Support information
for

The Total Synthesis of Immunostimulant *α*-Galactosylceramides from Naturally Configured *a*-Galactoside Raffinose

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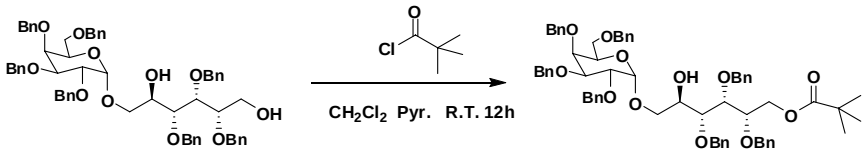


9 **10**

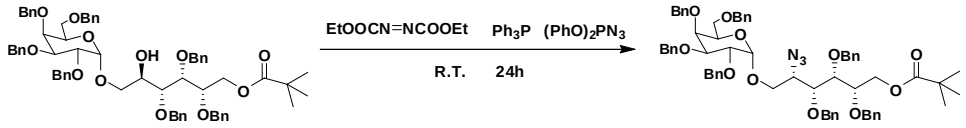
(2S,3R,4R,5R)-2,3,4-tris(benzyloxy)-5-hydroxy-6-(3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)hexyl pivalate 10

9 (6.555g, 6.72mmol**)** was dissolved in 150 mL of anhydrous DCM; 2.0mL of anhydrous pyridine were added and the solution was cooled-down to 0℃. Pivaloyl chloride (0.91 mL, 7.39mmol) were added dropwise and the solution was stirred overnight at room temperature. Solution was diluted with AcOEt and washed with a 1N solution of HCl, twice with water and with brine. After anhydrification with Na_2SO_4, solvent was evaporated and the crude was purified by flash chromatography (cyclohexane/EtoAc = 4:1) to give 6.89g of pure **10**, in 97% yield.

^{1}H NMR (400 MHz, CDCl3): δ 1.17 (s, 9H), 3.23 (br, 1H), 3.48 (d, 2H, J=6.3Hz), 3.80 (m, 5H,), 3.98 (m, 4H), 4.06 (dd, 1H, J=3.2Hz, J=9.9Hz), 4.16 (dd, 1H, J=6.6Hz, J=11.7Hz), 4.34 (m, 1H) 4.39 (dd, 2H, J=11.9Hz, J=30.9Hz), 4.66 (m, 10H), 4.83 (d, 1H, J=11.8Hz), 4.89 (d, 1H, J=3.2Hz), 4.92 (d, 1H, J=11.5Hz), 7.32 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 178.15, 138.56, 138.52, 138.19, 138.06, 137.81, 128.38, 128.33, 128.22, 128.08, 128.02, 127.87, 127.82, 127.78, 127.71, 127.64, 127.60, 127.53, 127.37, 99.06, 79.16, 78.32, 78.03, 77.63, 76.32, 74.75, 74.50, 73.71, 73.55, 73.41, 73.24, 72.81, 70.79, 70.48, 69.69, 68.76, 64.28, 60.41, 38.69, 27.21.

Exact mass (ESI-HRMS) for $C_{66}H_{74}NaO_{12}$ $[M+Na]^+$ found, 1081.5083; calcd, 1081.5072.



10 **11**

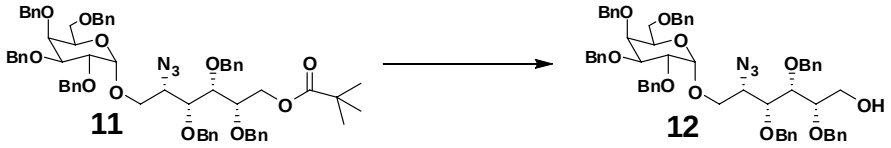
(2S,3S,4R,5S)-5-azido-2,3,4-tris(benzyloxy)-6-(3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)hexyl pivalate 11

To a well-stirred solution of alcohol **10** (6.6 g, 6.23 mmol) in dry THF (50 mL) at 0 °C was added diisopropyl azodicarboxylate (3.12 mL, 15.58 mmol) and triphenylphosphine (2.45g, 9.35 mmol), followed by dropwise addition of diphenylphosphoryl azide (4.00 mL, 18.56 mmol). After completion of addition, the reaction mixture was brought to room temperature and stirred for 24 h. Upon completion of the reaction (monitored by tlc), excess solvent was removed under vacuum and the residue was purified by flash chromatography (cyclohexane/EtOAc = 8:1) to obtain the azide **11** as an oil (6.2g, 92%).

^{1}H NMR (400 MHz, CDCl3): δ 1.18 (s, 9H), 3.47 (m, 3H), 3.60 (d, 2H, J=6.3Hz), 3.75 (m, 2H), 3.86 (m, 3H), 3.93 (s, 1H), 4.01 (dd, 1H, J=3.2Hz, J=10.0Hz), 4.28 (ddd, 2H, J=5.8Hz, J=11.5Hz, J=16.5Hz), 4.39 (q, 2H, J=11.8Hz), 4.66 (m, 12H), 4.93 (d, 1H, J=11.4Hz), 7.28 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 178.11, 138.84, 138.65, 137.95, 137.86, 137.75, 128.48, 128.38, 128.32, 128.26, 128.23, 127.93, 127.88, 127.82, 127.76, 127.70, 127.56, 127.51, 127.43, 98.80, 78.70, 78.50, 78.22, 76.33, 75.74, 75.01, 74.90, 74.74, 74.68, 73.42, 73.17, 73.06, 72.57, 69.70, 68.84, 68.72, 63.02, 61.33, 38.70, 27.19.

Exact mass (ESI-HRMS) for $C_{66}H_{77}N_4O_{11}$ $[M+NH_4]^+$ found, 1101.5586; calcd, 1101.5583.



11 **12**

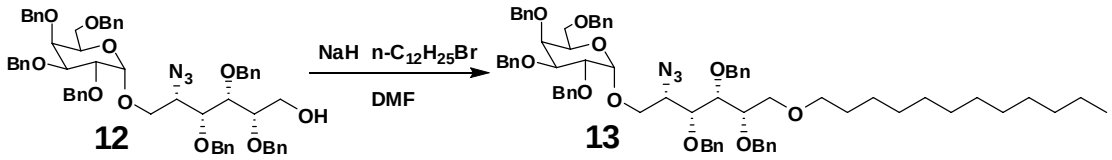
(2S,3S,4R,5S)-5-azido-2,3,4-tris(benzyloxy)-6-(3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)hexan-1-ol 12

11 (6.2 g, 5.7 mmol) was suspended in methanol (100 mL) at rt, and NaOMe (0.54g, 10 mmol) was added. The resulting solution was stirred at rt for 10 h. Acetic acid (0.63 mL, 11.2 mmol) was added, and the solvents were removed under reduced pressure. The residue was purified by filtration through silica gel (cyclohexane/EtOAc = 4:1) yielding **12** (5.56 g, 97%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 2.17 (br, 1H), 3.46 (p, 2H, J=9.5Hz), 3.58 (m, 3H), 3.71 (m, 3H), 3.82 (m, 1H), 3.90 (m, 4H), 4.02 (d, 1H, J=9.5Hz), 4.38 (q, 2H, J=11.8Hz), 4.63 (m, 9H), 4.78 (m, 3H), 4.93 (d, 1H, J=11.4Hz), 7.30 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 138.84, 138.66, 138.04, 138.01, 137.98, 128.56, 128.48, 128.42, 128.38, 128.33, 128.26, 128.03, 127.99, 127.90, 127.82, 127.72, 127.58, 98.81, 78.97, 78.78, 78.42, 78.31, 76.42, 75.08, 74.82, 74.74, 74.59, 73.51, 73.44, 73.14, 72.42, 69.88, 69.17, 68.50, 61.51, 61.30.

Exact mass (ESI-HRMS) for $C_{61}H_{69}N_4O_{10}$ $[M+NH_4]^+$ found, 1017.5005; calcd, 1017.5008.



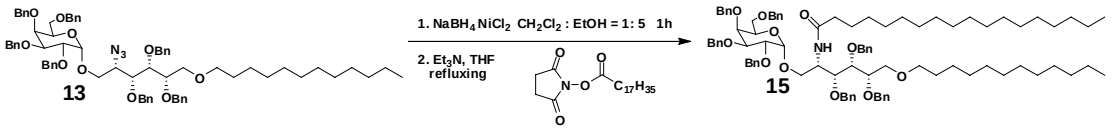
2-((2S,3R,4S,5S)-2-azido-3,4,5-tris(benzyloxy)-6-(dodecyloxy)hexyloxy)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran 13

12 (3g, 3mmol) was dissolved in anhydrous DMF (30mL) and cooled to 0°C; NaH (5mmol) was added, and after 20 min, *n*-dodecyl bromide (1.2mL, 5mmol) was added dropwise. Solution was allowed to warm to rt and stirred overnight. The reaction was quenched with 10 mL of an aqueous saturated solution of NH4Cl. Solution was diluted with AcOEt and washed three times with water and brine. After anhydrification with Na_2SO_4, the solvent was removed under vacuum, and the product was purified by flash chromatography (cyclohexane/EtOAc = 10:1) yielding **13** (2.69 g, 77%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.88 (t, 3H, J=6.6Hz), 1.25 (m, 18H), 1.53 (m, 2H) ppm 3.30 (sext., 2H, J=8.9Hz), 3.54 (m, 7H) ppm 3.70 (dd, 1H, J=4.8Hz, J=8.8Hz) ppm 3.76 (dd, 1H, J=2.3Hz, J=7.1Hz) ppm 3.88 (m, 4H) ppm 4.01 (dd, 1H, J=3.2Hz, J=10.0Hz) ppm 4.39 (dd, 2H, J=11.8Hz, J=27.6Hz) ppm 4.56 (m, 4H) ppm 4.73 (m, 8H) ppm 4.93 (d, 1H, J=11.5Hz) ppm 7.25 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 138.84, 138.67, 138.64, 138.27, 138.21, 138.11, 137.96, 128.35, 128.29, 128.26, 128.20, 127.84, 127.75, 127.69. 127.66, 127.58, 127.55, 127.48, 127.42, 98.76, 79.09, 78.69, 78.53, 76.79, 76.39, 75.01, 74.73, 74.70, 74.64, 73.38, 73.09, 72.46, 71.47, 70.54, 69.62, 68.86, 68.80, 61.48, 31.92, 29.70, 29.66, 29.52, 29.37, 26.20, 22.70, 14.14.

Exact mass (ESI-HRMS) for $C_{73}H_{93}N_4O_{10}$ $[M+NH_4]^+$ found, 1085.6892; calcd, 1085.6886.



N-((2S,3R,4S,5S)-3,4,5-tris(benzyloxy)-6-(dodecyloxy)-1-(3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)hexan-2-yl)stearamide 15

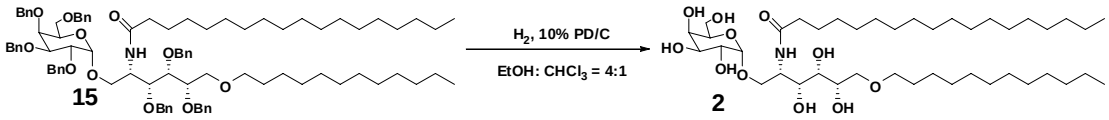
To a soln of **13** (1.169g, 1mmol) in 120 mL of a mixture DCM/methanol = 5:1 was added $NaBH_4$ (0.63g, 16.5mmol) and a catalytic amount of $NiCl_2$. The reaction mixture was stirred at room temperature for 1 h and concentrated. The residue was dissolved in CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated. This amine was dissolved in anhydrous THF (30mL), 2,5-dioxopyrrolidin-1-yl stearate (0.458g, 1.2mmol) and Et_3N (1mL) was added. The reaction mixture was stirred at 50°C for 14h, the solvents were removed under reduced pressure. The residue was purified by filtration through silica gel (cyclohexane/EtOAc = 8:1) yielding **15** (1.34g, 95%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.88 (t, 6H, J=6.7Hz), 1.24 (s, 46H), 1.47 (m, 2H), 1.57 (m, 2H), 2.09 (m, 2H), 3.30 (m, 3H), 3.44 (dd, 1H, J=6.3Hz, J=9.0Hz), 3.54 (m, 3H), 3.70 (m, 4H), 3.86 (m, 1H), 3.93 (m, 2H), 4.13 (d, 1H, J=8.2Hz), 4.28 (d, 1H, J=11.9Hz), 4.40 (m, 2H), 4.58 (m, 9H) 4.75 (d, 1H, J=11.1Hz), 4.80 (d, 1H, J=3.4Hz), 4.84 (d, 1H, J=8.0Hz), 4.87 (d, 1H, J=8.6Hz), 6.01 (d, 1H, J=9.3Hz), 7.19 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 172.89, 138.79, 138.75, 138.72, 138.60, 138.57, 137.89, 128.28, 127.26, 98.84, 80.27, 78.81, 78.49, 77.23, 76.59, 75.12, 74.95, 74.80, 74.63, 73.36, 73.29, 73.16,

72.94, 71.30, 69.92, 69.78, 69.06, 48.96, 36.69, 31.93, 29.84, 29.72, 29.67, 29.59, 29.46, 29.41, 29.37, 26.22, 25.74, 22.70, 14.14.

Exact mass (ESI-HRMS) for $C_{91}H_{126}NO_{11}$ $[M+H]^+$ found, 1408.9328; calcd, 1408.9325.



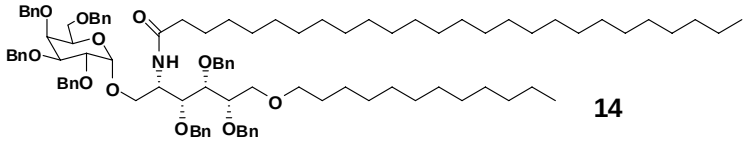
N-((2S,3R,4S,5S)-6-(dodecyloxy)-3,4,5-trihydroxy-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)hexan-2-yl)stearamide 2

To a solution of **15** (0.7g, 0.51mmol) in EtOH (10mL) and $CHCl_3$ (2.5mL) was added $Pd(OH)_2/C$ (10 wt% Pd dry basis on carbon, 100 mg), and the mixture was hydrogenated at r.t. for 5h. The suspension was diluted with pyridine (15mL) and filtered through Celite pad. The filter cake was rinsed with $CHCl_3$/MeOH (10:1, 4×10 mL) and pyridine (4×10 mL). The combined filtrate and washings were concentrated in vacuo. The residual solid was triturated with hexanes/EtOAc/CH_2Cl_2 (50:10:1, 3×2 mL) to give pure α-galactosylceramide **2** (240mg, 61%) as a white solid.

^{1}H NMR (400 MHz, pyridine-d5): δ 0.88 (t, 6H, J=6.3Hz), 1.26 (m, 46H), 1.60 (m, ,2H), 1.83 (td, 2H, J=7.9Hz, J=16.1Hz), 2.53 (t, 2H, J=7.4Hz), 3.52 (m, 2H), 4.03 (dd, 1H, J=6.9Hz, J=9.2Hz), 4.09 (dd, 1H, J=5.6Hz, J=9.5Hz), 4.17 (dd, 1H, J=5.3Hz, J=9.8Hz), 4.40 (d, 2H, J=5.9Hz), 4.52 (m, 5H), 4.66 (dd, 1H, J=3.4Hz, J=9.9Hz), 4.72 (t, 1H, J=6.0Hz), 4.90 (m, 1H), 5.19 (m, 1H), 5.46 (d, 1H, J=3.3Hz), 8.70 (d, 1H, J=8.8Hz).

^{13}C NMR (100 MHz, pyridine-d5): δ176.06, 103.01, 75.50, 74.79, 74.35, 74.07, 73.51, 73.48, 73.15, 72.73, 72.38, 70.89, 64.46, 53.43, 46.23, 38.74, 34.09, 32.25, 31.95, 31.90, 31.82, 31.77, 31.59, 28.49, 28.39, 24.91, 24.78, 16.27.

Exact mass (ESI-HRMS) for $C_{42}H_{84}NO_{11}$ $[M+H]^+$ found, 778.6051; calcd, 778.6039.



N-((2S,3R,4S,5S)-3,4,5-tris(benzyloxy)-6-(dodecyloxy)-1-(3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)hexan-2-yl)hexacosanamide 14

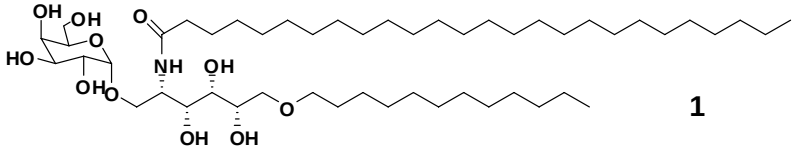
To a soln of **13** (1.169g, 1mmol) in 120 mL of a mixture DCM/methanol = 5:1 was added $NaBH_4$ (0.63g, 16.5mmol) and a catalytic amount of $NiCl_2$. The reaction mixture was stirred at room temperature for 1 h and concentrated. The residue was dissolved in CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated. This amine was dissolved in anhydrous THF (30mL), 2,5-dioxopyrrolidin-1-yl hexacosanoate (0.593g, 1.2mmol) and Et_3N (1mL) was added. The reaction mixture was stirred at 50°C for 14h, the solvents were removed under reduced pressure. The residue was purified by filtration through silica gel (cyclohexane/EtOAc = 8:1) yielding **14** (1.33g, 88%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.88 (t, 6H, J=6.7Hz), 1.28 (m, 60H), 1.47 (m, 2H), 1.56 (m, 2H), 1.74 (m, 2H), 2.08 (m, 2H), 3.28 (m, 2H), 3.40 (ddd, 2H, J=6.5Hz, J=9.2Hz, J=27.9Hz), 3.51 (m, 2H), 3.56 (dd, 1H, J=6.3Hz, J=9.6Hz), 3.65 (dd, 1H, J=6.4Hz, J=8.6Hz), 3.68 (dd, 1H, J=2.6Hz, J=8.2Hz), 3.74 (m, 2H), 3.85 (dt, 1H, J=2.6Hz, J=5.9Hz), 3.92 (ddd, 2H, J=4.9Hz, J=9.3Hz, J=14.5Hz), 4.12 (d, 1H, J=7.6Hz), 4.29 (d, 1H, J=11.9Hz), 4.39 (m, 2H), 4.48 (d, 1H, J=7.8Hz), 4.51 (d, 1H, J=8.1Hz), 4.62 (m, 7H), 4.75 (d, 1H, J=11.2Hz), 4.79 (d, 1H, J=3.6Hz), 4.84 (d, 1H, J=10.8Hz), 4.86 (d, 1H,

J=11.3Hz), 6.00 (d, 1H, J=9.3Hz), 7.23 (m, 35H)

^{13}C NMR (100 MHz, CDCl3): δ 172.98, 138.83, 138.76, 138.63, 137.94, 128.32, 128.28, 128.19, 128.11, 128.08, 128.01, 127.94, 127.83, 127.79, 127.63, 127.55, 127.50, 127.36, 127.30, 98.81, 80.30, 78.85, 78.48, 77.30, 76.62, 75.13, 75.00, 74.89, 74.68, 73.41, 73.31, 73.21, 72.98, 71.35, 69.99, 69.83, 69.08, 68.99, 49.04, 36.73, 31.95, 29.86, 29.73, 29.63, 29.49 29.39, 26.24, 25.78, 22.72, 14.15.

Exact mass (ESI-HRMS) for $C_{99}H_{142}NO_{11}$ $[M+H]^+$ found, 1521.0546; calcd, 1521.0577.



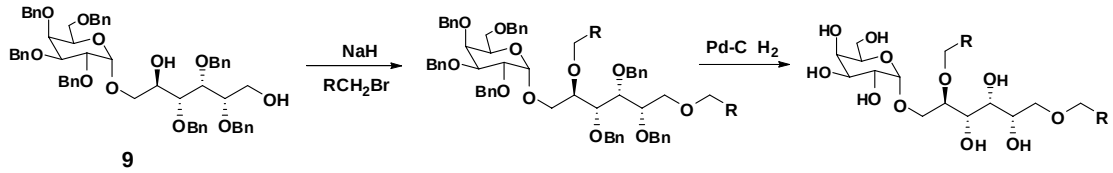
N-((2S,3R,4S,5S)-6-(dodecyloxy)-3,4,5-trihydroxy-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)hexan-2-yl)hexacosanamide 1

To a solution of **14** (0.76g, 0.50mmol) in EtOH (10mL) and $CHCl_3$ (2.5mL) was added $Pd(OH)_2/C$ (10 wt% Pd dry basis on carbon, 100 mg), and the mixture was hydrogenated at r.t. for 5h. The suspension was diluted with pyridine (15mL) and filtered through Celite pad. The filter cake was rinsed with $CHCl_3$/MeOH (10:1, 4×10 mL) and pyridine (4×10 mL). The combined filtrate and washings were concentrated in vacuo. The residual solid was triturated with hexanes/EtOAc/CH_2Cl_2 (50:10:1, 3×2 mL) to give pure α-galactosylceramide **2** (312mg, 70%) as a white solid.

^{1}H NMR (400 MHz, pyridine-d5): δ 0.88 (t, 6H, J=6.3Hz), 1.27 (m, 62H), 1.54 (td, 2H, J=6.9Hz, J=13.7Hz), 1.79 (m, 2H), 2.55 (m, 2H), 3.45 (m, 2H), 3.99 (m, 2H), 4.16 (dd, 1H, J=4.6Hz, J=9.9Hz), 4.46 (m, 9H), 4.89 (m, 1H), 5.10 (m, 1H), 5.44 (d, 1H, J=2.3Hz), 8.82 (d, 1H, J=8.1Hz)

^{13}C NMR (100 MHz, pyridine-d5): δ 176.33, 102.80, 75.03, 74.69, 74.50, 74.04, 73.57, 73.52, 73.35, 72.67, 72.29, 70.46, 64.41, 53.93, 38.71, 34.08, 32.16, 32.02, 31.93, 31.79, 31.55, 28.43, 24.89, 16.24.

Exact mass (ESI-HRMS) for $C_{42}H_{100}NO_{11}$ $[M+H]^+$ found, 890.7296; calcd, 890.7291.



3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)-6-((2R,3R,4R,5S)-3,4,5-tris(benzyloxy)-2,6-bis(octyloxy)hexyloxy)tetrahydro-2H-pyran 16

9 (0.65g, 0.67mmol**)** was dissolved in anhydrous DMF (10mL) and cooled to 0°C; NaH (48mg, 2mmol) was added, and after 20 min, 1-bromooctane (386mg, 2mmol) was added dropwise. Solution was allowed to warm to rt and stirred overnight. The reaction was quenched with 10 mL of an aqueous saturated solution of NH4Cl. Solution was diluted with AcOEt and washed three times with water and brine. After anhydrification with Na_2SO_4, the solvent was removed under vacuum, and the product was purified by flash chromatography (cyclohexane/EtOAc = 10:1) yielding **16** (0.60mg, 75%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.87 (m, 6H), 1.24 (m, 20H), 1.44 (m, 4H), 3.26 (m, 3H), 3.43 (td, 1H, J=6.6Hz, J=8.5Hz), 3.52 (m, 4H), 3.64 (dd, 1H, J=4.6Hz, J=9.2Hz), 3.82 (m, 4H), 3.91 (dd, 1H, J=2.7Hz, J=10.0Hz), 3.97 (m, 3H), 4.03 (dd, 1H, J=3.5Hz, J=10.0Hz), 4.38 (d, 1H, J=11.8Hz), 4.46 (m, 1H), 4.54 (d, 1H, J=7.7Hz), 4.57 (d, 1H, J=7.6Hz), 4.61 (d, 1H, J=11.8Hz), 4.69 (m, 5H), 4.75 (d, 1H, J=2.8Hz), 4.77 (d, 1H, J=2.2Hz), 4.85 (d, 1H, J=11.8Hz) 4.94 (d, 1H, J=6.6Hz), 4.95 (d, 1H, J=0.8Hz), 7.30 (m, 35H).
^{13}C NMR (100 MHz, CDCl3): δ 128.45, 128.42, 128.34, 128.26, 128.21, 128.08, 128.05, 127.81, 127.74, 127.62, 127.54, 127.49, 127.44, 97.61, 79.81, 79.19, 79.02, 78.82, 76.66, 75.21, 74.88, 74.37, 73.46, 73.17, 72.84, 72.81, 71.94, 71.58, 70.44, 69.27, 68.92, 66.22, 31.97, 30.40, 29.86, 29.66, 29.59, 29.45, 29.42, 26.37, 26.31, 22.79, 14.26
Exact mass (ESI-HRMS) for $C_{77}H_{99}O_{11}$ $[M+H]^+$ found, 1199.7188; calcd, 1199.7187.

3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)-6-((2R,3R,4R,5S)-3,4,5-tris(benzyloxy)-2,6-bis(decyloxy)hexyloxy)tetrahydro-2H-pyran 17

9 (0.65g, 0.67mmol**)** was dissolved in anhydrous DMF (10mL) and cooled to 0°C; NaH (48mg, 2mmol) was added, and after 20 min, 1-bromodecane (442mg, 2mmol) was added dropwise. Solution was allowed to warm to rt and stirred overnight. The reaction was quenched with 10 mL of an aqueous saturated solution of NH4Cl. Solution was diluted with AcOEt and washed three times with water and brine. After anhydrification with Na_2SO_4, the solvent was removed under vacuum, and the product was purified by flash chromatography (cyclohexane/EtOAc = 10:1) yielding **17** (0.65mg, 77%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.87 (t, 6H, J=6.5Hz), 1.23 (m, 36H), 1.48 (m, 4H), 3.26 (m, 3H), 3.44 (dd, 1H, J=6.9Hz, J=14.6Hz), 3.54 (m, 4H), 3.66 (dd, 1H, J=4.6Hz, J=8.8Hz), 3.84 (m, 4H), 3.93 (d, 1H, J=10.2Hz), 4.00 (m, 3H), 4.05 (dd, 1H, J=3.0Hz, J=9.9Hz), 4.42 (dd, 2H, J=11.8Hz, J=34.2Hz), 4.54 (d, 1H, J=7.7Hz), 4.56 (d, 1H, J=7.6Hz), 4.60 (d, 1H, J=11.8Hz), 4.69 (m, 5H), 4.75 (d, 1H, J=2.8Hz), 4.78 (d, 1H, J=2.2Hz), 4.82 (d, 1H, J=11.8Hz) 4.93 (d, 1H, J=6.6Hz), 4.94 (d, 1H, J=0.8Hz), 7.27 (m, 35H)
^{13}C NMR (100 MHz, CDCl3): δ 128.53, 128.44, 128.36, 128.30, 128.18, 128.15, 127.89, 127.82, 127.71, 127.64, 127.60, 127.53, 97.72, 79.93, 79.31, 79.10, 78.92, 76.81, 75.34, 75.02, 74.98, 74.49, 73.54, 73.28, 72.96, 72.89, 72.04, 71.66, 70.52, 69.42, 69.05, 66.29, 32.12, 30.50, 29.97, 29.90, 29.85, 29.82, 29.74, 29.56, 26.48, 26.42, 22.91, 14.38.
Exact mass (ESI-HRMS) for $C_{81}H_{107}O_{11}$ $[M+H]^+$ found, 1255.7804; calcd, 1255.7813.

3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)-6-((2R,3R,4R,5S)-3,4,5-tris(benzyloxy)-2,6-bis(dodecyloxy)hexyloxy)tetrahydro-2H-pyran 18

9 (0.65g, 0.67mmol**)** was dissolved in anhydrous DMF (10mL) and cooled to 0°C; NaH (48mg, 2mmol) was added, and after 20 min, 1-bromododecane (500mg, 2mmol) was added dropwise. Solution was allowed to warm to rt and stirred overnight. The reaction was quenched with 10 mL of an aqueous saturated solution of NH4Cl. Solution was diluted with AcOEt and washed three times with water and brine. After anhydrification with Na_2SO_4, the solvent was removed under vacuum, and the product was purified by flash chromatography (cyclohexane/EtOAc = 10:1) yielding **18** (0.624mg, 71%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3): δ 0.87 (m, 6H), 1.25 (m, 36H), 1.43 (m, 4H), 3.25 (m, 3H), 3.43 (td, 1H, J=6.6Hz, J=8.5Hz), 3.52 (m, 4H), 3.64 (dd, 1H, J=4.6Hz, J=9.2Hz), 3.82 (m, 4H), 3.91 (dd, 1H, J=2.7Hz, J=10.0Hz), 3.97 (m, 3H), 4.03 (dd, 1H, J=3.5Hz, J=10.0Hz), 4.38 (d, 1H, J=11.8Hz), 4.46 (m, 1H), 4.54 (d, 1H, J=7.7Hz), 4.56 (d, 1H, J=7.6Hz), 4.60 (d, 1H, J=11.8Hz), 4.69 (m, 5H), 4.75 (d, 1H, J=2.8Hz), 4.78 (d, 1H, J=2.2Hz), 4.82 (d, 1H, J=11.8Hz) 4.93 (d, 1H, J=6.6Hz), 4.94 (d, 1H, J=0.8Hz), 7.27 (m, 35H).
^{13}C NMR (100 MHz, CDCl3): δ 123.13, 123.10, 123.02, 122.94, 122.89, 122.76, 122.73, 122.49, 122.42, 122.29, 122.22, 122.17, 122.12, 92.28, 74.46, 73.87, 73.70, 73.50, 72.01, 71.32, 69.90, 69.57, 69.03, 68.14, 67.85, 67.51, 66.60, 66.27, 65.14, 63.93, 63.59, 60.91, 26.71, 25.09, 24.50, 24.46, 24.42, 24.34, 24.17, 21.06, 20.99, 17.49, 8.94
Exact mass (ESI-HRMS) for $C_{85}H_{115}O_{11}$ $[M+H]^+$ found, 1311.8443; calcd, 1311.8439.

2-(hydroxymethyl)-6-((2R,3S,4R,5S)-3,4,5-trihydroxy-2,6-bis(octyloxy)hexyloxy)tetrahydro-2H-pyran-3,4,5-triol 3

Deprotecting **16** (0.60mg, 0.5mmol) as the same procedure as for **2** produce **3** (0.202mg, 71%).
^{1}H NMR (400 MHz, CD_3OD): δ 0.80 (t, 6H, J=6.3Hz), 1.20 (m, 20H), 1.47 (m, 4H) , 3.46 (m, 6H), 3.67 (m, 7H), 3.84 (m, 4H), 3.91 (m, 1H), 4.81 (s, 1H)
^{13}C NMR (100 MHz, CD_3OD): δ 100.40, 79.4, 73.9, 73.71, 72.74, 72.62, 72.43, 71.92, 71.60, 71.15, 70.49, 69.60, 66.79, 62.90, 33.15, 31.35, 30.97, 30.83, 30.77, 30.56, 27.44, 27.39, 23.83, 14.58
Exact mass (ESI-HRMS) for $C_{28}H_{56}NaO_{11}$ $[M+Na]^+$ found, 591.3714; calcd, 591.3716.

2-((2R,3S,4R,5S)-2,6-bis(decyloxy)-3,4,5-trihydroxyhexyloxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol 4

Deprotecting **17** (0.627mg, 0.5mmol) as the same procedure as for **2** produce **4** (0.237mg, 76%).
^{1}H NMR (400 MHz, CD_3OD): δ 0.90 (m, 6H), 1.29 (m, 28H), 1.58 (m, 4H,), 3.56 (m, 6H), 3.80 (m, 7H,), 3.93 (m, 4H), 4.11 (s, 1H), 4.94 (s, 1H)。
^{13}C NMR (100 MHz, CD_3OD): δ 100.39, 79.33, 74.46, 74.14, 72.59, 72.46, 71.87, 71.53, 71.24, 70.45, 69.04, 66.55, 63.02, 58.36, 33.16, 31.39, 31.03, 30.90, 30.84, 30.61, 27.46, 27.42, 23.83, 18.43, 14.55.
Exact mass (ESI-HRMS) for $C_{32}H_{64}NaO_{11}$ $[M+Na]^+$ found, 647.4337; calcd, 647.4341.

2-((2R,3S,4R,5S)-2,6-bis(dodecyloxy)-3,4,5-trihydroxyhexyloxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol 5

Deprotecting **18** (0.60mg, 0.458mmol) as the same procedure as for **2** produce **5** (0.207mg, 66%).
^{1}H NMR (400 MHz, CD_3OD): δ 0.80 (t, 6H, J=6.6Hz), 1.19 (m, 36H), 1.48 (m, 4H), 3.45 (m, 6H), 3.65 (m, 7H), 3.80 (m, 5H), 4.78 (s, 1H).
^{13}C NMR (100 MHz, CD_3OD): δ 100.46, 79.73, 73.76, 72.94, 72.68, 72.33, 71.96, 71.72, 71.10, 70.55, 70.22, 67.21, 62.78, 33.17, 31.34, 30.92, 30.84, 30.61, 27.46, 27.39, 23.83, 14.58
Exact mass (ESI-HRMS) for $C_{36}H_{72}NaO_{11}$ $[M+Na]^+$ found, 703.4973; calcd, 703.4967.

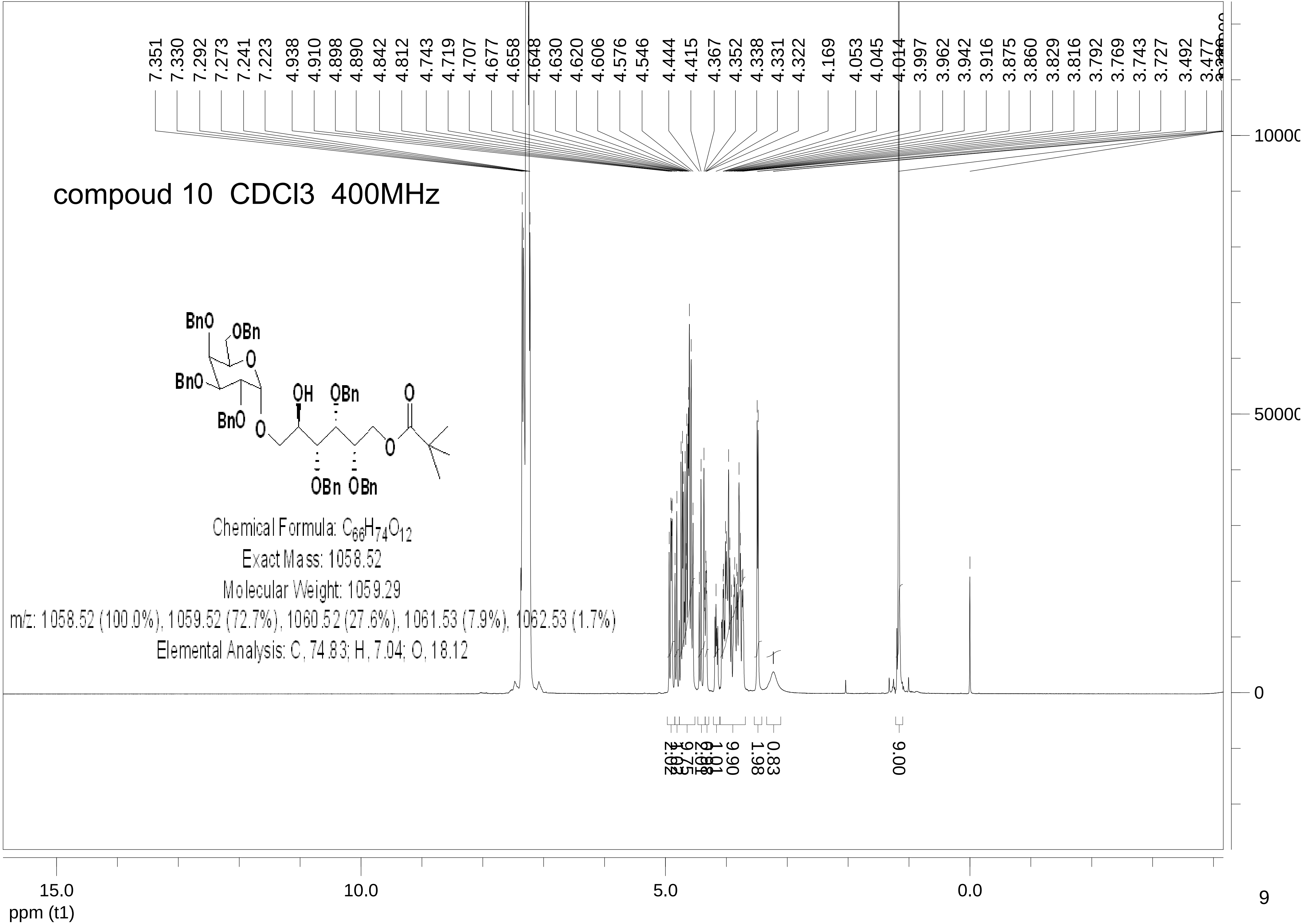
The detail exprimental procedures of the the biological activity:

For the *in vitro* hybridoma assay, the compounds were first cultured with CD1d expressing A20/CD1 cells at different concentration to load the glycolipids onto the cell surface CD1d protein. Then, the glycolipid-loaded A20/CD1 cells were separately cultured with two different NKT hybridoma cell lines, Hybridoma DN3A4-1.2, and N38-2H4. The culture supernatant was collected and the IL-2 concentrations in the culture was measured by ELISA.[1 (e)]

The compounds were also tested in the *in vivo* mouse splenocytes culture assay. Splenocytes from wild type mouse were cultured with the compounds at different concentration for three days. The cytokine (IFN-γ and IL-4) concentrations in the culture supernatants, which reflect the NKT stimulation efficiency, were measured by ELISA.[1.(c)]

1 (c) Zhang, W. P.; Xia, C. F.; Nadas, J.; Chen, W. L.; Gu, L.; Wang, P. G. *Bioorg. Med. Chem.* **2011**, *19,* 2726.

1 (e) Zhang, W. P.; Zheng, X. C.; Xia, C. F.; Perali, R. S.; Yao, Q. J.; Liu, Y.; Zheng, P.; Wang, P. G.. Chembiochem **2008**, *9* , 1423; (f)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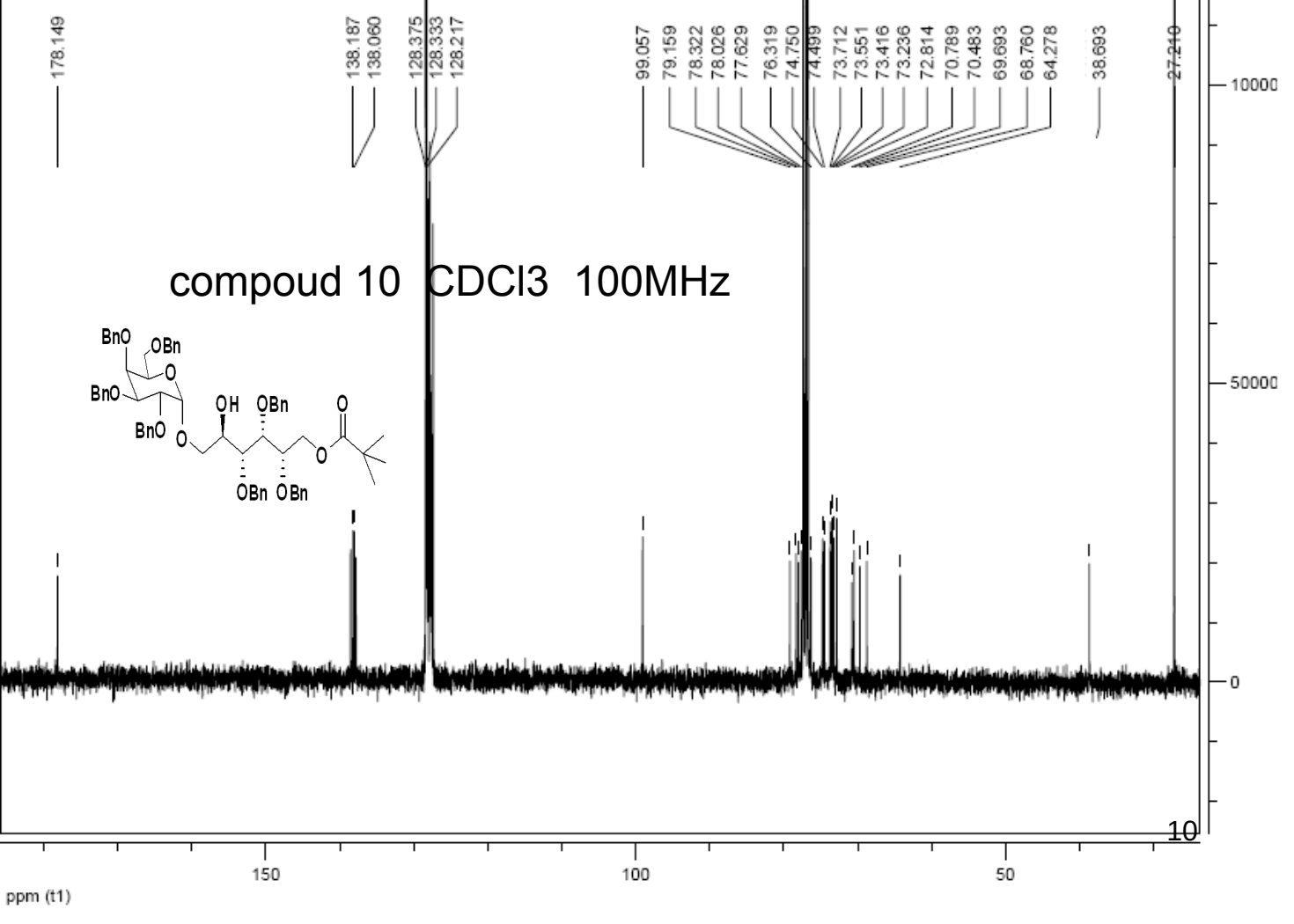
Molecular Weight: 1059.29
m/z: 1058.52 (100.0%), 1059.52 (72.7%), 1060.52 (27.6%), 1061.53 (7.9%), 1062.53 (1.7%)
Elemental Analysis: C, 74.83; H, 7.04; O, 18.12
ppm (t1)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74.499
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73.416
73.236
72.814
70.789
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69.693
68.760
64.278
38.693
27.210
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150
100
50
ppm (t1)
compoud 10 CDCl3 100MHz
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OBn
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BnO
OH
OBn
O
BnO
O
O
OBn
OBn
10

128.556
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99.305
79.331
78.506
78.220
77.836
76.584
74.963
74.879
74.709
73.925
73.765
73.607
73.422
72.996
70.975
70.712
69.944
68.995
64.470
27.440
compoud 10 CDCl3 100MHz
BnO
OBn
O
BnO
OH
OBn
O
BnO
O
O
OBn
OBn
Chemical Formula: C66H74O12
Exact Mass: 1058.52
Molecular Weight: 1059.29
m/z: 1058.52 (100.0%), 1059.52 (72.7%), 1060.52 (27.6%), 1061.53 (7.9%), 1062.53 (1.7%)
Elemental Analysis: C, 74.83; H, 7.04; O, 18.12
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100
50
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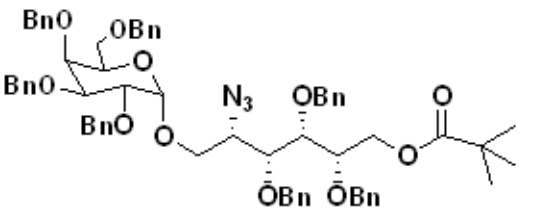
ppm (t1)

compoud 11 CDCl3 400MHz



$C_{66}H_{73}N_3O_{11}$
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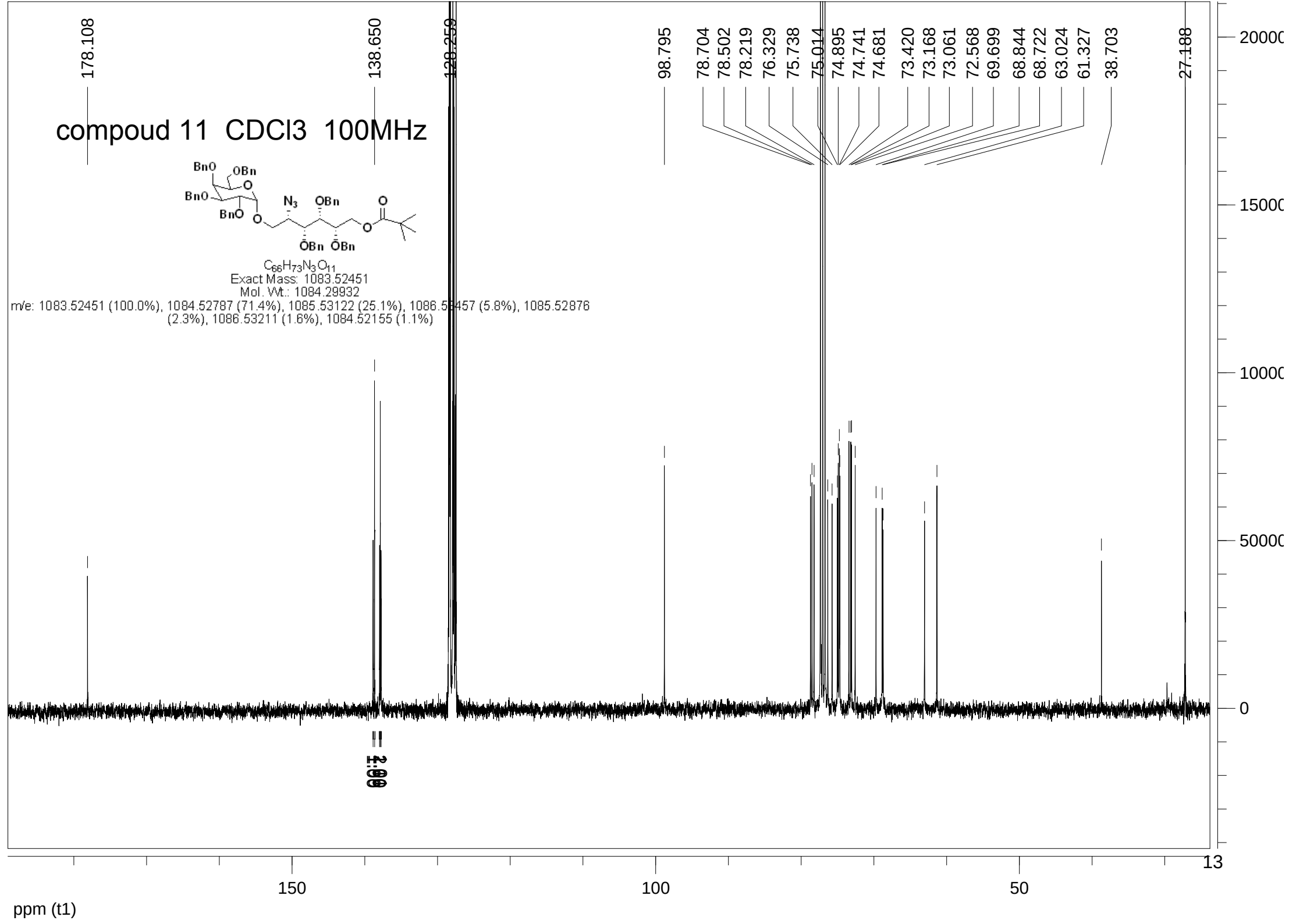
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78.502
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76.329
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74.681
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73.168
73.061
72.568
69.699
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63.024
61.327
38.703
27.188
compoud 11 CDCl3 100MHz
BnO
OBn
BnO
BnO
O
N3
OBn
O
O
OBn
OBn
C66H73N3O11
Exact Mass: 1083.52451
Mol. Wt.: 1084.29932
m/e: 1083.52451 (100.0%), 1084.52787 (71.4%), 1085.53122 (25.1%), 1086.53457 (5.8%), 1085.52876 (2.3%), 1086.53211 (1.6%), 1084.52155 (1.1%)
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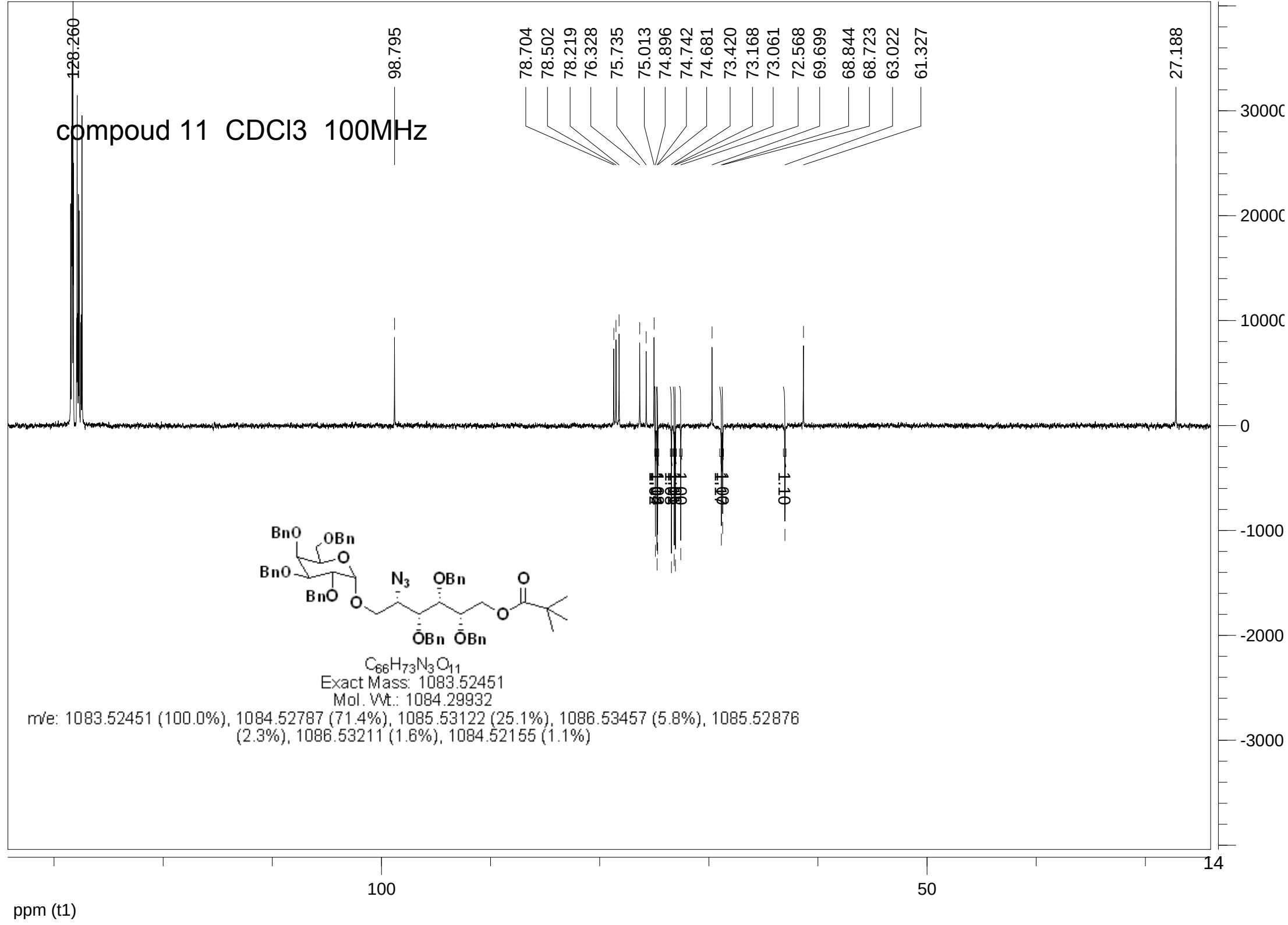
100
50
13
ppm (t1)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78.502
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75.013
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74.742
74.681
73.420
73.168
73.061
72.568
69.699
68.844
68.723
63.022
61.327
27.188
compoud 11 CDCl3 100MHz
1.00
1.00
1.10
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OBn
O
BnO
BnO
O
N3
OBn
O
O
OBn
OBn
C66H73N3O11
Exact Mass: 1083.52451
Mol. Wt.: 1084.29932
m/e: 1083.52451 (100.0%), 1084.52787 (71.4%), 1085.53122 (25.1%), 1086.53457 (5.8%), 1085.52876 (2.3%), 1086.53211 (1.6%), 1084.52155 (1.1%)
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20000
10000
0
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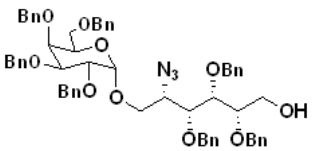
-3000
14
100
50
ppm (t1)

compoud 12 CDCl3 400MHz



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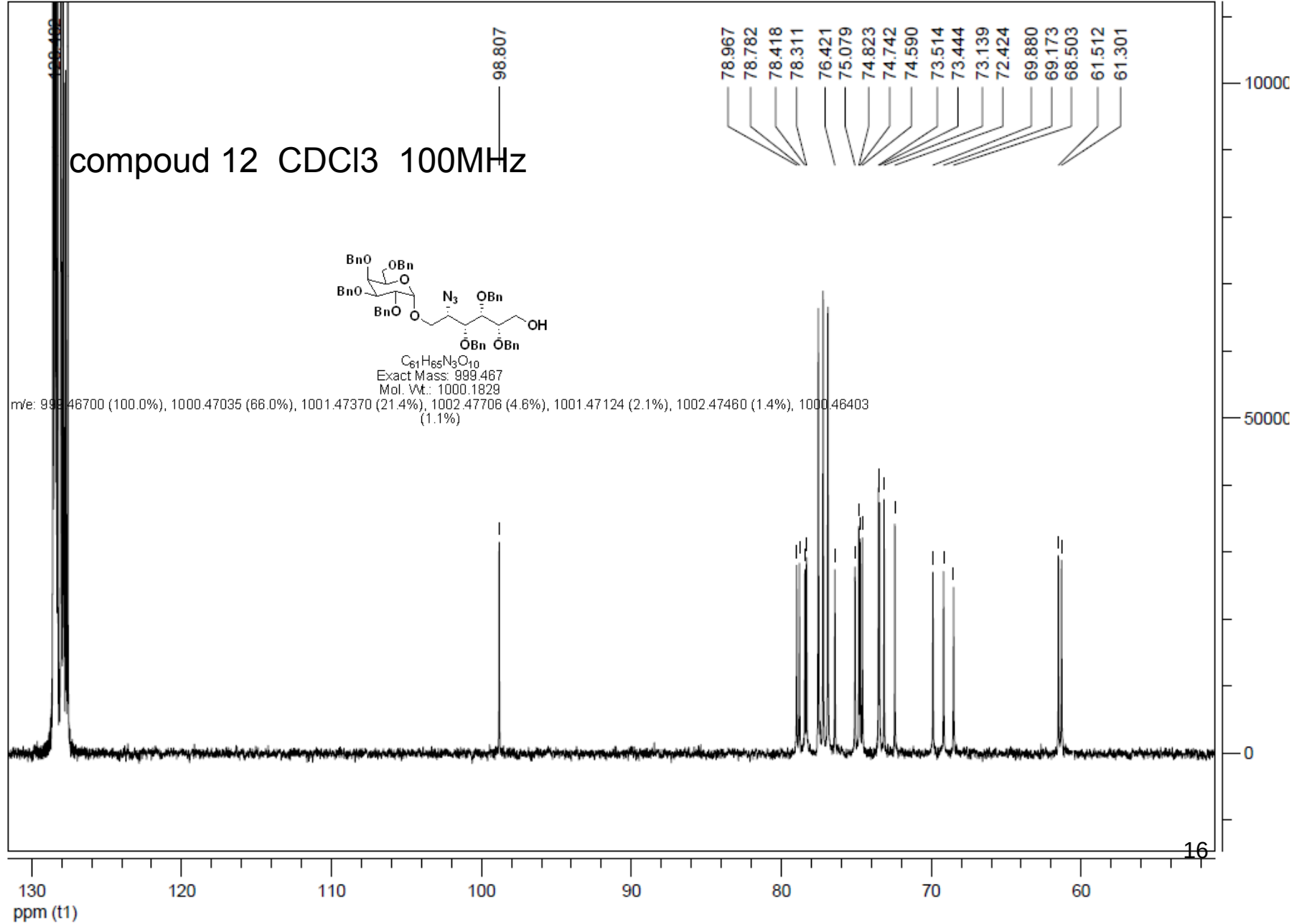
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72.424
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69.173
68.503
61.512
61.301
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OBn
BnO
BnO
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OBn
OH
OBn OBn
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Exact Mass: 999.467
Mol. Wt.: 1000.1829
m/e: 999.46700 (100.0%), 1000.47035 (66.0%), 1001.47370 (21.4%), 1002.47706 (4.6%), 1001.47124 (2.1%), 1002.47460 (1.4%), 1000.46403 (1.1%)
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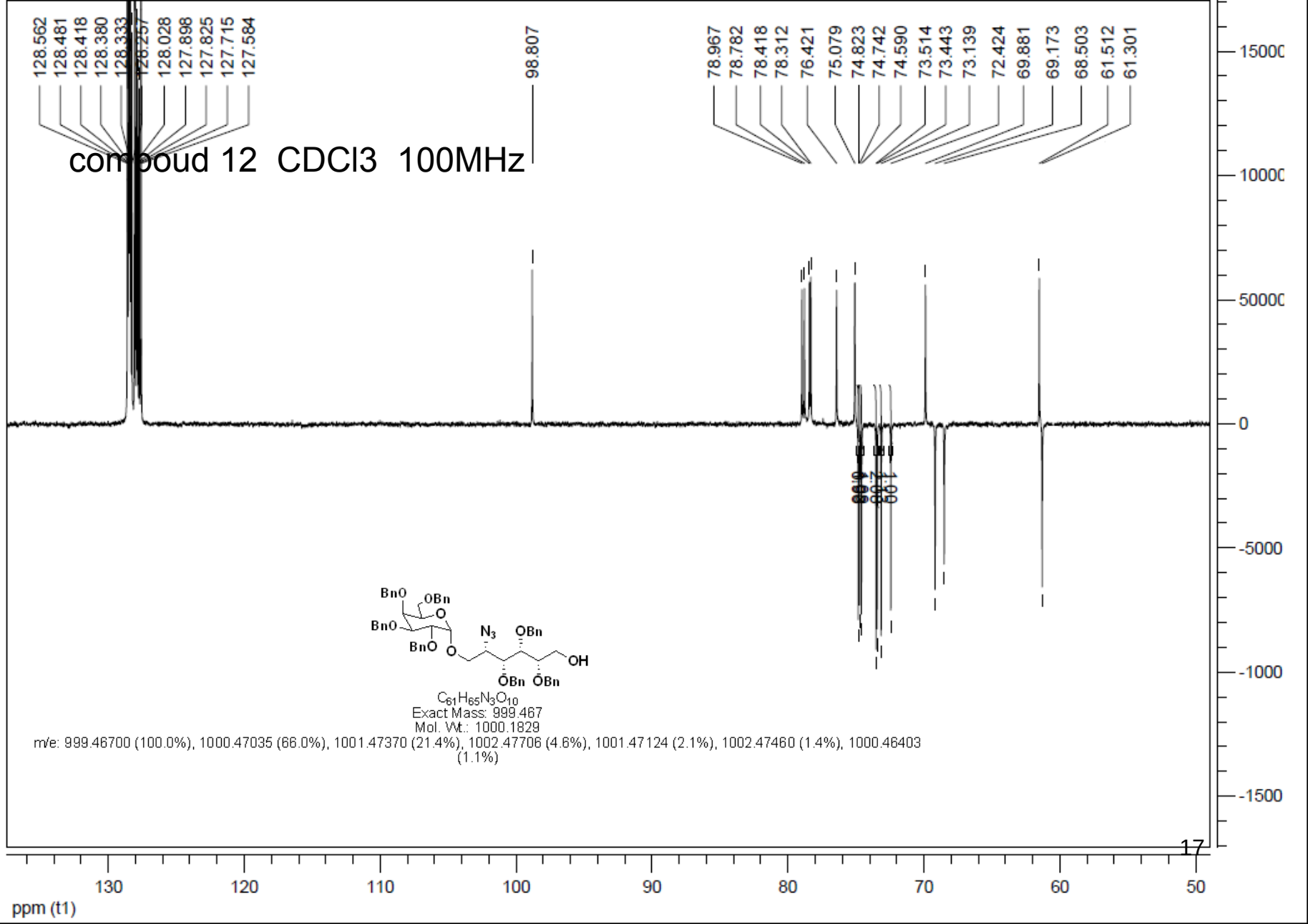
80
70
60
ppm (t1)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78.418
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75.079
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74.742
74.590
73.514
73.443
73.139
72.424
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69.173
68.503
61.512
61.301
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OBn
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BnO
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N3
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OH
OBn
OBn
C61H65N3O10
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Mol. Wt.: 1000.1829
m/e: 999.46700 (100.0%), 1000.47035 (66.0%), 1001.47370 (21.4%), 1002.47706 (4.6%), 1001.47124 (2.1%), 1002.47460 (1.4%), 1000.46403 (1.1%)
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60
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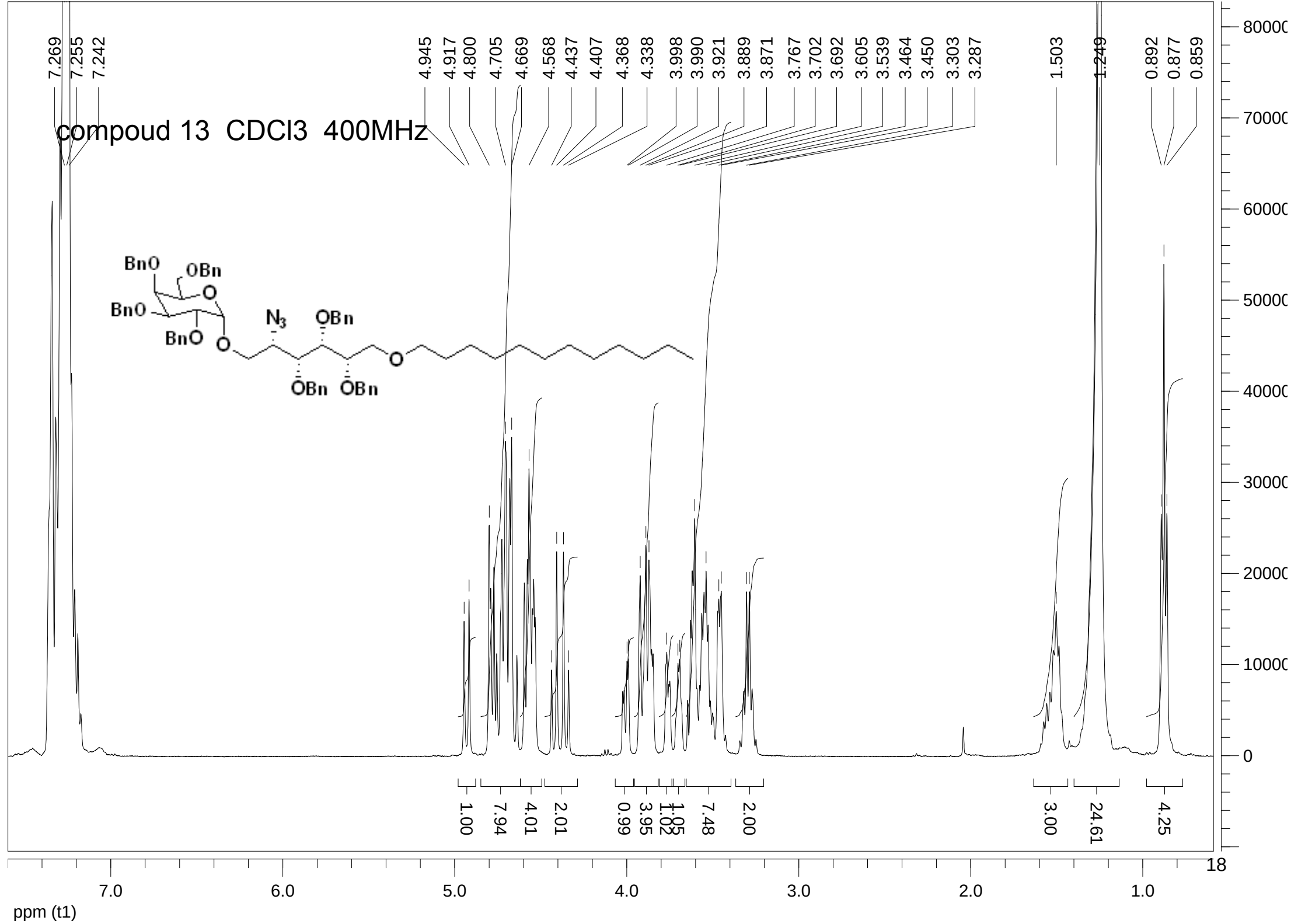
ppm (t1)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BnO
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OBn
OBn
OBn
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4.01
2.01
0.99
3.95
1.02
1.05
7.48
2.00
3.00
24.61
4.25
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70000
60000
50000
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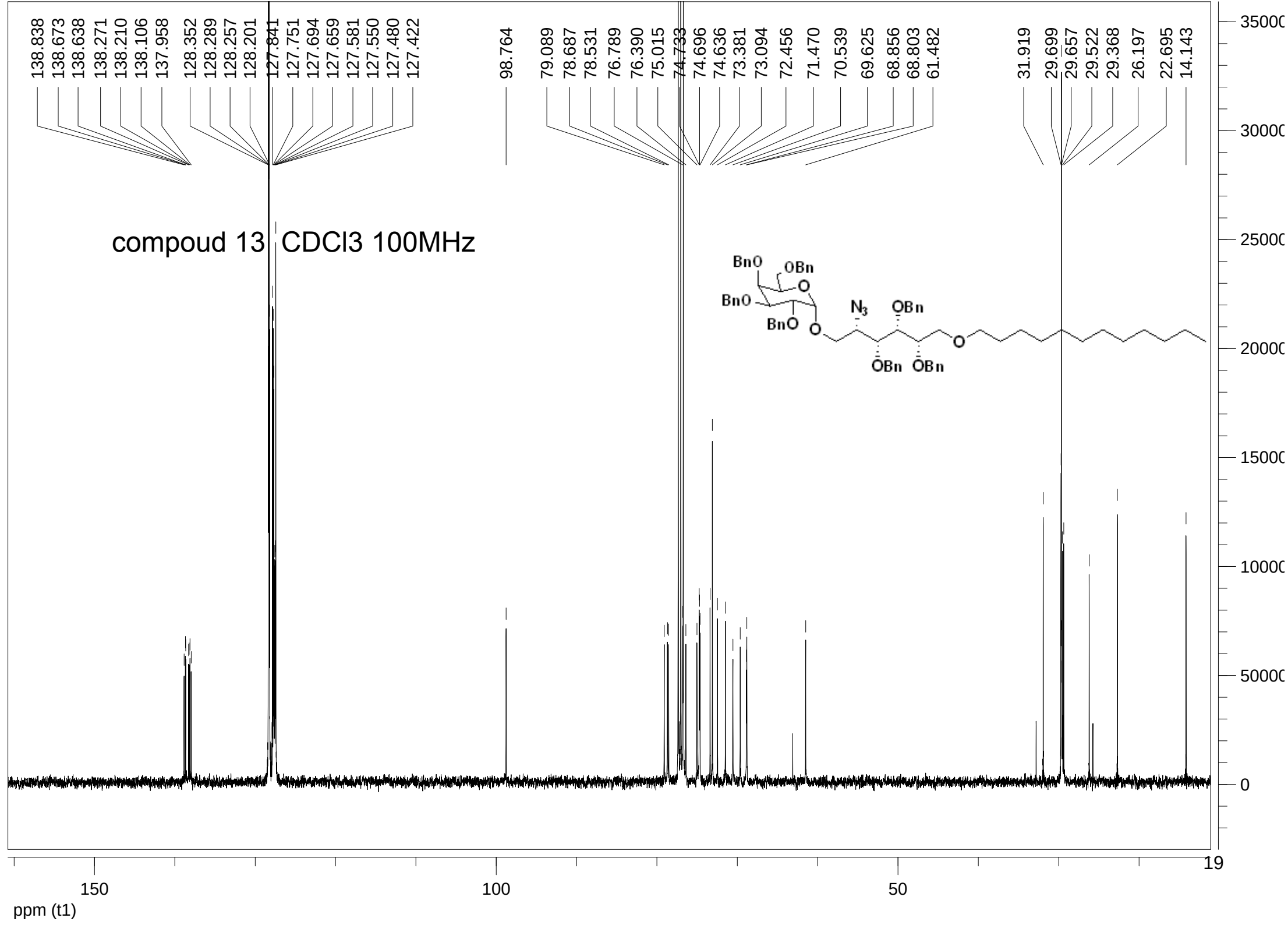
ppm (t1)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79.089
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74.696
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31.919
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29.368
26.197
22.695
14.143
compoud 13 CDCl3 100MHz
BnO
OBn
O
BnO
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2500
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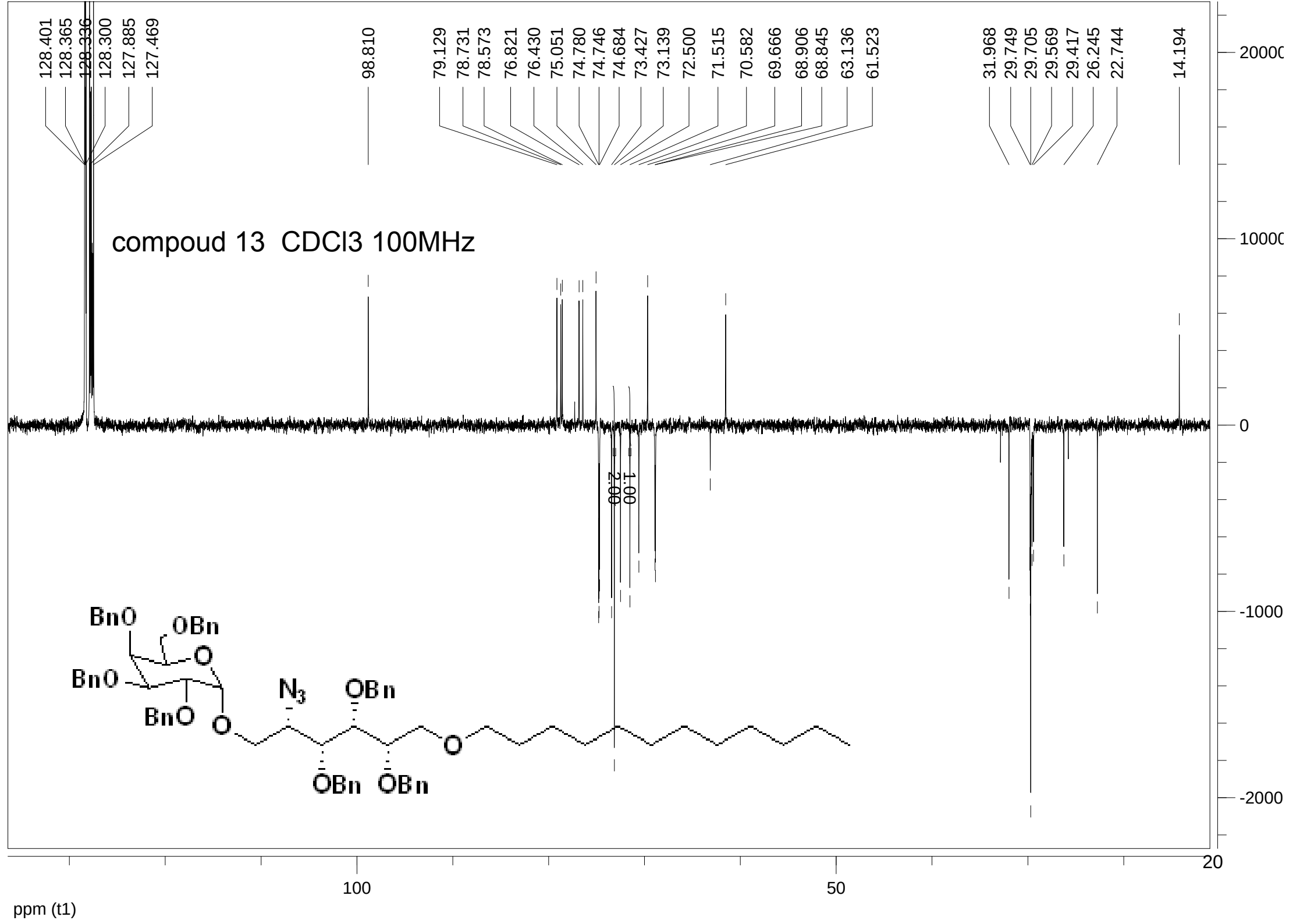
ppm (t1)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68.906
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61.523
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29.749
29.705
29.569
29.417
26.245
22.744
14.194
compoud 13 CDCl3 100MHz
2.00
1.00
BnO
OBn
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BnO
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OBn
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OBn
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-2000
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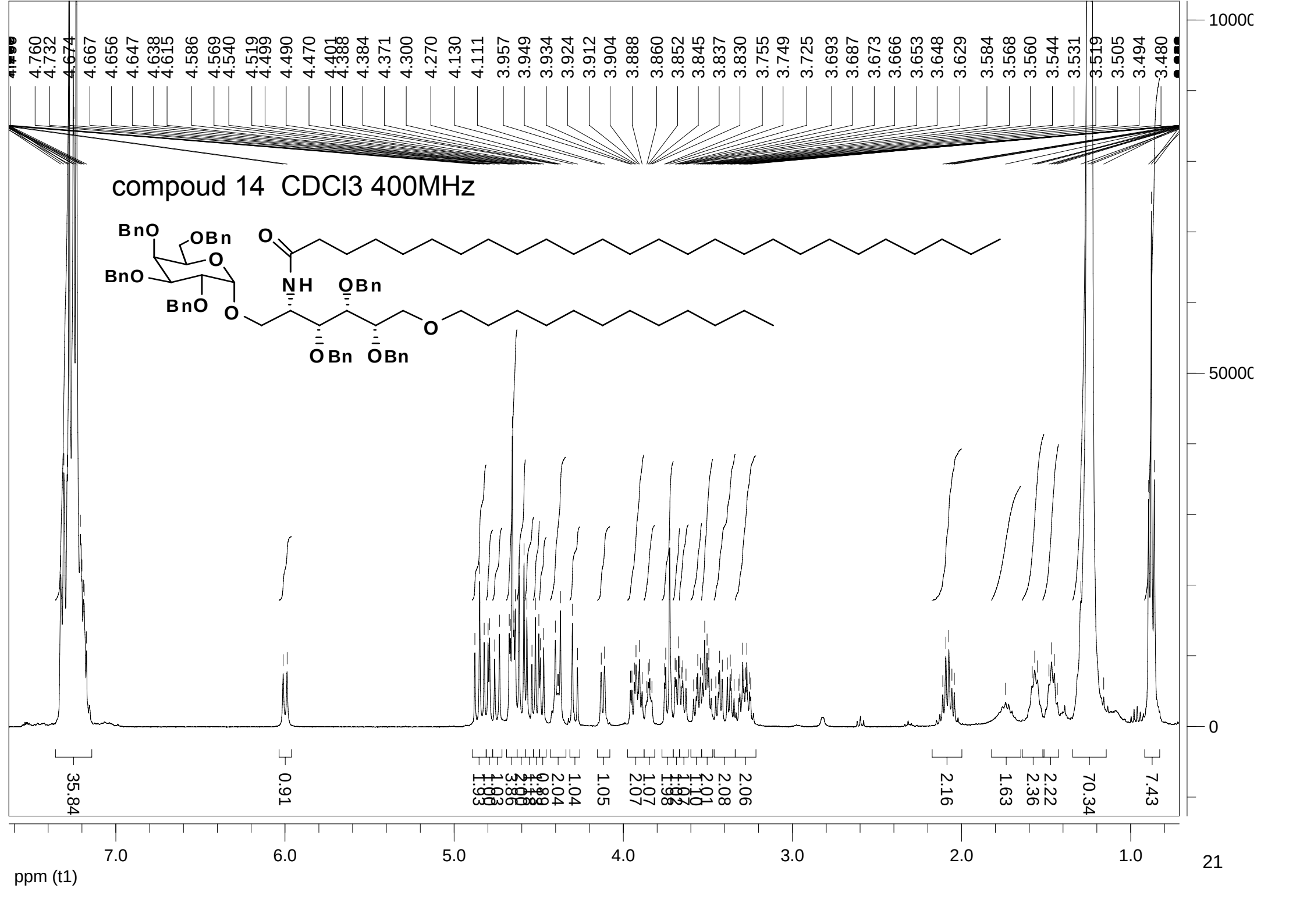
20
ppm (t1)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OBn
OBn
O
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3.666
3.653
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3.584
3.568
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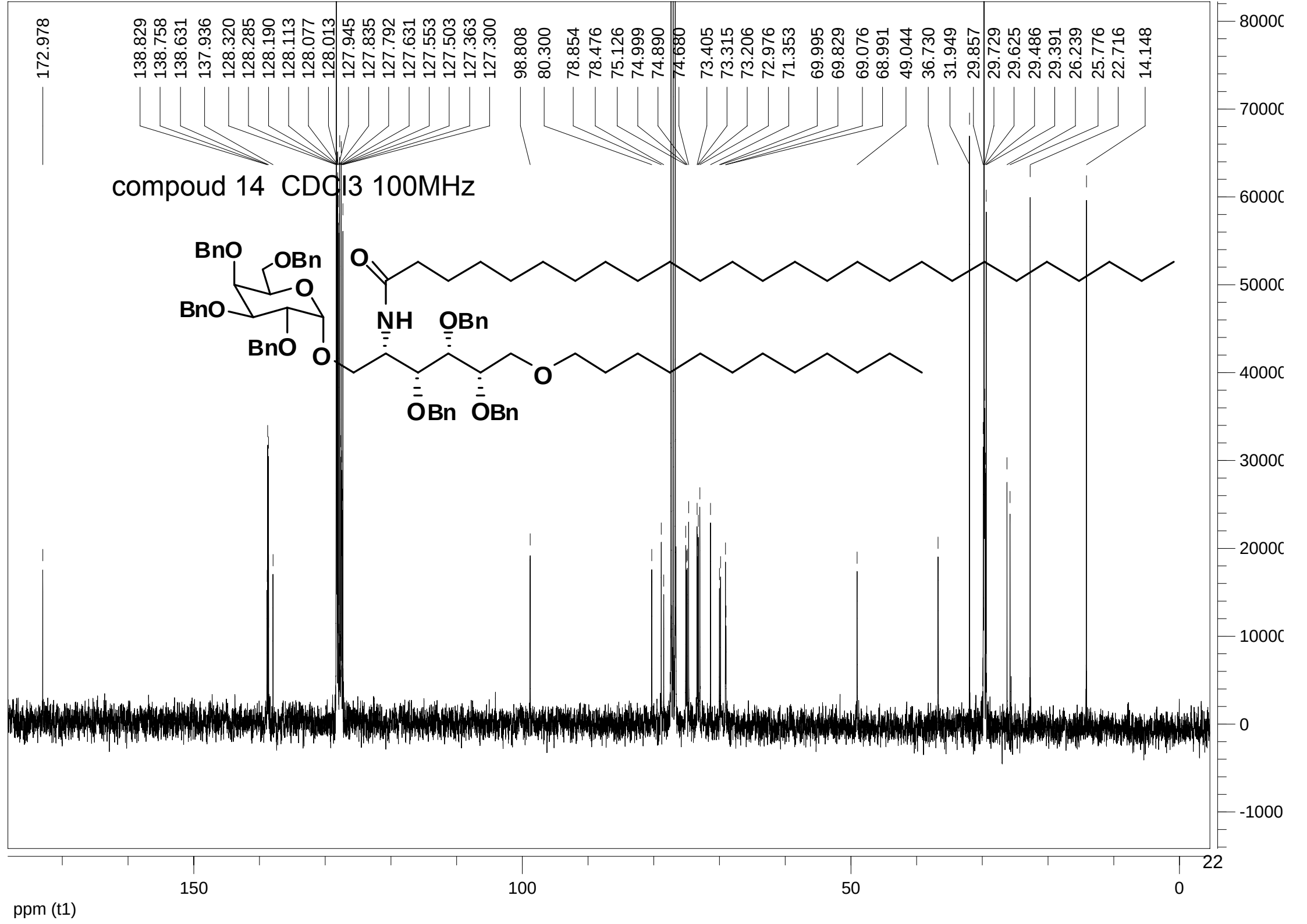
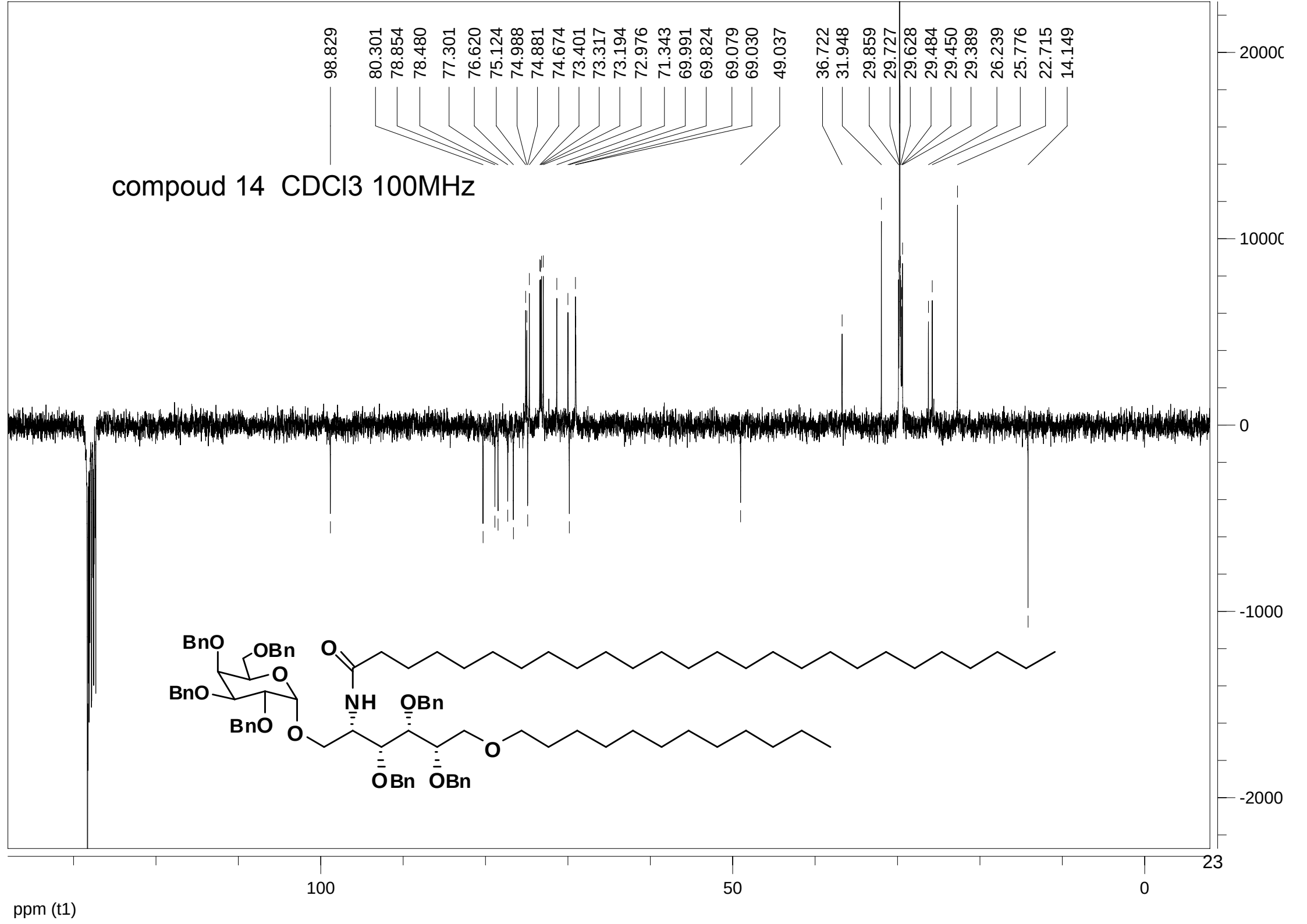
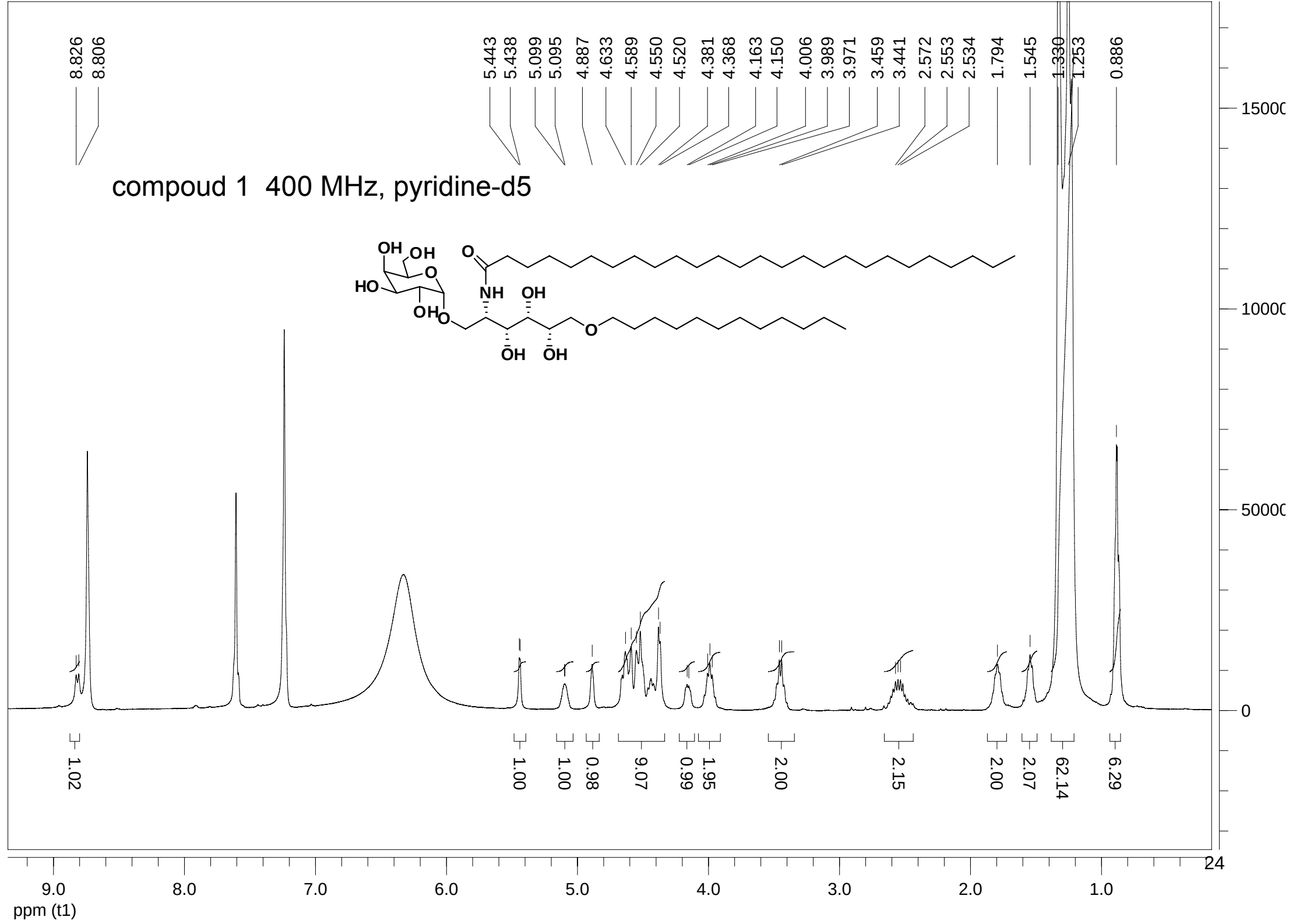
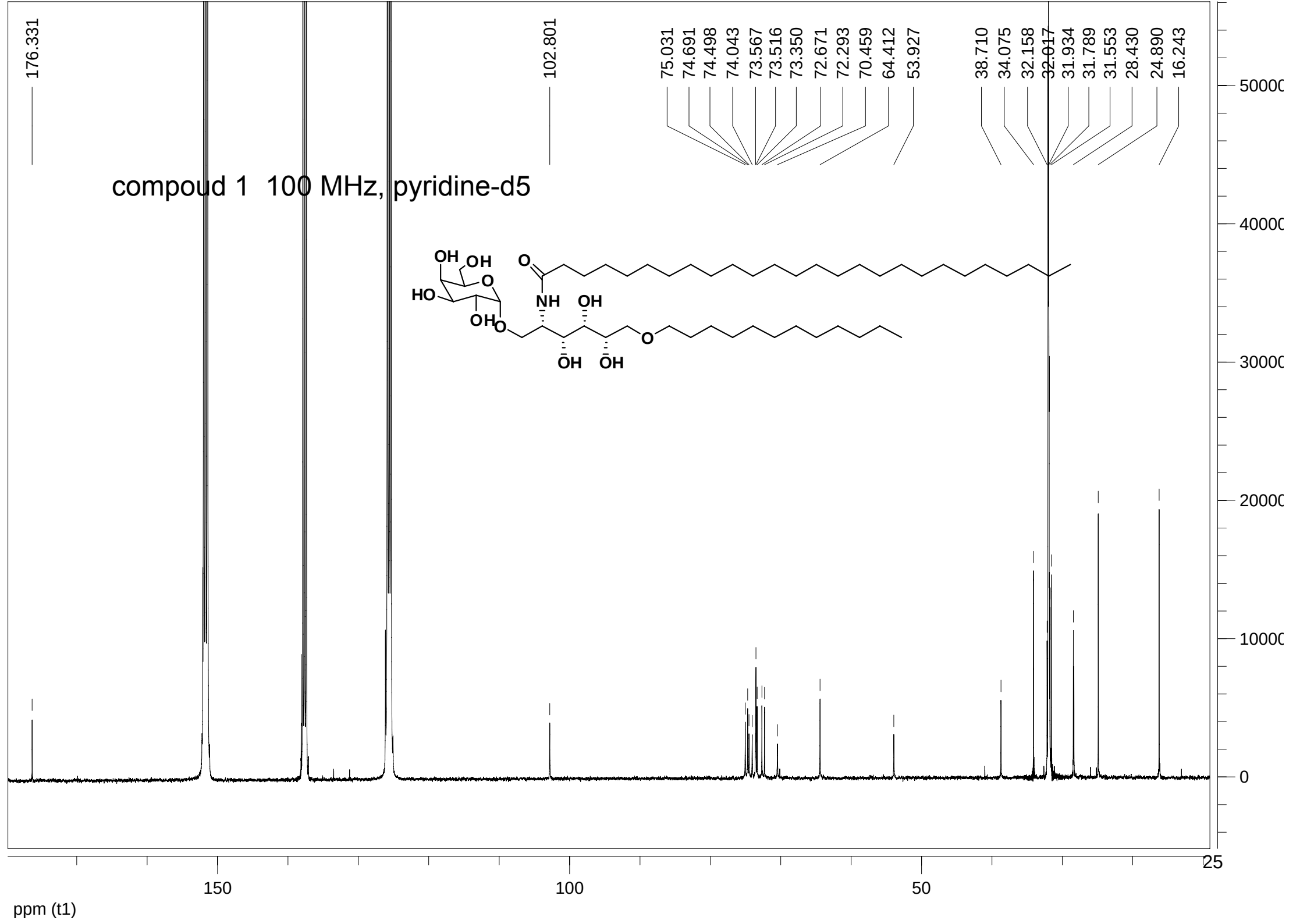
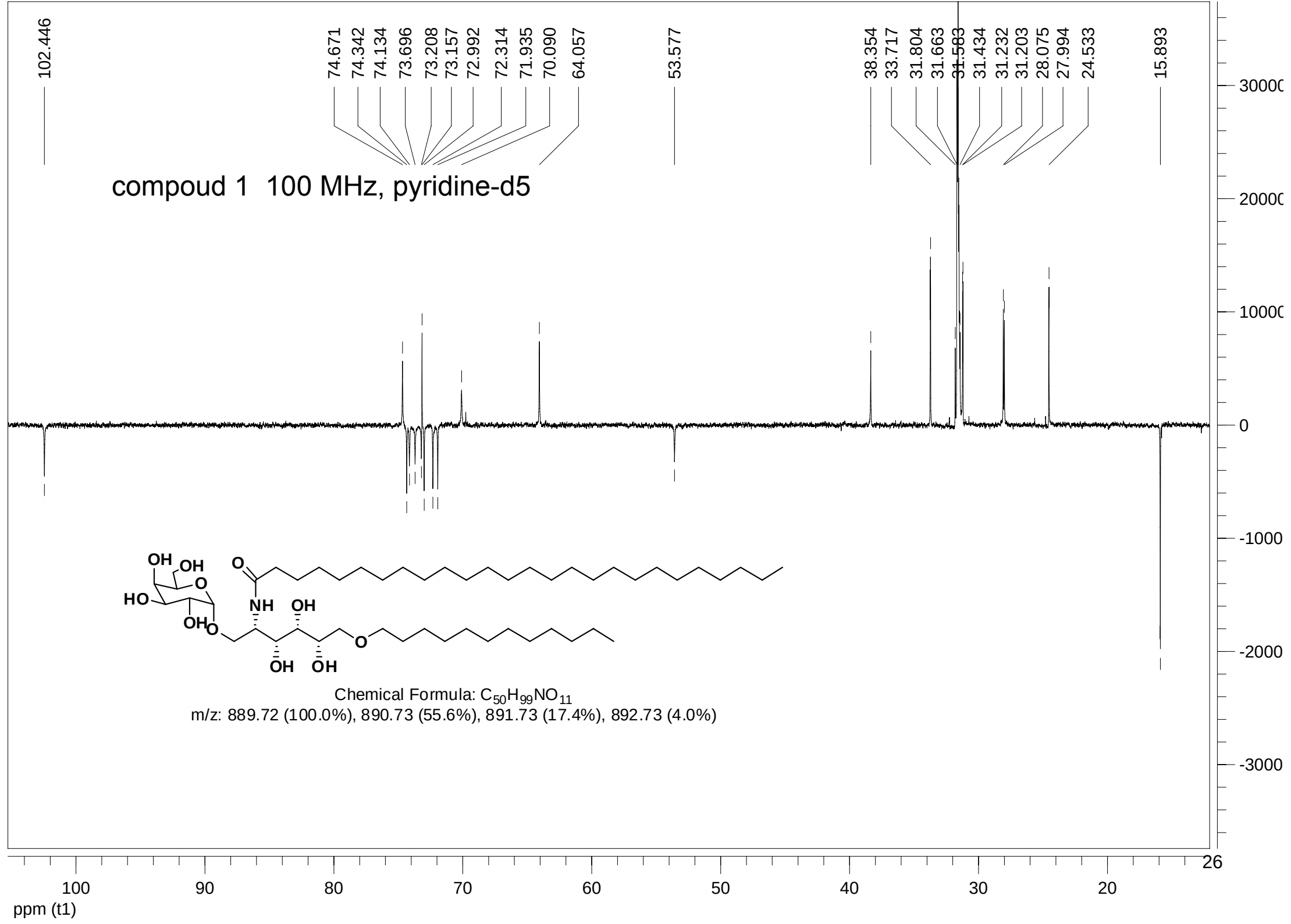
3.531
3.519
3.505
3.494
3.480
10000
50000
0
35.84
0.91
1.04
1.05
1.07
2.04
2.08
2.06
2.16
1.63
2.36
2.22
70.34
7.43
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
21


172.978
138.829
138.758
138.631
137.936
128.320
128.285
128.190
128.113
128.077
128.013
127.945
127.835
127.792
127.631
127.553
127.503
127.363
127.300
98.808
80.300
78.854
78.476
75.126
74.999
74.890
74.680
73.405
73.315
73.206
72.976
71.353
69.995
69.829
69.076
68.991
49.044
36.730
31.949
29.857
29.729
29.625
29.486
29.391
26.239
25.776
22.716
14.148
compoud 14 CDCl3 100MHz
BnO
OBn
O
BnO
BnO
O
O
NH
OBn
O
OBn
OBn
O
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000
150
100
50
0
22
ppm (t1)


98.829
80.301
78.854
78.480
77.301
76.620
75.124
74.988
74.881
74.674
73.401
73.317
73.194
72.976
71.343
69.991
69.824
69.079
69.030
49.037
36.722
31.948
29.859
29.727
29.628
29.484
29.450
29.389
26.239
25.776
22.715
14.149
compoud 14 CDCl3 100MHz
20000
10000
0
-1000
-2000
BnO
OBn
O
BnO
BnO
O
NH
OBn
O
OBn
OBn
O
100
50
0
23
ppm (t1)

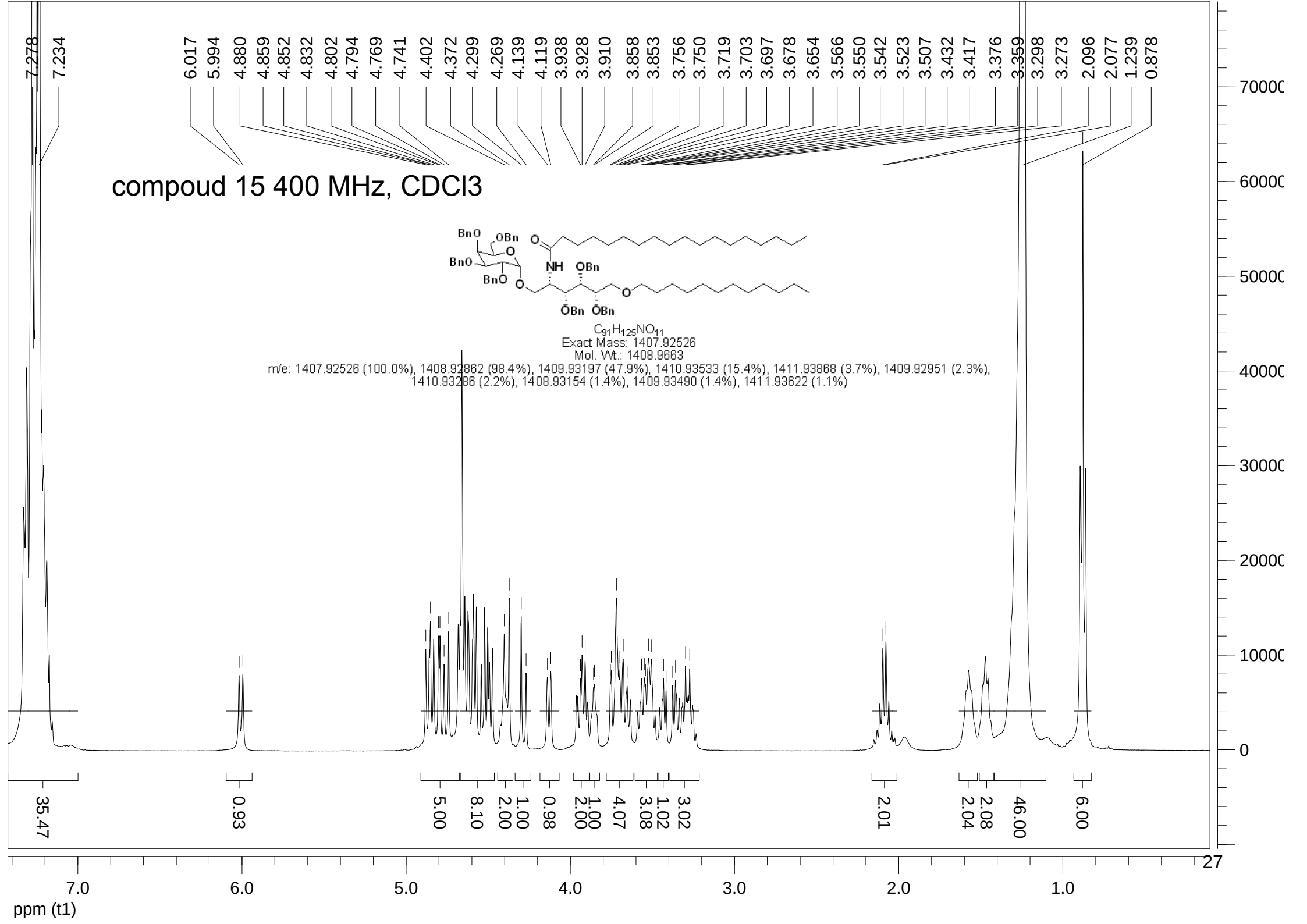

8.826
8.806
5.443
5.438
5.099
5.095
4.887
4.633
4.589
4.550
4.520
4.381
4.368
4.163
4.150
4.006
3.989
3.971
3.459
3.441
2.572
2.553
2.534
1.794
1.545
1.330
1.253
0.886
compoud 1 400 MHz, pyridine-d5
OH
OH
O
HO
OH
O
O
NH
OH
OH
OH
O
O
1.02
1.00
1.00
0.98
9.07
0.99
1.95
2.00
2.15
2.00
2.07
62.14
6.29
15000
10000
50000
0
24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

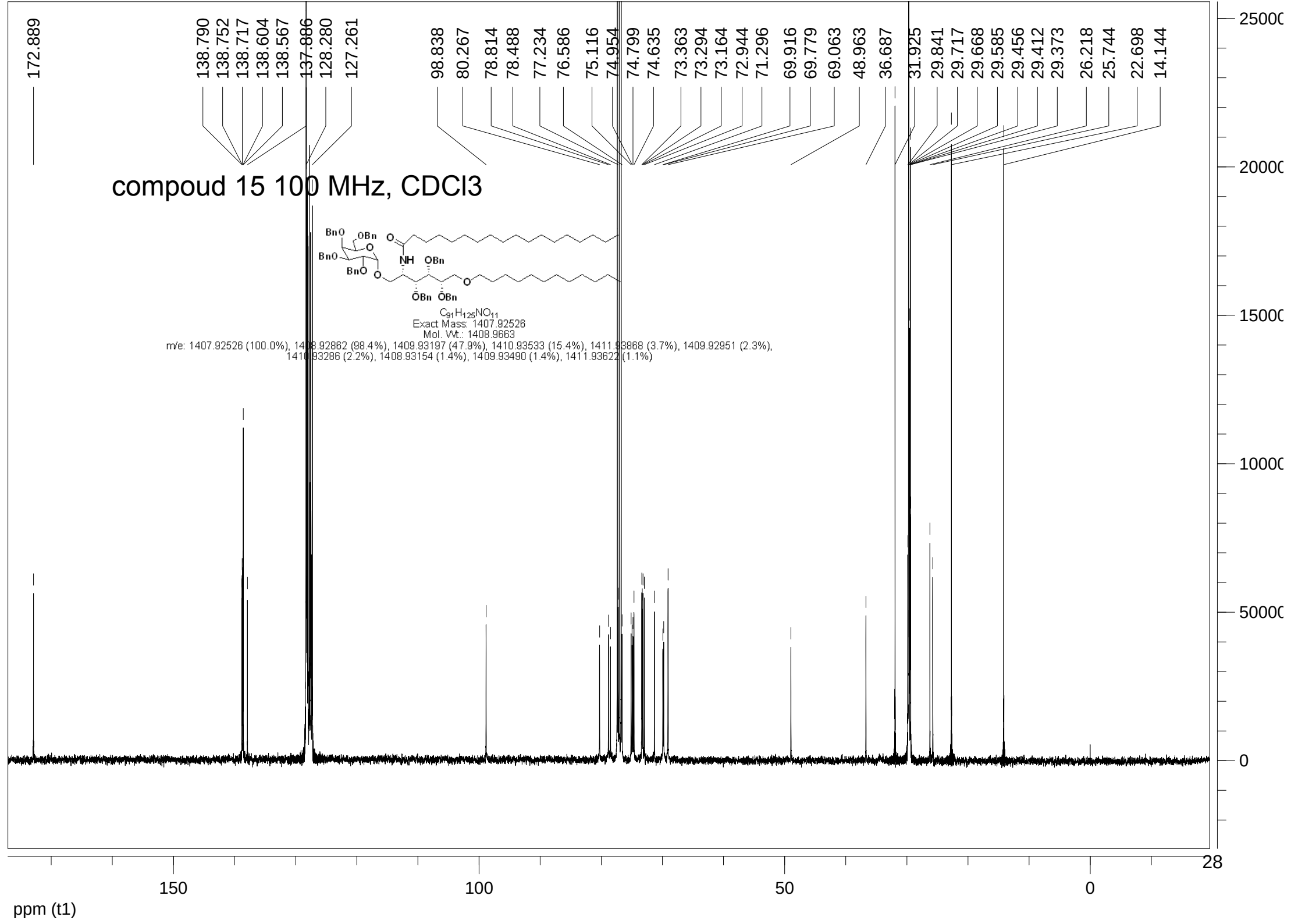

176.331
102.801
75.031
74.691
74.498
74.043
73.567
73.516
73.350
72.671
72.293
70.459
64.412
53.927
38.710
34.075
32.158
32.017
31.934
31.789
31.553
28.430
24.890
16.243
compoud 1 100 MHz, pyridine-d5
OH
OH
O
HO
OH
O
O
NH
OH
O
OH
OH
50000
40000
30000
20000
10000
0
150
100
50
25
ppm (t1)

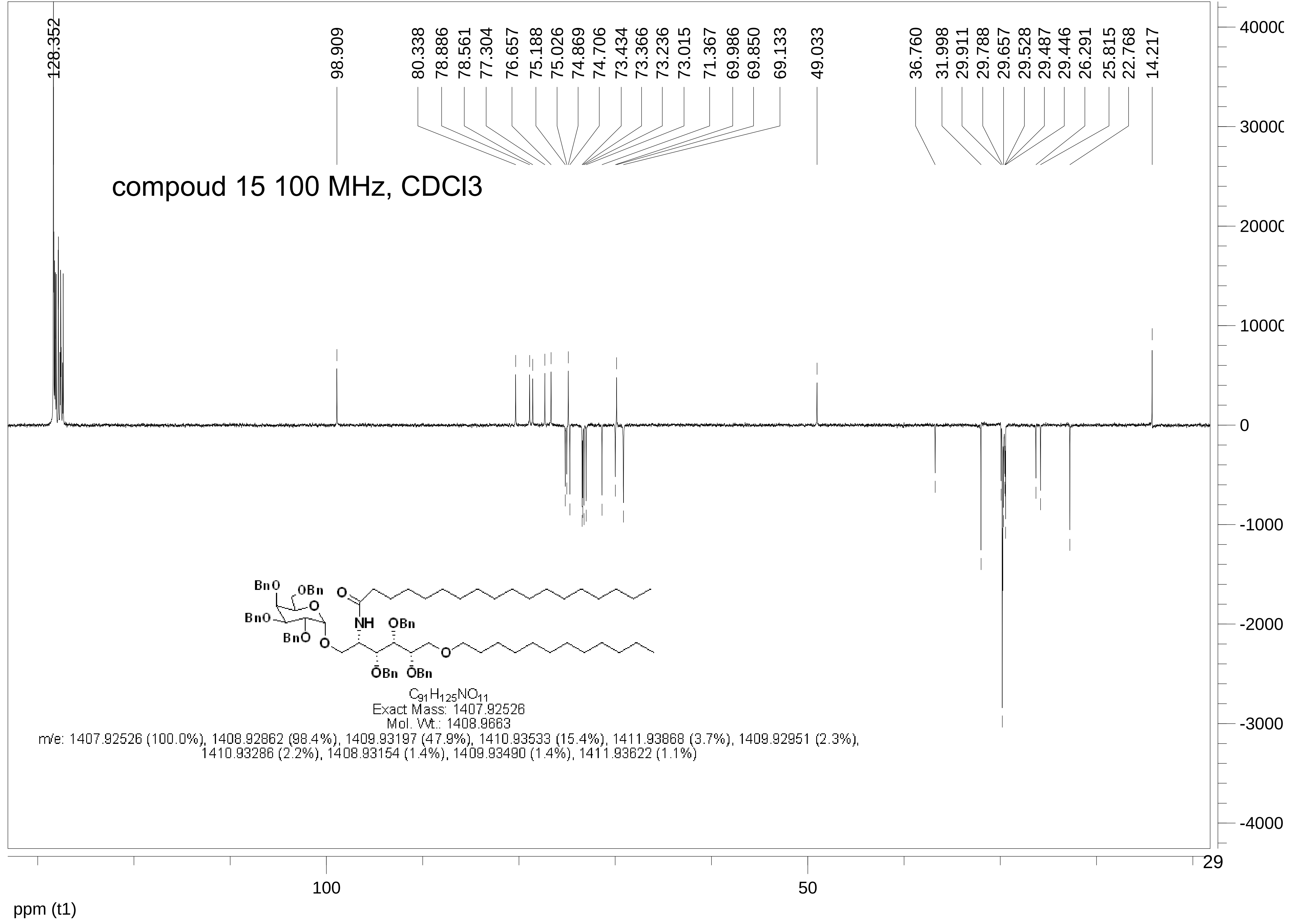


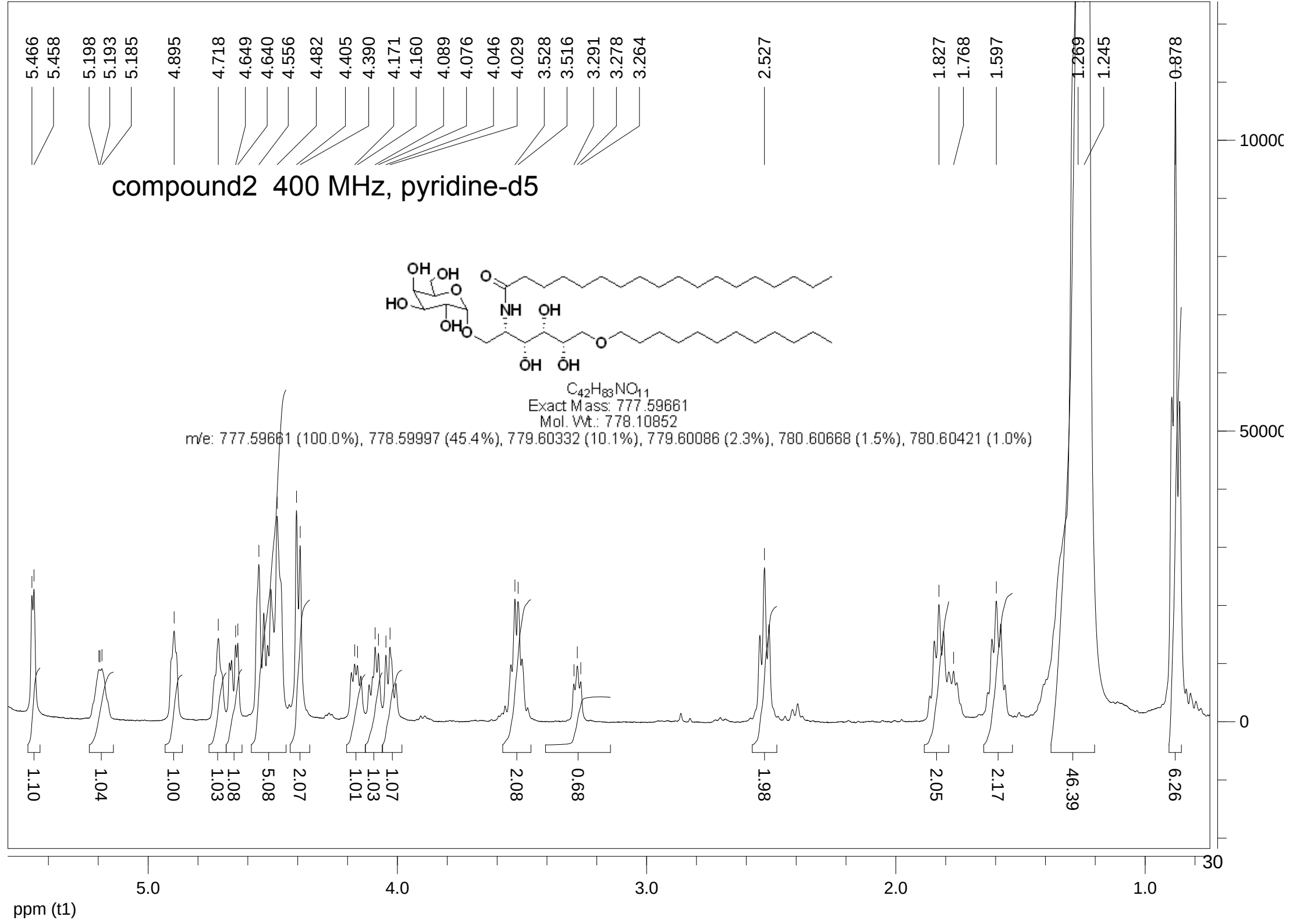
Chemical Formula: $C_{50}H_{99}NO_{11}$

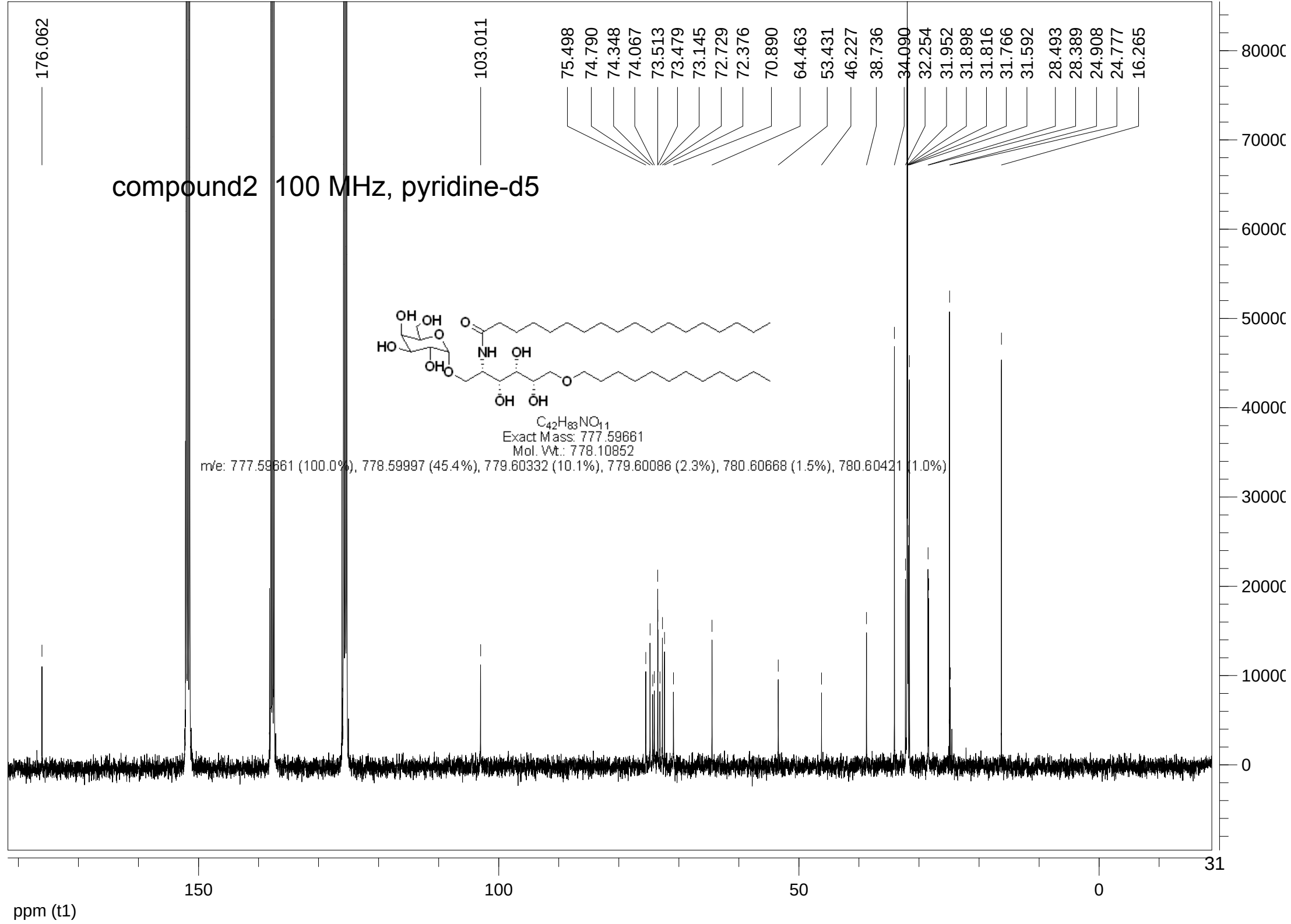
m/z: 889.72 (100.0%), 890.73 (55.6%), 891.73 (17.4%), 892.73 (4.0%)

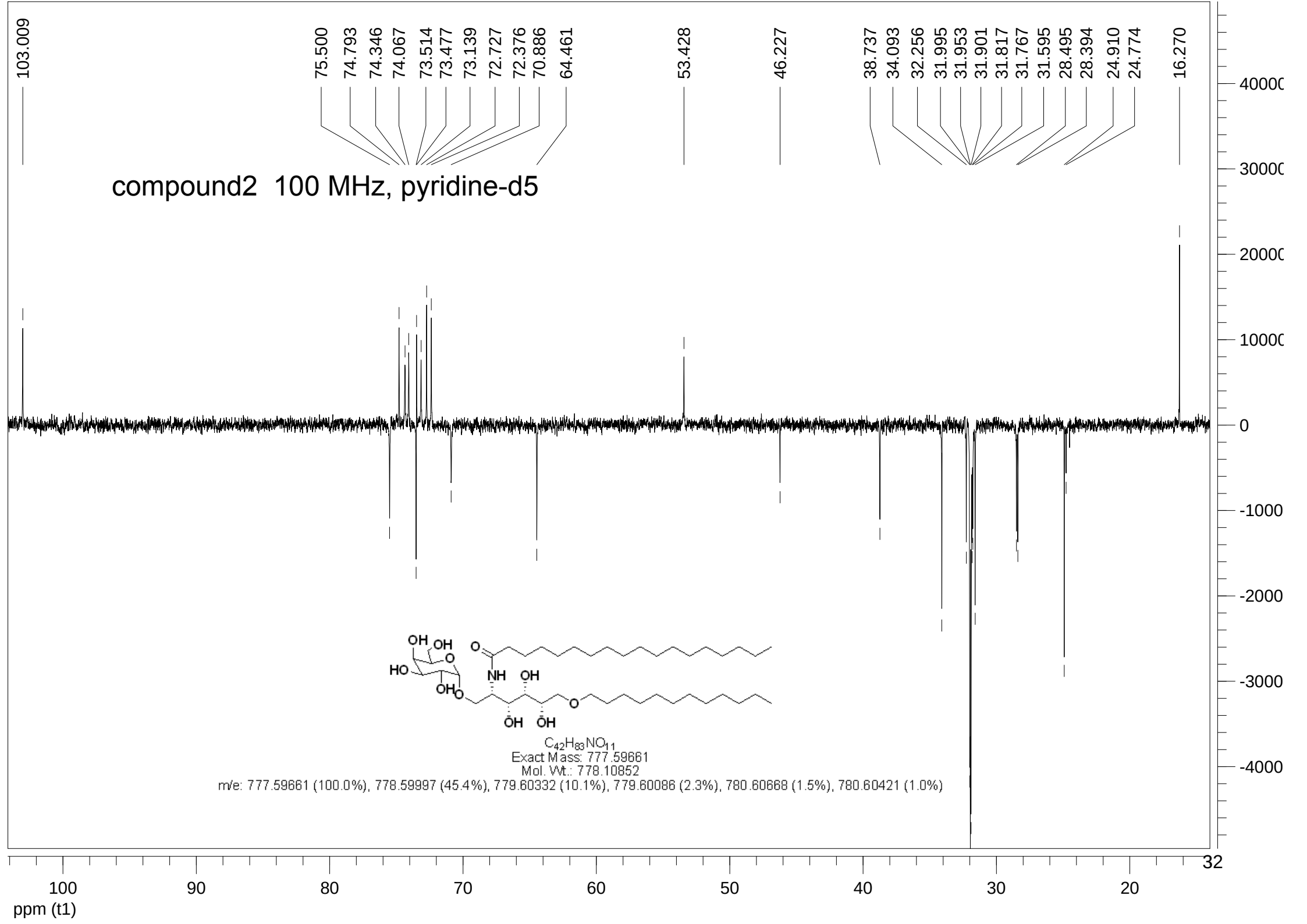

7.278
7.234
6.017
5.994
4.880
4.859
4.852
4.832
4.802
4.794
4.769
4.741
4.402
4.372
4.299
4.269
4.139
4.119
3.938
3.928
3.910
3.858
3.853
3.756
3.750
3.719
3.703
3.697
3.678
3.654
3.566
3.550
3.542
3.523
3.507
3.432
3.417
3.376
3.359
3.298
3.273
2.096
2.077
1.239
0.878
compoud 15 400 MHz, CDCl3
BnO
OBn
O
NH
OBn
OBn
OBn
OBn
C91H125NO11
Exact Mass: 1407.92526
Mol. Wt.: 1408.9663
m/e: 1407.92526 (100.0%), 1408.92862 (98.4%), 1409.93197 (47.9%), 1410.93533 (15.4%), 1411.93868 (3.7%), 1409.92951 (2.3%), 1410.93286 (2.2%), 1408.93154 (1.4%), 1409.93490 (1.4%), 1411.93622 (1.1%)
70000
60000
50000
40000
30000
20000
10000
0
35.47
0.93
5.00
8.10
2.00
1.00
0.98
2.00
1.00
4.07
3.08
1.02
3.02
2.01
2.04
2.08
46.00
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
27

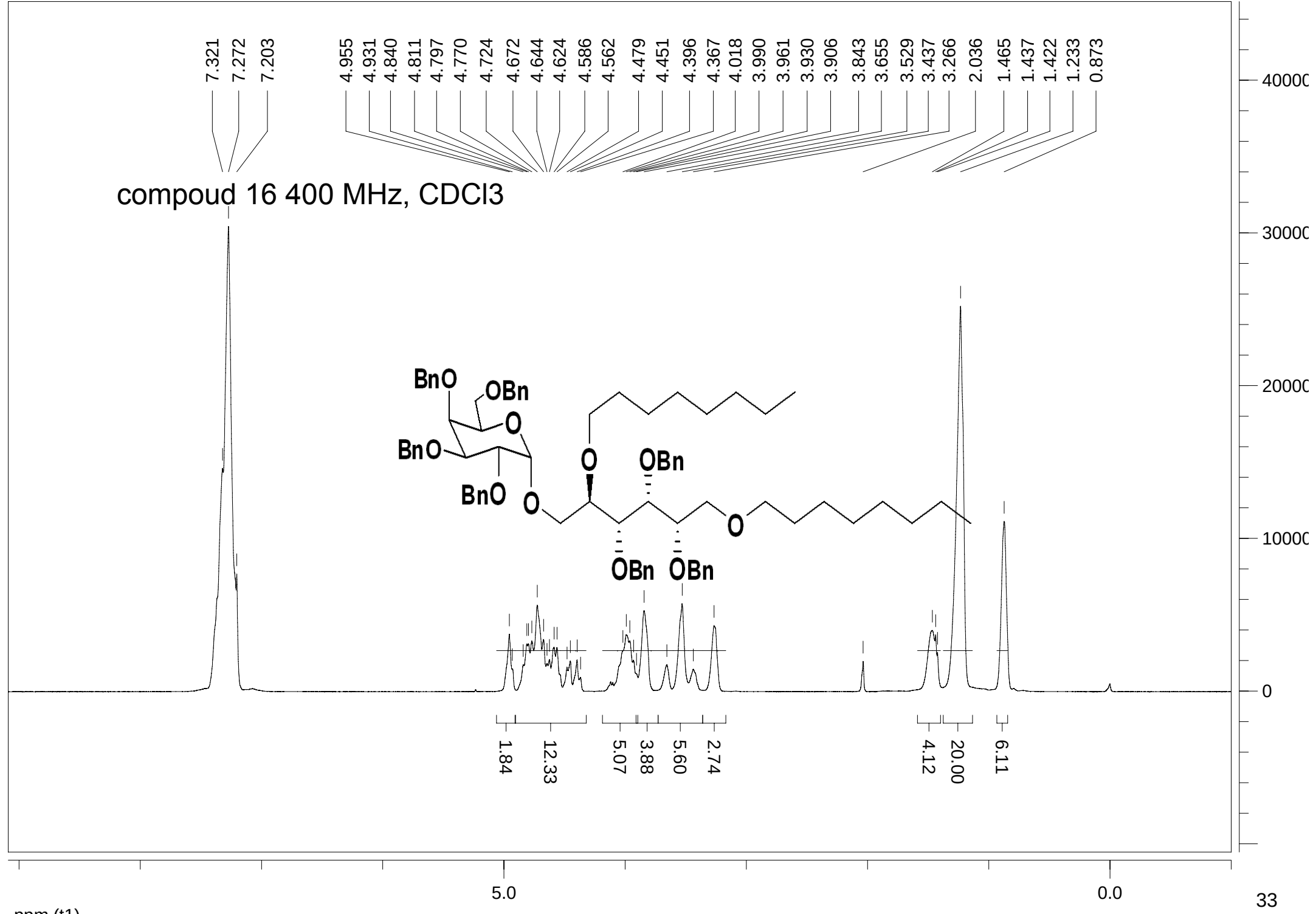

172.889
138.790
138.752
138.717
138.604
138.567
137.886
128.280
127.261
98.838
80.267
78.814
78.488
77.234
76.586
75.116
74.954
74.799
74.635
73.363
73.294
73.164
72.944
71.296
69.916
69.779
69.063
48.963
36.687
31.925
29.841
29.717
29.668
29.585
29.456
29.412
29.373
26.218
25.744
22.698
14.144
compoud 15 100 MHz, CDCl3
BnO
OBn
O
NH
OBn
OBn
OBn
C91H125NO11
Exact Mass: 1407.92526
Mol. Wt.: 1408.9663
m/e: 1407.92526 (100.0%), 1408.92862 (98.4%), 1409.93197 (47.9%), 1410.93533 (15.4%), 1411.93868 (3.7%), 1409.92951 (2.3%), 1410.93286 (2.2%), 1408.93154 (1.4%), 1409.93490 (1.4%), 1411.93622 (1.1%)
25000
20000
15000
10000
50000
0
28
150
100
50
0
ppm (t1)

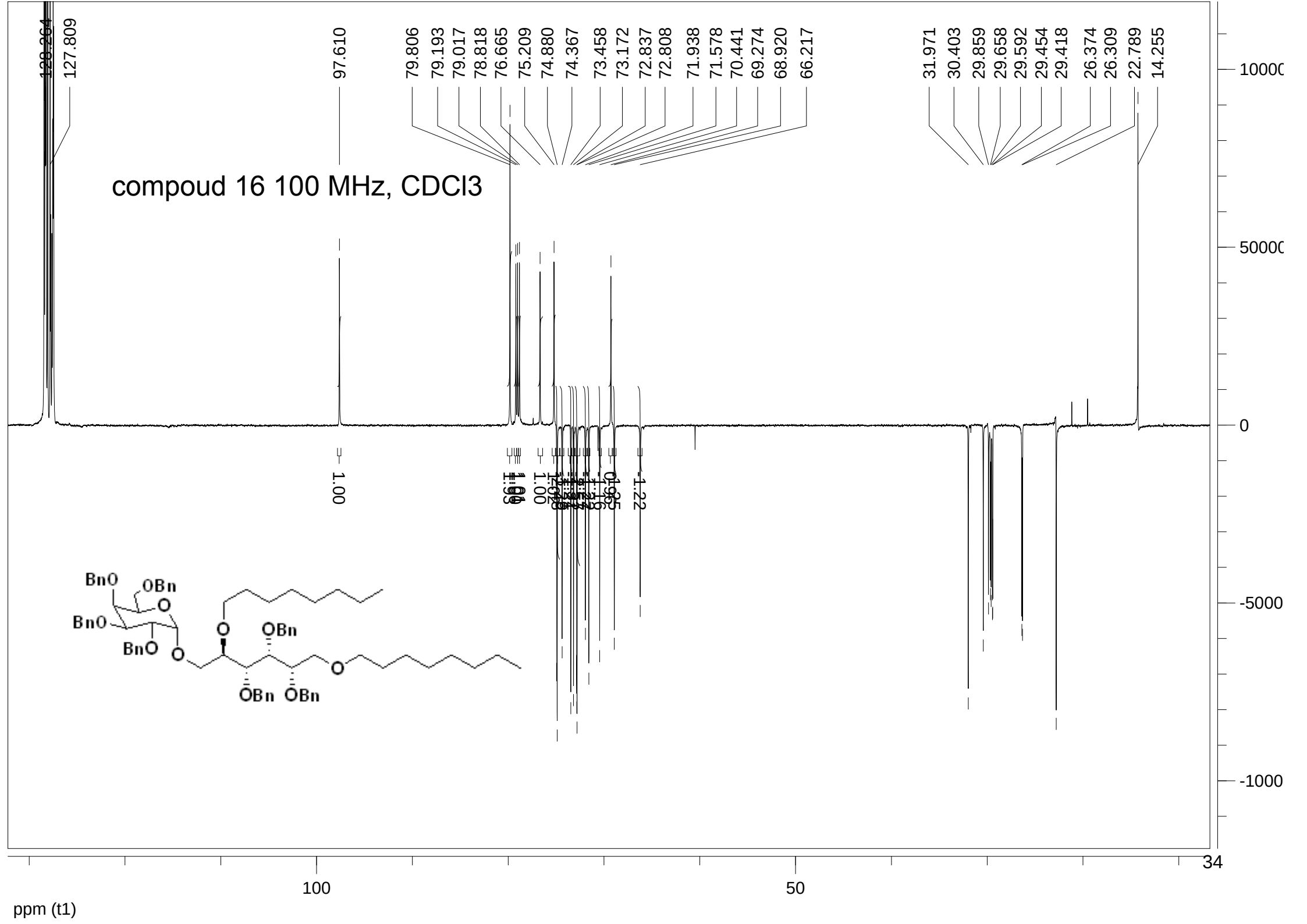

compoud 15 100 MHz, CDCl3
128.352
98.909
80.338
78.886
78.561
77.304
76.657
75.188
75.026
74.869
74.706
73.434
73.366
73.236
73.015
71.367
69.986
69.850
69.133
49.033
36.760
31.998
29.911
29.788
29.657
29.528
29.487
29.446
26.291
25.815
22.768
14.217
BnO
OBn
O
BnO
BnO
O
O
NH
OBn
O
OBn
OBn
$C_{91}H_{125}NO_{11}$
Exact Mass: 1407.92526
Mol. Wt.: 1408.9663
m/e: 1407.92526 (100.0%), 1408.92862 (98.4%), 1409.93197 (47.9%), 1410.93533 (15.4%), 1411.93868 (3.7%), 1409.92951 (2.3%), 1410.93286 (2.2%), 1408.93154 (1.4%), 1409.93490 (1.4%), 1411.93622 (1.1%)
100
50
ppm (t1)

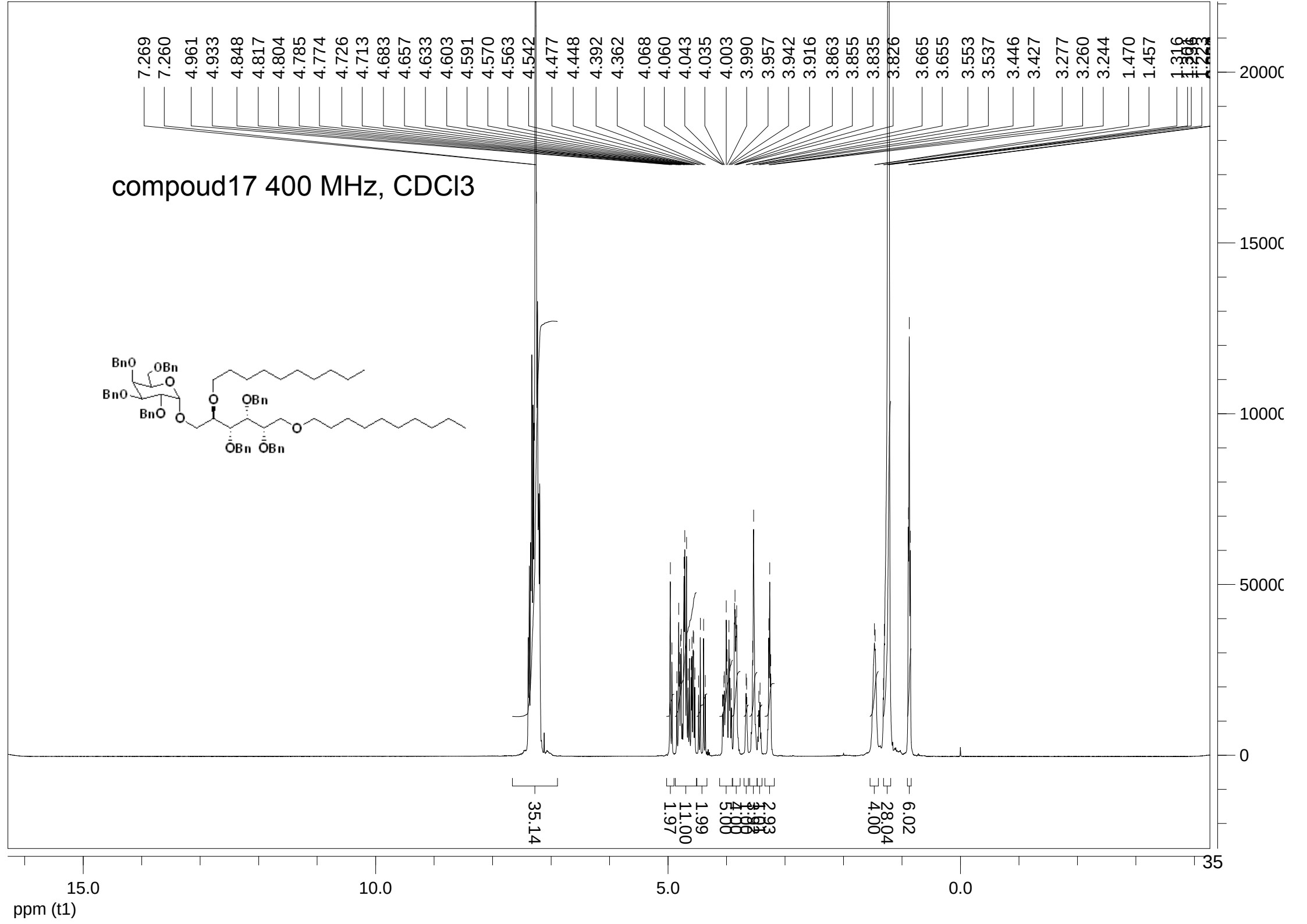

5.466
5.458
5.198
5.193
5.185
4.895
4.718
4.649
4.640
4.556
4.482
4.405
4.390
4.171
4.160
4.089
4.076
4.046
4.029
3.528
3.516
3.291
3.278
3.264
2.527
1.827
1.768
1.597
1.269
1.245
0.878
compound2 400 MHz, pyridine-d5
C42H83NO11
Exact Mass: 777.59661
Mol. Wt.: 778.10852
m/e: 777.59661 (100.0%), 778.59997 (45.4%), 779.60332 (10.1%), 779.60086 (2.3%), 780.60668 (1.5%), 780.60421 (1.0%)
1.10
1.04
1.00
1.03
1.08
5.08
2.07
1.01
1.03
1.07
2.08
0.68
1.98
2.05
2.17
46.39
6.26
10000
50000
0
30
5.0
4.0
3.0
2.0
1.0
ppm (t1)

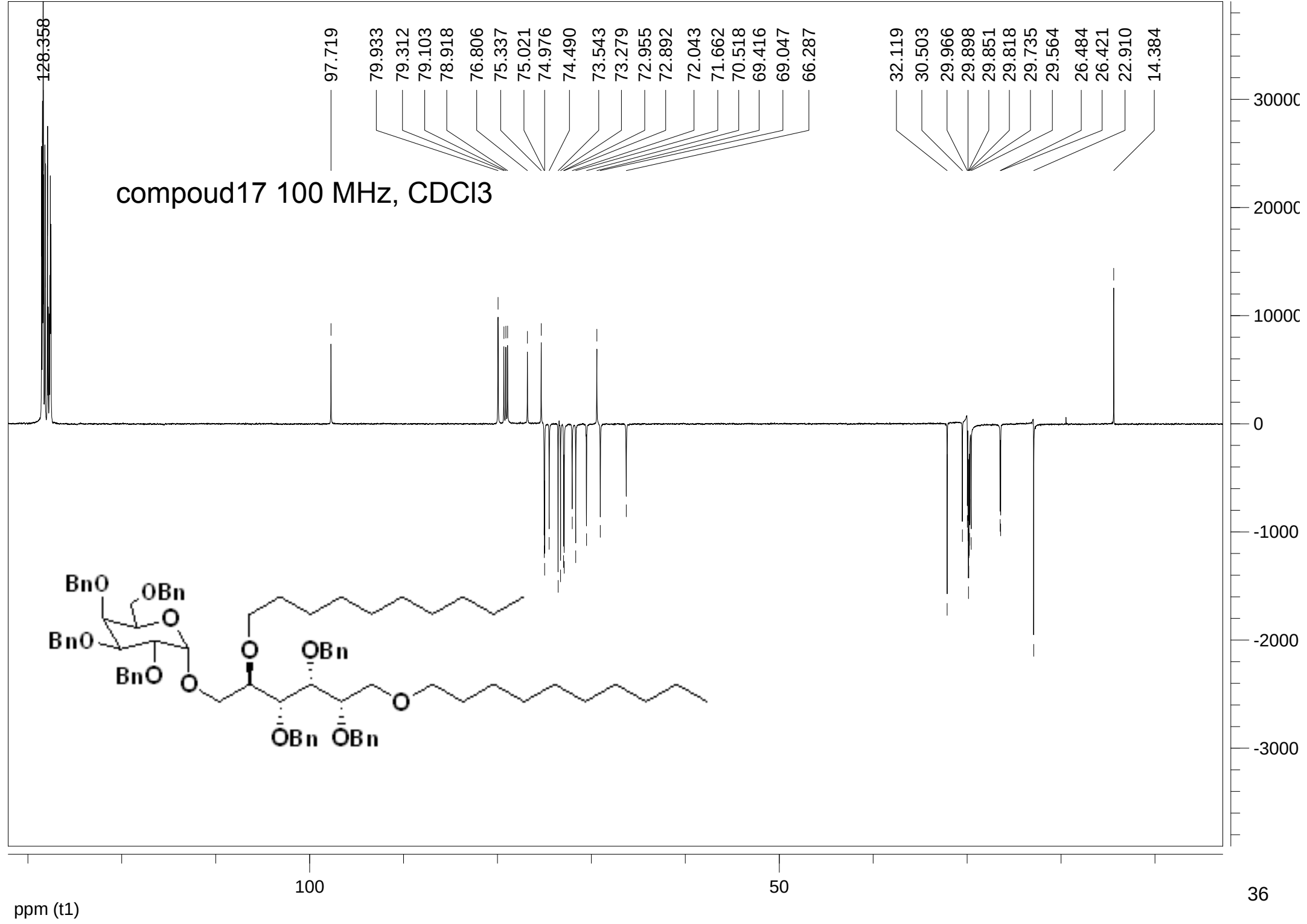

176.062
103.011
75.498
74.790
74.348
74.067
73.513
73.479
73.145
72.729
72.376
70.890
64.463
53.431
46.227
38.736
34.090
32.254
31.952
31.898
31.816
31.766
31.592
28.493
28.389
24.908
24.777
16.265
compound2 100 MHz, pyridine-d5
OH
OH
O
HO
OH
O
NH
OH
O
O
OH
OH
C42H83NO11
Exact Mass: 777.59661
Mol. Wt.: 778.10852
m/e: 777.59661 (100.0%), 778.59997 (45.4%), 779.60332 (10.1%), 779.60086 (2.3%), 780.60668 (1.5%), 780.60421 (1.0%)
80000
70000
60000
50000
40000
30000
20000
10000
0
31
150
100
50
0
ppm (t1)

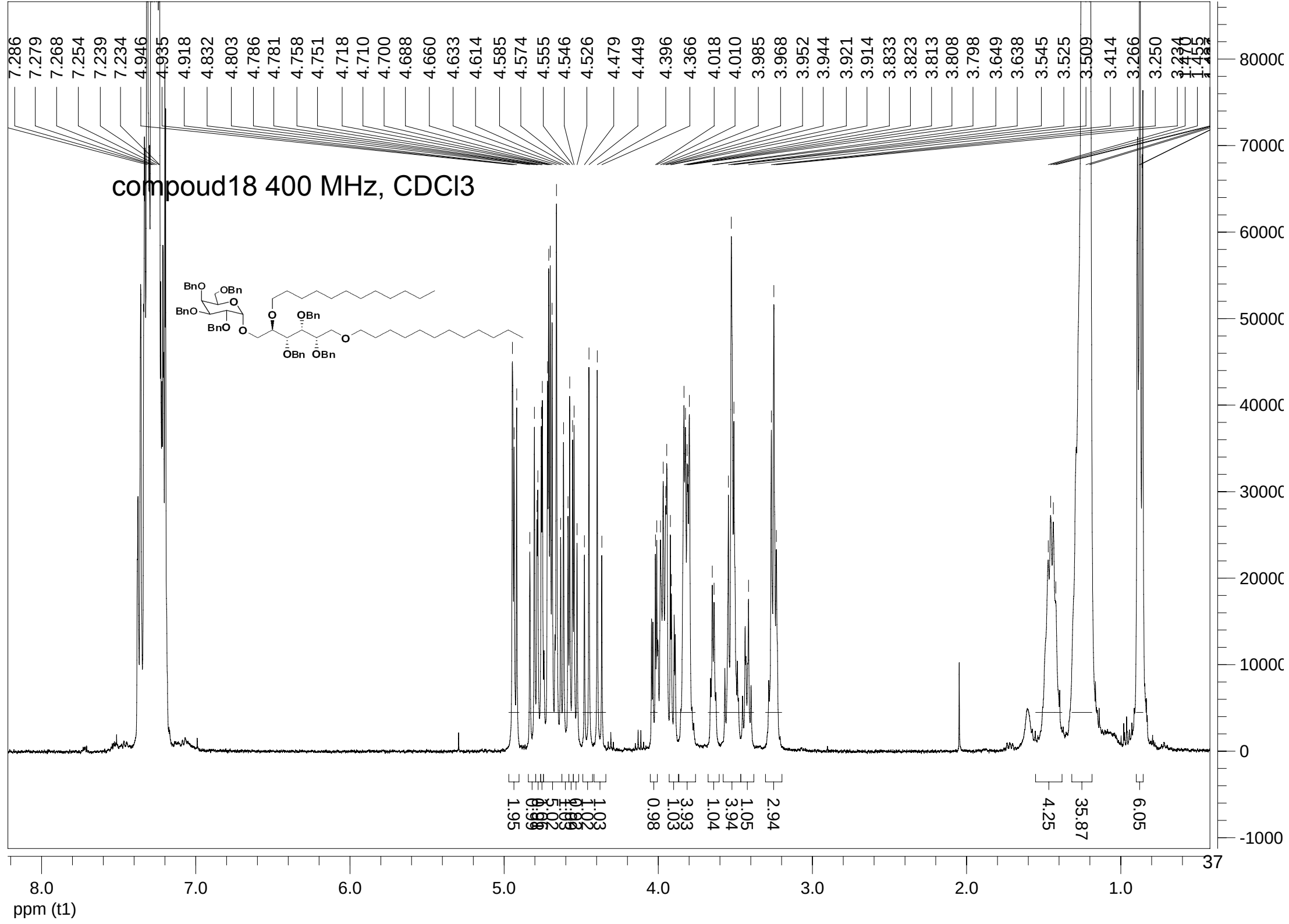

103.009
75.500
74.793
74.346
74.067
73.514
73.477
73.139
72.727
72.376
70.886
64.461
53.428
46.227
38.737
34.093
32.256
31.995
31.953
31.901
31.817
31.767
31.595
28.495
28.394
24.910
24.774
16.270
compound2 100 MHz, pyridine-d5
40000
30000
20000
10000
0
-1000
-2000
-3000
-4000
OH
OH
O
HO
OH
O
NH
OH
O
O
OH
OH
C42H83NO11
Exact Mass: 777.59661
Mol. Wt.: 778.10852
m/e: 777.59661 (100.0%), 778.59997 (45.4%), 779.60332 (10.1%), 779.60086 (2.3%), 780.60668 (1.5%), 780.60421 (1.0%)
32
100
90
80
70
60
50
40
30
20
ppm (t1)

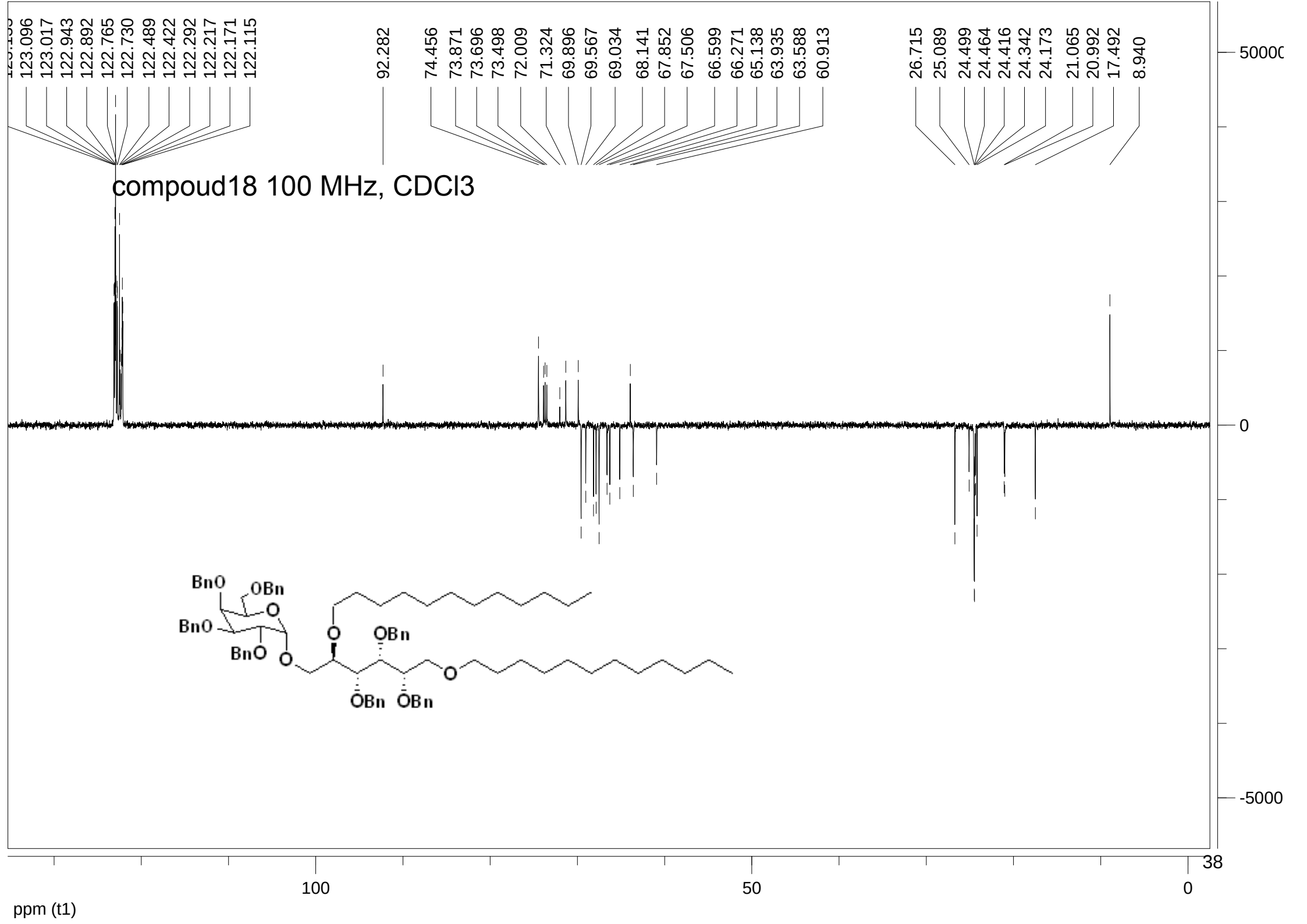

7.321
7.272
7.203
4.955
4.931
4.840
4.811
4.797
4.770
4.724
4.672
4.644
4.624
4.586
4.562
4.479
4.451
4.396
4.367
4.018
3.990
3.961
3.930
3.906
3.843
3.655
3.529
3.437
3.266
2.036
1.465
1.437
1.422
1.233
0.873
compoud 16 400 MHz, CDCl3
BnO
OBn
O
BnO
BnO
O
O
OBn
O
OBn
OBn
1.84
12.33
5.07
3.88
5.60
2.74
4.12
20.00
6.11
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)

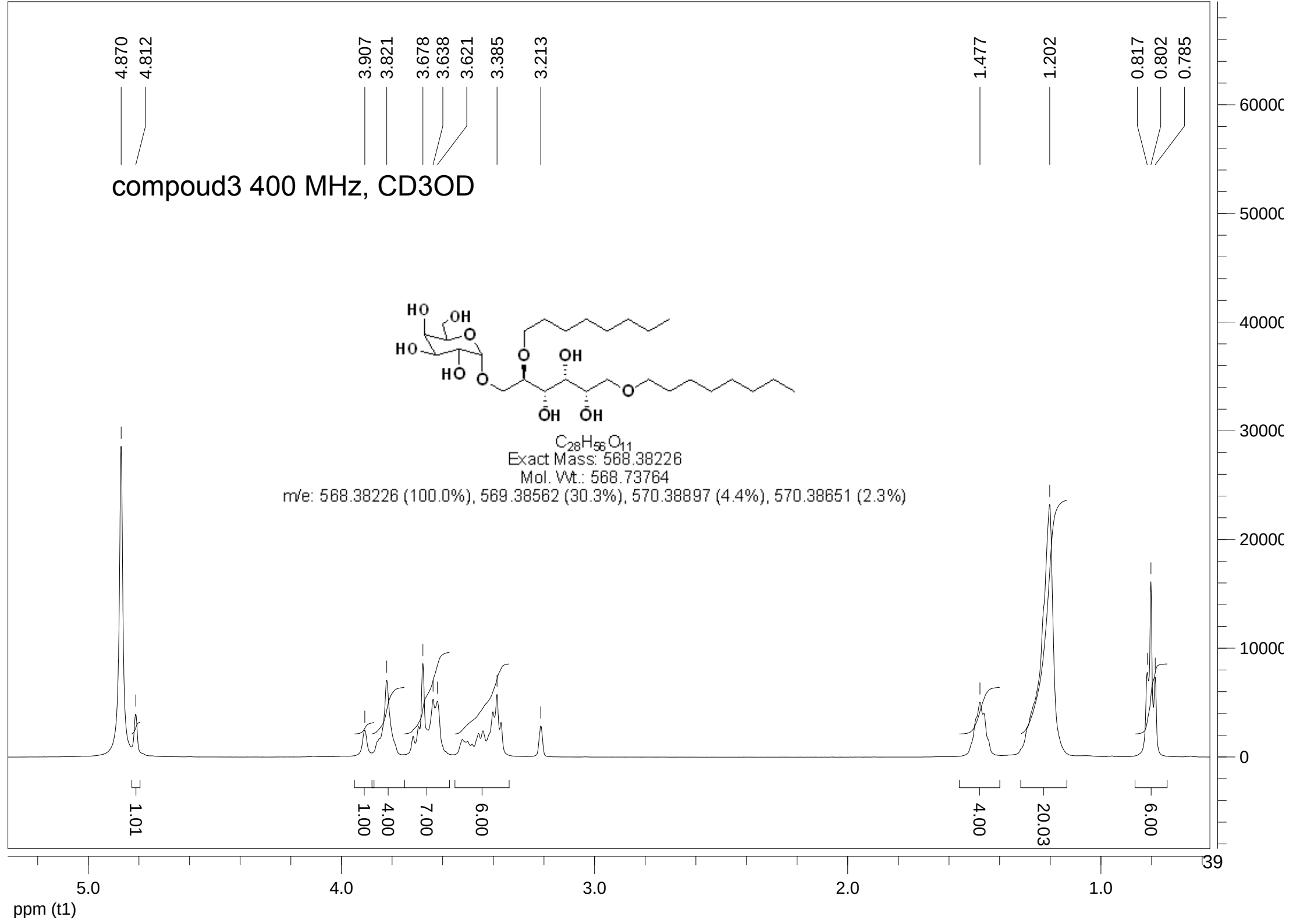

compoud 16 100 MHz, CDCl3
128.264
127.809
97.610
79.806
79.193
79.017
78.818
76.665
75.209
74.880
74.367
73.458
73.172
72.837
72.808
71.938
71.578
70.441
69.274
68.920
66.217
31.971
30.403
29.859
29.658
29.592
29.454
29.418
26.374
26.309
22.789
14.255
1.00
1.00
0.96
1.22
10000
50000
0
-5000
-10000
100
50
34
ppm (t1)
BnO
OBn
BnO
BnO
O
O
OBn
OBn
OBn
O

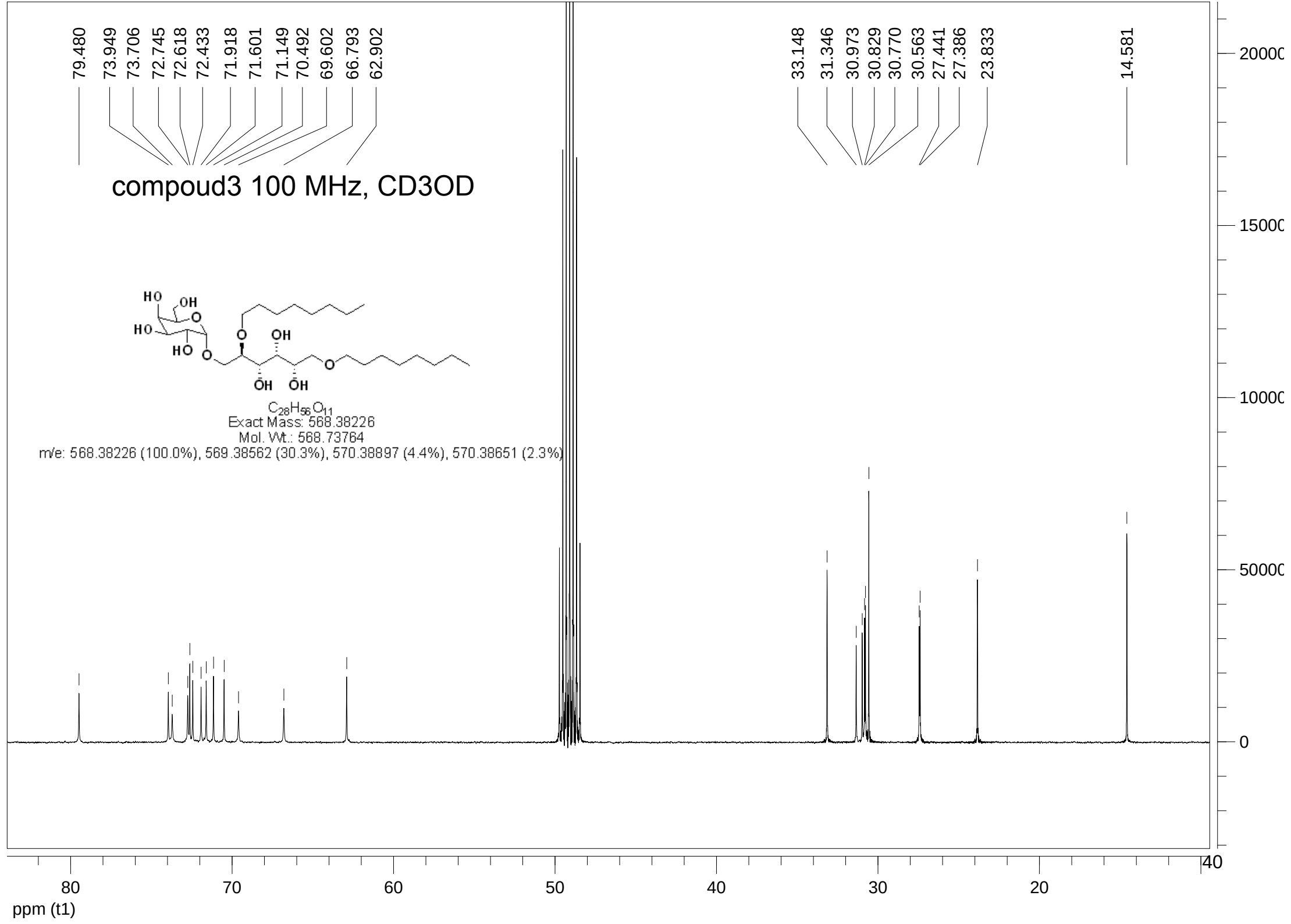

compoud17 400 MHz, CDCl3
7.269
7.260
4.961
4.933
4.848
4.817
4.804
4.785
4.774
4.726
4.713
4.683
4.657
4.633
4.603
4.591
4.570
4.563
4.542
4.477
4.448
4.392
4.362
4.068
4.060
4.043
4.035
4.003
3.990
3.957
3.942
3.916
3.863
3.855
3.835
3.826
3.665
3.655
3.553
3.537
3.446
3.427
3.277
3.260
3.244
1.470
1.457
1.316
BnO
OBn
O
OBn
35.14
1.97
11.00
1.99
5.00
4.00
28.04
6.02
20000
15000
10000
50000
0
35
15.0
10.0
5.0
0.0
ppm (t1)

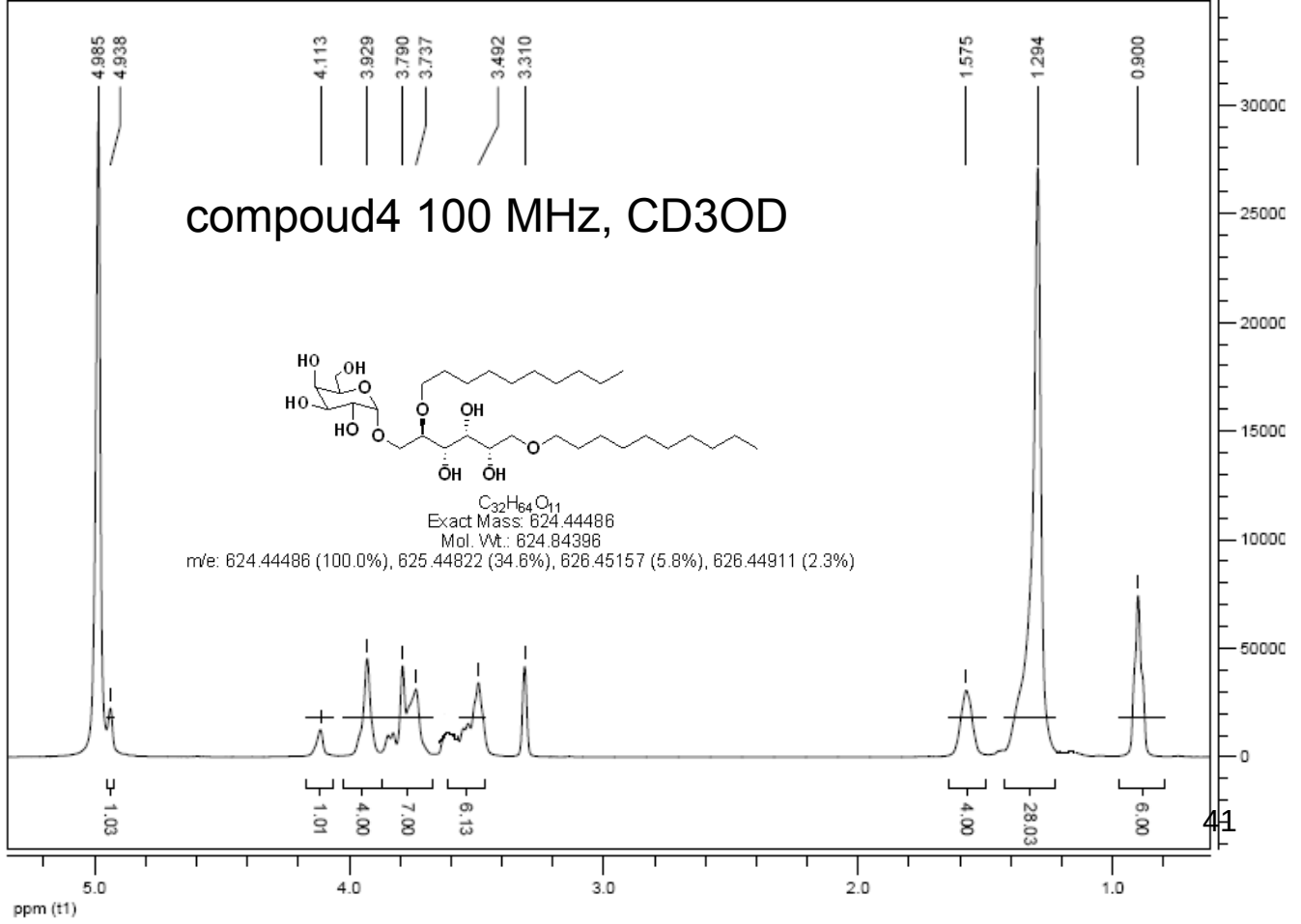

128.358
97.719
79.933
79.312
79.103
78.918
76.806
75.337
75.021
74.976
74.490
73.543
73.279
72.955
72.892
72.043
71.662
70.518
69.416
69.047
66.287
32.119
30.503
29.966
29.898
29.851
29.818
29.735
29.564
26.484
26.421
22.910
14.384
compoud17 100 MHz, CDCl3
30000
20000
10000
0
-1000
-2000
-3000
BnO
OBn
O
BnO
BnO
O
O
OBn
OBn
OBn
O
100
50
36
ppm (t1)

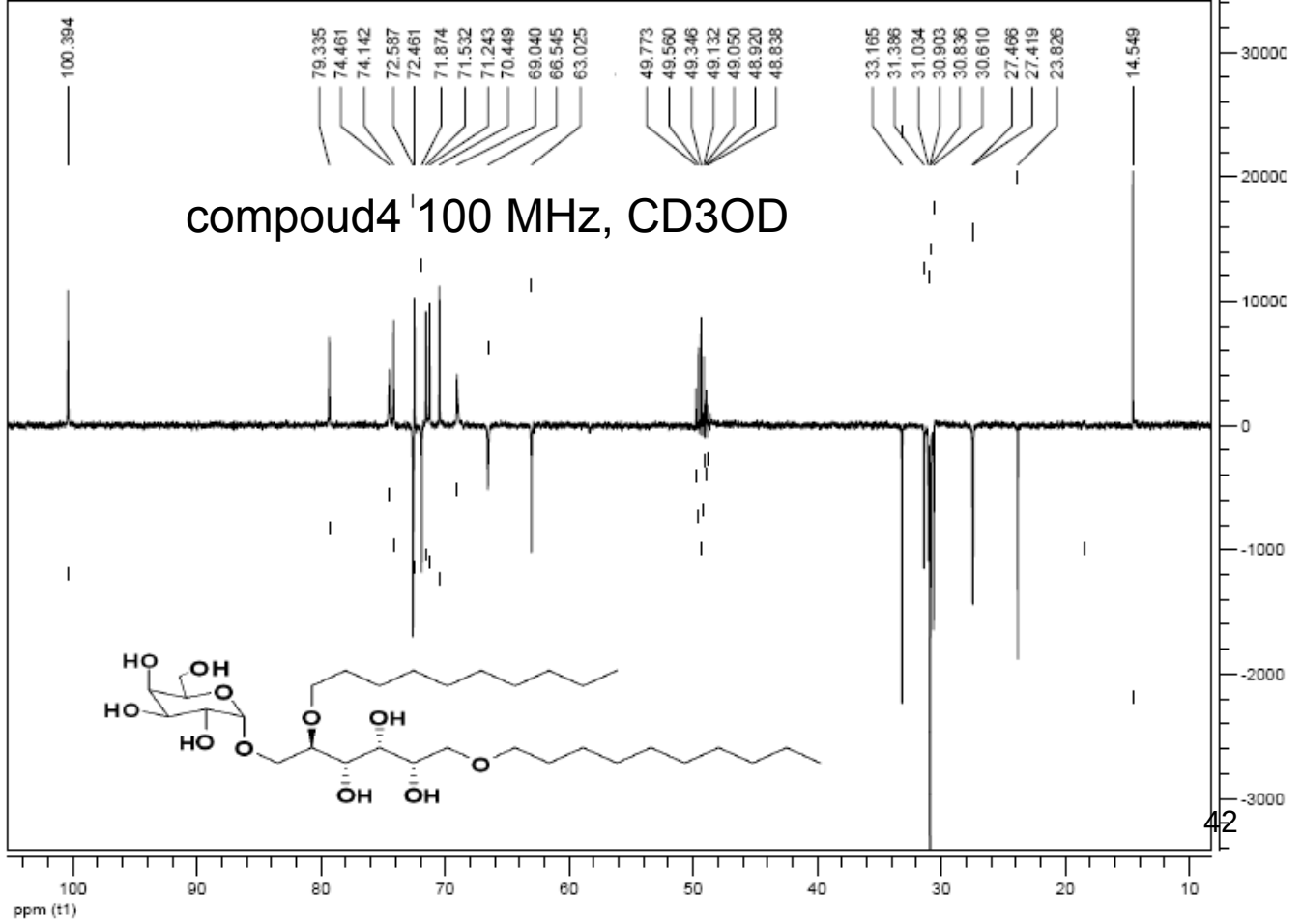

compoud18 400 MHz, CDCl3
7.286
7.279
7.268
7.254
7.239
7.234
4.946
4.935
4.918
4.832
4.803
4.786
4.781
4.758
4.751
4.718
4.710
4.700
4.688
4.660
4.633
4.614
4.585
4.574
4.555
4.546
4.526
4.479
4.449
4.396
4.366
4.018
4.010
3.985
3.968
3.952
3.944
3.921
3.914
3.833
3.823
3.813
3.808
3.798
3.649
3.638
3.545
3.525
3.509
3.414
3.266
3.250
BnO
OBn
O
OBn
1.95
0.98
1.03
3.93
1.04
3.94
1.05
2.94
4.25
35.87
6.05
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
37

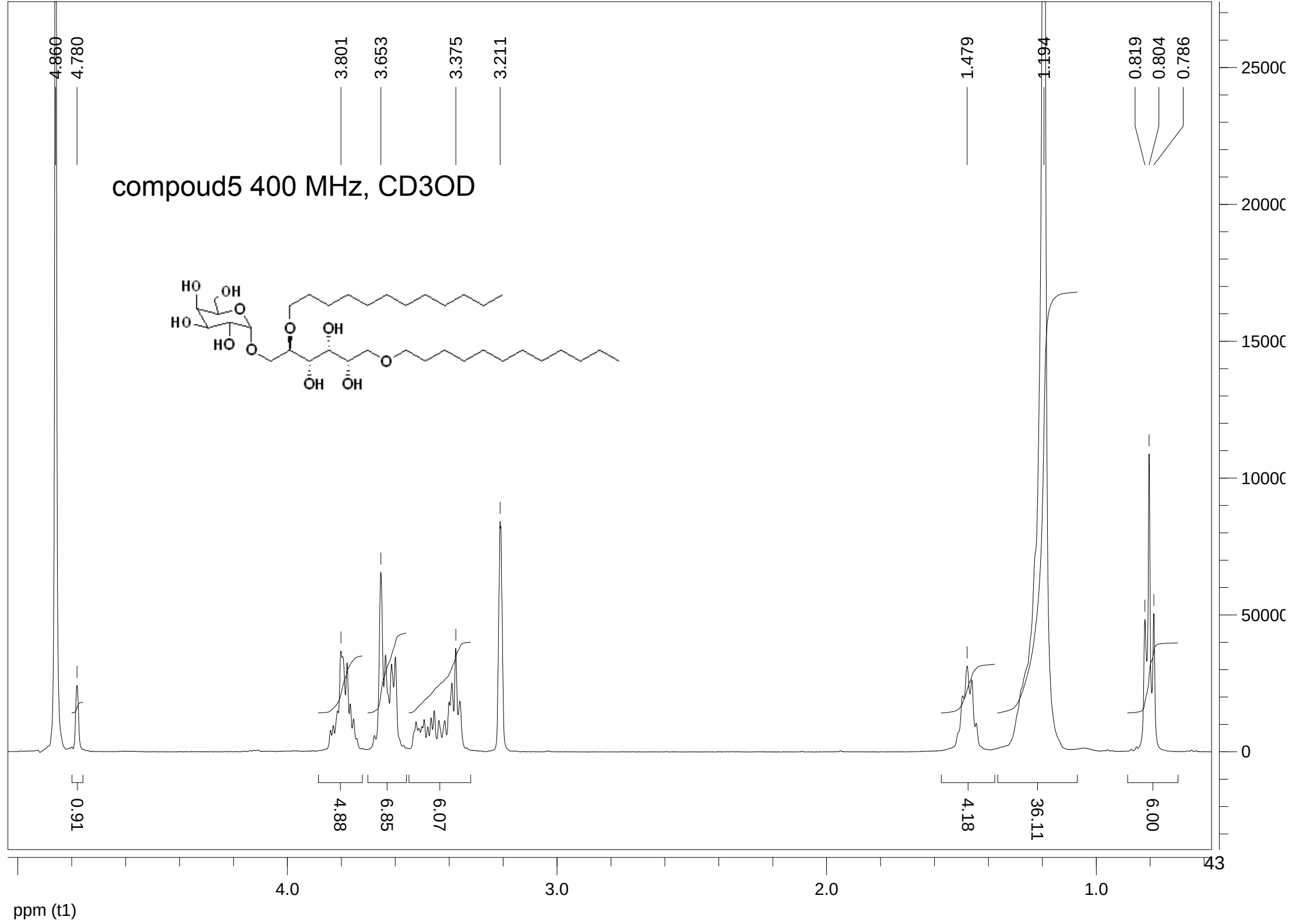

123.096
123.017
122.943
122.892
122.765
122.730
122.489
122.422
122.292
122.217
122.171
122.115
92.282
74.456
73.871
73.696
73.498
72.009
71.324
69.896
69.567
69.034
68.141
67.852
67.506
66.599
66.271
65.138
63.935
63.588
60.913
26.715
25.089
24.499
24.464
24.416
24.342
24.173
21.065
20.992
17.492
8.940
compoud18 100 MHz, CDCl3
50000
0
-5000
38
100
50
0
ppm (t1)
BnO
OBn
O
BnO
BnO
O
O
OBn
OBn
OBn
O

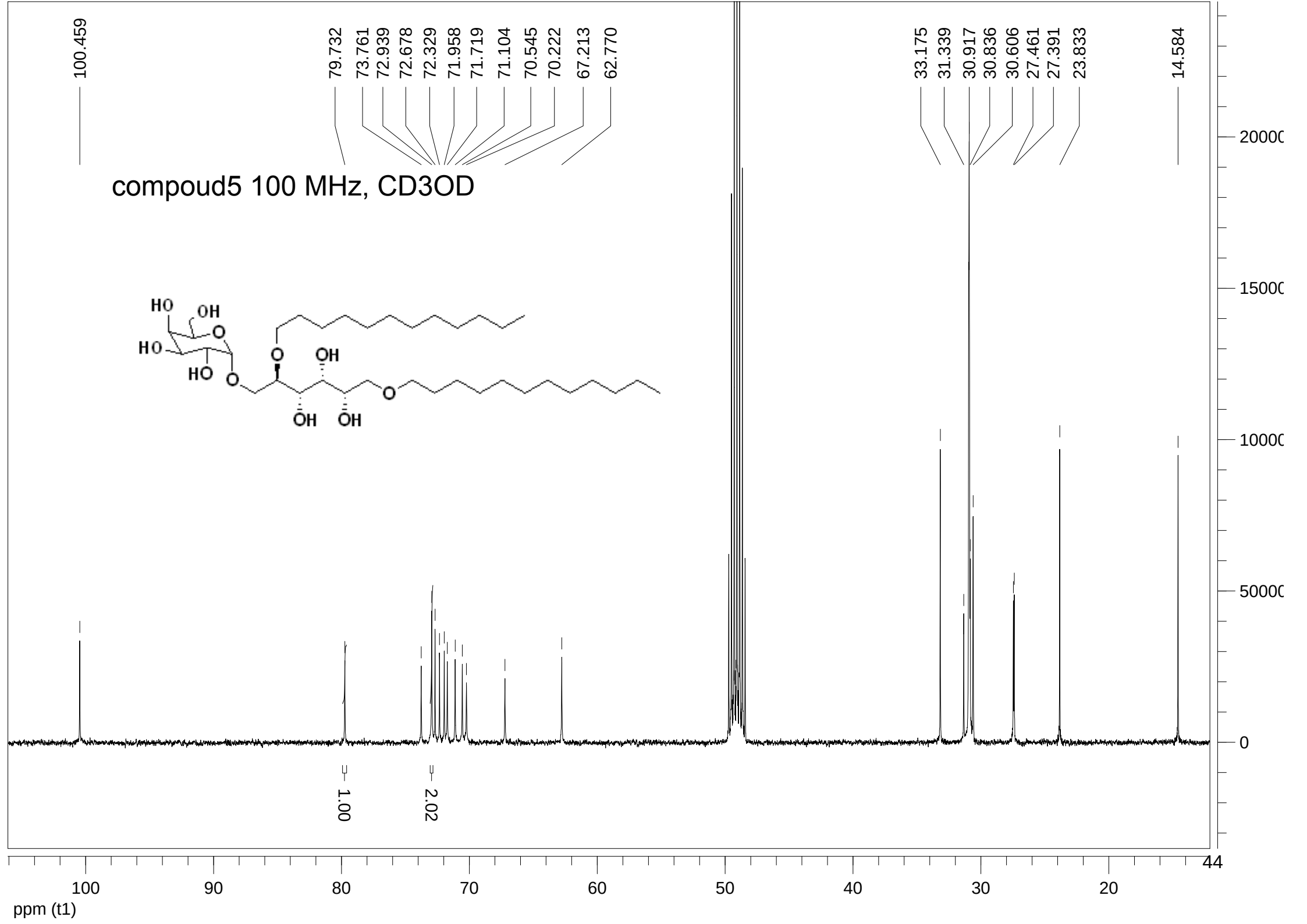

4.870
4.812
3.907
3.821
3.678
3.638
3.621
3.385
3.213
1.477
1.202
0.817
0.802
0.785
compoud3 400 MHz, CD3OD
C28H56O11
Exact Mass: 568.38226
Mol. Wt.: 568.73764
m/e: 568.38226 (100.0%), 569.38562 (30.3%), 570.38897 (4.4%), 570.38651 (2.3%)
1.01
1.00
4.00
7.00
6.00
4.00
20.03
6.00
60000
50000
40000
30000
20000
10000
0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
39


79.480
73.949
73.706
72.745
72.618
72.433
71.918
71.601
71.149
70.492
69.602
66.793
62.902
33.148
31.346
30.973
30.829
30.770
30.563
27.441
27.386
23.833
14.581
compoud3 100 MHz, CD3OD
C28H56O11
Exact Mass: 568.38226
Mol. Wt.: 568.73764
m/e: 568.38226 (100.0%), 569.38562 (30.3%), 570.38897 (4.4%), 570.38651 (2.3%)
20000
15000
10000
5000
0
80
70
60
50
40
30
20
40
ppm (t1)


4.985
4.938
4.113
3.929
3.790
3.737
3.492
3.310
1.575
1.294
0.900
compoud4 100 MHz, CD3OD
HO
OH
O
HO
HO
O
O
OH
O
OH
OH
C32H64O11
Exact Mass: 624.44486
Mol. Wt.: 624.84396
m/e: 624.44486 (100.0%), 625.44822 (34.6%), 626.45157 (5.8%), 626.44911 (2.3%)
1.03
1.01
4.00
7.00
9.13
4.00
28.03
6.00
30000
25000
20000
15000
10000
50000
0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


100.394
79.335
74.461
74.142
72.587
72.461
71.874
71.532
71.243
70.449
69.040
66.545
63.025
49.773
49.560
49.346
49.132
49.050
48.920
48.838
33.165
31.386
31.034
30.903
30.836
30.610
27.466
27.419
23.826
14.549
compoud4 '100 MHz, CD3OD
30000
20000
10000
0
-1000
-2000
-3000
100
90
80
70
60
50
40
30
20
10
ppm (t1)
HO
OH
O
HO
HO
O
O
OH
OH
OH
O


4.860
4.780
3.801
3.653
3.375
3.211
1.479
1.194
0.819
0.804
0.786
compoud5 400 MHz, CD3OD
HO
OH
O
HO
HO
O
O
OH
OH
OH
O
25000
20000
15000
10000
50000
0
0.91
4.88
6.85
6.07
4.18
36.11
6.00
43
4.0
3.0
2.0
1.0
ppm (t1)


100.459
79.732
73.761
72.939
72.678
72.329
71.958
71.719
71.104
70.545
70.222
67.213
62.770
33.175
31.339
30.917
30.836
30.606
27.461
27.391
23.833
14.584
compoud5 100 MHz, CD3OD
HO
OH
O
HO
HO
O
O
OH
OH
OH
O
1.00
2.02
20000
15000
10000
50000
0
100
90
80
70
60
50
40
30
20
44
ppm (t1)