General. All commercially available reagents were used without further purification. All solvents were used after distillation. Tetrahydrofuran (THF), diethyl ether, benzene, toluene, and dimethoxyethane (DME) were refluxed over and distilled from sodium-benzophenone ketyl. Dichloromethane was refluxed over and distilled from P_2O_5. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoric triamide (HMPA) were distilled from CaH_2 under reduced pressure. Methanol was refluxed over and distilled from $Mg(OMe)_2$. Triethylamine, diisopropylamine, and diisopropylethylamine were refluxed over and distilled from KOH.
Preparative separation was performed by column chromatography on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400MHz and 750 MHz spectrometer and chemical shifts were represented as δ-values relative to the internal standard TMS. IR spectra were recorded on a FT-IR Spectrometer. High-resolution mass spectra (HRMS) were measured on a ESI-TOF MS. Melting point was uncorrected.

(1*S*,2*R*,4*S*)-4-Acetoxy-1,2-Epoxy-1-ethynyl-2,6,6-trimethylcyclohexanol (15). To a solution of acetylene **14** (215 mg, 1.21 mmol) in pyridine (5 mL) was added acetic anhydride (0.18 mL, 1.94 mmol) at room temperature and the reaction mixture was stirred for 18 h at the same temperature. A saturated aqueous $CuSO_4$ solution was added, and then the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (5% ethyl acetate in hexane) afforded acetate **15** (209 mg, 77%): $[\alpha]^{24.0}_D$ –20.3 (*c* 1.18, $CHCl_3$); IR (neat, cm^{-1}) 3281, 2966, 2930, 2872, 1738, 1460, 1367, 1242, 1157, 1105, 1043; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.85 (m, 1H), 2.42 (s, 1H), 2.37 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.01 (s, 3H), 1.79 (dd, *J* = 15.1, 6.4 Hz, 1H), 1.60 (dd, *J* = 13.8, 3.4 Hz, 1H), 1.52 (s, 3H), 1.38 (dd, *J* = 13.5, 8.24 Hz, 1H), 1.27 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1, 80.2, 74.2, 66.9, 64.9, 63.1, 39.7, 35.6, 33.5, 28.4, 25.9, 21.7, 21.3; ESI-HRMS m/z calcd for $C_{13}H_{18}O_3Na$ $(M+Na)^+$ 245.1154, found 245.1164.

(2*E*,4*E*)-7-[(1'*S*,2'*R*,4'*S*)-4'-Acetoxy-1',2'-Epoxy-2',6',6'-trimethylcyclohexa-1'-yl]5-methylhepta-2,4-diene-6-yn-1-ol (18). To a solution of ester **16** (1.11 g, 1.89 mmol) in dichloromethane (18.9 mL) was added dropwise diisobutylaluminium hydride (1.0 M in toluene, 4.56 mL, 4.56 mmol) at –78 °C. After the reaction mixture was

stirred for 5 min at the same temperature, aqueous potassium sodium (+)-tartrate tetrahydrate solution were added and then resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*.to afford crude vinyl iodide **17**, which was used to the next reaction without further purification.

To a solution of crude vinyl iodide **17** and acetylene **15** (420 mg, 1.89 mmol) in diisopropylamine (9.45 mL) was added tetrakis(triphenylphosphine)palladium (262 mg, 0.23 mmol) and CuI (40 mg, 0.21 mmol). After being stirred for 1.5 h at room temperature, the reaction mixture was poured into a saturated aqueous NH_4Cl solution, and then the resulting mixture was extracted with diethyl ether. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 30% to 50% ethyl acetate in hexane) afforded the conjugated acetylene derivative **18** (484 mg, 81%): $[\alpha]^{24.0}_{D}$ +15.1 (*c* 1.07, $CHCl_3$); IR (neat, cm^{-1}) 3458, 2965, 2926, 1738, 1448, 1370, 1244, 1043; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.50 (dd, *J* = 14.8, 11.4 Hz, 1H), 6.39 (d, *J* = 11.2 Hz, 1H), 5.90 (dt, *J* = 14.9, 5.5 Hz, 1H), 4.87 (m, 1H), 4.23 (d, *J* = 5.5 Hz, 2H), 2.38 (dd, *J* = 14.9, 5.7 Hz, 1H), 2.01 (s, 3H), 1.91 (s, 3H), 1.80 (dd, *J* = 14.8, 6.4 Hz, 1H), 1.62 (dd, *J* = 13.8, 3.5 Hz, 1H), 1.51(s, 3H), 1.39 (dd,*J* = 13.5, 8.3 Hz, 1H), 1.27 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 135.4, 134.2, 125.9, 118.0, 89.3, 85.5, 67.1, 65.6, 63.9, 62.9, 39.8, 35.7, 34.0, 28.6, 26.1, 21.9, 21.3, 17.4; ESI-HRMS m/z calcd for $C_{19}H_{26}O_4Na$ $(M+Na)^+$ 341.1729, found 341.1740.

2-[(((2'*E*,4'*E*)-7'-((1''*S*,2''*R*,4''*S*)-4''-Acetoxy-1'',2''-Epoxy-2'',6'',6''-trimethylcyclohexylidene-1''-yl)-5'-methylhepta-2,4-diene-6-yn)sulfanyl) benzothiazole (19). To a solution of **18** (100 mg, 0.31 mmol), 2-mercaptobenzothiazole (68 mg, 0.41 mmol) and triphenylphosphine (107 mg, 0.41 mmol) in THF (4 mL) was added dropwise diisopropyl azodicarboxylate (0.09 mL, 0.44 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and the all solvents were removed *in vacuo*. To a residue was added diethyl ether and the precipitate was removed by filtration through a pad of Celite to give the crude products as a solution, which was concentrated *in vacuo*. Purification by short silica gel column chromatography (from 5% to 10% ethyl acetate in hexane) afforded the thioether **19** (127 mg, 87%): $[\alpha]^{26.0}_{D}$ +8.5 (*c* 0.97, $CHCl_3$); IR (neat, cm^{-1}) 2967, 2926, 1736, 1460,

1427, 1367, 1242, 1042; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (m, 1H), 7.75 (m, 1H), 7.42 (m, 1H), 7.30 (m, 1H), 6.60 (dd, *J* = 14.9, 11.2 Hz, 1H), 6.36 (d, *J* = 11.5 Hz, 1H), 5.93 (m, 1H), 4.87 (m, 1H), 4.08 (d, *J* = 7.6 Hz, 2H), 2.37 (ddd, *J* =14.9, 5.7, 0.9 Hz, 1H), 2.00 (s, 3H), 1.89 (s, 3H), 1.79 (dd, *J* = 15.1, 6.6 Hz, 1H), 1.61 (m, 1H), 1.48 (s, 3H), 1.38 (dd, *J* = 13.7, 8.2 Hz, 1H), 1.24 (s, 3H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 165.8, 153.2, 135.4, 135.0, 129.8, 128.9, 126.1, 124.3, 121.5, 120.9, 118.9, 89.2, 86.1, 67.1, 65.6, 63.9, 39.9, 35.9, 34.1, 28.7, 26.2, 21.9, 21.4, 17.5, -0.02; ESI-HRMS m/z calcd for $C_{26}H_{29}NO_3S_2Na$ $(M+Na)^+$ 490.1487, found 490.1467.

2-[(((2'*E*,4'*E*)-7'-((1''*S*,2''*R*,4''*S*)-4''-Acetoxy-1'',2''-Epoxy-2'',6'',6''-trimethylcyclohexylidene-1''-yl)-5'-methylhepta-2,4-diene-6-yn)sulfonyl)benzothiazole (6). To a solution of the thioether **19** (133 mg, 0.28 mmol) in ethanol (3 mL) was added dropwise a solution of ammonium heptamolybdate tetrahydrate (527 mg, 0.43 mmol) in hydrogen peroxide (30 wt.% in water, 1.4 mL) at 0 °C. After being stirred for 30 min at room temperature, the reaction mixture was poured into water and then extracted with diethyl ether. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography afforded the sulfone **6** (from 10% to 20% ethyl acetate in hexane) (79 mg, 58%): $[\alpha]^{24.0}_D$ +9.6 (*c* 0.29, $CHCl_3$); IR (neat, cm^{-1}) 2967, 2928, 1736, 1472, 1368, 1333, 1244, 1150, 1028; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (m, 1H), 8.02 (m, 1H), 7.64 (m, 2H), 6.46 (dd,*J* = 14.9, 11.5 Hz, 1H), 6.31 (d,*J* = 11.4 Hz, 1H), 5.69 (m, 1H), 4.87 (m, 1H), 4.31 (d, *J* = 7.8 Hz, 2H), 2.37 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.01 (s, 3H), 1.78 (dd, *J* = 15.1, 6.4 Hz, 1H), 1.72 (s, 3H), 1.60 (m, 1H), 1.47 (s, 3H), 1.37 (dd, *J* = 13.7, 8.4 Hz, 1H),1.23 (s, 3H), 1.13 (s, 3H); ^{13}C NMR $CDCl_3$, 100 MHz) δ 170.3, 165.4, 152.6, 135.7, 134.0, 128.1, 127.7, 125.4, 122.4, 121.5, 117.7, 88.7, 87.3, 67.1, 65.7, 63.8, 58.7, 39.9, 35.8, 34.1, 28.6, 26.2, 21.9, 21.4, 17.5, -0.02; ESI-HRMS m/z calcd for $C_{26}H_{29}NO_5S_2Na$ $(M+Na)^+$ 522.1385, found 522.1381.

Peridinin Derivative B (2). To a solution of acetylene segment **6** (22 mg, 0.044 mmol) and ylidenbutenolide segment **5** (15 mg, 0.044 mmol) in THF (0.87 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.12 mL, 0.12 mmol) at -78 °C in the dark. After being stirred for 5 min at the same temperature, the reaction

mixture was poured into water and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 30% to 50% ethyl acetate in hexane) in the dark afforded peridinin derivative **2** (5 mg, 18%) as a mixture of the isomers as a red film. A solution of a mixture of all-*trans*-peridinin derivative **2** and its *cis*-isomer in benzene was left at room temperature in the fluorescence light. After 11 days, partial separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1 / 10; flow rate: 2.0 mL / min.; UVdetect: 438 nm; retention time: (all-*trans*-isomer) 51 min., (9Z, 13E-isomer) 58 min.] in the dark, and HPLC [column: YMC Carotenoid C30 (10 x 250 mm); reverse phase: acetonitrile / methanol / water = 50 / 48 / 2; flow rate: 2.0 mL / min.; UVdetect: 438 nm; retention time: (all-*trans*-isomer) 22 min.] in the dark, was afforded the desired optically active peridinin derivative **2** as a red film: IR (neat, cm^{-1}) 3455, 2924, 2853, 2367, 1701, 1655, 1561, 1460, 1419, 1379, 1259, 1121, 1041; ^1H NMR (C_6D_6, 750 MHz) δ 7.57 (d, *J* = 15.5 Hz, 1H), 6.61 (d, *J* = 11.7 Hz, 1H), 6.56 (d, *J* =15.5 Hz, 1H), 6.42 (dd, *J* =13.9, 12.3 Hz, 1H), 6.38 (dd, *J* =14.3, 12.1 Hz, 1H), 6.30 (d, *J* =11.8 Hz, 1H), 6.26 (dd, *J* =14.2, 11.5 Hz, 1H), 6.15 (s, 1H), 6.13 (dd, *J* =14.2, 11.7 Hz, 1H), 5.18 (s, 1H), 5.07 (m, 1H), 3.75 (m, 1H), 2.25 (dd, *J* = 14.8, 3.5 Hz, 1H), 2.20 (ddd, *J* = 14.5, 4.2, 1.0 Hz, 1H), 2.11 (s, 3H), 1.79 (s, 3H), 1.68 (s, 3H), 1.62 (m, 1H), 1.46 (s, 3H), 1.41 (m, 2H), 1.35 (m, 1H), 1.34 (s, 3H), 1.31 (s, 3H), 1.13 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H), 1.06 (m, 1H); ^{13}C NMR (C_6D_6, 188 MHz) δ 169.3, 168.3, 147.7, 137.3,136.8, 136.4, 136.3, 135.1, 135.0, 134.9, 130.9, 130.0, 125.4, 122.3, 119.5, 118.2, 90.1, 89.1, 70.5, 67.4, 67.2, 65.6, 64.1, 63.9, 47.3, 41.1, 40.4, 36.2, 35.3, 34.4, 29.5, 29.0, 26.6, 25.3, 22.1, 20.9, 19.9, 17.7, 15.6; ESI-HRMS m/z calcd for $C_{39}H_{48}O_7Na$ $(M+Na)^+$ 651.3298, found 651.3276.

(trans)-2-[(1'*S*,2'*R*,4'*S*)-4'-Acetoxy-1',2'-Epoxy-2',6',6'-trimethylcyclohexyl]-1-(tributylstannyl)ethylene. To a solution of acetylene **15** (649 mg, 2.92 mmol), tetrakis(triphenylphosphine)palladium (169 mg, 0.15 mmol) in THF (29 mL) was added dropwise tributyltin hydride (1.55 mL, 5.84 mmol) at -78 °C. After being stirred for 15 min at room temperature and the reaction mixture was filtered through a pad of silica gel to give the crude products as a solution, which was concentrated *in vacuo*. Purification by silica gel column chromatography afforded **20** (1.31 g, 87%): $[\alpha]^{23.0}_D$ -

49.44 (*c* 0.89, $CHCl_3$); IR (neat, cm^{-1}) 3466, 2959, 2926, 2872, 2854, 1739, 1462, 1419, 1377, 1365, 1242, 1184, 1155, 1118, 1097, 1070, 1030; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.23 (d, *J* =19.0 Hz, 1H), 6.16 (d, *J* =19.2 Hz, 1H), 4.92 (m, 1H), 2.38 (dd, *J* =14.8, 5.7 Hz, 1H), 2.01 (s, 3H), 1.75 (dd, *J* =14.8, 6.8 Hz, 1H), 1.64 (dd, *J* =13.2, 3.4 Hz, 1H), 1.49 (m, 6H), 1.35 (m, 1H), 1.30 (m, 6H), 1.19 (s, 3H), 1.16 (s, 3H), 0.97 (s, 3H), 0.88 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.4, 142.1, 132.4, 72.2, 67.9, 64.7, 41.5, 36.8, 34.3, 29.2, 28.6, 27.3, 25.5, 21.5, 20.3, 13.8, 9.6; ESI-HRMS m/z calcd for $C_{25}H_{46}O_3SnNa$ $(M+Na)^+$ 537.2371, found 537.2363.

(trans)-2-[(1*S*,2*R*,4*S*)-4-Acetoxy-1,2-Epoxy-2,6,6-trimethylcyclohexyl]-1-iodoethylene (21). To a solution of iodine (445 mg, 1.75 mmol),Na_2CO_3 (372 mg, 3.51 mmol) in dichloromethane (7 mL) was added dropwise a solution of **20** (450 mg, 0.88 mmol) in dichloromethane (2 mL) at 0 °C. After stirred for 5 min at 0 °C, the mixture was poured into a saturated aqueous $Na_2S_2O_3$ solution and then extracted with Chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded iodide **21** (273 mg, 89%): $[\alpha]^{23.0}_D$ –68.0 (*c* 1.01, $CHCl_3$); IR (neat, cm^{-1}) 2965, 2932, 1736, 1603, 1468, 1365, 1242, 1032; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.77 (d, *J* =14.2 Hz, 1H), 6.28 (d, *J* =14.2 Hz, 1H), 4.89 (m, 1H), 2.37 (dd, *J* =14.9, 5.5 Hz, 1H), 2.01 (s, 3H), 1.76 (dd, *J* =15.1, 6.8 Hz, 1H), 1.63 (dd, *J* =13.5, 3.4 Hz, 1H), 1.35 (dd, *J* =13.5, 8.9 Hz, 1H), 1.22 (s, 3H), 1.15 (s, 3H), 0.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 141.3, 79.8, 72.5, 67.3, 65.1, 41.3, 36.6, 34.3, 28.4, 25.4, 21.5, 20.2; ESI-HRMS m/z calcd for $C_{13}H_{19}IO_3Na$ $(M+Na)^+$ 373.0277, found 373.0277.

Ethyl (2*E*,4*E*)-5-(tributylstannyl)hexa-2,4-dienate (22a). A mixture of **22** (1.0 g, 2.77 mmol) and manganese dioxide (16.6 g) in THF (17 mL) was stirred at room temperature for 6 h. The precipiate was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford crude aldehyde, which was used in the next reaction without further purification.

To a solution of triethyl phosphonoacetate (0.72 mL, 3.6 mmol) in THF (13 mL) was added sodium hydride (133 mg, 3.32 mmol) at 0 °C and the mixture was stirred for 10 min. To this mixture was added a solution of the crude aldehyde in THF

(3 mL) at 0 °C. After being stirred for 5 min at room temperature, the reaction mixture was poured into water and then extracted with ethyl acetate. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded ethyl ester **22a** (936 mg, 79% for 2 steps): IR (neat, cm^{-1}) 2961, 2928, 2870, 2852, 1716, 1620, 1462, 1419, 1367, 1340, 1304, 1265, 1234, 1180, 1132, 1095, 1076, 1043; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (dd, *J* = 15.3, 11.2 Hz, 1H), 6.34 (d, *J* = 11.3 Hz, 1H), 5.79 (d, *J* =15.1 Hz, 1H), 4.21 (q, *J* =7.1 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 157.9, 137.6, 136.5, 119.9, 60.1, 29.0, 27.3, 20.6, 14.3, 13.6, 9.2; ESI-HRMS m/z calcd for $C_{20}H_{38}O_2SnNa$ $(M+Na)^+$ 453.1795, found 453.1777.

(2*E*,4*E*)-5-(Tributylstannyl)hexa-2,4-dien-1-ol (23). To a suspension of lithium aluminum hydride (36 mg, 0.95 mmol) in THF (6 mL) was added dropwise a solution of **22a** (338 mg, 0.79 mmol) in THF (2 mL) at 0 °C. After being stirred for 10 min at the same temperature, Rochelle salt was carefully added. The reaction mixture was stirred for 30 min at room temperature and then extracted with ethyl acetate. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded **23** (223 mg, 73%): IR (neat, cm^{-1}) 3327, 2957, 2920, 2852, 1460, 1417, 1375, 1340, 1292, 1089, 1005; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.64 (dd, *J* = 15.1, 10.5 Hz, 1H), 6.19 (d, *J* = 10.5 Hz, 1H), 5.78 (dt, *J* = 14.8, 5.9 Hz, 1H), 4.22 (t, *J* = 5.8 Hz, 2H), 2.00 (s, 3H), 1.49 (m, 6H), 1.30 (m, 6H), 0.89 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 138.0, 130.9, 126.3, 63.7, 29.2, 27.5, 19.9, 13.8, 9.2.

(2*E*,4*E*,6*E*)-7-[(1'*S*,2'*R*,4'*S*)-4'-Acetoxy-1',2'-Epoxy-2',6',6'-trimethylcyclohexa-1'-yl]-5-methylhepta-2,4,6-triene-1-ol (24). To a solution of iodide **21** (560 mg, 1.6 mmol) and (2E,4E)-5-(tributyl stannyl)hexa-2,4-dien-1-ol **23** (915 mg, 2.40 mmol) in DMF (8 mL) was added bis(acetonitrile)dichloropalladium(II) (21 mg, 0.05 mmol) and lithium chloride (136 mg, 3.20 mmol). After being stirred for 10 min at 55 °C, the reaction mixture was poured into water and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded coupling product **24** (482 mg, 94%) as a yellow oil: $[\alpha]^{23.0}_D$ –41.6 (*c* 1.02, $CHCl_3$); IR

(neat, cm^{-1}) 3443, 2964, 2928, 1736, 1450, 1365, 1244, 1030; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.60 (dd, *J* = 14.2, 10.3 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.10 (d, *J* =11.2 Hz, 1H), 5.88 (d, *J* =15.8 Hz, 1H), 5.86 (m, 1H), 4.93 (m, 1H), 4.24 (m, 2H), 2.40 (dd, *J* =15.1, 5.8 Hz, 1H), 2.01 (s, 3H), 1.88 (s, 3H), 1.77 (dd, *J* =14.8, 6.8 Hz, 1H), 1.66 (dd, *J* =13.2, 3.4 Hz, 1H), 1.34(m, 1H), 1.18 (s, 3H), 1.15 (s, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 137.4, 134.5, 132.8, 130.4, 127.5, 123.7, 70.3, 67.7, 65.5, 63.5, 41.4, 36.8, 34.7, 28.6, 25.5, 21.4, 20.2, 12.8; ESI-HRMS m/z calcd for $C_{19}H_{28}O_4Na$ $(M+Na)^+$ 343.1885, found 343.1883.

2-[(((2'*E*,4'*E*,6'*E*)-7'-((1''*S*,2''*R*,4''*S*)-4''-Acetoxy-1'',2''-Epoxy-2'',6'',6''-trimethylcyclohexylidene-1''-yl)-5'-methylhepta-2,4,6-triene)sulfanyl) benzothiazole (25). To a solution of **24** (330 mg, 1.03 mmol), 2-mercaptobenzothiazole (241 mg, 1.44 mmol) and triphenylphosphine (378 mg, 1.44 mmol) in THF (10 mL) was added dropwise diisopropyl azodicarboxylate (0.32 mL, 1.65 mmol) at 0 °C. The reaction mixture was stirred for 10 min at room temperature and the all solvents were removed *in vacuo*. To a residue was added diethyl ether and the precipitate was removed by filtration through a pad of Celite to give the crude products as a solution, which was concentrated *in vacuo*. Purification by short silica gel column chromatography afforded the thioether **25** (444 mg, 92%): $[\alpha]^{23.0}_D$ -25.6 (*c* 1.08, $CHCl_3$); IR (neat, cm^{-1}) 2964, 2926, 1734, 1460, 1427, 1365, 1242, 1028; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87 (m, 1H), 7.75 (m, 1H), 7.40 (m, 1H), 7.28 (m, 1H), 6.71 (dd, *J* = 14.7, 11.3 Hz, 1H), 6.24 (d, *J* = 15.5 Hz, 1H), 6.07 (d, *J* =11.4 Hz, 1H), 5.88 (d, *J* =15.5 Hz, 1H), 5.86 (m, 1H), 4.93 (m, 1H), 4.11 (d, *J* =7.5 Hz, 2H), 2.38 (dd, *J* =15.8, 5.7 Hz, 1H), 2.01 (s, 3H), 1.87 (s, 3H), 1.76 (dd, *J* =14.8, 6.8 Hz, 1H), 1.65 (dd, *J* =13.2, 3.4 Hz, 1H), 1.33(m, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 166.1, 153.2, 137.2, 135.3, 134.9, 130.9, 129.9, 127.4, 125.9, 124.2, 124.1, 121.5, 120.9, 70.3, 67.6, 65.5, 41.4, 36.7, 36.1, 34.7, 28.5, 25.5, 21.4, 20.2, 12.8; ESI-HRMS m/z calcd for $C_{26}H_{31}NO_3S_2Na$ $(M+Na)^+$ 492.1643, found 492.1640.

2-[(((2'*E*,4'*E*,6'*E*)-7'-((1''*S*,2''*R*,4''*S*)-4''-Acetoxy-1'',2''-Epoxy-2'',6'',6''-trimethylcyclohexylidene-1''-yl)-5'-methylhepta-2,4,6-triene)sulfonyl) benzothiazole (7). To a solution of the thioether **25** (30 mg, 0.064 mmol) in ethanol (0.64 mL) was added dropwise a solution of sodium tungstate (VI) dihydrate (42 mg,

0.128 mmol) in hydrogen peroxide (30 wt.% in water, 0.51 mL) at 0 °C. After being stirred for 50 min at room temperature, the reaction mixture was poured into water and then extracted with diethyl ether. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography afforded the sulfone **7** (18 mg, 56%) as a yellow solid: $[\alpha]^{24.0}_D$ –22.5 (c 0.79, $CHCl_3$); IR (neat, cm^{-1}) 3471, 2930, 2865, 1736, 1637, 1473, 1381, 1334, 1240, 1147, 1116, 976, 763; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* =7.8 Hz, 1H), 8.01 (d, *J* =8.7 Hz, 1H), 7.65 (m, 2H), 6.59 (dd, *J* =14.7, 11.0 Hz, 1H), 6.20 (d, *J* =15.6, 1H), 6.02 (d, *J* =15.6 Hz, 1H), 5.90 (d, *J* =15.6 Hz, 1H), 5.64 (dt, *J* =15.1, 7.8 Hz, 1H), 4.91 (m, 1H), 4.31 (d, *J* =7.8 Hz, 1H), 2.36 (dd, J =15.1, 5.7, 1H), 2.00 (s, 3H), 1.78 (dd, *J* =15.2, 6.5 Hz, 1H), 1.71 (s, 3H), 1.63 (m, 1H), 1.37 (dd, *J* =13.7, 8.5 Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 0.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 165.9, 153.0, 137.5, 137.2, 129.5, 128.3, 128.0, 125.8, 125.7, 122.7, 116.5, 70.5, 67.9, 65.9, 59.3, 41.7, 37.1, 35.0, 28.9, 25.8, 21.7, 20.5, 13.1; ESI-HRMS m/z calcd for $_{26}H_{31}NO_5S_2Na$ $(M+Na)^+$ 524.1541, found 524.1524.

Peridinin Derivative C (3). To a solution of olefin segment **7** (22 mg, 0.044 mmol) and ylidenbutenolide segment **5** (15 mg, 0.044 mmol) in THF (0.65 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.13 mL, 0.13 mmol) at -78 °C in the dark. After being stirred for 5 min at the same temperature, the reaction mixture was poured into water and then extracted with diethyl ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 30% to 50% ethyl acetate in hexane) in the dark afforded peridinin derivative **2** (11 mg, 40%) as a mixture of the isomers as a red film. A solution of a mixture of all-*trans*-peridinin derivative **2** and its *cis*-isomer in benzene was left at room temperature in the fluorescence light. After 2 days, partial separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1 / 10; flow rate: 2.0 mL / min.; UVdetect: 450 nm; retention time: (all-*trans*-isomer) 49 min., (15-*cis*-isomer) 43 min.] in the dark, and HPLC [column: YMC Carotenoid C30 (10 x 250 mm); reverse phase: acetonitrile / methanol / water = 87 / 10 / 3; flow rate: 2.0 mL / min.; UVdetect: 450 nm; retention time: (all-*trans*-isomer) 30 min., (15-*cis*-isomer) 24 min.] in the dark, afforded the desired optically active peridinin derivative **2** as a red film: IR (neat, cm^{-1}) 3327, 2924,

1741, 1712, 1462, 1377, 1259, 1153, 1028; ^{1}H NMR (C_6D_6, 750 MHz) δ 7.57 (d, *J* = 15.5 Hz, 1H), 6.68 (d, *J* = 15.4 Hz, 1H), 6.62 (dd, *J* = 14.0, 12.3 Hz, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.45 (dd, *J* = 14.1, 11.9 Hz, 1H), 6.38 (dd, *J* = 14.3, 11.2 Hz, 1H), 6.33 (d, *J* = 11.7 Hz, 1H), 6.26 (dd, *J* = 14.2, 11.3 Hz, 1H), 6.17 (d, *J* = 11.7 Hz, 1H), 6.15 (s, 1H), 5.92 (d, *J* =15.5 Hz, 1H), 5.20 (s, 1H), 5.19 (m, 1H), 3.86 (m, 1H), 2.35 (dd, *J* = 14.7, 5.3 Hz, 1H), 2.19 (ddd, *J* = 14.7, 5.1, 1.1 Hz, 1H), 2.13 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.71 (m, 1H), 1.62 (dd, *J* =14.8, 7.2 Hz, 1H), 1.42 (m, 2H), 1.35 (m, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H), 1.05 (s, 3H), 1.05 (m, 1H); ^{13}C NMR (C_6D_6, 188 MHz) δ 169.3, 168.3, 147.5, 138.1, 137.7, 137.1, 136.4, 135.8, 134.7, 134.6, 134.4, 132.5, 131.4, 129.9, 125.1, 125.0, 122.4, 118.5, 70.5, 70.3, 67.7, 67.5, 65.8, 63.9, 47.3, 42.2, 41.2, 37.3, 35.3, 35.1, 29.5, 28.8, 25.7, 25.3, 21.0, 19.9, 15.6, 12.9; ESI-HRMS m/z calcd for $C_{39}H_{48}O_7Na$ $(M+Na)^+$ 651.3298, found 651.3276.

