Introduction of the (–)-Berkelic Acid Side Chain and Assignment of the C-22 Stereochemistry

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Supporting Information

General procedures. NMR spectra were recorded at 400 MHz in $CDCl_3$ with TMS as an internal standard unless otherwise indicated. Chemical shifts are reported in δ, coupling constants in Hz, and IR spectra in cm^{-1}. Spectra in $CDCl_3$ are referenced to the residual solvent peaks at δ 7.27 (^1H) and 77.00 (^{13}C). Spectra in CD_3OD are referenced to the residual solvent peaks at δ 3.30 (^1H) and δ 49.00 (^{13}C) to be consistent with the data for the natural product.[1] Spectra in acetone-d_6 are referenced to the residual solvent peaks at δ 2.05 (^1H). Spectra in benzene-d_6 are referenced to the residual solvent peaks at δ 7.16 (^1H) and δ 128.39 (^{13}C). COSY spectra were recorded for all compounds and used to assign ^1H NMR spectra. The atom numbering used in the spectral tabulation of all tetracyclic compounds is that used in the isolation of berkelic acid[1] rather than that of the systematic name given in the procedure heading.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-4-[2-[(1,1-Dimethylethyl)diphenylsilyloxy]ethyl]-3',3'a,4,5,5',6'-hexahydro-8'-hydroxy-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (11) and Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-3',3'a,4,5,5',6'-Hexahydro-8'-hydroxy-4-[2-hydroxyethyl]-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (12). A solution of freshly prepared acid (*R*)-(–)-**5** (37.8 mg, 141 μmol) and freshly prepared ketal aldehyde *ent*-**4b** (48.0 mg, 109 μmol) was treated with Dowex 50WX8-400-H^+ ion exchange resin (25 mg) at 25 °C and stirred at 25 °C for 60 h. The reaction mixture was filtered through Celite to remove the catalyst and the filtrate was concentrated to give 79.1 mg of crude product.

An ether solution (2 mL) of diazomethane (0.67 mmol) was added dropwise to an ether solution (2 mL) of the 79 mg of crude product at 25 °C. The resulting solution was stirred at 25 °C for 20 min and carefully concentrated to give crude ester. Flash chromatography on silica gel (50:1 to 2:1 hexanes/EtOAc) gave 22.1 mg (30%) of **11** followed by 10.6 mg (22%) of **12**.

Data for **11**: $[\alpha]_D^{22}$ –64.6 (*c* 1.11, $CHCl_3$); ^1H NMR 11.4 (s, 1, OH), 7.66 (d, 4, *J* = 7.8), 7.48-7.33 (m, 6), 6.31 (s, 1, H-4), 4.76 (dd, 1, *J* = 12.2, 5.4, H-15), 4.25 (dd, 1, *J* = 8.5, 8.5, H-26), 3.83-3.76 (m, 1, H-9), 3.82 (s, 3, OMe), 3.73-3.64 (m, 2, 2 H-21), 3.55 (dd, 1, *J* = 8.5, 8.5, H-26), 2.76 (dd, 1, *J* = 17.6, 3.9, H-8), 2.60 (dd, 1, *J* = 17.6, 10.7, H-8), 2.45-2.33 (m, 1, H-19),

2.16 (dd, 1, *J* = 12.2, 5.4, H-16), 1.95 (dd, 1, *J* = 12.2, 12.2, H-16), 1.95-1.87 (m, 1, H-20), 1.73 (dq, 1, *J* = 10.5, 6.7, H-18), 1.68-1.60 (m, 1, H-10), 1.58-1.46 (m, 3), 1.44-1.24 (m, 5), 1.06 (d, 3, *J* = 6.7, H-25), 1.055 (s, 9), 0.90 (t, 3, *J* = 6.6); ^{13}C NMR 171.6, 162.1, 152.1, 141.3, 135.5 (4 C), 133.5 (2 C), 129.71, 129.69, 127.7 (4 C), 112.7, 108.9, 108.3, 99.9, 75.1, 73.5, 68.2, 63.2, 52.0, 49.0, 41.6, 36.3, 35.5, 34.5, 34.0, 31.8, 26.8 (3 C), 25.1, 22.6, 19.1, 14.0, 11.7; IR (neat) 3398, 2957, 2932, 2859, 1660; HRMS (EI) calcd for $C_{40}H_{52}O_7Si$ (M^+) 672.3482, found 672.3480.

Data for **12**: $[\alpha]_D^{22}$ – 98.7 (*c* 0.53, $CHCl_3$); ^{1}H NMR 11.4 (s, 1, OH), 6.31 (s, 1, H-4), 4.76 (dd, 1, *J* = 12.2, 5.4, H-15), 4.25 (dd, 1, *J* = 8.5, 8.5, H-26), 3.91 (s, 3, OMe), 3.85-3.77 (m, 1, H-9), 3.72 (t, 2, *J* = 6.1, 2 H-21), 3.63 (dd, 1, *J* = 8.5, 8.5, H-26), 2.76 (dd, 1, *J* = 17.6, 3.9, H-8), 2.60 (dd, 1, *J* = 17.6, 10.7, H-8), 2.49-2.34 (m, 1, H-19), 2.18 (dd, 1, *J* = 12.2, 5.4, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 1.99-1.90 (m, 1, H-20), 1.76 (dq, 1, *J* = 10.7, 6.3, H-18), 1.68-1.60 (m, 1, H-10), 1.60-1.46 (m, 3), 1.45-1.24 (m, 5), 1.09 (d, 3, *J* = 6.8, H-25), 0.90 (t, 3, *J* = 6.6);^{13}C NMR 171.6, 162.1, 152.0, 141.3, 112.7, 109.1, 108.3, 99.9, 75.1, 73.1, 68.1, 61.9, 52.0, 48.9, 40.8, 36.3, 35.3, 34.5, 33.9, 31.8, 25.1, 22.6, 14.0, 11.7; IR (neat) 3406, 2953, 2933, 2860, 1660; HRMS (EI) calcd for $C_{24}H_{34}O_7$ (M^+) 434.2305, found 434.2305.

Deprotection of 11 to Give 12. To a solution of **11** (47.4 mg, 70.4 μmol) in THF (3 mL) was added TBAF (282 μL, 1 M in THF, 282 μmol) and AcOH (16.2 μL, 282 μmol). The solution was stirred at 25 °C for 12 h. The mixture was concentrated under reduced pressure at 25 °C. The residue was treated with brine (3 mL) and 40 drops of saturated $NaHCO_3$ to adjust the pH to 7 and the aqueous layer was extracted with ether (6 × 10 mL). The combined extracts were dried (Na_2SO_4) and concentrated to yield 54.6 mg of crude **12**. Flash chromatography on silica gel (2:1 Hexanes/EtOAc) gave 27.8 mg (91%) of pure **12**.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-Acetoxy-4-[2-[(1,1-dimethylethyl)diphenylsilyloxy]-ethyl]-3',3'a,4,5,5',6'-hexahydro-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (13). Acetic anhydride (0.2 mL) and pyridine (0.5 mL) were added to **11** (19 mg, 28 μmol) under N_2. The reaction mixture was stirred at 25 °C for 12 h. The solvent was removed under reduced pressure to give 22.8 mg of **13**: ^{1}H NMR 7.66 (d, 4, *J* =

7.3), 7.46-7.35 (m, 6), 6.43 (s, 1, H-4), 4.83 (dd, 1, *J* = 12.2, 5.5, H-15), 4.20 (dd, 1, *J* = 8.5, 8.5, H-26), 3.87-3.78 (m, 1, H-9), 3.78 (s, 3, OMe), 3.67 (t, 2, *J* = 5.8, 2 H-21), 3.61 (dd, 1, *J* = 8.5, 8.5, H-26), 2.79 (dd, 1, *J* = 17.1, 3.7, H-8), 2.63 (dd, 1, *J* = 17.1, 10.7, H-8), 2.33-2.24 (m, 1, H-19), 2.25 (s, 3, OAc), 2.17 (dd, 1, *J* = 12.2, 5.5, H-16), 1.99 (dd, 1, *J* = 12.2, 12.2, H-16), 1.92-1.83 (m, 1, H-20), 1.76-1.57 (m, 2, *J* = 10.5, 6.7, H-18), 1.59-1.44 (m, 3), 1.44-1.20 (m, 5), 1.05 (s, 9), 1.04 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.4); HRMS (EI) calcd for $C_{42}H_{54}O_8Si$ (M^+) 714.3588, found 714.3581.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-Acetoxy-3',3'a,4,5,5',6'-hexahydro-4-[2-hydroxyethyl]-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (14). To a solution of **13** in THF (3 mL) was added TBAF (113 μL, 1 M in THF, 113 μmol) and AcOH (6.5 μL, 113 μmol). The solution was stirred at 25 °C for 8 h. The mixture was concentrated under reduced pressure at 25 °C. The residue was treated with brine (3 mL) and 20 drops of saturated $NaHCO_3$ to adjust the pH to 7 and the aqueous layer was extracted with ether (5 × 10 mL). The combined extracts were dried (Na_2SO_4) and concentrated to yield 24.1 mg of crude **14**. Flash chromatography on silica gel (2:3 hexanes/EtOAc) gave 10.0 mg (74%) of pure **14**: ^{1}H NMR 6.43 (s, 1, H-4), 4.85 (dd, 1, *J* = 12.2, 5.5, H-15), 4.23 (dd, 1, *J* = 8.5, 8.5, H-26), 3.87-3.89 (m, 1, H-9), 3.84 (s, 3, OMe), 3.73-3.64 (m, 2, 2 H-21), 3.61 (dd, 1, *J* = 8.5, 8.5, H-26), 2.79 (dd, 1, *J* = 17.1, 3.1, H-8), 2.63 (dd, 1, *J* = 17.1, 11.0, H-8), 2.34-2.23 (m, 1, H-19), 2.25 (s, 3, OAc), 2.18 (dd, 1, *J* = 12.2, 5.5, H-16), 2.00 (dd, 1, *J* = 12.2, 12.2, H-16), 1.96-1.87 (m, 1, H-20), 1.74 (dq, 1, *J* = 10.5, 6.7, H-18), 1.69-1.60 (m, 1, H-10), 1.59-1.46 (m, 3), 1.45-1.23 (m, 5), 1.07 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.6); ^{13}C NMR 169.4, 164.9, 150.1, 148.3, 137.2, 119.7, 114.1, 111.9, 109.1, 75.2, 73.0, 68.2, 61.9, 51.9, 48.9, 40.8, 36.2, 35.6, 34.1, 33.9, 31.8, 25.1, 22.6, 20.8, 14.0, 11.7; HRMS (EI) calcd for $C_{26}H_{36}O_8$ (M^+) 476.2410, found 476.2413.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-Acetoxy-3',3'a,4,5,5',6'-hexahydro-4-[2-oxoethyl]-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (**15**). Dess–Martin periodinane (17.8 mg, 42 μmol) was added to a solution of alcohol **14**

(10 mg, 21 μmol) in CH_2Cl_2 (2 mL) at 0 °C. The suspension was warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ (3 mL) and stirred vigorously for another 30 min. The two layers were separated and the aqueous layer was extracted with ether (3 × 4 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated to yield 10.1 mg of crude aldehyde. Flash chromatography on MeOH-deactivated silica gel (4:1 hexanes/EtOAc) gave 8.7 mg (87%) of **15**: ^{1}H NMR 9.83 (s, 1), 6.44 (s, 1, H-4), 4.83 (dd, 1, *J* = 12.2, 5.5, H-15), 4.37 (dd, 1, *J* = 8.5, 8.5, H-26), 3.85 (s, 3, OMe), 3.87-3.78 (m, 1, H-9), 3.73-3.64 (m, 2, 2 H-21), 3.52 (dd, 1, *J* = 8.5, 8.5, H-26), 2.83 (dd, 1, *J* = 17.7, 3.7, H-20), 2.79 (dd, 1, *J* = 17.1, 3.3, H-8), 2.70-2.60 (m, 1, H-19), 2.64 (dd, 1, *J* = 17.1, 10.7, H-8), 2.46 (dd, 1, *J* = 17.7, 9.8, H-20), 2.26 (s, 3, OAc), 2.18 (dd, 1, *J* = 12.2, 5.5, H-16), 2.00 (dd, 1, *J* = 12.2, 12.2, H-16), 1.76 (dq, 1, *J* = 10.4, 6.1, H-18), 1.70-1.58 (m, 1, H-10), 1.62-1.46 (m, 2), 1.44-1.20 (m, 5), 1.06 (d, 3, *J* = 6.1, H-25), 0.90 (t, 3, *J* = 6.7).

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-[(1,1-Dimethylethyl)dimethylsilyl]oxy-4-[2-[[(1,1-dimethylethyl)dimethylsilyl]oxy]ethyl]-3',3'a,4,5,5',6'-hexahydro-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (16). To a solution of alcohol **12** (46.5 mg, 107 μmol) in CH_2Cl_2 (3.5 mL) was added 2,6-lutidine (70 μL, 589 μmol) and TBSOTf (123 μL, 535 μmol) under N_2 at 0 °C. The resulting solution was warmed to 25 °C and stirred for 12 h. The solvent was removed under reduced pressure. Flash chromatography on silica gel (40:1 hexanes/EtOAc) gave 58.6 mg (83%) of pure **16**: $[\alpha]_D^{22}$ -75.5 (*c* 2.93, $CHCl_3$); ^{1}H NMR 6.14 (s, 1, H-4), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.22 (dd, 1, *J* = 8.5, 8.5, H-26), 3.86-3.77 (m, 1, H-9), 3.81 (s, 3, OMe), 3.70-3.56 (m, 2, 2 H-21), 3.62 (dd, 1, *J* = 8.5, 8.5, H-26), 2.72 (dd, 1, *J* = 17.1, 3.7, H-8), 2.57 (dd, 1, *J* = 17.1, 11.0, H-8), 2.26-2.16 (m, 1, H-19), 2.14 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 1.88-1.79 (m, 1, H-20), 1.73-1.60 (m, 2, H-18), 1.58-1.23 (m, 8), 1.02 (d, 3, *J* = 6.7, H-25), 0.95 (s, 9), 0.90 (t, 3, *J* = 6.7), 0.89 (s, 9), 0.20 (s, 3), 0.18 (s, 3), 0.05 (s, 6); ^{13}C NMR 166.4, 152.4, 149.0, 135.5, 114.5, 112.1, 110.5, 108.6, 75.3, 73.3, 68.2, 62.2, 51.7, 48.9, 41.4, 36.3, 35.9, 34.6, 34.2,

31.8, 25.9 (3 C), 25.5 (3 C), 25.1, 22.6, 18.2, 18.0, 14.0, 11.6, -4.4, -4.5, -5.4, -5.5; IR (neat) 2954, 2931, 2858, 1738; HRMS (EI) calcd for $C_{36}H_{62}O_7Si_2$ (M^+) 662.4034, found 662.4038.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-[(1,1-Dimethylethyl)dimethylsilyl]oxy-3',3'a,4,5,5',6'-hexahydro-4-[2-hydroxyethyl]-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (**17**). $Ce(OTf)_n \bullet xH_2O$ (15.1 mg, 19-23% Ce basis) was added to a solution **16** (57.1 mg, 86 μmol) in THF/H_2O (5 mL, 4:1) at 25 °C. The solution was stirred vigorously at 25 °C for 55 h. Brine (3 mL) was added and the mixture was extracted with EtOAc (4 × 4 mL). The combined extracts were dried (Na_2SO_4) and concentrated to yield 53.3 mg of crude **17**. Flash chromatography on silica gel (3:1 Hexanes/EtOAc) gave 38.4 mg (81%) of pure **17**: $[\alpha]_D^{22}$ –98.0 (*c* 1.92, $CHCl_3$); ^{1}H NMR 6.14 (s, 1, H-4), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.22 (dd, 1, *J* = 8.5, 8.5, H-26), 3.86-3.78 (m, 1, H-9), 3.81 (s, 3, OMe), 3.72-3.62 (m, 2, 2 H-21), 3.59 (dd, 1, *J* = 8.5, 8.5, H-26), 2.73 (dd, 1, *J* = 17.1, 3.7, H-8), 2.58 (dd, 1, *J* = 17.1, 11.0, H-8), 2.28-2.18 (m, 1, H-19), 2.15 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 1.94-1.85 (m, 1, H-20), 1.76-1.58 (m, 2, H-18), 1.58-1.46 (m, 3), 1.45-1.24 (m, 5), 1.03 (d, 3, *J* = 6.7, H-25), 0.94 (s, 9), 0.90 (t, 3, *J* = 6.4), 0.20 (s, 3), 0.18 (s, 3); ^{13}C NMR 166.5, 152.4, 149.0, 135.5, 114.5, 112.0, 110.6, 108.7, 75.3, 72.9, 68.1, 61.8, 51.8, 48.9, 40.8, 36.3, 35.7, 34.5, 34.1, 31.8, 25.5 (3 C), 25.1, 22.6, 18.0, 14.0, 11.7, -4.4, -4.5; IR (neat) 3348, 2953, 2932, 2859, 1738, 1731; HRMS (EI) calcd for $C_{30}H_{48}O_7Si$ (M^+) 548.3169, found 548.3175.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-8'-[(1,1-Dimethylethyl)dimethylsilyl]oxy-3',3'a,4,5,5',6'-hexahydro-4-[2-oxoethyl]-3-methyl-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (**18**). Dess–Martin periodinane (57 mg, 134.5 μmol) was added to a solution of alcohol **17** (36.9 mg, 67.2μmol) in CH_2Cl_2 (4 mL) at 0 °C. The suspension was allowed to warm to 25 °C and stirred for 1 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ (4 mL) and stirred vigorously for another 30 min. The two layers were separated and the aqueous layer was extracted with ether (3 × 4 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated to yield 39.5 mg of crude aldehyde **18**. Flash chromatography on silica gel (5:1 Hexanes/EtOAc)

gave 27.6 mg (85%) of pure **18**: $[\alpha]_D^{22}$ –100.1 (*c* 1.38, $CHCl_3$); ^{1}H NMR 9.81 (s, 1), 6.15 (s, 1, H-4), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.36 (dd, 1, *J* = 8.5, 8.5, H-26), 3.83 (s, 3, OMe), 3.85-3.77 (m, 1, H-9), 3.51 (dd, 1, *J* = 8.5, 8.5, H-26), 2.81 (dd, 1, *J* = 17.7, 3.1, H-20), 2.73 (dd, 1, *J* = 17.1, 3.1, H-8), 2.58 (dd, 1, *J* = 17.1, 10.5, H-8), 2.65-2.57 (m, 1, H-19), 2.44 (dd, 1, *J* = 17.7, 9.8, H-20), 2.15 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 1.73 (dq, 1, *J* = 10.4, 6.7, H-18), 1.68-1.59 (m, 1), 1.58-1.45 (m, 2), 1.45-1.24 (m, 5), 1.03 (d, 3, *J* = 6.7, H-25), 0.95 (s, 9), 0.90 (t, 3, *J* = 6.7), 0.20 (s, 3), 0.18 (s, 3); ^{13}C NMR 200.6, 166.4, 152.5, 148.8, 135.6, 114.4, 112.1, 110.7, 108.3, 75.3, 72.2, 68.0, 51.8, 48.5, 47.2, 37.7, 36.3, 34.3, 34.1, 31.8, 25.5 (3 C), 25.1, 22.6, 18.0, 14.0, 11.5, -4.4, -4.5; IR (neat) 2957, 2933, 2860, 1739, 1732; HRMS (EI) calcd for $C_{30}H_{46}O_7Si$ (M^+) 546.3013, found 546.3016.

1-Methoxy-1-trimethylsiloxy-2-methyl-1-butene (19) was prepared by the literature procedure.[24] *n*-BuLi (12.6 mL, 1.6 M in hexane, 20 mmol) was added dropwise to a solution of diisopropylamine (2.82 mL, 20 mmol) in THF (15 mL) under N_2 at 0 °C. The resulting solution was stirred at 0 °C for 30 min and cooled to –78 °C. A solution of methyl 2-methylbutanoate (2.64 mL, 20 mmol) in THF (6 mL) was added dropwise to the reaction mixture and the reaction was stirred at –78 °C for 1 h. TMSCl (3 mL, 24 mmol) was added dropwise to the reaction mixture and the reaction was slowly warmed up to 25 °C over 3 h. The reaction was quenched with ice water (20 mL). The two layers were separated and the aqueous layer was extracted with hexanes (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated at 25 °C. The crude oil was purified by distillation (bp 95-97 °C/35 torr) to give 2.78 g (74%, 7:3 mixture of isomers) of **19** as a colorless oil: ^{1}H NMR 3.50 (s, 3), 1.99 (q, 0.3 × 2, *J* = 7.6), 1.94 (q, 0.7 × 2, *J* = 7.6), 1.55 (s, 0.7 × 3), 1.51 (s, 0.3 × 3), 0.94 (q, 0.3 × 2, *J* = 7.6), 0.93 (q, 0.7 × 2, *J* = 7.6), 0.208 (s, 0.3 × 3), 0.203 (s, 0.7 × 3). The ^{1}H NMR spectral data are identical to the literature data.[12]

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-α,3-Dimethyl-8'-[(1,1-dimethylethyl)dimethylsilyl]oxy-α-ethyl-3',3'a,4,5,5',6'-hexahydro-9'-(methoxycarbonyl)-3-methyl-β-oxo-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate (20). To a solution of

aldehyde **18** (6.0 mg, 11.0μmol), LiCl (1.5 mg, 35.5 μmol) and 4 Å molecular sieves (50 mg) in DMF (0.5 mL) was added silyl ketene acetal (**19**, 17.5 mg, 110μmol) and *N*-methylimidazole (2 μL, 25 μmol) under N_2 at 25 °C. The reaction mixture was stirred at 25 °C for 25 h. The mixture was quenched with 1 M HCl (3 mL) and extracted with EtOAc (4 × 4 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to yield 8.5 mg of crude aldol products that was used without further purification.

The above aldol products in CH_2Cl_2 (1 mL) were treated with Dess–Martin periodinane (9.3 mg, 22 μmol) at 0 °C. The suspension was allowed to warm to 25 °C and continued to stir for 12 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ (3 mL) and continued to stir vigorously for 30 min. The mixture was extracted with ether (4 × 3 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated to yield 7.9 mg of keto esters. Flash chromatography on silica gel (10:1 hexanes/EtOAc) gave 3.2 mg (44%) of **20** as a 1:1 inseparable mixture: ^{1}H NMR 6.14 (s, 1, H-4), 4.78 (dd, 1, *J* = 12.2, 5.2, H-15), 4.35 (dd, 1, *J* = 8.2, 8.2, H-26), 3.83 (s, 3, OMe), 3.85-3.76 (m, 1, H-9), 3.74 (s, 3, OMe), 3.44 (dd, 1, *J* = 8.2, 8.2, H-26), 2.84-2.68 (m, 2, H-20, H-8), 2.62-2.50 (m, 2, H-19, H-8), 2.44-2.31 (m, 1, H-20), 2.13 (dd, 1, *J* = 12.2, 5.2, H-16), 2.02-1.90 (m, 1, H-23), 1.95 (dd, 1, *J* = 12.2, 12.2, H-16), 1.88-1.76 (m, 1, H-23), 1.73-1.45 (m, 4, H-18), 1.45-1.19 (m, 5), 1.34 (s, 0.5 × 3), 1.32 (s, 0.5 × 3), 1.00 (d, 3, *J* = 6.7, H-25), 0.94 (s, 9), 0.93-0.76 (m, 6), 0.19 (s, 3), 0.18 (s, 3); HRMS (EI) calcd for $C_{36}H_{56}O_9Si$ (M^+) 660.3694, found 660.3688.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-α,3-Dimethyl-α-ethyl-3',3'a,4,5,5',6'-hexahydro-8'-hydroxy-9'-(methoxycarbonyl)-3-methyl-β-oxo-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate (21). To a solution of **20** (2.9 mg, 4.4μmol) in MeOH (1 mL) was treated with KF (10 mg, 65.8 μmol) at 25 °C. The suspension was stirred at 25 °C for 40 min. The solid was filtered off and the solvent was removed under reduced pressure. Flash chromatography on silica gel (7:1 Hexanes/EtOAc) gave 2.1 mg (88%) of **21** as an inseparable mixture of berkelic acid methyl ester and its 22-epimer: $[\alpha]_D^{22}$ –97.1 (*c* 0.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, the residual peak of solvent is referred as δ 7.24 rather than 7.27 to

facilitate comparison with the literature data[1]) 11.37 (s, 1, OH), 6.29 (s, 1, H-4), 4.73 (dd, 1, *J* = 12.2, 5.4, H-15), 4.32 (dd, 1, *J* = 8.3, 8.3, H-26), 3.93 (s, 3, OMe), 3.82-3.73 (m, 1, H-9), 3.73 (s, 3, OMe), 3.44 (dd, 1, *J* = 8.3, 8.3, H-26), 2.83-2.69 (m, 3, H-20, H-19, H-8), 2.58 (dd, 1, *J* = 17.6, 10.8, H-8), 2.43 (dd, 0.5 × 1, *J* = 17.6, 10.7, H-20), 2.41 (dd, 0.5 × 1, *J* = 17.6, 10.7, H-20), 2.14 (dd, 1, *J* = 12.2, 5.4, H-16), 2.02-1.90 (m, 1, H-23), 1.93 (dd, 1, *J* = 12.2, 12.2, H-16), 1.88-1.76 (m, 1, H-23), 1.74-1.62 (m, 1, H-18), 1.66-1.43 (m, 3), 1.43-1.20 (m, 5), 1.34 (s, 0.5 × 3), 1.32 (s, 0.5 × 3), 1.02 (d, 3, *J* = 6.4, H-25), 0.93-0.76 (m, 6); ^{13}C NMR 206.8 (tiny), 173.45 (0.5 × 1, C-28), 173.42 (0.5 × 1, C-28), 171.6, 162.1, 151.9, 141.2, 112.5, 108.6, 108.4, 100.0, 75.1, 72.87 (0.5 × 1, C-26), 72.81 (0.5 × 1, C-26), 68.1, 59.9, 52.4, 52.2, 48.3, 41.67 (0.5 × 1, C-20), 41.66 (0.5 × 1, C-20), 38.91 (0.5 × 1, C-19), 38.87 (0.5 × 1, C-19), 36.3, 34.5, 33.6, 31.8, 27.86 (0.5 × 1, C-23), 27.80 (0.5 × 1, C-23), 25.1, 22.6, 18.40 (0.5 × 1, C-27), 18.34 (0.5 × 1, C-27), 14.1, 11.6, 8.67 (0.5 × 1, C-24), 8.63 (0.5 × 1, C-24); IR (neat) 3390, 2953, 2934, 2860, 1715, 1660; HRMS (EI) calcd for $C_{30}H_{42}O_9$ (M^+) 546.2829, found 546.2827. The ^{1}H NMR spectral data in $CDCl_3$ match those of berkelic acid methyl ester.[1]

2-Propenyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-4-[2-[(1,1-Dimethylethyl)diphenylsilyloxy]ethyl]-3',3'a,4,5,5',6'-hexahydro-3-methyl-5'-pentyl-8'-(2-propenyloxy)-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (22) and 2-Propenyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-3',3'a,4,5,5',6'-Hexahydro-4-[2-hydroxyethyl]-3-methyl-5'-pentyl-8'-(2-propenyloxy)-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (23). A solution of freshly prepared acid (*R*)-(–)-**5** (42.0 mg, 157 μmol) and freshly prepared ketal aldehyde *ent*-**4b** (43 mg, 97.7 μmol) was treated with Dowex 50WX8-400-H^+ ion exchange resin (23 mg) at 25 °C and the solution was stirred for 60 h. The reaction mixture was filtered through Celite to remove the catalyst and the filtrate was concentrated to give 78.8 mg of crude product.

To a suspension of the above crude product and K_2CO_3 (108 mg, 784 μmol) in DMF (2 mL) was added allyl bromide (102 μL, 1.18 mmol) under N_2 at 25 °C. The reaction mixture was stirred at 25 °C for 12 h. H_2O (4 mL) was added and the mixture was extracted with CH_2Cl_2

(4 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (30:1 to 2:1 hexanes/EtOAc) gave 23.1 mg (32%) of **22** followed by 10.0 mg (20%) of **23**.

Data for **22**: $[\alpha]_D^{22}$ –60.0 (*c* 2.31, $CHCl_3$); ^{1}H NMR 7.66 (d, 4, *J* = 6.7), 7.47-7.34 (m, 6), 6.23 (s, 1, H-4), 6.02-5.90 (m, 2), 5.36 (br d, 1, *J* = 17.7), 5.33 (br d, 1, *J* = 17.1), 5.22 (br d, 1, *J* = 10.4), 5.15 (br d, 1, *J* = 10.4), 4.84-4.65 (m, 2, H-15), 4.71 (dd, 1, *J* = 12.3, 5.2), 4.51 (d, 2, *J* = 4.9), 4.20 (dd, 1, *J* = 8.5, 8.5, H-26), 3.83-3.78 (m, 1, H-9), 3.72-3.60 (m, 2, 2 H-21), 3.62 (dd, 1, *J* = 8.5, 8.5, H-26), 2.75 (dd, 1, *J* = 17.1, 3.7, H-8), 2.60 (dd, 1, *J* = 17.1, 10.7, H-8), 2.30-2.18 (m, 1, H-19), 2.15 (dd, 1, *J* = 12.2, 4.9, H-16), 1.97 (dd, 1, *J* = 12.2, 12.2, H-16), 1.89-1.80 (m, 1, H-20), 1.73-1.59 (m, 2, H-18, H-10), 1.58-1.46 (m, 3), 1.43-1.25 (m, 5), 1.05 (s, 9), 1.01 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.4); ^{13}C NMR 165.5, 155.5, 149.0, 135.8, 135.5 (4 C), 133.55, 133.52, 132.9, 132.3, 129.7 (2 C), 127.7 (4 C), 118.1, 117.1, 114.6, 109.6, 108.7, 104.2, 75.3, 73.3, 69.4, 68.1, 65.6, 63.2, 49.0, 41.3, 36.3, 35.6, 34.5, 34.4, 31.8, 26.8 (3 C), 25.1, 22.6, 19.1, 14.0, 11.6; IR (neat) 2957, 2932, 2859, 1739, 1732; HRMS (EI) calcd for $C_{45}H_{58}O_7Si$ (M^+) 738.3952, found 738.3953.

Data for **23**: $[\alpha]_D^{22}$ –88.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR 6.23 (s, 1, H-4), 6.06-5.92 (m, 2), 5.39 (br d, 1, *J* = 17.1), 5.36 (br d, 1, *J* = 17.1), 5.24 (br d, 1, *J* = 9.8), 5.23 (br d, 1, *J* = 10.4), 4.86-4.76 (m, 2, H-15), 4.74 (dd, 1, *J* = 13.4, 5.5), 4.51 (d, 2, *J* = 4.9), 4.20 (dd, 1, *J* = 8.2, 8.2, H-26), 3.86-3.77 (m, 1, H-9), 3.72-3.58 (m, 2, 2 H-21), 3.59 (dd, 1, *J* = 8.2, 8.2, H-26), 2.75 (dd, 1, *J* = 16.5, 4.0, H-8), 2.60 (dd, 1, *J* = 16.5, 11.0, H-8), 2.30-2.19 (m, 1, H-19), 2.16 (dd, 1, *J* = 12.2, 5.5, H-16), 1.97 (dd, 1, *J* = 12.2, 12.2, H-16), 1.92-1.85 (m, 1, H-20), 1.71 (dq, 1, *J* = 10.5, 6.7, H-18), 1.70-1.60 (m, 1, H-10), 1.58-1.46 (m, 3), 1.45-1.25 (m, 5), 1.03 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.7); ^{13}C NMR 165.6, 155.5, 149.0, 135.9, 132.9, 132.3, 118.1, 117.1, 114.6, 109.5, 108.8, 104.3, 75.3, 72.9, 69.4, 68.1, 65.6, 61.8, 48.9, 40.6, 36.3, 35.7, 34.43, 34.40, 31.8, 25.1, 22.6, 14.0, 11.7; IR (neat) 3432, 2932, 2876, 1739, 1732, 1714; HRMS (EI) calcd for $C_{29}H_{40}O_7$ (M^+) 500.2774, found 500.2769.

Deprotection of 22 to Give 23. To a solution of **23** (64.7 mg, 88 μmol) in THF (4 mL) was added TBAF (350 μL, 1 M in THF, 350 μmol) and AcOH (20 μL, 350 μmol). The solution was stirred at 25 °C for 12 h. The mixture was concentrated under reduced pressure at 25 °C. The residue was treated with brine (4 mL) and 45 drops of saturated $NaHCO_3$ to adjust the pH to 7 and the aqueous layer was extracted with distilled ether (6 × 10 mL). The combined extracts were dried (Na_2SO_4) and concentrated to yield 73.6 mg of crude **23**. Flash chromatography on silica gel (2:1 hexanes/EtOAc) gave 37.7 mg (86%) of pure **23**.

2-Propenyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-3',3'a,4,5,5',6'-Hexahydro-3-methyl-4-[2-oxoethyl]-5'-pentyl-8'-(2-propenyloxy)-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-9'-carboxylate (24). Dess–Martin periodinane (178 mg, 0.42 mmol) was added to a solution of alcohol **23** (105 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The suspension was allowed to warm to 25 °C and continued to stir for 1 h. The solvent was removed under reduced pressure at 25 °C. Flash chromatography on MeOH-deactivated silica gel (5:1 hexanes/EtOAc) gave 92.4 mg (88%) of pure **24**: $[\alpha]_D^{22}$ –103.9 (*c* 0.18, $CHCl_3$); ^{1}H NMR 9.81 (s, 1), 6.24 (s, 1, H-4), 6.08-5.92 (m, 2), 5.40 (br d, 1, *J* = 16.5), 5.36 (br d, 1, *J* = 15.9), 5.26 (br d, 1, *J* = 11.6), 5.23 (br d, 1, *J* = 11.0), 4.85 (dd, 1, *J* = 13.3, 6.1), 4.80 (dd, 1, *J* = 12.2, 5.5, H-15), 4.74 (dd, 1, *J* = 13.3, 5.8), 4.52 (d, 2, *J* = 4.9), 4.35 (dd, 1, *J* = 8.5, 8.5, H-26), 3.88-3.78 (m, 1, H-9), 3.51 (dd, 1, *J* = 8.5, 8.5, H-26), 2.80 (dd, 1, *J* = 17.7, 3.7, H-20), 2.75 (dd, 1, *J* = 16.5, 4.3, H-8), 2.61 (dd, 1, *J* = 16.5, 11.0, H-8), 2.66-2.57 (m, 1, H-19), 2.43 (dd, 1, *J* = 17.7, 9.8, H-20), 2.16 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 1.73 (dq, 1, *J* = 10.4, 6.7, H-18), 1.71-1.60 (m, 1, H-10), 1.58-1.46 (m, 2), 1.45-1.24 (m, 5), 1.04 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.7); ^{13}C NMR 200.5, 165.5, 155.6, 148.8, 135.9, 132.9, 132.3, 118.4, 117.2, 114.5, 109.6, 108.4, 104.5, 75.3, 72.2, 69.4, 68.0, 65.7, 48.5, 47.3, 37.6, 36.3, 34.4, 34.3, 31.8, 25.1, 22.6, 14.0, 11.5; IR (neat) 2957, 2932, 2860, 1738, 1732, 1716; HRMS (EI) calcd for $C_{29}H_{38}O_7$ (M^+) 498.2618, found 498.2611.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-α,3-Dimethyl-α-ethyl-3',3'a,4,5,5',6'-hexahydro-3-methyl-β-oxo-5'-pentyl-8'-(2-propenyloxy)-9'-(2-propenyloxycarbonyl)-spiro[furan-

2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate. To a solution of aldehyde **24** (12.0 mg, 24.0 μmol), LiCl (2.1 mg, 49.6 μmol) and 4 Å molecular sieves (50 mg) in DMF (0.5 mL) was added silyl ketene acetal **19** (38.2 mg, 240 μmol) and *N*-methylimidazole (4 μL, 50 μmol) under N_2 at 25 °C. The reaction mixture was stirred at 25 °C for 25 h. The mixture was quenched with 1 M HCl (3 mL) and extracted with EtOAc (4 × 4 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to yield 14.9 mg of crude aldol product that was used without further purification.

