Supporting Information for:

Syntheses of C33-, C35-, and C39-Peridinin and their Spectral Characteristics

Takayuki Kajikawa,[a] Shinji Hasegawa,[a] Takashi Iwashita,[b] Toshiyuki Kusumoto,[c] Hideki Hashimoto,[c] Dariusz M. Niedzwiedzki,[d] Harry A. Frank,[d] and Shigeo Katsumura[a*]

[a]School of Science and Technology, Kwansei Gakuin University, Gakuen 2-1, Sanda, Hyogo 669-1337 [b]Suntory Institute For Bioorganic Research, Wakayamadai 1-1-1, Shimamoto, Mishimagunn, Osaka 618-8503 [c]Department of Physics and CREST/JST, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan, and [d]Department of Chemistry, University of Connecticut, Storrs, CT, 06269-3060, USA

E-mail: katsumura@kwansei.ac.jp

General

All commercially available reagents were used without further purification. Tetrahydrofuran (THF) was refluxed over and distilled from sodium-benzophenone ketyl. 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.

Experimental

(1Z,3E)-6-(1'R,2'R,4S')-4'-Acetoxy-2'-hydroxy-2',6',6'-trimethylcyclohexylidene]-1-iodo-1,4-dimethylhexa-1,3,5-triene 5. To a suspention of ethylphosphonium bromide (651 mg, 2.24 mmol) in THF (7.04 mL) was added sodium bis(trimethylsilyl)amide (1.0M in THF, 4.47 mL, 4.47 mmol) at 0 ºC. The mixture was stirred for 15 min at the same temperature, and then to the resulting mixture was added N-iodosuccinimide (502 mg, 2.24 mmol) at 0 ºC. After the reaction mixture was stirred for 30 min, aldehyde **11** (237 mg, 0.75 mmol) was added at the same temperature, and then the mixture was stirred for 15 min at the same temperature. The resulting mixture was poured into water, and 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 vinyl iodide **5** (237 mg, 70%) as a yellow solid: $[\alpha]^{23}_D$ -16.4 (c 0.96, $CHCl_3$); IR (KBr disk, cm^{-1}) 3462, 2961, 2982, 2872, 2858, 1932, 1728, 1585, 1458, 1375, 1250, 1184, 1163, 1124, 1072, 1032, 972, 883, 856, 742; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.30 (dd, *J* =10.3, 1.4 Hz, 1H), 6.07 (s, 1H), 6.01 (d, *J* =10.3 Hz, 1H), 5.38 (m, 1H), 2.65 (s, 3H), 2.28 (ddd, *J* =12.8, 4.4, 2.1 Hz, 1H), 2.03 (s, 1H), 1.99 (ddd, *J* =12.4, 4.1, 2.3 Hz, 1H), 1.78 (s, 3H), 1.50 (dd, *J* =12.6, 11.5 Hz, 1H), 1.40(m, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.6, 170.7, 134.6, 130.8, 129.7, 118.0, 103.2, 103.1, 73.0, 68.3, 45.8, 45.6, 36.0, 34.7, 32.4, 31.6, 29.5, 21.8, 15.4; ESI-HRMS m/z Calcd for $C_{19}H_{27}IO_3$ $(M+Na)^+$ 453.0903, found 453.0892.

C33-peridinin 2. To a solution of iodide **5** (58 mg, 0.14 mmol) and alkyne **6** (43 mg, 0.14 mmol) in triethylamine (1.36 mL) was added tetrakis(triphenylphosphine)palladium (16 mg, 0.014 mmol) and cuprous iodide (8 mg, 0.042 mmol). After the reaction mixture was stirred for 10 min at 45 ºC, formic acid (0.015 mL, 0.41 mmol) was added at the same temperature, and then the resulting mixture was stirred for 10 min at the same temperature. The 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 30% to 75% ethyl acetate in hexane) in the dark afforded C33-peridinin **2** (29 mg, 35%) as a mixture of the isomers in a red film. A solution of the obtained mixture containing *all trans*-C33-peridinin **2** and its *cis*-isomer in benzene was left at room temperature under irradiation with fluorescence light. After 2 days, the 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: 430 nm; retention time: (all-*trans*-isomer) 80 min, (11Z, 11'Z-isomer) 82 min, (11E, 11'E-isomer) 85 min.] in the dark afforded the desired optically active C33-peridinin **2** as a red film: $[\alpha]^{23}_D$ -93.9 (c 0.98, $CHCl_3$); IR (KBr disk, cm^{-1}) 3449, 2961, 2926, 2855, 1925, 1751, 1748, 1736, 1655, 1637, 1560, 1458, 1377, 1303, 1261,1250, 1165, 1030; ^1H NMR ($CDCl_3$ 400 MHz) δ 7.17 (d, *J* =15.6 Hz, 1H), 7.02 (s, 1H), 6.65 (d, *J* =12.1 Hz, 1H), 6.38 (d, *J* =6.3 Hz, 1H), 6.37 (d, *J* =15.6 Hz, 1H), 6.12 (s, 1H), 5.78 (s, 1H), 5.72 (s, 1H), 5.38 (m, 1H), 3.90 (m, 1H), 2.40 (ddd,*J* =14.2, 5.0, 1.6 Hz, 1H), 2.29 (m, 1H), 2.23 (s, 3H), 2.04 (s, 3H), 2.00 (m, 1H) , 1.84 (s, 3H) , 1.65 (m, 2H), 1.51 (m, 1H) , 1.42 (m, 1H) , 1.39 (s, 3H), 1.35 (s, 3H) , 1.29 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.0, 170.3, 168.7, 146.5, 136.4, 136.3, 133.6, 133.6, 133.4, 124.7, 124.1, 121.7, 119.6, 117.7, 103.7, 72.6, 70.4, 67.9, 67.5, 64.2, 47.1, 45.4, 45.2, 40.9, 35.9, 35.3, 32.0, 31.2, 29.5, 29.1, 24.9, 21.4, 19.9, 15.2, 14.1; ESI-HRMS m/z Calcd for $C_{35}H_{46}O_7$ $(M+Na)^+$ 601.3141, found 601.3160.

