

General. All commercially available reagents were used without further purification. All solvents were used after distillation. Tetrahydrofuran (THF) were refluxed over and distilled from sodium-benzophenone ketyl. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were distilled from CaH₂ under reduced pressure. Preparative separation was performed by column chromatography on silica gel. ¹H NMR and ¹³C 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.

(3Z,5E)-6-[(1'S,2'R,4'S)-1',2'-epoxy-4'-Hydroxy-2',6',6'-trimethylcyclohex-1'-yl]-4-methoxycarbonylhexa-3,5-dien-1-yne (12). To a solution of dibromide **11** (684 mg, 1.21 mmol) in THF (12.1 mL) was added tetra-*n*-butylammonium fluoride (7.27 mL, 1.0 M solution in THF) at room temperature. After being stirred for 2 h at 55 °C, the reaction mixture was poured into a saturated aqueous NH₄Cl solution, and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 10% to 50% ethyl acetate in hexane) afforded alkyne **12** (144 mg, 41%): [α]_D²³ -64.7 (c 0.95, CHCl₃); IR (neat, cm⁻¹) 3424, 3291, 2961, 2782, 2097, 1782, 1578, 1437, 1375, 1229, 1159, 1049, 974; ¹H NMR (CDCl₃, 400 MHz) δ 6.24 (s, 2H), 5.83 (d, *J* = 2.7 Hz, 1H), 3.88 (m, 1H), 3.85 (s, 3H), 3.41 (d, *J* = 2.8 Hz, 1H), 2.36 (dd, *J* = 14.2, 4.5 Hz, 1H), 1.63-1.57 (m, 2H), 1.22 (dd, *J* = 12.8, 11.0 Hz, 1H), 1.18 (s, 3H), 1.12 (s, 3H), 0.96 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.8, 143.4, 132.2, 129.1, 113.4, 87.3, 80.4, 70.3, 67.7, 64.3, 52.4, 47.3, 41.1, 35.6, 29.6, 25.1, 20.1; ESI-HRMS *m/z* Calcd for C₁₇H₂₂O₄ (M+Na)⁺ 313.1416, found 313.1413.

(2E,6Z,8E)-9-[(1'S,2'R,4'S)-1',2'-Epoxy-4'-hydroxy-2',6',6'-trimethylcyclohex-1'-yl]-7-methoxycarbonyl-3-methylnona-2,6,8-trien-4-yn-1-ol (12'). To a solution of vinyl iodide **13** (174 mg, 0.878 mmol), tetrakis(triphenylphosphine)palladium (41 mg, 0.035 mmol) and triethylamine (0.15 mL, 1.05 mmol) in THF (2.2 mL) was added a solution of alkyne **12** (102 mg, 0.35 mmol) in THF (0.6 mL) and CuI (7 mg, 0.035 mmol). After being stirred for 40 min at room temperature, the reaction mixture was poured into a saturated aqueous NH₄Cl solution, and then the resulting mixture was extracted with ethyl acetate. The organic layers were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 50% to 70% ethyl acetate in hexane) afforded diol **12'** (83 mg, 66%): [α]_D²³ -77.9 (c 0.62, CHCl₃); IR (neat, cm⁻¹) 3395, 2962, 2930, 1722, 1437, 1379, 1219, 1157, 1047; ¹H NMR (400 MHz, CDCl₃) δ 6.26 (s, 2H), 6.03 (td, *J* = 6.4, 1.4 Hz, 1H), 6.00 (s, 1H), 4.26 (d, *J*

=6.6 Hz, 2H), 3.88 (m, 1H), 3.86 (s, 3H), 2.37 (ddd, $J=14.2, 5.0, 1.6$ Hz, 1H), 1.86 (s, 3H), 1.66-1.57 (m, 2H), 1.25-1.20 (m, 1H), 1.19 (s, 3H), 1.14 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 140.7, 137.4, 131.0, 129.5, 121.0, 115.1, 102.1, 85.3, 70.4, 67.7, 64.5, 59.6, 52.2, 47.4, 41.2, 35.6, 29.7, 25.1, 20.1, 17.7; ESI-HRMS m/z Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 383.1834, found 383.1846.

Acetylene Methyl Ester Derivative (2). To a solution of diol **12'** (30 mg, 0.08 mmol) in diethyl ether (0.8 mL) was added manganese dioxide (499 mg) at room temperature. After being stirred at the same temperature for 10 min, the reaction mixture was filtered through a pad of Celite. The solvents were removed *in vacuo* to afford crude aldehyde **6**, which was used to the next reaction without further purification.

To a solution of the sulfone **4** (40 mg, 0.083 mmol) and crude aldehyde **6** in THF (2 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.32 mL, 0.32 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 60% ethyl acetate in hexane) in the dark afforded a mixture of all-*trans*-peridinin derivative **2** and its *cis*-isomer (34 mg, 63%) as a red film. A solution of a mixture of peridinin derivative **2** in benzene was left at room temperature under fluorescent light. After 8 days, the separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1/6; flow rate: 2 mL / min.; UVdetect: 410 nm; retention time: (all-*trans*-isomer **2-1**) 40 min., (13Z-isomer **2-2**) 41 min.] in the dark gave crude peridinin derivative **2**, which was further purified by preparative HPLC [column: YMC Carotenoid C30 (10 x 250 mm); reverse phase: acetonitrile / methanol / water = 87 / 10 / 3; flow rate: 2 mL / min.; UVdetect: 410 nm; retention time: (all-*trans*-isomer) 15 min] in the dark, afforded the desired optically active peridinin derivative **2-1** as an orange powder: 13E-isomer **2-1**; IR (neat, cm^{-1}) 3505, 2929, 2161, 1931, 1713, 1437, 1363, 1223, 1161, 1032; ^1H NMR (750 MHz, CDCl_3) δ 6.58 (dd, $J=14.2, 11.9$ Hz, 1H), 6.49 (d, $J=11.4$ Hz, 1H), 6.46 (dd, $J=13.2, 13.2$ Hz, 1H), 6.41 (dd, $J=12.9, 12.9$ Hz, 1H), 6.32 (dd, $J=14.3, 11.0$ Hz, 1H), 6.27 (s, 2H), 6.08 (d, $J=11.8$ Hz, 1H), 6.07 (s, 1H), 6.04 (s, 1H), 5.38 (m, 1H), 3.89 (m, 1H), 3.87 (s, 3H), 2.37 (dd, $J=14.1, 4.8$ Hz, 1H), 2.28 (dd, $J=10.7$ Hz, 1H), 2.04 (s, 3H), 1.99 (m, 1H), 1.96 (s, 3H), 1.79 (s, 3H), 1.63 (m, 2H), 1.50 (dd, $J=12.0, 12.0$ Hz, 1H), 1.42 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.34 (m, 1H), 1.20 (s, 3H), 1.14 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (188 MHz, CDCl_3) δ 202.5, 170.4, 166.6, 137.8, 135.9, 132.7, 131.3, 130.3, 129.4, 128.0, 127.8, 117.7, 117.6, 115.4, 103.3, 87.6, 81.0, 72.7, 67.9, 67.6, 64.2, 51.6, 46.6, 45.4, 45.2, 40.9, 35.8, 35.3, 32.1, 29.4, 24.9, 21.4, 19.9, 17.5, 14.0; ESI-HRMS m/z Calcd for $\text{C}_{40}\text{H}_{52}\text{O}_7$ ($\text{M}+\text{Na}$) $^+$ 667.3611, found 667.3609; 13Z-isomer

2-2; ¹H NMR (750 MHz, CDCl₃) δ 6.93 (d, *J* = 9.7 Hz, 1H), 6.71 (dd, *J* = 14.2, 9.8 Hz, 1H), 6.59 (dd, *J* = 14.1, 11.6 Hz, 1H), 6.28 (s, 1H), 6.20 (m, 2H), 6.11 (d, *J* = 11.4 Hz, 1H), 6.08 (s, 1H), 6.05 (s, 1H), 5.38 (m, 1H), 3.90 (m, 1H), 3.88 (s, 3H), 2.38 (ddd, *J* = 14.5, 4.8, 1.4 Hz, 1H), 2.28 (m, 1H), 2.04 (s, 3H), 1.99 (m, 1H), 1.96 (s, 3H), 1.80 (s, 3H), 1.64 (m, 2H), 1.50 (dd, *J* = 11.7, 11.7 Hz, 1H), 1.40 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.25 (m, 1H), 1.20 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H), 0.98 (s, 3H); ¹³C NMR (188 MHz, CDCl₃) δ 202.6, 170.4, 166.6, 139.4, 134.0, 132.5, 132.0, 131.9, 130.5, 128.0, 127.6, 124.1, 119.0, 117.6, 115.3, 105.0, 103.3, 72.7, 70.1, 67.9, 67.4, 64.2, 51.8, 47.0, 45.4, 45.2, 40.9, 35.8, 35.3, 32.1, 31.3, 30.3, 30.1, 24.9, 21.4, 19.9, 17.2, 14.0.

(1Z,3Z,5E)-6-[(1'S,2'R,4'S)-4'-tert-Butyldimethylsiloxy-1',2'-epoxy-2',6',6'-trimethylcyclohex-1'-yl]-1-bromo-4-methoxycarbonyl-hexa-1,3,5-triene (15). To a suspension of bromomethyltriphenylphosphonium bromide (2.02 g, 4.63 mmol) in THF (7.72 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 4.32 mL, 4.32 mmol) at -30 °C. After the mixture was stirred for 5 min at -30 °C, a solution of γ -hydroxybutenolide **9** (609 mg, 1.54 mmol) and diisopropylethylamine (0.81 mL, 4.63 mmol) in DMF (7.72 mL) was added. After being stirred for 15 min at room temperature, methyl iodide (0.57 mL, 9.26 mmol) was added. After being stirred for 15 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 MgSO₄, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 5% to 10% ethyl acetate in hexane) afforded triene bromide **15** (511 mg, 69%) as a mixture of E and Z isomer: Z-isomer [α]_D²³ -35.7 (c 0.76, CHCl₃); IR (neat, cm⁻¹) 2957, 2930, 2858, 1726, 1462, 1381, 1257, 1151, 1078; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (dd, *J* = 11.0, 7.1 Hz, 1H), 6.77 (d, *J* = 11.2 Hz, 1H), 6.46 (d, *J* = 7.4, 0.9 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.24 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H), 3.83 (m, 1H), 2.25 (m, 1H), 1.64 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.51 (m, 1H), 1.26 (m, 1H), 1.19 (s, 3H), 1.13 (s, 3H), 0.97 (s, 3H), 0.88 (s, 9H), 0.07 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 134.1, 131.0, 130.9, 130.5, 129.2, 114.9, 70.6, 67.5, 65.0, 52.3, 47.4, 41.7, 35.5, 29.6, 26.2, 25.3, 20.4, 18.5, -4.4; ESI-HRMS *m/z* Calcd for C₂₃H₃₇BrO₄Si (M+Na)⁺ 507.1542, found 507.1530; E-isomer ¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, *J* = 13.5, 11.9 Hz, 1H), 6.63 (d, *J* = 14.2 Hz, 1H), 6.31 (d, *J* = 11.9 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 6.18 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.83 (m, 1H), 2.24 (m, 1H), 1.64 (m, 1H), 1.50 (m, 1H), 1.26 (m, 1H), 1.17 (s, 3H), 1.12 (s, 3H), 0.95 (s, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 134.6, 133.7, 133.4, 131.6, 130.2, 116.1, 70.7, 67.6, 65.0, 52.2, 47.3, 41.7, 35.5, 29.6, 26.2, 25.3, 20.4, 18.5, -4.4.

