Electronic Supplementary Material (ESI) for Chemical Communications

Total Synthesis of (+)-Chloranthalactone F

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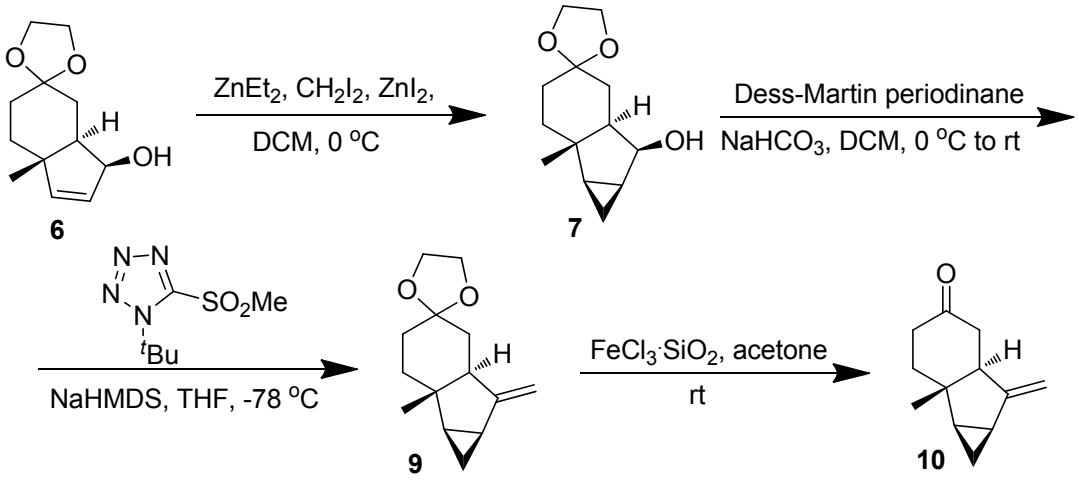
(A). General information

All reactions utilizing air- or moisture-sensitive reagents were carried out in flame-dried glassware under an argon atmosphere, unless otherwise stated. CH_2Cl_2, DMF and THF were distilled prior to use according to the standard protocols. Other reagents were purchased and used as received without further purification unless otherwise stated. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.15-0.2 mm pre-coated silica gel (10-40 μm) plates. Compounds were visualized with UV light and/or by staining with ethanolic phosphomolybdic acid (PMA) followed by heating on a hot plate. Flash chromatography was performed with silica gel (300-400 mesh) under pressure. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous compounds, unless otherwise stated. NMR spectra were recorded on Varian-300, Bruker-400 and Bruker-500 spectrometers in $CDCl_3$ (or CD_2Cl_2) with TMS as the internal standard. Chemical shifts (δ) are given in ppm relative to residual chloroform (δ 7.26 for ^{1}H NMR and 77.00 for ^{13}C NMR) and CD_2Cl_2 (δ 5.32 for ^{1}H NMR 53.84 for ^{13}C NMR), coupling constants (*J*) in Hz. Multiplicity is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were collected on Avatar 330 FT-IR spectrometer. Melting points were determined on SGW X-4 microscopic melting point apparatus and were uncorrected. Optical rotations were determined on JASCO P-1030 Polarimeter in the solvent indicated. High-resolution mass spectra were recorded on IonSpec 4.7 Tesla FTMS or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS.

(B). Experimental part



Scheme 1 Synthesis of Compound **10**

Sequential route to ketene 10. To a cooled (0 °C) solution of allylic alcohol **6** (55 mg, 0.26 mmol) (ref. Qian, S.; Zhao, G. *Synlett* **2011**, 722.) containing ZnI_2 (21 mg, 0.065 mmol) in DCM (7 mL) was added $ZnEt_2$ solution in hexanes (1.31 mL, 1.31 mmol), and the resultant mixture was kept for 10~15 min before the freshly distilled CH_2I_2 (0.11 mL, 1.31 mmol) was added. The resulting mixture was stirred for 12 h at 0 °C before being quenched with sat. NH_4Cl (aq.). The aqueous layer was extracted with DCM, washed with brine, dried over anhydrous $MgSO_4$. The filtrate was concentrated in vacuo and purified by flash column chromatography (EtOAc:Hexanes = 1:5) on silica gel to give 53 mg **7** in 99% yield as a single isomer. (NOTE: Alternatively, the residue before flash column chromatography can be used directly in the next step.)

(1aR,1bS,5aR,6S,6aS)-1b-methyloctahydro-1H-spiro[cyclopropa[a]indene-4,2'-[1,3]dioxolan]-6-ol (7): R_f = 0.45 (EtOAc:Hexanes = 1:1); $[\alpha]_D^{23}$ = +24.50 (*c* 1.70, $CHCl_3$); m.p. 100~102 °C; IR (KBr, cm^{-1}): 3488, 3008, 2984, 2900, 2876, 1443, 1349, 1104, 1048, 1009; ^1H NMR (300 MHz, $CDCl_3$) δ 4.34 (t, *J* = 5.1 Hz, 1H), 3.90 (s, 4H), 1.91 (dt, *J* = 12.6, 4.2 Hz, 1H), 1.86~1.76 (m, 1H), 1.75~1.42 (m, 7H), 1.34~1.16 (m, 2H), 0.94 (s, 3H), 0.66~0.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.0, 73.8, 64.2, 63.9, 60.1, 38.9, 37.1, 32.1, 30.5, 26.5, 17.8, 10.9; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1414.

To a stirred solution of alcohol **7** (180 mg, 0.80 mmol) in DCM (15 mL) at 0 °C was successively added $NaHCO_3$ (675 mg, 8.04 mmol) and Dess-Martin periodinane (681mg, 1.61 mmol). The resulting mixture was stirred at rt for 1 h before being quenched with sat. $Na_2S_2O_3$ (aq.) and sat. $NaHCO_3$ (aq.) carefully. The aqueous layers were extracted with DCM, washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The residue was used directly in the next reaction.

A cooled (-78 °C) solution of Julia methylenation reagent (492 mg, 2.41 mmol) in THF (15 mL) was added with NaHMDS solution (2.01 mL, 2.01 mmol, 1.0 M in THF). The resulting mixture was stirred at -78 °C for another 30 min followed by a slow addition of the above residue (in 2.0 mL of THF) obtained from the oxidation of alcohol **7** and an additional stirring at -78 °C for 2 h. The reaction mixture was quenched with sat. NH_4Cl (aq.). The aqueous layer was extracted with

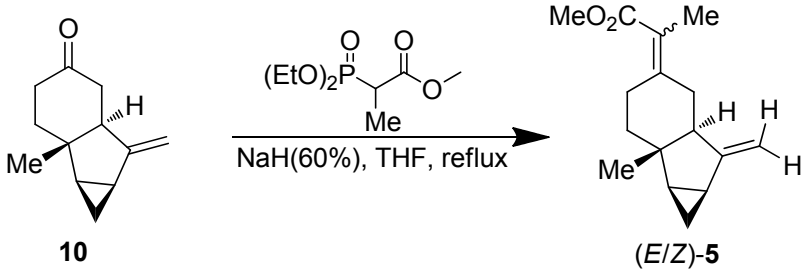
ethyl ether, washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The residue was taken directly into the next deprotectection reaction.

A sample (**9**) was purified by flash column chromatography (EtOAc:Hexanes = 1:100) on silica gel for characterization.

(1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydro-1H-spiro[cyclopropa[a]indene-4,2'-[1,3]dioxolane] (9): R_f = 0.75 (EtOAc:Hexanes = 1:10); $[\alpha]_D^{25}$ = +63.97 (*c* 1.13, $CHCl_3$); IR (neat, cm^{-1}): 3004, 2979, 2950, 2878, 1661, 1352, 1180, 1097, 1047, 1028; ^1H NMR (300 MHz, $CDCl_3$) δ 4.86 (t, *J* = 1.2 Hz, 1H), 4.55 (s, 1H), 3.93 (s, 4H), 2.73 (dd, *J* = 12.9, 2.7 Hz, 1H), 1.95~1.80 (m, 2H), 1.78~1.55 (m, 4H), 1.45~1.20 (m, 2H), 0.88~0.82 (m, 1H), 0.80~0.70 (m, 1H), 0.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 109.6, 104.2, 64.3, 64.1, 61.1, 37.4, 35.3, 32.4, 32.0, 27.9, 23.4, 16.5, 16.1; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1465.

The resultant methylenation mixture containing (**9**) was dissolved in acetone (10 mL) at rt, followed by the addition of pre-prepared $FeCl_3{\cdot}SiO_2$ (80 mg, 100 mg per mmol) in one portion. The mixture was stirred for another 3 h before being concentrated directly in vacuo at 30~35 °C. The residue was purified by flash column chromatography (EtOAc:Hexanes = 1:50) on silica gel to give ketene **10** 133 mg (93% and 6% alkene **9** was recovered) over 3 steps as an oil, the stereochemistry of which was mainly determined by nOe experiment and ^{13}C NMR comparision with the natural shizukanolide (60.7 ppm vs 64.0ppm).

(1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydrocyclopropa[a]inden-4(1bH)-one (10): R_f = 0.65 (EtOAc:Hexanes = 1:10); $[\alpha]_D^{27}$ = -5.96 (*c* 1.00, $CHCl_3$); IR (neat, cm^{-1}): 3006, 2968, 2926, 2863, 1711, 1662, 1416; ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H), 4.59 (s, 1H), 2.83 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.50~2.44 (m, 2H), 2.32 (brdd, *J* = 16.2, 4.0 Hz, 1H), 2.11 (bRT, 14.4 Hz, 1H), 2.05~1.91 (m, 3H), 1.43~1.35 (m, 1H), 0.90~0.80 (m, 2H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 151.9, 105.8, 60.7, 39.1, 38.0, 37.5, 36.2, 27.8, 23.9. 16.8, 16.4; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{16}O$ 176.1201, found 176.1198.



10 (*E*/*Z*)-**5**

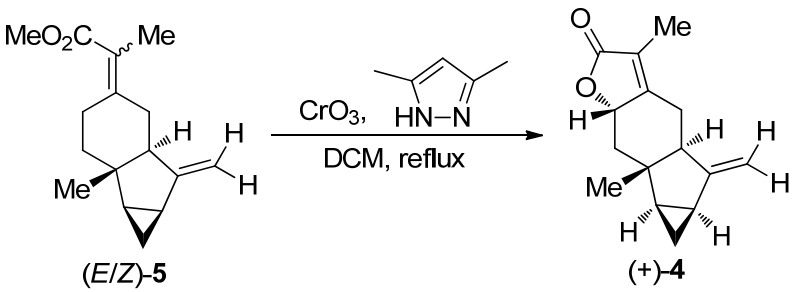
Scheme 2 Synthesis of Ester **5**

To a suspension of NaH (60%) (148 mg, 3.69 mmol) in THF (20 mL) cooled in a water-ice bath was added methyl 2-diethylphosphite propionate (995 mg, 4.44 mmol) slowly. The resulting mixture was stirred at rt for another 1 h before the ketene **10** (130 mg, 0.74 mmol) in THF (5 mL) was added in one portion. Then the reaction mixture was heated to reflux in a pre-heated oil-bath for 8 h. After cooling to rt, the mixture was quenched by brine. The aqueous layer was extracted with diethyl ether, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (EtOAc:Hexanes = 1:100) on silica gel to afford an inseparable 1.3:1.0 mixture of **5** in quantitative yield (180 mg, 99%) with the (*E*)-isomer favored, R_f = 0.65 (EtOAc:Hexanes = 1:10). The ratio of *E*/*Z* mixture can be improved to 2.0:1.0 after one

recrystallization in 81% yield. The stereochemistry of (*E*)- and (*Z*)- isomer (separated by reverse semi-preparative column: Agilent 1200HPLC using a Agilent 20RBAX Eclipse XDB-C_{18} 5 μm reversed-phase column measuring 4.6 mm × 150 mm with 20% MeCN/H_2O over 20 min. $t_R(Z)$ = 17.6 min, $t_R(E)$ = 18.9 min.) were determined by extensive spectroscopic studies along with a single crystal X-ray diffraction analysis of the (*Z*)-isomer.

(E)-methyl2-((1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydrocyclopropa[a]inden-4(1bH)-ylidene)propanoate (*E*)-5: $[\alpha]_D^{27}$ = +31.16 (*c* 0.30, $CHCl_3$); IR (neat, cm^{-1}): 3074, 2924, 2856, 1717, 1434, 1261, 1194, 1106; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94 (t, *J* = 1.5 Hz, 1H), 4.66 (s, 1H), 3.73 (s, 3H), 2.82 (dq, *J* = 16.0, 3.0 Hz, 1H), 2.56 (q, *J* = 8.5 Hz, 1H), 2.50 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.43 (dd, *J* = 15.2, 3.5 Hz, 1H), 1.93~1.81 (m, 5H), 1.77 (t, *J* = 15.0 Hz, 1H), 1.73~1.66 (m, 1H), 1.35~1.29 (m, 1H), 0.94~0.76 (m, 2H), 0.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 153.3, 145.3, 122.1, 104.6, 61.2, 51.3, 37.9, 37.5, 28.5, 27.4, 27.2, 23.2, 17.2, 16.6, 15.5; HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1625.

(Z)-methyl2-((1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydrocyclopropa[a]inden-4(1bH)-ylidene)propanoate (*Z*)-5: $[\alpha]_D^{27}$ = +18.55 (*c* 0.65, $CHCl_3$); m.p. 78~79 °C; IR (KBr, cm^{-1}): 3019, 2945, 1705, 1659, 1278, 1205, 1092, 1066, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (d, *J* = 1.6 Hz, 1H), 4.66 (s, 1H), 3.72 (s, 3H), 2.77 (dd, *J* = 15.6, 3.6 Hz, 1H), 2.61 (dd, *J* = 16.0, 4.8 Hz, 1H), 2.41 (dd, *J* = 13.2, 2.8 Hz, 1H), 2.34~2.22 (m, 1H), 2.00~1.84 (m, 6H), 1.74~1.64 (m, 1H), 1.33~1.27 (m, 1H), 0.94~0.75 (m, 2H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 152.9, 145.5, 122.0, 104.8, 62.1, 51.3, 37.6, 37.3, 28.3, 26.6, 23.2, 16.8, 16.5, 15.6; HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1617.

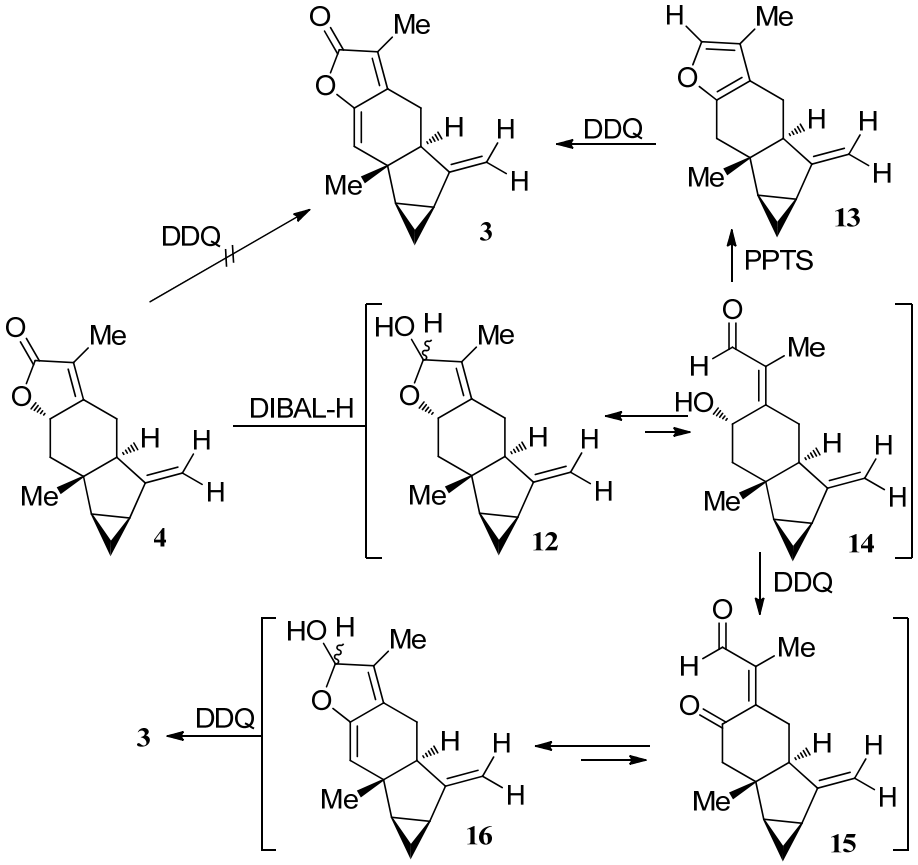


(*E*/*Z*)-**5** (+)-**4**

Scheme 3 Synthesis of Compound **4**

To a solution of *α*, *β*-unsaturated ester **5** (*E*/*Z* = 2.0:1.0) (19 mg, 0.0772 mmol) in freshly distilled DCM (10 mL) cooled in a water-ice bath was added CrO_3 (15 mg, 0.154 mmol) followed by 3, 5-dimethylpyrazole (30 mg, 0.309 mmol), and the resulting mixture was stirred at 0 °C for 30 min. Then, the reaction mixture was heated to reflux in a pre-heated oil-bath for 12 h. After cooling to rt, the reaction mixture was added Celite and stirred for another 15 min. The resulting mixture was filtered through a silica gel pad with ethyl ether as the washing solvent. The filtrate was concentrated in vacuo, and the residue was used for another two cycles. Finally, the residue obtained from the oxidative cycles was purified carefully by flash column chromatography (EtOAc:Hexanes = 1:120 to 1:30) on silica gel to furnish the synthetic shizukanolide (6.0 mg, 32%, 46% based on the recovered starting material) as a single isomer along with starting material (6 mg, 32% yield with the same ratio of *E*/*Z* (*ca*. 2.0:1.0)). (Lit. $[\alpha]_D^{20}$ = +200, (*c* 0.21, $CHCl_3$); m.p. 95~96.5 °C; *Agric. Biol. Chem.* **1979**, *43*, 885. & *Agric. Biol. Chem.* **1981**, *45*, 1447.)

