Electronic Supplementary Information

Synthesis and conformational analysis of vicinally branched trisaccharide β-D-Gal*f*-(1→2)-[β-D-Gal*f*-(1→3)-]-α-Gal*p* from *Cryptococcus neoformans* galactoxylomannan

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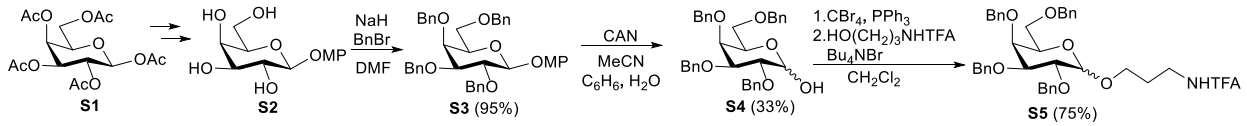
1. EXPERIMENTAL PROCEDURES

1.1. GENERAL METHODS

Molecular sieves AW-300 for glycosylation reactions were activated prior to application at 185 °C under high vacuum for 2 h. Dichloromethane was successively distilled from diethanolamine, P_2O_5, and CaH_2 under Ar. Pyridine was dried by distillation from P_2O_5. Acetonitrile was successively distilled from P_2O_5, and CaH_2 under Ar. Methanol was dried by distillation from Mg. Analytical TLC was performed on Silica Gel 60 Å F254 aluminium sheets (Merck), and visualization was accomplished using UV light or by charring at 150 °C with 10% (v/v) H_3PO_4 in isopropyl alcohol. TLC for water-soluble oligosaccharides were run in the mixture of BPS (^{n}BuOH-^{n}PrOH-HCl-H_2O 1:1:1:1) and AMW (MeCN-MeOH-H_2O1:1:1). Column chromatography was performed on Silica Gel 60 Å, 40–63 μm (Merck). Gel-permeation chromatography of water soluble compounds was carried out on TSK HW-40(S) columns in 0.1 M AcOH using a K-2401 (Knauer) refractometer to monitor the eluate. Optical rotations were measured using JASCO P-2000 polarimeter in solvents specified. NMR spectra were recorded on a Bruker AV-400 and Bruker AV-600 instruments. The spectra of protected carbohydrate derivatives were measured for solutions in $CDCl_3$ or pyridine-d5; ^{1}H NMR chemical shifts were referenced to the corresponding solvent residual signals (δH 7.27 and 8.74 ppm respectively). ^{13}C chemical shifts were referenced to the central resonances of $CDCl_3$ (δC 77.0) or *ortho*-carbons of pyridine-d5 (δC 150.35). NMR spectra of water soluble oligosaccharides were measured for solutions in D_2O using acetonitrile (δH 2.06, δC 1.47 ppm) as the internal standard. To assign NMR spectra for the obtained compounds we performed the following procedure for all monosaccharide rings: first determined H-1 signal by characteristic correlation in ^{1}H-^{13}C-HSQC spectra, then assigned all other hydrogen atoms of carbohydrate ring by ^{1}H-^{1}H-COSY. Ring carbon peaks in ^{13}C-NMR spectra were assigned according to correlations in ^{1}H-^{13}C-HSQC spectra. In the descriptions of the NMR spectra of galactose residues are denoted by Gal, Gal' and Gal" for galactopyranose, (1→2)-galactofuranose and (1→3)-galactofuranose, respectively. The HRMS (ESI) were obtained on a MicrOTOF II (Bruker Daltonics) instrument.

1.2.SYNTHESIS OF PERBEZYLATED PRECURSOR S5 FOR TRIOL ACCEPTOR 12

The direct path to acceptor **12** seemed to be through p-Methoxy tetrabenzyl β-D-galactopyranoside **S3** that was prepared from β-D-galactopyranose pentaacetate **S1** in three steps. First, anomeric acetyl group was substituted for p-methoxyphenyl group[1,2]. Then all other hydroxyl groups were deacetylated by treating with MeONa solution in methanol[1] and benzylated with BnBr. Interestingly, 3-trifluoroacetamidopropyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside **S5** was obtained as an inseparable anomeric mixture whereas 4,6-di-*O*-benzylidene protected analog **11** was formed as pure α-galactoside. Nevertheless we believe that both strategies are interesting in comparison and we publish them both.



***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (S3).**

Sodium hydride (60% suspension in mineral oil, 420 mg, 10.5 mmol) was added to a solution of **S2** (500 mg, 1.75 mmol) in dry DMF (16 mL) at 0 °C under argon atmosphere. The mixture was warmed to room temperature and stirred for 1 h. Then BnBr (1.0 mL, 8.39 mmol) was added at 0 °C, the mixture was stirred at room temperature for 1 h and the reaction was stopped by adding MeOH (0.9 mL) at 0°C. The mixture was diluted with EtOAc and washed with water. The aqueous phase was washed with EtOAc (50 mL) three times, the organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Column chromatography of the residue (petroleum ether:acetone 10:1→6:1) provided colorless oil **S3** (1.1 g,

95%). R_f = 0.18 (petroleum ether:acetone 10:1). $[\alpha]_D^{22}$=+0.14 ($CHCl_3$, 10 mg mL^{-1}). ^{1}H-NMR (600 MHz, $CDCl_3$): δ_H 7.39-7.24 (m, 24H, Ph), 7.03 (d, *J*=9.9 Hz, 2H, Ph(MP)), 6.79 (d, *J*=9.9 Hz, 2H, Ph(MP)), 5.02 (d, *J*=11.7 Hz, 1H, Bn^{1}A), 4.99 (d, *J*=11.7 Hz, 1H, Bn^{2}A), 4.88-4.85 (m, 2H, Bn^{1}B, H-1), 4.79 (d, *J*=12.0 Hz, 1H, Bn^{3}A), 4.75 (d, *J*=12.0 Hz, 1H, Bn^{3}B), 4.66 (d, *J*=12.0 Hz, 1H, Bn^{2}B), 4.46 (d, *J*=12.0 Hz, 1H, Bn^{4}A), 4.41 (d, *J*=12.0 Hz, 1H, Bn^{4}B), 4.10 (dd, $J_{2,3}$=9.7 Hz, $J_{2,1}$=7.8 Hz, 1H, H-2), 3.94 (d, $J_{4,3}$=2.9 Hz, 1H, H-4), 3.76 (s, 3H, CH_3(MP)), 3.66-3.62 (m, 3H, H-5, H-6A, H-6B), 3.61 (dd, $J_{3,4}$=2.9 Hz, $J_{3,2}$=9.7 Hz, 1H, H-3). ^{13}C-NMR (150 MHz, $CDCl_3$): δ_C 155.2, 151.8 (ipso Ph(MP)), 138.5, 138.4, 137.9 (ipso Ph), 128.4, 128.3, 128.2, 128.2, 127.8, 127.7, 127.6, 127.5 (Ph), 118.6 (Ph(MP)), 114.5 (Ph(MP)), 103.1 (C-1), 82.1 (C-3), 79.3 (C-2), 75.3 (Bn^1), 74.5 (Bn^2), 73.7 (C-5), 73.6 (Bn^3), 73.3 (C-4), 73.1 (Bn^4), 68.9 (C-6), 55.6 (CH_3(MP)). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{41}H_{42}O_7$ 669.2823; found 669.2827.

2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranose (S4).

Compound **S3** (59.2 mg, 0.092 mmol) was dissolved in acetonitrile (7 mL), then water (1.8 mL) and benzene (0.5 mL) were added. CAN (250 mg, 0.46 mmol) was added to the mixture at 0 °C and the mixture was stirred for 7 minutes, diluted with EtOAc and washed with saturated solution of $NaHCO_3$. The aqueous phase was washed with EtOAc (20 mL) three times; the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Column chromatography of the residue (petroleum ether:acetone 4:1→3:1) provided **S4** (16.5 mg, 33%) as a yellowish oil. R_f = 0.21 (petroleum ether:acetone 4:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.37-7.20 (m, 20H, Ph), 7.16-7.13 (m, 1.6H, Ph), 5.25 (br t, $J_{1,2}$=$J_{1,OH}$=3.0 Hz, 0.6H, H-1 α), 4.93-4.87 (m, 1.4H, Bn α, Bn β), 4.82-4.76 (m, 1H, Bn α, Bn β), 4.76-4.69 (m, 2.2H, Bn α, Bn α), 4.67-4.64 (m, 0.4H, Bn β), 4.63 (t, $J_{1,2}$=$J_{1,OH}$=7.3 Hz, 0.4H, H-1 β), 4.60-4.53 (m, 1H, Bn α, Bn β), 4.47-4.45 (m, 1H, Bn α, Bn β), 4.40-4.36 (m, 1H, Bn α, Bn β), 4.14 (t, *J*=6.5 Hz, 0.6H, H-5 α), 4.01 (dd, $J_{2,3}$=3.5 Hz, $J_{2,1}$=9.8 Hz, 0.6H, H-2 α), 3.94 (m, 0.6H, H-4 α), 3.88 (dd, $J_{3,4}$=9.6 Hz, $J_{3,2}$=3.5 Hz, 0.6H, H-3 α), 3.86 (m, 0.4H, H-4 β), 3.74 (dd, $J_{2,3}$=9.8 Hz, $J_{2,1}$=7.6 Hz, 0.4H, H-2 β), 3.60-3.54 (m, 2H, H-5 β, H-3), 3.53-3.43 (m, 2H, β, H-6A α, H-6B α), 3.22 (d, $J_{OH,1}$=7.0 Hz, 0.4H, OH β), 2.98 (d, $J_{OH,1}$=3.0 Hz, O.6H, OH α). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 138.5, 129.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (Ph), 97.8 (C-1 β), 91.9 (C-1 α), 82.2 (C-3 β), 80.7 (C-2 β), 78.7 (C-3 α), 76.6 (C-2 α), 75.0 (Bn), 74.7 (C-4 α), 74.6 (3 Bn), 73.6 (C-5 β), 73.5 (Bn, C-4 β), 73.4 (Bn), 72.9 (Bn), 72.9 (Bn), 69.5 (C-5 α), 69.0 (C-6 α), 68.9 (C-6 β). The spectral data matched those reported in the literature[3].

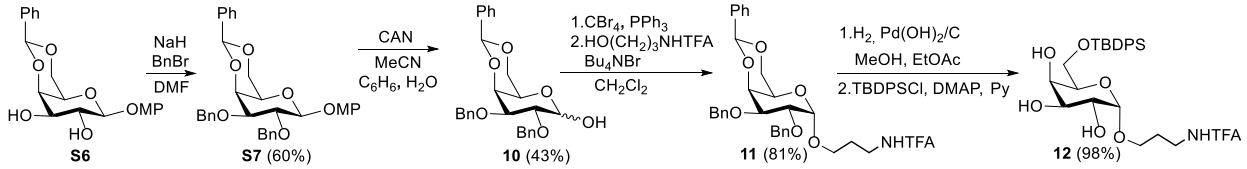
3-Trifluoroacetamidopropyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (S5).

CBr_4 (258 mg, 0.777 mmol) and PPh_3 (204 mg, 0.777 mmol) were added to a solution of **S4** (140 mg, 0.259 mmol) in dry CH_2Cl_2 (2.2 mL). The reaction mixture was stirred for 40 minutes, molecular sieves 4A (180 mg) were added and the mixture was stirred for another 40 minutes. Then 3-trifluoroacetamidopropanol (92 μL, 0.725 mmol) and Bu_4NBr (121 mg, 0.376 mmol) were added. The mixture was stirred overnight, diluted with CH_2Cl_2 and filtered through a layer of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography (toluene:EtOAc 30:1→9:1) to give yellowish oil **S5** (135 mg, 75%) as an inseparable mixture of α- and β-isomers (α:β≈10:1). R_f = 0.40 (toluene:EtOAc 1:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.83 (m, 1H, N*H*TFA), 7.43-7.09 (m, 20H, Ph), 4.94 (d, *J*=11.6 Hz, Bn^{1}A), 4.89-4.71 (m, 4H, Bn^{2}A, Bn^{3}A, Bn^{1}B, H-1), 4.66 (d, *J*=12.1 Hz, 1H, Bn^{2}B), 4.56 (d, *J*=12.1 Hz, 1H, Bn^{3}B), 4.48 (d, *J*=12.1 Hz, 1H, Bn^{4}A), 4.39 (d, *J*=12.1 Hz, 1H, Bn^{4}B), 4.05 (dd, $J_{2,3}$=10.1 Hz, $J_{2,1}$=4.0 Hz, 1H, H-2), 3.98-3.87 (m, 4H, H-4, H-5, OC*H*H'CH_2CH_2N, OCH_2CH_2C*H*H'N), 3.84 (dd, $J_{3,4}$=3.0 Hz, $J_{3,2}$=10.1 Hz, 1H, H-3), 3.54-3.45 (m, 2H, H-6A, H-6B), 3.38 (m, 1H, OCH*H'*CH_2CH_2N), 3.08 (m, 1H, OCH_2CH_2CH*H'*N), 1.82 (m, 2H, OCH_2C*H*$_2CH_2$N). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 138.5, 138.4, 137.8, 129.0, 128.4, 128.4, 128.0, 127.5 (Ph(Bn)), 99.0 (C-1), 79.5 (C-3), 76.2 (C-2), 74.8 (C-4), 74.7 (Bn), 74.5 (C-4), 74.1 (Bn),

73.45 (Bn), 73.0 (Bn), 69.2 (O*C*H_2C*H*$_2$CH$_2$N), 69.0 (C-6), 68.4 (C-6), 39.2 (OCH$_2$CH$_2$*C*H$_2$N), 37.9 (OCH$_2$CH$_2$CH$_2$N), 28.3 (OCH$_2$C*H*$_2$CH$_2$N). The proof of the structure of β-isomer was based on the following signals: 4.43 (d, 0.1H, Bn β), 4.34 (d, $J_{1,2}$-7.6 Hz, 0.1H, H-1 β), 3.80 (m, 0.1H, H-2 β), 3.54 (m, 0.1H, H-3 β) in ^{1}H-NMR spectrum; 104.1 (C-1 β), 82.2 (C-3 β), C-2 β, 75.3 (Bn β), 74.5 (C-4 β), 73.5 (Bn β), 73.3 (C-5 β), 72.4 (Bn β), 68.4 (C-6 β), 37.9 (OCH$_2$CH$_2$CH$_2$N β) in ^{13}C-NMR spectrum.

1.3.SYNTHESIS OF TRIOL ACCEPTOR 12 FROM 4,6-di-*O*-BENZYLIDENE PROTECTED PRECURSOR S6

p-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside **S7** for acceptor **12** was prepared from p-methoxyphenyl β-D-galactopyranoside **S2** in two steps: hydroxyl groups at C-4 and C-6 were protected with benzylidene group[4] and then free hydroxyl groups at O-2 and O-3 were benzylated with BnBr.



***p*-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (S7).**

Sodium hydride (60% suspension in mineral oil, 193 mg, 4.81 mmol) was added to a solution of **S6** (1.2 g, 3.21 mmol) in dry DMF (20 mL) at 0 °C under argon atmosphere. The mixture was warmed up to room temperature and stirred for 1 h. Then BnBr (0.92 mL, 7.70 mmol) was added at 0 °C, the mixture was stirred at room temperature for 20 h and the reaction was stopped by adding MeOH (5.8 mL) at 0 °C. The mixture was diluted with EtOAc and washed with water. The aqueous phase was washed with EtOAc (60 mL) three times; the organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Column chromatography of the residue (toluene:EtOAc 30:1→15:1) provided **S7** (1.1 g, 60%) as a white foam. R_f = 0.20 (toluene:EtOAc 15:1). $[\alpha]_D^{22}$= –10.7 ($CHCl_3$, 10 mg mL^{-1}). ^{1}H-NMR (600 MHz, $CDCl_3$): δ_H 7.58-7.54 (m, 2H, Ph), 7.39-7.23 (m, 13H, Ph), 7.05 (d, *J*=9.1 Hz, 2H, Ph(MP)), 6.80 (d, *J*=9.1 Hz, 2H, Ph(MP)), 5.50 (s, 1H, C*H*Ph), 4.98 (d, 1H, Bn^{1}A), 4.87-4.84 (m, 2H, Bn^{1}B, H-1), 4.78 (d, *J*=12.2 Hz, 1H, Bn^{2}A), 4.75 (d, *J*=12.2 Hz, 1H, Bn^{2}B), 4.30 (dd, $J_{6A,6B}$=12.3 Hz, $J_{6A,5}$=1.4Hz, 1H, H-6A), 4.14 (d, *J*=3.47 Hz, 1H, H-4), 4.08 (dd, $J_{2,3}$=9.7 Hz, $J_{2,1}$=7.8 Hz, 1H, H-2), 4.00 (dd, $J_{6B,6A}$=12.3, $J_{6B,5}$=1.7 Hz, 1H, H-6B), 3.75 (s, 3H, CH_3(MP)), 3.61 (dd, $J_{3,4}$=3.6 Hz, $J_{3,2}$=9.7 Hz, 1H, H-3), 3.36 (br s, 1H, H-5). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 155.4 (ipso Ph (MP)), 151.7 (ipso Ph (MP)), 138.5, 138.8, 137.8 (ipso Ph), 128.9, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.5, 126.5 (Ph(Bn)), 119.0 (Ph(MP)), 114.4 (Ph(MP)), 103.2 (C-1), 101.3 (*C*HPh), 79.3 (C-3), 78.1 (C-2), 75.5 (*C*H_2Ph), 73.8 (C-4), 72.1 (*C*H_2Ph), 69.2 (C-6), 66.6 (C-5), 55.7 (*C*H_3(MP)). HRMS (ESI): calcd *m/z* for [M+Na]$^+$ for $C_{34}H_{34}O_7$ 577.2197; found 577.2020.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranose (10).

Compound **S7** (1.0 g, 1.80 mmol) was dissolved in acetonitrile (100 mL), then water (26 mL) and benzene (7.6 mL) were added. CAN (4.9 g, 9.00 mmol) was added to the mixture at 0 °C and the mixture was stirred for 9 minutes until TLC showed disappearance of the starting material, then it was diluted with EtOAc and washed with saturated solution of $NaHCO_3$. The aqueous phase was washed with EtOAc (250 ml) three times, the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Column chromatography of the residue (toluene:MTBE 8:1→3:1) provided brownish oil **10** (350 mg, 43%) as a mixture of α and β isomers in ratio 4:1. R_f = 0.2 (toluene:EtOAc 3:1). ^{1}H-NMR (600 MHz, $CDCl_3$): δ_H 7.56-7.50 (m, 2H, Ph), 7.42-7.23 (m, 13H, Ph), 5.48 (s, 0.15H, C*H*Ph β), 5.47 (s, 0.85H, C*H*Ph α), 5.35 (d, $J_{1,2}$=3.4 Hz, 0.85H, H-1 α), 4.90-4.81 (m, 1.15H, Bn α,Bn β, Bn β), 4.81-4.72 (m, 2H, Bn α, Bn α, Bn β, Bn β), 4.69 (d,

0.85H, Bn α), 4.65 (br t, 0.15H, H-1 β), 4.28 (m, 1H, H-6A β), 4.21 (m, 0.85H, H-6A α), 4.18 (d, $J4_{,3}$=3.8 Hz, 0.85H, H-4 α), 4.10 (d, J=4.1 Hz, 1H, H-4 β), 4.04 (dd, $J_{2,3}$=9.8 Hz, $J_{2,1}$=3.4 Hz, 1H, H-2 α), 4.00-3.94 (m, 1.7H, H-3 α, H-6B α), 3.81 (br s, 1H, H-5 α), 3.76 (dd, $J_{2,3}$=9.6 Hz, $J_{2,1}$= 7.7 Hz, 1H, H-2 β), 3.56 (dd, $J_{3,4}$=3.6 Hz, $J_{3,2}$=9.6Hz, 1H, H-3 β), 3.36 (b s, 0.5H, OH β), 3.32 (s, 0.15H, H-5 β), 3.04 (br s, 0.67H, OH α). ^{13}C-NMR (150 MHz, $CDCl_3$): δ_C 138.5, 138.2, 137.8 (ipso Ph), 128.9, 128.8, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 126.3, 126.3 (Ph), 101.1 (*C*HPh β), 101.0 (*C*HPh α), 97.5 (C-1 β), 92.3 (C-1 α), 79.8 (C-2 β), 79.3 (C-3 β), 75.7 (C-2, C-3 α), 75.1 (CH_2Ph β), 74.2 (C-4 α), 73.8 (CH_2Ph α), 73.7 (C-4 β), 71.8 (CH_2Ph β), 71.7 (CH_2Ph α), 69.4 (C-6 β), 69.2 (C-6 α), 66.7 (C-5 β), 62.7 (C-5 α). The spectral data matched those reported in the literature.[5]

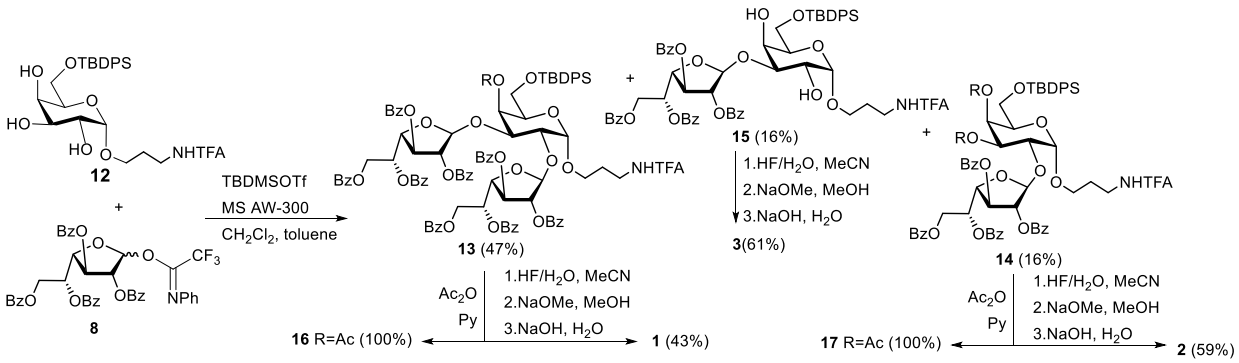
3-Trifluoroacetamidopropyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (11).

CBr_4 (774 mg, 2.33 mmol) and PPh_3 (612 mg, 2.33 mmol) were added to a solution of **10** (350 mg, 0.778 mmol) in dry CH_2Cl_2 (5.8 mL). The reaction mixture was stirred for 1.5 h, molecular sieves 4A (580 mg) were added and the mixture was stirred for another 1.5 h. Then 3-trifluoroacetamidopropanol (275 μL, 2.18 mmol) and Bu_4NBr (363 mg, 1.13 mmol) were added. The mixture was stirred overnight, diluted with CH_2Cl_2 and filtered through a layer of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography (petroleum ether:EtOAc 10:1→1.5:1) to give **11** (379 mg, 81%) as a yellowish oil. R_f = 0.24 (petroleum ether:EtOAc 1:1). $[\alpha]_D^{22}$=+101 ($CHCl_3$, 10 mg mL^{-1}). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.77 (br s, 0.77H, N*H*TFA), 7.46-7.43 (m, 2H, Ph), 7.37-7.17 (m, 13H, Ph), 5.39 (s, 1H, C*H*Ph), 4.82 (d, J=11.9 Hz, 1H, Bn^{1}A), 4.75 (d, $J_{1,2}$=3.8 Hz, 1H, H-1), 4.72 (d, J=12.0 Hz, 1H, Bn^{2}A), 4.63 (d, J=12.0 Hz, 1H, Bn^{2}B), 4.57 (d, J=11.9 Hz, 1H, Bn^{1}B), 4.15-4.10 (m, 2H, H-4, H-6A), 3.98 (dd, $J_{2,3}$=10.0 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 3.92 (dd, $J_{6B,6A}$=12.5, $J_{6B,5}$=1.0 Hz, 1H, H-6B), 3.87 (m, 1H, OC*H*'CH_2CH_2N), 3.82 (dd, $J_{3,4}$=3.5 Hz, $J_{3,2}$=10.0 Hz, 1H, H-3), 3.76 (m, 1H, OCH_2CH_2CH'N), 3.52 (br s, 1H, H-5), 3.32 (m, 1H, OCH*H*'CH_2CH_2N), 3.00 (m, 1H, OCH_2CH_2CH*H*'N), 1.73 (m, 2H, $OCH_2CH_2CH_2$N). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 138.6, 138.2, 137.7 (ipso Ph), 128.9, 128.4, 128.3, 128.1, 128.1, 128.0, 127.7, 127.6, 126.2 (Ph(Bn)), 101.1 (*C*HPh), 99.6 (C-1), 76.7 (C-3), 75.2 (C-2), 74.4 (Bn_1), 74.1 (C-4), 72.0 (Bn_2), 69.6 ($OCH_2CH_2CH_2$N), 69.3 (C-6), 62.8 (C-5), 39.2 ($OCH_2CH_2CH_2$N), 28.2 ($OCH_2CH_2CH_2$N). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{32}H_{34}F_3NO_7$ 624.2180; found 624.2185.

3-Trifluoroacetamidopropyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (12).

$Pd(OH)_2$/C (20 wt %, 50 mg) was added to a solution of **11** (258 mg, 0.430 mmol) in MeOH (2.0 mL) and EtOAc (0.3 mL). The reaction mixture was intensively stirred overnight under hydrogen atmosphere. Then the mixture was diluted with MeOH, the catalyst was filtered off and the filtrate was concentrated in vacuum to give tetraol **12a** as a white foam. TBDPSCl (175 mg, 0.636 mmol) and DMAP (10 mg) were added to a solution of **12a** (141 mg, 0.424 mmol) in dry pyridine (1.3 mL) under argon atmosphere and the mixture was stirred for 24 h. Then the mixture was diluted with EtOAc and washed with saturated solution of $NaHCO_3$. The aqueous layer was washed with EtOAc (15 mL) three times; the organic extracts were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Column chromatography of the residue ($CHCl_3$:MeOH 12:1→10:1) gave **12** (237 mg, 98%) as a white foam. R_f = 0.52 ($CHCl_3$:MeOH 6:1). $[\alpha]_D^{23}$=+59.9 ($CHCl_3$, 10 mg mL^{-1}). ^{1}H-NMR (400 MHz, Py-d_5): δ_H 7.93-7.90 (m, 4H, Ph), 7.48-7.42 (m, 6H, Ph), 6.74 (br s, OH), 6.04 (br s, OH), 5.29 (d, $J_{1,2}$=3.8 Hz, 1H, H-1), 4.63 (dd, $J_{2,3}$=9.8 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 4.55 (br s, 1H, H-4), 4.51-4.42 (m, 2H, H-3, H-6A), 4.39-4.32 (m, 2H, H-5, H-6B), 4.04 (m, 1H, OC*H*H'CH_2CH_2N), 3.78 (m, 1H, OCH_2CH_2CH*H*'N), 3.69-3.59 (m, 2H, OCH*H*'CH_2CH_2N, OCH_2CH_2CH*H*'N), 2.01 (m, 2H, $OCH_2CH_2CH_2$N), 1.14 (s, 9H, CH_3(^{t}Bu)). ^{13}C-NMR (100 MHz, Py-d_5): δ_C 136.5, 130.6, 128.7 (Ph), 101.2 (C-1), 73.0 (C-5), 71.9 (C-3), 70.8 (C-4), 70.6 (C-2), 66.7 ($OCH_2CH_2CH_2$N), 64.9 (C-6), 38.5 ($OCH_2CH_2CH_2$N), 29.7 ($OCH_2CH_2CH_2$N), 27.4 (CH_3(^{t}Bu)). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{27}H_{36}F_3NO_7Si$ 594.2105; found 594.2100.

1.4. GLYCOSYLATION REACTIONS AND DEPROTECTION OF DI- AND TRISACCHARIDES



3-Trifluoroacetamidopropyl 2,3-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-D-glalactofuranosyl)-6-*O*-*tert*-butyldiphenylsilyl-α-D-glalactopyranoside (13), 3-trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (14) and 3-trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (15).