(2E,4E,6E,8E)-9-[(1'S,2'R,4'S)-4'-tert-Butyldimethylsiloxy-1',2'-epoxy-2',6',6'-trimethylcyclohex-1'-yl]-7-methoxycarbonyl-3-methylnona-2,4,6,8-tetraen-1-ol (17). To a solution of triene bromide **15** (178 mg, 0.37 mmol) and vinylstannane **16** (398 mg, 1.10 mmol) in DMSO (1.84 mL) was added bis(acetonitrile)dichloropalladium(II) (5 mg, 0.02 mmol) and lithium chloride (31 mg, 0.73 mmol). After being stirred for 30 min at 60 °C, the reaction mixture was poured into water, and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 10% to 30% ethyl acetate in hexane) afforded coupling product **17** (87 mg, 50%): [α]_D²³ -18.7 (c 1.05, CHCl₃); IR (neat, cm⁻¹) 3449, 2957, 2930, 2858, 1714, 1597, 1435, 1363, 1228, 1084; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 11.2, 1H), 6.66 (dd, *J* = 15.1, 11.2, 1H), 6.59 (d, *J* = 15.1, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.46 (d, *J* = 15.8, 1H), 5.85 (t, *J* = 6.9 Hz, 1H), 4.34 (m, 2H), 3.85 (m, 1H), 3.78 (s, 3H), 2.26 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.84 (s, 3H), 1.67 (m, 1H), 1.55 (m, 1H), 1.26 (m, 1H), 1.24 (s, 3H), 1.17 (s, 3H), 1.01 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 144.8, 139.4, 136.0, 135.4, 132.0, 127.5, 124.9, 123.4, 71.0, 67.5, 65.0, 59.7, 52.1, 47.3, 41.7, 35.4, 29.8, 26.2, 25.3, 20.4, 18.4, 12.9, -4.5; ESI-HRMS *m/z* Calcd for C₂₇H₄₄O₅Si (M+Na)⁺ 499.2856, found 499.2845; 9'Z-isomer ¹H NMR (400 MHz, CDCl₃) δ 6.91 (dd, *J* = 15.4, 11.9, 1H), 6.53 (d, *J* = 11.7, 1H), 6.47 (d, *J* = 15.6, 1H), 6.26 (d, *J* = 15.5 Hz, 1H), 6.14 (d, *J* = 15.6, 1H), 5.81 (t, *J* = 6.9 Hz, 1H), 4.40 (m, 2H), 3.85 (m, 1H), 3.84 (s, 3H), 2.24 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.84 (s, 3H), 1.65 (m, 1H), 1.55 (m, 1H), 1.26 (m, 1H), 1.24 (s, 3H), 1.17 (s, 3H), 1.01 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H).

(2E,4E,6E,8E)-9-[(1'S,2'R,4'S)-1',2'-Epoxy-4'-hydroxy-2',6',6'-trimethylcyclohex-1'-yl]-7-methoxycarbonyl-3-methylnona-2,4,6,8-tetraen-1-ol (17'). To a solution of tetraene alcohol **17** (45 mg, 0.09 mmol) in THF (1 mL) was added tetra-*n*-butylammonium fluoride (1.0M in THF, 0.24 mL, 0.24 mmol) at 45 °C. After being stirred for 3 h at the same temperature, the reaction mixture was poured into a saturated aqueous NH₄Cl solution, and then extracted with diethyl ether. The organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 50% to 70% ethyl acetate in hexane) afforded tetraene diol **17'** (22 mg, 65%): [α]_D²⁴ -21.5 (c 0.61, CHCl₃); IR (neat, cm⁻¹) 3427, 2959, 1713, 1597, 1437, 1375, 1238, 1047, 974, 758; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 11.0, 1H), 6.67 (dd, *J* = 15.1, 11.0, 1H), 6.59 (d, *J* = 15.1, 1H), 6.48 (s, 2H), 5.85 (t, *J* = 6.9 Hz, 1H), 4.33 (d, *J* = 6.8 Hz, 2H), 3.90 (m, 1H), 3.78 (s, 3H), 2.39 (ddd, *J* = 14.2, 5.4, 1.8 Hz, 1H), 1.83 (s, 3H), 1.64 (m, 2H), 1.25 (m, 1H), 1.25 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 144.8, 139.5, 136.2, 135.2, 131.8, 127.5, 125.1, 123.6, 70.8, 67.5, 64.6, 59.9, 52.2, 47.4, 41.2, 35.6, 29.9, 25.2, 20.2, 13.0; ESI-HRMS *m/z* Calcd for C₂₁H₃₀O₅

(M+Na)⁺ 385.1991, found 385.1986.

9'E-Olefin methyl ester derivative (3). To a solution of **17'** (24 mg, 0.067 mmol) in diethyl ether (0.66 mL) was added manganese dioxide (0.397 g) at room temperature. After being stirred at the same temperature for 5 min, the reaction mixture was filtered through a pad of Celite. The solvents were removed *in vacuo* to afford crude aldehyde **7**, which was used to the next reaction without further purification.

To a solution of the sulfone **4** (34 mg, 0.067 mmol) and aldehyde **7** in THF (1.56 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.31 mL, 0.31 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 MgSO₄, filtered and concentrated *in vacuo*. Purification by short silica gel column chromatography (from 30% to 60% ethyl acetate in hexane) in the dark afforded a mixture of peridinin derivative **3** (20 mg, 46%) as a red film. A solution of a mixture of peridinin derivative **3** in benzene was left at room temperature under fluorescent light. After 5 days, the separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1/6; flow rate: 2 mL / min.; UVdetect: 430 nm; retention time: (13Z, 9'E)-isomer **3-1** 35 min., (13E, 9'E)-isomer **3-2** 37 min.] in the dark gave crude peridinin derivative **3**, which was further purified by preparative HPLC [column: YMC Carotenoid C30 (10 x 250 mm); reverse phase: acetonitrile / methanol / water = 87 / 10 / 3; flow rate: 2 mL / min.; UVdetect: 430 nm; retention time: (13E, 9'E)-derivative 31 min] in the dark, afforded the optically active 9'E-olefin methyl ester peridinin derivative **3-2** as a red powder: (13E, 9'E)-isomer **3-2**: IR (neat, cm⁻¹) 3433, 2926, 2855, 1929, 1711, 1437, 1364, 1246, 1163, 1032; ¹H NMR (750 MHz, CDCl₃) δ 7.24 (d, *J* = 11.7 Hz, 1H), 6.72 (dd, *J* = 15.1, 11.7 Hz, 1H), 6.65 (d, *J* = 15.4 Hz, 1H), 6.59 (m, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.47 (dd, *J* = 14.4, 11.3 Hz, 1H), 6.37 (dd, *J* = 14.4, 11.0 Hz, 1H), 6.32 (d, *J* = 11.0 Hz, 1H), 6.10 (d, *J* = 11.3 Hz, 1H), 6.05 (s, 1H), 5.38 (m, 1H), 3.93 (m, 1H), 3.78 (s, 3H), 2.41 (dd, *J* = 14.7, 4.5 Hz, 1H), 2.29 (m, 1H), 2.04 (s, 3H), 1.99 (m, 1H), 1.95 (s, 3H), 1.80 (s, 3H), 1.66 (m, 2H), 1.50 (m, 1H), 1.42 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.26 (m, 1H), 1.25 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H); ¹³C NMR (188 MHz, CDCl₃) δ 202.6, 170.7, 167.9, 139.6, 136.3, 136.1, 133.0, 131.1, 128.9, 127.9, 127.6, 126.2, 125.0, 123.0, 120.9, 117.3, 103.3, 80.4, 77.5, 67.1, 64.3, 51.8, 47.2, 45.4, 45.2, 41.0, 35.8, 31.9, 31.2, 29.3, 29.2, 25.0, 21.4, 20.0, 14.1, 14.0; ESI-HRMS *m/z* Calcd for C₄₀H₅₄O₇ (M+Na)⁺ 669.3767, found 669.3758; (13Z, 9'E)-isomer **3-1**: ¹H NMR (750 MHz, CDCl₃) δ 7.25 (d, *J* = 11.7 Hz, 1H), 6.75 (m, 3H), 6.71 (d, *J* = 14.7 Hz, 1H), 6.60 (dd, *J* = 14.1, 11.7 Hz, 1H), 6.51 (s, 1H), 6.38 (dd, *J* = 11.7, 11.7 Hz, 1H), 6.25 (dd, *J* = 11.3, 11.3 Hz, 1H), 6.15 (d, *J* = 11.7 Hz, 1H), 6.06 (s, 1H),

5.38 (m, 1H), 3.93 (m, 1H), 3.78 (s, 3H), 2.41 (ddd, $J=14.1, 5.7, 1.0$ Hz, 1H), 2.28 (m, 1H), 2.04 (s, 3H), 2.00 (m, 1H), 1.95 (s, 3H), 1.80 (s, 3H), 1.66 (m, 2H), 1.50 (m, 1H), 1.42 (m, 1H), 1.39 (s, 3H), 1.36 (s, 3H), 1.29 (m, 1H), 1.27 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (188 MHz, CDCl_3) δ 202.8, 179.1, 174.8, 167.8, 145.5, 143.5, 139.4, 136.0, 131.9, 131.7, 131.3, 130.7, 128.1, 127.8, 127.3, 124.8, 124.0, 117.2, 103.3, 72.7, 70.6, 68.0, 64.3, 47.1, 45.4, 45.2, 41.0, 35.8, 31.9, 31.2, 29.3, 29.1, 21.4, 20.0, 14.1, 12.5.