(4aS,5aS,6aR,6bS,7aS)-3,6b-dimethyl-5-methylene-4,4a,5,5a,6,6a,7,7a-octahydrocyclopropa[2,3]indeno[5,6-b]furan-2(6bH)-one (4): R_f = 0.60 (EtOAc:Hexanes = 1:5); $[\alpha]_D^{27}$= +184.08 (*c* 0.80, $CHCl_3$); m.p. 92~93 °C; IR (KBr, cm^{-1}): 3074, 3006, 2927, 1755, 1678, 1094, 1033, 886; ^1H NMR (500 MHz, $CDCl_3$) δ 5.04~4.97 (m, 2H), 4.73 (brs, 1H), 2.67 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.60 (dd, *J* = 12.0, 7.0 Hz, 1H), 2.46 (dq, *J* = 13.0, 3.0 Hz, 1H), 2.04 (tt, *J* = 13.5, 1.5 Hz, 1H), 1.97~1.91(m, 1H), 1.81 (t, *J* = 1.5 Hz, 3H), 1.47 (t, *J* = 11.0 Hz, 1H), 1.38~1.32 (m, 1H), 0.91~0.87 (m, 1H), 0.84~0.78 (m, 1H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 161.5, 150.3, 121.5, 106.1, 79.6, 64.0, 44.1, 38.6, 27.0, 23.9, 23.4, 17.2, 15.9, 8.4; HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{18}O_2$ 230.1307, found 230.1310.



Scheme 4 Oxidative enol-lactonization to **3**

1) To a stirred solution of **4** (2 mg, 8.70 μmol) in CH_2Cl_2 (2 mL) at rt was added DDQ (4 mg, 17.39 μmol) in one portion, 30 minutes' reaction resulted in no new product. The reaction mixture was then concentrated in the presence of silica gel (100-200 mesh). The residue was purified by flash column chromatography (EtOAc:Hexanes = 1:30) on silica gel to give starting material (2 mg).

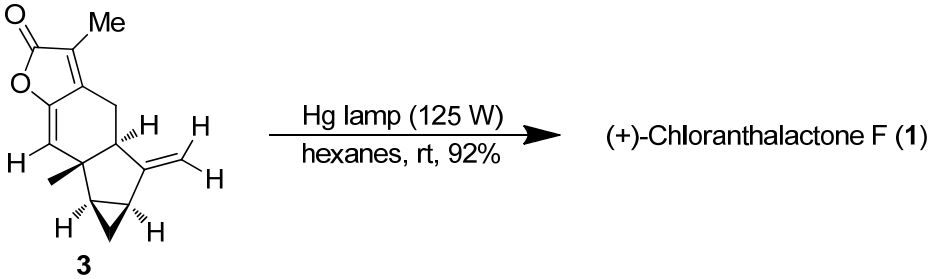
2) To a cooled (-78 °C) solution of **4** (20 mg, 0.0870 mmol) in DCM (10 mL) was added slowly a 1.0 M solution of DIBAL-H (0.87 mL) in toluene. The resulting solution was stirred at -78 °C for another 2 h before being quenched with sat. Roche salt (aq.). The mixture was allowed to warm to rt and stirred for hours until two layers were separated clearly. The aqueous layers were extracted with CH_2Cl_2, washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The lactol **12** was taken directly to the next reaction.

To a solution of hemiactetal **12** in CH_2Cl_2 (10 mL) cooled in a water-ice bath was added PPTS (2.2 mg, 0.0087 mmol) in one portion. The resulting solution was stirred for 5 min (NOTE: furan derivate **13** here could be isolated by flash column chromatography (EtOAc:Hexanes = 1:1000) on silica gel as an oil for characterization, although it is prone to decomposition for long-time storage even at 0 °C), and then DDQ (30 mg, 0.1305 mmol) was added in one portion. The reaction mixture was stirred for another 15 min and concentrated in the presence of silica gel (100-200 mesh). The residue was purified by flash column chromatography (EtOAc:Hexanes = 1:100) on silica gel to give **3** (7.2 mg, 36.3%).

3) A solution of crude mixture **12** (prepared as above on 5 mg (0.022 mmol) scale) in CH_2Cl_2 (5 mL) was added DDQ (20 mg, 0.088 mmol), the resulting solution was stirred at rt for 5 min before concentrated in the presence of silica gel (100-200 mesh). The residue was purified by flash column chromatography (EtOAc:Hexanes = 1:100) on silica gel to give **3** (4 mg, 80%). (Lit. $[\alpha]_D^{18}$ = +59.8, (*c* 1.02, $CHCl_3$); m.p. 64~65.5 °C; *Agric. Biol. Chem.* **1979**, *43*, 885. & *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3465.)

(4aS,5aS,6aR,6bS)-3,6b-dimethyl-5-methylene-4,4a,5,5a,6,6a,6b,7-octahydrocyclopropa[2,3]indeno[5,6-b]furan (13): R_f = 0.85 (EtOAc:Hexanes = 1:200); $[\alpha]_D^{27}$ = -41.24 (*c* 0.10, $CHCl_3$) (Lit. $[\alpha]_D^{24}$ = -50.1 (*c* 1.6, $CHCl_3$) *J. Chem. Soc.* (*C*) **1969**, 1920.); IR (neat, cm^{-1}): 3065, 2961, 1661, 881; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.07 (s, 1H), 5.00~4.70 (m, 1H), 4.77 (brs, 1H), 2.80~2.65 (m, 3H), 2.35 (ddd, *J* = 15.4, 4.6, 1.2 Hz, 1H), 2.04~1.96 (m, 1H), 1.92 (d, *J* = 1.2 Hz, 3H), 1.95~1.85 (m, 1H), 1.51~1.44 (m, 1H), 0.90~0.76 (m, 2H), 0.60 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 153.2, 152.2, 137.8, 120.4, 118.0, 105.5, 61.3, 39.3, 39.0, 28.1, 23.6, 18.9, 17.7, 16.6, 8.2; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{18}O$ 214.1358, found 214.1359.

(4aS,5aS,6aR,6bS)-3,6b-dimethyl-5-methylene-4,4a,5,5a,6,6a-hexahydrocyclopropa[2,3]indeno[5,6-b]furan-2(6bH)-one (3): R_f = 0.45 (EtOAc:Hexanes = 1:20); $[\alpha]_D^{26}$= +58.27 (*c* 0.19, $CHCl_3$); m.p. 60~62 °C; IR (KBr, cm^{-1}): 3075, 3008, 2965, 2924, 2855, 1770, 1661, 1645, 1141, 1103, 1064, 1018, 885; ^1H NMR (500 MHz, $CDCl_3$) δ 6.24 (s, 1H), 5.05 (s, 1H), 4.78 (s, 1H), 2.98 (dq, *J* = 13.5, 3.0 Hz, 1H), 2.70 (brdd, *J* = 17.0, 3.5 Hz, 1H), 2.27 (tq, *J* = 15.0, 2.0 Hz, 1H), 2.01~1.95 (m, 1H), 1.90 (d, *J* = 2.0 Hz, 3H), 1.68~1.62 (m, 1H), 0.94~0.85 (m, 2H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 150.1, 149.6, 148.0, 122.4, 119.7, 106.5, 62.0, 40.1, 26.4, 22.4, 22.1, 21.4, 17.0, 8.6; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1154.



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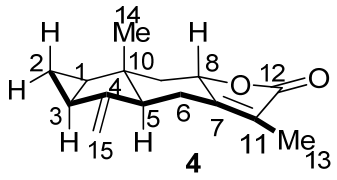
Scheme 5 Total Synthesis of Chloranthalactone F (**1**)

A solution of **3** (12 mg, 0.0524 mmol) in hexanes (13 mL, 0.004 M) in a quartz tube was irradiated by a high pressure Hg lamp (125 W) at rt for 4 h. After complete conversion, the reaction mixture was concentrated and directly purified by flash column chromatography (EtOAc:Hexanes = 1:50) on silica gel to furnish the synthetic chloranthalactone F in 92% (11 mg) yield as a white solid. (Lit. $[\alpha]_D^{23}$ = +20, (*c* 0.46, $CHCl_3$); m.p. 238~239 °C; *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3465.)

(1aS,5aR,5bR,9aS,10aS,11aR,11bS,11cS,11dS,11eS,11fR,12aS)-3,8,11b,11e-tetramethyl-1,10-dimethylene-1,1a,2,9,9a,10,10a,11,11a,11d,11e,11f,12,12a-tetradecahydrocyclopropa[3',4']cyclopenta[1',2':3,4]cyclopenta[1',2':5,6]biphenyleno[8a,8-b:8b,1-b']difuran-4,7(11bH,11cH)-dione (1): R_f = 0.40 (EtOAc:Hexanes = 1:10); $[\alpha]_D^{29}$ = +20.00 (*c* 0.17, $CHCl_3$); m.p. 223~225 ^oC; IR (KBr, cm^{-1}): 3073, 2964, 2927, 2854, 1762, 1667, 1090, 1049, 1023, 1010, 887; ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (brs, 2H), 4.80 (brs, 2H), 3.80~3.72 (m, 2H), 3.06 (s, 2H), 2.81 (ddd, *J* = 18.0, 6.4, 1.6 Hz, 2H), 2.31 (brdd, *J* = 18.0, 12.4 Hz, 2H), 2.14~2.06 (m, 2H), 1.77 (s, 6H), 1.45 (td, *J* = 7.0, 3.2 Hz, 2H), 0.92~0.78 (m, 4H), 0.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 160.5, 151.1, 124.9, 106.8, 91.1, 53.3, 48.2, 41.2, 24.2, 24.1, 23.9, 19.9, 16.3, 8.8; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{30}H_{32}O_4Na^+$ 479.2198, found 479.2200.

(C). Comparison of ^{1}H- and ^{13}C-NMR data for synthetic ones



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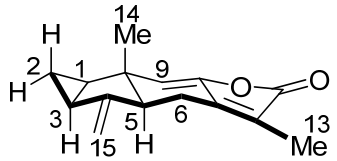
Comparison of ^{1}H NMR chemical shifts (δ: ppm)

No.	Natural (in $CDCl_3$, 100 MHz)	Synthetic (in $CDCl_3$, 500 MHz)
1	1.38 (ddd, *J* = 8.0, 7.0, 4.0 Hz)	1.38~1.32 (m)
2	0.93~0.80 (m)	0.84~0.78 (m)
5	2.80~2.40 (m)	2.46 (dq, *J* = 13.0, 3.0 Hz)
6α		2.67 (dd, *J* = 13.5, 3.0 Hz)
6β	2.20~2.00 (m)	1.97~1.91 (m)
3		2.04 (tt, *J* = 13.5, 1.5 Hz)
8	5.01 (brdd, *J* = 10.0, 7.0 Hz)	5.04~4.97 (m)
15	4.76 (brs), 5.01 (brs)	4.73 brs, 5.04~4.97 (m)
9α	1.49 (dd, *J* = 12.0, 10.0 Hz)	1.47 (t, *J* = 11.0 Hz)
9β	2.63 (dd, *J* = 12.0, 7.0 Hz)	2.60 (dd, *J* = 12.0, 7.0 Hz)
13	1.83 (t, 1.5 Hz)	1.81 (t, *J* = 1.5 Hz)
14	0.80 (s)	0.74 (s)

Comparison of ^{13}C NMR chemical shifts (δ: ppm)

Natural (in $CDCl_3$, 22 MHz)	Synthetic (in $CDCl_3$, 100 MHz)
174.0	174.5
161.4	161.5
150.2	150.3
121.4	121.5
106.0	106.1
79.5	79.6
63.9	64.0
44.1	44.1
38.6	38.6
27.0	27.0
23.8	23.9
23.4	23.4
17.2	17.2
15.9	15.9
8.4	8.4



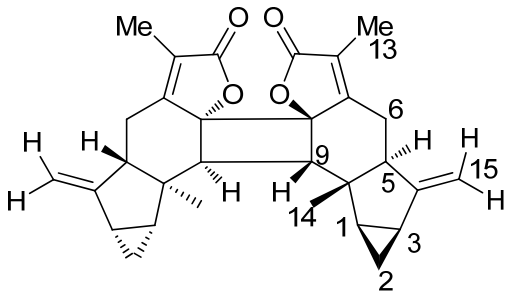
3

Comparison of ^{1}H NMR chemical shifts (δ: ppm)

No.	Natural (in $CDCl_3$, 400 MHz)	Synthetic (in $CDCl_3$, 500 MHz)
1	1.66 (dt, *J* = 7.3, 3.7 Hz)	1.68~1.62 (m)
2	0.94~0.88 (m)	0.94~0.85 (m)
3	2.00~1.95 (m)	2.01~1.95 (m)
5	2.97 (ddt, *J* = 13.6, 3.7, 2.2 Hz)	2.98 (dq, *J* = 13.5, 3.0 Hz)
6α	2.70 (dd, *J* = 16.9, 3.7 Hz)	2.70 (brdd, *J* = 17.0, 3.5 Hz)
6β	2.27 (ddq, *J* = 16.9, 13.6, 1.8 Hz)	2.27 (tq, *J* = 15.0, 2.0 Hz)
9	6.25 (s)	6.24 (s)
13	1.90 (d, *J* = 1.8 Hz)	1.90 (d, *J* = 2.0 Hz)
14	0.79 (s)	0.79 (s)
15	4.79 (brs), 5.06 (brs)	4.78 (brs), 5.05 (brs)

Comparison of ^{13}C NMR chemical shifts (δ: ppm)

Natural (in $CDCl_3$, 100 MHz)	Synthetic (in $CDCl_3$, 100 MHz)
169.0	171.1
150.1	150.1
149.6	149.6
148.0	148.0
122.4	122.4
119.8	119.7
106.5	106.5
62.0	62.0
40.1	40.1
26.4	26.4
22.4	22.4
22.1	22.1
21.4	21.4
17.0	17.0
8.6	8.6



Chloranthalactone F (**1**)

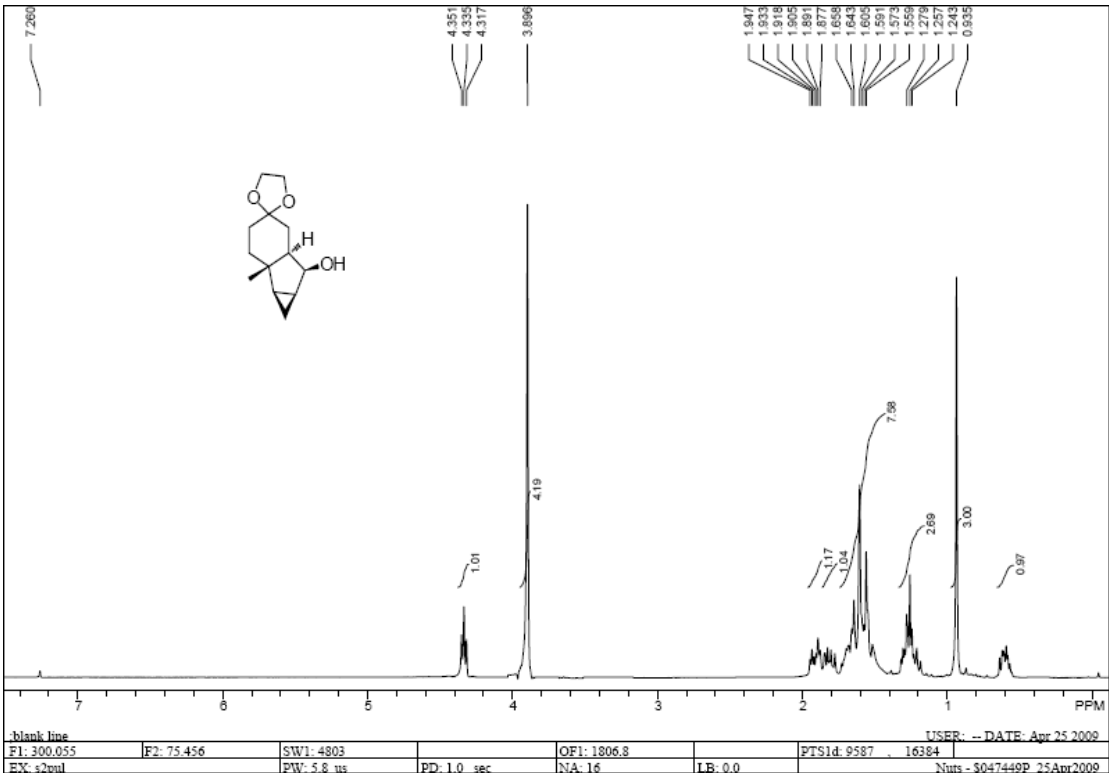
Comparison of ^{1}H NMR chemical shifts (δ: ppm)

