Supporting Information for

Design and synthesis of skeletal analogues of gambierol: Attenuation of amyloid-β and tau pathology with voltage-gated potassium channel and *N*-methyl-D-aspartate receptor implications

Eva Alonso[†], Haruhiko Fuwa[#], Carmen Vale[†], Yuto Suga[#], Tomomi Goto[#], Yu Konno[#], Makoto Sasaki[#], Frank M. LaFerla[£], Mercedes R. Vieytes[+], Lydia Giménez-Llort[¶], and Luis M. Botana[†,]*

[†]*Departamento de Farmacología, Facultad de Veterinaria, Universidad de Santiago de Compostela, Lugo, Spain,* [#]*Graduate School of Life Sciences, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan,* [£]*Department of Neurobiology and Behavior, University of California, Irvine, Irvine, California 92697, USA,* [+]*Departamento de Fisiología, Facultad de Veterinaria, Universidad de Santiago de Compostela, 27003 Lugo, Spain, and* [¶]*Departamento de Psiquiatría y Medicina Legal, Instituto de Neurociencias, Universidad Autonoma de Barcelona, 08193 Bellaterra, Spain.*

*Corresponding Author. E-mail: Luis.Botana@usc.es, Phone/Fax:+34982252242.

Contents

General remarks for synthetic chemistry. 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 (THF), diethyl ether (Et_2O), 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. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride under reduced pressure. All other chemicals were purchased at highest commercial grade and used directly. Analytical thin-layer chromatography (TLC) and preparative TLC were 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). Melting points are uncorrected. Chemical shift values of ^1H and ^{13}C NMR spectra are reported in ppm (δ) downfield from tetramethylsilane with reference to internal residual solvent [^1H NMR, $CHCl_3$ (7.24), C_6HD_5 (7.15); ^{13}C NMR, $CDCl_3$ (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.

Experimental procedure and characterization data for all new compounds.

Alcohol 6. To a solution of methyl ester **4** (2.31 g, 5.86 mmol) in CH_2Cl_2 (60 mL) at –78 °C was added DIBALH (1.02 M solution in *n*-hexane, 6.03 mL, 6.15 mmol), and the resultant solution was stirred at –78 °C for 35 min. The reaction was quenched with MeOH. The mixture was diluted with EtOAc and saturated aqueous potassium sodium tartrate solution and stirred vigorously at room temperature until the layers became clear. The organic layer was separated and washed with brine, dried (Na_2SO_4), and filtered. Concentration under reduced pressure afforded a crude aldehyde, which was used in the next reaction without further purification.

To a suspension of $Ph_3P^+CH_3Br^-$ (7.32 g, 20.5 mmol) in THF (60 mL) at 0 °C was added NaHMDS (1.0 M solution in THF, 17.6 mL, 17.6 mmol), and the resultant suspension was stirred at 0 °C for 1 h. To this suspension was added a solution of the above crude aldehyde in THF (10mL) via cannula, and the resultant solution was stirred at 0 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the resultant mixture was extracted with EtOAc. The organic layer was washed with H_2O and brine, dried (Na_2SO_4), and filtered. Concentration under reduced pressure gave olefin **5**, which was used in the next reaction without further purification.

To a solution of the above olefin **5** in THF (40 mL) was added TBAF (1.0 M solution in THF, 15.2 mL, 15.2 mmol). The resultant solution was stirred at room temperature overnight and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (30% EtOAc/hexanes) gave alcohol **6** (1.39 g,

82% for the three steps) as a colorless oil: $[\alpha]_D^{24}$ –40.2 (*c* 1.00, $CHCl_3$); IR (KBr) 3435, 2978, 2940, 2871, 1115, 1093 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49—7.47 (m, 2H), 7.37—7.31 (m, 3H), 5.90 (m, 1H), 5.51 (s, 1H), 5.13 (dddd, *J* = 17.2, 1.7, 1.7, 1.4 Hz, 1H), 5.07 (dddd, *J* = 10.0, 1.7, 1.4, 1.0 Hz, 1H), 4.30 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.69 (dd, *J* = 10.3, 10.3 Hz, 1H), 3.54 (ddd, *J* = 13.4, 8.4, 4.1 Hz, 1H), 3.35 (ddd, *J* = 10.3, 9.3, 4.8 Hz, 1H), 3.31 (dd, *J* = 9.3, 3.5 Hz, 1H), 2.44 (ddddd, *J* = 14.8, 8.9, 3.4, 1.4, 1.4 Hz, 1H), 2.20 (dd, *J* = 11.6, 4.1 Hz, 1H), 2.15 (m, 1H), 1.77 (dd, *J* = 12.1, 12.1 Hz, 1H), 1.59 (br s, 1H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.4, 135.6, 129.1, 128.3 (2C), 126.1 (2C), 116.7, 101.7, 84.4, 76.6, 74.3, 71.4, 69.3, 45.0, 33.4, 21.9; HRMS (ESI) calcd for $C_{17}H_{22}O_4Na$ $[(M + Na)^+]$ 313.1410, found 313.1421.

Dihydropyran 8. To a suspension of $[Ir(cod)Cl]_2$ (1.8 mg, 0.00266 mmol) and Na_2CO_3 (5.6 mg, 0.0531 mmol) in toluene (1 mL) was added a solution of alcohol **6** (25.7 mg, 0.0885 mmol) and vinyl acetate (40 μL, 0.44 mmol) in toluene (1 mL) via cannula, and the resultant solution was stirred at 100 °C for 10 h. The reaction mixture was quenched with moist Et_2O, and the mixture was concentrated under reduced pressure. The residue was passed through a plug of silica gel (eluted with 2% EtOAc/hexanes) to afford crude vinyl ether **7**, which was used in the next reaction without further purification.

To a solution of the above crude vinyl ether **7** in benzene (2 mL, degassed by repeating freeze-thaw cycle three times) was added the Grubbs second-generation catalyst (1.5 mg, 0.00177 mmol), and the resultant solution was stirred at 60 °C for 16 h.

The reaction was quenched with Et_3N, and the mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (1 to 2% EtOAc/hexanes) afforded dihydropyran **8** (18.6 mg, 73% for the two steps) as a colorless crystals: mp 141—143 °C (hexane/EtOAc); $[\alpha]_D^{26}$ –13.1 (*c* 0.30, $CHCl_3$); IR (KBr) 1637, 1109, 1078, 1019, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49—7.47 (m, 2H), 7.38—7.31 (m, 3H), 6.15 (m, 1H), 5.54 (s, 1H), 4.65 (ddd, *J* = 5.8, 5.8, 2.0 Hz, 1H), 4.32 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.73 (dd, *J* = 10.3, 10.3 Hz, 1H), 3.69 (ddd, *J* = 12.1, 9.3, 4.5 Hz, 1H), 3.54 (dd, *J* = 10.7, 5.8 Hz, 1H), 3.47 (ddd, *J* = 10.0, 10.0, 4.8 Hz, 1H), 2.30 (dd, *J* = 11.3, 4.5 Hz, 1H), 2.20 (dddd, *J* = 16.4, 5.1, 5.1, 0.7 Hz, 1H), 1.94 (dddd, *J* = 16.4, 11.0, 2.1, 2.1 Hz, 1H), 1.87 (dd, *J* = 11.7, 11.7 Hz, 1H), 1.28 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 141.3, 138.5, 129.0, 128.3 (2C), 126.7 (2C), 101.9, 97.9, 77.7, 76.8, 75.3, 74.2, 69.3, 42.5, 24.0, 16.9; HRMS (EI) calcd for $C_{17}H_{20}O_4$ (M^+) 288.1362, found 288.1365.

Acetal 9. To a solution of dihydropyran **8** (950 mg, 3.29 mmol) in EtOH/THF (2:1, v/v, 25 mL) was added Pd/C (300 mg) suspended in EtOH/THF (2:1, v/v, 5 mL), and the resultant suspension was stirred under an atmosphere of hydrogen (balloon) at room temperature for three days. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure to give a crude diol, which was used in the next reaction without further purification.

To a solution of the above diol in CH_2Cl_2 (25 mL) were added *p*-$MeOC_6H_4CH(OMe)_2$ (1.12 mL, 6.58 mmol) and PPTS (83 mg, 0.329 mmol), and the

resultant solution was stirred at room temperature for 3.5 h. The reaction was quenched with Et_3N, and the mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (10 to 20% EtOAc/hexanes) afforded acetal **9** (950 mg, 90% for the two steps) as a colorless oil: $[\alpha]_D^{26}$ –38.7 (*c* 0.16, $CHCl_3$); IR (KBr) 2941, 2872, 1517, 1249, 1093, 828 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41—7.38 (m, 2H), 6.88—6.85 (m, 2H), 5.48 (s, 1H), 4.28 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.78 (s, 3H), 3.73—3.67 (m, 3H), 3.61 (m, 1H), 3.47 (ddd, *J* = 9.7, 4.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 12.0, 3.8 Hz, 1H), 2.14 (dd, *J* = 11.3, 4.5 Hz, 1H), 1.88—1.68 (m, 3H), 1.63—1.55 (m, 2H), 1.30 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 160.5, 131.1, 128.1 (2C), 113.7 (2C), 102.1, 82.2, 77.6, 76.2, 73.1, 69.5, 59.5, 54.7, 43.9, 26.2, 24.4, 15.4; HRMS (ESI) calcd for $C_{18}H_{24}O_5Na$ $[(M + Na)^+]$ 343.1516, found 343.1519.

Iodide 10. To a solution of acetal **9** (950 mg, 2.97 mmol) in CH_2Cl_2 (30 mL) at –40 °C was added DIBALH (1.02 M solution in *n*-hexane, 11.7 mL, 11.9 mmol). The resultant solution was stirred at –40 °C for 10 min and then at 0 °C for 3 h. The reaction was quenched with MeOH and saturated aqueous potassium sodium tartrate solution. The mixture was diluted with EtOAc and stirred vigorously at room temperature until the layers became clear. The organic layer was separated and washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was passed through a plug of silica gel (50% EtOAc/hexanes) to give an alcohol, which was used in the next reaction without further purification.

To a solution of the above alcohol in THF (30 mL) were added imidazole (0.38 g, 5.64 mmol), PPh_3 (1.18 g, 4.51 mmol), and I_2 (0.93 g, 3.67 mmol), and the resultant mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous Na_2SO_3 solution and the mixture was extracted with EtOAc. 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 on silica gel (10 to 20% EtOAc/hexanes) gave iodide **10** (1.19 g, 98% for the two steps) as a colorless oil: $[\alpha]_D^{21}$ +43.3 (*c* 1.19, $CHCl_3$); IR (KBr) 2940, 2868, 1611, 1512, 1248, 1093, 1074, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25—7.21 (m, 2H), 6.88—6.85 (m, 2H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.40 (d, *J* = 11.0 Hz, 1H), 3.79 (s, 3H), 3.65 (ddd, *J* = 11.5, 11.5, 4.0 Hz, 1H), 3.58 (m, 1H), 3.53—3.42 (m, 3H), 3.23 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.97 (m, 1H), 2.24 (dd, *J* = 11.5, 5.0 Hz, 1H), 1.77 (m, 1H), 1.73—1.64 (m, 2H), 1.61—1.49 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 129.9, 129.6 (2C), 113.9 (2C), 80.4, 79.3, 75.7, 72.4, 70.9, 59.9, 55.3, 43.1, 25.8, 24.1, 15.1, 9.1; HRMS (EI) calcd for $C_{18}H_{25}IO_4$ (M^+) 432.0798, found 432.0793.

Exocyclic enol ether 11. To a solution of iodide **10** (1.19 g, 2.75 mmol) in THF (30 mL) at 0 °C was added KO*t*-Bu (925 mg, 8.25 mmol), and the resultant solution was stirred at 0 °C for 40 min. The reaction was quenched with H_2O, and the mixture was extracted with EtOAc. 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 on silica gel (10 to 20% EtOAc/hexanes) gave exocyclic enol

ether **11** (810 mg, 97%) as a colorless oil: $[\alpha]_D^{21}$ –49.1 (*c* 0.91, $CHCl_3$); IR (KBr) 2938, 2868, 1512, 1246, 1080, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28—7.22 (m, 2H), 6.88—6.83 (m, 2H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.51 (s, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.34 (s, 1H), 3.97 (dd, *J* = 7.0, 7.0 Hz, 1H), 3.87 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.79 (s, 3H), 3.65—3.55 (m, 2H), 2.12 (dd, *J* = 12.0, 6.5 Hz, 1H), 1.88 (m, 1H), 1.77 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.75—1.54 (m, 3H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 157.0, 130.2, 129.3 (2C), 113.8 (2C), 92.0, 77.3, 73.4, 72.3, 69.8, 60.3, 55.3, 44.2, 25.3, 24.3, 16.0; HRMS (FAB) calcd for $C_{18}H_{25}O_4$ $[(M + H)^+]$ 305.1753, found 305.1751.

Enol ether 14. To a solution of exocyclic enol ether **11** (163 mg, 0.536 mmol) in THF (5 mL) was added a solution of 9-BBN-H dimer (170 mg, 0.697 mmol) in THF (8 mL), and the resultant mixture was stirred at room temperature for 2.5 h. To the solution was added 3 M aqueous Cs_2CO_3 (0.450 mL, 1.35 mmol), and the resulting mixture was vigorously stirred at room temperature for 15 min. To this mixture were added $PdCl_2(dppf)\cdot CH_2Cl_2$ (74 mg, 0.0902 mmol) and a solution of the above crude enol phosphate **13** (275 mg, prepared from the corresponding lactone (185 mg, 0.451 mmol) according to the reported procedure[1] immediately before use) in DMF (5 mL) via cannula, and the resultant mixture was stirred at 50 °C for 10 h. The reaction mixture was extracted with EtOAc, washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column

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[1] Fuwa, H.; Kainuma, N.; Tachibana, K.; Sasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 14983.

chromatography on silica gel (10 to 20% EtOAc/hexanes) gave enol ether **14** (277 mg, 88%) as a colorless solid: mp 96—99 °C (hexane/EtOAc); $[\alpha]_D^{26}$ +8.3 (*c* 1.15, $CHCl_3$); IR (KBr) 2936, 2871, 1513, 1247, 1097, 1068, 819 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.20—7.15 (m, 2H), 6.81—6.75 (m, 2H), 5.01 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.42 (m, 1H), 4.16 (m, 1H), 3.90 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.83 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.63 (dd, *J* = 11.0, 8.5 Hz, 1H), 3.47 (ddd, *J* = 8.5, 8.5, 3.5 Hz, 1H), 3.43—3.31 (m, 3H), 3.31—3.18 (m, 5H), 3.16 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.03 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.95 (m, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.41 (m, 1H), 2.24—2.16 (m, 3H), 2.16—2.02 (m, 2H), 2.00—1.88 (m, 2H), 1.87—1.67 (m, 7H), 1.66—1.52 (m, 3H), 1.45 (s, 3H), 1.40—1.33 (m, 2H), 1.30 (s, 3H), 1.27 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.7, 151.9, 131.0, 129.5 (2C), 114.0 (2C), 108.3, 98.4, 88.7, 81.1, 80.9, 80.8, 79.9, 77.6, 76.5, 76.0, 73.09. 73.06, 72.6, 72.1, 70.3, 63.4, 59.7, 54.7, 53.9, 44.4, 41.4, 32.4, 30.1, 29.8, 28.8, 27.3, 26.2, 24.8, 23.0, 19.4, 18.9, 16.2, 15.4; HRMS (ESI) calcd for $C_{40}H_{58}O_{10}Na$ $[(M + Na)^+]$ 721.3928, found 721.3940.

Ketone 15. To a solution of enol ether **14** (1.36 g, 1.95 mmol) in THF (30 mL) at 0 °C was added $BH_3 \cdot SMe_2$ (1.9 M solution in THF, 5.10 mL, 9.75 mmol). After being stirred at room temperature for 5 h, the reaction mixture was treated successively with EtOH, saturated aqueous $NaHCO_3$ solution, and 30% aqueous H_2O_2 solution, and the resultant mixture was stirred at room temperature for 2 h. The reaction mixture was extracted with EtOAc, and the organic layer was washed successively with H_2O, saturated aqueous Na_2SO_3 solution, and brine. The aqueous layers were extracted with EtOAc.

The combined organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (40 to 70% EtOAc/hexanes) afforded an approximately 3:1 mixture of inseparable diastereomeric alcohols (1.26 g, 90%).

To a solution of the above mixture of alcohols (1.26 g, 1.75 mmol) in CH_2Cl_2 (20 mL) were added 4 Å molecular sieves (250 mg), NMO (615 mg, 5.25 mmol), and TPAP (92 mg, 0.26 mmol). After being stirred at room temperature for 30 min, the reaction mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (40% Et_2O/hexanes) afforded ketone **15** (881 mg, 70%) as a colorless oil along with its diastereomer (300 mg, 24%) as a colorless oil. Data for **15**: $[\alpha]_D^{26}$ –7.8 (*c* 1.32, $CHCl_3$); IR (KBr) 2943, 2872, 1707, 1513, 1248, 1077, 680 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.18—7.16 (m, 2H), 6.80—6.77 (m, 2H), 4.44 (dd, *J* = 6.5, 5.9 Hz, 1H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.14 (d, *J* = 11.3 Hz, 1H), 3.91 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.75 (ddd, *J* = 8.9, 8.6, 3.1 Hz, 1H), 3.69 (m, 1H), 3.64 (dd, *J* = 11.3, 8.9 Hz, 1H), 3.47—3.30 (m, 5H), 3.28 (s, 3H), 3.26—3.19 (m, 2H), 3.05—2.99 (m, 2H), 2.59 (ddd, *J* = 11.3, 11.3, 2.8 Hz, 1H), 2.36 (dd, *J* = 11.3, 5.0 Hz, 1H), 2.34—2.25 (m, 2H), 2.16—2.04 (m, 2H), 2.01 (d, *J* = 12.5 Hz, 1H), 1.97—1.88 (m, 3H), 1.79—1.62 (m, 6H), 1.50 (m, 1H), 1.45 (s, 3H), 1.39 (m, 1H), 1.29 (s, 3H), 1.22 (m, 1H), 1.16 (m, 1H), 1.10 (s, 3H), 1.04 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 214.7, 130.9, 129.6 (2C), 114.1 (2C), 98.4, 88.5, 81.3, 81.1, 80.9, 77.9, 77.8, 76.9, 76.4, 76.1, 73.0, 72.5, 72.1, 70.3, 63.4, 59.6, 54.7, 53.7, 44.3, 41.9, 38.1, 37.0,

32.3, 30.1, 29.8, 28.8, 26.1, 25.7, 24.5, 22.1, 19.4, 17.3, 16.6, 15.2; HRMS (ESI) calcd for $C_{40}H_{58}O_{11}Na$ [$(M + Na)^+$] 737.3877, found 737.3874. Data for the diastereomer: $[\alpha]_D^{26}$ –11.8 (*c* 1.10, $CHCl_3$); IR (KBr) 2948, 2868, 1700, 1511, 1248, 1079, 680 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.12—7.09 (m, 2H), 6.74—6.71 (m, 2H), 4.54 (dd, *J* = 11.3, 2.7 Hz, 1H), 4.35 (d, *J* = 11.3 Hz, 1H), 4.11 (d, *J* = 11.3 Hz, 1H), 3.95 (dd, *J* = 11.3, 5.8 Hz, 1H), 3.77—3.68 (m, 2H), 3.65 (dd, *J* = 11.3, 8.9 Hz, 1H), 3.47—3.30 (m, 5H), 3.28 (s, 3H), 3.26—3.20 (m, 2H), 3.04 (m, 1H), 2.87 (ddd, *J* = 10.3, 10.3, 10.3 Hz, 1H), 2.58 (dd, *J* = 12.7, 3.4 Hz, 1H), 2.38 (dd, *J* = 11.7, 4.9 Hz, 1H), 2.39 (ddd, *J* = 12.7, 11.7, 2.4 Hz, 1H), 2.16 (ddd, *J* = 12.7, 10.3, 2.4 Hz, 1H), 2.07—1.89 (m, 6H), 1.87—1.79 (m, 2H), 1.77—1.60 (m, 6H), 1.56—1.49 (m, 2H), 1.47 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 1.14 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 212.9, 131.9, 130.6 (2C), 116.7 (2C), 98.1, 88.5, 82.7, 81.8, 80.9, 78.2, 77.6, 76.3, 76.0, 75.7, 73.0, 72.1, 71.8, 70.7, 64.2, 59.1, 55.7, 53.7, 44.1, 41.7, 38.6, 37.0, 33.5, 31.1, 29.7, 28.8, 27.9, 25.1, 24.0, 20.7, 19.4, 17.9, 15.6, 15.1; HRMS (ESI) calcd for $C_{40}H_{58}O_{11}Na$ [$(M + Na)^+$] 737.3877, found 737.3880.

Mixed thioacetal 16. To a solution of ketone **15** (159 mg, 0.222 mmol) in CH_2Cl_2/pH 7 phosphate buffer (10:1, v/v, 10 mL) at 0 °C was added DDQ (76 mg, 0.333 mmol), and the resultant solution was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution at 0 °C. The mixture was extracted with EtOAc, and the organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was passed through a plug of silica

gel (eluted with 70% EtOAc/hexanes) to afford a hemiacetal, which was used in the next reaction without further purification.

To a solution of the above hemiacetal in CH_2Cl_2 (8 mL) were added EtSH (2 mL) and $Zn(OTf)_2$ (40.3 mg, 0.111 mmol), and the resultant mixture was stirred at room temperature overnight. The reaction was quenched with Et_3N, and the resulting mixture was concentrated under reduced pressure. The residue was immediately dissolved in CH_2Cl_2 (8 mL) and treated with Et_3N (0.460 mL, 3.33 mmol), Ac_2O (0.420 mL, 4.44 mmol), and DMAP (136 mg, 1.11 mmol). The resultant solution was stirred at room temperature for 45 min. The reaction was quenched with MeOH. The reaction mixture was diluted with EtOAc and washed successively with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (35 to 40% EtOAc/hexanes) gave mixed thioacetal **16** (144 mg, 95% for the three steps) as colorless crystals: mp 109—111 °C (hexanes/EtOAc); $[\alpha]_D^{21}$ –40.1 (*c* 1.11, $CHCl_3$); IR (KBr) 2943, 2873, 1741, 1234, 1079, 1045, 681 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.08 (m, 1H), 4.63 (dd, *J* = 10.5, 5.5 Hz, 1H), 4.21 (m, 1H), 4.16 (dd, *J* = 11.0, 6.5 Hz, 1H), 4.03 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.68 (m, 1H), 3.64 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.43—3.33 (m, 3H), 3.17 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.11 (ddd, *J* = 12.0, 10.0, 4.5 Hz, 1H), 3.06—2.99 (m, 2H), 2.43—2.30 (m, 3H), 2.26—2.12 (m, 5H), 2.04—1.97 (m, 2H), 1.86 (dd, *J* = 11.0, 11.0 Hz, 1H), 1.82—1.70 (m, 4H), 1.70—1.51 (m, 11H), 1.50—1.38 (m, 2H), 1.21 (s, 3H), 1.17 (s, 3H), 1.15 (s,

3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.4, 92.9, 83.4, 82.1, 81.4, 81.1, 80.4, 79.5, 77.3, 74.9, 73.7, 73.44, 73.37, 72.3, 69.1, 65.2, 59.7, 54.1, 44.2, 34.8, 34.7, 32.6, 27.7, 26.4, 25.6, 25.0, 24.6, 20.7, 20.3, 19.9, 17.7, 16.6, 15.6, 15.1; HRMS (FAB) calcd for $C_{35}H_{54}O_{11}SNa$ [$(M + Na)^+$] 705.3285, found 705.3294.

Heptacycle 17. To a solution of mixed thioacetal **16** (85.8 mg, 0.125 mmol) in CH_2Cl_2 (5 mL) at –40 °C were added Et_3SiH (0.40 mL, 2.5 mmol), NIS (84 mg, 0.375 mmol), and AgOTf (96 mg, 0.375 mmol), and the resultant solution was stirred at –40 °C for 1.5 h under exclusion of light. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ solution, and the mixture was extracted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (30 to 40% EtOAc/hexanes) afforded heptacycle **17** (70.2 mg, 90%) as colorless crystals: mp 145—147 °C (hexanes/EtOAc); $[\alpha]_D^{21}$ –4.8 (*c* 0.54, $CHCl_3$); IR (KBr) 2946, 2874, 1744, 1082, 1057, 772 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.98 (m, 1H), 4.12 (dd, *J* = 11.4, 6.6 Hz, 1H), 4.00 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.74 (ddd, *J* = 6.0, 4.2, 4.2 Hz, 1H), 3.67 (ddd, *J* = 12.0, 12.0, 3.6 Hz, 1H), 3.59 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.44 (m, 2H), 3.36 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.21 (ddd, *J* = 11.4, 9.6, 4.8 Hz, 1H), 3.17—3.05 (m, 4H), 3.02 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.20 (ddd, *J* = 12.6, 3.6, 3.6 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.04—1.94 (m, 5H), 1.90 (d, *J* = 13.2 Hz, 1H), 1.79—1.52 (m, 11H), 1.49—1.41 (m, 2H), 1.31 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.1, 84.8, 81.2, 81.1, 80.9, 79.7, 79.6, 78.2,

76.2, 75.8, 73.5, 73.1, 72.9, 72.2, 72.0, 65.0, 59.9, 53.9, 43.5, 37.4, 32.0, 28.5, 27.1, 25.9, 24.8, 24.3, 24.1, 21.2, 20.9, 18.2, 16.1, 15.2; HRMS (ESI) calcd for $C_{33}H_{50}O_{11}Na$ $[(M + Na)^+]$ 645.3245, found 645.3252.

Alcohol 18. To a solution of heptacycle **17** (278 mg, 0.446 mmol) in $MeOH/CH_2Cl_2$ (20 mL) was added NaOMe (12.1 mg, 0.223 mmol), and the resultant solution was stirred at room temperature for 9 h. The reaction was neutralized with Amberlyst® 15 ion-exchange resin, and the resultant mixture was filtered. The filtrate was concentrated under reduced pressure to afford a crude diol, which was used in the next reaction without further purification.

To a solution of the above material in DMF (20 mL) at 0 °C were added imidazole (304 mg, 4.46 mmol) and TBSCl (336 mg, 2.23 mmol), and the resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with Et_2O. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (30 to 40% EtOAc/hexanes) afforded alcohol **18** (233 mg, 80% for the two steps) as colorless crystals: mp 139—140 °C (hexanes/EtOAc); $[\alpha]_D^{26}$ –13.3 (*c* 0.52, $CHCl_3$); IR (KBr) 3446, 2950, 2875, 1081, 1057 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.89 (m, 1H), 3.74 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.67 (ddd, *J* = 12.4, 12.4, 3.8 Hz, 1H), 3.58 (dd, *J* = 12.4, 5.2 Hz, 1H), 3.50 (dd, *J* = 9.6, 7.9 Hz, 1H), 3.47—3.40 (m, 2H), 3.38—3.33 (m, 2H), 3.21 (ddd, *J* = 11.0, 9.6, 4.4 Hz, 1H), 3.17—3.12 (m, 2H),

3.12—3.05 (m, 2H), 3.02 (dd, *J* = 12.4, 3.4 Hz, 1H), 2.47 (s, 1H), 2.19 (ddd, *J* = 12.4, 4.1, 4.1 Hz, 1H), 2.06—1.95 (m, 4H), 1.90—1.42 (m, 15H), 1.31 (s, 3H), 1.21 (s, 6H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 85.1, 84.9, 83.0, 81.2, 80.0, 79.7, 78.3, 76.2, 75.8, 74.3, 73.1, 73.0, 72.2, 72.1, 65.9, 59.9, 53.9, 43.5, 37.4, 32.3, 29.5, 28.6, 27.3, 25.9, 25.8 (3C), 24.3, 24.2, 18.3, 18.2, 16.1, 15.2, –5.4, –5.5; HRMS (ESI) calcd for $C_{35}H_{60}O_9SiNa$ [$(M + Na)^+$] 675.3899, found 675.3902.

