Synthesis of an Advanced Intermediate for (+)-Pillaromycinone. Staunton-Weinreb Annulation Revisited

James D. White, F.W.J. Demnitz, Qing Xu, and William H.C. Martin*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003.

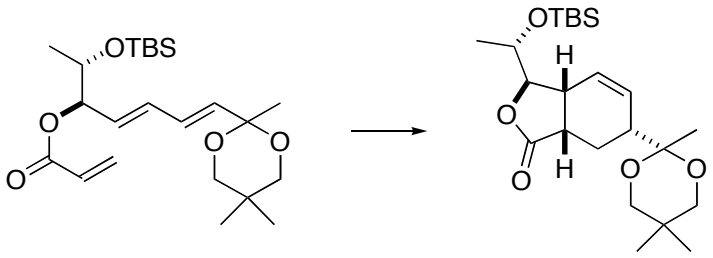
james.white@oregonstate.edu

SUPPORTING INFORMATION

General techniques: All reactions requiring anhydrous conditions were conducted in flame-dried glass apparatus under an atmosphere of argon. THF, Et_2O, CH_2Cl_2, DMF, benzene and acetonitrile were dried by passage through an activated alumina column under argon. DMSO was distilled from CaH_2 at 15 mm Hg and stored over activated 4Å molecular sieves. Anhydrous MeOH was freshly distilled from magnesium ethoxide. Preparative chromatographic separations were performed on silica gel (35-75 μm); reactions were followed by TLC analysis using silica plates with fluorescent indicator (254 nm) and visualized with a UV lamp or phosphomolybdic acid. All commercially available reagents were purchased from Aldrich and used as received unless stated otherwise.

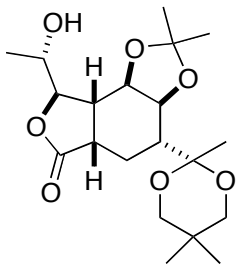
Optical rotations were measured with a polarimeter using a 1 mL capacity cell with 1 dm path length. Infrared spectra were recorded using a thin film supported on KBr discs or dispersed in a KBr pellet. ^1H and ^{13}C NMR spectra were recorded in Fourier transform mode at the field strength specified on either a 300 or 400 MHz spectrometer. Spectra were obtained on $CDCl_3$ solutions in 5 mm diameter tubes, and chemical shifts in ppm are quoted relative to the residual signals of chloroform (δ_H 7.26 ppm, or δ_C 77.0 ppm). Multiplicities in the ^1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra are reported with ion mass/charge (*m/z*) ratios as values in atomic mass units.

EXPERIMENTAL SECTION



8

Lactone 8. A solution of the acrylate[8] (2.57 g, 6.06 mmol) in toluene (60 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (100 mg) was heated in a sealed tube at 230 °C for 55 h. The solvent was evaporated leaving a yellow solid which was passed through a column of silica gel (hexane:EtOAc 85:15) to give a mixture of **8** and its trans fused isomer (1.29 g) as a colorless solid. The solid was taken up into benzene (50 mL) and NaH (7.4 mg, 0.1 mol%) and diisopropylethylamine (1.0 mg) were added. The mixture was heated at reflux for 12 h, after which the solvent was removed to leave a colorless crystalline solid. Recrystallization from hexane gave **8** (1.28 g, 50%) as colorless needles: mp 111-112 °C; $[\alpha]^{23}_{D}$ +20.8 (c 1.2 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.08 (3H, s), 0.09 (3H, s), 0.86 (3H, s), 0.88 (9H, s), 1.05 (3H, s), 1.22 (3H, d, *J* = 6 Hz), 1.34 (3H, s), 1.48 (1H, ddd, *J* = 13, 13, 11 Hz), 2.23 (1H, ddd, *J* = 13, 5.5 Hz), 2.56 (1H, m), 2.77 (1H, ddd, *J* = 13, 9.5 Hz), 3.08 (1H, m), 3.42 (2H, d, *J* = 12 Hz), 3.59 (1H, d, *J* = 12 Hz), 3.61 (1H, d, *J* = 12 Hz), 4.07 (2H, m), 5.76 (1H, ddd, *J* = 10, 3, 3 Hz), 6.01 (1H, d, *J* = 10 Hz); ^{13}C NMR ($CDCl_3$) δ -4.7, -4.6, 16.7, 18.0, 20.2, 22.5, 23.0, 23.6, 25.8, 30.0, 35.1, 39.7, 42.2, 69.0, 70.1, 70.4, 87.2, 99.6, 126.5, 129.8, 178.5; HRMS *m/z* 409.2408 (M^+ -15, calcd for $C_{22}H_{37}O_5Si$ *m/z* 409.2410). Anal. Calcd for $C_{23}H_{40}O_5Si$: C, 65.05; H, 9.49. Found: C, 64.85; H, 9.26



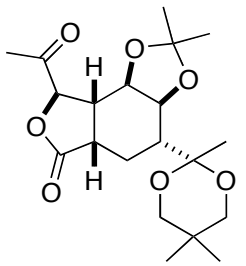
9

Alcohol 9. A solution of **8** (23 mg, 0.054 mol), N-methylmorpholine-N-oxide (14 mg, 0.119 mol) and OsO_4 (0.046M in *t*-BuOH, 0.06 mL, 0.0027 mmol) in THF (1 mL) and H_2O (0.2 mL) was stirred at room temperature for 21 h. The reaction was quenched with an aqueous slurry of $Na_2S_2O_3$ and Celite, and the resulting mixture was stirred vigorously for 10 min and was filtered. The filtrate was extracted with EtOAc (5x), the extract was washed with 1M HCl and then with satd. aqueous $NaHCO_3$, and was dried ($MgSO_4$). The filtrate was concentrated in vacuo to leave a pale yellow oil which was chromatographed on silica gel (hexane:EtOAc 1:1) to give a diol (23 mg, 94%) as a colorless oil: $[\alpha]^{23}_D$ +29.4 (c 9.6, $CHCl_3$); IR (film) 3468, 1772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (3H, s), 0.09 (3H, s), 0.88 (9H, s), 1.17 (3H, s), 1.20 (3H, d, *J* = 6 Hz), 1.28 (1H, ddd, *J* = 13, 13, 13 Hz), 1.42 (3H, s), 1.96 - 2.08 (2H, m), 2.69 (1H, ddd, *J* = 9, 8, 5 Hz), 2.88 (2H, m), 3.42 (2H, d, *J* = 12 Hz), 3.67 (1H, d, *J* = 12 Hz), 3.72 (1H, d, *J* = 12 Hz), 3.78 (1H, dd, *J* = 8, 4 Hz), 4.07 (1H, dq, *J* = 6, 4 Hz), 4.20 (1H, dd, *J* = 7, 4 Hz), 4.28 (1H, dd, *J* = 5, 4 Hz); ^{13}C NMR ($CDCl_3$) δ -4.8, -4.7, 15.6, 18.0, 19.8, 21.9, 22.3, 23.3, 25.8, 30.1, 38.0, 38.9, 48.3, 68.1, 68.6, 69.7, 70.2, 84.3, 101.0, 178.6; MS *m/z* 443 (M^+ -15), 129; HRMS *m/z* 443.2466 (calcd for $C_{22}H_{37}O_7Si$ 443.2465).

To a solution of the diol obtained above in CH_2Cl_2 (1.5 mL) containing 2,2-dimethoxypropane (0.28 mL, 2.28 mmol) was added a trace of *p*-toluenesulfonic acid and the solution was stirred at room temperature for 30 min, after which a further quantity of 2,2-dimethoxypropane (0.01 mL, 0.081 mmol) was added. Stirring was continued for 1 h, solid K_2CO_3 was added and the mixture was concentrated in vacuo. The residue was taken up in a small volume of hexane:EtOAc and was filtered through a short plug of silica gel. The filtrate was concentrated to give an acetonide (24 mg, 98%) as a colorless foam: $[\alpha]^{23}_D$ +39.0 (c 9.7, $CHCl_3$); IR (film) 1778 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.46 (3H, s), 0.72 (3H, s), 0.76 (3H, s), 0.86 (9H, s), 1.14 (3H, 2), 1.15 (3H, d, *J* = 6 Hz), 1.29 (1H, m), 1.36 (3H, s), 1.48 (3H, s), 1.49 (3H, s), 1.89 (1H, ddd, *J* = 14, 7, 2 Hz), 2.35 (1H, ddd, *J* = 14, 9, 2 Hz), 2.43 (1H, ddd, *J* = 11, 11, 1 Hz), 2.96 (1H, ddd, *J* = 11, 11, 9 Hz),

3.37 (2H, m), 3.69 (1H, d, *J* = 12 Hz), 3.72 (1H, d, *J* = 12 Hz), 3.91 (1H, dd, *J* = 11, 6 Hz), 4.14 (1H, dq, *J* = 6, 2 Hz), 4.24 (1H, broad s), 4.46 (1H, dd, *J* = 7, 6 Hz); ^{13}C NMR ($CDCl_3$) δ -4.9, 16.6, 17.9, 19.2, 19.6, 22.3, 23.3, 25.7 (x2), 28.3, 30.0, 36.7, 38.5, 48.4, 69.3, 70.2, 70.3, 74.1, 76.1, 86.0, 98.9, 109.1, 179.2; MS *m/z* 483 (M^+ -15), 129; HRMS *m/z* 483.2777 (calcd for $C_{25}H_{43}O_7Si$ 483.2778).

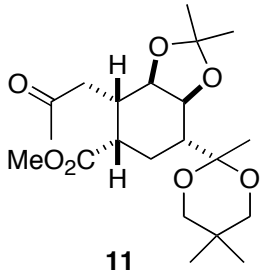
To a solution of the acetonide obtained above (20 mg, 0.04 mmol) in THF (1 mL) was added a solution of *tetra*-*N*-butylammonium fluoride in THF (1M, 0.05 mL, 0.05 mmol) and the mixture was stirred at room temperature for 5 h. Satd. aqueous NH_4Cl was added and the mixture was extracted with EtOAc (3x). The extract was washed with satd. aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated in vacuo to leave an oil which was chromatographed on silica gel to give **9** (15 mg, 98%) as a colorless oil: $[\alpha]^{23}_D$ +54.9 (c 8.2, $CHCl_3$); IR (film) 3470, 1771 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.77 (3H, s), 1.13 (3H, d, *J* = 6 Hz), 1.30 (1H, ddd, *J* = 14, 14, 3 Hz), 1.36 (3H, s), 1.46 (3H, s), 1.49 (3H, s), 1.91 (1H, ddd, *J* = 14, 7, 3 Hz), 2.08 (1H, d, *J* = 5 Hz), 2.33 (1H, ddd, *J* = 14, 9, 3 Hz), 2.48 (1H, ddd, *J* = 11, 10, 1 Hz), 3.07 (1H, ddd, *J* = 12, 10, 9 Hz), 3.37 (2H, m), 3.69 (1H, d, *J* = 12 Hz), 3.70 (1H, d, *J* = 12 Hz), 3.94 (1H, dd, *J* = 11, 6 Hz), 4.12 (1H, m), 4.29 (1H, dd, *J* = 2, 1 Hz), 4.48 (1H, dd, *J* = 7, 6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.7, 18.4, 19.6, 22.3, 23.3, 25.8, 28.3, 29.9, 37.0, 38.2, 48.1, 68.6, 70.2, 70.3, 74.1, 76.0, 85.9, 98.8, 109.2, 179.3; MS *m/z* 369 (M^+ -15), 129; HRMS *m/z* 369.1911 (calcd for $C_{19}H_{29}O_7$ 369.1913).



10

Ketone 10. To a solution of oxalyl chloride (0.045 mL, 0.516 mmol) in CH_2Cl_2 (1 mL) at -55 °C was added DMSO (0.075 mL, 1.057 mmol) followed by a solution of **9** (156 mg, 0.406 mmol) in CH_2Cl_2 (0.5 mL). The solution was allowed to warm to -25 °C during 0.5 h, after which Et_3N (0.3 mL, 2.15 mmol) was added. The solution was allowed to warm to room temperature, H_2O (5 mL) was added and the mixture was extracted with EtOAc (2x). The

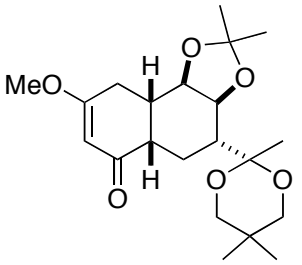
extract was washed with 5M HCl and satd. aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo. The resulting colorless foam was chromatographed on silica gel (EtOAc:hexane 55:45) to give **10** (114 mg, 73%) as a solid which crystallized as colorless plates from ethyl acetate – hexane: mp 135.5-136 °C; $[\alpha]^{23}_D$ +3.2 (c 7.6, $CHCl_3$); IR 1785, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3H, s), 1.13 (3H, s), 1.38 (1H, m), 1.38 (3H, s), 1.46 (3H, s), 1.51 (3H, s), 1.85 (1H, ddd, *J* = 14, 7, 3 Hz), 2.28 (3H, s), 2.38 (1H, ddd, *J* = 14, 9, 3 Hz), 2.50 (1H, ddd, *J* = 10, 10, 1 Hz), 2.83 (1H, ddd, *J* = 10, 9, 9 Hz), 3.36 (2H, m), 3.69 (1H, d, *J* = 12 Hz), 3.71 (1H, d, *J* = 12 Hz), 3.96 (1H, dd, *J* = 10, 6 Hz), 4.48 (1H, dd, *J* = 7, 6 Hz), 4.86 (1H, d, *J* = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 16.7, 19.2, 22.3, 23.3, 25.8, 26.1, 28.3, 30.0, 35.9, 40.3, 47.9, 70.3, 74.0, 75.0, 82.9, 98.7, 109.6, 177.8, 203.9; MS *m/z* 367 (M^+ -15), 129; HRMS *m/z* 367.1756 (calcd for $C_{19}H_{27}O_7$ 367.1757). Anal. Calcd for $C_{20}H_{30}O_7$: C, 62.81; H, 7.91. Found: C, 62.64; H, 7.98.



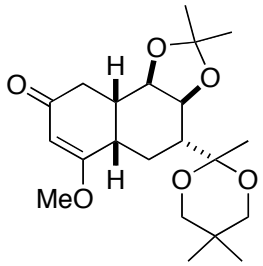
11

Keto Ester 11. To a solution of **10** (440 mg, 1.15 mmol) in THF (7 mL) containing anhydrous $FeCl_3$ (5 mg) was added a freshly prepared solution of SmI_2 (0.1M, 32 mL, 3.2 mmol). The initially brown solution changed to olive green then to blue-green during 15 min, after which the reaction was quenched with satd. aqueous NH_4Cl. The resulting two-phase mixture was separated, the aqueous phase was extracted with EtOAc (2x) and the combined organic solution was washed with aqueous sodium thiosulfate (2x), H_2O, and satd. aqueous NH_4Cl. The solution was dried ($MgSO_4$) and the solvent was removed in vacuo to leave a colorless oil that was taken up into Et_2O (10 mL). To the solution was added an excess of an ethereal solution of CH_2N_2. After 5 min, excess CH_2N_2 was removed in a stream of N_2 and the solution was passed through a short column of silica gel (EtOAc:hexane). The filtrate was concentrated to leave a solid which was crystallized from hexane to give **11** (356 mg, 78%) as colorless prisms:
mp 99-100 °C; $[\alpha]^{23}_D$ +9.4 (c 0.35, $CHCl_3$); IR (KBr) 1719, 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (3H, s); 1.11 (3H, s), 1.32 (3H, s), 1.43 (3H, s), 1.47 (3H, s), 1.59 (1H, ddd, *J* = 13, 12, 12 Hz),

1.98 (1H, ddd, *J* = 13, 9, 4 Hz), 2.19 (1H, m), 2.15 (3H, s), 2.50 (1H, d, *J* = 6 Hz), 2.51 (1H, d, *J* = 6 Hz), 2.75 (1H, dddd, *J* = 6, 6, 6, 6 Hz), 3.00 (1H, ddd, *J* = 12, 6, 6 Hz), 3.37 (2H, m), 3.65 (3H, s), 3.67 (1H, d, *J* = 11 Hz), 3.71 (1H, d, *J* = 11 Hz), 4.05 (1H, dd, *J* = 6, 6 Hz), 4.27 (1H, dd, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 17.3, 21.1, 22.4, 23.3, 26.1, 28.2, 30.0, 30.3, 32.9, 39.8, 42.1, 47.3, 51.6, 70.0, 70.1, 73.5, 76.5, 99.3, 108.2, 175.5, 207.0; MS *m/z* 398 (M^+), 129; HRMS *m/z* 398.2305 (calcd for $C_{21}H_{34}O_7$ 398.2304). Anal. Calcd for $C_{21}H_{34}O_7$: C, 63.29; H, 8.60. Found: C, 63.30; H, 8.80.



12



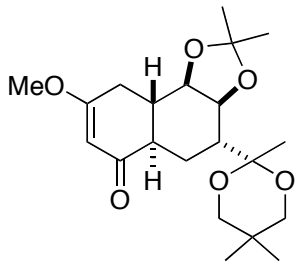
13

Methoxy Enones 12 and 13. To a solution of **11** (183 mg, 0.46 mmol) in benzene (25 mL) was added a solution of *t*-BuOK in *t*-BuOH (0.26M, 6 mL, 1.54 mmol) and the mixture was stirred at room temperature for 2.5 h. The reaction was quenched with satd. aqueous NH_4Cl and the mixture was extracted with Et_2O (3x). The extract was dried ($MgSO_4$) and concentrated to leave an oil that was taken up into Et_2O and treated with an excess of ethereal CH_2N_2. After 1 h, excess CH_2N_2 was removed in a stream of N_2, the solvent was removed in vacuo and the residue was chromatographed on silica gel to give less polar **12** (77 mg, 44%) followed by more polar **13** (84 mg, 48%), both as colorless oils.

12: $[\alpha]^{23}_D$ +31.6 (c 0.49, $CHCl_3$); IR 1653, 1612 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 0.76 (3H, s), 1.05 (3H, s), 1.33 (3H, s), 1.48 (3H, s), 1.49 (3H, s), 1.52 (1H, ddd, *J* = 14, 13, 13 Hz), 1.99 (1H, ddd, *J* = 13, 9, 4 Hz), 2.13 (1H, ddd, *J* = 14, 4, 4 Hz), 2.36 (1H, dd, *J* = 18, 6 Hz), 2.49 (1H, dd, *J* = 18, 10 Hz), 2.63 (2H, m), 3.65 (1H, d, *J* = 11 Hz), 3.69 (1H, d, *J* = 11 Hz), 3.71 (3H, s), 4.00 (1H, dd, *J* = 5, 4 Hz), 4.28 (1H, dd, *J* = 9, 5 Hz), 5.36 (1H, s); MS *m/z* 380 (M^+), 129; HRMS *m/z* 365.1962 (M^+ -15) (calcd for $C_{20}H_{29}O_6$ 365.1964).

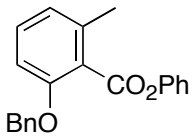
13: $[\alpha]^{23}_D$ -108.6 (c 0.22, $CHCl_3$); IR (film) 1656, 1606 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (3H, s), 1.07 (3H, s), 1.34 (3H, s), 1.49 (3H, s), 1.51 (3H, s), 1.53 (1H, m), 1.96 (1H, ddd, *J* = 13, 9, 4

Hz), 2.23 (1H, ddd, J = 14, 4, 4 Hz), 2.38 (2H, s), 2.69 (2H, m), 3.33 (2H, m), 3.67 (1H, d, J = 11 Hz), 3.71 (3H, s), 3.75 (1H, d, J = 11 Hz), 3.99 (1H, dd, J = 5, 2 Hz), 4.25 (1H, dd, J = 9, 5 Hz), 5.35 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.5, 22.3, 22.4, 23.4, 26.5, 28.4, 30.0, 34.9, 36.0, 36.3, 48.4, 56.0, 69.8, 70.0, 72.9, 77.3, 99.2, 101.5, 107.6, 181.8, 197.6; MS *m/z* 380 (M^+), 129; HRMS *m/z* 380.2198 (calcd for $C_{21}H_{32}O_6$ 380.2199).



14

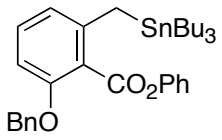
Isomerization of 12. Methoxy Enone 14. To a solution of **12** (170 mg, 0.46 mmol) in MeOH (10 mL) was added a solution of NaOMe (36 mg, 0.66 mmol) in MeOH (1.7 mL) and the mixture was stirred at room temperature for 3 h. The solution was diluted with Et_2O (20 mL), washed with brine and dried (Na_2SO_4). The solvent was removed in vacuo and the residual oil was chromatographed on silica gel (hexane:EtOAc 3:1) to give **14** (130 mg, 71%) as a colorless oil: $[\alpha]^{23}_D$ +68.6 (c 1.00 $CHCl_3$); IR (film) 1653, 1611 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (3H, s), 1.38 (3H, s), 1.46 (3H, s), 1.48 (3H, s), 1.58 (3H, s), 1.67 (1H, m), 1.87 (1H, m), 2.21 (1H, ddd, J = 17, 12, 2 Hz), 2.29 (2H, m), 2.36 (2H, m), 2.71 (1H, dd, J = 17, 5 Hz), 3.31 (1H, dd, J = 11, 2 Hz), 3.38 (1H, dd, J = 12, 2 Hz), 3.68 (3H, s), 3.61 (1H, d, J = 11 Hz), 3.72 (1H, d, J = 12 Hz), 3.92 (1H, dd, J = 9, 6 Hz), 4.64 (1H, dd, J = 5, 2 Hz), 5.34 (1H, d, J = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 16.6, 20.5, 22.4, 23.5, 28.6, 29.9, 33.3, 40.6, 42.9, 45.3, 55.7, 70.1, 70.4, 73.5, 79.4, 100.3, 102.0, 107.4, 177.0, 200.0; MS *m/z* 381 (M^+ +1), 307; HRMS *m/z* 381.2277 (calcd for $C_{21}H_{33}O_6$ 381.2277).



16

Benzoate 16. A mixture of ethyl 2-hydroxy-6-methylbenzoate (2.88 g, 16.0 mmol), benzyl bromide (2.40 mL, 20.2 mmol), tetra-*n*-butylammonium iodide (60 mg, 0.16 mmol) and sodium hydride (50% dispersion in mineral oil, 850 mg, 17.8 mmol) in THF (40 mL) was stirred at room temperature for 28 h. The mixture was diluted with EtOAc (30 mL), washed with satd. aqueous NH_4Cl and with satd. aqueous $NaHCO_3$, and dried ($MgSO_4$). After filtration and removal of the solvent, the residual crude benzyl ether was taken up into a mixture of EtOH (30 mL) and H_2O (20 mL) containing NaOH (2.0 g, 50 mmol). The mixture was refluxed for 48 h, cooled, acidified to pH 2, and extracted with EtOAc (3x). This solution was extracted with aqueous 1N NaOH (5x) and the combined basic extracts were acidified with concd HCl and extracted with EtOAc (5x). The extract was washed with brine and dried ($MgSO_4$), and the solvent was removed in vacuo to leave the crude carboxylic acid as a yellow-orange oil.

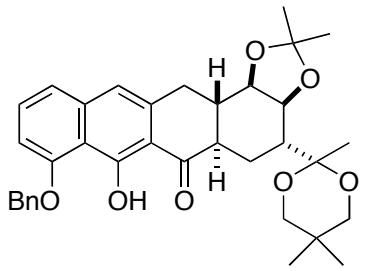
To a solution of the crude carboxylic acid obtained above in benzene (40 mL) was added $(COCl)_2$ (3.5 mL, 40 mmol) and the solution was stirred at room temperature for 24 h. The solvent was removed in vacuo, the residue was taken up into CH_2Cl_2 (30 mL), and phenol (1.65 g, 17.5 mmol) followed by dry pyridine (15 mL) were added. The solution was stirred at room temperature for 22 h, then was washed with 10% HCl (2x), satd. aqueous $CuSO_4$ and brine. The solution was dried ($MgSO_4$) and concentrated in vacuo to leave a reddish colored oil which was chromatographed on silica gel (hexane:EtOAc 9:1) to give **16** (3.40 g, 67%) as a solid. This material crystallized from hexane as colorless fluffy prisms: mp 81.5-82.5 °C; IR (KBr) 1746, 1587 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 5.16 (2H, s), 6.87 (1H, d, J = 8 Hz), 6.88 (1H, d, J = 8 Hz), 7.11 (1H, dd, J = 8, 2 Hz), 7.29 (9H, m), 7.45 (1H, d, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 19.3, 70.5, 109.9, 121.7, 122.7, 123.5, 125.9, 127.4, 128.0, 128.5, 129.4, 130.7, 136.6, 136.9, 150.8, 155.8, 166.9. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 78.82; H, 5.63.