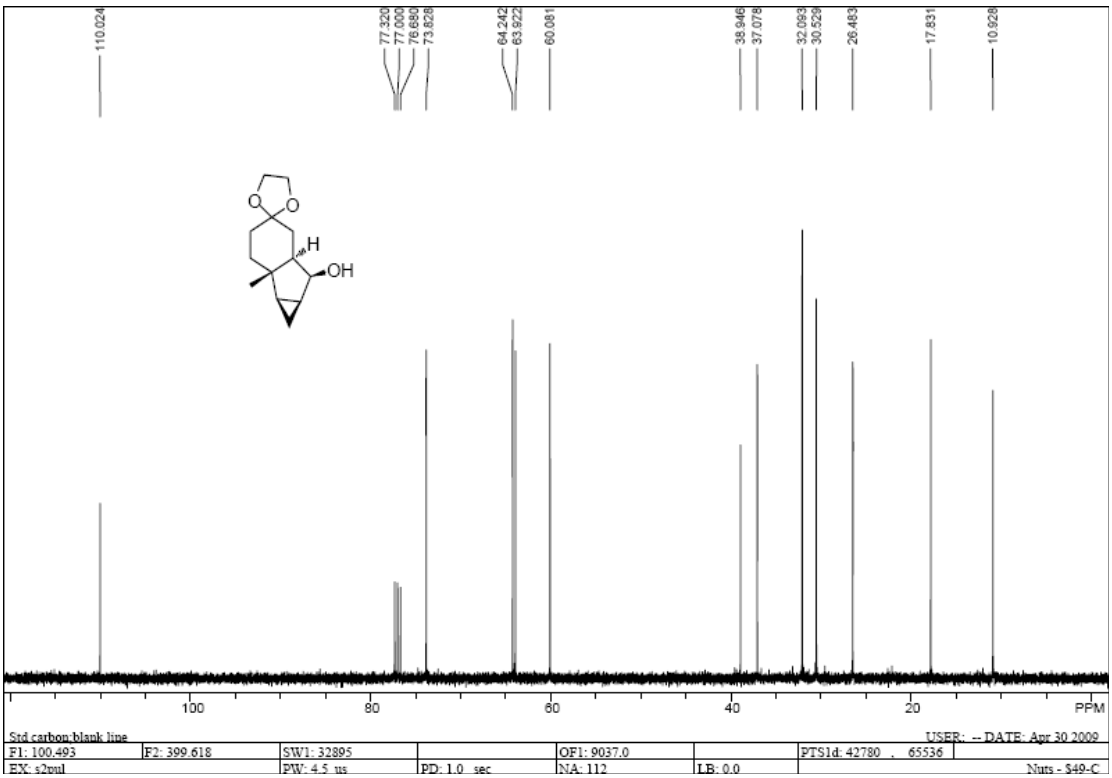
No.	Natural (in $CDCl_3$, 400 MHz)	Synthetic (in $CDCl_3$, 400 MHz)
1 (1')	1.45 (dt, *J* = 7.6, 3.7 Hz)	1.45 (dt, *J* = 7.0, 3.2 Hz)
2 (2')	0.92, 0.81 (m)	0.92~0.78 (m)
3 (3')	2.12, 2.06 (m)	2.14~2.06 (m)
5 (5')	3.77 (ddd, *J* = 12.1, 6.6, 2.2 Hz)	3.80~3.72 (m)
6a (6a')	2.81 (ddd, *J* = 18.3, 6.6, 2.2 Hz)	2.81 (ddd, *J* = 18.0, 6.4, 1.6 Hz)
6b (6b')	2.31 (brdd, *J* = 18.3, 12.1 Hz)	2.31 (brdd, *J* = 18.0, 12.4 Hz)
9 (9')	3.06 (s)	3.06 (s)
13 (13')	1.77 (d, *J* = 1.1 Hz)	1.77 (s)
14 (14')	0.53 (s)	0.53 (s)
15 (15')	5.09 (brs), 4.80 (brs)	5.08 (brs), 4.80 (brs)

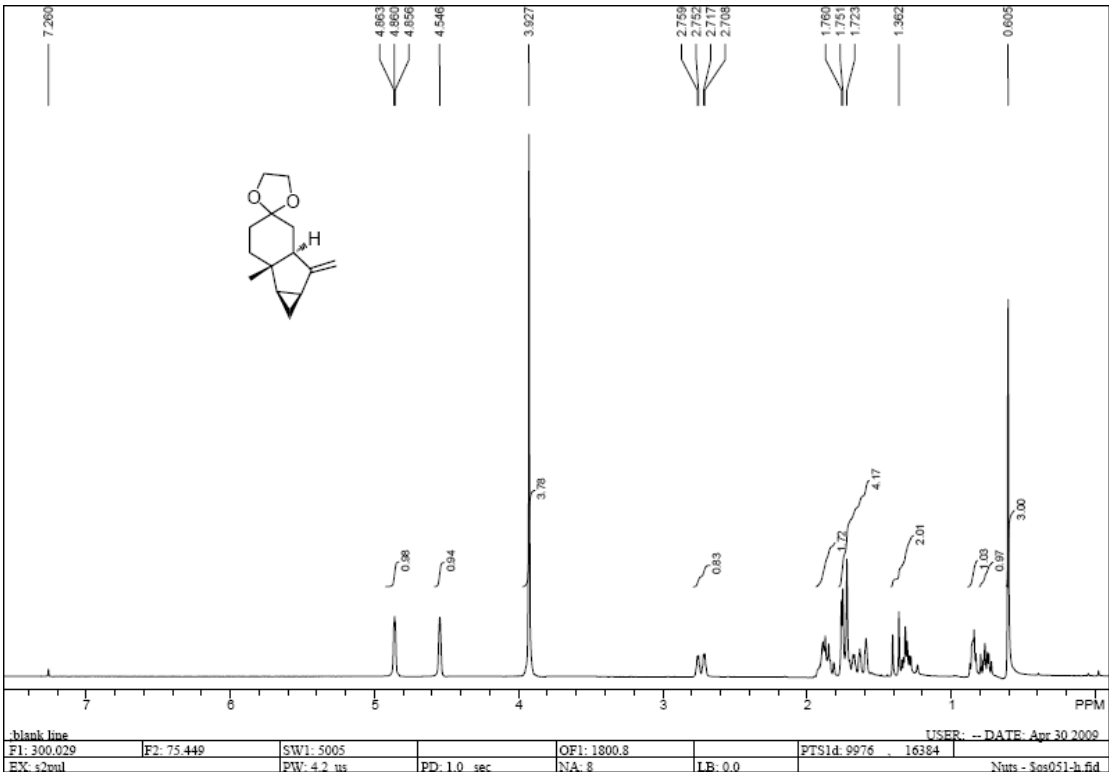
Comparison of ^{13}C NMR chemical shifts (δ: ppm)

Natural (in $CDCl_3$, 100 MHz)	Synthetic (in $CDCl_3$, 100 MHz)
172.3	172.3
160.5	160.5
152.1	151.1
124.8	124.9
106.8	106.8
91.0	91.1
53.3	53.3
48.1	48.2
41.1	41.2
24.4	24.2
24.1	24.1
23.9	23.9
19.9	19.9
16.3	16.3
8.8	8.8

(D). ^{1}H NMR and ^{13}C NMR spectra of new compounds



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4.856
4.546
3.927
2.759
2.752
2.717
2.708
1.760
1.751
1.723
1.362
0.605
O
O
H
0.88
0.94
3.78
0.83
1.72
4.17
2.01
1.03
0.97
3.00
7
6
5
4
3
2
1
PPM
blank line
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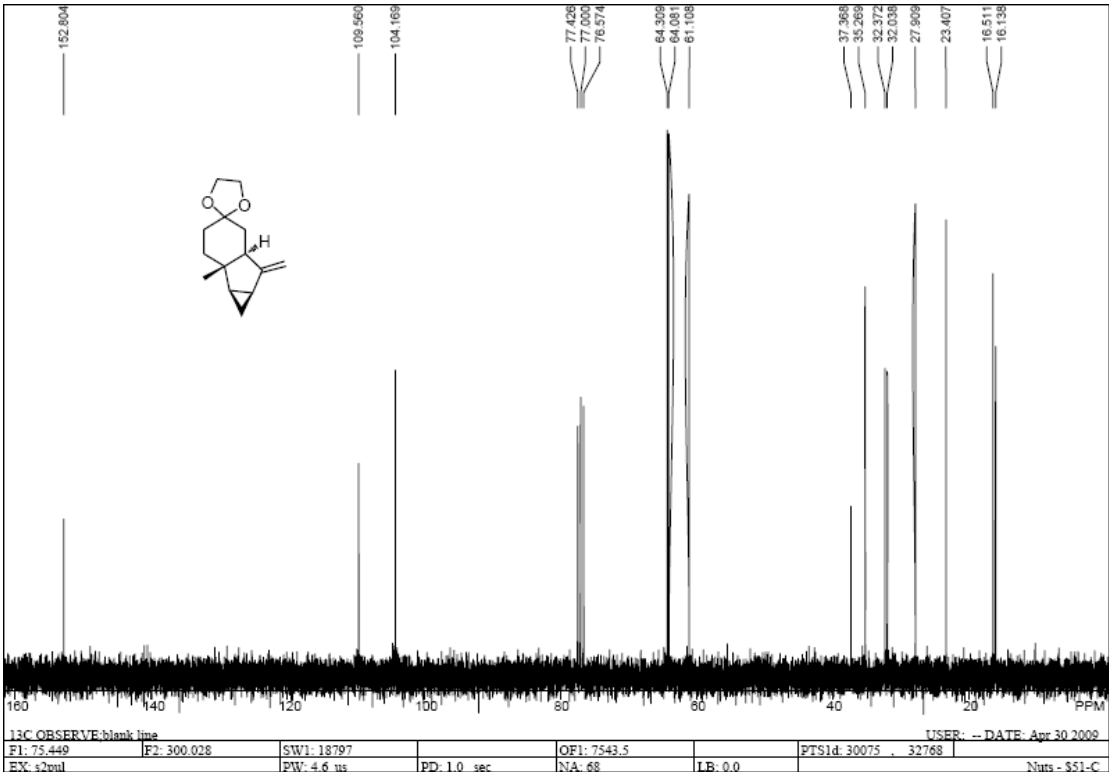
F1: 300.029
F2: 75.449
SW1: 5005
OF1: 1800.8
PTS1d: 9976 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $os051-h.fid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109.560
104.169
77.426
77.000
76.574
64.309
64.051
61.108
37.368
35.269
32.372
32.038
27.909
23.407
16.511
16.138
O
O
H
160
140
120
100
80
60
40
20
PPM
13C OBSERVE:blank line
USER: -- DATE: Apr 30 2009
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F2: 300.028
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OF1: 7543.5
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EX: s2pul
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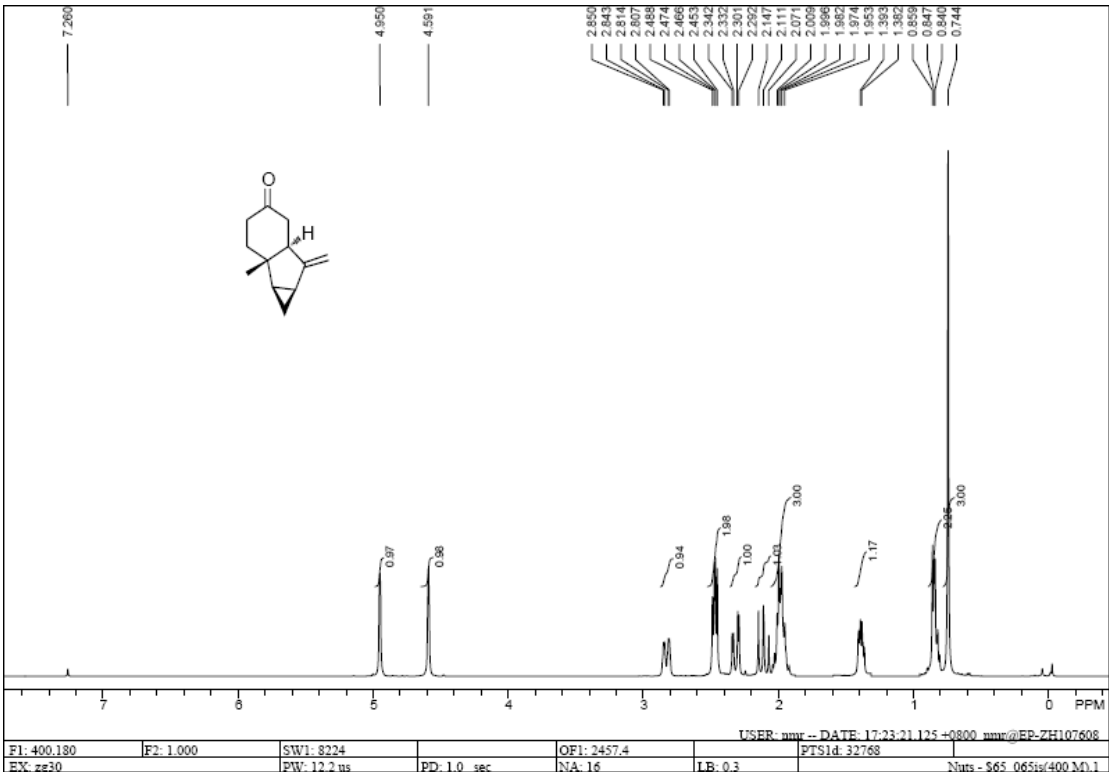
LB: 0.0
Nuts - $51-C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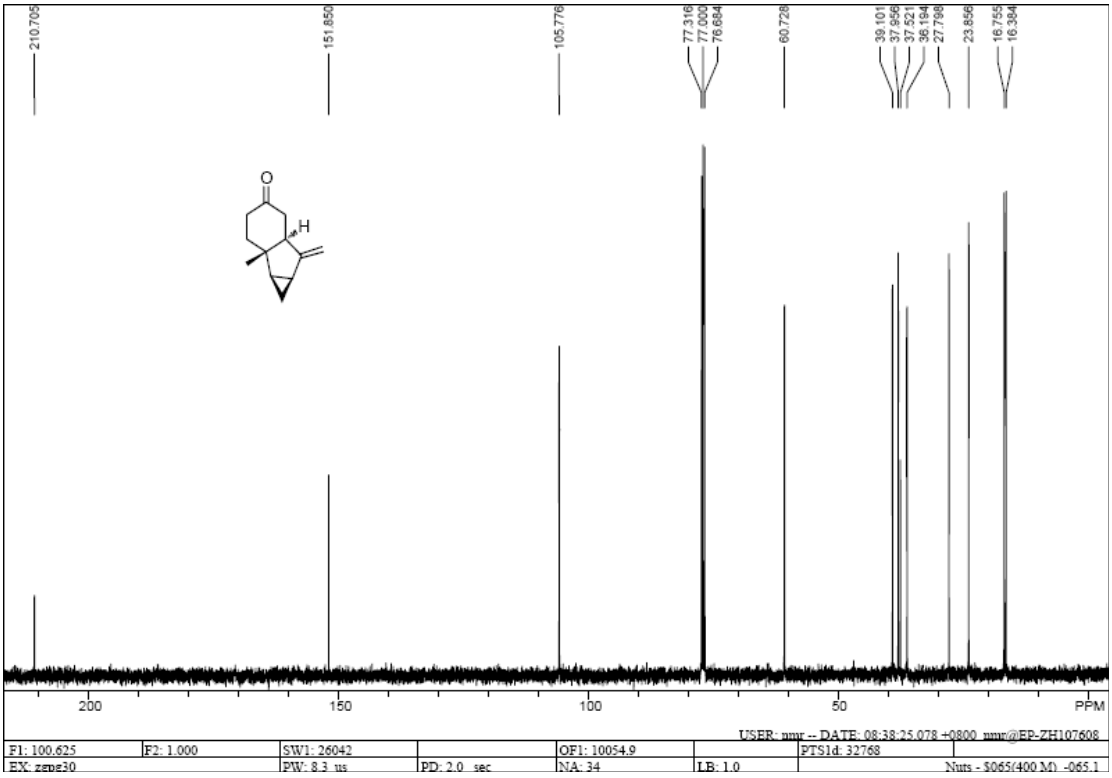
2.814
2.807
2.488
2.474
2.466
2.453
2.342
2.332
2.301
2.292
2.147
2.111
2.071
2.009
1.996
1.982
1.974
1.953
1.393
1.382
0.859
0.847
0.840
0.744
O
H
0.97
0.98
0.94
1.98
1.00
1.01
3.00
1.17
8.05
3.00
7
6
5
4
3
2
1
0
PPM
USER: nmr -- DATE: 17:23:21.125 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2457.4
PTS1d: 32768
EX: ze30
PW: 12.2 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $65_065is(400 M).1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105.776
77.316
77.000
76.684
60.728
39.101
37.956
37.521
36.194
27.798
23.856
16.755
16.384
O
H
200
150
100
50
PPM
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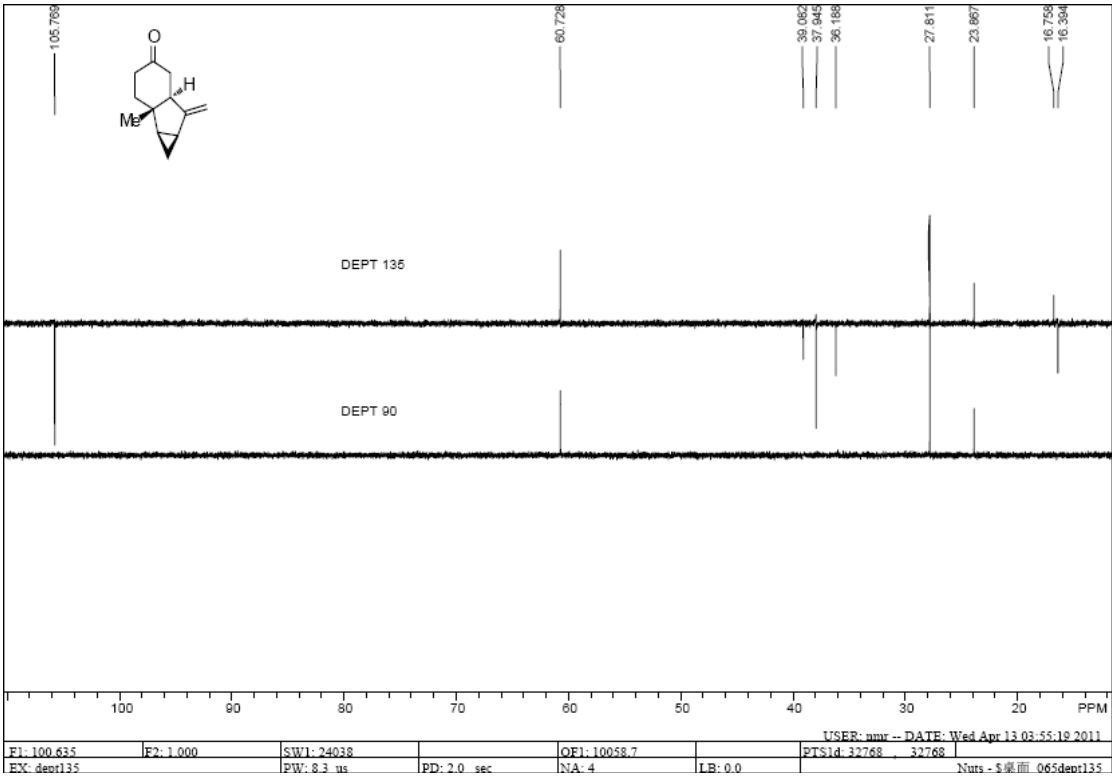
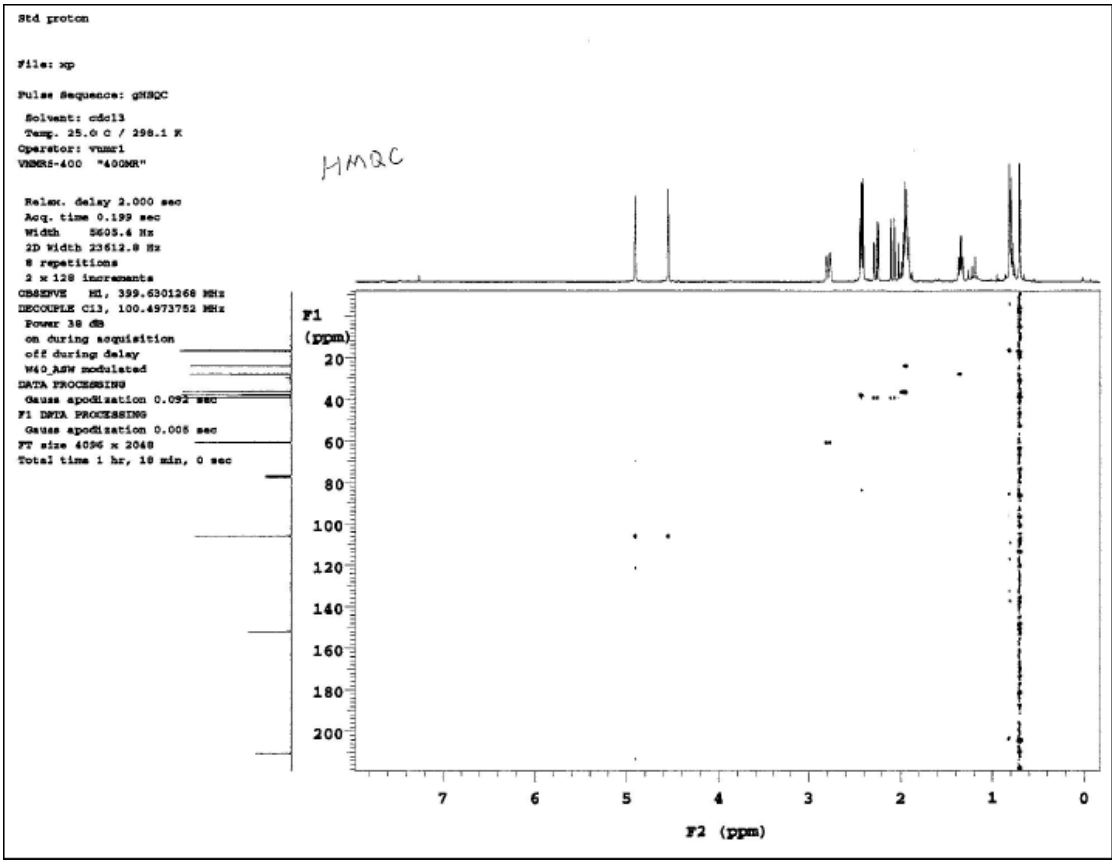
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10054.9
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 34
LB: 1.0
Nuts - $065(400 M) -065.1