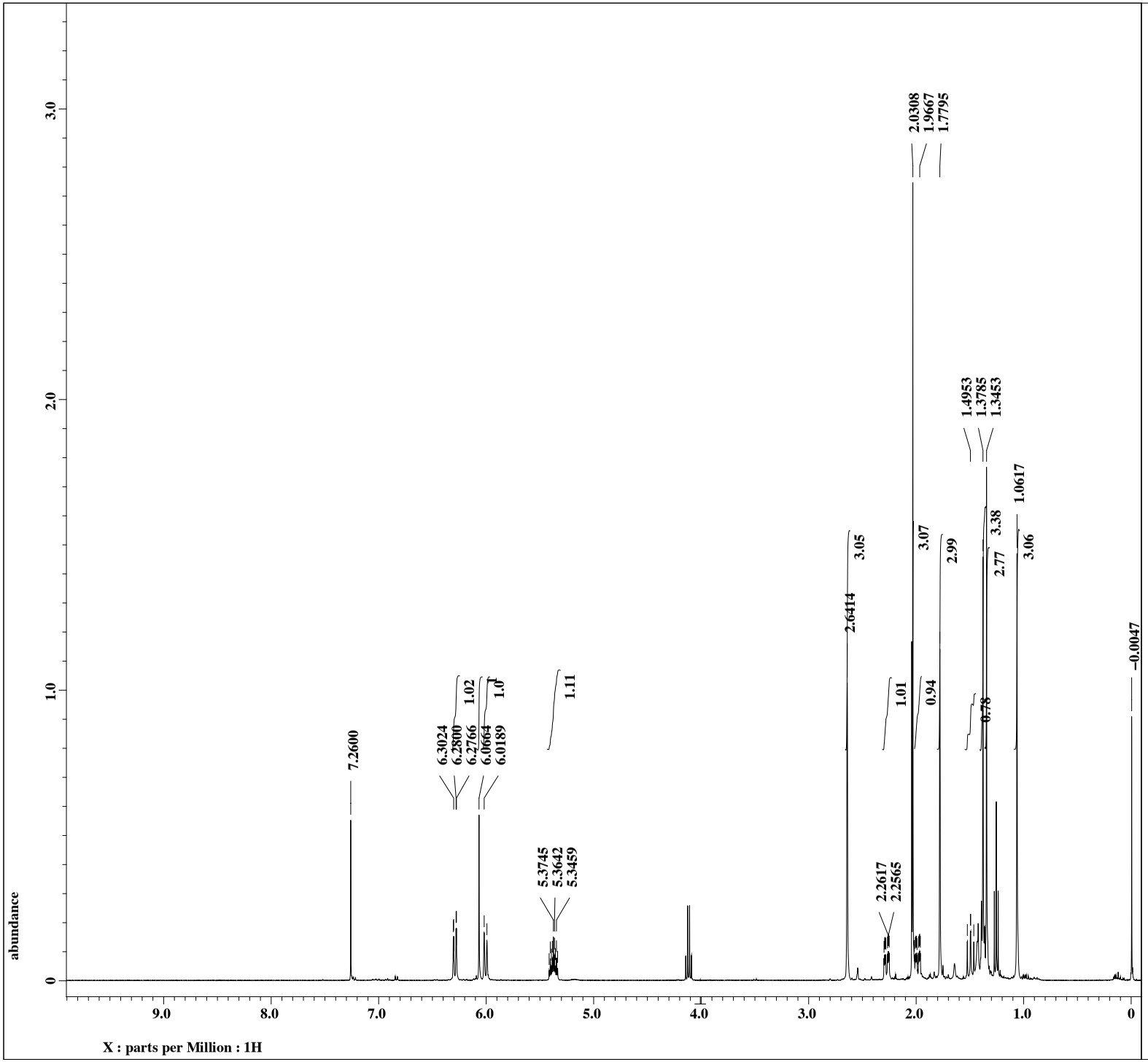
C35-peridinin 3. To a solution of sulfone **7** (43 mg, 0.090 mmol) and aldehyde **8** (31 mg, 0.090 mmol)

in THF (1.35 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.27 mL, 0.27 mmol) at -78 ºC 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 and THF (1:1). 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 15% to 30% acetone in hexane) in the dark afforded the C35-peridinin **3** (21 mg, 39%) as a mixture of the isomers in a red film. A solution of a mixture of the *all trans*-C35-peridinin **3** and its *cis*-isomer in benzene was left at room temperature under the irradiation with fluorescence light. After 2 days, the separation by preparative HPLC [column: Develosil CN-UG (0.6 x 25 cm); mobile phase: acetone / *n*-hexane = 1 / 8; flow rate: 1.5 mL / min.; UVdetect: 430 nm; retention time: (*all trans*-isomer) 66 min, (11Z-isomer) 69 min.] in the dark afforded the desired optically active C35-peridinin **3** as a red film: IR (KBr disk, cm^{-1}) 3449, 2914, 2855, 1736, 1464, 1377, 1261, 1161, 1095, 1034, 966, 860, 802; ^{1}H NMR ($CDCl_3$ 400 MHz) δ 7.14 (d, *J* =15.6 Hz, 1H), 7.02 (s, 1H), 6.69 (dd, *J* =13.7, 11.4 Hz, 1H), 6.59 (d, *J* =14.0, 11.2 Hz, 1H), 6.37 (d, *J* =15.6 Hz 1H), 6.17 (d, *J* =11.2 Hz 1H), 6.06 (s, 1H), 5.72 (s, 1H), 5.38 (m, 1H), 3.91 (m, 1H), 2.40 (ddd, *J* =14.2, 4.8, 1.4 Hz, 1H), 2.28 (m, 1H), 2.22 (s, 3H), 2.04 (s, 3H), 2.00 (m, 1H), 1.82 (s, 3H), 1.64 (m, 2H), 1.51 (m, 1H) , 1.39 (s, 3H), 1.35 (s, 3H) , 1.36 (m, 2H), 1.21 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 170.3, 168.7, 146.7, 138.1, 136.3, 134.6, 133.6, 133.0, 128.8, 128.3, 124.7, 121.7, 119.2, 117.6, 103.3, 72.6, 70.4, 67.9, 67.5, 64.2, 47.1, 45.4, 45.2, 40.9, 35.8, 35.3, 32.0, 31.3, 29.7, 29.5, 29.2, 24.9, 21.4, 19.9, 15.5, 14.1; ESI-HRMS m/z Calcd for $C_{37}H_{48}O_7$ $(M+Na)^+$ 627.3298, found 627.3282.

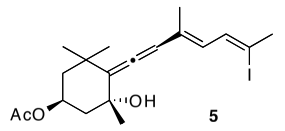
(5Z)-[(2'E,4'E)-6'-Hydroxy-2'-methyl-1'-hexanylidene]-3-[(1"E)-2"-(1"'S,2"'R,4"'S)-4"'hydroxy-1"',2"'-epoxy-2"',6"',6"'-trimethylcyclohex-1"'-ylethene-1"-yl]-2(5H)-furanone 13. To a solution of the alkyne **6** (48 mg, 0.16 mmol) and iodide **12** (80 mg, 0.24 mmol) in triethylamine (1.60 mL) was added tris(dibenzylideneacetone)dipalladium (15 mg, 0.016 mmol), tri(2-fulyl)phosphine (15 mg, 0.064 mmol) and cuprous iodide (9 mg, 0.048 mmol). After the reaction mixture was stirred for 10 min at 45 ºC, formic acid (0.18 ml 4.74 mmol) was added at the same temperature, and then the mixture was stirred for 10 min at the same temperature. The resulting mixture was poured into a saturated aqueous NH_4Cl solution, and 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 50% to 75% ethyl acetate in hexane) afforded alcohol **13** (24 mg, 44%) as a yellow solid: $[\alpha]^{23}_D$ -116.5 (c 0.98, $CHCl_3$); IR (KBr disk, cm^{-1}) 3422, 2961, 2928, 2870, 1749, 1458, 1601, 1554, 1458, 1381, 1363, 1184, 1149, 1049, 943, 767, 653; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (d, *J* =15.6 Hz, 1H), 7.03 (s, 1H), 6.67 (ddt, *J* =15.1, 11.4, 1.8 Hz, 1H), 6.38 (dd, *J* =9.61 Hz, 1H), 6.37 (d, *J* =15.6 Hz, 1H), 6.04 (dt, *J* =15.1, 5.5 Hz, 1H), 5.69 (s, 1H), 4.30 (d, *J* =5.03 Hz, 2H), 3.91 (m, 1H), 2.40 (ddd, *J* =14.6, 5.0, 1.8 Hz 1H), 2.21 (s, 3H), 2.21 (s, 3H), 1.65 (m, 2H), 1.27 (m, 1H), 2.21 (s, 6H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$,100