15

Stannane 15. To a solution of $(i\text{-Pr})_2NH$ (262 μL, 3.00 mmol) in THF (12 mL) at -78 °C was added *n*-BuLi (2.5M in hexanes, 1.12 mL, 2.80 mmol) followed, after 20 min, by a solution of **16** (760 mg, 2.00 mmol) in THF (1 mL) that had been precooled to -78 °C. The solution was stirred

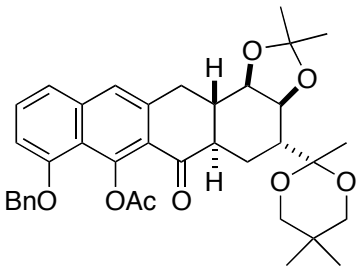
for 20 min at -78 °C and *n*-Bu_3SnCl (0.71 mL, 2.60 mmol) was added, after which the mixture was allowed to warm to room temperature. The mixture was diluted with Et_2O (30 mL), stirred vigorously for 4 h, then was washed with H_2O (2x) and brine. The solution was dried (Na_2SO_4) and concentrated to leave an oily residue which was chromatographed on silica gel (hexane:EtOAc 9:1) to give **15** (432 mg, 38%) as a colorless oil: IR (film) 1742, 1591 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (15H, m), 1.26 (6H, m), 1.45 (6H, m), 2.45 (2H, m), 5.17 (2H, s), 6.68 (1H, d, *J* = 8 Hz), 6.73 (1H, d, *J* = 8 Hz), 7.12 (2H, m), 7.24 (2H, m), 7.37 (2H, m), 7.47 (2H, m); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.7, 16.8, 27.7, 29.0, 70.5, 107.0, 120.6, 120.9, 121.8, 125.7, 127.5, 127.9, 128.5, 129.4, 130.6, 136.8, 144.1, 151.1, 156.4, 167.2; MS *m/z* 595 (M^+); HRMS *m/z* 595.2220 (calcd for $C_{32}H_{43}O_3Sn$ 595.2234).



17

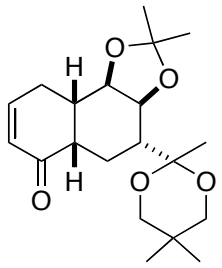
Tetracyclic Ketone 17. To a solution of **15** (94 mg, 0.16 mmol) in THF (0.5 mL) at -78 °C was added *n*-BuLi (1.57M in hexanes, 63 μL, 0.16 mmol). The solution became a deep red color and, after 5 min, a solution of **14** (27 mg, 0.072 mmol) in THF (0.3 mL) precooled to -78 °C was added. After 15 min, the solution was allowed to warm to room temperature and was stirred for 1 h. The mixture was diluted with Et_2O (10 mL) and the ethereal solution was washed with brine and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane:EtOAc 9:1 to 1:1) to give **17** (13 mg, 35%, 57% brsm) as a pale yellow, fluorescent oil: $[\alpha]^{23}_D$ +12.6 (c 1.00 $CHCl_3$); IR (film) 3379, 1733, 1700, 1624, 1617 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3H, s), 0.89 (3H, s), 1.16 (3H, s), 1.42 (3H, s), 1.46 (3H, s), 1.89 (1H, ddd, *J* = 15, 10, 6 Hz), 2.01 (1H, m), 2.36 (1H, m), 2.56 (1H, ddd, *J* = 15, 4, 4 Hz), 2.69 (1H, ddd, *J* = 14, 12, 1 Hz), 2.81 (1H, ddd, *J* = 10, 10, 4 Hz), 3.36 (3H, m), 3.68 (1H, d, *J* = 12 Hz), 3.76 (1H, d, *J* = 11 Hz), 4.01 (1H, dd, *J* = 9, 5 Hz), 4.67 (1H, dd, *J* = 5, 3 Hz), 5.29 (2H, s), 6.85 (1H, d, *J* = 8 Hz), 6.99 (1H, s), 7.22 (1H, dd, *J* = 8, 1 Hz), 7.38 (6H, m), 7.62 (1H, dd, *J* = 8, 1

Hz); MS *m/z* 572 (M^+), 381.307; HRMS *m/z* 572.2765 (calcd for $C_{35}H_{40}O_7$ 572.2774). There was also obtained 12 mg (44%) of recovered **14**.



18

Acetoxy Ketone 18. A solution of **17** (13 mg, 0.024 mol), Et_3N (0.32 mL, 2.31 mmol), DMAP (10 mg, 0.079 mmol) and Ac_2O (0.11 mL, 1.16 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 12 h. The solution was diluted with Et_2O (20 mL) and was washed with satd. aqueous $CuSO_4$ and brine. The solution was dried (Na_2SO_4), the solvent was removed in vacuo and the residual oil was chromatographed on silica gel (hexane:EtOAc 3:1) to give **18** (8 mg, 60%) as a colorless oil: $[\alpha]^{23}_D$ +21.0 (c 0.16 $CHCl_3$); IR (film) 1763, 1738, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (3H, s), 1.29 (3H, s), 1.44 (3H, s), 1.48 (3H, s), 1.79 (3H, s), 2.10 (2H, m), 2.32 (2H, m), 2.70 (1H, m), 2.86 (1H, m), 3.36 (1H, m), 3.44 (1H, dd, *J* = 13, 2 Hz), 3.49 (1H, m), 3.65 (1H, d, *J* = 11 Hz), 3.76 (1H, dd, *J* = 12, 2 Hz), 4.05 (1H, m), 4.70 (1H, m), 5.09 (1H, d, *J* = 10 Hz), 5.17 (1H, d, *J* = 10 Hz), 6.92 (1H, d, *J* = 8 Hz), 7.35-7.59 (9H, m); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.4, 26.3, 28.5, 29.7, 29.8, 40.4, 47.0, 53.5, 70.1, 70.3, 70.5, 71.3, 73.2, 73.4, 106.8, 120.0, 128.5, 128.7, 129.1, 136.1, 138.3, 138.4, 183.7, 197.6; MS *m/z* 614 (M^+), 572; HRMS *m/z* 614.2873 (calcd for $C_{37}H_{42}O_8$ 614.2880).

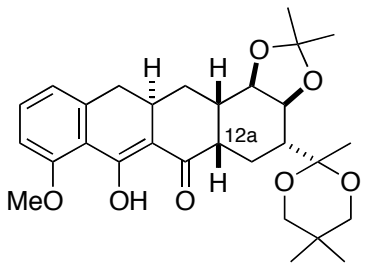


19

Enone 19. A. From 13. To a stirred suspension of $LiAlH_4$ (68 mg, 1.79 mmol) in dry Et_2O (10 mL) was added a solution of **13** (130 mg, 0.342 mmol) in dry Et_2O (8 mL) and the mixture was

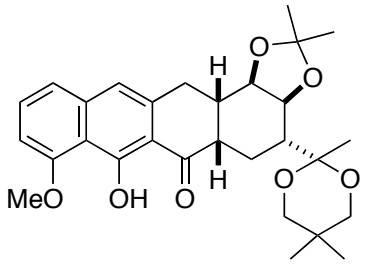
heated at reflux for 2 h. The reaction was quenched with wet Et_2O and the mixture was acidified to Congo Red with 1M HCl. The separated aqueous layer was extracted with EtOAc (2x) and the combined organic extract was washed with 1M HCl. The separated aqueous layer was extracted with EtOAc (2x) and the combined organic extract was washed with 1M HCl and satd. aqueous $NaHCO_3$ and dried ($MgSO_4$). The solvent was removed in vacuo to leave a solid which was crystallized from hexane to give **19** (84 mg, 70%) as colorless needles: mp 143-144 °C; $[\alpha]^{23}_D$ +50.1 (c 0.10, $CHCl_3$); IR (film) 1674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (3H, s) 1.04 (3H, s), 1.34 (3H, s), 1.48 (3H, s), 1.49 (3H, s), 1.58 (1H, ddd, *J* = 13, 12, 12 Hz), 2.01 (2H, m), 2.36 (2H, m), 2.70 (2H, m), 3.32 (2H, m), 3.65 (1H, d, *J* = 12 Hz), 3.70 (1H, d, *J* = 12 Hz), 4.03 (1H, dd, *J* = 5, 3 Hz), 4.28 (1H, dd, *J* = 9, 5 Hz), 6.03 (1H, ddd, *J* = 10, 2, 2 Hz), 6.90 (1H, ddd, *J* = 10, 4, 4 Hz); ^{13}C NMR ($CDCl_3$) δ 17.5, 20.8, 22.4, 23.4, 25.8, 26.4, 28.3, 29.9, 35.4, 43.1, 47.8, 69.9, 70.1, 73.1, 76.8, 99.4, 107.8, 129.3, 147.6, 201.6; MS *m/z* 335 (M^+ -15), 149.129; HRMS *m/z* 335.1860 (calcd for $C_{19}H_{27}O_5$ 335.1858). Anal. Calcd for $C_{20}H_{30}O_5$: C, 68.54; H, 8.63. Found: C, 68.14; H, 8.74.

B. From 12. A suspension containing **12** (104 mg, 0.274 mmol) and Pd/C (8 mg) in MeOH (5 mL) was stirred at room temperature under H_2 (1 atm) for 12 h. The suspension was filtered and the filtrate was concentrated to leave a mixture of saturated alcohol **21** and the saturated ketone (93 mg, ca 2:1 respectively, each as a mixture of diastereomers) as a pale yellow oil. The oil was taken up into CH_2Cl_2 (10 mL), Dess Martin periodinane (147 mg, 0.36 mmol) was added, and the solution was stirred at room temperature for 2 h. The mixture was poured into ice-cold satd. aqueous $NaHCO_3$ and was extracted with EtOAc (2x). The extract was dried (Na_2SO_4) and the solvent was removed in vacuo to leave crude **22** (74 mg, mixture of two diastereomers) as a colorless oil. The oil was taken up into THF (6 mL) and *t*-BuOK (56 mg, 0.50 mmol, sublimed) was added to the solution. The mixture was stirred at room temperature for 1.5 h then was poured into water and extracted with EtOAc (2x). The extract was washed with 1M HCl and brine, and was dried (Na_2SO_4). The solvent was removed in vacuo to leave a pale yellow solid which was crystallized from hexane to give **19** (51 mg, 53%) as colorless needles, identical with material prepared from **13** above.



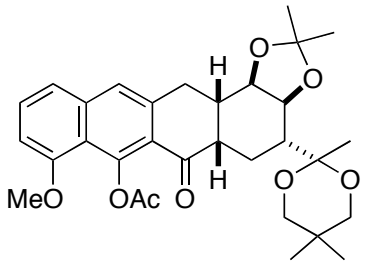
24

Diketone 24. To a freshly prepared solution of LDA (0.285 mmol) in THF (1.6 mL) at -78 °C was added a solution of **23** (69 mg, 0.285 mmol) in THF (0.8 mL). The resulting deep red solution was stirred for 15 min, after which a solution of **19** (30 mg, 0.086 mmol) and LiBr (76 mg, 0.868 mmol) in THF (1.6 mL) was added. The mixture was stirred at -78 °C for 2 h, during which the color changed from red to pale yellow. The mixture was allowed to warm to room temperature and the reaction was quenched with satd. aqueous NH_4Cl. The mixture was extracted with Et_2O (3x), and the extract was washed with H_2O and brine and was dried ($MgSO_4$). The solvent was removed in vacuo and the residual oil was chromatographed on silica gel (hexane:EtOAc 3:1) to give **24** (44 mg, 99%, keto-enol mixture) as a colorless oil: IR (film) 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3H, s), 1.13 (3H, s), 1.33 (3H, s), 1.40 (1H, m), 1.47 (6H, s), 2.05 (3H, m), 2.22 (1H, ddd, *J* = 13, 4, 4 Hz), 2.46 (1H, m), 2.54 (1H, dd, *J* = 14, 4 Hz), 2.81 (3H, m), 3.37 (2H, m), 3.68 (1H, d, *J* = 12 Hz), 3.70 (1H, d, *J* = 12 Hz), 3.90 (3H, s), 3.92 (3H, s), 3.92 (1H, m), 4.41 (1H, dd, *J* = 8, 8 Hz), 6.76 (1H, d, *J* = 11 Hz), 6.83 (1H, m), 7.34 (1H, m), 16.42 (1H, s); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.9, 22.3, 22.7, 22.8, 23.2, 25.7, 28.4, 28.7, 30.0, 31.6, 33.0, 35.3, 37.1, 37.5, 46.8, 56.0, 70.2, 70.3, 74.4, 77.2, 99.2, 108.6, 109.0, 110.4, 120.0, 121.1, 121.7, 121.9, 126.0, 129.5, 131.0, 133.6, 140.1, 144.7, 150.9, 156.8, 159.8, 183.1, 188.3; MS *m/z* 498 (M^+); HRMS *m/z* 498.2617 (calcd for $C_{29}H_{38}O_7$ 498.2617).



26

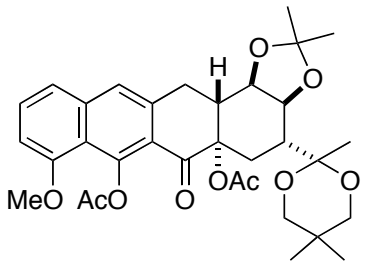
Naphthacenone 26. A solution of **24** (110 mg, 0.214 mmol) and **25** (526 mg, 2.14 mmol) in toluene (21 mL) was heated at reflux for 24 h. The solvent was removed in vacuo to leave a yellow oil which tlc showed to be a mixture of highly fluorescent **26** (less polar), unreacted **24** (weakly fluorescent, more polar) and **25**. Chromatography of the residual oil on silica gel (toluene:EtOAc 9:1) gave **26** (42 mg, 38%, 71% brsm) as an amorphous solid: $[\alpha]^{23}_{D}$ +2.7 (c 0.1, $CHCl_3$); IR (KBr) 2952 (br), 1623, 1576 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (3H, s), 1.00 (3H, s), 1.36 (3H, s), 1.51 (3H, s), 1.52 (3H, s), 1.74 (1H, ddd, *J* = 14, 13, 13 Hz), 2.09 (1H, m), 2.27 (1H, ddd, *J* = 14, 5, 5 Hz), 2.78 (1H, m), 2.92 (1H, dd, *J* = 16, 5 Hz), 3.01 (1H, ddd, *J* 12, 5, 5 Hz), 3.09 (1H, dd, *J* = 16, 12 Hz), 3.30 (2H, m), 3.65 (1H, d, *J* = 12 Hz), 3.70 (1H, d, *J* = 12 Hz), 4.02 (3H, s), 4.08 (1H, dd, *J* = 5, 5 Hz), 4.34 (1H, dd, *J* = 9, 5 Hz), 6.81 (1H, d, *J* = 8 Hz), 6.99 (1H, s), 7.21 (1H, d, *J* = 8 Hz), 7.49 (1H, dd, *J* = 8, 8 Hz); ^{13}C NMR ($CDCl_3$) δ 17.4, 21.7, 22.3, 23.4, 26.4, 28.4, 28.9, 29.9, 35.1, 43.5, 48.2, 56.1, 69.8, 70.1, 73.1, 77.2, 99.3, 105.5, 107.8, 110.8, 115.2, 116.8, 119.7, 131.1, 136.5, 140.3, 159.8, 166.3, 206.3; MS *m/z* 496 (M^+), 129; HRMS *m/z* 496.2459 (calcd for $C_{29}H_{36}O_7$ 496.2461).



27

Acetate 27. A solution of **26** (14.0 mg, 0.028 mol), DMAP (12 mg, 0.01 mmol), Et_3N (0.5 mL, 1.4 mmol) and Ac_2O (0.14 mL, 1.4 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 80 min. The reaction was quenched with satd. aqueous $NaHCO_3$ and the mixture was extracted with EtOAc. The extract was washed with brine and dried (Na_2SO_4), and the solvent was removed in vacuo to leave a colorless oil. This material was chromatographed on silica gel (hexane:EtOAc 2:1) to give **27** (10.0 mg, 70%) as a colorless, non-fluorescent oil: $[\alpha]^{20}_{D}$ +55.0 (c 0.40 $CHCl_3$); IR (film) 1767, 1681, 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (3H, s), 1.03 (3H, s), 1.32 (3H, s), 1.47 (3H, s), 1.50 (3H, s), 2.06 (1H, ddd, *J* = 12, 8, 4 Hz), 3.17 (1H, dd, *J* = 16, 8 Hz), 3.32 (2H, dd, *J* = 8, 8 Hz), 3.65 (2H, m), 3.88 (1H, m), 3.93 (3H, s), 4.35 (1H, t, *J* = 1 Hz), 6.79 (1H, d, *J* = 7 Hz), 7.33 (1H, d, *J* = 8 Hz), 7.44 (1H, dd, *J* = 8, 8 Hz), 7.56 (1H, s); ^{13}C NMR

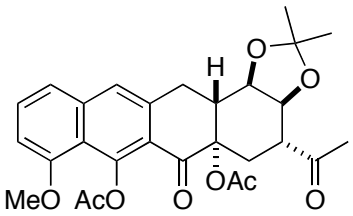
($CDCl_3$) δ 21.4, 22.4, 22.8, 23.8, 26.5, 28.8, 29.7, 30.1, 30.3, 34.8, 46.3, 48.0, 56.6, 70.4, 70.5, 74.0, 74.5, 76.1, 77.6, 99.7, 106.4, 108.6, 119.1, 120.4, 122.2, 125.8, 129.7, 138.9, 157.9, 170.4, 199.1; HRMS *m/z* 538.2560 (M^+) (calcd for $C_{31}H_{38}O_8$ 538.2567).



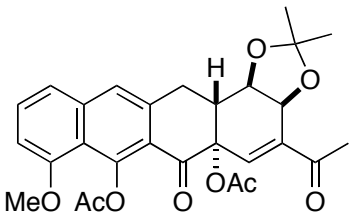
29

Diacetate 29. A solution of **27** (11.4 mg, 0.021 mmol), Et_3N (0.07 mL, 0.53 mmol) and trimethylsilyl triflate (0.04 mL, 0.22 mmol) in CH_2Cl_2 (3 mL) was stirred at 0 °C for 1h. The reaction was quenched with satd. aqueous $NaHCO_3$ and the separated aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried (Na_2SO_4). Removal of the solvent in vacuo gave crude enol ether which was taken up into CH_2Cl_2 (3 mL). The solution was cooled to -50 °C, *m*- chloroperbenzoic acid (40 mg, 0.23 mmol) was added and the mixture was stirred for 20 min, after which it was allowed to warm to -20 °C. The reaction was quenched at this temperature with an ice-cold satd. aqueous solution of Na_2SO_3 and the separated aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried (Na_2SO_4). Removal of the solvent in vacuo left pure α-hydroxy ketone **28** (9 mg, 80%) as a colorless oil. To a solution of **28** obtained above in pyridine (0.5 mL) containing DMAP (9 mg, 0.07 mol) was added Ac_2O (0.15 mL, 1.59 mmol) and the mixture was stirred at room temperature for 2.5 h. The solution was diluted with EtOAc, washed with satd. aqueous NH_4Cl and brine, and dried (Na_2SO_4). The solvent was removed in vacuo to leave an oil which was chromatographed on silica gel (hexane:EtOAc 3:2) to give **29** (9.0 mg, 72% from **27**) as a colorless oil: $[\alpha]^{20}_D$ +104.0 (c 0.35 $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.81 (3H, s), 1.14 (3H, s), 1.38 (3H, s), 1.43 (3H, s), 1.53 (3H, s), 1.75 (3H, s), 2.02 (1H, ddd, *J* = 14, 8, 4 Hz), 2.25 (1H, m), 2.37 (1H, d, *J* = 9 Hz), 2.45 (3H, s), 3.25 (2H, d, *J* = 9 Hz), 3.48 (3H, m), 3.72 (2H, m), 3.90 (3H, s), 4.29 (1H, dd, *J* = 11, 6 Hz), 4.62 (1H, dd, *J* = 8, 7 Hz), 6.76 (1H, d, *J* = 8 Hz), 7.31 (1H, d, *J* = 8 Hz), 7.42 (1H, dd, *J* = 8, 8 Hz), 7.49 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.6, 20.8, 21.4, 22.8, 23.7, 25.7, 25.9, 27.4, 28.5, 30.1, 30.4, 41.9, 45.4, 56.4, 70.6, 75.1, 75.7,

77.6, 82.2, 99.6, 106.0, 109.4, 118.9, 120.3, 123.0, 125.1, 129.3, 137.9, 138.3, 157.3, 170.0, 171.0, 192.4; HRMS (FAB) *m/z* 597.2704 (M^+ +1) (calcd for $C_{33}H_{41}O_{10}$ 597.2700).



Diketone. A solution of **29** (8.0 mg, 0.013 mol) and *p*-TsOH (2.6 mg, 0.013 mmol) in acetone (2 mL) was stirred at room temperature for 4 h. The mixture was diluted with EtOAc and the solution was washed with satd. aqueous $NaHCO_3$ and brine. The solution was dried (Na_2SO_4), the solvent was removed in vacuo and the residual oil was chromatographed on silica gel (hexane:EtOAc 3:2) to give diketone (5.1 mg, 73%) as a colorless oil: $[\alpha]^{23}_D$ +100.0 (c 0.35, $CHCl_3$); IR (film) 1746, 1706, 1625, 1568 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3H, s), 1.48 (3H, s), 1.76 (1H, dd, *J* = 15, 11 Hz), 1.80 (3H, s), 2.24 (1H, m), 2.34 (3H, s), 2.48 (3H, s), 2.92 (1H, ddd, *J* = 12, 7, 4 Hz), 3.28 (2H, m), 3.38 (1H, dd, *J* = 17, 6 Hz), 3.95 (3H, s), 4.36 (1H, dd, *J* = 10, 6 Hz), 4.61 (1H, t, *J* = 7 Hz), 6.81 (1H, d, *J* = 8 Hz), 7.36 (1H, d, *J* = 8 Hz), 7.47 (1H, dd, *J* = 8, 8 Hz), 7.53 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.2, 25.6, 27.5, 28.0, 28.6, 30.1, 30.3, 43.0, 48.9, 56.4, 74.6, 76.0, 77.6, 81.3, 106.2, 109.7, 120.3, 125.1, 129.6, 138.5, 170.9, 199.0, 209.1; HRMS (FAB) *m/z* 511.1959 (M^+ +1) (calcd for $C_{28}H_{31}O_9$ 511.1968).

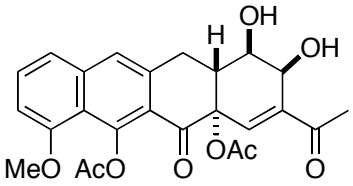


30

Enone 30. To a solution of diketone obtained above (6.0 mg, 0.011 mmol) in CH_2Cl_2 (2 mL) at 0 °C were added NaHMDS (0.046 mL, 0.24 mmol) followed by Me_3SiI (0.008 mL, 0.18 mmol). The mixture was stirred for 4 h at 0 °C and the reaction was quenched with satd. aqueous $NaHCO_3$. The mixture was extracted with EtOAc and the extract was washed with brine and dried (Na_2SO_4). The solvent was removed in vacuo to leave crude silyl enol ether, which was

taken up into CH_2Cl_2 (1.5 mL). To this solution at 0 °C was added solid K_2CO_3 (5 mg) followed by PhSeCl (5.9 mg, 0.030 mmol) and the mixture was stirred for 30 min. The solution was diluted with EtOAc and satd. aqueous $NaHCO_3$, the organic layer was separated and the aqueous layer was extracted with EtOAc (2x). The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo to leave an oil which was chromatograhed on silica gel (hexane:EtOAc 2:1) to give α-selenyl ketone (4 mg) as an oil.