105.769
60.728
39.062
37.945
36.188
27.811
23.867
16.759
16.394
O
H
Me
DEPT 135
DEPT 90
100
90
80
70
60
50
40
30
20
PPM
USER: nmr -- DATE: Wed Apr 13 03:55:19 2011
F1: 100.635
F2: 1.000
SW1: 24038
OF1: 10058.7
PTS1d: 32768 , 32768
EX: dept135
PW: 8.3 us
PD: 2.0 sec
NA: 4
LB: 0.0
Nuts - $桌面 065dept135


Std proton
File: xp
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. delay 2.000 sec
Acq. time 0.199 sec
Width 5605.4 Hz
2D Width 23612.8 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 399.6301268 MHz
DECOUPLE C13, 100.4973752 MHz
Power 38 dB
on during acquisition
off during delay
W40_ASW modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 1 hr, 10 min, 0 sec
HMQC
F1 (ppm)
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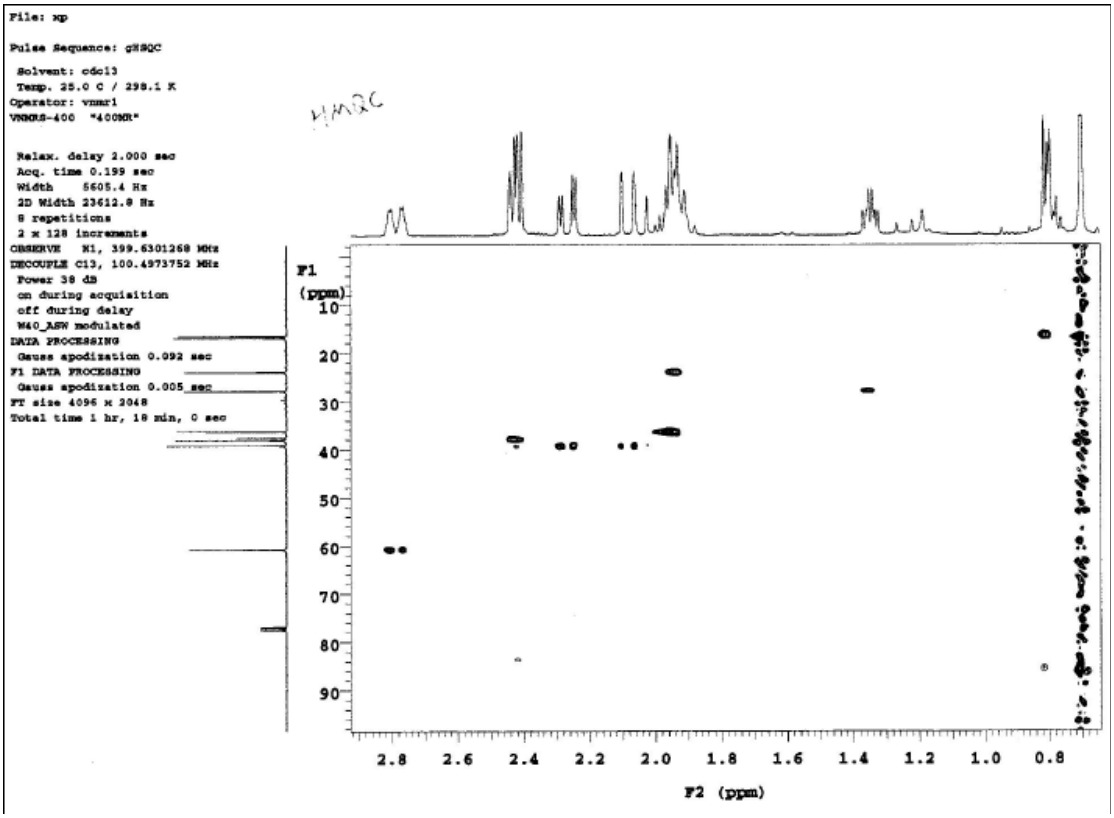
40
60
80
100
120
140
160
180
200
7
6
5
4
3
2
1
0
F2 (ppm)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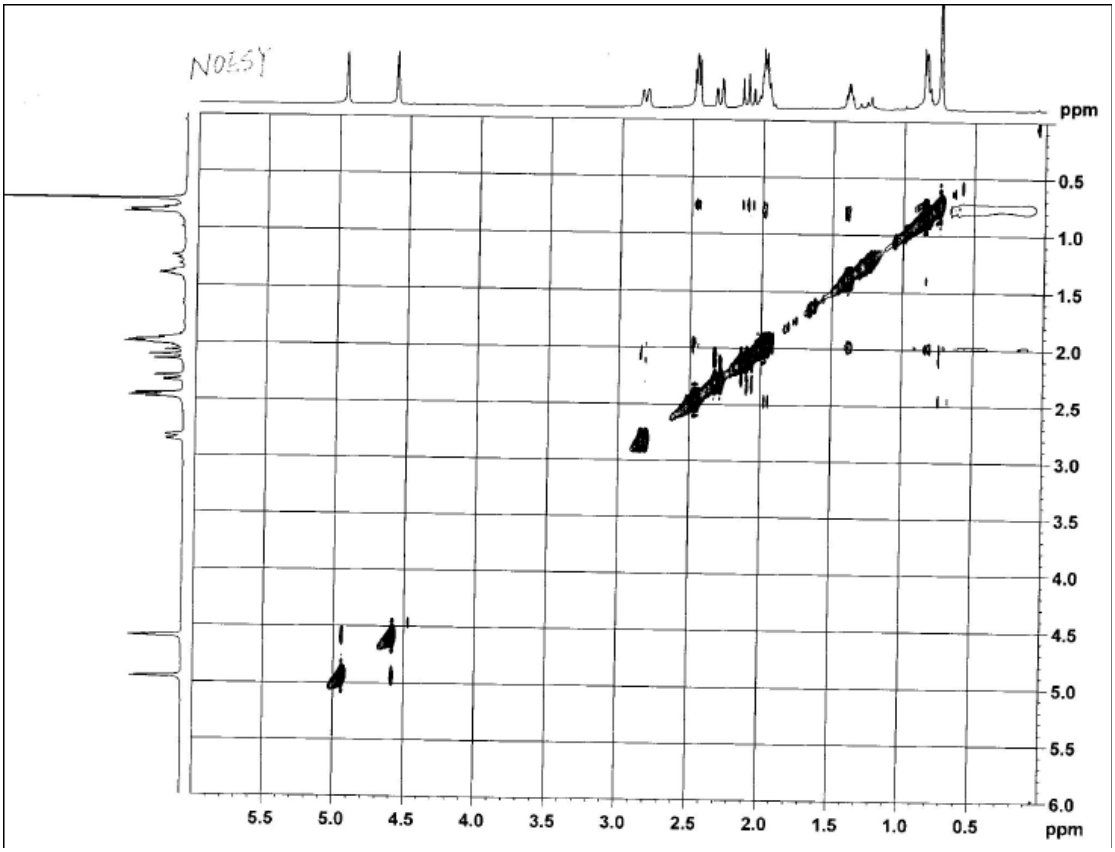
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. delay 2.000 sec
Acq. time 0.199 sec
Width 5605.4 Hz
2D Width 23612.8 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 399.6301268 MHz
DECOUPLE C13, 100.4973752 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ_ASW modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 1 hr, 18 min, 0 sec
HMQC
F1 (ppm)
F2 (ppm)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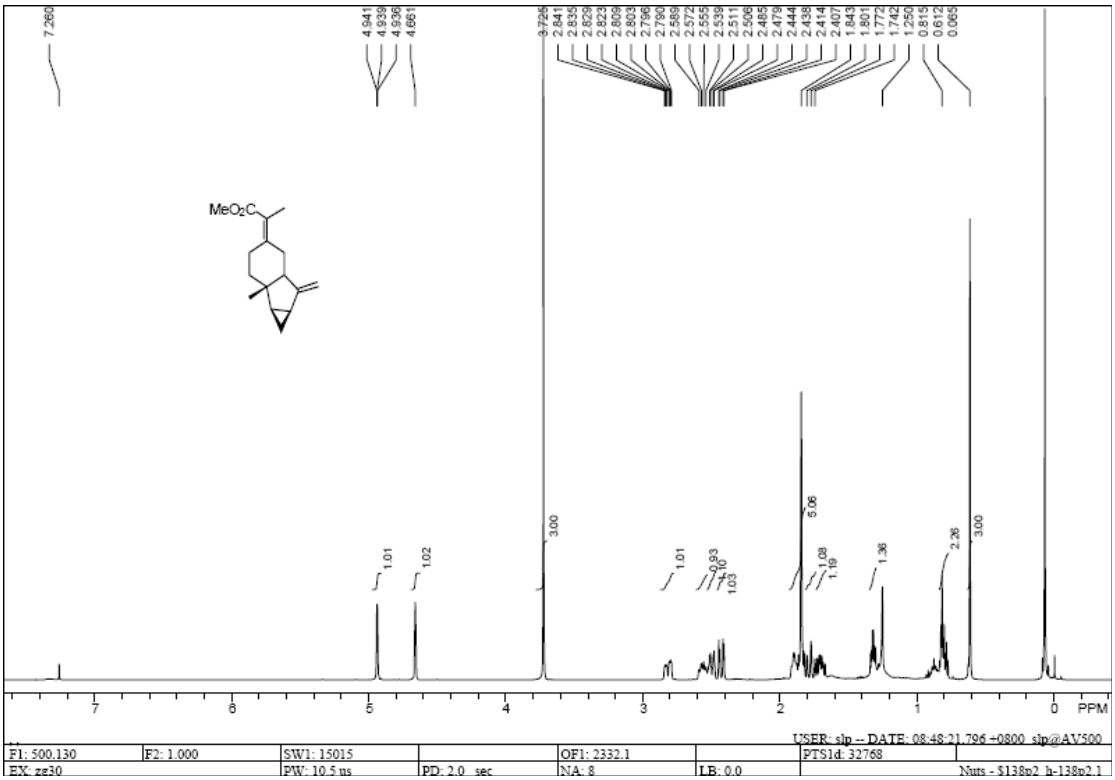
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2.823
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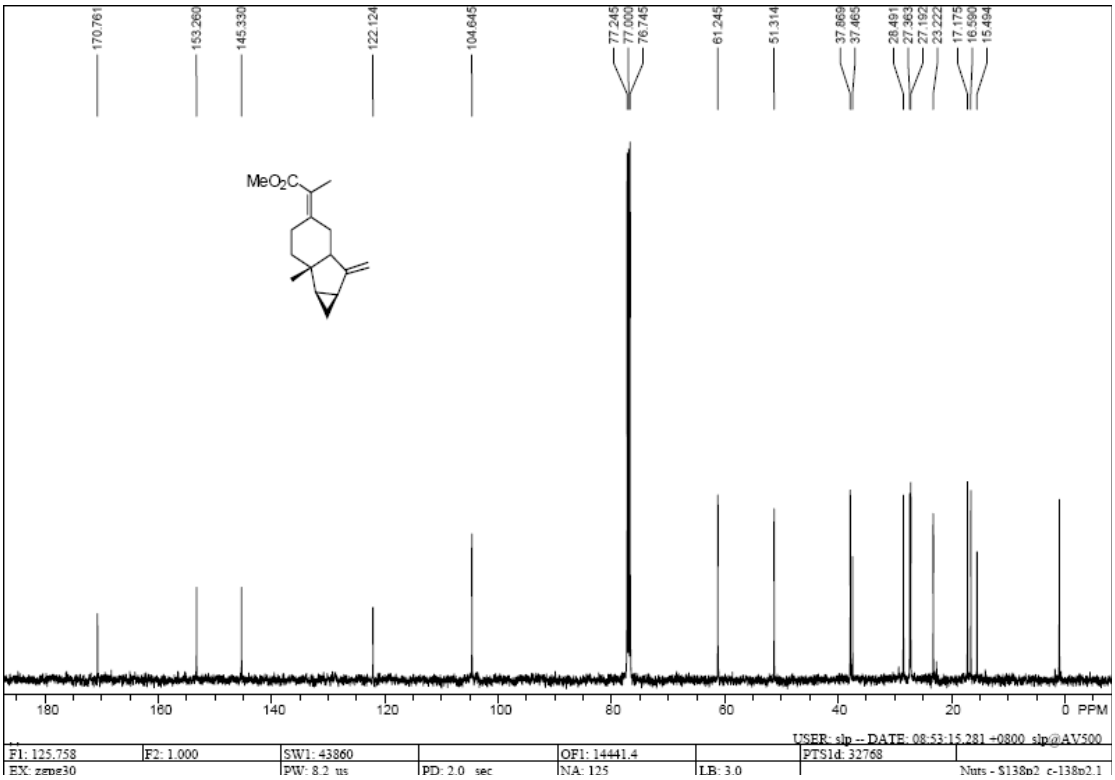
2.796
2.790
2.589
2.572
2.555
2.539
2.511
2.506
2.485
2.479
2.444
2.438
2.414
2.407
1.843
1.801
1.772
1.742
1.250
0.815
0.612
0.065
MeO2C
1.01
1.02
3.00
1.01
0.93
1.10
1.03
5.06
1.08
1.19
1.36
2.26
3.00
7
6
5
4
3
2
1
0 PPM
USER: slp -- DATE: 08:48:21.796 +0800 slp@AV500
F1: 500.130
F2: 1.000
SW1: 15015
OF1: 2332.1
PTS1d: 32768
EX: ze30
PW: 10.5 us
PD: 2.0 sec
NA: 8
LB: 0.0
Nuts - $138p2 h-138p2.1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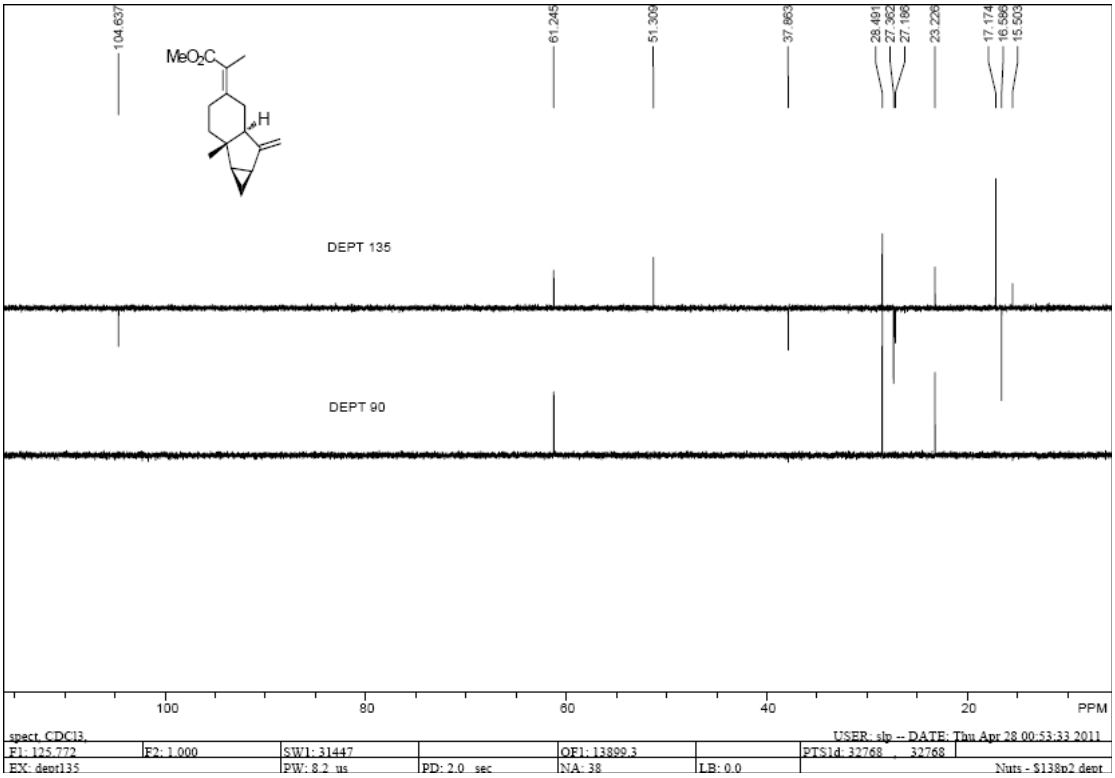
122.124
104.645
77.245
77.000
76.745
61.245
51.314
37.869
37.465
28.491
27.363
27.192
23.222
17.175
16.590
15.494
MeO2C
180
160
140
120
100
80
60
40
20
0 PPM
USER: slp -- DATE: 08:53:15.281 +0800 slp@AV500
F1: 125.758
F2: 1.000
SW1: 43860
OF1: 14441.4
PTS1d: 32768
EX: zgpg30
PW: 8.2 us
PD: 2.0 sec
NA: 125
LB: 3.0
Nuts - $138p2 c-138p2.1