Ketone 19. To a solution of alcohol **18** (557 mg, 0.853 mmol) in CH_2Cl_2 (20 mL) were added 4 Å molecular sieves (150 mg), NMO (300 mg, 2.56 mmol), and TPAP (45 mg, 0.128 mmol). After being stirred at room temperature for 10 min, the reaction mixture was filtered through a pad of Celite® and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (15% EtOAc/hexanes) afforded ketone **19** (531 mg, 96%) as colorless crystals: mp 120—122 °C (hexanes/EtOAc); $[\alpha]_D^{23}$ +18.3 (*c* 0.87, $CHCl_3$); IR (KBr) 2950, 2874, 1716, 1081, 838 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84—3.80 (m, 3H), 3.69—3.63 (m, 2H), 3.58 (dd, *J* = 12.0, 5.1 Hz, 1H), 3.45 (ddd, *J* = 10.7, 8.9, 4.8 Hz, 1H), 3.34 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.16—3.11 (m, 2H), 3.11—3.04 (m, 2H), 2.99 (dd, *J* = 12.7, 3.8 Hz, 1H), 2.97 (m, 1H), 2.85 (ddd, *J* = 14.0, 12.4, 2.4 Hz, 1H), 2.37 (ddd, *J* = 12.0, 7.2, 1.7 Hz, 1H), 2.19 (ddd, *J* = 12.0, 3.8, 3.8 Hz, 1H), 2.09 (ddd, *J* = 11.6, 3.8, 3.8 Hz, 1H), 2.04—3.11 (m, 3H), 1.78—1.40 (m, 13H), 1.31 (s, 3H), 1.26 (s, 3H), 1.20 (s, 3H), 0.84 (s, 9H), 0.02 (s, 3H), –0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.3, 88.3, 84.8, 82.2, 81.2, 79.6, 79.4, 78.2, 76.2, 75.7, 73.1, 72.7, 72.2, 72.1, 65.2, 59.9, 53.7, 43.4,

38.8, 37.4, 31.9, 30.0, 28.5, 25.9, 25.8 (3C), 24.2, 24.1, 18.3, 18.2, 16.0, 15.2, –5.3, –5.4; HRMS (ESI) calcd for $C_{35}H_{59}O_9Si$ [$(M + H)^+$] 651.3923, found 651.3928.

Enone 20. To a solution of ketone **19** (531 mg, 0.815 mmol) in THF (20 mL) at –78 °C were added Et_3N (0.900 mL, 6.52 mmol), TMSCl (0.830 mL, 2.44 mmol), and LHMDS (1.0 M solution in THF, 2.44 mL, 2.44 mmol), and the resultant solution was stirred at –78 °C for 30 min. The reaction was quenched with pH 7 phosphate buffer, and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered. The filtrate was concentrated under reduced pressure to afford a crude enol silyl ether, which was used in the next reaction without further purification.

To a solution of the above material in CH_3CN (20 mL) was added $Pd(OAc)_2$ (548 mg, 2.44 mmol). After being stirred at room temperature for 2 h, the reaction mixture was filtered through a plug of silica gel and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (20 to 30% EtOAc/hexanes) afforded enone **20** (516 mg, 98% for the two steps) as colorless crystals: mp 118—120 °C (hexanes/EtOAc); $[\alpha]_D^{27}$ –37.1 (*c* 0.56, $CHCl_3$); IR (KBr) 2950, 2875, 1665, 1117, 1059, 774 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 6.21 (dd, *J* = 12.7, 2.0 Hz, 1H), 5.98 (dd, *J* = 12.7, 2.8 Hz, 1H), 4.18 (ddd, *J* = 8.9, 2.4, 2.4 Hz, 1H), 4.03 (dd, *J* = 4.5, 2.0 Hz, 1H), 3.96 (dd, *J* = 11.0, 4.9 Hz, 1H), 3.89 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.43—3.34 (m, 4H), 3.17 (dd, *J* = 11.6, 3.8 Hz, 1H), 3.15—3.06 (m, 4H), 2.89 (dd, *J* = 12.7, 6.2 Hz, 1H), 2.44 (ddd, *J* = 12.0, 3.8, 3.8 Hz, 1H), 2.28 (dd, *J* = 11.7, 4.5 Hz, 1H), 2.09—1.98 (m, 5H), 1.83—1.52 (m, 6H), 1.50—1.38 (m, 2H), 1.18 (m,1H), 1.15

(s, 3H), 1.09 (s, 3H), 1.04 (s, 3H), 0.93 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 201.3, 145.1, 128.9, 88.4, 85.3, 81.9, 80.0, 79.6, 79.2, 78.9, 76.8, 76.0, 73.1, 73.0, 72.8 (2C), 65.7, 59.6, 54.2, 44.4, 38.1, 31.9, 29.0, 26.3, 26.0 (3C), 24.7, 24.6, 18.4, 18.2, 15.43, 15.42, –5.19, –5.22; HRMS (ESI) calcd for $C_{35}H_{56}O_9SiNa$ [(M + Na)$^+$] 671.3586, found 671.3597.

Alcohol 21. To a solution of α,β-unsaturated ketone **20** (516 mg, 0.795 mmol) in toluene (20 mL) at –78 °C was added MeMgBr (3.0 M solution in Et_2O, 1.06 mL, 3.18 mmol), and the resultant solution was stirred at –78 °C for 50 min. The reaction was quenched with saturated aqueous NH_4Cl solution, and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (20 to 40% EtOAc/hexanes) afforded alcohol **21** (495 mg, 94%) as colorless crystals: mp 125—127 °C (hexanes/EtOAc); $[\alpha]_D^{26}$ –53.9 (*c* 0.57, $CHCl_3$; IR (KBr) 3473, 2950, 2876, 1088, 1060, 837 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.59 (dd, *J* = 13.0, 2.7 Hz, 1H), 5.42 (dd, *J* = 13.0, 1.7 Hz, 1H), 4.21 (s, 1H), 4.10 (m, 1H), 3.78—3.64 (m, 3H), 3.64—3.56 (m, 2H), 3.45 (m, 1H), 3.35 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.30 (ddd, *J* = 11.3, 9.7, 5.2 Hz, 1H), 3.17—3.12 (m, 2H), 3.12—3.05 (m, 2H), 3.02 (dd, *J* = 12.7, 3.8 Hz, 1H), 2.20 (ddd, *J* = 12.4, 4.1, 4.1 Hz, 1H), 2.04—1.94 (m, 4H), 1.90 (d, *J* = 12.7 Hz, 1H), 1.78—1.43 (m, 10H), 1.30 (s, 3H), 1.27 (s, 3H), 1.21 (s, 3H), 0.88 (s, 3H), 0.087 (s, 3H), 0.085 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 139.9, 130.1, 85.2, 84.0, 82.0, 81.9, 80.0, 79.8, 78.9, 76.8, 76.3, 76.1, 73.1, 72.8, 72.2, 72.1,

64.4, 59.6, 54.4, 44.5, 38.2, 32.6, 29.1, 26.4, 25.8 (3C), 24.8, 24.6, 21.7, 18.3, 18.2, 15.6, 15.4, –5.6, –5.7; HRMS (ESI) calcd for $C_{36}H_{60}O_9SiNa$ [$(M + Na)^+$] 687.3899, found 687.3907.

Bis-TBS ether 22. To a solution of alcohol **21** (490 mg, 0.737 mmol) in CH_2Cl_2 (15 mL) at 0 °C were added Et_3N (0.500 mL, 3.69 mmol) and TBSOTf (0.500 mL, 2.21 mmol), and the resultant solution was stirred at room temperature for 1.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (10 to 15% EtOAc/hexanes) gave bis-TBS ether **22** (574 mg, 100%) as colorless crystals: mp 120—122 °C (hexanes/EtOAc); $[\alpha]_D^{23}$ –16.1 (*c* 0.31, $CHCl_3$); IR (KBr) 2952, 2857, 1255, 1084, 836 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 5.79 (dd, *J* = 13.1, 2.4 Hz, 1H), 5.72 (dd, *J* = 13.1, 1.7 Hz, 1H), 4.33 (ddd, *J* = 9.7, 2.0, 2.0 Hz, 1H), 4.16 (ddd, *J* = 8.9, 5.5, 5.5 Hz, 1H), 3.77—3.73 (m, 2H), 3.47—3.36 (m, 4H), 3.34 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.18—3.05 (m, 4H), 3.03 (dd, *J* = 12.7, 3.8 Hz, 1H), 2.44 (ddd, *J* = 12.1, 4.4, 4.1 Hz, 1H), 2.39 (ddd, *J* = 12.1, 4.4, 4.1 Hz, 1H), 2.28 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.08—1.94 (m, 5H), 1.86 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.80 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.75 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.67—1.52 (m, 3H), 1.49—1.37 (m, 2H), 1.31 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 1.11 (s, 3H), 1.00 (s, 9H), 0.96 (s, 9H), 0.16 (s, 3H), 0.14 (s, 6H), 0.11 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3, 129.2, 97.8, 89.1, 84.7, 81.6, 81.2, 79.7, 79.5, 78.2, 78.1, 76.2,

75.8, 73.1, 72.1, 72.0, 63.0, 59.9, 53.8, 43.5, 37.6, 31.8, 29.7, 28.6, 25.9 (3C), 25.7 (3C), 24.3, 24.1, 22.2, 18.3, 18.2, 18.1, 15.6, 15.2, –2.1, –2.3, –5.0, –5.3; HRMS (ESI) calcd for $C_{42}H_{74}O_9Si_2Na$ [$(M + Na)^+$] 801.4764, found 801. 4765.

Alcohol 23. To a solution of bis-TBS ether **22** (35.4 mg, 0.0454 mmol) in MeOH/CH_2Cl_2 (1:1, v/v, 2 mL) at 0 °C was added CSA (5.3 mg, 0.0227 mmol), and the resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with Et_3N, and the mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (30% EtOAc/hexanes) afforded alcohol **23** (29.9 mg, 99%) as colorless crystals: mp 123—125 °C (hexanes/EtOAc); $[\alpha]_D^{22}$ –16.4 (*c* 0.21, $CHCl_3$); IR (KBr) 3421, 2951, 2876, 1083, 1059 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.72 (dd, *J* = 13.0, 2.8 Hz, 1H), 5.38 (dd, *J* = 13.0, 2.0 Hz, 1H), 4.15 (ddd, *J* = 9.3, 2.4, 2.4 Hz, 1H), 3.78 (ddd, *J* = 10.7, 10.3, 2.0 Hz, 1H), 3.66 (ddd, *J* = 12.4, 12.4, 3.1 Hz, 1H), 3.58 (dd, *J* = 11.7, 5.2 Hz, 1H), 3.53—3.43 (m, 3H), 3.35 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.30 (ddd, *J* = 11.0, 9.3, 4.8 Hz, 1H), 3.18—3.12 (m, 2H), 3.12—3.04 (m, 2H), 3.02 (dd, *J* = 12.7, 3.8 Hz, 1H), 2.19 (ddd, *J* = 12.4, 4.4 Hz, 1H), 2.06 (ddd, *J* = 11.7, 4.4, 4.1 Hz, 1H), 2.04—1.94 (m, 4H), 1.96 (d, *J* = 13.1 Hz, 1H), 1.78—1.51 (m, 8H), 1.50—1.43 (m, 2H), 1.31 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 0.83 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 129.5, 87.3, 84.8, 81.5, 81.2, 79.7, 79.3, 78.2, 78.0, 76.2, 75.8, 73.1, 72.2, 72.0, 71.7, 61.7, 59.8, 53.7, 43.5, 37.4, 31.8, 28.6, 25.9, 25.7 (3C), 24.2, 24.1, 21.8, 18.2, 18.0, 15.6, 15.2, –2.0, –2.3; HRMS (ESI) calcd for $C_{36}H_{60}O_9SiNa$ [$(M + Na)^+$] 687.3899, found 687.3998.

Dibromoolefin 24. To a solution of alcohol **23** (29.9 mg, 0.045 mmol) in CH_2Cl_2/ DMSO (1:1, v/v, 2 mL) at 0 °C were added Et_3N (25 μL, 0.18 mmol) and SO_3·pyridine (25 mg, 0.16 mmol), and the resultant mixture was stirred at 0 °C for 4 h. The reaction mixture was diluted with Et_2O, washed with saturated aqueous NH_4Cl solution and brine, dried (Na_2SO_4), and filtered. The filtrate was concentrated under reduced pressure to afford a crude aldehyde (40.0 mg), which was used in the next reaction without further purification.

To a solution of CBr_4 (150 mg, 0.45 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added PPh_3 (235 mg, 0.90 mmol), and the resultant solution was stirred at 0 °C for 15 min. To the solution were added Et_3N (0.25 mL, 1.8 mmol) and a solution of the above crude aldehyde (40.0 mg) in CH_2Cl_2 (1 mL) via cannula. The resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the resultant mixture was extracted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (10 to 20% EtOAc/hexanes) afforded dibromoolefin **24** (37.2 mg, 100% for the two steps) as a pale yellow amorphous: $[\alpha]_D^{26}$ –8.1 (*c* 1.42, $CHCl_3$); IR (KBr) 2950, 2874, 1461, 1377, 1253, 1130, 1082, 1060, 835, 755 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 6.65 (d, *J* = 7.9 Hz, 1H), 5.82 (dd, *J* = 13.0, 2.8 Hz, 1H), 5.71 (dd, *J* = 13.0, 1.0 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 4.25 (d, *J* = 7.9 Hz, 1H), 3.47 (ddd, *J* = 11.2, 11.2, 4.8 Hz, 1H), 3.44—3.34 (m, 4H), 3.16 (dd, *J* = 11.6, 3.8 Hz, 1H),

3.14—3.06 (m, 3H), 3.02 (dd, *J* = 12.7, 3.8 Hz, 1H), 2.43 (m, 1H), 2.30—2.25 (m, 2H), 2.09—1.97 (m, 4H), 1.82—1.71 (m, 3H), 1.68—1.53 (m, 3H), 1.50—1.39 (m, 2H), 1.29 (s, 3H), 1.21 (m, 1H), 1.14 (s, 3H), 1.12 (s, 6H), 0.95 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 136.8, 131.2, 128.3, 95.8, 86.6, 85.3, 82.6, 81.9, 80.0, 79.8, 78.9, 78.5, 76.7, 76.1, 73.1, 72.8, 72.32, 72.29, 59.6, 54.5, 44.4, 38.1, 32.2, 29.1, 26.3, 25.9 (3C), 24.8, 24.6, 22.0, 18.3, 15.6, 15.4, –1.9, –2.2; HRMS (ESI) calcd for $C_{37}H_{59}Br_2O_8Si$ [$(M + H)^+$] 817.2340, found 817.2364.

(*Z*)-Vinyl bromide 25. To a solution of dibromoolefin **24** (13.2 mg, 0.0161 mmol) in benzene (1 mL) were added *n*-Bu_3SnH (20 mL, 0.081 mmol) and $Pd(PPh_3)_4$ (3.7 mg, 0.0032 mmol). After being stirred at room temperature for 75 min, the reaction mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (20 to 30% Et_2O/hexanes) afforded (*Z*)-vinyl bromide **25** (7.9 mg, 66%) as a colorless amorphous: $[\alpha]_D^{23}$ +6.4 (*c* 0.96, $CHCl_3$); IR (KBr) 2927, 2854, 1444, 1372, 1080 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 6.11 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.03 (d, *J* = 7.2 Hz, 1H), 5.89 (dd, *J* = 13.2, 2.8 Hz, 1H), 5.75 (dd, *J* = 13.2, 2.0 Hz, 1H), 4.51 (d, *J* = 7.6 Hz, 1H), 4.33 (ddd, *J* = 9.7, 2.4, 2.1 Hz, 1H), 3.58 (ddd, *J* = 11.0, 9.6, 4.8 Hz, 1H), 3.43—3.33 (m, 4H), 3.16 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.14—3.06 (m, 3H), 3.01 (dd, *J* = 12.7, 3.4 Hz, 1H), 2.43 (ddd, *J* = 12.0, 4.1, 3.8 Hz, 1H), 2.33 (ddd, *J* = 11.7, 4.1, 4.1 Hz, 1H), 2.27 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.09—1.95 (m, 5H), 1.81—1.72 (m, 3H), 1.67—1.52 (m, 3H), 1.48—1.37 (m, 5H), 1.14 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 0.93 (s, 9H), 0.11 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ

139.3, 132.8, 131.1, 113.0, 85.1, 84.2, 82.5, 81.9, 80.0, 79.9, 78.9, 78.6, 76.7, 76.1, 73.1, 72.7, 72.5, 72.3, 59.6, 54.5, 44.4, 38.2, 32.4, 29.1, 26.4, 26.0 (3C), 24.7, 24.6, 22.2, 18.33, 18.27, 15.7, 15.4, –1.8, –2.1; HRMS (ESI) calcd for $C_{37}H_{60}BrO_8Si$ $[(M + H)^+]$ 739.3235, found 739.3233.

Alcohol 26. To a solution of (*Z*)-vinyl bromide **25** (44.7 mg, 0.0604 mmol) in THF (3 mL) was added HF·pyridine (0.5 mL), and the resultant solution was stirred at room temperature for 17 h. The reaction mixture was carefully poured into saturated aqueous $NaHCO_3$ solution (20 mL) at 0 °C, and the resultant mixture was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (40% EtOAc/hexanes) gave alcohol **26** (37.0 mg, 98%) as a colorless amorphous: $[\alpha]_D^{23}$ +28.2 (*c* 0.37, $CHCl_3$); IR (KBr) 3512, 2945, 2869, 1458, 1380, 1079 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.47 (d, *J* = 7.6 Hz, 1H), 6.22 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.75 (dd, *J* = 13.1, 2.8 Hz, 1H), 5.50 (dd, *J* = 13.1, 1.7 Hz, 1H), 4.36 (d, *J* = 7.9 Hz, 1H), 4.21 (ddd, *J* = 9.6, 2.4, 2.1 Hz, 1H), 3.67 (ddd, *J* = 12.0, 12.0, 3.4 Hz, 1H), 3.59 (dd, *J* = 12.0, 5.1 Hz, 1H), 3.49—3.37 (m, 3H), 3.35 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.17—3.06 (m, 4H), 3.05 (dd, *J* = 12.7, 3.5 Hz, 1H), 2.20 (ddd, *J* = 12.0, 4.4, 3.8 Hz, 1H), 2.12 (ddd, *J* = 11.7, 4.8, 3.8 Hz, 1H), 1.91 (d, *J* = 13.0 Hz, 1H), 1.78—1.41 (m, 13H), 1.314 (s, 3H), 1.309 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 132.3, 131.5, 112.2, 85.2, 84.3, 82.1, 81.9, 80.0, 79.8, 78.9, 76.7, 76.1, 75.8, 73.1, 72.7, 72.4, 72.2, 59.6, 54.4, 44.4, 38.1, 32.3, 29.1, 26.3, 24.7, 24.6, 21.4,

18.2, 15.6, 15.4; HRMS (ESI) calcd for $C_{31}H_{46}BrO_8$ [(M + H)$^+$] 625.2371, found 625.2377.

Heptacyclic analogue 2. To a solution of alcohol **26** (3.4 mg, 0.00543 mmol) and vinyl stannane **27** (51.5 mg, 0.144 mmol) in degassed DMSO/THF (1:1, v/v, 2 mL) were added CuCl (32.0 mg, 0.326 mmol), LiCl (17.0 mg, 0.391 mmol), and $Pd(PPh_3)_4$ (5.0 mg, 0.0043 mmol). The resultant solution was stirred at 60 °C for 72 h. The reaction was quenched with 3% NH_4OH solution, and the mixture was extracted with EtOAc. The organic layer was washed with 3% NH_4OH solution and brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (20 to 30% EtOAc/hexanes) afforded heptacyclic analogue **2** (2.1 mg, 63%) as a colorless amorphous: $[\alpha]_D^{23}$ +36.3 (*c* 0.20, C_6H_6); IR (KBr) 3442, 2929, 2873, 1453, 1383, 1130, 1083, 1061, 835 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 6.51 (ddd, *J* = 11.4, 11.4, 0.6 Hz, 1H), 6.31 (dd, *J* = 11.4, 11.4 Hz, 1H), 5.96 (dd, *J* = 13.2, 1.8 Hz, 1H), 5.80 (dd, *J* = 13.2, 1.8 Hz, 1H), 5.68 (dddd, *J* = 17.4, 9.6, 6.6, 6.0 Hz, 1H), 5.51—5.45 (m, 2H), 5.01 (dd, *J* = 17.4, 1.8 Hz, 1H), 4.96 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.51 (d, *J* = 6.4 Hz, 1H), 4.39 (m, 1H), 3.44—3.34 (m, 5H), 3.18 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.15—3.04 (m, 3H), 3.01 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.76—2.72 (m, 2H), 2.46 (ddd, *J* = 12.0, 4.2, 3.6 Hz, 1H), 2.30 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.11—1.94 (m, 6H), 1.85—1.74 (m, 3H), 1.68—1.52 (m, 4H), 1.48—1.41 (m, 2H), 1.30 (s, 3H), 1.17 (s, 3H), 1.13 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 138.8, 136.2, 131.42, 131.39, 128.5, 127.0, 125.3, 115.4, 85.2, 83.1, 81.9, 81.8, 80.0, 79.9, 78.9, 76.7, 76.3,

76.1, 73.1, 72.8, 72.4, 72.1, 59.6, 54.5, 44.4, 38.1, 32.6, 31.8, 29.0, 26.3, 24.8, 24.6, 21.9, 18.2, 15.6, 15.4; HRMS (ESI) calcd for $C_{36}H_{53}O_8$ [$(M + H)^+$] 613.3735, found 613.3740.

Olefin 29. To a solution of ester **28** (1.29 g, 2.58 mmol) in toluene (30 mL) at −78 °C was added DIBALH (0.94 M solution in *n*-hexane, 3.00 mL, 2.82 mmol), and the resultant solution was stirred at −78 °C for 20 min. The reaction was quenched with saturated aqueous potassium sodium tartrate solution at −78 °C. The resultant mixture was diluted with EtOAc and stirred vigorously at room temperature until the layers became clear. The layers were separated, and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude aldehyde thus obtained was used in the next reaction without further purification.

To a suspension of $Ph_3P^+CH_3Br^-$ (2.77 g, 7.75 mmol) in THF (20 mL) at 0 °C was added NaHMDS (1.0 M solution in THF, 7.20 mL, 7.20 mmol), and the resultant suspension was stirred at 0 °C for 20 min. To this suspension was added a solution of the above aldehyde in THF (5 mL + 5 mL rinse), and the resultant mixture was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution at 0 °C. The resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (5 to 10% EtOAc/hexanes) gave olefin **29** (1.18 g, 100% for the two steps) as colorless crystals: mp 131—133 °C (hexanes/EtOAc); $[\alpha]_D^{23}$

−12.5 (*c* 0.61, benzene); IR (KBr) 3434, 2978, 2940, 2871, 1116, 1094 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.13 (m, 1H), 5.22 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 3.94 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.71 (m, 1H), 3.64 (dd, *J* = 11.5, 9.5 Hz, 1H), 3.48 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.44 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.25 (ddd, *J* = 9.5, 9.0, 5.5 Hz, 1H), 2.99 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.89 (m, 1H), 2.52 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.21 (m, 1H), 2.10 (d, *J* = 12.0 Hz, 1H), 2.04 (ddd, *J* = 11.5, 5.0, 3.5 Hz, 1H), 2.00—1.90 (m, 3H), 1.81—1.72 (m, 2H), 1.69 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.46 (s, 3H), 1.29 (s, 3H), 1.20 (s, 3H), 1.14 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 136.9, 116.1, 98.4, 87.9, 81.0, 80.5, 75.9, 74.3, 73.3, 73.1, 71.9, 63.5, 55.3, 33.7, 33.3, 30.2, 29.8, 28.9, 25.1, 19.4, 16.0, 2.7 (3C): HRMS (ESI) calcd for $C_{24}H_{42}O_6SiNa$ $[(M + Na)^+]$ 477.2643, found 477.2633.

Diene 30. To a solution of olefin **29** (1.15 g, 2.53 mmol) in THF (25 mL) was added TBAF (1.0 M solution in THF, 7.60 mL, 7.60 mmol), and the resultant solution was stirred at room temperature for 35 min. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (40 to 50% EtOAc/hexanes) to give an alcohol, which was used in the next reaction without further purification.

To a suspension of KH (30% in mineral oil, 1.00 g) in THF (10 mL) at 0 °C was added a solution of the above alcohol in THF (10 mL + 5 mL rinse), and the resultant mixture was stirred at 0 °C for 10 min. To the mixture was added allyl bromide (0.292 mL, 3.37 mmol), and the resultant mixture was stirred at room temperature for 3.5 h.

The reaction was quenched with MeOH and saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (5 to 15% EtOAc/hexanes) gave diene **30** (1.02 g, 96% for the two steps) as a colorless oil: $[\alpha]_D^{23}$ −13.0 (*c* 0.32, benzene); IR (KBr) 1638, 1109, 1078, 1019, 700 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 6.13 (m, 1H), 5.81 (m, 1H), 5.24 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.12 (d, *J* = 9.6 Hz, 1H), 5.02 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.95 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.75—3.60 (m, 4H), 3.51 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.47 (ddd, *J* = 9.0, 8.4, 3.6 Hz, 1H), 3.26 (ddd, *J* = 9.0, 9.0, 6.0 Hz, 1H), 2.92 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.86 (ddd, *J* = 10.2, 9.0, 4.8 Hz, 1H), 2.56 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.20 (m, 1H), 2.04—1.92 (m, 4H), 1.83—1.74 (m, 3H), 1.68 (ddd, *J* = 12.6, 12.0, 12.0 Hz, 1H), 1.47 (s, 3H), 1.29 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 136.7, 136.2, 116.1, 114.9, 98.3, 86.3, 80.9, 80.2, 75.7, 74.6, 73.2, 73.0, 71.8, 63.3, 62.1, 50.4, 33.8, 32.1, 30.1, 29.8, 28.8, 20.7, 19.2, 15.9; HRMS (ESI) calcd for $C_{24}H_{38}O_6Na$ [$(M + Na)^+$] 445.2561, found 445.2551.

Oxepene 31. To a solution of diene **30** (0.70 g, 1.7 mmol) in CH_2Cl_2 (66 mL) was added the Grubbs first-generation catalyst (136.6 mg, 0.1660 mmol), and the resultant solution was stirred at room temperature for 7 h. The reaction was quenched with Et_3N, and the resultant mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (10 to 20% EtOAc/hexanes) gave

oxepene **31** (0.58 g, 89%) as a colorless solid: $[\alpha]_D^{23}$ +19.8 (*c* 0.49, benzene); IR (KBr) 2941, 2872, 1517, 1250, 1093, 828 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.57—5.46 (m, 2H), 4.22—4.10 (m, 2H), 3.86 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.72 (m, 1H), 3.57 (dd, *J* = 11.4, 9.0 Hz, 1H), 3.50—3.42 (m, 2H), 3.34 (ddd, *J* = 9.6, 9.0, 6.0 Hz, 1H), 3.25 (ddd, *J* = 10.8, 9.0, 4.8 Hz, 1H), 3.09 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.50 (m, 1H), 2.18 (m, 1H), 2.09—1.99 (m, 2H), 1.84—1.69 (m, 3H), 1.57 (m, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 129.9, 123.2, 98.5, 85.0, 80.9, 79.4, 75.7, 75.5, 72.72, 72.65, 71.8, 63.2, 62.8, 53.0, 32.2, 31.8, 29.7, 29.3, 28.4, 19.5, 16.4, 16.1; HRMS (ESI) calcd for $C_{22}H_{34}O_6Na$ $[(M + Na)^+]$ 417.2248, found 417.2250.

