Rhenium(VII) Catalysis of Prins Cyclization Reactions

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SUPPORTING INFORMATION

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General Experimental Details. All moisture sensitive reactions were performed under a positive pressure of argon in flame- or oven-dried glassware using standard septa/syringe techniques. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), toluene (PhMe) were degassed and dried by filtration through alumina according to the procedure by Grubbs.[1] Chloroform ($CHCl_3$), ethyl acetate (EtOAc), nitromethane ($MeNO_2$), hexanes and acetonitrile (MeCN) were distilled over CaH_2 under nitrogen or argon at atmospheric pressure prior to use. All commercially available reagents were used as received, unless otherwise stated. Compounds **1**, **11-*R***, and **11-*S*** were prepared according to published procedures.[2] Thin layer chromatography (TLC) was performed on Whatman K6F (250 μm) silica gel plates and visualized using *p*-anisaldehyde stain. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 500 and 125 MHz, respectively. ^{1}H NMR spectra are reported in ppm on the δ scale and referenced to the internal tetramethylsilane. The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), coupling constant(s) in Hertz (Hz), and integration. ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.07 ppm). HPLC analysis was performed using a CHIRALCEL OD-H column and a hexane/isopropanol mobile phase.

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[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[2] (a) Nokami, J.; Nomiyama, K.; Matsuda, S.; Imai, N.; Kataoka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 1273–1276. (b) (b) Nokami, J.; Ohga, M.; Nakamoto, H.; Matsubara, T.; Hussain, I.; Kataoka, K. *J. Am. Chem. Soc.* **2001**, *123*, 9168–9169.

Experimental Procedures.

Preparation of Triphenylsilyl Perrhenate ($O_3ReOSiPh_3$)[3]

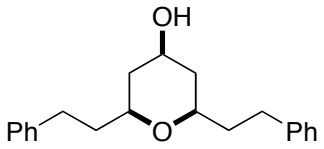
In a glove box, Re_2O_7 (0.53 g, 1.1 mmol) and triphenylsilanol (0.60 g, 2.2 mmol) was added to a 20-mL vial. The vial was removed from the glove box. Dry toluene (7 mL) was then added and the mixture was stirred at room temperature under argon for 1.5 h. The clear liquid portion of the mixture was transferred via a syringe to a flame dried flask. Solvent was then removed *in vacuo*. The crude product was dissolved in a small amount of dry ether and left in the freezer overnight. After removal of residual ether, $O_3ReOSiPh_3$ was obtained as white solids (0.63 g, 57%). Isolated $O_3ReOSiPh_3$ could be stored in the freezer (–20 °C) for approximately 3 months without decomposition. The complex decomposed slowly at ambient temperature, turning to greenish color. ^{1}H NMR (500 MHz, C_6D_6) δ 7.42–7.39 (m, 6H), 7.16–7.12 (m, 3H), 7.07–7.04 (m, 6H). ^{1}H NMR data matched those previously reported by Grubbs.[3]

General Procedure for $O_3ReOSiPh_3$–Catalyzed Prins Cyclization

To an oven-dried flask was added homoallylic alcohol (0.40 mmol, 1 equiv) and 4 mL of solvent (0.1 M). To this solution was added aldehyde (0.52–0.60 mmol, 1.3–1.5 equiv) and $O_3ReOSiPh_3$ (0.02 mmol, 5 mol%). The reaction mixture was stirred at room temperature under an atmosphere of argon and was judged complete upon disappearance of the homoallylic alcohol by TLC analysis. Solvent was then removed *in vacuo*, and the crude product was purified by flash chromatography (40–60% diethyl ether/hexanes).

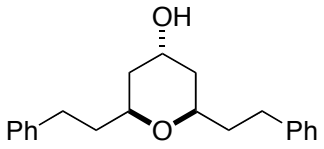
[3] Morrill, C.; Beutner, G. L.; Grubbs, R. H. *J. Org. Chem.* **2006**, *71*, 7813–7825.

Characterization Data.



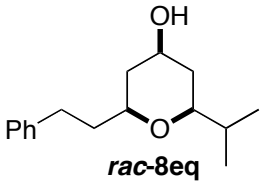
7eq

2,6-Diphenyltetrahydropyran-4-ol (7eq). White solid: mp 94–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.19 (m, 10H), 3.75 (tt, *J* = 10.7, 4.6 Hz, 1H), 3.27–3.23 (m, 2H), 2.87 (ddd, *J* = 14.0, 9.3, 5.3 Hz, 2H), 2.73 (ddd, *J* = 13.8, 8.7, 7.7 Hz, 2H), 1.98–1.91 (m, 4H), 1.75 (dddd, *J* = 13.5, 9.5, 7.4, 4.0 Hz, 2H), 1.41 (br s, 1H), 1.20 (q, *J* = 11.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 128.6, 128.4, 125.8, 74.4, 68.3, 41.5, 37.8, 32.0; IR (KBr) 3392, 3026, 2941, 2920, 1059, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{26}NaO_2$ $(M + Na)^+$ 333.1830, found 333.1835.



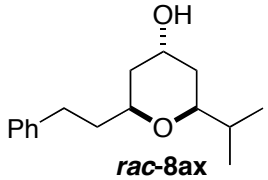
7ax

2,6-Diphenyltetrahydropyran-4-ol (7ax). White solid: mp 69–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.17 (m, 10H), 4.25 (quintet, *J* = 2.8 Hz, 1H), 3.76–3.71 (m, 2H), 2.89 (ddd, *J* = 14.3, 9.8, 5.2 Hz, 2H), 2.72 (ddd, *J* = 13.7, 9.4, 7.1 Hz, 2H), 1.86 (dtd, *J* = 14.2, 9.2, 5.2 Hz, 2H), 1.70 (dddd, J = 13.6, 10.7, 7.0, 3.8 Hz, 2H), 1.64 (dd, *J* = 14.7, 2.3 Hz, 2H), 1.54–1.49 (m, 2H), 1.30 (d, *J* = 2.90 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 128.60, 128.4, 125.8, 70.7, 65.0, 39.0, 38.1, 32.0; IR (KBr) 3392, 3026, 2918, 1093, 750, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{26}NaO_2$ $(M + Na)^+$ 333.1830, found 333.1836.



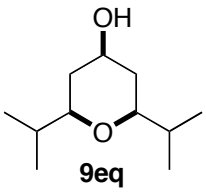
***rac*-8eq**

2-Isopropyl-6-phenethyltetrahydropyran-4-ol (8eq). Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.19–7.16 (m, 3H), 3.74 (tt, *J* = 10.7, 4.6 Hz, 1H), 3.22–3.17 (m, 1H), 2.92 (ddd, *J* = 11.1, 7.6, 1.6 Hz, 1H), 2.81 (ddd, *J* = 13.9, 9.0, 5.2 Hz, 1H), 2.70 (ddd, *J* = 13.8, 8.3, 8.3 Hz, 1H), 2.00–1.97 (m, 1H), 1.93–1.85 (m, 2H), 1.75–1.67 (m, 2H), 1.19–1.10 (m, 2H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 128.6, 128.4, 125.8, 80.7, 74.0, 68.8, 41.5, 38.4, 37.8, 33.2, 31.8, 19.0, 18.8; IR (thin film) 3367, 3028, 2951, 2871, 1050, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{16}H_{24}NaO_2$ $(M + Na)^+$ 271.1674, found 271.1676.



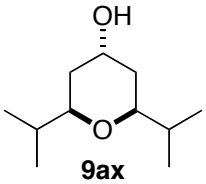
***rac*-8ax**

2-Isopropyl-6-phenethyltetrahydropyran-4-ol (8ax). Colorless oil (5:1 inseparable mixture with **7ax**): ^{1}H NMR (500 MHz, $CDCl_3$) *major component:* δ 7.29–7.25 (m, 2H), 7.22–7.15 (m, 3H), 4.26 (quintet, *J* = 2.8 Hz, 1H), 3.71–3.66 (m, 1H), 3.37 (ddd, *J* = 11.6, 7.3, 1.8 Hz, 1H), 2.83 (ddd, *J* = 14.2, 9.4, 5.1 Hz, 1H), 2.75–2.66 (m, 1H), 1.81 (dtd, *J* = 14.2, 9.1, 5.1 Hz, 1H), 1.68–1.63 (m, 2H), 1.62–1.56 (m, 2H), 1.50–1.42 (m, 2H), 1.35 (br s, 1H), 1.10 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *major component:* δ 142.5, 128.6, 128.3, 125.7, 76.7, 70.5, 65.2, 39.1, 38.1, 36.0, 33.4, 31.9, 19.0, 18.7; IR (thin film) 3390, 3028, 2947, 1057, 737, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{16}H_{24}NaO_2$ $(M + Na)^+$ 271.1674, found 271.1674.



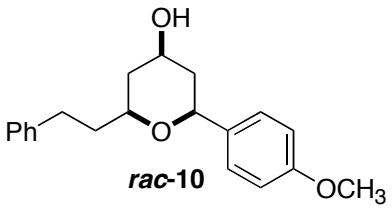
9eq

2,6-Diisopropyltetrahydropyran-4-ol (9eq). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (tt, *J* = 10.7, 4.6 Hz, 1H), 2.92 (ddd, *J* = 11.2, 6.6, 1.4 Hz, 2H), 1.95 (app dd, *J* = 11.7, 4.6 Hz, 2H), 1.47 (br s, 1H), 1.09 (ddd, *J* = 12.0, 11.3, 11.3 Hz, 2H), 0.95 (d, *J* = 6.7 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.5, 69.3, 38.4, 33.2, 18.8, 18.7; IR (thin film) 3351, 2958, 2875, 1469, 1367, 1047 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{11}H_{22}NaO_2$ $(M + Na)^+$ 209.1517, found 209.1522.



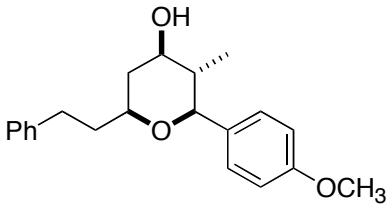
9ax

2,6-Diisopropyltetrahydropyran-4-ol (9ax). Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (quintet, *J* = 2.9 Hz, 1H), 3.34 (ddd, *J* = 11.7, 7.2, 1.3 Hz, 2H), 1.68 (dd, *J* = 14.0, 2.2 Hz, 2H), 1.64–1.58 (m, 2H), 1.45–1.39 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 6H), 0.87 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.6, 65.3, 35.9, 33.4, 18.8, 18.7; IR (thin film) 3365, 2958, 2875, 1471, 1385, 1070 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{11}H_{22}NaO_2$ $(M + Na)^+$ 209.1517, found 209.1520.



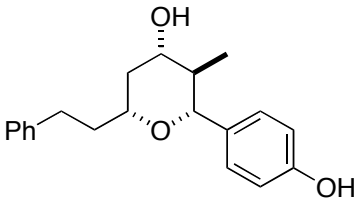
***rac*-10**

2-(4-Methoxyphenyl)-6-phenethyltetrahydropyran-4-ol (10). Light yellow solid: mp = 112–114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.29–7.26 (m, 2H), 7.20–7.17 (m, 3H), 6.90 (app d, *J* = 8.7 Hz, 2H), 4.30 (dd, *J* = 11.4, 1.6 Hz, 1H), 3.92 (tt, *J* = 10.8, 4.8 Hz, 1H), 3.81 (s, 3H), 3.48–3.43 (m, 1H), 2.81 (ddd, *J* = 14.1, 9.4, 5.7 Hz, 1H), 2.77–2.71 (m, 1H), 2.21–2.18 (m, 1H), 2.03–1.95 (m, 2H), 1.82 (dddd, *J* = 13.8, 9.4, 7.2, 4.5 Hz, 1H), 1.53–1.46 (m, 2H), 1.31 (ddd, *J* = 12.0, 11.3, 11.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 142.2, 134.4, 128.6, 128.4, 127.3, 125.8, 113.8, 74.8, 68.6, 55.4, 42.8, 41.0, 37.6, 31.7; IR (KBr) 3382, 3026, 2943, 1248, 829, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{20}H_{24}NaO_3$ $(M + Na)^+$ 335.1623, found 335.1625.

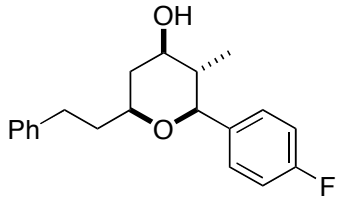


2-(4-Methoxyphenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. White solid: mp 85–86 °C; $[\alpha]^{25}_D$ = –78.3 (*c* 0.51, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 4H), 7.18–7.15 (m, 3H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.84 (d, *J* = 10.0 Hz, 1H), 3.81 (s, 3H), 3.49–3.44 (m, 2H), 2.73–2.68 (m, 2H), 2.04 (ddd, *J* = 12.3, 4.7, 1.7 Hz, 1H), 1.99–1.91 (m, 1H), 1.79 (dddd, *J* = 14.0, 9.2, 7.1, 5.0 Hz, 1H), 1.57–1.53 (m, 2H), 1.47 (ddd, *J* = 12.1, 11.3, 11.3 Hz, 1H), 0.77 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 142.2, 133.0, 128.8, 128.6, 128.3, 125.8, 113.8, 84.1, 74.8, 74.1, 55.3, 45.2, 41.0, 37.5, 31.5, 13.3; IR (KBr) 3424, 3022, 2962, 1456, 1047, 737 cm^{-1};

HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{26}NaO_3$ $(M + Na)^+$ 349.1780, found 349.1769. Enantiomeric excess was calculated from HPLC analysis using CHIRALCEL OD-H column eluting with 5% isopropanol/hexane (flow rate = 1 ml/min): retention time = 26.82 min, retention time of (+)-enantiomer = 19.99 min.

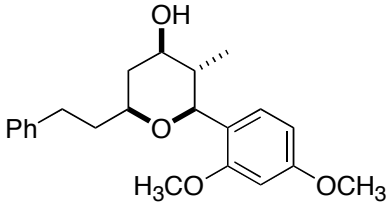


2-(4-Hydroxyphenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. Light yellow solid: mp 183–184 °C; $[\alpha]^{25}_D$ = +65.0 (*c* 0.50, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 3H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.76 (s, 1H), 3.83 (d, *J* = 10.0 Hz, 1H), 3.49–3.46 (m, 2H), 2.76–2.65 (m, 2H), 2.04 (ddd, *J* = 12.3, 4.7, 1.7 Hz, 1H), 1.99–1.91 (m, 1H), 1.79 (dddd, *J* = 13.8, 9.3, 7.1, 4.8 Hz, 1H), 1.60–1.52 (m, 2H), 1.47 (ddd, *J* = 12.1, 11.7. 11.3 Hz, 1H) 0.77 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 142.1, 132.5, 129.0, 128.6, 128.3, 125.8, 115.2, 84.0, 74.8, 74.1, 45.2, 41.0, 37.5, 31.5, 13.3; IR (KBr) 3237, 2914, 1227, 1038, 829, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{20}H_{24}NaO_3$ $(M + Na)^+$ 335.1623, found 335.1620.

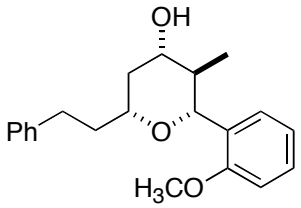


2-(4-Fluorophenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. White solid: mp 91–93 °C; $[\alpha]^{25}_D$ = –65.6 (*c* 0.51, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.25 (m, 4H), 7.19–7.15 (m,

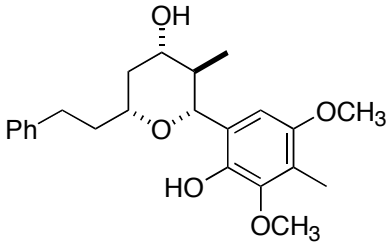
3H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.87 (d, *J* = 10.0 Hz, 1H), 3.49–3.46 (m, 2H), 2.76–2.65 (m, 2H), 2.05 (ddd, *J* = 12.4, 4.6, 1.8 Hz, 1H), 1.99–1.91 (m, 1H), 1.80 (dddd, *J* = 14.2, 9.2, 7.1, 5.1 Hz, 1H), 1.56–1.43 (m, 2H), 0.77 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, ^1J(CF) = 245.5), 142.0, 136.6, 129.2 (d, ^3J(CF) = 7.5), 128.5, 128.4, 125.8, 115.2 (d, ^2J(CF) = 21.4), 83.8, 74.9, 73.9, 45.4, 40.9, 37.5, 31.5, 13.2; IR (KBr) 3414, 2966, 2871, 1604, 1223, 837 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{20}H_{23}FNaO_2$ $(M + Na)^+$ 337.1580, found 337.1585. Enantiomeric excess was calculated from HPLC analysis using CHIRALCEL OD-H column eluting with 5% isopropanol/hexane (flow rate = 1 ml/min): retention time = 19.87 min, retention time of (+)-enantiomer = 15.08 min.



2-(2,4-Dimethoxyphenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. Colorless oil: $[\alpha]^{25}_D$ = –50.4 (*c* 0.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 1H), 7.27–7.24 (m, 2H), 7.18–7.17 (m, 3H), 6.53 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 4.43 (d, *J* = 10.1 Hz, 1H), 3.81 (s, 6H), 3.50–3.48 (m, 2H), 2.72–2.68 (m, 2H), 2.02 (app dd, *J* = 12.3, 3.5 Hz, 1H), 1.97–1.90 (m, 1H), 1.76 (dddd, *J* = 13.8, 8.9, 7.3, 5.1 Hz, 1H), 1.59–1.52 (m, 2H), 1.44 (ddd, *J* = 11.7, 11.6, 11.3 Hz, 1H), 0.78 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 158.0, 142.3, 128.6, 128.3, 125.7, 122.1, 104.9, 98.3, 74.7, 74.3, 55.5, 55.4, 45.4, 41.0, 37.6, 31.5, 12.7; IR (thin film) 3403, 2935, 2839, 1508, 1209, 1038 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{22}H_{28}NaO_4$ $(M + Na)^+$ 379.1885, found 379.1882.

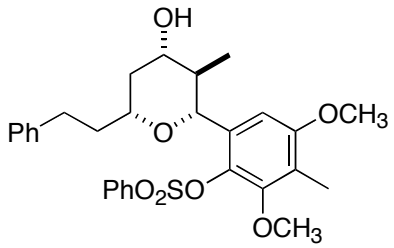


2-(2-Methoxyphenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. Pale yellow solid: mp 117–118 °C; $[\alpha]^{25}_{D}$ = +57.5 (*c* 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.27–7.24 (m, 3H), 7.18–7.15 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.54 (d, *J* = 10.1 Hz, 1H), 3.83 (s, 3H), 3.54–3.49 (m, 2H), 2.75–2.65 (m, 2H), 2.04 (ddd, *J* = 12.3, 4.6, 1.6 Hz, 1H), 1.98–1.91 (m, 1H), 1.78 (dddd, *J* = 13.9, 9.0, 7.2, 5.1 Hz, 1H), 1.56–1.54 (m, 1H), 1.53 (d, *J* = 5.4 Hz, 1H), 1.46 (ddd, *J* = 11.8, 11.4, 11.3 Hz, 1H), 0.78 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 142.3, 129.5, 128.6, 128.5, 128.3, 127.9, 125.7, 121.0, 110.5, 74.9, 74.3, 55.5, 45.6, 41.0, 37.6, 31.5, 12.6; IR (KBr) 3398, 2964, 2935, 1495, 1049, 754 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{26}NaO_3$ $(M + Na)^+$ 349.1780, found 349.1776.

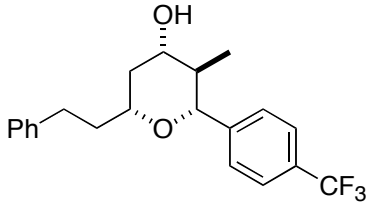


2-(2-Hydroxy-3,5-dimethoxy-4-methylphenyl)-3-methyl-6-phenethyltetrahydropyran-4-ol. Yellow oil: $[\alpha]^{25}_{D}$ = +52.9 (*c* 0.53, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 2H), 7.19–7.15 (m, 3H), 6.67 (br s, 1H), 6.41 (s, 1H), 4.22 (d, *J* = 10.2 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.56–3.51 (m, 1H), 3.48 (td, *J* = 10.2, 4.6 Hz, 1H), 2.79–2.66 (m, 2H), 2.15 (s, 3H), 2.08 (ddd, *J* = 12.3, 4.6, 1.6 Hz, 1H), 2.00–1.93 (m, 1H), 1.83 (dddd, *J* = 14.0, 9.6, 7.0, 4.8 Hz, 1H), 1.73 (m, 1H), 1.49 (ddd, *J* = 12.1, 11.5, 11.4 Hz, 1H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 151.1, 146.8, 141.9, 141.8, 128.5, 128.4, 125.9, 122.6, 120.0, 105.8, 82.0, 75.4, 73.7, 60.6, 56.2, 44.0, 41.0, 37.6, 31.5, 30.4, 13.3, 9.2; IR (thin film) 3392, 3028, 2937, 1120, 739, 702 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{23}H_{30}NaO_5$ $(M + Na)^+$ 409.1991, found 409.1978.

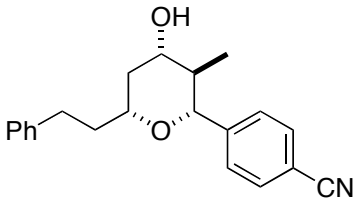


Benzenesulfonic acid 6-(4-hydroxy-3-methyl-6-phenethyltetrahydropyran-2-yl)-2,4-dimethoxy-3-methylphenyl ester. White solid: mp 58–60 °C; $[\alpha]^{25}_D$ = +31.1 (*c* 0.50, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.63 (app t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.30–7.26 (m, 2H), 7.22–7.17 (m, 3H), 6.71 (s, 1H), 4.20 (d, *J* = 10.1 Hz, 1H), 3.84 (s, 3H), 3.38–3.31 (m, 2H), 2.73 (s, 3H), 2.73–2.67 (m, 2H), 2.09 (s, 3H), 1.99 (ddd, *J* = 12.5, 4.8, 1.7 Hz, 1H), 1.96–1.90 (m, 1H), 1.79–1.72 (m, 1H), 1.59 (d, *J* = 5.0 Hz, 1H), 1.46–1.39 (m, 1H), 0.79 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 151.2, 142.2, 137.8, 135.7, 133.7, 132.7, 128.9, 128.7, 128.4, 128.3, 125.8, 121.0, 104.1, 74.9, 73.9, 60.3, 55.8, 45.0, 40.8, 37.5, 31.5, 12.7, 9.3; IR (KBr) 3401, 2937, 1456, 1176, 1130, 733 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{29}H_{34}NaO_7S$ $(M + Na)^+$ 549.1923, found 549.1934.