The above aldol adducts in CH_2Cl_2 (1.5 mL) were treated with Dess–Martin periodinane (20.4 mg, 48 μmol) at 0 °C. The suspension was allowed to warm to 25 °C and continued to stir for 12 h. The solvent was removed under reduced pressure at 25 °C. Flash chromatography on silica gel (10:1 hexanes/EtOAc) gave 8.8 mg (60%) of the allyl ether and ester of **25** as a 1:1 inseparable mixture: $[\alpha]_D^{22}$ –74.6 (*c* 0.19, $CHCl_3$); ^{1}HNMR 6.23 (s, 1, H-4), 6.08-5.92 (m, 2), 5.40 (br d, 1, *J* = 17.7), 5.36 (br d, 1, *J* = 17.1), 5.27 (br d, 1, *J* = 10.4), 5.23 (br d, 1, *J* = 10.4), 4.85 (dd, 1, *J* = 13.4, 6.1), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.74 (dd, 1, *J* = 13.1, 5.8), 4.51 (d, 2, *J* = 4.9), 4.35 (dd, 1, *J* = 8.5, 8.5, H-26), 3.86-3.78 (m, 1, H-9), 3.74 (s, 3, OMe), 3.45 (dd, 1, *J* = 8.5, 8.5, H-26), 2.81 (dd, 0.5 × 1, *J* = 17.7, 3.1, H-20), 2.77 (dd, 0.5 × 1, *J* = 17.7, 3.4, H-20), 2.75 (dd, 1, *J* = 16.5, 3.7, H-8), 2.60 (dd, 1, *J* = 17.1, 11.0, H-8), 2.62-2.50 (m, 1, H-19), 2.43 (dd, 0.5 × 1, *J* = 17.7, 10.4, H-20), 2.35 (dd, 0.5 × 1, *J* = 17.7, 10.4, H-20), 2.14 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 2.02-1.91 (m, 1, H-23), 1.82 (dq, 1, *J* = 14.0, 7.3, H-23), 1.72-1.58 (m, 2), 1.58-1.46 (m, 2), 1.45-1.24 (m, 5), 1.34 (s, 0.5 × 3, H-27), 1.33 (s, 0.5 × 3, H-27), 1.01 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.4), 0.84 (t, 0.5 × 3, *J* = 7.3), 0.83 (t, 0.5 × 3, *J* = 7.3); ^{13}C NMR 206.6 (0.5 × 1), 206.5 (0.5 × 1), 173.5, 165.5, 155.6, 148.9, 135.8, 132.9, 132.2, 118.5, 117.2, 114.5, 109.7, 108.4, 104.4, 75.3, 72.8, 69.4, 68.0, 65.7, 59.7, 52.4, 48.46 (0.5 × 1), 48.43 (0.5 × 1), 42.0, 38.9, 36.3, 34.41, 34.40, 31.8, 27.86 (0.5 × 1), 27.80 (0.5 × 1), 25.1, 22.6, 18.40 (0.5 × 1), 18.32 (0.5 × 1), 14.0, 11.6, 8.64 (0.5 × 1), 8.59 (0.5 × 1); IR (neat) 2953, 2932, 2856, 1739, 1732, 1714; HRMS (EI) calcd for $C_{35}H_{48}O_9$ (M^+) 612.3298, found 612.3302.

Methyl (2*S*,3*S*,3'a*S*,4*S*,5'*R*)-9'-Carboxy-α,3-dimethyl-α-ethyl-3',3'a,4,5,5',6'-hexahydro-8'-hydroxy-3-methyl-β-oxo-5'-pentyl-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate (25). To a solution of the allyl ester and ether (6.0 mg, 9.8 μmol) and $Pd(PPh_3)_4$ (3.4 mg, 2.9 μmol) in dry THF (1 mL) was added NEt_3 (123 μL, 0.88 mmol) and HCOOH (33 μL, 0.88 mmol) under N_2 at 25 °C. The yellow solution was stirred at 25 °C for 15 h and quenched with saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with ether (4 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Flash chromatography on silica gel (80:1:0 to 200:1:1 CH_2Cl_2/MeOH/AcOH) gave 4.2 mg (81%) of **25** as a 1:1 inseparable mixture of berkelic acid and its epimer: $[\alpha]_D^{22}$ – 104.6 (*c* 0.07, MeOH); ^{1}H NMR ($CDCl_3$, the residual peak of solvent is referred as δ 7.24 rather than 7.27 to facilitate comparison with the literature data[1]) 11.83 (s, 1, OH), 11.13-10.87 (br, 1, OH), 6.42 (s, 1, H-4), 4.77 (dd, 1, *J* = 12.2, 5.4, H-15), 4.45 (dd, 0.5 × 1, *J* = 8.5, 8.5, H-26), 4.44 (dd, 0.5 × 1, *J* = 8.5, 8.5, H-26), 3.85-3.76 (m, 1, H-9), 3.73 (s, 3, OMe), 3.59 (dd, 1, *J* = 8.5, 8.5, H-26), 2.90 (dd, 0.5 × 1, *J* = 17.6, 2.9, H-20), 2.85 (dd, 0.5 × 1, *J* = 17.0, 2.4, H-20), 2.79 (dd, 0.5 × 1, *J* = 17.6, 3.9, H-8), 2.78 (dd, 0.5 × 1, *J* = 17.7, 3.7, H-8), 2.60 (dd, 1, *J* = 17.7, 11.0, H-8), 2.54-2.45 (m, 1, H-19), 2.42 (dd, 0.5 × 1, *J* = 17.0, 9.8, H-20), 2.38 (dd, 0.5 × 1, *J* = 17.6, 10.0, H-20), 2.21 (dd, 1, *J* = 12.2, 5.4, H-16), 2.05 (dd, 1, *J* = 12.2, 12.2, H-16), 1.95 (dq, 1, *J* = 14.2, 7.3, H-23), 1.87 (dq, 1, *J* = 10.7, 6.8, H-18), 1.80 (dq, 1, *J* = 14.2, 7.3, H-23), 1.68-1.57 (m, 1), 1.58-1.43 (m, 2), 1.43-1.20 (m, 5), 1.33 (s, 0.5 × 3, H-27), 1.32 (s, 0.5 × 3, H-27), 1.09 (d, 3, *J* = 6.8, H-25), 0.88 (t, 3, *J* = 6.6), 0.83 (t, 0.5 × 3, *J* = 7.6, H-24), 0.81 (t, 0.5 × 3, *J* = 7.3, H-24); ^{1}H NMR (CD_3OD, 500 MHz) 6.27 (s, 1, H-4), 4.72 (dd, 1, *J* = 12.2, 5.4, H-15), 4.30 (dd, 1, *J* = 8.5, 8.5, H-26), 3.84-3.77 (m, 1, H-9), 3.73 (s, 3, OMe), 3.50 (dd, 1, *J* = 8.5, 8.5, H-26), 2.92 (dd, 0.5 × 1, *J* = 17.6, 3.0, H-20), 2.88 (dd, 0.5 × 1, *J* = 17.6, 3.1, H-20), 2.79 (dd, 0.5 × 1, *J* = 17.3, 3.6, H-8), 2.78 (dd, 0.5 × 1, *J* = 17.3, 3.7, H-8), 2.71-2.62 (m, 1, H-19), 2.55 (dd, 1, *J* = 17.3, 11.2, H-8), 2.53 (dd, 0.5 × 1, *J* = 17.6, 10.5, H-20), 2.49 (dd, 0.5 × 1, *J* = 17.6, 10.5, H-20), 2.14 (dd, 1, *J* = 12.2, 5.4, H-16), 1.94 (dq, 1, *J* = 14.2, 7.3, H-23), 1.91 (dd, 1, *J* = 12.2, 12.2, H-16), 1.88-1.78 (m, 2, H-23, H-18), 1.63-1.48 (m, 3), 1.46-1.27 (m, 5), 1.33 (s, 0.5 × 3, H-27), 1.32 (s,

0.5 × 3, H-27), 1.08 (d, 3, *J* = 6.3, H-25), 0.92 (t, 3, *J* = 6.8), 0.83 (t, 0.5 × 3, *J* = 7.6, H-24), 0.82 (t, 0.5 × 3, *J* = 7.3, H-24); ^{13}C NMR ($CDCl_3$) 206.04 (0.5 × 1), 205.98 (0.5 × 1), 173.4, 170.5, 162.5, 149.8, 142.2, 112.17, 112.16, 110.5, 98.6, 75.2, 73.5, 67.2, 59.74 (0.5 × 1), 59.73 (0.5 × 1), 52.5, 48.2, 41.6, 39.4, 36.2, 34.30, 34.29, 31.8, 27.92 (0.5 × 1), 27.85 (0.5 × 1), 25.0, 22.6, 18.41 (0.5 × 1), 18.34 (0.5 × 1), 14.0, 12.0, 8.67 (0.5 × 1), 8.61 (0.5 × 1); ^{13}C NMR (CD_3OD, 400 MHz) 208.82 (0.5 × 1), 208.76 (0.5 × 1), 174.8, 173.6, 163.4, 153.1, 142.3, 113.8, 110.7, 109.4, 101.1, 76.6, 74.16 (0.5 × 1), 76.13 (0.5 × 1), 69.5, 61.0, 52.9, 42.6, 40.48 (0.5 × 1), 40.46 (0.5 × 1), 37.4, 35.4, 35.0, 33.0, 28.90 (0.5 × 1), 28.83 (0.5 × 1), 26.2, 23.7, 18.89 (0.5 × 1), 18.78 (0.5 × 1), 14.4, 11.9, 8.98 (0.5 × 1), 8.94 (0.5 × 1) (a peak near δ 49.2 is obscured by the solvent peak); IR (neat) 3233, 2957, 2934, 2860, 1714, 1696. The ^{1}H and ^{13}CNMR spectral data in both $CDCl_3$ and CD_3OD correspond to those of the natural product.[1]

Methyl (α*S*,2*S*,3*S*,3'a*S*,4*S*,5'*R*)-α,3-Dimethyl-α-ethyl-3',3'a,4,5,5',6'-hexahydro-3-methyl-β-oxo-5'-pentyl-8'-(2-propenyloxy)-9'-(2-propenyloxycarbonyl)-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate. Aldol product **33** (20 mg, 32.5 μmol) in CH_2Cl_2 (2 mL) was treated with Dess–Martin periodinane (28 mg, 66 μmol) at 0 °C. The suspension was allowed to warm to 25 °C and continued to stir for 12 h. The solvent was removed under reduced pressure at 25 °C. Flash chromatography on silica gel (10:1 hexanes/EtOAc) gave 16.9 mg (85%) of the allyl ether and allyl ester of berkelic acid: $[\alpha]_D^{22}$ – 88.5 (*c* 0.73, $CHCl_3$); ^{1}H NMR 6.24 (s, 1, H-4), 6.08-5.92 (m, 2), 5.40 (br d, 1, *J* = 17.7), 5.36 (br d, 1, *J* = 17.1), 5.27 (br d, 1, *J* = 10.4), 5.23 (br d, 1, *J* = 10.4), 4.85 (dd, 1, *J* = 13.4, 6.1), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.74 (dd, 1, *J* = 13.1, 5.8), 4.51 (d, 2, *J* = 4.9), 4.35 (dd, 1, *J* = 8.5, 8.5, H-26), 3.86-3.78 (m, 1, H-9), 3.74 (s, 3, OMe), 3.45 (dd, 1, *J* = 8.5, 8.5, H-26), 2.77 (dd, 1, *J* = 17.7, 3.4, H-20), 2.75 (dd, 1, *J* = 16.5, 3.7, H-8), 2.60 (dd, 1, *J* = 17.1, 11.0, H-8), 2.62-2.51 (m, 1, H-19), 2.43 (dd, 1, *J* = 17.7, 10.4, H-20), 2.14 (dd, 1, *J* = 12.2, 5.5, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 2.02-1.91 (m, 1, H-23), 1.82 (dq, 1, *J* = 14.0, 7.3, H-23), 1.72-1.58 (m, 2), 1.58-1.46 (m, 2), 1.45-1.24 (m, 5), 1.33 (s, 3, H-27), 1.01 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.4), 0.84 (t, 3, *J* = 7.3); ^{13}C NMR 206.6, 173.5, 165.5, 155.6, 148.9, 135.8, 132.9, 132.2, 118.5,

117.1, 114.5, 109.7, 108.4, 104.4, 75.3, 72.8, 69.4, 68.0, 65.7, 59.7, 52.4, 48.4, 42.0, 38.9, 36.3, 34.42, 34.39, 31.8, 27.9, 25.1, 22.6, 18.4, 14.0, 11.6, 8.6; IR (neat) 2957, 2933, 2860, 1739, 1731, 1715; HRMS (EI) calcd for $C_{35}H_{48}O_9$ (M^+) 612.3298, found 612.3300.

Methyl (α*R*,2*S*,3*S*,3'a*S*,4*S*,5'*R*)-α,3-Dimethyl-α-ethyl-3',3'a,4,5,5',6'-hexahydro-3-methyl-β-oxo-5'-pentyl-8'-(2-propenyloxy)-9'-(2-propenyloxycarbonyl)-spiro[furan-2(3*H*),2'-[2*H*]pyrano[2,3,4-*de*][1]benzopyran]-4-butanoate. An identical reaction with **34** (20.2 mg, 32.9 μmol) afforded 15.6 mg (77%) of the allyl ether and allyl ester of 22-*epi*-berkelic acid: $[\alpha]_D^{22}$ –91.9 (*c* 0.70, $CHCl_3$); ^{1}H NMR 6.23 (s, 1, H-4), 6.08-5.92 (m, 2), 5.40 (br d, 1, *J* = 17.7), 5.36 (br d, 1, *J* = 17.1), 5.27 (br d, 1, *J* = 10.4), 5.23 (d, 1, *J* = 10.4), 4.85 (dd, 1, *J* = 13.4, 6.1), 4.79 (dd, 1, *J* = 12.2, 5.5, H-15), 4.74 (dd, 1, *J* = 13.1, 5.8), 4.51 (d, 2, *J* = 4.9), 4.35 (dd, 1, *J* = 8.5, 8.5, H-26), 3.86-3.78 (m, 1, H-9), 3.74 (s, 3, OMe), 3.45 (dd, 1, *J* = 8.5, 8.5, H-26), 2.81 (dd, 1, *J* = 17.7, 3.1, H-20), 2.75 (dd, 1, *J* = 17.1, 3.7, H-8), 2.60 (dd, 1, *J* = 17.1, 11.0, H-8), 2.60-2.50 (m, 1, H-19), 2.35 (dd, 1, *J* = 17.7, 10.4, H-20), 2.14 (dd, 1, *J* = 12.2, 4.9, H-16), 1.96 (dd, 1, *J* = 12.2, 12.2, H-16), 2.02-1.91 (m, 1, H-23), 1.82 (dq, 1, *J* = 14.7, 7.3, H-23), 1.72-1.58 (m, 2), 1.58-1.46 (m, 2), 1.45-1.24 (m, 5), 1.34 (s, 3, H-27), 1.00 (d, 3, *J* = 6.7, H-25), 0.90 (t, 3, *J* = 6.7), 0.83 (t, 3, *J* = 7.3); ^{13}C NMR 206.5, 173.5, 165.5, 155.6, 148.9, 135.8, 132.9, 132.2, 118.5, 117.2, 114.5, 109.7, 108.4, 104.4, 75.3, 72.8, 69.4, 68.0, 65.7, 59.7, 52.4, 48.5, 42.0, 38.9, 36.3, 34.42, 34.39, 31.8, 27.8, 25.1, 22.6, 18.3, 14.0, 11.6, 8.6; IR (neat) 2957, 2934, 2860, 1739, 1732, 1715; HRMS (EI) calcd for $C_{35}H_{48}O_9$ (M^+) 612.3298, found 612.3296.

Methyl (2*S*,3*R*,5*R*)- and (2*R*,3*S*,5*R*)-2-Ethyl-3-hydroxy-2,5,9-trimethyl-8-decenoate (42 and 43). *n*-BuLi (2.1 mL, 1.6 M in hexane, 3.36 mmol) was added dropwise to a solution of diisopropylamine (0.47 mL, 3.33 mmol) in THF (2 mL) under N_2 at 0 °C. The resulting solution was stirred at 0 °C for 30 min and cooled to –78 °C. A solution of methyl 2-methylbutanoate (0.44 mL, 3.33 mmol) in THF (2 mL) was added dropwise to the reaction mixture and the reaction was stirred at –78 °C for 1 h to generate enolate **38**. A solution of (*R*)-(+)-citronellal ((*R*)-**37**) (0.27 mL, 1.33 mmol) in THF (2 mL) was added dropwise to the reaction mixture and the reaction was slowly warmed up to 25 °C over 2 h. The reaction was quenched with saturated

NH_4Cl (10 mL) and extracted with ether (3 × 5 mL). The combined ether extracts were dried (Na_2SO_4) and concentrated to give 335 mg of crude **39**. Flash chromatography on silica gel (10:1 hexanes/EtOAc) gave 249.6 g (70%) of methyl (5*R*)-5,9-dimethyl-2-ethyl-3-hydroxy-8-decenoate (**39**) as a mixture of four diastereomers: ^{1}H NMR 5.13-5.04 (br, 1), 3.80-3.72 (m, 1), 3.71-3.68 (three singlets, 3), 2.19-1.06 (m, 7), 1.68 (3), 1.60 (3), 1.12-1.10 (four singlets, 3), 0.96-0.80 (m, 6).

n-BuLi (0.275 mL, 1.6 M in hexane, 0.44 mmol) was added dropwise to a solution of diisopropylamine (62 μL, 0.44 mmol) in THF (0.5 mL) under N_2 at 0 °C. The resulting solution was stirred at 0 °C for 30 min and cooled to -50 °C. A solution of **39** (51 mg, 0.2 mmol) in THF (0.5 mL) was added dropwise to the reaction mixture. The resulting solution was stirred at -50 °C for 30 min and at -20 °C for 1 h. A solution of MeI (25 μL, 0.61 mmol) and HMPA (0.21 mL, 1.2 mmol) in THF (0.3 mL) was added dropwise to the reaction mixture. The solution was stirred at -20 °C for 2 h and slowly warmed up to 25 °C over 1 h. The reaction mixture was quenched with saturated NH_4Cl (4 mL) and extracted with ether (4 × 4 mL). The combined ether extracts were dried ($MgSO_4$) and concentrated. Flash chromatography on silica gel (25:1 hexanes/EtOAc) gave 8.8 mg (16%) of 1:1 mixture of **42** and **43**.

Methyl (2*S*,3*R*,5*R*)-, (2*R*,3*R*,5*R*)-, (2*R*,3*S*,5*R*)-, and (2*S*,3*S*,5*R*)-2-Ethyl-3-hydroxy-2,5,9-trimethyl-8-decenoate (42, 43, 44, and 45, respectively). To a solution of *N*-Ts-(*S*)-valine ((*S*)-**32**)[22] (81 mg, 0.3 mmol) in dry CH_2Cl_2 (1 mL) was added BH_3•THF (0.3 mL, 1 M solution in THF, 0.3 mmol) by syringe over 3 min under N_2 at 0 °C. The solution was stirred for 30 min at 0 °C and additionally for 30 min at 25 °C. The solution was cooled –78 °C and a solution of (*R*)-(+)-citronellal ((*R*)-**37**) (16.3 μL, 90 μmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 3 min. After stirring for 5 min, silyl ketene acetal **19** (47 mg, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 3 min. The reaction mixture was stirred for 4 h at –78 °C and quenched with 1 M aqueous HCl (3 mL). The mixture was allowed to warm to 25 °C and the aqueous layer was extracted with CH_2Cl_2 (4 × 3 mL). The combined organic layers were washed with saturated $NaHCO_3$ (2 × 6 mL), dried ($MgSO_4$) and concentrated to yield

21.9 mg of crude aldol product. Flash chromatography (25:1 hexanes/EtOAc) gave 9.1 mg (38%) of **42** contaminated with 15% of **43**, followed by 10.0 mg (41%) of **44** contaminated with 15% of **45**.

Data for **42**: ^{1}H NMR 5.13-5.06 (m, 1), 3.789 (br d, 1, J = 9.8), 3.685 (s, 3), 2.07-1.85 (m, 3, including OH), 1.80 (dq, 1, J = 14.0, 7.3), 1.72-1.64 (m, 1), 1.68 (s, 3), 1.61 (s, 3), 1.54 (dq, 1, J = 13.4, 7.3), 1.52-1.42 (m, 1), 1.33-1.16 (m, 3), 1.113 (s, 3), 0.94 (d, 3, J = 6.7), 0.85 (t, 3, J = 7.3); ^{13}C NMR 177.05, 131.20, 124.78, 74.09, 51.62, 51.43, 40.16, 35.52, 29.60, 28.57, 25.72, 25.22, 20.76, 17.65, 16.22, 9.02; HRMS (EI) calcd for $C_{16}H_{30}O_3$ (M^+) 270.2195, found 270.2192.

Data for **44**: ^{1}H NMR 5.14-5.06 (m, 1), 3.755 (br, 1), 3.712 (s, 3), 2.34-2.26 (br, 1, OH), 2.09-1.96 (m, 1), 2.00-1.86 (m, 1), 1.74 (dq, 1, J = 14.0, 7.3), 1.76-1.68 (m, 1), 1.68 (s, 3), 1.61 (s, 3), 1.52 (dq, 1, J = 13.4, 7.3), 1.54-1.44 (m, 1), 1.37-1.22 (m, 2), 1.20-1.10 (m, 1), 1.095 (s, 3), 0.95 (d, 3, J = 6.7), 0.83 (t, 3, J = 7.3); ^{13}C NMR 177.72, 131.19, 124.79, 73.47, 51.73, 51.61, 39.23, 35.61, 29.50, 29.41, 25.72, 25.32, 20.82, 17.65, 16.53, 8.87; HRMS (EI) calcd for $C_{16}H_{30}O_3$ (M^+) 270.2195, found 270.2197.

An identical reaction from *N*-Ts-(*R*)-valine ((*R*)-**32**) afforded 5.0 mg (21%) of **43** contaminated with 15% of **42** and 4.4 mg (18%) of **45** contaminated with 15% of **44**.

Data for **43**: ^{1}H NMR 5.13-5.06 (m, 1), 3.784 (br d, 1, J = 10.4), 3.687 (s, 3), 2.08-1.91 (m, 3, including OH), 1.80 (dq, 1, J = 14.0, 7.3), 1.73-1.64 (m, 1), 1.68 (s, 3), 1.60 (s, 3), 1.55 (dq, 1, J = 14.0, 7.3), 1.47-1.38 (m, 1), 1.34-1.16 (m, 3), 1.119 (s, 3), 0.89 (d, 3, J = 6.7), 0.86 (t, 3, J = 7.3); ^{13}C NMR 177.07, 131.15, 124.70, 73.73, 51.60, 51.36, 39.82, 38.19, 29.10, 28.56, 25.70, 25.51, 18.68, 17.64, 16.25, 8.97; HRMS (EI) calcd for $C_{16}H_{30}O_3$ (M^+) 270.2195, found 270.2194.

Data for **45**: ^{1}H NMR 5.13-5.06 (m, 1), 3.760 (br d, 1, J = 10.4), 3.712 (s, 3), 2.36-2.27 (m, 1, OH), 2.07-1.90 (m, 2), 1.74 (dq, 1, J = 14.0, 7.3), 1.78-1.68 (m, 1), 1.68 (s, 3), 1.60 (s, 3), 1.53 (dq, 1, J = 13.4, 7.3), 1.38-1.18 (m, 1), 1.18-1.06 (m, 3), 1.099 (s, 3), 0.90 (d, 3, J = 6.7), 0.83 (t, 3, J = 7.3); ^{13}C NMR 177.74, 131.14, 124.72, 73.05, 51.70, 51.49, 38.80, 38.29, 29.41,

28.92, 25.70, 25.54, 18.75, 17.64, 16.58, 8.82; HRMS (EI) calcd for $C_{16}H_{30}O_3$ (M^+) 270.2195, found 270.2190.

Methyl (2*S*,5*R*)-2-Ethyl-2,5,9-trimethyl-3-oxo-8-decenoate (46). Dess–Martin periodinane (15.7 mg, 37 μmol) was added to a solution of **42** (5.0 mg, 18.5 μmol) in CH_2Cl_2 (1 mL) at 25 °C. The suspension was stirred at 25 °C for 12 h. The solvent was removed under reduced pressure at 25 °C. Flash chromatography on silica gel (40:1 hexanes/EtOAc) gave 4.3 mg (87%) of **46**: ^{1}H NMR 5.10-5.04 (m, 1), 3.71 (s, 3), 2.37 (dd, 1, *J* = 17.1, 5.5), 2.26 (dd, 1, *J* = 17.7, 7.9), 2.10-2.00 (m, 1), 2.00-1.89 (m, 3), 1.79 (dq, 1, *J* = 14.0, 7.3), 1.68 (s, 3), 1.59 (s, 3), 1.32-1.24 (m, 1), 1.30 (s, 3), 1.20-1.08 (m, 1), 0.85 (d, 3, *J* = 6.7), 0.82 (t, 3, *J* = 7.3); ^{13}C NMR 207.2, 173.6, 131.4, 124.3, 60.2, 52.2, 45.6, 36.7, 28.2, 27.6, 25.7, 25.5, 19.5, 18.1, 17.6, 8.6; HRMS (EI) calcd for $C_{16}H_{28}O_3$ (M^+) 268.2038, found 268.2031.

An identical reaction with **45** also afforded **46** (89%).

Methyl (2*R*,5*R*)-2-Ethyl-2,5,9-trimethyl-3-oxo-8-decenoate (47). An identical reaction with **44** afforded **47** (83%): ^{1}H NMR 5.11-5.04 (m, 1), 3.71 (s, 3), 2.41 (dd, 1, *J* = 17.1, 5.5), 2.24 (dd, 1, *J* = 17.7, 7.9), 2.11-2.00 (m, 1), 2.00-1.89 (m, 3), 1.78 (dq, 1, *J* = 14.0, 7.3), 1.68 (s, 3), 1.59 (s, 3), 1.33-1.24 (m, 1), 1.31 (s, 3), 1.19-1.08 (m, 1), 0.86 (d, 3, *J* = 6.7), 0.83 (t, 3, *J* = 7.3); ^{13}C NMR 207.2, 173.6, 131.4, 124.3, 60.1, 52.2, 45.6, 36.7, 28.1, 27.6, 25.7, 25.5, 19.5, 18.2, 17.6, 8.6; HRMS (EI) calcd for $C_{16}H_{28}O_3$ (M^+) 268.2038, found 268.2041.

An identical reaction with **43** also afforded **47** (84%).

(4*R*,5*R*)-4-((2*R*)-2,6-Dimethyl-5-hepten-1-yl)-5-ethyl-2,2,5-trimethyl-1,3-dioxane (48). To a stirred suspension of lithium aluminum hydride (44.5 mg, 1.17 mmol) in ether (1.5 mL) was added a solution of β-hydroxy ester **42** (78.5 mg, 0.29 mmol) in ether (3 mL) under N_2 at 25 °C. The suspension was stirred for 3 h and quenched by slow addition of H_2O (1 mL). The white precipitate was filtered off through a pad of Celite and rinsed with EtOAc (6 × 5 mL). The organic layer was washed with brine (5 mL), dried ($MgSO_4$), and concentrated to give 63.2 mg of diol.

A solution of the diol and TsOH•H_2O (6.0 mg, 32 μmol) in 2,2-dimethoxypropane (2.5 mL) was stirred under N_2 for 40 min. The reaction mixture was diluted with ether (20 mL) and washed with saturated $NaHCO_3$ (3 × 5 mL). The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography on silica gel (40:1 hexanes/EtOAc) gave 64.4 mg (79%) of **48**: ^{1}H NMR 5.13-5.06 (m, 1), 3.63 (dd, 1, *J* = 8.5, 2.4), 3.58 (d, 1, *J* = 11.6), 3.40 (d, 1, *J* = 11.6), 2.06-1.88 (m, 2), 1.93 (dq, 1, *J* = 14.0, 7.3), 1.69 (s, 3), 1.61 (s, 3), 1.63-1.51 (m, 1), 1.45-1.37 (m, 1), 1.42 (s, 3), 1.37 (s, 3), 1.32-1.21 (m, 2), 1.15 (dq, 1, *J* = 14.0, 6.7), 1.10-1.00 (m, 1), 0.91 (d, 3, *J* = 6.7), 0.85 (t, 3, *J* = 7.6), 0.62 (s, 3); ^{13}C NMR 131.1, 124.9, 98.3, 76.4, 67.2, 35.8, 35.7, 35.2, 29.6, 29.2, 25.7, 25.2, 21.4, 20.6, 18.9, 18.4, 17.6, 7.8. A 2D NOESY experiment showed NOEs from the three ring protons at δ 3.63, 3.58, and 3.40 to the methyl singlet at δ 0.62. Only the equatorial ring proton at δ 3.58 showed an NOE to the methyl triplet of the ethyl group at δ 0.91 and one methylene proton of the ethyl group at δ 1.93; HRMS (EI) calcd for $C_{18}H_{34}O_2$ (M^+) 282.2559, found 282.2554.

(4*R*,5*S*)-4-((2*R*)-2,6-Dimethyl-5-hepten-1-yl)-5-ethyl-2,2,5-trimethyl-1,3-dioxane (49). An identical series of reactions with **44** (63.5 mg, 0.24 mmol) afforded 53.7 mg (81%) of **49**: ^{1}H NMR 5.13-5.06 (m, 1), 3.69-3.62 (m, 2), 3.38 (d, 1, *J* = 11.6), 2.06-1.86 (m, 2), 1.68 (s, 3), 1.61 (s, 3), 1.64-1.55 (m, 1), 1.45-1.37 (m, 1), 1.40 (s, 3), 1.38 (s, 3), 1.30-1.19 (m, 3), 1.13 (dq, 1, *J* = 14.0, 7.3), 1.10-1.00 (m, 1), 0.97 (s, 3), 0.91 (d, 3, *J* = 6.7), 0.80 (t, 3, *J* = 7.3); ^{13}C NMR 131.1, 124.9, 98.2, 74.0, 69.9, 36.0, 35.7, 35.2, 29.4, 29.0, 28.4, 25.7, 25.2, 20.6, 19.1, 17.6, 15.7, 7.2; ^{1}H NMR (benzene-d_6) 5.29-5.20 (m, 1), 3.61 (br d, 1, *J* = 9.8), 3.52 (d, 1, *J* = 11.6), 3.38 (d, 1, *J* = 11.6), 2.16-1.99 (m, 2), 1.86-1.4 (m, 1), 1.70 (s, 3), 1.59 (s, 3), 1.59-1.49 (m, 1), 1.50 (s, 3), 1.39-1.29 (m, 1), 1.34 (s, 3), 1.23-1.10 (m, 2), 1.04 (s, 3), 0.97 (d, 3, *J* = 6.7), 1.09-0.99 (m, 1), 0.89 (dq, 1, *J* = 14.0, 7.3), 0.62 (t, 3, *J* = 7.6); ^{13}C NMR (benzene-d_6) 131.3, 125.9, 98.7, 74.8, 70.2, 36.9, 36.7, 35.7, 30.2, 29.9, 29.0, 26.3, 26.2, 21.3, 19.6, 18.1, 16.4, 7.7; HRMS (EI) calcd for $C_{18}H_{34}O_2$ (M^+) 282.2559, found 282.2563.

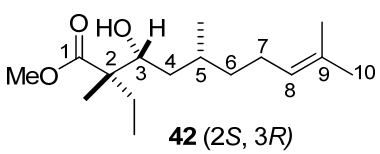
A 2D NOESY (run in benzene-d_6 because two ring protons overlapped in $CDCl_3$) experiment showed NOEs from all three ring protons at δ 3.61, 3.52, and 3.38 to the methyl

triplet of the ethyl group at δ 0.62, the ethyl methylene group multiplet at δ 0.89, and the ethyl methylene group multiplet at δ 1.09-0.99. Only the equatorial ring proton at δ 3.38 showed an NOE to the methyl singlet at δ 1.04. It is interesting to note that H-6e is downfield at δ 3.69-3.62 from H-6a at δ 3.38 in $CDCl_3$, but upfield at δ 3.38 from H-6a at δ 3.52 in C_6D_6 as has been previously observed.[30]

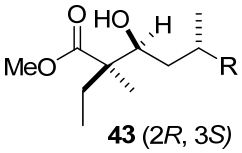
References

30. Pihlaja, K.; Äyräs, P. *Acta Chem. Scand.* **1970**, *24*, 531-549.

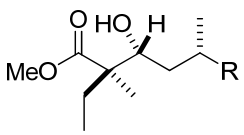
Table S1. Comparison of the ^{13}C and ^{1}H NMR Spectral Data Reported for Citronellal-derived Hydroxy Esters 42–45.



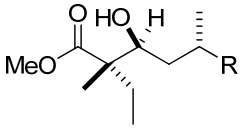
42 (2*S*, 3*R*)



43 (2*R*, 3*S*)



44 (2*R*, 3*R*)

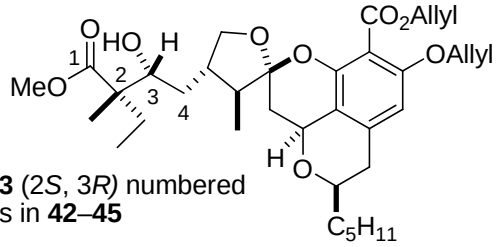


45 (2*S*, 3*S*)

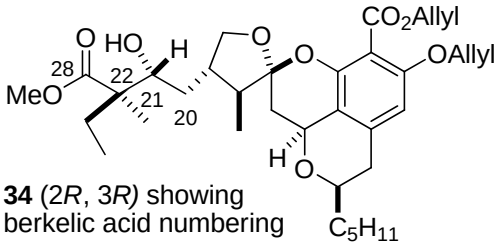
C (Roman)[a] *H(Italics)*[a]	**42** (2*S*,3*R*)	**43** (2*R*,3*S*)	**44** (2*R*,3*R*)	**45** (2*S*,3*S*)	
1	177.05	177.07	177.72	177.74	(2*R*,3*R*) and (2*S*,3*S*) 0.7 ppm downfield
2	51.6*	51.6*	51.73*	51.70*	
2-Me	16.21	16.25	16.53	16.58	(2*R*,3*R*) and (2*S*,3*S*) 0.3 ppm downfield
2-Me	*1.11*	*1.12*	*1.09*	*1.10*	*(2R,3R) and (2S,3S) 0.02 ppm upfield*
2-Et (CH_2)	28.57	28.56	29.41	29.41	(2*R*,3*R*) and (2*S*,3*S*) 0.85 ppm downfield
2-Et (CH_3)	9.0	9.0	8.87	8.82	(2*R*,3*R*) and (2*S*,3*S*) 0.15 ppm upfield
2-Et (CH_3)	*0.85*	*0.86*	*0.83*	*0.83*	*(2R,3R) and (2S,3S) 0.025 ppm upfield*
OMe	51.4*	51.4*	51.6*	51.5*	
OMe	*3.69*	*3.69*	*3.71*	*3.71*	*(2R,3R) and (2S,3S) 0.02 ppm downfield*
3	74.09	73.73	73.47	73.05	(2*R*,3*R*) and (2*S*,3*S*) 0.6-0.7 ppm upfield
3	*3.79*	*3.78*	*3.76*	*3.76*	*(2R,3R) and (2S,3S) 0.02 ppm upfield*
4	40.16	39.82	39.23	38.80	(2*R*,3*R*) and (2*S*,3*S*) 0.9-1.0 ppm upfield
5	29.60	29.10	29.50	28.92	(3*R*) 0.5 ppm downfield
5-Me	20.76	18.68	20.82	18.75	(3*R*) 2.1 ppm downfield
5-Me	*0.94*	*0.89*	*0.95*	*0.90*	*(3R) 0.05 ppm downfield*
6	35.52	38.19	35.61	38.29	(3*R*) 2.7 ppm upfield
7	25.2	25.5	25.3	25.5	
8	124.8	124.7	124.8	124.7	
9	131.2	131.2	131.2	131.1	
10	25.7	25.7	25.7	25.7	
9-Me	17.6	17.6	17.6	17.6	

* Data for C-2 and the OMe group may be switched. a) ^{13}C NMR data are in roman type and ^{1}H NMR data are in italic type.

Table S2. Comparison of the ^{13}C and ^{1}H NMR Spectral Data Reported for Berkelic Acid Intermediates 33 and 34.



33 (2*S*, 3*R)* numbered as in **42**–**45**



34 (2*R*, 3*R)* showing berkelic acid numbering

C (Roman)[a] *H (Italics)*[a]	**33** (2*S*,3*R*)	**34** (2*R*,3*R*)	
1	176.94	177.58	(2*R*,3*R*) 0.64 ppm downfield
2-Me	16.75	16.94	(2*R*,3*R*) 0.19 ppm downfield
2-Me	*1.14*	*1.13*	*(2R,3R) 0.01 ppm upfield*
2-Et (CH_2)	28.38	29.60	(2*R*,3*R*) 1.22 ppm downfield
2-Et (CH_3)	8.99	8.80	(2*R*,3*R*) 0.19 ppm upfield
2-Et (CH_3)	*0.87*	*0.85*	*(2R,3R) 0.02 ppm upfield*
OMe	*3.709*	*3.726*	*(2R,3R) 0.017 ppm downfield*
3	76.22	75.49	(2*R*,3*R*) 0.73 ppm upfield
3	*3.73*	*3.70*	*(2R,3R) 0.03 ppm upfield*
4	35.31	34.57	(2*R*,3*R*) 0.74 ppm upfield

a) ^{13}C NMR data are in roman type and ^{1}H NMR data are in italic type.