104.637
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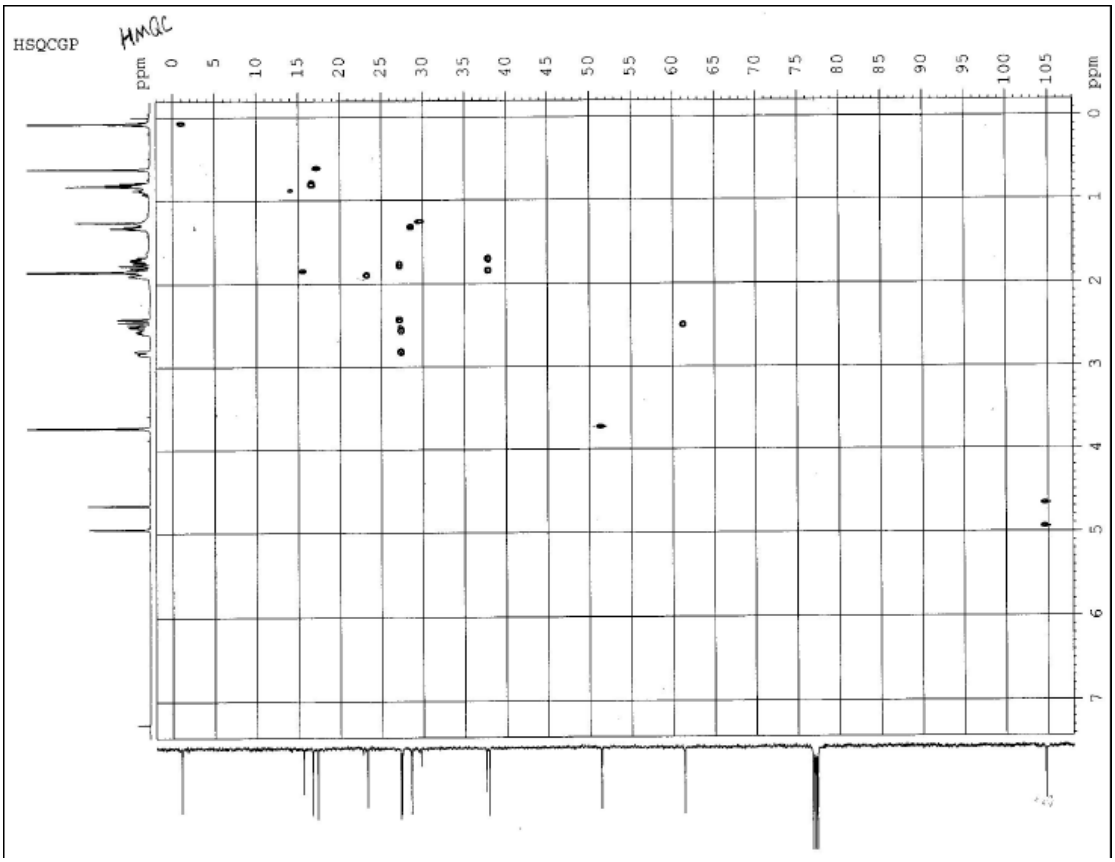
51.309
37.863
28.491
27.362
27.186
23.226
17.174
16.586
15.503
MeO2C
H
DEPT 135
DEPT 90
100
80
60
40
20
PPM
spect, CDCl3,
USER: slp -- DATE: Thu Apr 28 00:53:33 2011
F1: 125.772
F2: 1.000
SW1: 31447
OF1: 13899.3
PTS1d: 32768 , 32768
EX: dept135
PW: 8.2 us
PD: 2.0 sec
NA: 38
LB: 0.0
Nuts - S138p2 dept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HMQC
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10
15
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35
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45
50
55
60
65
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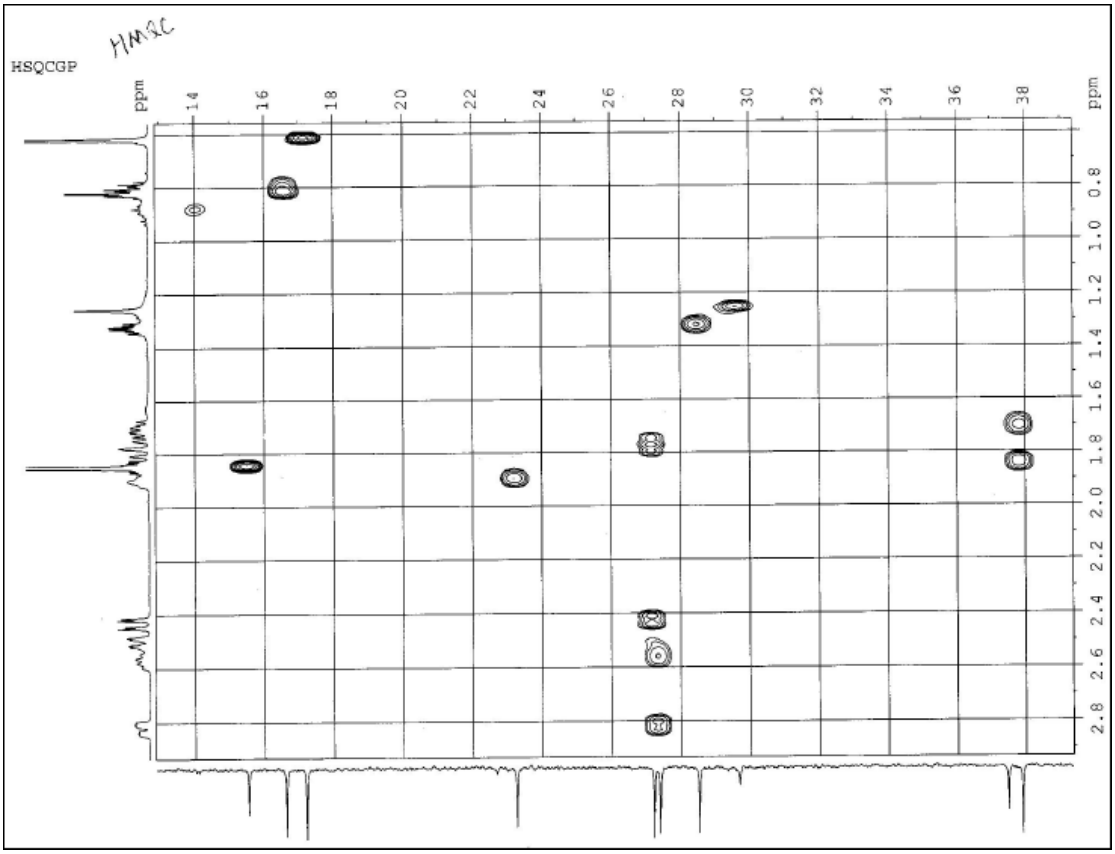
75
80
85
90
95
100
105
ppm
0
1
2
3
4
5
6
7