(4*S*)-4-hydroxy-2,6,6-trimethylcyclohex-1-enyltrifluoromethanesulfonate (10a). To a solution of **10** (200 mg, 0.50 mmol) in THF (2.47 mL) was added tetra-*n*-butylammonium fluoride (1.0M in THF, 1.49 mL, 1.49 mmol) at room temperature. After being stirred for 45 min at the same temperature, the reaction mixture was poured into a saturated aqueous NH_4Cl solution and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 10% to 50% ethyl acetate in hexane) afforded alcohol **10a** (112 mg, 78%) as a colorless oil: $[\alpha]_D^{23.0}$ -25.4 (c 0.99, $CHCl_3$); IR (neat, cm^{-1}) 3359, 2932, 2361, 1686, 1404, 1210, 1067, 913; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.11 (m, 1H), 2.50 (ddd, *J* = 17.0, 5.5, 1.9 Hz, 1H), 2.18 (ddd, *J* = 16.5, 9.2, 0.9 Hz, 1H), 1.86 (ddd, *J* = 12.4, 3.7, 0.3 Hz, 1H), 1.77 (s, 3H), 1.68 (dd, *J* = 11.9, 11.9 Hz, 1H), 1.22 (s, 3H), 1.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 123.9, 64.1, 49.0, 41.3, 37.1, 27.7, 27.0, 17.9; FAB-HRMS m/z calcd for $C_{39}H_{51}O_7Na$ $(M+H)^+$ 288.0716, found 289.0759.

(trans)-2-[(4*S*)-4-hydroxy-2,6,6-trimethylcyclohexene]-1-(tributylstannyl)ethylene (27). To a solution of alcohol **10a** (388 mg, 1.17 mmol) and bisstannane **26** (855 mg, 1.41 mmol) in DMF (5.86 mL) was added diisopropylethylamine (0.61 mL, 3.52 mmol), tetrakis(triphenylphosphine)palladium (67 mg, 0.059 mmol), and lithium chloride (99 mg, 2.34 mmol) After being stirred for 1

h at 90 °C, the reaction mixture was poured into water and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 0% to 30% ethyl acetate 3% triethylamine in hexane) afforded **27** (451 mg, 85%) as a colorless oil: $[\alpha]^{23.0}_D$ -72.0 (c 0.84, $CHCl_3$); IR (neat, cm^{-1}) 3360, 2924, 2855, 2361, 1579, 1464, 1174, 1045, 691; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.30 (d, *J* = 19.6 Hz, 1H), 5.90 (d, *J* = 19.2 Hz, 1H), 3.98 (m, 1H), 2.35 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.00 (dd, *J* = 16.1, 9.5 Hz, 1H), 1.75 (ddd, *J* = 19.0, 3.6, 2.3 Hz, 1H), 1.70 (s, 3H), 16.0-1.47 (m, 6H), 1.45 (dd, *J* = 12.3 Hz, 1H), 1.06 (s, 3H), 1.04 (s, 3H), 0.90 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 141.5, 133.9, 124.9, 65.5, 48.6, 42.5, 36.9, 30.4, 29.6, 28.8, 27.6, 21.7, 14.1, 9.9.

(trans)-2-[(4*S*)-4-hydroxy-2,6,6-trimethylcyclohexene]-1-iodoethylene (28). To a solution of iodide (728 mg, 2.87 mmol), Na_2CO_3 (608 mg, 5.74 mmol) in dichloromethane (11.4 mL) was added dropwise a solution of stannane **27** (654 mg, 1.44 mmol) in dichloromethane (3 mL) at 0 °C. After stirred for 5 min at 0 °C, the mixture was poured into a saturated aqueous $Na_2S_2O_3$ solution and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 5% to 30% ethyl acetate in hexane) afforded iodide **28** (379 mg, 94%) as a colorless oil: $[\alpha]^{23.0}_D$ -115.0 (c 0.64, $CHCl_3$); IR (neat, cm^{-1}) 3301, 2955, 1590, 1466, 1364, 1166, 1047, 945, 781; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.89 (d, *J* = 14.6 Hz, 1H), 5.96 (d, *J* = 14.6 Hz, 1H), 3.95 (m, 1H), 2.33 (dd, *J* = 17.0, 5.5 Hz,, 1H), 1.94 (ddd, *J* = 17.0, 9.6, 1.4 Hz, 1H), 1.73 (ddd, *J* = 12.4, 3.7, 1.4 Hz, 1H), 1.66 (s, 3H), 1.42 (dd, *J* = 11.9, 11.9 Hz, 1H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 139.0, 128.2, 79.5, 65.1, 48.2, 42.4, 36.8, 30.2, 28.7, 21.7; FAB-HRMS m/z calcd for $C_{11}H_{17}IO_7$ $(M+H)^+$ 293.0397, found 293.0423.

(trans)-2-[(4*S*)-4-Acetoxy-2,6,6-trimethylcyclohexene]-1-iodoethylene (29). To a solution of iodide **28** (379 mg, 1.30 mmol) in pyridine (5.19 mL) was added acetic anhydride (0.24 mL, 2.59 mmol) at room temperature, and the reaction mixture was stirred for 16 h at the same temperature. A saturated aqueous $CuSO_4$ solution was added and then the resulting mixture was extracted with ethyl acetate. The organic layers were

combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (30% ethyl acetate in hexane) afforded acetate **29** (374 mg, 86%) as a colorless oil: $[\alpha]^{25.0}_D$ -99.8 (c 1.10, $CHCl_3$); IR (neat, cm^{-1}) 2963, 2867, 1740, 1588, 1466, 1242, 1117, 1035, 968; NMR ($CDCl_3$, 400 MHz) δ 6.91 (d, *J*= 14.6 Hz, 1H), 6.00 (d, *J* = 15.1Hz, 1H), 5.02 (m, 1H), 2.39 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.04 (s, 3H), 2.01 (m, 1H), 1.76 (ddd, *J* = 11.9, 3.2, 1.8 Hz, 1H), 1.67 (s, 3H), 1.55 (dd, *J* = 11.5, 11.5 Hz, 1H), 1.07 (s, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 143.3, 139.2, 127.8, 79.8, 68.3, 43.9, 38.4, 36.4, 30.0, 28.5, 21.8, 21.6; FAB-HRMS m/z calcd for $C_{39}H_{51}O_7$ $(M+H)^+$ 335.0502, found 335.0541.

(2*E*,4*E*,6*E*)-7-[(4'*S*)-4'-Acetoxy-2',6',6'-trimethylcyclohexene]-5-methylhepta-2,4,6-triene-1-ol (30). To a solution of acetate **29** (194 mg, 0.58 mmol) and (2E,4E)-5-(tributylstannyl)hexa-2,4-dien-1-ol **23** (247 mg, 0.64 mmol) in DMF (2.9 mL) was added diisopropylethylamine (0.30 mL, 1.74 mmol), bis(acetonitrile)dichloropalladium(II) (7 mg, 0.03 mmol) and lithium chloride (49 mg, 1.16 mmol). After being stirred for 50 min at room temperature, the reaction mixture was poured into water and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 10% to 30% ethyl acetate in hexane) afforded **30** (151 mg, 85%) as a yellow oil: $[\alpha]^{23.0}_D$ -91.0 (c 1.33, $CHCl_3$); IR (neat, cm^{-1}) 3414, 2961, 2924, 1736, 1366, 1244, 1030; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.63 (dd, *J* = 15.1, 11.2 Hz, 1H), 6.13-5.96 (m, 3H), 5.88 (td, *J* = 12.1, 5.9 Hz, 1H), 5.06 (m, 1H), 4.24 (m, 1H), 2.44 (dd, *J* = 17.0, 5.72 Hz, 1H), 2.06 (m, 1H), 2.05 (s, 3H), 1.92 (s, 3H), 1.77 (ddd, *J* = 12.2, 3.4, 1.8 Hz, 1H), 1.71 (s, 3H), 1.56 (m, 1H), 1.10 (s, 3H), 1.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8, 138.3, 137.7, 135.9, 132.0, 129.3, 127.9, 125.8, 125.6, 68.4, 63.7, 43.9, 38.4, 36.6, 29.9, 28.4, 21.5, 21.4, 12.6; ESI-HRMS m/z calcd for $C_{19}H_{28}O_3Na$ $(M+Na)^+$ 327.1936, found 327.1940.

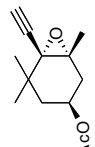
2-[(((2'*E*,4'*E*,6'*E*)-7'-((4''*S*)-4''-Acetoxy-1'',2''-Epoxy-2'',6'',6''-trimethylcyclohexene)-5'-methylhepta-2,4,6-triene)sulfanyl) benzothiazole (30a). To a solution of alcohol **30** (110 mg, 0.29 mmol), 2-mercaptobenzothiazole (68 mg, 0.41 mmol) and triphenylphosphine (107 mg, 0.41 mmol) in THF (3 mL) was added dropwise diisopropyl azodicarboxylate (0.09 mL, 0.47 mmol) at 0 °C. The reaction

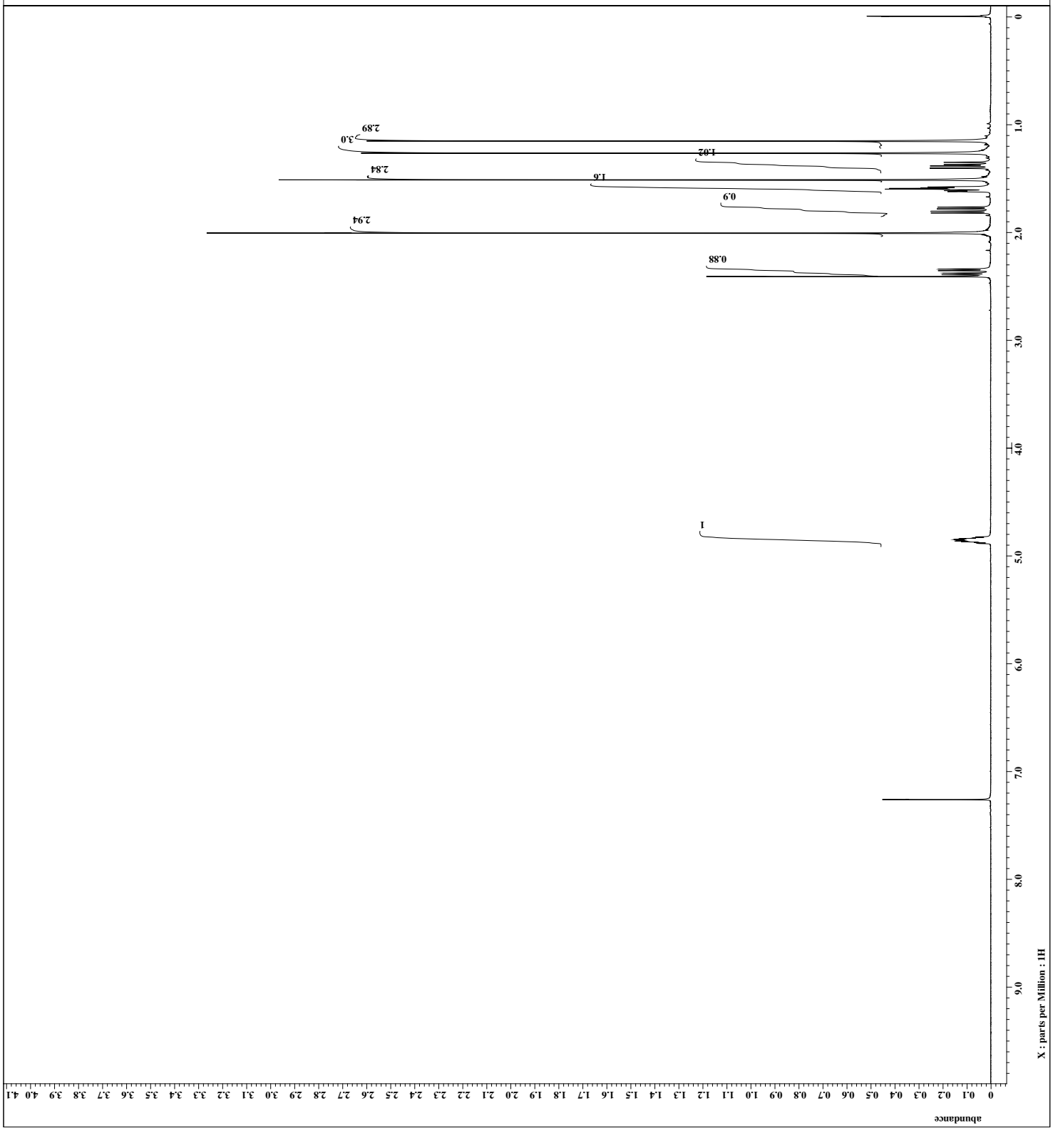
mixture was stirred for 10 min at room temperature and the all solvents were removed *in vacuo*. To a residue was added diethyl ether and the precipitate was removed by filtration through a pad of Celite to give the crude products as a solution, which was concentrated *in vacuo*. Purification by short silica gel column chromatography (from 10% to 30% ethyl acetate in hexane) afforded thioether **30a** (111 mg, 84%): $[\alpha]^{23.0}_{D}$ -64.1 (c 0.93, $CHCl_3$); IR (neat, cm^{-1}) 2963, 2926, 1734, 1460, 1427, 1363, 1244, 1030; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (m, 1H), 7.75 (m, 1H), 7.41 (m, 1H), 7.27 (m, 1H), 6.74 (dd, *J* = 14.6, 11.2 Hz, 1H), 6.09-6.04 (m, 2H), 6.02 (d, *J* =10.0 Hz, 1H), 5.88 (m, 1H), 5.04 (m, 1H), 4.11 (d, *J* =7.6 Hz, 2H), 2.43 (dd, *J* =17.0, 5.5 Hz, 1H), 2.08 (dd, *J* =17.0, 9.4 Hz, 1H), 2.04 (s, 3H), 1.91 (s, 3H), 1.73 (m, 1H), 1.69 (s, 3H), 1.56 (m, 1H), 1.08 (s, 3H), 1.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 166.2, 153.2, 138.2, 137.6, 136.3, 135.3, 131.2, 128.9, 126.7, 126.1, 125.9, 125.6, 124.2, 121.5, 120.9, 68.2, 43.9, 38.3, 36.6, 36.2, 29.9, 28.4, 21.4, 21.4, 12.56; ESI-HRMS m/z calcd for $C_{26}H_{31}NO_2S_2Na$ $(M+Na)^+$ 476.1694, found 476.1696.

2-[(((2'*E*,4'*E*,6'*E*)-7'-((4''*S*)-4''-Acetoxy-2'',6'',6''-trimethylcyclohexene)-5'-methylhepta-2,4,6-triene)sulfonyl) benzothiazole (8). To a solution of the thioether **30a** (205 mg, 0.45 mmol) in ethanol (9.0 mL) was added dropwise a solution of sodium tungstate (VI) dihydrate (164 mg, 0.50 mmol) in hydrogen peroxide (30 wt.% in water, 5,42 mL) at 0 °C. After being stirred for 50 min at room temperature, the reaction mixture was poured into water and then extracted with diethyl ether. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 10% to 30% ethyl acetate in hexane) afforded the sulfone **8** (68 mg, 31%): $[\alpha]^{23.0}_{D}$ -43.5 (c 1.50, $CHCl_3$); IR (neat, cm^{-1}) 2963, 1728, 1630, 1471, 1364, 1330, 1244, 1148, 1026, 970; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (m, 1H), 7.99 (m, 1H), 7.63 (m, 2H), 6.60 (dd, *J* = 14.9, 11.3 Hz, 1H), 6.10 (d, *J* = 16.2 Hz, 1H), 5.99 (d, *J* = 16.3 Hz, 1H), 5.98 (d, *J* = 11.4 Hz, 1H), 5.62 (m, 1H), 5.04 (m, 1H), 4.33 (d, *J* = 7.4 Hz, 2H), 2.37 (m, 1H), 2.09 (m, 1H), 2.04 (s, 3H), 1.80-1.65 (m, 1H), 1.74 (s, 3H), 1.60-1.50 (m, 1H), 1.43 (s, 3H), 0.97 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 166.3, 153.3, 139.2, 138.5, 137.8, 137.6, 133.9, 129.5, 128.6, 128.3, 128.2, 127.6, 126.1, 123.0, 116.1, 69.2, 59.8, 44.7, 38.7, 37.8, 29.5, 28.9, 22.12, 20.8, 13.2; ESI-HRMS m/z calcd for $C_{26}H_{31}NO_4S_2Na$ $(M+Na)^+$ 508.1592, found 508.1547.

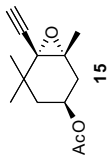
Peridinin derivative D (4). To a solution of sulfone **8** (22 mg, 0.045 mmol) and aldehyde **5** (16 mg, 0.045 mmol) in THF (0.68 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.14 mL, 0.14 mmol) at -78 °C in the dark. After being stirred for 5 min at the same temperature, the reaction mixture was poured into water and then extracted with diethyl ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 30% to 50% ethyl acetate in hexane) in the dark afforded peridinin derivative (13 mg, 47%) as a mixture of the isomers as a red film. A solution of a mixture of all-*trans*-peridinin derivative **4** and its isomer in benzene was left at room temperature in the fluorescence light. After 4 days, partial separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1 / 10; flow rate: 2 mL / min.; UVdetect: 459 nm; retention time: (all-*trans*-isomer) 68 min., (15-*cis*-isomer) 61 min.] in the dark, and HPLC [column: YMC Carotenoid C30 (10 x 250 mm); reverse phase: acetonitrile / methanol / water = 87 / 10 / 3; flow rate: 2.0 mL / min.; UVdetect: 459 nm; retention time: (all-*trans*-isomer) 34 min.] in the dark, afforded the desired optically active peridinin derivative **4** as a red film: IR (neat, cm^{-1}) 3449, 2924, 2853, 2363, 1751, 1655, 1509, 1364, 1242, 1124, 1034; ^1H NMR (C_6D_6, 750 MHz) δ 7.57 (d, *J* = 15.5 Hz, 1H), 6.68 (dd, *J* = 13.7, 12.3 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.49 (dd, *J* = 14.1, 12.0 Hz, 1H), 6.42 (dd, *J* = 14.1, 12.0 Hz, 1H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.34 (dd, *J* = 14.1, 11.0 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.26 (d, *J* = 11.4 Hz, 1H), 6.19 (d, *J* = 16.1 Hz, 1H), 6.17 (s, 1H), 5.29 (m, 1H), 5.22 (s, 1H), 3.76 (m, 1H), 2.46 (dd, *J* = 17.1, 5.9 Hz, 1H), 2.20 (ddd, *J* = 14.2, 4.8, 1.0 Hz, 1H), 2.15 (s, 3H), 2.13 (m, 1H), 1.87 (m, 1H), 1.84 (s, 3H), 1.68 (s, 3H), 1.64 (dd, *J* = 11.9, 11.9 Hz, 1H), 1.42 (m, 2H), 1.13 (s, 3H), 1.13 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 1.06 (m, 1.16); ^{13}C NMR (C_6D_6, 188 MHz) δ 169.8, 168.3, 147.4, 139.0, 138.1, 137.7, 137.2, 136.3, 134.6, 134.3, 134.1, 131.6, 129.6, 126.7, 126.4, 125.1, 122.4, 118.5, 70.4, 68.1, 67.4, 63.8, 47.3, 44.4, 41.2, 38.8, 36.8, 35.3, 30.1, 29.5, 28.6, 25.3, 21.5, 21.0, 19.9, 15.6, 12.7; ESI-HRMS m/z calcd for $C_{39}H_{50}O_6Na$ $(M+Na)^+$ 637.3505, found 637.3517.

```
Filename                = b1-acetyl-acetylene-1
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = 1
Solvent                 = CHLOROFORM-D
Creation_time           = 27-JUL-2006 19:48:01
Revision_time           = 29-OCT-2008 17:43:11
Current_time            = 29-OCT-2008 17:43:44

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 26214
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECX400M
Spectrometer            = DELTA2_NMR

Field_strength          = 9.389766[T] (400[MHz]
X_acq_duration          = 4.36731904[s]
X_domain                = 1H
X_freq                  = 399.78219838[MHz]
X_offset                = 4[ppm]
X_points                = 32768
X_prescans              = 1
X_resolution            = 0.22897343[Hz]
X_sweep                 = 7.5030012[kHz]
Irr_domain              = 1H
Irr_freq                = 399.78219838[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 399.78219838[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 12[us]
X_acq_time              = 4.36731904[s]
X_angle                 = 45[deg]
X_atn                   = 2.8[dB]
X_pulse                 = 6[us]
Tri_mode                = Off
Date_presat             = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 36
Relaxation_delay        = 5[s]
Repetition_time         = 9.36731904[s]
Temp_get                = 24.8[dC]
```

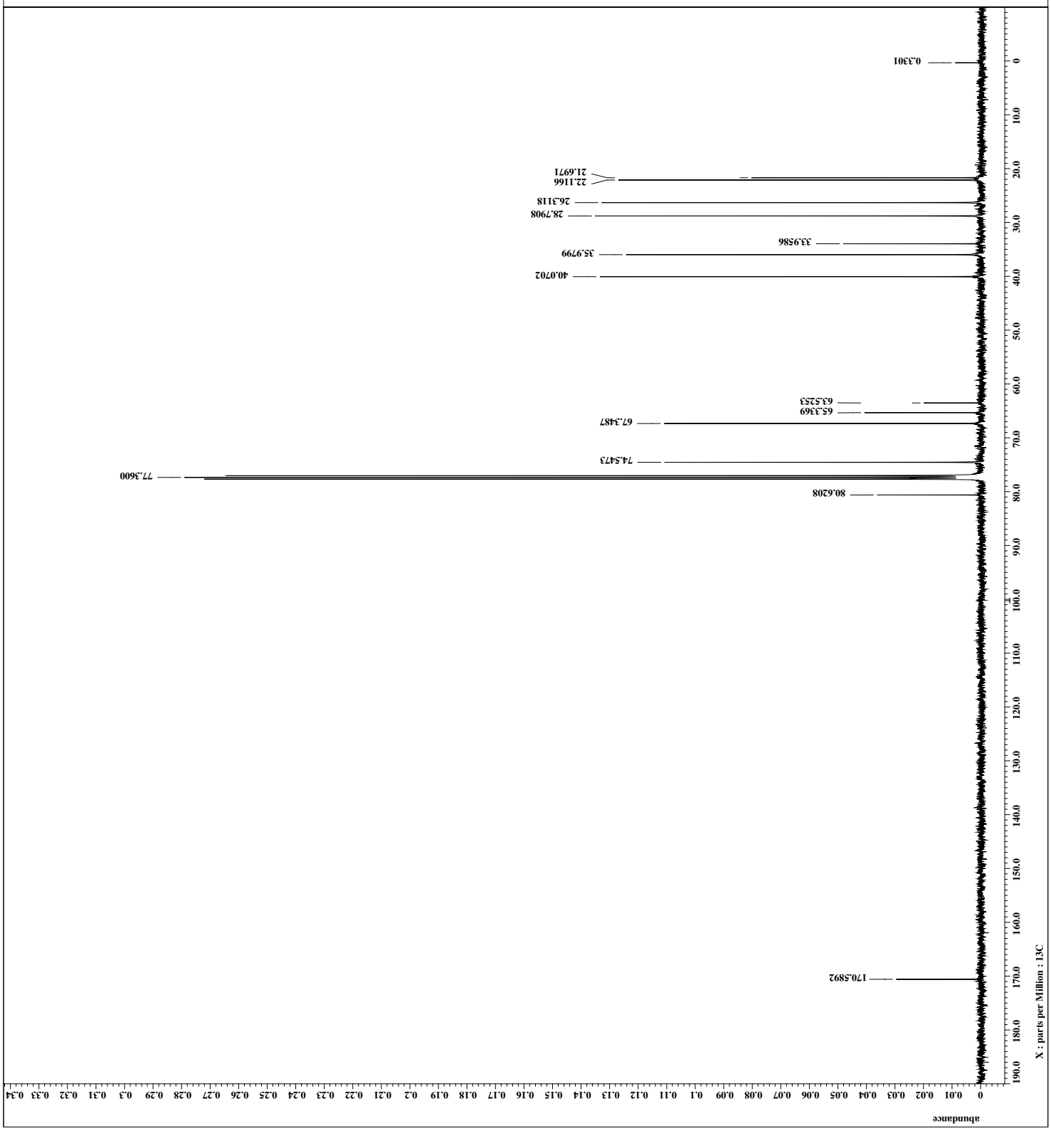


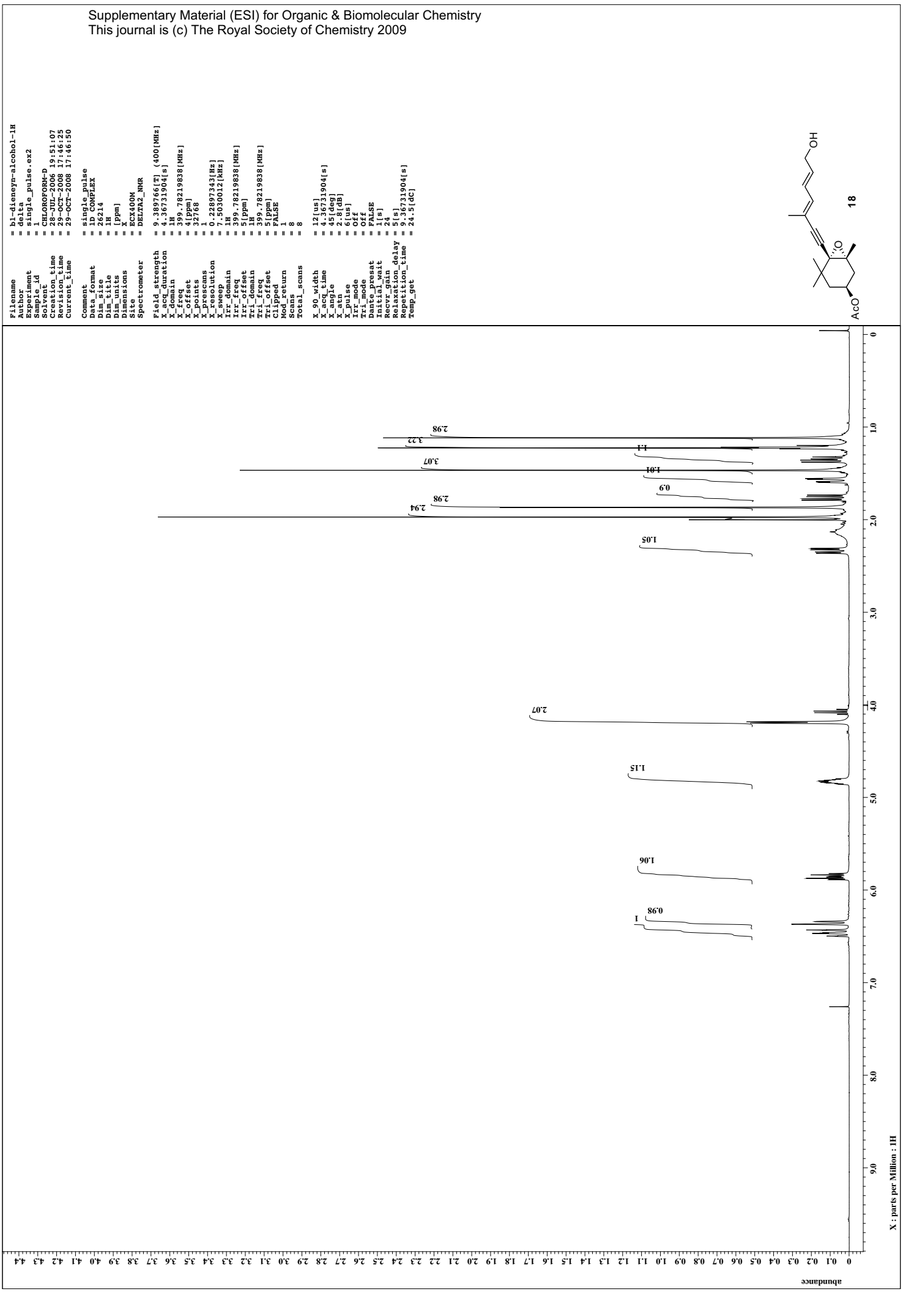


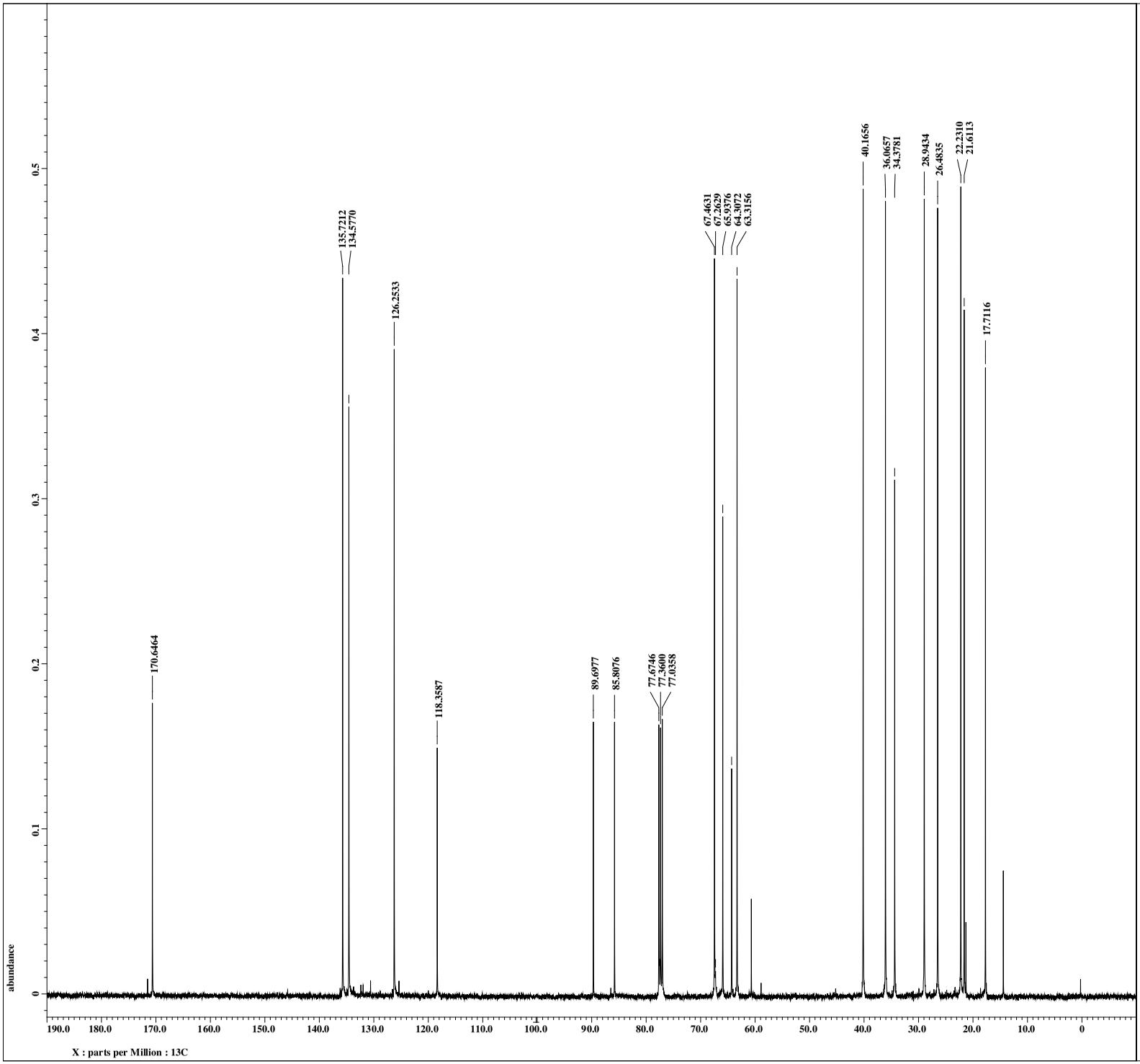
```
Filename          = bl-acetyl-acetylene-1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 27-JUL-2006 21:32:48
Revision_time     = 29-OCT-2008 16:29:12
Current_time      = 29-OCT-2008 16:29:58

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.043333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2000
Total_scans       = 2000

X_90_width        = 9.4[us]
X_acq_time        = 1.043333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_mode          = NNIRZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 54
Relaxation_delay  = 2[s]
Repetition_time   = 3.043333312[s]
Temp_get          = 25[dC]
```