Pentacycle 32. To a solution of oxepene **31** (77.4 mg, 0.196 mmol) in EtOAc (10 mL) were added Et_3N (0.060 mL, 0.43 mmol) and 10% Pd/C (24 mg), and the resultant suspension was stirred at room temperature under an atmosphere of hydrogen (ballon) overnight. The suspension was filtered through a pad of Celite®, and the filtrate was concentrated under reduced pressure to give pentacycle **32** (76.8 mg, 99%) as colorless crystals: mp 147—148 °C (hexanes/EtOAc); $[\alpha]_D^{23}$ +4.7 (*c* 0.24, benzene); IR (KBr) 2950, 2875, 1081, 1057 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.74—3.64 (m, 3H), 3.57 (dd, *J* = 11.5, 9.0 Hz, 1H), 3.47 (ddd, *J* = 9.0, 9.0, 4.0 Hz, 1H), 3.41 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.33 (ddd, *J* = 9.5, 9.0, 6.0 Hz, 1H), 3.23 (ddd, *J* = 10.5, 9.0, 5.0 Hz, 1H), 3.05 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.06 (m, 1H), 2.01 (m, 1H), 1.96—1.85 (m, 3H), 1.82—1.52 (m, 9H), 1.41 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.5, 86.0, 80.9, 80.3, 76.0, 75.7, 72.7, 72.6, 71.9,

64.2, 63.2, 53.6, 31.8, 29.9, 29.7, 29.3, 29.2, 28.4, 22.0, 19.53, 19.49, 16.1; HRMS (ESI) calcd for $C_{22}H_{36}O_6Na$ [$(M + Na)^+$] 419.2404, found 419.2395.

Ketone 33. To a solution of pentacycle **32** (76.8 mg, 0.194 mmol) in MeOH/$CHCl_3$ (2:1, v/v, 6 mL) was added CSA (10 mg), and the resultant solution was stirred at room temperature for 1.5 h. The reaction was quenched with Et_3N, and the resultant mixture was concentrated under reduced pressure. The residue was passed through a pad of silica gel (eluted with 5% MeOH/$CHCl_3$) to give a diol, which was used in the next reaction without further purification.

To a solution of the above diol in DMF (6 mL) at 0 °C were added imidazole (132.0 mg, 1.939 mmol) and TBSCl (87.7 mg, 0.582 mmol), and the resultant solution was stirred at 0 °C for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (30 to 45% EtOAc/hexanes) gave an alcohol, which was used in the next reaction without further purification..

To a solution of the above alcohol in CH_2Cl_2 (6 mL) were added 4 Å molecular sieves (100 mg), NMO (113.6 mg, 0.9697 mmol), and TPAP (ca. 10 mg). The resultant mixture was stirred at room temperature for 80 min and then filtered through a pad of silica gel (eluted with EtOAc). The filtrate was concentrated under reduced pressure to give ketone **33** (82.0 mg, 90% for the three steps) as a colorless oil: $[\alpha]_D^{23}$ +54.7 (*c* 0.20, benzene); IR (KBr) 2952, 2873, 1714, 1081, 838 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ

3.84 (dd, *J* = 10.5, 4.0 Hz, 1H), 3.76 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.67—3.54 (m, 3H), 3.50—3.41 (m, 2H), 2.95 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.78—2.66 (m, 2H), 2.30 (m, 1H), 2.13 (m, 1H), 2.12 (d, *J* = 12.5 Hz, 1H), 2.06 (d, *J* = 12.5 Hz, 1H), 1.97 (m, 1H), 1.85 (m, 1H), 1.80 (ddd, *J* = 13.0, 11.5, 11.0 Hz, 1H), 1.59 (m, 1H), 1.50—1.35 (m, 3H), 1.34—1.22 (m, 2H), 1.17 (s, 3H), 1.15 (s, 3H), 0.92 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 213.3, 88.5, 86.6, 82.6, 80.6, 76.1, 73.3, 72.3, 65.6, 64.2, 54.5, 39.2, 32.5, 30.4, 30.2, 29.5, 26.0 (3C), 22.2, 19.3, 18.5, 16.3, −5.2, −5.4; HRMS (ESI) calcd for $C_{25}H_{44}O_6SiNa$ [$(M + Na)^+$] 491.2799, found 491.2791.

Alcohol 34. To a solution of ketone **33** (82.0 mg, 0.175 mmol) in THF (5 mL) at −78 °C were added Et_3N (0.243 mL, 1.751 mmol), TMSCl (0.223 mL, 1.745 mmol), and LHMDS (1.0 M solution in THF, 0.524 mL, 0.524 mmol), and the resultant solution was stirred at −78 °C for 30 min. The reaction was quenched with aqueous pH 7 buffer solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give an enol silane. This material was immediately used in the next reaction without further purification.

To a solution of the above enol silane in CH_3CN (5 mL) was added $Pd(OAc)_2$ (117.5 mg, 0.5234 mmol), and the resultant mixture was stirred at room temperature for 40 min. Insoluble materials were filtered off, and the filtrate was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (15%

EtOAc/hexanes) gave an enone, which was used in the next reaction without further purification.

To a solution of the above enone in toluene (5 mL) at −78 °C was added MeMgBr (3.0 M solution in Et_2O, 0.175 mL, 0.525 mmol), and the resultant solution was stirred at −78 ° C for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (20 to 25% EtOAc/hexanes) gave alcohol **34** (88.9 mg, 100% for the three steps) as a colorless oil: $[\alpha]_D^{23}$ −8.0 (*c* 0.70, benzene); IR (KBr) 3473, 2950, 2875, 1088, 1060, 836 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.87 (dd, *J* = 12.5, 2.5 Hz, 1H), 5.78 (d, *J* = 12.5 Hz, 1H), 4.34 (d, *J* = 9.5 Hz, 1H), 3.89 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.81—3.73 (m, 2H), 3.65—3.58 (m, 2H), 3.48—3.40 (m, 2H), 3.37 (ddd, *J* = 11.5, 10.5, 5.5 Hz, 1H), 3.07 (dd, *J* = 12.5, 3.0 Hz, 1H), 2.20—2.10 (m, 3H), 1.92 (m, 1H), 1.82 (ddd, *J* = 12.0, 12.0, 11.5 Hz, 1H), 1.58 (m, 1H), 1.49—1.37 (m, 5H), 1.33—1.22 (m, 2H), 1.18 (s, 3H), 1.17 (s, 3H), 0.89 (s, 9H), −0.016 (s, 3H), −0.023 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 139.8, 130.2, 86.5, 84.1, 82.1, 80.5, 76.3, 76.1, 72.3, 64.4, 64.1, 54.4, 32.7, 30.2, 29.5, 25.8 (3C), 22.2, 21.7, 19.4, 18.2, 15.9, −5.6, −5.7 (one carbon missing presumably due to overlapping of signals); HRMS (ESI) calcd for $C_{26}H_{46}O_6SiNa$ [$(M + Na)^+$] 505.2956, found 505.2931.

Dibromoolefin 35. To a solution of alcohol **34** (740 mg, 1.54 mmol) in THF (15 mL) was added TBAF (1.0 M solution in THF, 4.62 mL, 4.62 mmol), and the resultant

solution was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (50 to 80% EtOAc/hexanes) to give a diol (505 mg, 89%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 13.0, 3.0 Hz, 1H), 5.47 (d, *J* = 13.0 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.74—3.63 (m, 2H), 3.59 (dd, *J* = 11.5, 9.0 Hz, 1H), 3.54 (dd, *J* = 7.0, 4.5 Hz, 1H), 3.40 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.33 (ddd, *J* = 11.0, 9.5, 5.0 Hz, 1H), 3.05 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.92—2.40 (br m, 2H), 2.08 (ddd, *J* = 11.5, 4.5, 4.0 Hz, 1H), 1.94—1.84 (m, 2H), 1.74—1.56 (m, 7H), 1.30 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 130.5, 86.1, 85.7, 81.6, 80.0, 76.1, 75.7, 72.1, 71.6, 64.2, 62.1, 53.4, 31.9, 29.8, 29.1, 21.9, 20.8, 19.4, 15.7.

To a solution of the above diol (505 mg, 1.37 mmol) in CH_2Cl_2/DMSO (4:1, v/v, 15 mL) was added Et_3N (0.95 mL, 6.8 mmol), and the solution was cooled to 0 °C. To this solution was added SO_3·pyridine complex (0.87 g, 5.5 mmol), and the resultant solution was stirred at 0 °C for 2 h. The reaction mixture was diluted with EtOAc, washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude aldehyde thus obtained was used in the next reaction without further purification.

To a solution of CBr_4 (1.36 g, 4.10 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added Ph_3P (2.16 g, 8.22 mmol), and the resultant solution was stirred at 0 °C for 20 min. To this solution were added Et_3N (1.53 mL, 11.0 mmol) and a solution of the above crude

aldehyde (5 mL + 5 mL rinse), and the resultant solution was stirred at 0 °C for 25 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resultant mixture was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (20 to 40% EtOAc/hexanes) gave dibromoolefin **35** (662.1 mg, 93% for the two steps) as a colorless oil: $[\alpha]_D^{22}$ +20.8 (*c* 0.19, benzene); IR (KBr) 3421, 2951, 2876, 1083, 1059 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.57 (m, 1H), 5.70 (d, *J* = 13.0 Hz, 1H), 5.57 (m, 1H), 4.27 (d, *J* = 9.5 Hz, 1H), 4.13 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.61 (ddd, *J* = 12.5, 7.0, 3.5 Hz, 1H), 3.48—3.34 (m, 3H), 3.03 (d, *J* = 13.0 Hz, 1H), 2.22 (m, 1H), 2.16—2.08 (m, 2H), 1.94 (m, 1H), 1.75 (ddd, *J* = 12.0, 12.0, 11.5 Hz, 1H), 1.58 (m, 1H), 1.50—1.38 (m, 2H), 1.34—1.22 (m, 3H), 1.17 (s, 3H), 1.13 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 138.8, 136.2, 131.7, 95.2, 86.5, 86.4, 82.5, 80.5, 76.1, 75.5, 72.4, 72.2, 64.2, 54.4, 32.3, 30.2, 29.5, 22.2, 21.2, 19.4, 15.8; HRMS (ESI) calcd for $C_{21}H_{30}Br_2O_5Na$ [$(M + Na)^+$] 543.0352, found 543.0342.

Silyl ether 36. To a solution of dibromoolefin **35** (46.2 mg, 0.0888 mmol) in CH_2Cl_2 (4 mL) at 0 °C were added 2,6-lutidine (0.100 mL, 0.859 mmol) and TMSOTf (0.080 mL, 0.44 mmol), and the resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with H_2O. The resultant mixture was extracted with EtOAc, and the organic layer was washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure.

Purification of the residue by flash chromatography on silica gel (10% EtOAc/hexanes) gave silyl ether **36** (52.6 mg, 100%) as a colorless oil: $[\alpha]_D^{22}$ +23.5 (*c* 0.26, benzene); IR (KBr) 2950, 2874, 1377, 1253, 1130, 1060, 835 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.65 (d, *J* = 9.0 Hz, 1H), 5.81 (dd, *J* = 13.0, 2.5 Hz, 1H), 5.73 (dd, *J* = 13.0, 1.5 Hz, 1H), 4.32—4.27 (m, 2H), 3.61 (ddd, *J* = 12.5, 6.5, 3.5 Hz, 1H), 3.48—3.38 (m, 3H), 2.99 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.21 (ddd, *J* = 11.5, 4.5, 4.0 Hz, 1H), 2.14 (d, *J* = 12.5 Hz, 1H), 2.12 (d, *J* = 12.5 Hz, 1H), 1.93 (m, 1H), 1.77 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.58 (m, 1H), 1.48—1.37 (m, 2H), 1.34—1.22 (m, 2H), 1.17 (s, 3H), 1.15 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 139.4, 136.9, 131.0, 86.7, 86.5, 82.6, 80.4, 79.0, 76.1, 72.41, 72.37, 64.2, 54.4, 32.3, 30.3, 29.5, 22.2, 22.0, 19.4, 15.8, 2.4 (3C); HRMS (ESI) calcd for $C_{24}H_{38}Br_2O_5SiNa$ $[(M + Na)^+]$ 615.0747, found 615.0749.

(*Z*)-Vinyl bromide 37. To a solution of silyl ether **36** (91.2 mg, 0.154 mmol) in benzene (5 mL) were added *n*-Bu_3SnH (0.083 mL, 0.31 mmol) and $Pd(PPh_3)_4$ (17.8 mg, 0.015 mmol), and the resultant mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (12 to 15% Et_2O/hexanes) gave (*Z*)-vinyl bromide **37** (70.2 mg, 89%) as a colorless oil: $[\alpha]_D^{22}$ +41.9 (*c* 1.35, benzene); IR (KBr) 2928, 2856, 1460, 1377, 1082 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.10 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.03 (d, *J* = 7.5 Hz, 1H), 5.90 (dd, *J* = 13.0, 2.5 Hz, 1H), 5.78 (dd, *J* = 13.0, 1.5 Hz, 1H), 4.59 (d, *J* = 7.5 Hz, 1H), 4.35 (m, 1H), 3.61 (ddd, *J* = 12.5, 7.0, 3.5 Hz, 1H), 3.55 (ddd, *J* = 11.0, 10.0, 5.0 Hz, 1H), 3.44 (ddd, *J* = 10.5, 8.0, 3.0 Hz, 1H), 3.39 (dd, *J* =

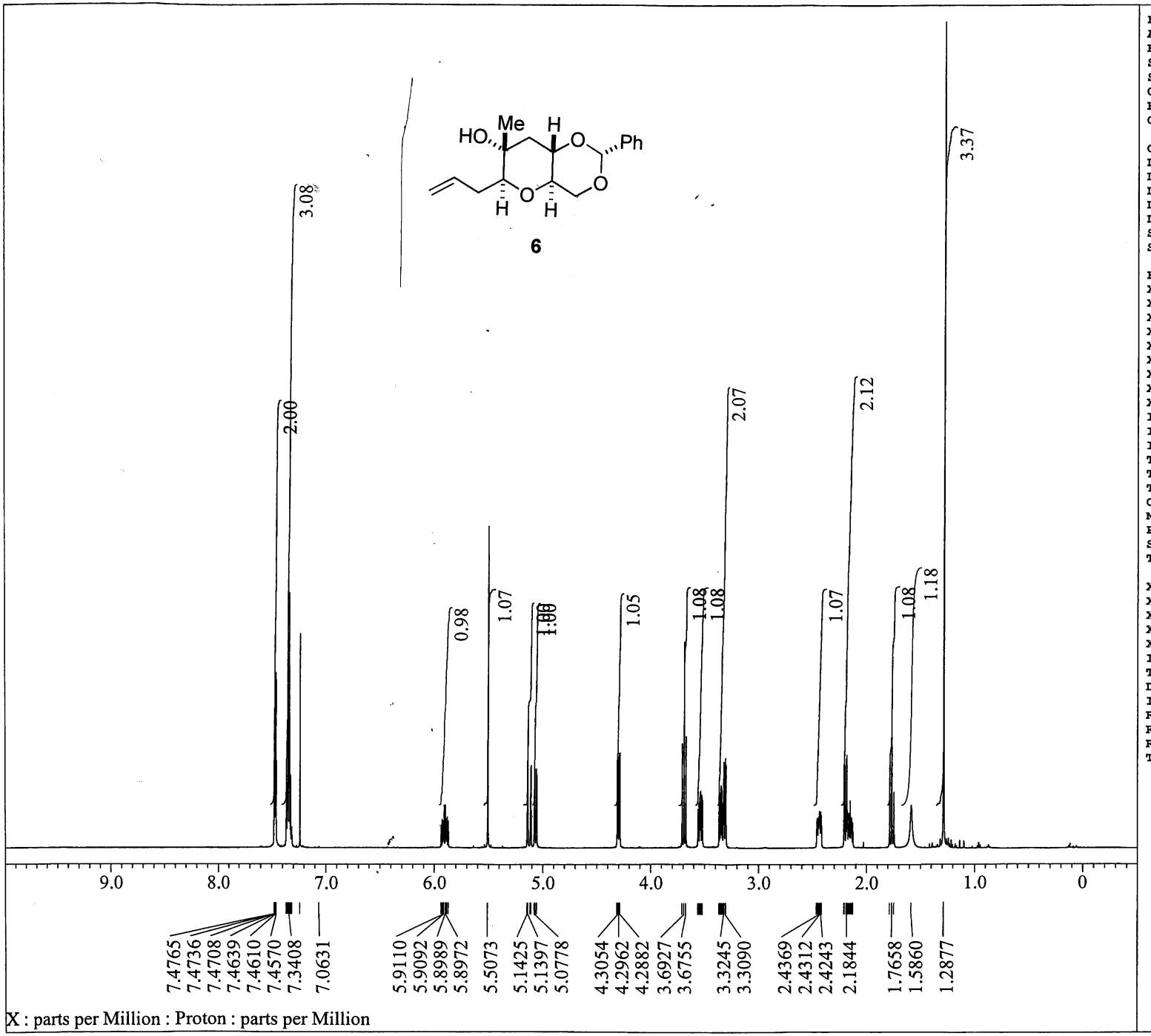
11.5, 4.0 Hz, 1H), 2.99 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.27 (ddd, *J* = 12.0, 4.5, 4.5 Hz, 1H), 2.16 (d, *J* = 12.5 Hz, 1H), 2.12 (d, *J* = 12.5 Hz, 1H), 1.92 (m, 1H), 1.81 (ddd, *J* = 13.0, 11.5, 11.0 Hz, 1H), 1.56 (m, 1H), 1.50—1.35 (m, 5H), 1.34—1.22 (m, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 139.4, 132.9, 131.0, 112.1, 86.3, 84.4, 82.5, 80.4, 79.1, 76.1, 72.6, 72.4, 64.1, 54.4, 32.5, 30.3, 29.5, 22.3, 22.2, 19.5, 15.9, 2.5 (3C); HRMS (ESI) calcd for $C_{24}H_{39}BrO_5SiNa$ [$(M + Na)^+$] 537.1642, found 537.1633.

Alcohol 38. To a solution of (*Z*)-vinyl bromide **37** (120.6 mg, 0.2346 mmol) in THF (5 mL) at 0 °C was added HF·pyridine complex (1.5 mL), and the resultant solution was stirred at room temperature overnight. The reaction was quenched with saturated aqueous $NaHCO_3$ solution at 0 °C. The resultant mixture was extracted with EtOAc, and the organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (30% EtOAc/hexanes) gave alcohol **38** (97.4 mg, 94%) as a colorless amorphous solid: $[\alpha]_D^{22}$ +78.8 (*c* 0.70, benzene); IR (KBr) 3510, 2947, 2873, 1458, 1379, 1079 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 5.97—5.72 (m, 2H), 5.75 (d, *J* = 12.5 Hz, 1H), 5.71 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.46 (m, 1H), 4.33 (d, *J* = 10.0 Hz, 1H), 3.61 (m, 1H), 3.48—3.37 (m, 3H), 2.99 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.18 (ddd, *J* = 11.5, 4.5, 4.0 Hz, 1H), 2.15 (d, *J* = 12.5 Hz, 1H), 2.11 (d, *J* = 12.5 Hz, 1H), 1.91 (m, 1H), 1.76 (ddd, *J* = 12.0, 12.0, 11.5 Hz, 1H), 1.57 (m, 1H), 1.50—1.38 (m, 2H), 1.33—1.22 (m, 5H), 1.20 (s, 1H), 1.17 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 131.9, 131.5,

113.0, 86.4, 84.1, 82.0, 80.4, 76.2, 76.2, 72.4, 72.0, 64.5, 53.8, 32.2, 30.2, 29.5, 22.2, 21.6, 19.8, 16.0; HRMS (ESI) calcd for $C_{21}H_{31}BrO_5Na$ [$(M + Na)^+$] 465.1247, found 465.1226.

Tetracyclic analogue 3. To a solution of alcohol **38** (37.6 mg, 0.0851 mmol) and vinyl stannane **27** (91.4 mg) in THF/DMSO (1:1, v/v, 2 mL, degassed by purging N_2 gas) were added LiCl (43.3 mg, 1.02 mmol), CuCl (84.2 mg, 0.851 mmol), and $Pd(PPh_3)_4$ (29.5 mg, 0.0255 mmol), and the resultant mixture was stirred at 60 °C for two days. The reaction was quenched with 3% NH_4OH solution at room temperature. The resultant mixture was stirred at room temperature for a while and then filtered through a pad of Celite®. The filtrate was diluted with EtOAc, washed with 3% NH_4OH solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (25% EtOAc/hexanes) gave tetracyclic analogue **3** (20.4 mg, 56%) as a colorless amorphous solid: $[\alpha]_D^{23}$ +97.0 (*c* 0.40, benzene); IR (KBr) 3442, 2928, 2873, 1457, 1382, 1130, 1082, 1060 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.51 (dd, *J* = 11.5, 11.0 Hz, 1H), 6.30 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.94 (dd, *J* = 13.0, 2.5 Hz, 1H), 5.82 (dd, *J* = 13.0, 1.5 Hz, 1H), 5.67 (m, 1H), 5.51—5.44 (m, 2H), 5.03—4.92 (m, 2H), 4.51 (d, *J* = 9.0 Hz, 1H), 4.40 (m, 1H), 3.61 (ddd, *J* = 13.0, 6.5, 4.0 Hz, 1H), 3.48—3.40 (m, 2H), 3.36 (ddd, *J* = 11.0, 9.5, 5.0 Hz, 1H), 3.03 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.76—2.70 (m, 2H), 2.16 (d, *J* = 12.5 Hz, 1H), 2.13 (d, *J* = 12.5 Hz, 1H), 2.10 (ddd, *J* = 12.0, 4.5, 4.5 Hz, 1H), 1.90 (m, 1H), 1.79 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.55 (m, 1H), 1.48—1.35 (m, 2H), 1.33—1.21 (m, 8H),

1.17 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 138.7, 136.2, 131.5, 131.4, 128.6, 127.0, 125.3, 115.4, 86.5, 83.1, 81.9, 80.6, 76.3, 76.1, 72.4, 72.3, 64.1, 54.4, 32.7, 31.8, 30.3, 29.5, 22.2, 21.9, 19.4, 15.9; HRMS (ESI) calcd for $C_{26}H_{38}O_5Na$ [$(M + Na)^+$] 453.2611, found 453.2609.

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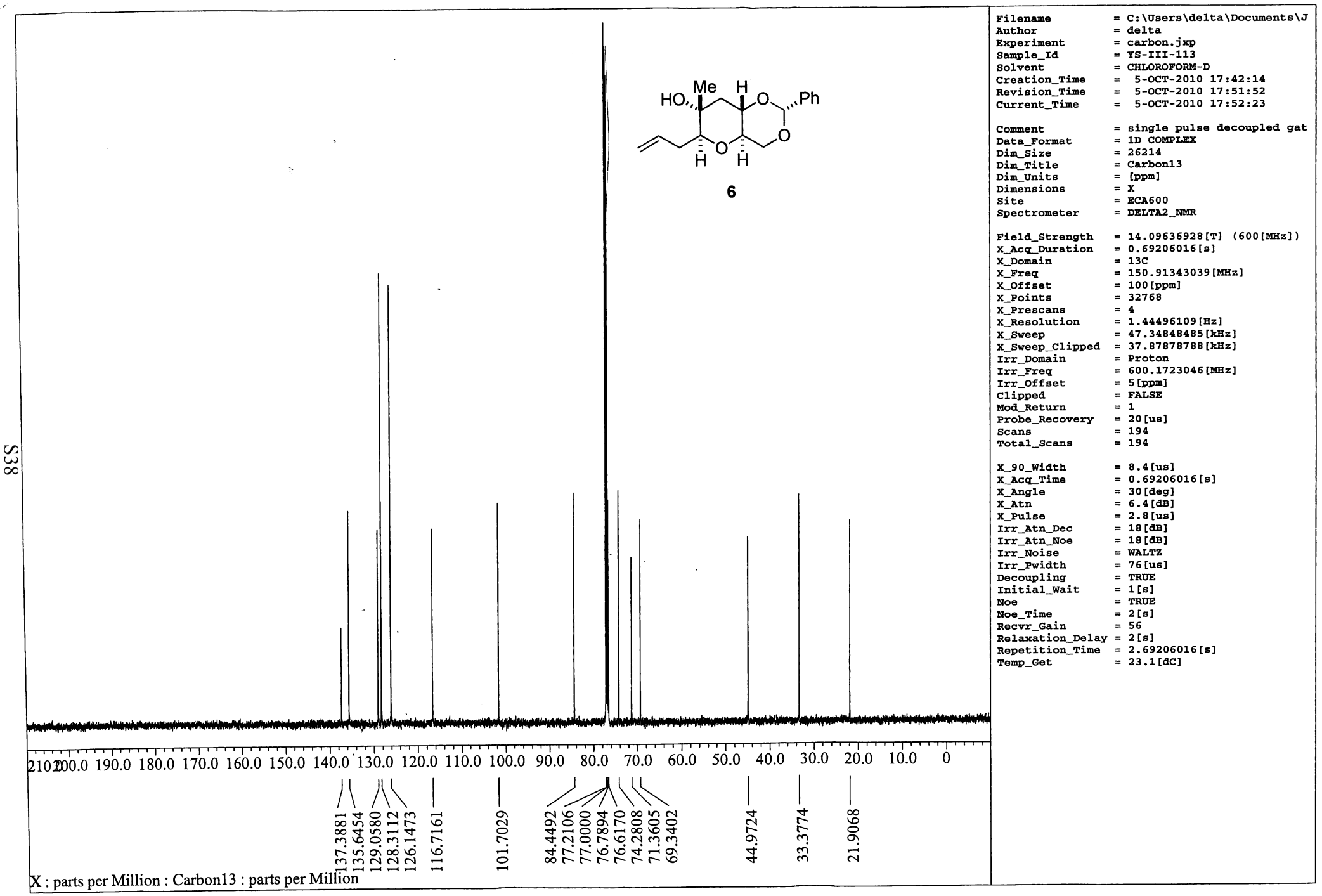


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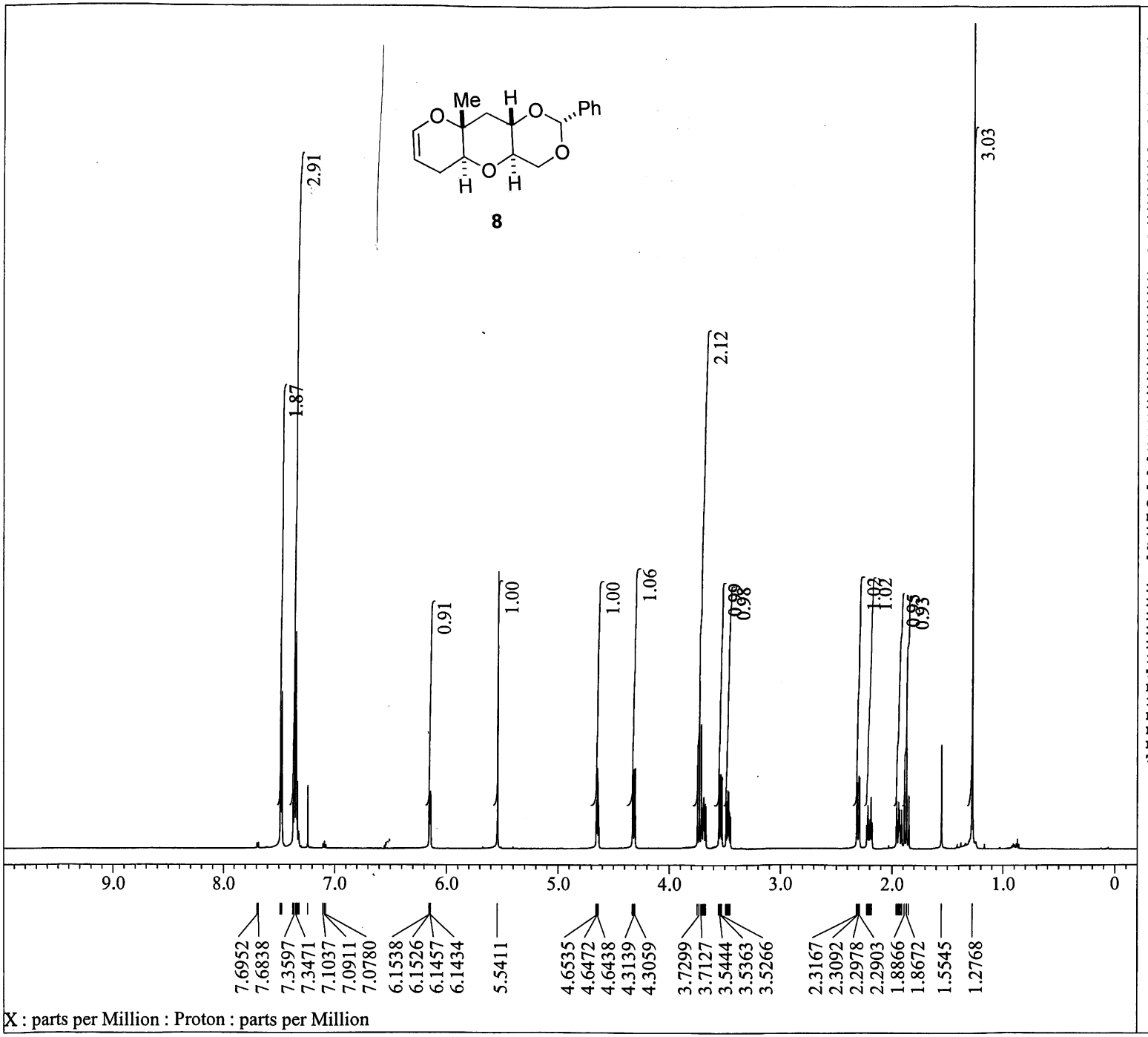