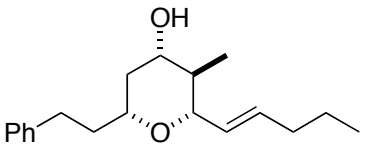


3-Methyl-6-phenethyl-2-(4-trifluoromethylphenyl)tetrahydropyran-4-ol. White solid: mp 99–100 °C; $[\alpha]^{25}_D$ = +71.9 (*c* 0.51, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz,

2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27–7.24 (m, 2H), 7.18–7.14 (m, 3H), 3.94 (d, *J* = 10.0 Hz, 1H), 3.51–3.46 (m, 2H), 2.76–2.65 (m, 2H), 2.05 (ddd, *J* = 12.4, 4.6, 1.8 Hz, 1H), 1.96 (dddd, *J* = 13.7, 8.8, 7.6, 5.9 Hz, 1H), 1.82 (dddd, *J* = 13.9, 9.2, 7.0, 4.8 Hz, 1H), 1.55–1.46 (m, 2H), 0.78 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.0, 131.1 (q, ^2J(CF) = 32.7), 128.5, 128.4, 127.9, 125.9, 125.3, 125.3 (q, ^3J(CF) = 3.8), 83.9, 75.0, 73.8, 45.3, 41.0, 37.5, 31.5, 13.1; IR (KBr) 3369, 2933, 1325, 1122, 835, 700 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{23}F_3NaO_2$ $(M + Na)^+$ 387.1548, found 387.1552.

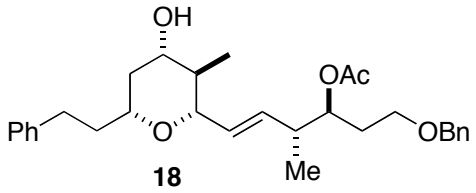


4-(4-Hydroxy-3-methyl-6-phenethyltetrahydropyran-2-yl)benzonitrile. Colorless oil: $[\alpha]^{25}_D$ = +78.9 (*c* 0.92, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.27–7.24 (m, 2H), 7.19–7.13 (m, 3H), 3.94 (d, *J* = 10.0 Hz, 1H), 3.52–3.46 (m, 2H), 2.76–2.64 (m, 2H), 2.04 (ddd, *J* = 12.4, 4.5, 1.6 Hz, 1H), 1.99–1.92 (m, 1H), 1.82 (dddd, *J* = 13.9, 9.2, 7.0, 4.8 Hz, 1H), 1.60 (d, *J* = 5.3 Hz, 1H), 1.53–1.46 (m, 2H), 0.78 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 141.8, 132.2, 128.44, 128.36, 128.3, 125.8, 118.8, 111.6, 83.7, 75.1, 73.5, 45.3, 40.9, 37.4, 31.4, 13.0; IR (thin film) 3460, 3028, 2922, 2229, 1610, 739 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{21}H_{23}NNaO_2$ 344.1627, found 344.1629.



14

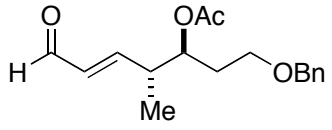
3-Methyl-2-pent-1-enyl-6-phenethyltetrahydropyran-4-ol (14). Light brown oil: $[\alpha]^{25}_{D}$ = +40.0 (*c* 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.26 (m, 2H), 7.19–7.17 (m, 3H), 5.72–5.67 (m, 1H), 5.43 (ddd, *J* = 15.3, 7.8, 1.4 Hz, 1H), 3.36–3.33 (m, 3H), 2.78–2.66 (m, 2H), 2.10–2.01 (m, 2H), 1.98–1.90 (m, 2H), 1.73–1.70 (m, 2H), 1.47–1.39 (m, 2H), 1.36–1.23 (m, 2H), 0.93–0.90 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 134.9, 129.2, 128.6, 128.4, 125.8, 82.8, 74.2, 73.8, 43.9, 40.9, 37.5, 34.5, 31.7, 22.3, 13.8, 13.4; IR (thin film) 3391, 3028, 2927, 1456, 1036, 746 cm^{-1}; HRMS (ES/MeOH) *m* / *z* calcd for $C_{19}H_{28}NaO_2$ $(M + Na)^+$ 311.1987, found 311.1985.



18

Acetic acid 1-(2-benzyloxylethyl)-4-(4-hydroxy-3-methyl-6-phenethyltetrahydropyran-2-yl)-2-methylbu-3-enyl ester (18). Yellow oil: $[\alpha]^{25}_{D}$ = +8.8 (*c* 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *mixture of E and Z isomers (ratio ca. 14:1):* δ 7.34–7.25 (m, 7H), 7.34–7.25 (m, 3H), 5.65–5.57 (m, 1H), 5.49–5.42 (m, 1H), 5.06–4.98 (m, 1H), 4.47 (s, 2H), 3.51–3.45 (m, 2H), 3.35–3.32 (m, 3H), 2.75–2.69 (m, 2H), 2.45–2.69 (m, 1H), 2.00 (s, 3H), 1.96–1.78 (m, 4H), 1.76–1.69 (m, 1H), 1.60 (br s, 1H), 1.33–1.24 (m, 2H), 1.06–1.03 (m, 3H), 0.92–0.90 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *major isomer:* δ 170.8, 142.1, 138.4, 135.0, 128.6, 128.41, 128.37, 127.8, 127.6, 125.8, 82.7, 74.2, 74.1, 73.7, 73.2, 67.0, 43.9, 41.0, 40.8, 37.6, 32.0, 31.7, 21.2,

16.2, 13.3; IR (thin film) 3446, 2933, 1732, 1242, 1095, 741 cm^{-1}; HRMS (ES/MeOH) *m / z* calcd for $C_{30}H_{40}NaO_5$ $(M + Na)^+$ 503.2773, found 503.2776.



17

Acetic acid 1-(2-benzyloxylethyl)-2-methyl-5-oxopent-3enyl ester (17). To a flame-dried flask equipped with a reflux condenser was added terminal alkene[4] (264.8 mg, 1.01 mmol, 1 equiv), crotonaldehyde (0.35 mL, 4.22 mmol, 4.2 equiv), Grubbs 2nd generation catalyst (70.0 mg, 0.08 mmol, 0.08 equiv) and dry CH_2Cl_2 (4 mL). The mixture was heated at 50 °C for 30 min and then cooled to room temperature before 5 mL of CH_2Cl_2 was added. The light brown mixture was heated at reflux (50 °C) for 18 h, cooled to room temperature, and concentrated *in vacuo*. Purification by flash chromatography (40% diethyl ether/hexanes) provided aldehyde **17** as a brown oil (150.4 mg, 54%, *E*/*Z* = 14:1). $[\alpha]^{25}_D$ = +33.0 (*c* 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *major isomer:* δ 9.51 (d, *J* = 7.8 Hz, 1H), 7.35–7.27 (m, 5H), 6.77 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.12 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.17–5.14 (m, 1H), 4.47 (s, 2H), 3.52–3.43 (m, 2H), 2.79–2.70 (m, 1H), 2.01 (s, 3H), 1.84–1.82 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 3H); *minor isomer diagnostic peaks:* δ 9.99 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *major isomer:* δ 193.9, 170.6, 158.2, 138.1, 133.6, 128.5, 127.9, 127.8, 73.4, 73.3, 66.4, 41.1, 32.2, 21.0, 15.6; *minor isomer diagnostic peaks:* 158.5, 133.2, 40.6, 31.6, 14.2; IR (thin film) 3032, 2864, 1734, 1684, 741, 700 cm^{-1}; HRMS (ES/MeOH) *m / z* calcd for $C_{17}H_{22}NaO_4$ $(M + Na)^+$ 313.1416, found 313.1409.

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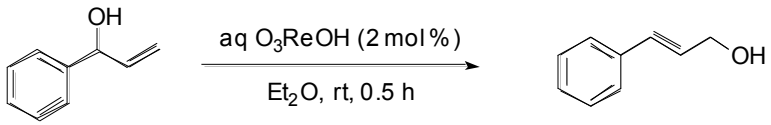
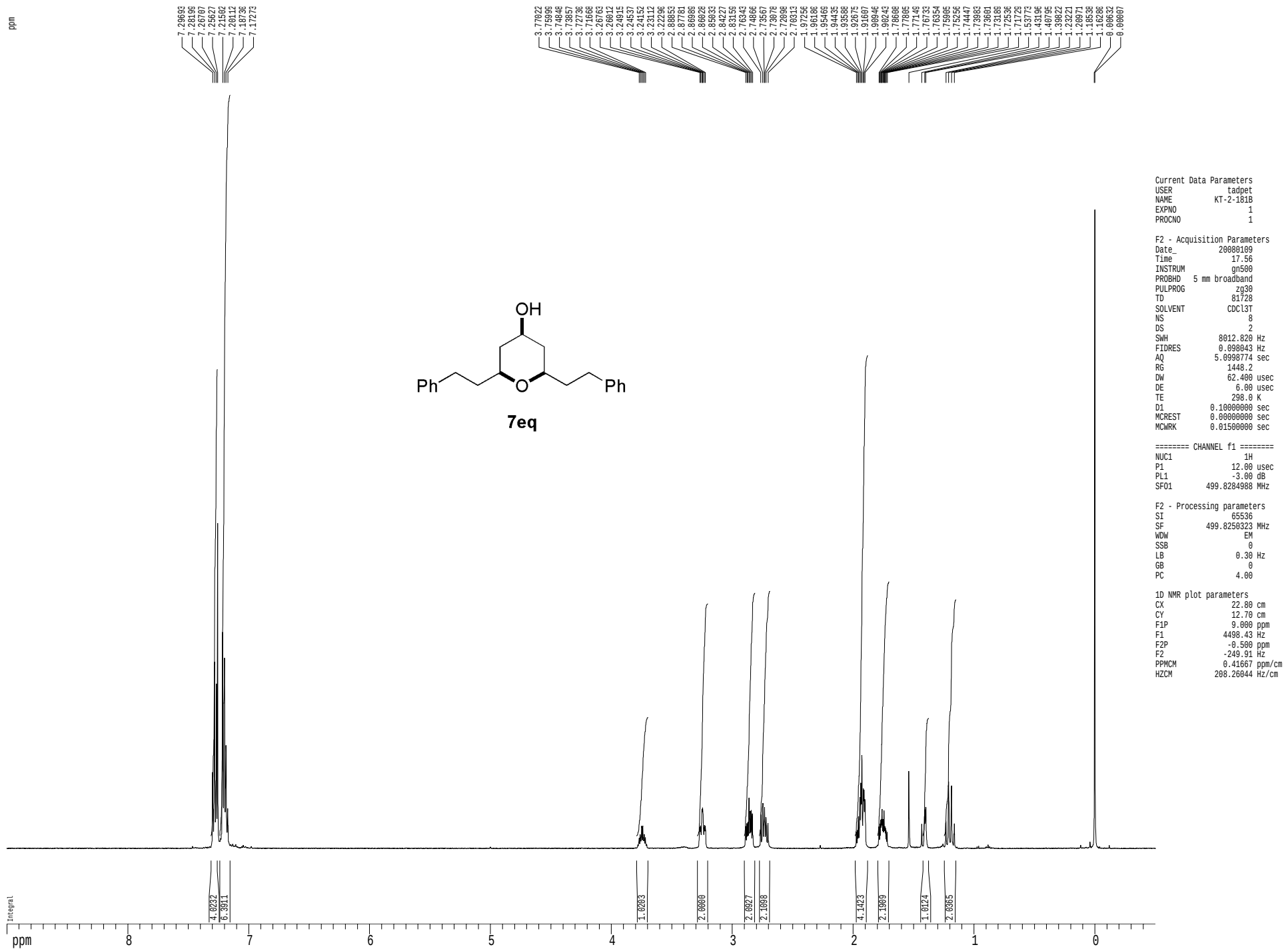
[4] Izzo, I.; Maulucci, N.; Bifulco, G.; De Riccardis, F. *Angew. Chem. Int. Ed.* **2006**, *45*, 7557–7560.



21 **22**

Cinnamyl Alcohol (22): To an oven-dried flask was added allylic alcohol **21** (67.6 mg, 0.50 mmol, 1 equiv) and 4 mL of Et_2O (0.1 M) and the solution was cooled to 0 °C in an ice-water bath for 10 min. To this solution was added 65–70 % aq O_3ReOH (2 μL, 0.011 mmol of O_3ReOH, 2 mol %) via a syringe. The reaction mixture was stirred at 0 °C for 30 min and 30 μL of triethylamine was added. The reaction mixture was then warmed to room temperature and concentrated *in vacuo*. Purification by flash chromatography (30% diethyl ether/hexanes) furnished **22** as a colorless oil (60.1 mg, 89%).

1H spectrum



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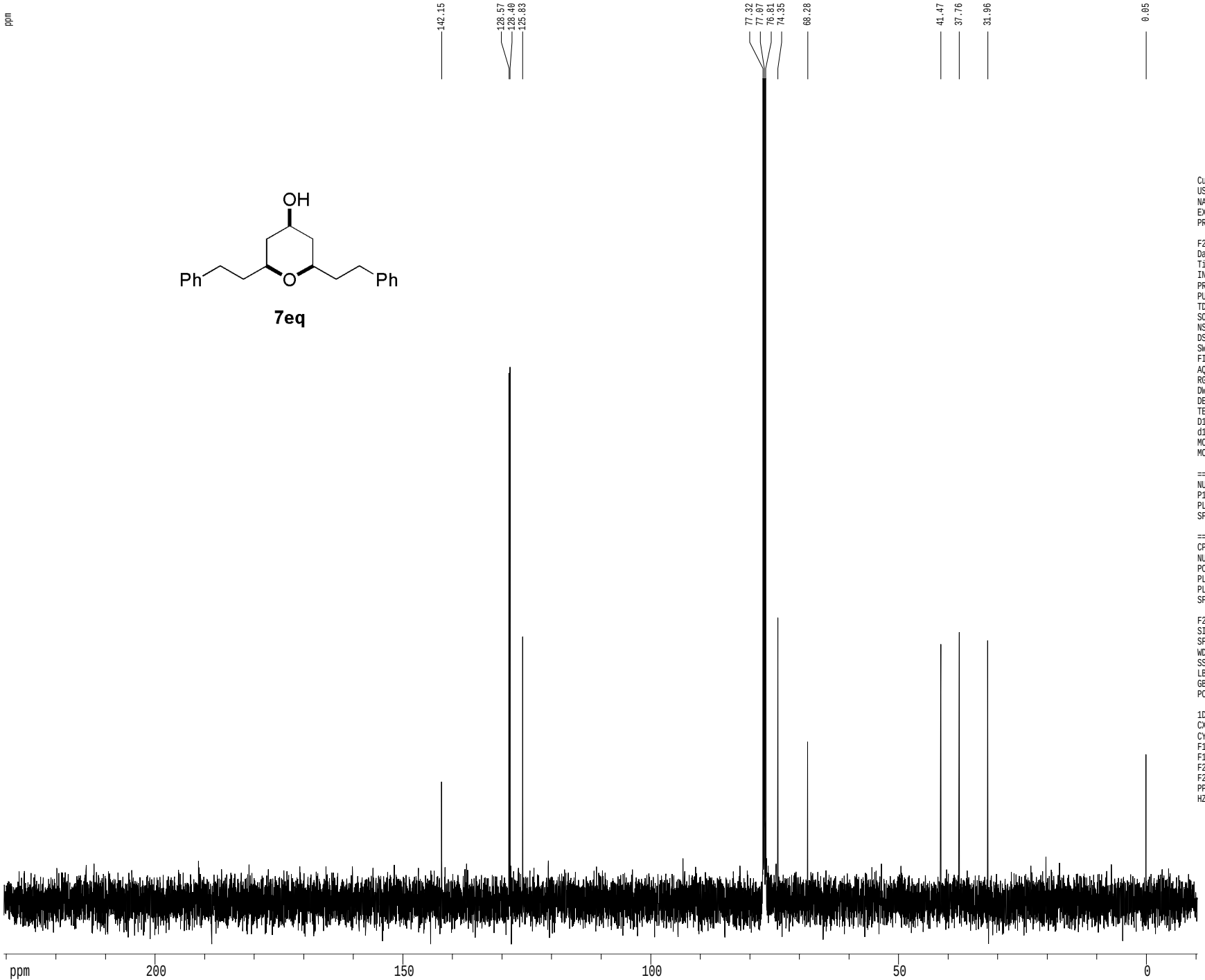
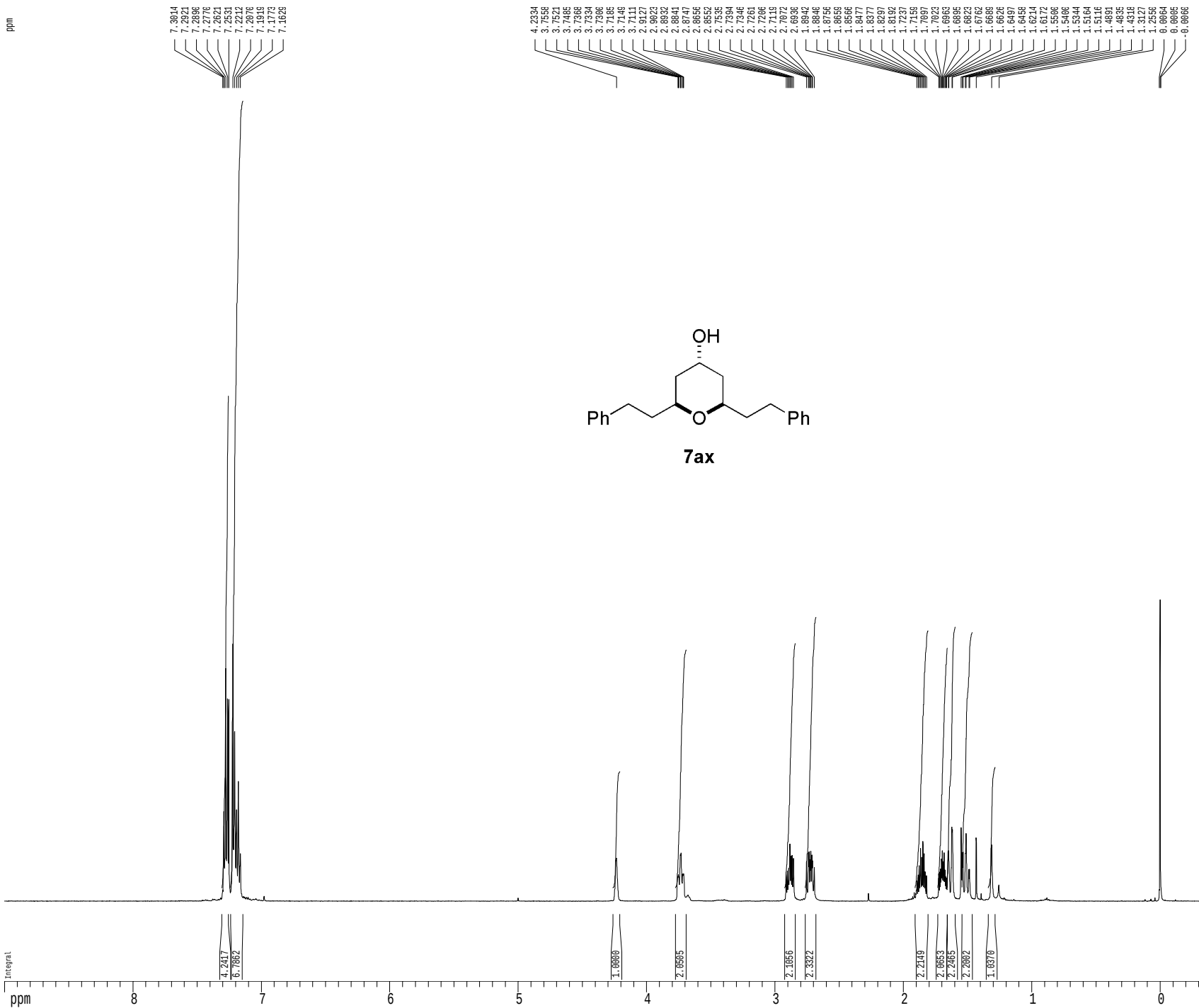
13C spectrum with 1H decoupling



