Total Synthesis of (±)Maoecrystal V

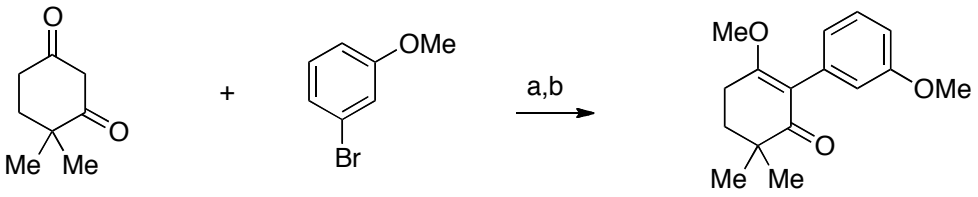
Feng Peng and Samuel J. Danishefsky*

Department of Chemistry, Columbia University, Havemeyer Hall, 3000 Broadway, New York, NY 10027; Laboratory for Bioorganic Chemistry, Sloan-Kettering Institute for Cancer Research, 1275 York Avenue, New York, NY 10065

Supplementary Information

General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium/benzophenone ketyl. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields reported are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer. Infrared spectra were taken on an Perkin-Elmer 1600 FT-IR spectrometer using thin neat film deposition on NaCl plates.



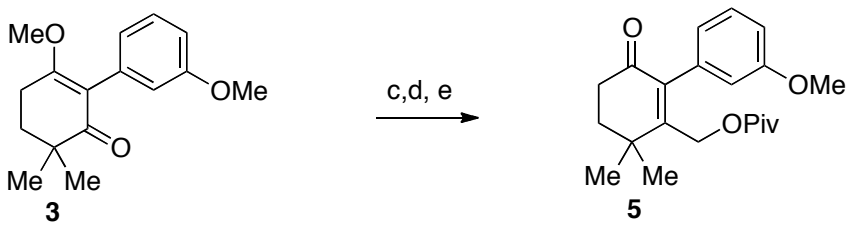
2 **3**

(a) $Pd(OAc)_2$, 2-di-*t*-butylphosphino-2'-methylbiphenyl, K_3PO_4,, THF, 80 ^oC, 12 h, 91%;

(b) $TMSCHN_2$, Hunig's base, CH_3CN/MeOH = 9:1, 6 h, 100%;

Compound 3: An oven-dried, 250 mL round bottom high-pressure flask containing a stir bar was capped with a rubber septum. This flask was then charged with 1,3-diketone **2** (5.1 g, 36 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), 2-di-*t*-butylphosphino-2'-methylbiphenyl (206 mg, 0.6 mmol), and K_3PO4 (14.6 g, 69 mmol). The flask was evacuated and backfilled with argon. 100 mL of THF and aryl bromide (3.8 mL, 30 mmol) were sequentially injected, and the septum was replaced with a Teflon screw cap. The flask was sealed and heated at 80 ^oC for 12 hours. The reaction mixture was then diluted with ethyl acetate and filtered. The filtrate was concentrated and dissolved in 27 mL of CH_3CN and 3 ml of MeOH under argon. To this mixture, Hünig's base (7.5 mL, 43 mmol) and a solution of $TMSCHN_2$ (21 mL, 2M) in hexane were injected sequentially at 0 ^oC. The reaction mixture was stirred at room temperature for additional 12 hours. Solvents were removed under reduced pressure using rotavap. The residues were purified by flash chromatography to give a colourless oil. (7.1g, 91% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.81-6.70 (m, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 2.70 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.93 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.7, 170.0, 158.9, 135.3, 128.4, 123.2, 118.4, 116.3, 112.3, 55.5,

55.1, 39.6, 34.0, 24.5, 22.7; HRMS (FAB, *m/z*) calcd. for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.1491, found 261.1485.



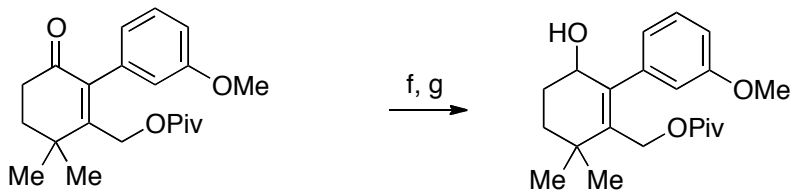
(c) Bu_3SnCH_2OMOM, BuLi, THF, -78 ^oC to -40 ^oC, 30 min, 0.5% HCl work-up, 75%; (d) HCl/MeOH, 50 ^oC, 75%; (e) PivCl, Py, DCM, 12 h, 96%

compound 4: A solution of Bu_3SnCH_2OMOM (5.9 g, 16 mmol) in 40 mL of anhydrous THF was cooled to -78 ^oC under argon. BuLi in hexane (6.45 ml, 2.5 M) was injected dropwise in 5 mins. The reaction mixture was stirred at this temperature for additional 10 min and a solution of **3** (2.6 g, 10 mmol) in 10 mL of THF was injected quickly. The reaction mixture was slowly warmed up to -40 ^oC in 30 min and stirred for additional 1 hour at this temperature. Then the reaction mixture was warmed up to 0 ^oC and acidified with 0.5% HCl solution until pH = 3. 30 min later, the reaction mixture was neutralized with saturated $NaHCO_3$ solution, extracted with ethyl acetate (3 x 20 mL) , and dried over $MgSO_4$. The extract was filtered over cotton and the solvent was removed under reduced pressure. The residue was put on a short silica gel column. The nonpolar impurity was removed by hexane and the polar part was collected using ethyl acetate as eluent. The ethyl acetate was removed under reduced pressure and the residue was dissolved in 50 mL of MeOH. 8 drops of concentrated HCl (37%) was added dropwise and the reaction mixture was stirred at 50 ^oC for 3 hours. Then the mixture was cooled to

room temperature, neutralized with saturated $NaHCO_3$ solution, and extracted with ethyl acetate (3 x 30 mL). The extract was dried over $MgSO_4$, filtered and the solvent was removed using rotovap. The residue was purified using flash chromatography to give a colorless oil **4** (1.5 g, 56% for two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.84 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.08 (d, *J* = 5.6 Hz, 2H), 3.77 (s, 3H), 2.61 (dd, *J* = 6.4, 6.4 Hz, 2H), 1.95 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.5, 162.7, 159.4, 138.5, 136.9, 129.3, 121.7, 115.1, 113.1, 60.4, 55.1, 37.6, 35.3, 34.6, 26.8; IR (neat): cm^{-1} 3441, 2960, 2926, 1701, 1670, 1596, 1484, 1466, 1287, 1256, 1047; HRMS (FAB, *m/z*) calcd for $C_{16}H_{20}O_3$ $[M+H]^+$ 261.1412, found 261.1417.

Compound 5: compound **4** (1.3 g, 5 mmol) was dissolved in 20 mL of anhydrous DCM under argon at 0 ^{o}C. Pyridine (2.4 mL, 30 mmol) was injected into this solution and 5 min later pivaloyl chloride (2.4 mL, 20 mmol) was injected into the mixture. The reaction mixture was stirred at this temperature for 12 hours, quenched with water, extracted with ether (3 x 20 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (1.65 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.58 (br s, 1H), 4.43 (s, 2H), 3.76 (s, 3H), 2.66 (dd, *J* = 6.4, 6.4 Hz, 2H), 2.13 (dd, *J* = 6.8, 6.8 Hz, 2H), 1.28 (s, 6H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.9, 177.6, 159.1, 157.3, 141.4, 136.2,

128.8, 122.0, 115.6, 113.1, 62.3, 55.1, 38.6, 37.5, 35.3, 34.7, 27.1; IR (neat): cm^{-1} 2952, 1724, 1667, 1453, 1437, 1301, 1259, 1156, 1034; HRMS (FAB, *m/z*) calcd for $C_{21}H_{28}O_4$ $[M]^+$ 344.1988, found 344.2001.

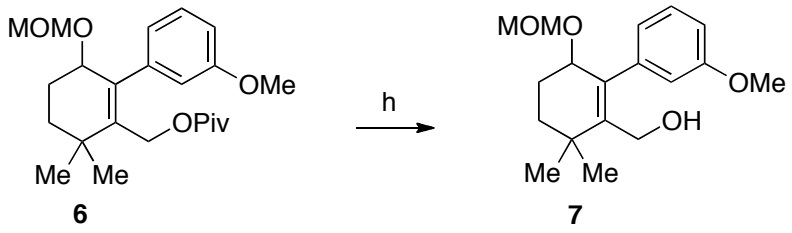


5 **6**

(f) $NaBH_4$, $CeCl_3$, MeOH, 0 ^oC, 2 h, 93%; (g) MOMCl, Hünig's base, DCM, 12 h, 95%;

Compound 6: compound **5** (3.4g, 10 mmol) and cerium chloride heptahydrate (5g, 13 mmol) were dissolved in 20 mL of methanol at 0 ^oC. 5 min later $NaBH_4$ (600 mg, 15 mmol) was added carefully in three portions. The reaction mixture was stirred at 0 ^oC for two hours and quenched with water. The product was extracted with ethyl acetate (3 x 30 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford a secondary alcohol (3.22 g, 93%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.20 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.79 (dd, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.32 (s, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 2.02-1.74 (m, 4H), 1.16 (s, 9H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.4, 143.1, 140.7, 138.3, 129.2, 121.4, 114.8, 112.6, 69.1, 62.0, 55.1, 38.5, 34.7, 34.4, 28.3, 27.5, 27.2, 27.1; IR (neat): cm^{-1} 3435, 2960, 2936, 2870, 1724, 1597, 1577, 1480, 1285; HRMS (FAB, *m/z*) calcd for $C_{21}H_{30}O_4$ $[M]^+$ 346.2144, found 346.2158. The resulting secondary alcohol (1.8 g, 5.2 mmol) and Hunig's base (2.72 mL, 15.6 mmol) were dissolved in anhydrous DCM under argon at room temperature.

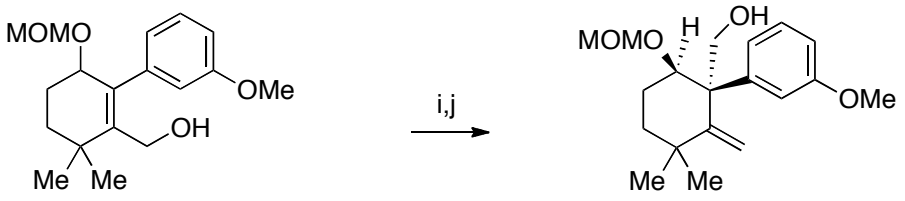
MOMCl (775 mL, 11 mmol) was injected into the solution and the reaction mixture was stirred at room temperature for 12 hours. Then the reaction was quenched with 2 drops of water. The solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford pure **6** (1.93 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.79-6.74 (m, 3H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.27-4.25 (m, 1H), 4.24 (d, *J* = 7.2 Hz, 1H), 4.10 (d, *J* = 11.6 Hz, 1H), 3.76 (s, 3H), 2.85 (s, 3H), 1.94-1.77 (m, 3H), 1.49-1.44 (m, 1H), 1.16 (s, 9H), 1.13 (s, 3H), 1.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.1, 143.8, 141.6, 139.4, 128.6, 121.7, 114.8, 112.3, 94.9, 73.4, 62.0, 55.2, 54.8, 38.5, 34.4, 34.3, 28.4, 27.1, 26.7, 25.1; IR (neat): cm^{-1} 2959, 2935, 1724, 1577, 1480, 1284, 1152, 1032; HRMS (FAB, *m/z*) calcd for $C_{23}H_{34}O_5$ $[M]^+$ 390.2406, found 390.2418.



(h) DIBAL-H, -78 ^{o}C, DCM, 30 min, 95%;

Compound 7: compound **6** (1.95 g, 5 mmol) was dissolved in anhydrous DCM under argon and cooled to -78 ^{o}C. 7.5 mL of DIBAL-H in hexane (2 M) was injected into the reaction mixture slowly and the reaction mixture was stirred for 30 min at this temperature. Then the reaction was quenched with 0.5 mL of methanol and 5 g of sodium sulfate decahydrate. After warming up to room temperature, the mixture was stirred for additional 1 hour and filtered. The solvent was removed using rotovap and the residue

was purified with flash chromatography to afford compound **7** (1.45, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.82-6.79 (m, 3H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.25 (d, *J* = 7.2 Hz, 1H), 4.21 (dd, *J* = 4.0, 4.0 Hz, 1H), 4.05 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.86 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.80 (s, 3H), 2.88 (s, 3H), 1.93-1.76 (m, 3H), 1.48-1.43 (m, 1H), 1.22 (s, 3H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 144.7, 142.5, 138.3, 129.2, 121.3, 114.4, 112.6, 94.9, 73.8, 59.7, 55.2, 54.9, 34.5, 34.4, 28.4, 26.8, 25.2; IR (neat): cm^{-1} 3458, 2936, 1597, 1577, 1483, 1149, 1027; HRMS (FAB, *m/z*) calcd for $C_{18}H_{26}O_4$ $[M]^+$ 306.1831, found 306.1836.



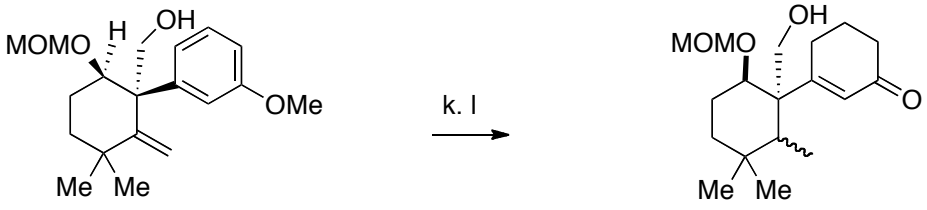
7 **8**

(i) KH, 18-crown-6, ICH_2SnBu_3, 0 ^{o}C, THF, 6 h, 90%; (j) BuLi, -78 ^{o}C to -20 ^{o}C, THF, 6 h, 88%;

Compound 8: an oven-dried round-bottomed flask was charged with KH (360 mg, 9 mmol) and 20 mL of THF under argon at 0 ^{o}C. A solution of compound **7** (920 mg, 3 mmol) in 5 mL of THF was injected slowly into the flask. 30 mins later, 18-crown-6 (780 mg, 3 mmol) was added. The reaction mixture was stirred for additional 5 min and then α-iodomethyl tributylstanne (3.9 g, 9 mmol) was injected and the reaction mixture was stirred at this temperature for 6 hours. After quenched with water carefully, the product was extracted with ether (3 x 20 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was concentrated using rotovap. The residue was

purified by flash chromatograph. And the desired product was dissolved in THF under argon. The mixture was cooled to -78 ^{o}C and BuLi in hexane (3.6 mL, 9 mmol) was injected dropwise. The temperature was slowly warmed up to -20 ^{o}C in 6 hours and the reaction was quenched with saturated NH_4Cl solution, extracted with ether (3 x 30 mL), and dried over $MgSO_4$. After filtration, the extract was concentrated and the residue was purified by chromatography to afford compound **8** (0.78g, 80% for 2 steps).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.14 (m, 3H), 6.75-6.71 (m, 1H), 5.37 (s, 1H), 5.34 (s, 1H), 4.78 (d, *J* = 10.4 Hz, 2H), 3.96 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.84-3.79 (m, 2H), 3.78 (s, 3H), 3.45 (s, 3H), 3.26 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.27 (dddd, *J* = 16.4, 16.4, 16.4, 6.8 Hz, 1H), 1.96 (dddd, *J* = 17.6, 6.0, 6.0, 6.0 Hz, 1H), 1.46-1.31 (m, 2H), 1.10 (s, 3H), 0.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 154.6, 143.0, 128.5, 121.4, 115.4, 110.8, 110.7, 96.8, 80.5, 66.5, 56.3, 55.9, 55.0, 38.5, 36.9, 31.3, 30.1, 24.9; IR (neat): cm^{-1} 3485, 2953, 1606, 1579, 1485, 1464, 1053, 1027; HRMS (FAB, *m/z*) calcd for $C_{19}H_{28}O_4$ $[M+Na]^+$ 343.1885, found 343.1868.

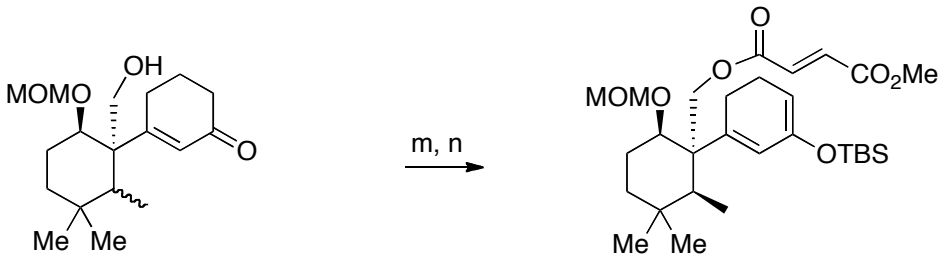


8 **10**

(k) Li, NH_3(l), *t*-BuOH/THF, -78 ^{o}C, 20 min, - 33 ^{o}C, 40min; (l) 1 N HCl, 0 ^{o}C, THF/MeOH (10/1), 8 h, 2 steps, 78%;

Compound 10: an oven-dried three-neck flash equipped with a dry ice acetone condenser was charged with 30 mg of compound **8**, 1 mL of THF, 1 mL of tertbutylol, and 2 mL of

liquid ammonia. Then 20 mg of lithium was added and the reaction mixture was stirred at -78 ^{o}C for 20 mins and -33 ^{o}C for 40 mins. Then ammonium chloride solid was added to quench the reaction until the blue color disappeared. The reaction mixture was then slowly warmed up to room temperature to vaporize the ammonia. The residue was extracted with ethyl acetate (3 x 20 mL) and dried over magnesium sulfate. After filtration of the drying agent, the solvent was removed under the reduced pressure and the residue was dissolved in THF/MeOH mixed solvent (THF/MeOH = 10: 1). The mixture was cooled to 0 ^{o}C and 2 drop of 1N HCl solution was added. The reaction mixture was stirred at 0 ^{o}C for 12 hours and quenched with saturated $NaHCO_3$. The extract was dried over $MgSO_4$. After filtration, the solvent was removed using rotovap and the residue was used without purification in the next step.

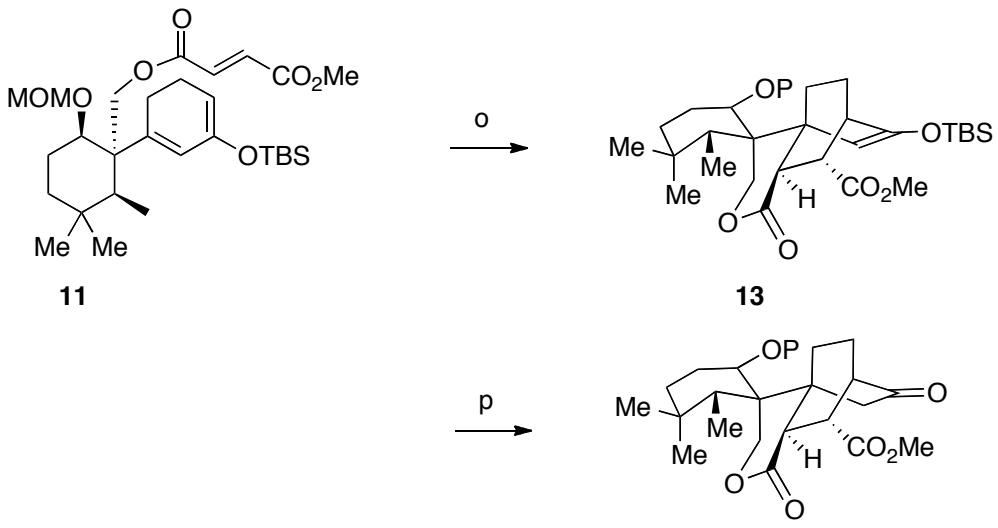


10 **11**

(m) methyl (2*E*)-4-4chloro-4-oxobut-2-enoate, Py, DCM, 0 ^{o}C; (d) TBSOTf, TEA, DCM, 0 ^{o}C, 15 h, 81%;

Compound 11: **10** (28 mg) and pyridine (73 μL, 0.9 mmol) was dissolved in DCM under argon at 0 ^{o}C. Acyl chloride (65 mg, 0.4 mmol) in 1 mL of DCM was injected slowly. After addition of acyl chloride solution, the reaction mixture was stirred at this temperature for 12 hours. The reaction was then quenched with methanol and the solvent was removed under the reduced pressure. The residue was purified using preparation

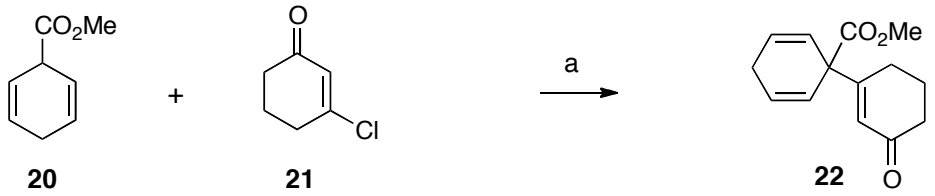
TLC to afford the corresponding ester: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, *J* =15.6 Hz, 2H), 6.52 (s, 1H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 12, 4 Hz, 1H), 3.29 (s, 3H), 2.63-2.56 (m, 1H), 2.52-2.29 (m, 3H), 2.13 (dddd, *J* = 13.2, 13.2, 13.2, 4 Hz, 1H), 2.00-1.97 (m, 1H), 1.92-1.84 (m, 2H), 1.67 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 1H), 1.53 (ddd, *J* = 13.6, 3.6, 3.6 Hz, 1H), 1.37 (ddd, *J* = 13.2, 13.2, 4 Hz, 1H), 1.04 (d, *J* = 7.6 Hz, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.8, 165.3, 164.5, 163.7, 133.7, 133.3, 131.4, 96.2, 80.1, 65.2, 55.9, 52.4, 52.1, 45.2, 40.1, 37.6, 34.4, 32.0, 29.1, 25.0, 23.7, 21.2, 12.4 ; IR (neat): cm^{-1} 2967, 1728, 1680, 1579, 1480, 1280, 1256, 1147; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2400. An oven-dried flask was charged with the resulting ester (22 mg, 0.05 mmol), TEA (22 μL, 0.15 mmol), and 5 mL of DCM under argon at 0 ^{o}C. TBSOTf (27 μL, 0.1 mmol) was added and the reaction mixture was stirred at this temperature for 12 hours. The product was purified using preparation TLC to afford compound **11**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, *J* =15.6 Hz, 2H), 6.18 (s, 1H), 4.91-4.89 (m, 1H), 4.69 (d, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.7 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 12.4, 4 Hz, 1H), 3.30 (s, 3H), 2.25-2.01 (m, 5H), 1.89-1.84 (m, 1H), 1.56 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 1H), 1.49 (ddd, *J* = 13.6, 3.6, 3.6 Hz, 1H), 1.35 (ddd, *J* = 13.2, 13.2, 4 Hz, 1H), 1.01 (d, *J* = 7.6 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 3H), 0.86 (s, 3H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 164.8, 148.9, 138.7, 133.8, 133.2, 127.4, 102.5, 96.5, 81.0, 65.5, 55.6, 52.3, 50.8, 44.8, 40.9, 34.3, 32.3, 26.4, 25.7, 25.3, 22.7, 20.6, 18.1, 12.1; IR (neat): cm^{-1} 2952, 2360, 1725, 1721, 1667, 1455, 1300, 1258, 1155, 1035; HRMS (FAB, *m/z*) calcd for $C_{29}H_{49}O_7Si$ $[M + H]^+$ 537.3248, found 537.3237.



(o) 180 ^{o}C, sealed tube, toluene, 12 h; (p) TBAF, 0 ^{o}C, THF, 2 steps, 48%.

Compound 13: compound **11** (37 mg, 0.07 mmol) was dissolved in 5 mL of anhydrous toluene in a high-pressure tube. The reactor was wash with BSA first and dried in oven for 12 hours. The reaction mixture was degassed with argon and then stirred at 180 ^{o}C for 16 hours. After cooling to room temperature and the mixture was transfer to a round bottom flask. The mixture was further cooled to 0 ^{o}C and TBAF in THF (70 μL, 0.07 mmol) was added. 5 mins later the reaction was quenched with saturated ammonium chloride solution. After extracting with ethyl acetate (3 x 10 mL), the solution was dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified using flash chromatography (14 mg, 48%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.76 (d, *J* = 7.2 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.12 (br s, 1H), 3.94 (dd, *J* = 3.2, 3.2 Hz, 1H), 3.88 (d, *J* = 12.0

Hz, 1H), 3.67 (s, 3H), 3.48 (dd, *J* = 18.8, 3.2 Hz, 1H), 3.44 (s, 3H), 3.11 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 2.74 (br s, 1H), 2.04-1.72 (m, 5H), 1.60-1.55 (m, 2H), 1.40-1.29 (m, 2H), 1.19 (d, *J* = 7.6 Hz, 3H), 0.97 (s, 3H), 0,88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.5, 175.7, 173.5, 96.0, 84.1, 78.0, 56.8, 56.6, 52.5, 48.7, 47.0, 44.7, 43.9, 43.3, 41.6, 40.7, 34.1, 32.7, 27.2, 25.9, 23.1, 21.9, 13.9; IR (neat): cm^{-1} 2952, 2850, 1740, 1665, 1461, 1311, 1184, 1023; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2396.

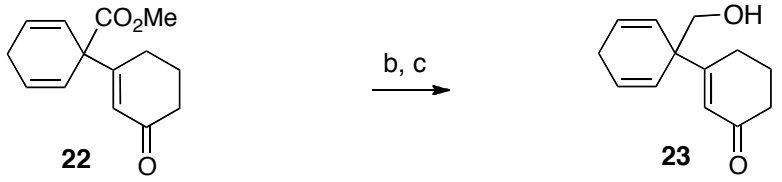


20 **21** **22**

(a) LDA, –78 °C, THF, 40%;

Compound 22: An oven-dried, 250 mL round bottom flask containing a stir bar was capped with a rubber septum. This flask was then charged with diisopropylamine (5.6 mL, 40 mmol) and 100 mL of anhydrous THF under argon. At 0 °C, n-BuLi (16 mL, 40 mmol) was injected dropwise in 10 mins. The reaction mixture was stirred at this temperature for additional 10 mins before cooled down to -78 °C. After stirring at -78 °C for 20 mins, a solution of **20** (5.2 g, 38 mmol) in 10 mL of THF was injected slowly to the flask in 15 mins. After addition of compound **20**, the reaction mixture was stirred at -78 °C for additional 40 mins. Then a solution of **21** (7.3 g, 57 mmol) in 15 mL of THF was injected in 5 mins. 30 mins later, the reaction was quenched by addition of 30 mL of water, extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The drying agent

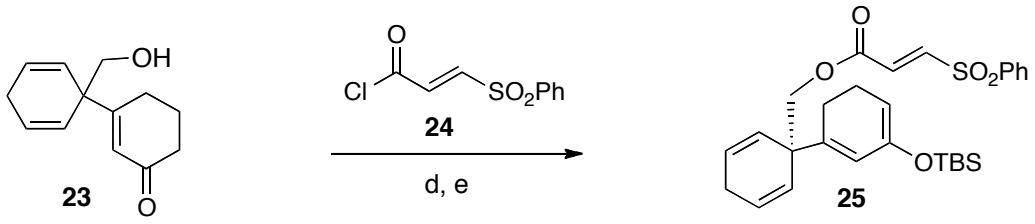
was filtered and solvents were removed under reduced pressure using rotavap. The residues were purified by flash chromatography to give a colourless oil. (3.5g, 40% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.03-5.97 (m, 2H), 5.90 (s, 1H), 5.87-5.82 (m, 2H), 3.73 (s, 3H), 2.69-2.67 (m, 2H), 2.38-2.34 (m, 2H), 2.30-2.26 (m, 2H), 2.00-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 199.7, 172.3, 164.6, 127.3, 126.2, 124.3, 54.3, 52.6, 37.4, 26.4, 25.9, 22.9; IR (neat): cm^{-1} 2951, 2869, 1734, 1671, 1250, 1225, 1040; HRMS (FAB, *m/z*) calcd for $C_{14}H_{17}O_3$ $[M+H]^+$ 233.113, found 233.118.