Developmental Therapeutics Program

Wu, Zhou, and Snider

One Dose Mean Graph

NSC: 744087 / 1 **Conc:** 1.00E-5 Molar **Test Date:** Apr 09, 2007

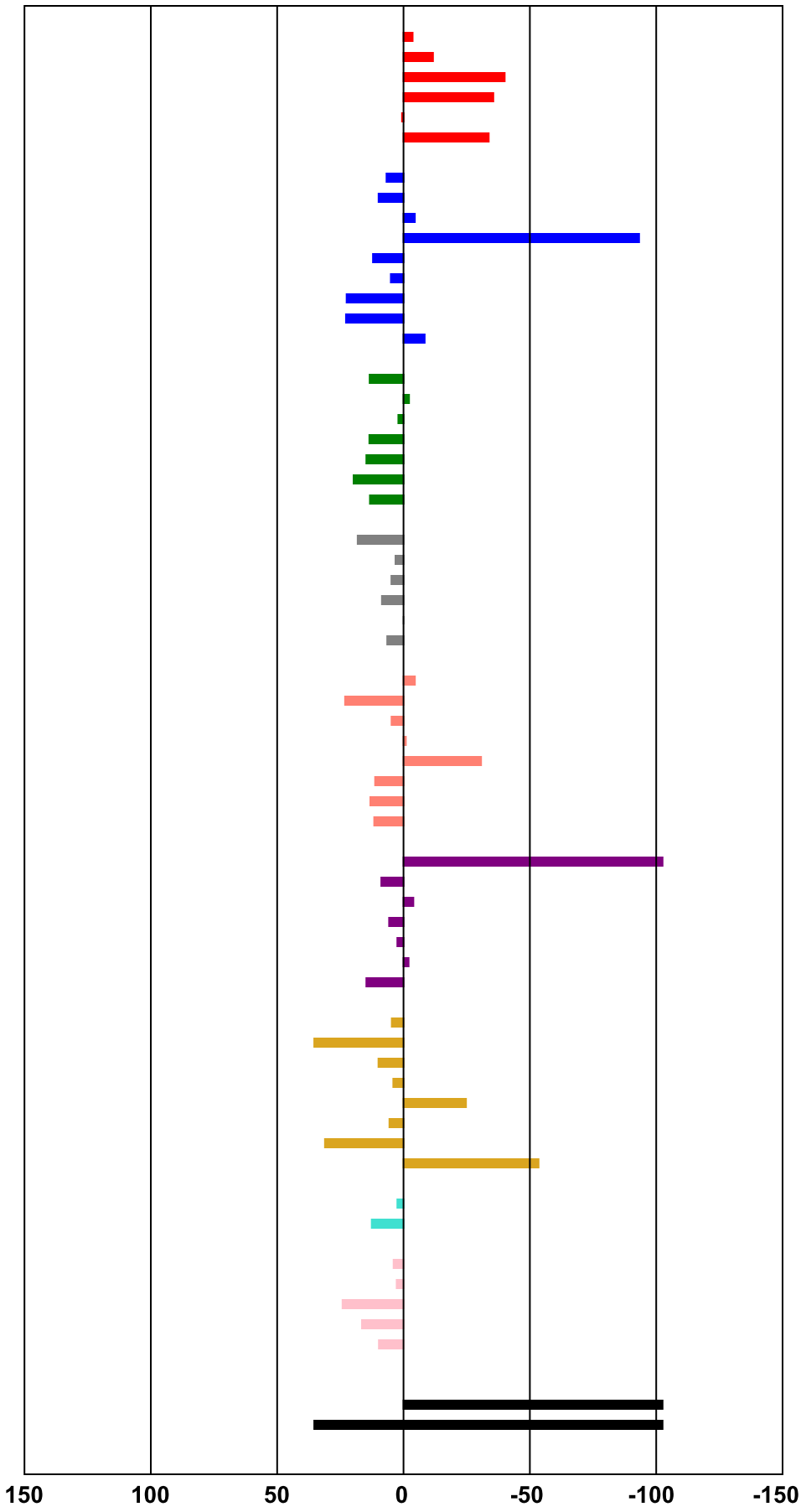
(-)-Berkelic Acid S23

Experiment ID: 0704OS63 **Report Date:** Mar 10, 2009

Data for model acid prepared by hydrolysis of **8a**

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	94.51
HL-60(TB)	86.45
K-562	58.08
MOLT-4	62.58
RPMI-8226	98.71
SR	64.40
Non-Small Cell Lung Cancer	
A549/ATCC	104.85
EKVX	107.99
HOP-62	93.63
HOP-92	4.89
NCI-H226	110.21
NCI-H23	103.14
NCI-H322M	120.64
NCI-H460	120.89
NCI-H522	89.75
Colon Cancer	
COLO 205	111.53
HCC-2998	95.93
HCT-116	100.17
HCT-15	111.64
HT29	112.83
KM12	117.89
SW-620	111.41
CNS Cancer	
SF-268	116.26
SF-295	101.30
SF-539	102.92
SNB-19	106.67
SNB-75	98.12
U251	104.57
Melanoma	
LOX IMVI	93.61
MALME-3M	121.25
M14	102.86
MDA-MB-435	97.19
SK-MEL-2	67.42
SK-MEL-28	109.36
SK-MEL-5	111.27
UACC-62	109.72
Ovarian Cancer	
IGROV1	-4.39
OVCAR-3	106.91
OVCAR-4	94.22
OVCAR-5	103.83
OVCAR-8	100.57
NCI/ADR-RES	96.11
SK-OV-3	112.83
Renal Cancer	
786-0	102.76
A498	133.44
ACHN	108.04
CAKI-1	102.17
RXF 393	73.39
SN12C	103.70
TK-10	129.21
UO-31	44.68
Prostate Cancer	
PC-3	100.56
DU-145	110.69
Breast Cancer	
MCF7	102.05
MDA-MB-231/ATCC	100.83
HS 578T	122.25
BT-549	114.58
T-47D	107.87
Mean	98.12
Delta	102.51
Range	137.83

Mean Growth Percent - Growth Percent



Testing Data for Berkelic acid MODEL (60953) NSC: 744087

Developmental Therapeutics Program

Wu, Zhou, and Snider (-)-Berkelic Acid S24

One Dose Mean Graph

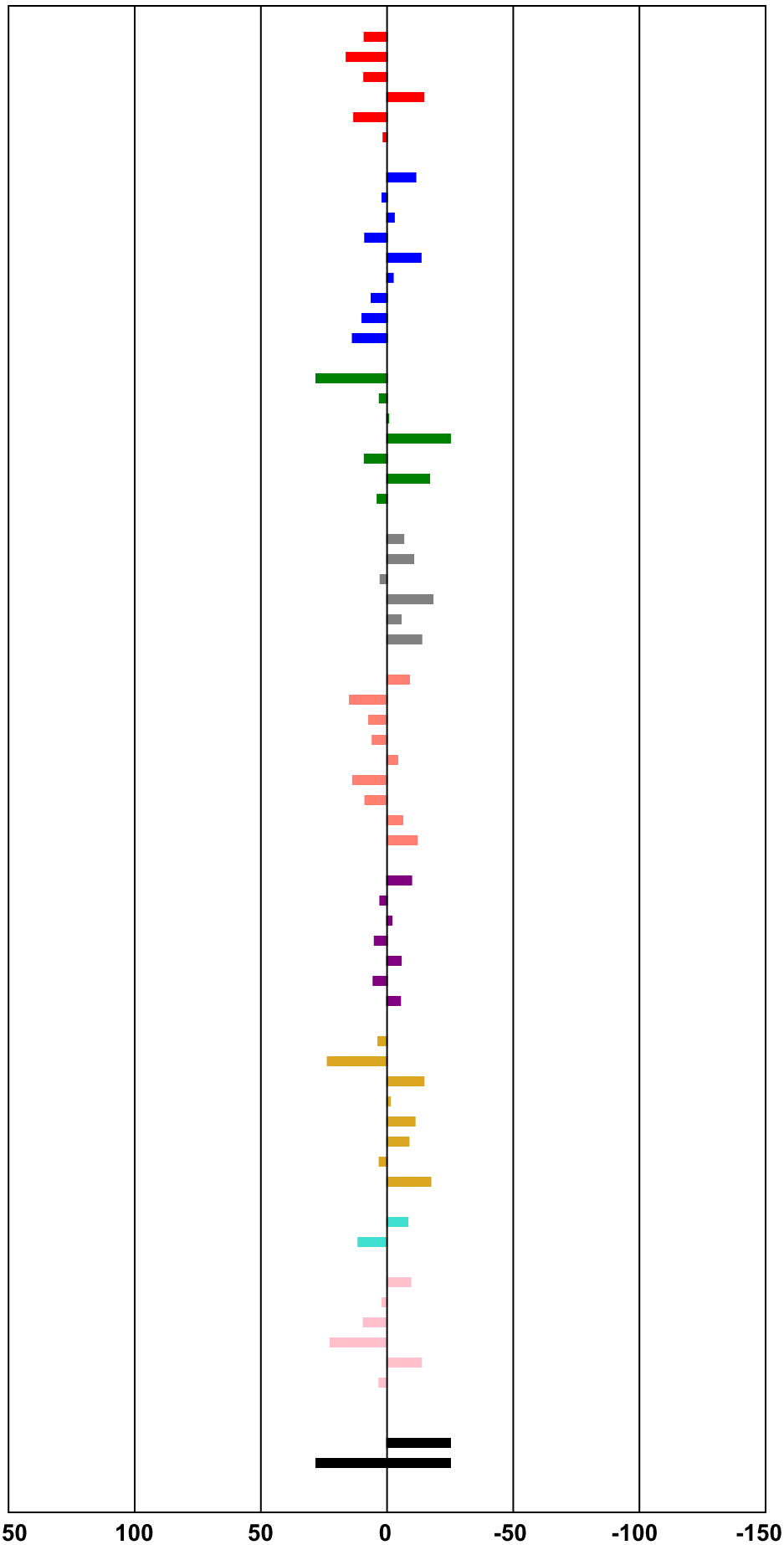
NSC: 749689 / 1 **Conc:** 1.00E-5 Molar **Test Date:** Feb 17, 2009

Experiment ID: 0902OS70 **Report Date:** Mar 10, 2009

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	117.97
HL-60(TB)	125.09
K-562	118.11
MOLT-4	94.62
RPMI-8226	122.10
SR	110.47
Non-Small Cell Lung Cancer	
A549/ATCC	97.75
EKVX	110.89
HOP-62	106.28
HOP-92	117.74
NCI-H226	95.67
NCI-H23	106.71
NCI-H322M	115.19
NCI-H460	118.85
NCI-H522	122.63
Colon Cancer	
COLO 205	137.06
HCC-2998	111.95
HCT-116	108.49
HCT-15	84.03
HT29	117.90
KM12	92.33
SW-620	112.82
CNS Cancer	
SF-268	102.53
SF-295	98.58
SF-539	111.63
SNB-19	90.94
SNB-75	103.61
U251	95.38
Melanoma	
LOX IMVI	100.29
MALME-3M	123.80
M14	116.19
MDA-MB-435	114.79
SK-MEL-2	104.93
SK-MEL-28	122.52
SK-MEL-5	117.68
UACC-257	102.91
UACC-62	97.18
Ovarian Cancer	
IGROV1	99.41
OVCAR-3	111.74
OVCAR-4	107.23
OVCAR-5	113.93
OVCAR-8	103.54
NCI/ADR-RES	114.42
SK-OV-3	103.82
Renal Cancer	
786-0	112.53
A498	132.57
ACHN	94.52
CAKI-1	107.86
RXF 393	98.06
SN12C	100.45
TK-10	112.01
UO-31	91.80
Prostate Cancer	
PC-3	100.92
DU-145	120.39
Breast Cancer	
MCF7	99.76
MDA-MB-231/ATCC	110.91
HS 578T	118.32
BT-549	131.45
T-47D	95.52
MDA-MB-468	112.12
Mean	109.02
Delta	24.99
Range	53.03

Data for berkelic acid (35)

Mean Growth Percent - Growth Percent



Testing Data for berkelic acid (83676) NSC: 749689

Developmental Therapeutics Program

One Dose Mean Graph

Wu, Zhou, and Snider

(-)-Berkelic Acid

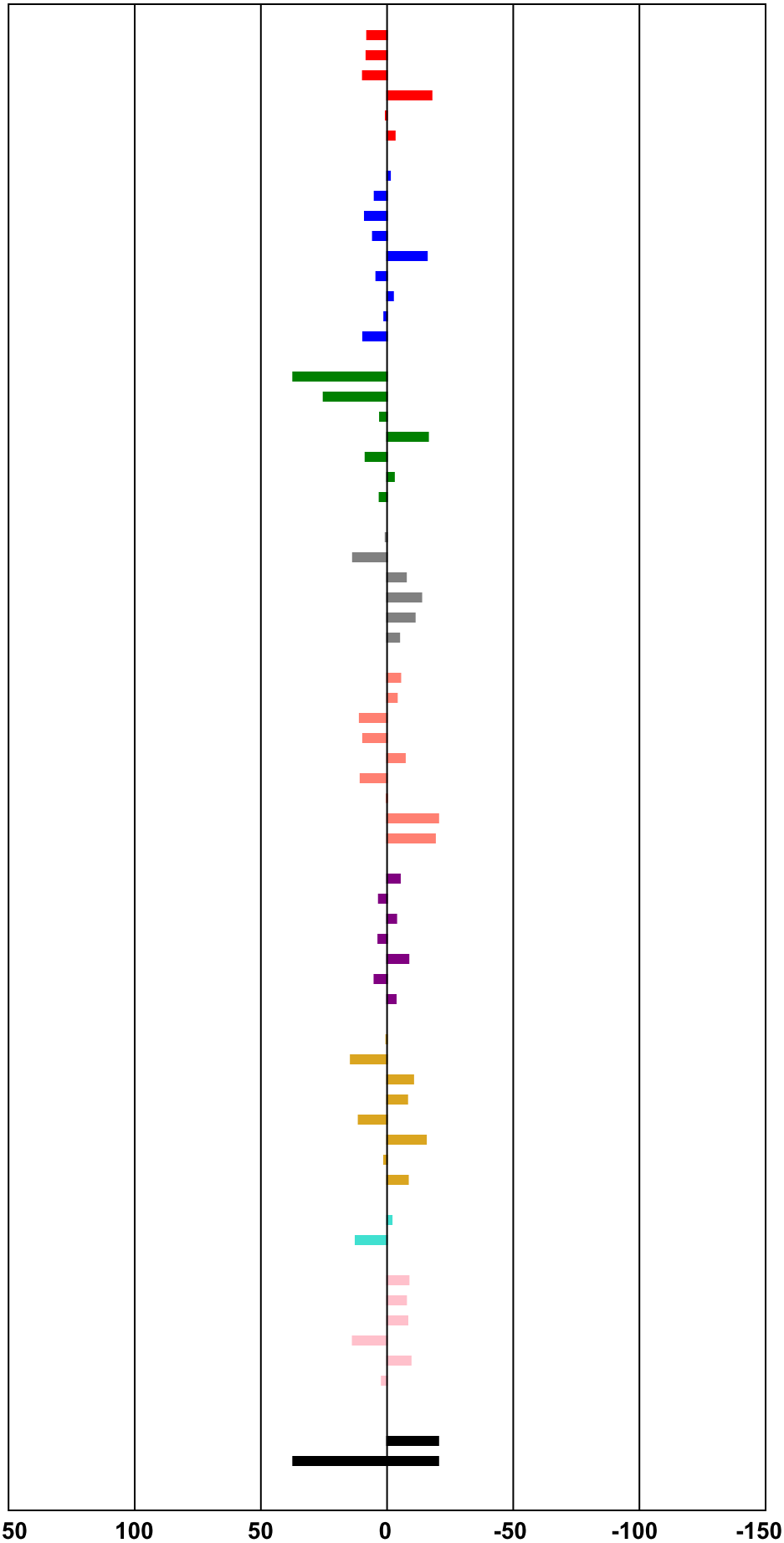
S25

NSC: 749690 / 1	Conc: 1.00E-5 Molar	Test Date: Feb 17, 2009
Experiment ID: 0902OS70		Report Date: Mar 10, 2009

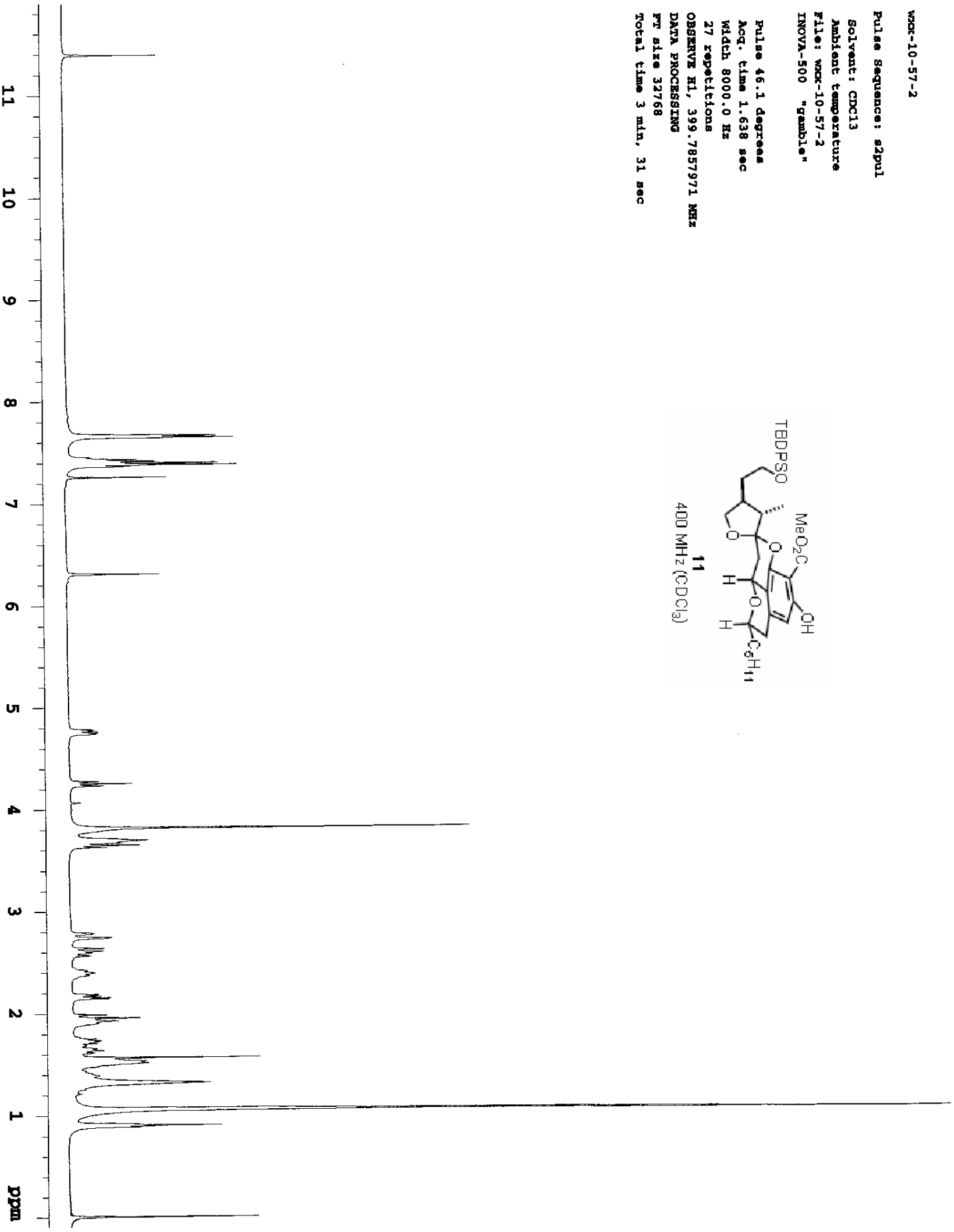
Data for 22-*epi*-berkelic acid (36)

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	115.78
HL-60(TB)	116.04
K-562	117.46
MOLT-4	90.23
RPMI-8226	108.37
SR	104.81
Non-Small Cell Lung Cancer	
A549/ATCC	106.70
EKVX	112.80
HOP-62	116.67
HOP-92	113.49
NCI-H226	92.08
NCI-H23	112.14
NCI-H322M	105.49
NCI-H460	109.00
NCI-H522	117.34
Colon Cancer	
COLO 205	145.08
HCC-2998	133.02
HCT-116	110.69
HCT-15	91.62
HT29	116.41
KM12	105.12
SW-620	110.84
CNS Cancer	
SF-268	108.45
SF-295	121.39
SF-539	100.37
SNB-19	94.28
SNB-75	96.88
U251	103.03
Melanoma	
LOX IMVI	102.60
MALME-3M	103.97
M14	118.70
MDA-MB-435	117.37
SK-MEL-2	100.79
SK-MEL-28	118.38
SK-MEL-5	107.96
UACC-257	87.57
UACC-62	88.86
Ovarian Cancer	
IGROV1	102.77
OVCAR-3	111.13
OVCAR-4	104.21
OVCAR-5	111.34
OVCAR-8	99.37
NCI/ADR-RES	112.87
SK-OV-3	104.42
Renal Cancer	
786-0	108.17
A498	122.26
ACHN	97.49
CAKI-1	99.86
RXF 393	119.13
SN12C	92.44
TK-10	109.04
UO-31	99.59
Prostate Cancer	
PC-3	106.04
DU-145	120.33
Breast Cancer	
MCF7	99.32
MDA-MB-231/ATCC	100.31
HS 578T	99.75
BT-549	121.47
T-47D	98.50
MDA-MB-468	109.97
Mean	107.86
Delta	20.29
Range	57.51

Mean Growth Percent - Growth Percent



Testing Data for 22-epiberkelic acid (83677) NSC: 749690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O
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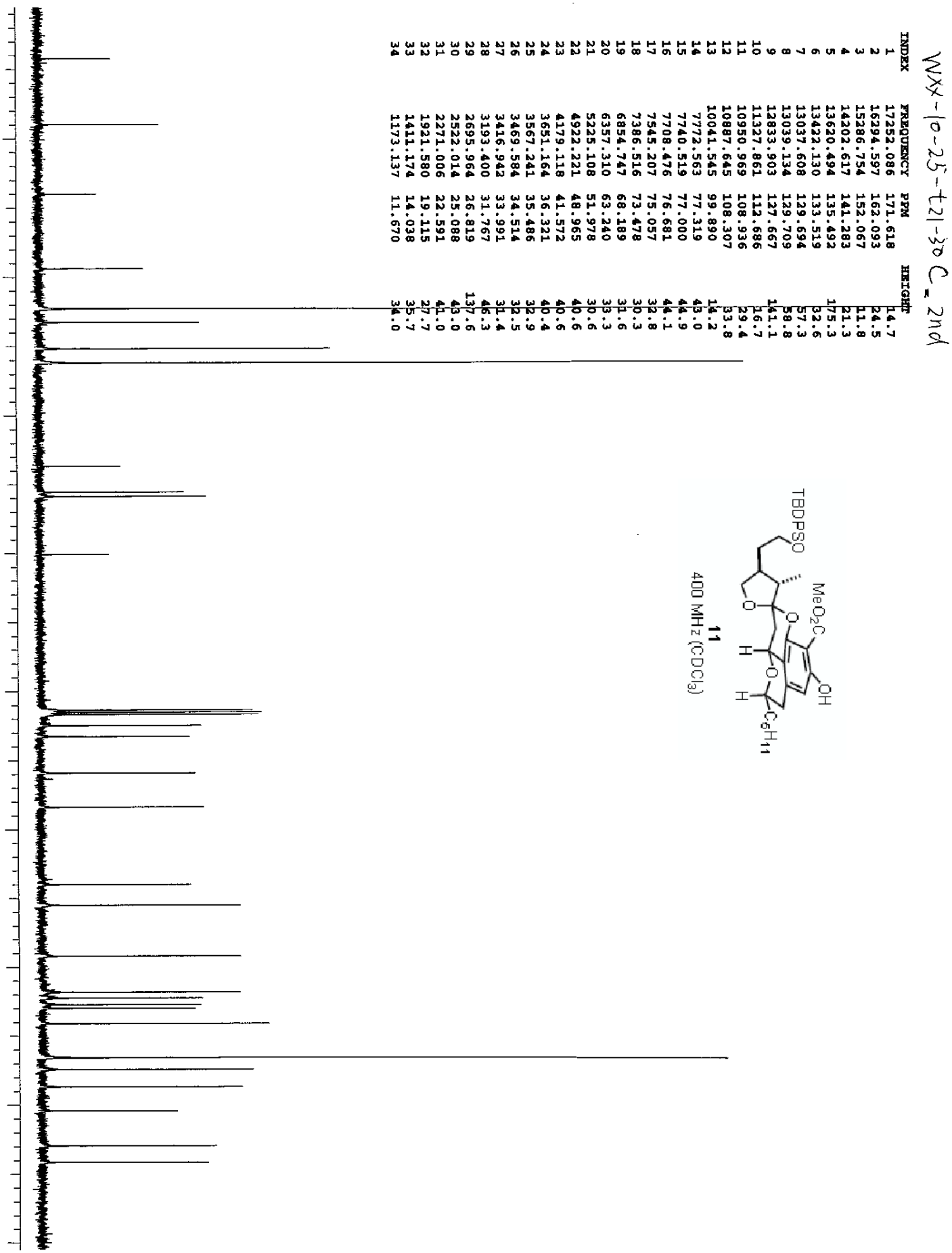
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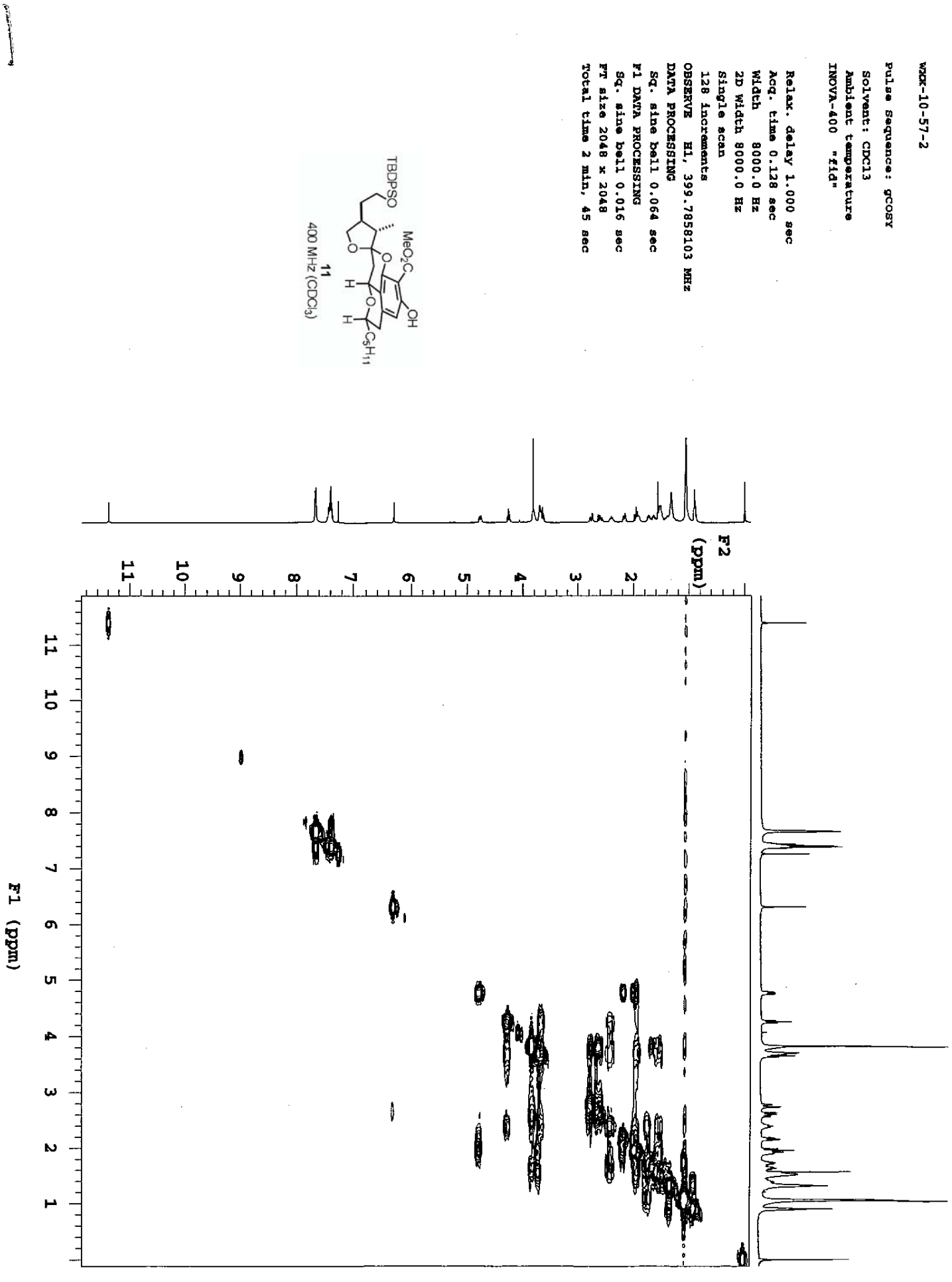
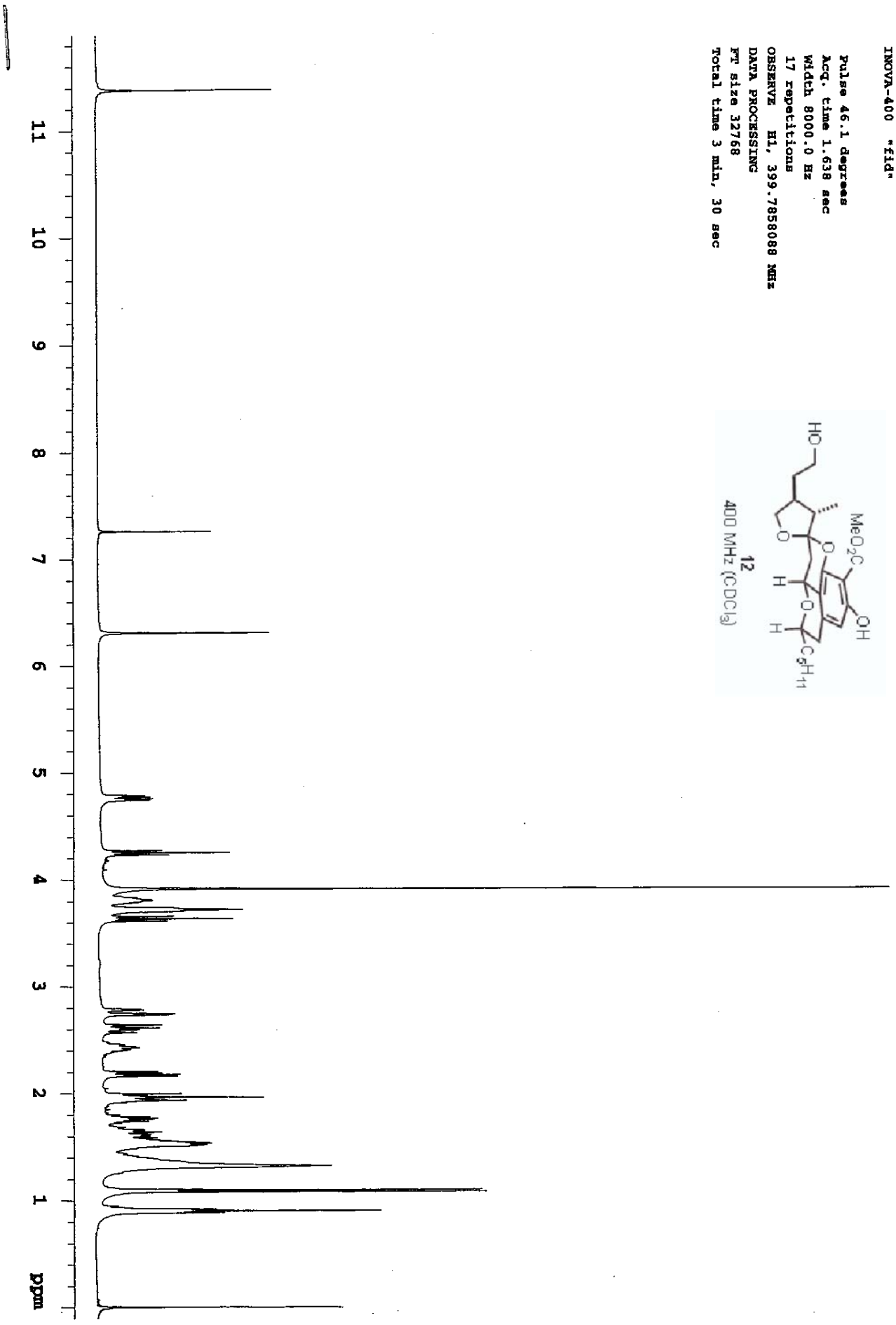
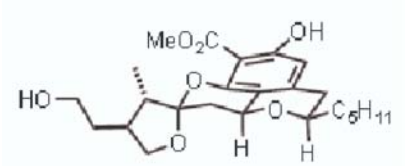
4 14202.617 141.283 21.3
5 13620.494 135.492 175.3
6 13422.130 133.519 32.6
7 13037.608 129.694 57.3
8 13039.134 129.709 58.8
9 12833.903 127.667 141.1
10 11327.861 112.686 16.7
11 10950.969 108.936 29.4
12 10887.645 108.307 33.8
13 10041.545 99.890 14.2
14 7772.563 77.319 43.0
15 7740.519 77.000 44.9
16 7708.476 76.681 44.1
17 7545.207 75.057 32.8
18 7386.516 73.478 30.3
19 6854.747 68.189 31.6
20 6357.310 63.240 33.3
21 5225.108 51.978 30.6
22 4922.221 48.965 40.6
23 4179.118 41.572 40.6
24 3651.164 36.321 40.4
25 3567.241 35.486 32.9
26 3469.584 34.514 32.5
27 3416.942 33.991 31.4
28 3193.400 31.767 46.3
29 2695.964 26.819 137.6
30 2522.014 25.088 43.0
31 2271.006 22.591 41.0
32 1921.580 19.115 27.7
33 1411.174 14.038 35.7
34 1173.137 11.670 34.0
TBDPSO
MeO2C
OH
C5H11
11
400 MHz (CDCl3)
160
140
120
100
80
60
40
20
ppm


WZK-10-57-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858103 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
TBDPSO
MeO2C
OH
C5H11
11
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

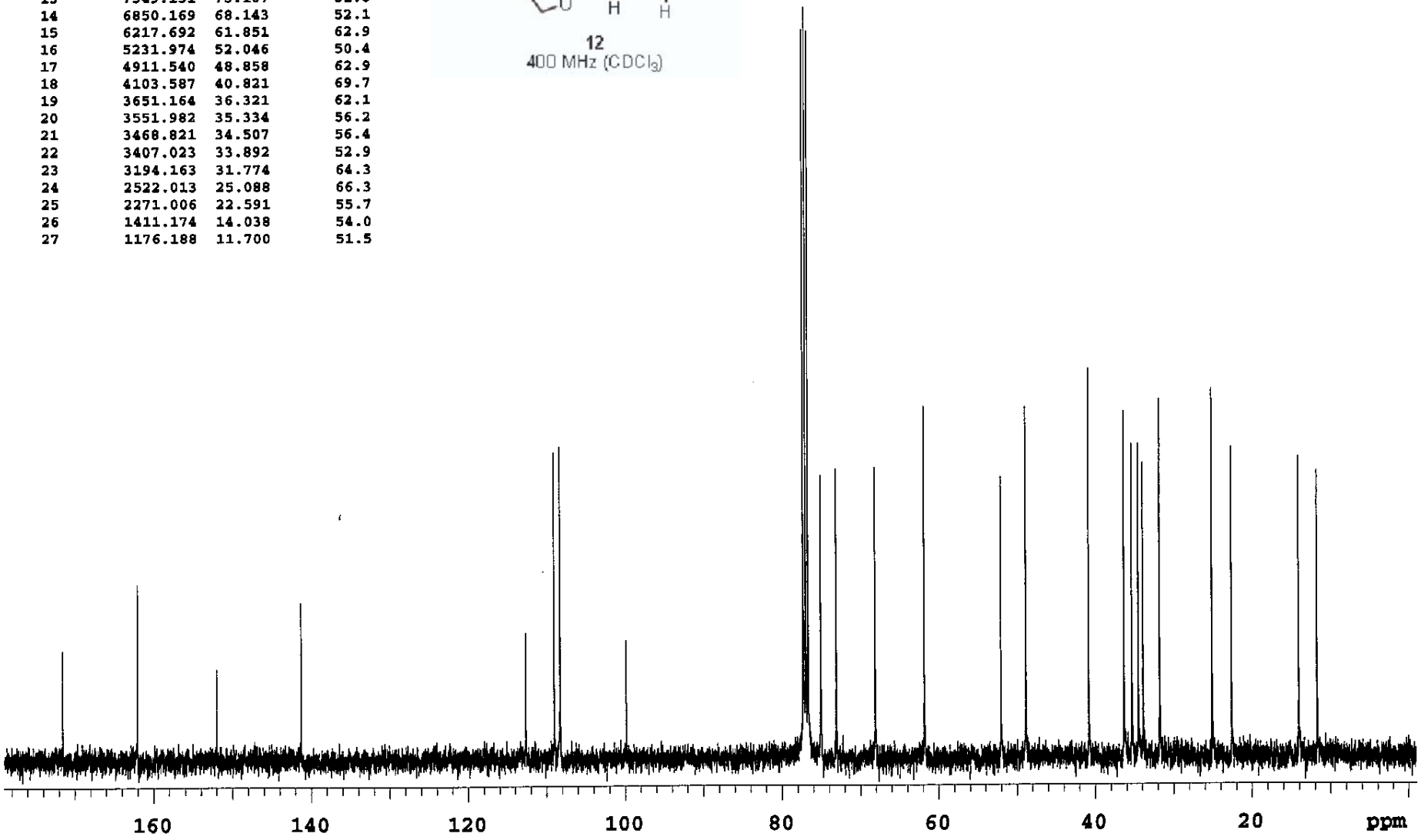

wzk-10-51-4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 8000.0 Hz
17 repetitions
OBSERVE H1, 399.7858088 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 30 sec
HO
MeO2C
OH
O
H
H
C5H11
12
400 MHz (CDCl3)
11
10
9
8
7
6
5
4
3
2
1
ppm