Molecular sieves AW-300 (85 mg) were added to a solution of donor **8** (26.0 mg, 0.034 mmol) and acceptor **12** (48.6 mg, 0.085 mmol) in dry toluene (1.0 mL) and CH_2Cl_2 (0.5 mL) under argon atmosphere at –20 °C. The mixture was stirred for 10 minutes and TBDMSOTf (8 μL, 0.034 mmol) was added. In 9 minutes a solution of donor **8** (13 mg, 0.017 mmol) in dry CH_2Cl_2 (0.1 mL) was added to the reaction mixture and the reaction was quenched with Et_3N (10 μL) in another 10 minutes. The mixture was warmed slowly to room temperature, diluted with CH_2Cl_2 and filtered through the layer of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography (toluene:EtOAc 30:1→1:1) to give trisaccharide **13** (20.9 mg, 47%), 1-2-linked disaccharide **14** (9.5 mg, 16%) and 1-3-linked disaccharide **15** (9.5 mg, 16%).

Data for trisaccharide **13**. Colorless oil. R_f = 0.23 (toluene:EtOAc 15:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07-7.89 (m, 8H, Ph), 7.96-7.91 (d, 4H, Ph), 7.79-7.65 (m, 9H, Ph), 7.59-7.27 (m, 22, Ph), 7.26-7.11 (m, 8H, Ph, N*H*TFA), 6.08 (m, 1H, H-5”). 6.04 (m, 1H, H-5’), 5.80 (s, 1H, H-1’ or H-1”), 5.68 (d, 1H, $J_{3,2}$= 4.1 Hz, H-3), 5.67-5.60 (m, 3H, H-3”, H-1”or H-1’, H-2” or H-2’), 5.50 (s, 1H, H-2’ or H-2”), 5.01 (d, $J_{1,2}$=4.2 Hz, 1H, H-1), 4.84-4.70 (m, 4H, H-6A’, H-6B’, H-6A”, H-6B”), 4.69-4.64 (m, 2H, H-4’, H-4”), 4.24 (dd, $J_{2,3}$=9.3 Hz, $J_{2,1}$=4.2 Hz, 1H, H-2), 4.15-4.10 (m, 2H, H-3, H-4), 3.91-3.79 (m, 4H, H-6A, H-5, H-6B, OC*H*H’CH_2CH_2N), 3.50 (m, 1H, OCH_2CH_2C*H*H’N), 3.37 (m, 1H, OCH*H’*CH_2CH_2N), 3.06 (m, 1H, OCH_2CH_2CH*H’*N), 2.66 (br s, 1H, OH), 1.67 (m, 2H, OCH_2CH_2CH_2N), 1.04 (s, 9H, CH_3(^{t}Bu)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 166.6, 166.2, 166.1, 165.9 (*C*=O (Ac)), 135.6, 135.5 (*ipso* Ph), 132.2, 136.1, 134.2, 134.1, 133.9, 133.7, 133.7, 133.0 (*ipso* Bz), 130.4, 130.4, 130.3, 130.2, 129.1, 129.1,129.0,128.9, 128.8, 128.7, 128.5, 128.4, 128.3 (Ph), 107.8, 107.4 (C-1’ and C-1”), 98.7 (C-1), 82.9 (C-4’ or C-4”), 82.8 (C-2”), 82.7 (C-2’), 81.4 (C-4” or C-4’), 77.9 (C-3”), 77.6 (C-3’), 75.5 (C-3), 74.8 (C-2), 70.4 (C-5’, C-5”), 70.1 (C-4, C-5), 67.4 (O$CH_2CH_2CH_2$N), 63.6 (C-6), 63.4, 63.2 (C-6’ and C-6”), 38.7 ($OCH_2CH_2CH_2$N), 28.3 ($OCH_2CH_2CH_2$N), 26.9 (CH_3(^{t}Bu)). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{95}H_{88}F_3NO_{25}Si$ 1750.5259; found 1750.5264.

Data for 1-2-linked disaccharide **14**. Colorless oil. R_f = 0.20 (toluene:EtOAc 4:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.06-7.89 (m, 9H, Ph), 7.73-7.65 (m, 4H, Ph), 7.59-7.49 (m, 5H, Ph, N*H*TFA), 7.48-7.29 (m, 17H, Ph), 5.95 (m, 1H, H-5’), 5.78 (dd, $J_{3,4}$=3.0 Hz, $J_{3,2}$=6.4 Hz, 1H, H-3’), 5.47 (br s, 1H, H-1’), 5.43 (m, 1H, H-2’), 4.99 (s, 1H, H-1), 4.80 (dd, $J_{6A,6B}$=12.7 Hz, $J_{6A,5}$=5.0 Hz, 1H, H-6A’), 4.72-4.66 (m, 2H, H-4’, H-6B’), 4.17 (s, 1H, H-4), 3.97 (s, 2H, H-

2, H-3), 3.95-3.74 (m, 4H, H-6A, H-6B, OC*H*H'CH_2CH_2N, H-5), 3.64 (m, 1H, OCH_2CH_2CHH'N), 3.38 (m, 1H, OCH*H'*CH_2CH_2N), 3.13 (m, 1H, OCH_2CH_2CH*H'*N), 2.67 (m, 0.9H, OH), 1.74 (m, 2H, $OCH_2CH_2CH_2$N), 1.06 (s, 9H, $CH_3(^tBu)$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 166.9, 166.2 (ipso Ph), 136.2, 136.1, 134.0, 133.9 (Ph), 130.6, 130.4, 130.3, 129.1, 129.0, 128.3 (Ph), 109.0 (C-1'), 98.6 (C-1), 83.6 (C-2'), 80.5 (C-4'), 78.4 (C-3), 76.4 (C-3'), 70.5 (C-5'), 70.4 (C-5), 69.2 (C-2, C-4), 68.0 ($OCH_2CH_2CH_2$N), 63.3 (C-6), 63.1 (C-6'), 39.1 ($OCH_2CH_2CH_2$N), 28.4 ($OCH_2CH_2CH_2$N), 26.8 ($CH_3(^tBu)$). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{61}H_{62}F_3NO_{16}Si$ 1172.3682; found 1172.3686.

Data for 1-3-linked disaccharide **15**. Colorless oil. R_f = 0.20 (toluene:EtOAc 8:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.06 (d, 2H, Ph), 8.02 (d, 2H, Ph), 7.97 (d, 2H, Ph), 7.94-7.87 (m, 3H, Ph, N*H*TFA), 7.72-7.66 (m, 5H, Ph), 7.59-7.28 (m, 17H, Ph), 5.94 (m, 1H, H-5"), 5.77 (dd, $J_{3,4}$=6.3 Hz, $J_{3,2}$=2.9 Hz, 1H, H-3"), 5.55 (s, 1H, H-1"), 5.53 (d, $J_{2,3}$=2.9 Hz, 1H, H-2"), 4.99 (d, $J_{1,2}$=3.8 Hz, 1H, H-1), 4.83 (dd, $J_{4,5}$=3.5 Hz, $J_{4,3}$=6.3 Hz, 1H, H-4"), 4.79-4.68 (m, 2H, H-6A", H-6B"), 4.23 (dd, $J_{2,3}$=10.0 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 4.20 (m, 1H, H-4), 4.00-3.73 (m, 6H, H-3, H-5, H-6A, H-6B, OC*H*H'CH_2CH_2N, OCH_2CH_2CHH'N), 3.49 (m, 1H, OCH*H'*CH_2CH_2N), 3.24 (m, 1H, OCH_2CH_2CH*H'*N), 2.89 (br s, 1H, OH), 1.84 (m, 2H, $OCH_2CH_2CH_2$N), 1.05 (s, 9H, $CH_3(^tBu)$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 166.5, 165.9, 165.5, 165.4 (ipso Ph), (Ph), 135.5, 135.4 (*ipso* (Ph)), 133.6, 133.5, 133.3, 133.0, 132.8 (*ipso* (Bz)), 129.8, 129.8, 127.7, 129.6, 129.3, 129.1, 128.6, 128.4, 128.3, 128.3, 128.2, 127.6, 127.6, 127.5 (Ph), 108.2 (C-1"), 98.8 (C-1), 83.5 (C-2"), 80.5 (C-4"), 79.5 (C-3), 76.6 (C-3"), 70.2 (C-5), 69.9 (C-4, C-5"), 68.4 ($OCH_2CH_2CH_2$N), 67.8 (C-2), 63.7 (C-6), 62.9 (C-6"), 39.1 ($OCH_2CH_2CH_2$N), 28.0 ($OCH_2CH_2CH_2$N), 26.6 ($CH_3(^tBu)$). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{61}H_{62}F_3NO_{16}Si$ 1172.3682; found 1172.3688.

3-Trifluoroacetamidopropyl 2,3-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-D-glalactofuranosyl)-4-O-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glalactopyranoside (16).

Trisaccharide **13** (10.0 mg, 0.006 mmol) was dissolved in the mixture of acetic anhydride (1.2 ml) and pyridine (1.2 ml) and left overnight. Then the reaction mixture was diluted with toluene and the solvents were removed in vacuum. After the residue was dried in vacuum acetylated disaccharide **16** (10.2 mg, 100%) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.11-7.90 (m, 12H, Ph), 7.79 (d, 2H, Ph), 7.69-7.27 (m, 31H, Ph), 7.24-7.13 (m, 9H, Ph), 7.12-7.03 (m, 1H, N*H*TFA), 6.18 (m, 1H, H-5'), 6.11 (m, 1H, H-5"), 5.69 (s, 1H, H-1" or H-1'), 5.66-5.60 (m, 2H, H-1' or H-1", H-3"), 5.58 (s, 1H, H-2' or H-2"), 5.53 (d, $J_{4,3}$=3.3 Hz, 1H, H-4), 5.44 (d, $J_{3,4}$=5.2 Hz, 1H, H-3'), 5.39 (s, 1H, H-2" or H-2'), 5.03-4.99 (m, 1H, H-1, H-4'), 4.88 (dd, $J_{6A,5}$=7.0 Hz, $J_{6A,6B}$=12.3 Hz, 1H, H-6A'), 4.83 (dd, $J_{6A,5}$=5.5 Hz, $J_{6A,6B}$=12.0 Hz, 1H, H-6A"), 4.75 (dd, $J_{6B,5}$=5.5 Hz, $J_{6B,6A}$=12.0 Hz, 1H, H-6B"), 4.69 (dd, $J_{6B,5}$=7.0 Hz, $J_{6B,6A}$=12.3 Hz, 1H, H-6B'), 4.63 (m, 1H, H-4"), 4.20 (dd, $J_{3,4}$=3.3 Hz, $J_{3,2}$ = 10,1 Hz, 1H, H-3), 4.11 (dd, $J_{2,3}$=10.1 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 3.97 (t, *J*=6.2 Hz, 1H, H-5), 3.78 (m, 1H, OC*H*H'CH_2CH_2N), 3.69-3.54 (m, 2H, H-6A, H-6B), 3.44 (m, 1H, OCH_2CH_2CHH'N), 3.34 (m, 1H, OCH*H'*CH_2CH_2N), 3.03 (m, 1H, OCH_2CH_2CH*H'*N), 1.75 (s, 3H, CH_3(Ac)), 1.70 (m, 2H, $OCH_2CH_2CH_2$N), 1.03 (s, 9H, $CH_3(^tBu)$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 169.5 (*C*=O (Ac)), 166.3, 166.1, 166.0, 165.7, 165.6, 165.4, 165.1 (*C*=O (Bz)), 135.4, 135.4 (*ipso* Ph), 133.4, 133.1, 133.1, 133.0, 132.9, 132.8, 132.7, 129.9, 129.8, 129.7, 126.6, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.6, 127.5 (Ph), 107.7, 107.6 (C-1', C-1"), 98.6 (C-1), 82.1 (C-2" or C-2'), 82.0 (C-4'), 81.8 (C-4" and C-2' or C-2"), 75.5 (C-3'), 77.9 (C-3"), 75.2 (C-2), 73.2 (C-3), 70.31 (C-5' and C-5"), 70.25 (C-4), 69.9 (C-5), 67.1 ($OCH_2CH_2CH_2$N), 63.9 (C-6'), 63.2 (C-6"), 62.2 (C-6), 38.4 ($OCH_2CH_2CH_2$N), 28.3 ($OCH_2CH_2CH_2$N), 26.6 ($CH_3(^tBu)$), 20.4 (CH_3(Ac)).

3-trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→2)-3,4-di-O-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranoside (17).

Disaccharide **14** (5.0 mg, 0.004 mmol) was dissolved in the mixture of acetic anhydride (1 mL) and pyridine (1 mL) and left overnight. Then the reaction mixture was diluted with toluene and the solvents were removed in vacuum. After the residue was dried in vacuum acetylated disaccharide **17** (4.0 mg, 100%) was obtained. ^{1}H-

NMR (400 MHz, $CDCl_3$): δ_H 8.06 (d, 2H, Ph), 7.99 (d, 2H, Ph), 7.93 (d, 2H, Ph), 7.86 (d, 2H, Ph), 7.66-7.28 (m, 22H, Ph), 6.07 (m, 1H, H-5'), 5.65 (m, 1H, H-3'), 5.56 (d, $J_{4,3}$=3.4 Hz, 1H, H-4), 5.44-5.40 (m, 2H, H-1', H-2'), 5.30 (dd, $J_{3,4}$=3.4 Hz, $J_{3,2}$=11.0 Hz, 1H, H-3), 4.99 (d, $J_{1,2}$=3.8 Hz, 1H, H-1), 4.83-4.72 (m, 2H, H-6A', H-6B'), 4.65 (m, 1H, H-4'), 4.06 (dd, $J_{2,3}$=11.0 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 3.99 (t, J=7.0Hz, 1H, H-5), 3.77 (m, 1H, OC*H*H'CH_2CH_2N), 3.70-3.58 (m, 2H, H-6), 3.50 (m, 1H, OCH_2CH_2CHH'N), 3.34 (m, 1H, OCH*H'*CH_2CH_2N), 3.04 (m, 1H, OCH_2CH_2CH*H'*N), 2.04 (s, 3H, CH_3(Ac)), 1.98 (s, 3H, CH_3(Ac)), 1.67 (m, 2H, $OCH_2CH_2CH_2N$), 1.02 (s, 9H, $CH_3(^tBu)$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 169.9, 169.8 (*C*=O (Ac)), 166.1, 165.6, 165.6, 165.0 (*C*=O (Bz)), 135.4 (ipso Ph), 133.6, 133.3, 133.1, 132.9, 132.7 (ipso Bz), 129.8, 129.7, 129.6, 129.5, 129.3, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 127.6, 127.6 (Ph), 107.4 (C-1'), 98.5 (C-1), 81.8 (C-2'), 81.4 (C-4'), 77.4 (C-3'), 73.0 (C-2), 70.3 (C-5'), 69.1 (C-3), 69.0 (C-5), 68.2 (C-4), 67.4 ($OCH_2CH_2CH_2N$), 63.2 (C-6'), 61.5 (C-6), 38.3 ($OCH_2CH_2CH_2N$), 28.5 ($OCH_2CH_2CH_2N$), 26.5 ($CH_3(^tBu)$), 20.5 (CH_3(Ac)). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{65}H_{66}F_3NO_{18}Si$ 1256.3893; found 1256.3930

3-Aminopropyl β-D-glalactofuranosyl-(1→2)-α-D-glalactopyranoside (2). Disaccharide **14** (16.0 mg, 0.014 mmol) was placed into a plastic flask, dissolved in acetonitrile (0.7 mL) and cooled to –20 °C. Then 40% aqueous HF (160 μL) was added dropwise until the solution became cloudy. The mixture was slowly warmed to room temperature and intensively stirred overnight. The reaction was diluted with EtOAc and washed with water. The organic phase was washed with saturated solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc, the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The dry residue was dissolved in dry MeOH (0.4 mL) and dry CH_2Cl_2 (0.1 mL) and 1M methanolic MeONa (2 μl, 0.0018 mmol) was added to the solution under argon atmosphere. The mixture was stirred overnight. Then CH_2Cl_2 was evaporated and water (200 μL) and 5M water solution of NaOH (200 μL) were added to the reaction mixture and stirring was continued for 2 h. The solvents were removed in vacuum and the residue was subjected to gel-permeation chromatography on the TSK HW-40(S) column; fractions containing the pure product were combined and freeze-dried to give disaccharide **2** (3.3 mg, 59%) as a fluffy solid. R_f = 0.2 (BPS:AMW=1:1). ^{1}H-NMR (600 MHz, D_2O, 303K): δ_H 5.12 (d, $J_{1,2}$=1.5Hz, 1H, H-1'), 5.05 (d, $J_{1,2}$=3.9 Hz, 1H, H-1), 4.12 (m, 1H, H-2'), 4.06 (m, 1H, H-3'), 3.97 (m, 1H, H-4), 3.94 (m, 1H, H-4'), 3.93-3.85 (m, 3H, H-3, H-5, OC*H*H'CH_2CH_2N), 3.82-3.78 (m, 2H, H-2, H-5'), 3.76-3.62 (m, 4H, H-6A, H-6B, H-6A', H-6B'), 3.59 (m, 1H, OCH*H'*CH_2CH_2N), 3.12 (m, 2H, $OCH_2CH_2CH_2N$), 2.00 (m, 2H, $OCH_2CH_2CH_2N$). ^{13}C-NMR (150 MHz, D_2O): δ_C 109.7 (C-1'), 98.6 (C-1), 83.3 (C-4'), 81.6 (C-2'), 76.8 (C-3'), 76.6 (C-2), 71.7 (C-5), 71.5 (C-5'), 70.1 (C-4), 68.9 (C-3), 66.5 ($OCH_2CH_2CH_2N$), 62.8 (C-6'), 61.5 (C-6), 38.4 ($OCH_2CH_2CH_2N$), 26.9 ($OCH_2CH_2CH_2N$). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{15}H_{29}NO_{11}$ 422.1633; found 422.1638.

3-Aminopropyl β-D-glalactofuranosyl-(1→3)-α-D-glalactopyranoside (3). Protecting groups of disaccharide **15** (28.6 mg, 0.025 mmol) were removed according to the procedure described for compound **2**. Disaccharide **3** was purified by gel-permeation chromatography on the TSK HW-40(S) column and isolated as a fluffy solid (3.4 mg, 61%). R_f = 0.2 (BPS:AMW 1:1). ^{1}H-NMR (600 MHz, D_2O): δ_H 5.19 (s, 1H, H-1"), 4.98 (d, $J_{1,2}$=3.5 Hz, 1H, H-1), 4.18 (m, 1H, H-2"), 4.11 (m, 1H, H-4), 4.08-4.01 (m, 2H, H-3", H-4"), 3.98-3.87 (m, 4H, H-2, H-3, H-5 OC*H*H'CH_2CH_2N), 3.83 (m, 1H, H-5"), 3.77-3.59 (m, 5H, H-6A, H-6B, H-6A", H-6B", OCH*H'*CH_2CH_2N), 3.16 (m, 2H, $OCH_2CH_2CH_2N$), 2.01 (m, 2H, $OCH_2CH_2CH_2N$). ^{13}C-NMR (150 MHz, D_2O): δ_C 109.5 (C-1"), 98.8 (C-1), 83.2 (C-4"), 81.8 (C-2"), 77.8 (C-3), 77.2 (C-3"), 71.3 (C-5), 71.1 (C-5"), 69.7 (C-4), 67.6 (C-2), 66.1 ($OCH_2CH_2CH_2N$), 63.1 (C-6"), 61.6 (C-6), 38.1 ($OCH_2CH_2CH_2N$), 27.0 ($OCH_2CH_2CH_2N$). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{15}H_{29}NO_{11}$ 422.1633; found 422.1635.

3-Aminopropyl 2,3-di-*O*-β-D-galactofuranosyl-α-D-galactopyranoside (1).

Protecting groups of trisaccharide **13** (80.0 mg, 0.046 mmol) were removed according to the procedure described for compound **2**. Trisaccharide **1** was purified by gel-permeation chromatography on the TSK HW-40(S) column and isolated as a fluffy solid (11 mg, 43%). R_f = 0.2 (BPS:AMW 1:1). ^{1}H-NMR (400 MHz, D_2O): δ_H 5.19 (s, 1H, H-1”), 5.15 (s, 1H, H-1’), 5.05 (d, $J_{1,2}$=3.6 Hz, H-1), 4.15 (m, 1H, H-2”), 4.12 (m, 1H, H-2’), 4.09 (m, 1H, H-4), 4.08-4.00 (m, 3H, H-3’, H-3”, H-4”), 4.00-3.87 (m, 5H, H-3, H-2, H-4’, H-5, OC*H*H’CH_2CH_2N), 3.84-3.80 (m, 2H, H-5’, H-5”), 3.76-3.56 (m, 7H, OCH*H*’CH_2CH_2N, H-6A, H-6B, H-6A’, H-6B’, H-6A”, H-6”), 3.21-3.07 (m, 2H, $OCH_2CH_2CH_2$N), 1.99 (m, 2H, $OCH_2CH_2CH_2$N). ^{13}C-NMR (100 MHz, D_2O): δ_C 109.8 (C-1’), 109.4 (C-1”), 98.6 (C-1), 83.7 (C-4’), 83.5 (C-4”), 82.0 (C-2”), 81.9 (C-2’), 77.6 (C-3”), 77.3 (C-3’), 76.2 (C-3), 75.5 (C-2), 77.3 (C-5’ or C-5”), 71.3 (C-5), 71.2 (C-5’ or C-5”), 70.0 (C-4), 66.6 ($OCH_2CH_2CH_2$N), 63.2 (C-6’ or C-6”), 63.0 (C-6’ or C-6”), 61.7 (C-6), 38.5 ($OCH_2CH_2CH_2$N), 27.1 ($OCH_2CH_2CH_2$N). HRMS (ESI): calcd *m/z* for $[M+Na]^+$ for $C_{21}H_{39}NO_{16}$ 584.2161; found 584.2161.

1.5. REFERENCES

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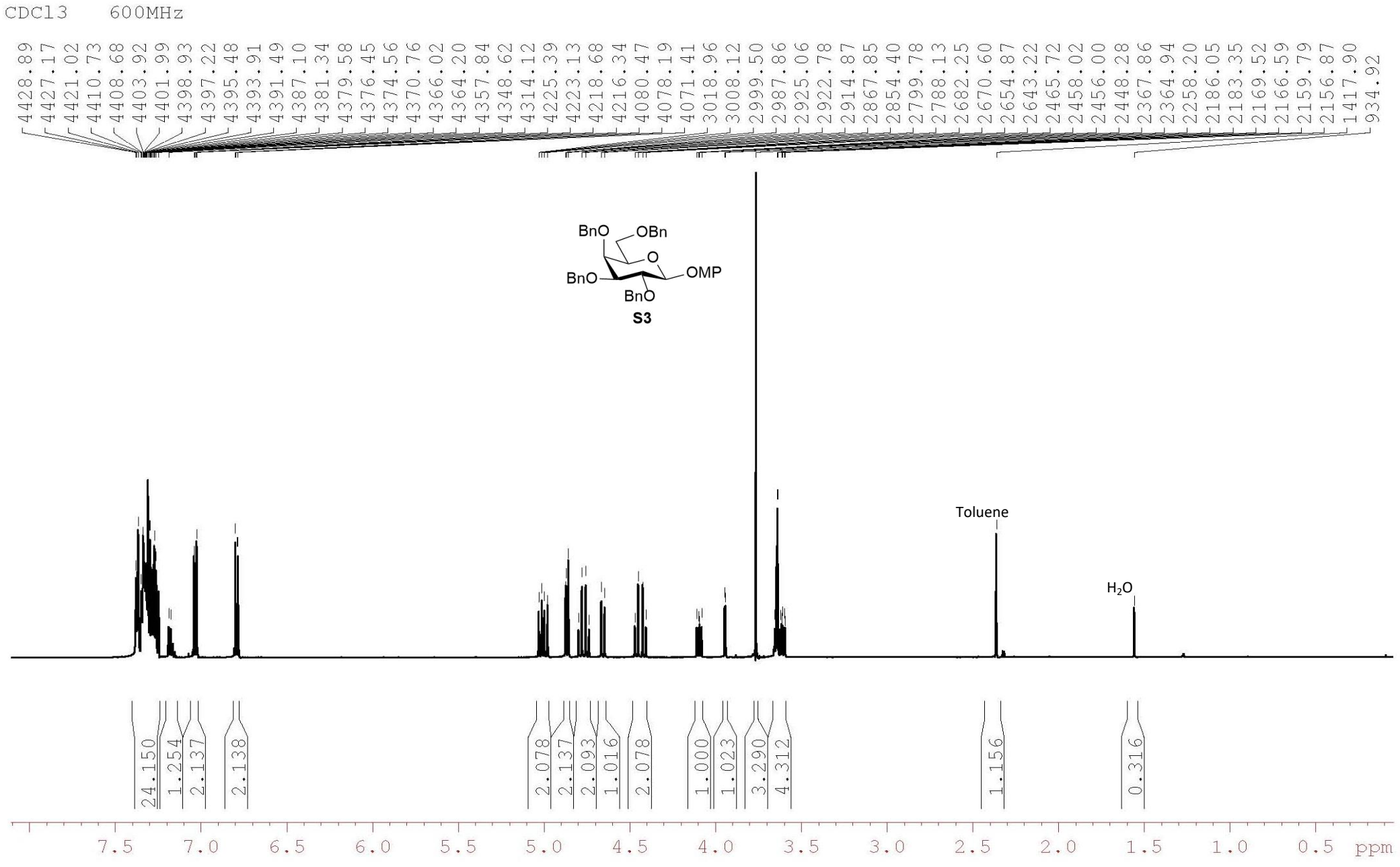
^{1}H-NMR spectrum of **S3**



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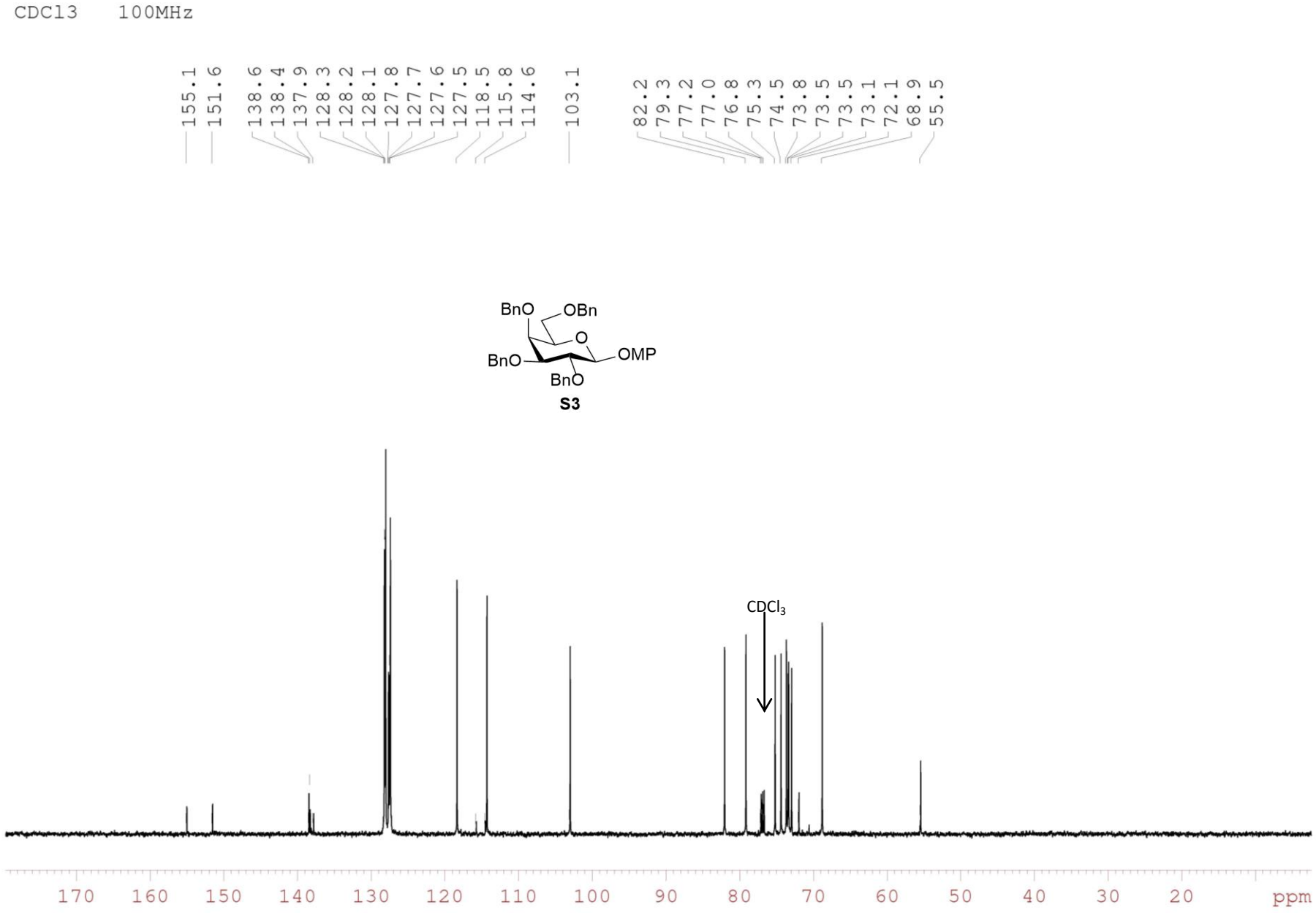

