Enantioselective Total Syntheses of (–)-Taiwaniaquinone H and (–)-Taiwaniaquinol B by Iridium-Catalyzed Borylation and Palladium-Catalyzed Asymmetric α-Arylation

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Supporting Information

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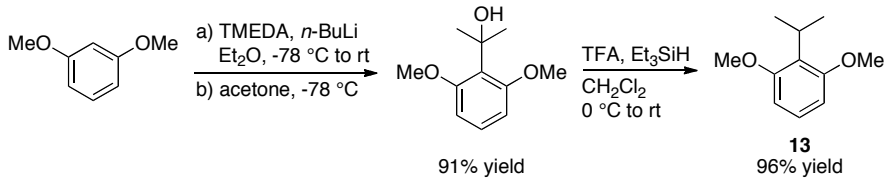
General Experimental Details

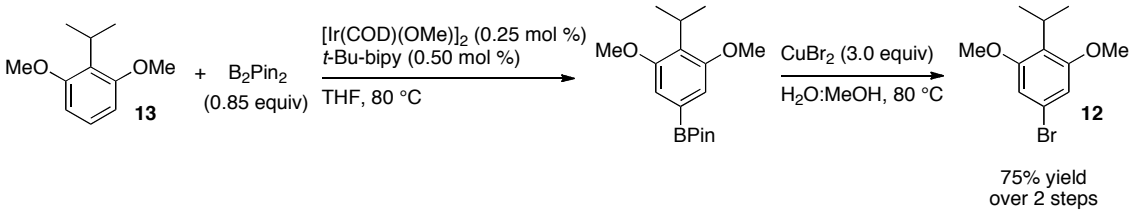
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. All reactions were performed under an atmosphere of nitrogen unless otherwise stated. All glassware for moisture-sensitive reactions was dried at 140 °C in an oven. Flash column chromatography was performed on Silicycle Siala-P siliga gel. Products were visualized on TLC plates by UV or by staining with $KMnO_4$ or ceric ammonium molybdate. Melting points were measured on a Thomas Hoover Unimelt capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the University of Illinois at Urbana-Champaign Microanalysis Laboratory or by Robertson Microlit Laboratories, Inc. (Madison, NJ). High-resolution MS analyses were performed by the University of Illinois at Urbana-Champaign Mass Spectrometry Center. GC/MS analyses were obtained on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector). Optical rotations were measured on a Rudolph Instruments (Denville, NJ) Autopol IV polarimeter. ^{1}H NMR spectra were acquired at 500 MHz and ^{13} NMR spectra were acquired at 125 MHz on Varian Unity and Varian Inova instruments in the University of Illinois VOICE NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C). Coupling constants are reported in hertz.

Materials

Tetrahydrofurn, diethyl ether, toluene, benzene, and dichloromethane were degassed by purging with argon for 45 minutes and dried with a solvent purification containing a one-meter column of activated alumina. 1,3-dimethoxybenzene, *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA, ≥99.5%), *n*-butyllithium (1.6 M in hexanes), trifluoroacetic acid, triethylsilane, 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*-Bu-bipy), copper(II) bromide, ethyl formate, 2-methylcyclohexanone, *N*-methylaniline, iodomethane, sodium hydride, trimethylsulfonium iodide, dimethyl sulfoxide (anhydrous), $BF_3{\cdot}OEt_2$ (purified by redistillation), $BBr_3{\cdot}SMe_2$ (1 M in CH_2Cl_2), 1,2-dichloroethane, salcomine, *N*,*N*-dimethylformamide (anhydrous), $BH_3{\cdot}THF$ (1 M in THF), 30% w/w H_2O_2, BCl_3 (1M in hexanes), ceric ammonium nitrate, and sodium hydrosulfite (technical grade) were purchased from Sigma-Aldrich and used without further purification. Acetone (Optima®), methanol (Optima®), and acetonitrile (Optima®) were purchased from Fisher Scientific and used without further purification. Potassium *t*-butoxide (KO*t*-Bu), sodium *t*-butoxide (NaO*t*-Bu), sodium hexamethyldisilazane (NaHMDS), $In(OTf)_3$, $InCl_3$, $Bi(OTf)_3$, and $BiCl_3$, (*R*)-Difluorphos, and $Pd(dba)_2$ were purchased from Strem and used without further purification. $[Ir(COD)(OMe)]_2$ was received as a gift from Johnson-Matthey and used without further purification. Bis(pinacolato)diboron (B_2pin_2) was received as a gift from Allychem and used without further purification. Methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR)[1] and IBX[2] were prepared according to a known procedures.

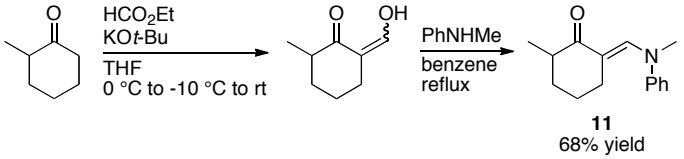


2-Isopropyl-1,3-dimethoxybenzene (13):[3] To a solution of 1,3-dimethoxybenzene (10.0 mL, 77.2 mmol) and TMEDA (13.0 mL, 86.7 mmol) in diethyl ether (250 mL) at -78 °C was added *n*-BuLi as a 1.6 M solution in hexanes (51.0 mL, 81.6 mmol) over 15 min. The reaction mixture was stirred at -78 °C for 30 minutes, then allowed to warm to room temperature over 1 h. The reaction mixture was stirred at room temperature for an additional 2 h, then cooled to -78 °C. Acetone (7.0 mL, 95 mmol) was added to the reaction mixture. The resulting solution was stirred at -78 °C for 30 min, then quenched with saturated aqueous ammonium chloride. The organic layer was separated, washed with saturated aqueous ammonium chloride, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column silica gel chromatography (90:10 to 80:20 hexanes:EtOAc) to yield 2-(2,6-dimethoxyphenyl)propan-2-ol as a colorless oil in 91% yield (13.8 g, 70.5 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.64 (s, 6H), 3.82 (s, 6H), 5.74 (s, 1H), 6.59 (d, J = 8.5 Hz, 2H), 7.14 (t, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.1, 56.2, 74.2, 106.1, 124.4, 127.7, 157.9. IR (NaCl) 3522 (br), 3048, 3006, 2973, 2944, 2841, 1594, 1582, 1475, 1435, 1388, 1368, 1248, 1101, 949. To a solution of 2-(2,6-dimethoxyphenyl)propan-2-ol (10.0 g, 51.0 mmol) in CH_2Cl_2 (500 mL) at 0 °C was added trifluoroacetic acid (18.1 mL, 243 mmol) and triethylsilane (23.1 mL, 145 mmol). The reaction mixture was stirred at 0 °C for 1 h, then removed from the ice-water bath and stirred for an additional 1 h. The reaction was concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (95:5 hexanes:EtOAc) to give **13** as a colorless oil in 96% yield (8.80 g, 48.8 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (d, J = 7.0 Hz, 6H), 3.64 (septet, J = 7.0 Hz, 1H), 3.83 (s, 6H), 6.57 (d, J = 8.5 Hz, 2H), 7.13 (t, J = 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 24.3, 55.9, 104.7, 124.6, 126.7, 158.8. IR (NaCl) 2986, 2959, 2940, 2873, 2839, 1593, 1474, 1438, 1360, 1249, 1142, 1113, 1088, 1054.

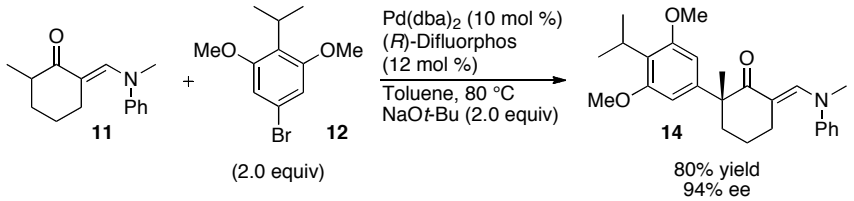


5-Bromo-2-isopropyl-1,3-dimethoxybenzene (12): In a nitrogen-filled glovebox, $[Ir(COD)(OMe)]_2$ (0.0341 g, 0.0514 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.0290 g, 0.108 mmol), B_2Pin_2 (4.32 g, 17.0 mmol), and THF (25 mL) were added to a 500-mL reaction vessel equipped with a vacuum valve. Arene **13** (3.60 g, 20.0 mmol) was added to the resulting reaction mixture, and the reaction vessel was sealed with a PTFE stopper. The reaction mixture was removed from the glovebox and heated at 80 °C for 40 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under vacuum. The crude arylboronate ester was dried under vacuum for 2 h. The crude arylboronate ester was dissolved in MeOH (150 mL). To the methanolic solution of the arylboronate ester was added copper(II) bromide (13.4 g, 60.0 mmol) as a solution in distilled water (150 mL). The reaction vessel was

sealed with a PTFE stopper and heated at 80 °C for 48 h. The reaction mixture was then cooled to room temperature and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (99:1 hexanes:EtOAc) to give aryl bromide **12** (3.91 g, 15.1 mmol) as a white amorphous solid in 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25 (d, J = 7.0 Hz, 6H), 3.54 (septet, J = 7.0 Hz, 1H), 3.79 (s, 6H), 6.68 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.6, 24.1, 56.0, 108.3, 119.6, 123.5, 159.2. IR (NaCl) 3004, 2988, 2961, 2941, 2873, 2838, 1580, 1463, 1450, 1407, 1360, 1228, 1145, 1125, 1101, 1056. Anal. Calcd. for $C_{11}H_{15}BrO$: C, 50.98; H, 5.83; found: C, 50.82; H, 5.87.

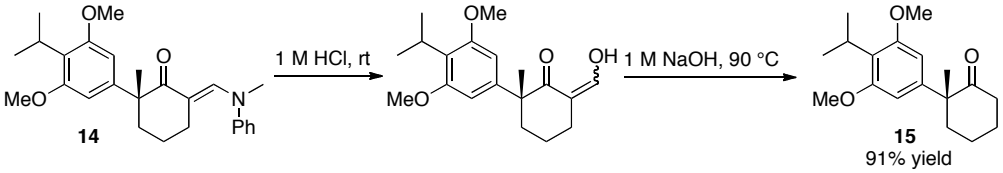


(*E*)-2-Methyl-6-((methyl(phenyl)amino)methylene)cyclohexanone (11):[4] To a stirred solution of KO*t*-Bu (3.70 g, 33.0 mmol) in THF (25 mL) at 0 °C was added ethyl formate (10 mL) dropwise. The resulting mixture was stirred at 0 °C until the evolution of gas had ceased. The mixture was then cooled to -10 °C and 2-methylcyclohexanone (3.64 mL, 33.0 mmol) in ethyl formate (20 mL) was added over 15 min. The reaction mixture was stirred at -10 °C for 30 min, then warmed to room temperature and stirred for 12 h. The mixture was acidified to pH = 1 with 1M HCl and extracted with Et_2O (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield crude hydroxymethylene ketone that was used without further purification. The crude ketone was dissolved in benzene (60 mL), and *N*-methylaniline (4.20 mL, 39.0 mmol) was added. The reaction flask was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was refluxed for 4 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was partially purified by flash column silica gel chromatography (80:20 hexanes:EtOAc) to give **11** as a pink-red solid. Recrystallization from hexane provided analytically pure **11** as off-white crystals in 68% yield (4.66 g, 20.3 mmol). m.p. = 51-52 °C (lit. values, 50-51 °C[4a] and 51-52.5 °C[4b]). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17 (d, J = 7.0 Hz, 3H), 1.41-1.55 (m, 2H), 1.67-1.76 (m, 1H), 1.86-1.97 (m, 1H), 2.02-2.16 (m, 2H), 2.29-2.38 (m, 1H), 3.39 (s, 3H), 7.01 (dd, J = 8.5, 1.0 Hz, 2H), 7.07 (t, J = 8.0, 1.0 Hz, 1H), 7.28 (ddd, J = 8.5, 8.0, 1.0 Hz, 2H), 7.50 (t, J = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.8, 22.5, 28.1, 31.6, 42.3, 42.7, 112.7, 121.1, 123.8, 129.0, 144.8, 146.3, 202.5. IR (NaCl) 3049, 2980, 2958, 2934, 2862, 1651, 1601, 1542 (br), 1494, 1455, 1425, 1370, 1319, 1294, 1237, 1193, 1107.

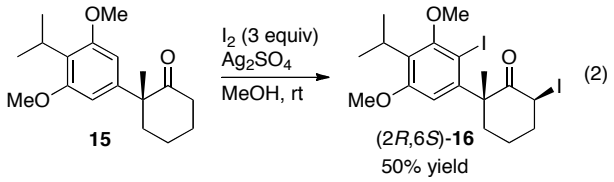


(*R*,*E*)-2-(4-Isopropyl-3,5-dimethoxyphenyl)-2-methyl-6-((methyl(phenyl)amino)methylene)-cyclohexanone (14): In a nitrogen-filled glovebox to a 100-mL reaction vessel equipped with a

vacuum valve were added (*R*)-Difluorphos (0.164 g, 0.240) $Pd(dba)_2$ (0.115 g, 0.200 mmol), ketone **11** (0.458 g, 0.200 mmol), and toluene (40 mL). To the resulting mixture was added aryl bromide **12**, followed by NaO*t*-Bu (0.384 g, 4.00 mmol). The reaction vessel was sealed with a PTFE stopper and removed from the glovebox. The reaction mixture was stirred at 80 °C for 72 h. The reaction mixture was then cooled to room temperature and quenched with cold water. The product was extracted from the resulting mixture with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (80:20 hexanes:EtOAc) to give α-aryl ketone **14** (0.650 g, 1.60 mmol) as a yellow foam in 80% yield. The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 6.2 min ((*S*)-enantiomer); t_R 16.6 min ((*R*)-enantiomer) [Chiralcel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexanes/*i*-PrOH, 90:10, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = +179.1 (c 0.90, $CHCl_3$, 94% ee). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.258 (d, *J* = 7.0 Hz, 3H), 1.259 (d, *J* = 7.0 Hz, 3H), 1.47 (s, 3H), 1.53 (m, 2H), 1.80-1.87 (m, 1H), 2.01-2.16 (m, 2H), 2.25-2.31 (m, 1H), 3.49 (s, 3H), 3.53 (septet, *J* = 7.0 Hz, 1H), 3.78 (s, 6H), 6.48 (s, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.29-7.34 (m, 2H), 7.57 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.9, 21.12, 21.14, 24.3, 27.5, 28.3, 37.5, 42.4, 51.5, 56.2, 104.1, 113.7, 121.3, 123.0, 124.0, 129.2, 144.8, 145.5, 146.6, 158.7, 202.8. IR (NaCl) 2984, 2960, 2938, 2872, 2838, 1649, 1603, 1573, 1542 (br), 1495, 1414, 1298, 1185, 1139, 1112, 1055. HRMS (ESI) calcd. for $C_{26}H_{34}NO_3^+$ $[M+H]^+$: 408.2539; found 408.2545.