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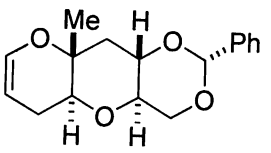

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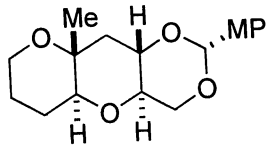
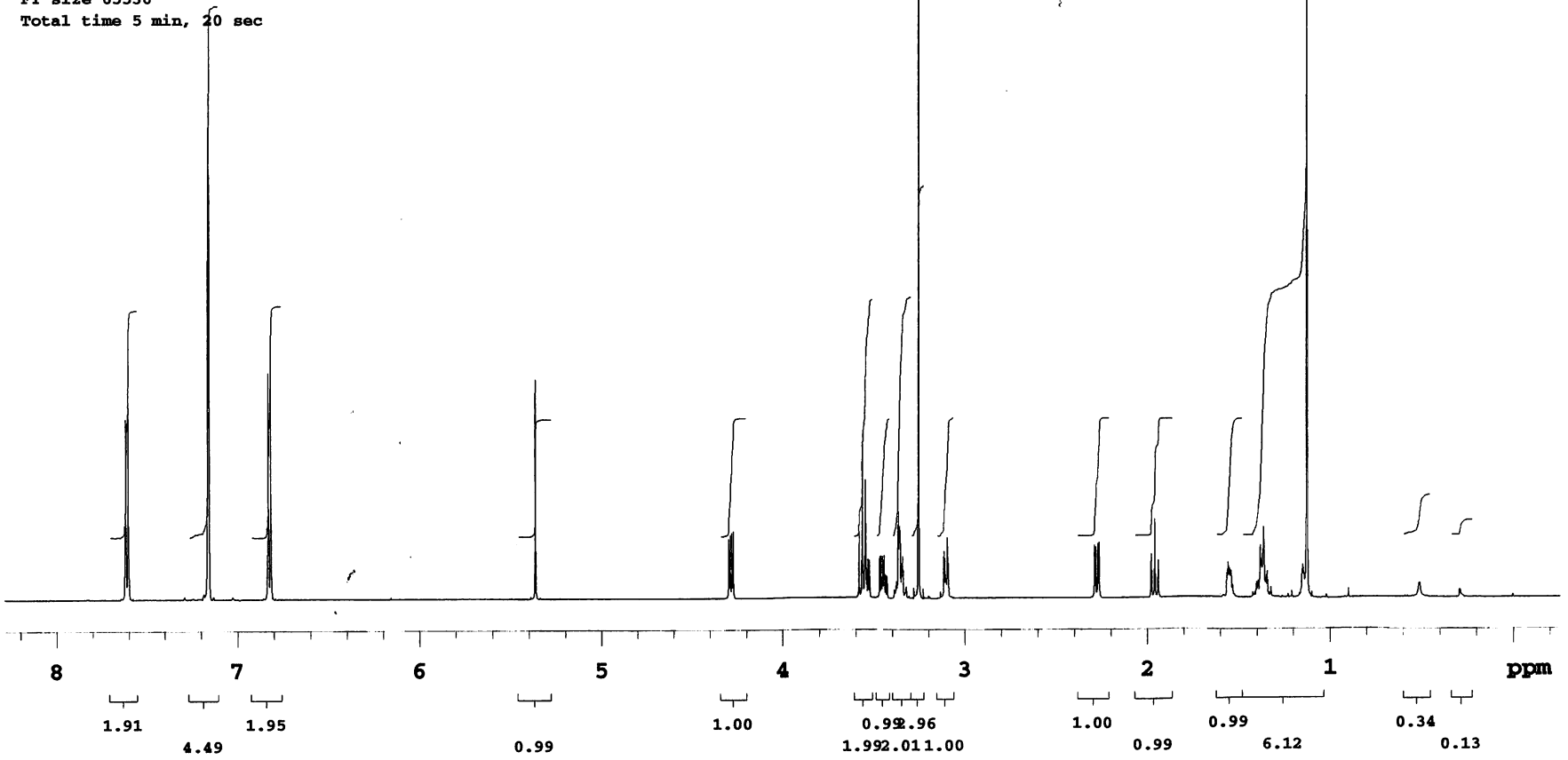


9



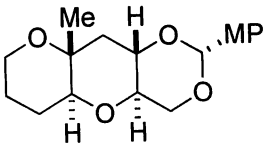
YS-IV-98

File: xp

Pulse Sequence: s2pul

Solvent: c6d6
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
200 repetitions
OBSERVE C13, 150.8369674 MHz
DECOUPLE H1, 599.8713508 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 min, 0 sec

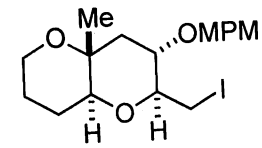


9

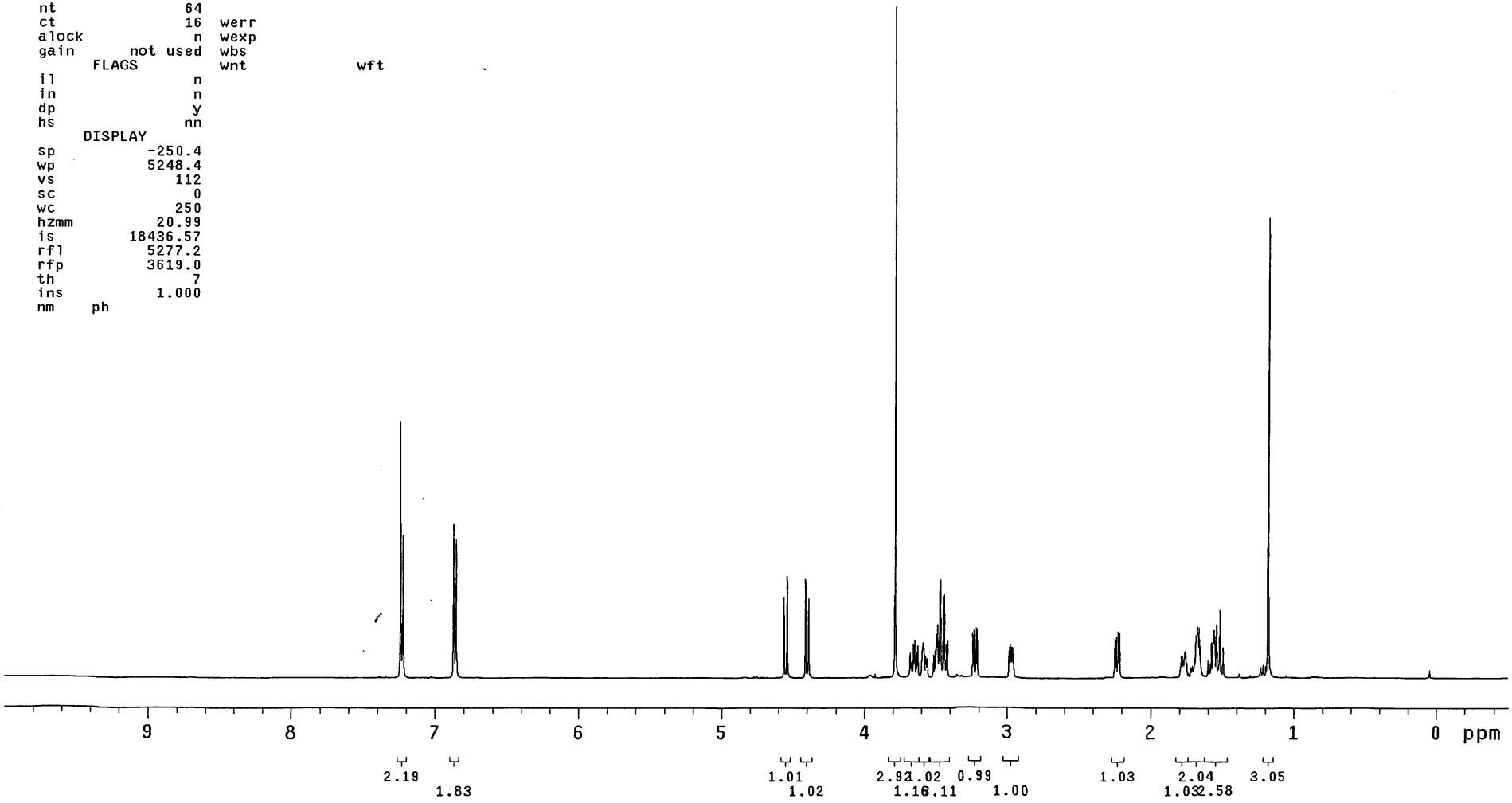
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 8 2007	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	54	wtfile	
pw	2.5	proc	lp
d1	1.000	fn	not used
tof	-140.0	math	f
nt	64		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	5248.4		
vs	112		
sc	0		
wc	250		
hzmm	20.99		
is	18436.57		
rfl	5277.2		
rfp	3619.0		
th	7		
ins	1.000		
nm	ph		



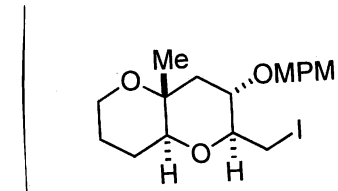
10



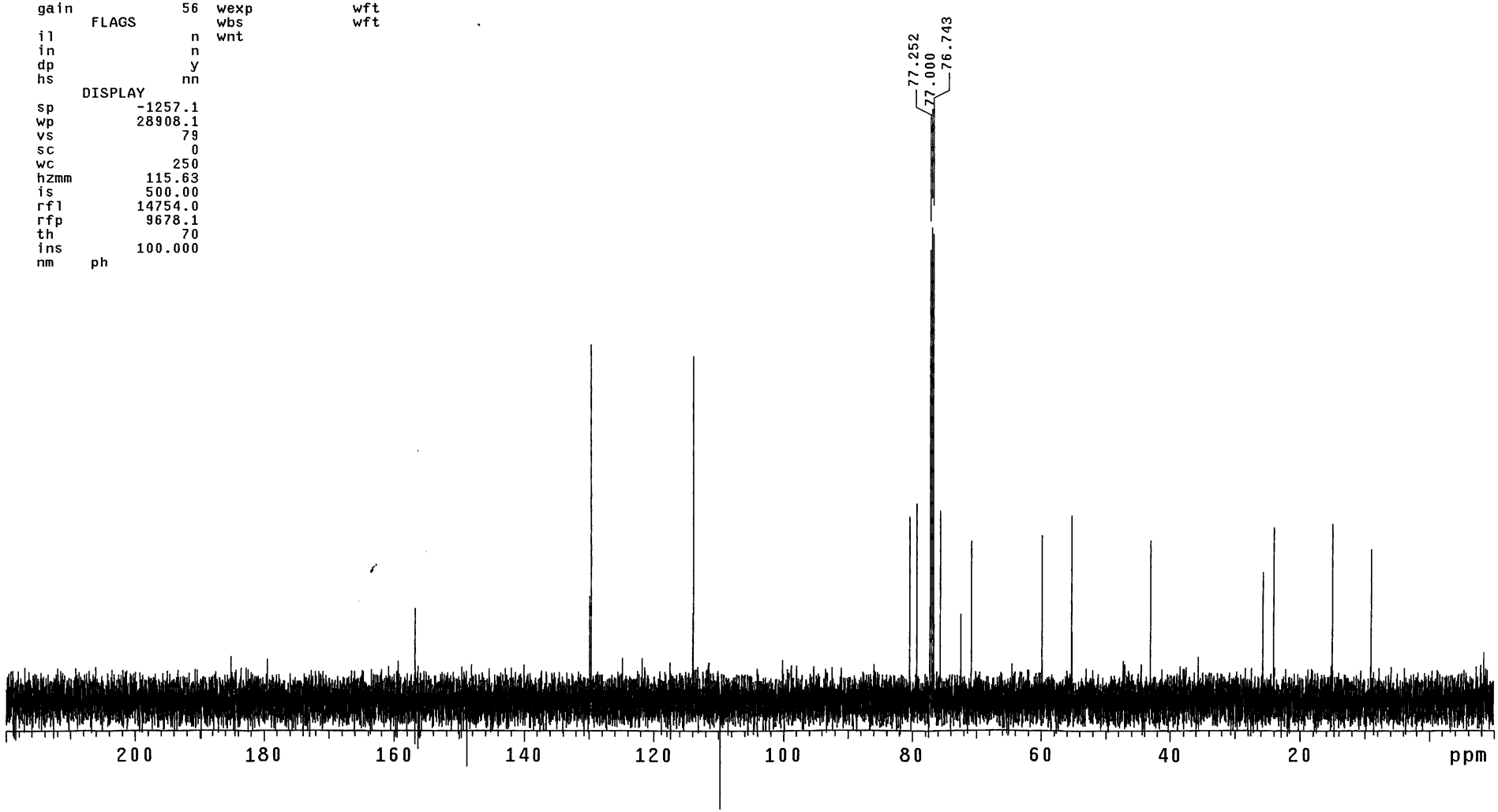
STANDARD CARBON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Dec 8 2007	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	8	PROCESSING	
tpwr	61	lb	0.50
pw	5.3	wtfile	
d1	0.700	proc	ft
tof	1883.8	fn	131072
nt	5120	math	f
ct	128		
alock	n	werr	
gain	56	wexp	wft
FLAGS		wbs	wft
il	n	wnt	
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1257.1		
wp	28908.1		
vs	79		
sc	0		
wc	250		
hzmm	115.63		
is	500.00		
rfl	14754.0		
rfp	9678.1		
th	70		
ins	100.000		
nm	ph		



10

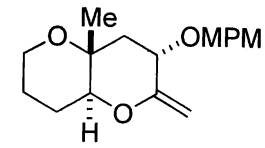


OMPM
Me
O
O
H
11
X : parts per Million : Proton : parts per Million
0.4825
1.0837
1.1307
1.1318
1.4199
1.4267
1.7039
1.7107
2.0955
2.1070
2.1282
2.1345
2.1362
3.2471
3.2517
3.2723
3.2860
3.3347
3.3438
3.8724
3.8758
4.1856
4.3493
4.5377
4.7290
6.1485
6.7641
6.7675
6.7789
7.1500
7.1981
7.2033
7.2067
7.2141
7.2176
0.96
3.00
2.10
1.03
2.08
1.02
3.93
1.00
0.96
1.04
1.02
1.03
1.01
95.23m
1.90
1.90

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
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
192 repetitions
OBSERVE C13, 125.6897254 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 5 hr, 34 min, 36 sec

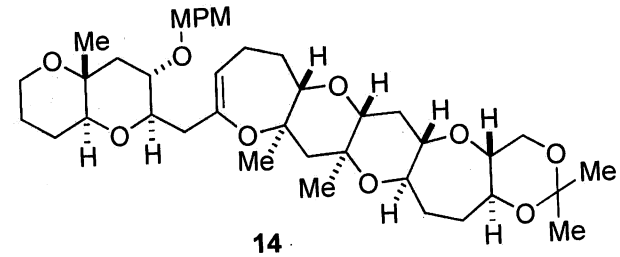


11

STANDARD PROTON PARAMETERS

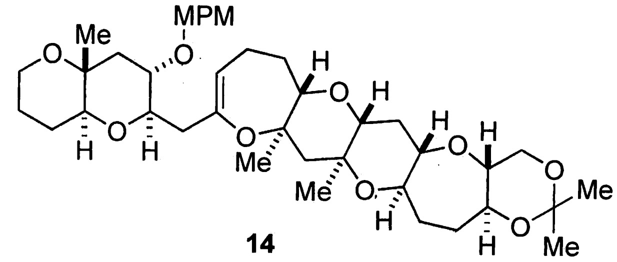
exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 10 2007	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	54	wtfile	
pw	2.5	proc	lp
d1	1.000	fn	not used
tof	-140.0	math	f
nt	64		
ct	20	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	5248.4		
vs	181		
sc	0		
wc	250		
hzmm	20.99		
is	19195.08		
rfl	5205.9		
rfp	3574.0		
th	69		
ins	1.000		
nm	ph		

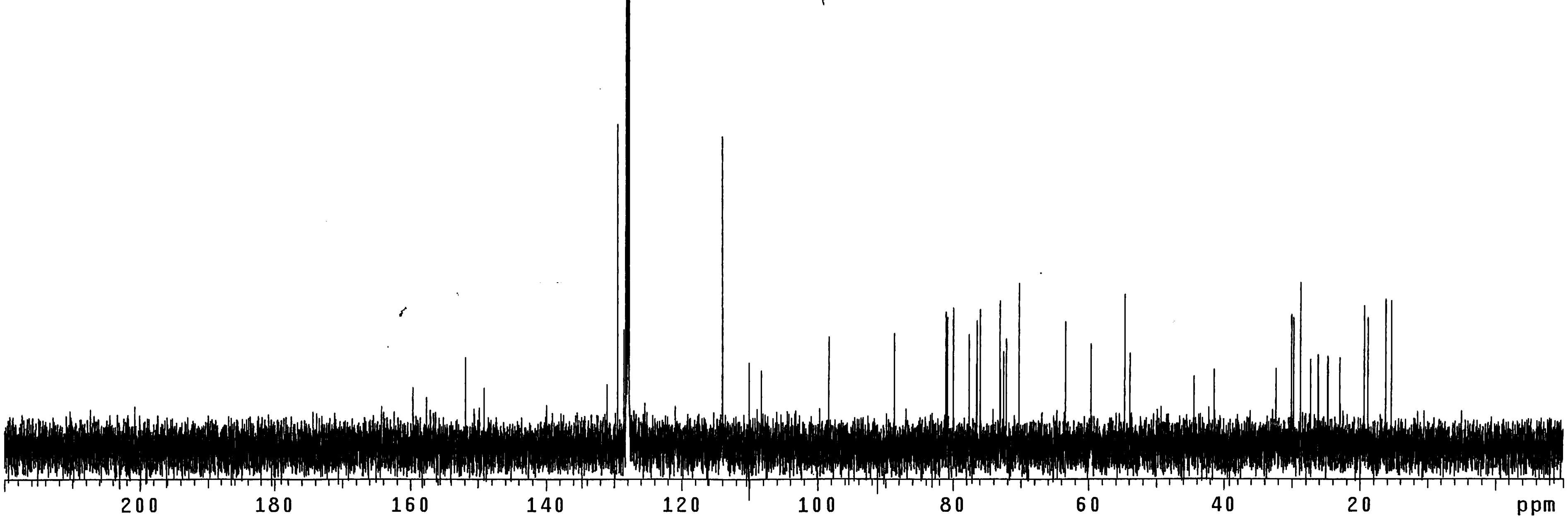


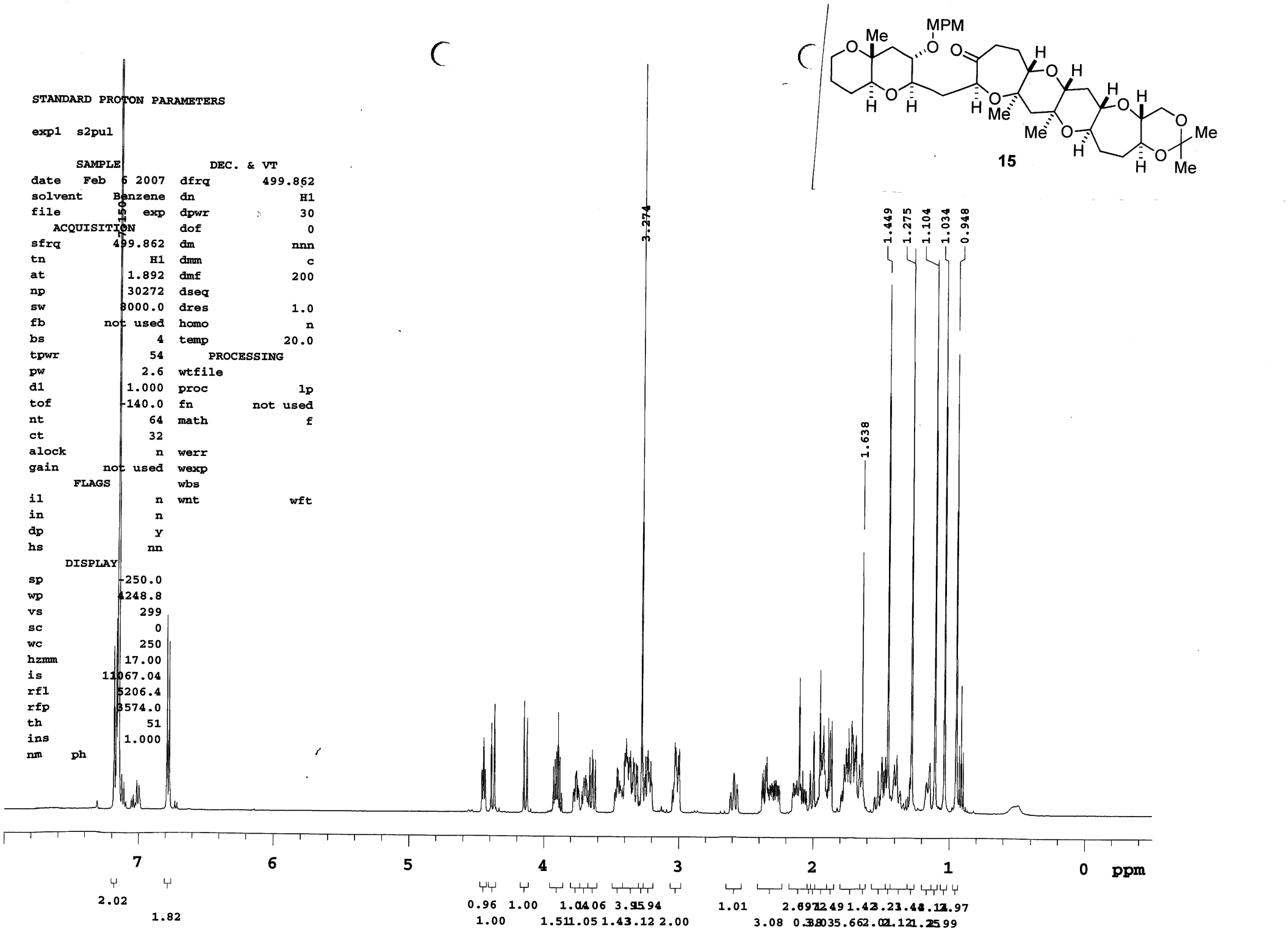
14

```
STANDARD CARBON PARAMETERS

exp3  s2pul

     SAMPLE                DEC. & VT
date    Dec 10 2007   dfrq        499.862
solvent    Benzene    dn               H1
file           exp    dpwr             27
   ACQUISITION        dof               0
sfrq       125.704    dm              yyy
tn             C13    dmm               w
at           1.298    dmf           12579
np           97994    dseq
sw         37735.8    dres            1.0
fb        not used    homo              n
bs               8       PROCESSING
tpwr            61    lb             0.50
pw             5.3    wtfile
d1           0.700    proc             ft
tof         1883.8    fn           131072
nt            5120    math              f
ct             256
alock            n    werr
gain            56    wexp            wft
     FLAGS            wbs             wft
il               n    wnt
in               n
dp               y
hs              nn
    DISPLAY
sp         -1256.9
wp         28908.1
vs             655
sc               0
wc             250
hzmm        115.63
is          500.00
rfl        21120.2
rfp        16088.3
th             102
ins        100.000
nm     ph
```



14

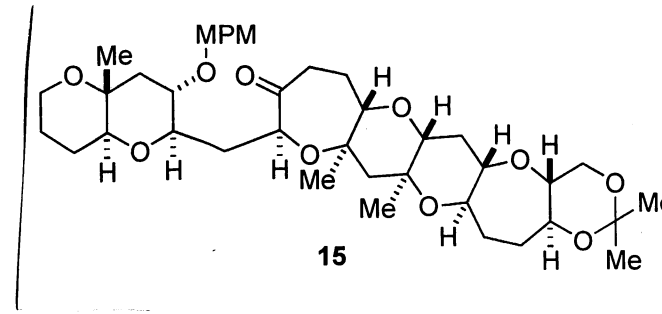


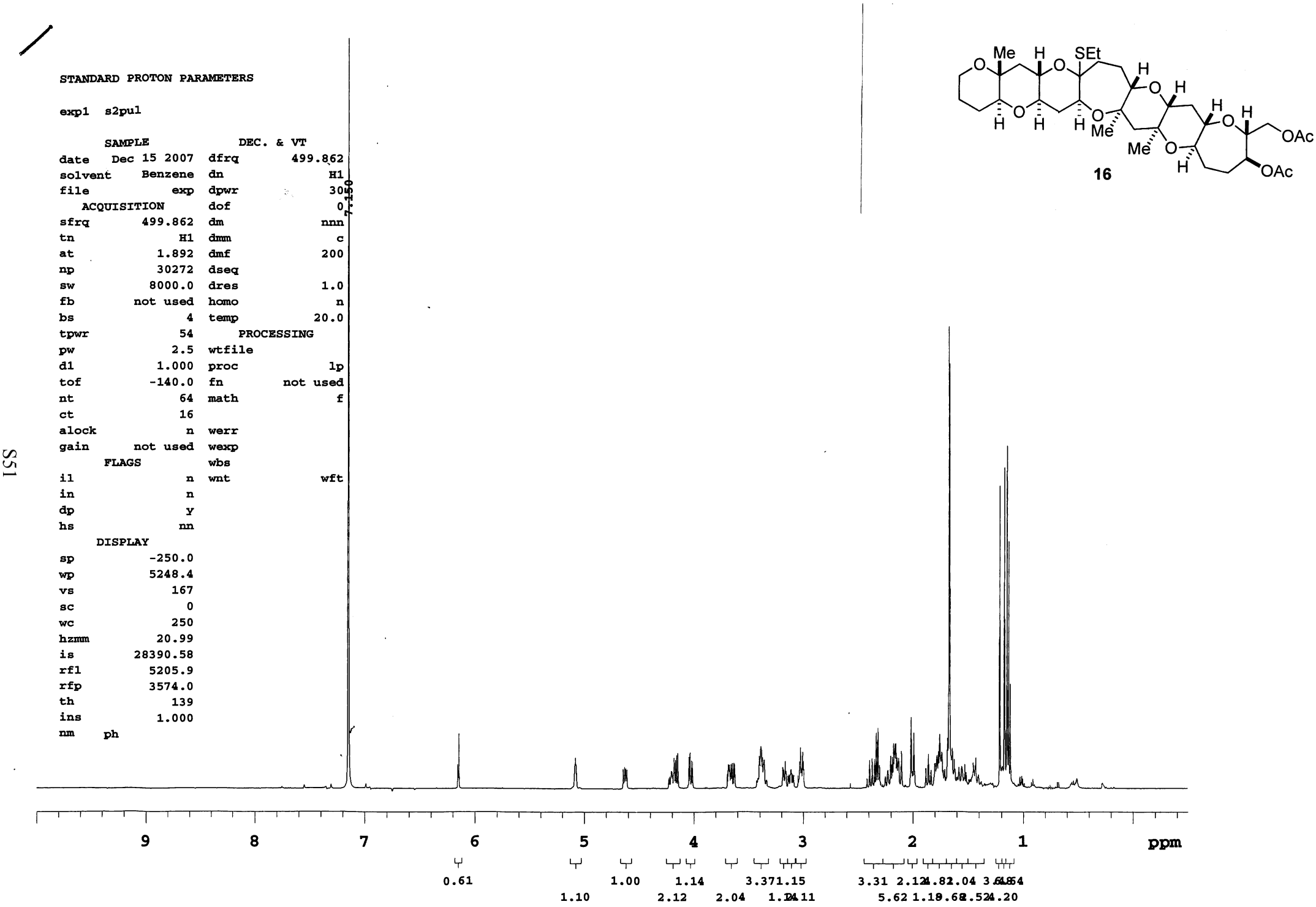

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Feb 6 2007
solvent Benzene
file exp
ACQUISITION
sfrq 499.862
tn H1
at 1.892
np 30272
sw 8000.0
fb not used
bs 4
tpwr 54
pw 2.6
d1 1.000
tof -140.0
nt 64
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 4248.8
vs 299
sc 0
wc 250
hzmm 17.00
is 11067.04
rfl 5206.4
rfp 3574.0
th 51
ins 1.000
nm ph
DEC. & VT
dfrq 499.862
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
wtfile
proc lp
fn not used
math f
werr
wexp
wbs
wnt wft
MPM
Me
15
3.274
1.638
1.449
1.275
1.104
1.034
0.948
7
6
5
4
3
2
1
0
ppm
2.02
1.82
0.96
1.00
1.00
1.51
1.05
1.43
3.12
2.00
1.01
3.08

