Supporting Information

Synthesis of Immunostimulatory α-*C*-Galactosylceramide Glycolipids via Sonogashira Coupling, Asymmetric Epoxidation, and Trichloroacetimidate-Mediated Epoxide Opening

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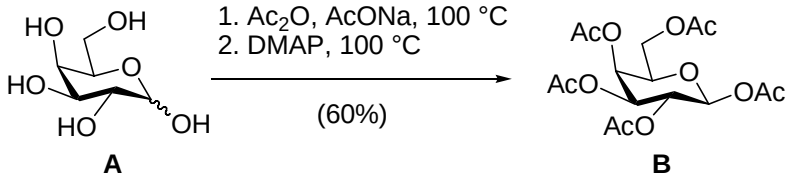
General Experimental Information

All reactions were carried out under a dry nitrogen atmosphere using oven-dried glassware and magnetic stirring. The solvents were dried as follows: THF was heated at reflux over sodium benzophenone ketyl; toluene was heated at reflux over sodium; CH_2Cl_2 were dried over CaH_2. Anhydrous *i*Pr_2NEt, CH_3CN, Et_3N, and benzene were used directly as purchased. Silica gel 60 F254 aluminum TLC plates of 0.2 mm thickness were used to monitor the reactions. The spots were visualized with short wavelength ultraviolet light or by charring after spraying with 15% H_2SO_4. Flash chromatography was carried out with silica gel 60 (230-400 ASTM mesh). ^1H NMR spectra were obtained on 400 MHz or 500 MHz spectrometers. Chemical shifts were referenced on residual solvent peaks: $CDCl_3$ (δ = 7.26 ppm for ^1H NMR and 77.00 ppm for ^{13}C NMR). Optical rotations were measured at rt in a 1.0-dm cell. High-resolution mass spectra were acquired by electrospray ionization.

Experimental Procedures

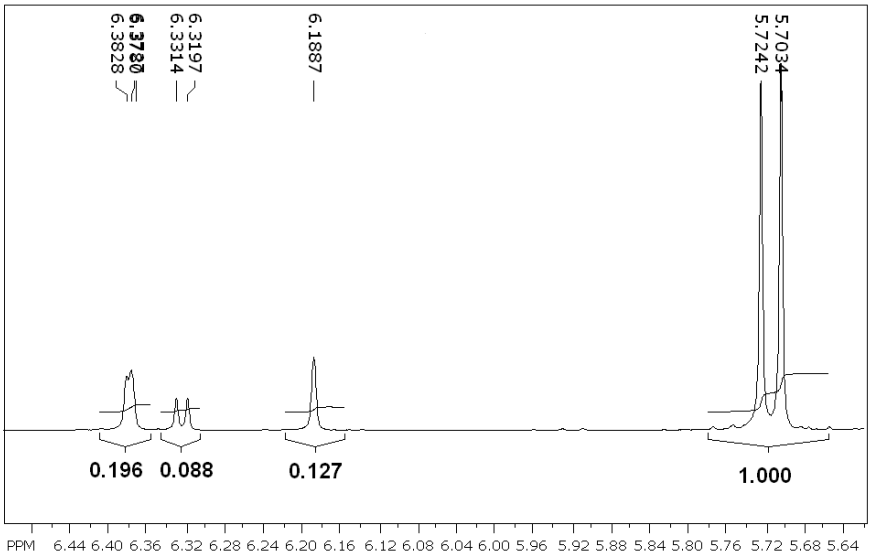


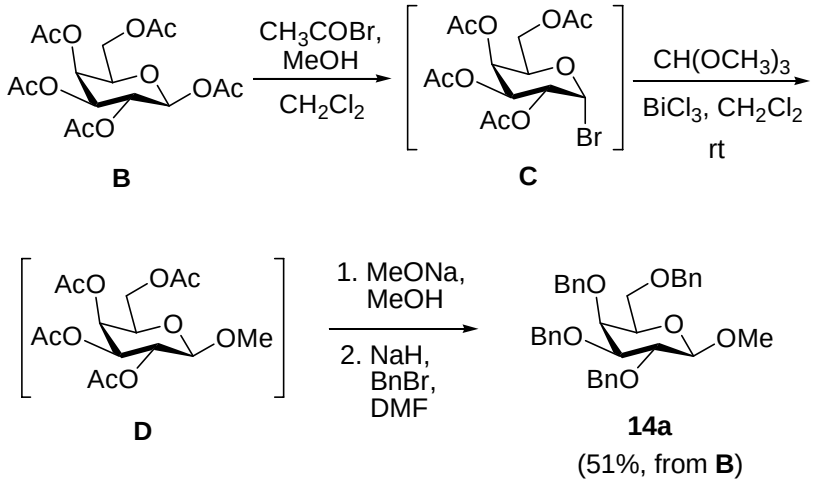
A **B**

Compound B.[S1, S2] A mixture of D-galactose (18.1 g, 0.10 mol) and sodium acetate (825 mg, 10.0 mmol) in 50 mL (0.528 mol) of Ac_2O was heated overnight at 100 °C (oil bath temperature). At this point, TLC showed the incomplete consumption of **A**. After addition of a catalytic amount of DMAP (1.22 g, 10.0 mmol), the mixture was stirred at same temperature and **A** was completely consumed overnight. The reaction mixture was diluted with EtOAc (250 mL) and washed with brine and then with water. The organic layer was dried over Na_2SO_4 and concentrated to give 39.21 g (100%) of an α- and β-mixture of D-galactopyranose pentaacetate and D-galactofuranose pentaacetate (see Figure S1). The product was purified by recrystallization from hexane/EtOAc (2:1) to give β-D-galactopyranose pentaacetate **B** (23.5 g, 60%): $[\alpha]^{23.5}_D$ +27.1 (*c* 1.03, $CHCl_3$) [lit.[S1h] $[\alpha]^{20}_D$ +25 ($CHCl_3$); lit.[S1i] $[\alpha]^{20}_D$

+25.2 ($CHCl_3$)]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.05 (s, 6H), 2.13 (s, 3H), 2.17 (s, 3H), 4.03-4.21 (m, 3H), 5.09 (dd, *J* = 3.4, 10.4 Hz, 1H), 5.30-5.37 (m, 1H), 5.43 (d, *J* = 2.4 Hz, 1H), 5.71 (d, *J* = 8.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.48, 20.57, 20.59, 20.75, 61.0, 66.7, 67.7, 70.8, 71.6, 92.1, 168.9, 169.3, 169.9, 170.1, 170.3.

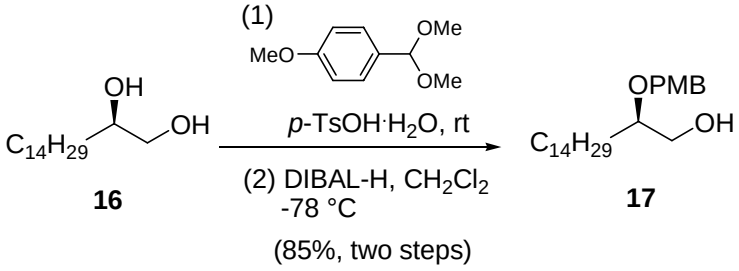
Figure S1. Partial ^{1}H NMR spectra of crude **B.** The signals of the anomeric protons of **B** and the other three isomers (α-D-galactopyranose and α- and β-D-galactofuranose pentaacetates) are shown.





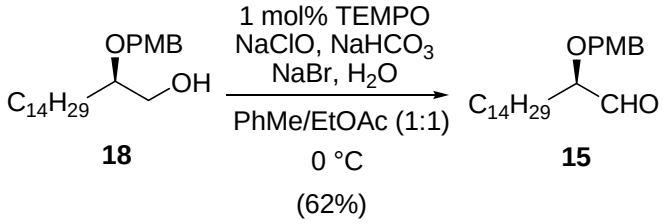
Compound 14a. To a solution of **B** (19.6 g, 50.2 mmol) in 50 mL of CH_2Cl_2 were added acetyl bromide (12 mL, 162 mmol) and MeOH (3.0 mL, 74.1 mmol) at 0 °C. After all of the starting pentaacetate was consumed, the mixture was concentrated to give crude α-D-galactosyl bromide **C**,[S3]

which was dried under high vacuum overnight. To a stirred solution of **C** and trimethyl orthoformate (10.0 mL, 91.4 mmol) in 50 mL of CH_2Cl_2 was added $BiCl_3$ (3.16 g, 10.0 mmol) at rt.[S4] After 5 h, the reaction mixture was diluted with CH_2Cl_2 (100 mL), and washed successively with saturated aqueous $NaHCO_3$ solution and water. After the organic layer was dried (Na_2SO_4) and concentrated, the residue was dried further under vacuum. The crude tetraacetate product **D**[S5] was dissolved in 100 mL of anhydrous MeOH and treated with MeONa (5 mL, 30% in MeOH) under reduced pressure in order to remove the methyl acetate formed. After **D** was dried under vacuum, *O*-benzylation was carried out using NaH (10.1 g, 252 mmol; 60% in white oil) and benzyl bromide (30 mL, 252 mmol) in 50 mL of DMF. The product was purified by column chromatography on silica gel (hexane/EtOAc 10:1 to 6:1) followed by recrystallization from hexane/EtOAc to give methyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside **14a**:[S6] (14.2 g, 51% overall yield): $[\alpha]^{24.2}_D$ -2.4 (*c* 1.08, $CHCl_3$) [lit.[S6b] $[\alpha]^{26.6}_D$ -0.84 (*c* 0.7, $CHCl_3$)]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.49-3.56 (m, 2H), 3.54 (s, 3H), 3.38-3.60 (m, 2H), 3.80 (dd, 1H, *J* = 2.32, 7.8 Hz), 3.89 (d, 1H, *J* = 2.32), 4.27 (d, 1H, *J* = 7.68 Hz), 4.40 (d, 1H, *J* = 19.2 Hz), 4.45 (d, 1H, *J* = 11.7 Hz), 4.61 (d, 1H, *J* = 11.7 Hz), 4.68-4.77 (m, 3H), 4.89 (d, 1H, *J* = 10.9 Hz), 4.94 (d, 1H, *J* = 11.7 Hz), 7.22-7.37 (m, 20H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 57.0, 68.8, 72.9, 73.27, 73.5, 74.4, 75.1, 79.6, 82.1, 105.0, 127.47, 127.50, 127.7, 127.8, 127.9, 128.07, 128.10, 128.22, 128.25, 128.30, 128.4, 137.9, 138.4, 138.6, 138.7.



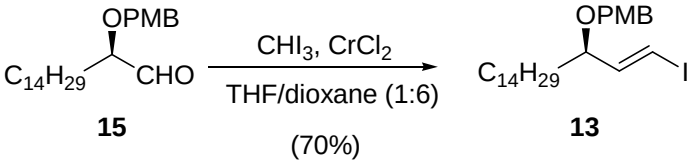
Compound 17. A solution of diol **16** (24.6 g, 95.2 mmol) in benzene (300 mL) was treated with *p*-methoxybenzaldehyde dimethylacetal (37.8 mL, 190 mmol) and *p*-toluenesulfonic acid monohydrate

(1.8 g, 9.5 mmol). The reaction mixture was stirred at rt overnight and then concentrated. The residue was used without purification in the next step. The crude acetonide (maximum 95.2 mmol) was dissolved in CH_2Cl_2 (500 mL), cooled to -78 °C, and treated with DIBAL-H (1.0 M in hexane; 333 mL, 333 mmol). After 30 min, the reaction mixture was gradually warmed to rt, quenched with MeOH (10 mL), diluted with Et_2O (700 mL), and treated with a saturated solution of Rochelle's salt (500 mL). The resultant biphasic mixture was stirred vigorously at rt until the organic phase turned clear. The organic phase was then dried with $MgSO_4$, filtered through Na_2SO_4, and concentrated. Flash chromatography (hexane/EtOAc 3:1) afforded **17** (30.6 g, 85% yield for two steps): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.40 (m, 24H), 1.43-1.52 (m, 1H), 1.57-1.66 (m, 1H), 2.02 (brs, 1H), 3.45-3.53 (m, 2H), 3.64-3.70 (m, 1H), 3.80 (s, 3H), 4.46 (d, *J* = 11.2 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 6.87-6.91 (m, 2H), 7.26-7.29 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.4, 29.3, 29.54, 29.58, 29.63, 29.66, 29.68, 29.8, 30.8, 31.9, 55.2, 64.2, 71.1, 79.4, 113.8, 129.4, 130.5, 159.2; **HRMS** (ESI, MNa^+) *m*/*z* calcd for $C_{24}H_{42}NaO_3^+$ 401.3026, found 401.3023.



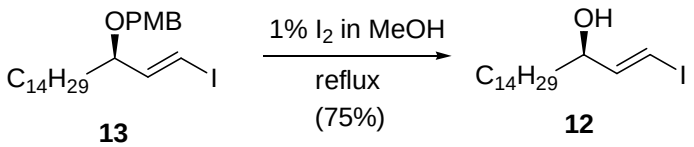
Compound 15. To a solution of 19 g (50.2 mmol) of alcohol **18** in 400 mL of EtOAc/PhMe (1:1) were added a solution of NaBr (10.8 g, 105 mmol in 50 mL H_2O) and TEMPO (235 mg, 1.51 mmol) at 0 °C. Clorox (76 mL) was diluted to 190 mL with H_2O and buffered by the addition of $NaHCO_3$ (12.3 g, 146 mmol). The bleach solution was added dropwise to the reaction flask over 1 h and stirred for an additional 10 min at 0 °C. The ice bath was removed, the reaction mixture was diluted with 800 mL of EtOAc, and the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash

chromatography (hexanes/EtOAc 20:1) to yield **15** (11.8 g, 62%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.46 (m, 24H), 1.61-1.68 (m, 2H), 3.70-3.75 (m, 1H), 3.81 (s, 3H), 4.48 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 6.86-6.91 (m, 2H), 7.25-7.30 (m, 2H), 9.61 (d, *J* = 2.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 29.34, 29.37, 29.51, 29.59, 29.63, 29.65, 29.66, 30.0, 31.9, 55.2, 72.2, 83.1, 113.8, 129.3, 129.7, 159.4, 204.2; **HRMS** (ESI, MNH_4^+) *m*/*z* calcd for $C_{24}H_{44}NO_3^+$ 394.3316, found 394.3302.



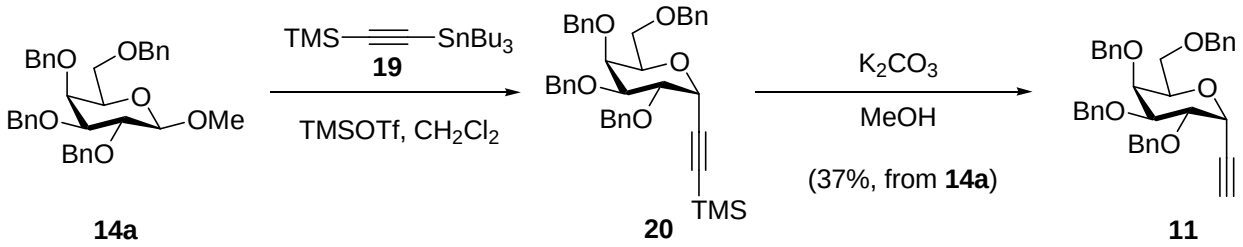
15 **13**

Compound 13. To a slurry of anhydrous chromium(II) chloride (27.5 g, 224 mmol) in THF (60 mL) was added a solution containing **15** (8.40 g, 22.3 mmol) and iodoform (26.3 g, 66.9 mmol) in dioxane (360 mL). The resulting brown suspension was stirred at rt overnight, and then was diluted with Et_2O (600 mL) and poured into 200 mL of water. The aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by flash chromatography (hexanes/EtOAc 40:1) afforded iodide **13** (7.81 g, 70%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.17-1.40 (m, 24H), 1.42-1.51 (m, 1H), 1.55-1.65 (m, 1H), 3.66-3.72 (m, 1H), 3.79 (s, 3H), 4.27 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 6.26 (d, *J* = 14.6 Hz, 1H), 6.45 (dd, *J* = 7.8, 14.6 Hz, 1H), 6.85-6.89 (m, 2H), 7.21-7.25 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.1, 29.3, 29.40, 29.49, 29.56, 29.61, 29.63, 29.66, 31.9, 34.9, 55.2, 70.0, 77.8, 81.0, 113.7, 129.3, 130.2, 147.2, 159.1; **HRMS** (ESI, MNa^+) *m*/*z* calcd for $C_{25}H_{41}INaO_2^+$ 523.2043, found 523.2042.



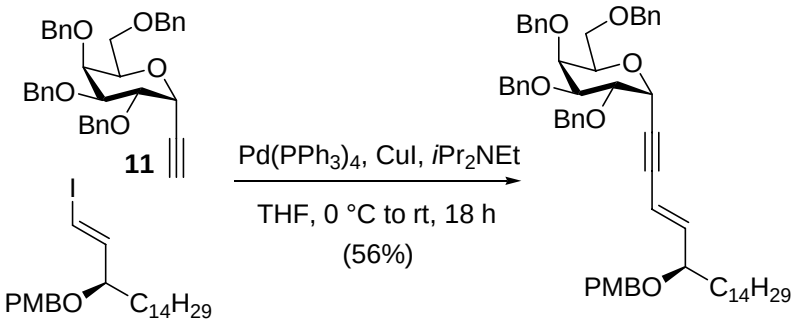
13 **12**

Compound 12. A solution of **13** (8.00 g, 16.0 mmol) in 200 mL of 1% I_2/MeOH (w/v) was heated at reflux for 2 h. After the reaction mixture was concentrated under reduced pressure, the residue was dissolved in EtOAc (200 mL) and washed with saturated aqueous $Na_2S_2O_3$ solution (50 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (hexanes/EtOAc 10:1) to give **12** (4.56 g, 75%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.40 (m, 24H), 1.49-1.57 (m, 2H), 4.07-4.13 (m, 1H), 6.35 (dd, *J* = 1.1, 14.4 Hz, 1H), 6.58 (dd, *J* = 6.4, 14.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.1, 29.35, 29.42, 29.51, 29.55, 29.62, 29.64, 29.67, 31.9, 36.6, 74.7, 77.1, 148.7; **HRMS** (ESI, MNa^+) *m*/*z* calcd for $C_{17}H_{33}INaO^+$ 403.1468, found 403.1460.



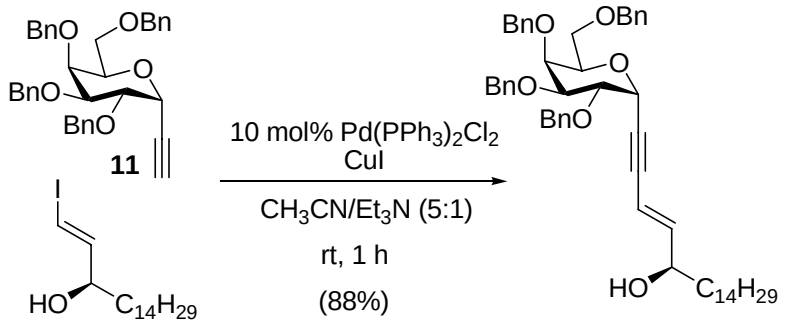
Compound 11.[S7] To a solution of **14a** (3.52 g, 6.35 mmol) in CH_2Cl_2 (100 mL) were added tributylstannyl(trimethylsilyl)ethyne **19** (5.49 g, 14.2 mmol) and TMSOTf (2.30 mL, 12.7 mmol) at rt. After the reaction mixture was stirred at rt for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$ solution (30 mL). The product was extracted with EtOAc (3×100 mL). The combined organic extracts were washed with H_2O (100 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 20:1) to afford **20** (2.02 g, 3.25 mmol) containing a small amount of stannane. The crude product was dissolved in MeOH (100 mL) and treated with K_2CO_3 (2.0 g) at rt for 4 h. The reaction was quenched with saturated aqueous NH_4Cl solution (30 mL), and extracted with EtOAc (3×100 mL). The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc 8:1) to afford α-*C*-ethynylgalactose **11** (1.30 g, 37% two steps): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.53 (d, *J* = 2.3 Hz, 1H), 3.48-3.56 (m, 2H), 3.89 (dd,

J = 2.8, 9.9 Hz, 1H), 3.97-3.99 (m, 1H), 4.07-4.15 (m, 2H), 4.40 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.7 Hz, 1H), 4.57 (d, J = 11.3 Hz, 1H), 4.71-4.81 (m, 4H), 4.86 (d, J = 11.7 Hz, 1H), 4.94 (d, J = 11.3 Hz, 1H), 7.23-7.41 (m, 20H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 67.3, 68.7, 72.6, 73.2, 73.3, 73.5, 74.8, 74.9, 75.1, 76.3, 78.9, 80.2, 127.4, 127.5, 127.6, 127.7, 127.9, 128.22, 128.27, 128.35, 128.36, 128.38, 137.9, 138.2, 138.5, 138.7.

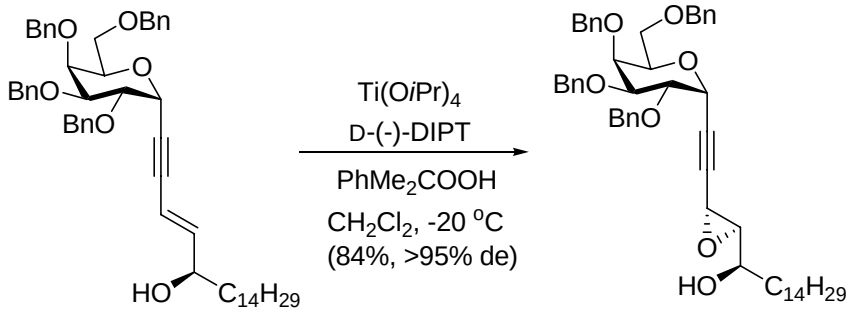


Compound 10. Compounds **11** (150 mg, 0.273 mmol) and **13** (164 mg, 0.328 mmol) were dissolved in THF (5 mL). The solution was degassed by two freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (31 mg, 27.3 μmol) and CuI (25 mg, 0.131 mmol) were added, and the mixture was degassed by one freeze-pump-thaw cycle, placed in a 0 °C bath under N_2, and treated with iPr$_2$NEt (285 μL, 1.64 mmol). The reaction was stirred at rt for 18 h, and then was quenched by the addition of half-saturated aqueous NH_4Cl solution and the mixture was extracted twice with Et_2O. The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 8:1) to afford **10** (140 mg, 56%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 3H), 1.20-1.41 (m, 24H), 1.45-1.53 (m, 1H), 1.58-1.66 (m, 1H), 3.54-3.57 (m, 2H), 3.72-3.77 (m, 1H), 3.78 (s, 3H), 3.89 (dd, J = 2.7, 9.9 Hz, 1H), 3.98-4.01 (m, 1H), 4.09-4.16 (m, 2H), 4.27 (d, J = 11.5 Hz, 1H), 4.40 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.3 Hz, 1H), 4.57 (d, J = 11.3 Hz, 1H), 4.71-4.80 (m, 3H), 4.84 (d, J = 11.7 Hz, 1H), 4.94 (d, J = 11.5 Hz, 1H), 4.96 (dd, J = 1.6, 5.7 Hz, 1H), 5.71 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 7.4, 16.0 Hz, 1H), 6.85-6.89 (m, 2H), 7.21-7.40 (m, 22H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.3, 29.3, 29.49, 29.52, 29.60, 29.64, 31.9, 35.3, 55.2, 67.8, 68.6, 70.1,

72.5, 72.9, 73.0, 73.4, 74.7, 74.8, 75.5, 78.8, 80.0, 84.7, 86.0, 110.8, 113.7, 127.4, 127.51, 127.59, 127.71, 127.78, 127.9, 128.15, 128.19, 128.25, 128.30, 128.34, 129.3, 130.5, 137.8, 138.3, 138.5, 138.6, 145.2, 159.1; **HRMS** (ESI, MNa^+) *m*/*z* calcd for $C_{61}H_{76}NaO_7^+$ 943.5483, found 943.5488.



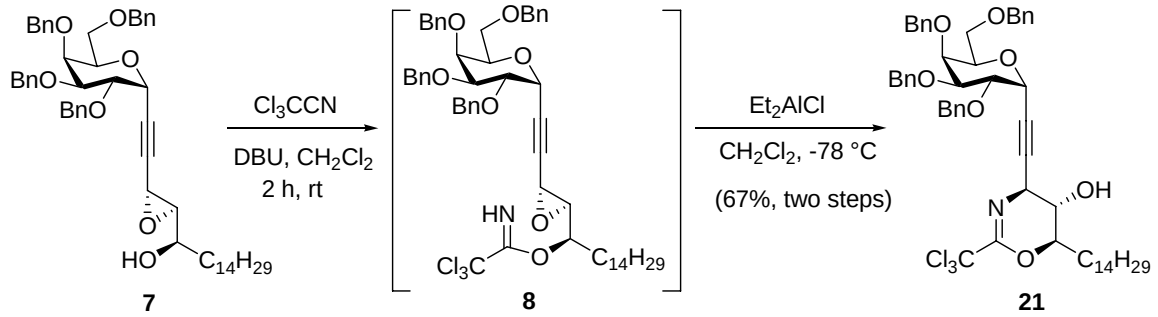
Compound 9. A mixture of **11** (870 mg, 1.59 mmol) and **12** (724 mg, 1.90 mmol) was azeotropically dried under reduced pressure with toluene, and then was dissolved in CH_3CN/Et_3N (30 mL, 5:1). The solution was degassed by two freeze-pump-thaw cycles. After $PdCl_2(PPh_3)_2$ (112 mg, 0.16 mmol) and CuI (182 mg, 0.954 mmol) were added, the reaction mixture was stirred at rt for 1 h, quenched with 0.05 M phosphate buffer (pH 7, 140 mL), and poured into water (250 mL). The product was extracted with EtOAc (3×200 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Purification by flash chromatography (hexanes/EtOAc 5:1) gave **9** (1.12 g, 88%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.18-1.62 (m, 26H), 3.50-3.56 (m, 2H), 3.86 (dd, *J* = 2.8, 9.8 Hz, 1H), 3.96-4.00 (m, 1H), 4.08-4.12 (m, 2H), 4.13-4.19 (m, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.70-4.78 (m, 3H), 4.83 (d, *J* = 11.7 Hz, 1H), 4.91-4.95 (m, 2H), 5.75 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.16 (dd, *J* = 6.1, 15.9 Hz, 1H), 7.22-7.40 (m, 20H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.3, 29.4, 29.53, 29.56, 29.62, 29.65, 29.69, 31.9, 36.9, 67.8, 68.7, 72.3, 72.5, 73.0, 73.1, 73.5, 74.7, 74.9, 75.5, 80.0, 84.9, 86.1, 109.2, 127.46, 127.56, 127.62, 127.75, 127.82, 127.9, 128.20, 128.26, 128.30, 128.31, 128.39, 137.9, 138.4, 138.6, 138.7, 146.7; **HRMS** (ESI, MNH_4^+) *m*/*z* calcd for $C_{53}H_{72}NO_6^+$ 818.5354, found 818.5351.