(*R*)-2-(4-Isopropyl-3,5-dimethoxyphenyl)-2-methylcyclohexanone (15): α-Aryl ketone **14** (0.650 g, 1.60 mmol) was dissolved in THF (50 mL). Aqueous 1 M HCl was added to the solution of **14**, and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with Et_2O (3x), and the combined organic layers were concentrated under reduced pressure. To the crude hydroxymethylene ketone was added aqueous 1 M NaOH (50 mL) and the reaction flask was equipped with a reflux condenser. The reaction mixture was heated at 90 °C. After 6 h, the reaction mixture was cooled to room temperature and neutralized with aqueous 1 M HCl. The reaction mixture was extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (98:2 hexanes:Et_2O) to give the deprotected ketone **15** (0.423 g, 1.46 mmol) as a white amorphous solid in 91% yield. $[\alpha]_D^{24}$ = +159.6 (c 0.50, $CHCl_3$, 94% ee). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25 (d, *J* = 7.0 Hz, 6H), 1.27 (s, 3H), 1.63-1.73 (m, 3H), 1.80-1.90 (m, 1H), 1.93-2.00 (m, 1H), 2.26-2.31 (m, 1H), 2.43 (ddd, *J* = 13.5, 13.5, 6.5 Hz, 1H), 2.62 (m, 1H), 3.53 (septet, 7.0 Hz, 1H), 3.76 (s, 6H), 6.32 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9 (2C, CHCH_3), 22.1, 24.2, 28.4, 28.6, 38.4, 40.1, 54.5, 56.1, 102.8, 123.1, 141.8, 159.1, 214.4. IR (NaCl) 2960, 2940, 2869, 2839, 1704, 1603, 1575, 1464, 1451, 1414, 1360, 1310, 1136, 1101, 1056. Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02; found: C, 74.22; H, 9.33.



(2*R*,6*S*)-6-Iodo-2-(2-iodo-4-isopropyl-3,5-dimethoxyphenyl)-2-methylcyclohexanone (16): To a solution of ketone **15** (0.0415 g, 0.143 mmol, 94% ee) in MeOH (5 mL) was added iodine (0.109 g, 0.429 mmol) and silver sulfate (0.133 g, 0.428 mmol). The resulting mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous sodium thiosulfate. The resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (98:2 hexanes:Et_2O) to give compound **16** as an amorphous solid. The resulting solid was dissolved in a minimal volume of hexane and the solution was stored in a freezer at -30 °C. After standing overnight at -30 °C, the mixture was filtered cold and washed with cold hexane (-30 °C) to provide crystals of **16** (0.0388 g, 0.0715 mmol, 50% yield) that were suitable for single-crystal X-ray diffraction. m.p. = 117-119 °C. $[\alpha]_D^{23}$ = +80.0 (c 0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (d, *J* = 7.0 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.62 (s, 3H), 1.70-1.80 (m, 2H), 1.90-2.01 (m, 1H), 2.20-2.32 (m, 1H), 2.59-2.80 (m, 2H), 3.46 (septet, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 3.84 (s, 3H), 4.91 (dd, *J* = 11.0, 5.0 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.00, 21.02, 23.3, 27.3, 27.5, 34.6, 41.7, 42.8, 55.7, 59.9, 61.9, 88.5, 108.5, 129.6, 144.8, 158.3, 160.5, 207.7. IR (NaCl) 3047, 2958, 2935, 2873, 2844, 1718, 1698, 1583, 1549, 1457, 1376, 1336, 1304, 1138, 1087, 1055, 1022.

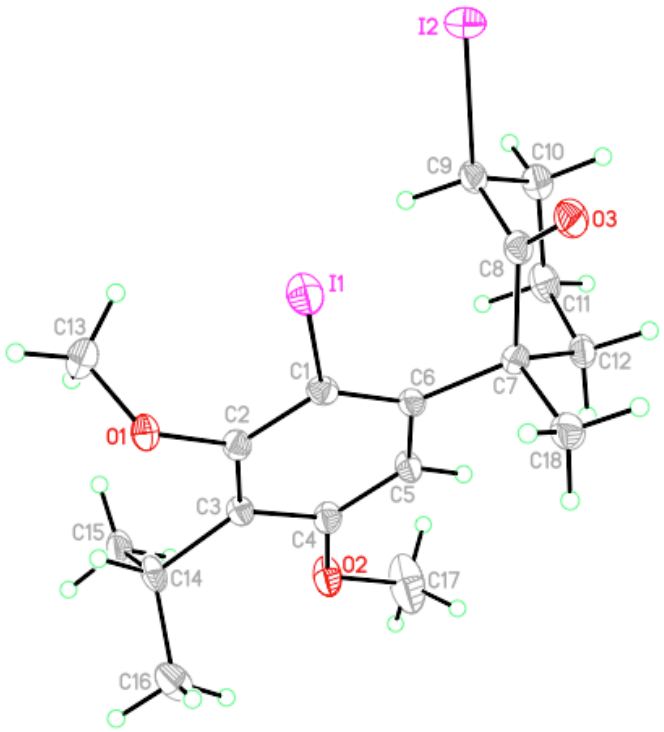
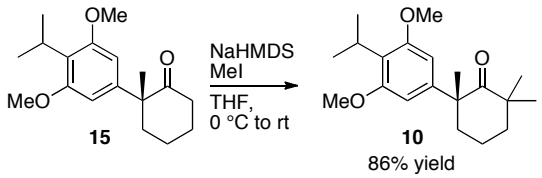
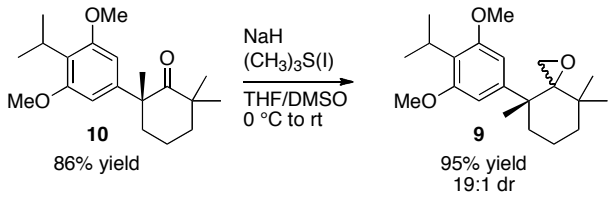


Figure S1. Ortep diagram of (2*R*,6*S*)-6-Iodo-2-(2-iodo-4-isopropyl-3,5-dimethoxyphenyl)-2-methylcyclohexanone **16**.



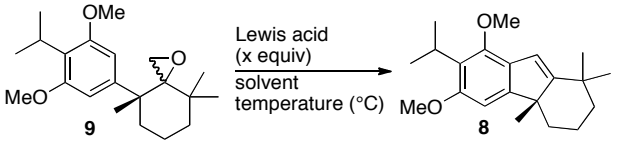
(*R*)-2-(4-Isopropyl-3,5-dimethoxyphenyl)-2,6,6-trimethylcyclohexanone (10): To a solution of NaHMDS (1.17 g, 6.38 mmol) in THF (10 mL) at 0 °C was added compound **15** (0.500 g, 1.72 mmol) as a solution in THF (5 mL). The resulting solution was stirred at 0 °C for 30 min. After 30 min the reaction mixture was allowed to warm to room temperature. The reaction was stirred an additional 1 h at room temperature. The reaction was quenched with cold water and extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated to give an approximately 80:20 mixture of dimethylated:monomethylated products. The crude mixture of products was added as a solution in THF (5 mL) to a solution of NaHMDS (0.630 g, 3.44 mmol) in THF (10 mL) at 0 °C. The resulting solution was stirred at 0 °C for 30 min. After 30 min, the reaction mixture was allowed to warm to room temperature. The reaction was stirred an additional 1 h at room temperature. The reaction was quenched with cold water and extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. Analysis by GC-MS showed complete conversion to the dimethylated product **10**. The crude product was purified by flash column silica gel chromatography (98:2 hexanes:Et_2O) to give compound **10** (0.470 g, 1.48 mmol) as a white amorphous solid in 86% yield. $[\alpha]_D^{25}$ = +139.6 (c 0.58, $CHCl_3$, 94% ee). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.72 (s, 3H), 1.08 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.28 (s, 3H), 1.55-1.75 (m, 4H), 1.97-2.07 (m, 1H), 2.57-2.64 (m, 1H), 3.52 (septet, *J* = 7.0 Hz, 1H), 3.76 (s, 6H), 6.42 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.4, 21.0 (2C, CH*CH₃*), 24.1, 27.4, 27.8, 30.6, 36.2, 40.3, 45.8, 52.6, 56.1, 102.6, 123.0, 141.4, 158.8, 217.5. IR (NaCl) 2986, 2960, 2939, 2870, 2838, 1693, 1604, 1574, 1465, 1454, 1413, 1136, 1103, 1056. Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50; found: C, 75.66; H, 9.29.



(4*R*)-4-(4-Isopropyl-3,5-dimethoxyphenyl)-4,8,8-trimethyl-1-oxaspiro[2.5]octane (9): A suspsension of NaH (0.248 g, 10.3 mmol) in THF (25 mL) and DMSO (23 mL) was stirred at room temperature for 20 min. The mixture was cooled to 0 °C, and a solution of trimethylsulfonium iodide (0.714 g, 3.50 mmol) in DMSO (10 mL) was added to the reaction flask. The reaction mixture was stirred at 0 °C for 10 min. Compound **10** (0.500 g, 1.57 mmol) in THF (13 mL) was added to the reaction mixture. The reaction mixture was stirred at 0 °C for 30 min. The reaction flask was removed from the cold bath and allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with cold water and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (96:4 hexanes:Et_2O) to

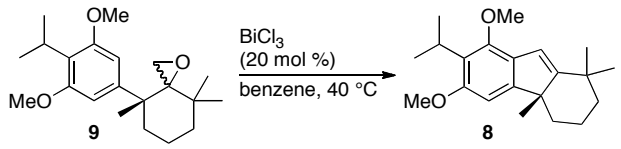
give a 19:1 mixture of diastereomers of epoxide **9** (0.495 g, 1.49 mmol) as a white amorphous solid in 95% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, major diastereomer) δ 0.53 (s, 3H), 0.77 (s, 3H), 1.01 (s, 3H), 1.26 (d, J = 7.0 Hz, 3H), 1.27 (d, J = 7.0 Hz, 3H), 1.49-1.76 (m, 4H), 1.81-1.91 (m, 1H), 2.22-2.27 (m, 1H), 3.00 (d, J = 4.0 Hz, 1H), 3.12 (d, = 4.0 Hz, 1H), 3.52 (septet, J = 7.0 Hz, 1H), 3.78 (s, 6H), 6.55 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5, 21.2 (2C, CH*CH$_3$*), 24.2, 26.3, 27.2, 29.6, 35.7, 35.9, 39.7, 42.7, 47.5, 56.2, 65.1, 103.7, 122.6, 146.1, 158.5. IR (NaCl) 2960, 2935, 2871, 1606, 1574, 1463, 1451, 1135. Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; found: C, 75.58; H, 10.04.

Table S1. Identification of Lewis Acid Promoters for the Synthesis of Tetrahydrofluorene **8** from Epoxide **9**[a]

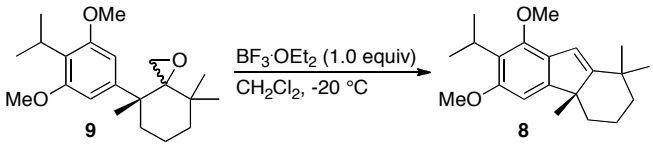


Entry	Lewis Acid (equiv)	Solvent	Temperature (°C)	Yield (%)[b]
1	$BF_3{\cdot}OEt_2$ (1.0)	CH_2Cl_2	rt	<5
2	$BF_3{\cdot}OEt_2$ (1.0)	CH_2Cl_2	0	15
3	**$BF_3{\cdot}OEt_2$ (1.0)**	**CH_2Cl_2**	**-20**	**50-70**
4	MABR (2.0)[c]	CH_2Cl_2	rt	<5
5	MABR (2.0)[c]	CH_2Cl_2	0	<5
6	MABR (2.0)[c]	CH_2Cl_2	-20	<5
7	$In(OTf)_3$ (1.0)	toluene	rt	15
8	$InCl_3$ (1.0)	toluene	rt	17
9	$Bi(OTf)_3$ (1.0)	toluene	rt	47
10	$Bi(OTf)_3$ (1.0)	benzene	rt	58
11	$Bi(OTf)_3$ (1.0)	CH_2Cl_2	rt	46
12	$Bi(OTf)_3$ (1.0)	THF	rt	43
13	$Bi(OTf)_3$ (1.0)	Et_2O	rt	55
14	$Bi(OTf)_3$ (1.0)	benzene	0	47
15	$Bi(OTf)_3$ (1.0)	benzene	40	64
16	$Bi(OTf)_3$ (0.50)	benzene	40	64
17	$Bi(OTf)_3$ (0.20)	benzene	40	60
18	$Bi(OTf)_3$ (2.0)	benzene	rt	56
19	$Bi(OTf)_3$ (0.50)	benzene	rt	54
20	$Bi(OTf)_3$ (0.20)	benzene	rt	56
21	$Bi(OTf)_3$ (0.10)	benzene	rt	50
22	$BiCl_3$ (1.0)	toluene	rt	47
23	$BiCl_3$ (1.0)	benzene	rt	52
24	$BiCl_3$ (1.0)	benzene	40	57
25	$BiCl_3$ (0.50)	benzene	40	61
26	**$BiCl_3$ (0.20)**	**benzene**	**40**	**67**

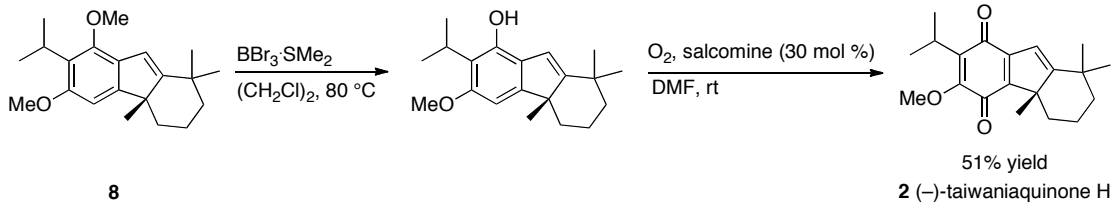
[a] Reactions conducted on 10 mg (0.030 mmol) of **9** in 1 mL of solvent. [b] Yields determined by GC-MS with dodecane (5 μL) as the internal standard. [c] MABR = methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide).



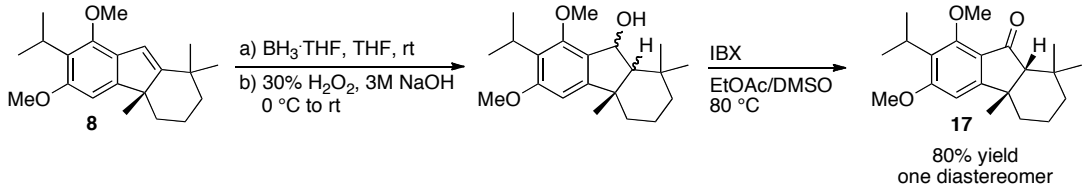
$BiCl_3$-Promoted Synthesis of (*R*)-7-isopropyl-6,8-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluorene (8):[5] In a nitrogen-filled glovebox to a 20 mL vial was added $BiCl_3$ (0.0379 g, 0.120 mmol), epoxide **9** (0.200 g, 0.602 mmol), and benzene (15 mL). The vial was sealed with a PTFE-lined cap and removed from the glovebox. The reaction mixture was heated in an oil bath at 40 °C for 8 h. The vial was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through a plug of silica gel (eluting with Et_2O) and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (99:1 hexanes:Et_2O) to give tetrahydrofluorene **8** (0.122 g, 0.388 mmol) as a white amorphous solid in 64% yield. *Note: A dry-packed silica gel column leads to improved separation of **8** from a byproduct of similar polarity.* $[\alpha]_D^{24}$ = +7.8 (c 0.21, $CHCl_3$, 94% ee). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.01 (ddd, *J* = 13.0, 13.0, 3.5 Hz, 1H), 1.10 (ddd, *J* = 13.0, 13.0, 4.0 Hz, 1H), 1.23 (s, 3H), 1.30 (s, 3H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.35 (s, 3H), 1.58-1.66 (m, 2H), 1.89-2.00 (m, 1H), 2.05-2.09 (m, 1H), 3.54 (septet, *J* = 7.0 Hz, 1H), 3.82 (s, 3H), 3.86 (s, 3H), 6.41 (s, 1H), 6.60 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.1, 21.6, 21.7, 24.0, 25.1, 25.7, 31.5, 35.7, 38.4, 43.0, 51.5, 56.2, 62.1, 101.7, 117.1, 126.7, 127.0, 151.8, 155.3, 157.1, 161.2. IR (NaCl) 2998, 2960, 2934, 2868, 1612, 1588, 1569, 1455, 1416, 1307, 1137, 1108, 1055, 1024. HRMS (ESI) calcd. for $C_{21}H_{31}O_2^+$ $[M+H]^+$: 315.2324; found 315.2328.



