Supporting Information for

A Convergent Synthesis of the C1—C16 Segment of Goniodomin A via Palladium-Catalyzed Organostannane—Thioester Coupling

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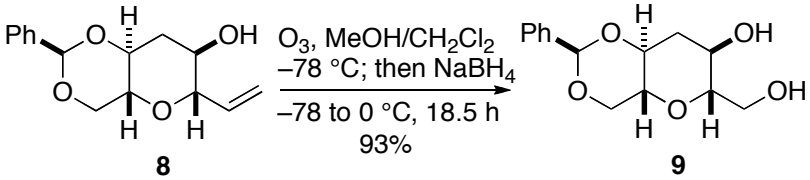
Contents

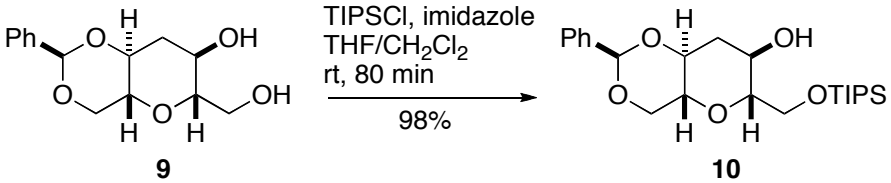
General methods. All reactions sensitive to moisture and/or air were carried out under an atmosphere of argon in dry, freshly distilled solvents under anhydrous conditions using oven-dried glassware unless otherwise noted. Anhydrous dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical Co. Inc. and used directly without further drying. Anhydrous tetrahydrofuran, diethyl ether, and toluene were purchased from Wako Pure Chemical Industries, Ltd. and further purified by a Glass Contour solvent purification system under an atmosphere of argon immediately prior to use. Diisopropylethylamine, triethylamine, 2,6-lutidine, acetonitrile (CH_3CN), benzene, and methanol were distilled from calcium hydride under an atmosphere of argon. Hexamethyphosphoramide (HMPA) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) were distilled from calcium hydride under reduced pressure. *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were distilled from magnesium sulfate under reduced pressure. All other chemicals were purchased at highest commercial grade and used directly. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} plates (0.25-mm thickness). Flash column chromatography was carried out using Kanto Chemical silica gel 60N (40-100 mesh, spherical, neutral) or Fuji Silysia silica gel BW-300 (200-400 mesh). Optical rotations were recorded on a JASCO P-1020 digital polarimeter. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA-600 spectrometer or a Varian Unity INOVA 600 spectrometer, and chemical shift values are reported in ppm (δ) downfield from tetramethylsilane with reference to internal solvent [^{1}H NMR, C*H*Cl_3 (7.24), C_6HD_5 (7.15); ^{13}C NMR, *C*DCl_3 (77.0), C_6D_6 (128.0)] unless otherwise noted. Coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations

were used to designate the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. EI and FAB mass spectra were recorded on a JEOL JMS-700 spectrometer and ESI mass spectra were measured on a Bruker microTOFfocus spectrometer.



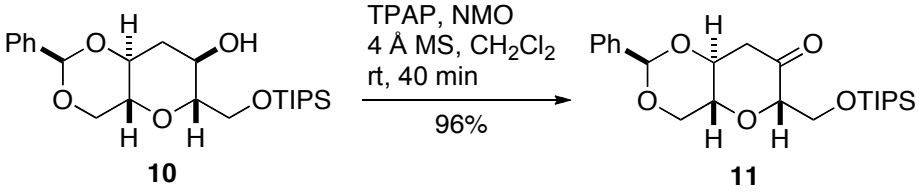
8 **9**

Diol 9. Ozone was bubbled through a solution of olefin **8** (2.53 g, 9.65 mmol) in MeOH/CH_2Cl_2 (1:1, v/v, 100 mL) at −78 °C until a pale blue color was persisted. Oxygen was bubbled through the solution to remove excess ozone. $NaBH_4$ (1.75 g, 46.3 mmol) was then added to the solution at −78 °C. The resultant solution was allowed to warm to 0 °C and stirred at that temperature for 18.5 h. The reaction mixture was quenched with H_2O. The mixture was diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give diol **9** (2.38 g, 93%) as colorless crystals. An analytically pure sample was obtained by recrystallization from EtOAc: mp 183—184 °C; $[\alpha]_D^{23}$ −30.4 (*c* 2.69, MeOH); IR (KBr) 3301, 2868, 1447, 1126, 1107, 1169, 1030, 1010, 982, 971, 745, 695, 647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48—7.46 (m, 2H), 7.37—7.33 (m, 3H), 5.51 (s, 1H), 4.30 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.88 (ddd, *J* = 11.5, 6.5, 4.5 Hz, 1H), 3.84—3.77 (m, 2H), 3.67 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.53 (ddd, *J* = 11.0, 9.5, 5.0 Hz, 1H), 3.40 (ddd, *J* = 10.0, 9.5, 5.0 Hz, 1H), 3.34 (ddd, *J* = 9.0, 5.0, 4.5 Hz, 1H), 2.49 (ddd, *J* = 11.0, 5.0, 4.0 Hz, 1H), 2.12 (d, *J* = 11.5 Hz, 1H), 1.93 (dd, *J* = 6.5, 5.5 Hz, 1H), 1.72 (ddd, *J* = 12.0, 11.0, 11.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 129.1, 128.4 (× 2), 126.1 (× 2), 101.7, 81.5, 76.4, 73.0, 69.2, 66.8, 63.0, 37.9; HRMS (FAB) calcd for $C_{14}H_{19}O_5$ [(M + H)$^+$] 267.1227, found 267.1236.



9 **10**

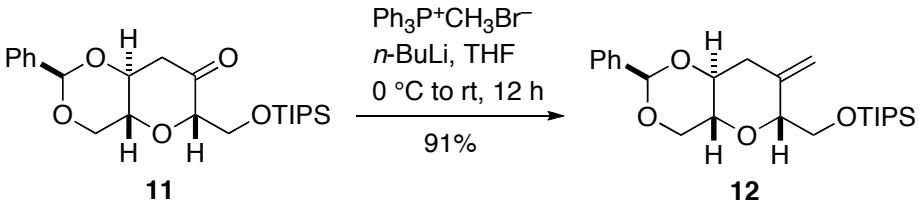
Alcohol 10. To a solution of diol **9** (500 mg, 1.87 mmol) in CH_2Cl_2/THF (3:2, v/v, 12.5 mL) at 0 °C were added imidazole (762 mg, 11.2 mmol) and TIPSCl (1.90 mL, 8.98 mmol), and the resultant solution was stirred at room temperature for 80 min. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 10 to 60% EtOAc/hexanes) gave alcohol **10** (775 mg, 98%) as colorless crystals: mp 71—72 °C; $[\alpha]_D^{23}$ +11.0 (*c* 2.09, $CHCl_3$); IR (KBr) 3417, 2941, 2865, 1461, 1383, 1366, 1100, 1015, 882, 760, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50—7.48 (m, 2H), 7.34—7.31 (m, 3H), 5.51 (s, 1H), 4.27 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.05 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.86 (d, *J* = 1.5 Hz, 1H), 3.83 (m, 1H), 3.79 (dd, *J* = 9.5, 8.0 Hz, 1H), 3.63 (dd, *J* = 10.5, 10.5 Hz, 1H), 3.52 (ddd, *J* = 11.5, 9.0, 4.5 Hz, 1H), 3.43—3.35 (m, 2H), 2.48 (ddd, *J* = 11.5, 4.5, 4.5 Hz, 1H), 1.72 (ddd, *J* = 11.5, 11.5, 11.5 Hz, 1H), 1.19—1.03 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 129.0, 128.2 (× 2), 126.1 (× 2), 101.6, 78.9, 76.3, 72.7, 70.4, 69.1, 66.6, 36.8, 17.8 (× 6), 11.6 (× 3); HRMS (ESI) calcd for $C_{23}H_{38}O_5SiNa$ $[(M + Na)^+]$ 445.2381, found 445.2389.



10 **11**

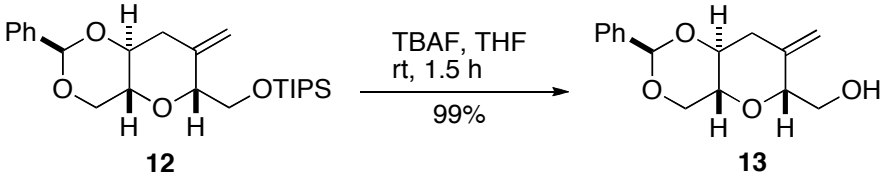
Ketone 11. To a solution of alcohol **10** (780 mg, 1.84 mmol) in CH_2Cl_2 (10 mL) were added 4 Å molecular sieves (700 mg), NMO (475 mg, 4.05 mmol), and TPAP (13.0 mg, 0.037 mmol), and the resultant solution was stirred at room temperature for 40 min. The reaction mixture was directly subjected to flash column chromatography (silica gel,

10% EtOAc/hexanes) to afford ketone **11** (743 mg, 96%) as colorless crystals: mp 73—74 °C; $[\alpha]_D^{23}$ −3.7 (*c* 0.52, benzene); IR (KBr) 3302, 2940, 2864, 1724, 1642, 1462, 1383, 1125, 1013 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50—7.48 (m, 2H), 7.39—7.33 (m, 3H), 5.57 (s, 1H), 4.44 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.07—4.02 (m, 3H), 3.97 (ddd, *J* = 11.0, 9.5, 6.0 Hz, 1H), 3.78 (dd, *J* = 10.5, 10.0 Hz, 1H), 3.66 (ddd, *J* = 10.0, 9.5, 5.0 Hz, 1H), 3.02 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.59 (dd, *J* = 17.0, 11.0 Hz, 1H), 1.13—1.01 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 137.0, 129.1, 128.3 (× 2), 126.1 (× 2), 101.2, 84.6, 75.4, 70.7, 69.2, 63.3, 44.6, 17.8 (× 6), 11.6 (× 3); HRMS (FAB) calcd for $C_{23}H_{37}O_5Si$ [$(M + H)^+$] 421.2405, found 421.2416.



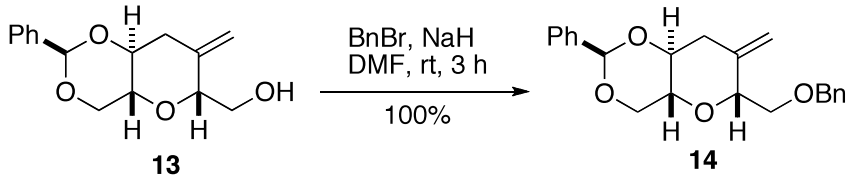
Olefin 12. To a suspension of $Ph_3P^+CH_3Br^-$ (539.9 mg, 1.511 mmol) in THF (15 mL) at 0 °C was added *n*-BuLi (2.64 M solution in hexane, 0.525 mL, 1.39 mmol), and the resulting ylide suspension was stirred at 0 °C for 30 min. To this solution was added a solution of ketone **11** (124.1 mg, 0.2950 mmol) in THF (2.5 mL + 1.0 mL × 2), and the resultant mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated. Purification of the residue by flash column chromatography (silica gel, 0 to 1% EtOAc/hexanes) gave olefin **12** (112.2 mg, 91%) as colorless crystals: mp 70—71 °C; $[\alpha]_D^{23}$ −39.2 (*c* 0.54, benzene); IR (KBr) 3269, 2942, 2867, 1643, 1631, 1451, 1383, 1107, 1002, 882, 748, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48—7.47 (m, 2H), 7.37—7.31 (m, 3H), 5.53 (s, 1H),

5.09 (s, 1H), 5.00 (s, 1H), 4.29 (dd, J = 10.5, 4.5 Hz, 1H), 4.00 (dd, J = 9.5, 5.5 Hz, 1H), 3.94—3.88 (m, 2H), 3.67 (dd, J = 10.5, 10.0 Hz, 1H), 3.58—3.49 (m, 2H), 2.74 (dd, J = 12.0, 4.5 Hz, 1H), 2.45 (dd, J = 12.0, 11.5 Hz, 1H), 1.14—1.00 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 137.5, 129.0, 128.3 (× 2), 126.1 (× 2), 111.6, 101.6, 79.1, 79.1, 73.3, 69.4, 63.7, 39.2, 18.0 (× 6), 12.0 (× 3); HRMS (FAB) calcd for $C_{24}H_{39}O_4Si$ [$(M + H)^+$] 419.2612, found 419.2615.

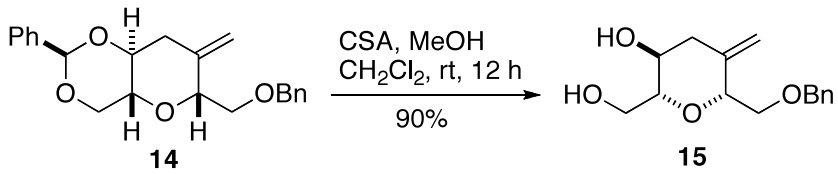


12 **13**

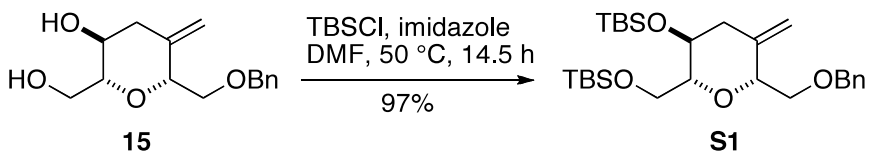
Alcohol 13. To a solution of olefin **12** (594 mg, 1.42 mmol) in THF (15 mL) was added TBAF (1.0 M solution in THF, 2.50 mL, 2.50 mmol), and the resultant solution was stirred at room temperature for 1.5 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 50 to 90% EtOAc/hexanes) gave alcohol **13** (372 mg, 99%) as colorless crystals: mp 125—126 °C; $[\alpha]_D^{23}$ −53.8 (*c* 0.29, $CHCl_3$); IR (KBr) 3396, 2915, 2872, 1643, 1383, 1330, 1105, 904, 752, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49—7.47 (m, 2H), 7.38—7.32 (m, 3H), 5.54 (s, 1H), 4.99 (s, 1H), 4.85 (s, 1H), 4.33 (dd, J = 10.5, 4.5 Hz, 1H), 3.99 (m, 1H), 3.93 (m, 1H), 3.81 (dd, J = 12.0, 7.0 Hz, 1H), 3.71 (dd, J = 10.5, 9.5 Hz, 1H), 3.61—3.53 (m, 2H), 2.75 (dd, J = 12.5, 4.5 Hz, 1H), 2.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 137.3, 129.0, 128.3 (× 2), 126.1 (× 2), 111.4, 101.5, 78.6, 78.4, 73.2, 69.2, 62.4, 38.8; HRMS (EI) calcd for $C_{15}H_{18}O_4$ (M^+) 262.1200, found 262.1205.



Benzyl ether 14. To a solution of alcohol **13** (1.10 g, 4.19 mmol) in DMF (50 mL) at 0 °C was added NaH (60% in mineral oil, 0.420 g, 8.75 mmol), and the resultant solution was stirred at 0 °C for 30 min. To this solution was added benzyl bromide (0.750 mL, 6.31 mmol), and the resultant mixture was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O, and the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 20% EtOAc/hexanes) gave benzyl ether **14** (1.49 g, 100%) as colorless crystals: mp 108—109 °C: $[\alpha]_D^{25}$ −25.9 (*c* 1.00, $CHCl_3$); IR (KBr) 3088, 3065, 3031, 2953, 2928, 2884, 2856, 1655, 1471, 1462, 1253, 1099, 836, 777, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48—7.37 (m, 2H), 7.37—7.27 (m, 8H), 5.53 (br s, 1H), 4.98 (s, 1H), 4.90 (s, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.35 (dd, *J* = 10.3, 4.8 Hz, 1H), 4.10 (dd, *J* = 4.5, 6.2 Hz, 1H), 3.80 (dd, *J* = 4.5, 10.3 Hz, 1H), 3.72 (dd, *J* = 10.3, 10.3 Hz, 1H), 3.67 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.61—3.52 (m 2H), 2.74 (dd, *J* = 12.4, 4.5 Hz, 1H), 2.44 (br dd, *J* = 12.4, 12.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 137.9, 137.5, 129.0, 128.4 (× 2), 128.3 (× 2), 127.9 (× 2), 127.8, 126.1 (× 2), 111.6, 101.5, 78.8, 77.4, 73.6, 73.5, 69.7, 69.3, 39.1; HRMS (ESI) calcd for $C_{22}H_{24}O_4Na$ [$(M + Na)^+$] 375.1567, found 375.1572.

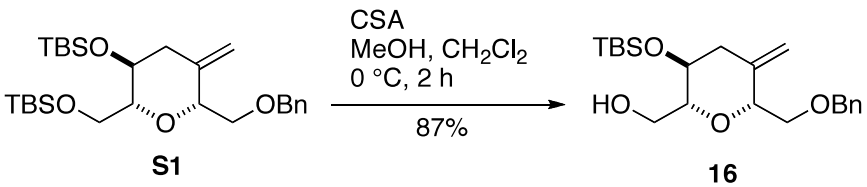


Diol 15. To a solution of benzyl ether **14** (54.9 mg, 0.156 mmol) in MeOH/CH_2Cl_2 (1:1, v/v, 2 mL) was added CSA (12.0 mg, 0.0520 mmol), and the resultant solution was stirred at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was diluted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 20% EtOAc/hexanes) gave diol **15** (37.0 mg, 90%) as colorless crystals: mp 118—119 °C; $[\alpha]_D^{25}$ +15.7 (*c* 1.00, $CHCl_3$); IR (KBr) 3295, 3088, 3065, 3031, 2953, 2928, 2884, 2856, 1655, 1471, 1462, 1253, 1099, 836, 777, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35—7.31 (m, 4H), 7.28 (m, 1H), 4.90 (br s, 1H), 4.80 (br s, 1H), 4.59 (d, *J* = 12.4 Hz, 1H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.02 (br dd, *J* = 4.4, 6.5 Hz, 1H), 3.84 (br dd, *J* = 11.7, 4.8 Hz, 1H), 3.76 (br dd, *J* = 11.7, 4.8 Hz, 1H), 3.74 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.64 (dd, *J* = 10.3, 6.5 Hz, 1H), 3.64 (m 1H), 3.32 (ddd, *J* = 8.9, 4.8, 4.8 Hz, 1H), 2.69 (dd, *J* = 13.1, 5.2 Hz, 1H), 2.57 (br s, 1H), 2.50 (m, 1H), 2.21 (br dd, *J* = 13.1, 11.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.6, 137.8, 128.4 (× 2), 127.9 (× 2), 127.8, 110.1, 81.4, 76.7, 73.5, 70.2, 68.4, 63.2, 41.8; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ [$(M + Na)^+$] 287.1254, found 287.1260.



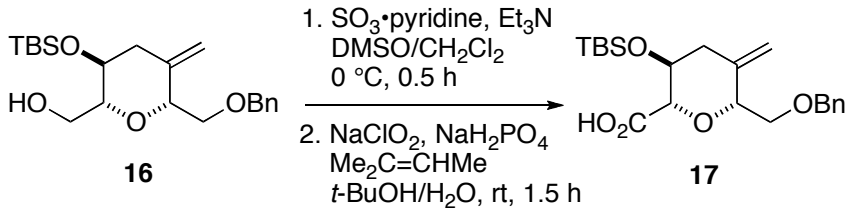
Bis-TBS ether S1. To a solution of diol **15** (100.3 mg, 0.379 mmol) in DMF (4 mL)

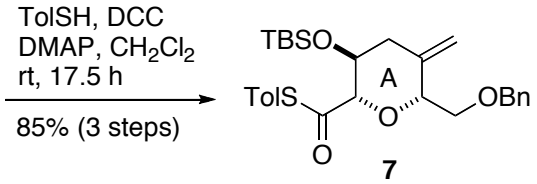
were added imidazole (105.5 mg, 1.55 mmol) and TBSCl (195.1 mg, 1.29 mmol), and the resultant solution was stirred at 50 °C for 14.5 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 2.5% EtOAc/hexanes) gave bis-TBS ether **S1** (182.0 mg, 97%) as a colorless oil: $[\alpha]_D^{23}$ +17.2 (*c* 1.29, $CHCl_3$); IR (film) 3088, 3065, 3031, 2953, 2928, 2884, 2856, 1655, 1471, 1462, 1253, 1099, 836, 777, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34—7.24 (m, 4H), 7.26 (m, 1H), 4.82 (br s, 1H), 4.79 (br s, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.98 (dd, *J* = 5.5, 5.5 Hz, 1H), 3.84 (dd, *J* = 11.3, 2.0 Hz, 1H), 3.75 (dd, *J* = 10.3, 5.5 Hz, 1H), 3.71 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.63 (dd, *J* = 10.3, 5.5 Hz, 1H), 3.62 (m 1H), 3.25 (ddd, *J* = 8.6, 4.9, 2.0 Hz, 1H), 2.56 (dd, *J* = 12.1, 5.2 Hz, 1H), 2.19 (dd, *J* = 12.1, 10.3 Hz, 1H), 0.86 (s, 18H), 0.05 (s, 3H), 0.043 (s, 3H), 0.038 (s, 3H), 0.029 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.9, 138.2, 128.3 (× 2), 127.8 (× 2), 127.5, 108.9, 83.0, 76.5, 73.6, 70.5, 68.0, 63.1, 42.8, 26.0 (× 3), 25.8 (× 3), 18.5, 17.9, −4.3, −4.9, −5.0, −5.2; HRMS (ESI) calcd for $C_{27}H_{48}O_4Si_2Na$ $[(M + Na)^+]$ 515.2983, found 515.2989.



Alcohol 16. To a solution of bis-TBS ether **S1** (1.30 g, 2.64 mmol) in MeOH/CH_2Cl_2 (1:1, v/v, 26 mL) was added CSA (66.1 mg, 0.285 mmol), and the resultant solution was stirred at 0 °C for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was diluted with EtOAc, and the organic layer was

washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 15% EtOAc/hexanes) gave alcohol **16** (0.870 g, 87%) as a colorless oil: $[\alpha]_D^{24}$ +10.8 (*c* 1.00, $CHCl_3$); IR (film) 3459, 3087, 3063, 3031, 2952, 2928, 2856, 1655, 1253, 1095, 837, 776 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.30—7.26 (m, 1H), 4.86 (br s, 1H), 4.80 (br s, 1H), 4.59 (d, *J* = 12.4 Hz, 1H), 4.56 (d, *J* = 12.4 Hz, 1H), 4.01 (br dd, *J* = 4.4, 5.8 Hz, 1H), 3.83 (br dd, *J* = 11.3, 3.1 Hz, 1H), 3.75 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.64 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.61 (br dd, *J* = 11.3, 5.8 Hz, 1H), 3.57 (ddd, *J* = 11.0, 8.9, 5.2 Hz, 1H), 3.34 (ddd, *J* = 8.9, 5.3, 3.1 Hz, 1H), 2.59 (dd, *J* = 13.0, 5.2 Hz, 1H), 2.22 (dd, *J* = 13.0, 11.0 Hz, 1H), 2.14 (br s, 1H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.0, 137.9, 128.4 (× 2), 127.84 (× 2), 127.77, 109.7, 82.1, 76.5, 73.5, 70.1, 68.7, 62.7, 43.0, 25.7 (× 3), 17.9, −4.2, −5.0; HRMS (ESI) calcd for $C_{21}H_{34}O_4SiNa$ $[(M + Na)^+]$ 401.2119, found 401.2124.





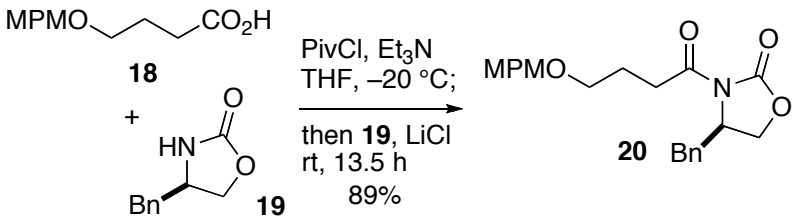
Thioester 7. To a solution of alcohol **16** (34.3 mg, 0.0906 mmol) in CH_2Cl_2/DMSO (1:1, v/v, 0.9 mL) was added Et_3N (0.0650 ml, 0.466 mmol). To this mixture cooled to 0 °C was added SO_3·pyridine (57.7 mg, 0.363 mmol), and the resultant solution was stirred at 0 °C for 0.5 h. The reaction mixture was extracted with Et_2O, and the organic layer

was washed successively with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude aldehyde was used immediately in the next reaction without purification.

To a solution of the above crude aldehyde, 2-methyl-2-butene (0.0950 mL, 0.897 mmol), and NaH_2PO_4 (12.0 mg, 0.100 mmol) in *t*-BuOH/H_2O (5:1, v/v, 0.9 mL) at 0 °C was added $NaClO_2$ (24.6 mg, 0.272 mmol), and the resultant mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into $CHCl_3$/H_2O. The aqueous layer was acidified (pH 3) with 1 M aqueous HCl solution, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude carboxylic acid **17** was used immediately in the next reaction without purification.

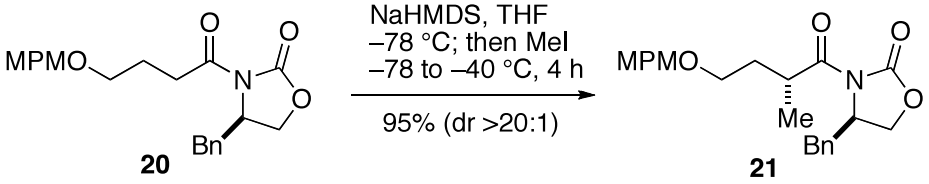
To a solution of the above crude carboxylic acid **17** in CH_2Cl_2 (0.9 mL) at 0 °C were added *p*-toluenethiol (12.4 mg, 0.0998 mmol), DMAP (1.2 mg, 0.0098 mmol), and DCC (20.6 mg, 0.0998 mmol), and the resultant solution was allowed to warm to room temperature and stirred for 17.5 h. The reaction mixture was diluted with Et_2O. Insoluble materials were filtered off, and the filtrate was washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduce pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 2% EtOAc/hexanes) gave thioester **7** (38.5 mg, 85% for the three steps) as a colorless oil: $[\alpha]_D^{25}$ −35.2 (*c* 0.84, $CHCl_3$); IR (film) 3734, 3063, 3028, 2951, 2927, 2884, 2856, 1707, 1253, 1109, 837, 808, 779 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39—7.38 (m, 2H), 7.35—7.32 (m, 2H), 7.28—7.26 (m, 3H), 7.20—7.19 (m, 2H), 4.93 (br s, 1H), 4.91

(br s, 1H), 4.68 (d, J = 12.4 Hz, 1H), 4.64 (d, J = 12.4 Hz, 1H), 4.18 (br dd, J = 6.2, 4.5 Hz, 1H), 4.01 (d, J = 7.6 Hz, 1H), 3.98 (ddd, J = 8.2, 7.6, 4.5 Hz, 1H), 3.82 (dd, J = 10.3, 4.5 Hz, 1H), 3.74 (dd, J = 10.3, 6.2 Hz, 1H), 2.66 (dd, J = 13.4, 4.5 Hz, 1H), 2.35 (s, 3H), 2.29 (dd, J = 13.4, 8.2 Hz, 1H), 0.84 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1, 140.8, 139.5, 138.1, 134.6 (× 2), 130.0 (× 2), 128.4 (× 2), 127.8 (× 2), 127.7, 123.7, 110.8, 86.9, 77.2, 73.6, 70.4, 70.1, 41.6, 25.7 (× 3), 21.3, 17.9, −4.6, −4.9; HRMS (ESI) calcd for $C_{28}H_{38}O_4SSiNa$ [$(M + Na)^+$] 521.2152, found 521.2158.



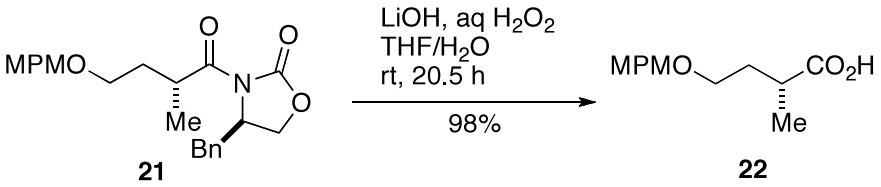
Oxazolidinone 20. To a solution of carboxylic acid **18**[1] (1.03 g, 4.59 mmol) and Et_3N (1.95 ml, 14.0 mmol) in THF (30 mL) cooled to −20 °C was added PivCl (0.675 ml, 5.54 mmol), and the resultant mixture was stirred at −20 °C for 2.5 h. To this mixture were added LiCl (292.0 mg, 6.888 mmol) and a solution of (*R*)-4-benzyl-2-oxazolidinone (**19**) (813.4 mg, 4.590 mmol) in THF (16 mL), and the resultant mixture was stirred at room temperature for 13.5 h. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 30% EtOAc/hexanes) to give oxazolidinone **20** (1.57 g, 89%) as a pale yellow oil: $[\alpha]_D^{24}$ −37.8 (*c* 1.00, $CHCl_3$); IR (film) 3061, 3028, 3001, 2931, 2859, 1780, 1699, 1513, 1388, 1248, 1211, 1097, 1032, 703 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32—7.29 (m, 2H), 7.26—7.23 (m, 3H), 7.17—7.16 (m,

2H), 6.85—6.83 (m, 2H), 4.57 (ddd, J = 13.4, 6.5, 3.5 Hz, 1H), 4.41 (s, 2H), 4.10—4.08 (m, 2H), 3.76 (s, 3H), 3.54—3.51 (m, 2H), 3.23 (dd, J = 13.4, 3.4 Hz, 1H), 3.04—3.02 (m, 2H), 2.65 (dd, J = 13.4, 9.6 Hz, 1H), 2.02—1.97 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 159.1, 153.4, 135.4, 130.5, 129.4 (× 2), 129.3 (× 2), 128.9 (× 2), 127.3, 113.7 (× 2), 72.5, 68.9, 66.1, 55.22, 55.15, 37.8, 32.5, 24.5; HRMS (ESI) calcd for $C_{22}H_{25}O_5NNa$ [$(M + Na)^+$] 406.1625, found 406.1622.



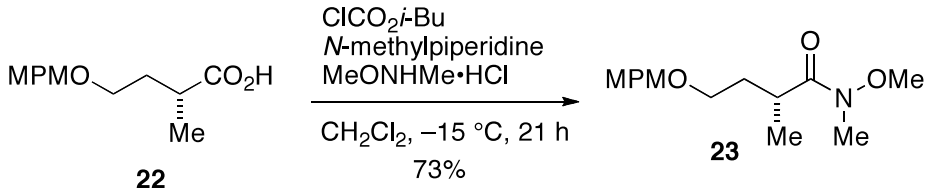
Methylated product 21. To a solution of oxazolidinone **20** (821.2 mg, 2.142 mmol) in THF (22 mL) at −78 °C was added NaHMDS (1.0 M solution in THF, 3.00 mL, 3.00 mmol), and the resultant solution was stirred at −78 °C for 1 h. To this mixture was added MeI (0.725 mL, 4.77 mmol), and the resultant solution was stirred at −78 °C for 3 h and then at −40 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 20 to 30% EtOAc/hexanes) to give methylated product **21** (805.6 mg, 95%, dr >20:1 by 600 MHz ^{1}H NMR analysis) as a yellow oil: $[\alpha]_D^{24}$ −57.7 (*c* 1.00, $CHCl_3$); IR (film) 3028, 2930, 2857, 1777, 1696, 1513, 1385, 1247, 1207, 1091, 1032, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32—7.28 (m, 2H), 7.25—7.20 (m, 3H), 7.15—7.13 (m, 2H), 6.82—6.79 (m, 2H), 4.38 (m, 1H), 4.33 (s, 2H), 3.97 (dd, J = 9.6, 3.1 Hz, 1H), 3.90 (m, 1H), 3.75 (m, 1H), 3.72 (s, 3H), 3.50 (m, 2H), 3.18 (dd, J = 13.4, 3.1 Hz, 1H), 2.68 (dd, J = 13.4, 9.6 Hz, 1H), 2.12 (dddd, J = 14.0, 8.2, 8.2, 5.5 Hz, 1H), 1.71 (dddd, J = 14.0, 5.5, 5.5, 4.8 Hz, 1H) 1.21 (d, J = 6.8

Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 159.1, 153.2, 135.4, 130.6, 129.4 (× 2), 129.2 (× 2), 128.8 (× 2), 127.2, 113.6 (× 2), 72.4, 68.1, 65.8, 55.24, 55.22, 38.0, 35.1, 33.6, 18.0; HRMS (ESI) calcd for $C_{23}H_{27}O_5NNa$ [(M + Na)$^+$] 420.1781, found 420.1779.

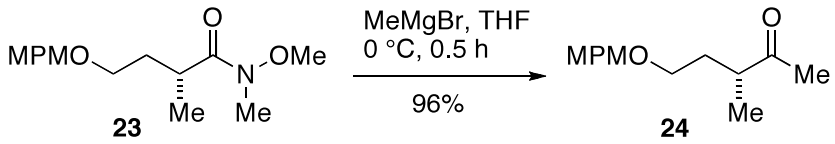


Carboxylic acid 22. To a solution of methylated product **21** (785.1 mg, 1.98 mmol) in THF/H_2O (4:1, v/v, 30 mL) at 0 °C were added 30% aqueous H_2O_2 solution (0.951 mL, 8.39 mmol) and a solution of LiOH·H_2O (140.5 mg, 3.348 mmol) in H_2O (4.2 mL), and the resultant solution was allowed to warm to room temperature and stirred for 20.5 h. The reaction mixture was cooled to 0 °C, quenched with saturated aqueous Na_2SO_3 solution, and stirred at 0 °C for 10 min. The reaction mixture was diluted with EtOAc and acidified with 0.1 M aqueous HCl solution (pH 3). The whole mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 15 to 30% EtOAc/hexanes) to give carboxylic acid **22** (462.5 mg, 98%) as a colorless oil: $[\alpha]_D^{25}$ −16.9 (*c* 1.00, $CHCl_3$); IR (film) 2935, 2859, 1811, 1742, 1612, 1513, 1458, 1362, 1302, 1248, 1173, 1096, 1033, 819 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23—7.20 (m, 2H), 6.86—6.83 (m, 2H), 4.40 (d, *J* = 12.9 Hz, 1H), 4.37 (d, *J* = 12.9 Hz, 1H), 3.77 (s, 3H), 3.47 (t, *J* = 6.2 Hz, 2H), 2.70 (ddq, *J* = 6.8, 6.8, 6.8 Hz, 1H), 2.02 (dddd, *J* = 13.7, 6.8, 6.2, 6.2 Hz, 1H), 1.69 (dddd, *J* = 13.7, 6.8, 6.2, 6.2 Hz, 1H), 1.18 (d, *J* = 6.8 Hz, 3H) (one proton missing presumably due to H/D exchange); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 159.2, 130.3, 129.3 (× 2), 113.8

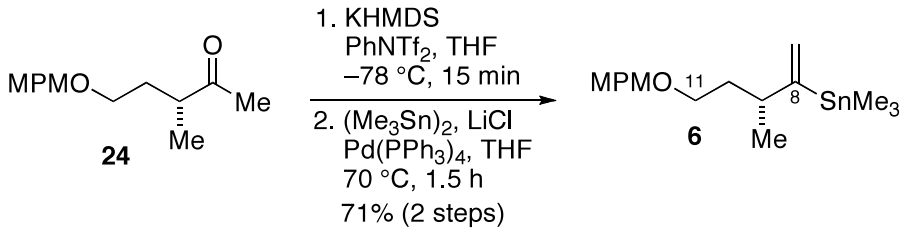
(× 2), 72.7, 67.0, 55.3, 37.5, 32.8, 16.3; HRMS (ESI) calcd for $C_{13}H_{18}O_4Na$ [$(M + Na)^+$] 261.1097, found 261.1097.



Weinreb amide 23. To a solution of carboxylic acid **22** (459.0 mg, 1.926 mmol) in CH_2Cl_2 (15 mL) at −15 °C were added *N*-methylpiperidine (0.725 mL, 5.94 mmol) and isobutyl chloroformate (0.385 mL, 2.93 mmol), and the resultant mixture was stirred at −15 °C for 80 min. To the mixture was added MeNHOMe·HCl (339.2 mg, 3.48 mmol), and the resultant mixture was stirred at −15 °C for 21 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 20 to 50% EtOAc/hexanes) to give Weinreb amide **23** (397.4 mg, 73%) as a colorless oil: $[\alpha]_D^{25}$ −19.4 (*c* 1.00, $CHCl_3$); IR (film) 2964, 2936, 2861, 1659, 1613, 1514, 1463, 1248, 1174, 1093, 1034, 994, 820 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.22—7.20 (m, 2H), 6.85—6.82 (m, 2H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.46 (ddd, *J* = 9.6, 5.8, 5.8 Hz, 1H), 3.39 (ddd, *J* = 9.6, 7.6, 5.2 Hz, 1H), 3.14 (s, 3H), 3.10 (m, 1H), 1.99 (dddd, *J* = 13.7, 8.6, 5.8, 5.2 Hz, 1H), 1.63 (dddd, *J* = 13.7, 7.6, 5.9, 5.8 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 159.6, 131.3, 129.3 (× 2), 128.2, 114.0 (× 2), 72.6, 68.2, 60.9, 54.7, 34.1, 32.4, 32.2, 17.9; HRMS (ESI) calcd for $C_{15}H_{23}O_4NNa$ [$(M + Na)^+$] 304.1519, found 304.1523.



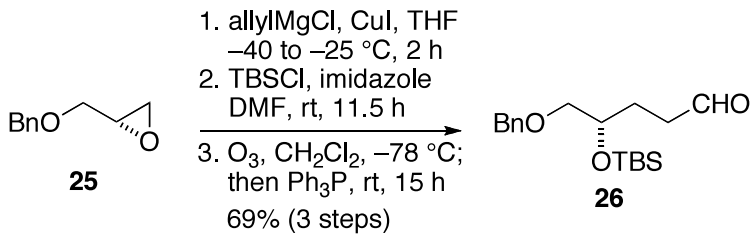
Methyl ketone 24. To a solution of Weinreb amide **23** (35.4 mg, 0.126 mmol) in THF (1.3 mL) at 0 °C was added MeMgBr (3.0 M solution in Et_2O, 0.130 mL, 0.390 mmol), and the resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc/hexanes) to give methyl ketone **24** (28.5 mg, 96%) as a colorless oil: $[\alpha]_D^{25}$ −8.0 (*c* 1.00, $CHCl_3$); IR (film) 2964, 2934, 2859, 1711, 1613, 1514, 1457, 1361, 1302, 1248, 1173, 1095, 1034, 820 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.22—7.20 (m, 2H), 6.86—6.84 (m, 2H), 4.37 (s, 2H), 3.78 (s, 3H), 3.42 (m, 2H), 2.69 (ddq, *J* = 6.8, 6.8, 6.8 Hz, 1H), 2.11 (s, 3H), 1.98 (dddd, *J* = 14.1, 7.2, 6.8, 5.8 Hz, 1H), 1.58 (dddd, *J* = 14.1, 6.8, 6.2, 6.2 Hz, 1H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.5, 159.1, 130.4, 129.3 (× 2), 113.7 (× 2), 72.6, 67.6, 55.3, 44.0, 32.7, 28.3, 16.3; HRMS (ESI) calcd for $C_{14}H_{20}O_3Na$ [$(M + Na)^+$] 259.1305, found 259.1304.



Vinylstannane 6. To a solution of methyl ketone **24** (688 mg, 2.91 mmol) and $PhNTf_2$ (1.37 g, 3.49 mmol) in THF (29 mL) at −78 °C was added KHMDS (7.00 mL, 0.5 M

solution in toluene, 3.50 mmol), and the resultant solution was stirred at −78 °C for 15 min. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 2 to 20% EtOAc/hexanes) to give an enol triflate, which was used immediately in the next reaction.

To a suspension of LiCl (1.23 g, 29.1 mmol) and $Pd(PPh_3)_4$ (336 mg, 0.291 mmol) in THF (15 mL) were added a solution of the above enol triflate in THF (14.2 mL) and hexamethylditin (1.20 mL, 5.82 mmol), and the resultant solution was stirred at 70 °C for 1.5 h. The reaction mixture was cooled to room temperature and diluted with Et_2O. Insoluble materials were filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 50 % benzene/hexanes, then 20% EtOAc/hexanes) to give vinylstannane **6** (847 mg, 71% for the two steps) as a colorless oil: $[\alpha]_D^{25}$ −12.1 (*c* 1.00, C_6H_6); IR (film) 3033, 2954, 2931, 2856, 1613, 1513, 1456, 1362, 1302, 1248, 1173, 1097, 1038, 917, 820, 768, 710, 526, 511 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.25—7.23 (m, 2H), 6.81—6.80 (m, 2H), 5.72 (dd, *J* = 1.3, 1.3 Hz, 1H), 5.19 (d, *J* = 1.3 Hz, 1H), 4.34 (s, 2H), 3.38 (m, 2H), 3.29 (s, 3H), 2.63 (m, 1H), 1.69 (m, 2H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6) δ 161.3, 159.7, 131.4, 129.3 (× 2), 124.0, 114.0 (× 2), 72.8, 68.5, 54.7, 42.7, 37.5, 22.1, −8.3 (× 3); HRMS (ESI) calcd for $C_{17}H_{28}O_2SnNa$ [$(M + Na)^+$] 407.1003, found 407.1009.

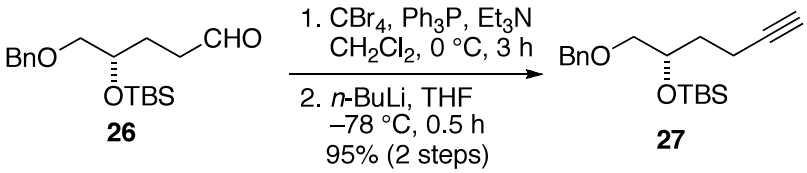


Aldehyde 26. To a suspension of copper(I) iodide (250 mg, 1.31 mmol) in THF (30 mL) at −40 °C was added allylmagnesium chloride (2.0 M solution in THF, 9.8 mL, 19.6 mmol), and the resultant mixture was stirred at −40 °C for 30 min. To the mixture was added a solution of benzyl (*S*)-glycidyl ether (**25**) (2.00 mL, 13.1 mmol) in THF (35 mL), and the resultant mixture was stirred at −40 °C for 15 min and then at −25 °C for 1.75 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 20% EtOAc/hexanes) to give an olefin (2.69 g) as a colorless oil.

To a solution of the above olefin (2.69 g) in DMF (65 mL) were added imidazole (1.78 g 26.2 mmol) and TBSCl (2.95 g, 19.6 mmol), and the resultant solution was stirred at room temperature for 11.5 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O, and the organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 15% EtOAc/hexanes) to give a TBS ether (4.19 g) as a colorless oil.

Ozone was bubbled through a solution of the above TBS ether (4.19 g) in CH_2Cl_2 (65 mL) at −78 °C until a pale blue color was persisted. Oxygen was bubbled

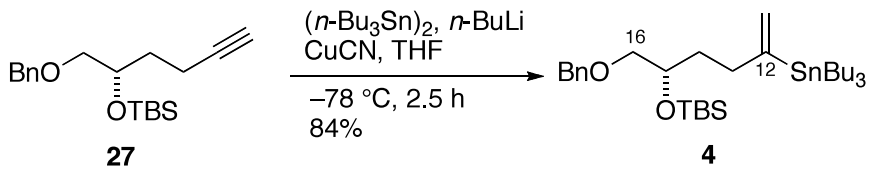
through the solution to remove excess ozone. To the solution was then added triphenylphosphine (13.78 g, 52.5 mmol), and the reaction mixture was gradually allowed to warm to room temperature and stirred for 15 h. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 15% EtOAc/hexanes) to give aldehyde **26** (2.91 g, 69% for the three steps) as a colorless oil: $[\alpha]_D^{20}$ −16.1 (*c* 1.01, $CHCl_3$); IR (film) 2953, 2928, 2893, 2856, 2717, 1726, 1472, 1362, 1254, 1099, 1041, 836, 776, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.75 (dd, *J* = 1.7, 1.7 Hz, 1H), 7.34—7.30 (m, 4H), 7.27 (m, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 3.88 (m, 1H), 3.40 (dd, *J* = 9.6, 5.5 Hz, 1H), 3.33 (dd, *J* = 9.6, 6.2 Hz, 1H), 2.49—2.46 (m, 2H), 1.94 (dddd, *J* = 14.5, 8.3, 7.2, 4.5 Hz, 1H), 1.78 (dddd, *J* = 14.5, 6.9, 6.9, 6.9 Hz, 1H), 0.86 (s, 9H), 0.033 (s, 3H), 0.028 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.5, 138.1, 128.3 (× 2), 127.59 (× 2), 127.57, 73.9, 73.3, 70.1, 39.4, 26.9, 25.8 (× 3), 18.0, −4.5, −4.9; HRMS (ESI) calcd for $C_{18}H_{30}O_3SiNa$ [$(M + Na)^+$] 345.1856, found 345.1858.