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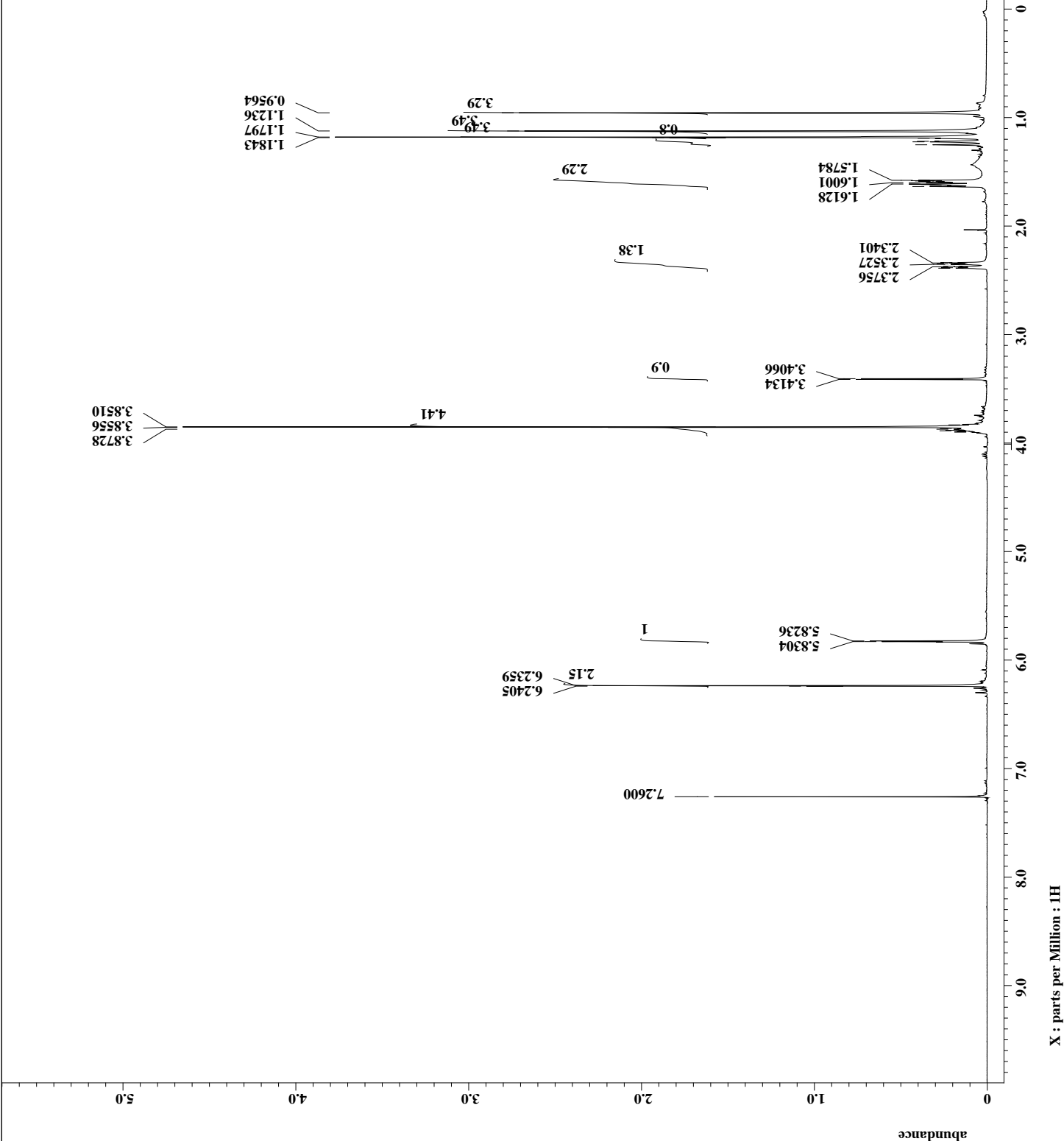
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12

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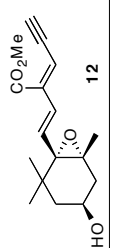
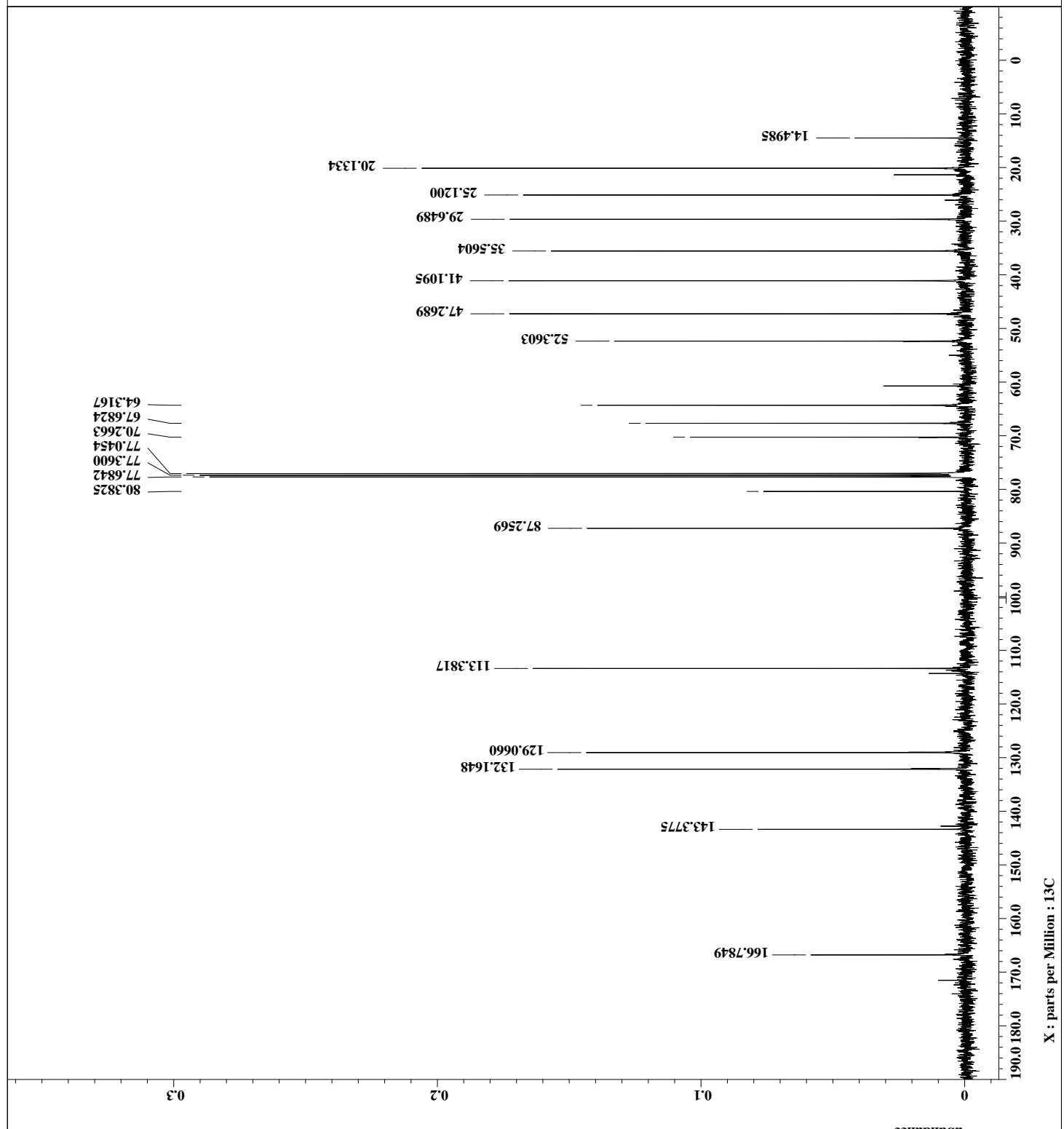
File name      = a2-alkyne-ester-13C-3
Author        = delta
Experiment    = single_pulse_dec
Sample ID     = S#354684
Solvent       = CHLOROFORM-D
Creation time = 11-DEC-2009 09:01:37
Revision time = 12-DEC-2009 18:16:51
Current time  = 12-DEC-2009 18:17:12

Comment       = single pulse decouple
Data format   = ID COMPLEX
Dim Size      = 26214
Dim Title     = 13C
Dim Units     = [ppm]
Dimensions    = X
Site          = ECX400M
Spectrometer = DELTA2_NMR

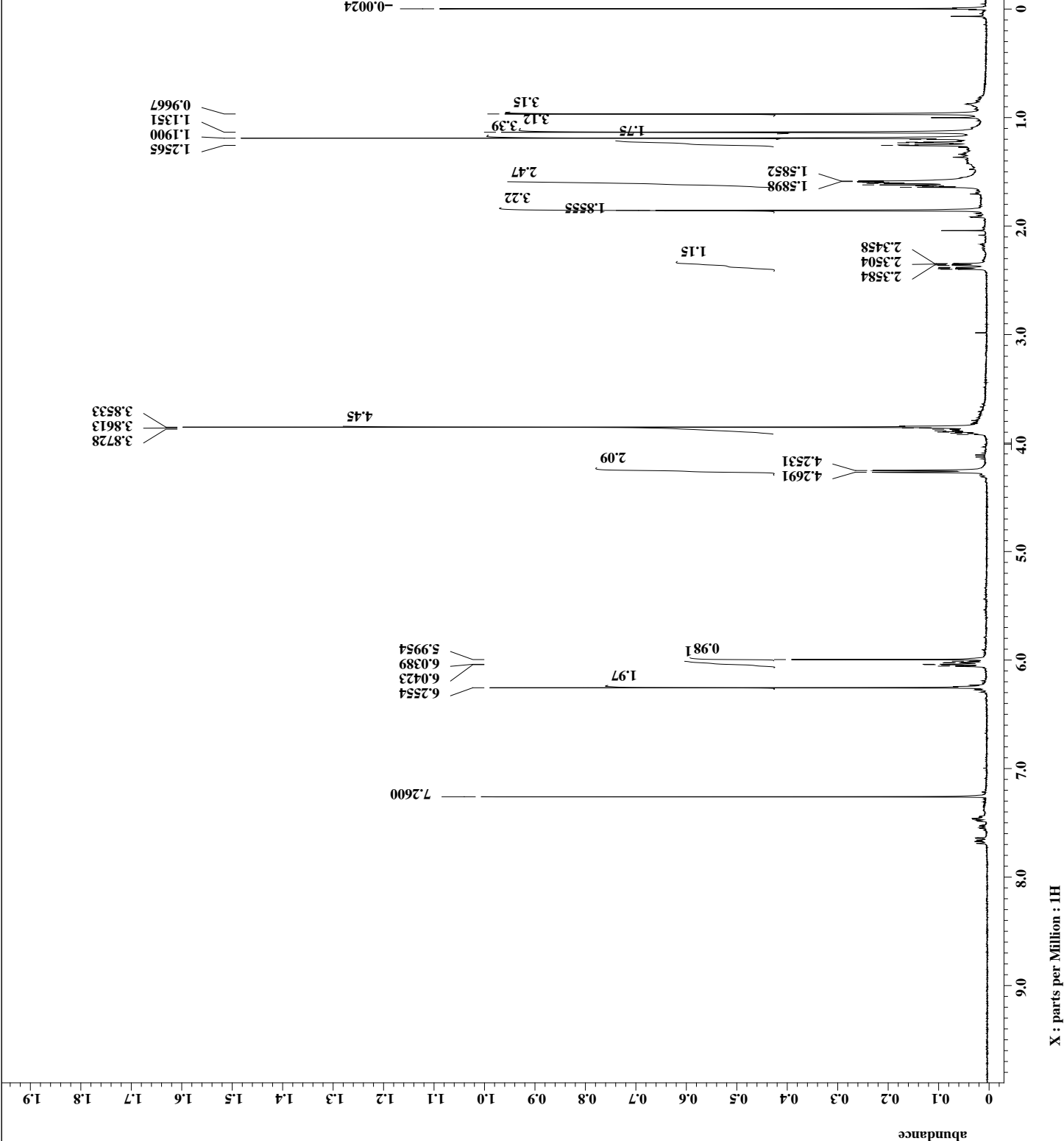
Field strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain       = 13C
X_freq         = 100.52530333[MHz]
X_offset       = 100[ppm]
X_points       = 32768
X_prescans     = 4
X_resolution   = 0.95846665[Hz]
X_sweep        = 31.40703518[kHz]
X_domain       = 1H
Irr_freq       = 399.78219838[MHz]
Irr_offset     = 5[ppm]
Clipped        = FALSE
Mod_return     = 1
Scans          = 153
Total_scans    = 153