$BF_3{\cdot}OEt_2$-Promoted Synthesis of (*R*)-7-isopropyl-6,8-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluorene (8):[5] To a solution of epoxide **9** (0.250 g, 0.753 mmol) in CH_2Cl_2 (20 mL) at -20 °C was added dropwise a pre-cooled solution of $BF_3{\cdot}OEt_2$ (95.0 μL 0.753 mmol) in CH_2Cl_2 (5 mL). The solution was stirred at -20 °C for 20 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (99:1 hexanes:Et_2O) to give tetrahydrofluorene **8** (0.177 g, 0.563 mmol) as a white amorphous solid in 75% yield. *Note: A dry-packed silica gel column leads to improved separation of **8** from a byproduct of similar polarity.* Spectroscopic data was identical to that reported for the $BiCl_3$-promoted synthesis of **8** (*vide supra*).

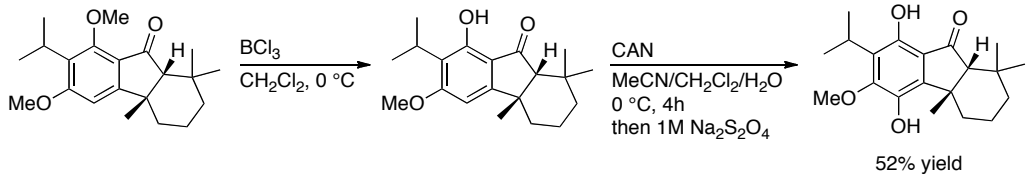


(–)-Taiwaniaquinone H (2):[5,6] Taiwaniaquinone was prepared according to a modified procedure based on methods reported by Trauner and coworkers.[5] To a solution of tetrahydrofluorene **8** (0.0200 g, 0.0636 mmol) in $(CH_2Cl)_2$ (3 mL) at room temperature was added $BBr_3{\cdot}SMe_2$ as a 1 M solution in CH_2Cl_2 (763 μL, 0.763 mmol). The resulting solution was heated in an oil bath at 80 °C for 2 h. The reaction mixture was cooled to room temperature, quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was filtered through a 1-inch column of silica gel (eluting with 90:10 hexanes:Et_2O) to remove baseline impurities. The solution containing the monodemethylated tetrahydrofluoren-1-ol was concentrated under reduced pressure, and the resulting residue was used without further purification.[7] To the crude tetrahydrofluoren-1-ol intermediate in DMF (1.5 mL) was added salcomine (0.0062 g, 0.019 mmol). Oxygen was bubbled through the resulting solution at room temperature for 6 h. The reaction was quenched with H_2O and extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (98:2 to 97:3 hexanes:Et_2O) to give (–)-taiwaniaquinone H **2** (0.0102 g, 0.0324 mmol) as an amorphous orange solid in 51% yield. m.p. = 81-83 °C (lit. values for racemic material, 83-84.5 °C[5] and 75-76 °C[6g]). $[\alpha]_D^{24}$ = -90.9 (c 0.13, $CHCl_3$, 94% ee). Published values of the optical rotation for Taiwaniaquinone H vary from $[\alpha]_D$ = -95.7 to -9.0 (see reference 6c); the value we report is consistent with that of the material prepared by Gademann and coworkers described in reference 6c. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.04-1.13 (m, 2H), 1.219 (s, 3H), 1.223 (d, *J* = 7.0 Hz, 3H), 1.226 (d, *J* = 7.0 Hz, 3H), 1.27 (s, 3H), 1.44 (s, 3H), 1.60-1.64 (m, 1H), 1.66-1.71 (m, 1H), 1.86-1.97 (m, 1H), 2.37-2.42 (m, 1H), 3.25 (septet, *J* = 7.0 Hz, 1H), 3.98 (s, 1H), 6.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.3, 20.4, 20.89, 20.91, 24.7, 25.0, 31.2, 36.9, 37.5, 43.6, 55.8, 61.6, 116.9, 136.2, 146.0, 150.8, 157.5, 176.0, 179.0, 186.5. IR (NaCl) 2934, 1646, 1538, 1465, 1294, 1159, 1029. HRMS (ESI) calcd. for $C_{20}H_{27}O_3^+$ $[M+H]^+$: 315.1960; found 315.1963.



(4a*S*,9a*R*)-7-isopropyl-6,8-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluoren-9(9a*H*)-one (17):[5,8] In a nitrogen-filled glovebox to a 20-mL vial was added tetrahydrofluorene **8** (0.0350 g, 0.111 mmol) and THF (3 mL). The vial was sealed with PTFE/silicone-lined septum cap and removed from the glovebox. A 1 M solution of $BH_3{\cdot}THF$ (900 μL, 0.900 mmol) was added to the reaction mixture at room temperature. The reaction mixture was stirred for 4 h

at room temperature, then cooled to 0 °C. The reaction was quenched by dropwise addition of H_2O (250 μL) at 0 °C. An aqueous solution of 3 M NaOH (1.80 mL, 5.40 mmol) was then added to the mixture, followed by addition of 30% w/w H_2O_2 (480 μL, 2.15 mmol). The resulting mixture was stirred at 0 °C for 30 min, then allowed to warm to room temperature and stirred for 1.5 h. The reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture containing a diastereomeric mixture of hexahydrofluoren-9-ols was filtered through a 1-inch column of silica gel (eluting with 90:10 hexanes:Et_2O) to remove baseline impurities. After concentration, the diastereomeric mixture of hexahydrofluoren-9-ols was used without further purification. To the diastereomeric mixture of hexahydrofluoren-9-ols in EtOAc (2.6 mL) and DMSO (1.3 mL) was added IBX (0.0343 g, 0.122 mmol). The vial was resealed with a PTFE-lined cap and heated in an oil bath at 80 °C for 2 h. The vial was removed from the oil bath and cooled to room temperature. The reaction mixture was quenched by addition of saturated aqueous Na_2SO_3 (0.5 mL) and stirred at room temperature for 10 min. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (4 mL) and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography to give diastereomerically pure tetrahydrofluoren-9-one **17** (0.0292 g, 0.0884 mmol) as a white amorphous solid in 80% yield. $[\alpha]_D^{25}$ = -35.5 (c 0.18, $CHCl_3$, 94% ee). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.70 (s, 3H), 1.22 (s, 3H), 1.25 (s, 3H), 1.28 (d, *J* = 7.0 Hz, 6H), 1.29-1.39 (m, 2H), 1.40-1.50 (m, 1H), 1.54-1.65 (m, 2H), 2.03-2.09 (m, 1H), 2.11 (s, 1H), 3.57 (septet, *J* = 7.0 Hz, 1H), 3.89 (s, 3H), 3.91 (s, 3H), 6.56 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.5, 21.3, 24.6, 24.7, 32.6, 33.4, 34.1, 34.6, 38.7, 41.5, 55.8, 62.2, 65.8, 99.8, 121.8, 128.2, 157.1, 164.1, 164.9, 204.6. IR (NaCl) 2959, 2936, 2872, 1690, 1588, 1461, 1322, 1137. HRMS (ESI) calcd. for $C_{21}H_{31}O_3^+$ $[M+H]^+$: 331.2273; found 331.2275.



17 **7** (–)-taiwaniaquinol B

(–)-Taiwaniaquinonol B (7):[5,8,9] To tetrahydrofluoren-9-one **17** (0.0150 g, 0.0454 mmol) in CH_2Cl_2 (1.2 mL) at 0 °C was added a 1 M solution of BCl_3 in hexanes (57 μL, 0.057 mmol). The resulting solution was stirred at 0 °C for 30 min. The reaction mixture was quenched with H_2O (3 mL) and extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to provide the 8-hydroxyfluoren-9-one intermediate,[10] which was used without further purification. To the 8-hydroxyfluoren-9-one intermediate in MeCN (1.4 mL) and CH_2Cl_2 (0.1 mL) at 0 °C was added ceric ammonium nitrate (0.0946 g, 0.173 mmol) as a solution in H_2O (0.7 mL). The reaction mixture was stirred at 0 °C for 4 h, then quenched with an aqueous 1M solution of $Na_2S_2O_4$ (1.0 mL). The reaction mixture was diluted with water (3 mL) and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel

chromatography (90:10 hexanes:EtOAc) to give (–)-taiwaniaquinonol B **7** (0.0078 g, 0.023 mmol) as an off-white solid in 52% yield. m.p. = 137-139 °C (lit. value from isolation of (–)-taiwaniaquinonol B,[9a] 142-144 °C; lit. values for racemic taiwaniaquinol B: 133.5-134.5 °C,[5] 140-141 °C,[6g] and 133-134 °C[8a]). $[\alpha]_D^{23}$ = -36.0 (c 0.15, $CHCl_3$, 94% ee) (lit. value, $[\alpha]_D^{31}$ = -37.7 (c 0.27, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (s, 3H), 1.26 (s, 3H), 1.385 (d, *J* = 7.0 Hz, 3H), 1.387 (d, *J* = 7.0 Hz, 3H), 1.37-1.44 (m, 2H), 1.45 (s, 3H), 1.52-1.64 (m, 1H), 1.66-1.76 (m, 1H), 1.95-2.10 (m, 2H), 2.12 (s, 1H), 3.27 (septet, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 5.25 (s, 1H), 9.52 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.8, 20.9 (2C, CH*CH₃*), 24.7, 26.2, 29.1, 30.7, 33.2, 34.6, 36.8, 43.0, 62.3, 65.5, 118.6, 126.5, 138.7, 143.0, 151.4, 152.7, 211.2. IR (NaCl) 3524 (br), 2960, 1661, 1629, 1428, 1331, 1117, 1015. HRMS (ESI) calcd. for $C_{20}H_{29}O_4^+$ $[M+H]^+$: 333.2066; found 333.2067.

References

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(10) For spectroscopic data of the 8-hydroxyfluoren-9-one intermediate, see reference 8a in the Supporting Information.

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tn             C13  dseq
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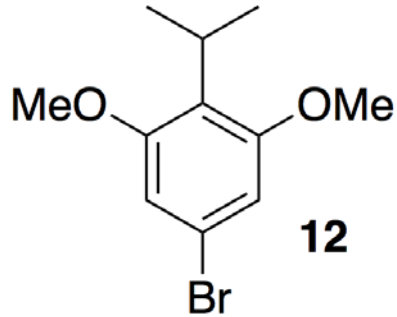

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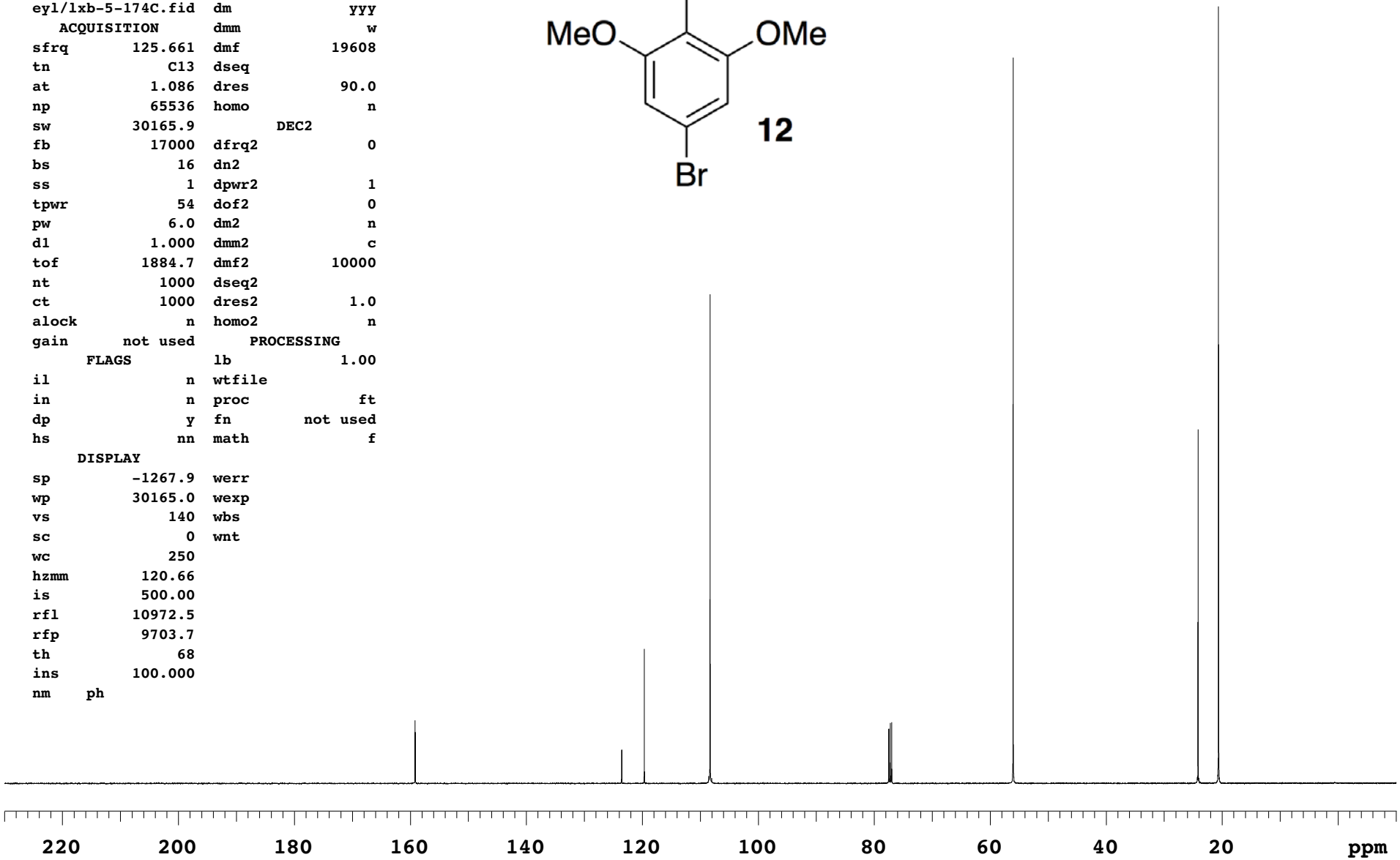