9 **7**

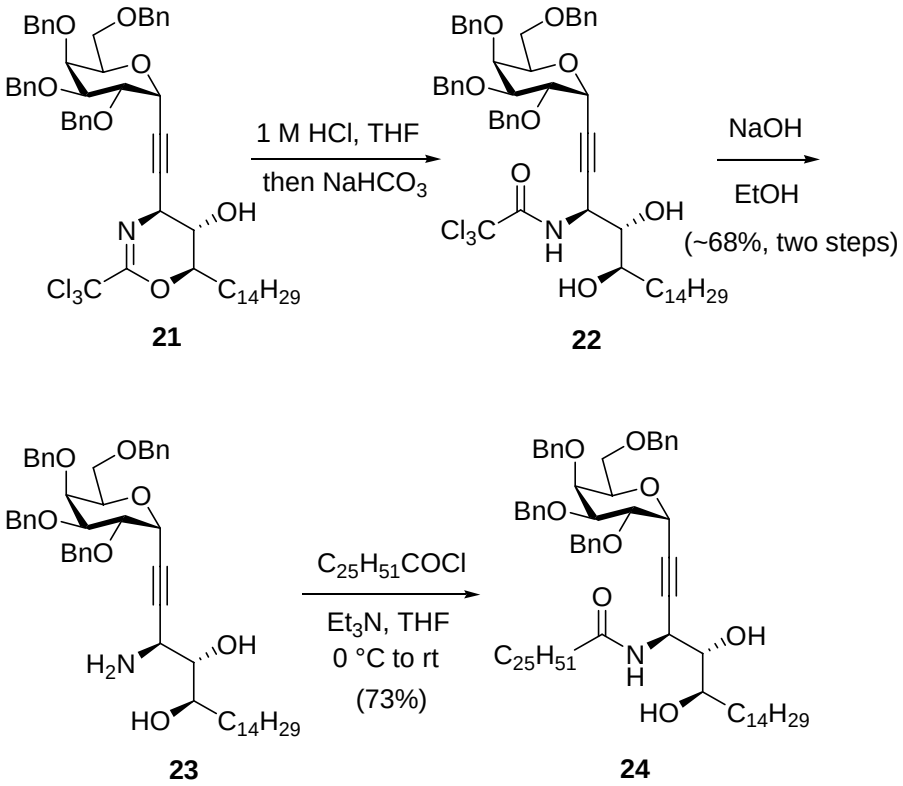
Compound 7. $Ti(OiPr)_4$ (887 mg, 3.12 mmol) was added dropwise to a solution of D-(-)-DIPT (761 mg, 3.25 mmol) and 4 Å molecular sieves (1.0 g) in CH_2Cl_2 (30 mL) at -20 °C. After the resultant mixture was allowed to stir at -20 °C for 50 min, a solution of **9** (1.0 g, 1.25 mmol) in CH_2Cl_2 (10 mL) was added over a period of 15 min. The reaction mixture was allowed to stir at -20 °C for another 30 min, and cumene hydroperoxide (924 μL, 5.00 mmol, 80% technical grade) was added via syringe. The reaction mixture was stirred at -20 °C for an additional 48 h, and 10% aqueous D-tartaric acid (5 mL) was added. The reaction mixture was stirred vigorously at rt for 30 min and filtered through a plug of Celite. The filtrate layers were separated and the aqueous layer was further extracted with CH_2Cl_2 (3× 10 mL). The combined organic phases were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography (hexane/EtOAc 5:1) afforded epoxide **7** (863 mg, 84%, >95% de; the chiral purity of **7** was determined by analysis of its (*S*)-MTPA ester, see ^{1}H NMR of its (*S*)-MTPA ester, p. S48): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.62 (m, 26H), 1.85 (d, *J* = 2.5 Hz, 1H), 3.15 (t, *J* = 2.5 Hz, 1H), 3.47-3.56 (m, 3H), 3.78-3.82 (m, 1H), 3.84 (dd, *J* = 2.8, 9.8 Hz, 1H), 3.95-3.98 (m, 1H), 4.03-4.11 (m, 2H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 7.6 Hz, 1H), 4.76 (d, *J* = 7.8 Hz, 1H), 4.80-4.85 (m, 2H), 4.91 (d, *J* = 11.3 Hz, 1H), 7.21-7.39 (m, 20H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.2, 29.3, 29.49, 29.57, 29.60, 29.64, 31.9, 33.1, 34.5, 41.6, 41.8, 62.4, 67.3, 67.9, 68.5, 72.7, 73.0, 73.4, 74.4, 74.5, 74.8, 75.2, 79.4, 79.9, 84.3, 126.0, 127.42, 127.45, 127.54, 127.6, 127.70, 127.74, 127.9, 128.0,

128.16, 128.20, 128.27, 128.3, 128.7, 128.9, 137.8, 138.2, 138.4, 138.5; **HRMS** (ESI, MNH_4^+) *m*/*z* calcd for $C_{53}H_{72}NO_7^+$ 834.5303, found 834.5293.



Compound 21. To a solution of **7** (425 mg, 0.52 mmol) in dry CH_2Cl_2 (10 mL) were added DBU (272 μL, 1.82 mmol) and Cl_3CCN (313 μL, 3.12 mmol). The reaction mixture was stirred at rt for 2 h, and then was quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 (3× 10 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl solution, dried (Na_2SO_4), and concentrated. The residue was dissolved in Et_2O and passed through a short column packed with anhydrous Na_2SO_4 and silica gel. Et_2O was evaporated to yield imidate **8** (403 mg) as a light yellow oil, which was dried under high vacuum overnight and used in the next reaction without further purification. To a solution of **8** in CH_2Cl_2 (10 mL) was added Et_2AlCl (1.0 M in hexane, 2.08 mL, 2.08 mmol) at -78 °C. After being stirred at -78 °C for 24 h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution and the product was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (hexane/EtOAc 4:1) afforded dihydrooxazine **21** (333 mg, 67%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.64 (m, 25H), 1.85-1.94 (m, 1H), 3.29 (d, *J* = 3.8 Hz, 1H), 3.39-3.47 (m, 2H), 3.53 (dd, *J* = 6.2, 9.4 Hz, 1H), 3.82 (dd, *J* = 2.8, 9.8 Hz, 1H), 3.91-3.95 (m, 1H), 4.03-4.14 (m, 3H), 4.27 (dd, *J* = 2.3, 8.4 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.68-4.80 (m, 4H), 4.85 (dd, *J* = 2.3, 5.8 Hz, 1H), 4.92 (d, *J* = 11.5 Hz, 1H), 7.23-7.40 (m, 20H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 24.0, 29.27, 29.34, 29.46, 29.55, 29.63,

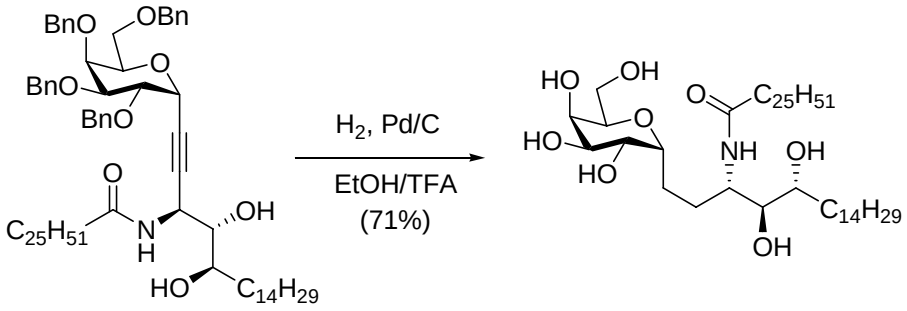
29.67, 31.4, 31.9, 53.5, 67.3, 68.9, 69.0, 72.75, 72.80, 73.3, 73.6, 74.3, 74.7, 75.4, 79.7, 80.1, 80.8, 86.0, 91.6, 127.5, 127.63, 127.69, 127.87, 127.96, 128.1, 128.2, 128.33, 128.39, 128.40, 128.43, 128.9, 137.6, 137.9, 138.3, 138.4, 153.8; **HRMS** (ESI, MH^+) *m*/*z* calcd for $C_{55}H_{69}Cl_3NO_7^+$ 960.4134, found 960.4130.



Compound 24. To a solution of **21** (333 mg, 0.346 mmol) in THF (15 mL) was added 1 M HCl (5 mL). After being stirred at rt for 30 min, the reaction mixture was carefully basified with saturated aqueous $NaHCO_3$ solution (5 mL). The product was extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated to obtain crude product **22**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.17-1.46 (m, 24H), 1.50-1.59 (m, 1H), 1.62-1.71 (m, 1H), 2.66 (d, *J* = 9.2 Hz, 1H), 3.06 (d, *J* = 9.1 Hz, 1H), 3.43 (dd, *J* = 6.9, 9.3 Hz, 1H), 3.49 (dd, *J* = 5.9, 9.3 Hz, 1H), 3.54-3.59 (m, 1H), 3.61-3.68 (m, 1H), 3.80 (dd, *J* = 2.7, 9.8 Hz, 1H), 3.91-3.93 (m, 1H), 3.97-4.01 (m, 1H), 4.10 (dd, *J* = 6.0, 9.8 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.74-4.84 (m, 4H), 4.89 (dt, *J* = 2.7, 8.5 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 7.23-7.44 (m, 21H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.7, 29.4, 29.51, 29.56,

29.61, 29.64, 29.68, 31.9, 33.3, 45.2, 67.3, 68.6, 72.2, 72.8, 72.9, 73.5, 73.7, 73.9, 74.3, 74.8, 75.5, 80.0, 81.3, 83.0, 92.1, 127.6, 127.7, 127.86, 127.97, 128.07, 128.16, 128.26, 128.31, 128.43, 128.47, 128.54, 137.4, 137.5, 138.2, 138.3, 161.0; **HRMS** (ESI, MNH_4^+) *m*/*z* calcd for $C_{55}H_{74}Cl_3N_2O_8^+$ 995.4505, found 995.4503.

To crude **22** in EtOH (10 mL) was added aqueous 6 *N* NaOH (5 mL). The air was replaced with nitrogen, and the solution was stirred at rt for 6 h. Et_2O (50 mL.) was added, the organic layer was separated, the aqueous layer was washed with Et_2O (2×50 mL), dried (K_2CO_3), and filtered. Concentration afforded **23** as a white solid residue (195 mg, 68% two steps from **21**). To a solution of the crude amine **23** in THF (5 mL) were added Et_3N (163 μL, 1.17 mmol) and *n*-hexacosanoyl chloride[S8,S9] (0.281 mmol, in 1 mL of THF) at 0 °C. The mixture was stirred at rt for 30 min, quenched with saturated aqueous NH_4Cl solution, and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by flash chromatography (EtOAc/hexanes 1:3 to 1:2) to yield amide **24** (208 mg, 73%): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 6H), 1.15-1.42 (m, 70H), 1.50-1.65 (m, 2H), 2.15 (t, *J* = 7.1 Hz, 2H), 2.65 (br s, 1H), 3.16 (br s, 1H), 3.42-3.53 (m, 1H), 3.55-3.63 (m, 1H), 3.78-3.83 (m, 1H), 3.90-3.93 (m, 1H), 3.98 (t, *J* = 5.8 Hz, 1H), 4.08 (dd, *J* = 5.8, 9.6 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.74-4.86 (m, 4H), 4.93 (d, *J* = 11.4 Hz, 1H), 5.00 (d, *J* = 7.7 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 7.22-7.46 (m, 20H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 25.9, 29.25, 29.32, 29.34, 29.48, 29.53, 29.59, 29.63, 29.68, 31.9, 33.5, 36.5, 42.9, 67.3, 68.6, 72.5, 72.7, 72.9, 73.5, 73.7, 74.4, 74.7, 74.8, 75.5, 79.79, 79.83, 85.0, 127.62, 127.95, 127.8, 127.96, 128.02, 128.08, 128.2, 128.4, 128.5, 137.4, 137.6, 138.3, 138.5, 146.1, 172.3; **HRMS** (ESI, MH^+) *m*/*z* calcd for $C_{79}H_{122}NO_8^+$ 1212.9165, found 1212.9184.



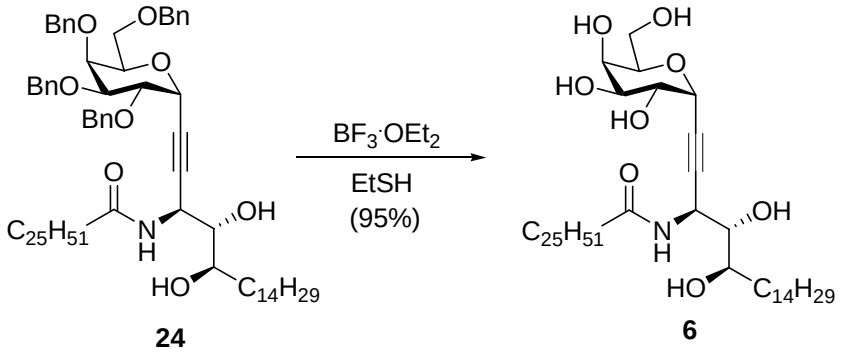
24 **2**

***N*-((3*S*,4*S*,5*R*)-1-(α-*C*-D-Galactopyranosyl)-nonadecane-4,5-diol-3-yl)-hexacosanamide (2).**

Amide **24** (48 mg, 0.040 mmol) was suspended in EtOH (95%)/TFA (30:1, 10.3 mL) at rt. After Pd/C (100 mg, 10% Pd) was added, the reaction vessel was purged with H_2 for 10 min. The mixture was stirred at rt for 48 h under a balloon filled with H_2. The suspension was filtered through Celite, which was washed with $CHCl_3$/MeOH (1:1, 30 mL) followed by pyridine (20 mL). The filtrate was concentrated, and the residue was purified by flash chromatography ($CHCl_3$/MeOH 8:1) and was then lyophilized with benzene to afford **2** (24 mg, 71%) as a white powder: $[\alpha]^{25}_D$ +33.7 (*c* 0.2, pyridine) [lit.[8] $[\alpha]^{25}_D$ +38.4 (*c* 0.13, pyridine); lit.[9] $[\alpha]^{25}_D$ +40.8 (*c* 0.13, pyridine)]; **^{1}H NMR** (500 MHz, d_5-pyridine) δ 0.87 (t, *J* = 6.4 Hz, 6H), 1.16-1.50 (m, 66H), 1.66-1.76 (m, 1H), 1.82-1.91 (m, 2H), 1.90-2.01 (m, 2H), 2.17-2.27 (m, 1H), 2.28-2.40 (m, 2H), 2.43-2.52 (m, 2H), 2.57-2.67 (m, 1H), 2.71-2.80 (m, 1H), 4.19-4.29 (m, 4H), 4.38 (dd, *J* = 4.6, 11.2 Hz, 1H), 4.50-4.57 (m, 3H), 4.76 (dd, *J* = 5.5, 8.9 Hz, 1H), 5.14-5.21 (m, 1H), 8.55 (d, *J* = 9.0 Hz, 1H); **^{13}C NMR** (125 MHz, d_5-pyridine) δ 14.8, 23.4, 26.9, 30.1, 30.1, 30.3, 30.5, 30.7, 32.6, 34.9, 37.4, 53.1, 63.2, 70.8, 71.1, 72.7, 73.0, 74.2, 77.6, 79.0, 173.8; **HRMS** (ESI, MH^+) *m*/*z* calcd for $C_{51}H_{101}NNaO_8^+$ 878.7419, found 878.7420. Table S1 shows that the ^{1}H and ^{13}C NMR spectra and the $[\alpha]^{25}_D$.value are in full agreement with the literature data.[S9,S10]

Table S1. Comparison of ^{1}H and ^{13}C NMR data and $[\alpha]^{25}_{D}$.value

	Ref. S10	Ref. S9	Our data
^{1}H (500 MHz, d_5-pyridine)	8.47 (d, *J* = 8.8 Hz, 1H) 5.14 (m, 1H) 4.74 (dd, *J* = 5.8, 8.8 Hz, 1H) 4.52 (m, 3H) 4.37 (dd, *J* = 4.3, 11.0 Hz, 1H) 4.25 (m, 4H) 2.72 (m, 1H) 2.59 (m, 1H) 2.48 (m, 1H) 2.33 (m, 2H) 2.22 (m, 1H) 1.94 (m, 2H) 1.86 (m, 3H) 1.71 (m, 1H) 1.37 (m, 64H) 0.88 (t, *J* = 6.4 Hz, 6H)	8.37 (d, 1 H, *J* = 8.9 Hz) 5.09 (dd, 1 H) 4.70 (dd, *J* = 5.5, 8.7 Hz, 1H) 4.55-4.43 (m, 3 H) 4.35 (dd, *J* = 4.5, 11.2 Hz, 1H) 4.26-4.15 (m, 4 H) 2.75-2.62 (m, 1 H) 2.61-2.51 (m, 1 H) 2.51-2.37 (m, 2 H) 2.37-2.25 (m, 2 H) 2.25-2.13 (m, 1 H) 2.00-1.78 (m, 4 H) 1.78-1.61 (m, 1 H) 1.50-1.21 (m, 68 H) 0.89 (t, *J* = 6.4 Hz, 6 H)	8.55 (d, J = 9.0 Hz, 1H) 5.21-5.14 (m, 1H) 4.76 (dd, *J* = 5.5, 8.9 Hz, 1H) 4.57-4.50 (m, 3H) 4.38 (dd, *J* = 4.6, 11.2 Hz, 1H) 4.29-4.19 (m, 4H) 2.80-2.71 (m, 1H) 2.67-2.57 (m, 1H) 2.52-2.43 (m, 2H) 2.40-2.28 (m, 2H) 2.27-2.17 (m, 1H) 2.01-1.90 (m, 2H) 1.91-1.82 (m, 2H) 1.76-1.66 (m, 1H) 1.50-1.16 (m, 66H) 0.87 (t, *J* = 6.4 Hz, 6H)
^{13}C (125 MHz, d_5-pyridine)	173.8, 78.8, 77.3, 74.0, 73.0, 72.5, 70.9, 70.7, 63.1, 53.0, 37.3, 34.8, 32.4, 30.7, 30.5, 30.3, 30.1, 29.9, 26.9, 23.3, 14.6	173.8, 78.8, 77.3, 74.1, 73.0, 72.5, 70.9, 70.8, 63.1, 53.1, 37.3, 34.8, 32.4, 30.7, 30.5, 30.3, 30.1, 29.9, 26.9, 23.0, 14.6	173.8, 79.0, 77.6, 74.2, 73.0, 72.7, 71.1, 70.8, 63.2, 53.1, 37.4, 34.9, 32.6, 30.7, 30.5, 30.3, 30.1, 30.1, 26.9, 23.4, 14.8
$[\alpha]^{25}_{D}$	+40.8 (*c* 0.13 pyridine)	+38.4 (*c* 0.13 pyridine)	+33.7 (*c* 0.20 pyridine)



24 **6**

***N*-((3*S*,4*S*,5*R*)-1-(α-*C*-D-Galactopyranosyl)-nonadec-1-ynyl-4,5-diol-3-yl)-hexacosanamide (6).**

A solution of **24** (9.5 mg, 7.83 μmol) in EtSH/BF_3·OEt_2 (3:1, 1.3 mL) was stirred at rt for 24 h. The solvent was evaporated, and the residue was purified by column chromatography ($CHCl_3$/MeOH 10:1) and lyophilized with benzene to afford **6** (6.3 mg, 95%) as a white powder: $[\alpha]^{25}_D$ +62.2 (*c* 0.09, pyridine); **^{1}H NMR** (400 MHz, d_5-pyridine) δ 0.85-0.90 (m, 6H), 1.16-1.52 (m, 66H), 1.65-1.84 (m, 3H), 1.86-1.98 (m, 2H), 2.29-2.38 (m, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 4.26 (dd, *J* = 3.1, 8.3 Hz, 1H), 4.33-4.43 (m, 2H), 4.47-4.57 (m, 3H), 4.70-4.79 (m, 2H), 5.30 (dd, *J* = 1.6, 5.9 Hz, 1H), 6.36 (dt, *J* = 2.2, 8.8 Hz, 1H), 9.23 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR** (100 MHz, d_5-pyridine) δ 14.7, 23.4, 26.7, 30.1, 30.22, 30.26, 30.30, 30.39, 30.46, 30.50, 30.6, 30.9, 32.6, 35.3, 37.1, 46.1, 63.0, 69.8, 71.0, 71.2, 73.1, 73.4, 76.2, 78.5, 81.5, 87.6, 172.8; **HRMS** (ESI, MH^+) *m*/*z* calcd for $C_{51}H_{98}NO_8^+$ 852.7287, found 852.7287.

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(S1) (a) Cohen, R. B.; Tsou, K.-C.; Rutenburg, S. H.; Seligman, A. M. *J. Biol. Chem.* **1952**, *195*, 239. (b) Hansen, R. G.; Rutter, W. J.; Krichevsky, P. *Biochem. Prep.* **1955**, *4*, 1. (c) Backinowsky, L. V.; Nepogod'ev, S. A.; Shashkov, A. S.; Kochetkov, N. K. *Carbohydr. Res.* **1985**, *138*, 41. (d) Maier, M. A.; Yannopoulos, C. G.; Mohamed, N.; Roland, A.; Fritz, H.; Mohan, V.; Just, G.; Manoharan, M. *Bioconj. Chem.* **2003**, *14*, 18. (e) Wang, Z. D.; Matin, M.; Sheikh, S. *Molecules* **2005**, *10*, 1325. (f) Bizier, N. P.; Atkins, S. R.; Helland, L. C.; Colvin, S. F.; Twitchell, J. R.; Cloninger, M. J. *Carbohydr.*

Res. **2008**, *343*, 1814. (g) Singh, U. P.; Brown, R. K. *Can. J. Chem.* **1971**, *49*, 1179. (h) Hudson, C. S.; Parker, H. O. *J. Am. Chem. Soc.* **1915**, *37*, 1589. (i) Ness, R. K.; Fletcher Jr., H. G.; Hudson, C. S. *J. Am. Chem. Soc.* **1951**, *73*, 3742.

(S2) Peracetylation of D-galactose (**A**) using Ac_2O as solvent proceeded in low yield (30% to 55%)[S1a,b] because of the formation of an α- and β-mixture of D-galactopyranose pentaacetate and D-galactofuranose pentaacetate.[S1c] Although the reaction in pyridine worked well,[S1d,e] pyridine is high boiling and noxious, and is also unsuitable for large-scale preparations.[S1f] In addition, the reaction in pyridine afforded the mixture of α and β-D-galactopyranose pentaacetates (α/β ratio 1.0:2.7) [S1g] as a colorless syrup. It was also reported that the reaction in pyridine delievered β-D-galactofuranose pentaacetes in 17% yield, which was recrystallized from 95% EtOH after removal of β-D-galactopyranose. [S1i]

(S3) (a) The preparation of **C** followed the reported procedure: Hunsen, M.; Long, D. A.; D'Ardenne, C. R.; Smith, A. L. *Carbohydr. Res*. **2005**, *340*, 2670.

(S4) (a) Mukherjee, D.; Yousut, S. K.; Taneja, S. C. *Tetradedron Lett*. **2008**, *49*, 4944. (b) Montero, J.-L.; Winum, J.-Y.; Leydet, A.; Kamal, M.; Pavia, A. A.; Roque, J.-P. *Carbohydr, Res*. **1997**, *297*, 175. (c) In addition to $InCl_3$,[S4a] we found that the use of $BiCl_3$[S4b] proceeded with high efficiency.

(S5) **D** may be directly prepared from **B** in one step. However, the R_f values of **B** and **D** are similar, making it difficult to monitor the reaction by TLC in the one-step procedure.

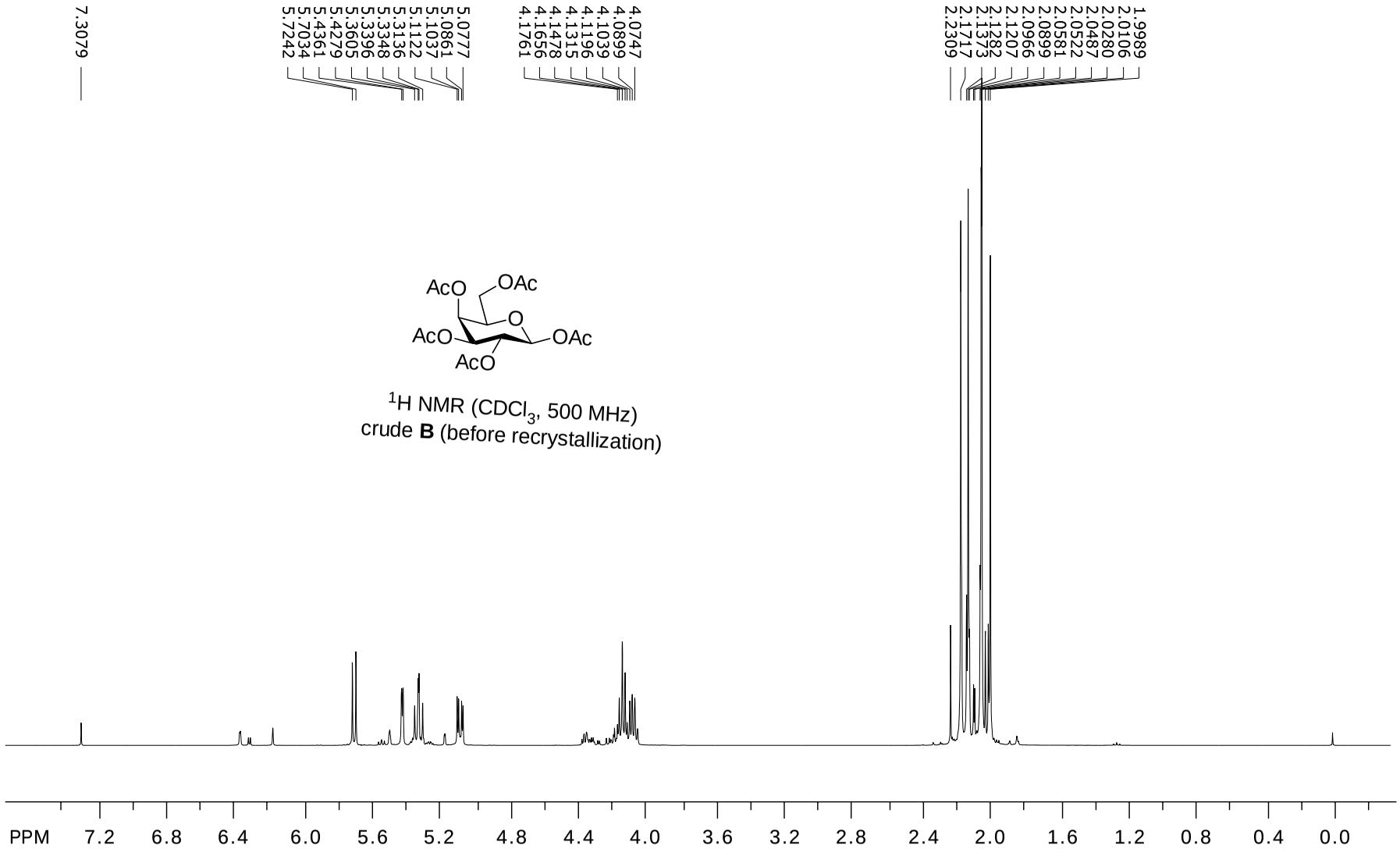
(S6) (a) Nokami, T.; Shibuya, A.; Tsuyama, H.; Suga, S.; Bowers, A. A.; Crich, D.; Yoshida, J.-I. *J. Am. Chem. Soc.* **2007**, *129*, 10922. (b) Grayson, E. J.; Ward, S. J.; Hall, A. L.; Rendle, P. M.; Gamblin, D. P.; Batsanov, A. S.; Davis, B. G. *J. Org. Chem.* **2005**, *70*, 9740. (c) Arya, P.; Barkley, A.; Randell, K. D. *J. Comb. Chem.* **2002**, *4*, 193.

(S7) (a) Nishikawa, T.; Koide, Y.; Kajii, S.; Wada, K.; Ishikawa, M.; Isobe, M. *Org. Biomol. Chem.* **2005**, *3*, 687. (b) Dondoni, A.; Moriotti, G.; Marra, A. *J. Org. Chem.* **2002**, *67*, 4475.

(S8) Heidelberg, T.; Martin, O. R. *J. Org. Chem.* **2004**, *69*, 2290.

(S9) Wipf, P.; Pierce, J. G. *Org. Lett.* **2006**, *8*, 3375.

(S10) (a) Yang, G.; Schmieg, J.; Tsuji, M.; Franck, R. W. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 3818. (b) Yang, G. Ph.D. Dissertation, The City University of New York, 2002.