Alkyne 27. To a solution of CBr_4 (1.29 g, 3.89 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added Ph_3P (2.02 g, 7.70 mmol), and the resultant solution was stirred at 0 °C for 30 min. To the solution were added Et_3N (1.45 mL, 10.4 mmol) and a solution of aldehyde **26** (0.540 g, 1.67 mmol) in CH_2Cl_2 (7 mL), and the resultant solution was stirred at 0 °C for 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated

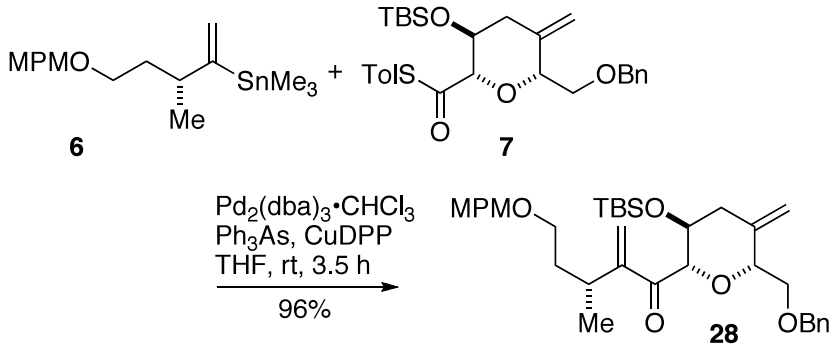
under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 5% EtOAc/hexanes) to give a dibromoolefin (0.77 g), which was contaminated with some impurities and used for the next reaction without further purification.

To a solution of the above dibromoolefin (0.77 g) in THF (16 mL) at −78 °C was added *n*-BuLi (2.69 M solution in hexanes, 1.50 mL, 4.04 mmol), and the resultant solution was stirred at −78 °C for 30 min. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 5% EtOAc/hexanes) to give alkyne **27** (0.51 g, 95% for the two steps) as a yellow oil: $[\alpha]_D^{20}$ −20.1 (*c* 1.37, $CHCl_3$); IR (film) 3310, 2954, 2928, 2894, 2856, 1471, 1362, 1254, 1127, 1093, 1029, 999, 836, 777, 735, 697, 633 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34—7.31 (m, 4H), 7.26 (m, 1H), 4.52 (d, *J* = 12.4 Hz, 1H), 4.50 (d, *J* = 12.4 Hz, 1H), 3.95 (dddd, *J* = 8.2, 5.5, 5.5, 4.1 Hz, 1H), 3.41 (dd, *J* = 9.6, 5.5 Hz, 1H), 3.35 (dd, *J* = 9.6, 5.5 Hz, 1H), 2.27—2.23 (m, 2H), 1.92 (dd, *J* = 2.8, 2.8 Hz, 1H), 1.79 (dddd, *J* = 13.7, 7.6, 7.6, 4.1 Hz, 1H), 1.66 (dddd, *J* = 13.7, 8.2, 7.3, 6.2 Hz, 1H), 0.89 (s, 9H) 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 128.3 (× 2), 127.6 (× 2), 127.5, 84.4, 74.4, 73.3, 69.9, 68.4, 33.4, 25.9 (× 3), 18.1, 14.4, −4.4, −4.9; HRMS (ESI) calcd for $C_{19}H_{30}O_2SiNa$ [(M + Na)$^+$] 341.1907, found 341.1912.



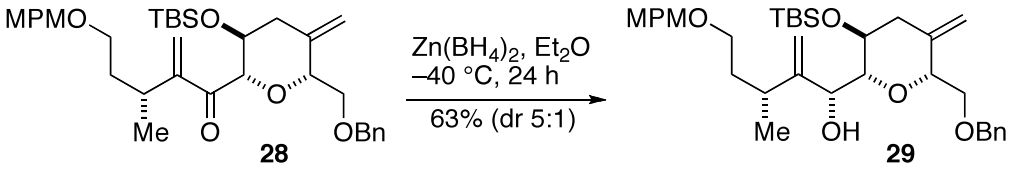
27 **4**

Vinylstannane 4. To a solution of bis(tri-*n*-butyltin) (3.00 mL, 6.00 mmol) in THF (7.0 mL) at −40 °C was added *n*-BuLi (2.69 M solution in hexanes, 2.20 mL, 5.92 mmol), and the resultant solution was stirred at −40 °C for 1 h. To the solution was added copper(I) cyanide (265.7 mg, 2.97 mmol), and the reaction mixture was cooled to −78 °C. To the resultant suspension was added a solution of alkyne **27** (308.2 mg 0.9676 mmol) in THF (2.0 mL + 1.0 mL rinse), and the resultant mixture was stirred at −78 °C for 2.5 h. The reaction mixture was quenched with H_2O. The mixture was extracted with Et_2O, and the organic layer was washed with saturated aqueous KF solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 5% benzene/hexanes) to give vinylstannane **4** (494.5 mg, 84%) as a colorless oil: $[\alpha]_D^{24}$ −1.7 (*c* 1.00, CH_2Cl_2); IR (film) 2955, 2927, 2854, 1457, 1253, 1115, 1003, 911, 835, 775, 696 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.28—7.27 (m, 2H), 7.20—7.17 (m, 2H), 7.09 (m, 1H), 5.89 (br s, 1H), 5.31 (br s, 1H) 4.35 (br d, *J* = 12.4 Hz, 1H), 4.32 (br d, *J* = 12.4 Hz, 1H), 3.92 (m, 1H), 3.40 (m, 1H), 3.34 (m, 1H), 2.61 (m, 1H), 2.44 (m, 1H), 1.85—1.71 (m, 2H), 1.68—1.55 (m, 6H), 1.42—1.35 (m, 6H), 1.05—1.01 (m, 15H), 0.95—0.92 (m, 9H), 0.14—0.12 (m, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 155.2, 139.0, 128.5 (× 2), 127.8 (× 2), 127.7, 125.2, 75.2, 73.4, 71.8, 37.5, 35.4, 29.6 (× 3), 27.8 (× 3), 26.2 (× 3), 18.4, 13.9 (× 3), 9.9 (× 3), −4.0, −4.5; HRMS (ESI) calcd for $C_{31}H_{58}O_2SiSnNa$ $[(M + Na)^+]$ 633.3120, found 633.3113.



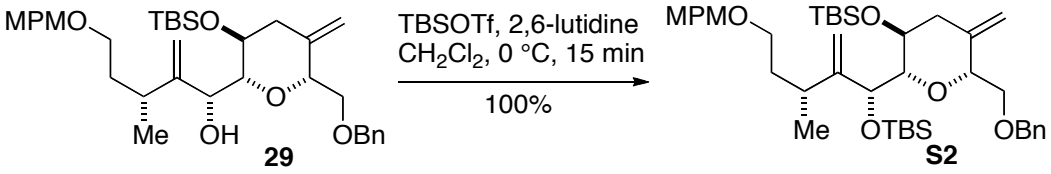
Enone 28. To a solution of thioester **7** (26.0 mg, 0.0521 mmol), copper(I) diphenylphosphinate (29.3 mg, 0.104 mmol), and $Pd_2(dba)_3$•$CHCl_3$ (2.70 mg, 0.00261 mmol) in THF (0.25 mL) were added a solution of Ph_3As (6.40 mg, 0.0209 mmol) in THF (0.1 mL + 0.05 mL rinse) and a solution of vinylstannane **6** (21.7 mg, 0.0566 mmol) in THF (0.1 mL + 0.05 mL rinse). The resultant solution was stirred at room temperature for 3.5 h. The reaction mixture was diluted with Et_2O. Insoluble materials were filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 10 % EtOAc/hexanes) to give enone **28** (29.8 mg, 96%) as a colorless oil: $[\alpha]_D^{30}$ +8.7 (*c* 1.00, $CHCl_3$); IR (film) 2954, 2928, 2855, 1645, 1613, 1514, 1249, 1098, 837, 778 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31—7.26 (m, 3H), 7.26—7.21 (m, 4H), 6.85—6.82 (m, 2H), 6.23 (s, 1H), 5.85 (s, 1H), 4.90 (d, *J* = 0.7 Hz, 1H), 4.84 (d, *J* = 0.7 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 1H), 4.33 (d, *J* = 11.7 Hz, 1H), 4.06 (br dd, *J* = 6.2, 5.2 Hz, 1H), 4.02 (ddd, *J* = 9.6, 8.6, 5.2 Hz, 1H), 3.77 (dd, *J* = 10.3, 5.2 Hz, 1H), 3.77 (s, 3H), 3.62 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.41 (ddd, *J* = 13.7, 7.2, 6.9 Hz, 1H), 3.40 (ddd, *J* = 13.7, 7.2, 6.8 Hz, 1H), 2.92 (ddq, *J* = 6.8, 6.8, 6.8 Hz, 1H), 2.66 (dd, *J* = 13.1, 5.2 Hz, 1H), 2.27 (m, 1H), 1.79 (dddd, *J* = 13.7, 6.9, 6.8, 6.8 Hz, 1H), 1.61 (dddd, *J* = 13.7, 7.2, 7.2, 6.8 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H),

0.79 (s, 9H), 0.04 (s, 3H), −0.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 159.0, 153.1, 141.3, 138.0, 130.7, 129.3 (× 2), 128.34, 128.31, 127.7 (× 2), 127.6, 125.4, 113.7 (× 2), 110.2, 80.6, 77.5, 73.5, 72.4, 70.2, 69.1, 68.3, 55.2, 42.5, 36.0, 30.3, 25.7 (× 3), 20.1, 17.8, −4.5, −5.0; HRMS (ESI) calcd for $C_{35}H_{50}O_6SiNa$ [$(M + Na)^+$] 617.3269, found 617.3290.



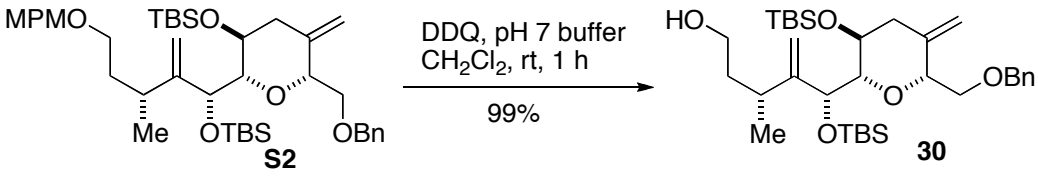
Allylic alcohol 29. To a solution of enone **28** (12.1 mg, 0.0203 mmol) in Et_2O (0.4 mL) at −40 °C was added $Zn(BH_4)_2$ (0.132 M solution in Et_2O, 0.775 mL, 0.102 mmol), and the resultant solution was stirred at −40 °C for 12 h. To this mixture was added $Zn(BH_4)_2$ (0.132 M solution in Et_2O, 0.775 mL, 0.102 mmol), and the resultant solution was stirred at −40 °C for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by column chromatography (silica gel, 0 to 20% EtOAc/hexanes) gave allylic alcohol **29** (7.6 mg, 63%, dr = 5 : 1 by 600 MHz ^{1}H NMR analysis) as a colorless oil: $[\alpha]_D^{30}$ –2.19 (*c* 1.00, $CHCl_3$); IR (film) 3441, 2953, 2927, 2856, 1513, 1249, 1094, 836 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32—7.29 (m, 4H), 7.27—7.21 (m, 3H), 6.85—6.82 (m, 2H), 5.12 (s, 1H), 4.99 (s, 1H), 4.85 (s, 1H), 4.83 (s, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.51 (d, *J* = 12.4 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 5.9 Hz, 1H), 3.98 (dd, *J* = 5.8, 4.8 Hz, 1H), 3.78—3.74 (m, 4H), 3.68 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.58 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.49—3.46 (m, 2H), 3.38 (dd, *J* = 7.9, 5.9 Hz, 1H), 2.59 (dd, *J* = 13.4, 4.8 Hz, 1H), 2.47

(ddq, J = 6.9, 6.9, 6.9 Hz, 1H), 2.25 (dd, J = 13.4, 8.9 Hz, 1H), 1.80 (dddd, J = 13.7, 7.6, 7.6, 6.9 Hz, 1H), 1.66 (dddd, J = 13.7, 6.9, 6.9, 6.9 Hz, 1H), 1.02 (d, J = 6.9 Hz, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H) (one proton missing presumably due to H/D exchange); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 154.1, 142.1, 138.2, 130.6, 129.3 (× 2), 128.3 (× 2), 127.6 (× 2), 127.5, 113.7 (× 2), 112.0, 109.7, 83.4, 76.90, 76.89, 73.4, 72.3, 71.6, 70.5, 68.6, 55.2, 42.2, 37.3, 31.6, 25.8 (× 3), 21.7, 17.9, –3.5, –4.6; HRMS (ESI) calcd for $C_{35}H_{52}O_6SiNa$ [$(M + Na)^+$] 619.3425, found 619.3410.



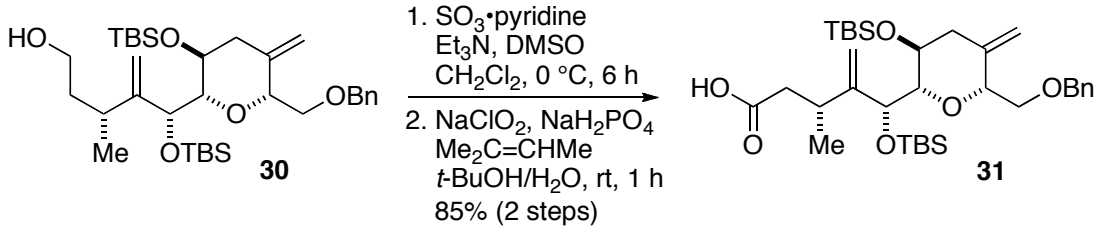
Bis-TBS ether S2. To a solution of allylic alcohol **29** (45.9 mg, 0.0769 mmol) in CH_2Cl_2 (0.8 mL) at 0 °C were added 2,6-lutidine (0.0500 mL, 0.429 mmol) and TBSOTf (0.0500 mL, 0.218 mmol), and the resultant solution was stirred at 0 °C for 15 min. The reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 5% Et_2O/hexanes) gave bis-TBS ether **S2** (54.8 mg, 100%) as a colorless oil: $[\alpha]_D^{30}$ –7.7 (*c* 0.69, $CHCl_3$); IR (film) 2954, 2927, 2885, 2855, 1514, 1471, 1457, 1361, 1249, 1093, 835, 775 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35—7.30 (m, 4H), 7.27—7.22 (m, 3H), 6.86—6.83 (m, 2H), 5.14 (s, 1H), 4.93 (s, 1H), 4.77 (s, 2H), 4.63 (d, J = 12.4 Hz, 1H), 4.56 (d, J = 12.4 Hz, 1H), 4.41 (d, J = 11.3 Hz, 1H), 4.35 (d, J = 11.3 Hz, 1H), 4.34 (s, 1H), 4.18 (m, 1H), 4.01 (dd, J = 9.3, 4.4 Hz, 1H), 3.77 (s, 3H), 3.69 (dd, J = 10.6, 3.8 Hz, 1H), 3.57 (dd, J = 10.6, 7.2 Hz, 1H), 3.43 (m, 3H), 2.53 (dd, J = 13.4, 2.4 Hz, 1H), 2.27 (m, 1H), 2.17

(dd, J = 13.4, 5.5 Hz, 1H), 1.87 (dddd, J = 13.4, 6.8, 6.8, 5.8 Hz, 1H), 1.59 (dddd, J = 13.4, 8.9, 7.6, 5.8 Hz, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.88 (s, 9H), 0.83 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H), –0.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 154.6, 143.5, 138.5, 130.9, 129.1 (× 2), 128.3 (× 2), 127.6 (× 2), 127.5, 113.7, 109.9, 108.6, 84.3, 76.5, 75.9, 73.5, 72.42, 72.37, 68.9, 66.7, 55.2, 39.7, 36.4, 32.0, 29.7, 25.9 (× 3), 25.9 (× 3), 21.5, 18.3, 17.9, –3.6, –4.4, –4.7, –4.8; HRMS (ESI) calcd for $C_{41}H_{66}O_6Si_2Na$ [$(M + Na)^+$] 733.4290, found 733.4283.



Alcohol 30. To a solution of bis-TBS ether **S2** (50.1 mg, 0.0705 mmol) in CH_2Cl_2/pH 7 buffer (10:1, v/v, 0.77 mL) at 0 °C was added DDQ (17.7 mg, 0.0780 mmol), and the resultant solution was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was cooled to 0 °C and quenched with saturated aqueous $NaHCO_3$ solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 10% EtOAc/hexanes) gave alcohol **30** (41.1 mg, 99%) as a colorless oil: $[\alpha]_D^{30}$ –15.3 (*c* 1.00, $CHCl_3$); IR (film) 3446, 3066, 3031, 2955, 2928, 2885, 2856, 1653, 1472, 1462, 1362, 1254, 1088, 836, 775, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35—7.31 (m, 4H), 7.27—7.24 (m, 1H), 5.14 (s, 1H), 4.95 (s, 1H), 4.79 (s, 1H), 4.78 (s, 1H), 4.62 (d, J = 12.4 Hz, 1H), 4.56 (d, J = 12.4 Hz, 1H), 4.41 (s, 1H), 4.09 (br dd, J = 8.9, 4.5 Hz, 1H), 3.85 (ddd, J = 6.9, 6.2, 3.4 Hz, 1H), 3.71 (dd, J = 10.7, 4.5 Hz, 1H), 3.63 (ddd, J = 10.7, 7.2, 5.9 Hz, 1H), 3.59 (dd, J = 10.7, 8.9 Hz, 1H), 3.54 (ddd, J = 10.7, 5.8, 5.8 Hz, 1H), 3.42 (dd, J =

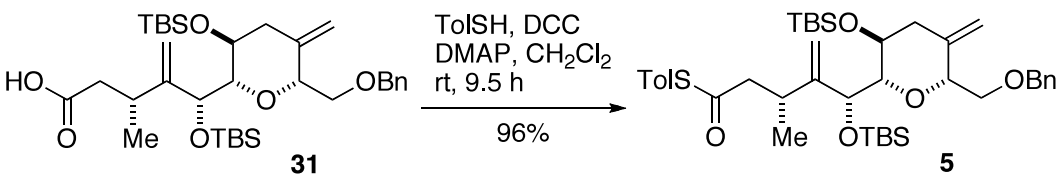
6.2, 2.0 Hz, 1H), 2.55 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.47 (ddq, *J* = 6.9, 6.9, 6.9 Hz, 1H), 2.18 (dd, *J* = 13.4, 6.9 Hz, 1H), 1.68 (dddd, *J* = 13.7, 6.9, 5.9, 5.8 Hz, 1H), 1.61 (dddd, *J* = 13.7, 7.2, 6.9, 5.8 Hz, 1H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.85 (s, 9H), 0.08 (s, 3H), 0.053 (s, 3H), 0.051 (s, 3H), 0.01 (s, 3H) (one proton missing presumably due to H/D exchange); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 142.9, 138.3, 128.3 (× 2), 127.7 (× 2), 127.5, 111.2, 109.0, 85.1, 76.7, 76.3, 73.5, 71.7, 67.8, 60.8, 40.7, 40.0, 30.7, 26.0 (× 3), 25.8 (× 3), 22.2, 18.4, 17.9, –3.5, –4.4, –4.5, –4.7; HRMS (ESI) calcd for $C_{33}H_{58}O_5Si_2Na$ [$(M + Na)^+$] 613.3715, found 613.3738.



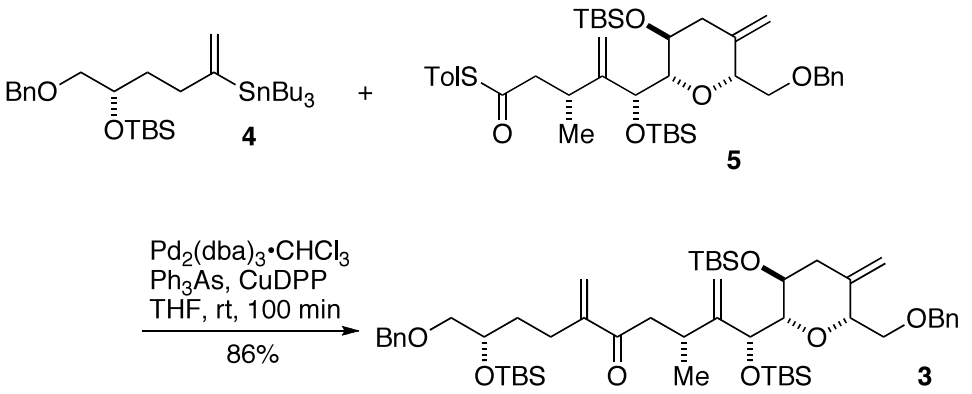
Carboxylic acid 31. To a solution of alcohol **30** (29.9 mg, 0.0506 mmol) in CH_2Cl_2/DMSO (1/1, v/v, 0.6 mL) was added Et_3N (0.0400 mL, 0.287 mmol). To the reaction mixture cooled to 0 °C was added SO_3·pyridine (32.4 mg, 0.204 mmol), and the resultant solution was stirred at 0 °C for 2 h. To the reaction mixture were added Et_3N (0.0700 mL, 0.502 mmol) and SO_3·pyridine (56.5 mg, 0.355 mmol) in two portions within 1 h, and the resultant solution was stirred at 0 °C for 3 h. The reaction mixture was diluted with Et_2O, washed successively with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 10% EtOAc/hexanes) gave aldehyde (26.9 mg, 90%) as a colorless oil, which was used immediately in the next reaction.

To a solution of the above aldehyde (26.9 mg, 0.0457 mmol), 2-methyl-2-butene

(0.0485 mL, 0.458 mmol), and NaH_2PO_4 (6.10 mg, 0.0508 mmol) in *t*-BuOH/H_2O (5:1, v/v, 0.48 mL) at 0 °C was added $NaClO_2$ (79% purity, 12.4 mg, 0.137 mmol), and the resultant solution was stirred at room temperature for 1 h. The reaction mixture was poured into $CHCl_3$/H_2O. The aqueous layer was acidified (pH 3) with 1 M aqueous HCl solution, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 20% EtOAc/hexanes) gave carboxylic acid **31** (26.0 mg, 94%) as a colorless oil: $[\alpha]_D^{26}$ –11.3 (*c* 1.50, $CHCl_3$); IR (film) 3503, 3087, 3033, 2955, 2929, 2895, 2857, 1710, 1652, 1471, 1463, 1254, 1094, 836, 775 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34—7.30 (m, 4H), 7.27—7.24 (m, 1H), 5.14 (s, 1H), 4.95 (s, 1H), 4.78 (s, 1H), 4.76 (s, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.42 (s, 1H), 4.14 (dd, *J* = 6.8, 3.8 Hz, 1H), 3.85 (ddd, *J* = 6.5, 5.8, 3.4 Hz, 1H), 3.72 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.58 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.42 (dd, *J* = 5.8, 2.0 Hz, 1H), 2.85 (m, 1H), 2.64 (dd, *J* = 15.1, 3.4 Hz, 1H), 2.53 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.25 (dd, *J* = 15.1, 11.0 Hz, 1H), 2.18 (dd, *J* = 13.4, 6.5 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.83 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H), –0.01 (s, 3H) (one proton missing presumably due to H/D exchange); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 153.0, 142.9, 138.3, 128.3 (× 2), 127.7 (× 2), 127.5, 111.4, 109.0, 84.9, 75.9, 73.6, 73.4, 72.0, 67.3, 41.9, 40.4, 31.4, 25.9 (× 3), 25.8 (× 3), 20.6, 18.3, 17.9, −3.5, −4.4, −4.7, −4.8; HRMS (ESI) calcd for $C_{33}H_{56}O_6Si_2Na$ [$(M + Na)^+$] 627.3508, found 627.3517.

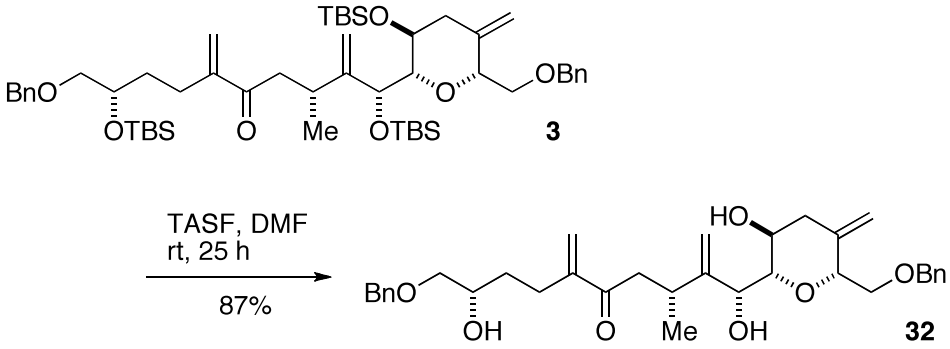


Thioester 5. To a solution of carboxylic acid **31** (22.0 mg, 0.0364 mmol) in CH_2Cl_2 (1 mL) at 0 °C were added *p*-toluenethiol (5.00 mg, 0.0403 mmol), DMAP (0.460 mg, 0.00377 mmol), and DCC (8.30 mg, 0.0402 mmol), and the resultant solution was stirred at room temperature for 9.5 h. The reaction mixture was diluted with Et_2O. Insoluble materials were filtered off, and the filtrate was washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduce pressure. Purification of the residue by flash column chromatography (silica gel, 0 to 2.5% EtOAc/hexanes) gave thioester **5** (24.9 mg, 96%) as a colorless oil: $[\alpha]_D^{25}$ −8.5 (*c* 1.12, $CHCl_3$); IR (film) 3077, 3030, 2955, 2928, 2896, 2856, 2033, 1709, 1471, 1462, 1255, 1094, 836, 806, 775 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35—7.29 (m, 4H), 7.25—7.22 (m, 3H), 7.19—7.18 (m, 2H) 5.15 (s, 1H), 4.95 (s, 1H), 4.79 (s, 2H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.41 (s, 1H), 4.15 (dd, *J* = 6.9, 4.1 Hz, 1H), 3.88 (m, 1H), 3.72 (dd, *J* = 10.7, 4.1 Hz, 1H), 3.60 (dd, *J* = 10.7, 6.9 Hz, 1H), 3.42 (dd, *J* = 5.9, 1.7 Hz, 1H), 2.95—2.90 (m, 2H), 2.56 (dd, *J* = 15.4, 11.6 Hz, 1H), 2.54 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.35 (s, 3H), 2.19 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.86 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 153.3, 143.1, 139.4, 138.5, 134.4 (× 2), 129.9 (× 2), 128.3 (× 2), 127.7 (× 2), 127.4, 124.5, 111.1, 108.9, 84.9, 76.8, 75.7, 73.6, 72.1, 67.2, 51.0, 40.3, 32.1, 25.93 (× 3), 25.86 (× 3), 21.3, 20.3, 18.3, 17.9, −3.5, −4.4, −4.7, −4.8; HRMS (ESI) calcd for $C_{40}H_{62}O_5Si_2SNa$ $[(M + Na)^+]$ 733.3749, found 733.3755.



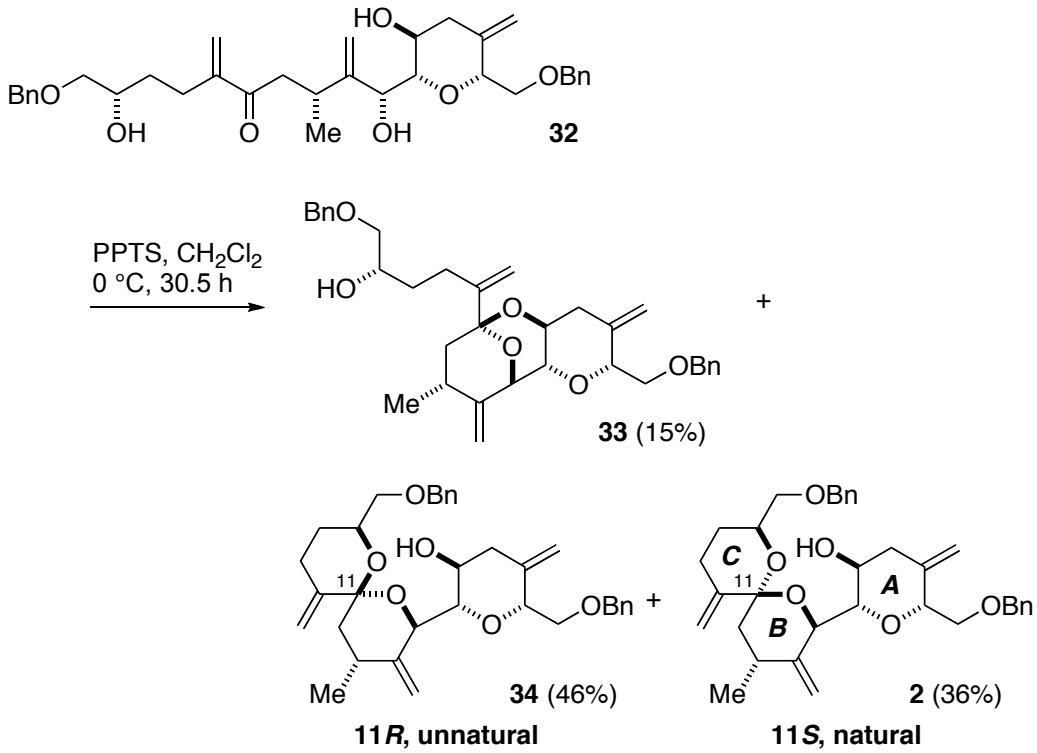
Enone 3. To a solution of thioester **5** (24.3 mg, 0.0342 mmol), copper(I) diphenylphosphinate (19.3 mg, 0.0688 mmol), and $Pd_2(dba)_3$•$CHCl_3$ (1.80 mg, 0.00174 mmol) in THF (0.2 mL) were added a solution of Ph_3As (4.20 mg, 0.0137 mmol) in THF (0.05 mL + 0.05 mL rinse) and a solution of vinylstannane **4** (23.0 mg, 0.0377 mmol) in THF (0.05 mL + 0.05 mL rinse), and the resultant solution was stirred at room temperature for 100 min. The reaction mixture was diluted with Et_2O. Insoluble materials were filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 0 to 2.5 % EtOAc/hexanes) to give enone **3** (26.6 mg, 86%) as a colorless oil: $[\alpha]_D^{25}$ –3.8 (*c* 1.08, $CHCl_3$); IR (film) 3088, 3065, 3031, 2954, 2928, 2894, 2856, 1682, 1471, 1462, 1362, 1254, 1094, 835, 775, 734, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35—7.30 (m, 8H), 7.26—7.23 (m, 2H), 5.97 (s, 1H), 5.66 (s, 1H), 5.16 (s, 1H), 4.95 (s, 1H), 4.78 (s, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.50 (s, 2H), 4.39 (s, 1H), 4.16 (dd, *J* = 6.9, 4.1 Hz, 1H), 3.94 (m, 1H), 3.83 (m, 1H), 3.68 (dd, *J* = 10.7, 4.1 Hz, 1H), 3.57 (dd, *J* = 10.7, 6.9 Hz, 1H), 3.38 (m, 3H), 2.86 (dd, *J* = 15.8, 2.5 Hz, 1H), 2.83 (m, 1H), 2.63 (dd, *J* = 15.8, 11.0 Hz, 1H), 2.52 (dd, *J* = 13.4, 2.8 Hz, 1H), 2.34 (ddd, *J* = 15.5, 11.7, 4.8 Hz, 1H), 2.23 (ddd, *J* = 15.5, 11.3, 5.2 Hz, 1H), 2.16 (dd, *J* = 13.4, 6.2 Hz, 1H), 1.63 (m, 1H), 1.50 (dddd, *J* = 13.1, 11.7, 7.2, 5.2 Hz, 1H), 0.97 (d, *J* = 6.5 Hz,

3H), 0.87 (s, 18H), 0.80 (s, 9H), 0.04 (s, 6H), 0.03 (s, 6H), 0.01 (s, 3H), –0.03 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 199.8, 155.0, 149.9, 143.7, 139.4, 139.1, 128.52 (× 2), 128.47 (× 2), 127.81 (× 2), 127.76 (× 2), 127.7, 127.5, 123.0, 110.7, 109.1, 85.4, 77.3, 76.4, 75.1, 73.6, 73.4, 72.5, 71.9, 67.8, 45.4, 40.8, 34.3, 31.6, 27.5, 26.2 (× 6), 26.1 (× 3), 21.2, 18.6, 18.4, 18.1, –3.4, –4.0, –4.2, –4.4, –4.6 (× 2); HRMS (ESI) calcd for $C_{52}H_{86}O_7Si_3Na$ [$(M + Na)^+$] 929.5574, found 929.5605.



Ketotriol 32. To a solution of enone **3** (10.2 mg, 0.0112 mmol) in DMF (1.2 mL) at 0 °C was added TASF (117 mg, 0.425 mmol) in four portions, and the resultant solution was stirred at room temperature for 25 h. The reaction mixture was diluted with Et_2O and quenched with saturated aqueous $NaHCO_3$ solution. The whole mixture was extracted with Et_2O, washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 20 to 100% EtOAc/hexanes) gave ketotriol **32** (5.6 mg, 87%) as a colorless oil: $[\alpha]_D^{25}$ +7.3 (*c* 0.20, CH_2Cl_2); IR (film) 3405, 3087, 3064, 3030, 2924, 2863, 1665, 1454, 1094, 907, 738, 698 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 7.29—7.28 (m, 2H), 7.21—7.15 (m, 6H), 7.12—7.08 (m, 2H), 5.52 (s, 1H), 5.42 (br s, 1H), 5.35 (s, 1H), 5.10 (s, 1H), 4.77 (m, 3H), 4.70 (d, *J* = 1.0 Hz, 1H), 4.39 (d, *J* = 12.4 Hz, 1H), 4.37 (d, *J* = 8.3 Hz, 1H), 4.34 (d, *J* = 12.4 Hz, 1H), 4.24 (s, 2H), 4.06 (ddd, *J* = 8.3, 7.2, 3.8 Hz, 1H), 3.99 (dd, *J* = 6.8,

4.1 Hz, 1H), 3.69 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.65 (m, 1H), 3.57 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.46 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.17 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.13 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.86 (dd, *J* = 13.4, 5.5 Hz, 1H), 2.80—2.70 (m, 2H), 2.48—2.41 (m, 2H), 2.35 (s, 1H), 2.33—2.26 (m, 2H), 1.49—1.40 (m, 2H), 1.00 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 202.8, 153.7, 148.8, 143.1, 139.3, 138.7, 128.6 (× 2), 128.4 (× 2), 128.3, 127.9 (× 2), 127.50 (× 2), 127.48, 125.1, 112.8, 109.0, 81.1, 80.4, 77.4, 74.8, 73.32, 73.30, 72.3, 70.9, 69.8, 45.6, 41.9, 32.5, 28.3, 27.3, 22.9; HRMS (ESI) calcd for $C_{34}H_{44}O_7Na$ [$(M + Na)^+$] 587.2979, found 587.2985.



Fused acetal 33 and spiroacetals 34 and 2. To a solution of triol **32** (2.0 mg, 0.0035 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C was added a solution of PPTS (1.3 mg, 0.0053 mmol) in CH_2Cl_2 (0.2 mL), and the resultant solution was stirred at 0 °C for 30.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried over

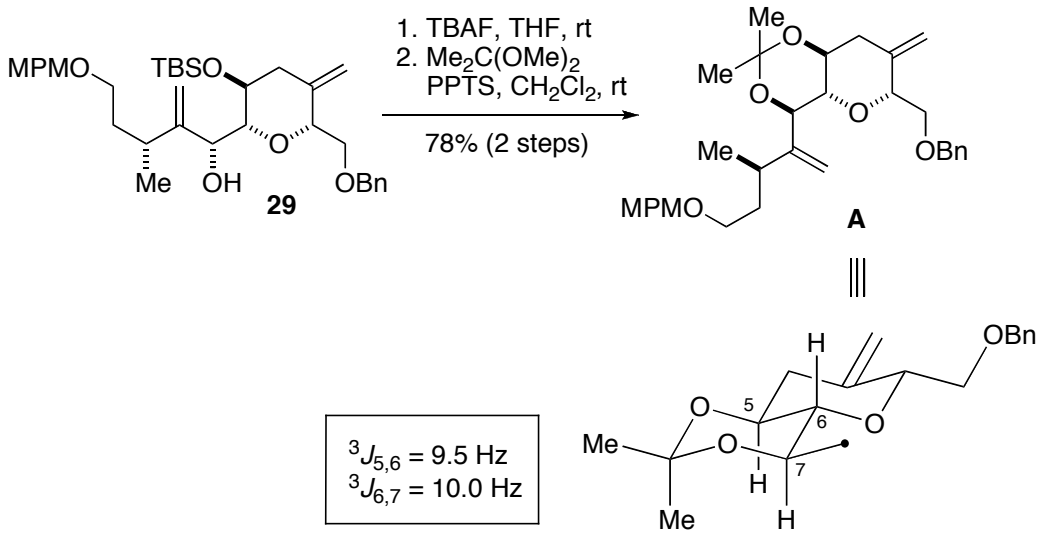
Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, $Et_2O/CHCl_3$/hexanes = 1:1:3) gave a mixture of spiroacetals **2** and **34**, along with fused acetal **33**. Further purification of the mixture of spiroacetals **2** and **34** by reverse-phase HPLC [COSMOSIL 5C_{18}-AR-II column, ø 10 × 250 mm, isocratic elution with 80% MeCN/H_2O, flow rate 3.0 mL/min, UV 220 nm] gave spiroacetal **2** (0.7 mg, 36%, t_R = 16 min, colorless oil) and spiroacetal **34** (0.9 mg, 46%, t_R = 20 min, colorless oil). Further purification of fused acetal **33** by reverse-phase HPLC [COSMOSIL 5C_{18}-AR-II column, ø 10 × 250 mm, isocratic elution with 80% MeCN/H_2O, flow rate 3.0 mL/min, UV 220 nm] gave analytically pure fused acetal **33** (0.3 mg, 15%, t_R = 16 min) as a colorless oil. Data for **2**: $[\alpha]_D^{24}$ –26.1 (*c* 0.18, C_6H_6); ^{1}H NMR (600 MHz, C_6D_6) δ 7.31—7.30 (m, 3H), 7.22—7.17 (m, 5H), 7.12—7.08 (m, 2H), 5.63 (s, 1H), 5.17 (s, 1H), 5.04—5.02 (m, 2H), 4.72 (d, *J* = 1.0 Hz, 1H), 4.67 (d, *J* = 1.0 Hz, 1H), 4.61 (s, 2H), 4.36 (d, *J* = 12.4 Hz, 1H), 4.36 (s, 1H), 4.32 (d, *J* = 12.4 Hz, 1H), 4.17 (ddd, *J* = 8.6, 8.2, 5.5 Hz, 1H), 4.07 (d, *J* = 1.4 Hz, 1H), 4.03 (br dd, *J* = 6.9, 4.4 Hz, 1H), 3.72 (dd, *J* = 8.2, 8.2 Hz, 1H), 3.66 (m, 1H), 3.65 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.59 (dd, *J* = 10.3, 6.9 Hz, 1H), 3.43 (dd, *J* = 9.6, 5.5 Hz, 1H), 3.25 (dd, *J* = 9.6, 5.5 Hz, 1H), 2.82 (dd, *J* = 13.4, 5.5 Hz, 1H), 2.42—2.34 (m, 2H), 2.06 (ddd, *J* = 14.8, 5.1, 4.8 Hz 1H), 1.95 (m, 1H), 1.74 (dd, *J* = 13.4, 4.8 Hz 1H) 1.57 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.45 (dddd, *J* = 13.1, 5.1, 2.7, 2.4 Hz, 1H), 1.35 (dddd, *J* = 13.1, 12.7, 11.3, 4.8 Hz, 1H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 150.3, 146.3, 143.0, 139.2, 128.6 (×2), 128.5 (×2), 128.4, 127.9, 127.7 (×2), 127.64 (×2), 127.56 108.7, 108.6, 107.8, 99.4, 82.2, 77.2, 74.3, 73.4, 73.34, 73.32, 72.6, 71.5, 71.0, 41.3, 39.2, 31.8, 30.2, 29.4, 19.0; HRMS (ESI) calcd for $C_{34}H_{42}O_6Na$ [$(M + Na)^+$] 569.2874, found 569.2877. Data for **33**: $[\alpha]_D^{24}$ –3.9 (*c* 0.09, C_6H_6); ^{1}H NMR (600 MHz, C_6D_6) δ 7.28—7.25 (m,

2H), 7.21—7.06 (m, 8H) 5.67 (s, 1H), 4.97 (d, *J* = 1.7 Hz, 1H), 4.93 (d, *J* = 1.4 Hz, 1H), 4.86 (s, 1H), 4.77 (s, 1H), 4.69 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 4.24 (s, 2H), 3.95 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.86 (ddd, *J* = 12.4, 9.3, 4.5 Hz, 1H), 3.78 (m, 1H), 3.76 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.68 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.37 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.21 (dd, *J* = 9.2, 3.8 Hz, 1H), 3.16 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.80 (m, 1H), 2.71 (dd, *J* = 12.4, 4.5 Hz, 1H), 2.51 (ddd, *J* = 15.5, 10.3, 5.2 Hz, 1H), 2.34—2.27 (m, 2H), 2.14 (d, *J* = 3.1 Hz, 1H) 1.85 (dd, *J* = 13.0, 5.1 Hz, 1H), 1.69 (dddd, *J* = 13.4, 10.0, 8.3, 5.2 Hz, 1H), 1.64 (dddd, *J* = 13.4, 10.3, 6.2, 4.1 Hz, 1H), 1.37 (dd, *J* = 13.0, 12.0 Hz, 1H), 0.898 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 149.5, 149.0, 142.4, 138.91, 138.86, 128.6 (×2), 128.5 (×2), 128.4, 127.9, 127.7 (×2), 127.6 (×2), 111.8, 110.6, 108.4, 101.0, 83.6, 80.2, 78.3, 75.0, 73.5, 73.2, 70.7, 70.0, 67.8, 43.4, 39.7, 32.7, 28.0, 26.7, 17.2; HRMS (ESI) calcd for $C_{34}H_{42}O_6Na$ [$(M + Na)^+$] 569.2874, found 569.2879.