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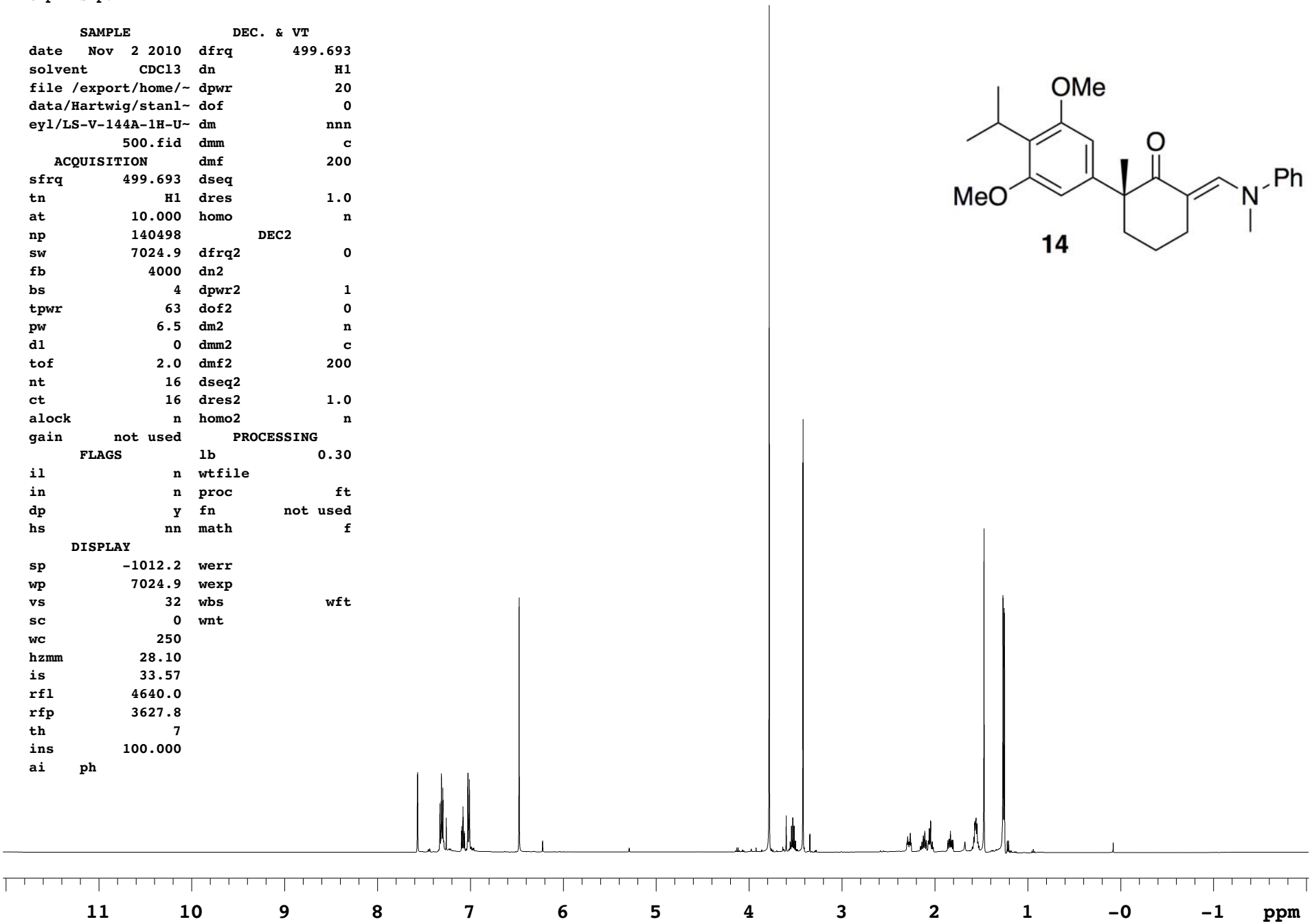

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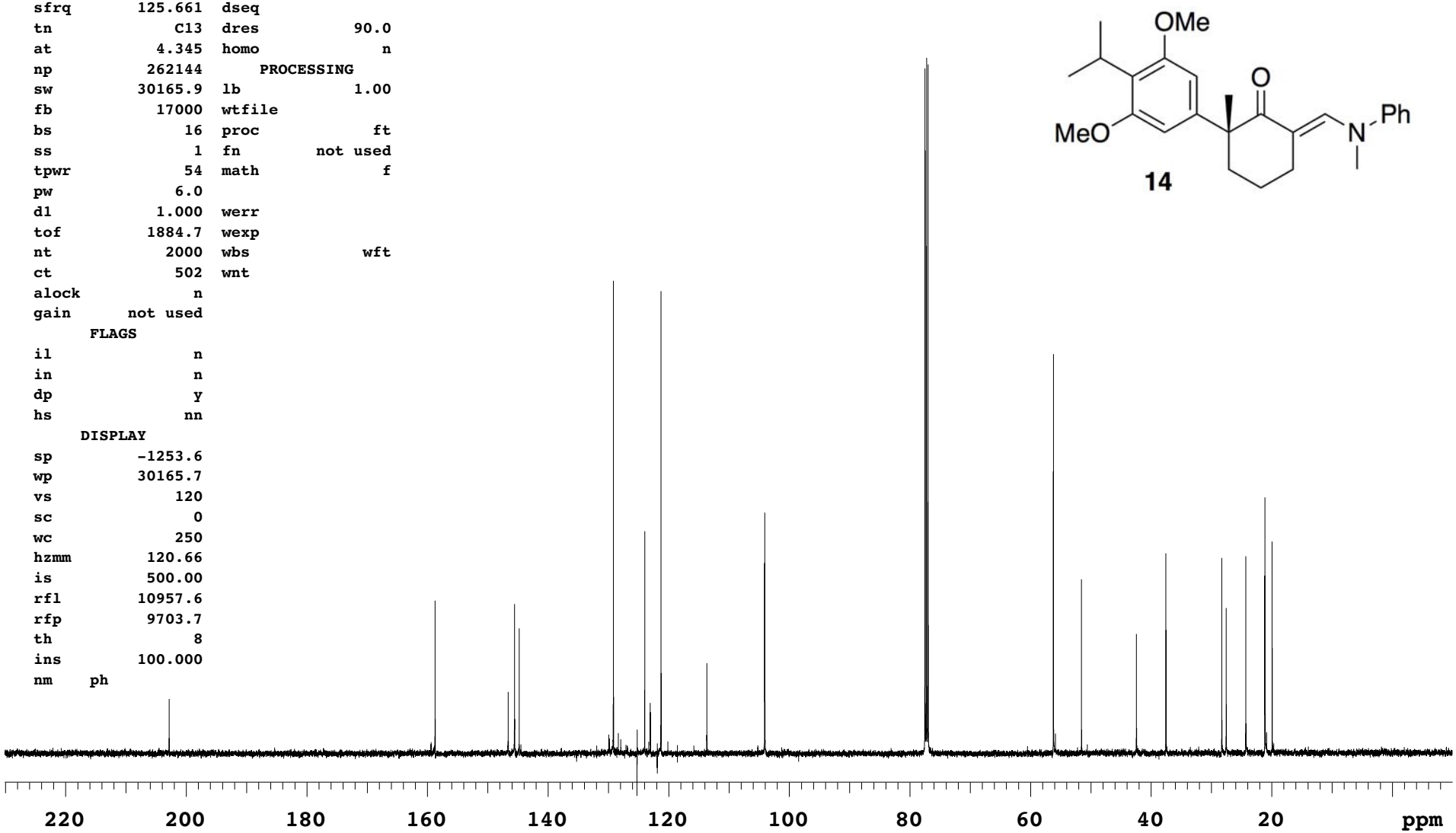
ins	100.000		
nm	ph		

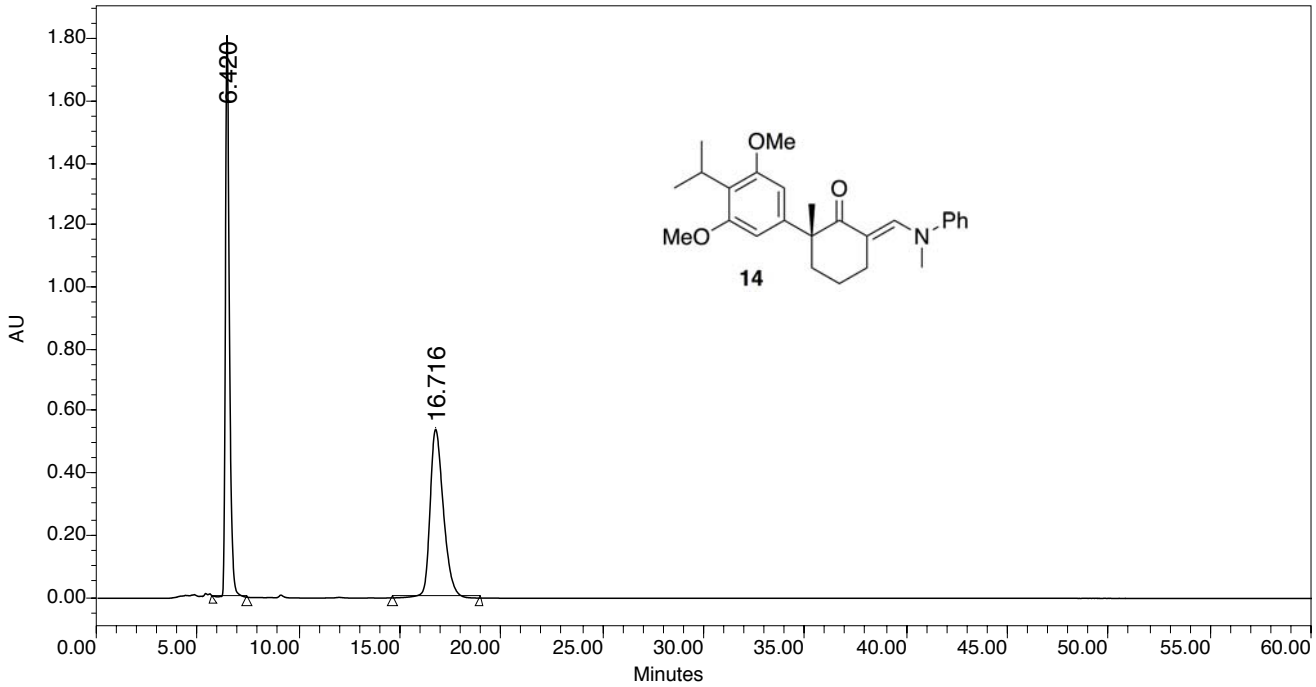


Yale University

Project Name: ColumnSelect
Reported by User: HartwigGRP

SAMPLE INFORMATION

Sample Name:	liu5-199-R	Acquired By:	HartwigGRP
Sample Type:	Unknown	Date Acquired:	4/2/2009 12:44:25 PM
Vial:	22	Acq. Method:	3_10ml_0A_100B_254_220
Injection #:	1	Date Processed:	7/6/2010 7:21:51 AM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	60.00 Minutes	Sample Set Name:	liu5199



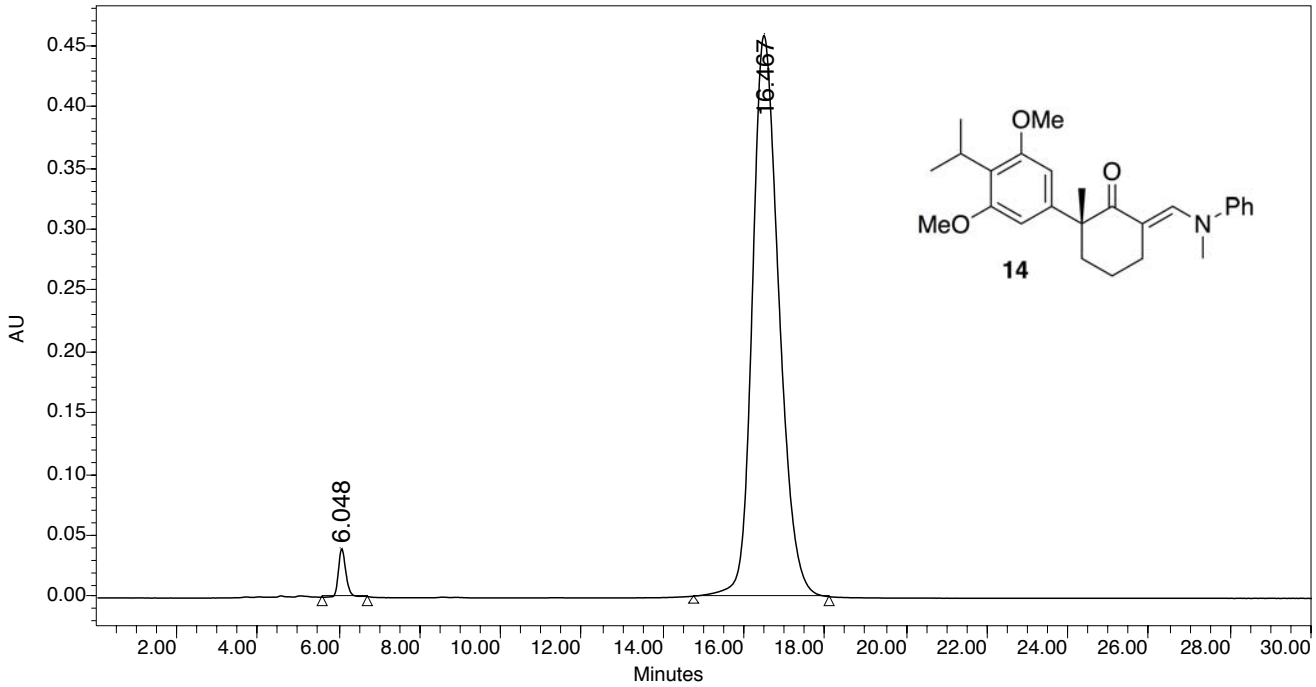
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.420	24827625	49.72	1810514	76.89
2	16.716	25108373	50.28	544100	23.11

Yale University

Project Name: ColumnSelect
Reported by User: HartwigGRP

SAMPLE INFORMATION

Sample Name:	liu5-200-E2	Acquired By:	HartwigGRP
Sample Type:	Unknown	Date Acquired:	4/9/2009 11:33:31 AM
Vial:	22	Acq. Method:	3_10ml_0A_100B_254_220
Injection #:	1	Date Processed:	11/4/2010 2:40:08 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	liu5200E