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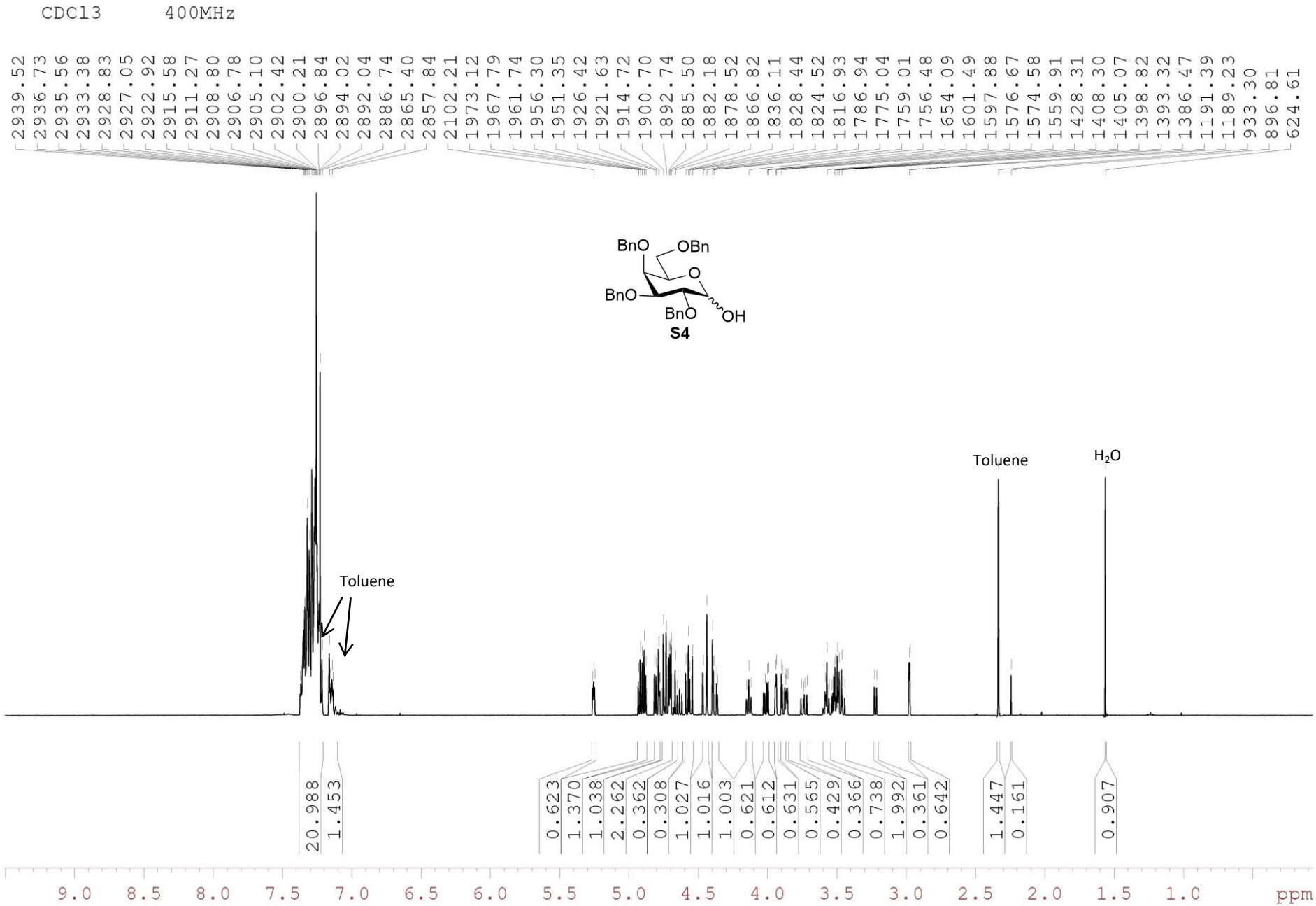

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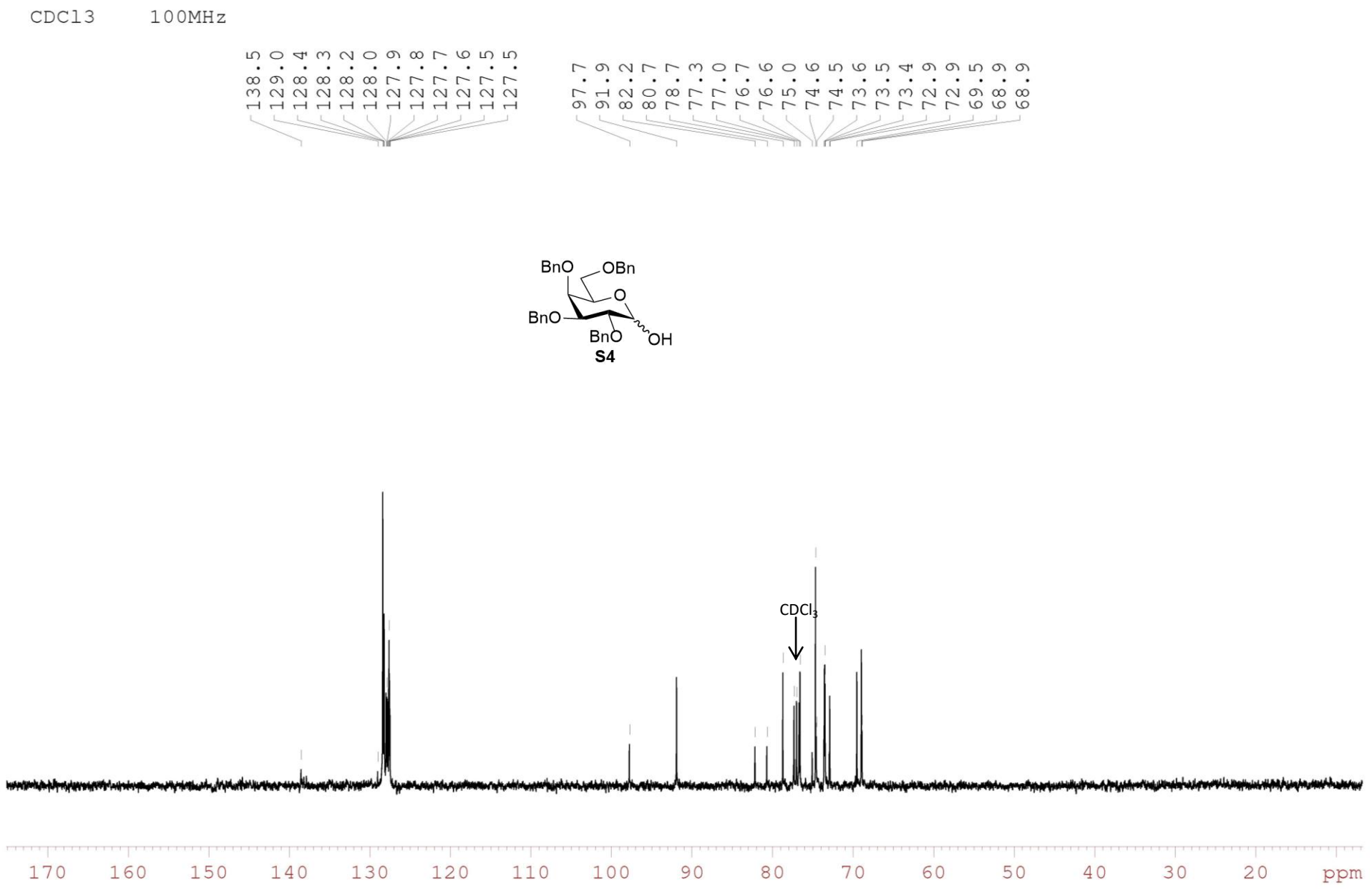

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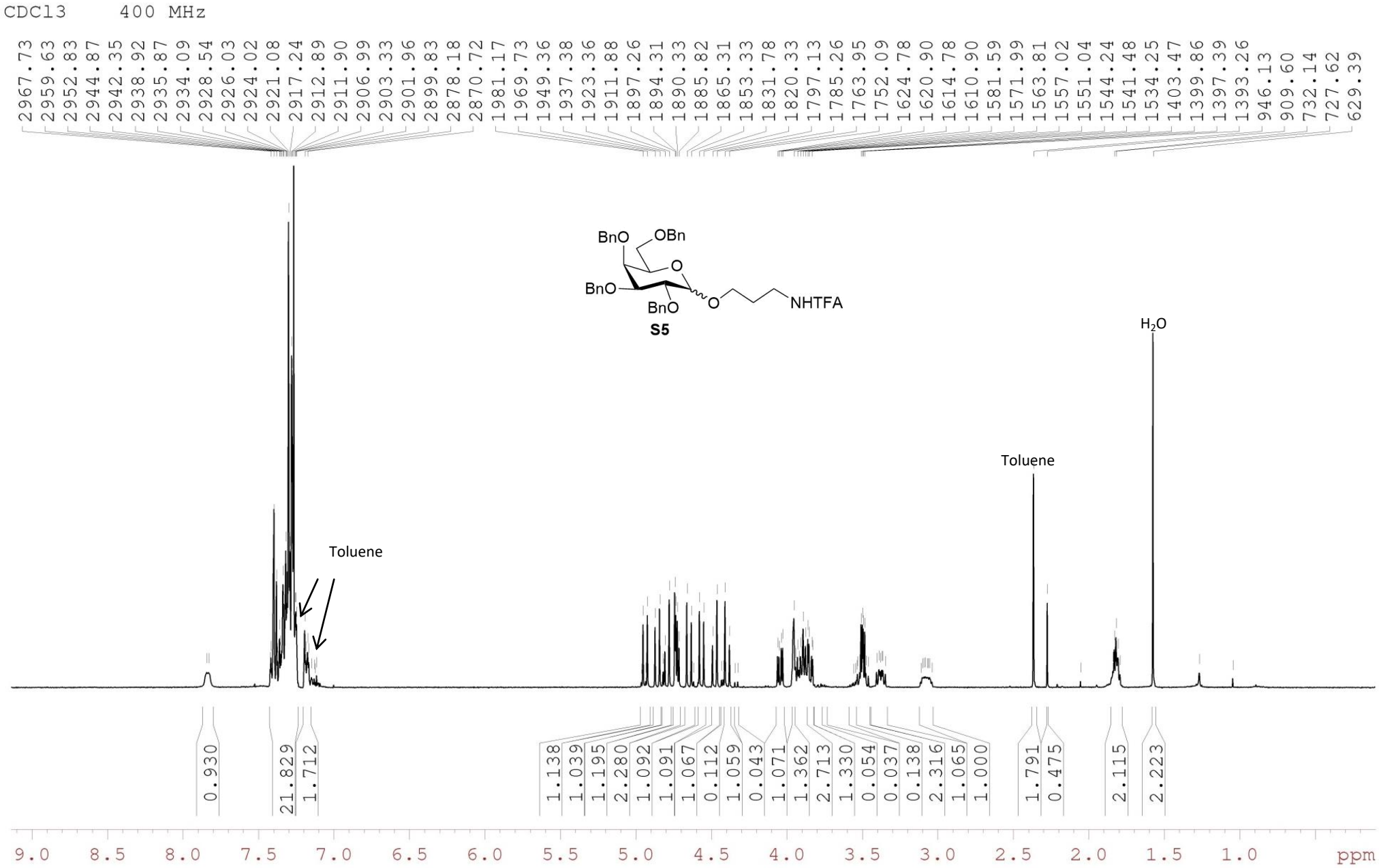

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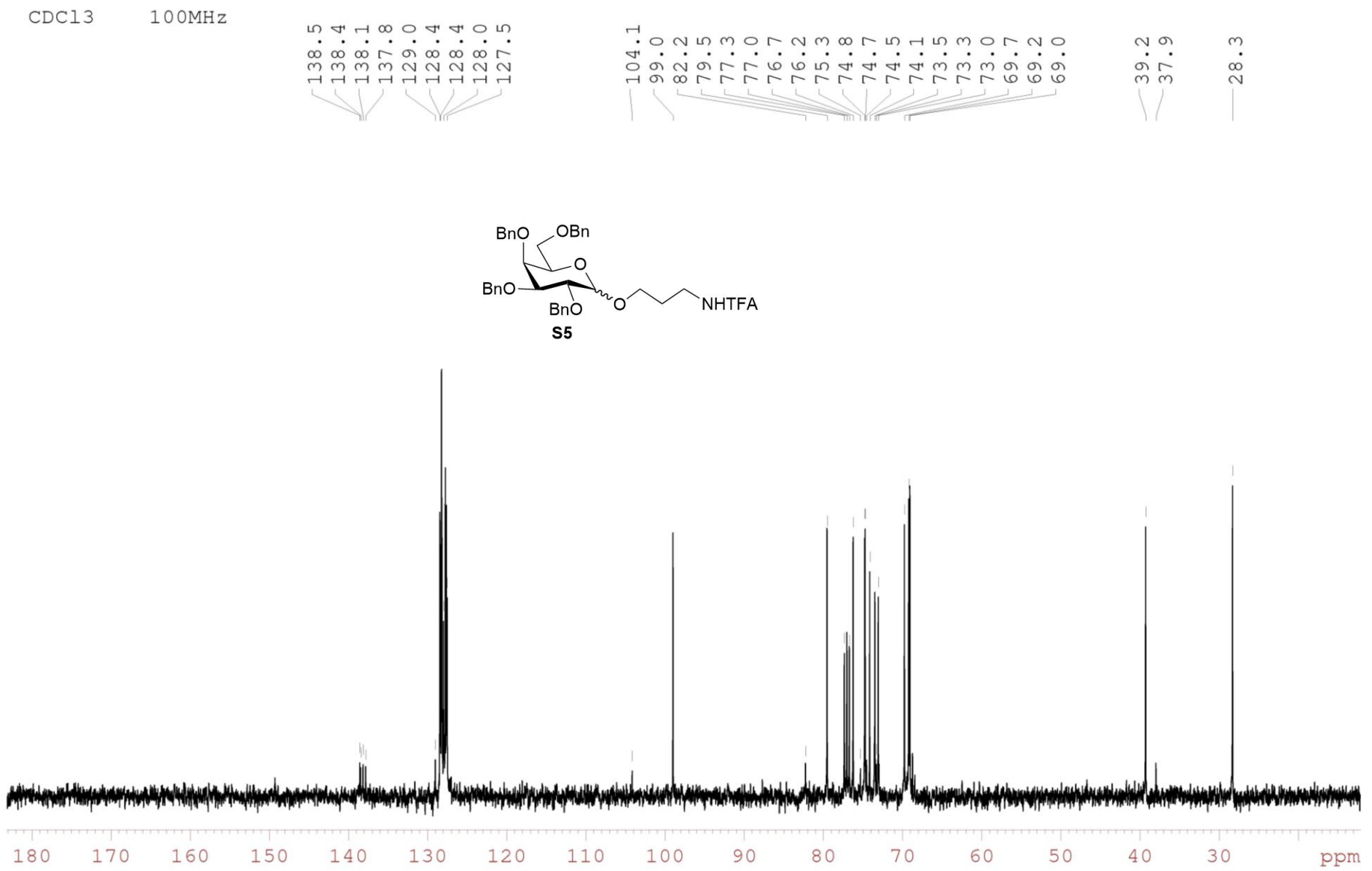

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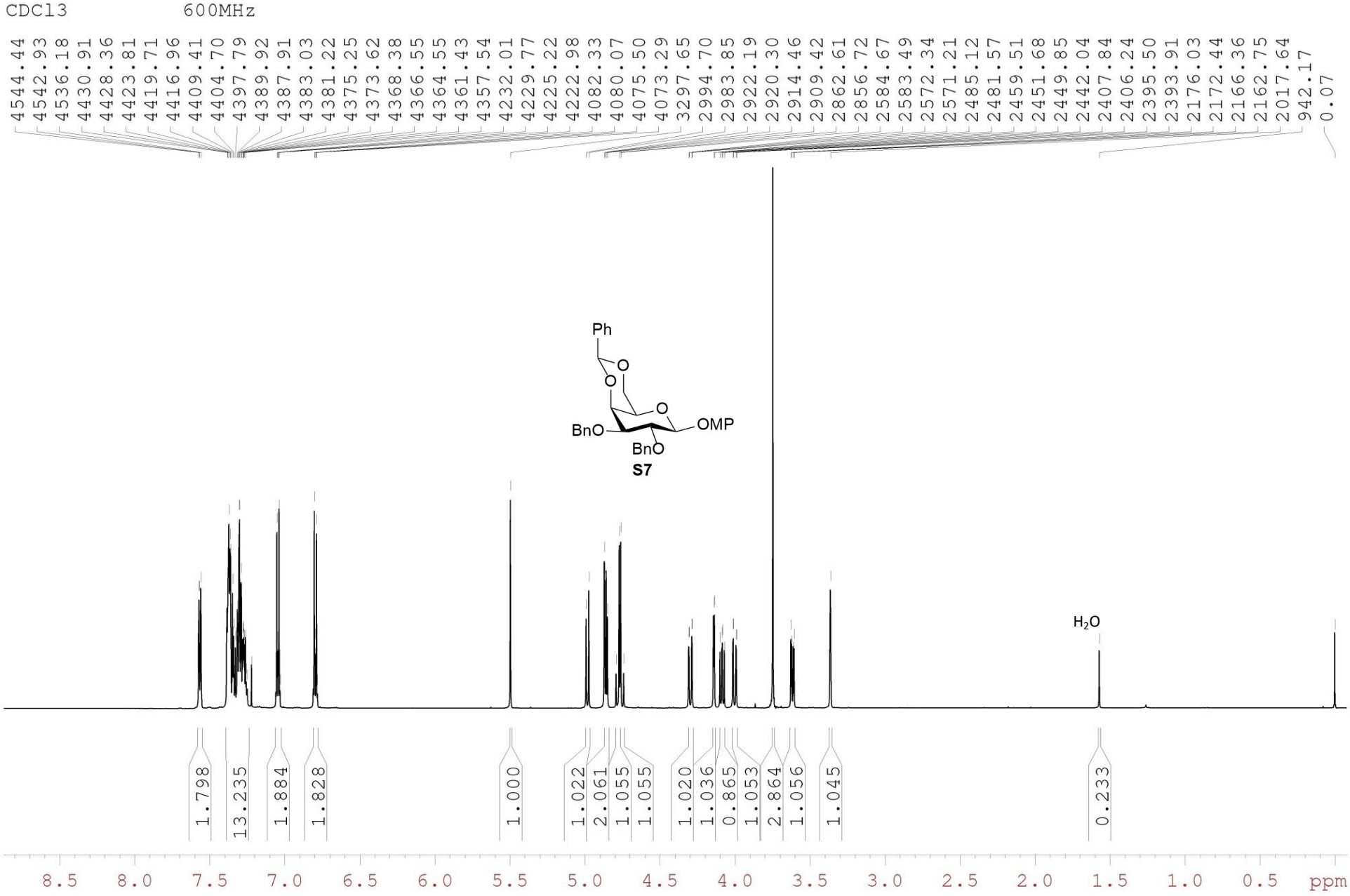

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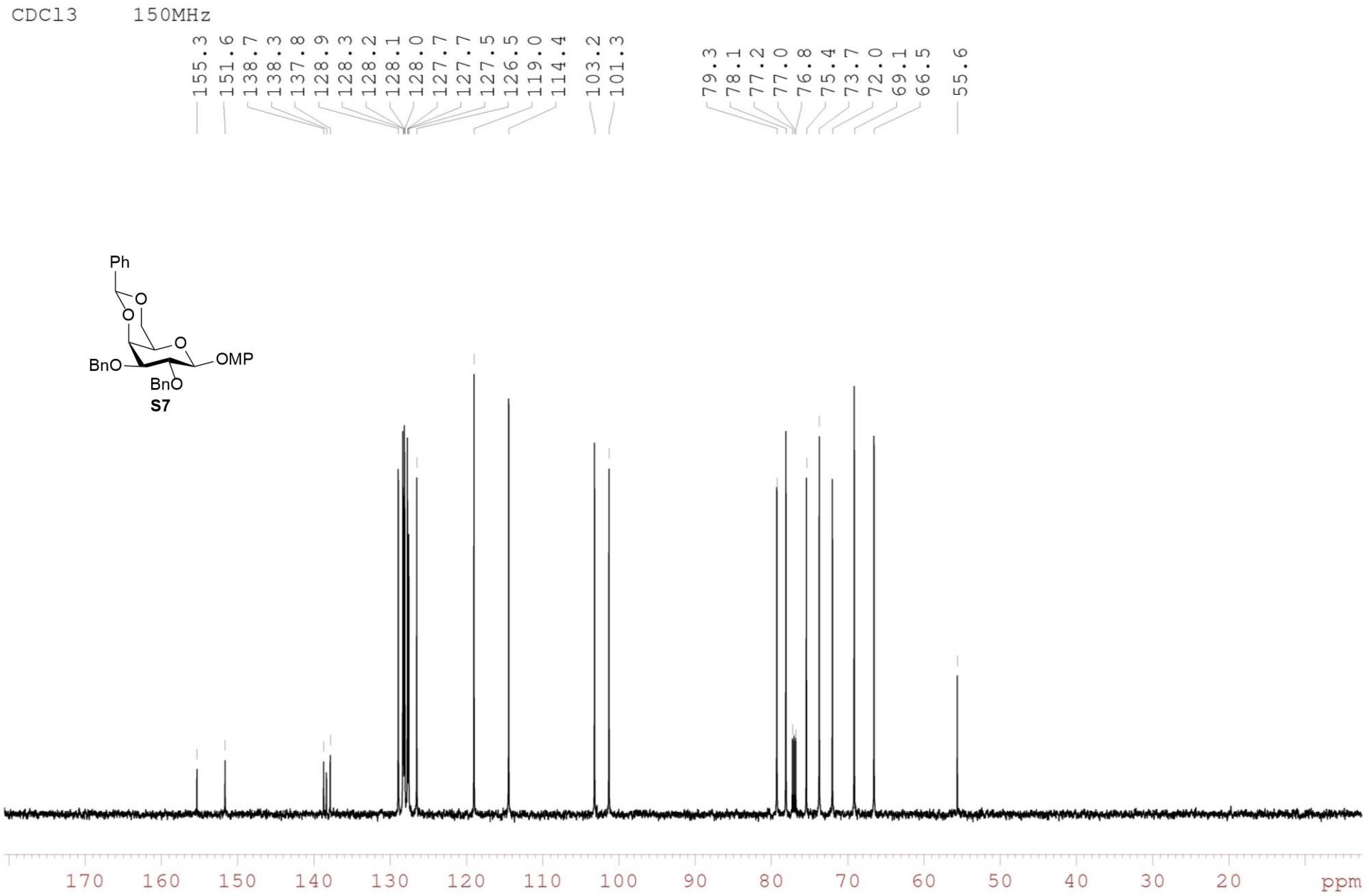

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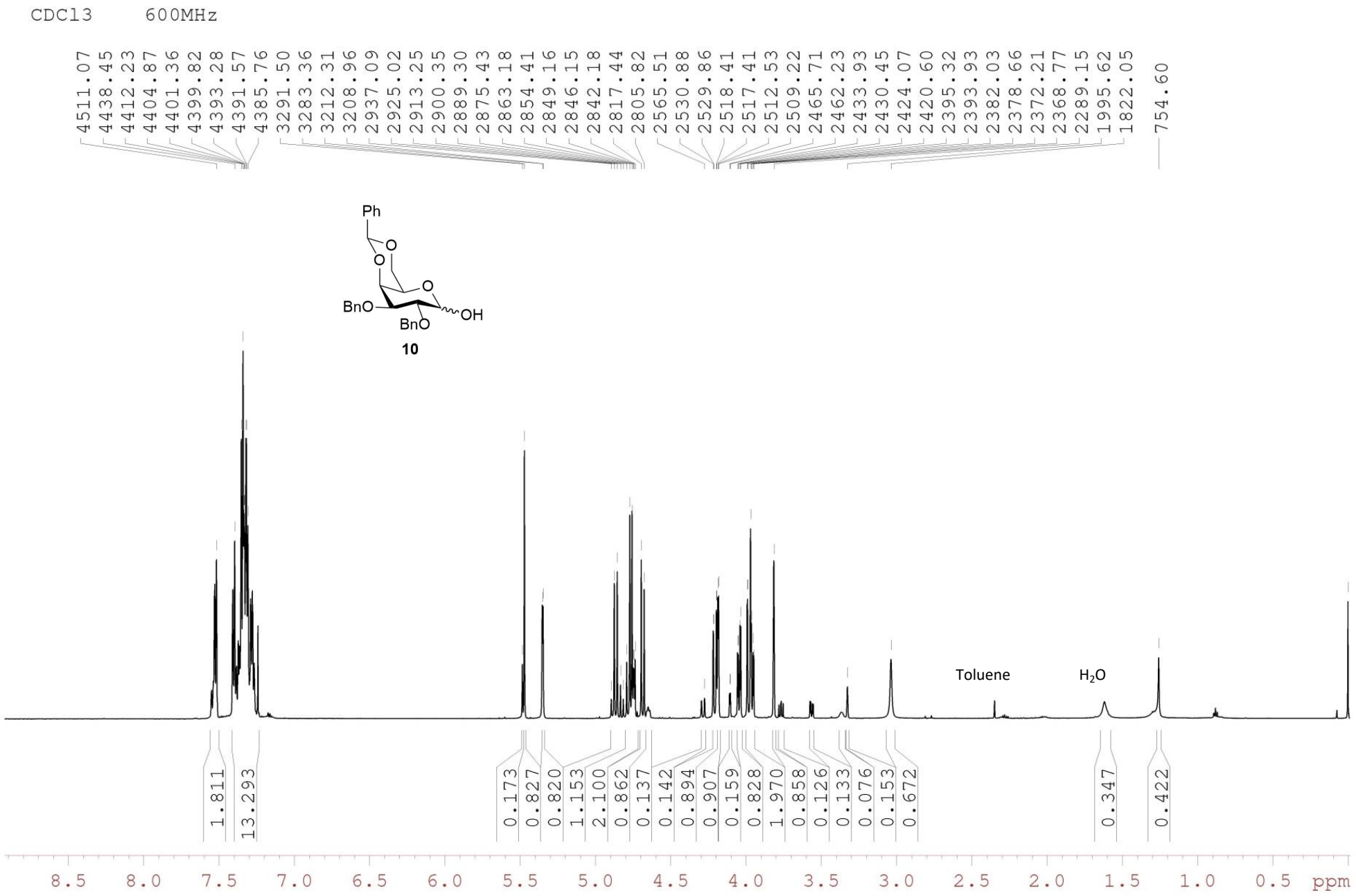