STANDARD CARBON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Dec 15 2007	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	YYY
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	8	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	536	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	wft
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	28908.1		
vs	420		
sc	0		
wc	250		
hzmm	115.63		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	154		
ins	100.000		
nm	ph		

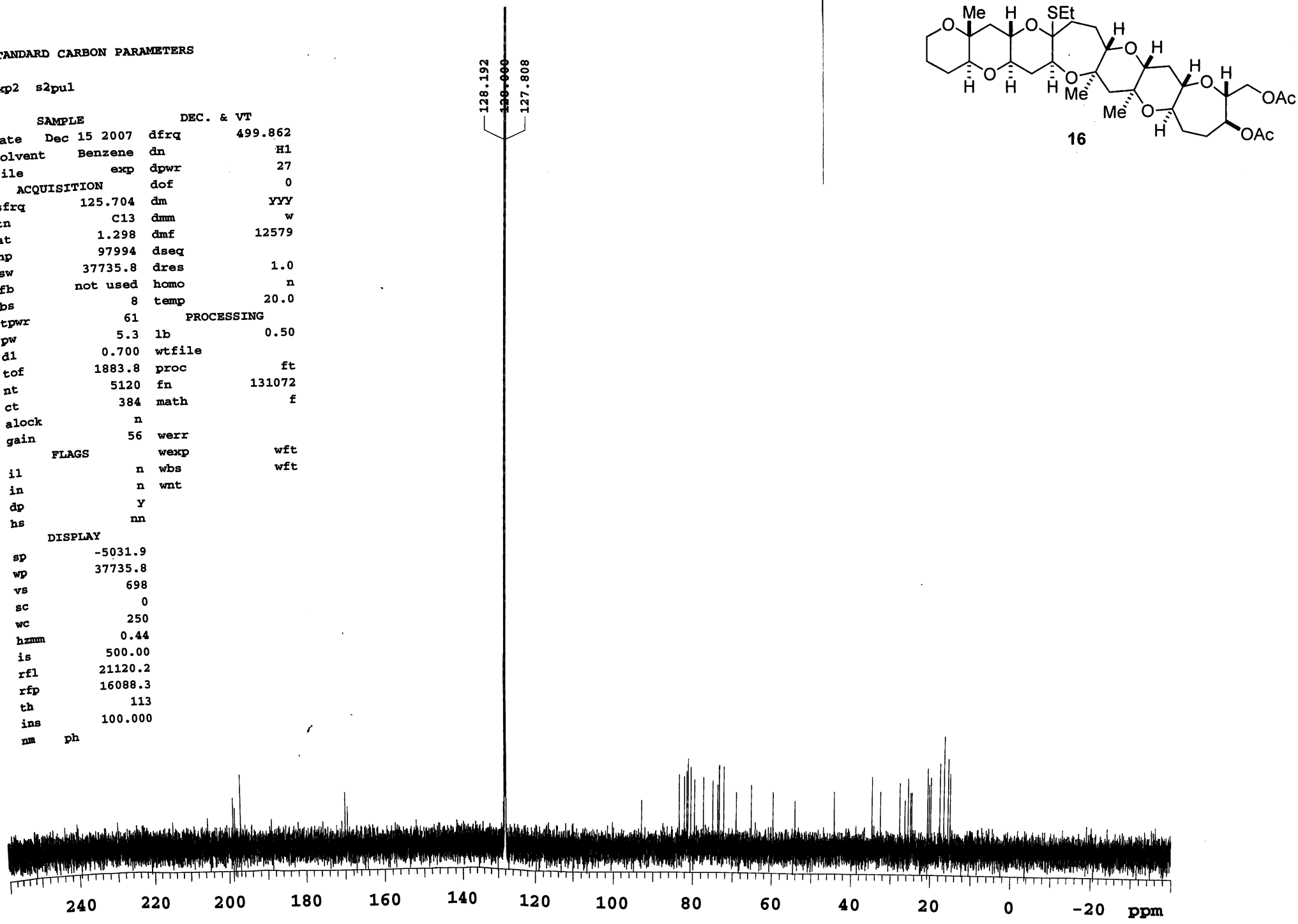



STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Dec 15 2007
solvent Benzene
file exp
ACQUISITION
sfrq 499.862
tn H1
at 1.892
np 30272
sw 8000.0
fb not used
bs 4
tpwr 54
pw 2.5
d1 1.000
tof -140.0
nt 64
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5248.4
vs 167
sc 0
wc 250
hzmm 20.99
is 28390.58
rfl 5205.9
rfp 3574.0
th 139
ins 1.000
nm ph
DEC. & VT
dfrq 499.862
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
wtfile
proc lp
fn not used
math f
werr
wexp
wbs
wnt wft
7.150
Me H SEt
OAc
OAc
16
9 8 7 6 5 4 3 2 1 ppm
0.61 1.10 1.00 2.12 1.14 2.04 3.37 1.15 3.31 2.12 5.62 1.18 4.82 2.04 3.68 2.52 4.20

STANDARD CARBON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Dec 15 2007	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	YYY
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	8	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	384	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	wft
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-5031.9		
wp	37735.8		
vs	698		
sc	0		
wc	250		
hzmm	0.44		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	113		
ins	100.000		
nm	ph		



16

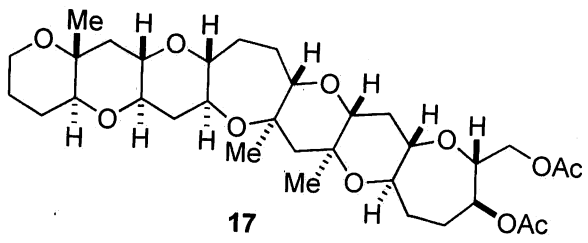
YS-IV-100

File: home/vnmr1/vnmrsys/data/operator/December/YS-IV-100-10127.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: vnmr1
File: YS-IV-100-10127
VNMRS-600 "varian2"

Relax. delay 1.592 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 9615.4 Hz
24 repetitions
OBSERVE H1, 599.8683082 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 5 min, 20 sec



17

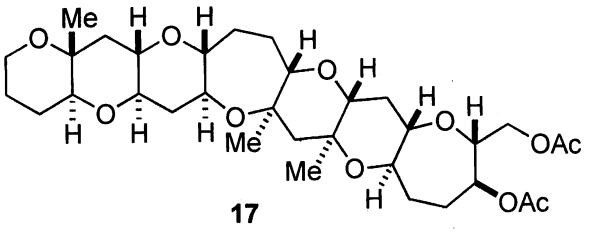
YS-IV-100-13C

File: xp

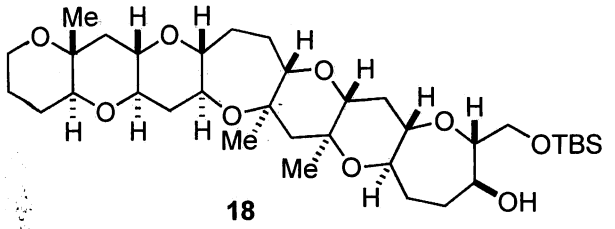
Pulse Sequence: s2pul

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
736 repetitions
OBSERVE C13, 150.8370053 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 4 hr, 10 min, 0 sec

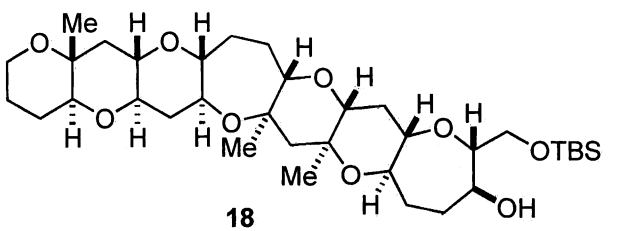


17



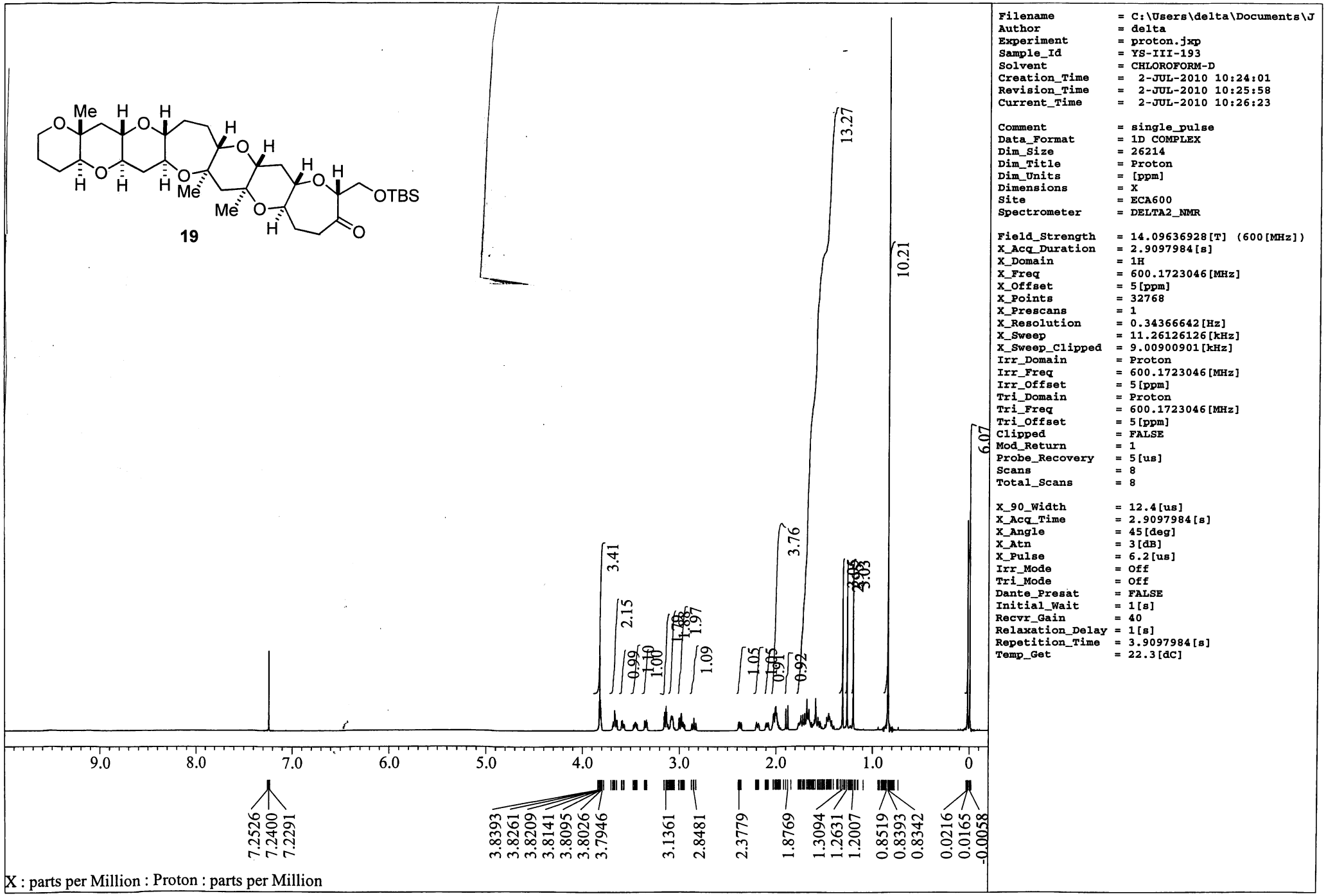
18


```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-III-186
Solvent           = CHLOROFORM-D
Creation_Time     = 22-SEP-2010 21:18:30
Revision_Time     = 22-SEP-2010 21:29:09
Current_Time      = 22-SEP-2010 21:29:34

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        = 44
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.3[dC]
```



18


```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = YS-III-186
Solvent           = CHLOROFORM-D
Creation_Time     = 22-SEP-2010 21:20:51
Revision_Time     = 22-SEP-2010 21:34:05
Current_Time      = 22-SEP-2010 21:35:07

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             = 269
Total_Scans       = 269

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]
```




```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-III-193
Solvent           = CHLOROFORM-D
Creation_Time     =  2-JUL-2010 10:24:01
Revision_Time     =  2-JUL-2010 10:25:58
Current_Time      =  2-JUL-2010 10:26:23

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          = 22.3[dC]
```

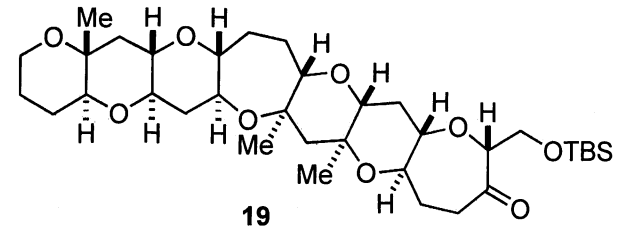
YS-III-193-13C

File: xp

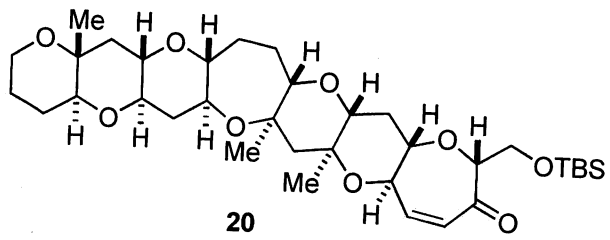
Pulse Sequence: s2pul

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
488 repetitions
OBSERVE C13, 150.8370056 MHz
DECOUPLE H1, 599.8712968 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 40 min, 0 sec

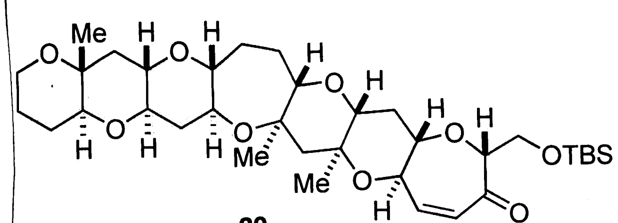


19

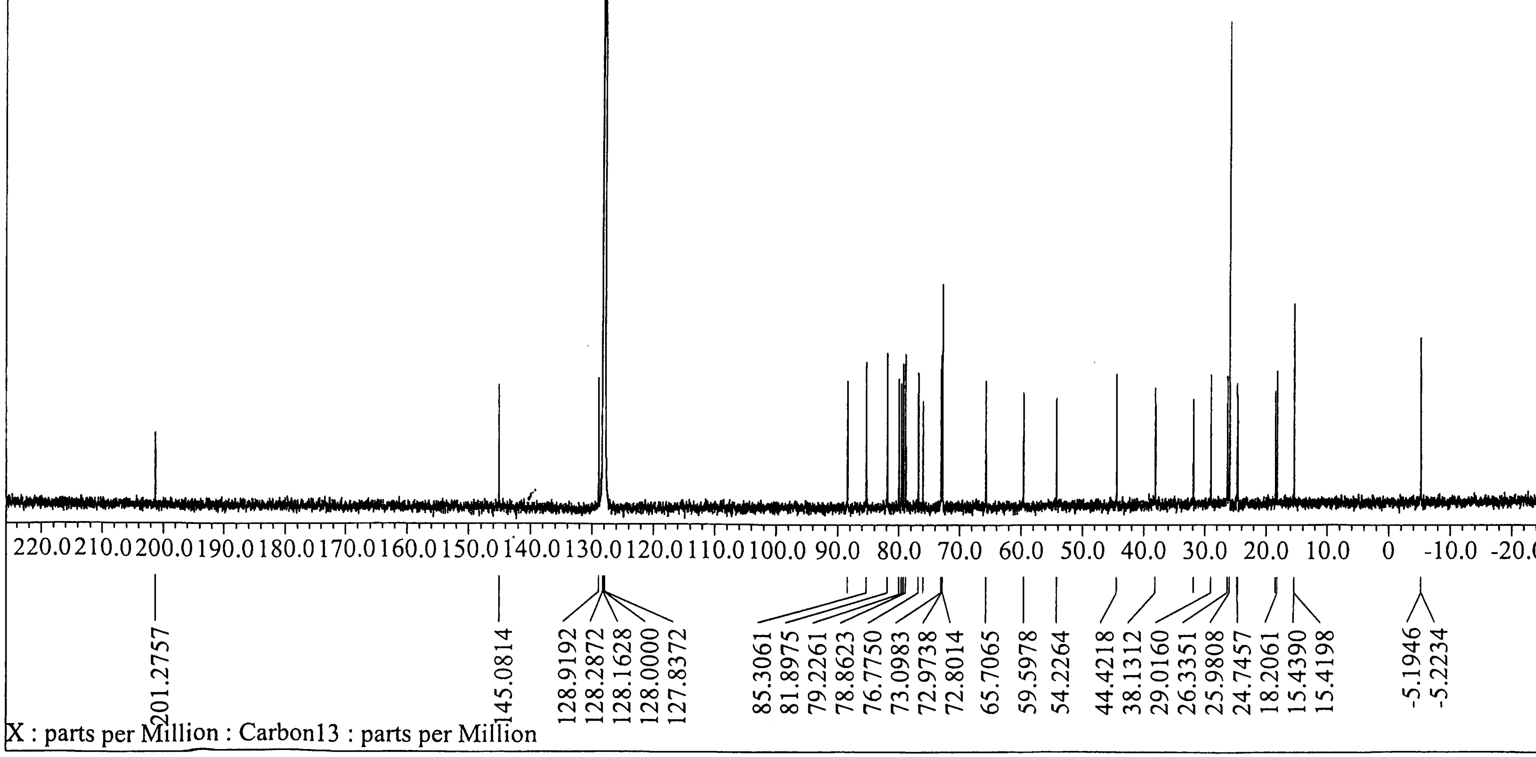



```
Filename          = C:\Users\delta\Desktop\dat
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-IV-6
Solvent           = BENZENE-D6
Creation_Time     = 16-JUL-2010 18:42:58
Revision_Time     =  6-JAN-2012 02:40:24
Current_Time      =  6-JAN-2012 02:40:35

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        = 36
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]
```

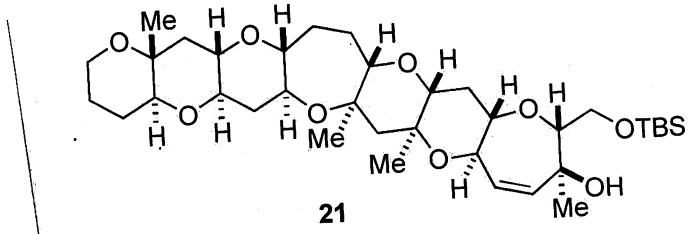
X : parts per Million : Proton : parts per Million



20



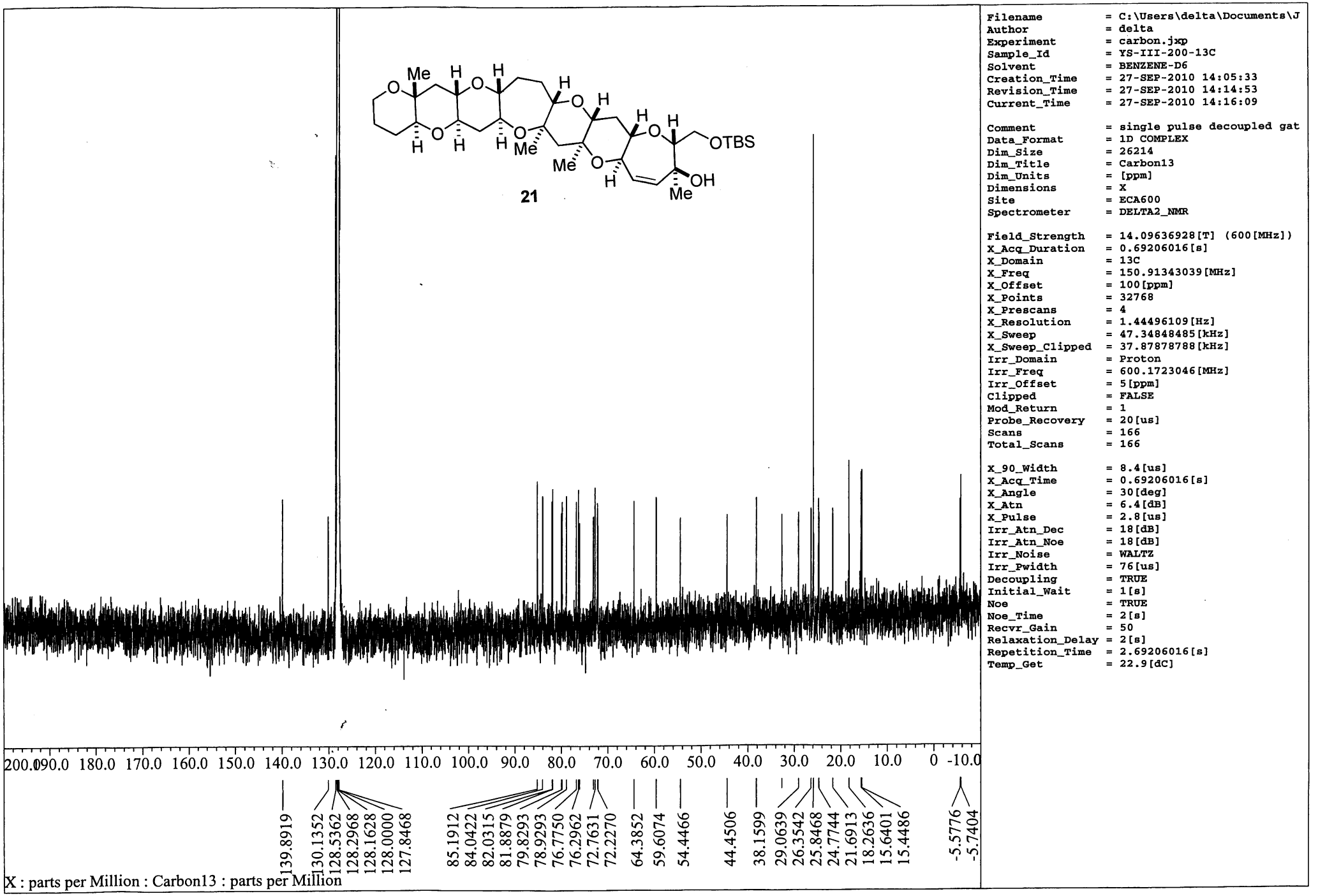
Filename	= C:\Users\delta\Desktop\dat
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= YS-IV-6
Solvent	= BENZENE-D6
Creation_Time	= 16-JUL-2010 18:45:13
Revision_Time	= 6-JAN-2012 02:41:26
Current_Time	= 6-JAN-2012 02:41:39
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
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	= 292
Total_Scans	= 292
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]



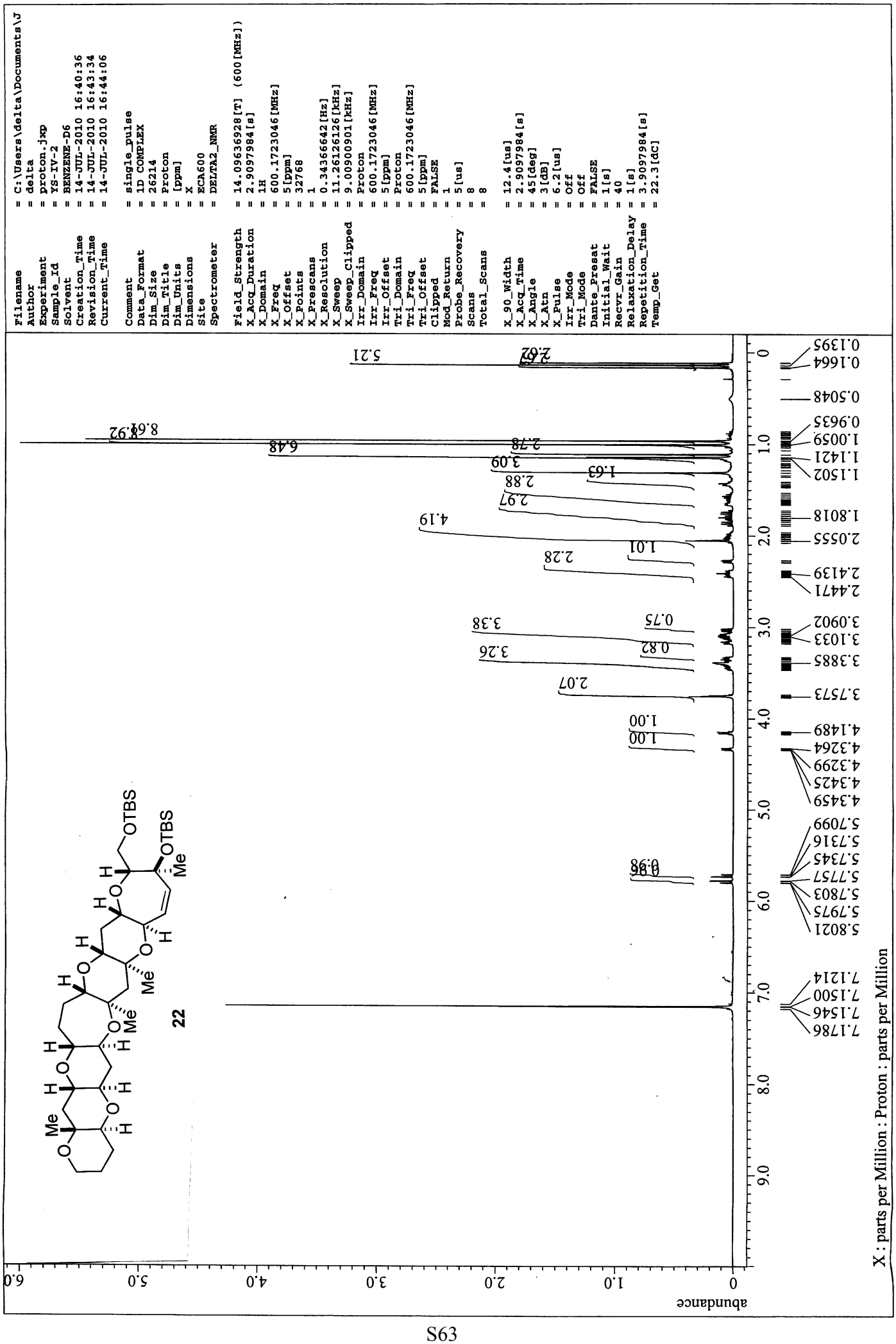
21

X : parts per Million : Proton : parts per Million

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-III-200
Solvent           = CHLOROFORM-D
Creation_Time     = 15-JUL-2010 16:06:04
Revision_Time     = 15-JUL-2010 16:08:34
Current_Time      = 15-JUL-2010 16:08:55

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          = 22.2[dC]
```




```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = YS-III-200-13C
Solvent           = BENZENE-D6
Creation_Time     = 27-SEP-2010 14:05:33
Revision_Time     = 27-SEP-2010 14:14:53
Current_Time      = 27-SEP-2010 14:16:09

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             = 166
Total_Scans       = 166

