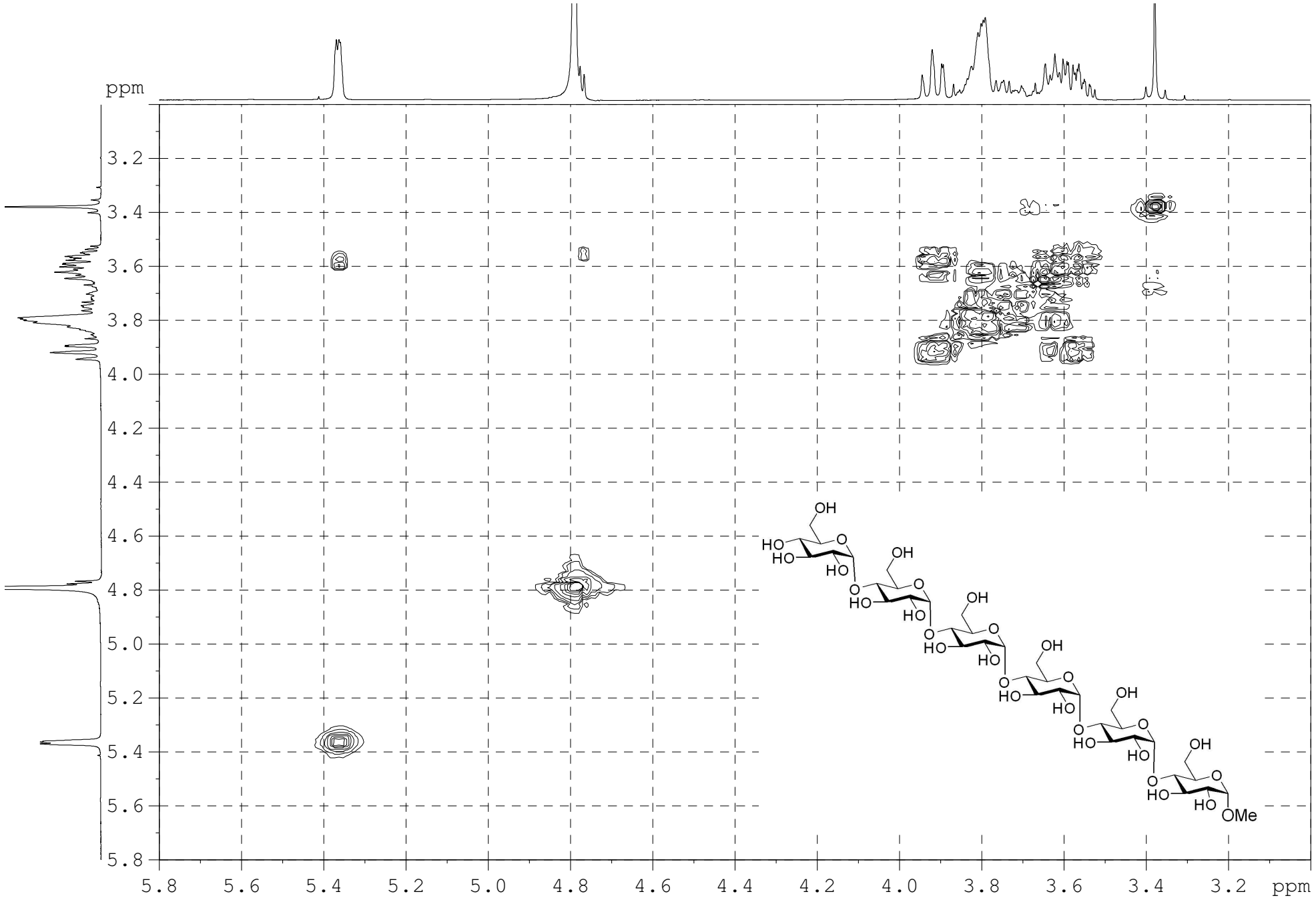

ppm
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
OBn
NapO
BnO
BnO
O
OBn
BnO
O
BnO
OBn
O
4
O
BnO
BnO
OMe

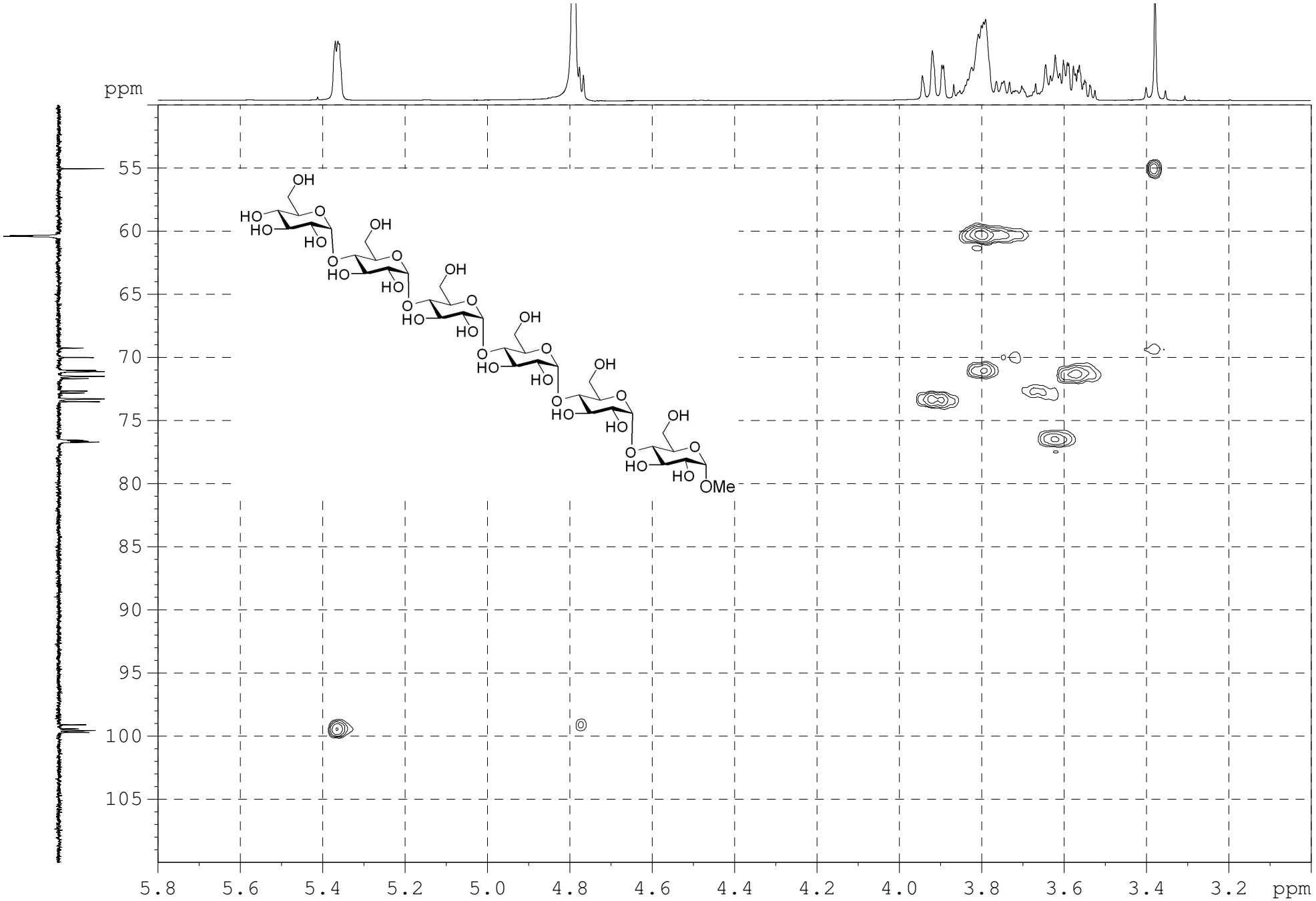

ppm
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
171.2 Hz
170.7 Hz
172.5 Hz
170.5 Hz
168.1 Hz
OBn
NapO
BnO
O
4
OMe
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4 ppm

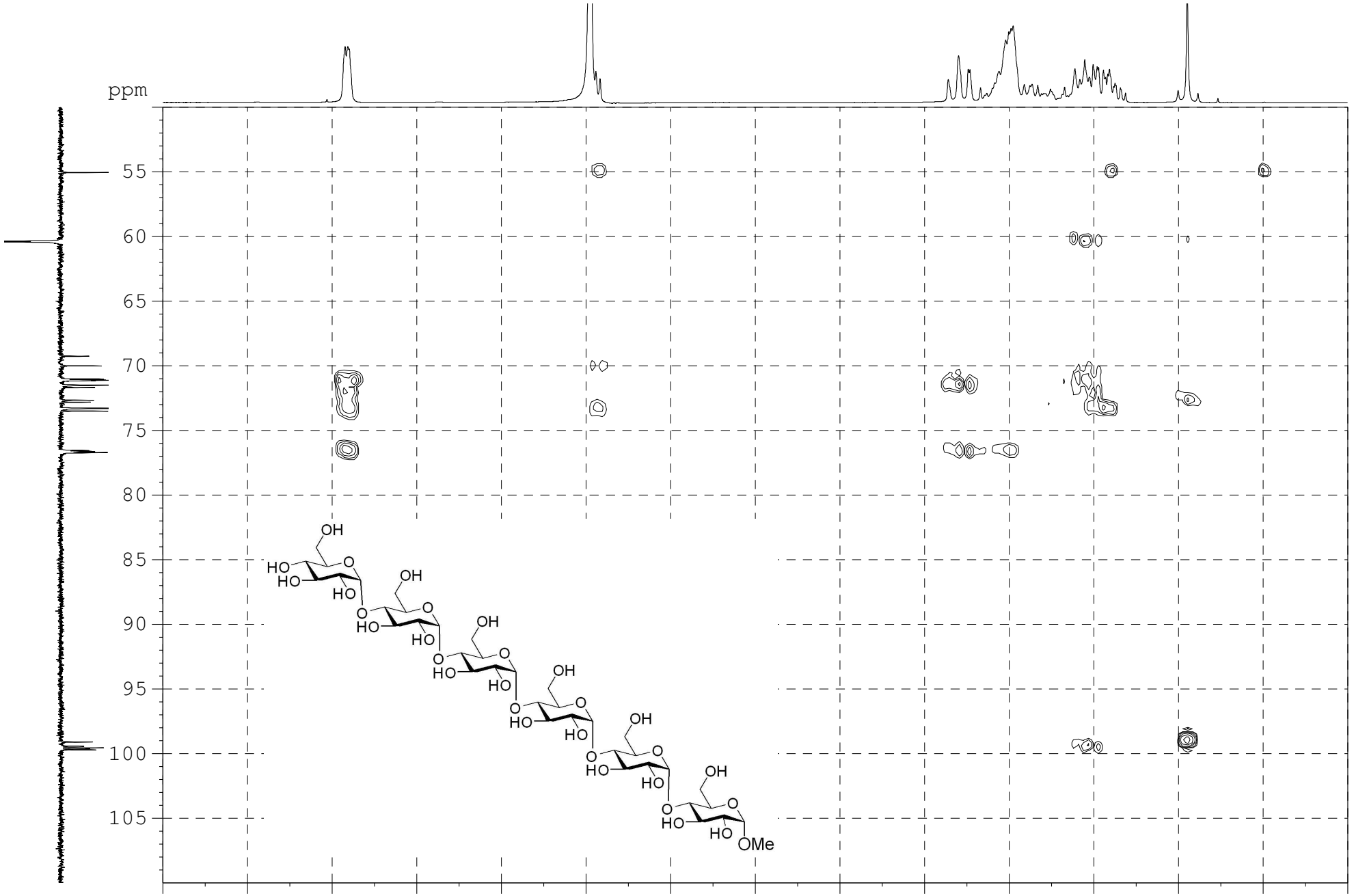
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **21**

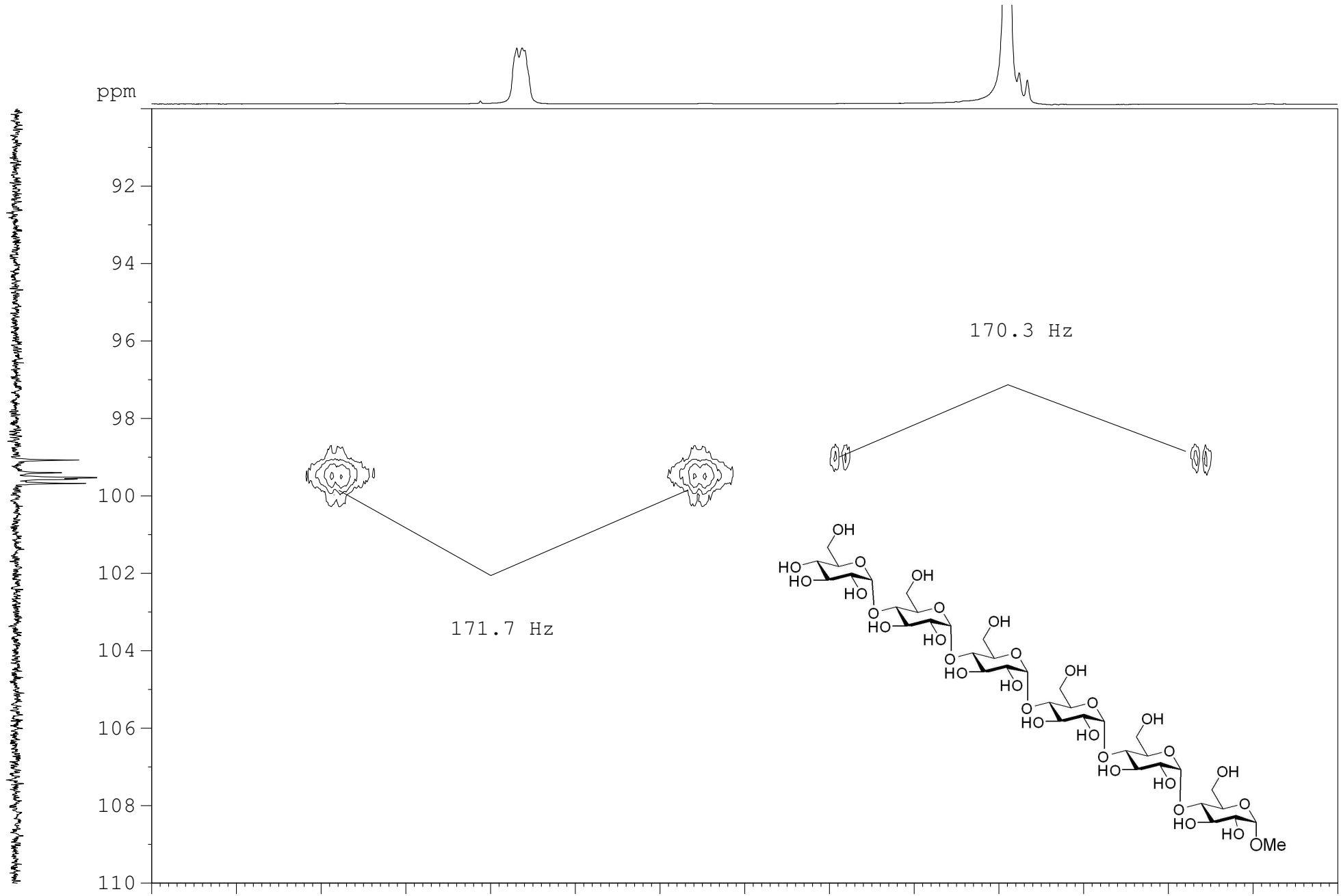



99.68
99.53
99.40
99.07
76.71
76.64
76.55
73.50
73.29
72.81
72.66
71.68
71.50
71.12
71.01
70.00
69.26
60.41
60.34
55.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

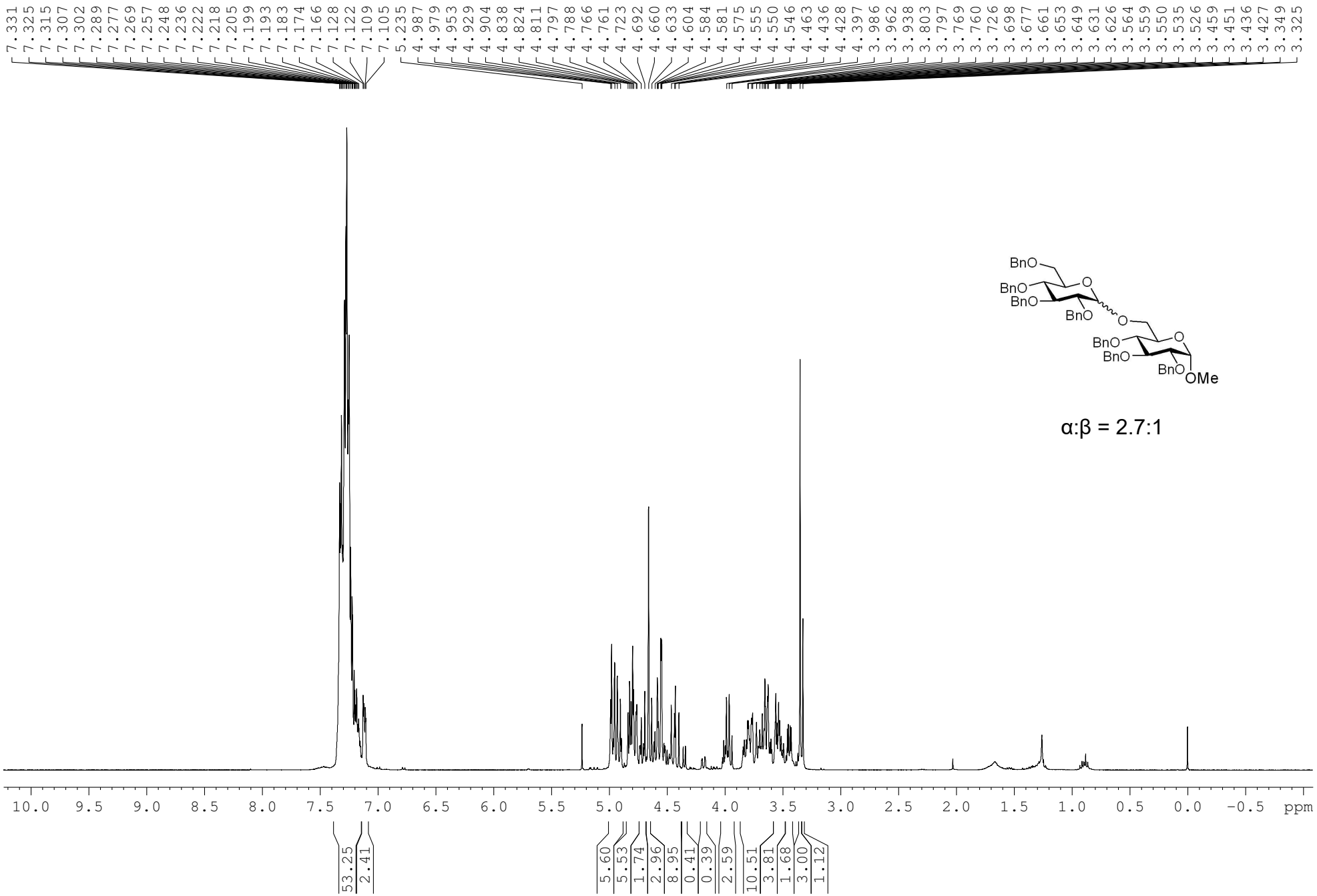

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm
OH
HO
O
OMe


ppm
55
60
65
70
75
80
85
90
95
100
105
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
OH
HO
O
OMe

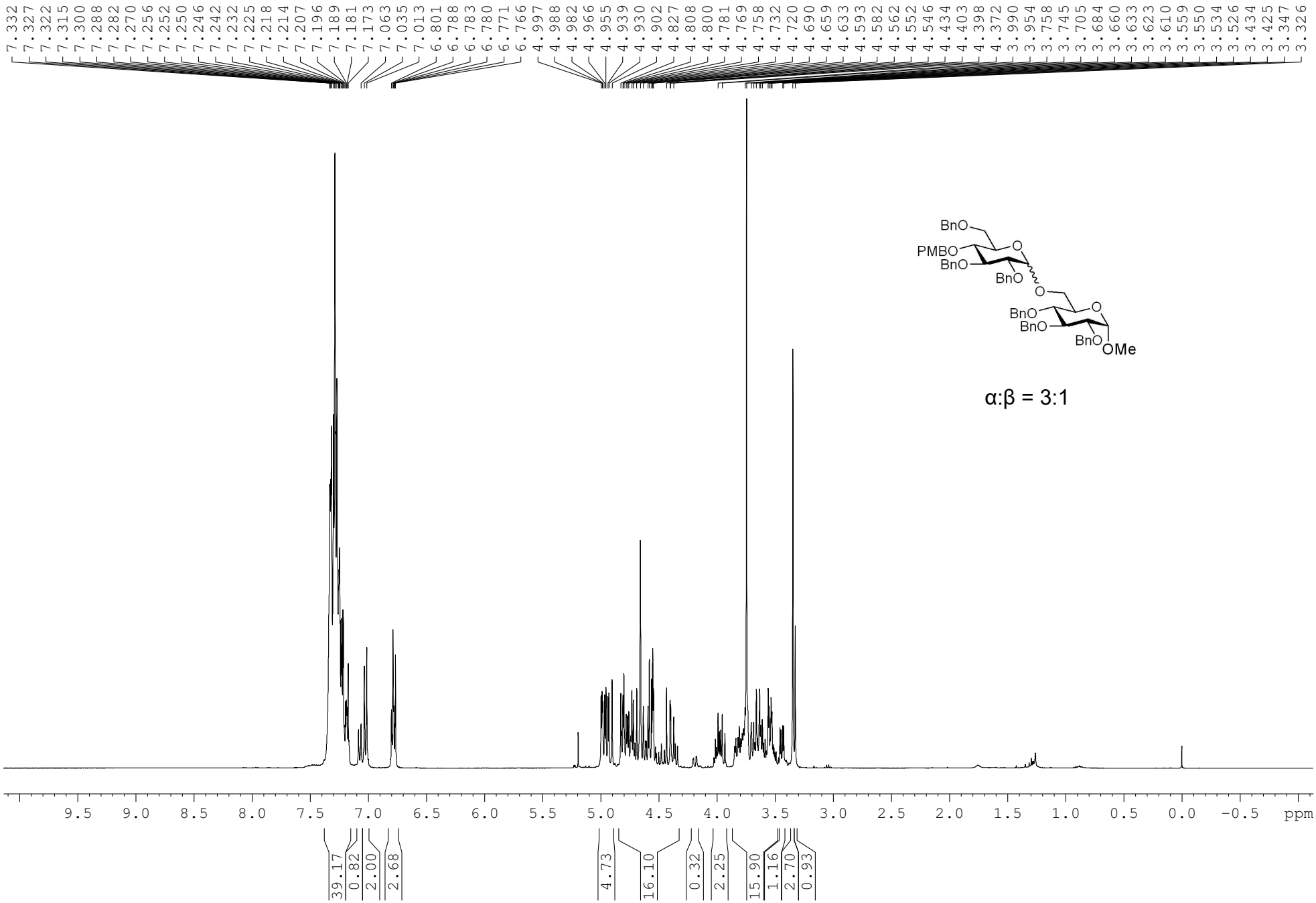

ppm
55
60
65
70
75
80
85
90
95
100
105
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
OH
HO
O
OMe

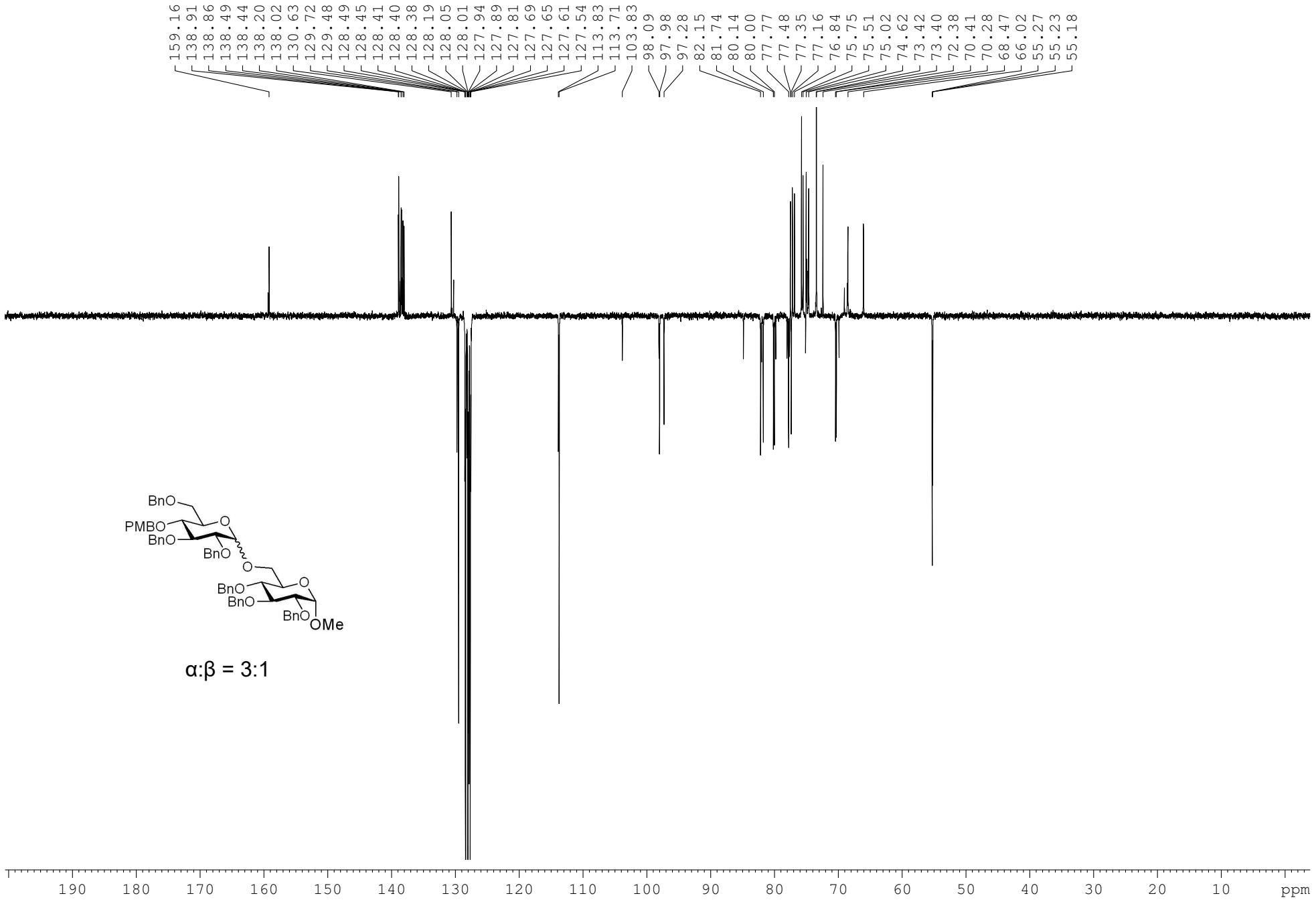

ppm
92
94
96
98
100
102
104
106
108
110
170.3 Hz
171.7 Hz
OH
HO
O
OMe
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
ppm

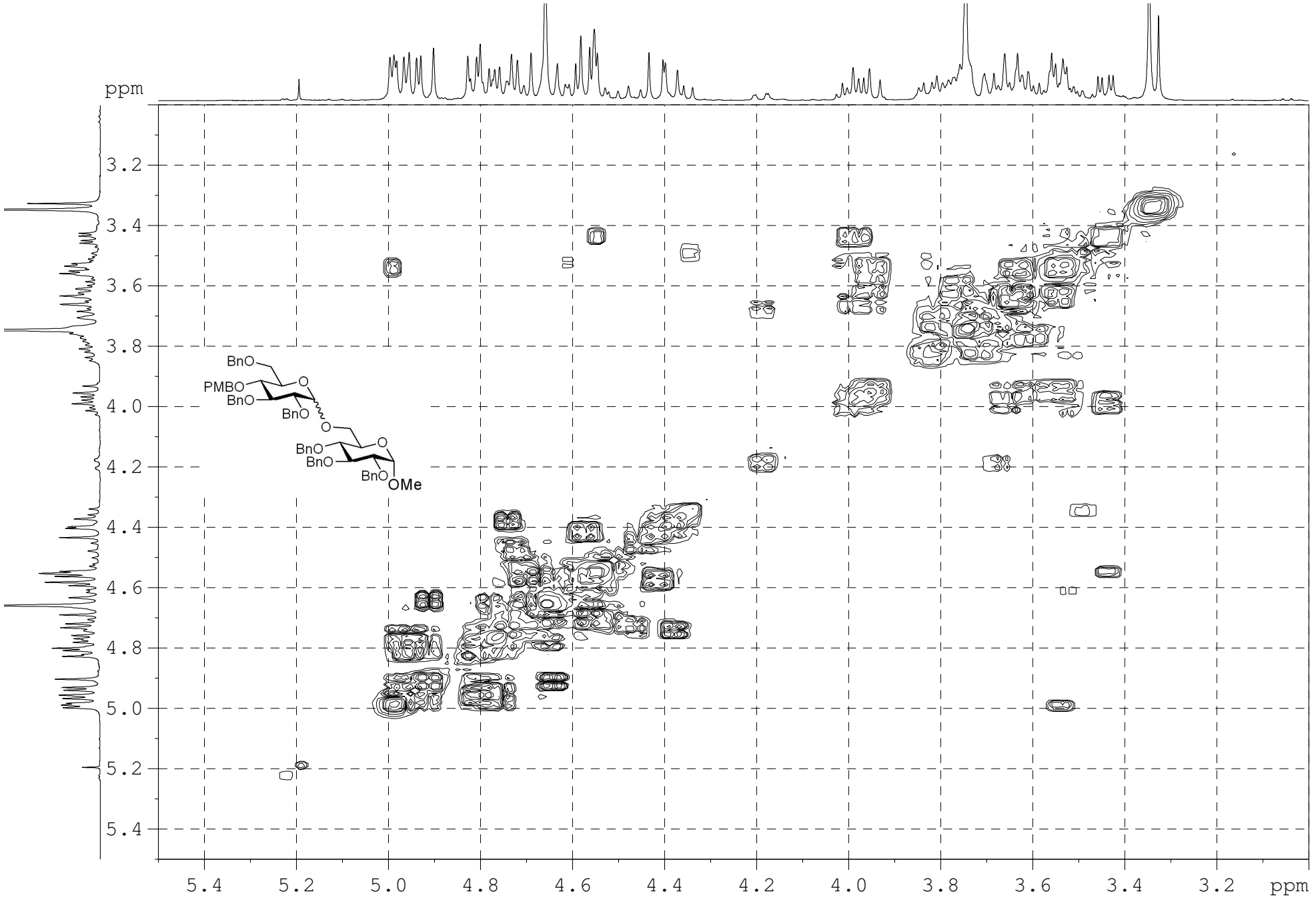
^{1}H-NMR of **23**

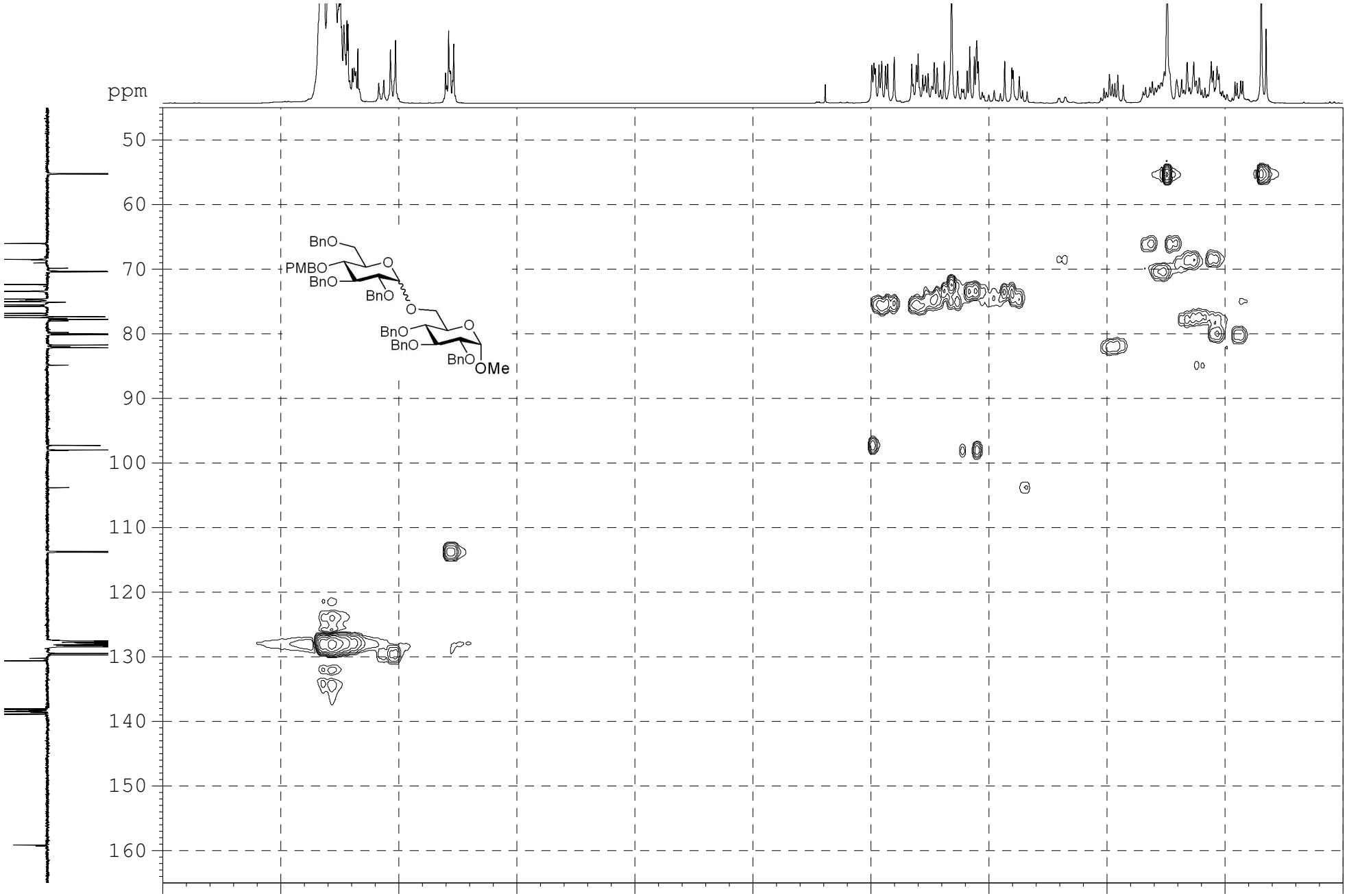

7.331
7.325
7.315
7.307
7.302
7.289
7.277
7.269
7.257
7.248
7.236
7.222
7.218
7.205
7.199
7.193
7.183
7.174
7.166
7.128
7.122
7.109
7.105
5.235
4.987
4.979
4.953
4.929
4.904
4.838
4.824
4.811
4.797
4.788
4.766
4.761
4.723
4.692
4.660
4.633
4.604
4.584
4.581
4.575
4.555
4.550
4.546
4.463
4.436
4.428
4.397
3.986
3.962
3.938
3.803
3.797
3.769
3.760
3.726
3.698
3.677
3.661
3.653
3.649
3.631
3.626
3.564
3.559
3.550
3.535
3.526
3.459
3.451
3.436
3.427
3.349
3.325
BnO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
BnO
OMe
α:β = 2.7:1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm
53.25
2.41
5.60
5.53
1.74
2.96
8.95
0.41
0.39
2.59
10.51
3.81
1.68
3.00
1.12

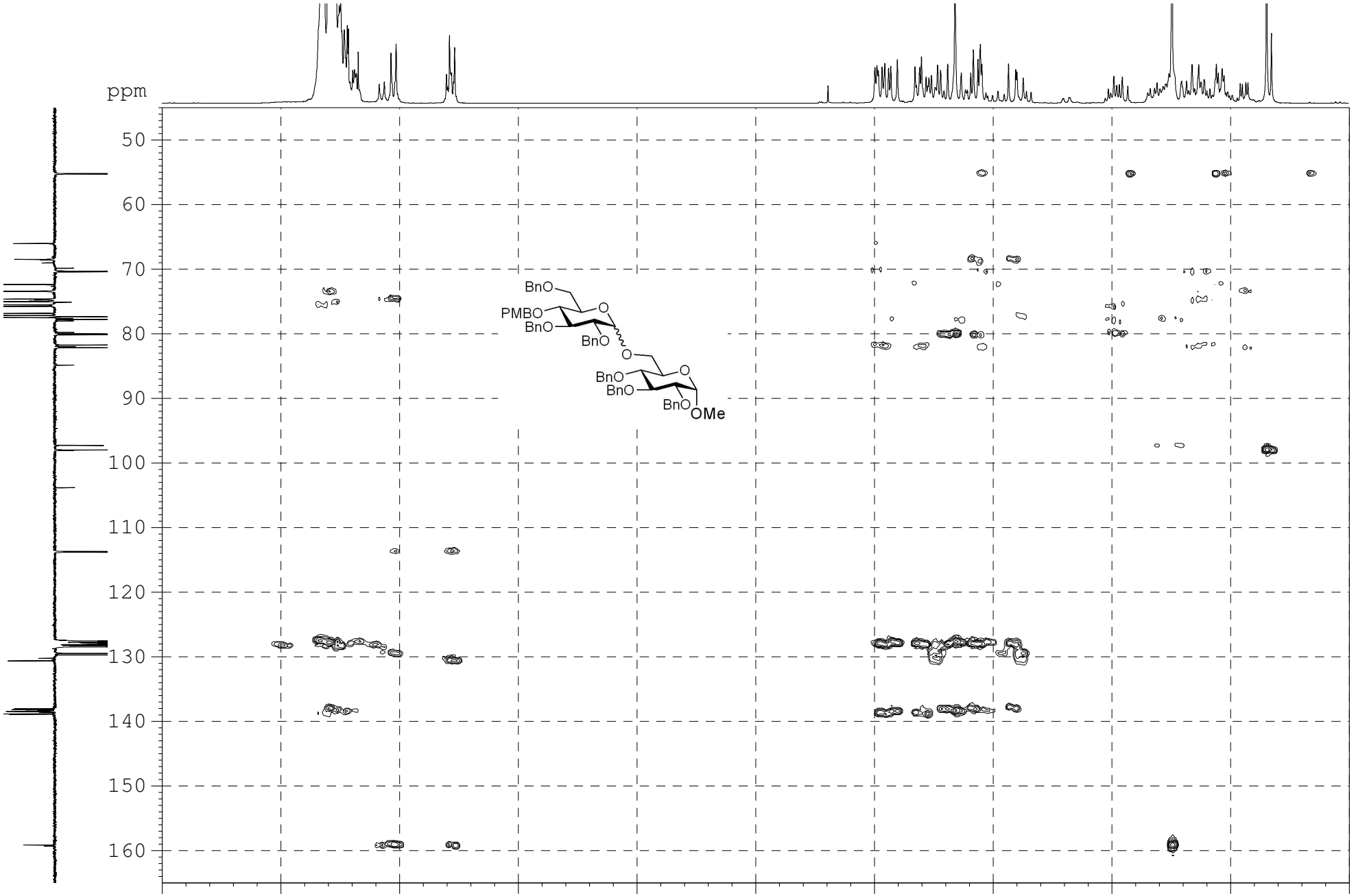
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **24**, α:β = 3:1

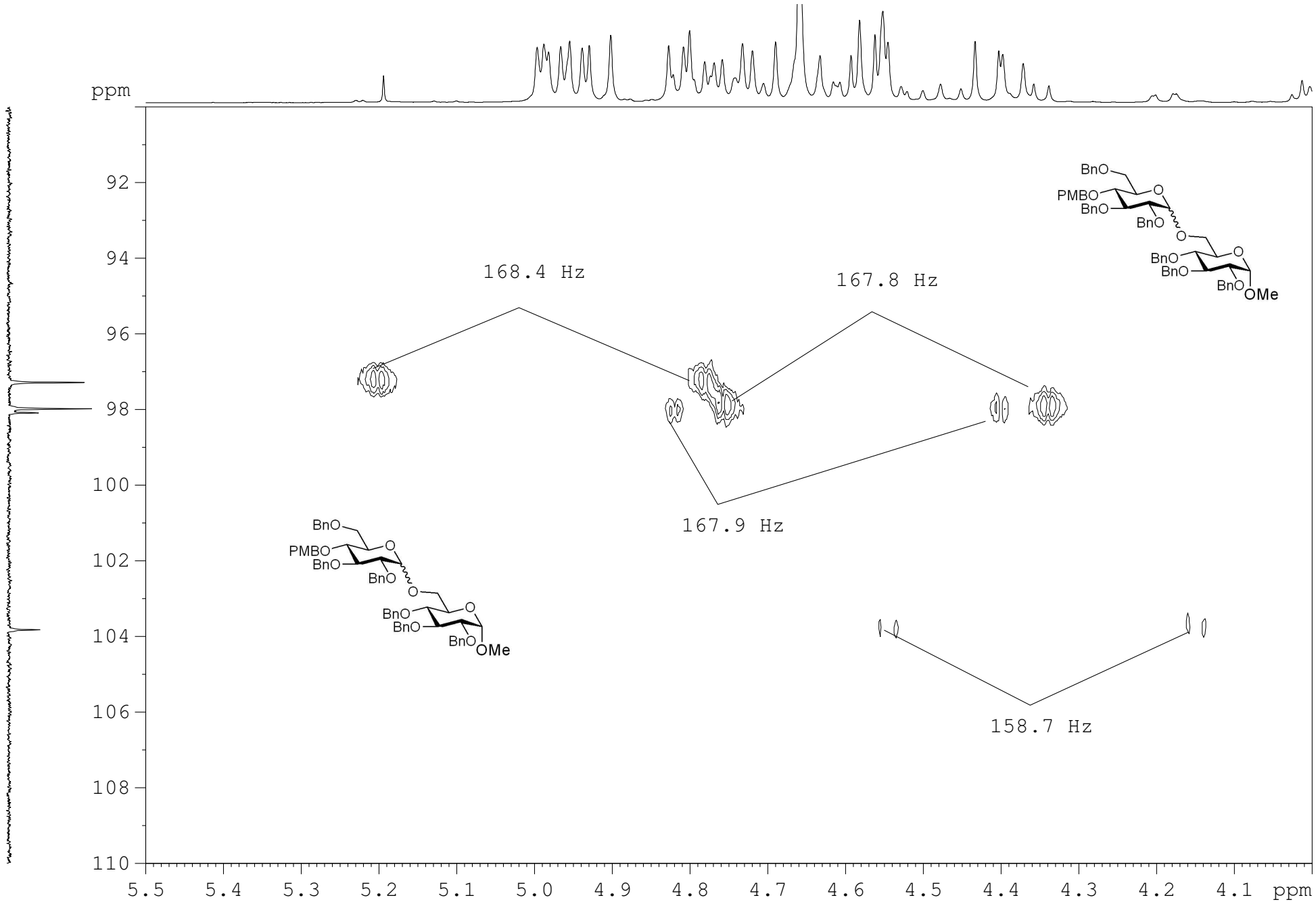



159.16
138.91
138.86
138.49
138.44
138.20
138.02
130.63
129.72
129.48
128.49
128.45
128.41
128.40
128.38
128.19
128.05
128.01
127.94
127.89
127.81
127.69
127.65
127.61
127.54
113.83
113.71
103.83
98.09
97.98
97.28
82.15
81.74
80.14
80.00
77.77
77.48
77.35
77.16
76.84
75.75
75.51
75.02
74.62
73.42
73.40
72.38
70.41
70.28
68.47
66.02
55.27
55.23
55.18
BnO
PMBO
BnO
O
BnO
O
O
BnO
BnO
BnO
OMe
α:β = 3:1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

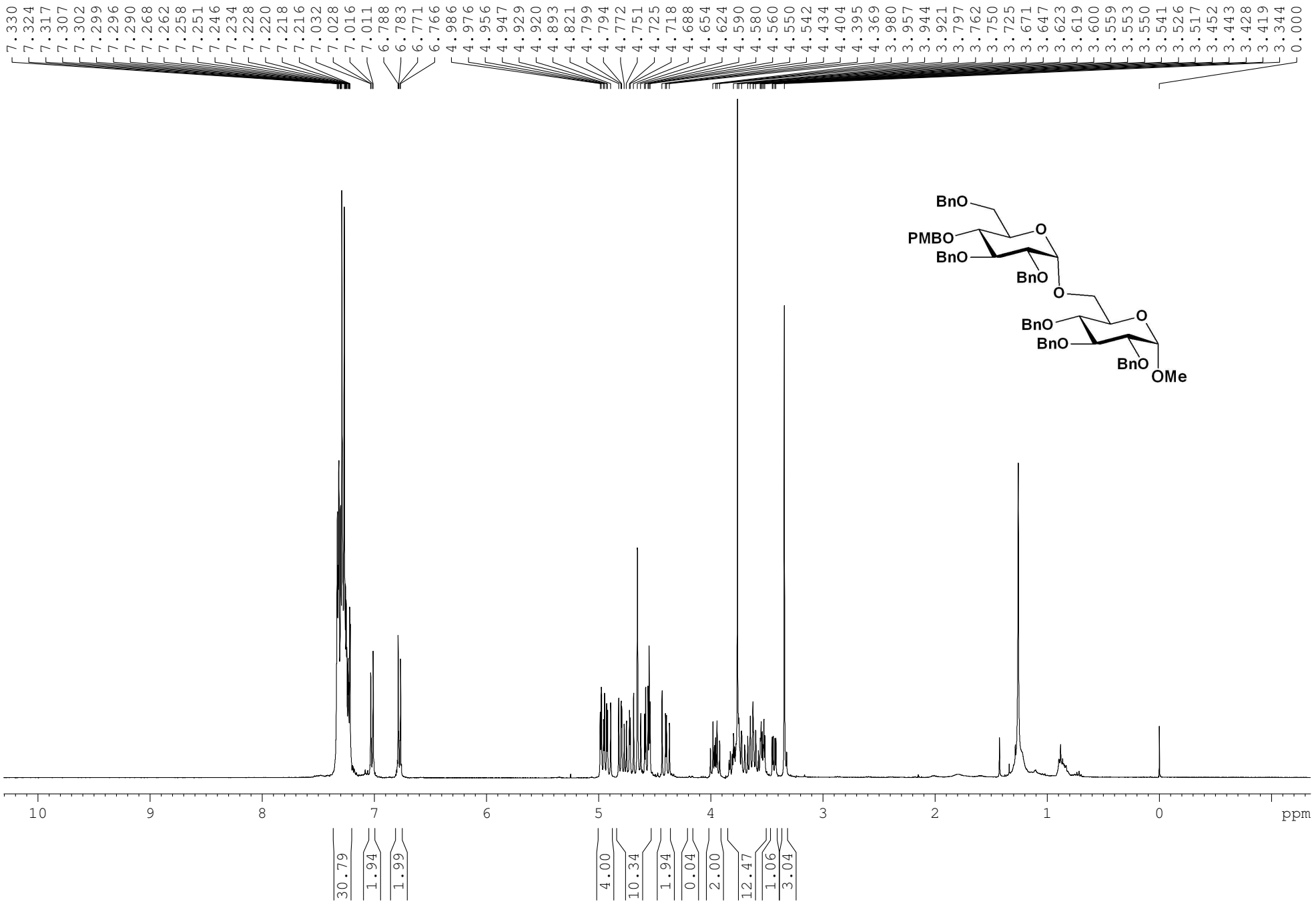

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
BnO
PMBO
BnO
BnO
O
BnO
BnO
BnO
O
OMe

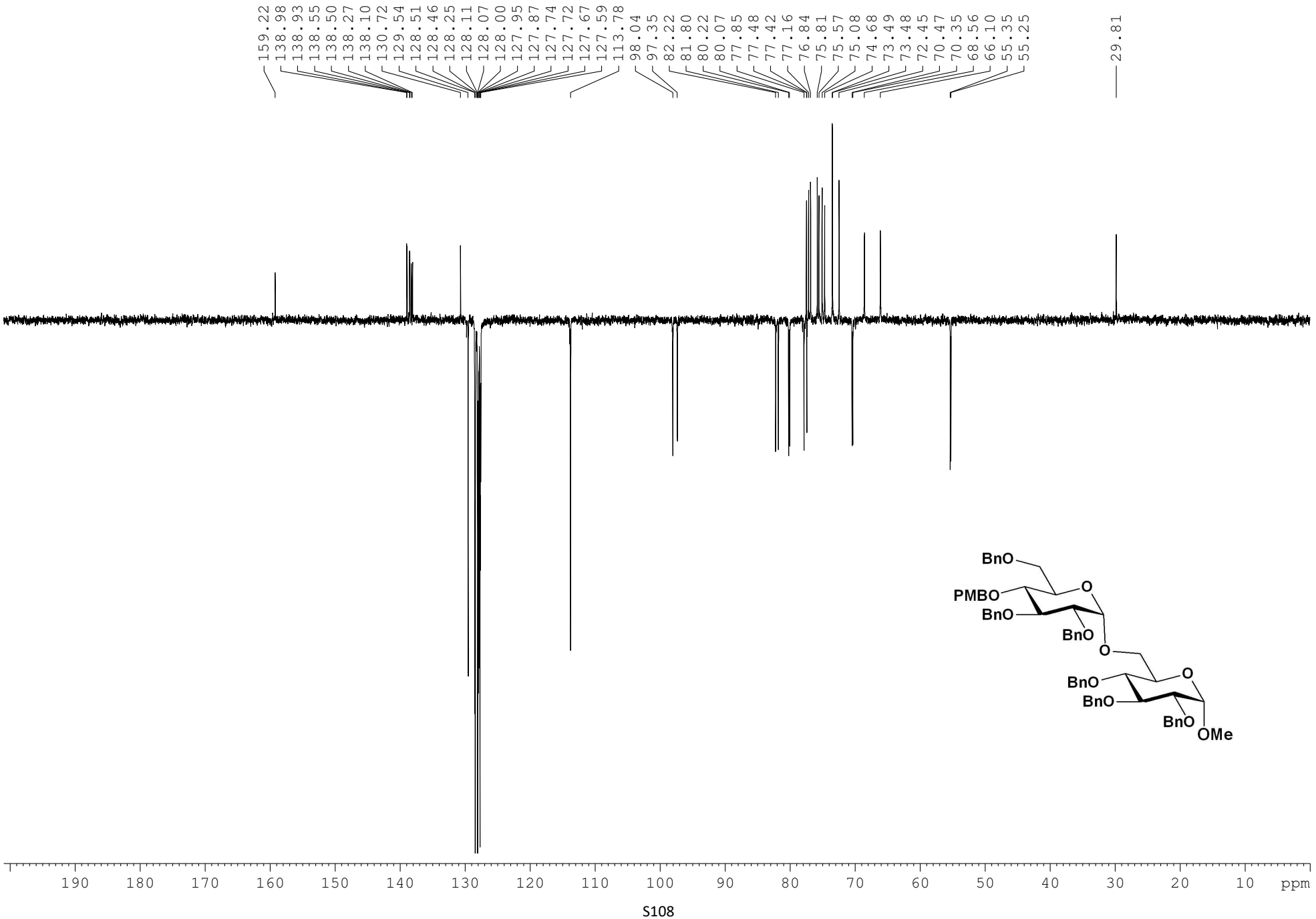

ppm
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
PMBO
BnO
BnO
O
O
BnO
BnO
BnO
OMe

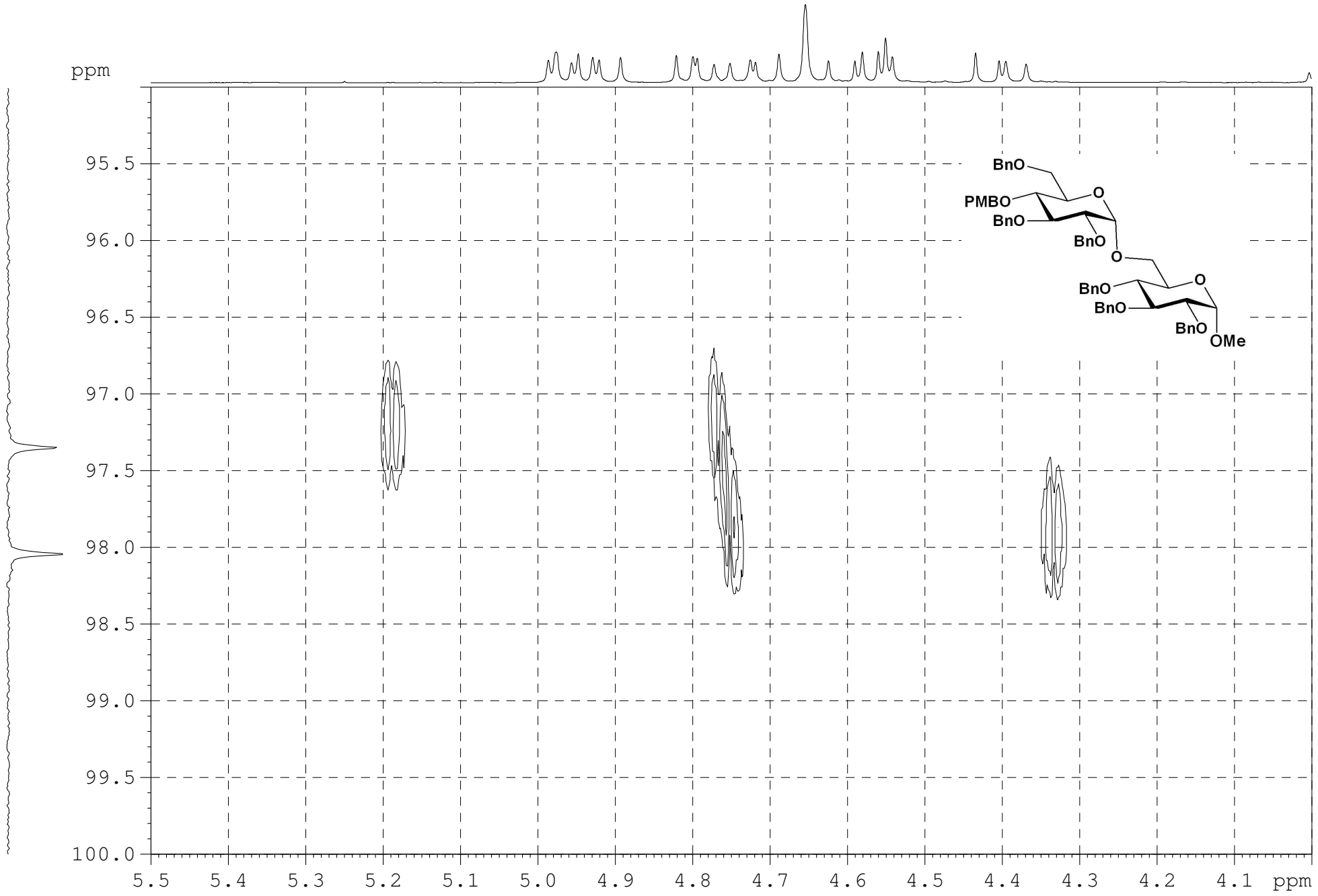

ppm
50
60
70
80
90
100
110
120
130
140
150
160
BnO
PMBO
BnO
BnO
O
O
BnO
BnO
BnO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

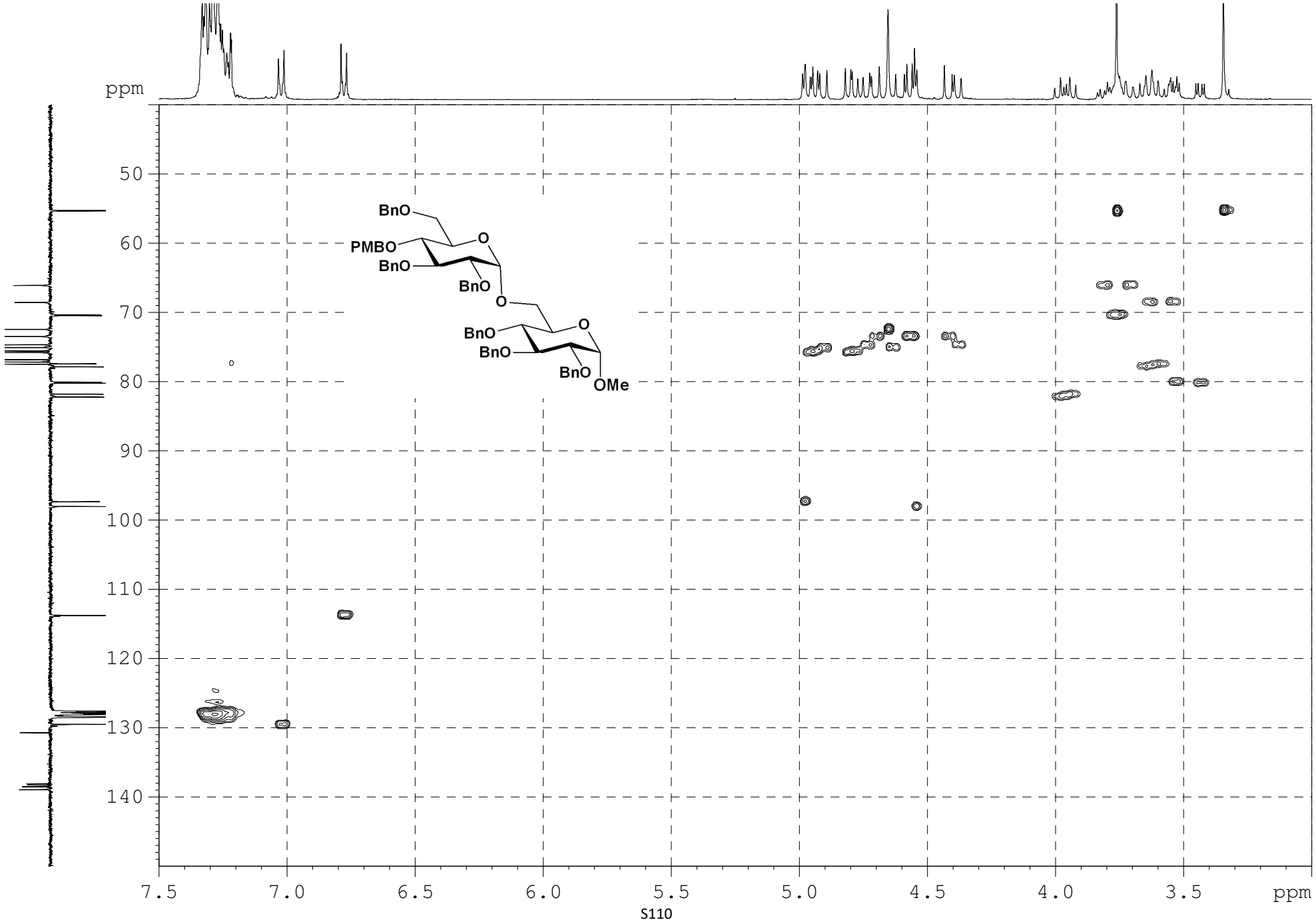

ppm
92
94
96
98
100
102
104
106
108
110
168.4 Hz
167.8 Hz
167.9 Hz
158.7 Hz
BnO
PMBO
BnO
BnO
O
BnO
BnO
BnO
OMe
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
ppm

^{1}H-NMR, ^{13}C-APT, HSQC, GATED of **24**

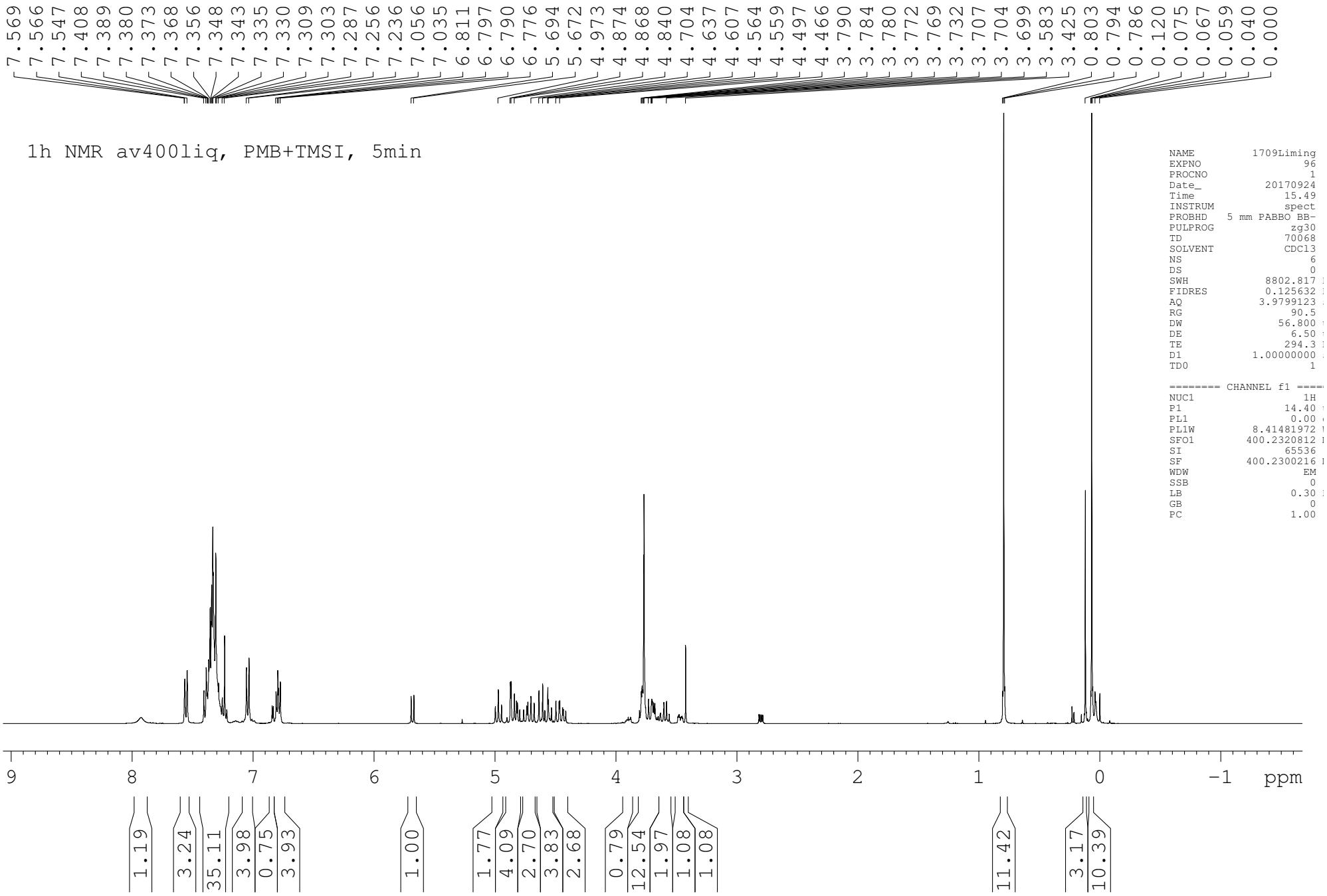


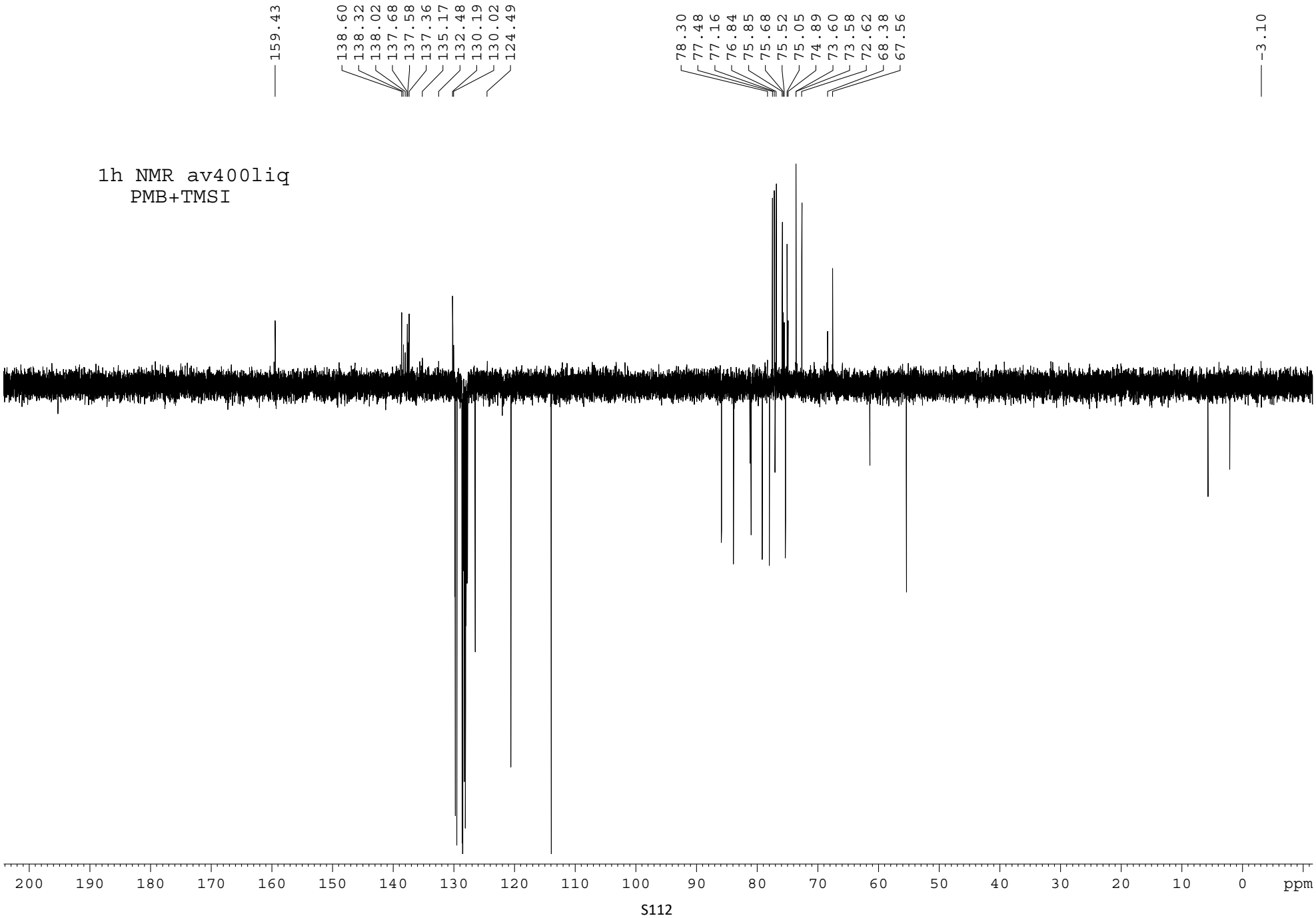

159.22
138.98
138.93
138.55
138.50
138.27
138.10
130.72
129.54
128.51
128.46
128.25
128.11
128.07
128.00
127.95
127.87
127.74
127.72
127.67
127.59
113.78
98.04
97.35
82.22
81.80
80.22
80.07
77.85
77.48
77.42
77.16
76.84
75.81
75.57
75.08
74.68
73.49
73.48
72.45
70.47
70.35
68.56
66.10
55.35
55.25
29.81
BnO
PMBO
BnO
O
BnO
O
BnO
BnO
O
BnO
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