^{1}H NMR ($CDCl_3$, 500 MHz)
crude **B** (before recrystallization)

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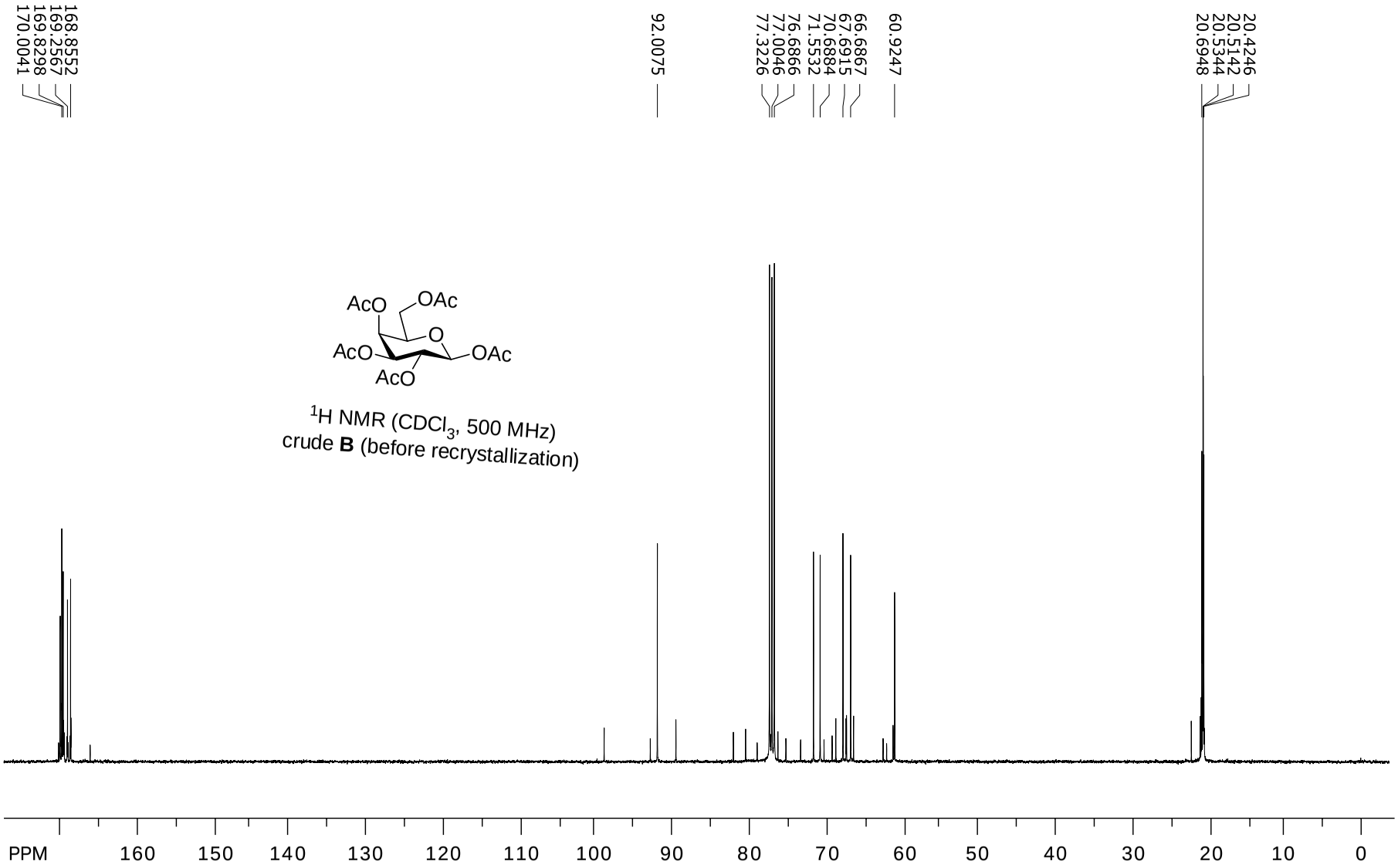
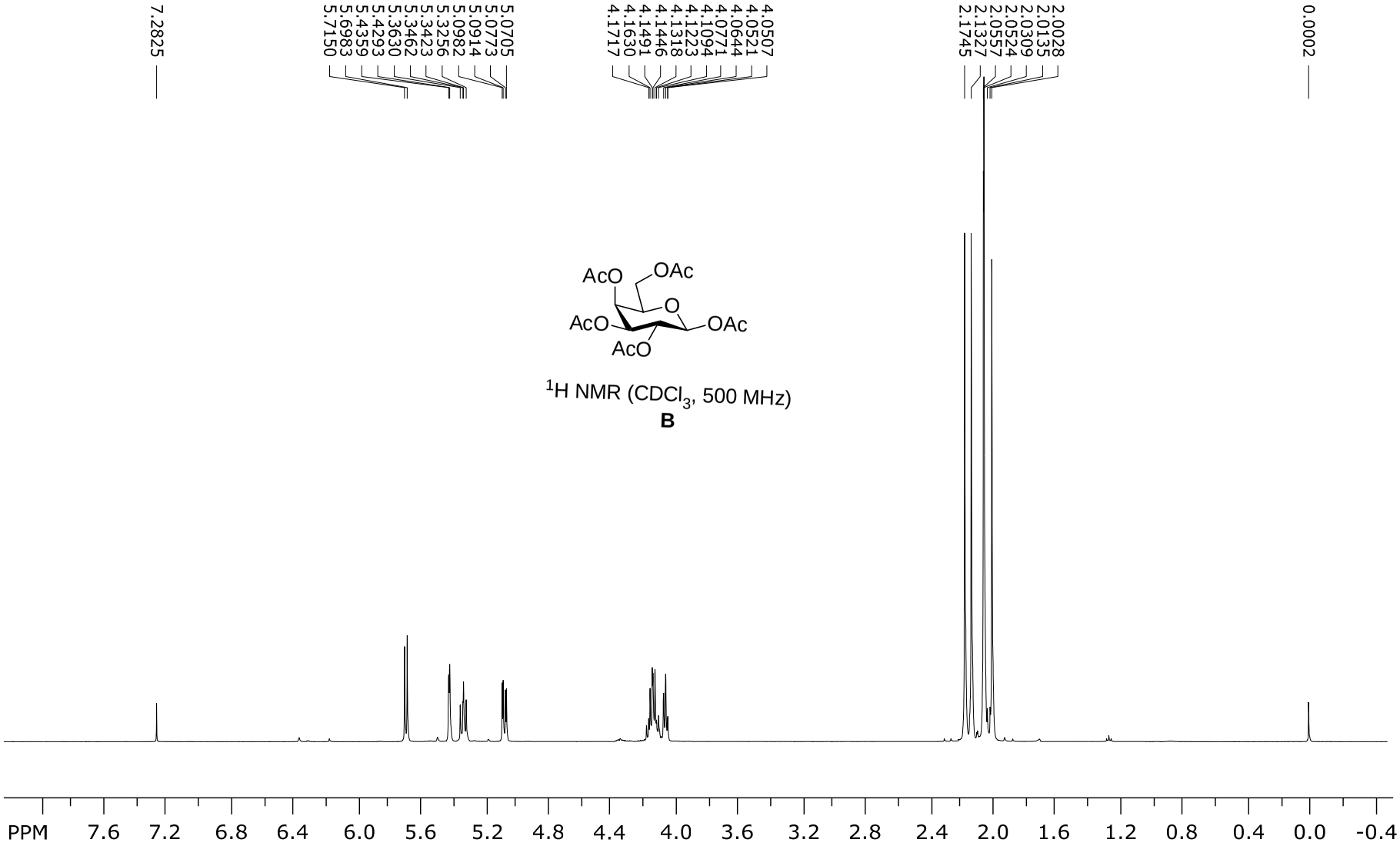
Hz/cm: 129.506 ppm/cm: 0.32366



^{1}H NMR ($CDCl_3$, 500 MHz)
crude **B** (before recrystallization)

file: ...ettings\zliu\Desktop\hb0129\11\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612778 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 730.087 ppm/cm: 7.25568

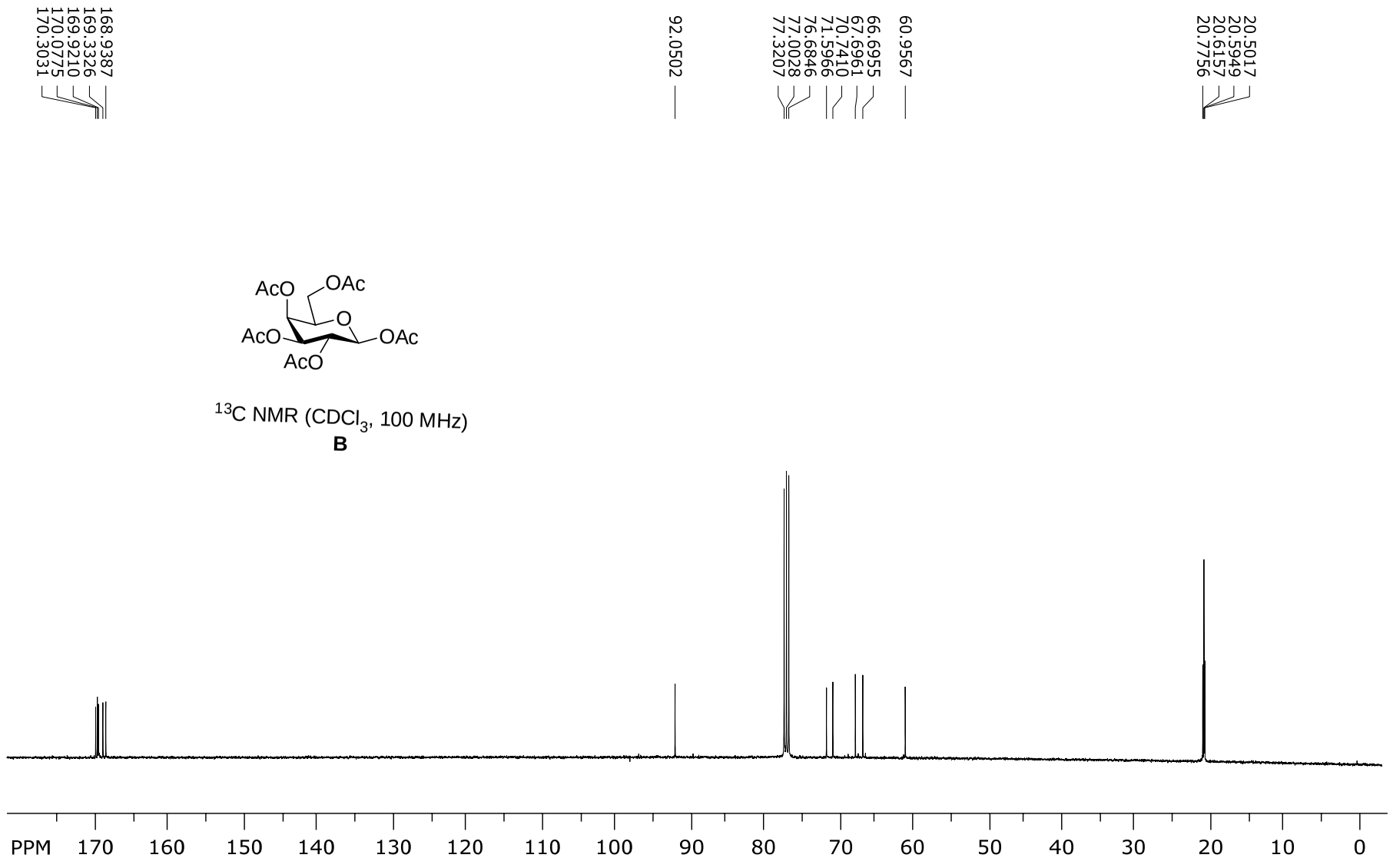


^{1}H NMR ($CDCl_3$, 500 MHz)

B

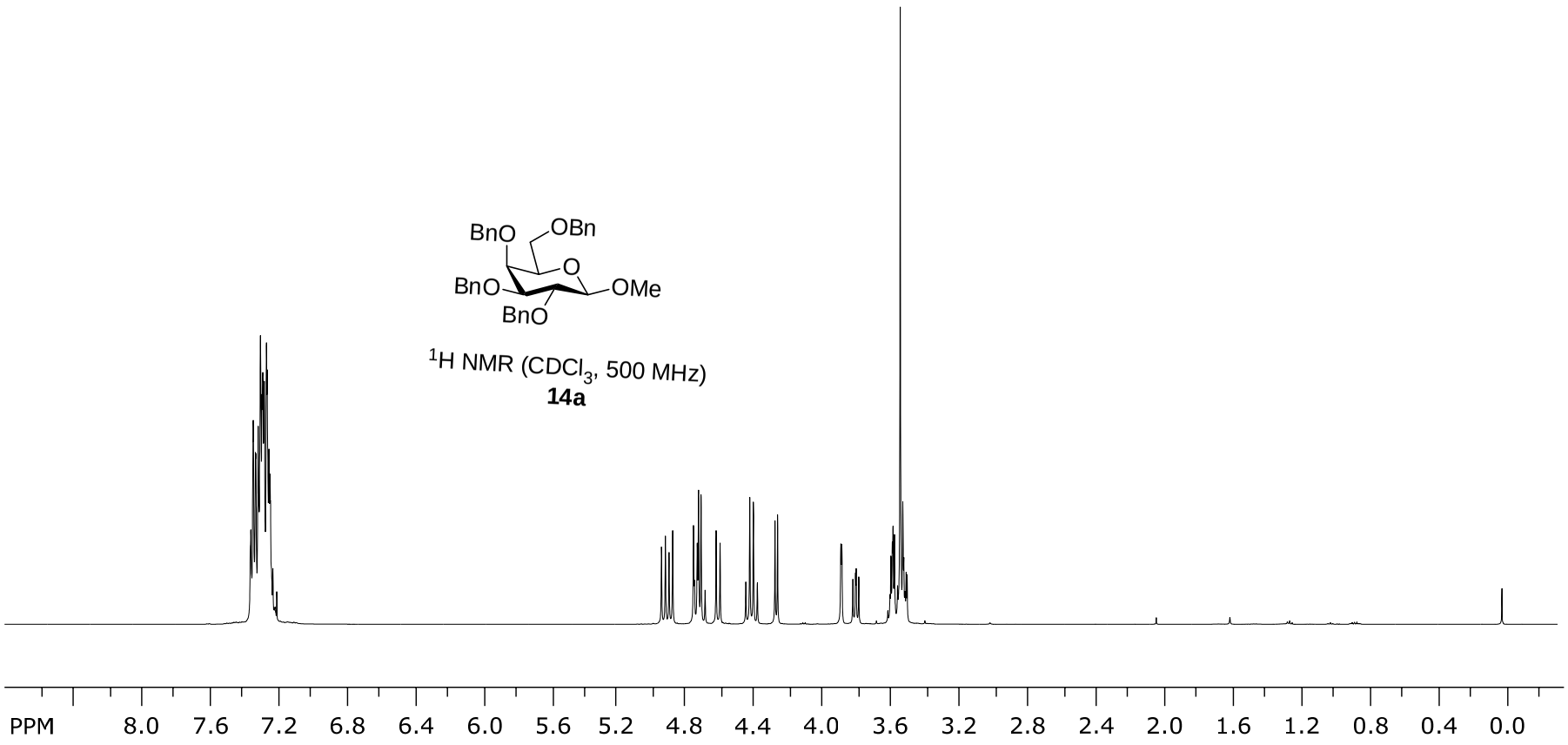
file: ... 500 3-1-2010\zh-hb-100427-2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130003 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 175.005 ppm/cm: 0.34992



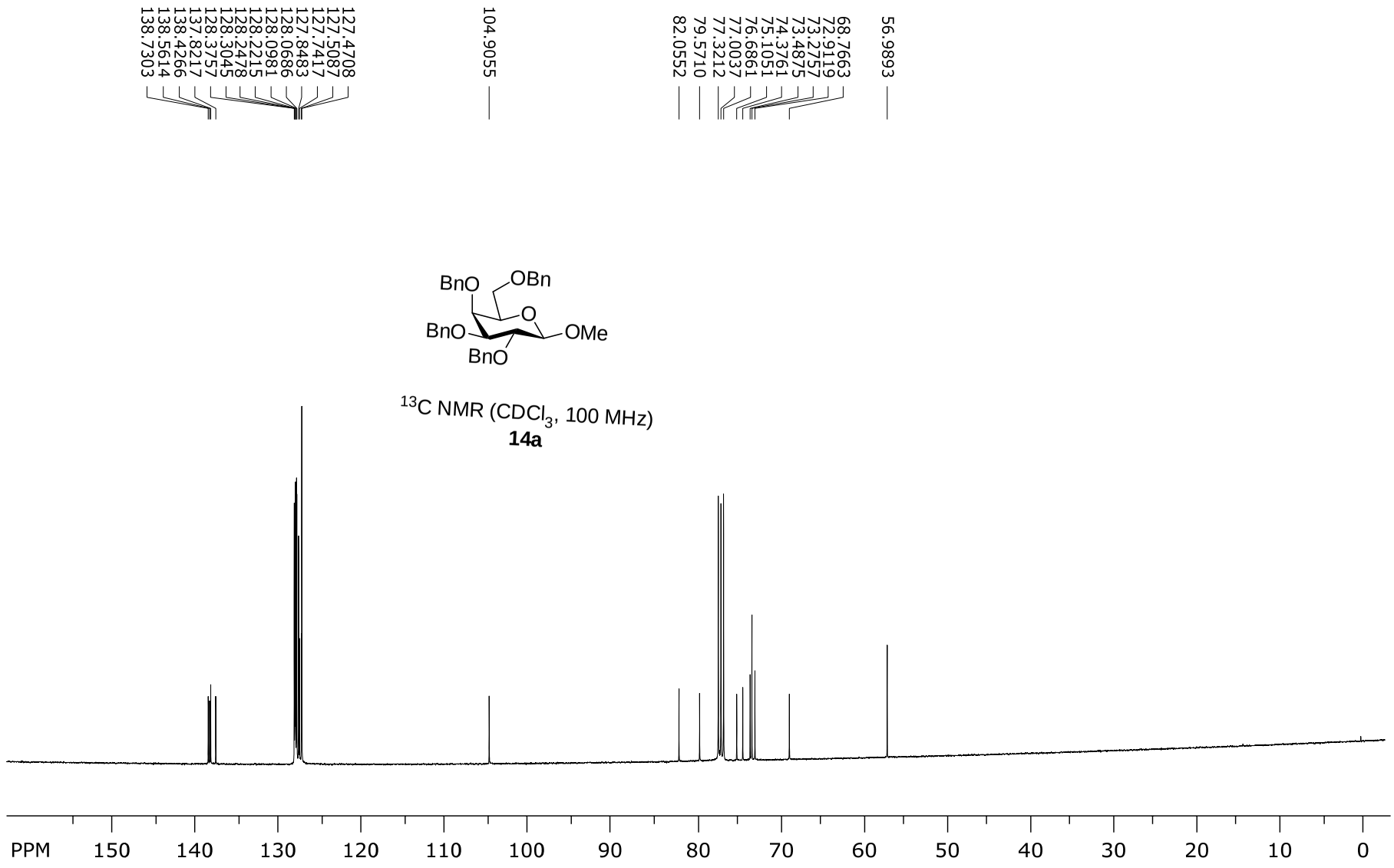
file: ... 400 3-13-10\zh-hb-100427-2\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612776 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 747.435 ppm/cm: 7.42809



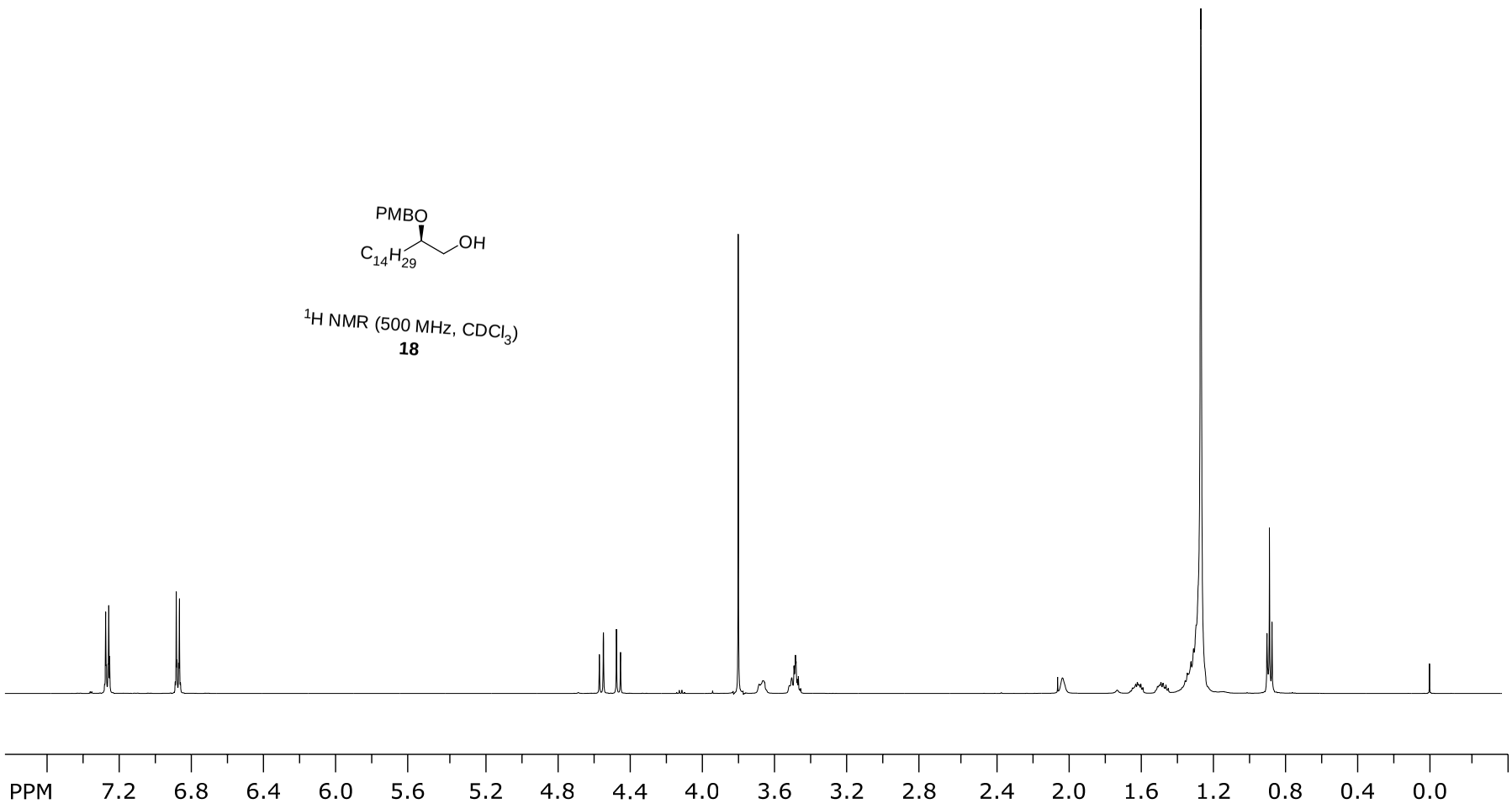
file: ... 500 3-1-2010\zh-hb-100427-1\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130034 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 183.101 ppm/cm: 0.36610



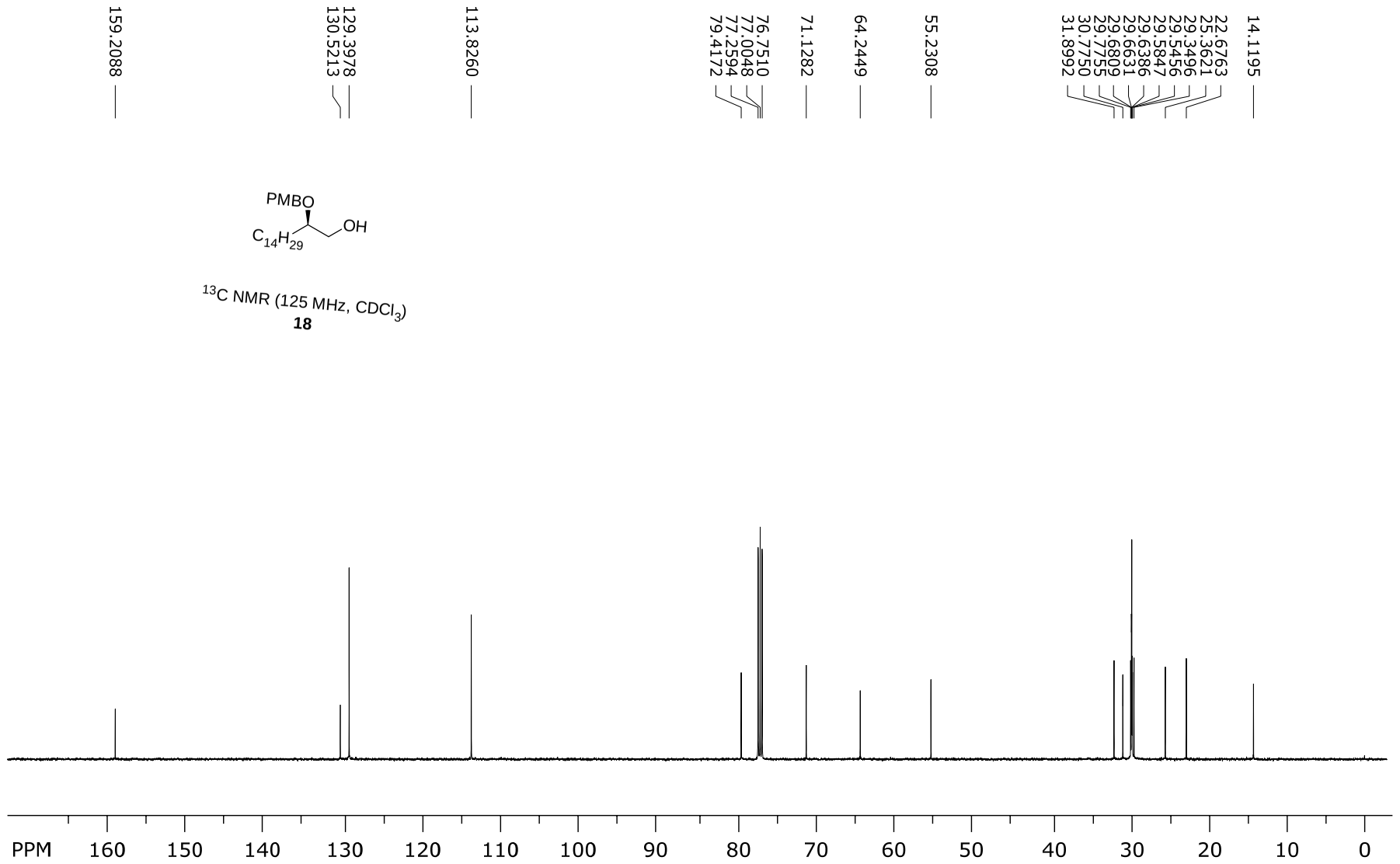
file: ... 400 3-13-10\zh-hb-100427-1\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612781 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 667.921 ppm/cm: 6.63787



file: ...\NMR 500 3-1-2010\zh091030s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

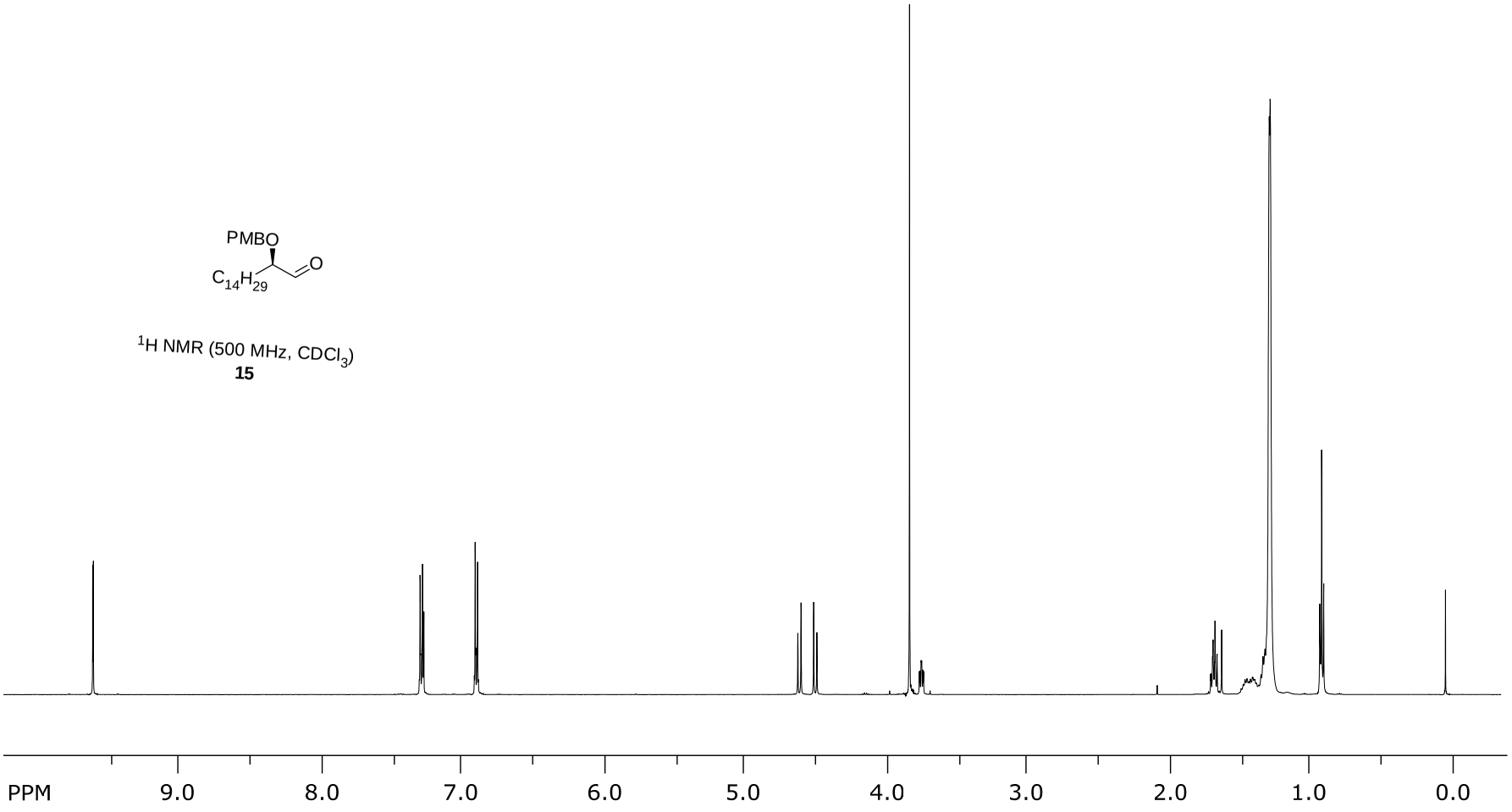
freq. of 0 ppm: 500.130013 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 164.729 ppm/cm: 0.32937