(b) DIBAL-H, –78 ^{o}C, DCM, 2 h; (c) MnO_2, rt, DCM, 40 min, 2 steps, 68%;

Compound 23: compound **22** (1.5 g, 6.4 mmol) was dissolved in anhydrous DCM under argon and cooled to -78 ^{o}C. 25.8 mL of DIBAL-H in hexane (1 M) was injected into the solution slowly and the reaction mixture was stirred for 50 mins at this temperature. Then the reaction was quenched with 0.5 mL of ethyl acetate and 5 g of sodium sulfate decahydrate. After warming up to room temperature, the mixture was stirred for additional 1 hour, dried over $MgSO_4$ and filtered. The solvent was removed using rotovap and the residue was used directly in the next step. The residue was dissolved in DCM in a round bottom flask and 30 g of MnO_2 was added. The reaction mixture was stirred for 40 min and the solid was filtered (The reaction process was monitored carefully under TLC). After removing of the solvent with rotavap, the residues were purified with flash

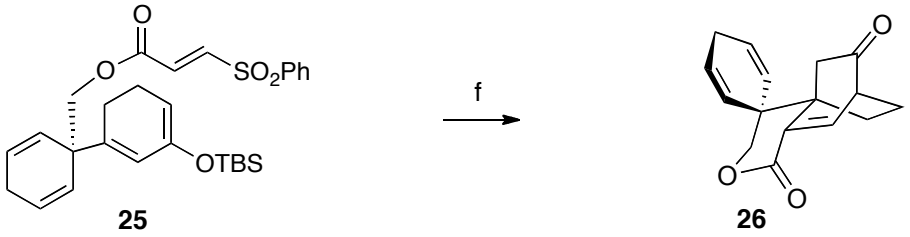
chromatography to give a colourless oil. (890 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.03 (ddd, *J* = 10.4, 3.2, 3.2 Hz, 2H), 5.91 (s, 1H), 5.51 (ddd, *J* = 10.4, 2.0, 2.0 Hz, 2H), 3.65 (d, *J* = 5.6 Hz, 2H), 2.70 (dd, *J* = 3.2, 3.2 Hz, 2H), 2.35-2.30 (m, 4H), 1.95-1.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.2, 167.1, 128.2, 126.7, 125.2, 67.1, 48.6, 37.4, 26.7, 26.2, 22.9; IR (neat): cm^{-1} 3416, 2944, 2869, 1652, 1348, 1033; HRMS (FAB, *m/z*) calcd for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.123, found 205.122.



(d) **24**, Py, 0 °C, DCM, 30 min, 86%; (e) TBSOTf, TEA, DCM, –78 °C, 12 h, 91%;

Compound 25: compound **23** (1.35 g, 6.6 mmol) and pyridine (10.4 mL, 12 mmol) was dissolved in DCM under argon at 0 °C. Acyl chloride **24** (1.67 g, 7.2 mmol) in 5 mL of DCM was injected slowly. After addition of acyl chloride solution, the reaction mixture was stirred at this temperature for 1 hour. The reaction was then quenched by addition of methanol and the solvent was removed under the reduced pressure. The residue was purified using flash chromatography. The pure product and TEA (1.6 mL, 12 mmol) was dissolved in anhydrous DCM under argon at -78 °C, TBSOTf (2.3 mL, 10 mmol) was injected dropwise and the reaction mixture was stirred at this temperature for 12 hours. The reaction mixture was quenched with water, extracted with ether and dried over $MgSO_4$. The solid was filtered and the solvent was removed with rotavap. Then the residues were purified by flash chromatography using TEA deactivated silica gel and

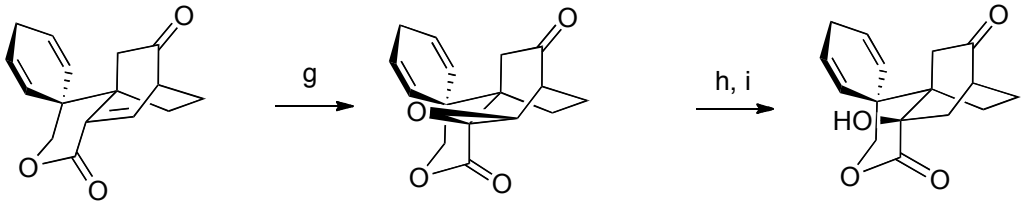
afforded a colourless oil. (2,4 g, 72% yield for two steps). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.71-7.67 (m, 1H), 7.61-7.57 (m, 2H), 7.29 (d, *J* = 15.2 Hz, 1H), 6.82 (d, *J* = 15.2 Hz, 1H), 5.92-5.89 (m, 2H), 5.49-5.46 (m, 3H), 4.80-4.78 (m, 1H), 4.27 (s, 2H), 2.62 (br s, 2H), 2.12-1.99 (m, 4H), 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.4, 148.7, 143.3, 143.0, 138.5, 134.4, 130.9, 129.6, 128.3, 127.4, 126.7, 121.1, 101.1, 69.5, 45.1, 26.2, 25.7, 24.1, 22.4, 18.1, –4.5; IR (neat): cm^{-1} 2951, 2858, 1729, 1670, 1448, 1294; HRMS (FAB, *m/z*) calcd for $C_{28}H_{37}O_5SiS$ $[M+H]^+$ 513.2131, found 513.2131.



(f) toluene, sealed tube, 166 ^{o}C, 1 h, then TBAF, THF, 62%;

Compound 26: compound **25** (513 mg, 1 mmol) was dissolved in 50 mL of anhydrous toluene in a high-pressure tube. The reaction mixture was degassed with argon and then stirred at 170 ^{o}C for 1 hour. After cooling to room temperature and the mixture was transferred to a round bottom flask and the solvent was removed with rotavap. The residue was dissolved in THF and cooled to 0 ^{o}C. Then TBAF in THF (1.5 mL, 1.5 mmol) was added. 2 hours later the reaction was quenched with saturated ammonium chloride solution, extracted with ethyl acetate (3 x 10 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was removed under reduced

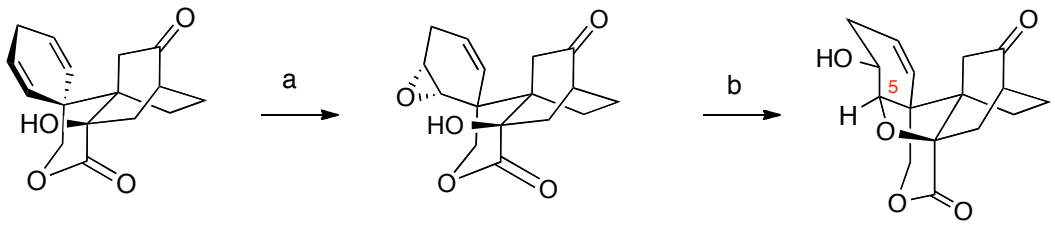
pressure. The residue was purified using flash chromatography (156 mg, 62%) ^{1}H NMR ($CDCl_3$, 400 MHz): 7.55 (d, *J* = 6.8 Hz, 1H), 6.12-6.07 (m, 2H), 5.68-5.60 (m, 2H), 4.30 (d, *J* = 10.0 Hz, 1H), 4.15 (d, *J* = 10.0 Hz, 1H), 3.49-3.47 (m, 1H), 2.78-2.76 (m, 2H), 2.15 (d, *J* = 18 Hz, 1H), 2.08-1,99 (m, 2H), 1.88-1.60 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 163.5, 143.1, 135.7, 129.3, 128.6, 124.4, 123.3, 71.7, 50.1, 46.5, 41.3, 38.9, 26.9, 25.9, 23.1; IR (neat): cm^{-1} 2946, 1720, 1616, 1242, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.1178, found 257.1178.



(g) H_2O_2, NaOH, MeOH, 0 ^{o}C; (h) MgI_2, 40 ^{o}C, CH_2Cl_2; (i) Bu_3SnH, AIBN, toluene, 80 ^{o}C, 3 steps, 47%.

Compound 28: Compound **26** (64 mg, 0.25 mmol) was dissolved in 5 mL of methanol at 0 ^{o}C under argon. 30% H_2O_2 (32 μL, 0.28 mmol) was injected into the reaction flask followed by an addition of 3 N NaOH aqueous solution (20 μL, 0.06 mmol). 3 hours later, 3 N NaOH solution (20 μL, 0.06 mmol) was added again to the reaction mixture and the reaction was stirred at 0 ^{o}C for additional 3 hours. The reaction was quenched with 200 μL of 1N HCl solution, extracted with ethyl acetate and the extract was dried over $MgSO_4$. After filtration of the drying agent and removing of the solvent, the residue was purified with flash chromatography to afford **27** (65 mg, 95%). Compound **27** (14

mg, 0.05 mmol) was dissolved in 5 mL of anhydrous DCM and magnesium diiodide (42 mg, 0.15 mmol) was added to this solution. The reaction mixture was stirred at 45 ^{o}C for about 40 mins (Monitored under TLC). After cooling down to room temperature, the reaction mixture was filtered and the solvent was removed using rotavap. The residue and Bu_3SnH (43 μL, 0.15 mmol) were dissolved in anhydrous toluene and the solution was degassed three times with argon. After addition of 5 mg of AIBN, the reaction mixture was heated under reflux for 1 hour. Then the reaction mixture cooled down to room temperature and the toluene was removed with rotavap. The residue was purified with flash chromatography to afford **28** (7 mg, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06-6.02 (m, 2H), 5.96-5.92 (m, 1H), 5.60 (dd, *J* = 10.4, 2 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 2.77 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.70 (dd, *J* = 18.8, 3.2 Hz, 1H), 2.62 (br s, 2H), 2.45 (br s, 1H), 2.29 (br s, 1H), 2.00 (d, *J* = 18.4 Hz, 1H), 1.95-1.60 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.6, 172.9, 128.9, 128.3, 126.3, 125.7, 76.1, 73.9, 45.8, 41.9, 39.8, 39.7, 39.4, 26.2, 23.0, 22.1; IR (neat): cm^{-1} 3401, 2916, 2849,1728, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_4$ $[M + H]^+$ 275.1283, found 275.1278.



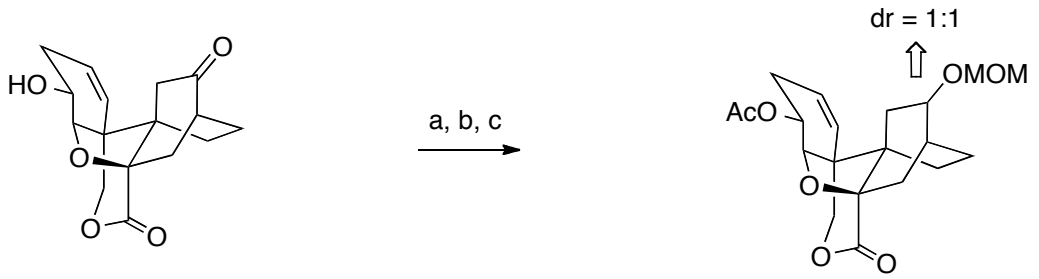
28 **29** **30**

(a) *m*-CPBA, DCM, rt, 18 h, 72%; (b) *p*-TsOH•H_2O, DCM, rt, 12 h, 90%.

Compound 30: *m*-CPBA (42 mg, 0.18 mmol) was added to a solution of **28** (33 mg, 0.12 mmol) in 5 mL of anhydrous DCM at 0 ^{o}C. 12 hour later, the ice-bath was removed and

the reaction mixture was stirred at room temperature for additional 6 hours. The reaction process was monitored under TLC until the disappearance of starting material. Then the reaction was quenched with $Na_2S_2O_3$ solution, extracted with ethyl acetate and the extract was dried over $MgSO_4$. The drying agent was filtered and the solvent was removed under reduced pressure. The residue was purified using flash chromatography to afford **29** (25 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.72-5.67 (m, 1H), 5.22 (d, *J* = 10.8 Hz 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.15-4.13 (m, 1H), 3.40-3.39 (m, 1H), 2.82-2.72 (m, 2H), 2.62 (dd *J* = 18.4, 5.6 Hz, 1H), 2.51-2.41 (m, 3H), 2.10 (d, *J* = 18 Hz, 1H), 2.00-1.65 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.5, 172.5, 125.8, 124.5, 73.5, 65.8, 60.4, 54.5, 51.9, 45.0, 41.6, 40.0, 38.9, 25.1, 23.5, 21.7; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1219, found 291.1232.

Compound 30: compound **29** (12 mg, 0.04 mmol) dissolved in anhydrous DCM at room temperature and p-TSA monohydrate (2 mg, 0.01 mmol) was added to this solution. The reaction mixture was stirred at this temperature for about 12 hours. The solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford compound **30** (11 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.99-5,95 (m, 1H), 5.37 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.17 (d, *J* = 9.2 Hz, 1H), 4.00-3.97 (m, 2H), 3.09 (dd, *J* = 15.2, 4 Hz, 1H), 2.48 (ddd, *J* = 17.2, 6.0, 6.0 Hz, 1H), 2.45-2.30 (m, 2H), 2.12-2.04 (m, 1H), 1.96-1.67 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.4, 169.1, 131.1, 121.1, 88.3, 83.4, 76.1, 69.8, 49.2, 46.5, 42.9, 41.6, 30.7, 29.2, 21.4 , 20.2; IR (neat): cm^{-1} 3401, 2916, 2849,1728, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1219, found 291.1232.

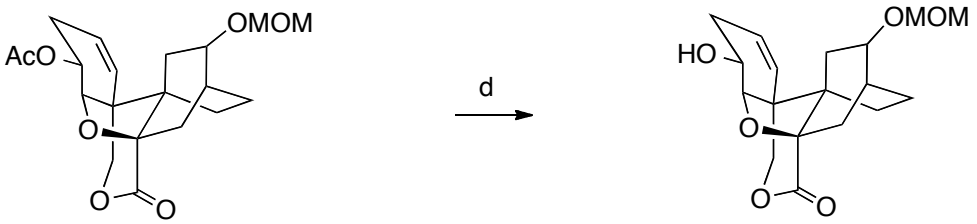


30

(a) Ac_2O, Py, CH_2Cl_2; (b) $NaBH_4$, CH_2Cl_2/EtOH; (c) MOMCl, $^{i}Pr_2NEt$, 3 steps, 82%;

Protected Secondary Alcohol: To a solution of ketone 30 (1 g, 3.4 mmol) in anhydrous CH2Cl2 was added acetic anhydride (1.38 mL, 13.8 mmol), pyridine (1.2 mL, 15 mmol) and DMAP (24.4 mg, 0.2 mmol). The reaction mixture was stirred for 2 h at room temperature and the solvent was removed under vacuum. The residue was then subjected to flash chromatography purification. The resultant acetate was dissolved in a mixture solvent of CH_2Cl_2/EtOH (2:1). To this solution at -78 ^{o}C was added $NaBH_4$ and the reaction was slowly warmed up to -20 ^{o}C in 3 h. The reaction was then quenched with acetone and water, extracted with ethyl acetate, and dried over MgSO4. The drying agent was filtered and the solution was concentrated under vacuum. The residue was purified using flash chromatography. The resultant pure secondary alcohol was dissolved in anhydrous CH_2Cl_2 and MOMCl and $^{i}Pr_2NEt$ was injected. The reaction was stirred at room temperature for 24 h before quenched with water. The solvent was removed under vacuum and the residue was directly purified via flash chromatography to give a colourless oil. (1.05 g, 82% yield, 1:1 diastereoisomers). One of the diastereomers was

isolated as pure compound: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.87 (ddd, *J* = 9.9, 6.6, 2.0 Hz, 1H), 5.38 (dd, *J* = 9.9, 3.2 Hz, 1H), 5.10 (td, *J* = 10.1, 5.8 Hz, 1H), 4.62 (s, 2H), 4.34 (d, *J* = 10.7 Hz, 1H), 4.24 (d, *J* = 9.7 Hz, 1H), 3.89 (d, *J* = 10.7 Hz, 2H), 3.35 (s, 3H), 2.80 (dd, *J* = 14.7, 5.0 Hz, 1H), 2.62 (dt, *J* = 16.8, 6.2 Hz, 1H), 2.09 (s, 3H), 2.05-1.90 (m, 4H), 1.77-1.55 (m, 3H), 1.40 (dt, *J* = 14.8, 1.9 Hz, 1H), 1.36-1.24 (m, 1H), 1.23-1.18 (m, 1H).; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.7, 169.9, 129.1, 122.3, 94.8, 84.1, 76.0, 71.9, 55.5, 49.8, 42.6, 33.7, 29.8, 28.6, 28.5, 21.2, 20.9, 17.9; IR (neat): cm^{-1} 2942, 1745, 1370, 1038; HRMS (FAB, *m/z*) calcd for $C_{20}H_{27}O_7$ $[M+H]^+$ 379.1757, 72.9, found 379.1758.

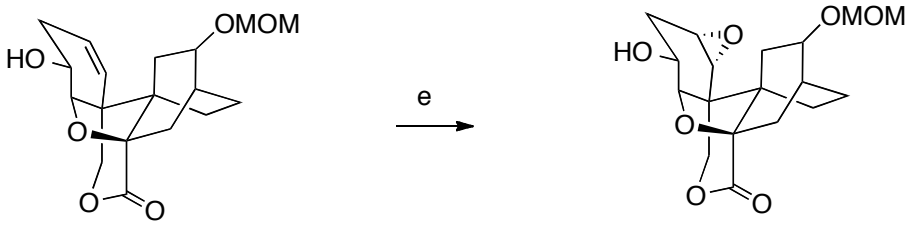


36

(d) K_2CO_3, MeOH, 97%;

Compound **36**: To a solution of the corresponding protected secondary alcohol (1 g, 2.6 mmol) in 5 mL of MeOH was added 20 mg of K_2CO_3. The reaction mixture was quenched with water 30 min later and extracted with ethyl acetate. The solvent was removed under vacuum and the residue was purified directly using flash chromatography to afford alcohol **36** as 1:1 diastereomers (845 mg, 97% yield). One of the diastereomer was isolated as partial pure compound: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (ddd, *J* = 9.9, 6.6, 2.0 Hz, 1H), 5.32 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.63 (s, 2H), 4.29 (d, *J* = 10.7 Hz, 1H),

4.17-3.99 (m, 2H), 3.89 (d, J = 10.7 Hz, 1H), 3.74 (ddd, J = 9.6, 5.7, 2.3 Hz, 1H), 3.36 (s, 3H), 2.67-2.57 (m, 1H), 2.53-2.38 (m, 1H), 2.17-1.91 (m, 3H), 1.77-1.42 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 130.3, 121.8, 94.9, 88.2, 84.3, 77.2, 76.3, 73.3, 69.5, 55.4, 49.3, 42.5, 33.4, 30.7, 30.0, 25.3, 20.9, 20.7; IR (neat): cm^{-1} 3500, 2970, 1750, 1030; HRMS (FAB, *m/z*) calcd for $C_{18}H_{25}O_6$ $[M+H]^+$ 337.1651, found 337.1647.

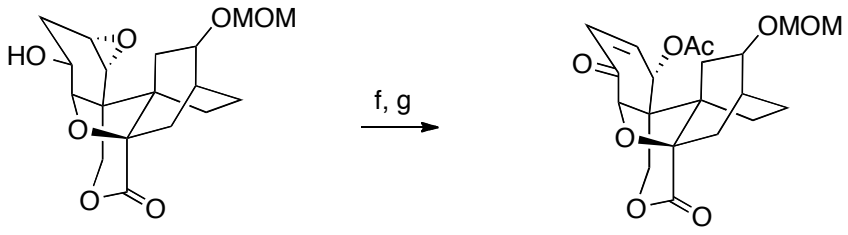


36 **37**

(e) *m*-CPBA (10 eq), rt, 7 d, 95%;

Compound **37**: To a solution of compound **36** (700 mg, 2.1 mmol) in anhydrous CH_2Cl_2 was added *m*-CPBA (4.8 g, 21 mmol). The reaction mixture was stirred at room temperature for about 7 days and nights. Then the solvent was removed under vacuum and the residue was purified via flash chromatography to give epoxide **37** as 1:1 C-16 epimers (702 mg, 95% yield). One of the diastereomers was isolated as pure compound: ^{1}H NMR (CDCl3, 400 MHz) δ 4.71-4.58 (m, 1H), 4.51 (d, J = 11.1 Hz, 1H), 4.24 (d, J = 11.1 Hz, 1H), 4.14-3.99 (m, 1H), 3.85 (d, J = 8.8 Hz, 1H), 3.81-3.70 (m, 1H), 3.38 (s, 3H), 3.32 (ddd, J = 6.1, 3.7, 1.6 Hz, 1H), 2.95 (d, J = 3.7 Hz, 1H), 2.64 (ddd, J = 14.3, 4.4, 1.6 Hz, 1H), 2.46 (dt, J = 15.2, 6.2 Hz, 1H), 2.33 (d, J = 26.1 Hz, 1H), 2.09-1.85 (m, 3H), 1.79-1.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.7, 95.1, 87.6, 84.2, 74.6,

73.2, 69.3, 55.5, 51.1, 51.0, 45.3, 42.5, 32.3, 30.5, 29.8, 25.1, 20.9, 20.8; IR (neat): cm^{-1} 3520, 2970, 1753, 1032; HRMS (FAB, *m/z*) calcd for $C_{18}H_{25}O_7$ $[M+H]^+$ 353.1600, found 353.1610.

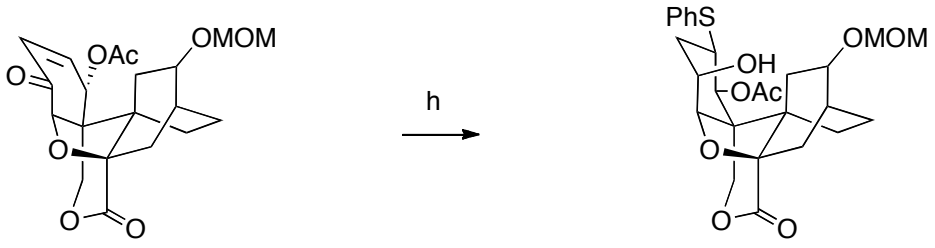


37 **38**

(f) DMP, CH_2Cl_2, 85%; (g) Ac_2O, Py, CH_2Cl_2, 90%;

Compound **38**: To a solution of epoxide **37** (700 mg, 2 mmol) in CH_2Cl_2 at 0 ^oC was added Dess-Martin reagent (2.5 g, 6 mmol) and $NaHCO_3$ (840 mg, 10 mmol). The reaction mixture was stirred at this temperature for additional 10 h before quenching with NaS_2O_3 solution. The liquid mixture was then extracted with ethyl acetate, dried over $MgSO_4$ and filtered. The solution was then concentrated under vacuum and the residue was purified via flash chromatography to give an enone as 1:1 C-16 epimers (592 mg, 85%). One of the diatereomers was isolated as pure compound: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.97-6.82 (m, 1H), 6.24 (d, *J* = 10.3 Hz, 1H), 4.74-4.48 (m, 6H), 4.39 (d, *J* = 4.9 Hz, 1H), 3.73-3.52 (m, 1H), 3.28 (s, 3H), 2.72-2.62 (m, 1H), 2.04-1.88 (m, 2H), 1.69-1.47 (m, 8H), 1.15-1.01 (m, 1H).; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.7, 169.5, 145.5, 129.7, 95.3, 82.7, 81.2, 73.9, 73.5, 63.2, 55.5, 48.1, 43.6, 33.7, 29.9, 24.8, 20.7, 20.1; HRMS (FAB, *m/z*) calcd for $C_{18}H_{23}O_7$ $[M+H]^+$ 351.1444, found 353.1447. To a solution of this enone (590 mg, 1.7 mmol) in anhydrous DCM was added acetic anhydride and

pyridine. The reaction mixture was then stirred under argon at room temperature for additional 12 h. The solvent was removed under vacuum and the residue was purified via flash chromatography to afford compound **38** as 1:1 C-16 epimers (600 mg, 90% yield). One of the epimers was isolated as pure compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, *J* = 10.3, 4.8 Hz, 1H), 6.32 (dd, *J* = 10.3, 1.0 Hz, 1H), 5.58 (dd, *J* = 4.8, 1.0 Hz, 1H), 4.60 (d, *J* = 7.0 Hz, 1H), 4.56-4.52 (m, 2H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.25 (d, *J* = 11.5 Hz, 1H), 3.75-3.60 (m, 1H), 3.29 (s, 3H), 2.68 (ddd, *J* = 14.6, 4.7, 1.6 Hz, 1H), 2.13 (s, 3H), 2.08-1.93 (m, 2H), 1.77-1.62 (m, 1H), 1.21-1.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.95, 169.50, 168.86, 141.88, 131.28, 95.37, 82.68, 80.96, 73.37, 72.61, 64.02, 55.52, 46.85, 43.82, 33.70, 29.87, 24.75, 20.66, 20.56, 20.03; IR (neat): cm^{-1} 2975, 1750, 1722, 1683, 1030; HRMS (FAB, *m/z*) calcd for $C_{20}H_{25}O_8$ $[M+H]^+$ 393.1549, found 393.1554.

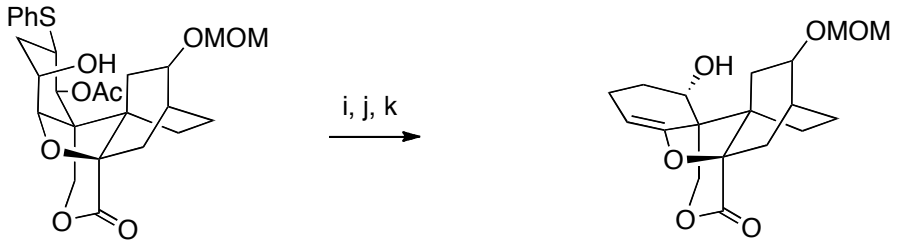


38 **39**

(h) PhSH, then $NaBH_4$, 78%;

Compound **39**: To a solution of enone **38** (600 mg, 1.5 mmol) in CH_2Cl_2 was added PhSH (190 mg, 1.2 eq) and triethylamine (30 mg, 0.2 eq) at 0 ^{o}C. 30 min later, the reaction temperature was cooled to -50 ^{o}C and EtOH(CH_2Cl_2 :EtOH = 1:1) was injected. To this reaction mixture was added $NaBH_4$ (200 mg, 6 eq) and reaction temperature was

slowly warmed up to 0 ^{o}C in 2 h. Acetone was added to quench the excess $NaBH_4$. 20 min later water was added and the reaction mixture was extracted with ethyl acetate. The organic layer was collected and dried over $MgSO_4$. After filtration of the solid, the solvent was removed under reduced pressure. The residue was purified via flash chromatography to afford compound **39** as 1:1 C-16 epimers (597 mg, 78% yield). These two epimers could not be separated and characterized as mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 6H), 7.33 (m, 3H), 7.29-7.25 (m, 6H), 5.41 (dd, *J* = 3.1, 1.1 Hz, 2H), 5.37 (dd, *J* = 3.1, 1.1 Hz, 1H), 4.65 (d, *J* = 6.9 Hz, 1H), 4.61 (d, *J* = 6.9 Hz, 1H), 4.58 (d, *J* = 0.9 Hz, 2H), 4.31 (ddt, *J* = 9.4, 6.2, 3.0 Hz, 2H), 4.25-4.19 (m, 4H), 4.17-4.07 (m, 3H), 3.86 (dd, *J* = 9.5, 3.9 Hz, 2H), 3.67 (ddt, *J* = 28.7, 12.8, 3.1 Hz, 3H), 3.36 (s, 3H), 3.33 (s, 6H), 2.88 (dd, *J* = 14.6, 5.1 Hz, 2H), 2.82-2.71 (m, 3H), 2.64 (ddd, *J* = 14.7, 4.7, 1.6 Hz, 1H), 2.57 (s, 1H), 2.39 (dd, *J* = 13.9, 4.5 Hz, 1H), 2.29-2.17 (m, 3H), 2.15 (d, *J* = 1.6 Hz, 8H), 2.09-1.90 (m, 9H), 1.76 (ddd, *J* = 13.5, 10.8, 8.0 Hz, 2H), 1.65-1.45 (m, 8H), 1.40-1.25 (m, 3H), 1.12-1.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.9, 169.4, 169.3, 134.2, 134.1, 131.7, 131.6, 129.1, 127.5, 127.4, 95.4, 94.5, 83.8, 83.2, 81.5, 81.5, 74.9, 75.0, 73.2, 72.7, 68.8, 68.8, 64.4, 64.3, 55.5, 55.4, 47.7, 47.6, 43.6, 43.5, 42.4, 42.1, 31.7, 31.6, 30.2, 30.1, 29.9, 29.9, 28.6, 24.8, 21.8, 21.8, 20.6, 20.4, 17.8; IR (neat): cm^{-1} 3460, 2965, 1750, 1722, 1620, 1030; HRMS (FAB, *m/z*) calcd for $C_{26}H_{33}O_8S$ 505.1896, found 505.1891.