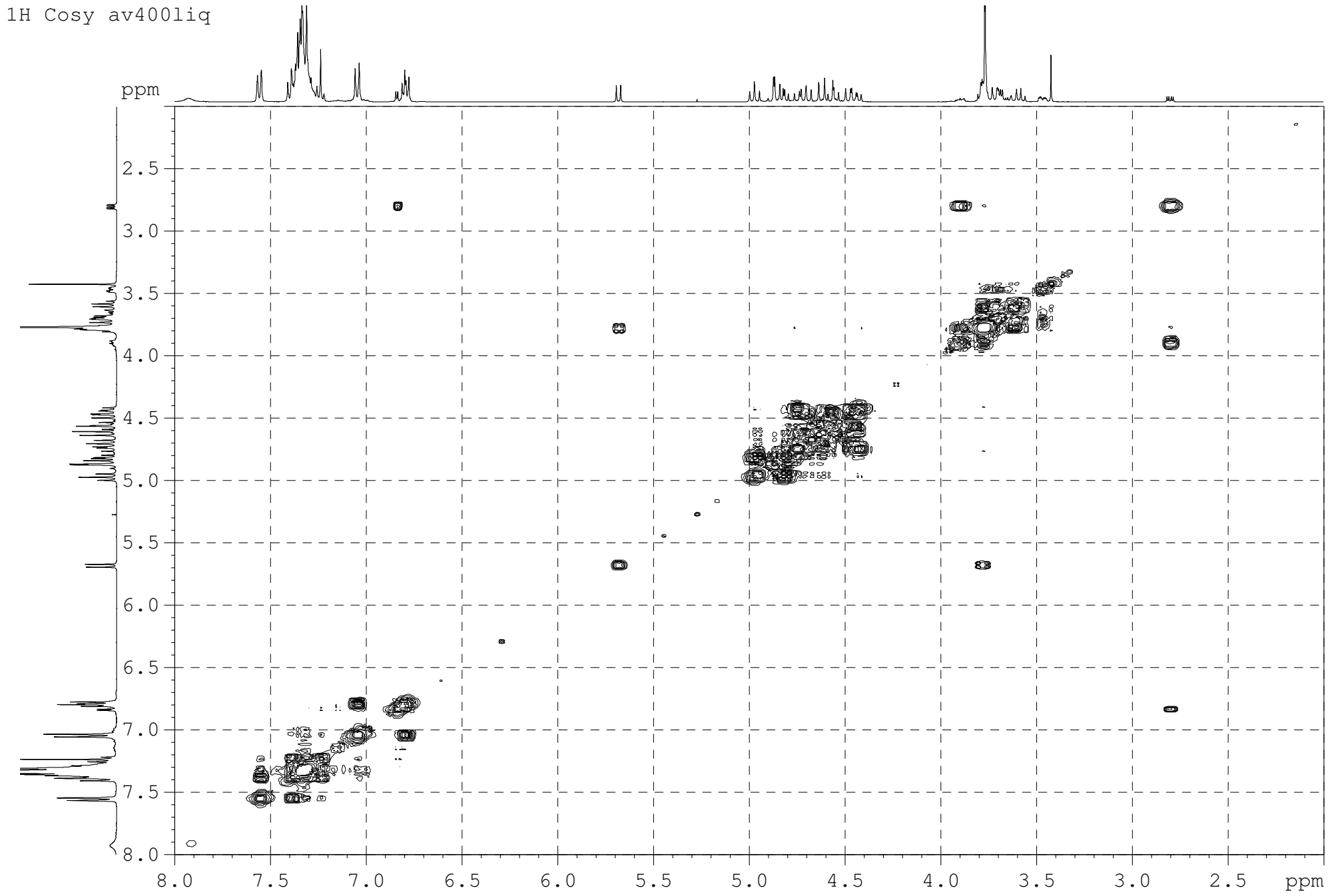

ppm
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
ppm
BnO
PMBO
BnO
O
BnO
O
BnO
BnO
O
BnO
OMe

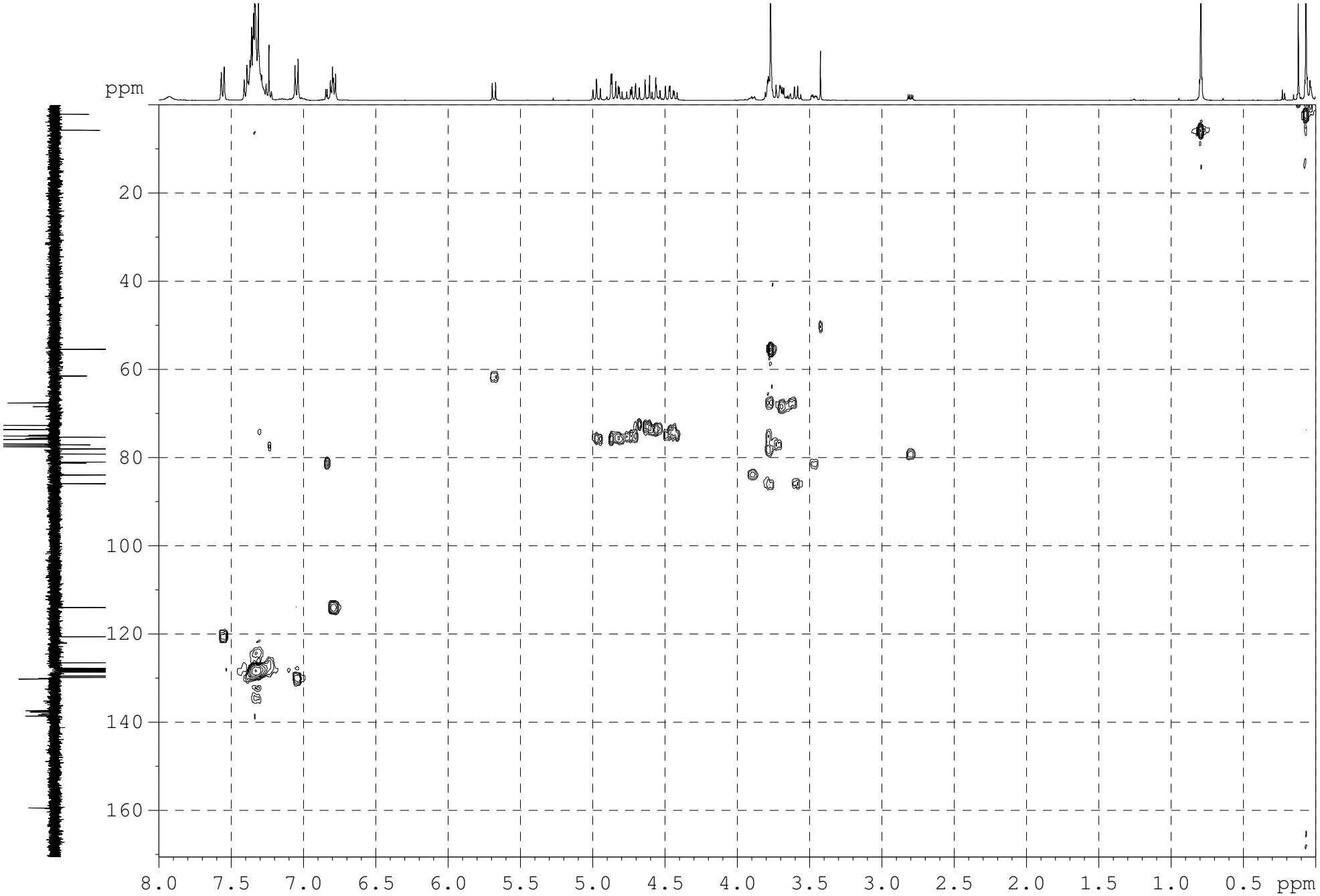

ppm
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
BnO
PMBO
BnO
O
BnO
O
O
BnO
BnO
BnO
OMe

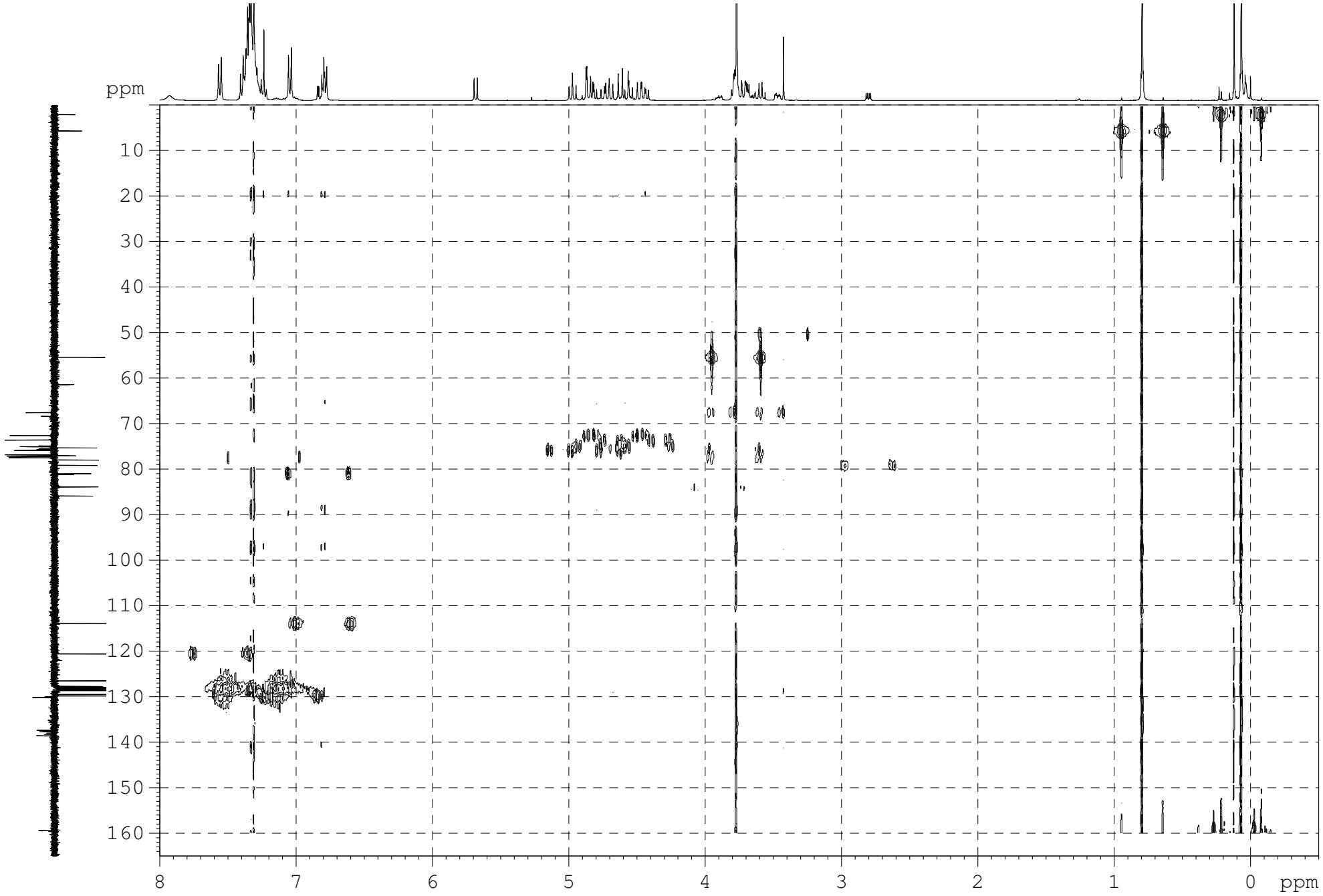
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC of **25**



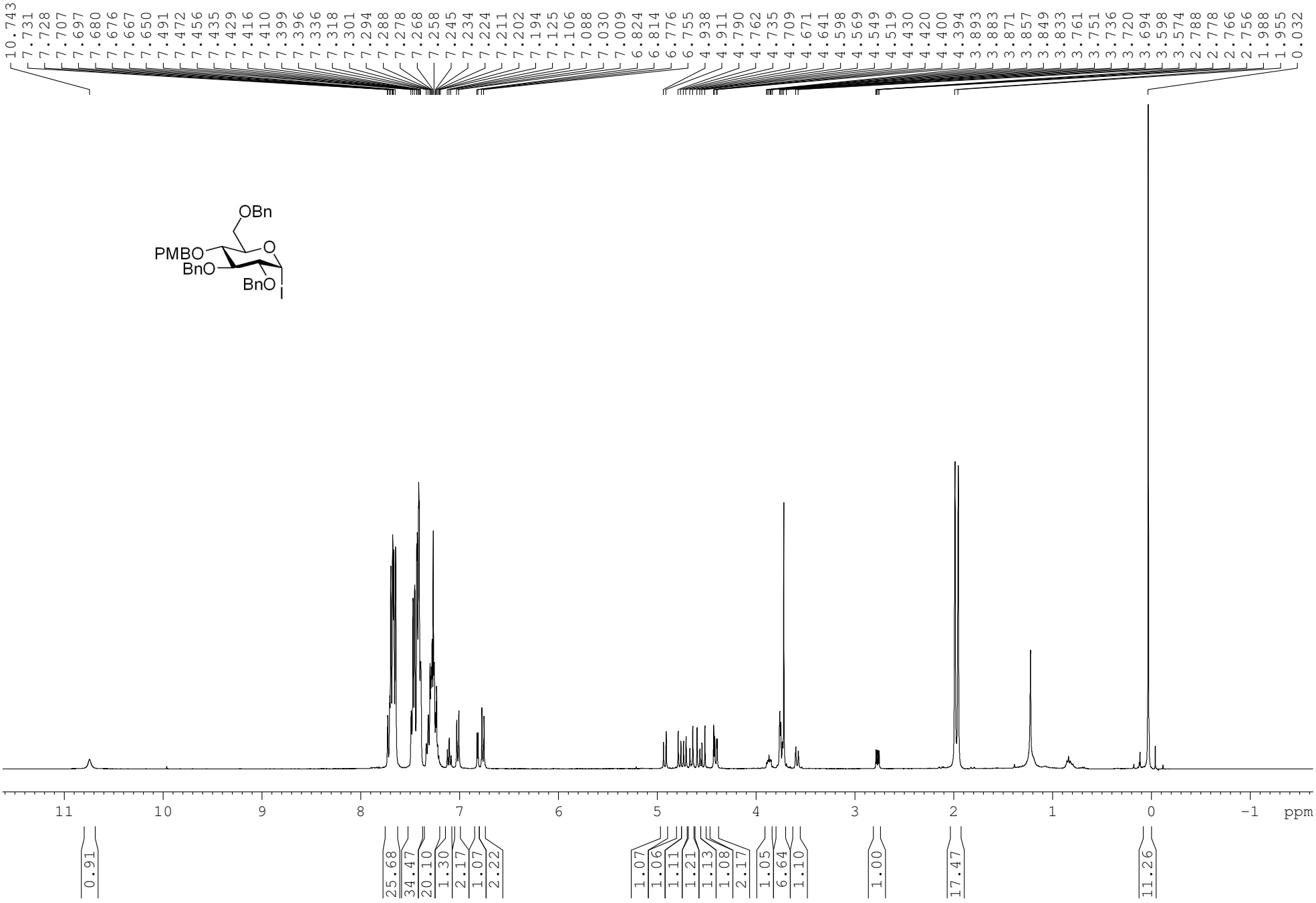

159.43
138.60
138.32
138.02
137.68
137.58
137.36
135.17
132.48
130.19
130.02
124.49
78.30
77.48
77.16
76.84
75.85
75.68
75.52
75.05
74.89
73.60
73.58
72.62
68.38
67.56
-3.10
1h NMR av400liq
PMB+TMSI
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

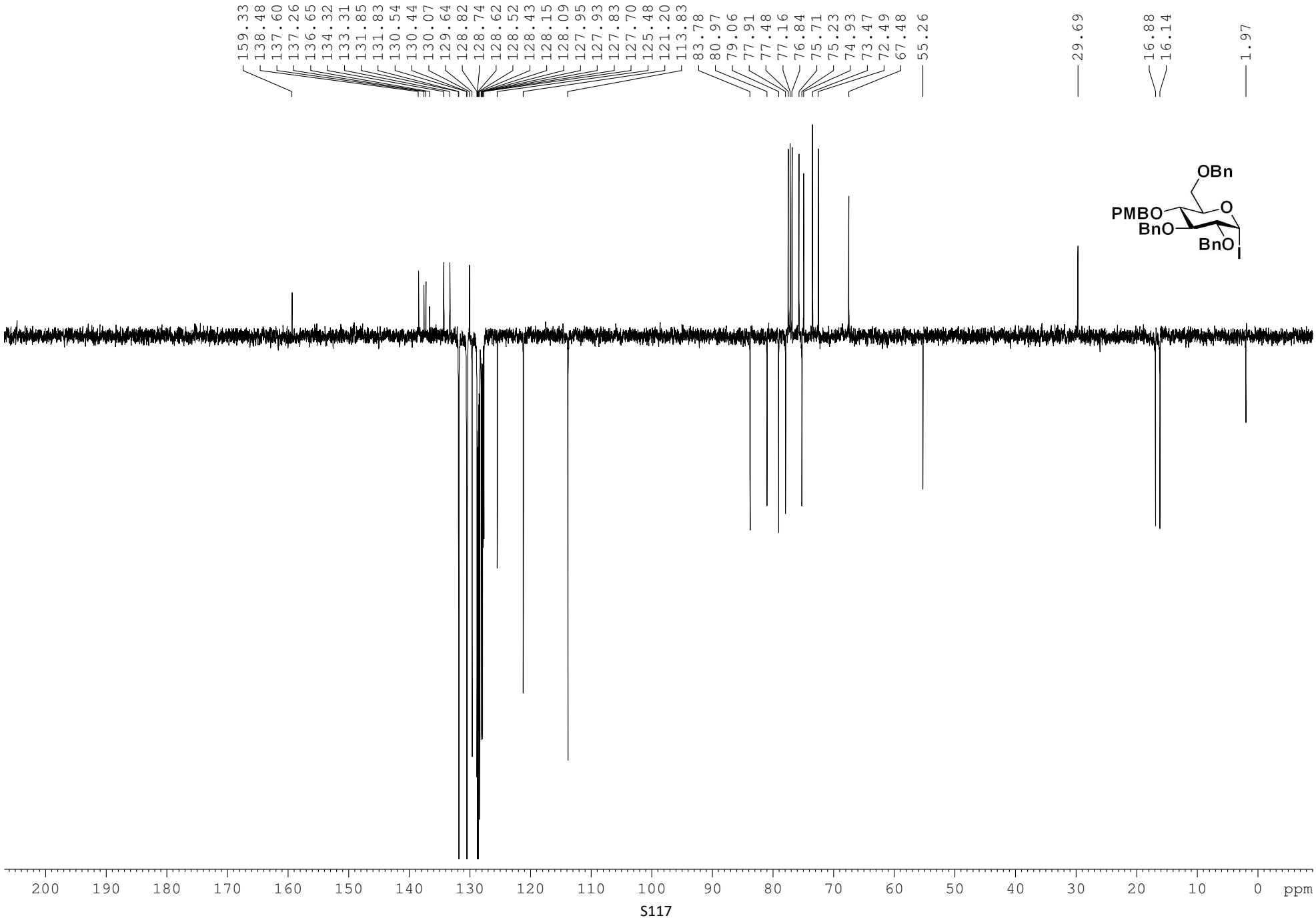

1H Cosy av400liq
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

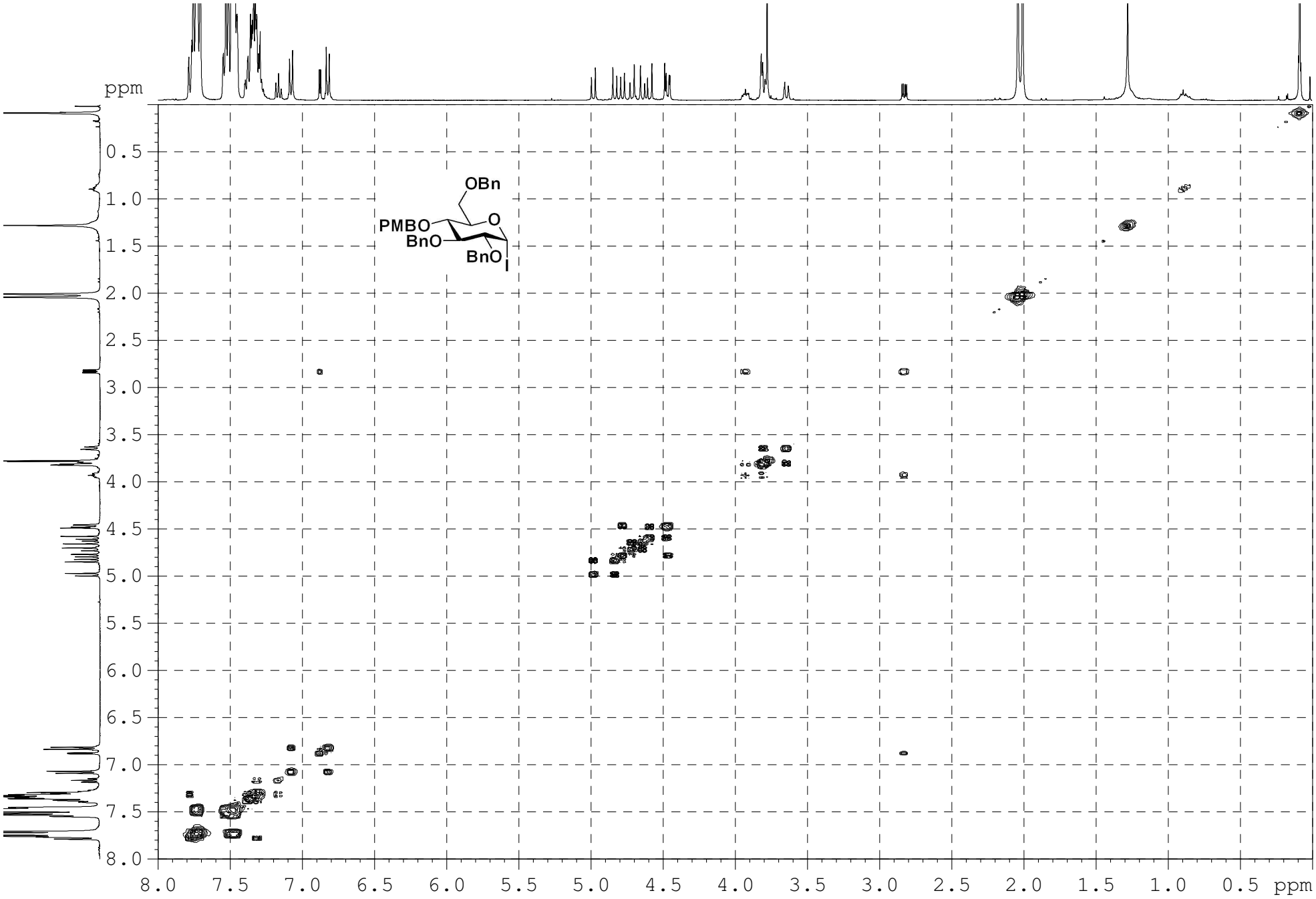

ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

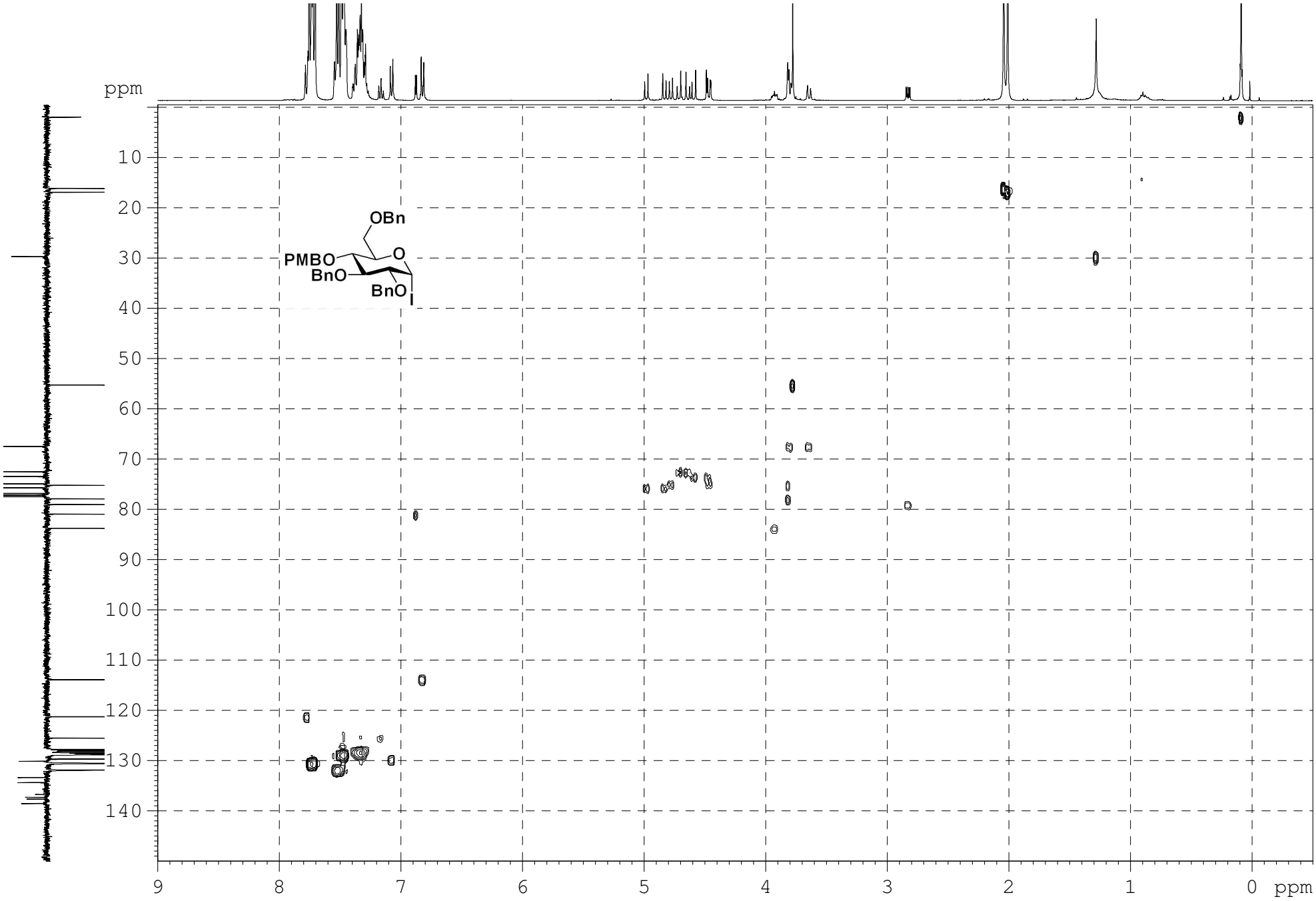

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8
7
6
5
4
3
2
1
0
ppm

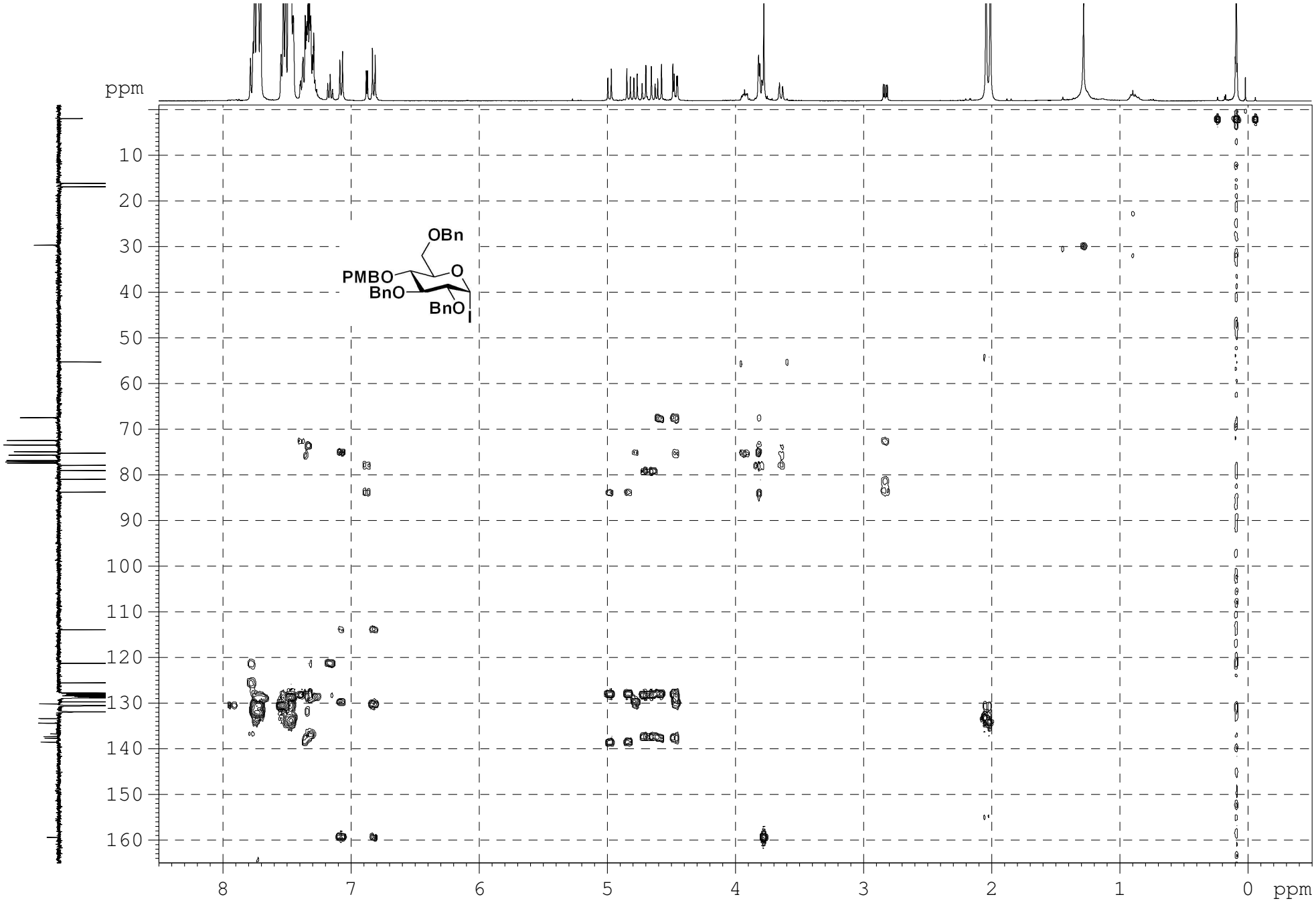
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **26**



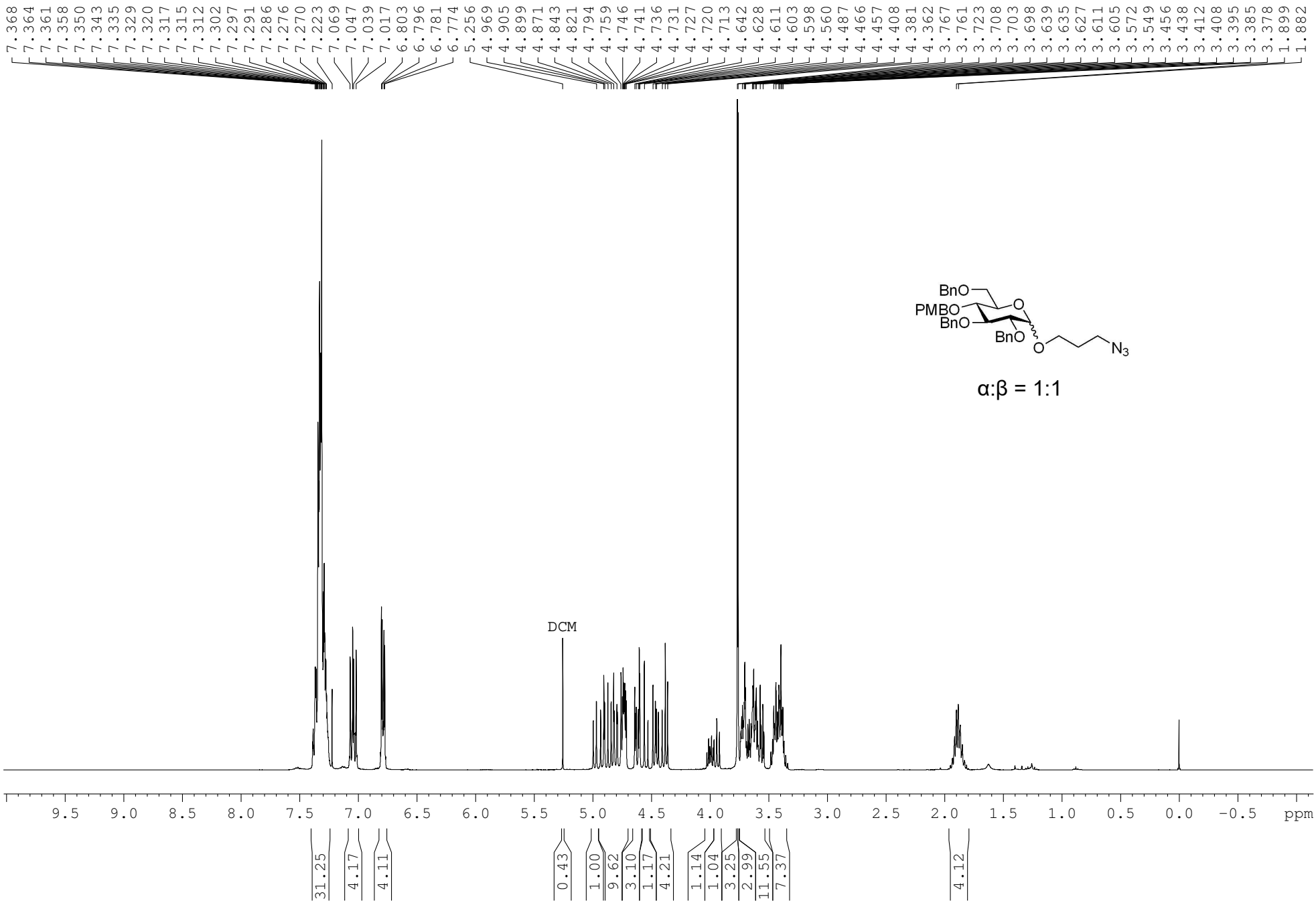

159.33
138.48
137.60
137.26
136.65
134.32
133.31
131.85
131.83
130.54
130.44
130.07
129.64
128.82
128.74
128.62
128.52
128.43
128.15
128.09
127.95
127.93
127.83
127.70
125.48
121.20
113.83
83.78
80.97
79.06
77.91
77.48
77.16
76.84
75.71
75.23
74.93
73.47
72.49
67.48
55.26
29.69
16.88
16.14
1.97
OBn
PMBO
BnO
BnO
O
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

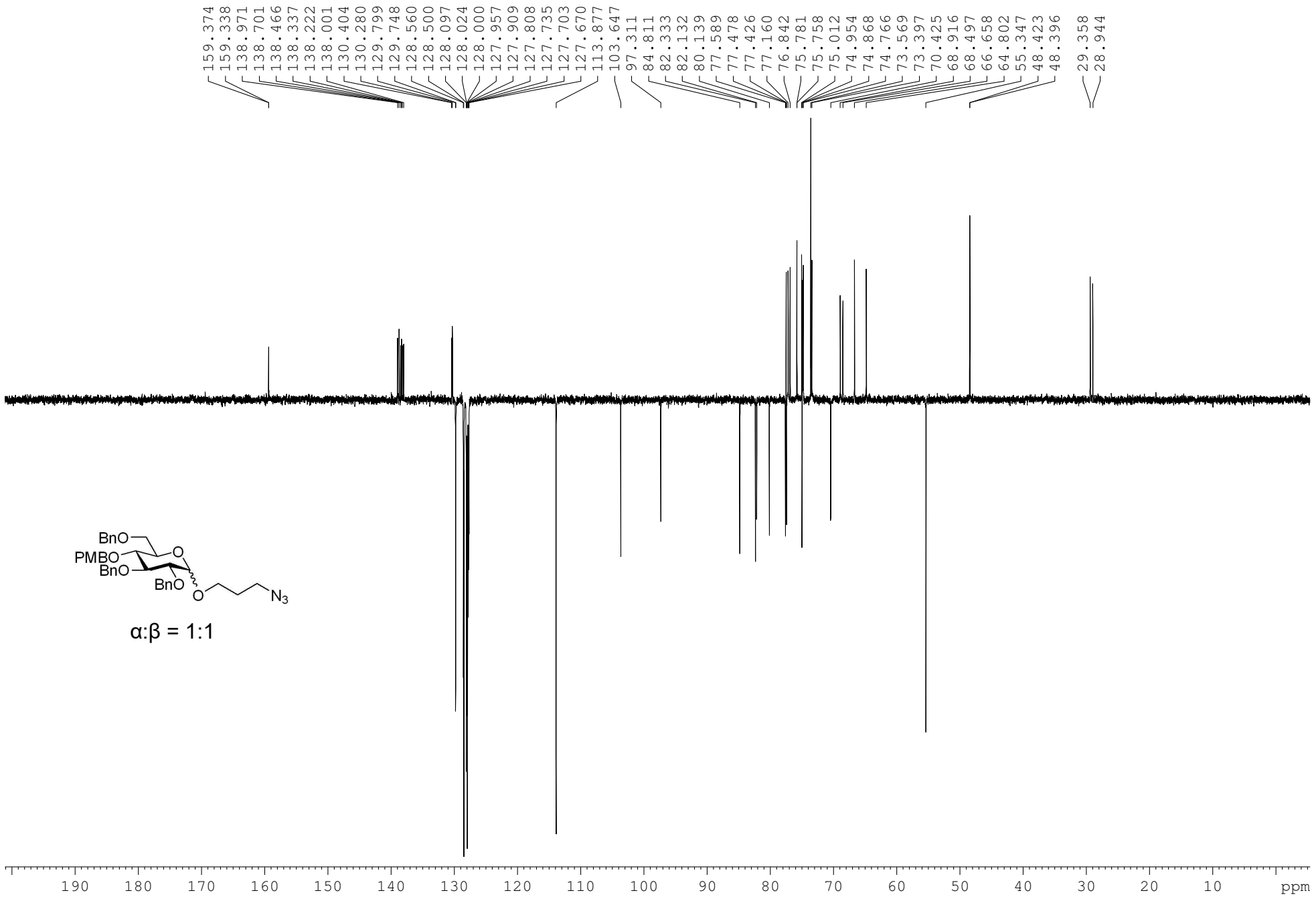

ppm
OBn
PMBO
BnO
BnO
I
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

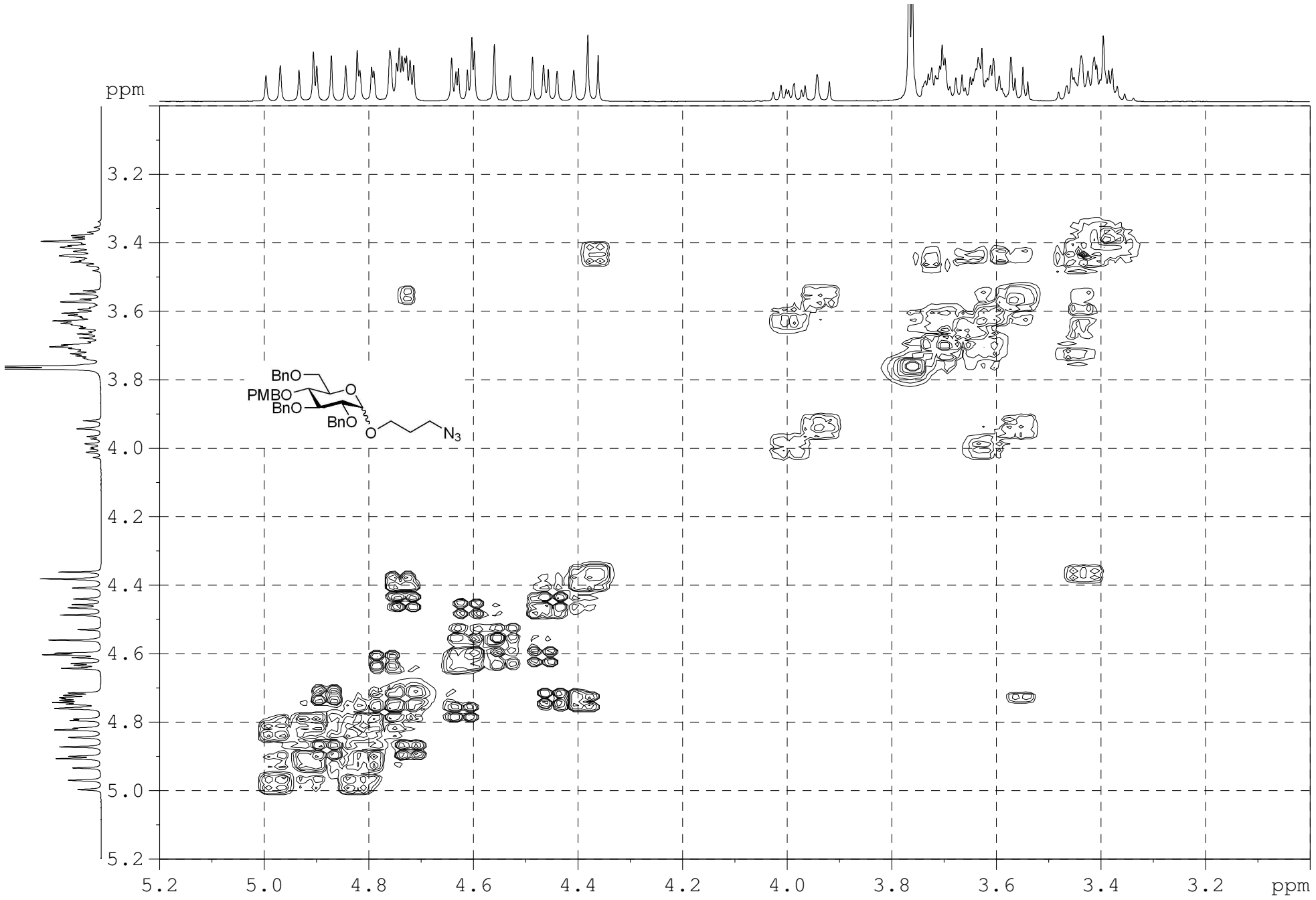

ppm
OBn
PMBO
O
BnO
BnO
I
10
20
30
40
50
60
70
80
90
100
110
120
130
140
9
8
7
6
5
4
3
2
1
0
ppm

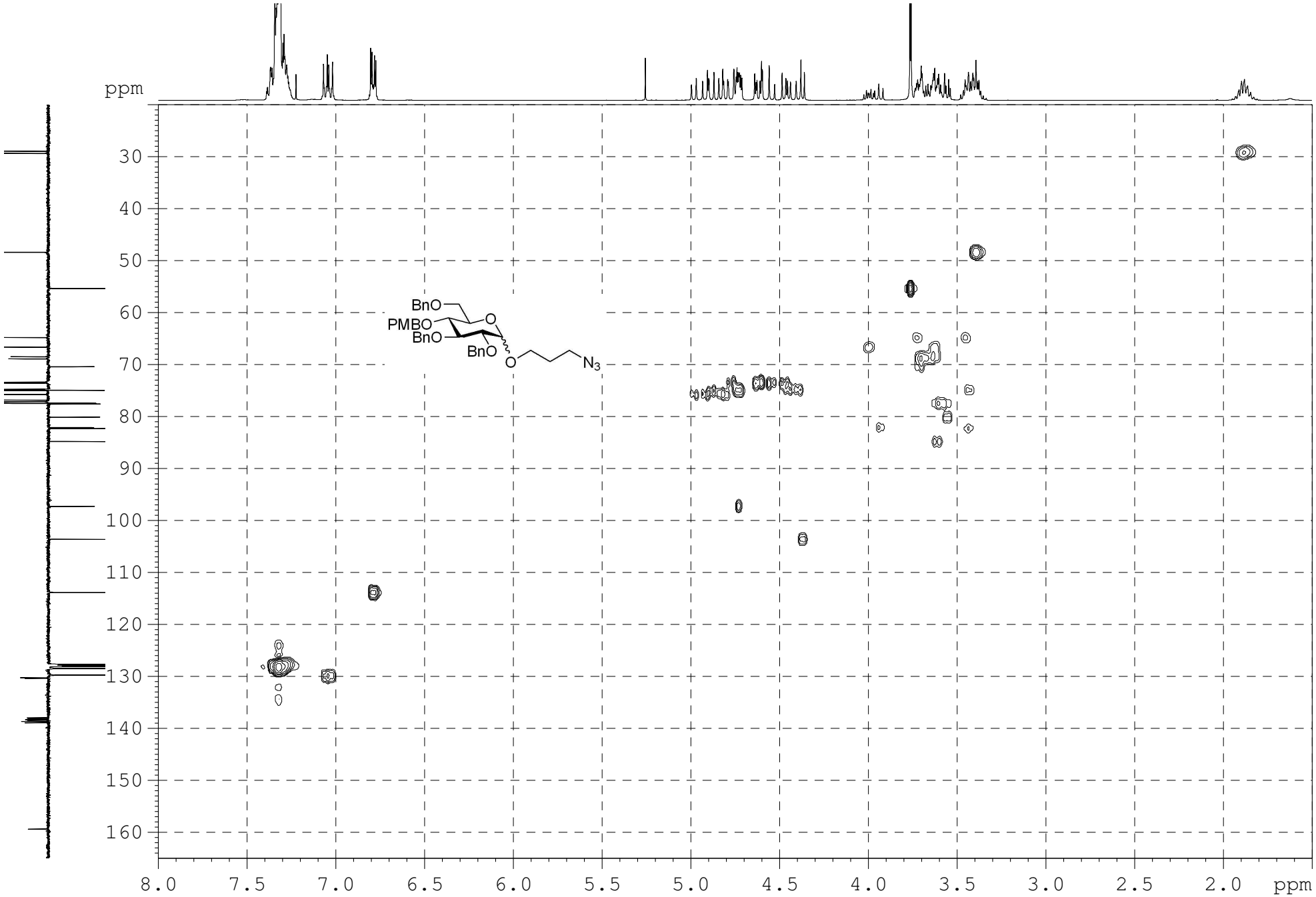

ppm
OBn
PMBO
O
BnO
BnO
I
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8
7
6
5
4
3
2
1
0
ppm

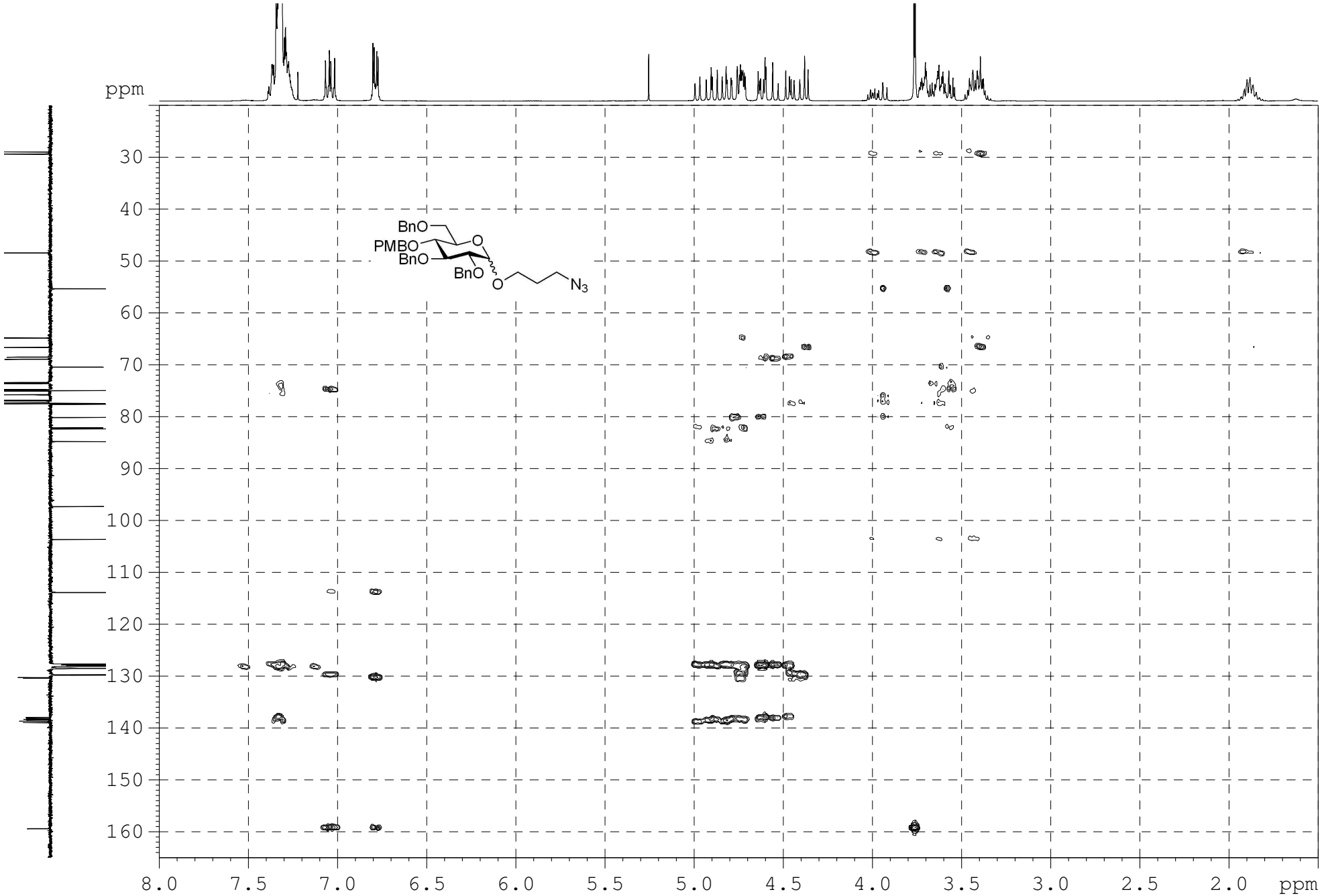
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **27**, α:β = 1:1

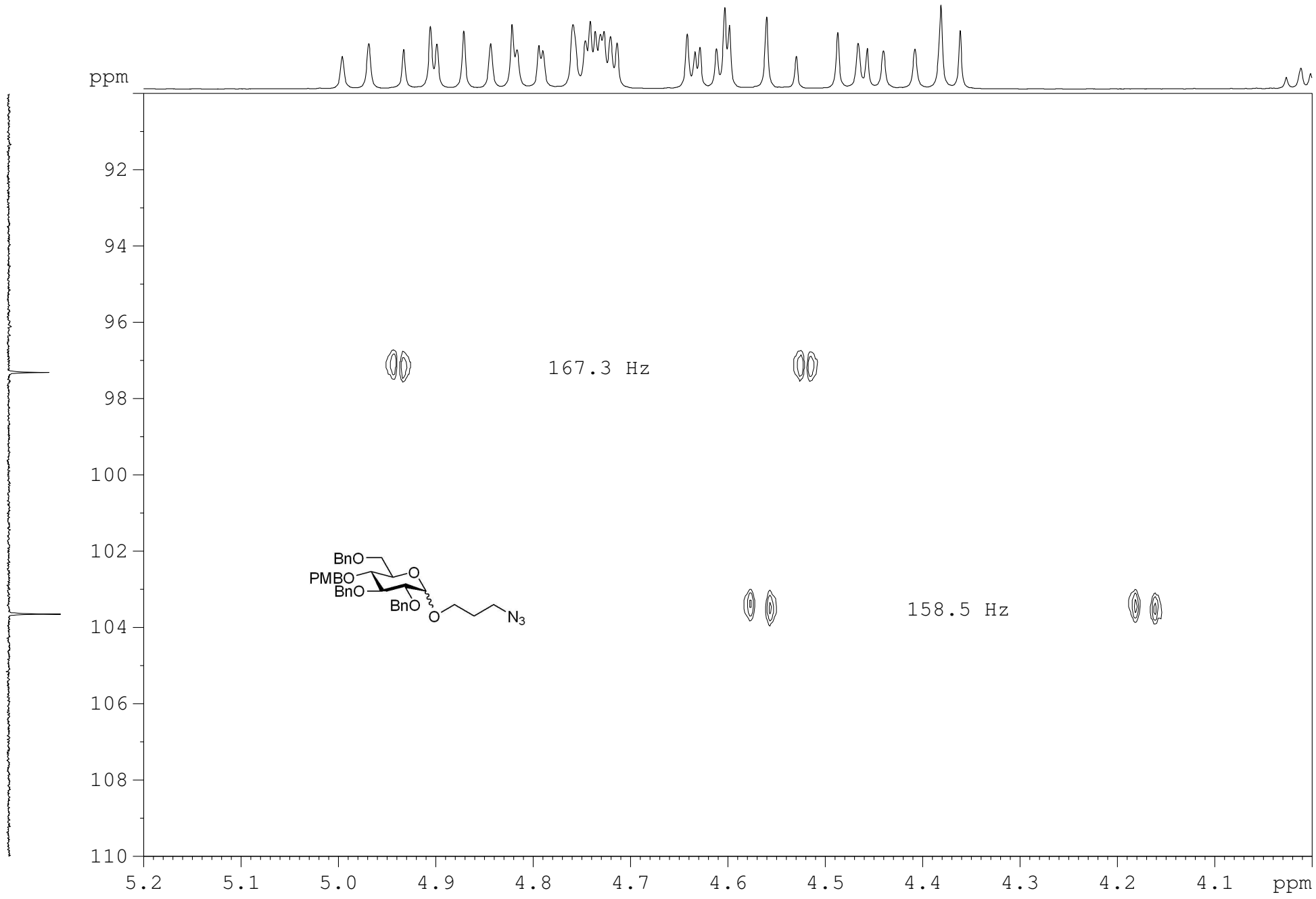



159.374
159.338
138.971
138.701
138.466
138.337
138.222
138.001
130.404
130.280
129.799
129.748
128.560
128.500
128.097
128.024
128.000
127.957
127.909
127.808
127.735
127.703
127.670
113.877
103.647
97.311
84.811
82.333
82.132
80.139
77.589
77.478
77.426
77.160
76.842
75.781
75.758
75.012
74.954
74.868
74.766
73.569
73.397
70.425
68.916
68.497
66.658
64.802
55.347
48.423
48.396
29.358
28.944
BnO
PMBO
BnO
BnO
O
O
N3
α:β = 1:1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

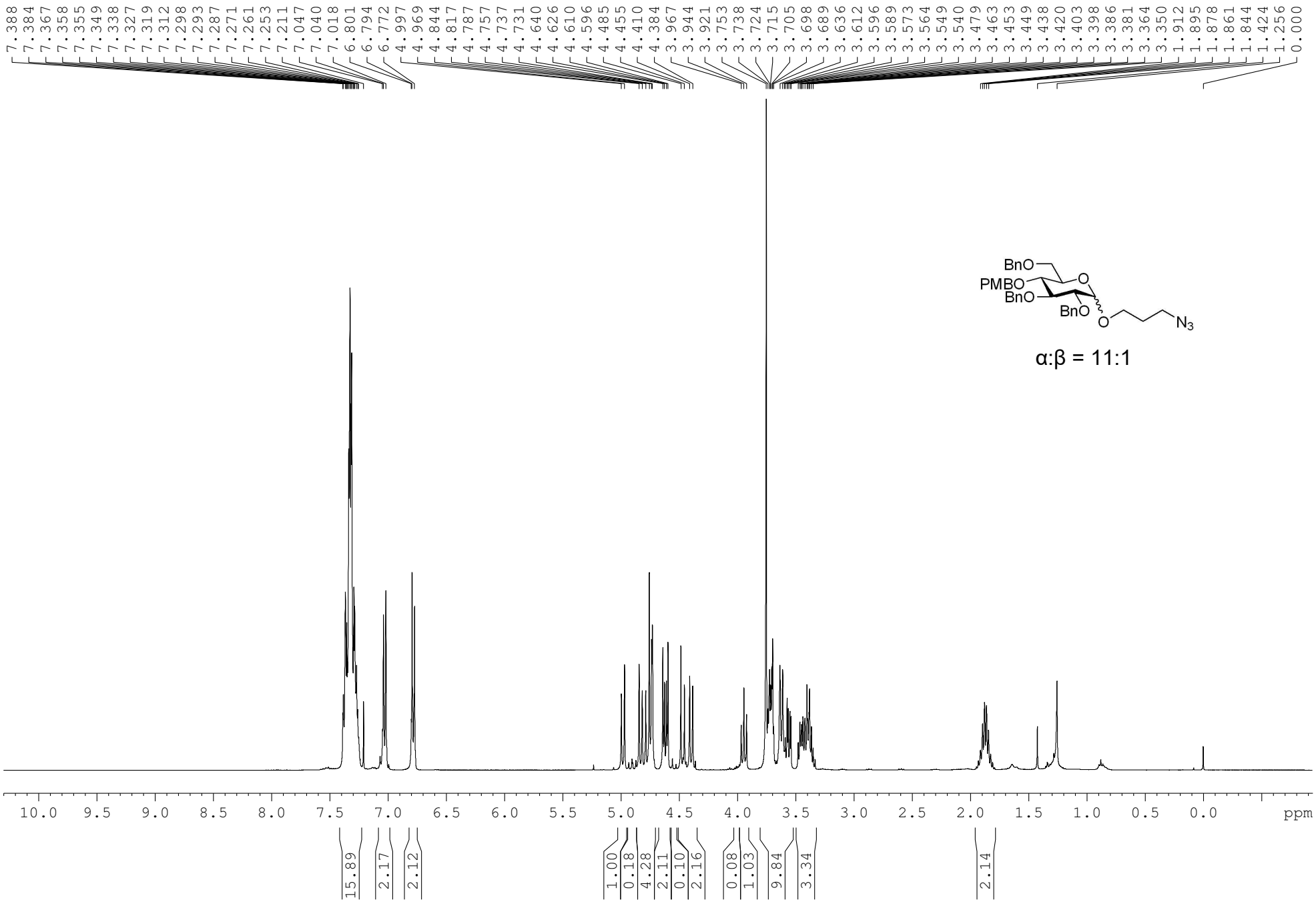

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
BnO
PMBO
BnO
BnO
O
O
N3
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

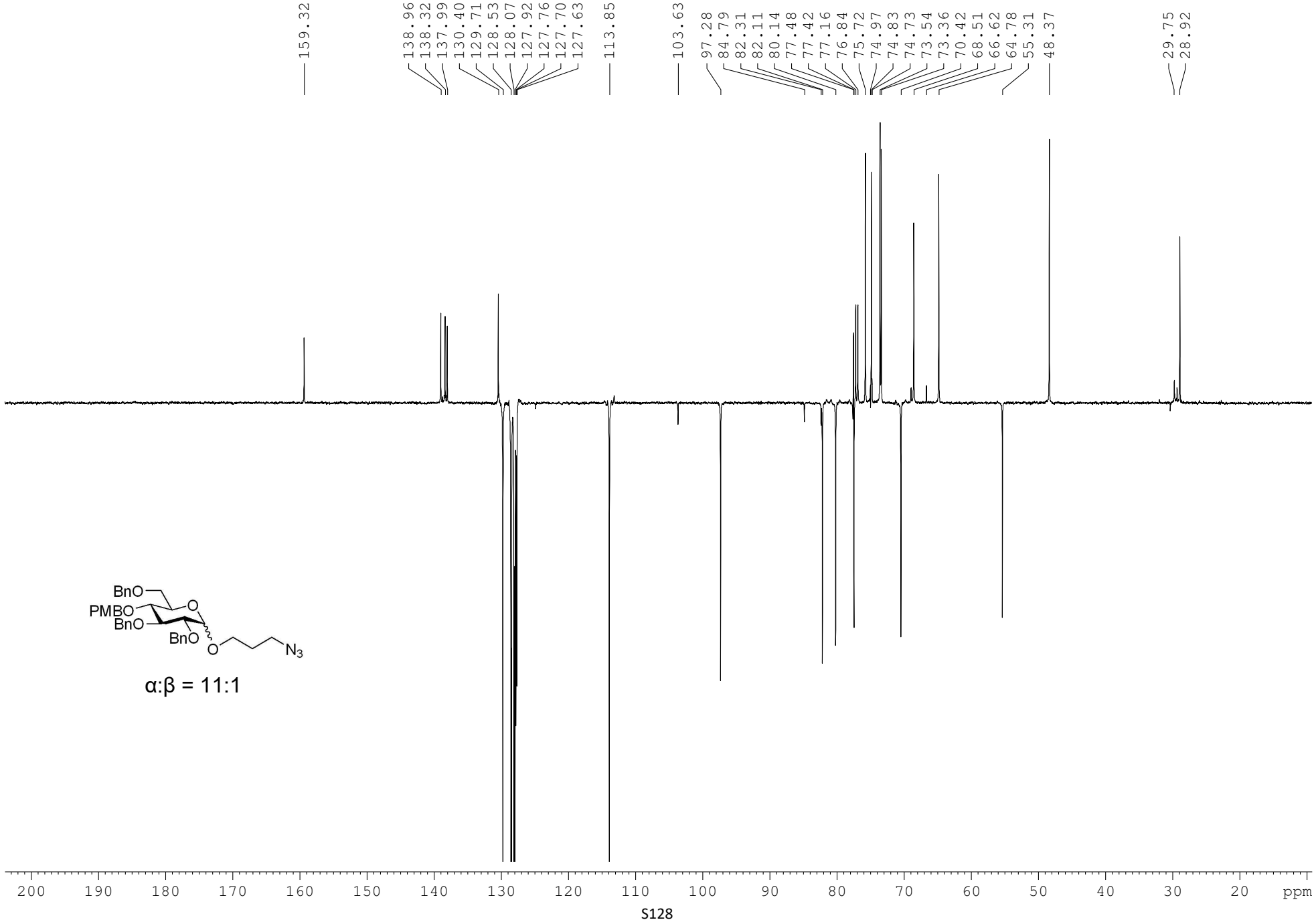

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
BnO
PMBO
BnO
BnO
O
O
N3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
BnO
PMBO
BnO
BnO
O
O
N3
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
ppm

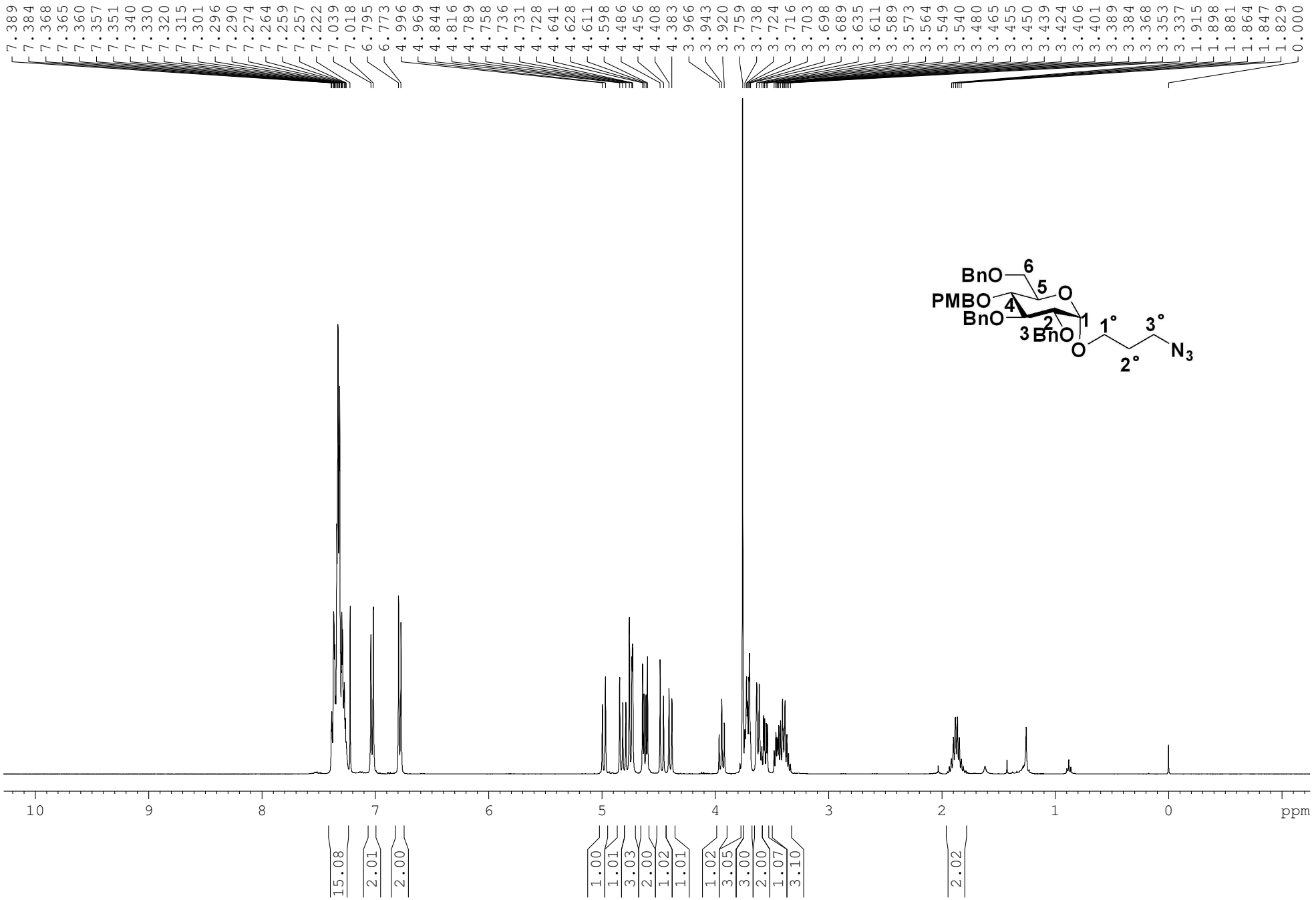

ppm
92
94
96
98
100
102
104
106
108
110
167.3 Hz
158.5 Hz
BnO
PMBO
BnO
BnO
O
O
N3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
ppm

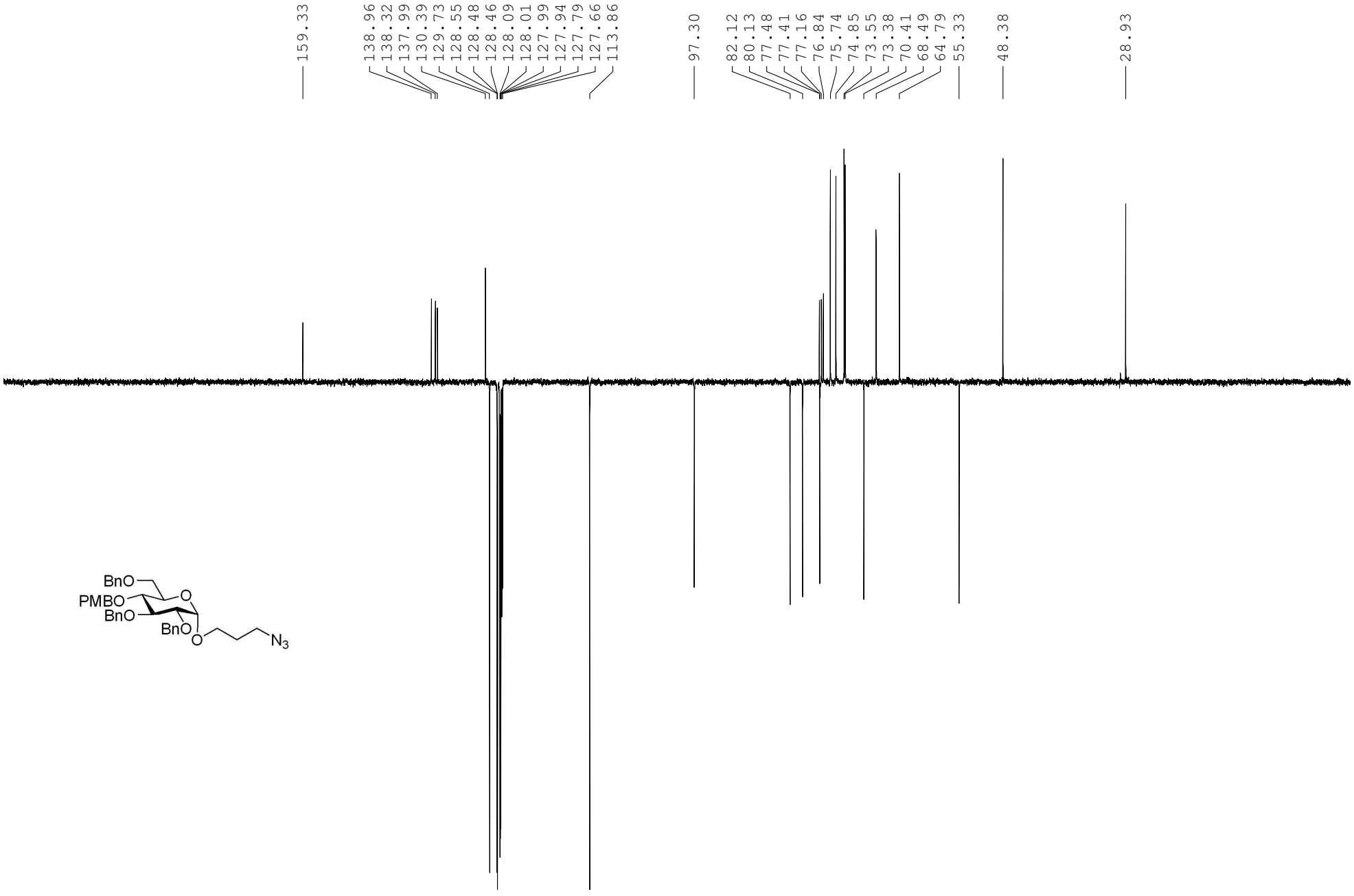
^{1}H-NMR, ^{13}C-APT of **27**, α:β = 1:1