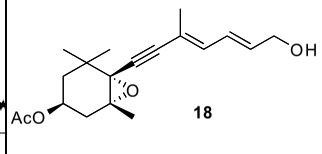
15



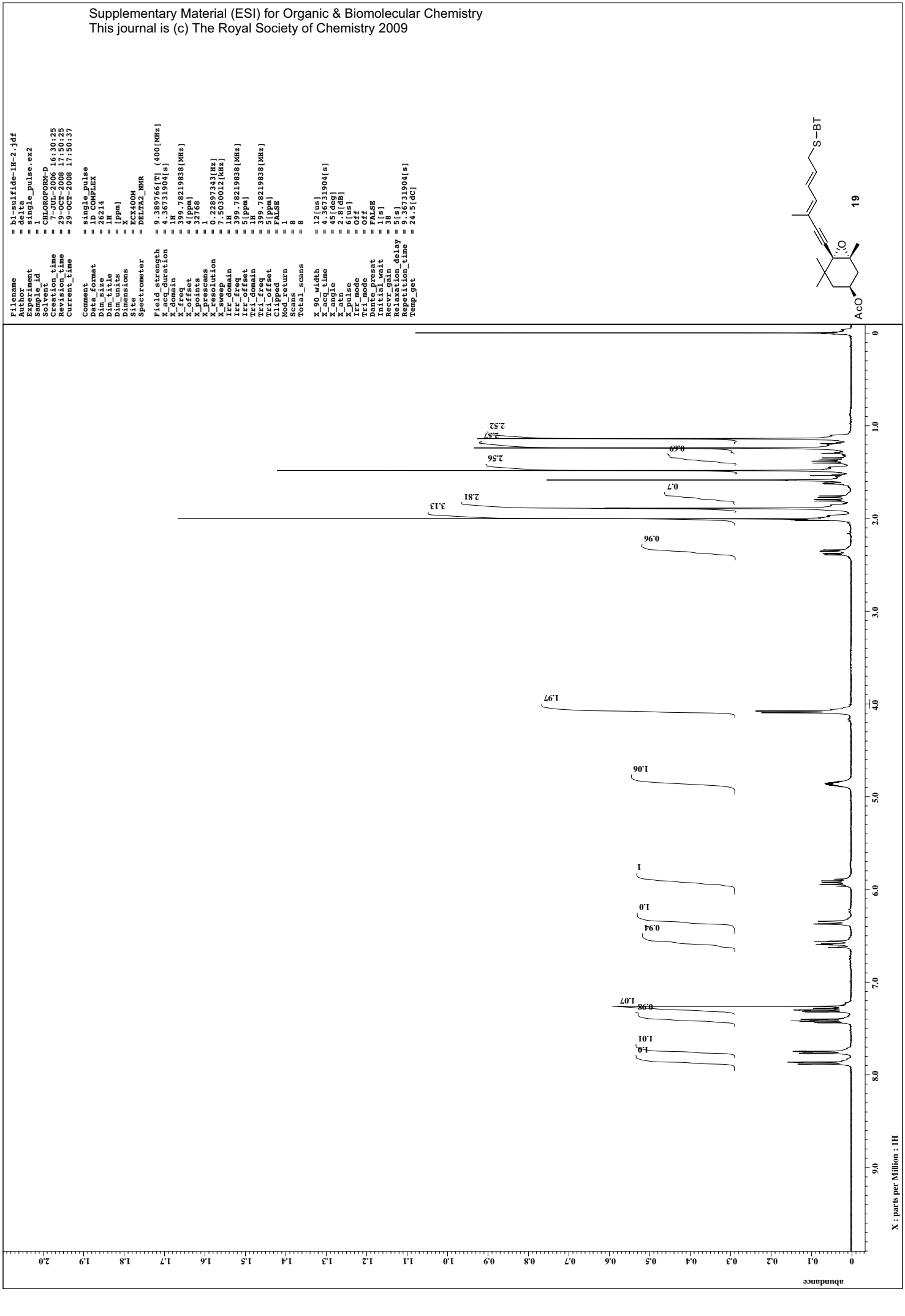

Filename = b1-dieneyn-alcohol-1H
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 28-JUL-2006 19:51:07
Revision_time = 29-OCT-2008 17:46:25
Current_time = 29-OCT-2008 17:46:50
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 4.36731904[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 4[ppm]
X_points = 32768
X_prescans = 1
X_resolution = 0.22897343[Hz]
X_sweep = 7.50300012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12[us]
X_acq_time = 4.36731904[s]
X_angle = 45[deg]
X_atn = 2.8[dB]
X_pulse = 6[us]
Irr_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 24
Relaxation_delay = 5[s]
Repetition_time = 9.36731904[s]
Temp_get = 24.5[dC]
OH
AcO
18
2.98
3.22
1.1
3.07
1.81
0.9
2.98
2.94
1.05
2.07
1.15
1.06
0.98
1
abundance
X : parts per Million : 1H

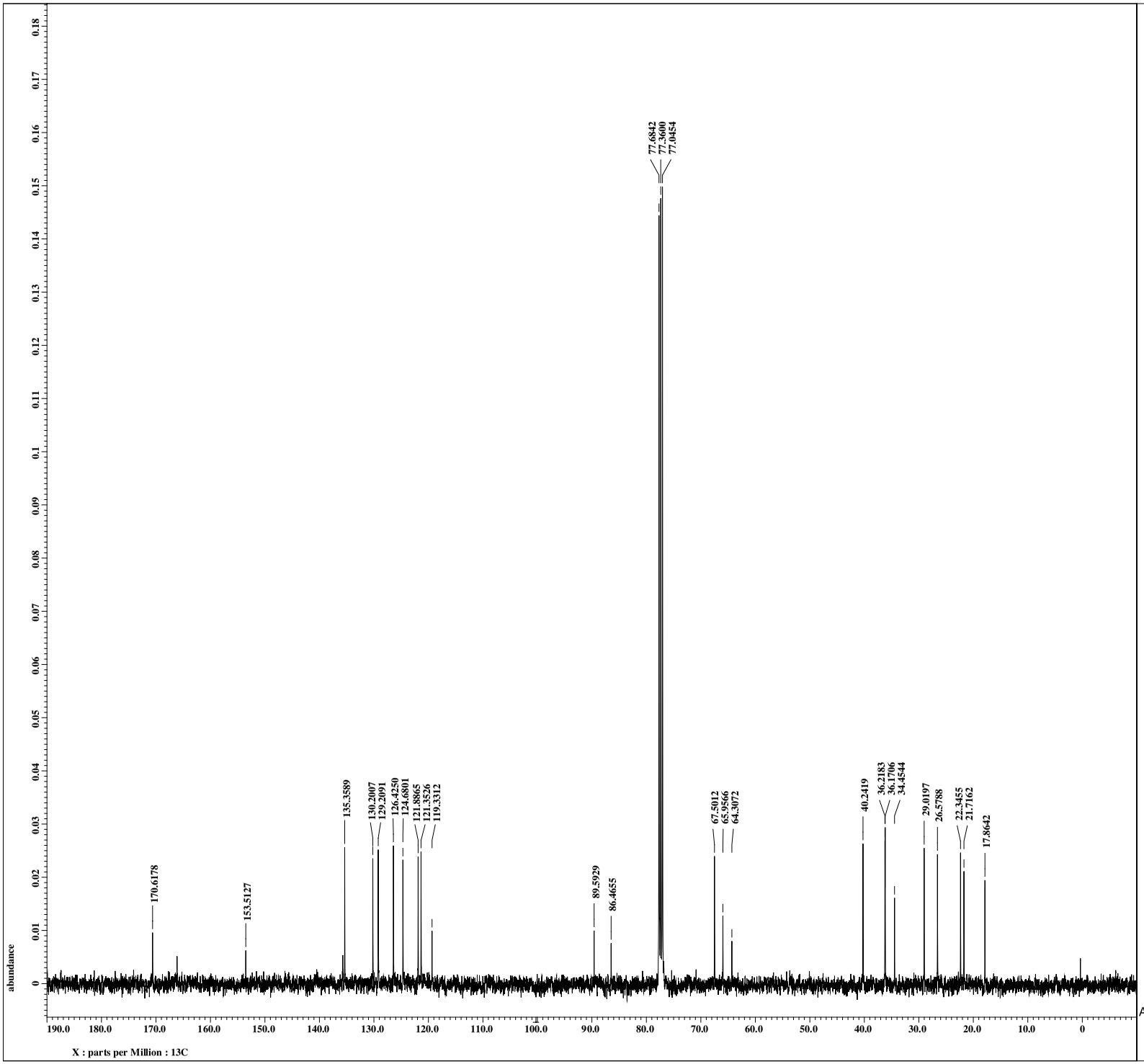



```
Filename          = b1-dieneyn-alcohol-13
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 28-JUL-2006 21:35:09
Revision_time     = 29-OCT-2008 16:31:54
Current_time      = 29-OCT-2008 16:32:42

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2000
Total_scans       = 2000

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 54
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.7[dC]
```

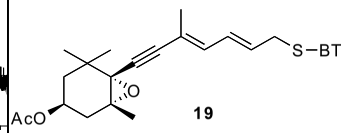


18

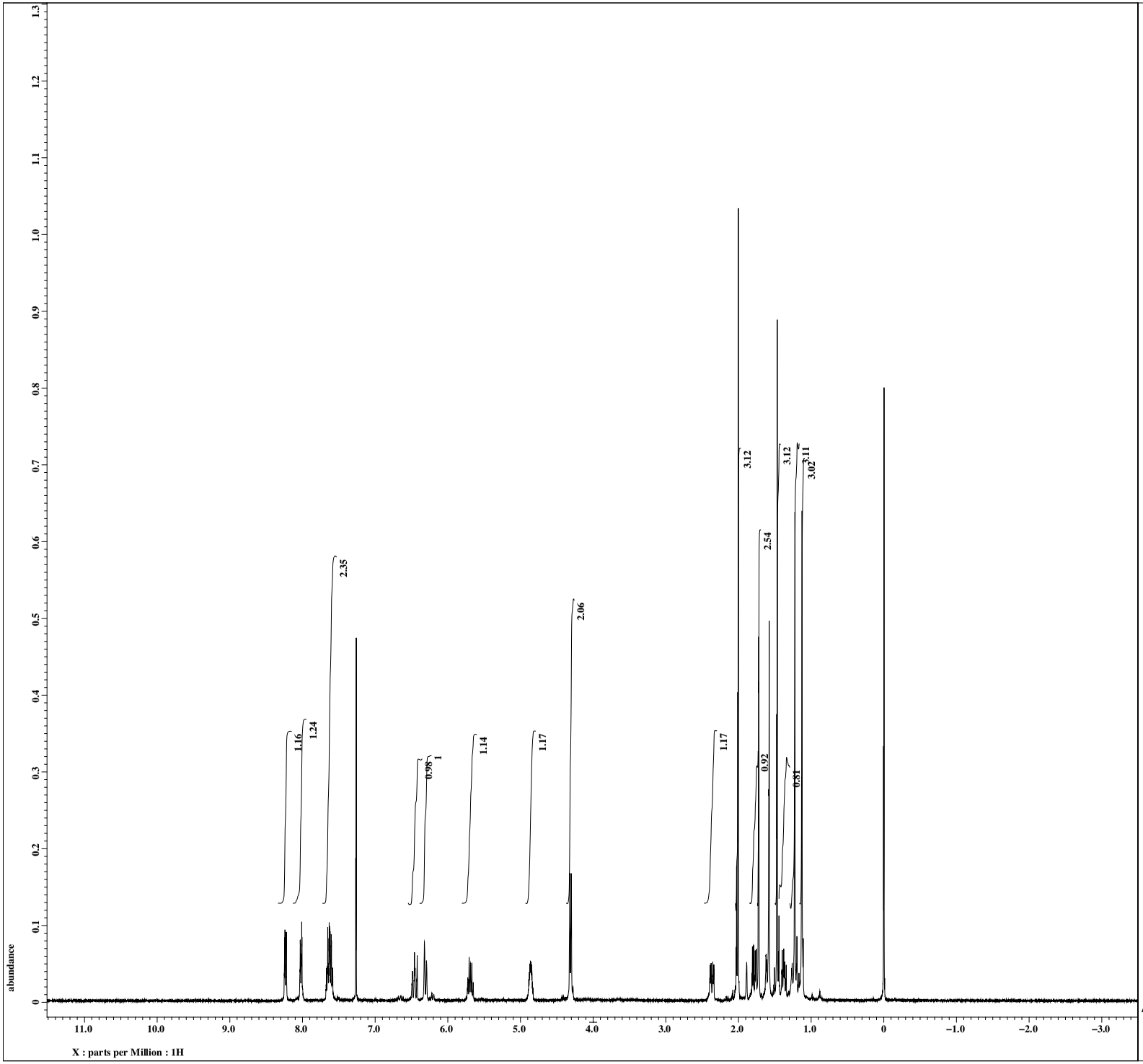

Filename = b1-sulfide-1H-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 7-JUL-2006 16:30:25
Revision_time = 29-OCT-2008 17:50:25
Current_time = 29-OCT-2008 17:50:37
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 4.36731904[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 4[ppm]
X_points = 32768
X_prescans = 1
X_resolution = 0.22897343[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12[us]
X_acq_time = 4.36731904[s]
X_angle = 45[deg]
X_atn = 2.8[dB]
X_pulse = 6[us]
Irr_mode = Off
Tri_mode = Off
Date_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 5[s]
Repetition_time = 9.36731904[s]
Temp_get = 24.5[dC]
S−BT
O
AcO
19
3.13
2.81
2.57
2.52
2.56
0.7
0.69
0.96
1.97
1.06
1
0.94
1.0
0.98
1.07
1.0
1.01
abundance
X : parts per Million : 1H



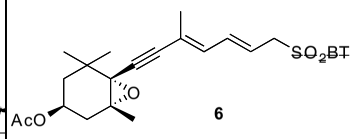

```
Filename          = b1-sulfide-13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#609547
Solvent           = CHLOROFORM-D
Creation_time     =  7-JUL-2006 17:10:23
Revision_time     = 29-OCT-2008 17:06:45
Current_time      = 29-OCT-2008 17:07:05

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 571
Total_scans       = 571

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.8[dC]
```



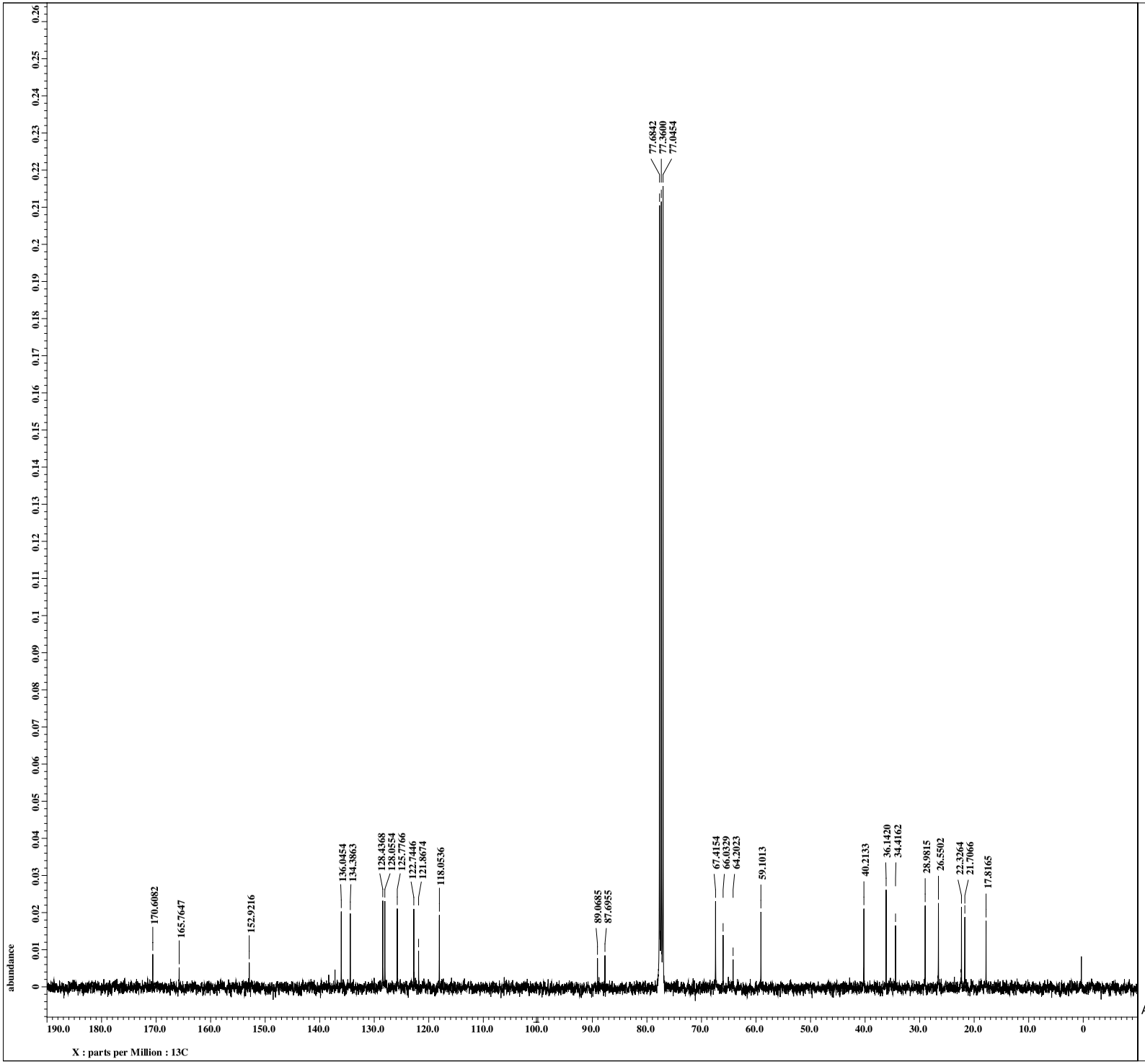
19



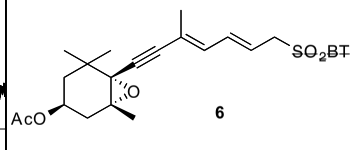

```
Filename          = b1-sulfone-1H-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  8-JUL-2006 12:07:32
Revision_time     = 29-OCT-2008 17:53:57
Current_time      = 29-OCT-2008 17:54:13

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.8[dB]
X_pulse           = 6[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 24.3[dC]
```



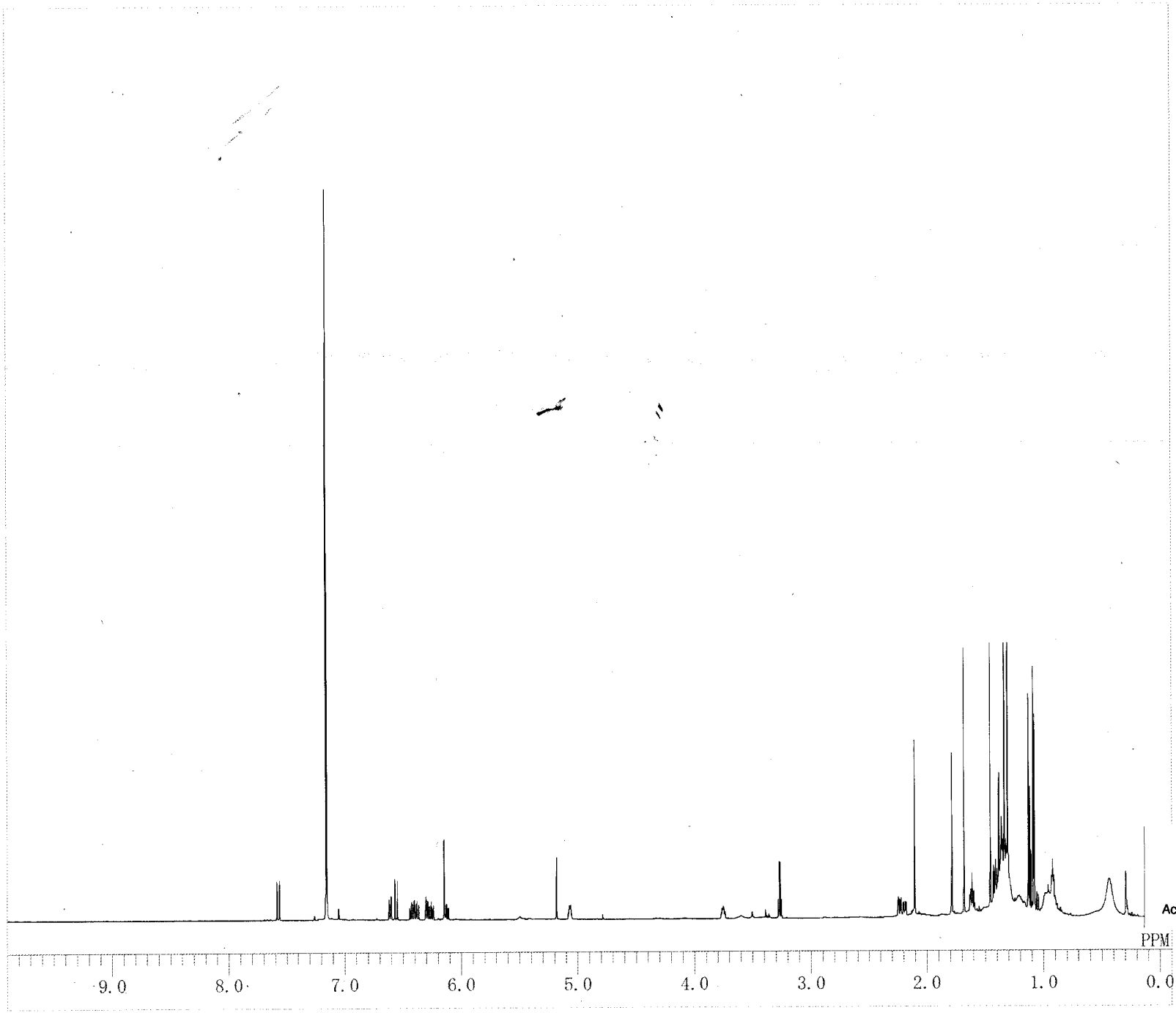
6



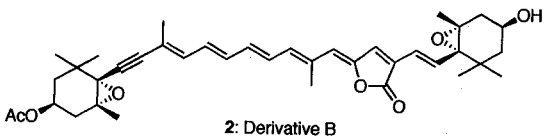

```
Filename          = b1-sulfone-13C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#450415
Solvent           = CHLOROFORM-D
Creation_time     =  8-JUL-2006 12:55:53
Revision_time     = 29-OCT-2008 17:07:52
Current_time      = 29-OCT-2008 17:08:14

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 781
Total_scans       = 781

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 52
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.6[dC]
```