Data for **34**: $[\alpha]_D^{24}$ –13.6 (*c* 0.31, C_6H_6); ^{1}H NMR (600 MHz, C_6D_6) δ 7.32—7.31 (m, 2H), 7.27—7.26 (m, 2H), 7.20—7.15 (m, 4H), 7.11—7.05 (m, 2H), 5.18 (s, 1H), 4.95 (s, 1H), 4.87 (s, 1H), 4.79 (s, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.45 (dddd, *J* = 11.3, 6.5, 3.8, 3.8 Hz, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.37 (d, *J* = 12.4 Hz, 1H), 4.34 (d, *J* = 12.4 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 4.30 (d, *J* = 12.4 Hz, 1H), 4.09 (dd, *J* = 6.2, 4.4 Hz, 1H), 4.06 (ddd, *J* = 8.6, 6.8, 4.5 Hz, 1H), 4.00 (dd, *J* = 7.9, 6.8 Hz, 1H), 3.82 (br s, 1H), 3.71 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.60 (dd, *J* = 10.6, 6.2 Hz, 1H), 3.37 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.25 (dd, *J* = 10.0, 3.8 Hz, 1H), 2.99 (m, 1H), 2.75 (dd, *J* = 13.4, 4.5 Hz, 1H), 2.47 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.40 (m, 1H), 2.03 (ddd, *J* = 13.4, 4.8, 4.8 Hz, 1H), 1.98 (dd, *J* = 13.1, 4.8 Hz, 1H), 1.68 (dd, *J* = 13.1, 13.1 Hz, 1H), 1.42 (dddd, *J* = 13.0, 5.5, 4.8, 3.8 Hz, 1H), 1.35 (dddd, *J* = 13.0, 12.4, 11.3, 4.8 Hz, 1H), 0.95 (d, *J* = 6.5 Hz, 3H); ^{13}C

NMR (150 MHz, C_6D_6) δ 149.2, 146.2, 143.7, 139.5, 138.7, 128.6 (× 2), 128.5 (× 2), 127.9 (× 2), 127.7 (× 2), 127.6, 127.5, 109.8, 108.9, 108.6, 99.5, 80.5, 80.1, 77.2, 73.6, 73.4, 73.4, 71.8, 71.3, 70.0, 41.9, 40.2, 29.6, 29.3, 28.2, 18.2; HRMS (ESI) calcd for $C_{34}H_{42}O_6Na$ [$(M + Na)^+$] 569.2874, found 569.2879.

Scheme S1. Stereochemical Assignment of Allylic Alcohol **29**



Alcohol **29** was transformed into acetonide **A** via desilylation and acetalization. ^{1}H NMR analysis on **A** based on $^{3}J_{H,H}$ values established the stereochemistry of the C7 stereogenic center as shown.

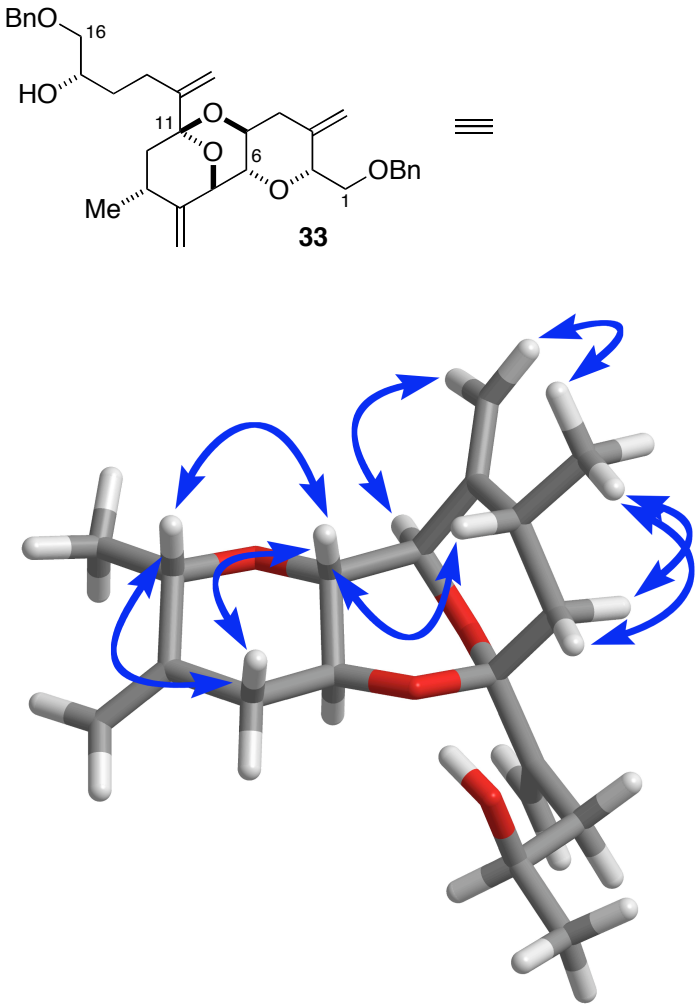
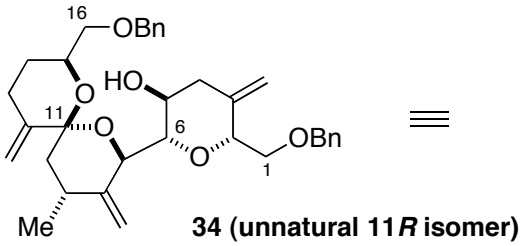


Figure S1. Stereochemical assignment of fused acetal **33**. The double-ended blue arrows denote important NOEs. The benzyloxy groups are omitted for clarity in the 3D model. The structure of the 3D model was generated by MMFF94s conformational searches followed by geometry optimization (HF6-31G*//PM3 level of theory).



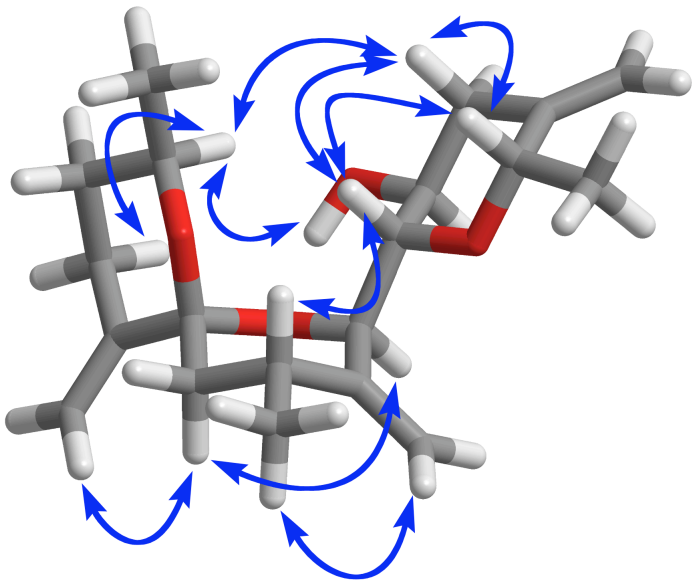
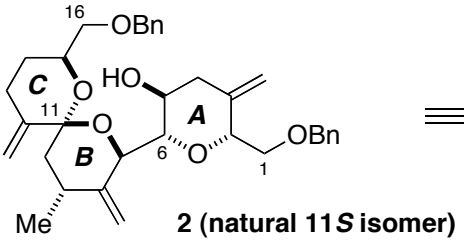


Figure S2. Stereochemical assignment of unnatural spiroacetal **34**. The double-ended blue arrows denote important NOEs. The benzyloxy groups are omitted for clarity in the 3D model. The structure of the 3D model was generated by MMFF94s conformational searches followed by geometry optimization (HF6-31G*//PM3 level of theory).



2 (natural 11*S* isomer)

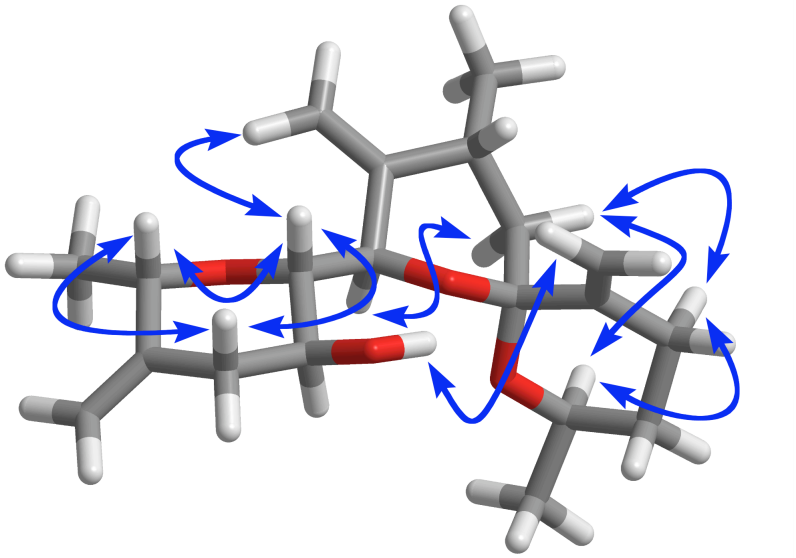


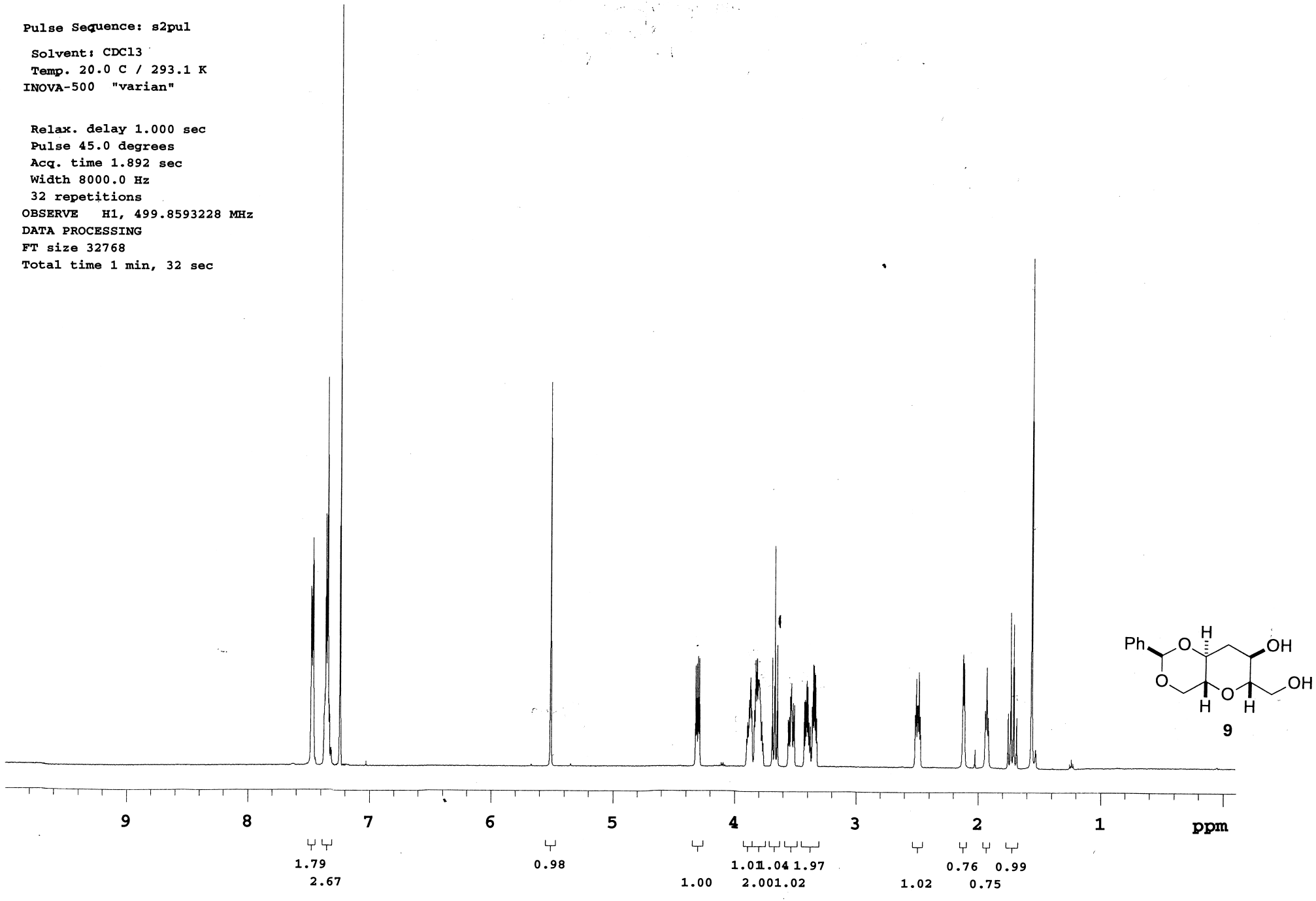
Figure S3. Stereochemical assignment of natural spiroacetal **2**. The double-ended blue arrows denote important NOEs. The benzyloxy groups are omitted for clarity in the 3D model. The structure of the 3D model was generated by MMFF94s conformational searches followed by geometry optimization (HF6-31G*//PM3 level of theory).

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
INOVA-500 "varian"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.8593228 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



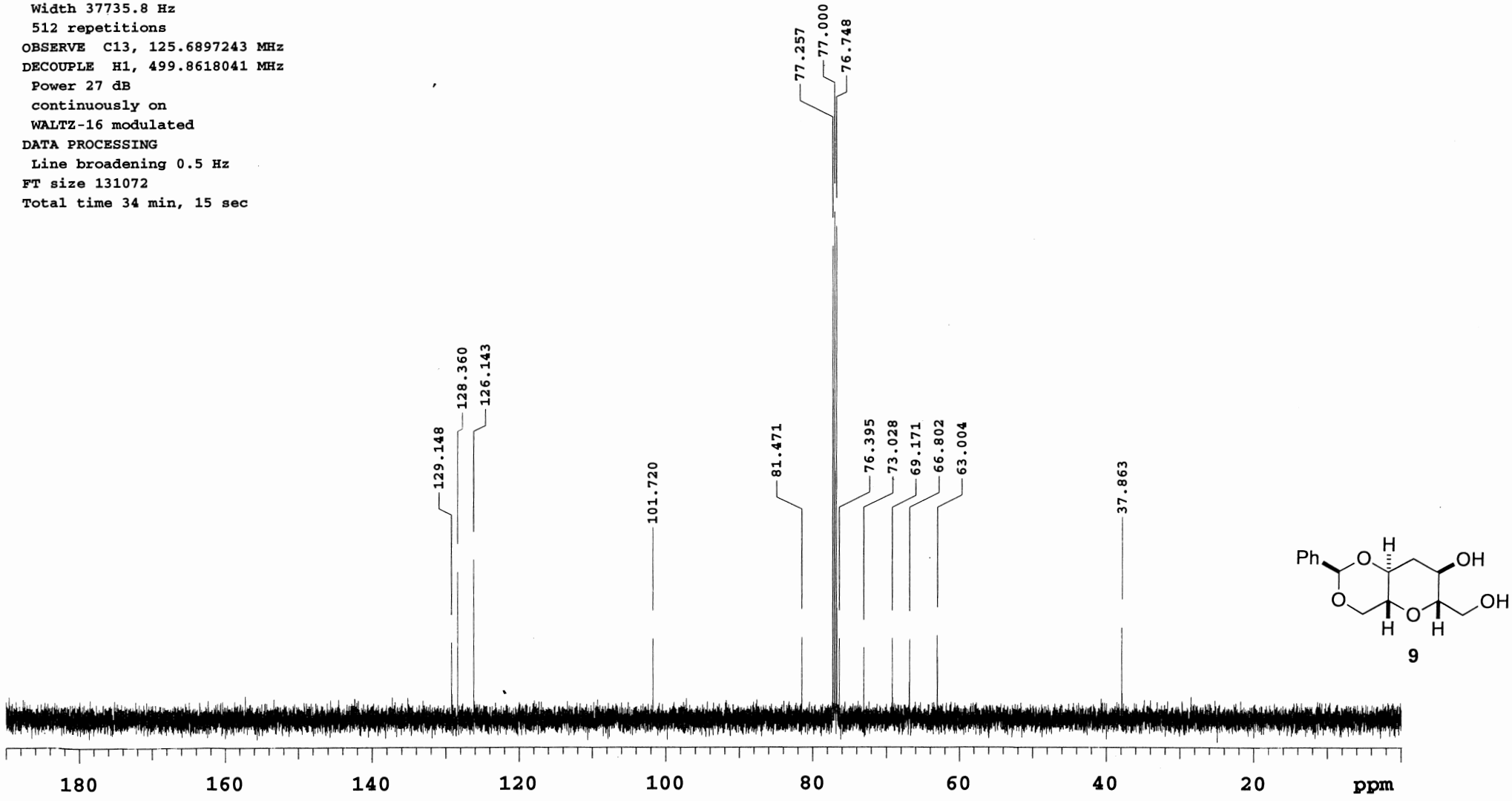
9

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "varian"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.298 sec
Width 37735.8 Hz
512 repetitions
OBSERVE C13, 125.6897243 MHz
DECOUPLE H1, 499.8618041 MHz
Power 27 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 34 min, 15 sec



9

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: ~~Benzene~~ CDCl3

Temp. 20.0 C / 293.1 K

INOVA-500 "varian"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

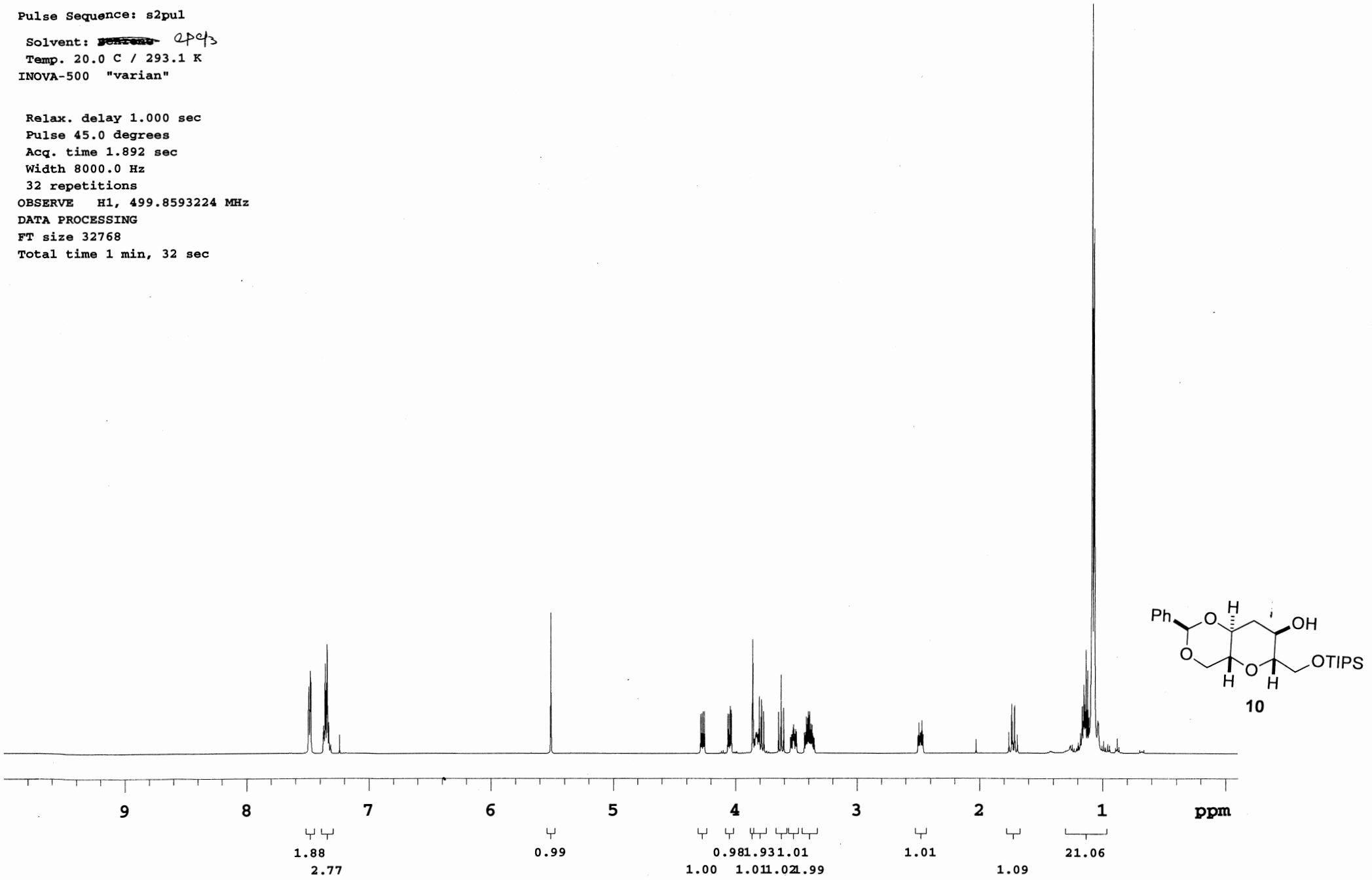
32 repetitions

OBSERVE H1, 499.8593224 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 32 sec



10

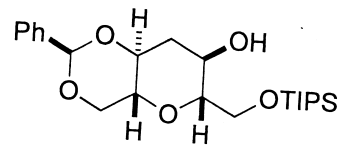
1/π – 9a

STANDARD CARBON PARAMETERS

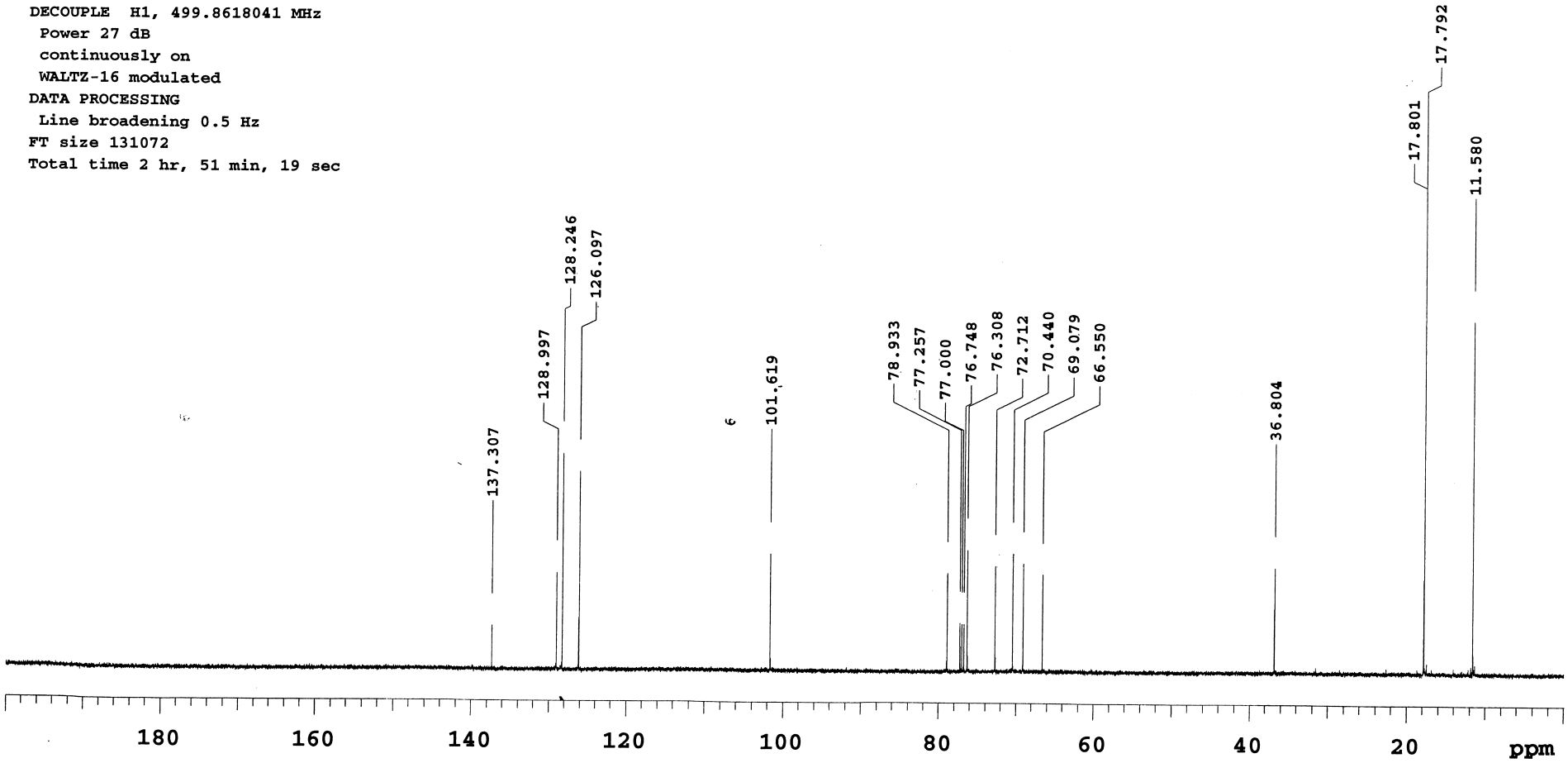
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "varian"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.298 sec
Width 37735.8 Hz
96 repetitions
OBSERVE C13, 125.6897352 MHz
DECOUPLE H1, 499.8618041 MHz
Power 27 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 51 min, 19 sec



10

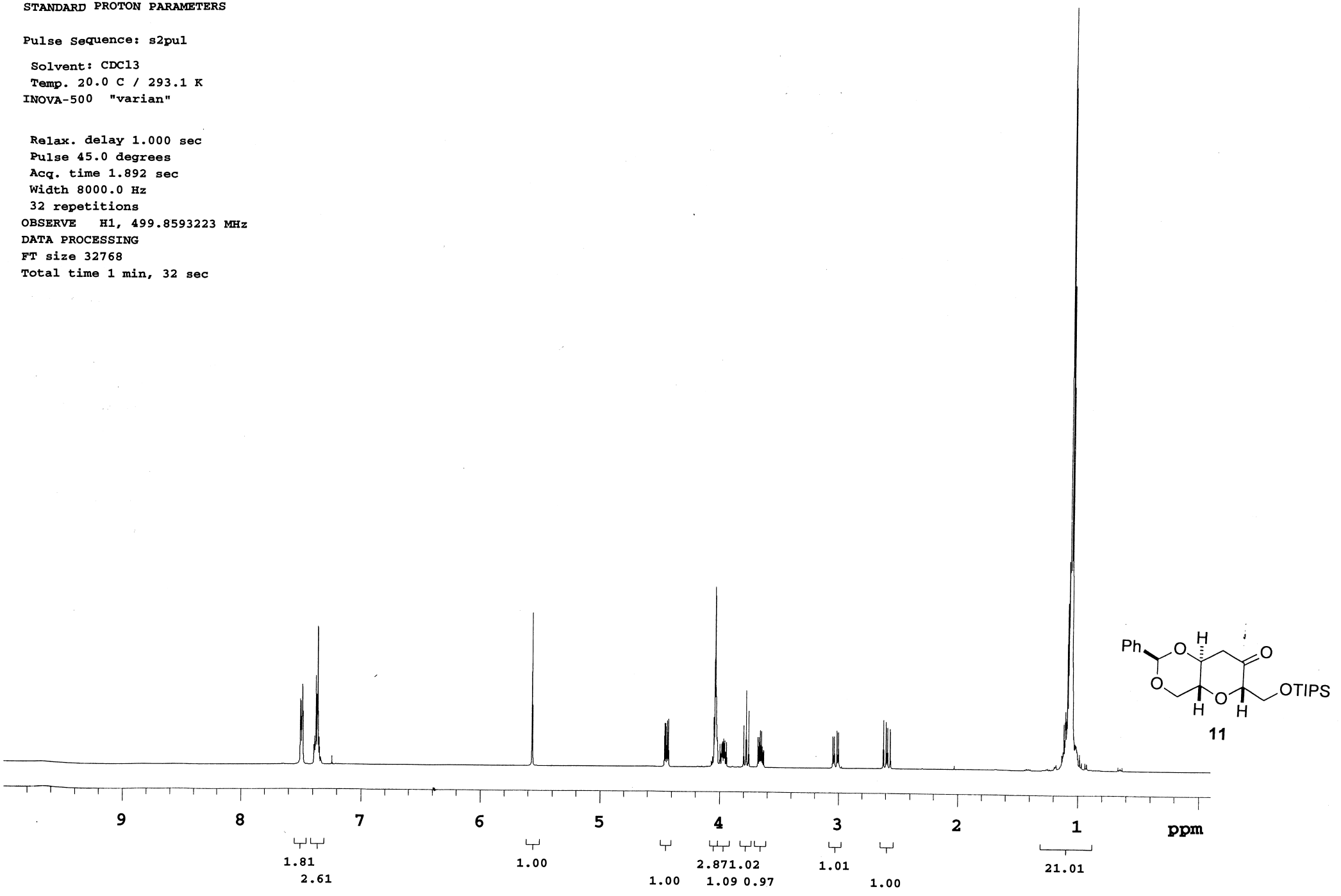


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
INOVA-500 "varian"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.8593223 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



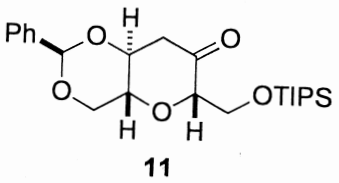
II-91

STANDARD CARBON PARAMETERS

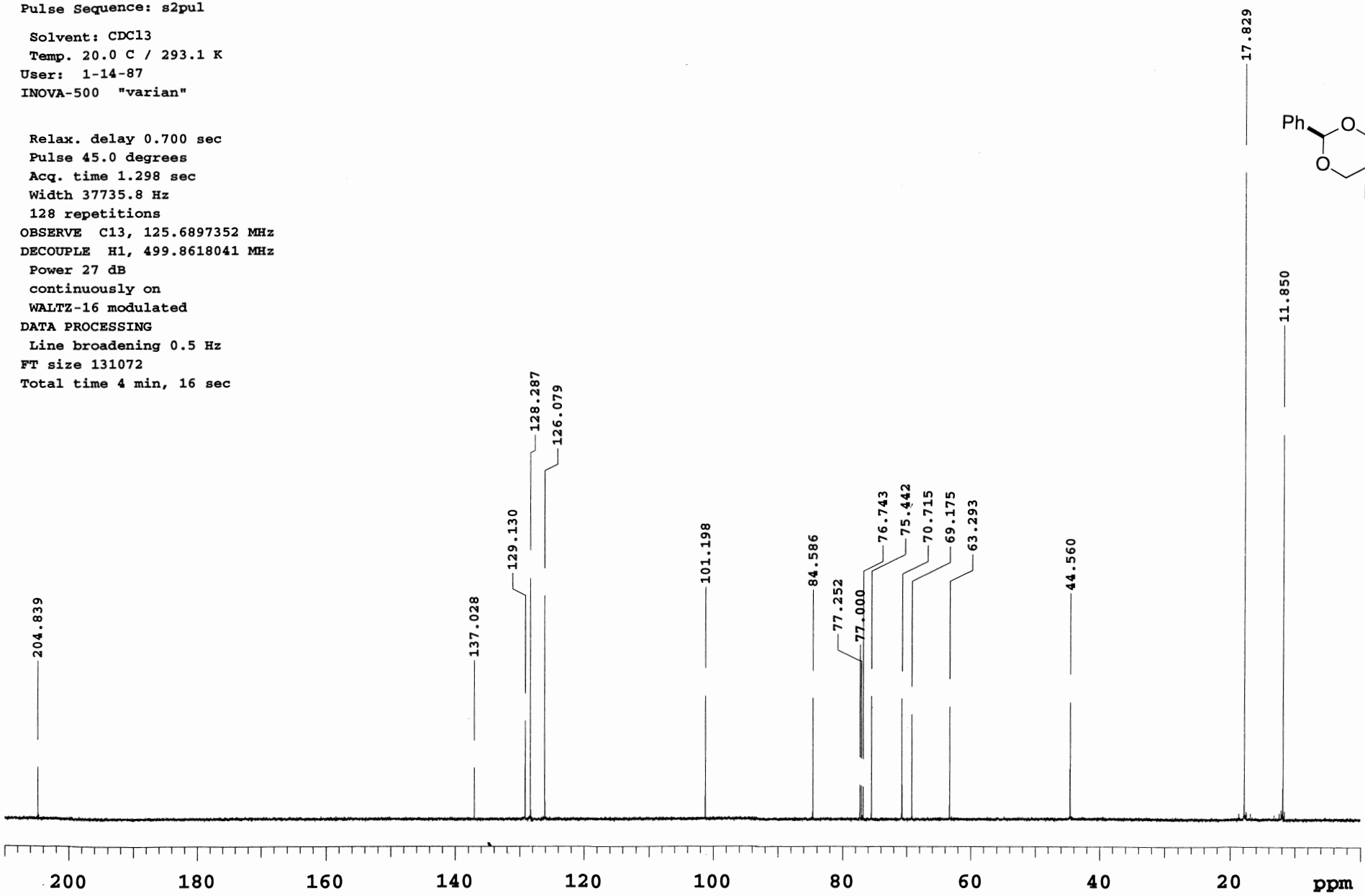
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "varian"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.298 sec
Width 37735.8 Hz
128 repetitions
OBSERVE C13, 125.6897352 MHz
DECOUPLE H1, 499.8618041 MHz
Power 27 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 4 min, 16 sec



11

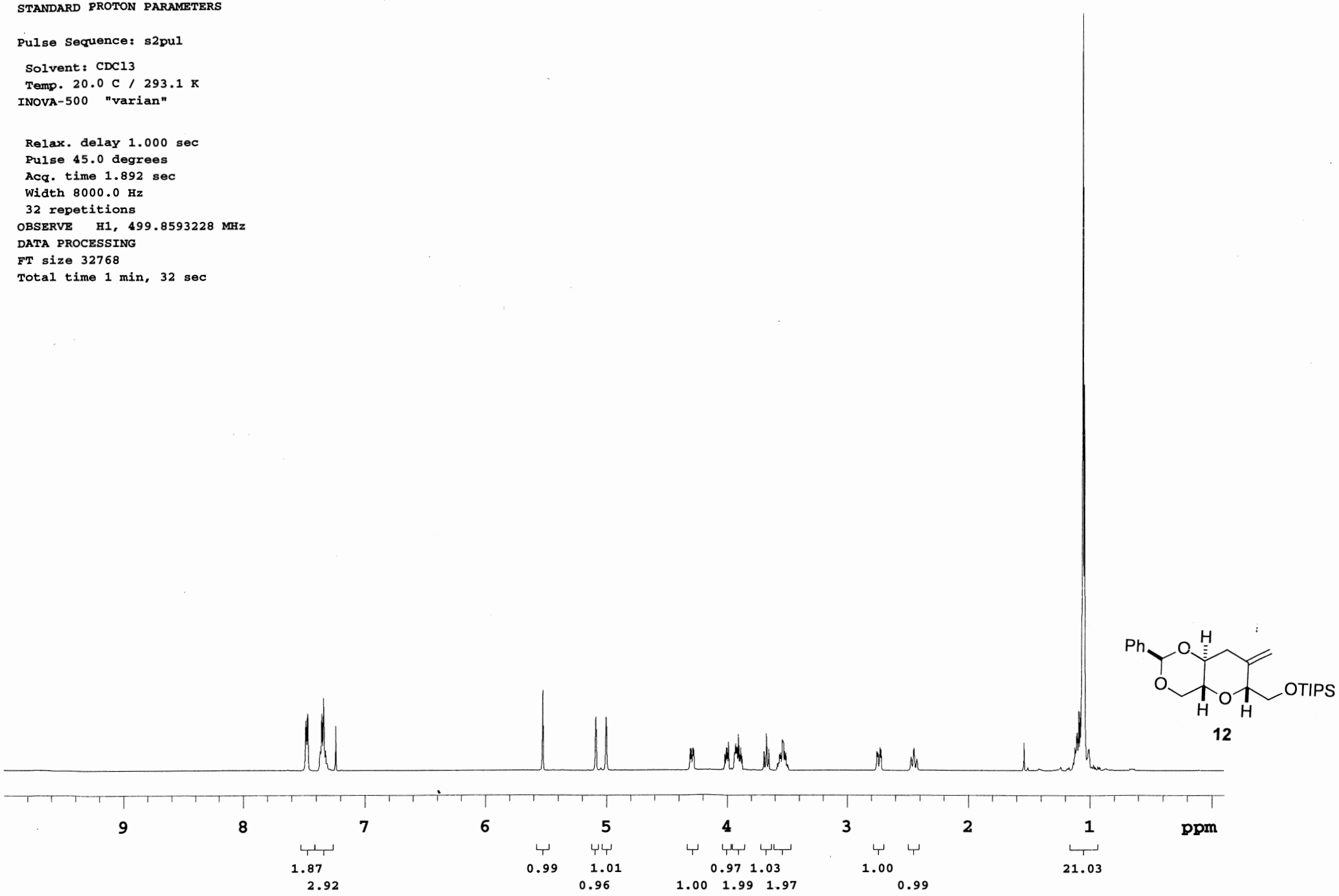


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
INOVA-500 "varian"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.8593228 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



12

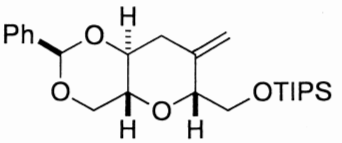
VII-92

STANDARD CARBON PARAMETERS

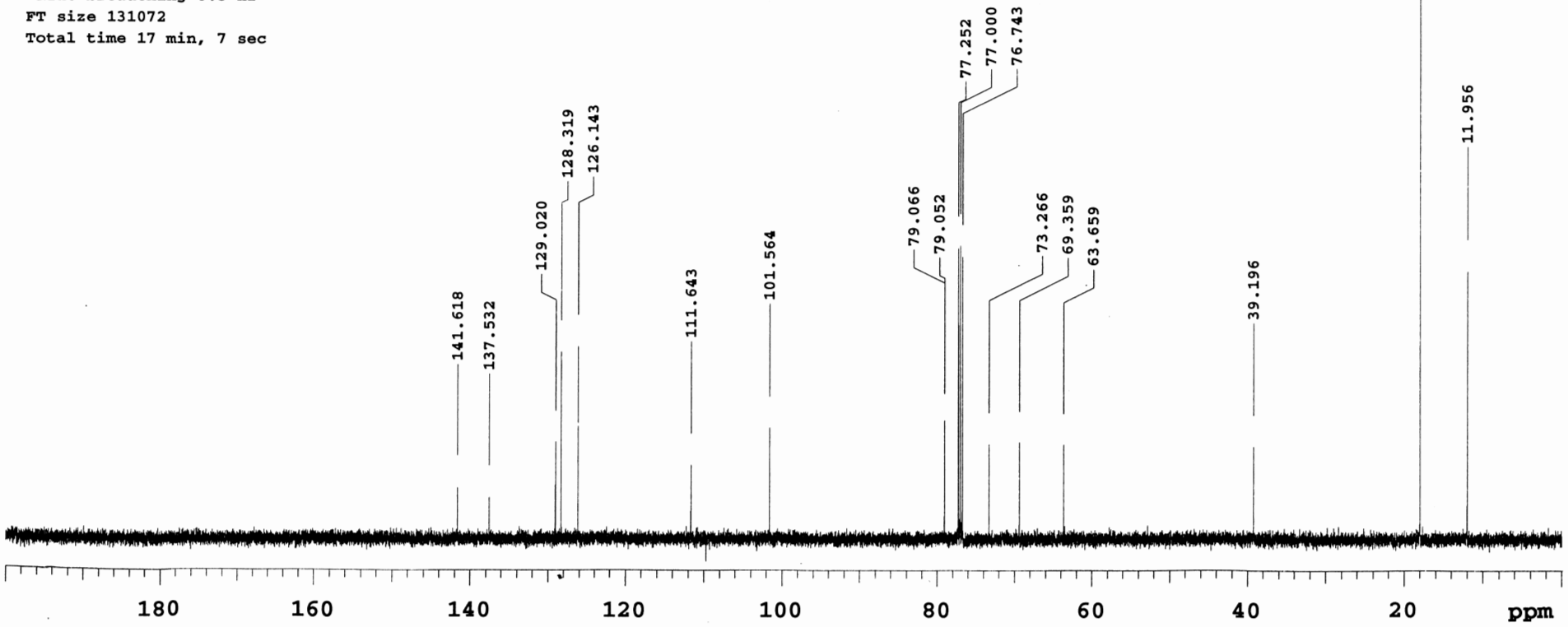
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "varian"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.298 sec
Width 37735.8 Hz
288 repetitions
OBSERVE C13, 125.6897260 MHz
DECOUPLE H1, 499.8618041 MHz
Power 27 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 17 min, 7 sec



12

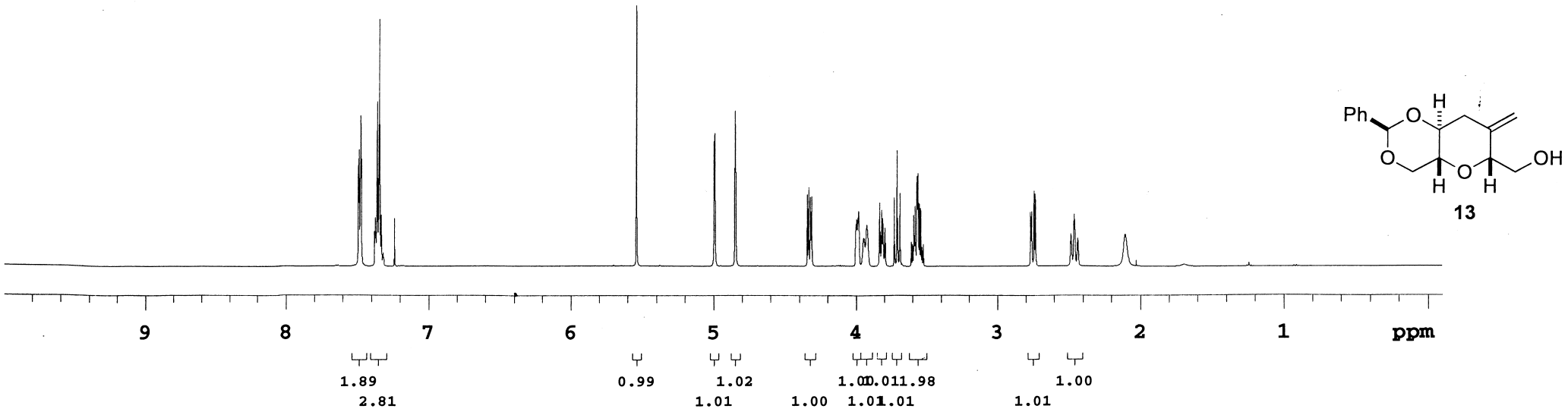


STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
INOVA-500 "varian"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.8593228 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