1H spectrum

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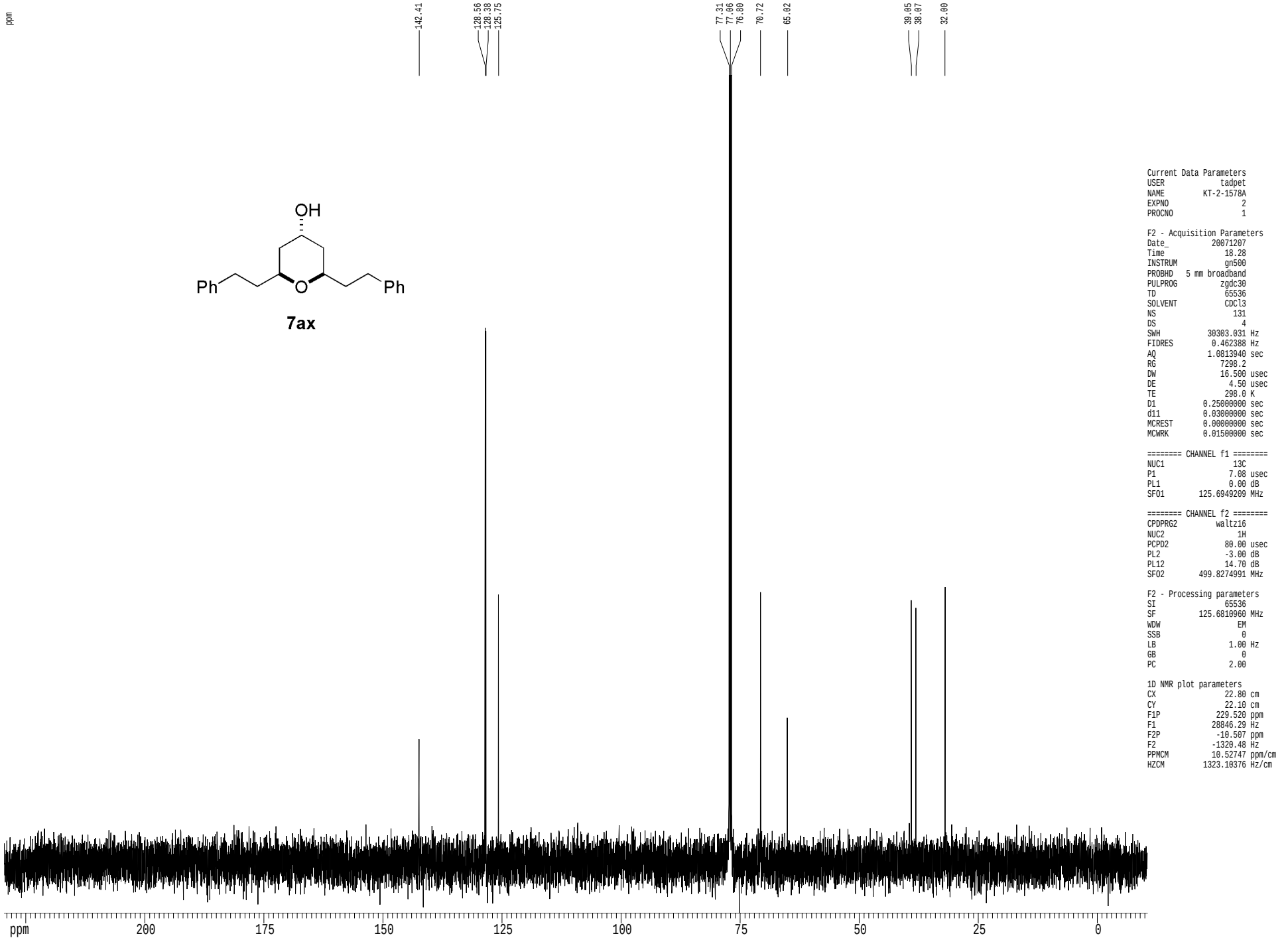
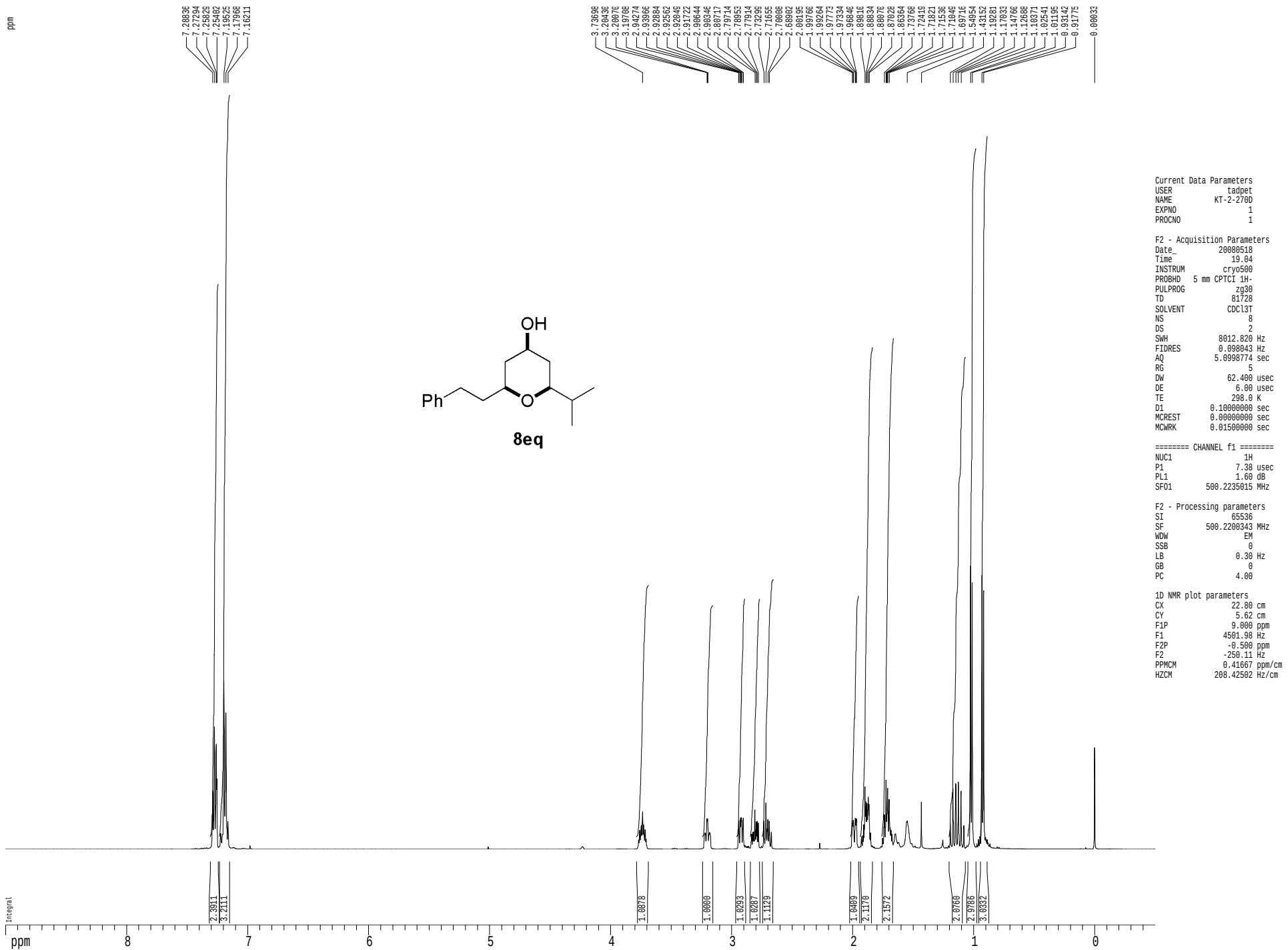
13C spectrum with 1H decoupling



1H spectrum

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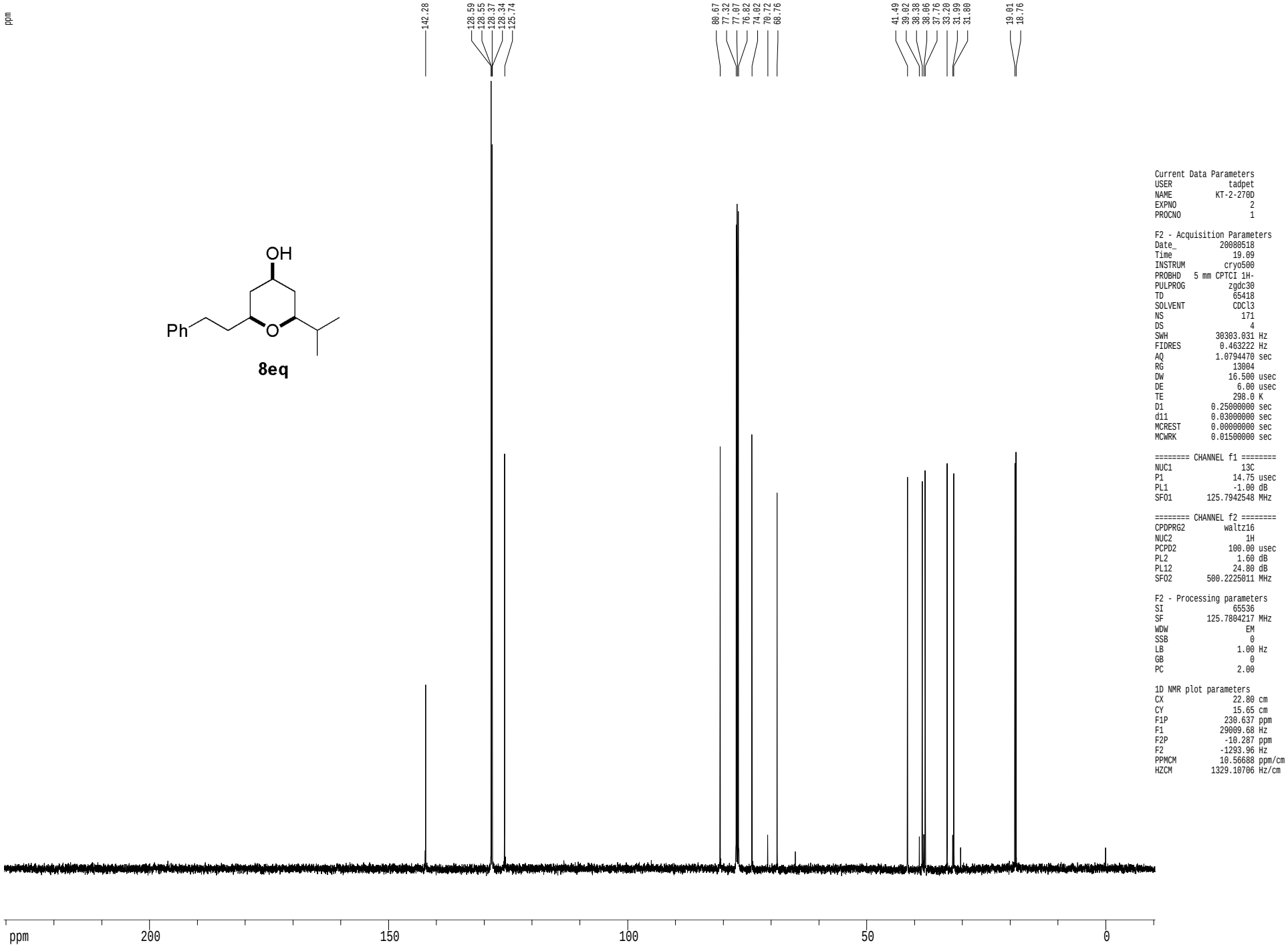
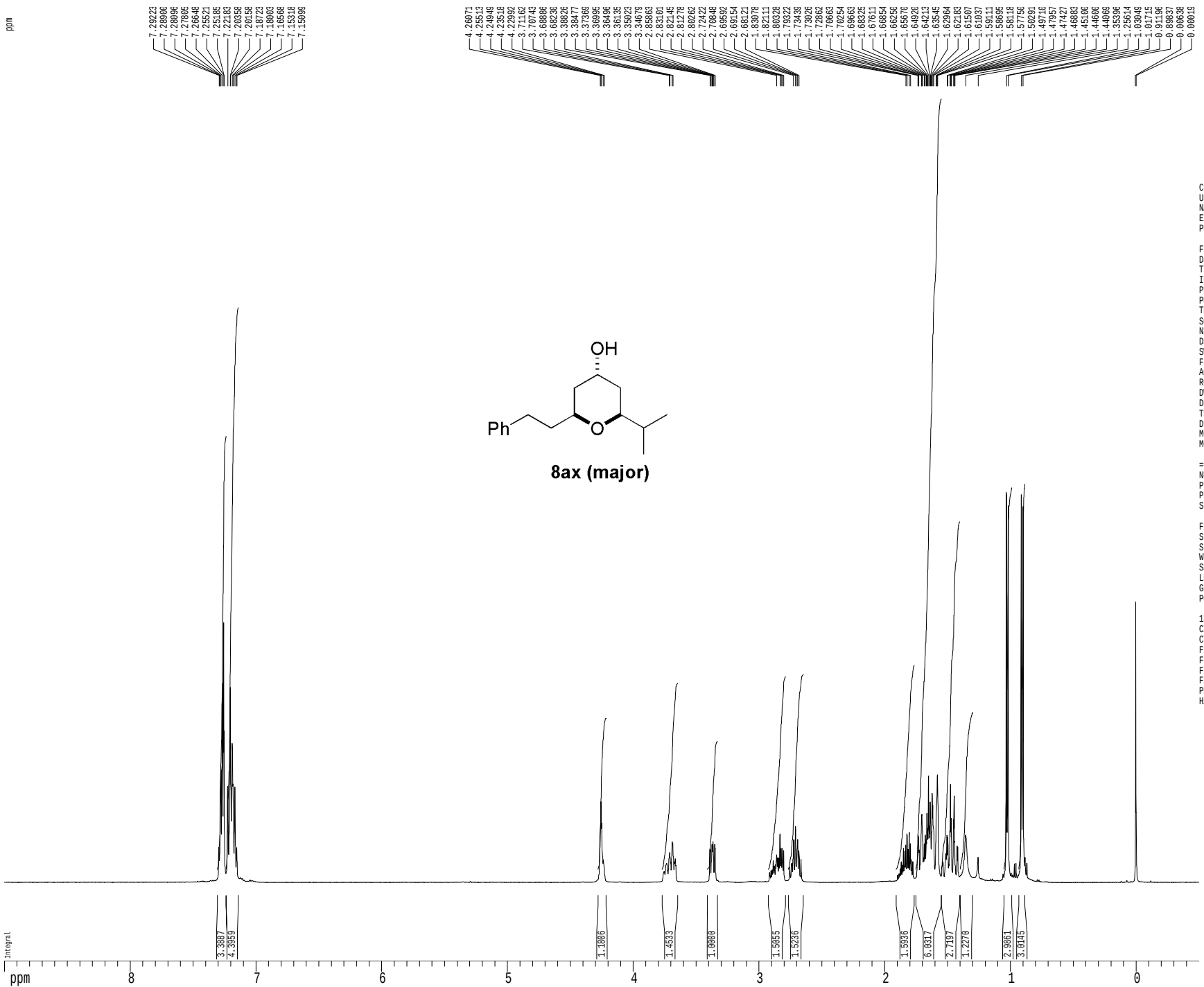
13C spectrum with 1H decoupling



1H spectrum

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1D NMR plot parameters
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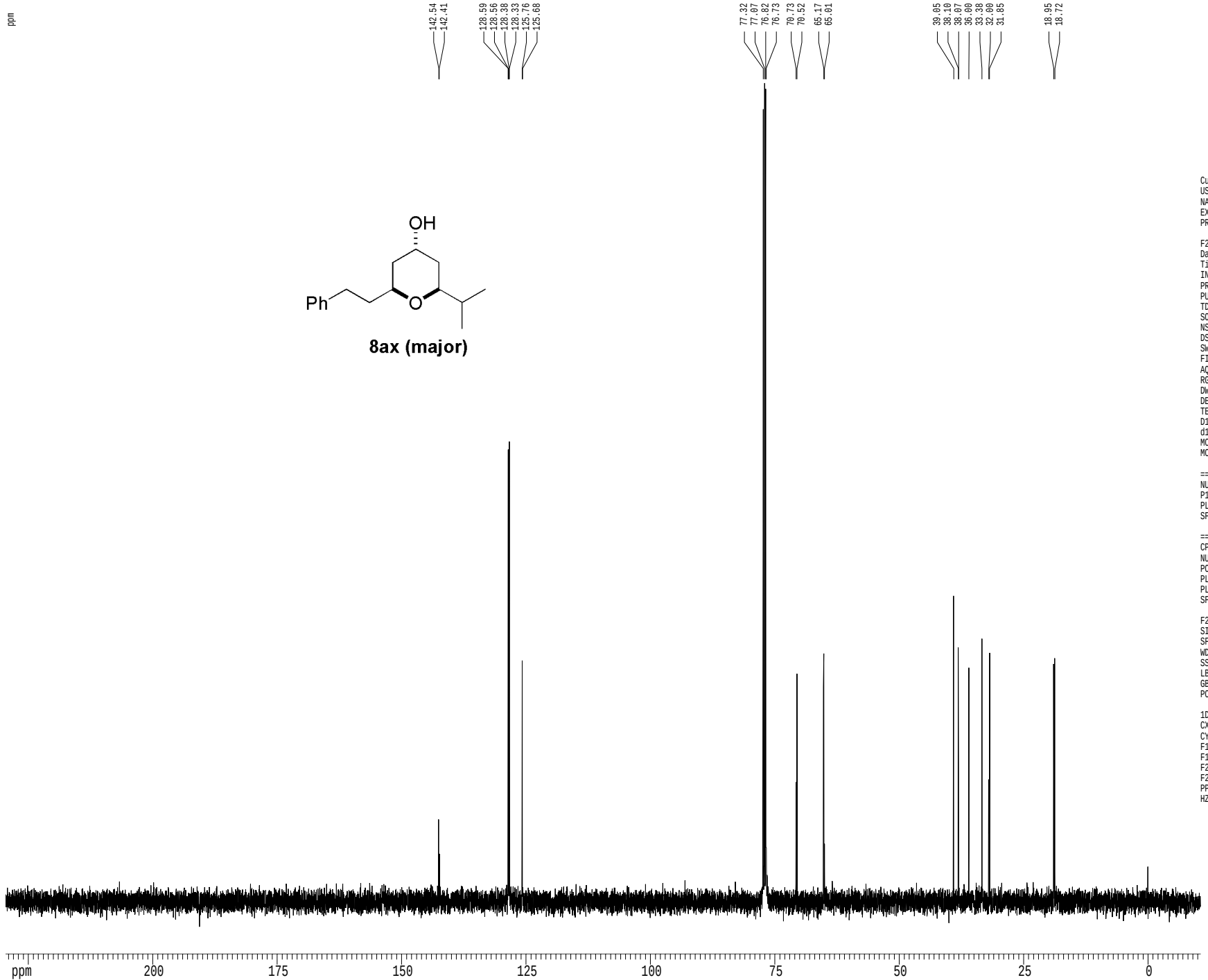
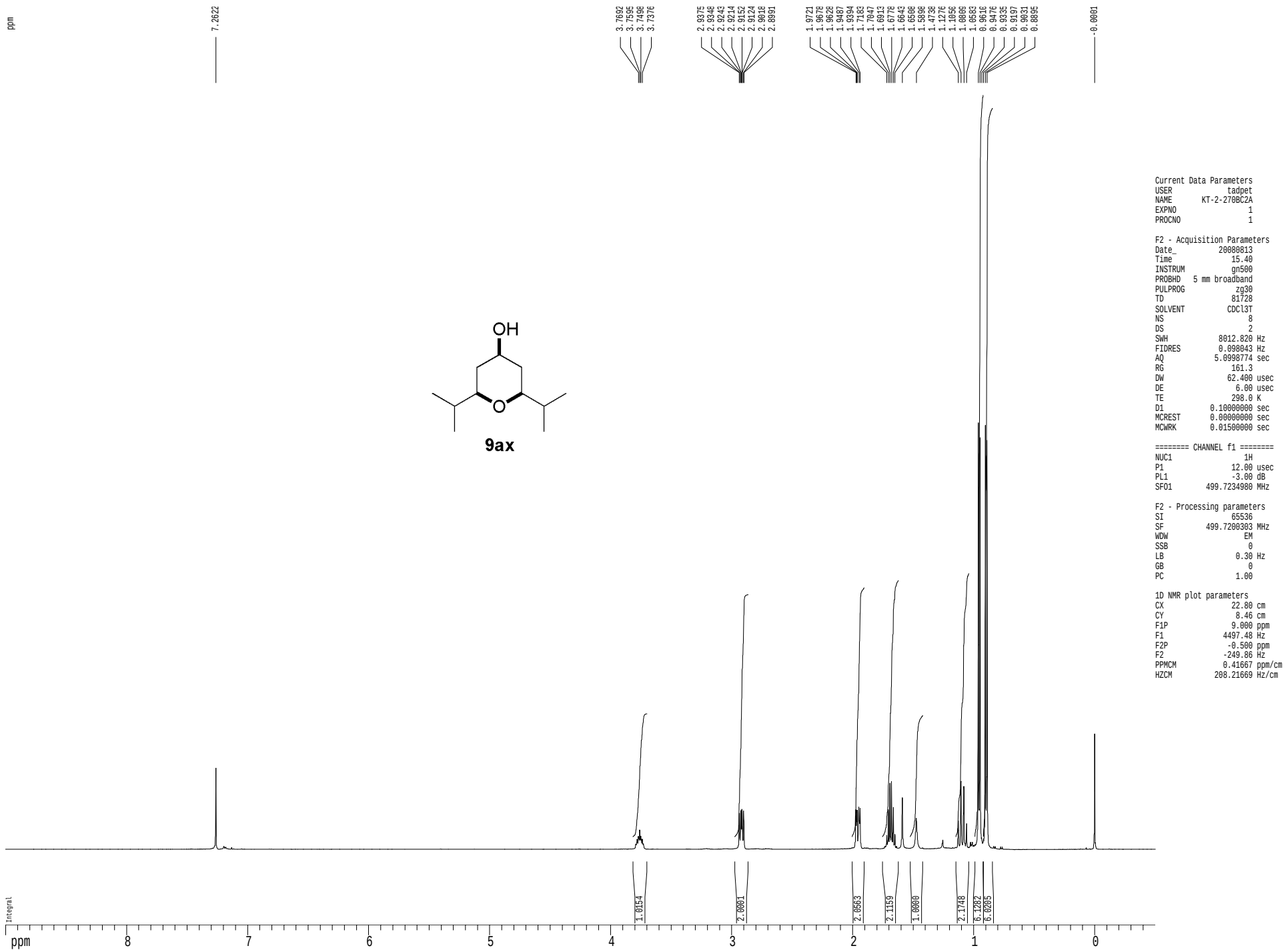
13C spectrum with 1H decoupling