6

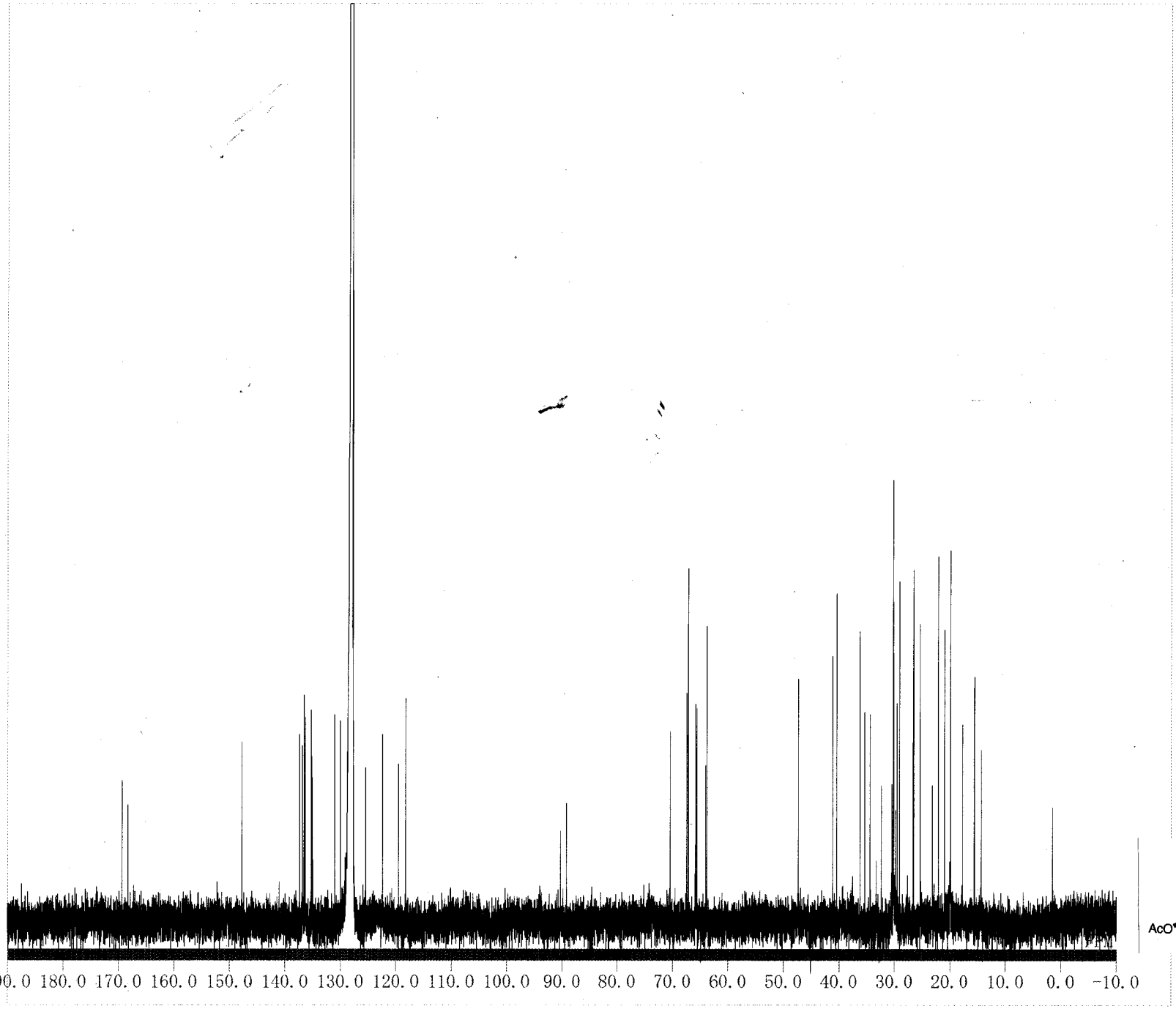


DFILE	1r
COMNT	katsum750_12.1.1
DATIM	Thu Sep 18 11:07:06 2008
OBNUC	1H
EXMOD	zg30
OBFRQ	750.13 MHz
OBSET	3.60 KHz
OBFIN	0.62 Hz
POINT	32768
FREQU	11261.26 Hz
SCANS	16
ACQTM	2.9098 sec
PD	1.0000 sec
PW1	10.55 usec
IRNUC	
CTEMP	26.9 c
SLVNT	C6D6
EXREF	7.16 ppm
BF	0.30 Hz
RGAIN	128

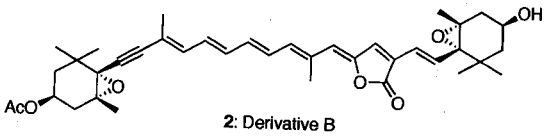


2: Derivative B

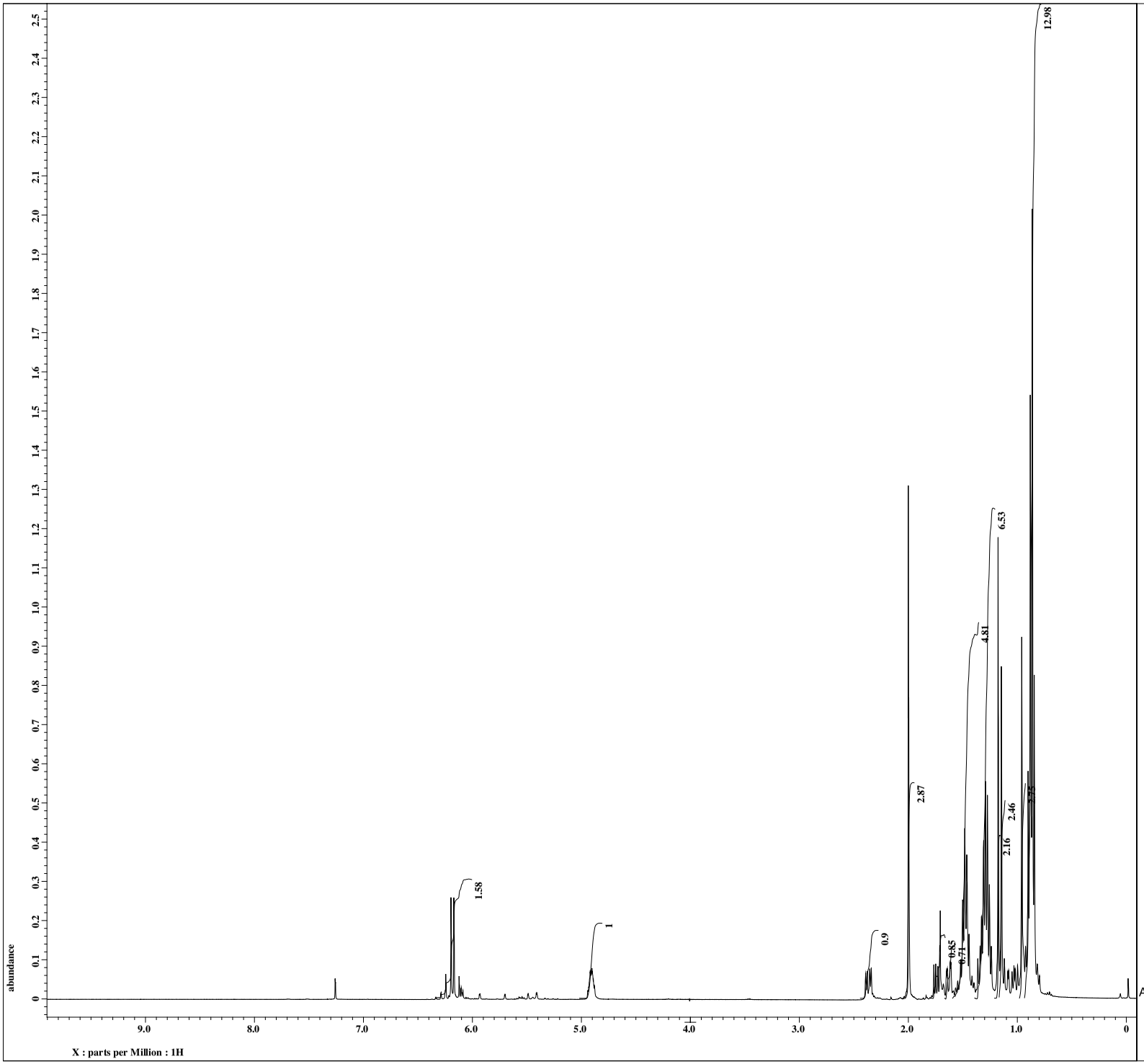
katsum750_12.1000.1



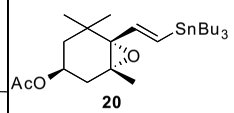
DFILE	1r
COMNT	katsum750_12.1000.1
DATIM	Thu Sep 18 13:19:12 2008
OBNUC	13C
EXMOD	zgpg30
OBFRQ	188.63 MHz
OBSET	9.20 KHz
OBFIN	0.56 Hz
POINT	32768
FREQU	45045.05 Hz
SCANS	16384
ACQTM	0.7275 sec
PD	2.0000 sec
PW1	15.00 usec
IRNUC	
CTEMP	26.9 c
SLVNT	CDCl3
EXREF	219.62 ppm
BF	1.00 Hz
RGAIN	4096



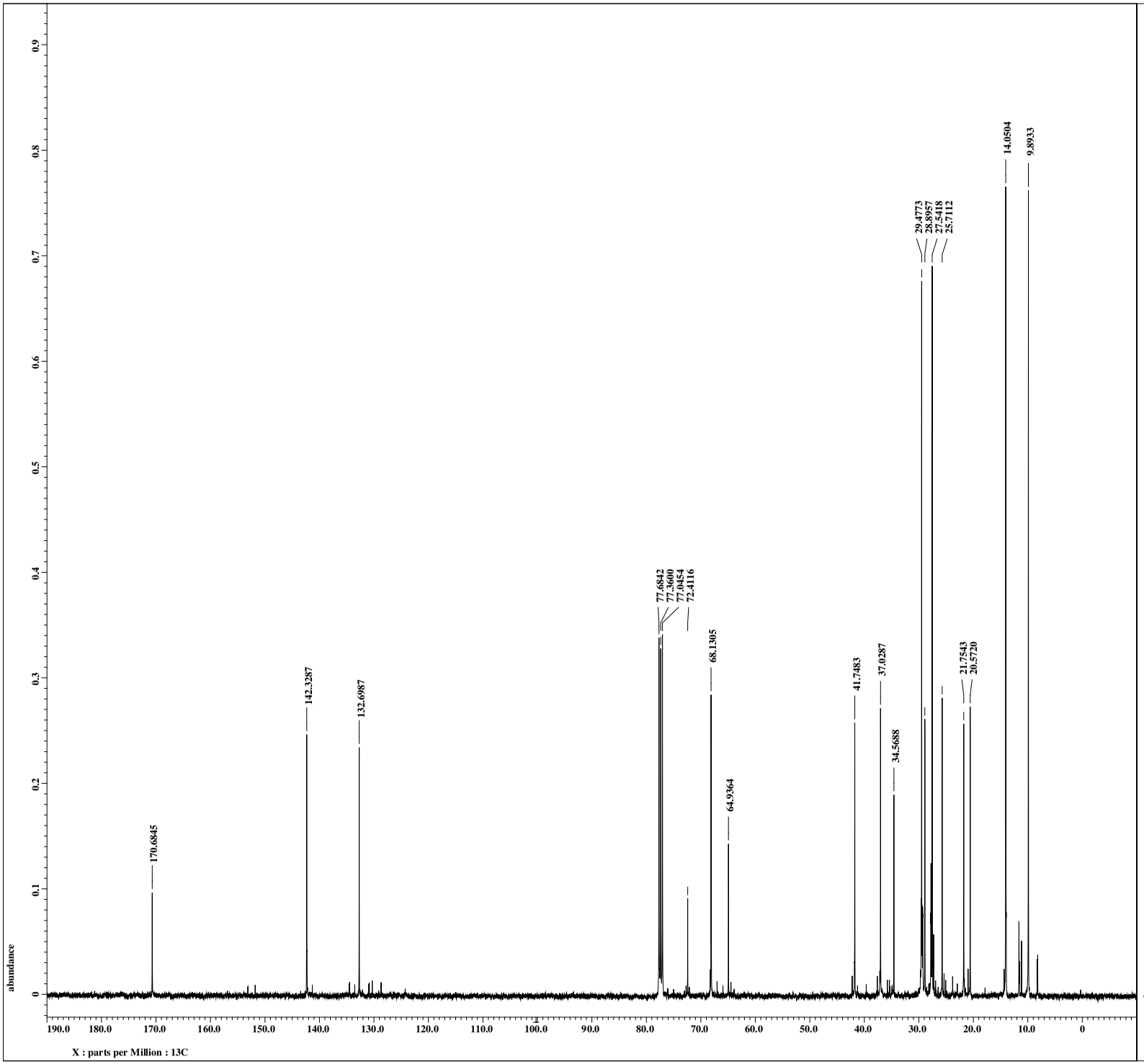
2: Derivative B



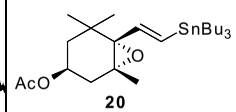

```
Filename          = c1-acetyl-stannane-1H
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 31-JUL-2006 09:35:13
Revision_time     = 30-OCT-2008 10:12:18
Current_time      = 30-OCT-2008 10:12:44

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.8[dB]
X_pulse           = 6[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 24
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 22.4[dC]
```



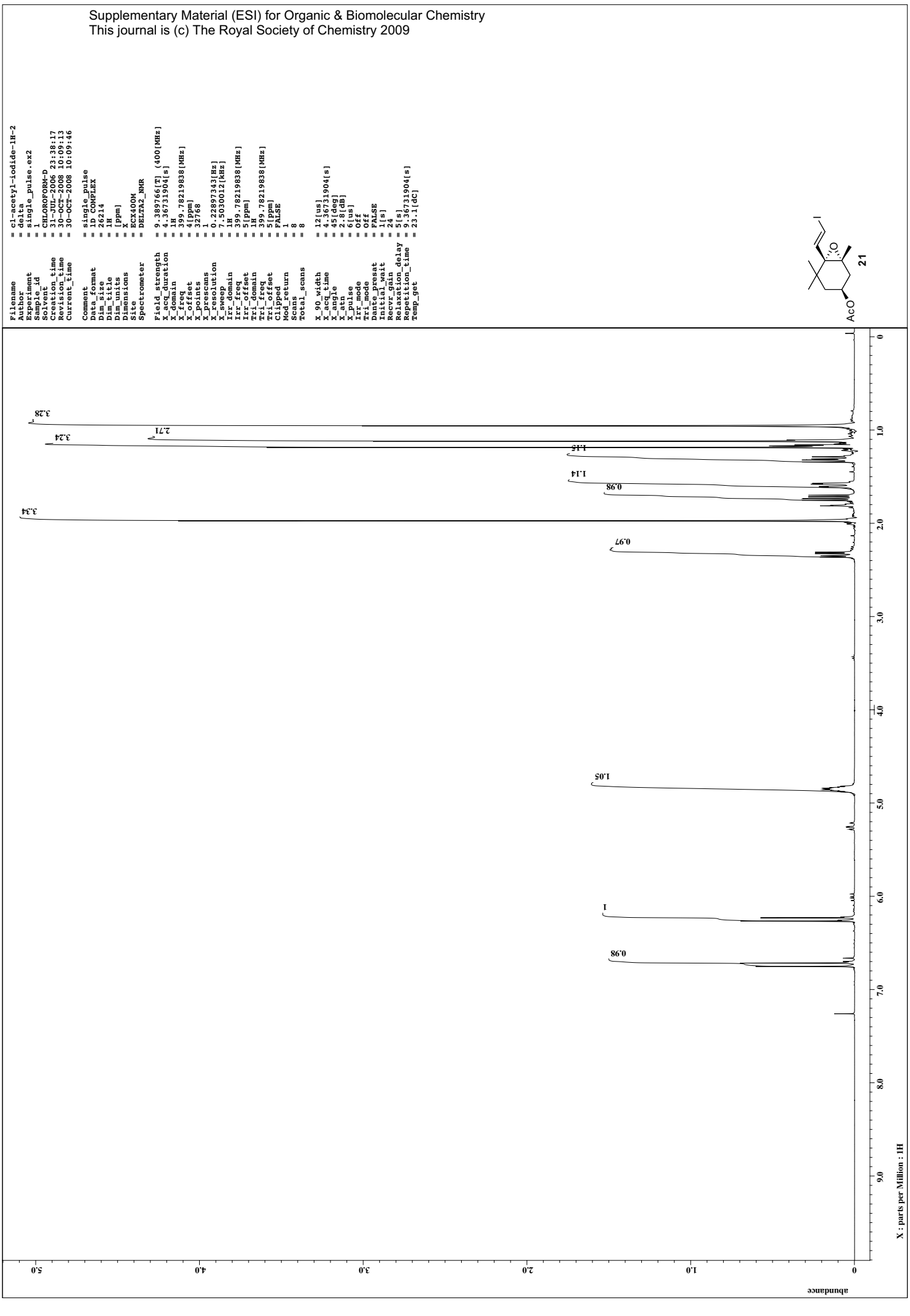
20

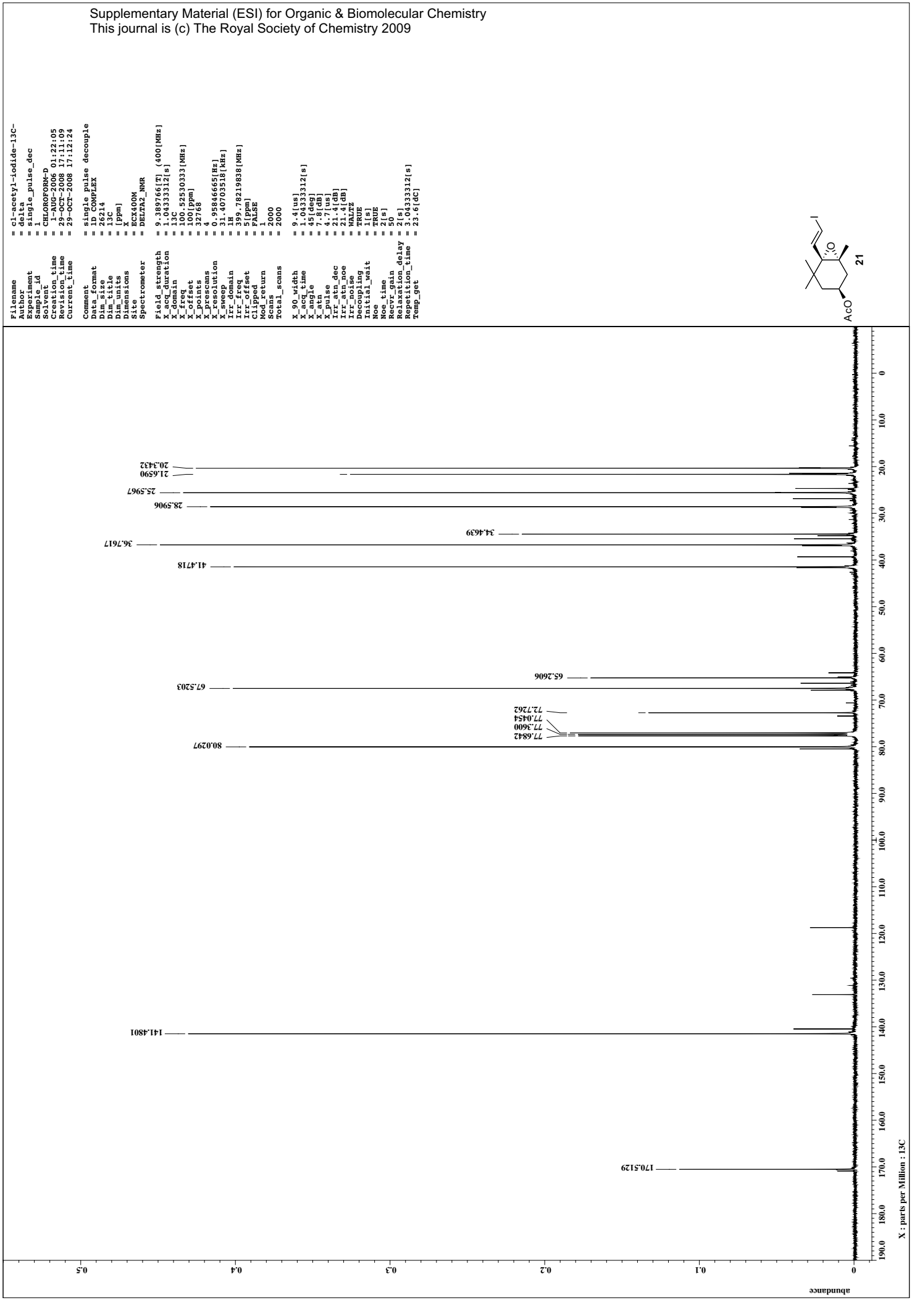


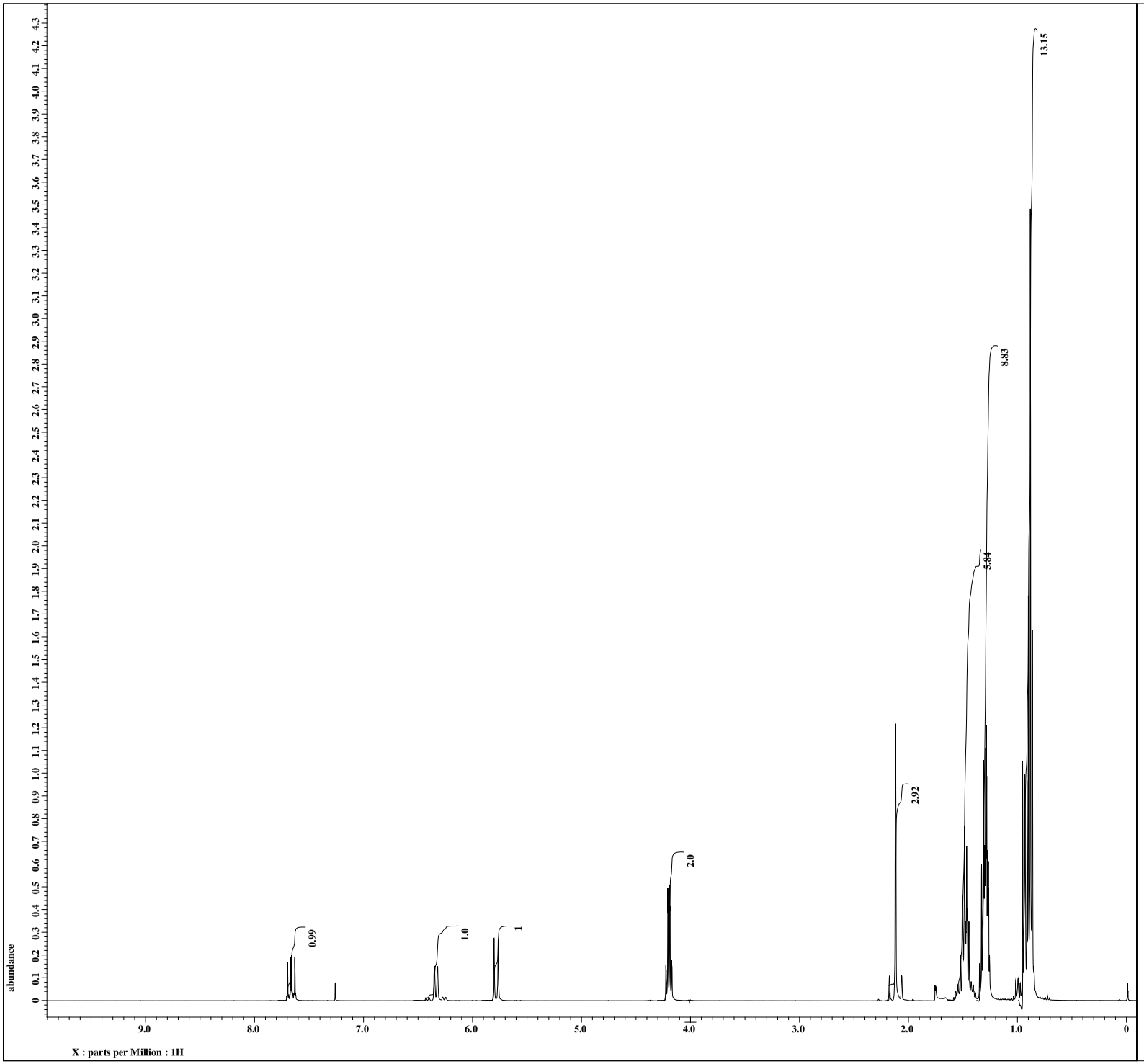

```
Filename          = c1-acetyl-stannane-13
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 31-JUL-2006 10:35:24
Revision_time     = 29-OCT-2008 17:02:06
Current_time      = 29-OCT-2008 17:03:59

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1143
Total_scans       = 1143

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 22.9[dC]
```



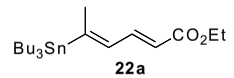
20


Filename = c1-acetyl-iodide-1H-2
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 31-JUL-2006 23:38:17
Revision_time = 30-OCT-2008 10:09:13
Current_time = 30-OCT-2008 10:09:46
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 4.36731904[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 4[ppm]
X_points = 32768
X_prescans = 1
X_resolution = 0.22897343[Hz]
X_sweep = 7.50300012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12[us]
X_acq_time = 4.36731904[s]
X_angle = 45[deg]
X_atn = 2.8[dB]
X_pulse = 6[us]
Irr_mode = Off
Tri_mode = Off
Date_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 24
Relaxation_delay = 5[s]
Repetition_time = 9.36731904[s]
Temp_get = 23.1[dC]
AcO
21
3.28
3.24
2.71
1.15
1.14
0.98
3.34
0.97
1.05
1
0.98
abundance
X : parts per Million : 1H

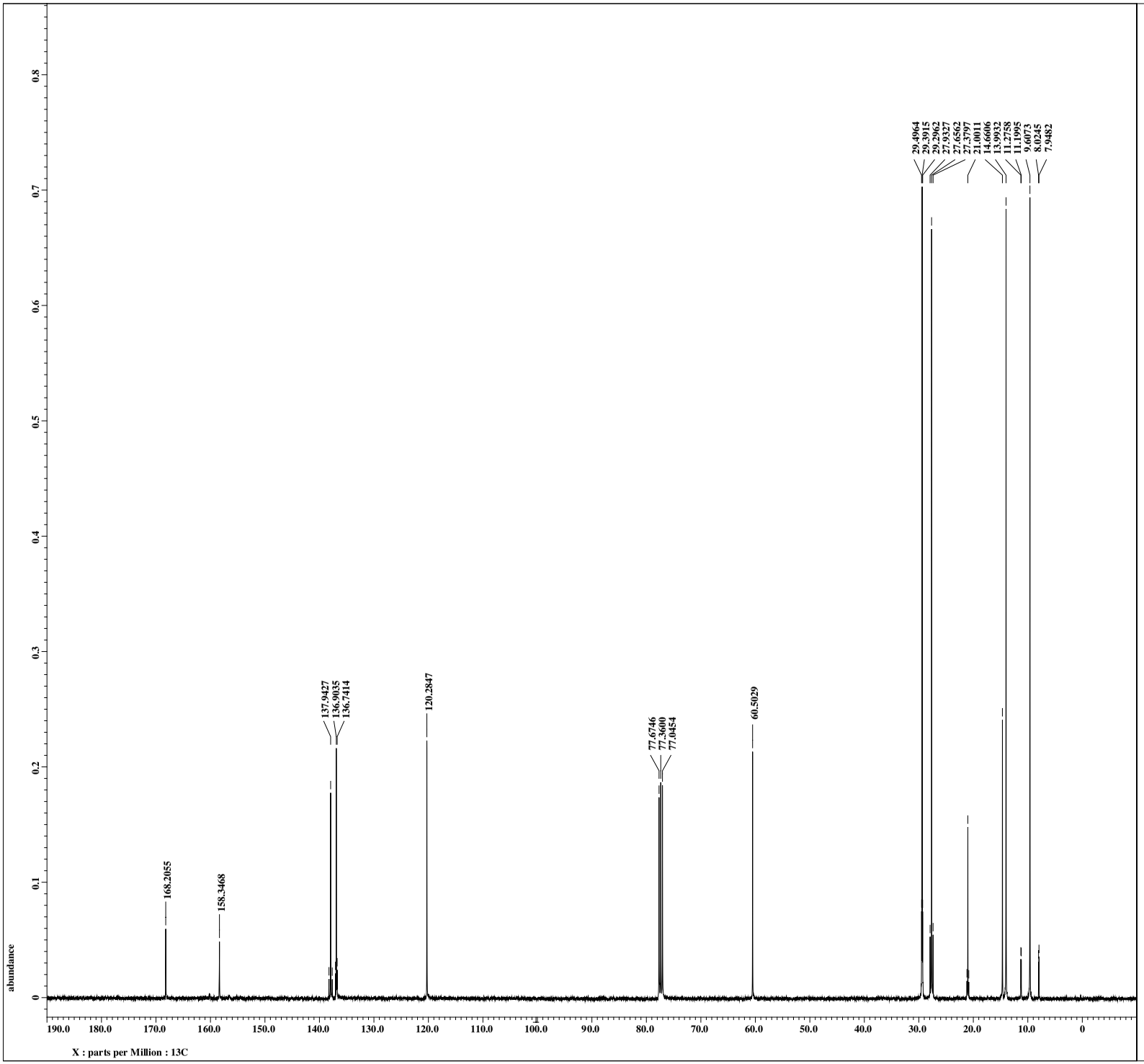

Filename = cl-acetyl-iodide-13C-
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 1-AUG-2006 01:22:05
Revision_time = 29-OCT-2008 17:11:09
Current_time = 29-OCT-2008 17:12:24
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2000
Total_scans = 2000
X_90_width = 9.4[us]
X_acq_time = 1.043333312[s]
X_angle = 45[deg]
X_atn = 7.8[dB]
X_pulse = 4.7[us]
Irr_atn_dec = 21.4[dB]
Irr_atn_noe = 21.4[dB]
Irr_mode = NNLEVEL
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 23.6[dC]
AcO
21
20.3432
21.6590
25.5967
28.5906
34.4639
36.7617
41.4718
65.2606
67.5203
72.7262
77.0454
77.3600
77.6842
80.0297
141.4801
170.5129
abundance
X : parts per Million : 13C