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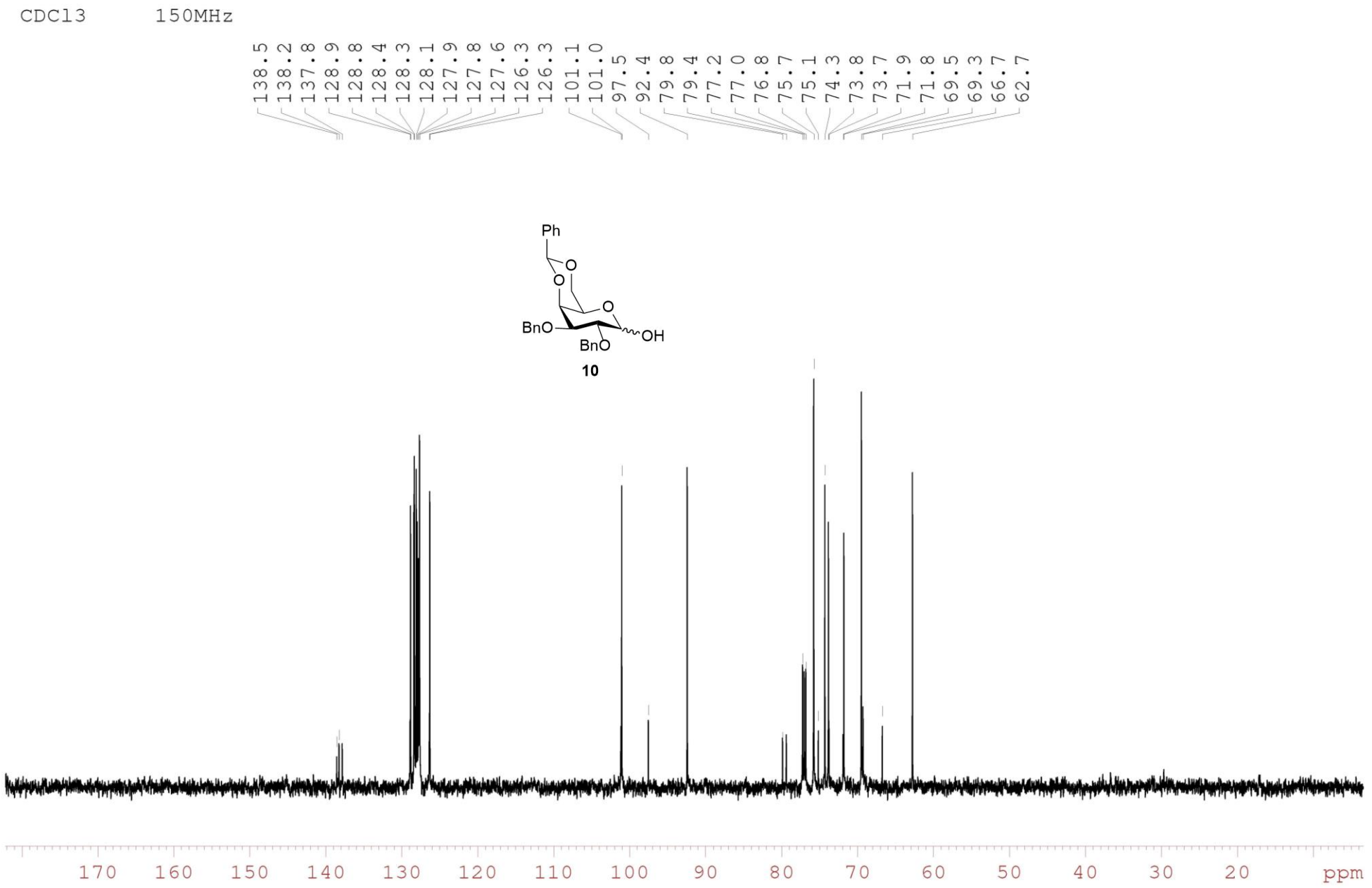

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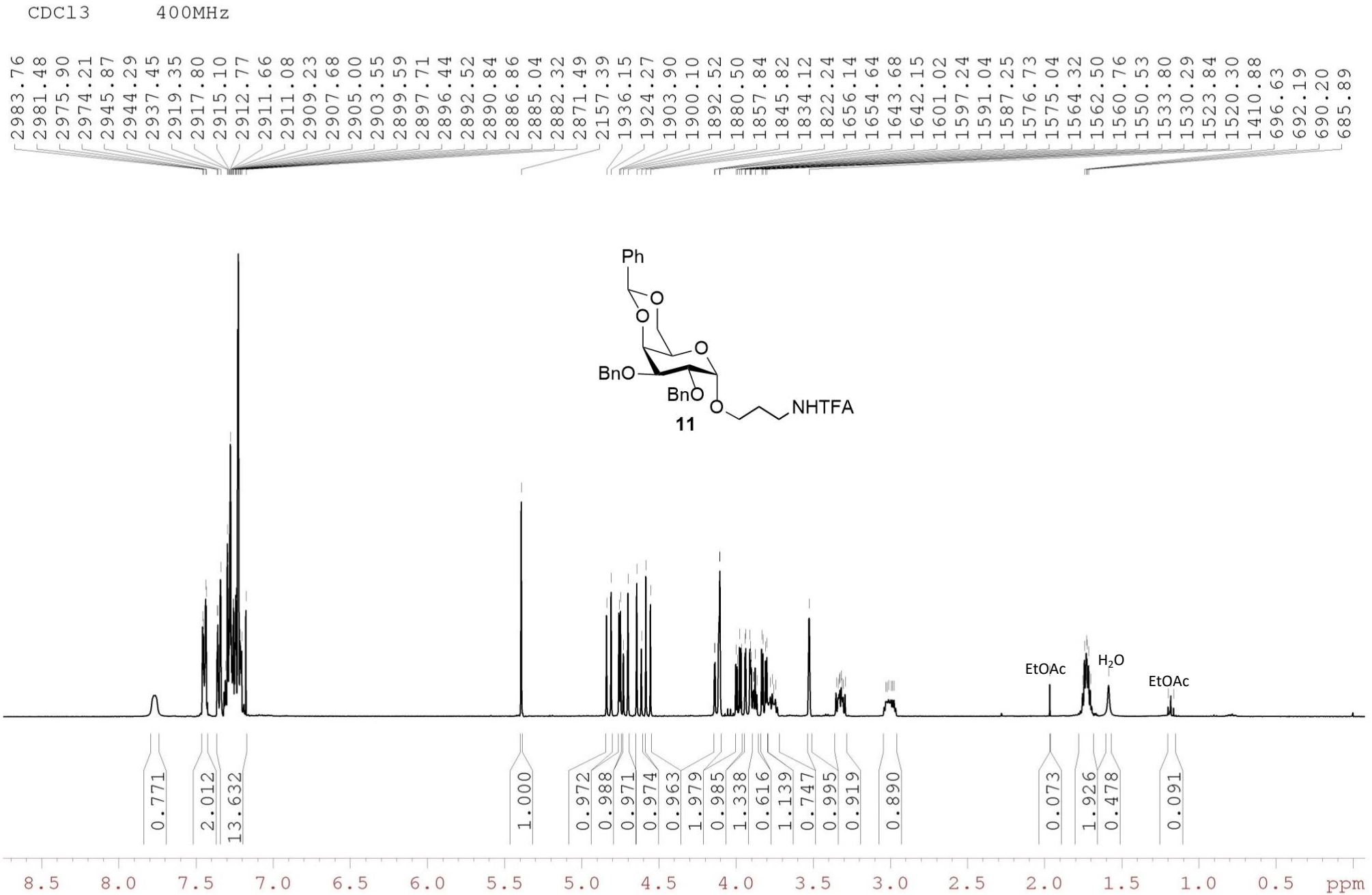

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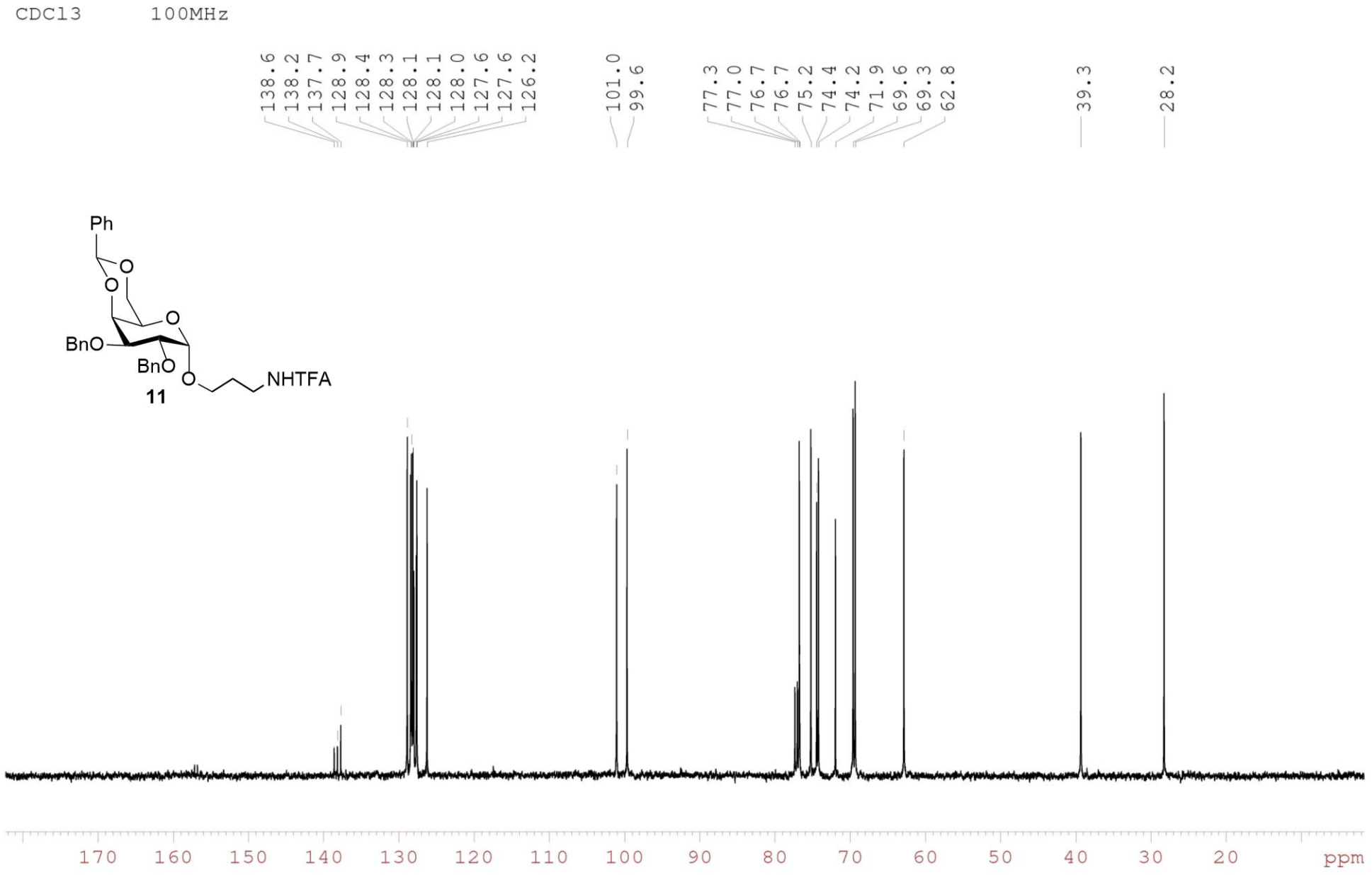

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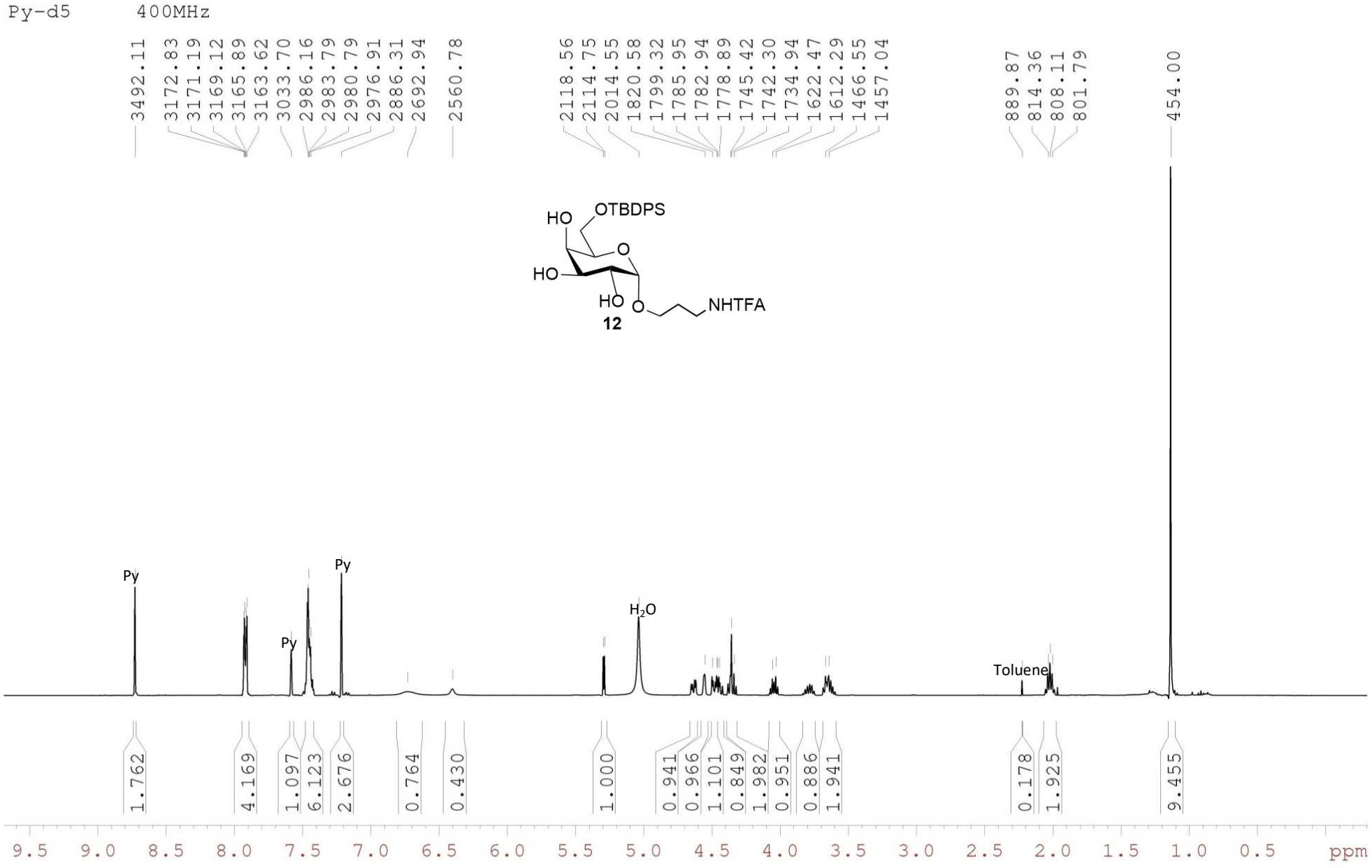

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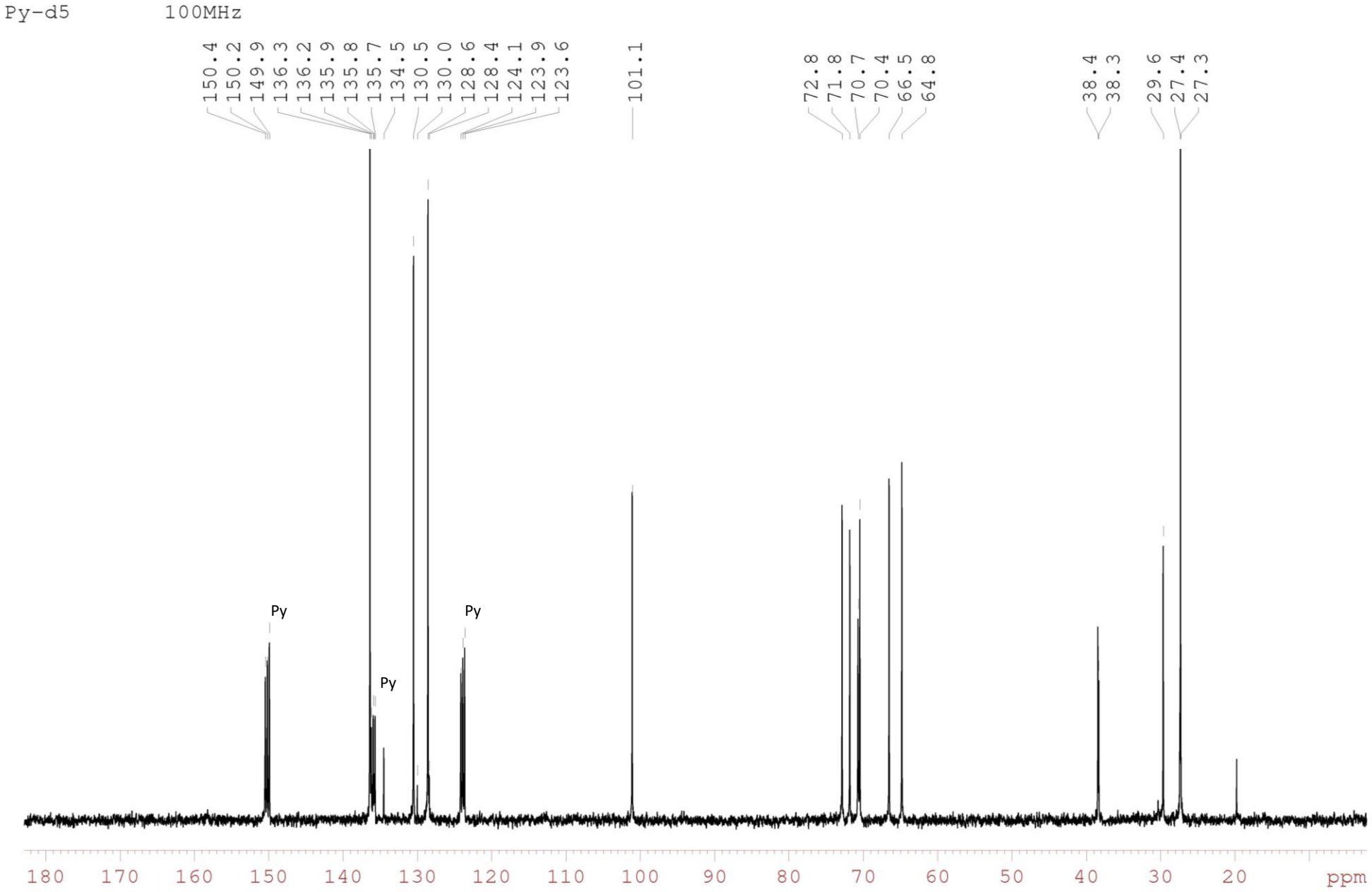

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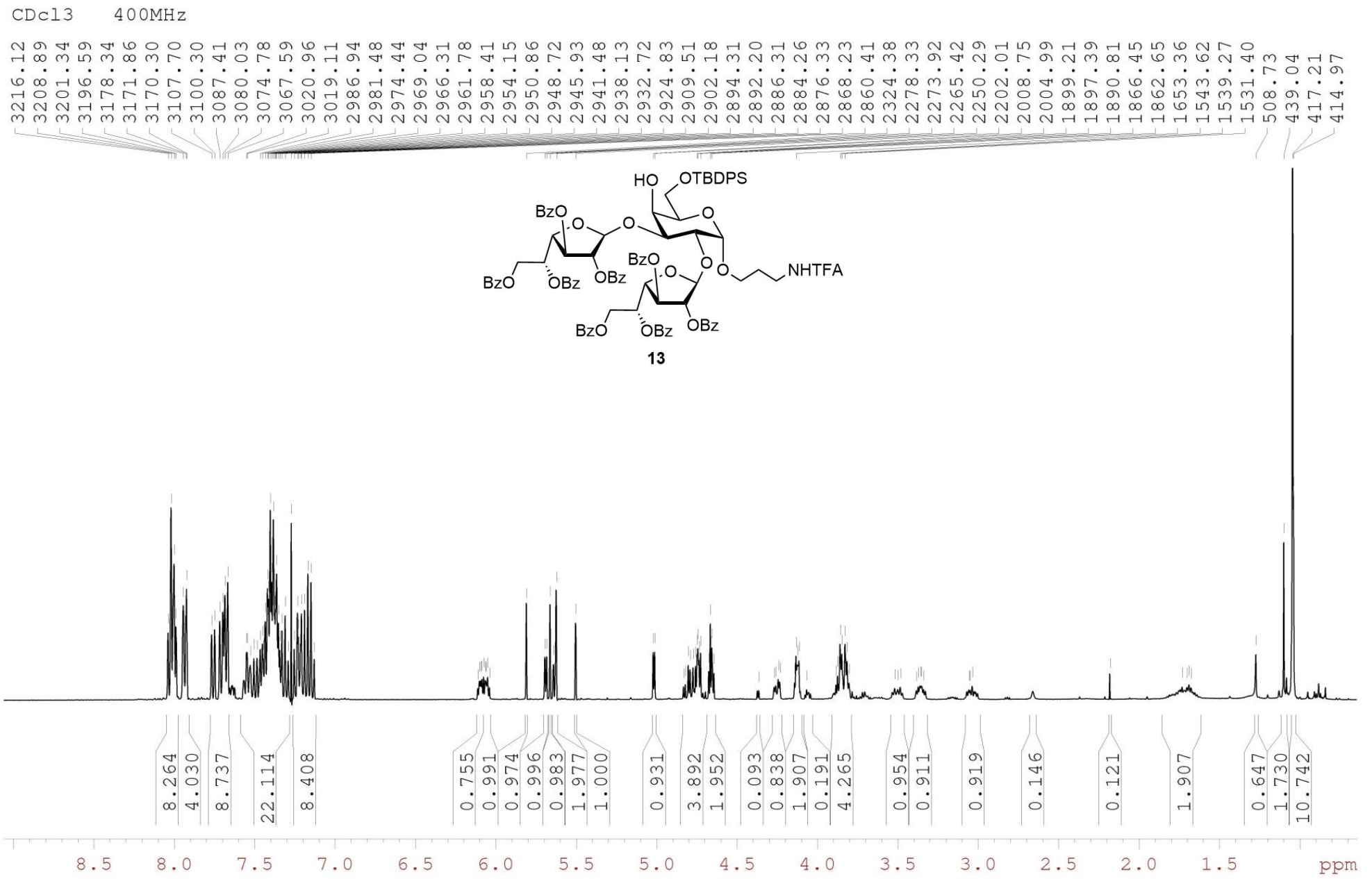

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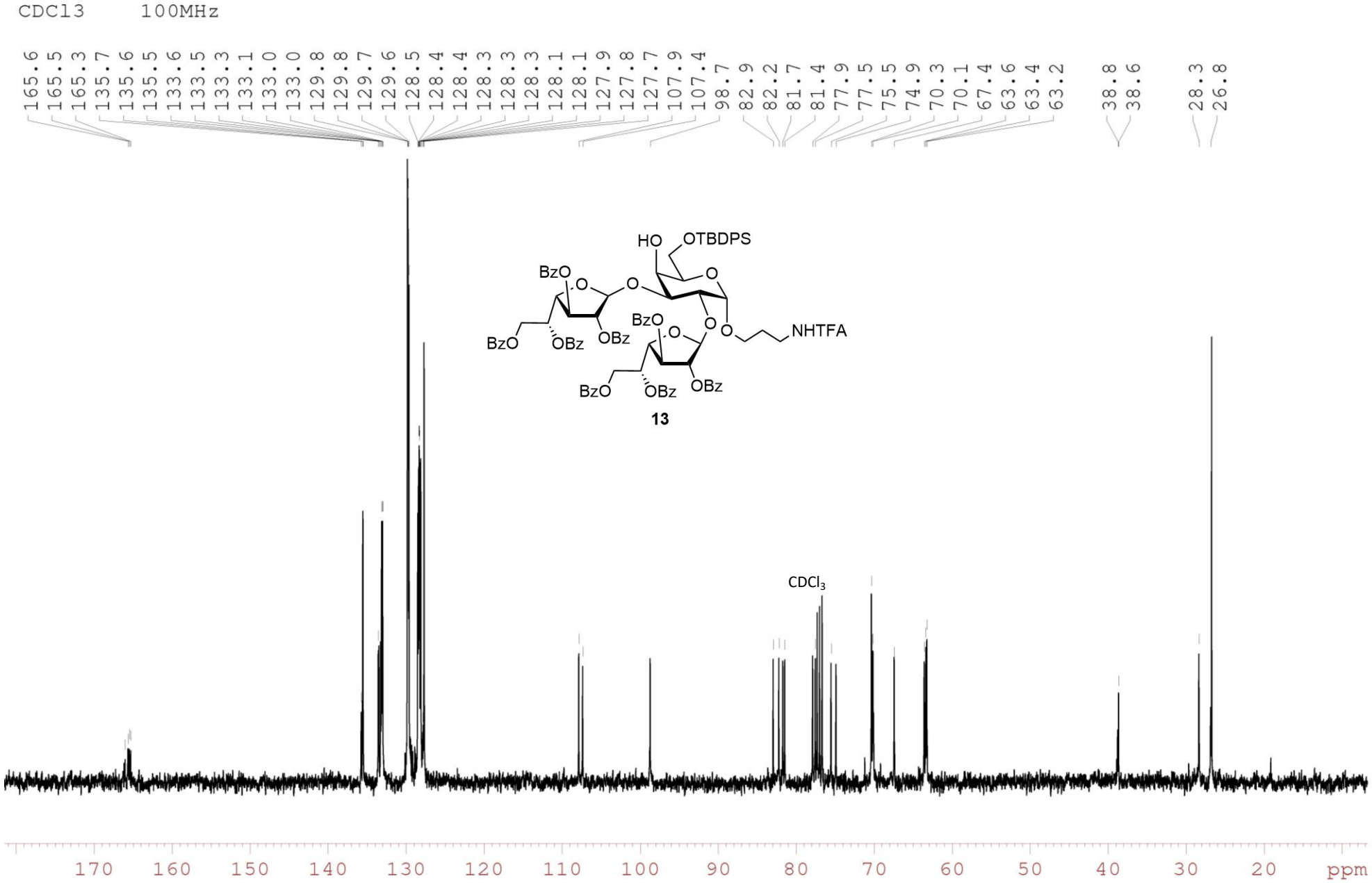