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      = WAITZ
Decoupling     = TRUE
Initial_wait   = 1[s]
Noe            = TRUE
Noe_time       = 5[s]
Recvr_gain     = 50
Relaxation_delay = 5[s]
Repetition_time = 6.04333312[s]
Temp_get       = 24.1[dc]

```



X : parts per Million : 13C



```

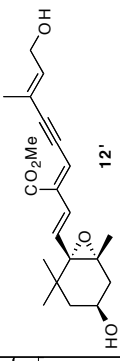
Filename = a2-alcohol-ester-1H-4
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 5-DEC-2009 11:32:21
Revision_time = 12-DEC-2009 14:36:43
Current_time = 12-DEC-2009 14:38:08

Comment = single_pulse
Data_format = ID 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

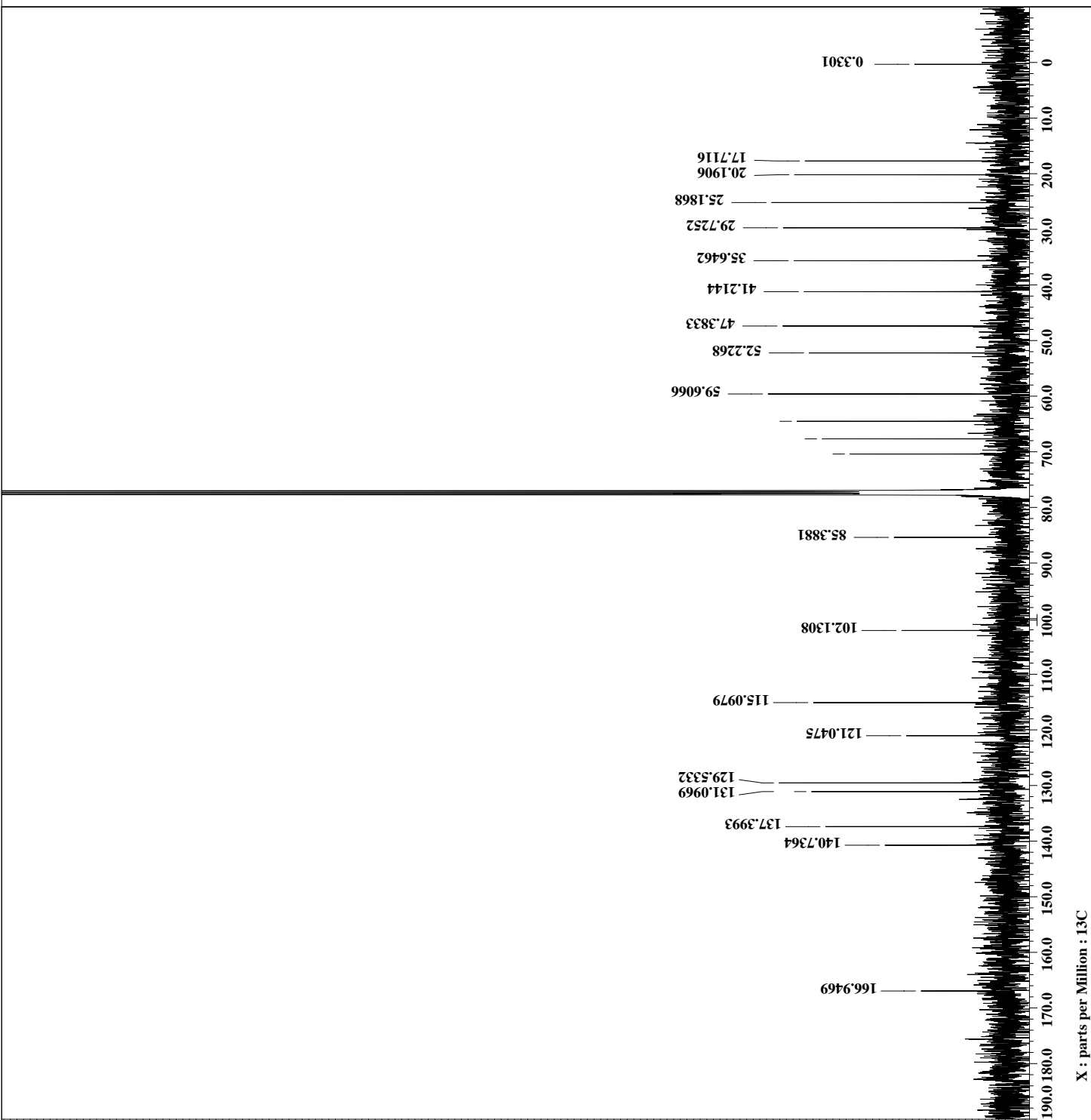
x_90_width = 10.5[us]
x_acq_time = 2.18365952[s]
x_angle = 45[deg]
x_atn = 1.4[dB]
x_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 1[s]
Repetition_time = 3.18365952[s]
Temp_get = 25.6[dC]

```



X : parts per Million : 1H

abundance



X : parts per Million : 13C

```

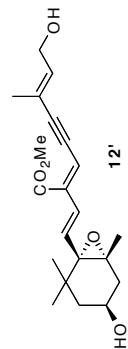
Filename = a2-alcohol-ester-13C-
Author = delta
Experiment = single_pulse_dec
Sample_id = S#456123
Solvent = CHLOROFORM-D
Creation_time = 5-DEC-2009 12:34:50
Revision_time = 12-DEC-2009 18:14:14
Current_time = 12-DEC-2009 18:15:05

Comment = single pulse decouple
Data_format = ID 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 = 584
Total_scans = 584