HSQCGP
HMBC
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18
20
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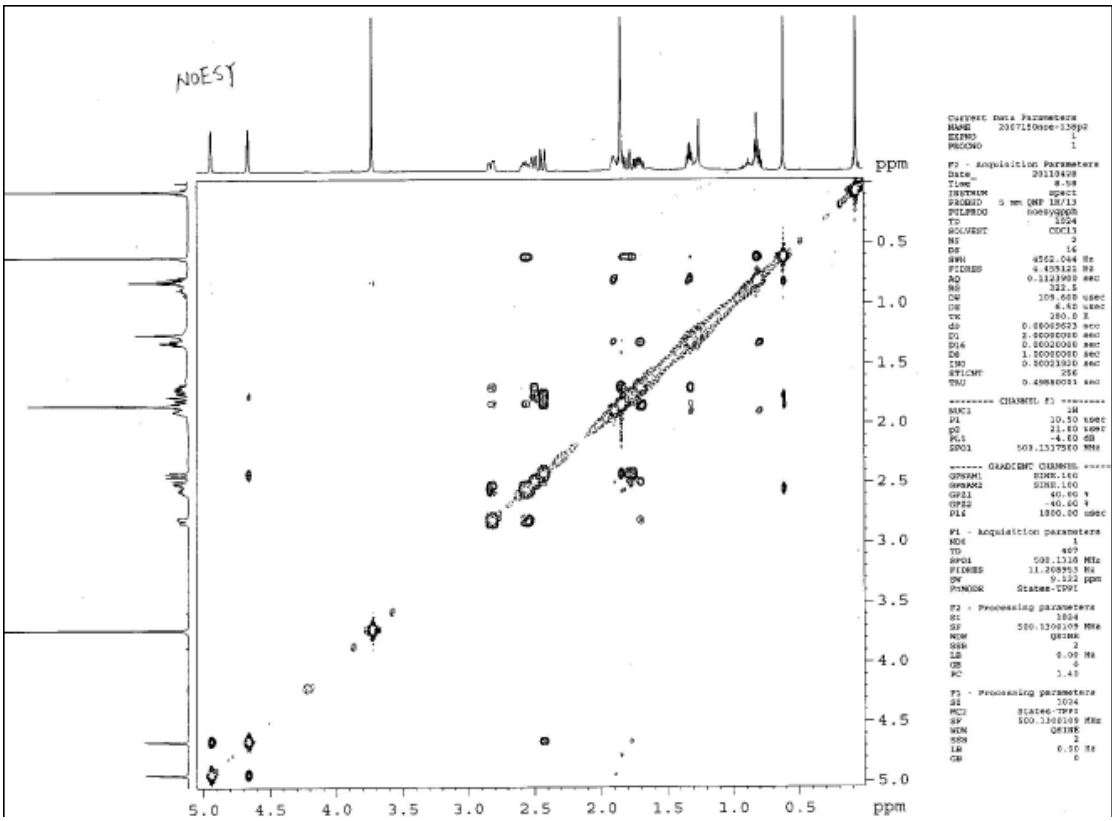
1.8
2.0
2.2
2.4
2.6
2.8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3.5
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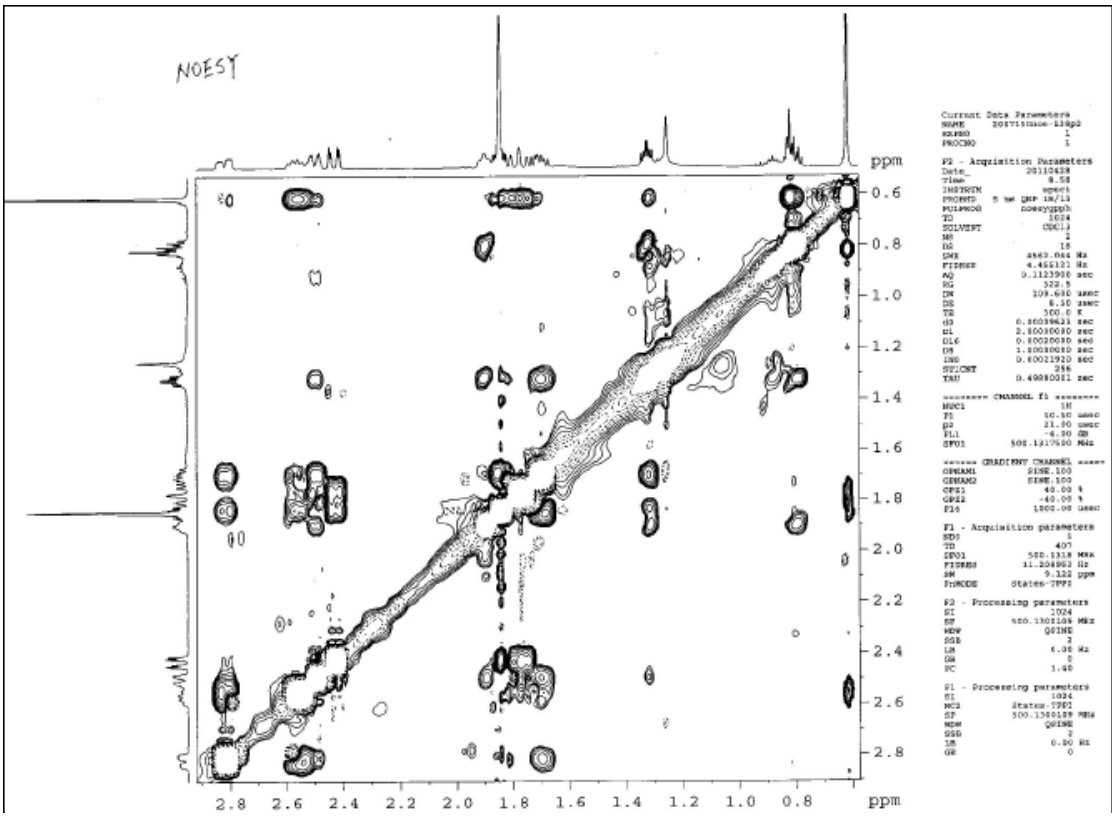
2.5
2.0
1.5
1.0
0.5
ppm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ppm
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1.2
1.4
1.6
1.8
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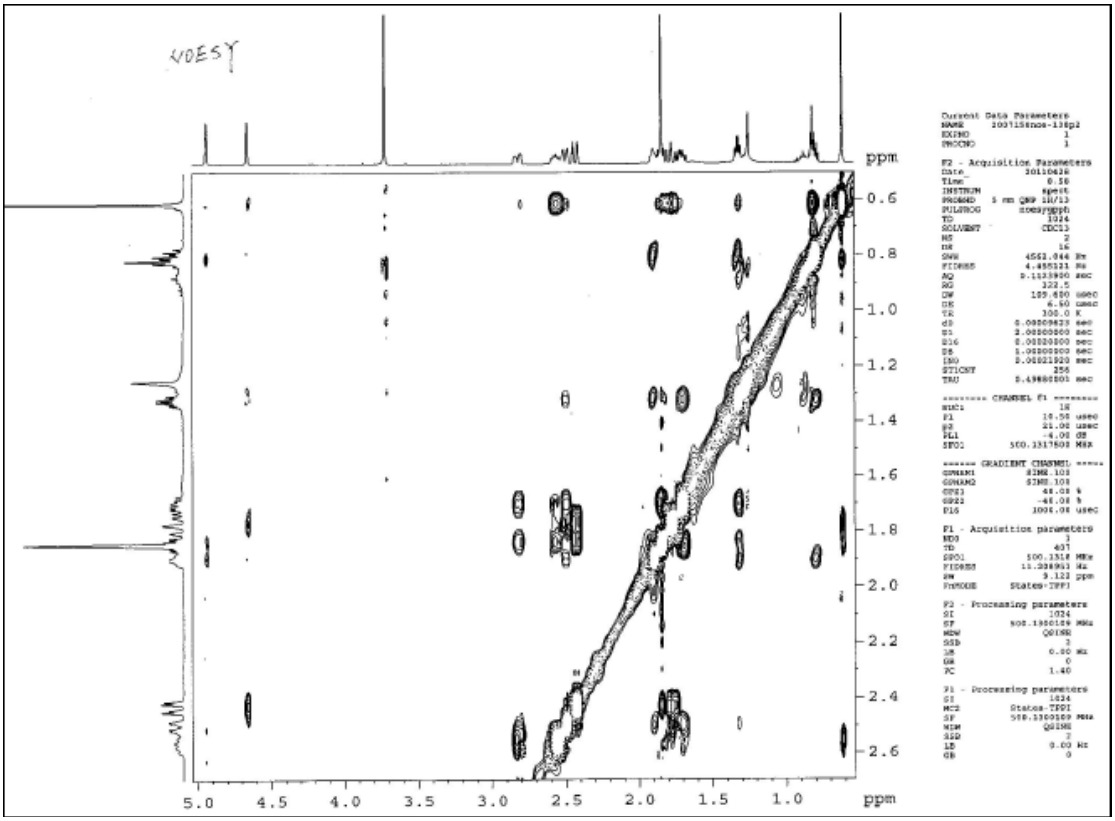
2.4
2.6
2.8
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
ppm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1.0
1.2
1.4
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1.8
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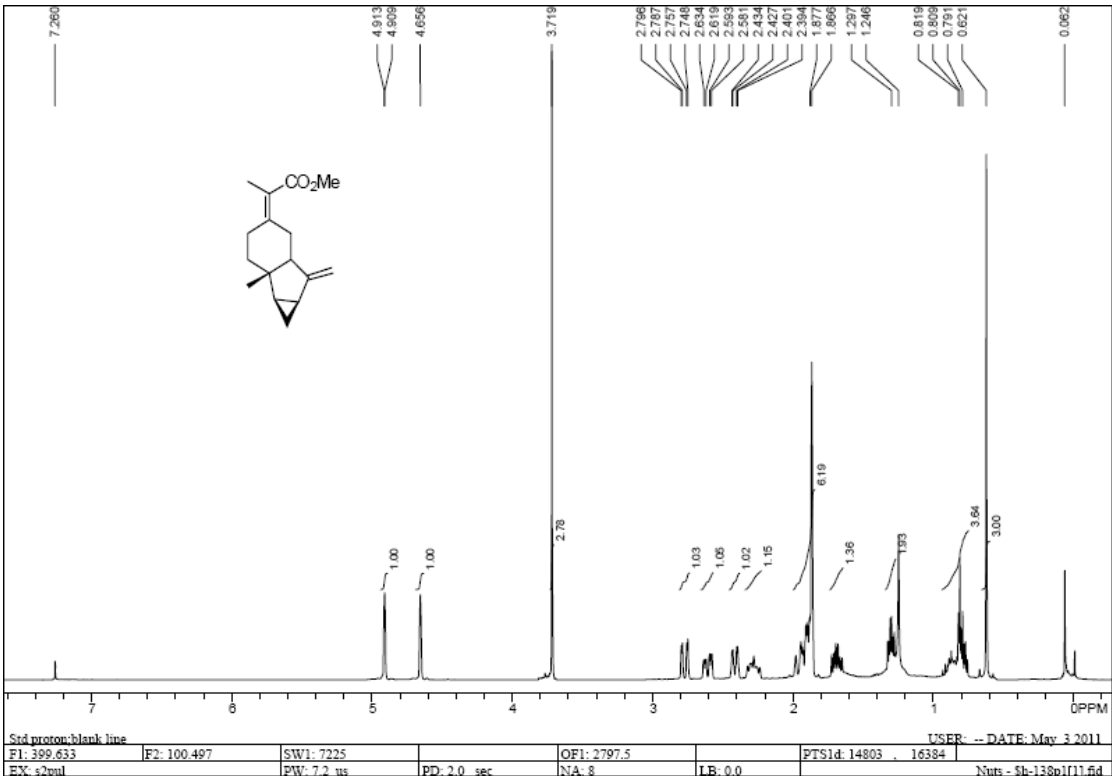
2.2
2.4
2.6
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm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2.593
2.581
2.434
2.427
2.401
2.394
1.877
1.866
1.297
1.246
0.819
0.809
0.791
0.621
0.062
CO2Me
1.00
1.00
2.78
1.03
1.05
1.02
1.15
6.19
1.36
1.93
3.64
3.00
7
6
5
4
3
2
1
0PPM
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USER: -- DATE: May 3 2011
F1: 399.633
F2: 100.497
SW1: 7225
OF1: 2797.5
PTS1d: 14803 , 16384
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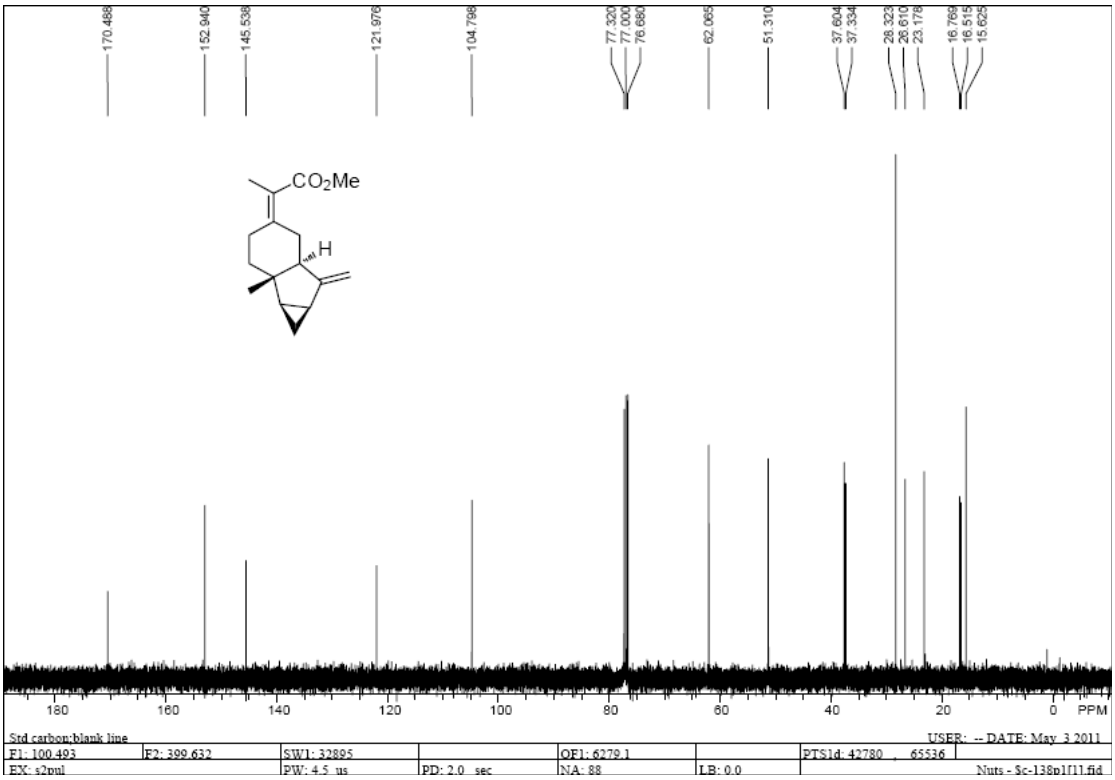
PW: 7.2 us
PD: 2.0 sec
NA: 8
LB: 0.0
Nuts - $h-138p1f11.fid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76.680
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51.310
37.604
37.334
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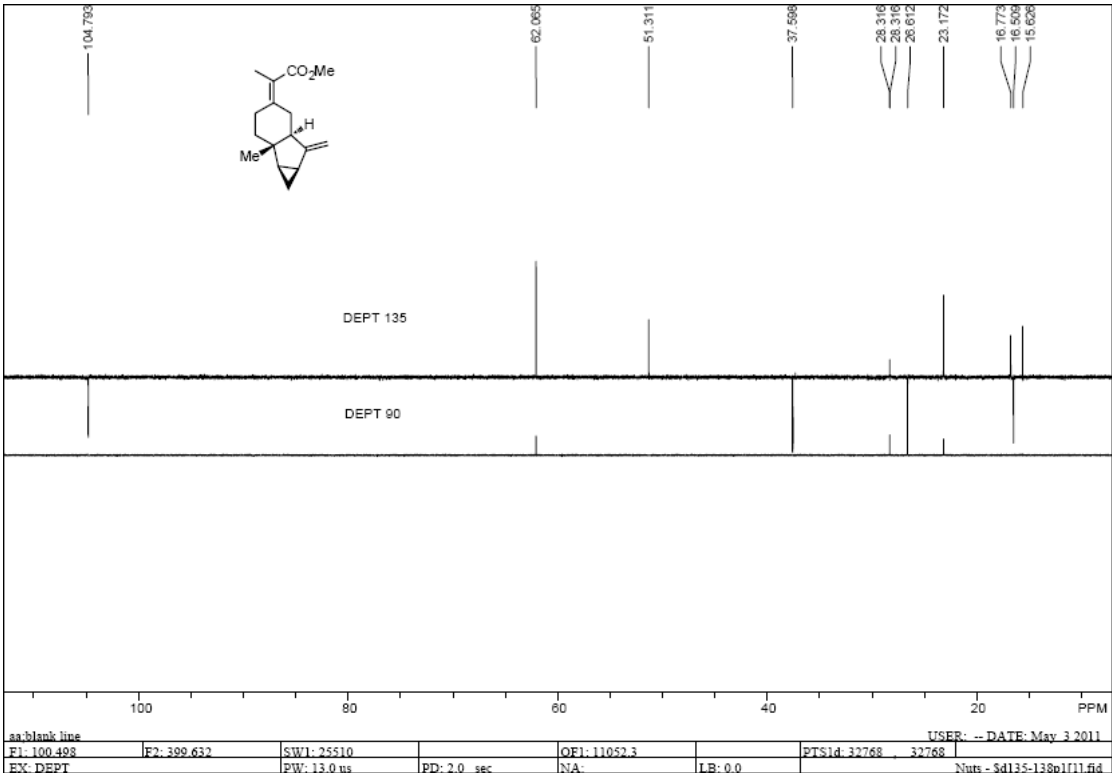
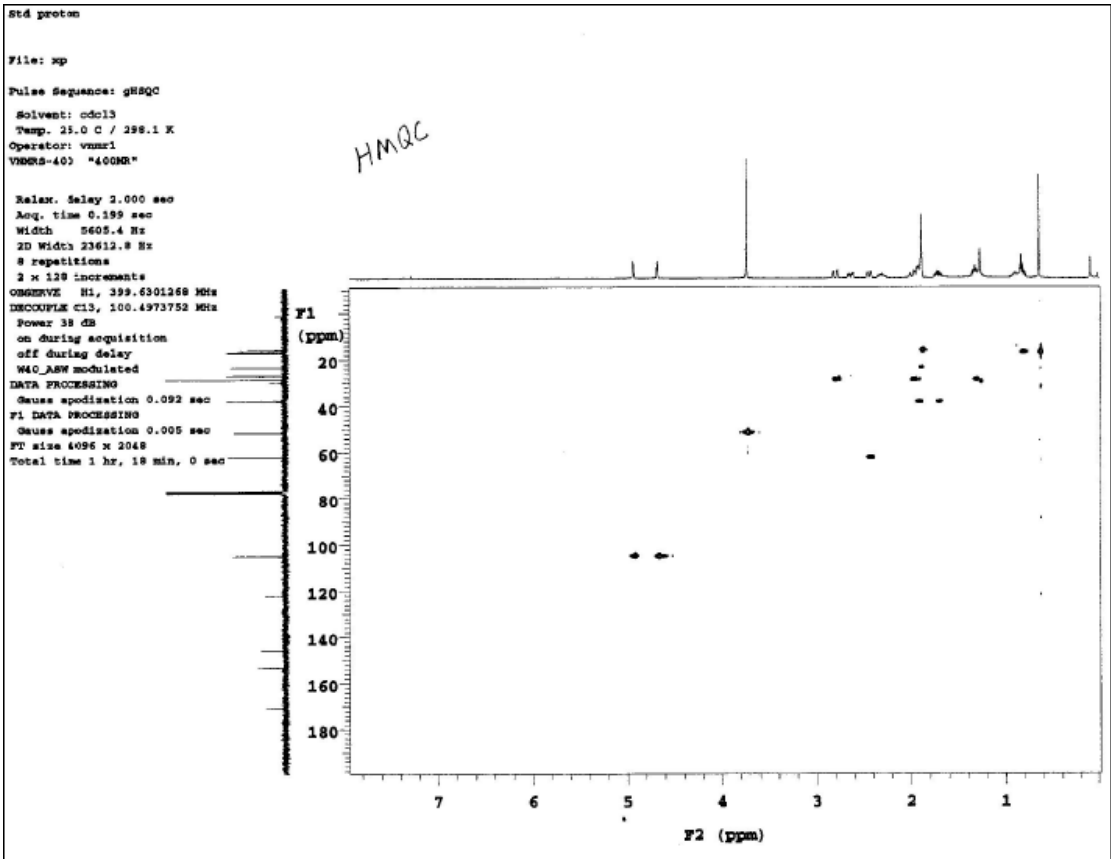
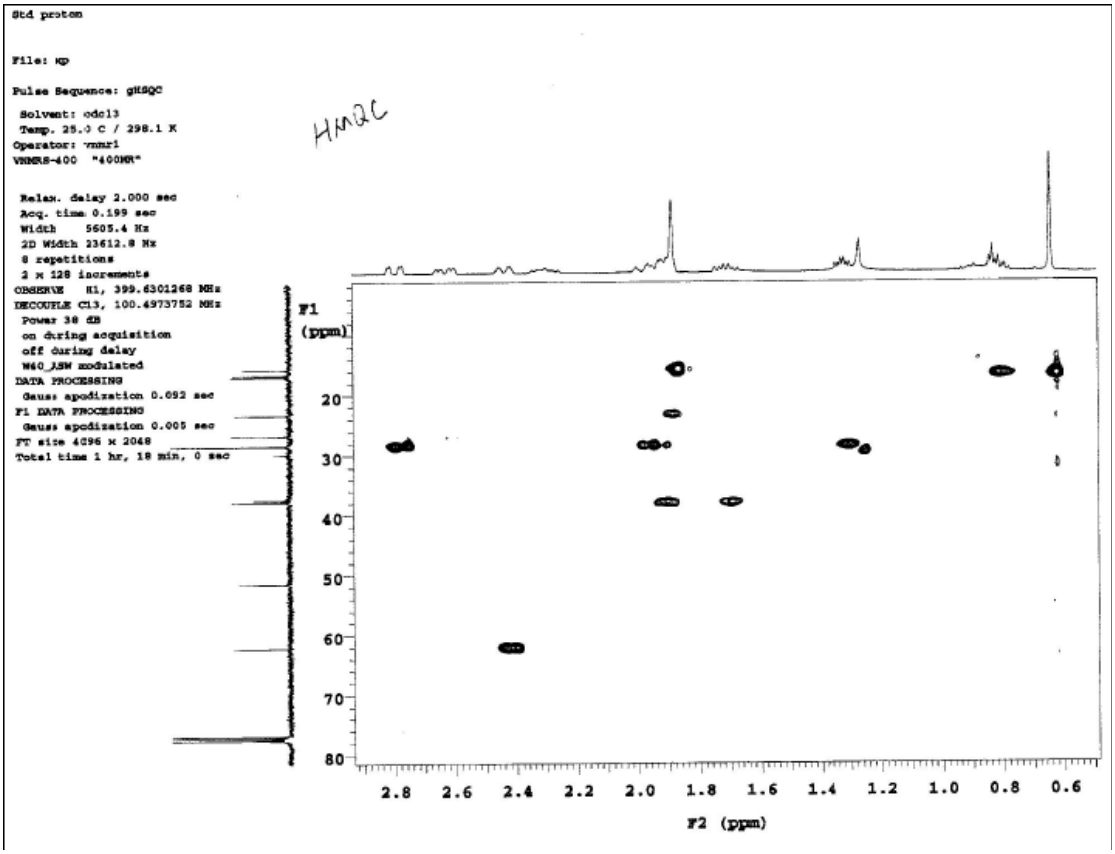
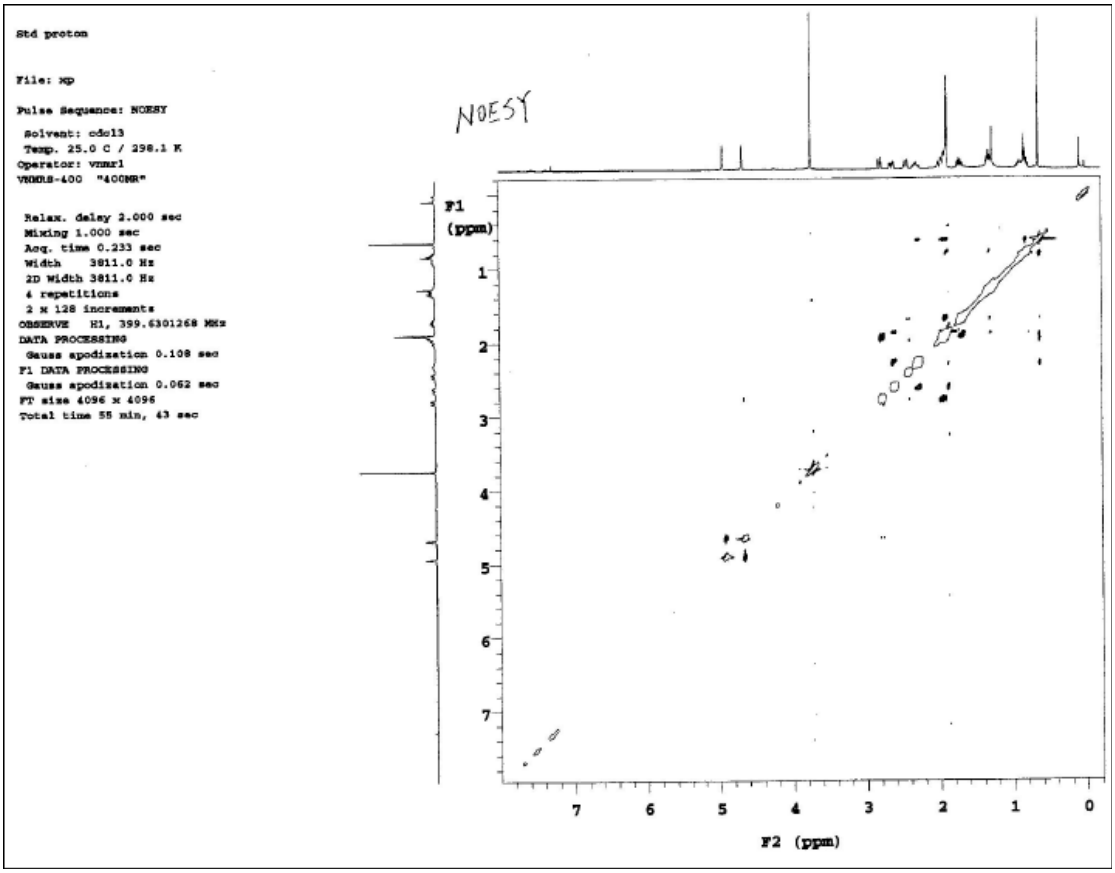
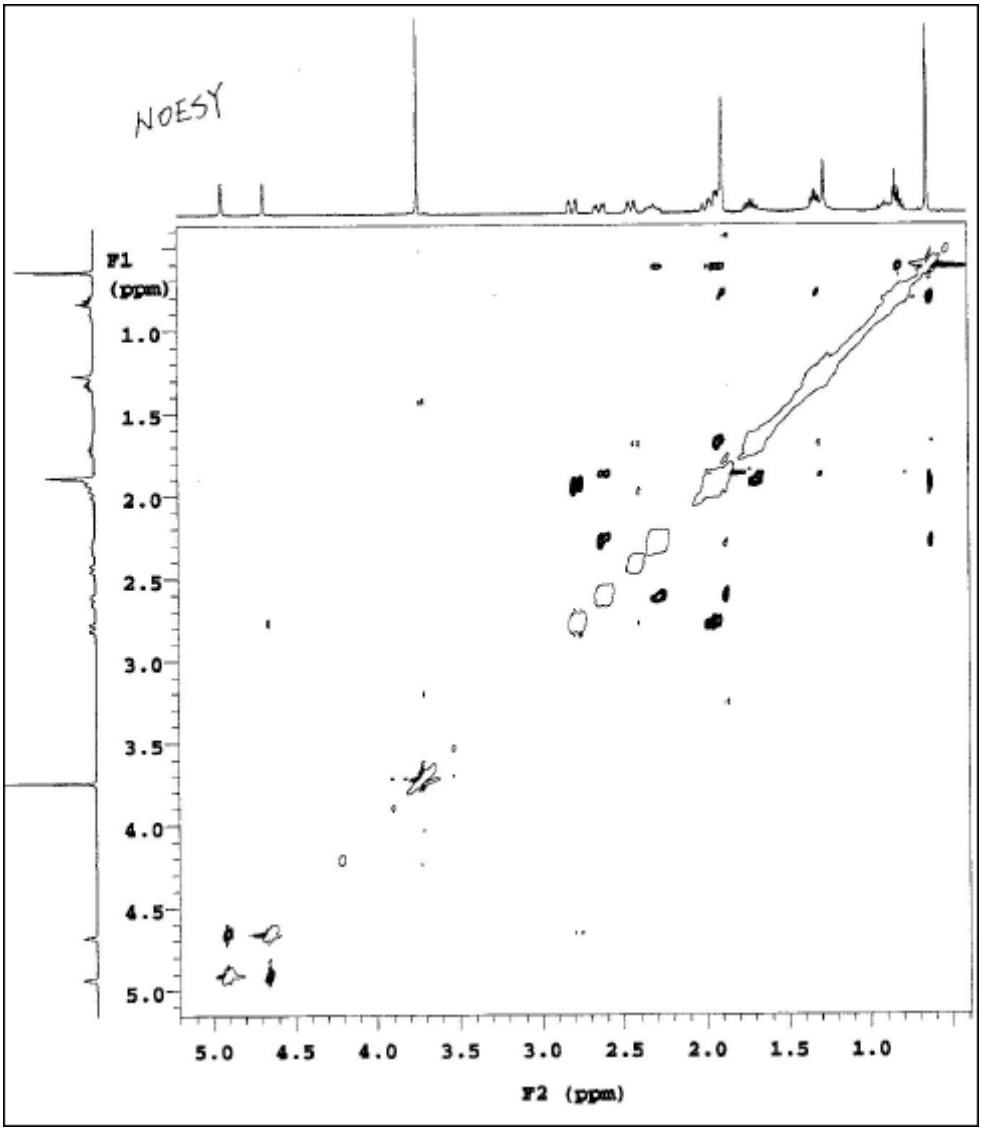
26.610
23.178
16.769
16.515
15.625
CO2Me
H
180
160
140
120
100
80
60
40
20
0
PPM
Std carbon:blank line
USER: -- DATE: May 3 2011
F1: 100.493
F2: 399.632
SW1: 32895
OF1: 6279.1
PTS1d: 42780 , 65536
EX: s2pul
PW: 4.5 us
PD: 2.0 sec
NA: 88
LB: 0.0
Nuts - $c-138p1f11.fid