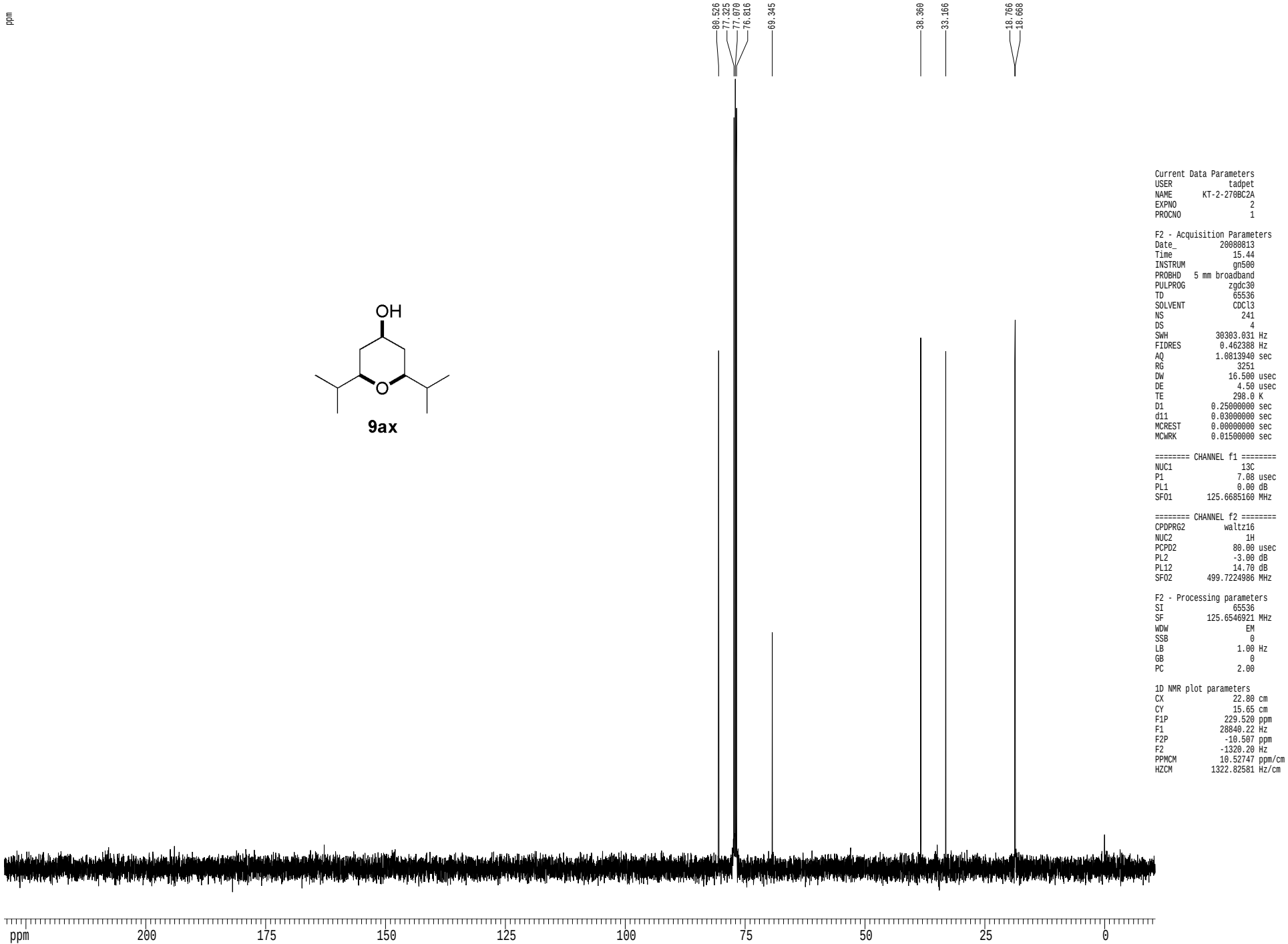


1H spectrum

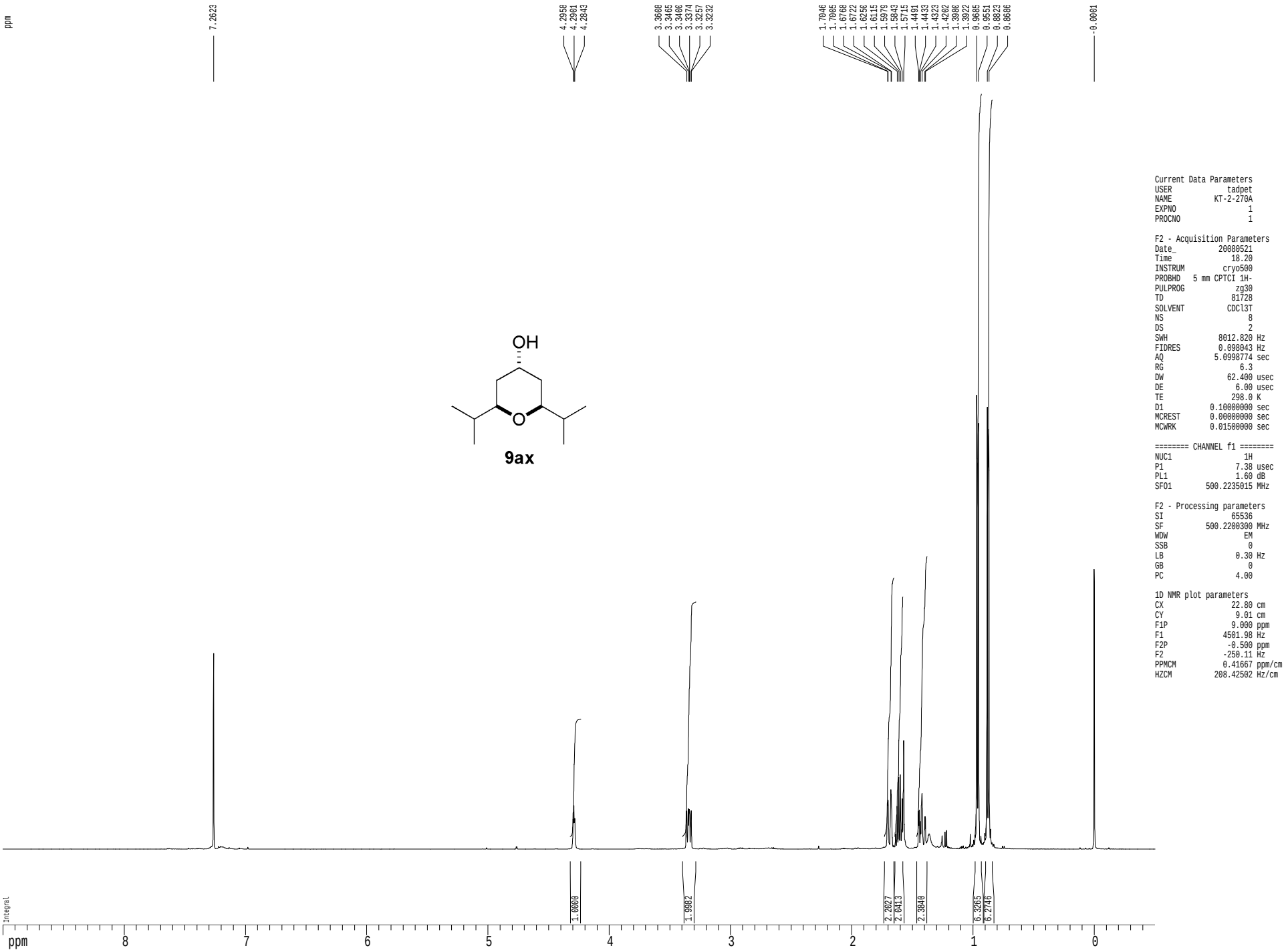



```
Current Data Parameters
USER              tadpet
NAME       KT-2-270BC2A
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20080813
Time              15.40
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                161.3
DW               62.400 usec
DE                6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -3.00 dB
SFO1         499.7234980 MHz

F2 - Processing parameters
SI                65536
SF           499.7200303 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                 8.46 cm
F1P               9.000 ppm
F1              4497.48 Hz
F2P              -0.500 ppm
F2             -249.86 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.21669 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER tadpet
NAME KT-2-270A
EXPNO 1
PROCNO 1

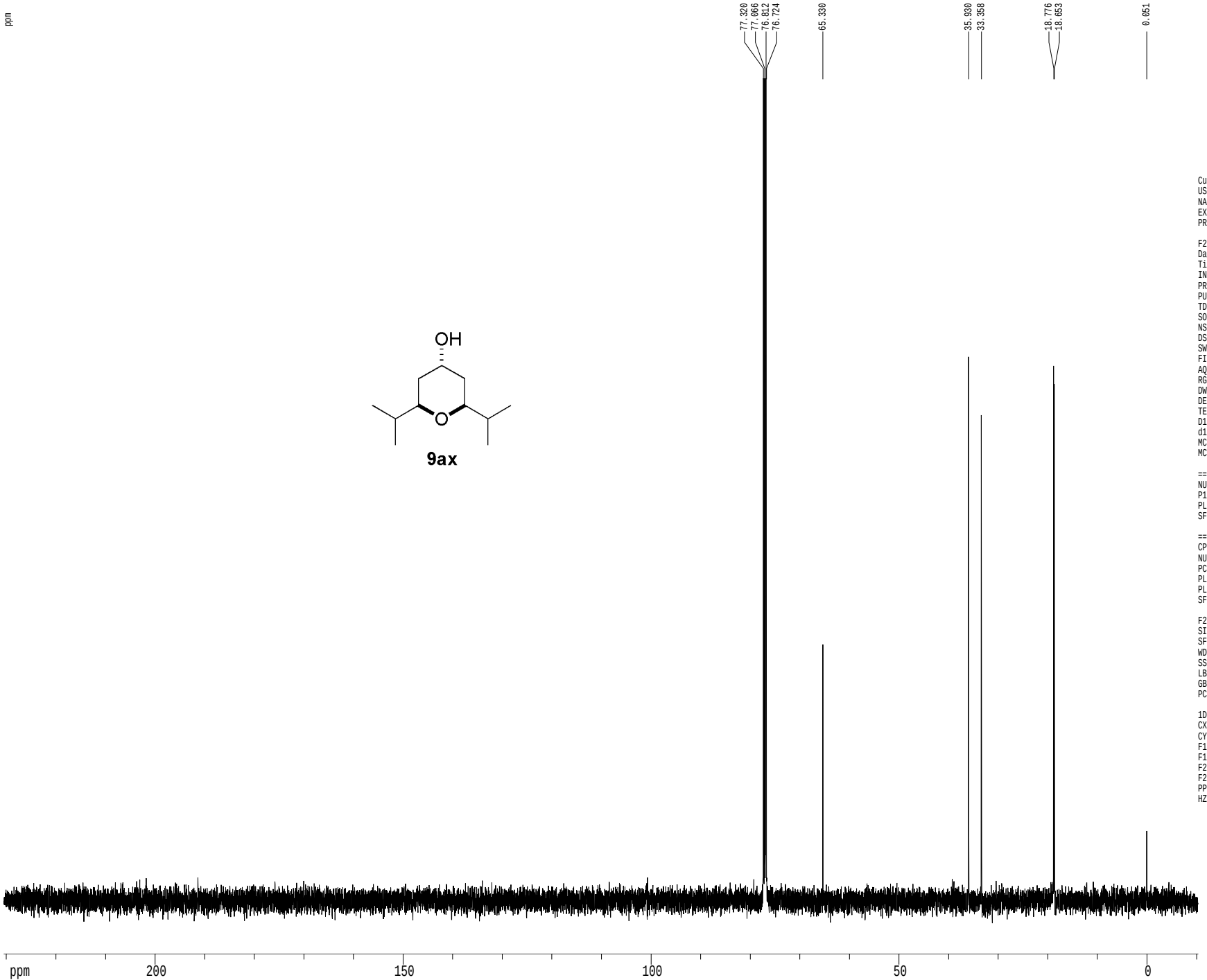
F2 - Acquisition Parameters
Date_ 20080521
Time 18.20
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

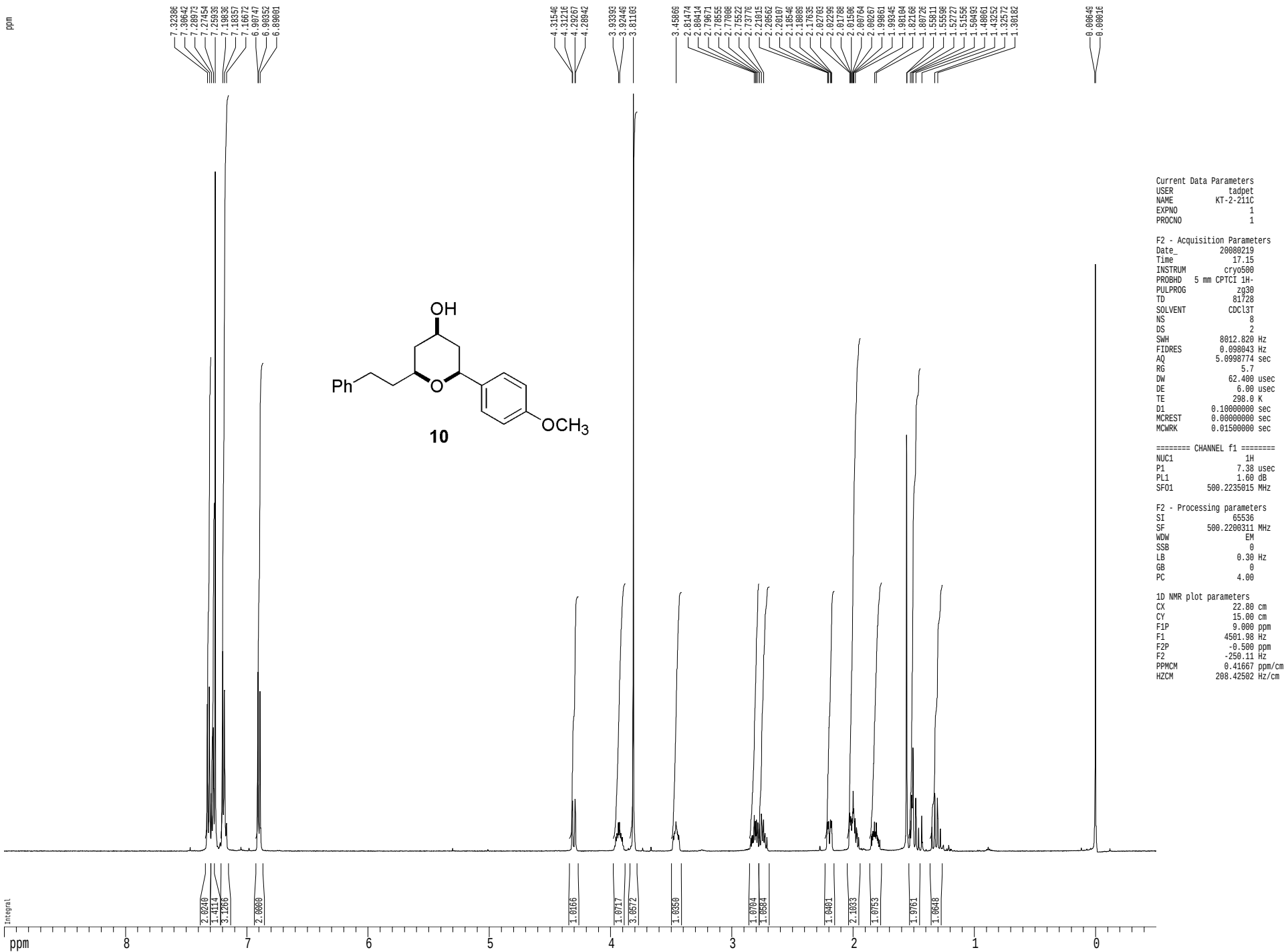
F2 - Processing parameters
SI 65536
SF 500.2200300 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 9.01 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling

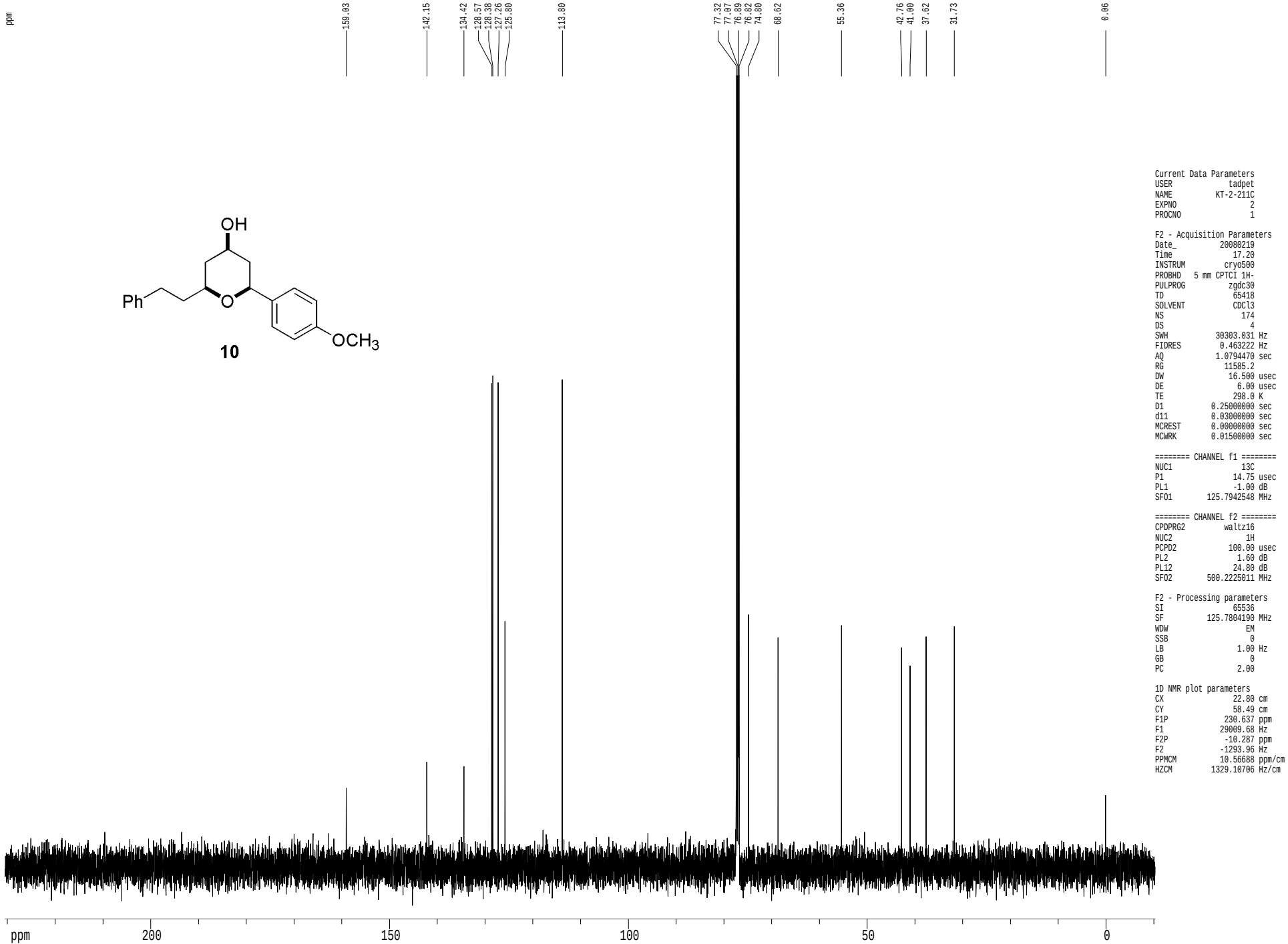


1H spectrum



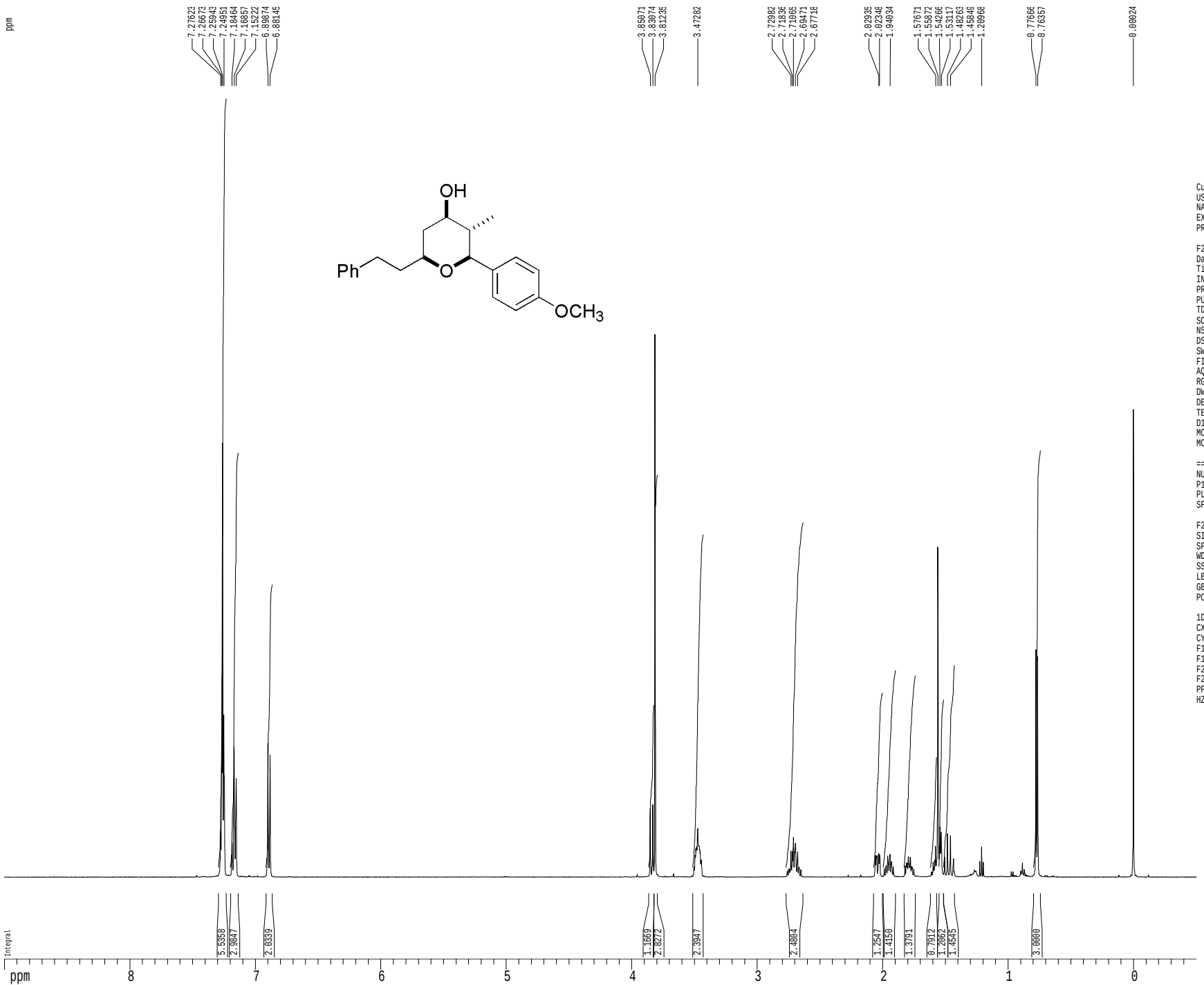

```
Current Data Parameters
USER              tadpet
NAME           KT-2-211C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080219
Time               17.15
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                   5.7
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.38 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