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 = WAITZ
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 = 26.2[dc]

```



katsum750_03.1000.1
 Iridinin Derivative 15E-A-2 /CDCI3 /298K(TE=300.5)
 C{1H} 1Pulse with CPD (zpgp30):CPTCI-Z

202.563
 202.544
 170.400
 166.638
 135.857
 132.692
 132.678
 131.287
 130.315
 128.013
 118.066
 117.708
 117.597
 115.396
 103.272
 87.617
 81.021
 77.404
 77.374
 77.353
 77.322
 77.307
 77.178
 77.009
 76.839
 76.729
 76.692
 72.682
 70.131
 67.947
 67.674
 64.214
 51.802
 51.578
 47.648
 47.086
 46.598
 45.411
 45.221
 40.909
 35.784
 35.346
 33.743
 32.059
 31.930
 31.275
 29.708
 29.686
 29.666
 29.412
 29.173
 28.931
 28.917
 28.677

Current Data Parameters
 NAME katsum750_03
 EXPNO 1000
 PROCNO 1

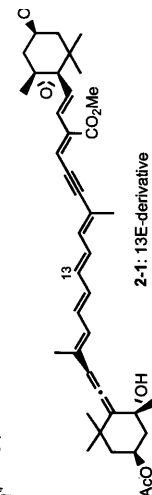
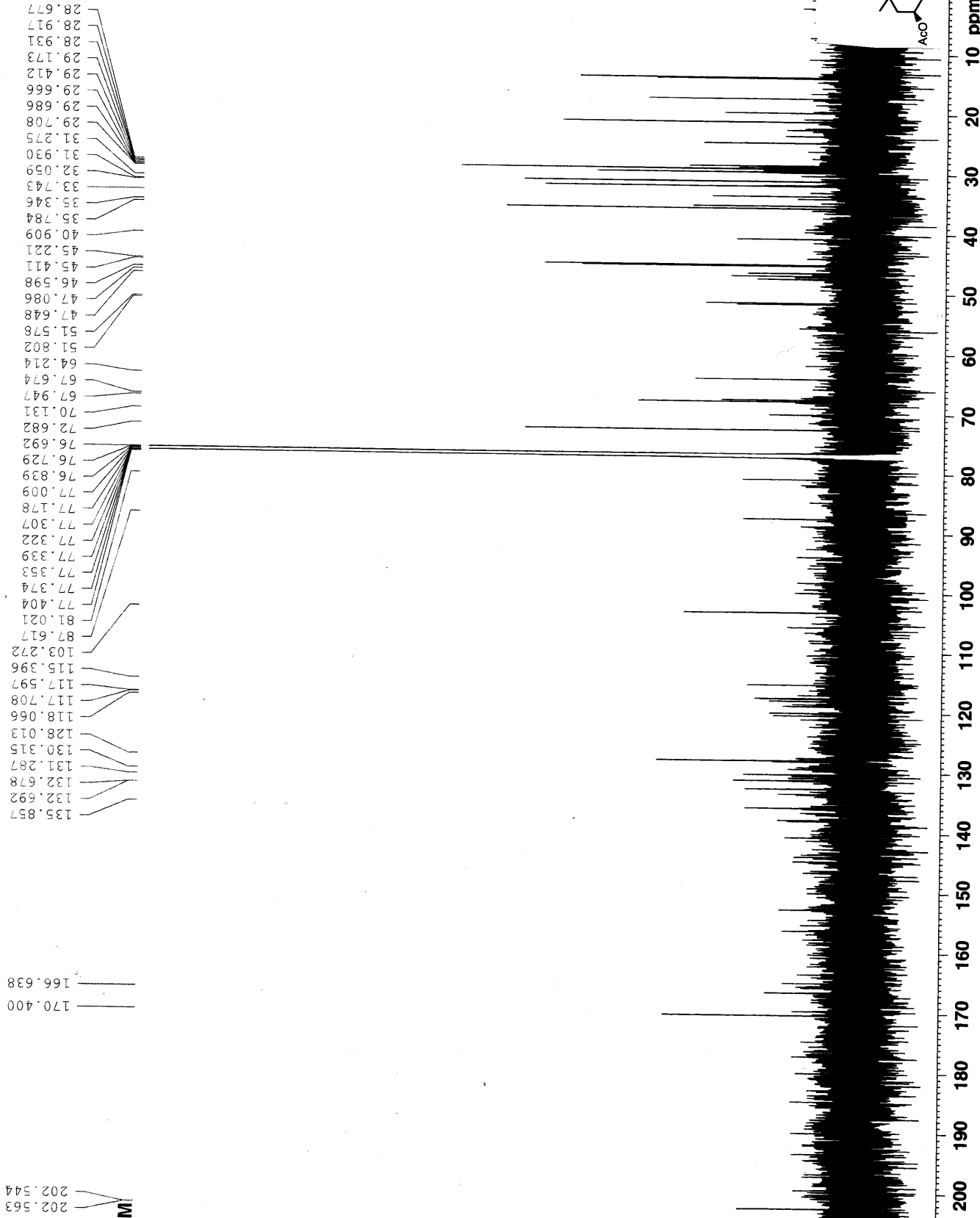
F2 - Acquisition Parameters
 Date_ 20070724

Time 5.52
 INSTRUM Spect
 PROBHD 5 mm CPTCI 1H-
 PULPROG zpgp30
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 4
 SWH 45045.047 Hz
 FIDRES 0.687333 Hz
 AQ 0.7274996 sec
 RG 4096
 DW 11.100 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

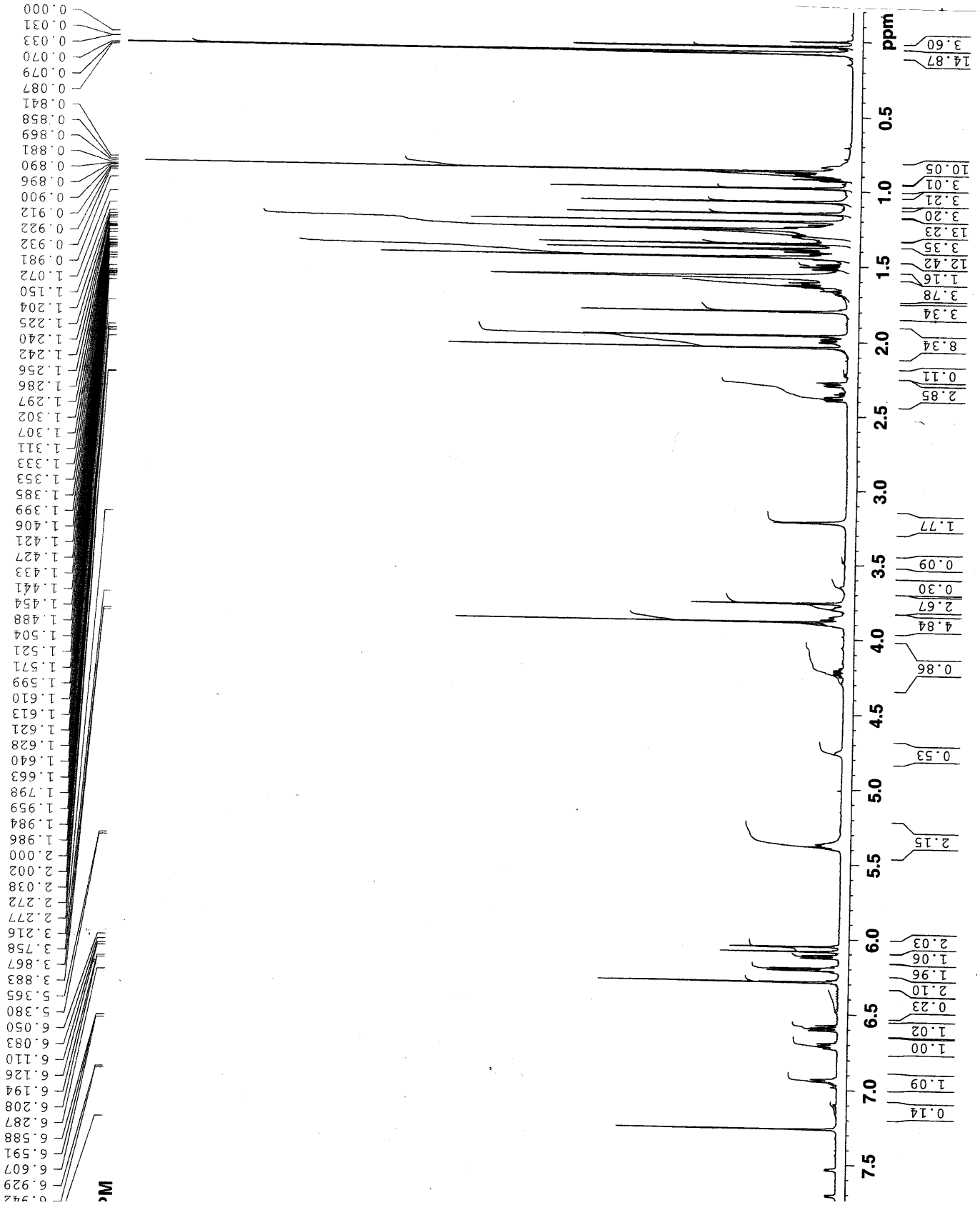
=====
 CHANNEL f1
 NUC1 13C
 P1 15.00 usec
 PL1 -4.90 dB
 SFO1 188.632006 MHz

=====
 CHANNEL f2
 waltz16
 CPDPRG2 1H
 NUC2 13C
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 16.80 GB
 PL13 16.80 GB
 SFO2 750.1330005 MHz

F2 - Processing parameters
 SI 32768
 SF 188.6203390 MHz
 EM
 WDW 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.00



iridinin Derivative 15Z-A-2 /CDC13 /298K(TE=300.5)
 | 1Pulse (zg30):CPTCI-Z

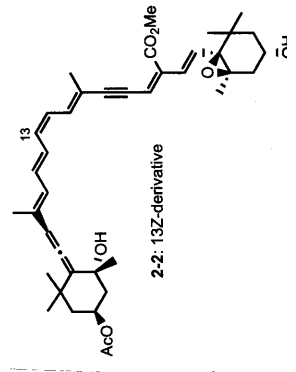


Current Data Parameters
 NAME Katsum750_04
 EXPNO 1
 PROCNO 1

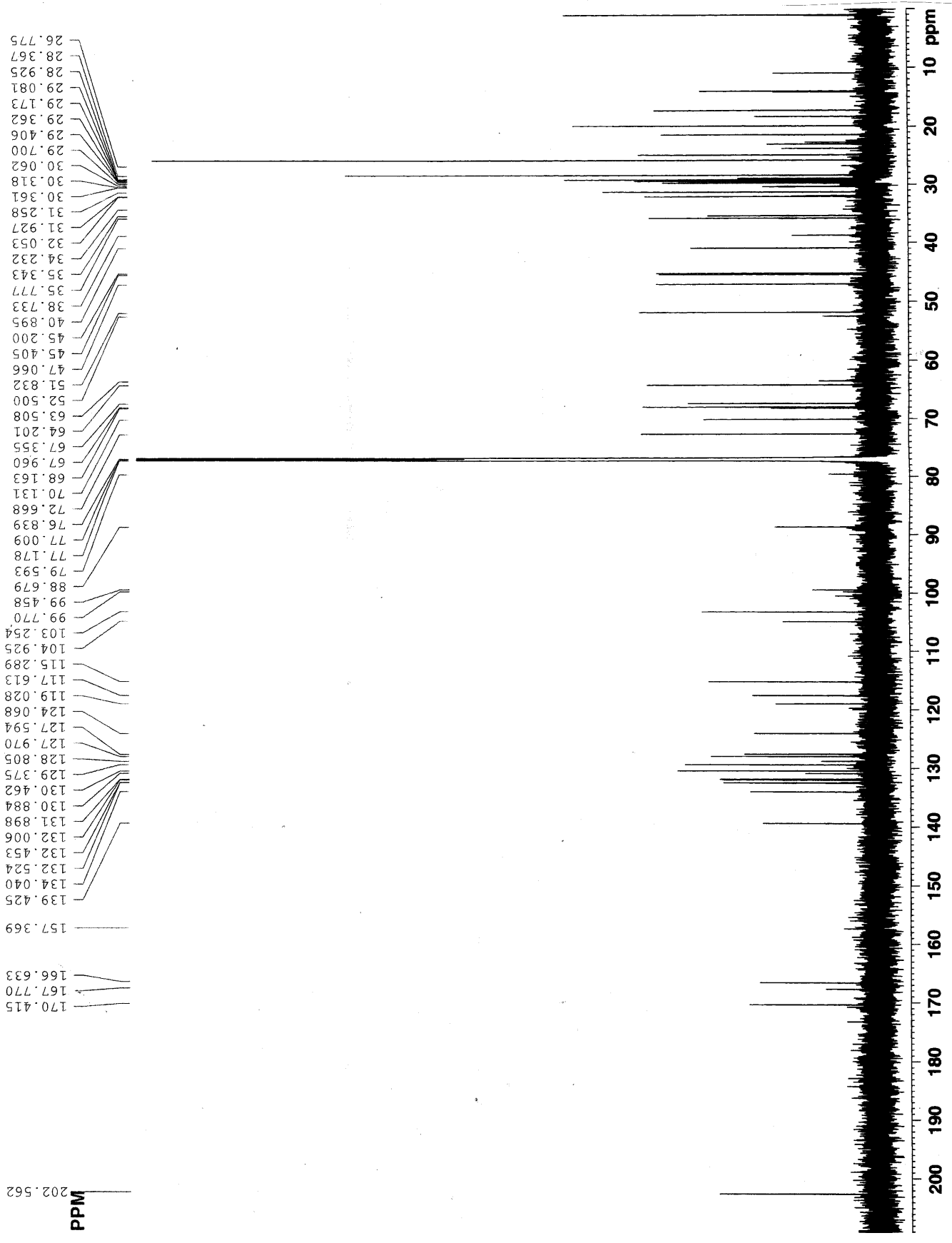
F2 - Acquisition Parameters
 Date_ 20070724
 Time 14.43
 INSTRUM spect
 PROBHD 5 mm CPTCI 1H-
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 4
 SMH 11261.262 Hz
 FIDRES 0.171833 Hz
 AQ 2.9098485 sec
 RG 64
 DW 44.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCWRK 0.0150000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -3.00 dB
 SFO1 750.1336006 MHz

F2 - Processing parameters
 SI 32768
 SF 750.1300165 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 0.10



Peridinin Derivative 15Z-A-2 /CDC13 /298K(TE=300.5)
 13C{1H} 1Pulse with CPD (zgpg30):CPTCI-Z



Current Data Parameters
 NAME katsu750_04
 EXPNO 1000
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070725
 Time 2.51
 INSTRUM spect
 PROBHD 5 mm CPTCI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 4096
 DS 4
 SWH 45045.047 Hz
 FIDRES 0.687333 Hz
 AQ 0.727496 sec
 RG 16384
 DW 11.100 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

==== CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 -4.30 dB
 SFO1 188.6392006 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 16.80 dB
 PL13 16.80 dB
 SFO2 750.1330005 MHz

F2 - Processing parameters
 SI 32768
 SF 188.6203403 MHz
 EM
 WDW 0
 SSB 1.00 Hz
 LB 0
 GB 0
 PC 1.00