MHz) δ 169.0, 147.1, 137.0, 136.6, 134.3, 134.1, 132.4, 127.3, 125.6, 121.9, 119.1, 70.8, 67.9, 64.5, 63.7, 47.4, 41.2, 35.6, 29.8, 25.2, 20.2, 15.7; ESI-HRMS m/z Calcd for $C_{22}H_{28}O_5$ $(M+Na)^+$ 395.1834, found 395.1848.

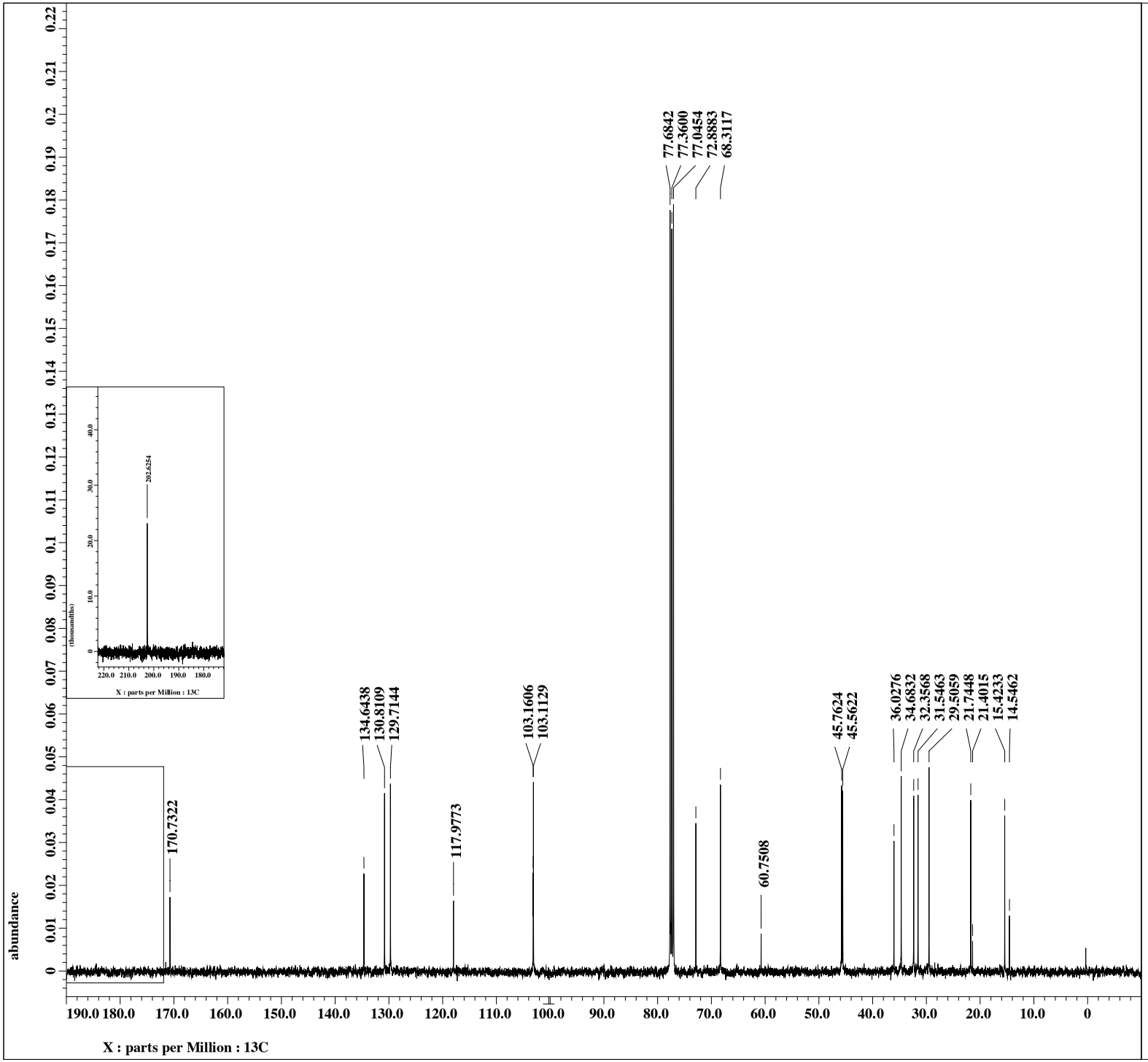
C39-peridinin 4. To a solution of sulfone **9** (56 mg, 0.11 mmol) and aldehyde **10** (39 mg, 0.11 mmol) in THF (1.68 mL) was added dropwise sodium bis(trimethylsilyl)amide (1.0M in THF, 0.11 mL, 0.11 mmol) at -78 ºC in the dark. After being stirred for 5 min at the same temperature, the reaction mixture was poured into water, and then extracted with ethyl acetate and THF (1:1). 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 10% to 20% acetone in hexane) in the dark afforded C39-peridinin **4** (25 mg, 35%) as a mixture of the isomers in a red film. A solution of the obtained mixture containing *all trans*-C39-peridinin **4** and its *cis*-isomer in benzene was left at room temperature under the irradiation with fluorescence light. After 2 days, the 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: 469 nm; retention time: (all-*trans*-isomer) 80 min, (9Z,13E-isomer) 89 min.] in the dark gave crude C39-peridinin **4**, which was further purified by preparative HPLC [column: YMC Carotenoid C30 (1.0 x 25 cm); reverse phase: acetonitrile / methanol / water = 87 / 10 / 3; flow rate: 2.5 mL / min.; UVdetect: 469 nm; retention time: (*all trans*-isomer) 118 min.] in the dark afforded the desired optically active C39-peridinin **4** as a red film: IR (KBr disk, cm^{-1}) 3422, 2928, 2851, 1741, 1664, 1464, 1377, 1261, 1093, 1206, 800; ^1H NMR ($CDCl_3$, 750 MHz) δ 7.17 (d, *J* =15.5 Hz, 1H), 7.02 (s, 1H), 6.61 (dd, *J* =13.4, 13.1 Hz, 1H), 6.57 (dd, *J* =15.1, 12.0 Hz, 1H), 6.48 (dd, *J* =13.7, 11.3, Hz, 1H), 6.46 (d, *J* =11.7 Hz, 1H), 6.45 (dd, *J* =14.8, 11.7 Hz, 1H), 6.39 (dd, *J* =14.4, 11.0 Hz, 1H), 6.38 (d, *J* =15.5 Hz, 1H), 6.10 (d, *J* =11.7 Hz, 1H), 5.73 (s, 1H), 5.38 (m, 1H), 3.91 (m, 1H), 2.40 (dd,*J* =14.4, 4.8 Hz, 1H), 2.28 (m, 1H), 2.23 (s, 3H), 2.04 (s, 3H), 2.01 (m, 1H), 1.79 (s, 3H), 1.64 (m, 2H), 1.50 (m, 1H), 1.41 (m, 1H) , 1.38 (s, 3H), 1.35 (s, 3H) , 1.30 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 188MHz) δ 202.6, 170.4, 168.8, 146.8, 138.0, 137.0, 136.3, 135.6, 134.1, 133.7, 133.4, 133.1, 132.9, 130.9, 129.2, 128.2, 124.8, 121.8, 119.2, 117.6, 103.3, 72.7, 70.5, 68.0, 67.5, 64.2, 47.1, 45.4, 45.2, 41.0, 35.8, 35.3, 32.1, 31.3, 29.5, 29.2, 24.9, 21.4, 19.9, 15.4, 14.0; ESI-HRMS m/z Calcd for $C_{41}H_{52}O_7$ $(M+Na)^+$ 679.3611, found 679.3585.