^{13}C NMR (125 MHz, $CDCl_3$)
18

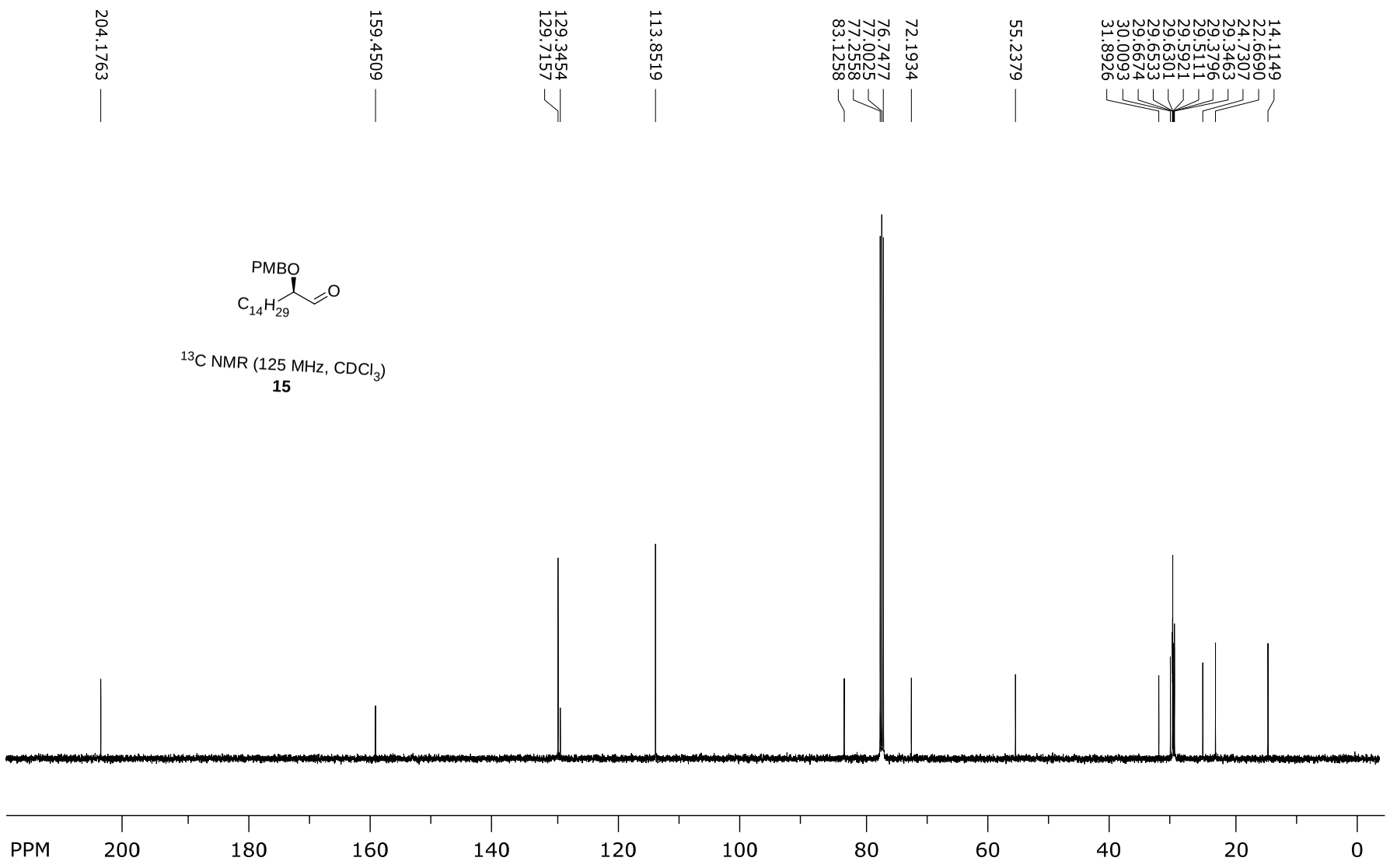
file: ...\NMR 500 3-1-2010\zh091030s2\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 1024

freq. of 0 ppm: 125.757798 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 884.514 ppm/cm: 7.03270



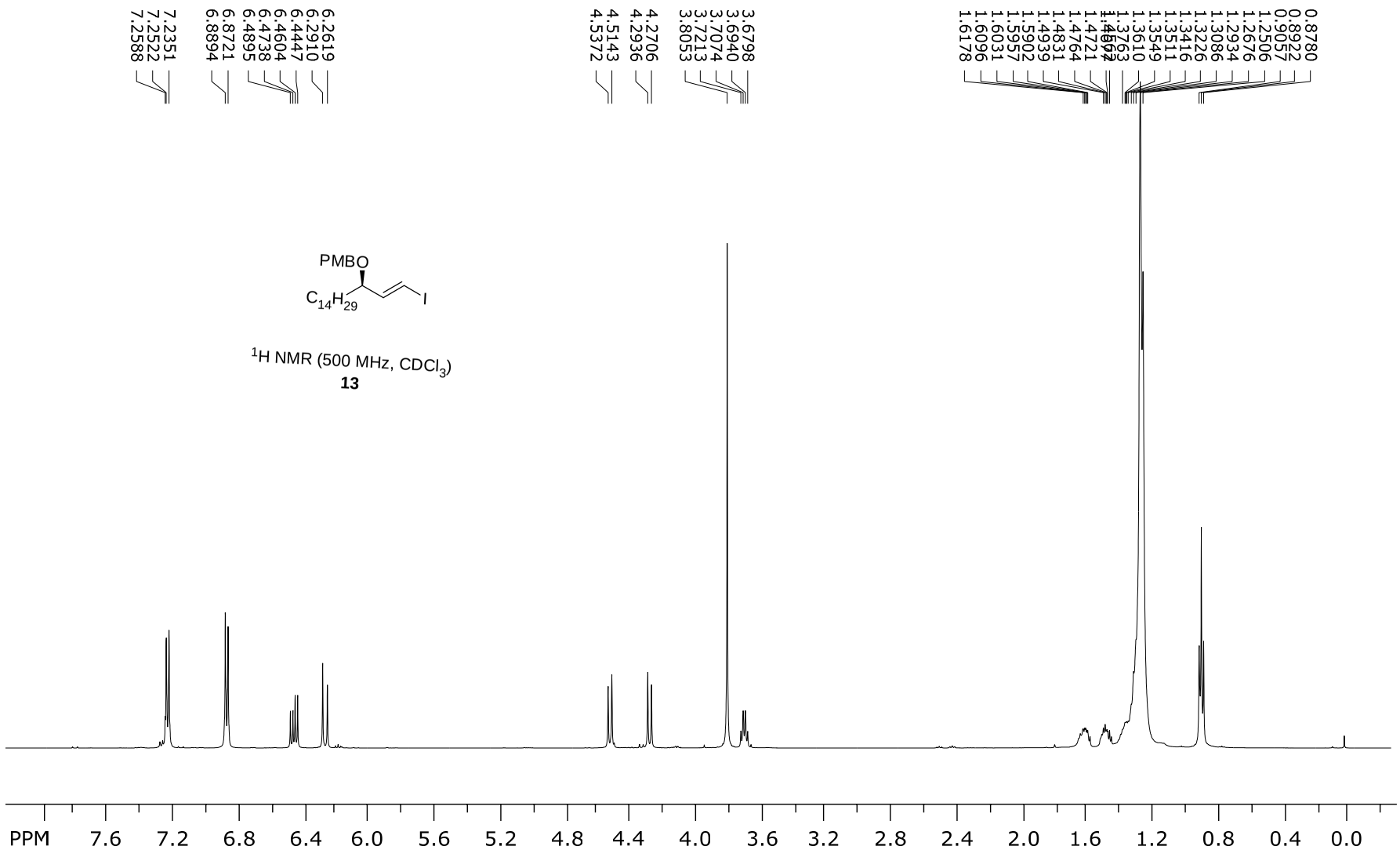
file: ...\NMR 500 3-1-2010\zh091101s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 212.995 ppm/cm: 0.42588



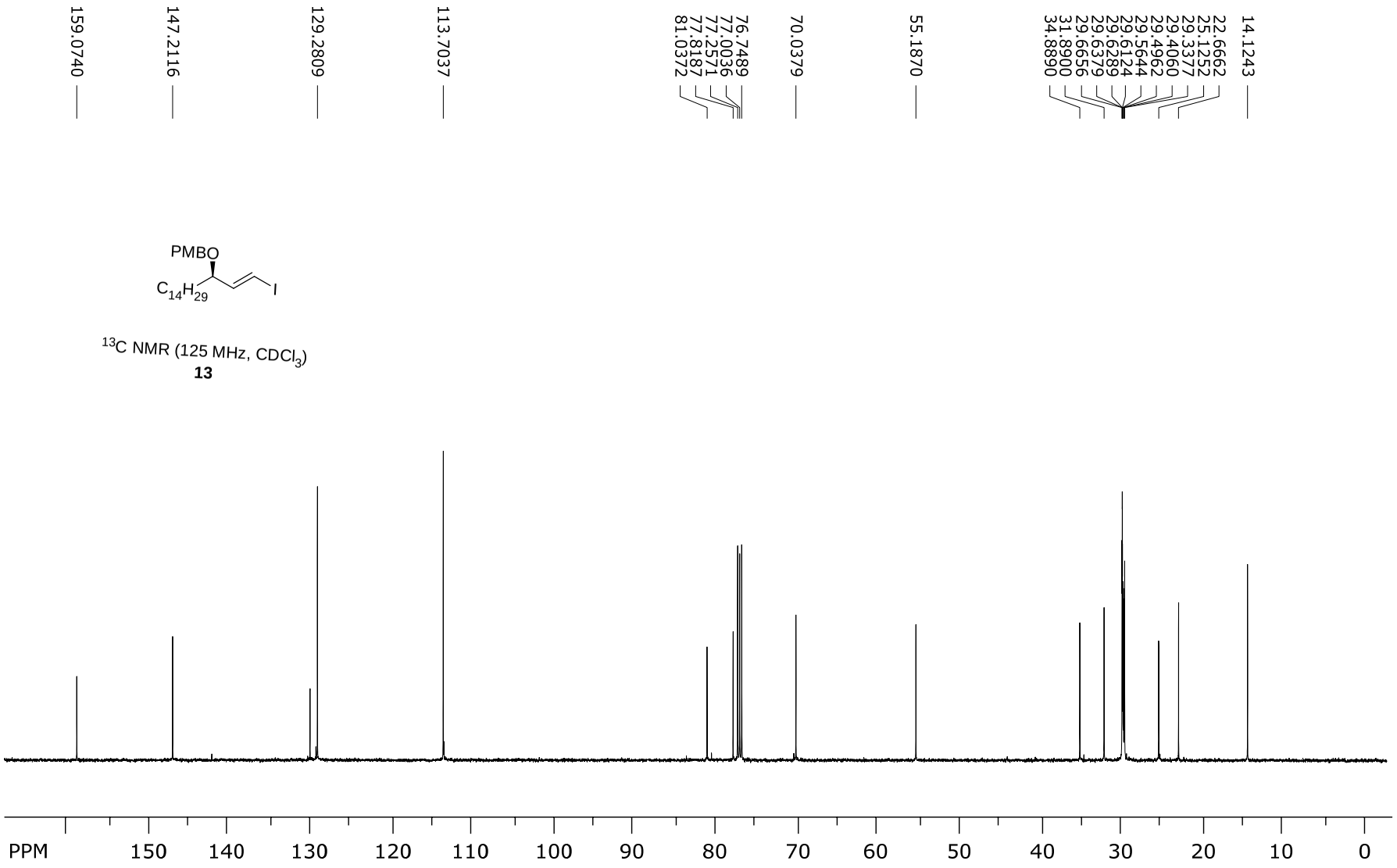
file: ...\NMR 500 3-1-2010\zh091101s2\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757798 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 1124.717 ppm/cm: 8.94254



file: ...\NMR 500 3-1-2010\zh091107s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

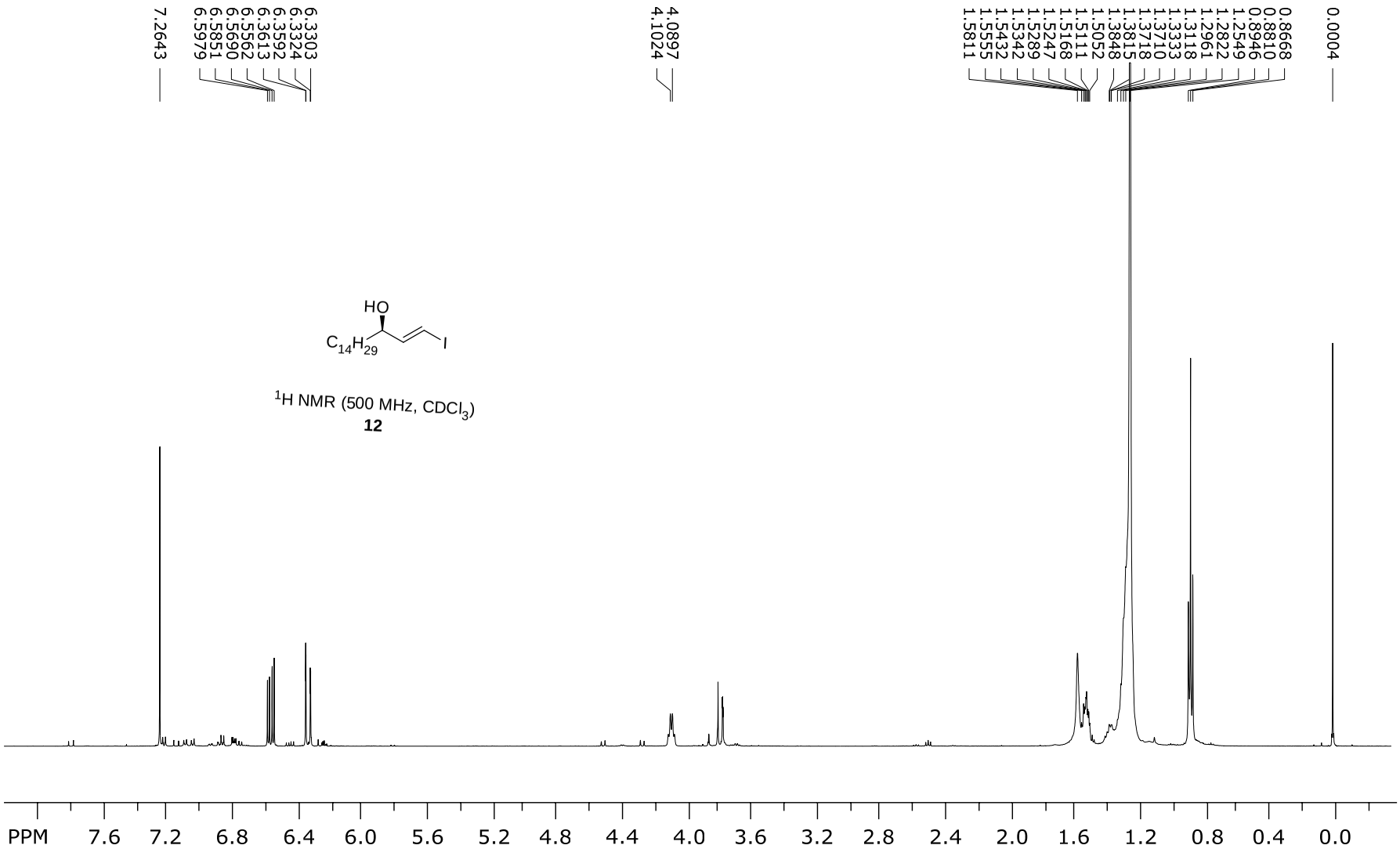
freq. of 0 ppm: 500.130015 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 170.334 ppm/cm: 0.34058



^{13}C NMR (125 MHz, $CDCl_3$)
13

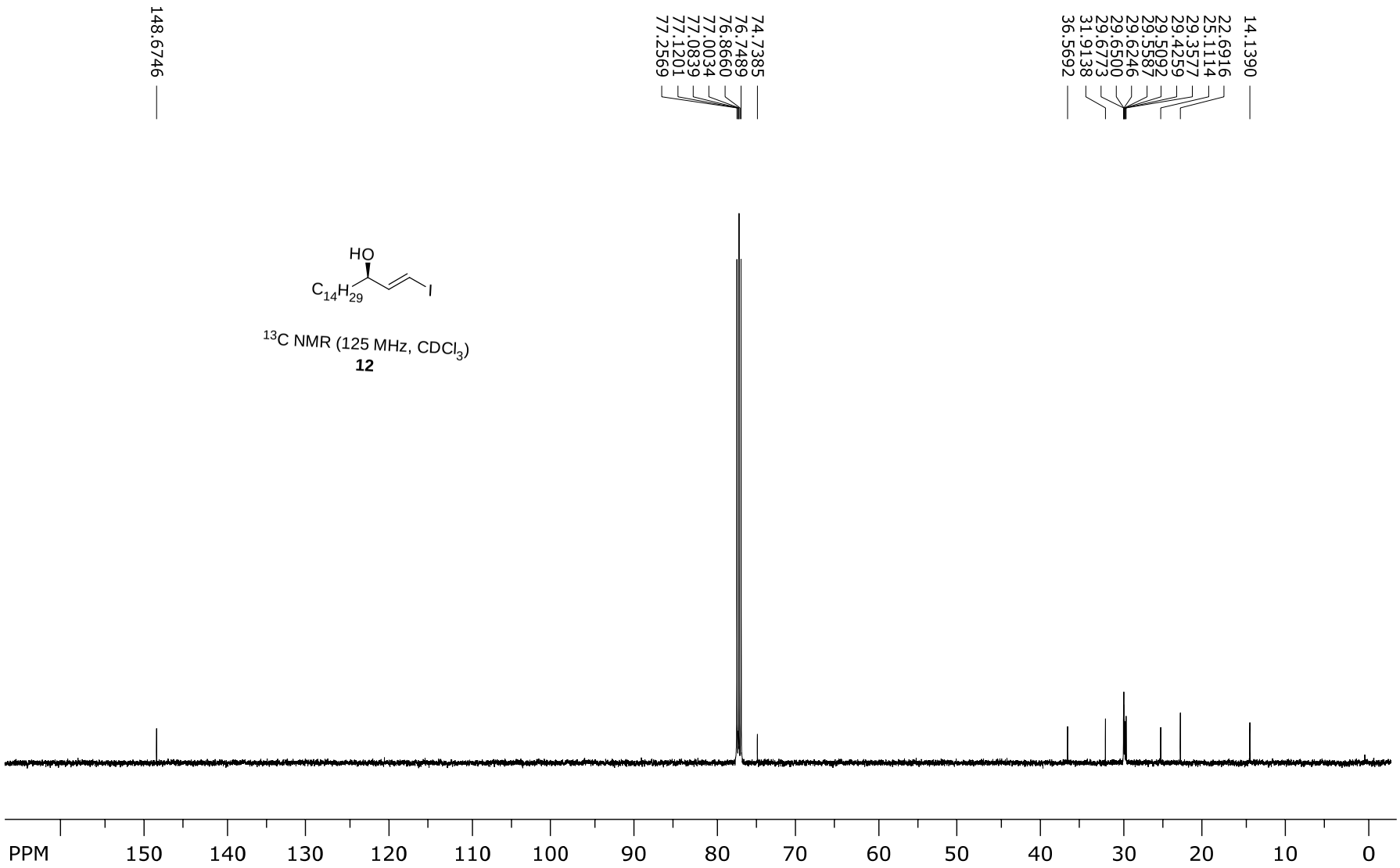
file: ...\NMR 500 3-1-2010\zh091107s2\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757802 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 860.965 ppm/cm: 6.84546



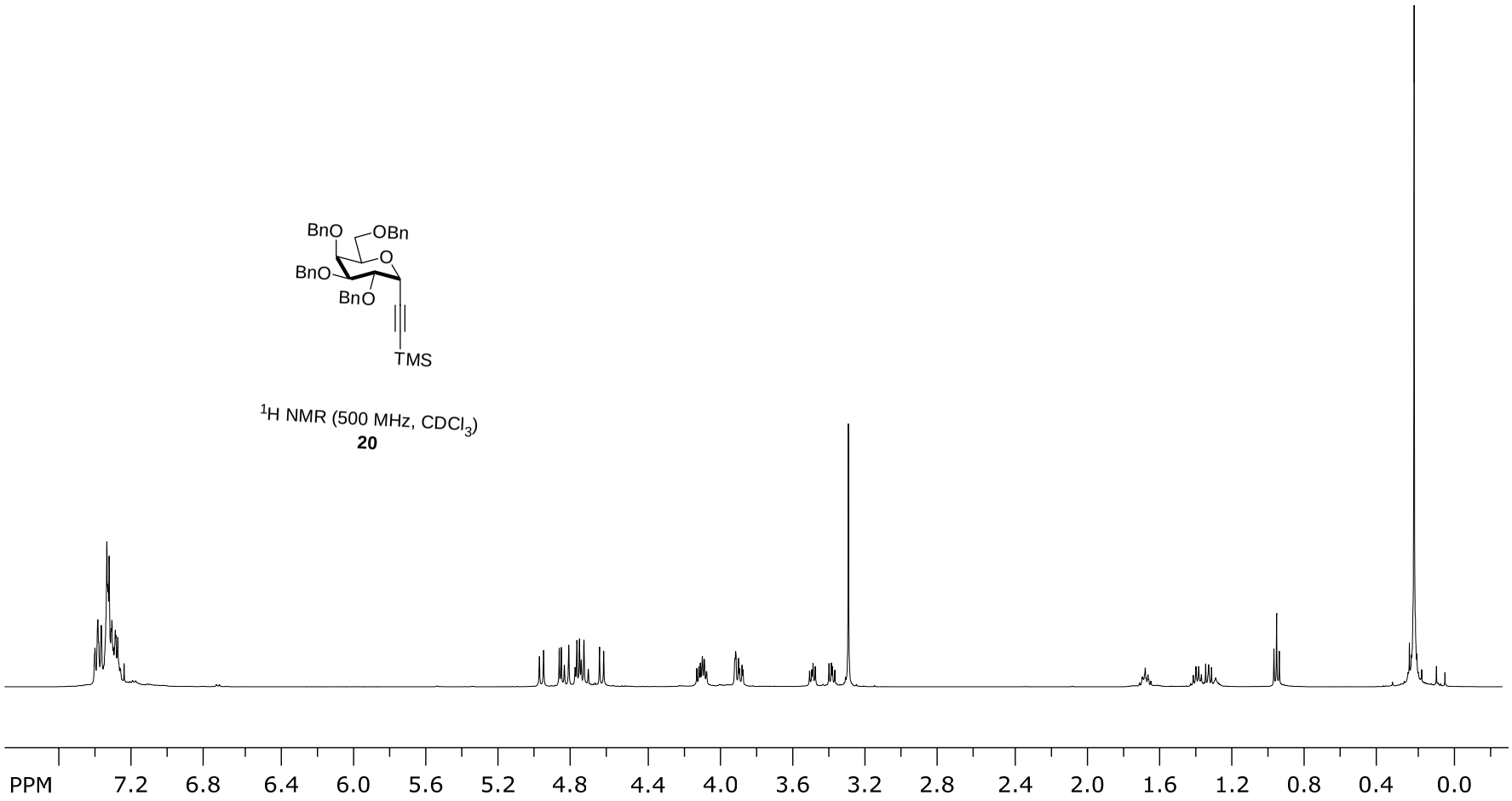
file: ...\NMR 500 3-1-2010\zh091113s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 171.891 ppm/cm: 0.34369



file: ...\NMR 500 3-1-2010\zh091113s2\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 1024

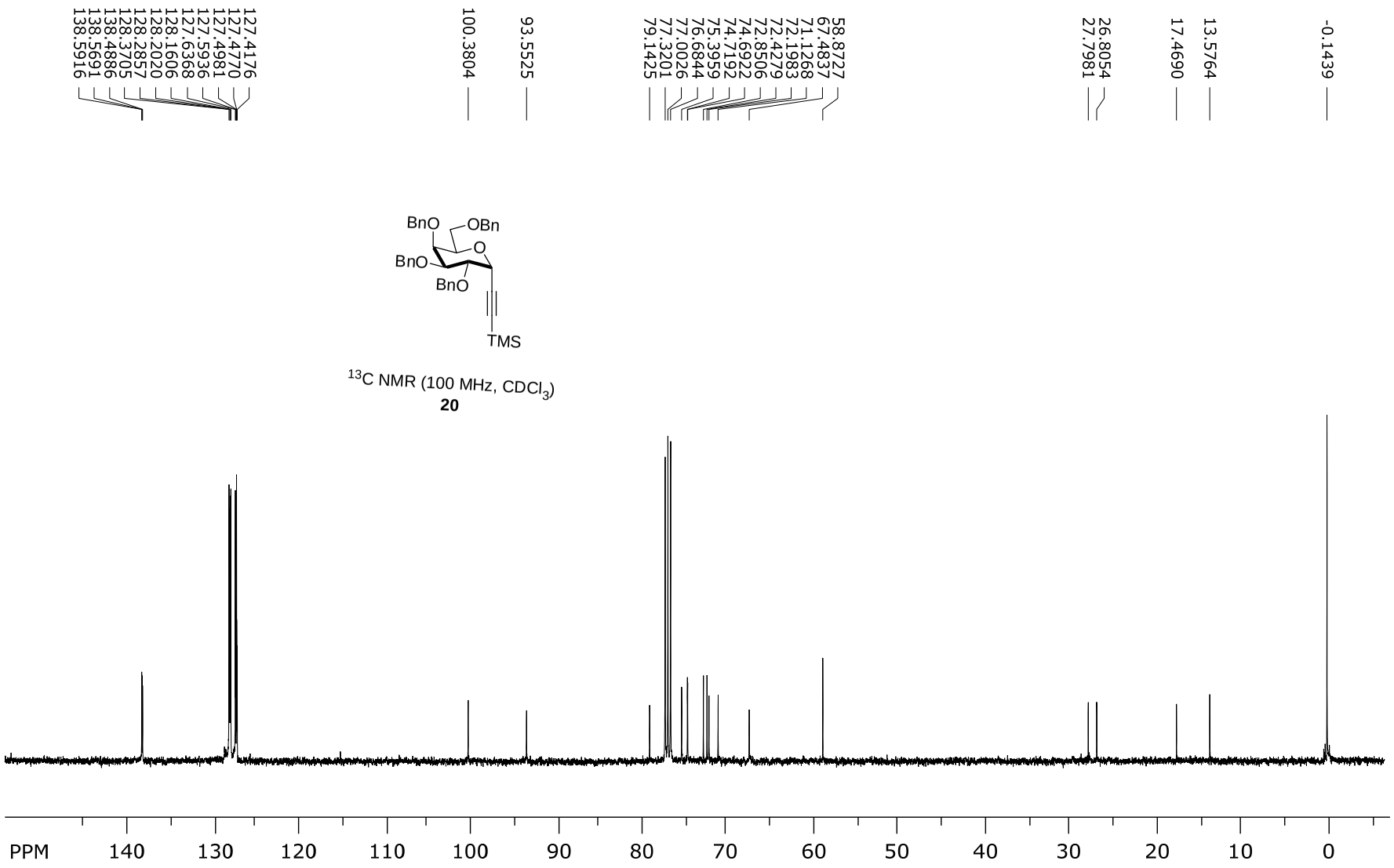
freq. of 0 ppm: 125.757795 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 858.139 ppm/cm: 6.82299