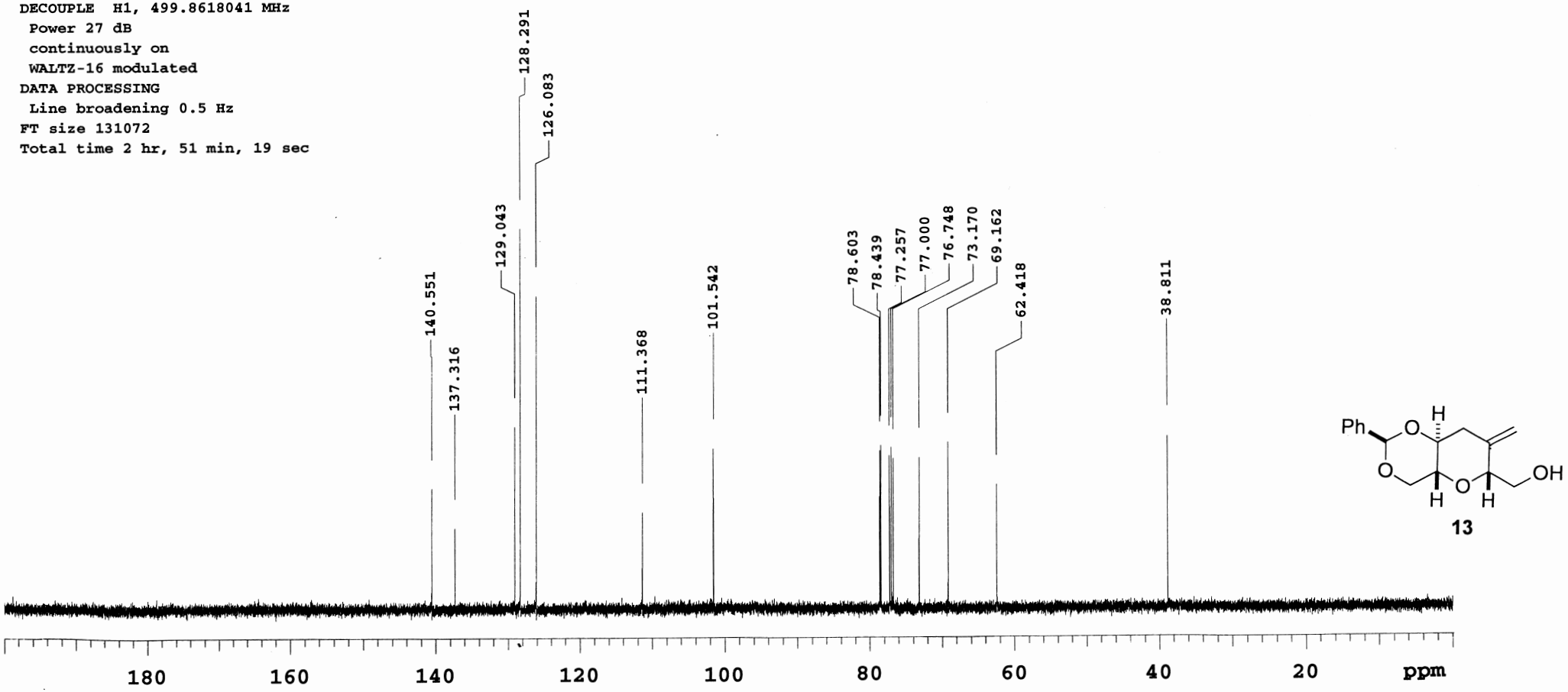
13

STANDARD CARBON PARAMETERS

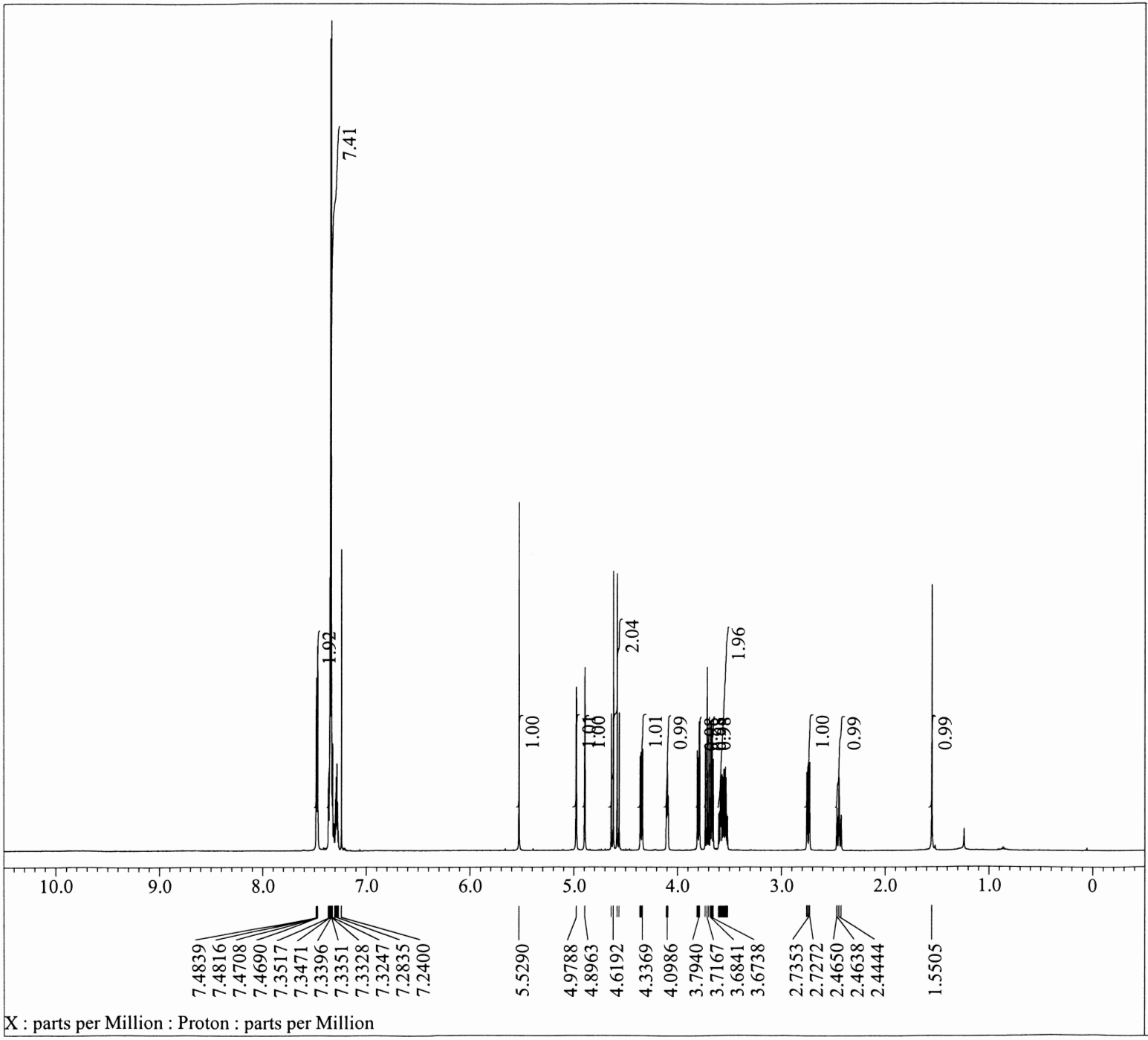
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "varian"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.298 sec
Width 37735.8 Hz
96 repetitions
OBSERVE C13, 125.6897329 MHz
DECOUPLE H1, 499.8618041 MHz
Power 27 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 51 min, 19 sec



13



X : parts per Million : Proton : parts per Million

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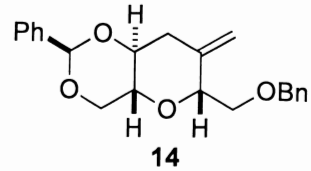
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-I-84
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 19:52:55
Revision_Time     =  7-OCT-2010 19:57:15
Current_Time      =  7-OCT-2010 19:57:36

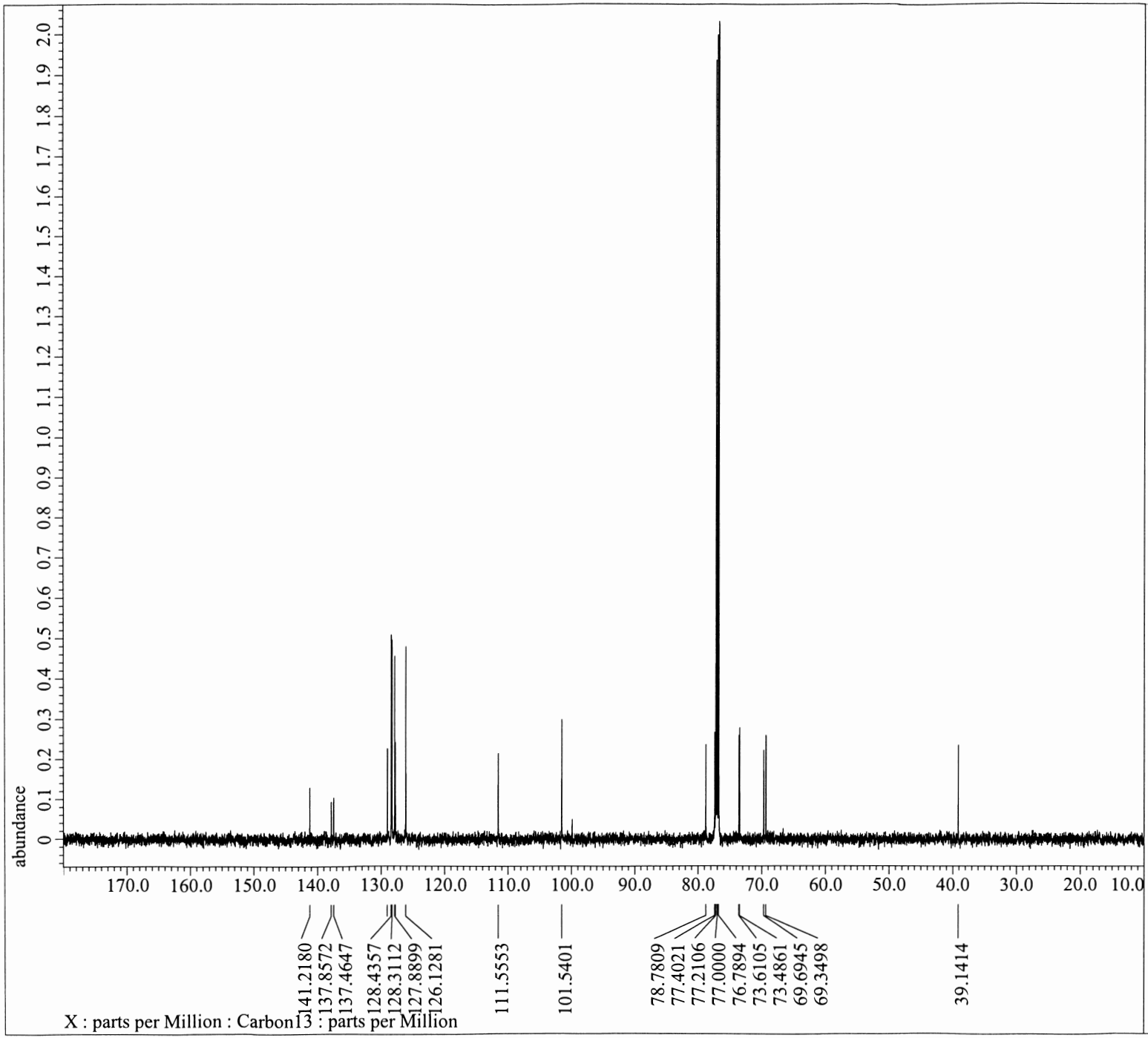
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 44
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
```



14

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Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-I-84
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 19:55:50
Revision_Time     =  7-OCT-2010 20:03:54
Current_Time      =  7-OCT-2010 20:04:34

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 121
Total_Scans       = 121

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23[dC]
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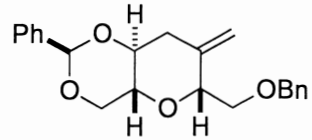
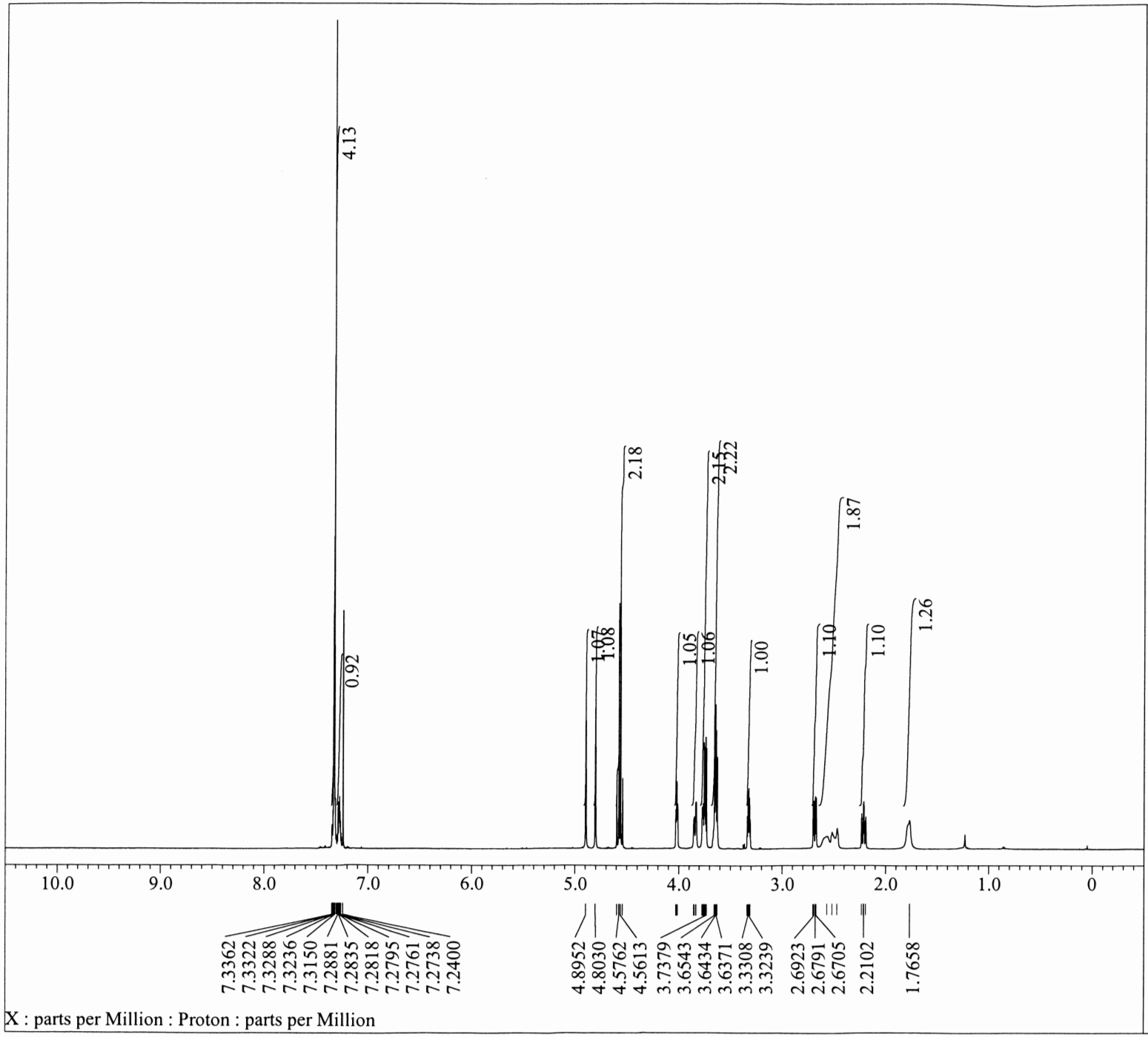


14

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Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-I-86
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 20:08:56
Revision_Time     =  7-OCT-2010 20:13:30
Current_Time      =  7-OCT-2010 20:13:54

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 44
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
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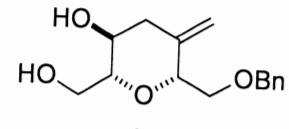

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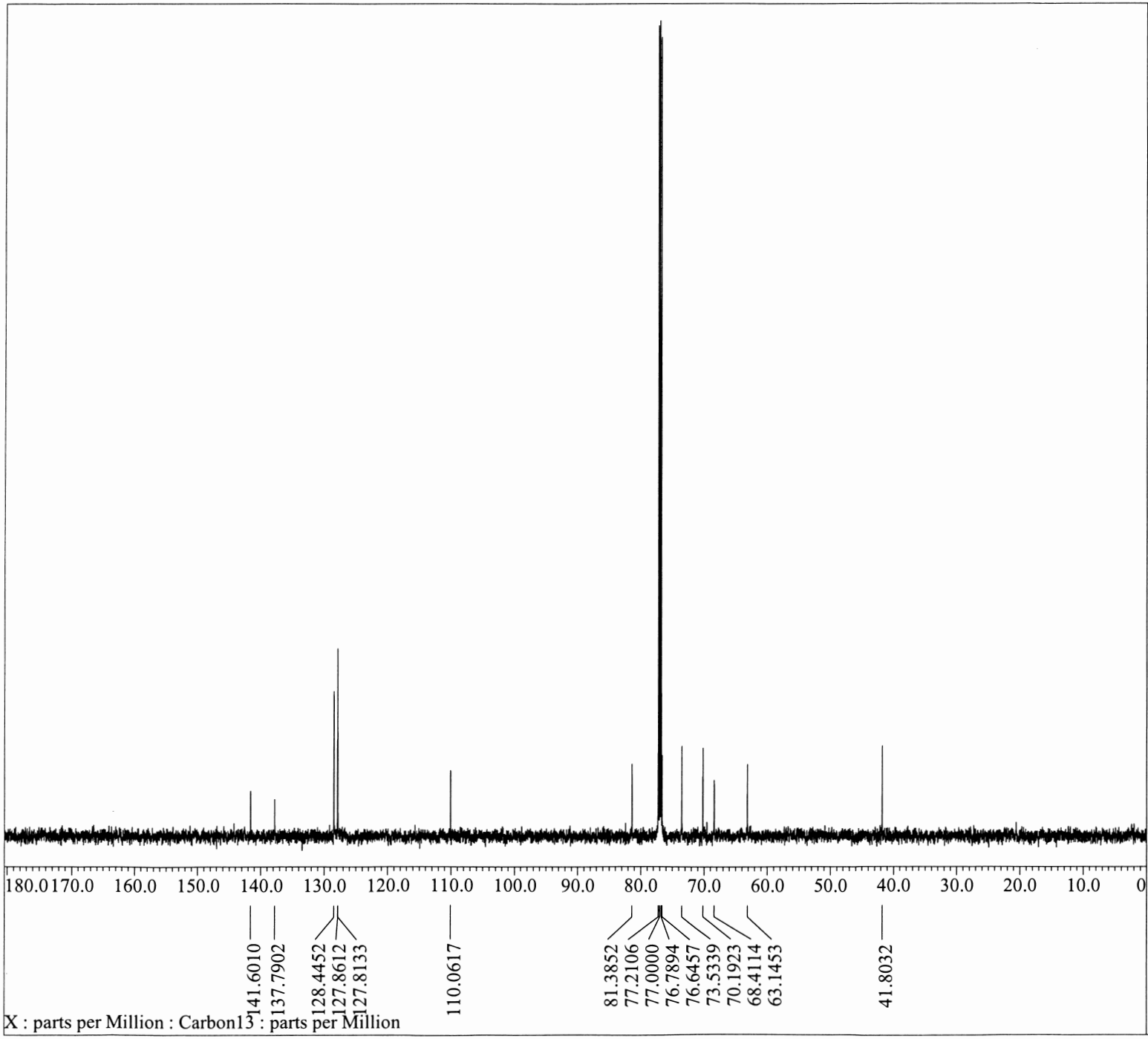


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Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-I-86
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 20:11:50
Revision_Time     =  7-OCT-2010 20:16:00
Current_Time      =  7-OCT-2010 20:16:48

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 77
Total_Scans       = 77

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 22.9[dC]
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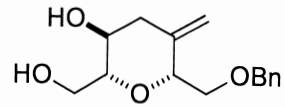
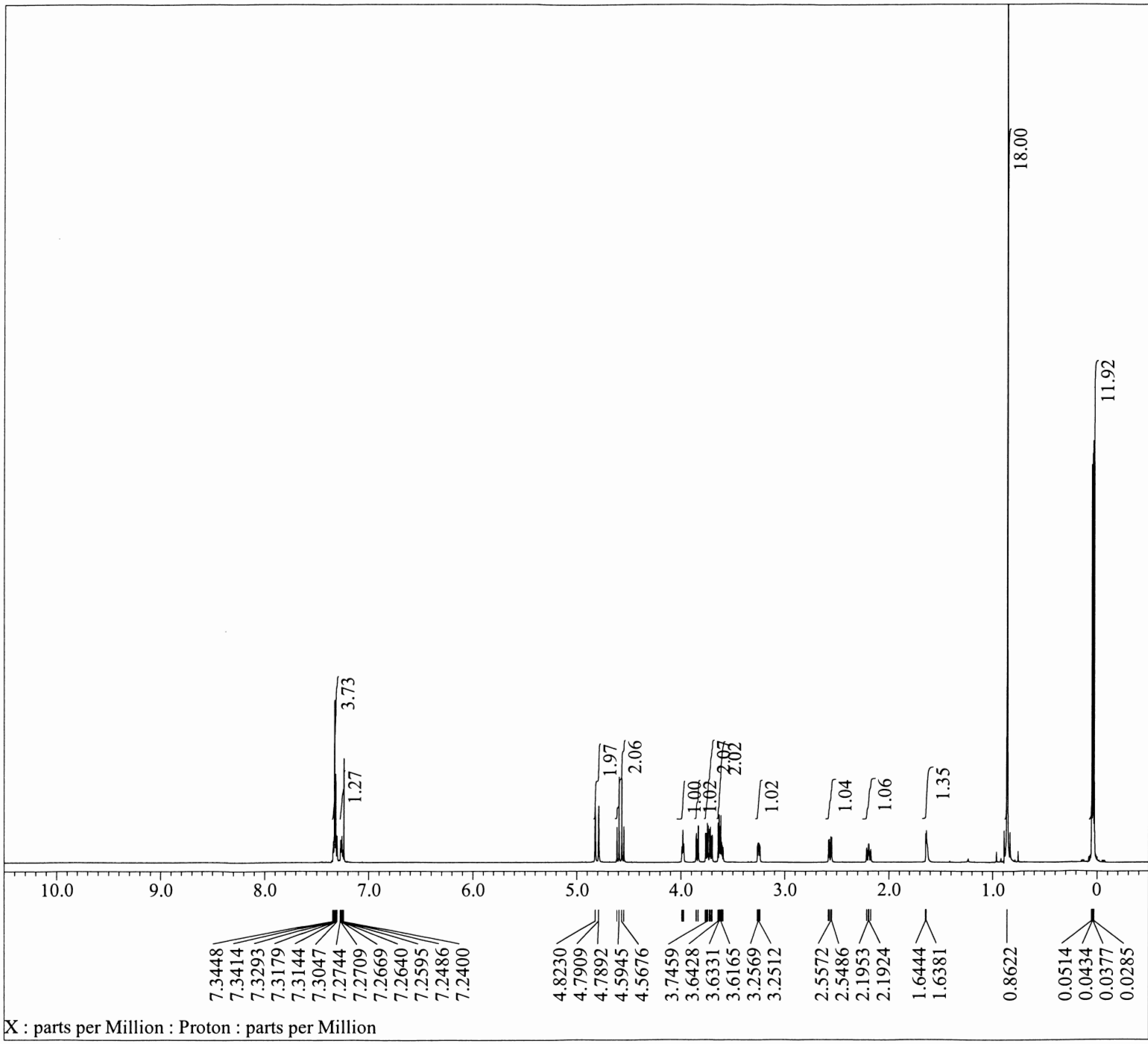


15



X : parts per Million : Proton : parts per Million

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Experiment	= proton.jxp
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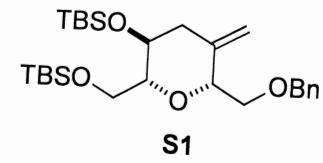
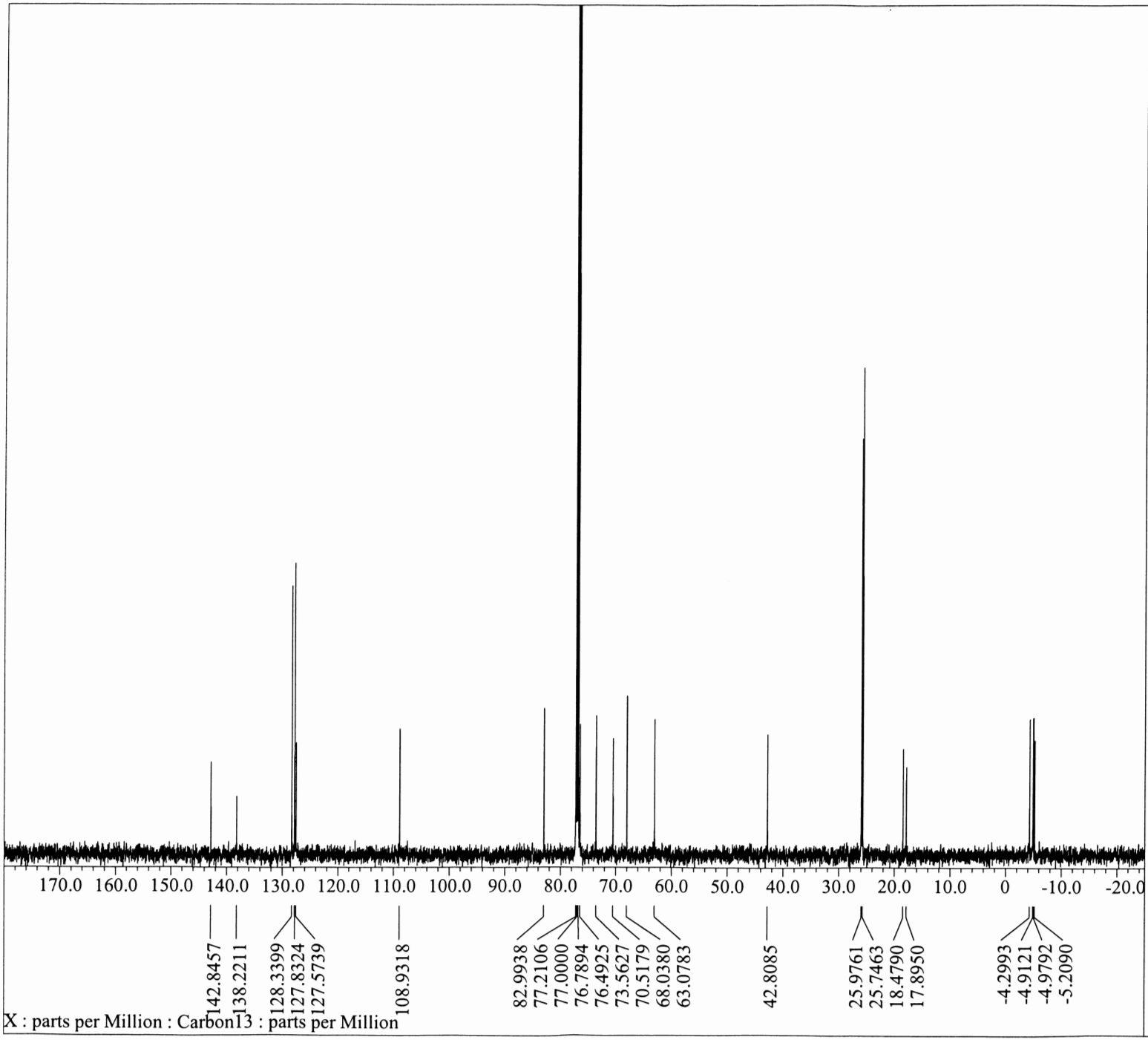
Solvent	= CHLOROFORM-D
Creation_Time	= 27-SEP-2010 14:54:54
Revision_Time	= 27-SEP-2010 15:03:00
Current_Time	= 27-SEP-2010 15:03:57
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 2.9097984[s]
X_Domain	= 1H
X_Freq	= 600.1723046[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.34366642[Hz]
X_Sweep	= 11.26126126[kHz]
X_Sweep_Clipped	= 9.00900901[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 600.1723046[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Mod_Return	= 1
Probe_Recovery	= 5[us]
Scans	= 8
Total_Scans	= 8
X_90_Width	= 12.4[us]
X_Acq_Time	= 2.9097984[s]
X_Angle	= 45[deg]
X_Atn	= 3[dB]
X_Pulse	= 6.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Recvr_Gain	= 40
Relaxation_Delay	= 1[s]
Repetition_Time	= 3.9097984[s]
Temp_Get	= 22.6[dC]



S1

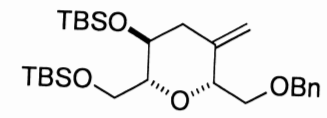



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-I-100
Solvent           = CHLOROFORM-D
Creation_Time     = 27-SEP-2010 21:09:04
Revision_Time     = 27-SEP-2010 21:19:21
Current_Time      = 27-SEP-2010 21:20:18

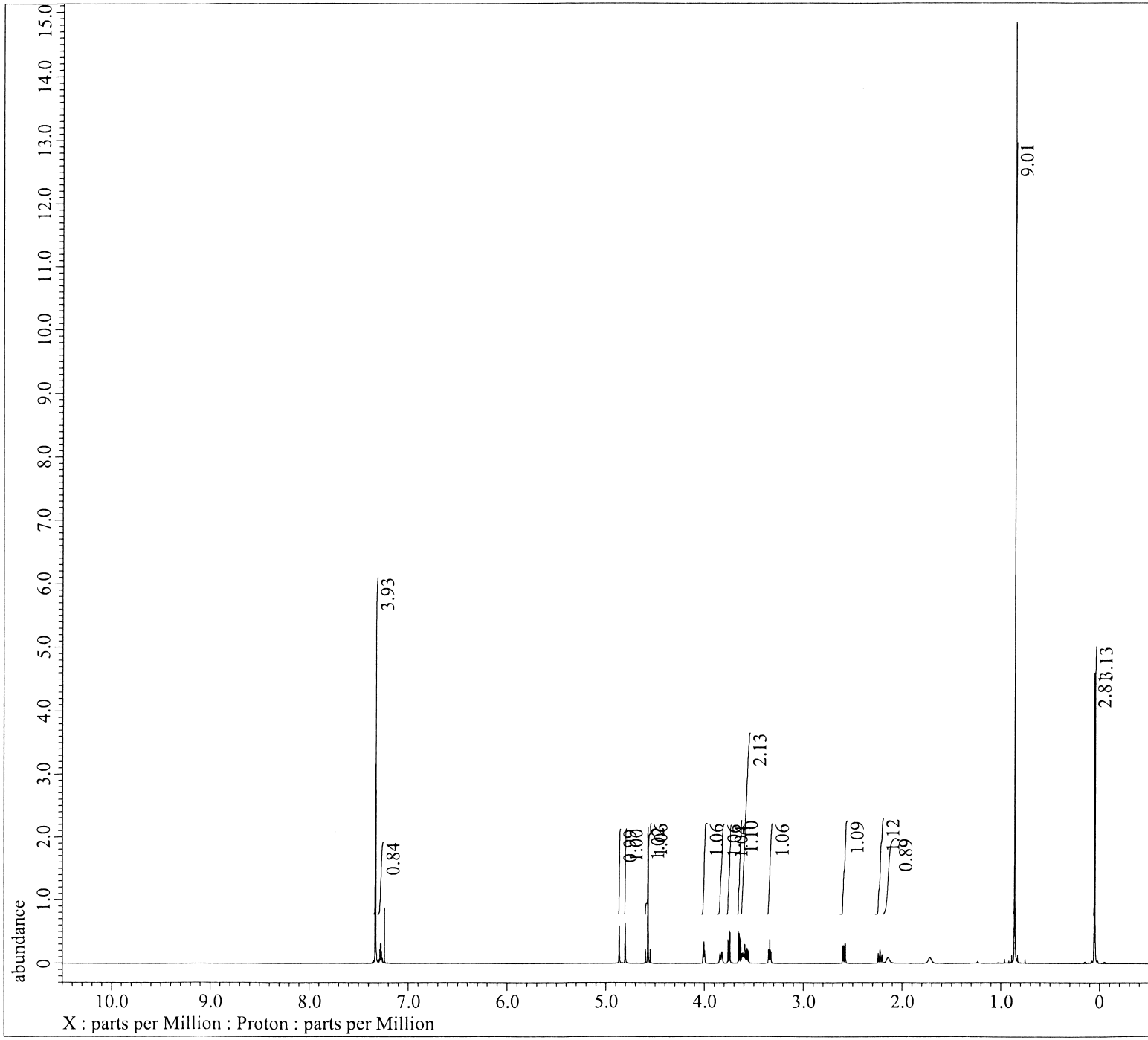
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 181
Total_Scans       = 181

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23.3[dC]
```



S1

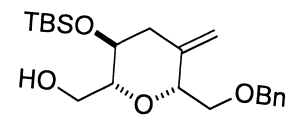



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-I-104
Solvent           = CHLOROFORM-D
Creation_Time     = 27-SEP-2010 15:04:05
Revision_Time     = 24-NOV-2010 20:51:26
Current_Time      = 24-NOV-2010 20:51:49

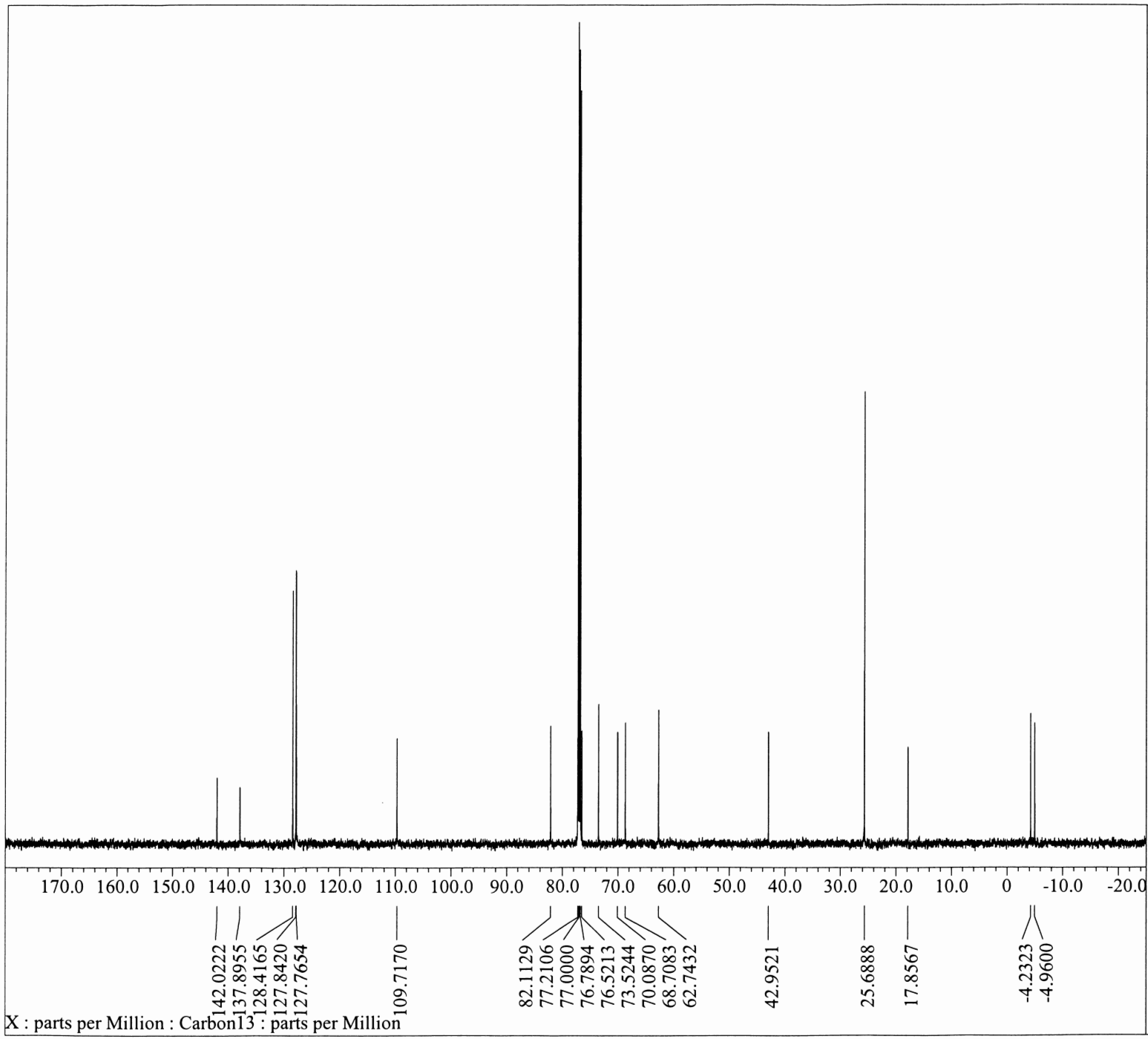
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

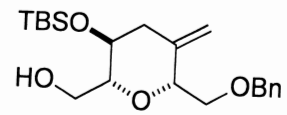
Relaxation_Delay  = 1[s]
Recvr_Gain        = 38
Temp_Get          = 22.2[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



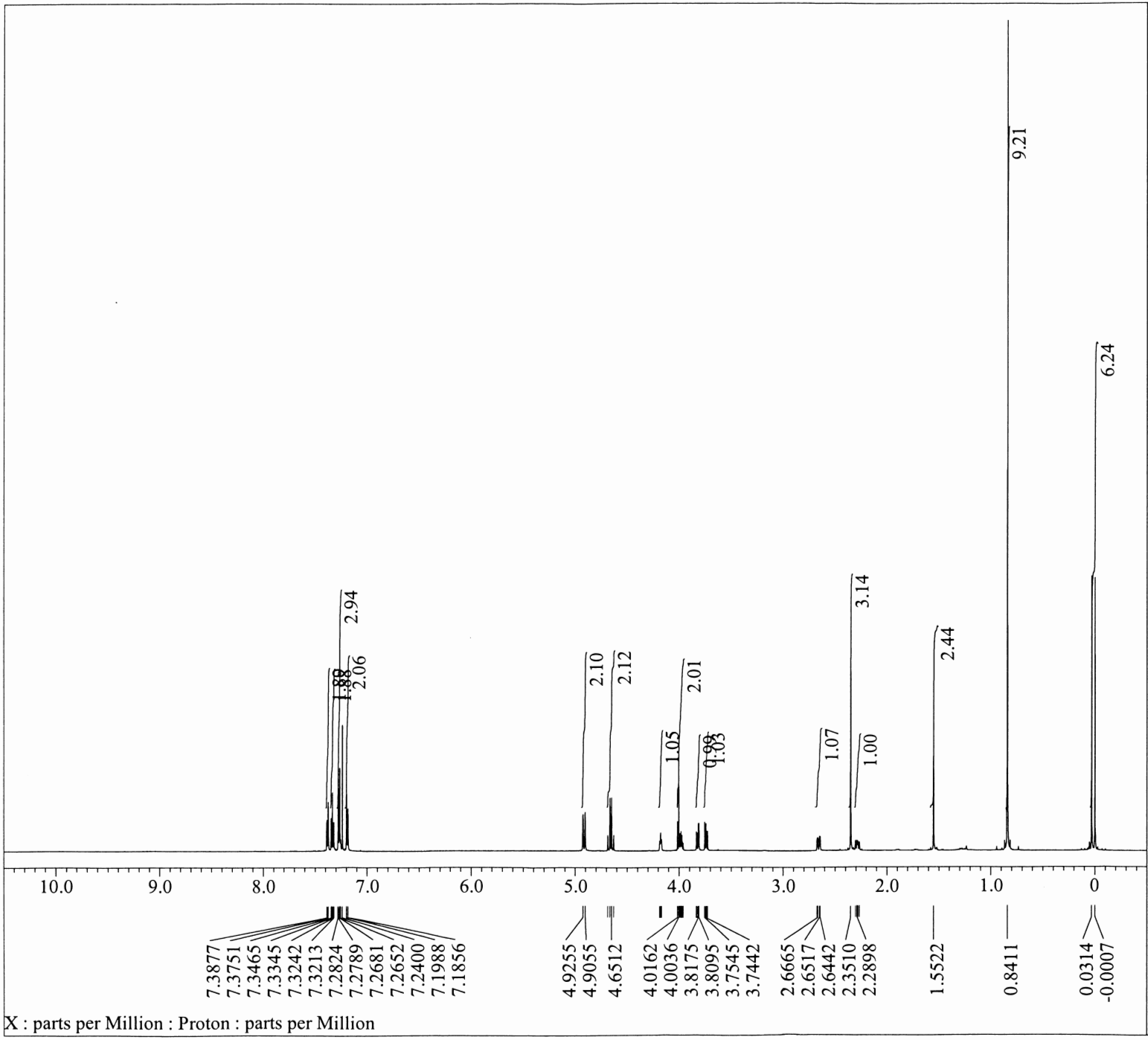
16



Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= MN-I-104
Solvent	= CHLOROFORM-D
Creation_Time	= 27-SEP-2010 21:30:47
Revision_Time	= 27-SEP-2010 21:42:20
Current_Time	= 27-SEP-2010 21:43:12
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 0.69206016[s]
X_Domain	= 13C
X_Freq	= 150.91343039[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.44496109[Hz]
X_Sweep	= 47.34848485[kHz]
X_Sweep_Clipped	= 37.87878788[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Mod_Return	= 1
Probe_Recovery	= 20[us]
Scans	= 240
Total_Scans	= 240
X_90_Width	= 8.4[us]
X_Acq_Time	= 0.69206016[s]
X_Angle	= 30[deg]
X_Atn	= 6.4[dB]
X_Pulse	= 2.8[us]
Irr_Atn_Dec	= 18[dB]
Irr_Atn_Noe	= 18[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 76[us]
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Recvr_Gain	= 56
Relaxation_Delay	= 2[s]
Repetition_Time	= 2.69206016[s]
Temp_Get	= 23.1[dC]



16

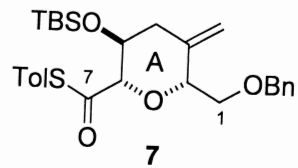



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-104
Solvent           = CHLOROFORM-D
Creation_Time     =  4-OCT-2010 21:57:16
Revision_Time     =  4-OCT-2010 22:02:48
Current_Time      =  4-OCT-2010 22:03:06