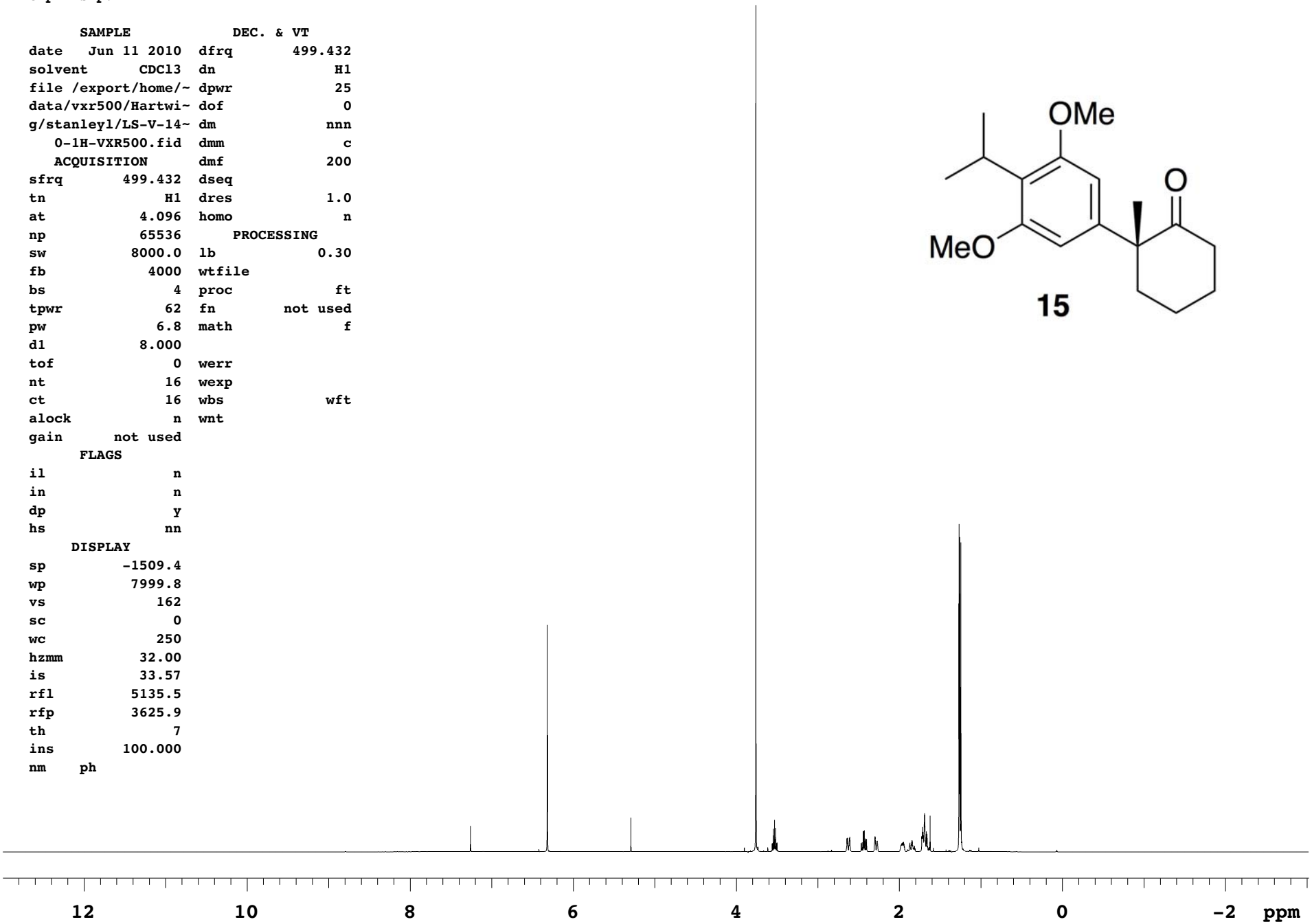


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.048	511511	2.40	39409	7.92
2	16.467	20824944	97.60	457977	92.08

```
LS-V-140-1H-VXR500

exp1  s2pul

      SAMPLE            DEC. & VT
date   Jun 11 2010  dfrq       499.432
solvent      CDCl3  dn              H1
file /export/home/~ dpwr            25
data/vxr500/Hartwi~ dof              0
g/stanleyl/LS-V-14~ dm             nnn
   0-1H-VXR500.fid  dmm              c
   ACQUISITION      dmf            200
sfrq       499.432  dseq
tn              H1  dres           1.0
at           4.096  homo             n
np           65536      PROCESSING
sw          8000.0  lb            0.30
fb            4000  wtfile
bs               4  proc            ft
tpwr            62  fn        not used
pw             6.8  math             f
d1           8.000
tof              0  werr
nt              16  wexp
ct              16  wbs            wft
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -1509.4
wp          7999.8
vs             162
sc               0
wc             250
hzmm         32.00
is           33.57
rfl         5135.5
rfp         3625.9
th               7
ins        100.000
nm    ph
```

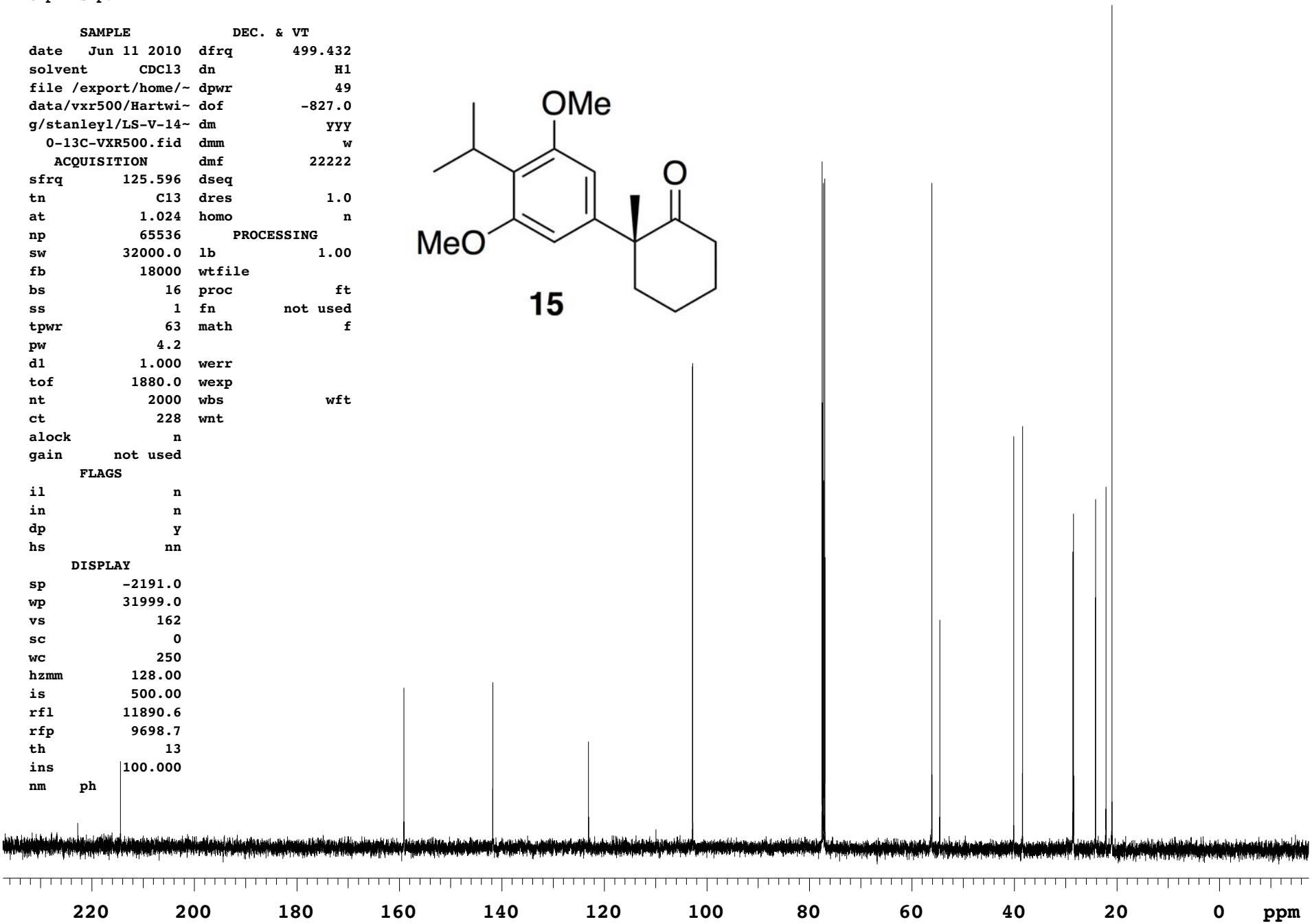



LS-V-140-13C-VXR500

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jun 11 2010	dfrq	499.432
solvent	CDCl3	dn	H1
file /export/home/~		dpwr	49
data/vxr500/Hartwi~		dof	-827.0
g/stanleyl/LS-V-14~		dm	yyy
0-13C-VXR500.fid		dmm	w
ACQUISITION		dmf	22222
sfrq	125.596	dseq	
tn	C13	dres	1.0
at	1.024	homo	n
np	65536	PROCESSING	
sw	32000.0	lb	1.00
fb	18000	wtfile	
bs	16	proc	ft
ss	1	fn	not used
tpwr	63	math	f
pw	4.2		
d1	1.000	werr	
tof	1880.0	wexp	
nt	2000	wbs	wft
ct	228	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2191.0		
wp	31999.0		
vs	162		
sc	0		
wc	250		
hzmm	128.00		
is	500.00		
rfl	11890.6		
rfp	9698.7		
th	13		
ins	100.000		
nm	ph		

15

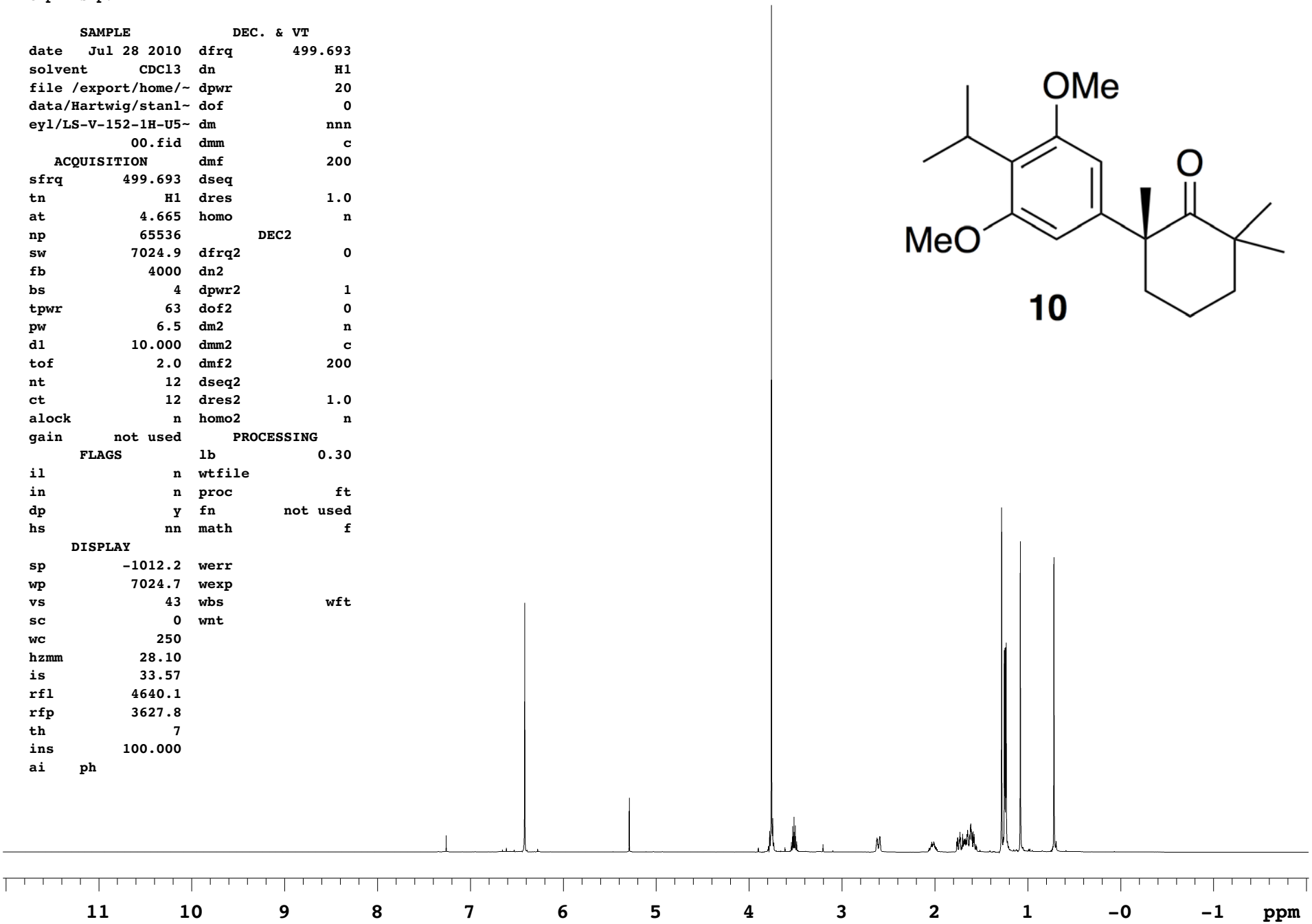


LS-V-152-1H-U500

exp2 s2pul

	SAMPLE		DEC. & VT
date	Jul 28 2010	dfrq	499.693
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
data/Hartwig/stanl~		dof	0
eyl/LS-V-152-1H-U5~		dm	nnn
	00.fid	dmm	c
	ACQUISITION	dmf	200
sfrq	499.693	dseq	
tn	H1	dres	1.0
at	4.665	homo	n
np	65536		DEC2
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	6.5	dm2	n
d1	10.000	dmm2	c
tof	2.0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
	FLAGS	lb	0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
	DISPLAY		
sp	-1012.2	werr	
wp	7024.7	wexp	
vs	43	wbs	wft
sc	0	wnt	
wc	250		
hzmm	28.10		
is	33.57		
rfl	4640.1		
rfp	3627.8		
th	7		
ins	100.000		
ai	ph		