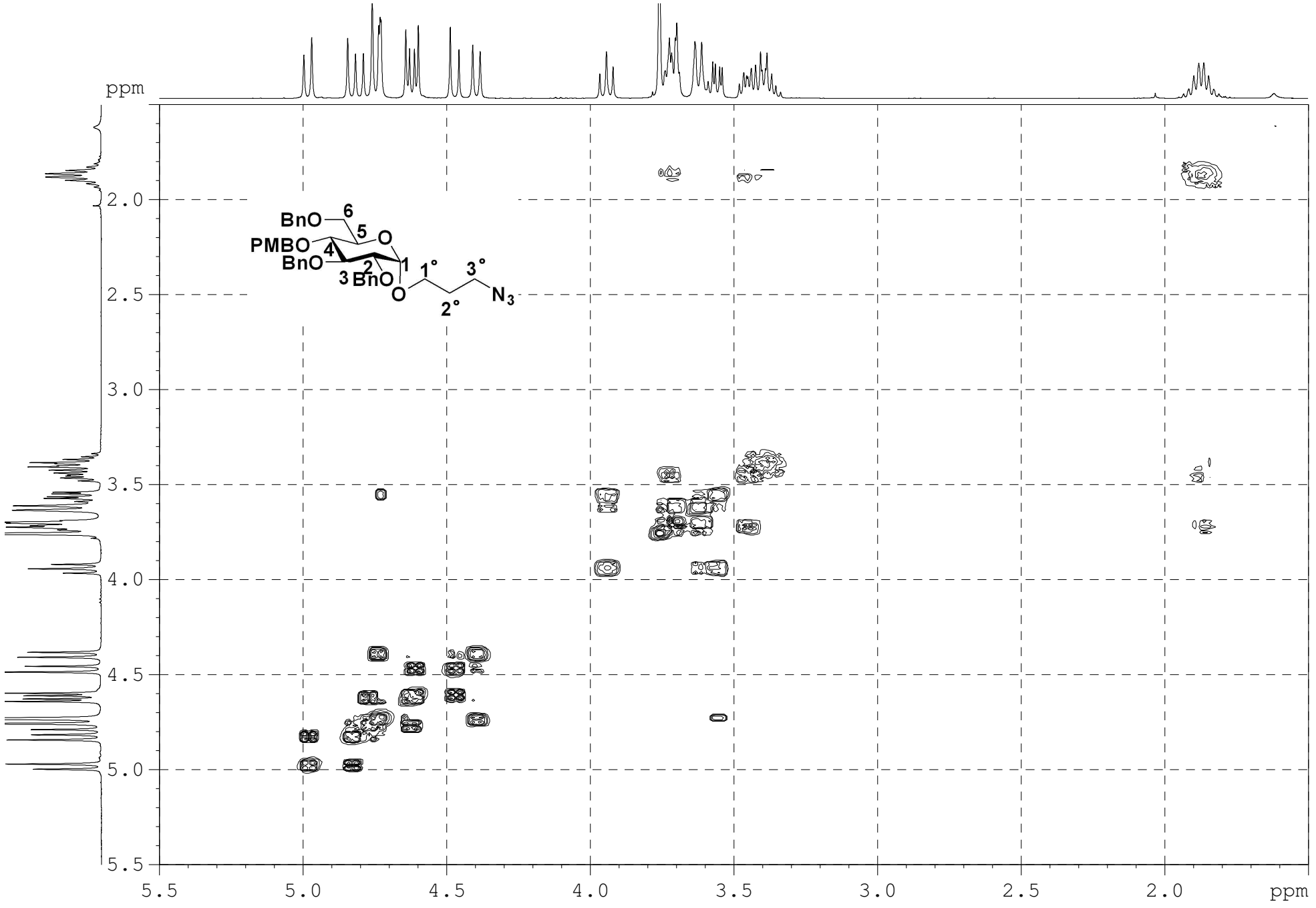


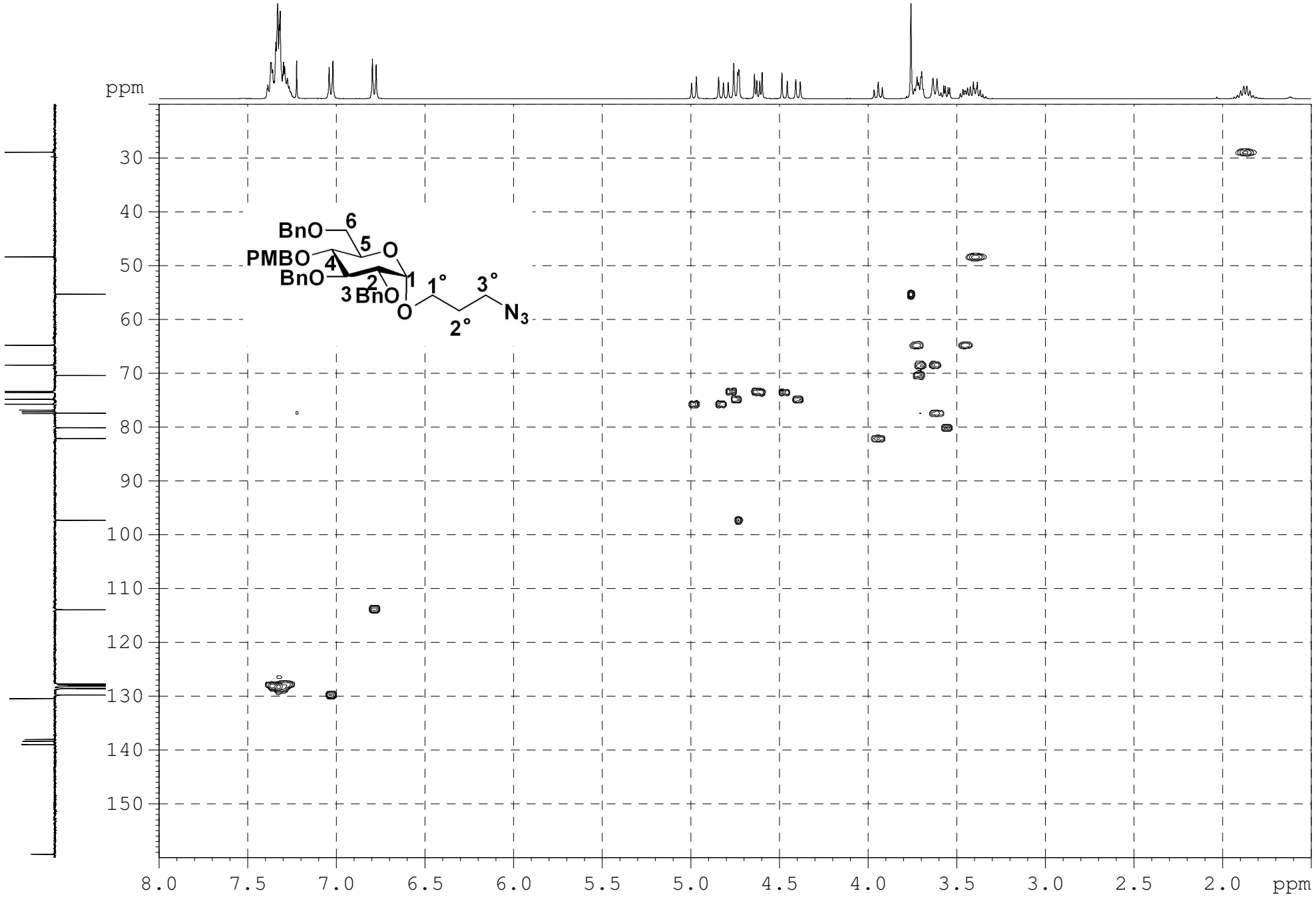

159.32
138.96
138.32
137.99
130.40
129.71
128.53
128.07
127.92
127.76
127.70
127.63
113.85
103.63
97.28
84.79
82.31
82.11
80.14
77.48
77.42
77.16
76.84
75.72
74.97
74.83
74.73
73.54
73.36
70.42
68.51
66.62
64.78
55.31
48.37
29.75
28.92
BnO
PMBO
BnO
BnO
O
O
N3
α:β = 11:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

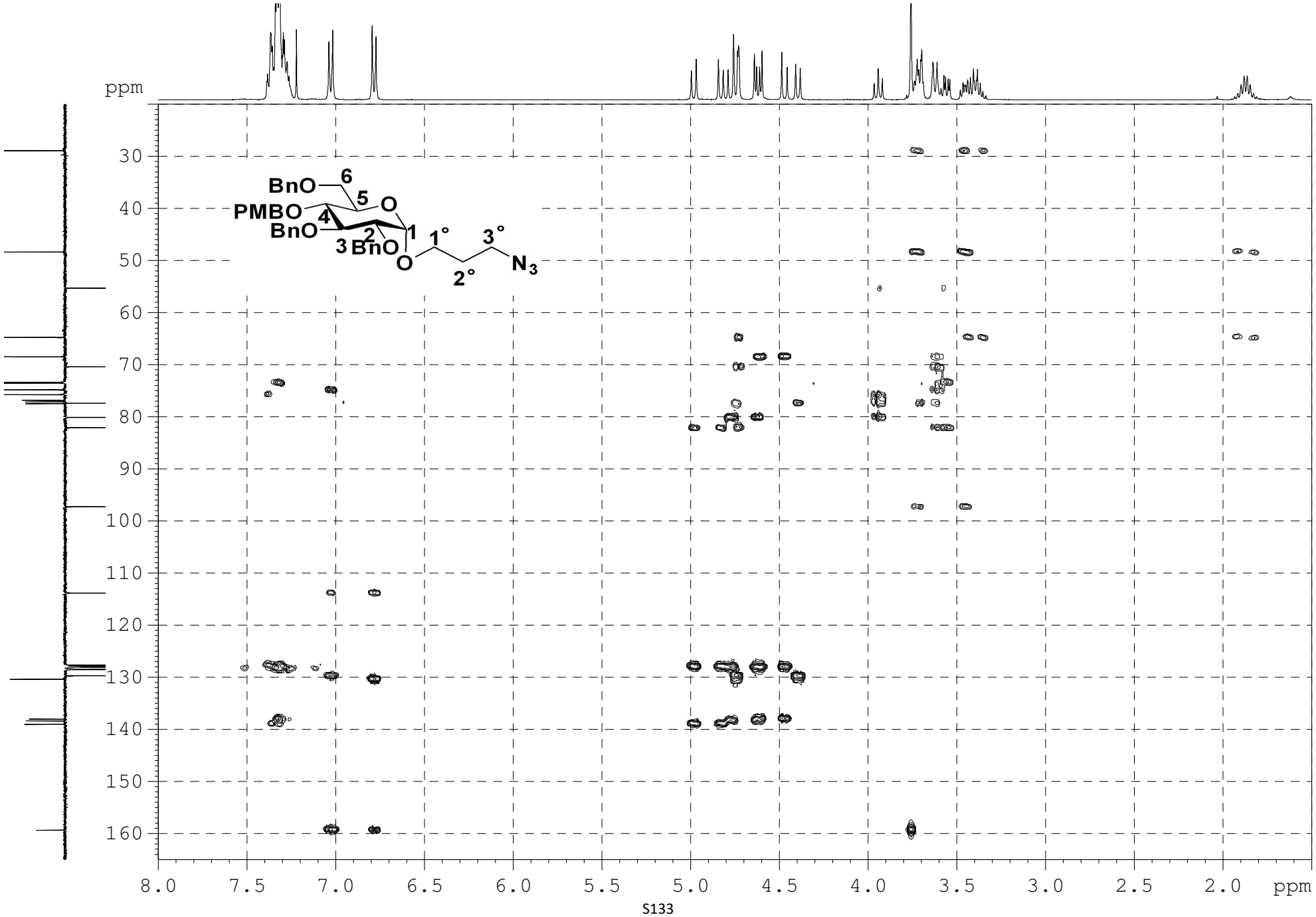
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **27**

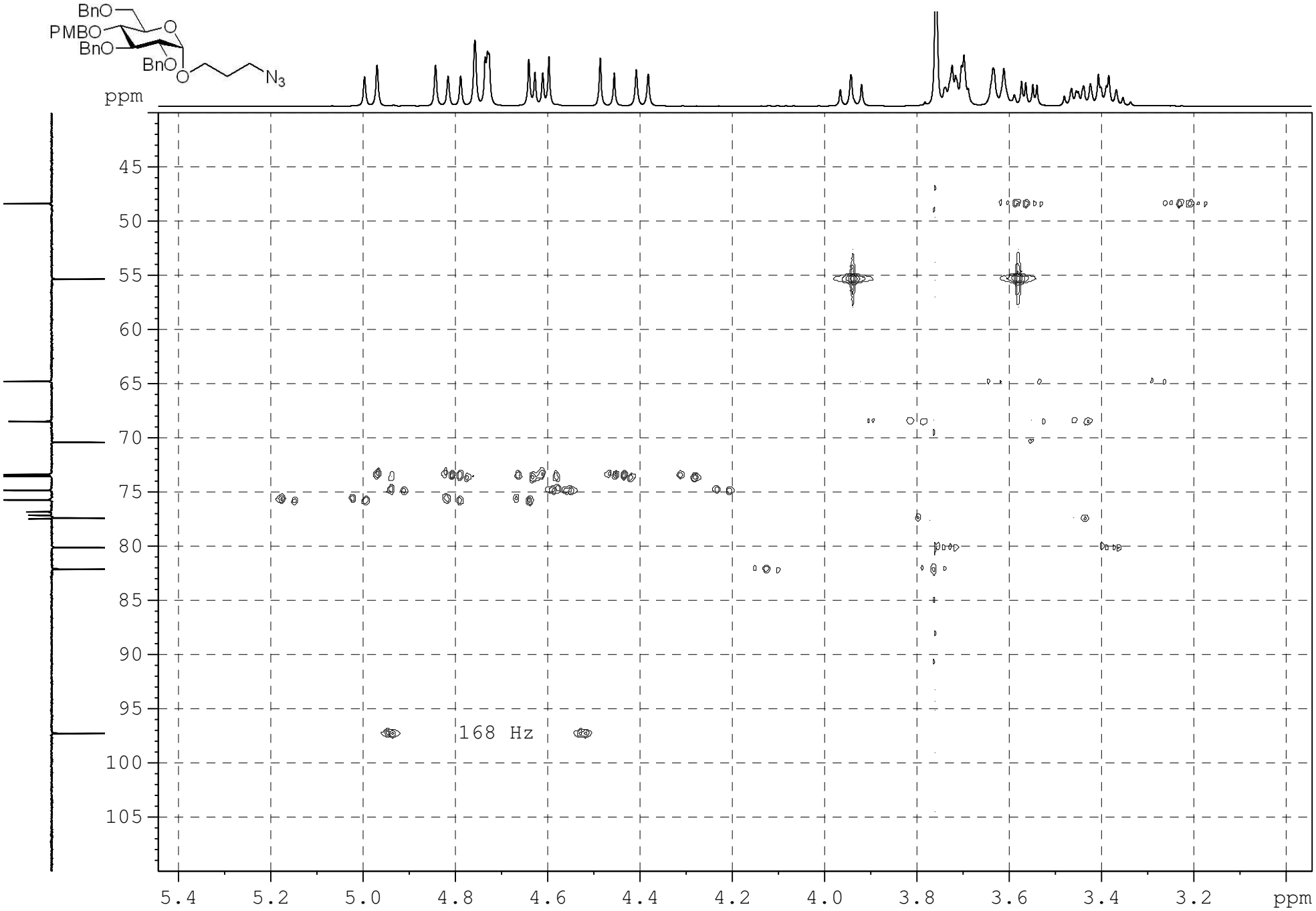



159.33
138.96
138.32
137.99
130.39
129.73
128.55
128.48
128.46
128.09
128.01
127.99
127.94
127.79
127.66
113.86
97.30
82.12
80.13
77.48
77.41
77.16
76.84
75.74
74.85
73.55
73.38
70.41
68.49
64.79
55.33
48.38
28.93
BnO
PMBO
BnO
BnO
O
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

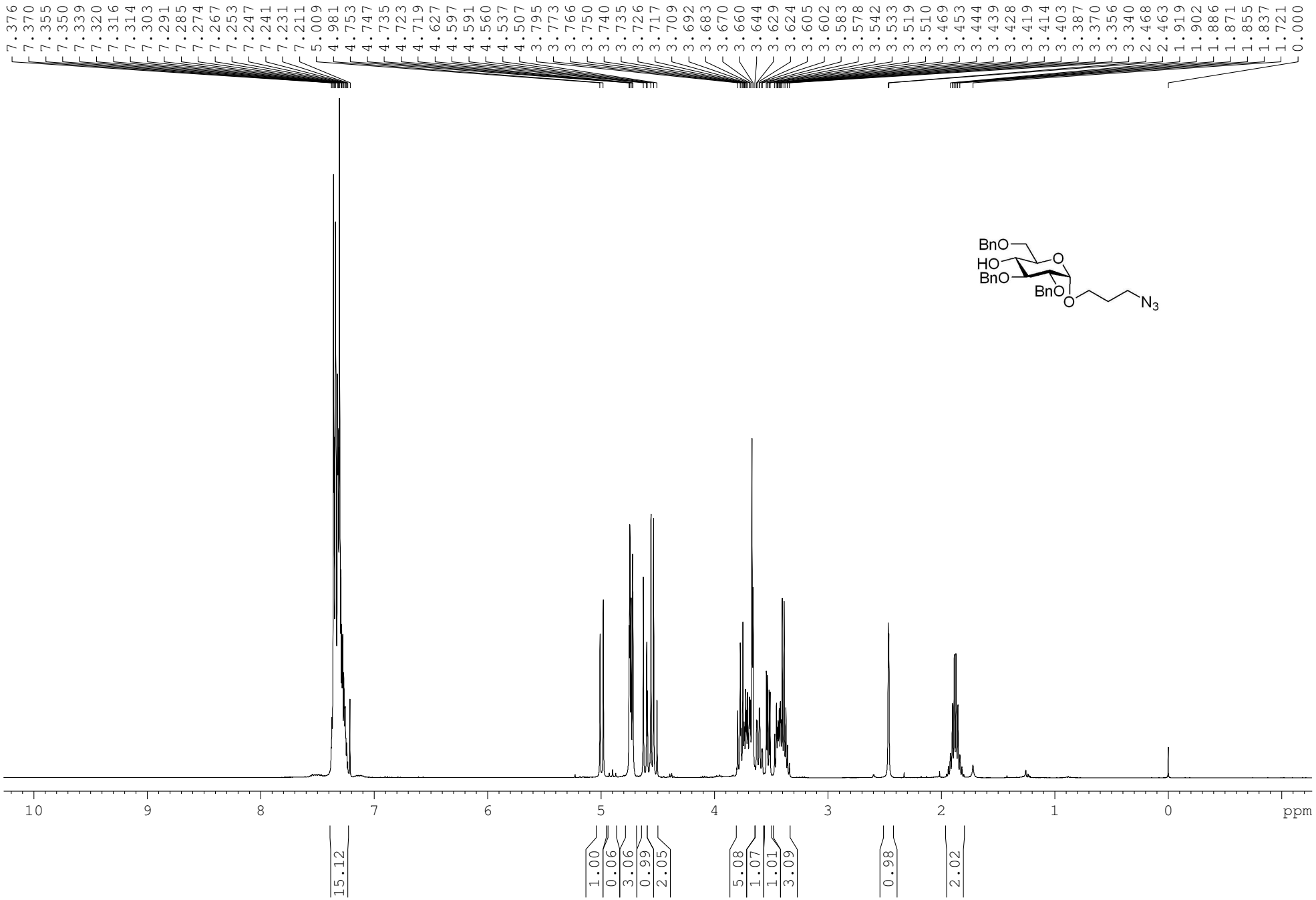

ppm
BnO
6
5
O
PMBO
4
BnO
2
1
3 BnO
1°
3°
O
N3
2°
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

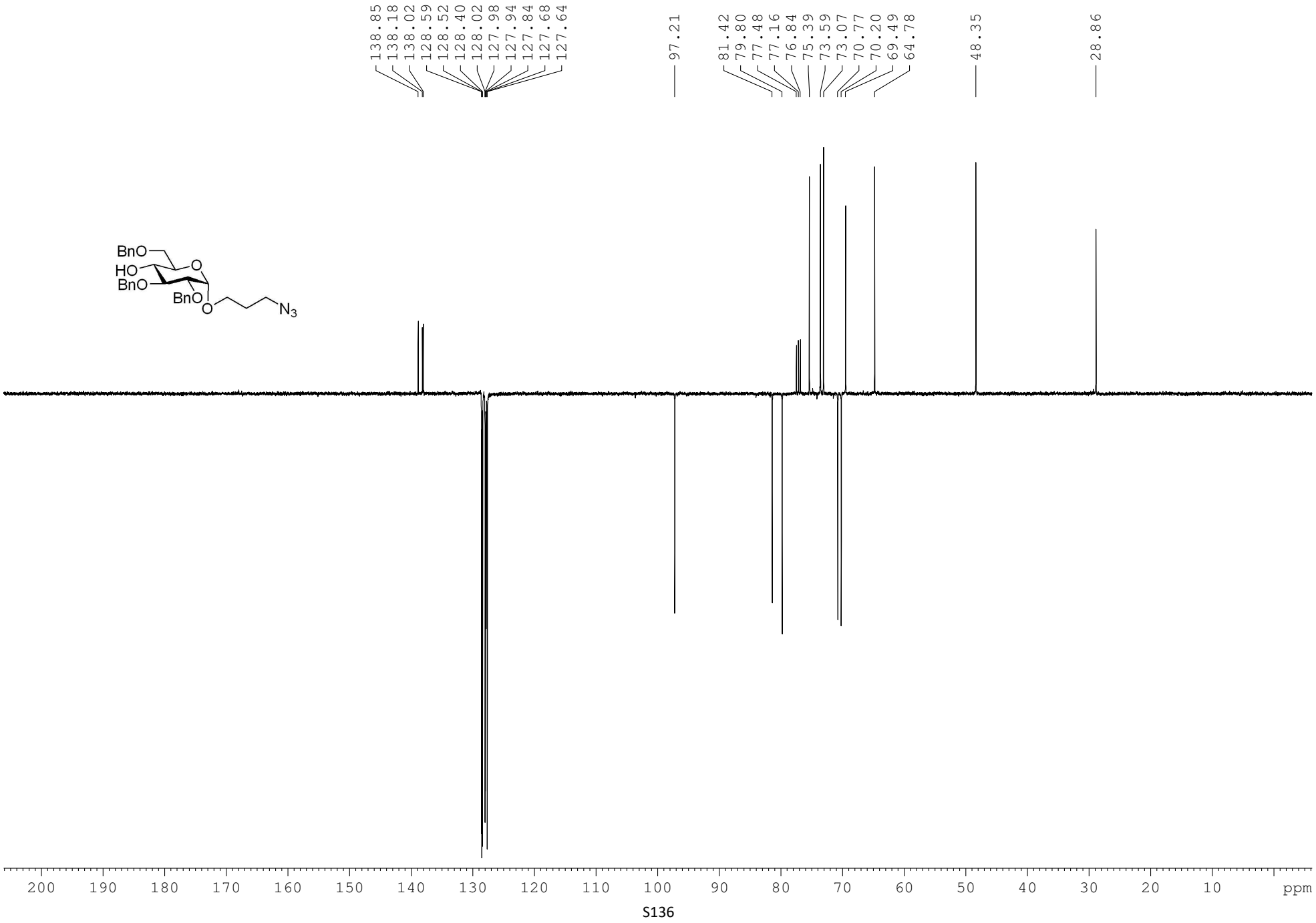

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
6
5
O
PMBO
4
BnO
2
1
3
BnO
O
1°
2°
3°
N3

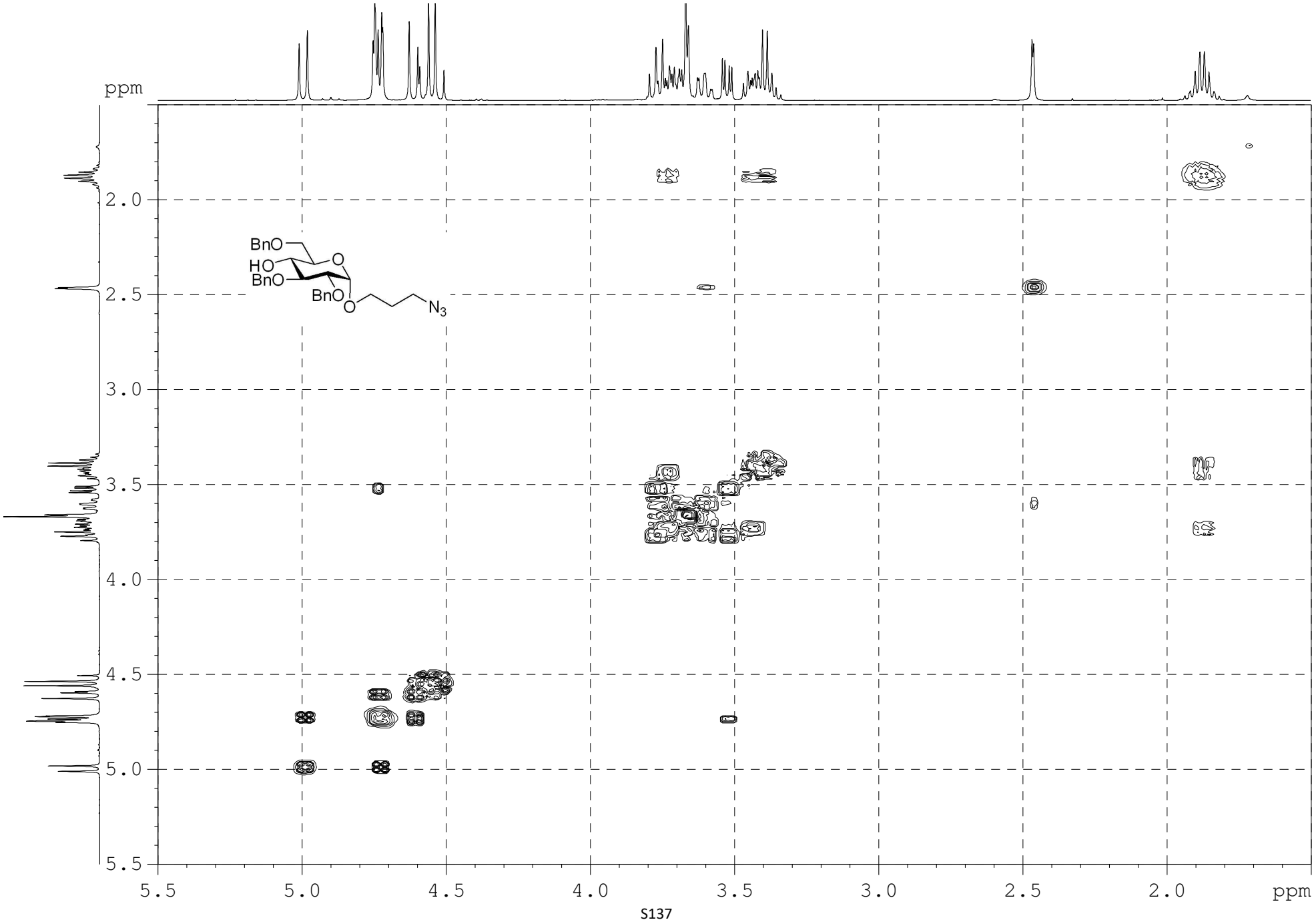

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
6
5
O
PMBO
4
BnO
2
1
3 BnO
O
1°
2°
3°
N3

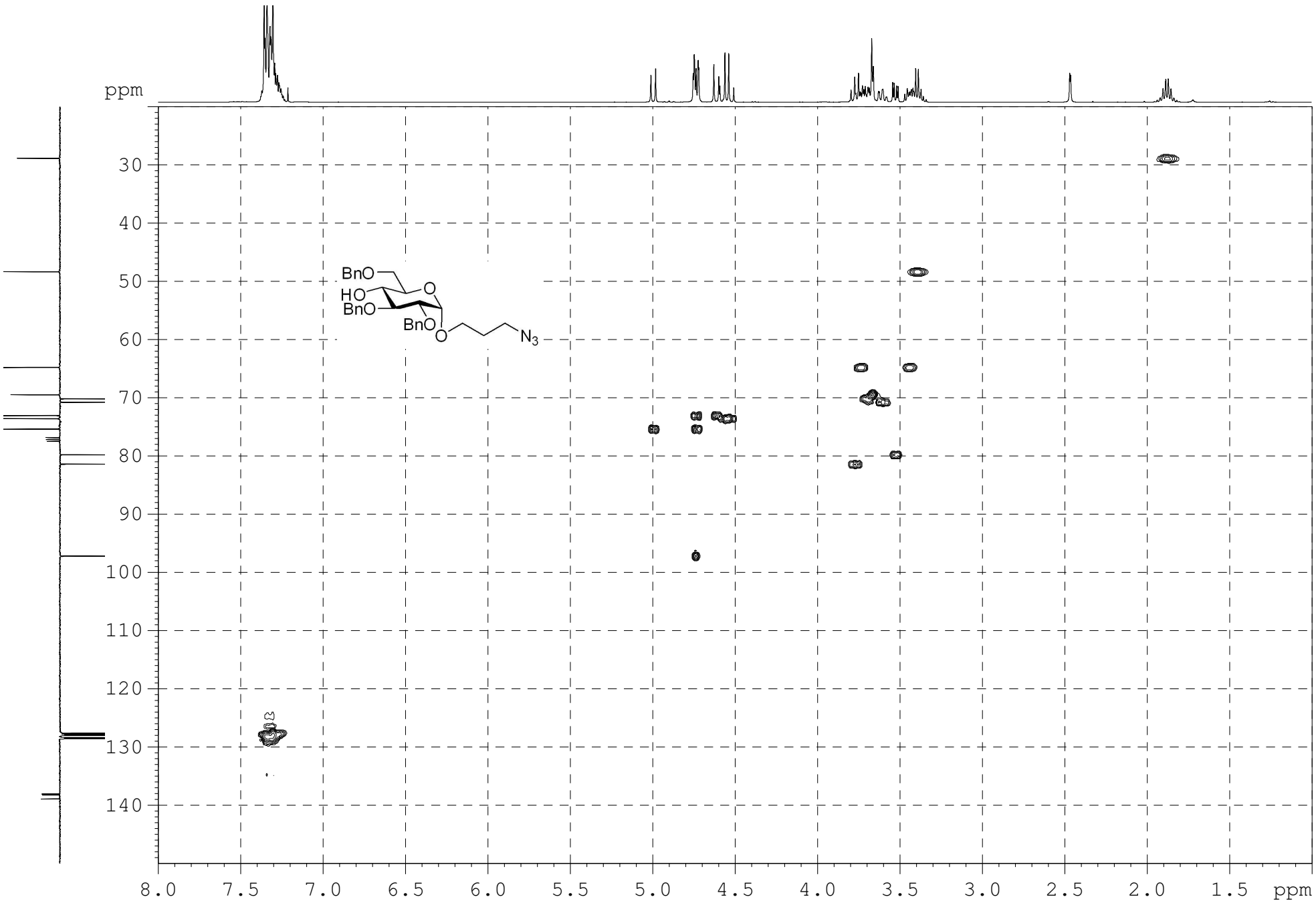

BnO
PMBO
BnO
BnO
O
O
N3
ppm
45
50
55
60
65
70
75
80
85
90
95
100
105
168 Hz
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC of **28**

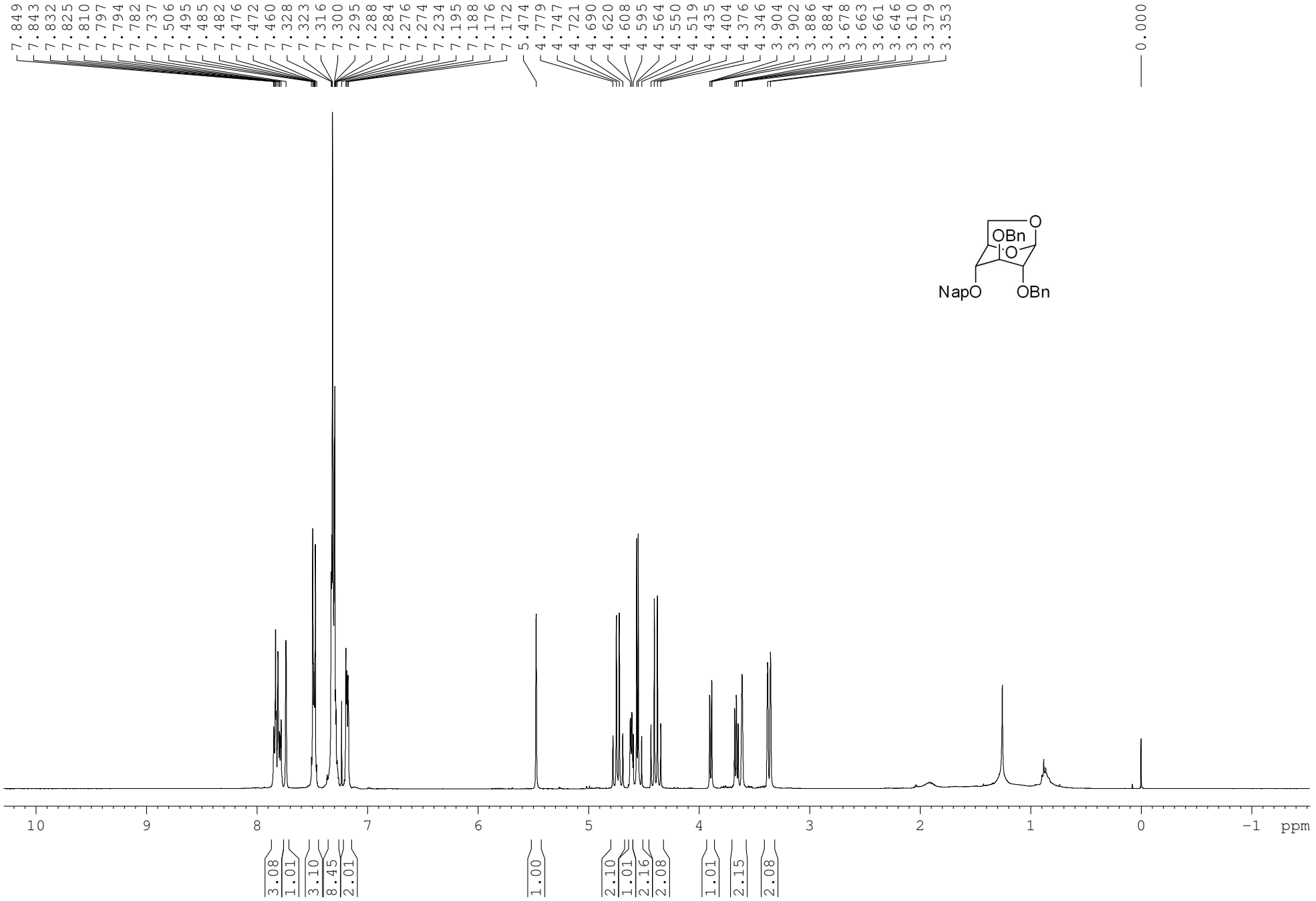


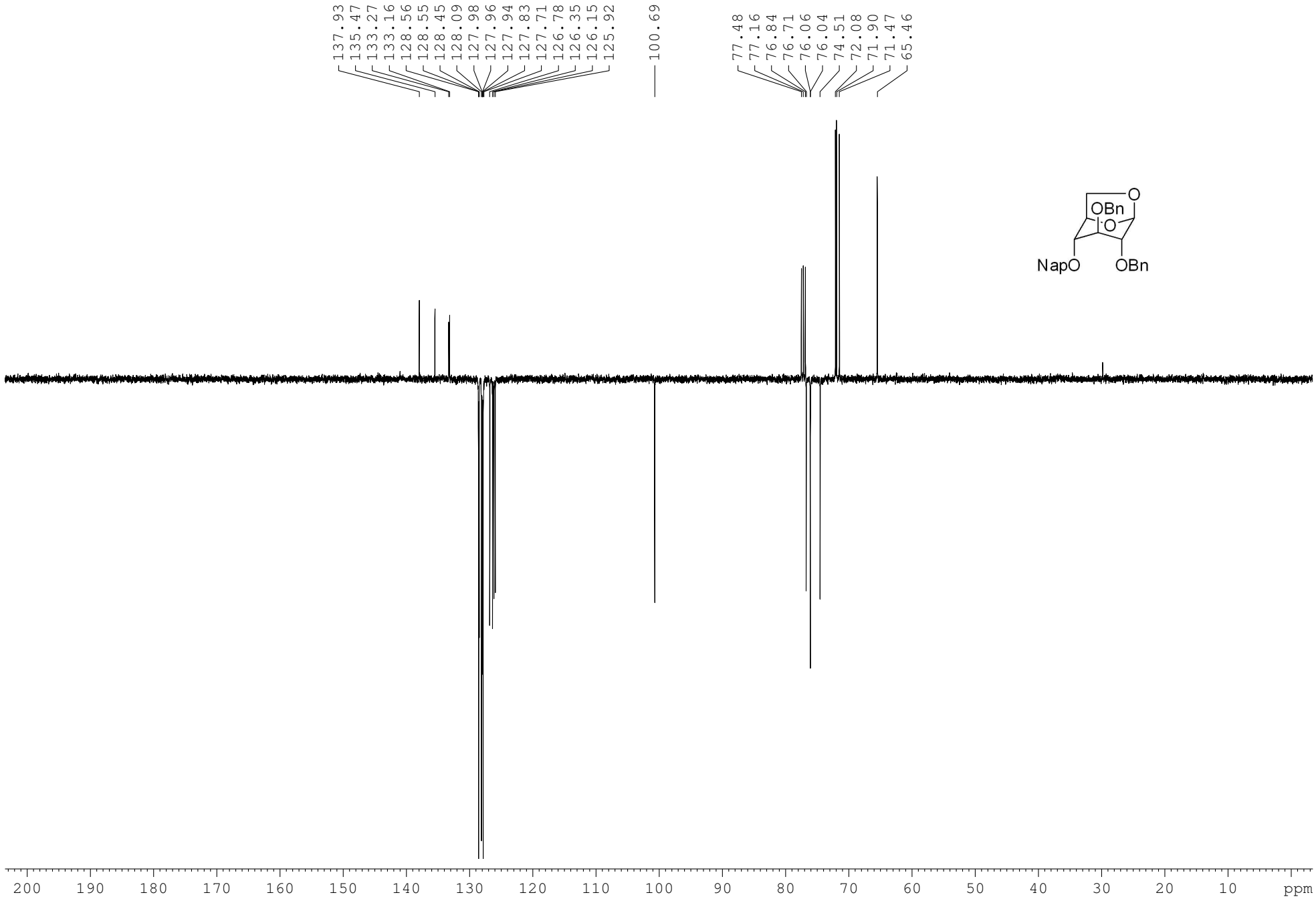

138.85
138.18
138.02
128.59
128.52
128.40
128.02
127.98
127.94
127.84
127.68
127.64
97.21
81.42
79.80
77.48
77.16
76.84
75.39
73.59
73.07
70.77
70.20
69.49
64.78
48.35
28.86
BnO
HO
BnO
BnO
O
O
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

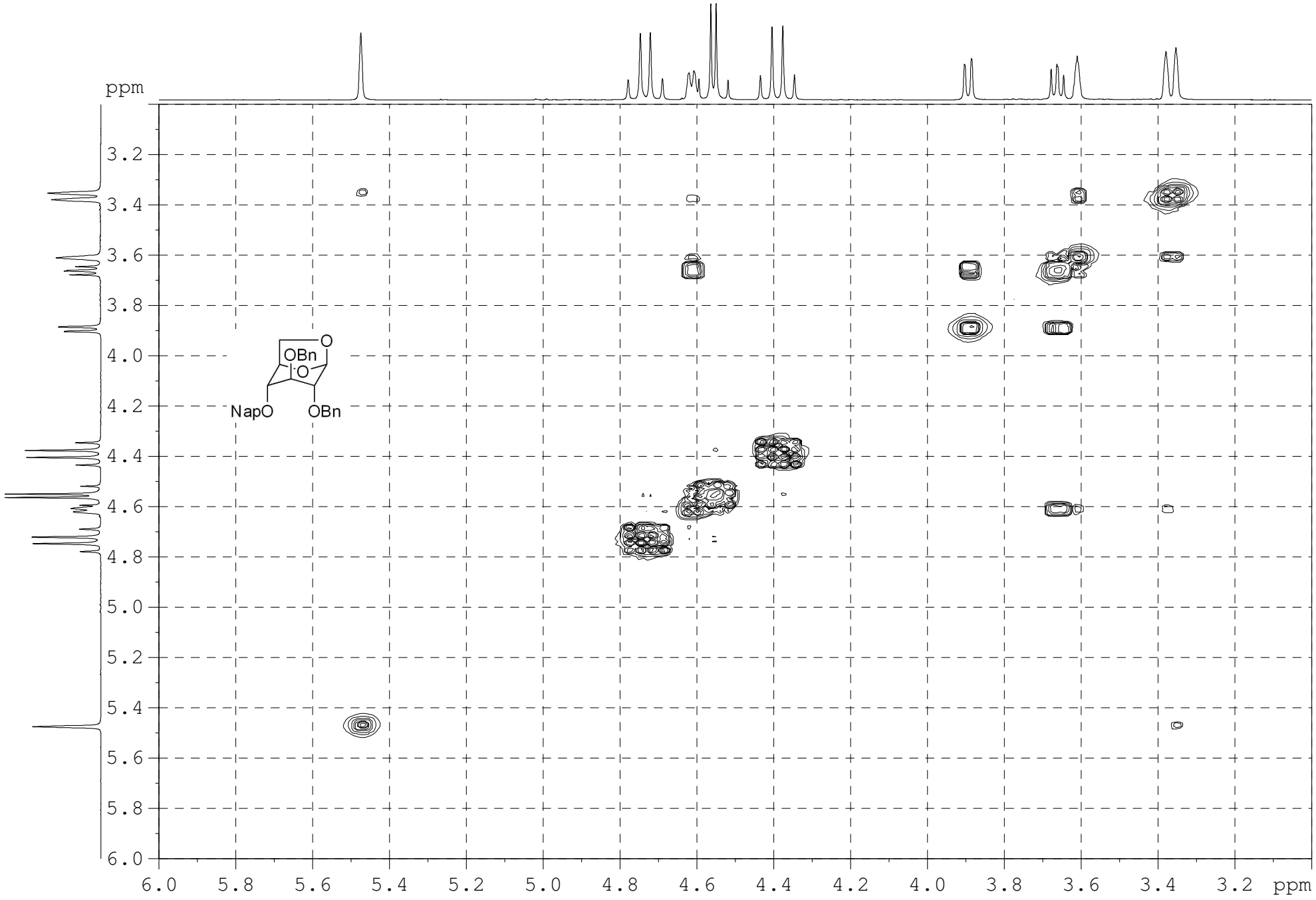

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
BnO
HO
BnO
BnO
O
O
N_3
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

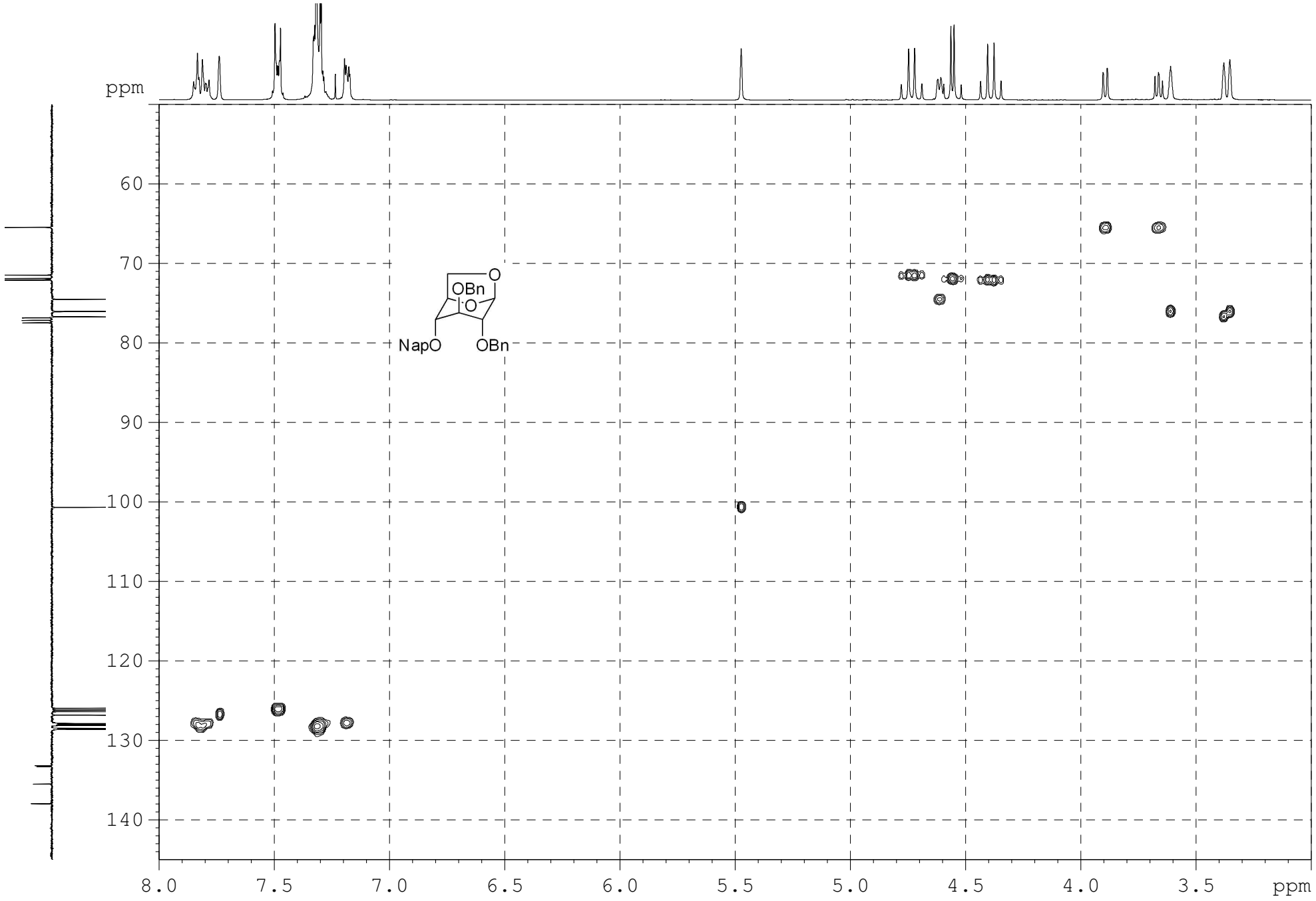

ppm
30
40
50
60
70
80
90
100
110
120
130
140
BnO
HO
BnO
BnO
O
O
N_3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

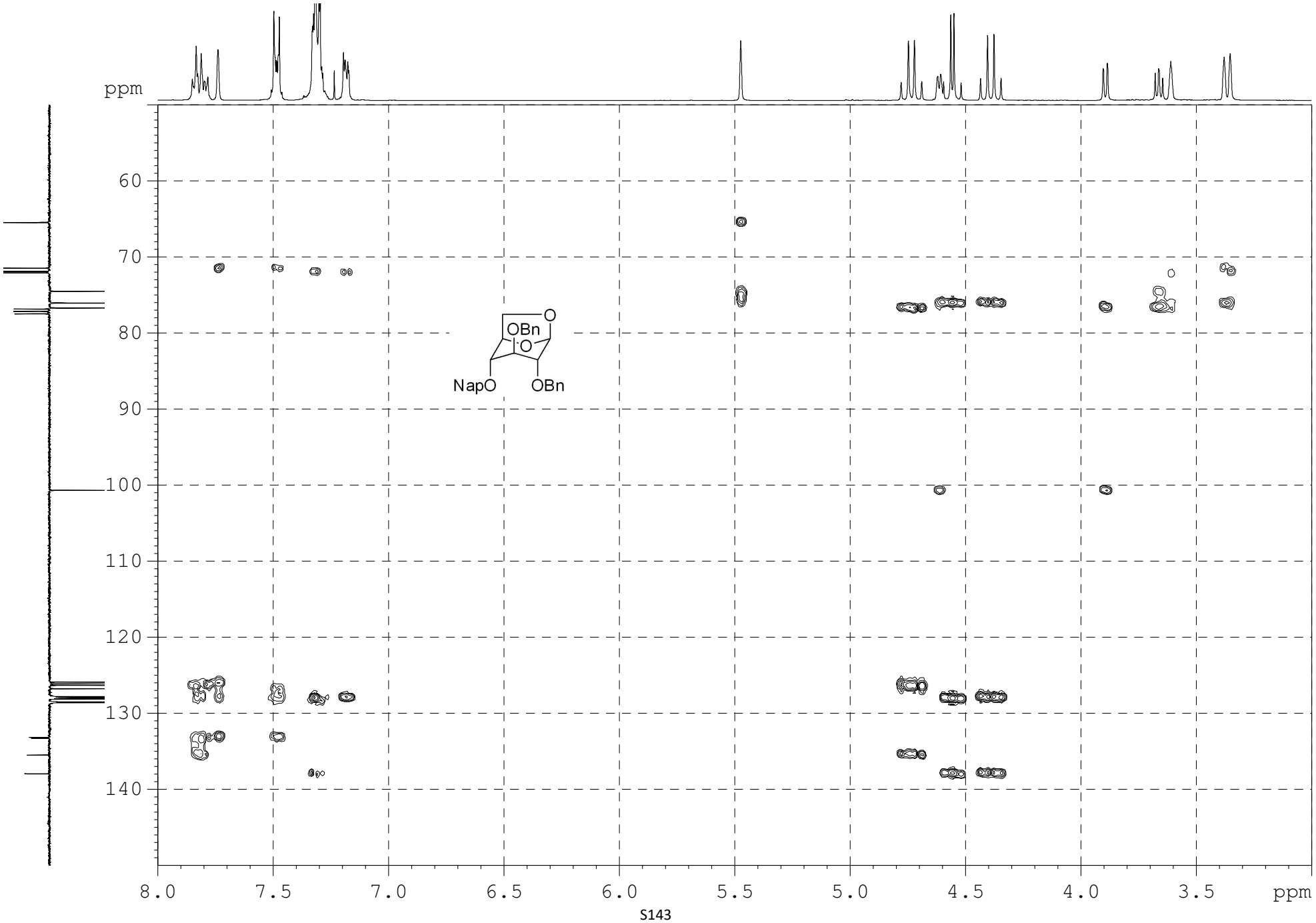
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **29**



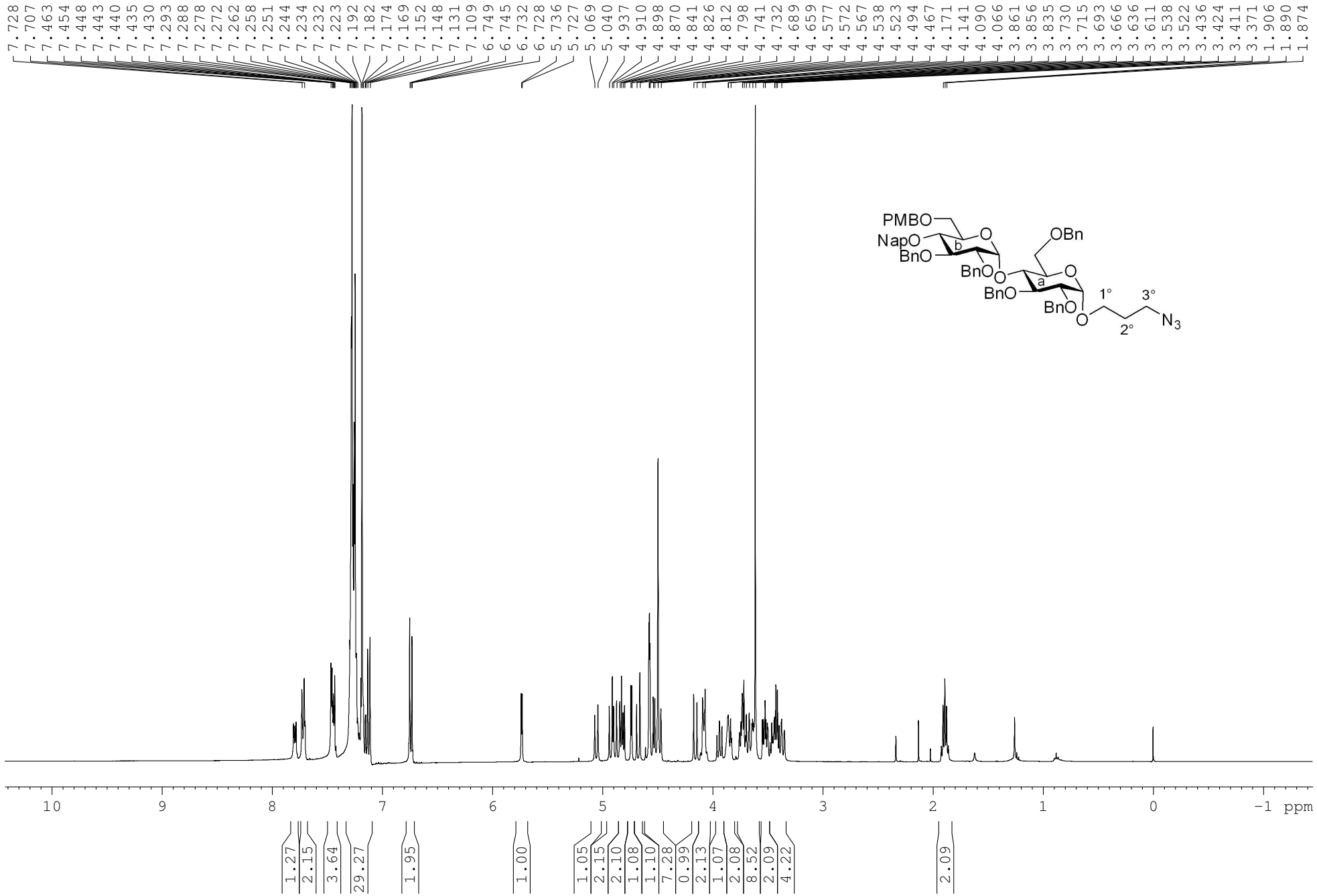

137.93
135.47
133.27
133.16
128.56
128.55
128.45
128.09
127.98
127.96
127.94
127.83
127.71
126.78
126.35
126.15
125.92
100.69
77.48
77.16
76.84
76.71
76.06
76.04
74.51
72.08
71.90
71.47
65.46
OBn
O
O
NapO
OBn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

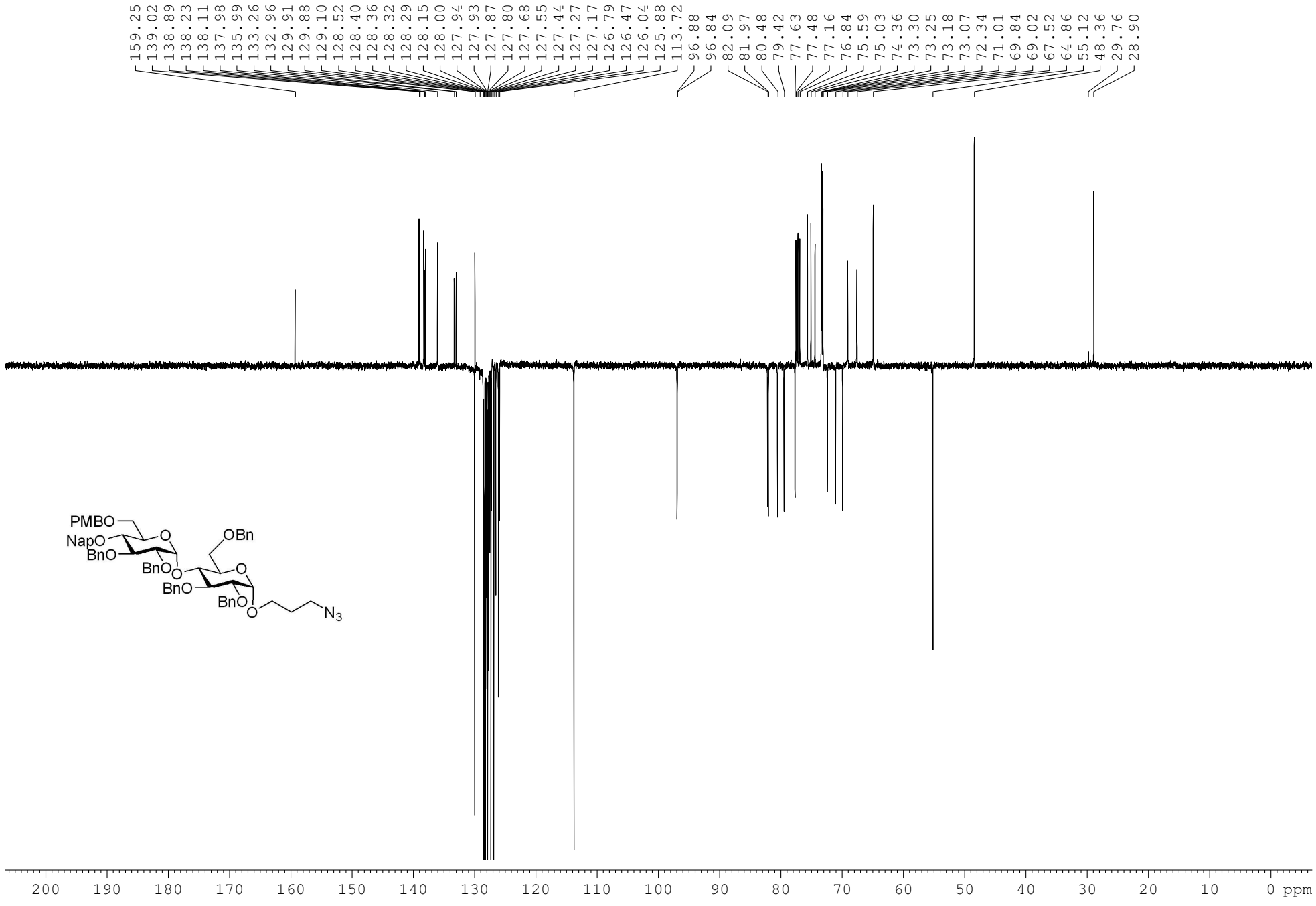

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
O
OBn
O
NapO
OBn

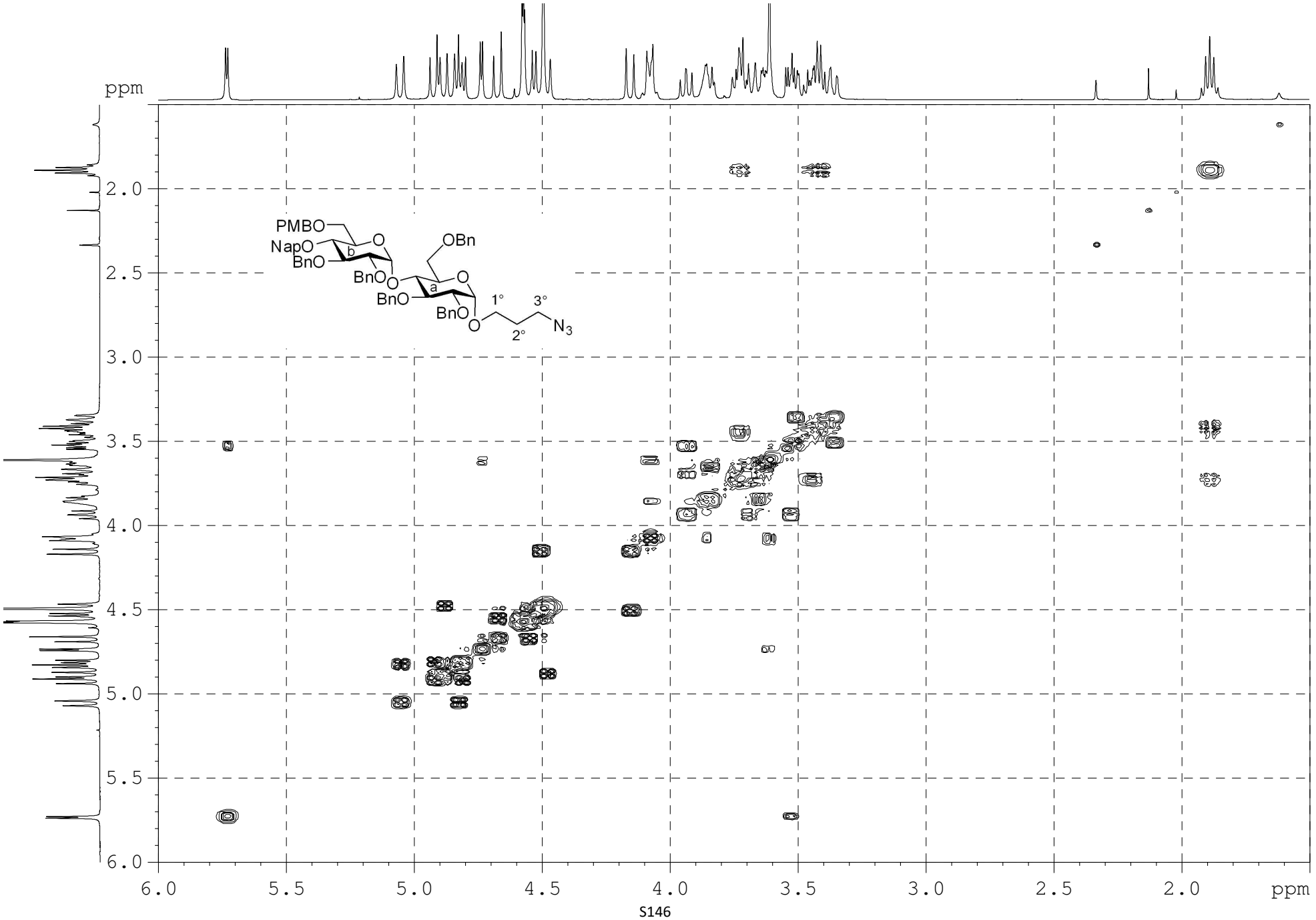

ppm
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
O
OBn
O
NapO
OBn

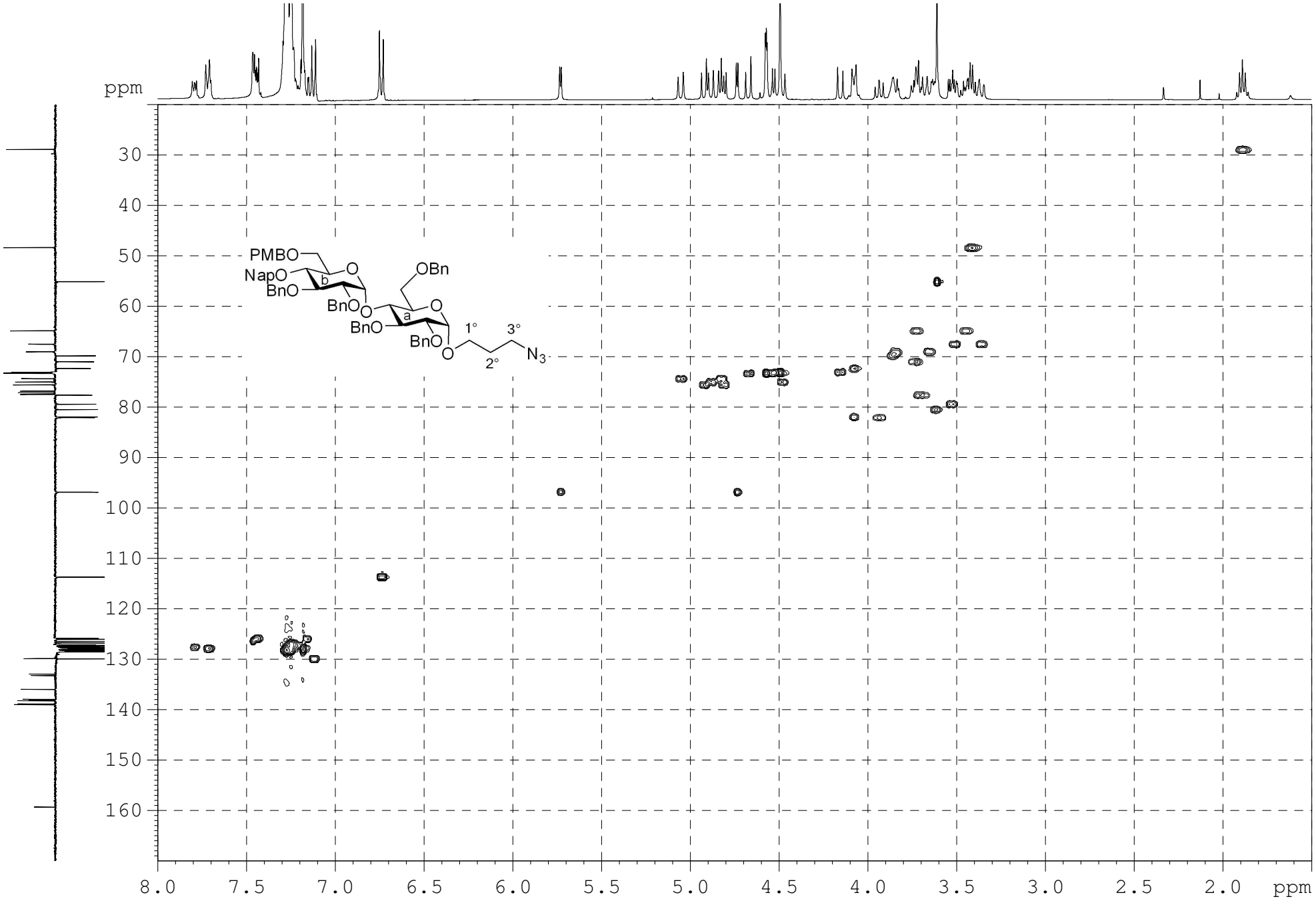

ppm
60
70
80
90
100
110
120
130
140
OBn
O
O
NapO
OBn
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

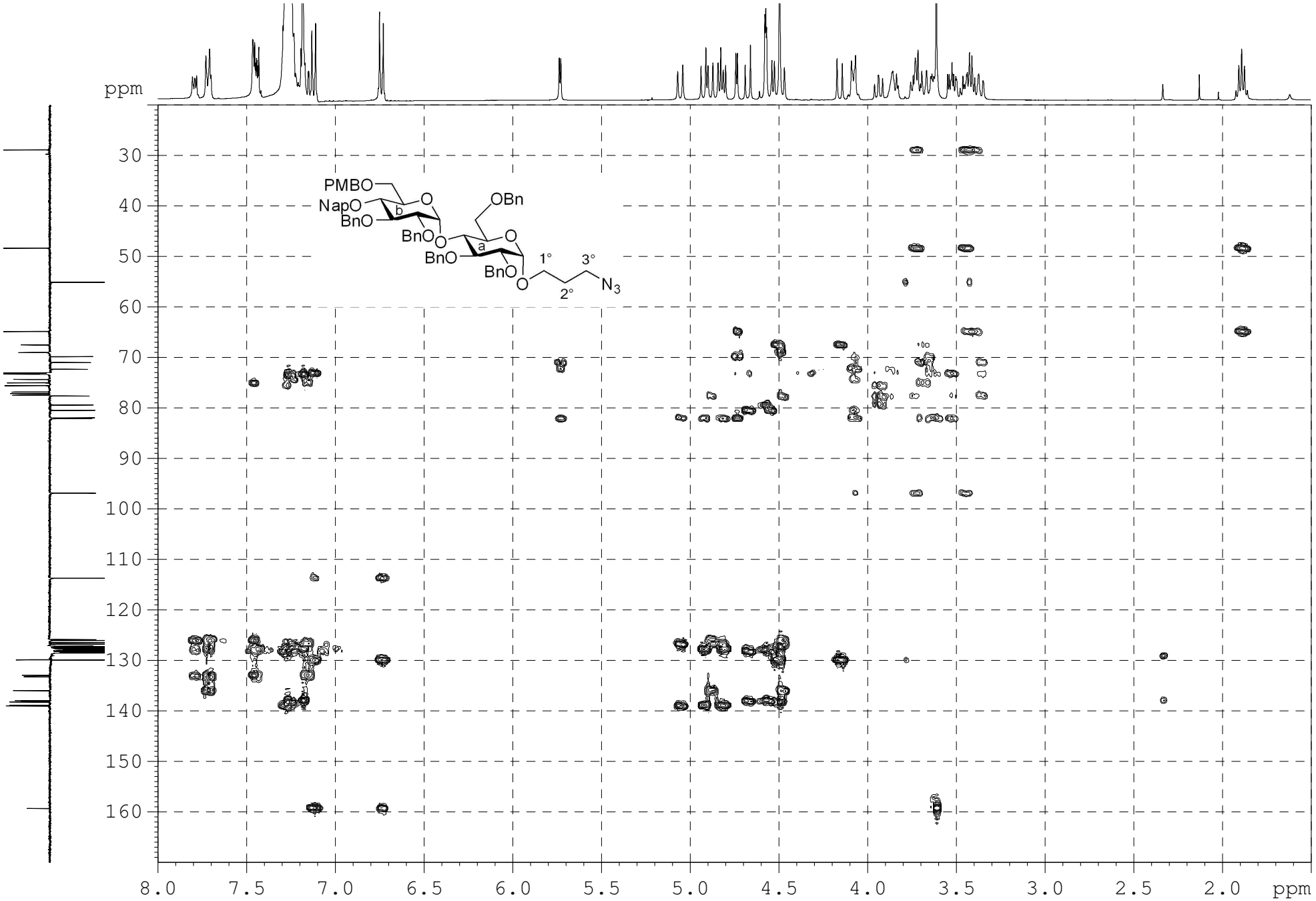
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **30**