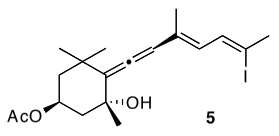

```
Filename          = iodide methyl C33 for
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  9-JAN-2009 11:06:19
Revision_time     = 24-AUG-2009 11:07:43
Current_time      = 24-AUG-2009 11:14:53

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        = 10.5[us]
X_acq_time        = 4.36731904[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        = 36
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 23.8[dC]
```



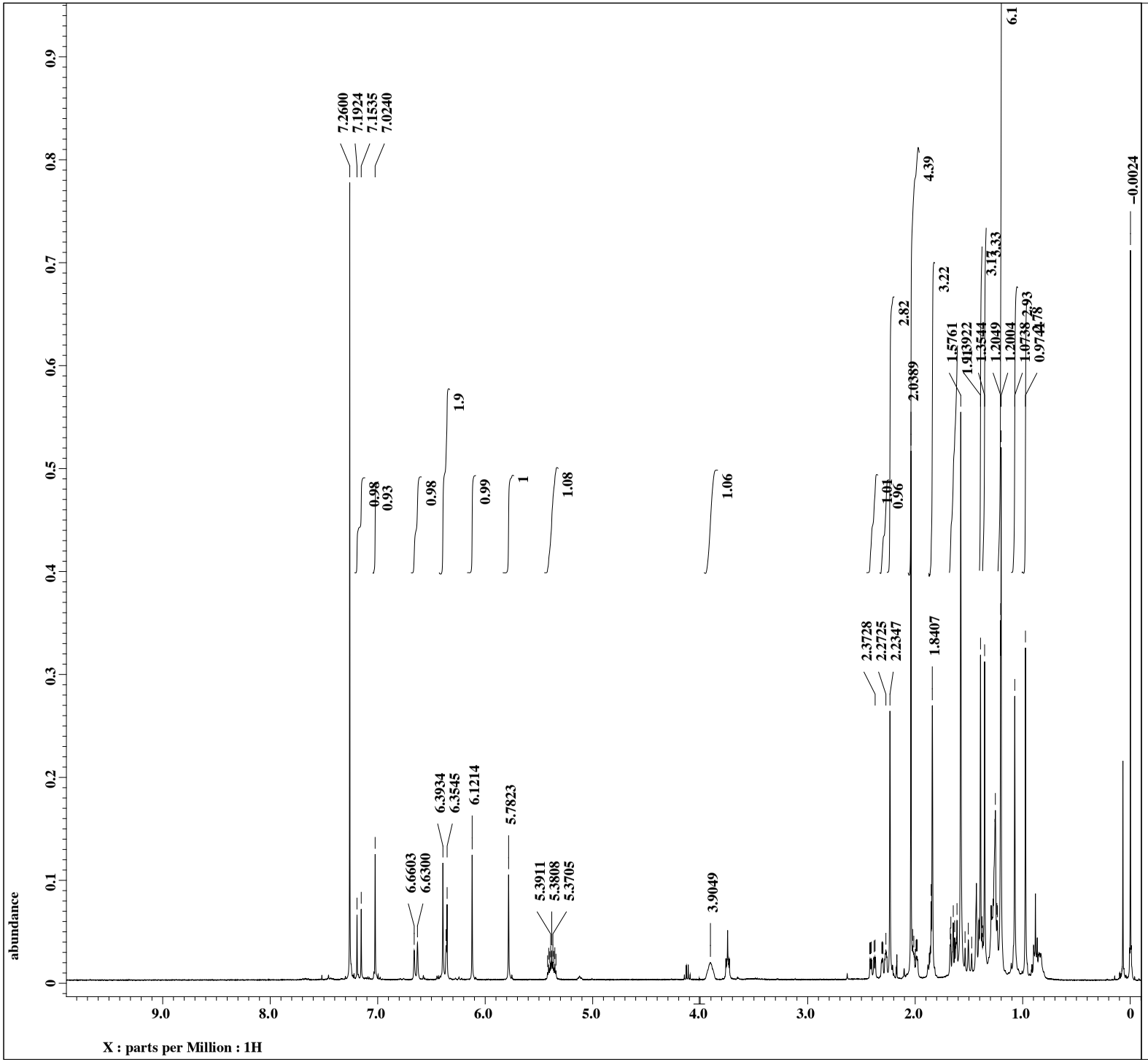
5




```
Filename          = iodide methyl 13C for
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#402267
Solvent           = CHLOROFORM-D
Creation_time     =  9-JAN-2009 12:05:58
Revision_time     = 24-AUG-2009 10:57:43
Current_time      = 24-AUG-2009 10:59:21

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             = 1120
Total_scans       = 1120

X_90_width        = 8.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.2[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        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.4[dC]
```



5

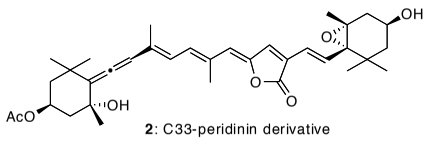


Filename = C33 peridinin derivat
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 11-DEC-2008 17:05:46
Revision_time = 24-AUG-2009 11:53:08
Current_time = 24-AUG-2009 11:53:37