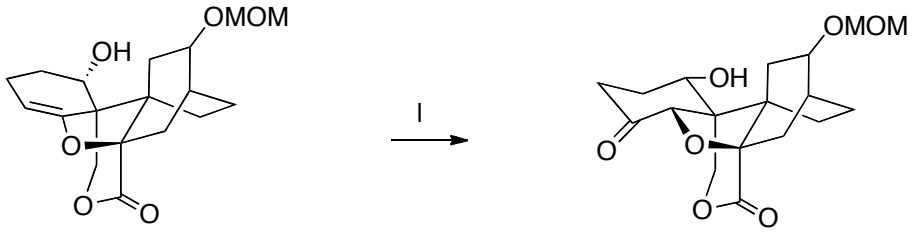


39 **40**

(i) Raney-Ni; (j) MsCl, DMAP, rt to 80 ^{o}C; (k) K_2CO_3, MeOH, 3 steps, 61%;

Compound **40**: To a mixture of Raney-Ni (ca. 20 mg) in reagent acetone was added a solution of compound **39** (30 mg, 0.06 mmol) in acetone. The reaction was stirred at room temperature for 15 min and filtered. The solvent was removed under vacuum and the residue was used directly in the next step. To this residue was added DMAP (12 eq) and CH_2Cl_2. Then MsCl (12 eq) was injected and the reaction mixture was stirred at 60 ^{o}C for 20 h and at 80 ^{o}C for additional 6 h. Then the reaction mixture was purified directly using flash chromatography to afford the dehydration product. To a solution of this dehydration product in MeOH was added K_2CO_3. The reaction mixture was quenched with water 30 min later and extracted with ethyl acetate. The solvent was removed under vacuum and the residue was purified directly using flash chromatography to afford enol ether **40** as 1:1 C-16 epimers (12 mg, 61%). One of the epimers was isolated as a pure compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (t, J = 3.6 Hz, 1H), 4.72 (d, J = 10.7 Hz, 1H), 4.65 (s, 2H), 4.39 (d, J = 10.7 Hz, 1H), 4.03 (dq, J = 12.0, 3.9 Hz, 1H), 3.84 (ddt, J = 9.4, 5.2, 1.9 Hz, 1H), 3.36 (s, 3H), 2.68 (ddd, J = 14.2, 4.2, 1.8 Hz, 1H), 2.30-2.16 (m, 2H), 2.11-1.95 (m, 3H), 1.85-1.74 (m, 2H), 1.73-1.62 (m, 2H), 1.59-1.52 (m, 2H), 1.44 (dddd, J = 17.0, 13.5, 5.5, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 155.84, 94.90, 94.80, 83.32, 72.70, 72.18, 68.34, 55.43, 47.71, 42.85, 30.47,

30.06, 27.56, 24.20, 21.52, 21.48, 21.29. IR (neat): cm^{-1} 3452, 2941, 1745, 1147, 1042; HRMS (FAB, *m/z*) calcd for $C_{18}H_{24}O_6$ $[M]^+$ 336.1573, found 336.1566.

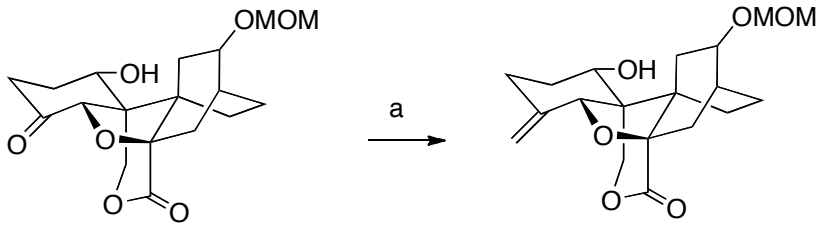


40 **41**

(l) DMDO, then BF_3•Et_2, 82%

Compound **41**: At 0 ^oC, compound **40** (26 mg,100 μmol) dissolved in anhydrous CH_2Cl_2 under argon. 50 mg of 4 Å molecular sieve was added to the solution and the mixture was stirred for 1 hour. Then fresh-prepared dimethyldioxirane in acetone (120 μmol, 1.2 eq) was injected dropwise to the reaction mixture. 10 min later, the solvent was blown out using argon flow and 2 mL of anhydrous ether was injected to the residue. Boron trifluoride etherate (30 μL, 3 eq) was added sequentially to the reaction mixture slowly. 15 min later the reaction was quenched with saturated $NaHCO_3$, extracted with ethyl acetate, and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford a white solid (22 mg, 82% yield) as 1:1 C-16 epimers. One of the epimers was isolated as a pure compound: ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, *J* = 2.2 Hz, 1H), 4.67 (s, 2H), 4.65-4.59 (m, 1H), 4.51 (ddd, *J* = 14.7, 7.1, 4.0 Hz, 1H), 4.20 (dd, *J* = 12.2, 2.6 Hz, 1H), 3.87 (ddt, *J* = 9.8, 5.9, 2.1 Hz, 1H), 3.38 (s, 3H), 2.70 (ddd, *J* = 14.2, 4.7, 1.6 Hz, 1H), 2.48-2.37 (m, 2H), 2.32-2.18 (m, 2H), 2.06-1.90 (m, 3H), 1.86-1.62 (m, 4H),

1.53 (ddd, J = 9.7, 5.2, 1.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.61, 169.18, 95.06, 85.67, 85.12, 72.64, 68.03, 66.68, 55.52, 52.55, 43.85, 35.49, 30.72, 30.24, 24.59, 22.19, 20.92; IR (neat): cm^{-1} 3480, 2946, 1740, 1039; HRMS (FAB, *m/z*) calcd for $C_{18}H_{25}O_7$ $[M+H]^+$ 353.1600, found 353.1588.

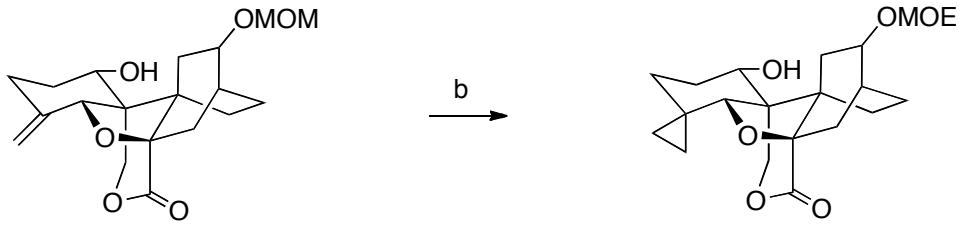


41 **42**

(a) Lombardo reagent, rt, 8 min, 85%;

Compound **42**: To a solution of compound **41** (15 mg, 0.04 mmol) in anhydrous CH_2Cl_2 was added one pipette of fresh-prepared Lombardo reagent at room temperature. The reaction mixture was stirred for additional 8 min and quenched with saturated $NaHCO_3$ solution. The mixture was extracted with ethyl acetate, dried over $MgSO_4$. After filtration of the solid, the liquid mixture was concentrated under vacuum and the residue was purified via flash chromatography to afford olefin **42** as 1:1 C-16 epimers (13 mg, 85% yield). One of the epimers was isolated as a pure compound: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.11 (q, J = 1.8 Hz, 1H), 5.01 (q, J = 1.8 Hz, 1H), 4.68 (s, 2H), 4.54-4.39 (m, 3H), 4.16-4.05 (m, 1H), 3.87 (ddd, J = 9.7, 5.5, 2.2 Hz, 1H), 3.38 (s, 3H), 2.71 (ddd, J = 14.3, 4.6, 1.8 Hz, 1H), 2.40 (ddd, J = 14.7, 6.0, 1.5 Hz, 1H), 2.19 (dd, J = 13.1, 9.5 Hz, 1H), 2.10-1.94 (m, 3H), 1.91-1.72 (m, 3H), 1.58-1.35 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.75, 141.53, 107.62, 95.01, 84.75, 84.11, 72.95, 69.04, 66.96, 55.48, 50.05, 43.17,

30.94, 30.39, 30.25, 29.42, 24.93, 23.13, 21.18; IR (neat): cm^{-1} 3475, 2950, 1738, 1030; HRMS (FAB, *m/z*) calcd for $C_{19}H_{27}O_6$ $[M+H]^+$ 351.1808, found 351.1812.

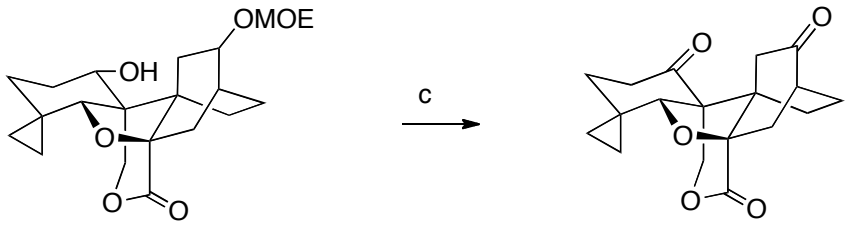


42 **43**

(b) CH_2I_2, Zn/Ag couple, ether, 42 ^oC, 96 h, 88%;

Compound **43**: To a solution of compound **42** (40 mg, 0.11 mmol) in anhydrous ether was added Zn/Ag (300 mg, 4.6 mmol) couple. Then a solution of CH_2I_2 (200 μL, 4.2 mmol) in ether was injected in 1 h via syringe pump. Then the reaction mixture was stirred at 42 ^oC for 96 h. Then the reaction mixture was cooled down to rt and quenched with saturated $NaHCO_3$ solution. The mixture was extracted with ethyl acetate and dried over $MgSO_4$. After filtration, the liquid mixture was concentrated under vacuum and the residue was purified via flash chromatography to give cyclopropane **43** as 1:1 C-16 epimers (36 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, *J* = 11.4 Hz, 3H), 4.79-4.70 (s, 6H), 4.54 (dd, *J* = 11.4, 1.6 Hz, 3H), 4.24 (s, 2H), 4.18 (s, 1H), 4.06-3.95 (m, 2H), 3.89 (br s, 1H), 3.70-3.59 (qt, *J* = 6.9, 1.8 Hz, 6H), 2.89 (dd, *J* = 14.4, 5.4 Hz, 1H), 2.65 (ddd, *J* = 14.1, 4.7, 1.6 Hz, 2H), 2.25-2.13 (m, 2H), 2.05 (d, *J* = 11.5 Hz, 4H), 1.96-1.74 (m, 8H), 1.66-1.49 (m, 6H), 1.33-1.11 (m, 9H), 0.88 (dd, *J* = 14.1, 7.6 Hz, 3H), 0.71-0.48 (m, 6H), 0.30-0.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 170.8,

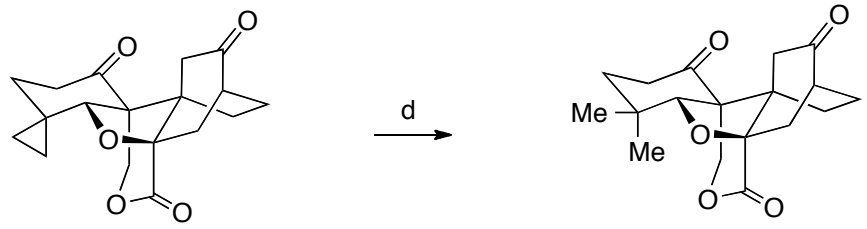
93.5, 93.4, 84.0, 83.6, 83.2, 82.6, 72.9, 72.8, 69.7, 69.6, 67.5, 67.4, 63.5, 63.4, 49.7, 49.5, 43.5, 43.3, 31.5, 30.8, 30.3, 30.2, 30.1, 29.9, 28.8, 24.9, 22.9, 22.6, 21.2, 18.1, 17.7, 17.6, 15.1, 14.1; IR (neat): cm^{-1} 3500, 2955, 1752, 1030; HRMS (FAB, *m/z*) calcd for $C_{21}H_{31}O_6$ $[M+H]^+$ 379.2121, found 379.2117.



43 **44**

(c) PCC, CH_2Cl_2, rt, 76%;

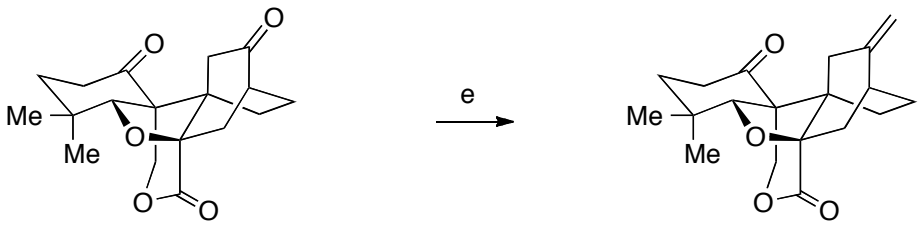
Compound **44**: To a solution of compound **43** (20 mg, 0.05 mmol) in CH_2Cl_2 at room temperature was added PCC (43 mg, 0.2 mmol). The reaction mixture was stirred at this temperature for 12 h. Then celite was added and the reaction mixture was filtered via a short silica gel column to give compound **44** (12 mg, 76% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 5.26 (d, *J* = 11.3 Hz, 1H), 4.60 (s, 1H), 4.24 (dd, *J* = 11.3, 1.6 Hz, 1H), 3.14 (dd, *J* = 14.9, 4.5 Hz, 1H), 2.88-2.72 (m, 1H), 2.59 (dd, *J* = 18.5, 3.6 Hz, 1H), 2.51-2.30 (m, 2H), 2.20 (dt, *J* = 13.5, 8.8 Hz, 1H), 2.10-1.71 (m, 3H), 1.65-1.44 (m, 3H), 0.99-0.72 (m, 4H), 0.55-0.38 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.3, 168.9, 83.2, 82.3, 68.2, 41.5, 40.3, 38.9, 30.9, 29.3, 22.1, 20.3, 17.6, 14.1, 8.2, 5.5; IR (neat): cm^{-1} 2955, 1755, 1742, 1723, 1035; HRMS (FAB, *m/z*) calcd for $C_{18}H_{21}O_5$ $[M+H]^+$ 317.1389, found 317.1392.



44 **45**

(d) PtO_2, H_2, HOAc, 40 ^oC, 40%;

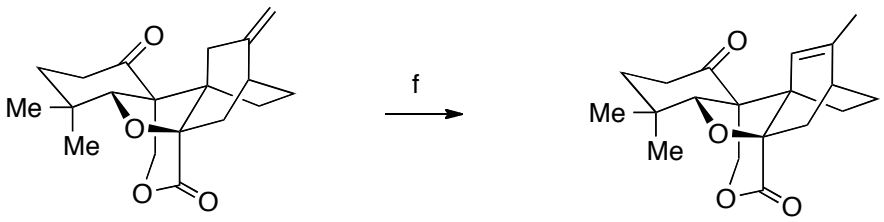
Compound **45**: To a solution of compound **44** (10 mg, 0.027 mmol) in anhydrous acetic acid was added PtO_2 (1 eq). The reaction mixture was first degassed with H_2 for about 30 min. Then the reaction was stirred at 40 ^oC for additional 40 mins, filtered, and concentrated. The residue was purified via flash chromatography (4.1 mg, 40%). ^1H NMR (CDCl3, 400 MHz) δ 4.90 (d, *J* = 12.2 Hz, 1H), 4.30-4.25 (m, 2H), 3.14 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.63-2.53 (m, 1H), 2.50-2.34 (m, 4H), 2.06-1.91 (m, 4H), 1.86-1.69 (m, 2H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.8, 94.9, 94.8, 83.3, 72. 7, 72.2, 68. 3, 55.4, 47.7, 42.8, 30. 5, 30.0, 27.5, 24. 2, 21.5, 21. 5, 21.3; IR (neat): cm^{-1} 2950, 1755, 1743, 1716, 1040; HRMS (FAB, *m/z*) calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1545, found 319.1559.



45 **46**

(e) Lombardo reageant, 0 ^oC, CH_2Cl_2, 80%;

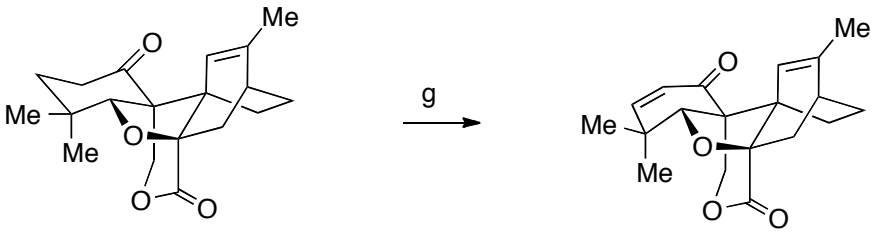
Compound **46**: At 0 °C, to a solution of compound **45** (12 mg 0.037 mmol), in anhydrous CH_2Cl_2 was added a pipette of fresh-prepared Lombardo reagent. The reaction mixture was stirred at this temperature for additional 10 min and quenched with saturated $NaHCO_3$ solution. The liquid mixture was extracted with ethyl acetate and dried over $MgSO_4$. After filtration of the drying agent, the residue was purified via flash chromatography to give compound **46** (9.5 mg, 80%). ^{1}H NMR (500 MHz, CDCl3) δ 4.86-4.83 (m, 1H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.68 (dt, *J* = 2.8, 1.5 Hz, 1H), 4.32 (d, *J* = 1.7 Hz, 1H), 4.23 (dd, *J* = 11.8, 1.8 Hz, 1H), 2.92 (dd, *J* = 14.1, 4.5 Hz, 1H), 2.60 (dq, *J* = 16.4, 3.1 Hz, 1H), 2.45-2.29 (m, 4H), 1.98 (ddd, *J* = 14.7, 11.3, 5.2 Hz, 1H), 1.94-1.83 (m, 2H), 1.76 (dt, *J* = 14.6, 5.5 Hz, 1H), 1.70 (dt, *J* = 14.1, 1.9 Hz, 1H), 1.61 (tdt, *J* = 9.8, 4.8, 2.4 Hz, 1H), 1.25 (d, *J* = 2.4 Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.41, 169.91, 147.30, 106.22, 87.52, 84.32, 68.07, 57.55, 44.55, 37.57, 35.41, 35.20, 32.30, 31.78, 31.73, 31.38, 24.78, 22.22, 22.11; IR (neat): cm^{-1} 2912, 2850, 1750, 1718, 1462, 1261, 1145; HRMS (FAB, *m/z*) calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1753, found 317.1748.



46 **47**

(f) *p*-TsOH•H_2O, benzene, 76 °C, 50 min, 85%;

Compound **47**: To a solution of compound **46** (9.7 mg, 0.03 mmol) in anhydrous benzene was added *p*-TsOH•H_2O (1 mg, 10% eq). The reaction mixture was stirred at 76 ^oC for about 50 min. After it cooled down to room temperature, the liquid mixture was directly loaded to a flash chromatography column and purified to afford olefin **47** (8.2 mg, 85%). ^1H NMR (500 MHz, CDCl3) δ 5.41 (t, *J* = 1.7 Hz, 1H), 4.83 (d, *J* = 11.7 Hz, 1H), 4.26 (dd, *J* = 11.7, 1.7 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 2.78 (dd, *J* = 13.8, 3.5 Hz, 1H), 2.47 (dq, *J* = 3.6, 1.9 Hz, 1H), 2.43 (dd, *J* = 7.7, 6.1 Hz, 2H), 1.96 (dt, *J* = 14.8, 7.2 Hz, 1H), 1.84 (d, *J* = 1.6 Hz, 3H), 1.81-1.68 (m, 3H), 1.53-1.42 (m, 1H), 1.26 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8, 170.4, 145.7, 122.4, 88.4, 86.5, 68.2, 57.1, 48.4, 37.9, 35.7, 35.5, 35.4, 32.6, 31.2, 23.2, 22.0, 21.5, 19.8; IR (neat): cm^{-1} 2924, 2853, 1754, 1720, 1261, 1148; HRMS (FAB, *m/z*) calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1754, found 317.1749.

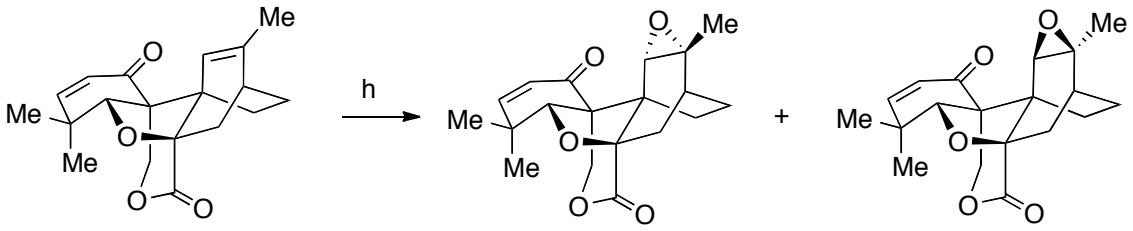


47 **48**

(g) TMSCl, LDA, then $Pd(TFA)_2$, 70 ^oC, 5 h, 72%;

Compound **48**: To a fresh prepared LDA solution in THF was added a solution of compound **47** (8 mg, 0.025 mmol) in THF at -78 ^oC. 1 h later, TMSCl was injected via syringe and the reaction mixture was stirred for additional 1 h. Then the reaction mixture

was quenched with $NaHCO_3$ solution. The reaction mixture was then extracted with ether and dried over $MgSO_4$. After filtration of the drying agent, the liquid mixture was concentrated and the residue dissolved in anhydrous CH_3CN. $Pd(TFA)_2$ (8 eq) was added and the reaction mixture was then heated to 70 ^oC and stirred at this temperature for about 5 h. The solvent was removed via rotovap and the residue was purified via direct flash chromatography to afford enone 48 (7.2 mg, 72%). ^1H NMR (400 MHz, CDCl3) δ 6.70 (d, J = 10.1 Hz, 1H), 5.92 (d, J = 10.1 Hz, 1H), 5.48 (d, J = 2.0 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.29 (d, J = 1.5 Hz, 1H), 4.26 (dd, J = 11.8, 1.6 Hz, 1H), 2.79 (dd, J = 13.8, 3.5 Hz, 1H), 2.50 (dt, J = 3.9, 2.0 Hz, 1H), 2.46-2.28 (m, 1H), 1.84 (dd, J = 4.5, 1.6 Hz, 3H), 1.82-1.75 (m, 2H), 1.50 (td, J = 6.2, 3.0 Hz, 1H), 1.34 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.81, 170.44, 157.72, 145.79, 126.84, 122.47, 86.69, 86.62, 68.59, 54.42, 47.76, 38.63, 35.65, 35.21, 30.71, 23.14, 22.06, 19.83, 18.59; IR (neat): cm^{-1} 2918, 2850, 1755, 1691, 1265, 1154; HRMS (FAB, m/z) calcd for $C_{19}H_{22}O_4$ $[M]^+$ 314.1518, found 314.1515.



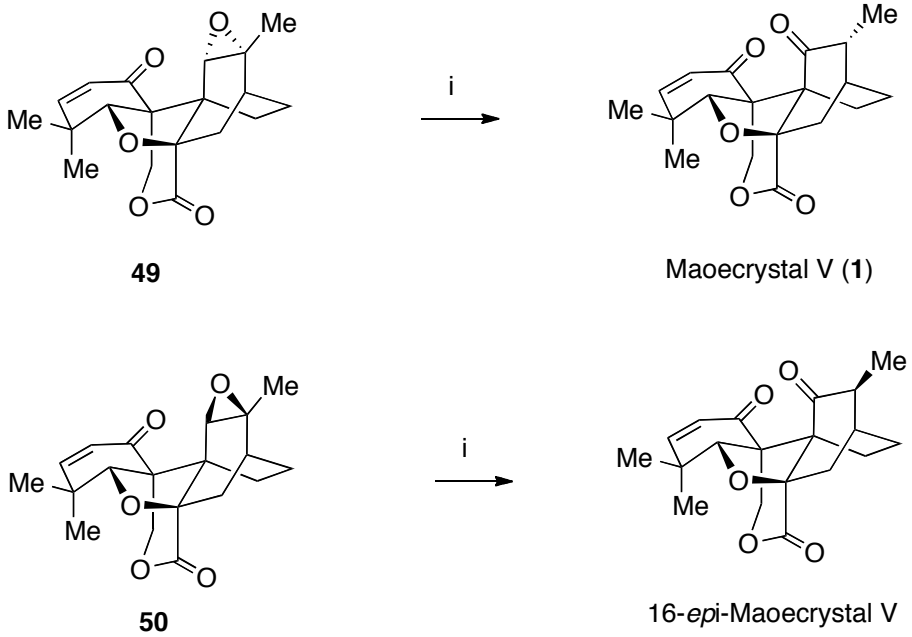
48 **49** **50**

(h) TFDO, CH_2Cl_2, -78 ^oC to 0 ^oC, 90%;

Compound **49**: To a solution of compound **48** (7.2 mg, 0.023 mmol) in CH_2Cl_2 at -78 ^oC was added fresh-prepared TFDO (1.1 eq). The reaction mixture was then warmed up to 0 ^oC and stirred for additional 5 mins. The liquid mixture was then concentrated under

vacuum and the residue was purified via flash chromatography to afford a separable 1:1 epoxides (3.45 mg each, 90% yield). α-epoxide **50**: ^{1}H NMR (400 MHz, CDCl3) δ 6.73 (d, J = 10.1 Hz, 1H), 5.91 (d, J = 10.1 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.50 (d, J = 1.6 Hz, 1H), 4.13 (dt, J = 11.7, 1.8 Hz, 1H), 3.20 (s, 1H), 2.55 (dd, J = 14.0, 3.7 Hz, 1H), 2.19-2.00 (m, 4H), 1.86-1.55 (m, 5H), 1.43 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 169.5, 158.4, 126.6, 87.0, 83.9, 68.4, 57.8, 57.5, 54.7, 45.8, 38.5, 33.6, 30.6, 28.8, 21.6, 19.4, 18.7, 18.3; IR (neat): cm^{-1} 2920, 1754, 1692, 1264, 1155; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M]^+$ 330.1467, found 330.1455.

β-epoxide **49**: ^{1}H NMR (400 MHz, CDCl3) δ 6.70 (d, J = 10.1 Hz, 1H), 5.93 (d, J = 10.1 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.28 (d, J = 1.6 Hz, 1H), 4.21-4.04 (m, 1H), 2.98 (d, J = 1.2 Hz, 1H), 2.93 (dd, J = 14.8, 4.0 Hz, 1H), 2.48-2.23 (m, 2H), 2.13 (tt, J = 3.9, 2.2 Hz, 1H), 1.81-1.63 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 169.6, 157.1, 126.7, 87.1, 86.1, 68.3, 60.3, 57.3, 54.7, 46.3, 39.0, 34.2, 31.2, 30.7, 20.7, 20.5, 18.5, 18.4; IR (neat): cm^{-1} 2917, 1753, 1690, 1263, 1154; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M]^+$ 330.1467, found 330.1458.



49 Maoecrystal V (**1**)

50 16-*epi*-Maoecrystal V

(i) BF_3•Et_2, CH_2Cl_2, rt, 1 h.

Maoecrystal V (**1**) and 16-*epi*-maoecrystal V

To a solution of epoxide **49** in CH_2Cl_2 at 0 ^oC was added molecular sieve. The reaction was stirred at this temperature for additional 1 h. Then BF_3 etherate (3 eq) was added. 20 mins later, the reaction temperature was warmed up to room temperature and additional BF_3 etherate (3 eq) was added and the reaction was stirred for additional 1 h. Then it was quenched with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The liquid mixture was dried over $MgSO_4$, filtered, concentrated and the residue was purified using preparative TLC.

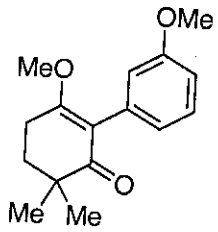
Maoecrystal V: 2 mg, 85% yield. ^1H NMR (500 MHz, CDCl3) δ 6.66 (d, J = 10.2 Hz, 1H), 5.95 (d, J = 10.2 Hz, 1H), 4.63 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 1.6 Hz, 1H), 4.13 (dd, J = 12.1, 1.7 Hz, 1H), 3.19 (dd, J = 14.6, 4.7 Hz, 1H), 2.42-2.25 (m, 2H), 2.21-2.06

(m, 3H), 1.98 (dddd, J = 13.9, 11.5, 6.1, 3.1 Hz, 1H), 1.70 (dt, J = 14.6, 2.1 Hz, 1H), 1.67-1.61 (m, 1H), 1.30 (s, 3H), 1.25 (d, J = 7.5 Hz, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 194.8, 169.0, 156.7, 127.1, 84.9, 84.1, 69.2, 56.6, 51.9, 48.3, 38.3, 34.6, 32.7, 30.6, 18.6, 18.5, 18.0, 15.1; ^{13}C NMR (101 MHz, C_5D_5N) δ 211.8, 194.8, 169.6, 156.8, 127.3, 85.6, 84.7, 69.6, 57.0, 52.5, 48.4, 38.4, 34.9, 33.0, 30.5, 30.1, 18.8, 18.4, 18.3, 15.1;IR (neat): cm^{-1} 2920, 1754, 1719, 1688, 1264, 1155; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M]^+$ 330.1467, found 330.1472.