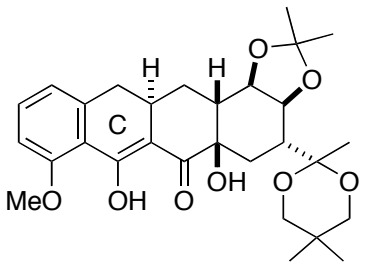
The ketone obtained above was taken up into CH_2Cl_2 (1 mL), the solution was cooled to -78 °C and *m*-chloroperbenzoic acid (0.2M in CH_2Cl_2, 0.04 mL, 0.005 mmol) was added. The solution was stirred at -78 °C for 30 min, (*i*-Pr)$_2$NH (0.02mL) was added and the mixture was allowed to warm to room temperature. The solution was diluted with EtOAc, dried (Na_2SO_4) and concentrated in vacuo to leave an oil which was chromatographed on silica gel (hexane:EtOAc 3:2) to give **30** (2.0 mg, 40% over three steps) as a colorless oil: $[\alpha]^{20}_D$ +48.0 (c 0.25, $CHCl_3$); IR (film) 1760, 1742, 1690, 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (3H, s), 1.52 (3H, s), 1.86 (3H, s), 2.40 (1H, m), 2.50 (3H, s), 2.56 (3H, s), 3.30 (1H, dd, *J* = 17, 11 Hz), 3.51 (1H, dd, *J* = 17, 7 Hz), 3.96 (3H, s), 4.30 (1H, dd, *J* = 10, 6 Hz), 5.09 (1H, d, *J* = 6 Hz), 6.84 (1H, d, *J* = 8 Hz), 7.38 (1H, d, *J* = 8 Hz), 7.50 (1H, dd, *J* = 8, 8 Hz), 7.58 (1H, s), 7.78 (1H, s); HRMS *m/z* 508.1725 (M^+) (calcd for $C_{28}H_{28}O_9$ 508.1733).



31

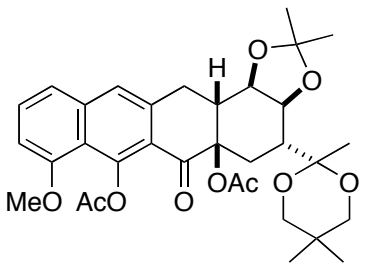
Diol 31. A solution of **30** (4.4 mg, 0.008 mmol) and trifluoroacetic acid (0.7 m) in CH_2Cl_2 (1 mL) was stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel (EtOAc:hexane 2:1 to 3:1) to give **31** (2.2 mg, 55%) as a colorless oil: $[\alpha]^{20}_D$ +76.4 (c 0.11, $CHCl_3$); IR (film) 3424, 1765, 1751, 1676, 1650, 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.85 (3H, s), 2.49 (3H, s), 2.55 (3H, s), 2.62 (1H, m), 3.37 (1H, dd, *J* = 16, 11 Hz), 3.50 (1H, dd, *J* = 18, 6 Hz), 3.96 (3H, s), 4.07 (1H, m), 4.72 (1H, d, *J* = 4 Hz), 6.83 (1H,

d, J = 8 Hz), 7.39 (1H, d, J = 8 Hz), 7.50 (1H, t, J = 8 Hz), 7.61 (1H, s), 7.66 (1H, s); HRMS (ES) *m/z* 491.1339 (M^+ +23) (calcd for $C_{25}H_{24}O_9Na$ 491.1318).



32

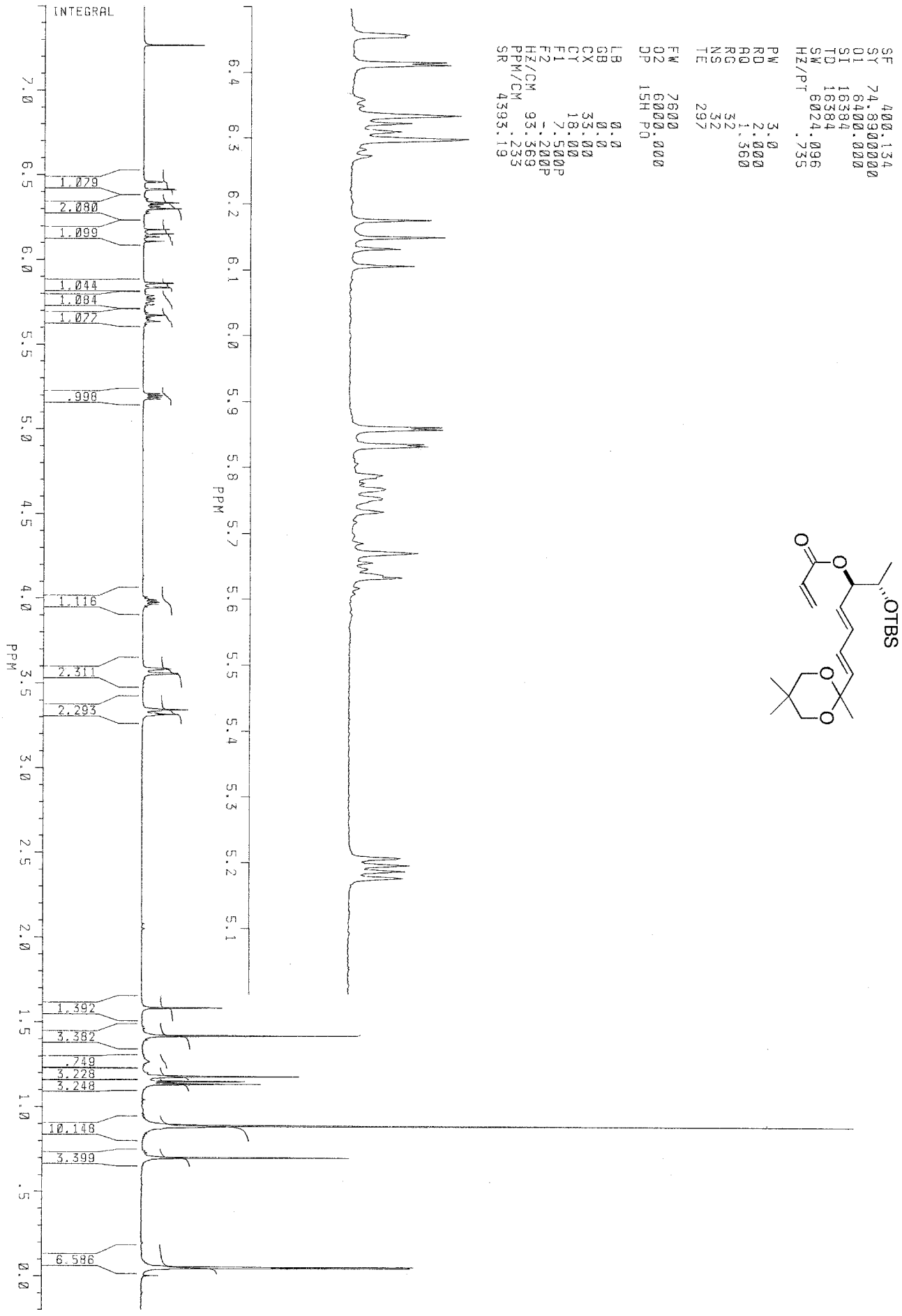
Hydroxy Ketone 32. To a solution of **24** (15 mg, 0.034 mmol) in dioxane (1 mL) was added SeO_2 (19 mg, 0.17 mmol) and the mixture was heated at reflux for 1.5 h. The resulting red solution was allowed to cool to room temperature, the solvent was removed and the residual oil was chromatographed on silica gel (hexane:EtOAc 2:1) to yield **32** (6 mg, 40%) as a colorless oil: $[\alpha]^{20}_D$ +16.7 (c 0.15, $CHCl_3$); IR (film) 3444, 2935, 1617, 1596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (3H, s), 1.14 (3H, s), 1.36 (3H, s), 1.51 (6H, s), 1.56 (1H, m), 1.70 (1H, dt, J = 13, 4 Hz), 2.28 (1H, dd, J = 15, 2 Hz), 2.38 (1H, ddd, J = 13, 8, 2 Hz), 2.46 (1H, s), 2.61 (1H, dd, J = 14, 14 Hz), 2.84 (2H, m), 3.43 (2H, dd, J = 17, 12 Hz), 3.70 (2H, dd, J = 12, 9 Hz), 3.84 (1H, dd, J = 12, 6 Hz), 3.93 (3H, s), 4.45 (1H, dd, J = 7, 7 Hz), 6.81 (1H, d, J = 7 Hz), 6.90 (1H, d, J = 8 Hz), 7.41 (1H, dd, J = 8, 7 Hz), 16.10 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.4, 22.8, 23.5, 26.3, 26.6, 28.8, 29.3, 30.1, 30.4, 33.2, 37.4, 41.3, 44.1, 56.5, 70.6, 71.3, 73.9, 75.2, 77.6, 99.5, 108.4, 109.8, 110.9, 120.5, 134.5, 145.3, 160.2, 179.6, 190.2; HRMS (FAB) *m/z* 515.2659 (M^+ +1) (calcd for $C_{29}H_{39}O_8$ 515.2645).

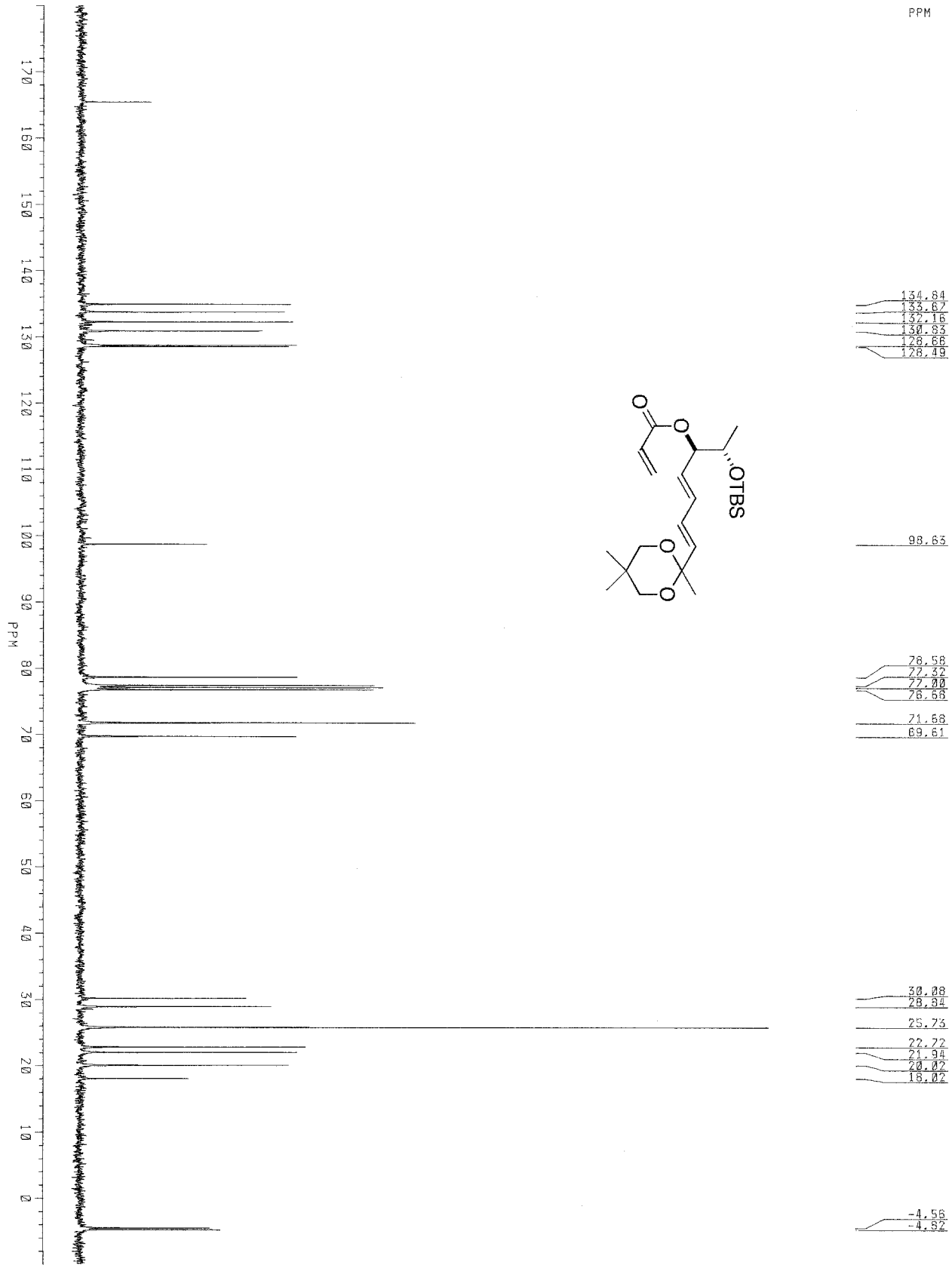


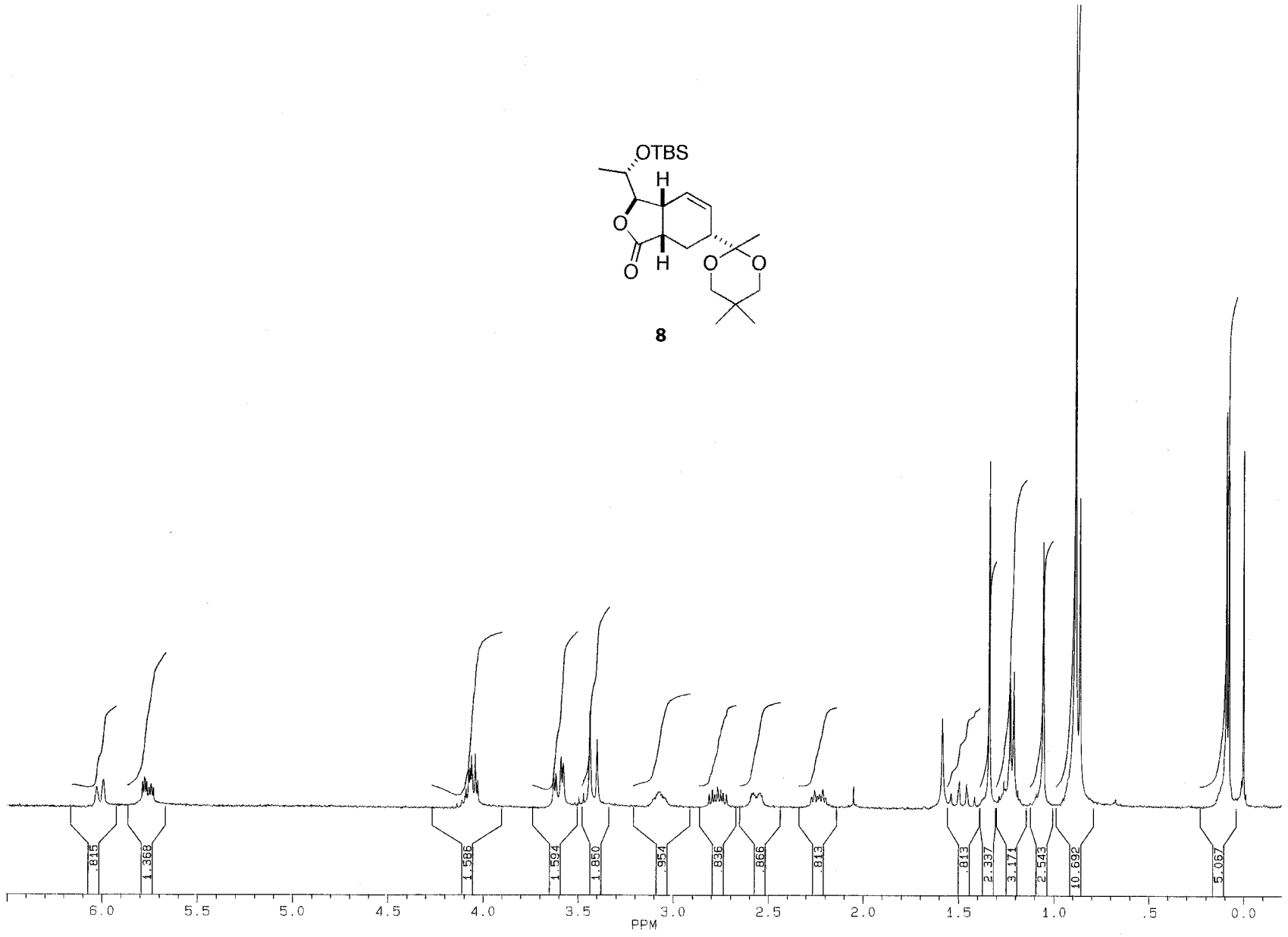
34

Diacetate 34. A solution of **32** (3.0 mg, 0.006 mmol), Ac_2O (29 mg, 0.28 mmol), pyridine (0.2 mL) and DMAP (2 mL) was stirred at room temperature for 15 h. The reaction was quenched

with satd. aqueous $NaHCO_3$ and the mixture was extracted with Et_2O. The extract was washed with satd. aqueous $CaSO_4$ and brine and was dried (Na_2SO_4). The solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane:EtOAc 1:1) to give **33** (1.8 mg) admixed with a small quantity of a monoacetate. The mixture was taken up in toluene (0.5 mL), **25** (5 mg, 0.02 mmol) was added and the solution was heated at 105 °C for 15 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel (pentane:EtOAc 4:1) to give **34** (1.9 mg, 55%) as a colorless oil: $[\alpha]^{20}_D$ +38.2 (c 0.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.80 (3H, s), 1.29 (3H, s), 1.42 (3H, s), 1.47 (3H, s), 1.51 (3H, s), 1.84 (3H, s), 2.40 (2H, d, *J* = 7 Hz), 2.50 (3H, s), 2.58 (3H, s), 3.39 (1H, m), 3.52 (2H, m), 3.97 (3H, s), 4.41 (1H, dd, *J* = 12, 8 Hz), 5.10 (1H, dd, *J* = 8, 8 Hz), 6.81 (1H, d, *J* = 6 Hz), 7.36 (1H, dd, *J* = 8, 8 Hz), 7.44 (1H, s), 7.58 (1H, d, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 17.1, 21.5, 21.9, 22.9, 23.5, 26.1, 27.3, 28.6, 29.2, 30.1, 42.4, 44.9, 56.6, 71.0, 75.5, 76.1, 77.2, 84.2, 100.3, 106.4, 109.3, 119.9, 121.8, 123.7, 124.8, 130.2, 138.8, 139.2, 156.6, 171.5, 171.7, 196.0; HRMS (FAB) *m/z* 597.2712 (M^+ +1) (calcd for $C_{33}H_{41}O_{10}$ 597.2700).


SBHIV11A.101
DATE 10-6-88
SF 400.134
SY 74.8300000
01 6400.000
SI 16384
TD 16384
SW 6024.096
HZ/PT .735
PW 3.0
RD 2.000
AQ 1.360
RG 32
NS 32
TE 297
FW 7600
O2 6000.000
DP 15H PO
LB 0.0
GB 0.0
CX 33.00
CY 18.00
F1 7.500P
F2 -.200P
HZ/CM 93.369
PPM/CM .233
SR 4393.19
INTEGRAL
1.079
2.080
1.099
1.044
1.084
1.077
.998
1.116
2.311
2.293
1.392
3.382
.749
3.228
3.248
10.148
3.399
6.586
PPM
OTBS


PPM
134.84
133.67
132.16
130.83
128.66
128.49
98.63
78.58
77.32
77.00
76.66
71.68
69.61
30.08
28.34
25.73
22.72
21.94
20.02
18.02
-4.56
-4.82
OTBS
JD170.201
DATE 22-6-88
SF 100.614
SY 74.890000
O1 54000.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 1333
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 179.998P
F2 -9.998P
HZ/CM 579.279
PPM/CM 5.757
SR 4387.89



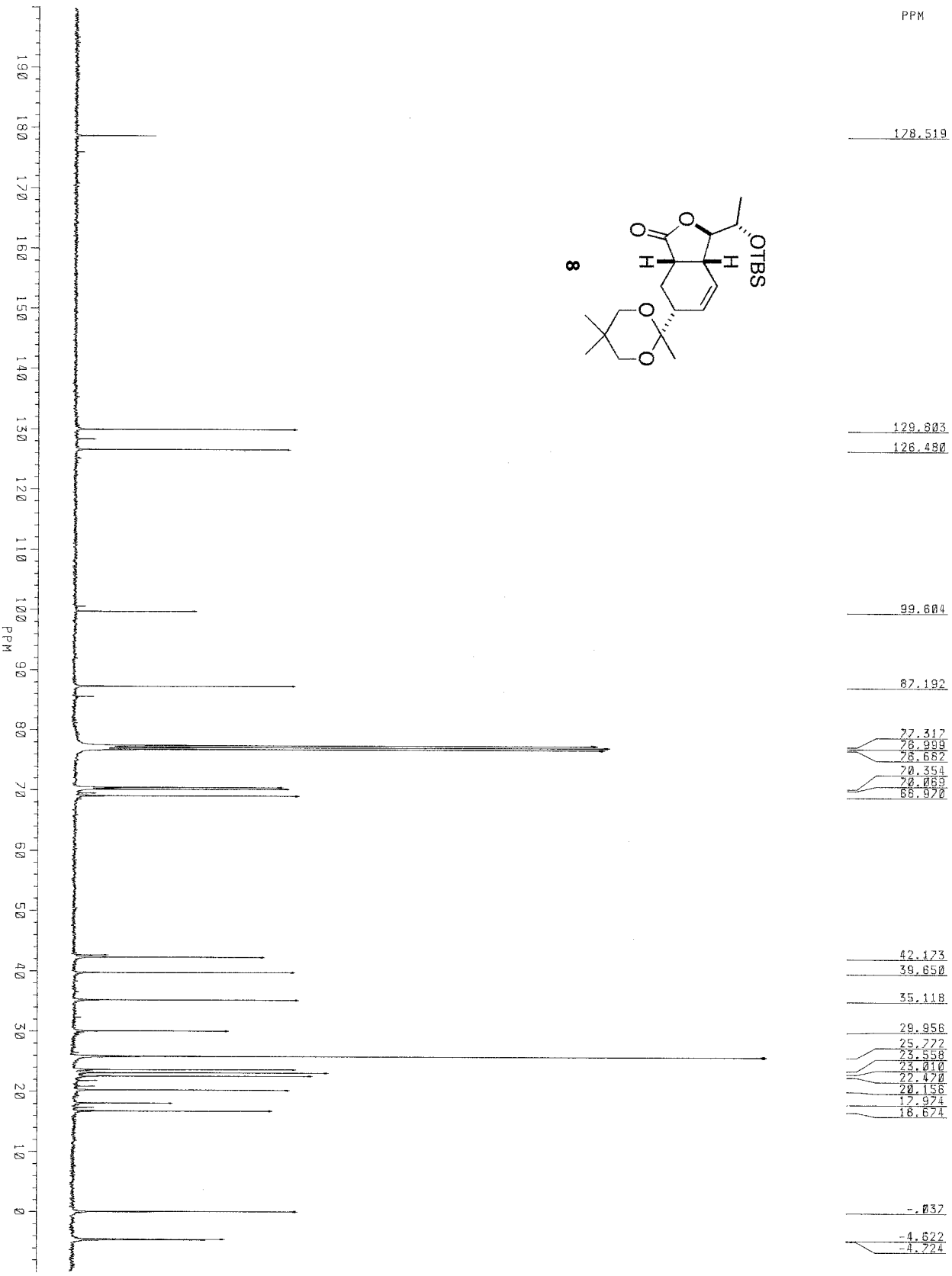
SPC2
DATE 31-12-88

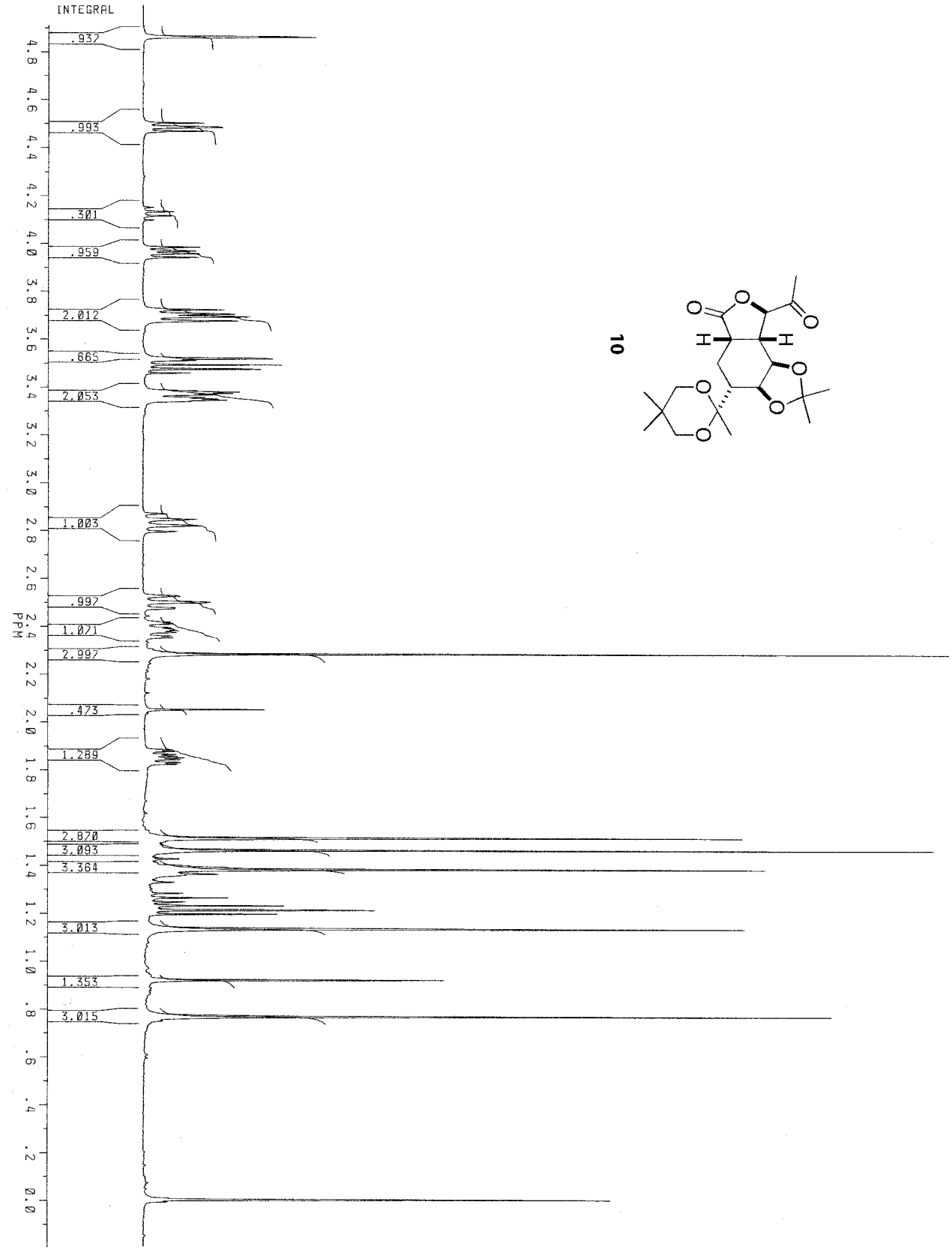
SF 300.133
SY 210.0
O1 5200.000
SI 16384
TD 16384
SW 4504.505
HZ/PT .550