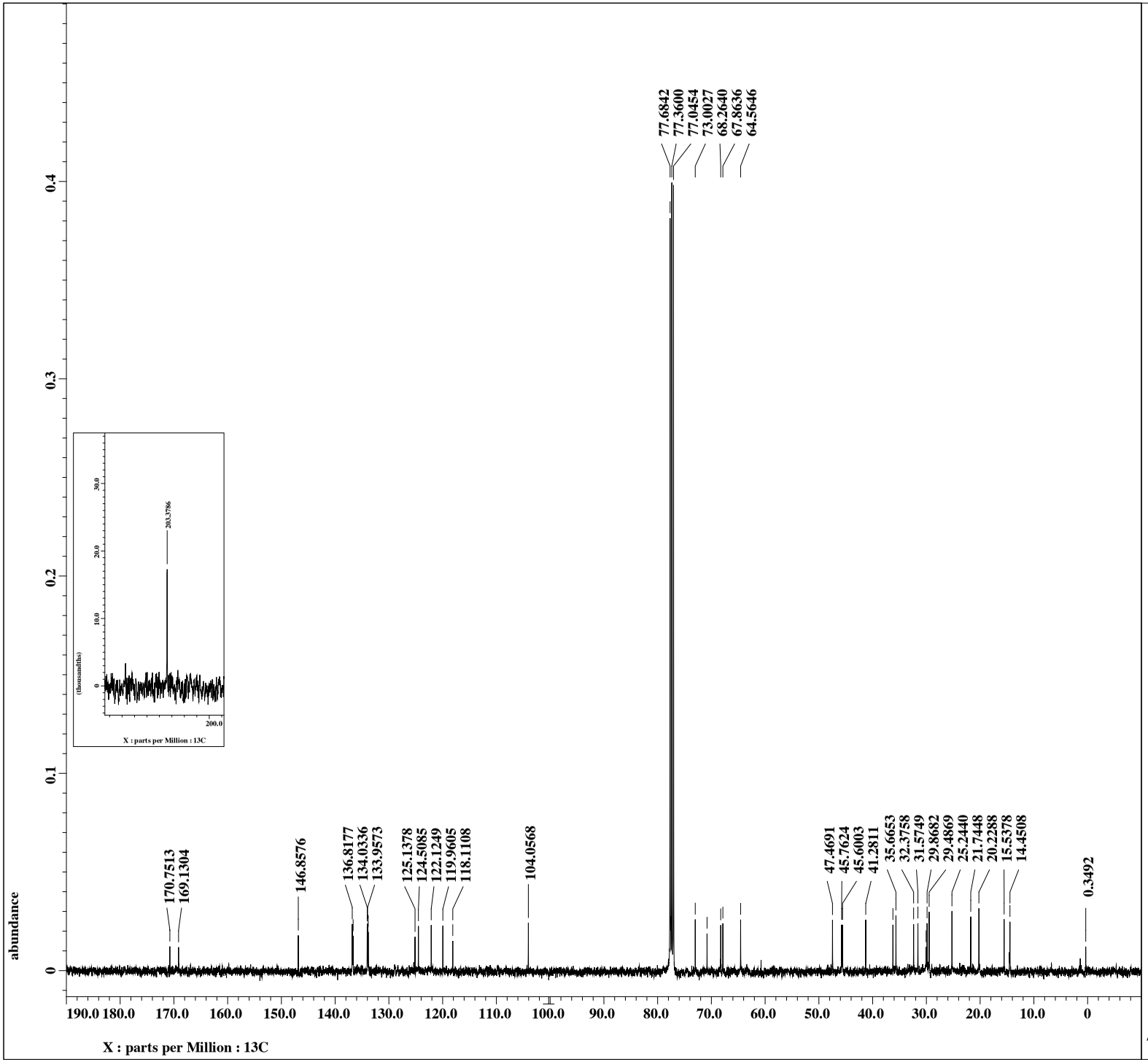
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR

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 = 100
Total_scans = 100

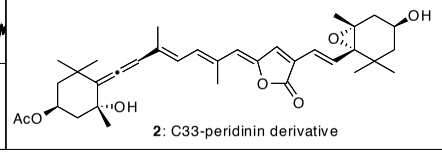
X_90_width = 10.5[us]
X_acq_time = 4.36731904[s]
X_angle = 45[deg]
X_atn = 1.4[dB]
X_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 9.36731904[s]
Temp_get = 24.8[dC]



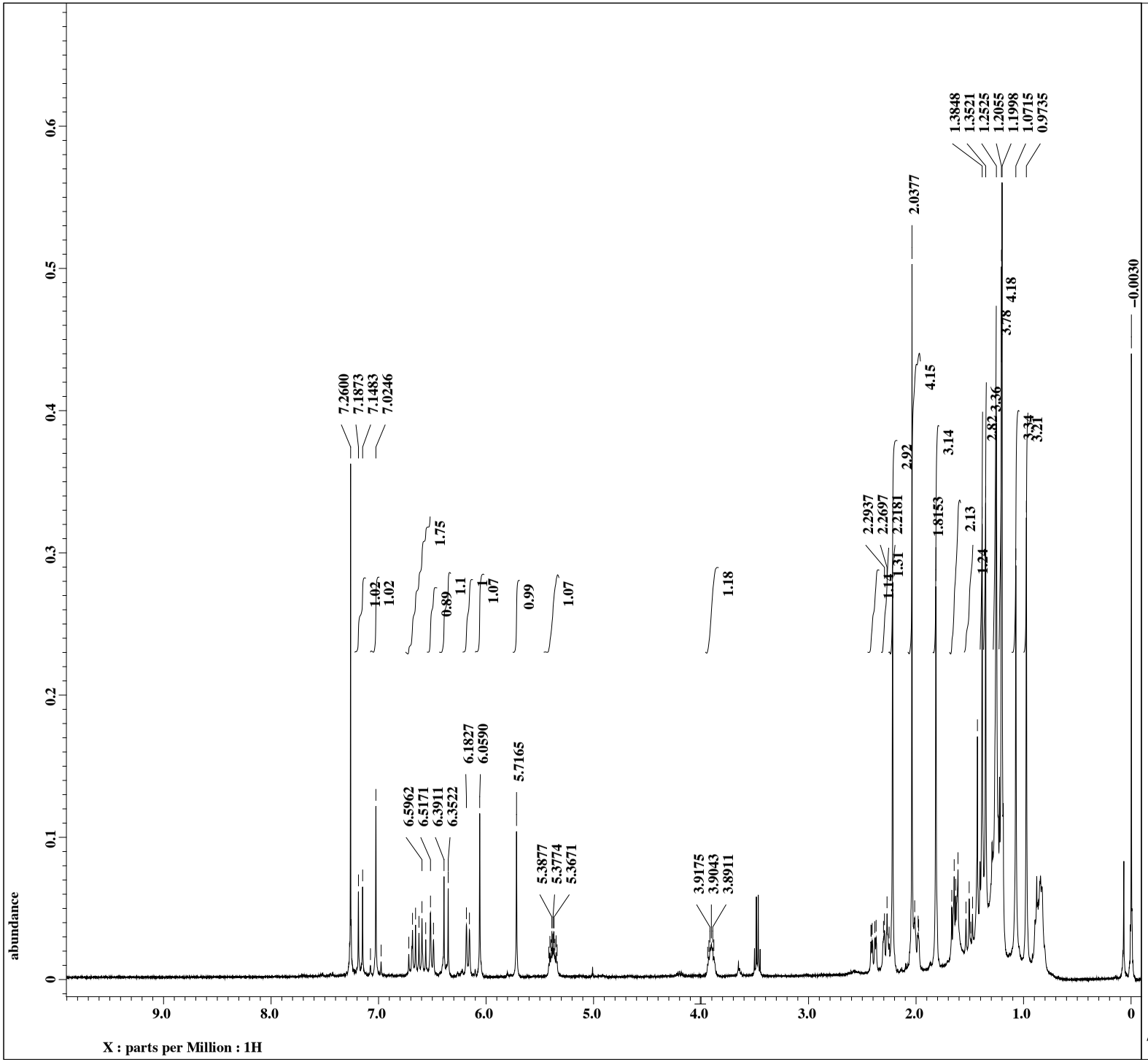
2: C33-peridinin derivative




```
Filename          = C33-peridinin derivat
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 11-DEC-2008 23:01:59
Revision_time     = 24-AUG-2009 11:42:04
Current_time      = 24-AUG-2009 11:43:05

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           = TRUE
Mod_return        = 1
Scans             = 1800
Total_scans       = 1800

X_90_width        = 8.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 45[deg]
X_atn             = 6.6[dB]
X_pulse           = 4.2[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        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 24.4[dC]
```