^{1}H NMR (500 MHz, $CDCl_3$)
20

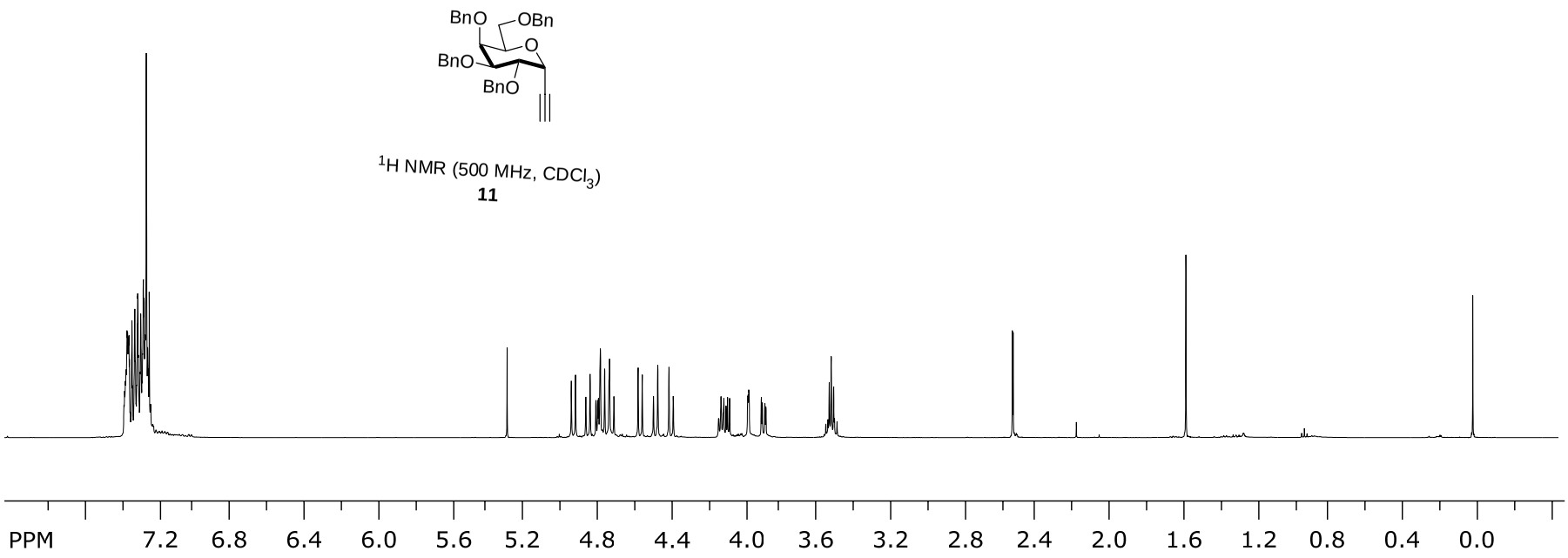
file: ...\NMR 500 3-1-2010\zh091103s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130015 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 164.106 ppm/cm: 0.32812



file: ...iu\NMR 400Hz new\zh091103s2\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

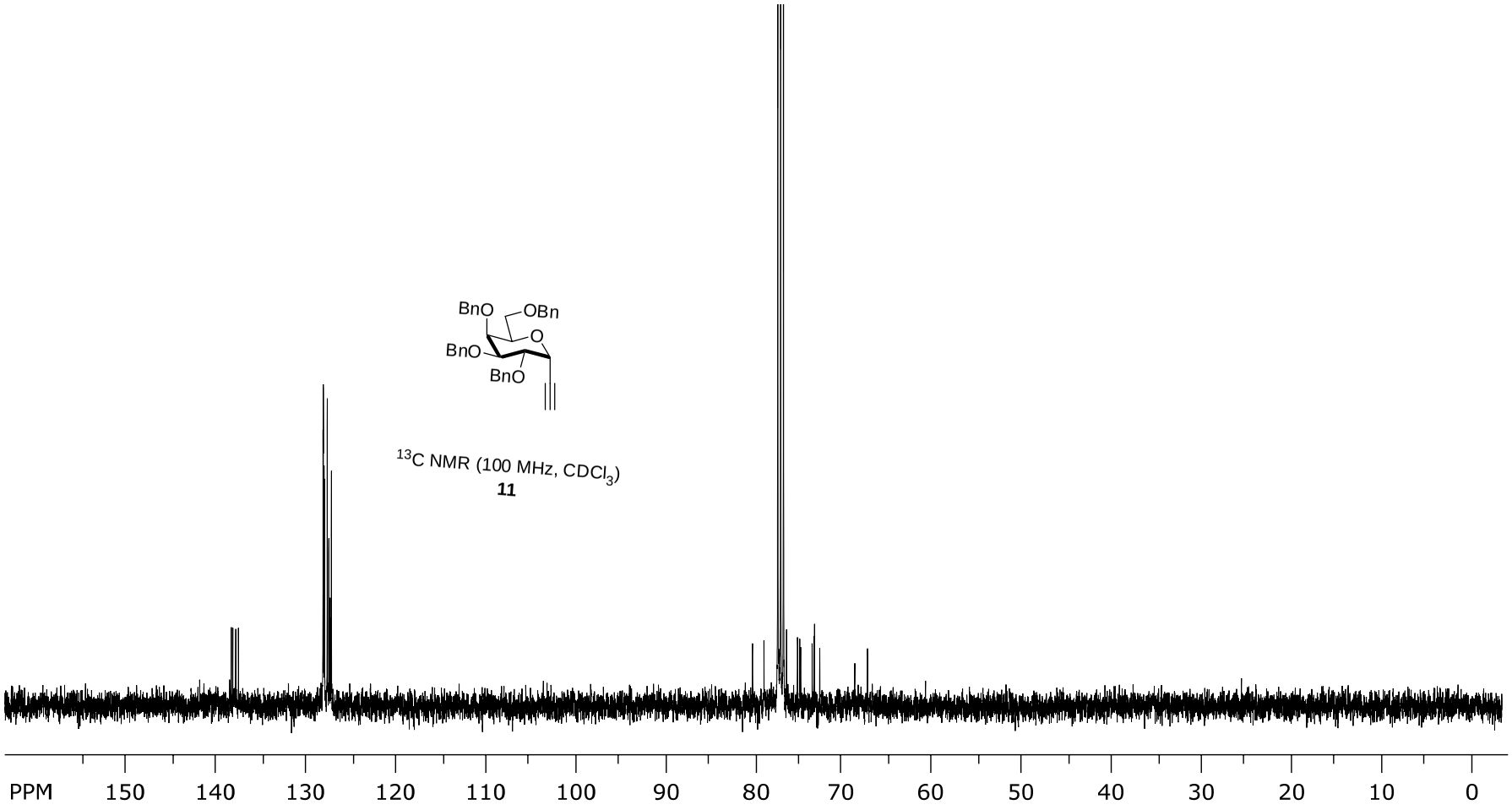
freq. of 0 ppm: 100.612778 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 649.849 ppm/cm: 6.45827



^{1}H NMR (500 MHz, $CDCl_3$)
11

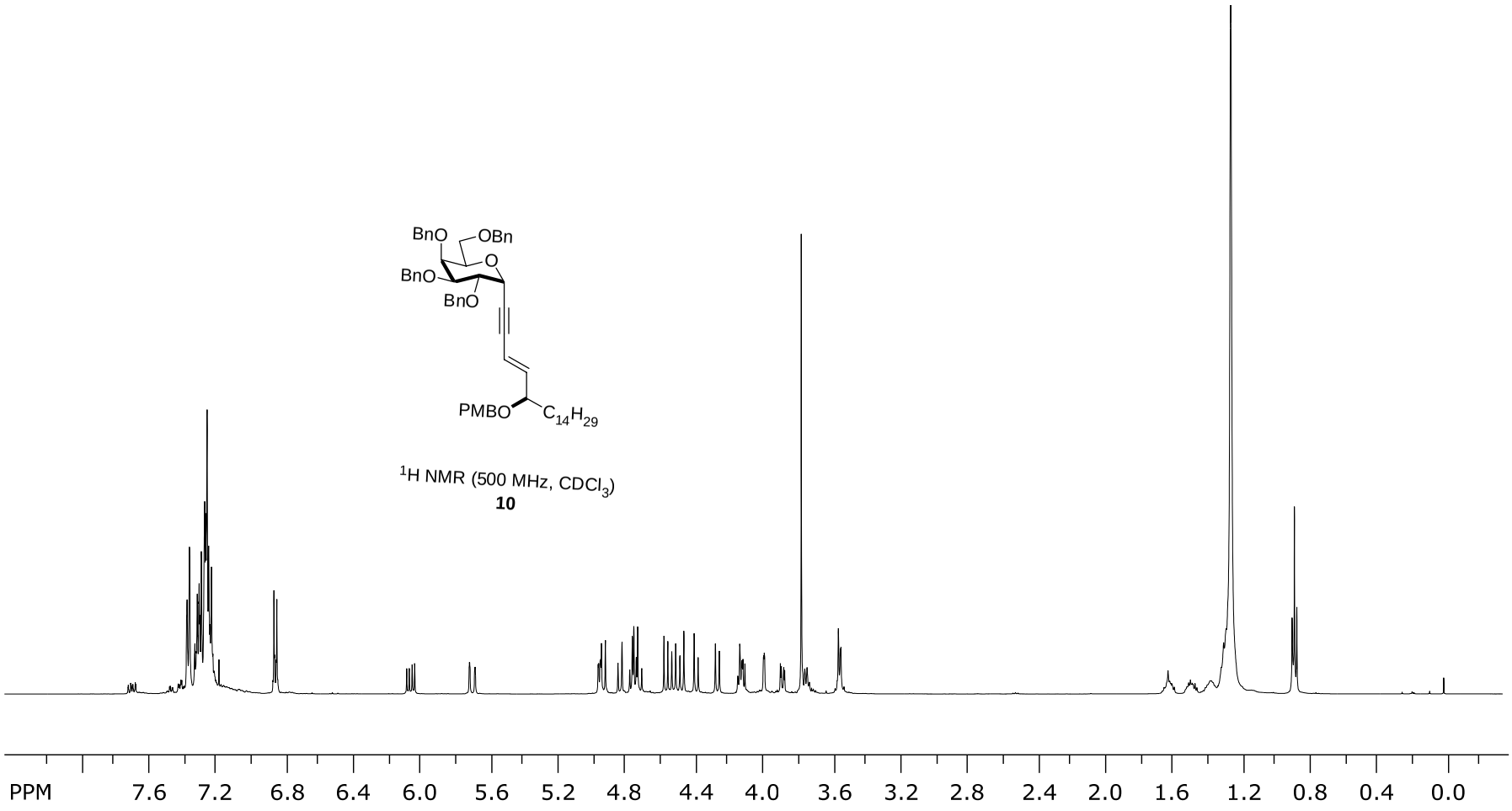
file: ...Zheng Liu\NMR 500\zh091114s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130015 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 170.334 ppm/cm: 0.34058



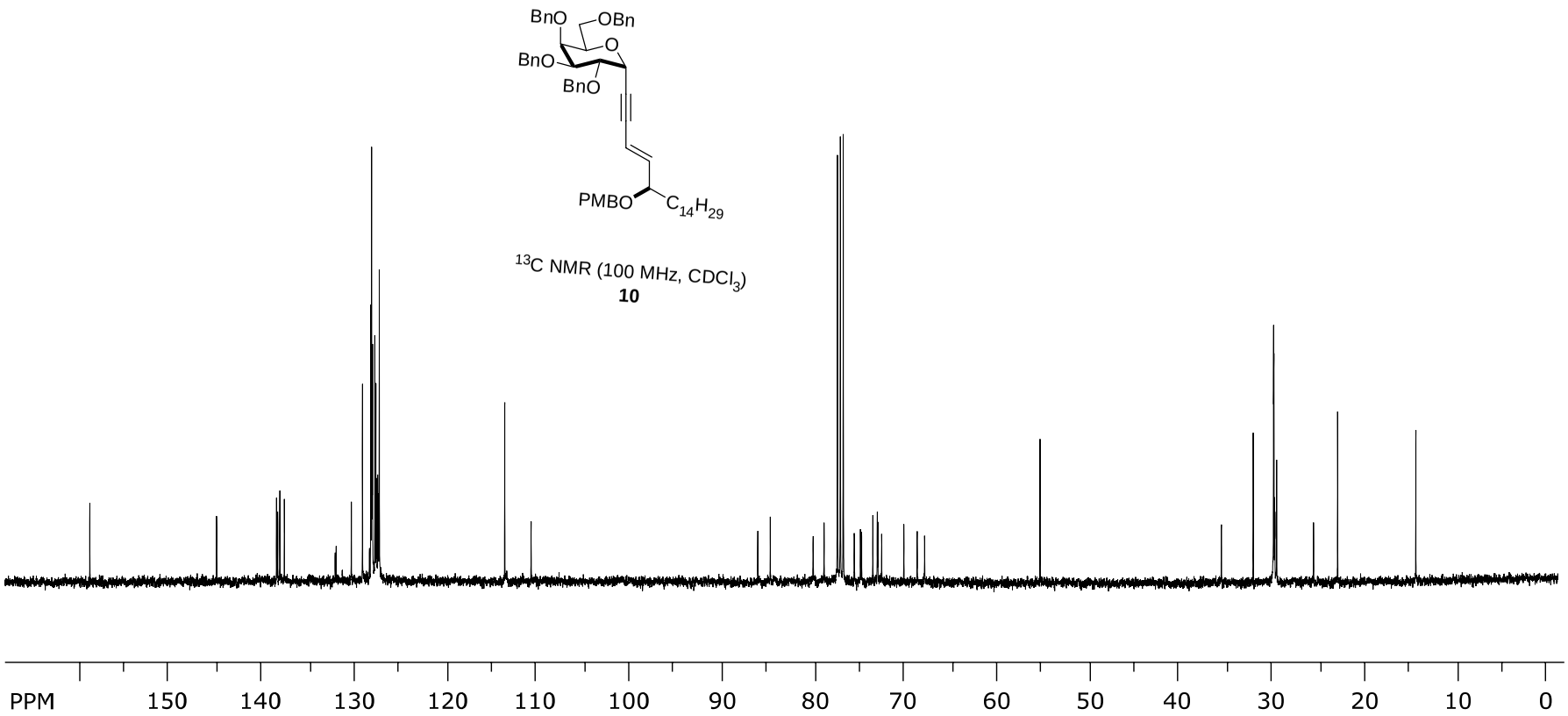
file: I:\400 MHz\zh091114s2\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612773 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 676.484 ppm/cm: 6.72296



file: ...Zheng Liu\NMR 500\zh091116s3\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

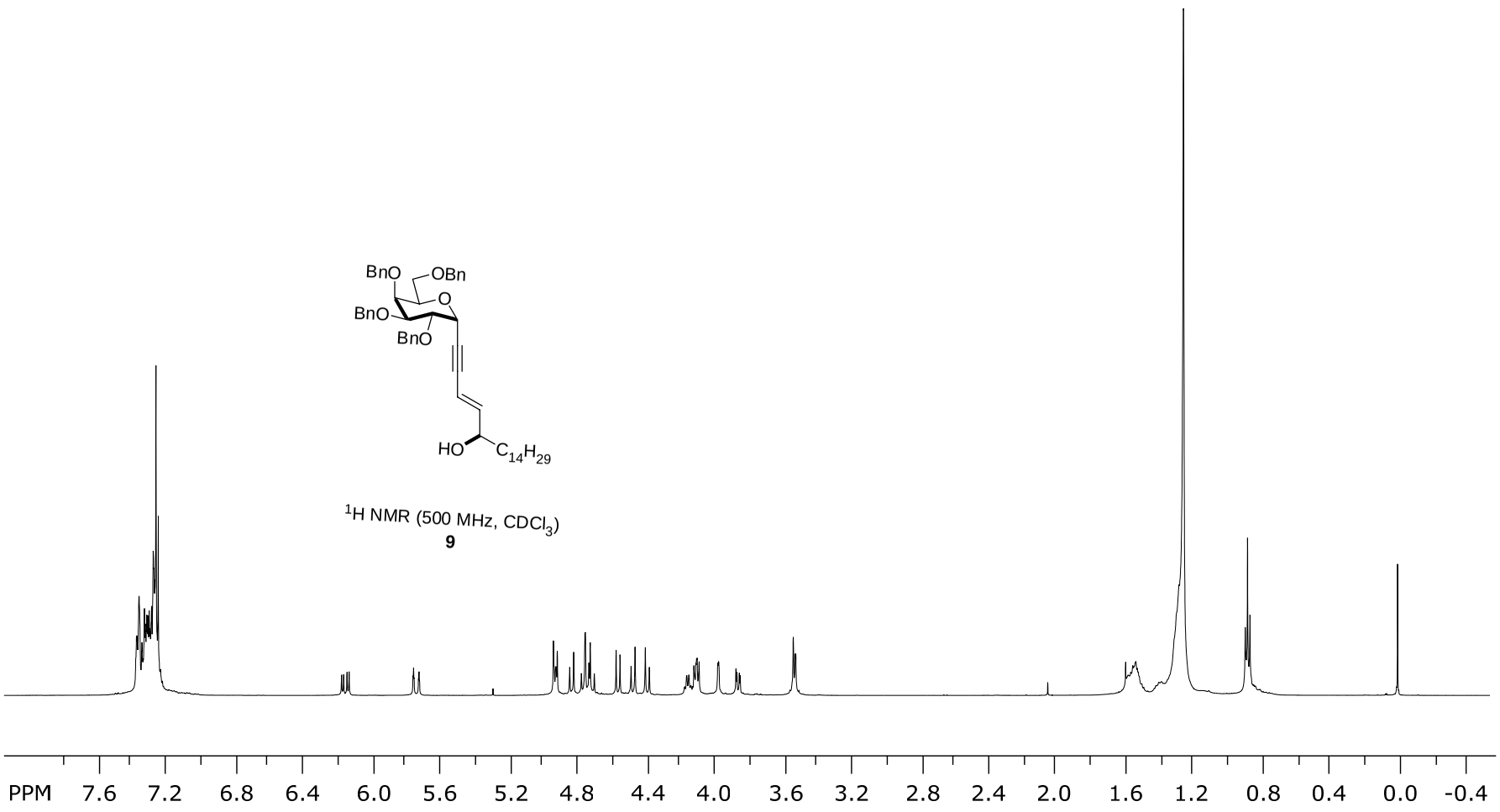
freq. of 0 ppm: 500.130043 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 176.250 ppm/cm: 0.35241



^{13}C NMR (100 MHz, $CDCl_3$)
10

file: I:\400 MHz\zh091116s3\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612784 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 683.354 ppm/cm: 6.79124



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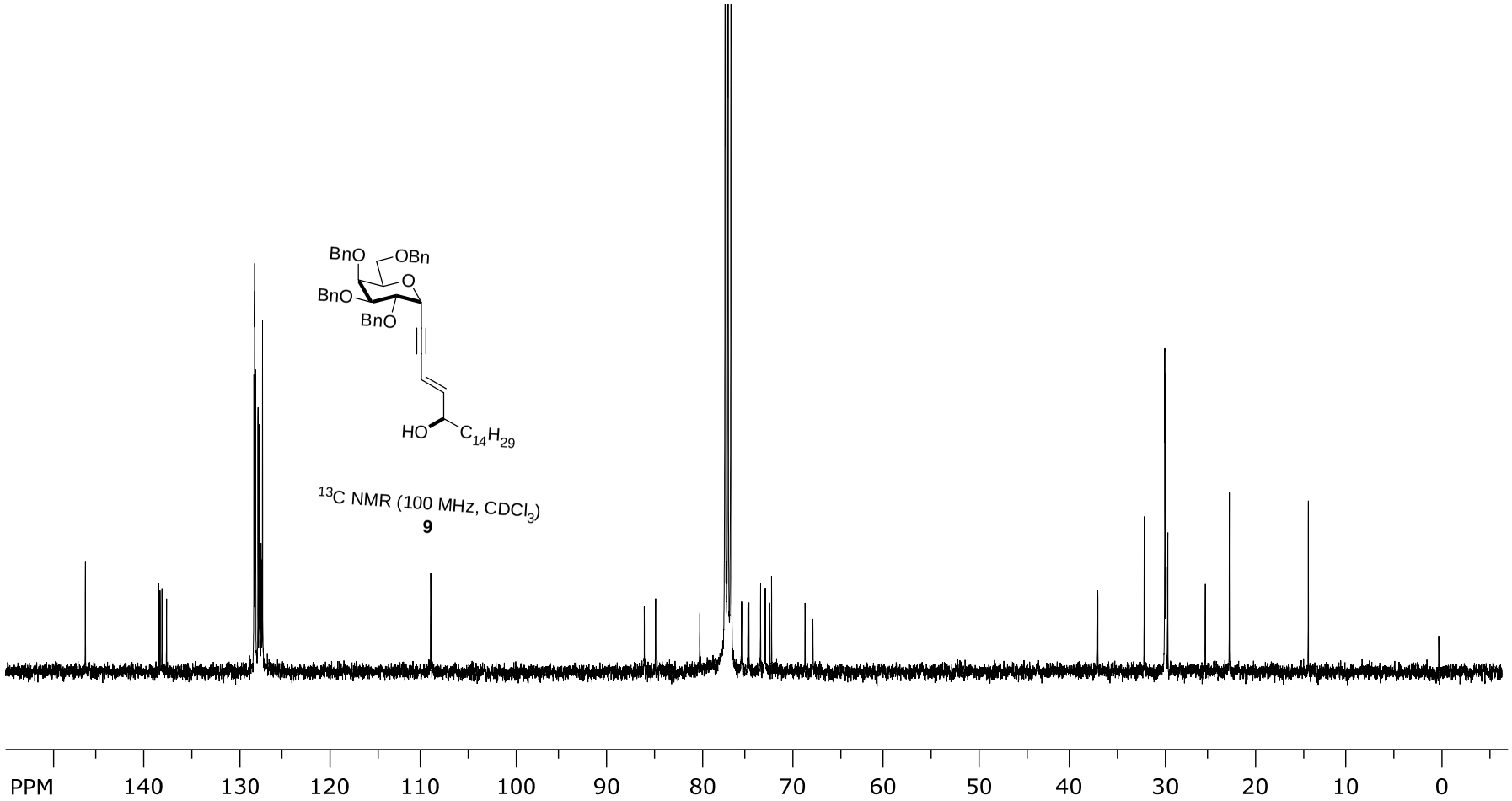
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130015 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 174.071 ppm/cm: 0.34805



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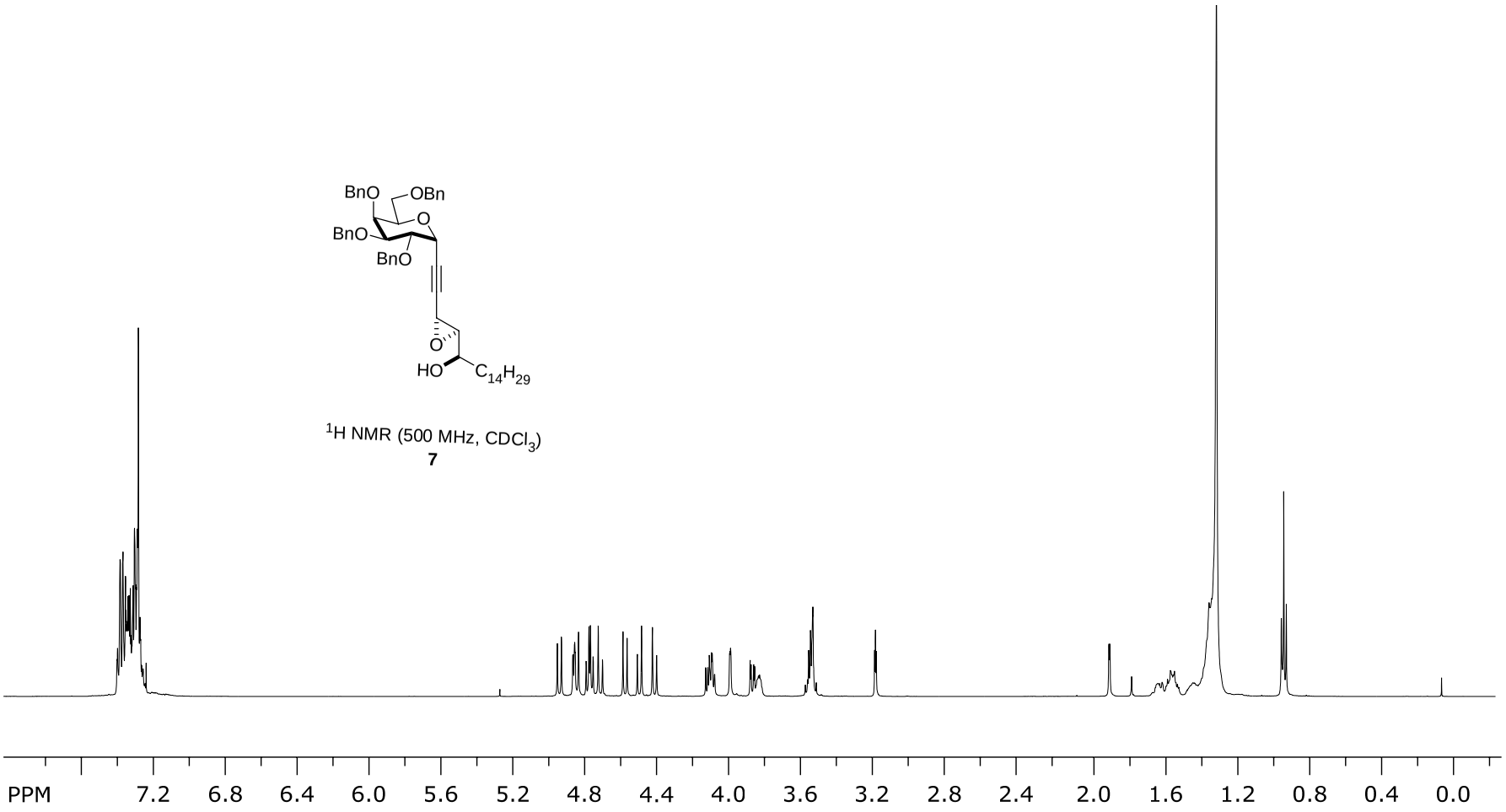
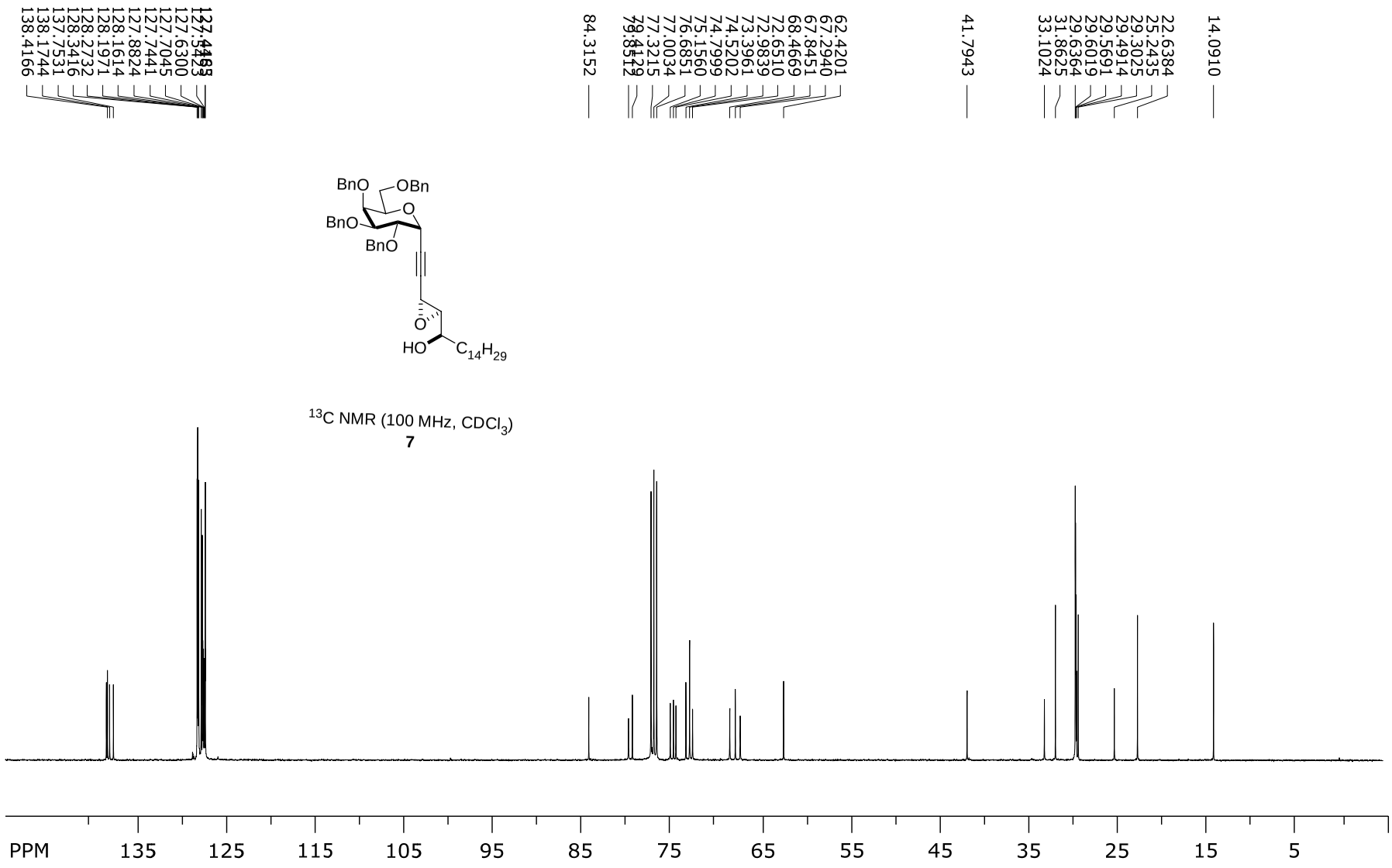
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612772 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 652.701 ppm/cm: 6.48661