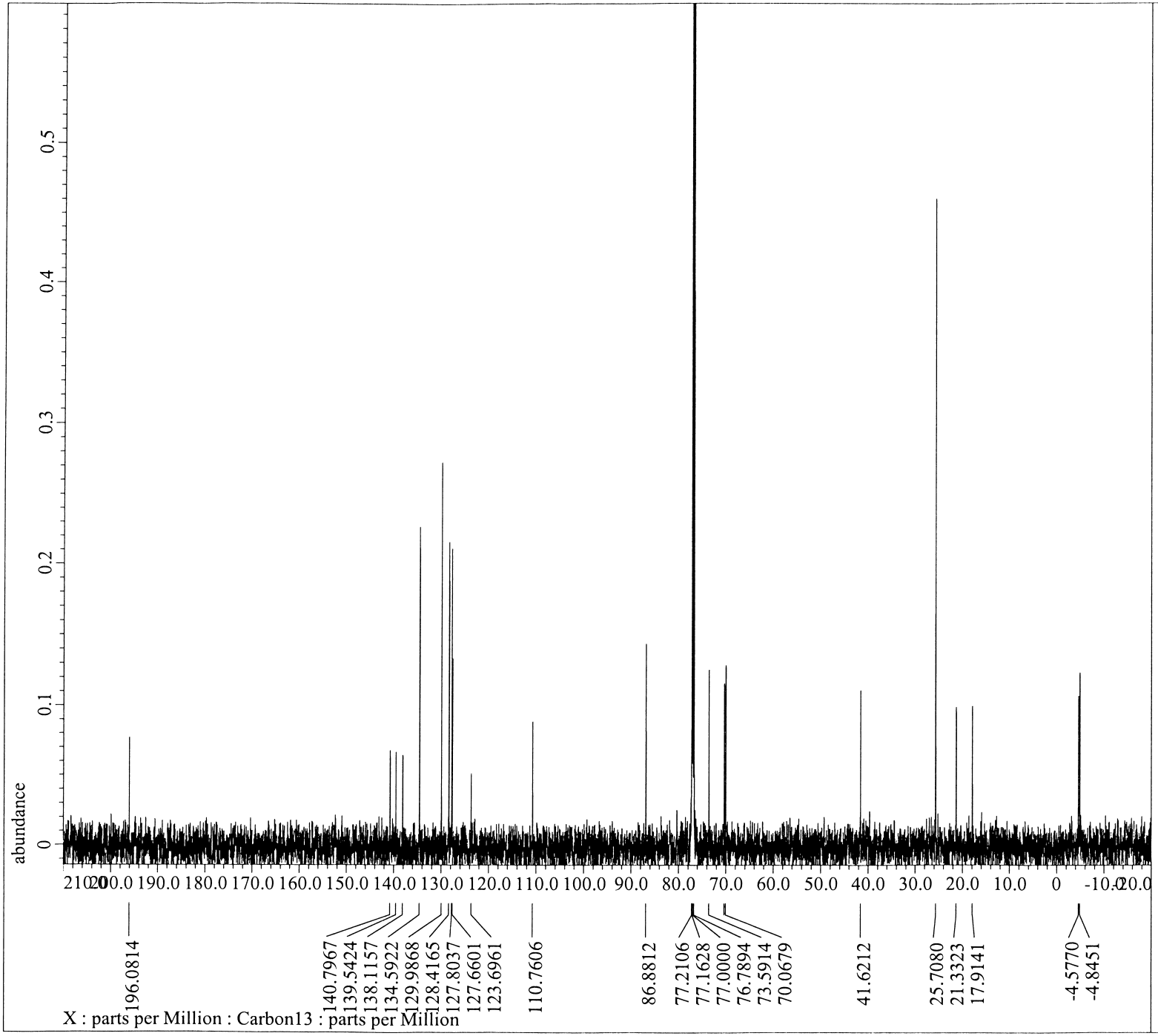
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 44
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
```



7

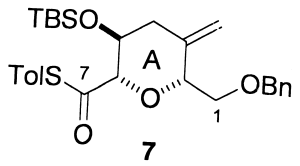



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-104
Solvent           = CHLOROFORM-D
Creation_Time     =  4-OCT-2010 22:00:13
Revision_Time     = 26-NOV-2010 17:23:42
Current_Time      = 26-NOV-2010 17:24:21

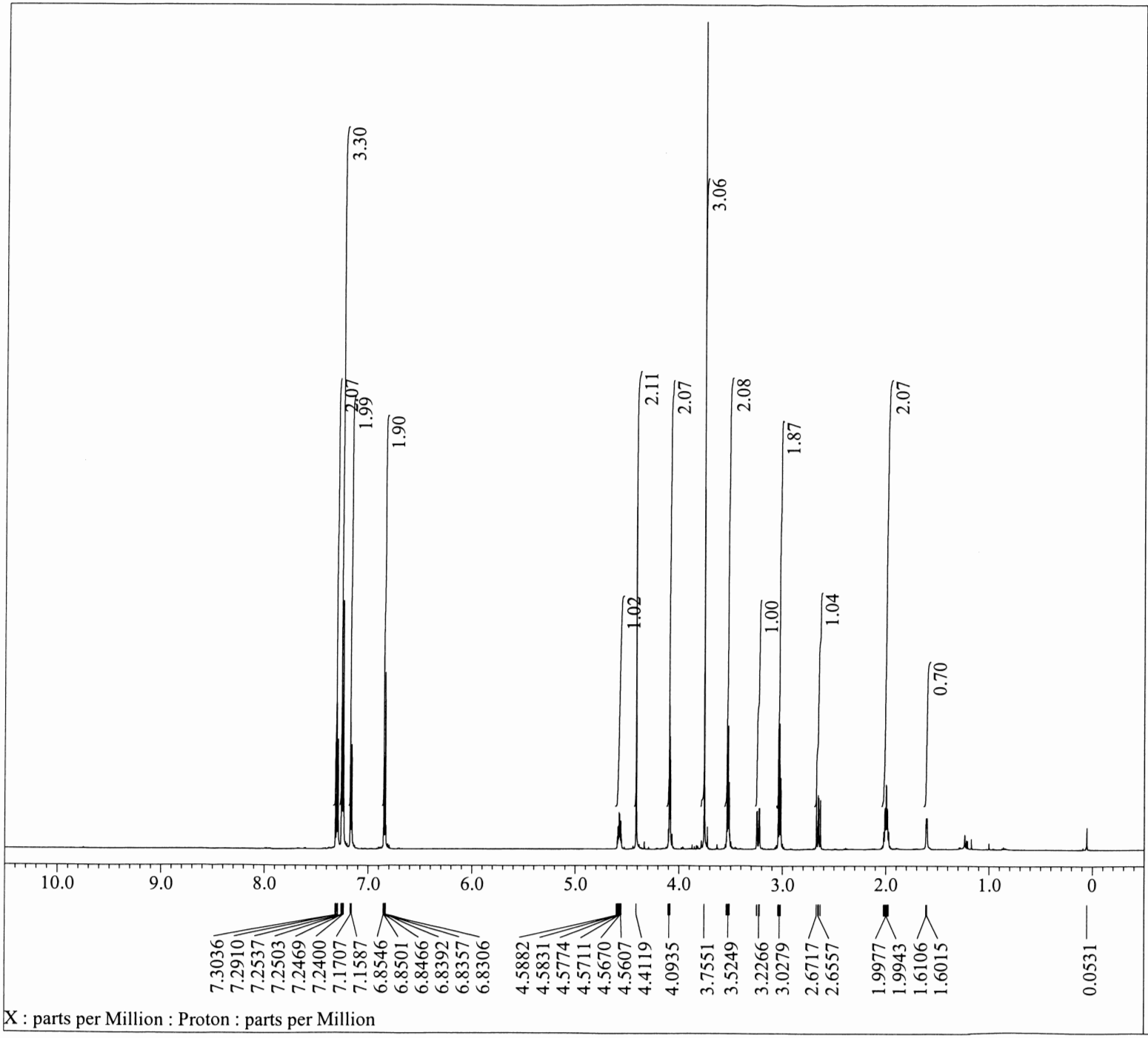
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 126
Total_Scans       = 126

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 22.9[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



7

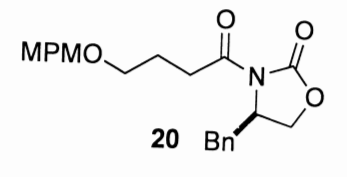


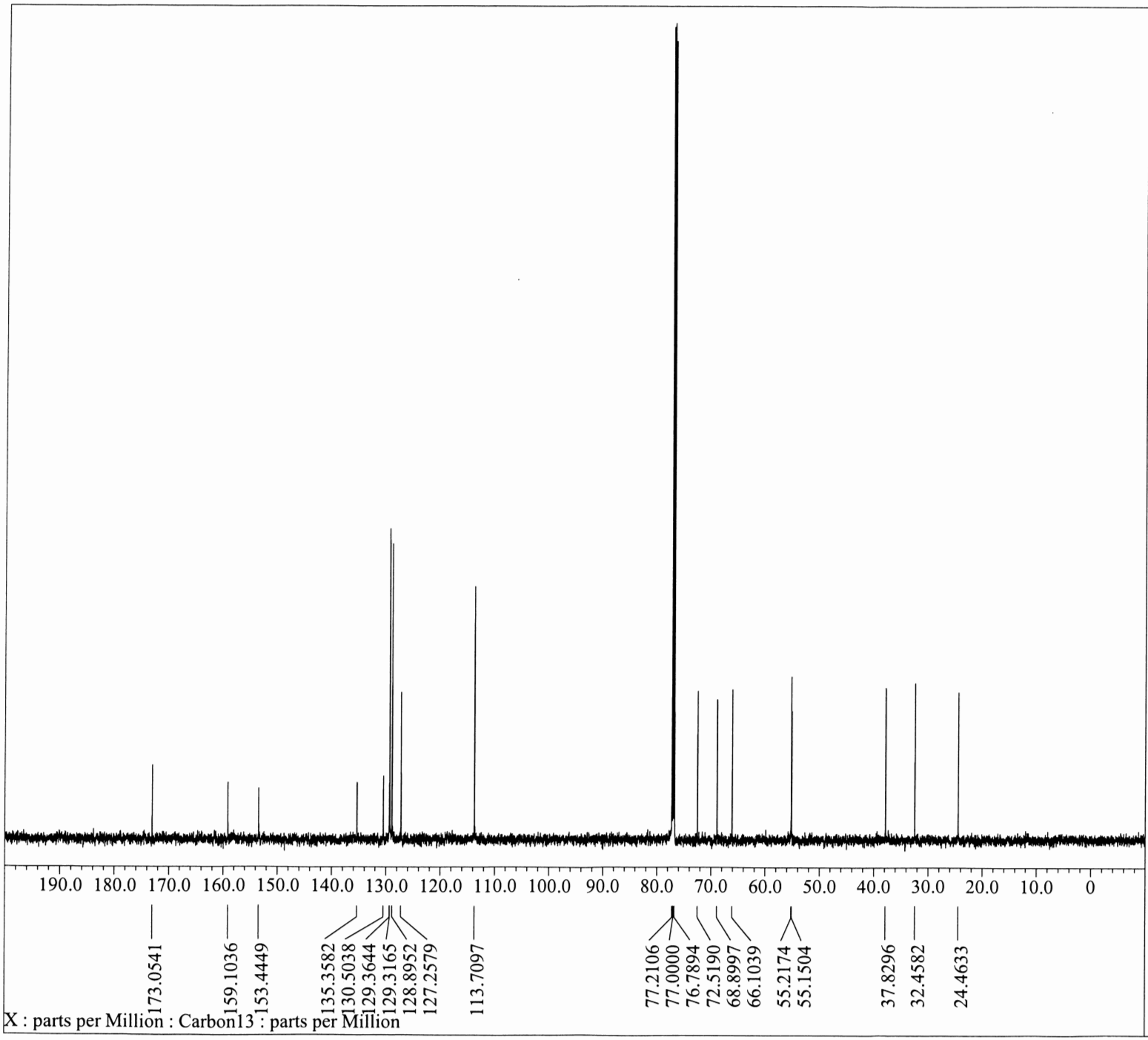

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = HI-I-13-2
Solvent           = CHLOROFORM-D
Creation_Time     =  5-OCT-2010 16:19:27
Revision_Time     =  5-OCT-2010 16:26:37
Current_Time      =  5-OCT-2010 16:27:09

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 40
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.1[dC]
```



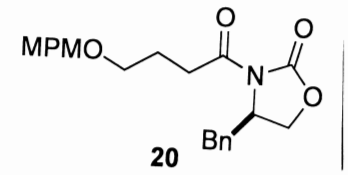



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HI-I-13-2
Solvent           = CHLOROFORM-D
Creation_Time     =  5-OCT-2010 20:22:04
Revision_Time     =  5-OCT-2010 20:30:05
Current_Time      =  5-OCT-2010 20:30:52

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 145
Total_Scans       = 145

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23.1[dC]
```



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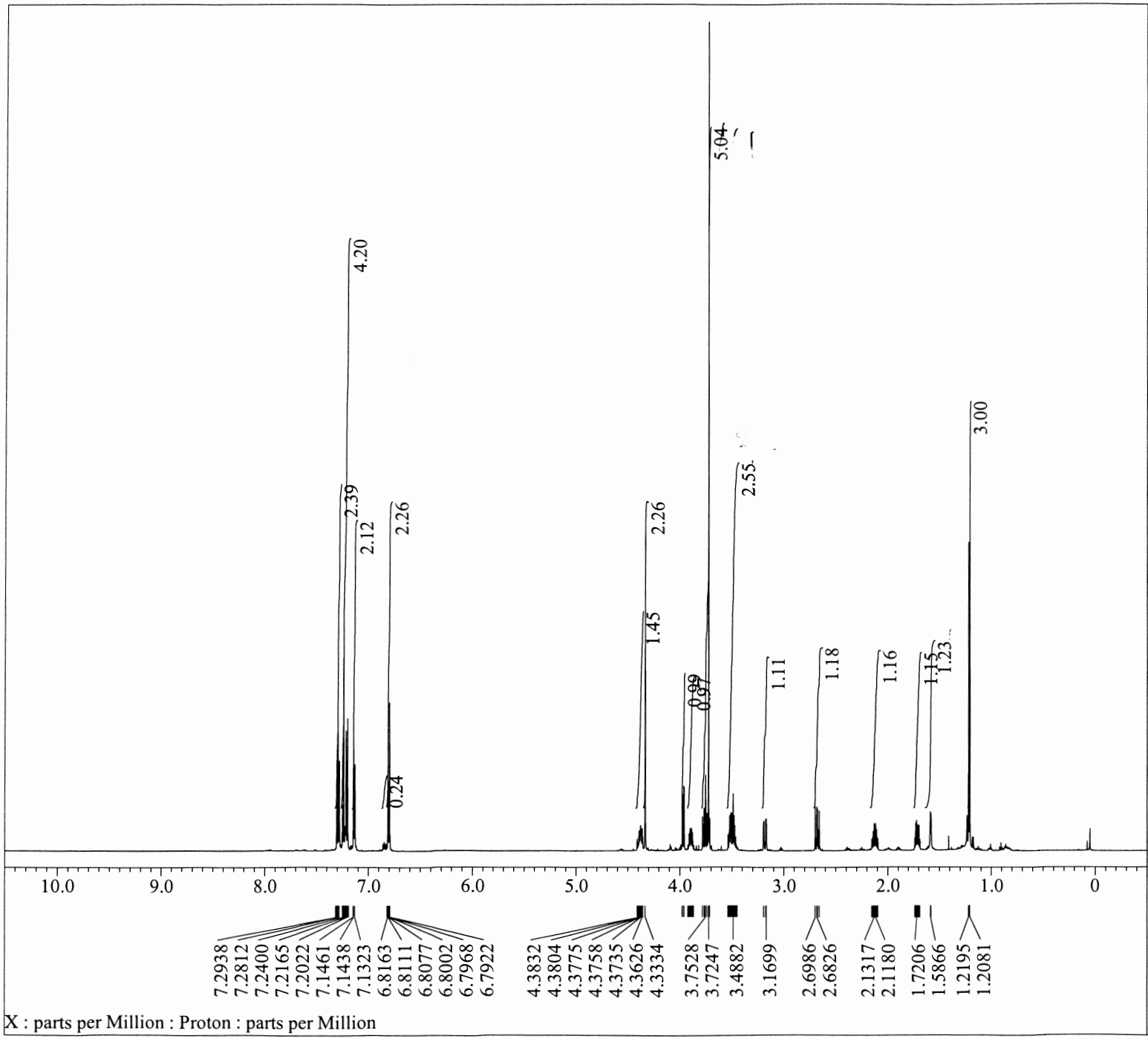
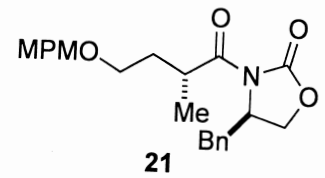


Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= proton.jxp
Sample_Id	= HI-I-13-1
Solvent	= CHLOROFORM-D
Creation_Time	= 5-OCT-2010 16:10:14
Revision_Time	= 5-OCT-2010 16:17:58
Current_Time	= 5-OCT-2010 16:18:34
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 2.9097984[s]
X_Domain	= 1H
X_Freq	= 600.1723046[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.34366642[Hz]
X_Sweep	= 11.26126126[kHz]
X_Sweep_Clipped	= 9.00900901[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 600.1723046[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Mod_Return	= 1
Probe_Recovery	= 5[us]
Scans	= 8
Total_Scans	= 8
X_90_Width	= 12.4[us]
X_Acq_Time	= 2.9097984[s]
X_Angle	= 45[deg]
X_Atn	= 3[dB]
X_Pulse	= 6.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Recvr_Gain	= 42
Relaxation_Delay	= 1[s]
Repetition_Time	= 3.9097984[s]
Temp_Get	= 22.2[dC]



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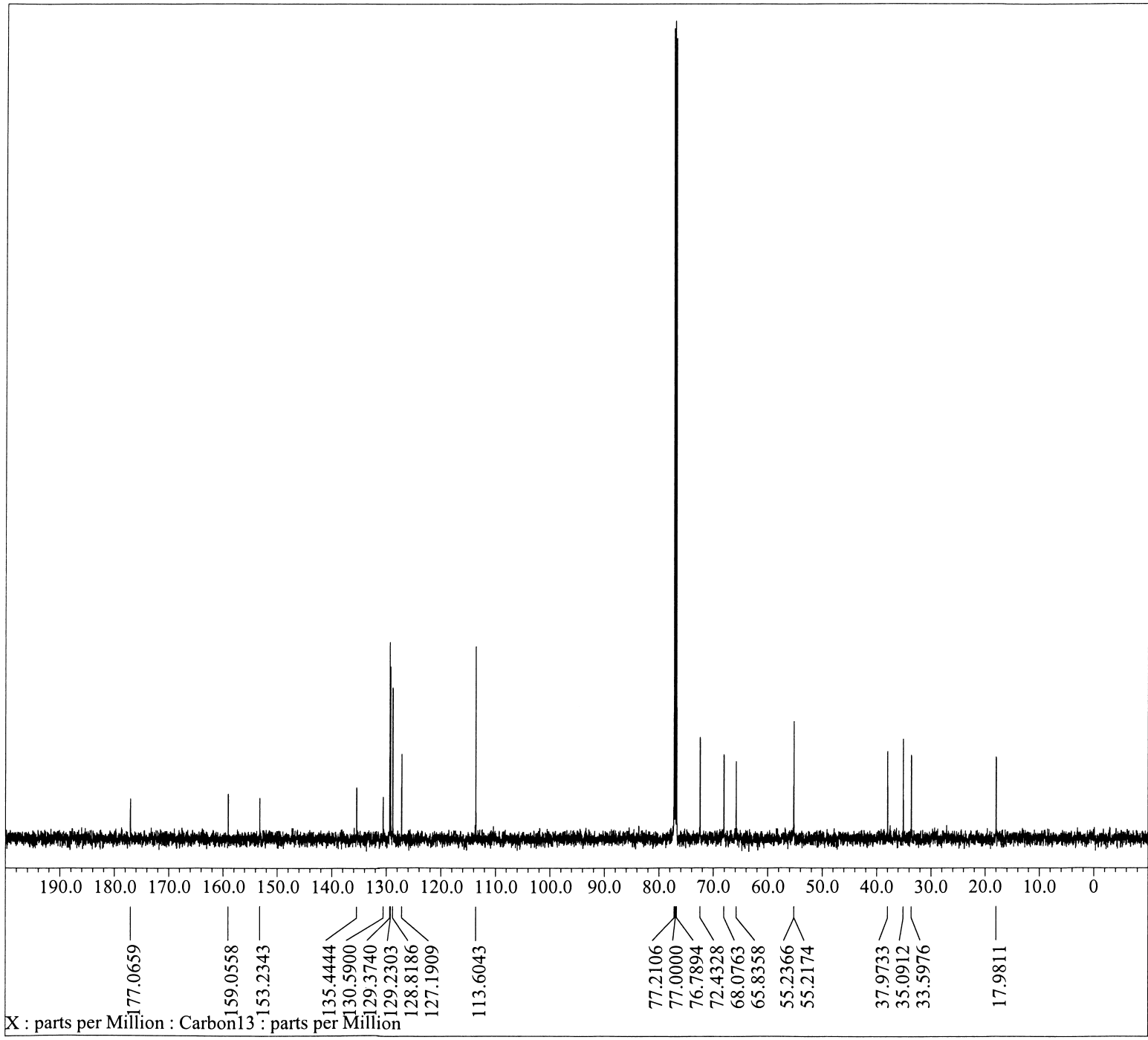
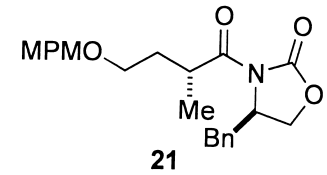



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HI-I-13-1
Solvent           = CHLOROFORM-D
Creation_Time     =  5-OCT-2010 20:10:35
Revision_Time     =  5-OCT-2010 20:15:22
Current_Time      =  5-OCT-2010 20:17:14

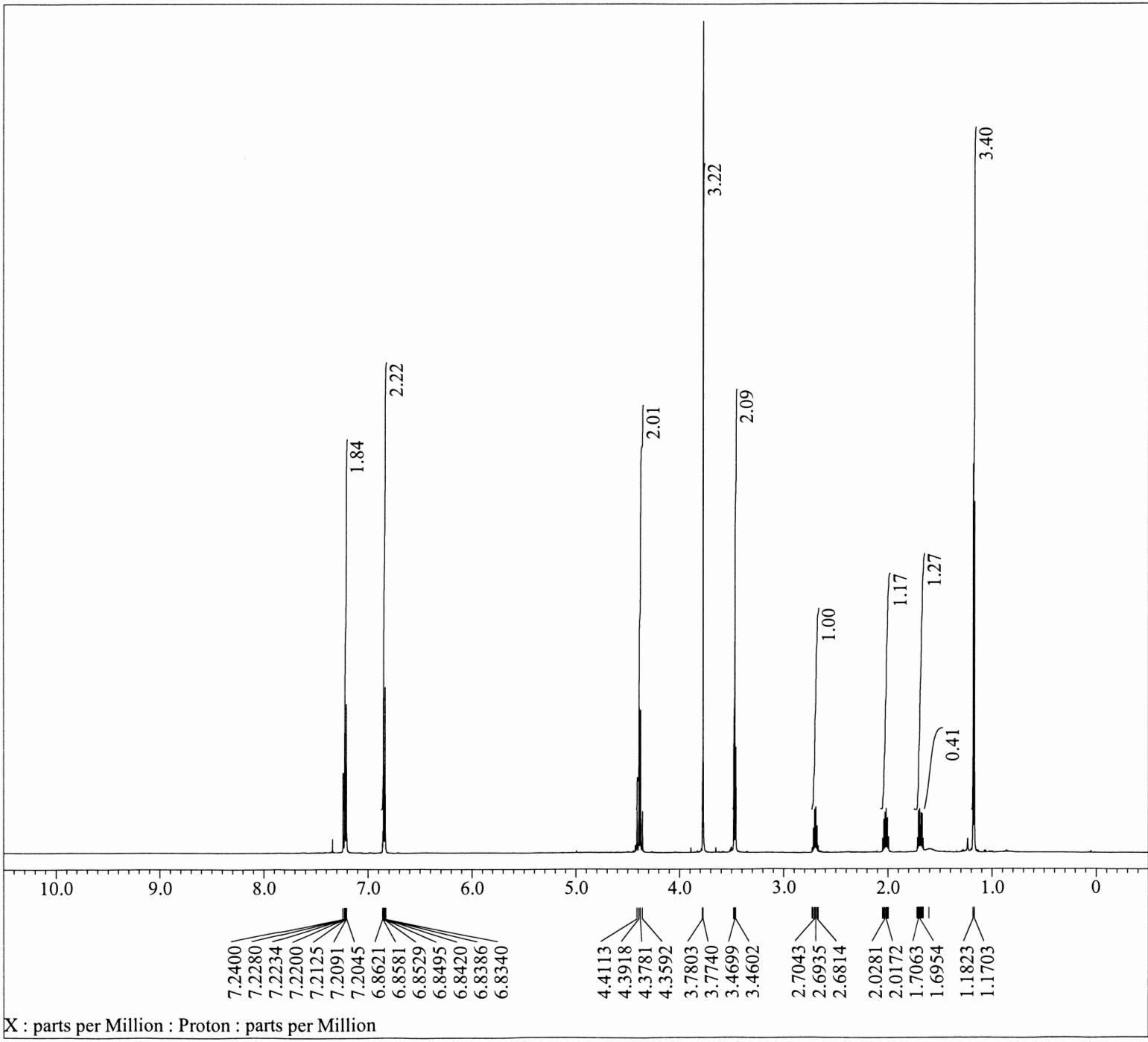
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = TRUE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 72
Total_Scans       = 72

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 58
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 22.8[dC]
```



21

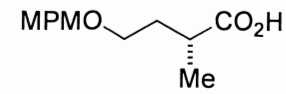



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-81
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 19:36:22
Revision_Time     =  7-OCT-2010 19:42:38
Current_Time      =  7-OCT-2010 19:43:03

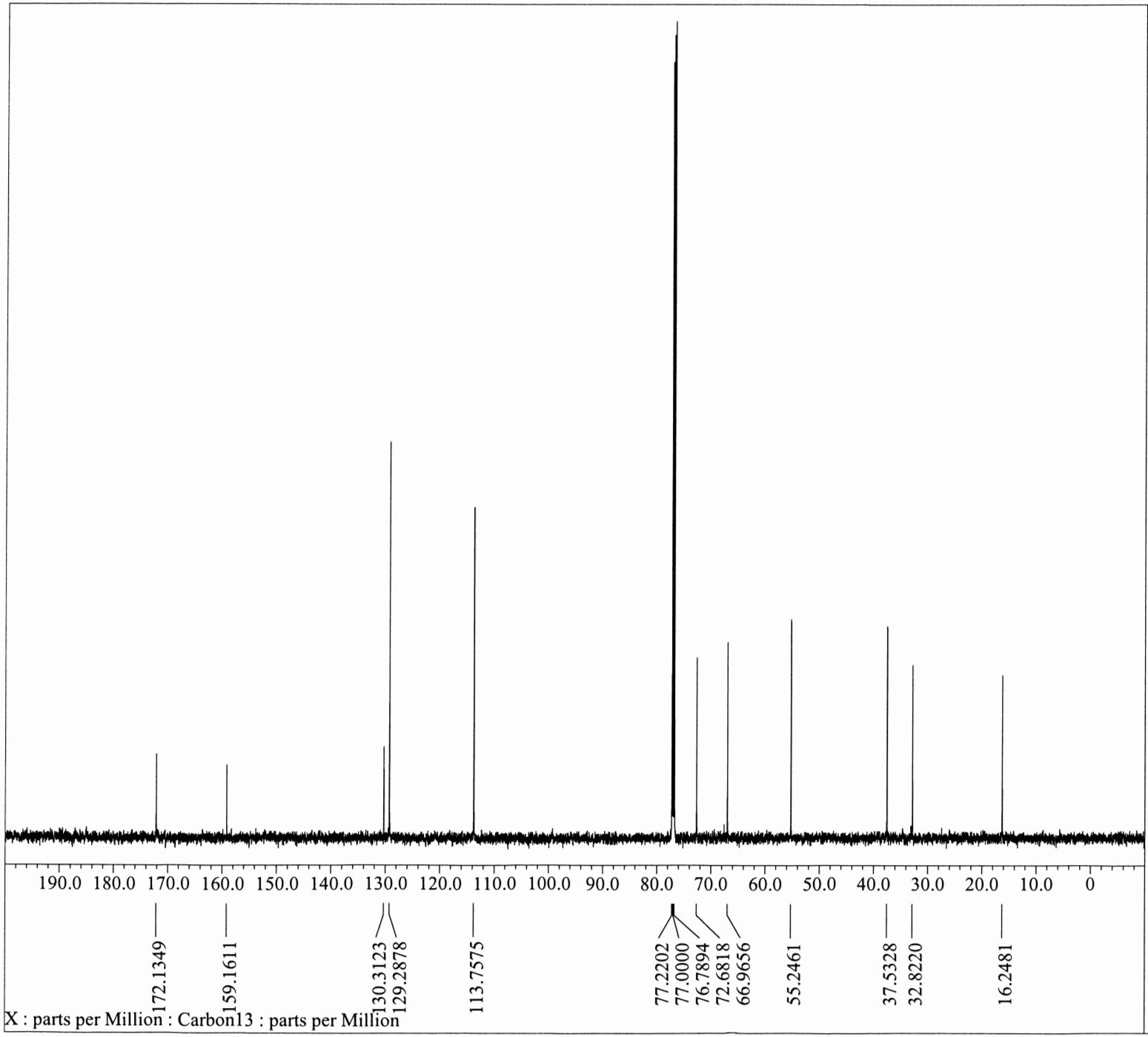
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 40
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.6[dC]
```



22

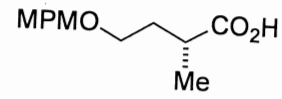



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-81
Solvent           = CHLOROFORM-D
Creation_Time     =  7-OCT-2010 19:39:16
Revision_Time     =  7-OCT-2010 19:46:48
Current_Time      =  7-OCT-2010 19:47:23

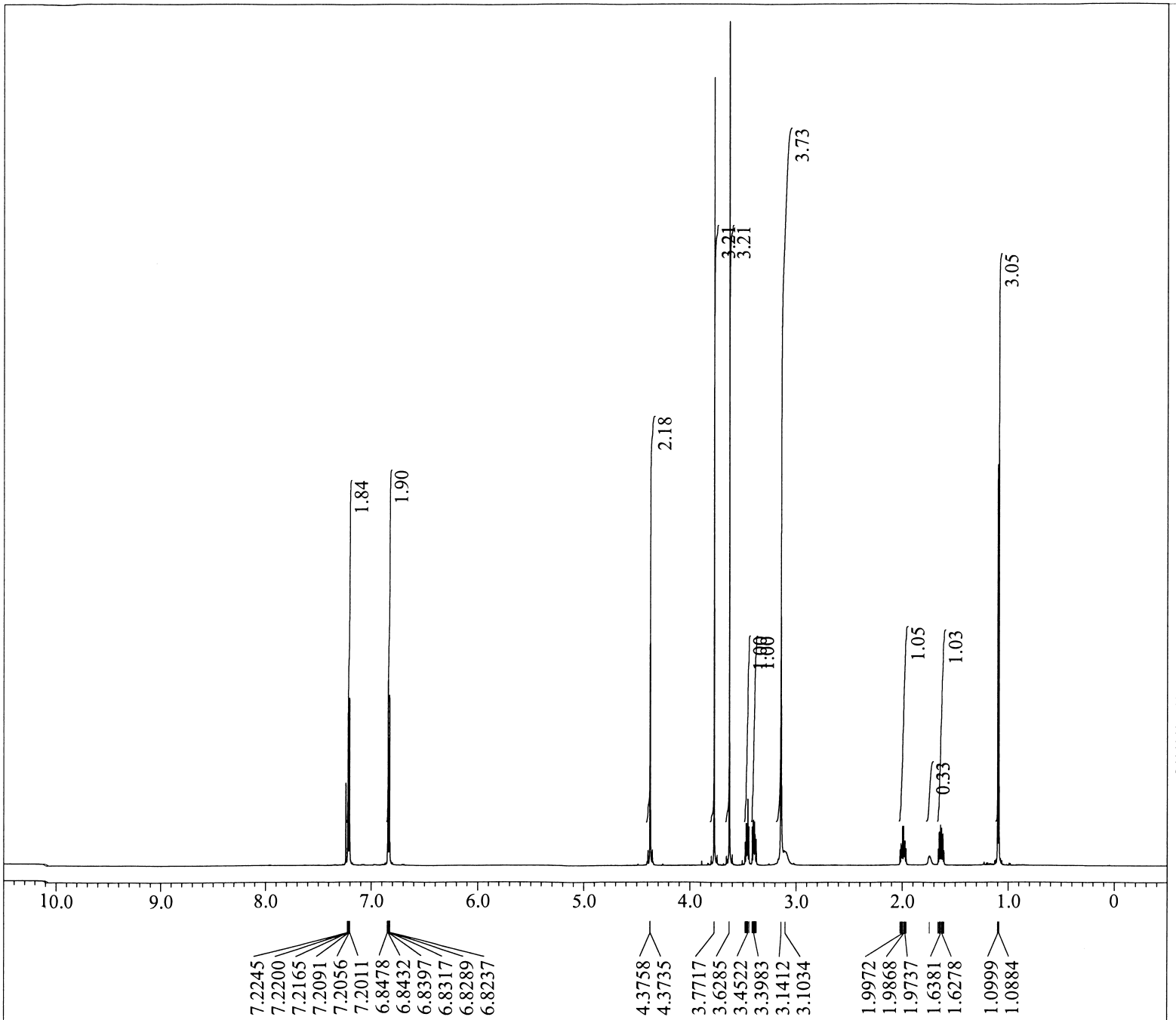
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 132
Total_Scans       = 132

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23.1[dC]
```

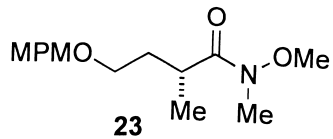


22

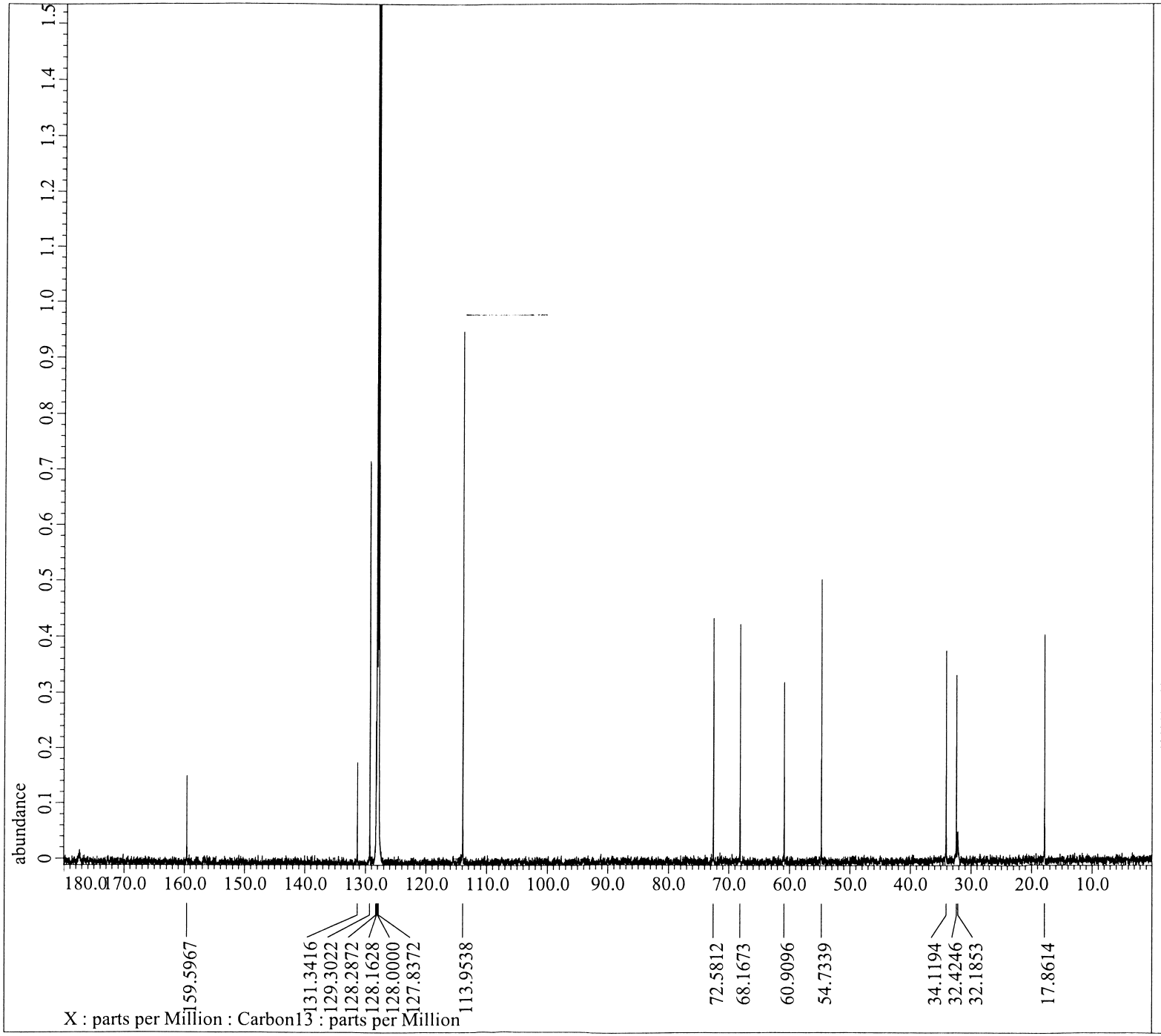


X : parts per Million : Proton : parts per Million

Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= proton.jxp
Sample_Id	= HI-I-24
Solvent	= CHLOROFORM-D
Creation_Time	= 5-OCT-2010 16:28:31
Revision_Time	= 5-OCT-2010 20:09:28
Current_Time	= 5-OCT-2010 20:09:51
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 2.9097984[s]
X_Domain	= 1H
X_Freq	= 600.1723046[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.34366642[Hz]
X_Sweep	= 11.26126126[kHz]
X_Sweep_Clipped	= 9.00900901[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 600.1723046[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Mod_Return	= 1
Probe_Recovery	= 5[us]
Scans	= 8
Total_Scans	= 8
X_90_Width	= 12.4[us]
X_Acq_Time	= 2.9097984[s]
X_Angle	= 45[deg]
X_Atn	= 3[dB]
X_Pulse	= 6.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Recvr_Gain	= 36
Relaxation_Delay	= 1[s]
Repetition_Time	= 3.9097984[s]
Temp_Get	= 22.1[dC]



23

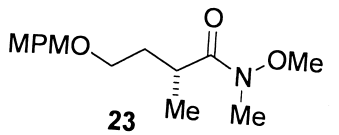



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HI-I-24
Solvent           = BENZENE-D6
Creation_Time     =  6-OCT-2010 22:51:58
Revision_Time     = 26-NOV-2010 17:27:56
Current_Time      = 26-NOV-2010 17:29:22

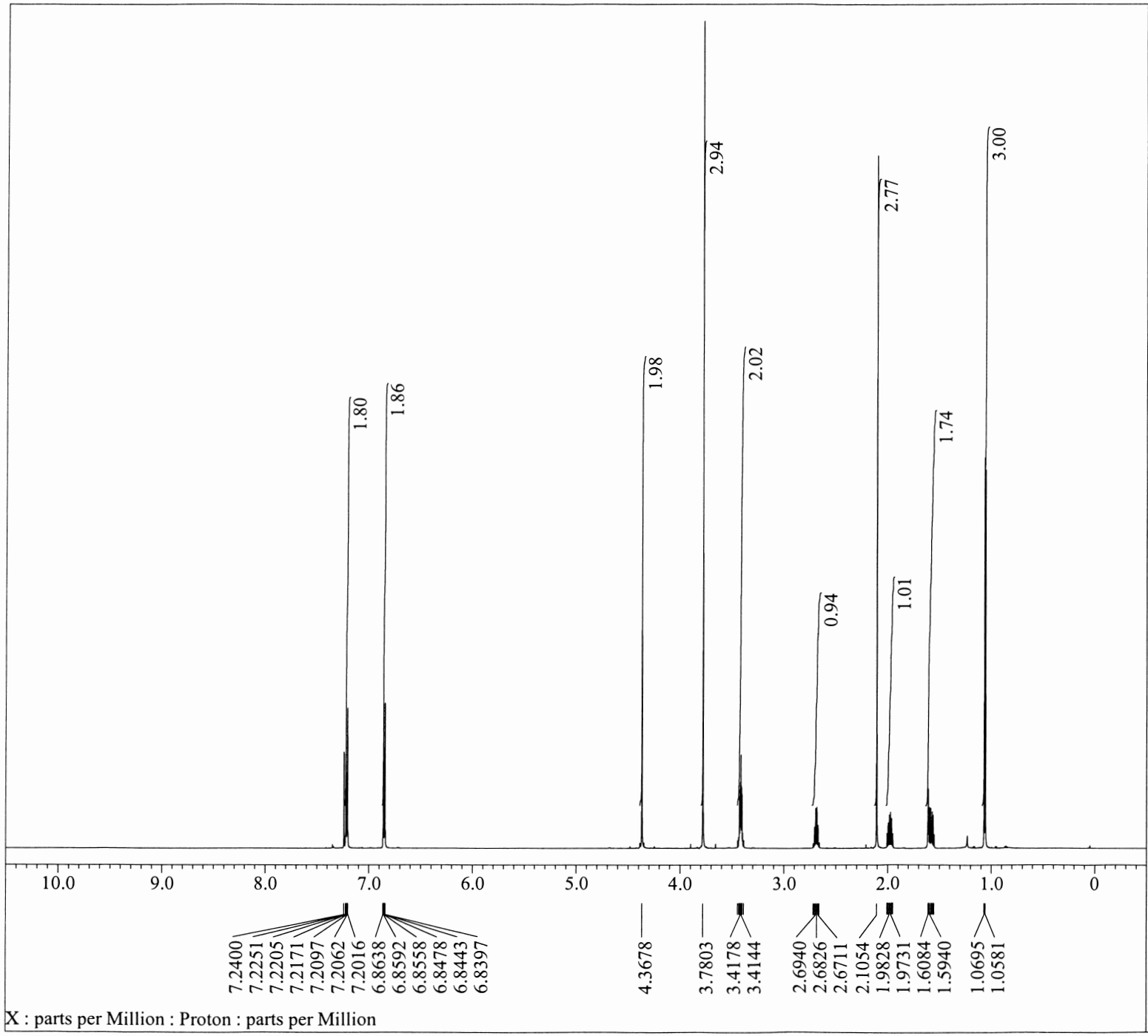
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 102
Total_Scans       = 102

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 23.3[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



23

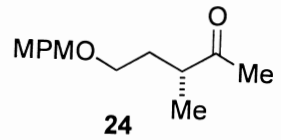



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-70 & 82
Solvent           = CHLOROFORM-D
Creation_Time     =  8-OCT-2010 15:51:17
Revision_Time     =  8-OCT-2010 16:00:54
Current_Time      =  8-OCT-2010 16:01:15

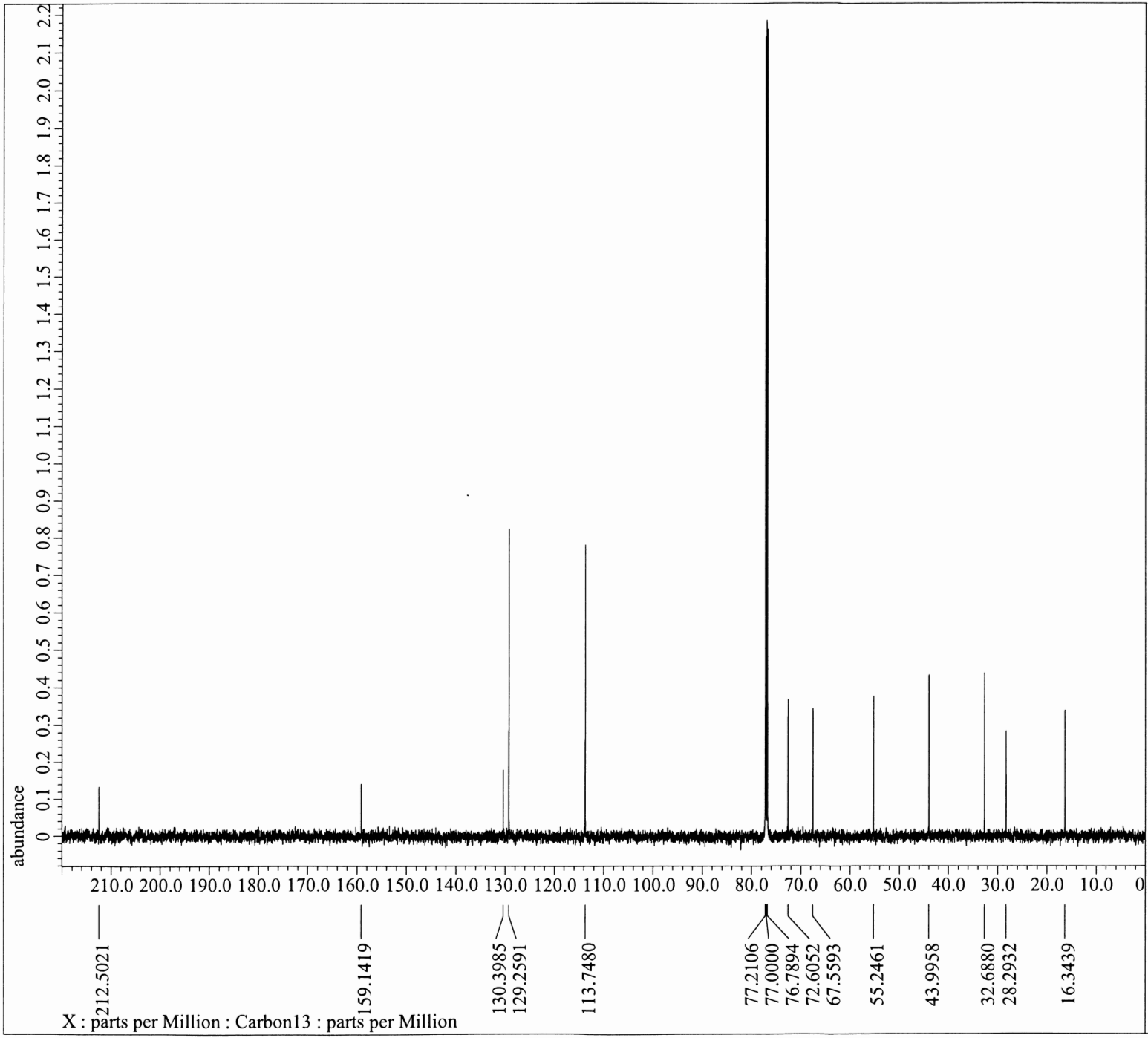
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 42
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
```



24

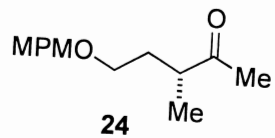



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-70 & 82
Solvent           = CHLOROFORM-D
Creation_Time     =  8-OCT-2010 17:31:05
Revision_Time     =  8-OCT-2010 17:37:19
Current_Time      =  8-OCT-2010 17:37:59

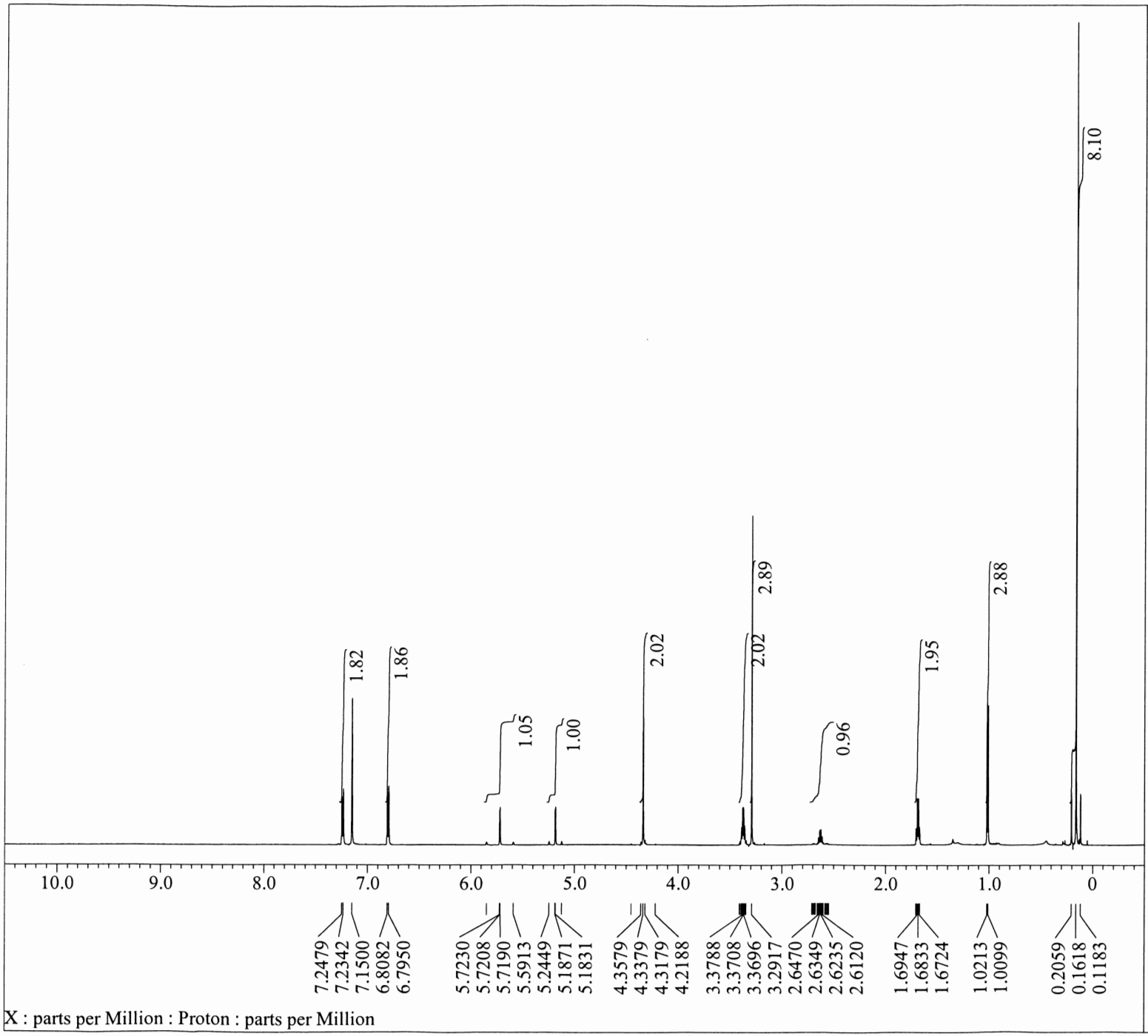
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 103
Total_Scans       = 103

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 22.9[dC]
```