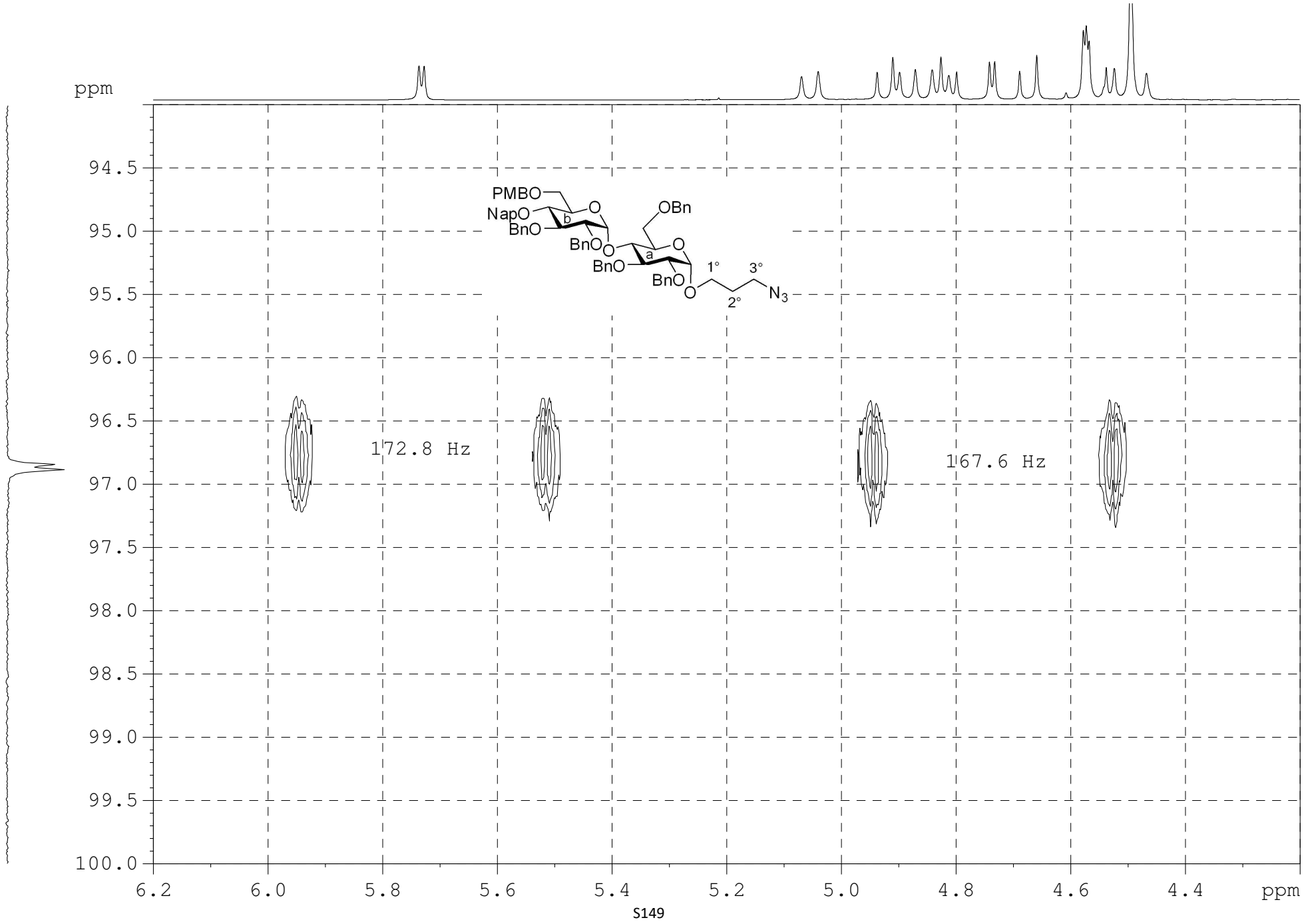



159.25
139.02
138.89
138.23
138.11
137.98
135.99
133.26
132.96
129.91
129.88
129.10
128.52
128.40
128.36
128.32
128.29
128.15
128.00
127.94
127.93
127.87
127.80
127.68
127.55
127.44
127.27
127.17
126.79
126.47
126.04
125.88
113.72
96.88
96.84
82.09
81.97
80.48
79.42
77.63
77.48
77.16
76.84
75.59
75.03
74.36
73.30
73.25
73.18
73.07
72.34
71.01
69.84
69.02
67.52
64.86
55.12
48.36
29.76
28.90
PMBO
NapO
BnO
BnO
BnO
BnO
BnO
OBn
O
O
O
O
O
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

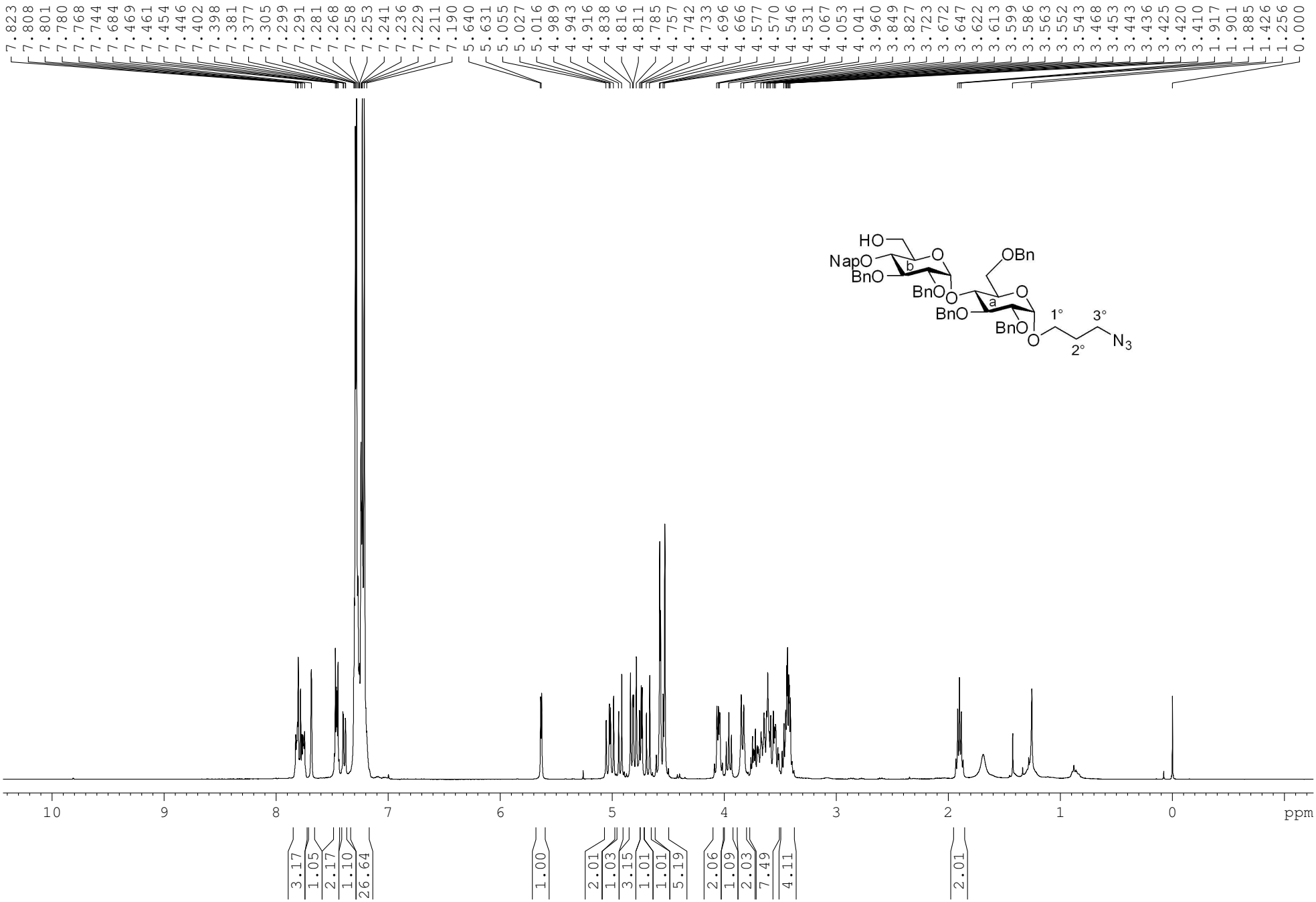

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
PMBO
NapO
BnO
b
BnO
OBn
a
BnO
BnO
1°
2°
3°
N3

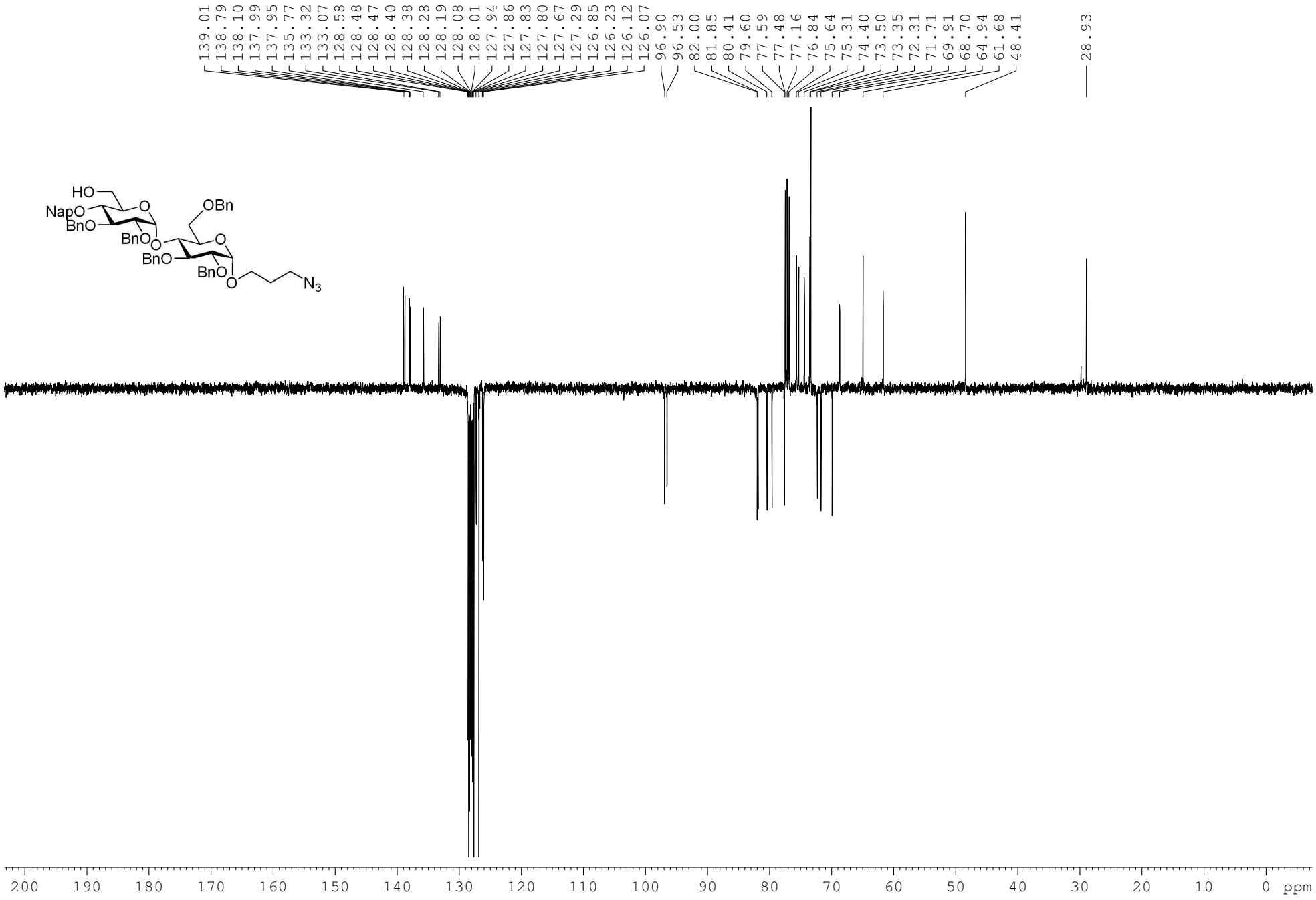

ppm
PMBO
NapO
BnO
BnO
BnO
BnO
OBn
O
a
b
1°
2°
3°
N_3
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

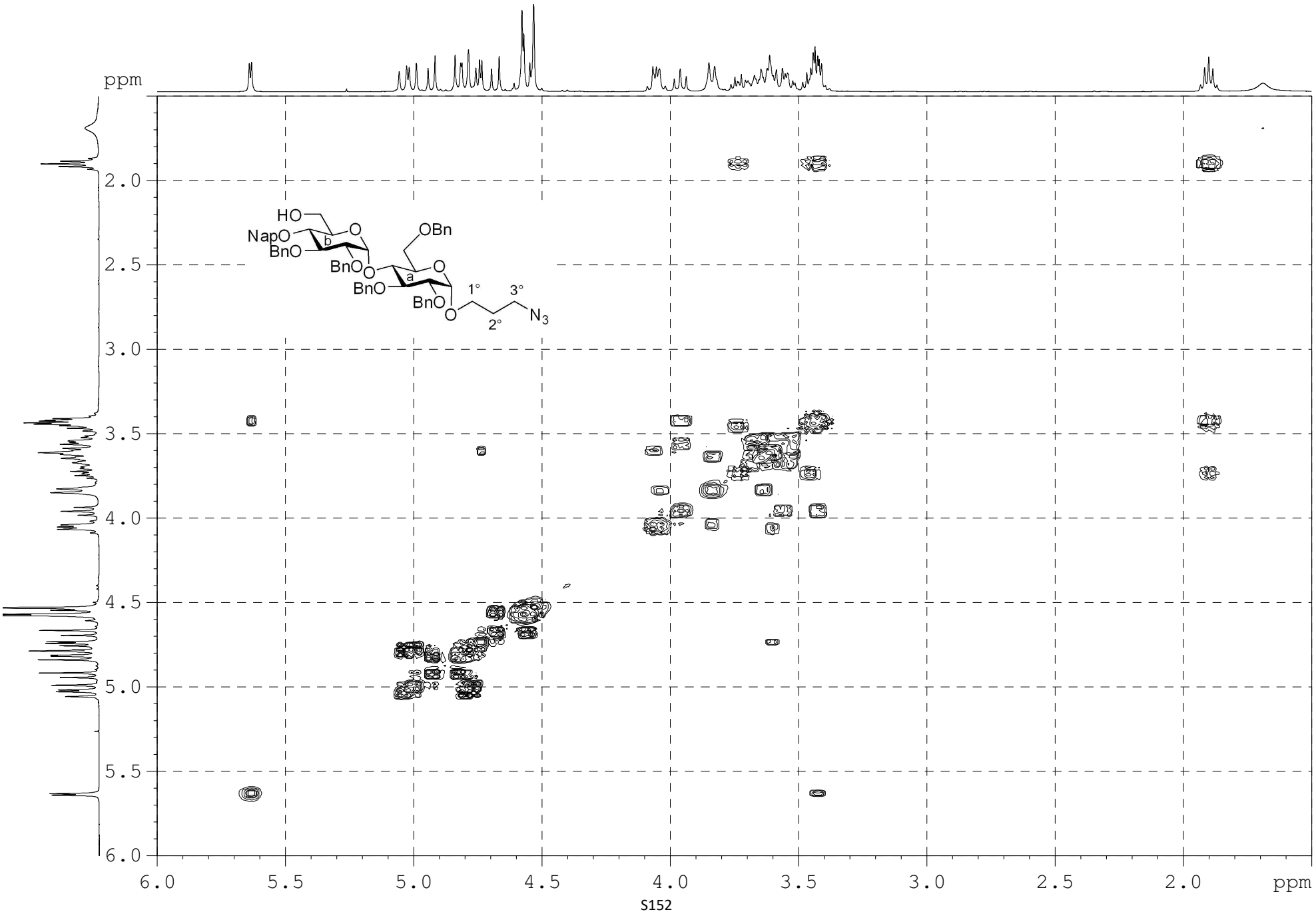

ppm
PMBO
NapO
BnO
BnO
BnO
BnO
OBn
a
b
1°
2°
3°
N_3
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

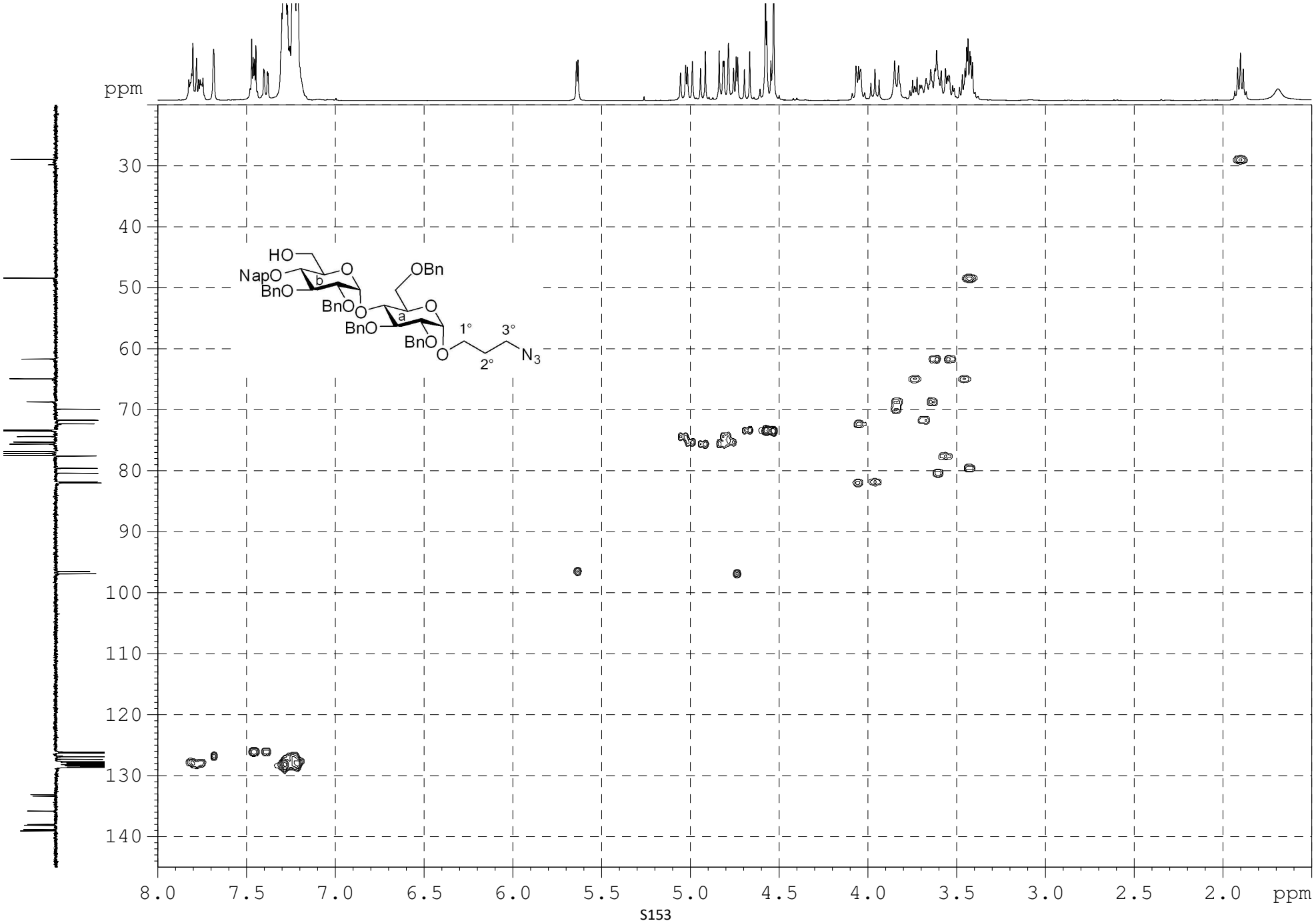

ppm
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
ppm
PMBO
NapO
BnO
b
O
OBn
BnO
O
a
O
BnO
BnO
O
1°
3°
2°
N3
172.8 Hz
167.6 Hz

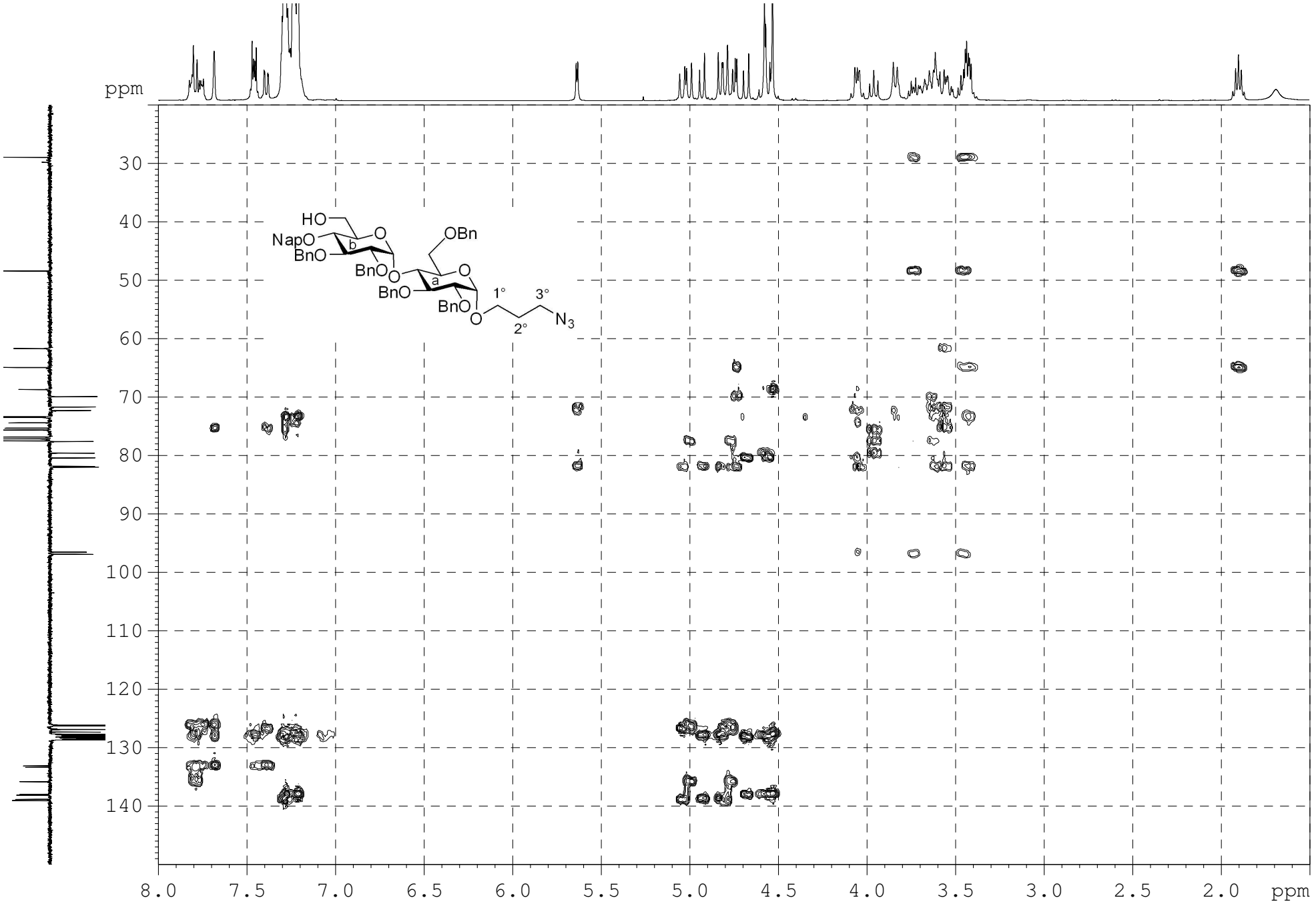
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **31**



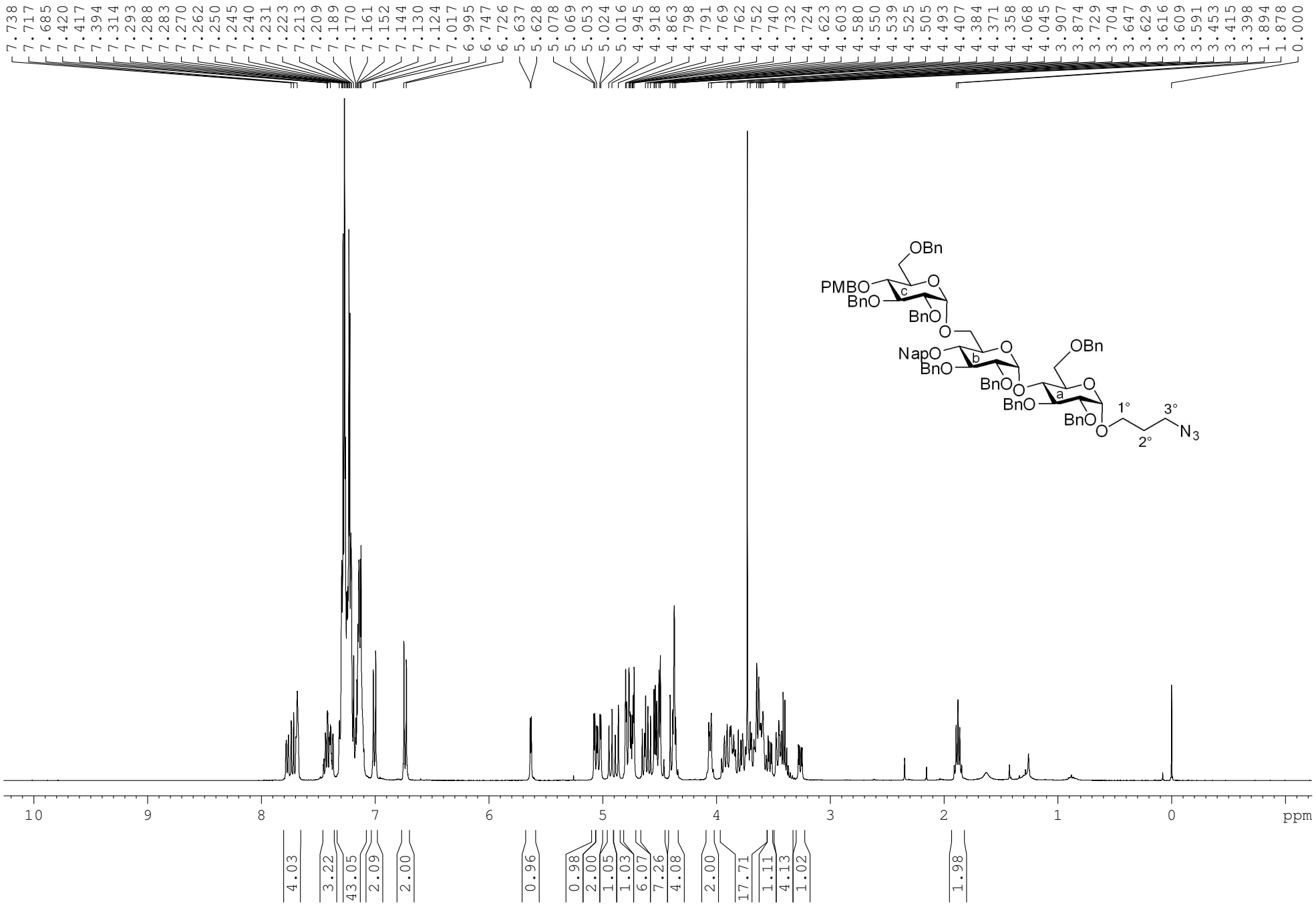

139.01
138.79
138.10
137.99
137.95
135.77
133.32
133.07
128.58
128.48
128.47
128.40
128.38
128.28
128.19
128.08
128.01
127.94
127.86
127.83
127.80
127.67
127.29
126.85
126.23
126.12
126.07
96.90
96.53
82.00
81.85
80.41
79.60
77.59
77.48
77.16
76.84
75.64
75.31
74.40
73.50
73.35
72.31
71.71
69.91
68.70
64.94
61.68
48.41
28.93
HO
NapO
BnO
BnO
BnO
BnO
BnO
O
O
O
O
O
OBn
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

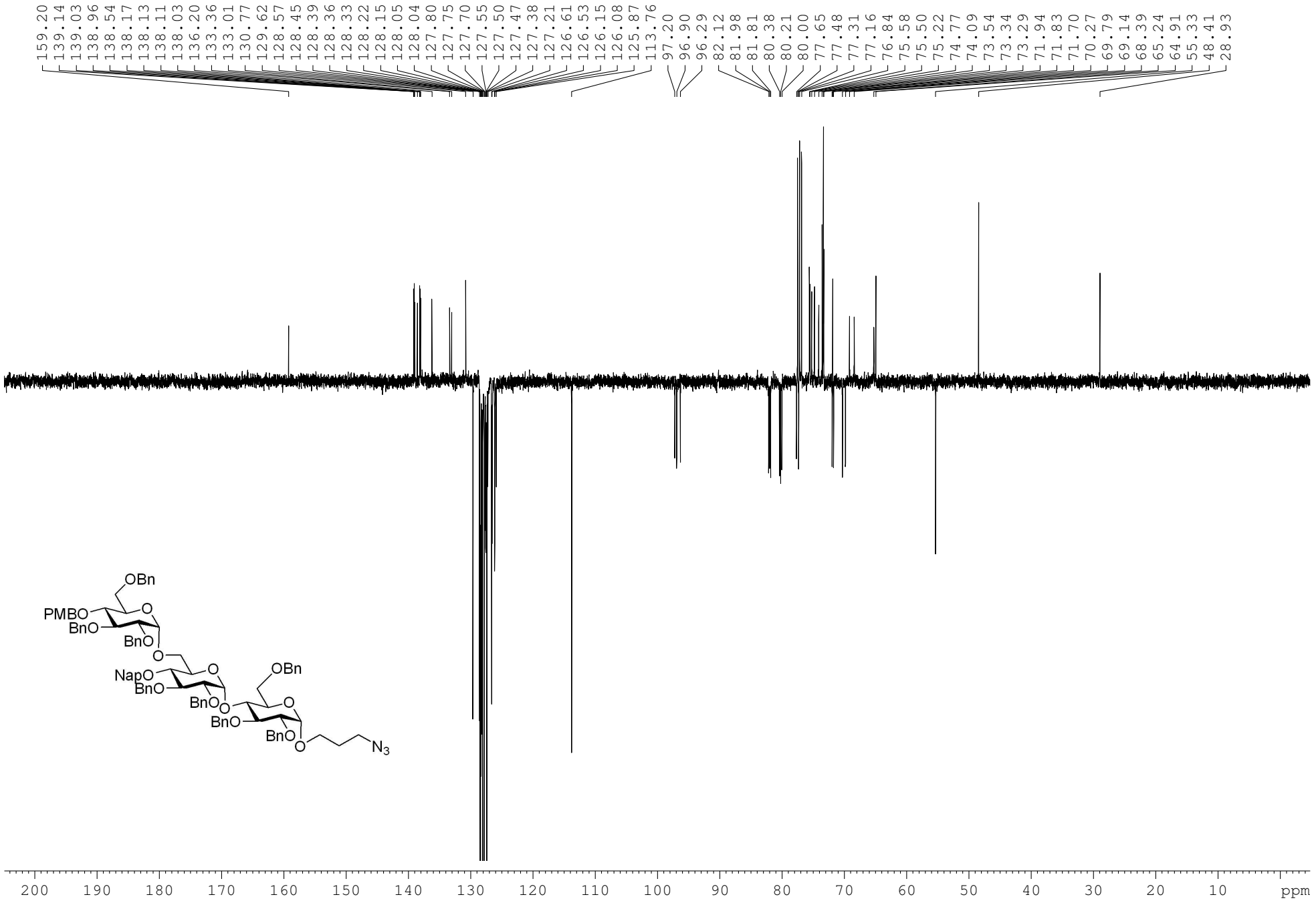

ppm
HO
NapO
BnO
O
b
OBn
BnO
O
O
a
BnO
1°
3°
BnO
O
2°
N3
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

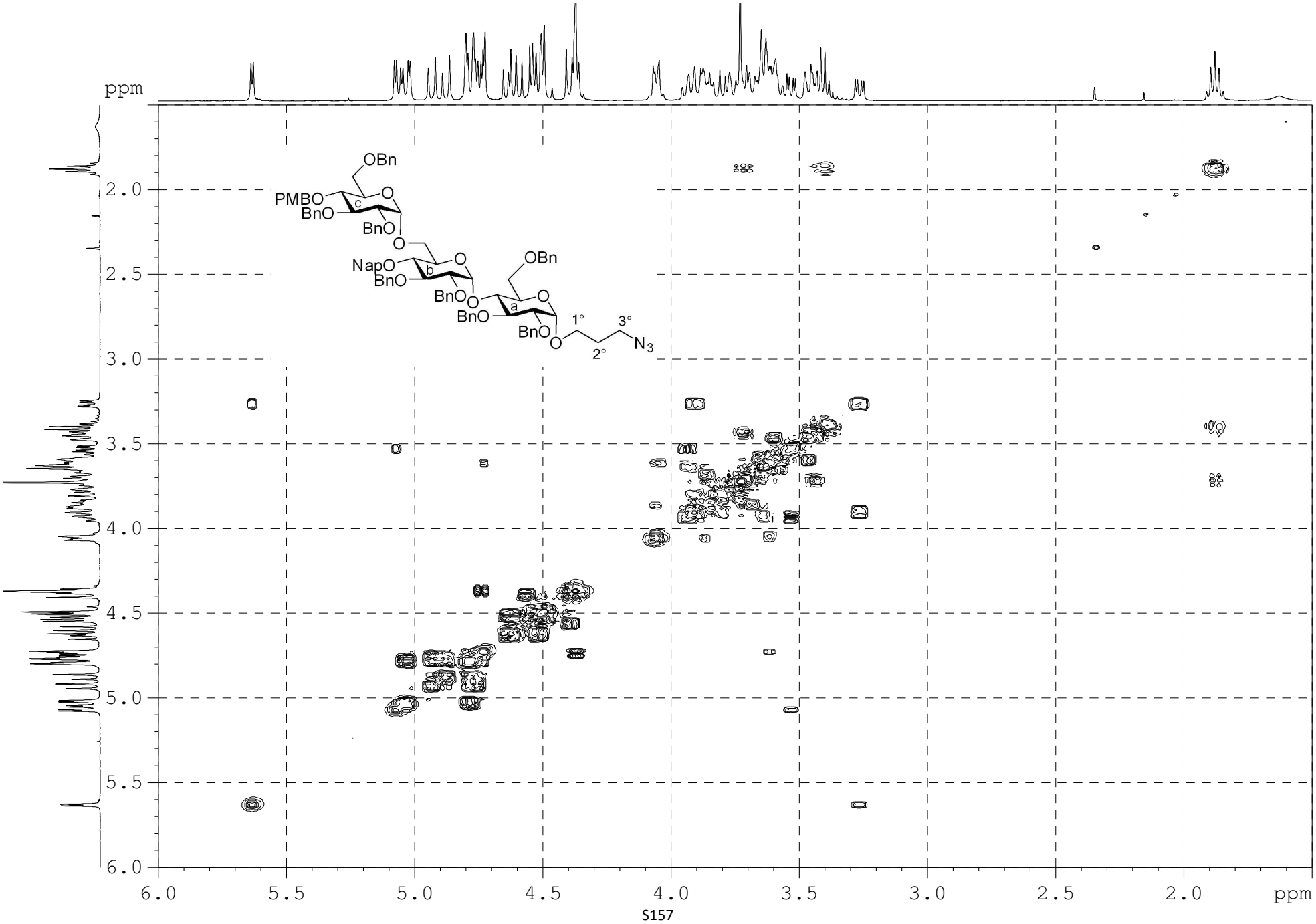

ppm
HO
NapO
BnO
O
b
OBn
BnO
O
O
a
BnO
BnO
O
1°
3°
2°
N3
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

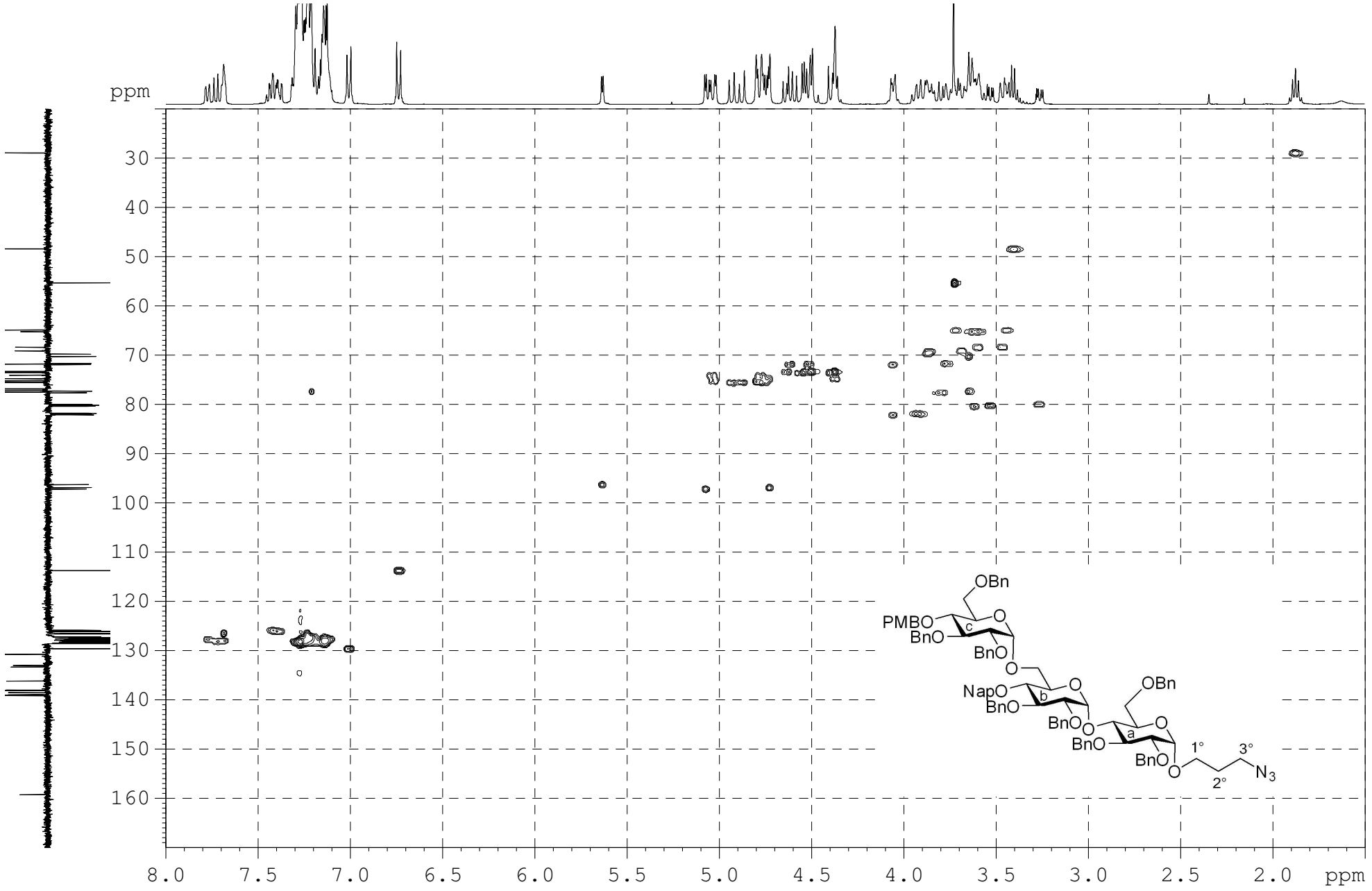

ppm
HO
NapO
BnO
O
b
BnO
O
OBn
O
a
BnO
BnO
O
1°
2°
3°
N3
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

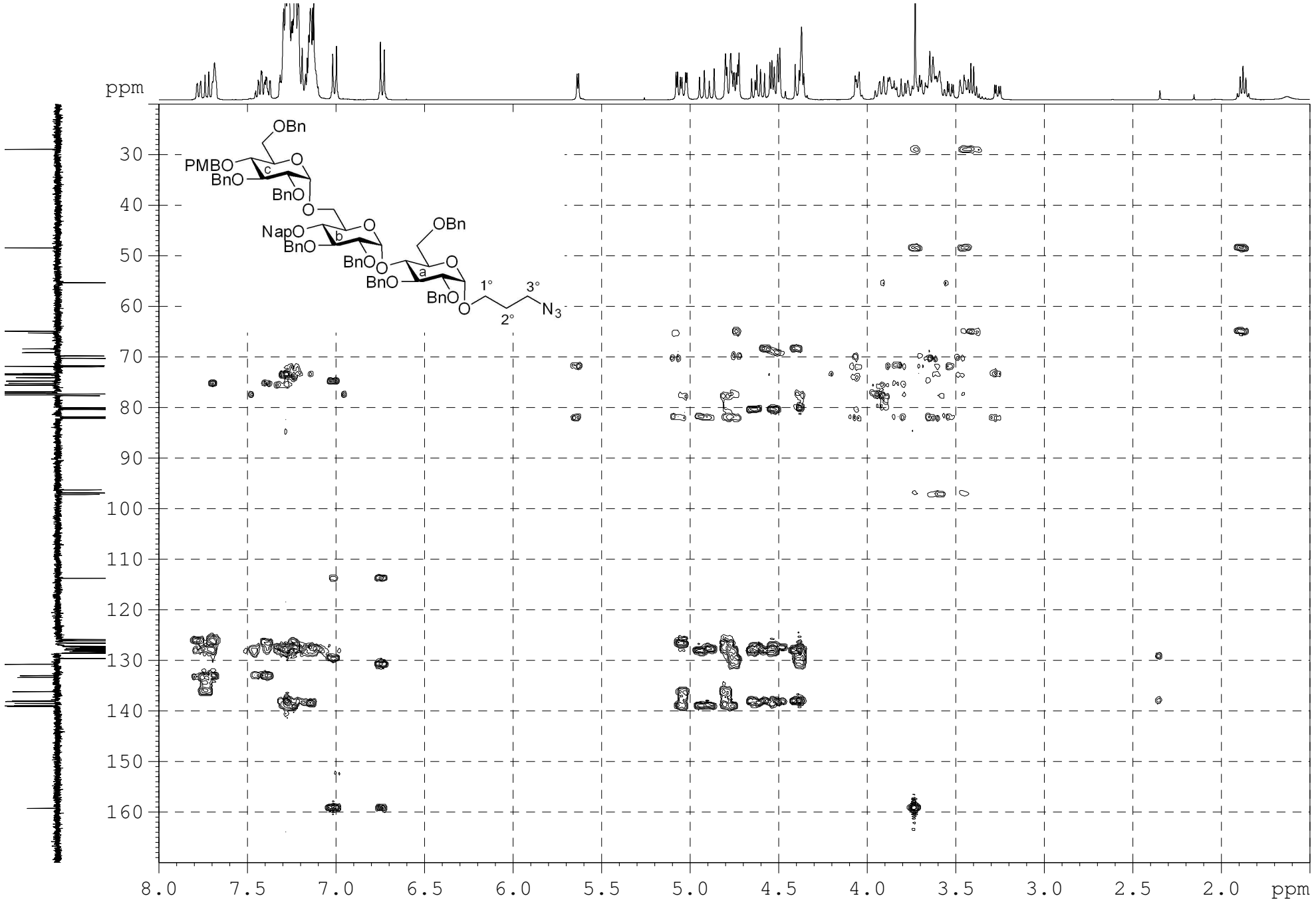
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **32**

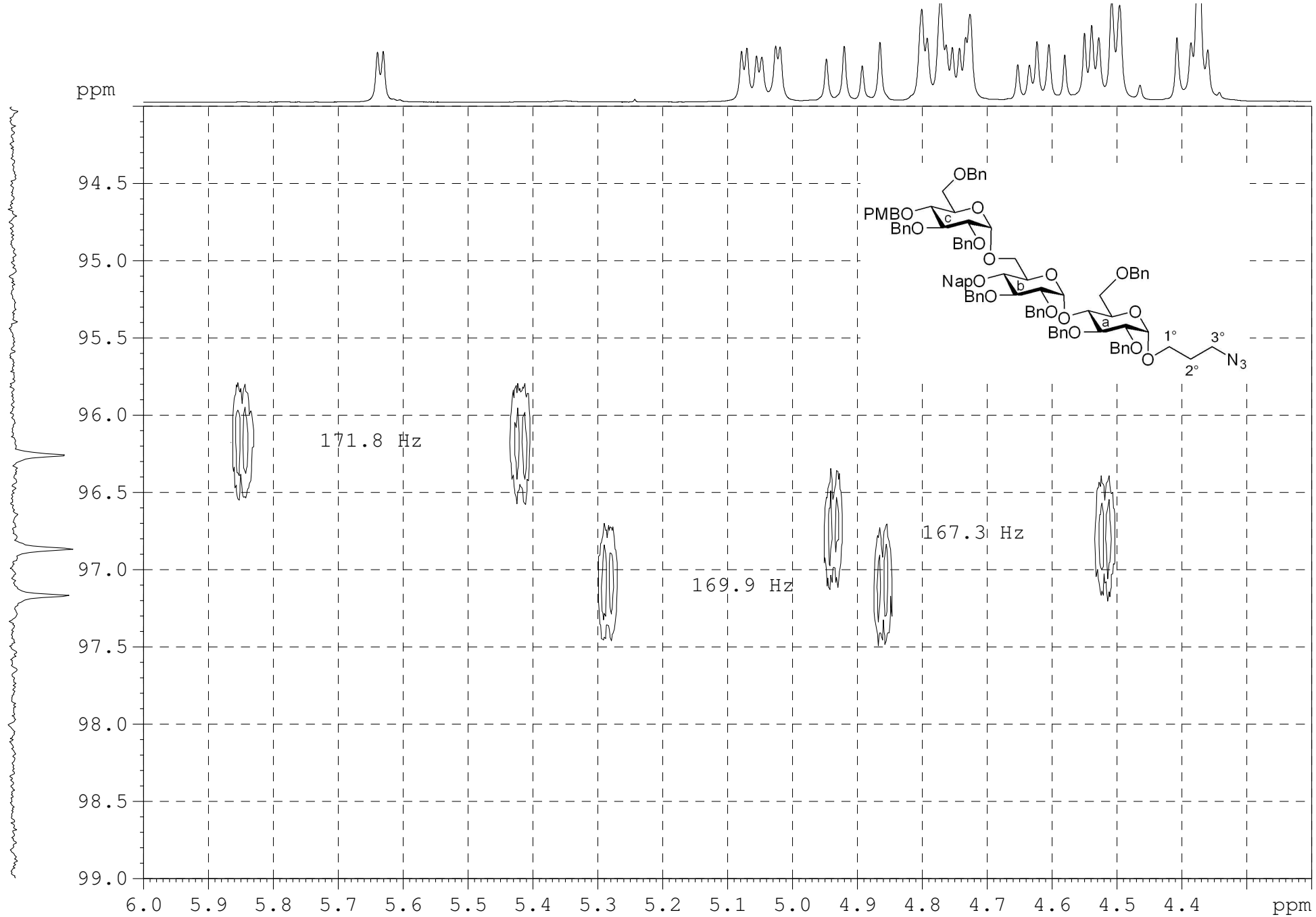



159.20
139.14
139.03
138.96
138.54
138.17
138.13
138.11
138.03
136.20
133.36
133.01
130.77
129.62
128.57
128.45
128.39
128.36
128.33
128.22
128.15
128.05
128.04
127.80
127.75
127.70
127.55
127.50
127.47
127.38
127.21
126.61
126.53
126.15
126.08
125.87
113.76
97.20
96.90
96.29
82.12
81.98
81.81
80.38
80.21
80.00
77.65
77.48
77.31
77.16
76.84
75.58
75.50
75.22
74.77
74.09
73.54
73.34
73.29
71.94
71.83
71.70
70.27
69.79
69.14
68.39
65.24
64.91
55.33
48.41
28.93
OBn
PMBO
BnO
BnO
O
NapO
BnO
O
BnO
O
OBn
O
BnO
BnO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

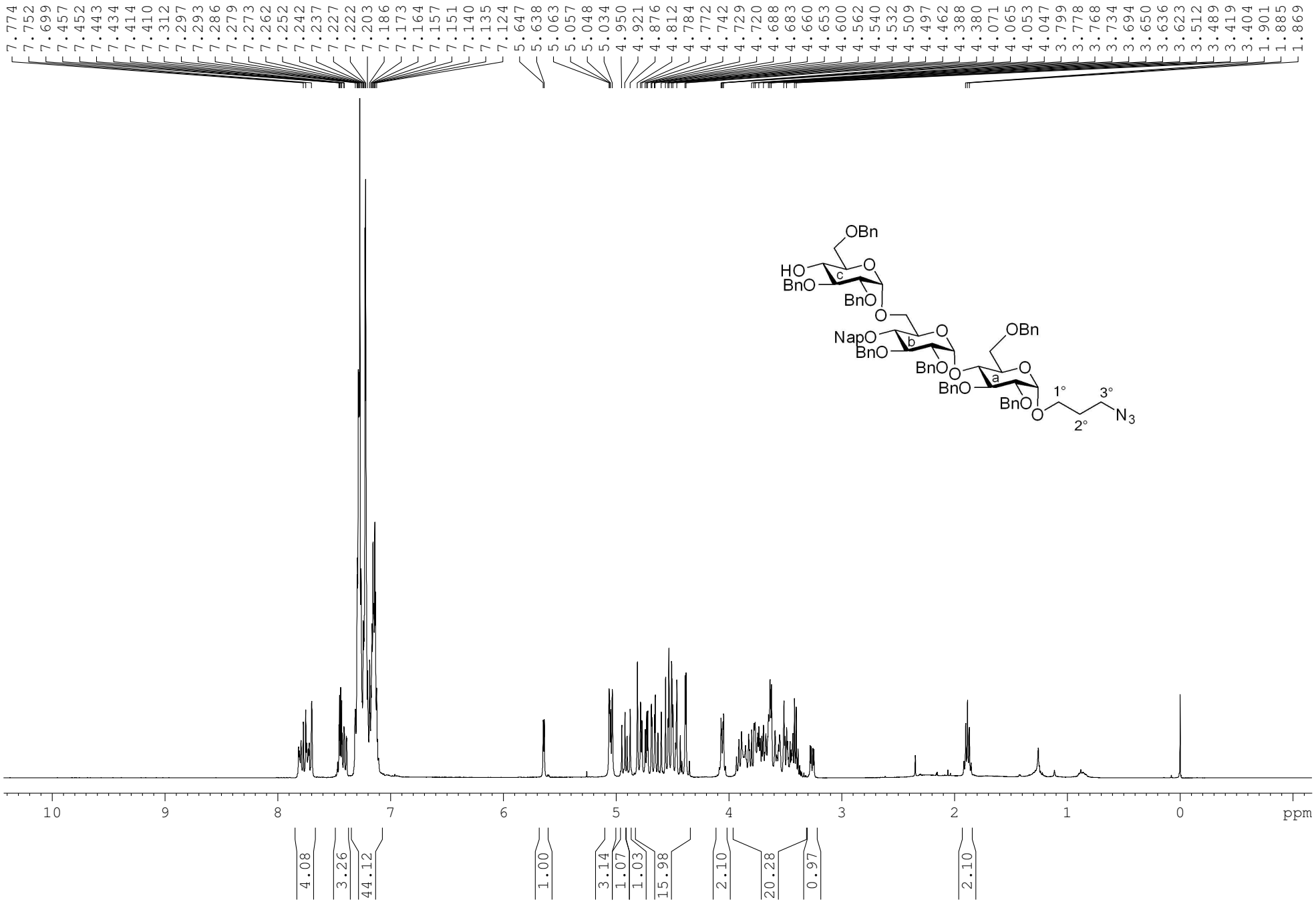

ppm
OBn
PMBO
BnO
BnO
O
NapO
BnO
BnO
BnO
BnO
OBn
1°
2°
3°
N_3
a
b
c
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

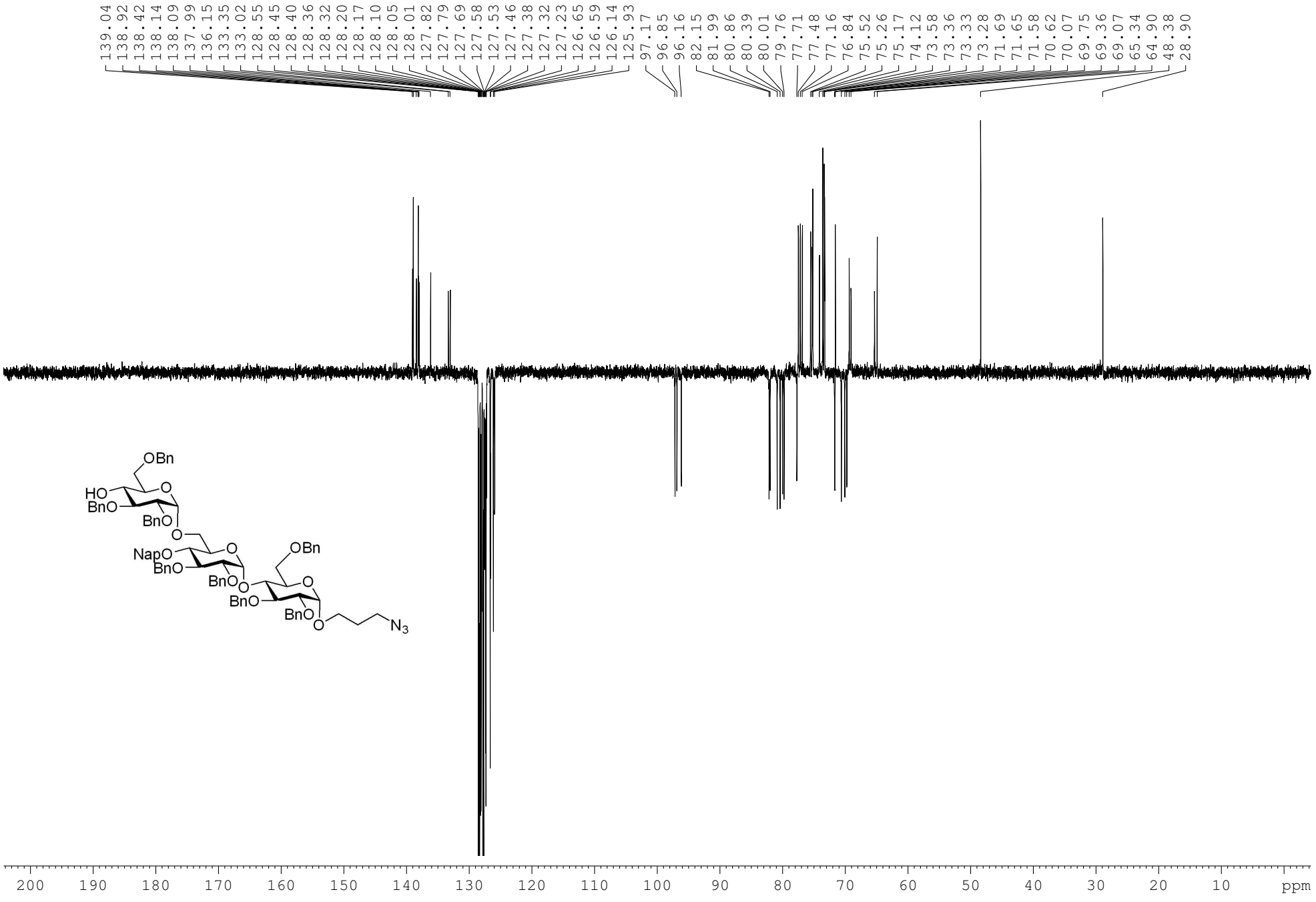

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
PMBO
BnO
c
BnO
O
NapO
BnO
b
BnO
O
OBn
BnO
a
O
BnO
O
1°
2°
3°
N3

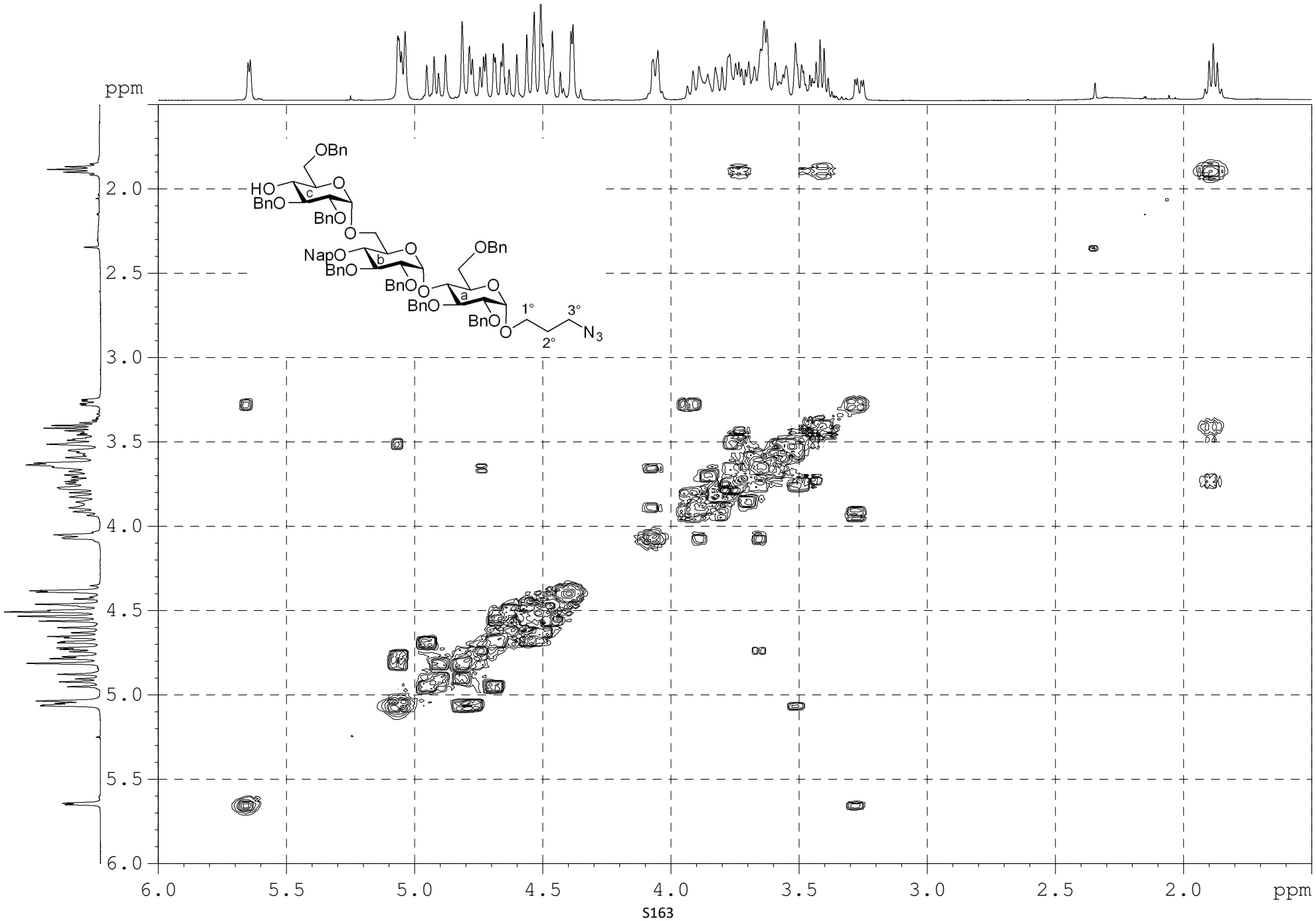

ppm
OBn
PMBO
BnO
c
BnO
O
NapO
BnO
b
O
OBn
BnO
O
a
O
BnO
BnO
1°
3°
O
2°
N3
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

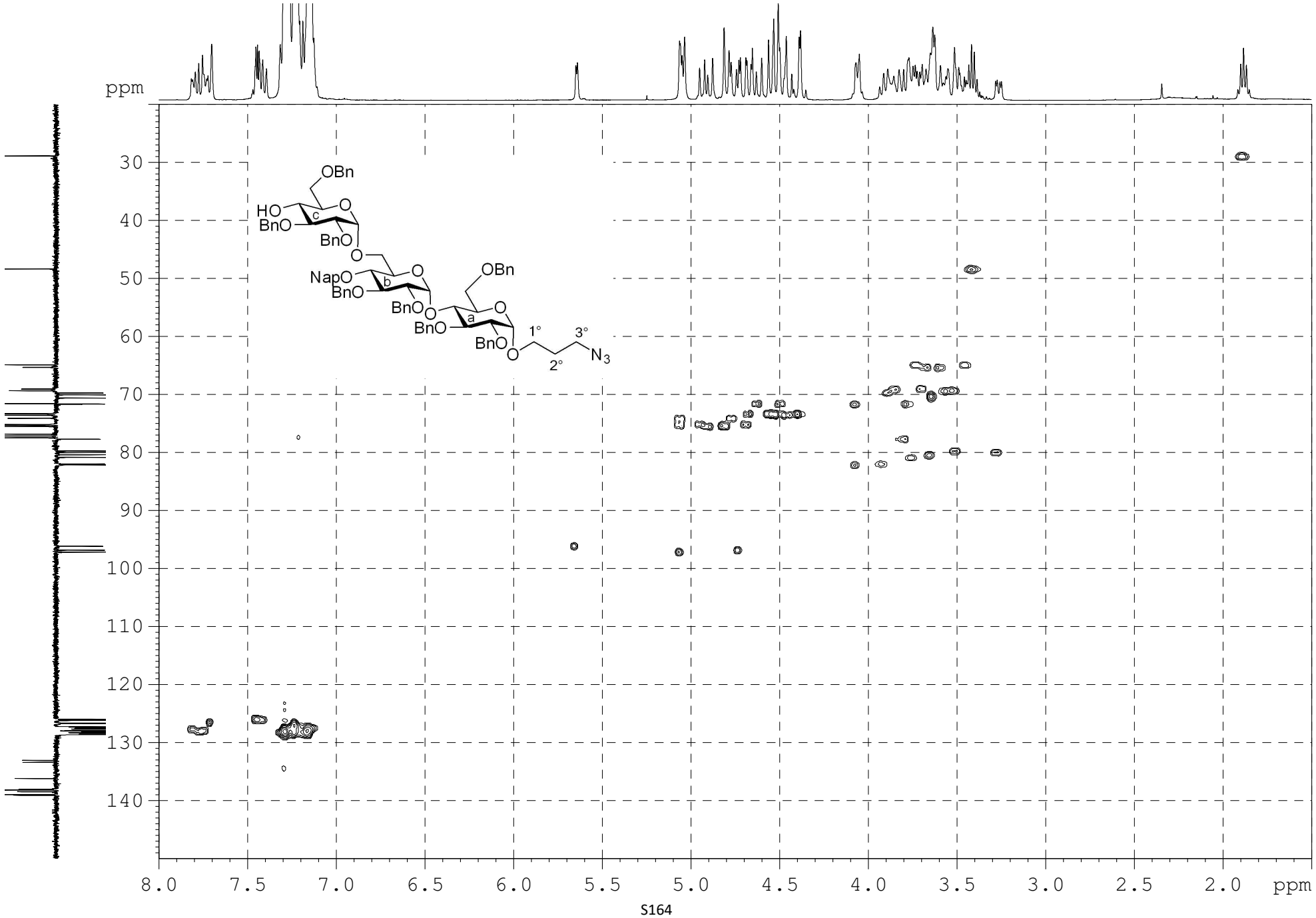

ppm
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
171.8 Hz
169.9 Hz
167.3 Hz
OBn
PMBO
BnO
BnO
O
NapO
BnO
BnO
BnO
BnO
a
b
c
1°
2°
3°
N3
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
ppm

^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC of **33**

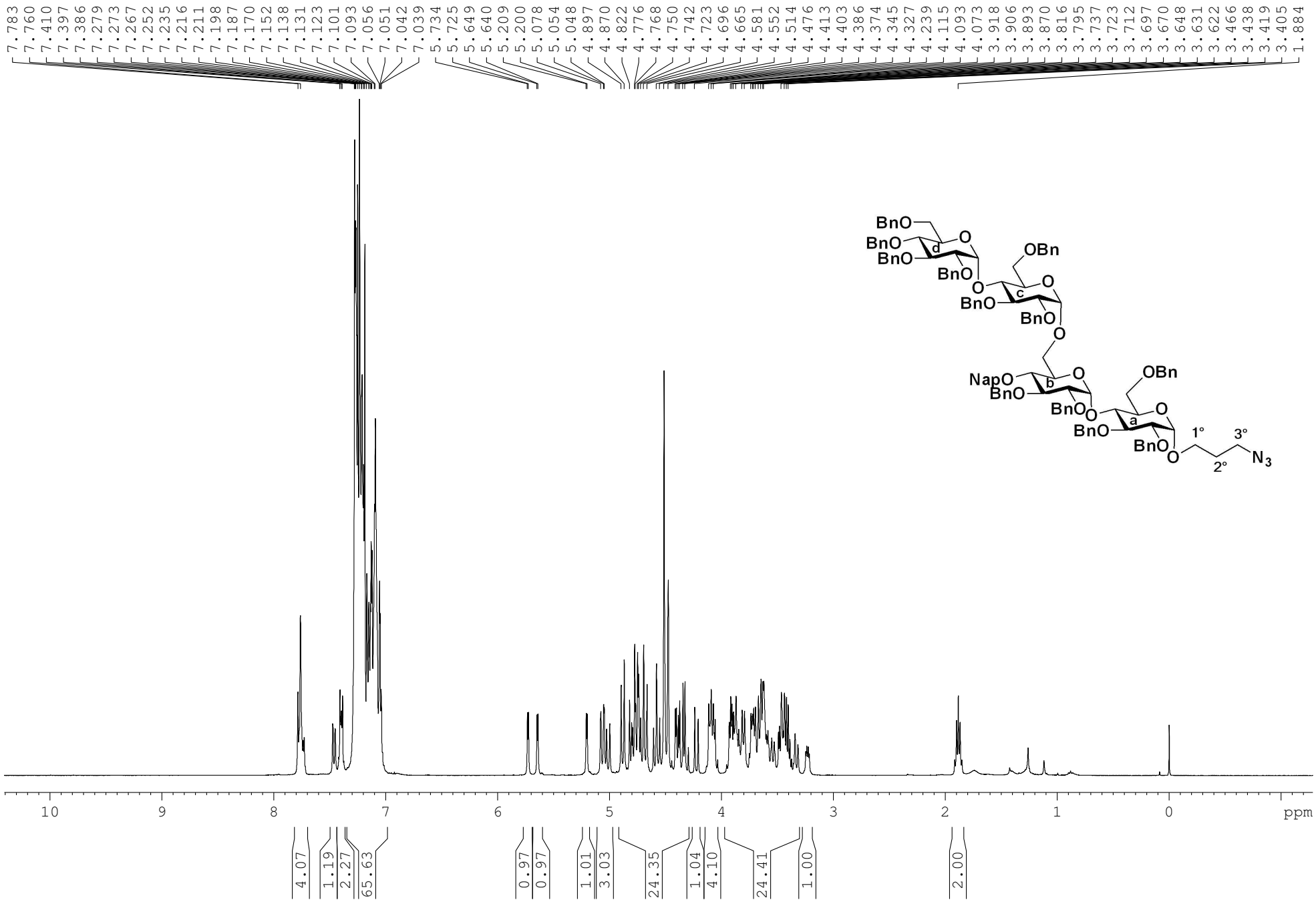


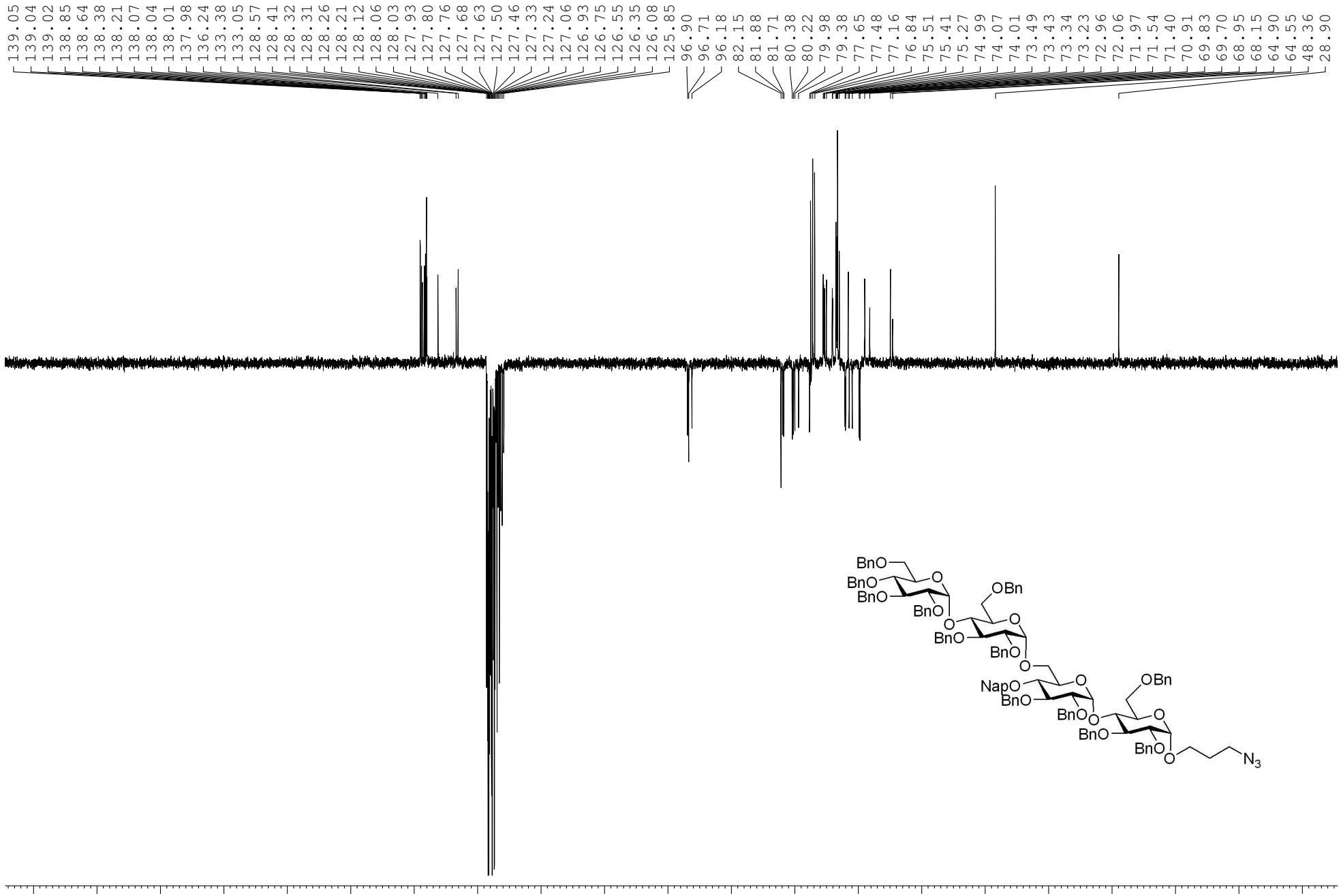

139.04
138.92
138.42
138.14
138.09
137.99
136.15
133.35
133.02
128.55
128.45
128.40
128.36
128.32
128.20
128.17
128.10
128.05
128.01
127.82
127.79
127.69
127.58
127.53
127.46
127.38
127.32
127.23
126.65
126.59
126.14
125.93
97.17
96.85
96.16
82.15
81.99
80.86
80.39
80.01
79.76
77.71
77.48
77.16
76.84
75.52
75.26
75.17
74.12
73.58
73.36
73.33
73.28
71.69
71.65
71.58
70.62
70.07
69.75
69.36
69.07
65.34
64.90
48.38
28.90
OBn
HO
BnO
BnO
O
NapO
BnO
BnO
O
BnO
BnO
O
OBn
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