16-*epi*-Maoecrystal V: 2.8 mg, 90% yield. ^{1}H NMR (500 MHz, CDCl3) δ 6.66 (d, J = 10.1 Hz, 1H), 5.94 (d, J = 10.1 Hz, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.52 (d, J = 1.5 Hz, 1H), 4.13 (dd, J = 12.1, 1.7 Hz, 1H), 2.94 (ddd, J = 14.8, 4.6, 2.0 Hz, 1H), 2.47 (qt, J = 7.2, 2.1 Hz, 1H), 2.21 (ddd, J = 14.8, 10.8, 8.3 Hz, 1H), 2.13-2.03 (m, 2H), 1.93-1.73 (m, 3H), 1.30 (s, 3H), 1.24 (s, 3H), 1.21 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 194.9, 169.0, 156.8, 126.9, 85.2, 85.0, 69.3, 55.3, 52.1, 46.0, 38.4, 33.2, 30.8, 27.7, 23.3, 18.5, 18.3, 12.6; IR (neat): cm^{-1} 2924, 1755, 1725, 1692, 1154; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M]^+$ 330.1467, found 330.1476.

NAME	PFD-II-25
EXPNO	1
PROCNO	1
Date_	20081104
Time	19.27
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	22
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200133 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



carbon NMR

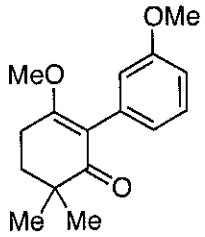
201.719 170.023 158.904 135.260 128.401 123.204 118.367 116.285 112.348 77.322 77.004 76.685 55.545 55.065 39.645 33.995 24.536 22.719

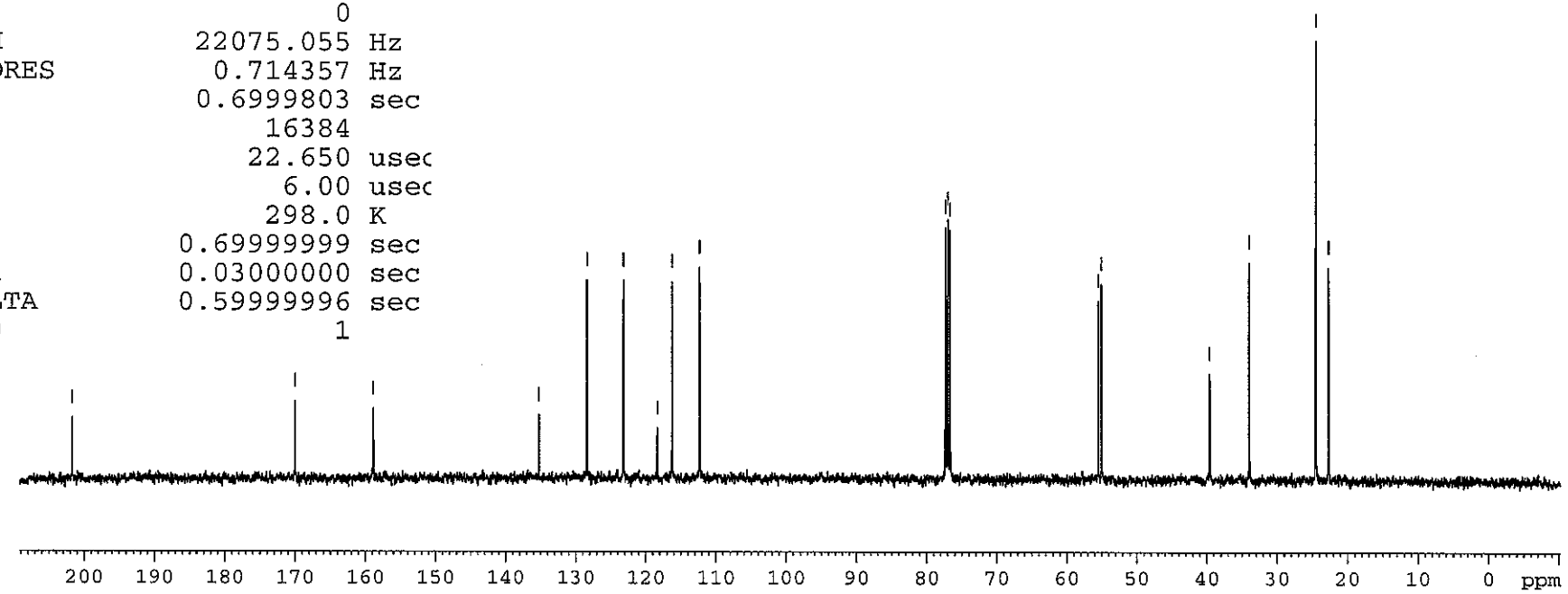
carbon NMR

Current Data Parameters
NAME PFD-II-25-C13
EXPNO 1
PROCNO 1

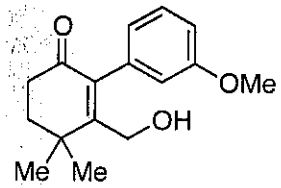
F2 - Acquisition Parameters

Date_	20081008	
Time	18.01	
INSTRUM	spect	
PROBHD	5 mm Multinucl	
PULPROG	zgpg30	
TD	30902	
SOLVENT	Aceton	
NS	385	
DS	0	
SWH	22075.055	Hz
FIDRES	0.714357	Hz
AQ	0.6999803	sec
RG	16384	
DW	22.650	usec
DE	6.00	usec
TE	298.0	K
D1	0.69999999	sec
d11	0.03000000	sec
DELTA	0.59999996	sec
TD0	1	

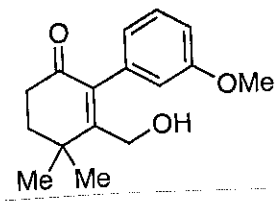




NAME	PFD-II-45
EXPNO	1
PROCNO	1
Date_	20081104
Time	19.18
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200095 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



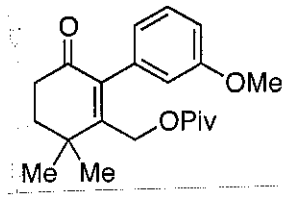
NAME	PFD-II-45-C13
EXPNO	1
PROCNO	1
Date_	20081104
Time	19.21
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	181
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	298.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599749 MHz
WDW	EM
SSB	0



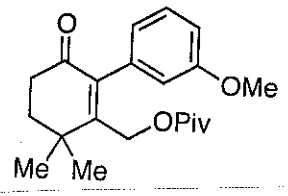
NAME	PFD-I-173
EXPNO	1
PROCNO	1
Date_	20090727
Time	23.46
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	26
DS	0
SWH	10416.667 Hz
FIDRES	0.317891 Hz
AQ	1.5729140 sec
RG	10.1
DW	48.000 usec
DE	6.00 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1

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

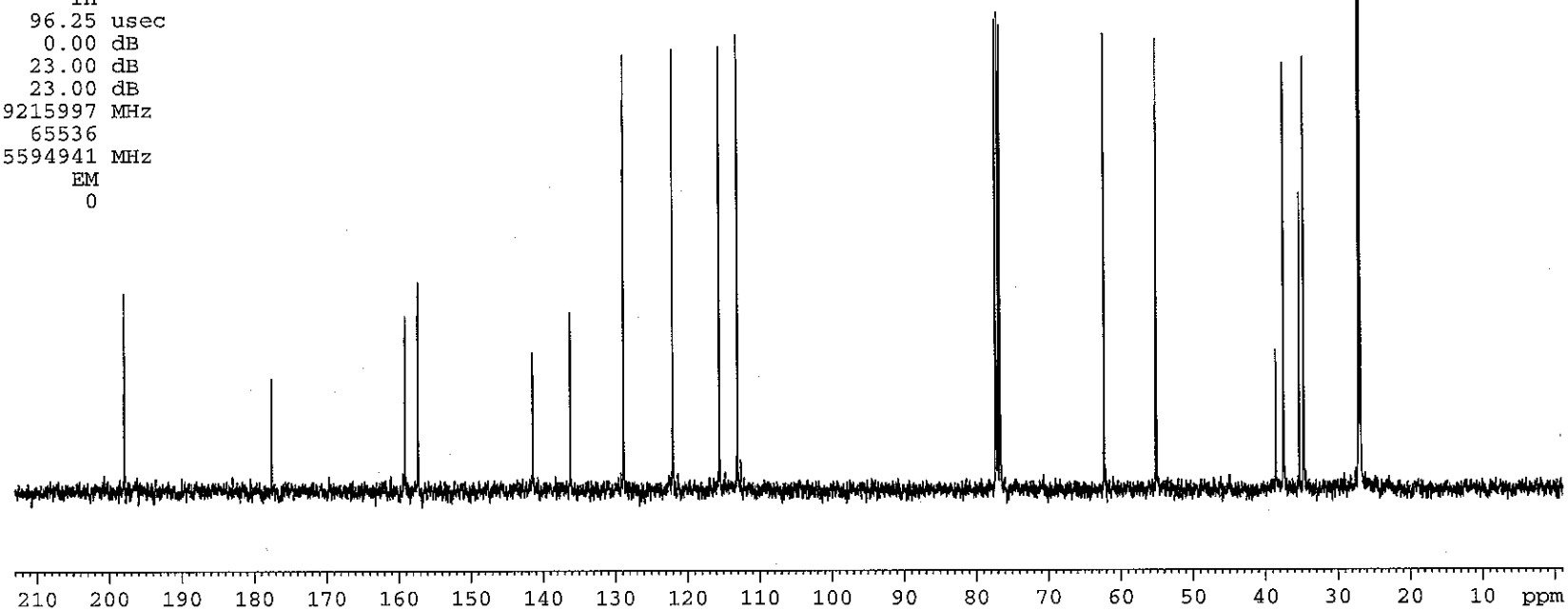
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9181115 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



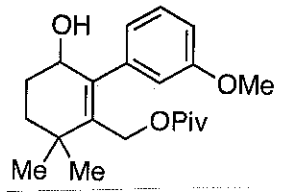
NAME	PFD-I-173
EXPNO	2
PROCNO	1
Date_	20090727
Time	23.48
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	1003
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5594941 MHz
WDW	EM
SSB	0



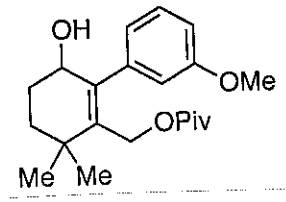
197.939
177.593
159.113
157.297
141.416
136.209
128.805
122.016
115.588
113.067
77.317
76.999
76.681
62.283
55.064
38.578
37.510
35.313
34.721
27.086



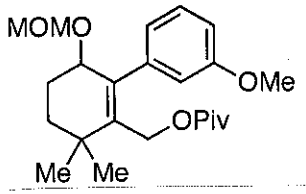
NAME	PFD-I-179
EXPNO	1
PROCNO	1
Date_	20090727
Time	23.08
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	10416.667 Hz
FIDRES	0.317891 Hz
AQ	1.5729140 sec
RG	10.1
DW	48.000 usec
DE	6.00 usec
TE	299.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9181113 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



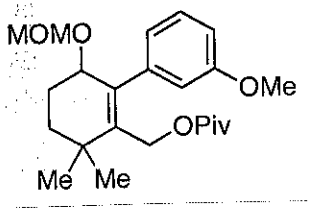
NAME	PFD-I-179
EXPNO	2
PROCNO	1
Date_	20090727
Time	23.10
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	1399
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5594938 MHz
WDW	EM
SSB	0



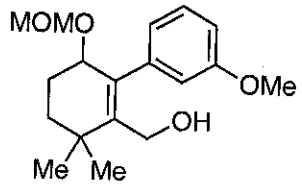
NAME	PFD-I-253
EXPNO	1
PROCNO	1
Date_	20090728
Time	23.34
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	26
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200111 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



NAME	PFD-I-253
EXPNO	2
PROCNO	1
Date_	20090728
Time	23.37
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	411
DS	0
SWH	26178.010 Hz
FIDRES	0.847130 Hz
AQ	0.5902782 sec
RG	16384
DW	19.100 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599695 MHz
WDW	EM
SSB	0

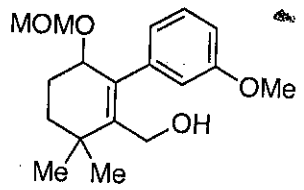


NAME	PFD-II-52
EXPNO	1
PROCNO	1
Date_	20090729
Time	21.44
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	299.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200110 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

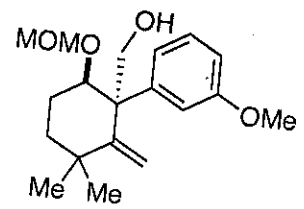


NAME	PFD-II-52
EXPNO	2
PROCNO	1
Date_	20090729
Time	21.48
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	1484
DS	0
SWH	26178.010 Hz
FIDRES	0.847130 Hz
AQ	0.5902782 sec
RG	16384
DW	19.100 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599671 MHz
WDW	EM
SSB	0

159.457
144.749
142.455
138.268
129.205
121.293
114.439
112.624
94.905
77.320
77.002
76.685
73.782
59.743
55.242
54.890
34.468
34.356
28.414
26.815
25.171



NAME	PFD-I-220
EXPNO	1
PROCNO	1
Date_	20080714
Time	9.22
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	30
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40



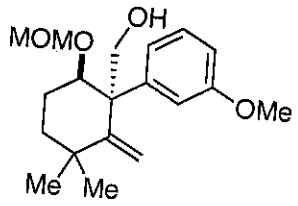
S50

NAME	PFD-I-220-C13
EXPNO	1
PROCNO	1
Date_	20080714
Time	9.25
INSTRUM	spect
PROBHD	5 mm Multinuc1
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	397
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1

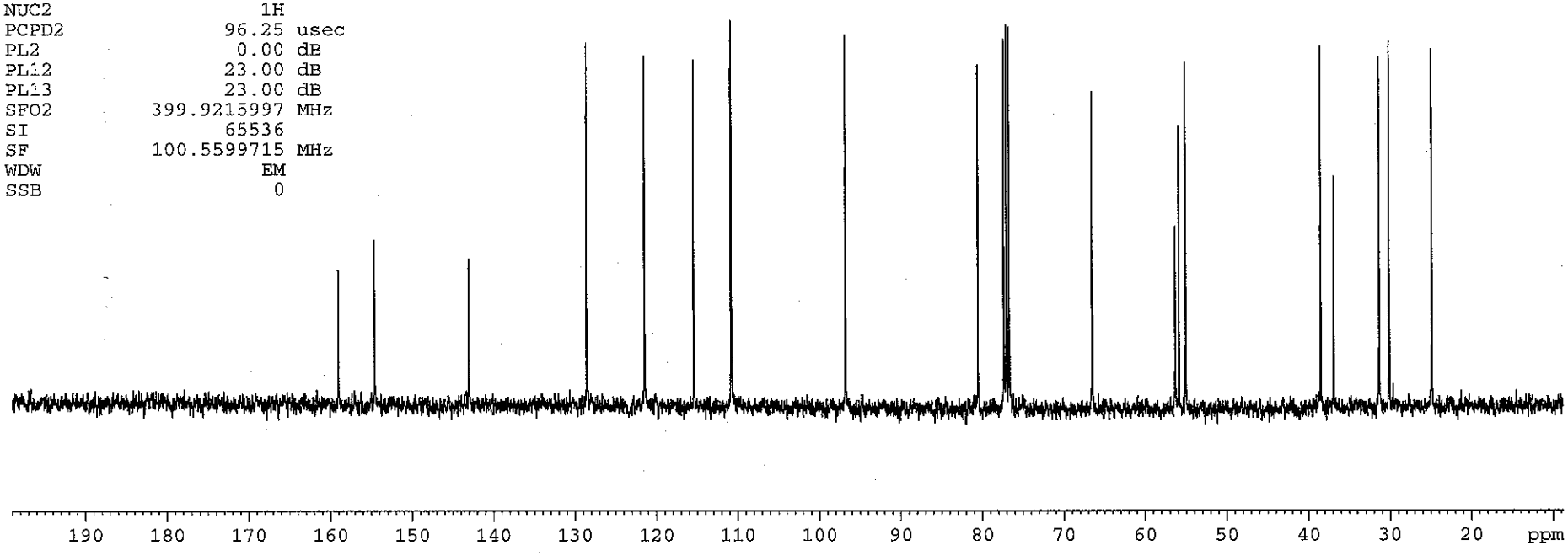
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz

======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599715 MHz
WDW	EM
SSB	0

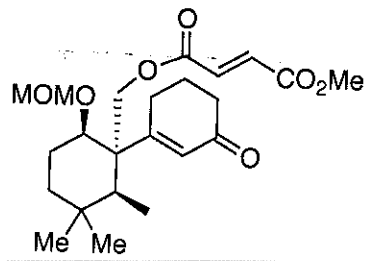
159.015 154.594 143.037 128.546 121.423 115.392 110.822 110.759 96.773 80.509 77.321 77.002 76.684 66.493 56.304 55.857 55.040 38.481 36.890 31.326 30.083 24.866



S51

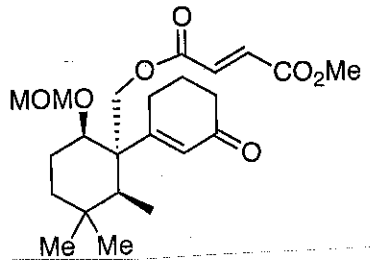


NAME	PFD-I-296
EXPNO	1
PROCNO	1
Date_	20090728
Time	14.06
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	30
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200111 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

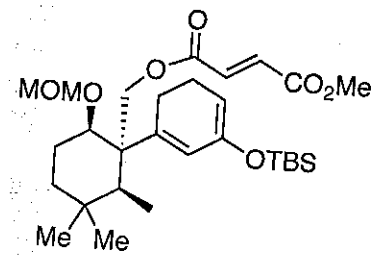


NAME	PFD-I-296
EXPNO	2
PROCNO	1
Date_	20090728
Time	14.09
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	738
DS	0
SWH	26178.010 Hz
FIDRES	0.847130 Hz
AQ	0.5902782 sec
RG	16384
DW	19.100 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599670 MHz
WDW	EM
SSB	0

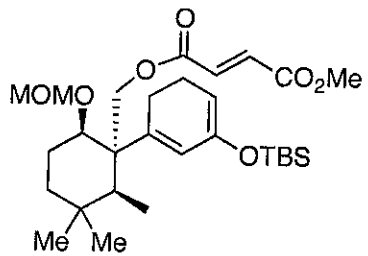
199.804
165.267
164.536
163.665
133.664
133.308
131.406
96.209
80.095
77.319
77.001
76.684
65.227
55.858
52.374
52.081
45.202
40.052
37.562
34.372
31.987
29.091
25.021
23.712
21.179
12.396



NAME	PFD-I-297
EXPNO	2
PROCNO	1
Date_	20081002
Time	15.16
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200116 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

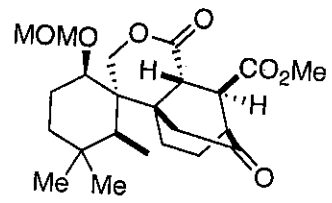


NAME	PFD-I-297-C13
EXPNO	2
PROCNO	1
Date_	20081002
Time	15.19
INSTRUM	spect
PROBHD	5 mm Multinuc1
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	1688
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	298.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599240 MHz
WDW	EM
SSB	0



proton 400Mhz

```
Current Data Parameters
NAME      PFD-I-298-r2-product
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20081006
Time              21.00
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG             zg
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            5995.204 Hz
FIDRES        0.182959 Hz
AQ            2.7329011 sec
RG                 10.1
DW               83.400 usec
DE                6.00 usec
TE                298.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                2.50 usec
PL1               0.00 dB
SFO1        399.9225995 MHz

F2 - Processing parameters
SI                32768
SF          399.9200000 MHz
```

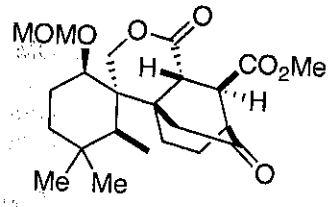


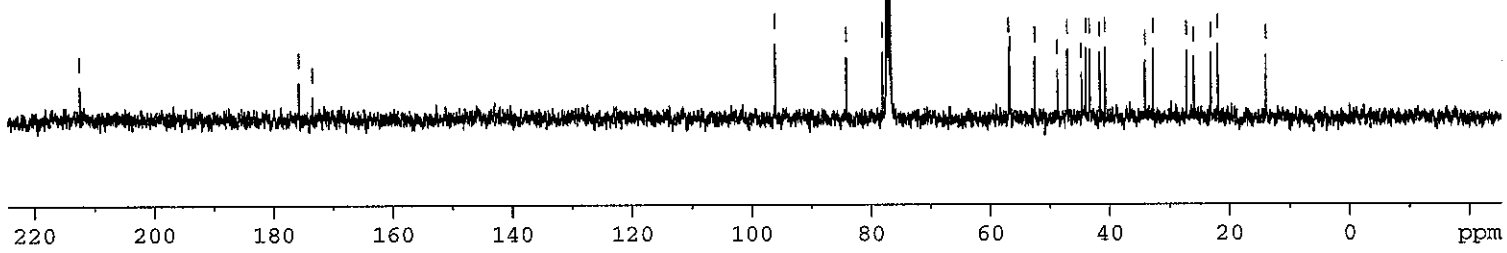
NAME	PFD-I-298-r2-produc
EXPNO	1
PROCNO	1
Date_	20081006
Time	21.15
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	4614
DS	0
SWH	25125.629 Hz
FIDRES	0.813074 Hz
AQ	0.6149998 sec
RG	16384
DW	19.900 usec
DE	6.00 usec
TE	298.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599669 MHz
WDW	EM
SSB	0

212.466

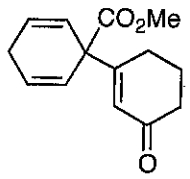
175.742
173.491

96.032
84.093
78.041
77.317
76.999
76.681
56.832
56.604
52.496
48.691
47.039
44.661
43.925
43.320
41.623
40.741
34.060
32.693
27.155
25.935
23.085
21.920
13.893

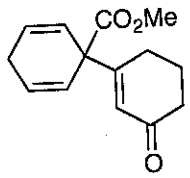




NAME	PFD-II-197-1
EXPNO	1
PROCNO	1
Date_	20090611
Time	0.14
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	22522
SOLVENT	CDCl3
NS	27
DS	0
SWH	4496.403 Hz
FIDRES	0.199645 Hz
AQ	2.5044963 sec
RG	256
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	3.00 dB
SFO1	300.1321009 MHz
SI	32768
SF	300.1300063 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



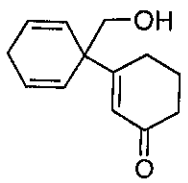
NAME	PFD-II-197-1
EXPNO	2
PROCNO	1
Date_	20090611
Time	0.19
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	288
DS	0
SWH	23809.523 Hz
FIDRES	0.726609 Hz
AQ	0.6881780 sec
RG	16384
DW	21.000 usec
DE	21.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.12 usec
PL1	5.00 dB
SFO1	75.4763978 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	3.00 dB
PL12	24.25 dB
PL13	24.25 dB
SFO2	300.1312005 MHz
SI	65536
SF	75.4677522 MHz
WDW	EM
SSB	0

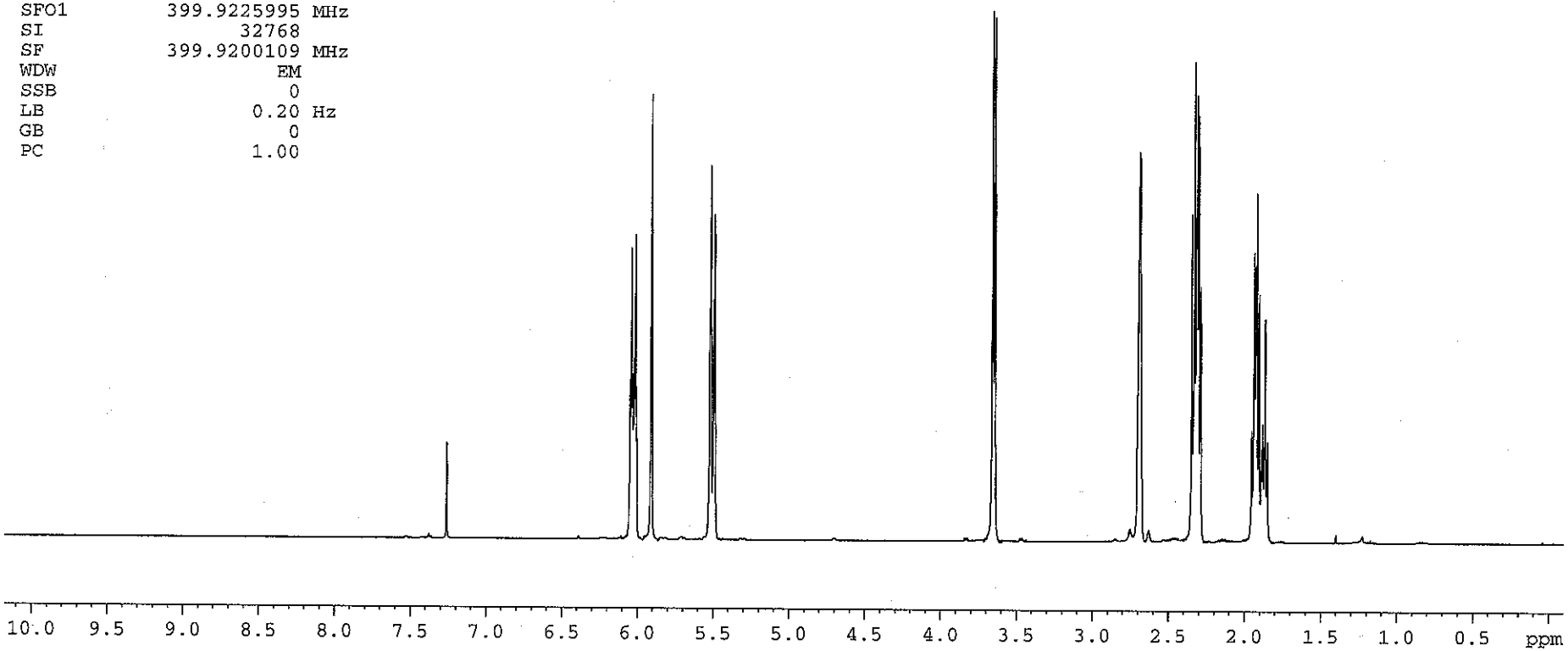


NAME	PFD-II-199
EXPNO	1
PROCNO	1
Date_	20090719
Time	12.11
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	299.9 K
D1	1.00000000 sec
TD0	1

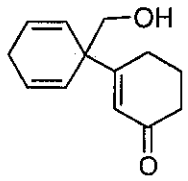
======== CHANNEL f1 ========

NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200109 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00





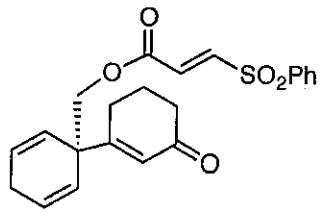
NAME	PFD-II-199
EXPNO	2
PROCNO	1
Date_	20090719
Time	12.14
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	147
DS	0
SWH	22075.055 Hz
FIDRES	0.714357 Hz
AQ	0.6999803 sec
RG	16384
DW	22.650 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599732 MHz
WDW	EM
SSB	0



NAME	PFD-II-213
EXPNO	1
PROCNO	1
Date_	20090719
Time	20.14
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	22522
SOLVENT	CDCl3
NS	32
DS	0
SWH	4496.403 Hz
FIDRES	0.199645 Hz
AQ	2.5046077 sec
RG	256
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
TD0	1

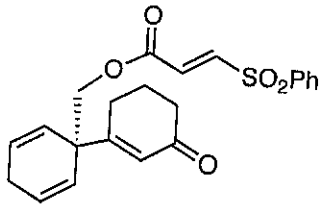
======== CHANNEL f1 ========

NUC1	1H
P1	2.50 usec
PL1	3.00 dB
SFO1	300.1321009 MHz
SI	32768
SF	300.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

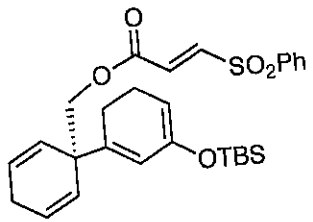


NAME	PFD-II-213
EXPNO	2
PROCNO	1
Date_	20090719
Time	20.18
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	275
DS	0
SWH	23809.523 Hz
FIDRES	0.726609 Hz
AQ	0.6881990 sec
RG	16384
DW	21.000 usec
DE	21.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.12 usec
PL1	5.00 dB
SFO1	75.4763978 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	3.00 dB
PL12	24.25 dB
PL13	24.25 dB
SFO2	300.1312005 MHz
SI	65536
SF	75.4677565 MHz
WDW	EM
SSB	0