13C spectrum with 1H decoupling




```
Current Data Parameters
USER              tadpet
NAME           KT-2-211C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20080219
Time               17.20
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          zgdc30
TD                65418
SOLVENT           CDCl3
NS                  174
DS                    4
SWH           30303.031 Hz
FIDRES         0.463222 Hz
AQ             1.0794470 sec
RG               11585.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.75 usec
PL1               -1.00 dB
SFO1        125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.80 dB
SFO2        500.2225011 MHz

F2 - Processing parameters
SI                 65536
SF          125.7804190 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 58.49 cm
F1P              230.637 ppm
F1             29009.68 Hz
F2P              -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

1H spectrum



Current Data Parameters
USER tadpet
NAME KT-2-257
EXPNO 1
PROCNO 1

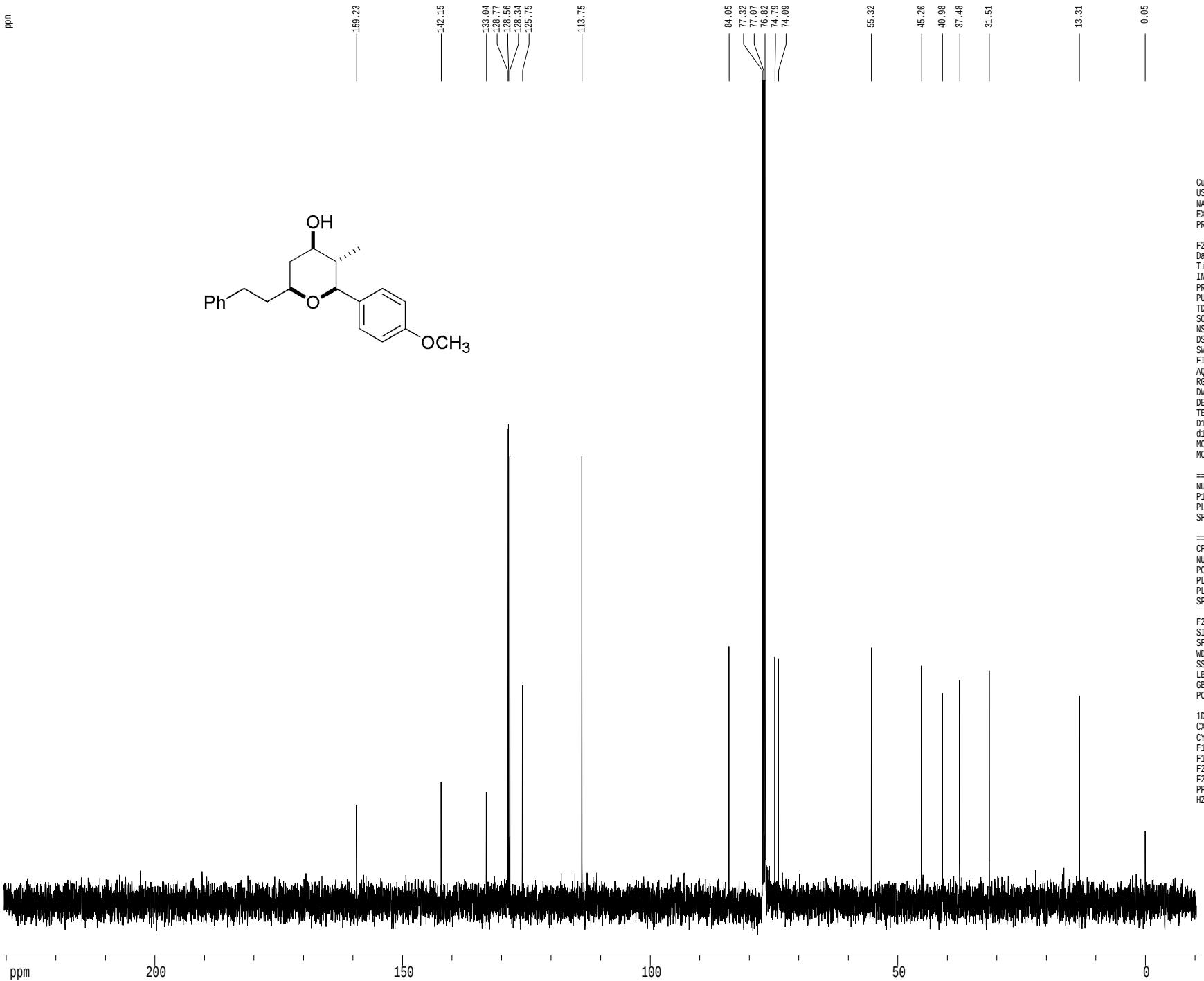
F2 - Acquisition Parameters
Date_ 20080421
Time 10.43
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

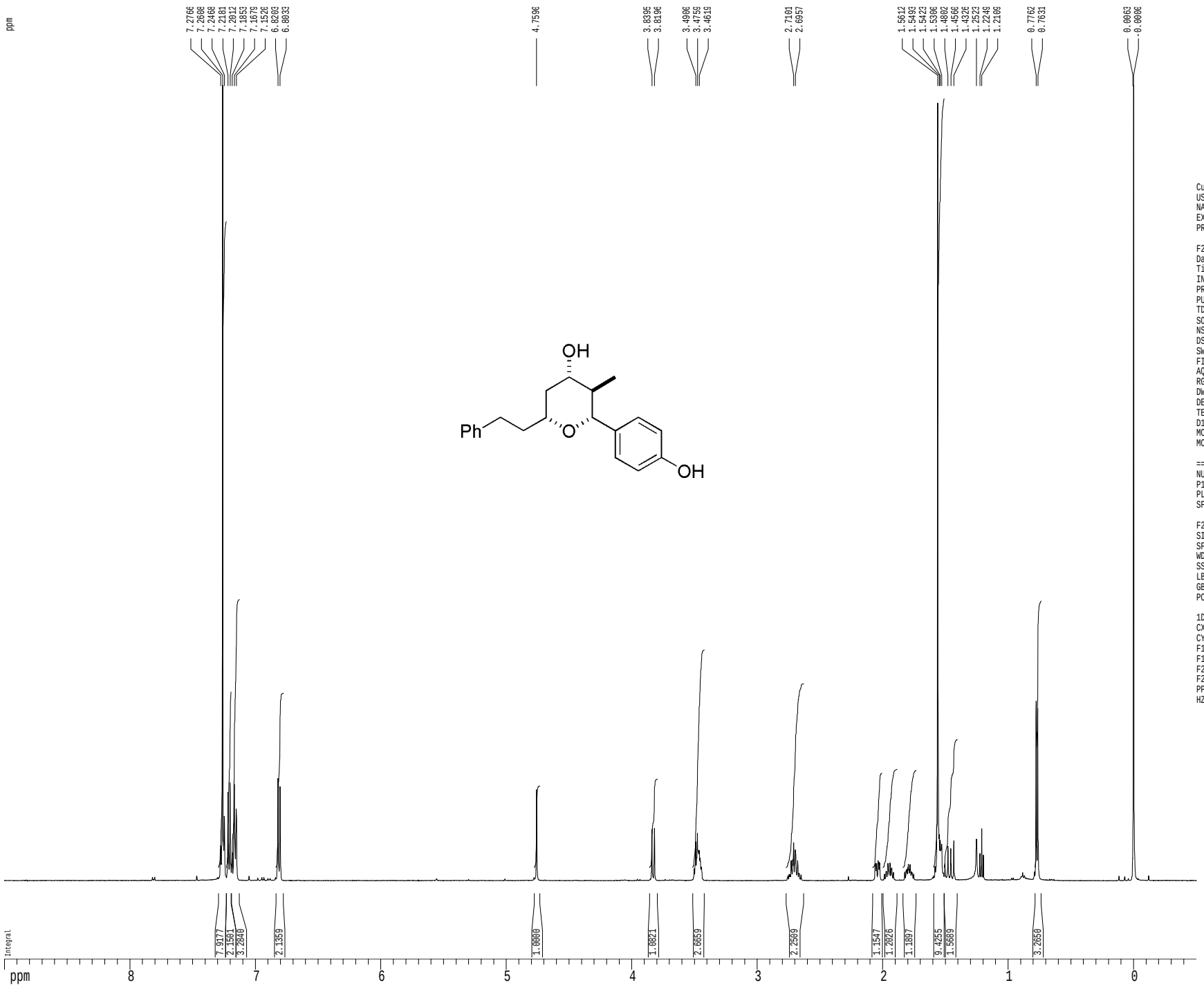
F2 - Processing parameters
SI 65536
SF 500.2200314 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 10.46 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling

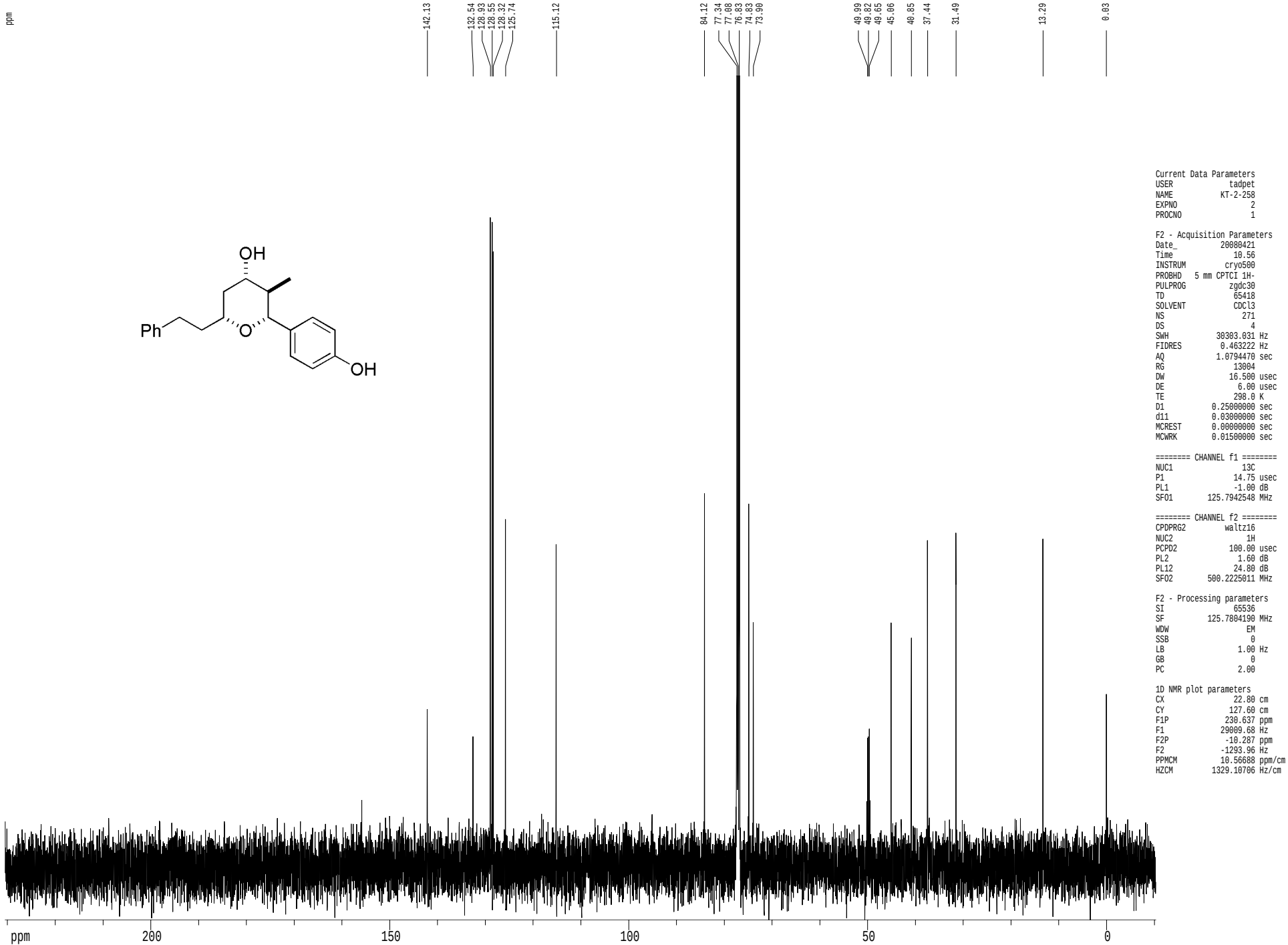


1H spectrum

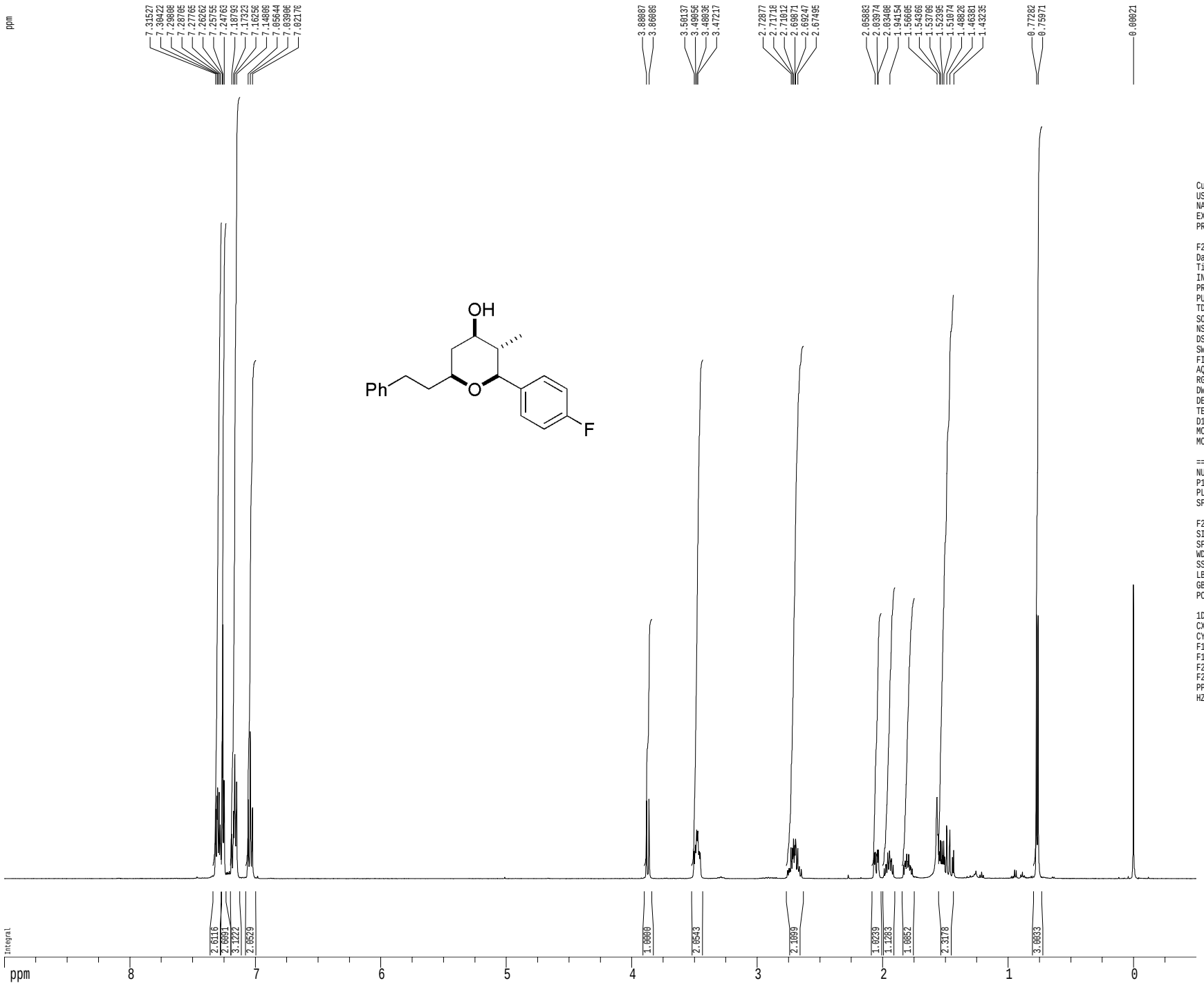



```
Current Data Parameters
USER              tadpet
NAME           KT-2-239
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080402
Time              11.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                   6.3
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.38 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200307 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                18.73 cm
F1P                9.000 ppm
F1              4501.98 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER tadpet
NAME KT-2-260
EXPNO 1
PROCNO 1

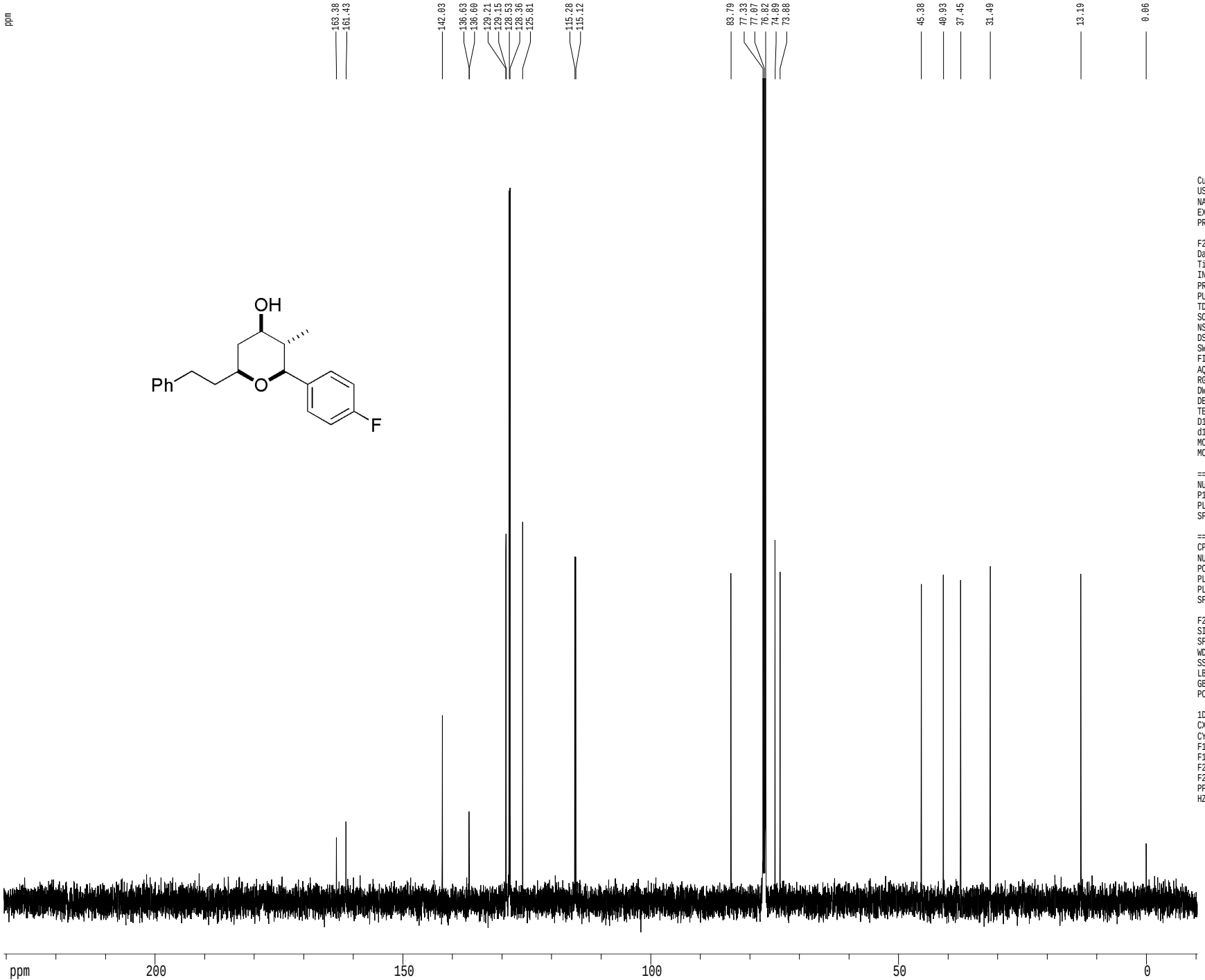
F2 - Acquisition Parameters
Date_ 20080424
Time 18.03
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200322 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