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          = 22.9[dC]
```


Filename = C:\Users\delta\Documents\J
Author = delta
Experiment = proton.jxp
Sample_Id = YS-IV-2
Solvent = BENZENE-D6
Creation_Time = 14-JUL-2010 16:40:36
Revision_Time = 14-JUL-2010 16:43:34
Current_Time = 14-JUL-2010 16:44:06
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 = 2.90979841[s]
X_Domain = 1H
X_Freq = 600.17230461[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 = 600.17230461[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 600.17230461[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 = 2.90979841[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 = 3.90979841[s]
Temp_Get = 22.3[dC]
OTBS
OTBS
Me
Me
Me
22
abundance
X : parts per Million : Proton : parts per Million

YS-IV-2-13C

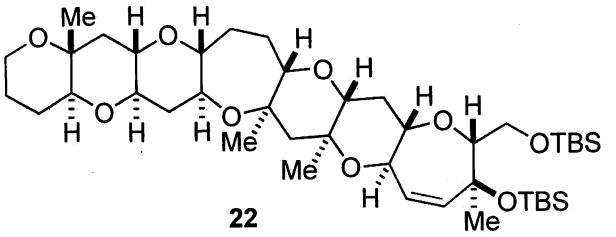
1000回 積算

File: xp

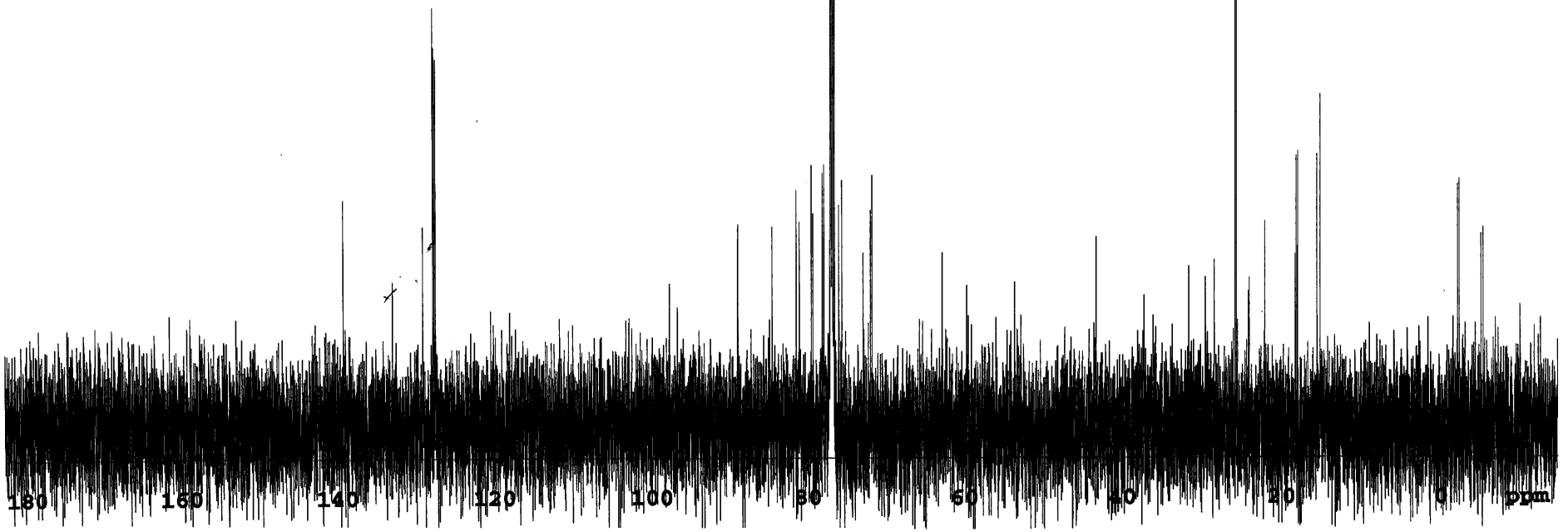
Pulse Sequence: s2pul

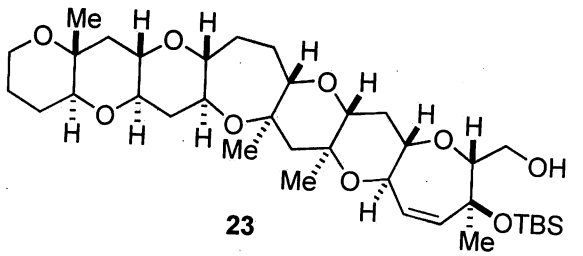
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: vnmr1
VNMRS-600 "varian600"

Relax. delay 1.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 36764.7 Hz
1200 repetitions
OBSERVE C13, 150.8370071 MHz
DECOUPLE H1, 599.8712968 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 40 min, 0 sec



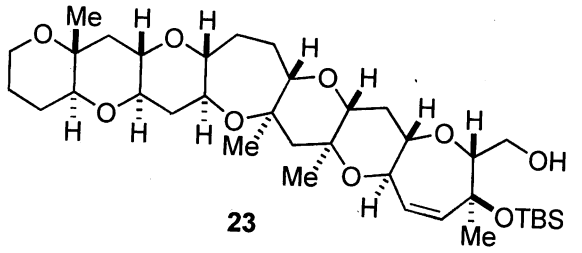
22





23


```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-IV-16
Solvent           = CHLOROFORM-D
Creation_Time     = 20-JUL-2010 20:14:35
Revision_Time     = 20-JUL-2010 20:16:49
Current_Time      = 20-JUL-2010 20:17:00

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]
```



23

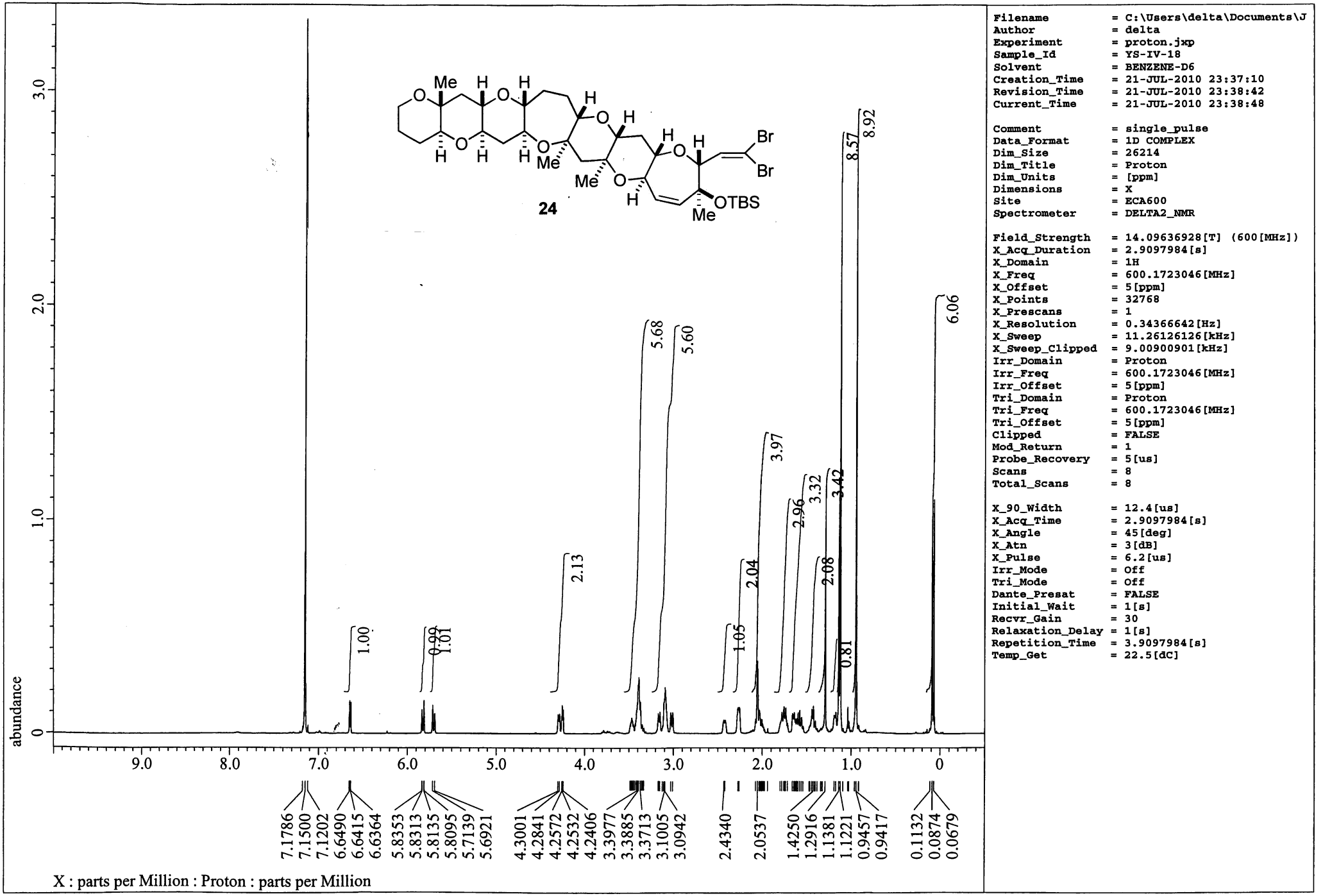
abundance

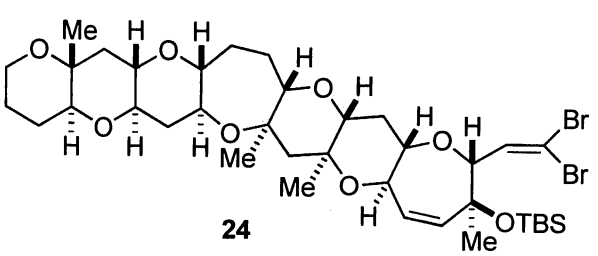
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

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

X : parts per Million : Carbon13 : parts per Million

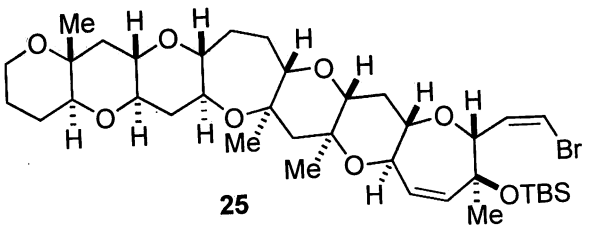
Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= YS-IV-16
Solvent	= CHLOROFORM-D
Creation_Time	= 20-JUL-2010 20:17:49
Revision_Time	= 20-JUL-2010 20:28:06
Current_Time	= 20-JUL-2010 20:28:42
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 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	= 245
Total_Scans	= 245
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]


24
abundance
X : parts per Million : Proton : parts per Million
Filename = C:\Users\delta\Documents\J
Author = delta
Experiment = proton.jxp
Sample_Id = YS-IV-18
Solvent = BENZENE-D6
Creation_Time = 21-JUL-2010 23:37:10
Revision_Time = 21-JUL-2010 23:38:42
Current_Time = 21-JUL-2010 23:38:48
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 = 30
Relaxation_Delay = 1[s]
Repetition_Time = 3.9097984[s]
Temp_Get = 22.5[dC]



24

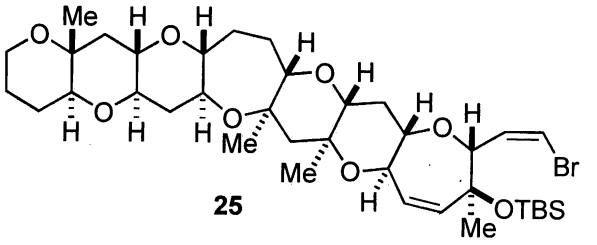
Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= YS-IV-18
Solvent	= BENZENE-D6
Creation_Time	= 21-JUL-2010 23:39:31
Revision_Time	= 21-JUL-2010 23:45:27
Current_Time	= 21-JUL-2010 23:46:23
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 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	= 120
Total_Scans	= 120
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	= 23.2[dC]



25

X : parts per Million : Proton : parts per Million

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-IV-81
Solvent           = BENZENE-D6
Creation_Time     = 14-SEP-2010 17:51:45
Revision_Time     = 14-SEP-2010 17:57:20
Current_Time      = 14-SEP-2010 17:57:45

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          = 22.2[dC]
```



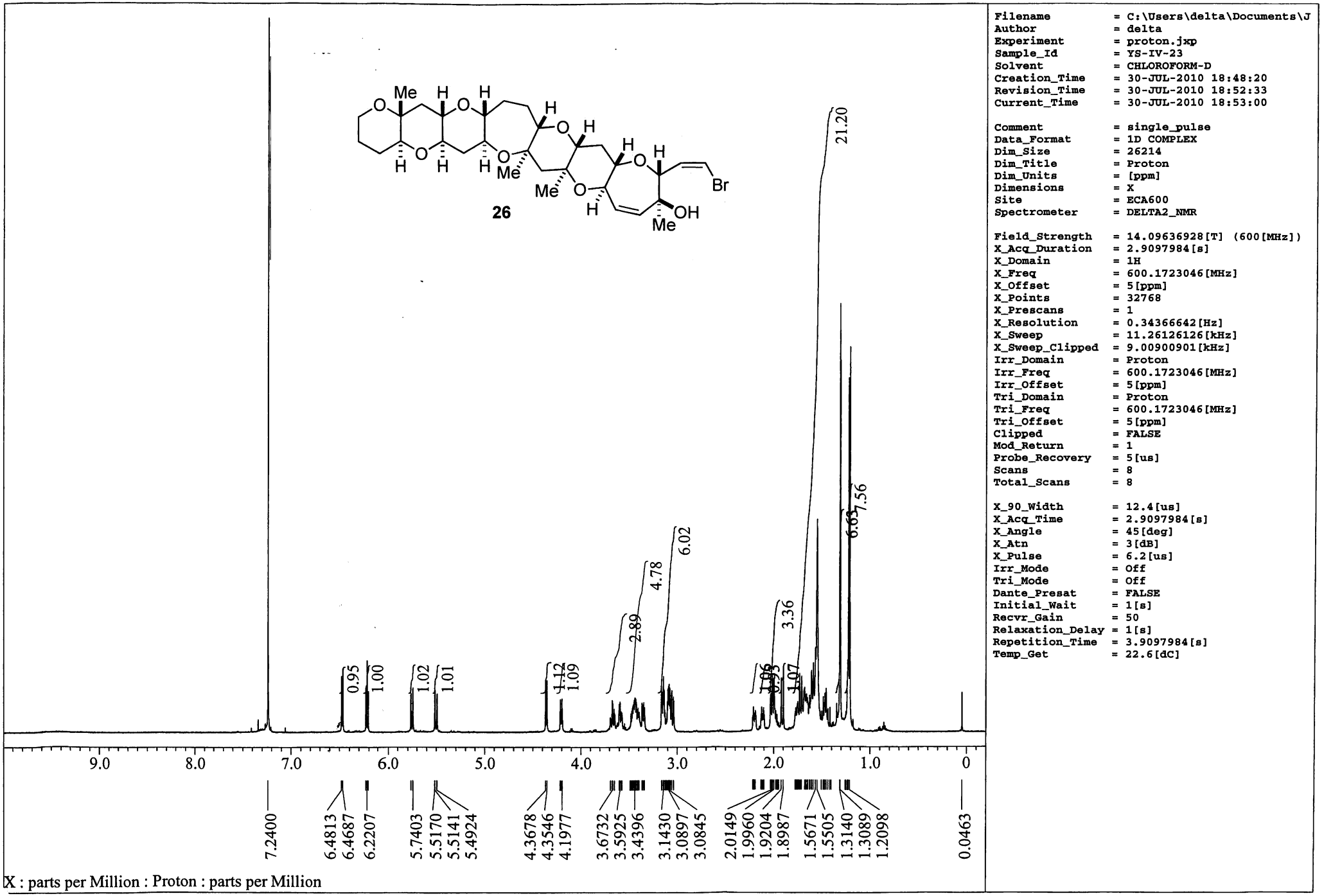
25

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = YS-IV-81
Solvent           = BENZENE-D6
Creation_Time     = 14-SEP-2010 16:47:17
Revision_Time     = 14-SEP-2010 16:53:34
Current_Time      = 14-SEP-2010 16:57:18

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             = 102
Total_Scans       = 102

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          = 23.2[dC]
```

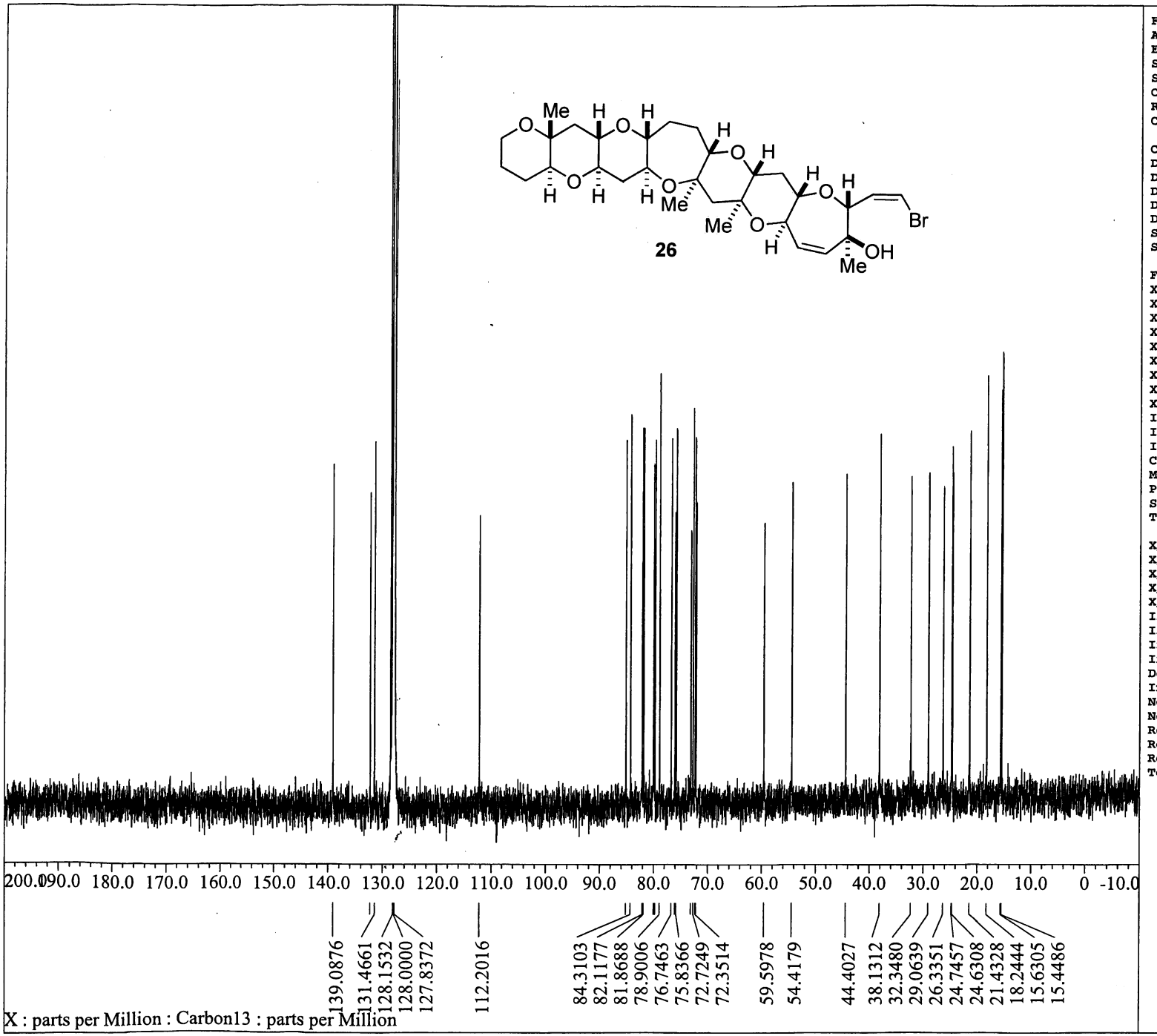
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

139.2599
128.1628
128.0000
127.8468
112.9580
85.1338
82.4720
81.8783
80.0304
78.9197
76.7463
72.7249
72.2844
59.5978
54.4849
44.4218
38.1504
29.0735
26.3542
26.0287
22.2084
18.2731
15.6879
15.4486
-1.8147
-2.1020

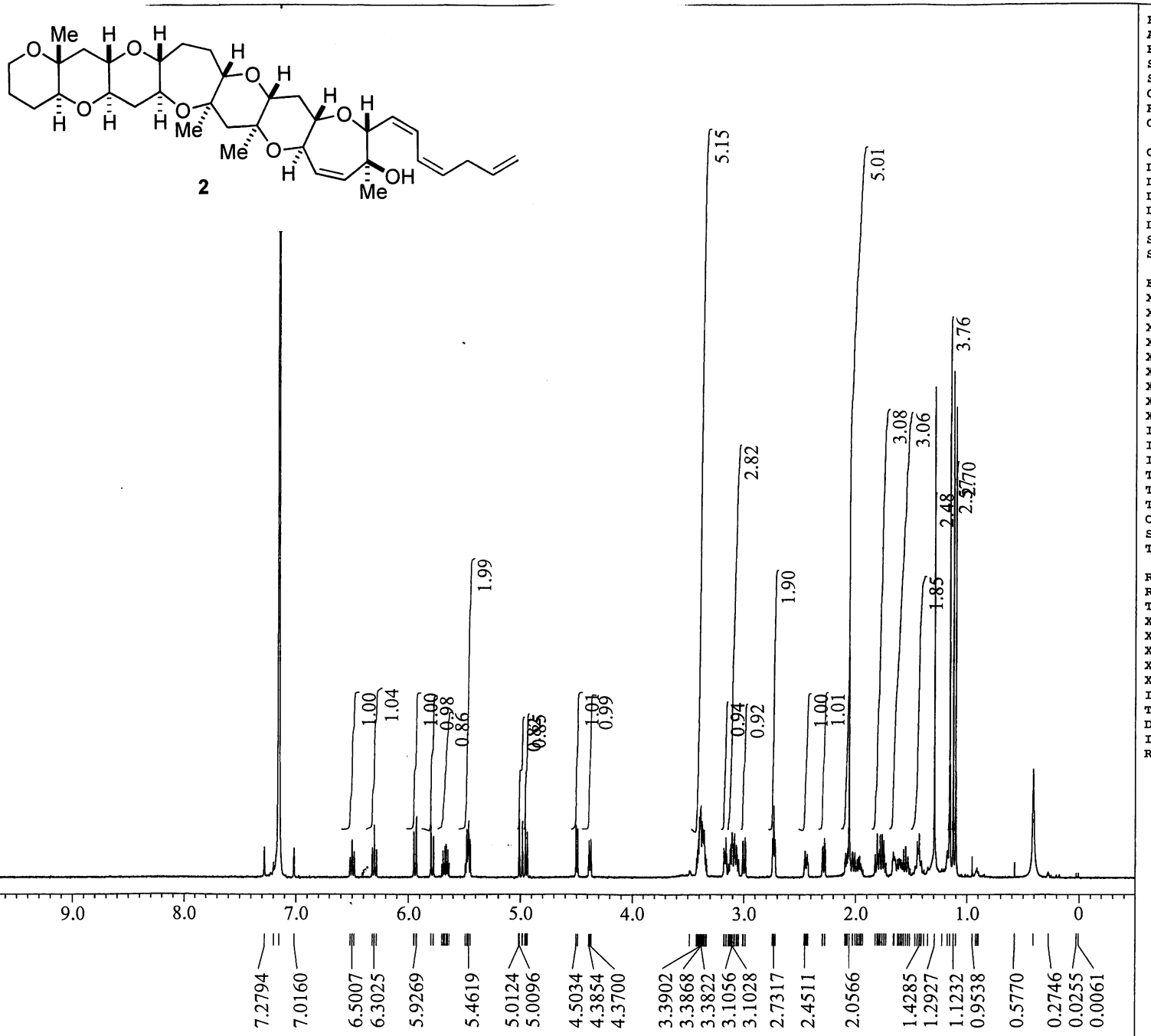
X : parts per Million : Carbon13 : parts per Million



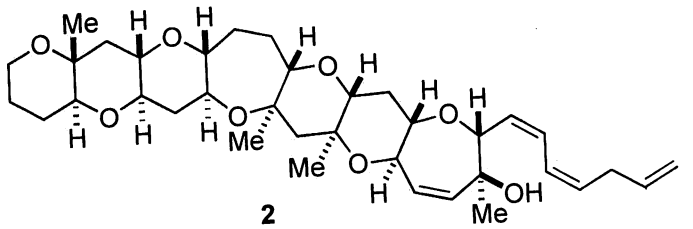

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-IV-23
Solvent           = CHLOROFORM-D
Creation_Time     = 30-JUL-2010 18:48:20
Revision_Time     = 30-JUL-2010 18:52:33
Current_Time      = 30-JUL-2010 18:53:00

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        = 50
Relaxation_Delay  = 1[s]
Repetition_Time   = 3.9097984[s]
Temp_Get          = 22.6[dC]
```



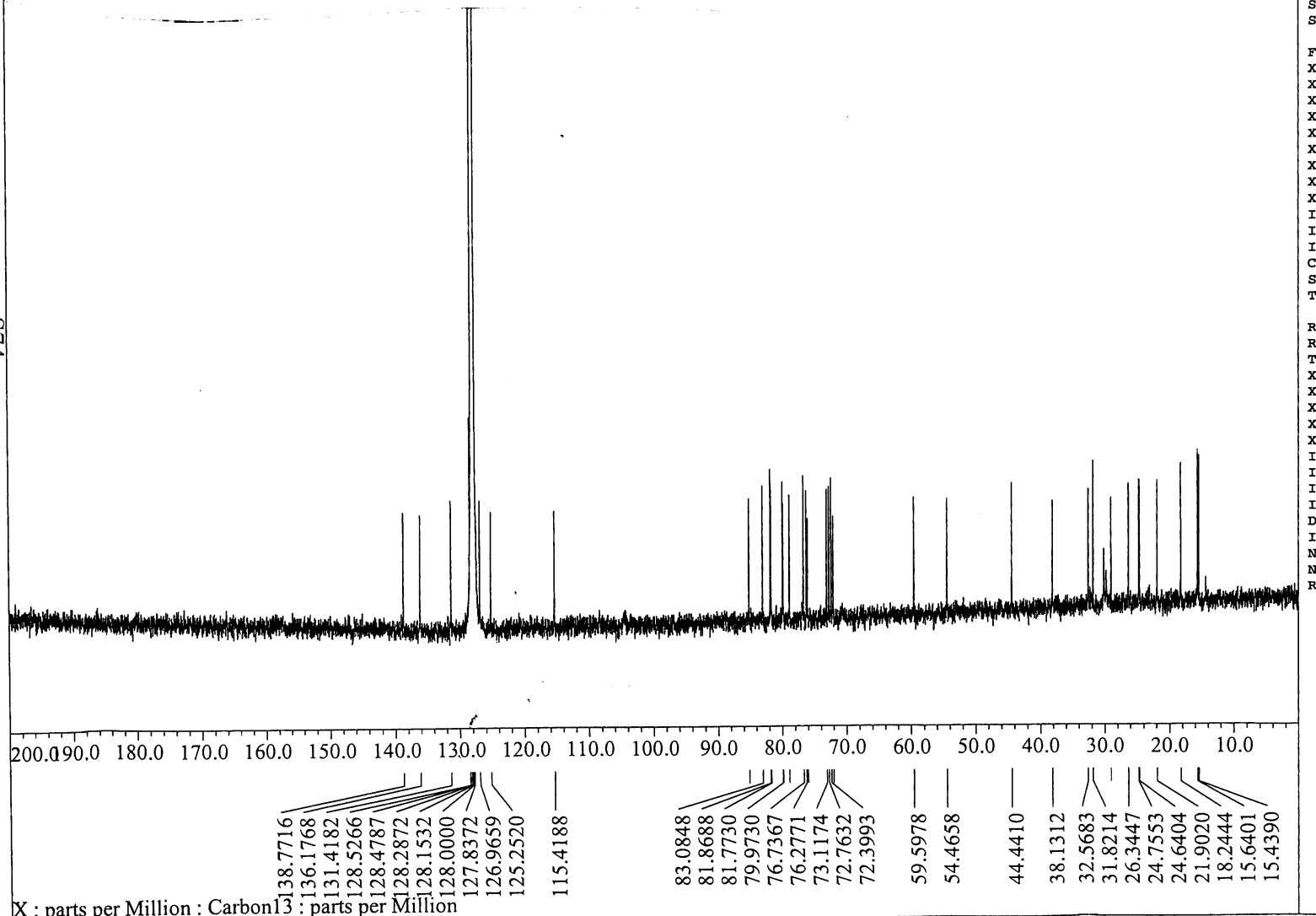

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = YS-IV-82
Solvent           = BENZENE-D6
Creation_Time     = 21-SEP-2010 20:21:33
Revision_Time     = 21-SEP-2010 20:27:31
Current_Time      = 21-SEP-2010 20:28:49