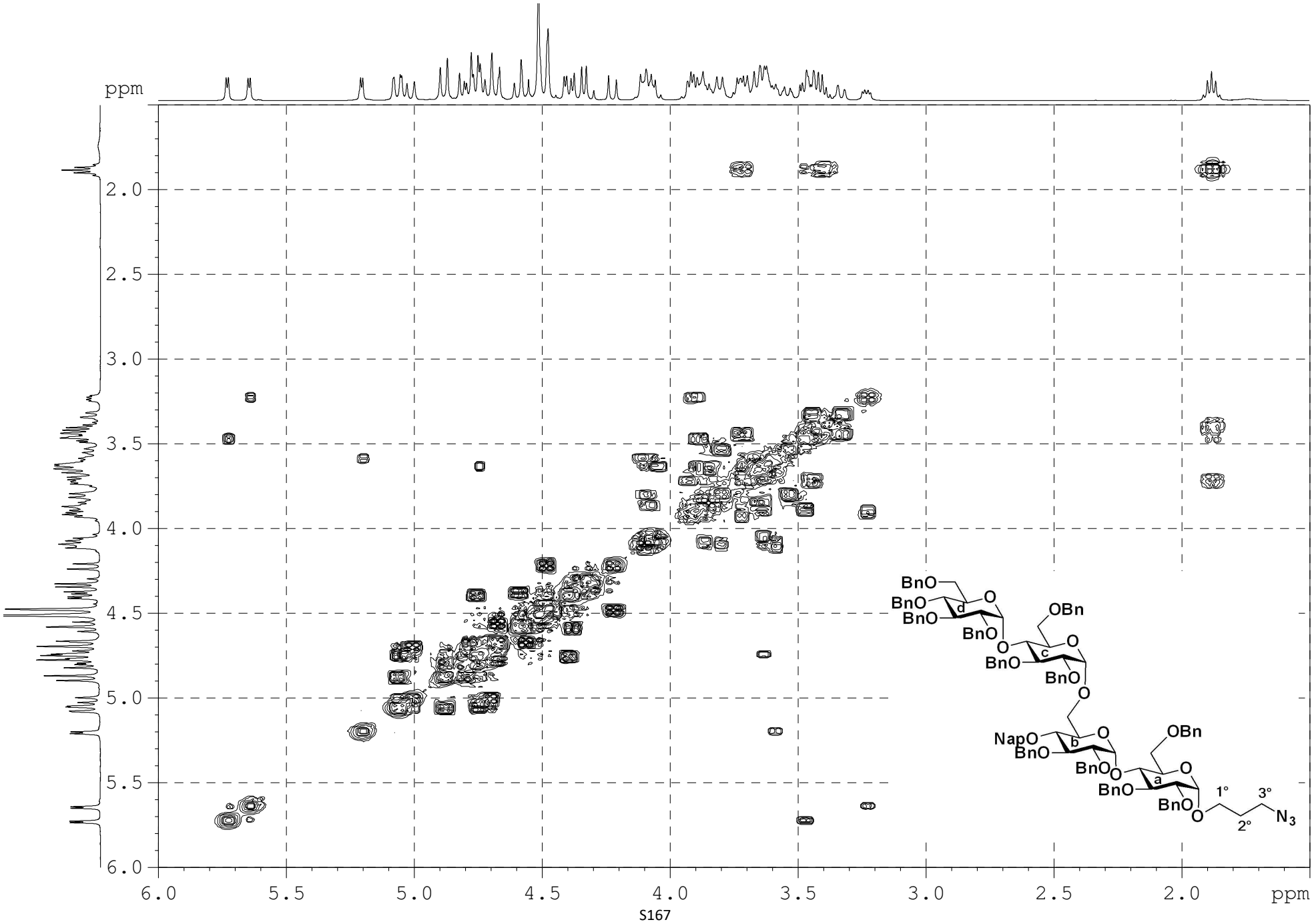

ppm
OBn
HO
BnO
BnO
O
NapO
BnO
BnO
BnO
BnO
OBn
BnO
1°
2°
3°
N3
a
b
c
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

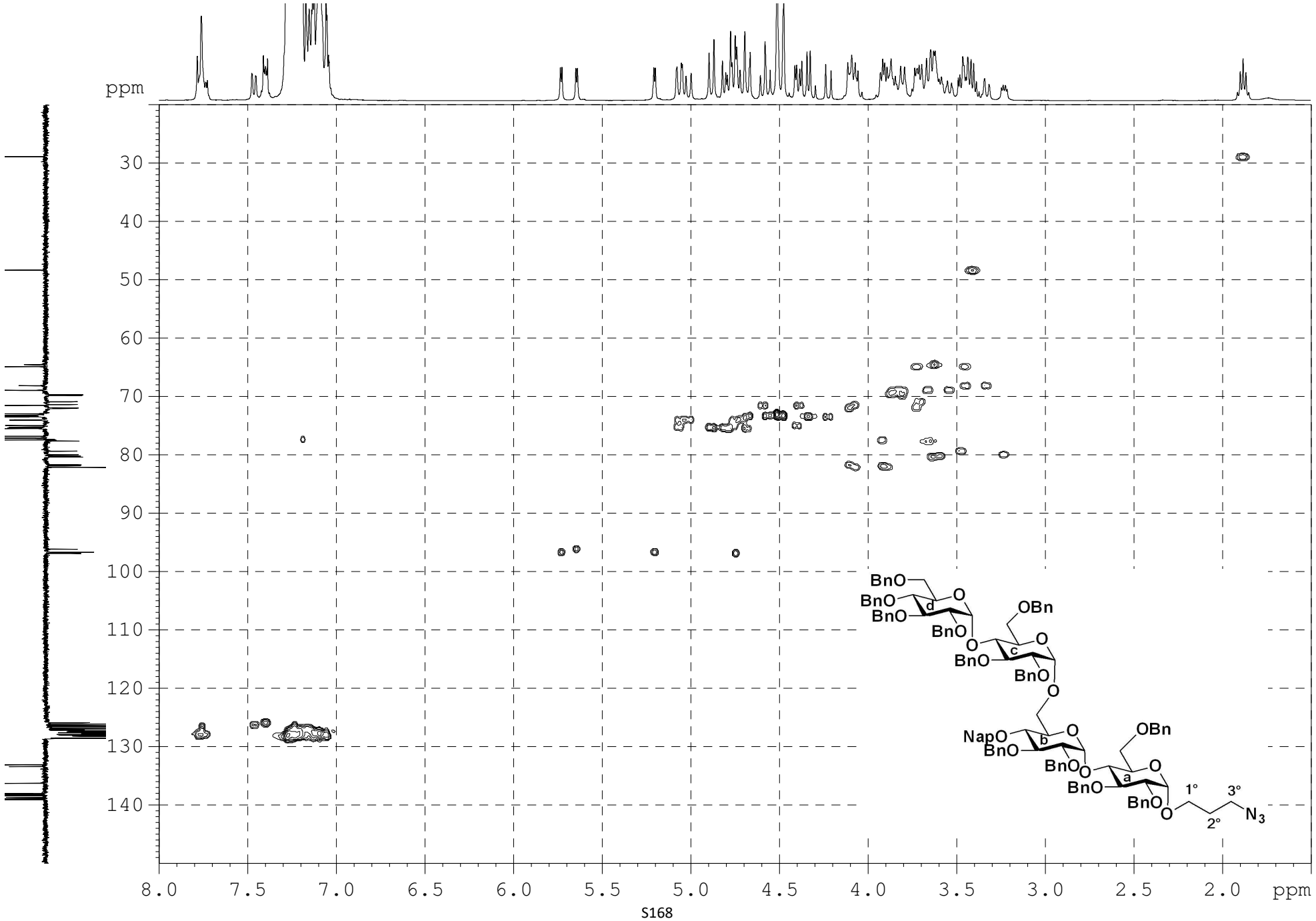

ppm
30
40
50
60
70
80
90
100
110
120
130
140
OBn
HO
BnO
c
O
BnO
O
NapO
BnO
b
O
BnO
O
a
OBn
O
BnO
O
1°
2°
3°
N3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

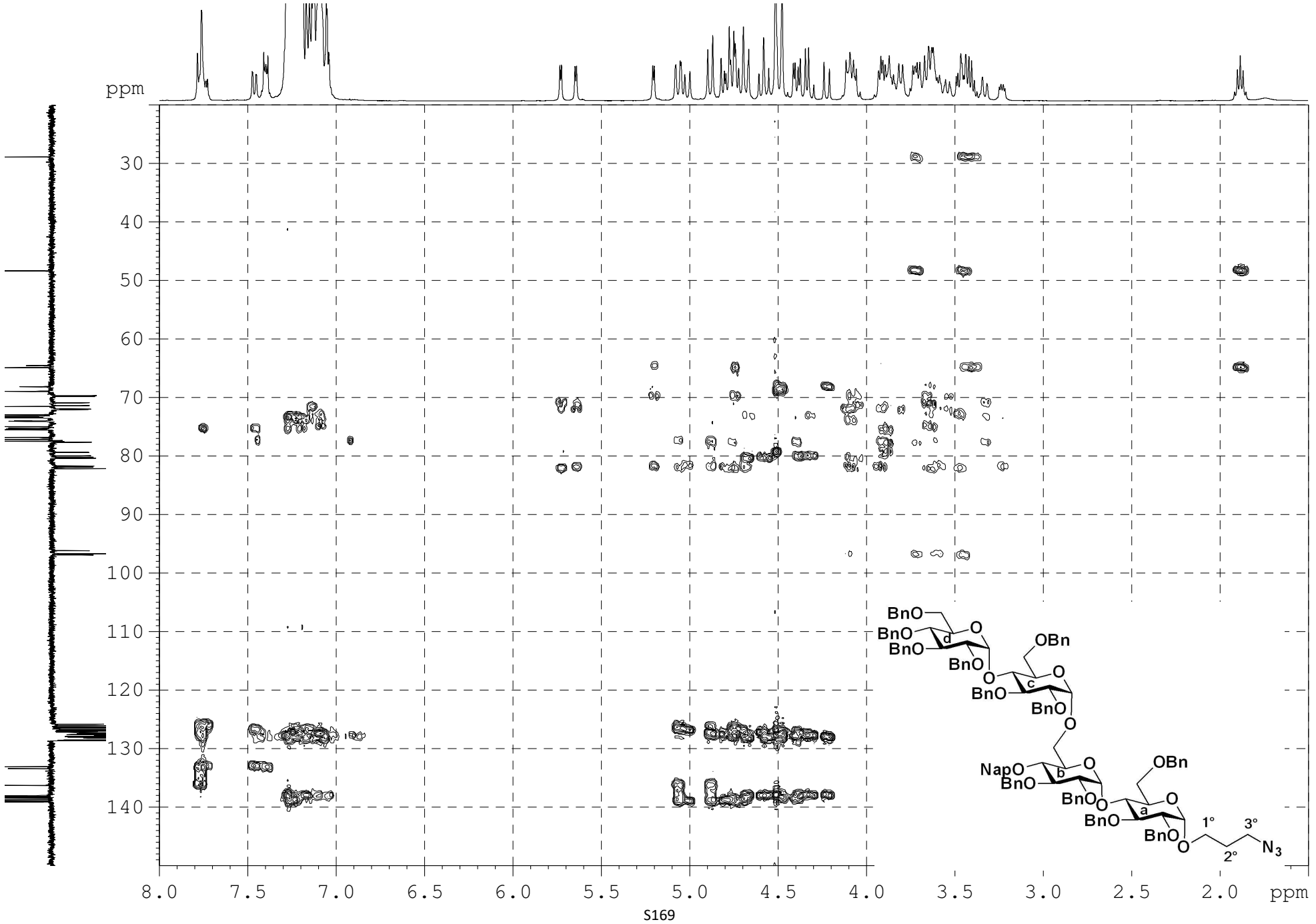
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **34**

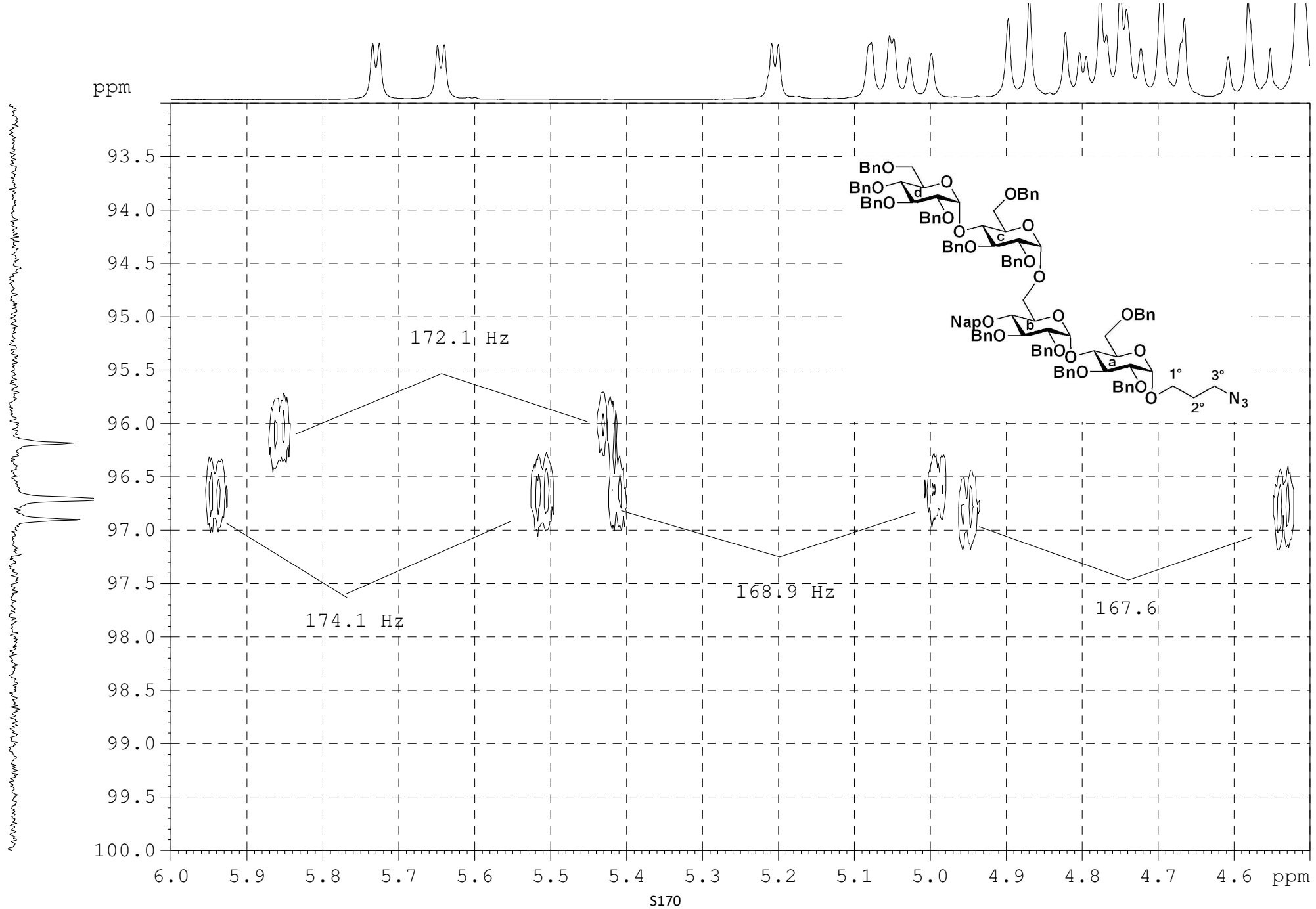



139.05
139.04
139.02
138.85
138.64
138.38
138.21
138.07
138.04
138.01
137.98
136.24
133.38
133.05
128.57
128.41
128.32
128.31
128.26
128.21
128.12
128.06
128.03
127.93
127.80
127.76
127.68
127.63
127.50
127.46
127.33
127.24
127.06
126.93
126.75
126.55
126.35
126.08
125.85
96.90
96.71
96.18
82.15
81.88
81.71
80.38
80.22
79.98
79.38
77.65
77.48
77.16
76.84
75.51
75.41
75.27
74.99
74.07
74.01
73.49
73.43
73.34
73.23
72.96
72.06
71.97
71.54
71.40
70.91
69.83
69.70
68.95
68.15
64.90
64.55
48.36
28.90
BnO
BnO
BnO
BnO
O
OBn
O
BnO
BnO
O
NapO
BnO
O
BnO
OBn
O
BnO
BnO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

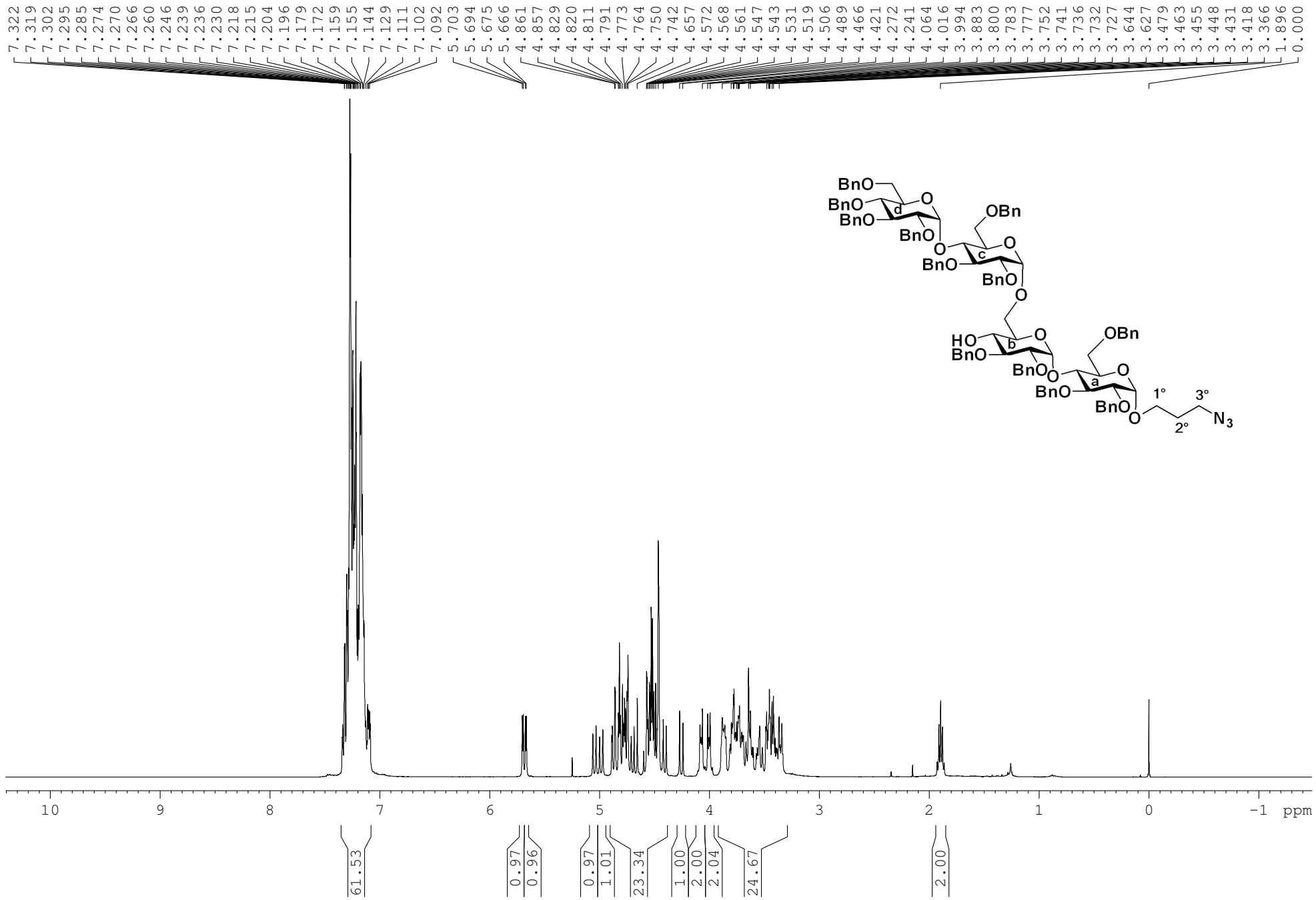

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
O
BnO
OBn
c
O
BnO
O
NapO
BnO
b
O
BnO
O
OBn
BnO
a
O
BnO
O
1°
2°
3°
N3

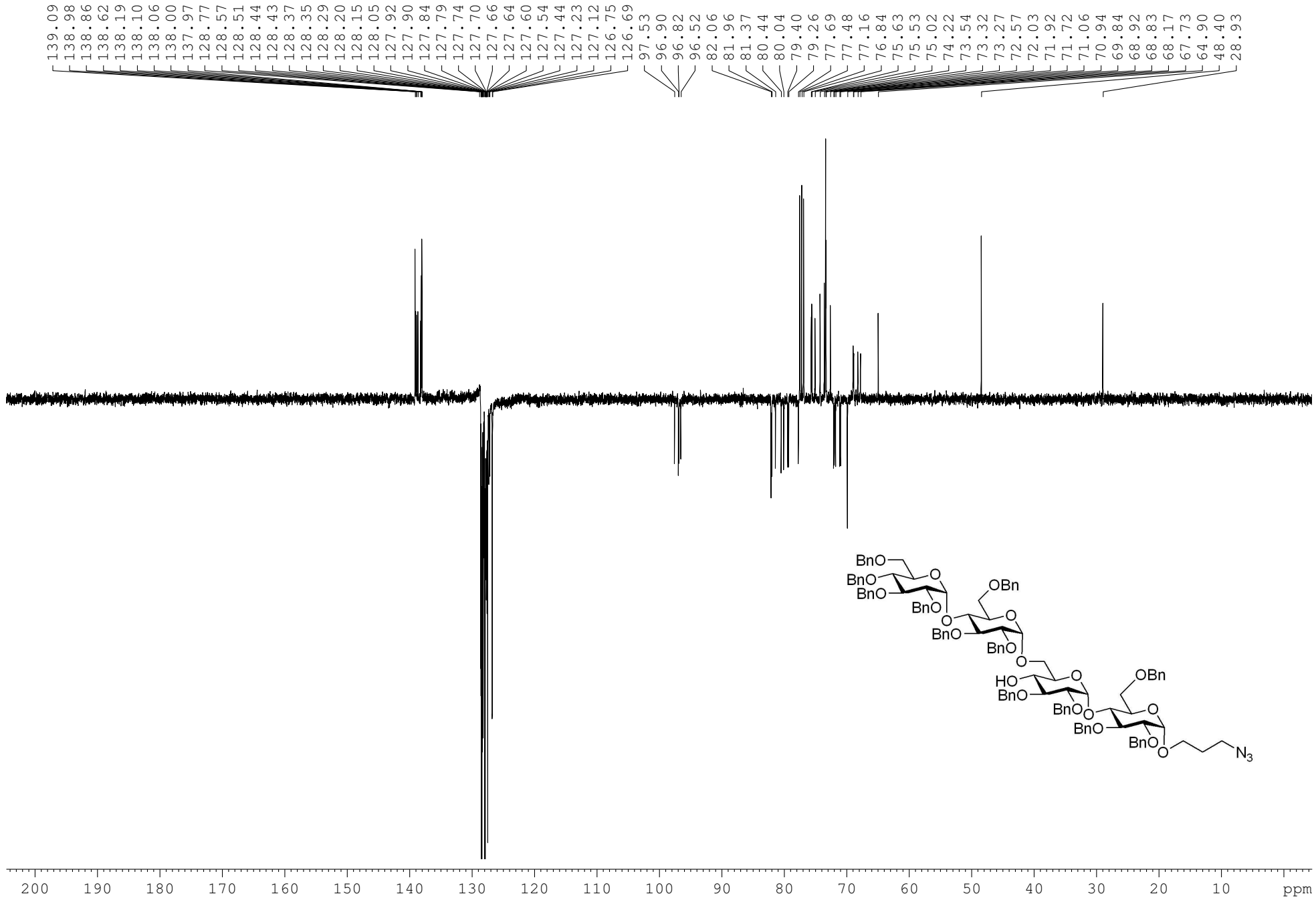

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
OBn
O
BnO
c
O
BnO
O
NapO
BnO
b
O
BnO
O
OBn
BnO
a
O
BnO
O
1°
2°
3°
N3

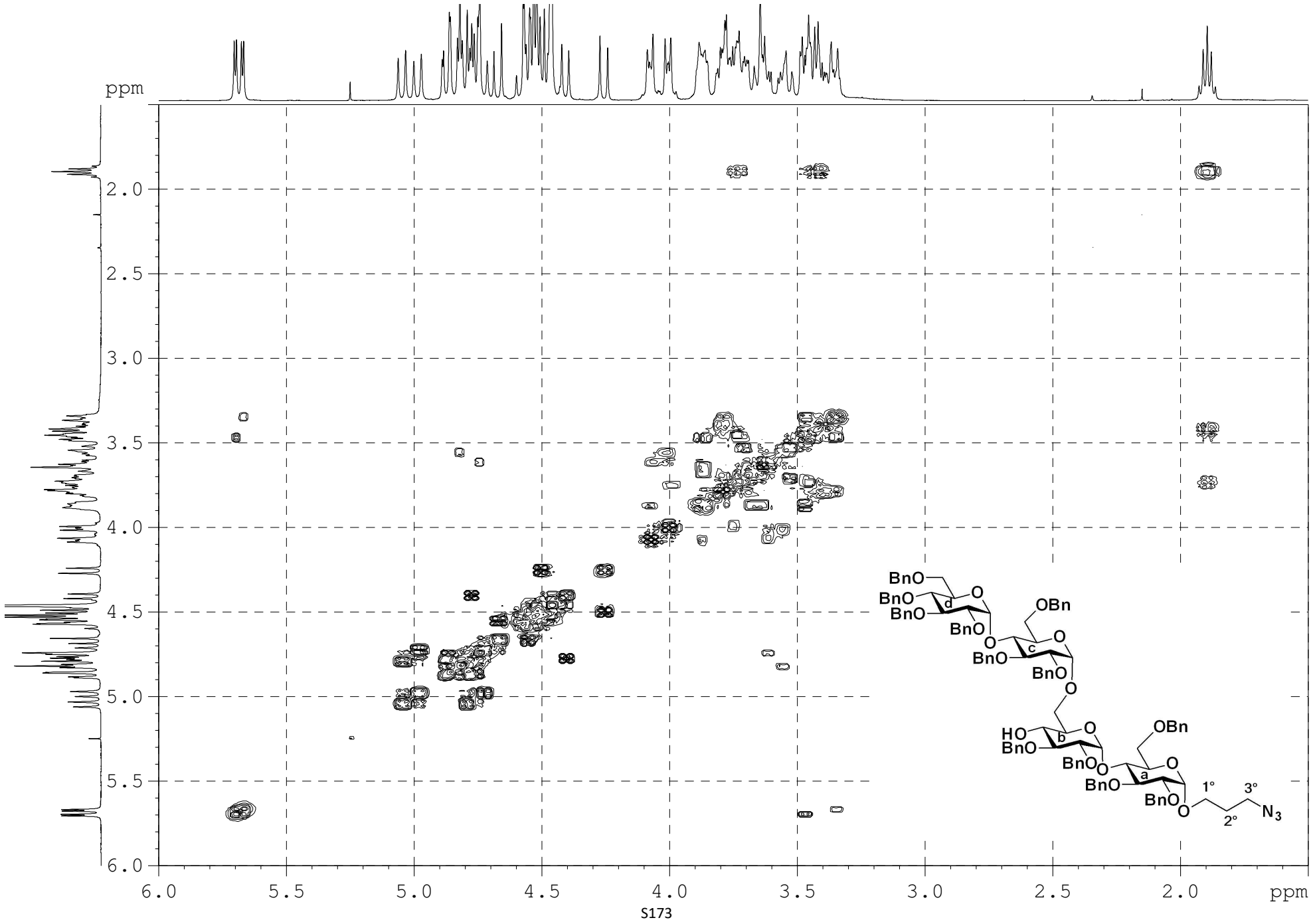

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
OBn
BnO
O
c
O
BnO
BnO
O
NapO
BnO
b
O
OBn
BnO
O
BnO
a
O
BnO
O
1°
3°
2°
N3

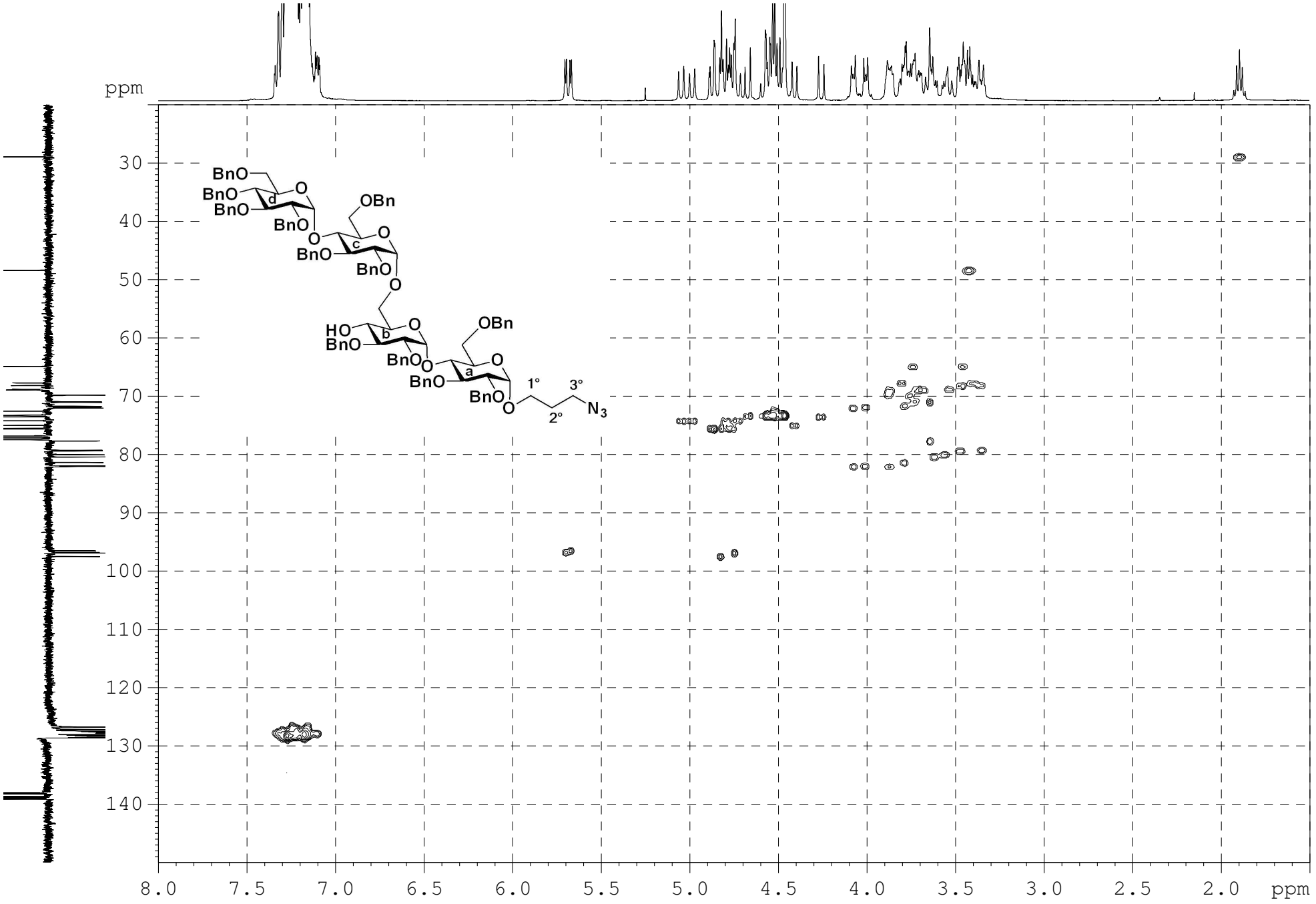

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
172.1 Hz
174.1 Hz
168.9 Hz
167.6
BnO
OBn
NapO
N3
1°
2°
3°
a
b
c
d
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
ppm

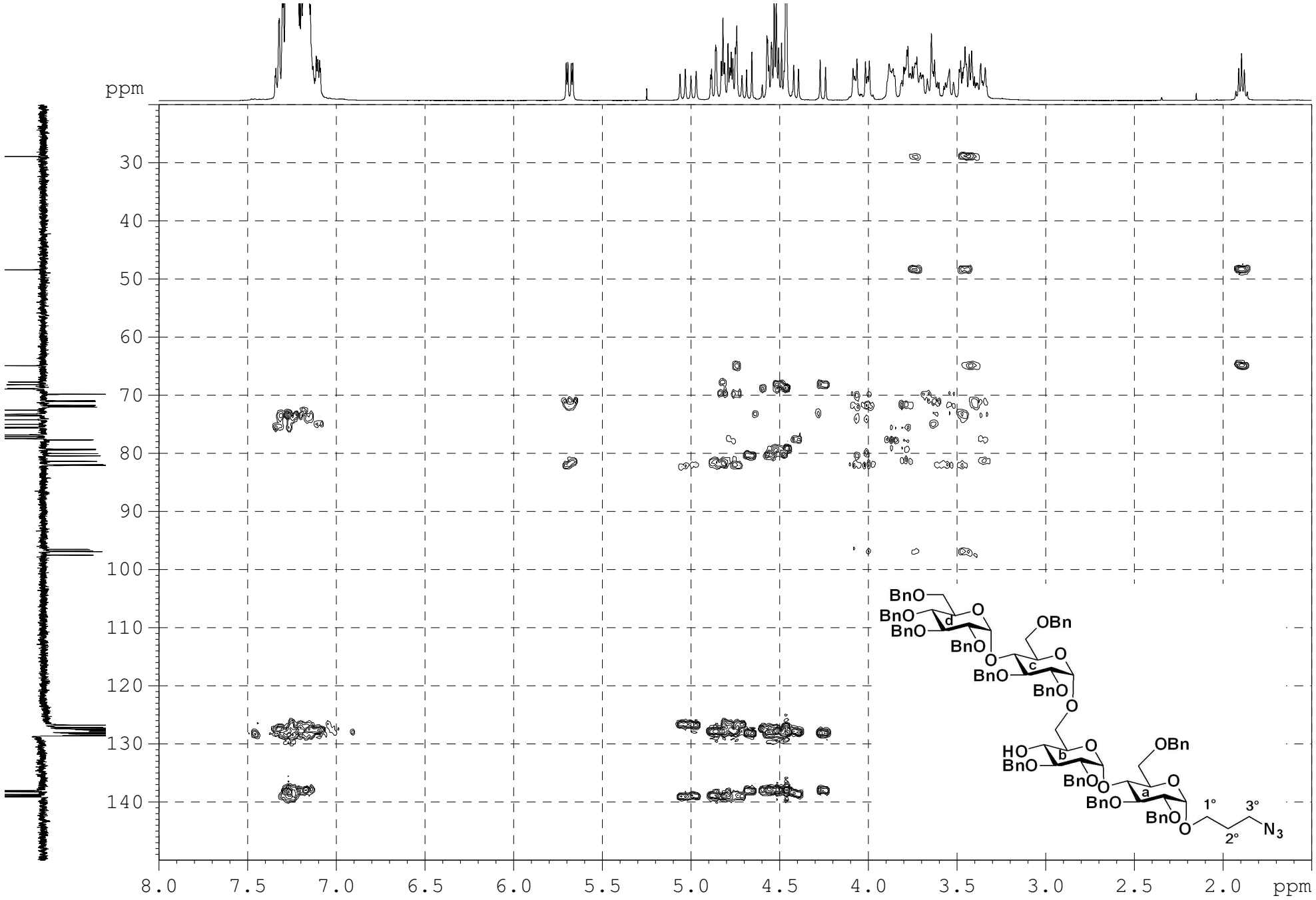
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **35**



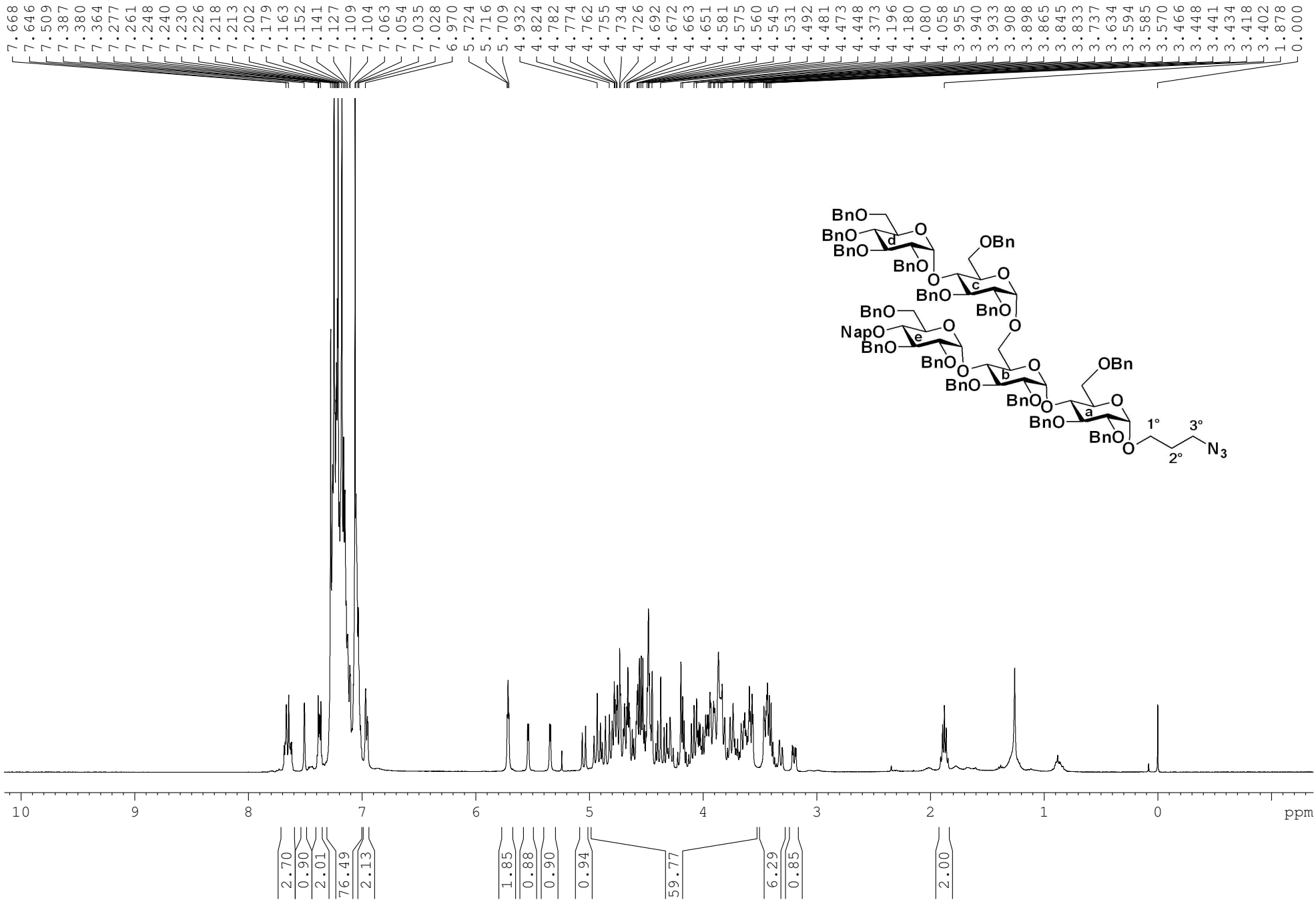

139.09
138.98
138.86
138.62
138.19
138.10
138.06
138.00
137.97
128.77
128.57
128.51
128.44
128.43
128.37
128.35
128.29
128.20
128.15
128.05
127.92
127.90
127.84
127.79
127.74
127.70
127.66
127.64
127.60
127.54
127.44
127.23
127.12
126.75
126.69
97.53
96.90
96.82
96.52
82.06
81.96
81.37
80.44
80.04
79.40
79.26
77.69
77.48
77.16
76.84
75.63
75.53
75.02
74.22
73.54
73.32
73.27
72.57
72.03
71.92
71.72
71.06
70.94
69.84
68.92
68.83
68.17
67.73
64.90
48.40
28.93
BnO
BnO
BnO
BnO
O
OBn
O
BnO
BnO
O
HO
BnO
O
OBn
BnO
O
O
BnO
BnO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

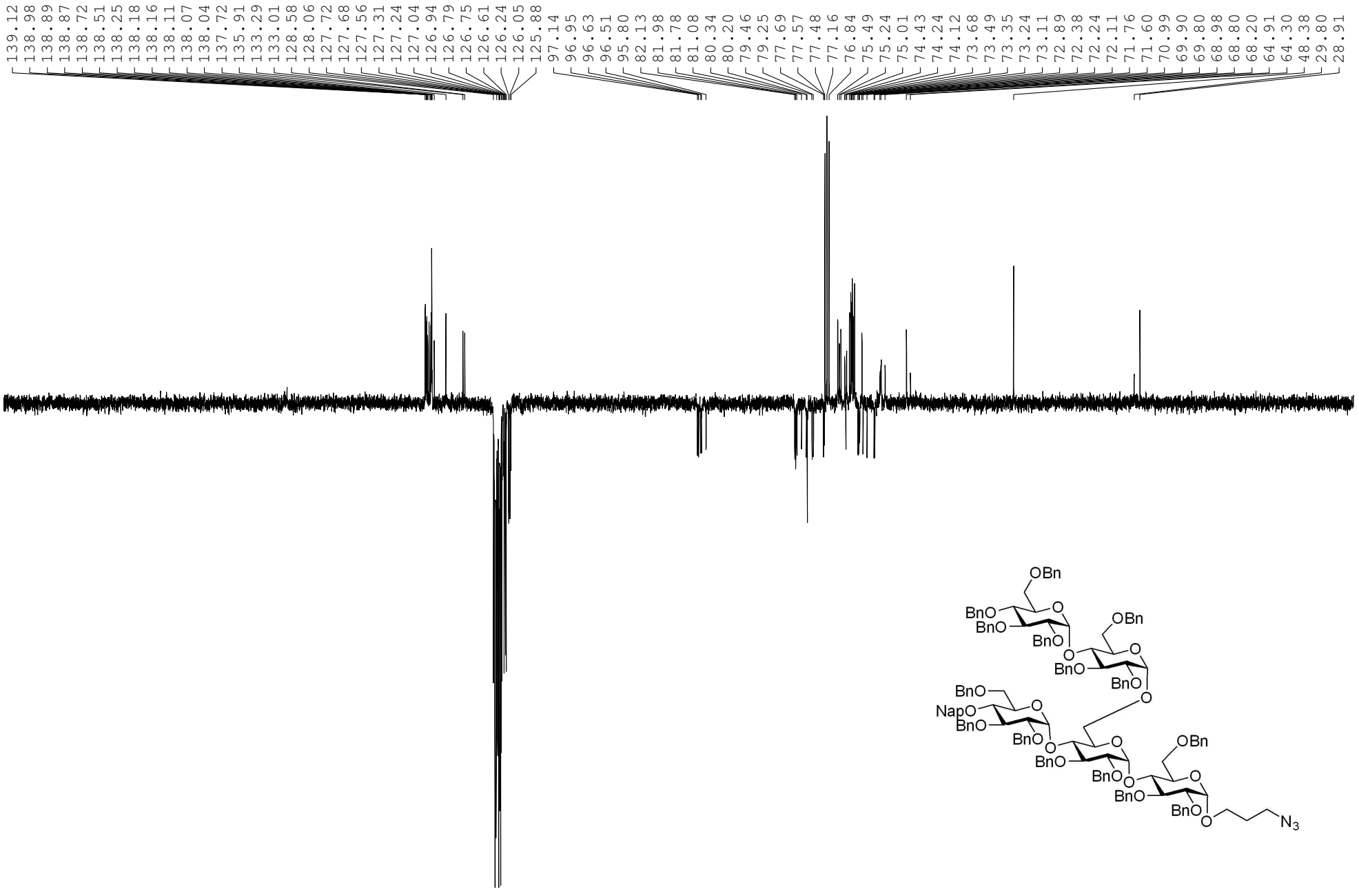

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
O
OBn
c
O
BnO
BnO
O
HO
BnO
b
O
BnO
O
OBn
a
O
BnO
BnO
O
1°
2°
3°
N3

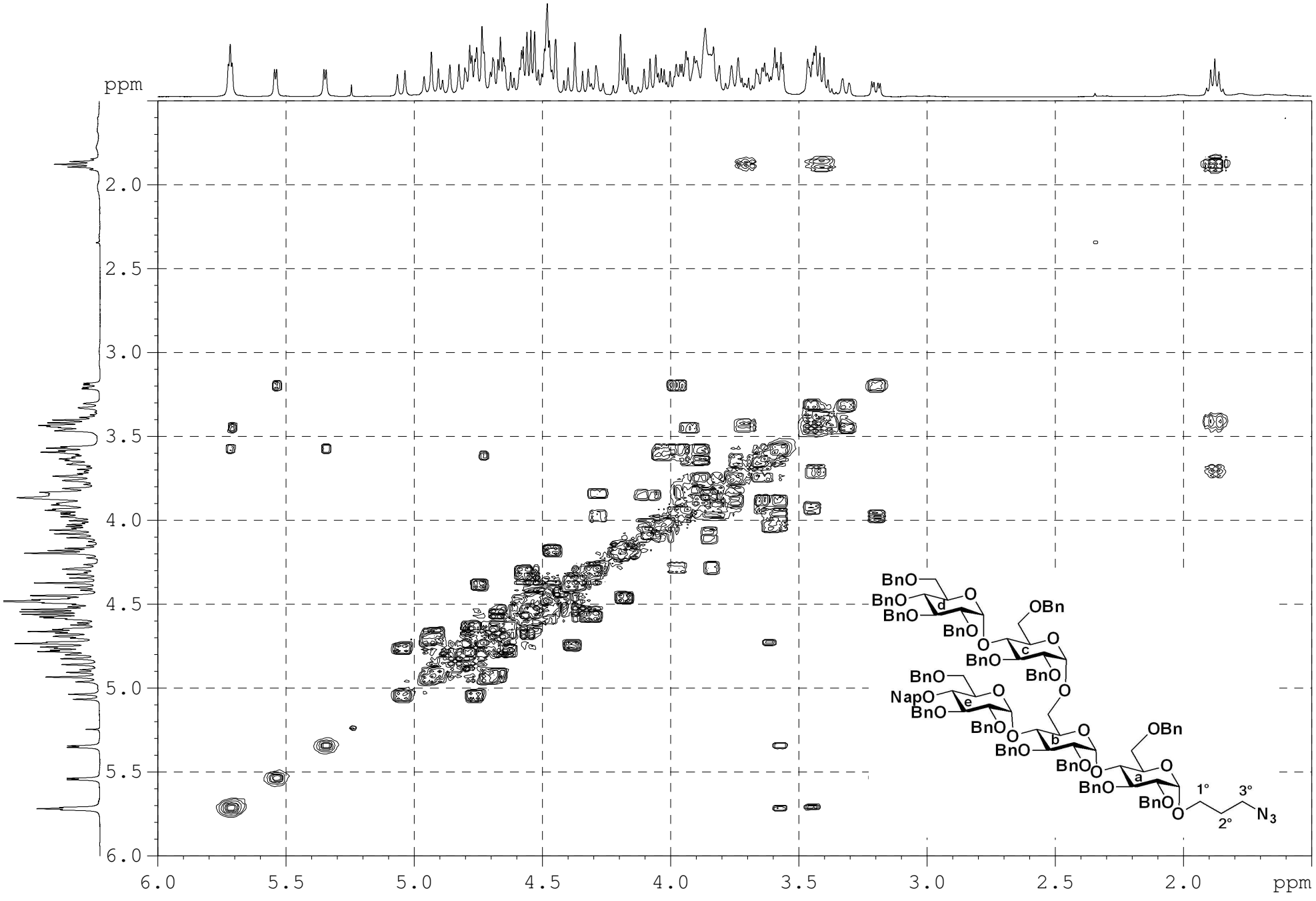

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
OBn
O
c
O
BnO
BnO
O
HO
BnO
b
O
BnO
OBn
O
a
O
BnO
BnO
O
1°
2°
3°
N3

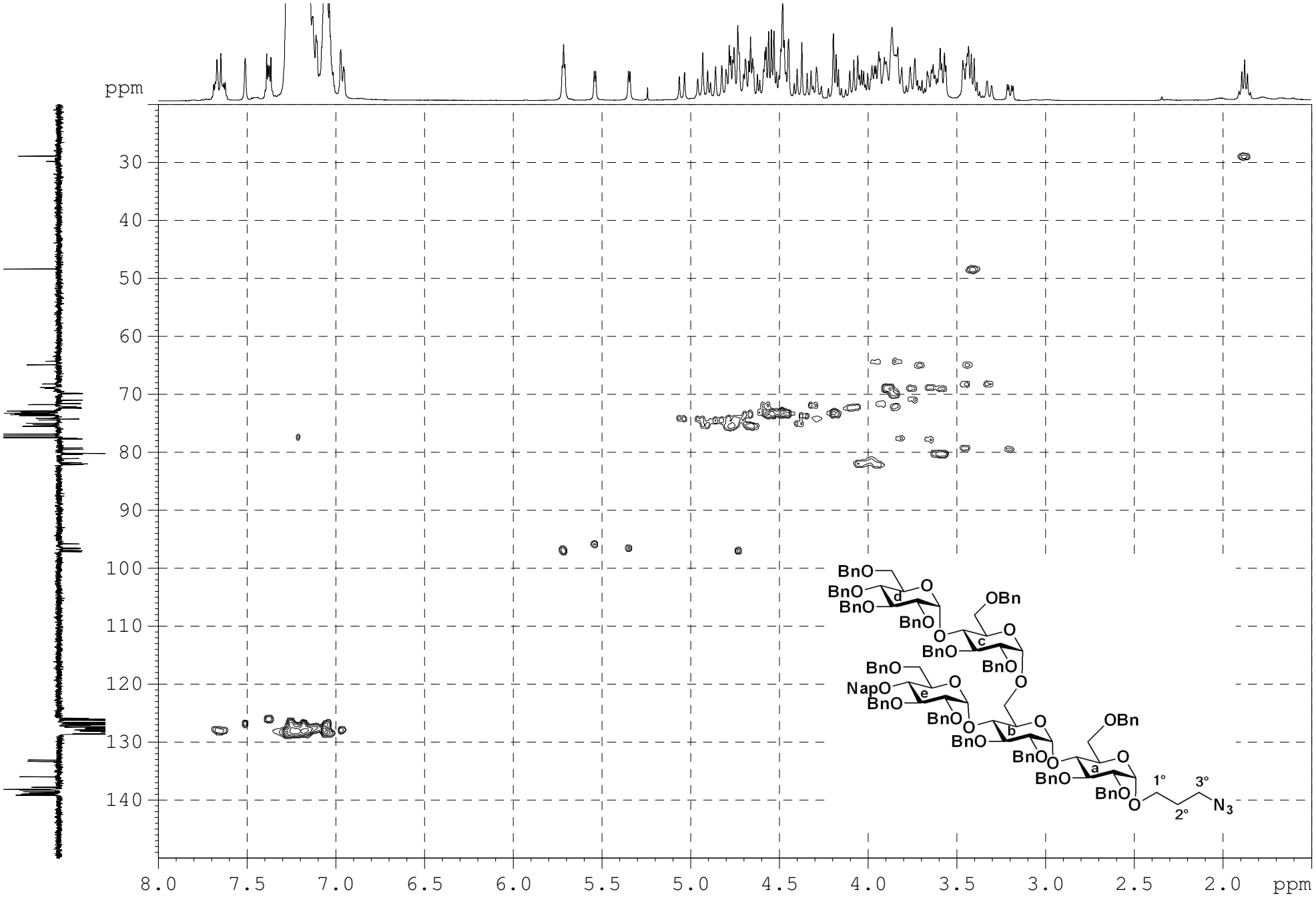

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
O
d
OBn
BnO
O
BnO
c
BnO
O
HO
BnO
O
b
OBn
BnO
O
BnO
a
O
BnO
O
1°
2°
3°
N3

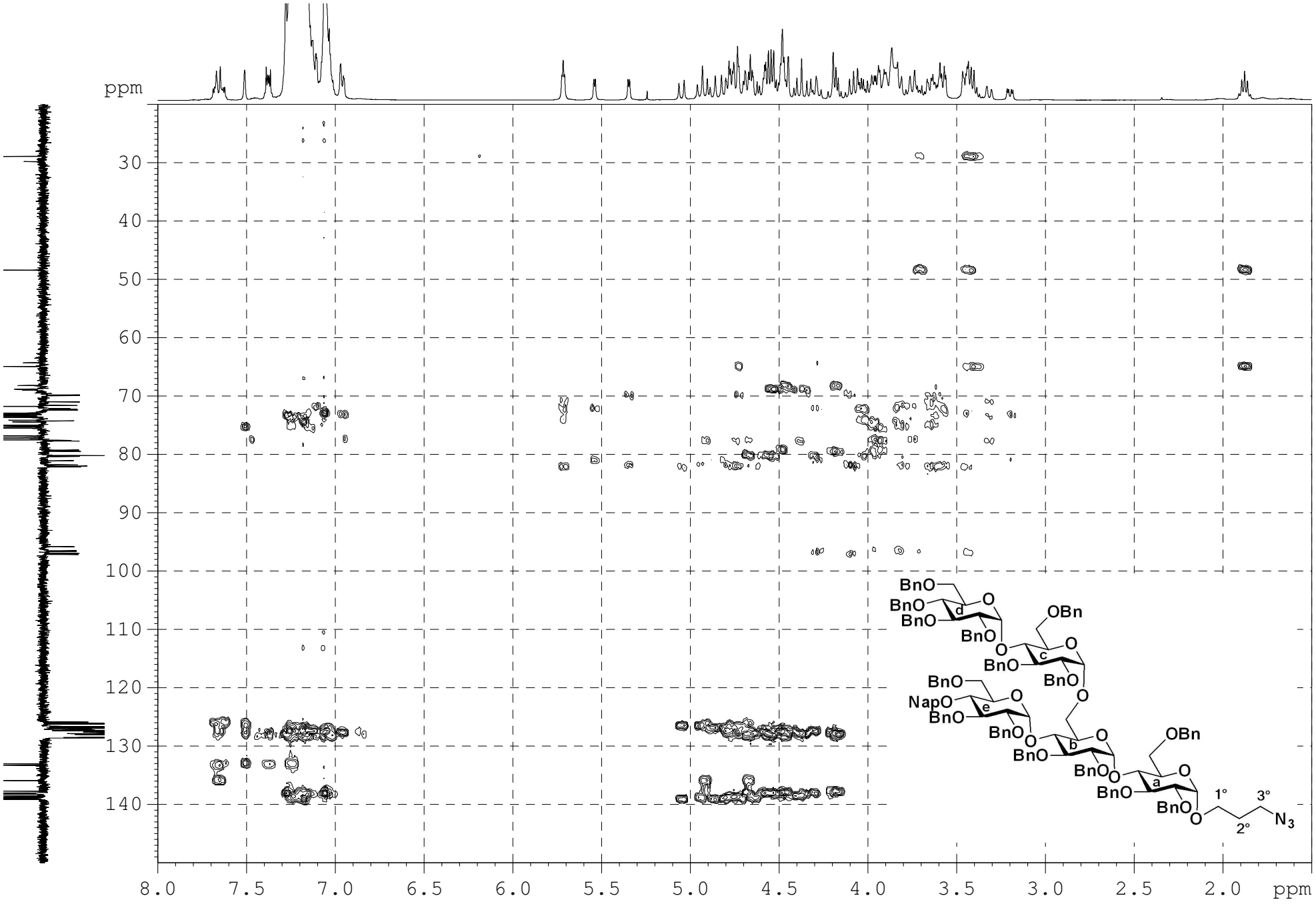
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **36**

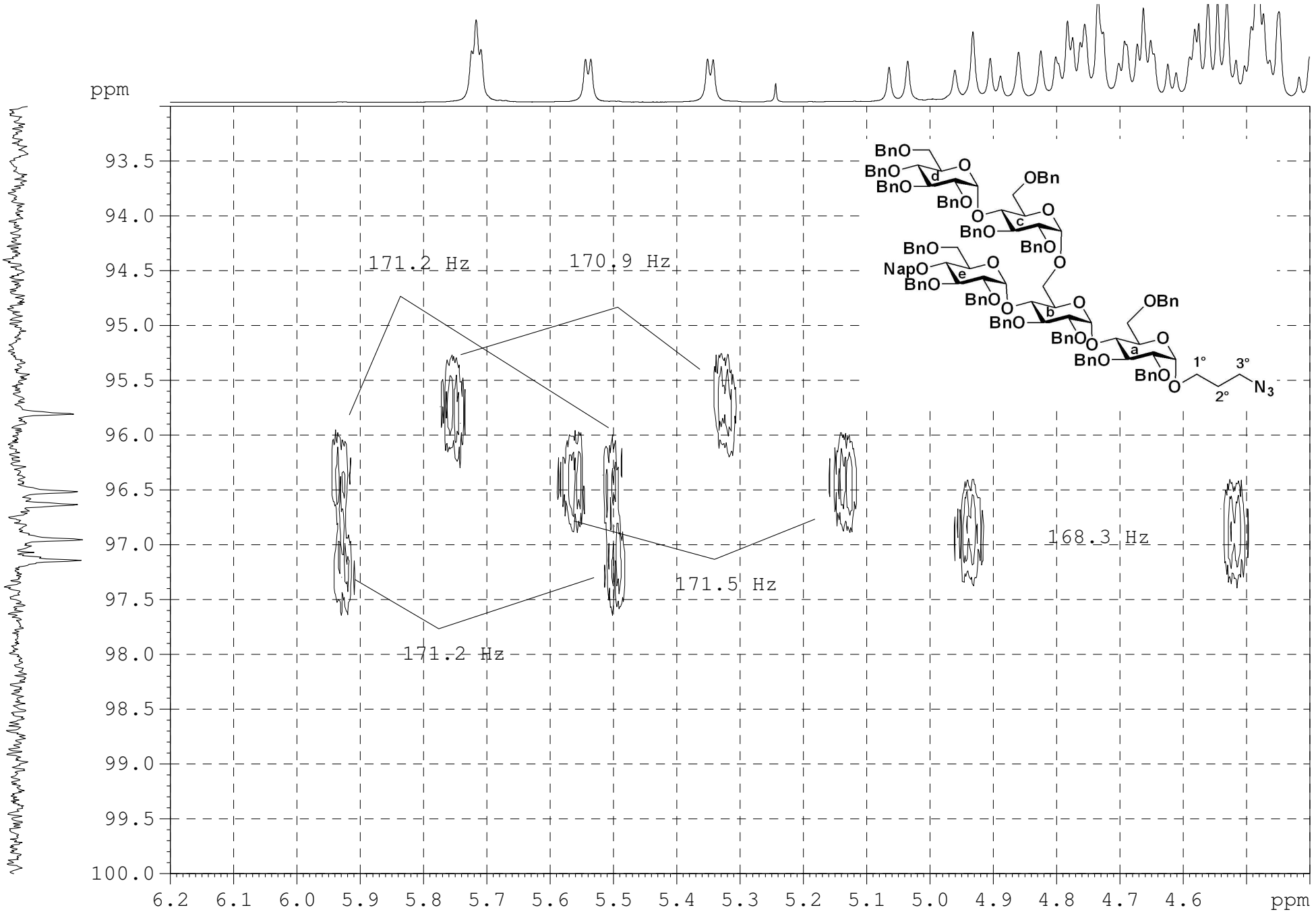



139.12
138.98
138.89
138.87
138.72
138.51
138.25
138.18
138.16
138.11
138.07
138.04
137.72
135.91
133.29
133.01
128.58
128.06
127.72
127.68
127.56
127.31
127.24
127.04
126.94
126.79
126.75
126.61
126.24
126.05
125.88
97.14
96.95
96.63
96.51
95.80
82.13
81.98
81.78
81.08
80.34
80.20
79.46
79.25
77.69
77.57
77.48
77.16
76.84
75.49
75.24
75.01
74.43
74.24
74.12
73.68
73.49
73.35
73.24
73.11
72.89
72.38
72.24
72.11
71.76
71.60
70.99
69.90
69.80
68.98
68.80
68.20
64.91
64.30
48.38
29.80
28.91
OBn
BnO
NapO
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

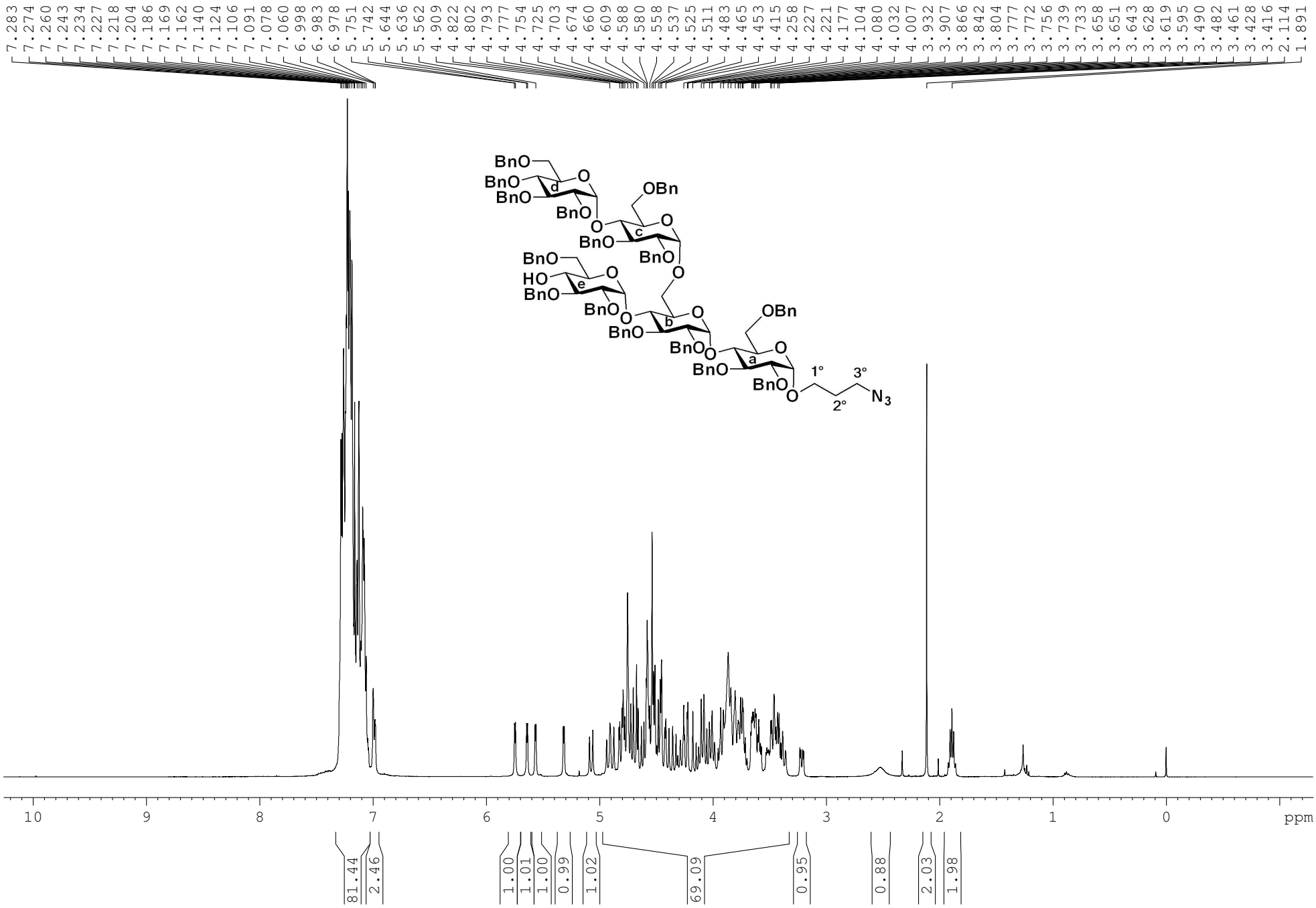

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
OBn
O
c
O
BnO
BnO
O
BnO
NapO
BnO
e
O
BnO
O
b
O
BnO
OBn
BnO
O
a
O
BnO
BnO
O
1°
2°
3°
N3