24

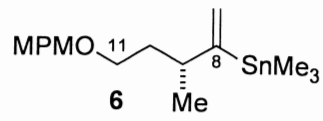


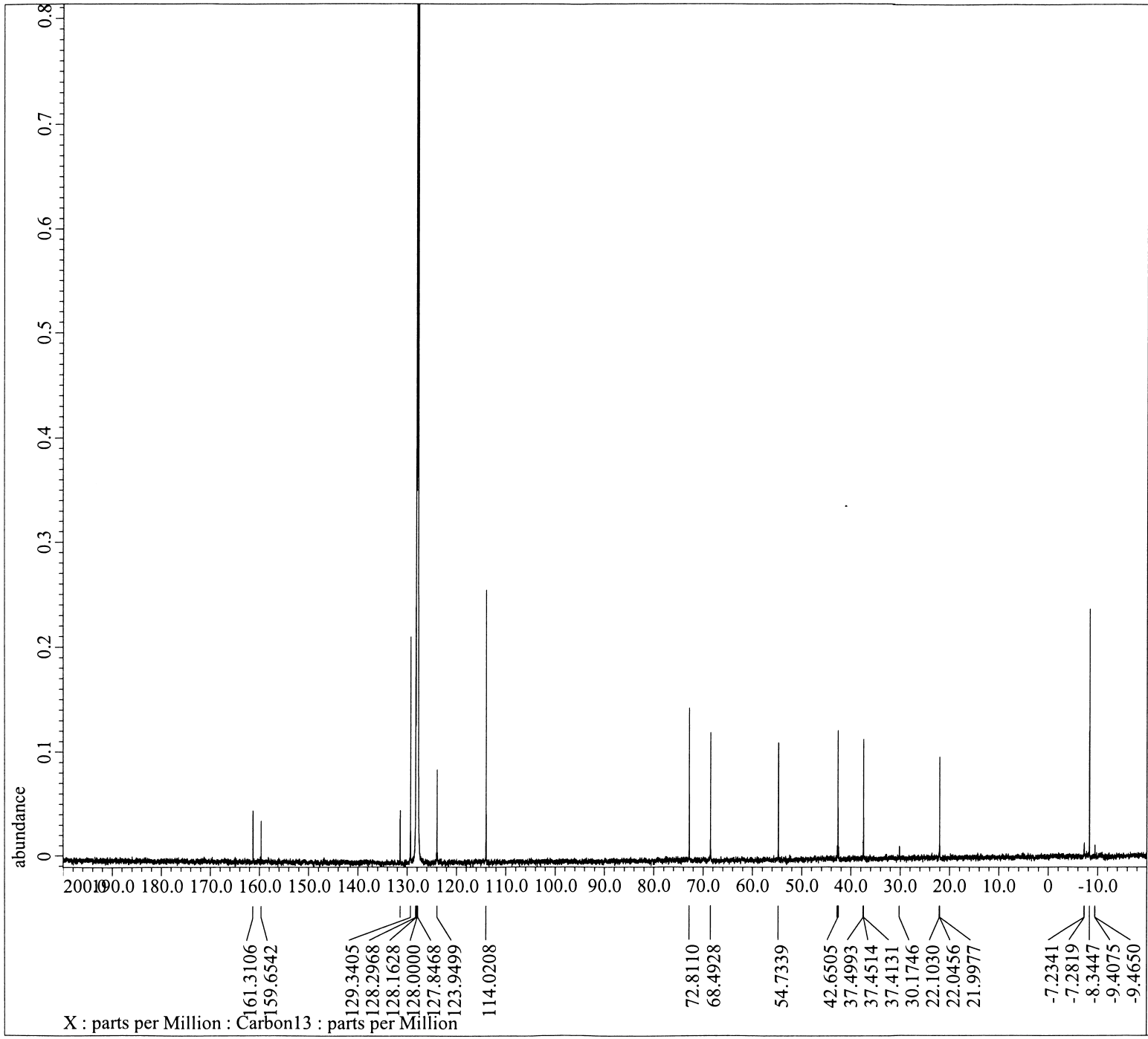

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-94 & 95
Solvent           = BENZENE-D6
Creation_Time     =  8-OCT-2010 15:57:28
Revision_Time     =  8-OCT-2010 17:23:11
Current_Time      =  8-OCT-2010 17:23:43

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 40
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.2[dC]
```



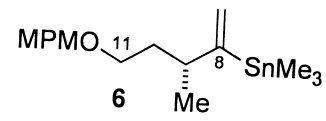


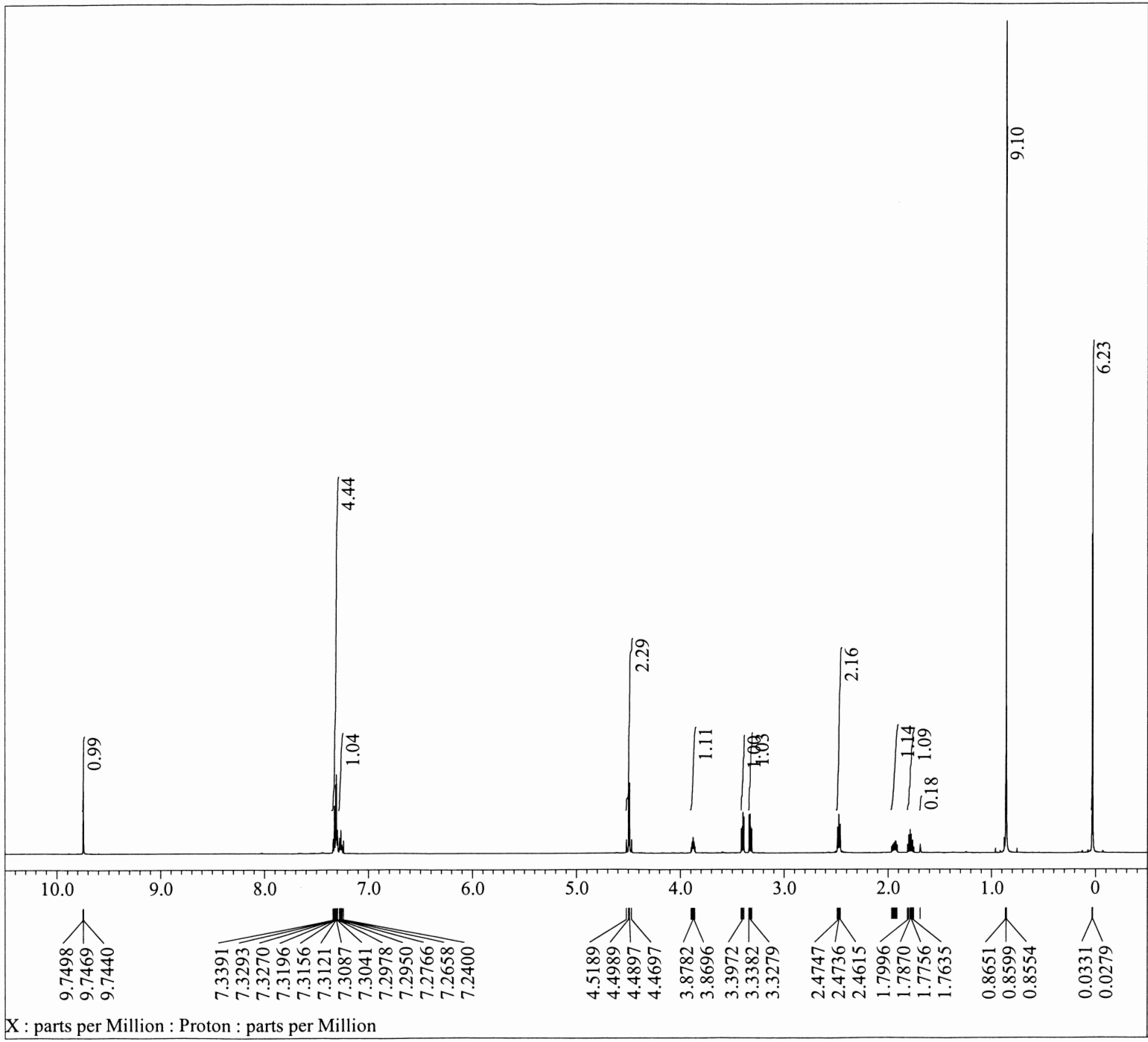

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-95
Solvent           = BENZENE-D6
Creation_Time     =  8-OCT-2010 20:40:29
Revision_Time     =  8-OCT-2010 21:26:28
Current_Time      =  8-OCT-2010 21:27:11

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

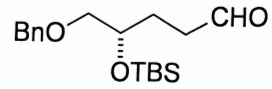
Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 961
Total_Scans       = 961

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 50
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23.3[dC]
```





Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= proton.jxp
Sample_Id	= MN-I-190
Solvent	= CHLOROFORM-D
Creation_Time	= 13-OCT-2010 17:06:54
Revision_Time	= 13-OCT-2010 17:15:29
Current_Time	= 13-OCT-2010 17:15:48
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 2.9097984[s]
X_Domain	= 1H
X_Freq	= 600.1723046[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.34366642[Hz]
X_Sweep	= 11.26126126[kHz]
X_Sweep_Clipped	= 9.00900901[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 600.1723046[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Mod_Return	= 1
Probe_Recovery	= 5[us]
Scans	= 8
Total_Scans	= 8
X_90_Width	= 12.4[us]
X_Acq_Time	= 2.9097984[s]
X_Angle	= 45[deg]
X_Atn	= 3[dB]
X_Pulse	= 6.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Recvr_Gain	= 28
Relaxation_Delay	= 1[s]
Repetition_Time	= 3.9097984[s]
Temp_Get	= 22.3[dC]



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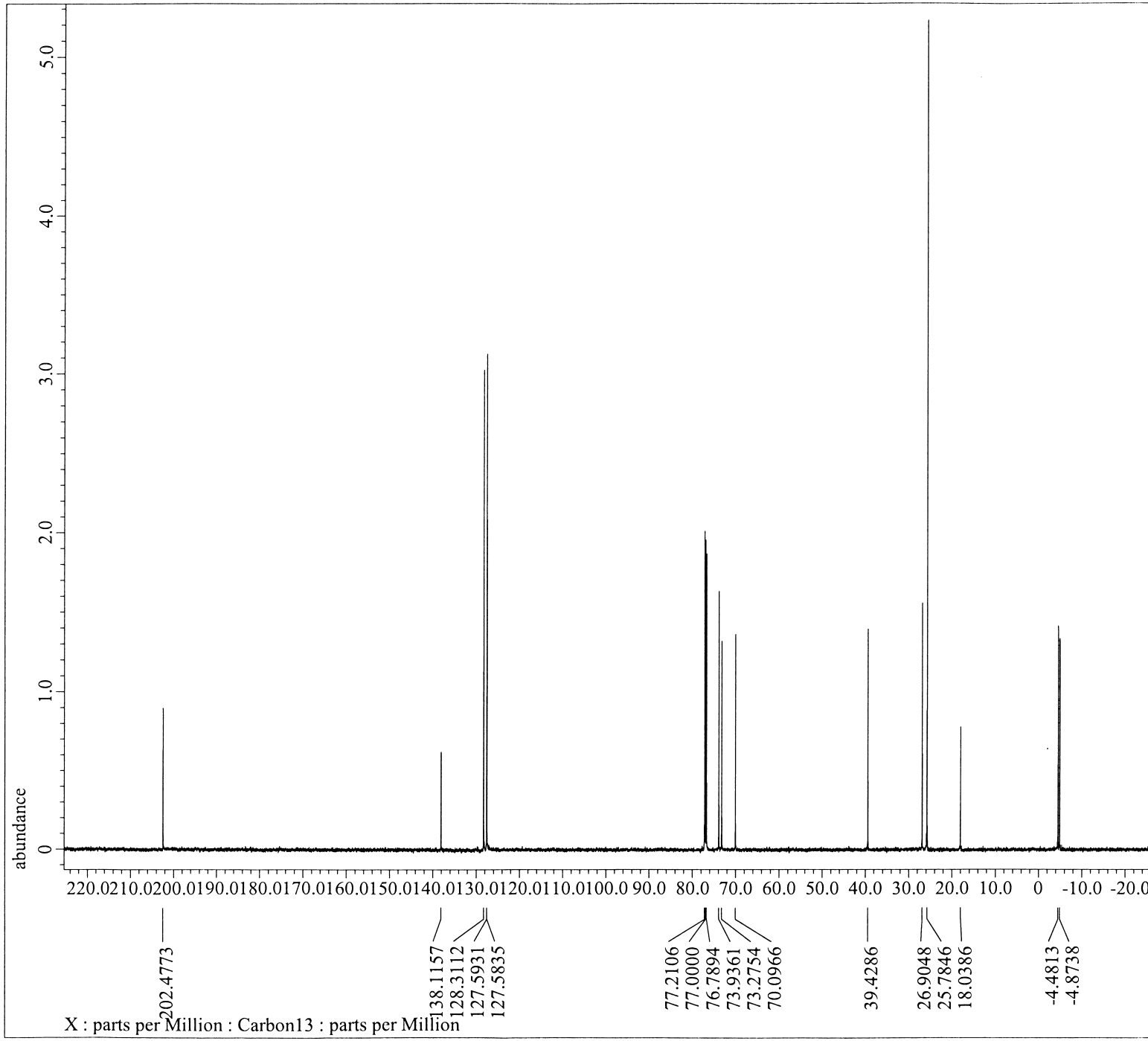
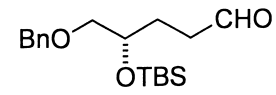



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-I-190
Solvent           = CHLOROFORM-D
Creation_Time     = 13-OCT-2010 17:09:50
Revision_Time     = 22-NOV-2010 05:57:47
Current_Time      = 22-NOV-2010 05:58:15

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 217
Total_Scans       = 217

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 23.3[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



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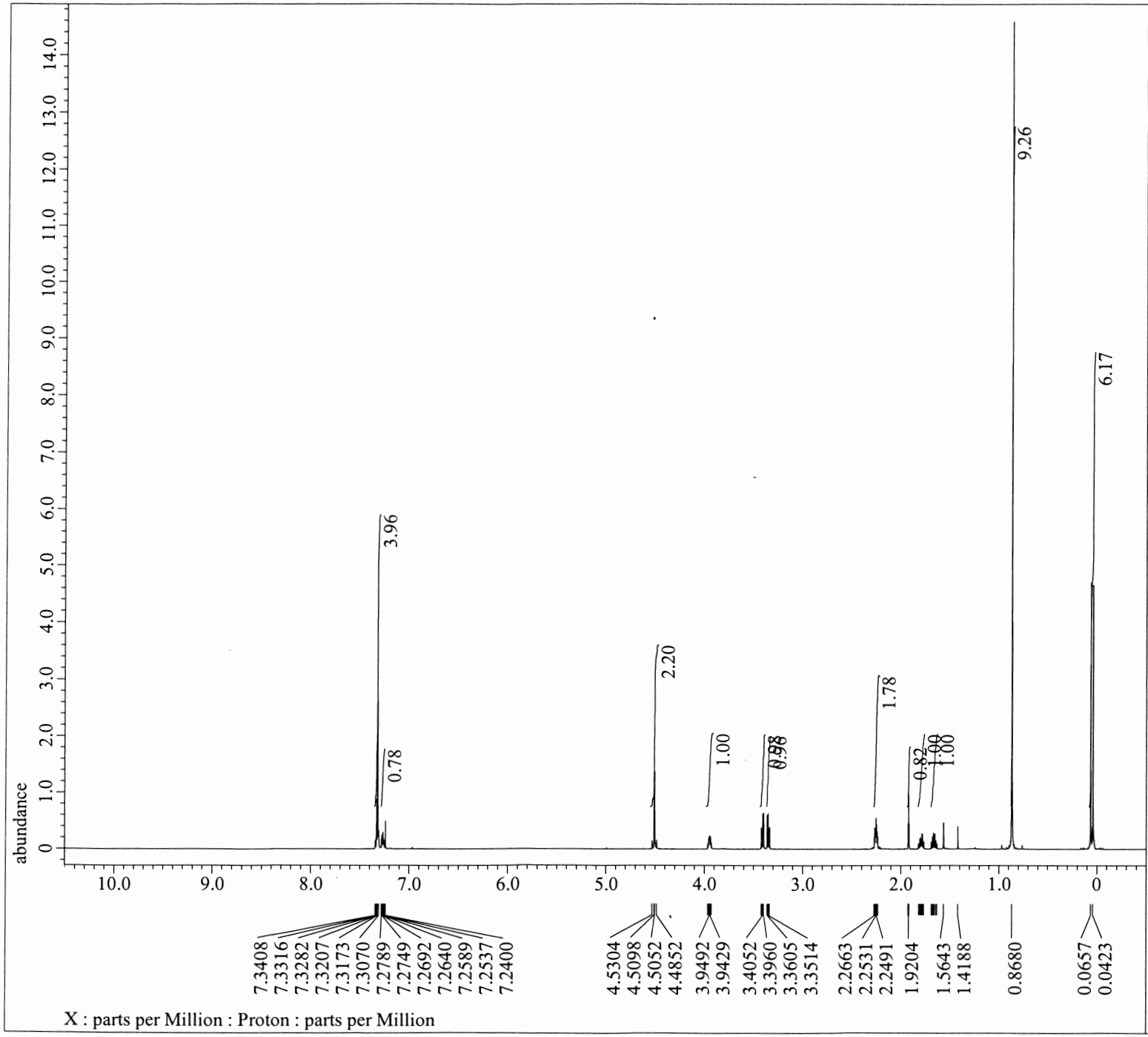
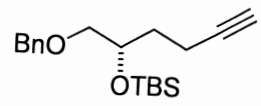



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-I-196
Solvent           = CHLOROFORM-D
Creation_Time     = 13-OCT-2010 17:47:41
Revision_Time     = 13-OCT-2010 17:54:05
Current_Time      = 13-OCT-2010 17:54:33

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 34
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.4[dC]
```



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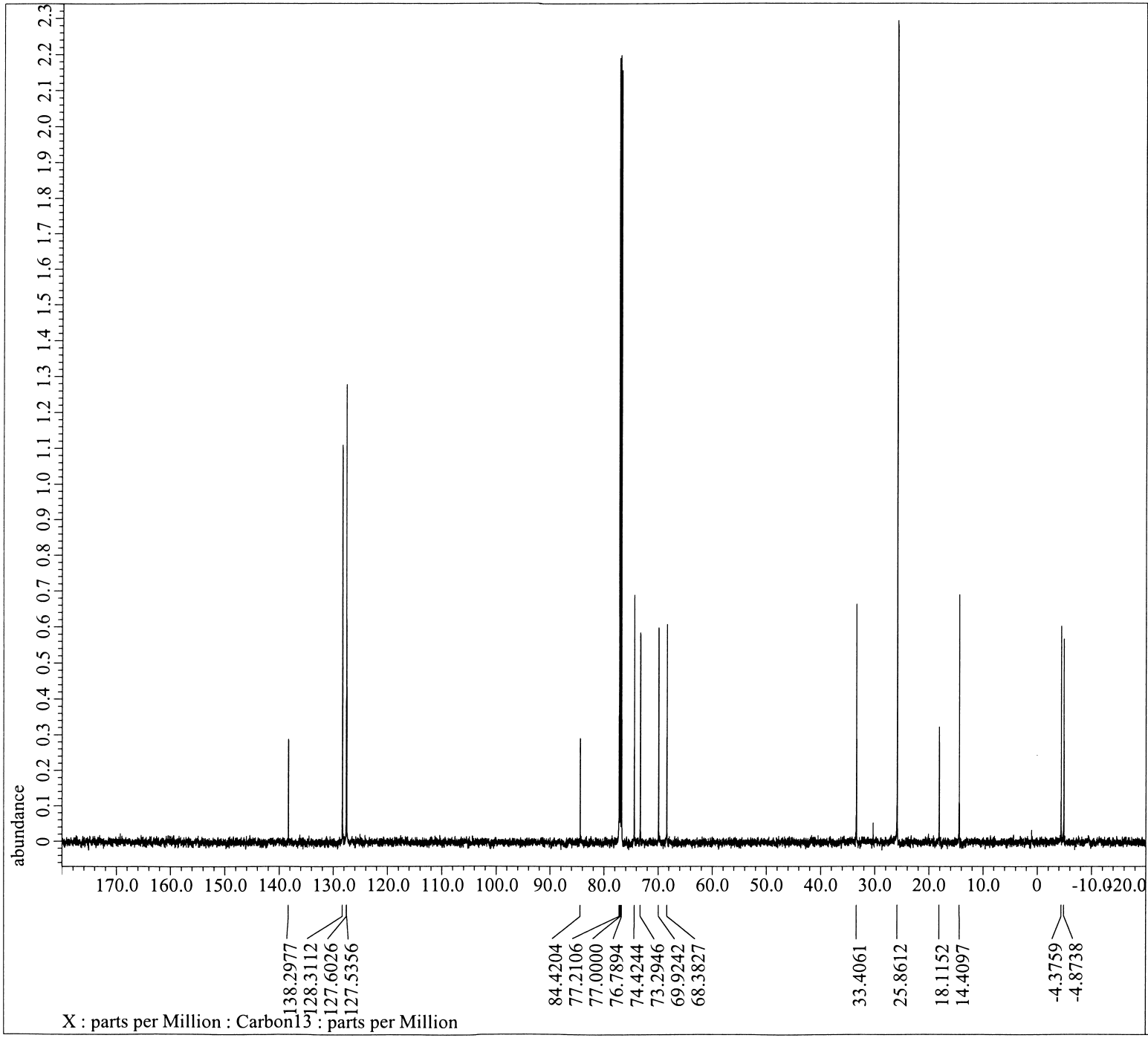
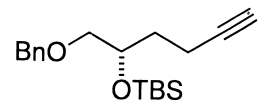



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-I-196
Solvent           = CHLOROFORM-D
Creation_Time     = 13-OCT-2010 17:50:34
Revision_Time     = 13-OCT-2010 17:59:35
Current_Time      = 13-OCT-2010 18:00:01

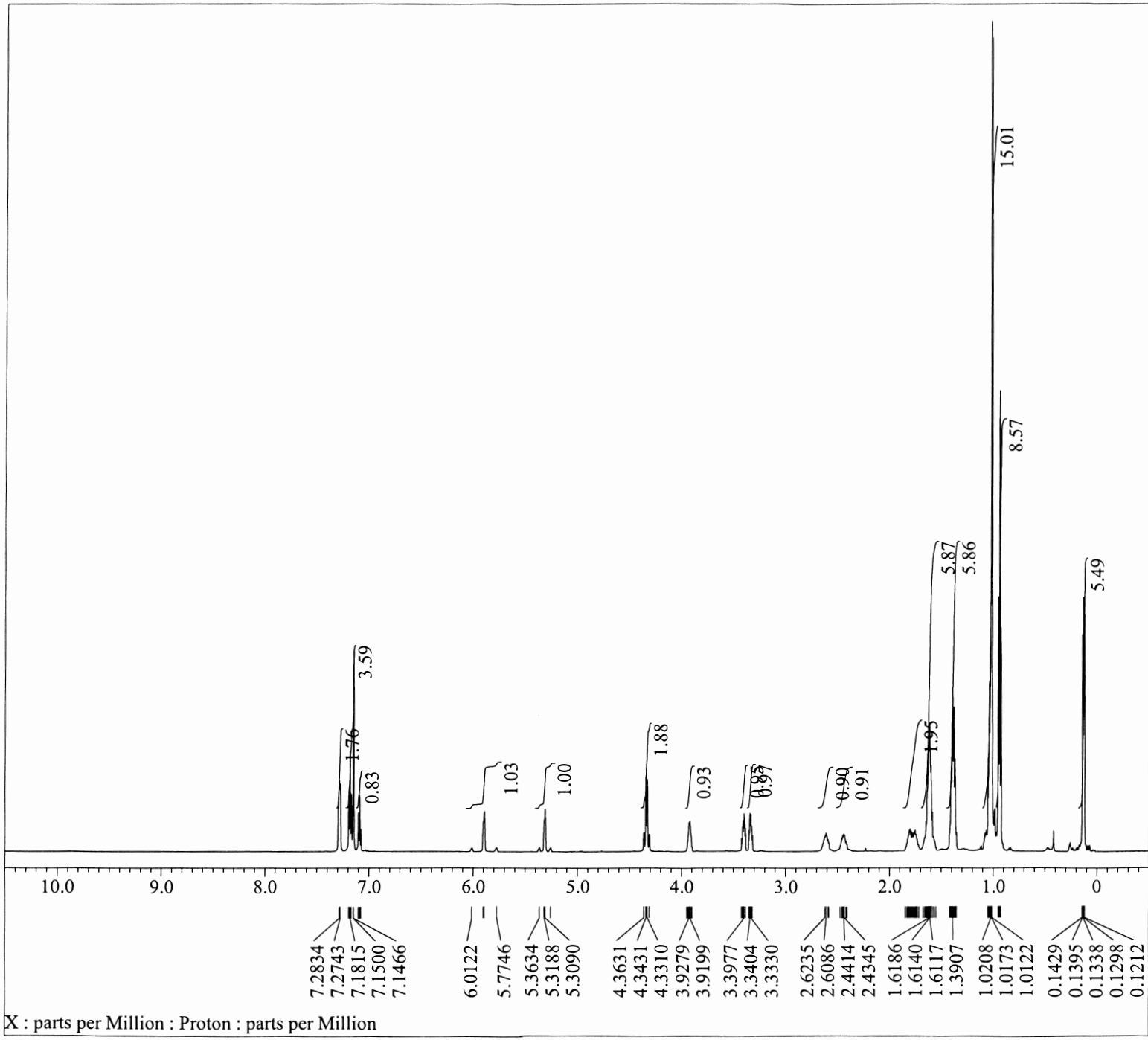
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 181
Total_Scans       = 181

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23[dC]
```



27

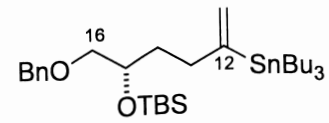



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-II-43
Solvent           = BENZENE-D6
Creation_Time     = 13-OCT-2010 23:17:04
Revision_Time     = 13-OCT-2010 23:34:32
Current_Time      = 13-OCT-2010 23:34:52