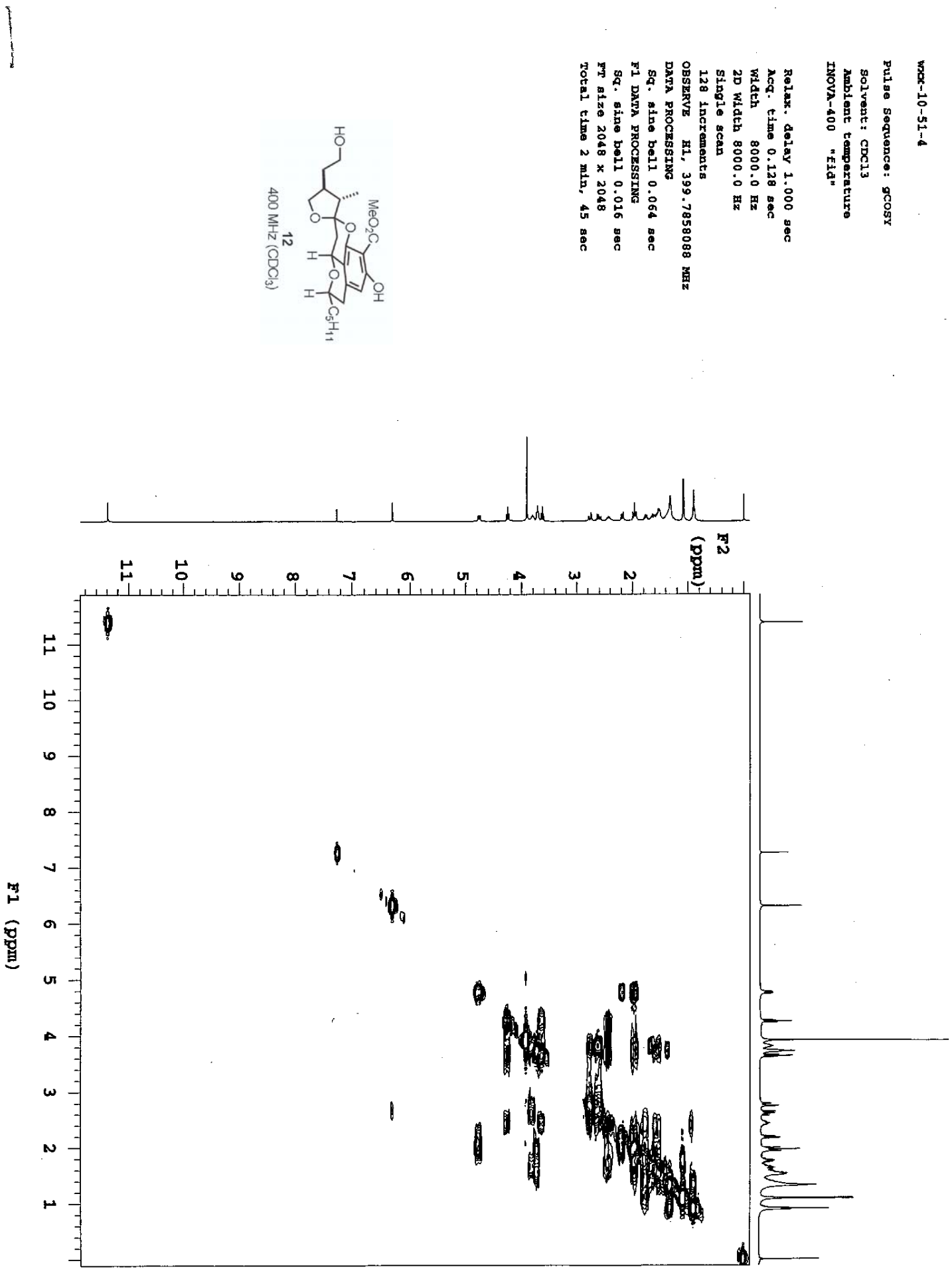
WXX-10-51-t19-20C

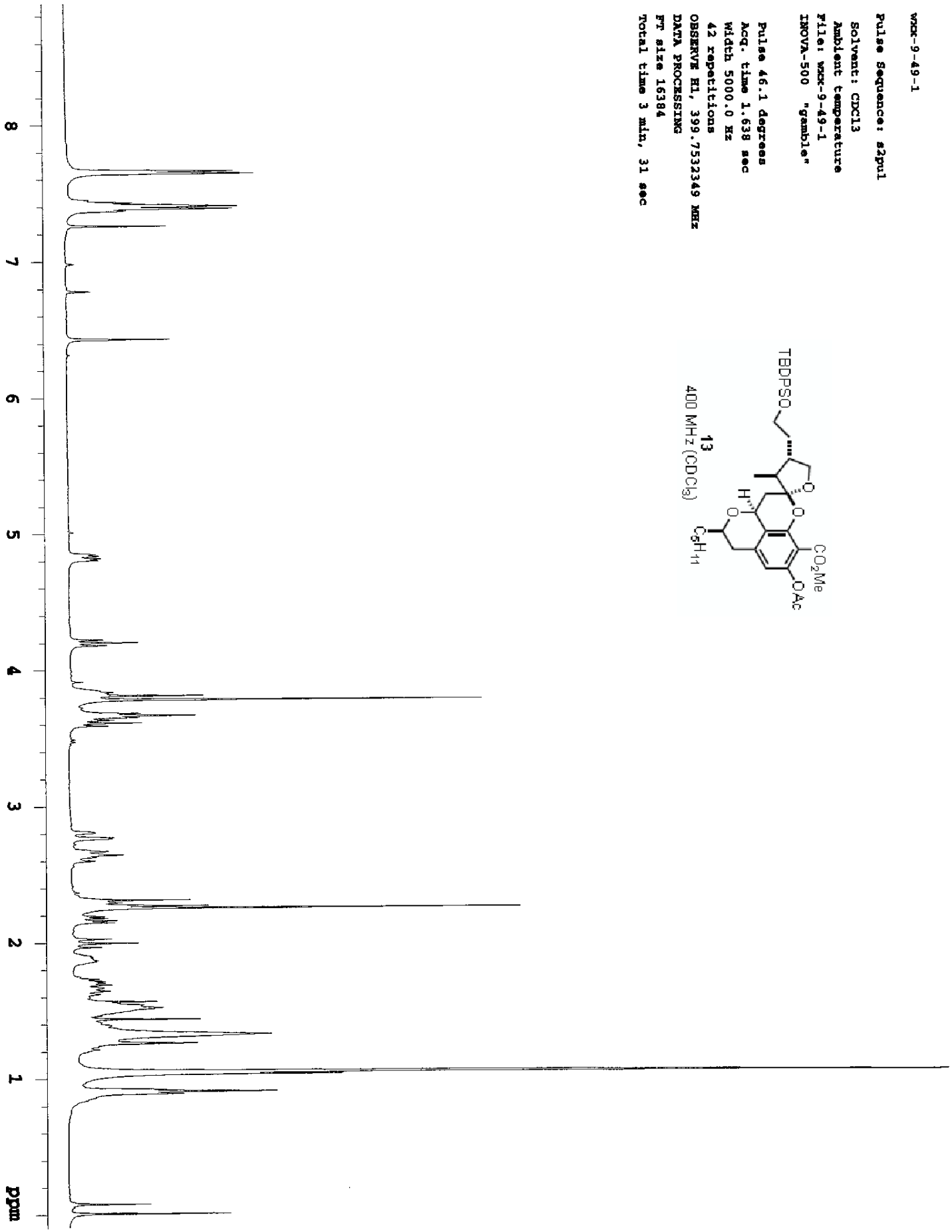
INDEX	FREQUENCY	PPM	HEIGHT
1	17249.034	171.587	20.1
2	16292.308	162.070	32.0
3	15284.465	152.045	16.8
4	14204.142	141.298	28.6
5	11327.861	112.686	23.1
6	10963.938	109.065	54.9
7	10889.170	108.322	55.9
8	10040.782	99.882	21.6
9	7772.563	77.319	129.1
10	7740.519	77.000	132.9
11	7708.476	76.681	128.7
12	7546.733	75.072	50.8
13	7349.131	73.107	51.8
14	6850.169	68.143	52.1
15	6217.692	61.851	62.9
16	5231.974	52.046	50.4
17	4911.540	48.858	62.9
18	4103.587	40.821	69.7
19	3651.164	36.321	62.1
20	3551.982	35.334	56.2
21	3468.821	34.507	56.4
22	3407.023	33.892	52.9
23	3194.163	31.774	64.3
24	2522.013	25.088	66.3
25	2271.006	22.591	55.7
26	1411.174	14.038	54.0
27	1176.188	11.700	51.5

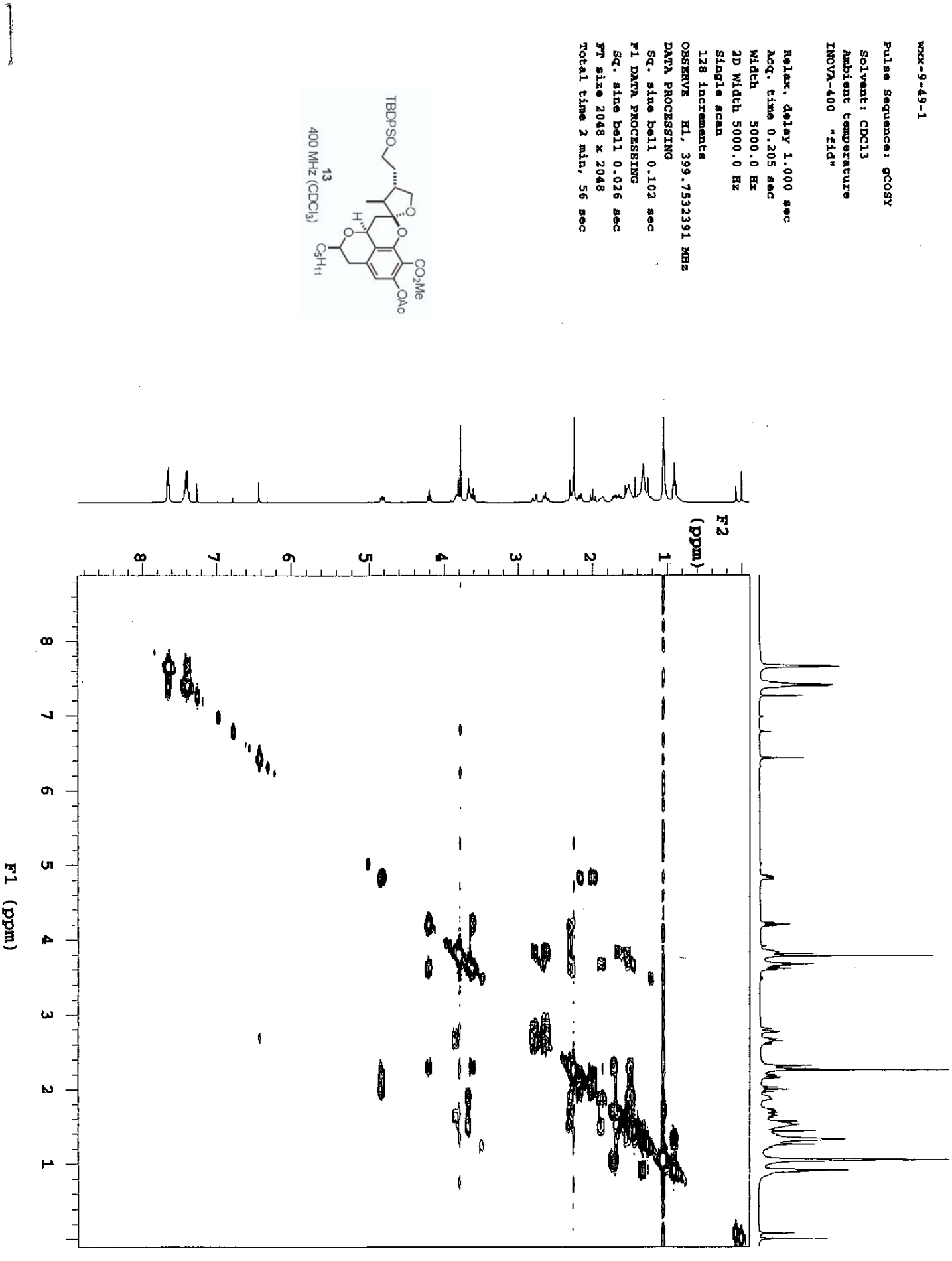


12
400 MHz ($CDCl_3$)

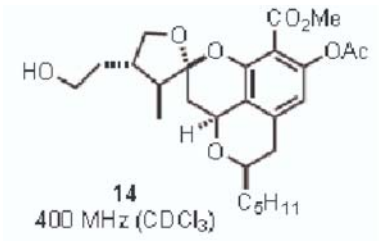



WSK-10-51-4
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858088 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
HO
MeO2C
OH
O
O
O
H
H
C5H11
12
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)
11
10
9
8
7
6
5
4
3
2
1

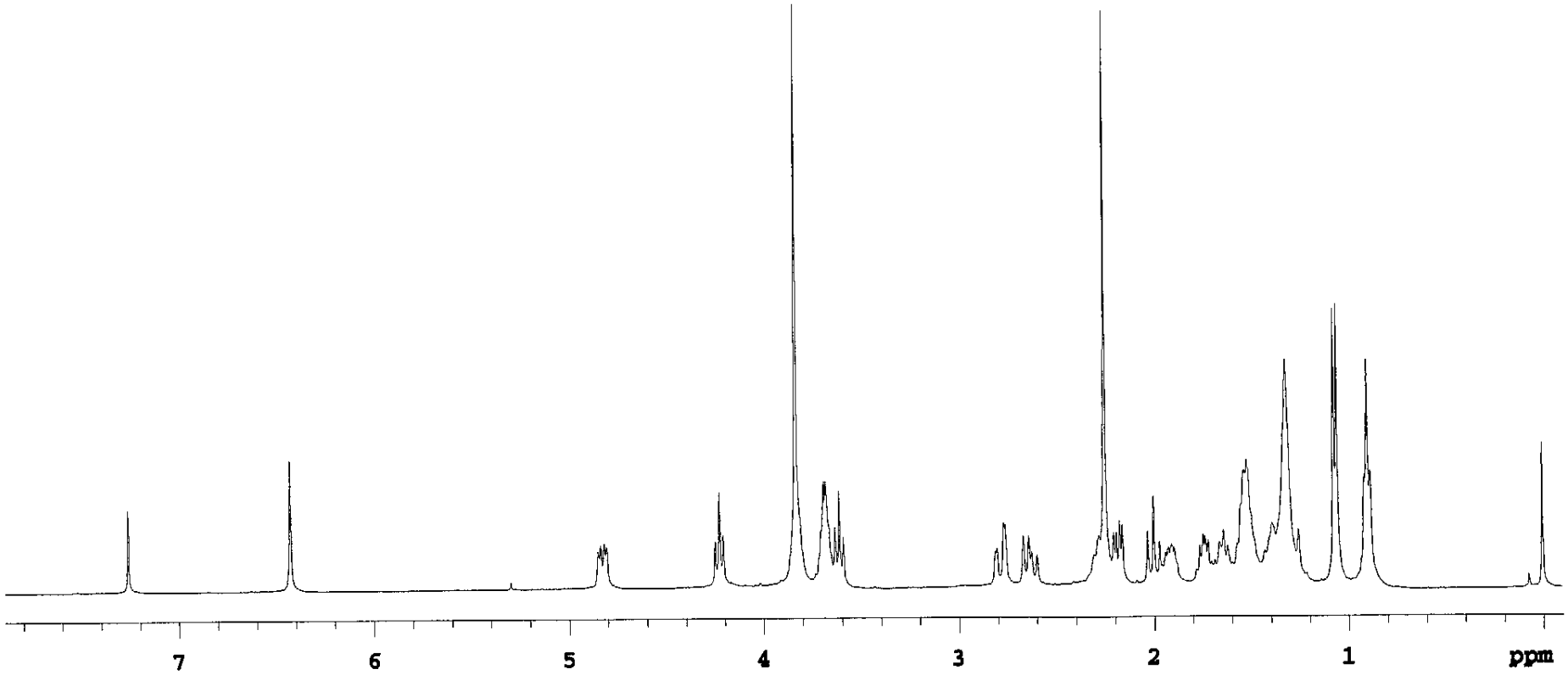

wzk-9-49-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-9-49-1
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
42 repetitions
OBSERVE H1, 399.7532349 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
TBDPSO
O
H
O
O
CO2Me
OAc
C5H11
13
400 MHz (CDCl3)
8
7
6
5
4
3
2
1
ppm


WZK-9-49-1
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7532391 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
TBDPSO
CO2Me
OAc
C5H11
13
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

```
wux-9-89-3

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
File: wux-9-89-3
INOVA-500  "gamble"

 Pulse 46.1 degrees
 Acq. time 1.638 sec
 Width 5000.0 Hz
 55 repetitions
OBSERVE H1, 399.7532349 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
```



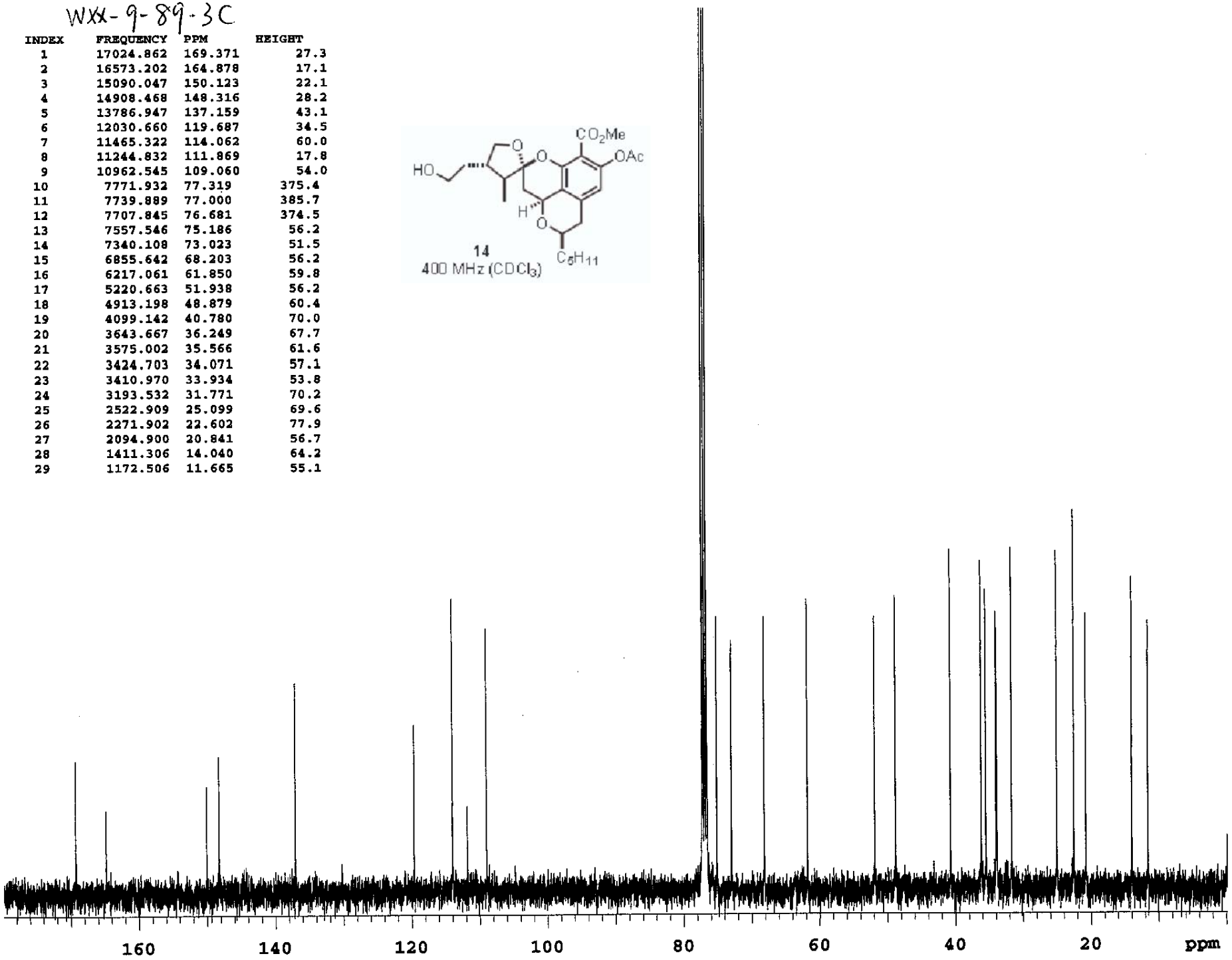
14
400 MHz ($CDCl_3$)

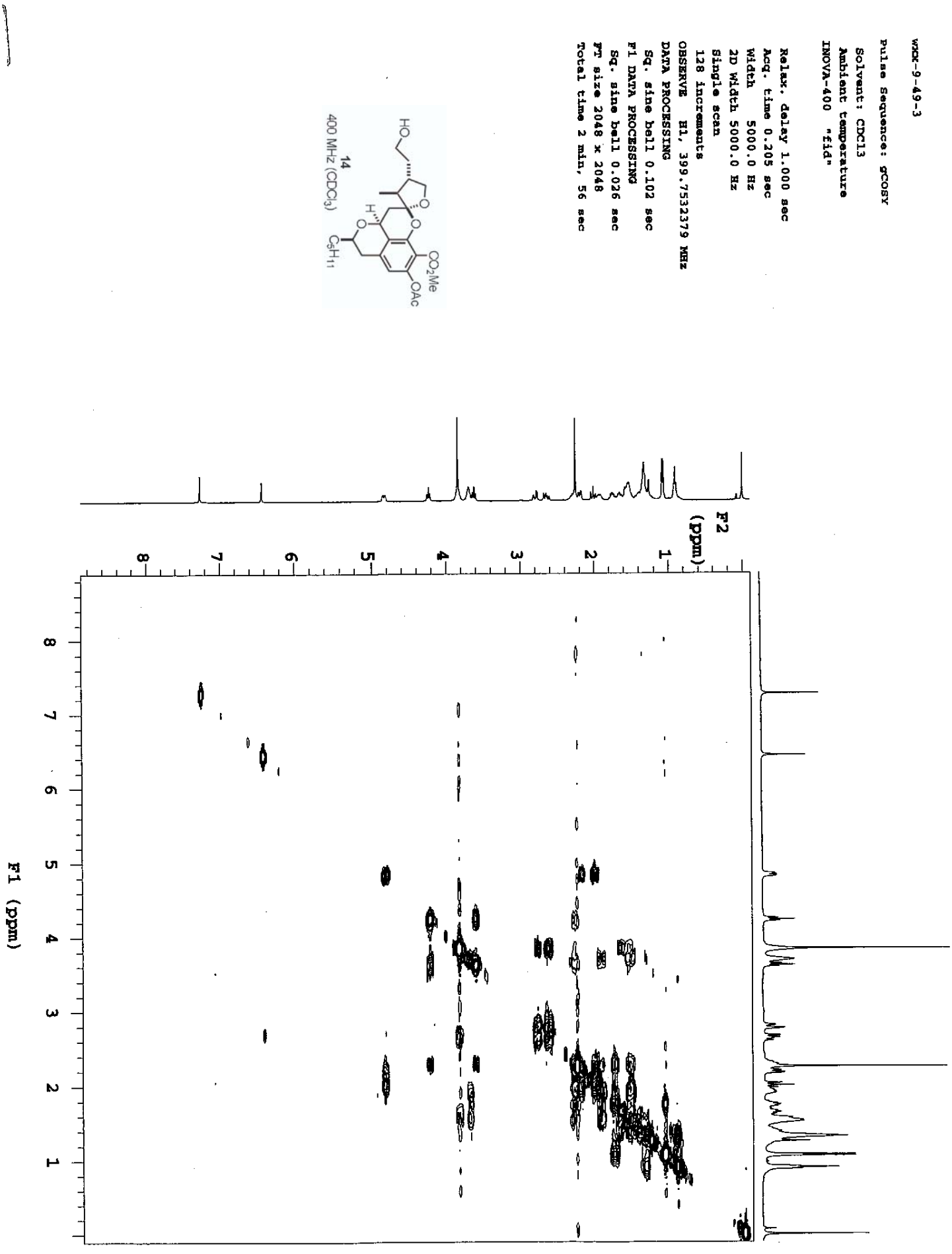


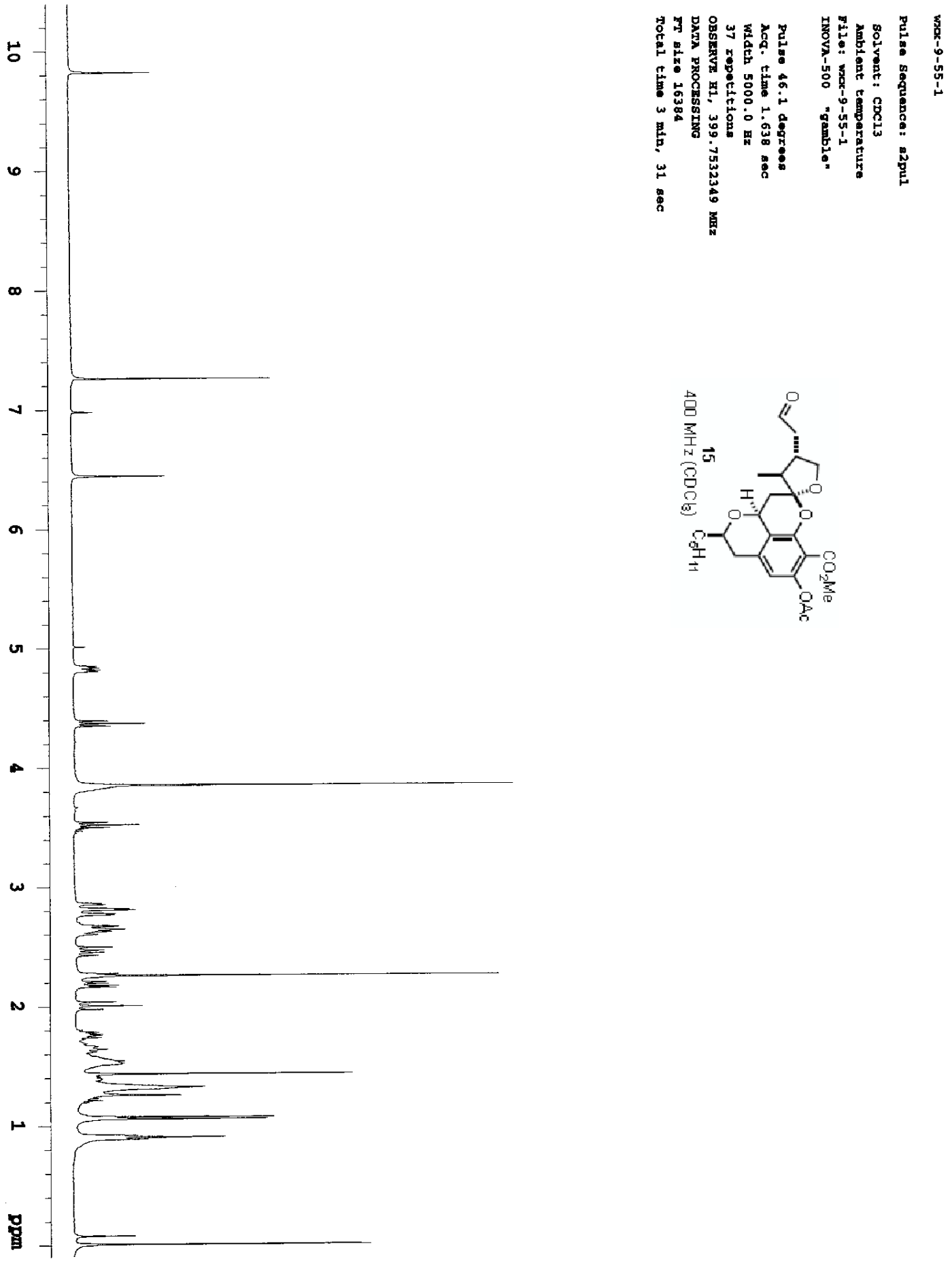
WXX-9-89-3C

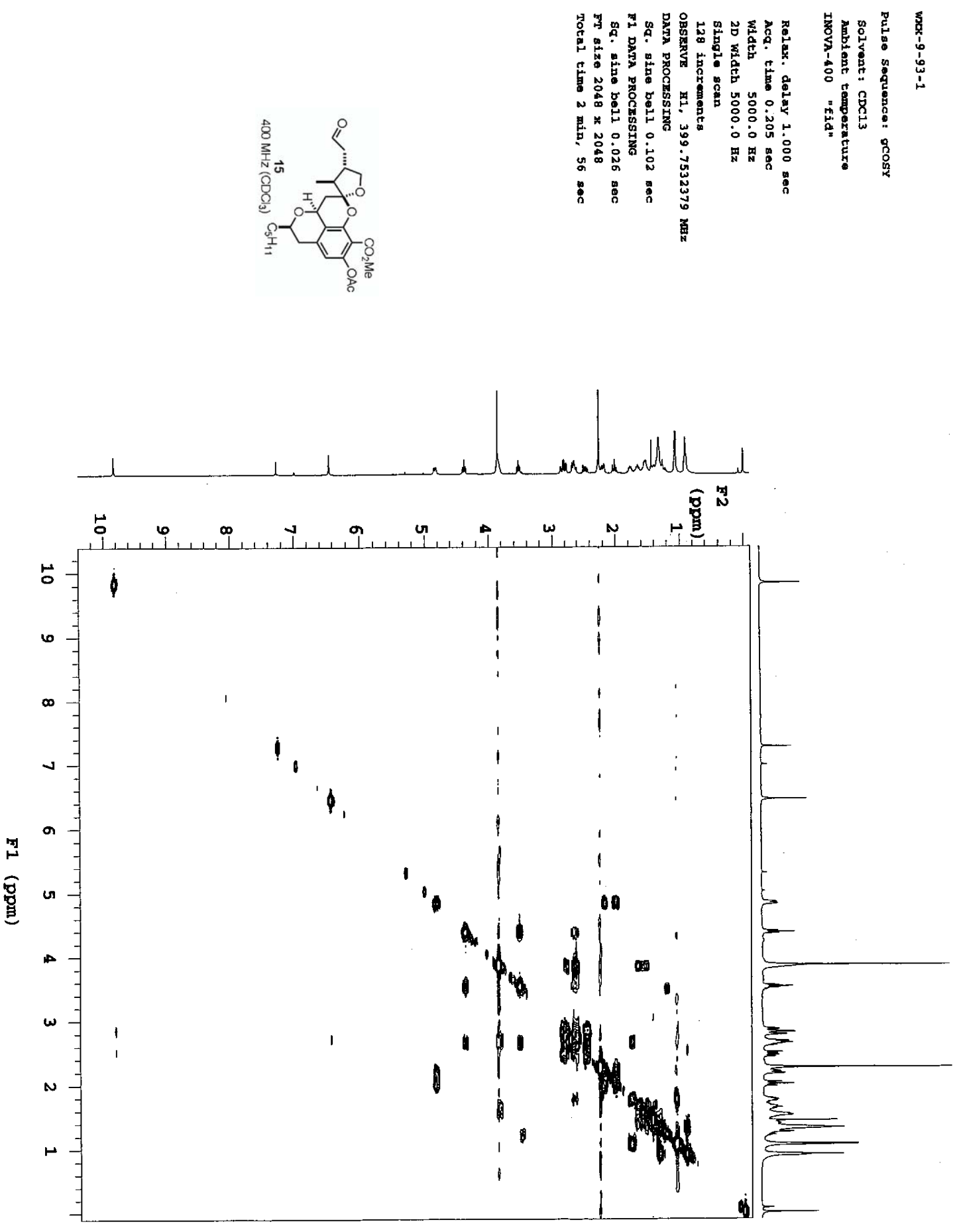
INDEX	FREQUENCY	PPM	HEIGHT
1	17024.862	169.371	27.3
2	16573.202	164.878	17.1
3	15090.047	150.123	22.1
4	14908.468	148.316	28.2
5	13786.947	137.159	43.1
6	12030.660	119.687	34.5
7	11465.322	114.062	60.0
8	11244.832	111.869	17.8
9	10962.545	109.060	54.0
10	7771.932	77.319	375.4
11	7739.889	77.000	385.7
12	7707.845	76.681	374.5
13	7557.546	75.186	56.2
14	7340.108	73.023	51.5
15	6855.642	68.203	56.2
16	6217.061	61.850	59.8
17	5220.663	51.938	56.2
18	4913.198	48.879	60.4
19	4099.142	40.780	70.0
20	3643.667	36.249	67.7
21	3575.002	35.566	61.6
22	3424.703	34.071	57.1
23	3410.970	33.934	53.8
24	3193.532	31.771	70.2
25	2522.909	25.099	69.6
26	2271.902	22.602	77.9
27	2094.900	20.841	56.7
28	1411.306	14.040	64.2
29	1172.506	11.665	55.1

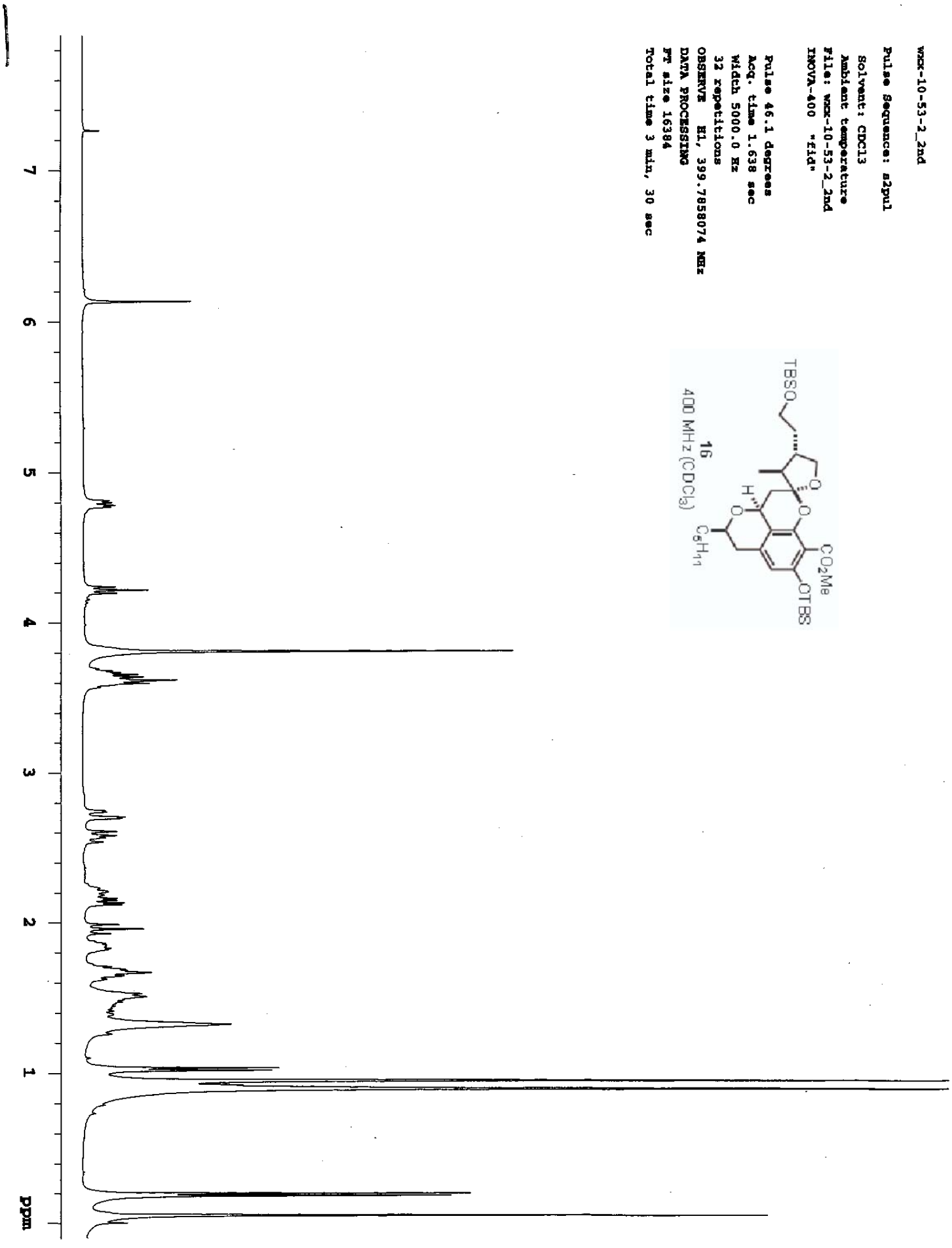
14
400 MHz ($CDCl_3$)




wzk-9-49-3
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7532379 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
HO
H
O
O
O
CO2Me
OAc
C5H11
14
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)
8
7
6
5
4
3
2
1


wzk-9-55-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-9-55-1
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
width 5000.0 Hz
37 repetitions
OBSERVE H1, 399.7532349 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
15
400 MHz (CDCl3)
C9H11
CO2Me
OAc
10
9
8
7
6
5
4
3
2
1
ppm