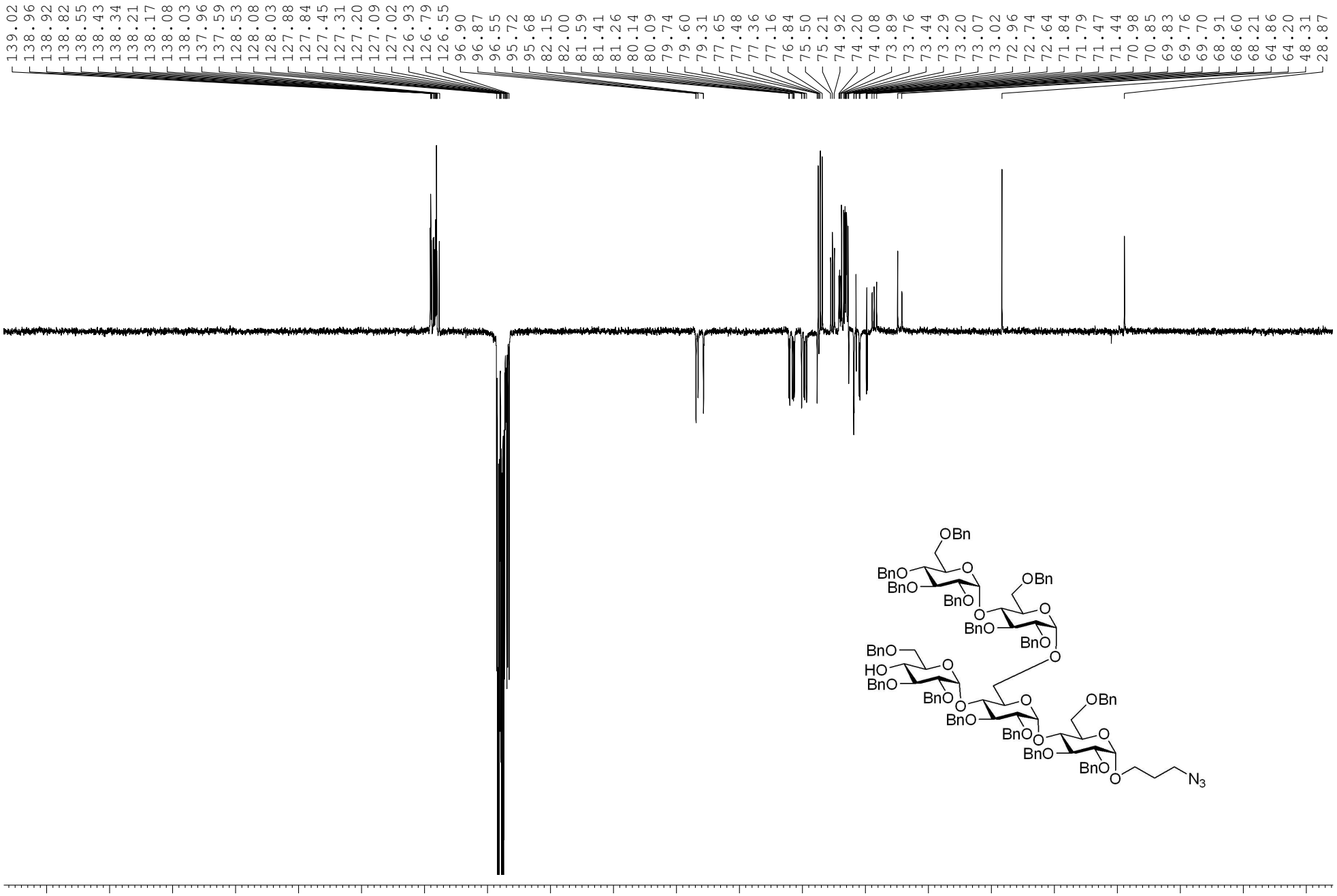

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
O
d
BnO
OBn
O
O
c
BnO
BnO
BnO
NapO
BnO
O
e
BnO
O
b
O
BnO
OBn
BnO
O
a
O
BnO
O
1°
2°
3°
N3

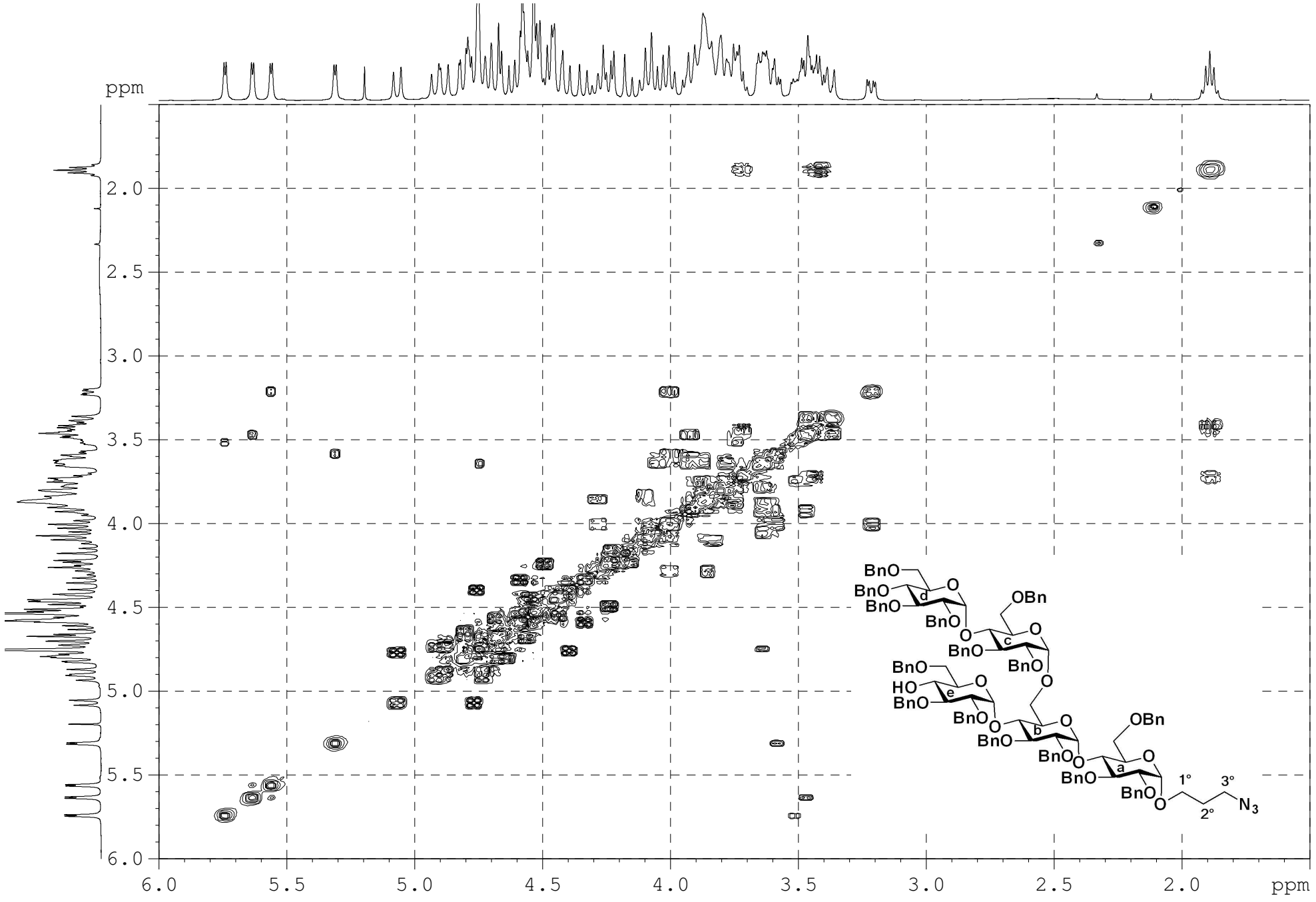

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
OBn
O
BnO
c
O
BnO
BnO
O
BnO
NapO
BnO
e
O
BnO
O
BnO
b
O
BnO
OBn
BnO
O
a
O
BnO
BnO
O
1°
2°
3°
N3

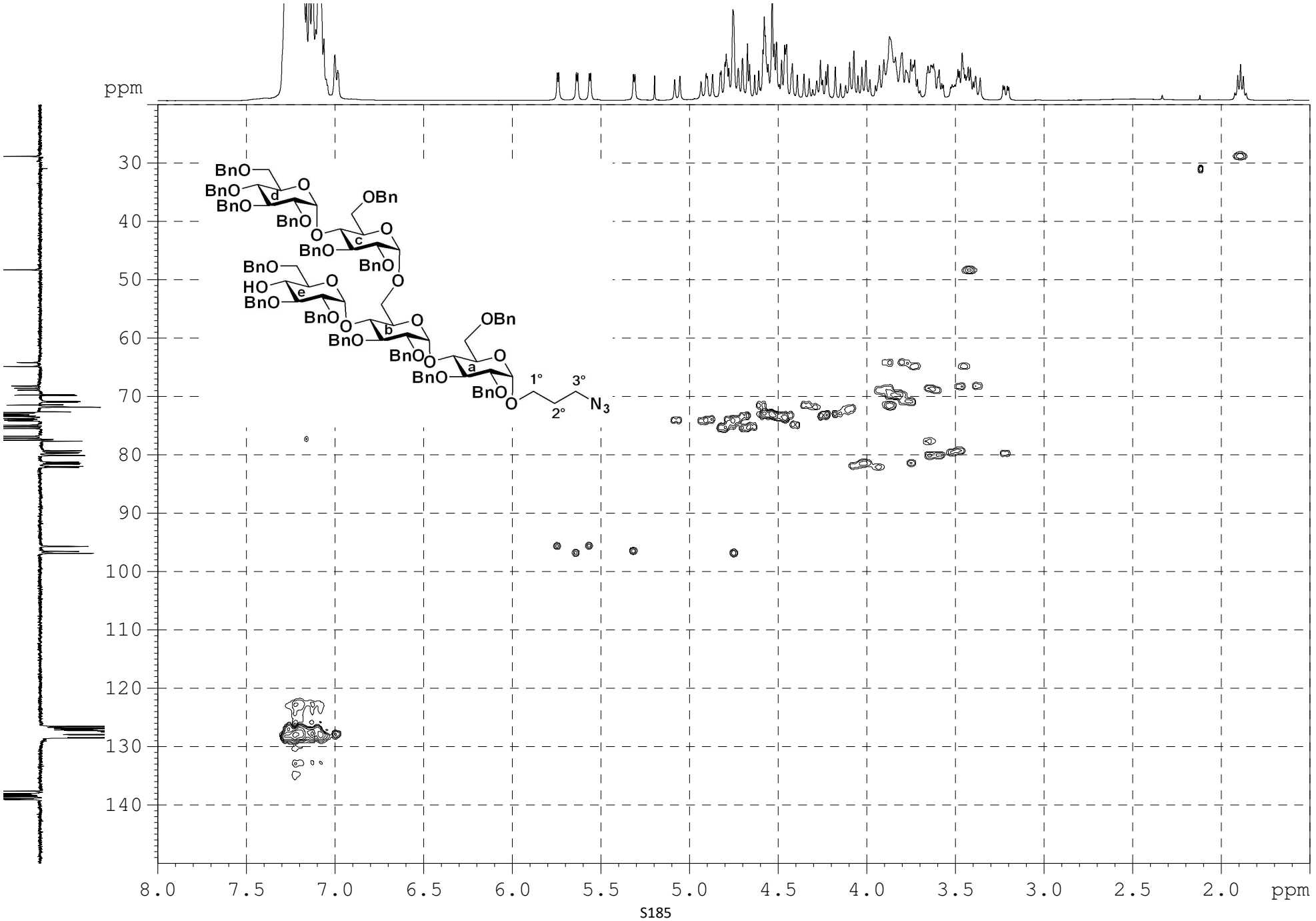

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
171.2 Hz
170.9 Hz
171.5 Hz
171.2 Hz
168.3 Hz
BnO
NapO
OBn
1°
2°
3°
N_3
6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6
ppm

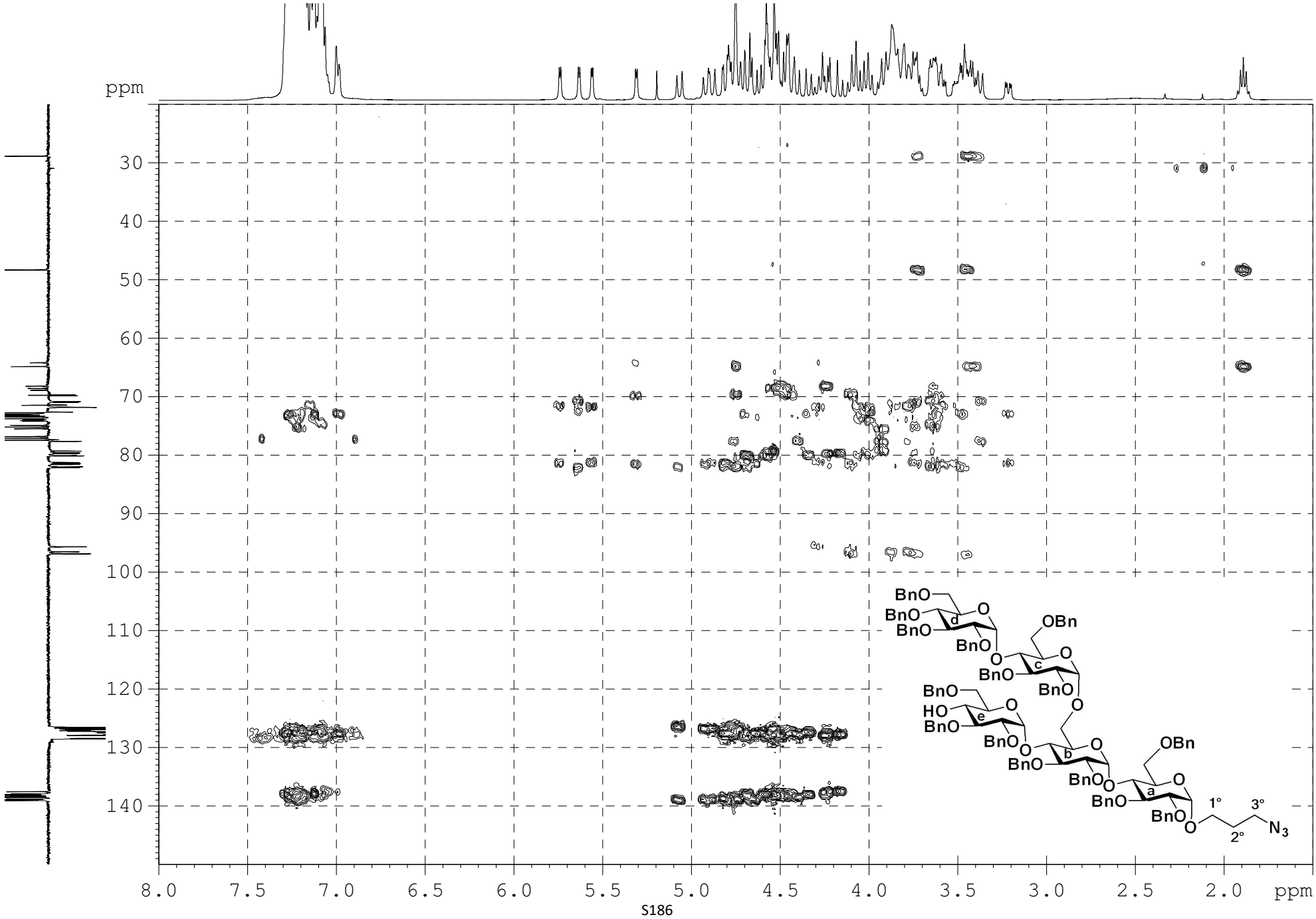
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC of **37**



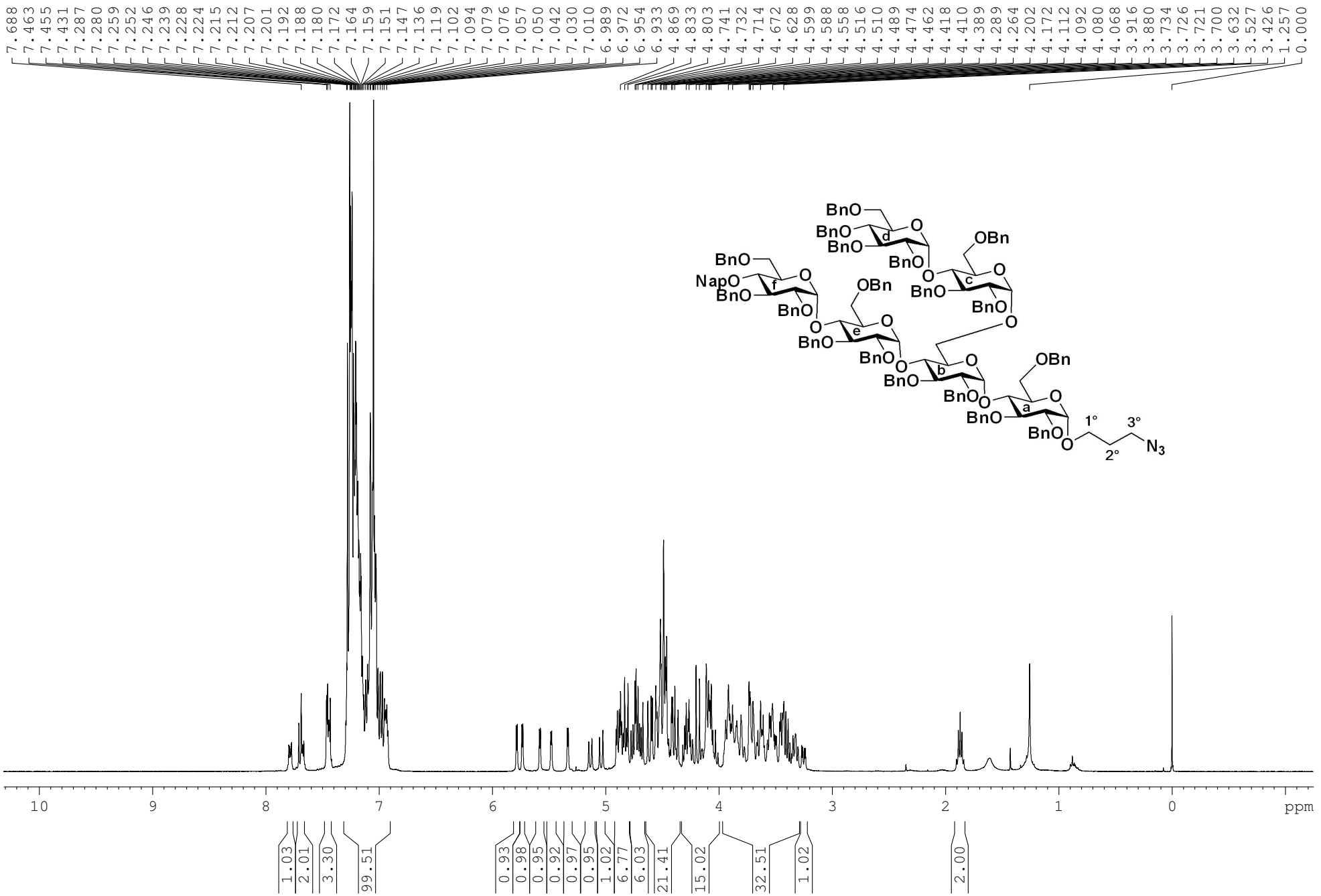

139.02
138.96
138.92
138.82
138.55
138.43
138.34
138.21
138.17
138.08
138.03
137.96
137.59
128.53
128.08
128.03
127.88
127.84
127.45
127.31
127.20
127.09
127.02
126.93
126.79
126.55
96.90
96.87
96.55
95.72
95.68
82.15
82.00
81.59
81.41
81.26
80.14
80.09
79.74
79.60
79.31
77.65
77.48
77.36
77.16
76.84
75.50
75.21
74.92
74.20
74.08
73.89
73.76
73.44
73.29
73.20
73.07
73.02
72.96
72.74
72.64
71.84
71.79
71.47
71.44
70.98
70.85
69.83
69.76
69.70
68.91
68.60
68.21
64.86
64.20
48.31
28.87
OBn
BnO
BnO
BnO
O
OBn
O
BnO
BnO
O
BnO
HO
BnO
O
BnO
BnO
O
O
OBn
BnO
BnO
O
BnO
O
BnO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

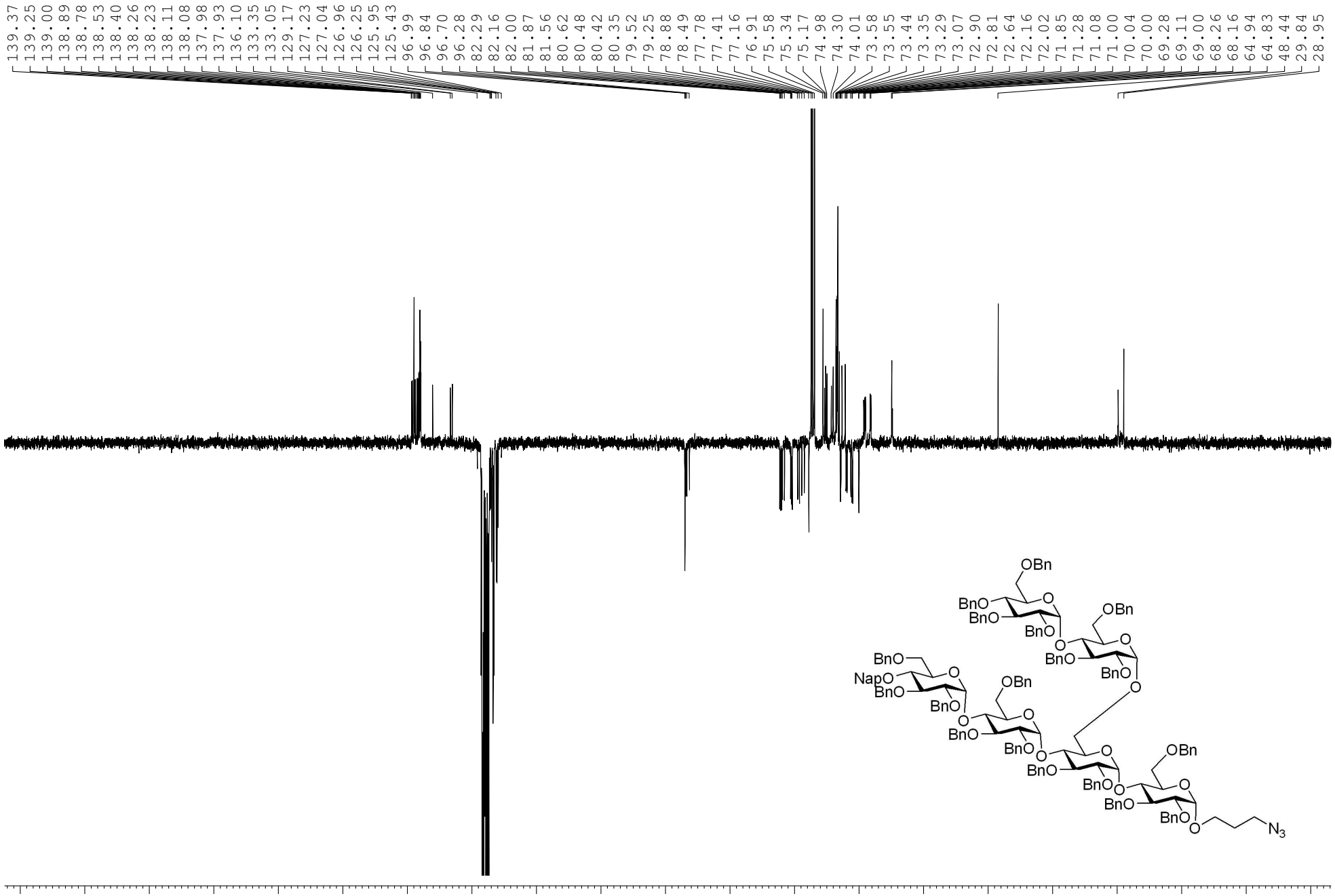

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
O
d
OBn
BnO
O
BnO
c
O
BnO
O
BnO
HO
BnO
e
O
BnO
O
b
O
BnO
OBn
BnO
O
a
O
BnO
O
1°
3°
2°
N3

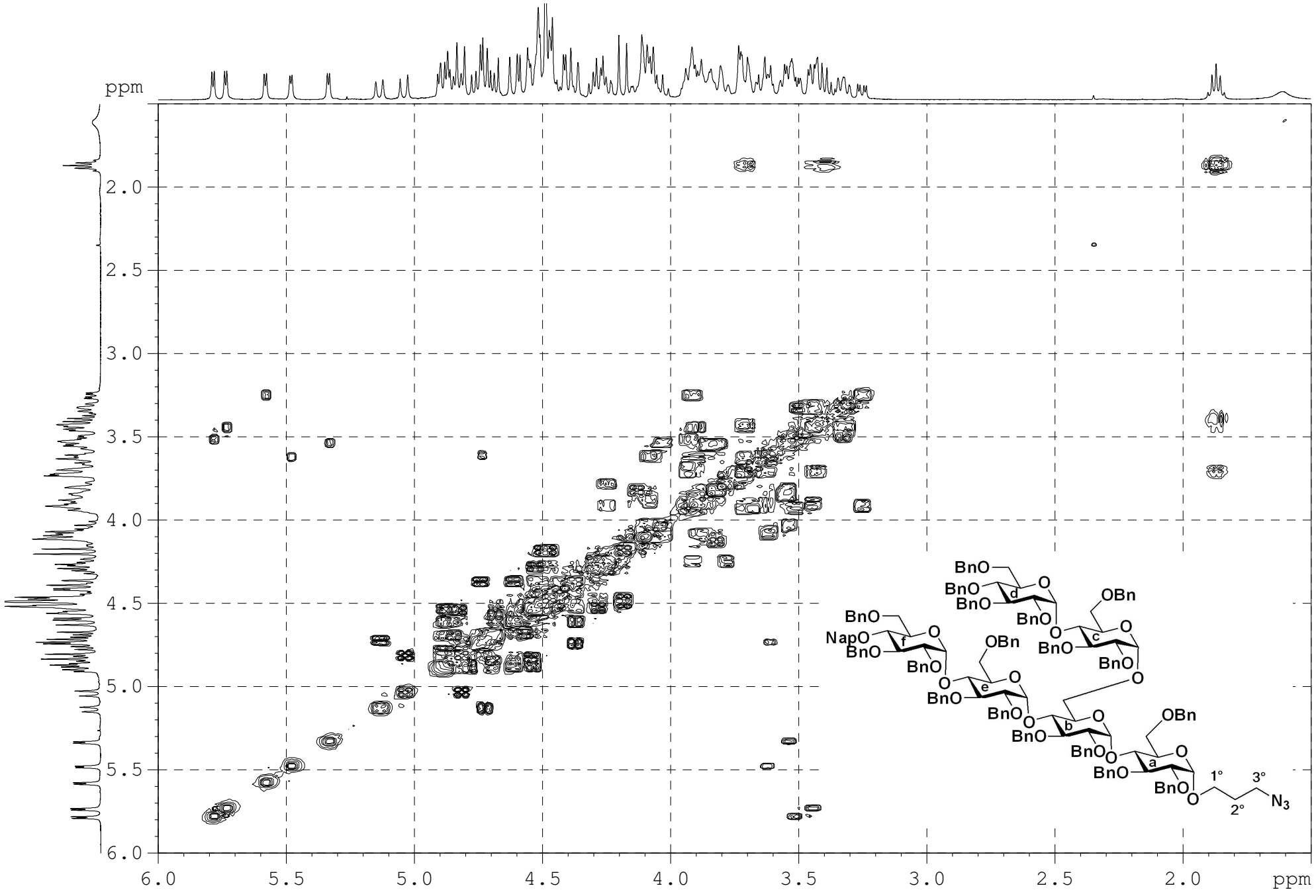

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
OBn
HO
1°
2°
3°
N3
a
b
c
d
e

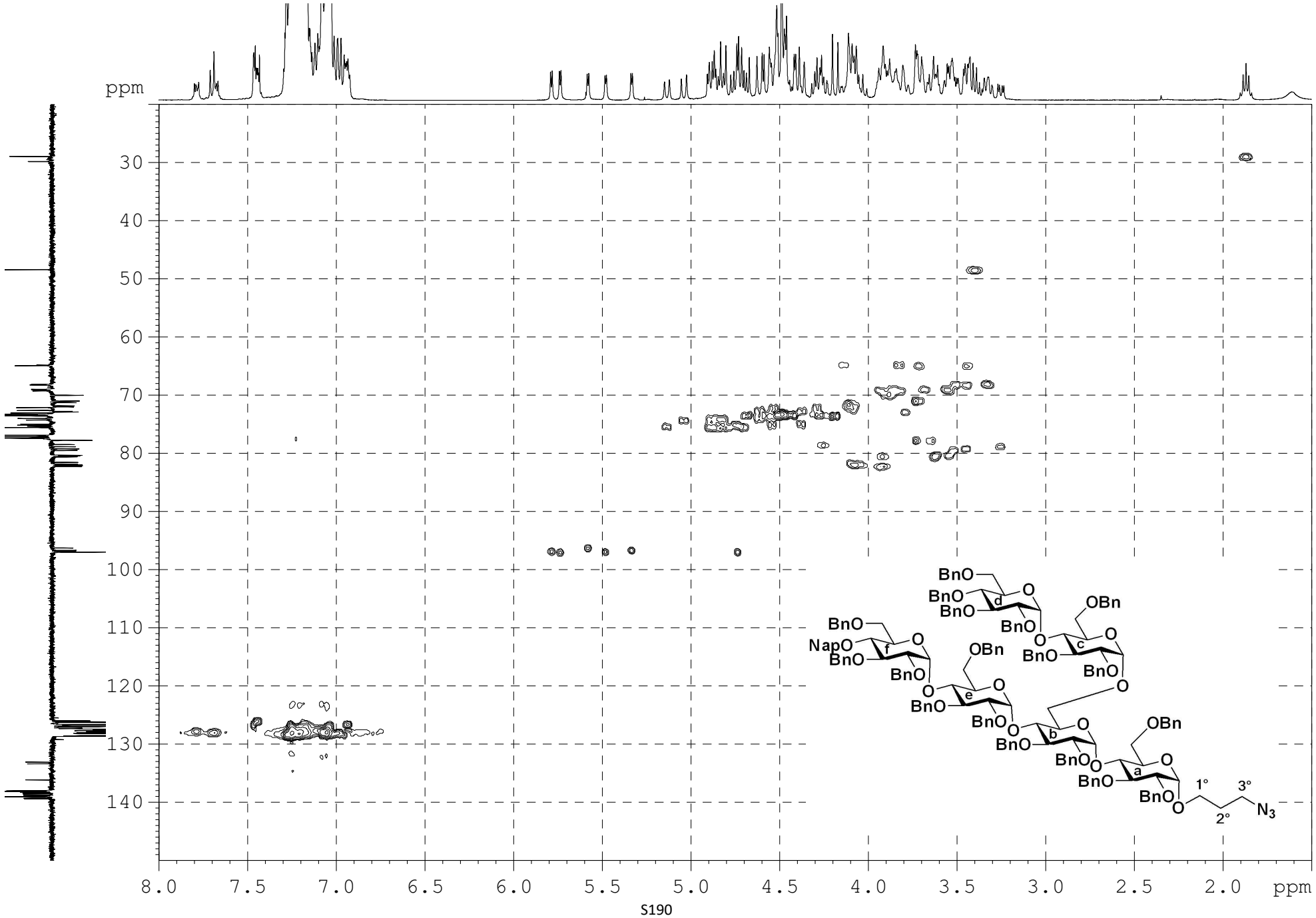

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
d
O
BnO
OBn
O
c
BnO
BnO
O
BnO
HO
BnO
e
O
BnO
O
b
BnO
O
OBn
BnO
O
a
O
BnO
BnO
O
1°
2°
3°
N3

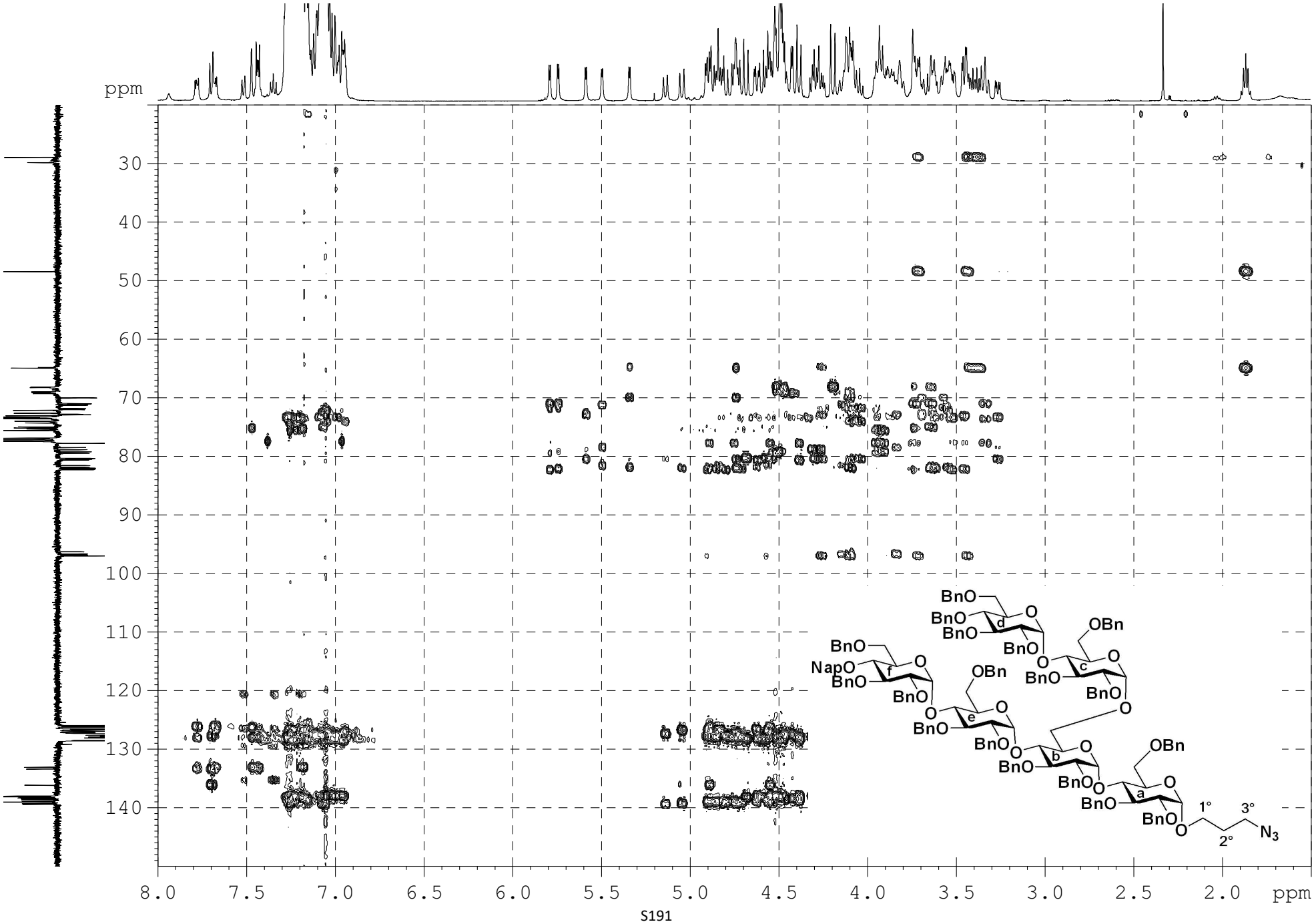
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED, ^{1}H-^{1}H cleantocsy **38**

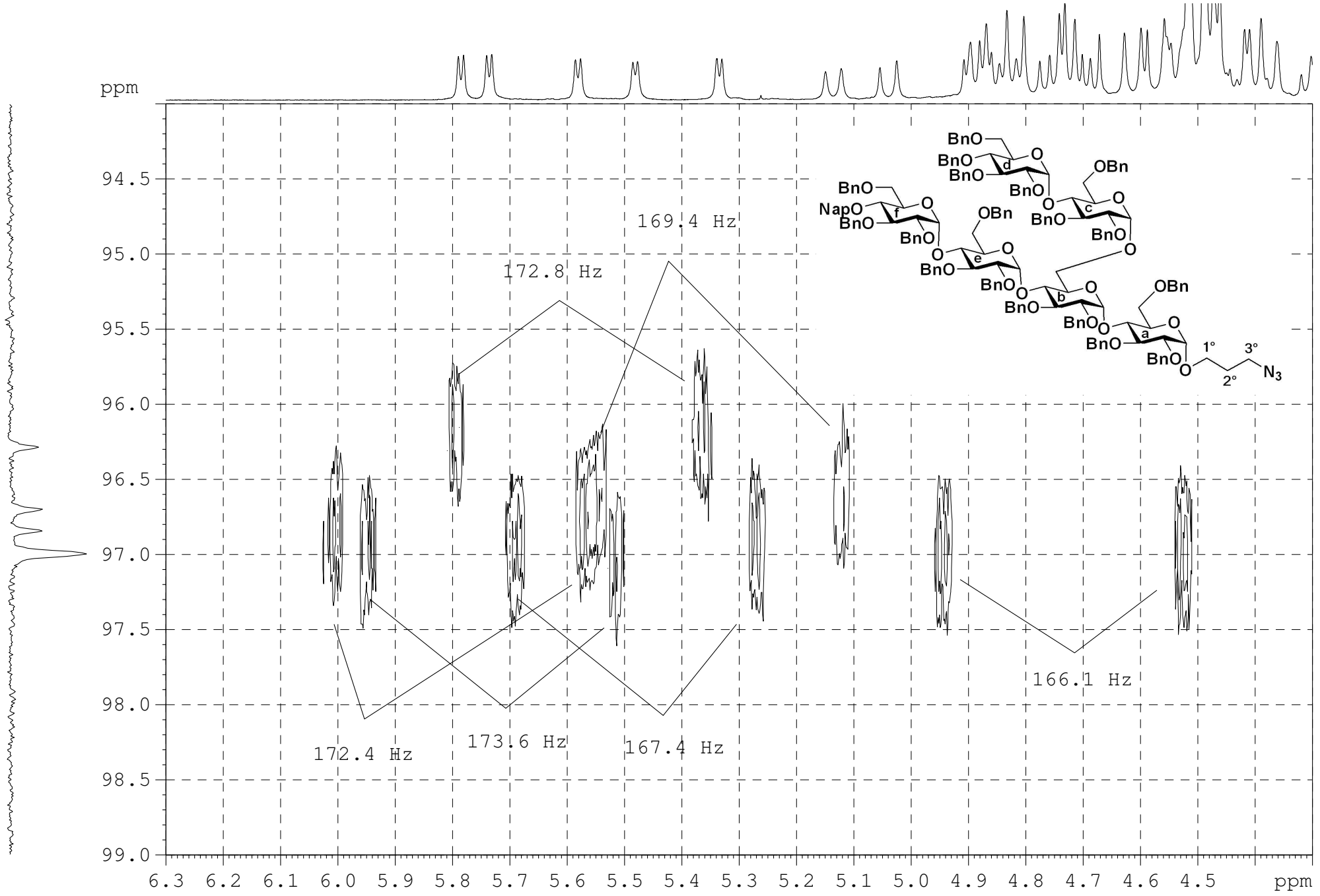


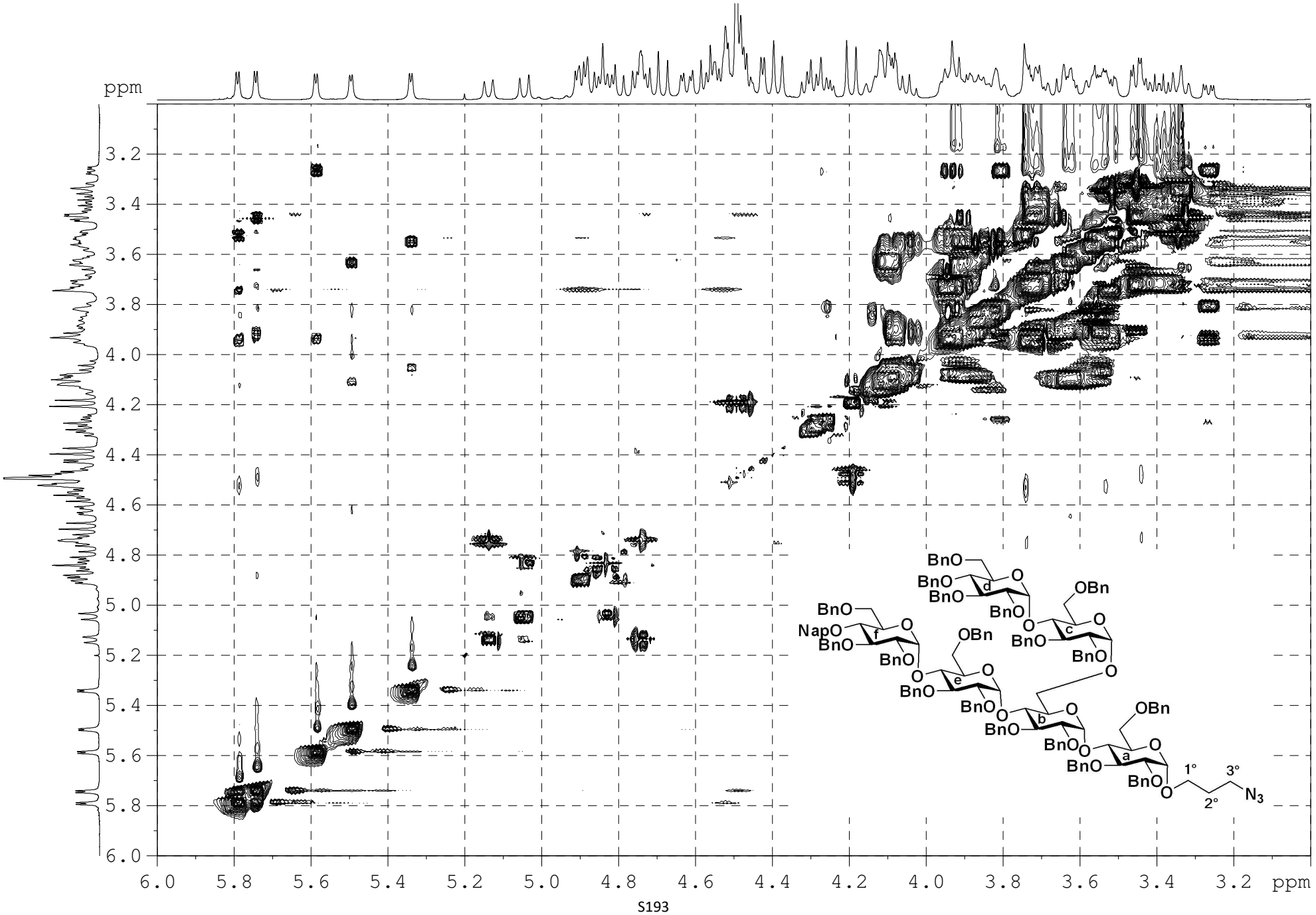

139.37
139.25
139.00
138.89
138.78
138.53
138.40
138.26
138.23
138.11
138.08
137.98
137.93
136.10
133.35
133.05
129.17
127.23
127.04
126.96
126.25
125.95
125.43
96.99
96.84
96.70
96.28
82.29
82.16
82.00
81.87
81.56
80.62
80.48
80.42
80.35
79.52
79.25
78.88
78.49
77.78
77.41
77.16
76.91
75.58
75.34
75.17
74.98
74.30
74.01
73.58
73.55
73.44
73.35
73.29
73.07
72.90
72.81
72.64
72.16
72.02
71.85
71.28
71.08
71.00
70.04
70.00
69.28
69.11
69.00
68.26
68.16
64.94
64.83
48.44
29.84
28.95
OBn
BnO
NapO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
NapO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

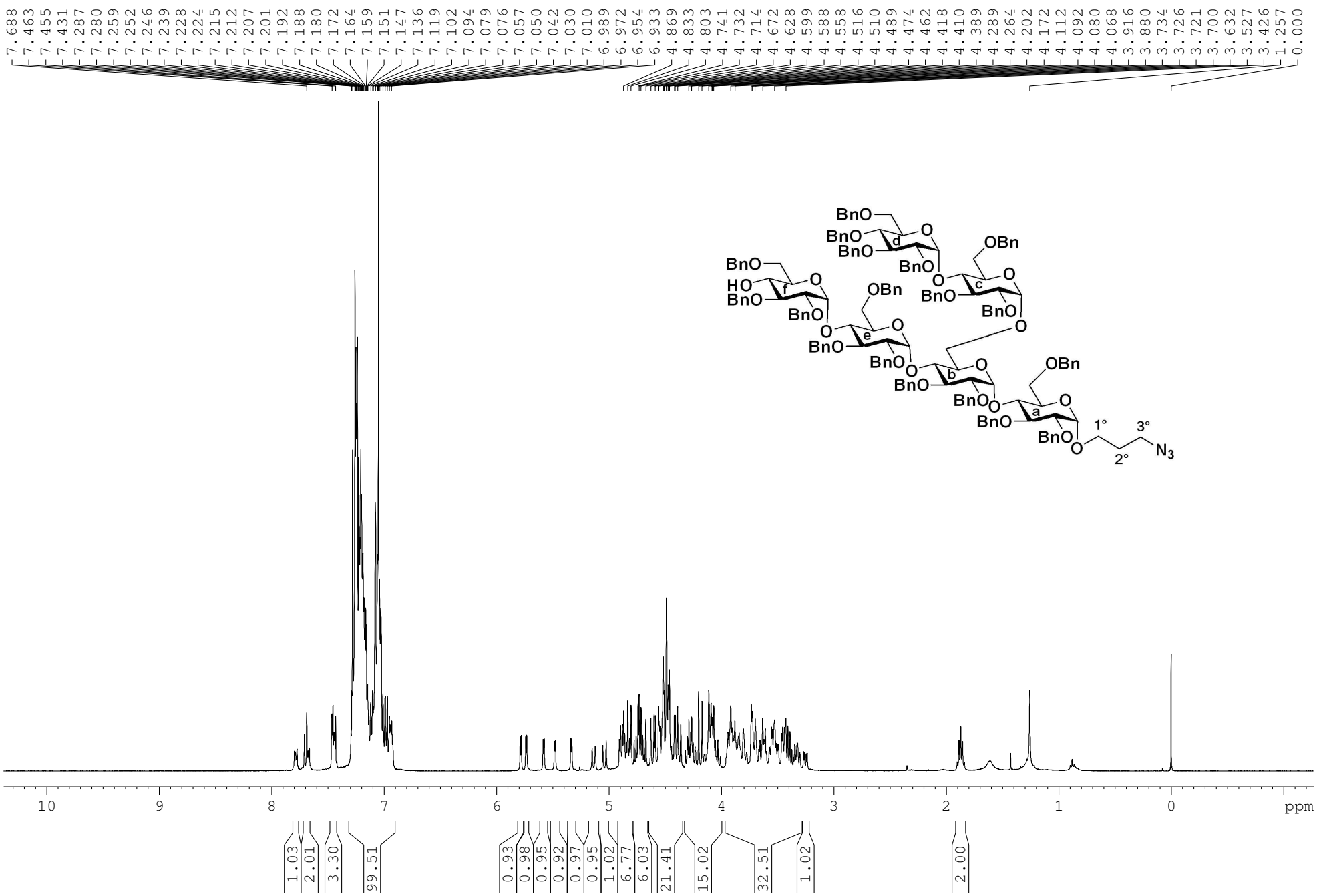

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
NapO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

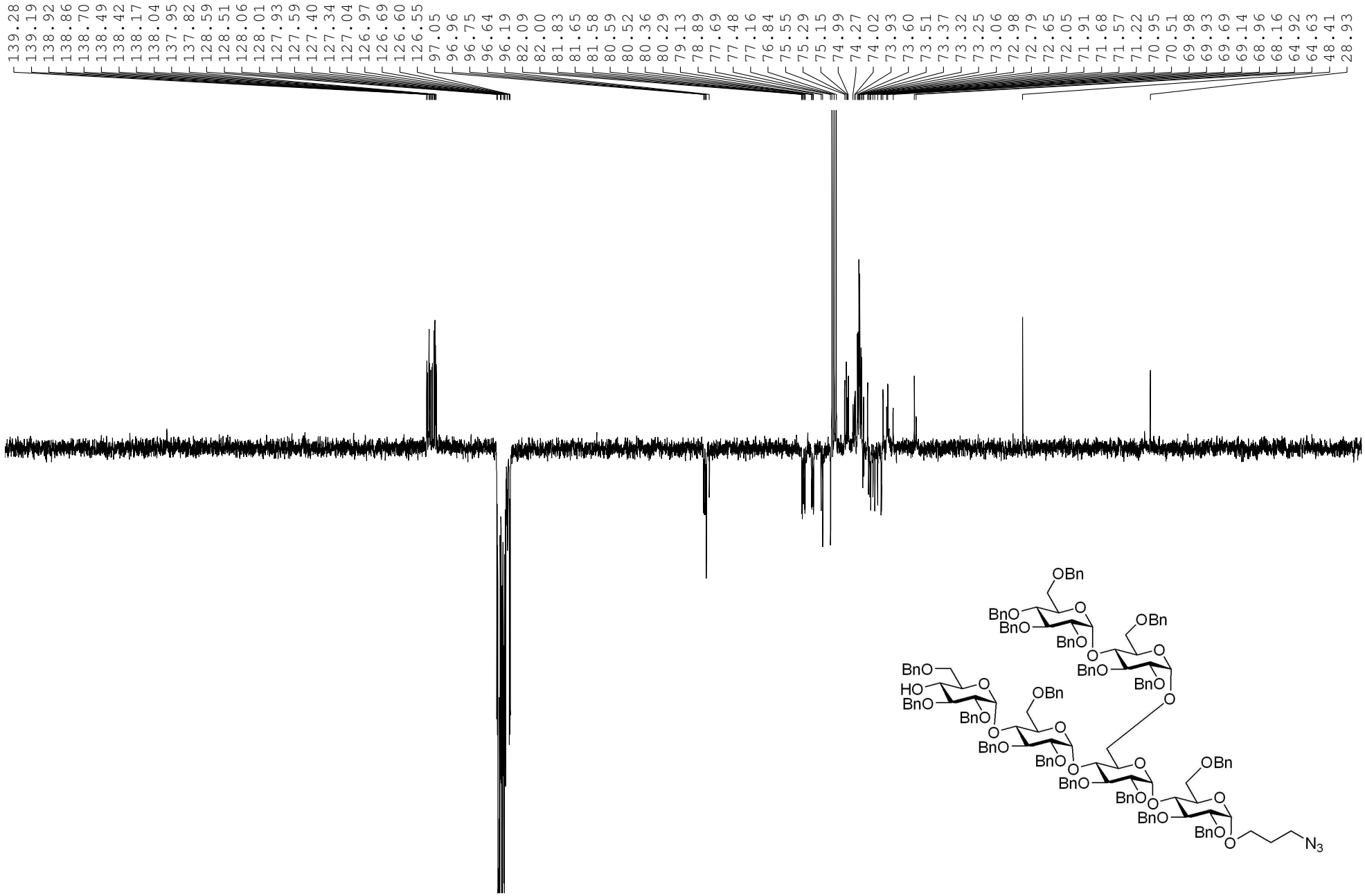

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
NapO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

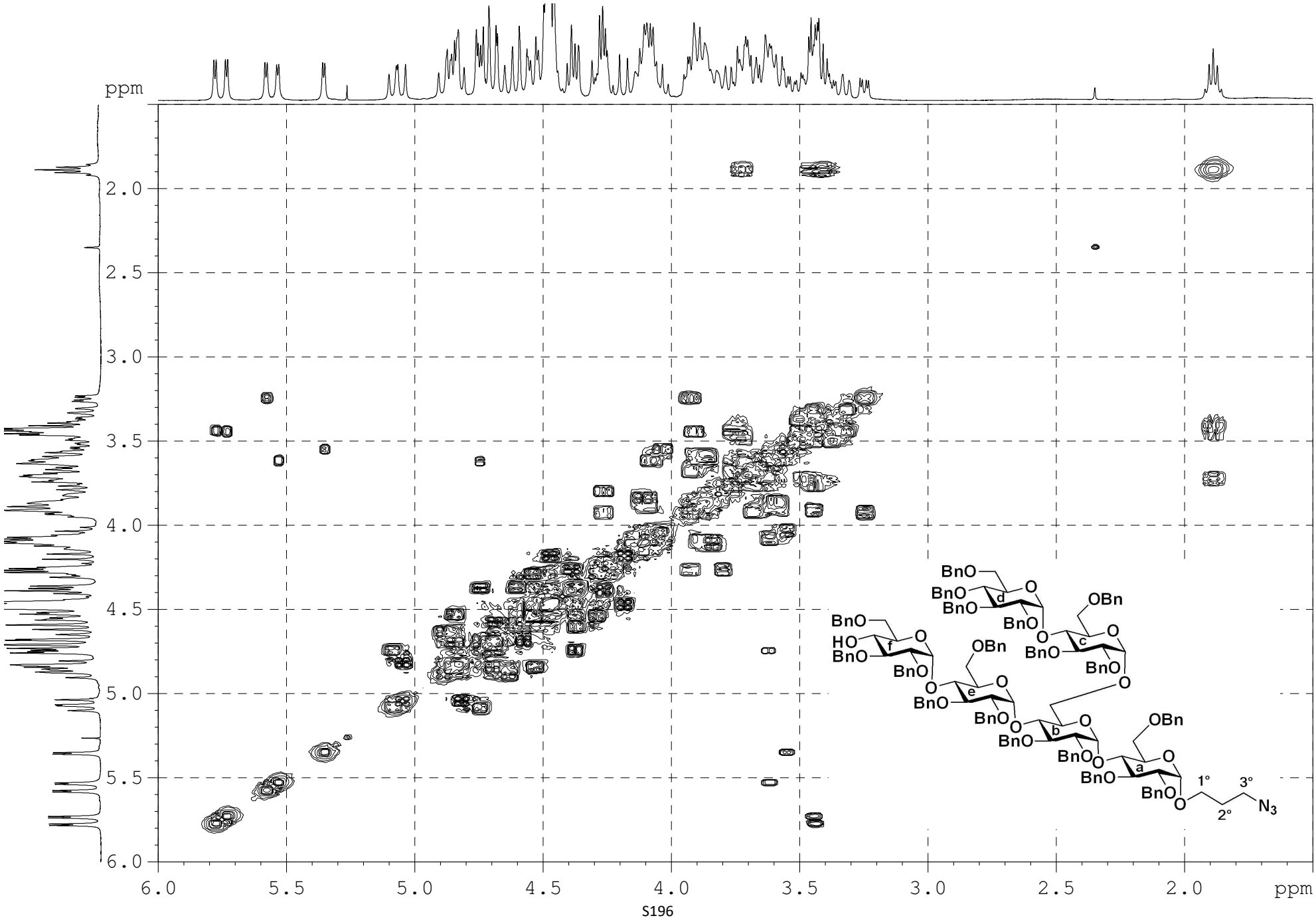

ppm
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
ppm
169.4 Hz
172.8 Hz
172.4 Hz
173.6 Hz
167.4 Hz
166.1 Hz
BnO
NapO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

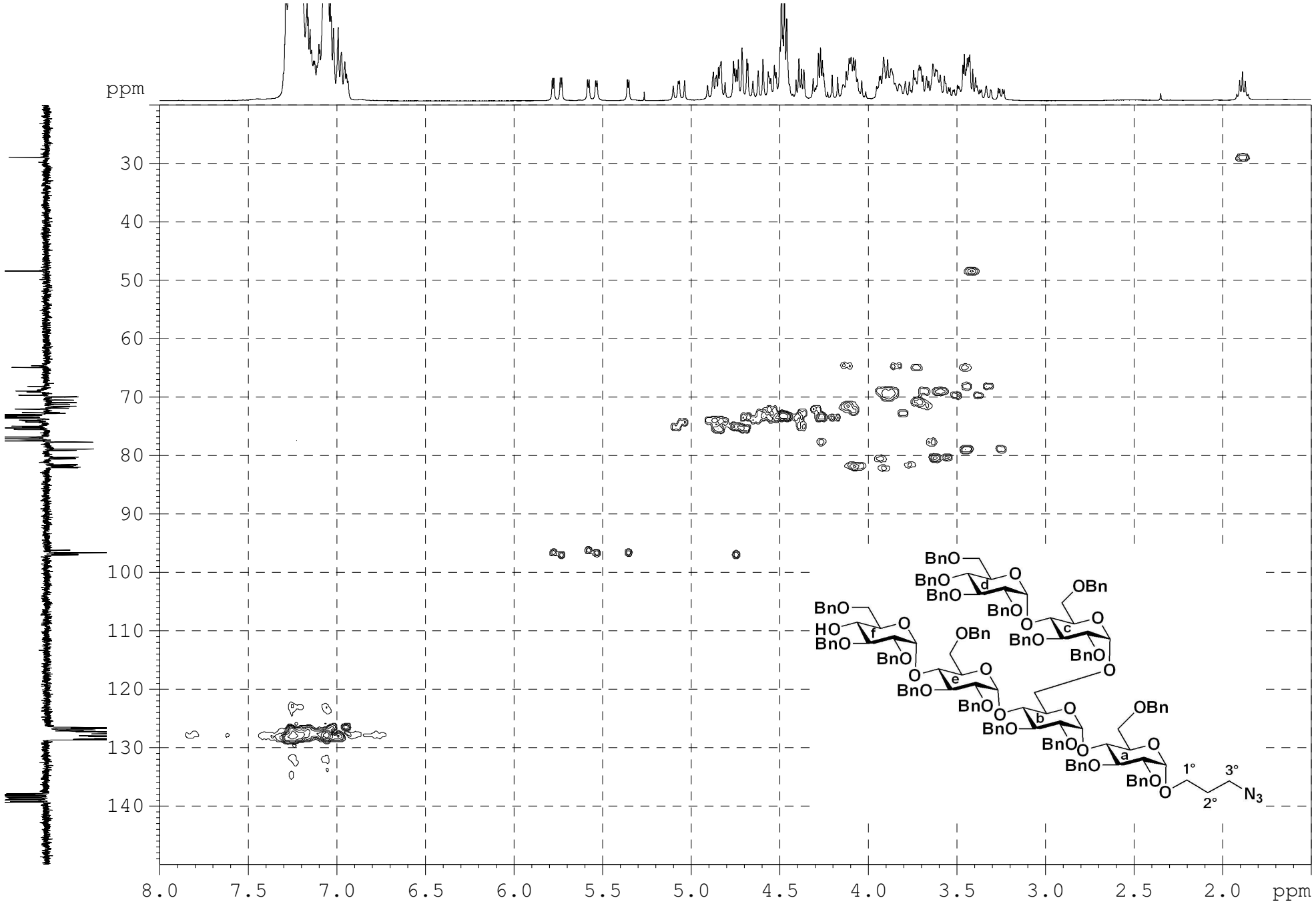

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm
BnO
NapO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

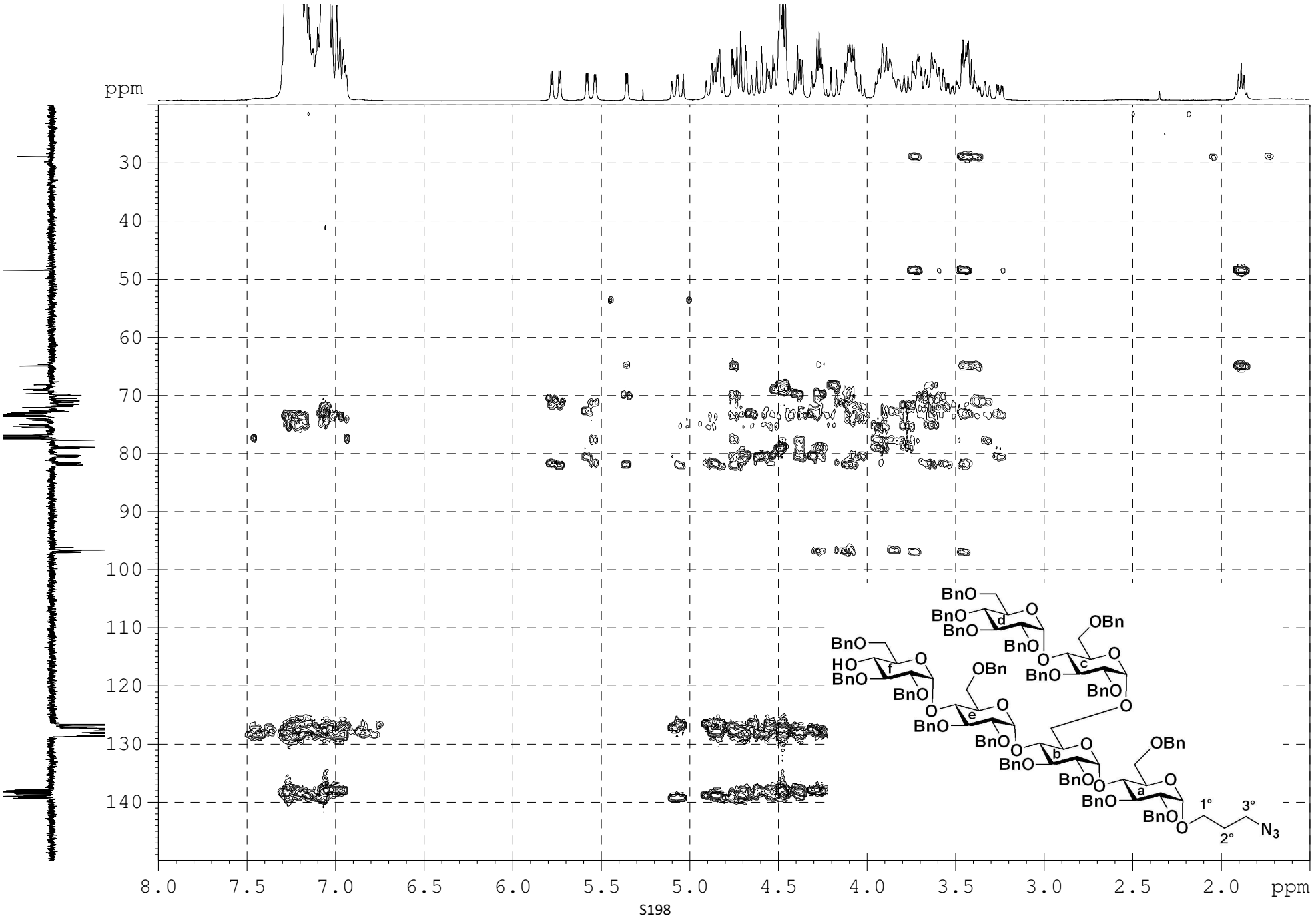
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, ^{1}H-^{1}H cleantocsy **39**

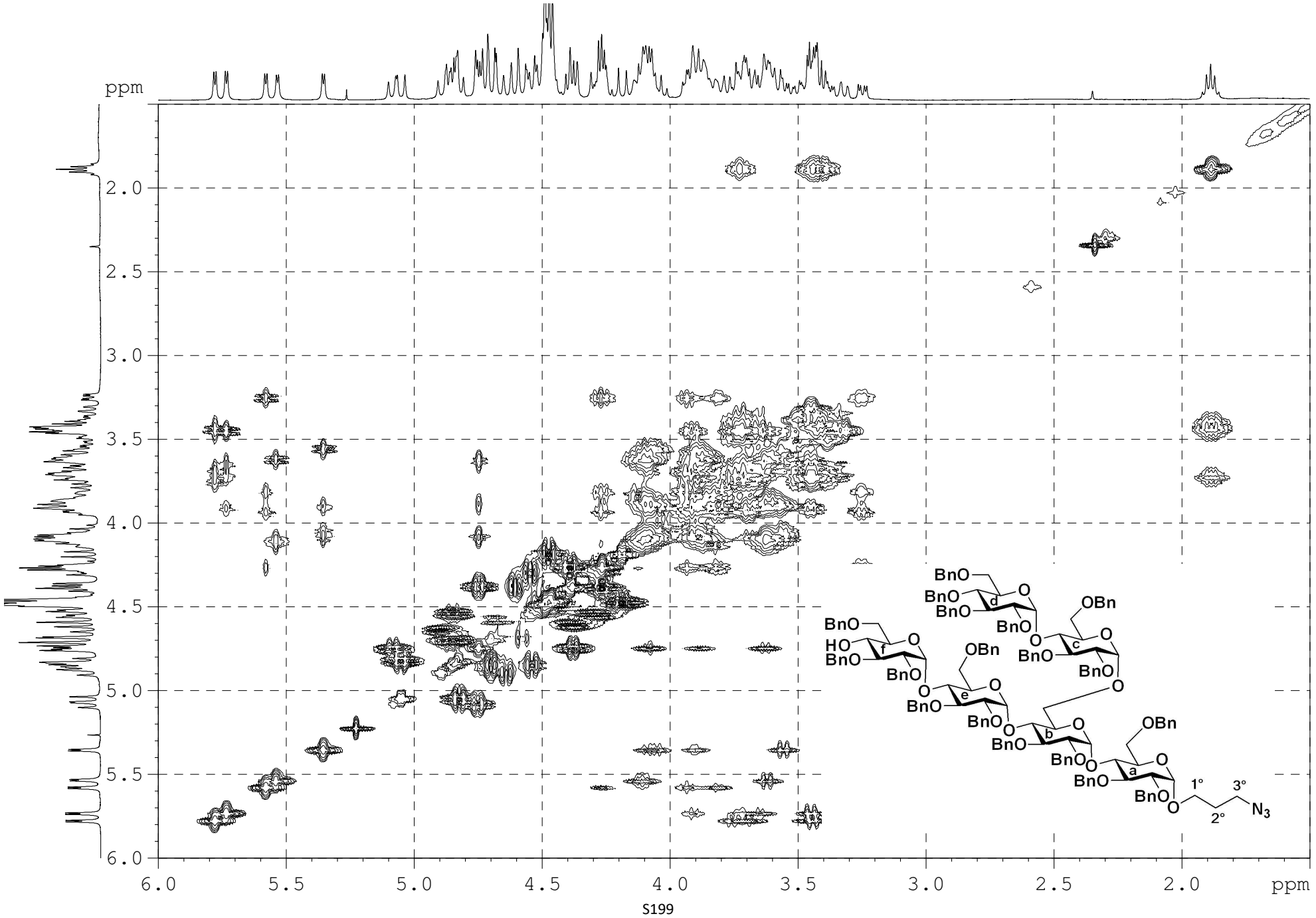



139.28
139.19
138.92
138.86
138.70
138.49
138.42
138.17
138.04
137.95
137.82
128.59
128.51
128.06
128.01
127.93
127.59
127.40
127.34
127.04
126.97
126.69
126.60
126.55
97.05
96.96
96.75
96.64
96.19
82.09
82.00
81.83
81.65
81.58
80.59
80.52
80.36
80.29
79.13
78.89
77.69
77.48
77.16
76.84
75.55
75.29
75.15
74.99
74.27
74.02
73.93
73.60
73.51
73.37
73.32
73.25
73.06
72.98
72.79
72.65
72.05
71.91
71.68
71.57
71.22
70.95
70.51
69.98
69.93
69.69
69.14
68.96
68.16
64.92
64.63
48.41
28.93
OBn
BnO
HO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