```

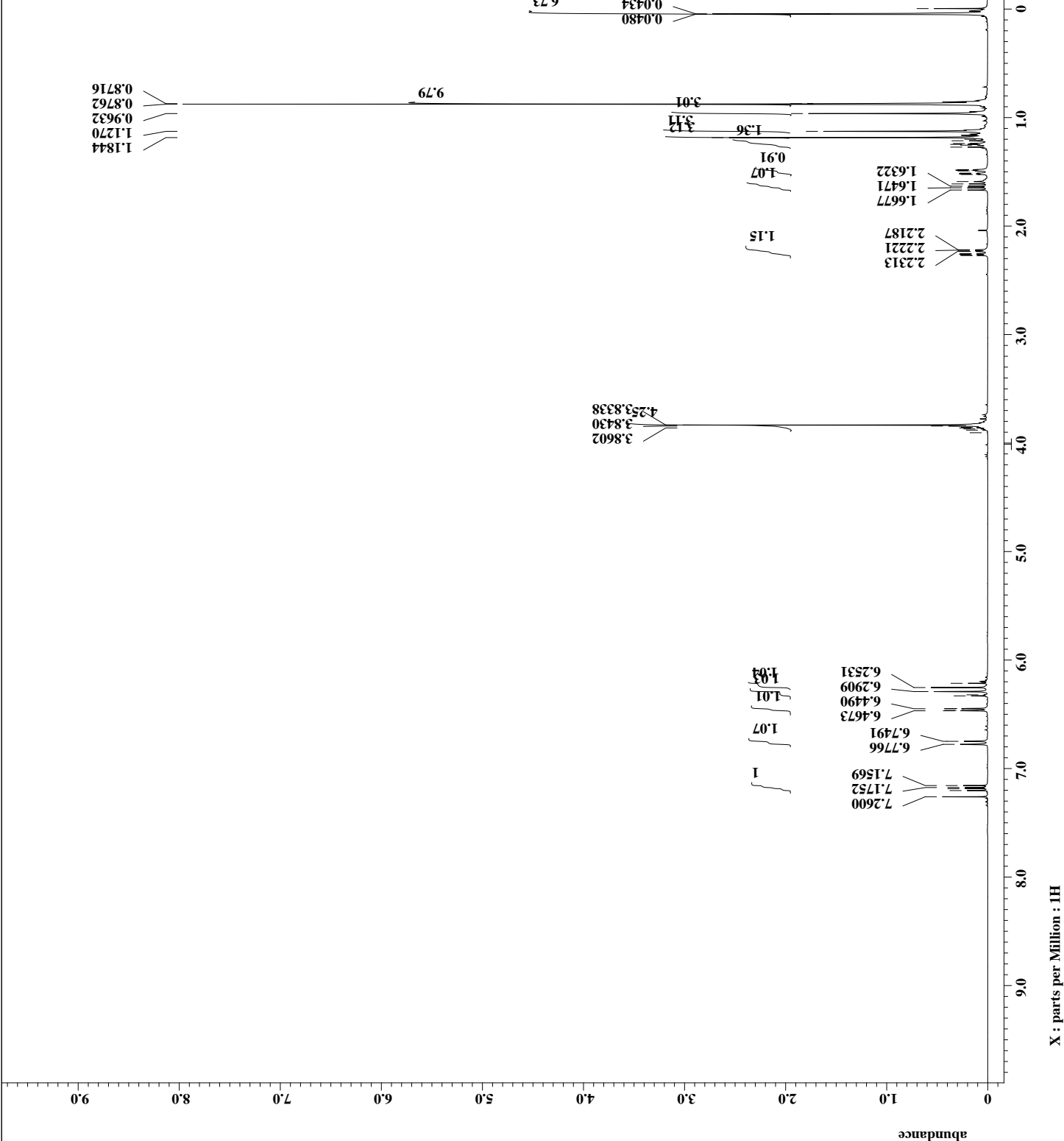
Filename = a3-cis-bromide-1H-4.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 7-DEC-2009 20:19:01
Revision_time = 12-DEC-2009 14:48:06
Current_time = 12-DEC-2009 14:48:39

Comment = single_pulse
Data_format = ID 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 = 10.5[us]
x_acq_time = 2.18365952[s]
x_angle = 45[deg]
x_atn = 1.4[dB]
x_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 1[s]
Repetition_time = 3.18365952[s]
Temp_get = 24[dc]

```



X : parts per Million : 1H

```

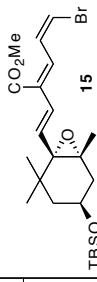
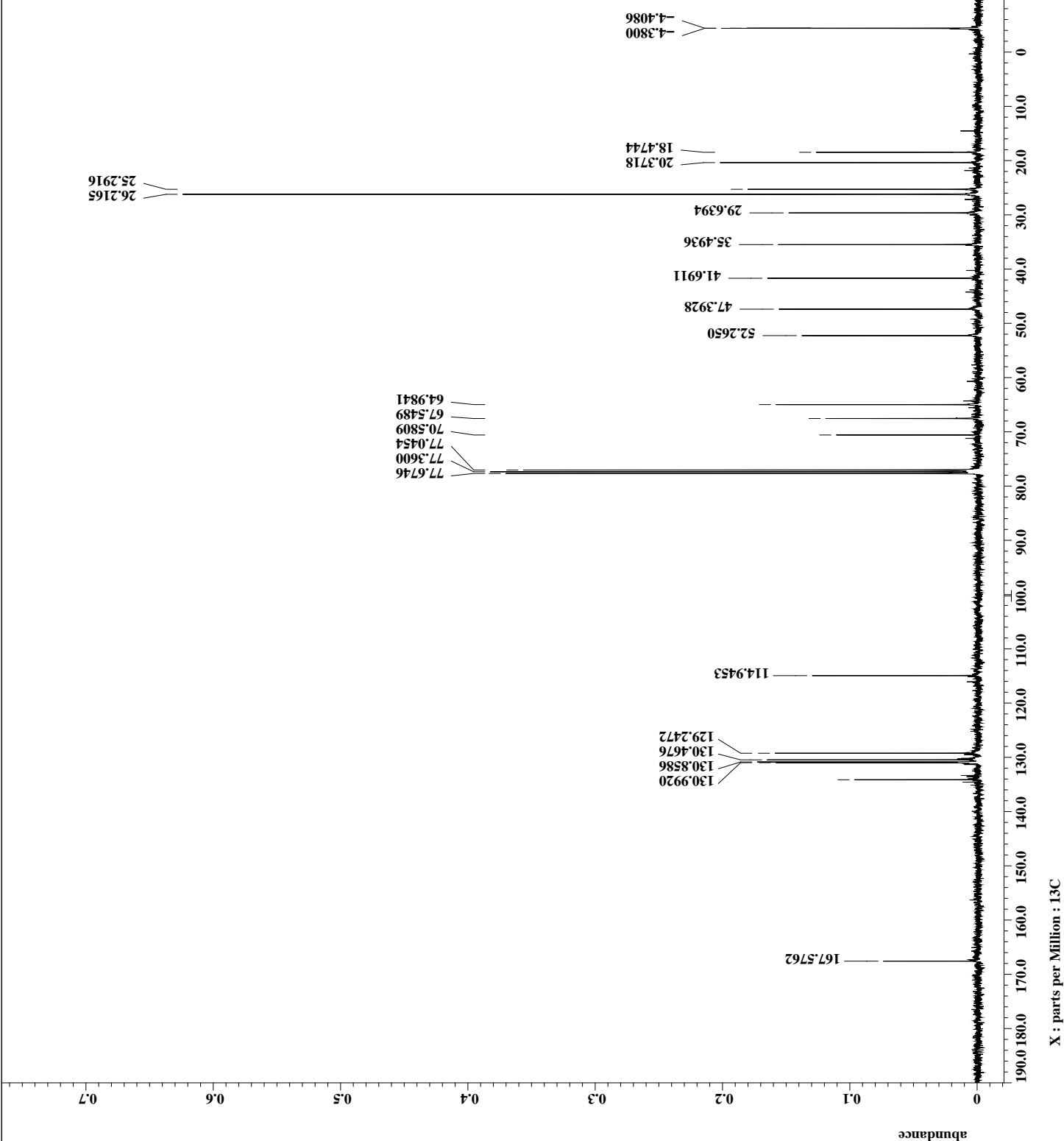
Filename = a3-cis-bromide-13C-3.
Author = delta
Experiment = single_pulse_dec
Sample_id = S#435638
Solvent = CHLOROFORM-D
Creation_time = 8-DEC-2009 11:22:43
Revision_time = 12-DEC-2009 18:17:33
Current_time = 12-DEC-2009 18:17:59