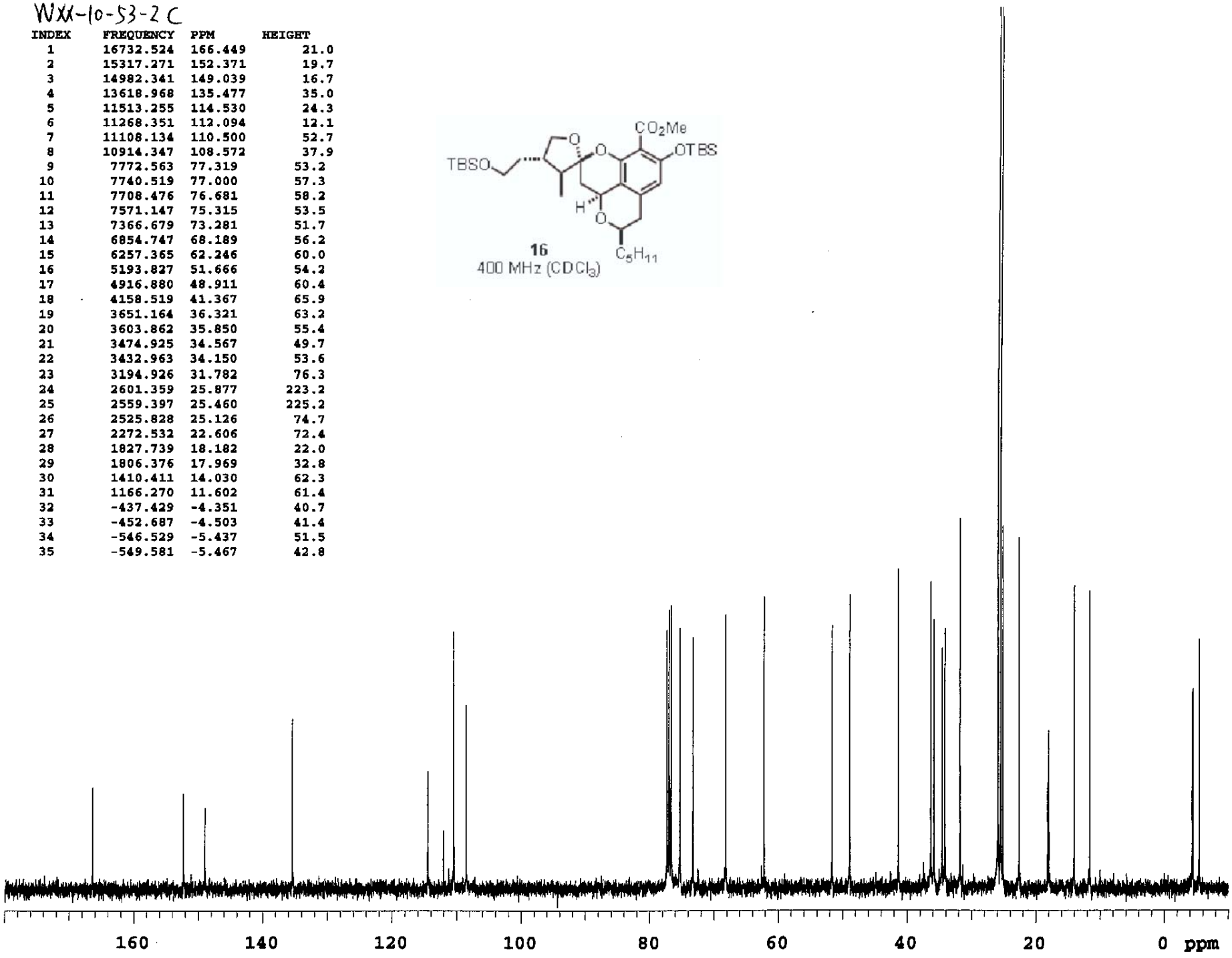

WZK-9-93-1
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7532379 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
15
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

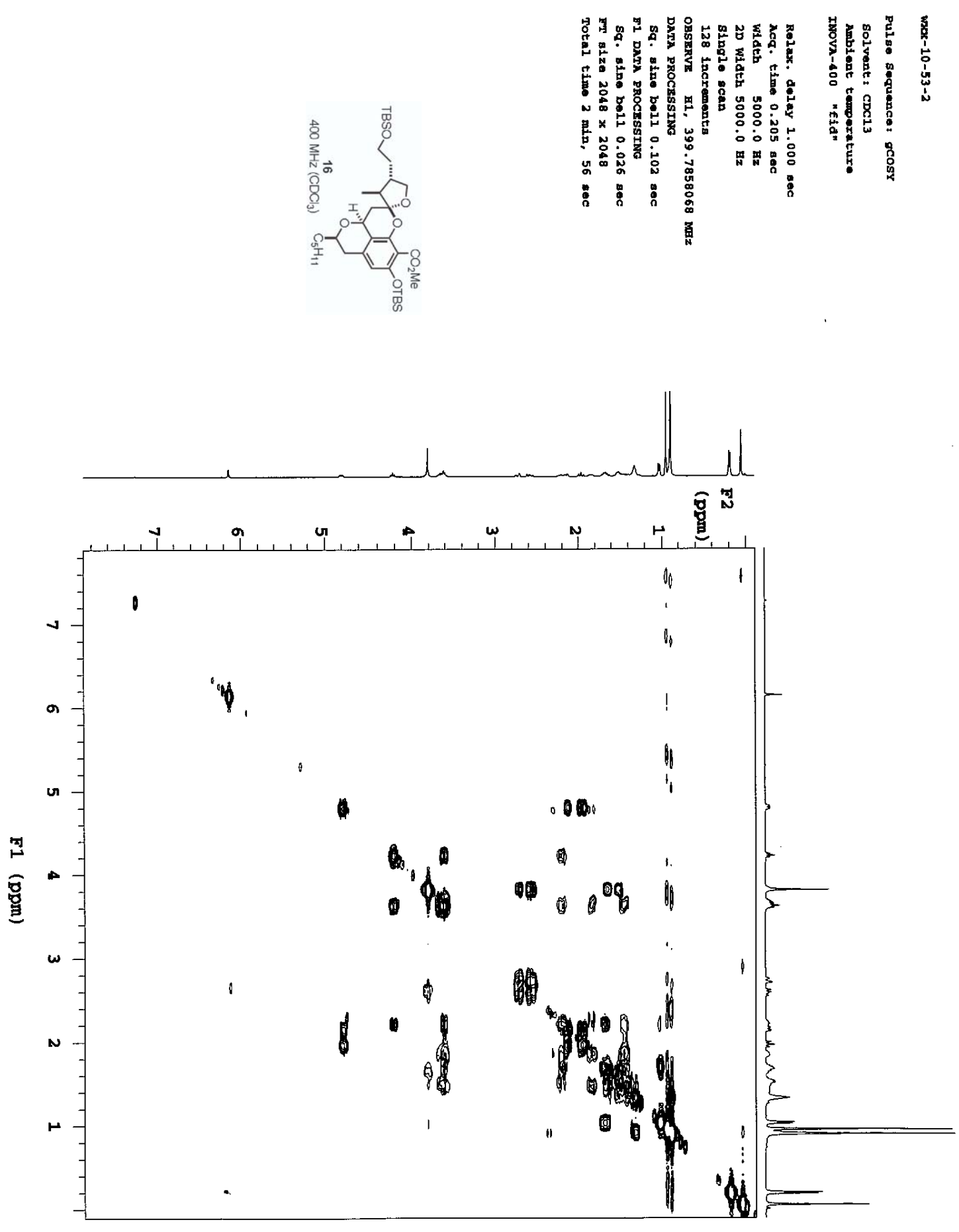

wzk-10-53-2_2nd
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-10-53-2_2nd
INOVA-400 "fid"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
32 repetitions
OBSERVE H1, 399.7858074 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 30 sec
TBSO
CO2Me
OTBS
H
O
C5H11
16
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm

WXX-10-53-2C

INDEX	FREQUENCY	PPM	HEIGHT
1	16732.524	166.449	21.0
2	15317.271	152.371	19.7
3	14982.341	149.039	16.7
4	13618.968	135.477	35.0
5	11513.255	114.530	24.3
6	11268.351	112.094	12.1
7	11108.134	110.500	52.7
8	10914.347	108.572	37.9
9	7772.563	77.319	53.2
10	7740.519	77.000	57.3
11	7708.476	76.681	58.2
12	7571.147	75.315	53.5
13	7366.679	73.281	51.7
14	6854.747	68.189	56.2
15	6257.365	62.246	60.0
16	5193.827	51.666	54.2
17	4916.880	48.911	60.4
18	4158.519	41.367	65.9
19	3651.164	36.321	63.2
20	3603.862	35.850	55.4
21	3474.925	34.567	49.7
22	3432.963	34.150	53.6
23	3194.926	31.782	76.3
24	2601.359	25.877	223.2
25	2559.397	25.460	225.2
26	2525.828	25.126	74.7
27	2272.532	22.606	72.4
28	1827.739	18.182	22.0
29	1806.376	17.969	32.8
30	1410.411	14.030	62.3
31	1166.270	11.602	61.4
32	-437.429	-4.351	40.7
33	-452.687	-4.503	41.4
34	-546.529	-5.437	51.5
35	-549.581	-5.467	42.8

16
400 MHz ($CDCl_3$)




WZK-10-53-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858068 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
TBSO
CO2Me
OTBS
C5H11
16
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

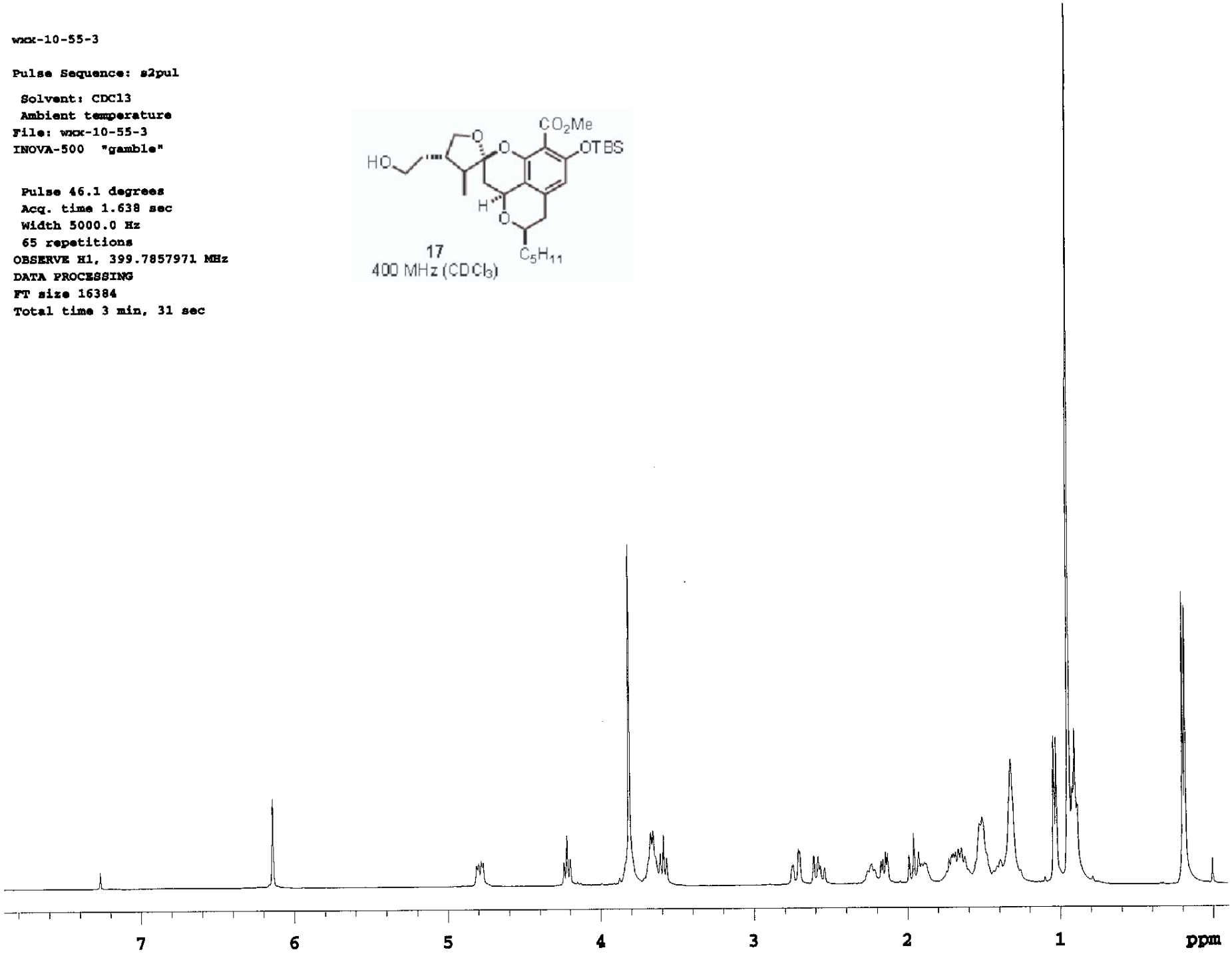
wox-10-55-3

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wox-10-55-3
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
65 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

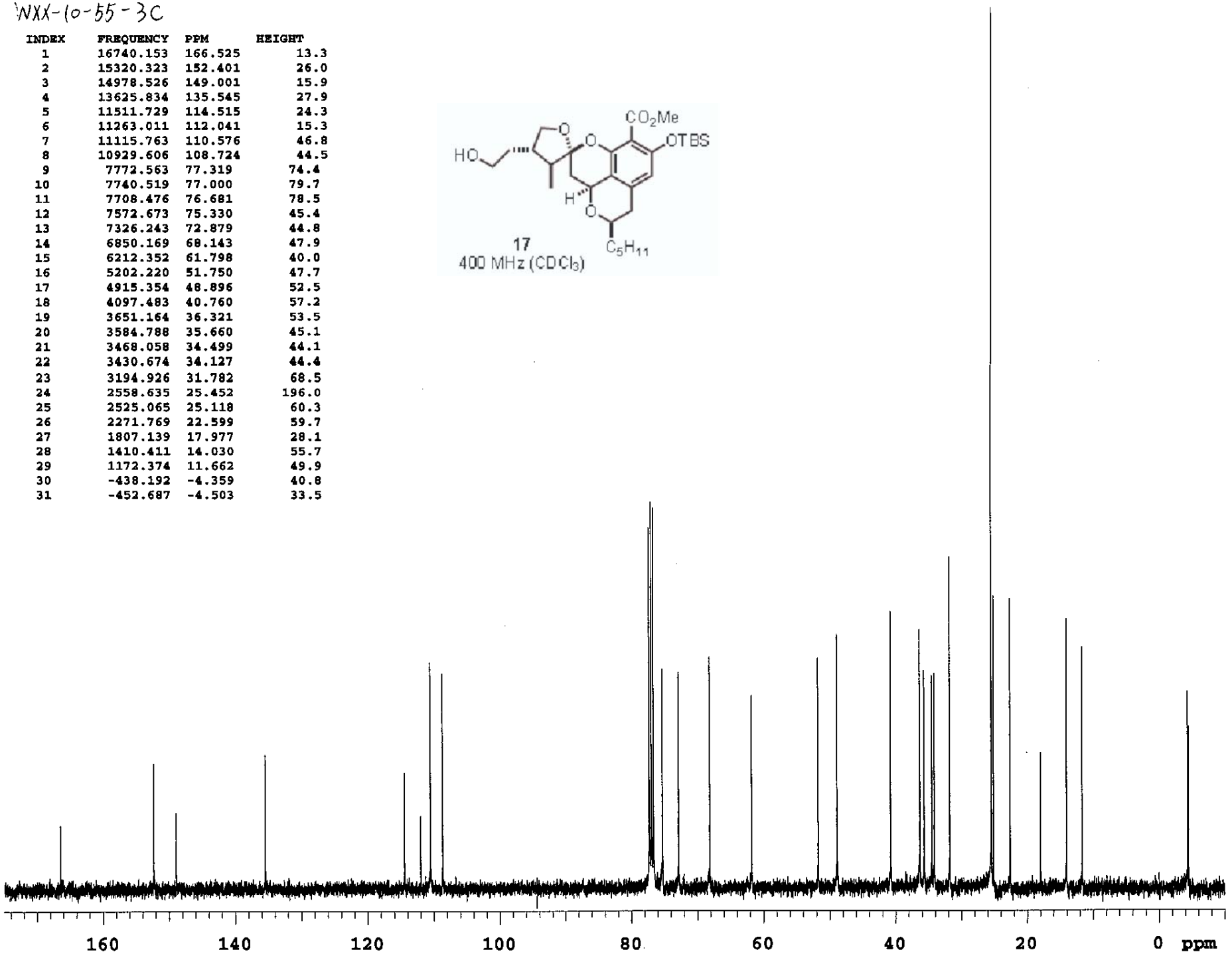
17
400 MHz ($CDCl_3$)

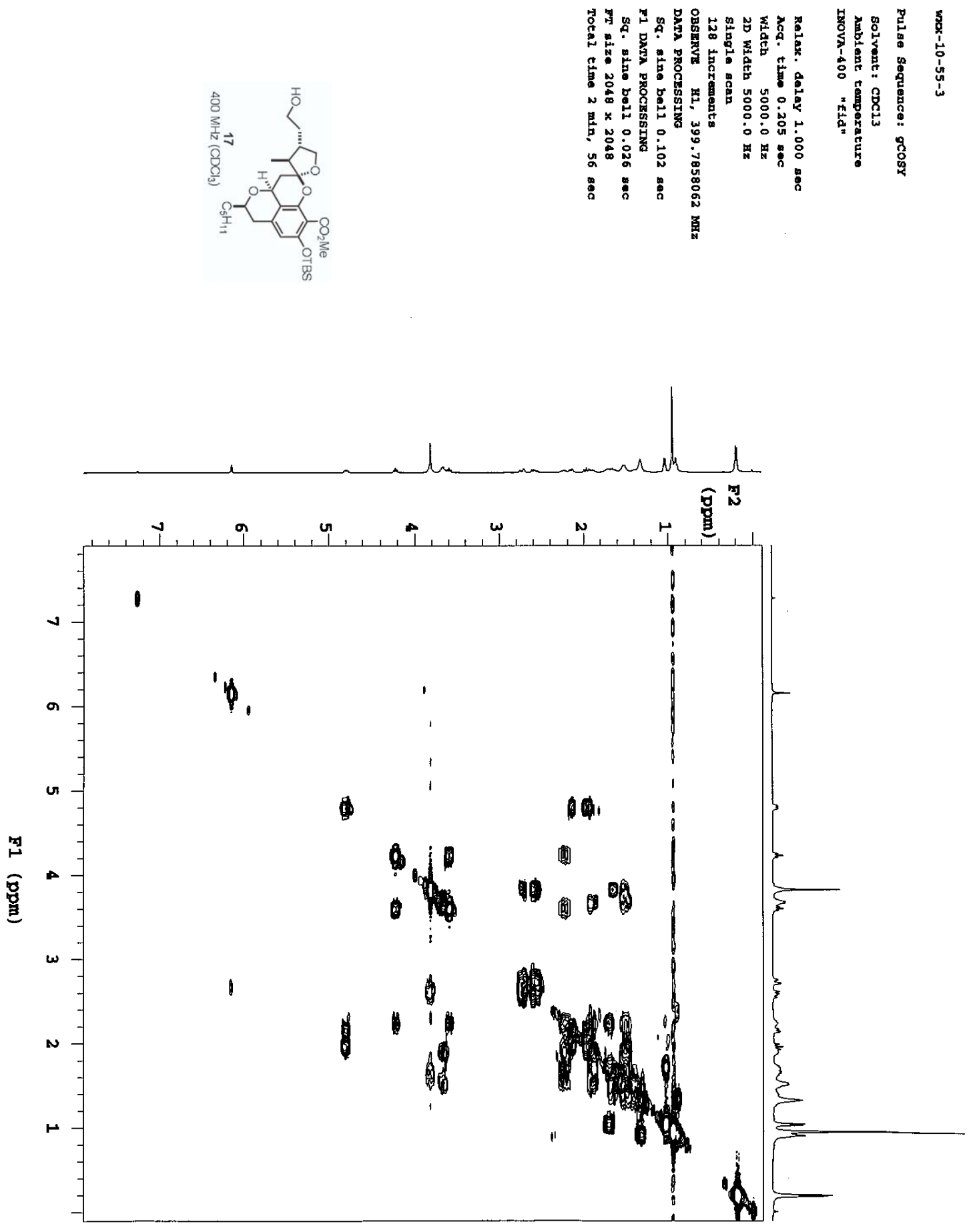


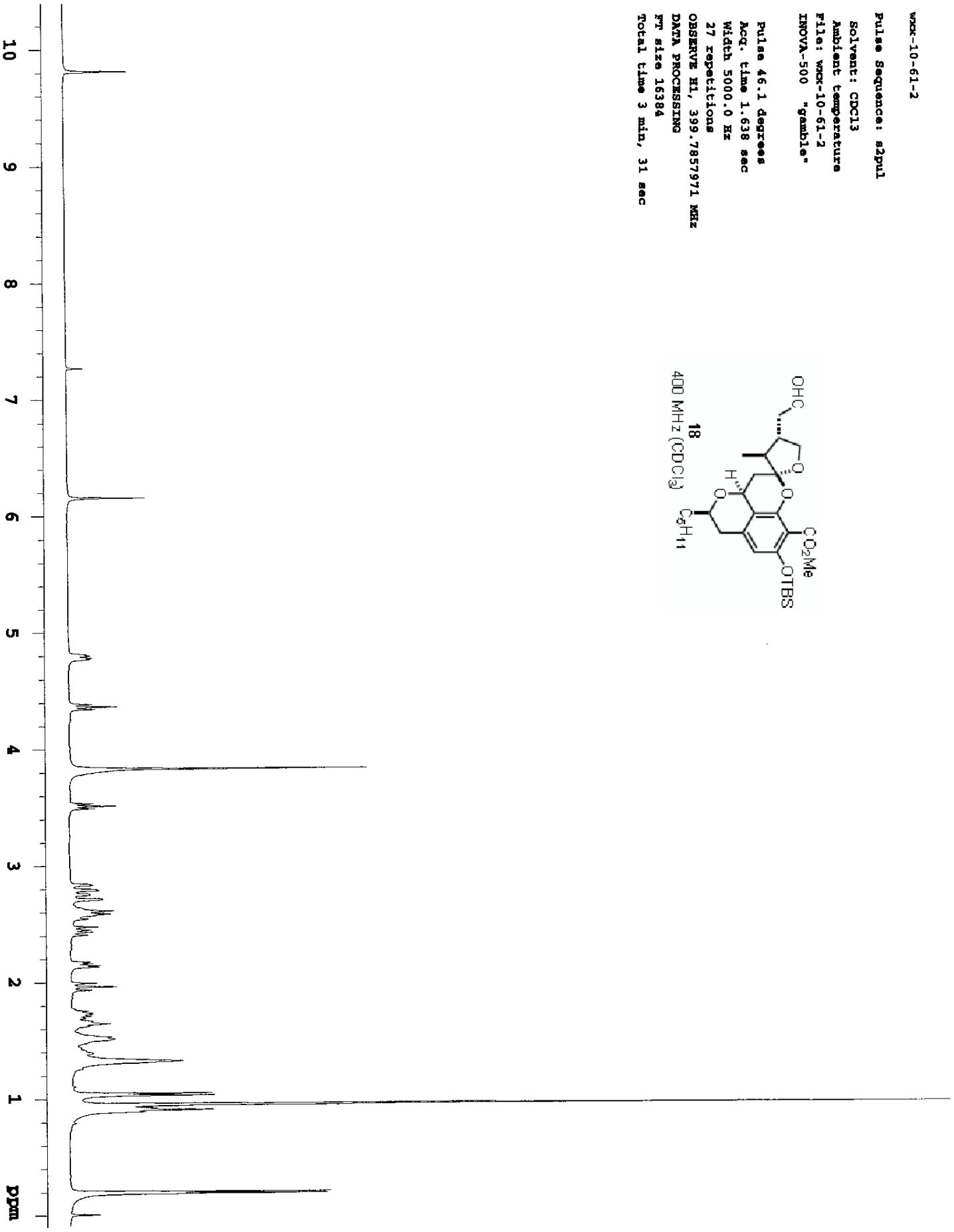
WXX-10-55-3C

INDEX	FREQUENCY	PPM	HEIGHT
1	16740.153	166.525	13.3
2	15320.323	152.401	26.0
3	14978.526	149.001	15.9
4	13625.834	135.545	27.9
5	11511.729	114.515	24.3
6	11263.011	112.041	15.3
7	11115.763	110.576	46.8
8	10929.606	108.724	44.5
9	7772.563	77.319	74.4
10	7740.519	77.000	79.7
11	7708.476	76.681	78.5
12	7572.673	75.330	45.4
13	7326.243	72.879	44.8
14	6850.169	68.143	47.9
15	6212.352	61.798	40.0
16	5202.220	51.750	47.7
17	4915.354	48.896	52.5
18	4097.483	40.760	57.2
19	3651.164	36.321	53.5
20	3584.788	35.660	45.1
21	3468.058	34.499	44.1
22	3430.674	34.127	44.4
23	3194.926	31.782	68.5
24	2558.635	25.452	196.0
25	2525.065	25.118	60.3
26	2271.769	22.599	59.7
27	1807.139	17.977	28.1
28	1410.411	14.030	55.7
29	1172.374	11.662	49.9
30	-438.192	-4.359	40.8
31	-452.687	-4.503	33.5

17
400 MHz ($CDCl_3$)



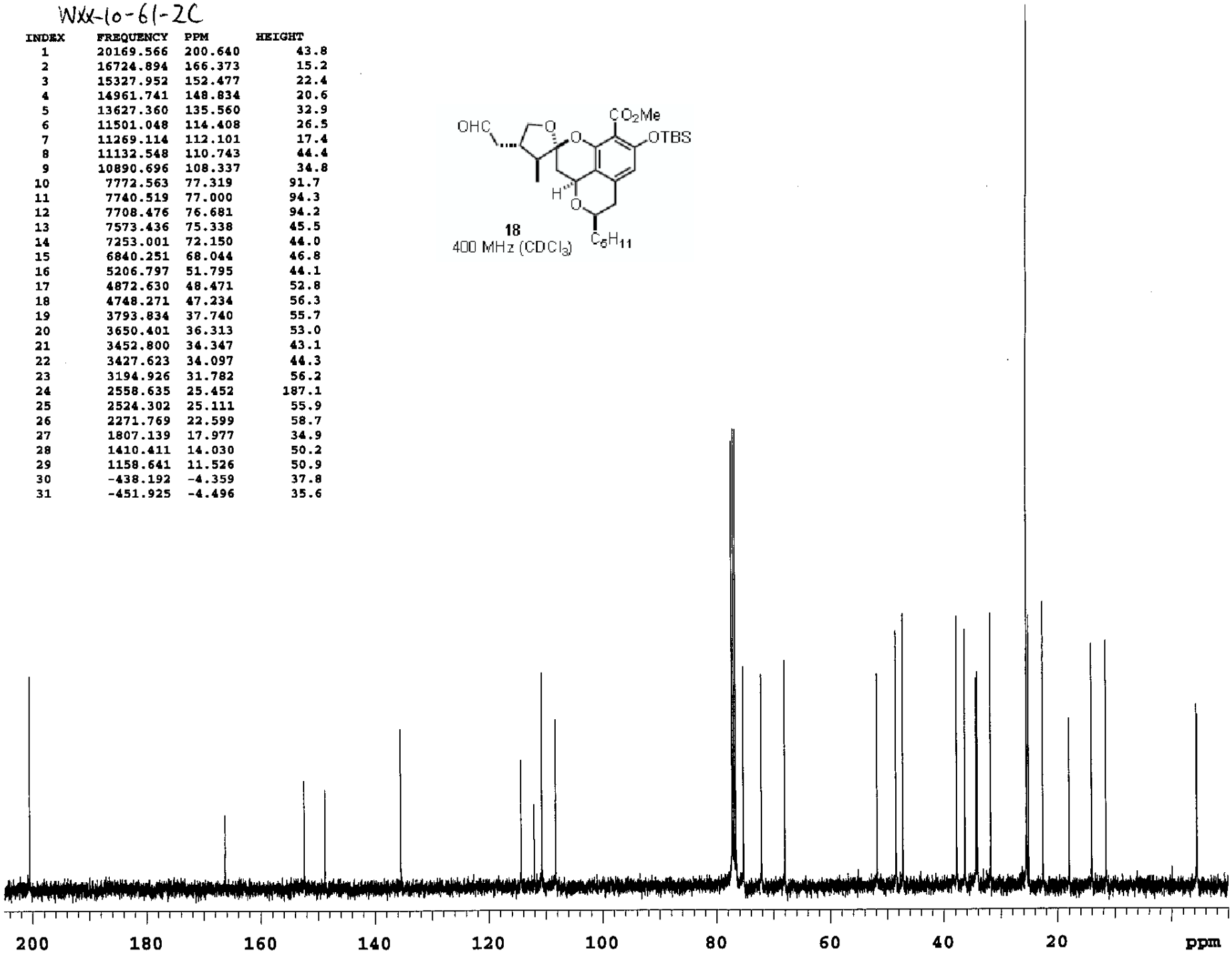

wzk-10-55-3
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858062 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
17
400 MHz (CDCl3)
HO
H
O
O
O
CO2Me
OTBS
C5H11
F2 (ppm)
F1 (ppm)
1
2
3
4
5
6
7

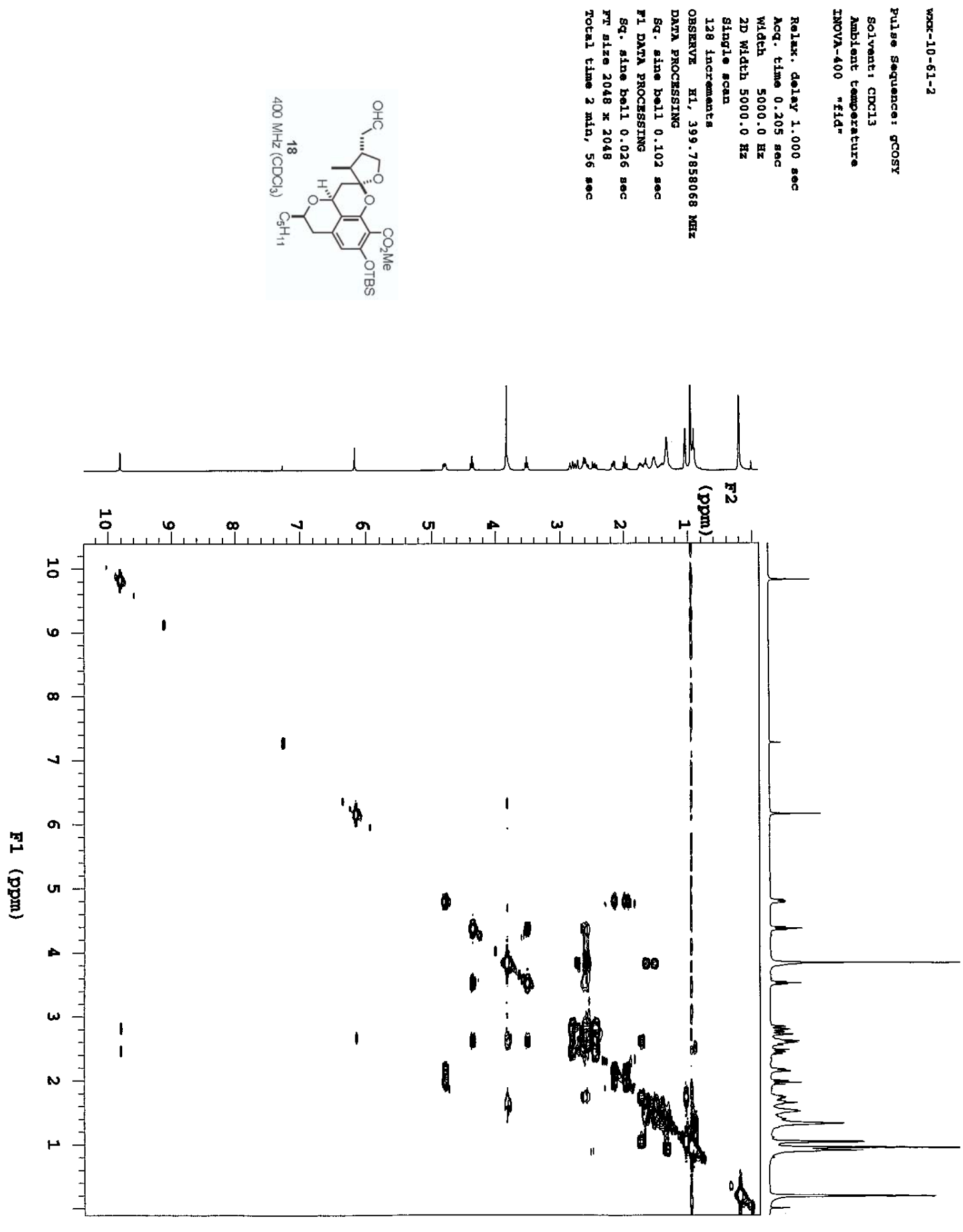

wzk-10-61-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-10-61-2
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
27 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
OHC
O
H
O
O
O
CO2Me
OTBS
C5H11
18
400 MHz (CDCl3)
10
9
8
7
6
5
4
3
2
1
ppm