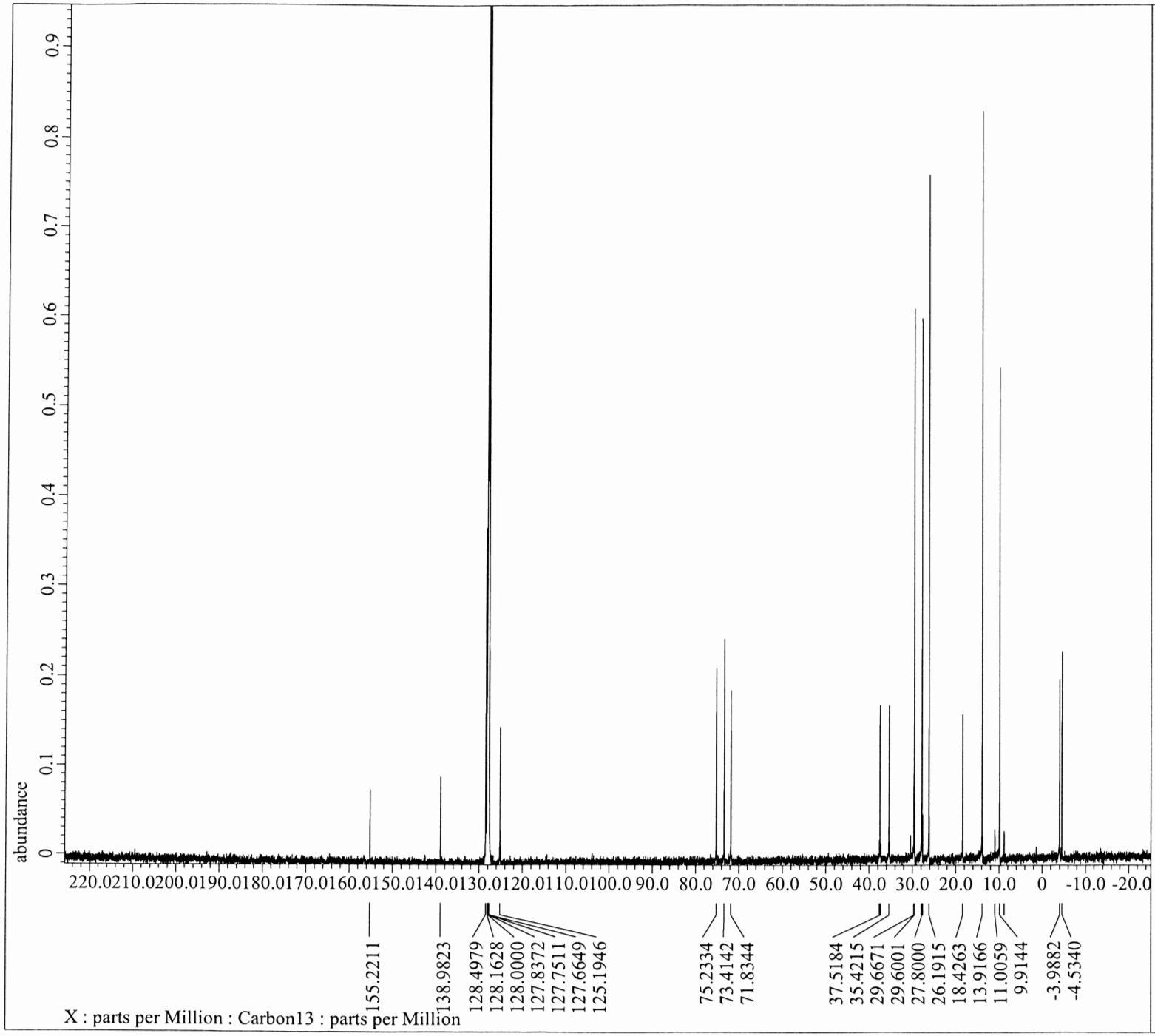
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 30
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
```



4

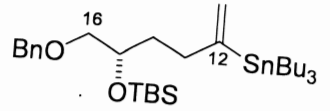



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-II-43
Solvent           = BENZENE-D6
Creation_Time     = 13-OCT-2010 23:20:02
Revision_Time     = 26-NOV-2010 17:34:38
Current_Time      = 26-NOV-2010 17:35:18

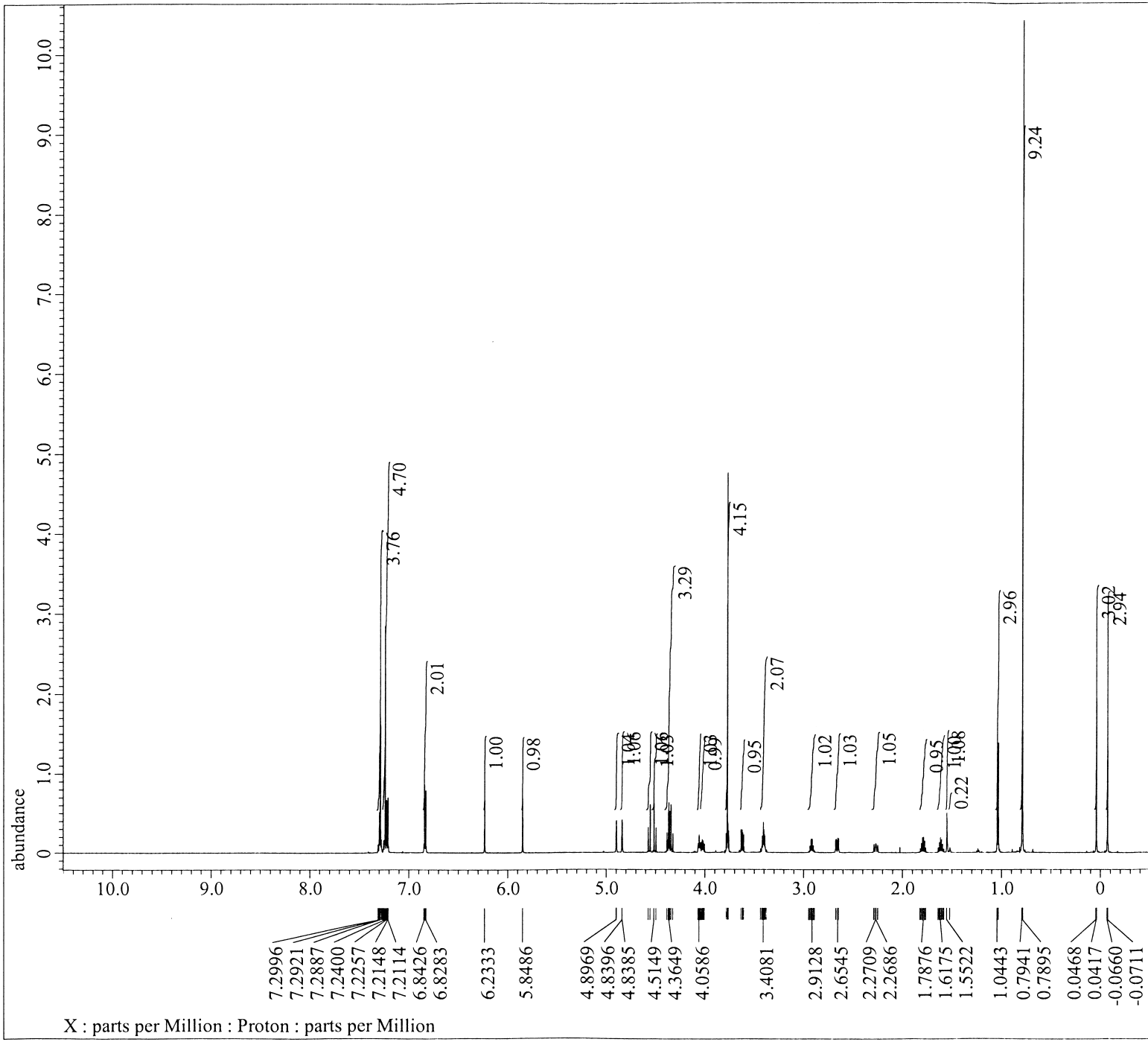
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 423
Total_Scans       = 423

Relaxation_Delay  = 2[s]
Recvr_Gain        = 52
Temp_Get          = 23.1[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



4

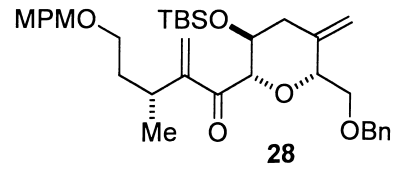



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-107
Solvent           = CHLOROFORM-D
Creation_Time     = 27-MAY-2010 21:11:29
Revision_Time     = 10-NOV-2010 18:55:42
Current_Time      = 10-NOV-2010 18:56:09

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 46
Temp_Get          = 21.8[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



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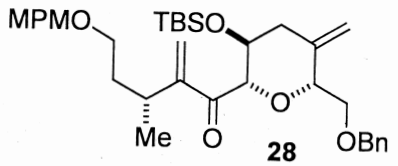
MN-3-183

File: xp

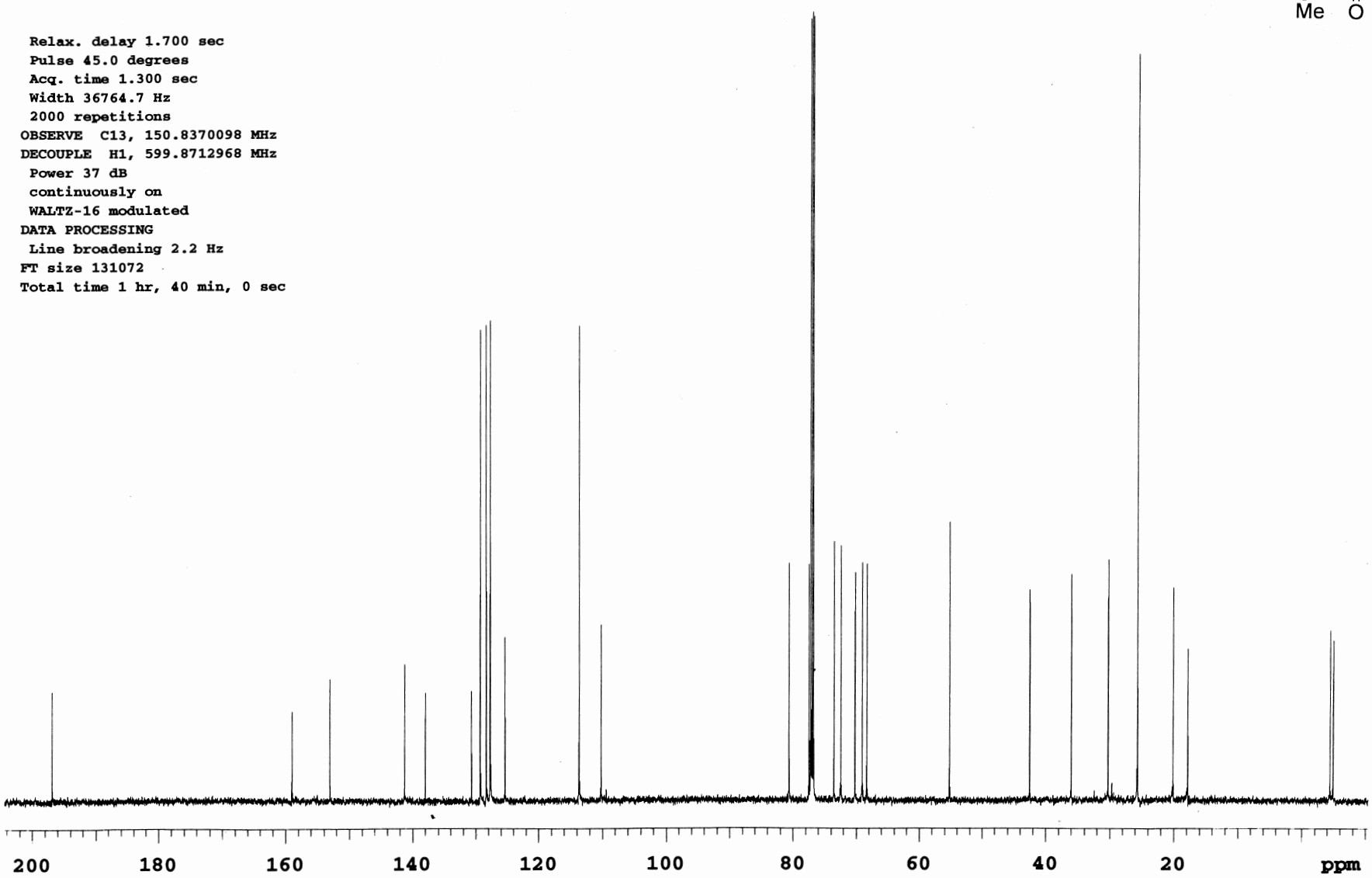
Pulse Sequence: s2pul

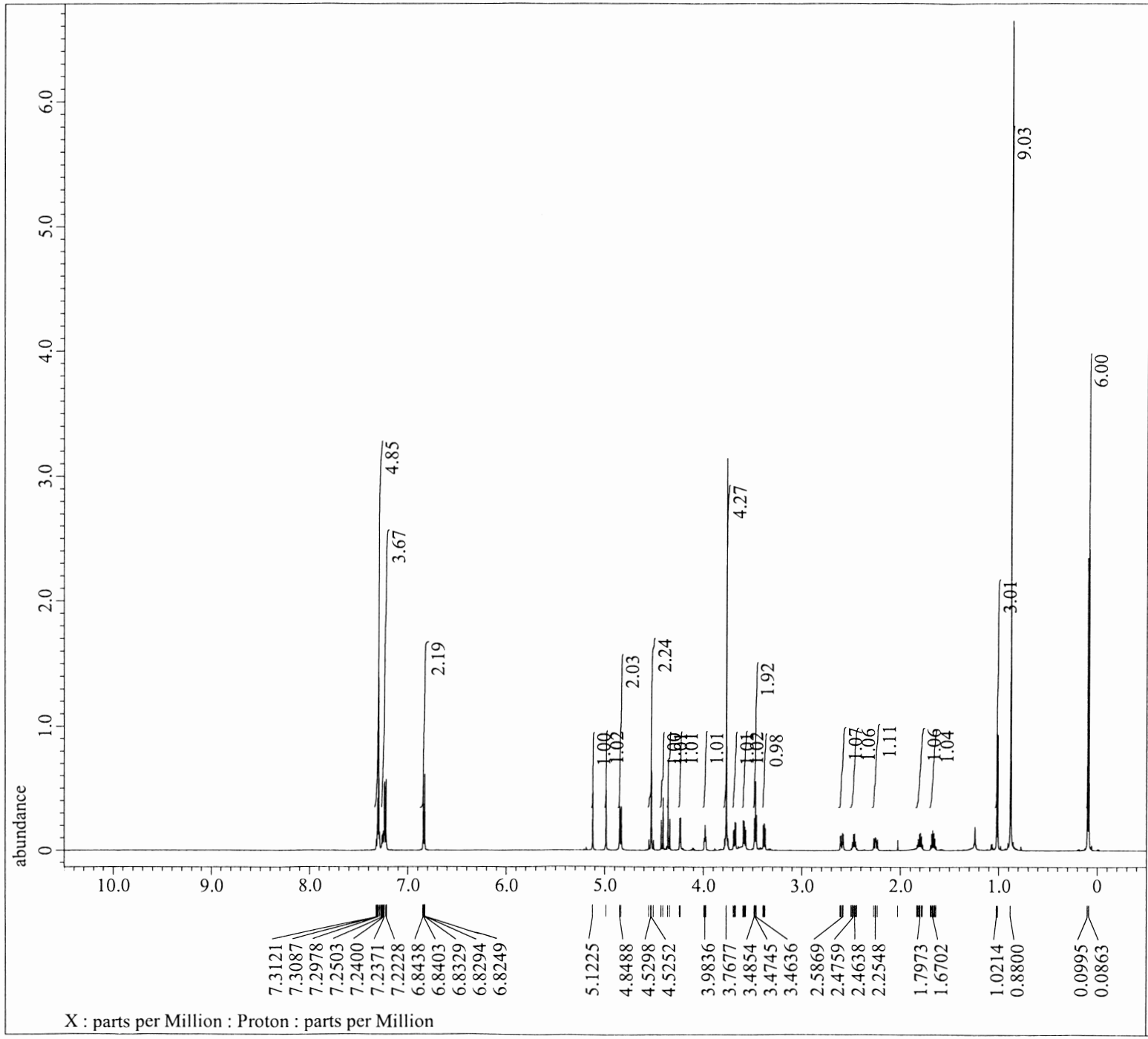
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: vnmr1
VNMRS-600 "varian600"

Relax. delay 1.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 36764.7 Hz
2000 repetitions
OBSERVE C13, 150.8370098 MHz
DECOUPLE H1, 599.8712968 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.2 Hz
FT size 131072
Total time 1 hr, 40 min, 0 sec



28



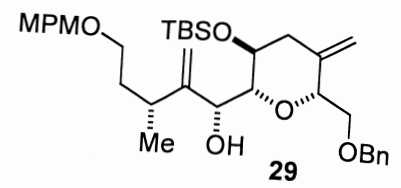



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-149-2
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUN-2010 19:58:28
Revision_Time     = 10-NOV-2010 21:19:37
Current_Time      = 10-NOV-2010 21:19:56

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 32
Temp_Get          = 22.6[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



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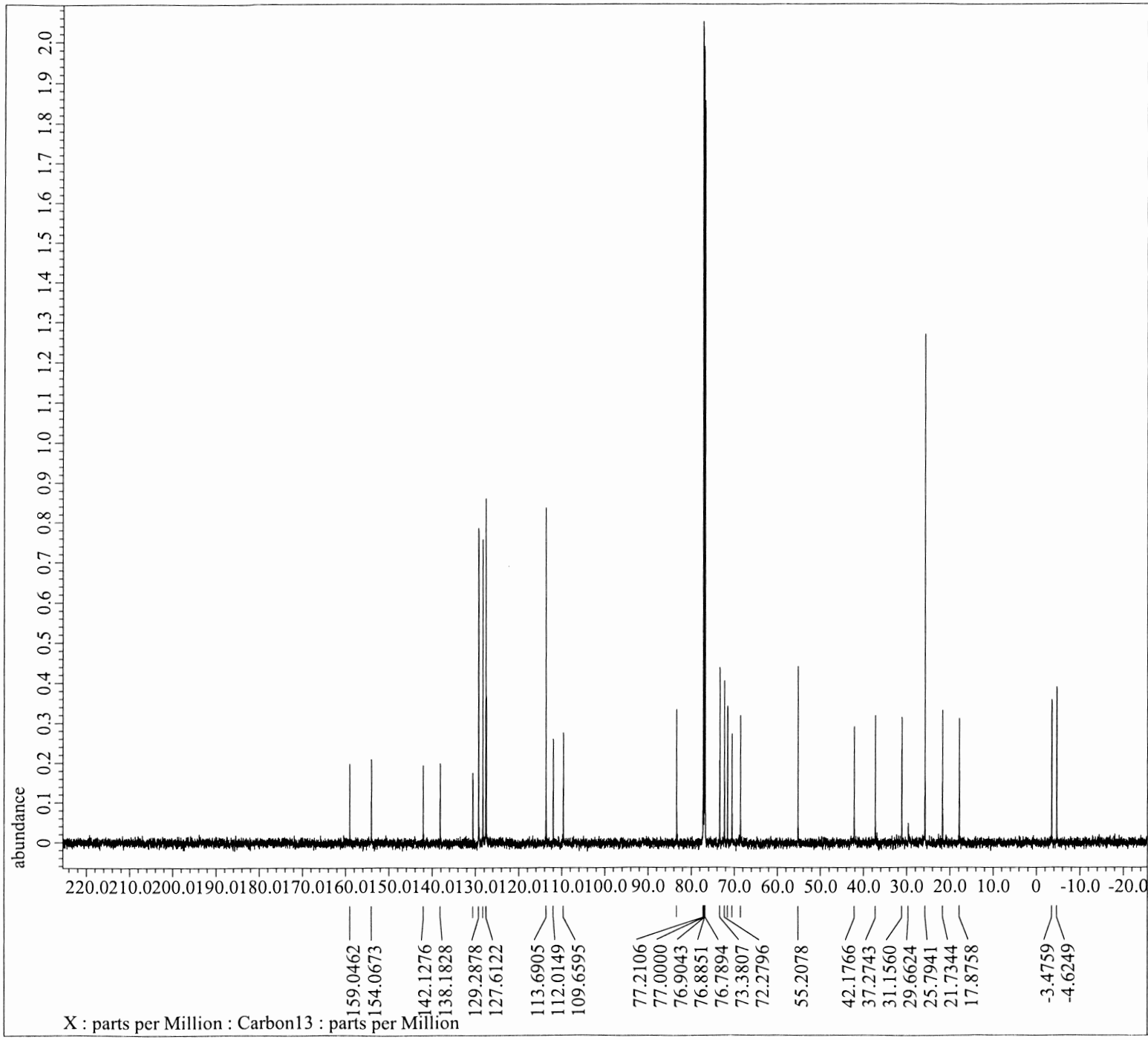
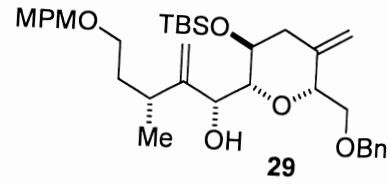



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-149-2
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUN-2010 20:04:49
Revision_Time     = 15-NOV-2010 12:31:02
Current_Time      = 15-NOV-2010 12:31:17

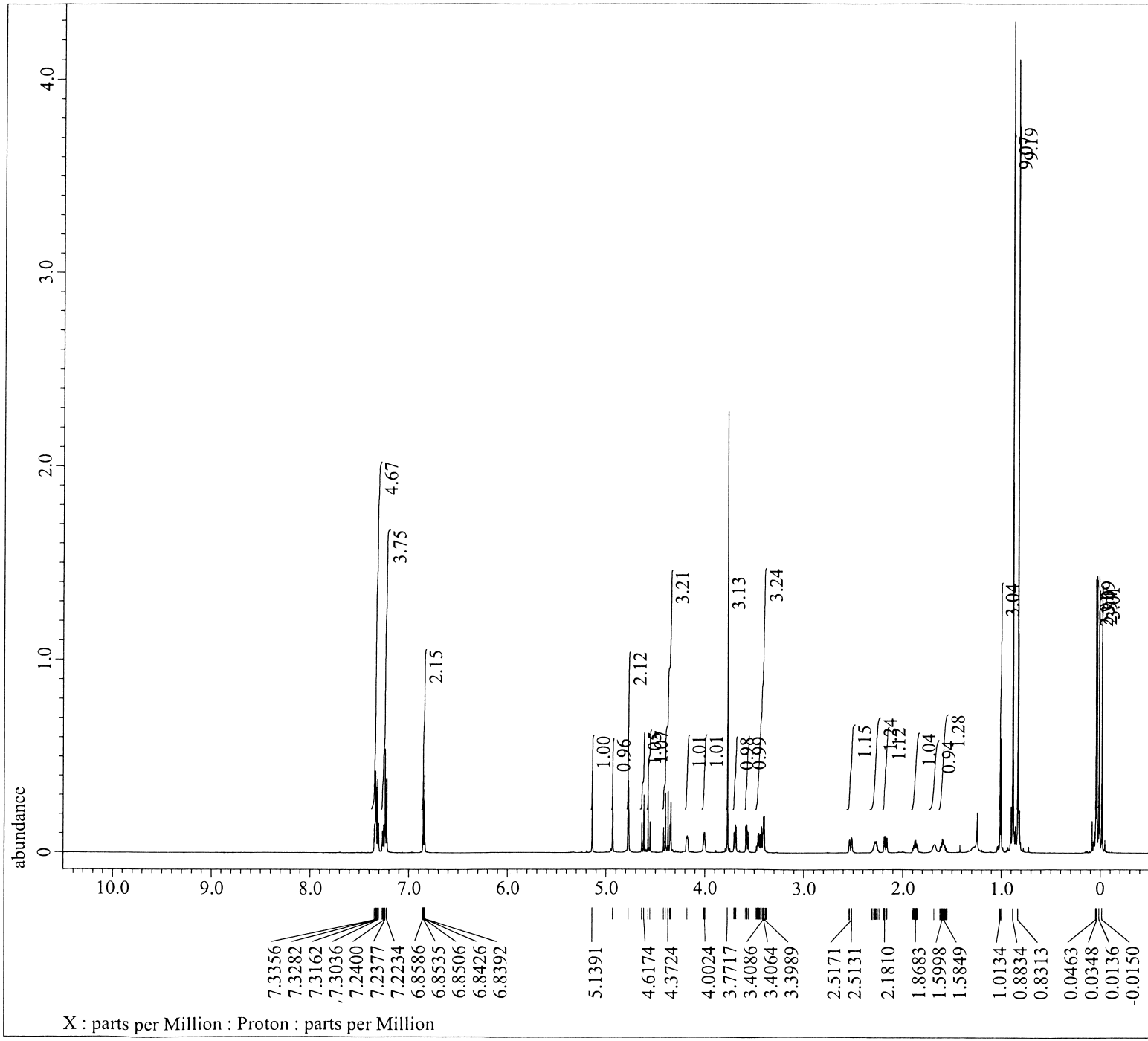
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 205.0
Total_Scans       = 205.0

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 23.4[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



29

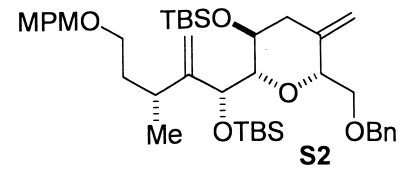



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-153-2
Solvent           = CHLOROFORM-D
Creation_Time     = 18-JUL-2010 02:38:52
Revision_Time     = 10-NOV-2010 21:36:15
Current_Time      = 10-NOV-2010 21:36:35

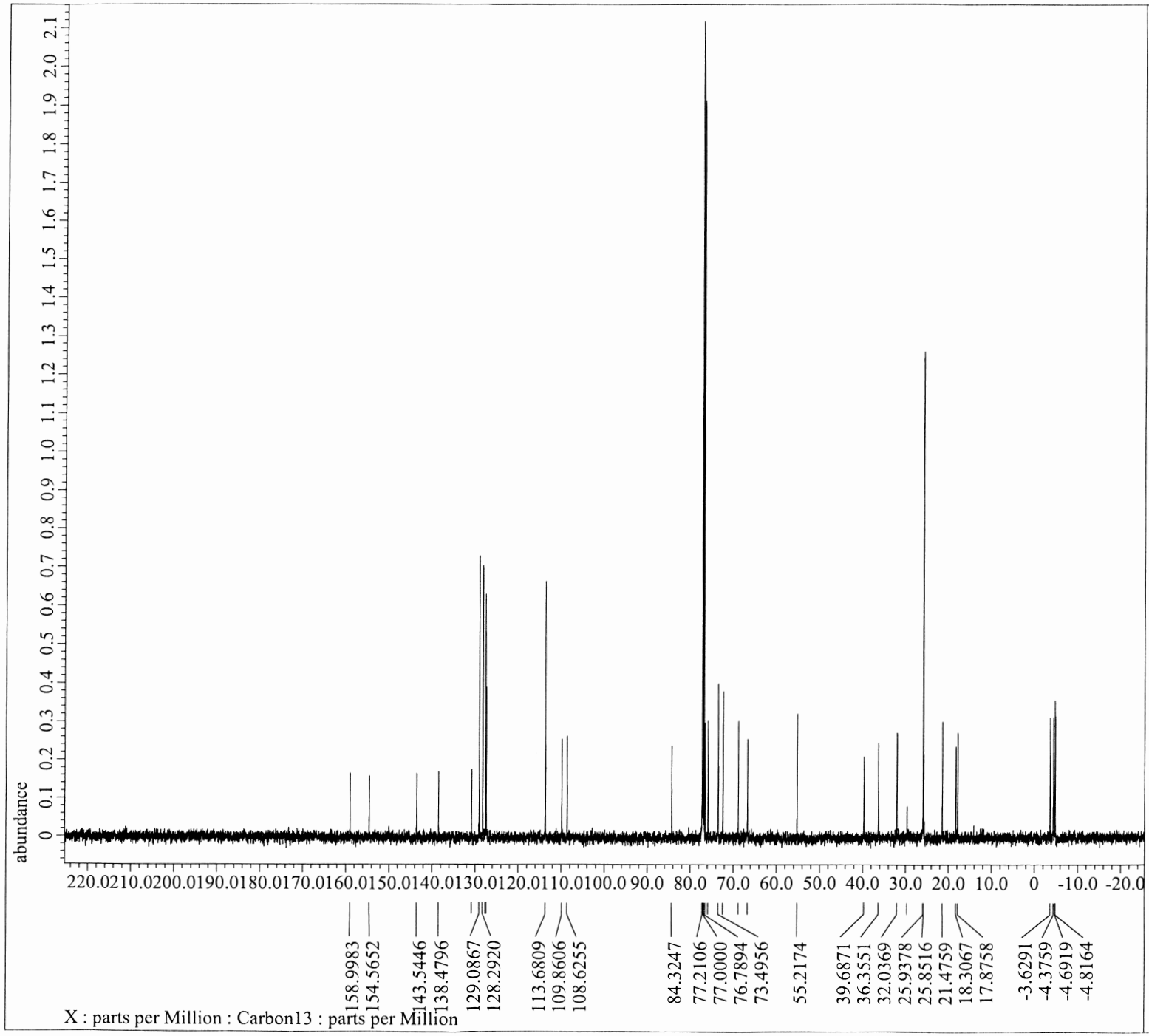
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 30
Temp_Get          = 22.4[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



S2

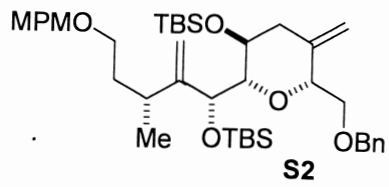



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-153-2
Solvent           = CHLOROFORM-D
Creation_Time     = 18-JUL-2010 02:41:18
Revision_Time     = 15-NOV-2010 13:43:49
Current_Time      = 15-NOV-2010 13:44:27

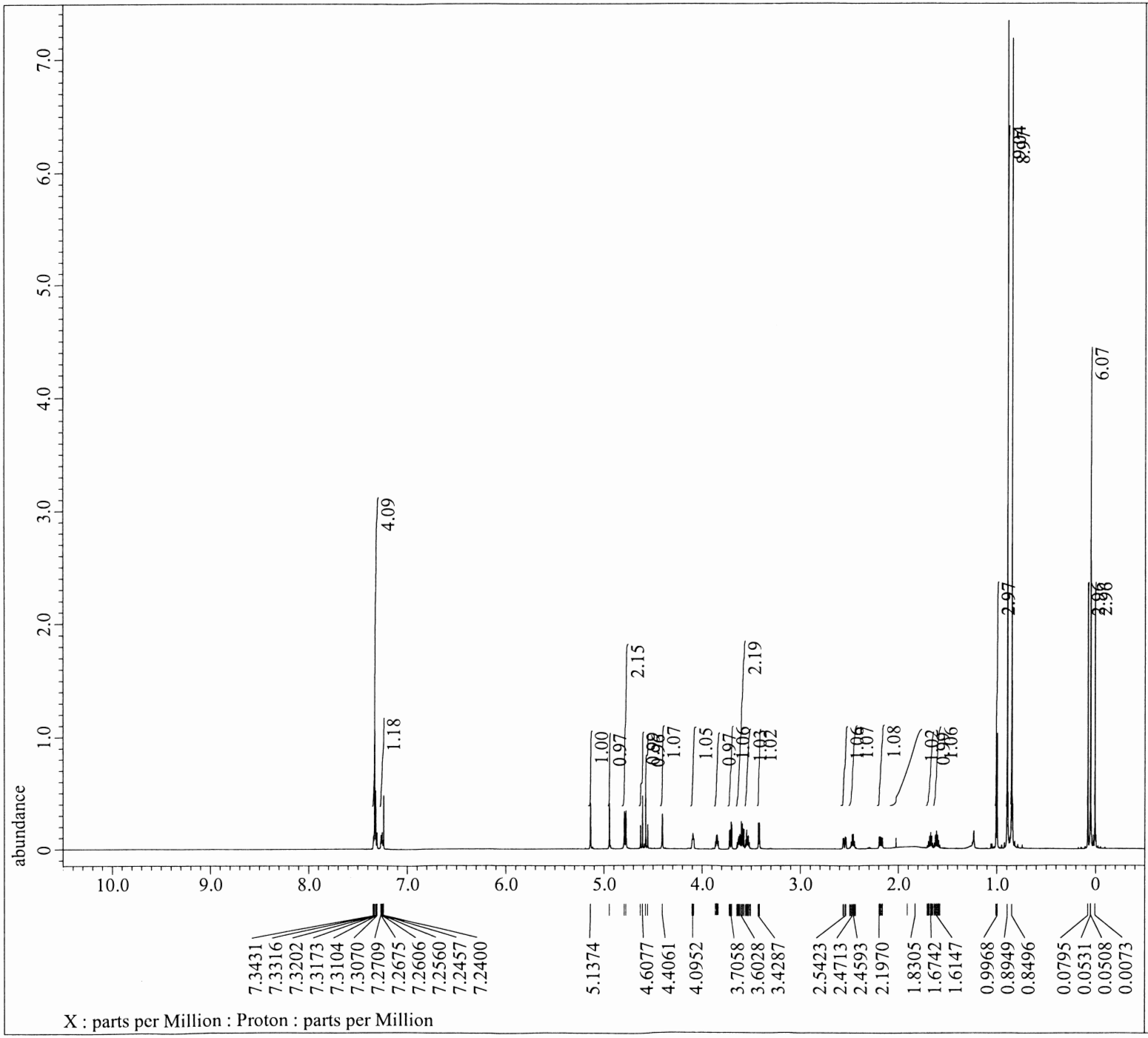
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 121
Total_Scans       = 121

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 22.9[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



S2

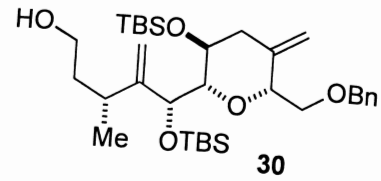



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-154
Solvent           = CHLOROFORM-D
Creation_Time     = 19-JUL-2010 00:19:20
Revision_Time     = 10-NOV-2010 21:51:08
Current_Time      = 10-NOV-2010 21:51:26

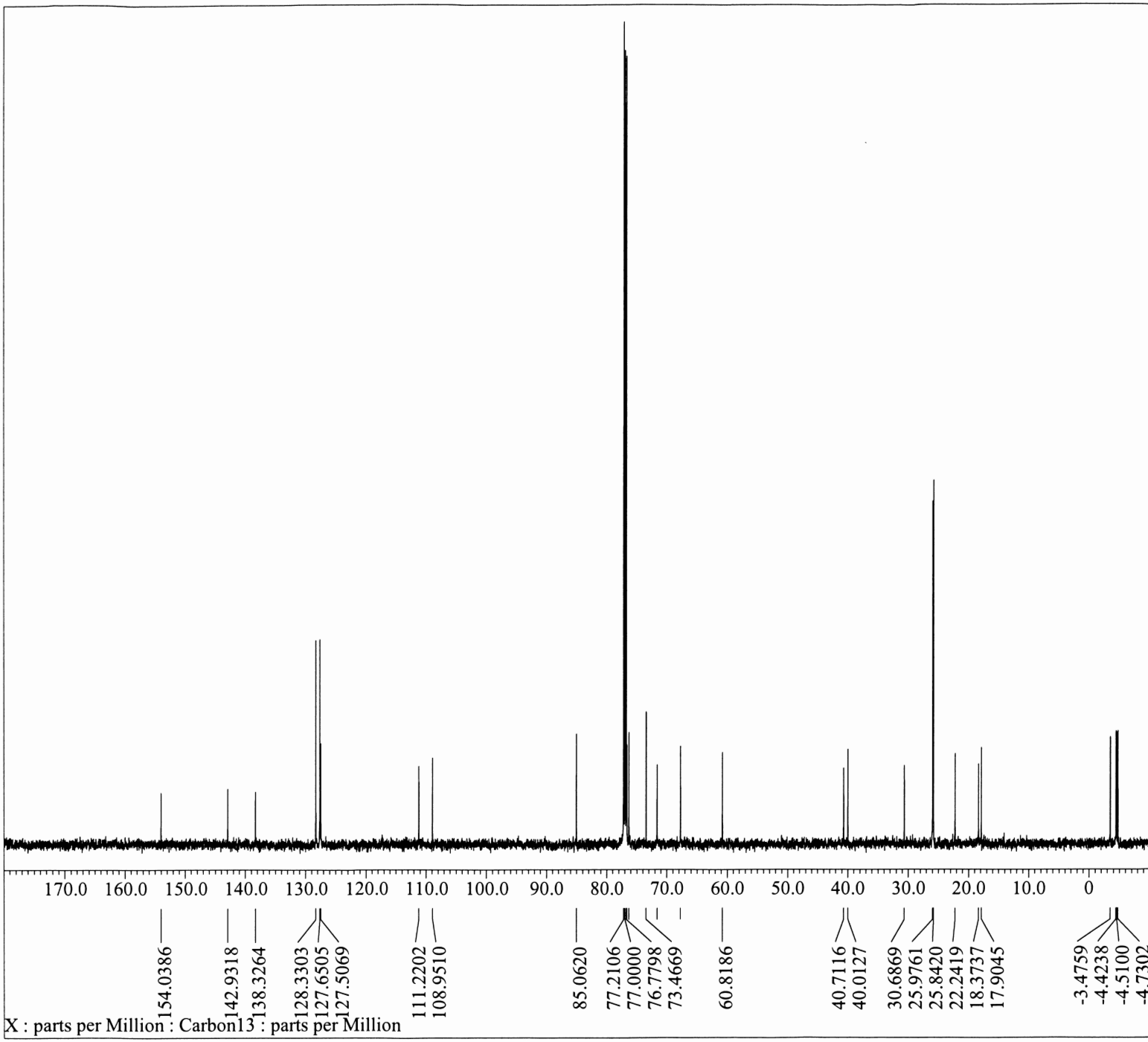
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 34
Temp_Get          = 22.3[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



30

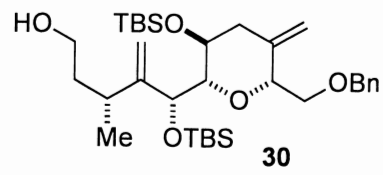



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-154
Solvent           = CHLOROFORM-D
Creation_Time     = 19-JUL-2010 00:21:47
Revision_Time     = 19-JUL-2010 00:35:42
Current_Time      = 19-JUL-2010 00:35:50

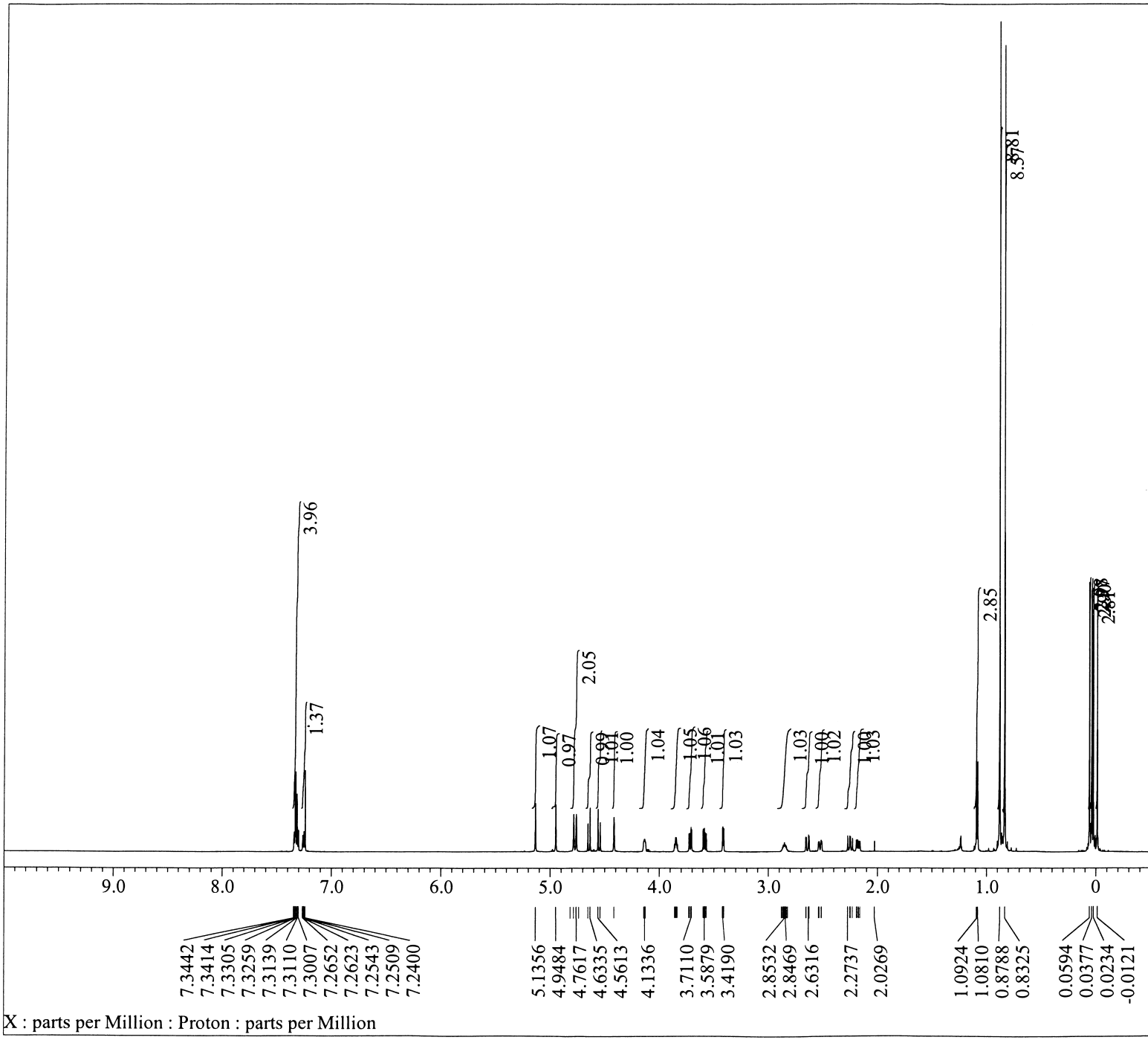
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 181
Total_Scans       = 181

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23[dC]
```



30

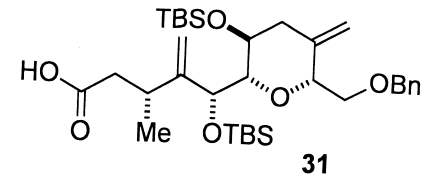



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-158
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUL-2010 18:06:39
Revision_Time     = 23-JUL-2010 18:13:40
Current_Time      = 23-JUL-2010 18:14:09

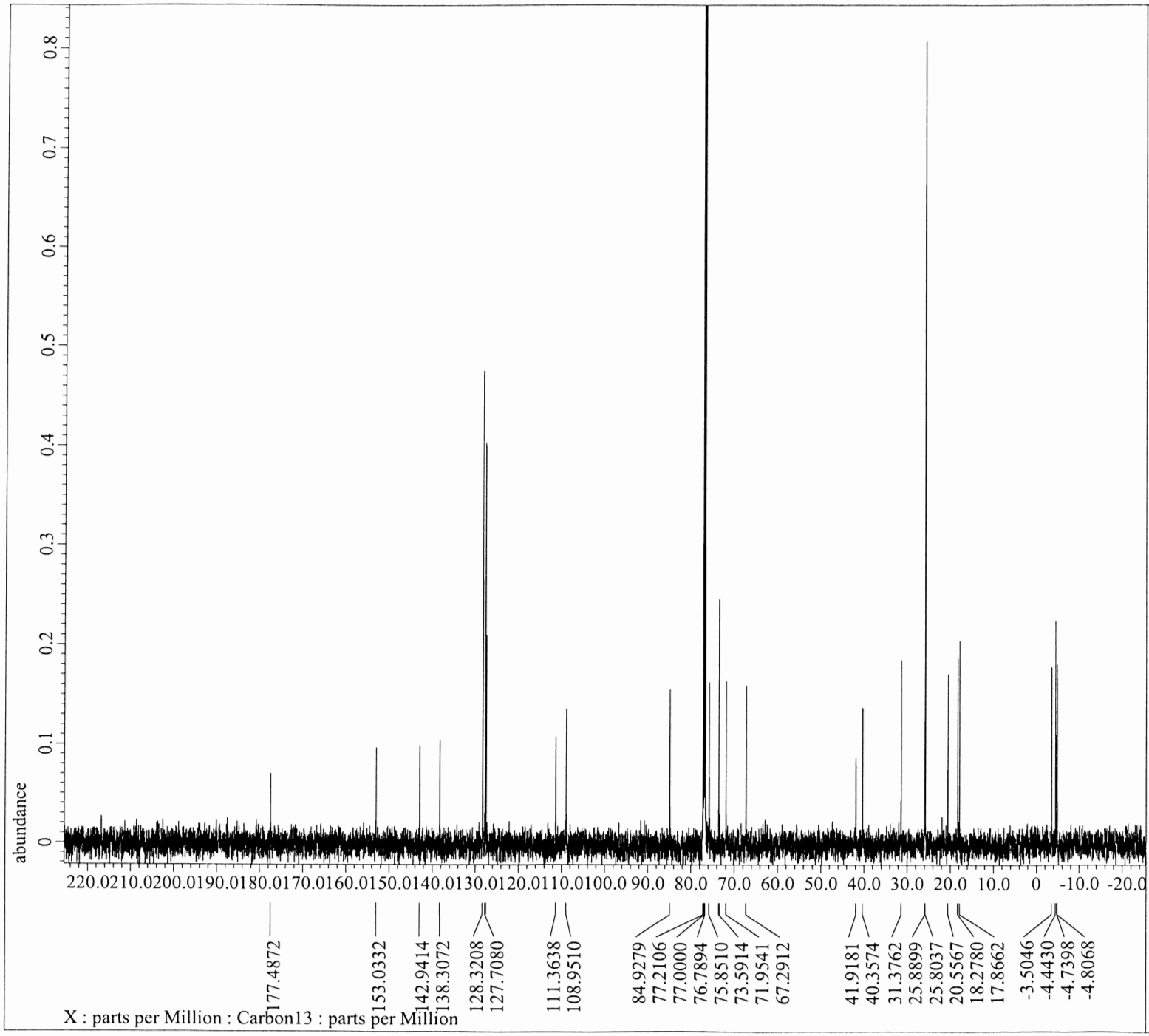
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 36
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.5[dC]
```



31

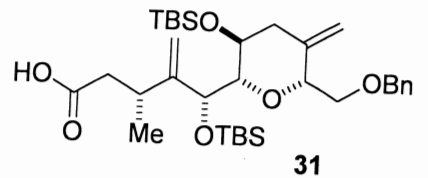



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-158
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUL-2010 18:09:58
Revision_Time     = 26-NOV-2010 17:39:18
Current_Time      = 26-NOV-2010 18:29:14

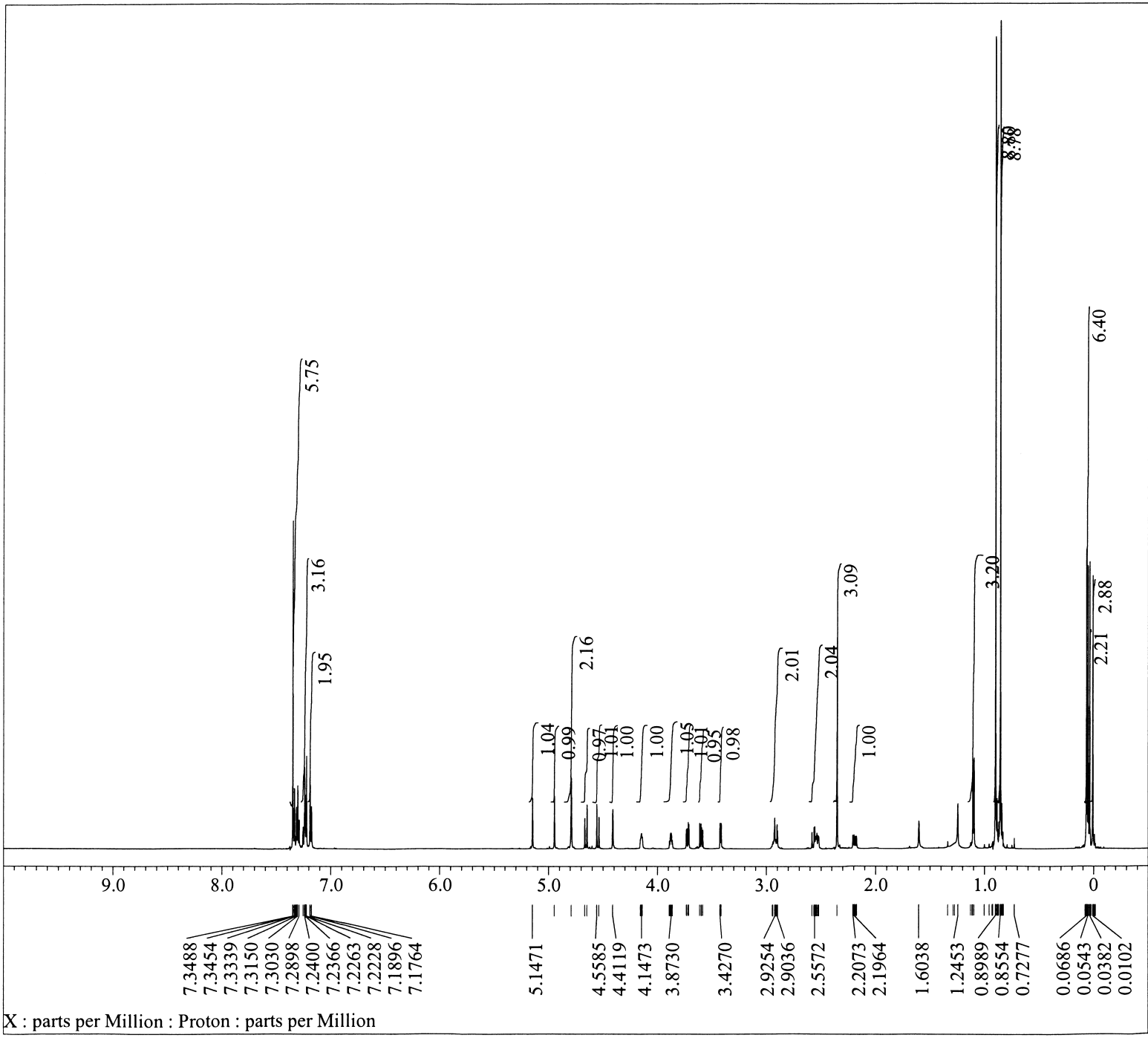
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 128
Total_Scans       = 128

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 23.4[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



31

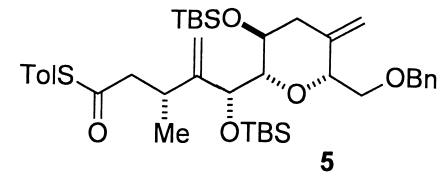



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-160
Solvent           = CHLOROFORM-D
Creation_Time     = 28-JUL-2010 13:26:18
Revision_Time     = 28-JUL-2010 13:29:12
Current_Time      = 28-JUL-2010 13:29:22

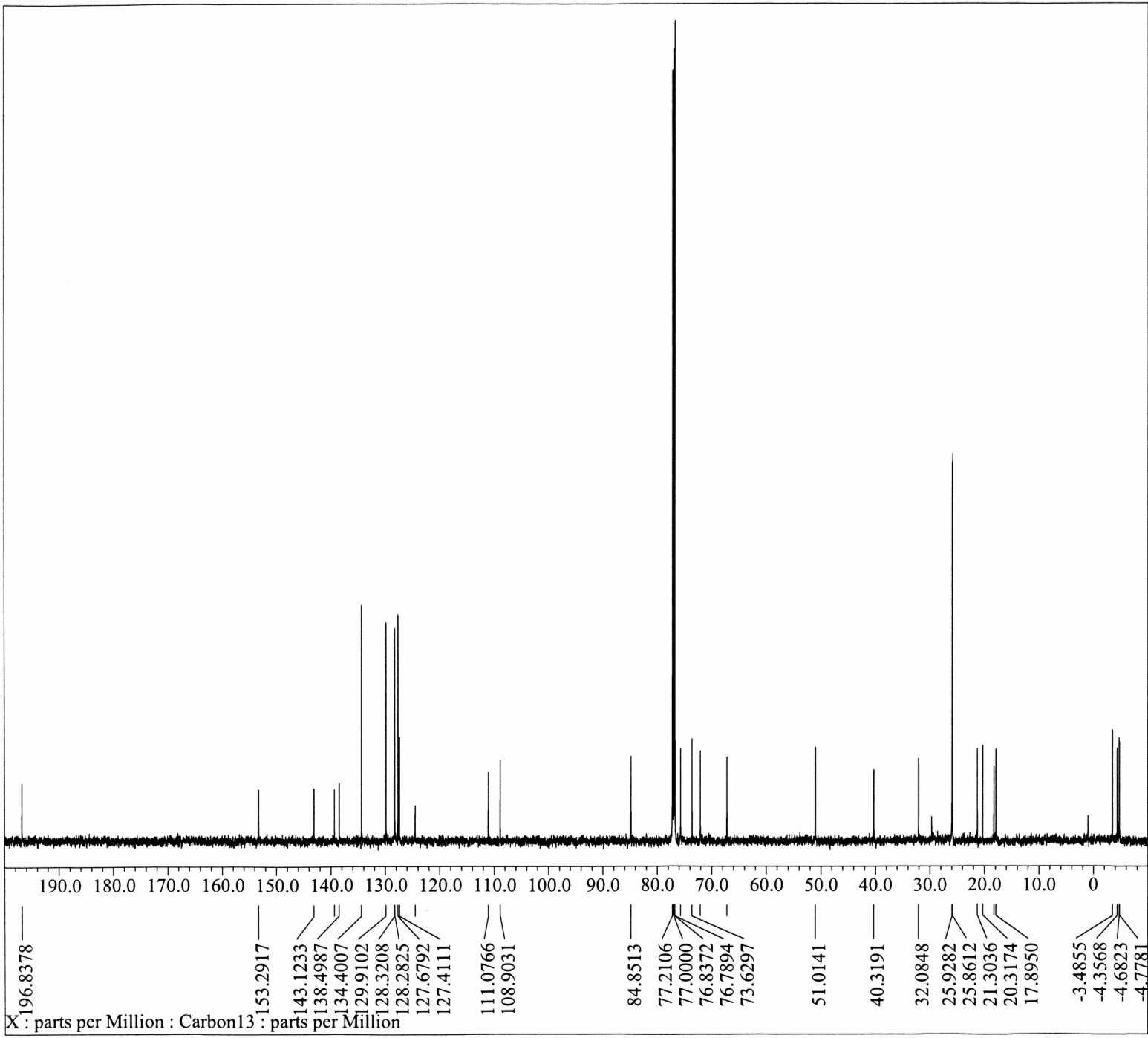
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 5[us]
Scans             = 8
Total_Scans       = 8

X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Recvr_Gain        = 34
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.6[dC]
```



5

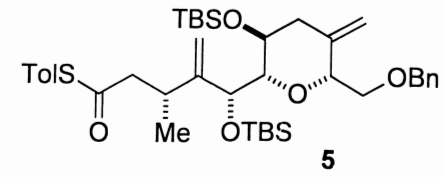



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-160
Solvent           = CHLOROFORM-D
Creation_Time     = 28-JUL-2010 13:28:36
Revision_Time     = 28-JUL-2010 13:37:09
Current_Time      = 28-JUL-2010 13:37:43

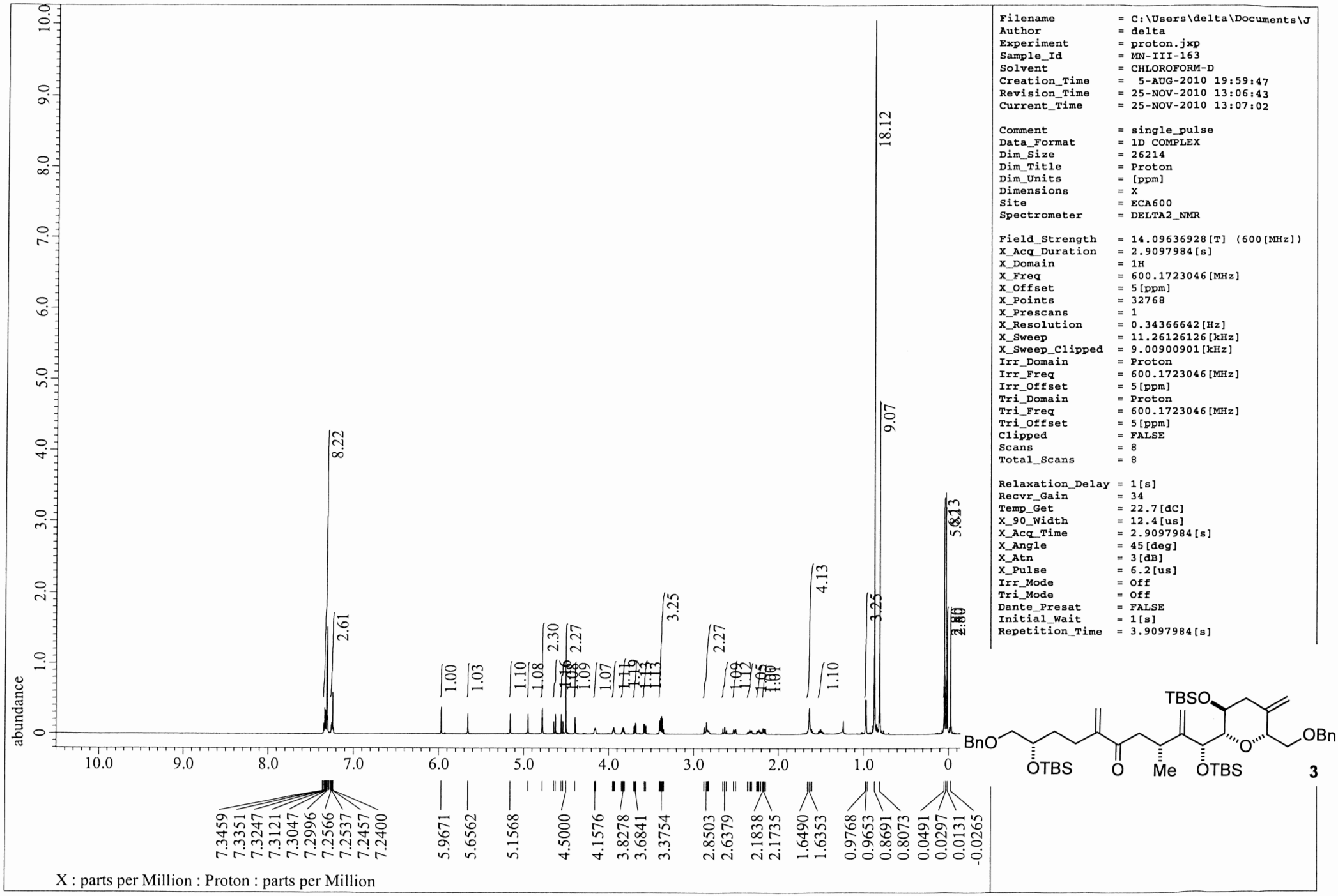
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