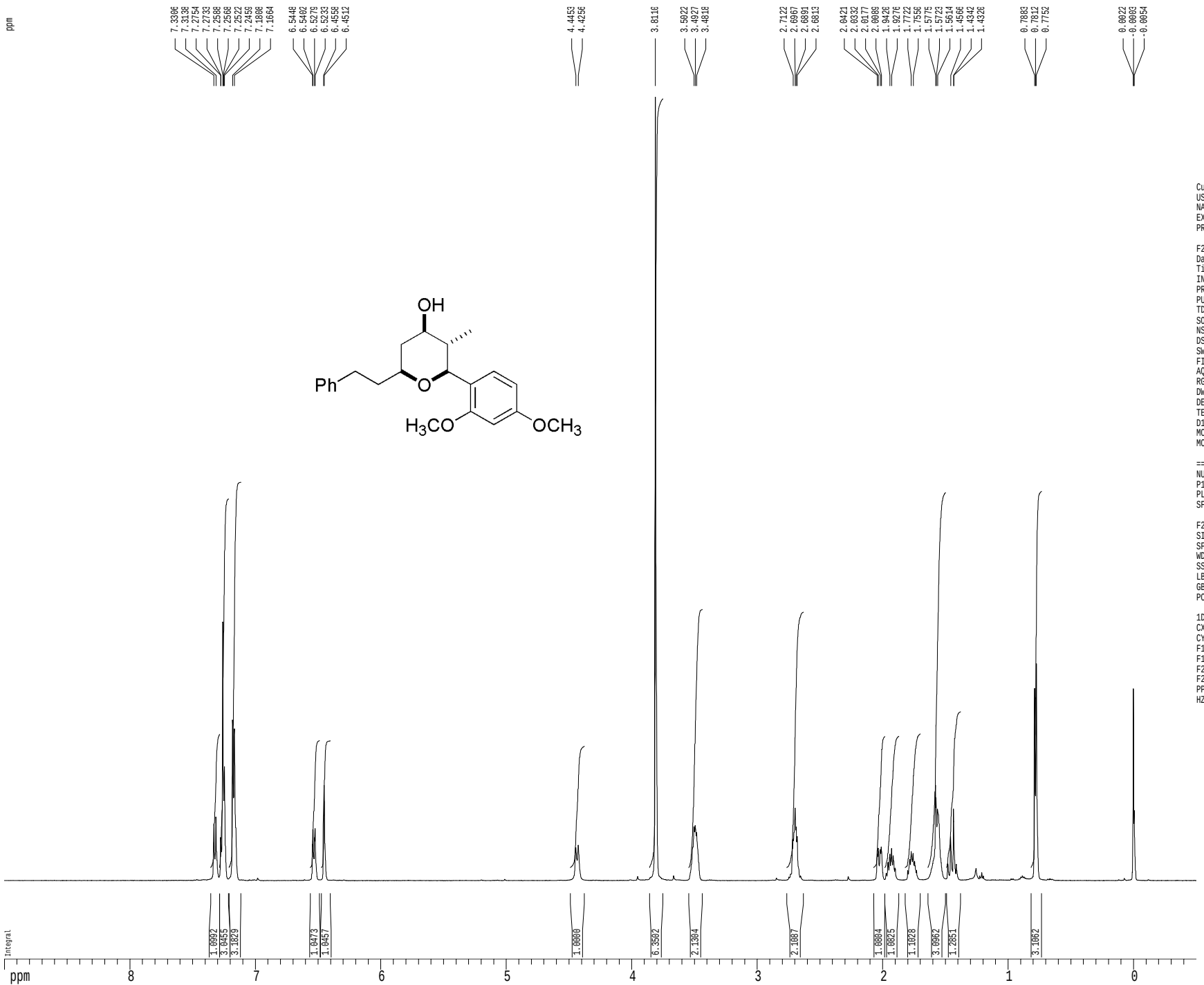
1D NMR plot parameters
CX 22.80 cm
CY 5.63 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling




```
Current Data Parameters
USER              tadpet
NAME            KT-2-260
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080424
Time               18.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zgdc30
TD                 65418
SOLVENT            CDCl3
NS                   165
DS                     4
SWH            30303.031 Hz
FIDRES          0.463222 Hz
AQ              1.0794470 sec
RG                 13004
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.75 usec
PL1               -1.00 dB
SFO1         125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12               24.80 dB
SFO2         500.2225011 MHz

F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 44.34 cm
F1P              230.637 ppm
F1             29009.68 Hz
F2P              -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

1H spectrum



Current Data Parameters
USER tadpet
NAME KT-2-263
EXPNO 1
PROCNO 1

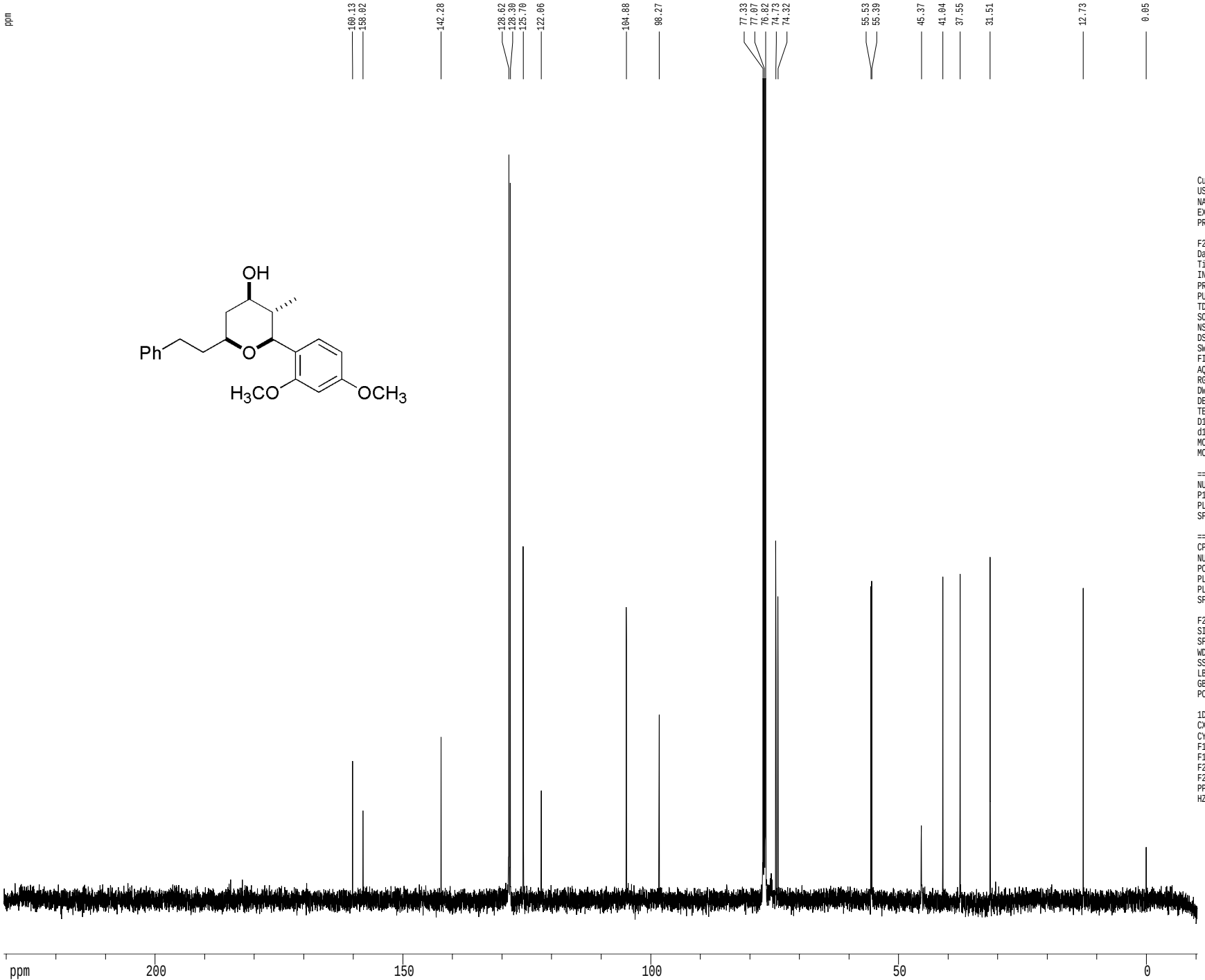
F2 - Acquisition Parameters
Date_ 20080427
Time 16.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200320 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

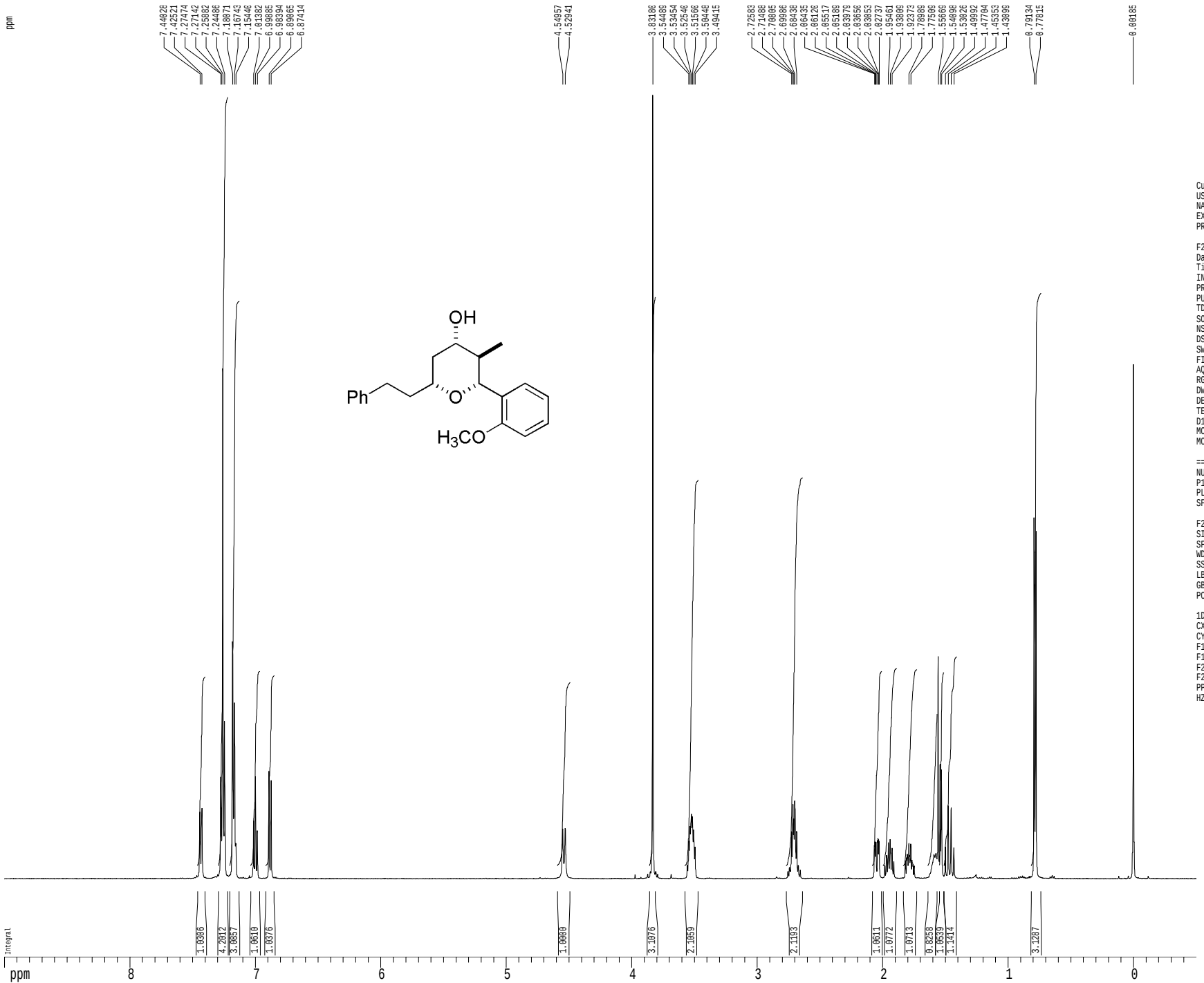
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling



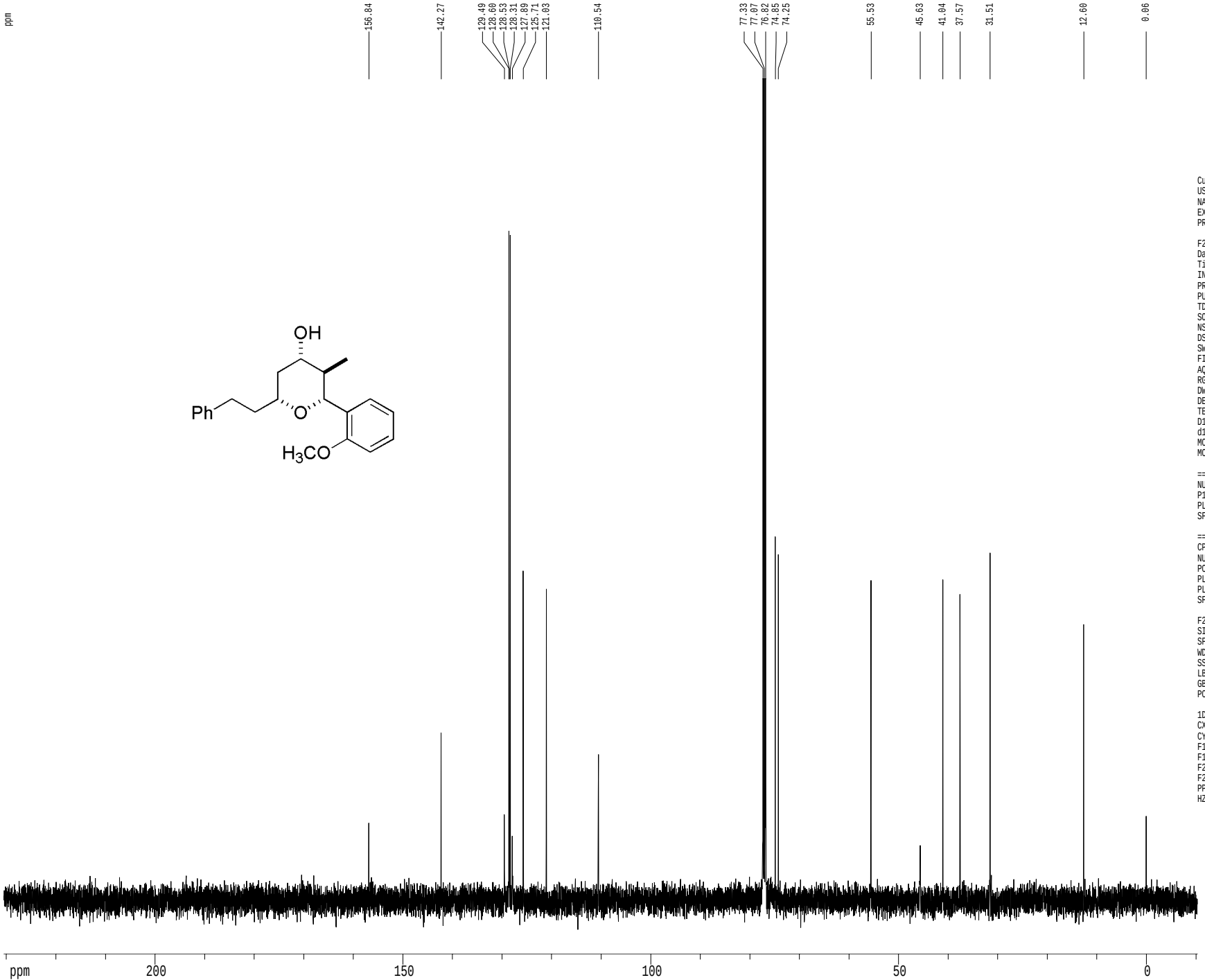

```
Current Data Parameters
USER              tadpet
NAME            KT-2-263
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080427
Time               16.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zgdc30
TD                 65418
SOLVENT            CDCl3
NS                   651
DS                     4
SWH            30303.031 Hz
FIDRES          0.463222 Hz
AQ             1.0794470 sec
RG               11585.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.75 usec
PL1               -1.00 dB
SFO1         125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.80 dB
SFO2         500.2225011 MHz

F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 41.95 cm
F1P              230.637 ppm
F1             29009.68 Hz
F2P              -10.287 ppm
F2             -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10706 Hz/cm
```

1H spectrum




```
Current Data Parameters
USER              tadpet
NAME           KT-2-276
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20080522
Time              15.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                81728
SOLVENT           CDCl3T
NS                   8
DS                   2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                 4.5
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                7.38 usec
PL1               1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF           500.2200319 MHz
WDW                  EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

13C spectrum with 1H decoupling



Current Data Parameters
USER tadpet
NAME KT-2-276
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080522
Time 15.06
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 201
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

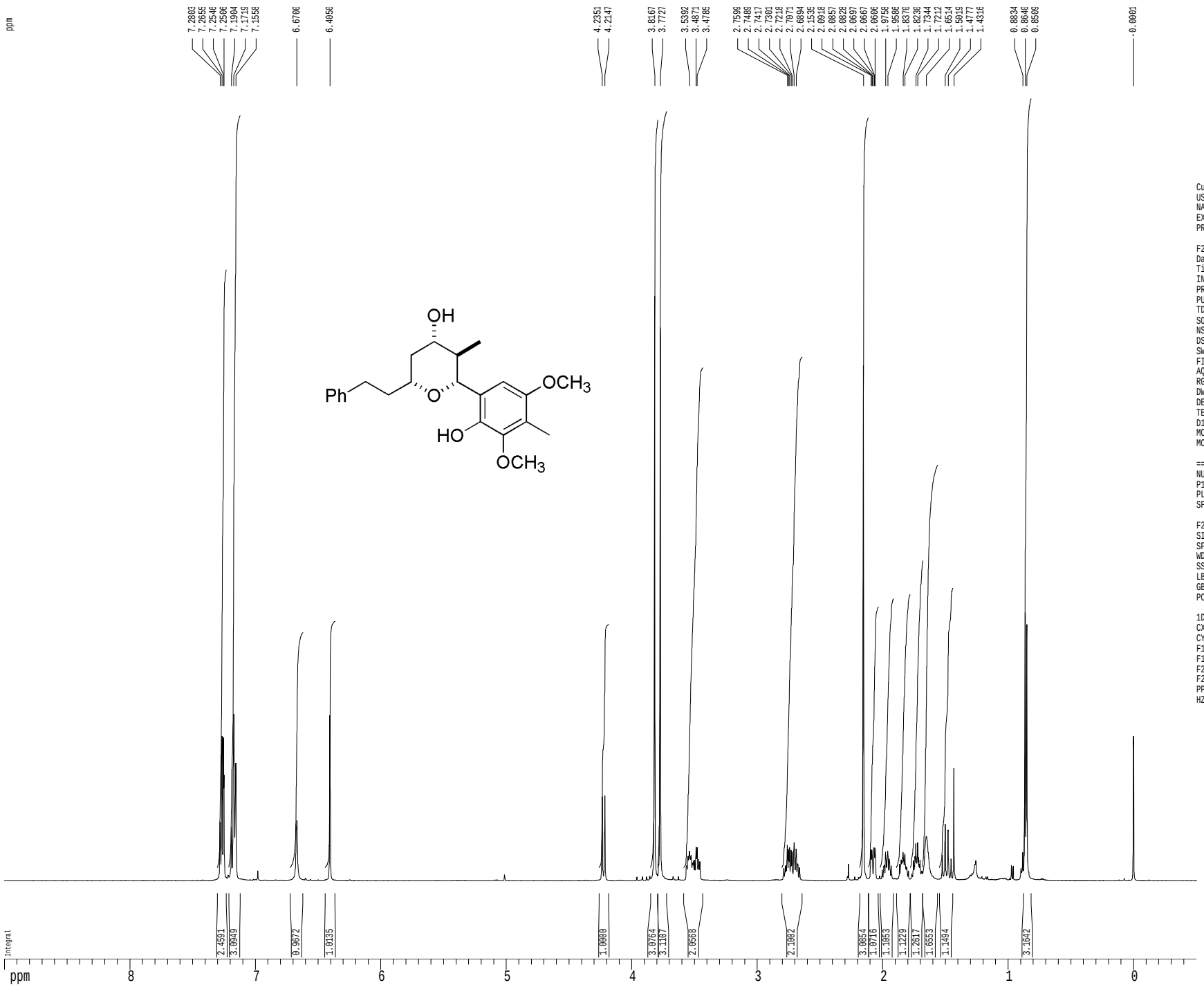
======== CHANNEL f1 ========
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

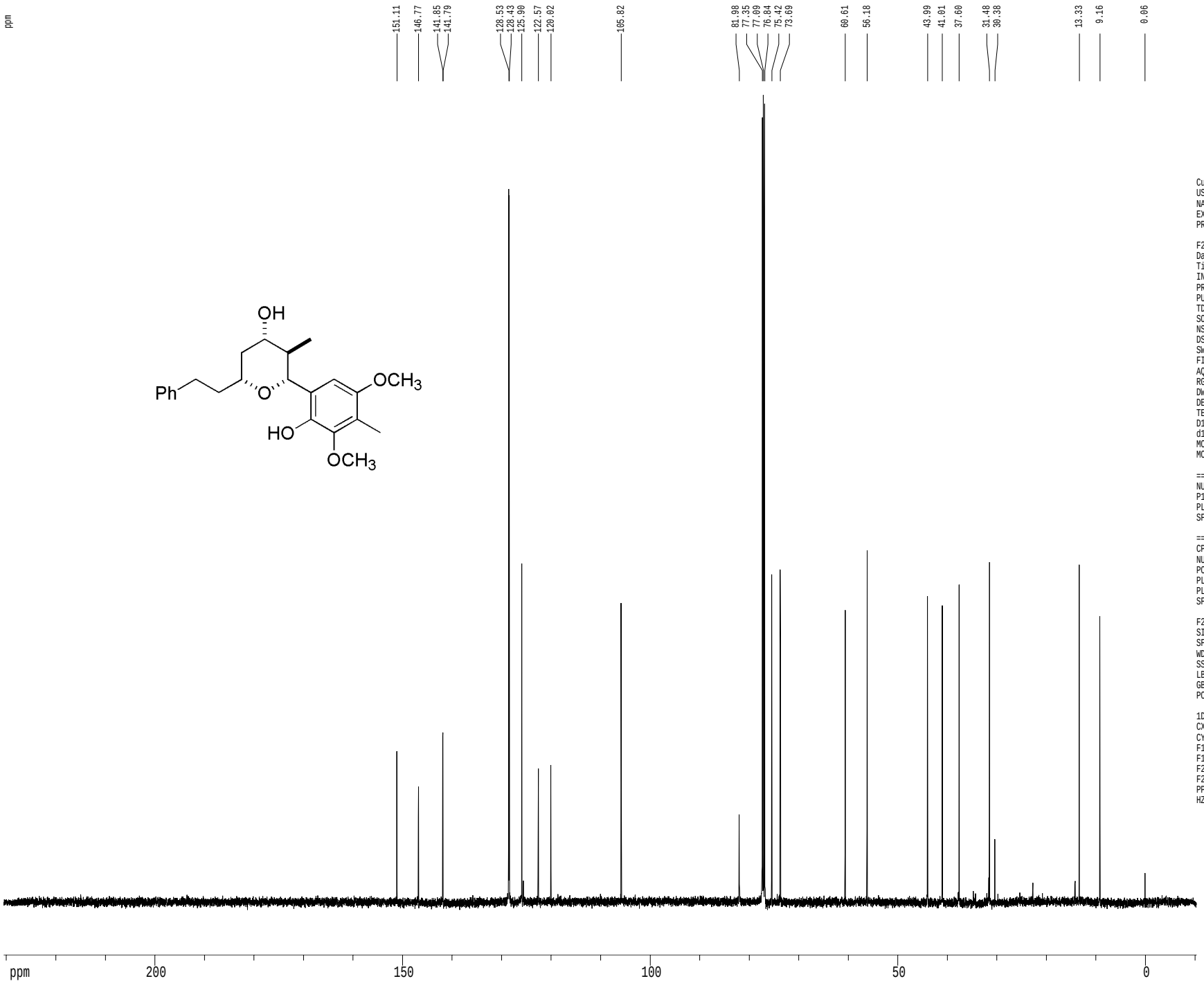
1D NMR plot parameters
CX 22.80 cm
CY 47.32 cm
F1P 230.637 ppm
F1 29009.68 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10706 Hz/cm