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             = 106
Total_Scans       = 106

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          = 23.1[dC]
```




```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = YS-IV-137
Solvent           = BENZENE-D6
Creation_Time     =  7-FEB-2011 23:08:47
Revision_Time     =  7-FEB-2011 23:12:56
Current_Time      =  7-FEB-2011 23:13:24

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          = 22.3[dC]
X_90_Width        = 13.3[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.65[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



2

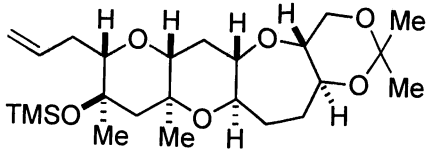



```
Filename          = C:\Users\delta\Desktop\dat
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = YS-GBR-7analog
Solvent           = BENZENE-D6
Creation_Time     = 27-FEB-2011 17:11:18
Revision_Time     =  6-JAN-2012 02:44:50
Current_Time      =  6-JAN-2012 02:44:54

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
Scans             = 1889
Total_Scans       = 1889

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 21.7[dC]
X_90_Width        = 8.8[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.93333333[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]
```

HF18102/C6D6

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 5 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	4248.8		
vs	311		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5203.9		
rfp	3574.0		
th	7		
ins	1.000		
nm	ph		

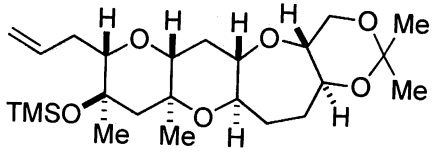


29

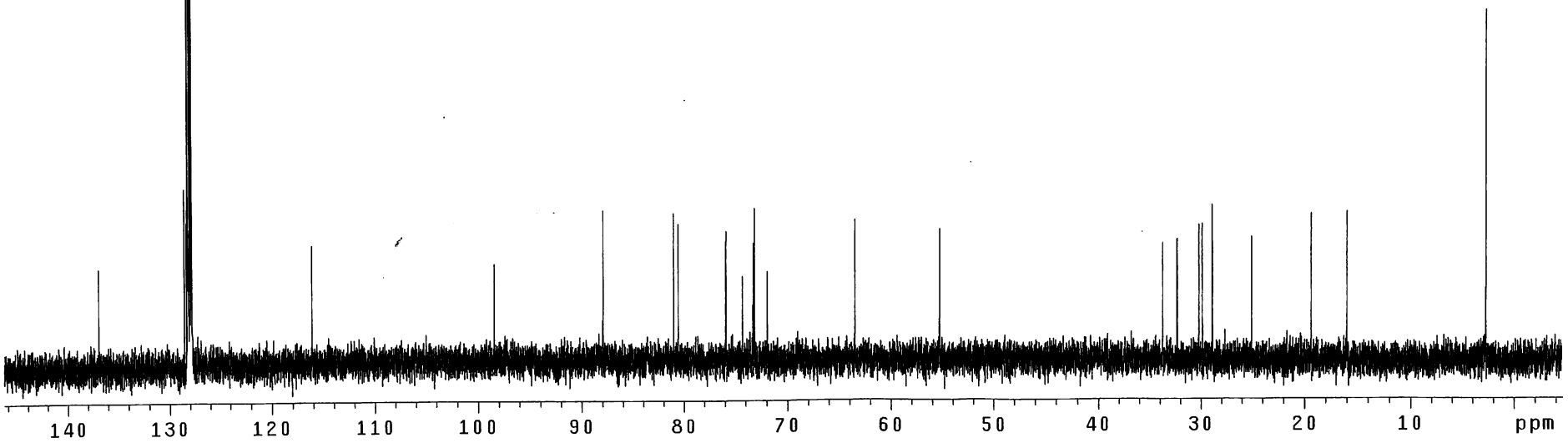
HF18102/C6D6

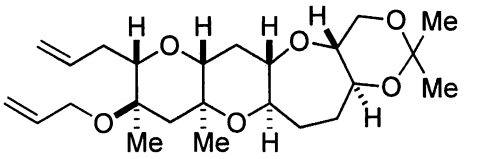
exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 5 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	224	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-579.8		
wp	18975.9		
vs	423		
sc	0		
wc	250		
hzmm	75.90		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	32		
ins	100.000		
nm	ph		



29



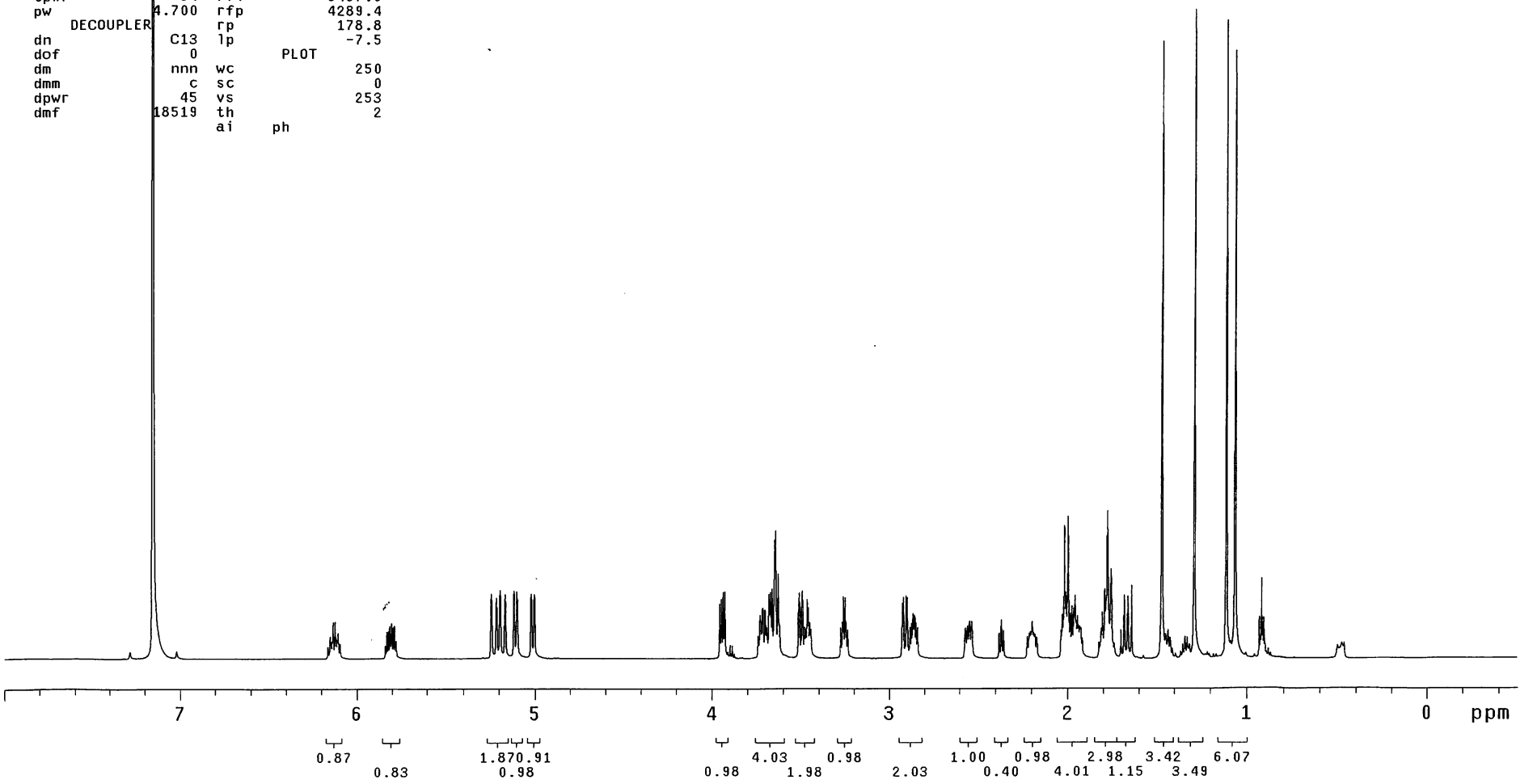


30

HF18104/C6D6

exp1 PROTON

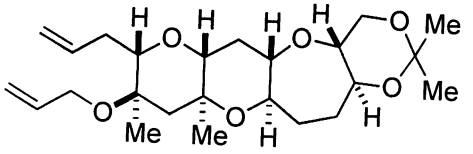
SAMPLE		SPECIAL	
date	Nov 7 2005	temp	20.0
solvent	Benzene	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	9611.9	pw90	9.400
at	1.820	alfa	3.812
np	34992	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	65536
tn	H1	DISPLAY	
sfrq	599.917	sp	-300.2
tof	599.7	wp	5099.2
tpwr	54	rfl	5457.6
pw	4.700	rfp	4289.4
DECOUPLER		rp	178.8
dn	C13	lp	-7.5
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	45	vs	253
dmf	18519	th	2
		ai	ph



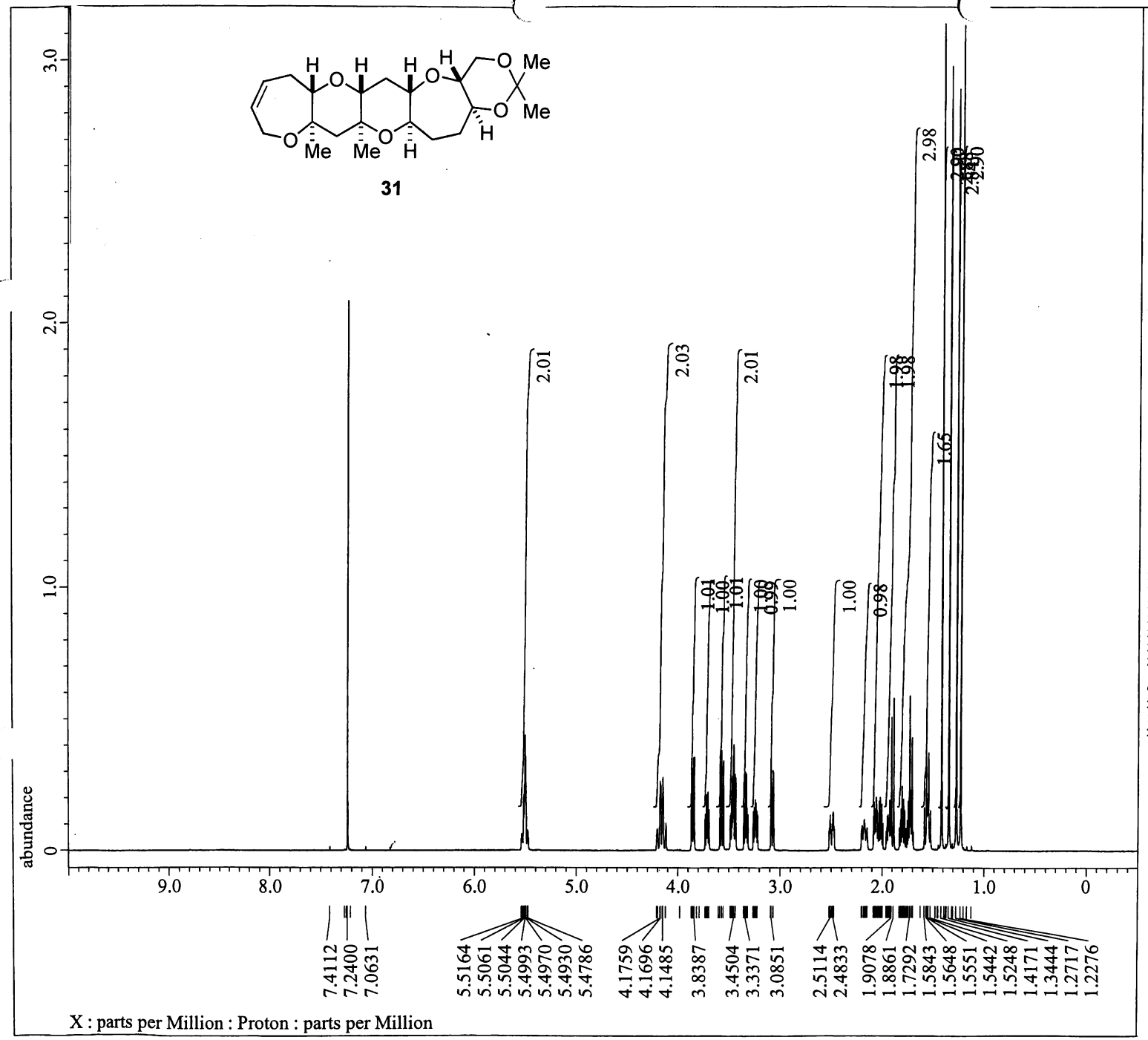
C13 STD parameter

exp3 s2pul

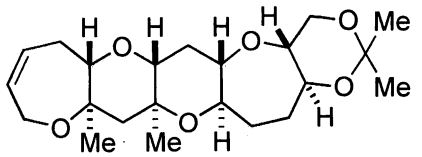
SAMPLE		DEC. & VT	
date	Nov 7 2005	dfrq	599.915
solvent	Benzene	dn	H1
file	exp	dpwr	38
ACQUISITION		dof	-1000.0
sfrq	150.865	dm	yyy
tn	C13	dmm	w
at	0.867	dmf	13163
np	60032	dseq	
sw	34632.0	dres	1.0
fb	not used	homo	n
bs	64	temp	20.0
tpwr	56	DEC2	
pw	6.8	dfrq2	0
d1	0.689	dn2	
tof	3000.0	dpwr2	1
nt	50000	dof2	0
ct	128	dm2	n
alock	n	dmm2	c
gain	56	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-816.6	dpwr3	1
wp	34632.0	dof3	0
vs	606	dm3	n
sc	0	dmm3	c
wc	250	dmf3	12346
hzmm	138.53	dseq3	
is	500.00	dres3	1.0
rfl	816.6	homo3	n
rfp	0	PROCESSING	
th	13	lb	0.50
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	131072
		math	f
		werr	
		wexp	wft
		wbs	
		wnt	



30




```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = HF18105
Solvent           = CHLOROFORM-D
Creation_Time     = 24-MAY-2011 16:04:33
Revision_Time     = 24-MAY-2011 16:06:14
Current_Time      = 24-MAY-2011 16:06:29

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          = 21.5[dC]
X_90_Width        = 13.3[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.65[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



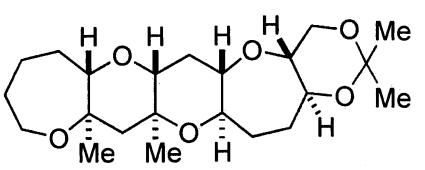
31


```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HF18105
Solvent           = CHLOROFORM-D
Creation_Time     = 24-MAY-2011 16:06:54
Revision_Time     = 24-MAY-2011 16:12:55
Current_Time      = 24-MAY-2011 16:13:10

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          = 22.1[dC]
X_90_Width        = 8.8[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.93333333[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]
```

HF18107/CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 10 2005	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	2.00
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	4248.8		
vs	176		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5277.2		
rfp	3619.0		
th	7		
ins	1.000		
nm	ph		

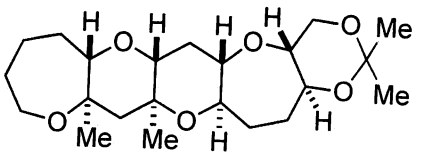


32

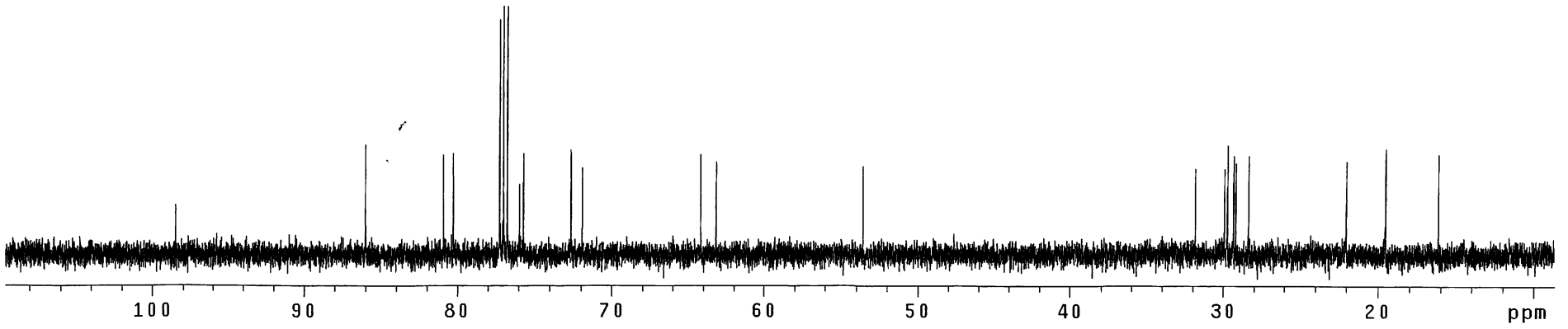
STANDARD CARBON PARAMETERS

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 10 2005	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	96	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	1089.3		
wp	12680.5		
vs	40		
sc	0		
wc	250		
hzmm	50.72		
is	500.00		
rfl	14754.0		
rfp	9678.1		
th	7		
ins	100.000		
nm	ph		



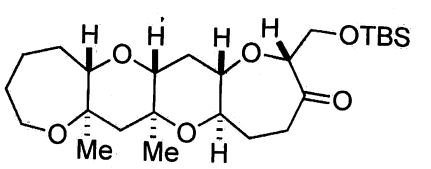
32



HF18110/C6D6

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 12 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	4248.8		
vs	324		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5205.4		
rfp	3574.0		
th	7		
ins	1.000		
nm	ph		

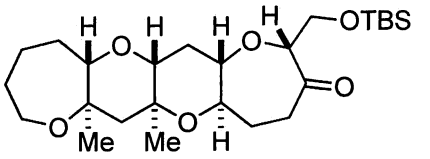


33

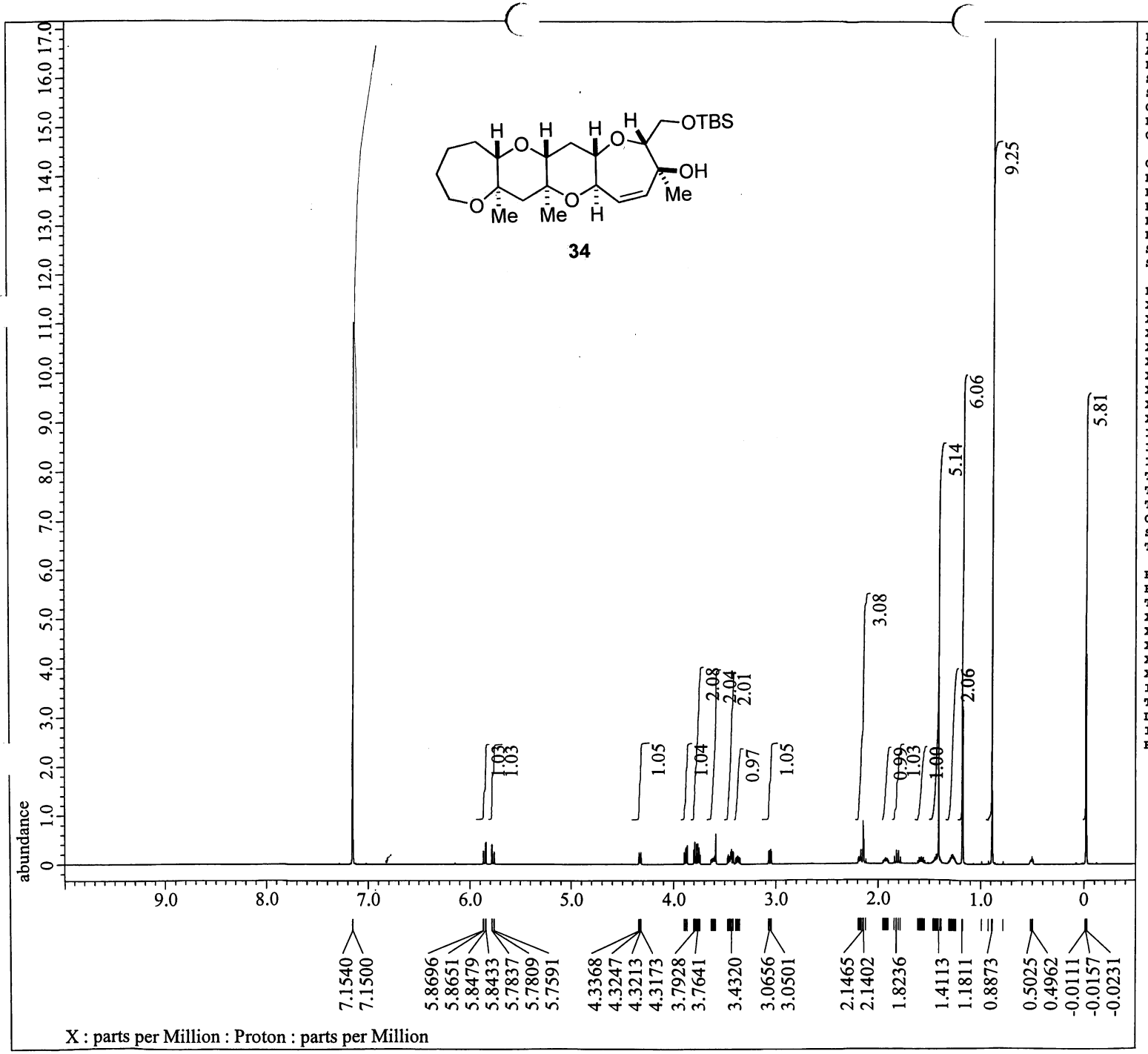
STANDARD CARBON PARAMETERS

exp3 s2pul

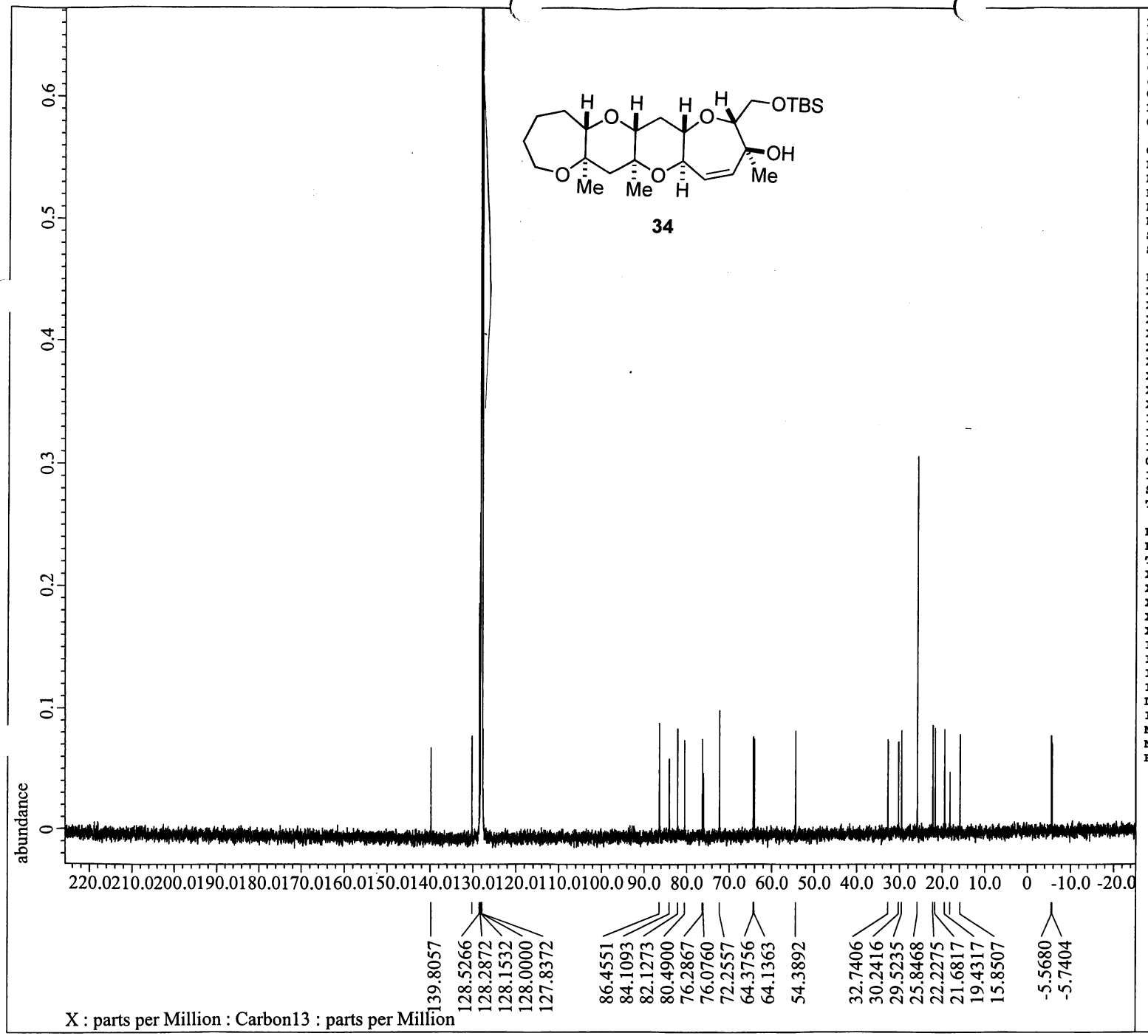
SAMPLE		DEC. & VT	
date	Nov 12 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	192	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-5031.9		
wp	37735.8		
vs	343		
sc	0		
wc	250		
hzmm	150.94		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	8		
ins	100.000		
nm cdc ph			



33

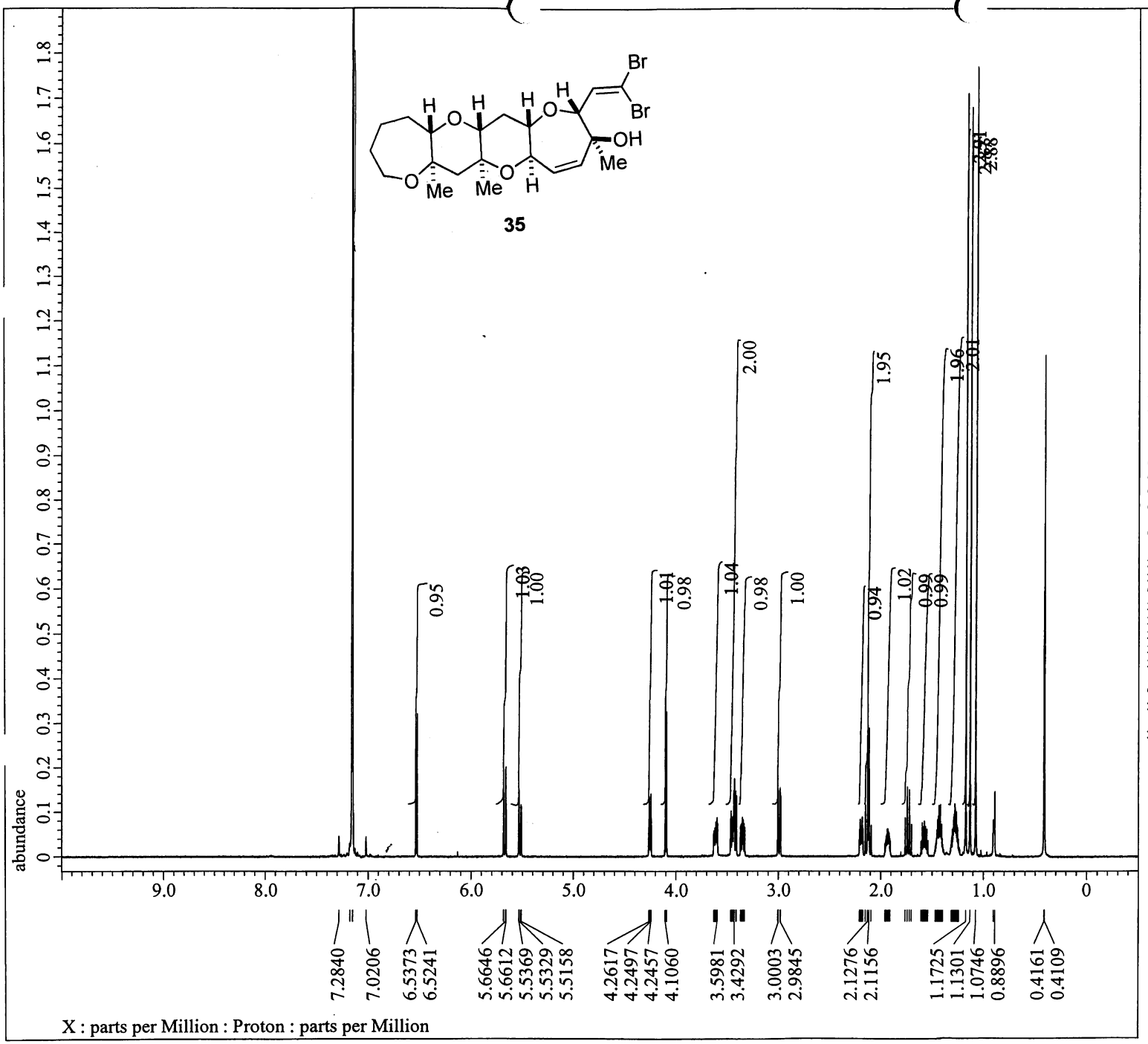