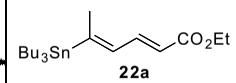

```
Filename          = c1-tin-ester-1H-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 29-JUL-2006 13:36:30
Revision_time     = 30-OCT-2008 11:12:29
Current_time      = 30-OCT-2008 11:12:55

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.8[dB]
X_pulse           = 6[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 24
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 23.6[dC]
```



22a

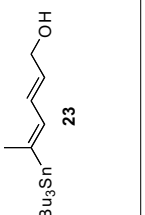



```
Filename          = c1-tin-ester-13C-2.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 29-JUL-2006 14:39:22
Revision_time     = 29-OCT-2008 17:13:59
Current_time      = 29-OCT-2008 17:14:48

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1200
Total_scans       = 1200

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.1[dC]
```

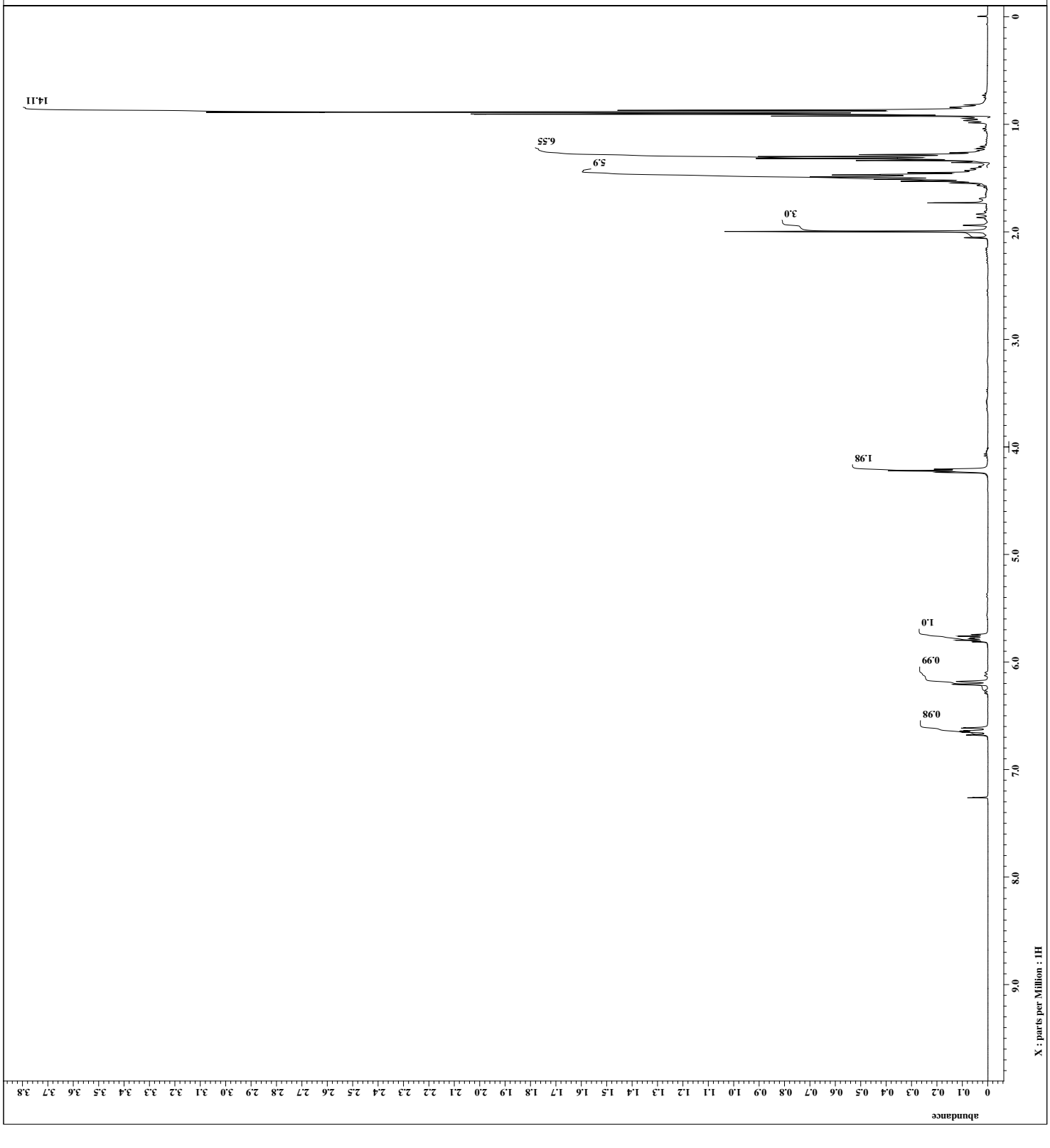


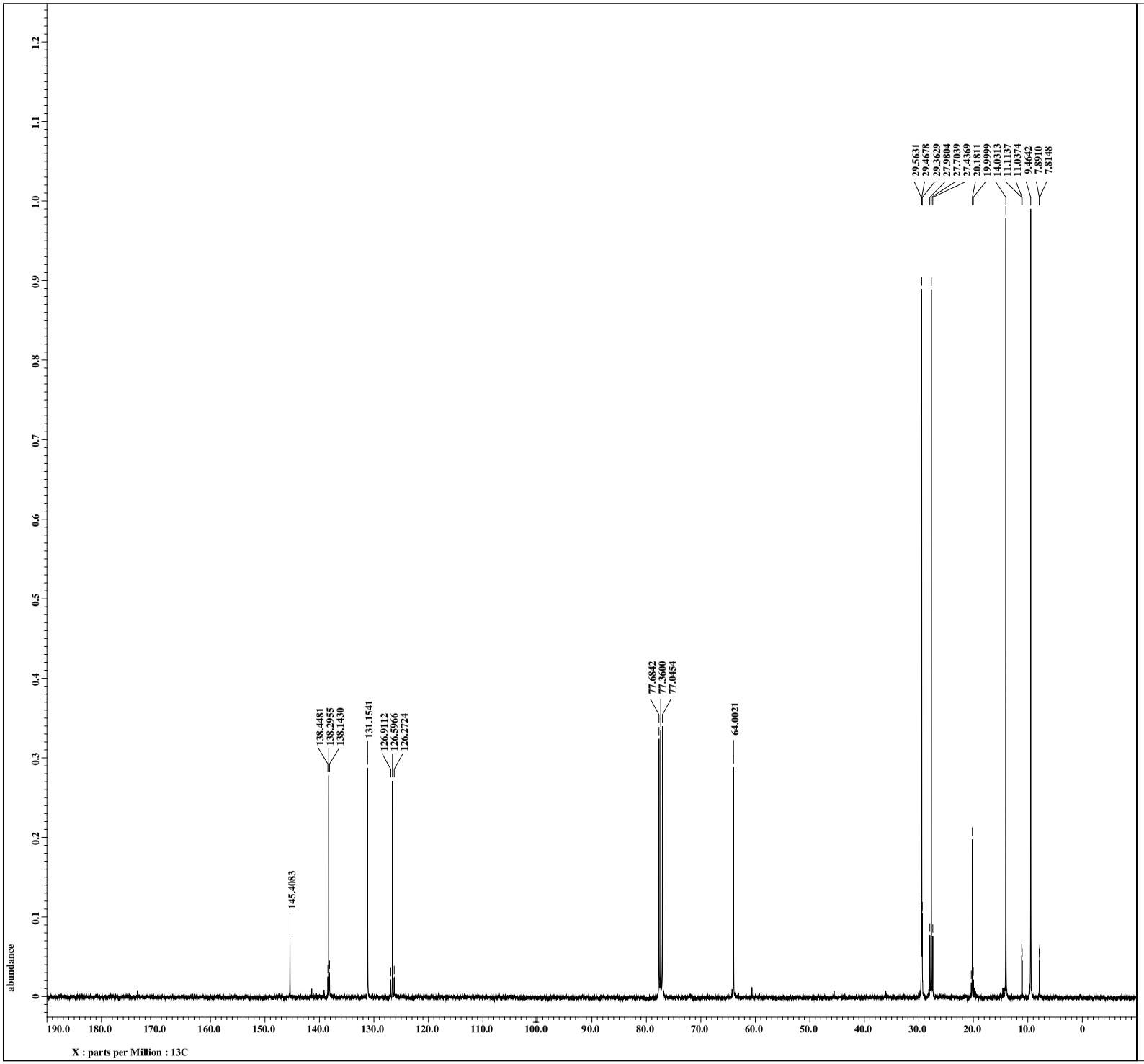
22a

```
Filename              = c1-tin-alcohol-1H-2.j
Author                = delta
Experiment            = single_pulse.ex2
Sample_id             = 1
Solvent               = CHLOROFORM-D
Creation_time         = 31-JUL-2006 16:06:37
Revision_time         = 30-OCT-2008 11:10:11
Current_time          = 30-OCT-2008 11:10:41

Comment               = single_pulse
Data_format           = 1D COMPLEX
Dim_size              = 26214
Dim_title             = 1H
Dim_units             = [ppm]
Dimensions            = X
Site                  = ECX400M
Spectrometer          = DELTA2_NMR

Field_strength        = 9.389766[T] (400[MHz]
X_acq_duration        = 4.36731904[s]
X_domain              = 1H
X_freq                = 399.78219838[MHz]
X_offset              = 4[ppm]
X_points              = 32768
X_prescans            = 1
X_resolution          = 0.22897343[Hz]
X_sweep               = 7.5030012[kHz]
Irr_domain            = 1H
Irr_freq              = 399.78219838[MHz]
Irr_offset            = 5[ppm]
Tri_domain            = 1H
Tri_freq              = 399.78219838[MHz]
Tri_offset            = 5[ppm]
Clipped               = FALSE
Mod_return            = 1
Scans                 = 8
Total_scans           = 8

X_90_width            = 12[us]
X_acq_time            = 4.36731904[s]
X_angle               = 45[deg]
X_atn                 = 2.8[dB]
X_pulse               = 6[us]
Tri_mode              = Off
Dante_presat          = FALSE
Initial_wait          = 1[s]
Recvr_gain            = 26
Relaxation_delay      = 5[s]
Repetition_time       = 9.36731904[s]
Temp_get              = 23.1[dC]
```

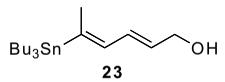


23





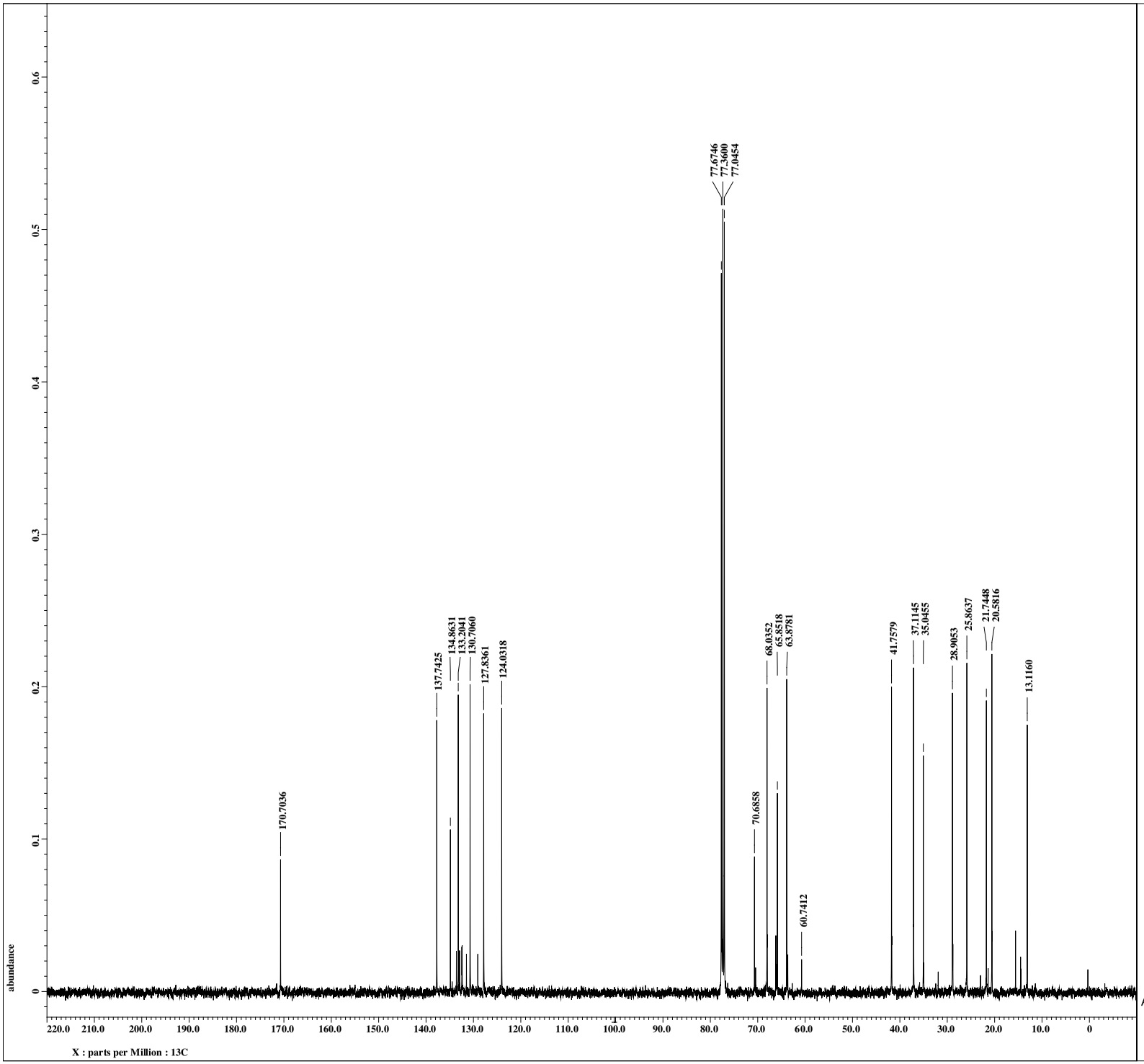

```
Filename          = c1-tin-alcohol-13C-2.
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 31-JUL-2006 17:09:50
Revision_time     = 29-OCT-2008 17:25:55
Current_time      = 29-OCT-2008 17:26:34

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1200
Total_scans       = 1200

X_90_width        = 9.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.7[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 23.4[dC]
```



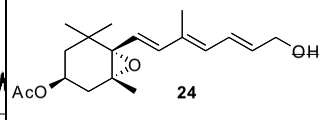
23

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2009

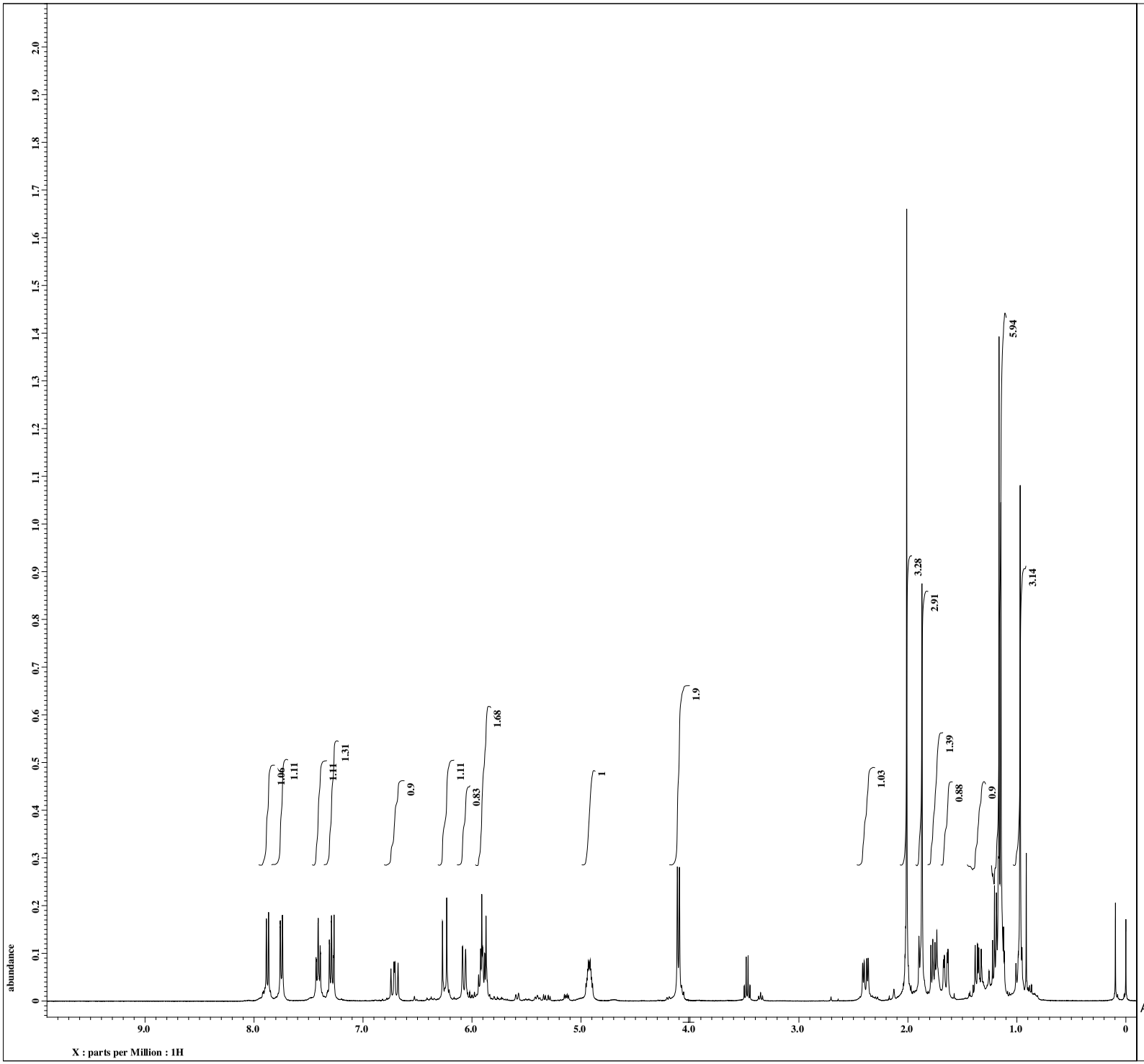
```
Filename              = c1-triene-alcohol-1H-
Author                = delta
Experiment            = single_pulse.ex2
Sample_id             = 1
Solvent               = CHLOROFORM-D
Creation_time         = 20-SEP-2006 21:22:54
Revision_time         = 30-OCT-2008 13:35:33
Current_time          = 30-OCT-2008 13:35:47

Comment               = single_pulse
Data_format           = 1D COMPLEX
Dim_size              = 26214
Dim_title             = 1H
Dim_units             = [ppm]
Dimensions            = X
Site                  = ECX400M
Spectrometer          = DELTA2_NMR

Field_strength        = 9.389766[T] (400[MHz]
X_acq_duration        = 4.367319904[s]
X_domain              = 1H
X_freq                = 399.78219838[MHz]
X_offset              = 4[ppm]
X_points              = 32768
X_prescans            = 1
X_resolution          = 0.22897343[Hz]
X_sweep               = 7.5030012[kHz]
Irr_domain            = 1H
Irr_freq              = 399.78219838[MHz]
Irr_offset            = 5[ppm]
Tri_domain            = 1H
Tri_freq              = 399.78219838[MHz]
Tri_offset            = 5[ppm]
Clipped               = FALSE
Mod_return            = 1
Scans                 = 8
Total_scans           = 8

X_90_width            = 11.2[us]
X_acq_time            = 4.367319904[s]
X_angle               = 45[deg]
X_atn                 = 2.8[dB]
X_pulse               = 5.6[us]
Irr_mode              = Off
Date_presat           = FALSE
Initial_wait          = 1[s]
Recvr_gain            = 30
Relaxation_delay      = 5[s]
Repetition_time       = 9.367319904[s]
Temp_get              = 25.3[dC]
```



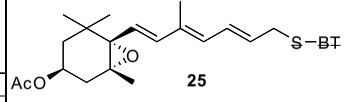

```
Filename          = c1-triene-alcohol-13C
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 20-SEP-2006 22:17:11
Revision_time     = 29-OCT-2008 17:27:47
Current_time      = 29-OCT-2008 17:28:13

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1014
Total_scans       = 1014

X_90_width        = 9.6[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.8[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 25.4[dC]
```



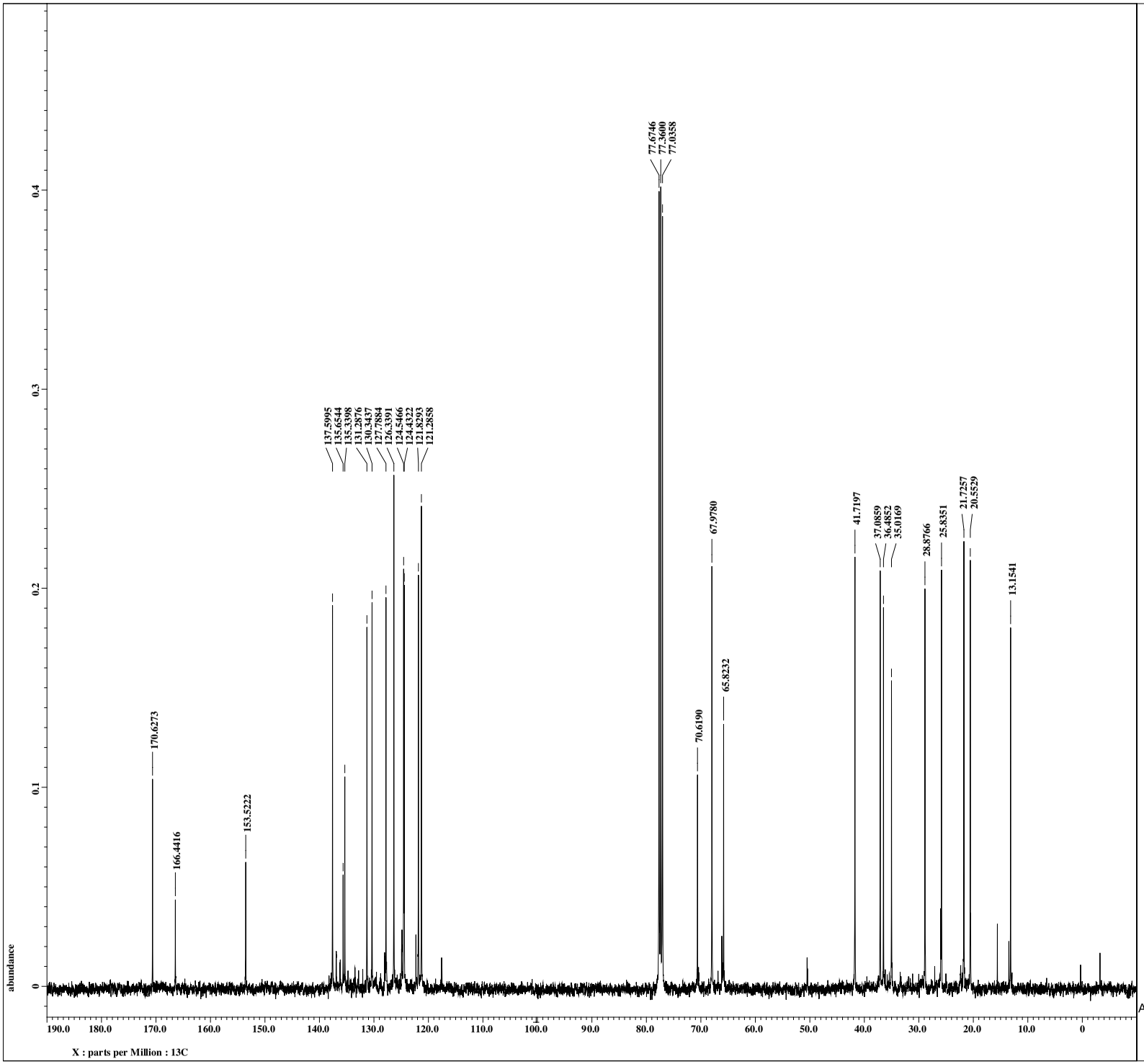
24



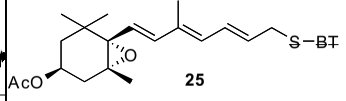

```
Filename          = c1-sulfide-1H-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 21-SEP-2006 17:47:23
Revision_time     = 30-OCT-2008 10:15:46
Current_time      = 30-OCT-2008 10:16:31

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 11.2[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.8[dB]
X_pulse           = 5.6[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 25.1[dC]
```