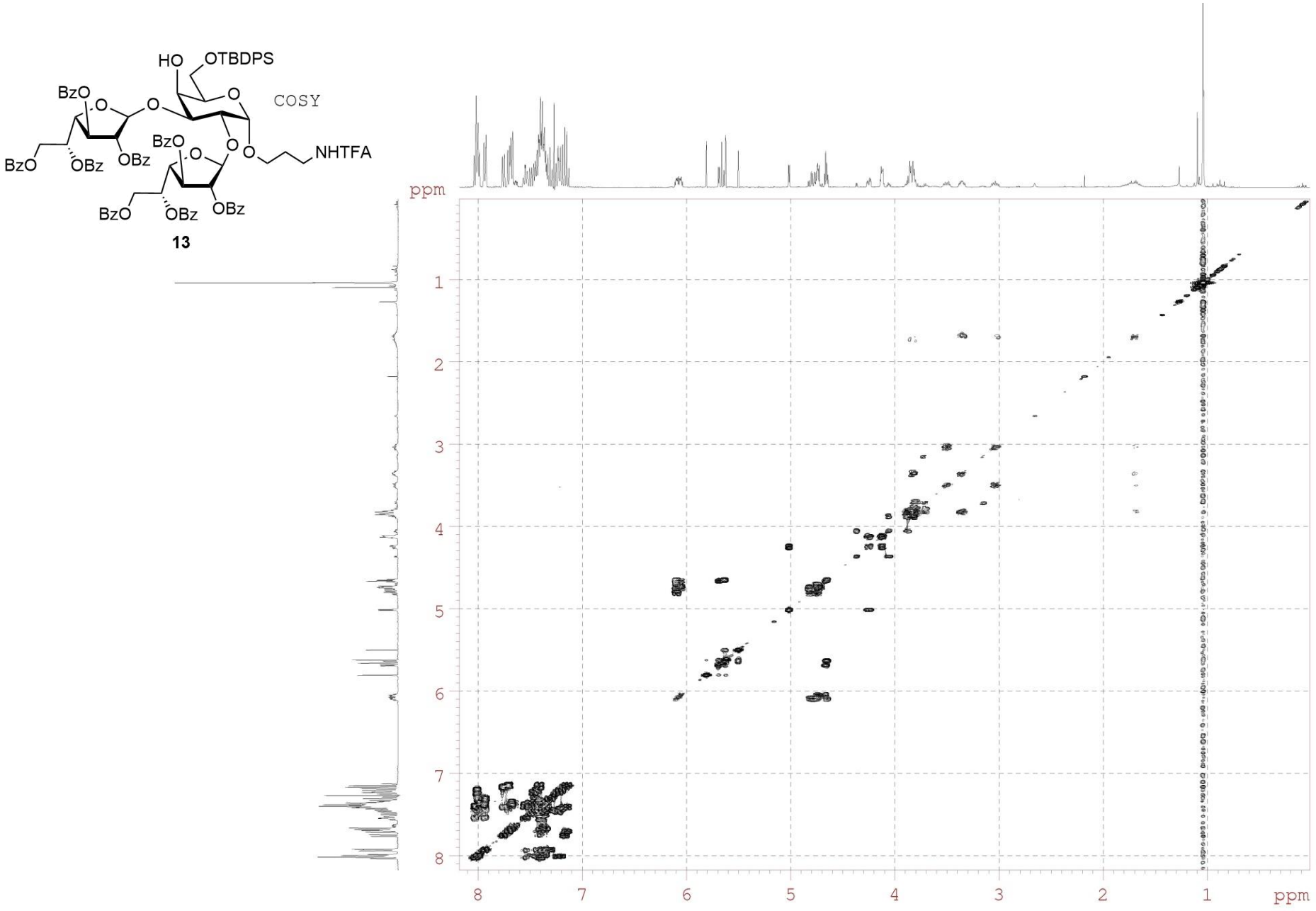
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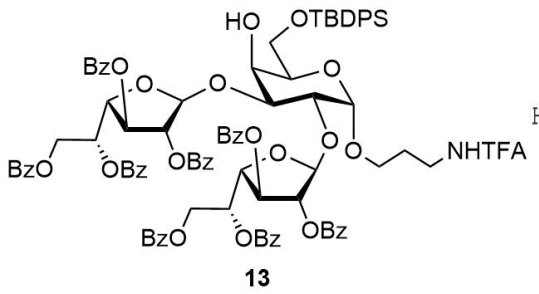
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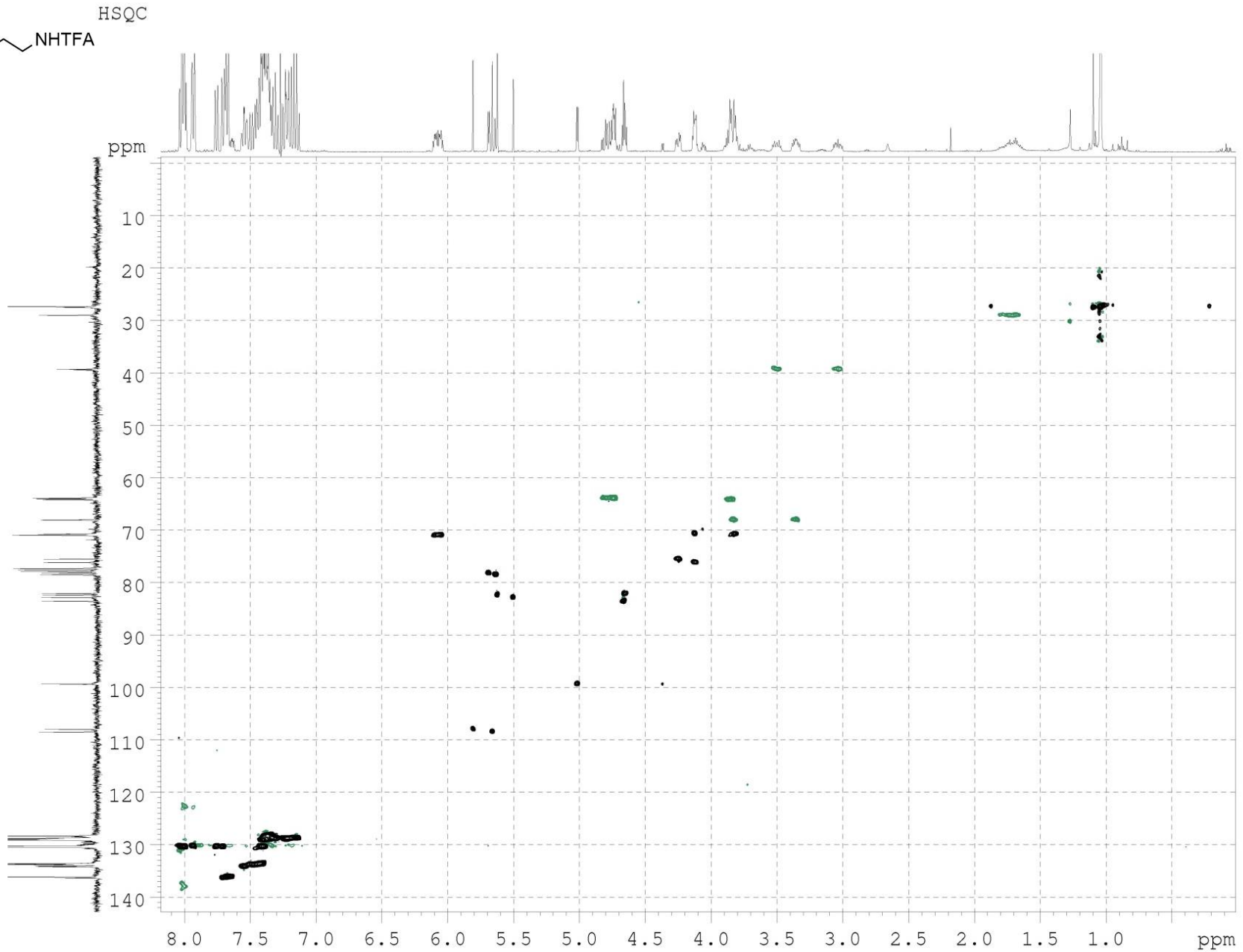
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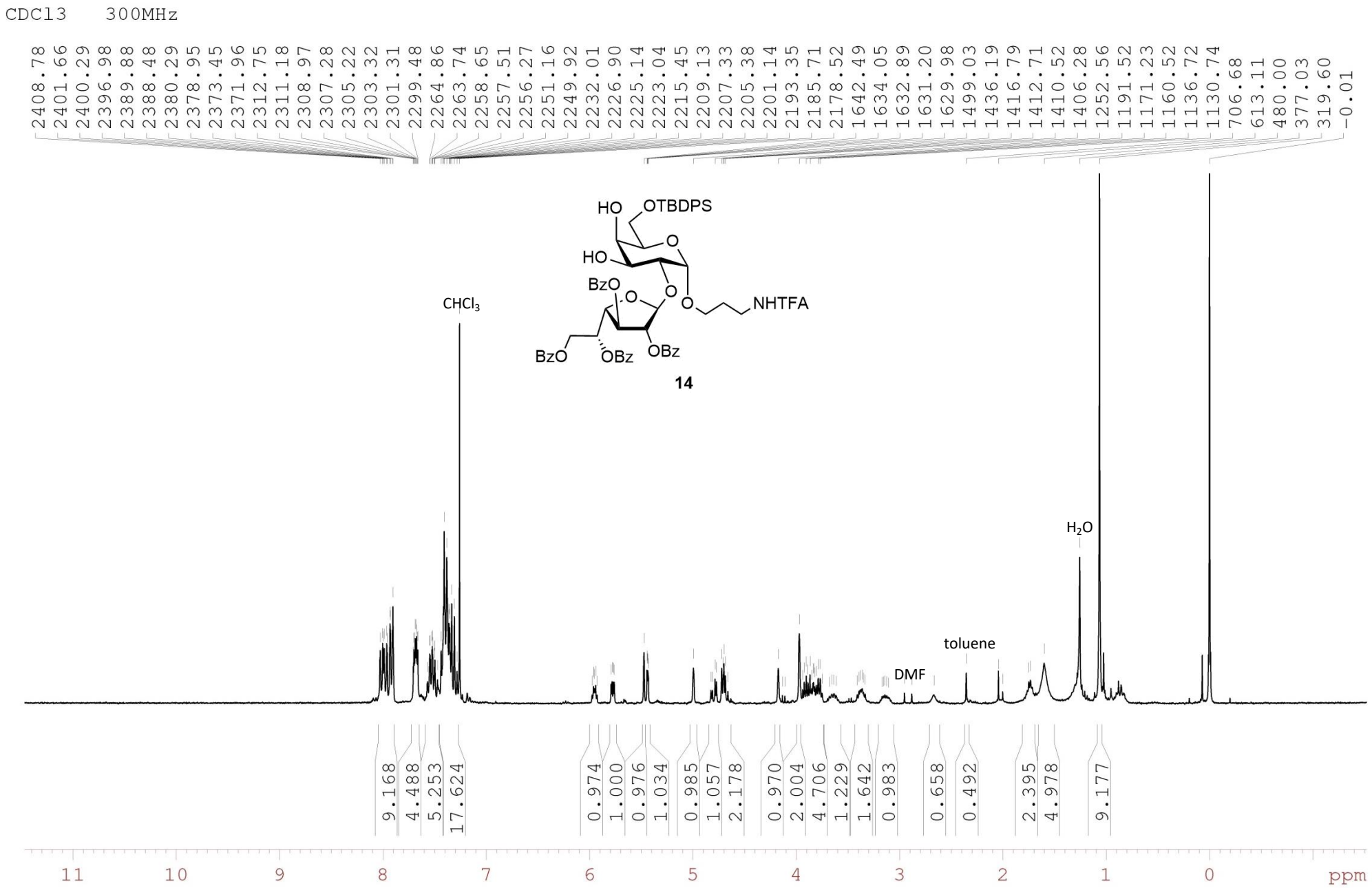
^{1}H-NMR spectrum of **14**



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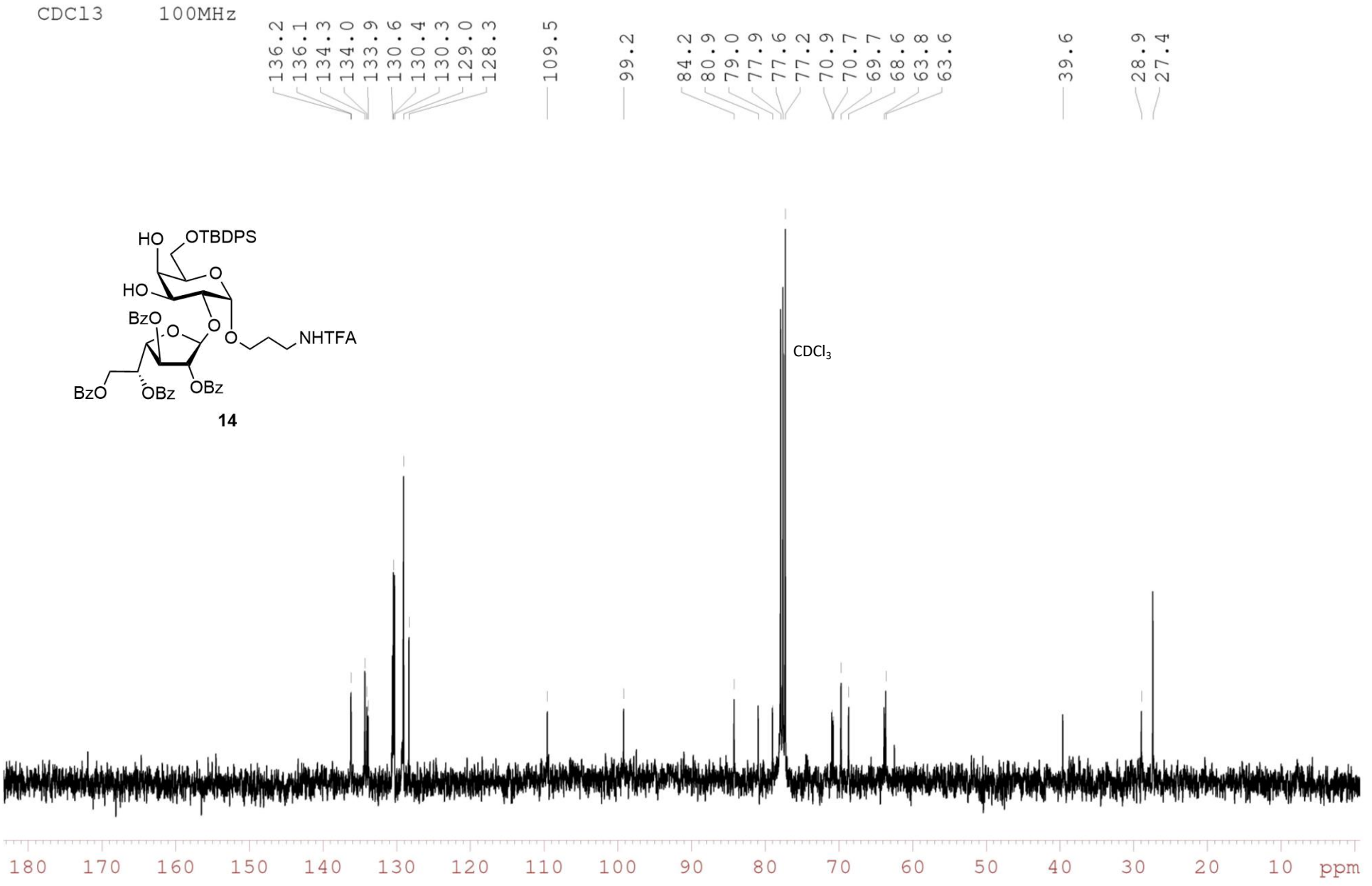

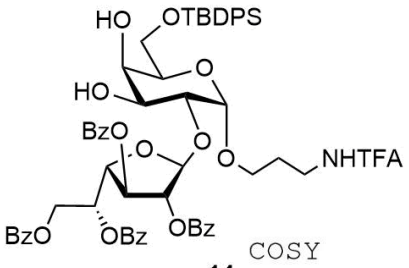
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14

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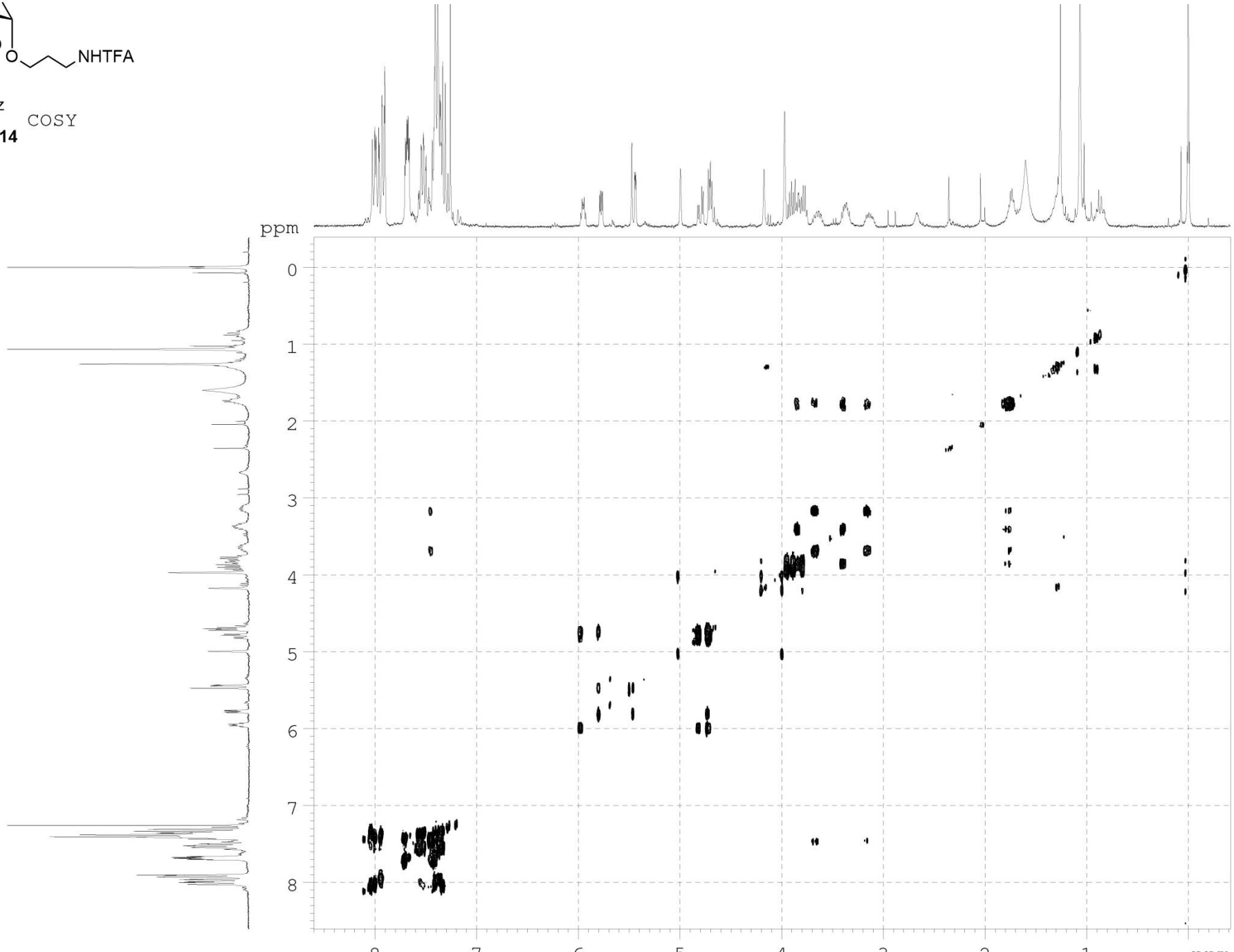
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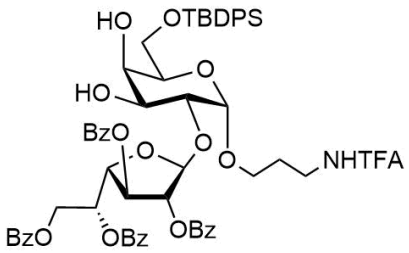
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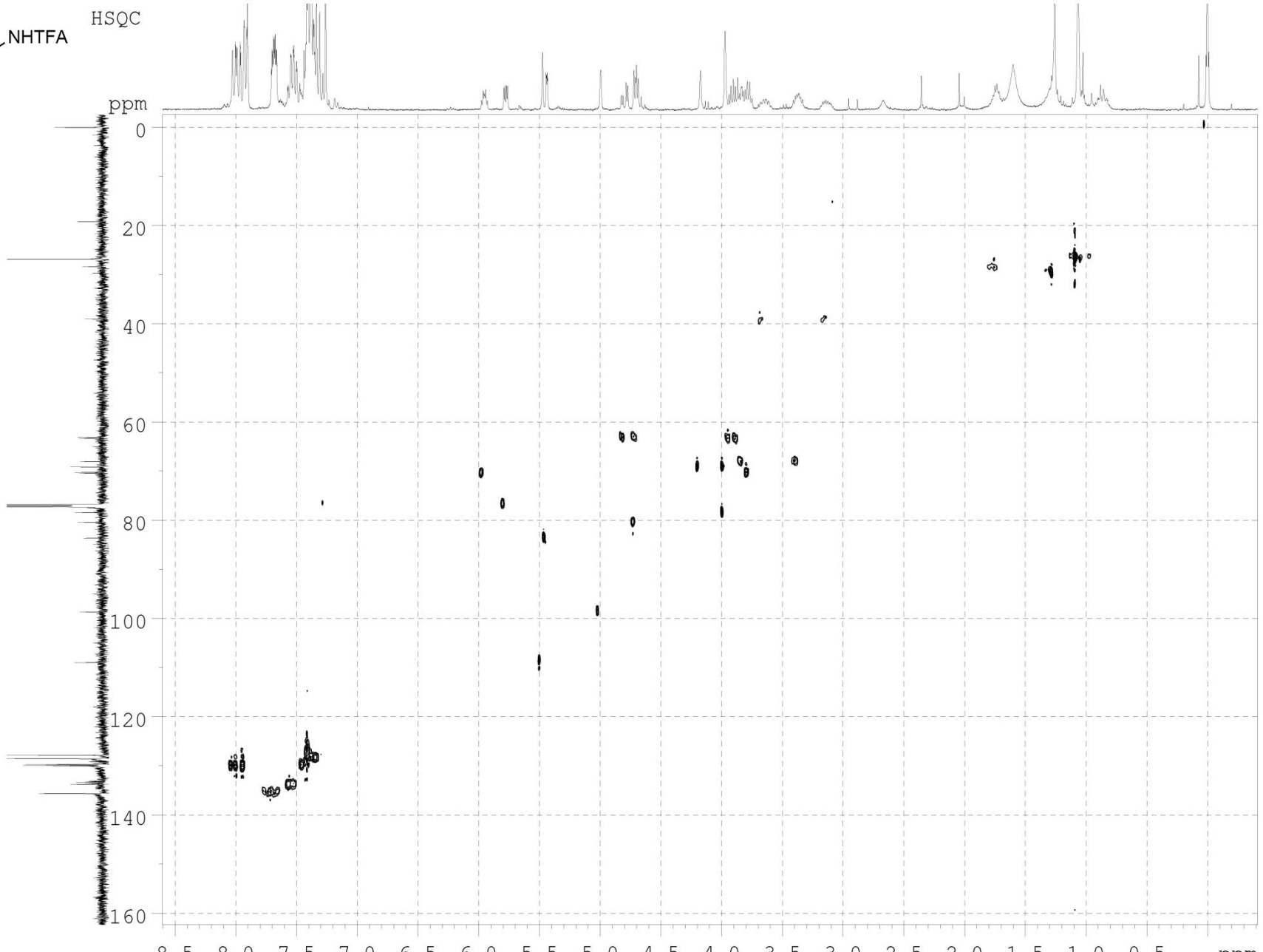
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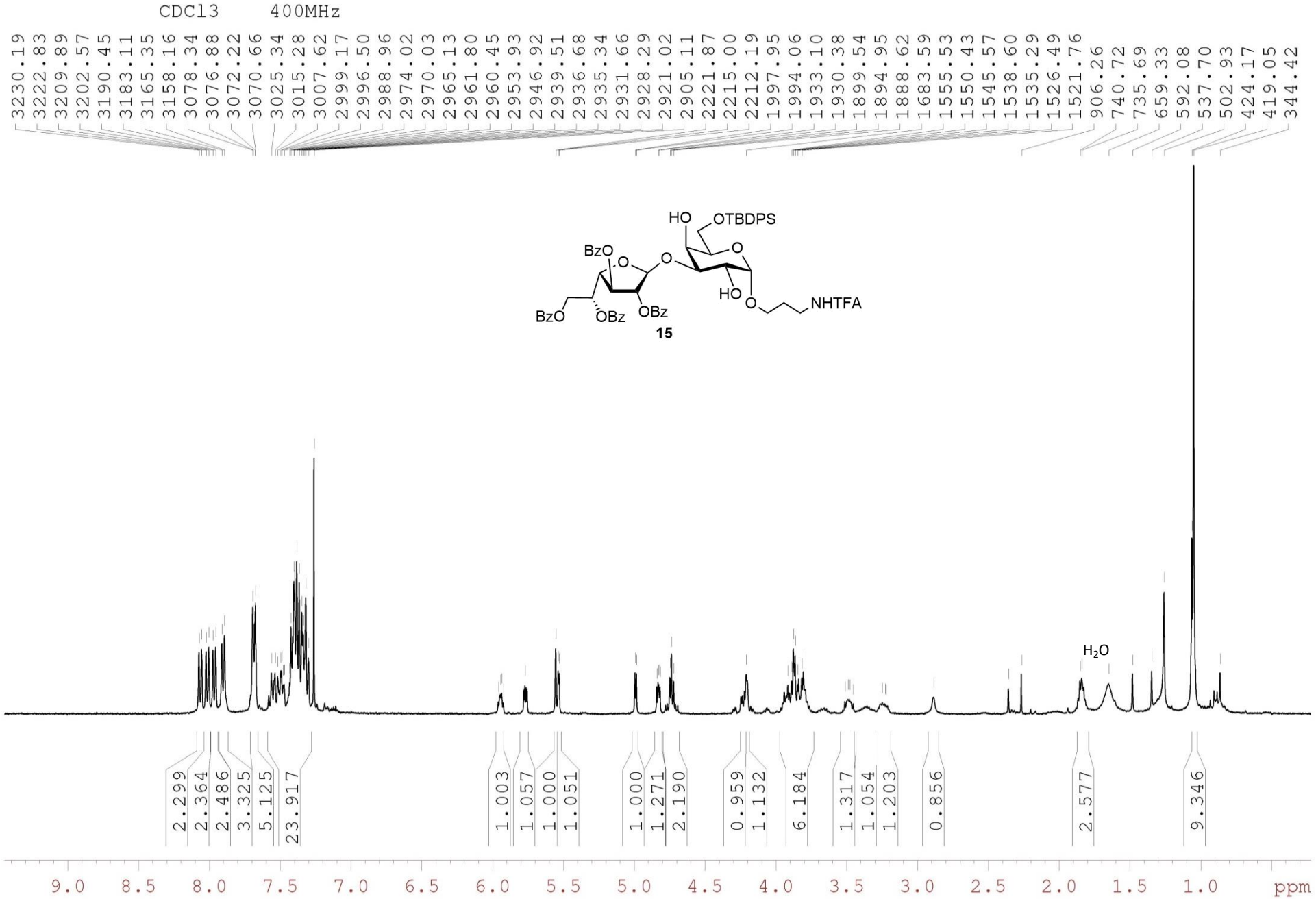
^{1}H-NMR spectrum of **15**



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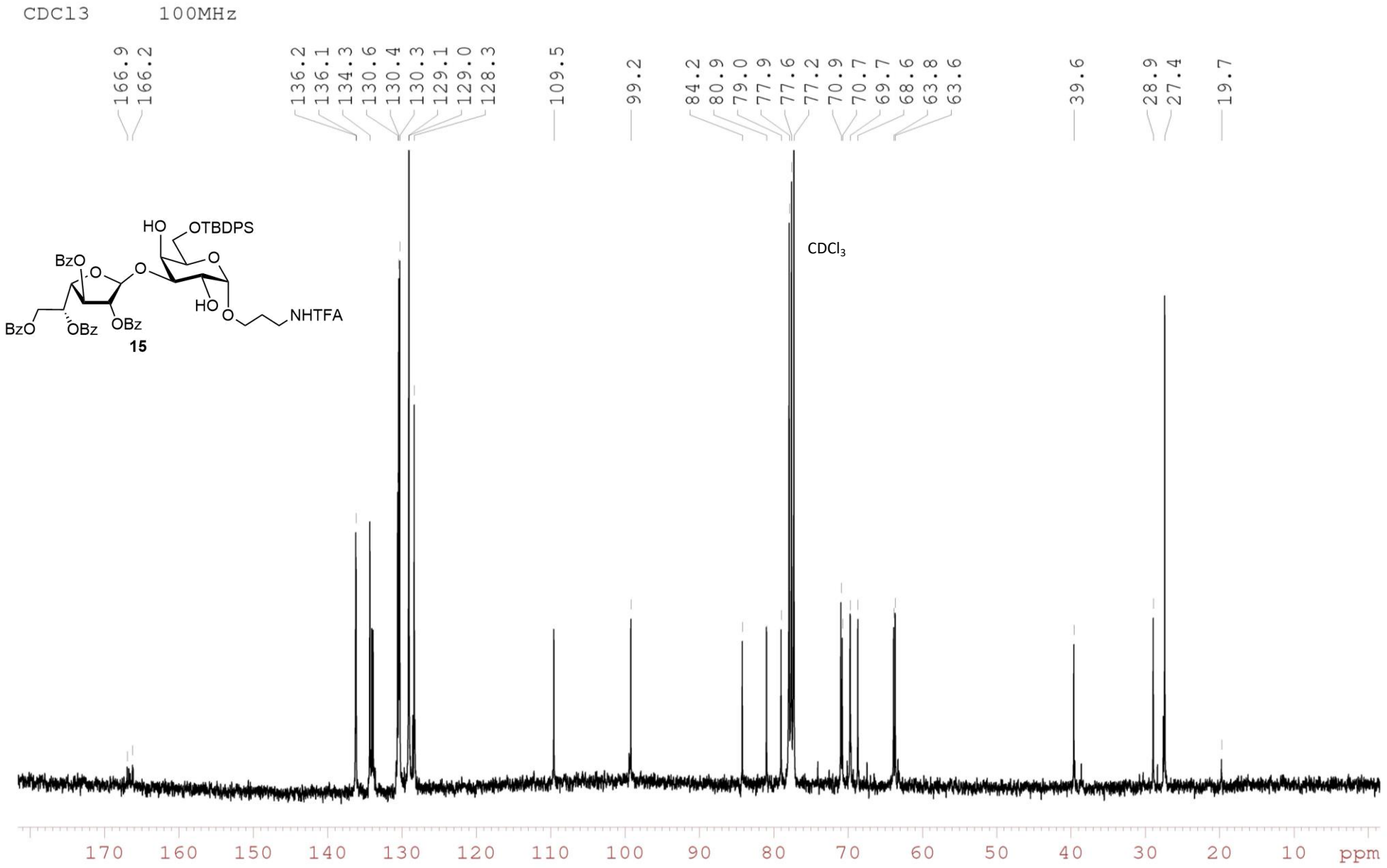