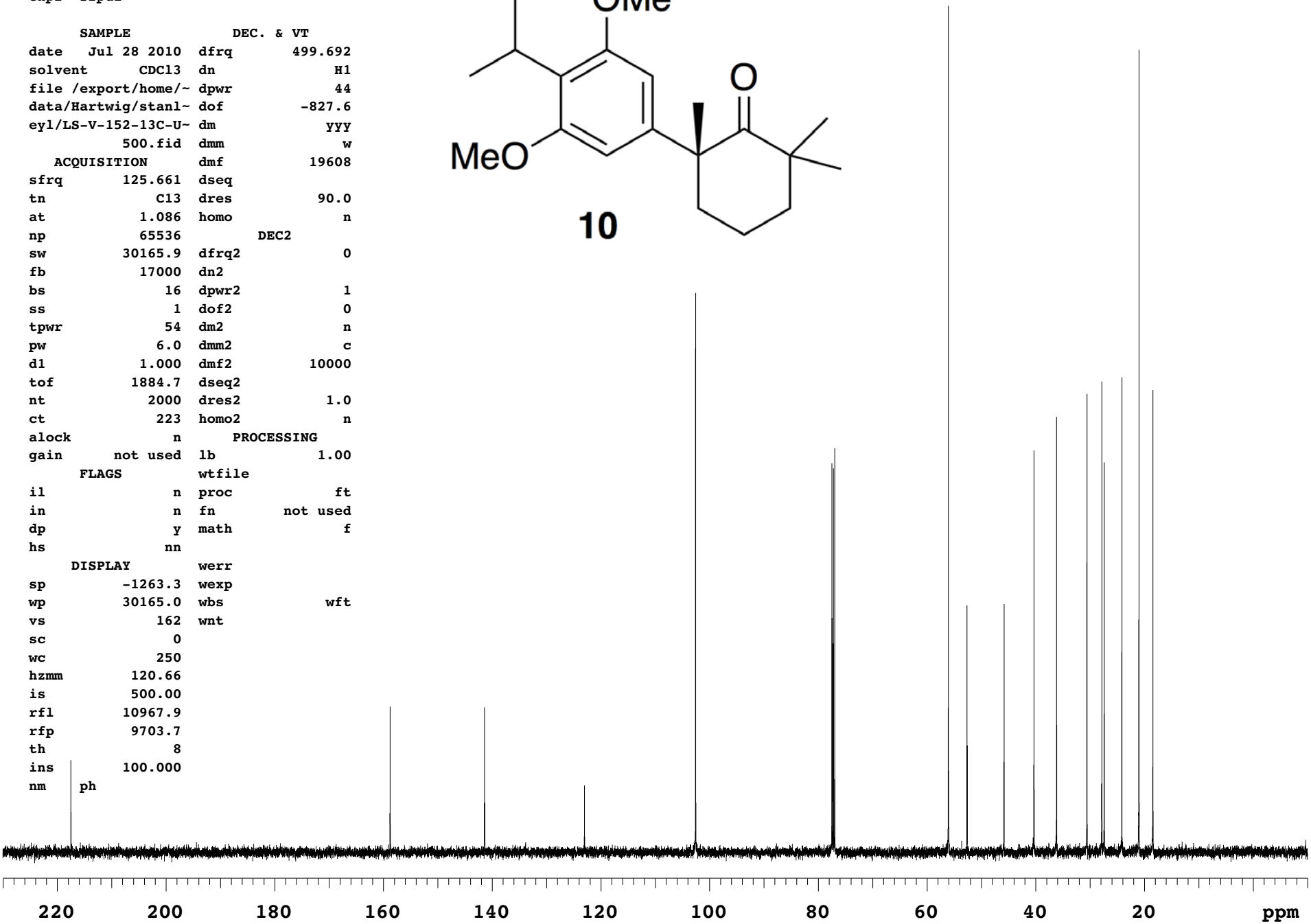
10



LS-V-152-13C-U500

exp2 s2pul

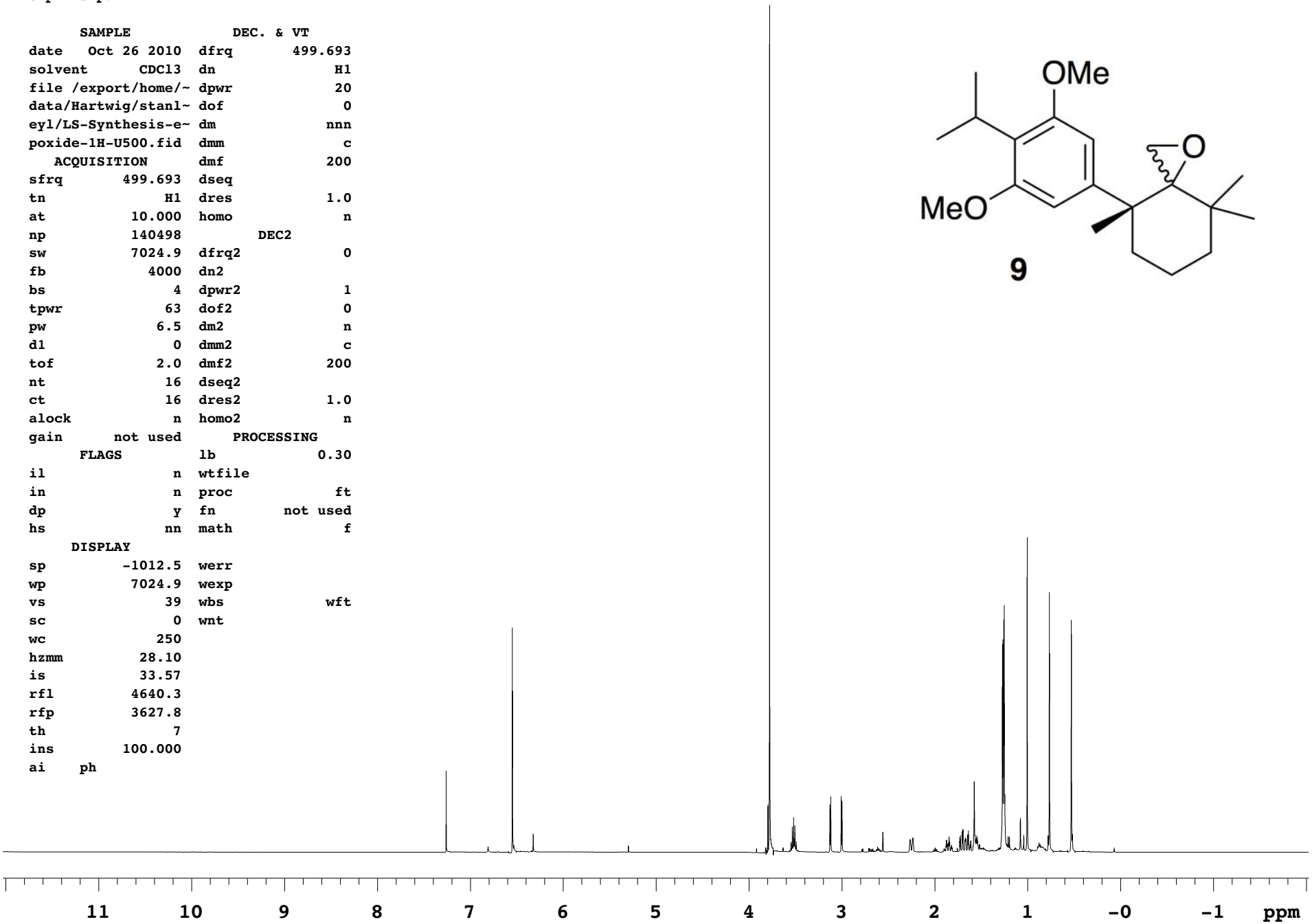
SAMPLE		DEC. & VT	
date	Jul 28 2010	dfrq	499.692
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	44
data/Hartwig/stanl~		dof	-827.6
eyl/LS-V-152-13C-U~		dm	yyy
	500.fid	dmm	w
ACQUISITION		dmf	19608
sfrq	125.661	dseq	
tn	C13	dres	90.0
at	1.086	homo	n
np	65536	DEC2	
sw	30165.9	dfrq2	0
fb	17000	dn2	
bs	16	dpwr2	1
ss	1	dof2	0
tpwr	54	dm2	n
pw	6.0	dmm2	c
d1	1.000	dmf2	10000
tof	1884.7	dseq2	
nt	2000	dres2	1.0
ct	223	homo2	n
alock	n	PROCESSING	
gain	not used	lb	1.00
FLAGS		wtfile	
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nn		
DISPLAY		werr	
sp	-1263.3	wexp	
wp	30165.0	wbs	wft
vs	162	wnt	
sc	0		
wc	250		
hzmm	120.66		
is	500.00		
rfl	10967.9		
rfp	9703.7		
th	8		
ins	100.000		
nm	ph		



LS-Synthesis-epoxide-1H-U500

exp2 s2pul

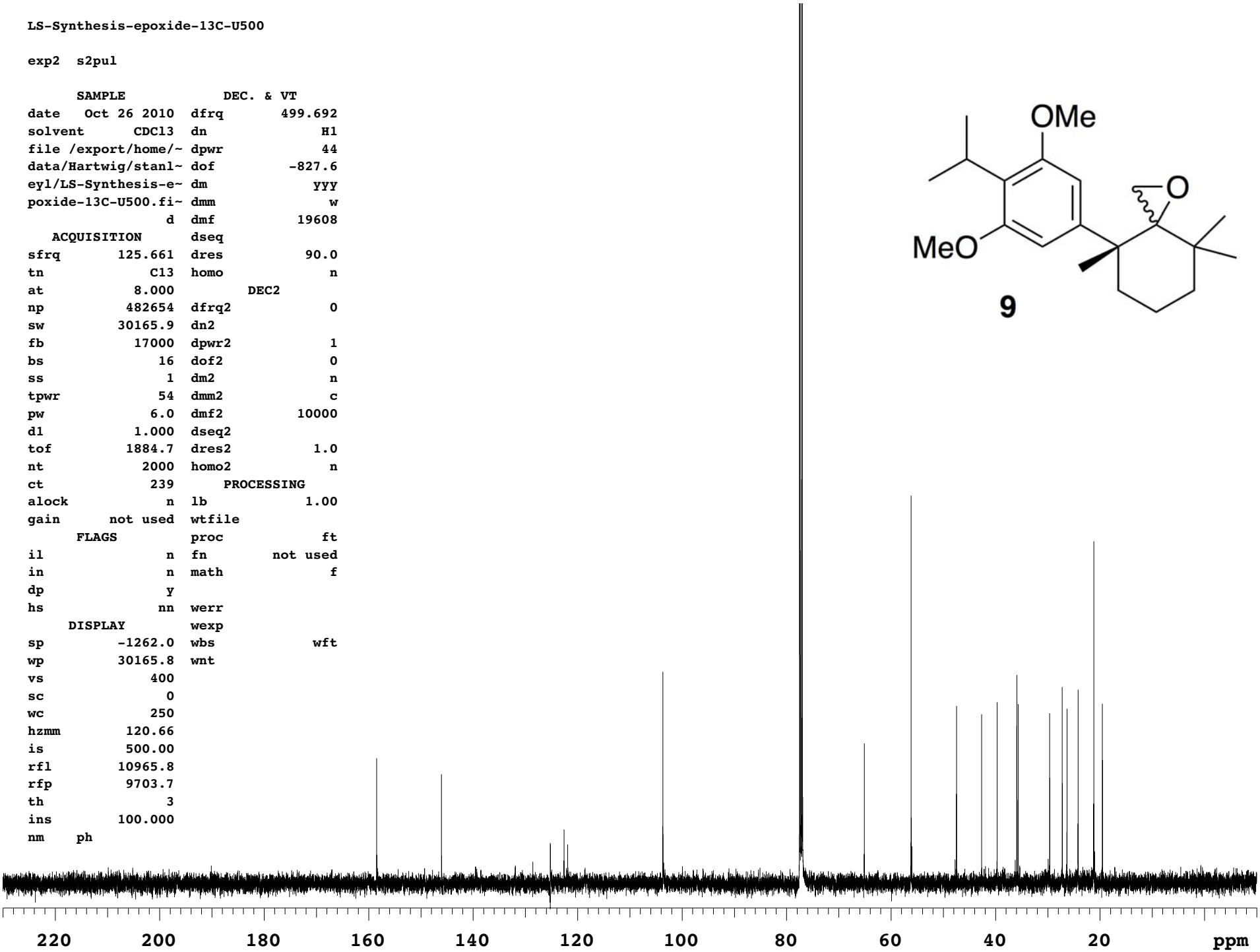
	SAMPLE		DEC. & VT
date	Oct 26 2010	dfrq	499.693
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
data/Hartwig/stanl~		dof	0
eyl/LS-Synthesis-e~		dm	nnn
poxide-1H-U500.fid		dmm	c
	ACQUISITION	dmf	200
sfrq	499.693	dseq	
tn	H1	dres	1.0
at	10.000	homo	n
np	140498		DEC2
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	6.5	dm2	n
d1	0	dmm2	c
tof	2.0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
	FLAGS	lb	0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
	DISPLAY		
sp	-1012.5	werr	
wp	7024.9	wexp	
vs	39	wbs	wft
sc	0	wnt	
wc	250		
hzmm	28.10		
is	33.57		
rfl	4640.3		
rfp	3627.8		
th	7		
ins	100.000		
ai	ph		



LS-Synthesis-epoxide-13C-U500

exp2 s2pul

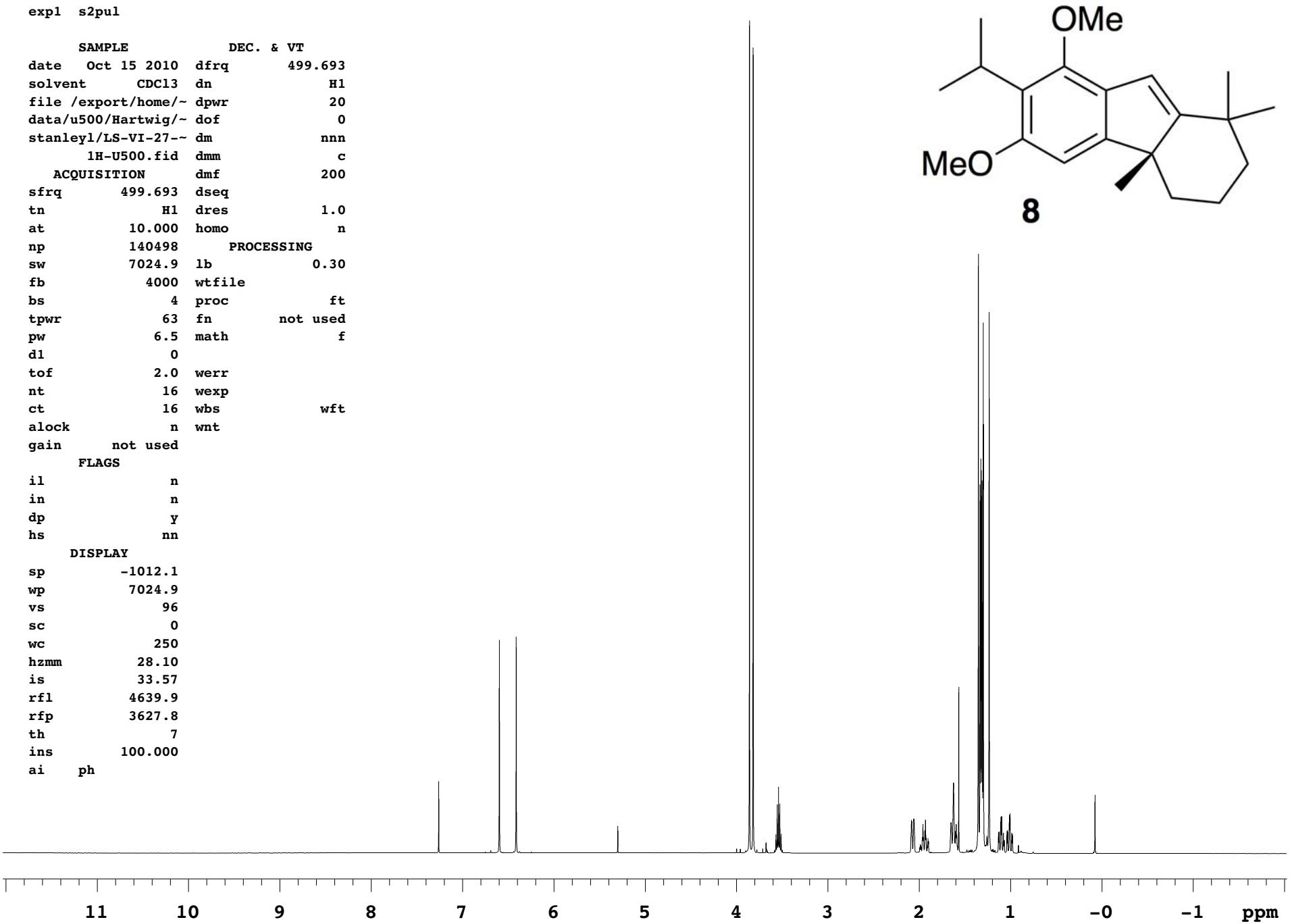
	SAMPLE		DEC. & VT
date	Oct 26 2010	dfrq	499.692
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	44
data/Hartwig/stanl~		dof	-827.6
eyl/LS-Synthesis-e~		dm	yyy
poxide-13C-U500.fi~		dmm	w
	d	dmf	19608
	ACQUISITION	dseq	
sfrq	125.661	dres	90.0
tn	C13	homo	n
at	8.000		DEC2
np	482654	dfrq2	0
sw	30165.9	dn2	
fb	17000	dpwr2	1
bs	16	dof2	0
ss	1	dm2	n
tpwr	54	dmm2	c
pw	6.0	dmf2	10000
d1	1.000	dseq2	
tof	1884.7	dres2	1.0
nt	2000	homo2	n
ct	239		PROCESSING
alock	n	lb	1.00
gain	not used	wtfile	
	FLAGS	proc	ft
il	n	fn	not used
in	n	math	f
dp	y		
hs	nn	werr	
	DISPLAY	wexp	
sp	-1262.0	wbs	wft
wp	30165.8	wnt	
vs	400		
sc	0		
wc	250		
hzmm	120.66		
is	500.00		
rfl	10965.8		
rfp	9703.7		
th	3		
ins	100.000		
nm	ph		