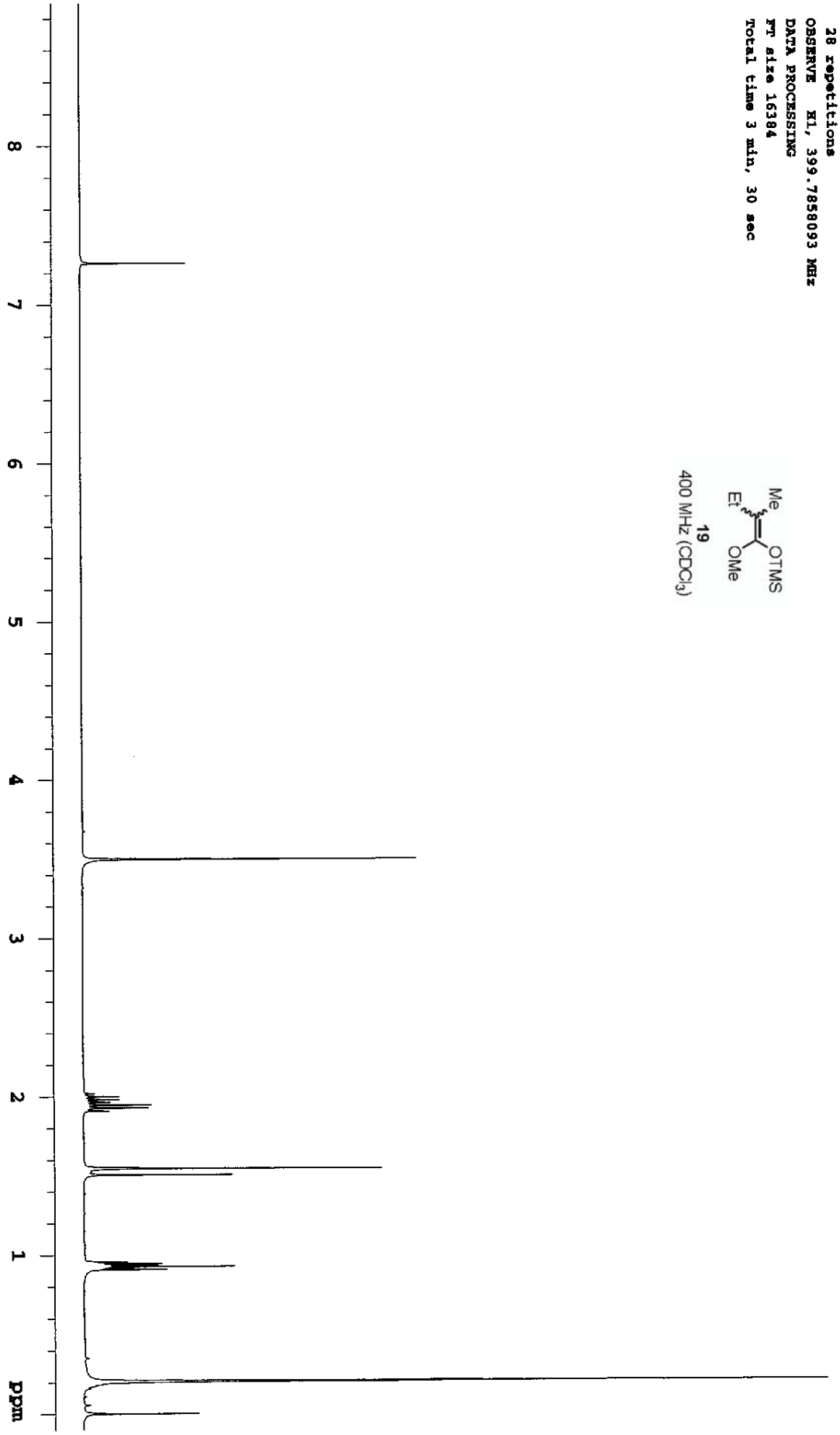
WXX-10-61-2C

INDEX	FREQUENCY	PPM	HEIGHT
1	20169.566	200.640	43.8
2	16724.894	166.373	15.2
3	15327.952	152.477	22.4
4	14961.741	148.834	20.6
5	13627.360	135.560	32.9
6	11501.048	114.408	26.5
7	11269.114	112.101	17.4
8	11132.548	110.743	44.4
9	10890.696	108.337	34.8
10	7772.563	77.319	91.7
11	7740.519	77.000	94.3
12	7708.476	76.681	94.2
13	7573.436	75.338	45.5
14	7253.001	72.150	44.0
15	6840.251	68.044	46.8
16	5206.797	51.795	44.1
17	4872.630	48.471	52.8
18	4748.271	47.234	56.3
19	3793.834	37.740	55.7
20	3650.401	36.313	53.0
21	3452.800	34.347	43.1
22	3427.623	34.097	44.3
23	3194.926	31.782	56.2
24	2558.635	25.452	187.1
25	2524.302	25.111	55.9
26	2271.769	22.599	58.7
27	1807.139	17.977	34.9
28	1410.411	14.030	50.2
29	1158.641	11.526	50.9
30	-438.192	-4.359	37.8
31	-451.925	-4.496	35.6

18
400 MHz ($CDCl_3$)

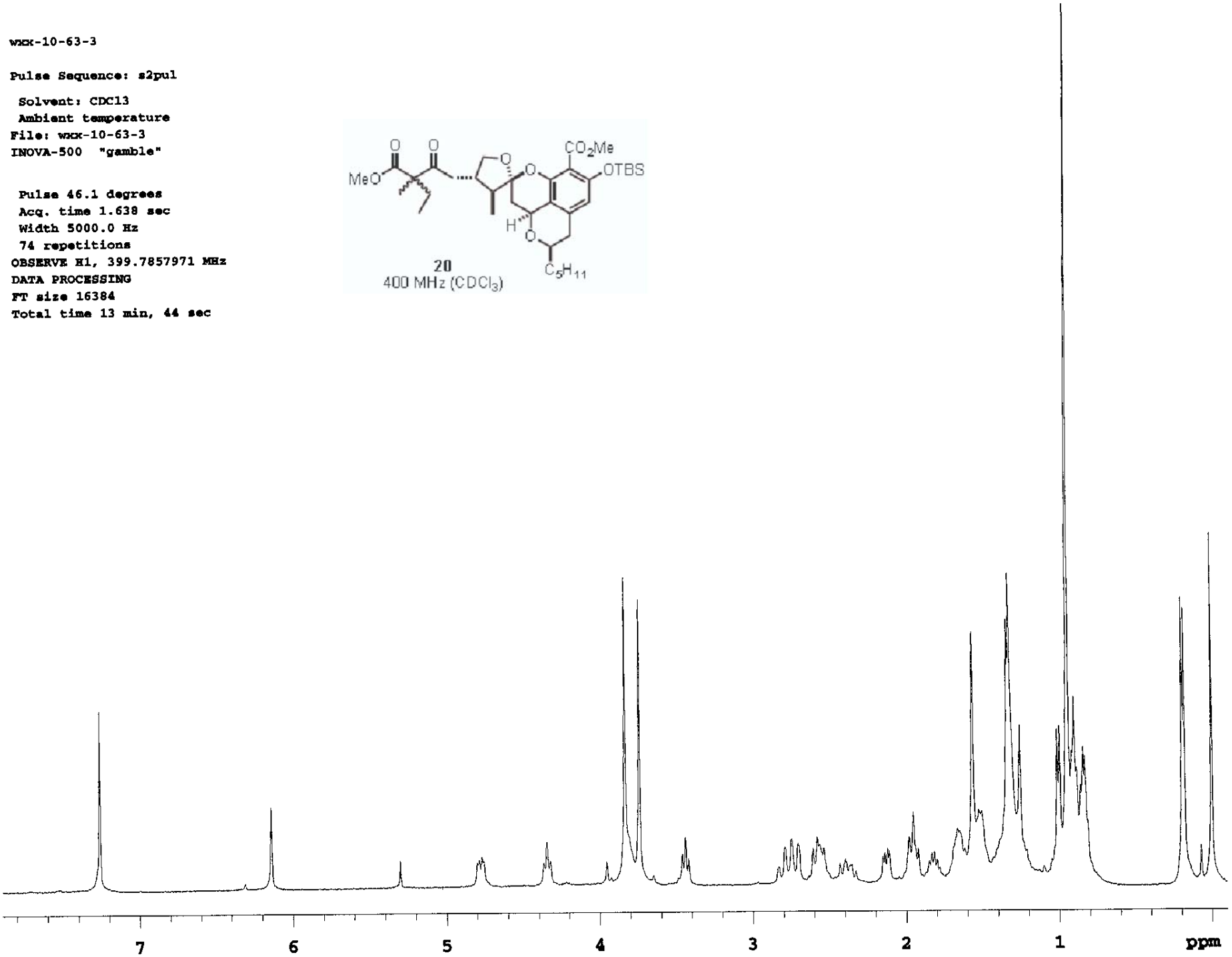


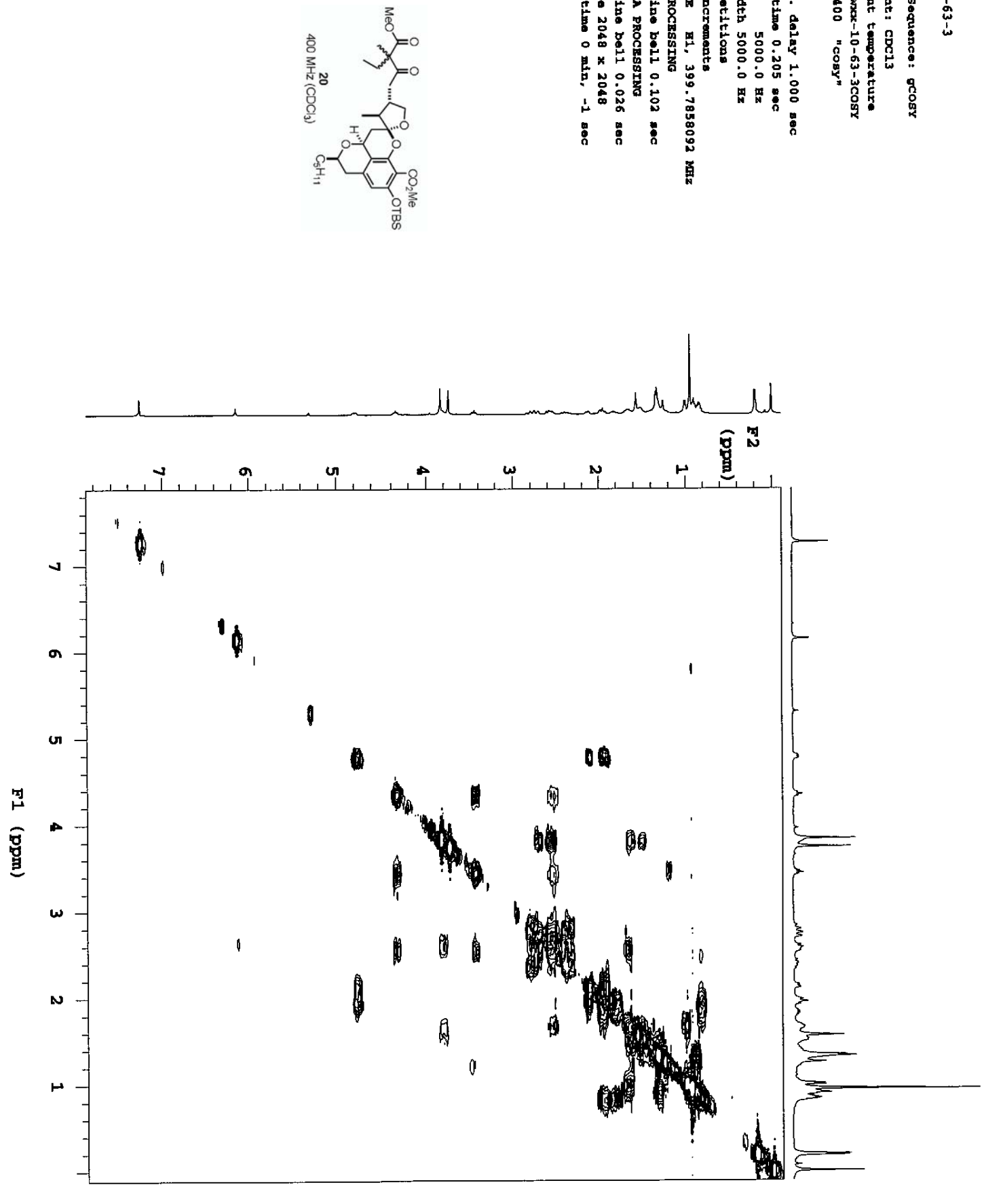

wsk-10-61-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858068 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
OHC
H
O
O
O
CO2Me
OTBS
C5H11
18
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)


WSK-10-149-3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: WSK-10-149-3
INOVA-400 "cosy"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
28 repetitions
OBSERVE H1, 399.7858093 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 30 sec
Me
Et
OTMS
OMe
19
400 MHz (CDCl3)
8
7
6
5
4
3
2
1
ppm

```
wxx-10-63-3

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
File: wxx-10-63-3
INOVA-500  "gamble"

 Pulse 46.1 degrees
 Acq. time 1.638 sec
 Width 5000.0 Hz
 74 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 13 min, 44 sec
```


20
400 MHz ($CDCl_3$)



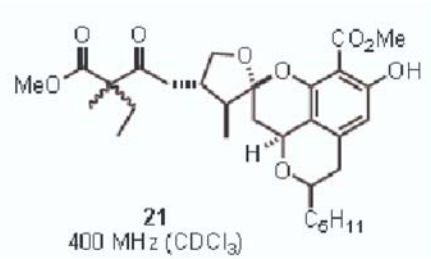

wzx-10-63-3
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: wzx-10-63-3COSY
INOVA-400 "cosy"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
6 repetitions
256 increments
OBSERVE H1, 399.7858092 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 0 min, -1 sec
MeO
CO2Me
OTBS
C5H11
20
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-10-71-2

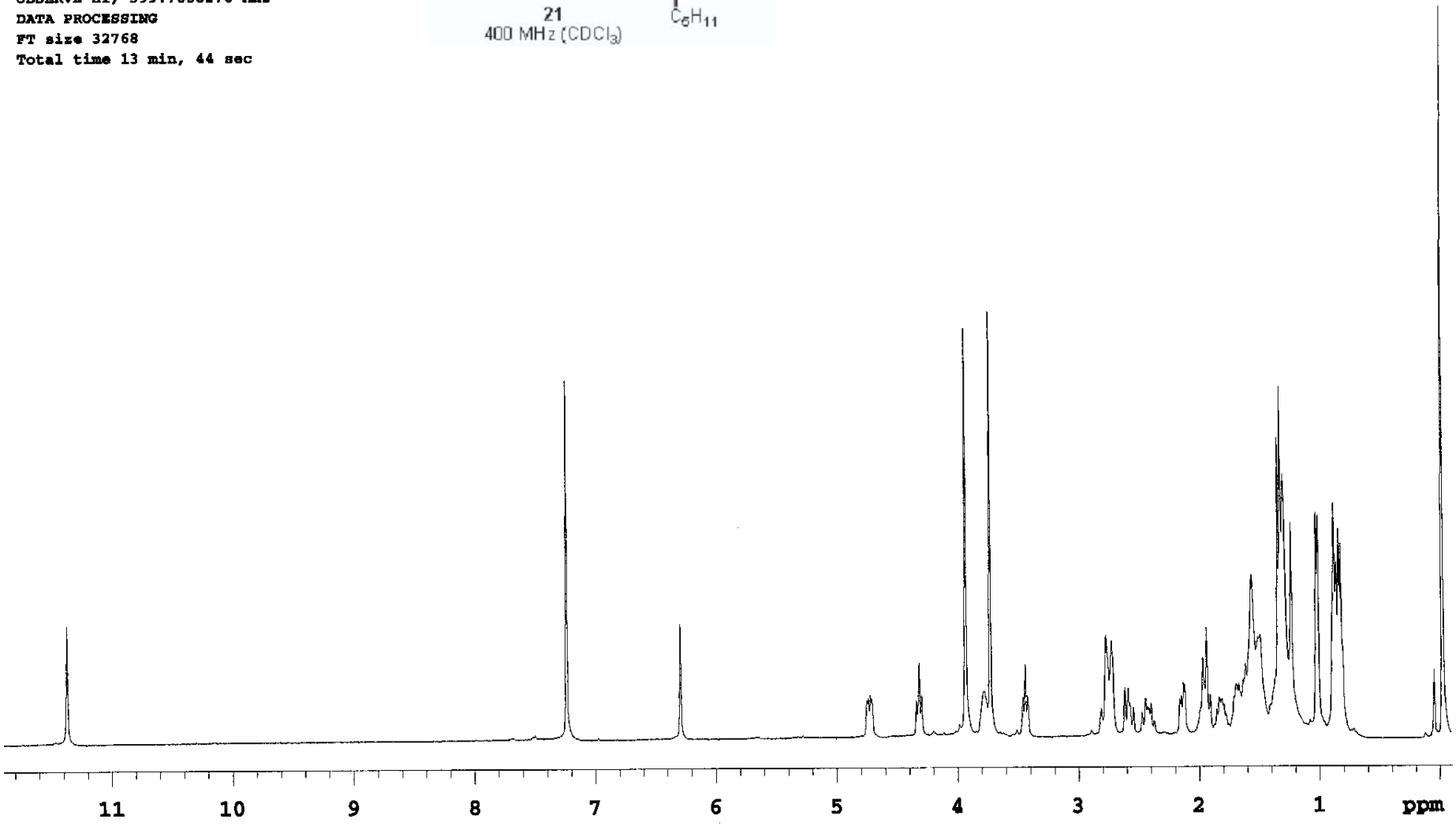
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-10-71-2
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 8000.0 Hz
371 repetitions
OBSERVE H1, 399.7858276 MHz
DATA PROCESSING
FT size 32768
Total time 13 min, 44 sec



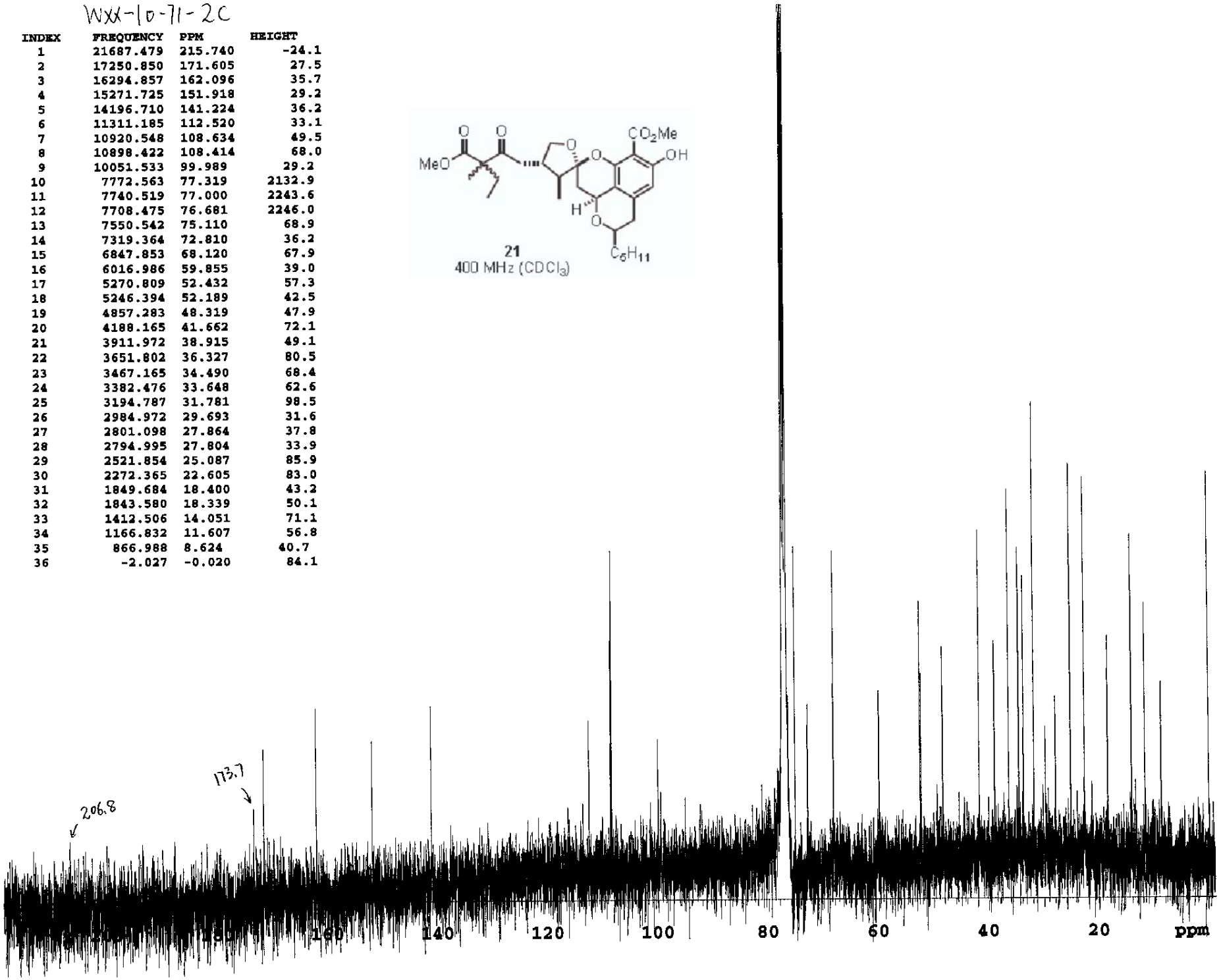
21
400 MHz ($CDCl_3$)

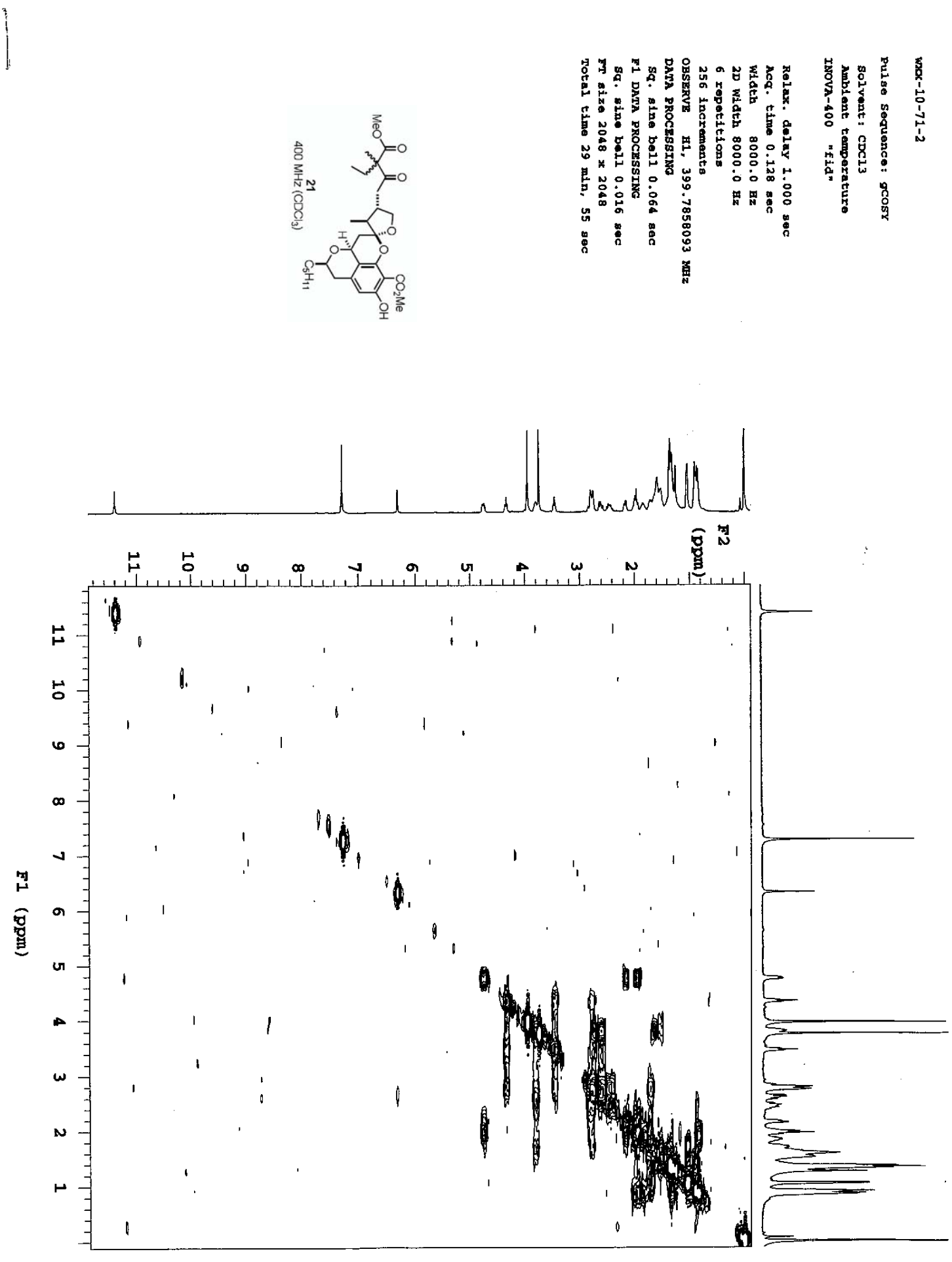


WXX-10-71-2C

INDEX	FREQUENCY	PPM	HEIGHT
1	21687.479	215.740	-24.1
2	17250.850	171.605	27.5
3	16294.857	162.096	35.7
4	15271.725	151.918	29.2
5	14196.710	141.224	36.2
6	11311.185	112.520	33.1
7	10920.548	108.634	49.5
8	10898.422	108.414	68.0
9	10051.533	99.989	29.2
10	7772.563	77.319	2132.9
11	7740.519	77.000	2243.6
12	7708.475	76.681	2246.0
13	7550.542	75.110	68.9
14	7319.364	72.810	36.2
15	6847.853	68.120	67.9
16	6016.986	59.855	39.0
17	5270.809	52.432	57.3
18	5246.394	52.189	42.5
19	4857.283	48.319	47.9
20	4188.165	41.662	72.1
21	3911.972	38.915	49.1
22	3651.802	36.327	80.5
23	3467.165	34.490	68.4
24	3382.476	33.648	62.6
25	3194.787	31.781	98.5
26	2984.972	29.693	31.6
27	2801.098	27.864	37.8
28	2794.995	27.804	33.9
29	2521.854	25.087	85.9
30	2272.365	22.605	83.0
31	1849.684	18.400	43.2
32	1843.580	18.339	50.1
33	1412.506	14.051	71.1
34	1166.832	11.607	56.8
35	866.988	8.624	40.7
36	-2.027	-0.020	84.1

21
400 MHz ($CDCl_3$)




WZK-10-71-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
6 repetitions
256 increments
OBSERVE H1, 399.7858093 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 29 min, 55 sec
MeO
CO2Me
OH
C5H11
21
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

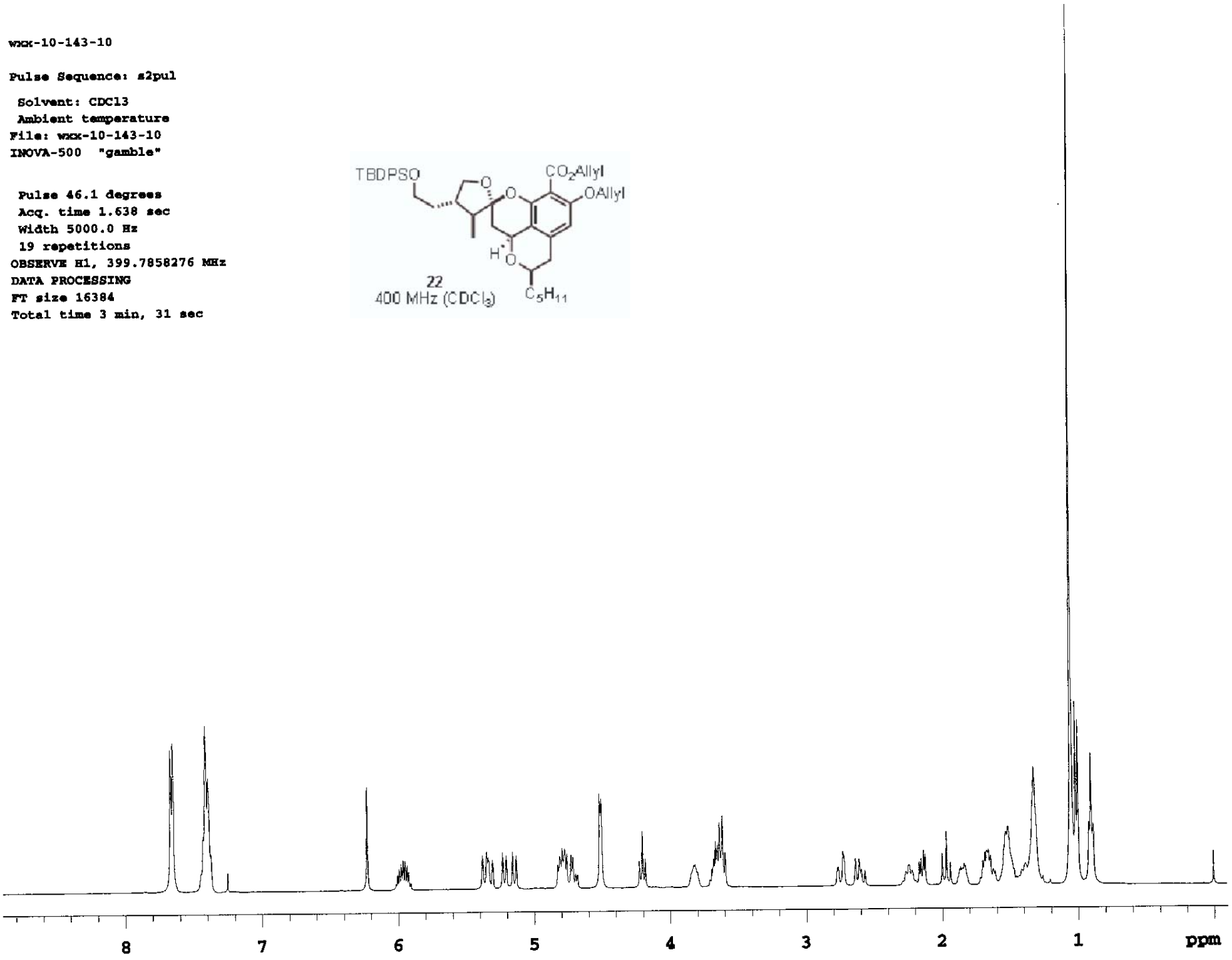
wxx-10-143-10

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-10-143-10
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
19 repetitions
OBSERVE H1, 399.7858276 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

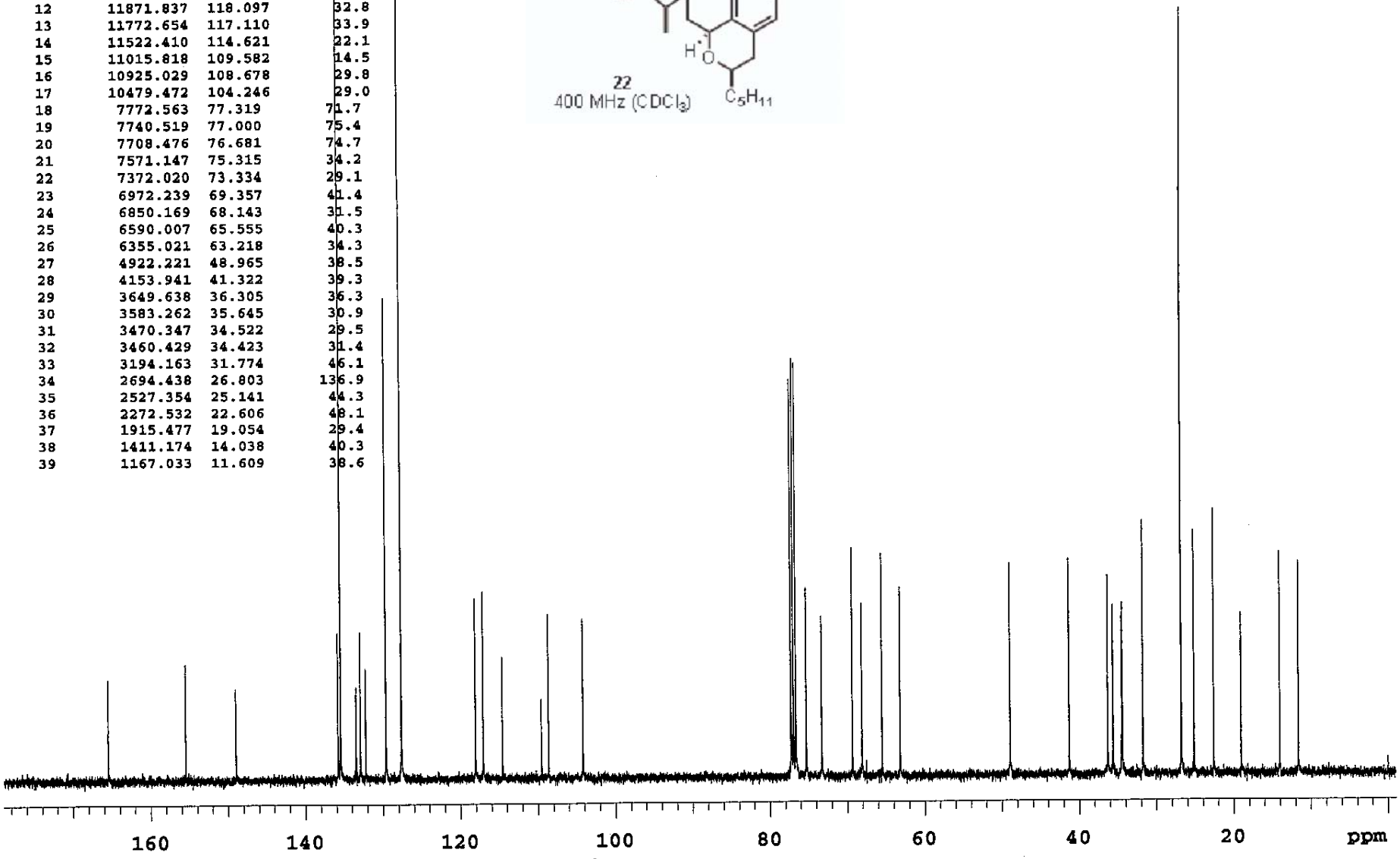
22
400 MHz ($CDCl_3$)

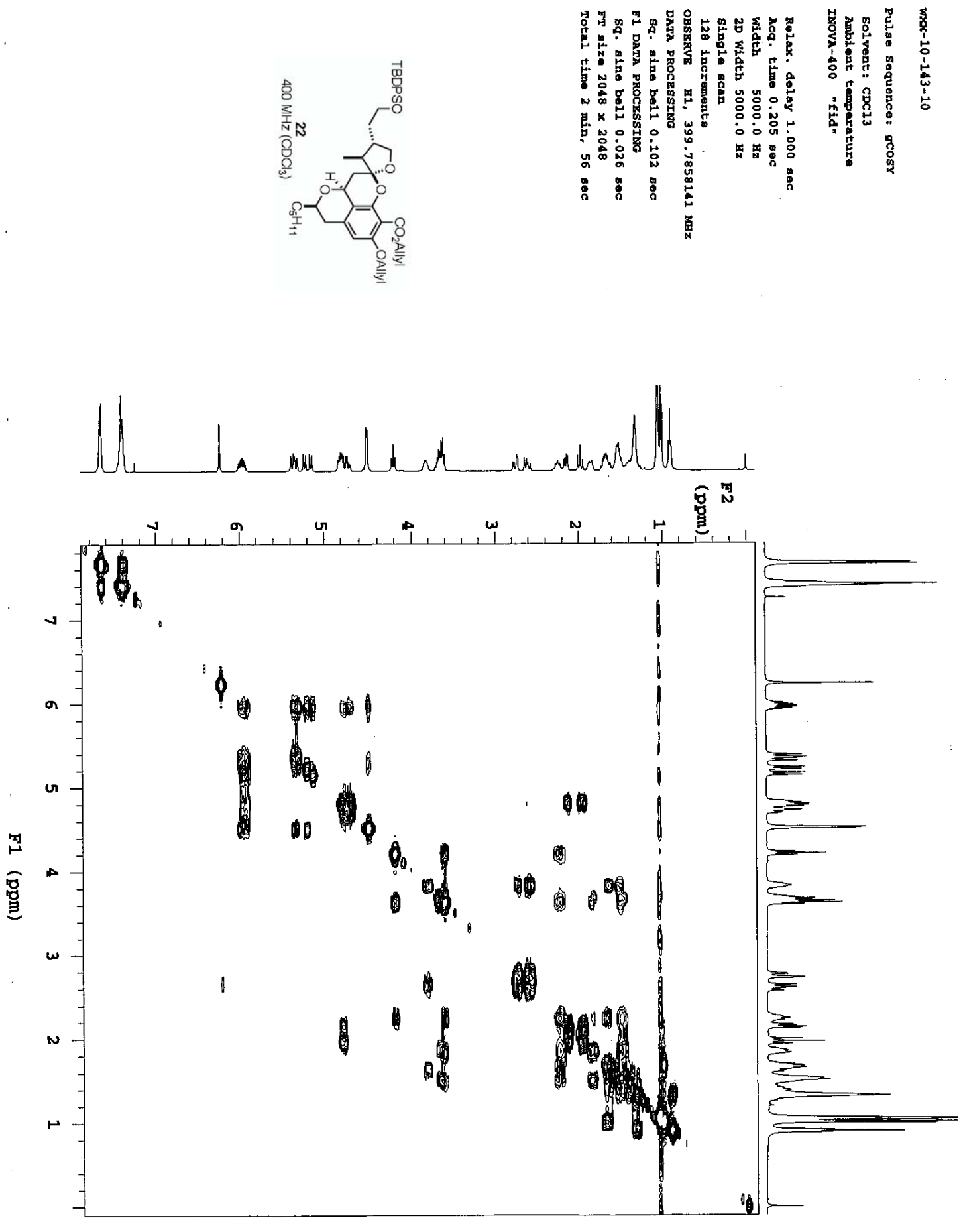


WXY-10-143-10C

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	16640.971	165.539	18.2				
2	15636.180	155.543	21.1				
3	14983.104	149.047	16.6				
4	13656.352	135.849	26.6				
5	13622.020	135.507	172.8				
6	13425.181	133.549	15.4				
7	13422.130	133.519	16.9				
8	13364.909	132.949	26.7				
9	13297.007	132.274	20.2				
10	13033.793	129.656	86.7				
11	12834.666	127.675	170.0				
12	11871.837	118.097	32.8				
13	11772.654	117.110	33.9				
14	11522.410	114.621	22.1				
15	11015.818	109.582	14.5				
16	10925.029	108.678	29.8				
17	10479.472	104.246	29.0				
18	7772.563	77.319	71.7				
19	7740.519	77.000	75.4				
20	7708.476	76.681	74.7				
21	7571.147	75.315	34.2				
22	7372.020	73.334	29.1				
23	6972.239	69.357	41.4				
24	6850.169	68.143	31.5				
25	6590.007	65.555	40.3				
26	6355.021	63.218	34.3				
27	4922.221	48.965	38.5				
28	4153.941	41.322	39.3				
29	3649.638	36.305	36.3				
30	3583.262	35.645	30.9				
31	3470.347	34.522	29.5				
32	3460.429	34.423	31.4				
33	3194.163	31.774	46.1				
34	2694.438	26.803	136.9				
35	2527.354	25.141	44.3				
36	2272.532	22.606	48.1				
37	1915.477	19.054	29.4				
38	1411.174	14.038	40.3				
39	1167.033	11.609	38.6				