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

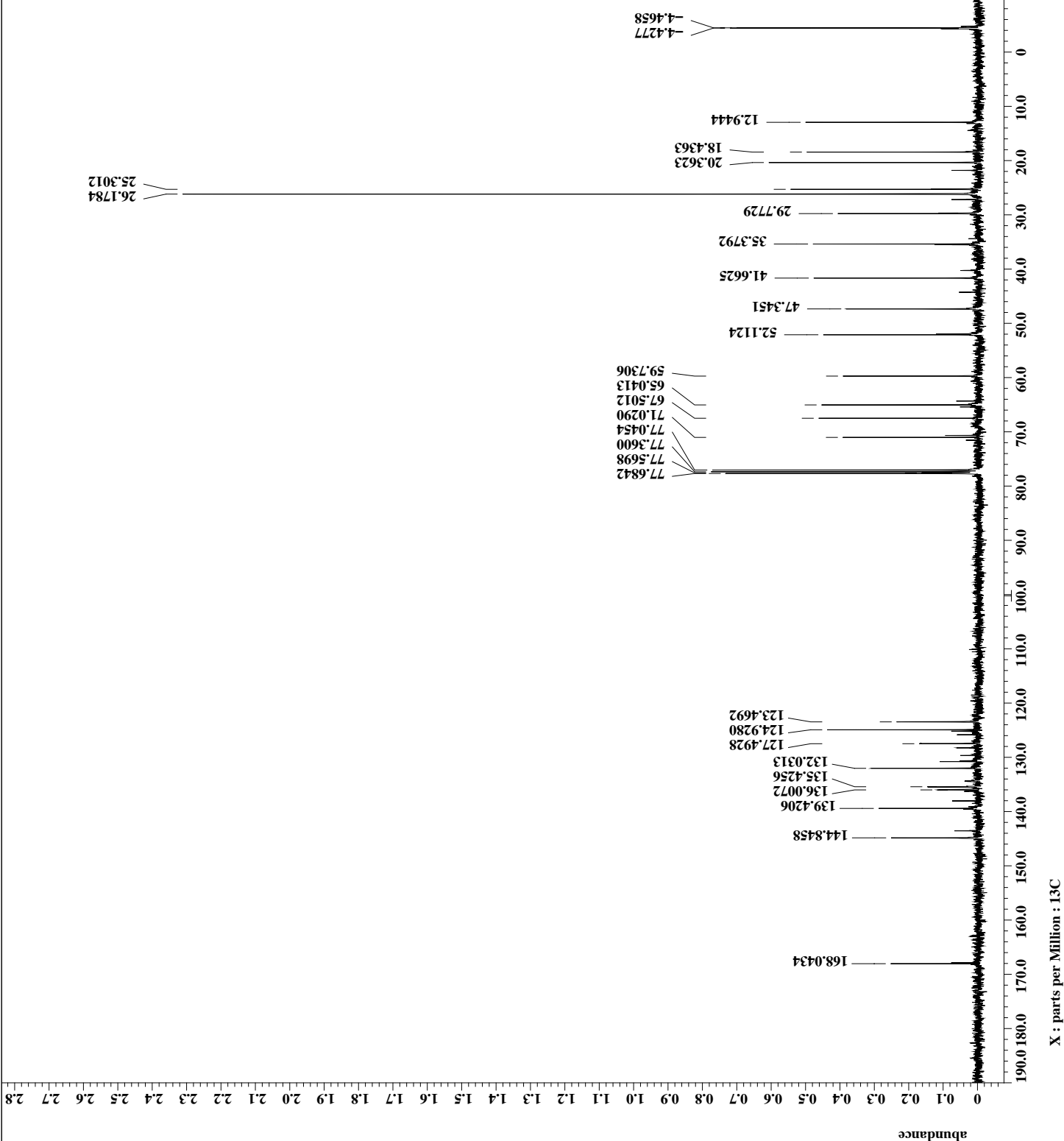
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 213
Total_scans = 213

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 = WAITZ
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 = 24.9[dc]

```



X : parts per Million : 13C



```

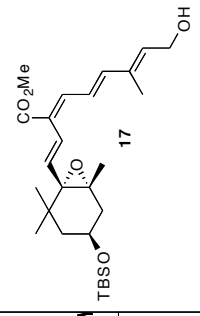
Filename = a3-tetraene-alcohol-1
Author = delta
Experiment = single_pulse_dec
Sample_id = S#705366
Solvent = CHLOROFORM-D
Creation_time = 8-DEC-2009 18:37:37
Revision_time = 12-DEC-2009 18:19:37
Current_time = 12-DEC-2009 18:20:13

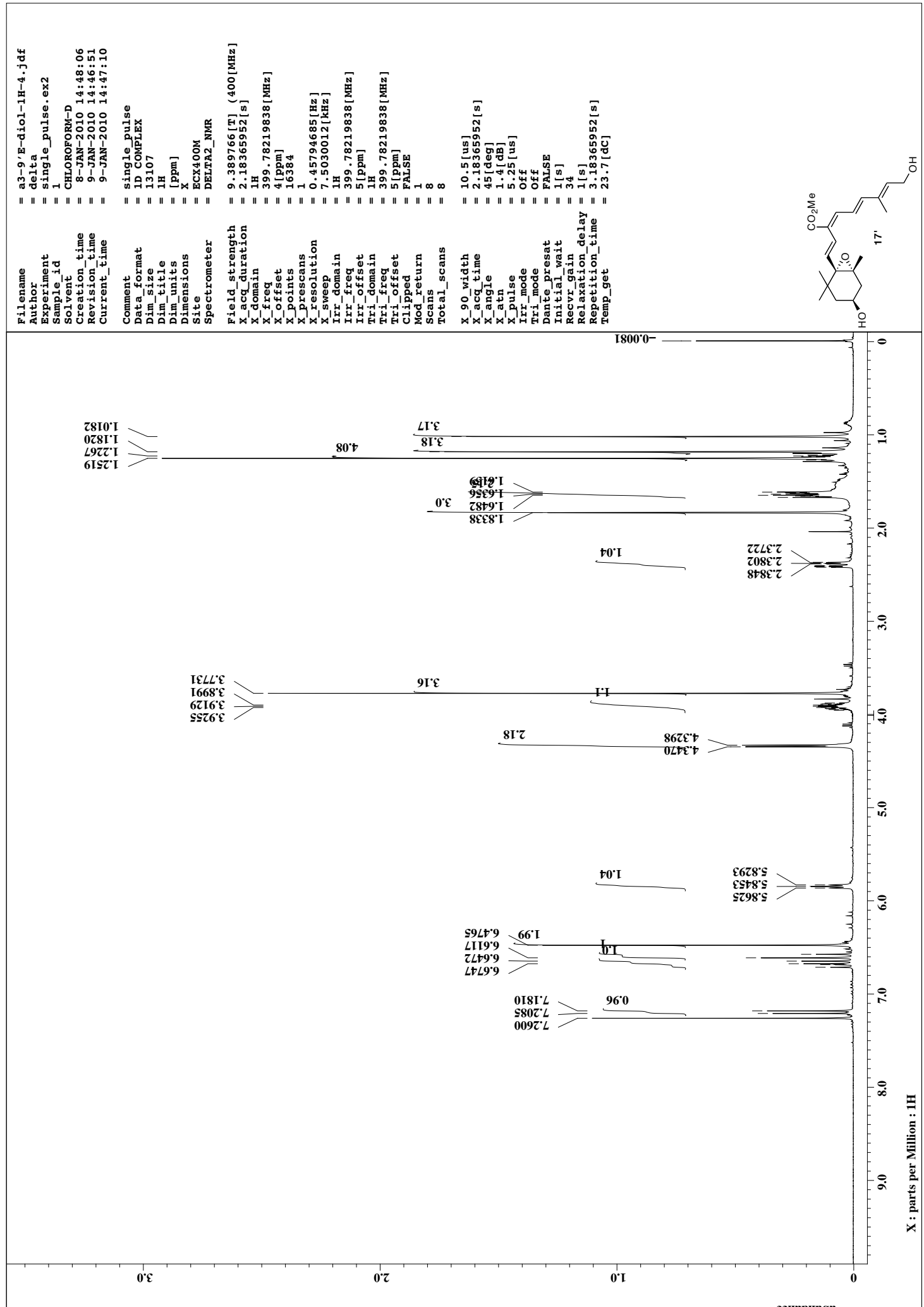
Comment = single pulse decouple
Data_format = ID COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR

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 = 69
Total_scans = 69

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 = WAITZ
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 = 24.9[dc]

```





```

Filename = a3-9'E-diol-1H-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 8-JAN-2010 14:48:06
Revision_time = 9-JAN-2010 14:46:51
Current_time = 9-JAN-2010 14:47:10

Comment = single_pulse
Data_format = ID 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
Total_scans = 8

x_90_width = 10.5[us]
x_acq_time = 2.18365952[s]
x_angle = 45[deg]
x_atn = 1.4[dB]
x_pulse = 5.25[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 = 23.7[degC]

```

```

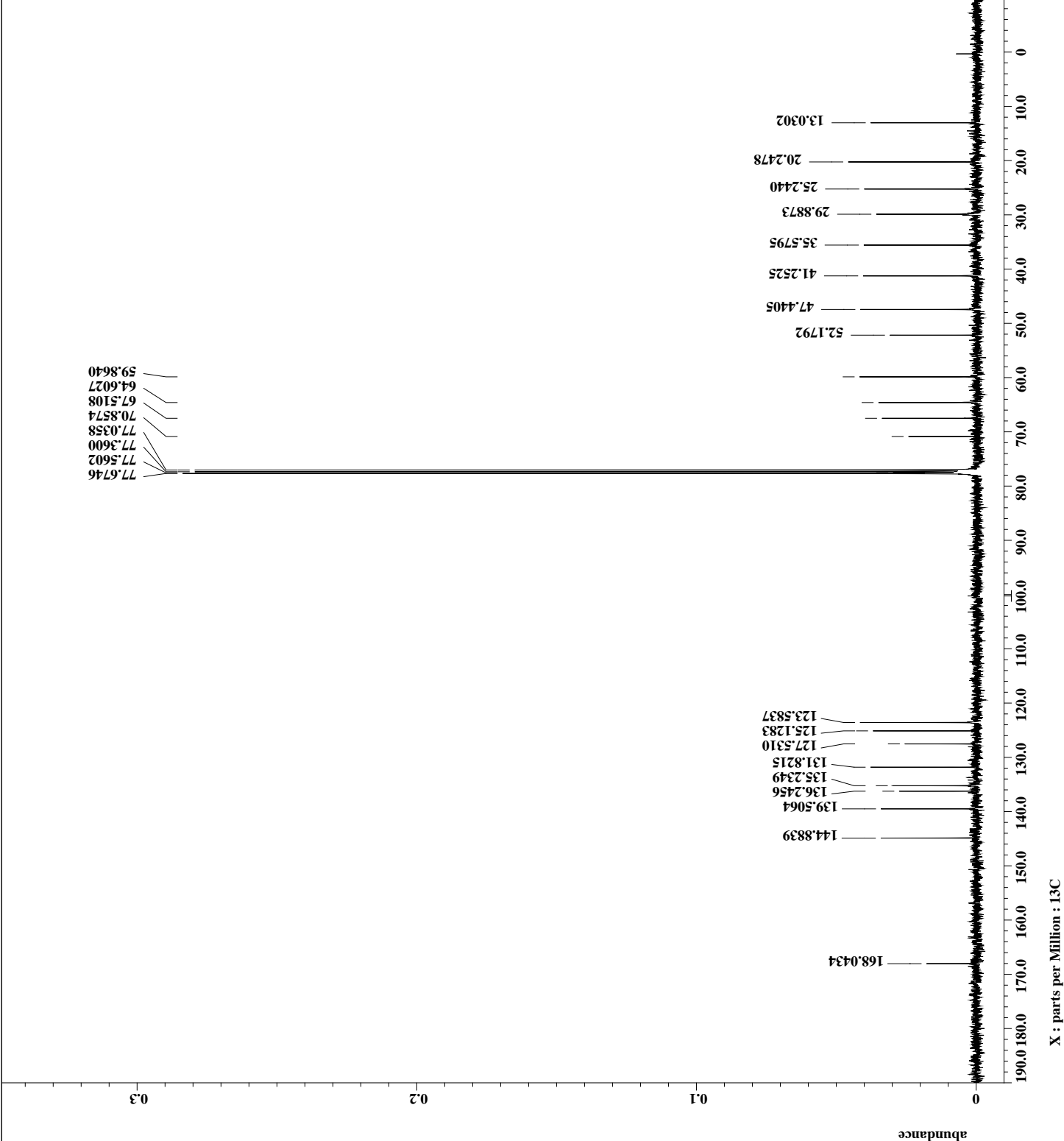
Filename = a3-9'E-diol-13C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#581989
Solvent = CHLOROFORM-D
Creation_time = 8-JAN-2010 15:42:17
Revision_time = 9-JAN-2010 14:37:58
Current_time = 9-JAN-2010 14:40:01