2: C33-peridinin derivative

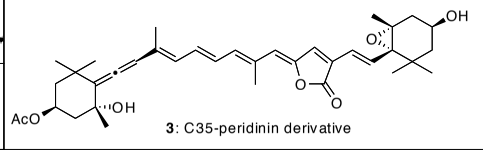


Filename = C35derivative-1H-3.jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 17-FEB-2008 05:21:58
Revision_time = 24-AUG-2009 10:53:52
Current_time = 24-AUG-2009 10:54:31

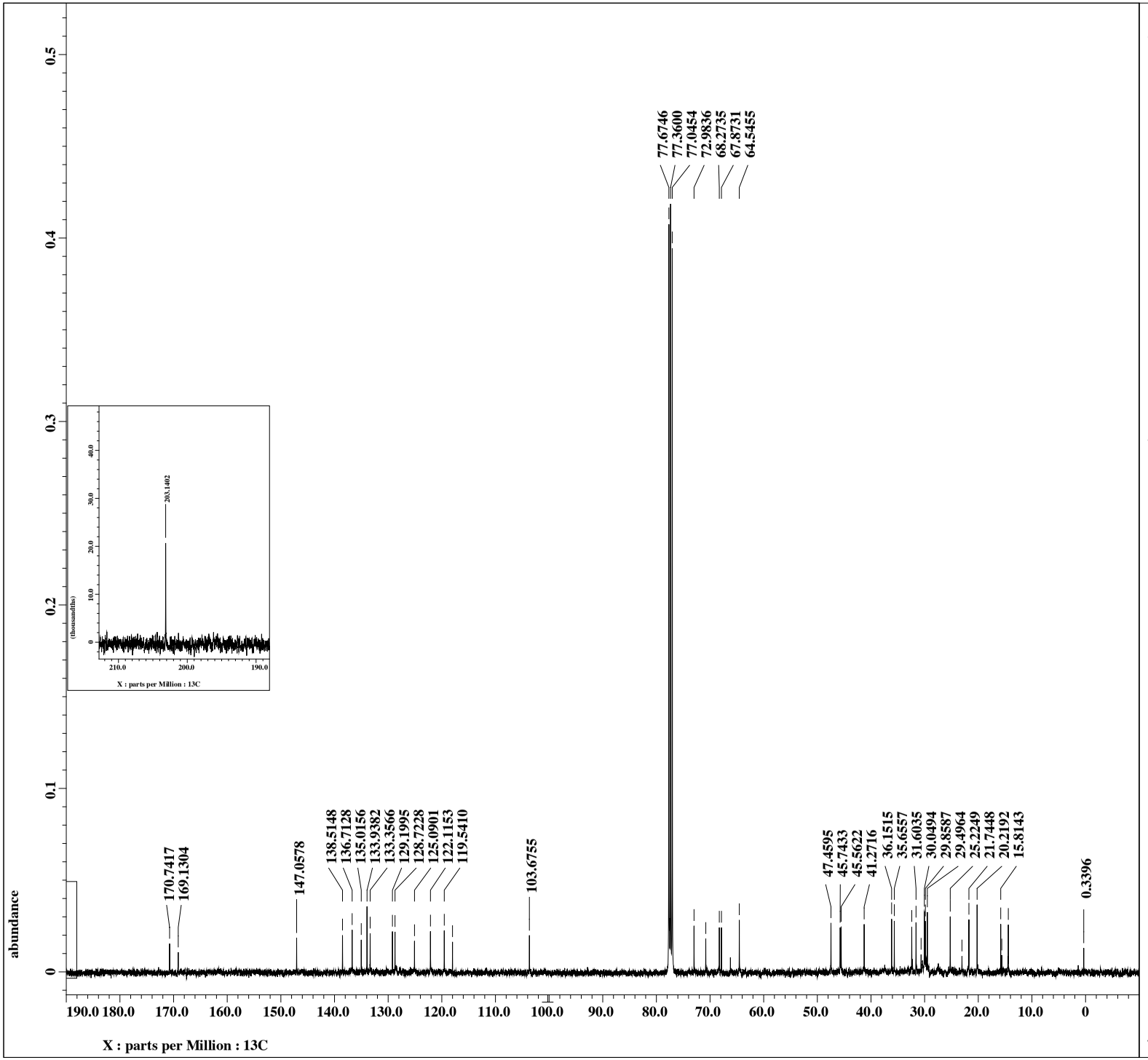
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX400M
Spectrometer = DELTA2_NMR

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

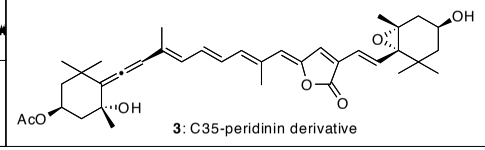
X_90_width = 11.2[us]
X_acq_time = 4.36731904[s]
X_angle = 45[deg]
X_atn = 2.8[dB]
X_pulse = 5.6[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 9.36731904[s]
Temp_get = 23.2[dC]