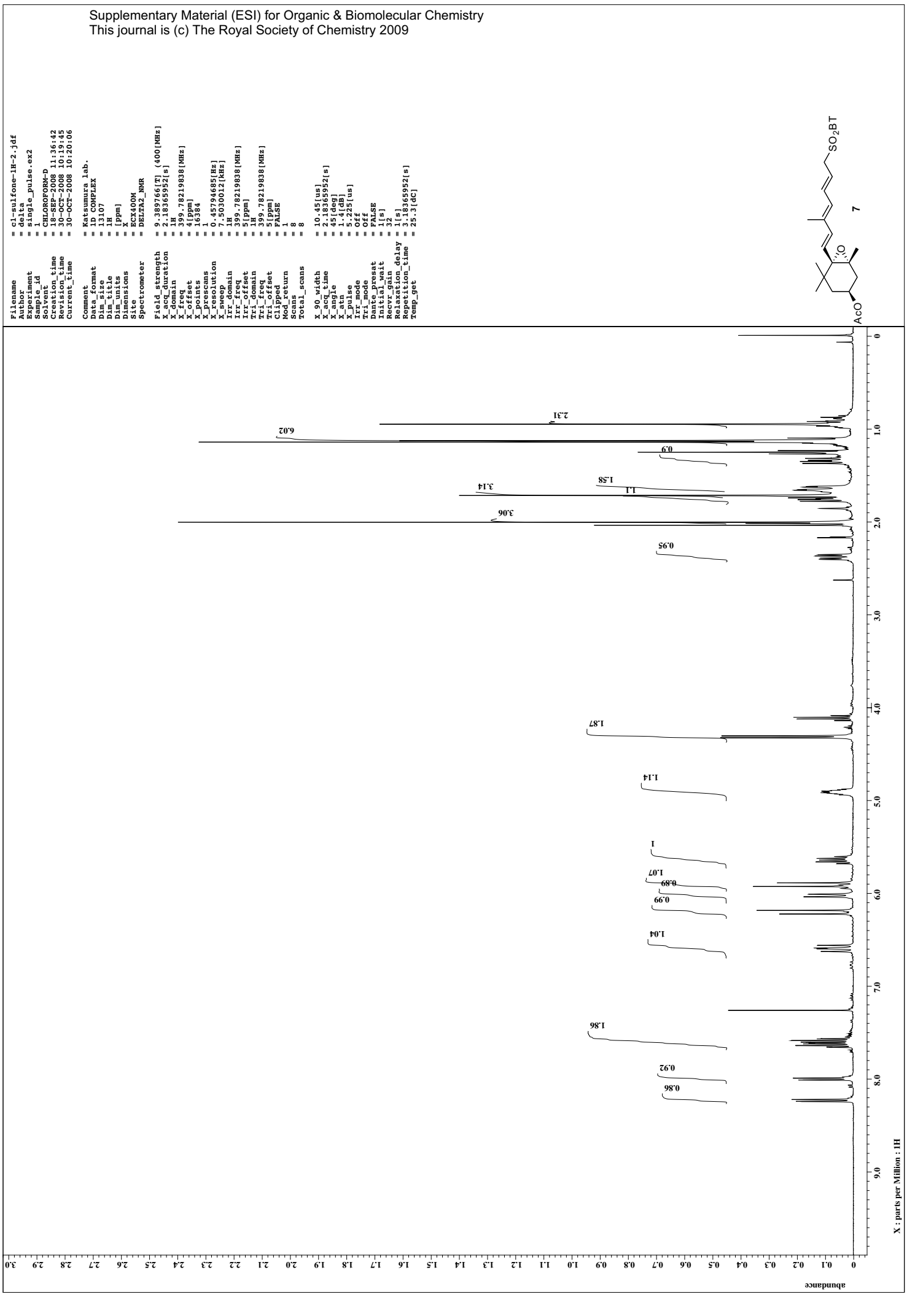
25

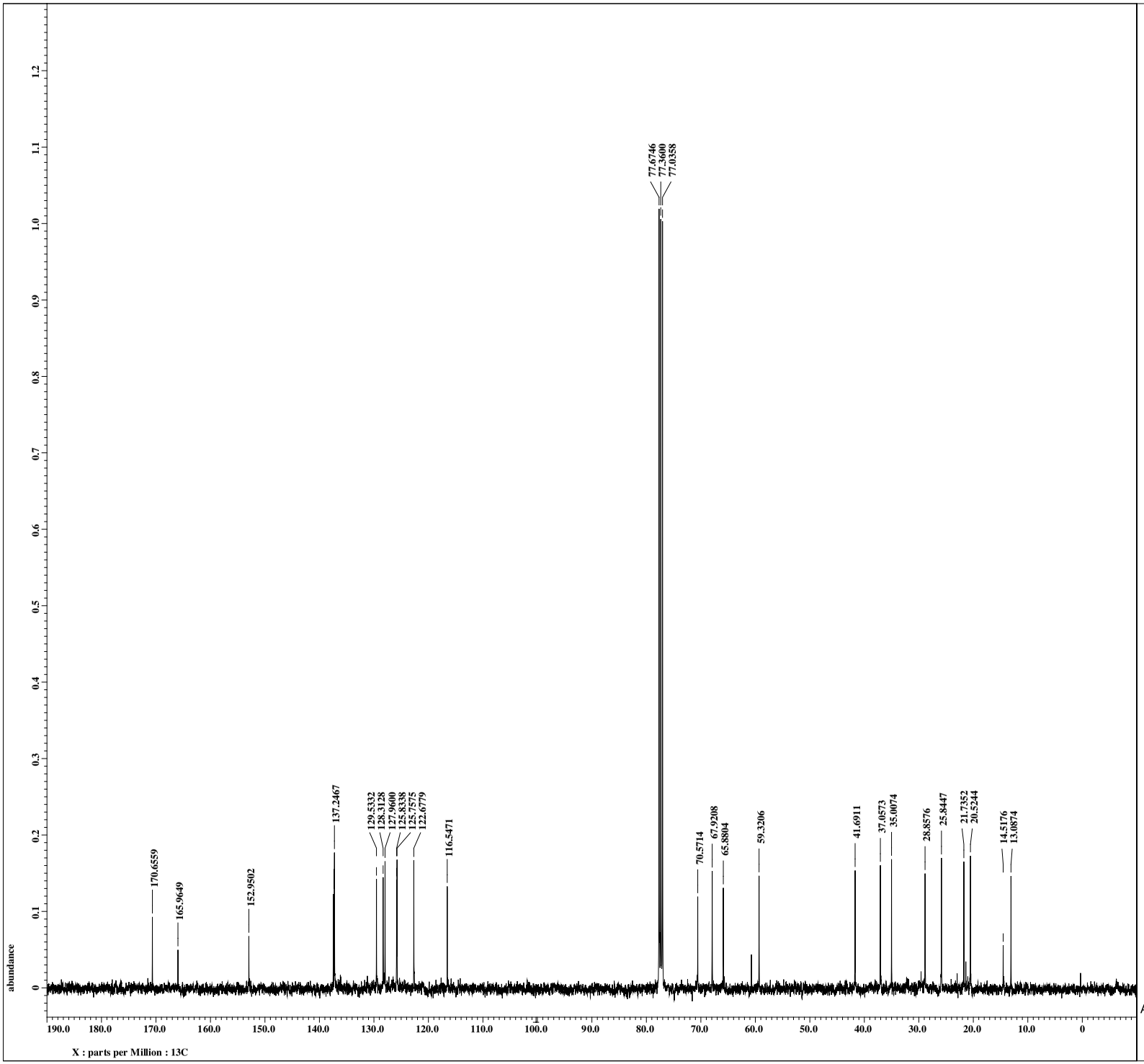



```
Filename          = c1-sulfide-13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 21-SEP-2006 18:40:29
Revision_time     = 29-OCT-2008 17:15:56
Current_time      = 29-OCT-2008 17:16:25

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1000
Total_scans       = 1000

X_90_width        = 9.6[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 7.8[dB]
X_pulse           = 4.8[us]
Irr_atn_dec       = 21.4[dB]
Irr_atn_noe       = 21.4[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 25.6[dC]
```

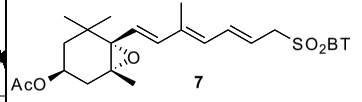


25

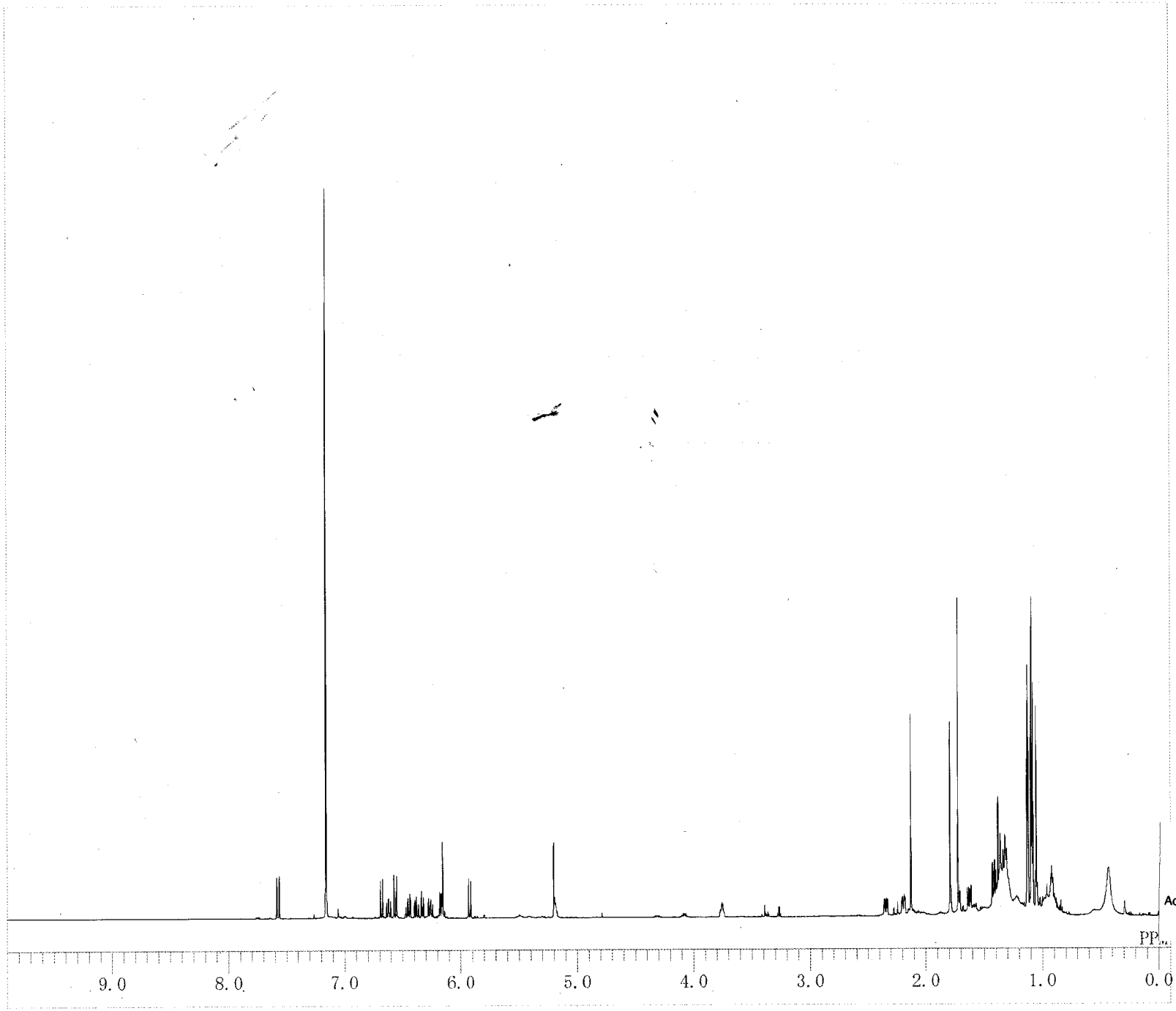

Filename = c1-sulfone-1H-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 18-SEP-2008 11:36:42
Revision_time = 30-OCT-2008 10:19:45
Current_time = 30-OCT-2008 10:20:06
Comment = Katsumura lab.
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 4[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.45[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1.4[dB]
X_pulse = 5.225[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 32
Relaxation_delay = 1[s]
Repetition_time = 3.18365952[s]
Temp_get = 25.3[dC]
AcO
O
SO2BT
7
6.02
2.31
3.14
3.06
1.58
1.1
0.9
0.95
1.87
1.14
1
1.07
0.89
0.99
1.04
1.86
0.92
0.86
abundance
X : parts per Million : 1H



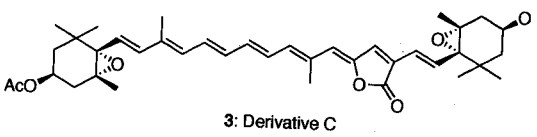

```
Filename          = c1-sulfone-13C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#447052
Solvent           = CHLOROFORM-D
Creation_time     = 18-SEP-2008 12:07:39
Revision_time     = 29-OCT-2008 17:18:41
Current_time      = 29-OCT-2008 17:19:06

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 281
Total_scans       = 281

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 5[s]
Recvr_gain        = 60
Relaxation_delay  = 5[s]
Repetition_time   = 6.04333312[s]
Temp_get          = 25.8[dC]
```



7

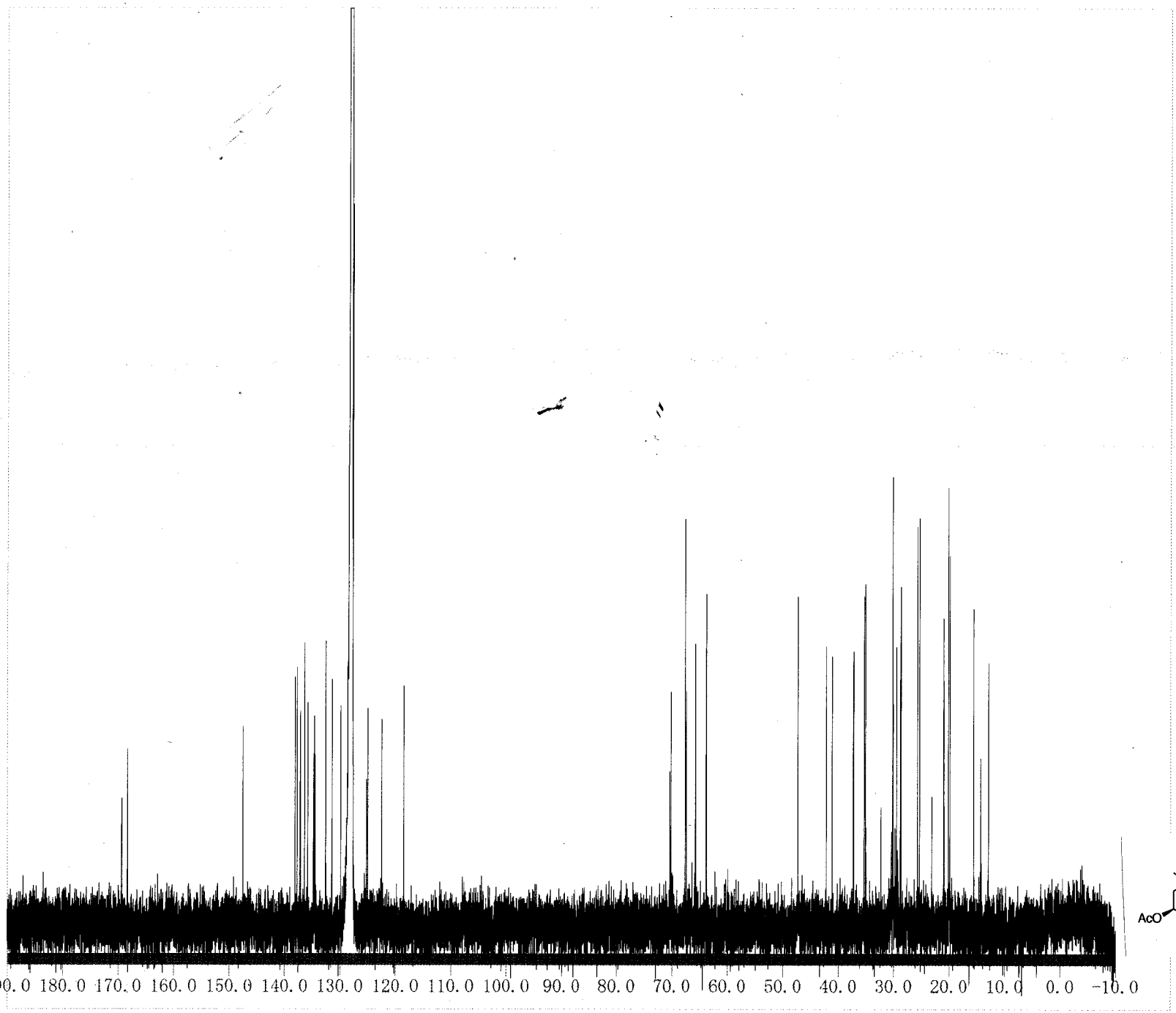


DFILE	1r
COMNT	katsum750_13.1.1
DATIM	Thu Nov 6 10:05:29 2008
OBNUC	1H
EXMOD	zg30
OBFRQ	750.13 MHz
OBSET	3.60 KHz
OBFIN	0.62 Hz
POINT	32768
FREQU	11261.26 Hz
SCANS	16
ACQTM	2.9098 sec
PD	1.0000 sec
PW1	10.15 usec
IRNUC	
CTEMP	26.9 c
SLVNT	C6D6
EXREF	7.16 ppm
BF	0.30 Hz
RGAIN	128

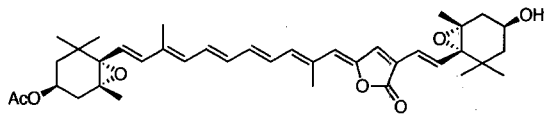


3: Derivative C

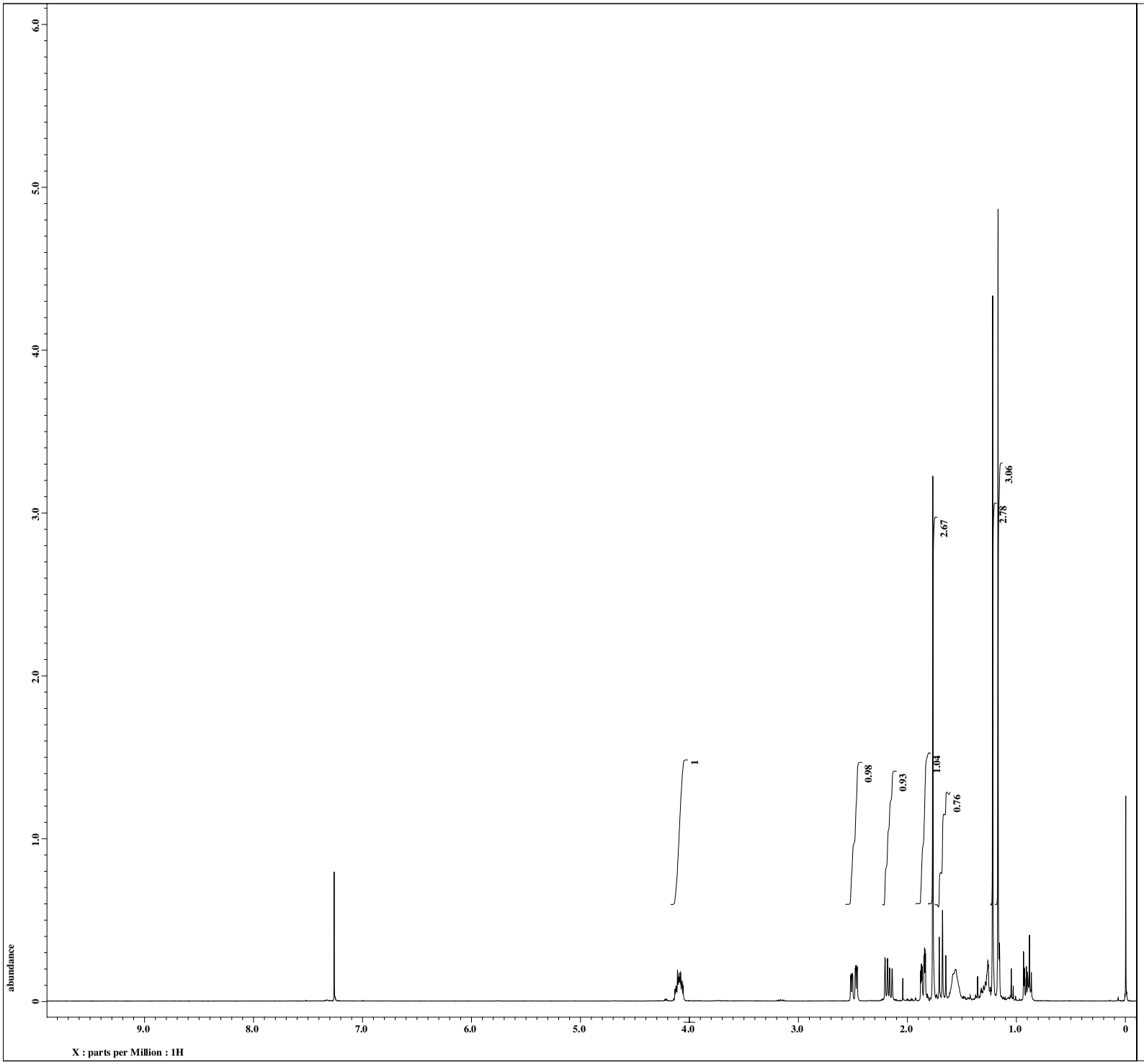
katsum750_13.1000.1



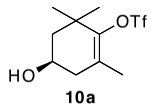
DFILE	1r
COMNT	katsum750_13.1000.1
DATIM	Thu Nov 6 10:52:00 2008
OBNUC	13C
EXMOD	zgpg30
OBFRQ	188.63 MHz
OBSET	9.20 KHz
OBFIN	0.56 Hz
POINT	32768
FREQU	45045.05 Hz
SCANS	8192
ACQTM	0.7275 sec
PD	2.0000 sec
PW1	15.00 usec
IRNUC	
CTEMP	26.9 c
SLVNT	CDCl3
EXREF	219.62 ppm
BF	1.00 Hz
RGAIN	4096



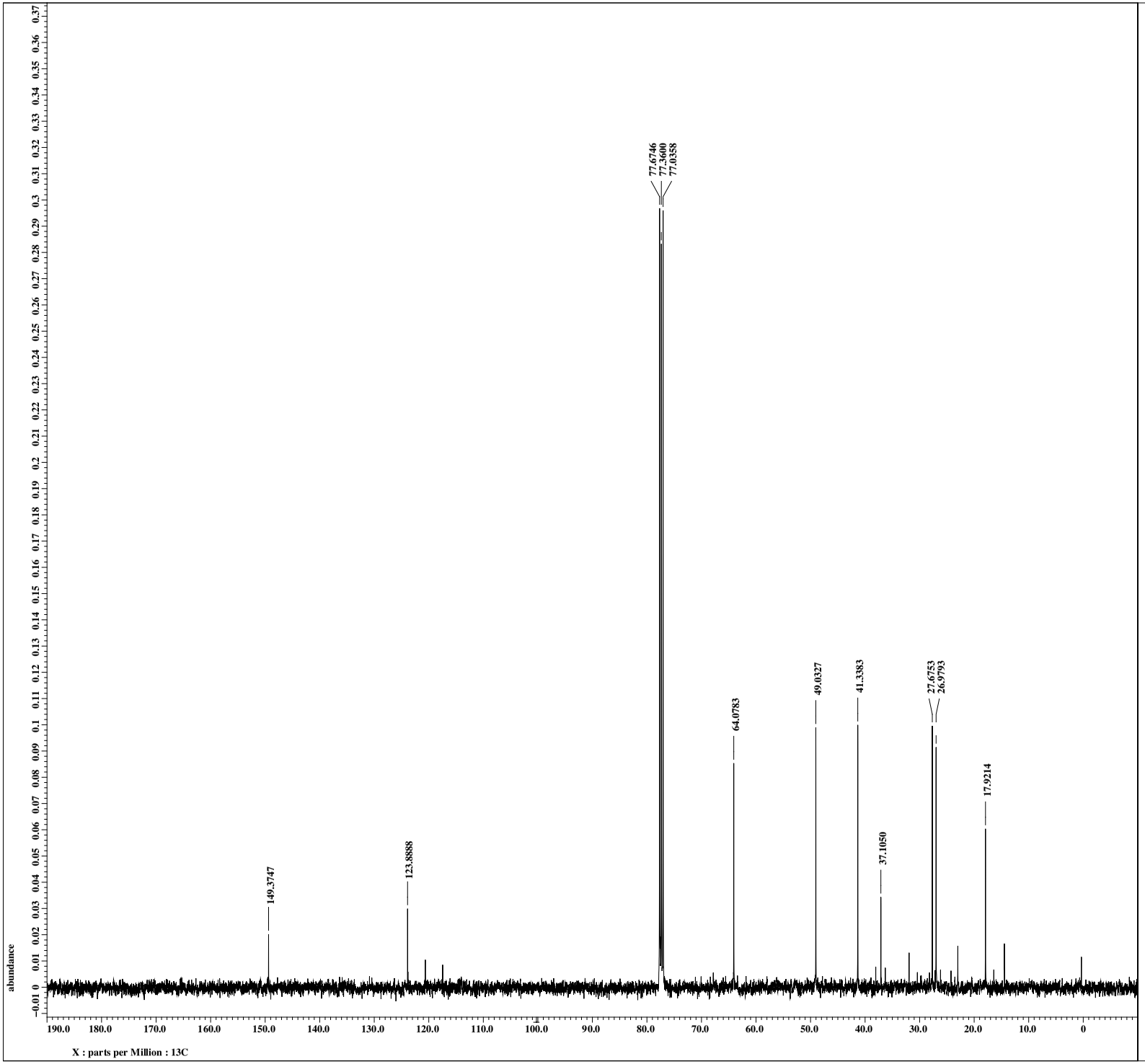
3: Derivative C



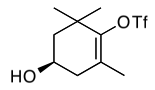

```
Filename          = d1-triflate-alcohol-1
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 11-AUG-2008 13:27:28
Revision_time     = 30-OCT-2008 17:13:44
Current_time      = 30-OCT-2008 17:14:07

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.45[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1.4[dB]
X_pulse           = 5.225[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 1[s]
Repetition_time   = 3.18365952[s]
Temp_get          = 24.5[dC]
```



10a

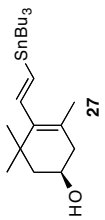



```
Filename          = dl-triflate-alcohol-1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#484875
Solvent           = CHLOROFORM-D
Creation_time     = 11-AUG-2008 13:54:00
Revision_time     = 29-OCT-2008 17:35:05
Current_time      = 29-OCT-2008 17:35:27

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 471
Total_scans       = 471

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 54
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.7[dC]
```

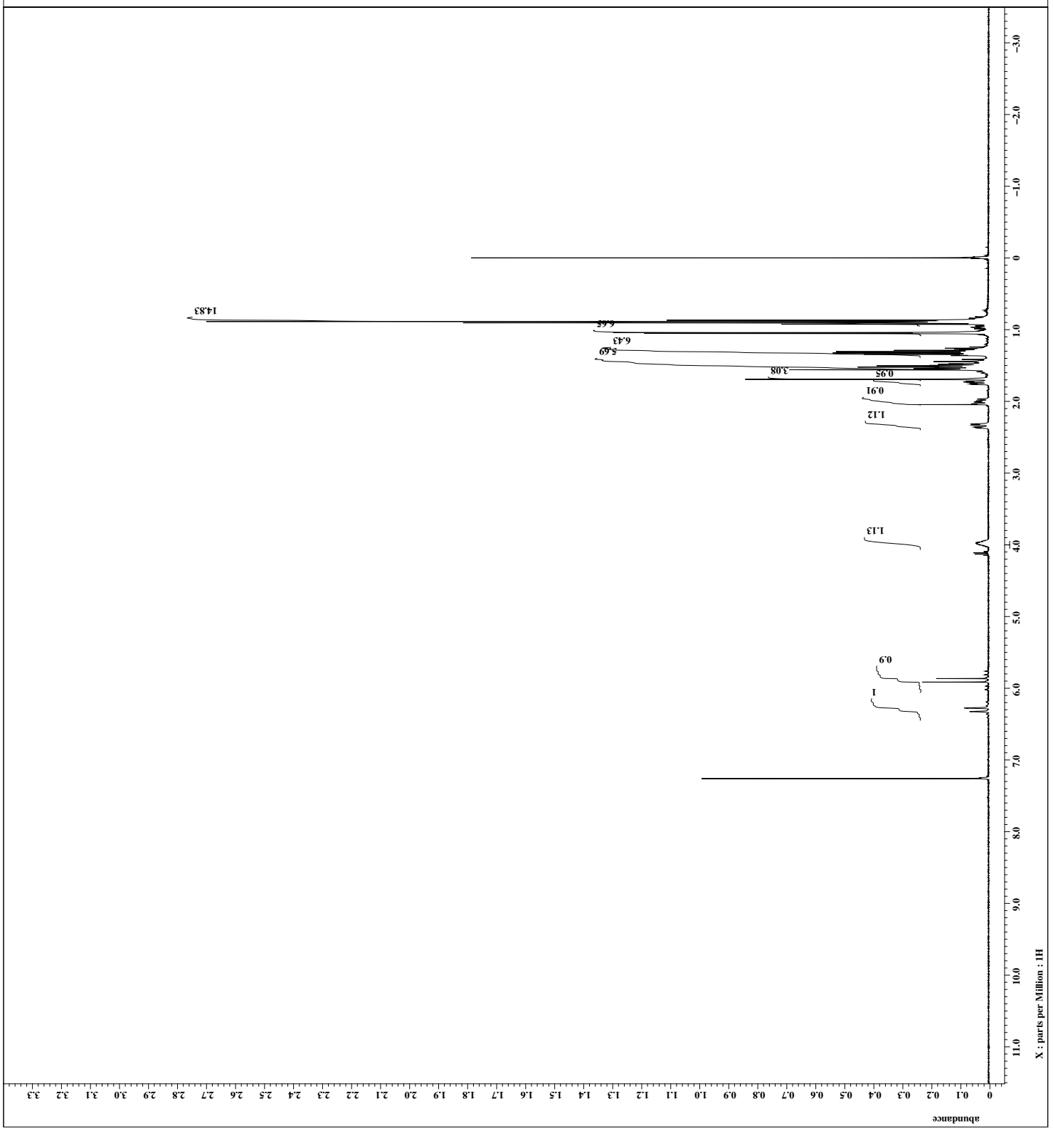



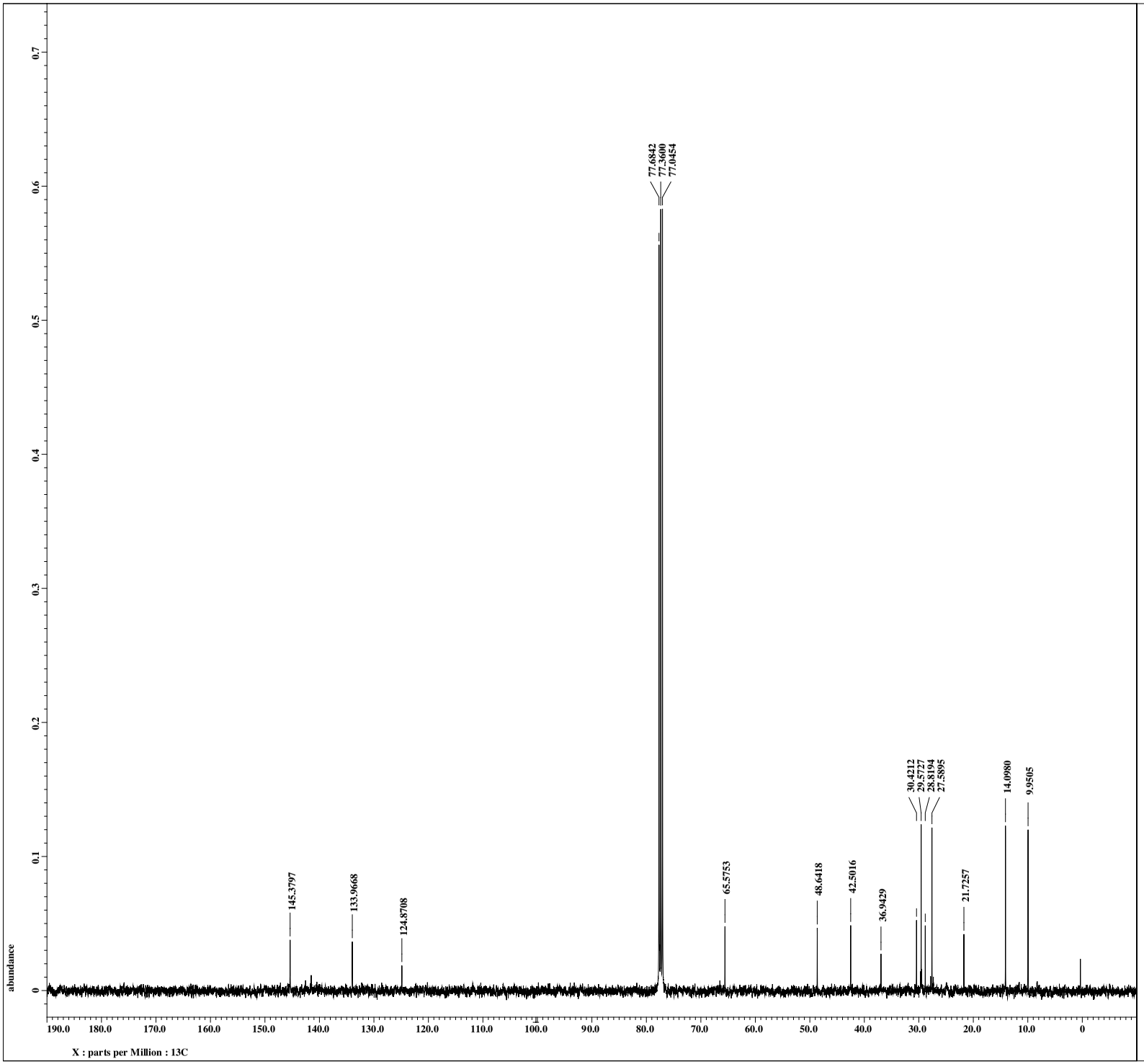
10a

```
Filename                = dl-alcohol-stannane-1
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = 1
Solvent                 = CHLOROFORM-D
Creation_time           = 11-AUG-2008 17:54:25
Revision_time           = 30-OCT-2008 17:00:02
Current_time            = 30-OCT-2008 17:00:19

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECX400M
Spectrometer            = DELTA2_NMR

Field_strength          = 9.389766[T] (400[MHz]
X_acq_duration          = 2.18365952[s]
X_domain                = 1H
X_freq                  = 399.78219838[MHz]
X_offset                = 4[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.45794685[Hz]
X_sweep                 = 7.5030012[kHz]
Irr_domain              = 1H
Irr_freq                = 399.78219838[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 399.78219838[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 10.45[us]
X_acq_time              = 2.18365952[s]
X_angle                 = 45[deg]
X_atn                   = 1.4[dB]
X_pulse                 = 5.225[us]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 38
Relaxation_delay        = 1[s]
Repetition_time         = 3.18365952[s]
Temp_get                = 24.4[dC]
```