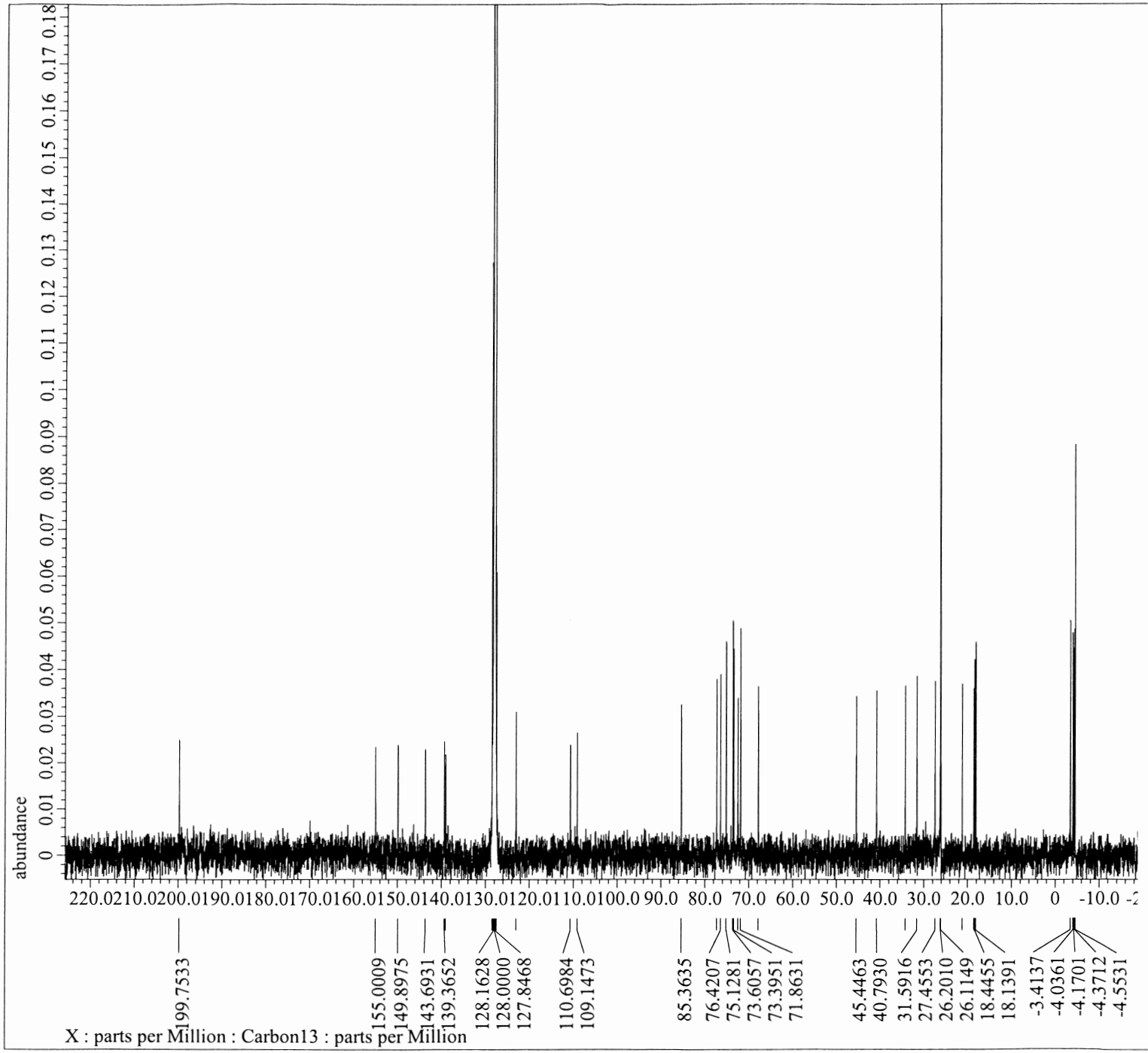
Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Mod_Return        = 1
Probe_Recovery    = 20[us]
Scans             = 196
Total_Scans       = 196

X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Recvr_Gain        = 56
Relaxation_Delay  = 2[s]
Repetition_Time   = 2.69206016[s]
Temp_Get          = 23.4[dC]
```



5


abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.22
2.61
2.30
2.27
3.25
4.13
18.12
9.07
5.61
5.13
1.00
1.03
1.10
1.08
1.09
1.07
1.10
2.27
3.25
4.13
1.10
7.3459
7.3351
7.3247
7.3121
7.3047
7.2996
7.2566
7.2537
7.2457
7.2400
5.9671
5.6562
5.1568
4.5000
4.1576
3.8278
3.6841
3.3754
2.8503
2.6379
2.1838
2.1735
1.6490
1.6353
0.9768
0.9653
0.8691
0.8073
0.0491
0.0297
0.0131
-0.0265
X : parts per Million : Proton : parts per Million
Filename = C:\Users\delta\Documents\J
Author = delta
Experiment = proton.jxp
Sample_Id = MN-III-163
Solvent = CHLOROFORM-D
Creation_Time = 5-AUG-2010 19:59:47
Revision_Time = 25-NOV-2010 13:06:43
Current_Time = 25-NOV-2010 13:07:02
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = ECA600
Spectrometer = DELTA2_NMR
Field_Strength = 14.09636928[T] (600[MHz])
X_Acq_Duration = 2.9097984[s]
X_Domain = 1H
X_Freq = 600.1723046[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.34366642[Hz]
X_Sweep = 11.26126126[kHz]
X_Sweep_Clipped = 9.00900901[kHz]
Irr_Domain = Proton
Irr_Freq = 600.1723046[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 600.1723046[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 1[s]
Recvr_Gain = 34
Temp_Get = 22.7[dC]
X_90_Width = 12.4[us]
X_Acq_Time = 2.9097984[s]
X_Angle = 45[deg]
X_Atn = 3[dB]
X_Pulse = 6.2[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 3.9097984[s]
TBSO
BnO
OBn
OTBS
O
Me
OTBS
3

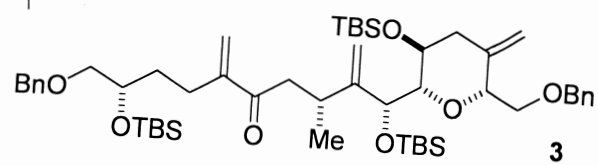



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-163_c6d6
Solvent           = BENZENE-D6
Creation_Time     =  6-AUG-2010 17:21:39
Revision_Time     = 26-NOV-2010 18:47:21
Current_Time      = 26-NOV-2010 18:47:39

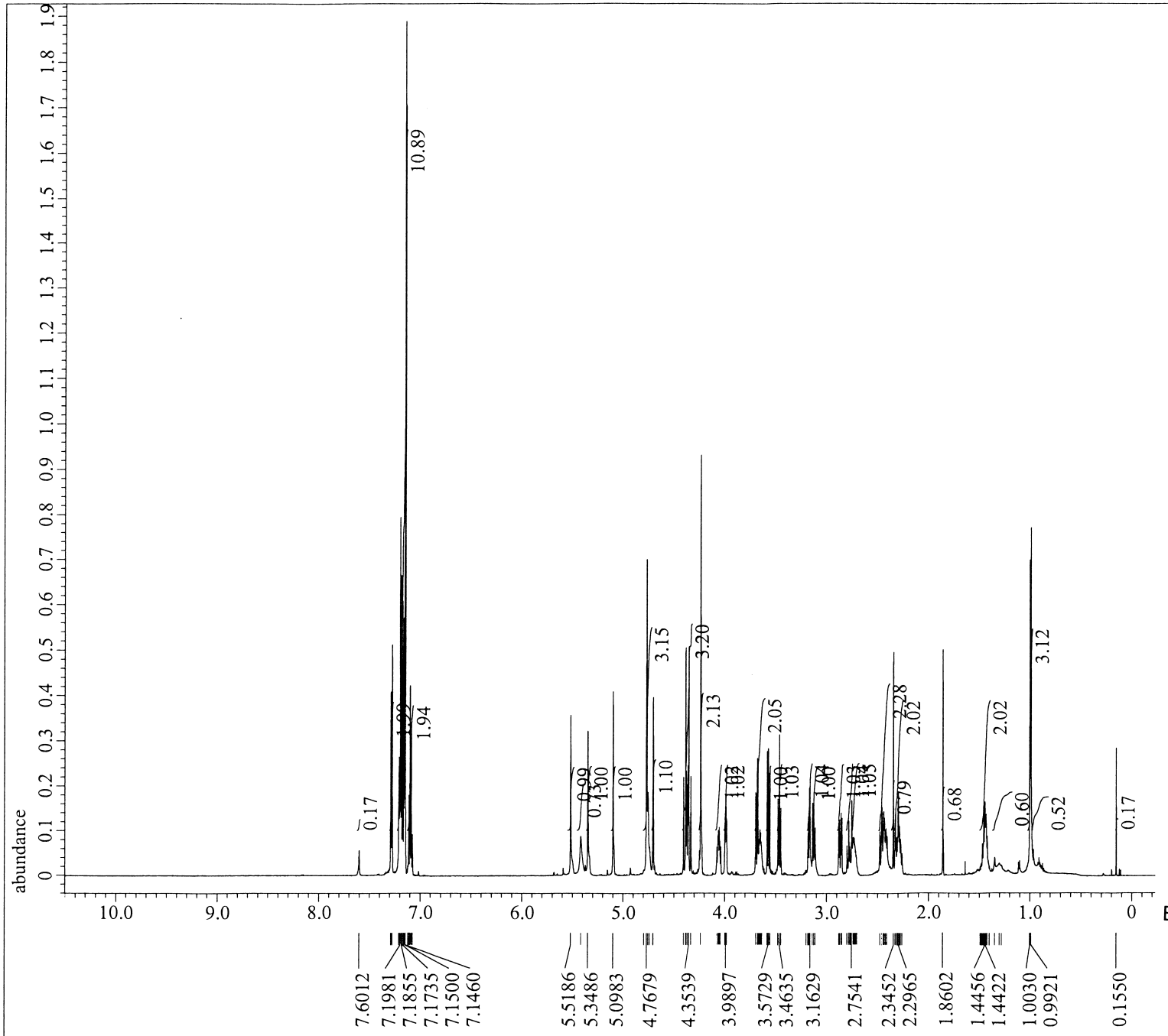
Comment           = single pulse decoupled gat
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 480
Total_Scans       = 480

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 23.6[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



3

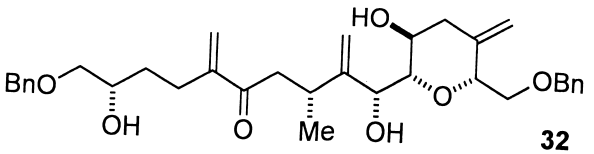



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-165
Solvent           = BENZENE-D6
Creation_Time     = 11-AUG-2010 20:13:09
Revision_Time     = 15-NOV-2010 19:28:43
Current_Time      = 15-NOV-2010 19:29:08

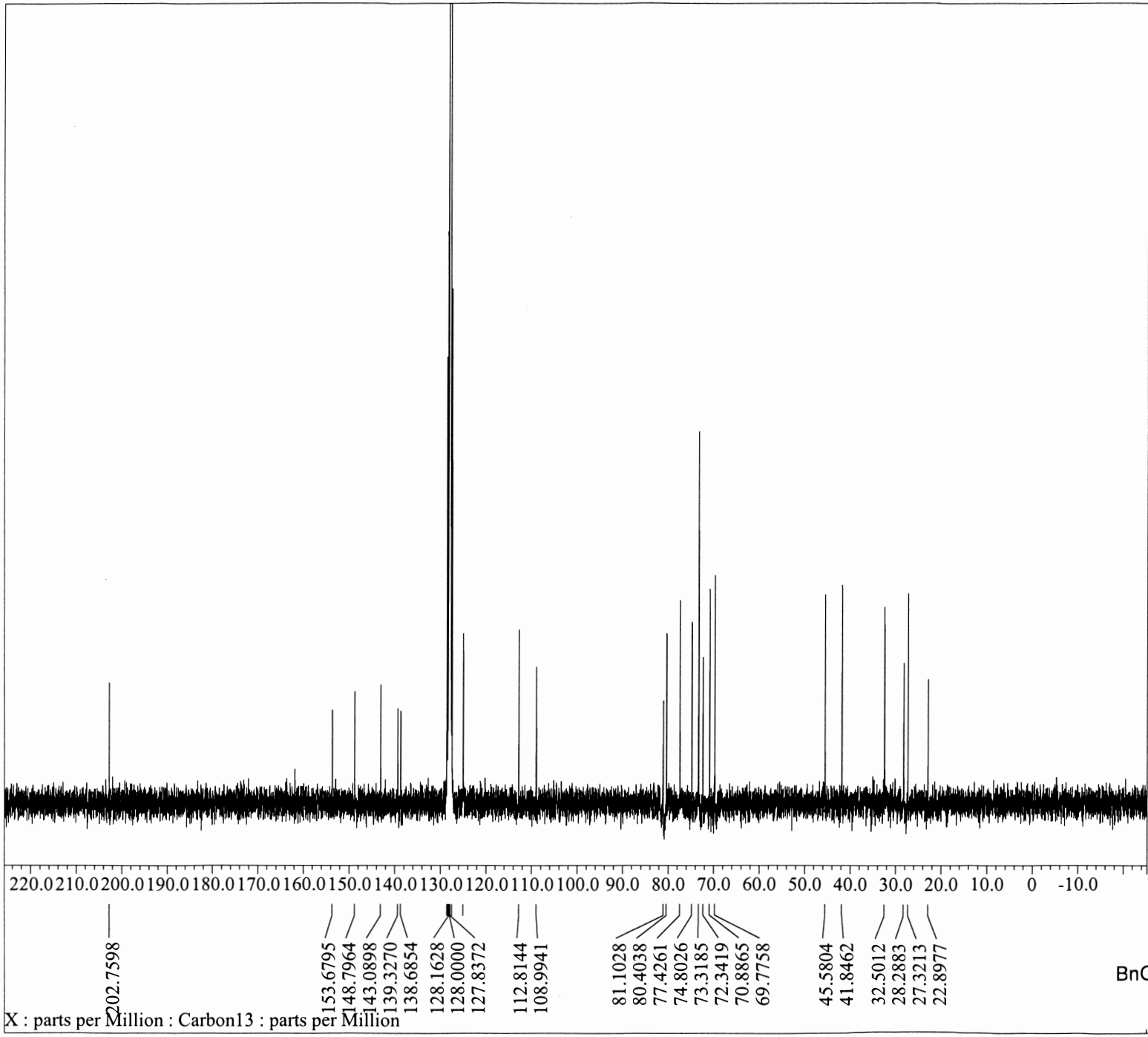
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

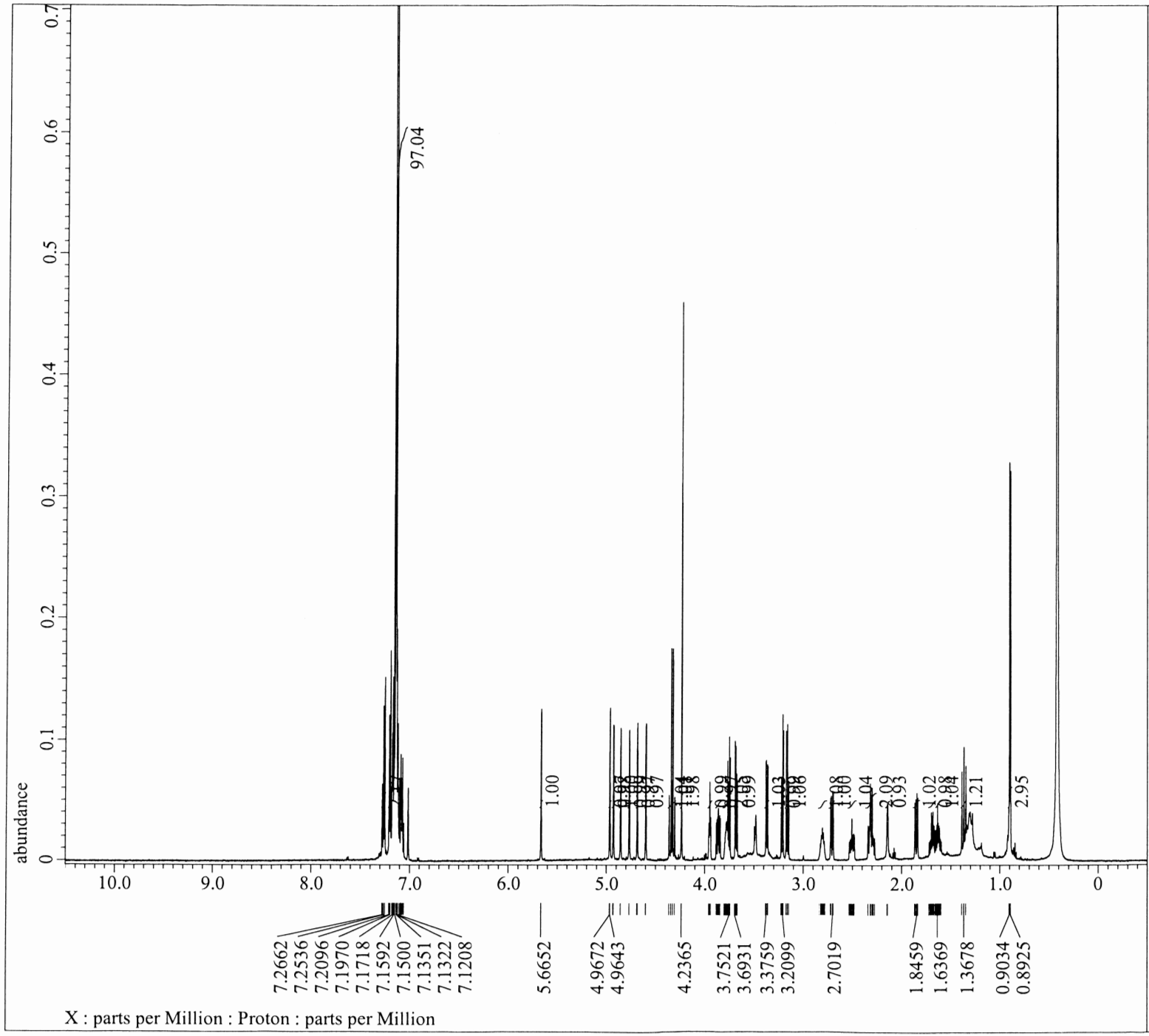
Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 38
Temp_Get          = 22.8[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



32


Filename = C:\Users\delta\Documents\J
Author = delta
Experiment = carbon.jxp
Sample_Id = MN-III-165
Solvent = BENZENE-D6
Creation_Time = 11-AUG-2010 20:15:29
Revision_Time = 11-AUG-2010 20:29:36
Current_Time = 11-AUG-2010 20:31:33
Comment = single pulse decoupled gat
Data_Format = 1D REAL
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = ECA600
Spectrometer = DELTA2_NMR
Field_Strength = 14.09636928[T] (600[MHz])
X_Acq_Duration = 0.69206016[s]
X_Domain = 13C
X_Freq = 150.91343039[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.44496109[Hz]
X_Sweep = 47.34848485[kHz]
X_Sweep_Clipped = 37.87878788[kHz]
Irr_Domain = Proton
Irr_Freq = 600.1723046[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Mod_Return = 1
Probe_Recovery = 20[us]
Scans = 188
Total_Scans = 188
X_90_Width = 8.4[us]
X_Acq_Time = 0.69206016[s]
X_Angle = 30[deg]
X_Atn = 6.4[dB]
X_Pulse = 2.8[us]
Irr_Atn_Dec = 18[dB]
Irr_Atn_Noe = 18[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 76[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Recvr_Gain = 50
Relaxation_Delay = 2[s]
Repetition_Time = 2.69206016[s]
Temp_Get = 23.5[dC]
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
202.7598
153.6795
148.7964
143.0898
139.3270
138.6854
128.1628
128.0000
127.8372
112.8144
108.9941
81.1028
80.4038
77.4261
74.8026
73.3185
72.3419
70.8865
69.7758
45.5804
41.8462
32.5012
28.2883
27.3213
22.8977
X : parts per Million : Carbon13 : parts per Million
HO
BnO
OBn
OH
O
Me
OH
O
32

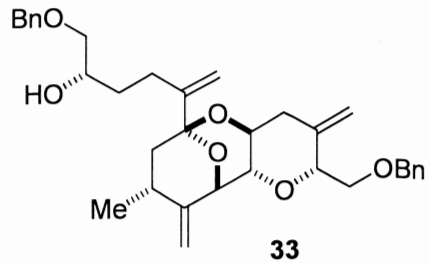



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-180-B
Solvent           = BENZENE-D6
Creation_Time     = 16-SEP-2010 10:19:05
Revision_Time     = 26-NOV-2010 20:50:12
Current_Time      = 26-NOV-2010 20:51:14

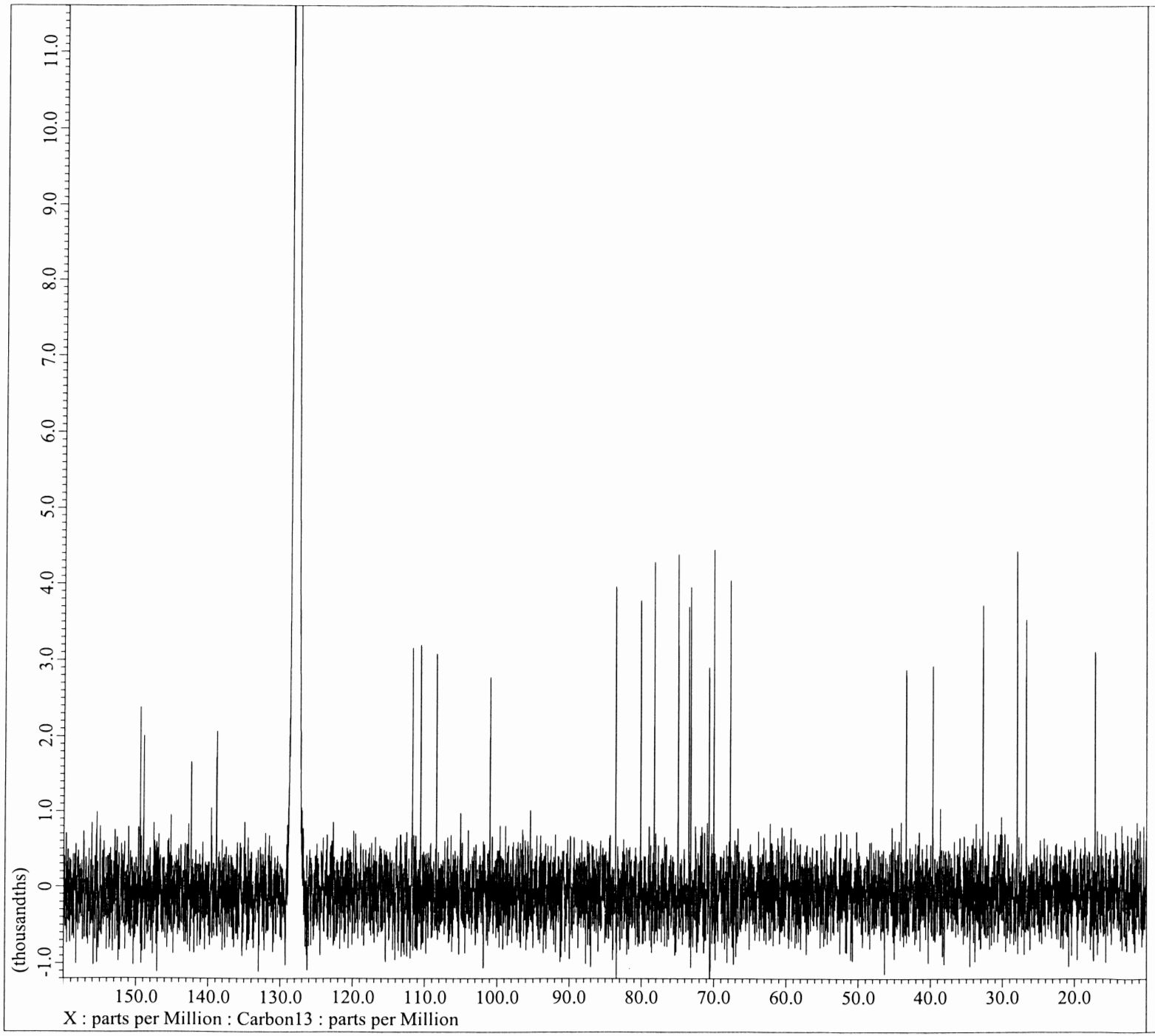
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 133
Total_Scans       = 133

Relaxation_Delay  = 1[s]
Recvr_Gain        = 54
Temp_Get          = 22.2[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



33

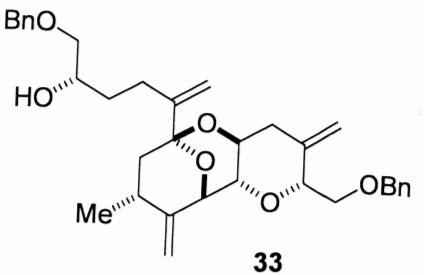



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-180-B
Solvent           = BENZENE-D6
Creation_Time     = 20-SEP-2010 20:32:33
Revision_Time     = 26-NOV-2010 19:14:33
Current_Time      = 26-NOV-2010 19:14:43

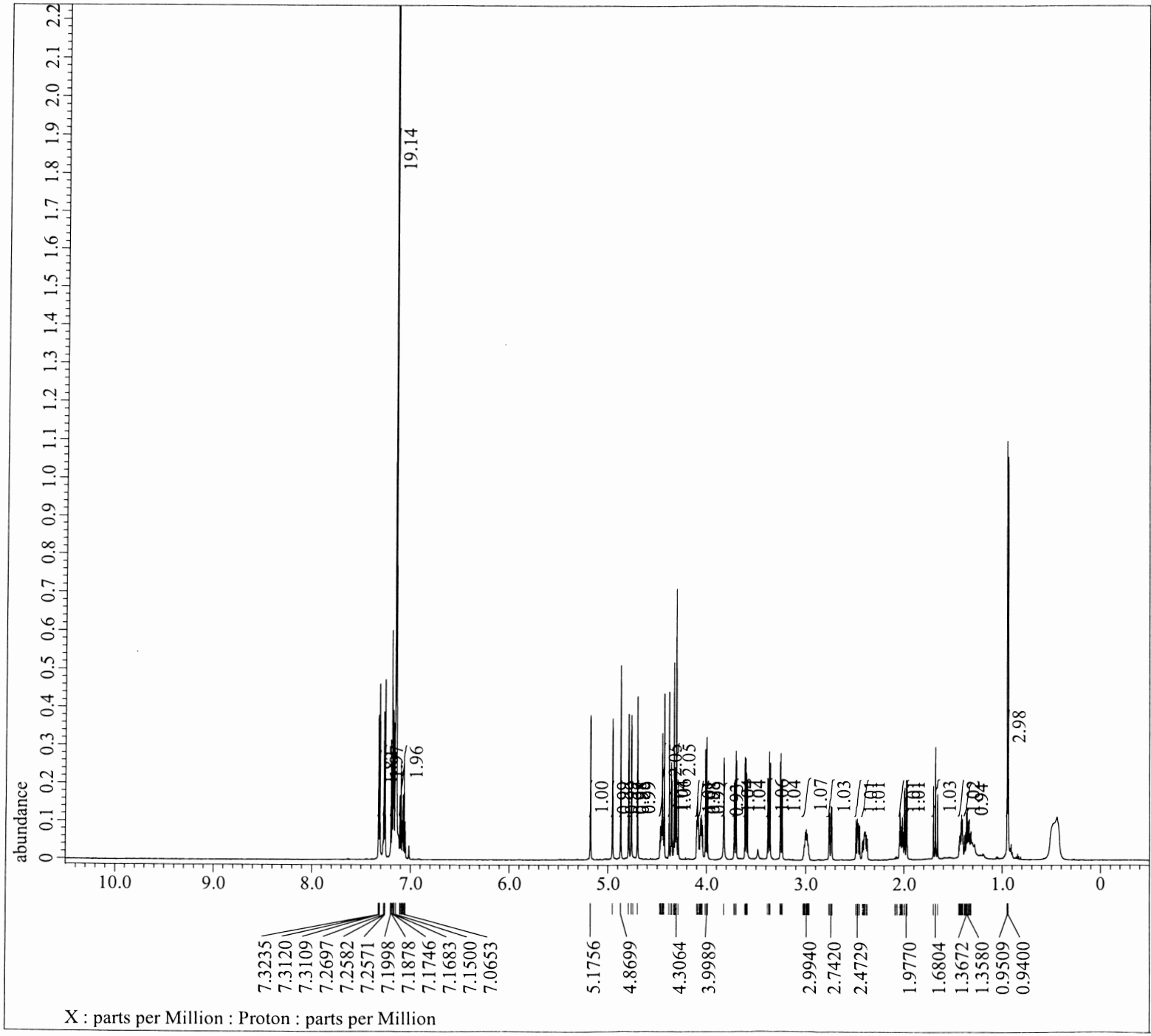
Comment           = single pulse decoupled gat
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16816
Total_Scans       = 16816

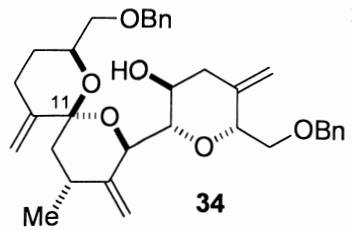
Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 23[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



33

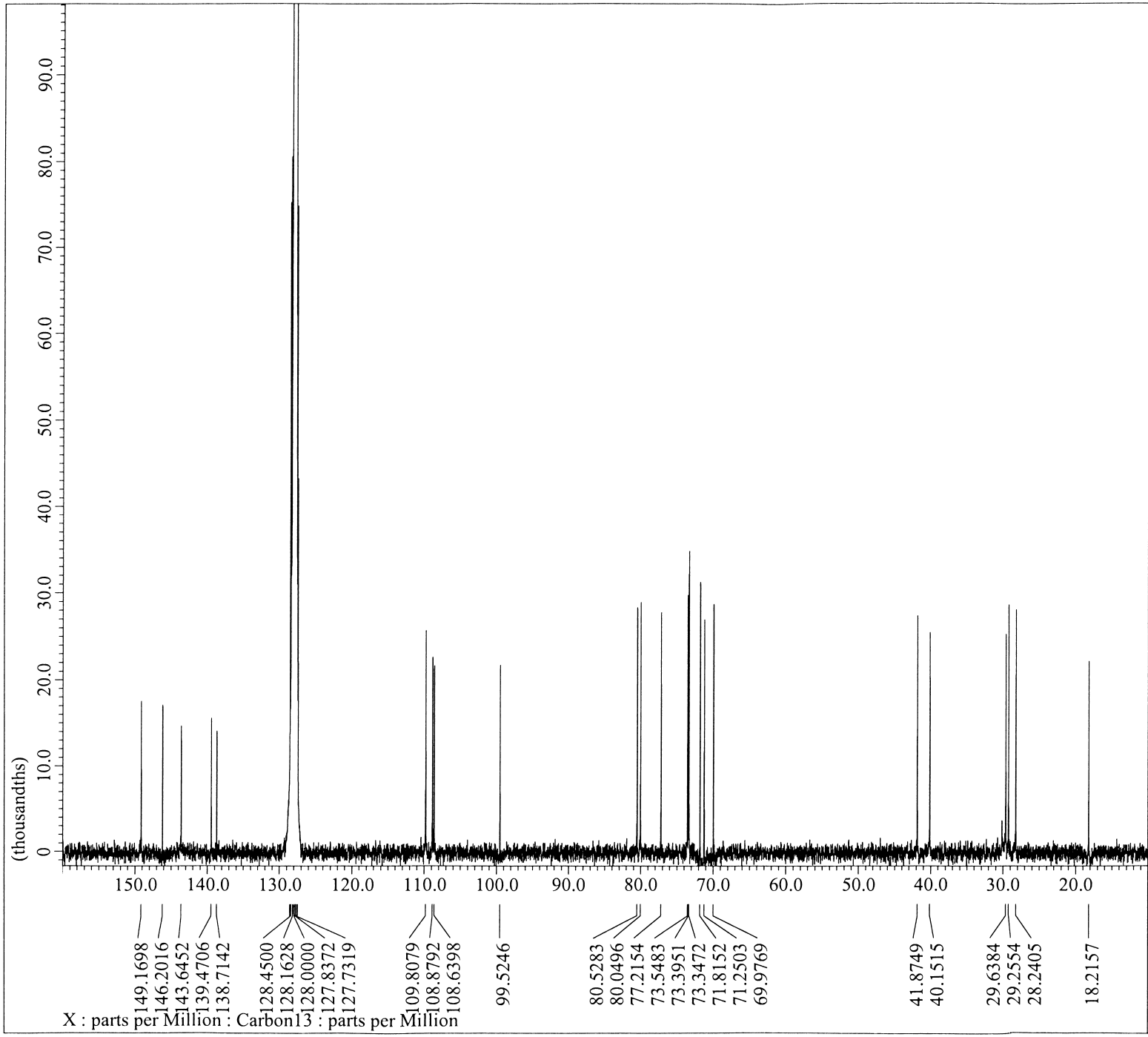


Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= proton.jxp
Sample_Id	= MN-III-180-A-ushiro
Solvent	= BENZENE-D6
Creation_Time	= 16-SEP-2010 10:10:23
Revision_Time	= 26-NOV-2010 20:40:08
Current_Time	= 26-NOV-2010 20:40:36
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 2.9097984[s]
X_Domain	= 1H
X_Freq	= 600.1723046[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.34366642[Hz]
X_Sweep	= 11.26126126[kHz]
X_Sweep_Clipped	= 9.00900901[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 600.1723046[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 45
Total_Scans	= 45
Relaxation_Delay	= 1[s]
Recvr_Gain	= 50
Temp_Get	= 22.1[dC]
X_90_Width	= 12.4[us]
X_Acq_Time	= 2.9097984[s]
X_Angle	= 45[deg]
X_Atn	= 3[dB]
X_Pulse	= 6.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Repetition_Time	= 3.9097984[s]



34

11*R*, unnatural

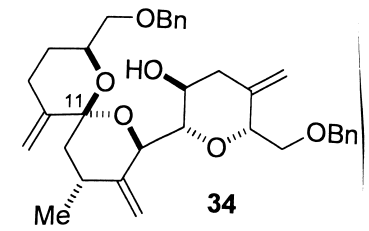



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-180-A-ushiro
Solvent           = BENZENE-D6
Creation_Time     = 19-SEP-2010 15:31:08
Revision_Time     = 26-NOV-2010 19:36:02
Current_Time      = 26-NOV-2010 19:36:56

Comment           = single pulse decoupled gat
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

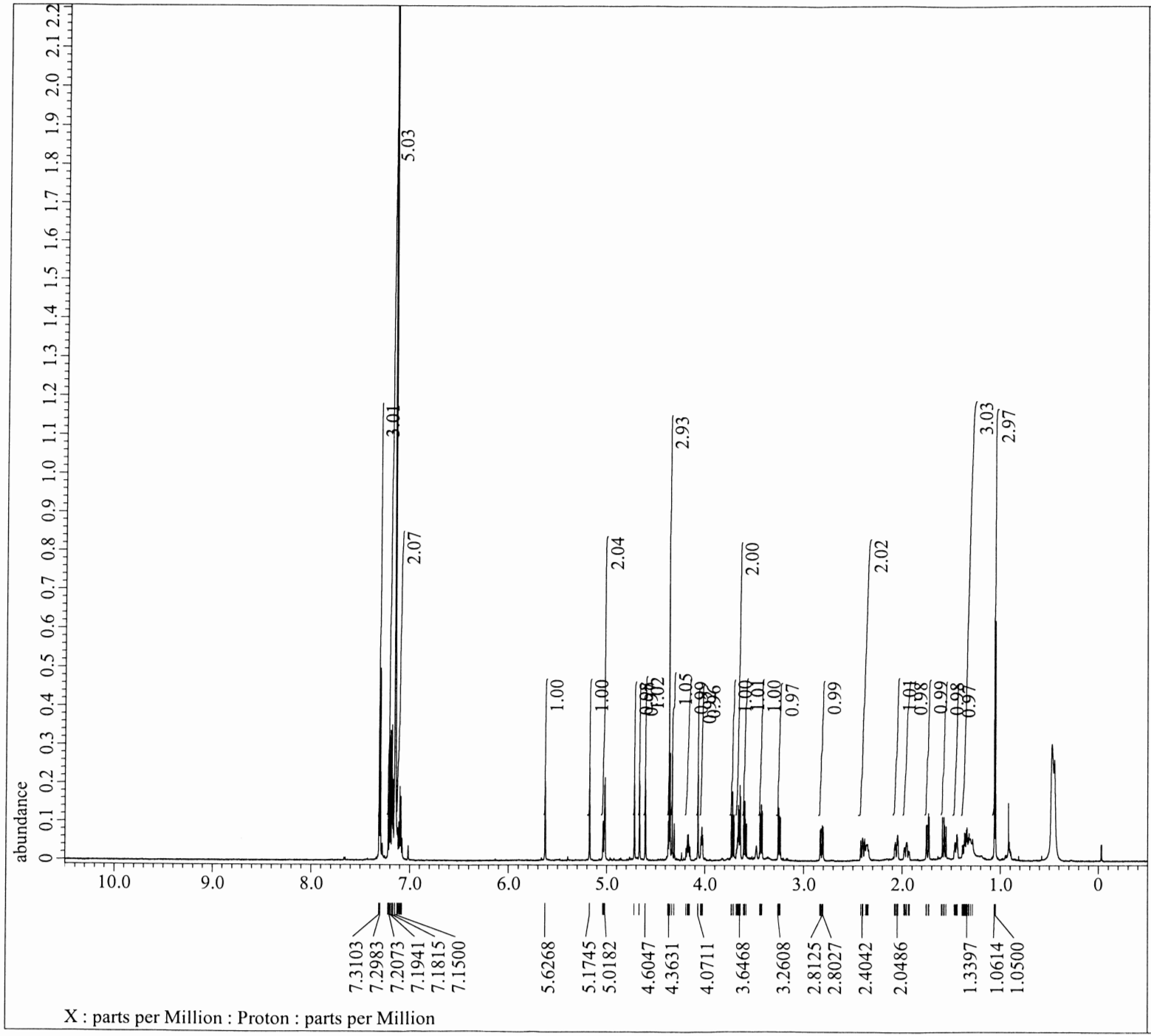
Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 10000
Total_Scans       = 10000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 52
Temp_Get          = 23.5[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



34

11*R*, unnatural

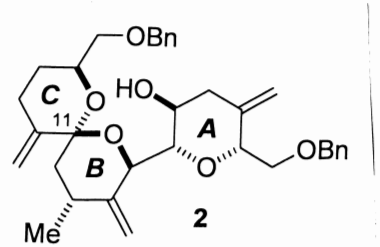



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MN-III-180-A-before
Solvent           = BENZENE-D6
Creation_Time     = 17-SEP-2010 00:50:45
Revision_Time     = 26-NOV-2010 20:29:23
Current_Time      = 26-NOV-2010 20:40:49

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

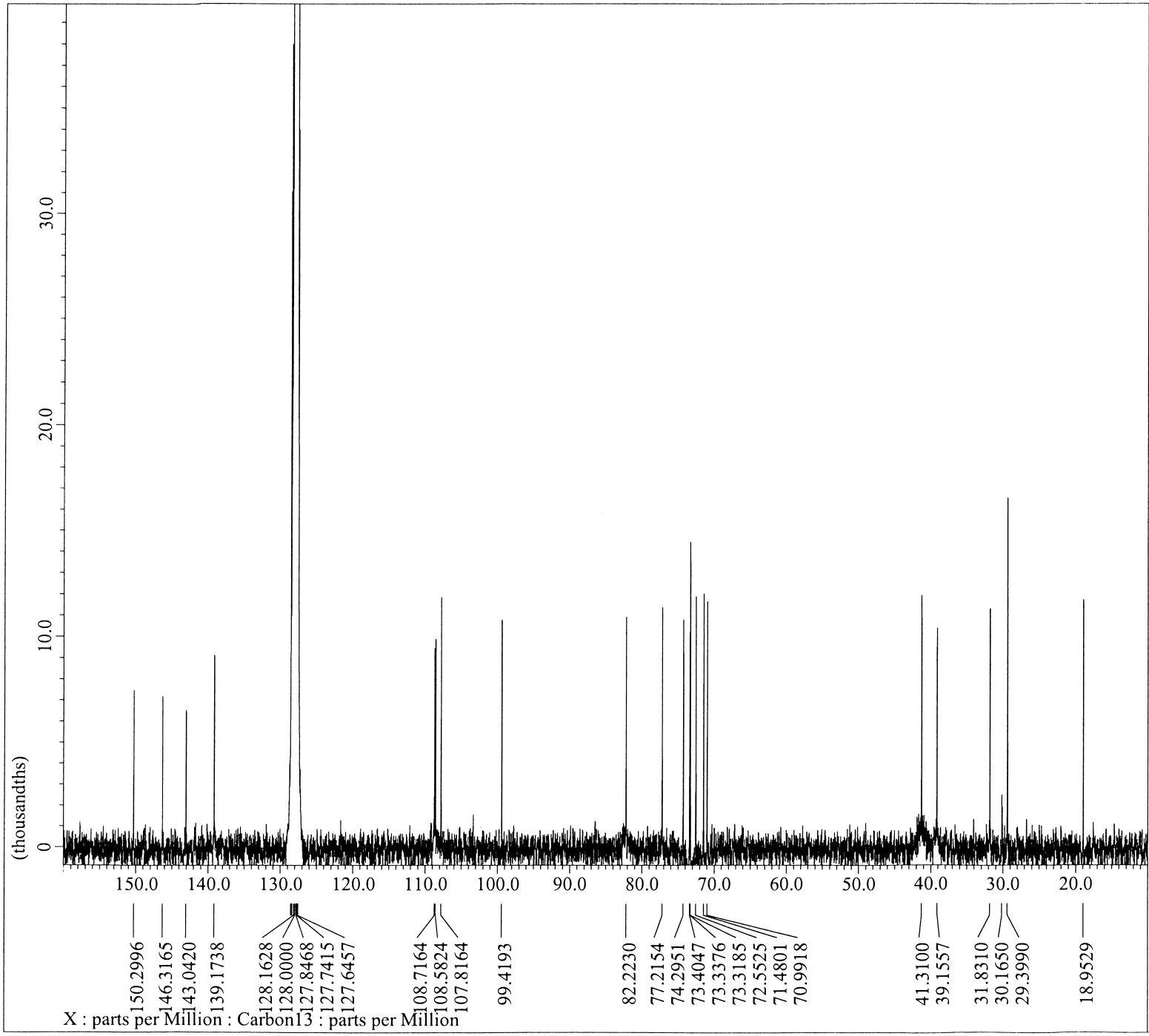
Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 2.9097984[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.34366642[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 1[s]
Recvr_Gain        = 50
Temp_Get          = 22.1[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



2

11*S*, natural

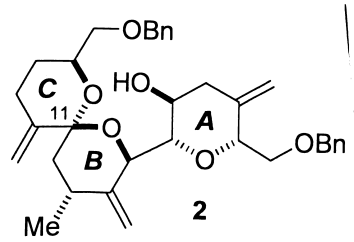



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = MN-III-180-A-before
Solvent           = BENZENE-D6
Creation_Time     = 17-SEP-2010 00:53:05
Revision_Time     = 26-NOV-2010 19:40:13
Current_Time      = 26-NOV-2010 19:41:02

Comment           = single pulse decoupled gat
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA600
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 10921
Total_Scans       = 10921

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 23.2[dC]
X_90_Width        = 8.4[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.8[us]
Irr_Atn_Dec       = 18[dB]
Irr_Atn_Noe       = 18[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 76[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```



2

11*S*, natural