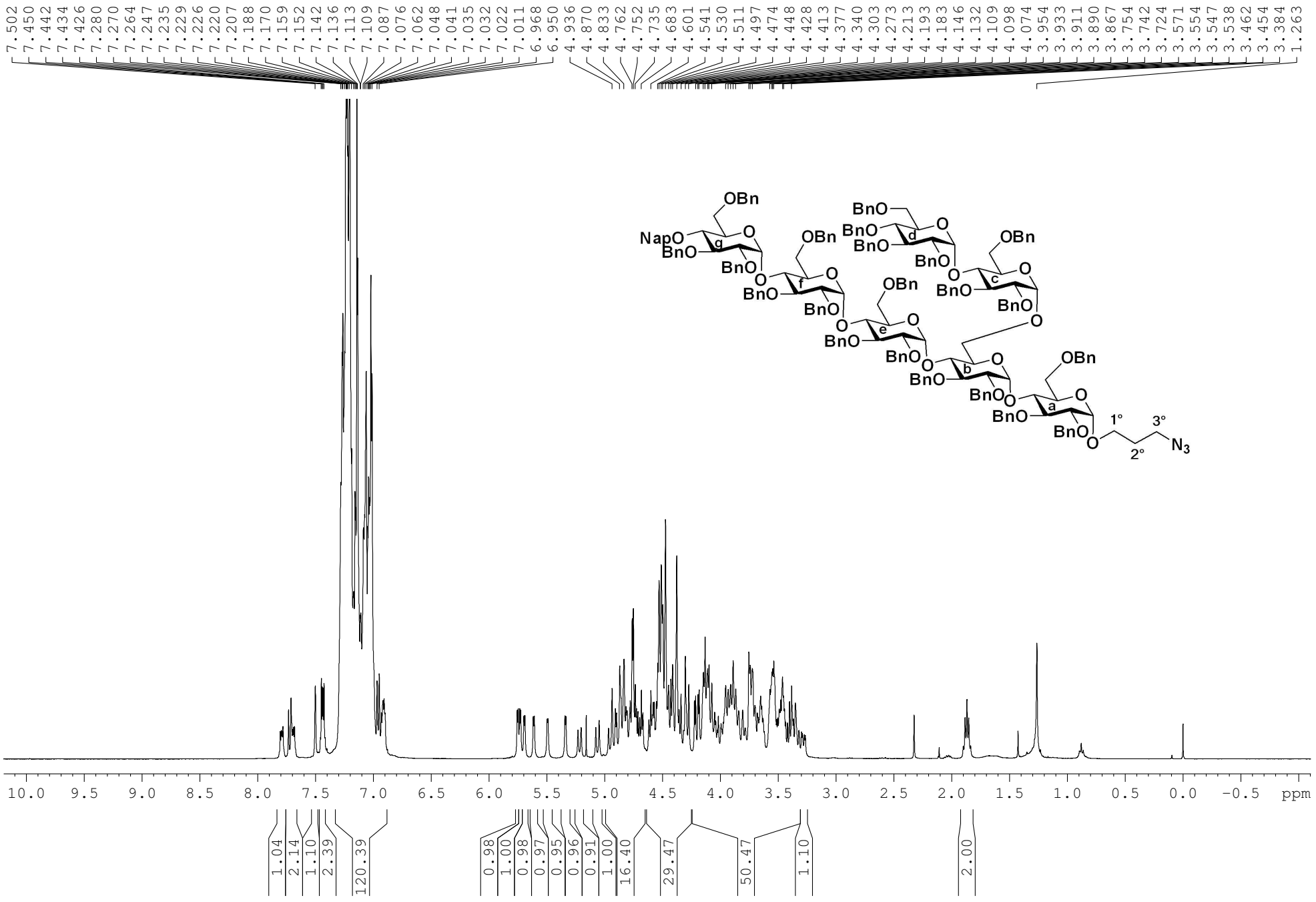

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
OBn
O
a
b
c
d
e
f
1°
2°
3°
N3

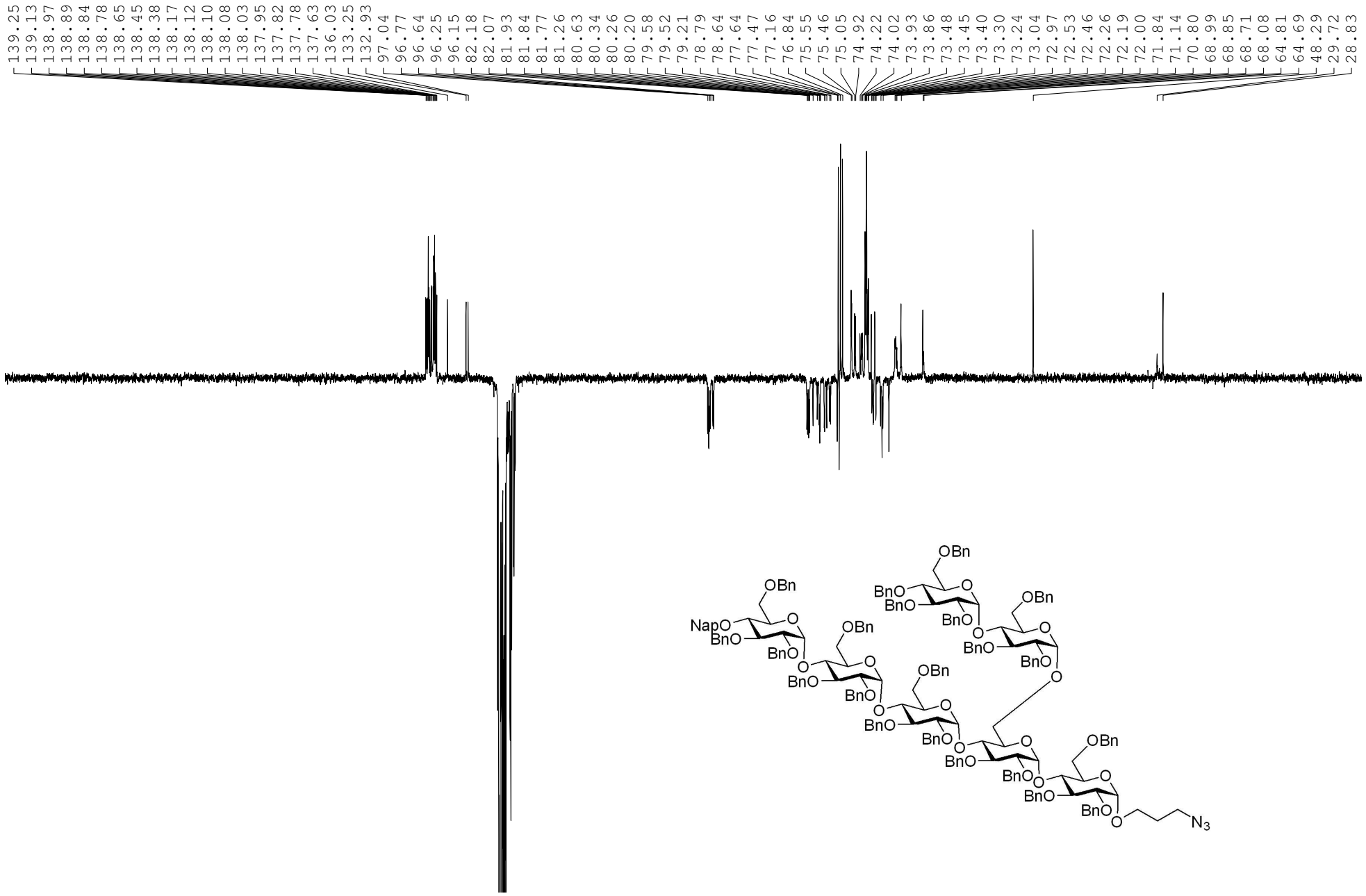

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
OBn
O
N3
1°
2°
3°
a
b
c
d
e
f

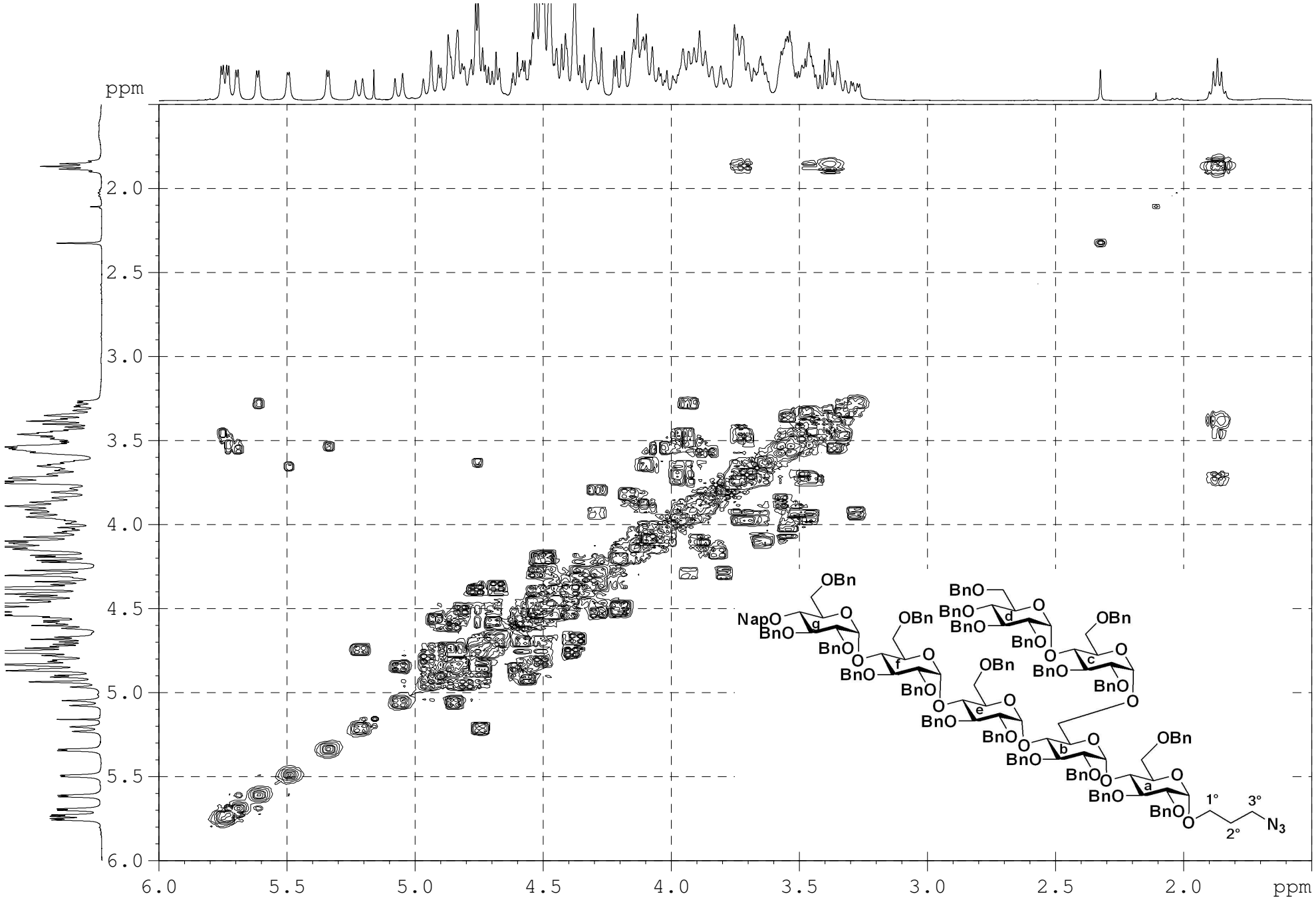

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

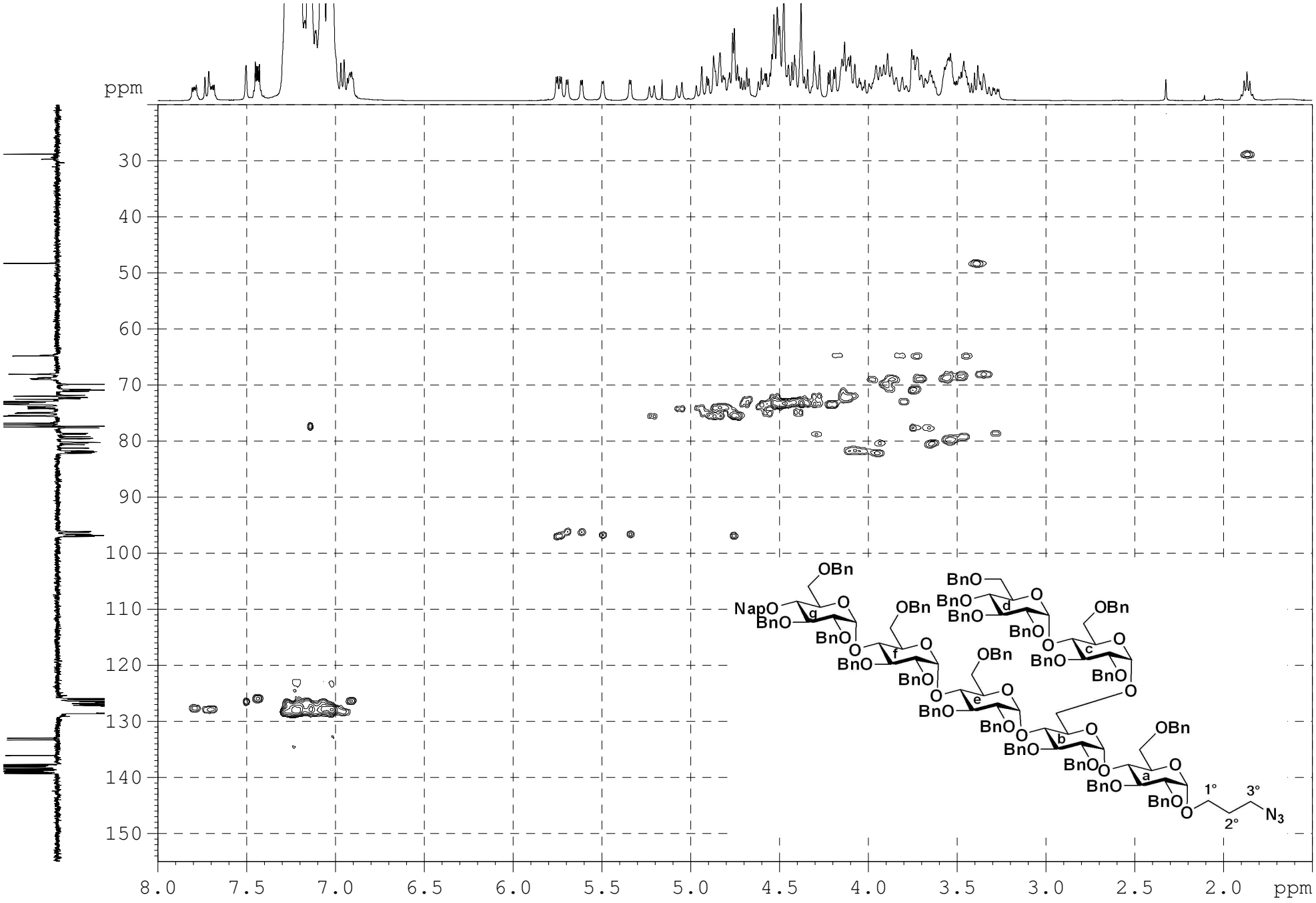

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
OBn
N3
1°
2°
3°
a
b
c
d
e
f

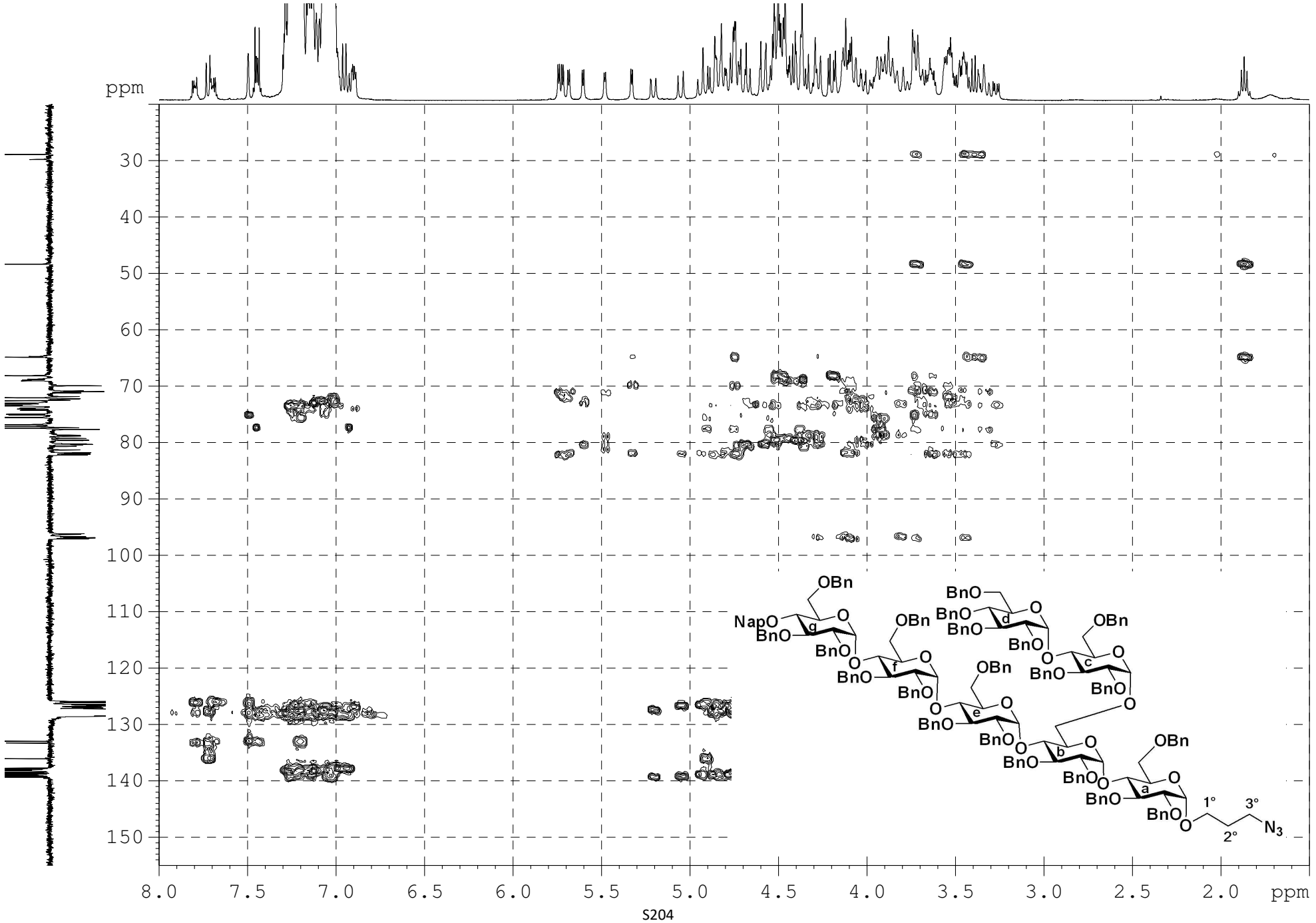
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED, ^{1}H-^{1}H cleantocsy **40**

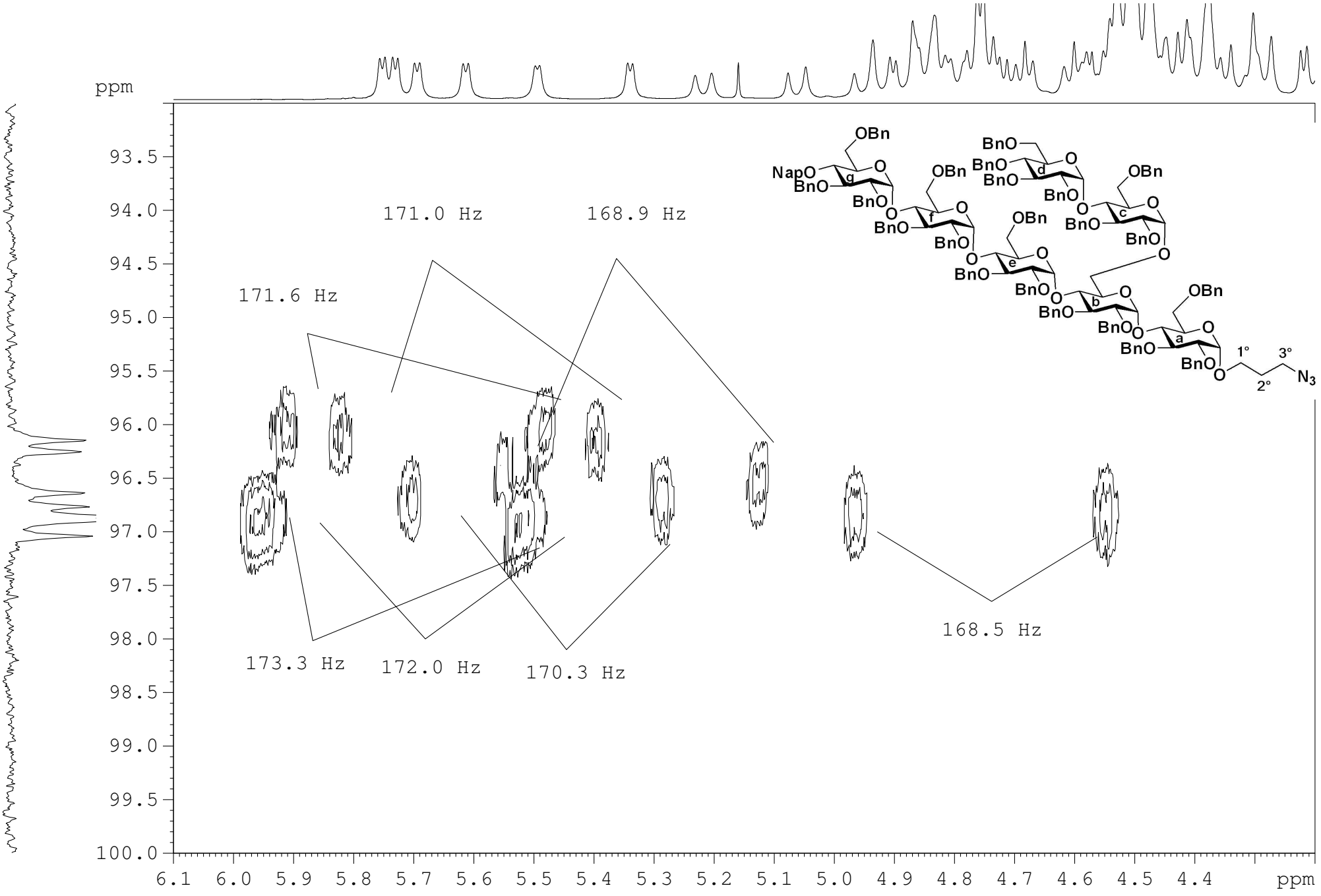


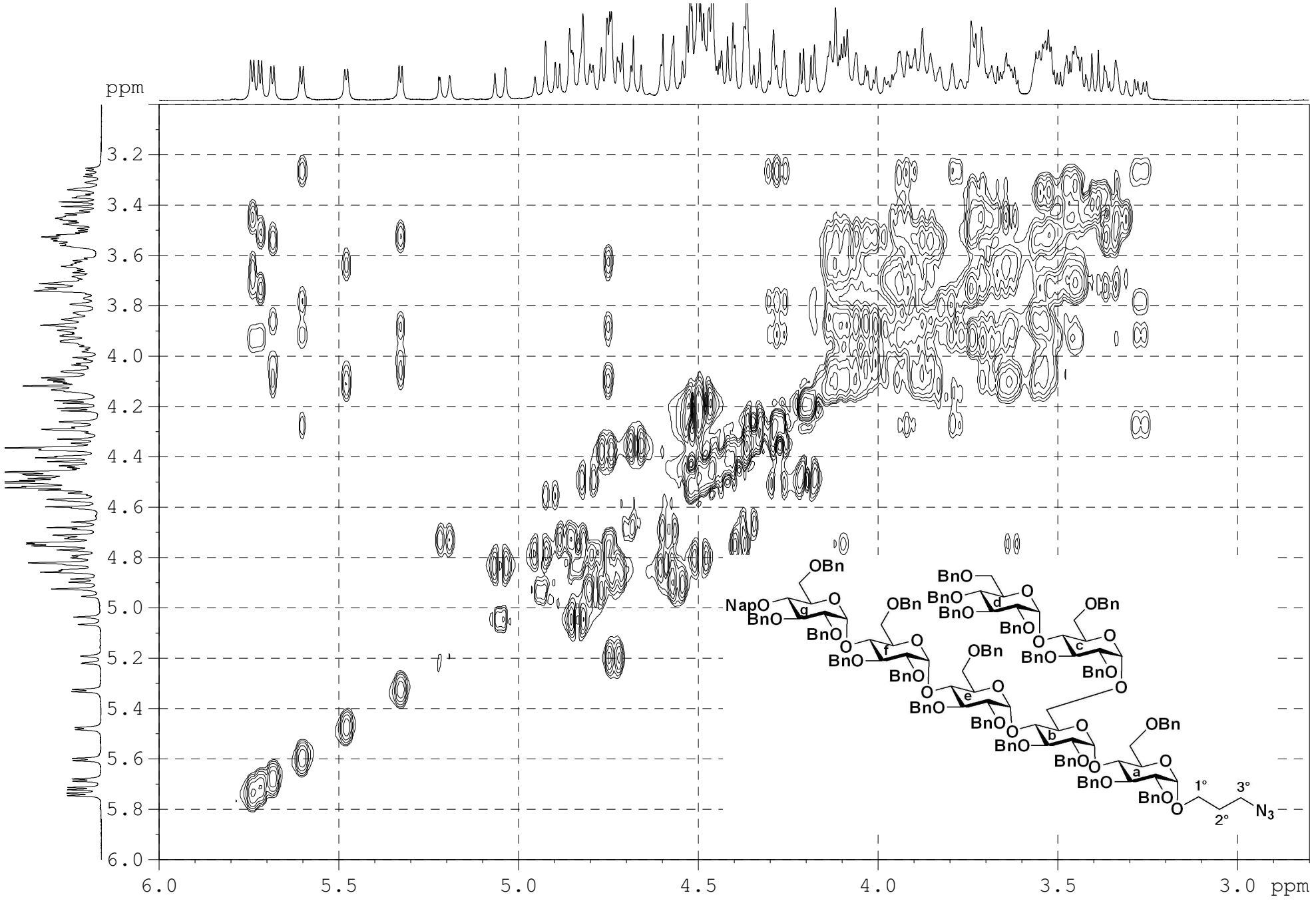

139.25
139.13
138.97
138.89
138.84
138.78
138.65
138.45
138.38
138.17
138.12
138.10
138.08
138.03
137.95
137.82
137.78
137.63
136.03
133.25
132.93
97.04
96.77
96.64
96.25
96.15
82.18
82.07
81.93
81.84
81.77
81.26
80.63
80.34
80.26
80.20
79.58
79.52
79.21
78.79
78.64
77.64
77.47
77.16
76.84
75.55
75.46
75.05
74.92
74.22
74.02
73.93
73.86
73.48
73.45
73.40
73.30
73.24
73.04
72.97
72.53
72.46
72.26
72.19
72.00
71.84
71.14
70.80
68.99
68.85
68.71
68.08
64.81
64.69
48.29
29.72
28.83
OBn
NapO
BnO
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
NapO
BnO
g
f
e
d
c
b
a
1°
2°
3°
N3

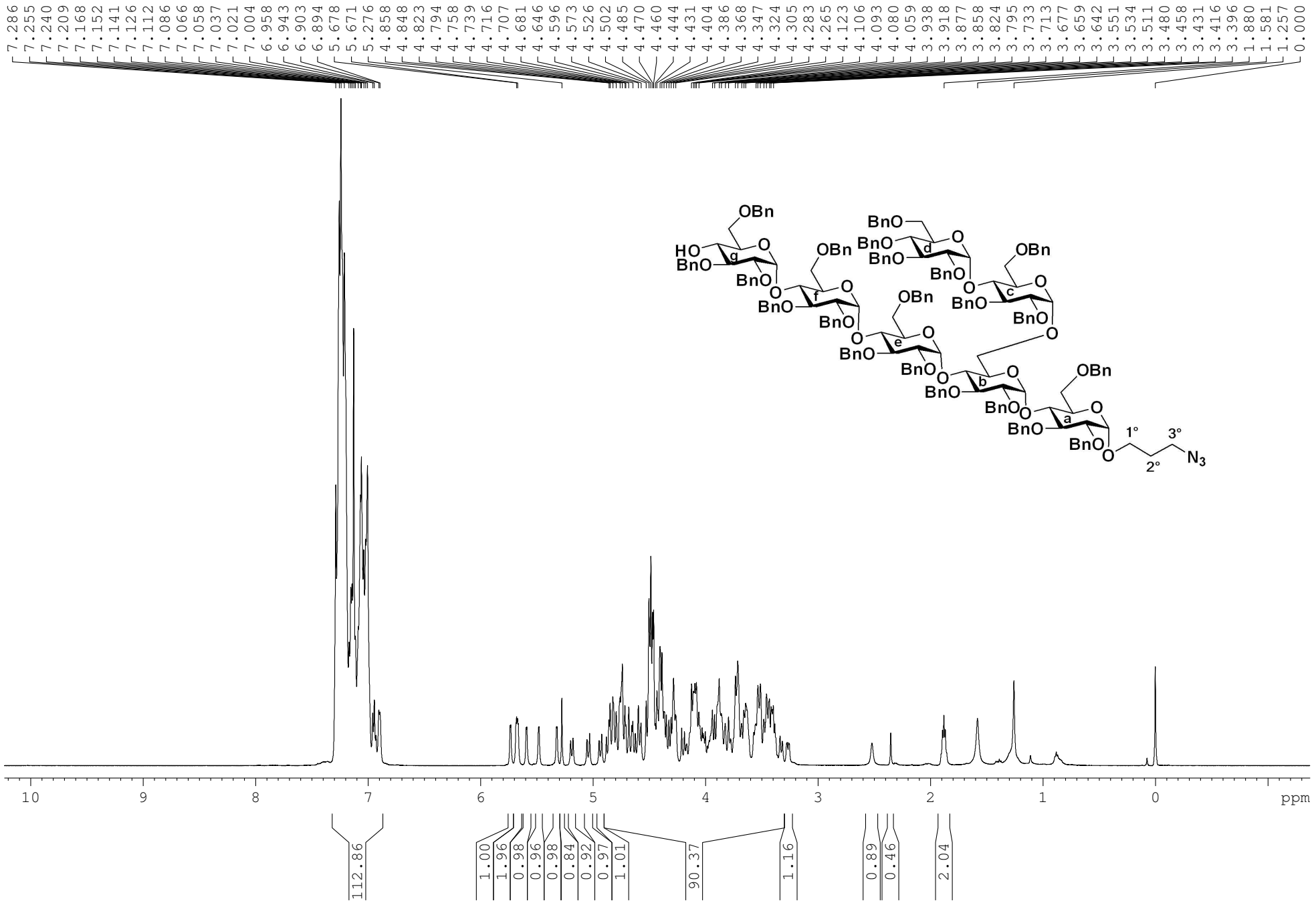

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
NapO
BnO
O
g
f
d
c
e
b
a
1°
2°
3°
N3

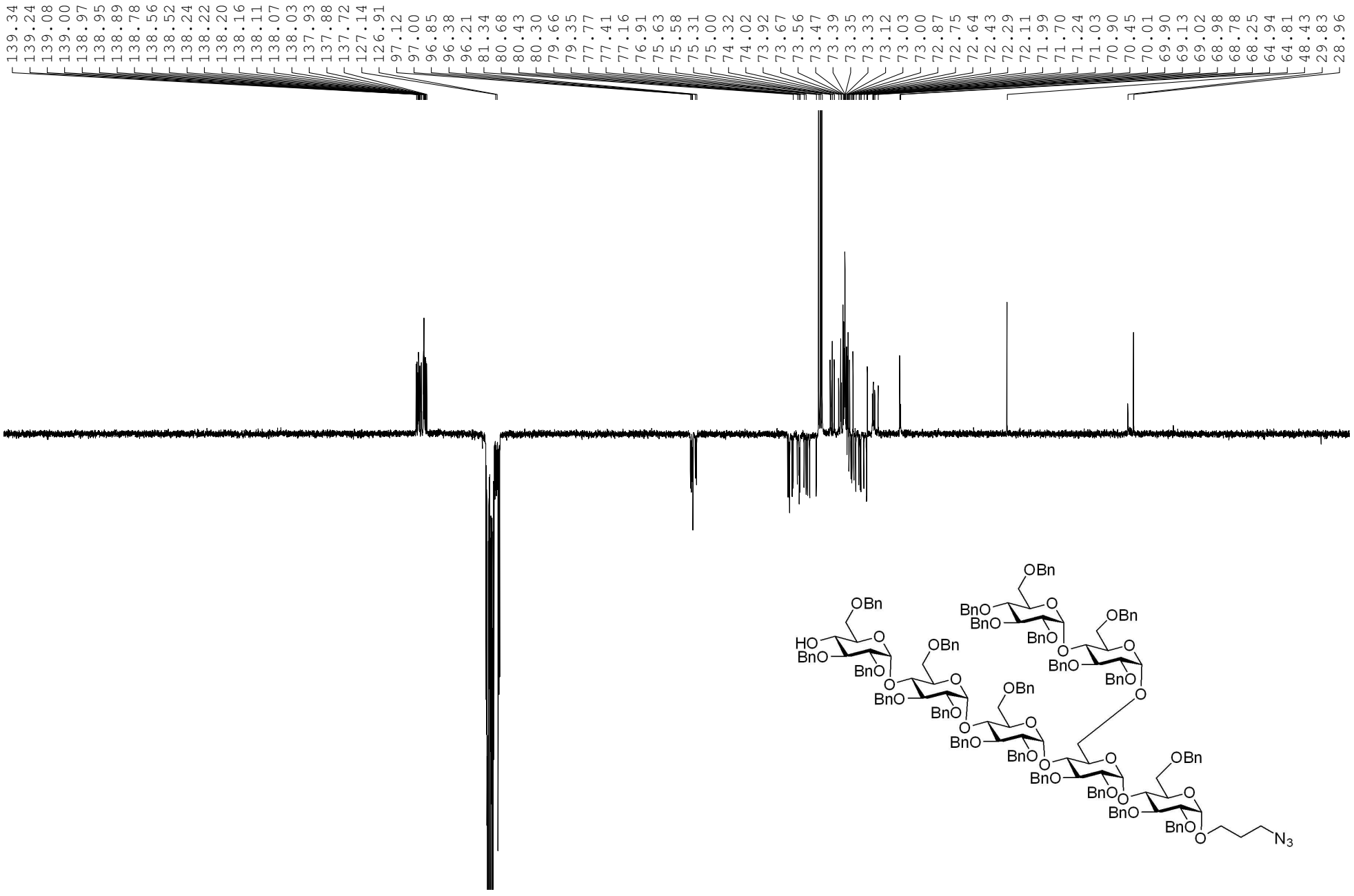

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
NapO
BnO
g
f
e
d
c
b
a
1°
2°
3°
N3

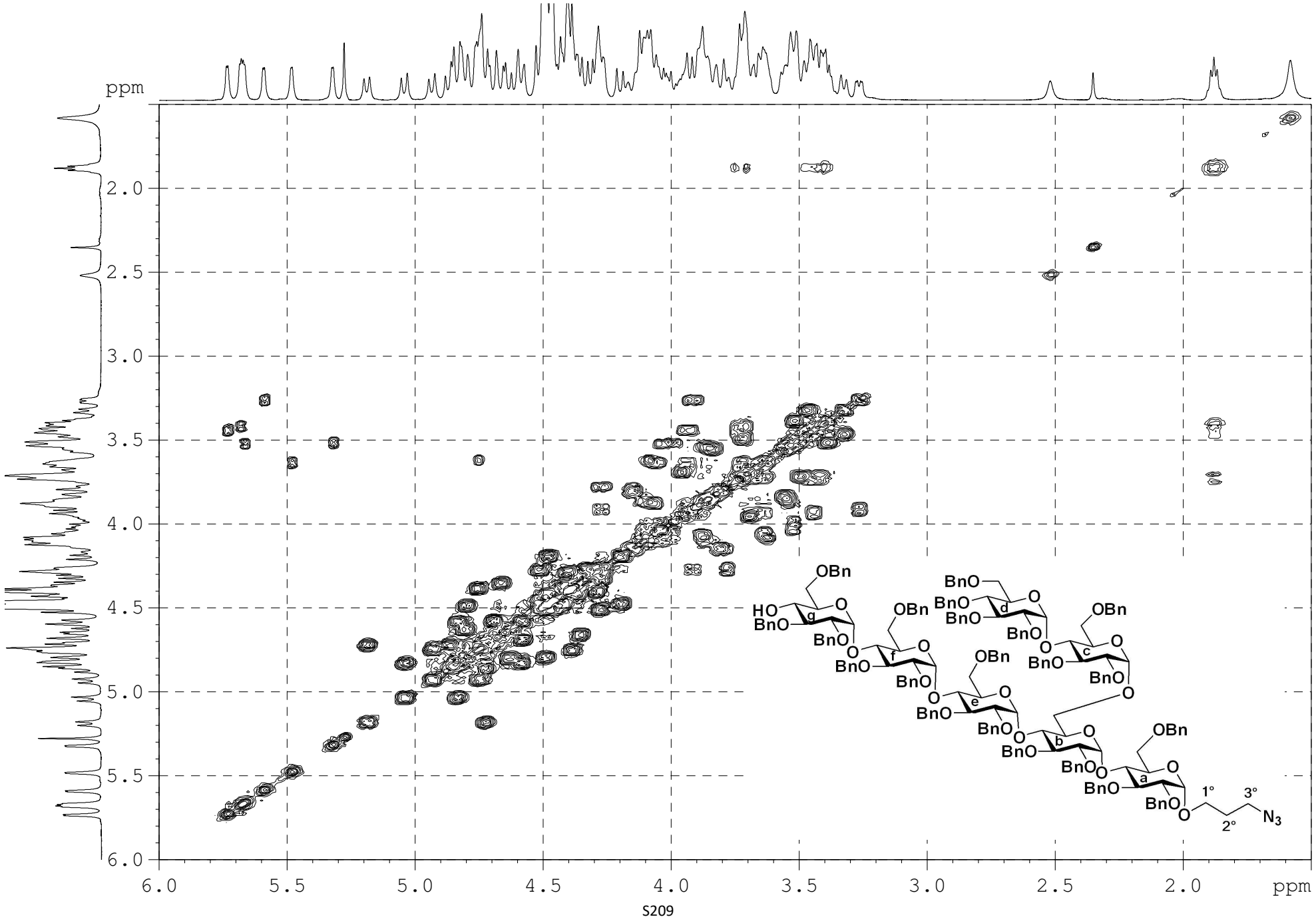

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
171.0 Hz
168.9 Hz
171.6 Hz
173.3 Hz
172.0 Hz
170.3 Hz
168.5 Hz
OBn
NapO
BnO
a
b
c
d
e
f
g
1°
2°
3°
N3
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
ppm

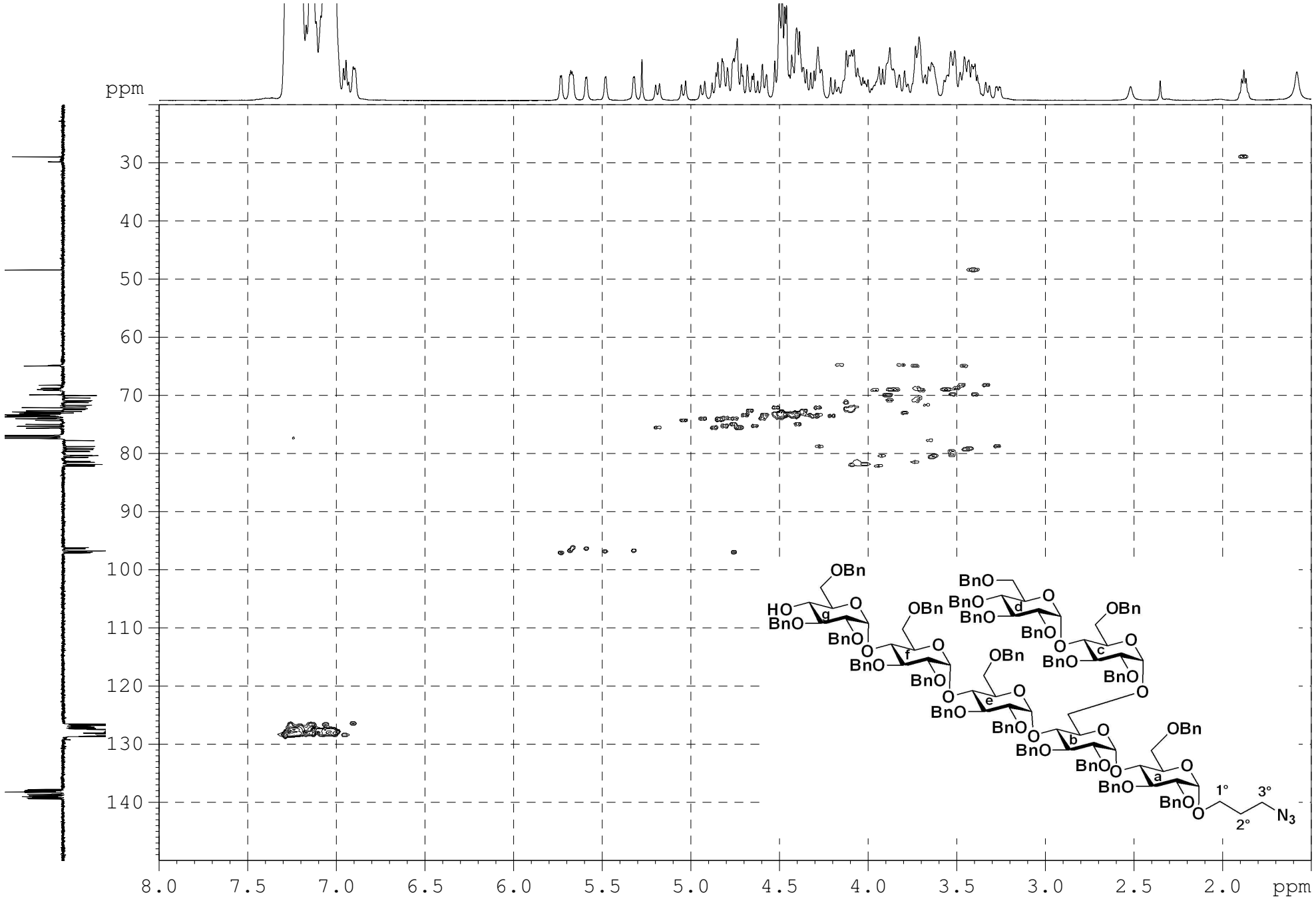

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0 ppm
OBn
NapO
BnO
O
a
b
c
d
e
f
g
1°
2°
3°
N3

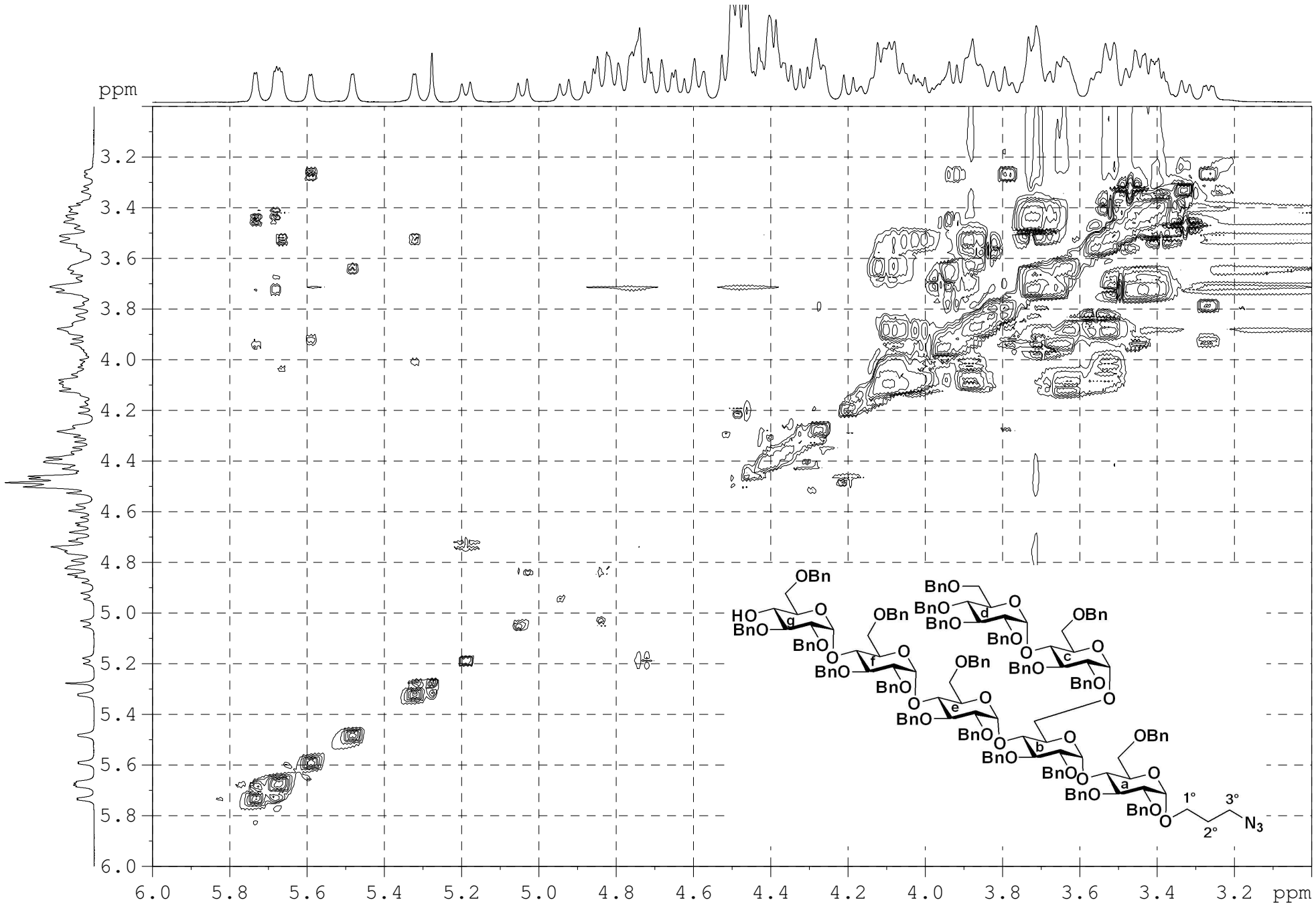
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, ^{1}H-^{1}H cleantocsy **41**



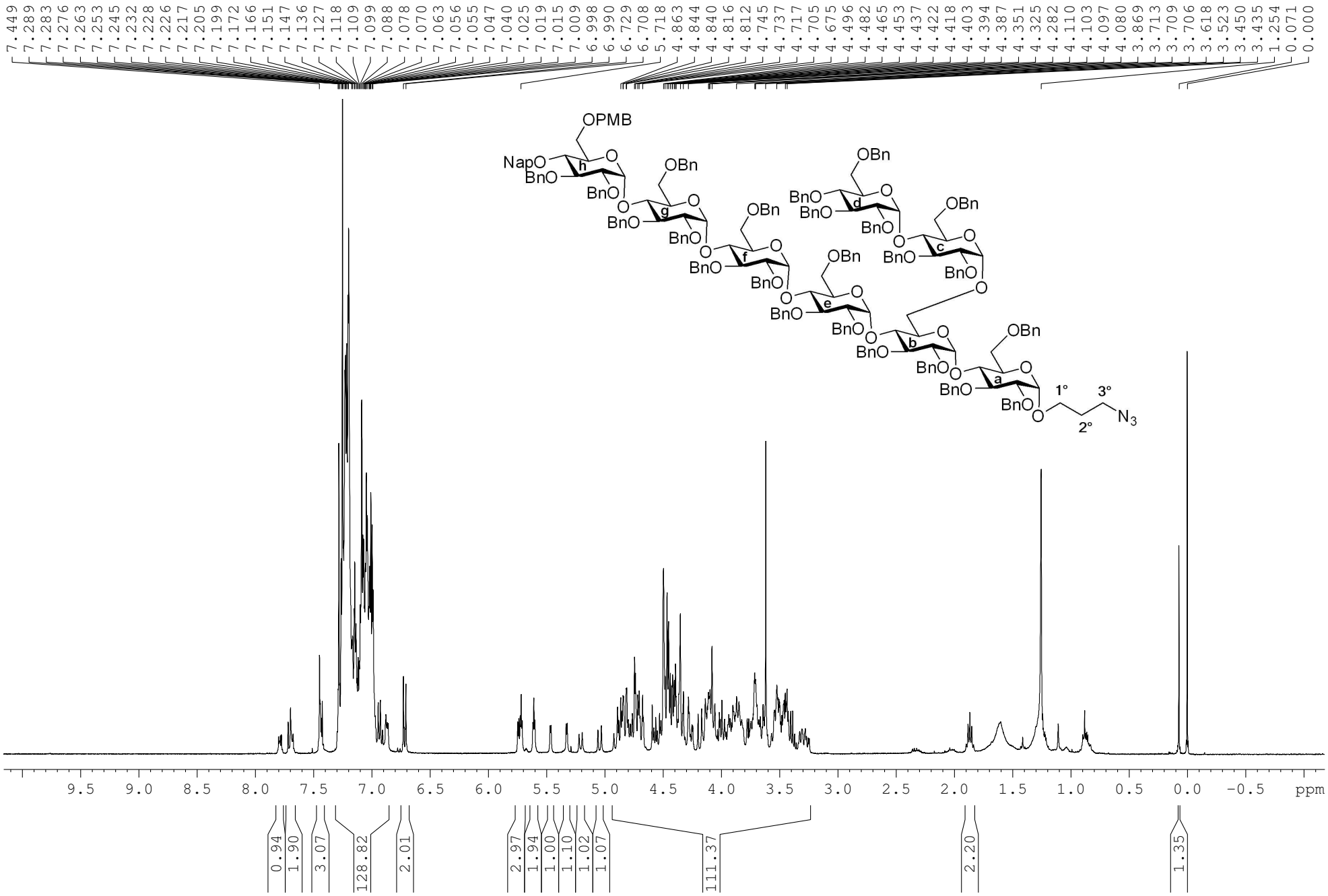

139.34
139.24
139.08
139.00
138.97
138.95
138.89
138.78
138.56
138.52
138.24
138.22
138.20
138.16
138.11
138.07
138.03
137.93
137.88
137.72
127.14
126.91
97.12
97.00
96.85
96.38
96.21
81.34
80.68
80.43
80.30
79.66
79.35
77.77
77.41
77.16
76.91
75.63
75.58
75.31
75.00
74.32
74.02
73.92
73.67
73.56
73.47
73.39
73.35
73.33
73.12
73.03
73.00
72.87
72.75
72.64
72.43
72.29
72.11
71.99
71.70
71.24
71.03
70.90
70.45
70.01
69.90
69.13
69.02
68.98
68.78
68.25
64.94
64.81
48.43
29.83
28.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

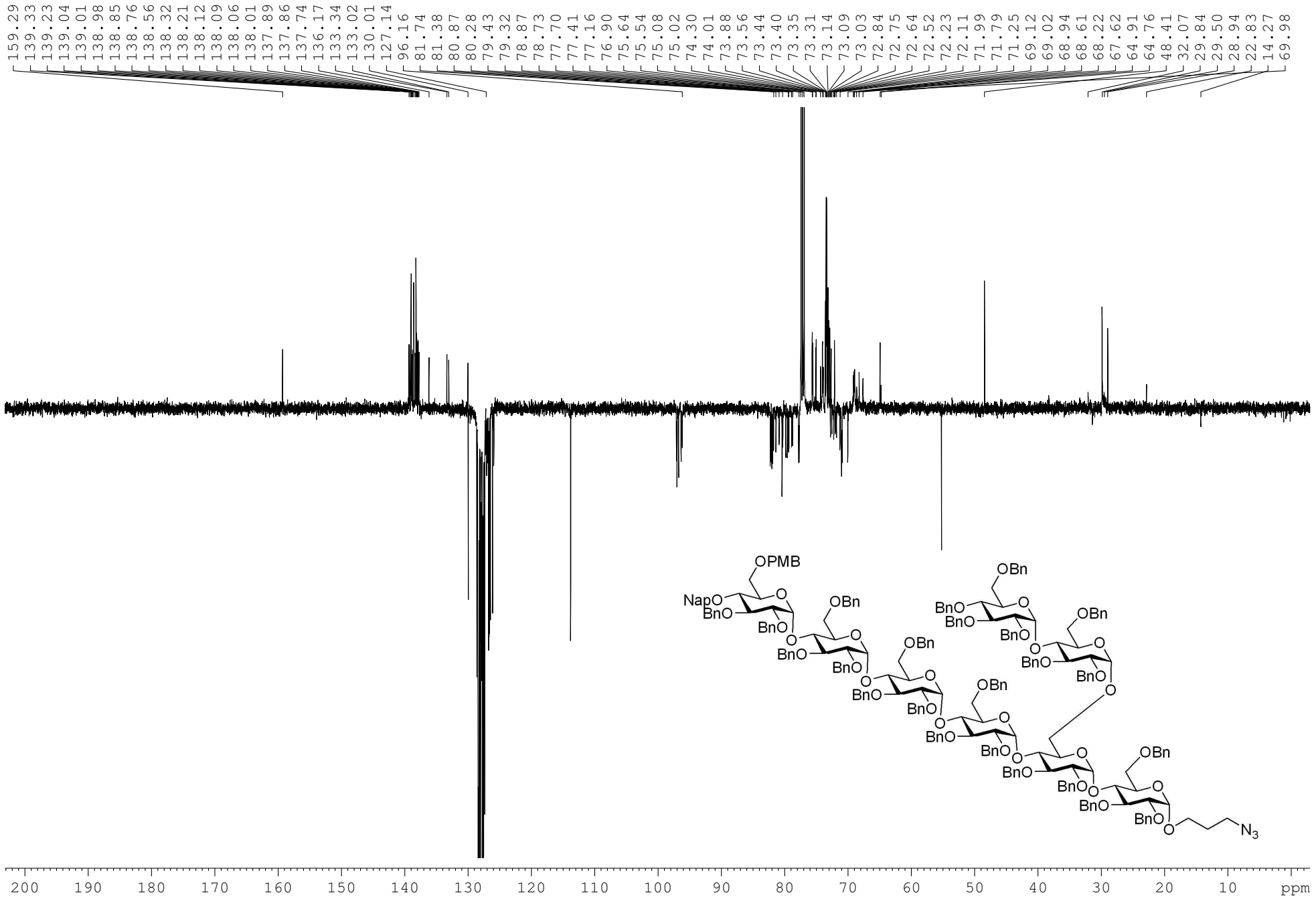

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
HO
BnO
g
f
e
d
c
b
a
1°
2°
3°
N3

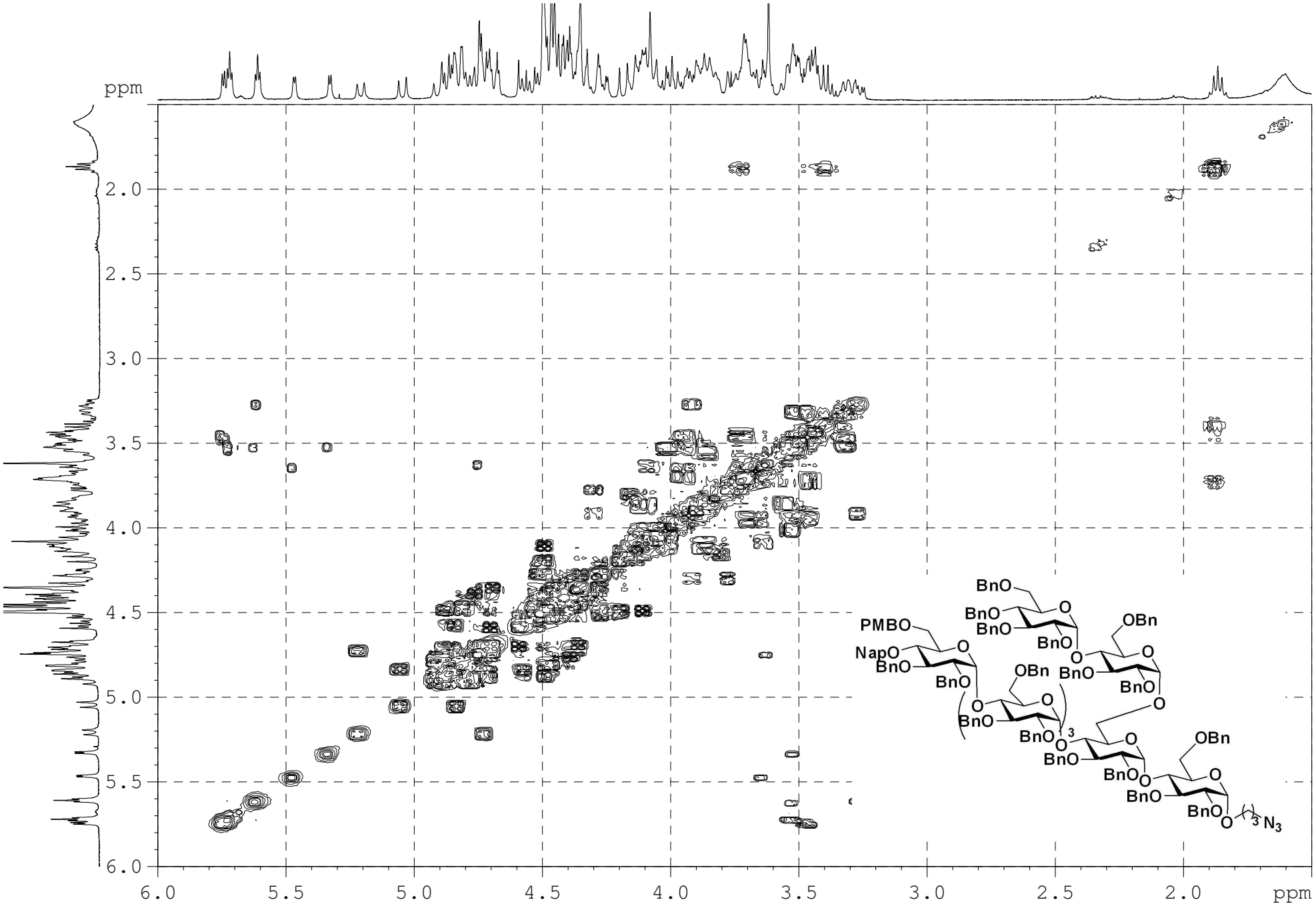

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
OBn
HO
BnO
O
g
f
d
c
e
b
a
1°
2°
3°
N3

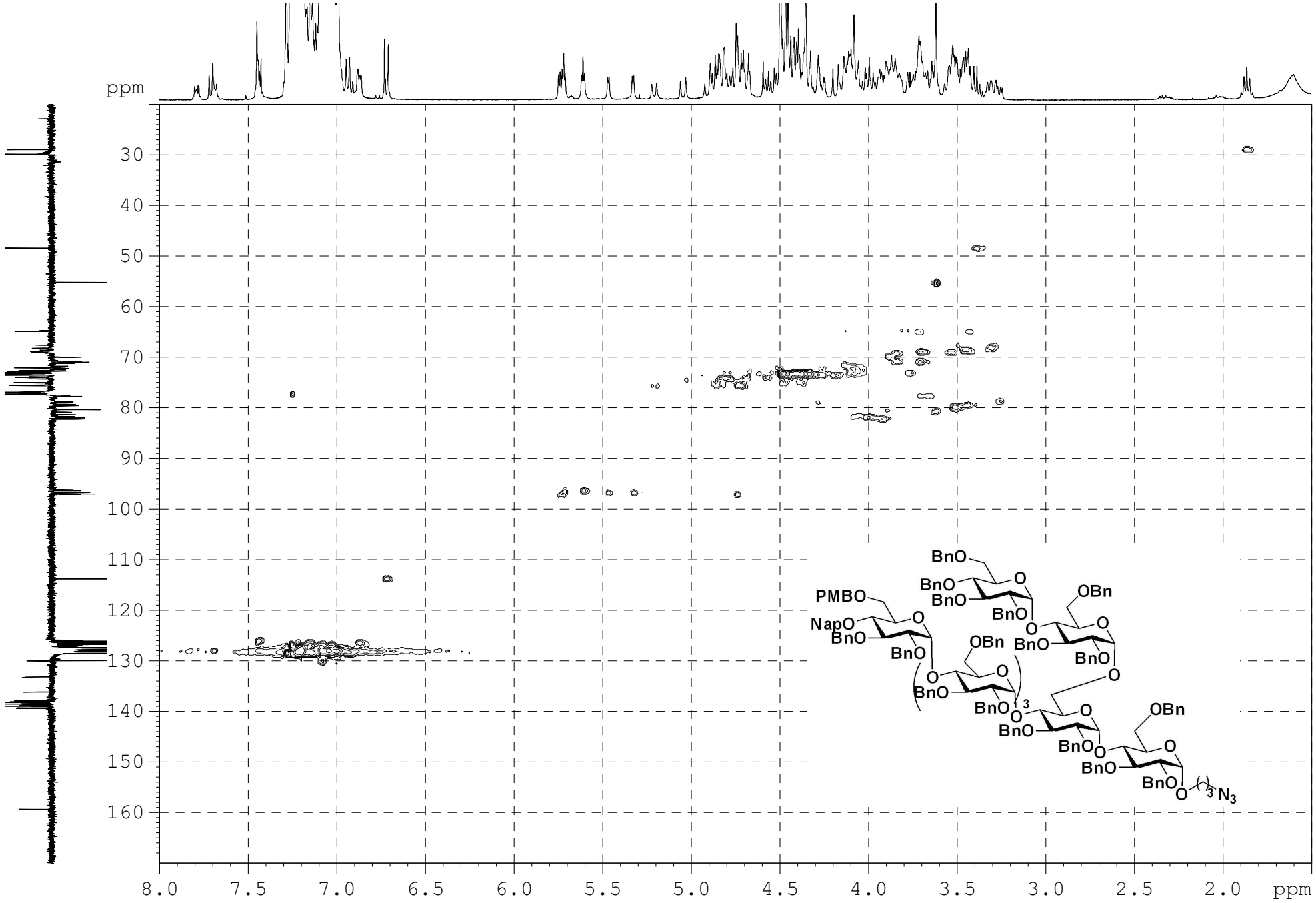

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm
OBn
HO
BnO
O
g
f
e
d
c
b
a
1°
2°
3°
N_3

^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC **42**

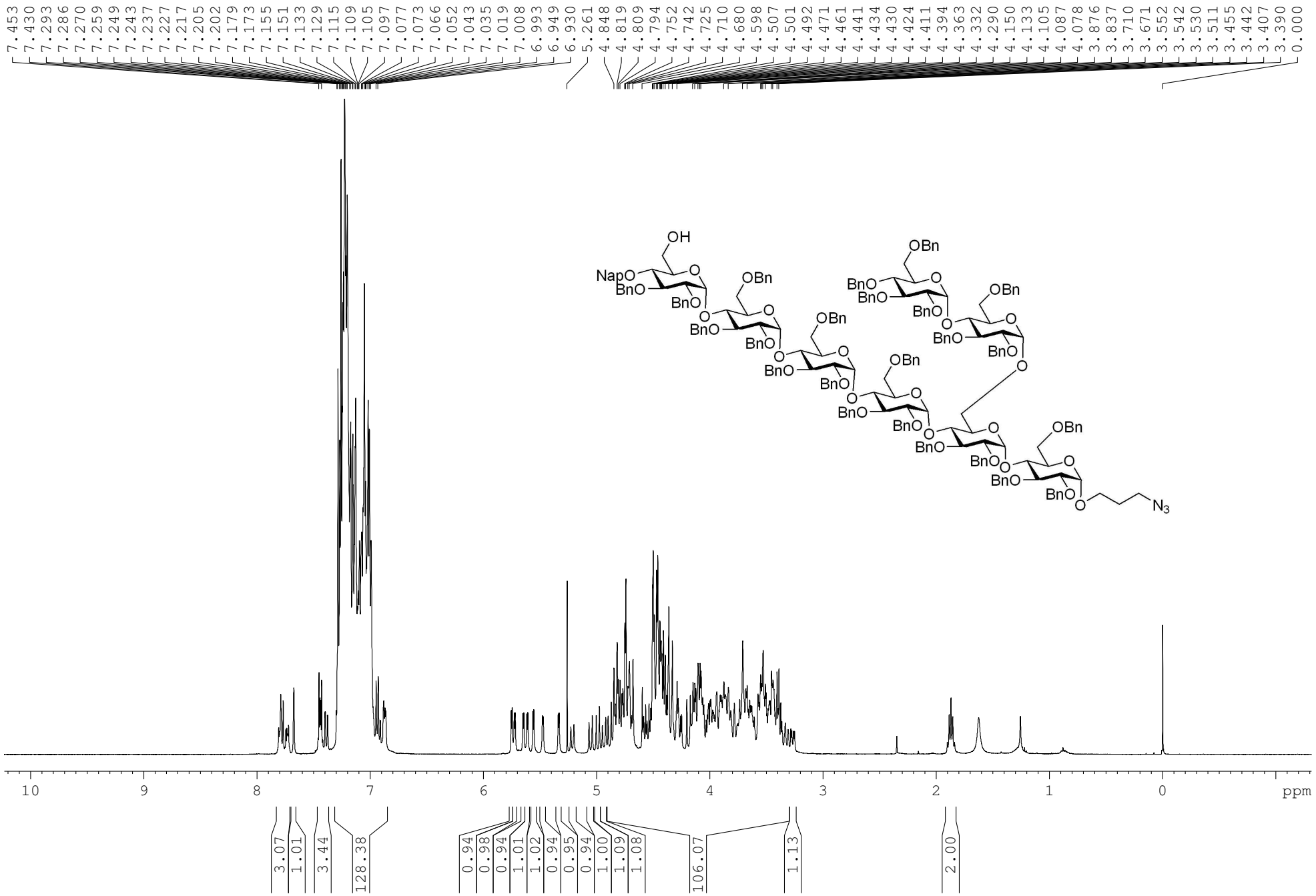


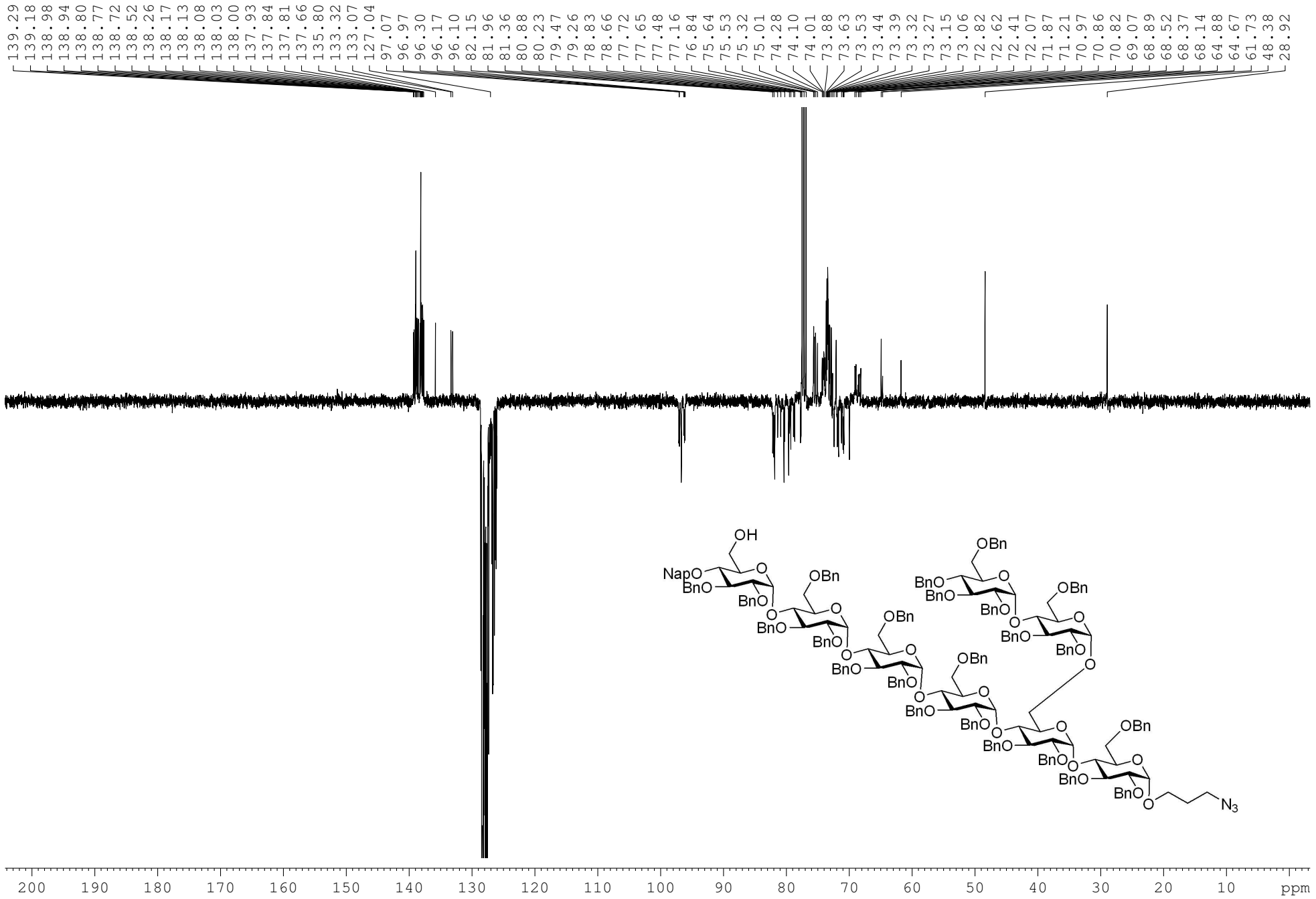

159.29
139.33
139.23
139.04
139.01
138.98
138.85
138.76
138.56
138.32
138.21
138.12
138.09
138.06
138.01
137.89
137.86
137.74
136.17
133.34
133.02
130.01
127.14
96.16
81.74
81.38
80.87
80.28
79.43
79.32
78.87
78.73
77.70
77.41
77.16
76.90
75.64
75.54
75.08
75.02
74.30
74.01
73.88
73.56
73.44
73.40
73.35
73.31
73.14
73.09
73.03
72.84
72.75
72.64
72.52
72.23
72.11
71.99
71.79
71.25
69.12
69.02
68.94
68.61
68.22
67.62
64.91
64.76
48.41
32.07
29.84
29.50
28.94
22.83
14.27
69.98
OPMB
NapO
BnO
OBn
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