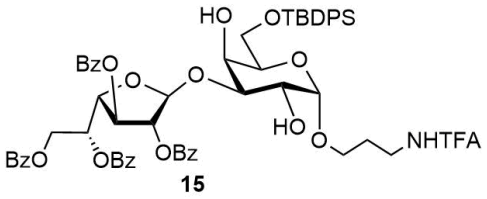
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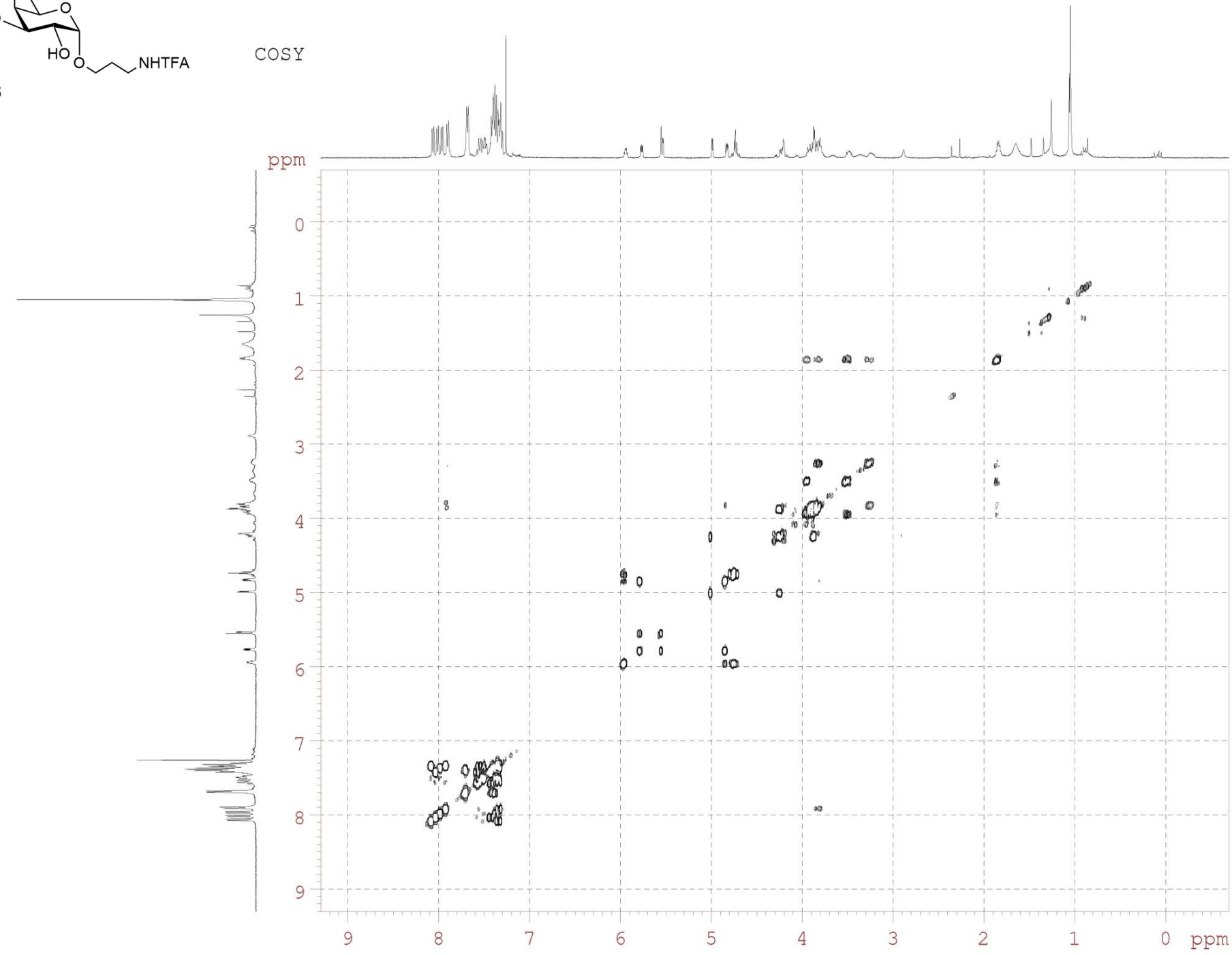
15

COSY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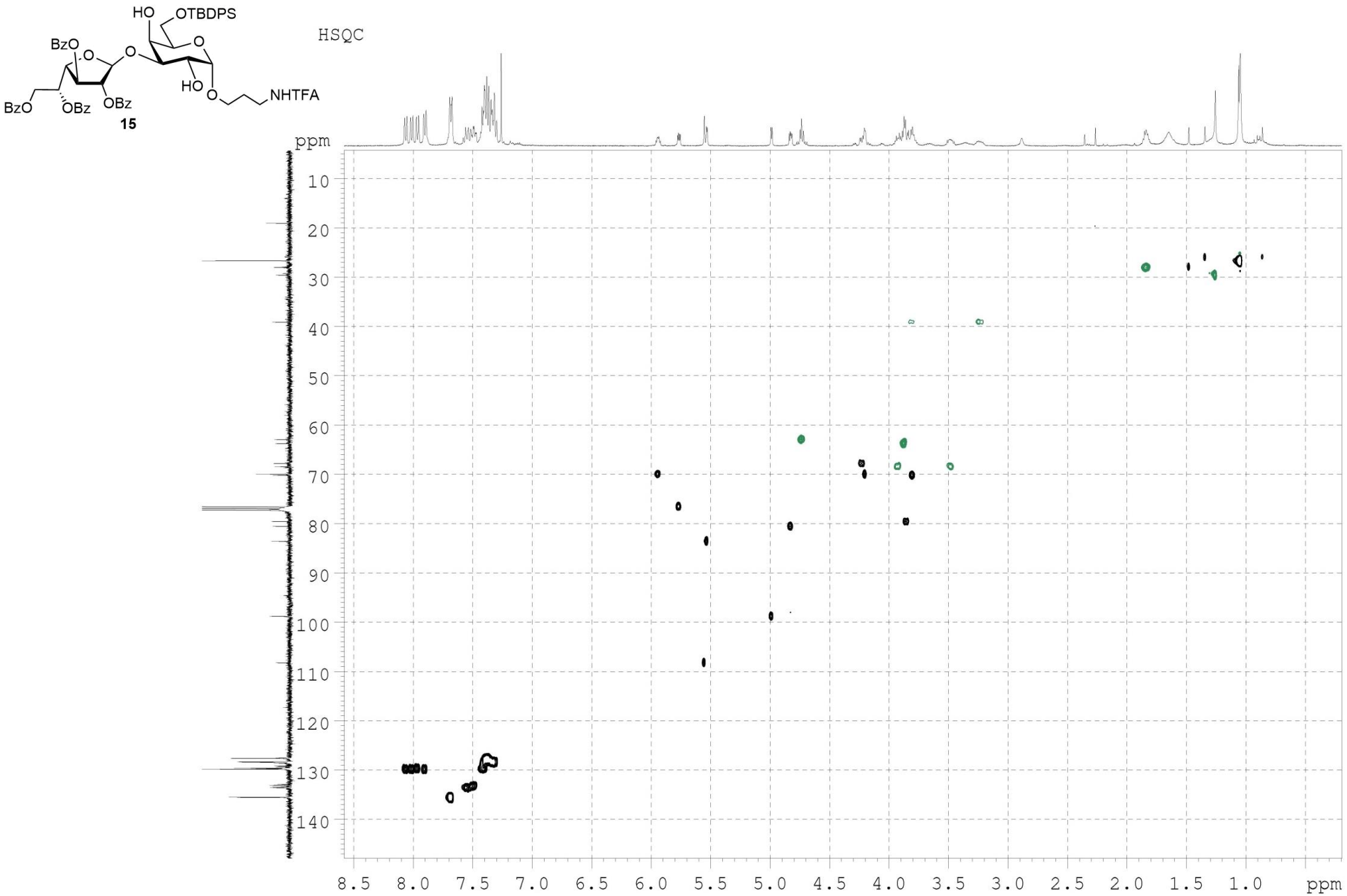
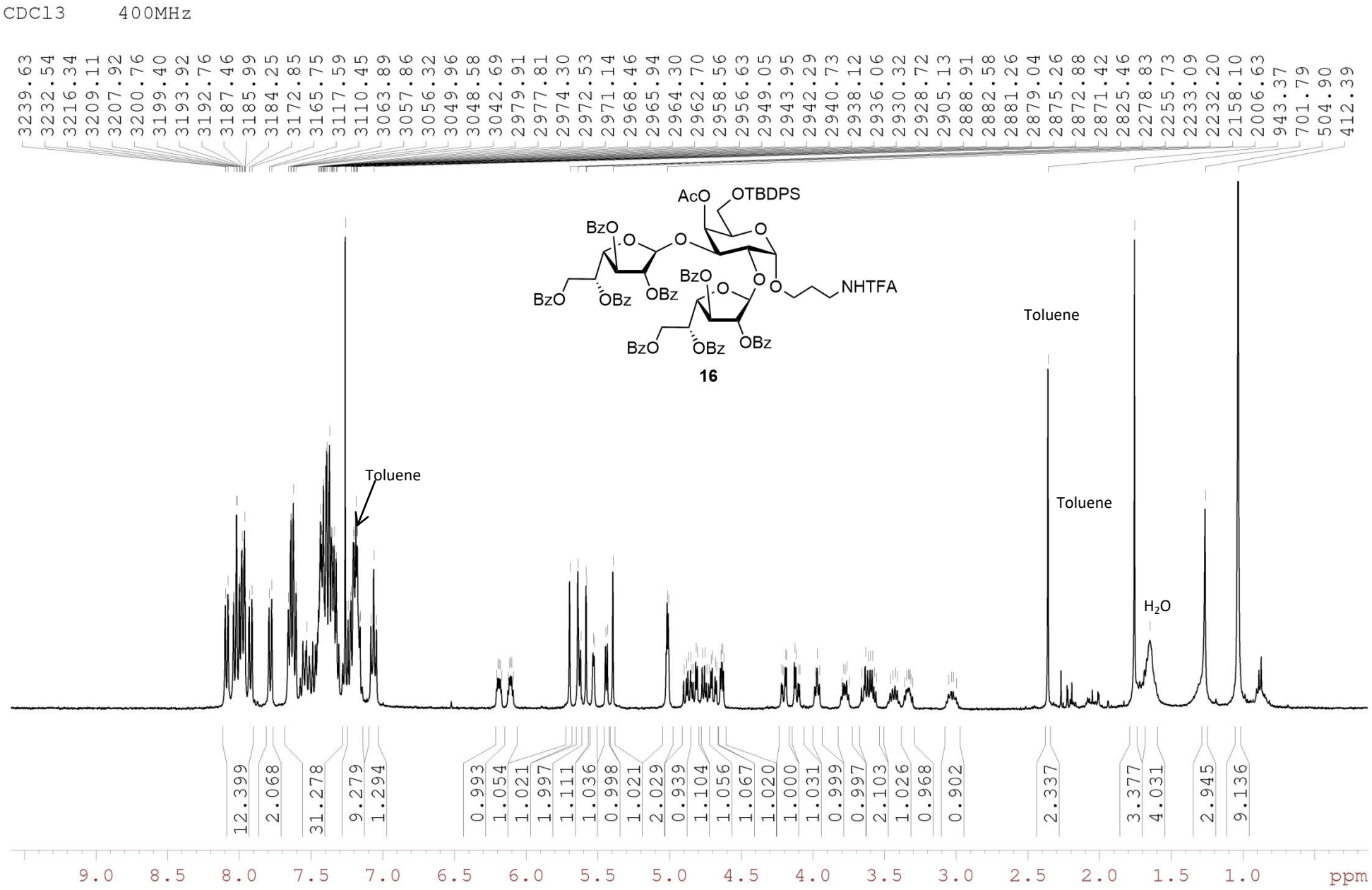
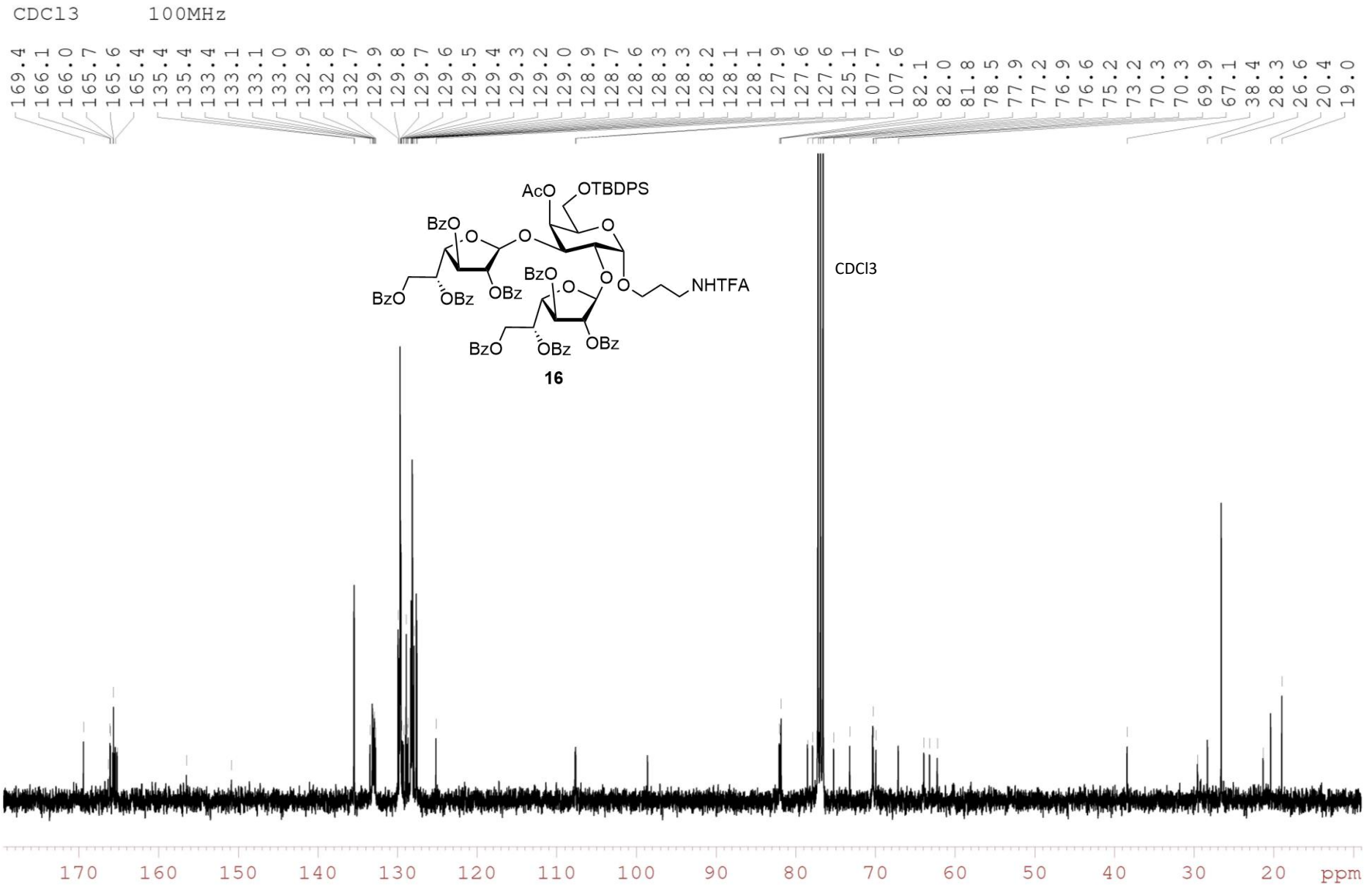
ppm

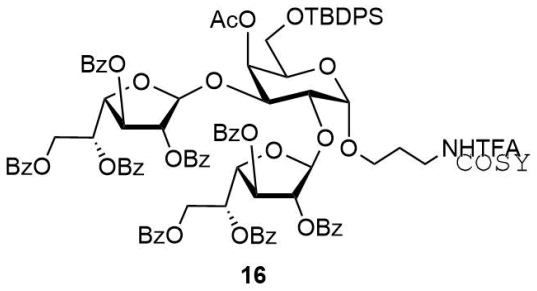

HO
OTBDPS
BzO
O
O
O
HO
O
NHTFA
BzO
OBz
OBz
15
HSQC
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-NMR spectrum of **16**