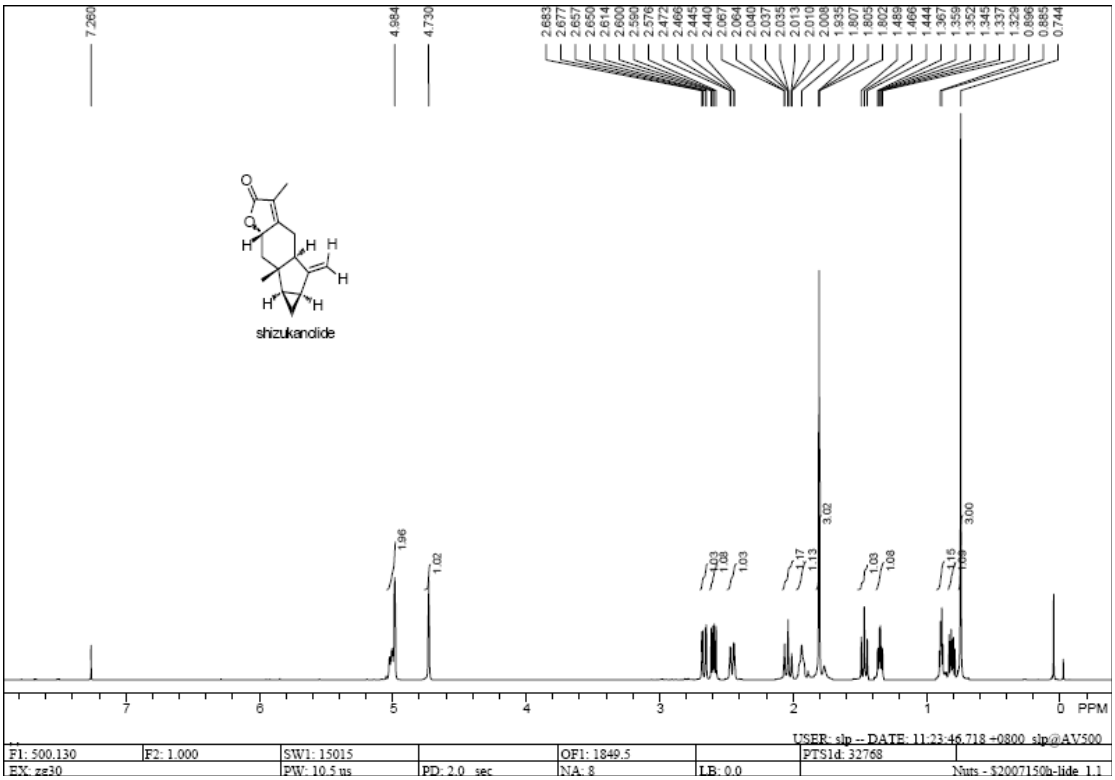

104.793
62.065
51.311
37.598
28.316
28.316
26.612
23.172
16.773
16.509
15.626
CO2Me
H
Me
DEPT 135
DEPT 90
100
80
60
40
20
PPM
aa:blank line
USER: -- DATE: May 3 2011
F1: 100.498
F2: 399.632
SW1: 25510
OF1: 11052.3
PTS1d: 32768 , 32768
EX: DEPT
PW: 13.0 us
PD: 2.0 sec
NA:
LB: 0.0
Nuts - $d135-138p1f11.fid

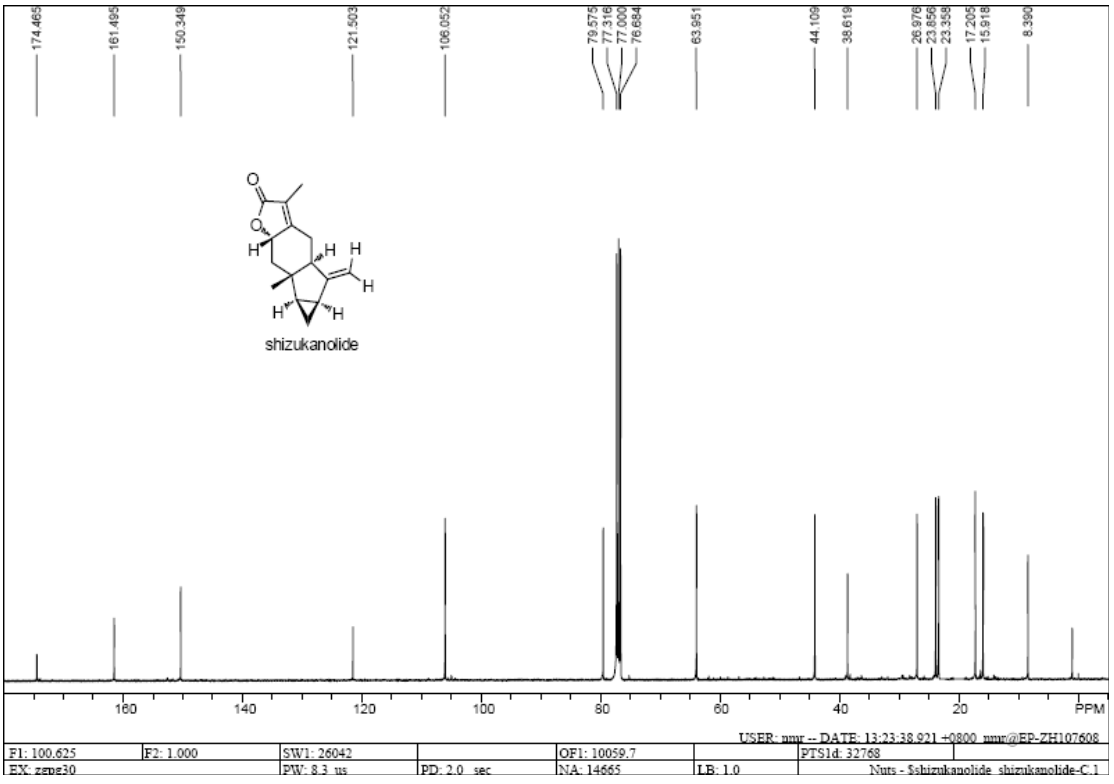

Std proton
File: xp
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. Delay 2.000 sec
Acq. time 0.199 sec
Width 5605.4 Hz
2D Width 23612.8 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 399.6301268 MHz
DECOUPLE C13, 100.4973752 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ16 modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 1 hr, 18 min, 0 sec
HMQC
F1
(ppm)
20
40
60
80
100
120
140
160
180
7
6
5
4
3
2
1
F2 (ppm)

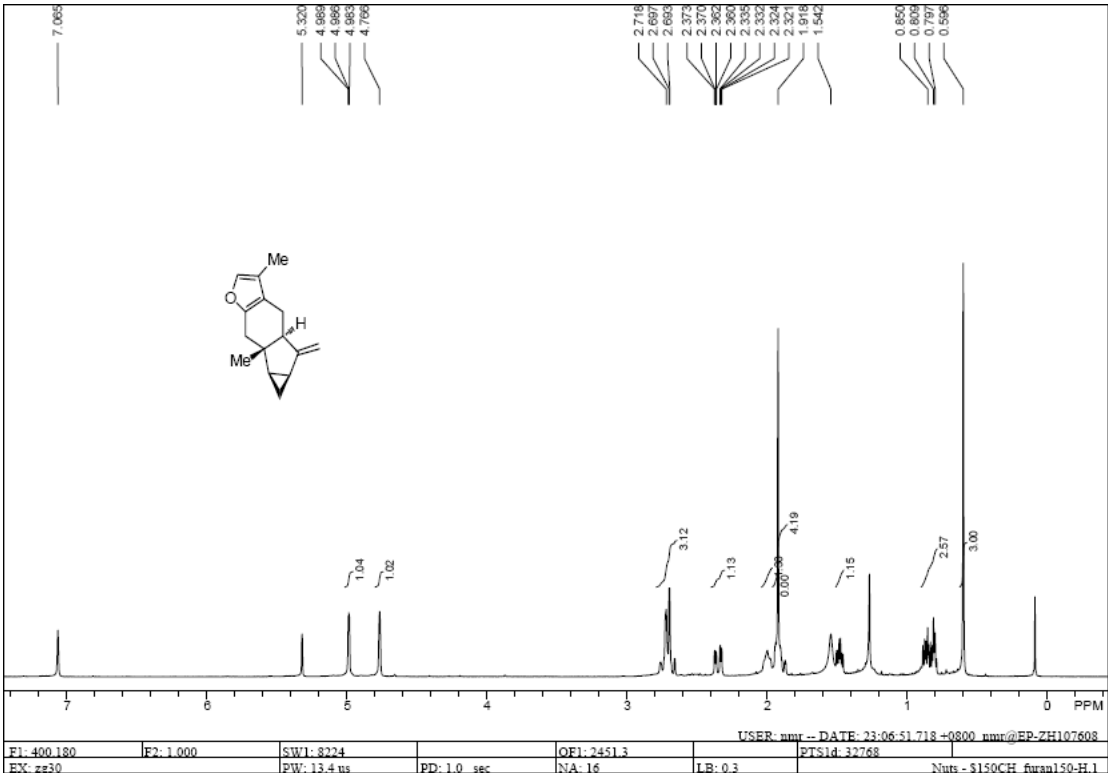

Std proton
File: KP
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. delay 2.000 sec
Acq. time 0.199 sec
Width 5605.4 Hz
2D Width 23612.8 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 399.6301268 MHz
DECOUPLE C13, 100.4973752 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ16 modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 1 hr, 18 min, 0 sec
HMQC
F1 (ppm)
F2 (ppm)

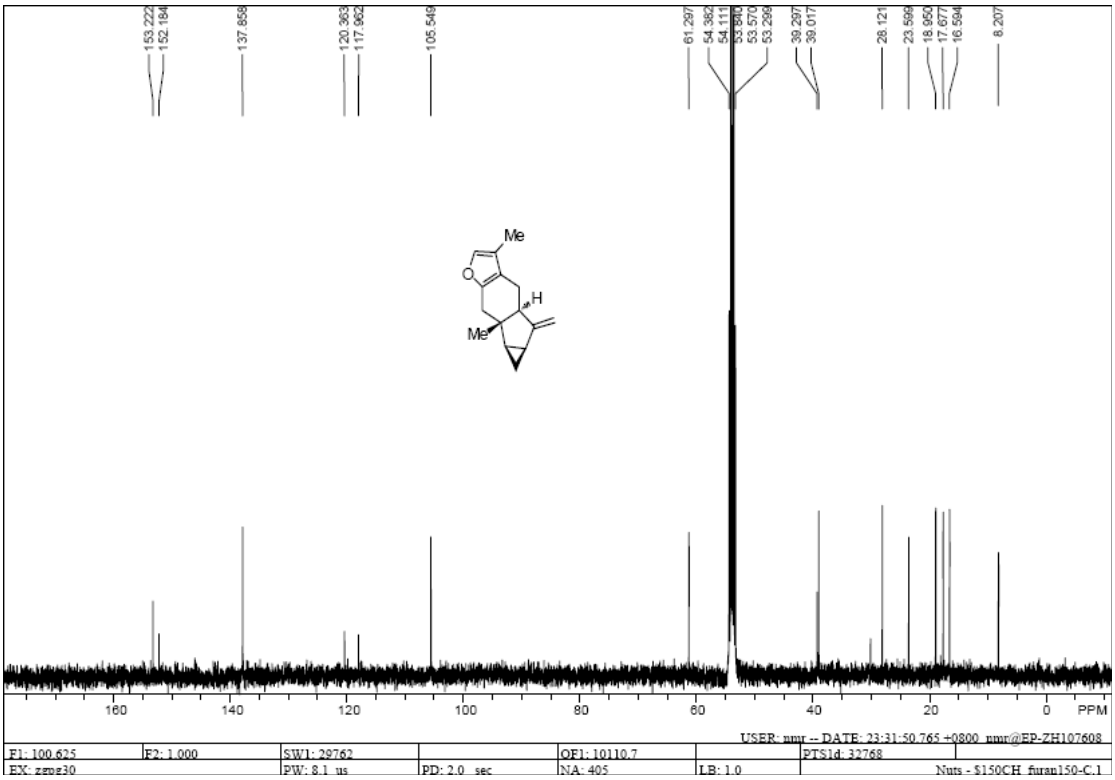

Std proton
File: KP
Pulse Sequence: NOESY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. delay 2.000 sec
Mixing 1.000 sec
Acq. time 0.233 sec
Width 3811.0 Hz
2D Width 3811.0 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.6301268 MHz
DATA PROCESSING
Gauss apodization 0.108 sec
F1 DATA PROCESSING
Gauss apodization 0.062 sec
FT size 4096 x 4096
Total time 55 min, 43 sec
NOESY
F1 (ppm)
F2 (ppm)