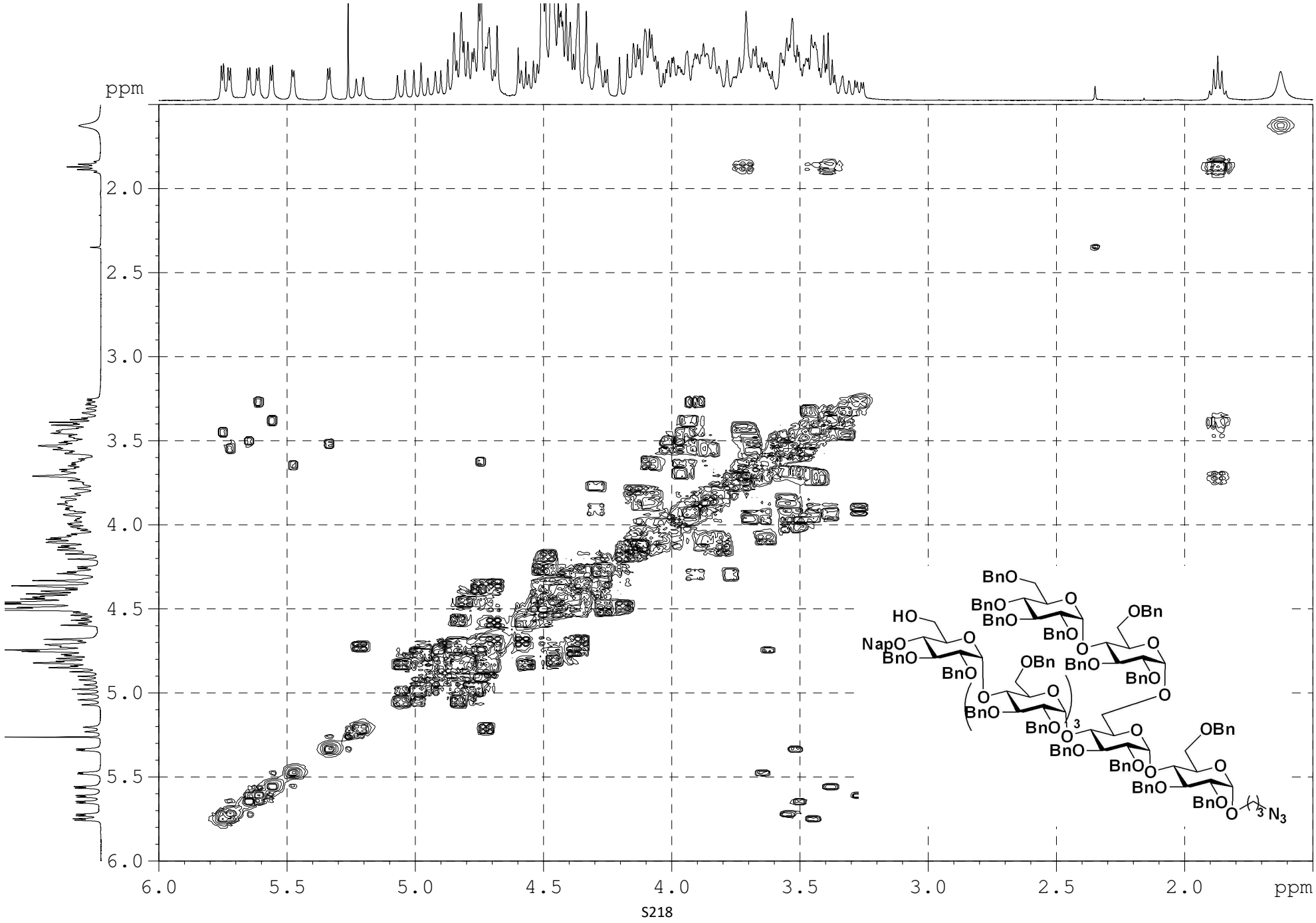

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
O
BnO
PMBO
OBn
NapO
O
O
BnO
BnO
BnO
OBn
BnO
BnO
O
O
BnO
O
BnO
3
O
BnO
O
OBn
BnO
BnO
O
O
BnO
BnO
O
3
N3

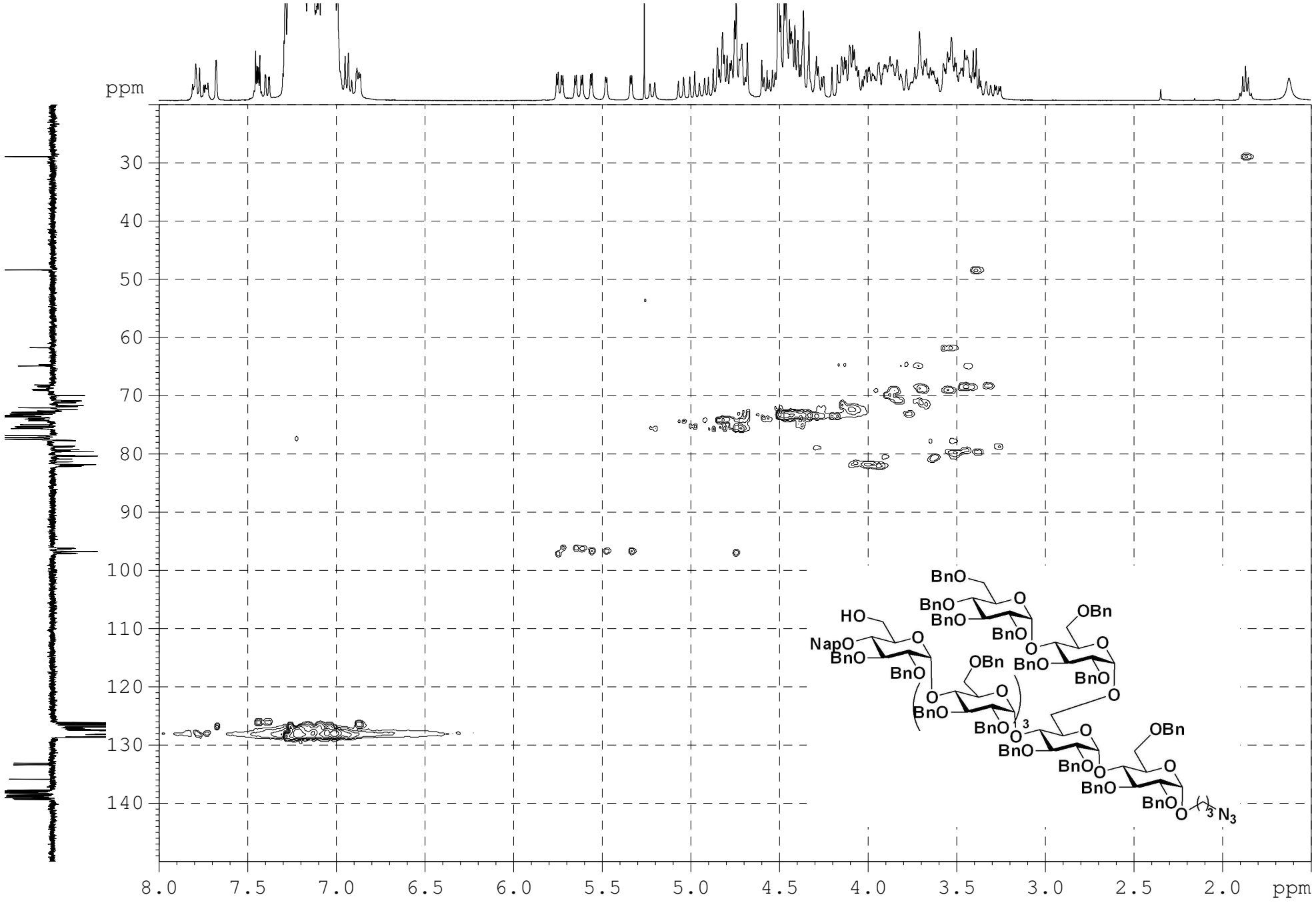

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
BnO
BnO
O
BnO
OBn
PMBO
NapO
BnO
O
BnO
O
BnO
OBn
BnO
O
BnO
BnO
O
BnO
3
O
BnO
O
BnO
OBn
BnO
O
BnO
O
BnO
O
3
N3

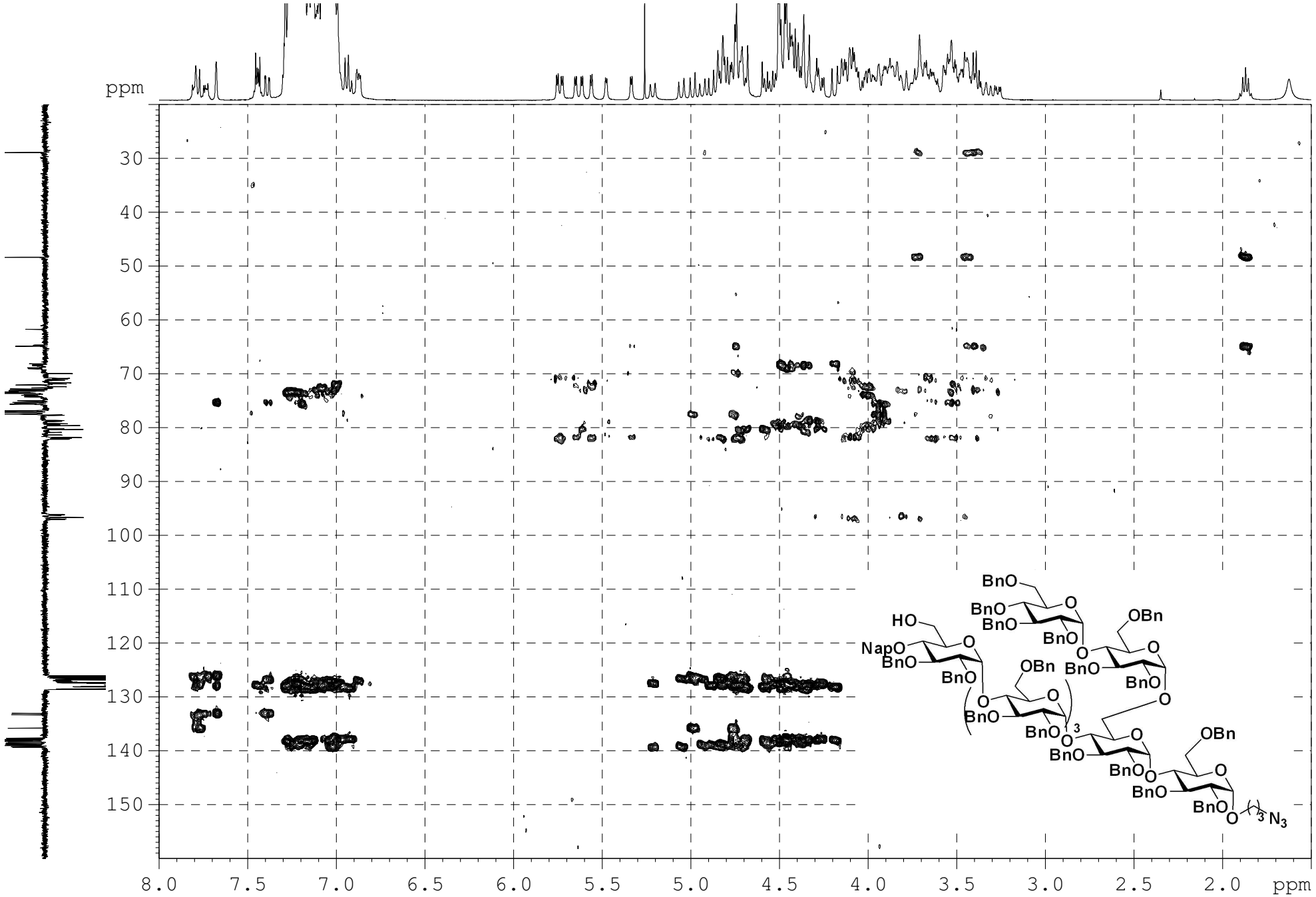
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED, ^{1}H-^{1}H cleantocsy **43**

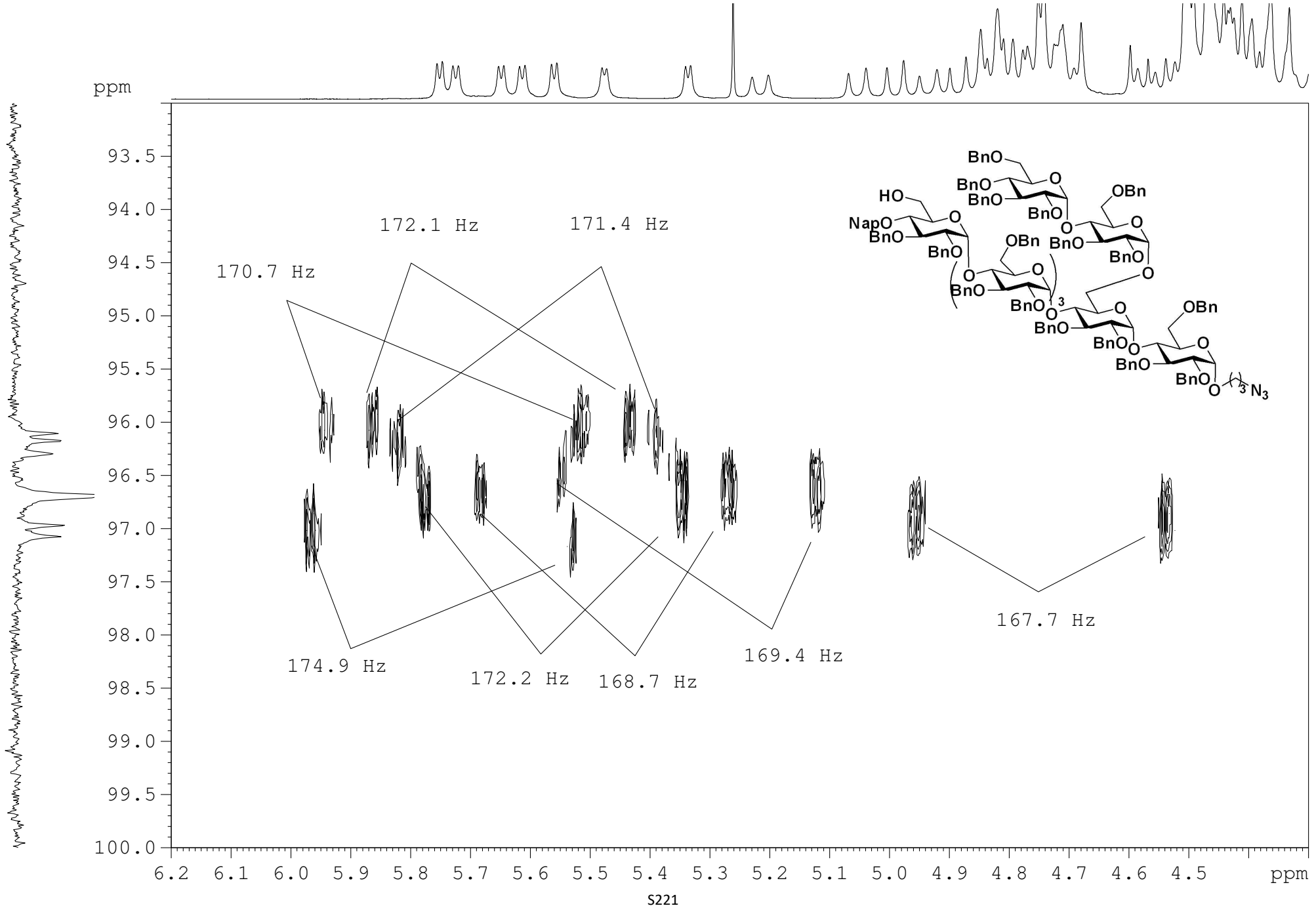


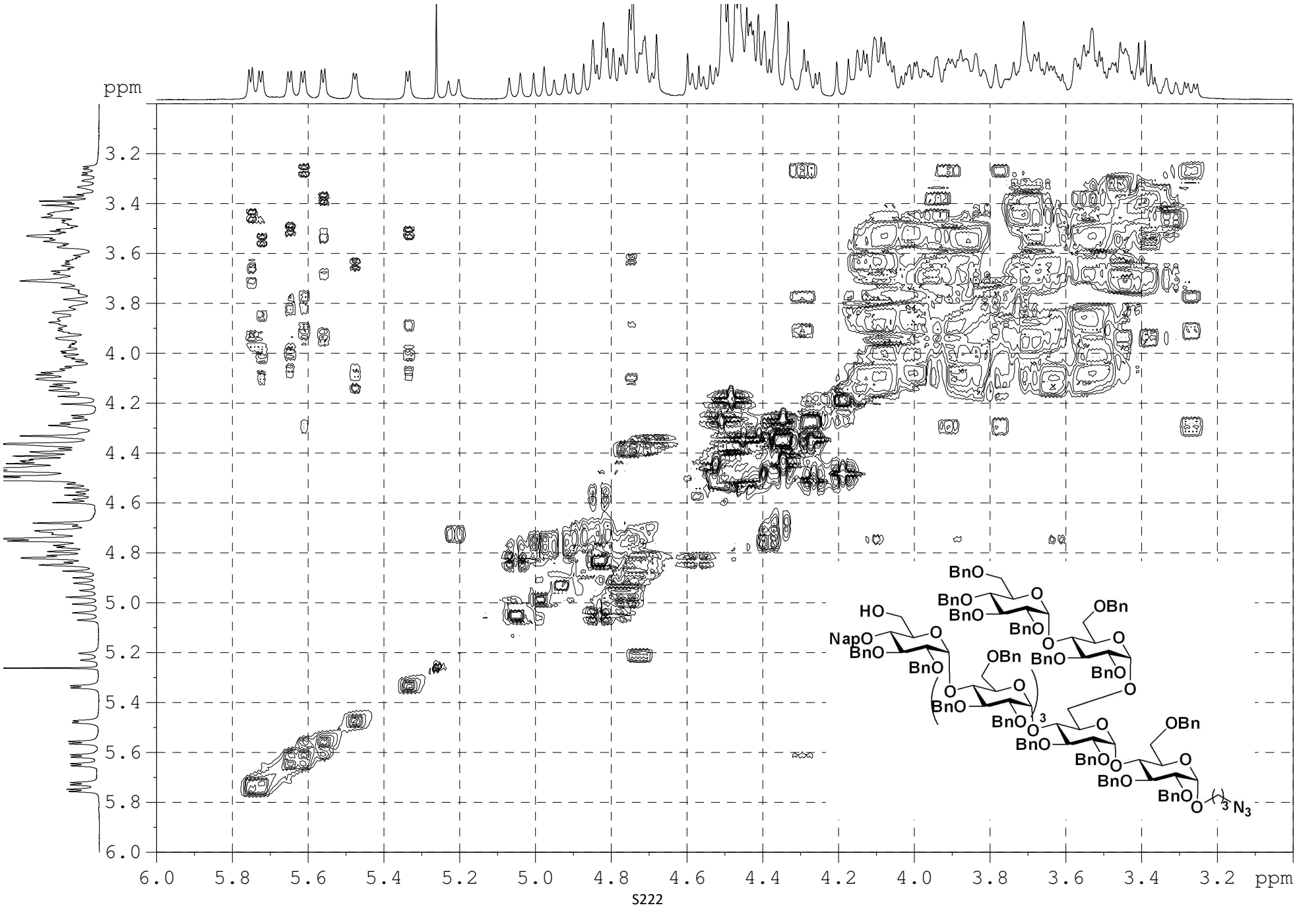

139.29
139.18
138.98
138.94
138.80
138.77
138.72
138.52
138.26
138.17
138.13
138.08
138.03
138.00
137.93
137.84
137.81
137.66
135.80
133.32
133.07
127.04
97.07
96.97
96.30
96.17
96.10
82.15
81.96
81.36
80.88
80.23
79.47
79.26
78.83
78.66
77.72
77.65
77.48
77.16
76.84
75.64
75.53
75.32
75.01
74.28
74.10
74.01
73.88
73.63
73.53
73.44
73.39
73.32
73.27
73.15
73.06
72.82
72.62
72.41
72.07
71.87
71.21
70.97
70.86
70.82
69.07
68.89
68.52
68.37
68.14
64.88
64.67
61.73
48.38
28.92
OH
NapO
BnO
OBn
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
NapO
OBn
N3

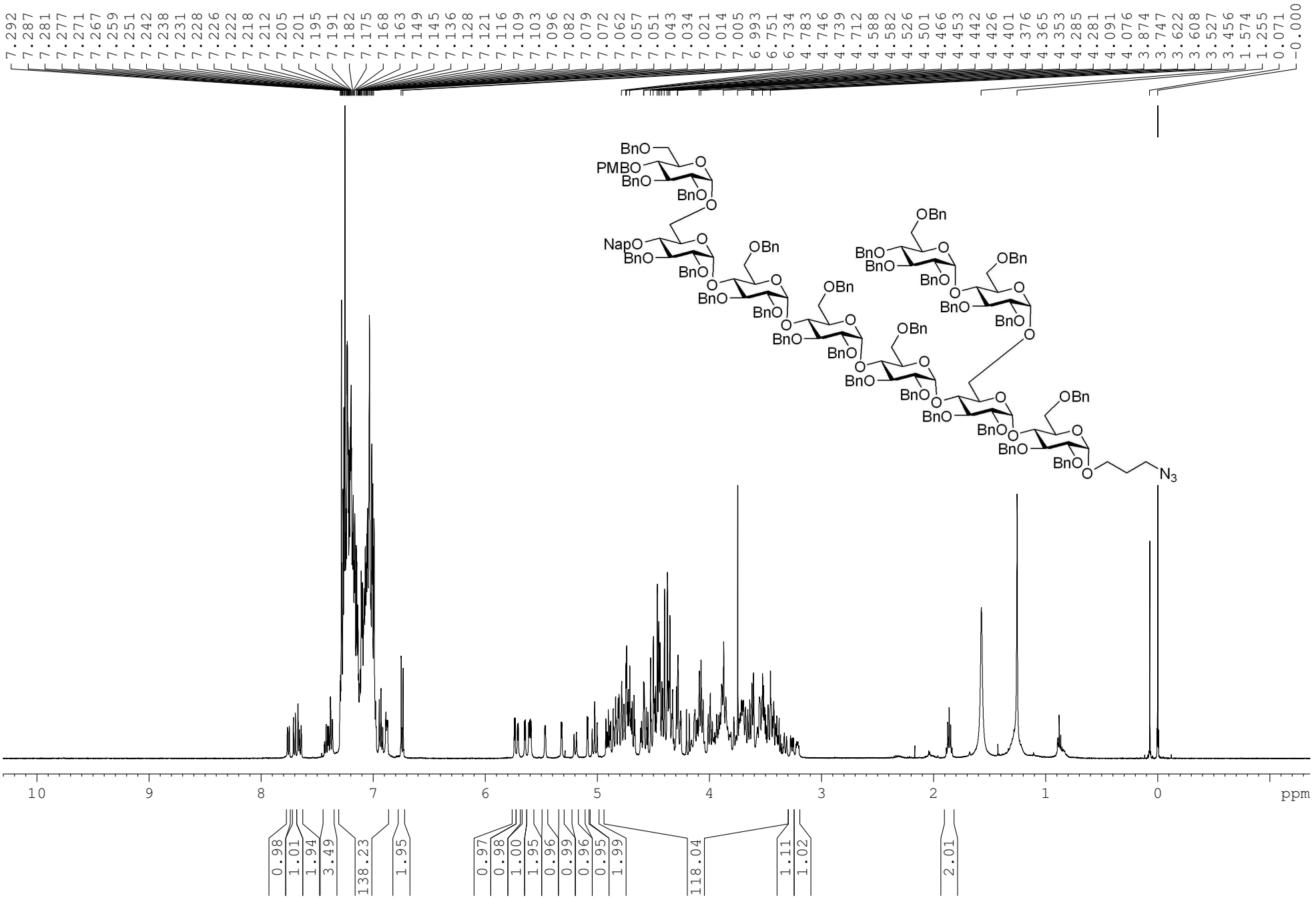

ppm
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
NapO
OBn
N3

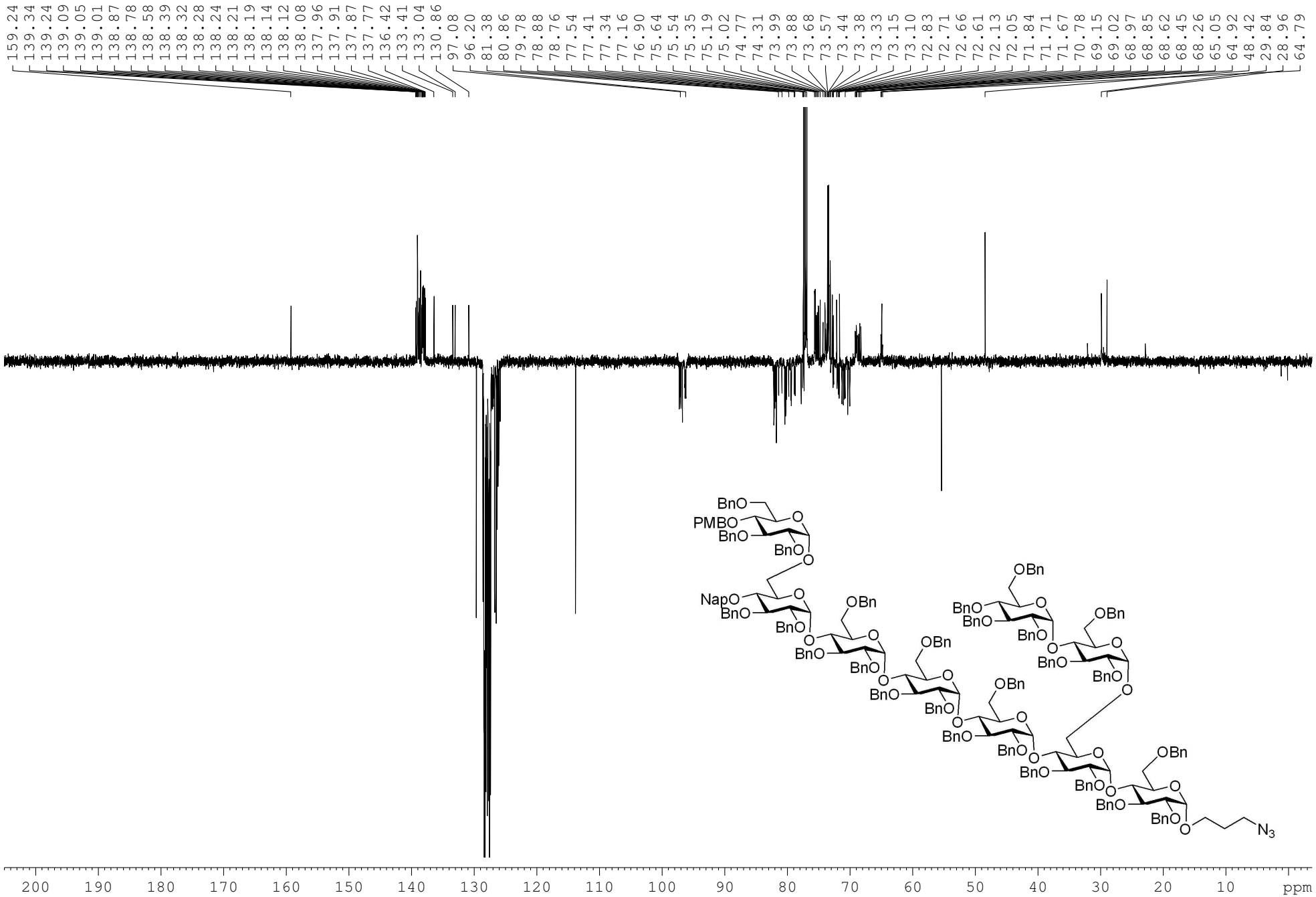

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
HO
NapO
OBn
N3

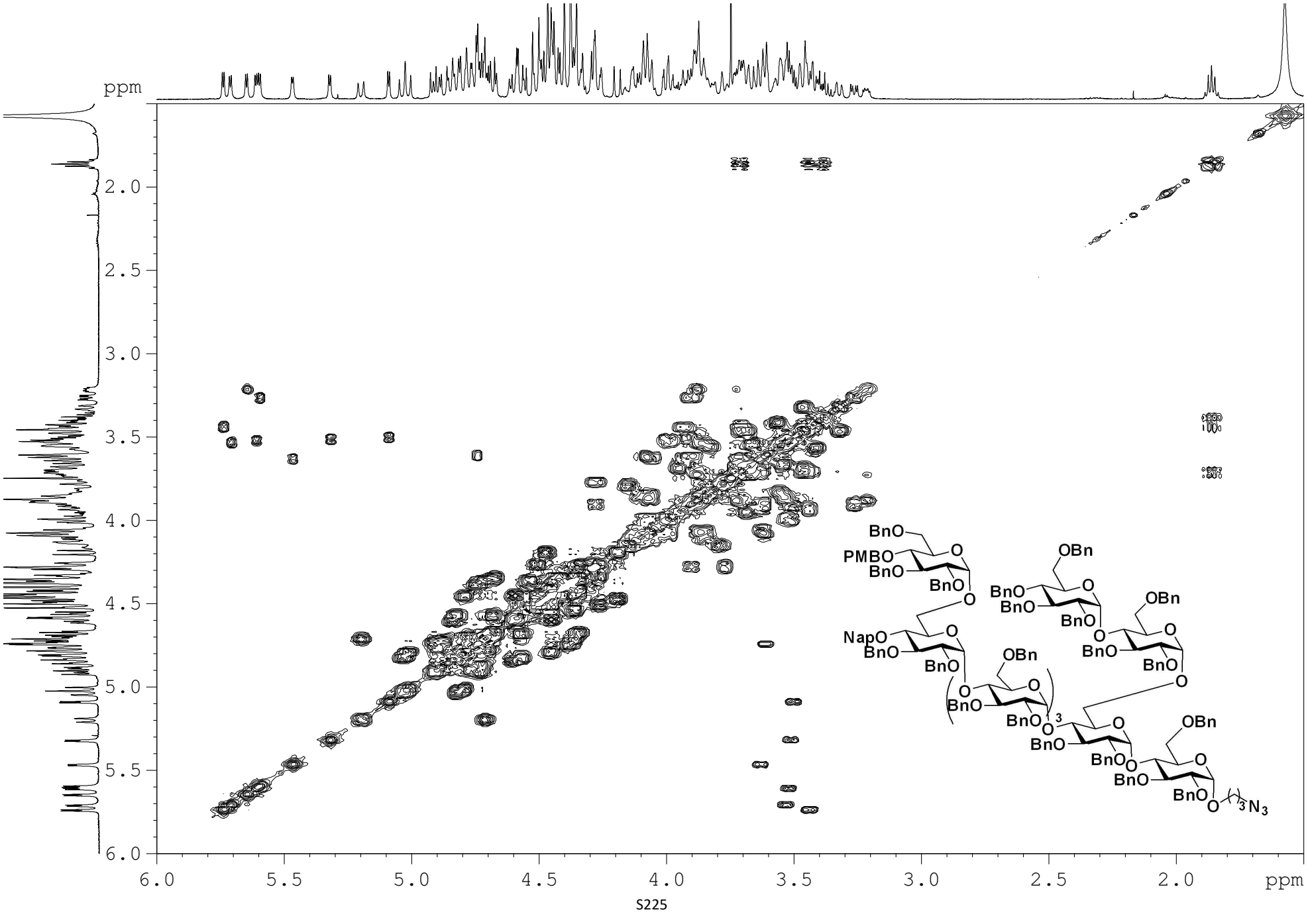

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
172.1 Hz
171.4 Hz
170.7 Hz
174.9 Hz
172.2 Hz
168.7 Hz
169.4 Hz
167.7 Hz
BnO
HO
NapO
OBn
N3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
ppm

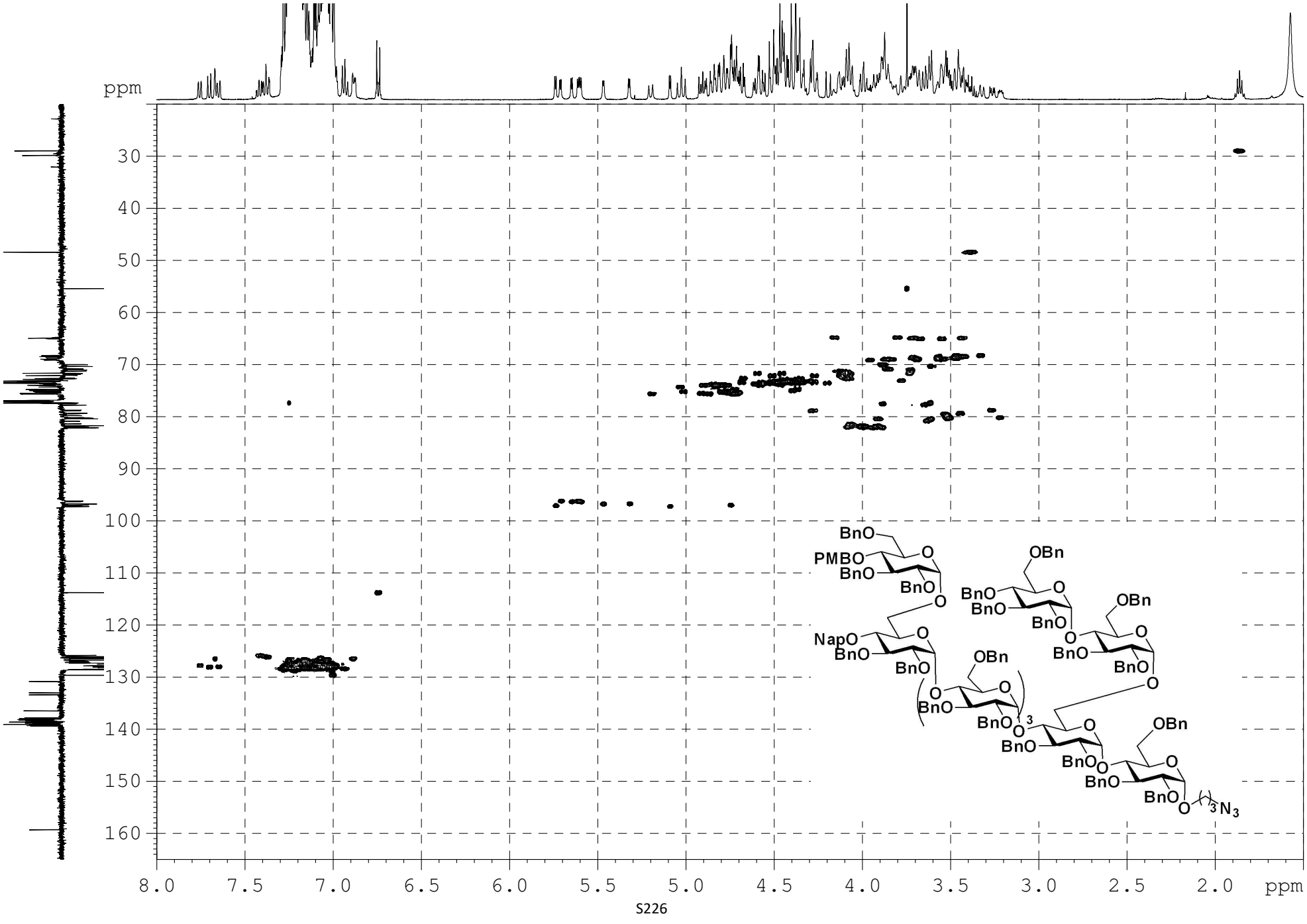

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm
BnO
HO
NapO
OBn
N3

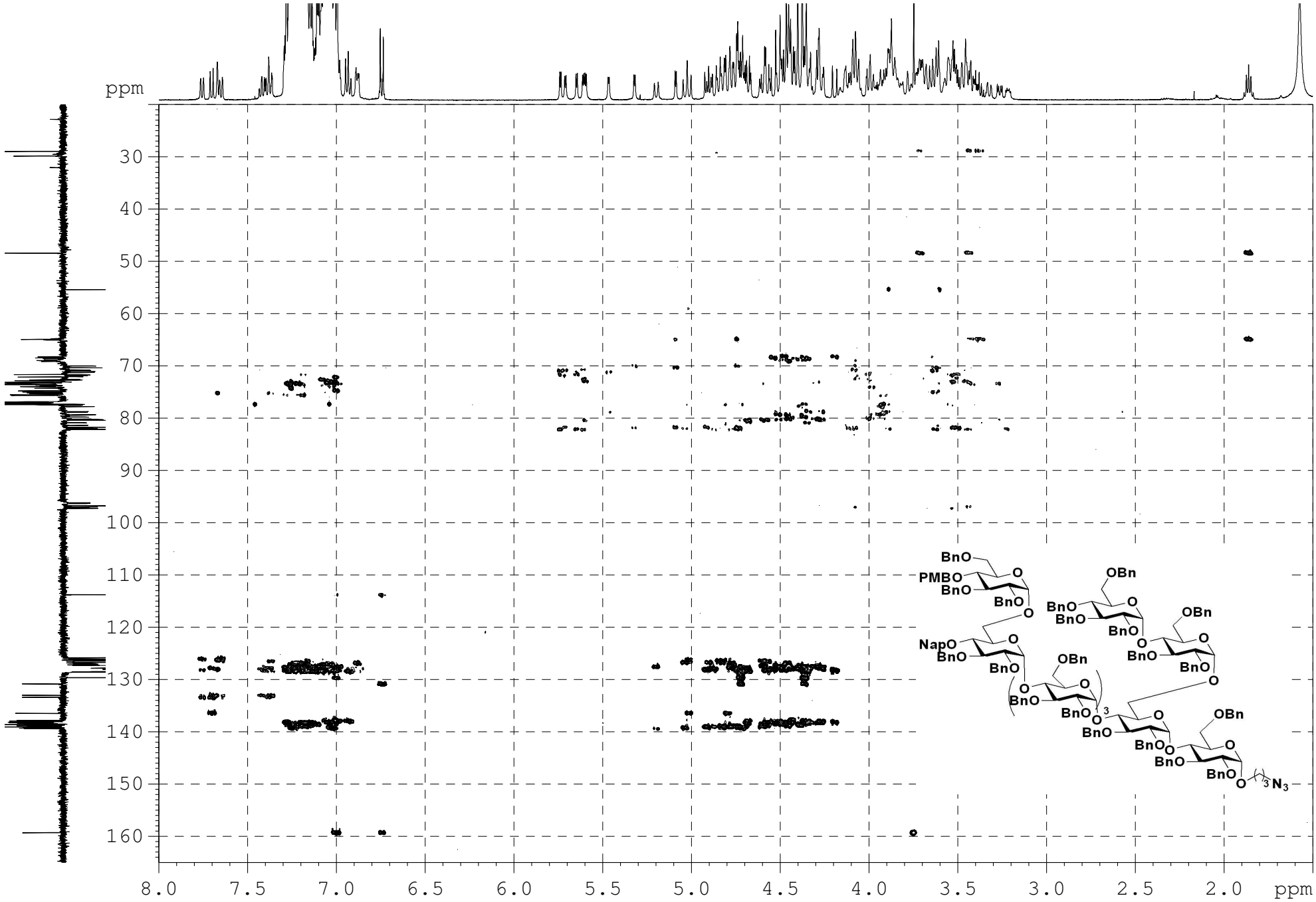
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **44**

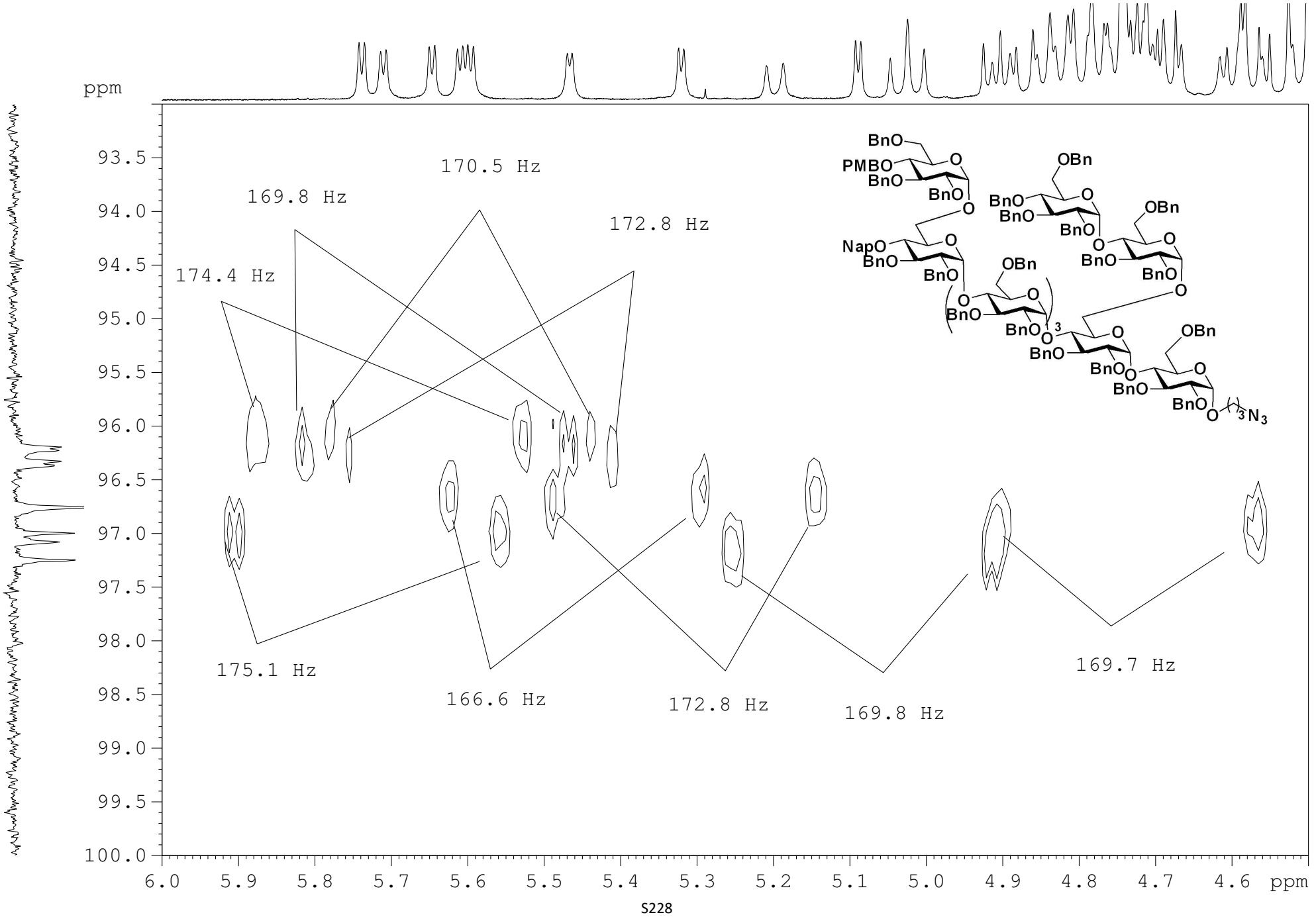



159.24
139.34
139.24
139.09
139.05
139.01
138.87
138.78
138.58
138.39
138.32
138.28
138.24
138.21
138.19
138.14
138.12
138.08
137.96
137.91
137.87
137.77
136.42
133.41
133.04
130.86
97.08
96.20
81.38
80.86
79.78
78.88
78.76
77.54
77.41
77.34
77.16
76.90
75.64
75.54
75.35
75.19
75.02
74.77
74.31
73.99
73.88
73.68
73.57
73.44
73.38
73.33
73.15
73.10
72.83
72.71
72.66
72.61
72.13
72.05
71.84
71.71
71.67
70.78
69.15
69.02
68.97
68.85
68.62
68.45
68.26
65.05
64.92
48.42
29.84
28.96
64.79
BnO
PMBO
BnO
BnO
O
NapO
BnO
BnO
OBn
O
BnO
BnO
OBn
O
BnO
BnO
OBn
O
BnO
BnO
OBn
O
BnO
BnO
OBn
O
BnO
BnO
OBn
O
BnO
BnO
O
N3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

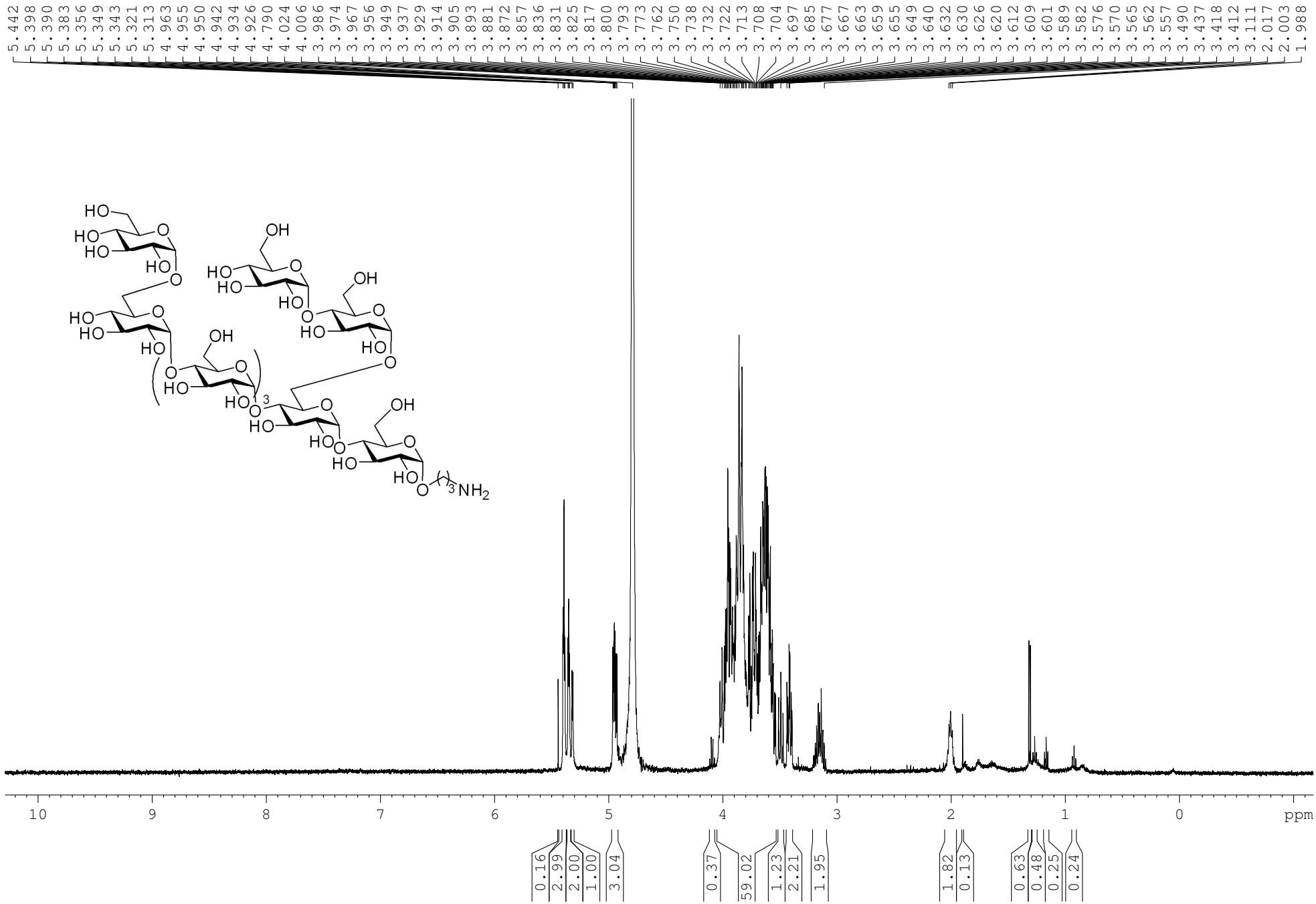

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
PMBO
BnO
BnO
O
NapO
BnO
BnO
O
BnO
OBn
BnO
BnO
O
BnO
OBn
O
BnO
BnO
O
BnO
OBn
O
BnO
BnO
3
O
BnO
OBn
O
BnO
BnO
O
BnO
O
3
N3

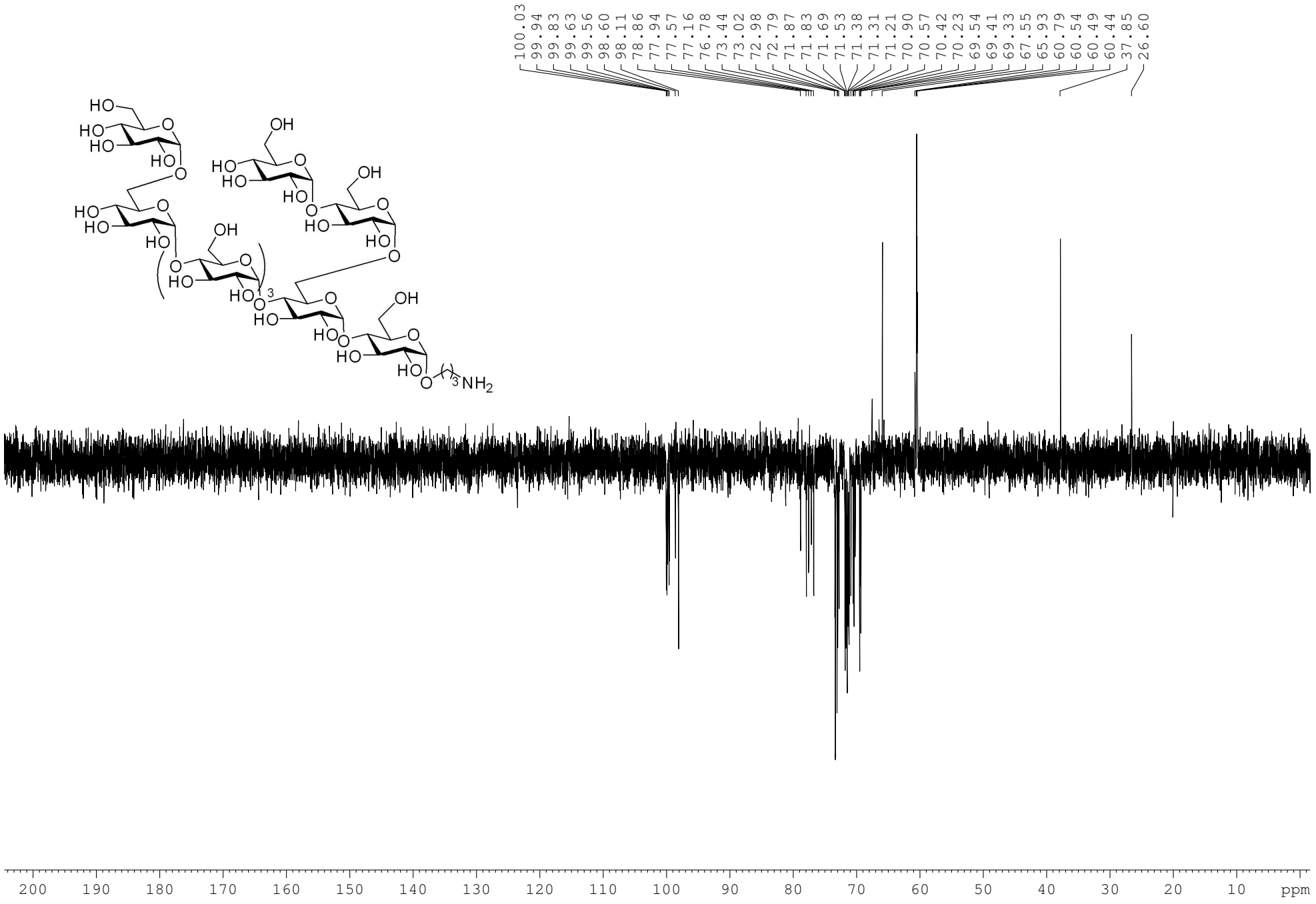

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
PMBO
BnO
BnO
O
NapO
BnO
BnO
O
BnO
BnO
O
OBn
BnO
BnO
O
BnO
BnO
O
OBn
BnO
BnO
O
BnO
BnO
O
3
OBn
BnO
BnO
O
BnO
BnO
O
OBn
BnO
O
3
N3

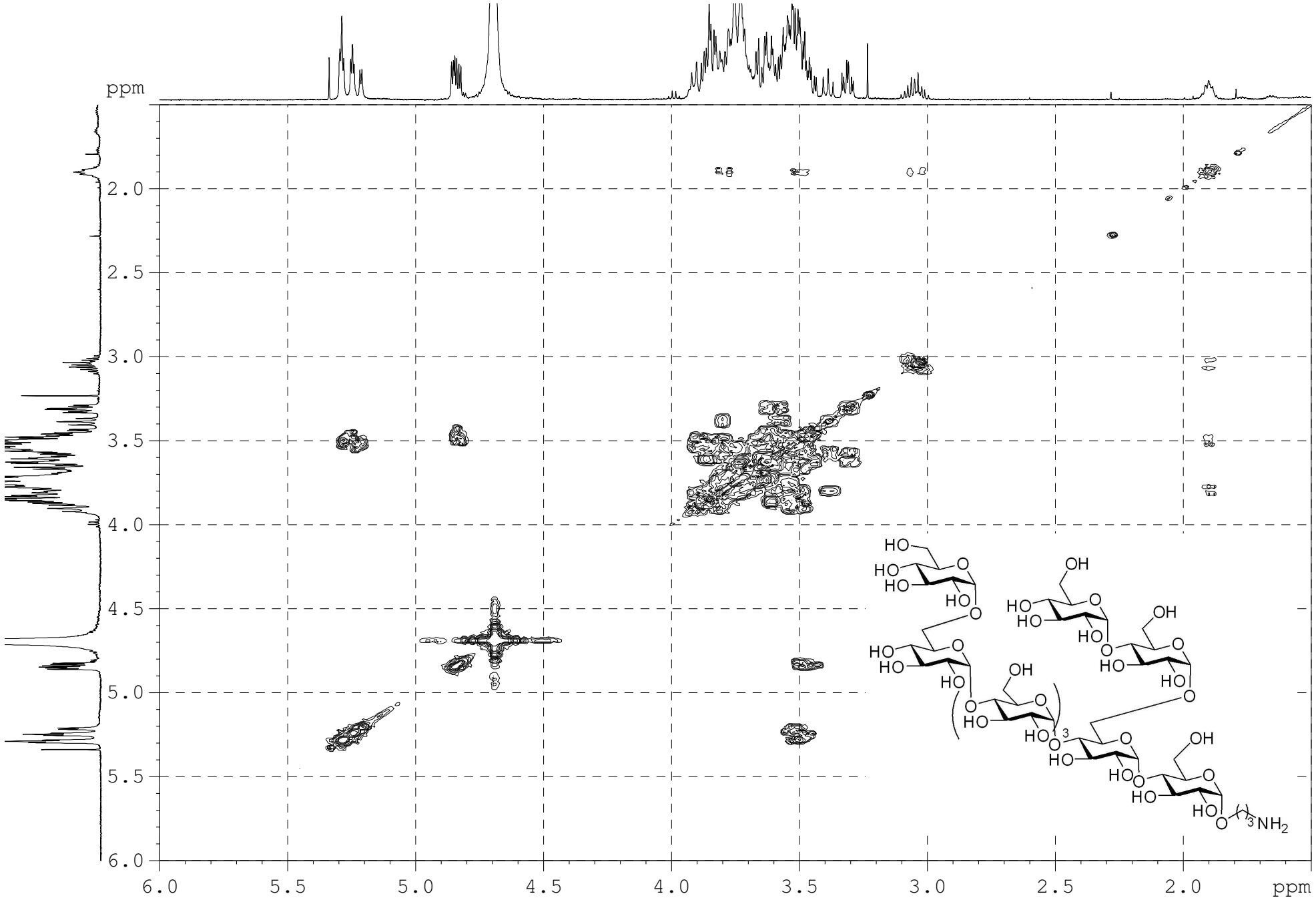

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
BnO
PMBO
BnO
BnO
O
NapO
BnO
BnO
O
BnO
OBn
BnO
BnO
O
OBn
BnO
BnO
O
BnO
O
BnO
O
3
O
BnO
BnO
O
BnO
OBn
O
BnO
O
3
N3

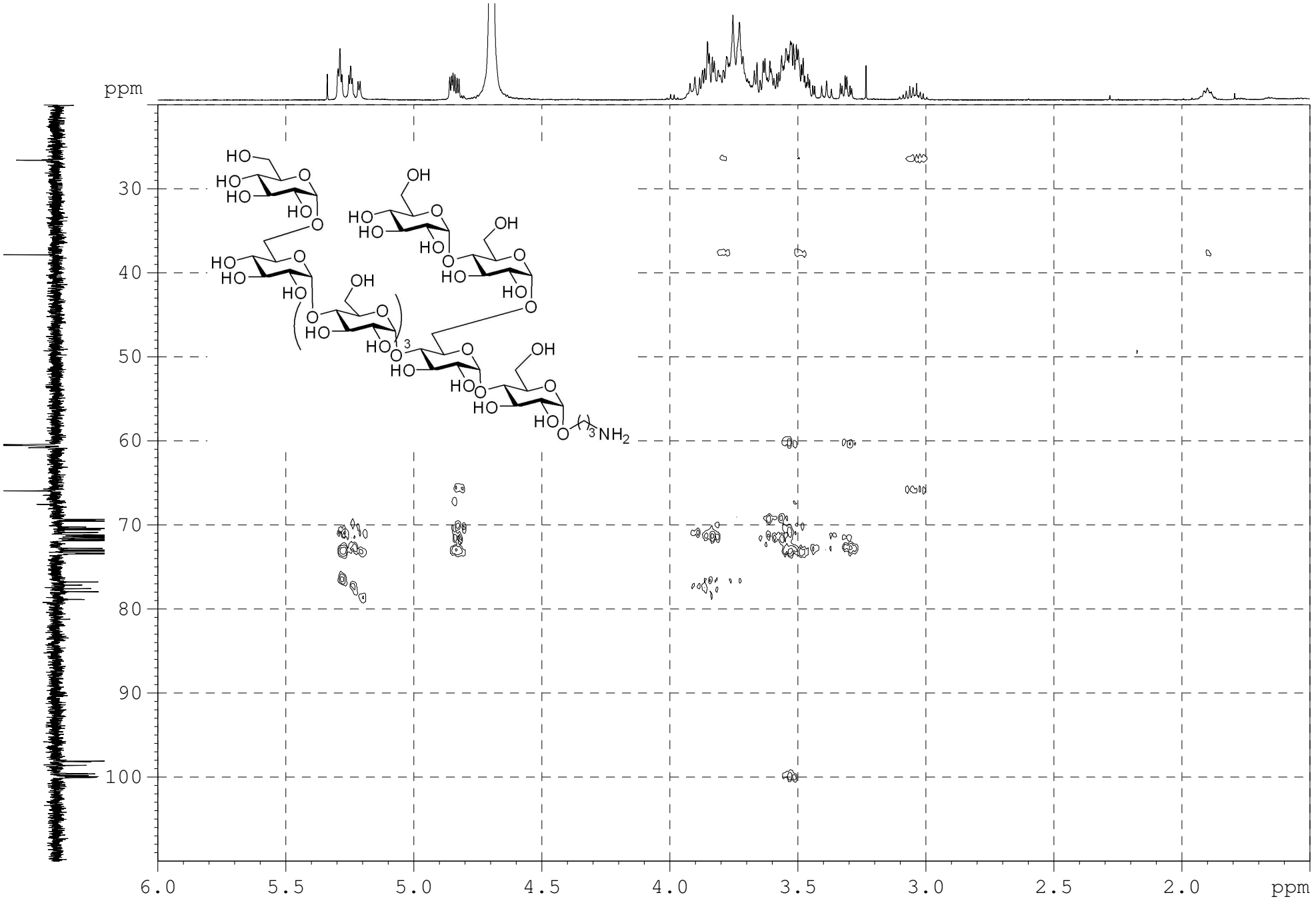

ppm
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0
170.5 Hz
169.8 Hz
172.8 Hz
174.4 Hz
175.1 Hz
166.6 Hz
172.8 Hz
169.8 Hz
169.7 Hz
BnO
PMBO
NapO
OBn
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
ppm

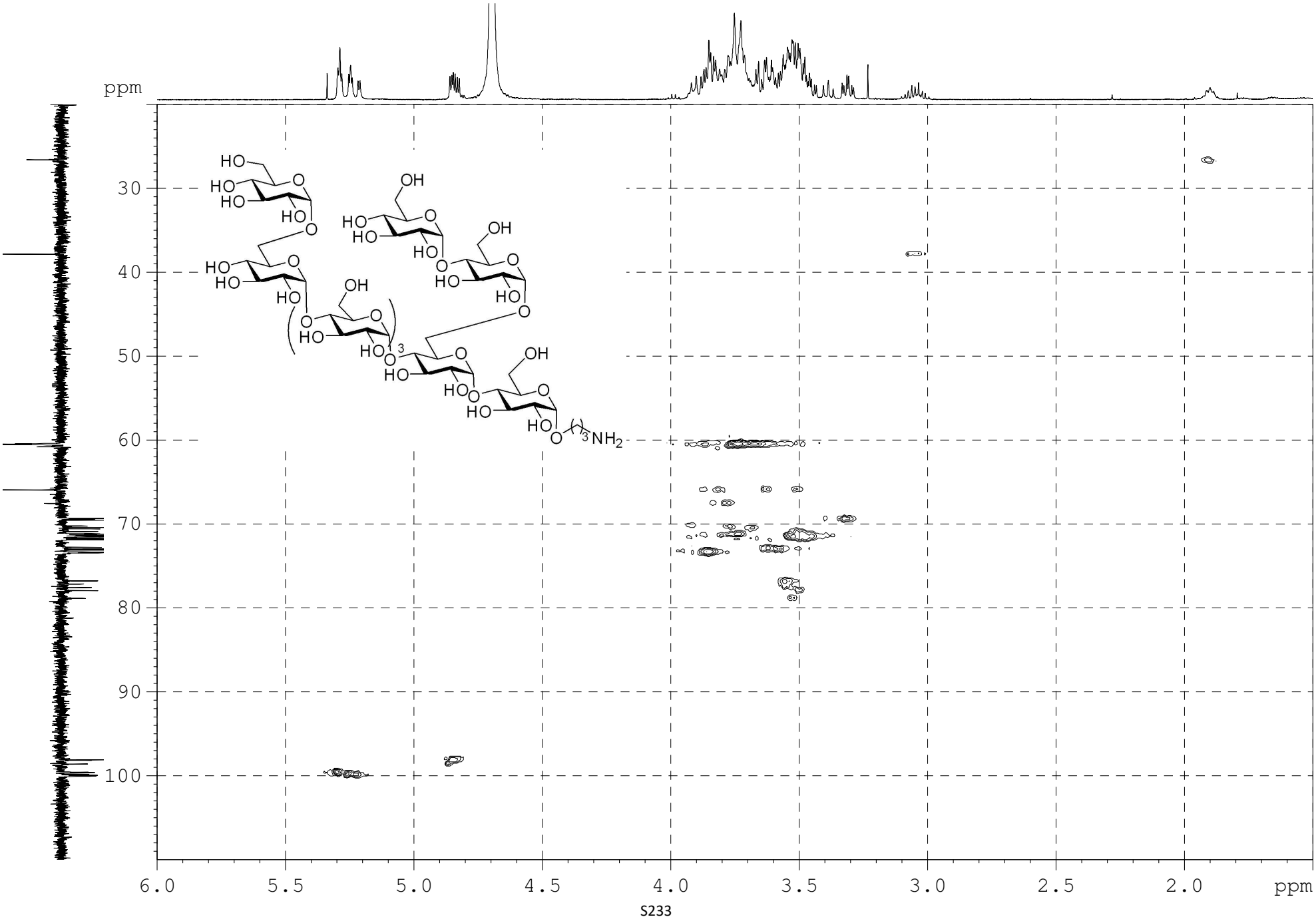
^{1}H-NMR, ^{13}C-APT, ^{1}H-^{1}H COSY, HSQC, HMBC, GATED of **1**

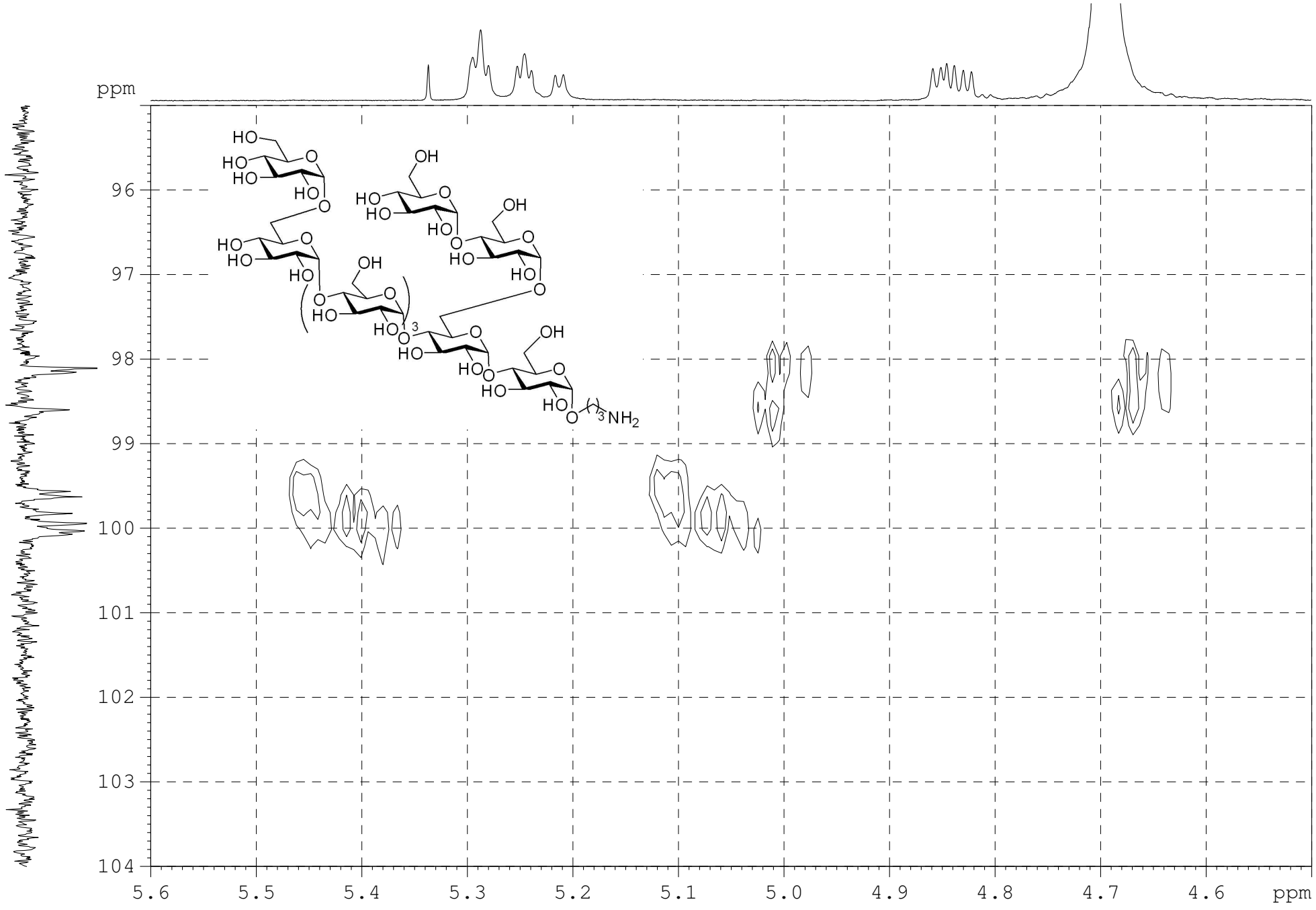



100.03
99.94
99.83
99.63
99.56
98.60
98.11
78.86
77.94
77.57
77.16
76.78
73.44
73.02
72.98
72.79
71.87
71.83
71.69
71.53
71.38
71.31
71.21
70.90
70.57
70.42
70.23
69.54
69.41
69.33
67.55
65.93
60.79
60.54
60.49
60.44
37.85
26.60
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
HO
HO
HO
O
HO
O
OH
HO
HO
O
HO
O
OH
HO
HO
O
HO
O
OH
HO
HO
O
HO
O
OH
HO
HO
O
HO
O
HO
3
O
OH
HO
HO
O
HO
O
HO
O
3
NH2


ppm
30
40
50
60
70
80
90
100
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


ppm
30
40
50
60
70
80
90
100
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


ppm
96
97
98
99
100
101
102
103
104
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
ppm