^{13}C-NMR spectrum of **16**

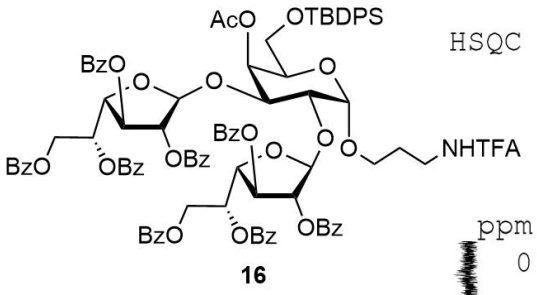



AcO
OTBDPS
BzO
BzO
OBz
OBz
BzO
BzO
OBz
OBz
NHTFA

16

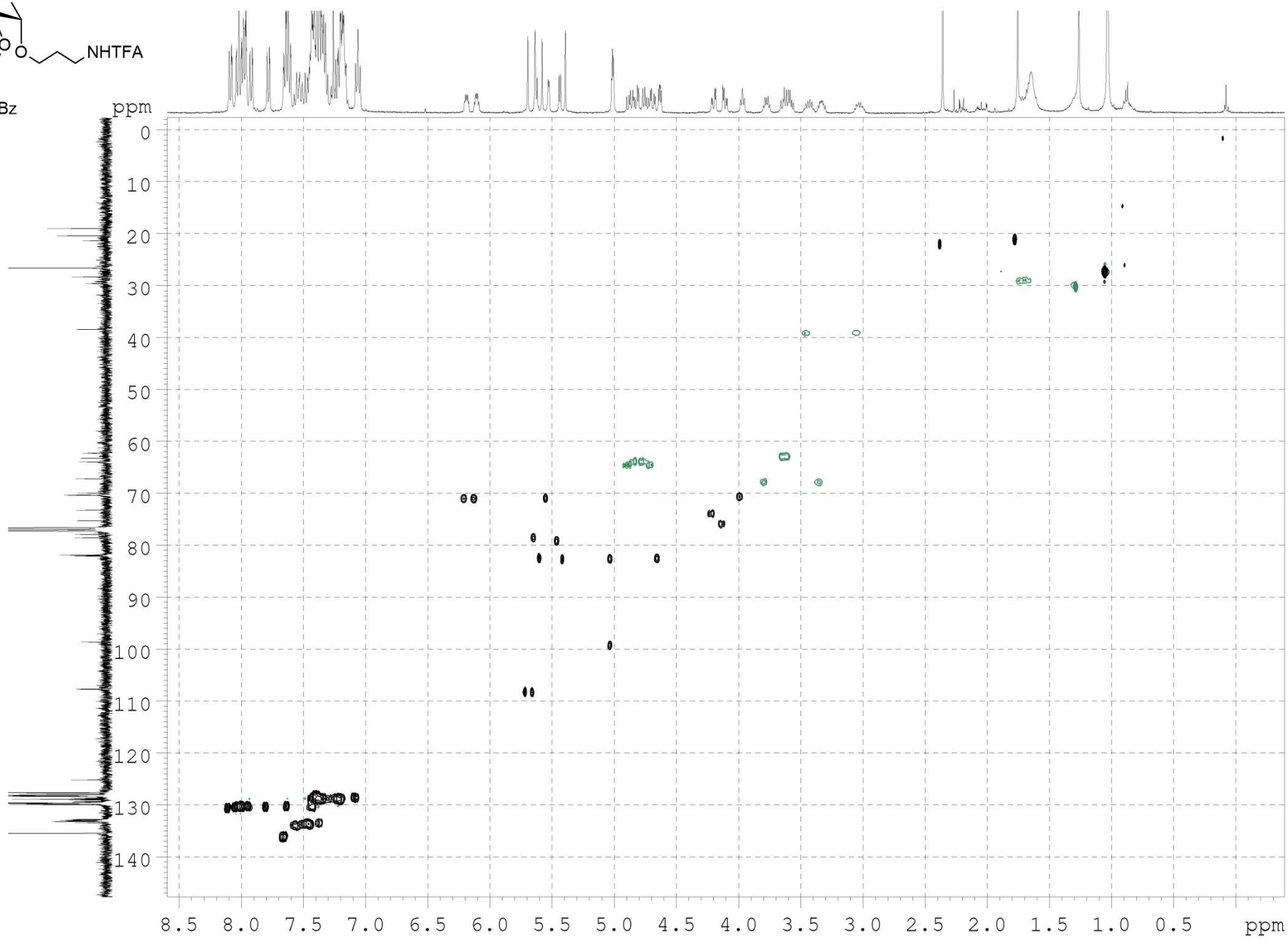
COSY

ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm

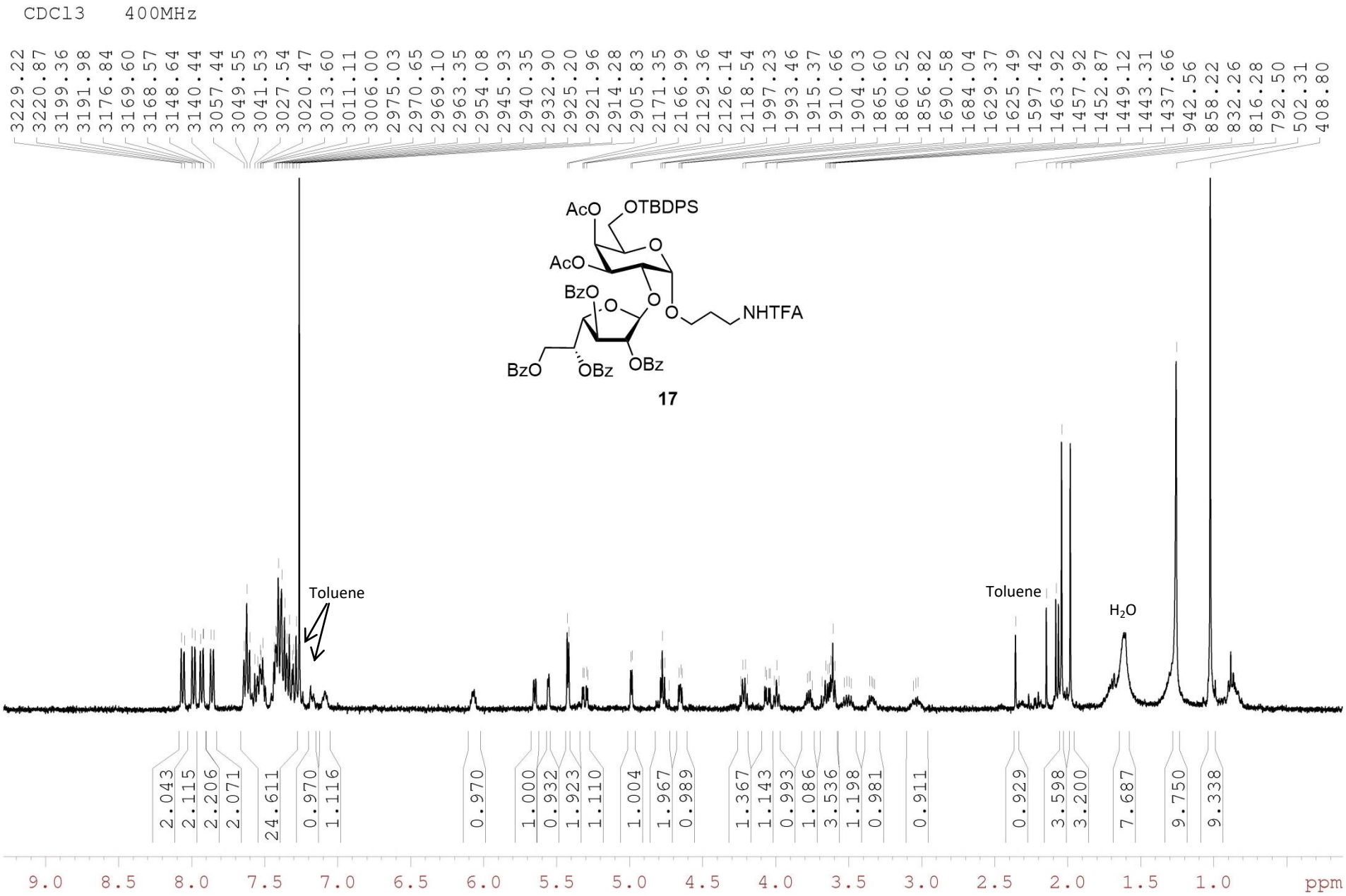

AcO
OTBDPS
BzO
BzO
OBz
OBz
BzO
BzO
OBz
OBz
NHTFA

16

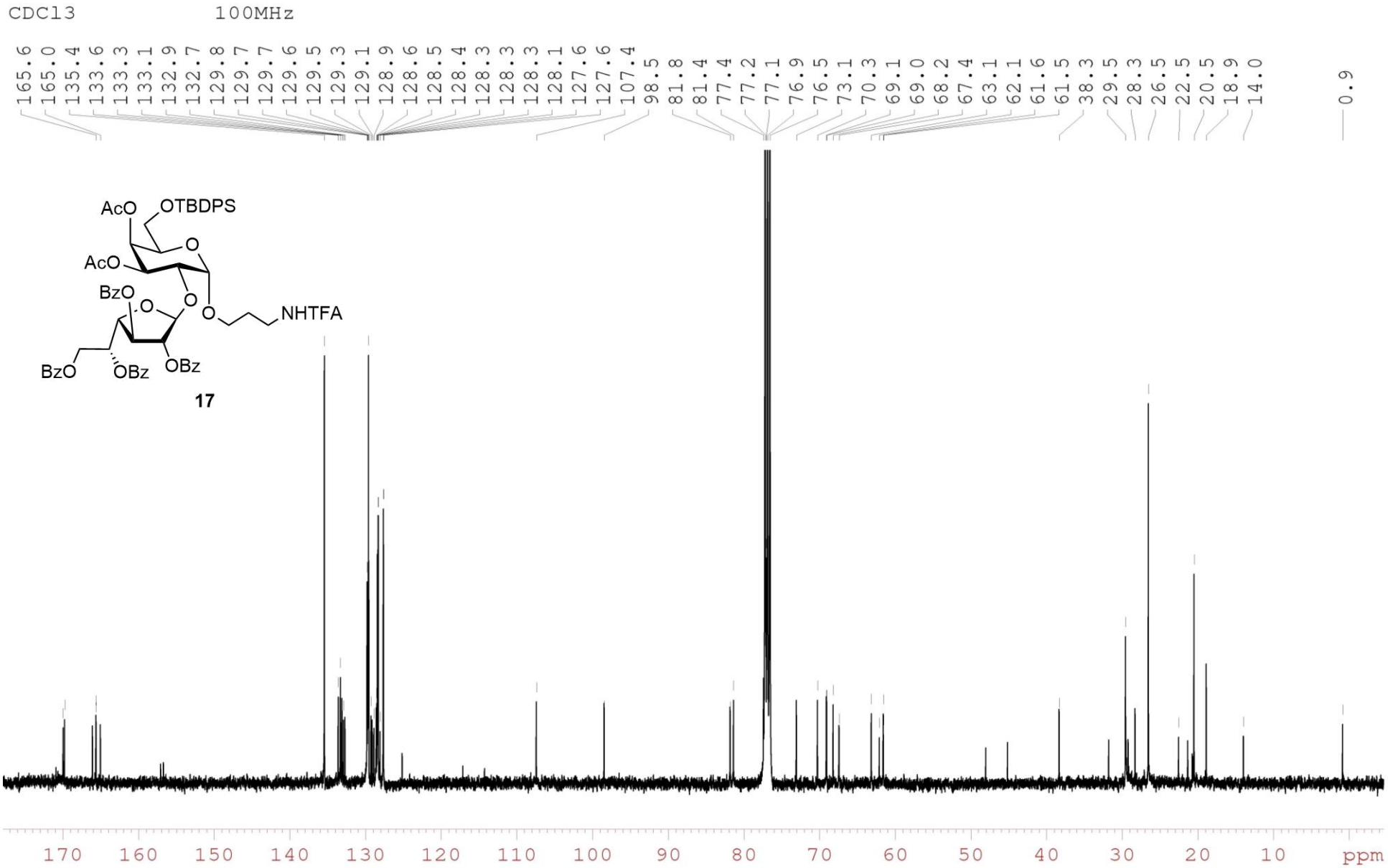
HSQC

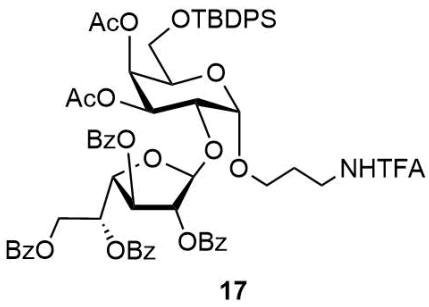

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-NMR spectrum of **17**



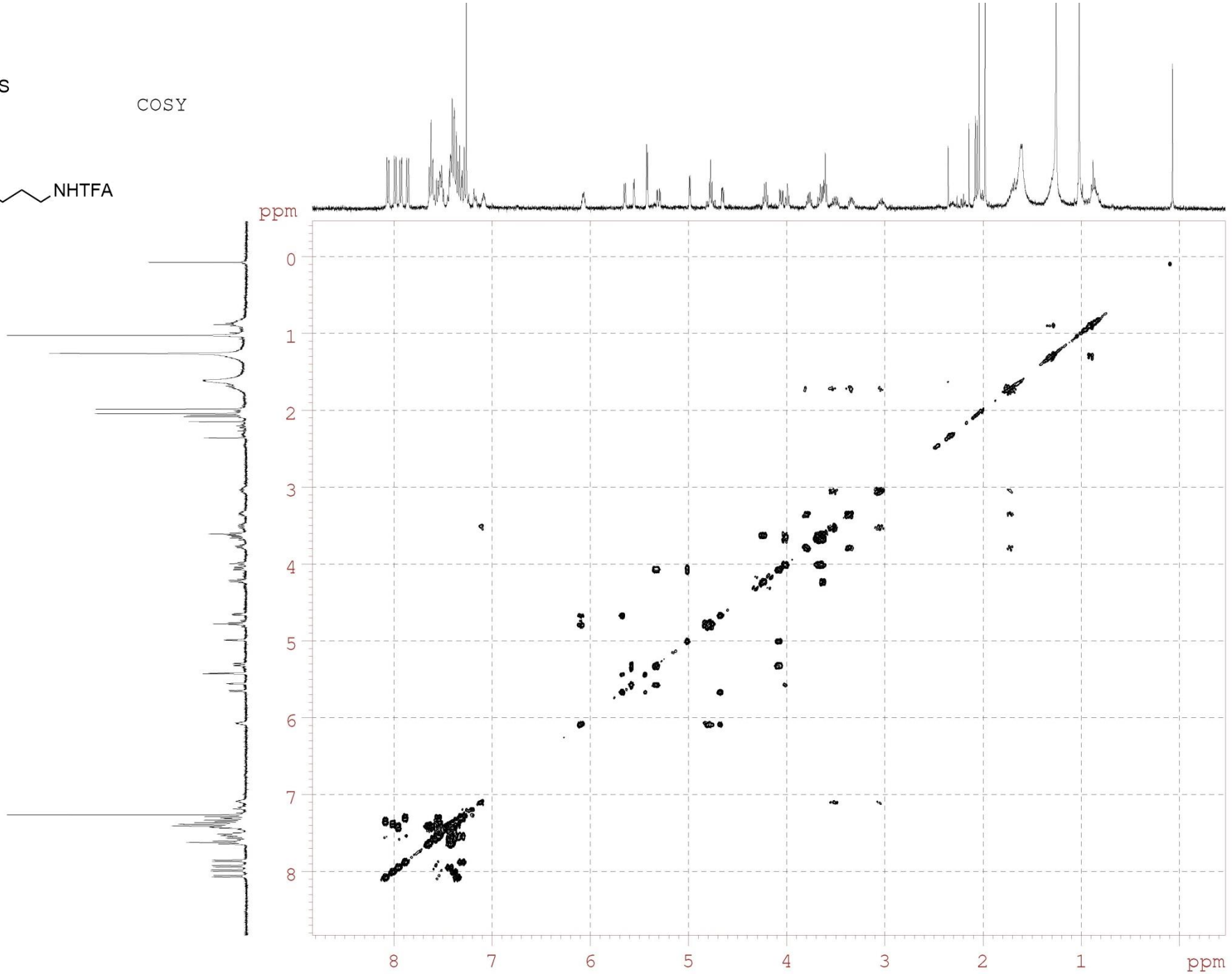
^{13}C-NMR spectrum of **17**

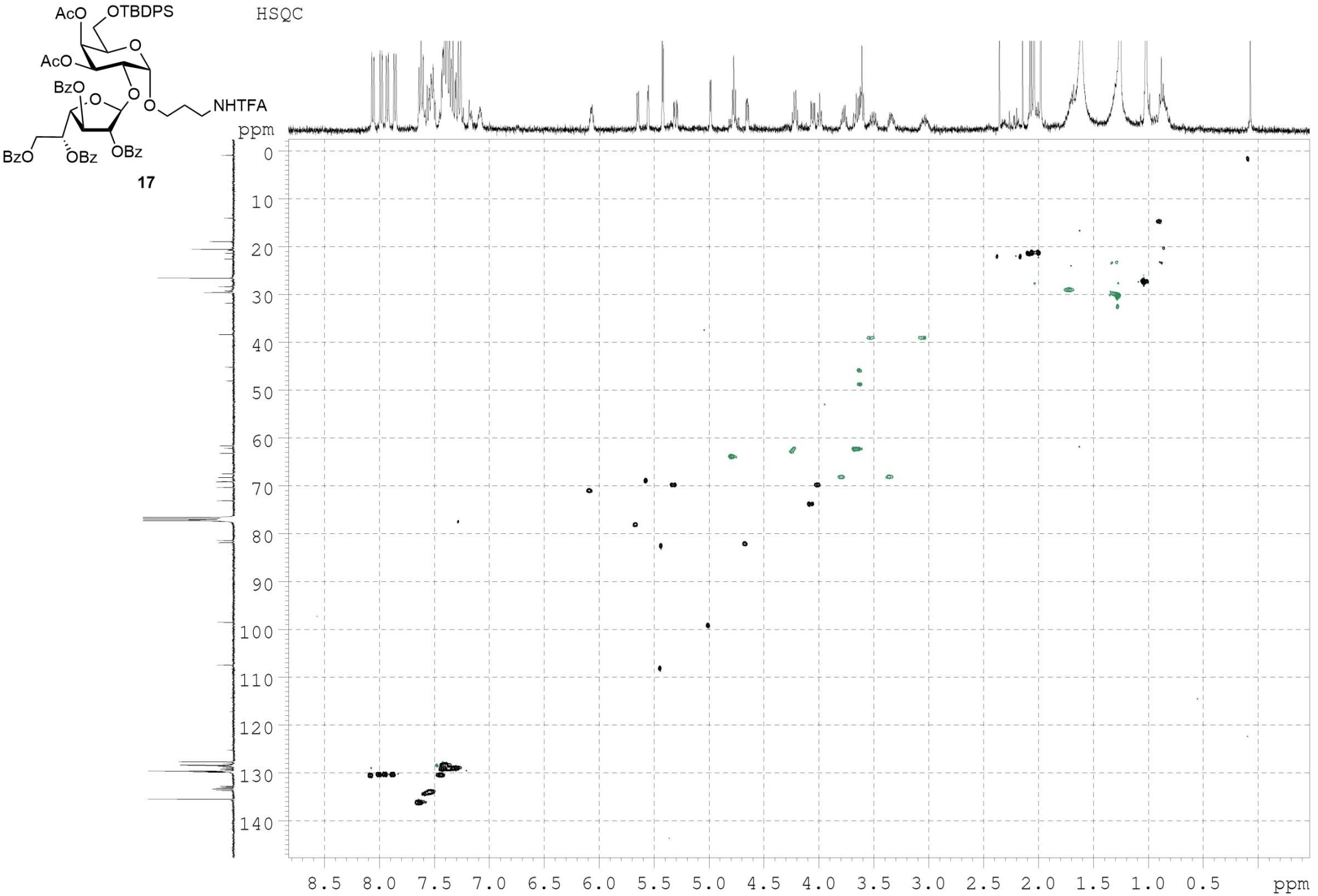



AcO
OTBDPS
AcO
BzO
NHTFA
BzO
OBz
OBz

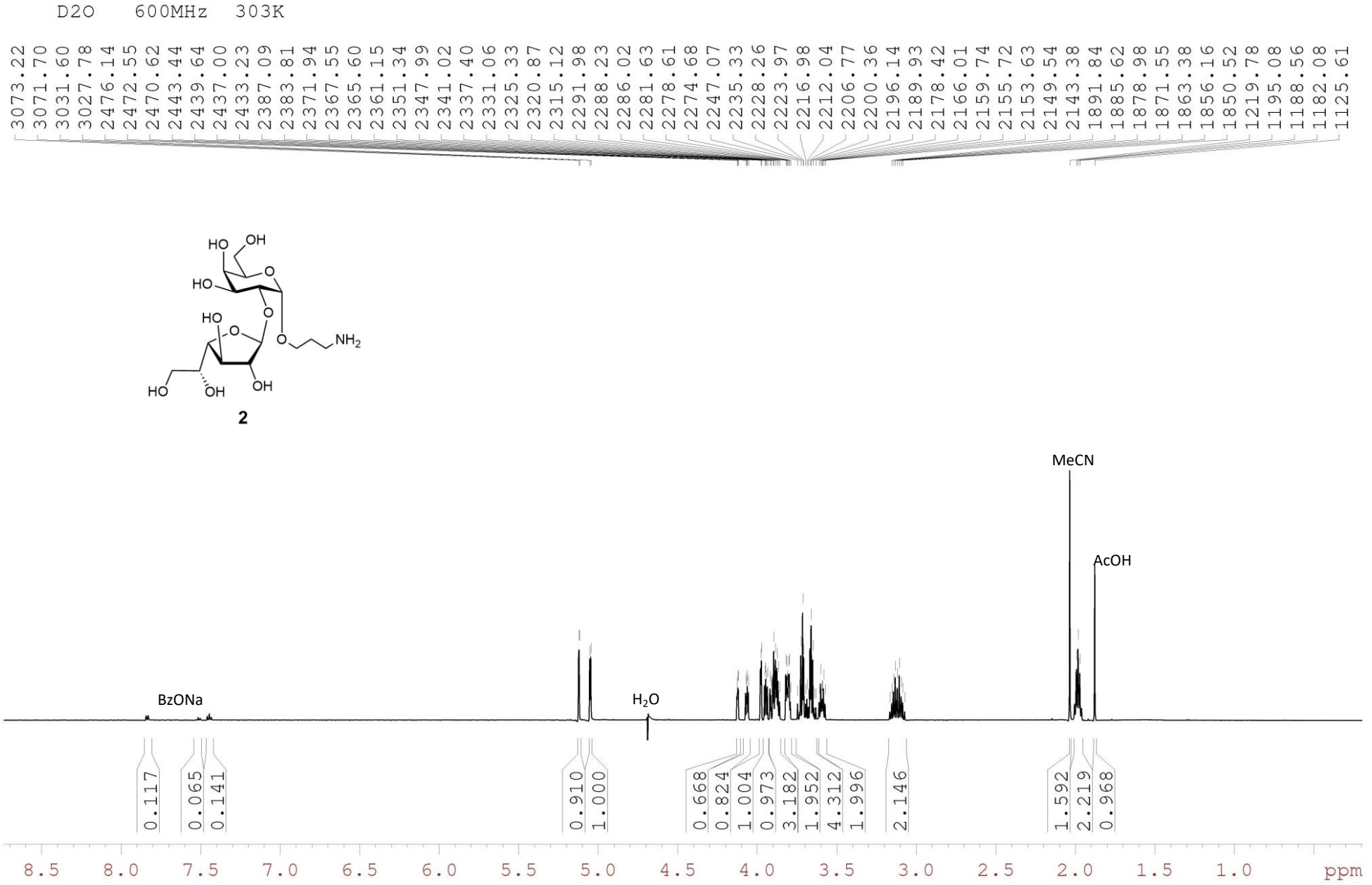
17

COSY

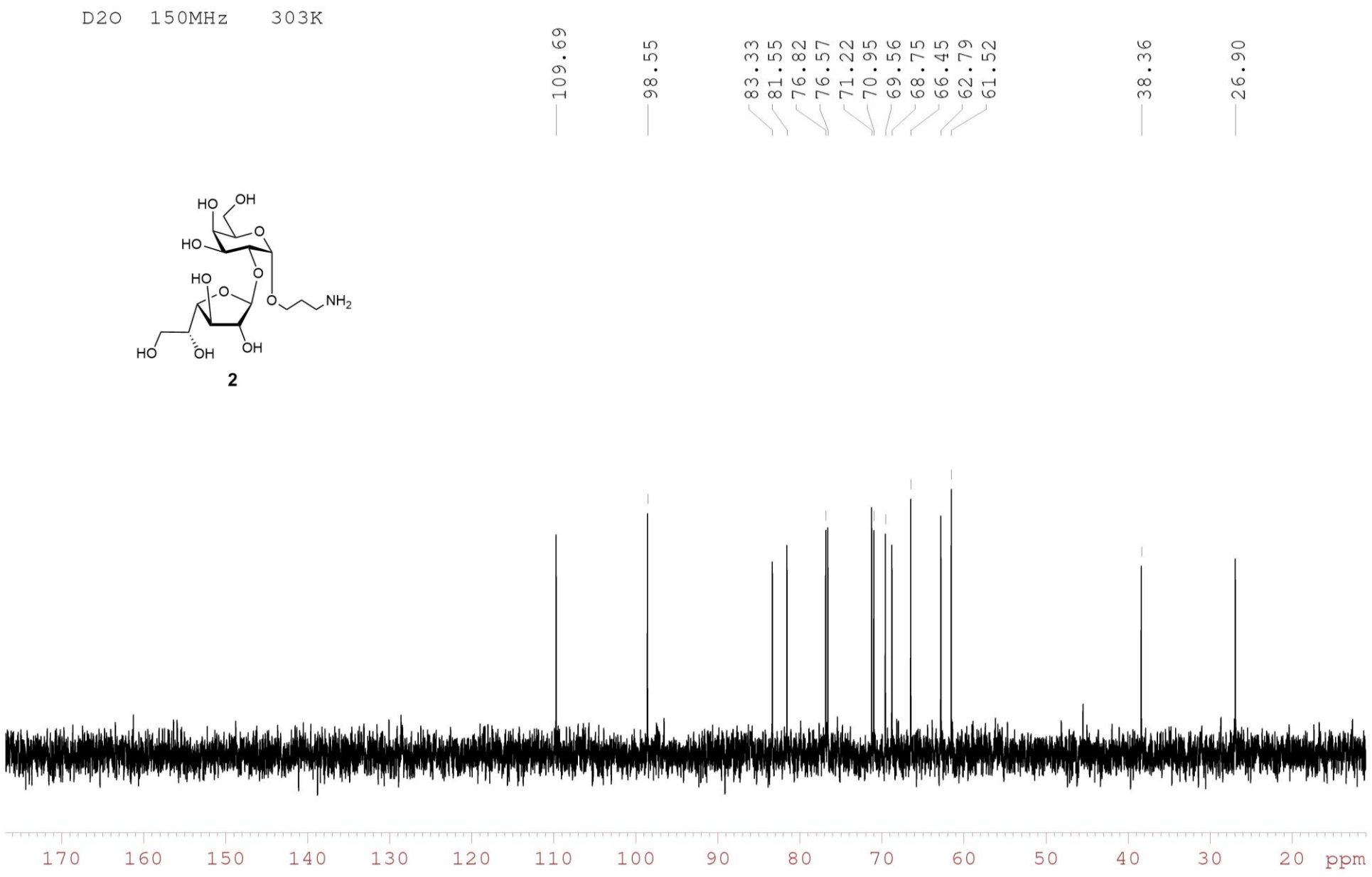

ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm

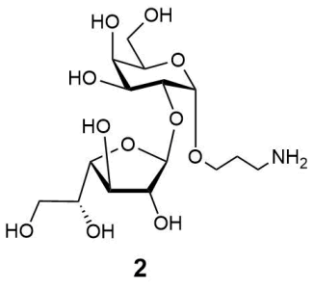

AcO
OTBDPS
AcO
BzO
NHTFA
BzO
OBz
OBz
17
HSQC
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

^{1}H-NMR spectrum of **2**



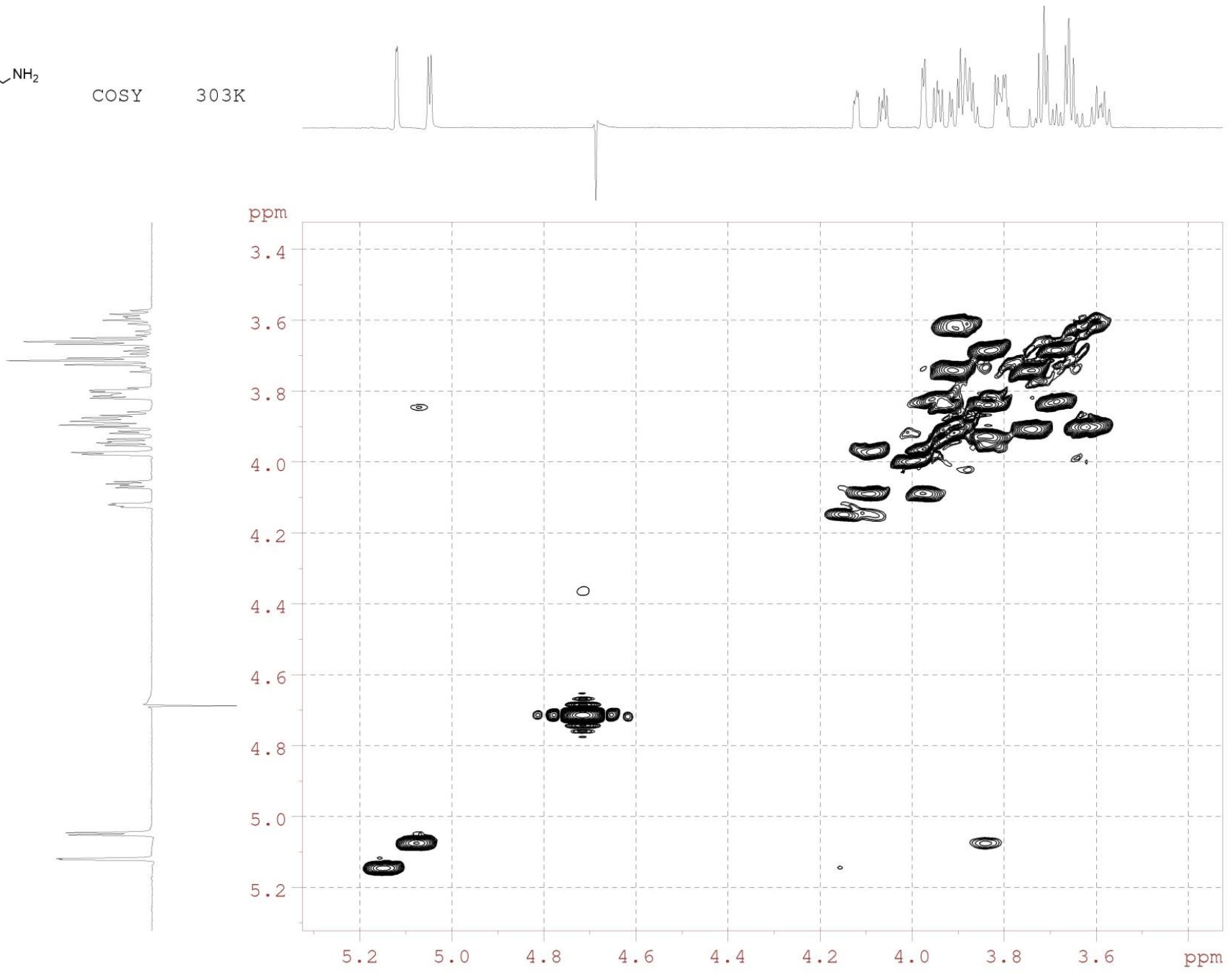
^{13}C-NMR spectrum of **2**

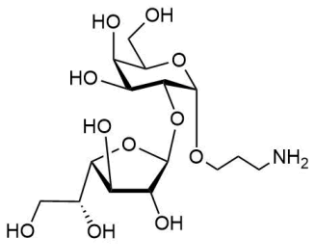



HO
OH
HO
O
HO
O
O
NH2
HO
O
HO
OH
OH

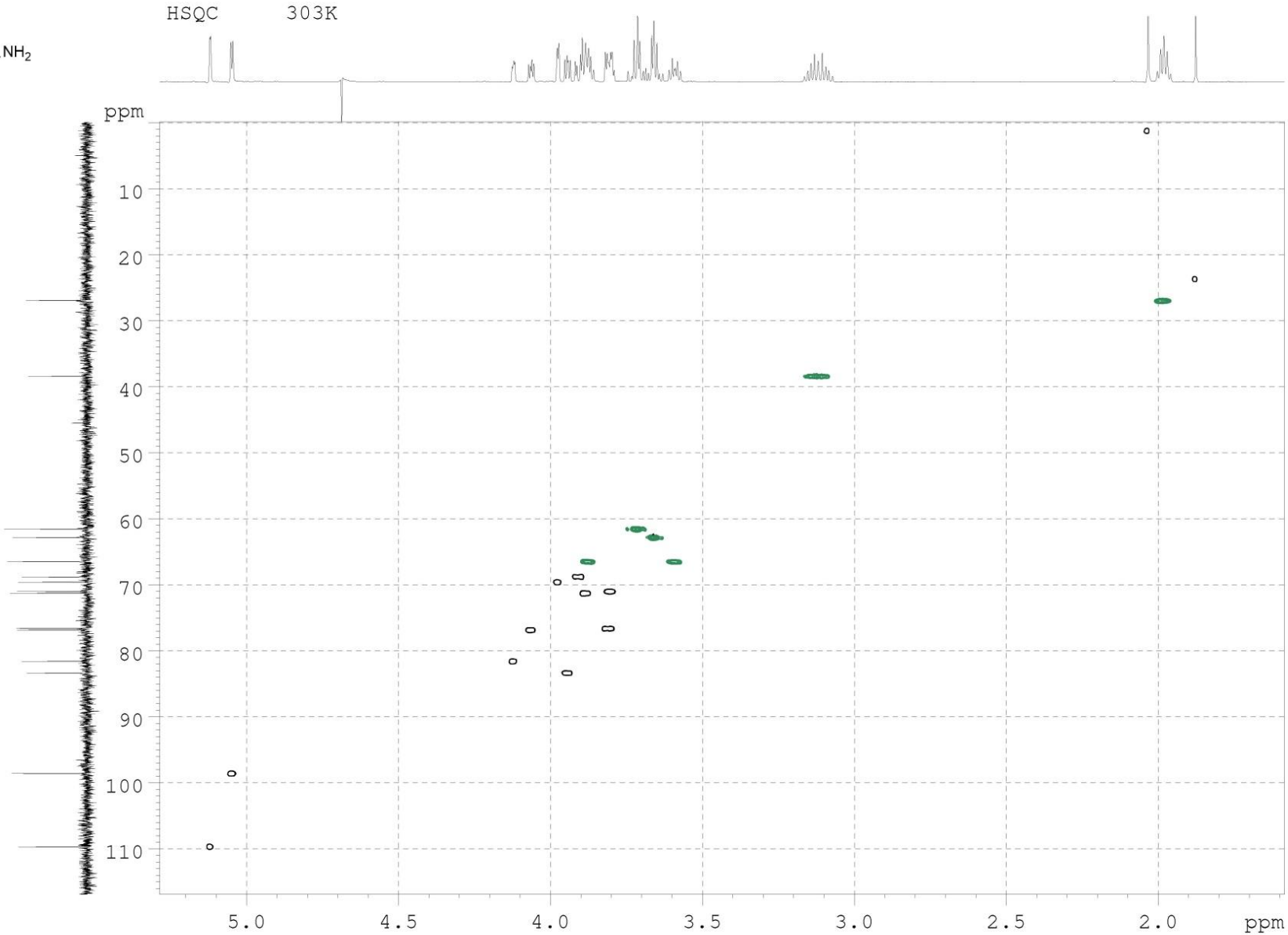
2

COSY 303K

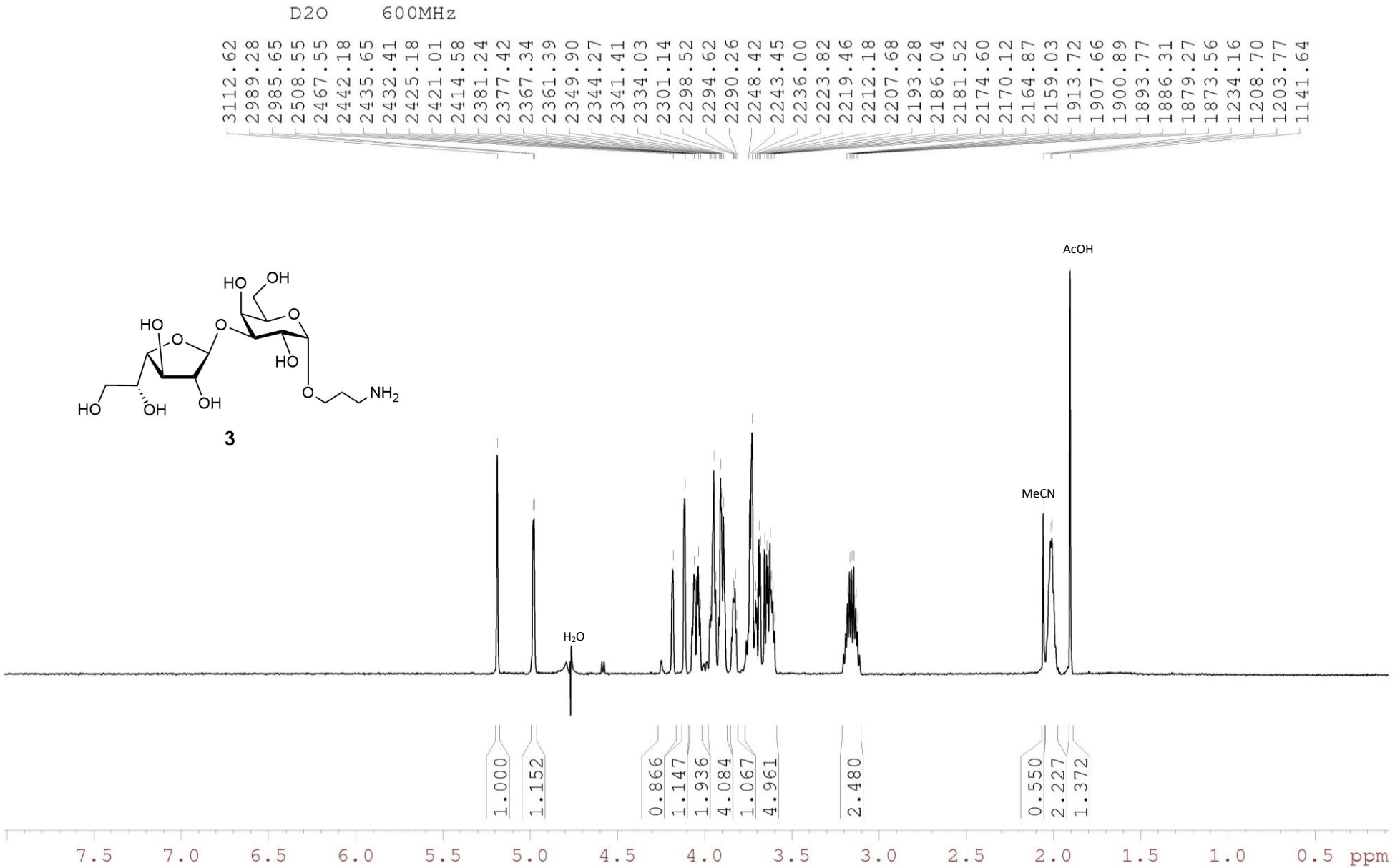

ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm


HO
OH
HO
O
HO
O
HO
O
O
NH2
HO
OH
OH

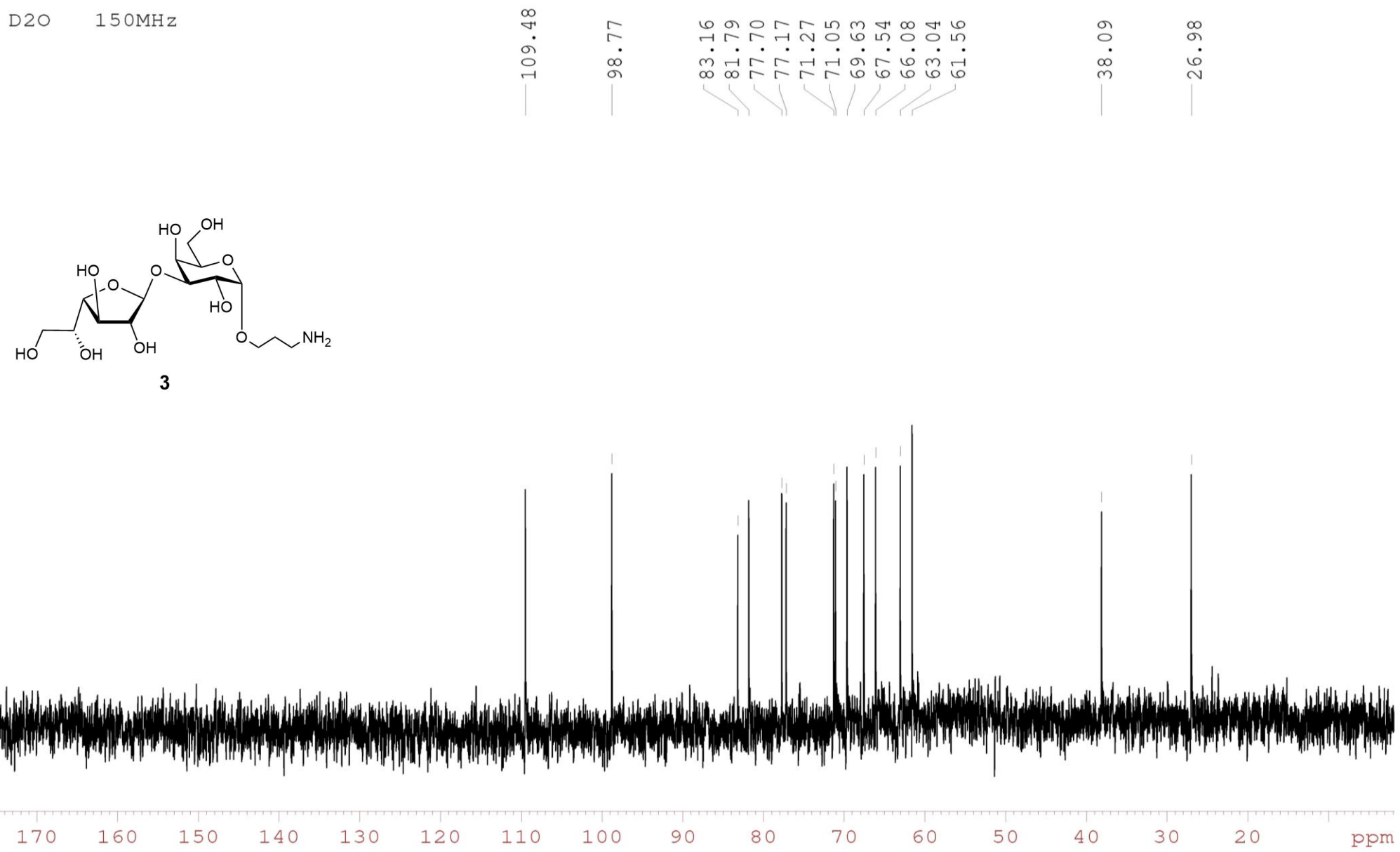
2

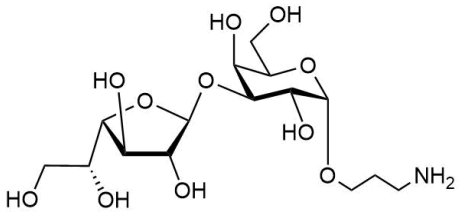

HSQC
303K
ppm
10
20
30
40
50
60
70
80
90
100
110
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