PW 3.0
RD 2.000
AQ 1.819
RG 40
NS 32
TE 297

FW 5700
O2 3200.000
DP 63L PO

LB 0.0
GB 0.0
CX 35.00
CY 35.00
F1 6.500P
F2 -.198P
HZ/CM 57.437
PPM/CM .191
SR 3366.20


PPM
178.519
129.803
126.480
99.604
87.192
77.317
76.999
76.682
70.354
70.069
68.970
42.173
39.650
35.118
29.956
25.772
23.558
23.010
22.470
20.156
17.974
16.674
-.037
-4.622
-4.724
8
OTBS
O
H
H
O
O
O
PPM
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
JDI100.222
DATE 21-9-88
SF 100.614
SY 24.890000
O1 54000.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 32194
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 200.001P
F2 -9.998P
HZ/CM 640.268
PPM/CM 6.364
SR 43871.60



10

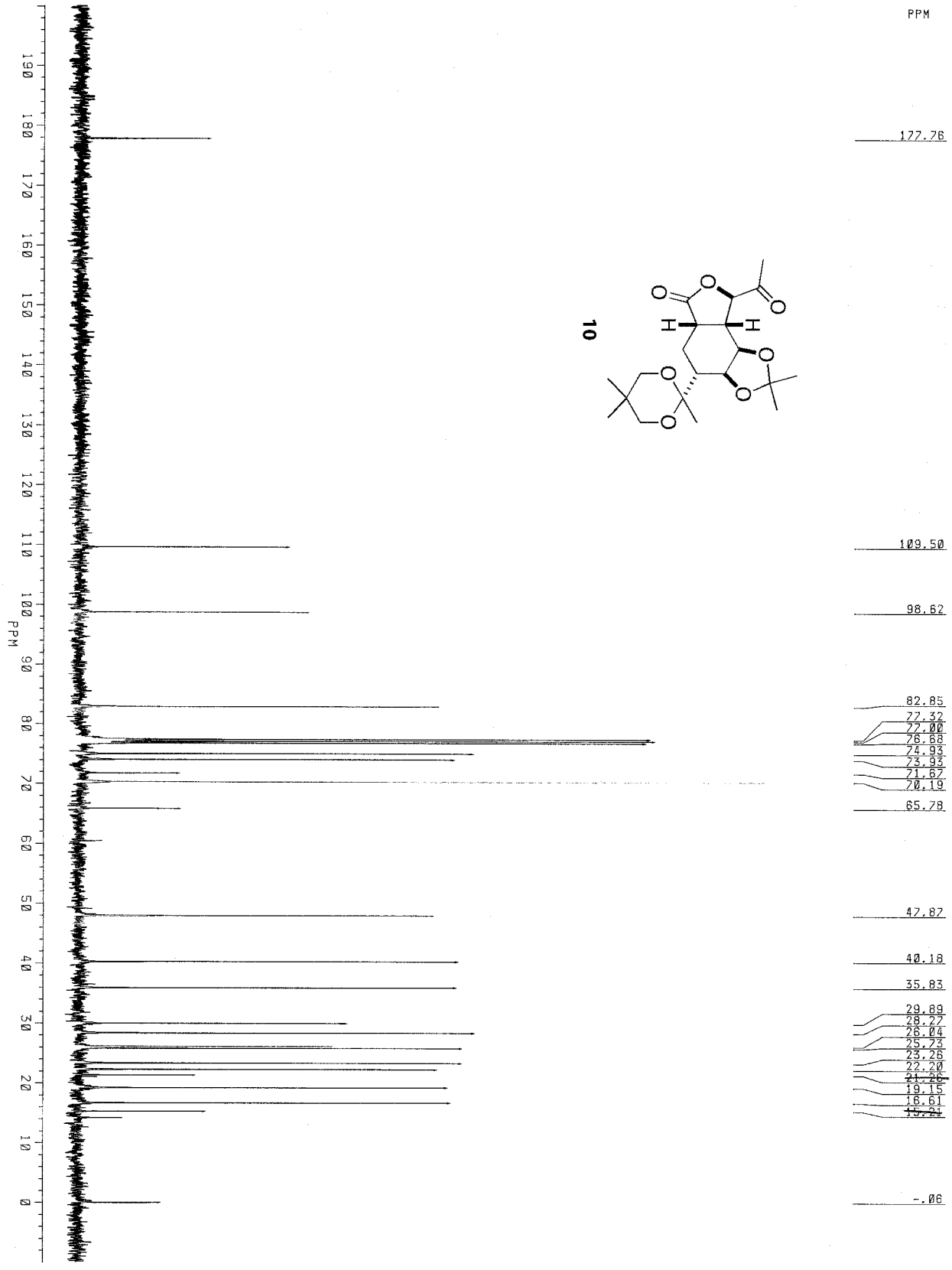
LMII17.401
DATE 27-8-88

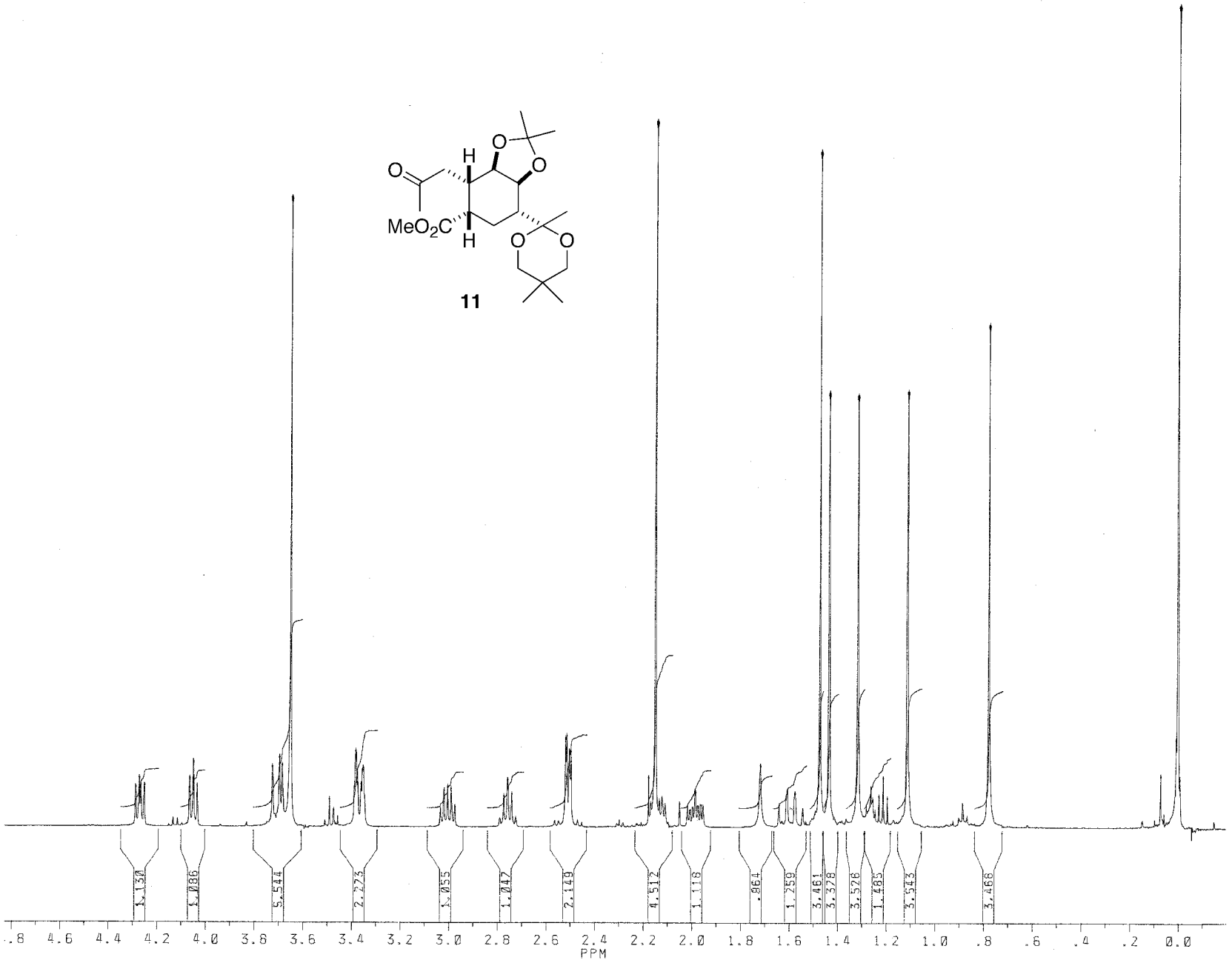
SF 400.134
SY 74.890000
O1 6400.000
SI 16384
TD 16384
SW 6024.096
HZ/PT .735

PW 3.0
RD 2.000
AQ 1.360
RG 16
NS 32
TE 297

FW 7600
O2 6000.000
DP 15H PO

LB 0.0
GB 0.0
CX 33.00
CY 0.0
F1 5.001P
F2 -.195P
HZ/CM 62.996
PPM/CM .157
SR 4387.31


PPM
177.76
109.50
98.62
82.85
77.32
77.00
76.68
74.95
73.95
71.67
70.19
65.78
47.87
40.18
35.83
29.89
28.27
26.04
25.73
23.26
22.20
21.26
19.15
16.61
15.21
-.06
10
JDII54-201
DATE 25-8-88
SF 100.614
SY 74.890000
O1 5400.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 1880
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 200.001P
F2 -9.998P
HZ/CM 640.268
PPM/CM 6.364
SR 43975.41



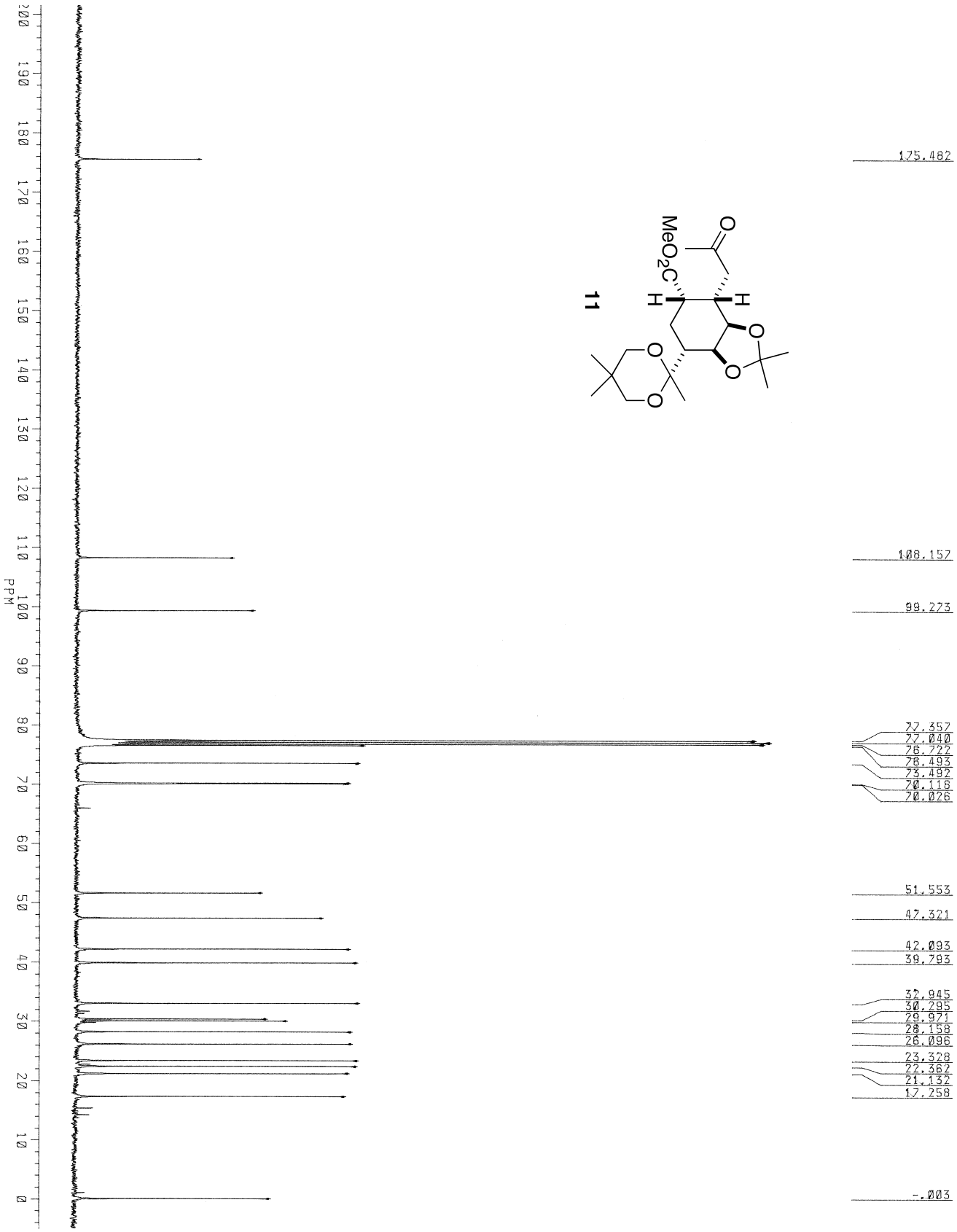
JDII87.101
DATE 5-10-88

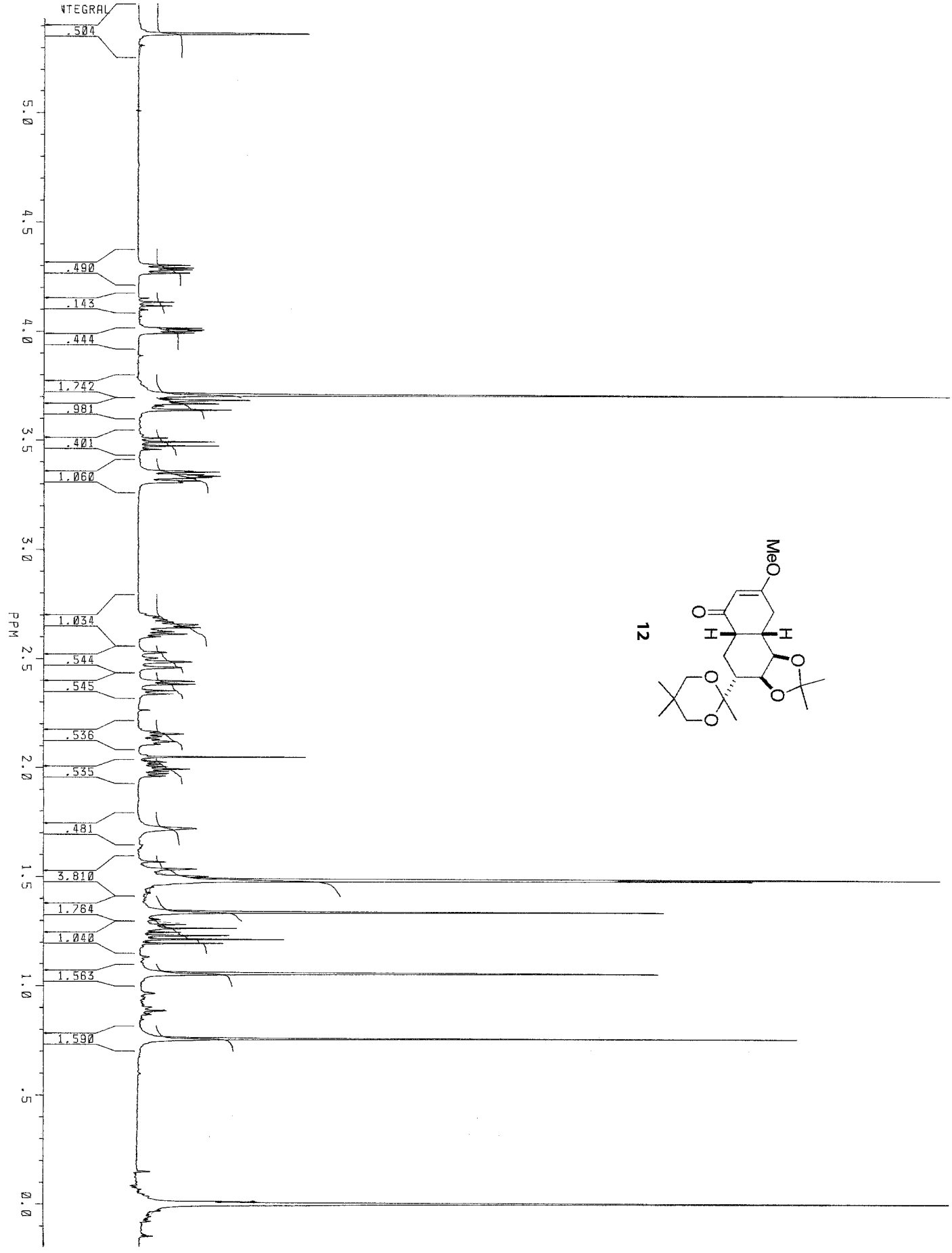
SF 400.134
SY 74.8900000
O1 6400.000
SI 16384
TD 16384
SW 6024.096
HZ/PT .735

PW 3.0
RD 2.000
AQ 1.360
RG 10
NS 32
TE 297

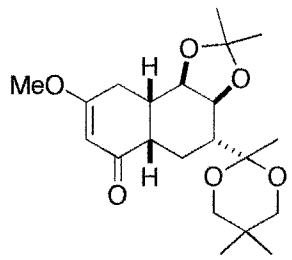
FW 7600
O2 6000.000
DP 15H PO

LB 0.0
GB 0.0
CX 33.00
CY 0.0
F1 5.001P
F2 -.197P
HZ/CM 63.018
PPM/CM .157
SR 4388.05

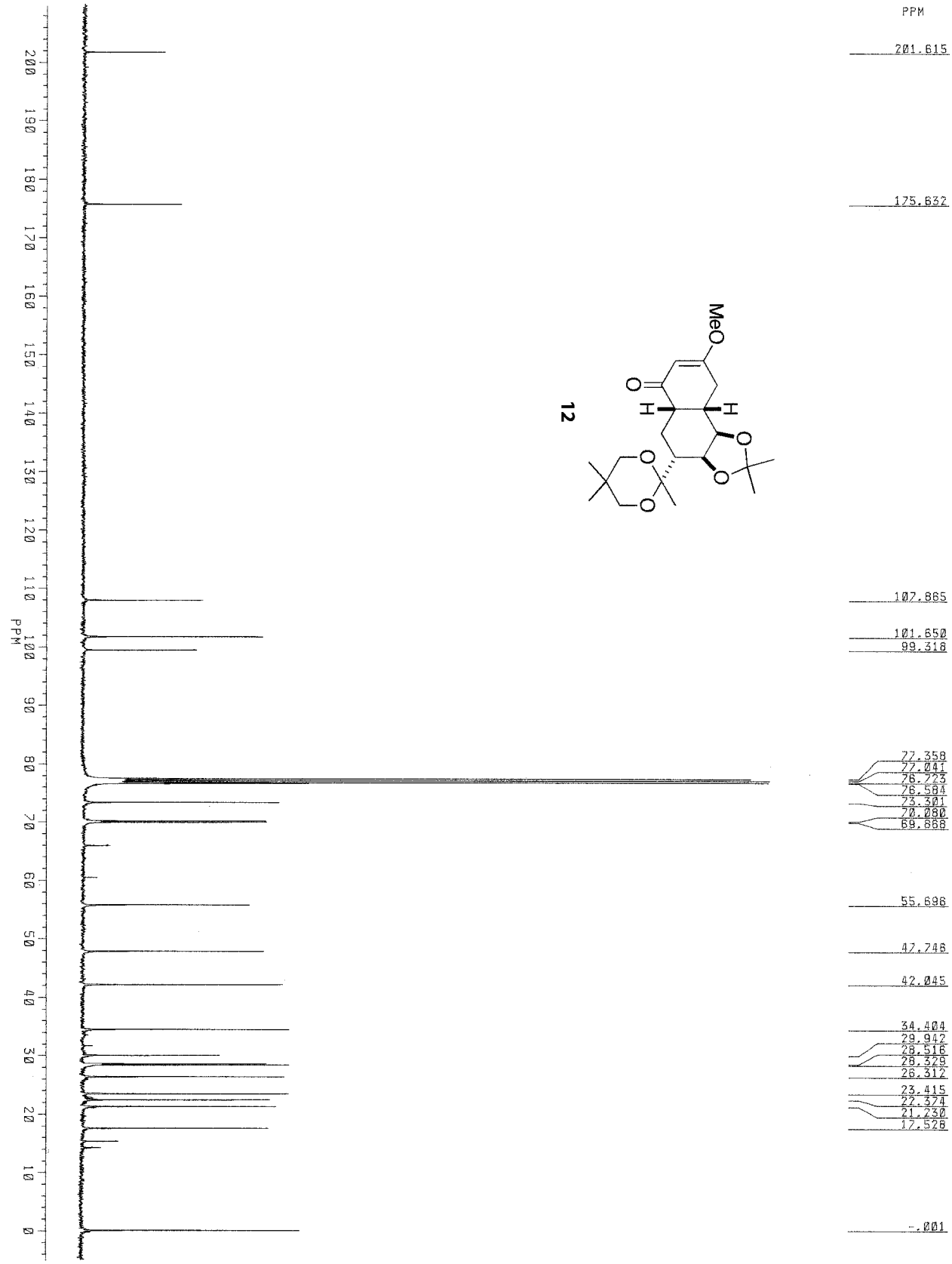

175.482
108.157
99.273
77.357
77.040
76.722
76.493
73.492
70.116
70.026
51.553
47.321
42.093
39.793
32.945
30.295
29.971
28.158
26.096
23.328
22.362
21.132
17.258
-.003
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
MeO2C
H
H
O
O
O
O
O
11
JDII87.201
DATE 6-10-88
SF 100.614
SY 74.890000
O1 5400.000
SI 65536
TD 65536
SW 2500.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 23813
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 209.999P
F2 14.997P
HZ/CM 655.504
PPM/CM 6.515
SR 43989.69

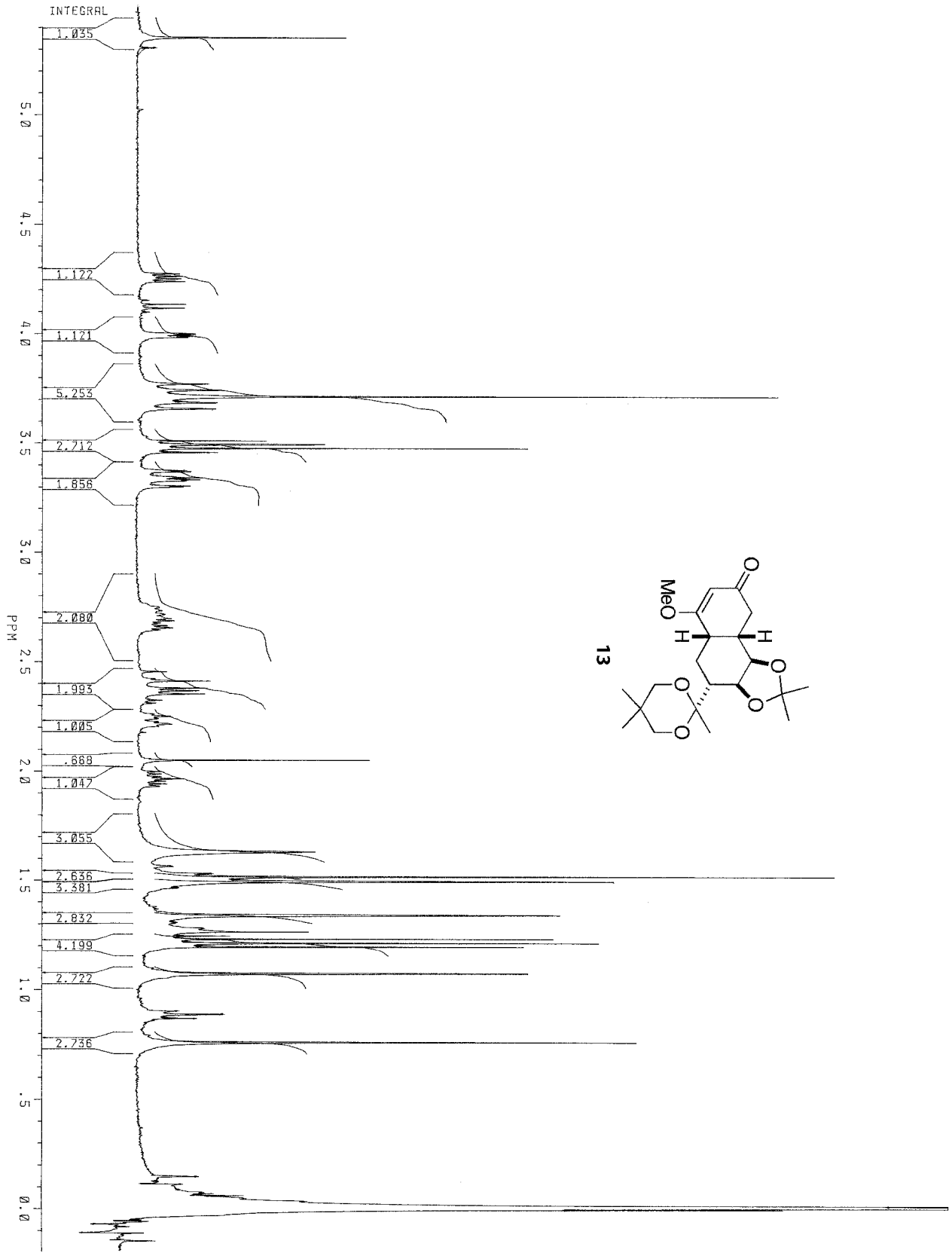

INTEGRAL
.504
.490
.143
.444
1.242
.981
.401
1.060
1.034
.544
.545
.536
.535
.481
3.810
1.764
1.040
1.563
1.590
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM
MeO
O
H
H
O
O
O
O

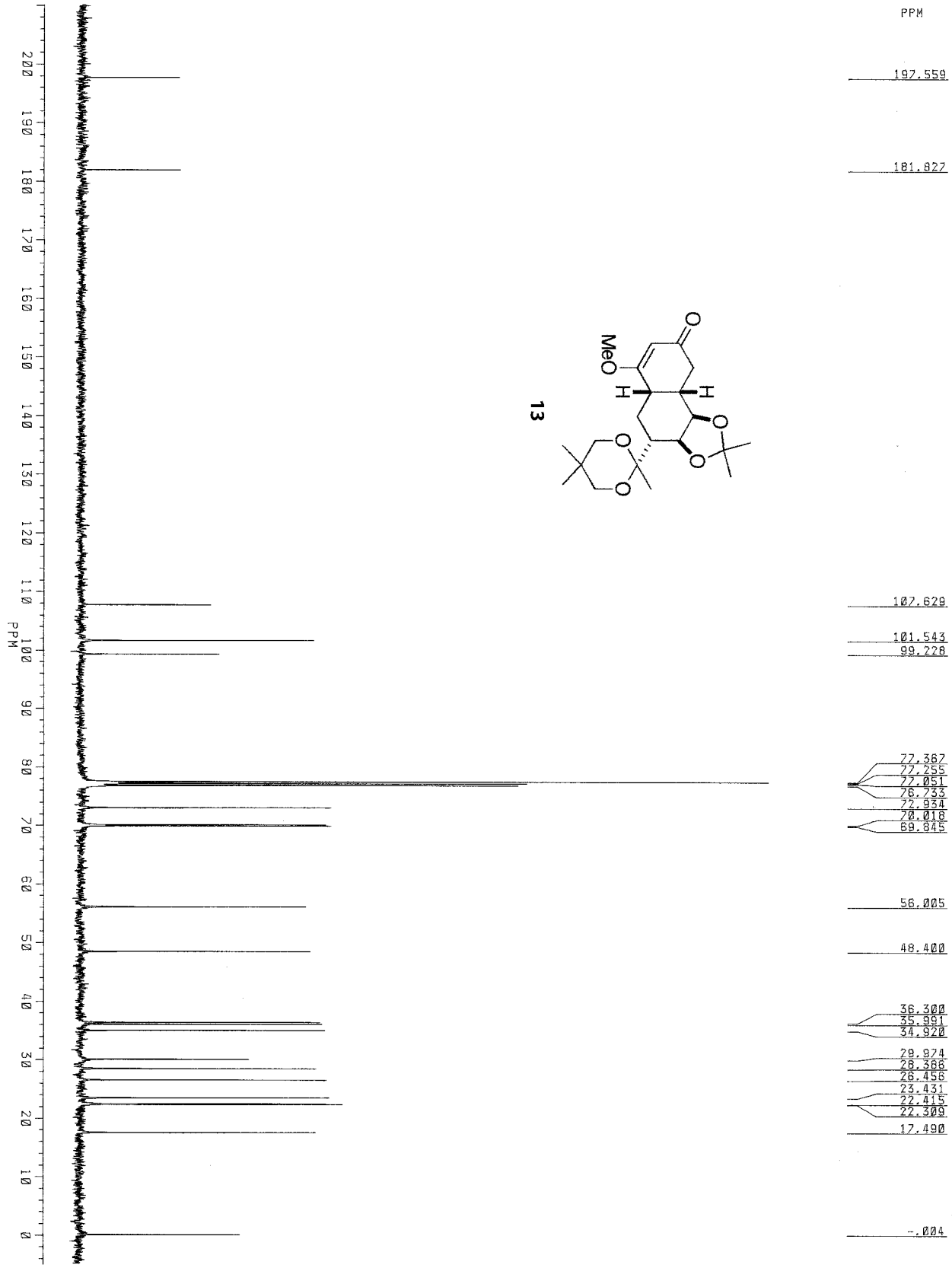
12

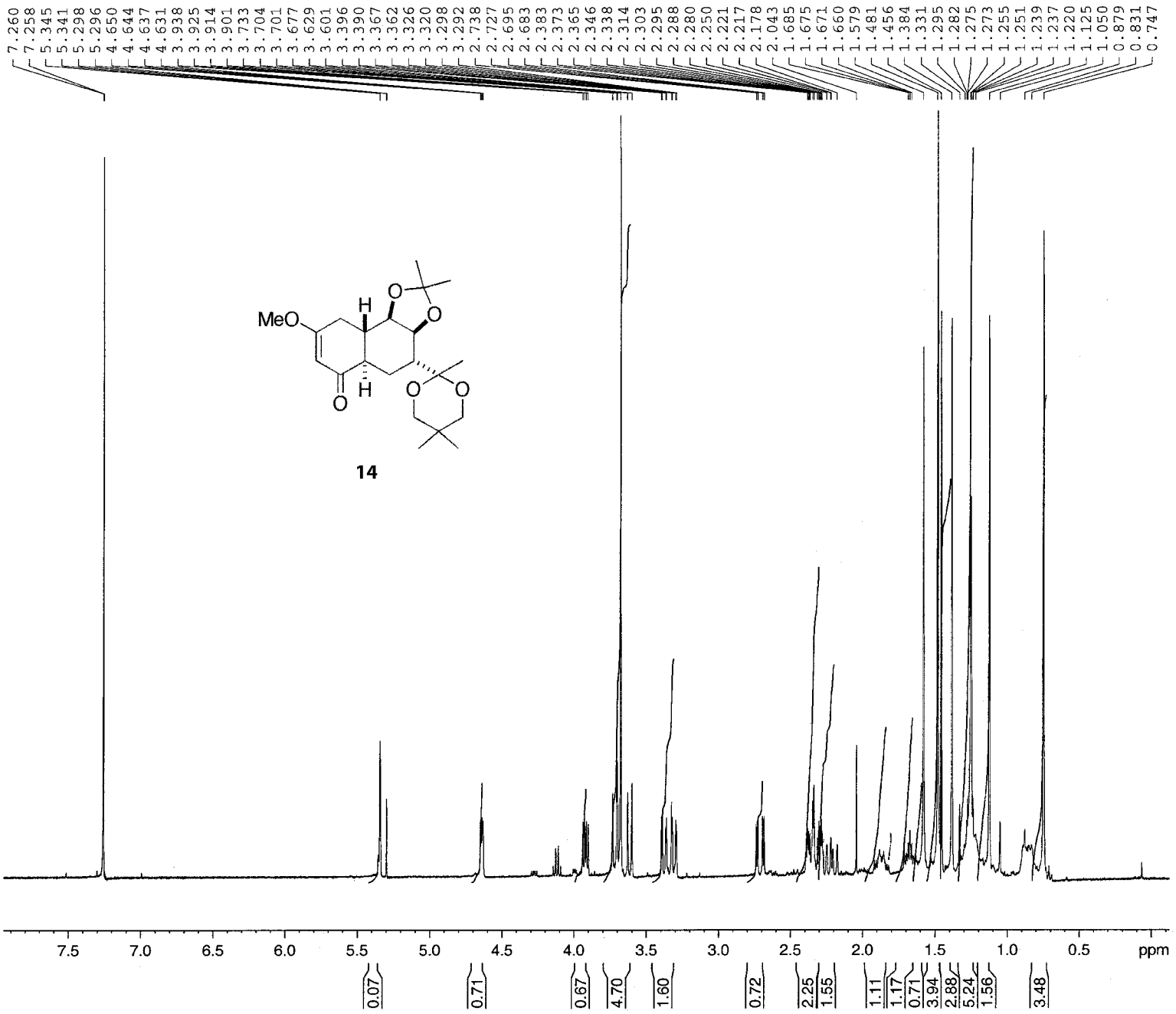


12

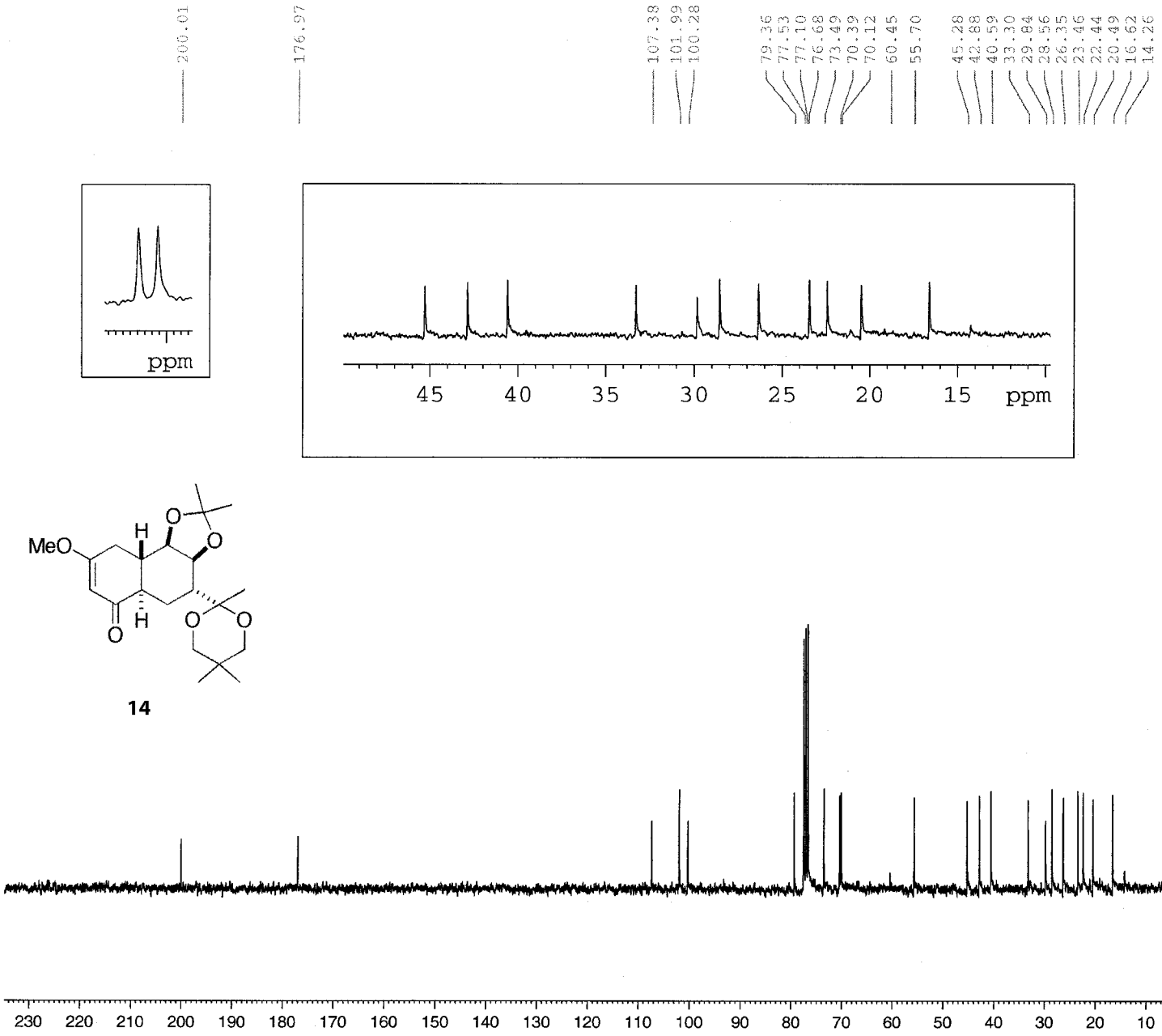

PPM
201.615
175.632
107.865
101.650
99.318
77.358
77.041
76.725
76.584
73.301
70.080
69.868
55.696
47.746
42.045
34.404
29.942
28.516
28.329
26.312
23.415
22.374
21.230
17.528
-.001
MeO
O
H
H
O
O
O
O
12
JDIII94.201
DATE 23-10-88
SF 100.614
SY 74.890000
O1 54000.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 33516
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 209.999P
F2 -4.997P
HZ/CM 655.504
PPM/CM 6.515
SR 43868.93


INTEGRAL
1.035
1.122
1.121
5.253
2.712
1.856
2.080
1.993
1.005
.689
1.047
3.055
2.636
3.381
2.832
4.199
2.722
2.736
PPM
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
MeO
H
H
O
O
O
O
O
13
JDII94.102
DATE 21-10-88
SF 400.134
SY 74.890000
01 6400.000
SI 16384
TD 16384
SW 6024.096
HZ/PT .735
PW 3.0
RD 2.000
AQ 1.360
RG 32
NS 32
TE 297
FW 7600
O2 6000.000
DP 15H PO
LB 0.0
GB 0.0
CX 33.00
CY 0.0
F1 5.501P
F2 -.195P
HZ/CM 69.057
PPM/CM .173
SR 4592.46


PPM
197.559
181.827
107.629
101.543
99.228
77.367
77.255
77.051
76.733
72.934
70.016
69.845
56.005
48.400
36.300
35.991
34.920
29.974
28.386
26.456
23.431
22.415
22.309
17.490
-.004
MeO
H
H
O
O
O
O
13
JDII94A.002
AU PROG: WALTZ.AU
DATE 25-10-88
SF 100.614
SY 74.690000
O1 5400.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 2200
TE 297
FW 31300
O2 5500.000
DP 15H DD
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 210.052P
F2 14.936P
HZ/CM 65.481
PPM/CM 6.515
SR 43869.69

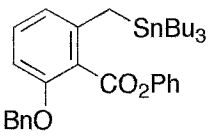



```
Current Data Parameters
NAME                wm-I-21-1
EXPNO                       1
PROCNO                      1
DU                         /m
USER                william

F2 - Acquisition Parameters
Date_              20060331
Time                  17.57
INSTRUM              DPX400
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT
NS                      32
DS                       2
SWH               6410.256 Hz
FIDRES            0.195625 Hz
AQ                2.5559540 sec
RG                     512
DW                78.000 usec
DE                 6.00 usec
TE                 298.2 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                 14.70 usec
PL1                 0.00 dB
SFO1          400.0128001 MHz

F2 - Processing parameters
SI                   32768
SF            400.0100146 MHz
WDW                     no
SSB                      0
LB                  0.00 Hz
GB                       0
PC                    1.00
```



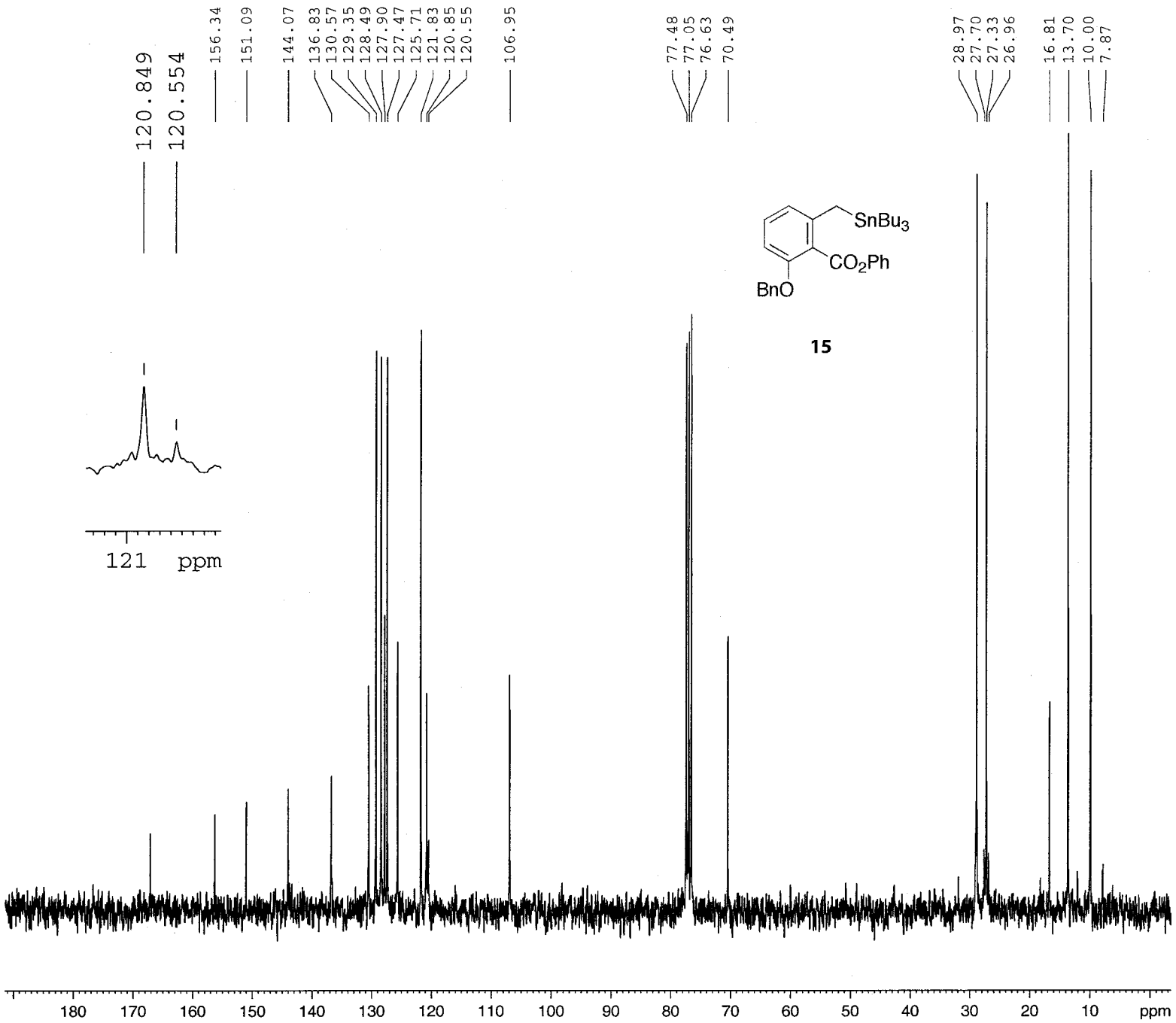
14

```
Current Data Parameters
NAME                  wm-I-24-1
EXPNO                         2
PROCNO                        1
DU                           /n
USER                   william

F2 - Acquisition Parameter
Date_                  20060404
Time                      16.18
INSTRUM                  DPX300
PROBHD    5 mm QNP  1H/1
PULPROG                 zgpg30
TD                         65536
SOLVENT                  CDCl3
NS                           466
DS                             4
SWH                  18832.393 Hz
FIDRES                0.287360 Hz
AQ                    1.7400308 se
RG                       9195.2
DW                       26.550 us
DE                        6.00 us
TE                       296.2 K
D1                  0.15000001 se
d11                 0.03000000 se
DELTA               0.05000000 se
TD0                           1

======== CHANNEL f1 ======
NUC1                        13C
P1                         8.80 us
PL1                       -3.00 dB
SFO1                75.4760505 MH

======== CHANNEL f2 ======
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 us
PL2                       -3.00 dB
PL12                      17.55 dB
PL13                      17.55 dB
SFO2               300.1312005 MH

F2 - Processing parameters
SI                         32768
SF                  75.4677434 MH
WDW                           EM
SSB                            0
LB                         3.00 Hz
GB                             0
PC                          1.40
```

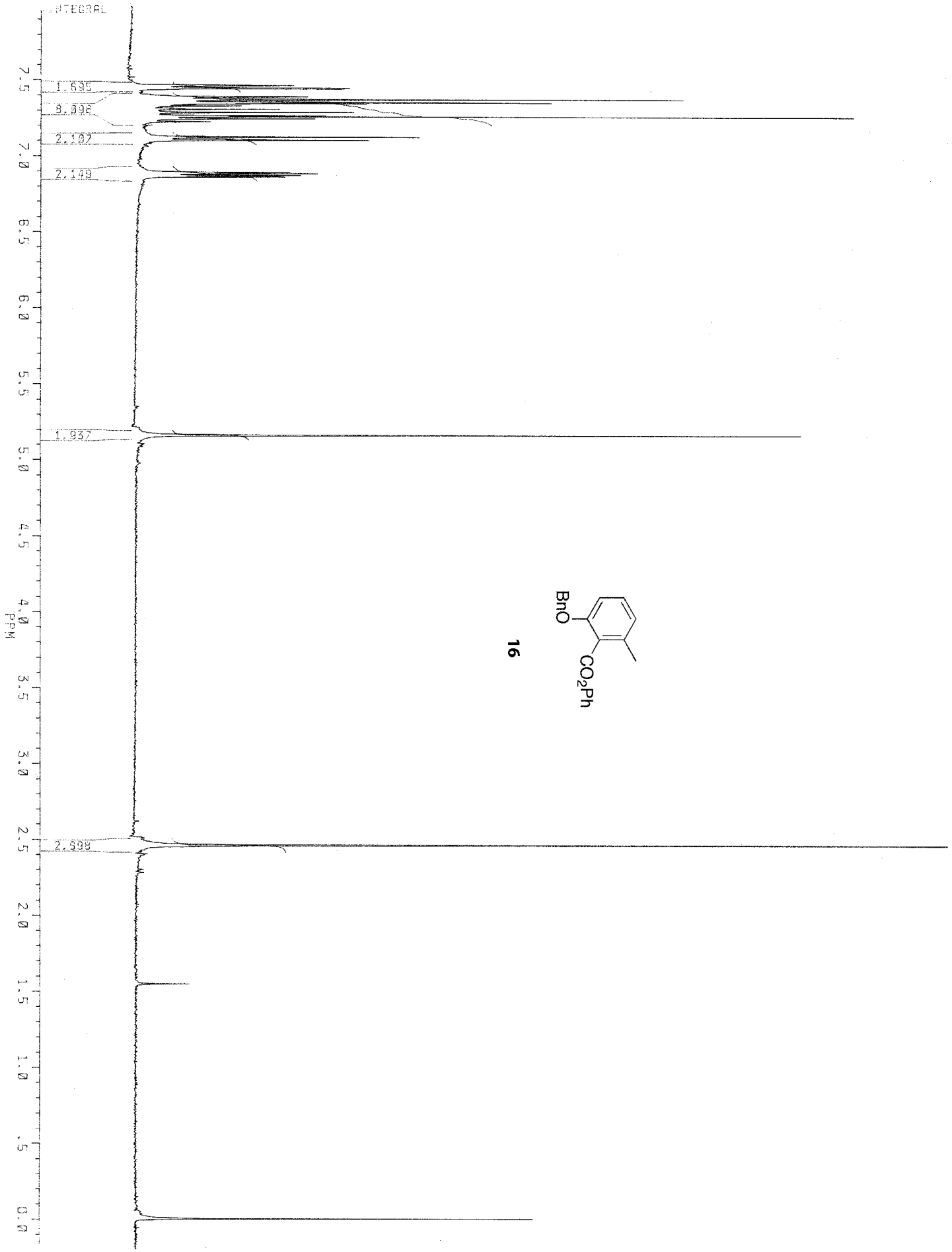


15


```
Current Data Parameters
NAME                 wm-I-39-1
EXPNO                        1
PROCNO                       1
DU                          /m
USER                   william

F2 - Acquisition Parame
Date_                 20060418
Time                     19.19
INSTRUM                DPX300
PROBHD    5 mm QNP  1H/1
PULPROG                  zg30
TD                      32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   4789.272
FIDRES                0.146157
AQ                    3.4210291
RG                         80.6
DW                       104.400
DE                          6.00
TE                         296.2
D1                    2.00000000
TD0                          1

======== CHANNEL f1 ===
NUC1                        1H
P1                        9.00
PL1                      -3.00
SFO1                300.1321009

F2 - Processing paramet
SI                       32768
SF                  300.1300000
WDW                         no
SSB                          0
LB                        0.00
GB                           0
PC                        1.00
```

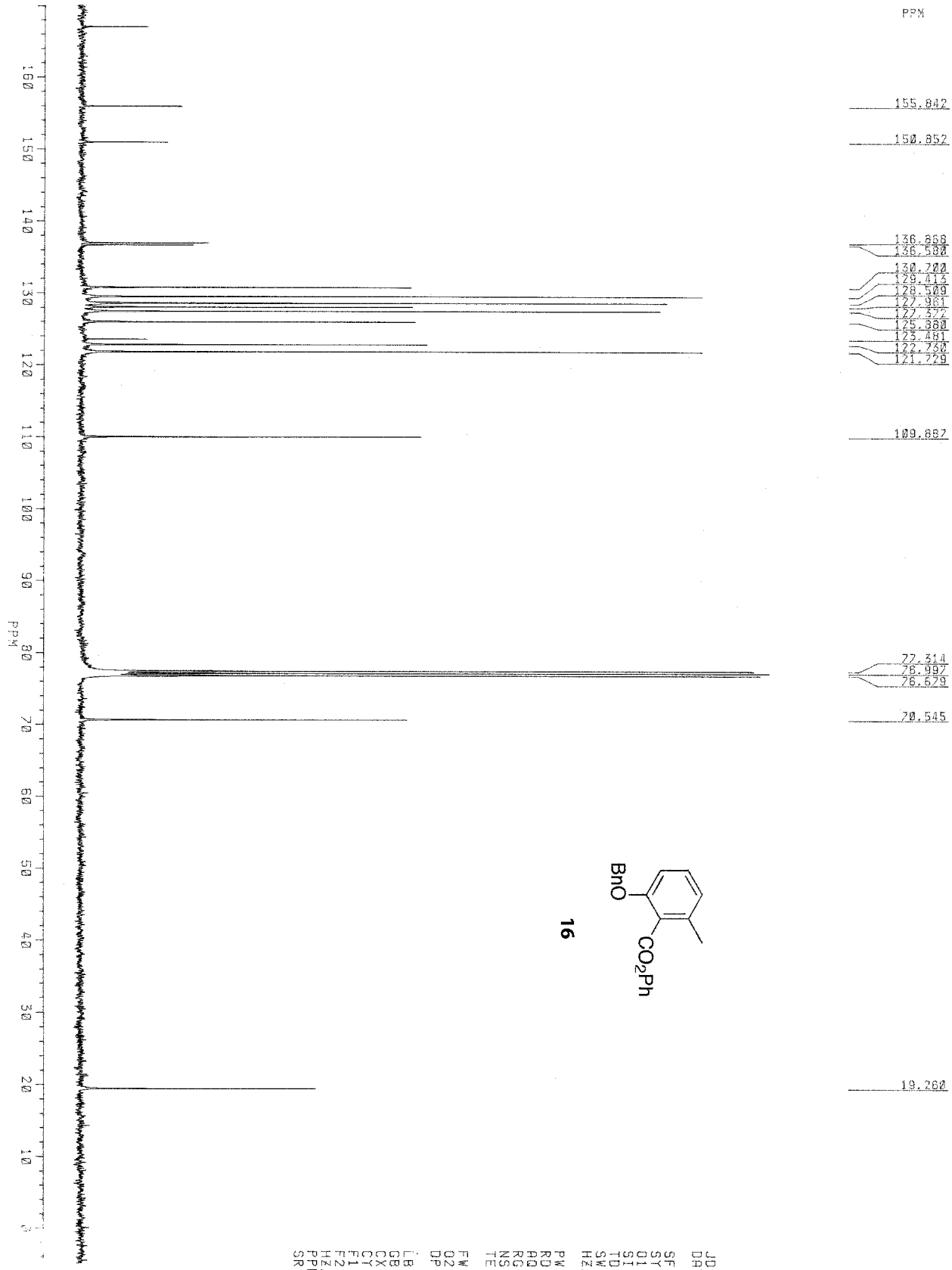


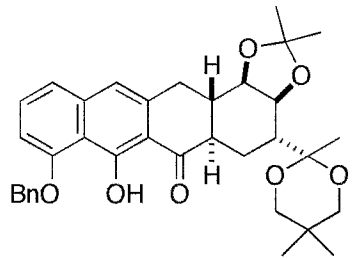

```
Current Data Parameters
NAME                  wm-I-39-1
EXPNO                         2
PROCNO                        1
DU                           /m
USER                   william

F2 - Acquisition Parameters
Date_                  20060418
Time                      19.23
INSTRUM                  DPX300
PROBHD    5 mm QNP  1H/1
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         208
DS                           4
SWH                  18832.393 Hz
FIDRES                0.287360 Hz
AQ                    1.7400308 sec
RG                       9195.2
DW                       26.550 usec
DE                        6.00 usec
TE                       296.2 K
D1                 0.15000001 sec
d11                0.03000000 sec
DELTA              0.05000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.80 usec
PL1                      -3.00 dB
SFO1                75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -3.00 dB
PL12                     17.55 dB
PL13                     17.55 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                  75.4677490 MHz
WDW                           EM
SSB                            0
LB                        3.00 Hz
GB                             0
PC                          1.40
```


INTEGRAL
1.635
9.096
2.107
2.149
1.937
2.598
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
.5
0.0
PPM

BnO
CO2Ph

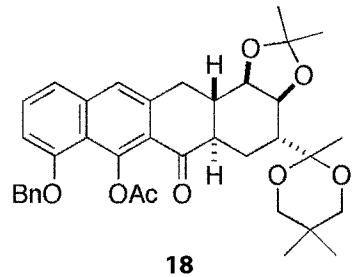
16


PPM
155.842
150.852
136.858
136.580
130.700
129.414
128.509
127.961
127.352
125.980
123.481
122.750
121.729
109.867
77.314
76.997
76.679
70.545
19.260
BnO
CO2Ph
16
JDIV024.201
DATE 1-3-89
SF 100.614
SY 74.890000
O1 54000.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 800
NS 8837
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 18.00
F1 170.004P
F2 -4.986P
HZ/CM 533.526
PPM/CM 5.303
SR 43876.94



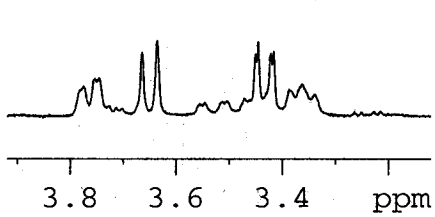
17

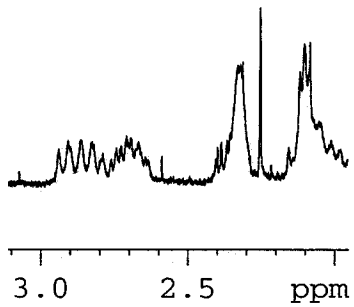
```
Current Data Parameters
NAME                 wm-I-40-1
EXPNO                        1
PROCNO                       1
DU                          /m
USER                   william

F2 - Acquisition Parameters
Date_               20060420
Time                   10.56
INSTRUM              DPX300
PROBHD    5 mm QNP  1H/1
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                     574.7
DW                   104.400 usec
DE                     6.00 usec
TE                     296.2 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.00 usec
PL1                   -3.00 dB
SFO1           300.1321009 MHz

F2 - Processing parameters
SI                     32768
SF                300.1300000 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.00
```

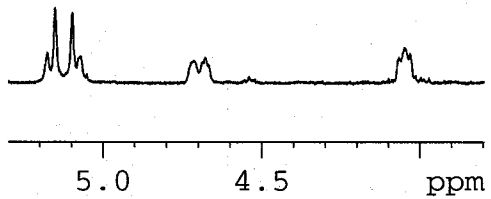


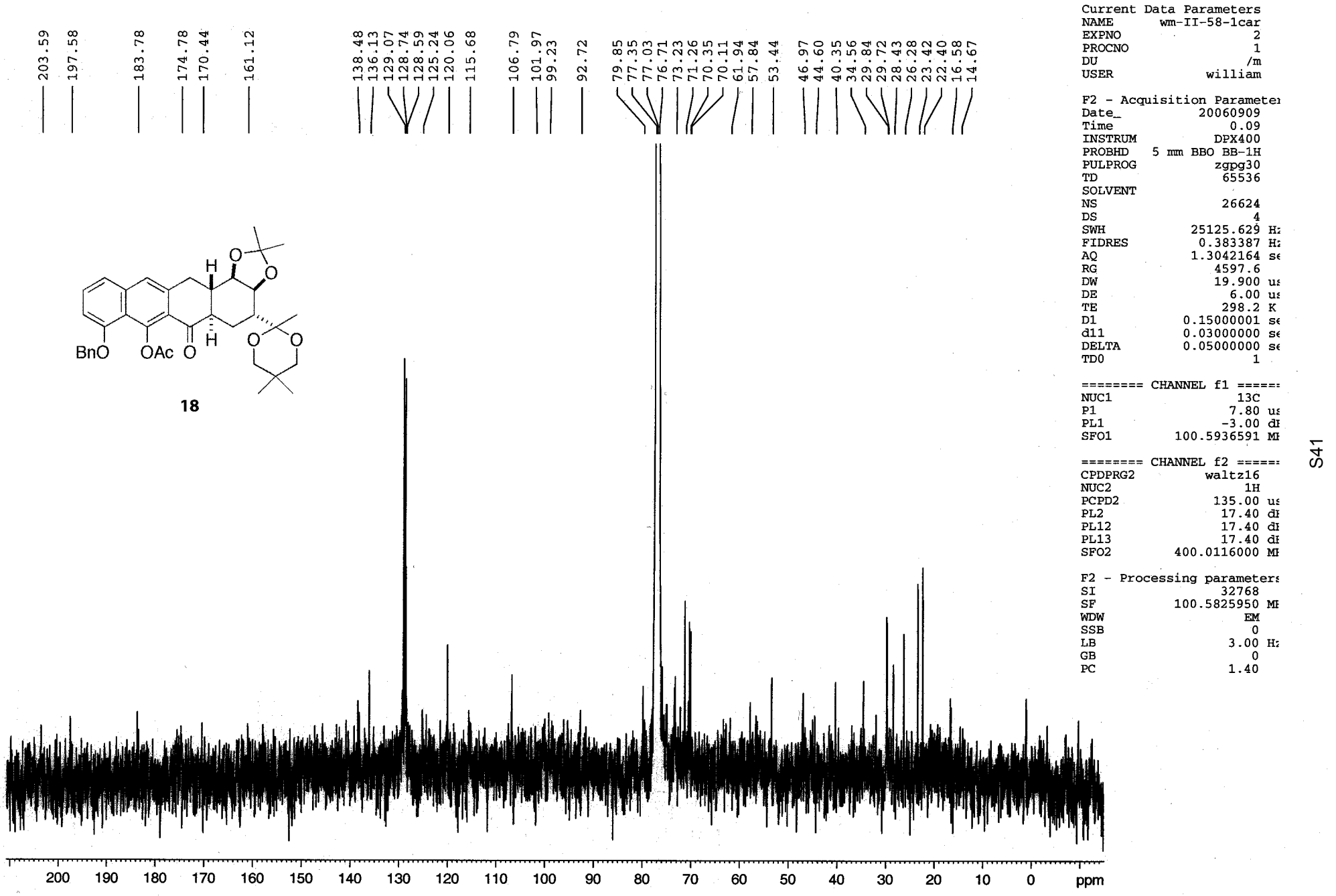
18

```
Current Data Parameters
NAME          wm-I-70-car
EXPNO                   2
PROCNO                  1
DU                     /m
USER             william

F2 - Acquisition Parameters
Date_           20060526
Time               20.58
INSTRUM          DPX400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT
NS                   32
DS                    2
SWH            6410.256 Hz
FIDRES        0.195625 Hz
AQ            2.5559540 sec
RG                  512
DW               78.000 usec
DE                6.00 usec
TE               298.2 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
SFO1        400.0128001 MHz

F2 - Processing parameters
SI                32768
SF        400.0100000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```

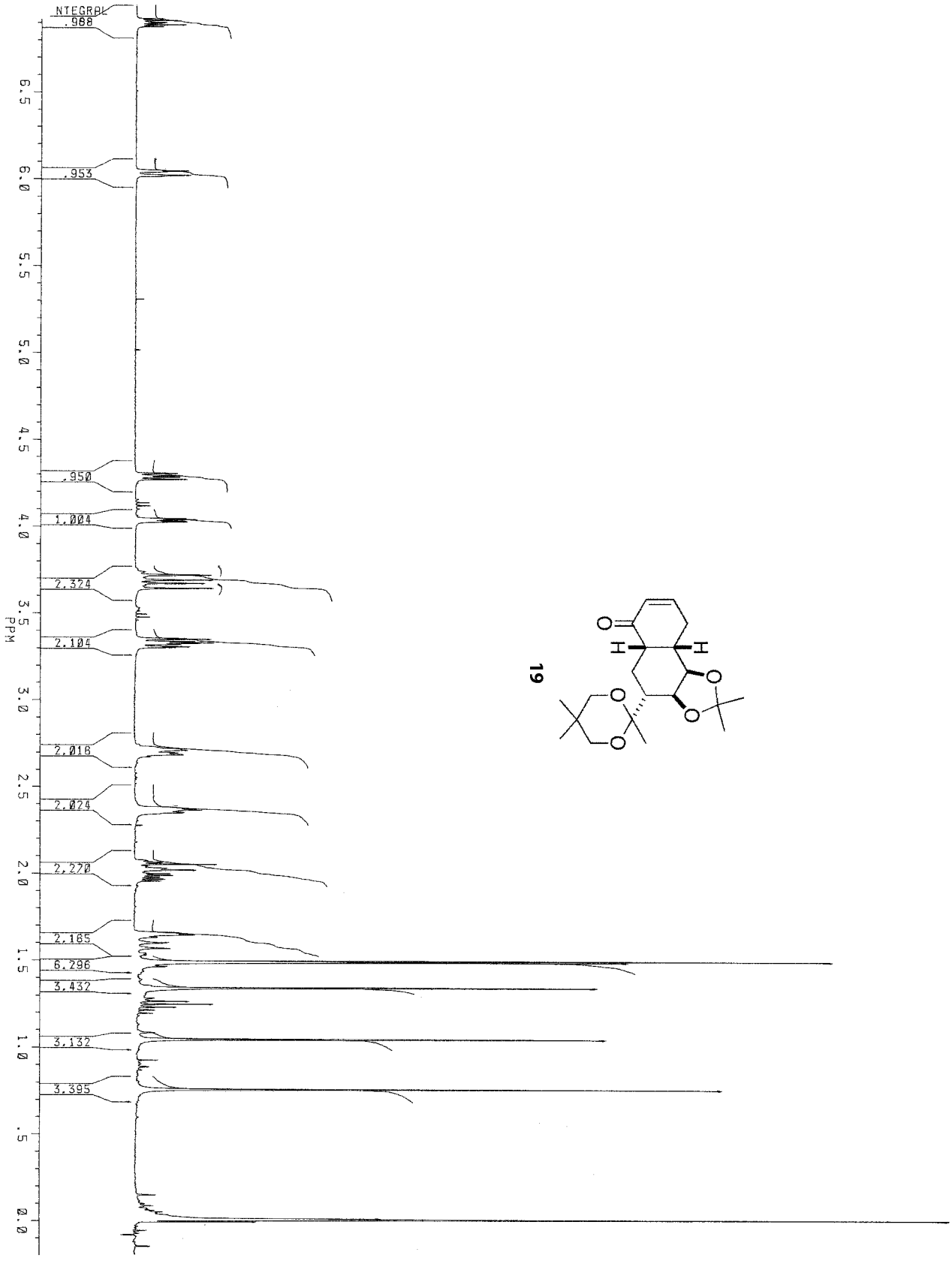




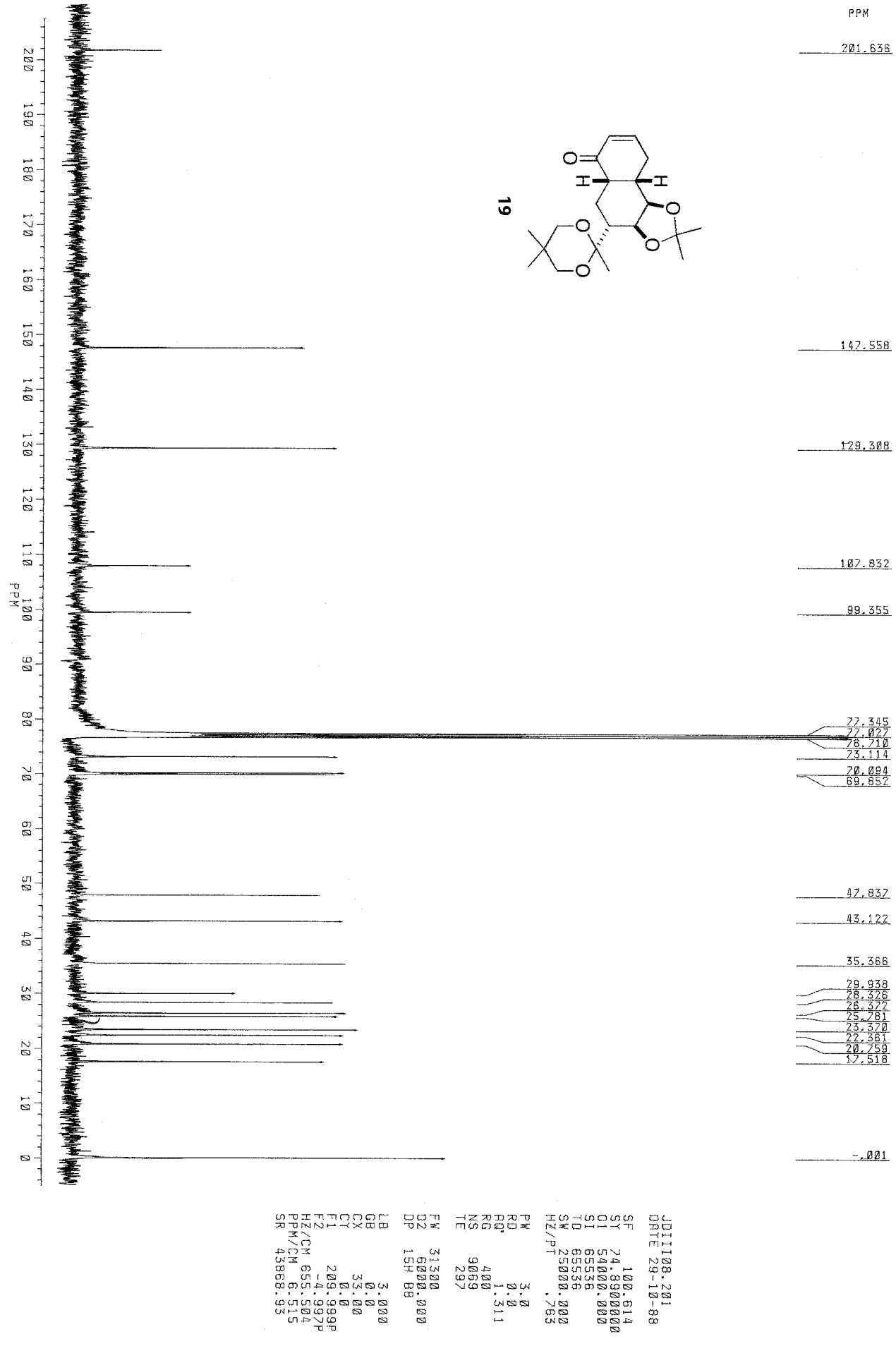