1H spectrum

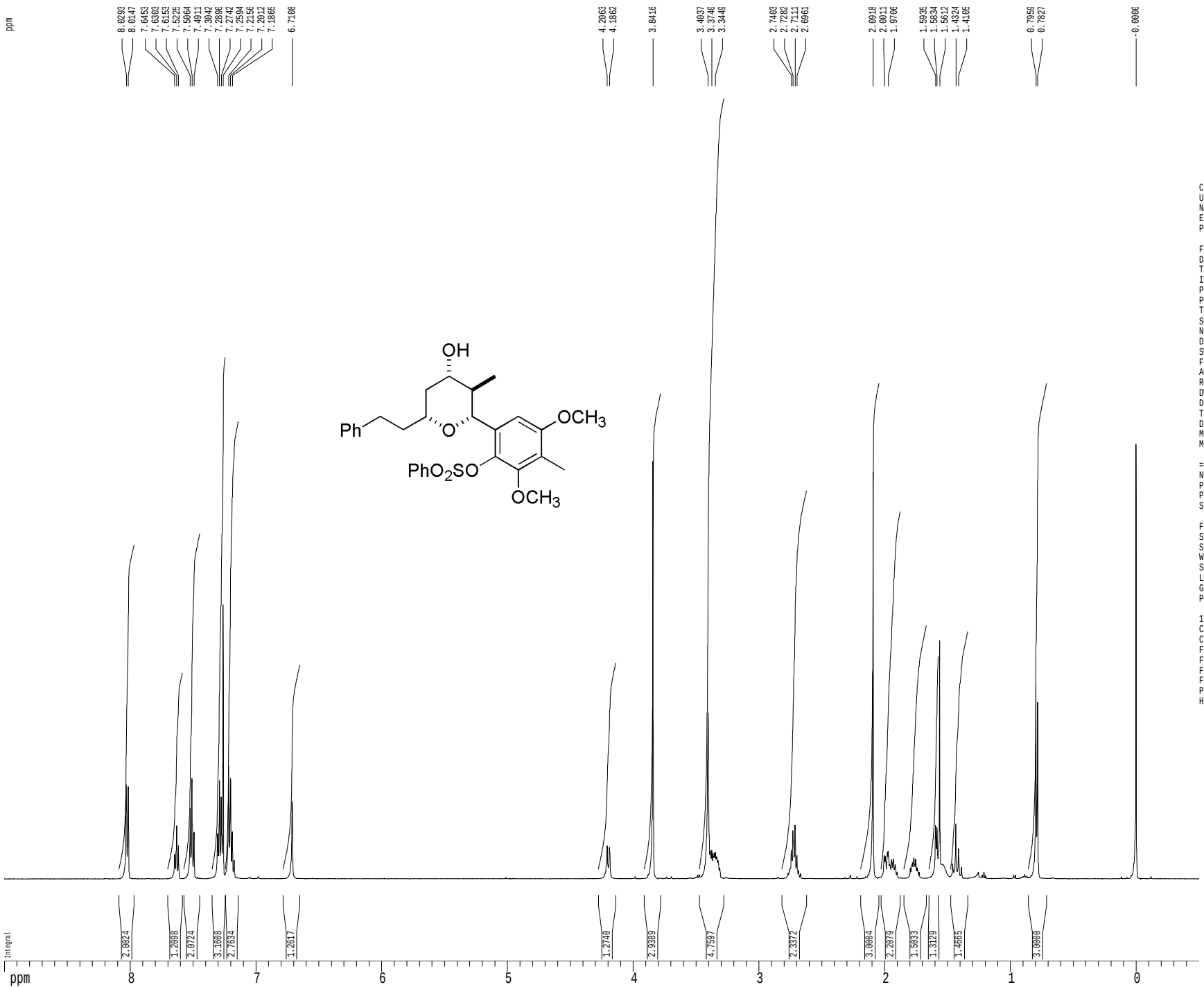



```
Current Data Parameters
USER              tadpet
NAME           KT-2-241
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080411
Time              16.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                81728
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                    4
DW               62.400 usec
DE                6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.38 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF           500.2200333 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                11.17 cm
F1P                9.000 ppm
F1              4501.98 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

13C spectrum with 1H decoupling

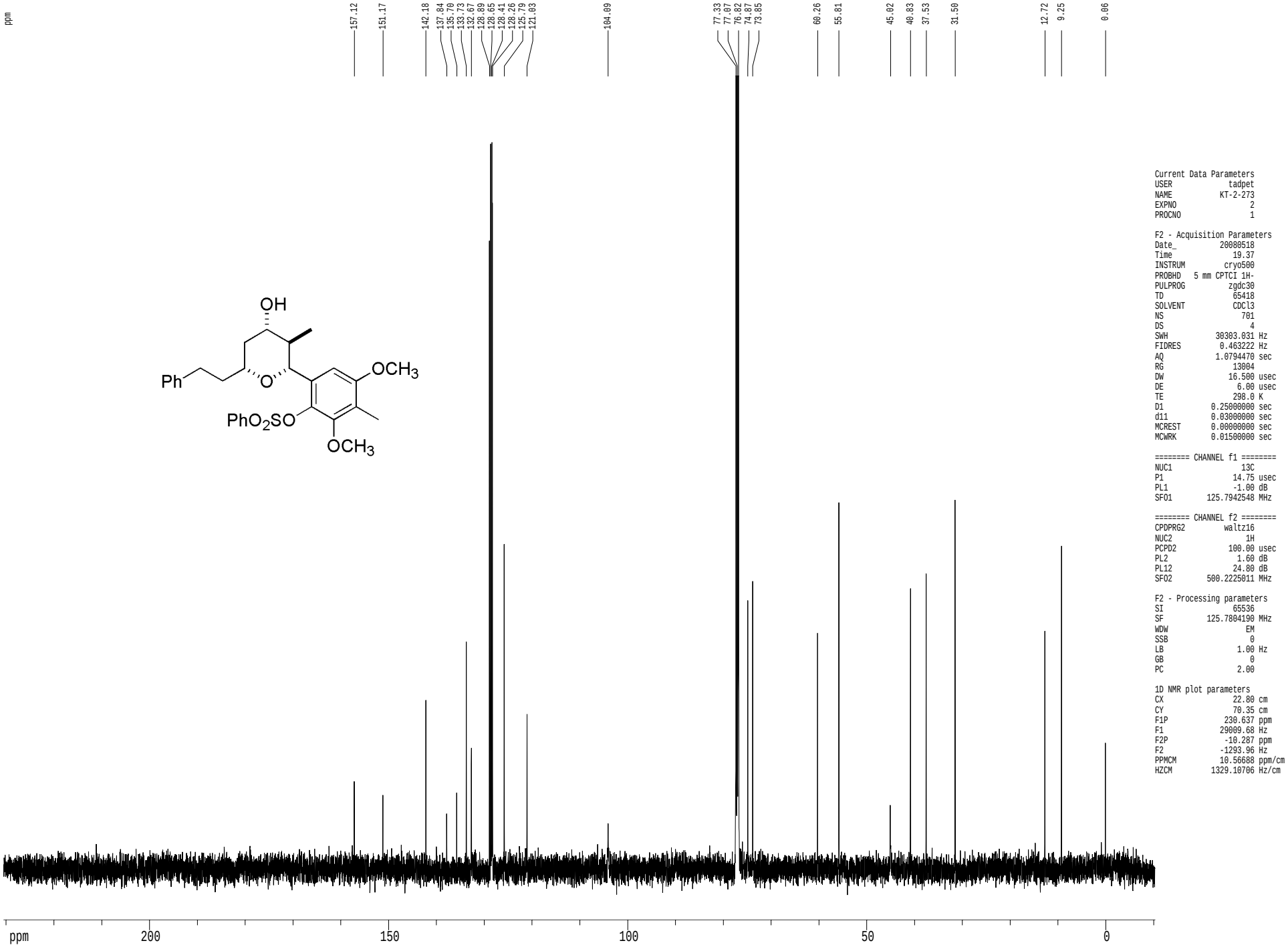


1H spectrum

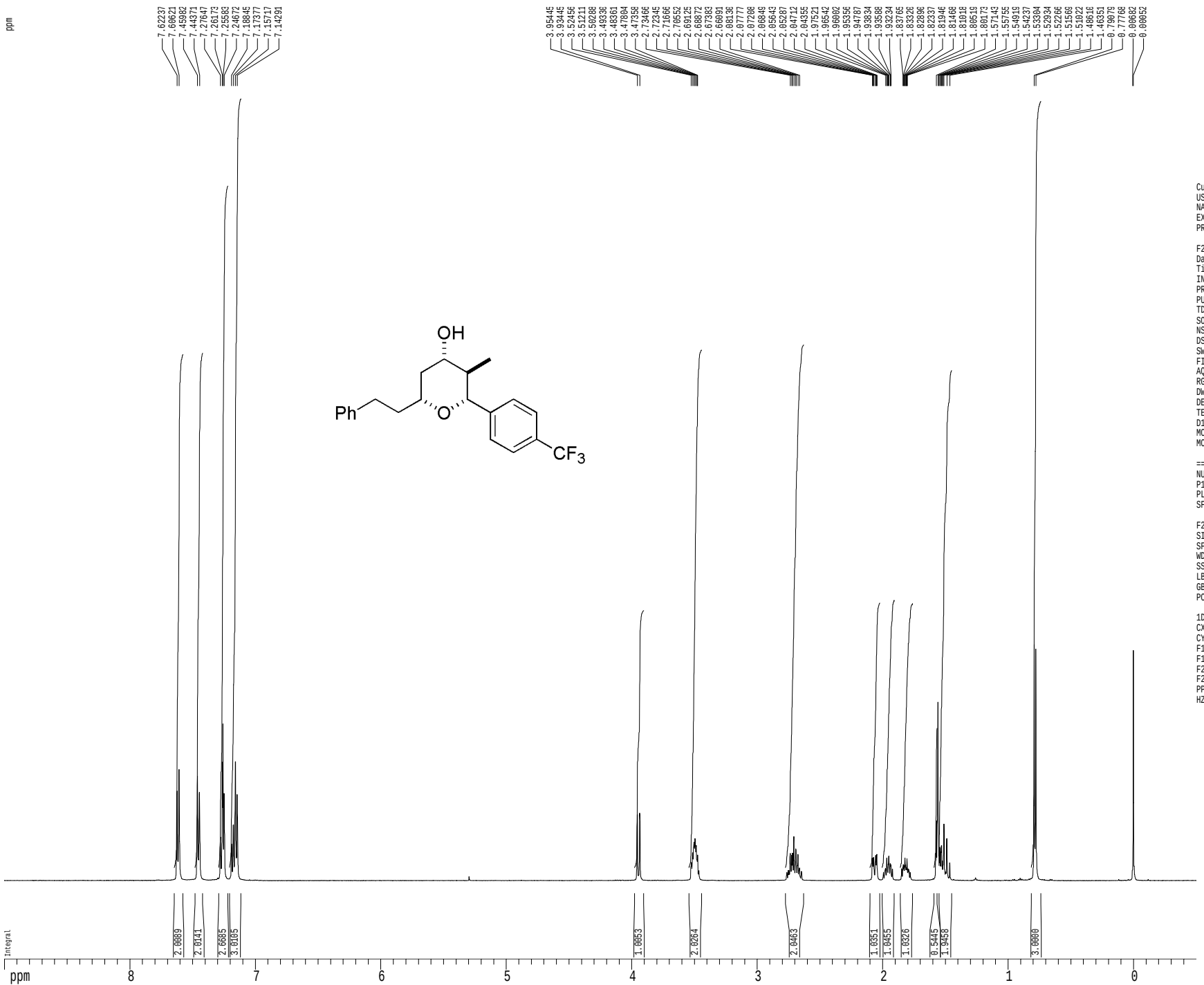



```
Current Data Parameters
USER              tadpet
NAME           KT-2-273
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080518
Time              19.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   6.3
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.38 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF            500.2200313 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                 8.37 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER tadpet
NAME KT-3-050A
EXPNO 1
PROCNO 1

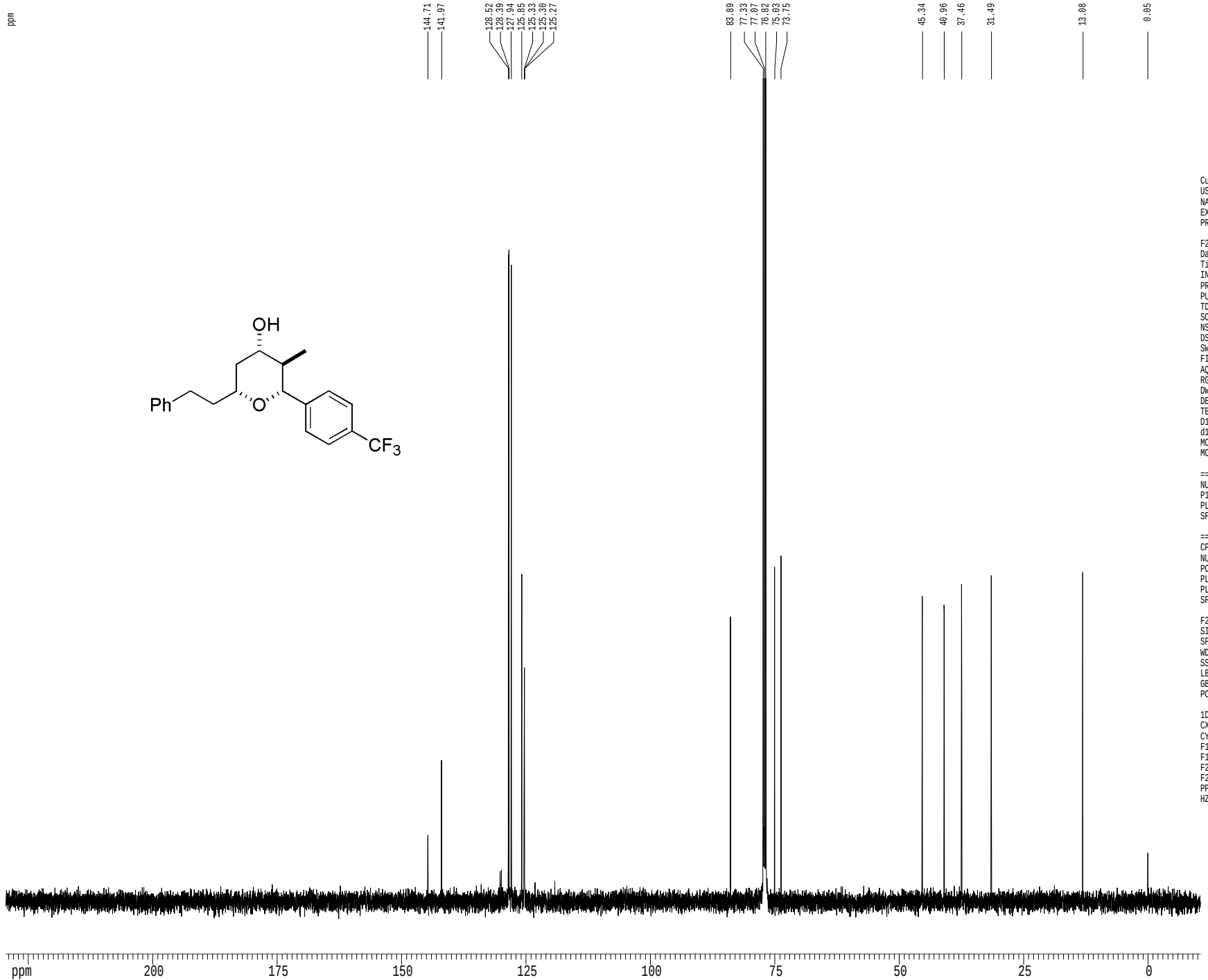
F2 - Acquisition Parameters
Date_ 20080813
Time 17.41
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 812.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -3.00 dB
SFO1 499.7234980 MHz

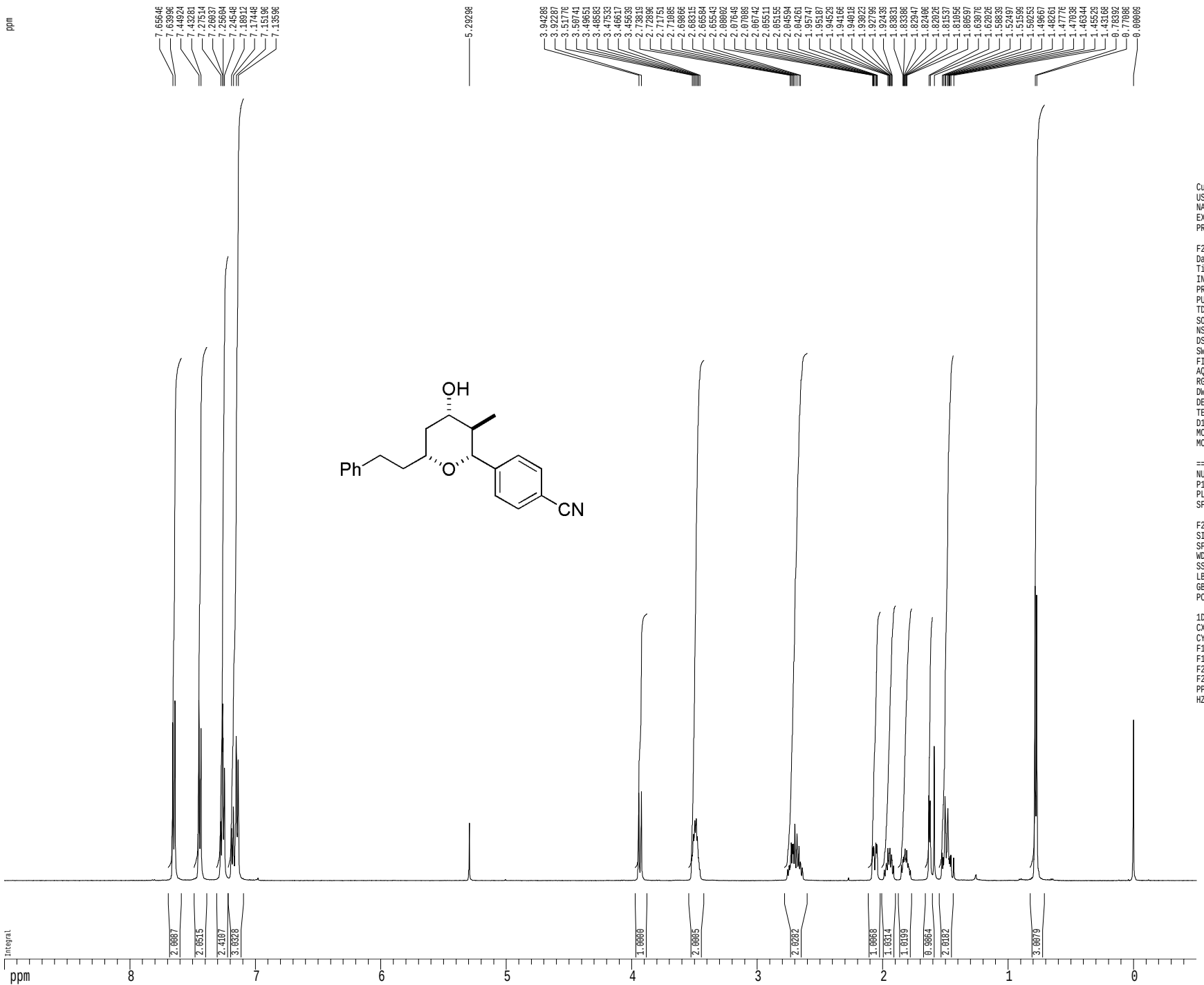
F2 - Processing parameters
SI 65536
SF 499.7200336 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 4.51 cm
F1P 9.000 ppm
F1 4497.48 Hz
F2P -0.500 ppm
F2 -249.86 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.21669 Hz/cm