^{1}H-NMR spectrum of **3**

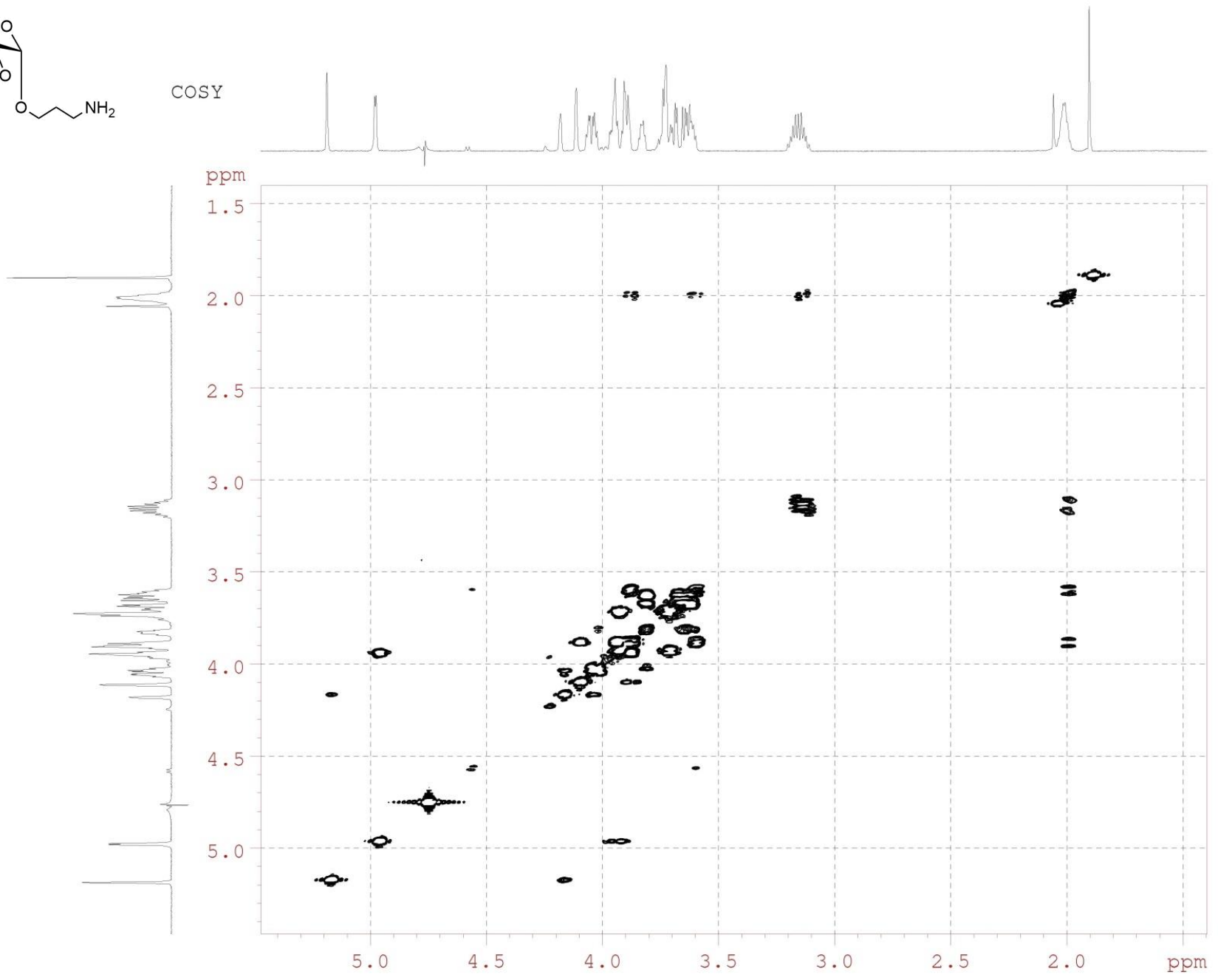


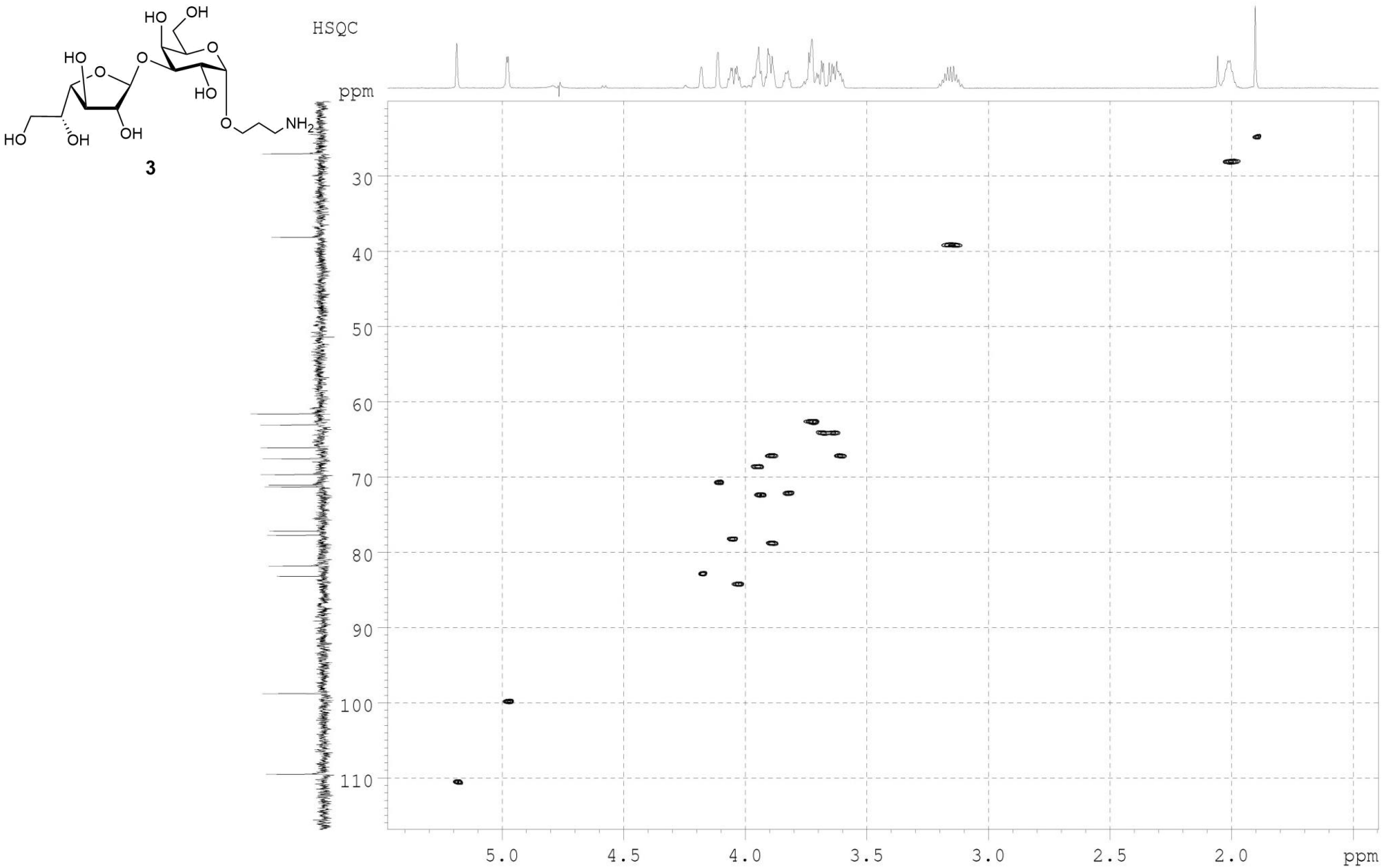
^{13}C-NMR spectrum of **3**




HO
OH
HO
O
O
O
HO
HO
OH
OH
O
NH2

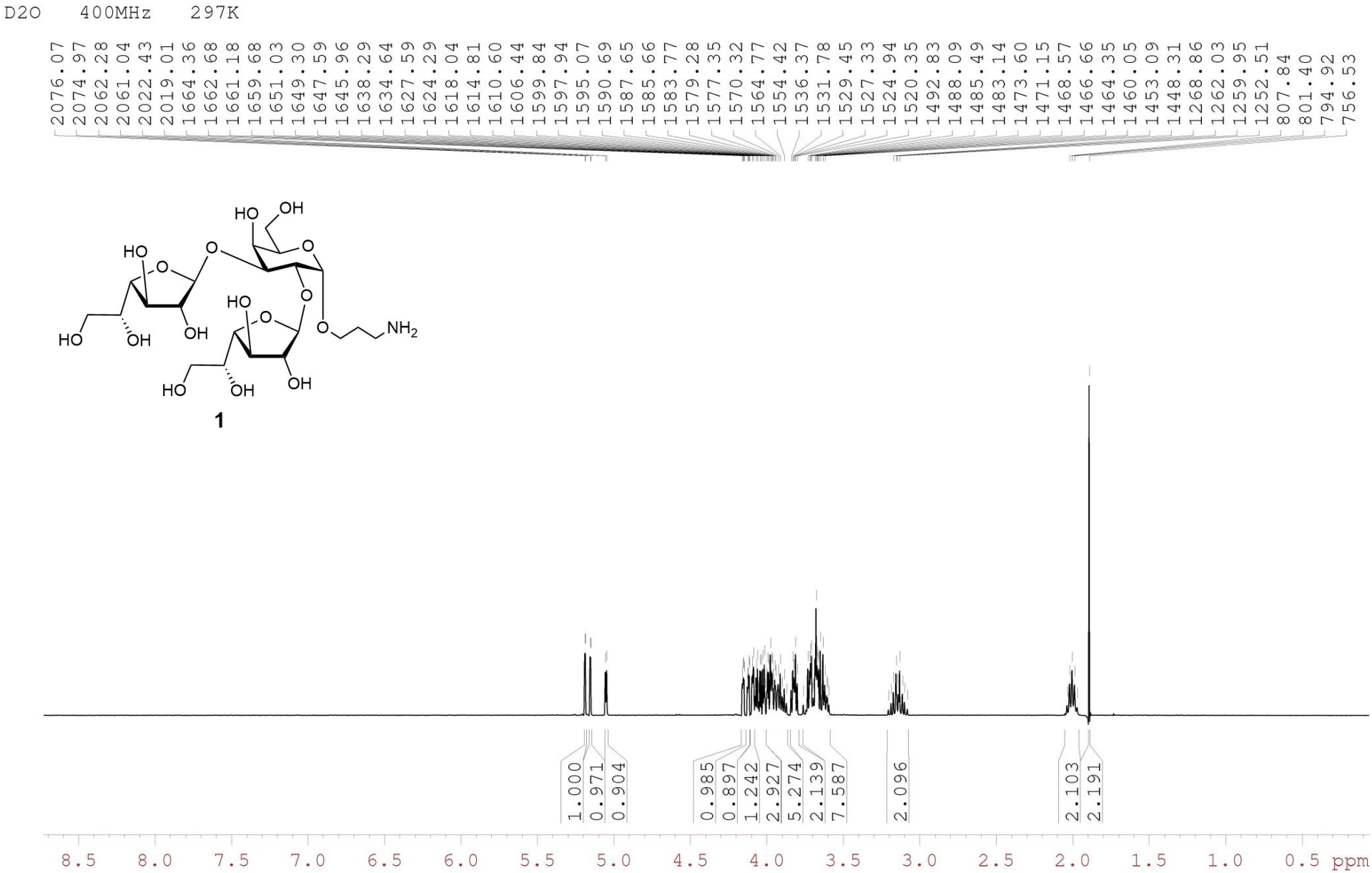
3


COSY
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

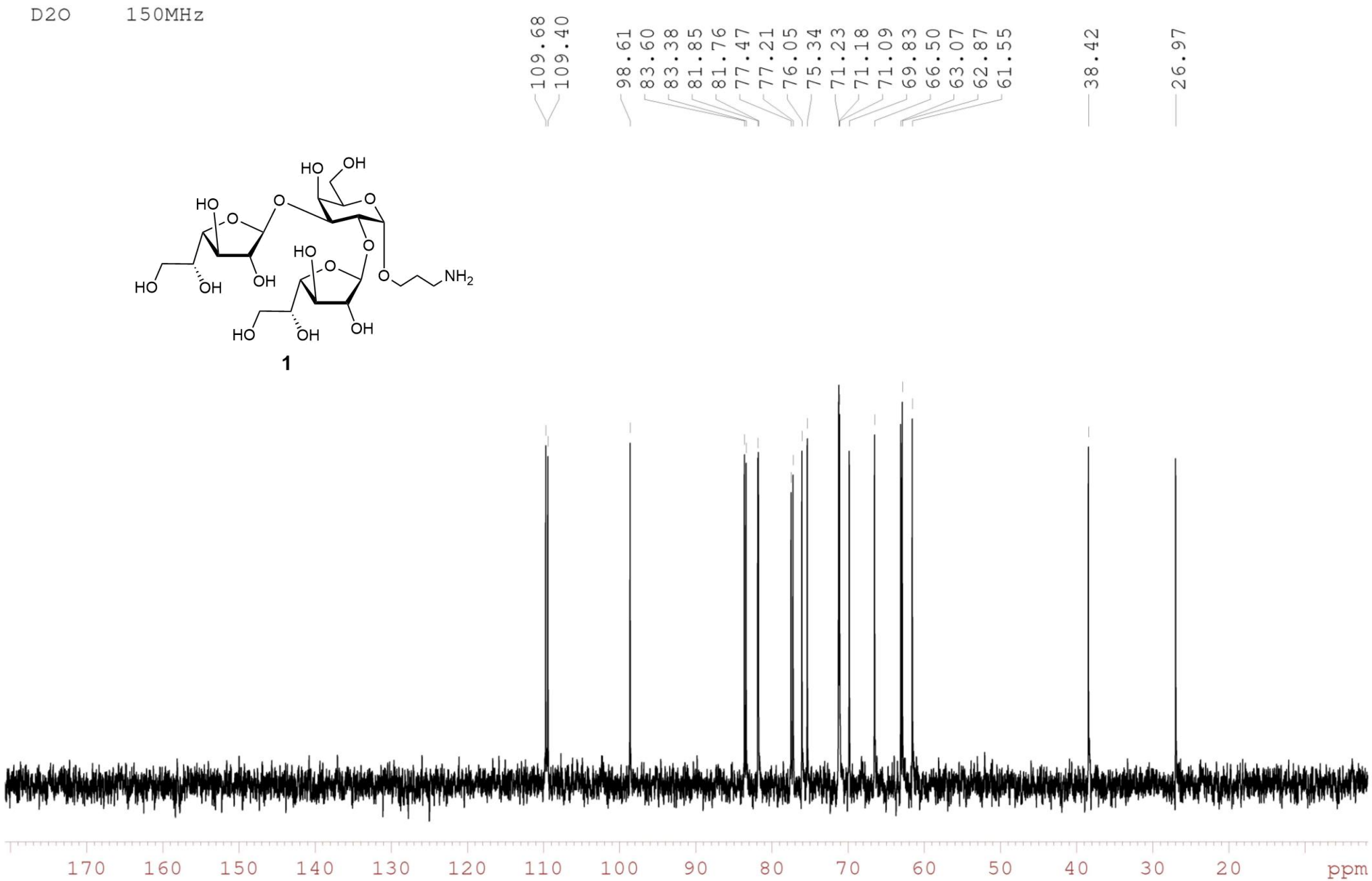


3

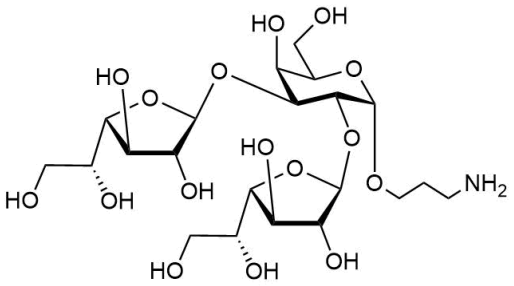
^{1}H-NMR spectrum of **1**



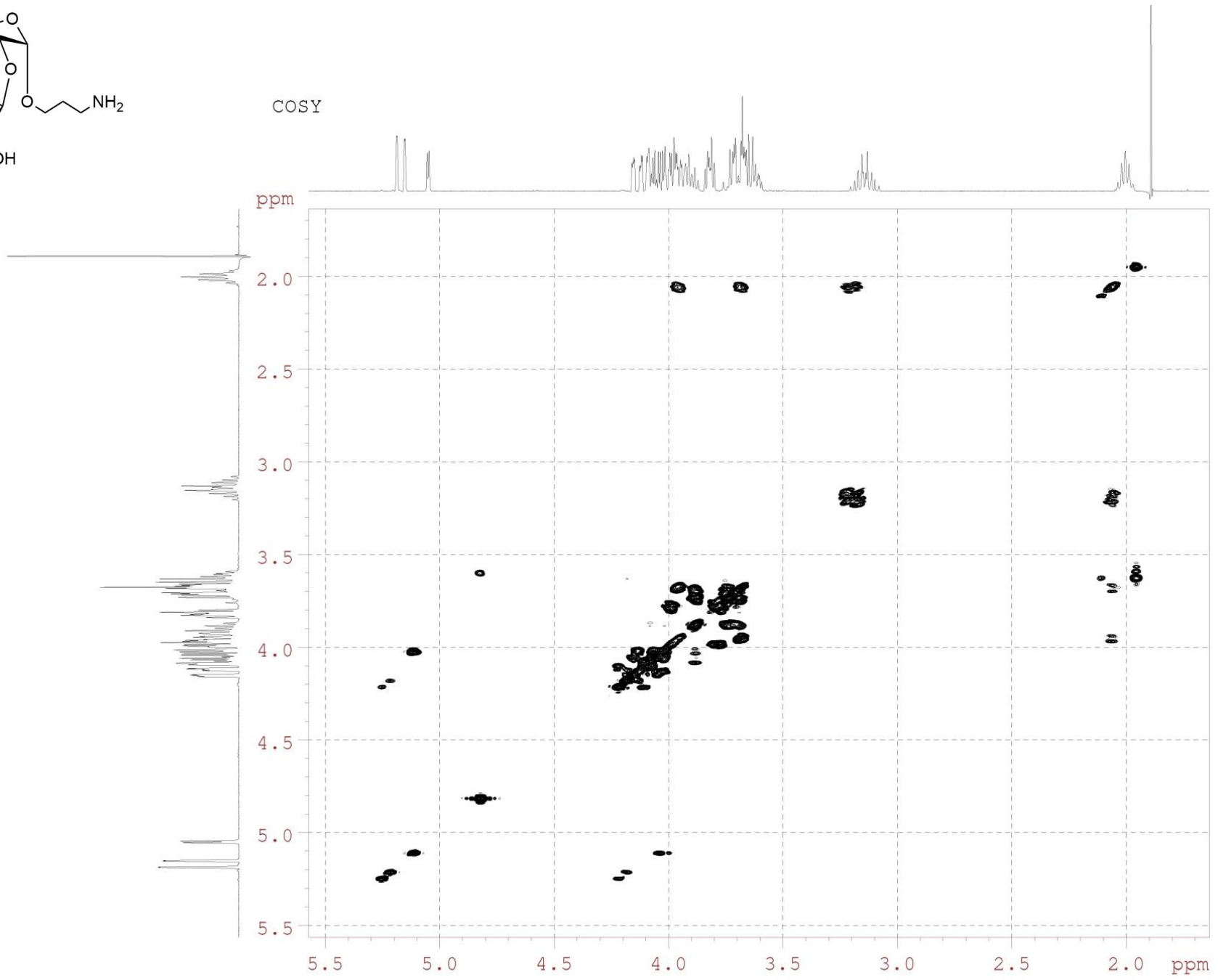
^{13}C-NMR spectrum of **1**

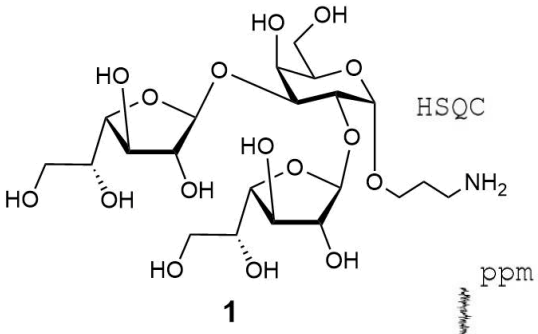


1


HO
OH
HO
O
O
HO
O
O
HO
O
NH2
HO
OH
OH
HO
OH
OH

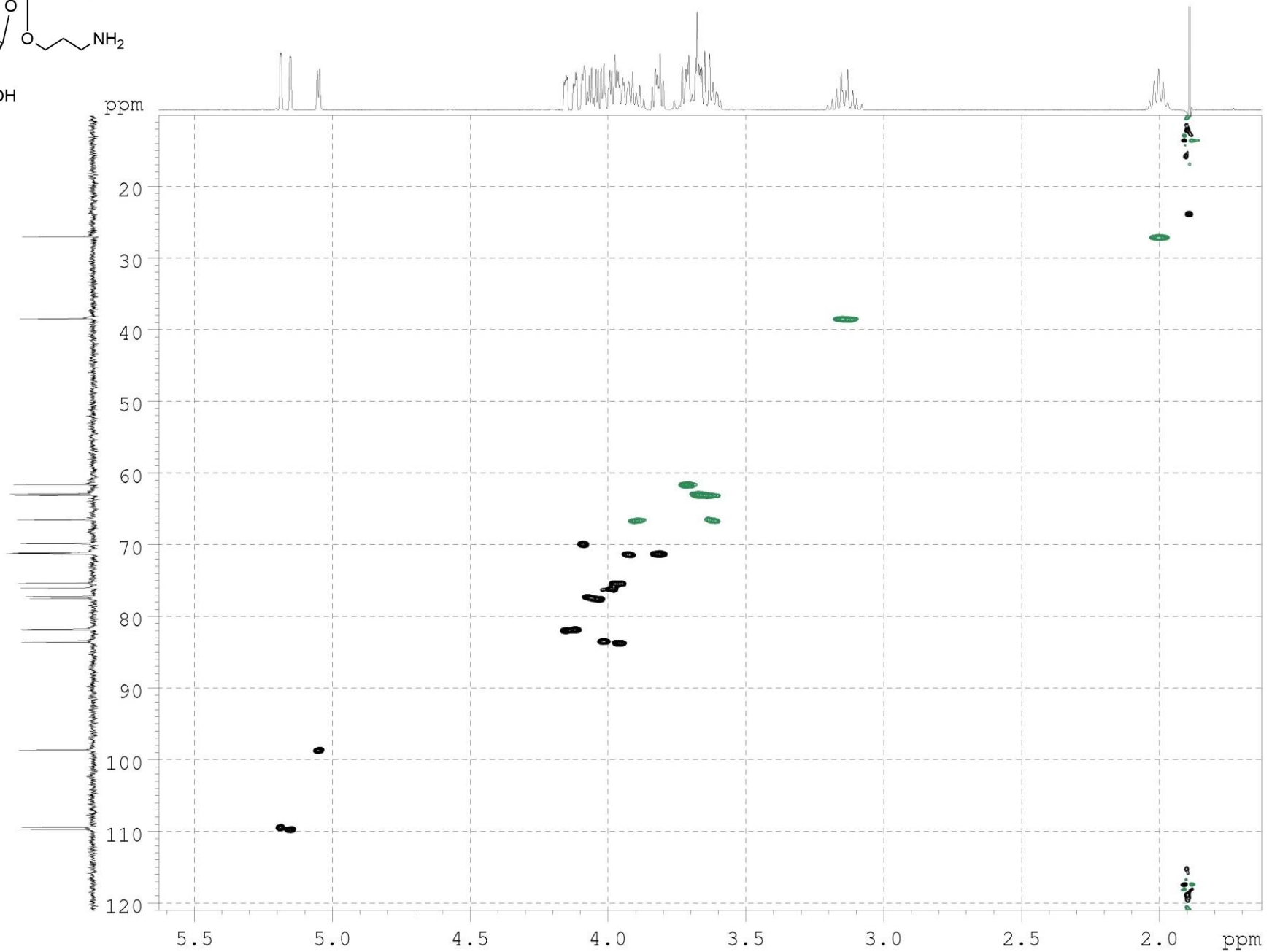
1


COSY
ppm
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


HO
OH
HO
O
O
HO
O
O
HO
OH
OH
HO
O
O
NH2
HO
OH
OH

1

HSQC 297K


ppm
20
30
40
50
60
70
80
90
100
110
120
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm