Supporting Information

Isolated Polar Amino Acid Residues Modulate Lipid Binding in the Large Hydrophobic Cavity of CD1d

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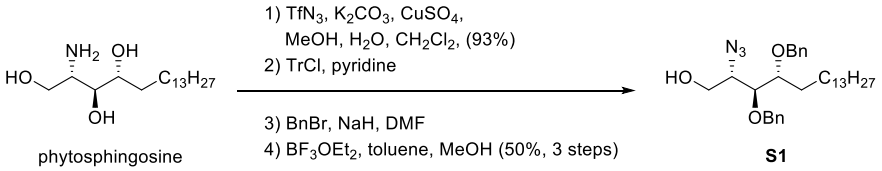
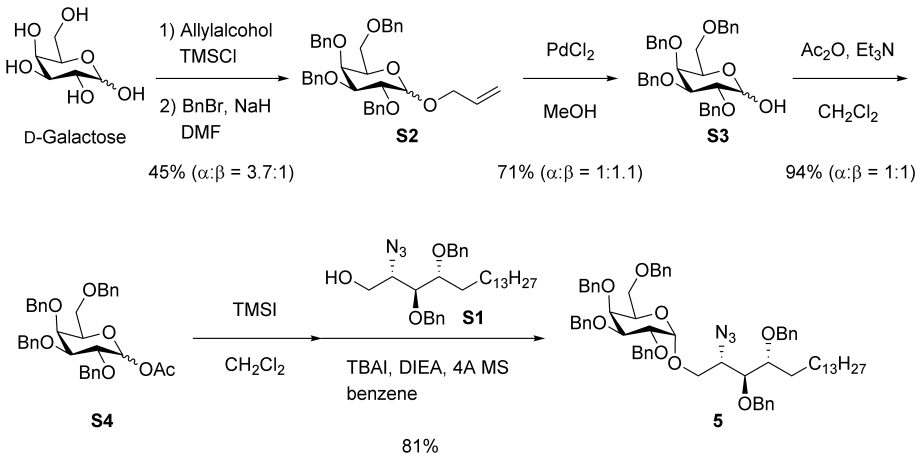
Experimental Section

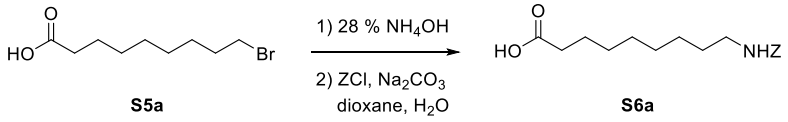
General Methods. All moisture-sensitive reactions were performed using syringe-septum cap techniques under an argon atmosphere and all glassware was dried in an oven at 80 °C for 2 h prior to use. Reactions at –78 °C employed a CO_2–MeOH bath. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F_{254} Plates (Merck, 0.25 mm thickness). For flash chromatography, Silica gel 60 N [spherical neutral (Kanto Chemical Co., 40-50 μm)] was employed. All NMR spectral data were recorded on a JEOL ECX-400 spectrometer for ^1H (400 MHz) and ^{13}C (100 MHz). Chemical shifts are reported in δ (ppm) relative to TMS in $CDCl_3$ as internal standard (^1H NMR) or the residual $CHCl_3$ signal (^{13}C NMR). ^1H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Exact mass (HRMS) spectra were recorded on an electronspray ionization quadrupole time of flight (ESI-QTOF) mass spectrometer (micrOTOF-QII-HC; BRUKER).



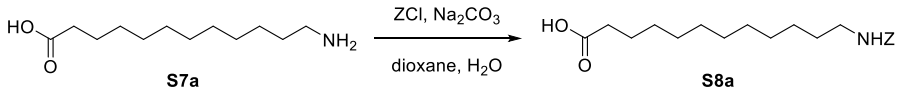
Scheme S1. Synthesis of a known ceramide derivative **S1**.[1]



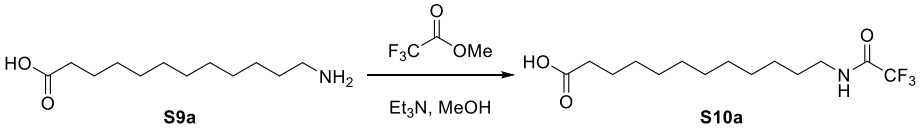
Scheme S2. Synthesis of a known compound **5**.[2, 3]



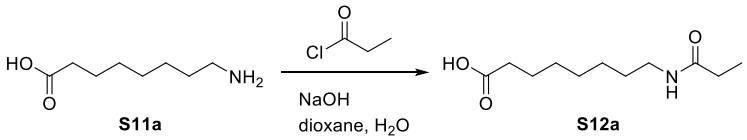
Scheme S3. Synthesis of **S6**.



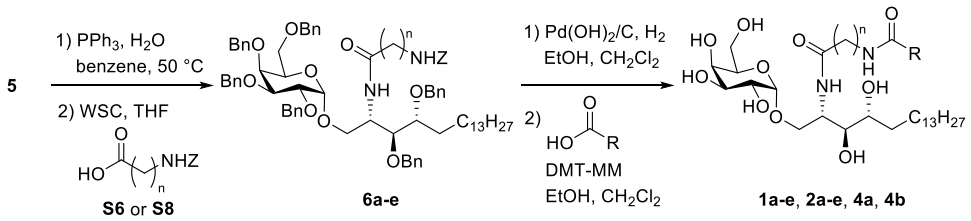
Scheme S4. Synthesis of **S8**.



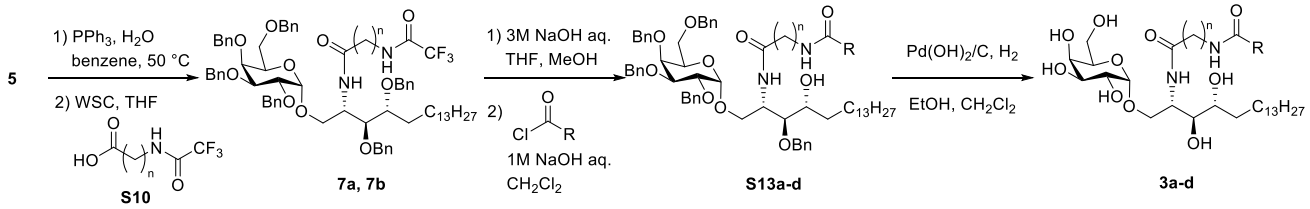
Scheme S5. Synthesis of **S10**.



Scheme S6. Synthesis of **S12**.

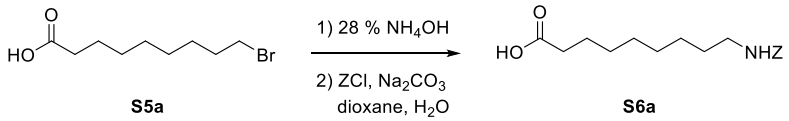


Scheme S7. Synthesis of **1a-e**, **2a-e**, **4a** and **4b** from **5**.



Scheme S8. Synthesis of **3a-d** from **5**.

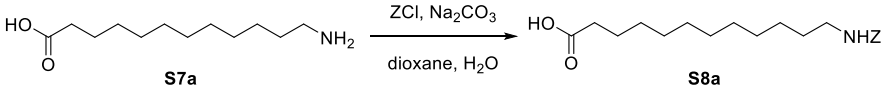
General Procedure for the Preparation of (Z)-Protected Amino Acid Derivatives S6 from Bromocarboxylic Acids S5.



S5a S6a

S6a: The preparation of 9-aminononanoic acid was carried out according to the method of Meijler, M. M. *et al.*[4] A solution of **S5a** (300 mg, 1.27 mmol) in 28% NH_4OH was stirred at 50 °C for 46 h. The mixture was concentrated under reduced pressure to give a crude amine as a white solid, which was used without further purification. To a stirred suspension of this amine in dioxane (2.5 mL) and H_2O (2.5 mL) were added Na_2CO_3 (1.35 g, 12.7 mmol) and ZCl (0.90 mL, 6.36 mmol) at room temperature. After stirring for 25 h at this temperature, the mixture was diluted with EtOAc and washed with saturated $KHSO_4$ aq., and dried over Mg_2SO_4. Concentration under reduced pressure followed by recrystallization from hexane/EtOAc (8/1) gave **S6a** as white solid (181 mg, 46% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27-1.34 (m, 8H), 1.45-1.52 (m, 2H), 1.60-1.66 (m, 2H), 2.34 (t, J = 7.3 Hz, 2H), 3.16-3.21 (m, 2H), 4.71-4.77 (m, 1H), 5.09-5.11 (m, 2H), 7.30-7.38 (m, 5H).

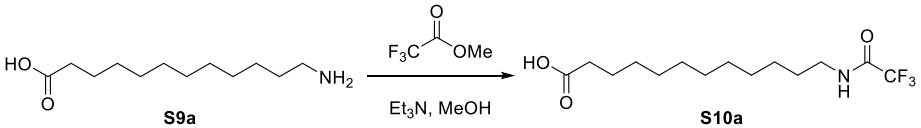
General Procedure for the Preparation of (Z)-Protected Amino Acid Derivative S8 from Amino Acids S7.



S7a S8a

S8a: To a stirred suspension of **S7a** (1.0 g, 4.6 mmol) in dioxane (7.0 mL) and H_2O (7.0 mL) were added Na_2CO_3 (2.4 g, 23 mmol) and ZCl (0.76 mL, 5.5 mmol) at room temperature. After stirring for 31 h at this temperature, the mixture was diluted with EtOAc and washed with saturated $KHSO_4$ aq., and dried over Mg_2SO_4. Concentration under reduced pressure followed by recrystallization from hexane/EtOAc (8/1) gave **S8a** as white solid (550 mg, 34% yield). All the spectral data were in agreement with those reported by Suzuki, M. *et al.* (*Tetrahedron* **2007**, *63*, 7302-7308): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25-1.35 (m, 14H), 1.45-1.51 (m, 2H), 1.60-1.65 (m, 2H), 2.34 (t, J = 7.6 Hz, 2H), 3.18 (dt, J = 7.3, 6.3 Hz, 2H), 4.73-4.77 (m, 1H), 5.09-5.15 (m, 2H), 7.30-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 26.7, 28.8, 29.0, 29.1, 29.2, 29.3, 29.4 (2C), 34.0, 41.1, 66.6, 128.1 (3C), 128.5 (2C), 136.6, 156.4, 179.3; HRMS (ESI-TOF) calcd $C_{20}H_{30}NO_4$: $(M-H)^-$, 348.2180; found: $(M-H)^-$, 348.2188.

General Procedure for the Preparation of Trifluoroacetyl-Protected Amino Acid Derivative S10 from Amino Acids S9.

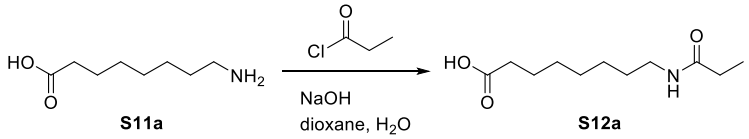


S9a S10a

S10a: The preparation of **S10a** was carried out according to the method of Durand, A.; Brown, T. (*Nucleos. Nucleot. Nucl.* **2007**, *26*, 785–794). To a stirred suspension of **S9a** (1.0 g, 4.6 mmol) in MeOH (7.0 mL) and Et_3N (0.70 mL) were added methyl 2,2,2-trifluoroacetate (0.68 mL, 6.9 mmol) at room temperature. After stirring for 18 h at this temperature, the mixture was diluted with EtOAc and washed with saturated $KHSO_4$ aq., and dried

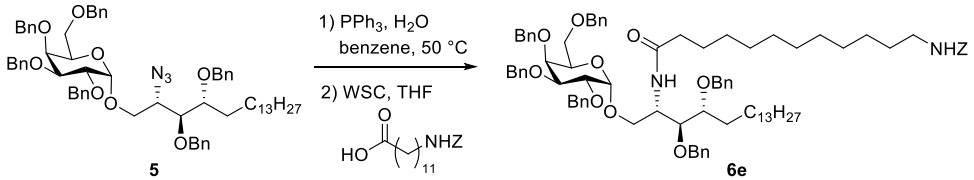
over Mg_2SO_4. Concentration under reduced pressure gave **S10a** as white solid (1.32 g, 92% yield). All the spectral data were in agreement with those reported by Durand, A.; Brown, T.: ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H-NMR ($CDCl_3$) δ: 1.26-1.35 (m, 14H), 1.57-1.64 (m, 4H), 2.35 (t, J = 7.6 Hz, 2H), 3.36 (dt, J = 6.8, 6.8 Hz, 2H), 6.29-6.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 26.6, 28.9 (2C), 29.0, 29.1, 29.3 (3C), 34.0, 40.0, 115.8 (q, J_{C-F} = 286.3 Hz), 157.2 (q, J_{C-F} = 37.2 Hz), 180.1; HRMS (ESI-TOF) calcd $C_{14}H_{23}F_3NO_3$: $(M-H)^-$, 310.1636; found: $(M-H)^-$, 310.1639.

General Procedure for the Preparation of Amide Derivative S12.



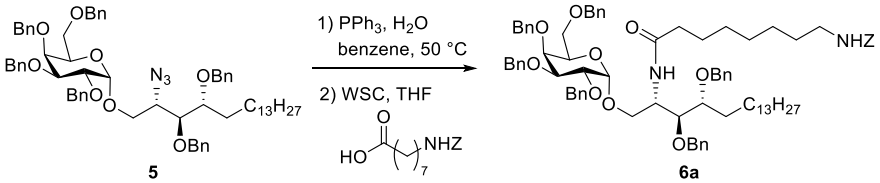
S12a: To a stirred solution of **S11a** (300 mg, 1.88 mmol) in CH_2Cl_2 (1.5 mL) and H_2O (1.5 mL) were added NaOH (188 mg, 4.7 mmol) and acryloyl chloride (0.18 mL, 2.26 mmol), and the mixture was stirred at room temperature for 7.5 h. and diluted with saturated $KHSO_4$ aq. The whole was extract with EtOAc. The extract was washed with saturated $KHSO_4$ aq., and dried over $MgSO_4$, and concentrated under reduced pressure followed by recrystallization from hexane/EtOAc (5/1) gave **S12a** as white solid (292 mg, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J = 7.6 Hz, 3H), 1.29-1.36 (m, 6H), 1.46-1.52 (m, 2H), 1.60-1.66 (m, 2H), 2.22 (q, J = 7.6 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 3.24 (td, J = 6.7, 6.7 Hz, 2H), 5.66-5.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 24.6, 26.6, 28.8, 28.9, 29.5, 29.7, 34.0, 39.5, 174.2, 178.8; HRMS (ESI-TOF) calcd $C_{11}H_{20}NO_3$: $(M-H)^-$, 214.1449; found: $(M-H)^-$, 214.1452.

General Procedure for the Preparation of Ceramide Derivatives 6 from the Azide 5.

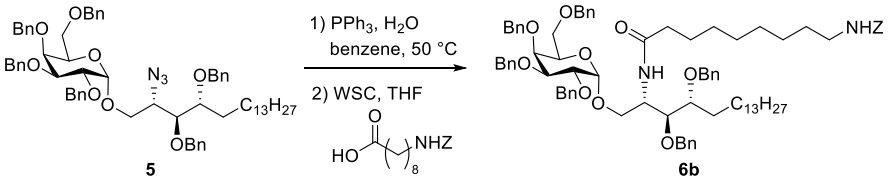


6e: To a stirred solution of **5** (200 mg, 0.19 mmol) in benzene (12 mL) and H_2O (0.48 mL) was added PPh_3 (125 mg, 0.48 mmol), and the mixture was stirred at 50 °C for 12 h. The mixture was concentrated under reduced pressure, and azeotroped three times with benzene. The residue was dissolved in THF (14 mL). 12-{[(Benzyloxy)carbonyl]amino}dodecanoic acid (179 mg, 0.51 mmol) and WSCI·H_2O (98 mg, 0.51 mmol) were added to the stirred mixture at room temperature. The mixture was stirred at this temperature for 24 h, and diluted with saturated $NaHCO_3$ aq. The whole was extract with EtOAc. The extract was washed with saturated $NaHCO_3$, brine, and dried over $MgSO_4$, and concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **6e** as a white solid (195 mg, 76% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ : 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.29 (m, 38H), 1.42-1.53 (m, 6H), 1.88-1.98 (m, 2H), 3.14-3.20 (m, 2H), 3.41 (dd, J = 8.7, 6.3 Hz, 1H), 3.41 (dd, J = 8.7, 6.3 Hz, 1H), 3.51-3.47 (m, 2H), 3.73 (dd, J = 10.0, 5.0 Hz, 1H), 3.86 (dd, J = 10.0, 3.4 Hz, 1H), 3.88-3.95 (m, 2H), 4.00-4.06 (m, 2H),

4.13-4.17 (m, 1H), 4.35-4.38 (m, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.47 (d, J = 11.7 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.60-4.54 (m, 2H), 4.64 (d, J = 11.7 Hz, 1H), 4.68-4.73 (m, 1H), 4.72-4.82 (m, 4H), 4.85 (d, J = 3.4 Hz, 1H), 4.92 (d, J = 11.7 Hz, 1H), 5.09 (s, 2H), 6.15 (d, J = 8.3 Hz, 1H), 7.38-7.22 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.0, 26.7, 29.3, 29.4 (3C), 29.5, 29.6, 29.7 (12C), 29.8, 29.9, 31.9, 36.6, 41.1, 50.3, 66.5, 67.9, 69.2, 69.9, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 76.6, 78.6, 78.9, 80.1, 99.6, 127.4 (2C), 127.5 (3C), 127.6, 127.7, 127.8 (8C), 127.9 (2C), 128.0, 128.1, 128.2 (2C), 128.3 (8C), 128.4 (4C), 128.5 (2C), 136.6, 137.5, 138.4, 138.6, 138.7 (2C), 139.8, 156.8, 172.7; HRMS (ESI-TOF) calcd $C_{86}H_{114}N_2NaO_{11}$: $(M+Na)^+$, 1373.8315; found: $(M+Na)^+$, 1373.8315.

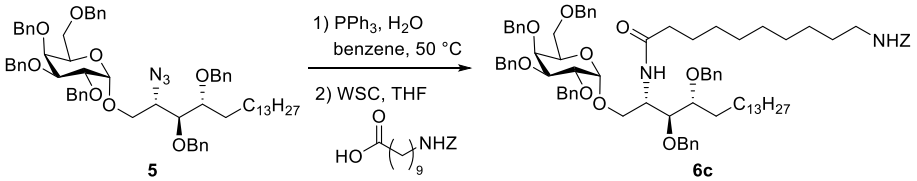


6a: By a procedure identical with that described for synthesis of **6e** from **5**, the azide **5** (20 mg, 0.019 mmol) was converted into **6a** as colorless oil (16.1 mg, 65% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.28 (m, 30H), 1.40-1.51 (m, 6H), 1.88-1.95 (m, 2H), 3.10-3.16 (m, 2H), 3.41 (dd, J = 10.9, 6.4 Hz, 1H), 3.46-3.52 (m, 2H), 3.73 (dd, J = 10.9, 3.7 Hz, 1H), 3.85 (dd, J = 6.4, 2.6 Hz, 1H), 3.87-3.94 (m, 3H), 3.98-4.02 (m, 1H), 4.04 (dd, J = 10.9, 3.7 Hz, 1H), 4.13-4.20 (m, 1H), 4.36 (d, J = 11.7 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.46 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.53-4.60 (m, 2H), 4.64 (d, J = 11.7 Hz, 1H), 4.65-4.72 (m, 1H), 4.70-4.81 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 4.91 (d, J = 11.7 Hz, 1H), 5.08 (s, 2H), 6.18 (d, J = 8.8 Hz, 1H), 7.37-7.21 (35H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.4, 26.5, 29.0, 29.1, 29.3, 29.6, 29.7 (9C), 29.8, 31.9, 36.4, 41.0, 50.2, 66.5, 69.2 (2C), 69.9, 71.6, 72.8, 73.5 (3C), 74.7 (2C), 76.6, 78.6, 78.8, 80.1, 99.5, 127.4 (2C), 127.5 (3C), 127.6, 127.7, 127.8 (8C), 127.9 (2C), 128.0, 128.1, 128.2 (2C), 128.3 (8C), 128.4 (4C), 128.5 (2C), 136.6, 137.5, 138.3, 138.4, 138.6 (3C), 156.3, 172.6; HRMS (ESI-TOF) calcd $C_{83}H_{107}N_2O_{13}$: $(M+HCO_2)^-$, 1339.7779; found: $(M+HCO_2)^-$, 1339.7781.

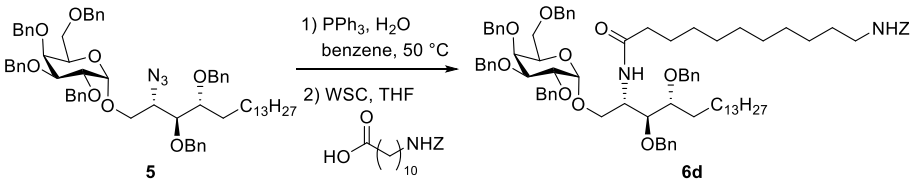


6b: By a procedure identical with that described for synthesis of **6e** from **5**, the azide **5** (100 mg, 0.096 mmol) was converted into **6b** as colorless oil (117 mg, 93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.16-1.30 (m, 32H), 1.42-1.50 (m, 4H), 1.56-1.70 (m, 2H), 1.87-1.98 (m, 2H), 3.11-3.18 (m, 2H), 3.41 (dd, J = 10.2, 6.4 Hz, 1H), 3.46-3.52 (m, 2H), 3.73 (dd, J = 10.2, 3.8 Hz, 1H), 3.83-3.95 (m, 4H), 3.99-4.07 (m, 2H), 4.13-4.19 (m, 1H), 4.36 (d, J = 11.7 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.46 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.54-4.60 (m, 2H), 4.64 (d, J = 11.7 Hz, 1H), 4.70-4.72 (m, 1H), 4.73-4.82 (m, 4H), 4.85 (d, J = 3.4 Hz, 1H), 4.92 (d, J = 11.7 Hz, 1H), 5.07-5.11 (m, 2H), 6.19 (d, J = 8.5 Hz, 1H), 7.43-7.15 (m, 35H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.7, 29.0, 29.1, 29.3 (2C), 29.4, 29.7 (9C), 29.9, 31.9, 36.5, 41.0, 50.3, 66.6, 69.3, 69.4, 69.9, 71.7, 72.9, 73.5, 73.6 (2C), 74.7 (2C), 76.6, 78.6, 78.9, 80.1, 99.6, 127.4 (2C), 127.5 (2C), 127.6, 127.7 (2C), 127.8 (2C), 127.9 (8C), 128.1 (2C), 128.3 (8C), 128.4 (6C), 128.5 (2C), 136.6, 137.6, 138.4 (2C), 138.6, 138.7 (2C), 156.4, 172.8; HRMS (ESI-TOF) calcd $C_{83}H_{108}N_2NaO_{11}$: $(M+Na)^+$, 1331.7845; found: $(M+Na)^+$, 1331.7838.



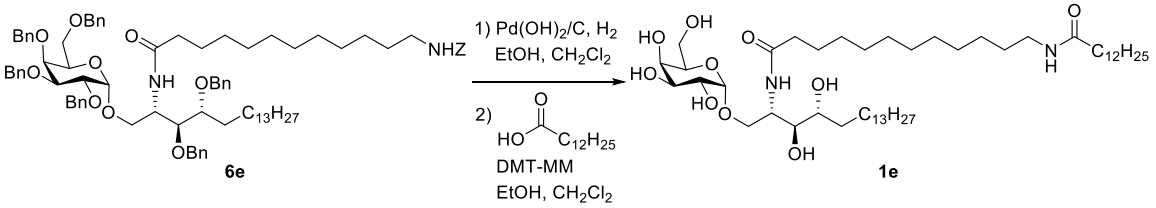
6c: By a procedure identical with that described for synthesis of **6c** from **5**, the azide **5** (20.0 mg, 0.019 mmol) was converted into **6c** as colorless oil (18.4 mg, 73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.27 (m, 34H), 1.44-1.50 (m, 4H), 1.84-1.87 (m, 2H), 1.90-1.96 (m, 2H), 3.12-3.18 (m, 2H), 3.41 (dd, J = 9.2, 6.3 Hz, 1H), 3.46-3.51 (m, 2H), 3.71-3.76 (m, 1H), 3.84-3.93 (m, 4H), 3.98-4.06 (m, 2H), 4.13-4.18 (m, 1H), 4.36 (d, J = 11.4 Hz, 1H), 4.42 (d, J = 11.4 Hz, 1H), 4.46 (d, J = 11.4 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.54-4.60 (m, 2H), 4.64 (d, J = 11.4 Hz, 1H), 4.66-4.71 (m, 1H), 4.73-4.82 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 4.91 (d, J = 11.4 Hz, 1H), 5.09 (s, 2H), 6.17 (d, J = 8.5 Hz, 1H), 7.21-7.37 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.0, 26.7, 29.2, 29.3 (3C), 29.4, 29.6, 29.7 (9C), 29.8, 29.9, 31.9, 36.6, 41.0, 50.2, 66.5, 67.9, 69.2, 69.9, 71.6, 72.8, 73.5, 73.6 (2C), 74.7 (2C), 76.6, 78.6, 78.8, 80.1, 99.4, 127.4 (2C), 127.5 (3C), 127.6, 127.7, 127.8 (8C), 127.9 (2C), 128.0, 128.1, 128.2 (4C), 128.3 (6C), 128.4 (4C), 128.5 (2C), 136.6, 137.5, 138.3, 138.4, 138.6 (2C), 138.7, 156.3, 172.8; HRMS (ESI-TOF) calcd $C_{84}H_{110}N_2NaO_{11}$: $(M+Na)^+$, 1345.8002; found: $(M+Na)^+$, 1345.8001.



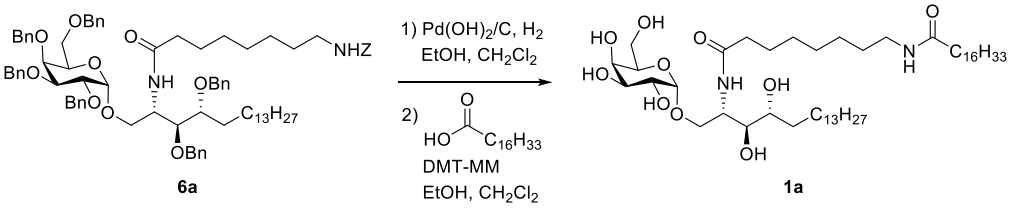
6d: By a procedure identical with that described for synthesis of **6e** from **5**, the azide **5** (20.0 mg, 0.019 mmol) was converted into **6d** as colorless oil (19.8 mg, 78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.29 (m, 36H), 1.44-1.50 (m, 4H), 1.62-1.68 (m, 2H), 1.88-1.98 (m, 2H), 3.13-3.20 (m, 2H), 3.41 (dd, J = 9.2, 6.3 Hz, 1H), 3.46-3.52 (m, 2H), 3.73 (dd, J = 10.8, 3.8 Hz, 1H), 3.84-3.87 (m, 1H), 3.90-3.94 (m, 3H), 3.98-4.06 (m, 2H), 4.13-4.19 (m, 1H), 4.36 (d, J = 11.7 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.47 (d, J = 11.7 Hz, 1H) , 4.51 (d, J = 11.7 Hz, 1H), 4.54-4.60 (m, 2H), 4.64 (d, J = 11.7 Hz, 1H), 4.68-4.72 (m, 1H), 4.73-4.82 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 4.91 (d, J = 11.7 Hz, 1H), 5.09 (s, 2H), 6.17 (d, J = 8.8 Hz, 1H),.7.21-7.37 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.1, 26.7, 29.2, 29.3, 29.4 (2C), 29.5, 29.6, 29.7 (8C), 29.8, 29.9, 31.9, 36.6, 41.1, 50.2, 66.5, 69.2 (2C), 69.9, 71.6, 72.8, 73.5, 73.5 (2C), 74.7 (2C), 76.6, 78.6, 78.8, 80.1, 99.5, 127.4 (2C), 127.5 (3C), 127.6, 127.7, 127.8 (8C), 127.9 (2C), 128.0, 128.1, 128.2 (4C), 128.3 (6C),

128.4 (4C), 128.5 (2C), 136.6, 137.5, 138.3, 138.4, 138.6 (2C), 138.7, 156.3, 172.8; HRMS (ESI-TOF) calcd $C_{85}H_{112}N_2NaO_{11}$: $(M+Na)^+$, 1359.8158; found: $(M+Na)^+$, 1359.8150.

General Procedure for the Preparation of Galactosyl Ceramide Derivatives 1a-e from Compounds 6a-e.

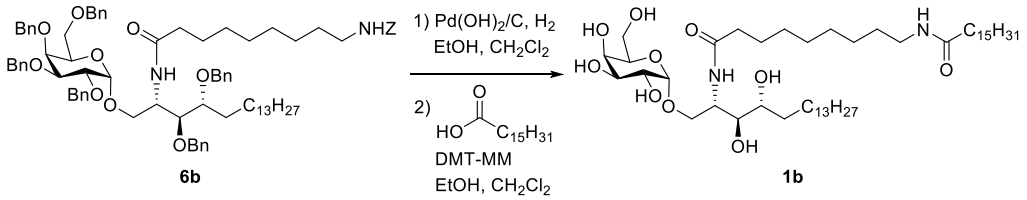


1e: A mixture of **6e** (15 mg, 0.010 mmol) and $Pd(OH)_2/C$ (20% wt on carbon, 5 mg, 0.007 mmol) in EtOH (1.2 mL) and CH_2Cl_2 (0.4 mL) was stirred for 7 h at room temperature under H_2 atmosphere (0.5 MPa), and then filtrated through a short pad of Celite with EtOH/CH_2Cl_2 (3:1). The filtrate was concentrated under reduced pressure to give a crude amine as a colorless oil. This amine was dissolved in EtOH (1.5 mL) and CH_2Cl_2 (0.5 mL). tridecanoic acid (6.4 mg, 0.030 mmol) and DMT-MM (8.3 mg, 0.030 mmol) were added to the stirred mixture at room temperature. The mixture was stirred at this temperature for 12 h, and diluted with saturated $NaHCO_3$ aq. The whole was extract with EtOAc. The extract was washed with saturated $NaHCO_3$, brine, and dried over $MgSO_4$, and concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with $CHCl_3$–MeOH (9:1) to give **1e** as a white solid (4.7 mg, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.5 Hz, 6H), 1.20-1.35 (m, 56H), 1.43-1.53 (m, 2H), 1.55-1.70 (m, 6H), 2.15 (t, J = 8.1 Hz, 2H), 2.19 (t, J = 8.1 Hz, 2H), 3.15-3.23 (m, 2H), 3.50-3.56 (m, 2H), 3.65-3.75 (m, 3H), 3.76-3.83 (m, 3H), 3.89 (dd, J = 10.1, 4.0 Hz, 1H), 3.96 (d, J = 4.0 Hz, 1H), 4.16-4.22 (m, 1H), 4.91 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 14.1 (2C), 22.8, 25.9 (2C), 26.0, 26.9, 29.3 (2C), 29.4 (6C), 29.5 (2C), 29.7 (2C). 29.8 (12C), 29.9, 32.0, 32.8, 36.6, 36.8, 39.5, 50.4, 62.1, 67.7, 69.0, 69.9, 70.3, 70.7, 72.2, 75.0, 99.7, 174.3, 174.4; HRMS (ESI-TOF) calcd $C_{49}H_{96}N_2NaO_{10}$: $(M+Na)^+$, 895.6957; found: $(M+Na)^+$, 895.6972.

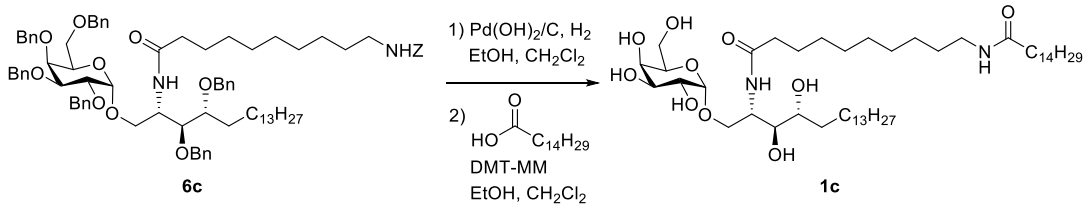


1a: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6a** (13.3 mg, 0.010 mmol) was converted into **1a** as white solid (1.8 mg, 21% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.8 Hz, 6H), 1.25-1.31 (m, 56H), 1.45-1.50 (m, 2H), 1.58-1.66 (m, 6H), 2.15 (t, J = 7.7 Hz, 2H), 2.20 (t, J = 7.7 Hz, 2H), 3.16-3.21 (m, 2H), 3.51-3.57 (m, 2H), 3.68-3.75 (m, 3H), 3.76-3.82 (m, 3H), 3.90 (dd, J = 10.5, 3.6 Hz, 1H), 3.95 (d, J = 3.6 Hz, 1H), 4.19-4.20 (m, 1H), 4.92 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5, 25.4, 25.7, 25.8, 26.3, 28.4, 28.6, 29.1, 29.2 (3C), 29.4, 29.5, 29.6 (16C),

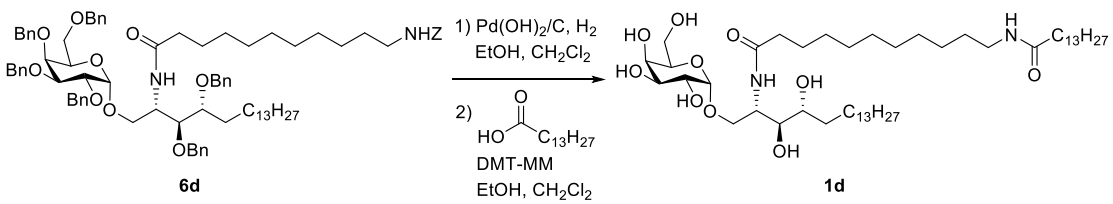
29.9, 31.8, 32.7, 36.1, 36.5, 39.2, 50.2, 61.8, 67.3, 68.8, 69.6, 70.1, 70.5, 72.0, 74.7, 99.5, 174.2 (2C); HRMS (ESI-TOF) calcd $C_{49}H_{96}N_2NaO_{10}$: $(M+Na)^+$, 895.6957; found: $(M+Na)^+$, 895.6955.



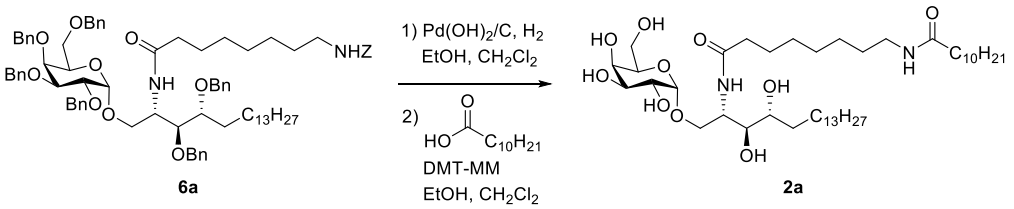
1b: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6b** (15.0 mg, 0.011 mmol) was converted into **1b** as white solid (3.3 mg, 38% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.80 (t, J = 6.8 Hz, 6H), 1.20 (d, J = 19.0 Hz, 56H), 1.35-1.44 (m, 2H), 1.49-1.55 (m, 6H), 2.08 (t, J = 7.8 Hz, 2H), 2.12 (t, J = 7.8 Hz, 2H), 3.09-3.13 (m, 2H), 3.39-3.48 (m, 2H), 3.60-3.66 (m, 3H), 3.68-3.73 (m, 3H), 3.81 (dd, J = 10.0, 3.9 Hz, 1H), 3.87 (d, J = 3.9 Hz, 1H), 4.09-4.13 (m, 1H), 4.83 (d, J = 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 14.2 (2C), 22.8, 25.7, 25.9, 26.0, 26.7, 28.9, 29.0, 29.1, 29.4 (2C), 29.5 (2C), 29.6, 29.7 (2C), 29.3, 29.8 (12C), 29.9, 32.0 (2C), 32.9, 36.5, 36.8, 39.4, 50.4, 62.1, 67.6, 69.0, 69.9, 70.3, 70.7, 72.2, 75.0, 99.8, 174.4 (2C); HRMS (ESI-TOF) calcd $C_{49}H_{96}N_2NaO_{10}$: $(M+Na)^+$, 895.6957; found: $(M+Na)^+$, 895.6964.



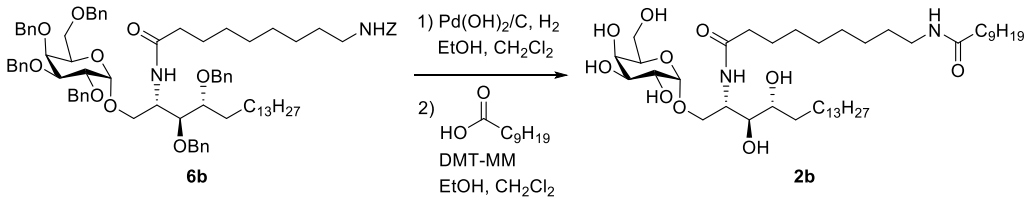
1c: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6c** (15.0 mg, 0.011 mmol) was converted into **1c** as white solid (2.0 mg, 21% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.7 Hz, 6H), 1.25-1.29 (m, 56H), 1.45-1.49 (m, 2H), 1.55-1.67 (m, 6H), 2.15 (t, J = 7.7 Hz, 2H), 2.20 (t, J = 7.7 Hz, 2H), 3.18-3.22 (m, 2H), 3.48-3.59 (m, 2H), 3.67-3.74 (m, 3H), 3.76-3.82 (m, 3H), 3.89 (dd, J = 10.8, 3.8 Hz, 1H), 3.95 (d, J = 3.8 Hz, 1H), 4.19 (d, J = 3.8 Hz, 1H), 4.91 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5 (2C), 25.6, 25.7 (2C), 26.6, 28.9 (2C), 29.0, 29.1, 29.2 (2C), 29.4, 29.6, 29.5 (3C), 29.6 (12C), 31.8 (2C), 32.6, 36.3, 36.5, 39.2, 50.2, 61.8, 67.4, 68.8, 69.6, 70.1, 70.5, 72.0, 74.7, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{49}H_{96}N_2NaO_{10}$: $(M+Na)^+$, 895.6957; found: $(M+Na)^+$, 895.6961.



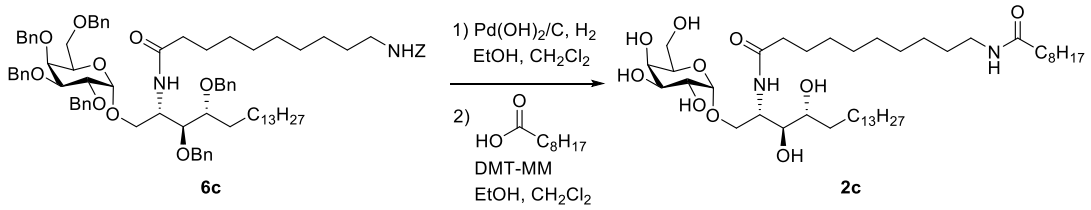
1d: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6d** (14.3 mg, 0.011 mmol) was converted into **1d** as white solid (4.6 mg, 48% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.5 Hz, 6H), 1.24-1.29 (m, 56H), 1.47-1.49 (m, 2H), 1.58-1.62 (m, 6H), 2.15 (t, J = 7.7 Hz, 2H), 2.19 (t, J = 7.7 Hz, 2H), 3.16-3.22 (m, 2H), 3.52-3.55 (m, 2H), 3.68-3.73 (m, 3H), 3.77-3.80 (m, 3H), 3.88 (dd, J = 10.0, 3.6 Hz, 1H), 3.94-3.97 (m, 1H), 4.17-4.19 (m, 1H), 4.90-4.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5 (2C), 25.6, 25.7 (2C), 26.6, 28.7 (2C), 29.0 (2C), 29.2 (2C), 29.4, 29.5 (3C), 29.6 (13C), 31.8 (2C), 32.4, 36.3, 36.5, 39.3, 50.1, 61.8, 67.4, 68.7, 69.7, 70.0, 70.4, 71.9, 74.5, 99.5, 174.0, 174.2; HRMS (ESI-TOF) calcd $C_{49}H_{96}N_2NaO_{10}$: $(M+Na)^+$, 895.6957; found: $(M+Na)^+$, 895.6961.



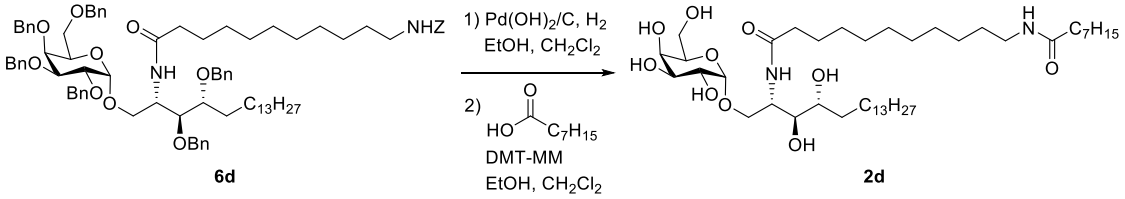
2a: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6a** (20.0 mg, 0.015 mmol) was converted into **2a** as white solid (4.4 mg, 37% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.7 Hz, 6H), 1.25-1.31 (m, 44H), 1.46-1.49 (m, 2H), 1.57-1.63 (m, 6H), 2.15 (t, J = 7.7 Hz, 2H), 2.20 (t, J = 7.7 Hz, 2H), 3.18 (t, J = 7.7 Hz, 2H), 3.49-3.54 (m, 2H), 3.68-3.72 (m, 3H), 3.75-3.81 (m, 3H), 3.89 (dd, J = 10.0, 3.8 Hz, 1H), 3.95 (d, J = 3.8 Hz, 1H), 4.19 (d, J = 3.8 Hz, 1H), 4.91 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 14.0 (2C), 22.5, 22.6, 25.5, 25.8, 26.5, 28.3, 28.7, 28.8 (2C), 29. 2 (2C), 29.3, 29.4, 29.6 (8C), 29.7 (2C), 31.7, 31.8, 32.7, 36.3, 36.6, 39.2, 50.2, 61.8, 67.6, 68.8, 69.7, 70.1, 70.5, 72.0, 74.5, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{84}N_2NaO_{10}$: $(M+Na)^+$, 811.6018; found: $(M+Na)^+$, 811.6026.



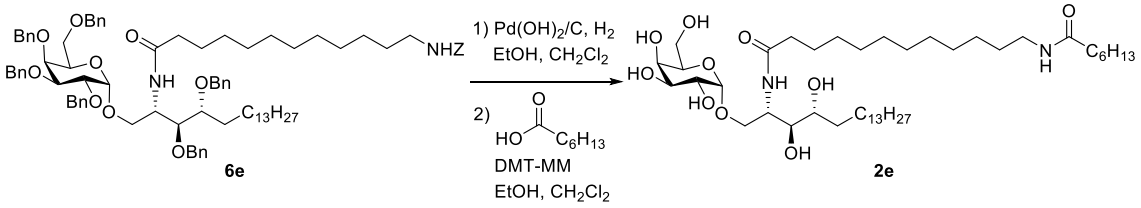
2b: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6b** (17.0 mg, 0.013 mmol) was converted into **2b** as white solid (2.1 mg, 20% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.7 Hz, 6H), 1.26-1.31 (m, 44H), 1.47-1.50 (m, 2H), 1.57-1.64 (m, 6H), 2.16 (t, J = 8.2 Hz, 2H), 2.20 (t, J = 8.2 Hz, 2H), 3.16-3.20 (m, 2H), 3.52-3.57 (m, 2H), 3.68-3.74 (m, 3H), 3.78-3.88 (m, 4H), 3.93-3.96 (m, 1H), 4.18-4.21 (m, 1H), 4.91 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 14.0 (2C), 22.5, 22.6, 25.5, 25.8, 26.5, 28.3, 28.7, 28.8 (2C), 29. 2 (2C), 29.3, 29.4, 29.6 (8C), 29.7 (2C), 31.7, 31.8, 32.7, 36.3, 36.6, 39.2, 50.2, 61.8, 67.6, 68.8, 69.7, 70.1, 70.5, 72.0, 74.5, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{84}N_2NaO_{10}$: $(M+Na)^+$, 811.6018; found: $(M+Na)^+$, 811.6017.



2c: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6c** (20.0 mg, 0.015 mmol) was converted into **2c** as white solid (3.5 mg, 30% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.3 Hz, 6H), 1.23-1.31 (m, 44H), 1.46-1.49 (m, 2H), 1.57-1.63 (m, 6H), 2.15 (t, J = 7.7 Hz, 2H), 2.20 (t, J = 7.7 Hz, 2H), 3.16-3.22 (m, 2H), 3.48-3.55 (m, 2H), 3.69-3.74 (m, 3H), 3.76-3.81 (m, 3H), 3.89 (dd, J = 10.0, 3.8 Hz, 1H), 3.94-3.97 (m, 1H), 4.17-4.20 (m, 1H), 4.90-4.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5 (2C), 25.5, 25.6, 26.7 (2C), 28.9, 29.0 (2C), 29. 2 (2C), 29.4, 29.5, 29.6 (10C), 31.7, 31.8, 32.5, 36.3, 36.6, 39.3, 50.1, 61.9, 67.5, 68.8, 69.7, 70.1, 70.4, 72.0, 74.7, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{84}N_2NaO_{10}$: $(M+Na)^+$, 811.6018; found: $(M+Na)^+$, 811.6022.

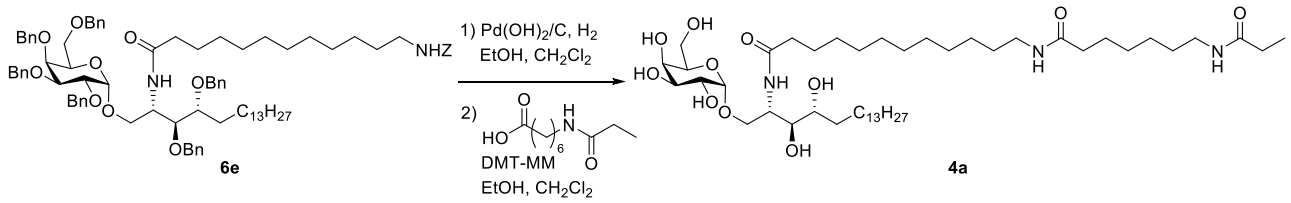


2d: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6d** (20.0 mg, 0.015 mmol) was converted into **2d** as white solid (2.2 mg, 19% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 7.1 Hz, 6H), 1.23-1.32 (m, 44H), 1.47-1.49 (m, 2H), 1.58-1.66 (m, 6H), 2.16 (t, J = 7.9 Hz, 2H), 2.20 (t, J = 7.9 Hz, 2H), 3.19 (t, J = 7.2 Hz, 2H), 3.50-3.54 (m, 2H), 3.67-3.74 (m, 3H), 3.76-3.81 (m, 3H), 3.89 (dd, J = 10.8, 3.8 Hz, 1H), 3.94-3.97 (m, 1H), 4.19 (d, J = 3.8 Hz, 1H), 4.92 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.4, 22.5, 25.6, 25.7 (2C), 26.6, 28.9, 29.0 (2C), 29.1, 29. 2 (2C), 29.5, 29.6 (9C), 31.6, 31.8 (2C), 32.6, 36.4, 36.6, 39.3, 50.1, 61.9, 67.5, 68.8, 69.6, 70.1, 70.4, 72.0, 74.7, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{84}N_2NaO_{10}$: $(M+Na)^+$, 811.6018; found: $(M+Na)^+$, 811.6022.

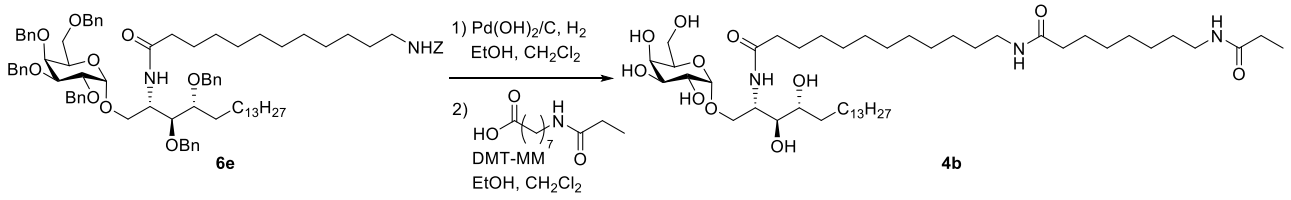


2e: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6e** (25.8 mg, 0.019 mmol) was converted into **2e** as white solid (3.8 mg, 25% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.4 Hz, 6H), 1.24-1.31 (m, 44H), 1.45-1.50 (m, 2H), 1.57-1.64 (m, 6H), 2.16 (t, J = 7.7 Hz, 2H), 2.20 (t, J = 7.7

Hz, 2H), 3.16-3.22 (m, 2H), 3.51-3.55 (m, 2H), 3.69-3.73 (m, 3H), 3.75-3.81 (m, 3H), 3.89 (dd, J = 10.0, 3.8 Hz, 1H), 3.94-3.97 (m, 1H), 4.17-4.20 (m, 1H), 4.90-4.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5 (2C), 25.4, 25.7, 25.8, 26.2, 26.5, 28.5, 28.6, 29.1, 29.2 (2C), 29.4 (2C), 29.5, 29.6 (7C), 29.7, 31.7, 31.8, 32.6, 36.2, 36.5, 39.1, 50.2, 61.8, 67.4, 68.8, 69.6, 70.1, 70.5, 72.0, 74.8, 99.5, 174.1, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{84}N_2NaO_{10}$: $(M+Na)^+$, 811.6018; found: $(M+Na)^+$, 811.6024.

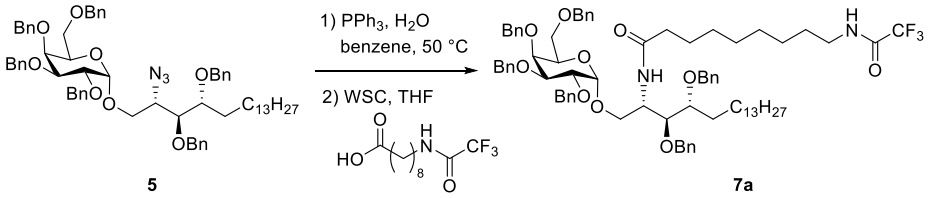


4a: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6e** (10.0 mg, 0.0067 mmol) was converted into **4a** as white solid (2.4 mg, 42% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.92 (t, J = 7.6 Hz, 3H), 1.14 (t, J = 7.6 Hz, 3H), 1.25-1.32 (m, 44H), 1.45-1.51 (m, 4H), 1.60-1.68 (m, 4H), 2.14-2.23 (m, 6H), 3.16-3.22 (m, 4H), 3.48-3.53 (m, 2H), 3.69-3.73 (m, 3H), 3.76-3.82 (m, 3H), 3.89 (dd, J = 10.0, 3.8 Hz, 1H), 3.95 (d, J = 3.8 Hz, 1H), 4.18-4.21 (m, 1H), 4.91 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9 (2C), 22.5, 22.8, 23.6, 25.3, 25.6, 25.7, 26.0, 26.6, 28.3, 28.8 (2C), 28.9, 29.0 (2C), 29.2 (2C), 29.4, 29.6 (5C), 30.2, 31.8 (2C), 32.7, 36.1, 36.3, 38.6, 39.0, 39.3, 50.1, 61.9, 68.1, 68.8, 69.7, 70.1, 70.4, 72.0, 74.8, 99.5, 174.0, 174.9 (2C); HRMS (ESI-TOF) calcd $C_{46}H_{89}N_3NaO_{11}$: $(M+Na)^+$, 882.6389; found: $(M+Na)^+$, 882.6400.

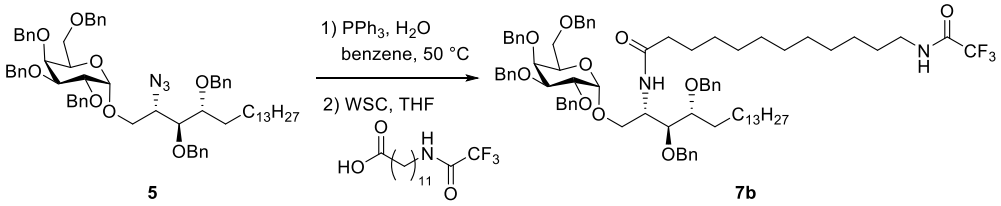


4b: By a procedure identical with that described for synthesis of **1e** from **6e**, the amine **6e** (10.0 mg, 0.0067 mmol) was converted into **4b** as white solid (2.1 mg, 36% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.8 Hz, 3H), 1.14 (t, J = 7.7 Hz, 3H), 1.25-1.31 (m, 46H), 1.47-1.49 (m, 4H), 1.59-1.61 (m, 4H), 2.16-2.20 (m, 6H), 3.18-3.21 (m, 4H), 3.48-3.54 (m, 2H), 3.67-3.74 (m, 3H), 3.76-3.82 (m, 3H), 3.89 (dd, J = 10.5, 3.8 Hz, 1H), 3.95 (d, J = 3.8 Hz, 1H), 4.18-4.21 (m, 1H), 4.91 (d, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.2 (2C), 22.7 (2C), 25.5, 25.6, 25.8, 25.9, 26.4, 26.8, 28.6, 28.8, 29.2 (2C), 29.3, 29.4 (2C), 29.7 (2C), 29.6 (8C), 32.0 (2C), 32.9, 36.5, 36.6, 39.3, 39.5, 50.3, 62.1, 67.7, 69.0, 69.9, 70.3, 70.6, 72.2, 75.0, 99.7, 174.2, 174.4, 175.0; HRMS (ESI-TOF) calcd $C_{47}H_{91}N_3NaO_{11}$: $(M+Na)^+$, 896.6546; found: $(M+Na)^+$, 896.6559.

General Procedure for the Preparation of Ceramide Derivative 7 from the Azide 5.

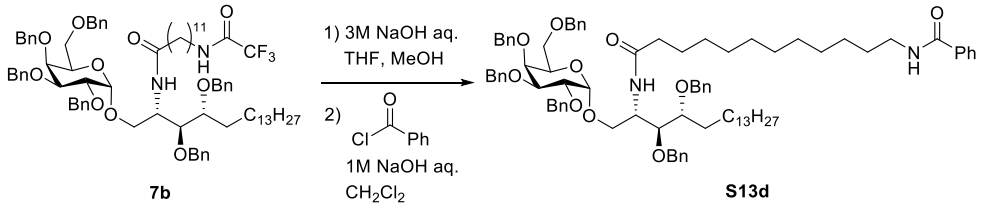


7a: By a procedure identical with that described for synthesis of **6e** from **5**, the amine **5** (80.0 mg, 0.077 mmol) was converted into **7a** as colorless oil (32.6 mg, 33% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.19-1.30 (m, 32H), 1.46-1.53 (m, 4H), 1.58-1.66 (m, 2H), 1.89-1.96 (m, 2H), 3.29 (dt, J = 6.7, 6.7 Hz, 2H), 3.40 (dd, J = 9.2, 6.3 Hz, 1H), 3.46-3.52 (m, 2H), 3.73 (dd, J = 11.0, 3.8 Hz, 1H), 3.85-3.87 (m, 2H), 3.90-3.94 (m, 2H), 4.00-4.06 (m, 2H), 4.14-4.20 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.47 (d, J = 11.9 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.57 (d, J = 11.9 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.71-4.81 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 4.92 (d, J = 11.9 Hz, 1H), 6.18 (d, J = 8.5 Hz, 1H), 6.31-6.34 (m, 1H), 7.24-7.37 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.4, 26.1, 26.5, 28.8, 28.9, 29.1 (2C), 29.4, 29.6 (6C), 29.8 (2C), 29.9, 31.9, 36.5, 39.9, 50.3, 66.6, 69.3, 69.5, 70.0, 71.7, 72.9, 73.4, 73.6, 74.7 (2C), 76.6, 78.6, 78.9, 80.1, 99.6, 115.8 (q, $J_{C\text{-}F}$ = 285.6 Hz), 127.4 (2C), 127.5 (3C), 127.7 (3C), 127.8 (6C), 127.9 (2C), 128.2 (2C), 128.3 (8C), 128.4 (4C), 137.5, 138.4 (2C), 138.6 (3C), 157.6 (q, $J_{C\text{-}F}$ = 36.6 Hz), 172.7; HRMS (ESI-TOF) calcd $C_{77}H_{101}F_3N_2NaO_{10}$: $(M+Na)^+$, 1293.7301; found: $(M+Na)^+$, 1293.7311.

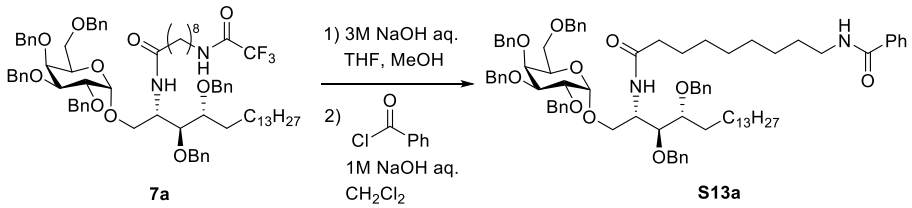


7b: By a procedure identical with that described for synthesis of **6e** from **5**, the amine **5** (40.0 mg, 0.038 mmol) was converted into **7b** as colorless oil (22.6 mg, 45% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.22-1.28 (m, 40H), 1.48-1.68 (m, 4H), 1.90-1.96 (m, 2H), 3.33 (td, J = 6.8, 6.8 Hz, 2H), 3.41 (dd, J = 9.4, 6.3 Hz, 1H), 3.48-3.50 (m, 2H), 3.73 (dd, J = 11.0, 3.6 Hz, 1H), 3.84-3.88 (m, 2H), 3.89-3.93 (m, 2H), 4.00-4.06 (m, 2H), 4.14-4.17 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.47 (d, J = 11.9 Hz, 2H), 4.51 (d, J = 11.9 Hz, 1H), 4.54-4.60 (m, 2H), 4.64 (d, J = 11.9 Hz, 1H), 4.71-4.81 (m, 3H), 4.84 (d, J = 3.6 Hz, 1H), 4.92 (d, J = 11.9 Hz, 1H), 6.15 (d, J = 8.5 Hz, 1H), 6.28-6.31 (m, 1H), 7.21-7.38 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.1, 26.6, 28.9 (2C), 29.1, 29.3 (3C), 29.4, 29.7 (15C), 29.8, 31.9, 36.6, 39.9, 50.3, 69.3, 69.5, 70.0, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 76.7, 78.6, 78.9, 80.1, 99.6, 115.8 (q, $J_{C\text{-}F}$ = 287.5 Hz), 127.4 (2C), 127.5 (2C), 127.7 (2C), 127.8 (6C), 127.9 (2C), 128.2 (2C), 128.3 (6C), 128.4 (2C), 137.5, 138.4 (2C), 138.6 (3C), 157.1 (q, $J_{C\text{-}F}$ = 36.6 Hz), 172.8; HRMS (ESI-TOF) calcd $C_{80}H_{107}F_3N_2NaO_{10}$: $(M+Na)^+$, 1335.7770; found: $(M+Na)^+$, 1335.7763.

General Procedure for the Preparation of Bn-Protected Ceramide derivative S13 from Compounds 7.

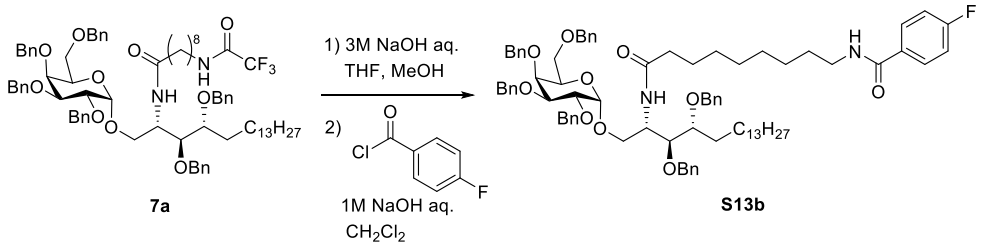


S13d: A mixture of **7b** (10 mg, 0.0076 mmol) in 3M NaOH aq. (0.2 mL), MeOH (0.4 mL) and THF (0.4 mL) was stirred at 40 °C for 0.5 h, and then concentrated under reduced pressure to give a crude amine. This amine was dissolved in 1M NaOH aq. (0.2 mL) and CH_2Cl_2 (0.2 mL). Benzoyl chloride (8.8 μL, 0.076 mmol) was added to the stirred mixture at room temperature. The mixture was stirred at this temperature for 0.5 h, and diluted with saturated $NaHCO_3$ aq. The whole was extract with EtOAc. The extract was washed with saturated $NaHCO_3$, brine, and dried over $MgSO_4$, and concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **S13d** as a colorless oil (6.7 mg, 68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3H), 1.22-1.25 (m, 40H), 1.46-1.50 (m, 2H), 1.58-1.63 (m, 2H), 1.90-1.96 (m, 2H), 3.38-3.51 (m, 5H), 3.73 (dd, J = 10.7, 3.7 Hz, 1H), 3.84-3.88 (m, 2H), 3.89-3.94 (m, 2H), 4.01-4.04 (m, 2H), 4.14-4.17 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42-4.47 (m, 2H), 4.51 (d, J = 11.9 Hz, 1H), 4.55-4.58 (m, 2H), 4.64 (d, J = 11.9 Hz, 1H), 4.73 (d, J = 11.9 Hz, 1H), 4.76-4.81 (m, 3H), 4.84 (d, J = 3.4 Hz, 1H), 4.91 (d, J = 11.9 Hz, 1H), 6.06-6.09 (m, 1H), 6.13 (d, J = 8.5 Hz, 1H), 7.23-7.35 (m, 30H), 7.41-7.43 (m, 2H), 7.48-7.50 (m, 1H), 7.73-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 26.1, 27.0, 29.3, 29.4 (2C), 29.5 (2C), 29.6, 29.7 (10C), 29.8, 31.9, 36.6, 40.1, 50.3, 69.2, 69.5, 69.9, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 76.6, 78.6, 78.9, 80.1, 99.6, 126.8 (2C), 127.4 (2C), 127.5 (3C), 127.6, 127.7, 127.8 (6C), 127.9 (2C), 128.2 (2C), 128.3 (8C), 128.4 (4C), 128.5 (2C), 131.3 (2C), 134.8, 137.5, 138.4 (2C), 138.6 (2C), 138.7, 167.4, 172.8; HRMS (ESI-TOF) calcd $C_{85}H_{112}N_2NaO_{10}$: $(M+Na)^+$, 1343.8209; found: $(M+Na)^+$, 1343.8214.

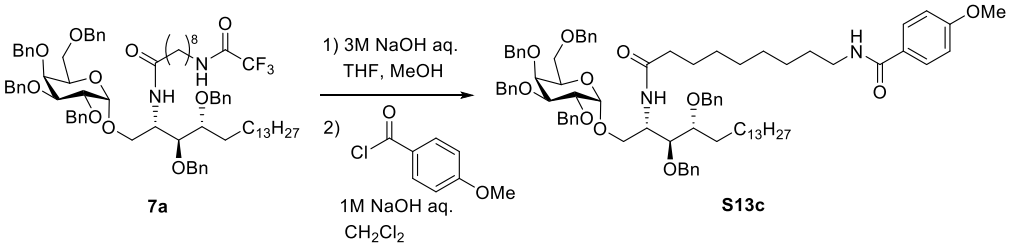


S13a: By a procedure identical with that described for synthesis of **S13d** from **7b**, the amine **7a** (10.0 mg, 0.0079 mmol) was converted into **S13a** as colorless oil (8.2 mg, 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.21-1.30 (m, 33H), 1.46-1.68 (m, 4H), 1.87-1.97 (m, 2H), 3.41-3.44 (m, 1H), 3.41 (td, J = 6.1, 6.1 Hz, 2H), 3.47-3.51 (m, 2H), 3.73 (dd, J = 11.0, 3.8 Hz, 1H), 3.84-3.88 (m, 2H), 3.91-3.94 (m, 3H), 4.00-4.06 (m, 2H), 4.15-4.18 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.46 (d, J = 11.9 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.55-4.58 (m, 2H), 4.64 (d, J = 11.9 Hz, 1H), 4.71-4.81 (m, 4H), 4.85 (d, J = 3.8 Hz, 1H), 4.91 (d, J = 11.9 Hz, 1H), 6.05-6.07 (m, 1H), 6.15 (d, J = 8.8 Hz, 1H), 7.21-7.38 (m, 30H), 7.40-7.44 (m, 2H), 7.47-7.49 (m, 1H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 26.1, 26.9, 29.1, 29.2, 29.4, 29.6,

29.7 (7C), 29.8 (2C), 29.9, 31.9, 36.5, 40.0, 50.3, 69.3, 69.5, 70.0, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 77.2, 78.6, 78.9, 80.1, 99.6, 126.8 (2C), 127.4 (2C), 127.6, 127.5 (3C), 127.7 (2C), 127.8 (6C), 127.9 (2C), 128.2 (2C), 128.3 (8C), 128.4 (4C), 128.5 (2C), 131.3, 134.8, 137.5, 138.4 (2C), 138.6 (2C), 138.7, 167.4, 172.7; HRMS (ESI-TOF) calcd $C_{82}H_{106}N_2NaO_{10}$: $(M+Na)^+$, 1301.7740; found: $(M+Na)^+$, 1301.7748.



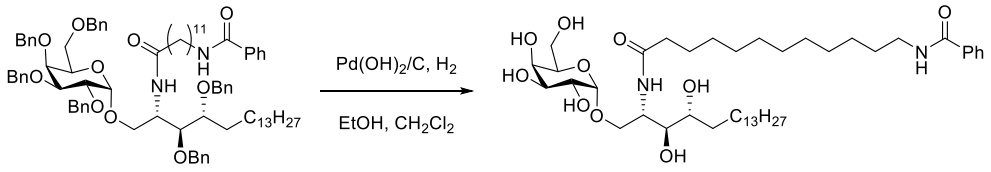
S13b: By a procedure identical with that described for synthesis of **S13d** from **7b**, the amine **7a** (10.0 mg, 0.0079 mmol) was converted into **S13b** as colorless oil (5.1 mg, 50% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.23-1.28 (m, 34H), 1.48-1.65 (m, 4H), 1.90-1.96 (m, 2H), 3.38-3.42 (m, 3H), 3.48-3.50 (m, 2H), 3.73 (dd, J = 10.9, 3.9 Hz, 1H), 3.84-3.88 (m, 2H), 3.88-3.94 (m, 2H), 4.01-4.04 (m, 2H), 4.15-4.18 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.46 (d, J = 11.9 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.55-4.58 (m, 2H), 4.64 (d, J = 11.9 Hz, 1H), 4.71-4.81 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 4.91 (d, J = 11.9 Hz, 1H), 5.99-6.02 (m, 1H), 6.15 (d, J = 8.3 Hz, 1H), 7.08-7.10 (m, 2H), 7.21-7.35 (m, 30H), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 26.1, 26.9, 29.1, 29.2 (2C), 29.4, 29.6, 29.7 (7C), 29.8 (2C), 31.9, 36.5, 40.1, 50.3, 69.3, 69.5, 70.0, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 76.6, 78.6, 78.9, 80.1, 99.6, 115.5 (d, $J_{C\text{-}F}$ = 22.6 Hz, 2C), 127.4 (2C), 127.5 (3C), 127.7 (3C), 127.8 (6C), 127.9 (2C), 128.2 (2C), 128.3 (8C), 128.4 (4C), 129.1 (d, $J_{C\text{-}F}$ = 9.4 Hz, 2C), 130.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 137.5, 138.4 (2C), 138.6 (2C), 138.7, 164.6 (d, $J_{C\text{-}F}$ = 251.8 Hz), 166.4, 172.7; HRMS (ESI-TOF) calcd $C_{82}H_{105}FN_2NaO_{10}$: $(M+Na)^+$, 1319.7645; found: $(M+Na)^+$, 1319.7638.



S13c: By a procedure identical with that described for synthesis of **S13d** from **7b**, the amine **7a** (10.0 mg, 0.0079 mmol) was converted into **S13c** as colorless oil (5.1 mg, 71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.26 (t, J = 14.6 Hz, 34H), 1.48-1.61 (m, 4H), 1.90-1.96 (m, 2H), 3.38-3.41 (m, 3H), 3.48-3.50 (m, 2H), 3.73 (dd, J = 11.0, 3.6 Hz, 1H), 3.83 (s, 3H), 3.84-3.88 (m, 2H), 3.89-3.94 (m, 2H), 4.01-4.04 (m, 2H), 4.15-4.18 (m, 1H), 4.36 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.47 (d, J = 11.9 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.55-4.58 (m, 2H), 4.64 (d, J = 11.9 Hz, 1H), 4.71-4.81 (m, 4H), 4.85 (d, J = 3.6 Hz, 1H), 4.91 (d, J = 11.9 Hz, 1H), 5.96-5.99 (m, 1H), 6.15 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.21-7.37 (m, 30H), 7.71 (d,

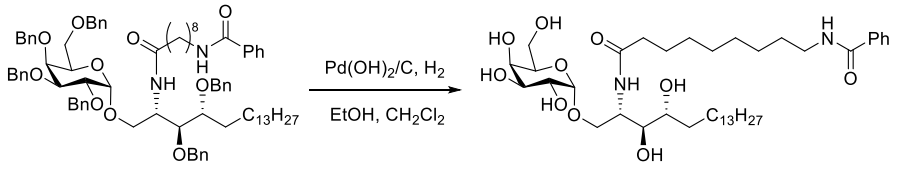
J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 26.1, 26.9, 29.1, 29.2, 29.4, 29.7 (10C), 29.8, 31.9, 36.5, 39.9, 50.3, 55.4, 69.3, 69.5, 70.0, 71.7, 72.9, 73.4, 73.6 (2C), 74.7 (2C), 77.2, 78.6, 78.9, 80.1, 99.6, 113.7, 127.1 (2C), 127.4 (2C), 127.5 (3C), 127.7 (2C), 127.8 (5C), 127.9 (4C), 128.2 (2C), 128.3 (8C), 128.4 (4C), 128.6 (2C), 137.6, 138.4 (2C), 138.6 (2C), 138.7, 162.0, 166.9, 172.7; HRMS (ESI-TOF) calcd $C_{83}H_{108}N_2NaO_{11}$: $(M+Na)^+$, 1319.7645; found: $(M+Na)^+$, 1319.7638.

General Procedure for the Preparation of Galactosyl Ceramide Derivative 3a-d from Compounds S13a-d.



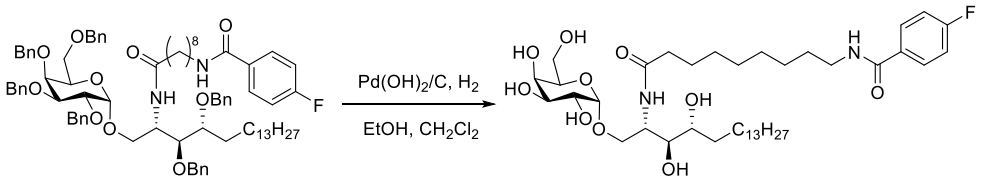
S13d **3d**

3d: A mixture of **S13d** (6.0 mg, 0.0033 mmol) and $Pd(OH)_2/C$ (20% wt on carbon, 5 mg, 0.007 mmol) in EtOH (1.2 mL) and CH_2Cl_2 (0.4 mL) was stirred for 22 h at room temperature under H_2 atmosphere (0.5 MPa), and then filtrated through a short pad of Celite with EtOH/CH_2Cl_2 (3:1). The filtrate was concentrated under reduced pressure to give **3d** as white solid (2.6 mg, 99% yield): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.5 Hz, 3H), 1.25-1.28 (m, 38H), 1.58-1.63 (m, 6H), 2.19 (t, J = 7.4 Hz, 2H), 3.38-3.43 (m, 2H), 3.51-3.54 (m, 2H), 3.70-3.73 (m, 3H), 3.77-3.81 (m, 3H), 3.89 (dd, J = 10.0, 5.0 Hz, 1H), 3.94-3.96 (m, 1H), 4.17-4.20 (m, 1H), 4.91 (d, J = 3.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9, 22.5, 25.6, 25.7, 26.8, 29.0, 29.1 (2C), 29.2 (2C), 29.3, 29.5. 29.6 (11C), 31.8, 32.7, 36.4, 39.9, 50.2, 61.9, 67.5, 68.8, 69.6, 70.4, 72.0, 74.9, 99.6, 126.7 (2C), 128.4 (2C), 134.4, 168.2, 174.2; HRMS (ESI-TOF) calcd $C_{43}H_{76}N_2NaO_{10}$: $(M+Na)^+$, 803.5392; found: $(M+Na)^+$, 803.5395.



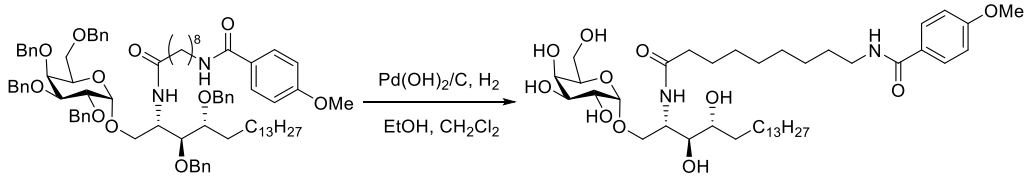
S13a **3a**

3a: By a procedure identical with that described for synthesis of **3d** from **S13d**, the amine **S13a** (10.0 mg, 0.0079 mmol) was converted into **3a** as white solid (5.0 mg, quant.): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.7 Hz, 3H), 1.25-1.32 (m, 32H), 1.60-1.62 (m, 6H), 2.19 (t, J = 6.7 Hz, 2H), 3.38-3.43 (m, 2H), 3.52-3.54 (m, 2H), 3.69-3.74 (m, 3H), 3.77-3.82 (m, 3H), 3.89 (dd, J = 10.3, 4.0 Hz, 1H), 3.94-3.96 (m, 1H), 4.18-4.20 (m, 1H), 4.91 (d, J = 3.1 Hz, 1H), 7.44 (dd, J = 7.4, 7.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.76 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9, 22.5, 25.5, 25.8, 26.6, 28.8 (2C), 28.9, 29.2 (3C), 29.5. 29.6 (5C), 29.7, 31.8, 32.4, 36.2, 39.8, 50.2, 61.8, 67.4, 68.7, 69.7, 70.1, 70.4, 72.0, 74.5, 99.5, 126.8 (2C), 128.4 (2C), 131.3, 134.3, 168.3, 174.2; HRMS (ESI-TOF) calcd $C_{40}H_{70}N_2NaO_{10}$: $(M+Na)^+$, 761.4923; found: $(M+Na)^+$, 761.4921.



S13b **3b**

3b: By a procedure identical with that described for synthesis of **3d** from **S13d**, the amine **S13b** (5.0 mg, 0.0039 mmol) was converted into **3b** as white solid (3.6 mg, quant.): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.8 Hz, 3H), 1.25-1.33 (m, 32H), 1.50-1.68 (m, 6H), 2.20 (t, J = 7.3 Hz, 2H), 3.38-3.42 (m, 2H), 3.52-3.56 (m, 2H), 3.69-3.74 (m, 3H), 3.77-3.81 (m, 3H), 3.89 (dd, J = 10.3, 3.6 Hz, 1H), 3.94-3.97 (m, 1H), 4.18-4.21 (m, 1H), 4.91 (d, J = 3.6 Hz, 1H), 7.10-7.12 (m, 2H), 7.79-7.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD = 10:1) δ 13.9, 22.5, 24.5, 25.7, 26.6, 28.7, 28.8 (2C), 29.2 (2C), 29.5, 29.6 (6C), 31.8 (2C), 32.6, 36.2, 39.9, 50.2, 61.8, 67.4, 68.8, 69.6, 70.1, 70.5, 71.9, 74.7, 99.5, 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 129.2 (d, $J_{C\text{-}F}$ = 8.5 Hz, 2C), 130.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 164.5 (d, $J_{C\text{-}F}$ = 251.8 Hz), 167.1, 174.2; HRMS (ESI-TOF) calcd $C_{40}H_{69}FN_2NaO_{10}$: $(M+Na)^+$, 779.4828; found: $(M+Na)^+$, 779.4834.



S13c **3c**

3c: By a procedure identical with that described for synthesis of **3d** from **S13d**, the amine **S13c** (5.0 mg, 0.0039 mmol) was converted into **3c** as white solid (4.1 mg, quant.): ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD = 10:1) δ 0.88 (t, J = 6.6 Hz, 3H), 1.25-1.33 (m, 32H), 1.58-1.65 (m, 6H), 2.19-2.26 (m, 2H), 3.38-3.41 (m, 2H), 3.53-3.56 (m, 2H), 3.72-3.86 (m, 6H), 3.86 (s, 3H), 3.86-3.91 (m, 1H), 3.95-3.98 (m, 1H), 4.19-4.21 (m, 1H), 4.91-4.93 (m, 1H), 6.93 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.5, 25.5, 25.7, 26.6, 28.8, 28.9, 29.2 (2C), 29.3, 29.5, 29.6 (4C), 29.7, 31.8 (2C), 32.5, 35.2, 36.4, 39.8, 50.2, 55.3, 62.0, 67.5, 68.8, 70.4, 70.5, 71.2, 72.0, 74.7, 99.5, 113.6 (2C), 126.5, 128.7 (2C), 162.0, 164.7, 175.8; HRMS (ESI-TOF) calcd $C_{41}H_{72}N_2NaO_{11}$: $(M+Na)^+$, 791.5028; found: $(M+Na)^+$, 791.5034.

General Molecular Modeling Work

For general molecular modeling work described below, the Maestro molecular modeling suite (Maestro version 10.4; Schrödinger, LLC: New York) with OPLS3 force field[5] was used through out. The same force field was used also for the WaterMap calculations and the MD simulations.

WaterMap Calculation

The protocols involved in the WaterMap calculations are described in details in previous works.[6, 7] It involves a grand canonical Monte Carlo equilibration for the regions of the ligand binding site that may not allow for easy exchange of the solvating water molecules with the bulk water.[8, 9] Default settings were used for all calculations. The calculated thermodynamic parameters are relative to those of bulk water. The coordinates of the protein and the ligand, an α-GalCer derivative with a saturated acyl chain (C24:0), were obtained from the X-ray crystal structure (PDB: 3g08). The input structures were prepared using the Protein Preparation Wizard.[10] For the preparation of the apo protein, the ligand was simply deleted from the complex structure. The structure of the mCD1d in complex with the amide-containing ligand (C24 equivalent to **1d**) was generated by editing the same template. The initial structure was relaxed by a MD simulation for 200 ps, and used for the WaterMap calculation.

Molecular Dynamics Simulations

Molecular dynamics simulations were performed using Desmond (Desmond version 4.4; Schrödinger, LLC: New York).[11] The coordinates of mCD1d in complex with α-GalCer are taken from the X-ray crystal structure (PDB: 3he6), and were prepared using Maestro as described above. The structures of **1a-d** bound in mCD1d were also modeled based on this structure. The system was solvated in a TIP4P[12] water box extending 10 Å beyond the protein, and the system was relaxed using the default relaxation protocol as implemented within Desmond. For the regions of the ligand binding site that may not allow for easy exchange of the solvating water molecules with the bulk water, a grand canonical Monte Carlo equilibration protocol implemented in Desmond was used.[8, 9] Molecular dynamics simulations were performed in the NPT ensemble at 300K and 1.01 bar using the default settings, described briefly below. The temperature and pressure were controlled using a Nose-Hoover chain thermostat[13] and Martyna-Tobias-Klein barostat,[14] respectively. Van der Waals and short range electrostatic interactions were cut off at 9 Å and smooth particle mesh Ewald (PME) method[15] was employed for calculation of long range electrostatic interacts. The reversible reference system propagation algorithm (RESPA) multiple time step method was used. The time step was set at 2 ps, and long-ranged electrostatic interactions were computed every 6 ps.[16]

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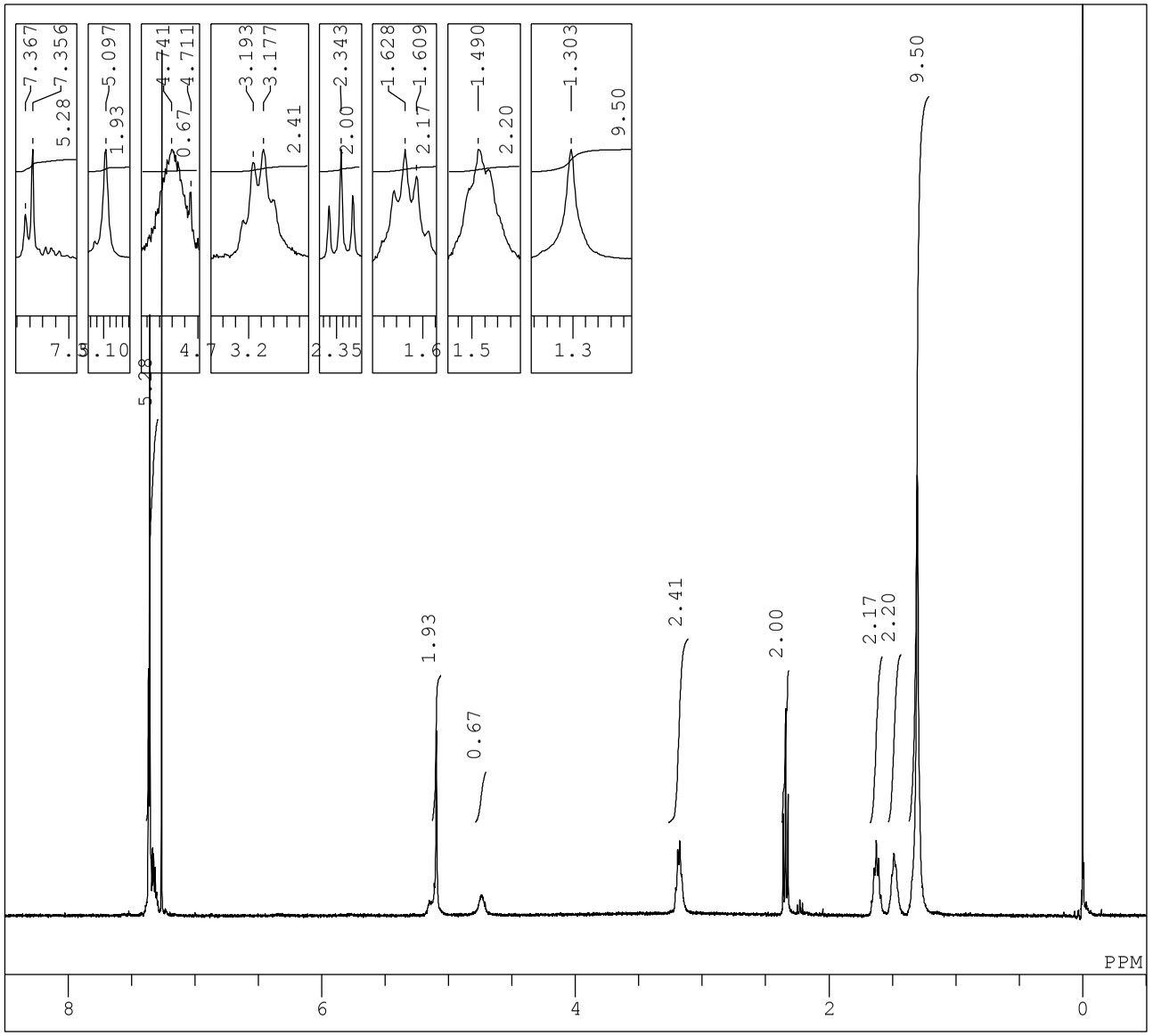

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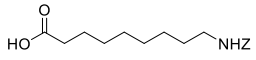

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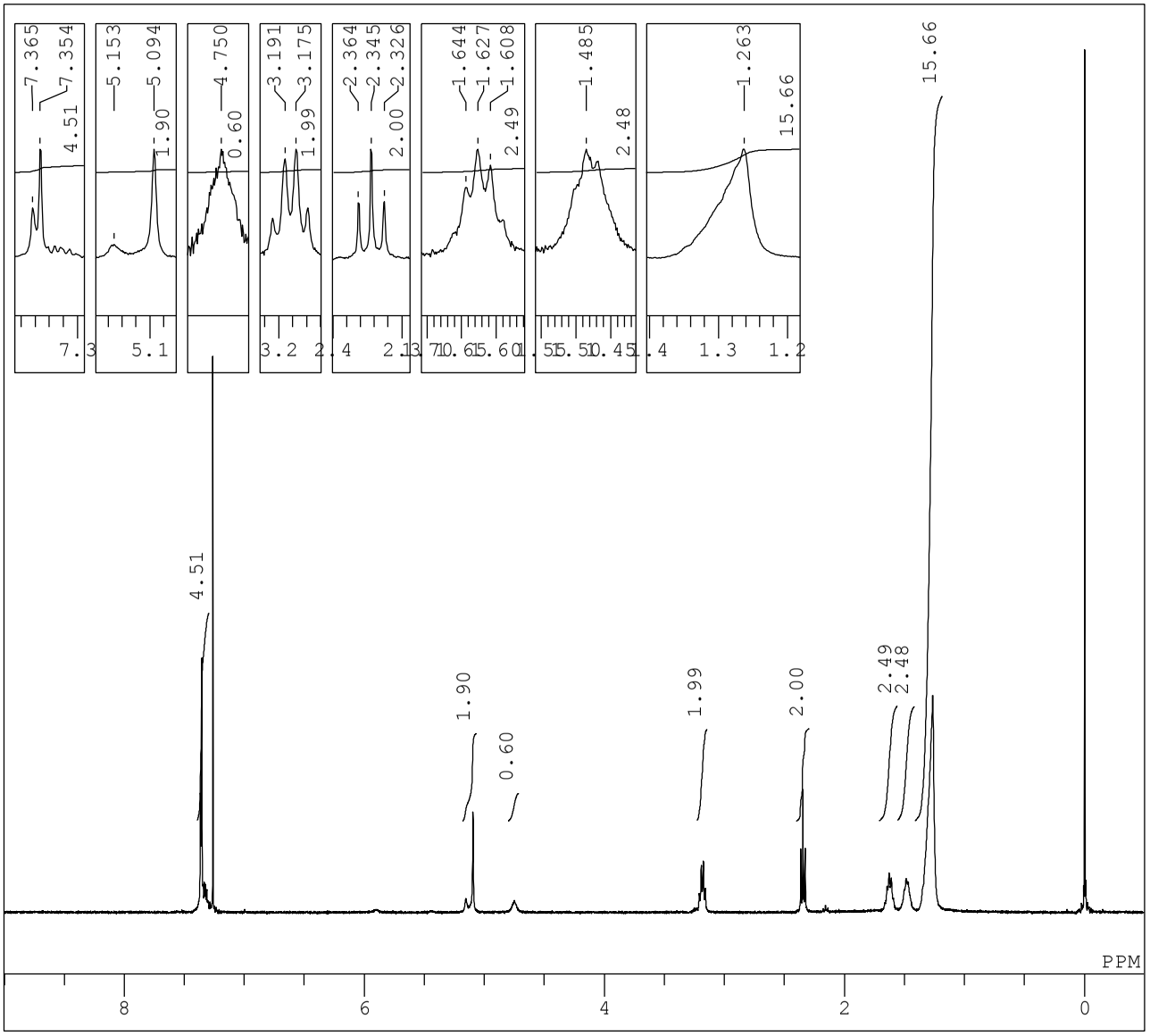

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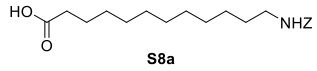

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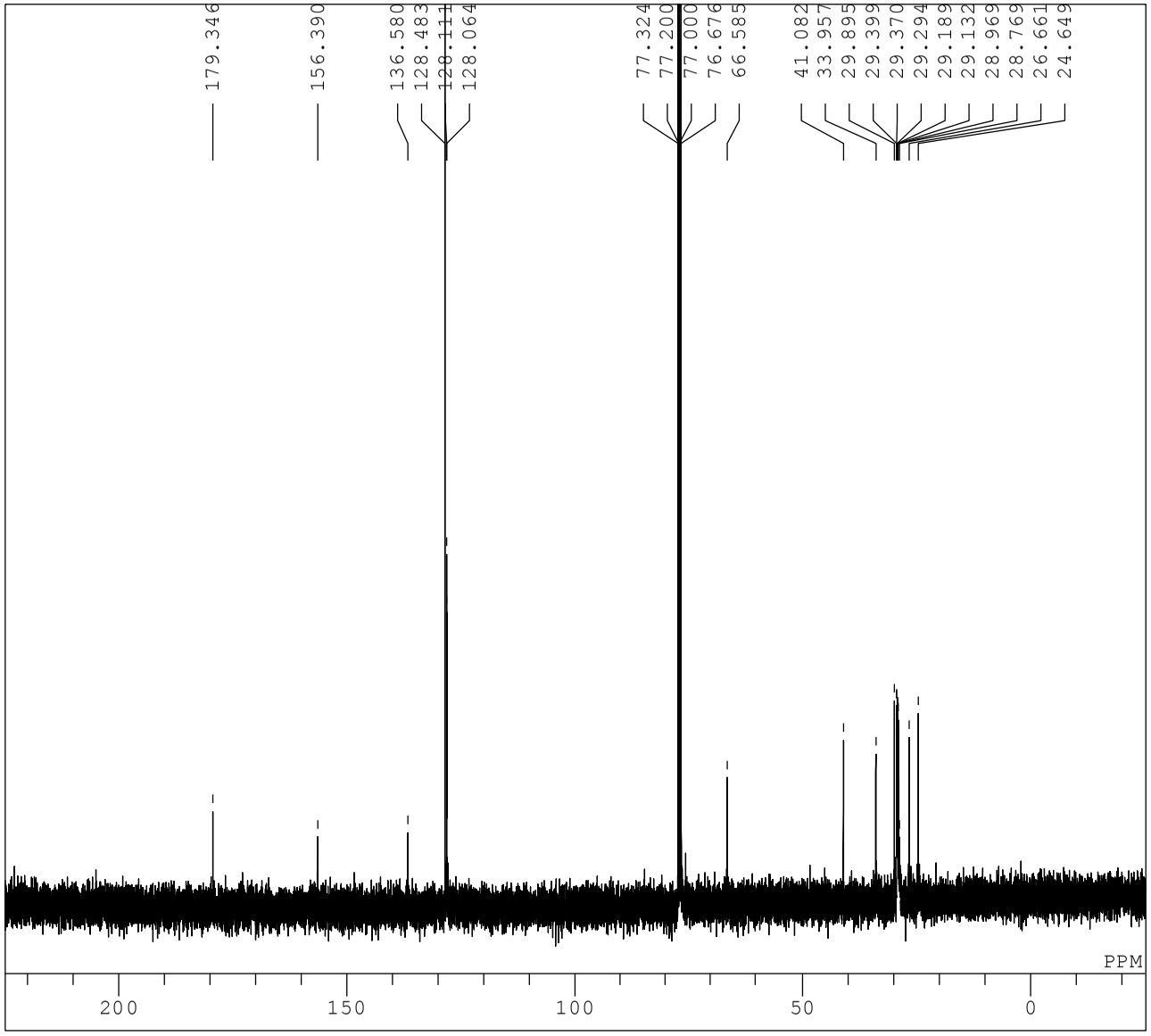


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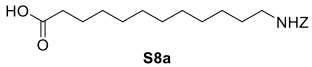

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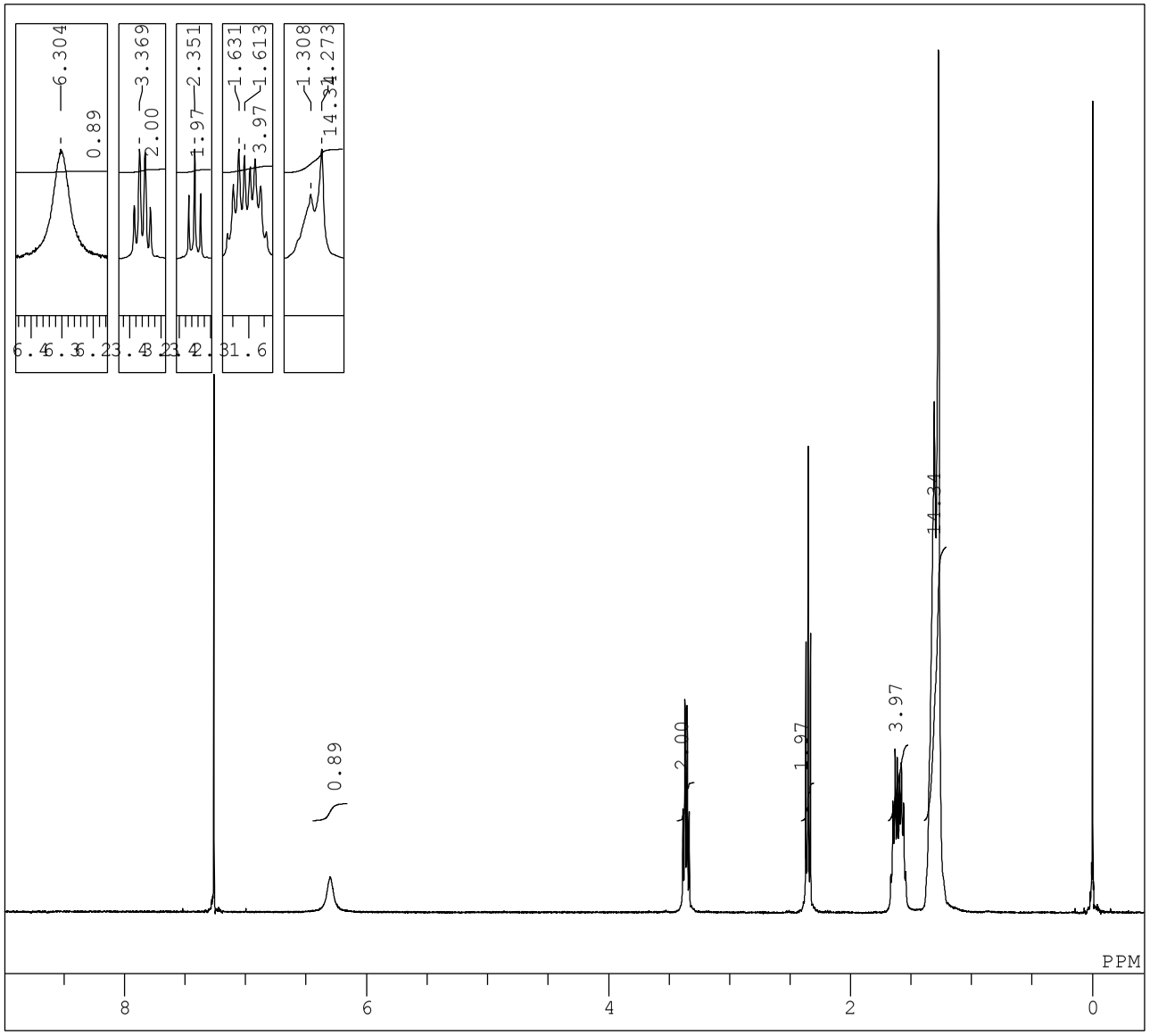

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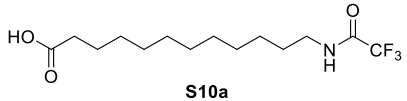

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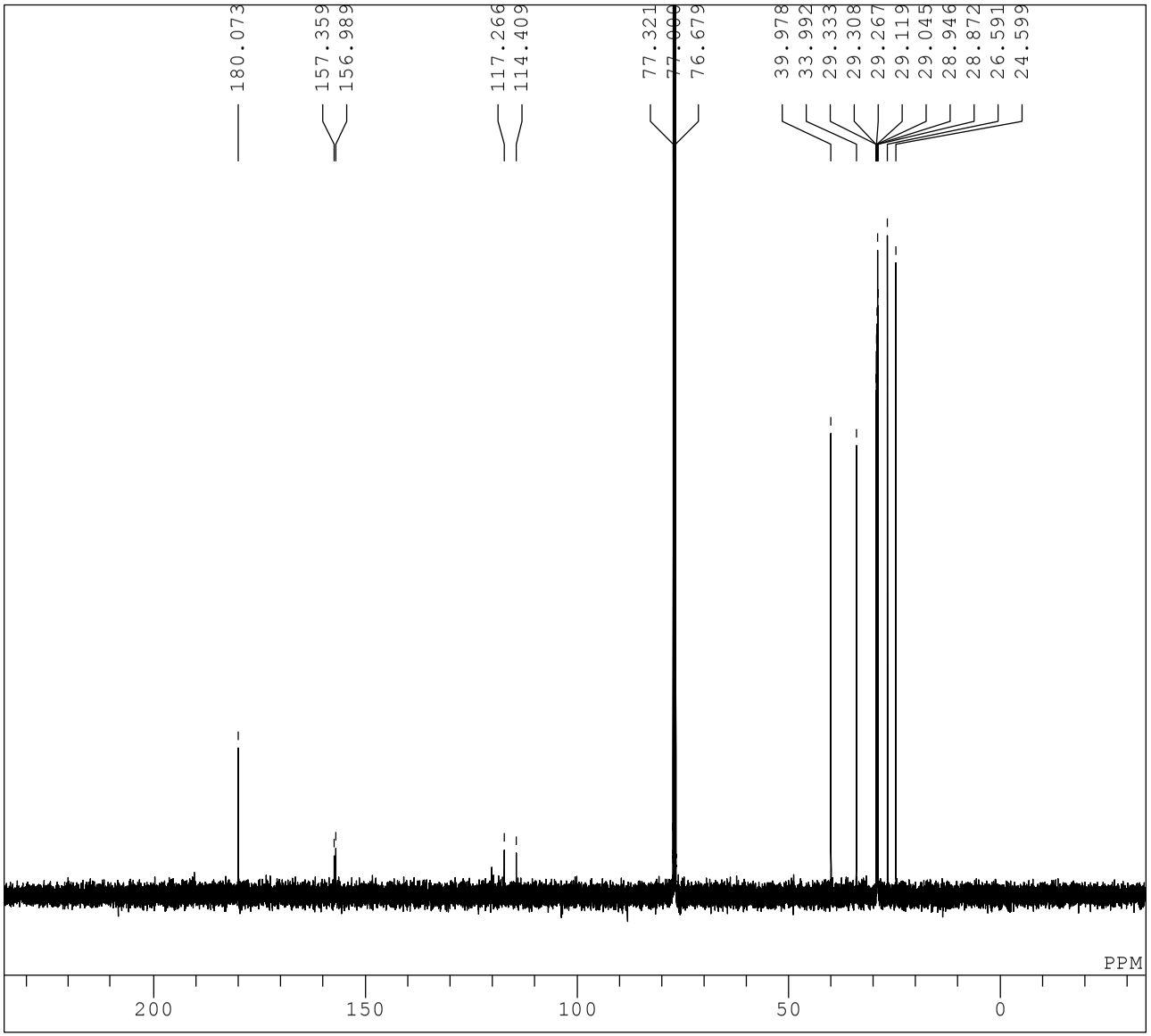

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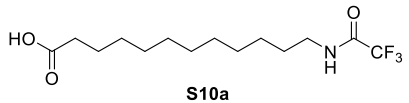

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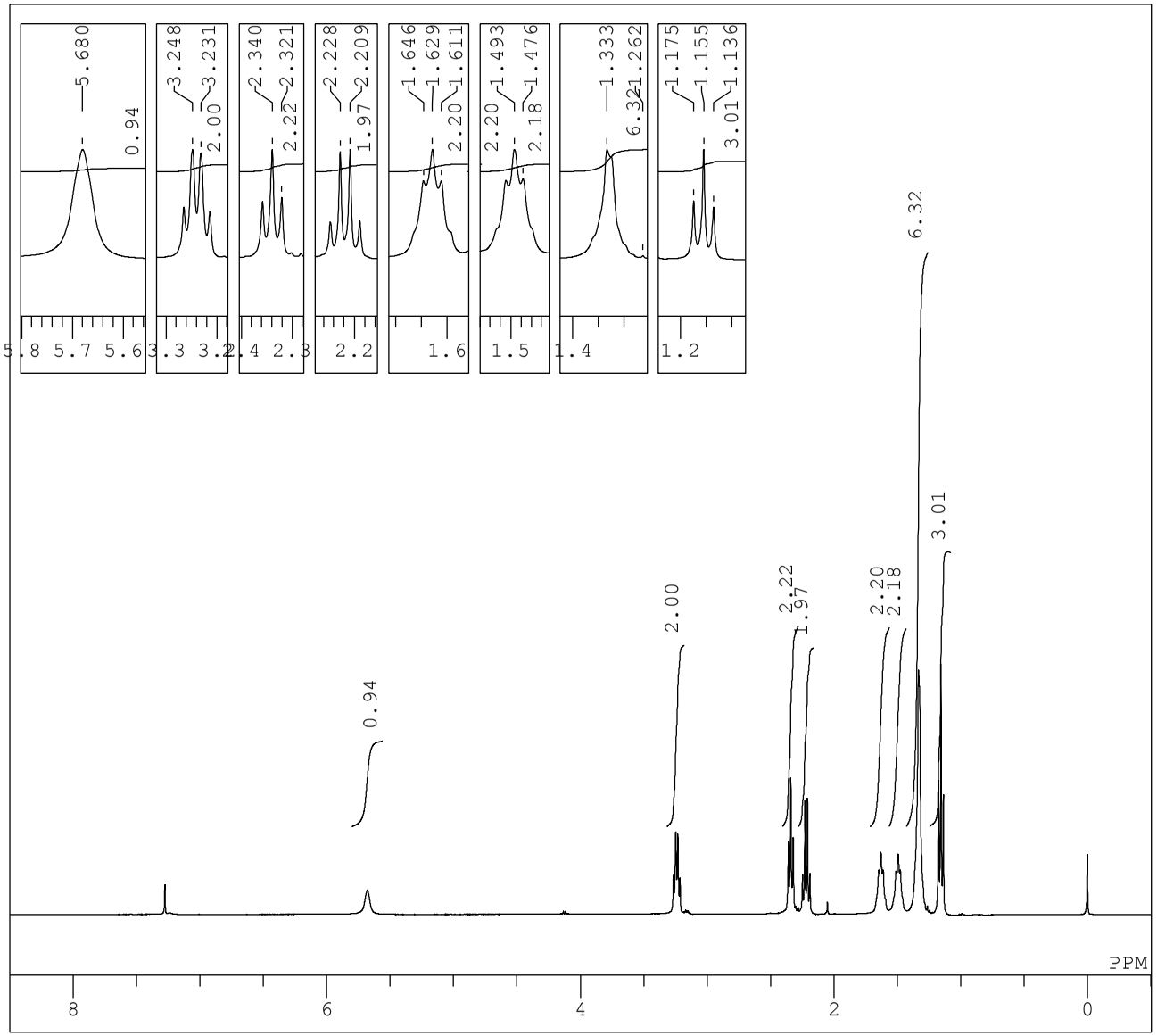

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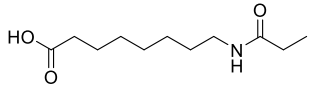

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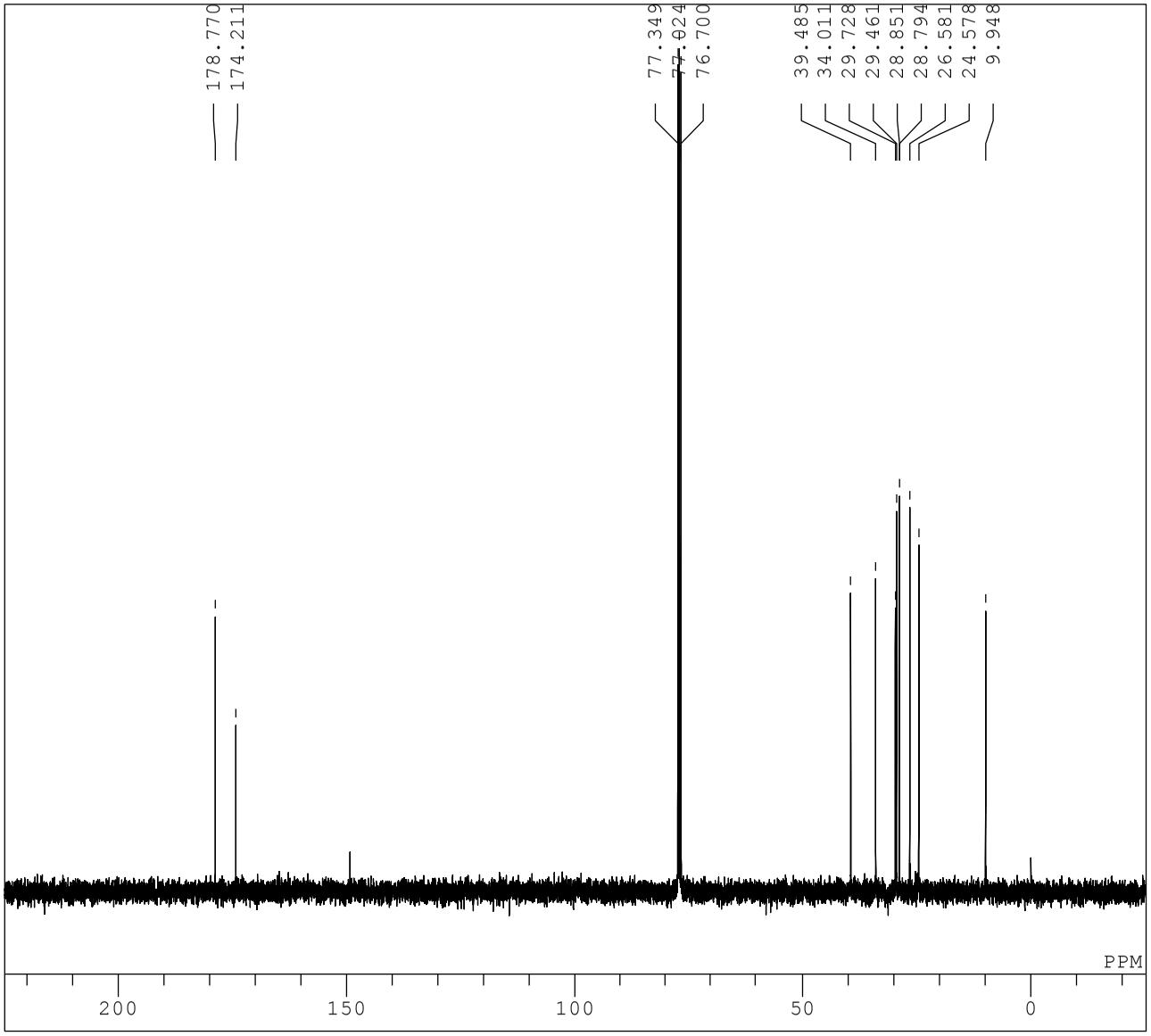


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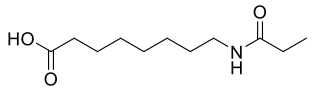

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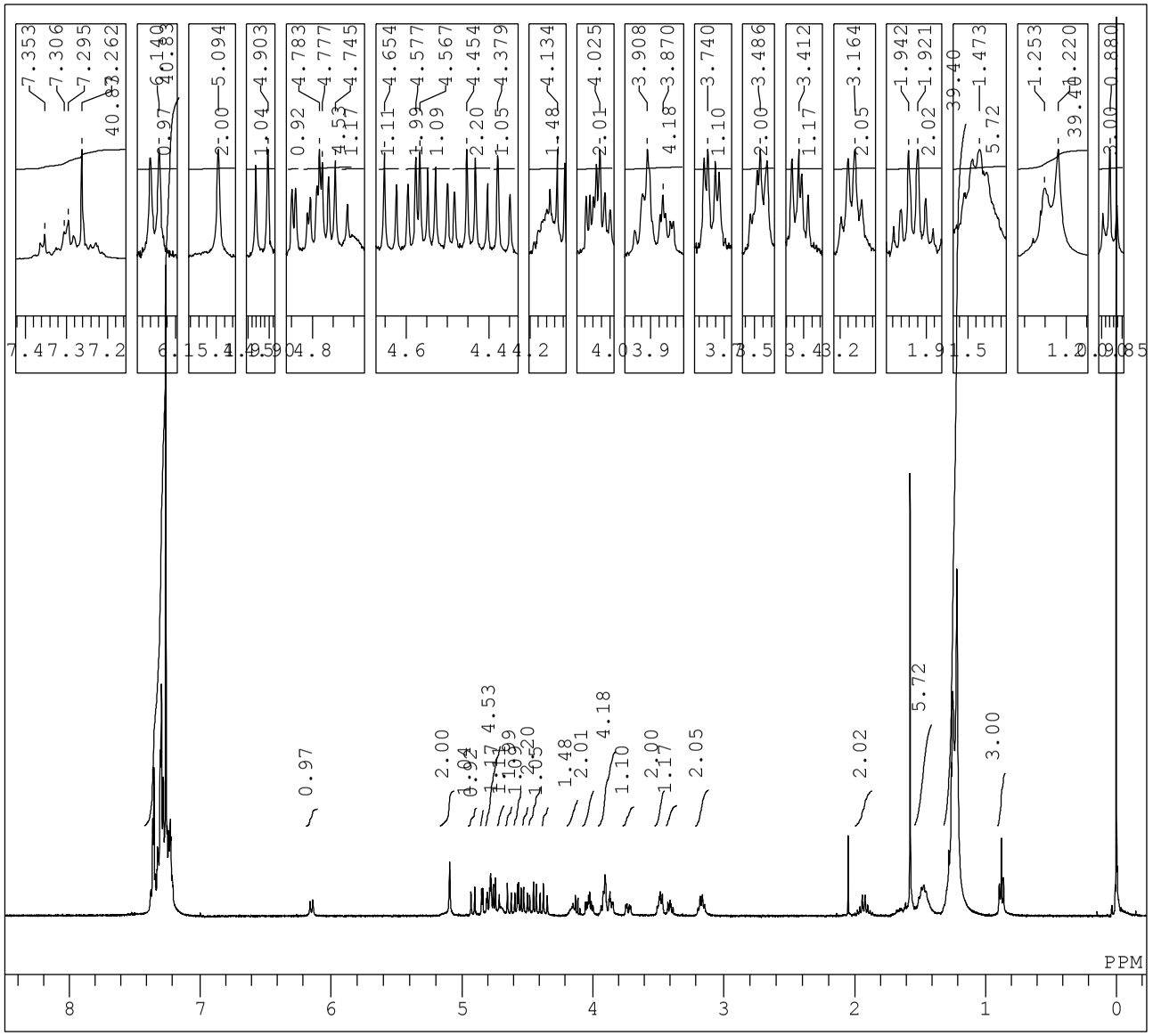

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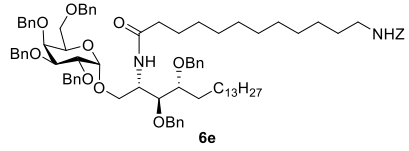

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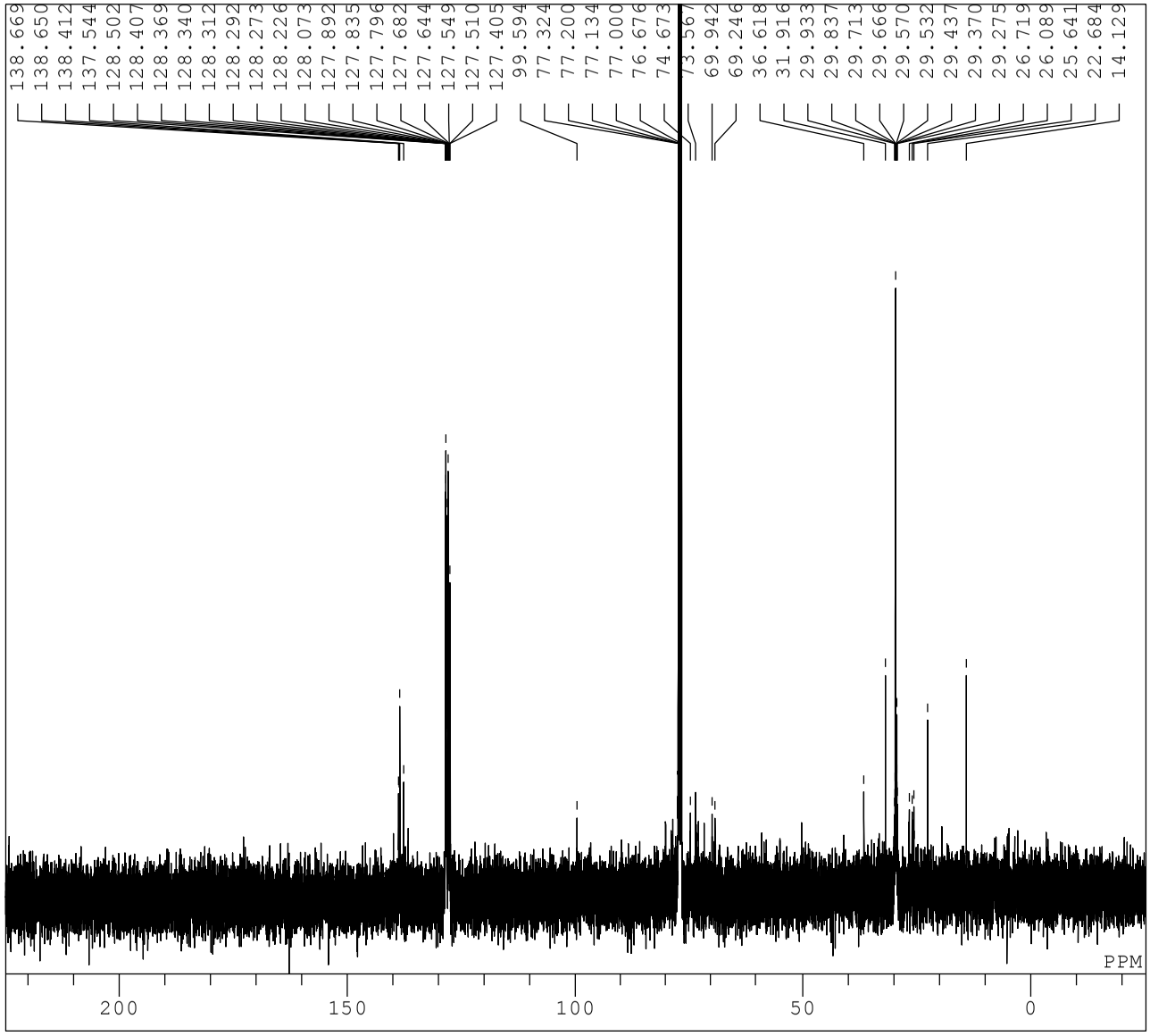

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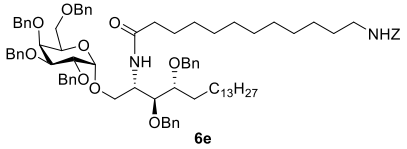
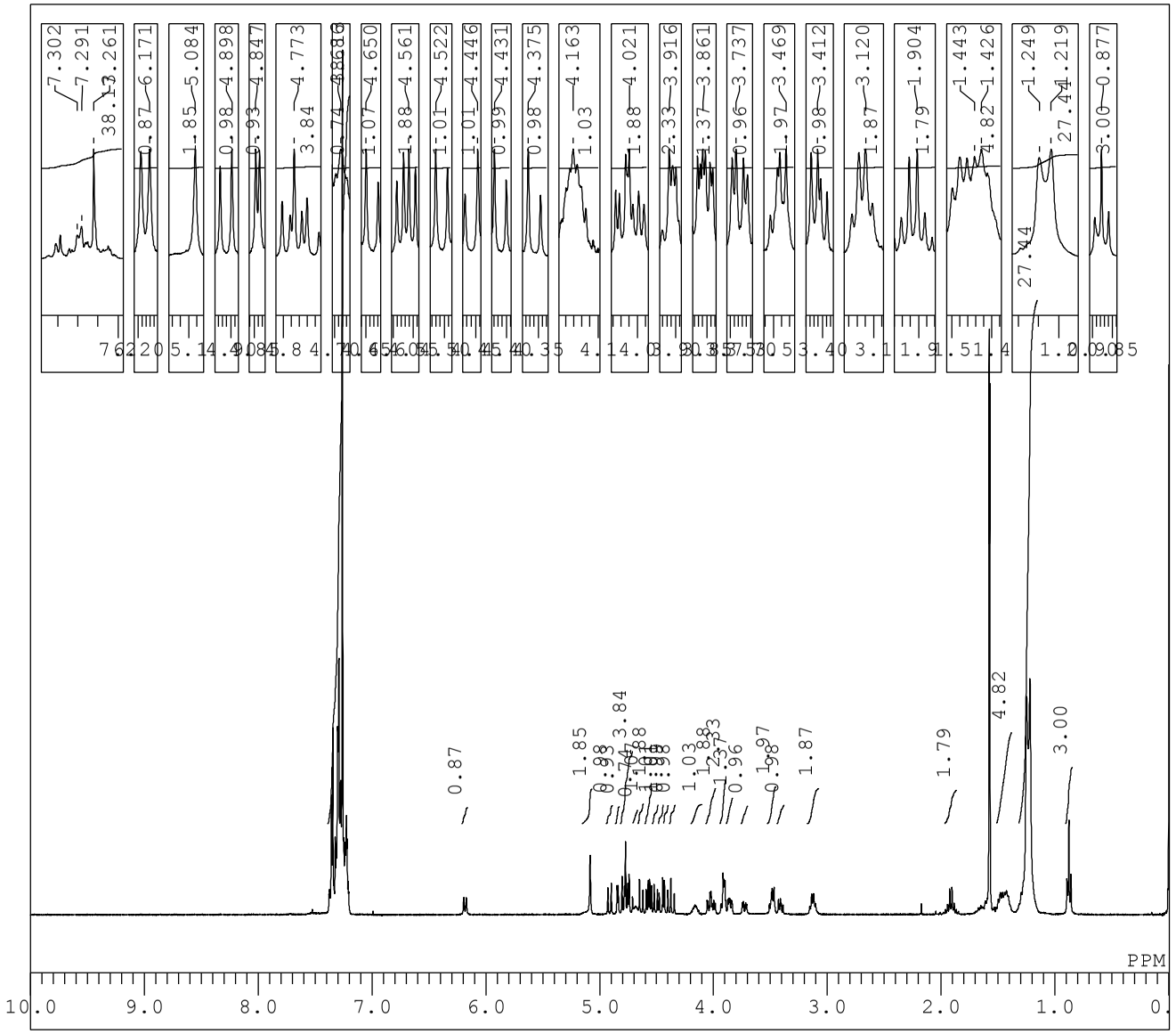
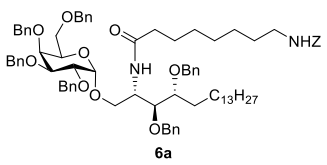
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 2425
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 34



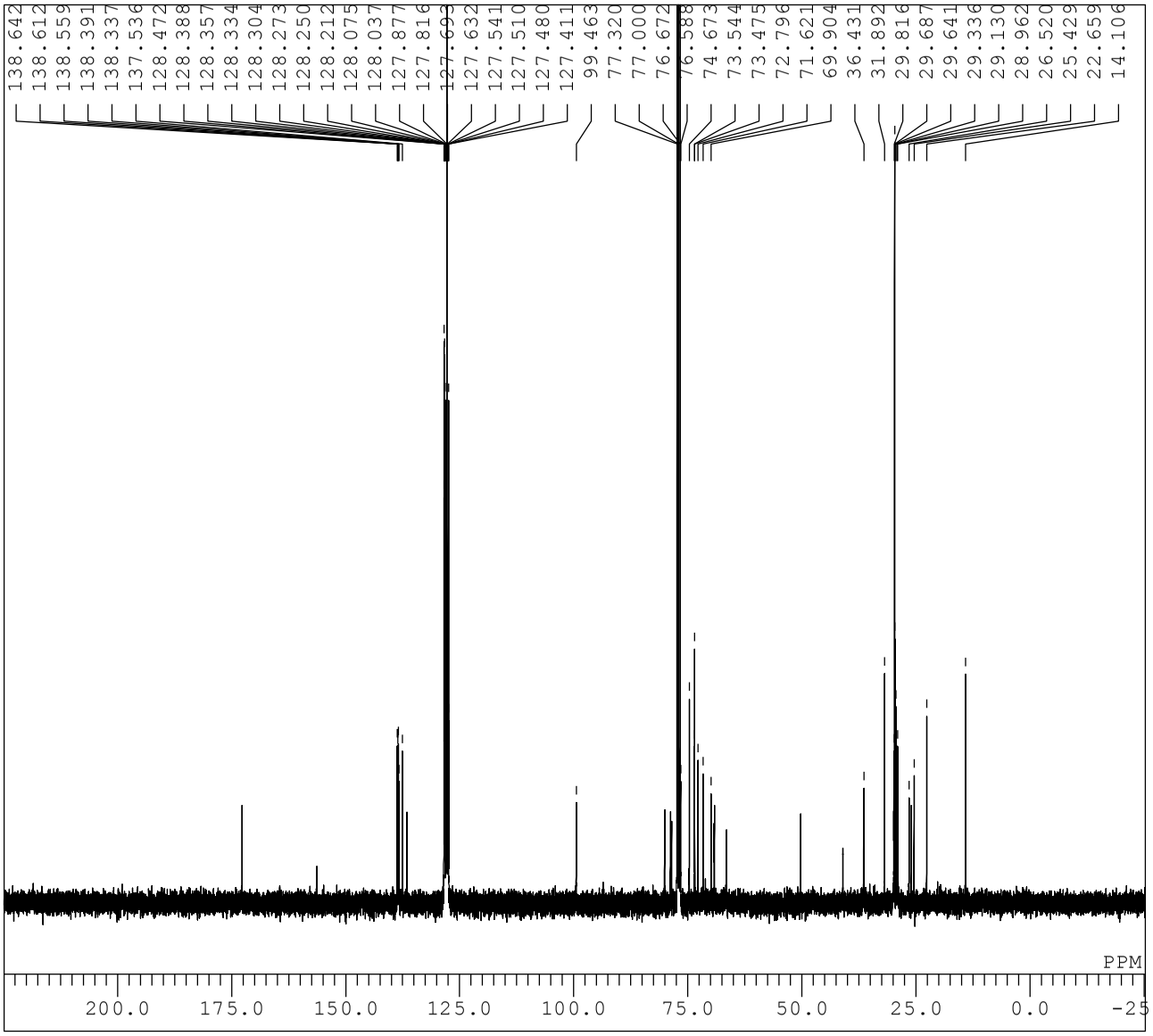
6e



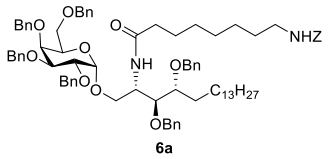
DFILE 102B-145a-1.als
COMNT single_pulse
DATIM 2015-07-13 12:38:57
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 50



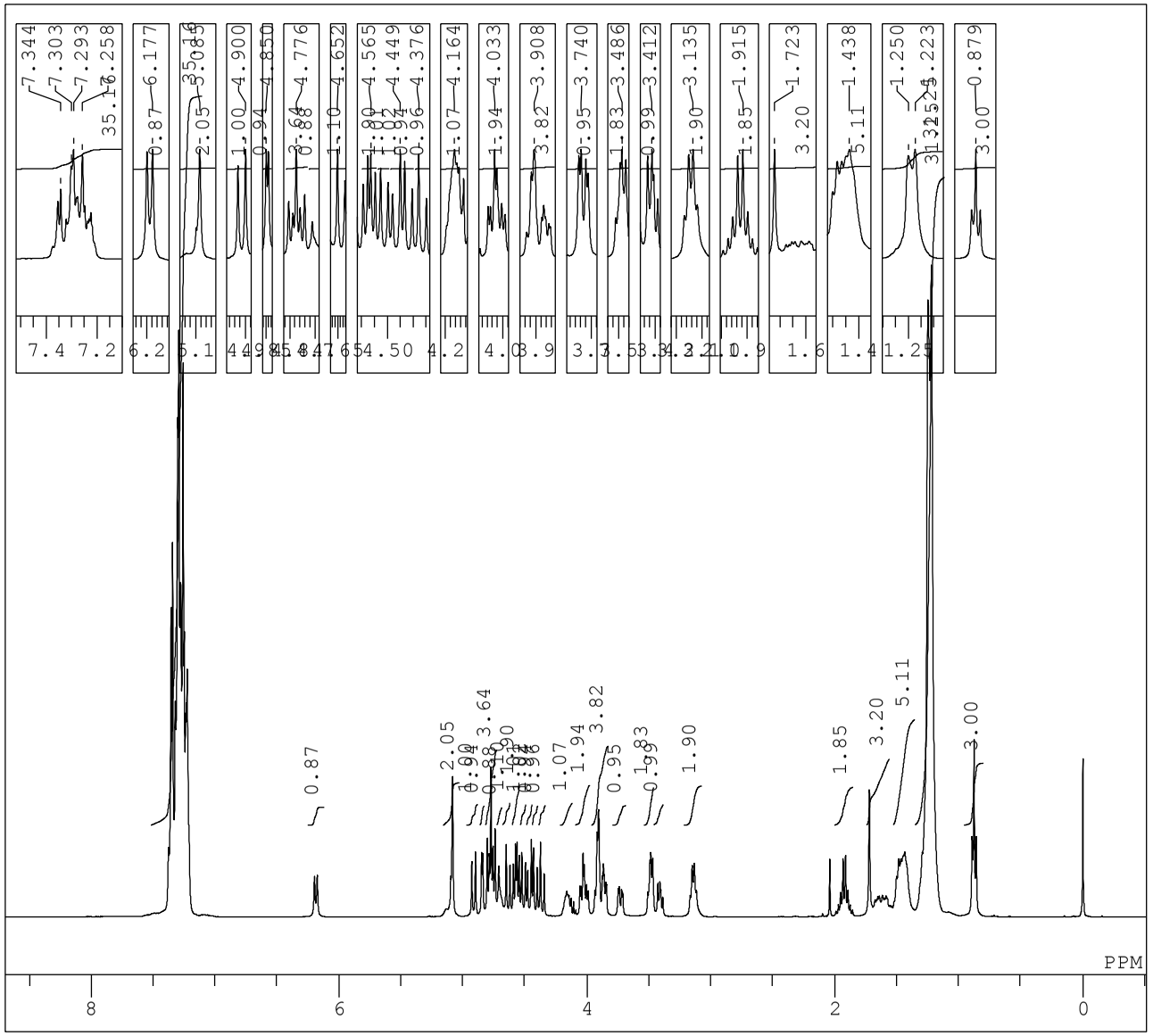
6a



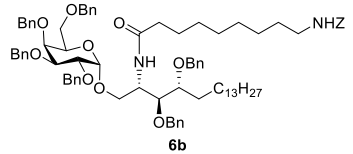
DFILE 102B-145a BCM -1.als
COMNT single pulse decoupled
DATIM 2015-07-13 13:43:10
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 32768
FREQU 24630.54 Hz
SCANS 1000
ACQTM 1.3304 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 66



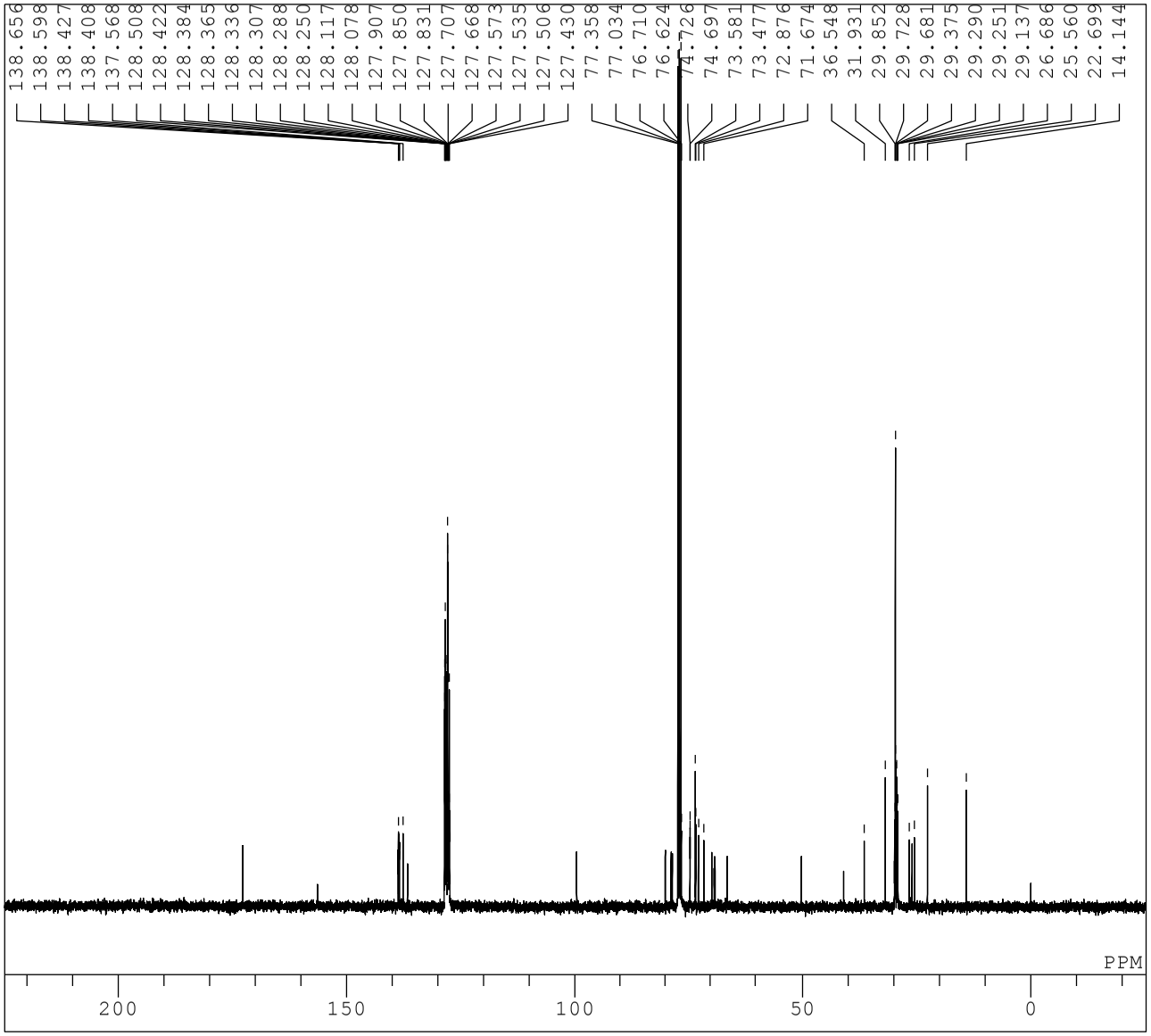
6a



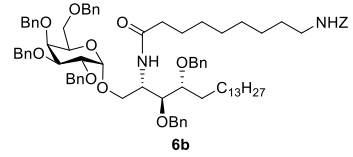
DFILE 102A-090a-1.als
COMNT single_pulse
DATIM 2014-10-02 13:42:34
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.25 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.10 Hz
RGAIN 30



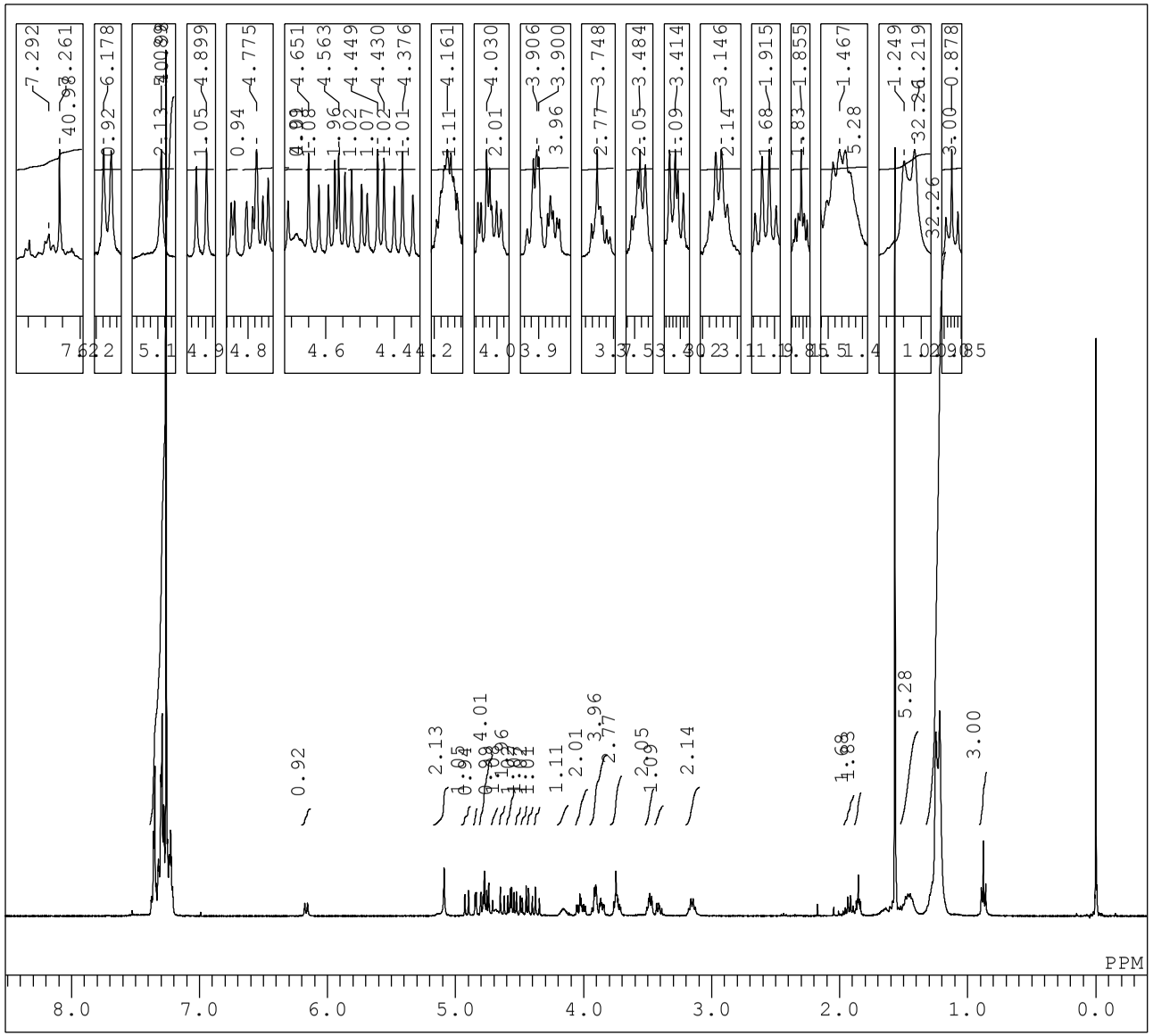
6b



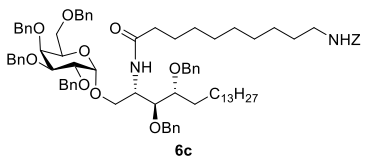
DFILE 102A-090a BCM-2.als
COMNT single pulse decoupled c
DATIM 2014-10-02 14:16:16
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 502
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.10 Hz
RGAIN 34



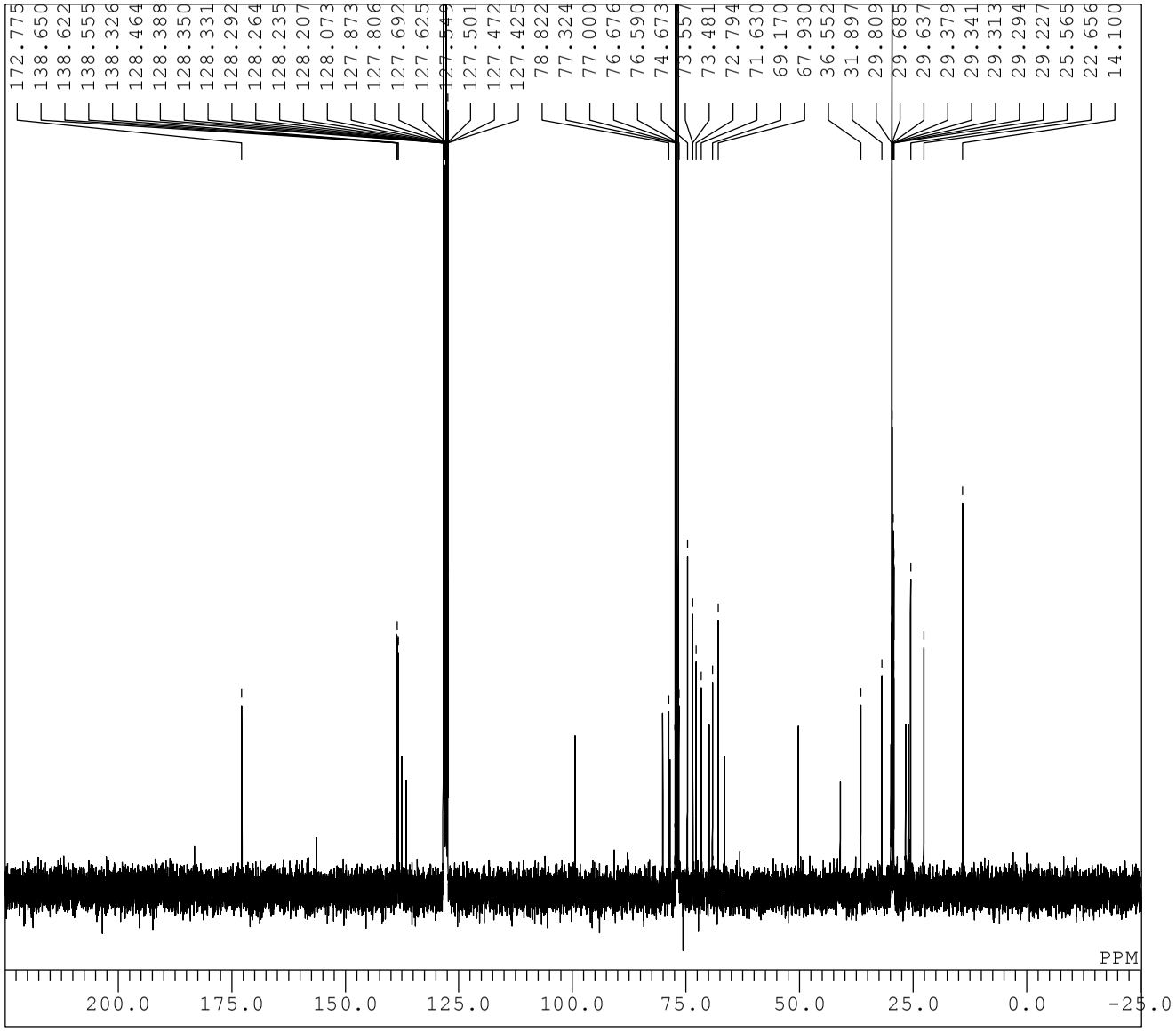
6b



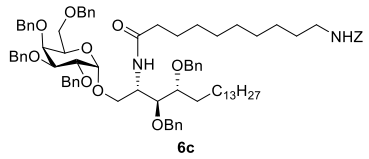
DFILE 102B-143a 150711-1.als
COMNT single_pulse
DATIM 2015-07-11 09:35:09
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 50



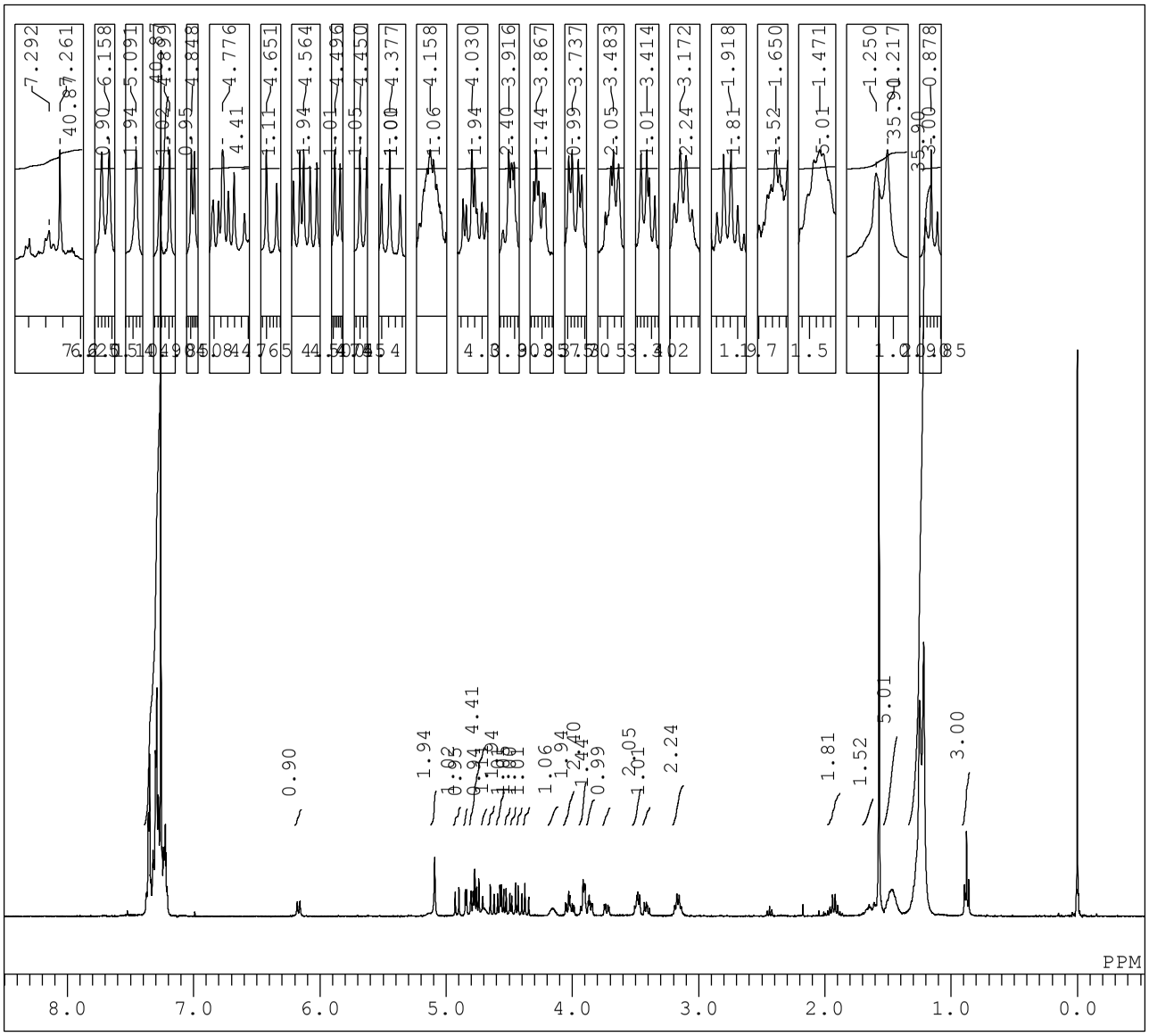
6c



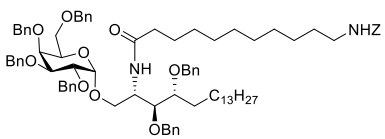
DFILE 102B-143a BCM 150711-1.a
COMNT single pulse decoupled c
DATIM 2015-07-11 10:35:22
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 1000
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 36



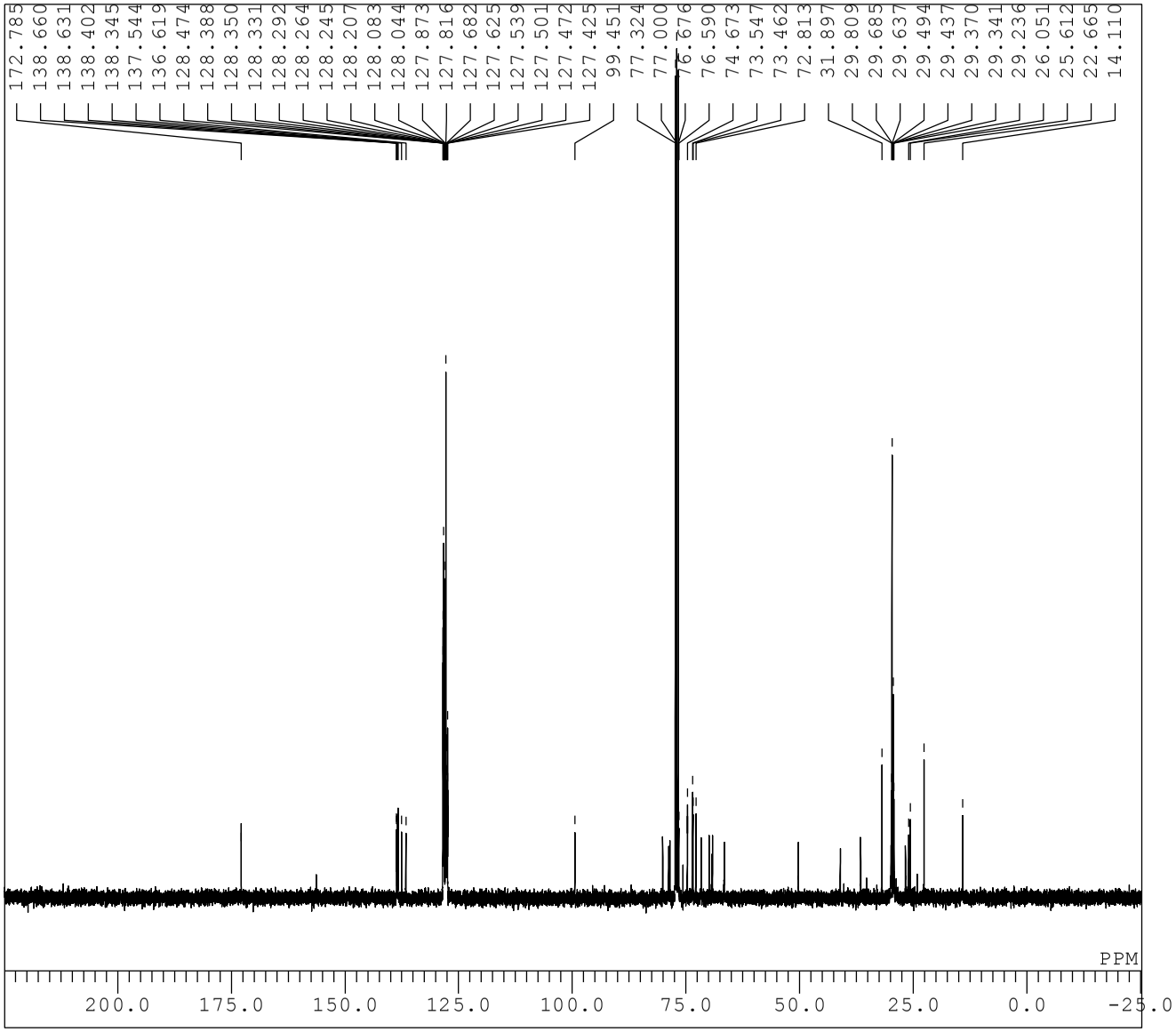
6c



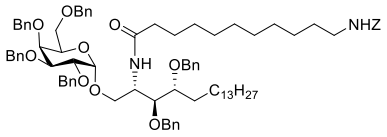

```
DFILE 102B-144a-1.als
COMNT single_pulse
DATIM 2015-07-11 14:09:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.35 usec
IRNUC 1H
CTEMP         21.3 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.42 Hz
RGAIN           48
```



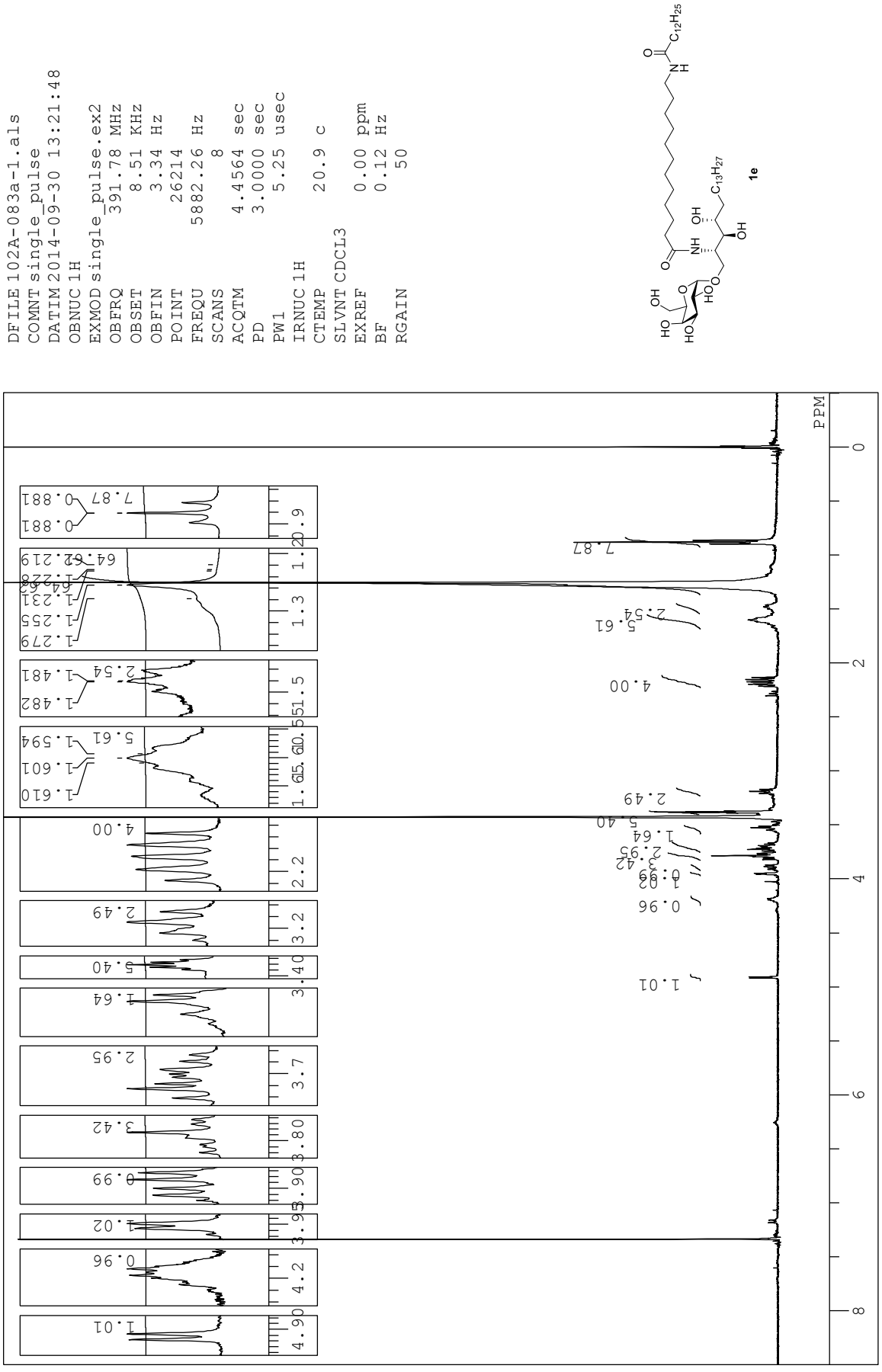
6d

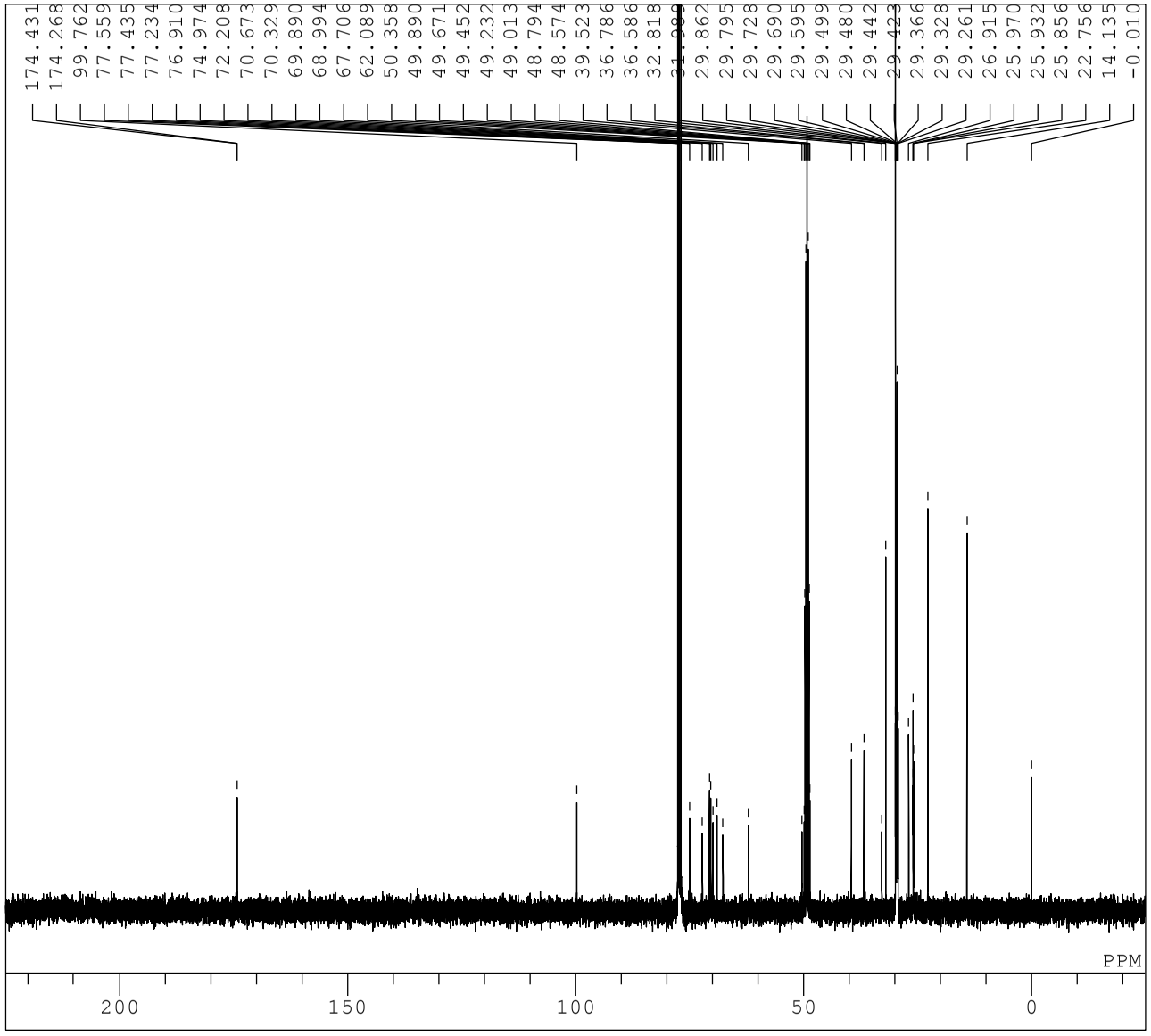


DFILE 102B-144 BCM-1.als
COMNT single pulse decoupled c
DATIM 2015-07-11 15:09:11
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 1000
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 44

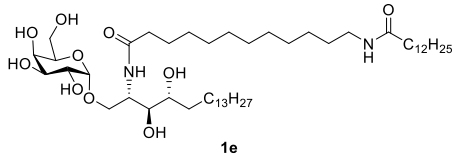


6d

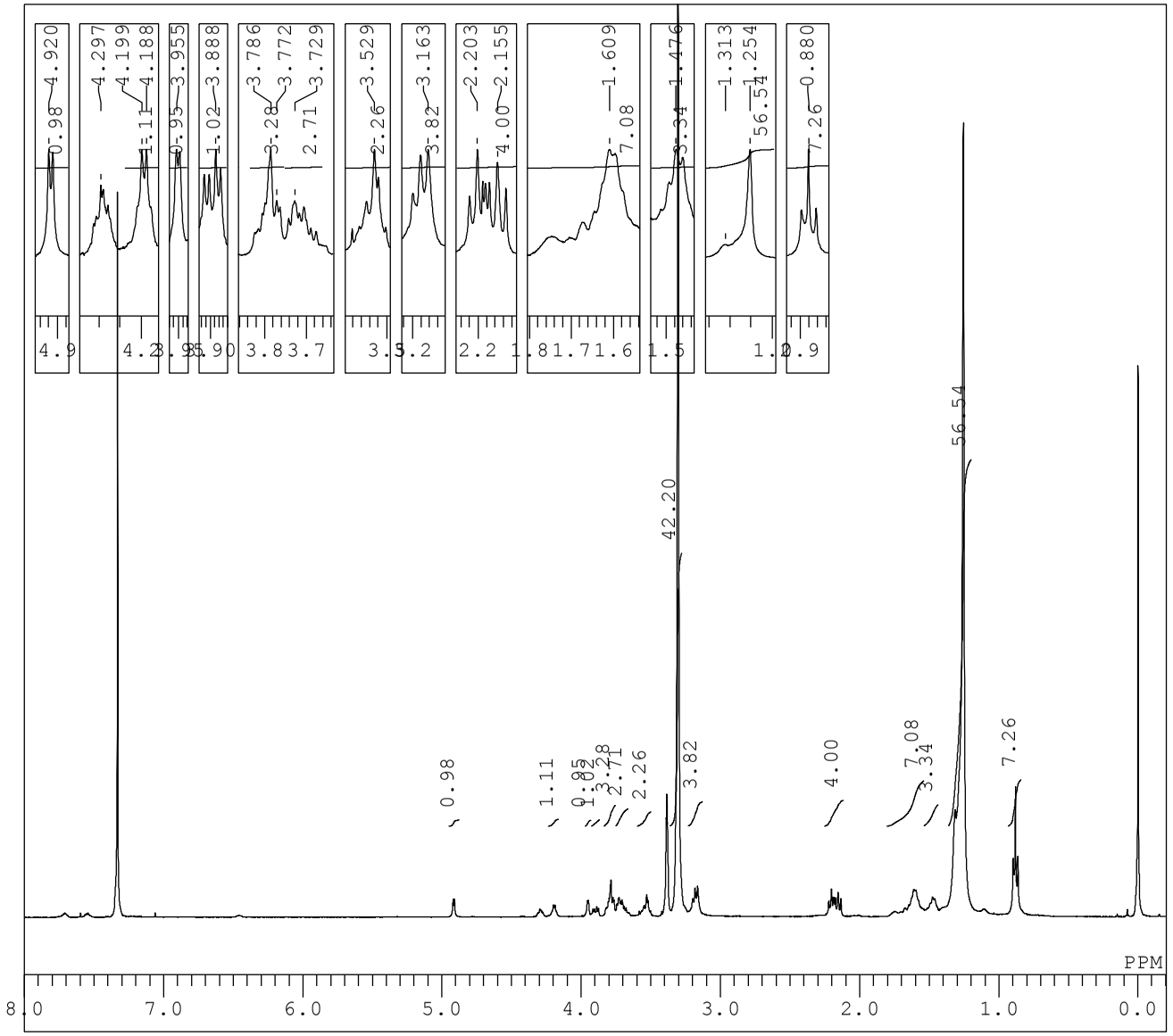

DFILE 102A-083a-1.als
COMNT single_pulse
DATIM 2014-09-30 13:21:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.25 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
1e
PPM



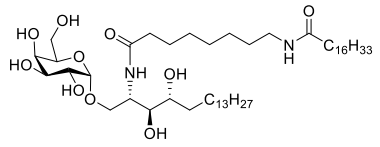

```
DFILE 102A-083a BCM-1.als
COMNT single pulse decoupled c
DATIM 2014-10-29 08:47:03
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS        13136
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.17 usec
IRNUC 1H
CTEMP         21.4 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           46
```



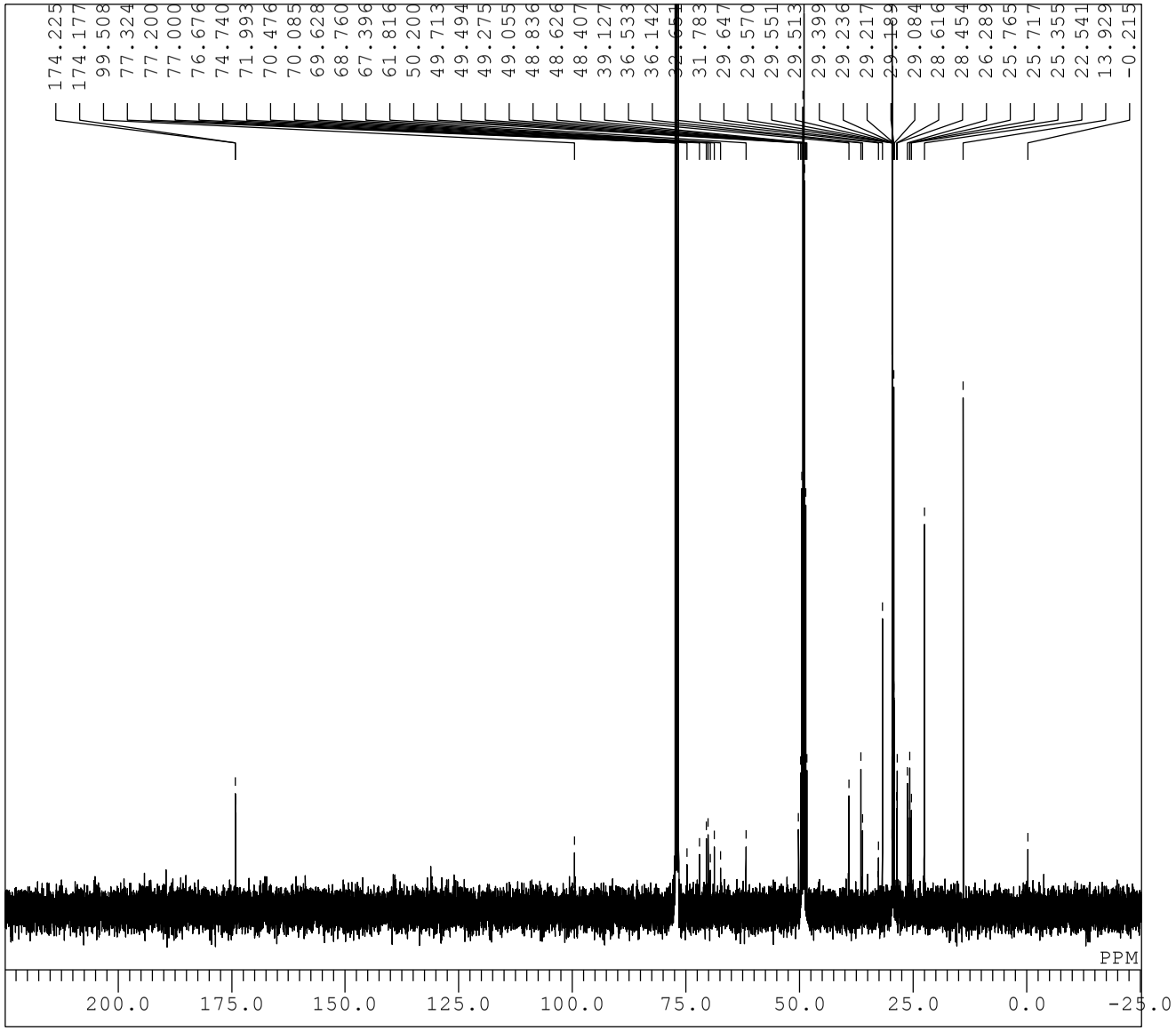
1e



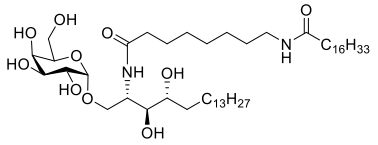
DFILE 102B-154a 150723-1.als
COMNT single_pulse
DATIM 2015-07-22 11:36:33
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 128
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 50



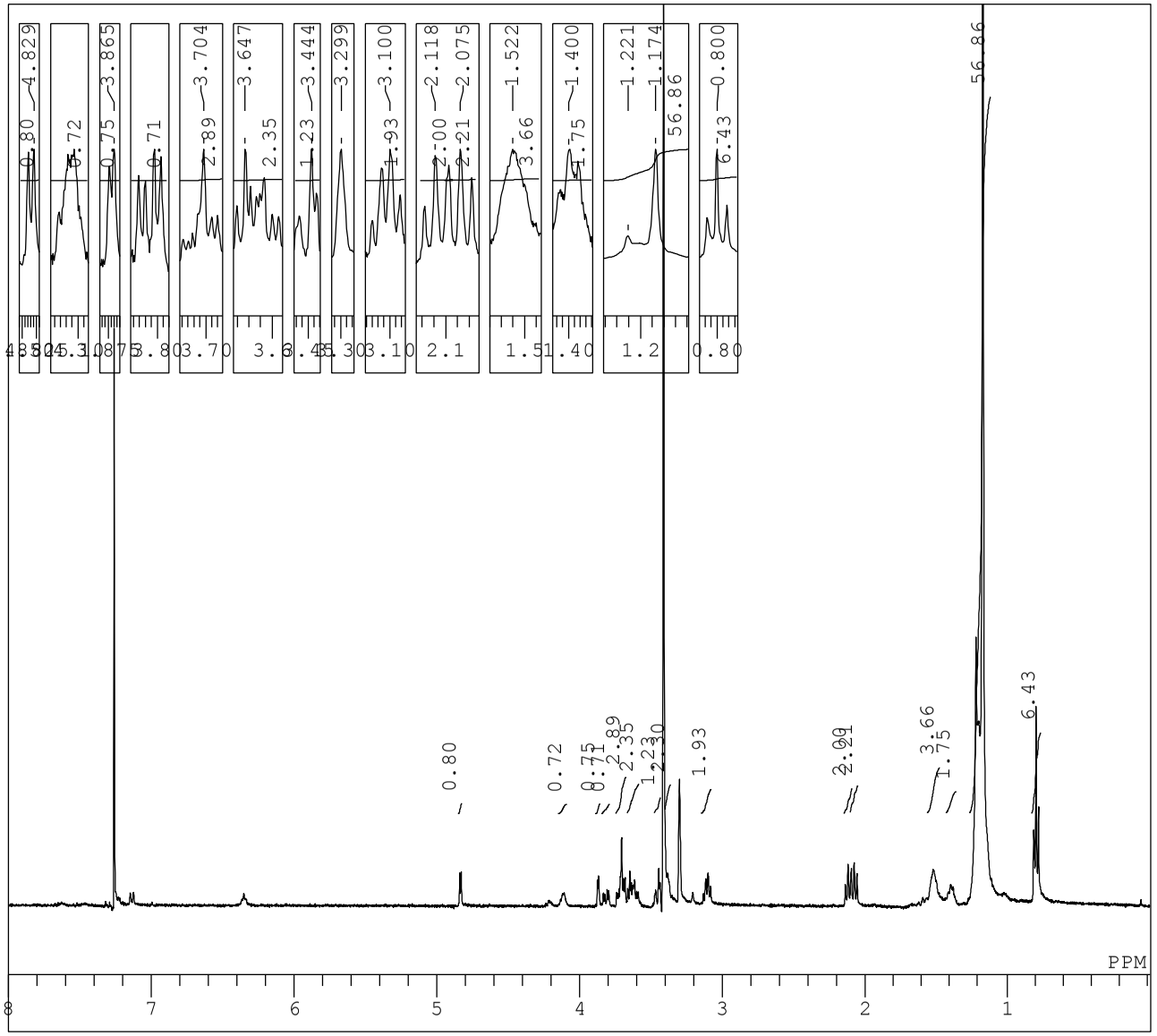
1a



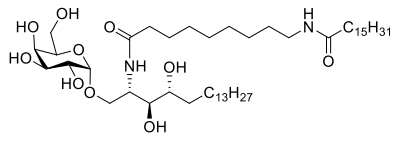
DFILE 102B-154a BCM 150726-1.a
COMNT single pulse decoupled c
DATIM 2015-07-27 08:24:59
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13174
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 34



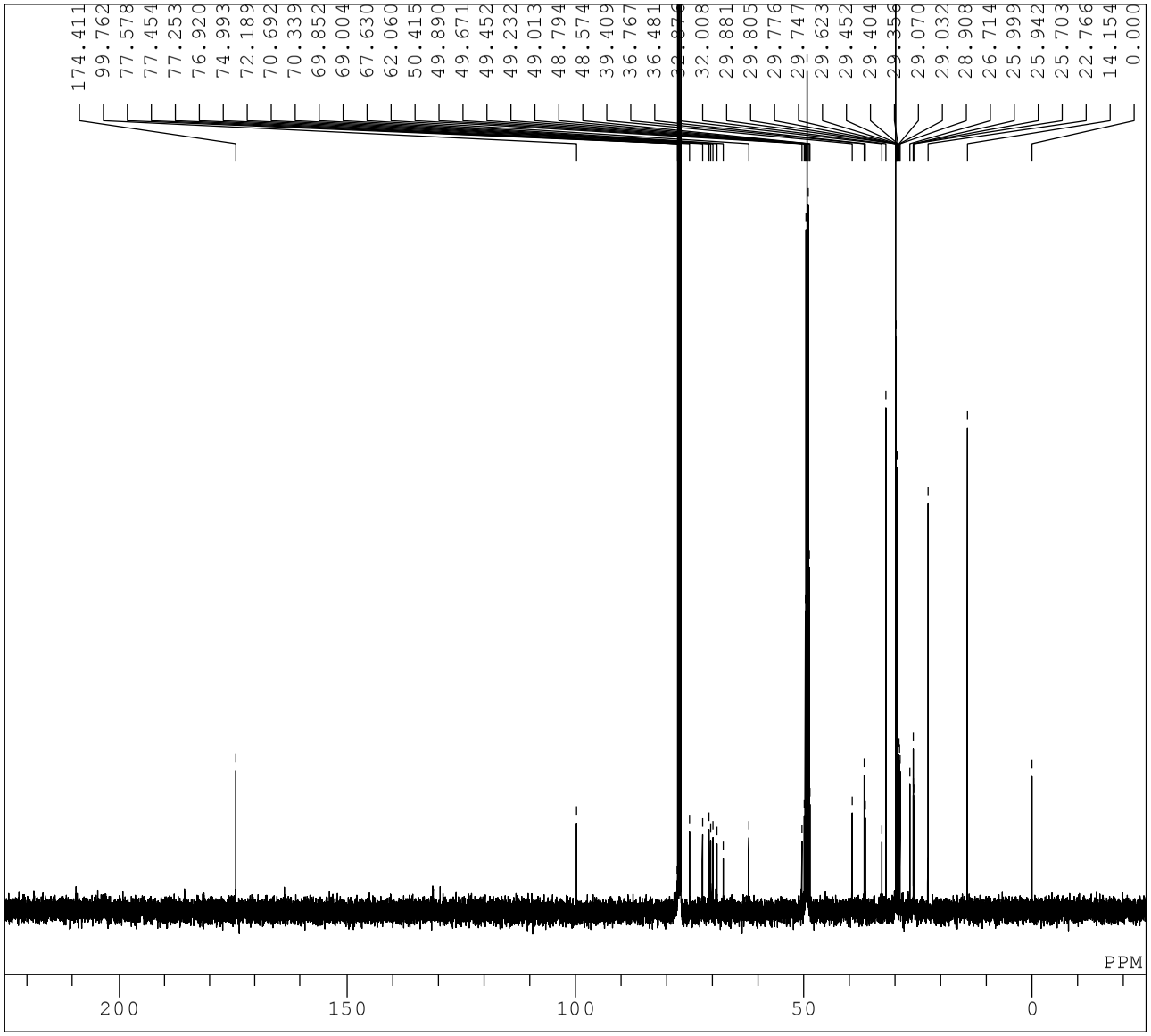
1a



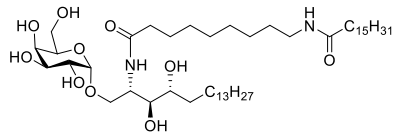
DFILE 102A-095a.als
COMNT
DATIM Fri Oct 10 15:50:41 201
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 2.0000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20



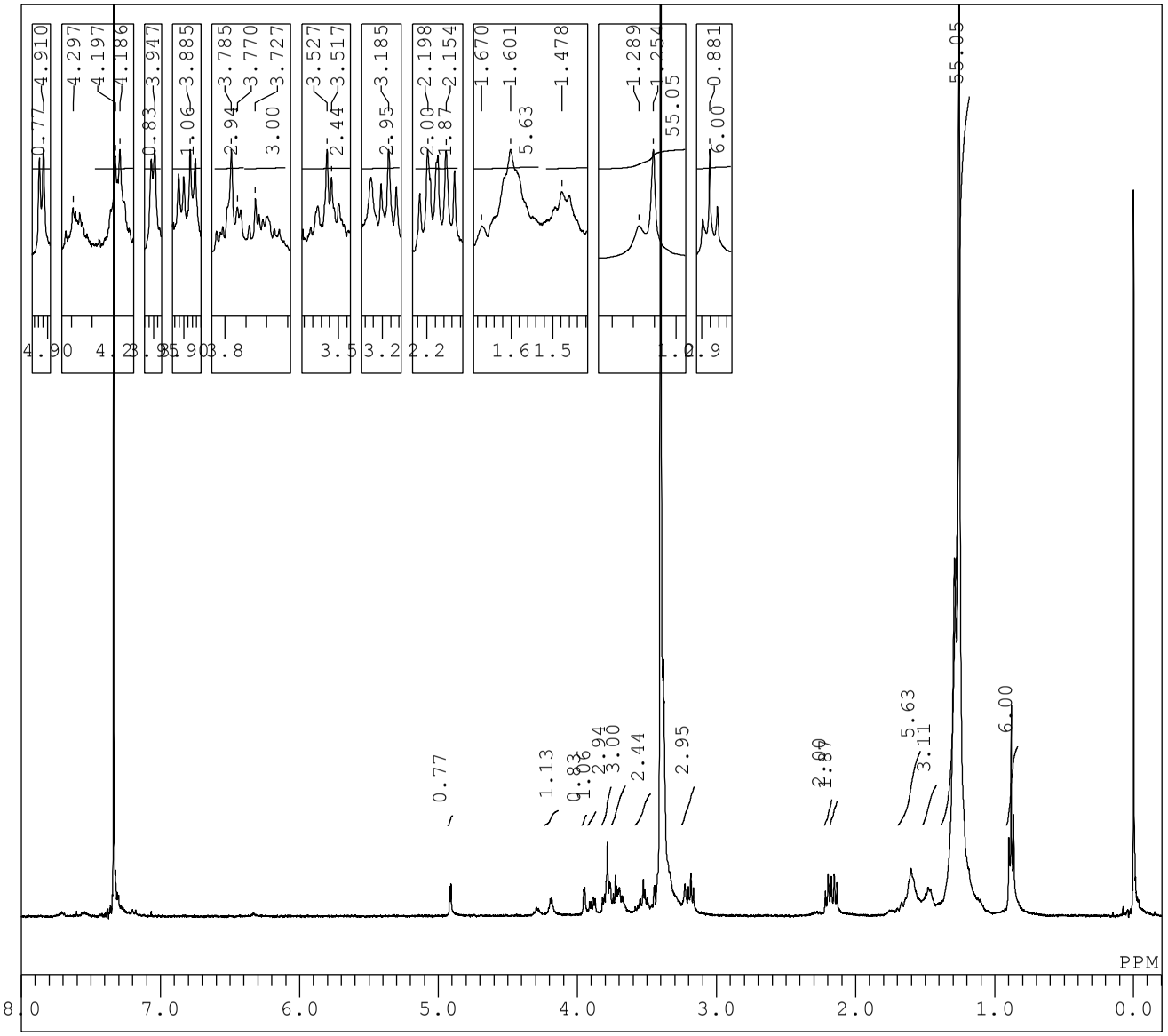
1b



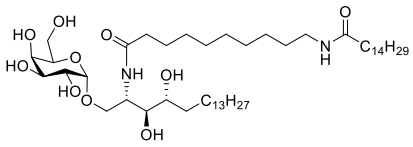
DFILE 102A-095a BCM-1.als
COMNT single pulse decoupled c
DATIM 2014-11-18 08:40:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 12329
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 36



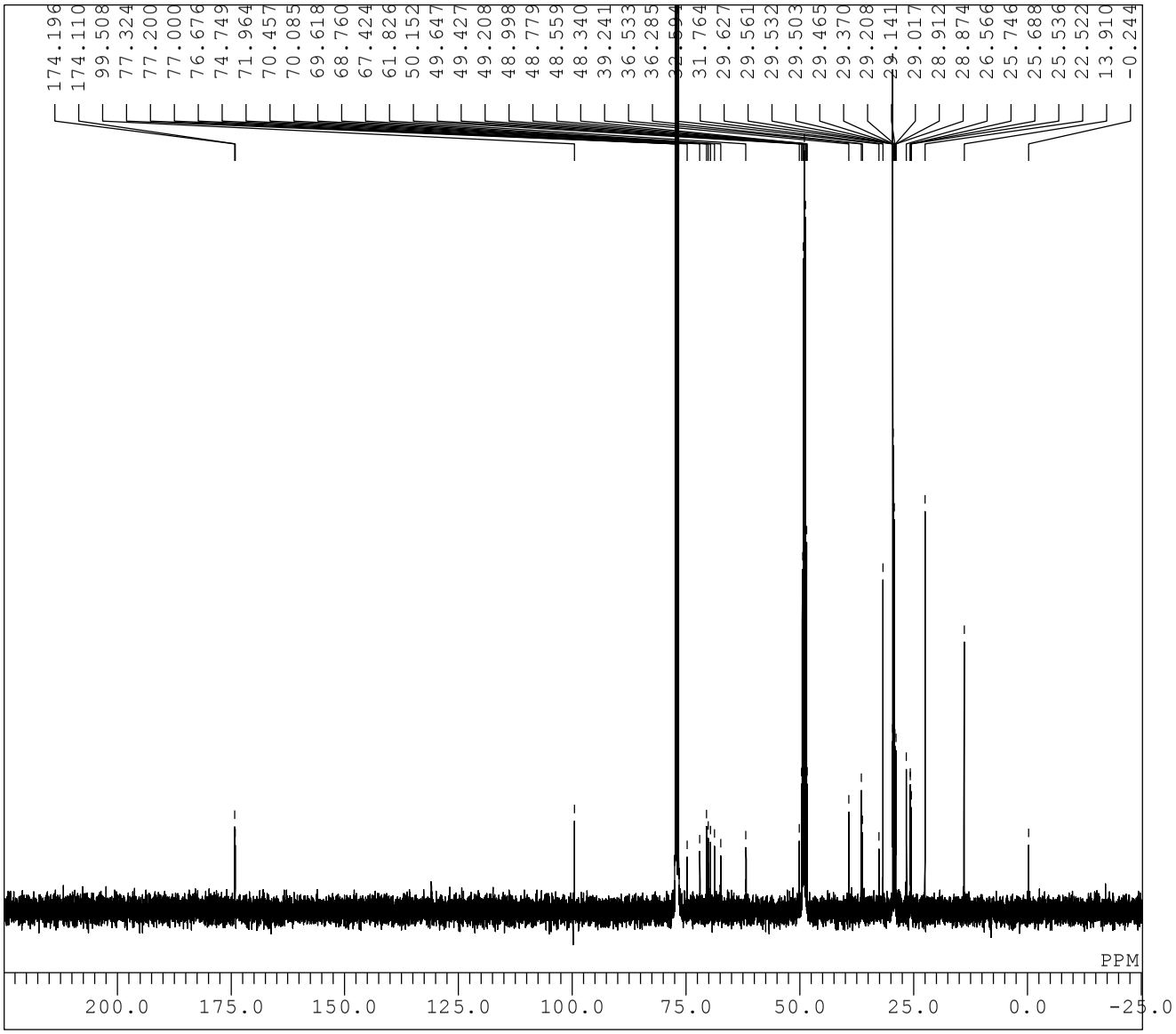
1b



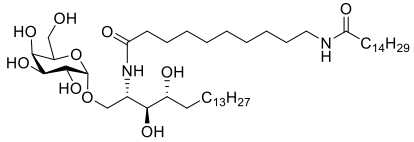

```
DFILE 102B-151a 150720-3.als
COMNT single_pulse
DATIM 2015-07-20 19:35:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.35 usec
IRNUC 1H
CTEMP         20.8 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.42 Hz
RGAIN           50
```



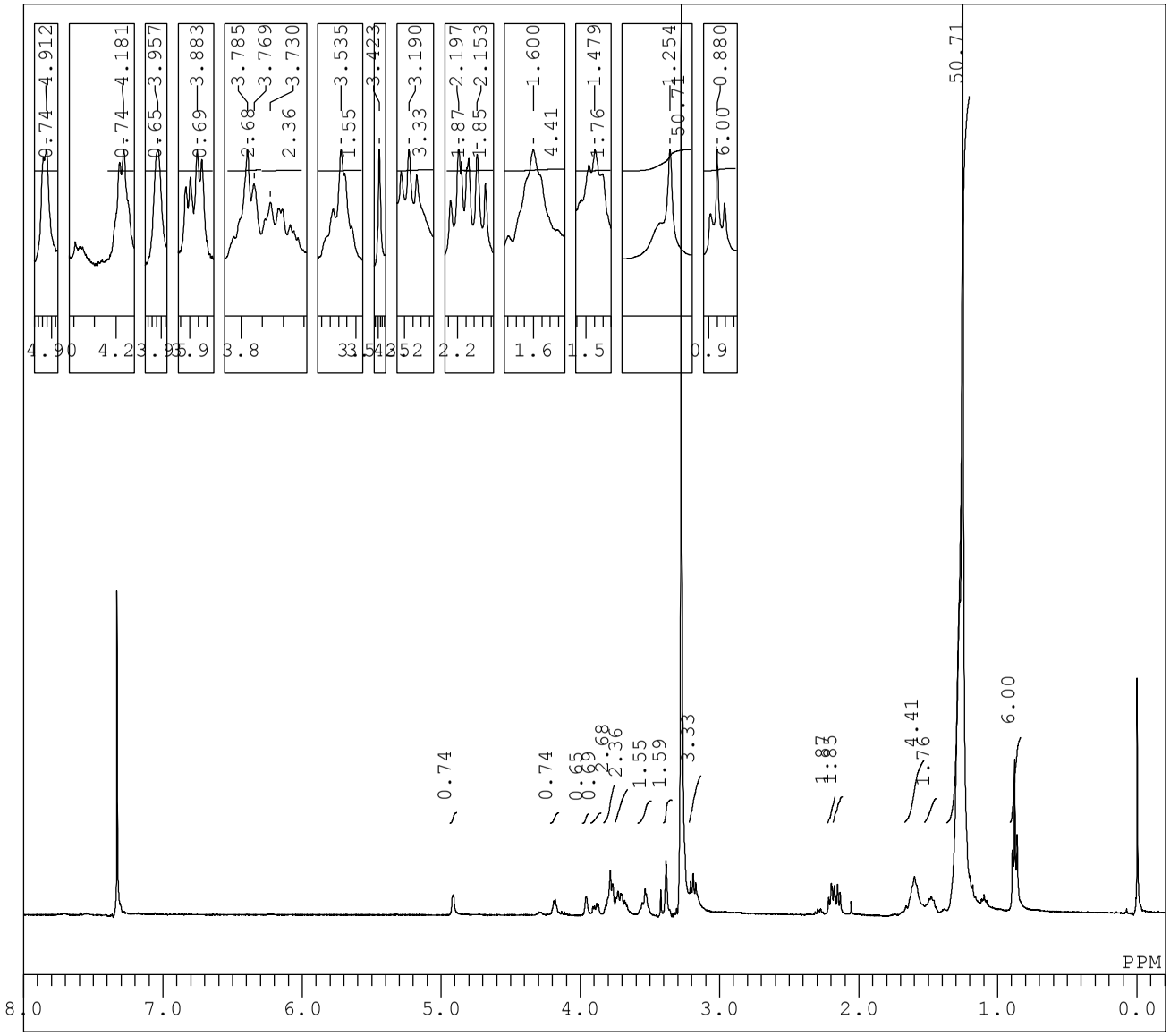
1c



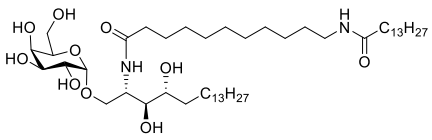
DFILE 102B-151a BCM 150720-1.a
COMNT single pulse decoupled c
DATIM 2015-07-21 08:28:26
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13570
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 36



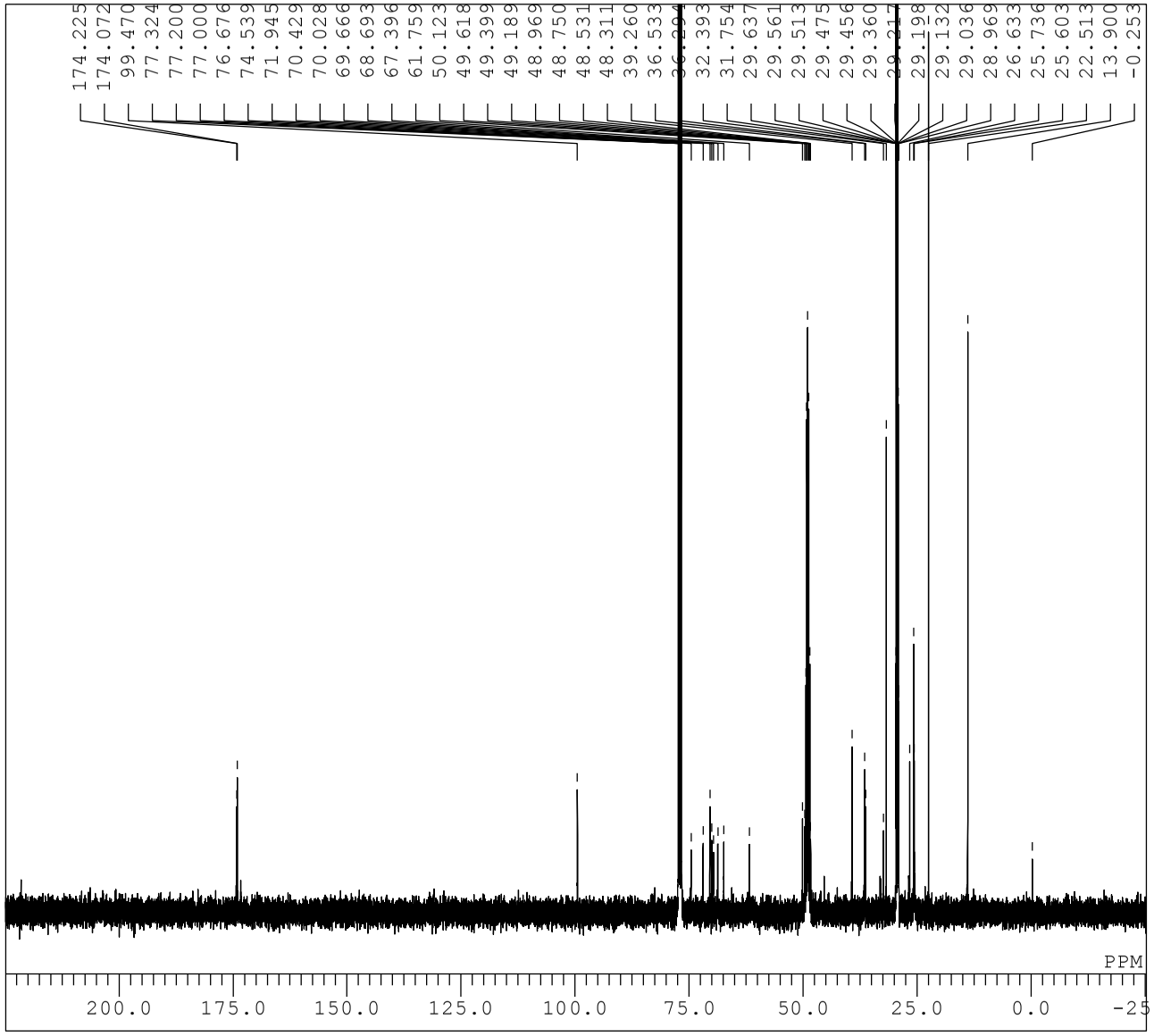
1c



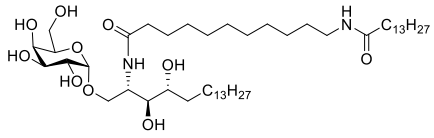

```
DFILE 102B-153a-1.als
COMNT single_pulse
DATIM 2015-07-22 11:15:12
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.35 usec
IRNUC 1H
CTEMP         20.9 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.42 Hz
RGAIN           46
```



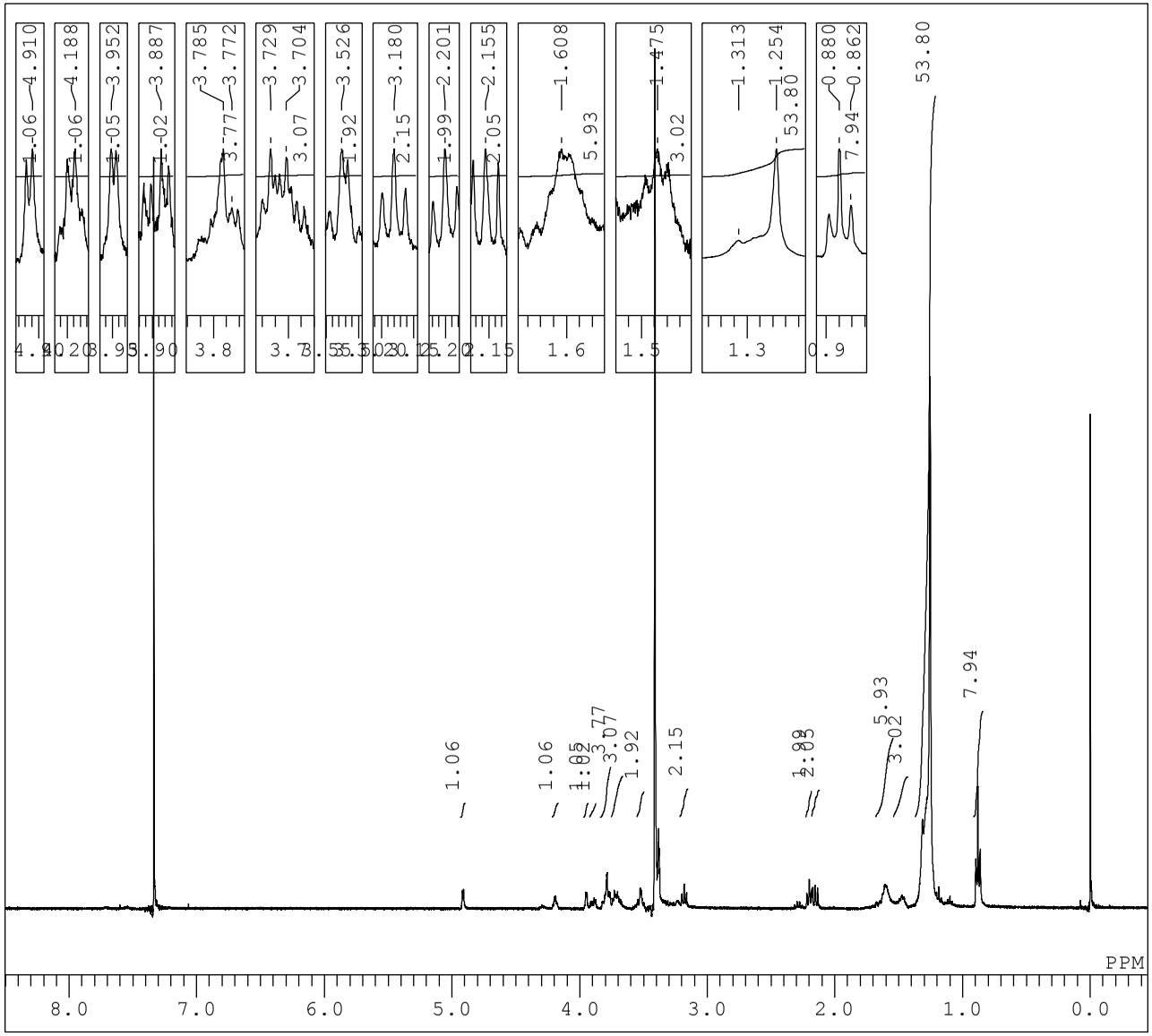
1d



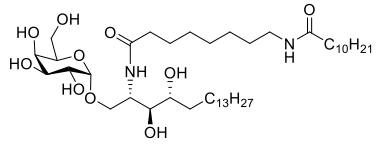
DFILE 102B-153a BCM 150726-1.a
COMNT single pulse decoupled c
DATIM 2015-07-26 08:53:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13220
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 36



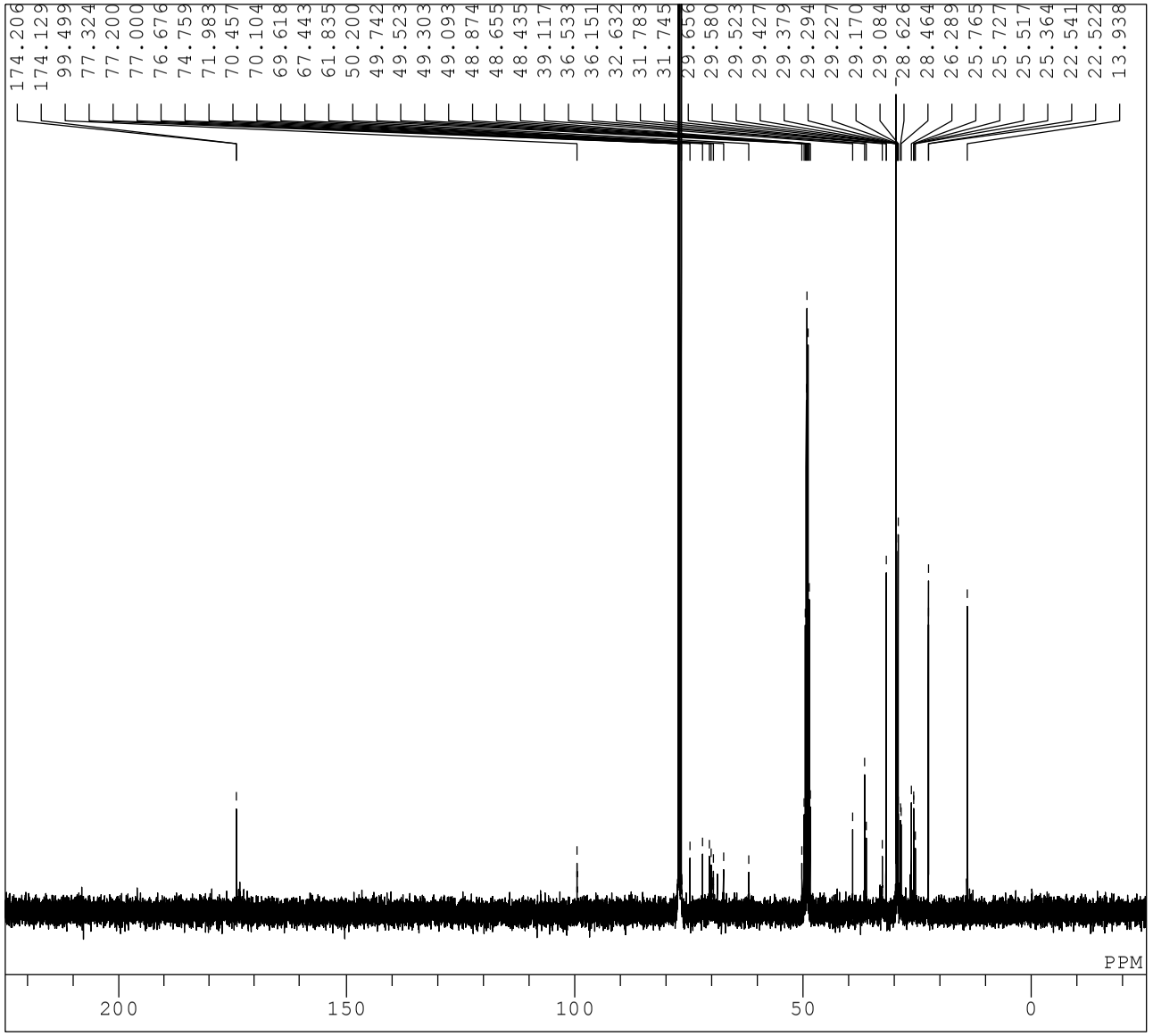
1d



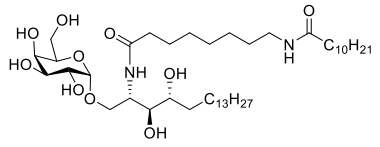

```
DFILE 102C-051a-1.als
COMNT single_pulse
DATIM 2016-01-16 22:00:32
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.55 usec
IRNUC 1H
CTEMP         20.2 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.00 Hz
RGAIN           54
```



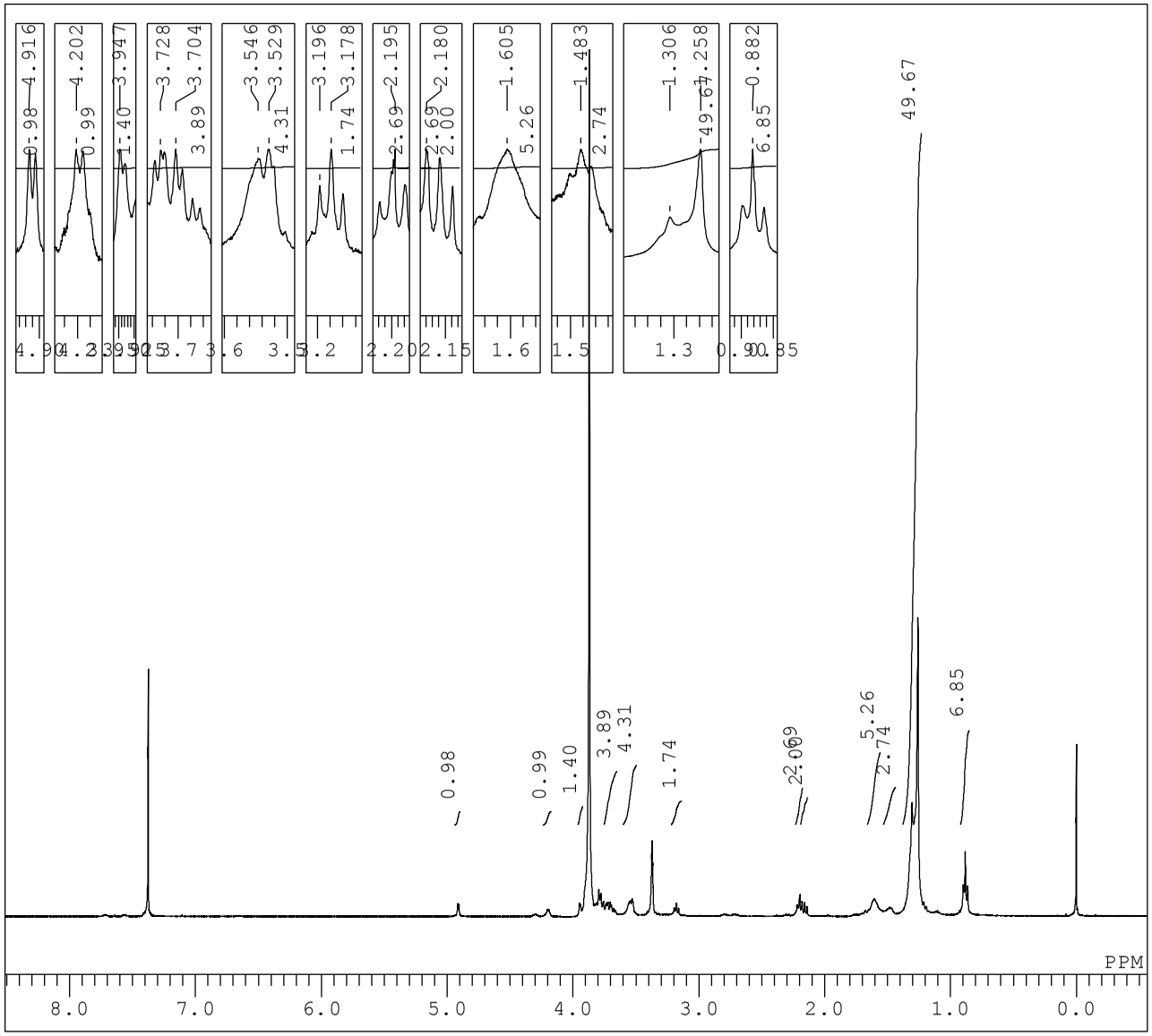
2a



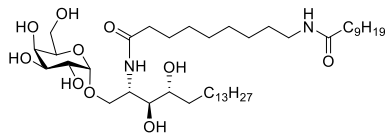
DFILE 102C-051a BCM 160128-1.a
COMNT single pulse decoupled c
DATIM 2016-01-29 08:40:15
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 12888
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 36



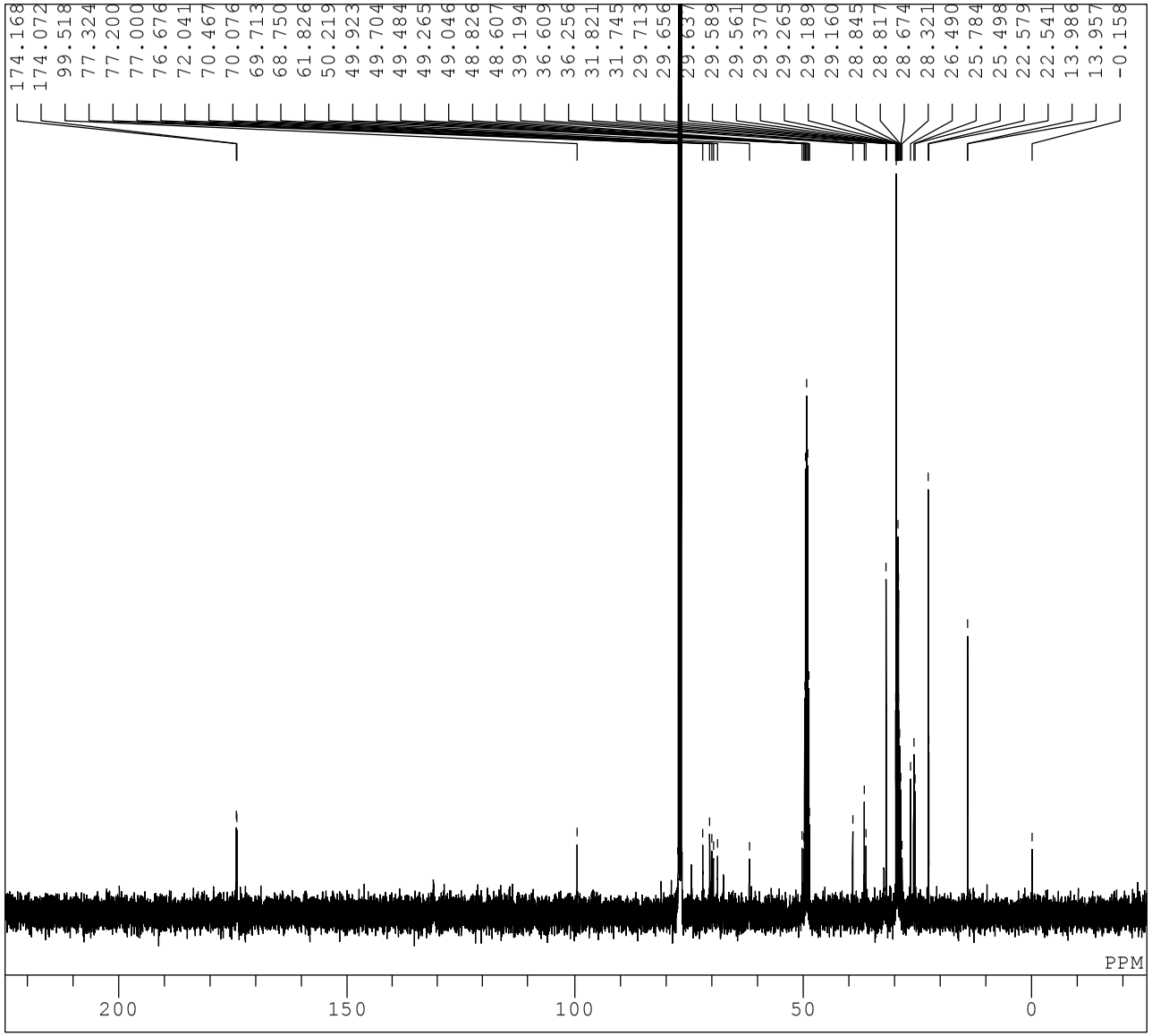
2a



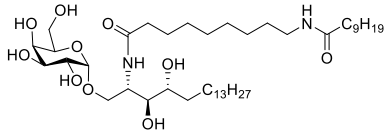
DFILE 102B-158a 150726-1.als
COMNT single_pulse
DATIM 2015-07-26 10:17:36
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 16
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48



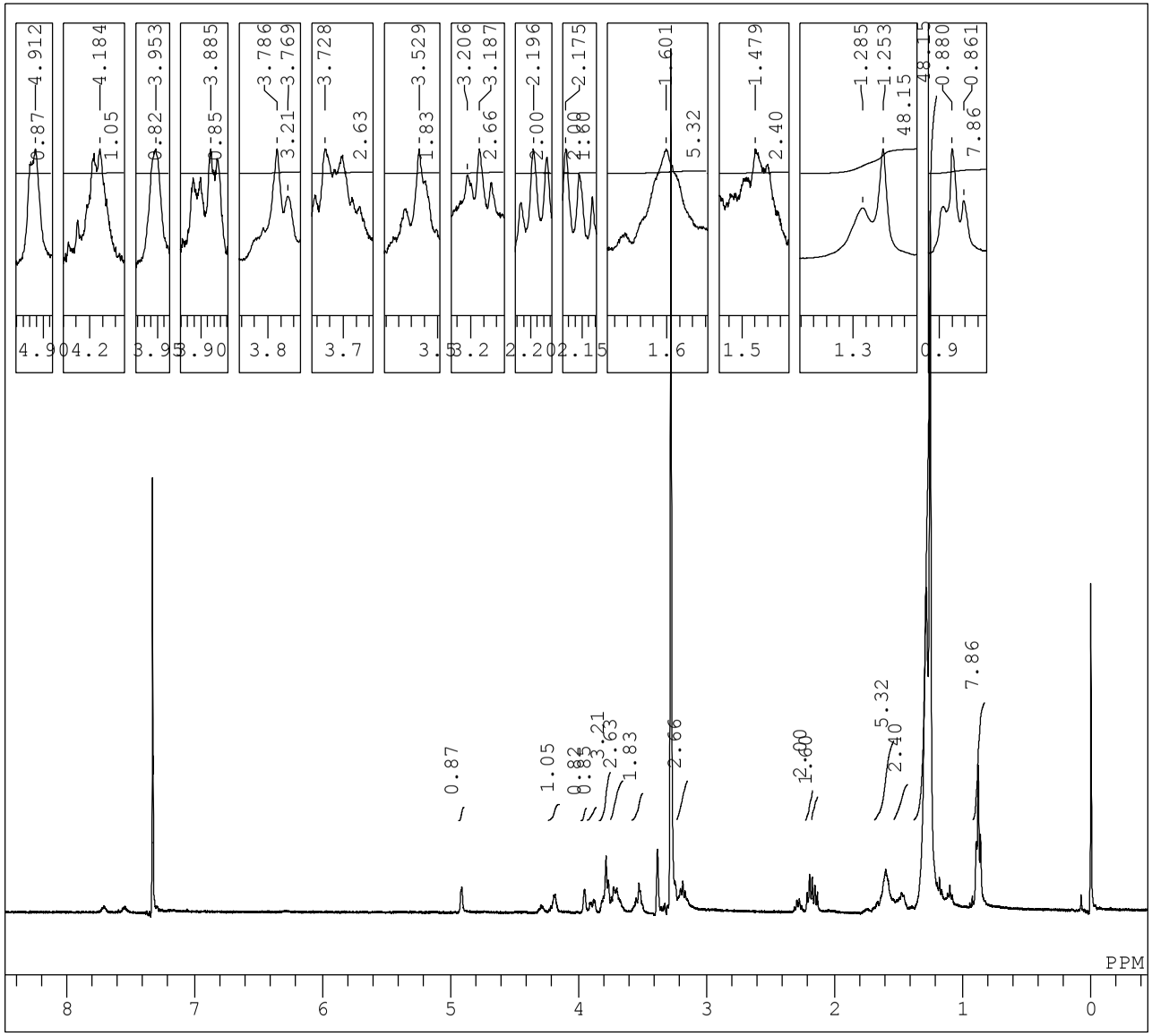
2b



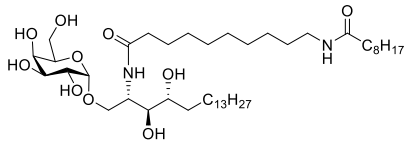

```
DFILE 102B-158a BCM 150730-1.a
COMNT single pulse decoupled c
DATIM 2015-07-31 07:02:52
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ         98.52 MHz
OBSET          4.64 KHz
OBFIN          8.74 Hz
POINT         26214
FREQU      24630.17 Hz
SCANS         11633
ACQTM        1.0643 sec
PD           2.0000 sec
PW1            3.17 usec
IRNUC 1H
CTEMP          21.9 c
SLVNT CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            32
```



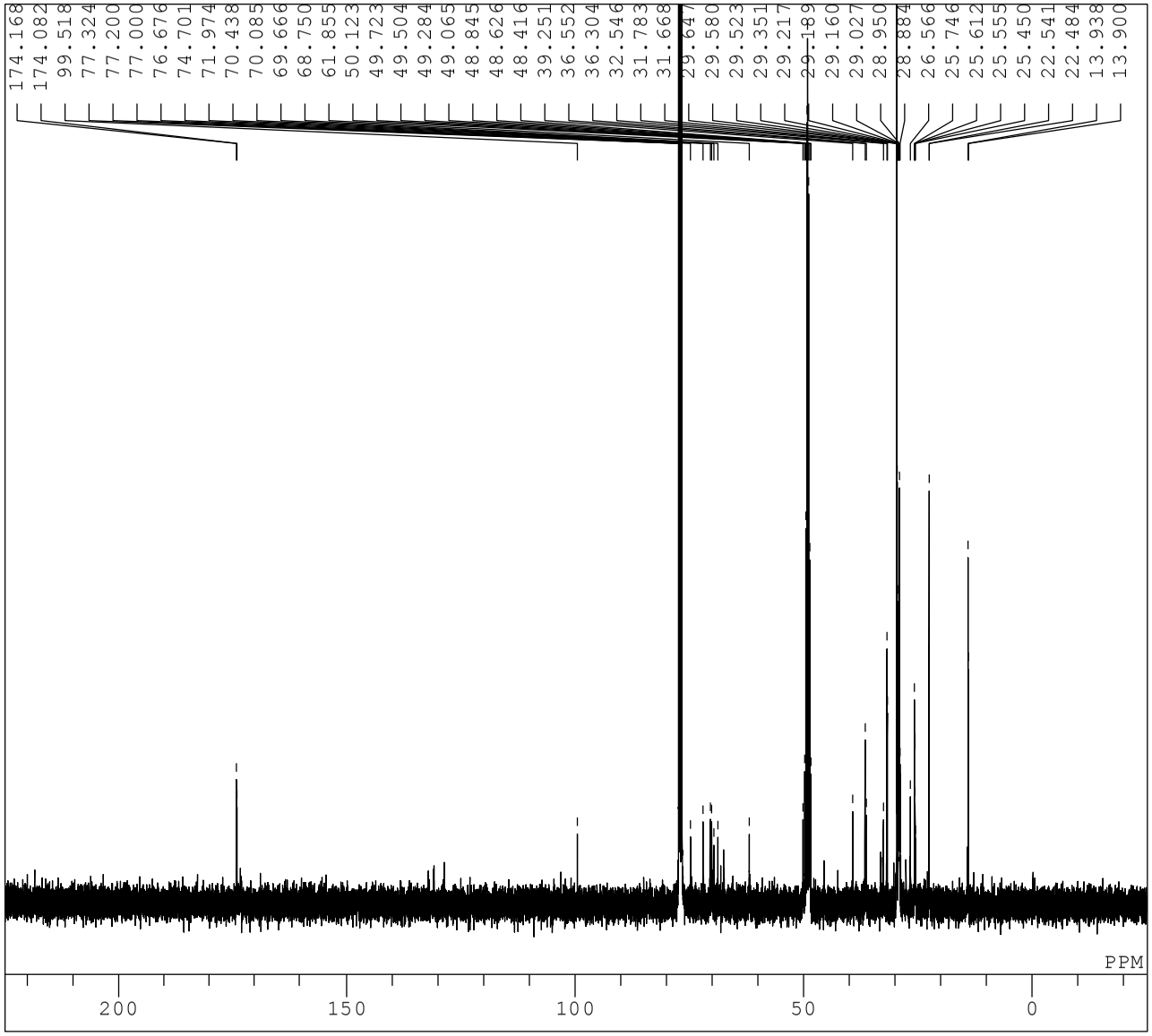
2b



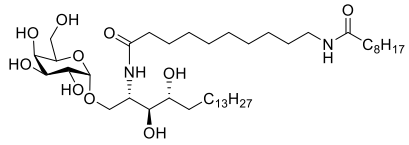
DFILE 102C-055a-1.als
COMNT single_pulse
DATIM 2016-01-18 20:57:43
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 52



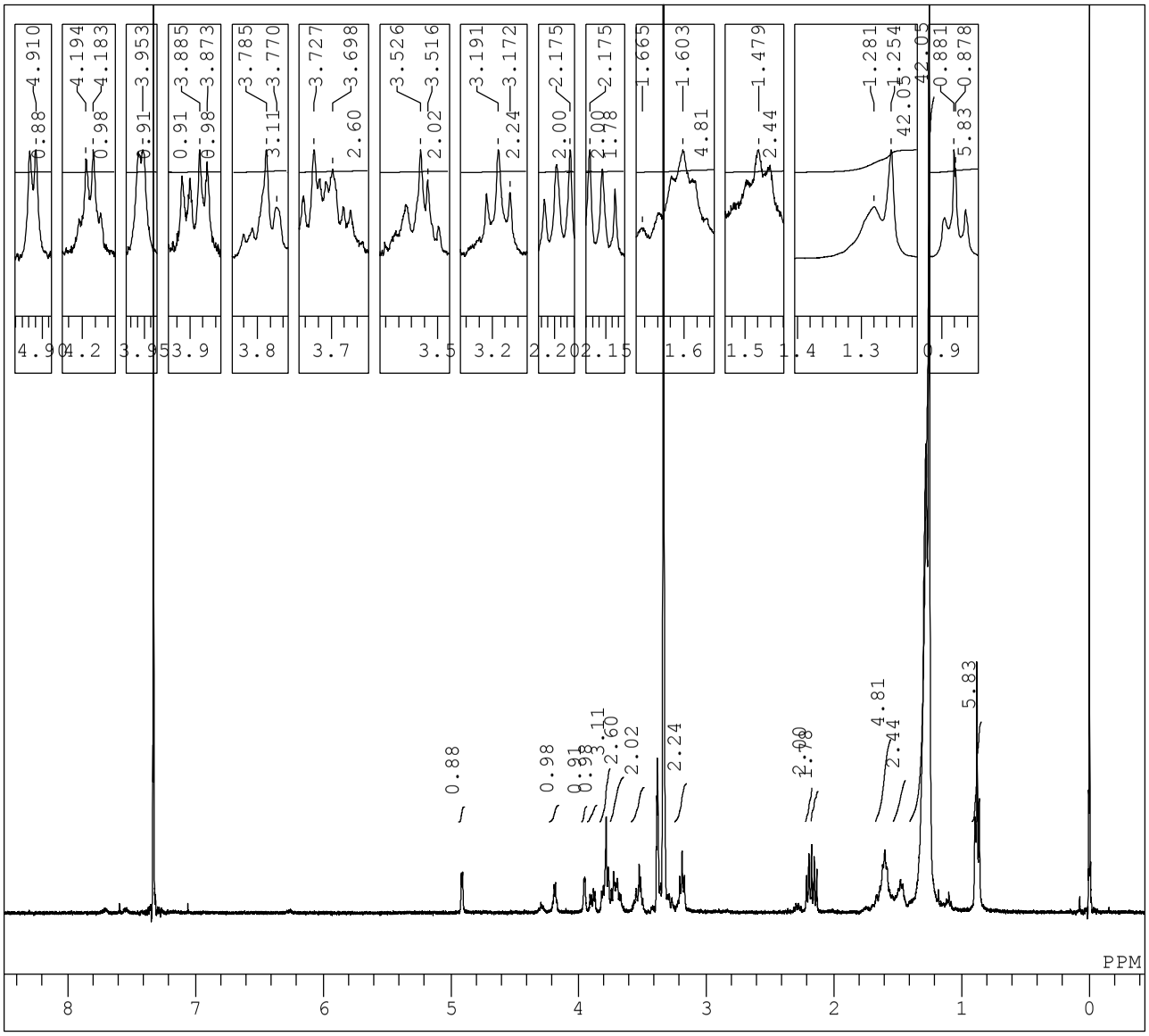
2c



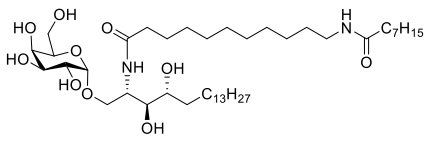

```
DFILE 102C-055a BCM 160130-1.a
COMNT single pulse decoupled c
DATIM 2016-01-31 10:00:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS        12469
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         19.9 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           36
```



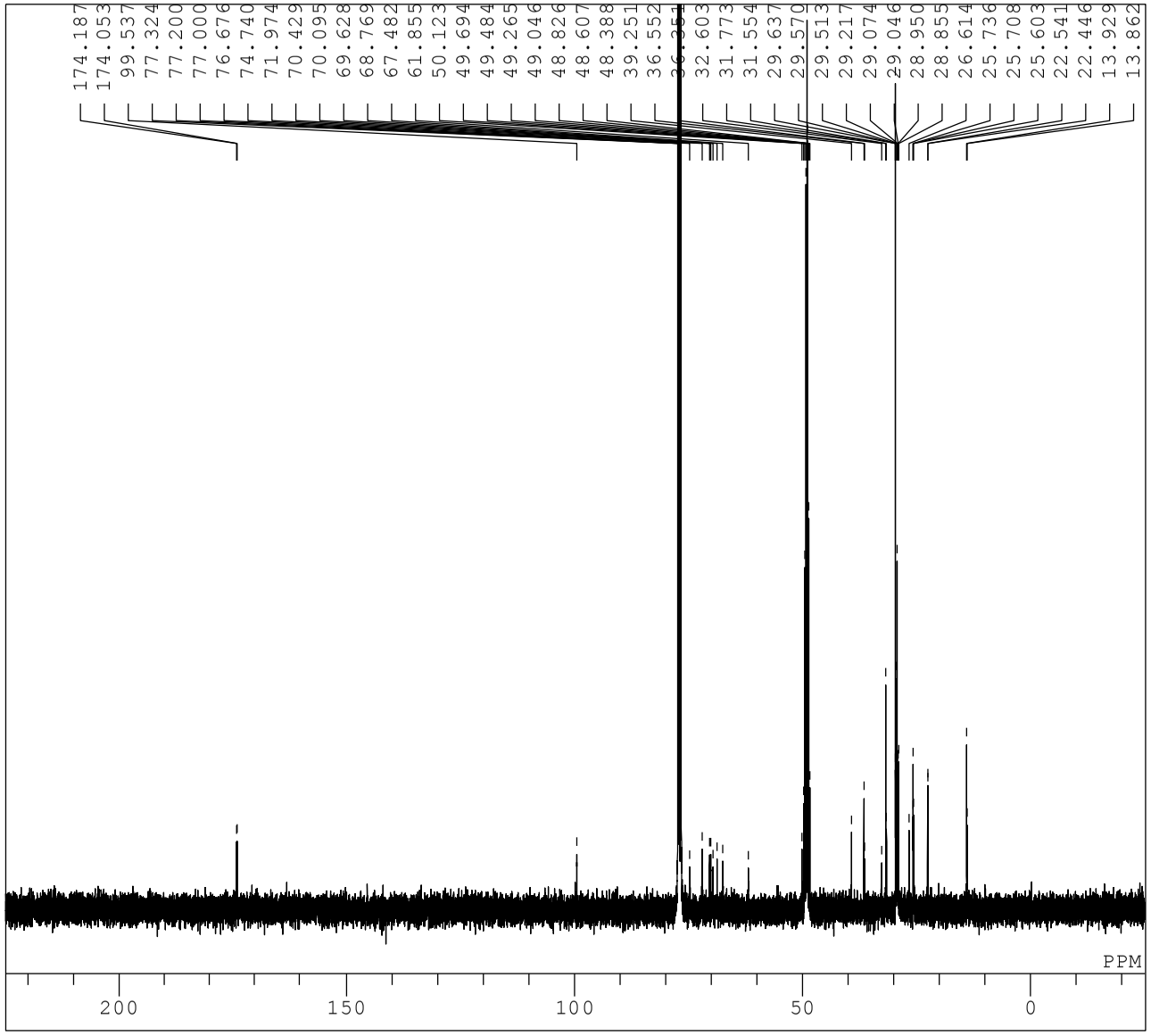
2c



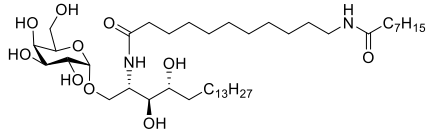

```
DFILE 102C-056a-1.als
COMNT single_pulse
DATIM 2016-01-18 21:05:32
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.55 usec
IRNUC 1H
CTEMP         20.0 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           54
```



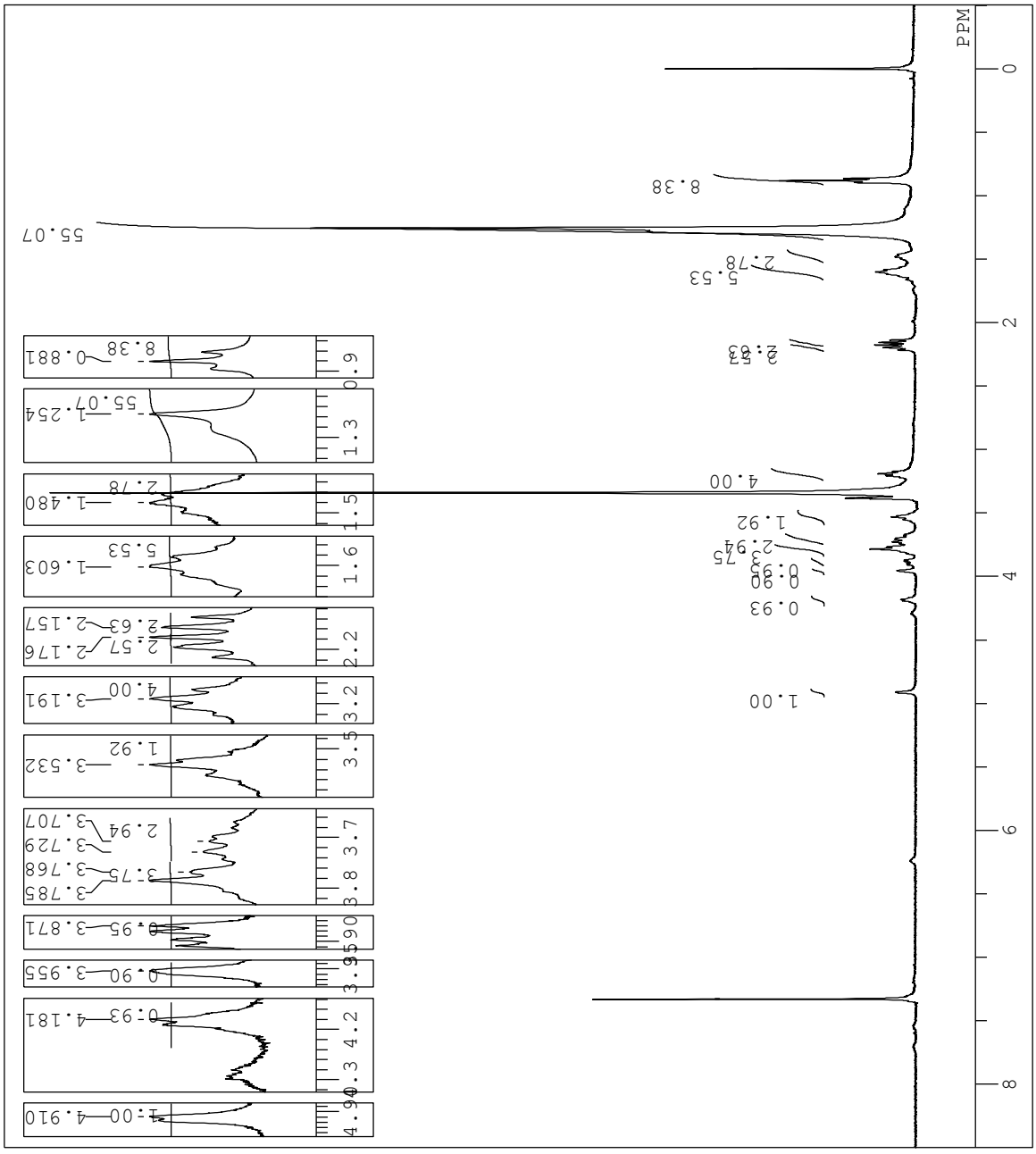
2d

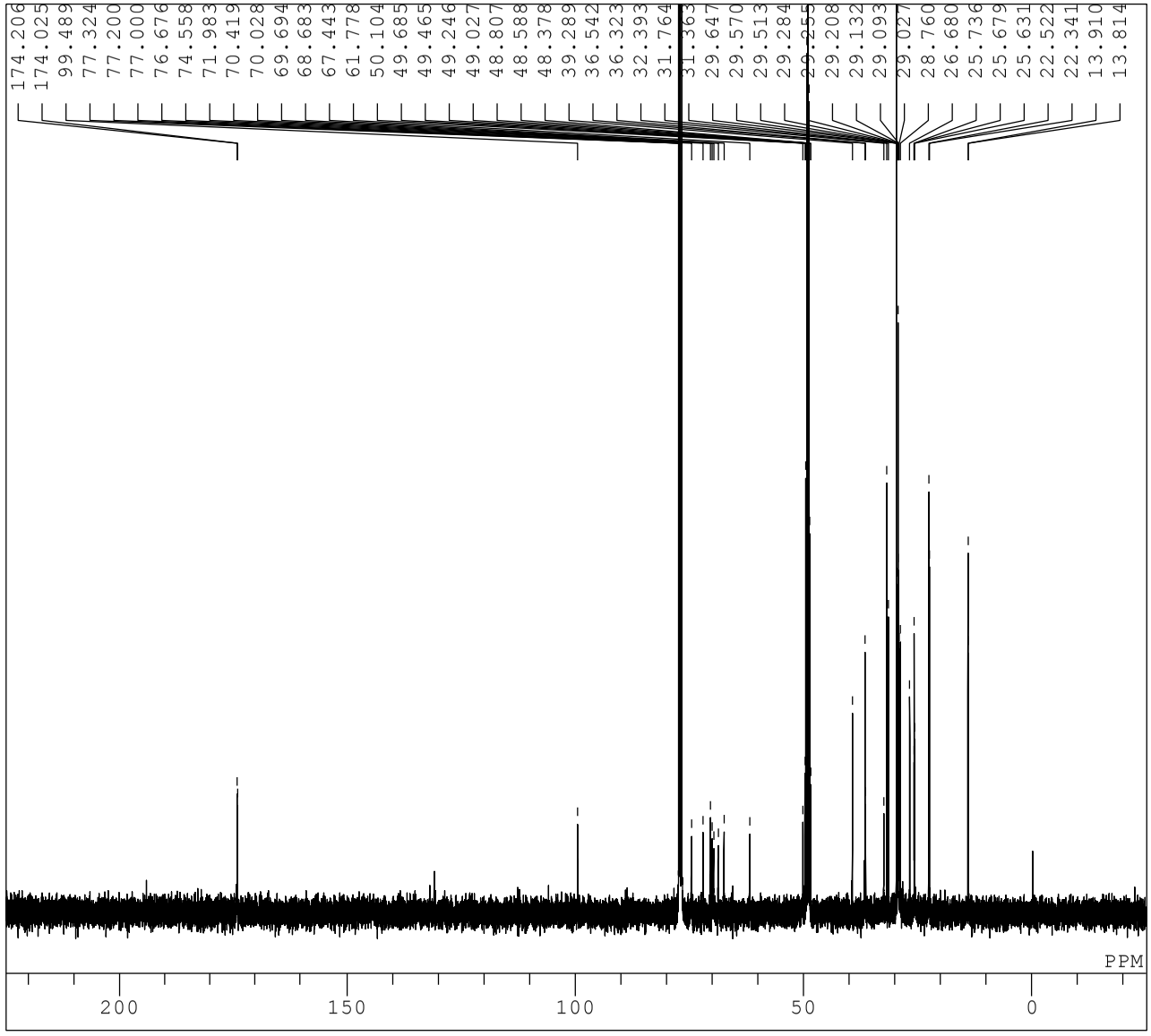


DFILE 102C-056a BCM 160131-1.a
COMNT single pulse decoupled c
DATIM 2016-02-01 08:33:45
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13115
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 42

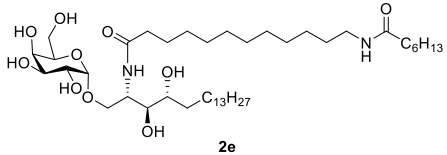


2d

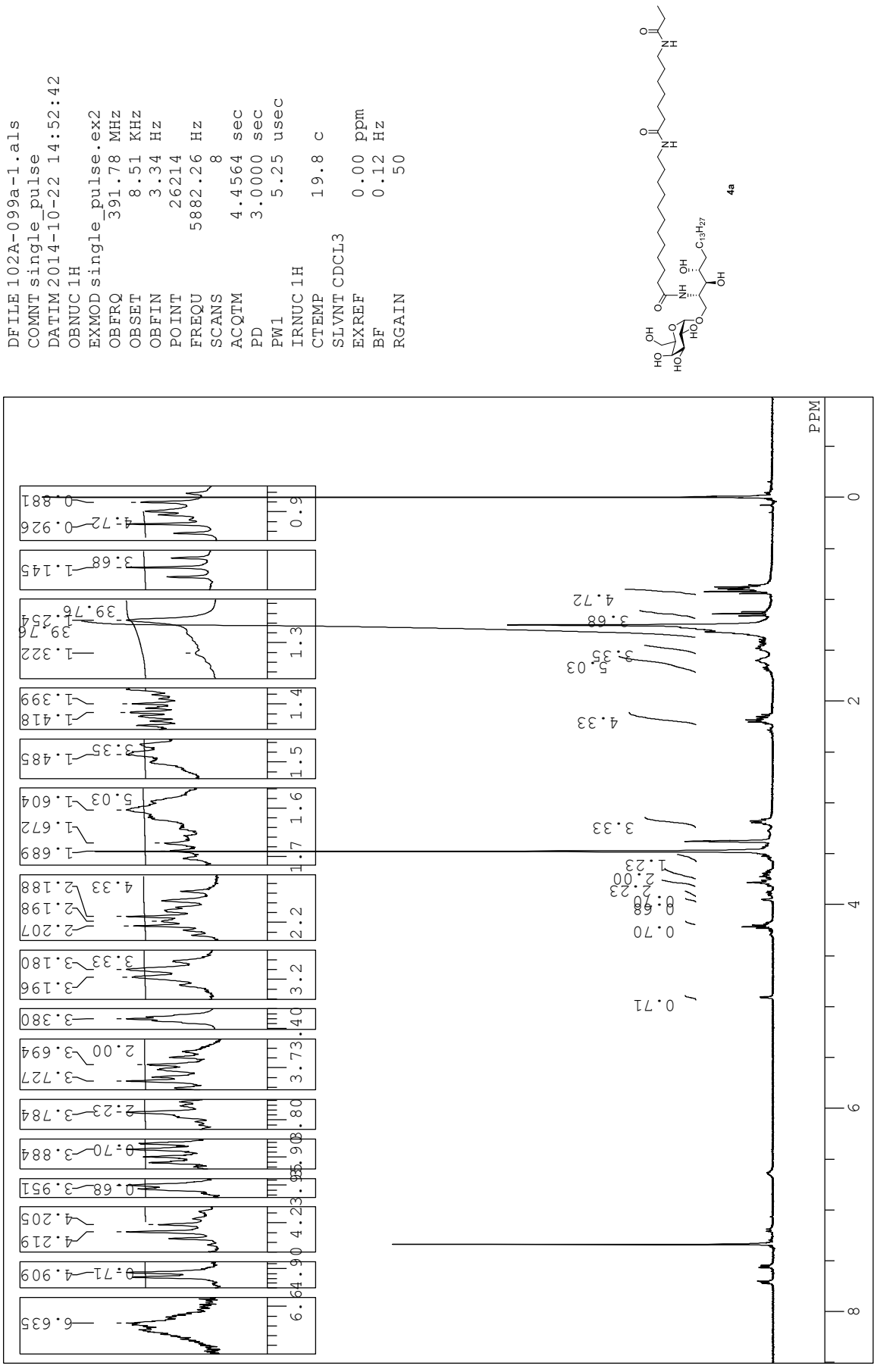

DFILE 102B-164a-1.als
COMNT single_pulse
DATIM 2015-07-30 19:15:32
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.35 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
2e
PPM

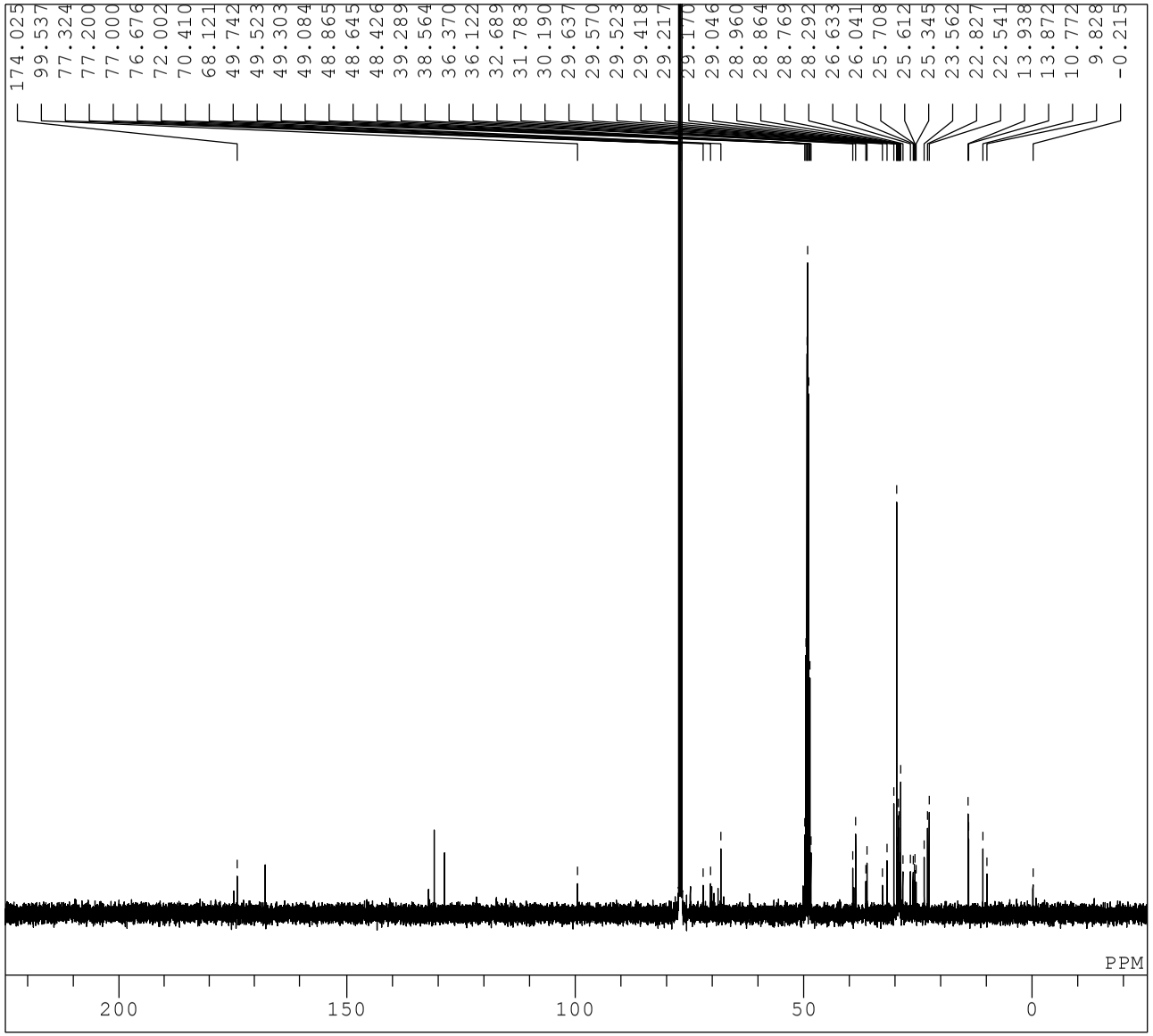


DFILE 102B-164a BCM 150803-1.a
COMNT single pulse decoupled c
DATIM 2015-08-04 08:13:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 12459
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 32

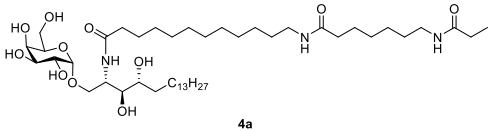


2e

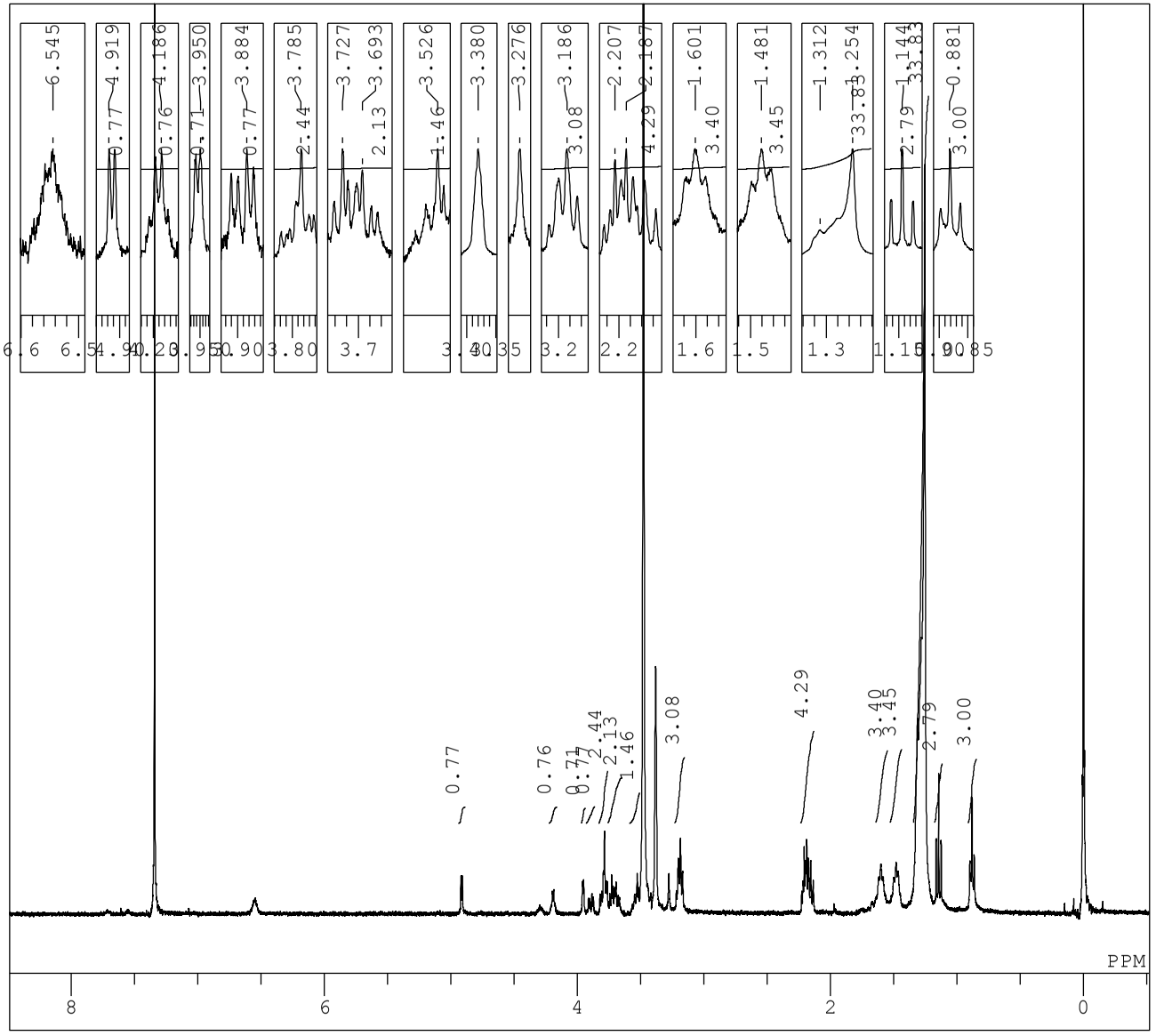

DFILE 102A-099a-1.als
COMNT single_pulse
DATIM 2014-10-22 14:52:42
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.25 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
4a
PPM



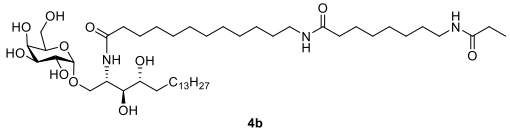

```
DFILE 102A-099a BCM 160203-1.a
COMNT single pulse decoupled c
DATIM 2016-02-04 08:28:26
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS        13305
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         19.6 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           34
```



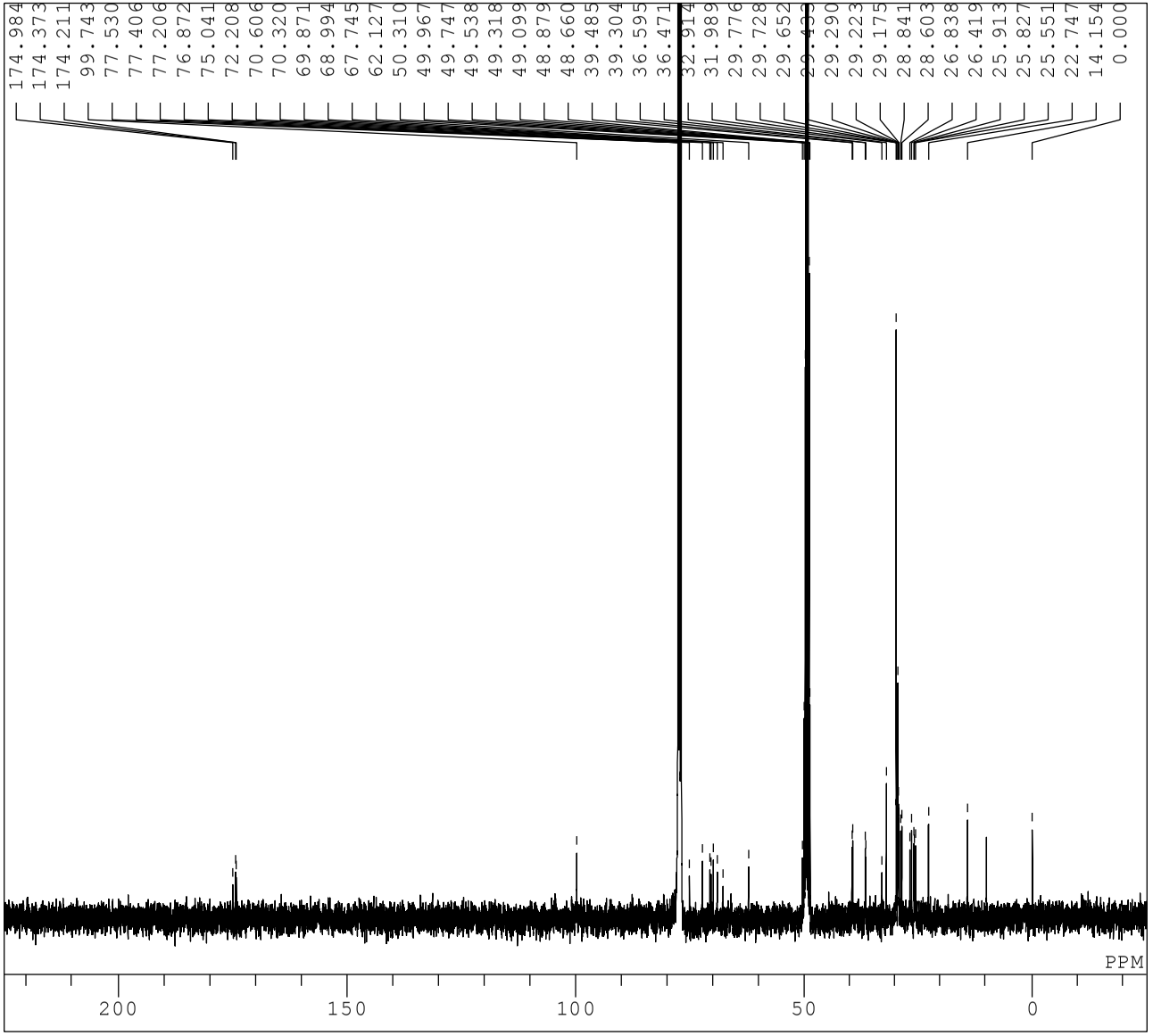
4a



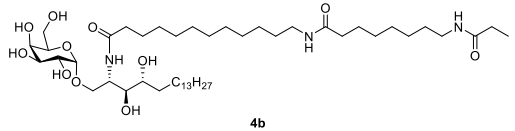
DFILE 102A-100a-1.als
COMNT single_pulse
DATIM 2014-10-22 14:56:51
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.25 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50



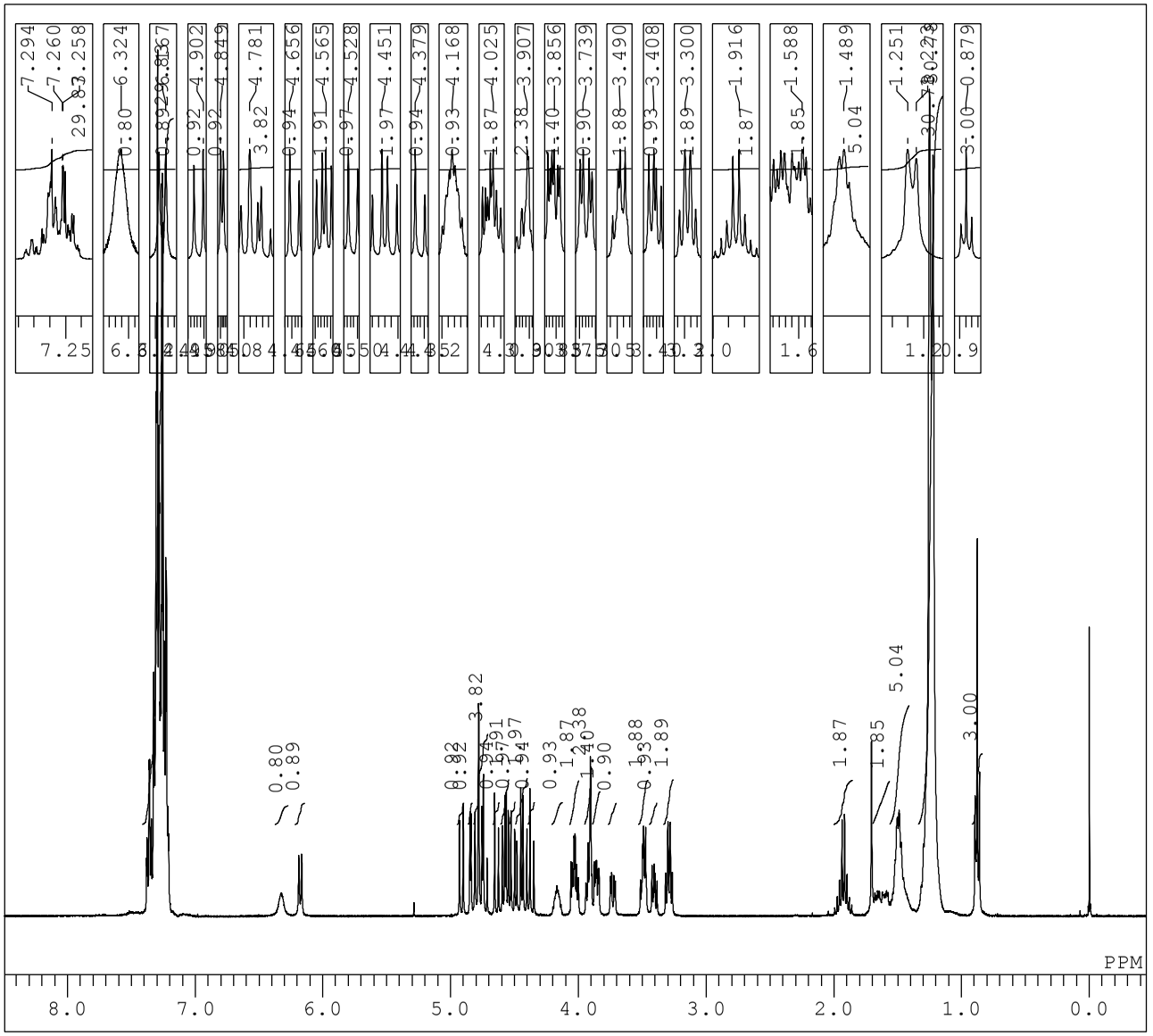
4b



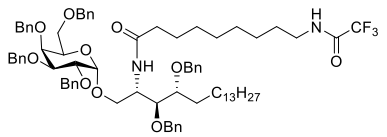

```
DFILE 102A-100a BCM 160207-1.a
COMNT single pulse decoupled c
DATIM 2016-02-08 08:37:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS        12977
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         19.9 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           48
```



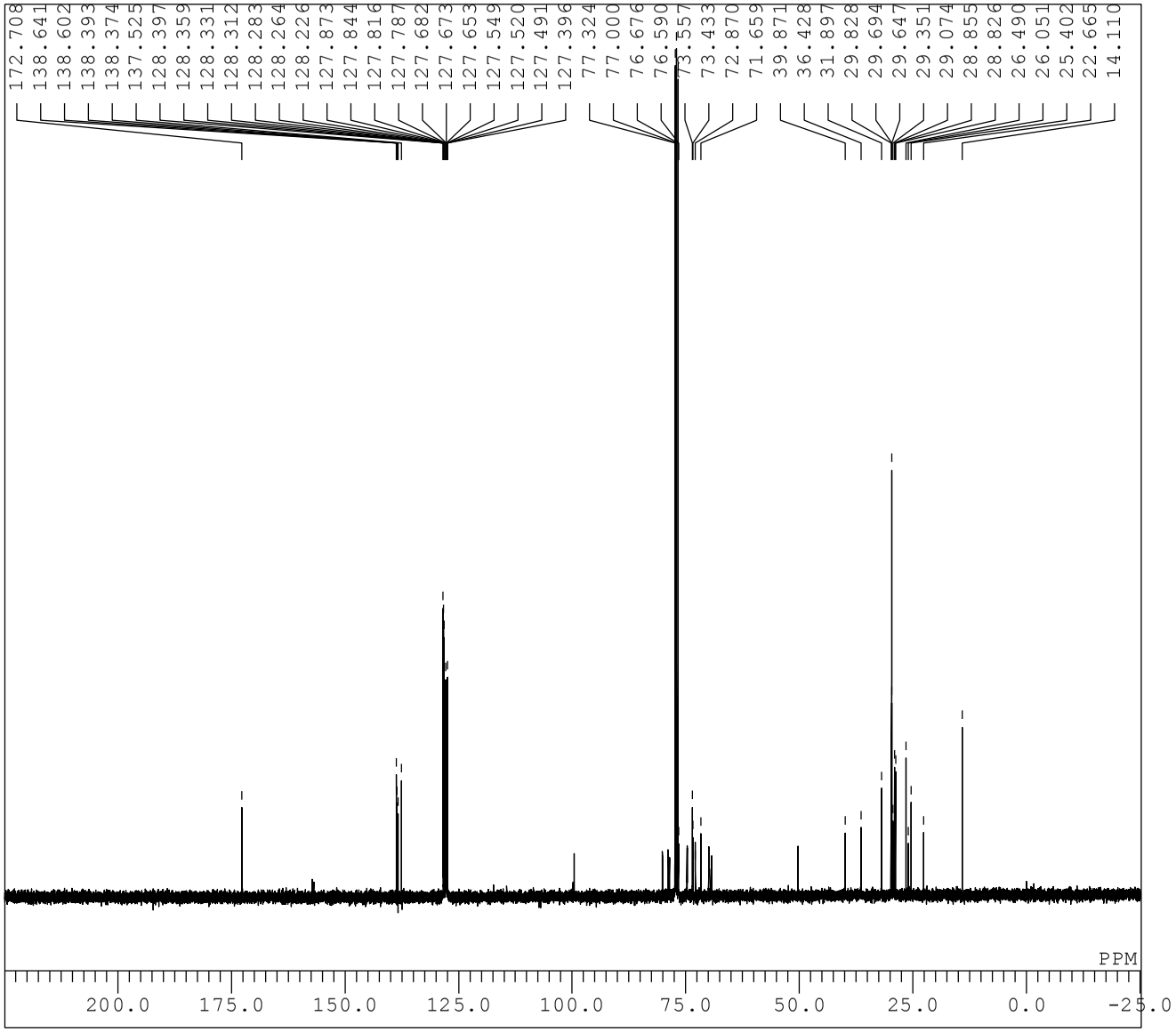
4b



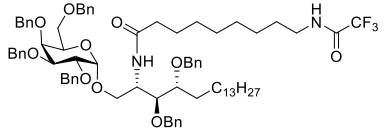
DFILE 102C-046a 160114-1.als
COMNT single_pulse
DATIM 2016-01-14 21:29:37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 36



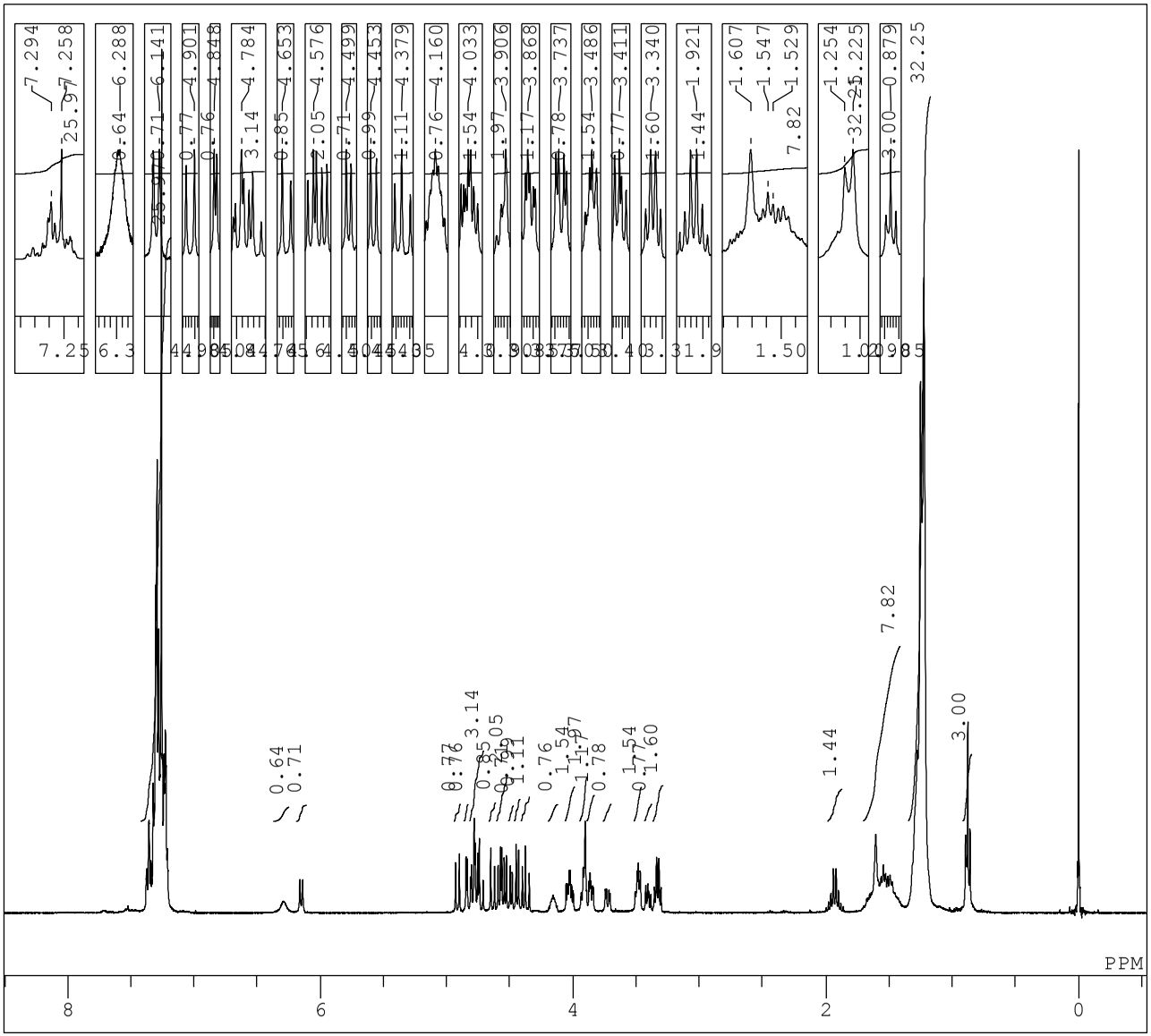
7a



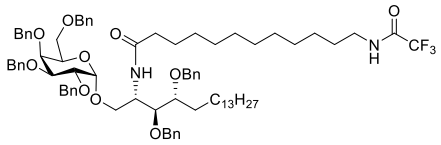
DFILE 102C-046a BCM 160114-1.a
COMNT single pulse decoupled c
DATIM 2016-01-14 22:26:50
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 1043
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 38



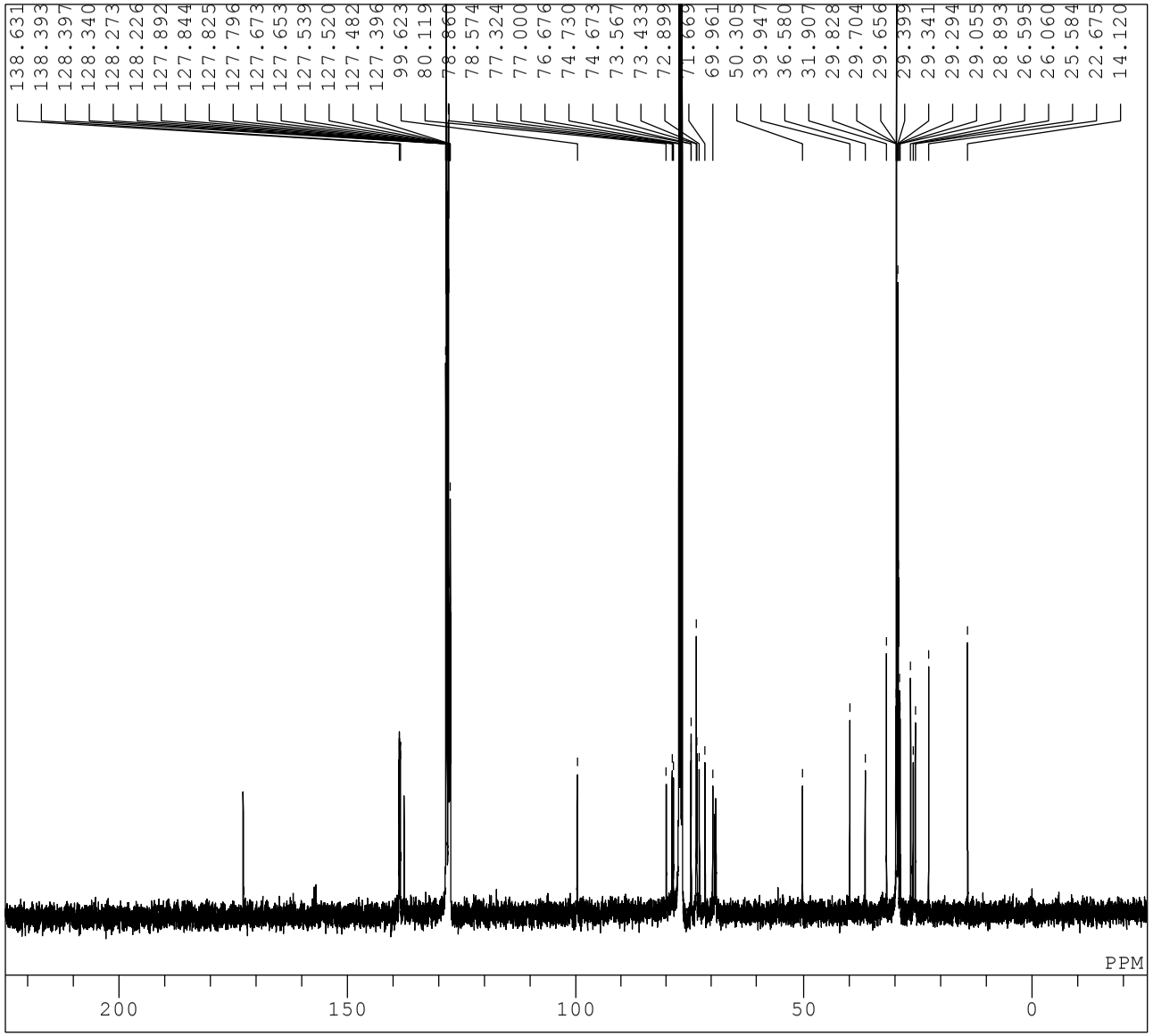
7a



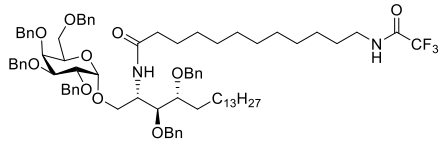

```
DFILE 102A-047a-1.als
COMNT single_pulse
DATIM 2014-07-28 17:15:18
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.25 usec
IRNUC 1H
CTEMP         21.2 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           40
```



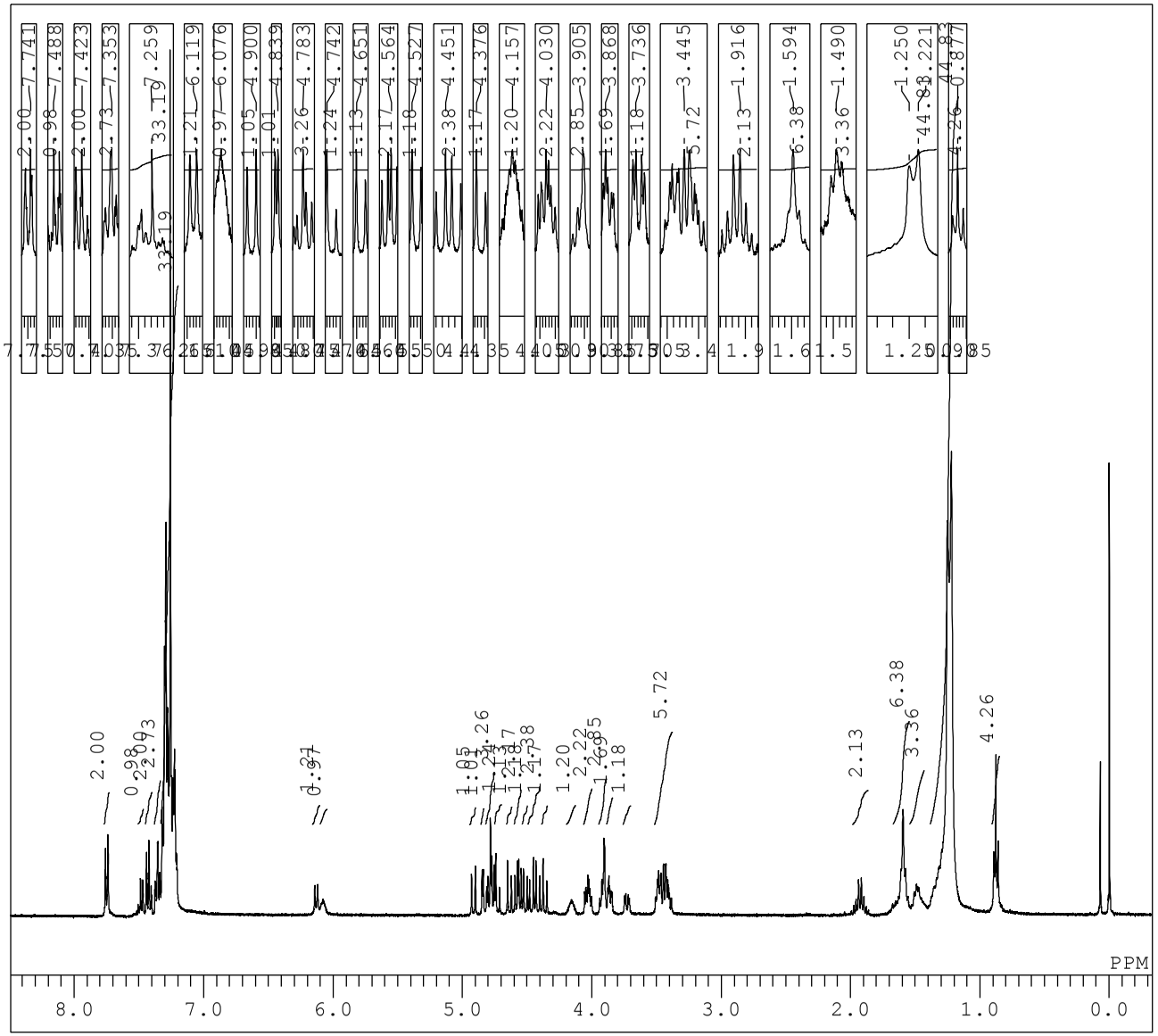
7b



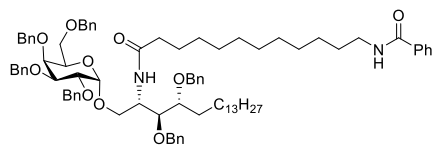
DFILE 102C-063a BCM 160206-1.a
COMNT single pulse decoupled c
DATIM 2016-02-07 01:47:44
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 6478
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 34



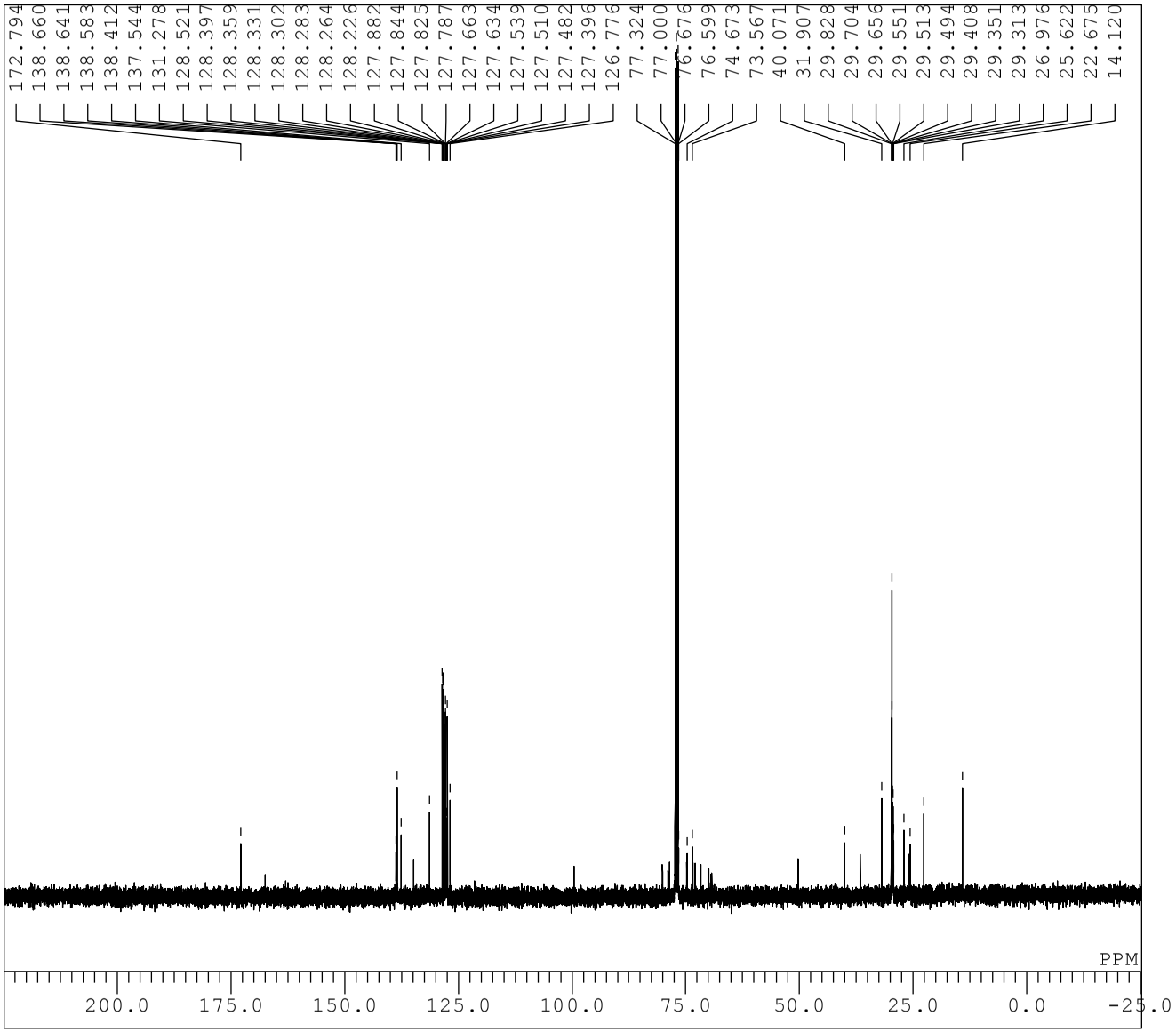
7b



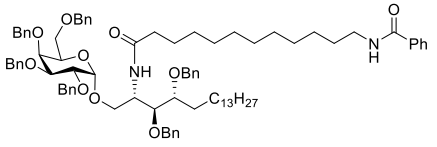

```
DFILE 102C-044a.als
COMNT
DATIM Sat Jan 09 17:55:03 201
OBNUC 1H
EXMOD SINGL
OBFRQ        400.05 MHz
OBSET          0.00 KHz
OBFIN     130800.00 Hz
POINT        131072
FREQU      31948.88 Hz
SCANS             8
ACQTM        4.1026 sec
PD           2.0000 sec
PW1             5.30 usec
IRNUC 1H
CTEMP          21.3 c
SLVNT CDCL3
EXREF          0.00 ppm
BF             0.00 Hz
RGAIN            18
```



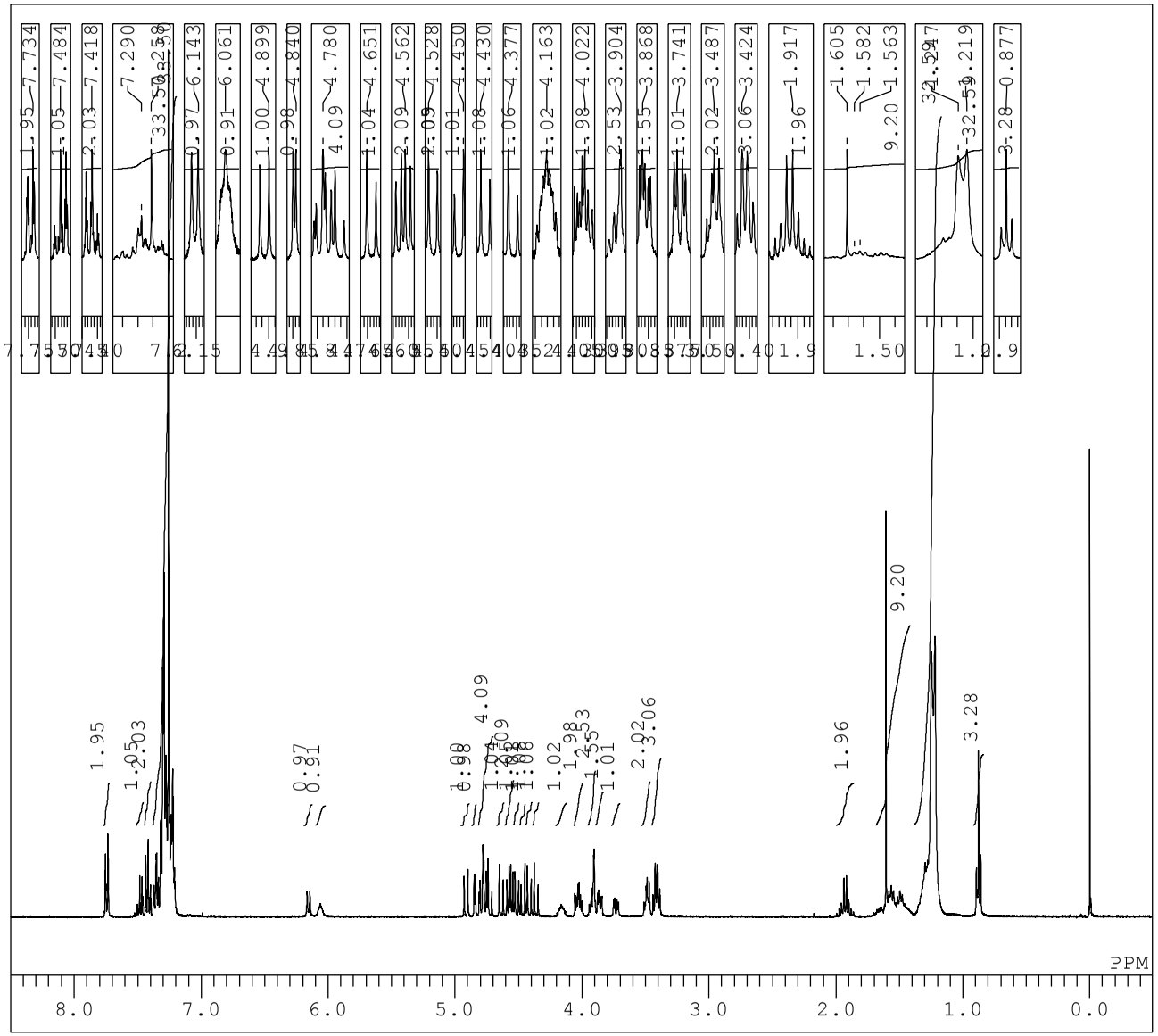
S13d



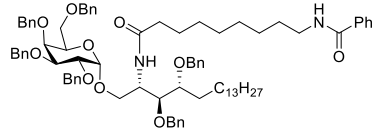

```
DFILE 102C-044a BCM 160110-1.a
COMNT single pulse decoupled c
DATIM 2016-01-10 14:45:31
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS         2000
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         20.8 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            0.00 Hz
RGAIN           34
```



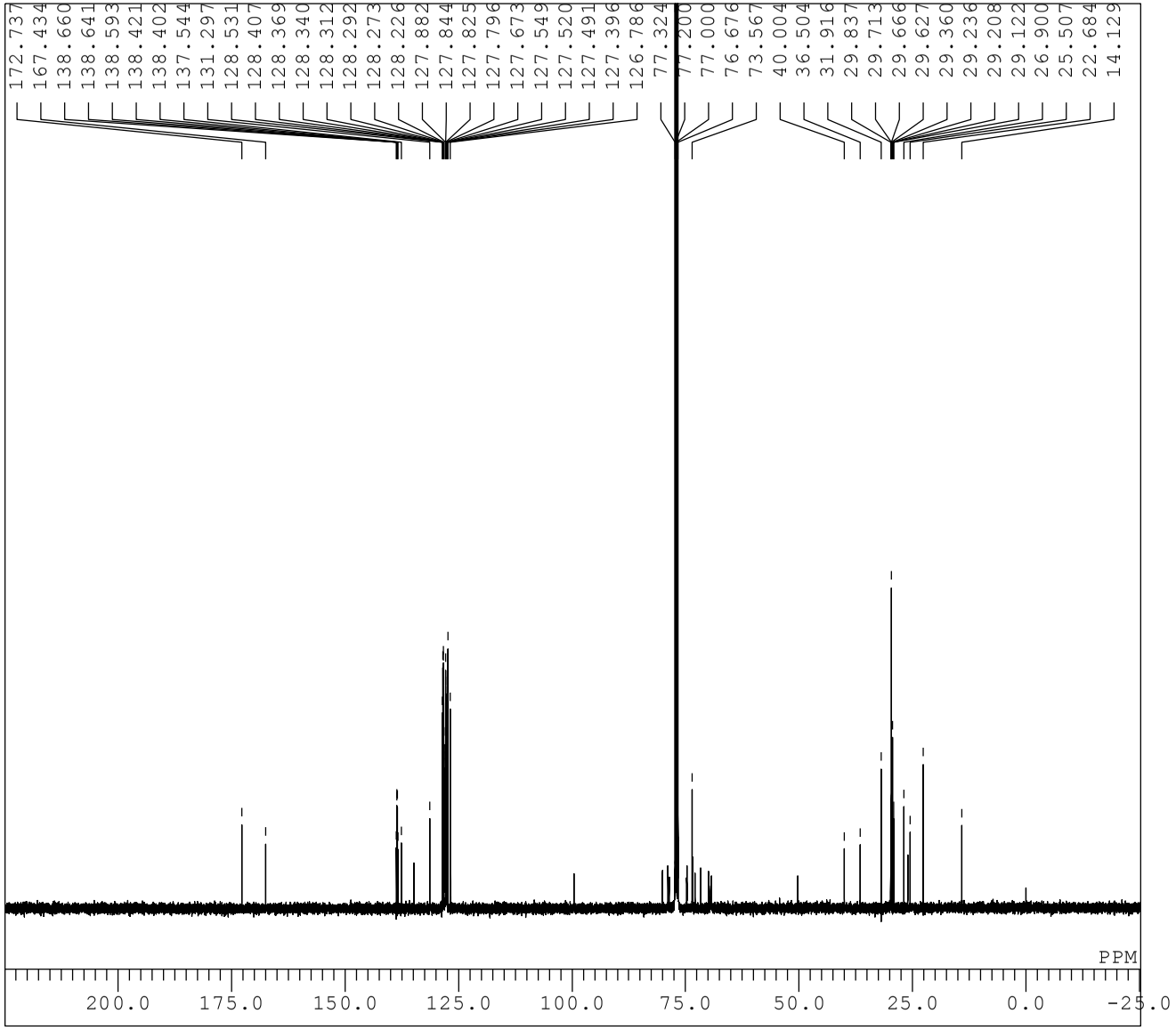
S13d



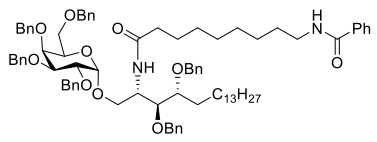

```
DFILE 102C-052a-1.als
COMNT single_pulse
DATIM 2016-01-16 19:04:29
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.55 usec
IRNUC 1H
CTEMP         20.5 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.00 Hz
RGAIN           46
```



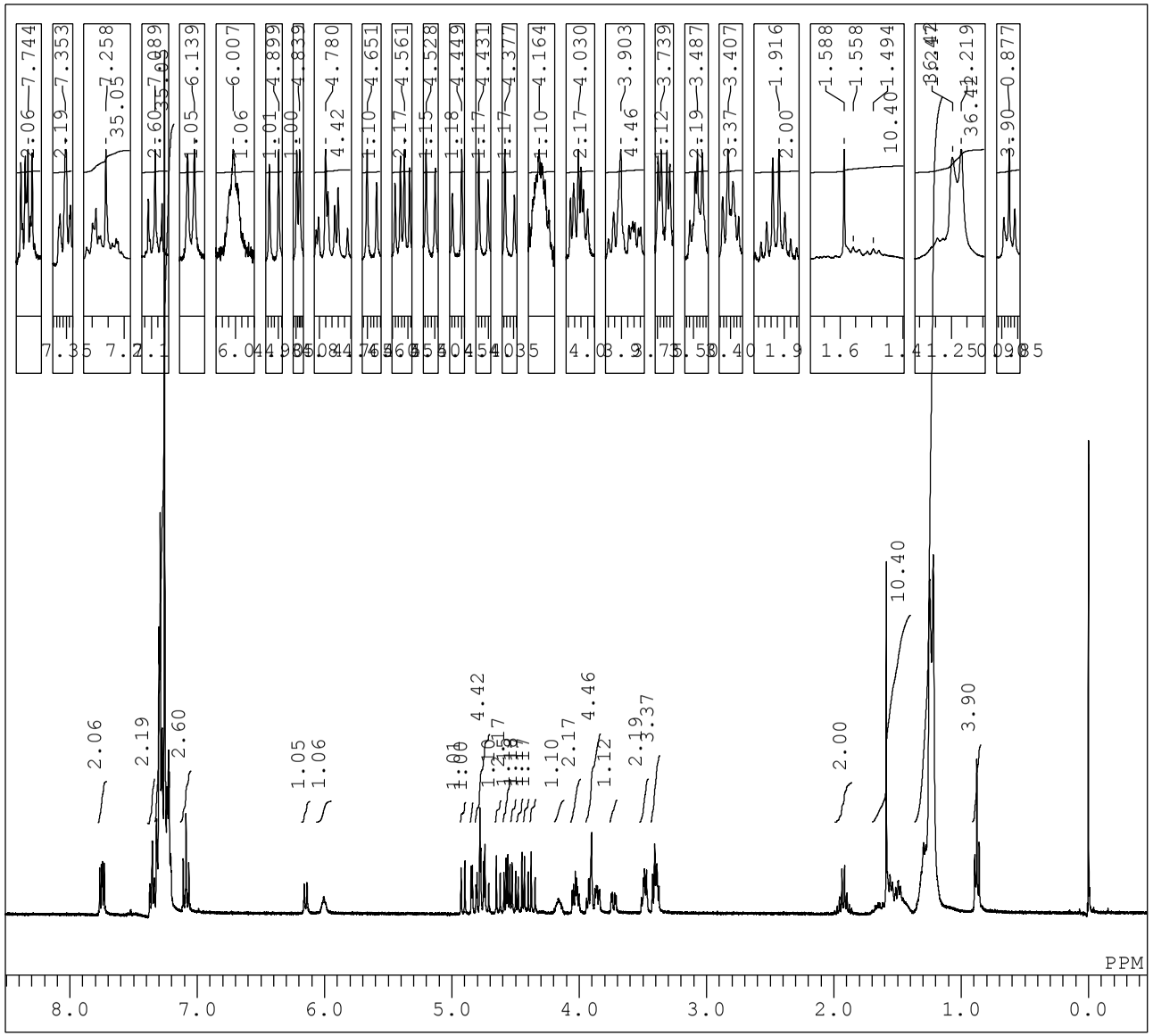
S13a



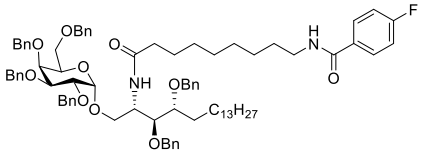
DFILE 102C-052a BCM-1.als
COMNT single pulse decoupled
DATIM 2016-01-17 09:44:49
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 11304
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 36



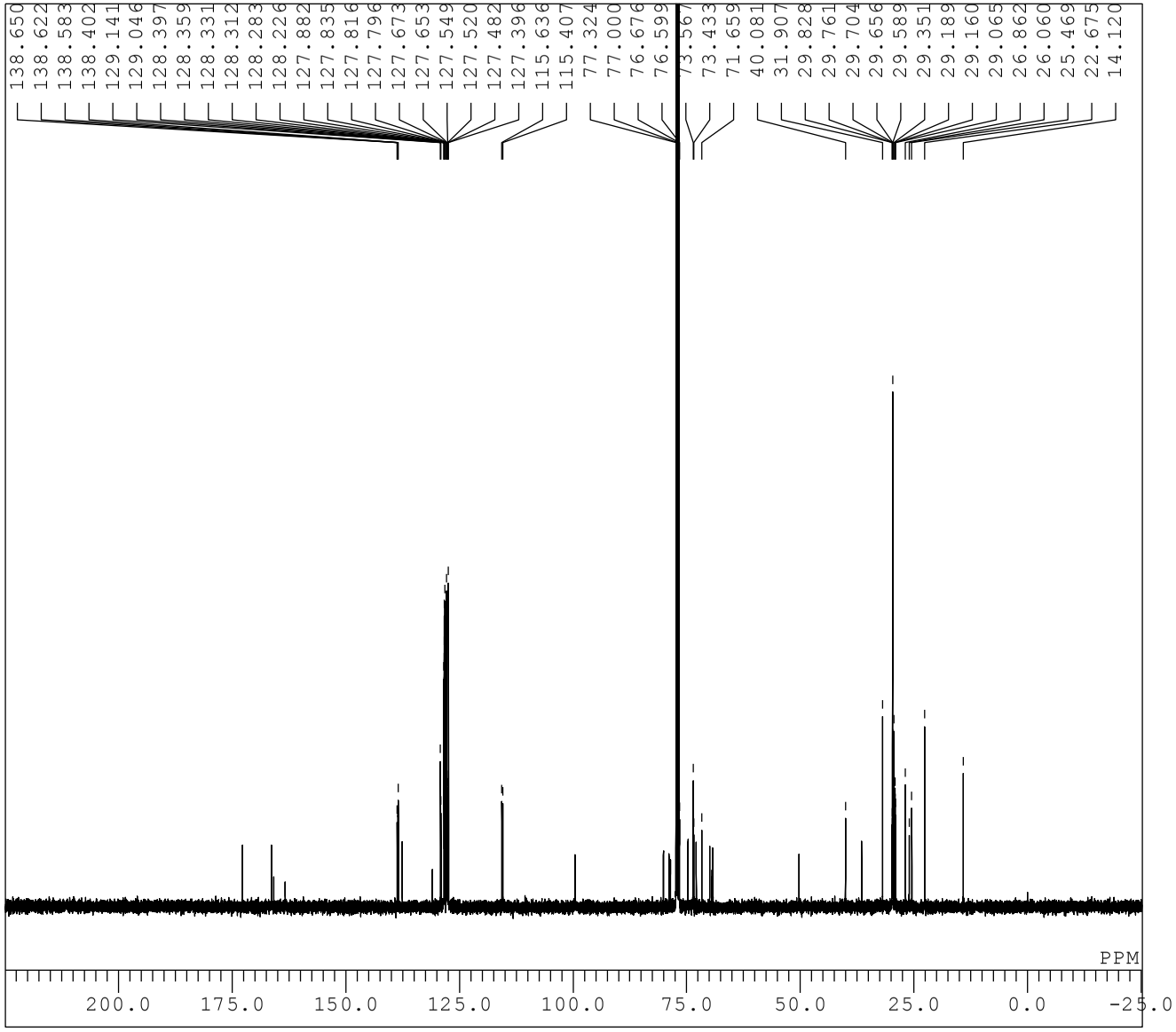
S13a



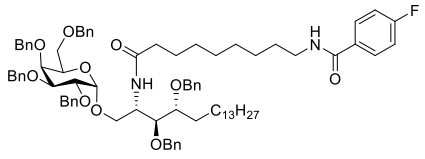

```
DFILE 102C-053a-1.als
COMNT single_pulse
DATIM 2016-01-16 19:09:28
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ       391.78 MHz
OBSET         8.51 KHz
OBFIN         3.34 Hz
POINT        26214
FREQU      5882.26 Hz
SCANS            8
ACQTM       4.4564 sec
PD          3.0000 sec
PW1            5.55 usec
IRNUC 1H
CTEMP         20.5 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.00 Hz
RGAIN           50
```