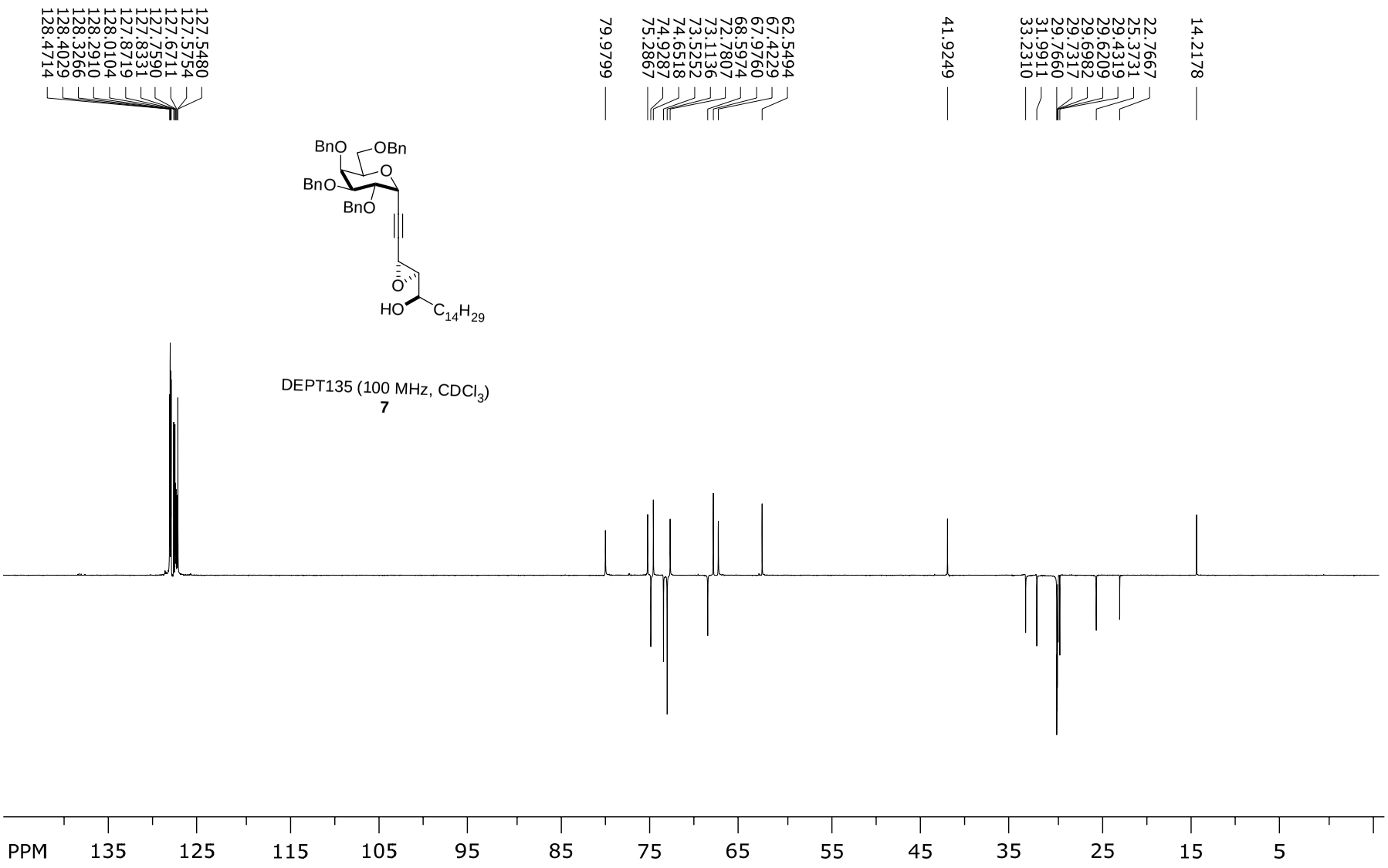
file: ...\NMR 500 3-1-2010\zh091216s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130015 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 166.286 ppm/cm: 0.33248



file: E:\NMR 400\zh091216s2\10\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

freq. of 0 ppm: 100.612782 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 623.104 ppm/cm: 6.19247



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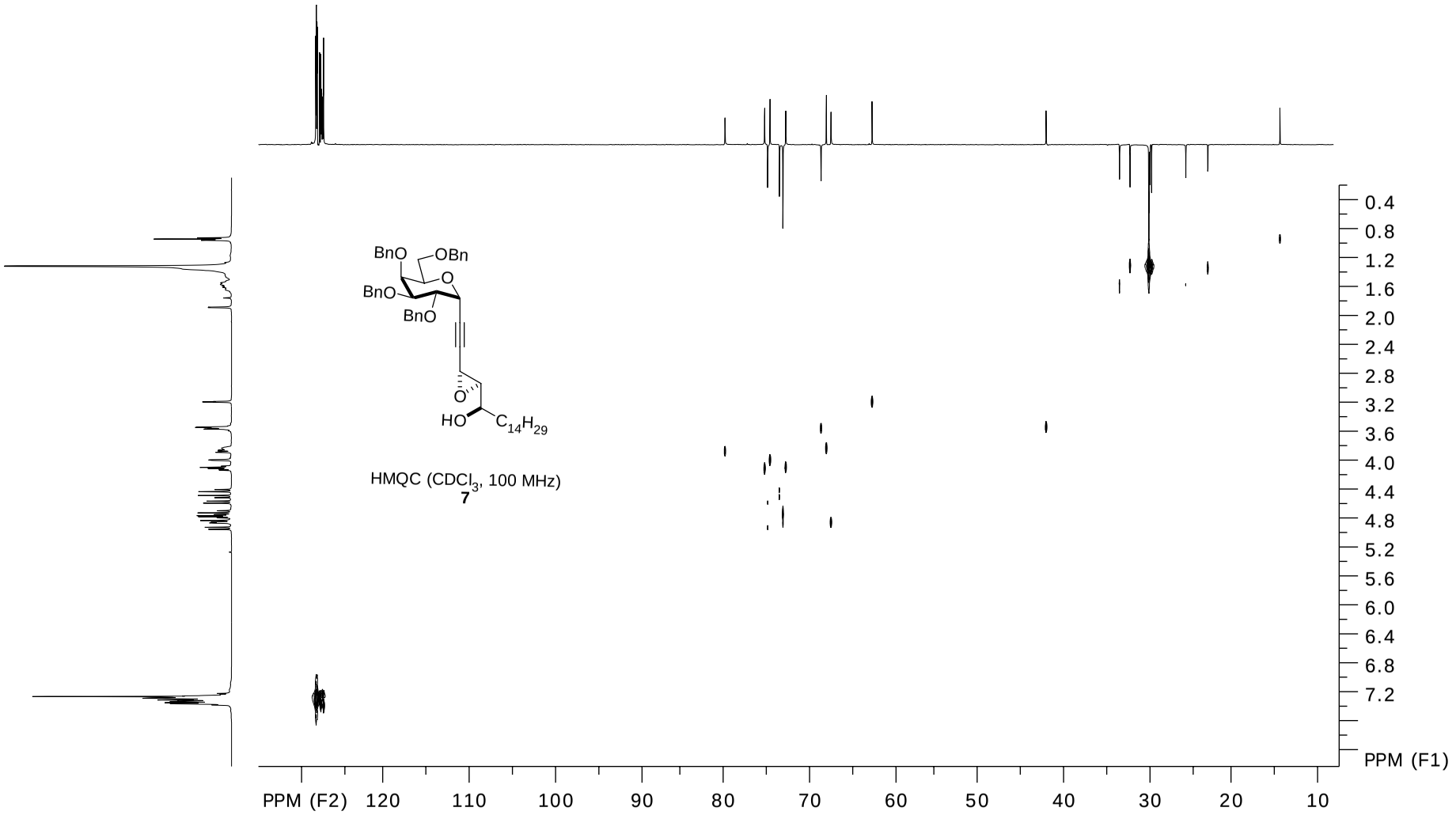
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

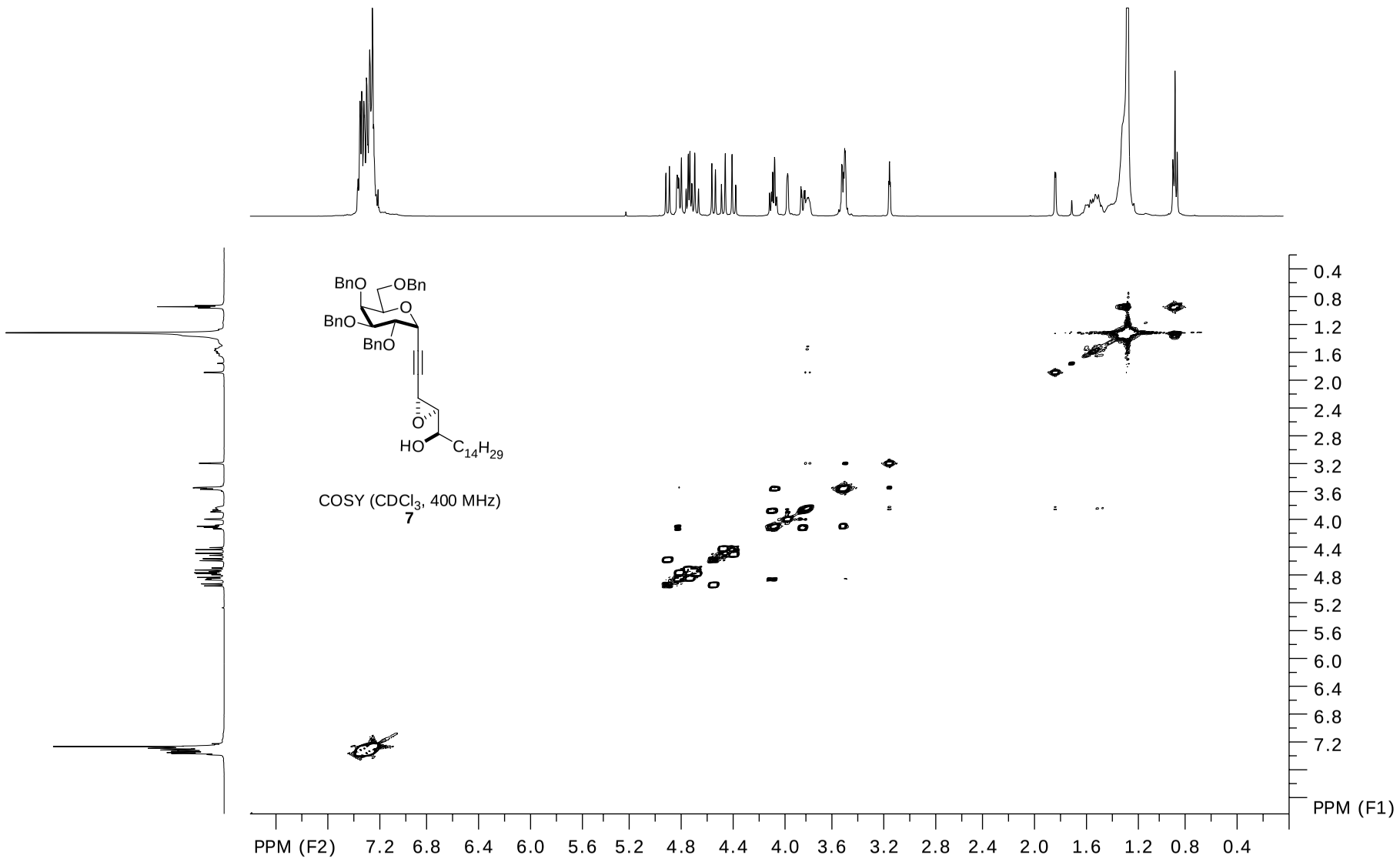
freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 615.875 ppm/cm: 6.12063



file: E:\NMR 400\zh091216s2\16\ser
expt: <hxcoqf>
transmitter freq: 100.619968 MHz
time domain size: 4096 by 128 points
width (F2): 12820.51 Hz = 127.4152 ppm = 3.1300 Hz/pt
number of scans: 64

F2: freq. of 0 ppm: 100.6127690 MHz
processed size: 2048 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 641.026 ppm/cm: 6.37076

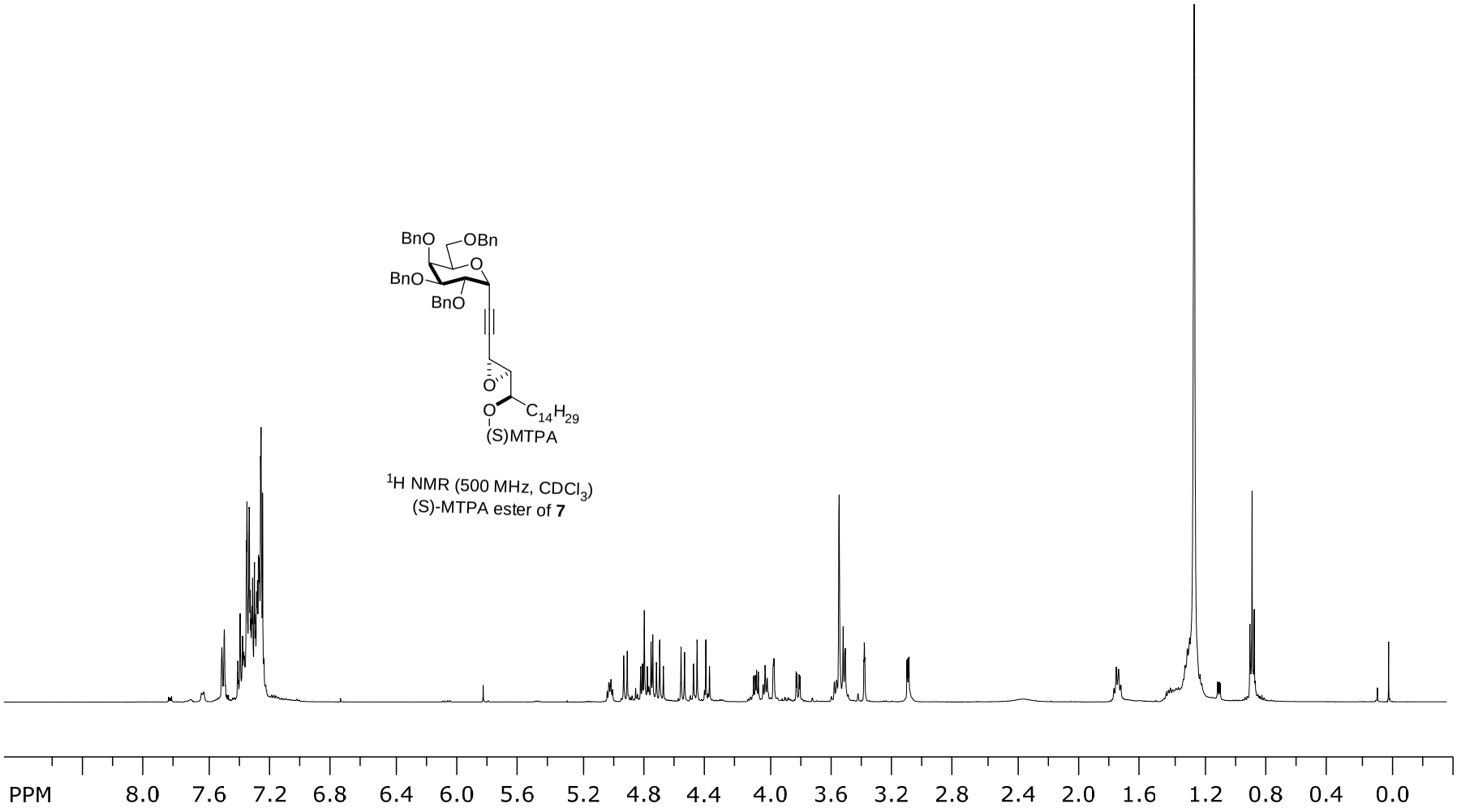
F1: freq. of 0 ppm: 400.1300270 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 299.043 ppm/cm: 0.74736



file: E:\NMR 400\zh091216s2\13\ser
expt: <cosyqf90>
transmitter freq: 400.131677 MHz
time domain size: 2048 by 256 points
width (F2): 3289.47 Hz = 8.2210 ppm = 1.6062 Hz/pt
number of scans: 16

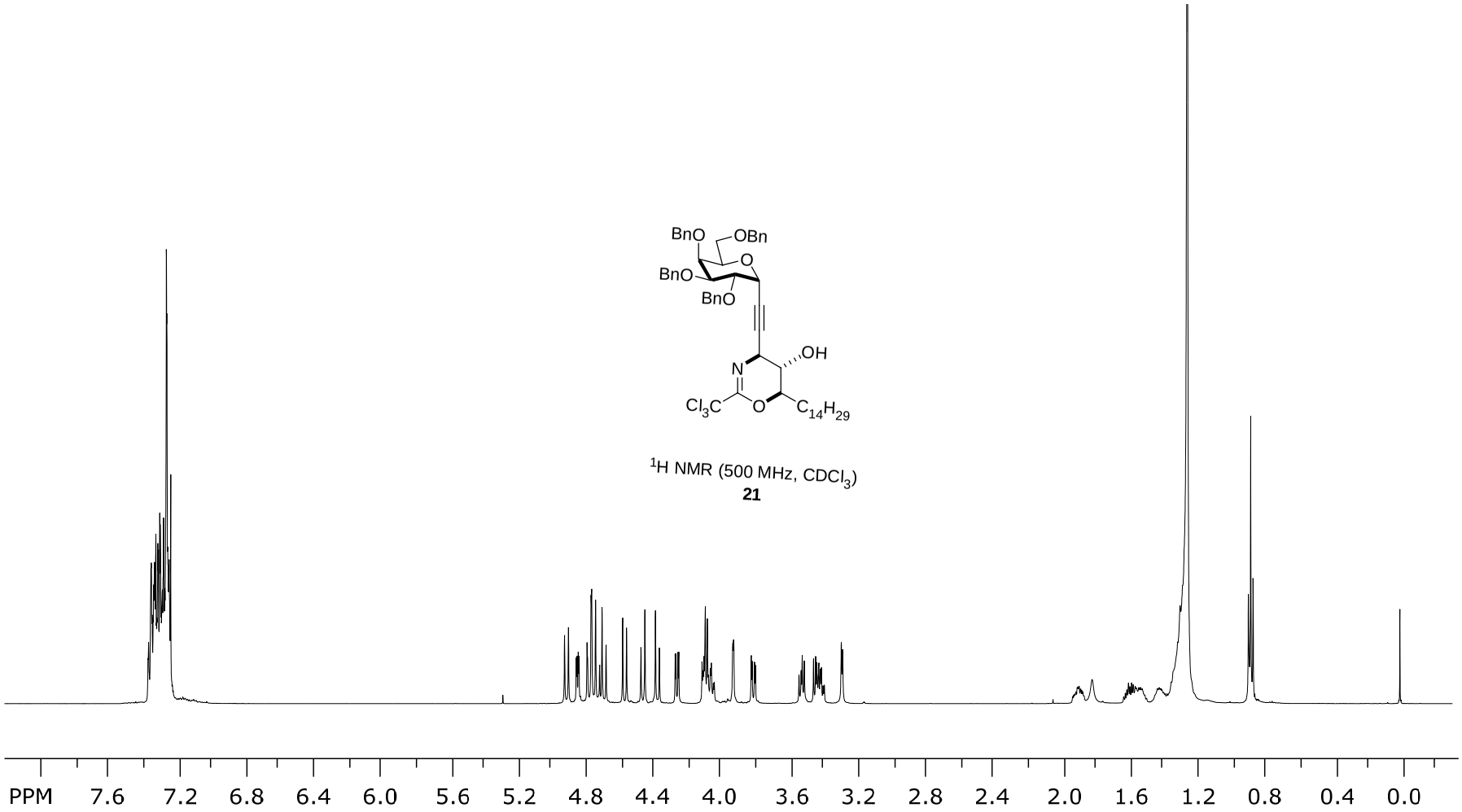
F2: freq. of 0 ppm: 400.1300270 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 164.474 ppm/cm: 0.41105

F1: freq. of 0 ppm: 400.1300270 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 299.043 ppm/cm: 0.74736



file: ...\NMR 500 3-1-2010\zh100226s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

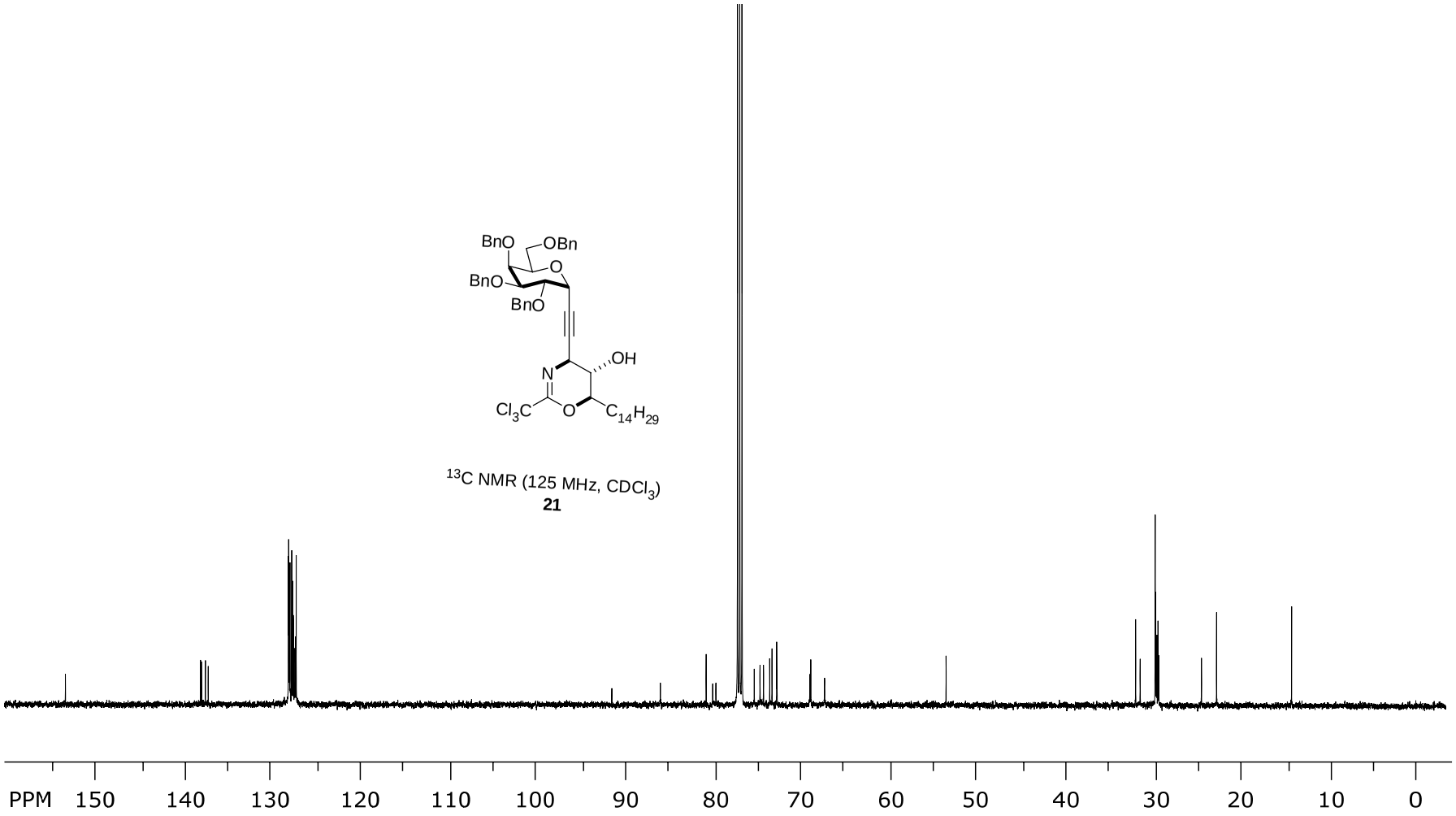
freq. of 0 ppm: 500.130018 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 193.650 ppm/cm: 0.38720