22
400 MHz ($CDCl_3$)



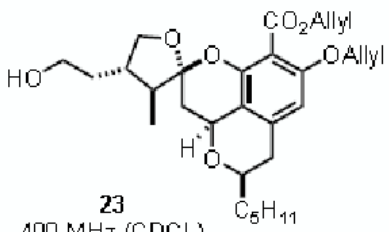

wkk-10-143-10
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858141 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
TBDPSO
CO2Allyl
OAllyl
C5H11
22
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-10-147-2

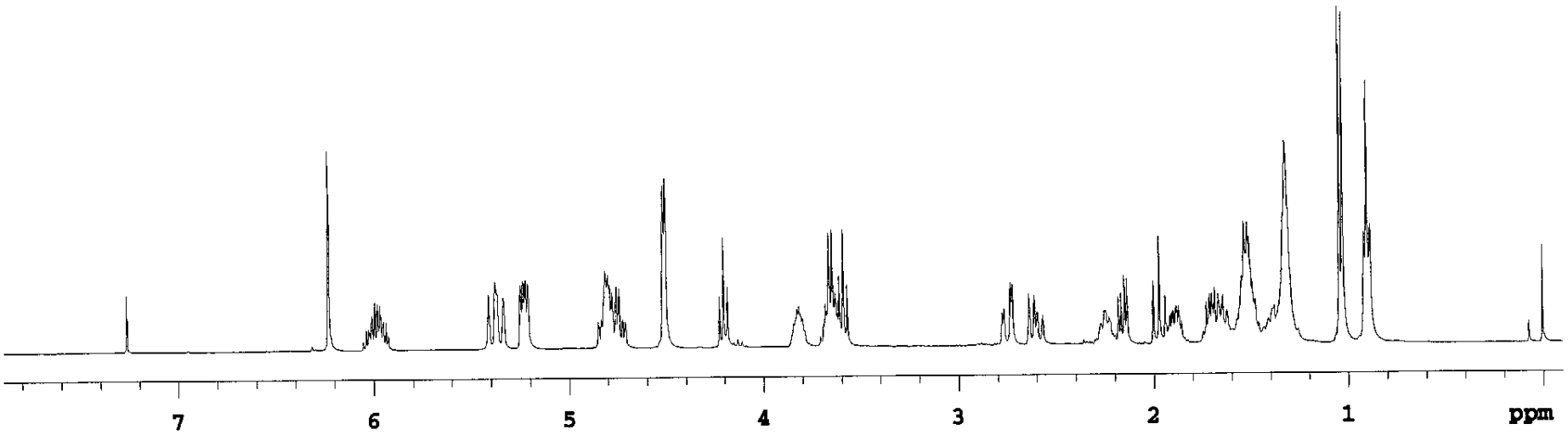
Pulse Sequence: s2pul

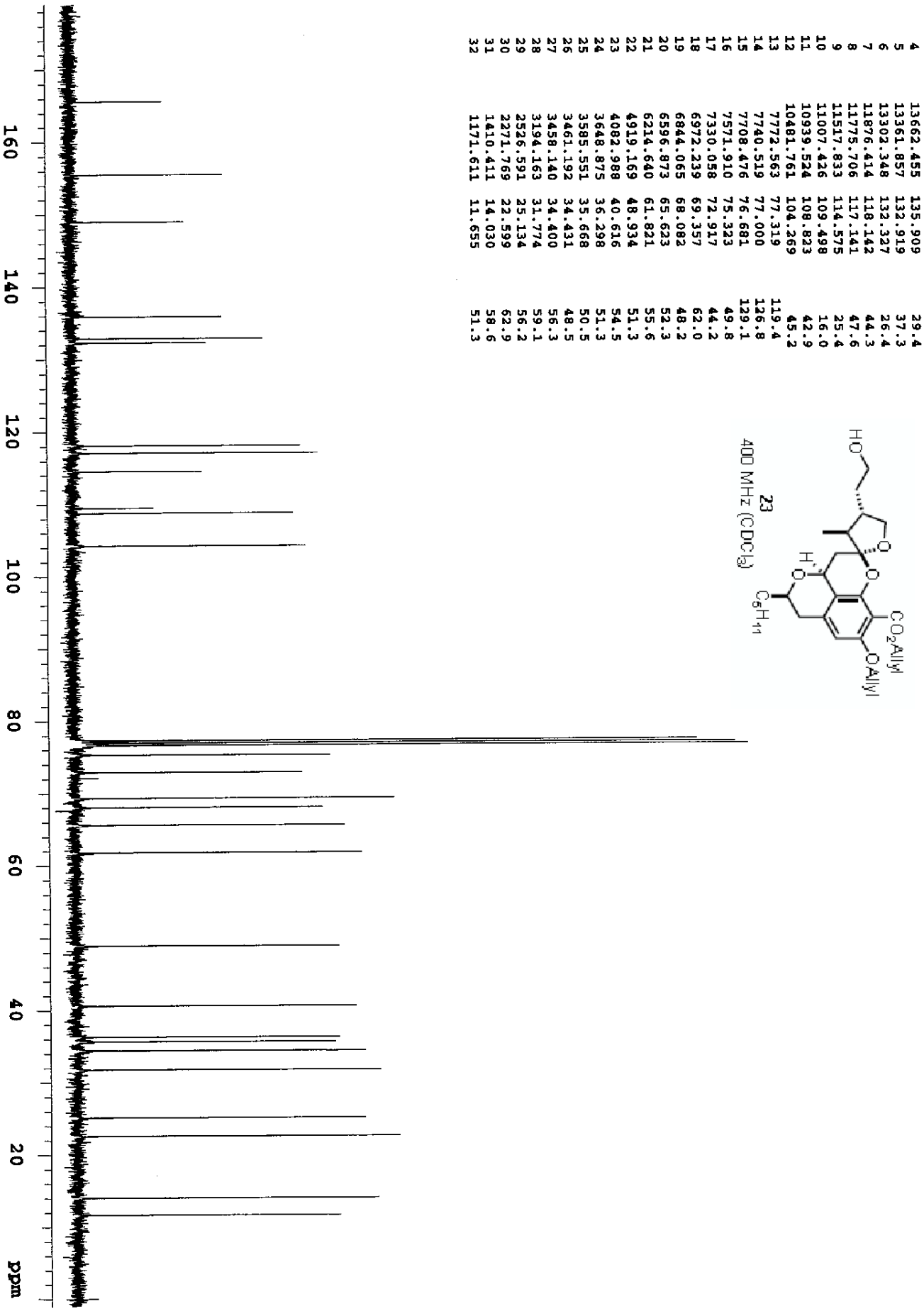
Solvent: CDCl3
Ambient temperature
File: wxx-10-147-2
INOVA-500 "gamble"

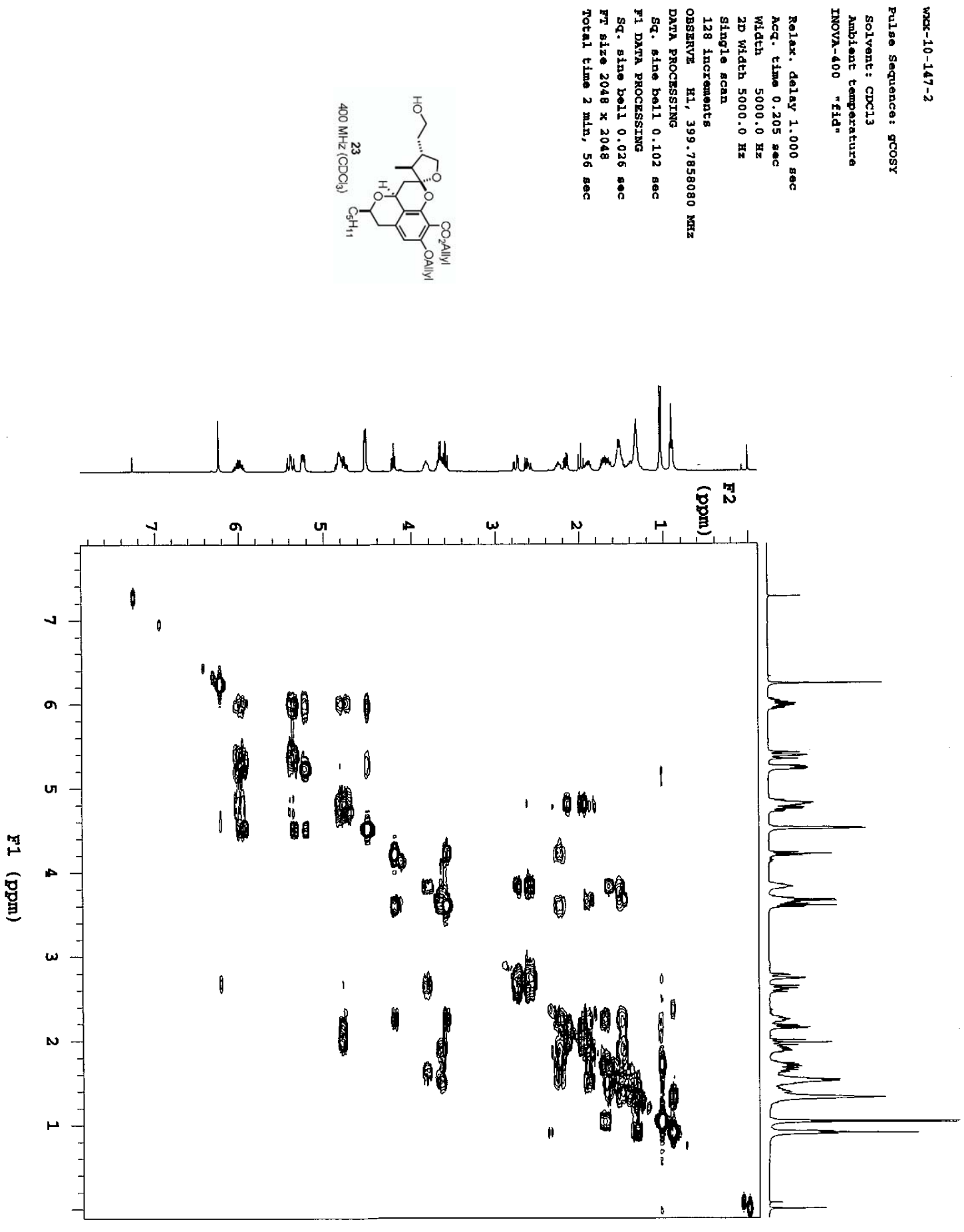
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
47 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec



23
400 MHz ($CDCl_3$)




WX-10-147-2C
INDEX FREQUENCY PPM HEIGHT
1 16650.889 165.637 18.0
2 15636.180 155.543 29.7
3 14980.052 149.016 22.2
4 13662.455 135.909 29.4
5 13361.857 132.919 37.3
6 13302.348 132.327 26.4
7 11876.414 118.142 44.3
8 11775.706 117.141 47.6
9 11517.833 114.575 25.4
10 11007.426 109.498 16.0
11 10939.524 108.823 42.9
12 10481.761 104.269 45.2
13 7772.563 77.319 119.4
14 7740.519 77.000 126.8
15 7708.476 76.681 129.1
16 7571.910 75.323 49.8
17 7330.058 72.917 44.2
18 6972.239 69.357 62.0
19 6844.065 68.082 48.2
20 6596.873 65.623 52.3
21 6214.640 61.821 55.6
22 4919.169 48.934 51.3
23 4082.988 40.616 54.5
24 3648.875 36.298 51.3
25 3585.551 35.668 50.5
26 3461.192 34.431 48.5
27 3458.140 34.400 56.3
28 3194.163 31.774 59.1
29 2526.591 25.134 56.2
30 2271.769 22.599 62.9
31 1410.411 14.030 58.6
32 1171.611 11.655 51.3
23
400 MHz (CDCl3)
HO
O
O
H
O
C6H11
CO2Allyl
OAllyl
160
140
120
100
80
60
40
20
ppm


WSK-10-147-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858080 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
HO
H
O
O
O
O
CO2Allyl
OAllyl
C5H11
23
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

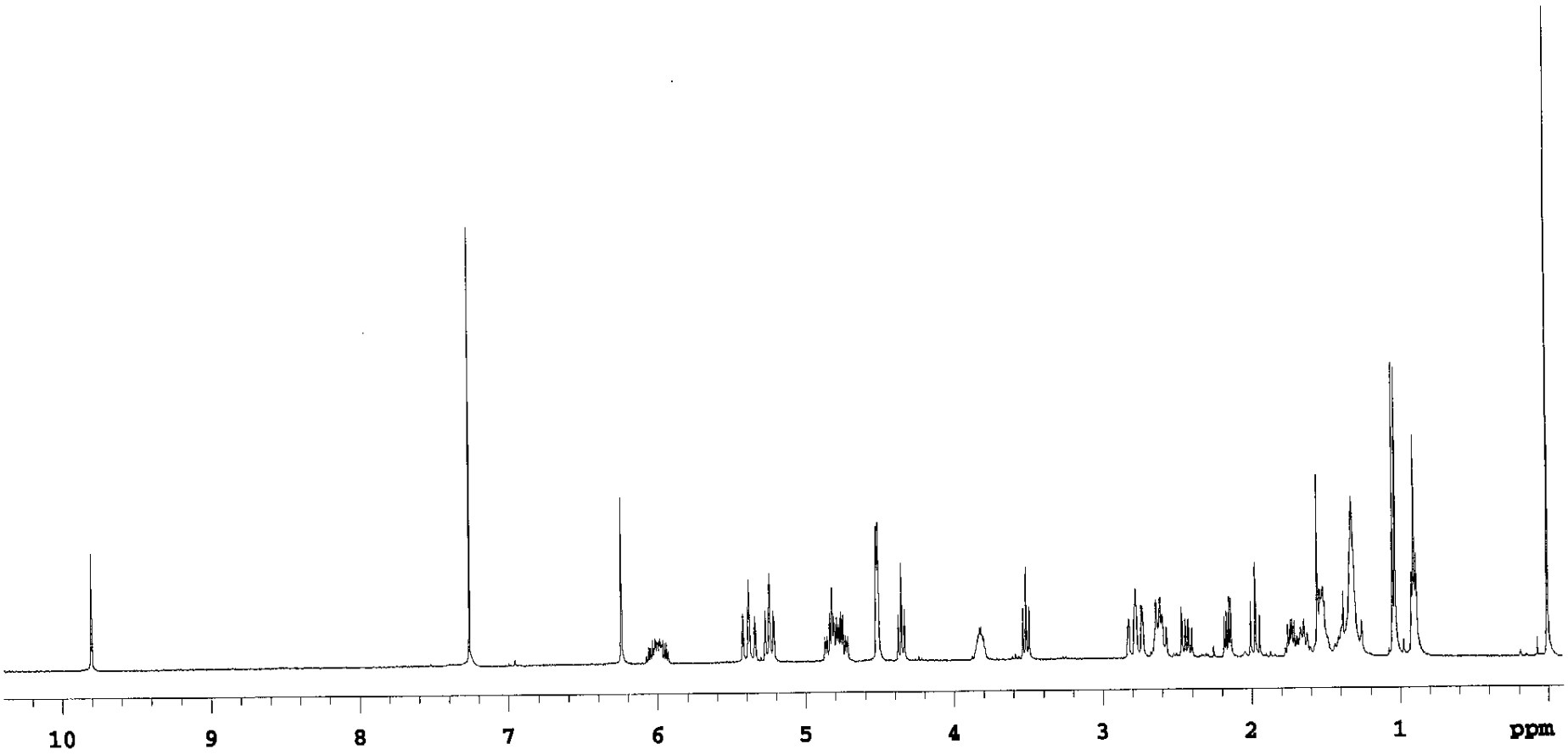
wxx-11-1-4

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-11-1-4
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
21 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

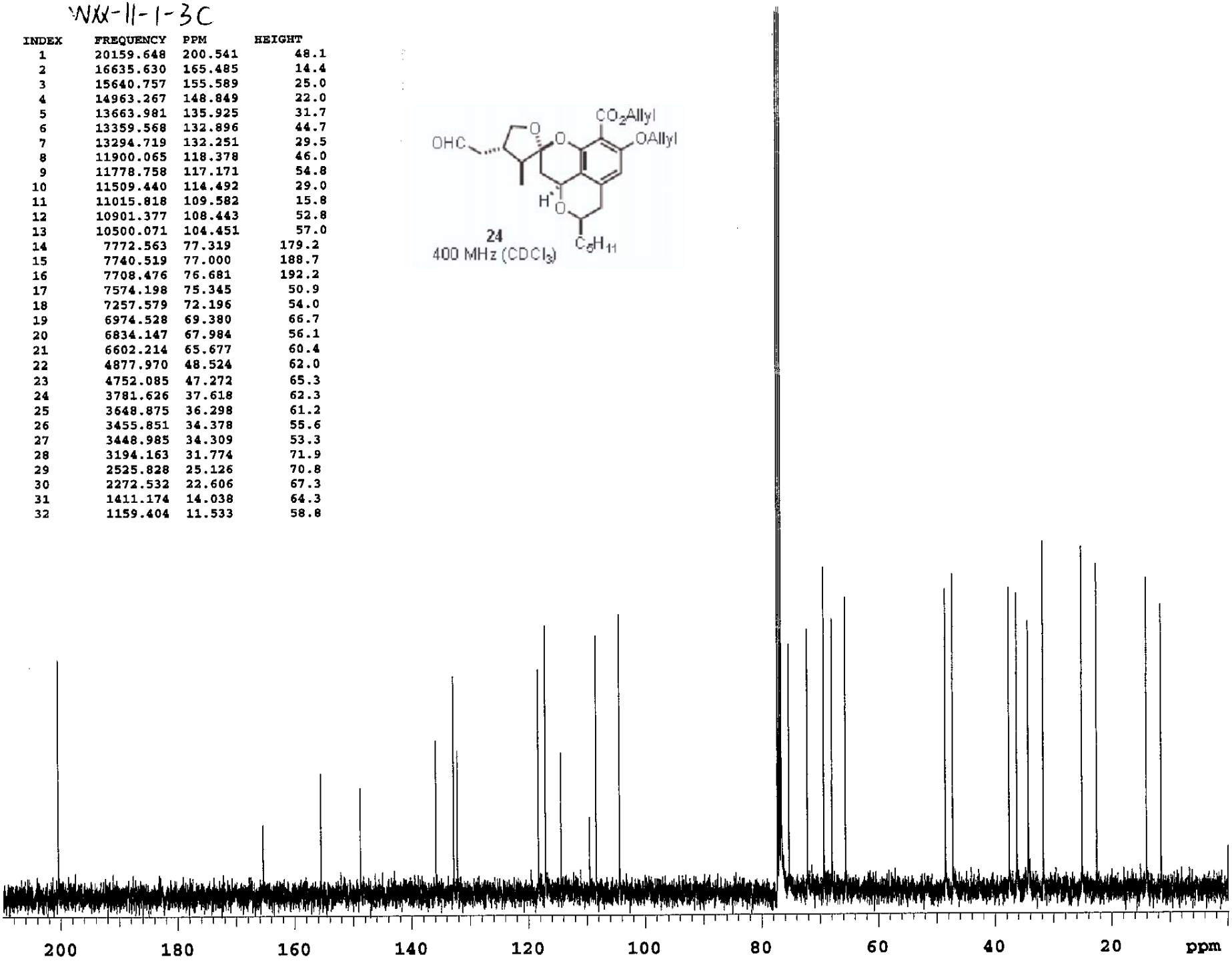
24
400 MHz ($CDCl_3$)

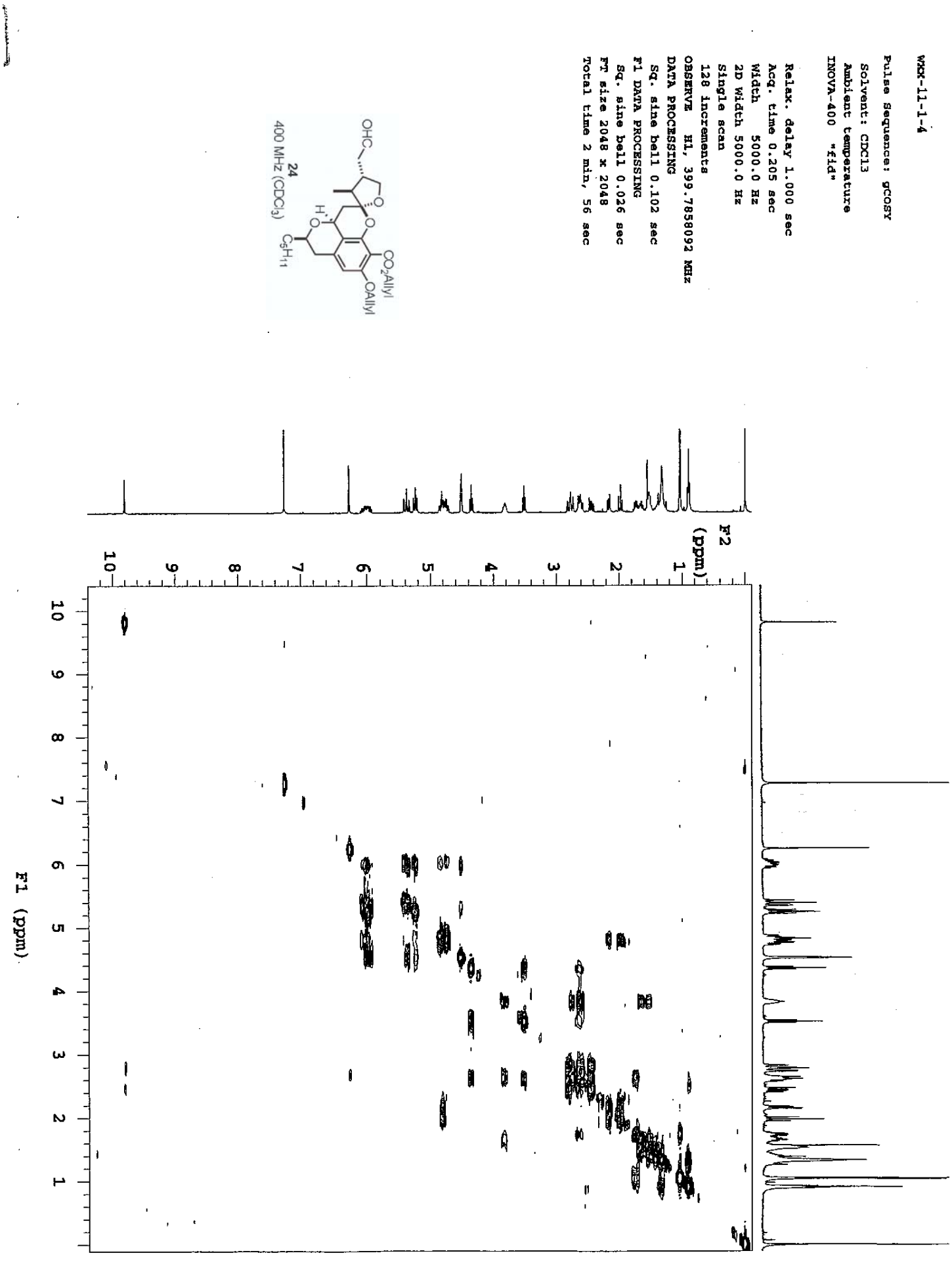


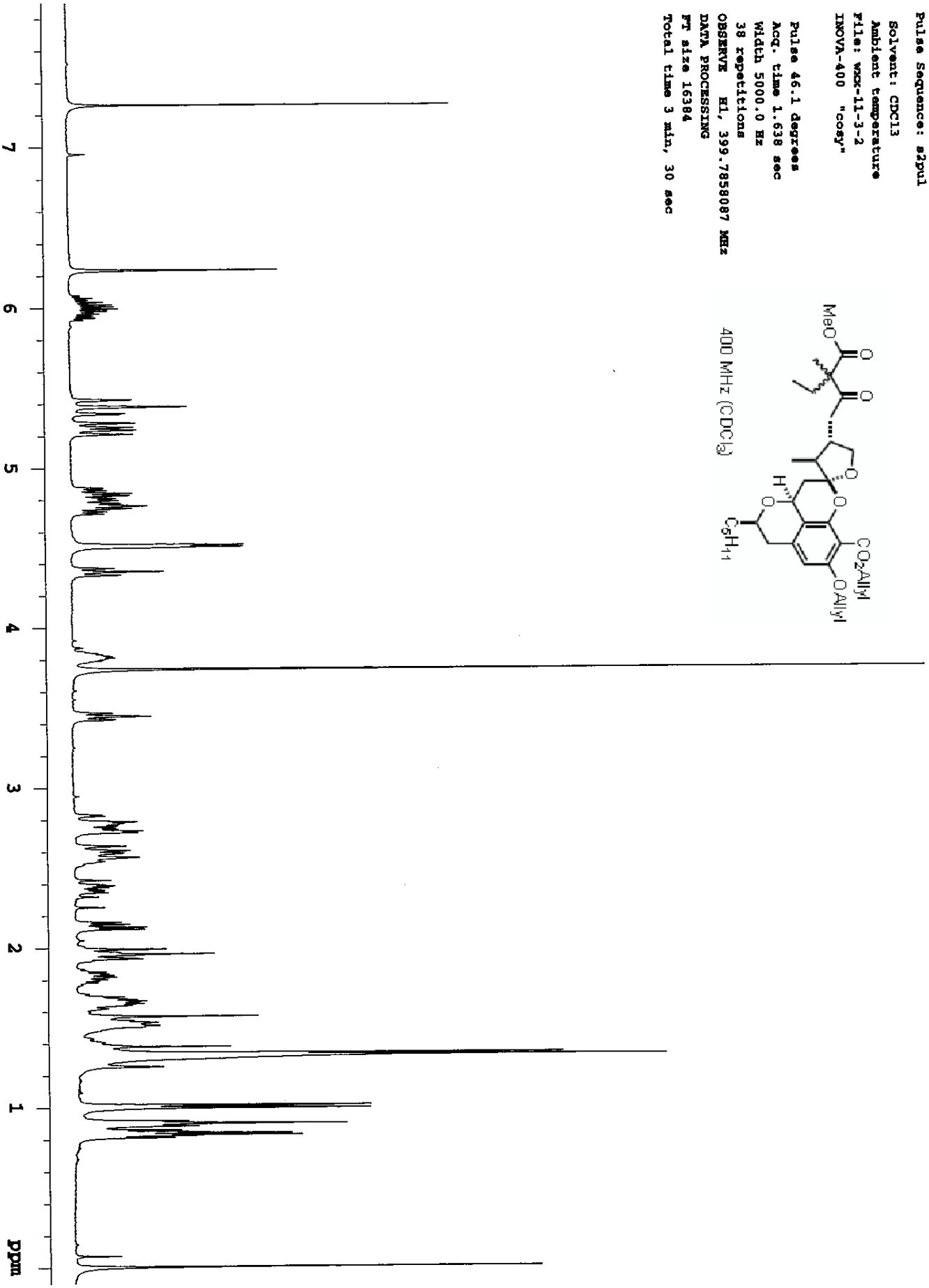
WX-11-1-3C

INDEX	FREQUENCY	PPM	HEIGHT
1	20159.648	200.541	48.1
2	16635.630	165.485	14.4
3	15640.757	155.589	25.0
4	14963.267	148.849	22.0
5	13663.981	135.925	31.7
6	13359.568	132.896	44.7
7	13294.719	132.251	29.5
8	11900.065	118.378	46.0
9	11778.758	117.171	54.8
10	11509.440	114.492	29.0
11	11015.818	109.582	15.8
12	10901.377	108.443	52.8
13	10500.071	104.451	57.0
14	7772.563	77.319	179.2
15	7740.519	77.000	188.7
16	7708.476	76.681	192.2
17	7574.198	75.345	50.9
18	7257.579	72.196	54.0
19	6974.528	69.380	66.7
20	6834.147	67.984	56.1
21	6602.214	65.677	60.4
22	4877.970	48.524	62.0
23	4752.085	47.272	65.3
24	3781.626	37.618	62.3
25	3648.875	36.298	61.2
26	3455.851	34.378	55.6
27	3448.985	34.309	53.3
28	3194.163	31.774	71.9
29	2525.828	25.126	70.8
30	2272.532	22.606	67.3
31	1411.174	14.038	64.3
32	1159.404	11.533	58.8

24
400 MHz ($CDCl_3$)



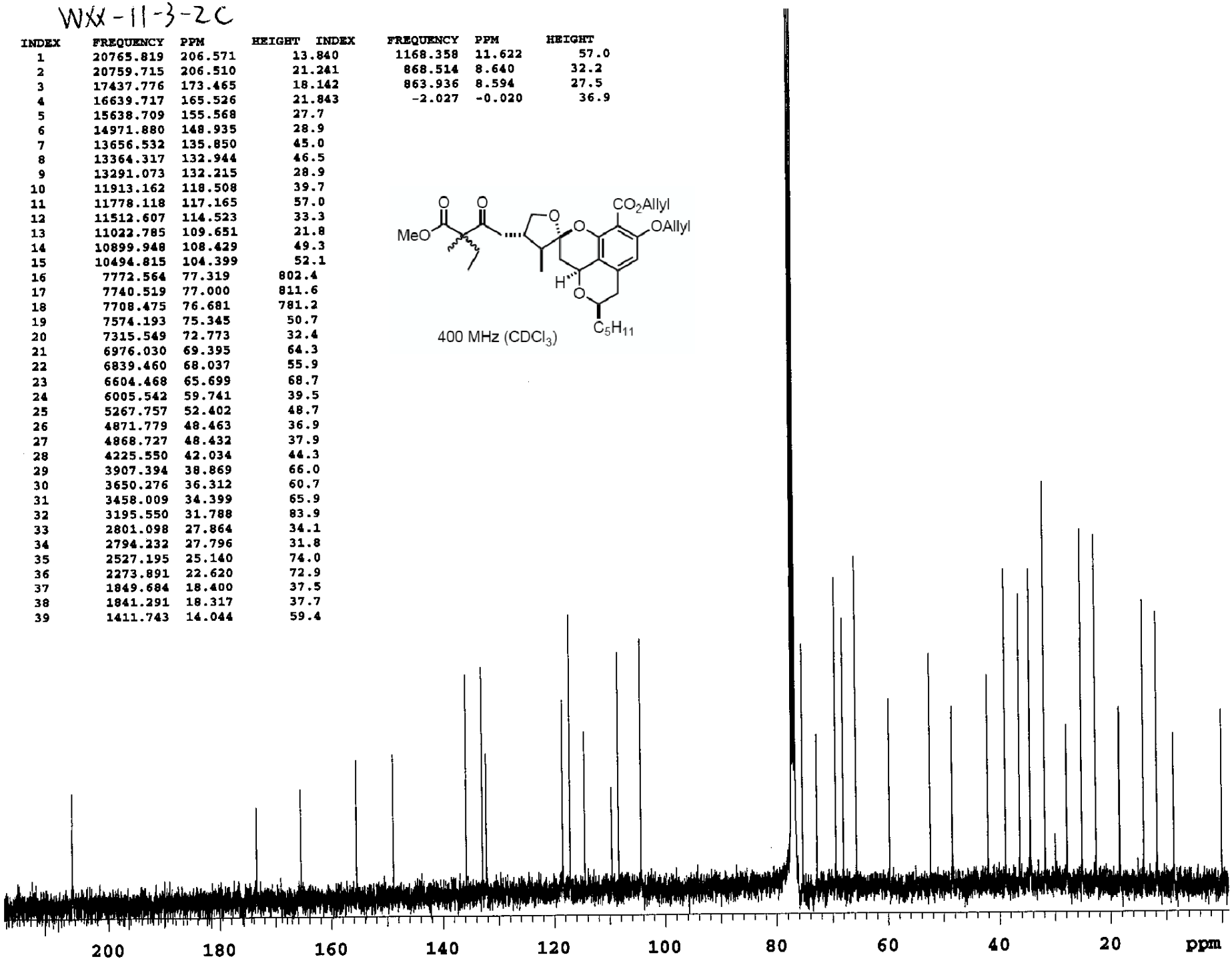

WSX-11-1-4
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858092 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
OHC
CO2Allyl
OAllyl
C5H11
24
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

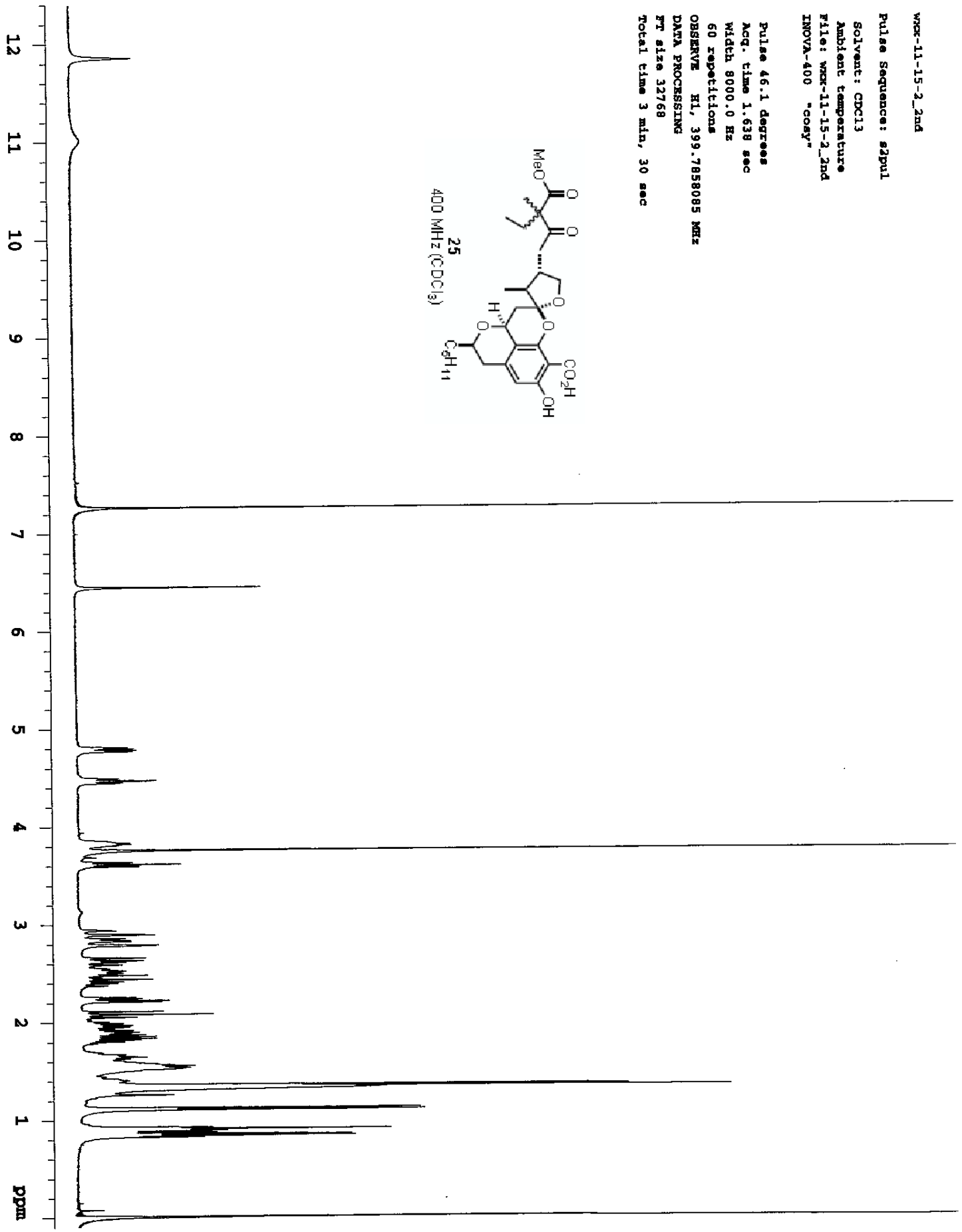

wzx-11-3-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzx-11-3-2
INOVA-400 "cosy"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
38 repetitions
OBSERVE H1, 399.7858087 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 30 sec
400 MHz (CDCl3)
MeO
O
O
O
O
H
O
O
C5H11
CO2Allyl
OAllyl
7
6
5
4
3
2
1
ppm