```
Current Data Parameters
NAME       wm-II-58-1car
EXPNO                 2
PROCNO                1
DU                   /m
USER           william

F2 - Acquisition Parameter
Date_          20060909
Time               0.09
INSTRUM          DPX400
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD               65536
SOLVENT
NS               26624
DS                   4
SWH          25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 se
RG               4597.6
DW               19.900 us
DE                6.00 us
TE               298.2 K
D1           0.15000001 se
d11          0.03000000 se
DELTA        0.05000000 se
TD0                  1

======== CHANNEL f1 ======
NUC1                13C
P1                7.80 us
PL1              -3.00 dB
SFO1        100.5936591 MH

======== CHANNEL f2 ======
CPDPRG2         waltz16
NUC2                1H
PCPD2           135.00 us
PL2              17.40 dB
PL12             17.40 dB
PL13             17.40 dB
SFO2        400.0116000 MH

F2 - Processing parameters
SI                32768
SF          100.5825950 MH
WDW                EM
SSB                 0
LB               3.00 Hz
GB                  0
PC               1.40
```

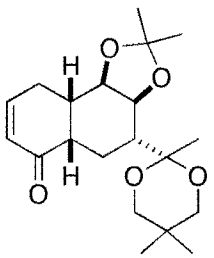

INTEGRAL
.988
.953
.950
1.004
2.324
2.104
2.016
2.024
2.270
2.165
6.296
3.432
3.132
3.395
PPM
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
JDIII08-101
DATE 28-10-88
SF 400.134
SY 74.890000
D1 6400.000
SI 16384
TD 16384
SW 6024.096
HZ/PT .735
PW 3.0
RD 2.000
AQ 1.360
RG 20
NS 32
TE 297
FW 7600
O2 6000.000
DP 15H PO
LB 0.0
GB 0.0
CX 33.00
CY 0.0
F1 7.000P
F2 -.198P
HZ/CM 87.285
PPM/CM .218
SR 4390.99

19


PPM
201.636
147.556
129.308
107.832
99.355
77.345
77.027
76.710
73.114
70.094
69.852
47.837
43.122
35.366
29.938
28.326
26.372
25.781
23.570
22.361
20.759
17.518
-.001
19
JDIII08.201
DATE 29-10-88
SF 100.614
SY 74.8900000
O1 5400.000
SI 65536
TD 65536
SW 25000.000
HZ/PT .763
PW 3.0
RD 0.0
AQ 1.311
RG 400
NS 9069
TE 297
FW 31300
O2 6000.000
DP 15H BB
LB 3.000
GB 0.0
CX 33.00
CY 0.0
F1 209.999P
F2 -4.997P
HZ/CM 655.504
PPM/CM 6.515
SR 43868.93

RPM

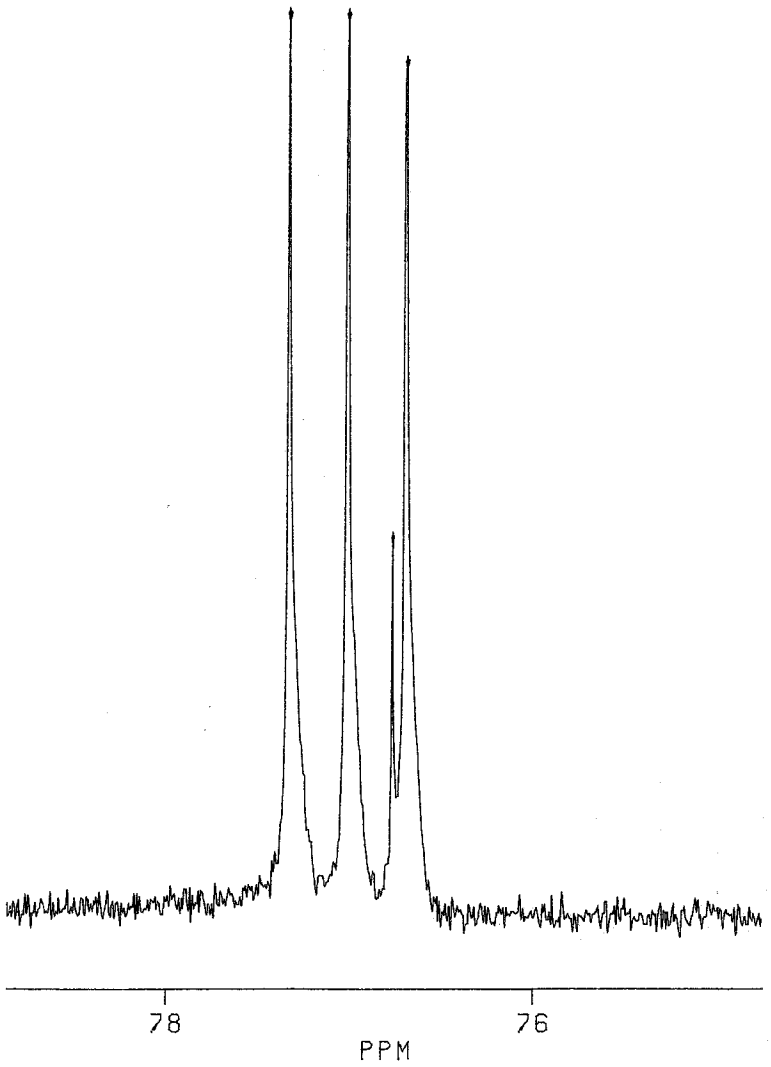
77.3192
77.0016
76.7571
76.6845

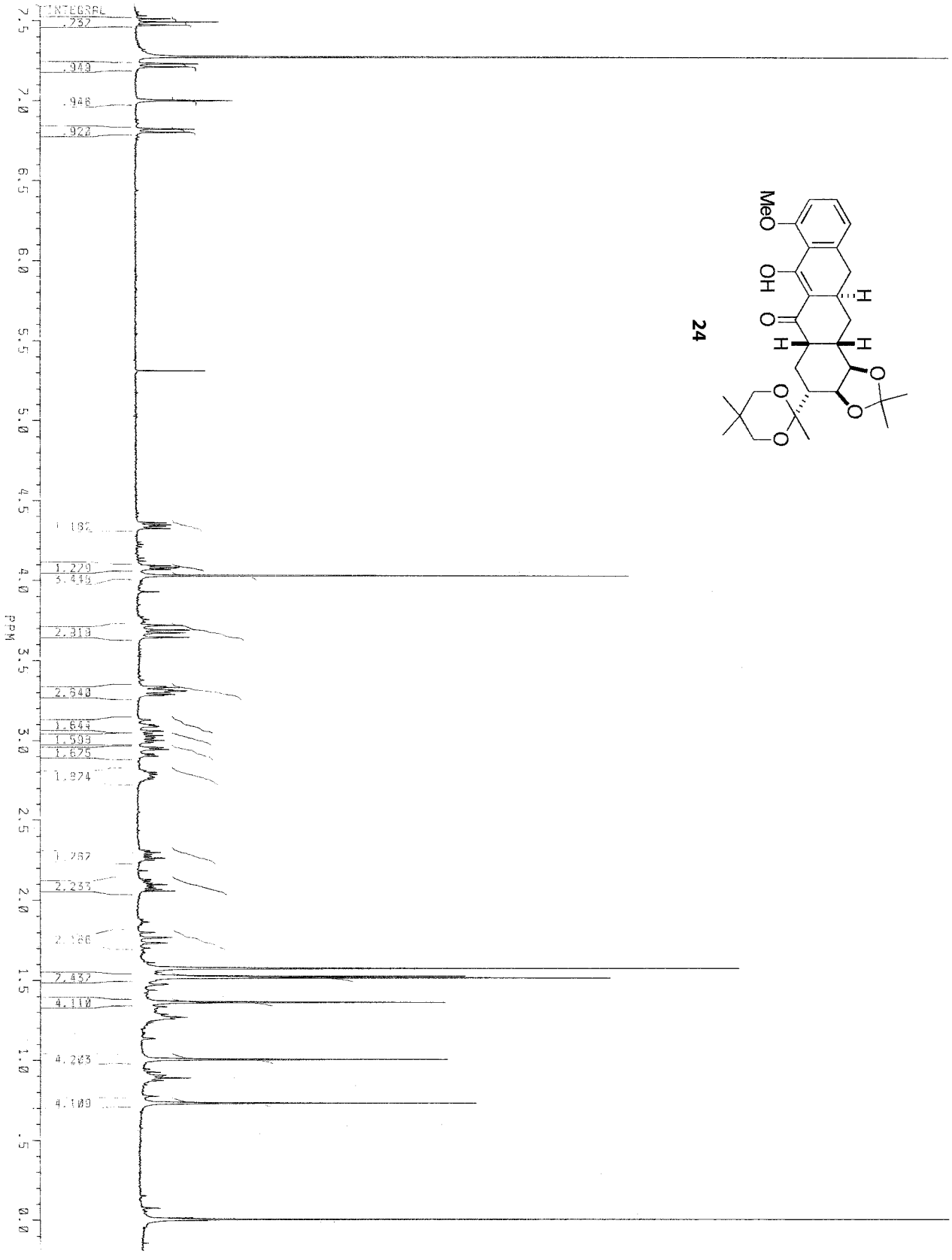


19

JDIII08.201
DATE 29-10-88

SF	100.614
SY	74.8900000
O1	54000.000
SI	65536
TD	65536
SW	25000.000
HZ/PT	.763
PW	3.0
RD	0.0
AQ	1.311
RG	400
NS	9069
TE	297
FW	31300
O2	6000.000
DP	15H BB
LB	0.0
GB	0.0
CX	10.00
CY	12.00
F1	78.858P
F2	74.740P
HZ/CM	41.428
PPM/CM	.412
SR	43871.60

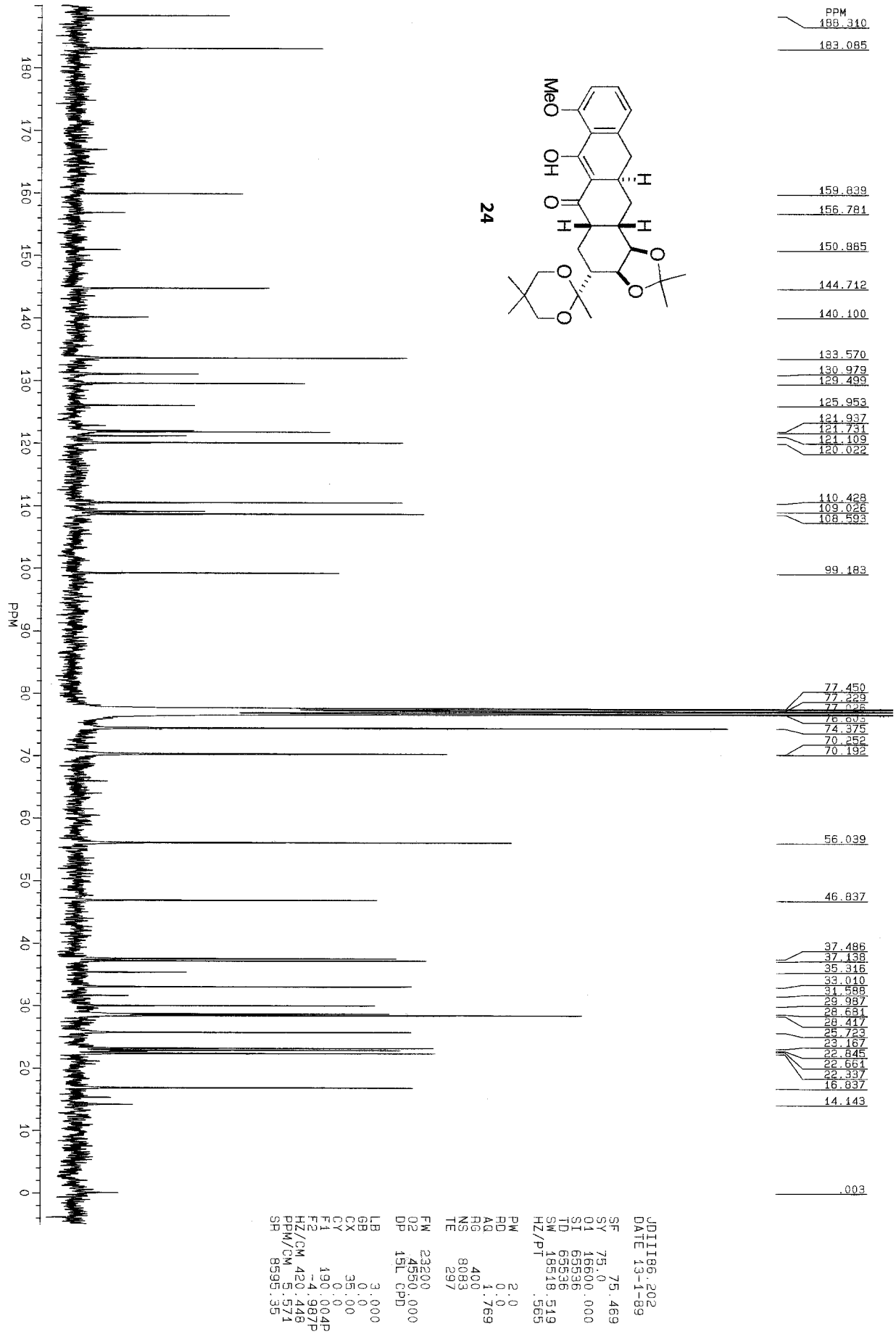


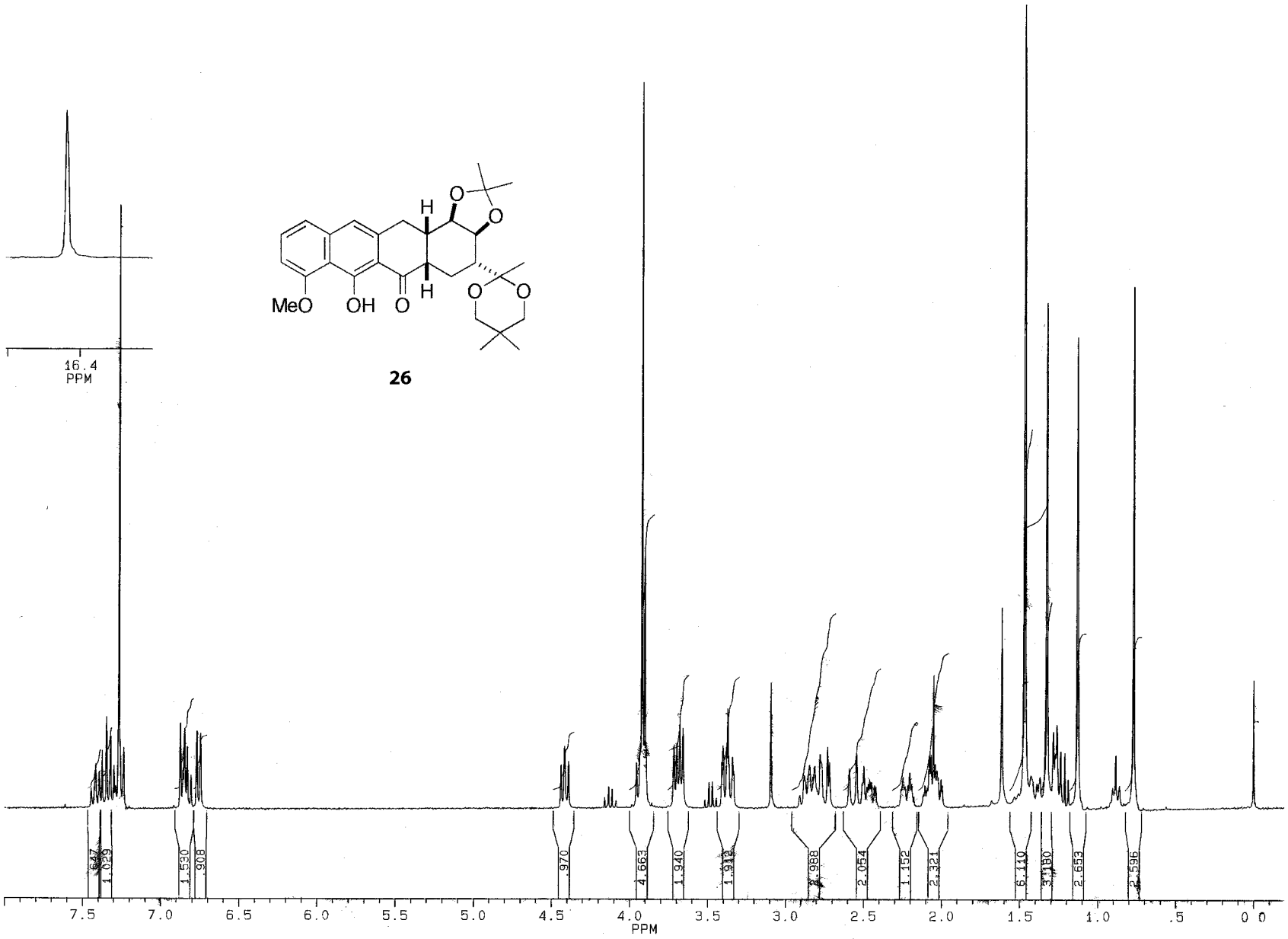


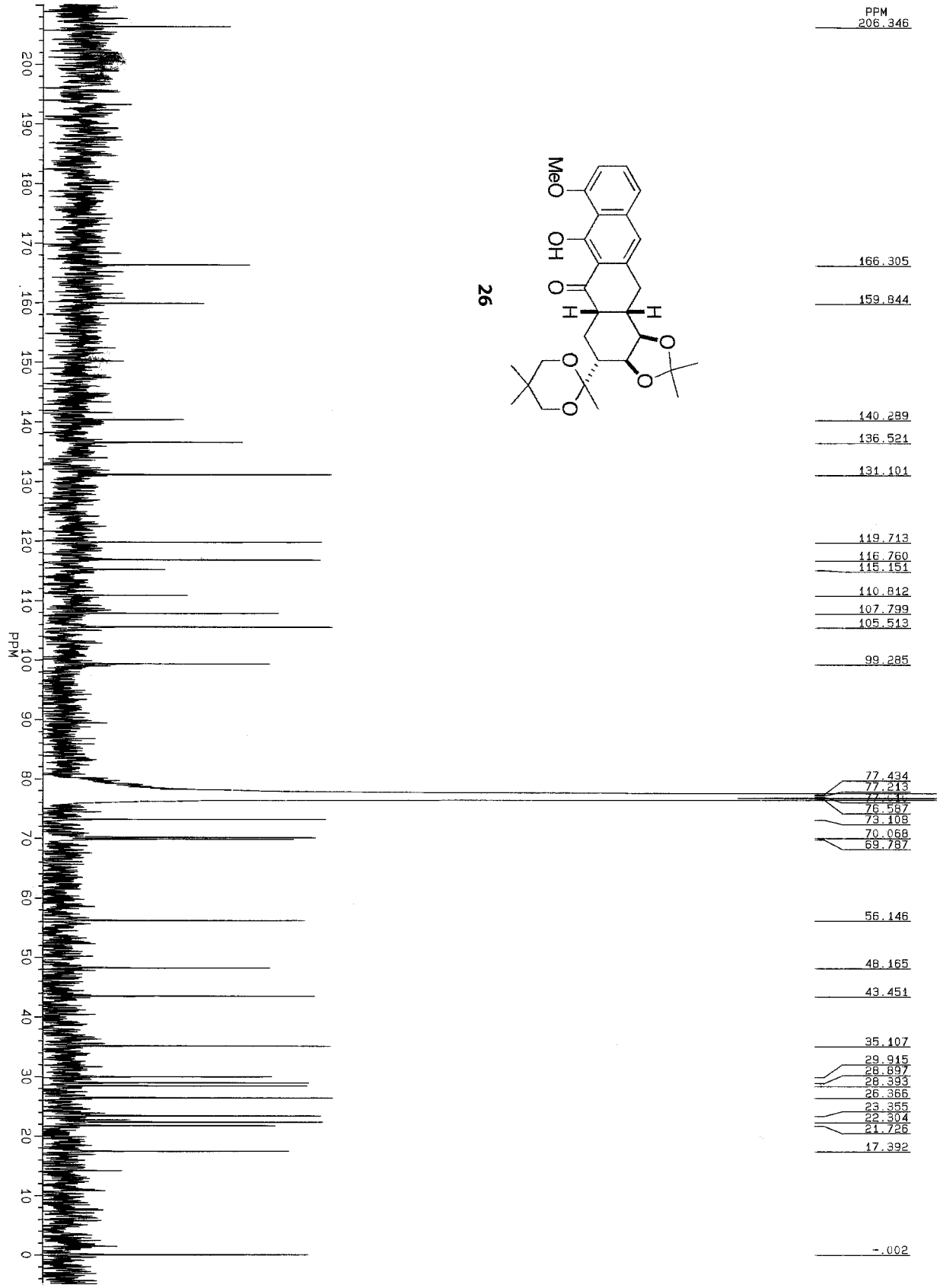
24

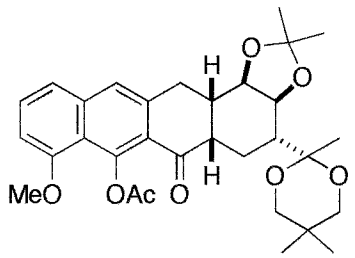
JDIV024-201
DATE 1-3-89

SF	400.134
SY	74.8900000
O1	6400.000
SI	16384
TD	16384
SW	6024.096
HZ/PT	.735
PW	3.0
RD	2.000
AQ	1.360
RG	100
NS	160
TE	297
FW	7600
O2	6000.000
DP	15H PO
LB	0.0
GB	0.0
CX	33.00
CY	0.0
F1	7.601P
F2	-.197P
HZ/CM	94.550
PPM/CM	.236
SR	4392.46


MeO
OH
O
H
H
H
O
O
O
O
24
PPM
188.310
183.085
159.839
156.781
150.885
144.712
140.100
133.570
130.979
129.499
125.953
121.937
121.731
121.109
120.022
110.428
109.026
108.593
99.183
77.450
77.229
77.025
76.603
74.375
70.252
70.192
56.039
46.837
37.486
37.138
35.316
33.010
31.586
29.987
28.651
28.417
25.723
23.167
22.845
22.661
22.337
16.837
14.143
.003
PPM
JDIII86.202
DATE 13-1-89
SF 75.469
SY 75.0
D1 16600.000
SI 65536
TD 65536
SW 18518.519
HZ/PT .565
PW 2.0
RD 0.0
AQ 1.769
RG 400
NS 8083
TE 297
FW 23200
O2 4550.000
DP 15L CPD
LB 3.000
GB 0.0
CX 35.00
CY 0.0
F1 190.004P
F2 -4.987P
HZ/CM 420.448
PPM/CM 5.571
SR 8595.35

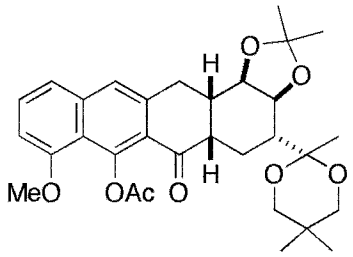

MeO
OH
O
H
H
O
O
O
O
16.4
PPM
26
A.002
DATE 19-1-89
SF 300.133
SY 210.0
O1 6112.778
SI 16384
TD 16384
SW 6024.096
HZ/PT .735
PW 3.0
RD 2.000
AQ 1.360
RG 4
NS 32
TE 297
FW 7600
O2 3200.000
DP 63L PO
LB 0.0
GB 0.0
CX 35.00
CY 24.00
F1 8.000P
F2 -.196P
HZ/CM 70.280
PPM/CM .234
SR 3366.20
.647
1.029
1.530
.908
.970
4.663
1.940
1.913
8.968
2.054
1.152
2.321
6.110
3.180
2.653
2.596
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
.5
0 0
PPM


PPM
206.346
166.305
159.844
140.289
136.521
131.101
119.713
116.760
115.151
110.812
107.799
105.513
99.285
77.434
77.213
76.992
76.567
73.109
70.068
69.787
56.146
48.165
43.451
35.107
29.915
28.897
28.393
26.366
23.355
22.304
21.726
17.392
-.002
MeO
OH
O
H
H
O
O
O
26
JDIV004:201
DATE 20-2-89
SF 75.469
SY 75.0
01 16600.000
SI 65536
TD 65536
SW 18518.519
HZ/PT .565
PW 2.0
RD 0.0
AQ 1.769
RG 400
NS 37231
TE 297
FW 23200
O2 4550.000
DP 15L CPD
LB 3.000
GB 0.0
CX 35.00
CY 0.0
F1 210.005P
F2 -4.987P
HZ/CM 463.577
PPM/CM 6.143
SR 8595.35



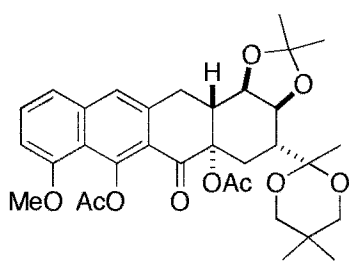
27