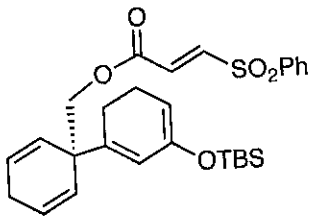
199.710
165.306
163.084
143.559
138.202
134.392
130.316
129.588
128.211
127.928
125.602
125.313
77.423
76.999
76.575
68.813
46.057
37.293
26.468
26.050
22.848



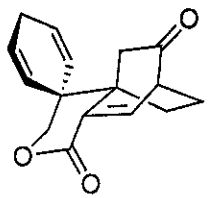
NAME	PFD-II-214
EXPNO	1
PROCNO	1
Date_	20100713
Time	21.03
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	32
DW	83.200 usec
DE	6.50 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



NAME	PFD-II-214
EXPNO	2
PROCNO	1
Date_	20100713
Time	21.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	3734
DS	0
SWH	28409.092 Hz
FIDRES	0.866977 Hz
AQ	0.5767668 sec
RG	1820
DW	17.600 usec
DE	6.50 usec
TE	300.2 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127695 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

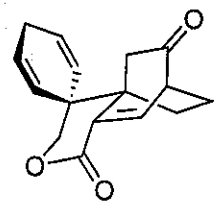


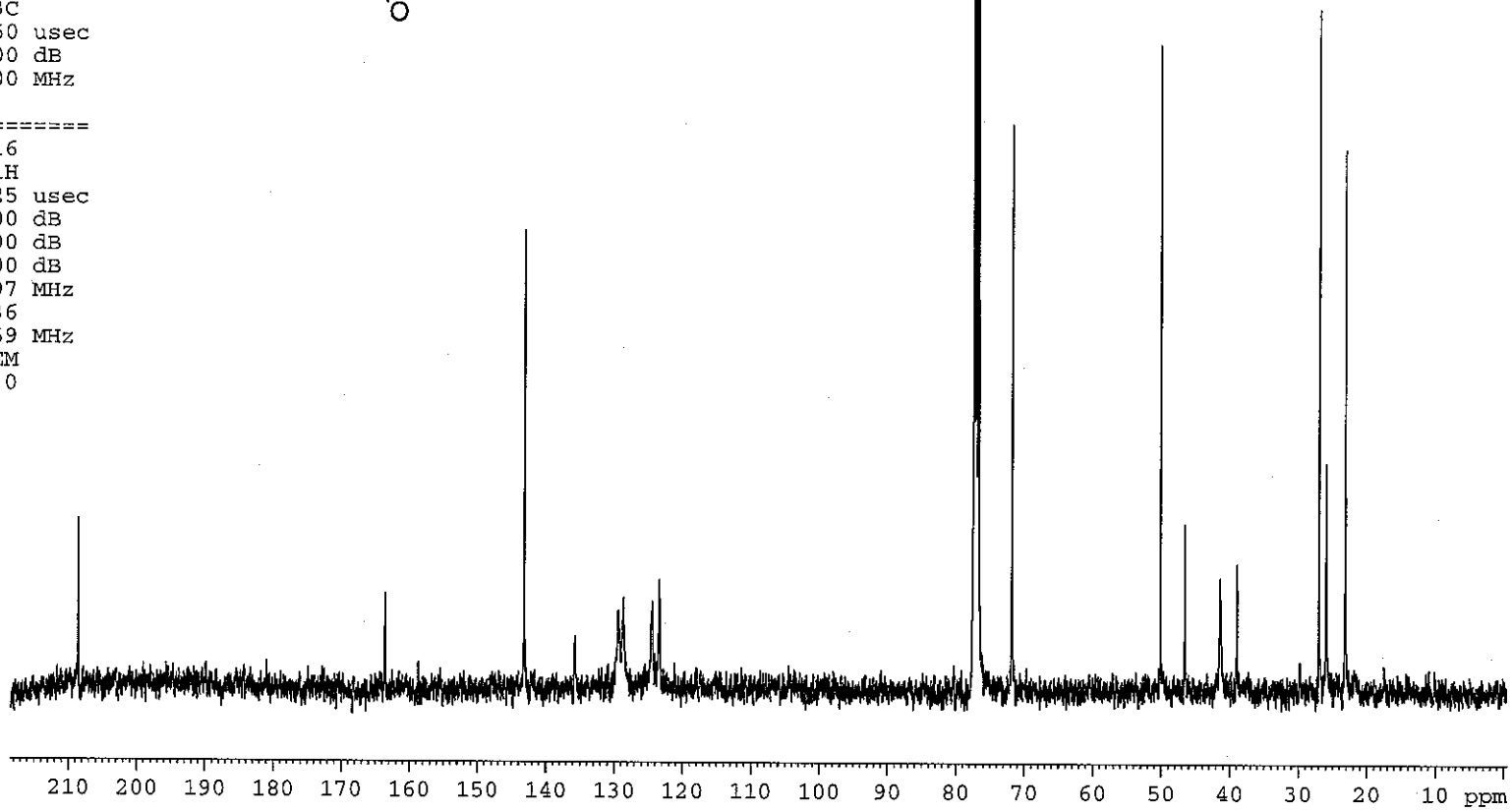
NAME	PFD-II-217
EXPNO	1
PROCNO	1
Date_	20090725
Time	18.20
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200118 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



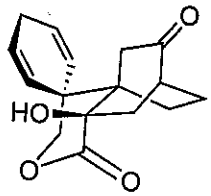
NAME	PFD-II-217	
EXPNO	2	
PROCNO	1	
Date_	20090725	
Time	20.23	
INSTRUM	spect	
PROBHD	5 mm Multinucl	
PULPROG	zgpg30	
TD	30902	
SOLVENT	Aceton	
NS	35631	
DS	0	
SWH	25125.629	Hz
FIDRES	0.813074	Hz
AQ	0.6149998	sec
RG	16384	
DW	19.900	usec
DE	6.00	usec
TE	300.0	K
D1	0.69999999	sec
d11	0.03000000	sec
DELTA	0.59999996	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	17.50	usec
PL1	-1.00	dB
SFO1	100.5699800	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	96.25	usec
PL2	0.00	dB
PL12	23.00	dB
PL13	23.00	dB
SFO2	399.9215997	MHz
SI	65536	
SF	100.5599659	MHz
WDW	EM	
SSB	0	

208.520
163.517
143.093
135.690
129.346
128.561
124.353
123.302
77.321
77.003
76.685
71.733
50.065
46.486
41.329
38.856
26.901
25.870
23.101

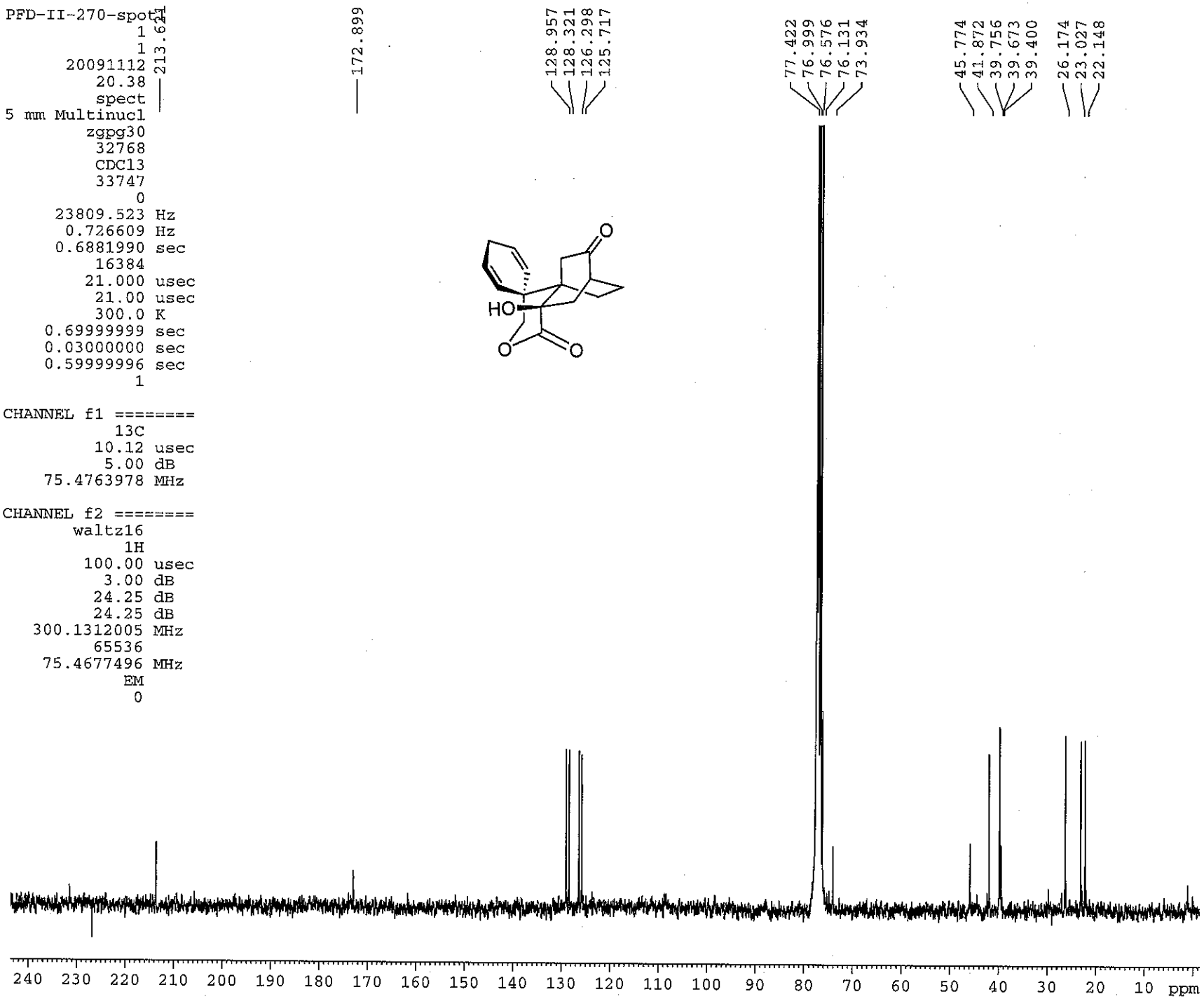




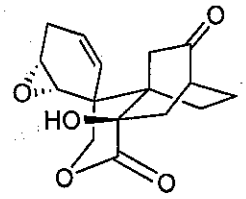
NAME	PFD-II-270-spot1
EXPNO	1
PROCNO	1
Date_	20091112
Time	20.38
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200111 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



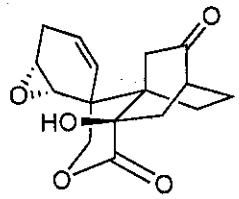
NAME	PFD-II-270-spot
EXPNO	1
PROCNO	1
Date_	20091112
Time	20.38
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	33747
DS	0
SWH	23809.523 Hz
FIDRES	0.726609 Hz
AQ	0.6881990 sec
RG	16384
DW	21.000 usec
DE	21.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.12 usec
PL1	5.00 dB
SFO1	75.4763978 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	3.00 dB
PL12	24.25 dB
PL13	24.25 dB
SFO2	300.1312005 MHz
SI	65536
SF	75.4677496 MHz
WDW	EM
SSB	0



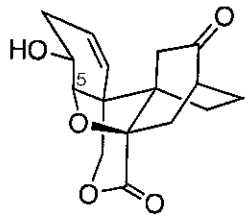
NAME	PFD-II-252-pure
EXPNO	1
PROCNO	1
Date_	20091125
Time	14.58
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	100
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200112 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



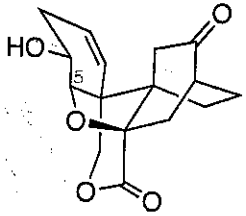
NAME	PFD-II-252-pure
EXPNO	2
PROCNO	1
Date_	20091125
Time	22.06
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	32594
DS	0
SWH	30120.482 Hz
FIDRES	0.974710 Hz
AQ	0.5130232 sec
RG	16384
DW	16.600 usec
DE	6.00 usec
TE	300.1 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599651 MHz
WDW	EM
SSB	0



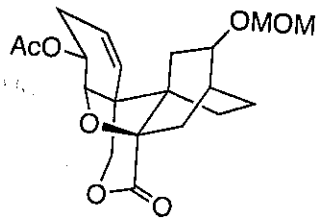
NAME	PFD-II-52-pureprodu
EXPNO	1
PROCNO	1
Date_	20091127
Time	22.01
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	22522
SOLVENT	CDCl3
NS	32
DS	0
SWH	4496.403 Hz
FIDRES	0.199645 Hz
AQ	2.5046077 sec
RG	256
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	3.00 dB
SFO1	300.1321009 MHz
SI	32768
SF	300.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40



NAME	PFD-II-52-pureprodu
EXPNO	2
PROCNO	1
Date_	20091127
Time	22.03
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	91514
DS	0
SWH	23809.523 Hz
FIDRES	0.726609 Hz
AQ	0.6881990 sec
RG	16384
DW	21.000 usec
DE	21.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.12 usec
PL1	5.00 dB
SFO1	75.4763978 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	3.00 dB
PL12	24.25 dB
PL13	24.25 dB
SFO2	300.1312005 MHz
SI	65536
SF	75.4677491 MHz
WDW	EM
SSB	0



```
Current Data Parameters
NAME       PFD-IV-191-R1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120607
Time               3.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  24
DS                   0
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ           2.7263477 sec
RG                  32
DW             83.200 usec
DE              6.50 usec
TE              300.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               9.50 usec
PLW1       26.94187927 W
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               32768
SF         400.1300090 MHz
WDW                 EM
SSB       0
LB             0.20 Hz
GB        0
PC             1.00
```

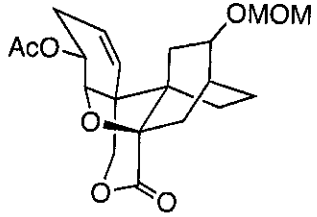


Current Data Parameters
NAME PFD-IV-191-R1
EXPNO 2
PROCNO 1

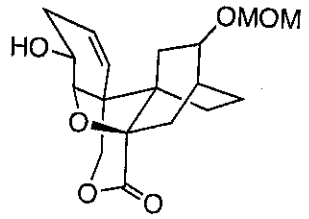
F2 - Acquisition Parameters

Date_	20120606	
Time	21.56	
INSTRUM	spect	
PROBHD	5 mm Multinucl	
PULPROG	zgpg30	
TD	32768	
SOLVENT	CDCl3	
NS	1308	
DS	0	
SWH	21186.441	Hz
FIDRES	0.646559	Hz
AQ	0.7733748	sec
RG	32768	
DW	23.600	usec
DE	21.00	usec
TE	300.0	K
D1	0.69999999	sec
d11	0.03000000	sec
DELTA	0.59999996	sec

S75



NAME	PFD-IV-191-R2	
EXPNO	1	
PROCNO	1	
Date_	20110715	
Time	22.03	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	32	
DS	0	
SWH	6009.615	Hz
FIDRES	0.183399	Hz
AQ	2.7263477	sec
RG	575	
DW	83.200	usec
DE	6.50	usec
TE	295.0	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.50	usec
PL1	-4.00	dB
PL1W	26.94187927	W
SFO1	400.1328009	MHz
SI	32768	
SF	400.1300092	MHz
WDW	EM	
SSB	0	
LB	0.20	Hz
GB	0	
PC	1.00	

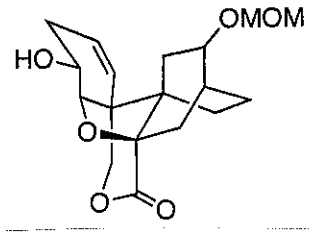


proton

S76

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

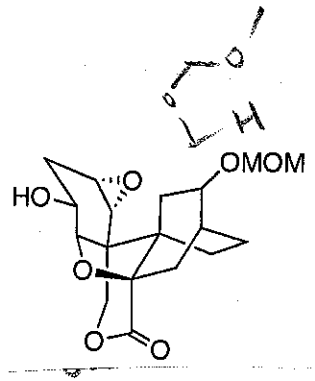
NAME	PFD-IV-191-R2
EXPNO	2
PROCNO	1
Date_	20110715
Time	22.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	4004
DS	0
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	0.6816244 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	295.1 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



NAME	PFD-IV-197
EXPNO	1
PROCNO	1
Date_	20110724
Time	16.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	456
DW	83.200 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

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

NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

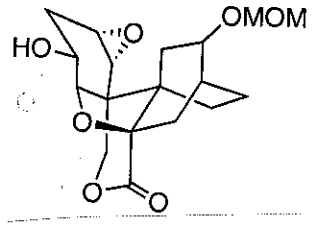


proton

S78

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

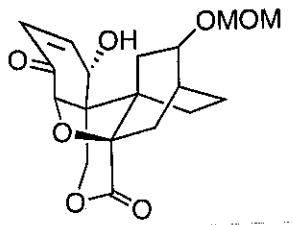
NAME	PFD-IV-197
EXPNO	2
PROCNO	1
Date_	20110724
Time	17.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	4346
DS	0
SWH	28409.092 Hz
FIDRES	0.866977 Hz
AQ	0.5767668 sec
RG	2050
DW	17.600 usec
DE	6.50 usec
TE	298.2 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127700 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



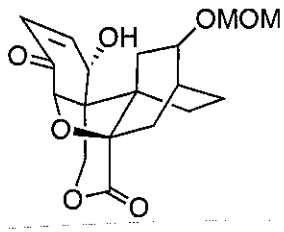
NAME	PFD-IV-197-R2
EXPNO	1
PROCNO	1
Date_	20110809
Time	21.01
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDC13
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	362
DW	83.200 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

S80

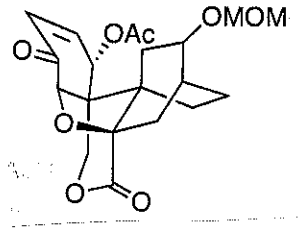
proton

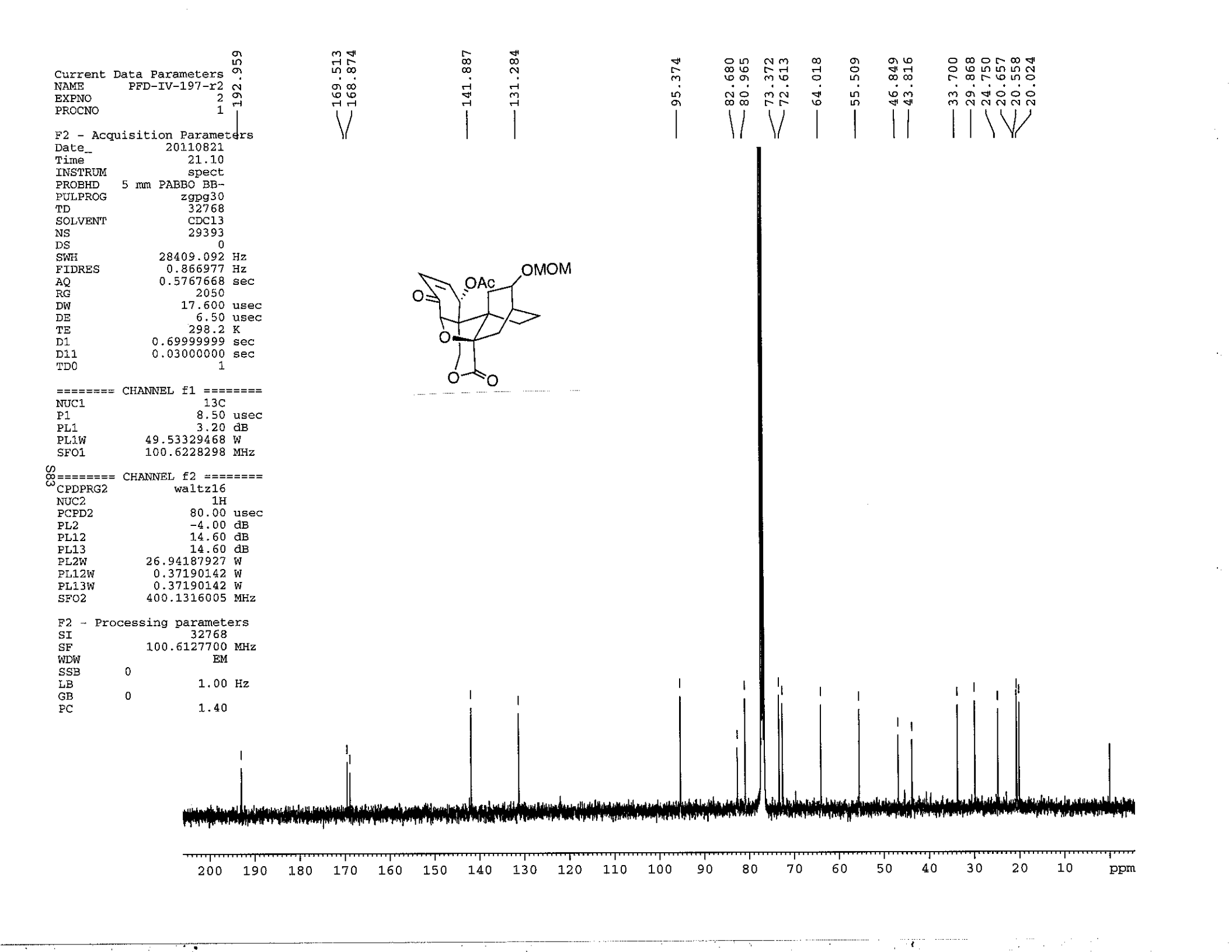


NAME	PFD-IV-197-R2
EXPNO	4
PROCNO	1
Date_	20110810
Time	22.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	22335
DS	0
SWH	28409.092 Hz
FIDRES	0.866977 Hz
AQ	0.5767668 sec
RG	2050
DW	17.600 usec
DE	6.50 usec
TE	298.3 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127700 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



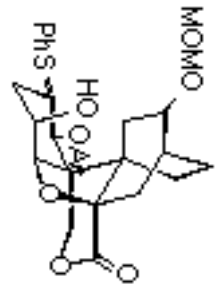
NAME	PFD-IV-197-R2	
EXPNO	1	
PROCNO	1	
Date_	20110821	
Time	11.08	
INSTRUM	spect	
PROBHD	5 mm PABBI 1H/	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	52	
DS	0	
SWH	12019.230	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	41.600	usec
DE	6.50	usec
TE	300.2	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	7.25	usec
PL1	0.00	dB
PL1W	12.20776844	W
SFO1	399.9225995	MHz
SI	32768	
SF	399.9200000	MHz
WDW	EM	
SSB	0	
LB	0.20	Hz
GB	0	
PC	1.00	

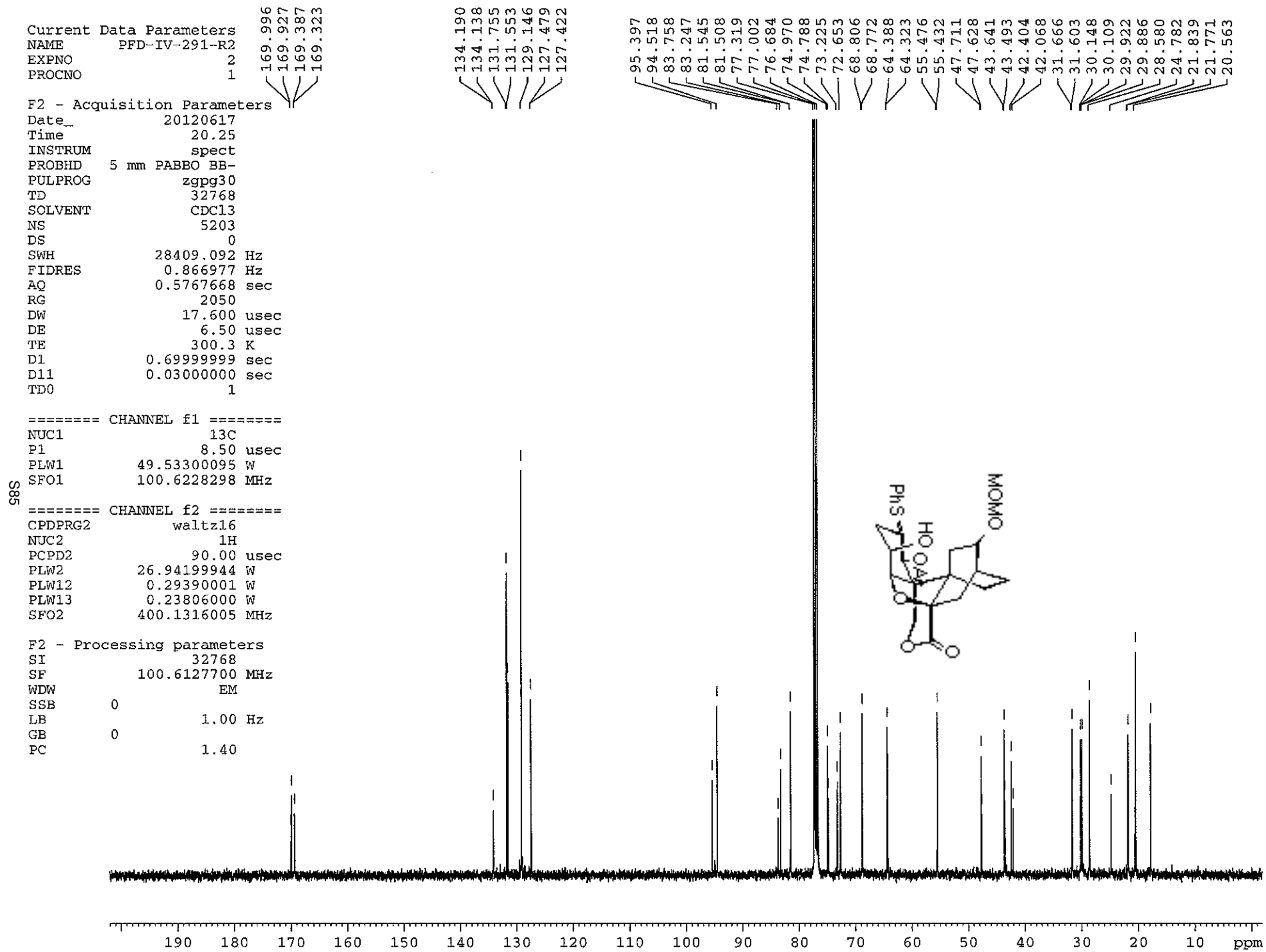



Current Data Parameters
NAME PFD-IV-197-r2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110821
Time 21.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 29393
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
192.959
169.513
168.874
141.887
131.284
95.374
82.680
80.965
73.372
72.613
64.018
55.509
46.849
43.816
33.700
29.868
24.750
20.657
20.558
20.024
OAc
OMOM
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

proton

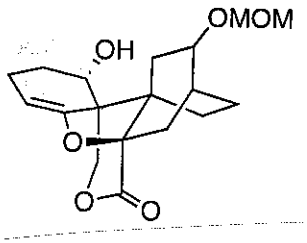
```
Current Data Parameters
NAME      PFD-IV-291-R2
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20120617
Time              20.21
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                  362
DW               83.200 usec
DE                6.50 usec
TE               300.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                9.50 usec
PLW1        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB       0
LB                0.20 Hz
GB        0
PC                1.40
```




Current Data Parameters
NAME PFD-IV-291-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120617
Time 20.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 5203
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
169.996
169.927
169.387
169.323
134.190
134.138
131.755
131.553
129.146
127.479
127.422
95.397
94.518
83.758
83.247
81.545
81.508
77.319
77.002
76.684
74.970
74.788
73.225
72.653
68.806
68.772
64.388
64.323
55.476
55.432
47.711
47.628
43.641
43.493
42.404
42.068
31.666
31.603
30.148
30.109
29.922
29.886
28.580
24.782
21.839
21.771
20.563
PhS
HO
OAc
MOMO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

proton

```
Current Data Parameters
NAME       PFD-IV-212-R1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120502
Time              10.27
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   33
DS                    0
SWH            6009.615 Hz
FIDRES         0.183399 Hz
AQ             2.7263477 sec
RG                  406
DW               83.200 usec
DE                6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W       26.94187927 W
SFO1       400.1328009 MHz

F2 - Processing parameters
SI                32768
SF         400.1300088 MHz
WDW                  EM
SSB       0
LB                0.20 Hz
GB        0
PC                1.00
```