3: C35-peridinin derivative

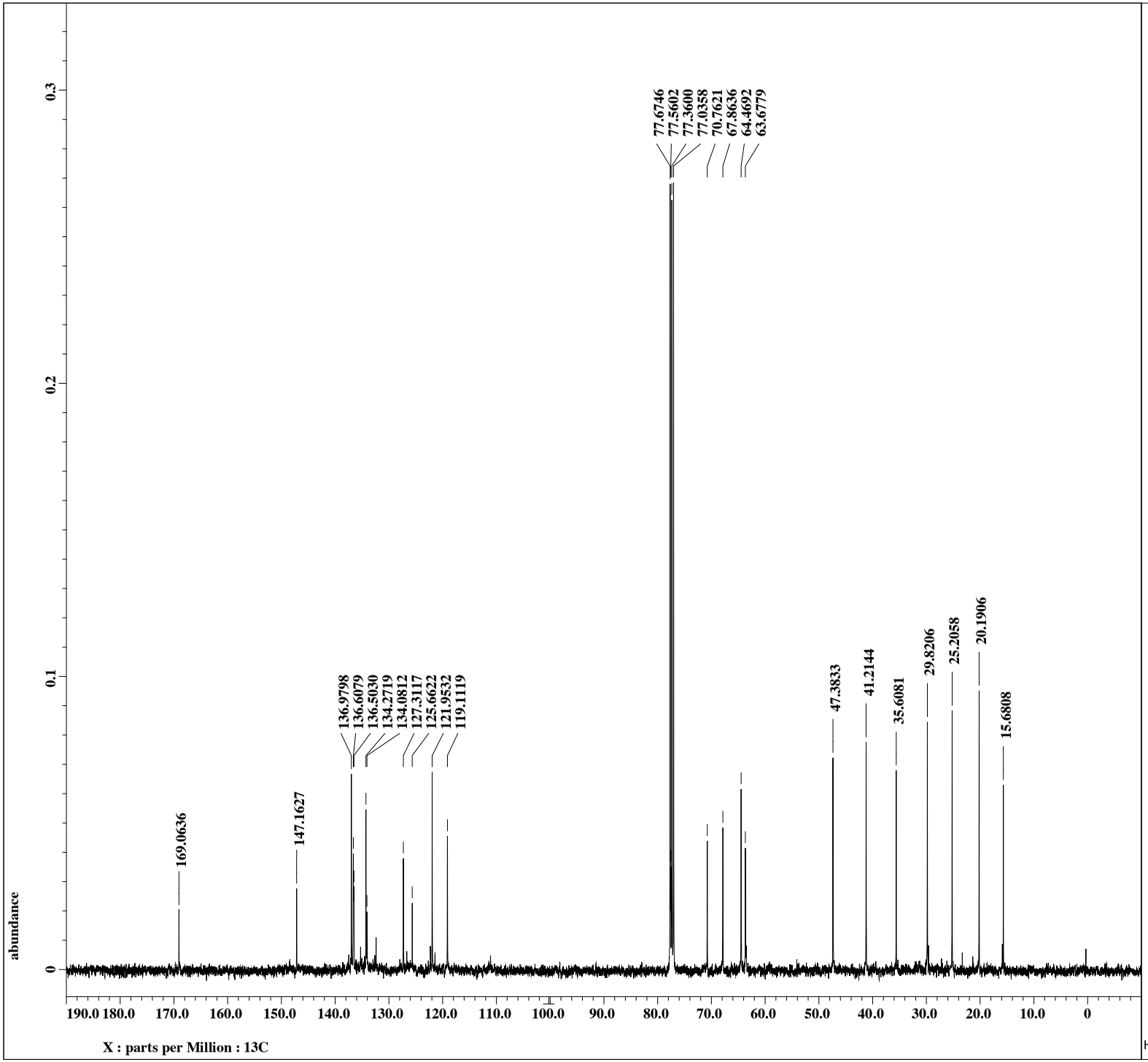


Filename	= C35derivative-13C-2.j
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= 1
Solvent	= CHLOROFORM-D
Creation_time	= 16-FEB-2008 23:26:37
Revision_time	= 24-AUG-2009 10:37:51
Current_time	= 24-AUG-2009 10:40:32
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 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	= 9.6[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	= 56
Relaxation_delay	= 2[s]
Repetition_time	= 3.04333312[s]
Temp_get	= 22.9[dC]

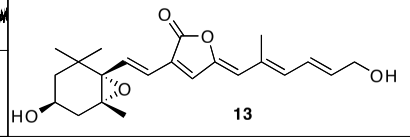


3: C35-peridinin derivative

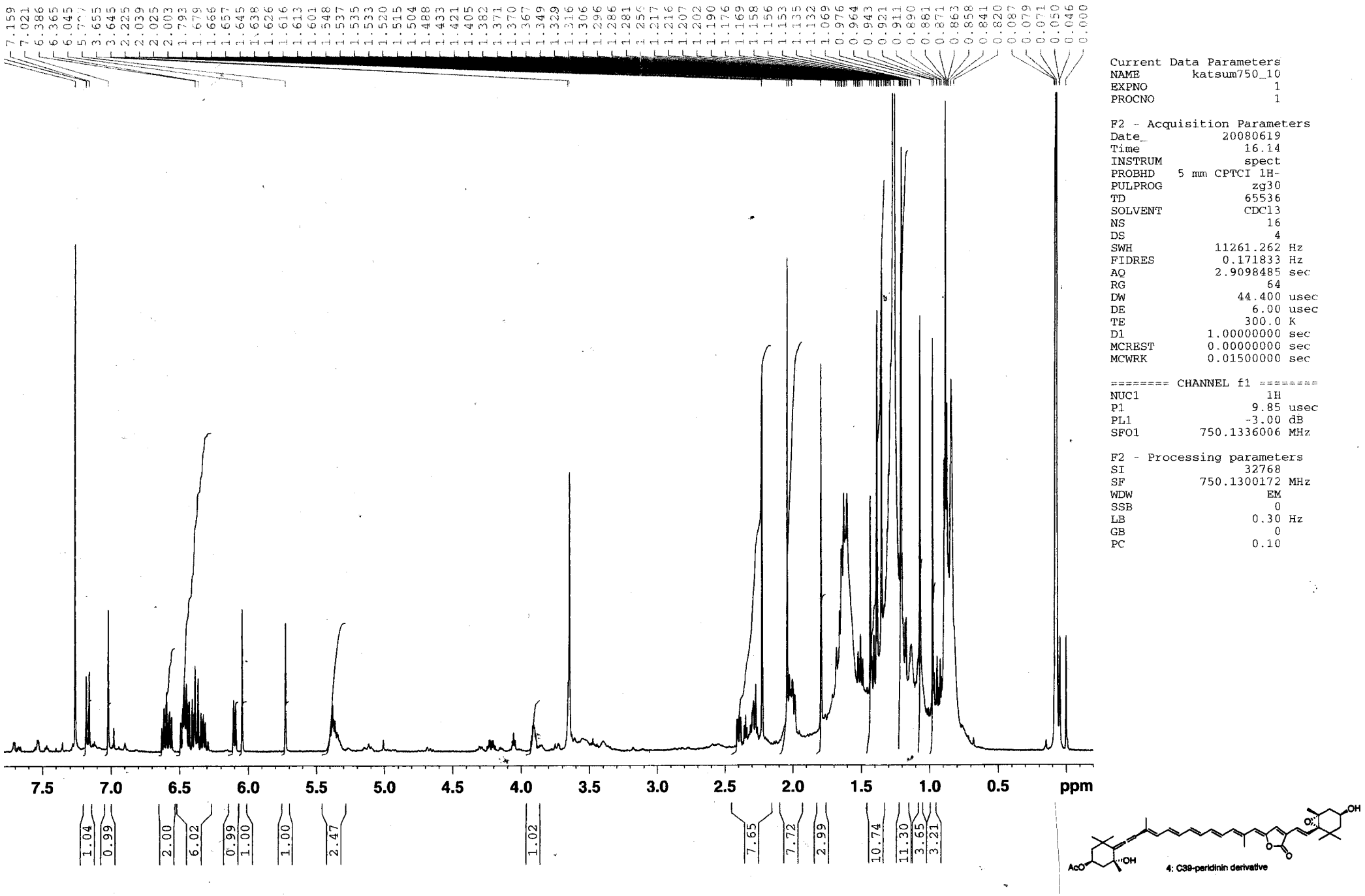
Filename = C22 yliden 1H-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 23-MAY-2009 12:05:03
Revision_time = 24-AUG-2009 10:34:53
Current_time = 24-AUG-2009 10:35:43
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
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 = 200
Total_scans = 200
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 = 40
Relaxation_delay = 1[s]
Repetition_time = 3.18365952[s]
Temp_get = 26.1[dC]
OH
O
O
HO
13
abundance
X : parts per Million : 1H
7.2600
7.2016
7.1627
7.0287
1.16
0.86
1.17
2.63
1
0.93
6.6701
6.6323
6.3918
6.3528
6.0527
6.0149
5.6930
4.3012
4.2886
3.9187
3.9049
3.8923
1.45
2.87
2.3837
2.3711
2.3677
2.2073
1.41
2.97
1.6460
1.6139
1.6105
2.18
1.2038
1.1981
6.78
0.9740
4.16
-0.0012




```
Filename          = C22 ylidenbutnolide-1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#556336
Solvent           = CHLOROFORM-D
Creation_time     = 29-SEP-2008 15:44:07
Revision_time     = 24-AUG-2009 11:39:16
Current_time      = 24-AUG-2009 11:39:57

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        = 9.2[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          = 25.6[dC]
```