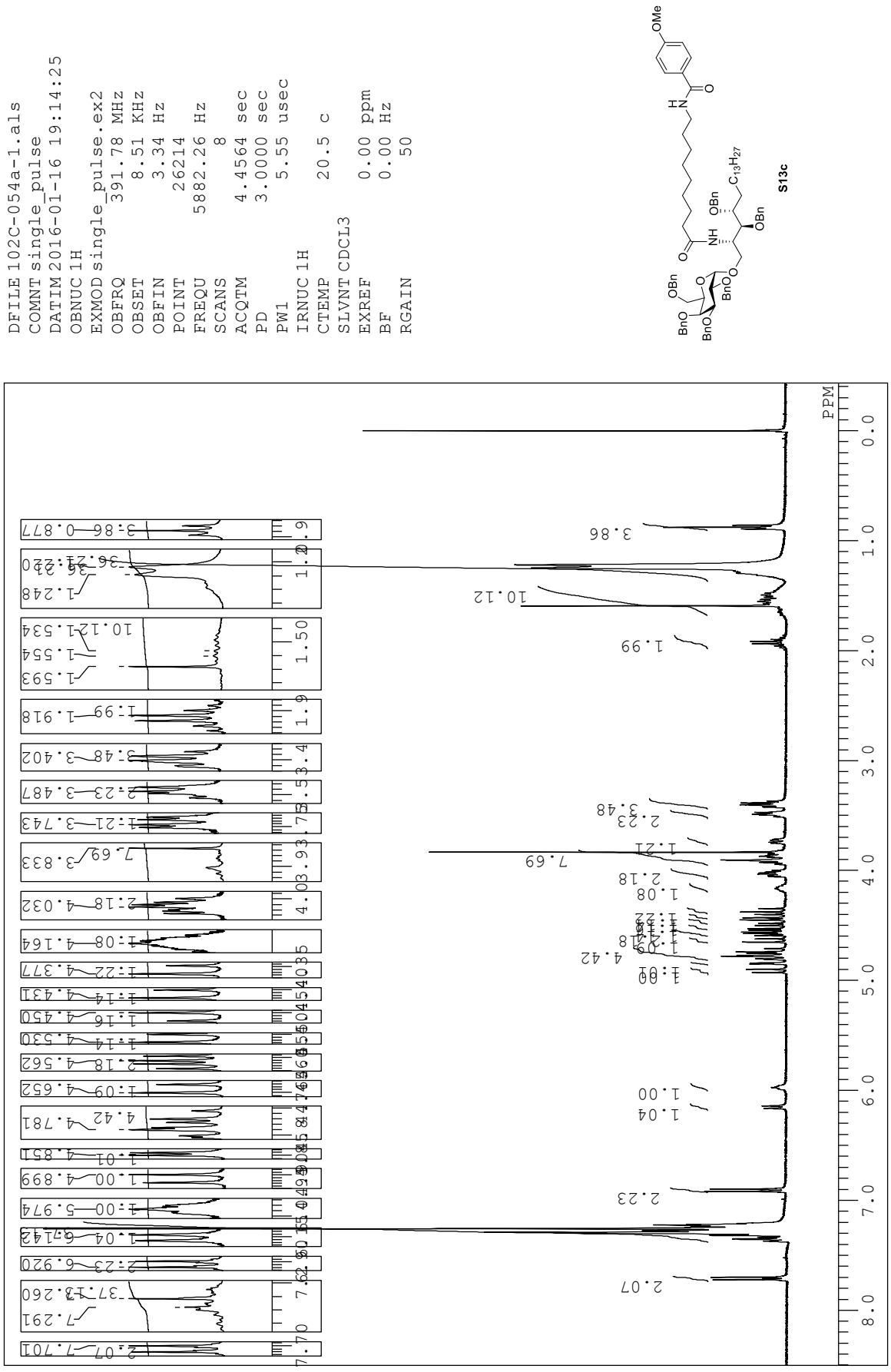
S13b

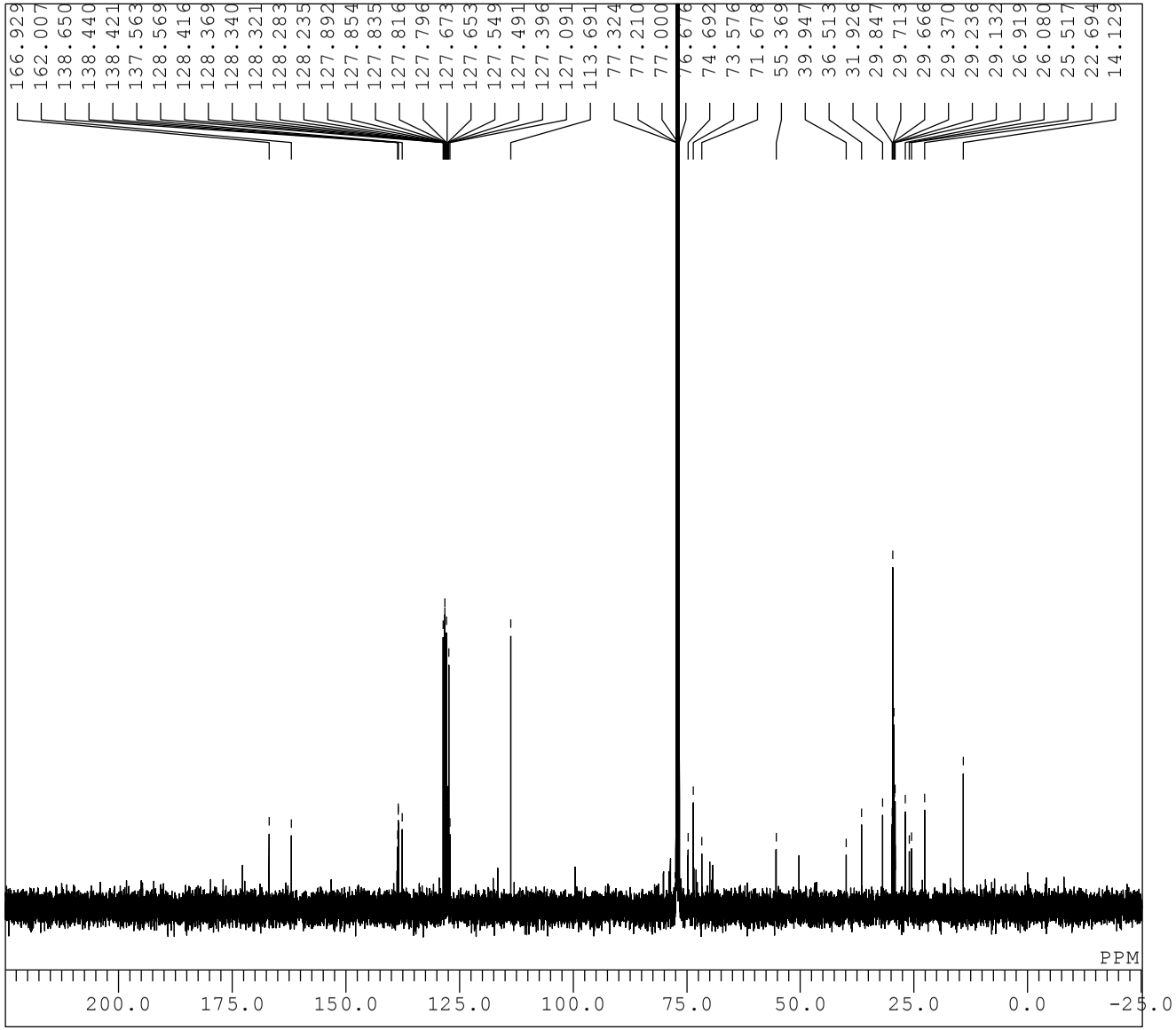



```
DFILE 102C-053a BCM 160117-1.a
COMNT single pulse decoupled c
DATIM 2016-01-18 08:40:05
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        98.52 MHz
OBSET         4.64 KHz
OBFIN         8.74 Hz
POINT        26214
FREQU     24630.17 Hz
SCANS        12906
ACQTM       1.0643 sec
PD          2.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         20.7 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            0.00 Hz
RGAIN           38
```

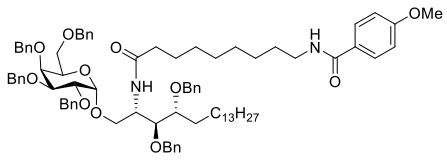


S13b

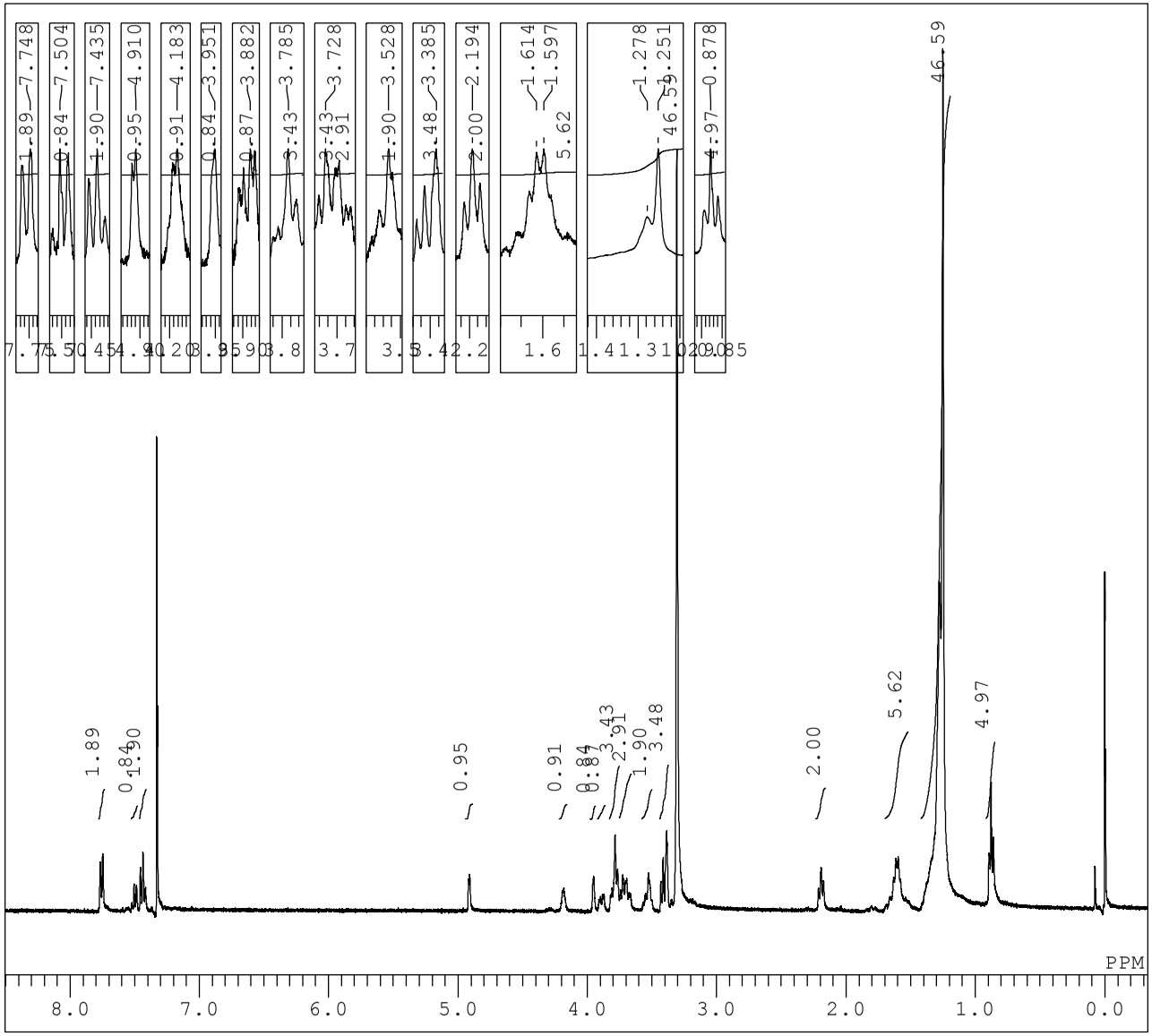

DFILE 102C-054a-1.als
COMNT single_pulse
DATIM 2016-01-16 19:14:25
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 50
OMe
O
H
N
O
OBn
BnO
BnO
O
O
NH
OBn
OBn
C13H27
S13c
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



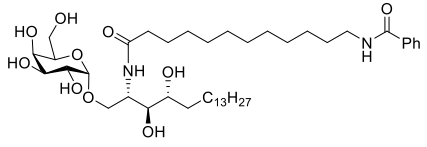
DFILE 102C-054a BCM-1.als
COMNT single pulse decoupled
DATIM 2016-01-16 21:51:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 3000
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 50



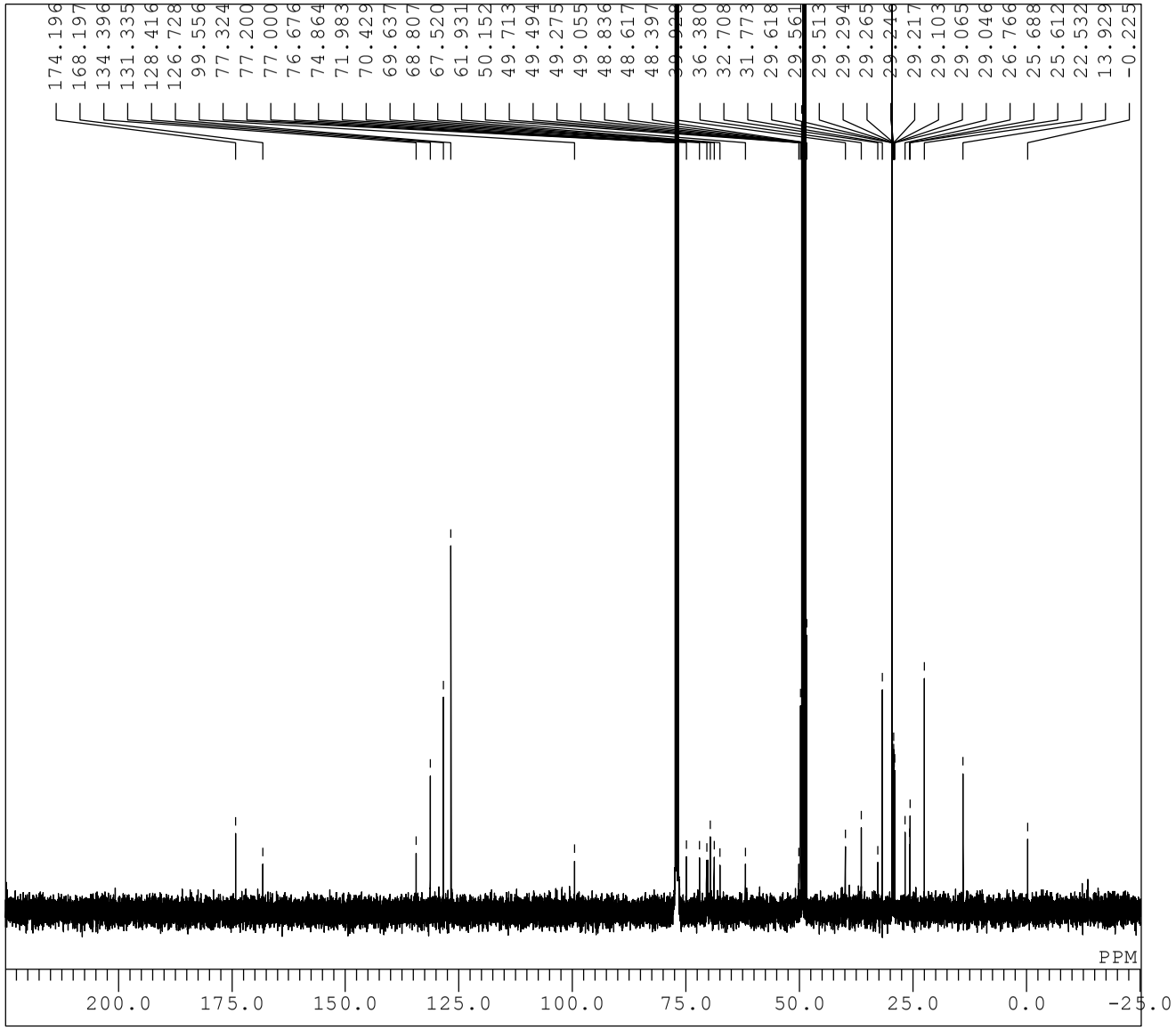
S13c



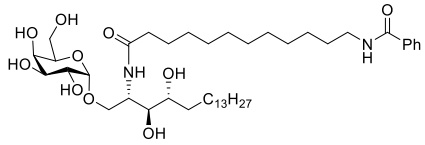
DFILE 102C-050a 160112-1.als
COMNT single_pulse
DATIM 2016-01-12 10:15:37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 50



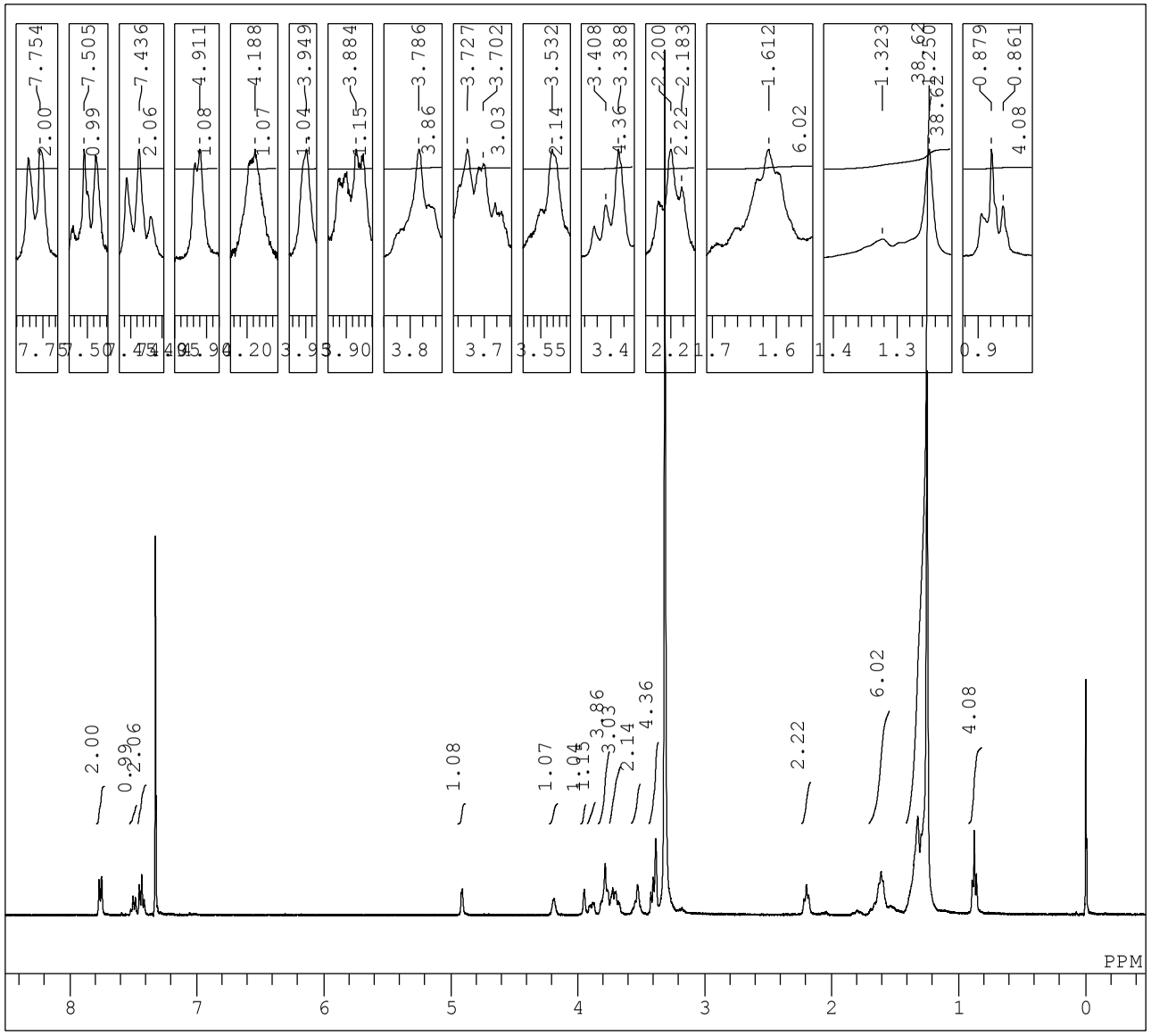
3d



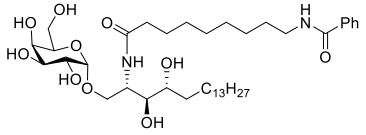
DFILE 102C-050a BCM 160114-1.a
COMNT single pulse decoupled c
DATIM 2016-01-15 08:26:31
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 11524
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 34



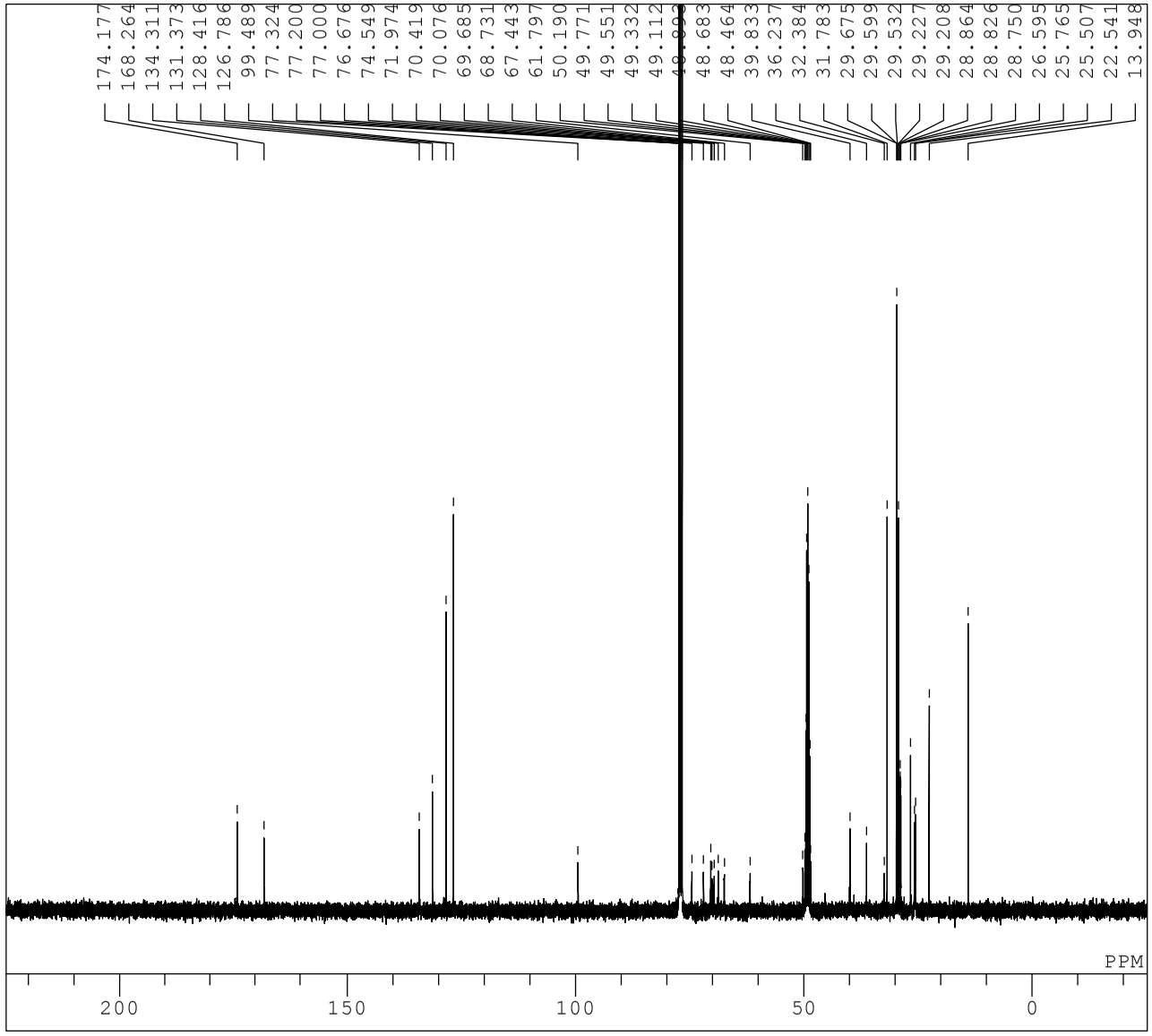
3d



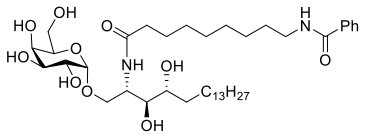
DFILE 102C-057a-2.als
COMNT single_pulse
DATIM 2016-01-18 21:16:06
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 54



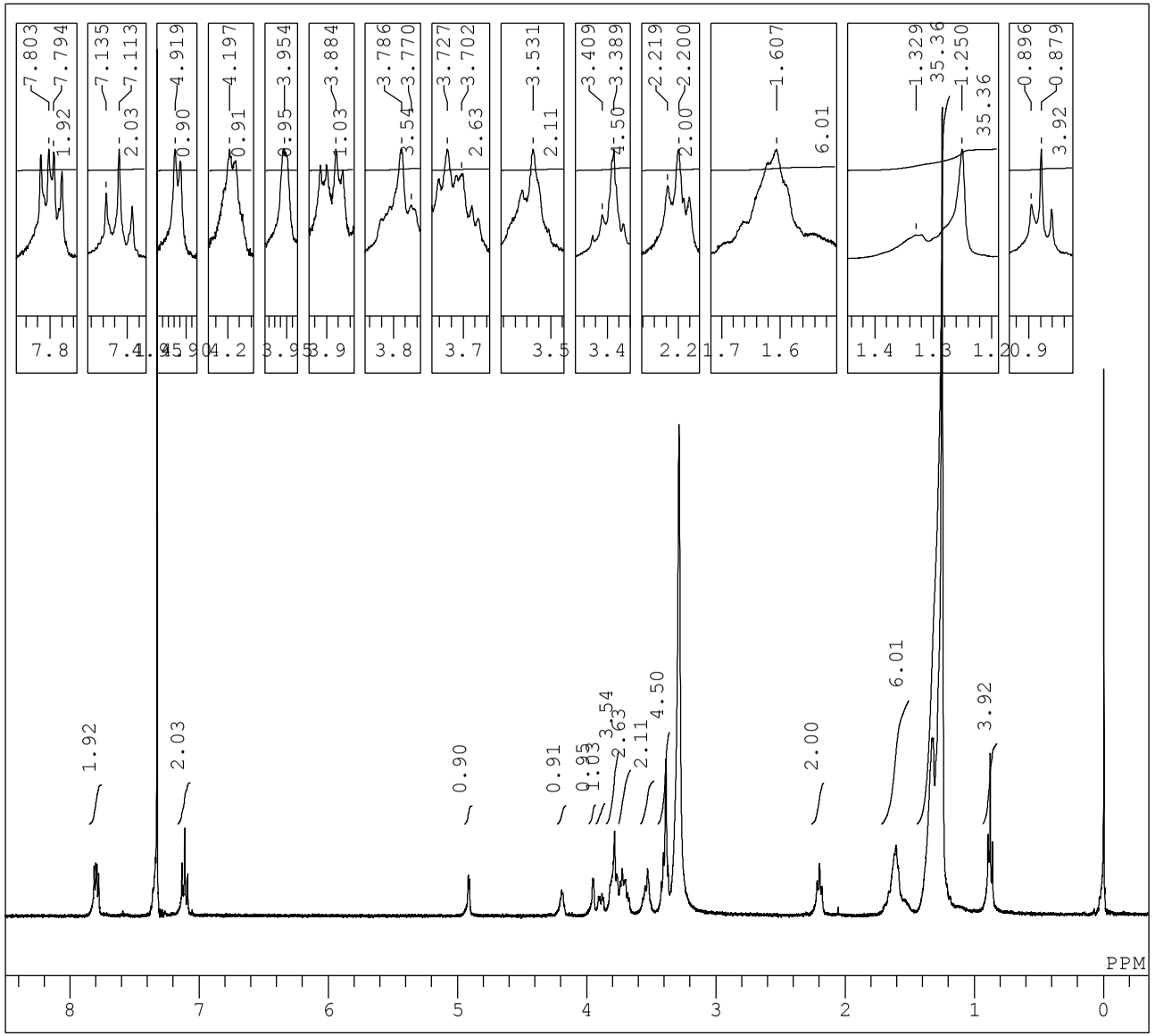
3a



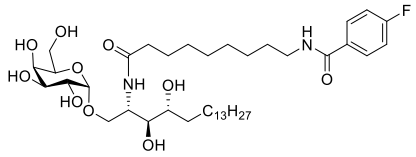
DFILE 102C-057a BCM 160123-1.a
COMNT single pulse decoupled g
DATIM 2016-01-24 09:42:53
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13475
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.10 Hz
RGAIN 34



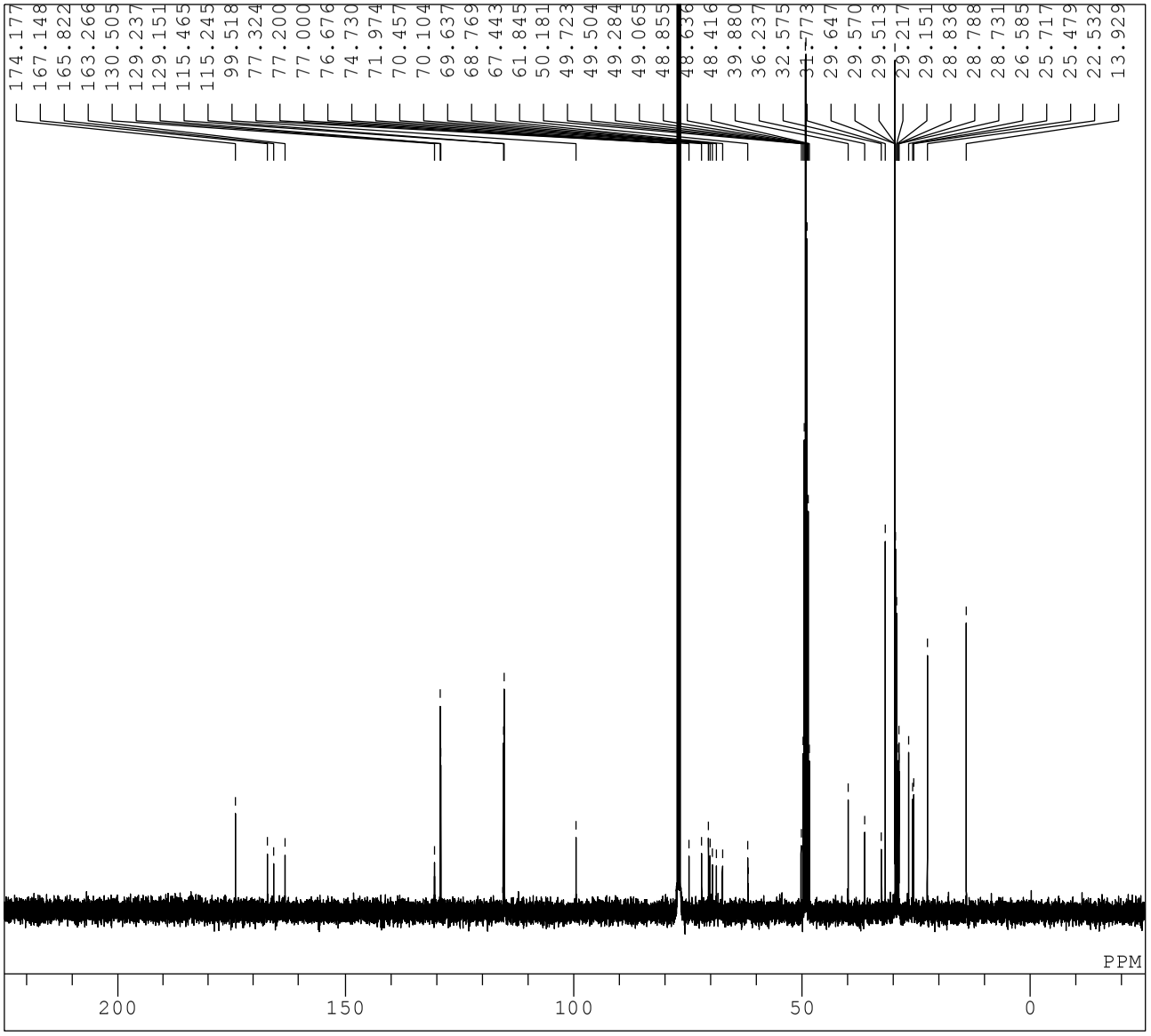
3a



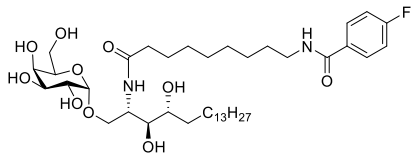
DFILE 102C-058a-1.als
COMNT single_pulse
DATIM 2016-01-19 17:56:19
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 54



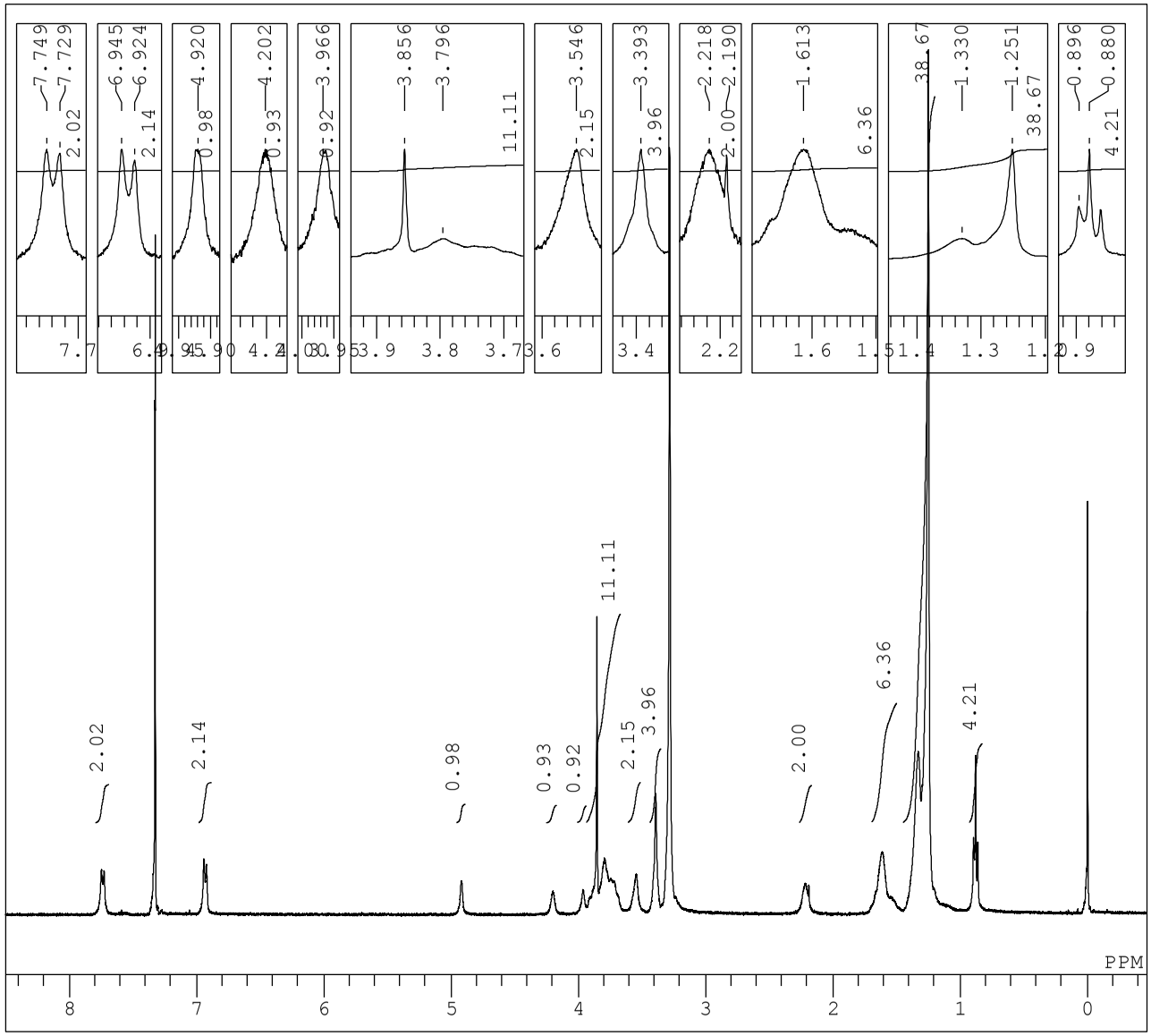
3b



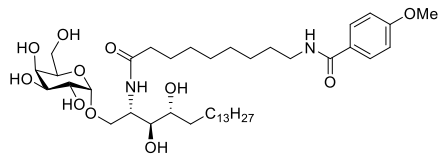
DFILE 102C-058a BCM 160124-1.a
COMNT single pulse decoupled c
DATIM 2016-01-25 08:30:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13078
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.10 Hz
RGAIN 34



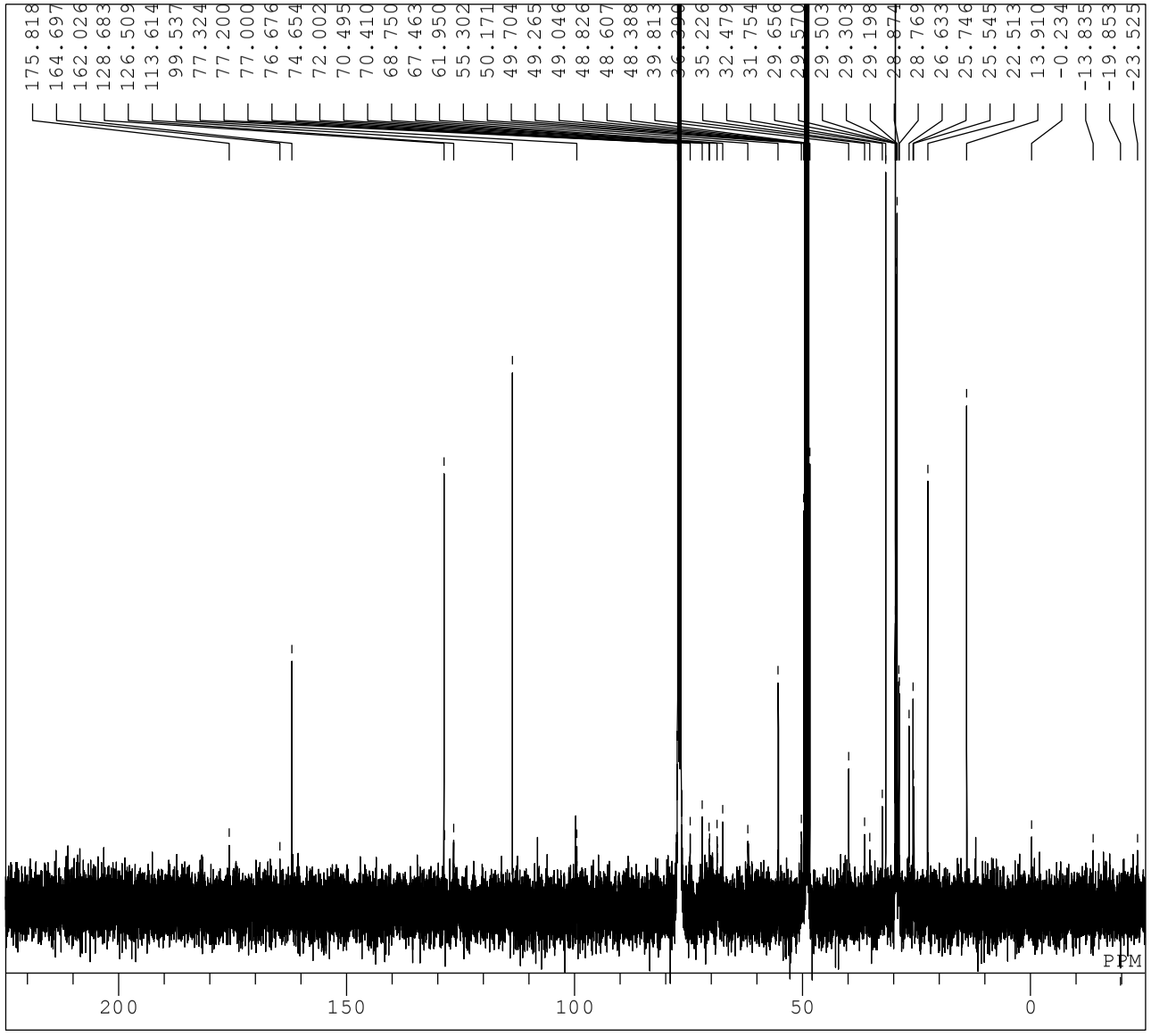
3b



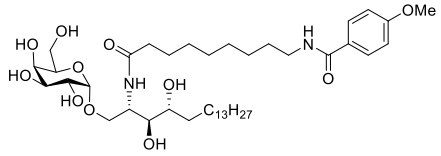
DFILE 102C-059a 160121-2.als
COMNT single_pulse
DATIM 2016-01-21 12:44:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 26214
FREQU 5882.26 Hz
SCANS 8
ACQTM 4.4564 sec
PD 3.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 54



3c



DFILE 102C-059a BCM 160126-1.a
COMNT single pulse decoupled c
DATIM 2016-01-27 08:26:58
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 98.52 MHz
OBSET 4.64 KHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.17 Hz
SCANS 13141
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 40



3c