Current Data Parameters
NAME PFD-IV-212-R1
EXPNO 2
PROCNO 1

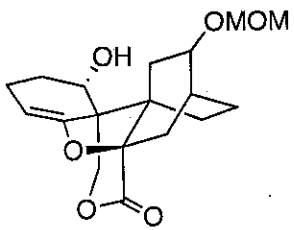
F2 - Acquisition Parameters
Date_ 20120502
Time 10.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1296
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1

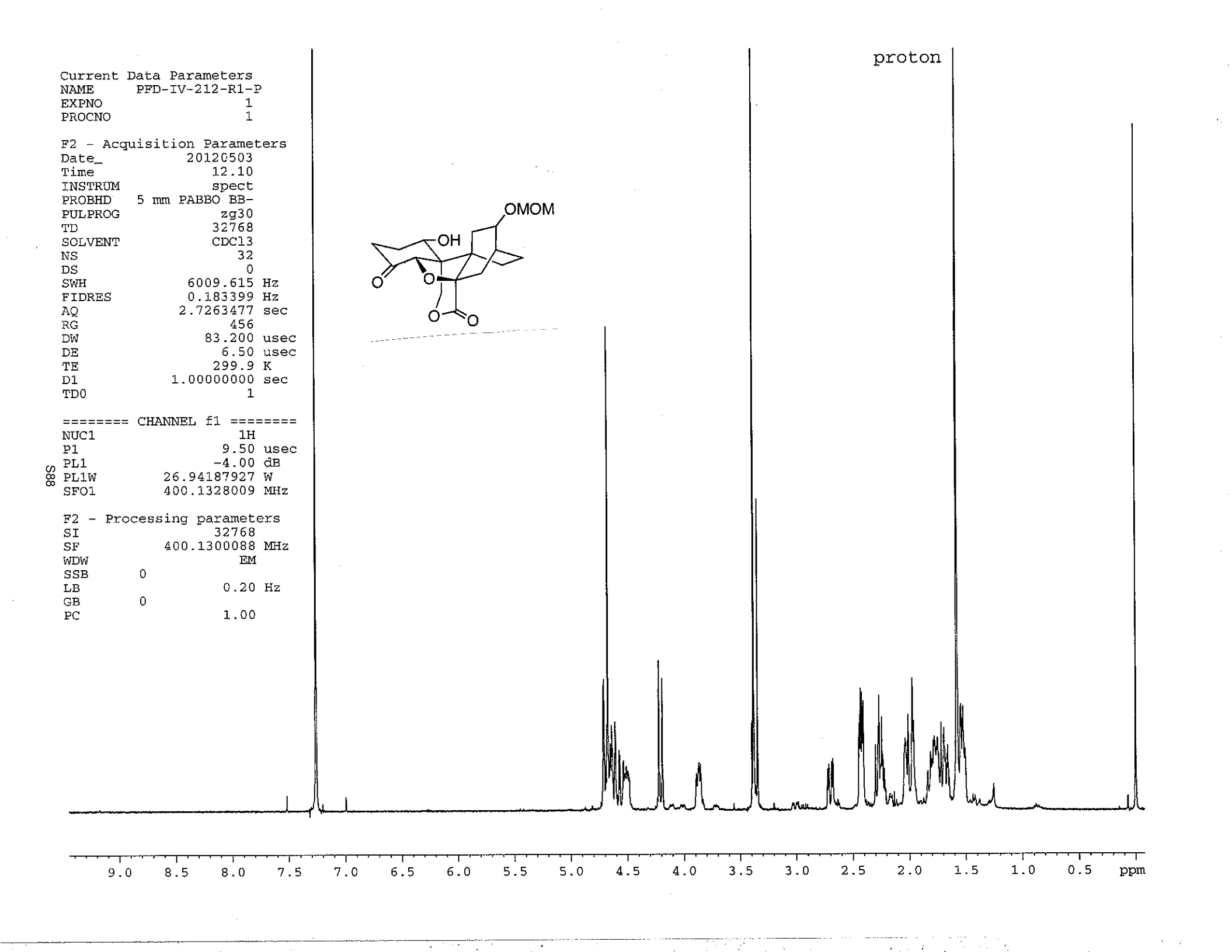
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz

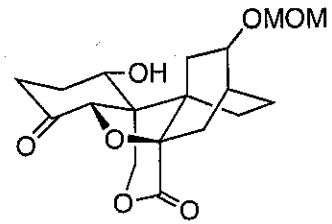
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

169.362
155.849
94.898
94.802
83.322
77.318
77.000
76.682
72.700
72.174
68.341
55.431
47.714
42.843
30.470
30.051
27.556
24.191
21.512
21.469
21.286

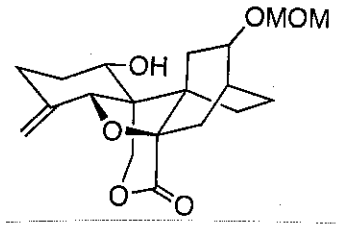



Current Data Parameters
NAME PFD-IV-212-R1-P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 12.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 456
DW 83.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S88
OMOM
OH
O
O
O
O
proton
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

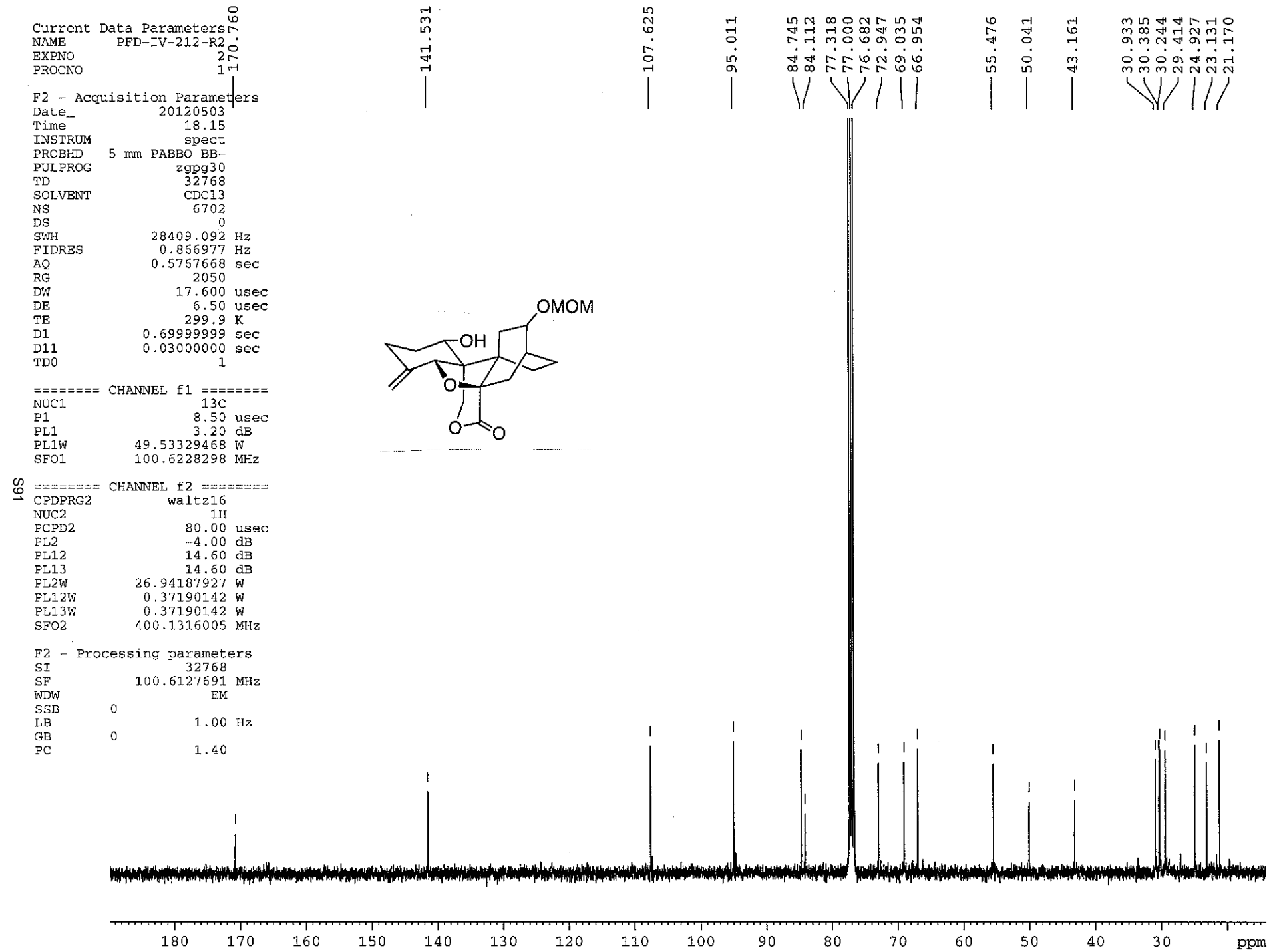
```
Current Data Parameters
NAME      PFD-IV-212-R1-P
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120503
Time               12.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                 5893
DS                    0
SWH           28409.092 Hz
FIDRES         0.866977 Hz
AQ            0.5767668 sec
RG                 2050
DW               17.600 usec
DE                6.50 usec
TE               300.4 K
D1            0.69999999 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.50 usec
PL1                3.20 dB
PL1W        49.53329468 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -4.00 dB
PL12              14.60 dB
PL13              14.60 dB
PL2W        26.94187927 W
PL12W        0.37190142 W
PL13W        0.37190142 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127691 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



```
Current Data Parameters
NAME       PFD-IV-212-R2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120503
Time              18.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                  575
DW               83.200 usec
DE                6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W       26.94187927 W
SFO1       400.1328009 MHz

F2 - Processing parameters
SI                32768
SF        400.1300089 MHz
WDW                  EM
SSB       0
LB                0.20 Hz
GB        0
PC                1.40
```

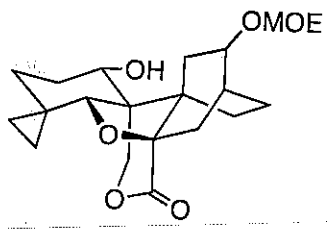


proton


Current Data Parameters
NAME PFD-IV-212-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 18.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 6702
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.760
141.531
107.625
95.011
84.745
84.112
77.318
77.000
76.682
72.947
69.035
66.954
55.476
50.041
43.161
30.933
30.385
30.244
29.414
24.927
23.131
21.170
OMOM
OH
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

proton

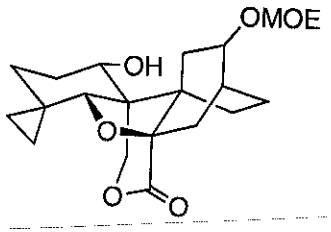
```
Current Data Parameters
NAME          PFD-IV-219
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20111006
Time               23.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    28
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   512
DW                83.200 usec
DE                 6.50 usec
TE                300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.40
```



```
Current Data Parameters
NAME          PFD-IV-219
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20111007
Time                0.07
INSTRUM            spect
PROBHD  5 mm PABBO BB-
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 24964
DS                     0
SWH            28409.092 Hz
FIDRES          0.866977 Hz
AQ              0.5767668 sec
RG                  2050
DW                17.600 usec
DE                 6.50 usec
TE                300.0 K
D1             0.69999999 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                 3.20 dB
PL1W         49.53329468 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W         26.94187927 W
PL12W         0.37190142 W
PL13W         0.37190142 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127687 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

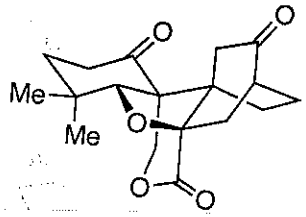
170.896
170.799

93.519
93.437
84.044
83.609
83.026
82.597
72.947
72.851
69.710
69.671
67.529
67.395
63.518
63.420
49.724
49.496
43.487
43.379
31.469
30.796
30.333
30.243
30.129
29.931
28.789
24.943
22.924
22.552
21.194
18.123
17.715
17.678
15.167
14.193

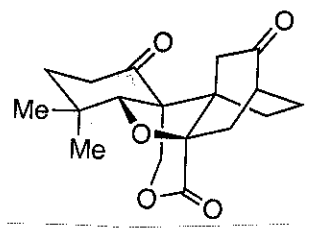


NAME	PFD-IV-256-R2	
EXPNO	6	
PROCNO	1	
Date_	20120403	
Time	11.39	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	32	
DS	0	
SWH	6009.615	Hz
FIDRES	0.183399	Hz
AQ	2.7263477	sec
RG	575	
DW	83.200	usec
DE	6.50	usec
TE	298.0	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.50	usec
PL1	-4.00	dB
PL1W	26.94187927	W
SFO1	400.1328009	MHz
SI	32768	
SF	400.1300089	MHz
WDW	EM	
SSB	0	
LB	0.20	Hz
GB	0	
PC	1.00	

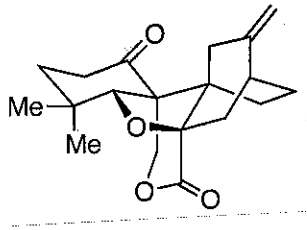
proton



```
Current Data Parameters
NAME       PFD-IV-256-R2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120403
Time              18.14
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              32768
SOLVENT          CDCl3
NS                8247
DS                   0
SWH          28409.092 Hz
FIDRES        0.866977 Hz
AQ            0.5767668 sec
RG                2050
DW              17.600 usec
DE               6.50 usec
TE               298.0 K
D1           0.69999999 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                3.20 dB
PL1W       49.53329468 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W       26.94187927 W
PL12W       0.37190142 W
PL13W       0.37190142 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127695 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

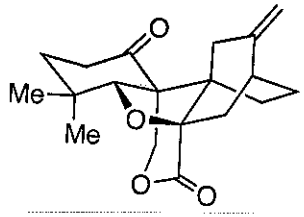


```
Current Data Parameters
NAME       PFD-IV-258-R2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120405
Time              22.24
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  34
DS                   0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG               203.12
DW               48.400 usec
DE                6.50 usec
TE               298.1 K
D1           1.50000000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                8.00 usec
PLW1        14.79100037 W
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                65536
SF          500.1300130 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



```
Current Data Parameters
NAME       PFD-IV-282-R2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120528
Time              11.52
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               41662
SOLVENT          CDCl3
NS                5423
DS                   0
SWH          35714.285 Hz
FIDRES        0.857239 Hz
AQ            0.5833180 sec
RG                 912
DW              14.000 usec
DE               6.50 usec
TE              300.3 K
D1          1.00000000 sec
D11         0.03000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                9.13 usec
PLW1     123.02999878 W
SFO1      125.7703637 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2            80.00 usec
PLW2       19.15500069 W
PLW12       0.43459001 W
PLW13       0.27814001 W
SFO2      500.1320005 MHz

F2 - Processing parameters
```

207.431 169.927 147.317 106.228 87.524 84.325 68.083 57.562 44.548 37.577 35.411 35.202 32.307 31.781 31.733 31.383 24.785 22.222 22.113

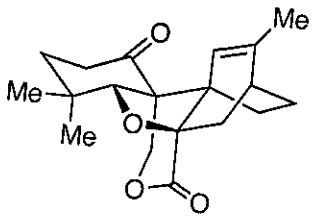


Current Data Parameters
NAME PFD-IV-261
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120406
Time 10.54
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.50000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 65536
SF 500.1300129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



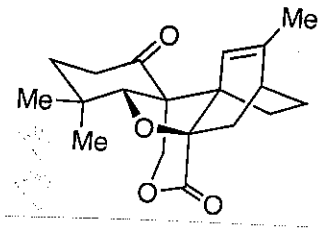
Current Data Parameters
NAME PFD-IV-283
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120529
Time 0.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 41662
SOLVENT CDCl3
NS 1524
DS 0
SWH 35714.285 Hz
FIDRES 0.857239 Hz
AQ 0.5833180 sec
RG 912
DW 14.000 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.13 usec
PLW1 123.02999878 W
SFO1 125.7703637 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.15500069 W
PLW12 0.43459001 W
PLW13 0.27814001 W
SFO2 500.1320005 MHz

F2 - Processing parameters



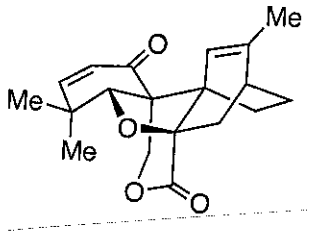
207.833
170.357
145.656
122.421
88.449
86.472
77.251
76.998
76.743
68.220
57.125
48.365
37.878
35.754
35.528
35.359
32.569
31.198
23.214
22.017
21.505
19.829

Current Data Parameters
NAME PFD-IV-264-R2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120616
Time 23.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 512
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PLW1 26.94187927 W
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40



Current Data Parameters
NAME PFD-IV-264-R2
EXPNO 2
PROCNO 1

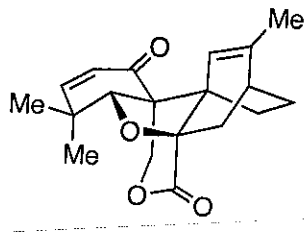
F2 - Acquisition Parameters
Date_ 20120617
Time 2.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 13744
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz

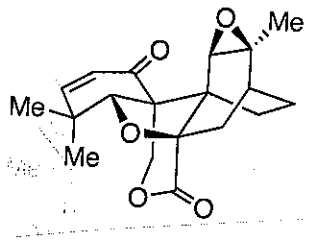
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127687 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

196.821
170.454
157.739
145.804
126.846
122.474
86.689
86.628
77.317
77.000
76.683
68.592
54.422
47.756
38.635
35.652
35.208
30.708
23.137
22.063
19.825
18.588



```
Current Data Parameters
NAME        PFD-IV-273-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120629
Time                4.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   575
DW                83.200 usec
DE                 6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PLW1        26.94187927 W
SFO1       400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300088 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.40
```



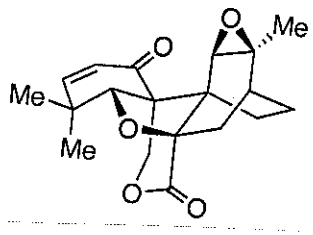
Current Data Parameters
NAME PFD-IV-273-2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120629
Time 4.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 30584
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1

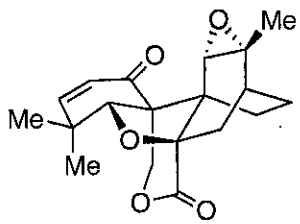
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

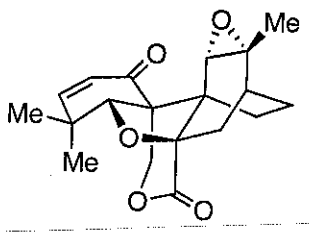


```
Current Data Parameters
NAME        PFD-IV-273-3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120701
Time               23.47
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   406
DW                83.200 usec
DE                 6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PLW1        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300087 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.40
```



```
Current Data Parameters
NAME        PFD-IV-273-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120701
Time              23.54
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              32768
SOLVENT         CDCl3
NS              42230
DS                  0
SWH         28409.092 Hz
FIDRES        0.866977 Hz
AQ           0.5767668 sec
RG                2050
DW              17.600 usec
DE               6.50 usec
TE               299.9 K
D1          0.69999999 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               13C
P1                8.50 usec
PLW1        49.53300095 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           90.00 usec
PLW2        26.94199944 W
PLW12        0.29390001 W
PLW13        0.23806000 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127691 MHz
WDW                EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

195.621
169.614
157.176
126.730
87.056
86.130
68.296
60.306
57.288
54.659
46.264
39.016
34.173
31.158
30.730
20.679
20.463
18.456
18.416

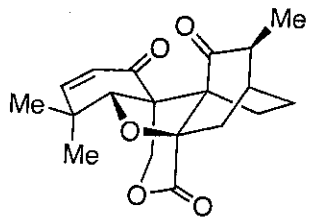


Current Data Parameters
NAME PFD-IV-275-p
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120703
Time 20.15
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 46
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.50000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 65536
SF 500.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

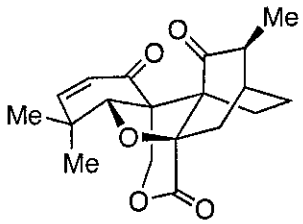


16-*epi*-Maoecrystal V

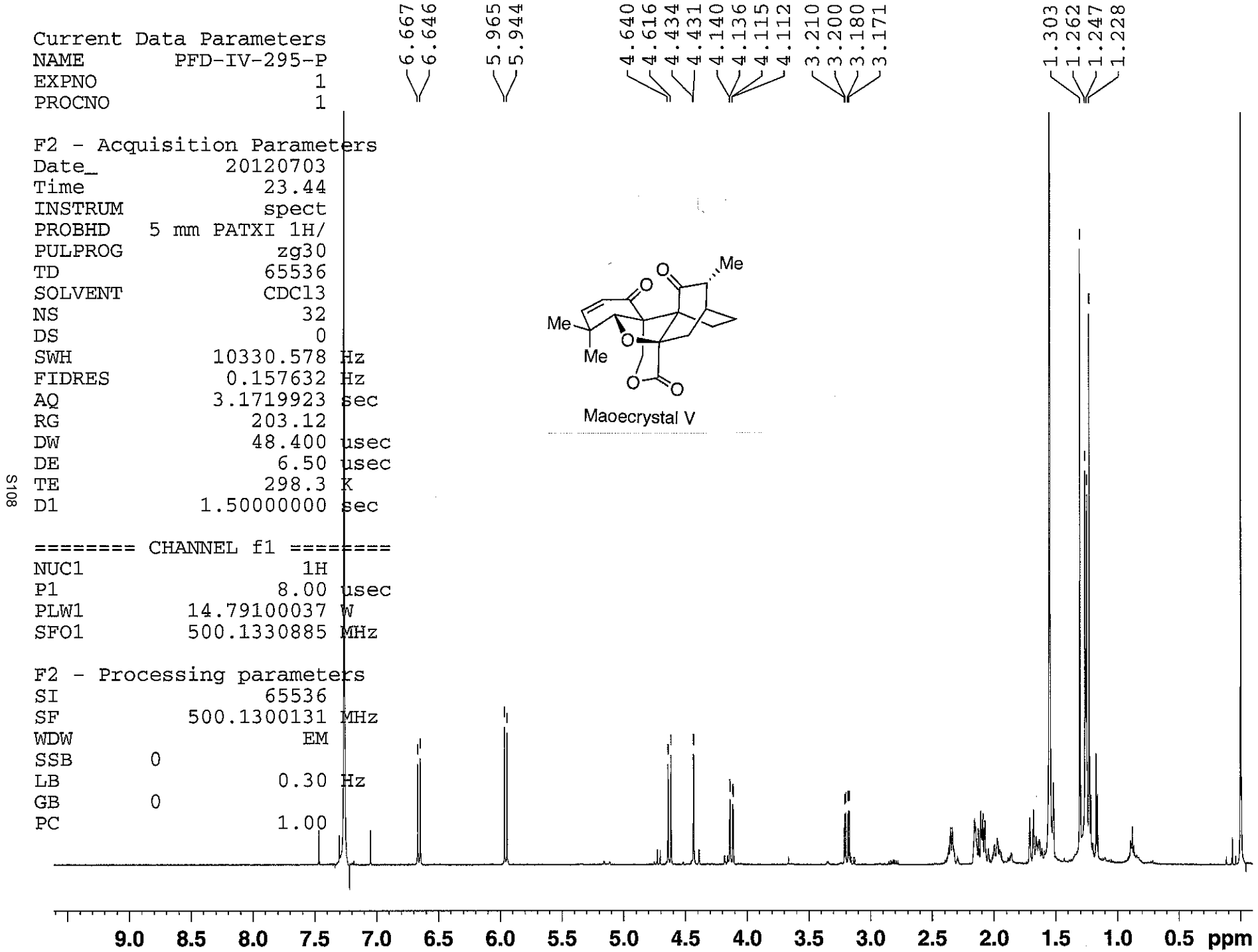
```
Current Data Parameters
NAME        PFD-IV-275-P
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120704
Time               3.22
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                32768
SOLVENT           CDCl3
NS                34984
DS                    0
SWH           28409.092 Hz
FIDRES         0.866977 Hz
AQ             0.5767668 sec
RG                 2050
DW                17.600 usec
DE                 6.50 usec
TE                299.9 K
D1             0.69999999 sec
D11            0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PLW1         49.53300095 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              90.00 usec
PLW2         26.94199944 W
PLW12         0.29390001 W
PLW13         0.23806000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127691 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

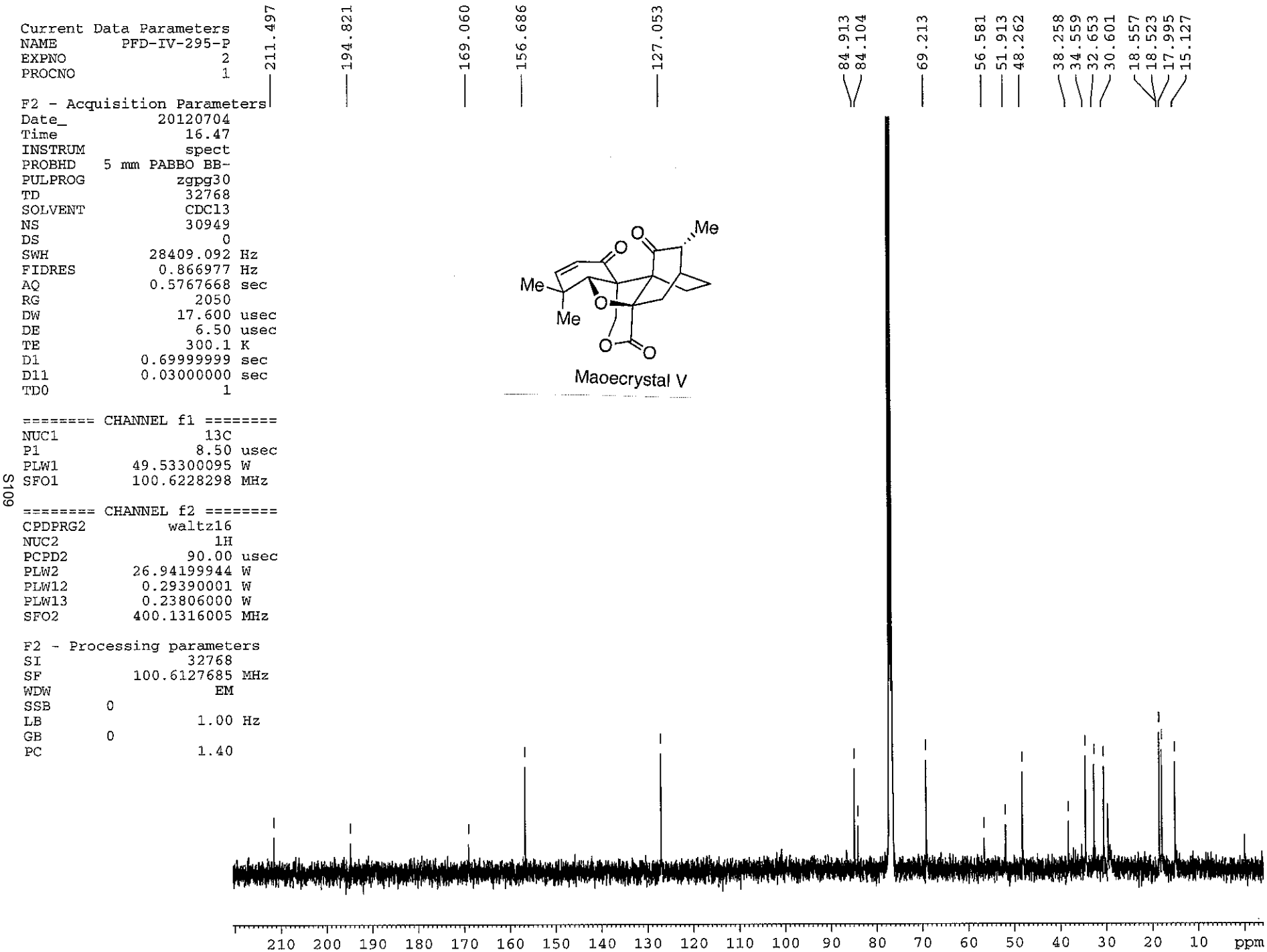
211.435 194.874 169.006 156.836 126.920

85.226 84.978 77.316 76.999 76.681 69.331 55.323 52.090 45.991 38.388 33.183 30.770 27.680 23.301 18.526 18.305 12.644