13



Current Data Parameters

NAME	katsum750_10
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080619
Time	16.14
INSTRUM	spect
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	4
SWH	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	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

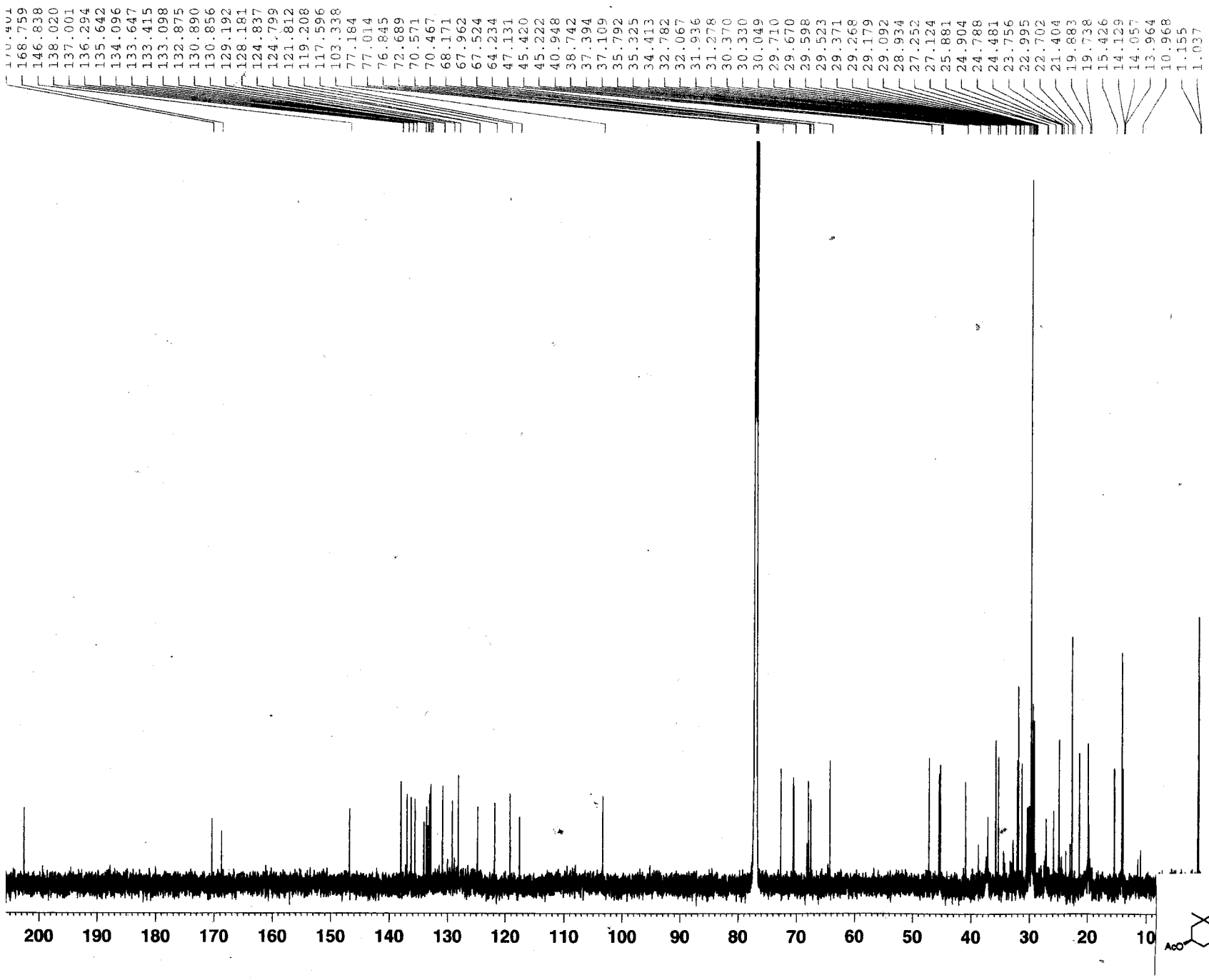
======== CHANNEL f1 ========

NUC1	1H
P1	9.85 usec
PL1	-3.00 dB
SFO1	750.1336006 MHz

F2 - Processing parameters

SI	32768
SF	750.1300172 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.10

4: C39-peridinin derivative



14

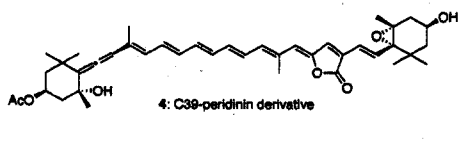
Current Data Parameters
NAME katsum750_10
EXPNO 2000
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080621
Time 1.13
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16384
DS 4
SWH 45045.047 Hz
FIDRES 0.687333 Hz
AQ 0.7274996 sec
RG 8192
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 16.80 dB
PL13 16.80 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 1.00



4: C39-peridinin derivative