^{1}H NMR (500 MHz, $CDCl_3$)
21

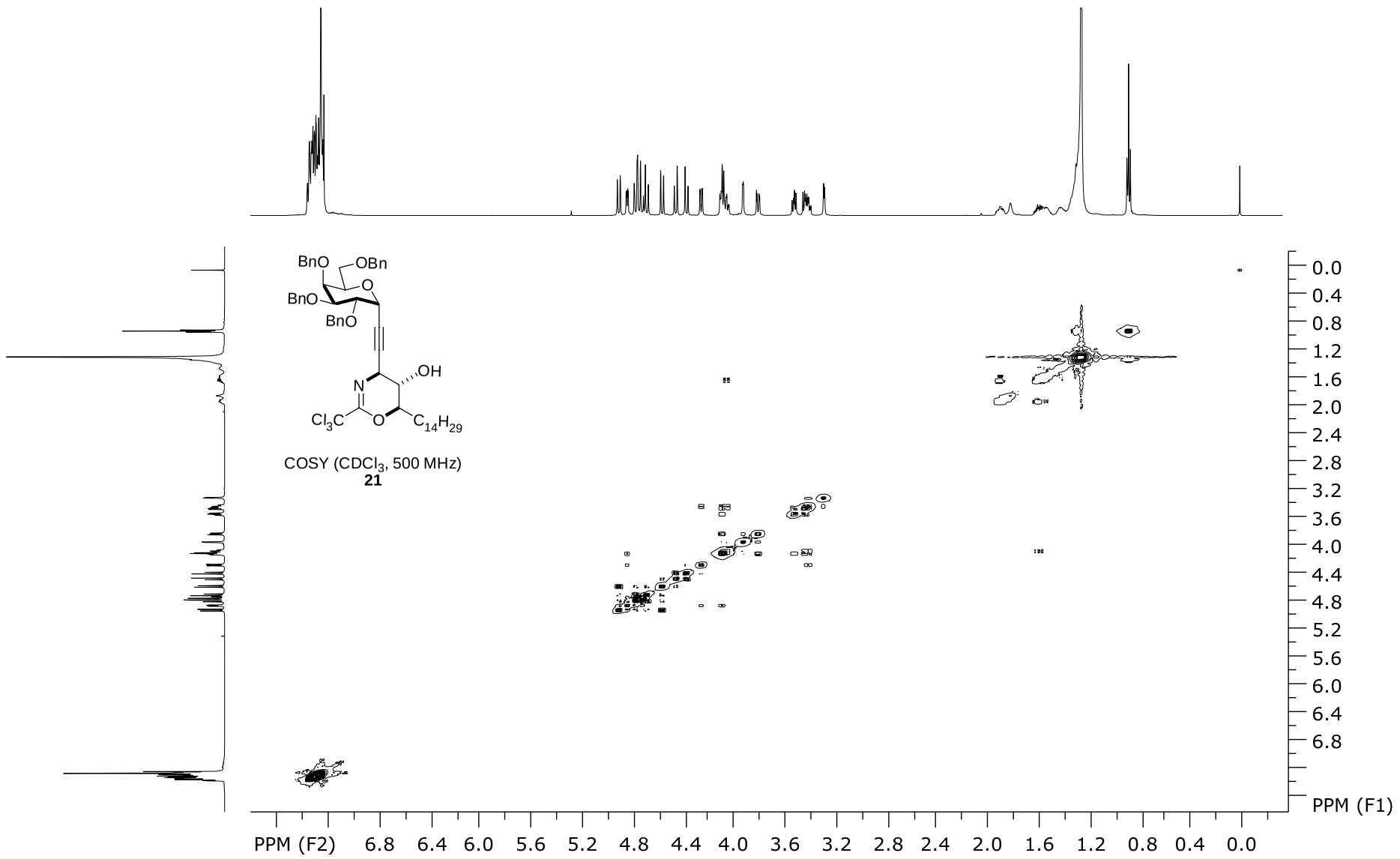
file: ...\NMR 500 3-1-2010\zh100224s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130017 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 178.080 ppm/cm: 0.35606



file: ...\NMR 500 3-1-2010\zh100224s2\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 2048

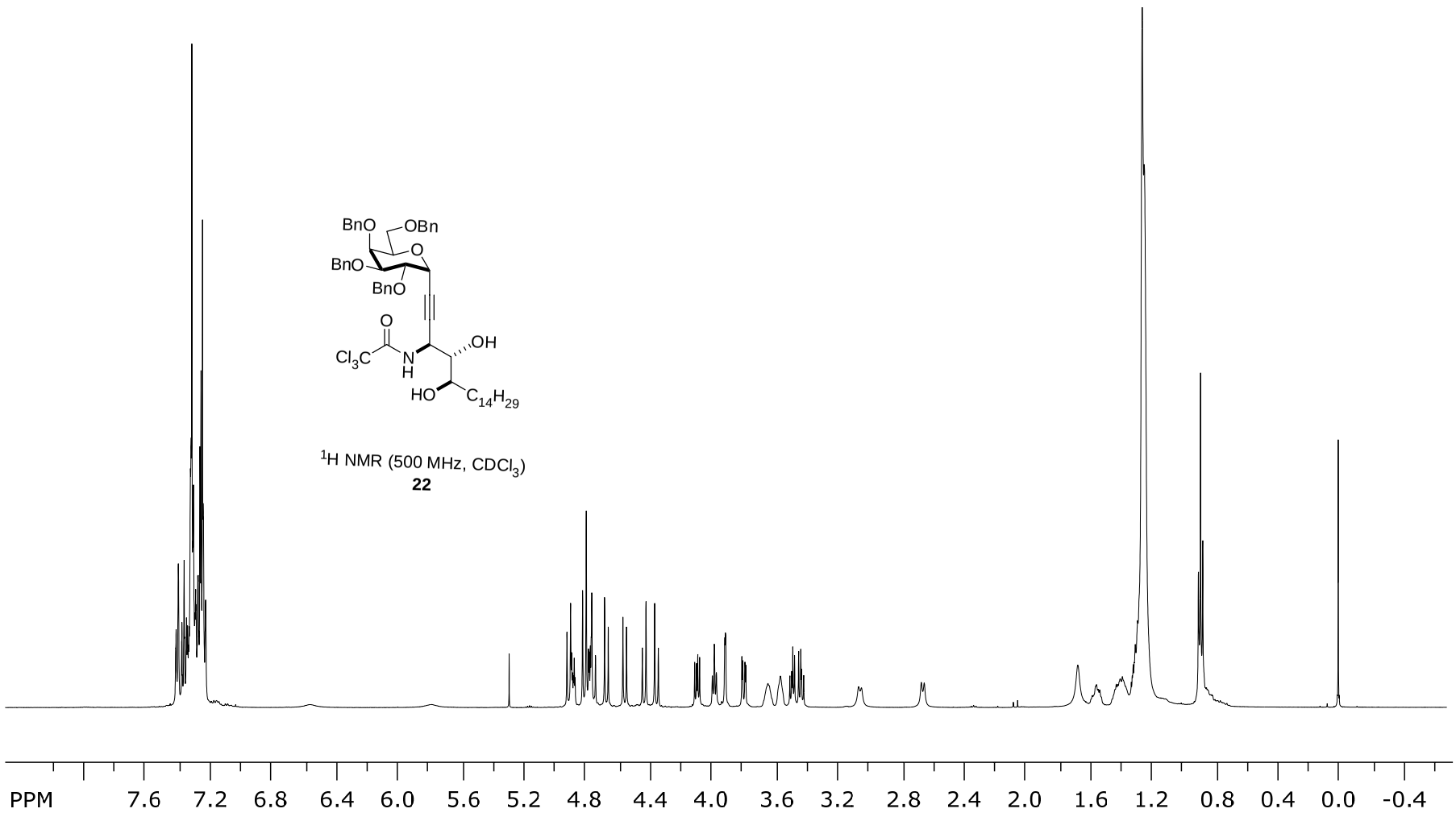
freq. of 0 ppm: 125.757797 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 860.533 ppm/cm: 6.84203



file: ...\NMR 500 3-1-2010\zh100224s2\3\ser
expt: <cosygpqf>
transmitter freq: 500.131890 MHz
time domain size: 2048 by 128 points
width (F2): 4091.65 Hz = 8.1811 ppm = 1.9979 Hz/pt
number of scans: 8

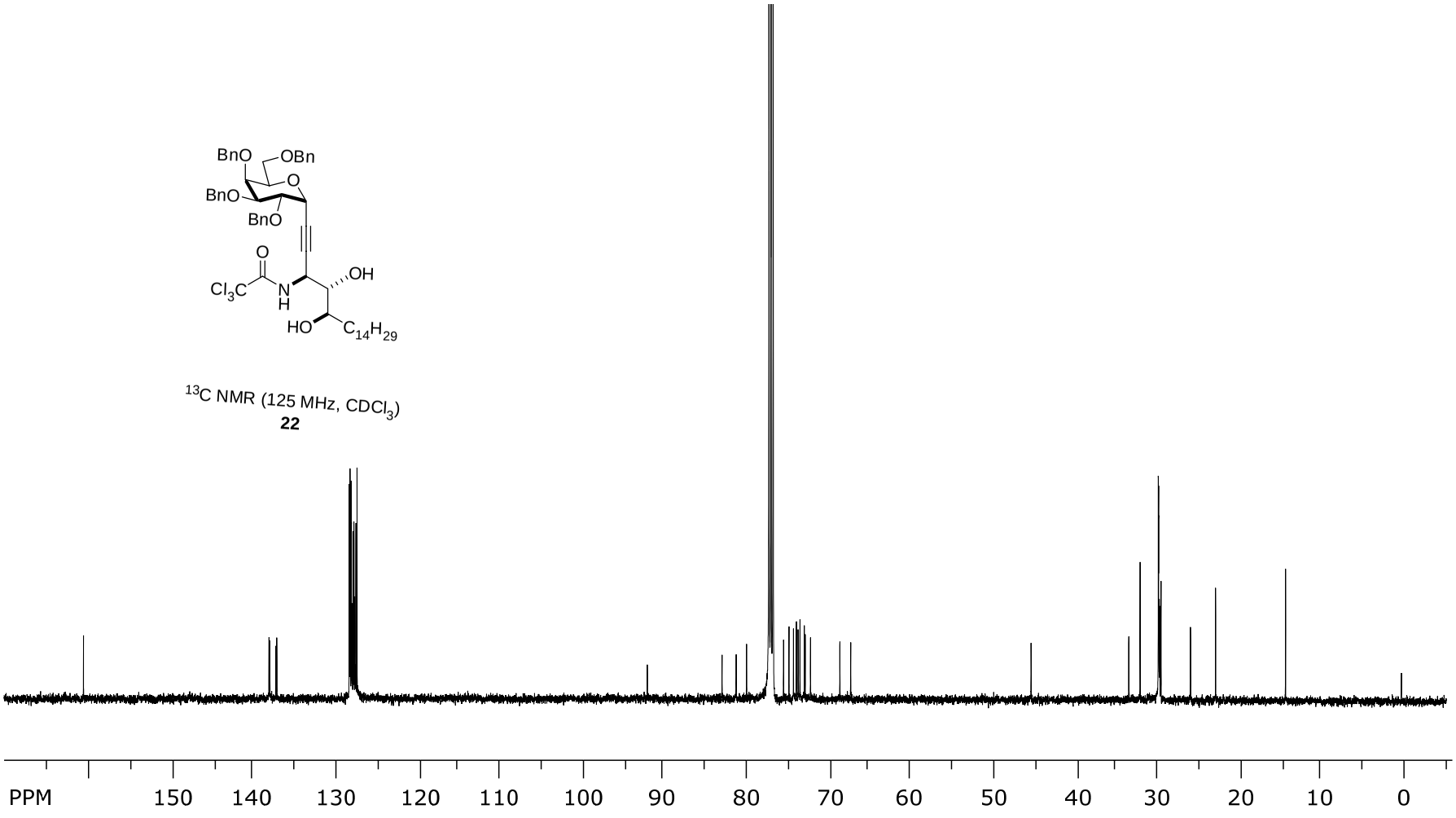
F2: freq. of 0 ppm: 500.1300167 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 204.583 ppm/cm: 0.40906

F1: freq. of 0 ppm: 500.1300167 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 371.966 ppm/cm: 0.74374



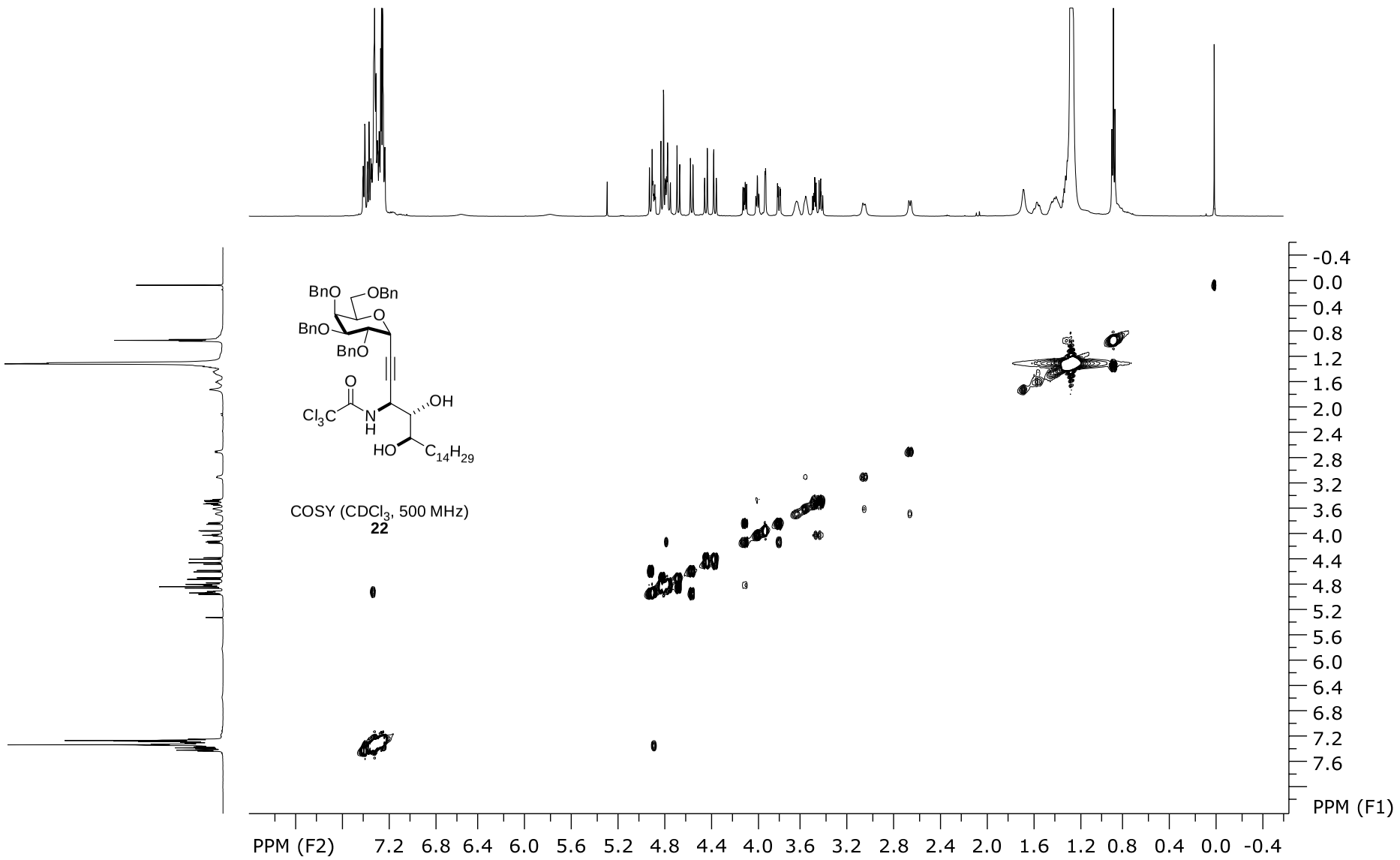
file: ...\NMR 500 3-1-2010\zh091203s4\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130014 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 192.028 ppm/cm: 0.38395



file: ...\NMR 500 3-1-2010\zh091203s4\2\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 8192

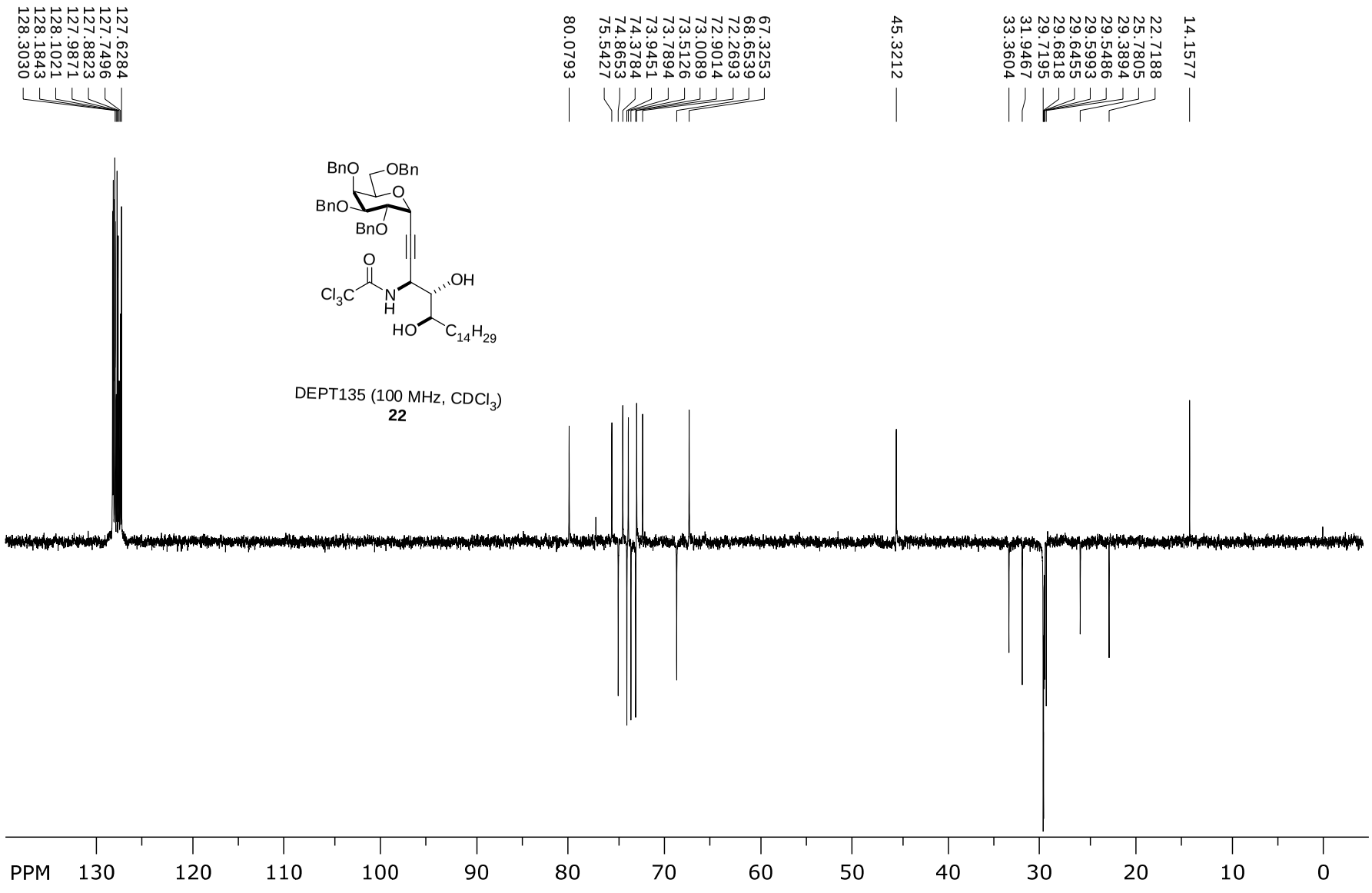
freq. of 0 ppm: 125.757796 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 923.331 ppm/cm: 7.34133



file: ...\NMR 500 3-1-2010\zh091203s4\3\ser
expt: <cosygpqf>
transmitter freq: 500.131970 MHz
time domain size: 2048 by 128 points
width (F2): 4518.07 Hz = 9.0338 ppm = 2.2061 Hz/pt
number of scans: 16

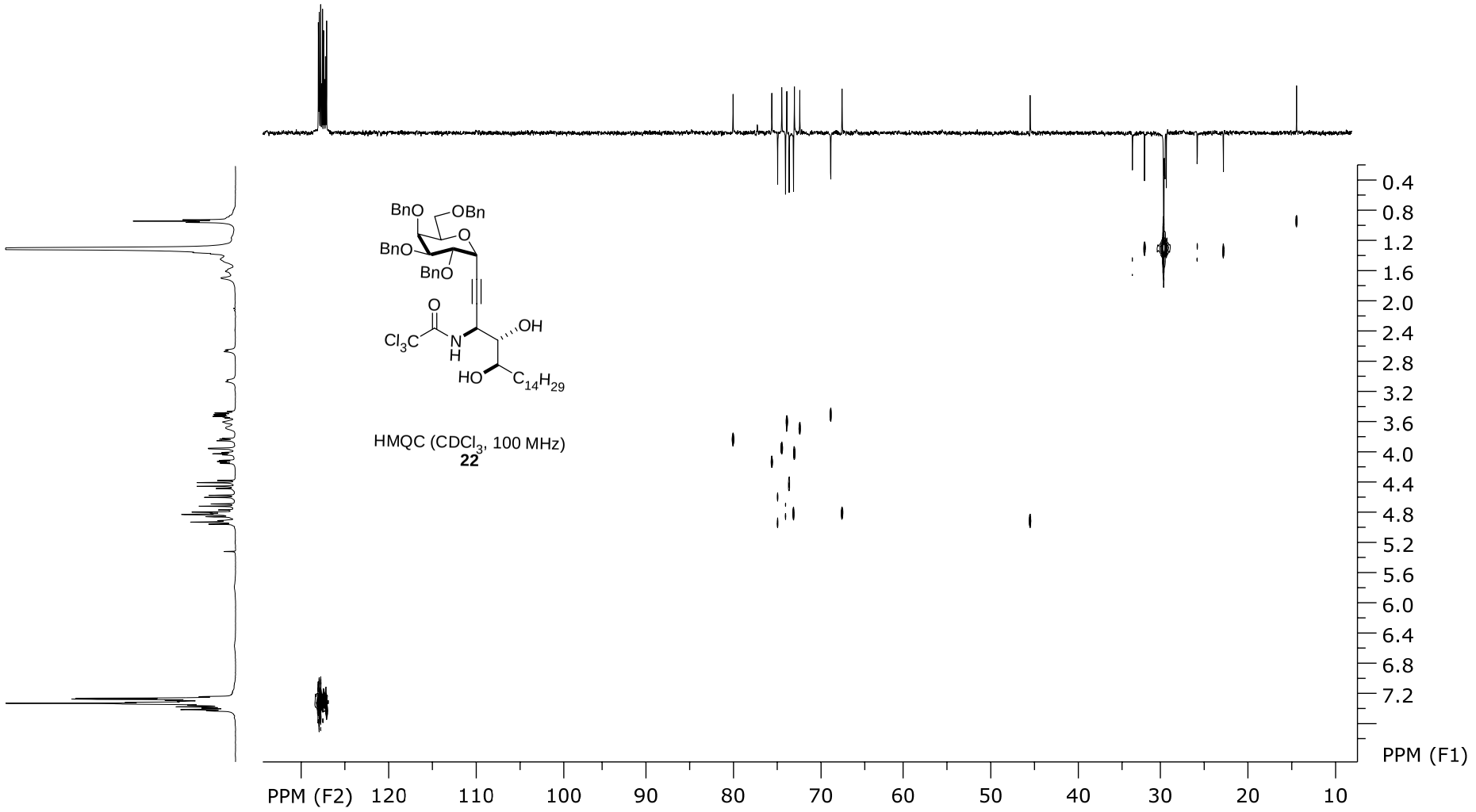
F2: freq. of 0 ppm: 500.1300139 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 225.904 ppm/cm: 0.45169

F1: freq. of 0 ppm: 500.1300139 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 410.733 ppm/cm: 0.82125



file: ...500 3-1-2010\zh091203s4-400\10\fid expt: <dept135>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 4096

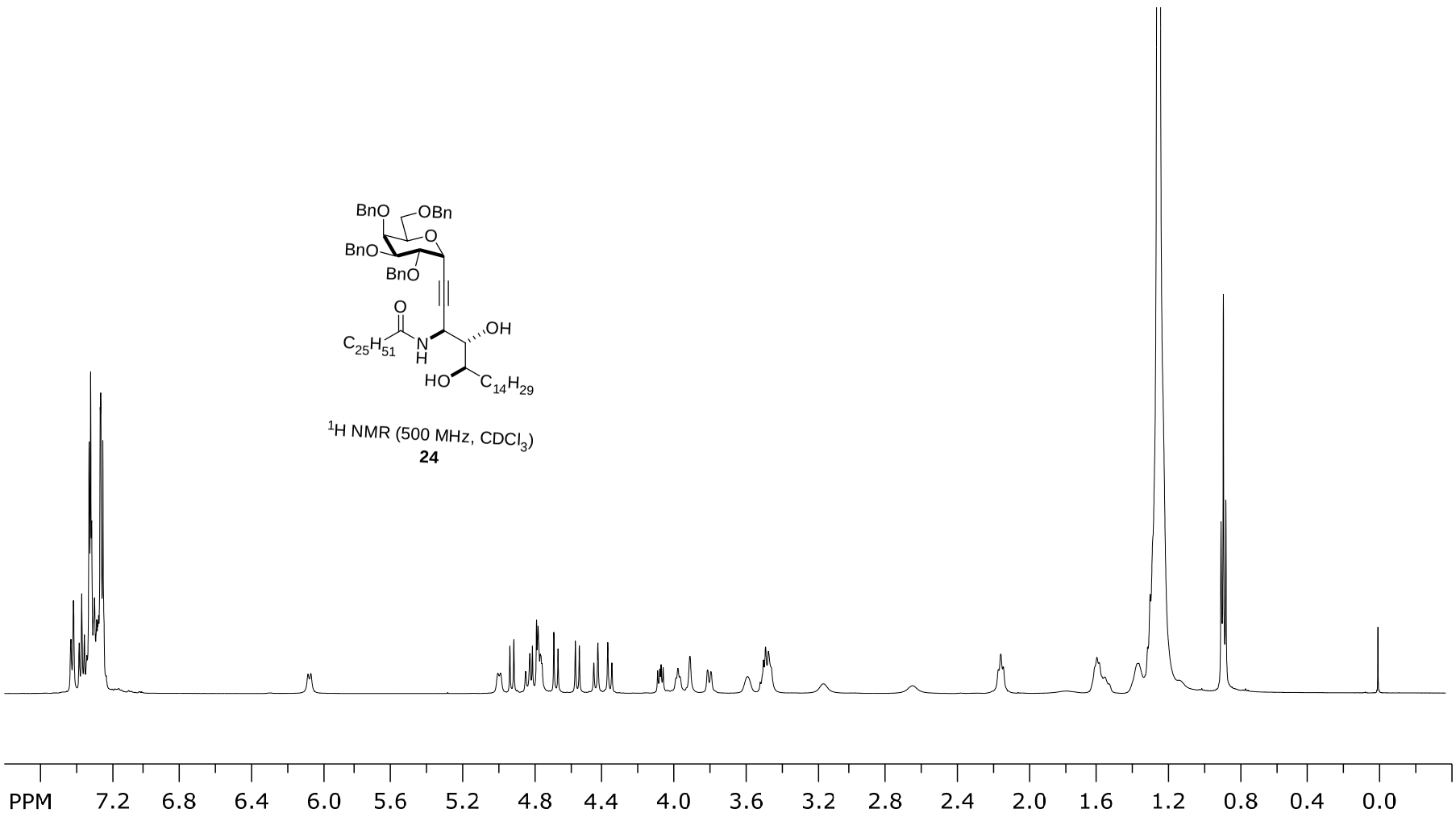
freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 604.641 ppm/cm: 6.00898



file: ...500 3-1-2010\zh091203s4-400\13\ser
expt: <hxcoqf>
transmitter freq: 100.619951 MHz
time domain size: 4096 by 128 points
width (F2): 12820.51 Hz = 127.4152 ppm = 3.1300 Hz/pt
number of scans: 64