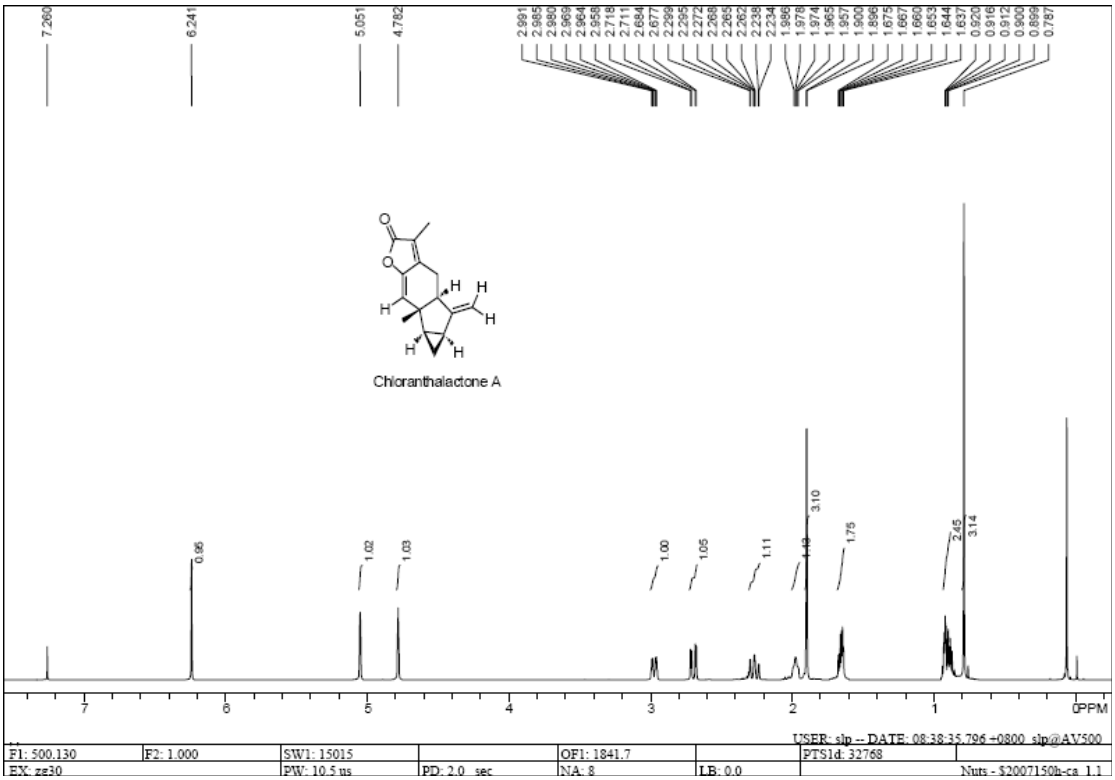

NOESY
F1
(ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 (ppm)

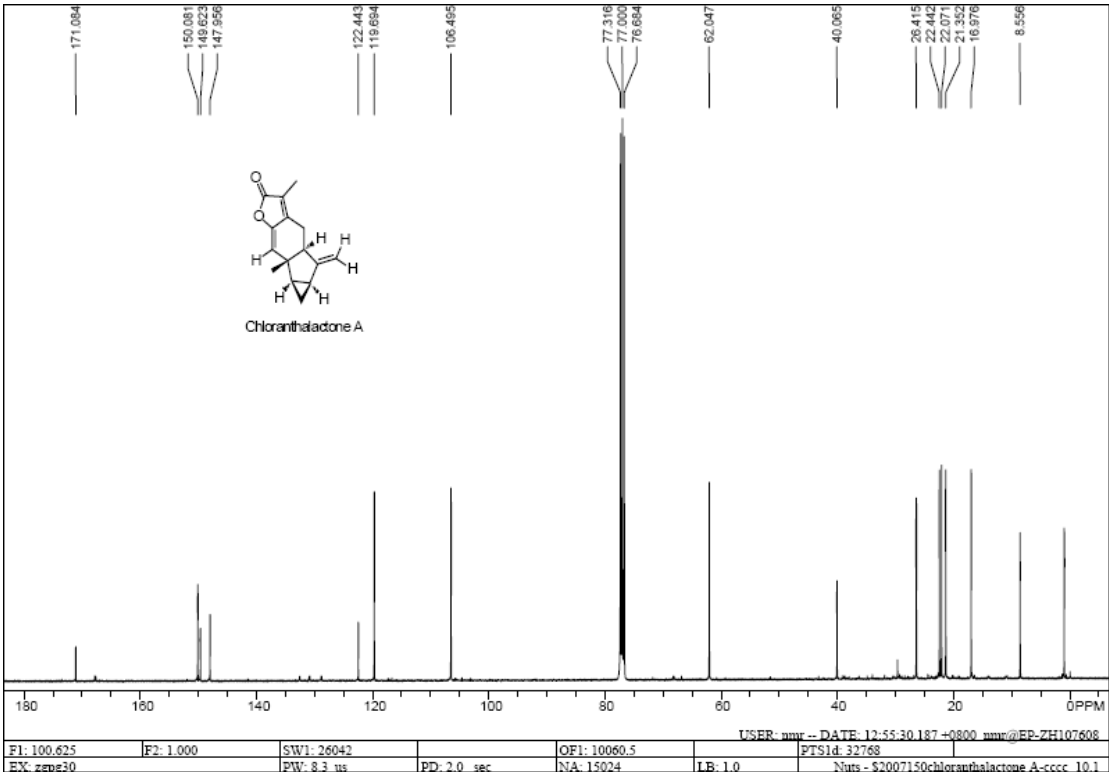

shizukanolide
PPM
F1: 500.130
F2: 1.000
SW1: 15015
OF1: 1849.5
PTS1d: 32768
EX: ze30
PW: 10.5 us
PD: 2.0 sec
NA: 8
LB: 0.0
Nuts - $2007150h-lide 1.1

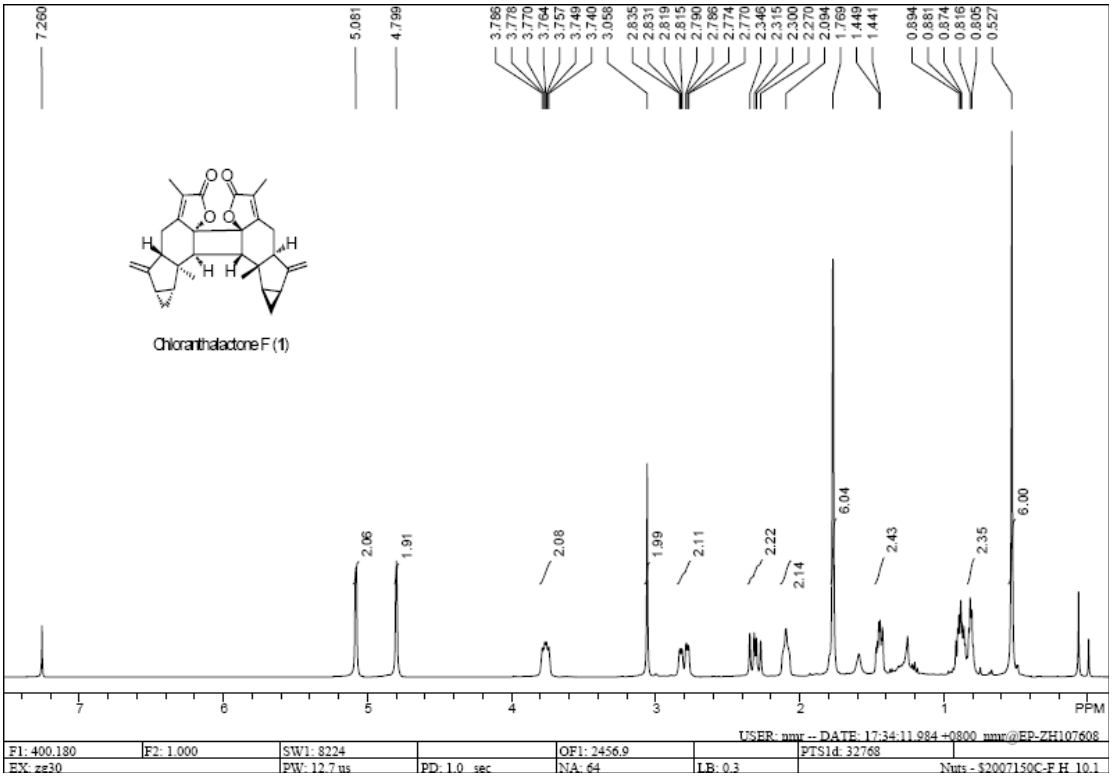

shizukanolide
PPM
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10059.7
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 14665
LB: 1.0
Nuts - $shizukanolide_shizukanolide-C.1

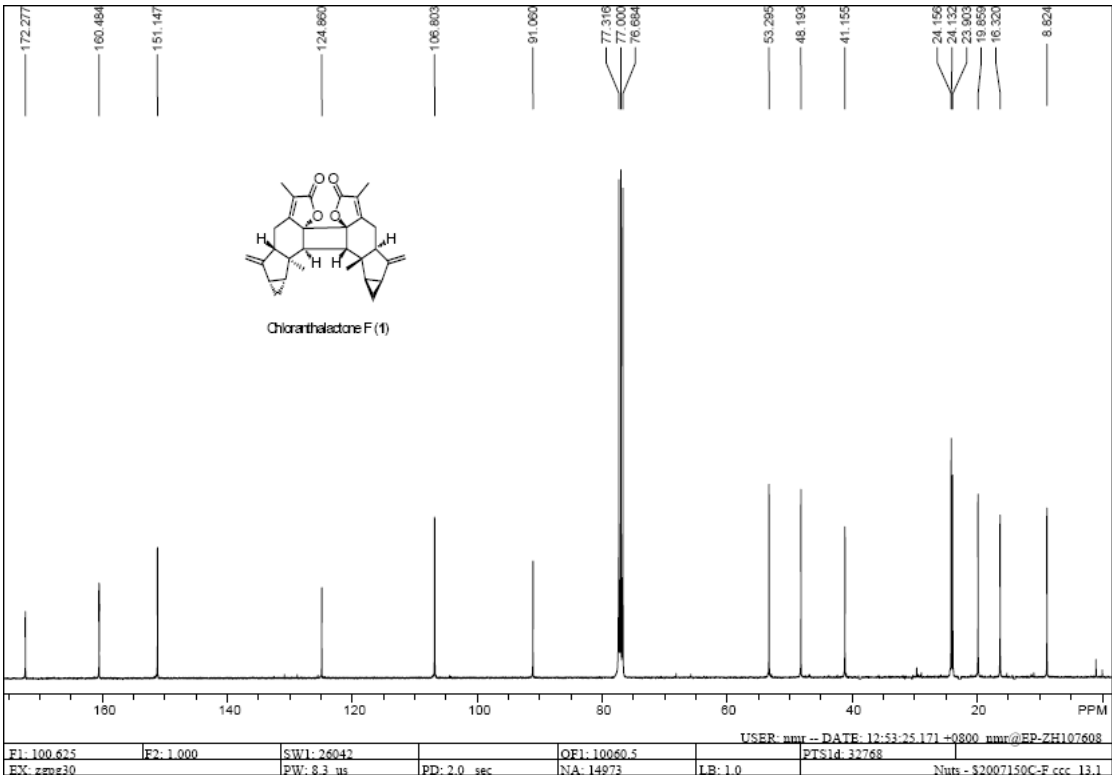

7.065
5.320
4.989
4.986
4.983
4.766
2.718
2.697
2.693
2.373
2.370
2.362
2.360
2.335
2.332
2.324
2.321
1.918
1.542
0.850
0.809
0.797
0.596
Me
O
H
Me
1.04
1.02
3.12
1.13
0.00
4.19
1.15
2.57
3.00
PPM
USER: nmr -- DATE: 23:06:51.718 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2451.3
PTS1d: 32768
EX: zg30
PW: 13.4 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $150CH furan150-H.1


153.222
152.184
137.858
120.363
117.962
105.549
61.297
54.382
54.111
53.840
53.570
53.299
39.297
39.017
28.121
23.599
18.950
17.677
16.594
8.207
Me
O
H
Me
PPM
USER: nmr -- DATE: 23:31:50.765 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 29762
OF1: 10110.7
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 sec
NA: 405
LB: 1.0
Nuts - $150CH furan150-C.1


Chloranthalactone A
USER: slp -- DATE: 08:38:35.796 +0800 slp@AV500
F1: 500.130 F2: 1.000 SW1: 15015 OF1: 1841.7 PTS1d: 32768
EX: ze30 PW: 10.5 us PD: 2.0 sec NA: 8 LB: 0.0 Nuts - $2007150h-ca 1.1


Chloranthalactone A
USER: nmr -- DATE: 12:55:30.187 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10060.5 PTS1d: 32768
EX: zgpg30 PW: 8.3 us PD: 2.0 sec NA: 15024 LB: 1.0 Nuts - $2007150chloranthalactone A-cccc 10.1


7.260
5.081
4.799
3.786
3.778
3.770
3.764
3.757
3.749
3.740
3.058
2.835
2.831
2.819
2.815
2.790
2.786
2.774
2.770
2.346
2.315
2.300
2.270
2.094
1.769
1.449
1.441
0.894
0.881
0.874
0.816
0.805
0.527
Chloranthalactone F (1)
2.06
1.91
2.08
1.99
2.11
2.22
2.14
6.04
2.43
2.35
6.00
PPM
USER: nmr -- DATE: 17:34:11.984 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2456.9
PTS1d: 32768
EX: ze30
PW: 12.7 us
PD: 1.0 sec
NA: 64
LB: 0.3
Nuts - $2007150C-F H 10.1


172.277
160.484
151.147
124.860
106.803
91.060
77.316
77.000
76.684
53.295
48.193
41.155
24.156
24.132
23.903
19.859
16.320
8.824
Chloranthalactone F (1)
PPM
USER: nmr -- DATE: 12:53:25.171 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10060.5
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 14973
LB: 1.0
Nuts - $2007150C-F ccc 13.1

(E). X-ray structure of (Z)-5 and 1

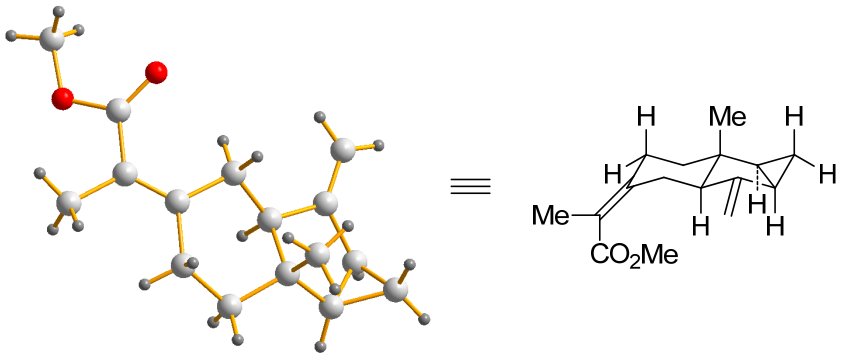


Fig 1. X-ray structure of (*Z*)-**5**

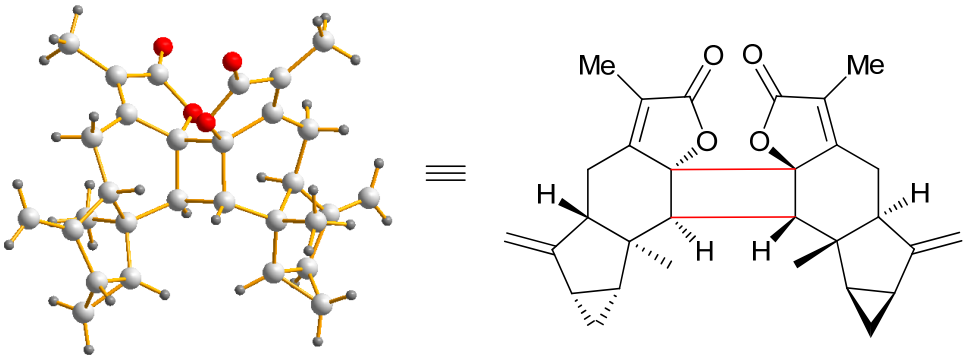


Fig 2. X-ray structure of **1**