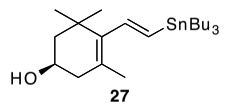


27

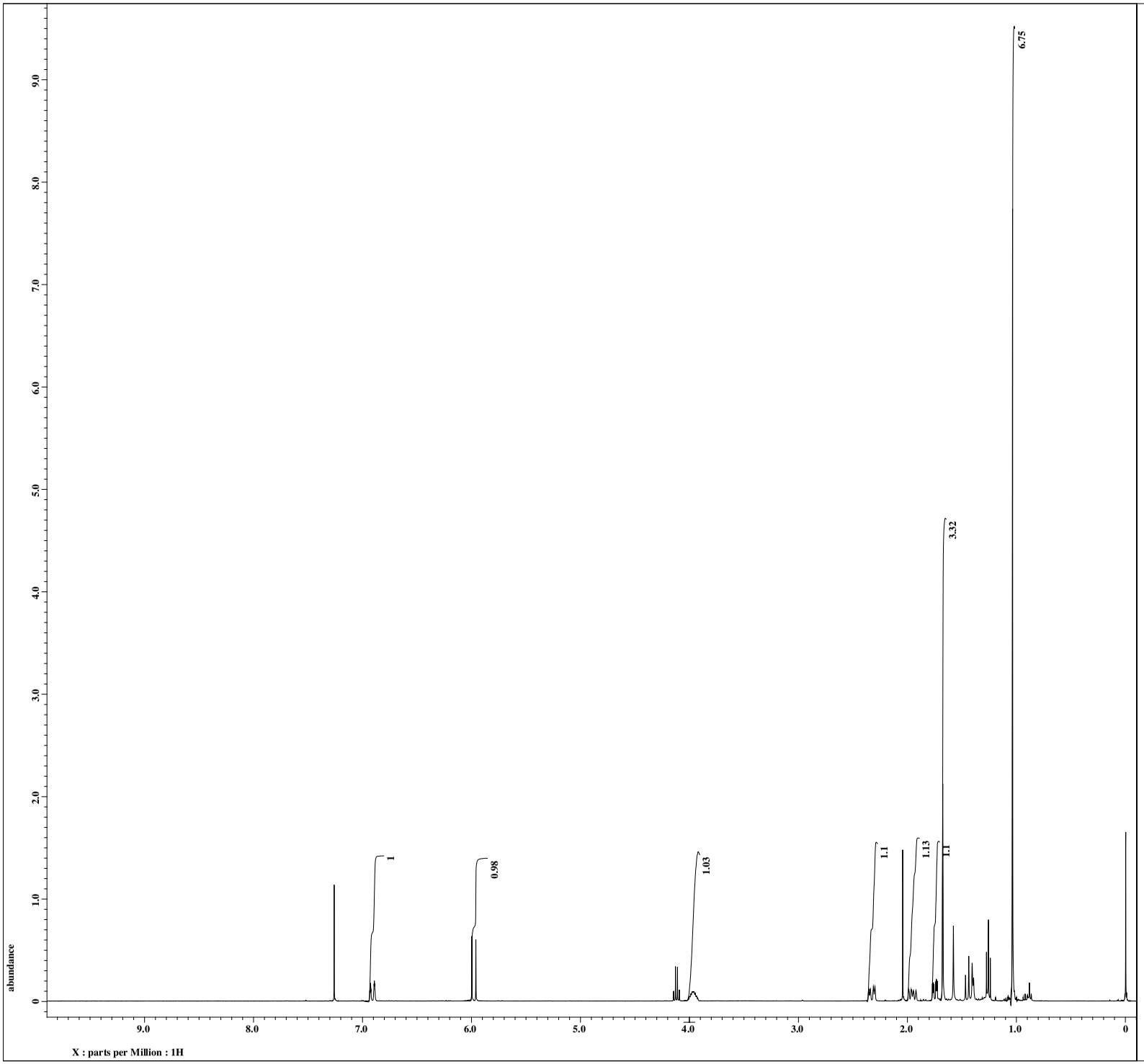




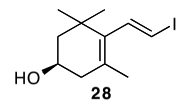

```
Filename          = d1-alcohol-stannane-1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#645271
Solvent           = CHLOROFORM-D
Creation_time     = 11-AUG-2008 18:48:35
Revision_time     = 29-OCT-2008 17:32:17
Current_time      = 29-OCT-2008 17:32:44

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1000
Total_scans       = 1000

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.1[dC]
```



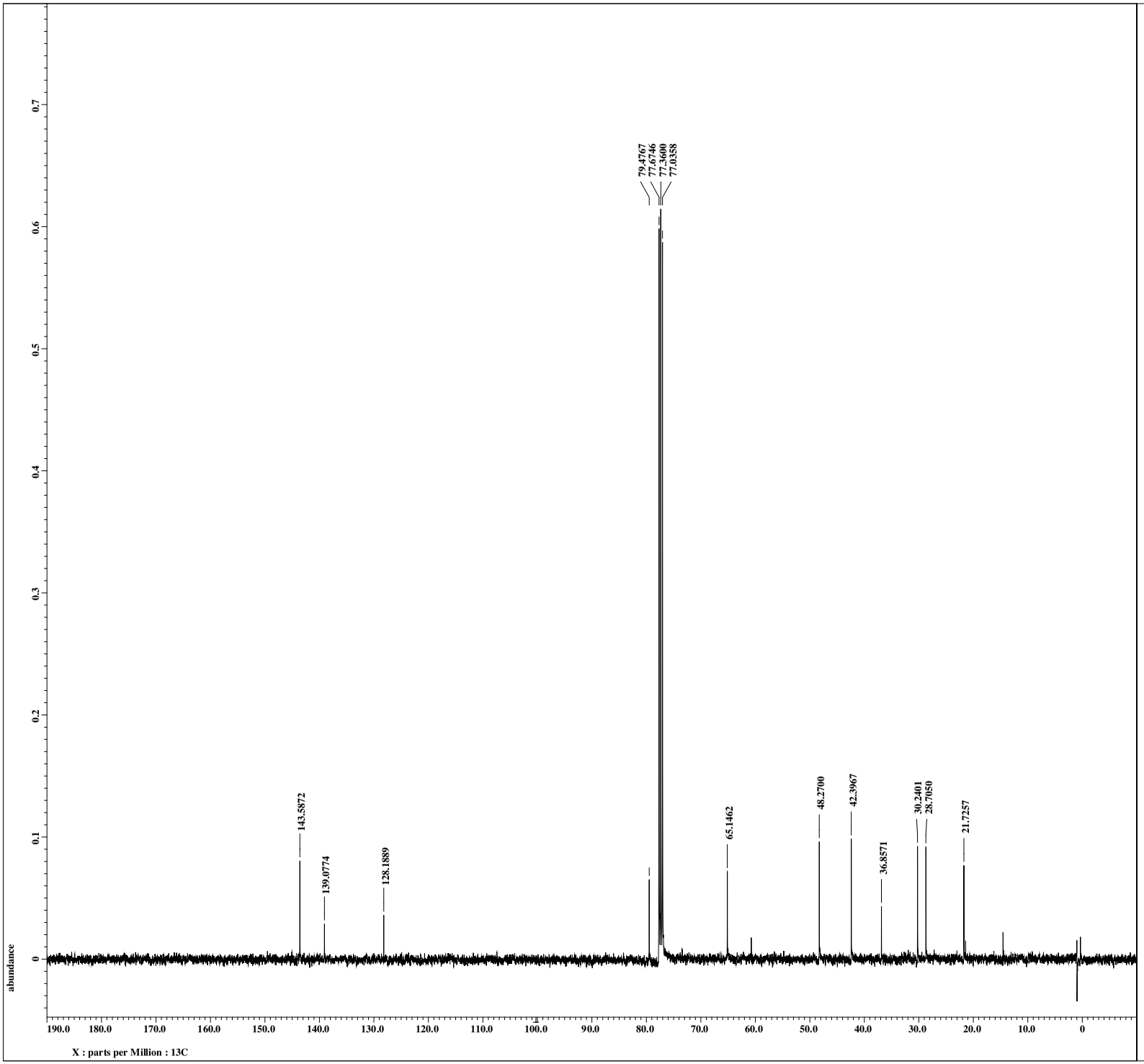
27



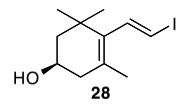

```
Filename          = d1-alcohol-iodide-1H-
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 11-AUG-2008 20:06:55
Revision_time     = 30-OCT-2008 16:57:04
Current_time      = 30-OCT-2008 16:57:41

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.45[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1.4[dB]
X_pulse           = 5.225[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 3.18365952[s]
Temp_get          = 24.1[dC]
```



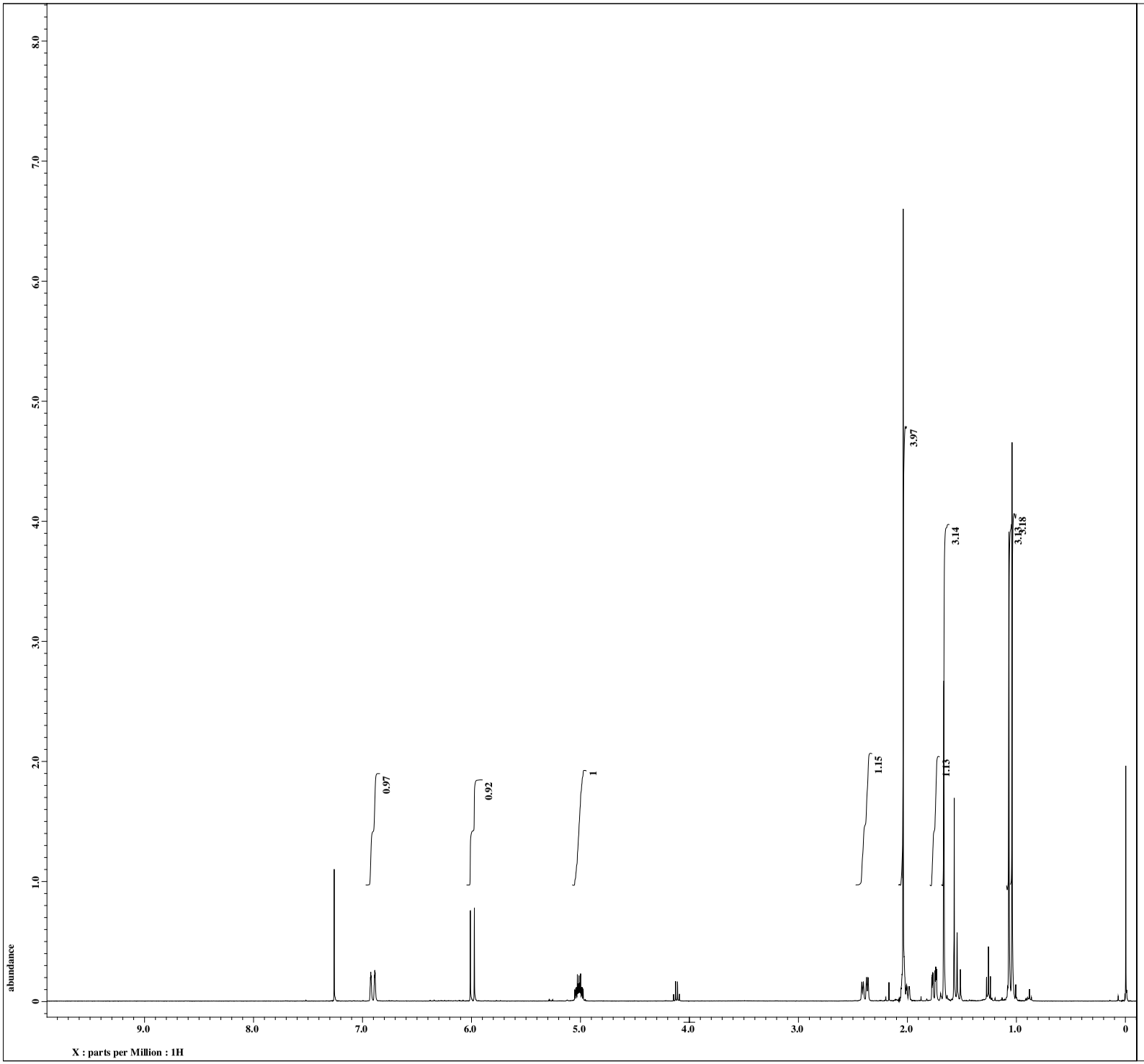
28



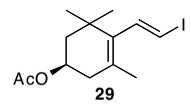

```
Filename          = d1-alcohol-iodide-13C
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#724508
Solvent           = CHLOROFORM-D
Creation_time     = 11-AUG-2008 20:50:05
Revision_time     = 29-OCT-2008 17:30:54
Current_time      = 29-OCT-2008 17:31:20

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 605
Total_scans       = 605

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 58
Relaxation_delay  = 3[s]
Repetition_time   = 4.04333312[s]
Temp_get          = 24.5[dC]
```



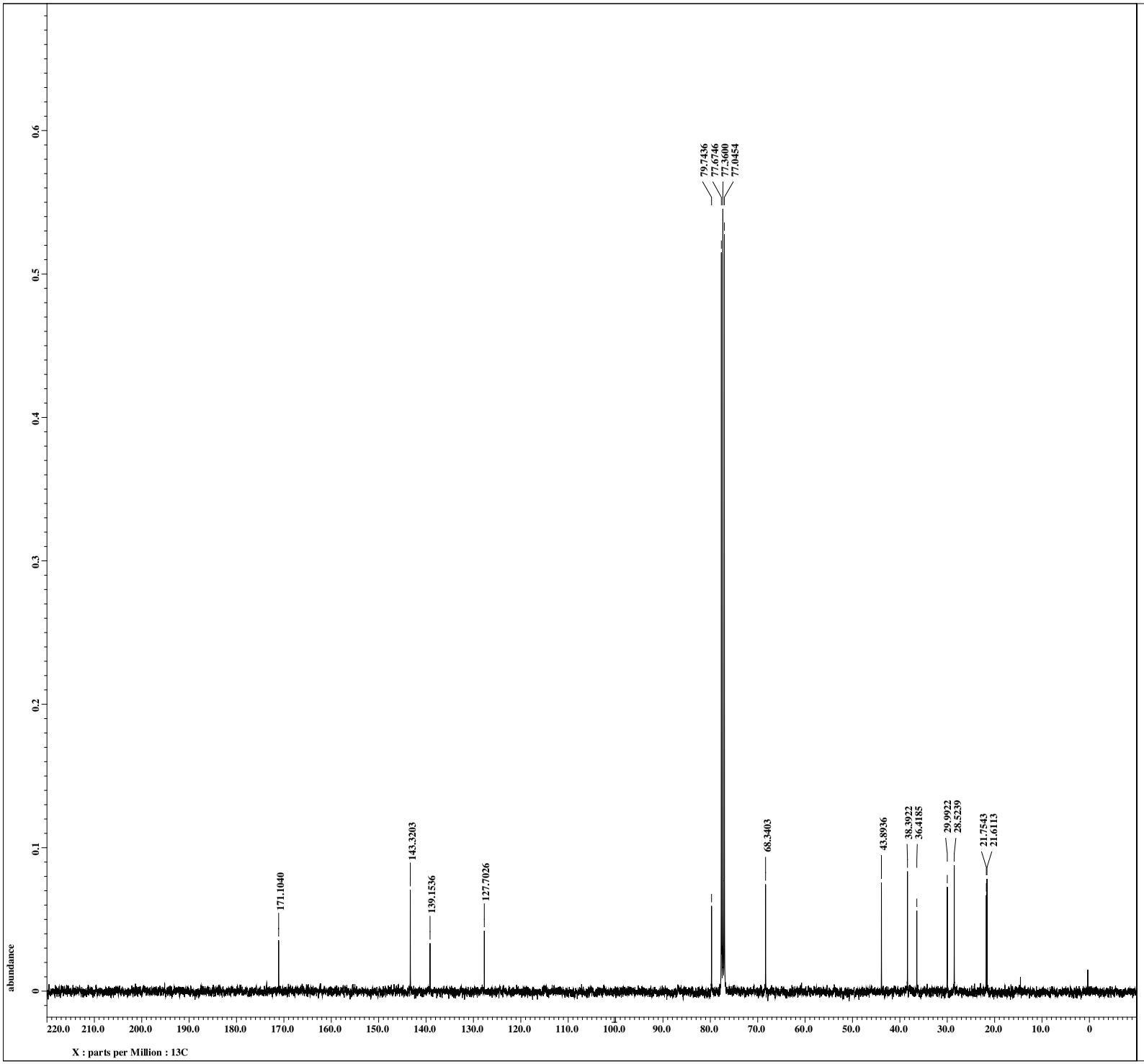
28



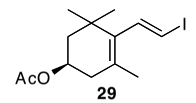

```
Filename          = d1-acetyl-iodide-1H-2
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 12-AUG-2008 12:53:35
Revision_time     = 30-OCT-2008 16:55:18
Current_time      = 30-OCT-2008 16:55:39

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.45[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1.4[dB]
X_pulse           = 5.225[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 3.18365952[s]
Temp_get          = 23.6[dC]
```



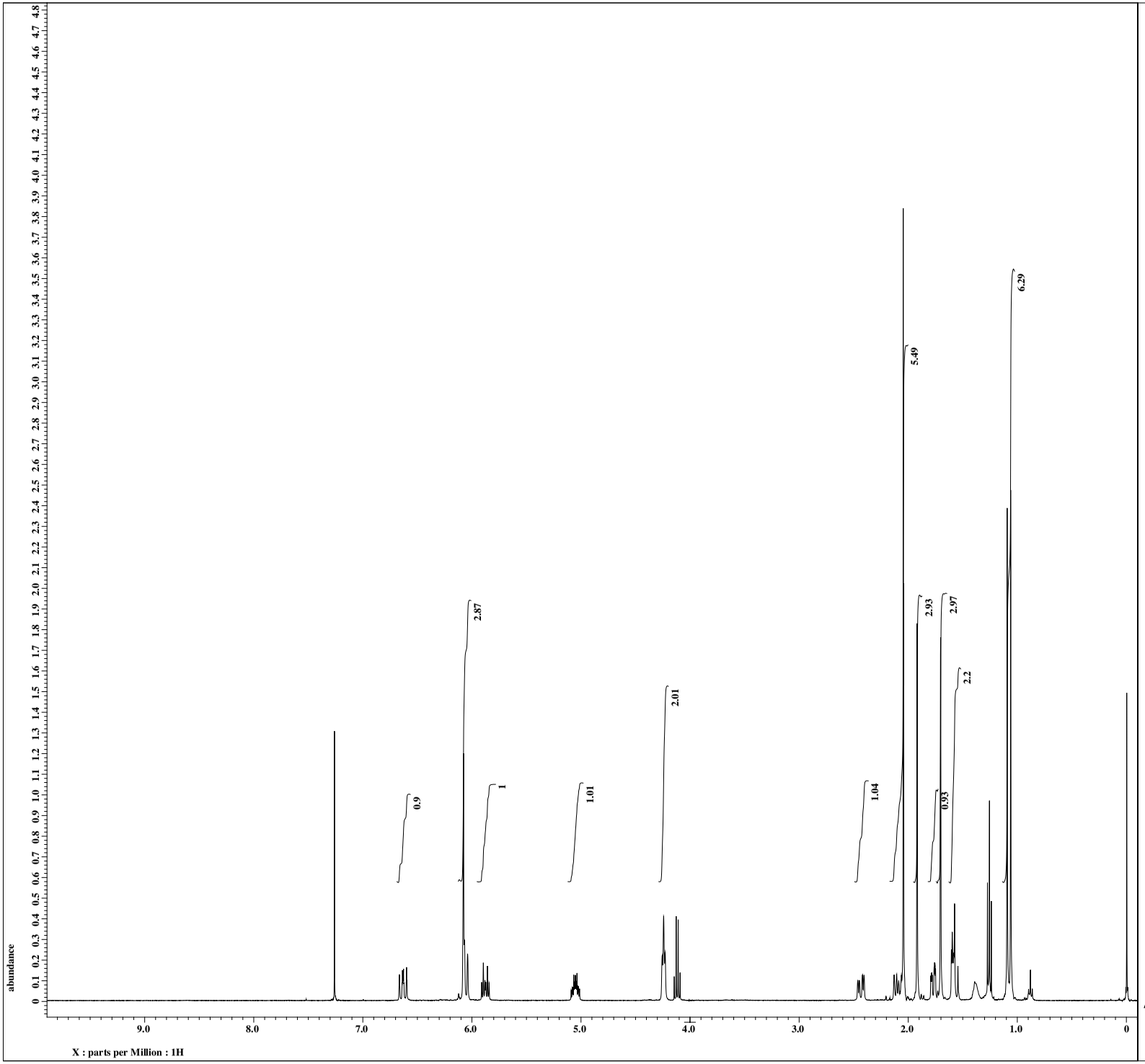
29



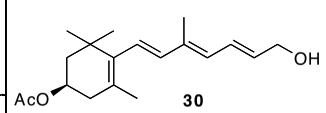

```
Filename          = d1-acetyl-iodide-13C-
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#464539
Solvent           = CHLOROFORM-D
Creation_time     = 12-AUG-2008 13:30:38
Revision_time     = 29-OCT-2008 17:28:53
Current_time      = 29-OCT-2008 17:29:19

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 337
Total_scans       = 337

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 5[s]
Recvr_gain        = 54
Relaxation_delay  = 5[s]
Repetition_time   = 6.04333312[s]
Temp_get          = 23.8[dC]
```



29

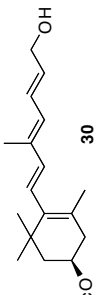



```
Filename          = d1-tetraene-alcohol-1
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 12-AUG-2008 18:25:29
Revision_time     = 30-OCT-2008 17:12:03
Current_time      = 30-OCT-2008 17:12:23

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.45[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1.4[dB]
X_pulse           = 5.225[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 3.18365952[s]
Temp_get          = 24[dC]
```