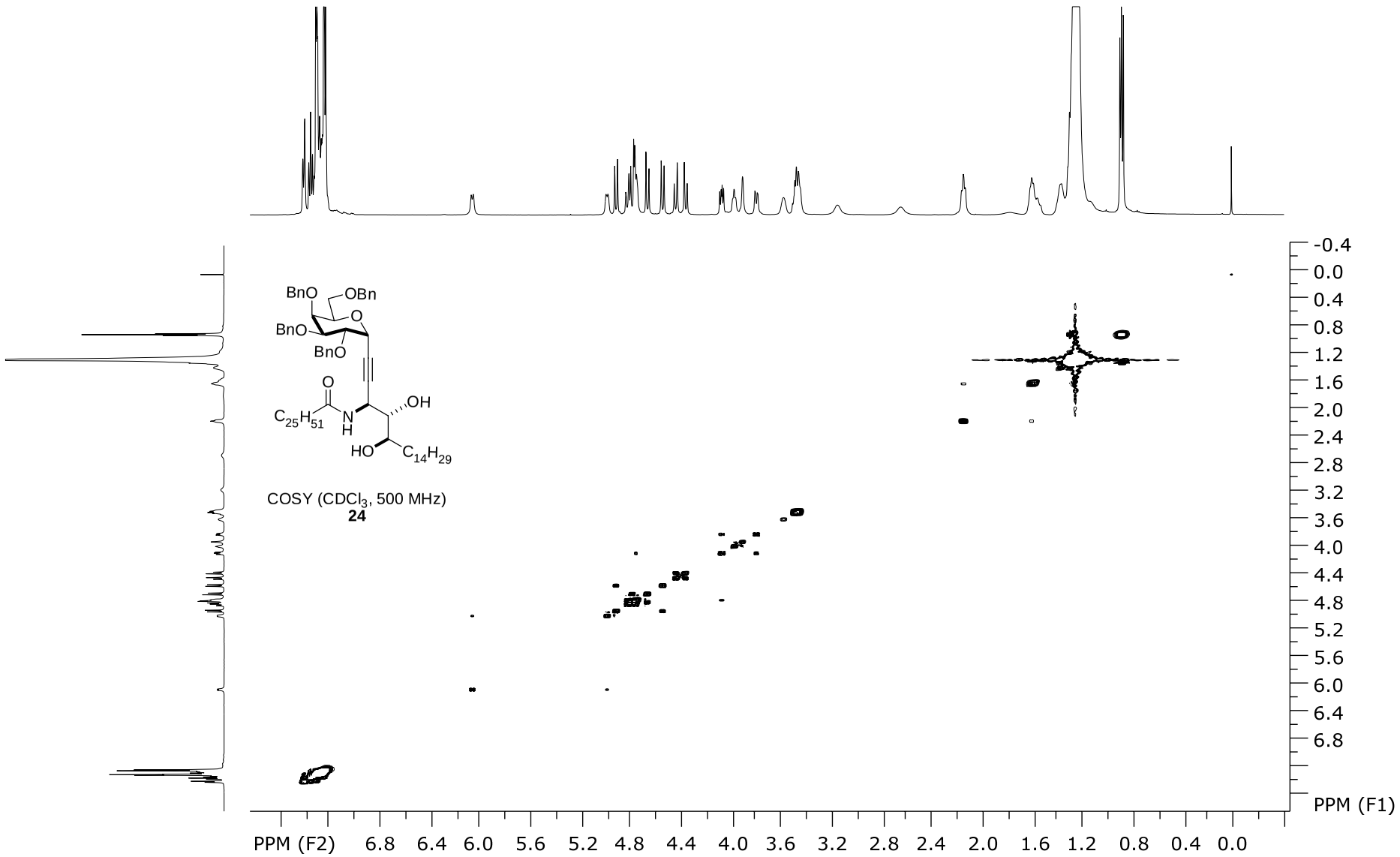
F2: freq. of 0 ppm: 100.6127690 MHz
processed size: 2048 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 641.026 ppm/cm: 6.37076

F1: freq. of 0 ppm: 400.1300108 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 289.889 ppm/cm: 0.72448



file: ...\NMR 500 3-1-2010\zh100308s2\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

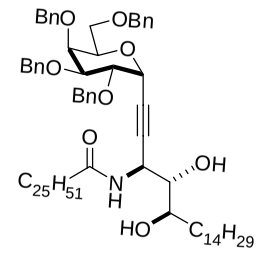
freq. of 0 ppm: 500.130016 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 170.944 ppm/cm: 0.34180



file: ...\NMR 500 3-1-2010\zh100308s2\2\ser
expt: <cosygpqf>
transmitter freq: 500.131875 MHz
time domain size: 2048 by 128 points
width (F2): 4145.94 Hz = 8.2897 ppm = 2.0244 Hz/pt
number of scans: 8

F2: freq. of 0 ppm: 500.1300161 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 207.297 ppm/cm: 0.41448

F1: freq. of 0 ppm: 500.1300161 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 376.904 ppm/cm: 0.75361

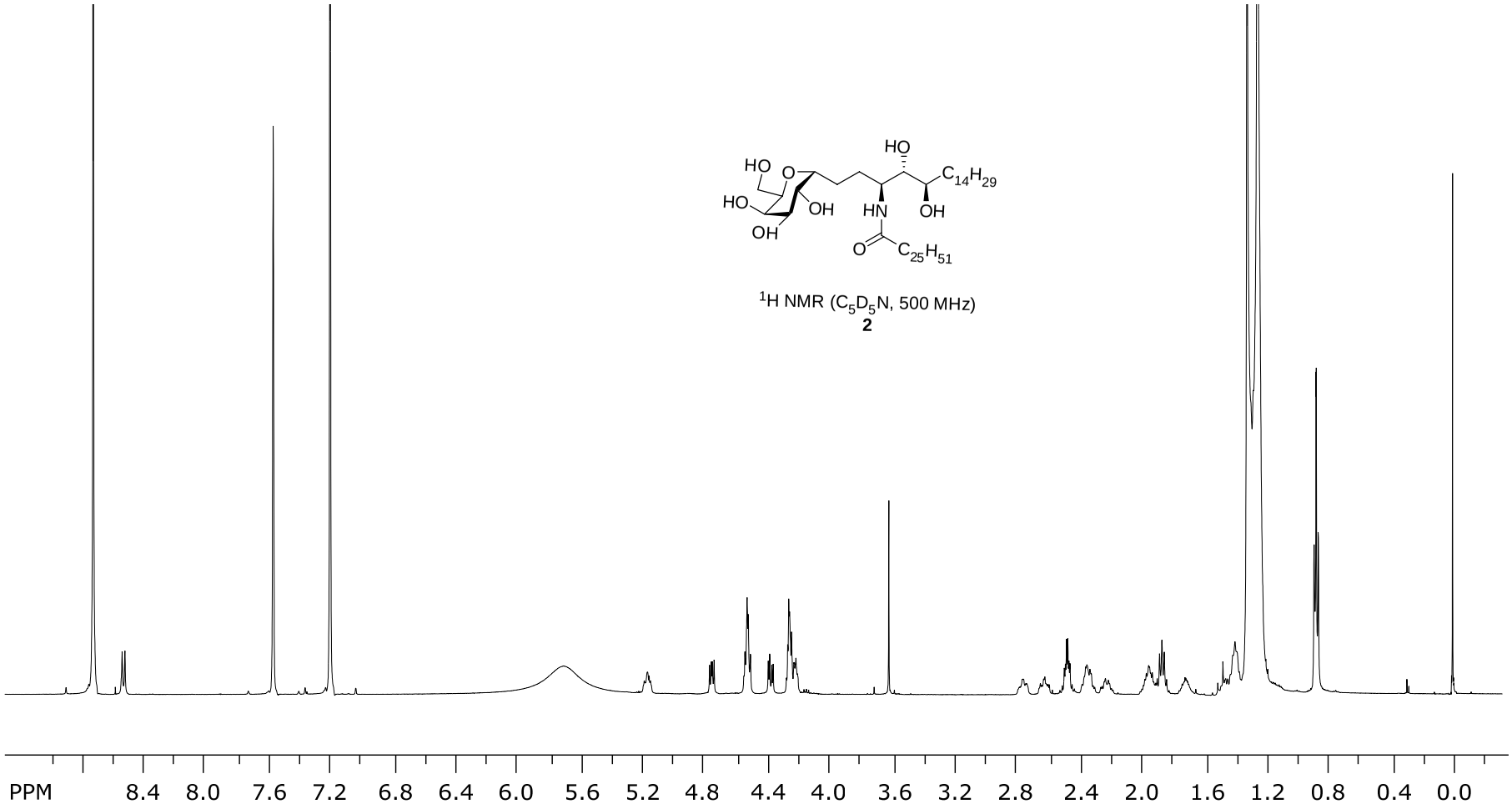


^{13}C NMR (125 MHz, $CDCl_3$)

24

file: ...\NMR 500 3-1-2010\zh100308s2\3\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 8192

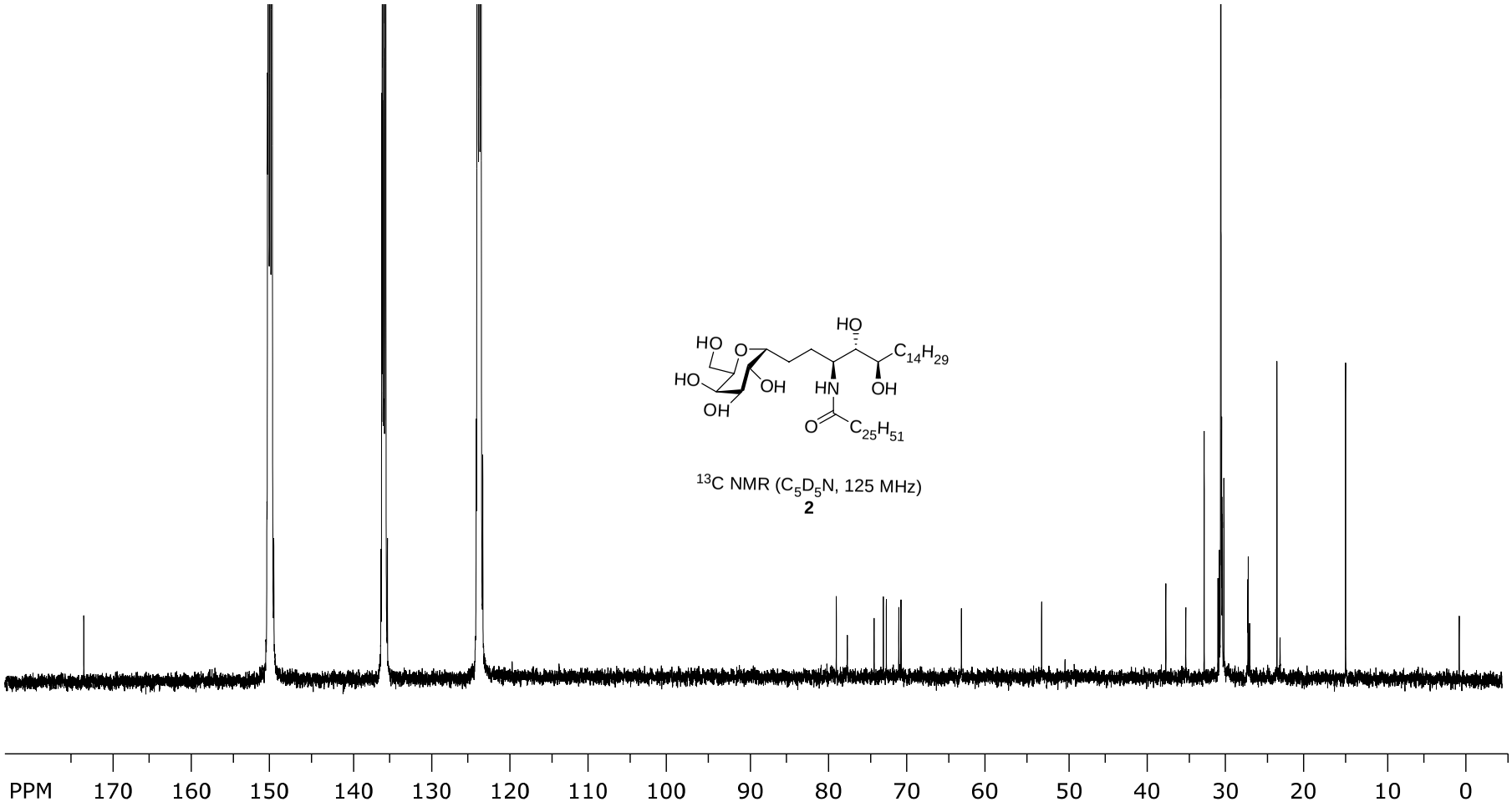
freq. of 0 ppm: 125.757798 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 966.505 ppm/cm: 7.68460



^{1}H NMR (C_5D_5N, 500 MHz)
2

file: ...\NMR 500 3-1-2010\zh100315s2\2\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16

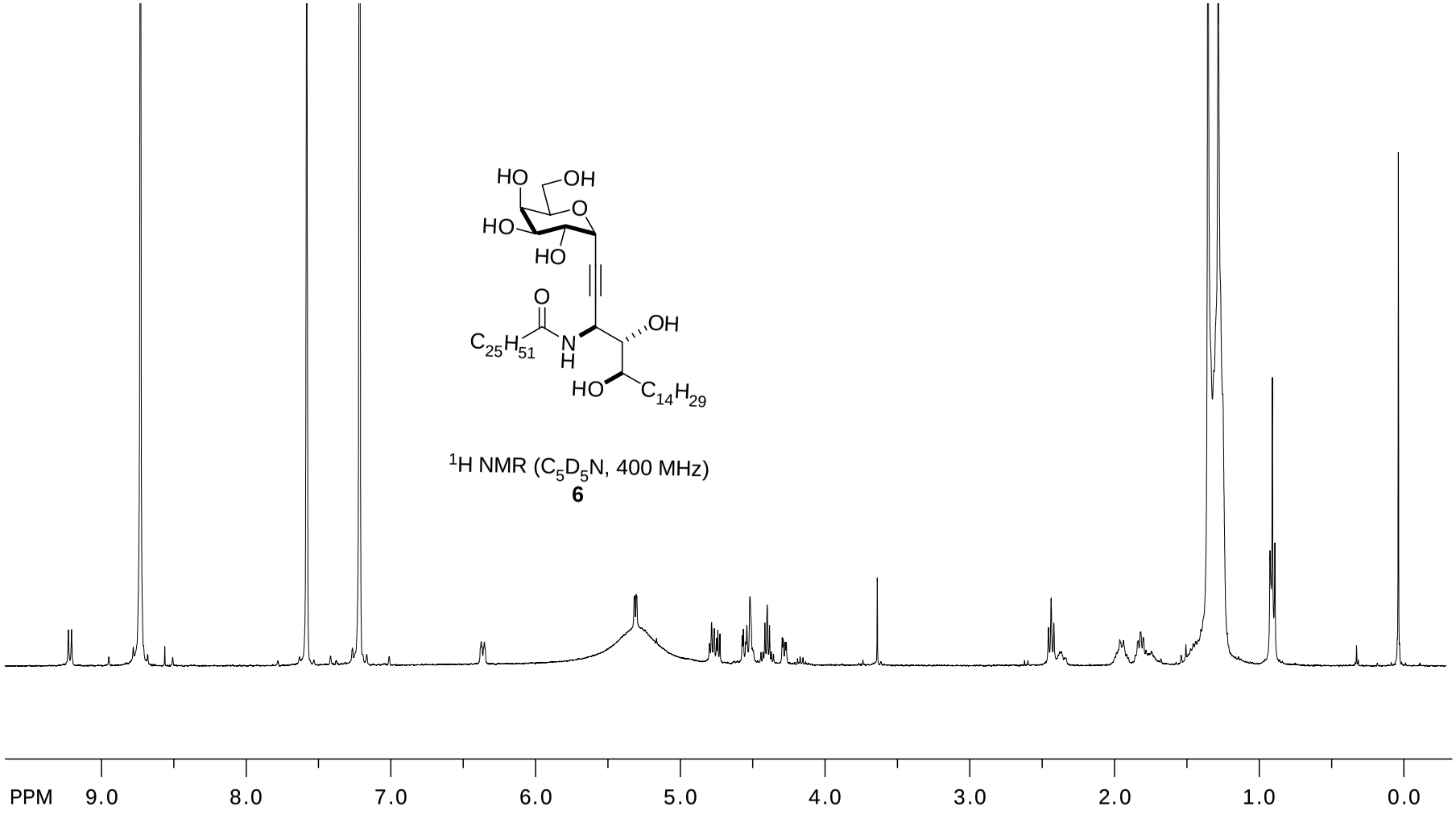
freq. of 0 ppm: 500.130741 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 192.754 ppm/cm: 0.38541



^{13}C NMR (C_5D_5N, 125 MHz)
2

file: ...\NMR 500 3-1-2010\zh100315s2\4\fid expt: <zgpg30>
transmitter freq.: 125.771622 MHz
time domain size: 65536 points
width: 31250.00 Hz = 248.4662 ppm = 0.476837 Hz/pt
number of scans: 24576

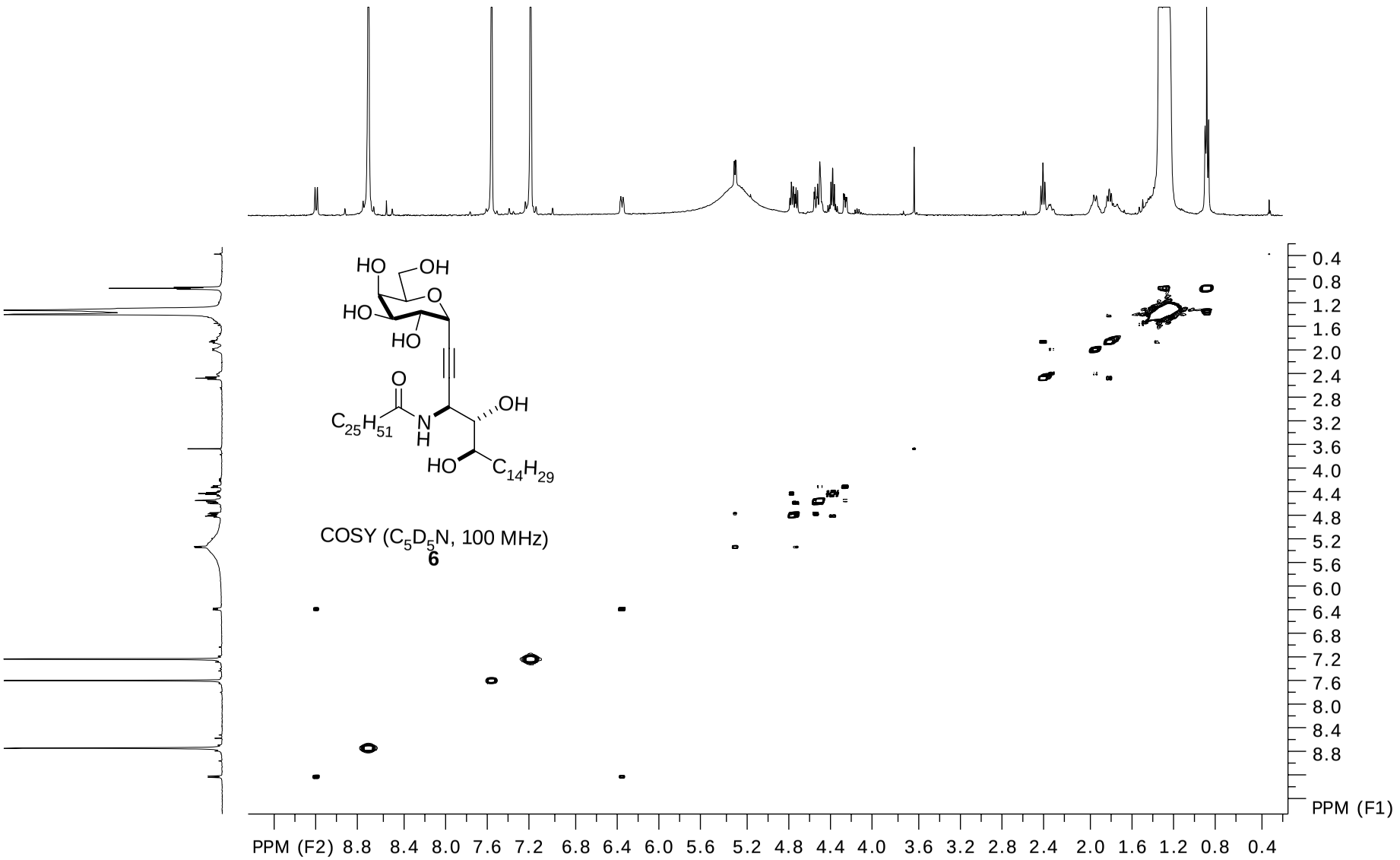
freq. of 0 ppm: 125.757892 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 949.510 ppm/cm: 7.54948



^{1}H NMR (C_5D_5N, 400 MHz)
6

file: ...\NMR 400 3-13-10\zh100310s2\10\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.6885 ppm = 0.126314 Hz/pt
number of scans: 16

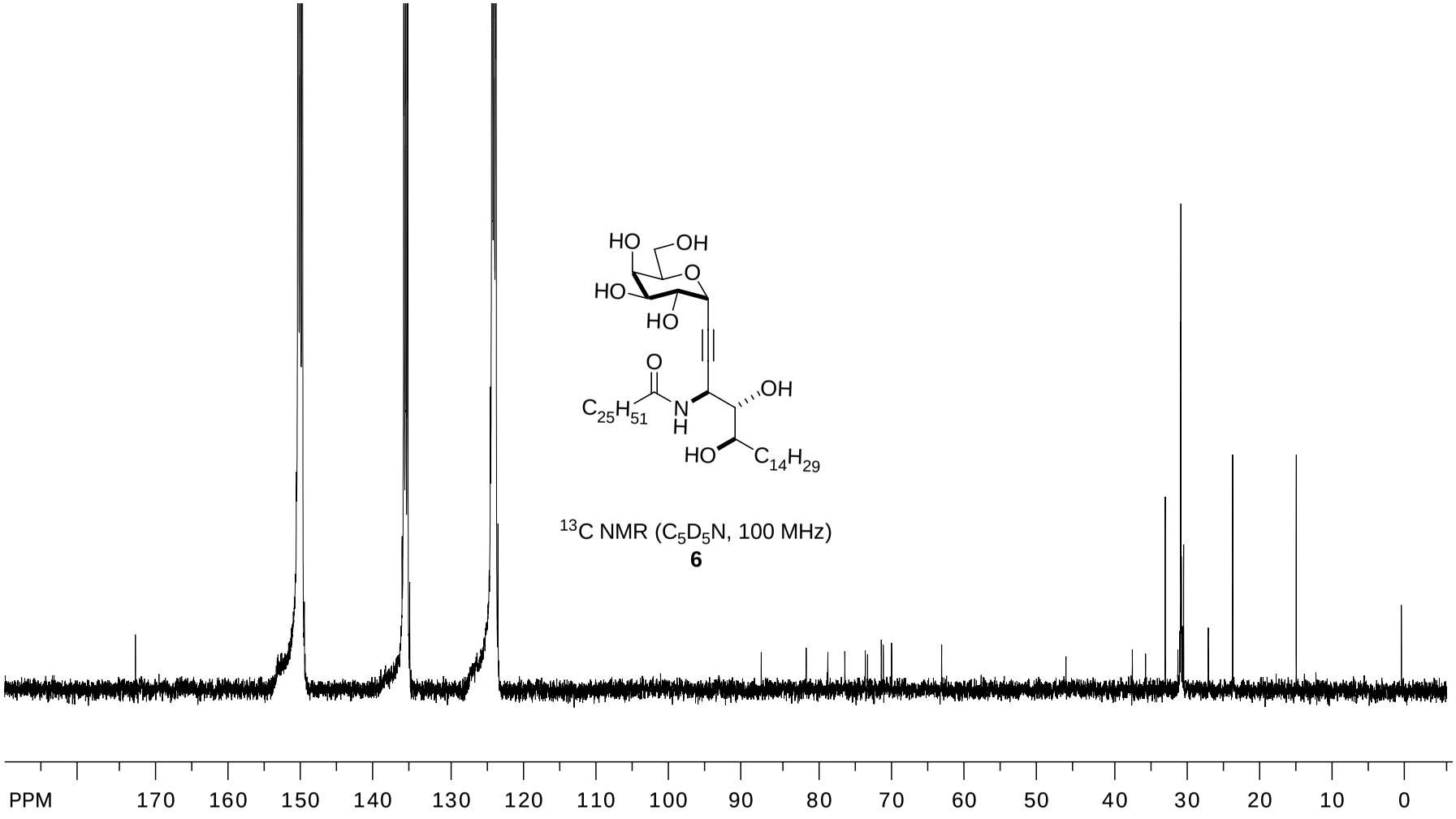
freq. of 0 ppm: 400.129987 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 166.873 ppm/cm: 0.41704



file: ...\NMR 400 3-13-10\zh100310s2\11\ser
expt: <cosyqf45>
transmitter freq: 400.131993 MHz
time domain size: 2048 by 128 points
width (F2): 3881.99 Hz = 9.7018 ppm = 1.8955 Hz/pt
number of scans: 16

F2: freq. of 0 ppm: 400.1299870 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 194.099 ppm/cm: 0.48509

F1: freq. of 0 ppm: 400.1299870 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 352.908 ppm/cm: 0.88198

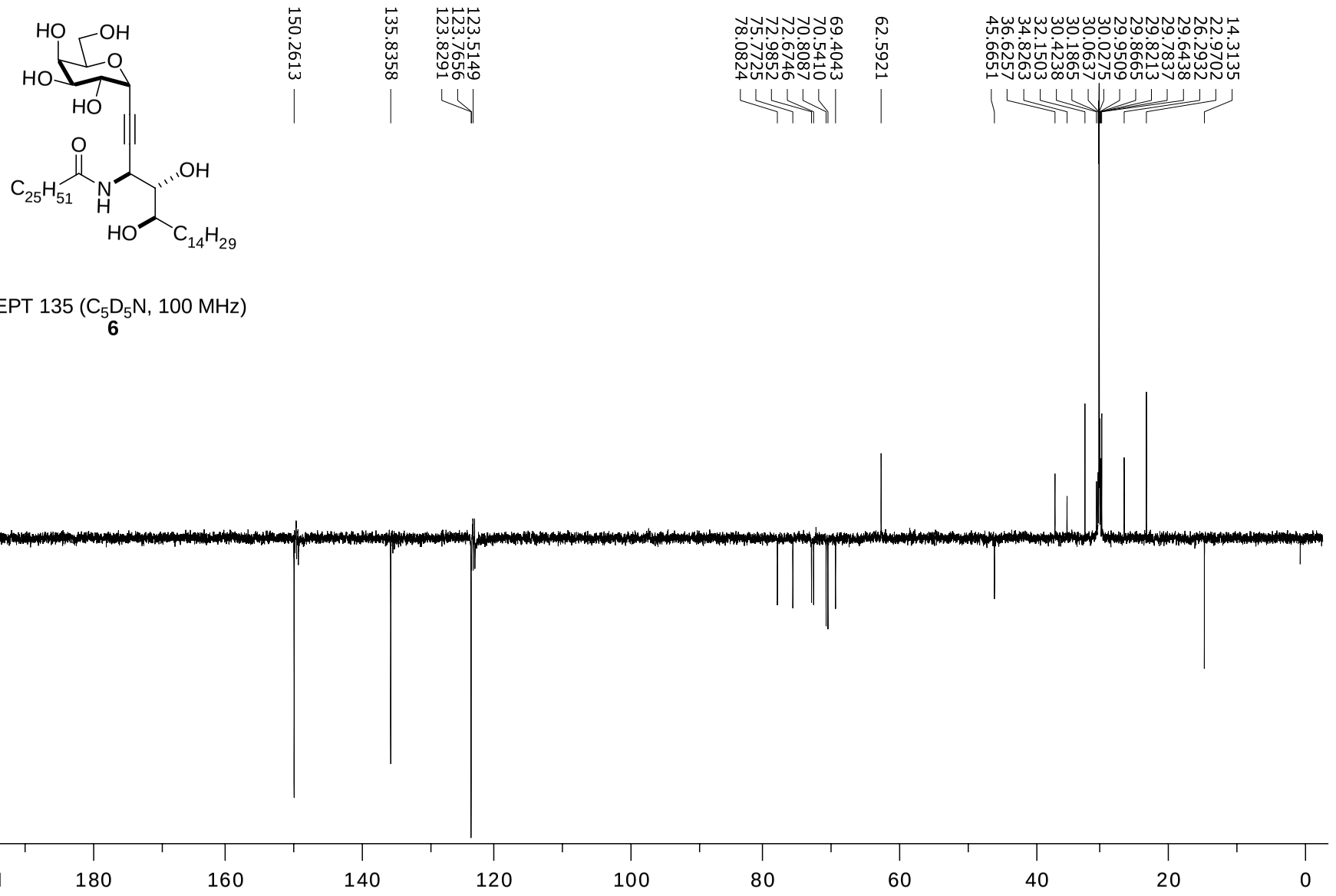


^{13}C NMR (C_5D_5N, 100 MHz)

6

file: ...\NMR 400 3-13-10\zh100310s2\12\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 16384

freq. of 0 ppm: 100.612699 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 823.004 ppm/cm: 8.17910



DEPT 135 (C_5D_5N, 100 MHz)
6

file: ...\NMR 400 3-13-10\zh100310s2\13\fid expt: <dept135>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23980.82 Hz = 238.3238 ppm = 0.365918 Hz/pt
number of scans: 16384

freq. of 0 ppm: 100.612858 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 855.382 ppm/cm: 8.50087