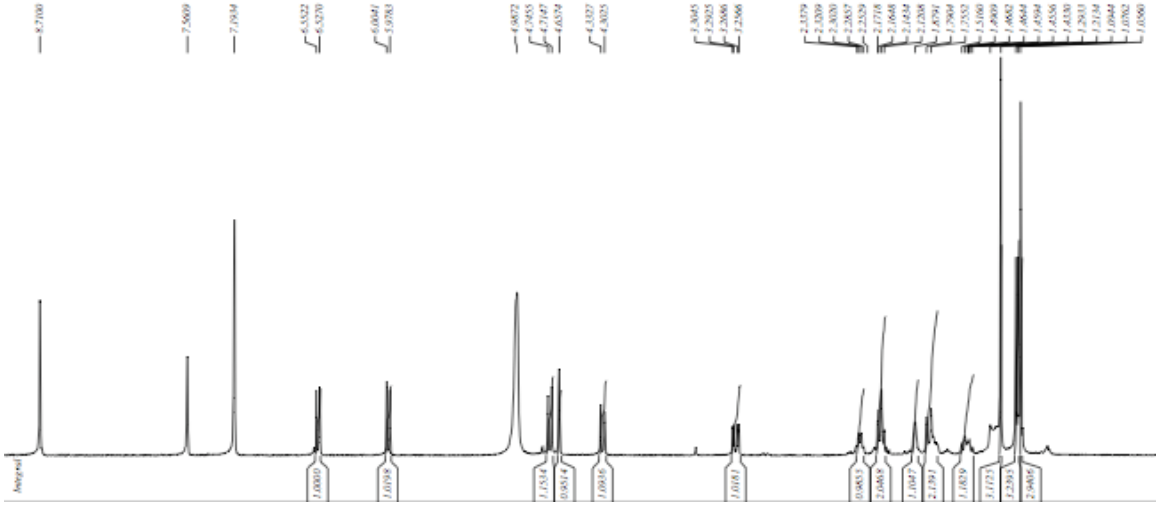


16-*epi*-Maoecrystal V

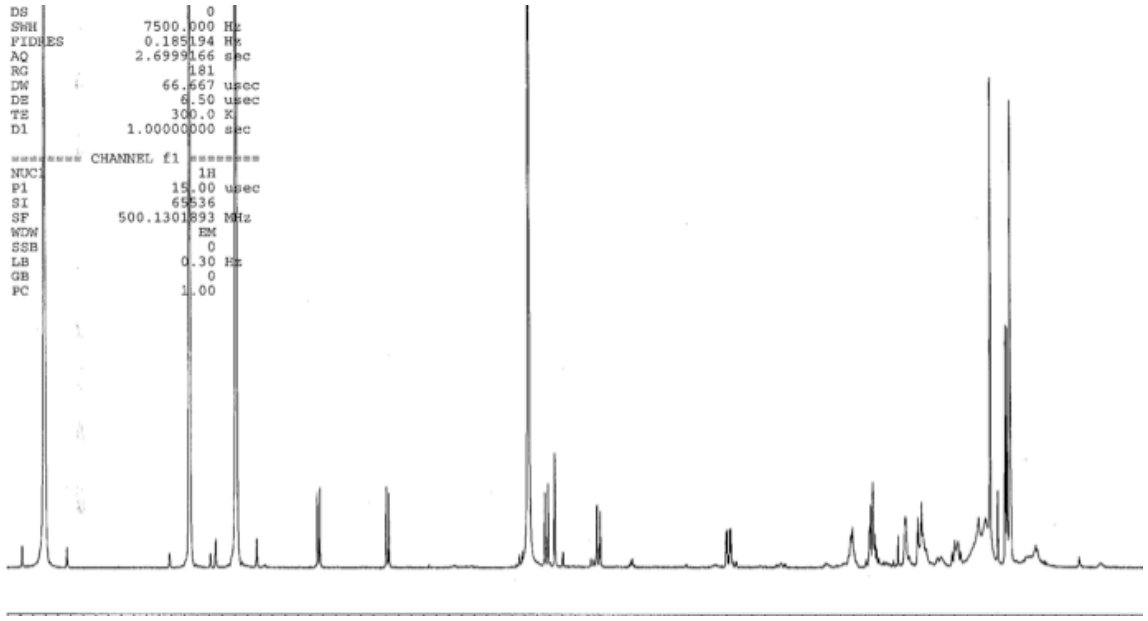

6.667
6.646
5.965
5.944
4.640
4.616
4.434
4.431
4.140
4.136
4.115
4.112
3.210
3.200
3.180
3.171
1.303
1.262
1.247
1.228
Current Data Parameters
NAME PFD-IV-295-P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120703
Time 23.44
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Me
Me
Me
O
O
O
O
O
Maoecrystal V
S108
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


211.497
194.821
169.060
156.686
127.053
84.913
84.104
69.213
56.581
51.913
48.262
38.258
34.559
32.653
30.601
18.557
18.523
17.995
15.127
Current Data Parameters
NAME PFD-IV-295-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120704
Time 16.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 30949
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
Me
Me
Maoecrystal V
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

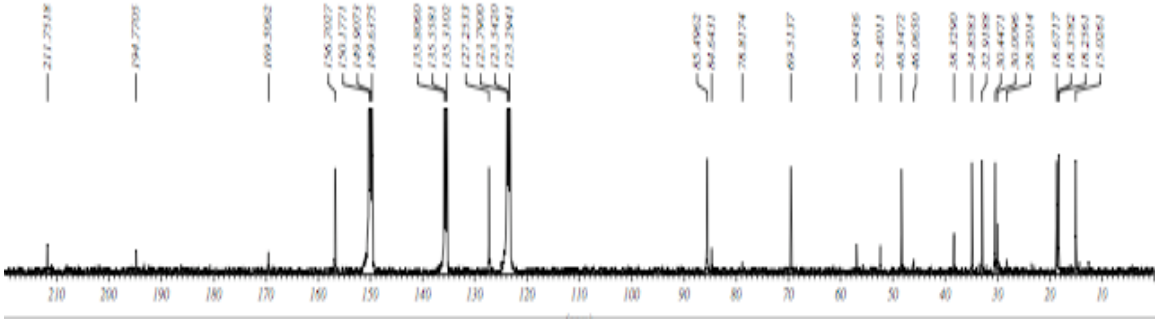
Maoecrystal V (Isolated)



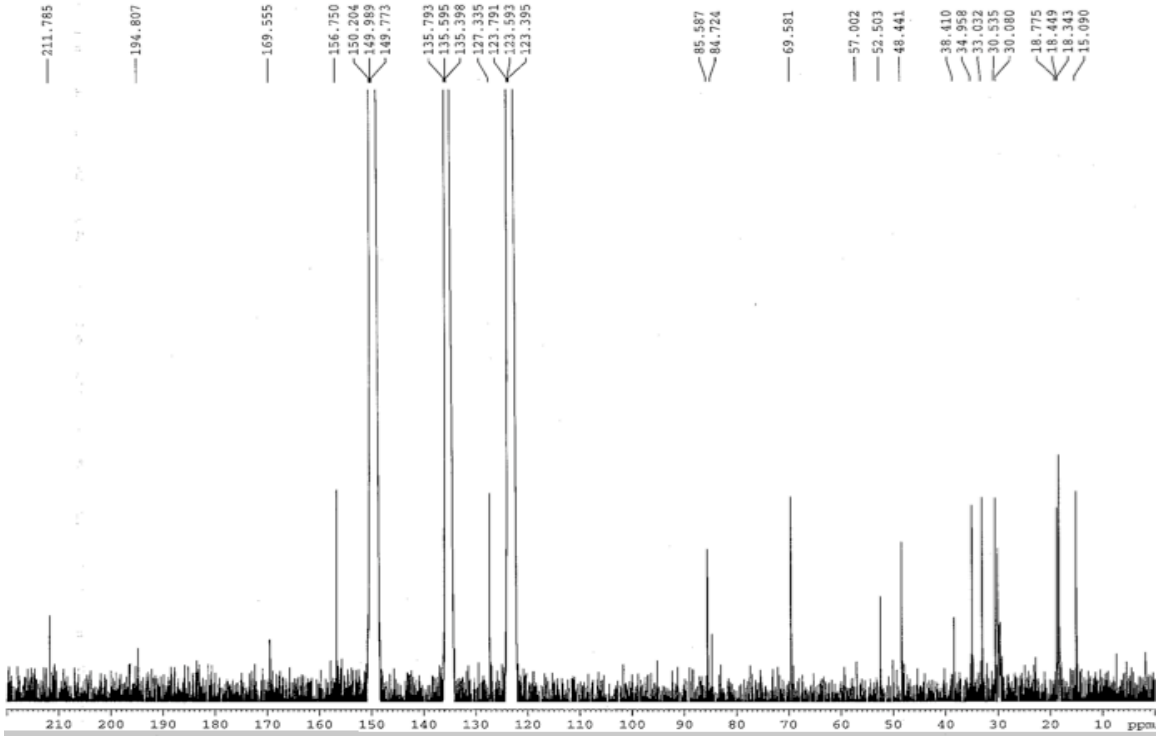
Maoecrystal V (Synthetic)



Maecrystal V (Isolated)



Maocrystal V (Synthetic)



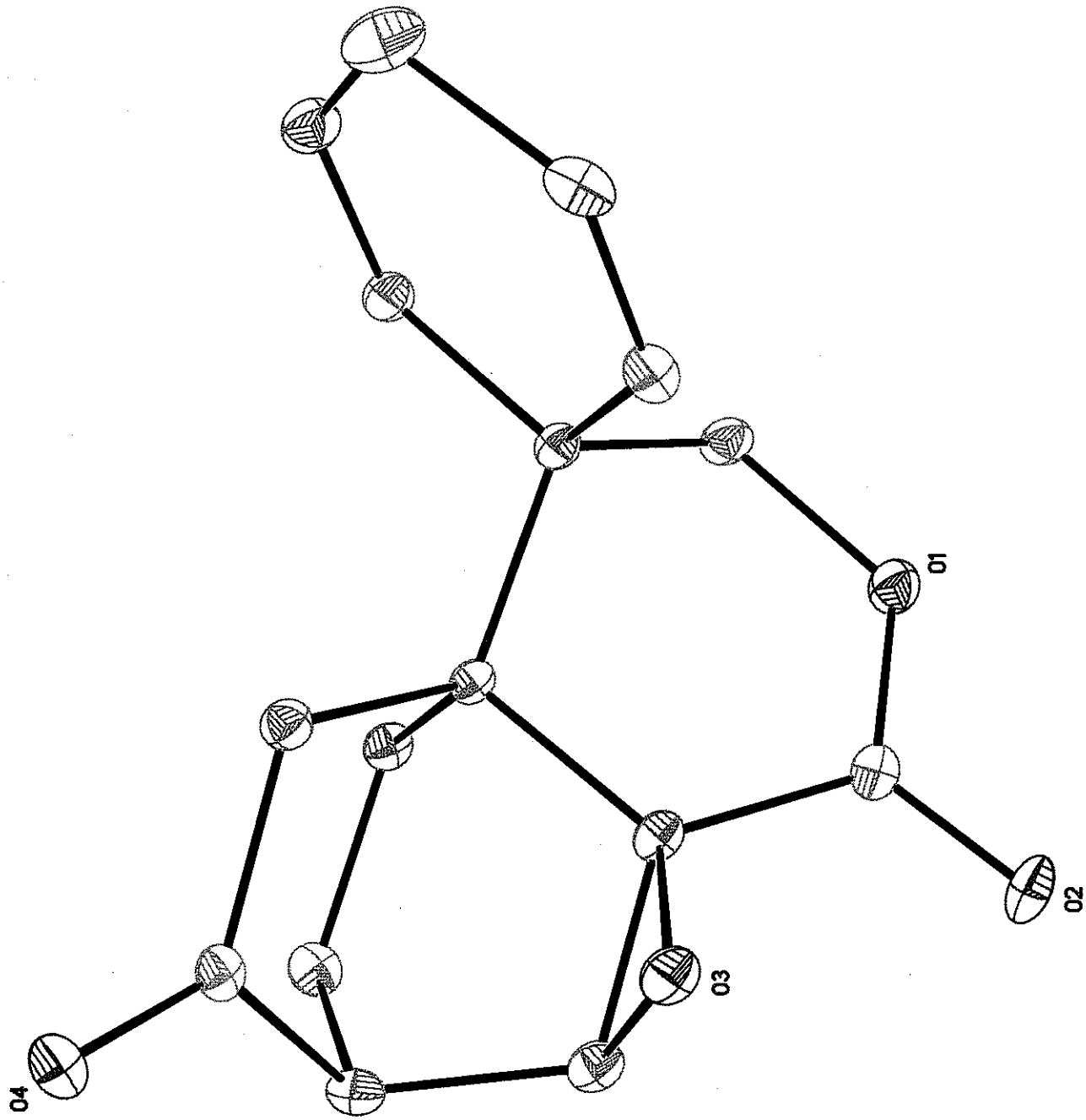

O1
O2
O3
O4

Table 1. Crystal data and structure refinement for FENG3WS10.

Identification code	feng3ws10
Empirical formula	$C_{16}H_{16}O_4$
Formula weight	272.29
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.837(3) Å alpha = 90° b = 9.269(4) Å beta = 93.680(7)° c = 20.261(8) Å gamma = 90°
Volume, Z	1281.3(9) $Å^3$, 4
Density (calculated)	1.412 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	576
Crystal size	0.12 x 0.03 x 0.03 mm
Θ range for data collection	2.01 to 28.28°
Limiting indices	$-9 \le h \le 9$, $-12 \le k \le 12$, $-26 \le l \le 26$
Reflections collected	17277
Independent reflections	3181 (R_{int} = 0.1389)
Completeness to Θ = 28.28°	100.0 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9970 and 0.9880
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3181 / 0 / 181
Goodness-of-fit on F^2	1.031
Final R indices [I>2σ(I)]	R1 = 0.0730, wR2 = 0.1549
R indices (all data)	R1 = 0.1497, wR2 = 0.1846
Largest diff. peak and hole	0.297 and -0.328 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FENG3WS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	4434(3)	5833(2)	1112(1)	31(1)
O(2)	6850(3)	4965(3)	573(1)	32(1)
O(3)	5896(3)	2123(2)	938(1)	27(1)
O(4)	2687(3)	-852(2)	922(1)	29(1)
C(1)	2373(4)	4158(3)	1742(2)	22(1)
C(2)	375(5)	4123(4)	2023(2)	27(1)
C(3)	89(5)	3815(4)	2642(2)	32(1)
C(4)	1674(6)	3479(5)	3150(2)	46(1)
C(5)	3668(5)	3598(4)	2895(2)	31(1)
C(6)	3967(5)	3881(3)	2273(2)	27(1)
C(7)	2629(5)	5659(4)	1446(2)	27(1)
C(8)	5330(5)	4731(3)	832(2)	24(1)
C(9)	4433(4)	3252(3)	852(2)	22(1)
C(10)	4736(5)	2240(3)	316(2)	26(1)
C(11)	3047(5)	1196(3)	212(2)	26(1)
C(12)	2729(4)	451(3)	859(2)	23(1)
C(13)	2378(5)	1490(3)	1412(2)	24(1)
C(14)	2500(4)	3046(3)	1170(1)	18(1)
C(15)	915(4)	3235(3)	601(2)	24(1)
C(16)	1183(5)	2110(4)	51(2)	29(1)

Table 3. Bond lengths [Å] and angles [°] for FENG3WS10.

O(1)-C(8)	1.336(4)	O(1)-C(7)	1.454(4)
O(2)-C(8)	1.213(4)	O(3)-C(10)	1.449(4)
O(3)-C(9)	1.450(4)	O(4)-C(12)	1.215(4)
C(1)-C(6)	1.503(4)	C(1)-C(2)	1.514(4)
C(1)-C(7)	1.530(4)	C(1)-C(14)	1.558(4)
C(2)-C(3)	1.313(5)	C(3)-C(4)	1.478(5)
C(4)-C(5)	1.494(5)	C(5)-C(6)	1.316(5)
C(8)-C(9)	1.504(4)	C(9)-C(10)	1.460(4)
C(9)-C(14)	1.519(4)	C(10)-C(11)	1.511(5)
C(11)-C(12)	1.510(4)	C(11)-C(16)	1.548(4)
C(12)-C(13)	1.507(4)	C(13)-C(14)	1.527(4)
C(14)-C(15)	1.541(4)	C(15)-C(16)	1.546(4)

C(8)-O(1)-C(7)	122.6(3)	C(10)-O(3)-C(9)	60.47(19)
C(6)-C(1)-C(2)	110.9(3)	C(6)-C(1)-C(7)	109.9(3)
C(2)-C(1)-C(7)	107.2(3)	C(6)-C(1)-C(14)	110.3(2)
C(2)-C(1)-C(14)	111.1(2)	C(7)-C(1)-C(14)	107.3(2)
C(3)-C(2)-C(1)	123.9(3)	C(2)-C(3)-C(4)	124.3(3)
C(3)-C(4)-C(5)	112.8(3)	C(6)-C(5)-C(4)	123.2(3)
C(5)-C(6)-C(1)	124.7(3)	O(1)-C(7)-C(1)	113.9(3)
O(2)-C(8)-O(1)	118.4(3)	O(2)-C(8)-C(9)	122.4(3)
O(1)-C(8)-C(9)	119.1(3)	O(3)-C(9)-C(10)	59.75(19)
O(3)-C(9)-C(8)	112.4(2)	C(10)-C(9)-C(8)	119.3(3)
O(3)-C(9)-C(14)	118.1(2)	C(10)-C(9)-C(14)	113.8(3)
C(8)-C(9)-C(14)	119.6(3)	O(3)-C(10)-C(9)	59.79(19)
O(3)-C(10)-C(11)	116.3(3)	C(9)-C(10)-C(11)	111.8(3)
C(12)-C(11)-C(10)	108.9(3)	C(12)-C(11)-C(16)	105.8(3)
C(10)-C(11)-C(16)	106.9(3)	O(4)-C(12)-C(13)	123.4(3)
O(4)-C(12)-C(11)	123.5(3)	C(13)-C(12)-C(11)	113.0(3)
C(12)-C(13)-C(14)	110.5(2)	C(9)-C(14)-C(13)	108.8(2)
C(9)-C(14)-C(15)	104.9(2)	C(13)-C(14)-C(15)	107.3(3)
C(9)-C(14)-C(1)	108.9(2)	C(13)-C(14)-C(1)	112.3(2)
C(15)-C(14)-C(1)	114.3(2)	C(14)-C(15)-C(16)	110.7(2)
C(15)-C(16)-C(11)	110.5(3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FENG3WS10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	32(1)	25(1)	37(1)	1(1)	8(1)	-1(1)
O(2)	18(1)	35(1)	44(2)	11(1)	5(1)	-1(1)
O(3)	19(1)	30(1)	32(1)	2(1)	1(1)	6(1)
O(4)	30(1)	23(1)	34(1)	-2(1)	-2(1)	-1(1)
C(1)	18(2)	24(2)	23(2)	-1(1)	3(1)	1(1)
C(2)	20(2)	31(2)	30(2)	-5(2)	4(1)	1(1)
C(3)	30(2)	32(2)	35(2)	-2(2)	10(2)	2(2)
C(4)	54(3)	55(3)	30(2)	8(2)	10(2)	5(2)
C(5)	39(2)	27(2)	27(2)	-4(2)	-6(2)	7(2)
C(6)	24(2)	24(2)	31(2)	-2(1)	-2(1)	2(1)
C(7)	26(2)	26(2)	31(2)	-1(1)	8(1)	5(1)
C(8)	22(2)	26(2)	25(2)	5(1)	-1(1)	1(1)
C(9)	16(2)	24(2)	24(2)	4(1)	1(1)	5(1)
C(10)	26(2)	26(2)	27(2)	4(1)	5(1)	6(1)
C(11)	30(2)	26(2)	21(2)	-2(1)	2(1)	4(1)
C(12)	14(2)	25(2)	29(2)	-1(1)	-4(1)	0(1)
C(13)	24(2)	24(2)	23(2)	1(1)	3(1)	0(1)
C(14)	14(2)	22(2)	19(2)	2(1)	1(1)	3(1)
C(15)	18(2)	29(2)	24(2)	1(1)	-1(1)	4(1)
C(16)	30(2)	30(2)	26(2)	0(2)	-3(1)	0(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FENG3WS10.

	x	y	z	U(eq)
H(2A)	-738	4335	1735	33
H(3A)	-1221	3808	2772	39
H(4A)	1487	2486	3315	55
H(4B)	1582	4148	3528	55
H(5A)	4776	3463	3196	37
H(6A)	5285	3911	2150	32
H(7A)	1504	5857	1126	33
H(7B)	2601	6384	1804	33
H(10A)	5386	2598	-81	31
H(11A)	3273	487	-147	31
H(13A)	3370	1331	1782	28
H(13B)	1067	1312	1576	28
H(15A)	1000	4219	415	28
H(15B)	-399	3120	773	28
H(16A)	1292	2611	-377	35
H(16B)	22	1470	9	35

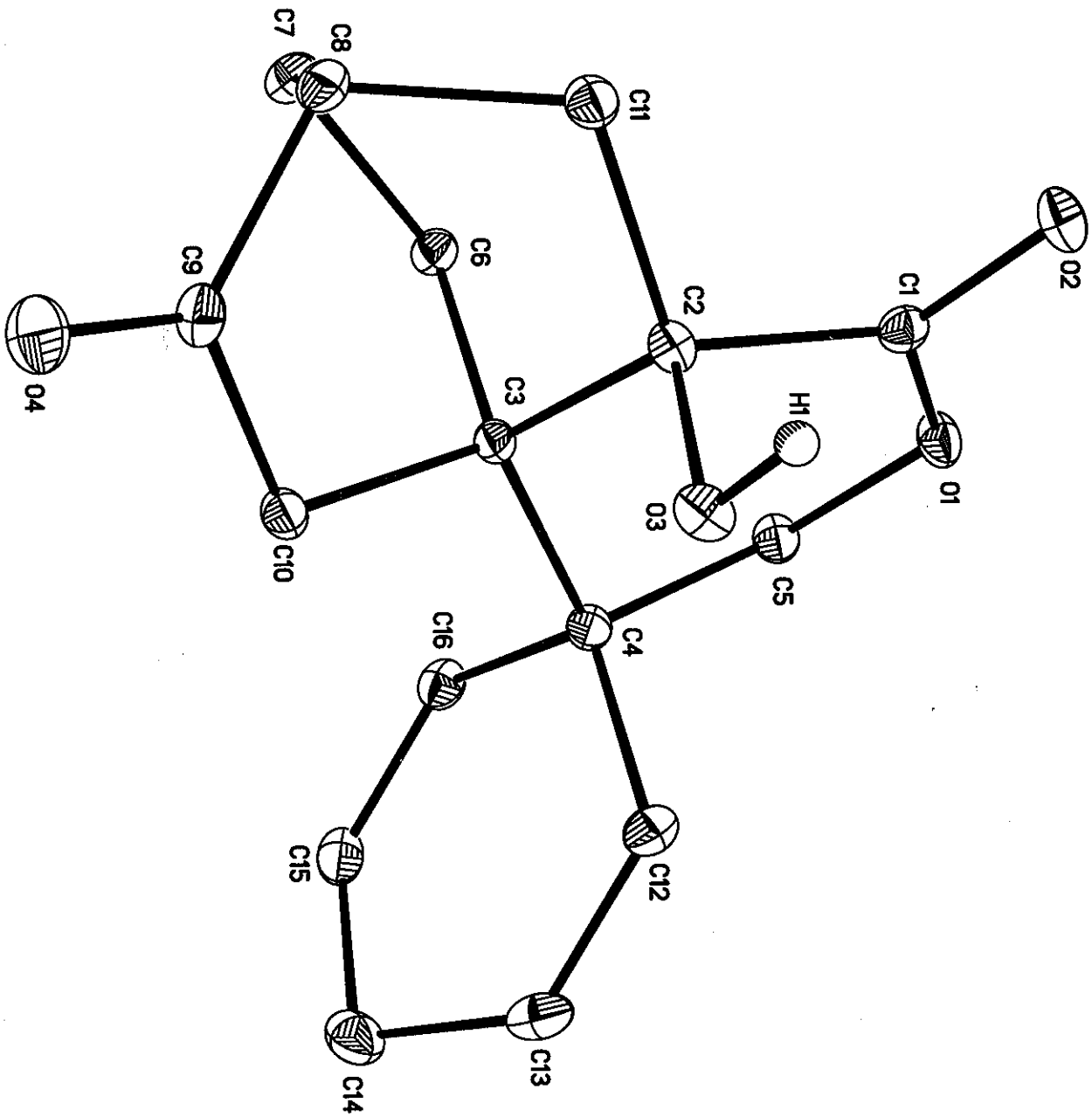

C7
C8
C11
C6
C9
C2
C1
O2
O4
C3
H1
O1
O3
C10
C5
C16
C4
C15
C12
C13
C14

Table 1. Crystal data and structure refinement for fpta5.

Identification code	fpta5
Empirical formula	$C_{16}H_{18}O_4$
Formula weight	274.30
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.281(2) Å alpha = 90° b = 7.951(3) Å beta = 92.835(6)° c = 25.900(10) Å gamma = 90°
Volume, Z	1291.9(8) $Å^3$, 4
Density (calculated)	1.410 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	584
Crystal size	0.60 x 0.05 x 0.05 mm
Θ range for data collection	1.57 to 26.49°
Limiting indices	$-7 \le h \le 7$, $0 \le k \le 9$, $0 \le l \le 32$
Reflections collected	12681
Independent reflections	2657 (R_{int} = 0.0639)
Completeness to Θ = 26.49°	99.2 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9950 and 0.9420
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2648 / 0 / 187
Goodness-of-fit on F^2	1.143
Final R indices [I>2σ(I)]	R1 = 0.0432, wR2 = 0.1004
R indices (all data)	R1 = 0.0513, wR2 = 0.1044
Extinction coefficient	0.0069(17)
Largest diff. peak and hole	0.307 and -0.265 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for fpta5. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-4472(3)	11340(2)	4231(1)	22(1)
O(2)	-2672(3)	10819(2)	4954(1)	22(1)
O(3)	-127(3)	9187(2)	4178(1)	20(1)
O(4)	183(3)	4528(2)	3872(1)	31(1)
C(1)	-3202(4)	10341(3)	4519(1)	17(1)
C(2)	-2261(4)	8732(3)	4297(1)	16(1)
C(3)	-3458(4)	8116(3)	3792(1)	15(1)
C(4)	-4051(4)	9638(3)	3425(1)	17(1)
C(5)	-5425(4)	10843(3)	3729(1)	19(1)
C(6)	-5484(4)	7190(3)	3965(1)	18(1)
C(7)	-4882(4)	5496(3)	4226(1)	22(1)
C(8)	-2517(4)	5580(3)	4423(1)	20(1)
C(9)	-1235(4)	5528(3)	3941(1)	21(1)
C(10)	-1993(4)	6825(3)	3541(1)	18(1)
C(11)	-2205(4)	7294(3)	4702(1)	20(1)
C(12)	-2081(4)	10535(3)	3243(1)	21(1)
C(13)	-1433(4)	10436(3)	2764(1)	25(1)
C(14)	-2597(5)	9489(3)	2337(1)	30(1)
C(15)	-4773(4)	8970(3)	2482(1)	25(1)
C(16)	-5432(4)	9058(3)	2960(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for fpta5.