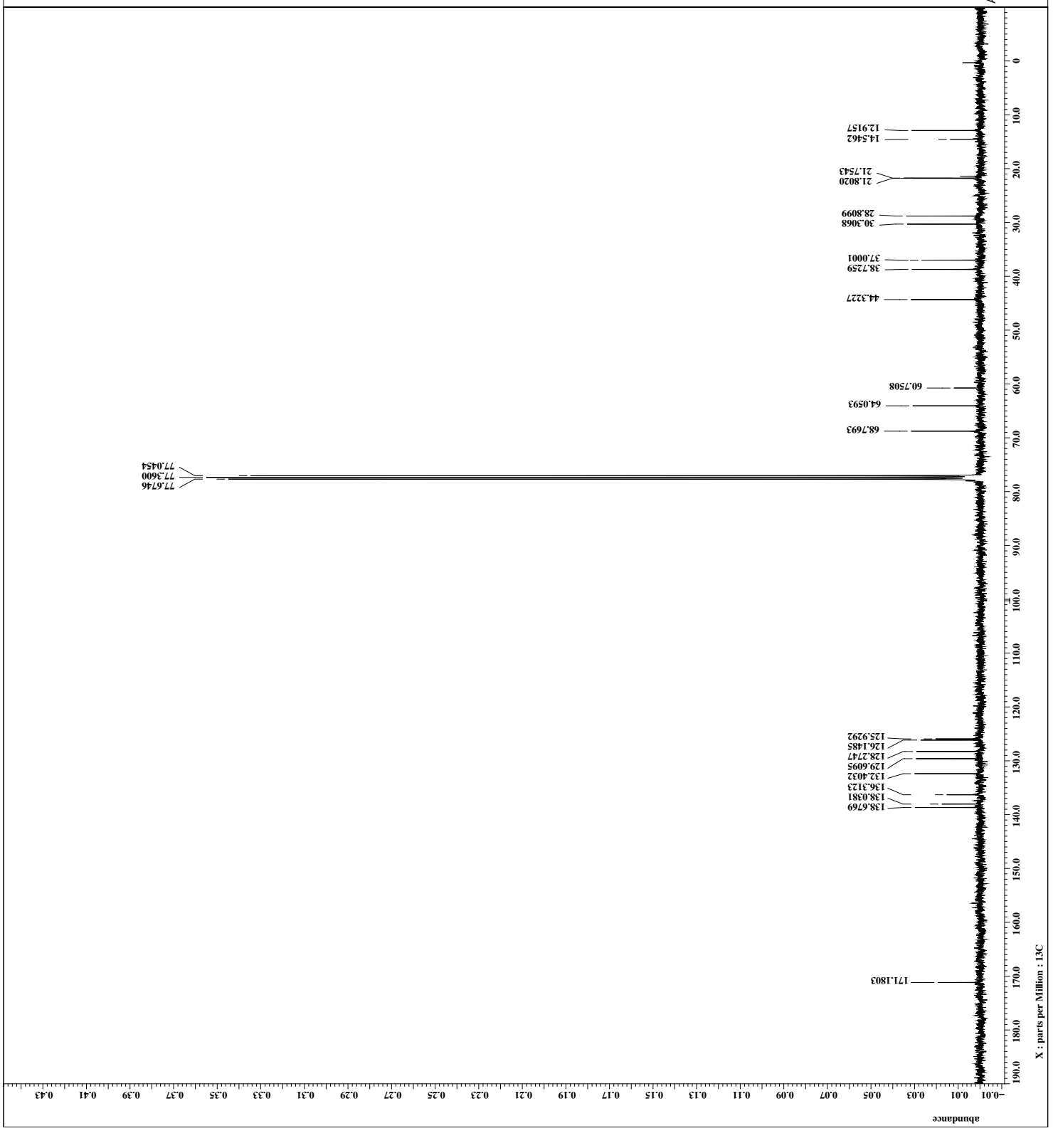


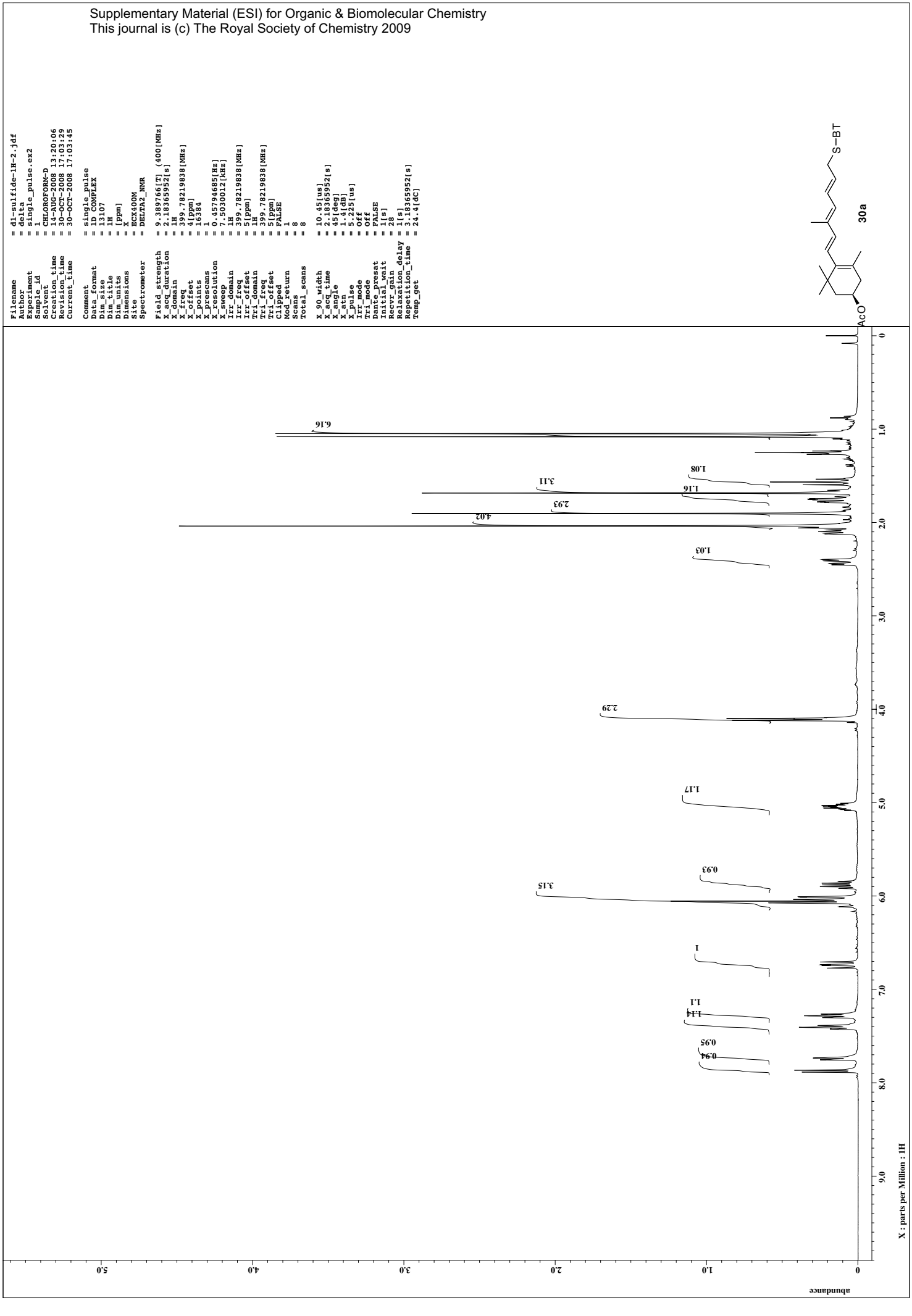
30

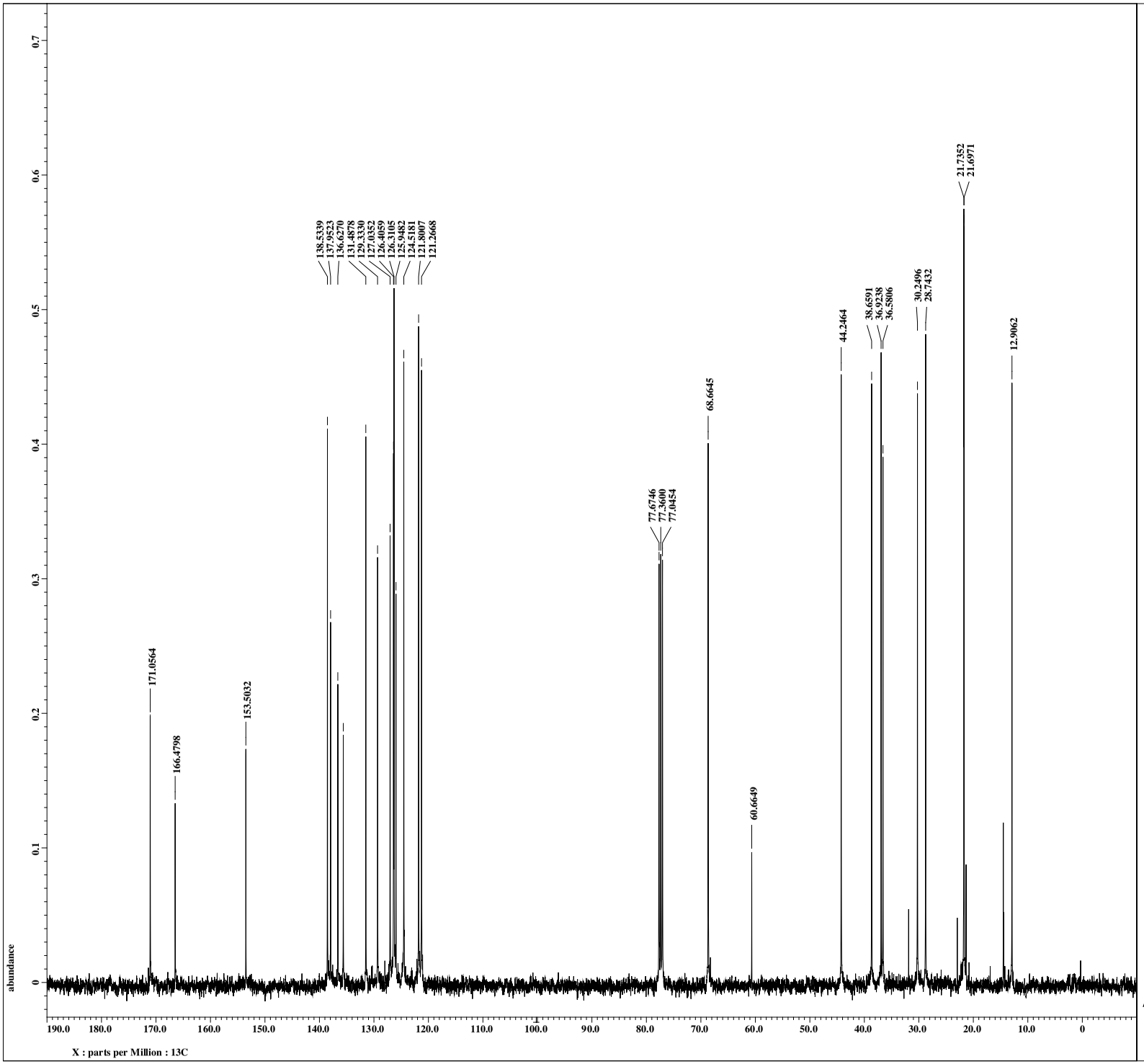
```
Filename          = d1-tetraene-alcohol-1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#663/36
Solvent           = CHLOROFORM-D
Creation_time     = 12-AUG-2008 19:04:57
Revision_time     = 29-OCT-2008 17:33:47
Current_time      = 29-OCT-2008 17:34:30

Comment           = single_pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.043333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 365
Total_scans       = 365

X_90_width        = 9.2[us]
X_acq_time        = 1.043333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_mode          = WALTZ16
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 5[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 6.043333312[s]
Temp_get          = 24.5[dC]
```



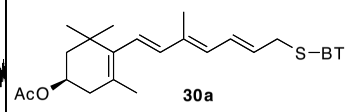
30



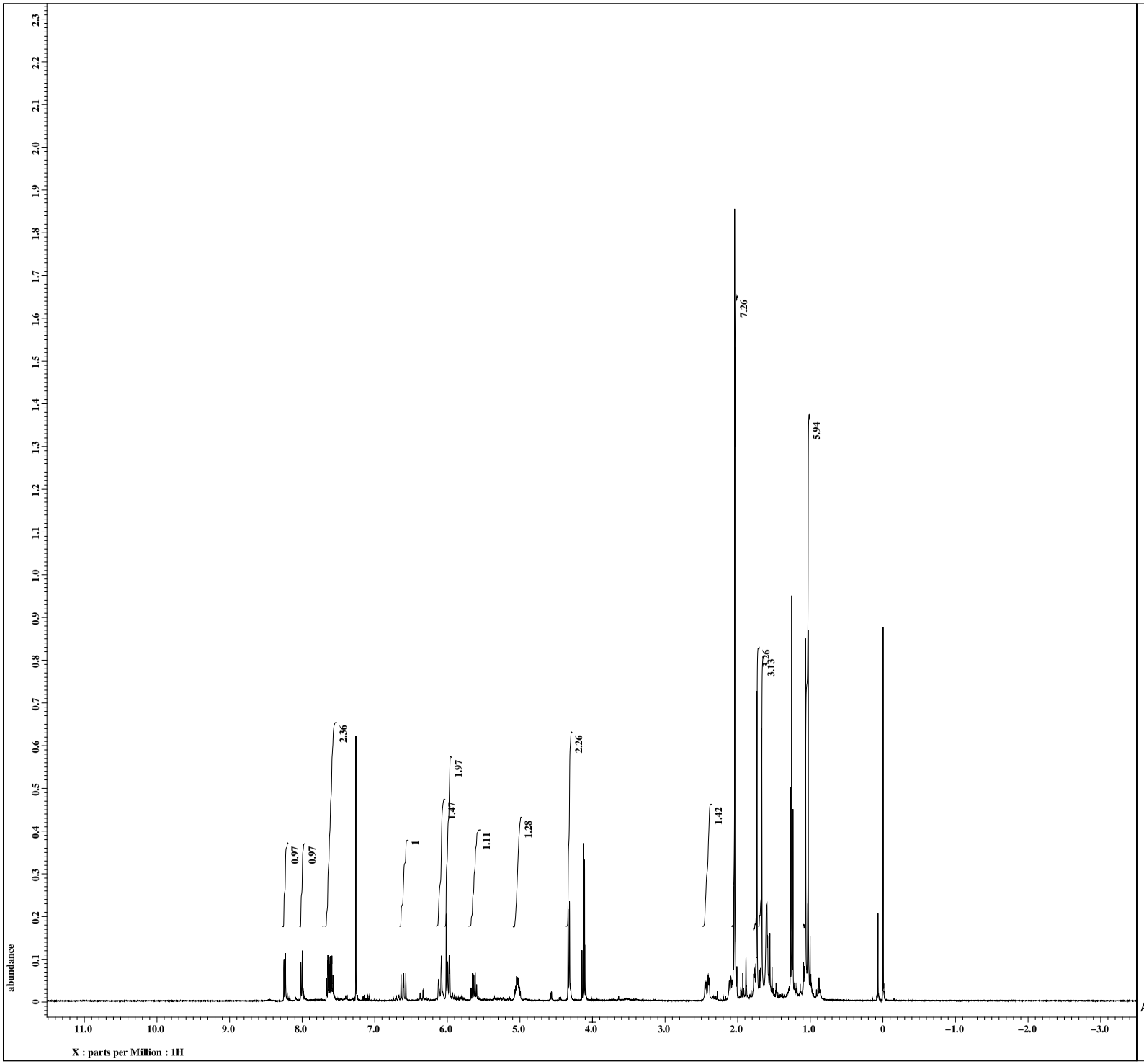

Filename = dl-sulfide-1H-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 14-AUG-2008 13:20:06
Revision_time = 30-OCT-2008 17:03:29
Current_time = 30-OCT-2008 17:03:45
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 4[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.45[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1.4[dB]
X_pulse = 5.225[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 28
Relaxation_delay = 1[s]
Repetition_time = 3.18365952[s]
Temp_get = 24.4[dC]
S–BT
AcO
30a
6.16
3.11
1.08
1.16
2.93
4.02
1.03
2.29
1.17
0.93
3.15
1
1.14
1.1
0.94
0.95
abundance
X : parts per Million : 1H



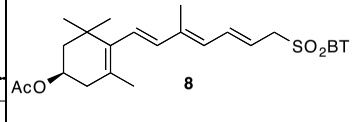

```
Filename          = d1-sulfide-13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#480788
Solvent           = CHLOROFORM-D
Creation_time     = 14-AUG-2008 13:50:28
Revision_time     = 29-OCT-2008 17:39:07
Current_time      = 29-OCT-2008 17:39:28

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 268
Total_scans       = 268

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 5[s]
Recvr_gain        = 58
Relaxation_delay  = 5[s]
Repetition_time   = 6.04333312[s]
Temp_get          = 24.3[dC]
```



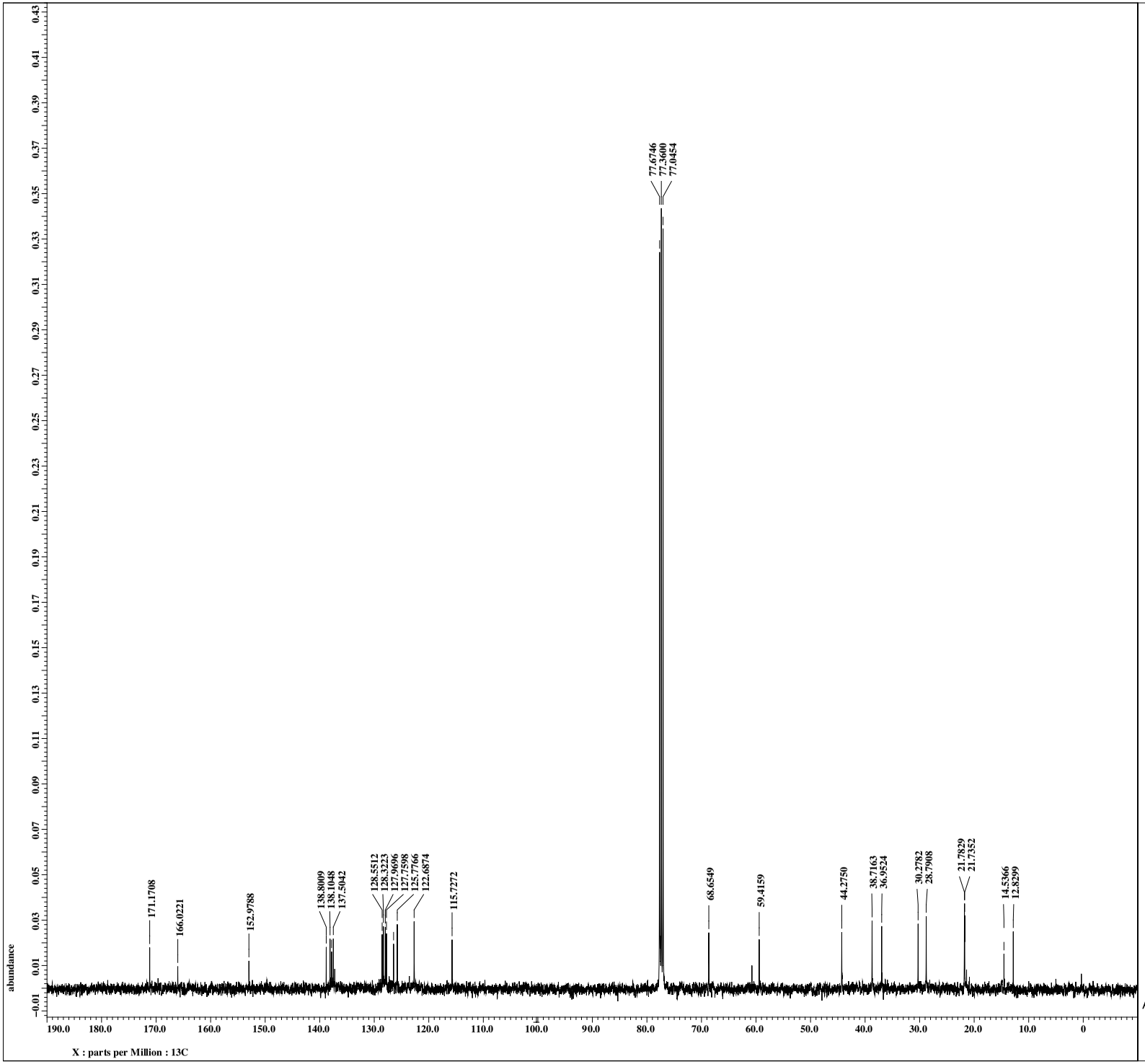
30a



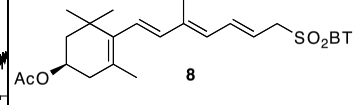

```
Filename          = d1-sulfone-1H-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 20-AUG-2008 14:06:52
Revision_time     = 30-OCT-2008 17:09:47
Current_time      = 30-OCT-2008 17:10:00

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 4[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.45[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1.4[dB]
X_pulse           = 5.225[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 34
Relaxation_delay  = 1[s]
Repetition_time   = 3.18365952[s]
Temp_get          = 24.6[dC]
```



8

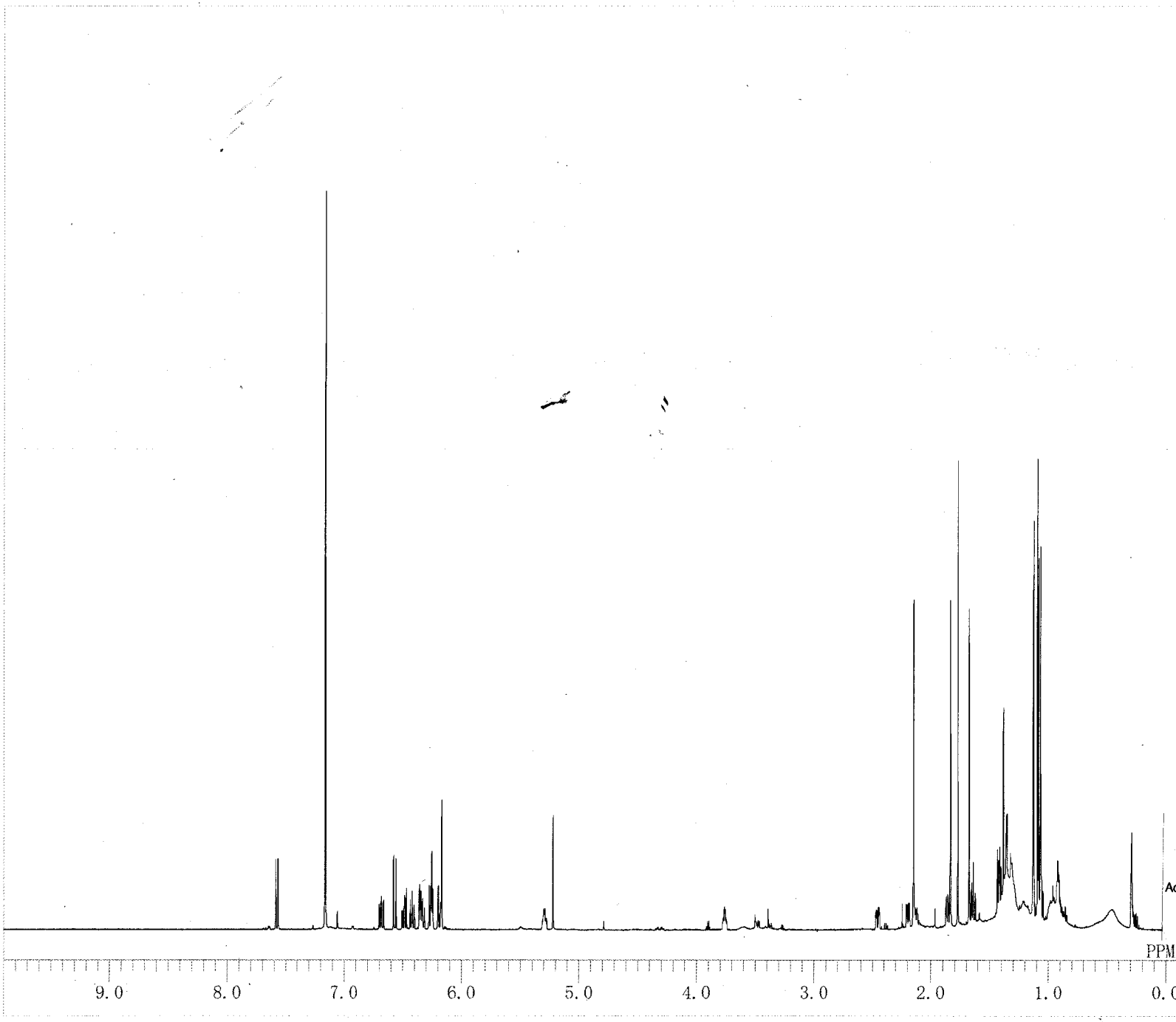



```
Filename          = d1-sulfone-13C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#573846
Solvent           = CHLOROFORM-D
Creation_time     = 20-AUG-2008 15:50:57
Revision_time     = 29-OCT-2008 17:40:29
Current_time      = 29-OCT-2008 17:40:50

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX400M
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 374
Total_scans       = 374

X_90_width        = 9.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.6[us]
Irr_atn_dec       = 22.2[dB]
Irr_atn_noe       = 22.2[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 5[s]
Recvr_gain        = 52
Relaxation_delay  = 5[s]
Repetition_time   = 6.04333312[s]
Temp_get          = 25.2[dC]
```

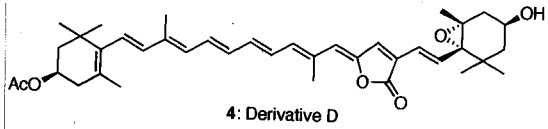


8

katsum750_09.1.1

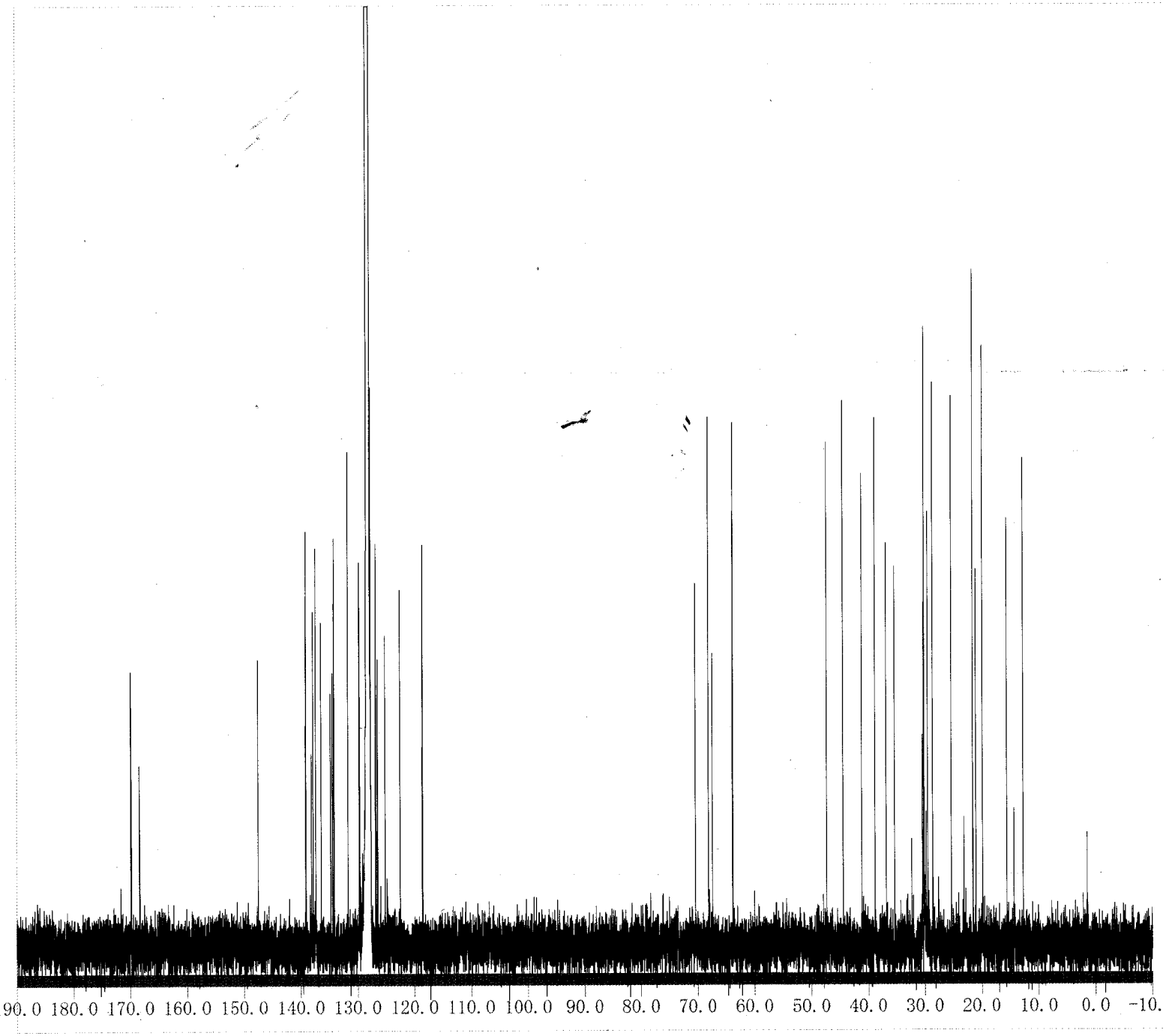


DFILE	1r
COMNT	katsum750_09.1.1
DATIM	Thu Mar 27 16:43:07 2008
OBNUC	1H
EXMOD	zg30
OBFRQ	750.13 MHz
OBSET	3.60 KHz
OBFIN	0.62 Hz
POINT	32768
FREQU	11261.26 Hz
SCANS	16
ACQTM	2.9098 sec
PD	2.0000 sec
PW1	10.20 usec
IRNUC	
CTEMP	26.9 c
SLVNT	CDC13
EXREF	7.16 ppm
BF	0.30 Hz
RGAIN	32

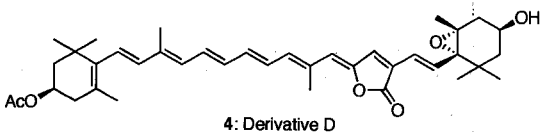


4: Derivative D

katsum750_09.1000.1



DFILE	1r
COMNT	katsum750_09.1000.1
DATIM	Thu Mar 27 17:12:15 2008
OBNUC	13C
EXMOD	zgpg30
OBFRQ	188.63 MHz
OBSET	9.20 KHz
OBFIN	0.56 Hz
POINT	32768
FREQU	45045.05 Hz
SCANS	8192
ACQTM	0.7275 sec
PD	2.0000 sec
PW1	15.00 usec
IRNUC	
CTEMP	26.9 c
SLVNT	CDCl3
EXREF	219.62 ppm
BF	1.00 Hz
RGAIN	8192



4: Derivative D