13C spectrum with 1H decoupling

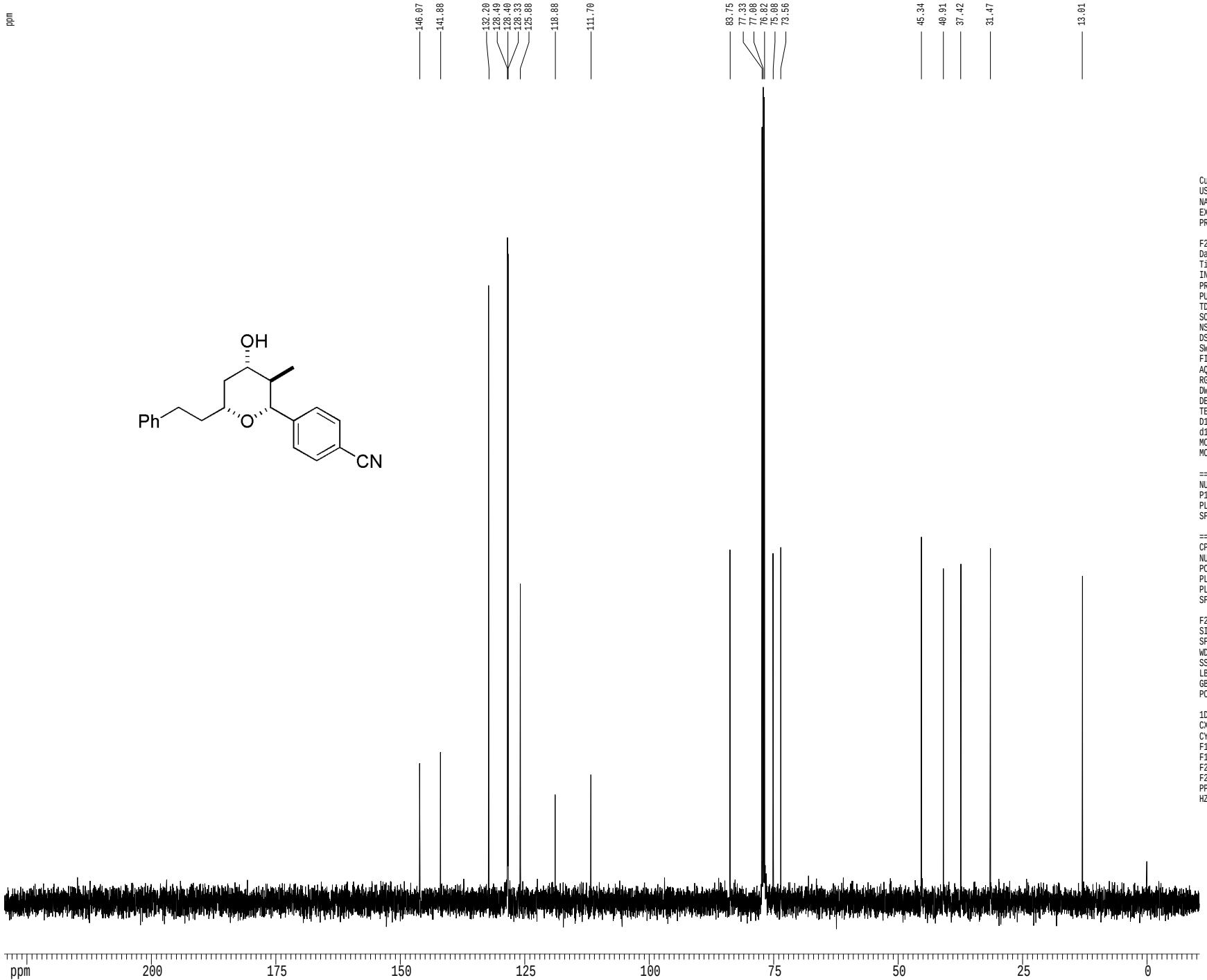


1H spectrum



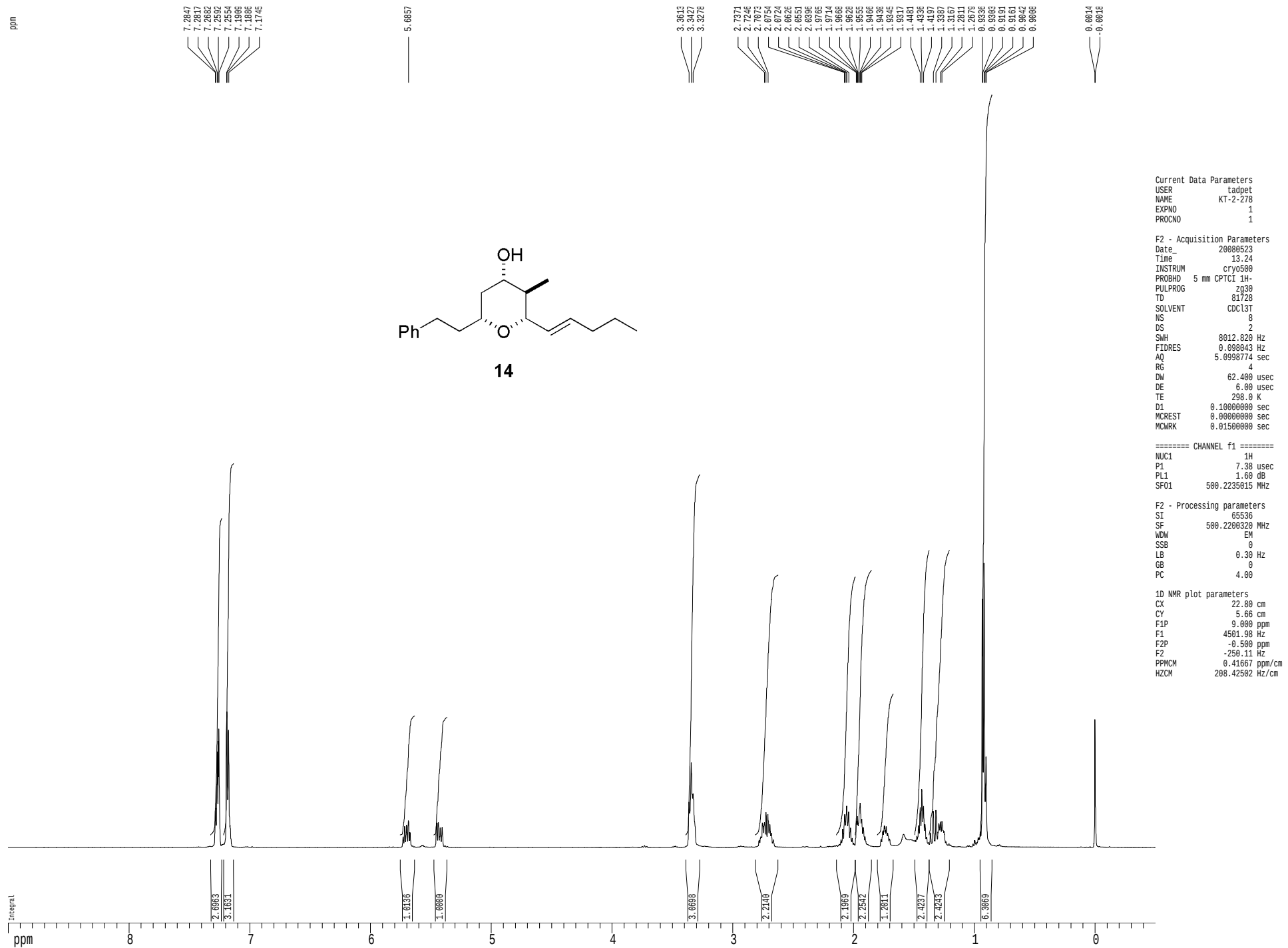

```
Current Data Parameters
USER              tadpet
NAME           KT-3-049A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080813
Time               17.31
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                 143.7
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                 12.00 usec
PL1                -3.00 dB
SFO1         499.7234980 MHz

F2 - Processing parameters
SI                 65536
SF           499.7200331 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  5.63 cm
F1P                9.000 ppm
F1              4497.48 Hz
F2P               -0.500 ppm
F2              -249.86 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.21669 Hz/cm
```

13C spectrum with 1H decoupling

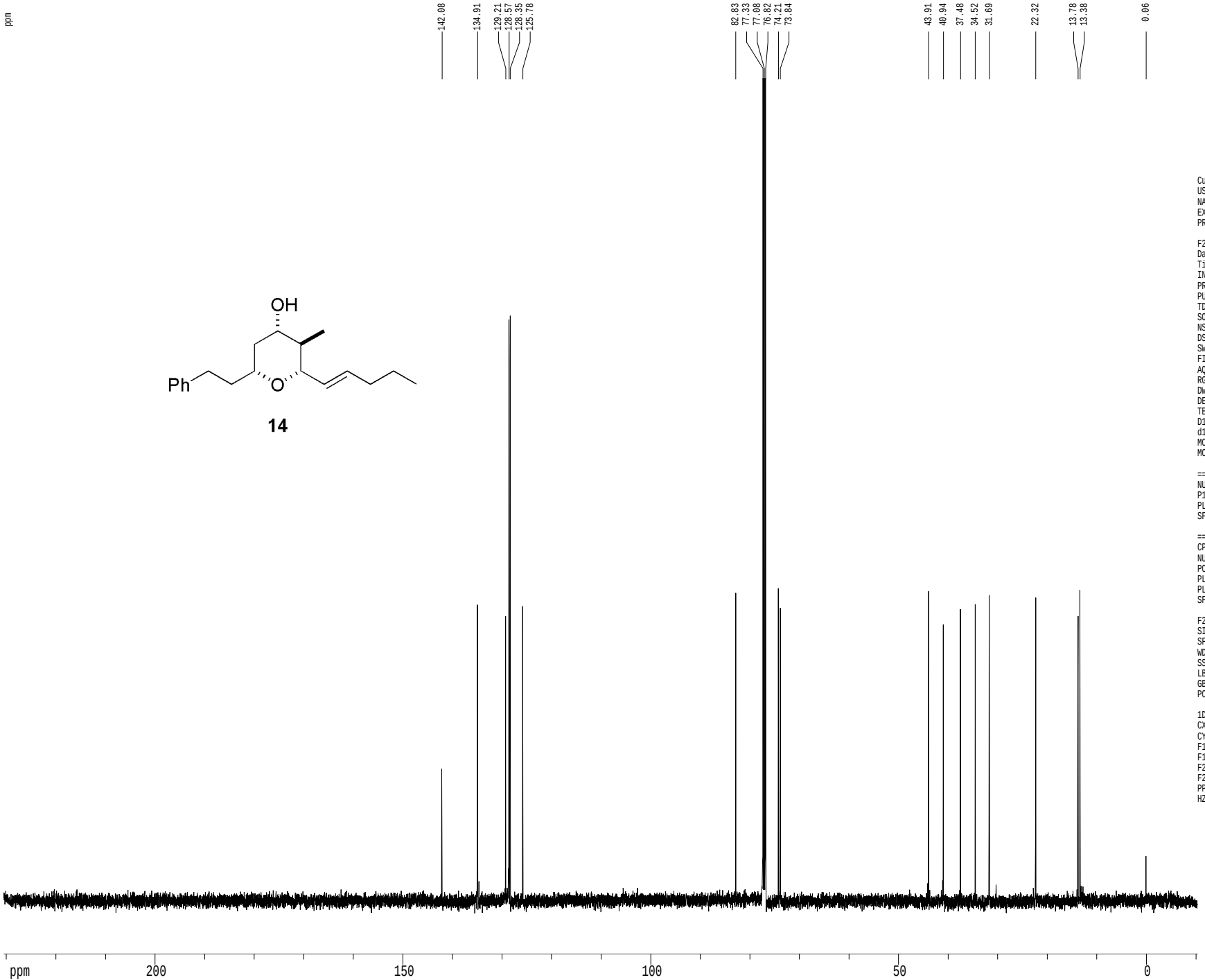



```
Current Data Parameters
USER             tadpet
NAME          KT-3-049A
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20080813
Time              17.34
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  201
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                4597.6
DW                16.500 usec
DE                 4.50 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                7.08 usec
PL1               0.00 dB
SFO1        125.6685160 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              14.70 dB
SFO2        499.7224986 MHz

F2 - Processing parameters
SI                65536
SF          125.6546939 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P              229.520 ppm
F1             28840.22 Hz
F2P              -10.507 ppm
F2             -1320.20 Hz
PPMCM          10.52747 ppm/cm
HZCM         1322.82581 Hz/cm
```

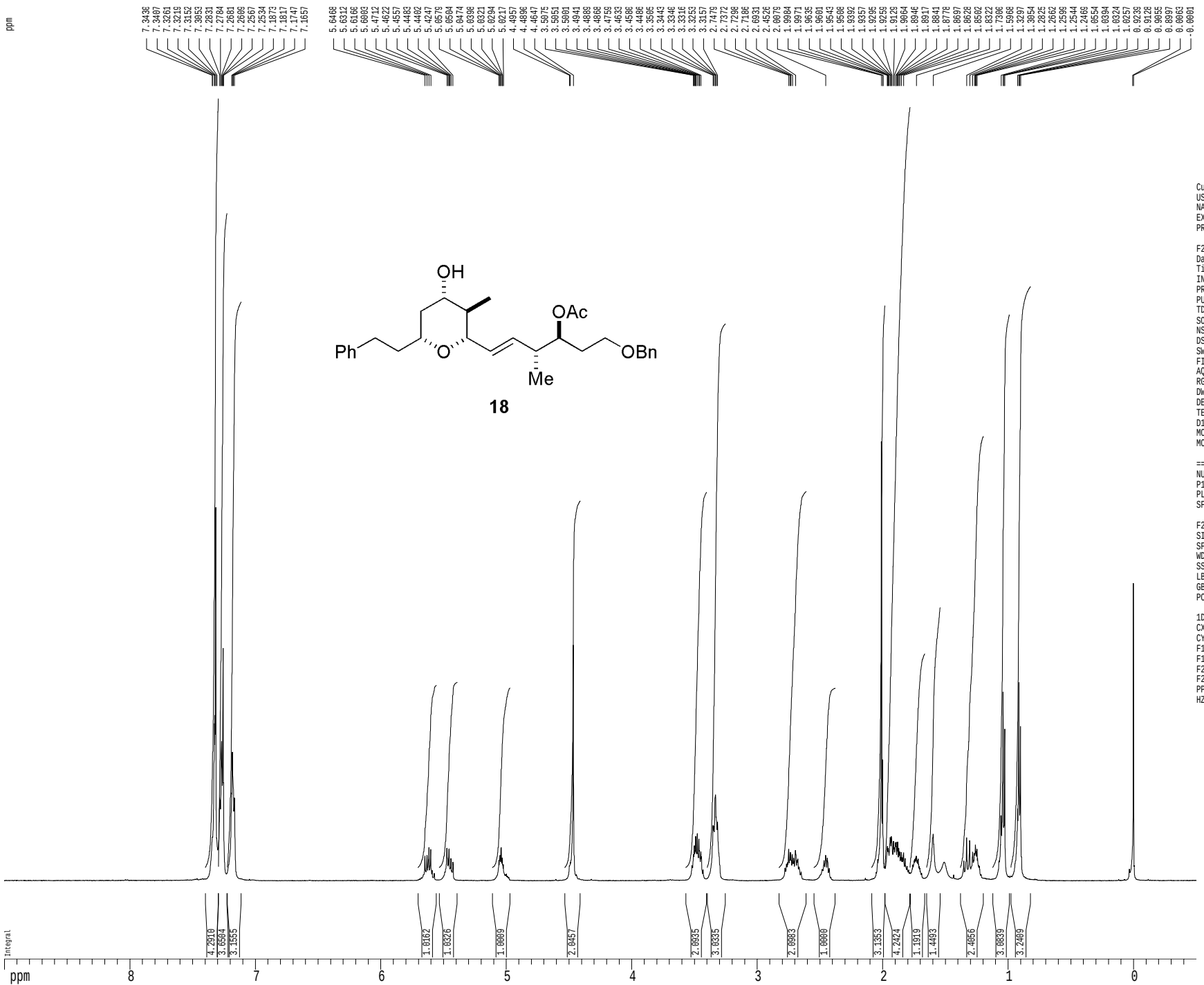
1H spectrum


ppm
7.2847
7.2817
7.2682
7.2592
7.2554
7.1908
7.1886
7.1745
5.6857
3.3613
3.3427
3.3278
2.7371
2.7246
2.7073
2.0754
2.0724
2.0628
2.0551
2.0396
1.9765
1.9714
1.9668
1.9628
1.9555
1.9466
1.9436
1.9345
1.9317
1.4481
1.4336
1.4197
1.3387
1.3167
1.2811
1.2679
0.9336
0.9303
0.9191
0.9161
0.9042
0.9008
0.0014
-0.0018
OH
Ph
O
14
Current Data Parameters
USER tadpet
NAME KT-2-278
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080523
Time 13.24
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200320 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 5.66 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Integral
2.6963
3.1831
1.0136
1.0000
3.0698
2.2140
2.1969
2.2542
1.2011
2.4237
2.4243
6.3069
ppm
8
7
6
5
4
3
2
1
0

13C spectrum with 1H decoupling

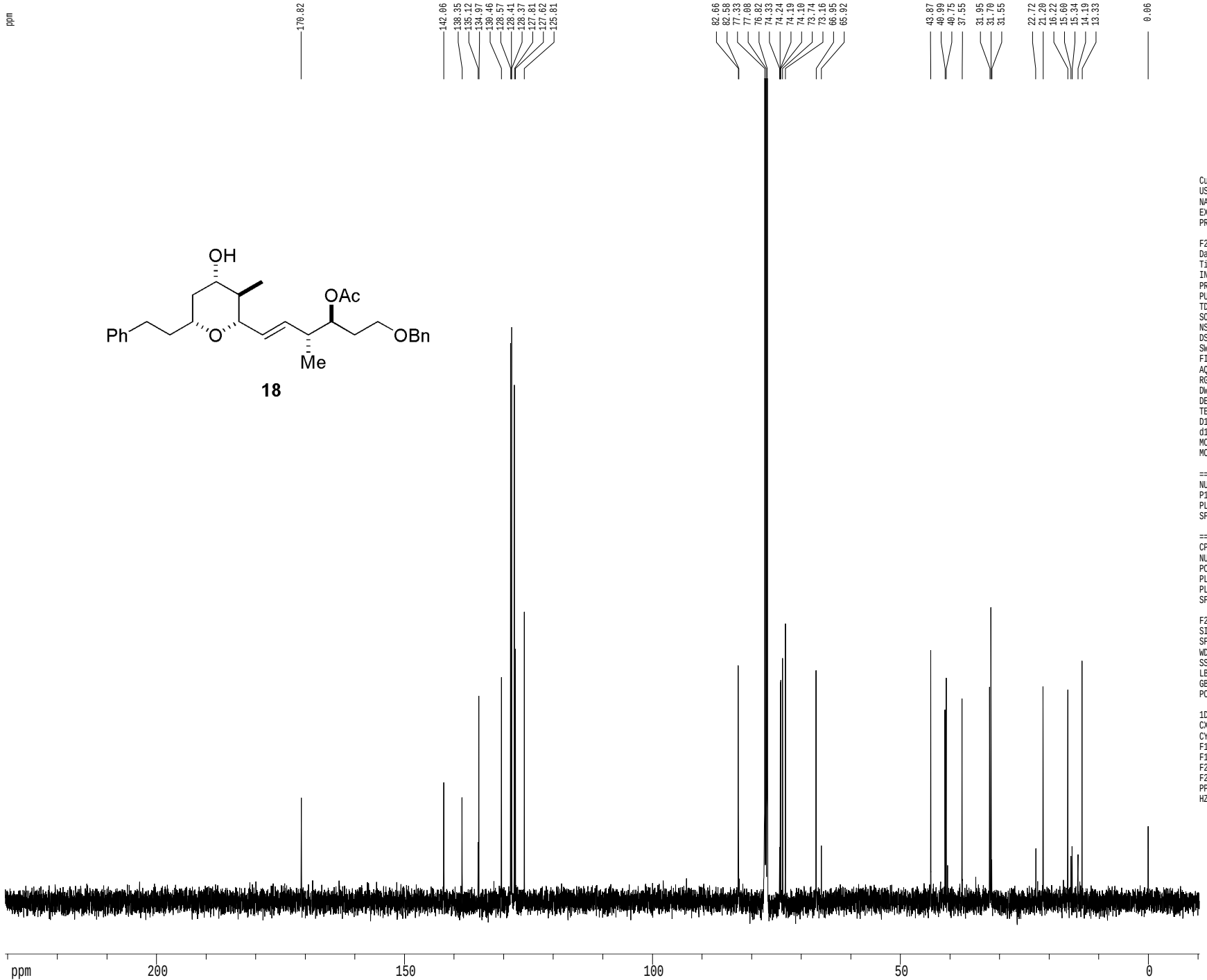


1H spectrum

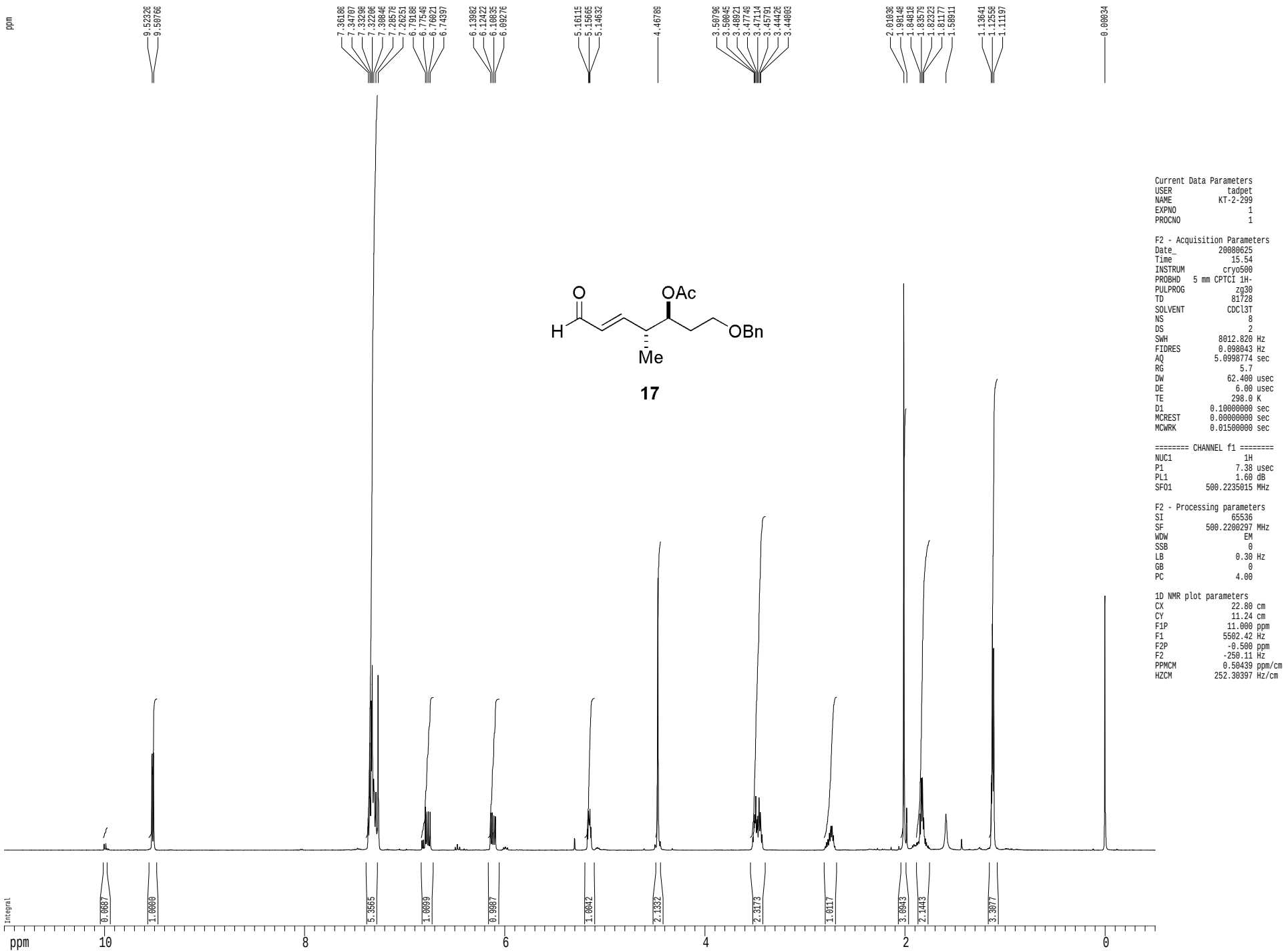



```
Current Data Parameters
USER              tadpet
NAME          KT-2-300B2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080805
Time               17.27
INSTRUM            gn500
PROBHD    5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   128
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
SFO1          499.7234980 MHz

F2 - Processing parameters
SI                 65536
SF            499.7200325 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  8.42 cm
F1P                9.000 ppm
F1              4497.48 Hz
F2P               -0.500 ppm
F2              -249.86 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.21669 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum




```
Current Data Parameters
USER              tadpet
NAME            KT-2-299
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080625
Time               15.54
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   5.7
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.38 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF            500.2200297 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                11.24 cm
F1P               11.000 ppm
F1              5502.42 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM           0.50439 ppm/cm
HZCM          252.30397 Hz/cm
```

13C spectrum with 1H decoupling