LS-VI-27-1H-U500

exp1 s2pul

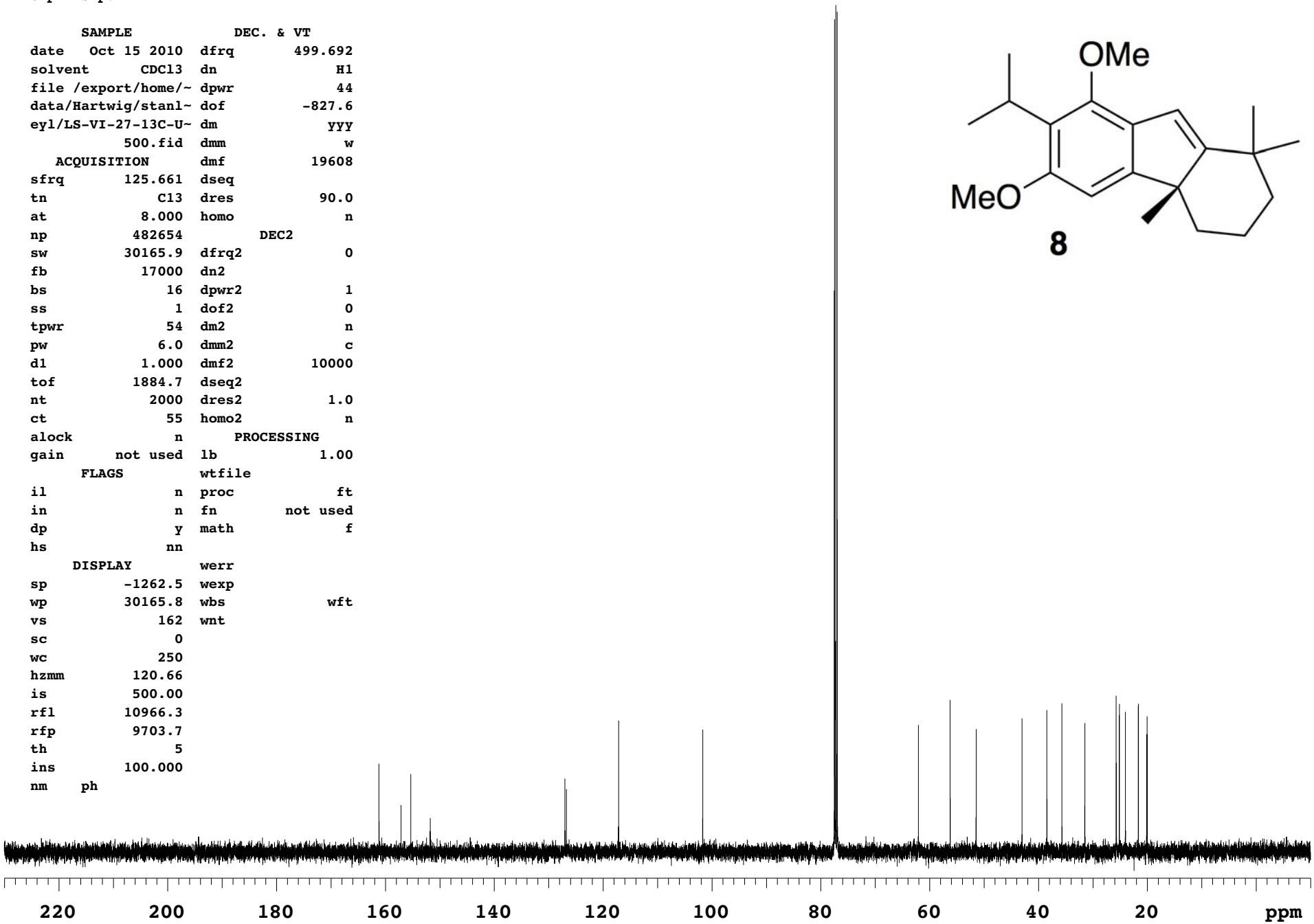
	SAMPLE		DEC. & VT
date	Oct 15 2010	dfrq	499.693
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
data/u500/Hartwig/~		dof	0
stanleyl/LS-VI-27-~		dm	nnn
	1H-U500.fid	dmm	c
	ACQUISITION	dmf	200
sfrq	499.693	dseq	
tn	H1	dres	1.0
at	10.000	homo	n
np	140498		PROCESSING
sw	7024.9	lb	0.30
fb	4000	wtfile	
bs	4	proc	ft
tpwr	63	fn	not used
pw	6.5	math	f
d1	0		
tof	2.0	werr	
nt	16	wexp	
ct	16	wbs	wft
alock	n	wnt	
gain	not used		
	FLAGS		
il	n		
in	n		
dp	y		
hs	nn		
	DISPLAY		
sp	-1012.1		
wp	7024.9		
vs	96		
sc	0		
wc	250		
hzmm	28.10		
is	33.57		
rfl	4639.9		
rfp	3627.8		
th	7		
ins	100.000		
ai	ph		



LS-VI-27-13C-U500

exp2 s2pul

	SAMPLE		DEC. & VT
date	Oct 15 2010	dfrq	499.692
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	44
data/Hartwig/stanl~		dof	-827.6
eyl/LS-VI-27-13C-U~		dm	yyy
	500.fid	dmm	w
	ACQUISITION	dmf	19608
sfrq	125.661	dseq	
tn	C13	dres	90.0
at	8.000	homo	n
np	482654		DEC2
sw	30165.9	dfrq2	0
fb	17000	dn2	
bs	16	dpwr2	1
ss	1	dof2	0
tpwr	54	dm2	n
pw	6.0	dmm2	c
d1	1.000	dmf2	10000
tof	1884.7	dseq2	
nt	2000	dres2	1.0
ct	55	homo2	n
alock	n		PROCESSING
gain	not used	lb	1.00
	FLAGS	wtfile	
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nn		
	DISPLAY	werr	
sp	-1262.5	wexp	
wp	30165.8	wbs	wft
vs	162	wnt	
sc	0		
wc	250		
hzmm	120.66		
is	500.00		
rfl	10966.3		
rfp	9703.7		
th	5		
ins	100.000		
nm	ph		

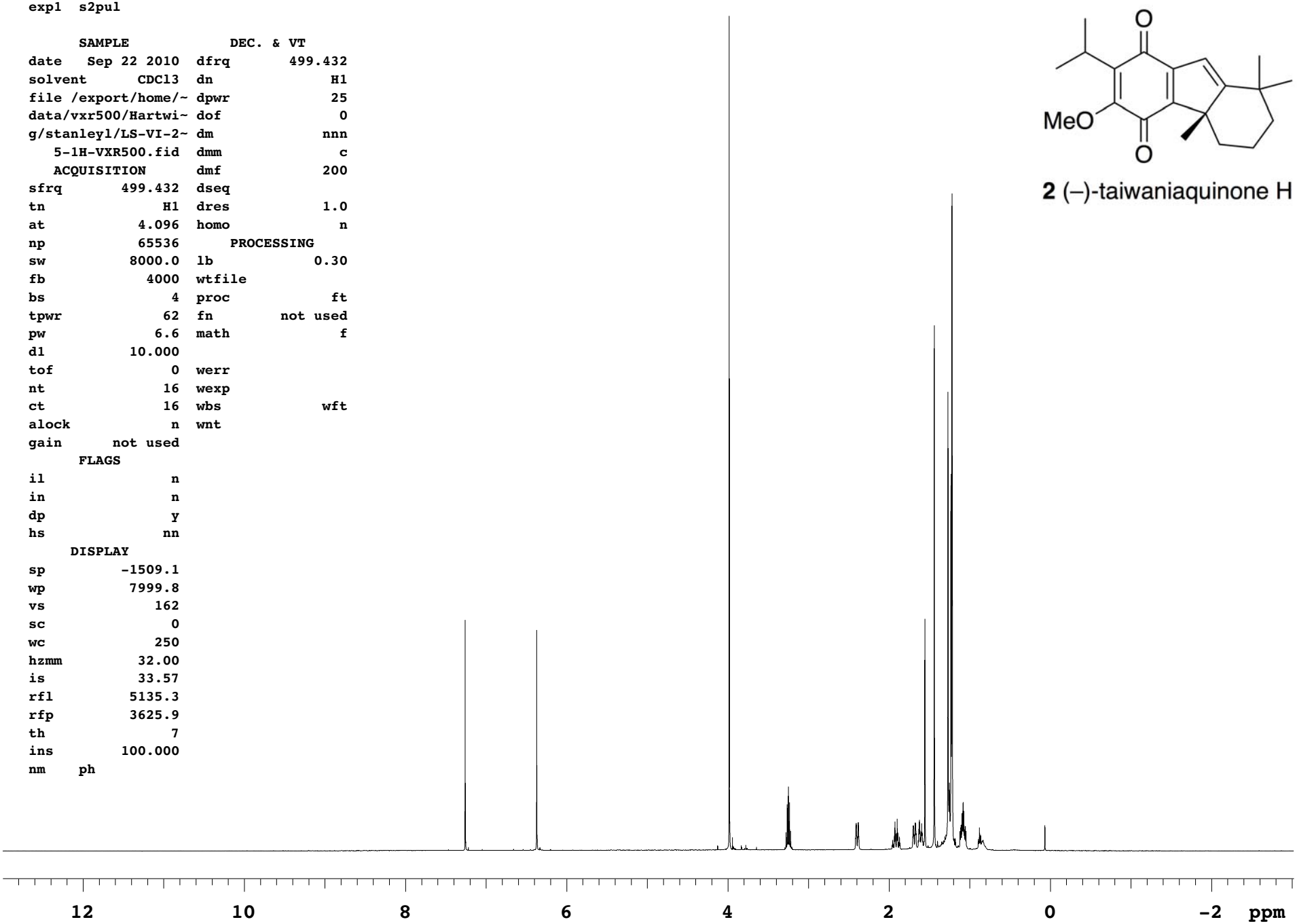


LS-VI-25-1H-VXR500

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 22 2010	dfrq	499.432
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	25
data/vxr500/Hartwi~		dof	0
g/stanleyl/LS-VI-2~		dm	nnn
5-1H-VXR500.fid		dmm	c
ACQUISITION		dmf	200
sfrq	499.432	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	PROCESSING	
sw	8000.0	lb	0.30
fb	4000	wtfile	
bs	4	proc	ft
tpwr	62	fn	not used
pw	6.6	math	f
d1	10.000		
tof	0	werr	
nt	16	wexp	
ct	16	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1509.1		
wp	7999.8		
vs	162		
sc	0		
wc	250		
hzmm	32.00		
is	33.57		
rfl	5135.3		
rfp	3625.9		
th	7		
ins	100.000		
nm	ph		