```
Current Data Parameters
NAME                  qx354y.101
EXPNO                          1
PROCNO                         1
DU                            /m
USER                       qing

F2 - Acquisition Parameters
Date_                   20030903
Time                       21.37
INSTRUM                  dpx300
PROBHD        5 mm QNP  1H
PULPROG                    zg30
TD                        32768
SOLVENT                   CDCl3
NS                           65
DS                            2
SWH                   4496.403 Hz
FIDRES                0.137219 Hz
AQ                    3.6438515 sec
RG                        574.7
DW                      111.200 usec
DE                        6.00 usec
TE                       300.0 K
D1                    1.50000000 sec

============ CHANNEL f1 =========
NUC1                         1H
P1                        8.20 usec
PL1                      -3.00 dB
SFO1                300.1319000 MHz

F2 - Processing parameters
SI                        32768
SF                  300.1300063 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



27

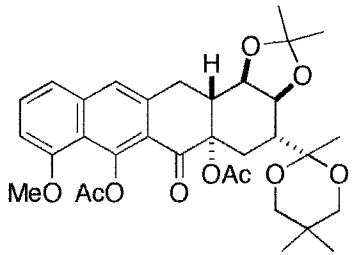
```
Current Data Parameters
NAME          qx354y.101
EXPNO                  2
PROCNO                 1
DU                    /m
USER               qing

F2 - Acquisition Parameters
Date_           20030903
Time               21.48
INSTRUM          dpx300
PROBHD     5 mm QNP  1H
PULPROG          zgpg30
TD                65536
SOLVENT
NS                21388
DS                    2
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                 8192
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1            0.00300000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ==========
NUC1                13C
P1                 7.60 usec
PL1               -3.00 dB
SFO1         75.4756431 MHz

============ CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               17.55 dB
PL13               19.00 dB
SFO2        300.1315007 MHz

F2 - Processing parameters
SI                131072
SF           75.4677190 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.40
```



29

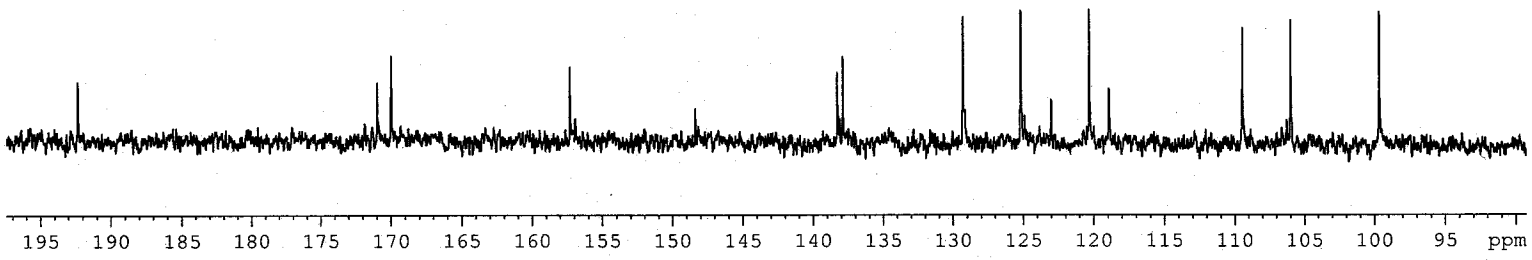

```
Current Data Parameters
NAME                 qx358w.101
EXPNO                         1
PROCNO                        1
DU                           /m
USER                      qing

F2 - Acquisition Parameters
Date_                  20030908
Time                      22.12
INSTRUM                  dpx300
PROBHD       5 mm QNP   1H
PULPROG                   zg30
TD                       32768
SOLVENT
NS                          100
DS                            2
SWH                   4496.403 Hz
FIDRES                0.137219 Hz
AQ                    3.6438515 sec
RG                        574.7
DW                      111.200 usec
DE                        6.00 usec
TE                       300.0 K
D1                    1.50000000 sec

============ CHANNEL f1 =========
NUC1                         1H
P1                        8.20 usec
PL1                      -3.00 dB
SFO1                300.1319000 MHz

F2 - Processing parameters
SI                           32768
SF                  300.1300063 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.40
```

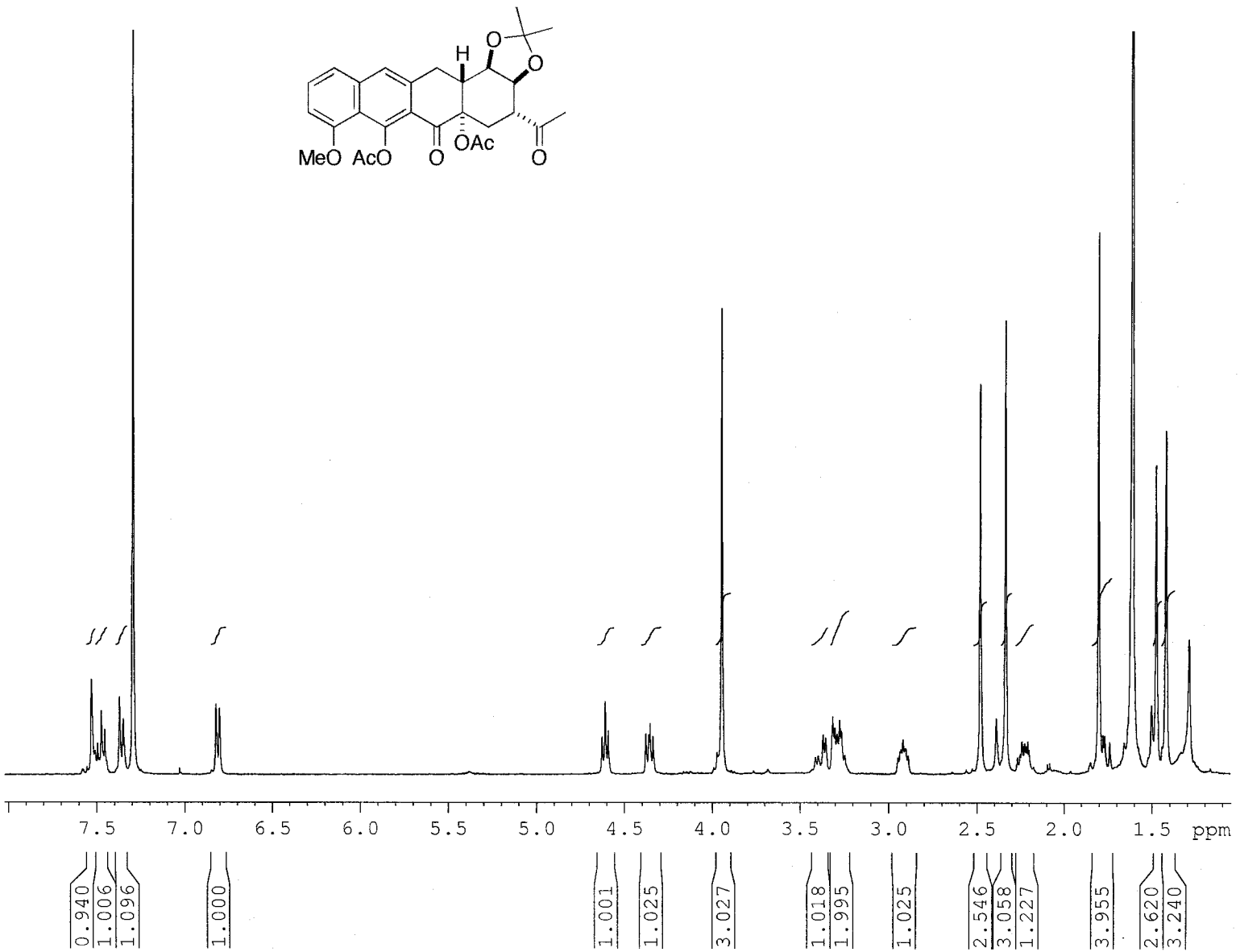
192.360
170.951
169.979
157.299
138.282
137.874
129.271
125.148
122.973
120.277
118.886
109.421
105.961
99.632



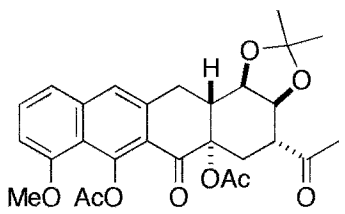
29

```
Current Data Parameters
NAME                 qx358w.101
EXPNO                         2
PROCNO                        1
DU                           /m
USER                      qing

F2 - Acquisition Parameters
Date_                  20030908
Time                      22.26
INSTRUM                 dpx300
PROBHD       5 mm QNP  1H
PULPROG                 zgpg30
TD                       65536
SOLVENT
NS                       20084
DS                           2
SWH                  18832.393 Hz
FIDRES               0.287360 Hz
AQ                   1.7400308 sec
RG                        8192
DW                      26.550 usec
DE                       6.00 usec
TE                      300.0 K
D1                   0.00300000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec

============ CHANNEL f1 ==========
NUC1                       13C
P1                        7.60 usec
PL1                      -3.00 dB
SFO1                75.4756431 MHz

============ CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                       2.00 dB
PL12                     17.55 dB
PL13                     19.00 dB
SFO2               300.1315007 MHz

F2 - Processing parameters
SI                       131072
SF                  75.4677190 MHz
WDW                         EM
SSB                          0
LB                        3.00 Hz
GB                           0
PC                        1.40
```

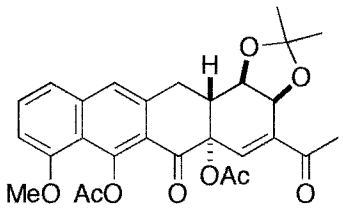





```
Current Data Parameters
NAME          qx359w.101
EXPNO                  1
PROCNO                 1
DU                    /m
USER               qing

F2 - Acquisition Parameters
Date_          20030910
Time              22.41
INSTRUM         dpx400
PROBHD    5 mm BBO Z-G
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                100
DS                  2
SWH          5995.204 Hz
FIDRES       0.182959 Hz
AQ           2.7329011 sec
RG              1149.4
DW              83.400 usec
DE               6.00 usec
TE              300.0 K
D1          2.00000000 sec

============ CHANNEL f1 =========
NUC1                1H
P1              11.30 usec
PL1              0.00 dB
SFO1       400.0126001 MHz

F2 - Processing parameters
SI                65536
SF       400.0100000 MHz
WDW                  EM
SSB                   0
LB               0.70 Hz
GB                    0
PC                 1.00
```

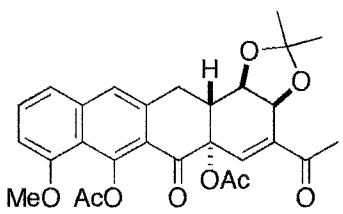



```
Current Data Parameters
NAME                 qx366y.101
EXPNO                         2
PROCNO                        1
DU                           /m
USER                      qing

F2 - Acquisition Parameters
Date_                  20031004
Time                       8.00
INSTRUM                  dpx300
PROBHD      5 mm QNP  1H
PULPROG                 zgpg30
TD                       65536
SOLVENT
NS                       20000
DS                           2
SWH                  18832.393 Hz
FIDRES                0.287360 Hz
AQ                    1.7400308 sec
RG                        8192
DW                      26.550 usec
DE                       6.00 usec
TE                      300.0 K
D1                 0.00300000 sec
D11                0.03000000 sec
D12                0.00002000 sec

============ CHANNEL f1 ==========
NUC1                       13C
P1                        7.60 usec
PL1                      -3.00 dB
SFO1                75.4756431 MHz

============ CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                       2.00 dB
PL12                     17.55 dB
PL13                     19.00 dB
SFO2               300.1315007 MHz

F2 - Processing parameters
SI                       131072
SF                  75.4677190 MHz
WDW                          EM
SSB                           0
LB                         3.00 Hz
GB                            0
PC                         1.40
```



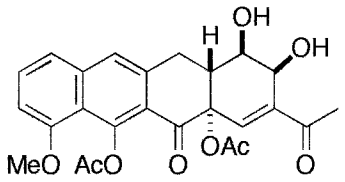
30


```
Current Data Parameters
NAME                 qx361w.101
EXPNO                         2
PROCNO                        1
DU                           /m
USER                      qing

F2 - Acquisition Parameters
Date_                  20030915
Time                      12.07
INSTRUM                 dpx400
PROBHD       5 mm BBO Z-G
PULPROG                  zg30
TD                       32768
SOLVENT                  CDC13
NS                        1357
DS                           2
SWH                   5995.204 Hz
FIDRES                0.182959 Hz
AQ                    2.7329011 sec
RG                       1149.4
DW                       83.400 usec
DE                        6.00 usec
TE                       300.0 K
D1                    2.00000000 sec

============ CHANNEL f1 =========
NUC1                         1H
P1                       11.30 usec
PL1                       0.00 dB
SFO1                400.0126001 MHz

F2 - Processing parameters
SI                       65536
SF                  400.0100000 MHz
WDW                         EM
SSB                          0
LB                        0.70 Hz
GB                           0
PC                        1.00
```



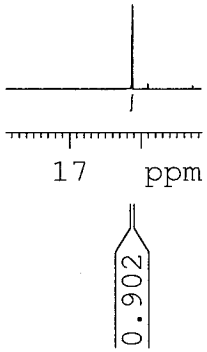
30

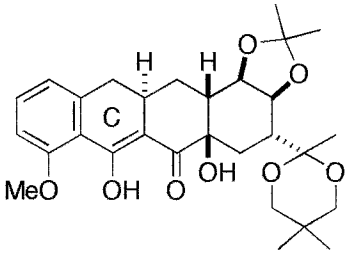

```
Current Data Parameters
NAME          qx558w.101
EXPNO                  3
PROCNO                 1
DU                    /m
USER                qing

F2 - Acquisition Parameters
Date_           20040711
Time                8.11
INSTRUM          dpx300
PROBHD     5 mm QNP  1H
PULPROG          zgpg30
TD                65536
SOLVENT
NS                21000
DS                    2
SWH           18832.393 Hz
FIDRES         0.287360 Hz
AQ             1.7400308 sec
RG                 8192
DW                26.550 usec
DE                 6.00 usec
TE                300.0 K
D1            0.00300000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ==========
NUC1                13C
P1                 7.60 usec
PL1               -3.00 dB
SFO1         75.4756431 MHz

============ CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               17.55 dB
PL13               19.00 dB
SFO2        300.1315007 MHz

F2 - Processing parameters
SI                131072
SF           75.4677190 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.00
```



31

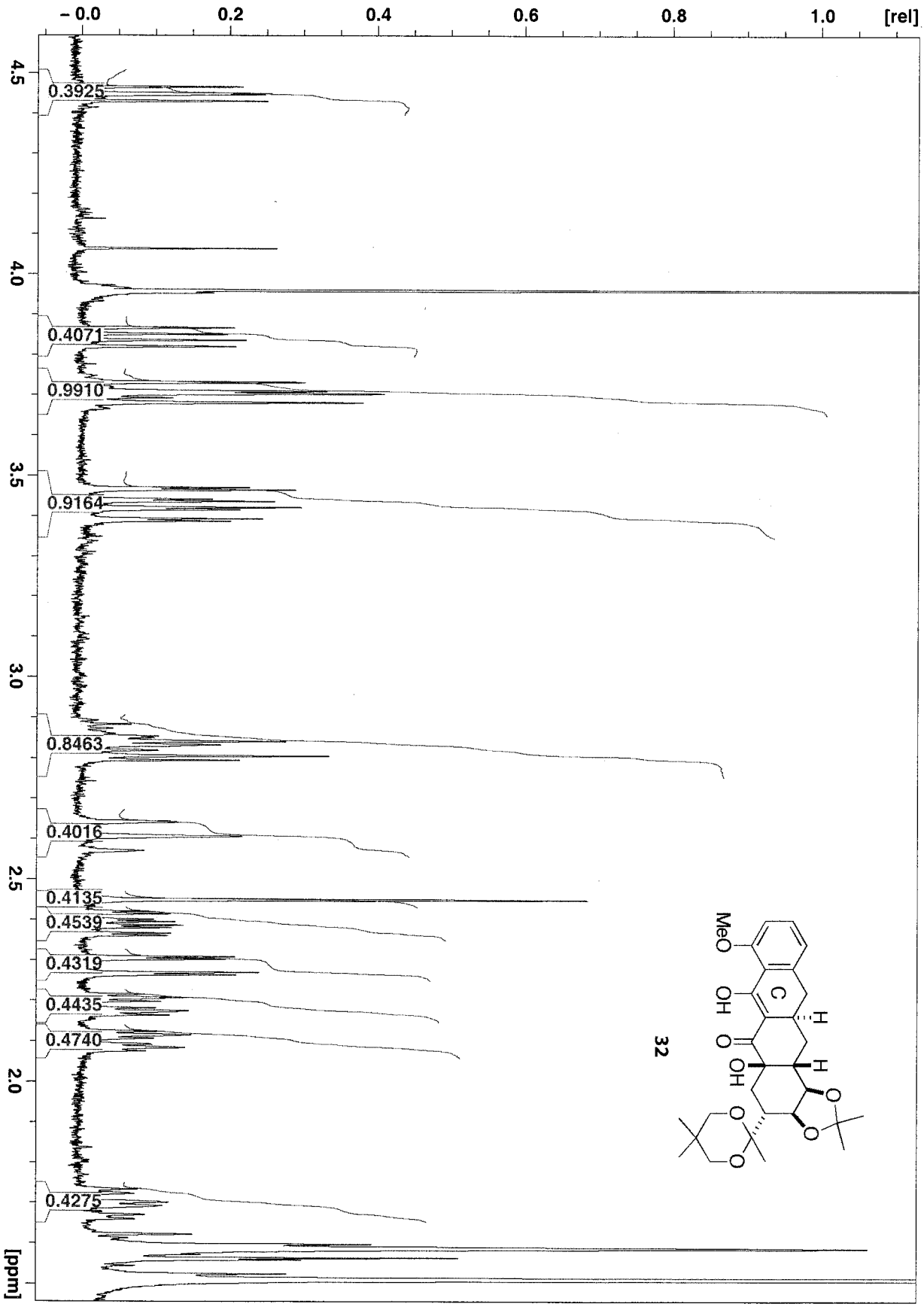

```
Current Data Parameters
NAME          qx560w.101
EXPNO                  1
PROCNO                 1
DU                    /m
USER               qing

F2 - Acquisition Parameters
Date_           20040713
Time               20.01
INSTRUM          dpx400
PROBHD     5 mm BBO Z-G
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  505
DS                    2
SWH            5995.204 Hz
FIDRES         0.182959 Hz
AQ             2.7329011 sec
RG                2580.3
DW                83.400 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec

========== CHANNEL f1 =========
NUC1                  1H
P1                11.30 usec
PL1                0.00 dB
SFO1         400.0126001 MHz

F2 - Processing parameters
SI                 65536
SF          400.0100000 MHz
WDW                   EM
SSB                    0
LB                0.70 Hz
GB                     0
PC                1.00
```

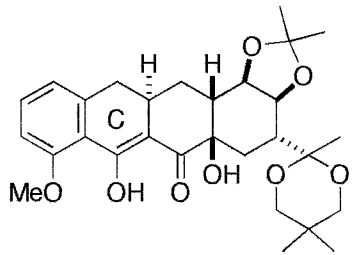




32

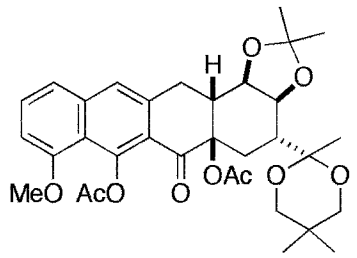
```
Current Data Parameters
NAME          qx318y.101
EXPNO                  1
PROCNO                 1
DU                    /m
USER                qing

F2 - Acquisition Parameters
Date_           20030505
Time               20.08
INSTRUM          dpx400
PROBHD     5 mm BBO Z-G
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  175
DS                    2
SWH            8012.820 Hz
FIDRES            0.244532 Hz
AQ             2.0447731 sec
RG                  362
DW                62.400 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                11.30 usec
PL1                0.00 dB
SFO1         400.0140001 MHz

F2 - Processing parameters
SI                65536
SF           400.0100000 MHz
WDW                  EM
SSB                   0
LB                 0.70 Hz
GB                    0
PC                 1.00
```


– 0.0
0.2
0.4
0.6
0.8
1.0
[rel]
4.5
4.0
3.5
3.0
2.5
2.0
[ppm]
0.3925
0.4071
0.9910
0.9164
0.8463
0.4016
0.4135
0.4539
0.4319
0.4435
0.4740
0.4275
MeO
OH
O
OH
C
H
H
O
O
O
O
32



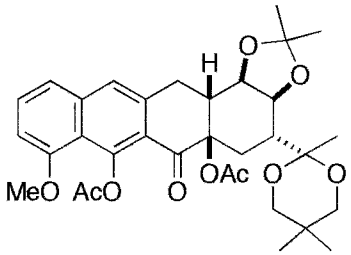
32

```
Current Data Parameters
NAME          qx318y.101
EXPNO                  2
PROCNO                 1
DU                    /m
USER                qing

F2 - Acquisition Parameters
Date_           20030517
Time               22.29
INSTRUM          dpx300
PROBHD     5 mm QNP  1H
PULPROG            zg30
TD                32768
SOLVENT
NS                    32
DS                     2
SWH             4496.403 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                 406.4
DW               111.200 usec
DE                 6.00 usec
TE                300.0 K
D1             1.50000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 8.20 usec
PL1               -3.00 dB
SFO1         300.1319000 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300063 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                 7.472 ppm
F1               2242.52 Hz
F2P                 4.695 ppm
F2               1409.14 Hz
PPMCM            0.13884 ppm/cm
HZCM            41.66925 Hz/cm
```



34

```
Current Data Parameters
NAME          qx363y.101
EXPNO                  1
PROCNO                 1
DU                    /m
USER               qing

F2 - Acquisition Parameters
Date_           20030922
Time               14.16
INSTRUM          dpx400
PROBHD     5 mm BBO Z-G
PULPROG            zg30
TD                32768
SOLVENT           CDC13
NS                  157
DS                    2
SWH            5995.204 Hz
FIDRES        0.182959 Hz
AQ            2.7329011 sec
RG                 2048
DW               83.400 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec

============ CHANNEL f1 =========
NUC1                1H
P1              11.30 usec
PL1              0.00 dB
SFO1       400.0126001 MHz

F2 - Processing parameters
SI                 65536
SF         400.0100000 MHz
WDW                   EM
SSB                    0
LB                0.70 Hz
GB                     0
PC                1.00
```



34

```
Current Data Parameters
NAME          qx358w.101
EXPNO                  2
PROCNO                 1
DU                    /m
USER                qing

F2 - Acquisition Parameters
Date_           20030908
Time               22.26
INSTRUM          dpx300
PROBHD     5 mm QNP  1H
PULPROG         zgpg30
TD               65536
SOLVENT
NS               20084
DS                   2
SWH          18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                8192
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1          0.00300000 sec
D11         0.03000000 sec
D12         0.00002000 sec

============ CHANNEL f1 ==========
NUC1                13C
P1                 7.60 usec
PL1               -3.00 dB
SFO1         75.4756431 MHz

============ CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                2.00 dB
PL12               17.55 dB
PL13               19.00 dB
SFO2        300.1315007 MHz

F2 - Processing parameters
SI                131072
SF           75.4677190 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.40
```