Comment = single pulse decouple
Data_format = ID 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 = 388
Total_scans = 388

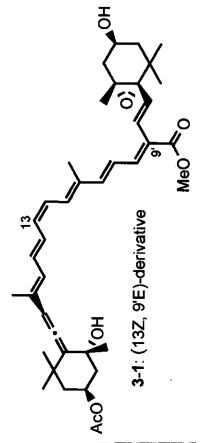
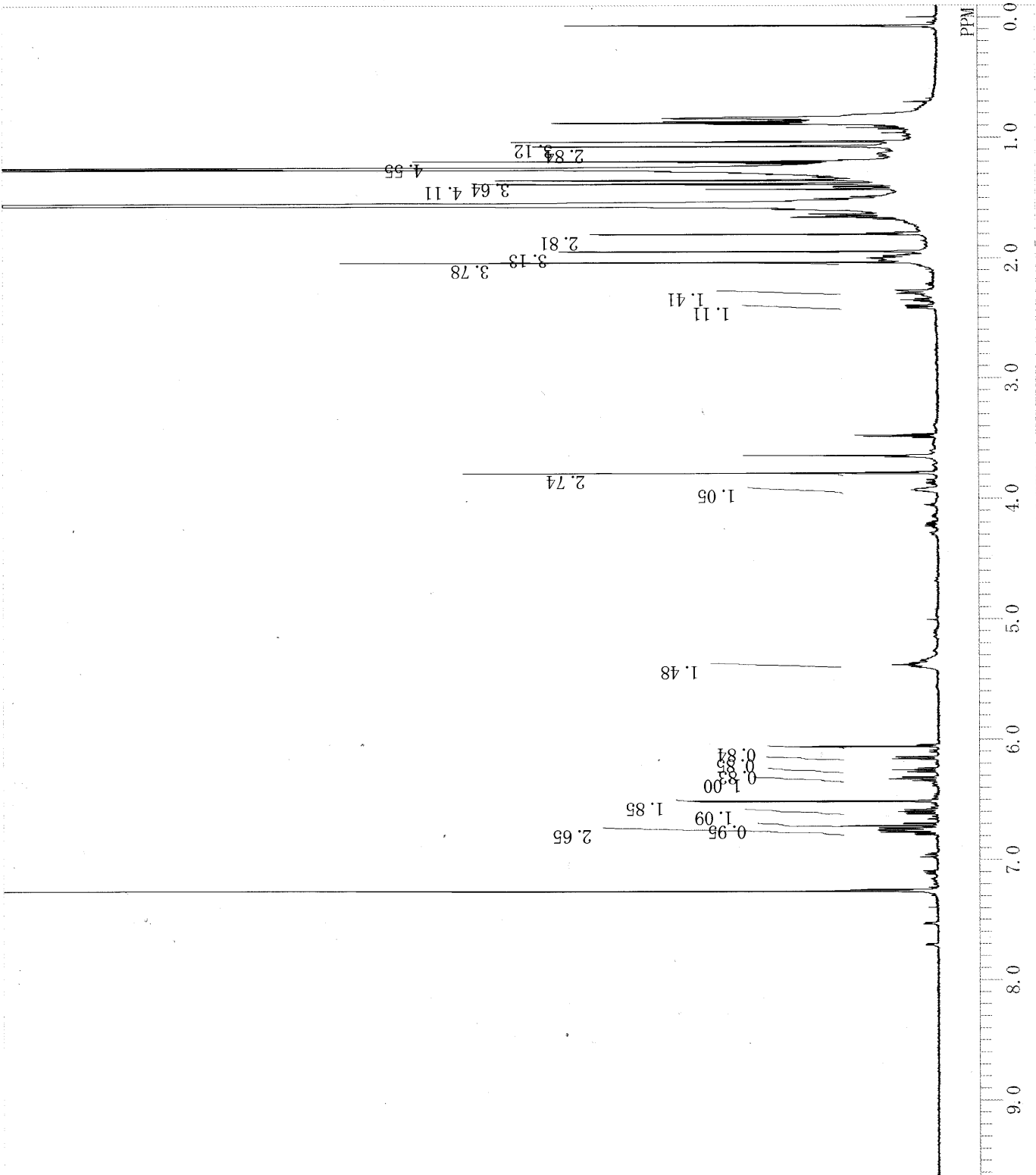
X_90_width = 9.2[us]
X_acq_time = 1.04333312[s]
X_angle = 45[deg]
X_atn = 6.6[db]
X_pulse = 4.6[us]
Irr_atn_dec = 22.2[db]
Irr_atn_noe = 22.2[db]
Irr_noise = WAITZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 5[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 6.04333312[s]
Temp_get = 23.4[dc]

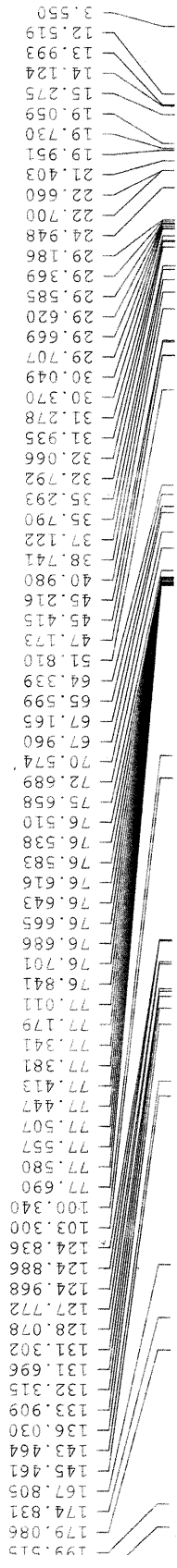
```



X : parts per Million : 13C

Ir
 katsum750_08.1.1
 Thu Aug 23 14:36:01 2007
 OBNUC IH
 EXMOD zg30
 OBFREQ 750.13 MHz
 OBSETE 3.60 KHz
 OBFIN 0.62 Hz
 POINT 32768
 FREQU 11261.26 Hz
 SCANS 16
 ACQTM 2.9098 sec
 PD 1.0000 sec
 PW1 9.85 usec
 IRNUC 26.9 c
 CTEMP 7.26 ppm
 SLVNT CDC13
 EXREF 0.30 Hz
 BF 64
 RGAIN





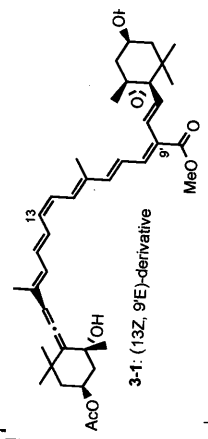
Current Data Parameters
 NAME katsum750_08
 EXPNO 2000
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070805
 Time 23.53
 INSTRUM spect
 PROBD 5 mm CPTCI IH-
 PULPROG zgpg30
 TD 65402
 SOLVENT CDCl3
 NS 4096
 DS 4
 SWH 45045.047 Hz
 FIDRES 0.688741 Hz
 AQ 0.7260122 sec
 RG 16384
 DW 11.100 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

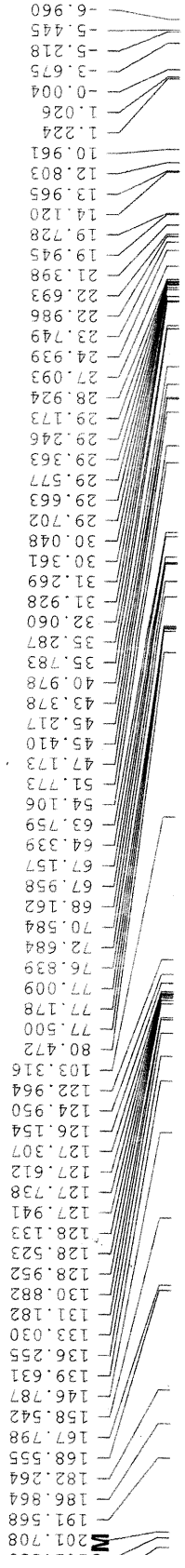
=====
 CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 -4.90 dB
 SFO1 188.6392006 MHz

=====
 CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 16.95 dB
 PL13 16.95 dB
 SFO2 750.1330005 MHz

F2 - Processing parameters
 SI 32768
 SF 188.6203390 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.01



sum/50.0/1.1000.7
 Z,15'E)-(A-3)/CDC13 /298K(TE=300.5)
 2{1H} 1Pulse with CPD (zgpg30):CPTCl-Z



Current Data Parameters
 NAME katsum750_07
 EXPNO 1000
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070803
 Time 23.23

INSTRUM spect
 PROBHD 5 mm CPYCI 1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 4096
 DS 4
 SWH 45045.047 Hz
 FIDRES 0.667333 Hz
 AQ 0.7274996 sec
 RG 16384
 DW 11.100 usec
 DE 6.00 usec
 TE 300.0 K
 DI 2.00000000 sec
 GLL 0.03000000 sec
 DELTA 1.89999998 sec
 ACRESST 0.00000000 sec
 PCWRRK 0.01500000 sec

===== CHANNEL f1 =====
 NUQC1 L3C
 FL 15.00 usec
 PLL1 -4.90 dB
 SFO1 188.6392006 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUQC2 IH
 PCPD2 100.00 usec
 PLL2 120.00 dB
 PLL3 16.95 dB
 PLL4 16.95 dB
 SFO2 750.1330005 MHz

F2 - Processing parameters
 SI 32768
 SF 188.6203403 MHz
 EN
 SSB EN
 LB 1.00 Hz
 GB 0
 PC 0.30