O(1)-C(1)	1.329(3)	O(1)-C(5)	1.459(3)
O(2)-C(1)	1.218(3)	O(3)-C(2)	1.436(3)
O(4)-C(9)	1.214(3)	C(1)-C(2)	1.534(3)
C(2)-C(11)	1.552(3)	C(2)-C(3)	1.554(3)
C(3)-C(10)	1.543(3)	C(3)-C(6)	1.555(3)
C(3)-C(4)	1.572(3)	C(4)-C(16)	1.520(3)
C(4)-C(12)	1.524(3)	C(4)-C(5)	1.532(3)
C(6)-C(7)	1.546(3)	C(7)-C(8)	1.547(3)
C(8)-C(9)	1.518(3)	C(8)-C(11)	1.551(3)
C(9)-C(10)	1.521(3)	C(12)-C(13)	1.326(3)
C(13)-C(14)	1.497(4)	C(14)-C(15)	1.493(4)
C(15)-C(16)	1.327(3)		

C(1)-O(1)-C(5)	123.17(18)	O(2)-C(1)-O(1)	117.5(2)
O(2)-C(1)-C(2)	121.0(2)	O(1)-C(1)-C(2)	121.28(19)
O(3)-C(2)-C(1)	104.58(18)	O(3)-C(2)-C(11)	109.93(18)
C(1)-C(2)-C(11)	110.87(17)	O(3)-C(2)-C(3)	108.48(17)
C(1)-C(2)-C(3)	113.54(18)	C(11)-C(2)-C(3)	109.30(18)
C(10)-C(3)-C(2)	106.83(18)	C(10)-C(3)-C(6)	108.64(18)
C(2)-C(3)-C(6)	106.08(17)	C(10)-C(3)-C(4)	112.67(18)
C(2)-C(3)-C(4)	110.86(17)	C(6)-C(3)-C(4)	111.44(18)
C(16)-C(4)-C(12)	109.64(18)	C(16)-C(4)-C(5)	106.41(19)
C(12)-C(4)-C(5)	110.69(19)	C(16)-C(4)-C(3)	110.75(18)
C(12)-C(4)-C(3)	112.10(18)	C(5)-C(4)-C(3)	107.08(17)
O(1)-C(5)-C(4)	114.22(19)	C(7)-C(6)-C(3)	110.62(19)
C(6)-C(7)-C(8)	108.49(19)	C(9)-C(8)-C(7)	105.55(18)
C(9)-C(8)-C(11)	110.33(19)	C(7)-C(8)-C(11)	106.74(19)
O(4)-C(9)-C(8)	124.2(2)	O(4)-C(9)-C(10)	123.4(2)
C(8)-C(9)-C(10)	112.3(2)	C(9)-C(10)-C(3)	109.72(18)
C(8)-C(11)-C(2)	109.49(17)	C(13)-C(12)-C(4)	123.7(2)
C(12)-C(13)-C(14)	123.9(2)	C(15)-C(14)-C(13)	111.9(2)
C(16)-C(15)-C(14)	123.5(2)	C(15)-C(16)-C(4)	124.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for fpta5.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	29(1)	18(1)	19(1)	-3(1)	-1(1)	6(1)
O(2)	19(1)	26(1)	20(1)	-8(1)	-2(1)	1(1)
O(3)	13(1)	27(1)	18(1)	-1(1)	0(1)	0(1)
O(4)	28(1)	27(1)	38(1)	-1(1)	7(1)	11(1)
C(1)	14(1)	18(1)	19(1)	1(1)	1(1)	-3(1)
C(2)	14(1)	19(1)	16(1)	-2(1)	0(1)	1(1)
C(3)	18(1)	14(1)	13(1)	-1(1)	0(1)	0(1)
C(4)	19(1)	17(1)	15(1)	1(1)	-1(1)	0(1)
C(5)	22(1)	18(1)	17(1)	0(1)	-2(1)	3(1)
C(6)	17(1)	16(1)	20(1)	1(1)	2(1)	0(1)
C(7)	22(1)	18(1)	26(1)	4(1)	3(1)	0(1)
C(8)	22(1)	16(1)	21(1)	3(1)	1(1)	3(1)
C(9)	20(1)	17(1)	25(1)	-4(1)	0(1)	-1(1)
C(10)	18(1)	18(1)	18(1)	-3(1)	3(1)	0(1)
C(11)	22(1)	19(1)	17(1)	1(1)	0(1)	3(1)
C(12)	20(1)	20(1)	22(1)	4(1)	-2(1)	-2(1)
C(13)	20(1)	25(1)	31(1)	11(1)	6(1)	2(1)
C(14)	41(2)	29(1)	21(1)	4(1)	6(1)	8(1)
C(15)	37(2)	19(1)	19(1)	0(1)	-6(1)	2(1)
C(16)	23(1)	18(1)	21(1)	2(1)	-4(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for fpta5.

	x	y	z	U(eq)
H(1)	600(50)	9340(30)	4468(11)	26(7)
H(5A)	-5702	11867	3519	23
H(5B)	-6815	10299	3782	23
H(6A)	-6235	7906	4210	21
H(6B)	-6463	6983	3660	21
H(7A)	-5091	4565	3975	26
H(7B)	-5801	5288	4519	26
H(8A)	-2139	4620	4659	24
H(10A)	-2781	6259	3250	22
H(10B)	-749	7409	3404	22
H(11A)	-821	7303	4902	24
H(11B)	-3351	7464	4946	24
H(12A)	-1272	11202	3485	25
H(13A)	-153	10999	2687	30
H(14A)	-2720	10207	2025	36
H(14B)	-1767	8476	2253	36
H(15A)	-5736	8555	2218	30
H(16A)	-6859	8738	3016	25

Table 6. Hydrogen bonds for fpta5 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(1)...O(2)#1	0.87(3)	1.94(3)	2.786(2)	165(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

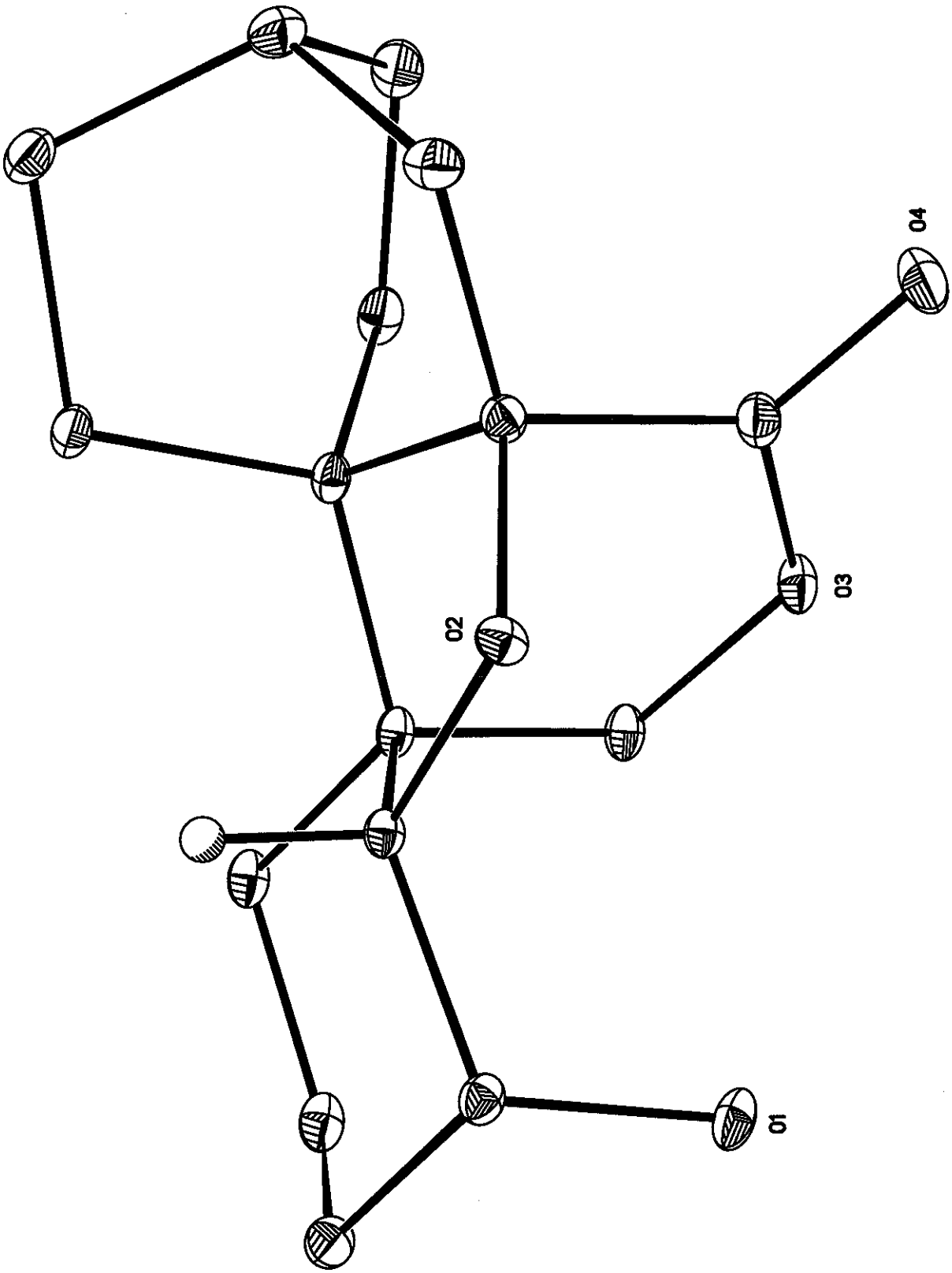

O4
O3
O2
O1

Table 1. Crystal data and structure refinement for FPEWS10.

Identification code	fpews10
Empirical formula	$C_{16}H_{22}O_4$
Formula weight	278.34
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.2174(9) Å alpha = 90° b = 11.2661(9) Å beta = 90° c = 21.3465(17) Å gamma = 90°
Volume, Z	2697.7(4) $Å^3$, 8
Density (calculated)	1.371 Mg/m^3
Absorption coefficient	0.097 mm^{-1}
F(000)	1200
Crystal size	0.25 x 0.23 x 0.16 mm
⊛ range for data collection	1.91 to 31.66°
Limiting indices	$-16 \le h \le 16$, $-16 \le k \le 16$, $-31 \le l \le 31$
Reflections collected	41822
Independent reflections	4542 (R_{int} = 0.0393)
Completeness to ⊛ = 31.66°	99.5 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9846 and 0.9761
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4542 / 0 / 182
Goodness-of-fit on F^2	1.081
Final R indices [I>2σ(I)]	R1 = 0.0407, wR2 = 0.1007
R indices (all data)	R1 = 0.0568, wR2 = 0.1137
Largest diff. peak and hole	0.517 and -0.221 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FPEWS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	3478(1)	1153(1)	5360(1)	21(1)
O(2)	5403(1)	1020(1)	4366(1)	16(1)
O(3)	2997(1)	963(1)	3834(1)	23(1)
O(4)	3950(1)	-476(1)	3353(1)	30(1)
C(1)	4512(1)	1890(1)	5342(1)	17(1)
C(2)	4211(1)	3135(1)	5595(1)	21(1)
C(3)	3453(1)	3895(1)	5149(1)	23(1)
C(4)	3977(1)	3978(1)	4481(1)	20(1)
C(5)	4194(1)	2728(1)	4220(1)	15(1)
C(6)	5008(1)	2084(1)	4686(1)	14(1)
C(7)	5160(1)	1195(1)	3698(1)	17(1)
C(8)	6175(1)	777(1)	3274(1)	23(1)
C(9)	6290(1)	1687(1)	2734(1)	26(1)
C(10)	6833(1)	2838(1)	2995(1)	24(1)
C(11)	6134(1)	3203(1)	3592(1)	19(1)
C(12)	4930(1)	2538(1)	3613(1)	16(1)
C(13)	4342(1)	2726(1)	2968(1)	23(1)
C(14)	5046(1)	1996(1)	2473(1)	28(1)
C(15)	2975(1)	2138(1)	4121(1)	20(1)
C(16)	4001(1)	490(1)	3599(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for FPEWS10.

O(1)-C(1)	1.4270(13)	O(2)-C(6)	1.4488(12)
O(2)-C(7)	1.4639(12)	O(3)-C(16)	1.3429(14)
O(3)-C(15)	1.4587(13)	O(4)-C(16)	1.2102(14)
C(1)-C(6)	1.5224(14)	C(1)-C(2)	1.5404(14)
C(2)-C(3)	1.5358(17)	C(3)-C(4)	1.5459(16)
C(4)-C(5)	1.5334(14)	C(5)-C(6)	1.5338(14)
C(5)-C(15)	1.5354(14)	C(5)-C(12)	1.5504(14)
C(7)-C(8)	1.5286(15)	C(7)-C(16)	1.5385(15)
C(7)-C(12)	1.5457(14)	C(8)-C(9)	1.5479(17)
C(9)-C(10)	1.5363(17)	C(9)-C(14)	1.5432(18)
C(10)-C(11)	1.5519(15)	C(11)-C(12)	1.5453(14)
C(12)-C(13)	1.5415(14)	C(13)-C(14)	1.5545(19)

C(6)-O(2)-C(7)	106.93(7)	C(16)-O(3)-C(15)	122.07(8)
O(1)-C(1)-C(6)	113.95(8)	O(1)-C(1)-C(2)	110.02(8)
C(6)-C(1)-C(2)	105.76(8)	C(3)-C(2)-C(1)	114.31(9)
C(2)-C(3)-C(4)	113.27(9)	C(5)-C(4)-C(3)	109.89(8)
C(4)-C(5)-C(6)	107.07(8)	C(4)-C(5)-C(15)	107.80(8)
C(6)-C(5)-C(15)	114.47(8)	C(4)-C(5)-C(12)	120.99(8)
C(6)-C(5)-C(12)	99.21(8)	C(15)-C(5)-C(12)	107.45(8)
O(2)-C(6)-C(1)	115.30(8)	O(2)-C(6)-C(5)	105.49(8)
C(1)-C(6)-C(5)	116.54(8)	O(2)-C(7)-C(8)	113.36(9)
O(2)-C(7)-C(16)	102.78(8)	C(8)-C(7)-C(16)	112.87(9)
O(2)-C(7)-C(12)	106.13(8)	C(8)-C(7)-C(12)	110.90(8)
C(16)-C(7)-C(12)	110.35(8)	C(7)-C(8)-C(9)	107.41(9)
C(10)-C(9)-C(14)	107.35(10)	C(10)-C(9)-C(8)	108.83(9)
C(14)-C(9)-C(8)	110.05(10)	C(9)-C(10)-C(11)	108.73(9)
C(12)-C(11)-C(10)	109.69(9)	C(13)-C(12)-C(11)	106.31(8)
C(13)-C(12)-C(7)	108.16(8)	C(11)-C(12)-C(7)	109.37(8)
C(13)-C(12)-C(5)	119.99(9)	C(11)-C(12)-C(5)	115.00(8)
C(7)-C(12)-C(5)	97.22(7)	C(12)-C(13)-C(14)	108.48(9)
C(9)-C(14)-C(13)	109.48(9)	O(3)-C(15)-C(5)	115.82(8)
O(4)-C(16)-O(3)	118.65(10)	O(4)-C(16)-C(7)	124.33(11)
O(3)-C(16)-C(7)	116.93(9)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FPEWS10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	20(1)	13(1)	29(1)	4(1)	6(1)	-1(1)
O(2)	20(1)	12(1)	16(1)	0(1)	-1(1)	3(1)
O(3)	19(1)	20(1)	31(1)	0(1)	-1(1)	-8(1)
O(4)	37(1)	22(1)	31(1)	-6(1)	-3(1)	-9(1)
C(1)	18(1)	13(1)	19(1)	1(1)	2(1)	0(1)
C(2)	25(1)	15(1)	24(1)	-3(1)	6(1)	-1(1)
C(3)	19(1)	14(1)	35(1)	-2(1)	5(1)	2(1)
C(4)	16(1)	12(1)	32(1)	3(1)	0(1)	2(1)
C(5)	12(1)	12(1)	21(1)	3(1)	-1(1)	0(1)
C(6)	13(1)	10(1)	18(1)	1(1)	0(1)	1(1)
C(7)	18(1)	16(1)	16(1)	1(1)	-1(1)	-2(1)
C(8)	25(1)	23(1)	21(1)	-3(1)	4(1)	1(1)
C(9)	27(1)	32(1)	18(1)	-1(1)	4(1)	-5(1)
C(10)	20(1)	31(1)	19(1)	4(1)	2(1)	-6(1)
C(11)	17(1)	20(1)	20(1)	3(1)	0(1)	-5(1)
C(12)	15(1)	15(1)	17(1)	4(1)	-3(1)	-3(1)
C(13)	23(1)	27(1)	20(1)	8(1)	-6(1)	-6(1)
C(14)	32(1)	35(1)	18(1)	3(1)	-5(1)	-10(1)
C(15)	14(1)	17(1)	28(1)	3(1)	-2(1)	-1(1)
C(16)	24(1)	18(1)	19(1)	2(1)	-3(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FPEWS10.

	x	y	z	U(eq)
H(1A)	3686	438	5380	31
H(1B)	5145	1528	5611	20
H(2A)	3779	3048	5996	26
H(2B)	4965	3561	5682	26
H(3A)	3382	4705	5325	27
H(3B)	2642	3552	5125	27
H(4A)	3415	4410	4205	24
H(4B)	4737	4423	4491	24
H(6A)	5731	2595	4737	17
H(8A)	5995	-21	3104	28
H(8B)	6929	733	3514	28
H(9A)	6807	1359	2394	31
H(10A)	6781	3475	2677	28
H(10B)	7683	2711	3099	28
H(11A)	6608	3007	3969	23
H(11B)	5991	4070	3588	23
H(13A)	4356	3579	2856	28
H(13B)	3501	2461	2980	28
H(14A)	4607	1258	2373	34
H(14B)	5130	2464	2083	34
H(15A)	2574	2073	4533	23
H(15B)	2483	2666	3856	23

Table 6. Hydrogen bonds for FPEWS10 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(2)#1	0.84	2.01	2.8132(10)	159.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

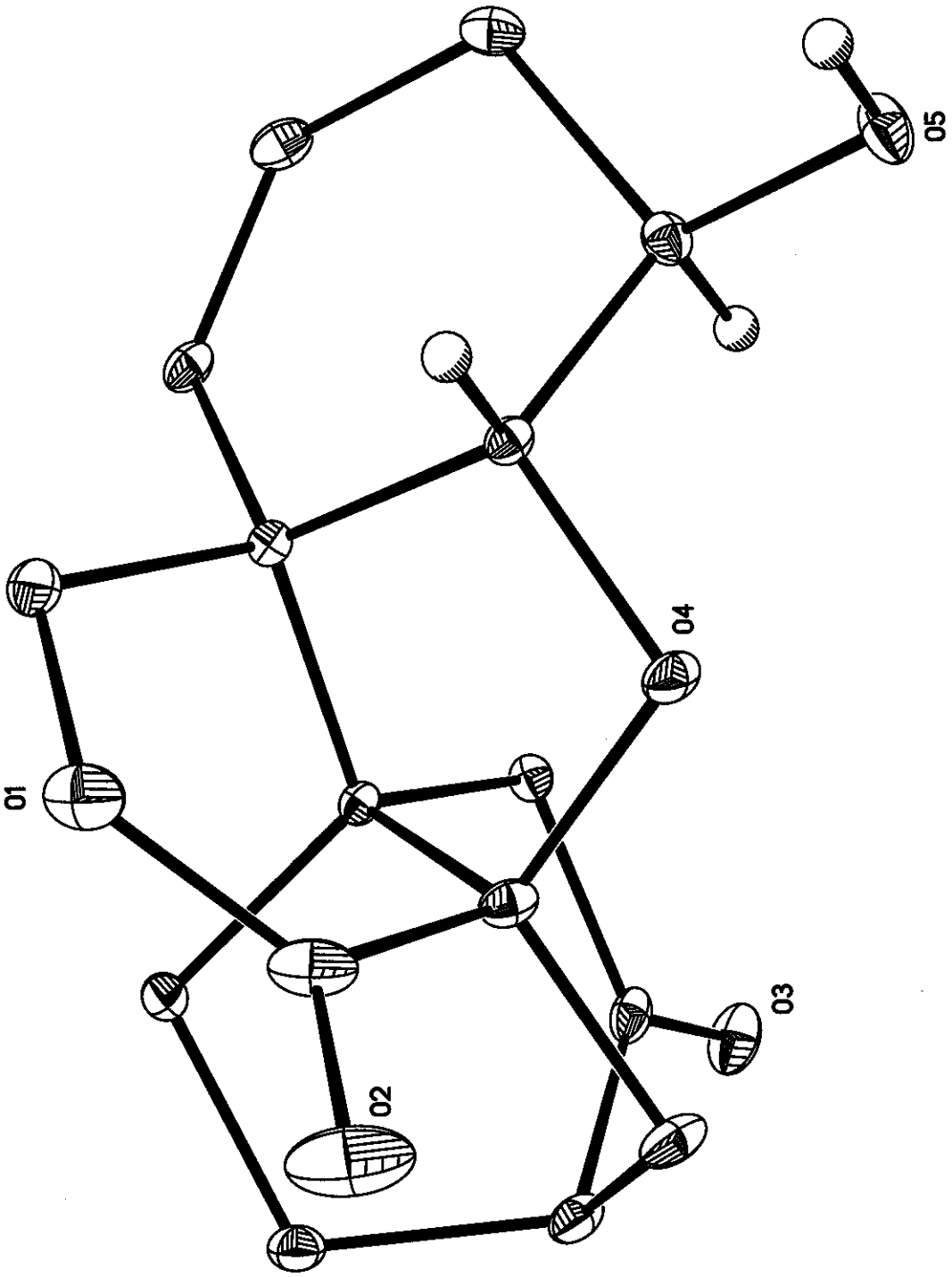

O1
O2
O3
O4
O5

Table 1. Crystal data and structure refinement for FPAS10.

Identification code	fpas10
Empirical formula	$C_{16}H_{18}O_5$
Formula weight	290.30
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.0107(8) Å alpha = 89.325(2)° b = 9.3430(11) Å beta = 77.850(2)° c = 10.1589(12) Å gamma = 89.200(2)°
Volume, Z	650.42(13) $Å^3$, 2
Density (calculated)	1.482 Mg/m^3
Absorption coefficient	0.110 mm^{-1}
F(000)	308
Crystal size	0.50 x 0.25 x 0.20 mm
⊙ range for data collection	2.05 to 30.61°
Limiting indices	$-10 \le h \le 10$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	10421
Independent reflections	3979 (R_{int} = 0.0207)
Completeness to ⊙ = 30.61°	99.2 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9783 and 0.9471
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3979 / 0 / 194
Goodness-of-fit on F^2	1.081
Final R indices [I>2σ(I)]	R1 = 0.0387, wR2 = 0.1054
R indices (all data)	R1 = 0.0474, wR2 = 0.1114
Largest diff. peak and hole	0.432 and -0.187 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FPAS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	2159(1)	10509(1)	2954(1)	28(1)
O(2)	-301(2)	10499(1)	1948(1)	44(1)
O(3)	2702(1)	4376(1)	352(1)	30(1)
O(4)	70(1)	7702(1)	3660(1)	20(1)
O(5)	-438(1)	6456(1)	6359(1)	25(1)
C(1)	918(2)	9801(1)	2353(1)	26(1)
C(2)	1036(1)	8151(1)	2330(1)	17(1)
C(3)	111(2)	7519(1)	1234(1)	23(1)
C(4)	1737(2)	6842(1)	144(1)	21(1)
C(5)	3415(2)	7915(1)	-296(1)	22(1)
C(6)	4393(2)	8273(1)	898(1)	17(1)
C(7)	3147(1)	7638(1)	2194(1)	13(1)
C(8)	3238(2)	6004(1)	2050(1)	15(1)
C(9)	2569(1)	5587(1)	783(1)	19(1)
C(10)	3456(1)	8161(1)	3570(1)	14(1)
C(11)	5162(1)	7527(1)	4059(1)	18(1)
C(12)	5003(2)	6881(1)	5252(1)	21(1)
C(13)	3078(2)	6651(1)	6200(1)	22(1)
C(14)	1410(2)	6569(1)	5455(1)	17(1)
C(15)	1452(1)	7862(1)	4526(1)	14(1)
C(16)	3697(2)	9782(1)	3477(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for FPAS10.

O(1)-C(1)	1.3480(15)	O(1)-C(16)	1.4550(14)
O(2)-C(1)	1.2052(14)	O(3)-C(9)	1.2137(13)
O(4)-C(2)	1.4378(12)	O(4)-C(15)	1.4498(11)
O(5)-C(14)	1.4259(12)	C(1)-C(2)	1.5430(16)
C(2)-C(7)	1.5283(13)	C(2)-C(3)	1.5287(14)
C(3)-C(4)	1.5465(15)	C(4)-C(9)	1.5027(16)
C(4)-C(5)	1.5461(16)	C(5)-C(6)	1.5557(14)
C(6)-C(7)	1.5361(13)	C(7)-C(8)	1.5336(13)
C(7)-C(10)	1.5451(13)	C(8)-C(9)	1.5167(14)
C(10)-C(11)	1.5007(13)	C(10)-C(16)	1.5258(14)
C(10)-C(15)	1.5573(13)	C(11)-C(12)	1.3315(15)
C(12)-C(13)	1.4997(16)	C(13)-C(14)	1.5243(15)
C(14)-C(15)	1.5206(14)		

C(1)-O(1)-C(16)	122.34(8)	C(2)-O(4)-C(15)	107.07(7)
O(2)-C(1)-O(1)	117.39(11)	O(2)-C(1)-C(2)	124.12(12)
O(1)-C(1)-C(2)	118.30(9)	O(4)-C(2)-C(7)	104.74(8)
O(4)-C(2)-C(3)	112.41(9)	C(7)-C(2)-C(3)	111.36(8)
O(4)-C(2)-C(1)	105.00(8)	C(7)-C(2)-C(1)	110.47(9)
C(3)-C(2)-C(1)	112.42(9)	C(2)-C(3)-C(4)	108.86(8)
C(9)-C(4)-C(5)	106.80(8)	C(9)-C(4)-C(3)	107.38(9)
C(5)-C(4)-C(3)	109.94(9)	C(4)-C(5)-C(6)	111.02(8)
C(7)-C(6)-C(5)	108.39(8)	C(2)-C(7)-C(8)	109.17(8)
C(2)-C(7)-C(6)	109.09(8)	C(8)-C(7)-C(6)	107.23(8)
C(2)-C(7)-C(10)	97.83(7)	C(8)-C(7)-C(10)	113.76(8)
C(6)-C(7)-C(10)	119.10(8)	C(9)-C(8)-C(7)	109.70(8)
O(3)-C(9)-C(4)	124.88(10)	O(3)-C(9)-C(8)	123.10(10)
C(4)-C(9)-C(8)	112.02(8)	C(11)-C(10)-C(16)	108.21(8)
C(11)-C(10)-C(7)	116.59(8)	C(16)-C(10)-C(7)	107.79(8)
C(11)-C(10)-C(15)	113.60(8)	C(16)-C(10)-C(15)	107.21(8)
C(7)-C(10)-C(15)	102.94(7)	C(12)-C(11)-C(10)	123.35(9)
C(11)-C(12)-C(13)	122.79(9)	C(12)-C(13)-C(14)	111.85(9)
O(5)-C(14)-C(15)	110.99(8)	O(5)-C(14)-C(13)	111.92(8)
C(15)-C(14)-C(13)	109.77(8)	O(4)-C(15)-C(14)	110.76(8)
O(4)-C(15)-C(10)	105.88(7)	C(14)-C(15)-C(10)	115.45(8)
O(1)-C(16)-C(10)	113.03(8)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FPAS10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	44(1)	15(1)	26(1)	-2(1)	-12(1)	8(1)
O(2)	59(1)	42(1)	38(1)	-8(1)	-24(1)	34(1)
O(3)	25(1)	28(1)	35(1)	-16(1)	-3(1)	-3(1)
O(4)	11(1)	34(1)	16(1)	-2(1)	-3(1)	0(1)
O(5)	25(1)	21(1)	23(1)	-3(1)	7(1)	-5(1)
C(1)	35(1)	25(1)	19(1)	-3(1)	-8(1)	14(1)
C(2)	14(1)	22(1)	15(1)	-3(1)	-4(1)	5(1)
C(3)	15(1)	37(1)	20(1)	-8(1)	-8(1)	5(1)
C(4)	16(1)	31(1)	16(1)	-5(1)	-6(1)	0(1)
C(5)	23(1)	27(1)	15(1)	1(1)	-6(1)	0(1)
C(6)	19(1)	18(1)	15(1)	1(1)	-3(1)	-3(1)
C(7)	11(1)	13(1)	14(1)	-1(1)	-3(1)	0(1)
C(8)	16(1)	14(1)	16(1)	-2(1)	-2(1)	0(1)
C(9)	12(1)	23(1)	19(1)	-7(1)	0(1)	-3(1)
C(10)	13(1)	14(1)	14(1)	-1(1)	-4(1)	0(1)
C(11)	12(1)	22(1)	20(1)	-4(1)	-6(1)	0(1)
C(12)	20(1)	23(1)	23(1)	-4(1)	-11(1)	6(1)
C(13)	28(1)	22(1)	17(1)	1(1)	-6(1)	4(1)
C(14)	18(1)	16(1)	16(1)	-2(1)	0(1)	-1(1)
C(15)	12(1)	16(1)	15(1)	-2(1)	-4(1)	1(1)
C(16)	28(1)	15(1)	21(1)	-1(1)	-8(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FPAS10.

	x	y	z	U(eq)
H(1)	-650(30)	7240(20)	6827(18)	47(5)
H(3A)	-580	8281	827	28
H(3B)	-848	6782	1630	28
H(4A)	1206	6532	-646	25
H(5B)	2895	8806	-633	26
H(5C)	4403	7501	-1040	26
H(6A)	5729	7860	739	21
H(6B)	4482	9323	982	21
H(8A)	4592	5658	2002	19
H(8B)	2389	5555	2845	19
H(11A)	6420	7589	3489	21
H(12A)	6157	6552	5515	26
H(13A)	2819	7447	6850	26
H(13B)	3141	5751	6714	26
H(14A)	1617	5691	4885	21
H(15A)	1063	8726	5096	17
H(16A)	3706	10155	4384	25
H(16B)	4973	10004	2885	25