```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = HF18116
Solvent           = BENZENE-D6
Creation_Time     = 24-MAY-2011 17:33:49
Revision_Time     = 24-MAY-2011 17:36:33
Current_Time      = 24-MAY-2011 17:36:49

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        = 42
Temp_Get          = 21.2[dC]
X_90_Width        = 13.3[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.65[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```

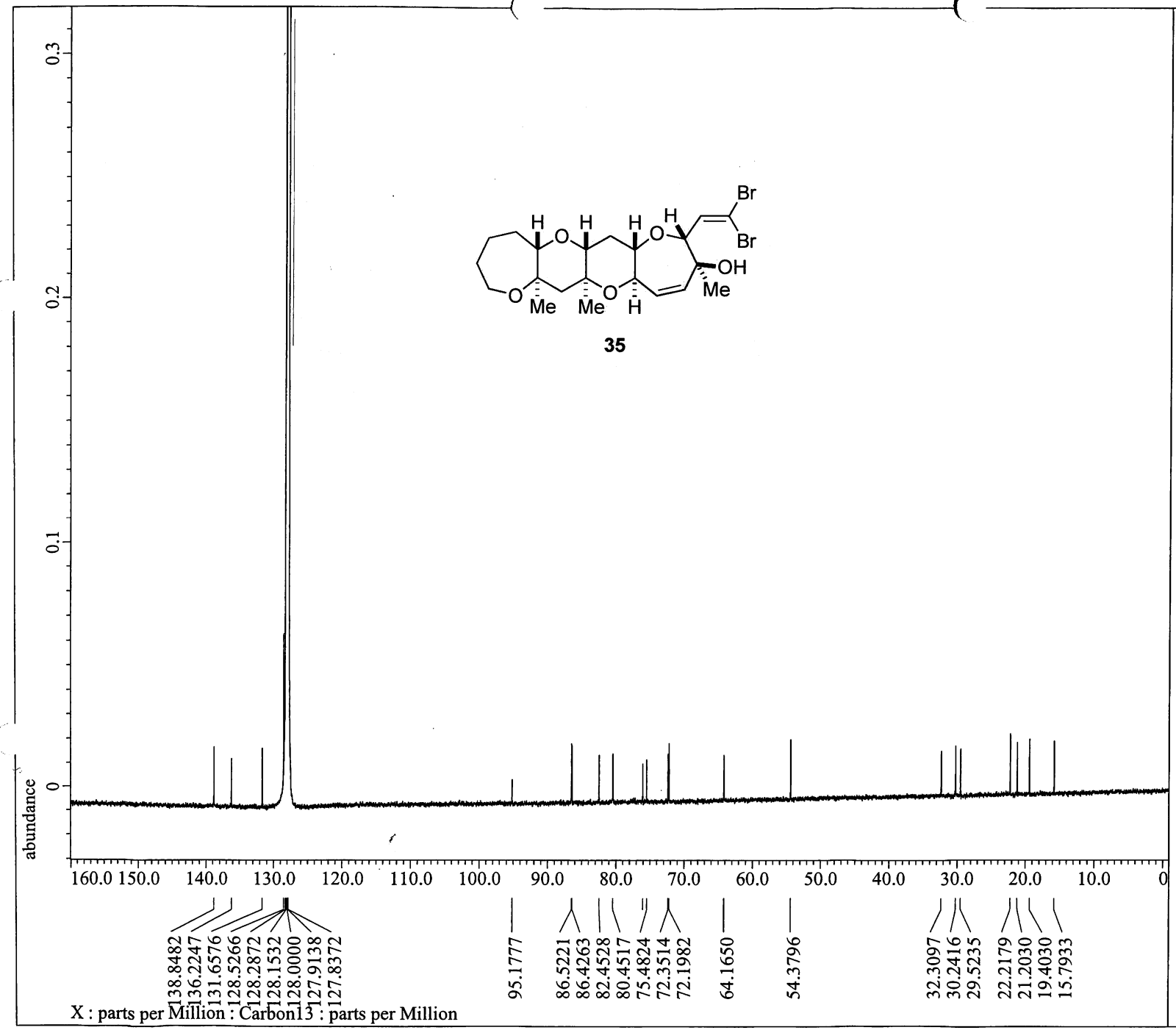


34

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HF18116
Solvent           = BENZENE-D6
Creation_Time     = 24-MAY-2011 17:36:07
Revision_Time     = 24-MAY-2011 17:49:00
Current_Time      = 24-MAY-2011 17:49:20

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[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
Incomplete_Copy   = TRUE
Scans             = 256
Total_Scans       = 256

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 22.2[dC]
X_90_Width        = 8.8[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 2.93333333[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]
```




```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = proton.jxp
Sample_Id         = HF18118
Solvent           = BENZENE-D6
Creation_Time     = 24-MAY-2011 17:55:06
Revision_Time     = 24-MAY-2011 17:57:12
Current_Time      = 24-MAY-2011 17:57:46

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          = 21.4[dC]
X_90_Width        = 13.3[us]
X_Acq_Time        = 2.9097984[s]
X_Angle           = 45[deg]
X_Atn             = 3[dB]
X_Pulse           = 6.65[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 3.9097984[s]
```



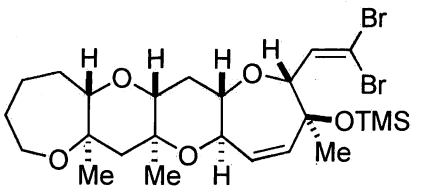
35

Filename	= C:\Users\delta\Documents\J
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= HF18118
Solvent	= BENZENE-D6
Creation_Time	= 24-MAY-2011 22:06:20
Revision_Time	= 25-MAY-2011 08:55:17
Current_Time	= 25-MAY-2011 08:55:50
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	= TRUE
Scans	= 14412
Total_Scans	= 14412
Relaxation_Delay	= 2[s]
Recvr_Gain	= 52
Temp_Get	= 22.2[dC]
X_90_Width	= 8.8[us]
X_Acq_Time	= 0.69206016[s]
X_Angle	= 30[deg]
X_Atn	= 6.4[dB]
X_Pulse	= 2.93333333[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]

HF18120/C6D6

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 21 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	8	math	f
ct	8		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	4248.8		
vs	271		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5205.9		
rfp	3574.0		
th	7		
ins	1.000		
nm	ph		

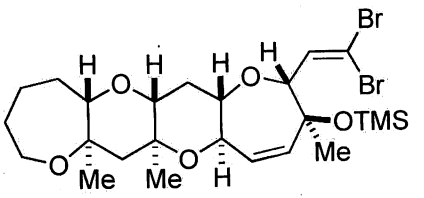


36

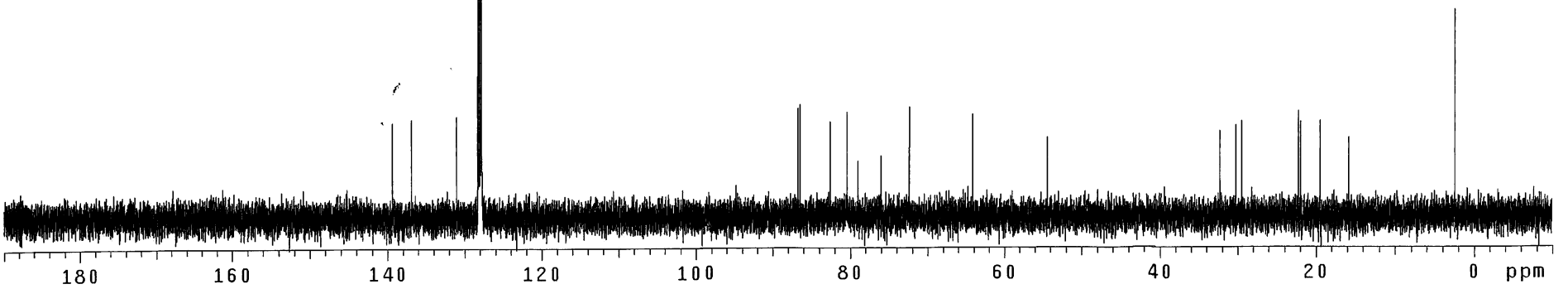
STANDARD CARBON PARAMETERS

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 21 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	224	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	25137.7		
vs	452		
sc	0		
wc	250		
hzmm	100.55		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	8		
ins	100.000		
nm	ph		



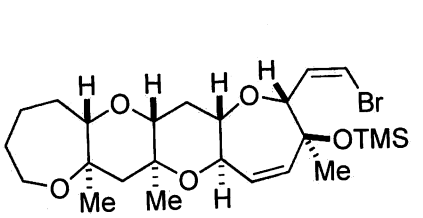
36



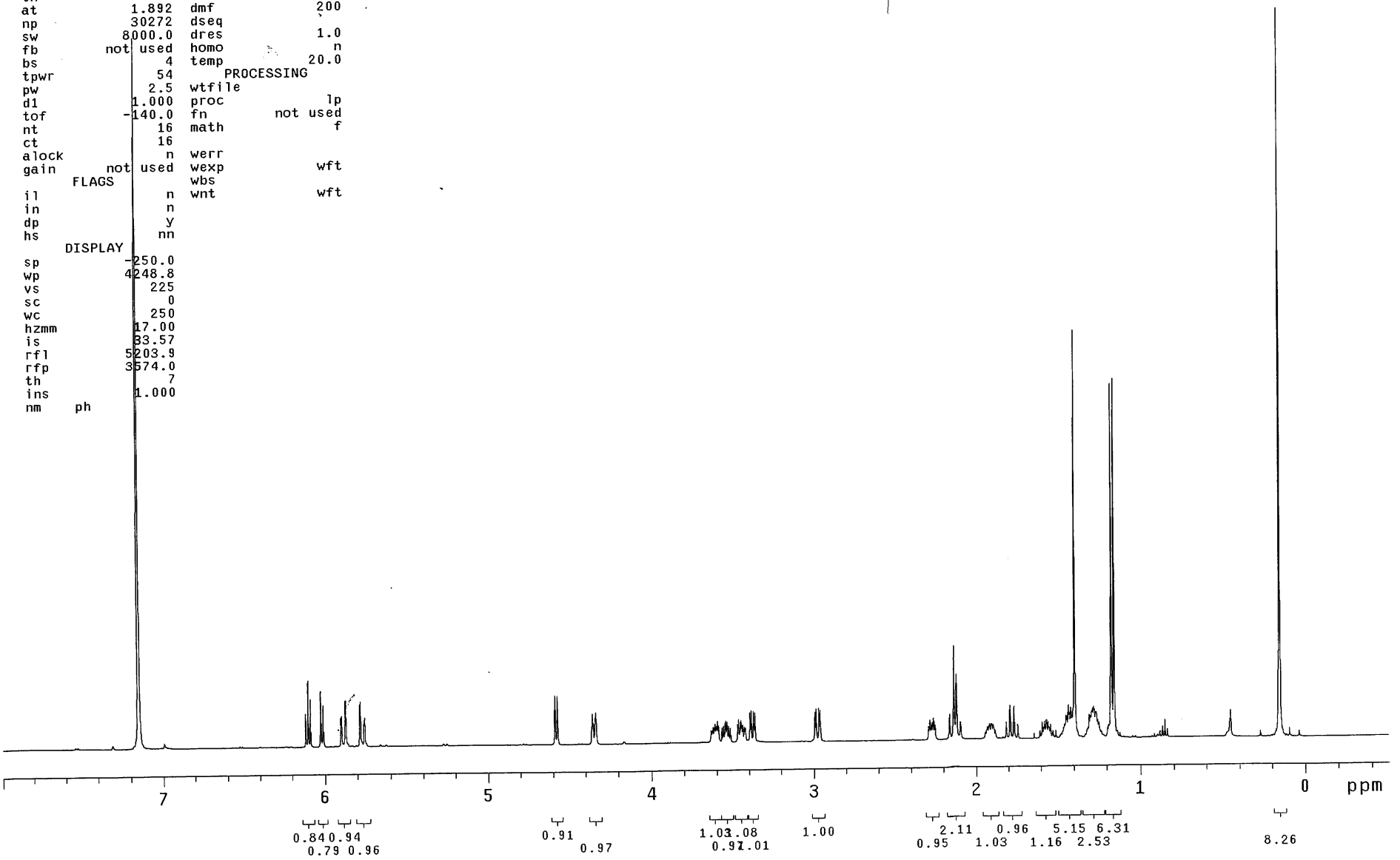
HF18121/C6D6

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 22 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	4248.8		
vs	225		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5203.9		
rfp	3574.0		
th	7		
ins	1.000		
nm	ph		



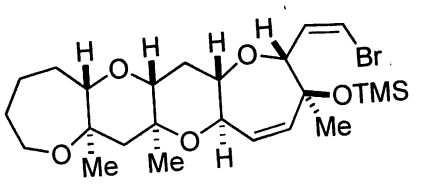
37



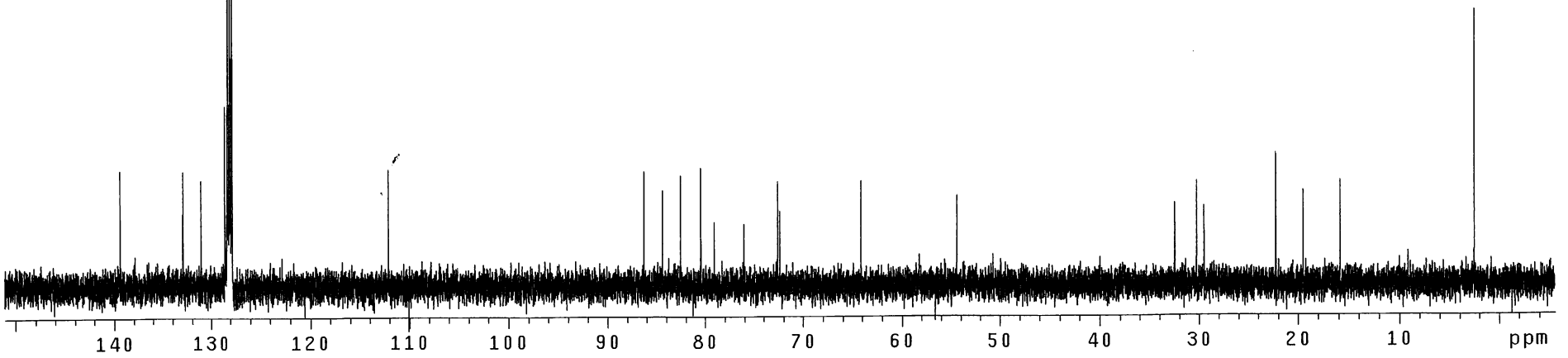
STANDARD CARBON PARAMETERS

exp5 s2pul

SAMPLE		DEC. & VT	
date	Nov 22 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	192	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-702.4		
wp	19695.7		
vs	428		
sc	0		
wc	250		
hzmm	78.78		
is	500.00		
rfl	21120.2		
rfp	16088.3		
th	9		
ins	100.000		
nm	ph		



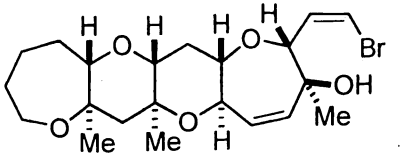
37



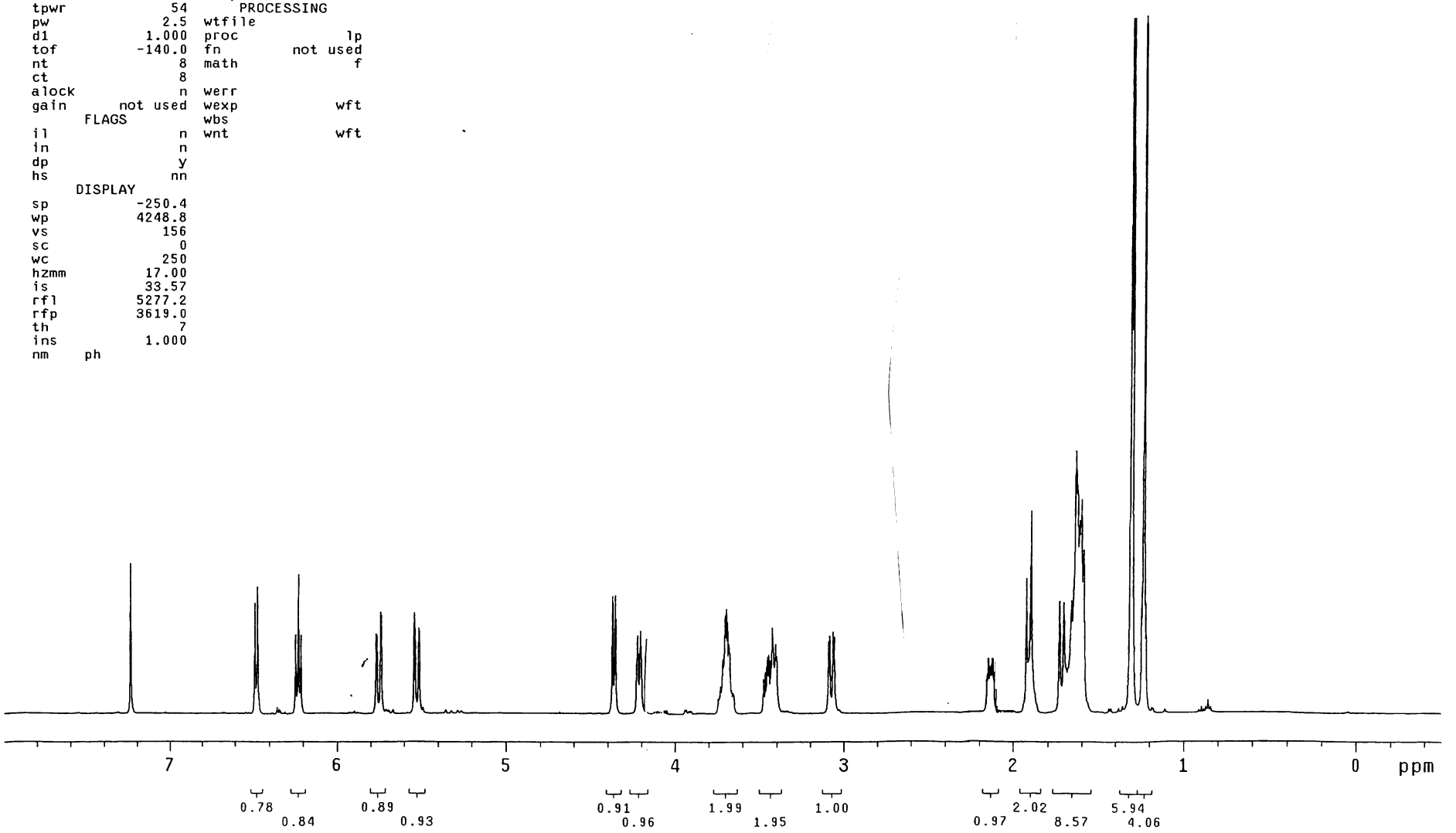
HF18127/CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 26 2005	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	8	math	f
ct	8		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	4248.8		
vs	156		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5277.2		
rfp	3619.0		
th	7		
ins	1.000		
nm	ph		



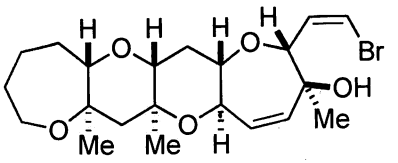
38



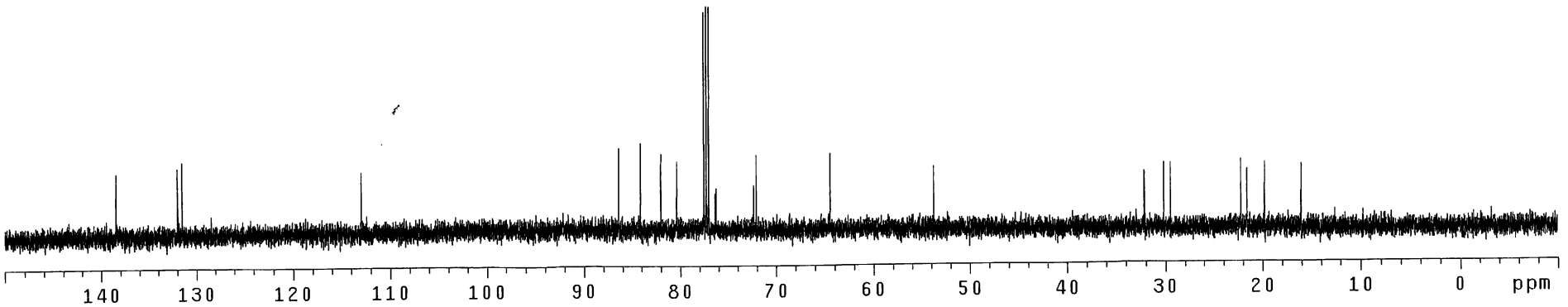
STANDARD CARBON PARAMETERS

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 26 2005	dfrq	499.862
solvent	CDCl3	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	192	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-1257.2		
wp	20110.2		
vs	667		
sc	0		
wc	250		
hzmm	80.44		
is	500.00		
rfl	5042.1		
rfp	0		
th	7		
ins	100.000		
ai	ph		



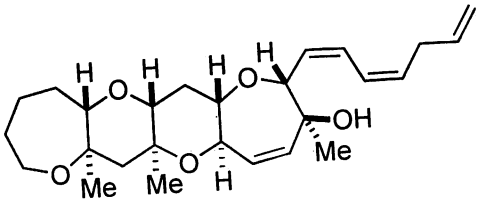
38



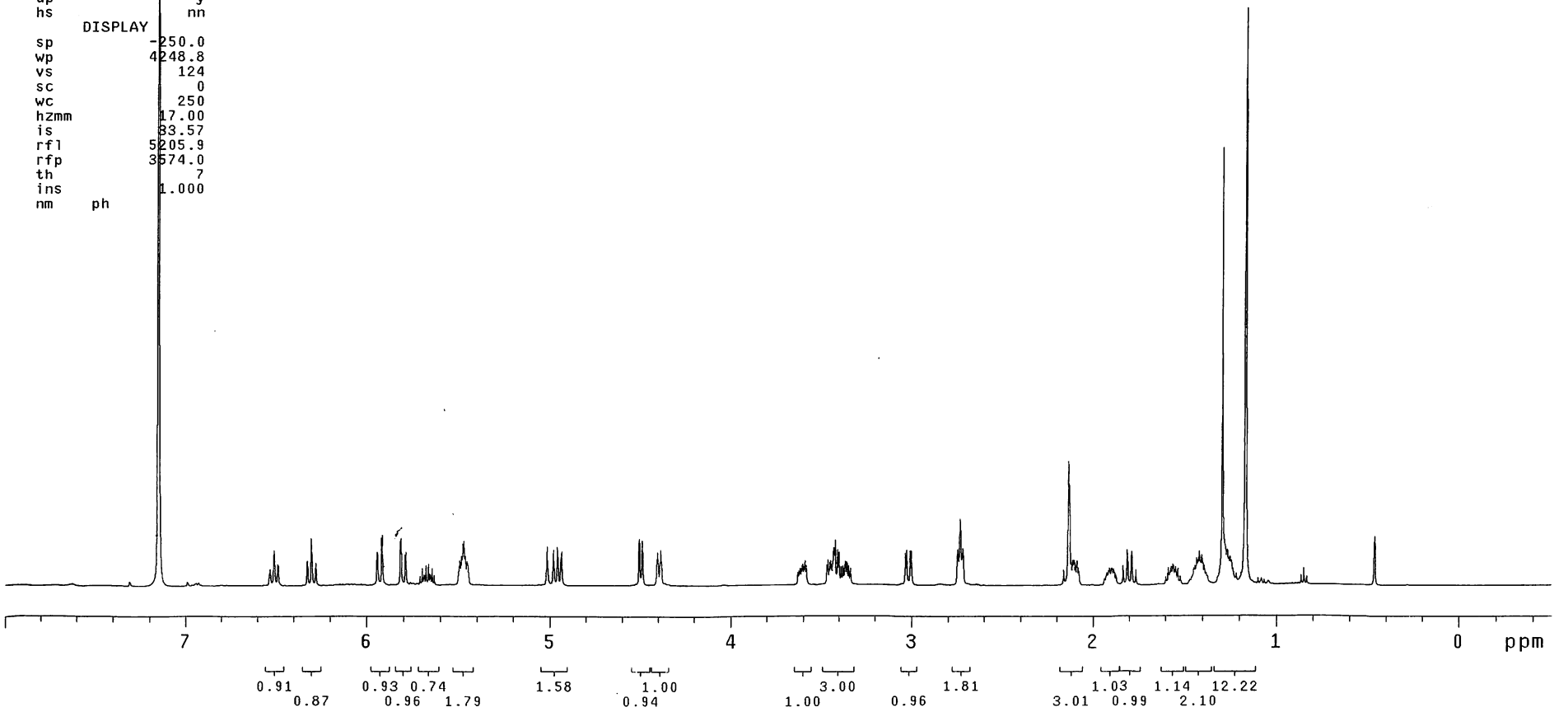
HF18129/C6D6

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 1 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.862	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	temp	20.0
tpwr	54	PROCESSING	
pw	2.5	wtfile	
d1	1.000	proc	lp
tof	-140.0	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	4248.8		
vs	124		
sc	0		
wc	250		
hzmm	17.00		
is	33.57		
rfl	5205.9		
rfp	3574.0		
th	7		
ins	1.000		
nm	ph		



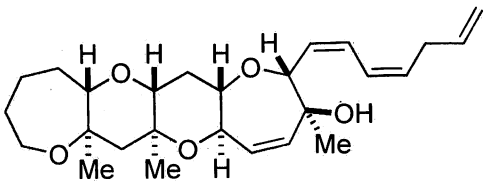
3



STANDARD CARBON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Dec 1 2005	dfrq	499.862
solvent	Benzene	dn	H1
file	exp	dpwr	27
ACQUISITION		dof	0
sfrq	125.704	dm	yyy
tn	C13	dmm	w
at	1.298	dmf	12579
np	97994	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	32	temp	20.0
tpwr	61	PROCESSING	
pw	5.3	lb	0.50
d1	0.700	wtfile	
tof	1883.8	proc	ft
nt	5120	fn	131072
ct	288	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	wft
il	n	wbs	wft
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-5031.4		
wp	37735.8		
vs	410		
sc	0		
wc	250		
hzmm	150.94		
is	500.00		
rfl	21119.6		
rfp	16088.3		
th	7		
ins	100.000		
nm	ph		



3