2 (–)-taiwaniaquinone H



```
LS-VI-25-13C-U500

exp2  s2pul

      SAMPLE            DEC. & VT
date   Sep 24 2010  dfrq       499.692
solvent      CDCl3  dn              H1
file /export/home/~ dpwr            44
data/Hartwig/stanl~ dof         -827.6
eyl/LS-VI-25-13C-U~ dm             yyy
           500.fid  dmm              w
   ACQUISITION      dmf          19608
sfrq       125.661  dseq
tn             C13  dres          90.0
at           6.000  homo             n
np          361990        DEC2
sw         30165.9  dfrq2            0
fb           17000  dn2
bs              16  dpwr2            1
ss               1  dof2             0
tpwr            54  dm2              n
pw             6.0  dmm2             c
d1           1.000  dmf2         10000
tof         1884.7  dseq2
nt            3000  dres2          1.0
ct            1405  homo2            n
alock            n     PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               y  math             f
hs              nn
     DISPLAY        werr
sp         -1262.0  wexp
wp         30165.8  wbs            wft
vs             400  wnt
sc               0
wc             250
hzmm        120.66
is          500.00
rfl        10965.8
rfp         9703.7
th               6
ins        100.000
nm    ph
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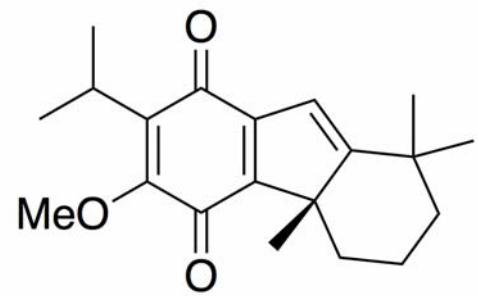
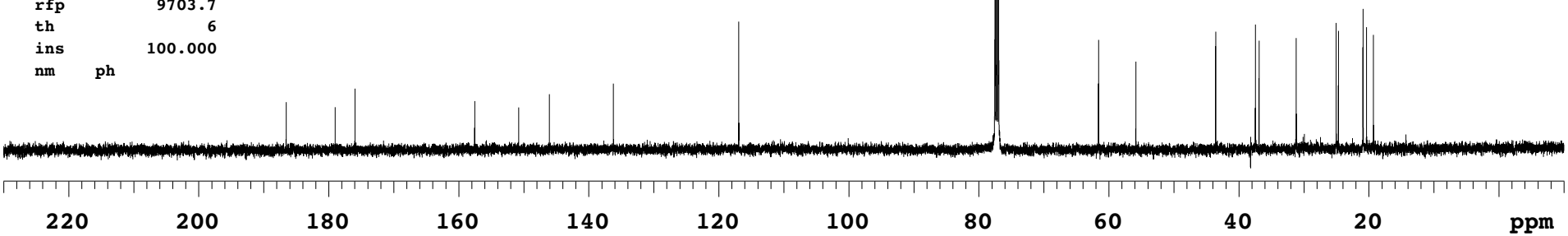


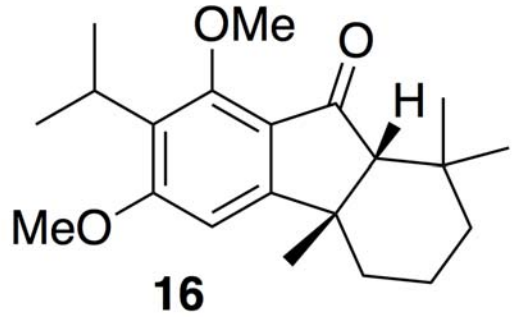
2 (–)-taiwaniaquinone H

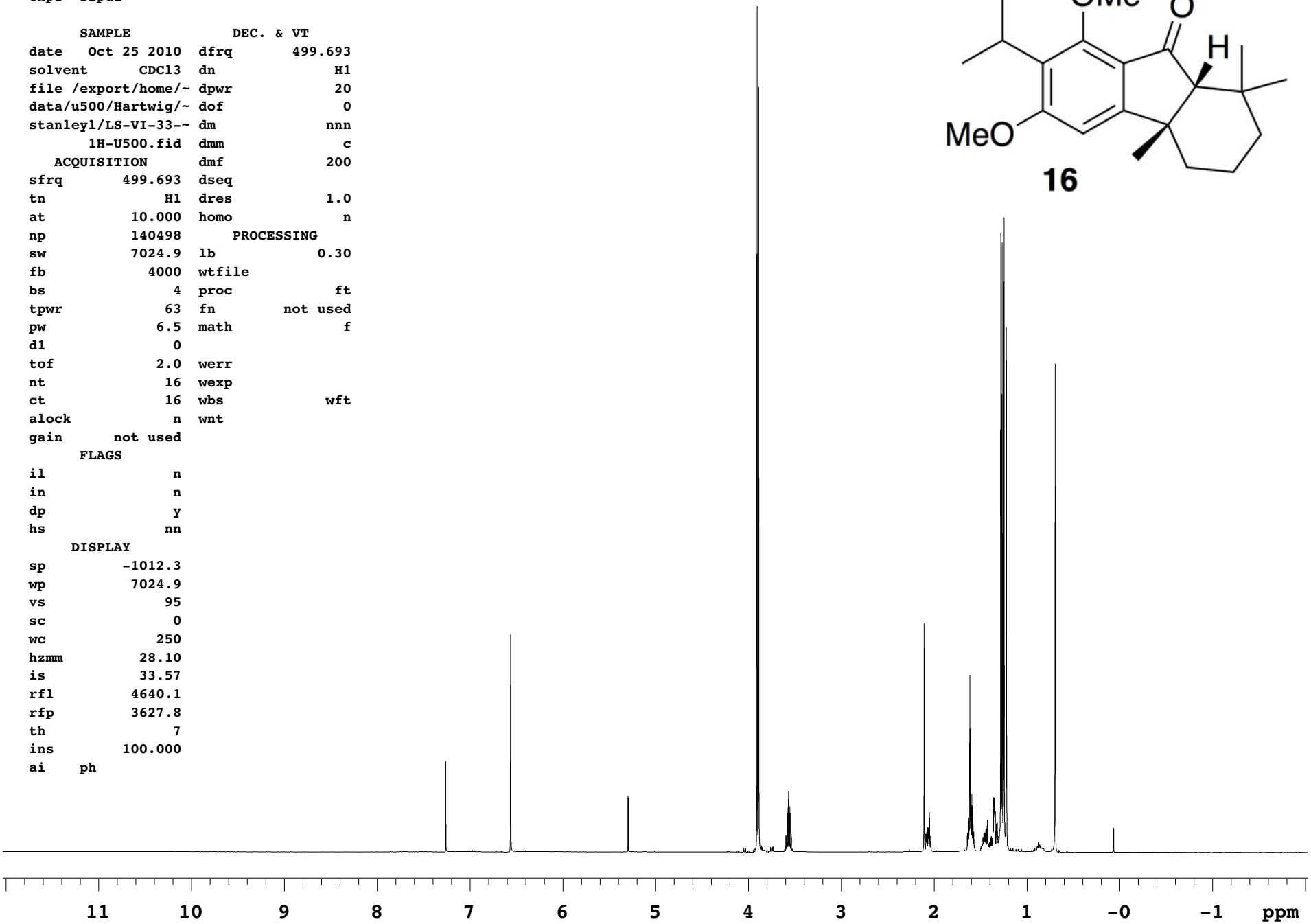


LS-VI-33-1H-U500

exp1 s2pul

	SAMPLE		DEC. & VT
date	Oct 25 2010	dfrq	499.693
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
data/u500/Hartwig/~		dof	0
stanleyl/LS-VI-33-~		dm	nnn
	1H-U500.fid	dmm	c
	ACQUISITION	dmf	200
sfrq	499.693	dseq	
tn	H1	dres	1.0
at	10.000	homo	n
np	140498		PROCESSING
sw	7024.9	lb	0.30
fb	4000	wtfile	
bs	4	proc	ft
tpwr	63	fn	not used
pw	6.5	math	f
d1	0		
tof	2.0	werr	
nt	16	wexp	
ct	16	wbs	wft
alock	n	wnt	
gain	not used		
	FLAGS		
il	n		
in	n		
dp	y		
hs	nn		
	DISPLAY		
sp	-1012.3		
wp	7024.9		
vs	95		
sc	0		
wc	250		
hzmm	28.10		
is	33.57		
rfl	4640.1		
rfp	3627.8		
th	7		
ins	100.000		
ai	ph		

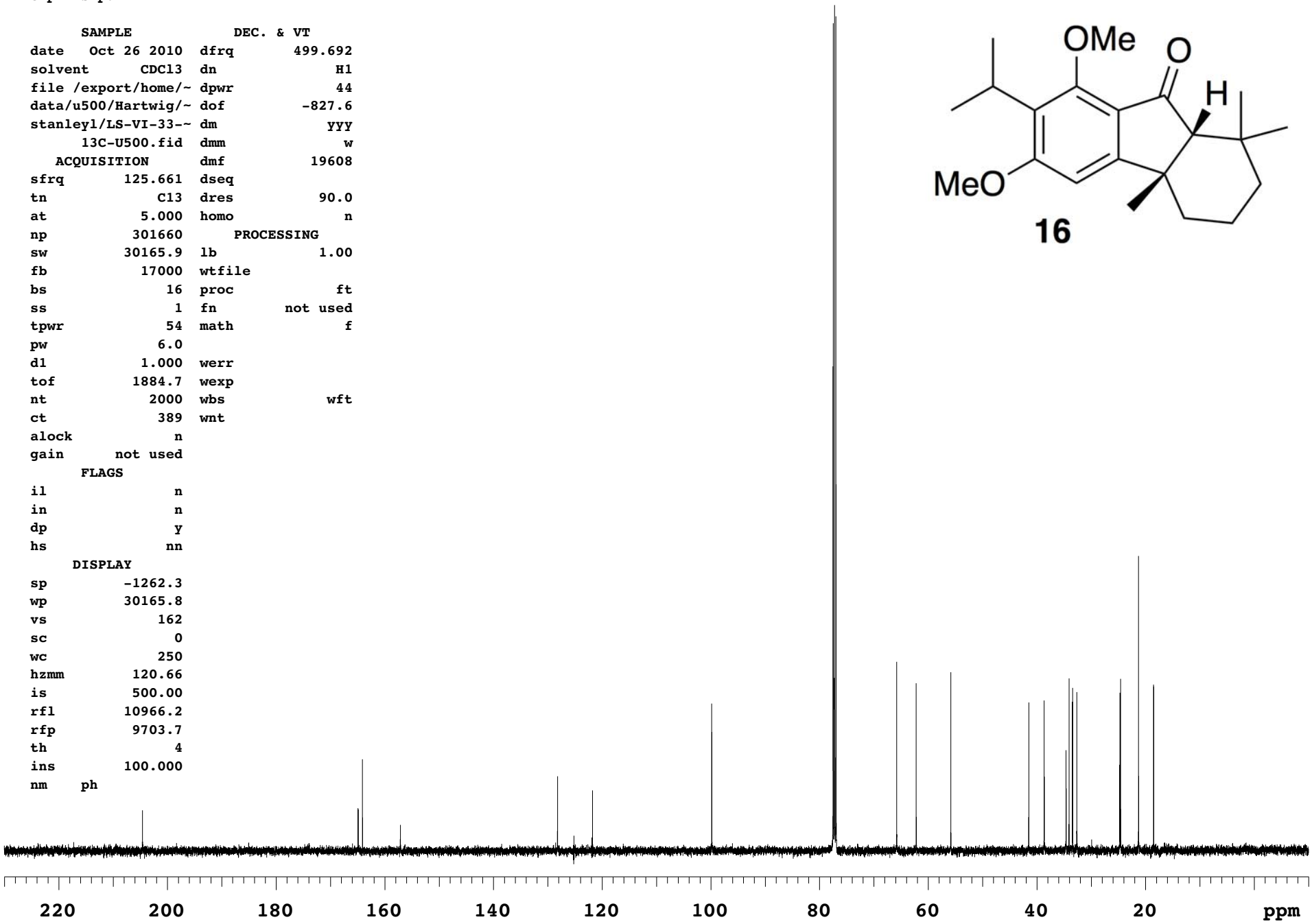




LS-VI-33-13C-U500

exp1 s2pul

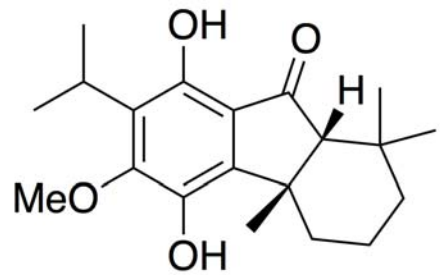
	SAMPLE		DEC. & VT
date	Oct 26 2010	dfrq	499.692
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	44
data/u500/Hartwig/~		dof	-827.6
stanleyl/LS-VI-33-~		dm	yyy
	13C-U500.fid	dmm	w
	ACQUISITION	dmf	19608
sfrq	125.661	dseq	
tn	C13	dres	90.0
at	5.000	homo	n
np	301660		PROCESSING
sw	30165.9	lb	1.00
fb	17000	wtfile	
bs	16	proc	ft
ss	1	fn	not used
tpwr	54	math	f
pw	6.0		
d1	1.000	werr	
tof	1884.7	wexp	
nt	2000	wbs	wft
ct	389	wnt	
alock	n		
gain	not used		
	FLAGS		
il	n		
in	n		
dp	y		
hs	nn		
	DISPLAY		
sp	-1262.3		
wp	30165.8		
vs	162		
sc	0		
wc	250		
hzmm	120.66		
is	500.00		
rfl	10966.2		
rfp	9703.7		
th	4		
ins	100.000		
nm	ph		



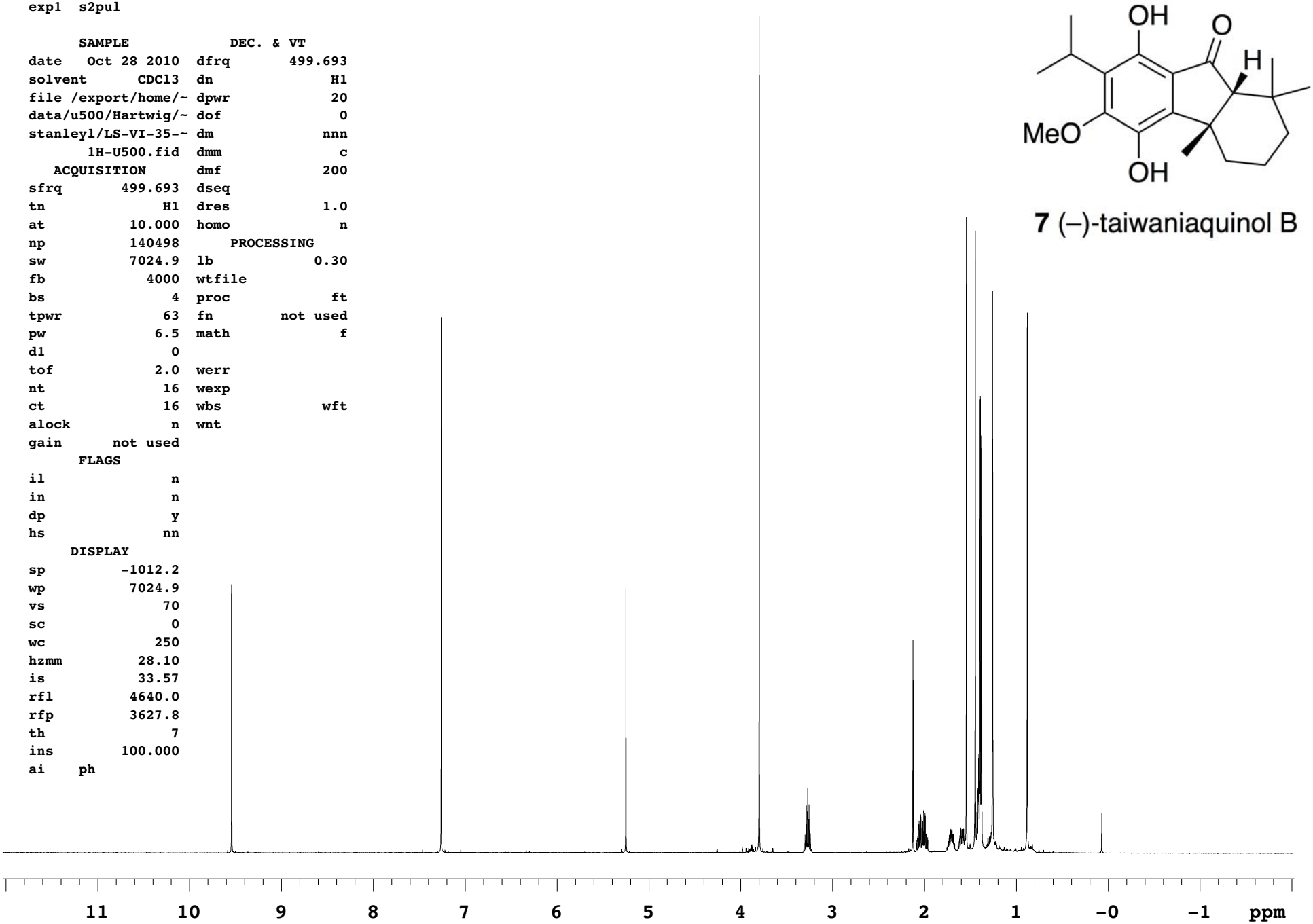
LS-VI-35-1H-U500

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2010	dfrq	499.693
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
data/u500/Hartwig/~		dof	0
stanleyl/LS-VI-35-~		dm	nnn
1H-U500.fid		dmm	c
ACQUISITION		dmf	200
sfrq	499.693	dseq	
tn	H1	dres	1.0
at	10.000	homo	n
np	140498	PROCESSING	
sw	7024.9	lb	0.30
fb	4000	wtfile	
bs	4	proc	ft
tpwr	63	fn	not used
pw	6.5	math	f
d1	0		
tof	2.0	werr	
nt	16	wexp	
ct	16	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1012.2		
wp	7024.9		
vs	70		
sc	0		
wc	250		
hzmm	28.10		
is	33.57		
rfl	4640.0		
rfp	3627.8		
th	7		
ins	100.000		
ai	ph		



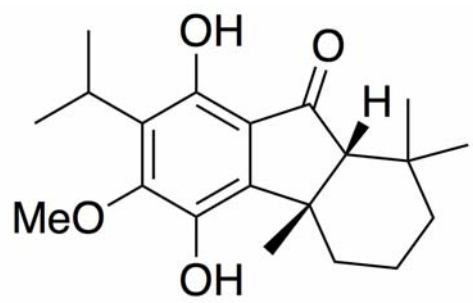
7 (–)-taiwaniaquinol B



LS-VI-35-13C-U500

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2010	dfrq	499.692
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	44
data/u500/Hartwig/~		dof	-827.6
stanleyl/LS-VI-35-~		dm	yyy
13C-U500.fid		dmm	w
ACQUISITION		dmf	19608
sfrq	125.661	dseq	
tn	C13	dres	90.0
at	7.000	homo	n
np	422322	PROCESSING	
sw	30165.9	lb	1.00
fb	17000	wtfile	
bs	16	proc	ft
ss	1	fn	not used
tpwr	54	math	f
pw	6.0		
d1	1.000	werr	
tof	1884.7	wexp	
nt	2000	wbs	wft
ct	1332	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1250.8		
wp	30165.8		
vs	1500		
sc	0		
wc	250		
hzmm	120.66		
is	500.00		
rfl	10954.7		
rfp	9703.7		
th	6		
ins	100.000		
nm	ph		



7 (–)-taiwaniaquinol B