WXX-11-3-2C

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20765.819	206.571	13.840		1168.358	11.622	57.0
2	20759.715	206.510	21.241		868.514	8.640	32.2
3	17437.776	173.465	18.142		863.936	8.594	27.5
4	16639.717	165.526	21.843		-2.027	-0.020	36.9
5	15638.709	155.568	27.7				
6	14971.880	148.935	28.9				
7	13656.532	135.850	45.0				
8	13364.317	132.944	46.5				
9	13291.073	132.215	28.9				
10	11913.162	118.508	39.7				
11	11778.118	117.165	57.0				
12	11512.607	114.523	33.3				
13	11022.785	109.651	21.8				
14	10899.948	108.429	49.3				
15	10494.815	104.399	52.1				
16	7772.564	77.319	802.4				
17	7740.519	77.000	811.6				
18	7708.475	76.681	781.2				
19	7574.193	75.345	50.7				
20	7315.549	72.773	32.4				
21	6976.030	69.395	64.3				
22	6839.460	68.037	55.9				
23	6604.468	65.699	68.7				
24	6005.542	59.741	39.5				
25	5267.757	52.402	48.7				
26	4871.779	48.463	36.9				
27	4868.727	48.432	37.9				
28	4225.550	42.034	44.3				
29	3907.394	38.869	66.0				
30	3650.276	36.312	60.7				
31	3458.009	34.399	65.9				
32	3195.550	31.788	83.9				
33	2801.098	27.864	34.1				
34	2794.232	27.796	31.8				
35	2527.195	25.140	74.0				
36	2273.891	22.620	72.9				
37	1849.684	18.400	37.5				
38	1841.291	18.317	37.7				
39	1411.743	14.044	59.4				

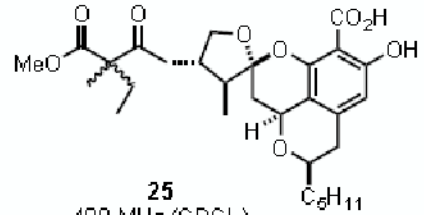
400 MHz ($CDCl_3$)



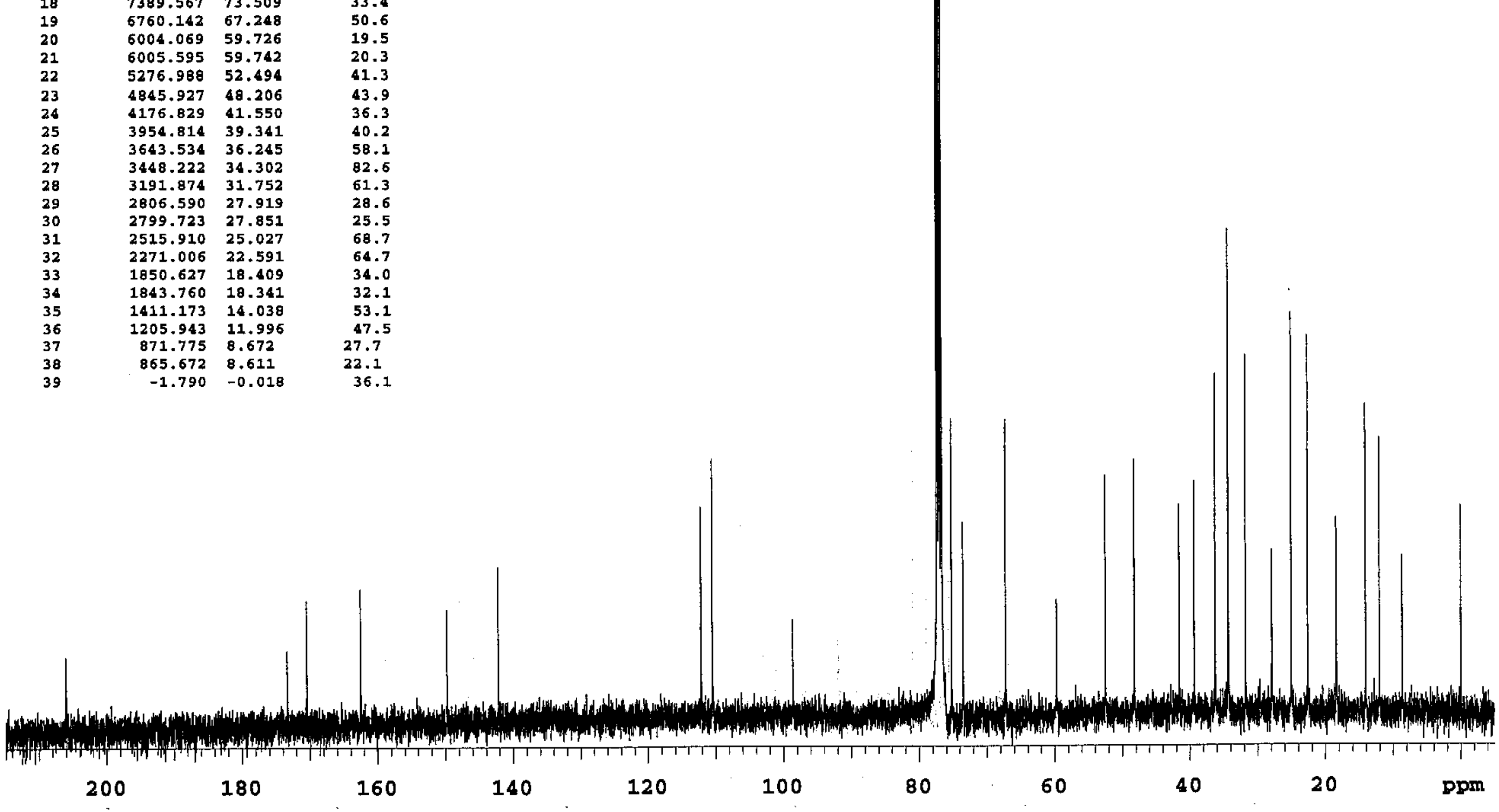

wzk-11-15-2_2nd
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-11-15-2_2nd
INOVA-400 "cosy"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 8000.0 Hz
60 repetitions
OBSERVE H1, 399.7858085 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 30 sec
MeO
O
O
O
O
H
O
C5H11
CO2H
OH
25
400 MHz (CDCl3)
12
11
10
9
8
7
6
5
4
3
2
1
ppm

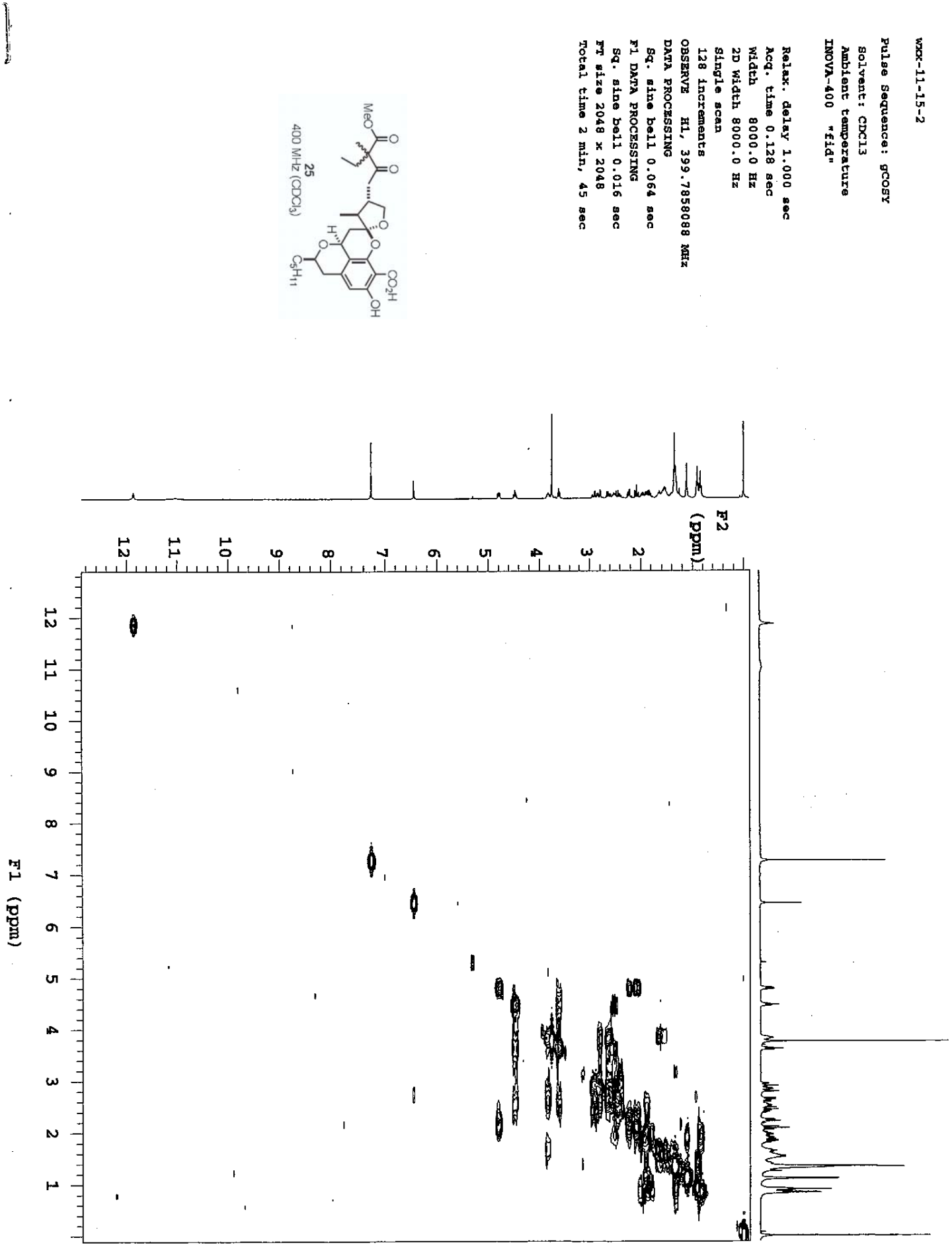
WXX-11-15-2C in $CDCl_3$

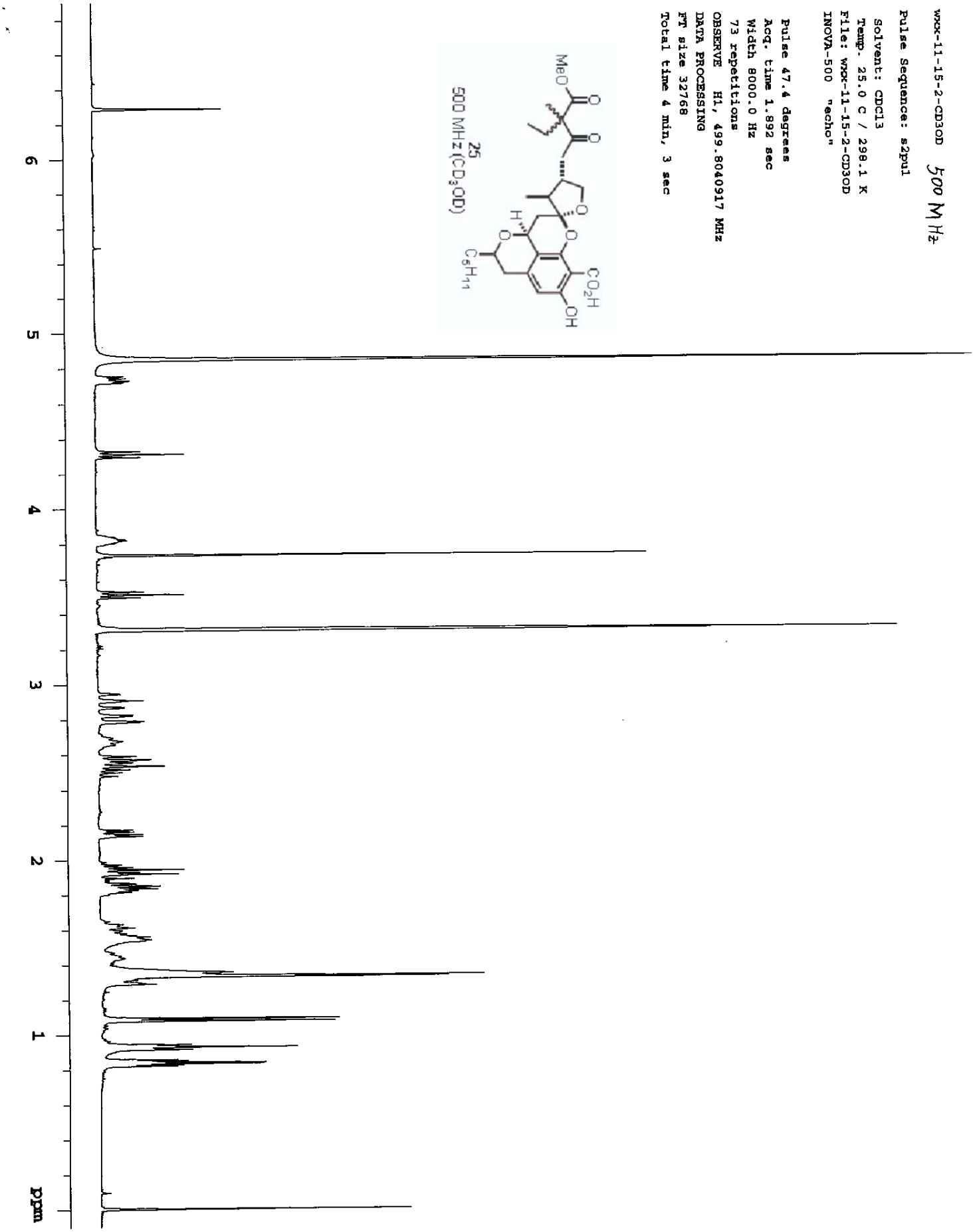
INDEX	FREQUENCY	PPM	HEIGHT
1	21358.988	212.472	-7.5
2	20712.016	206.036	10.9
3	20705.912	205.975	7.6
4	19229.624	191.290	-7.1
5	18792.460	186.941	-7.2
6	17427.561	173.363	11.9
7	17139.170	170.495	20.3
8	16338.847	162.533	22.3
9	15056.346	149.775	18.7
10	14294.932	142.201	26.0
11	11274.455	112.154	36.0
12	11107.371	110.492	44.1
13	9916.422	98.645	17.0
14	7771.800	77.311	647.6
15	7740.519	77.000	673.0
16	7708.476	76.681	677.9
17	7560.465	75.209	50.6
18	7389.567	73.509	33.4
19	6760.142	67.248	50.6
20	6004.069	59.726	19.5
21	6005.595	59.742	20.3
22	5276.988	52.494	41.3
23	4845.927	48.206	43.9
24	4176.829	41.550	36.3
25	3954.814	39.341	40.2
26	3643.534	36.245	58.1
27	3448.222	34.302	82.6
28	3191.874	31.752	61.3
29	2806.590	27.919	28.6
30	2799.723	27.851	25.5
31	2515.910	25.027	68.7
32	2271.006	22.591	64.7
33	1850.627	18.409	34.0
34	1843.760	18.341	32.1
35	1411.173	14.038	53.1
36	1205.943	11.996	47.5
37	871.775	8.672	27.7
38	865.672	8.611	22.1
39	-1.790	-0.018	36.1



25
400 MHz ($CDCl_3$)

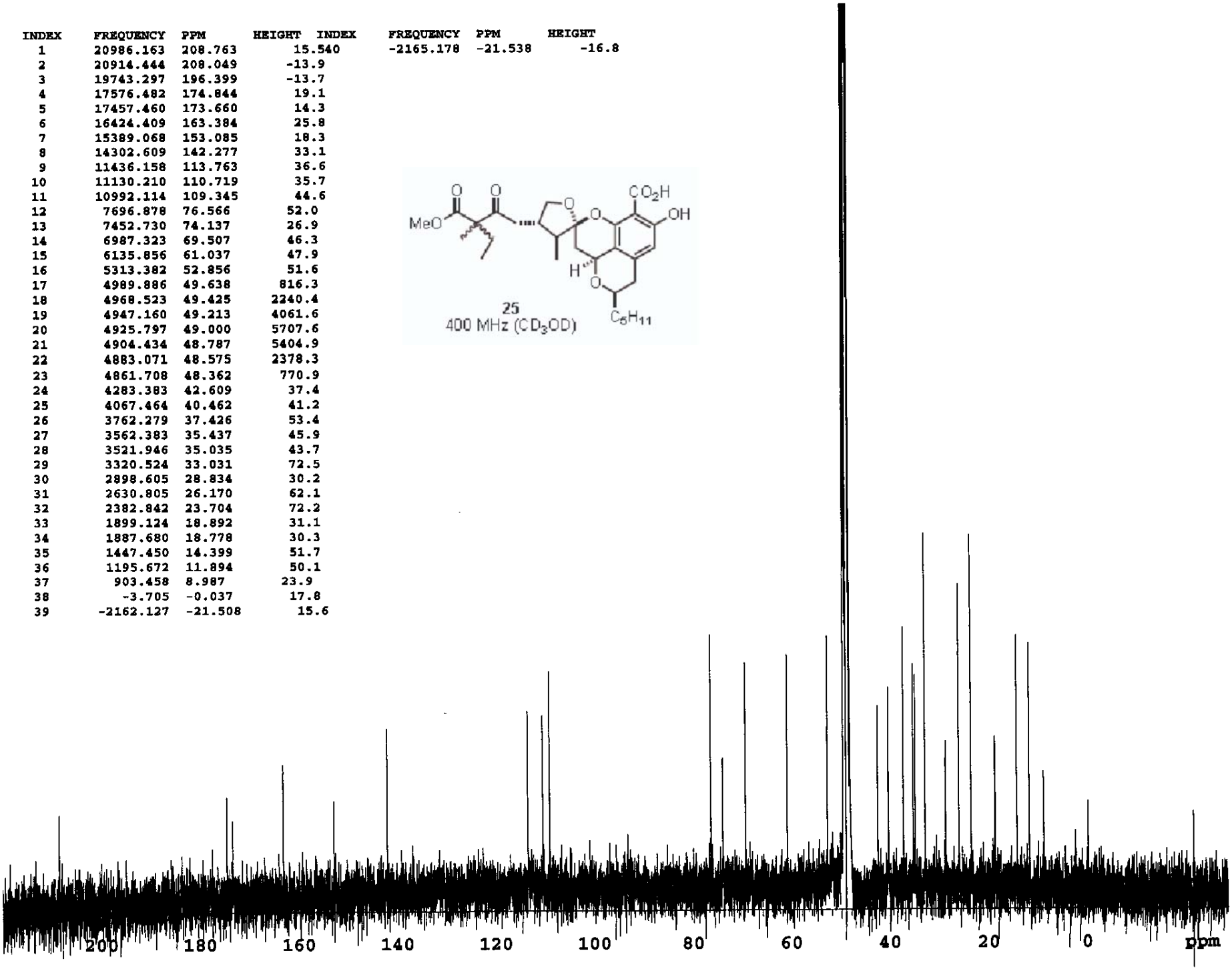


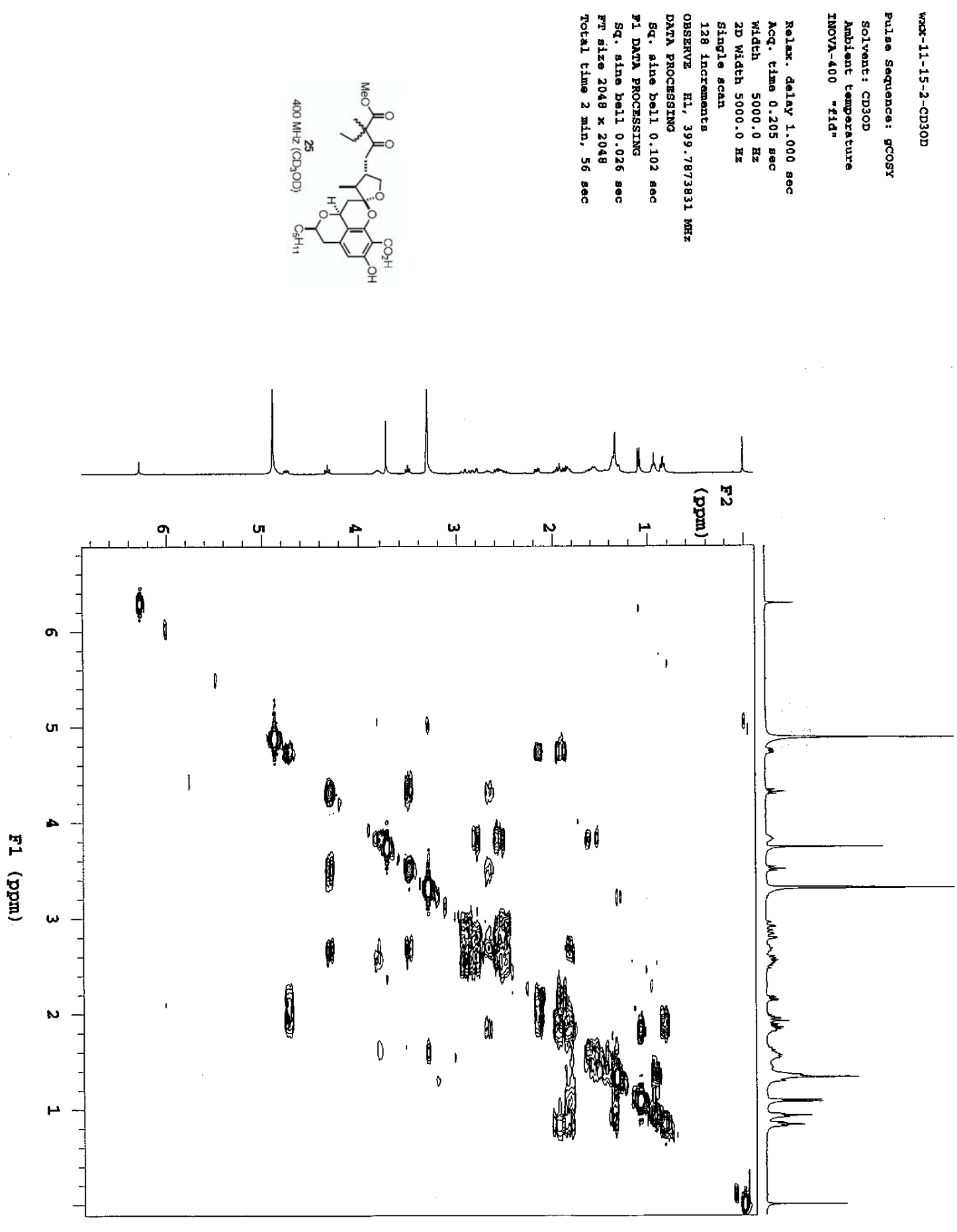

WZK-11-15-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858088 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
MeO
CO2H
OH
C5H11
25
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)


wxx-11-15-2-CD3OD 500 MHz
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: wxx-11-15-2-CD3OD
INOVA-500 "echo"
Pulse 47.4 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
73 repetitions
OBSERVE H1, 499.8040917 MHz
DATA PROCESSING
FT size 32768
Total time 4 min, 3 sec
MeO
CO2H
OH
C5H11
25
500 MHz (CD3OD)
6
5
4
3
2
1
ppm

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20986.163	208.763	15.540		-2165.178	-21.538	-16.8
2	20914.444	208.049	-13.9				
3	19743.297	196.399	-13.7				
4	17576.482	174.844	19.1				
5	17457.460	173.660	14.3				
6	16424.409	163.384	25.8				
7	15389.068	153.085	18.3				
8	14302.609	142.277	33.1				
9	11436.158	113.763	36.6				
10	11130.210	110.719	35.7				
11	10992.114	109.345	44.6				
12	7696.878	76.566	52.0				
13	7452.730	74.137	26.9				
14	6987.323	69.507	46.3				
15	6135.856	61.037	47.9				
16	5313.382	52.856	51.6				
17	4989.886	49.638	816.3				
18	4968.523	49.425	2240.4				
19	4947.160	49.213	4061.6				
20	4925.797	49.000	5707.6				
21	4904.434	48.787	5404.9				
22	4883.071	48.575	2378.3				
23	4861.708	48.362	770.9				
24	4283.383	42.609	37.4				
25	4067.464	40.462	41.2				
26	3762.279	37.426	53.4				
27	3562.383	35.437	45.9				
28	3521.946	35.035	43.7				
29	3320.524	33.031	72.5				
30	2898.605	28.834	30.2				
31	2630.805	26.170	62.1				
32	2382.842	23.704	72.2				
33	1899.124	18.892	31.1				
34	1887.680	18.778	30.3				
35	1447.450	14.399	51.7				
36	1195.672	11.894	50.1				
37	903.458	8.987	23.9				
38	-3.705	-0.037	17.8				
39	-2162.127	-21.508	15.6				

25
400 MHz (CD_3OD)



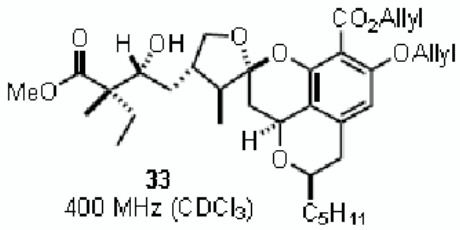

wsk-11-15-2-CD3OD
Pulse Sequence: gCOSY
Solvent: CD3OD
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7873831 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
O
O
H
O
O
O
CO2H
OH
C5H11
25
400 MHz (CD3OD)
F2 (ppm)
F1 (ppm)
6
5
4
3
2
1

wxx-11-13-2

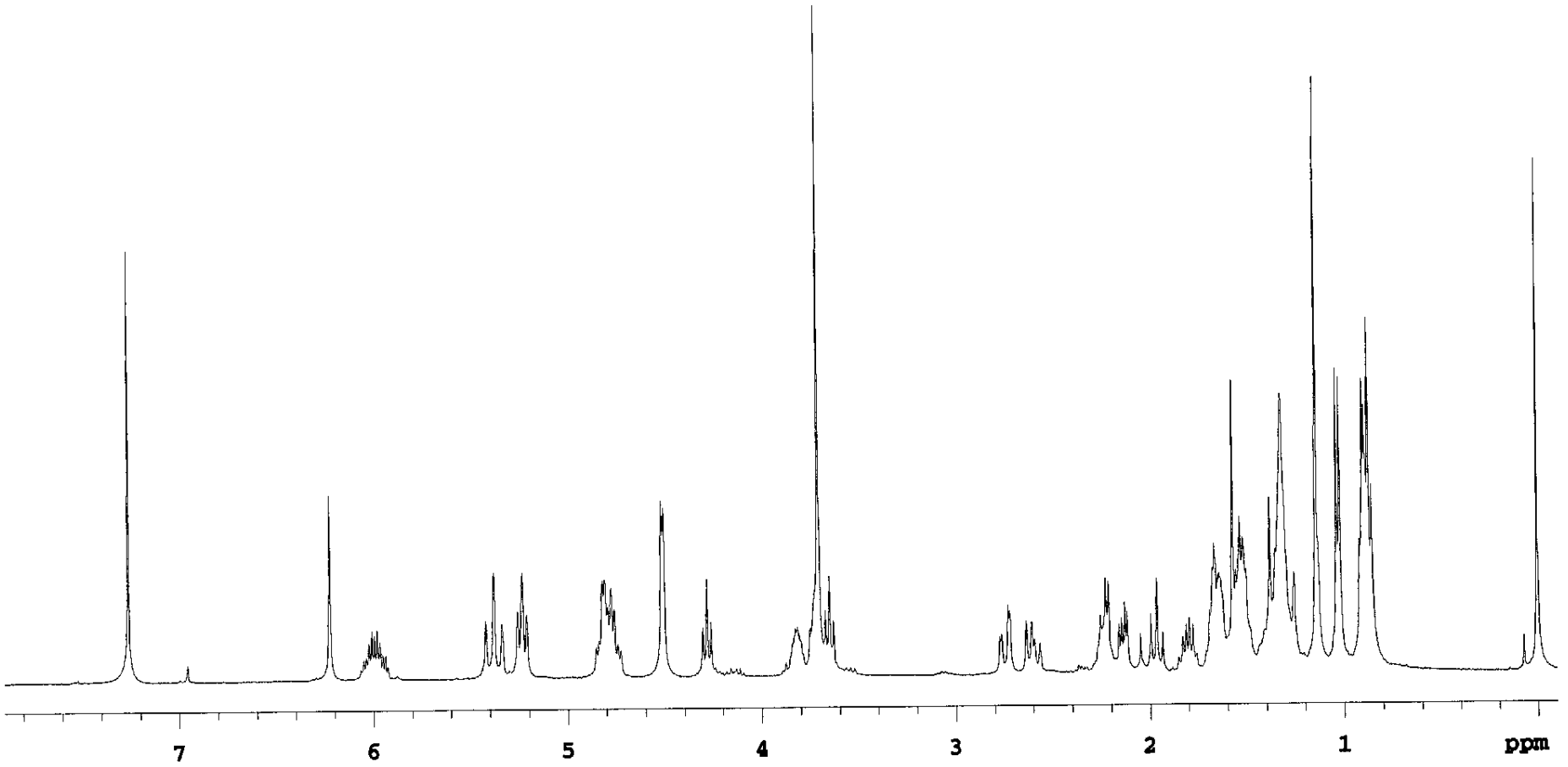
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-11-13-2
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
69 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

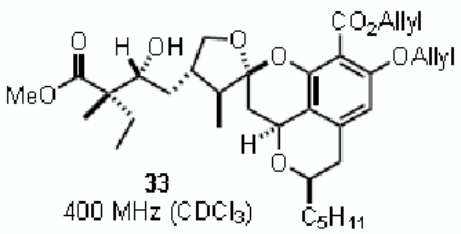


33
400 MHz ($CDCl_3$)

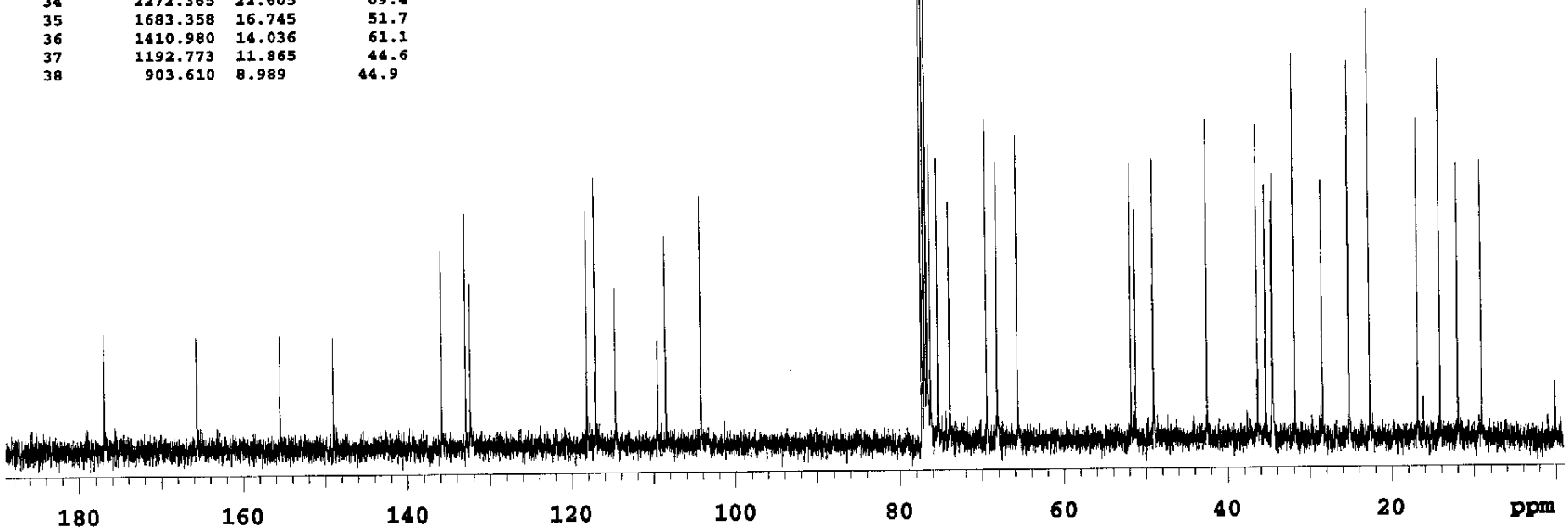


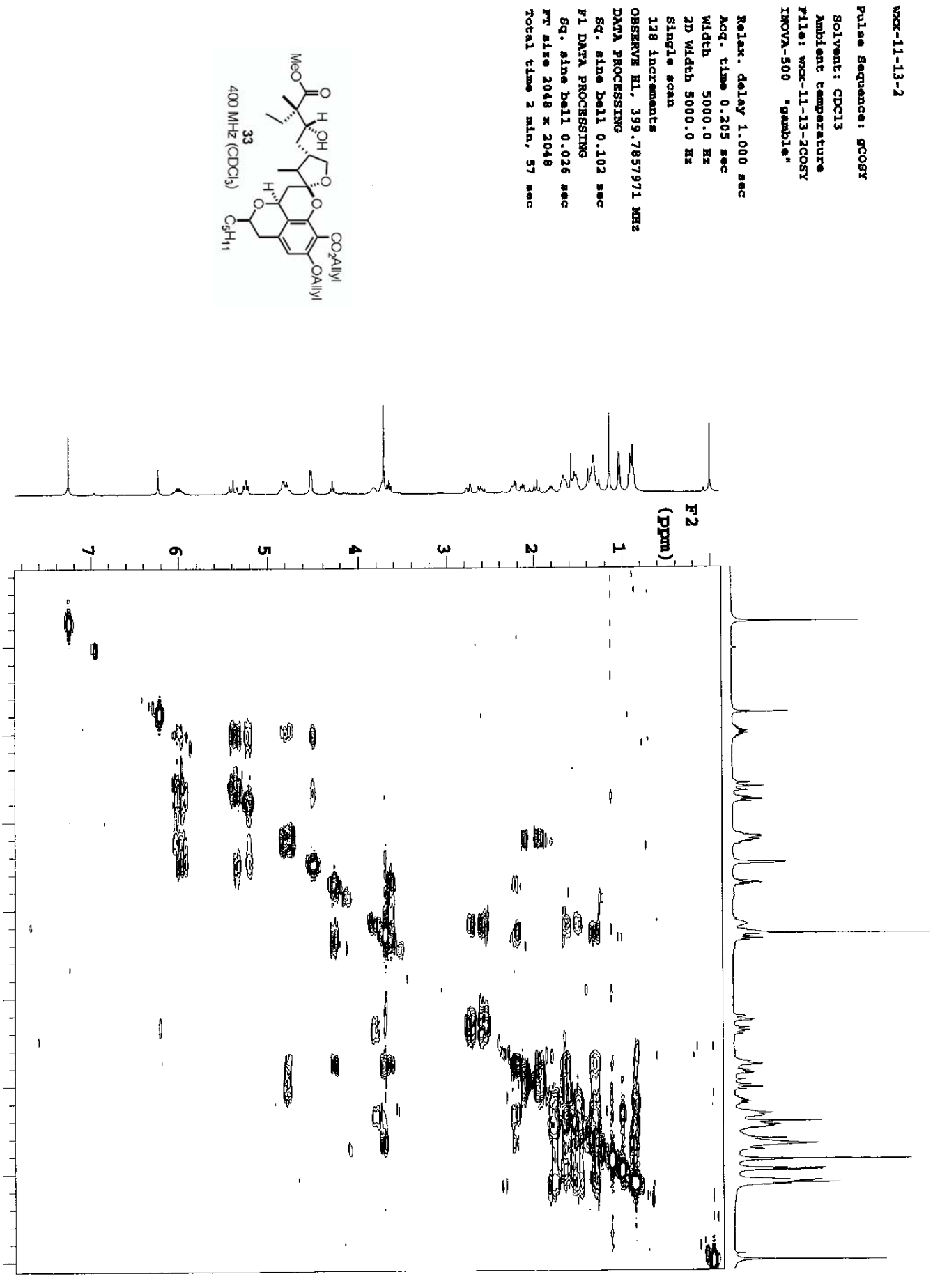
WXX-11-19-2C

INDEX	FREQUENCY	PPM	HEIGHT
1	17787.213	176.941	18.6
2	16653.449	165.663	18.0
3	15636.421	155.546	18.1
4	14987.140	149.087	17.8
5	13660.347	135.888	31.9
6	13365.844	132.959	37.6
7	13309.384	132.397	26.5
8	11878.829	118.166	37.9
9	11775.066	117.134	43.1
10	11524.814	114.645	25.6
11	11009.814	109.522	16.9
12	10909.104	108.520	33.7
13	10478.029	104.232	40.1
14	7772.563	77.319	133.2
15	7740.519	77.000	138.5
16	7708.475	76.681	133.9
17	7661.934	76.218	48.1
18	7570.378	75.308	45.9
19	7425.416	73.865	38.9
20	6974.504	69.380	52.0
21	6847.090	68.112	45.3
22	6598.364	65.638	49.4
23	5205.957	51.787	44.7
24	5149.498	51.225	41.7
25	4929.765	49.040	45.4
26	4269.802	42.475	51.8
27	3651.039	36.319	50.9
28	3549.565	35.310	41.3
29	3473.269	34.551	35.7
30	3459.535	34.414	43.2
31	3195.550	31.788	62.4
32	2852.980	28.380	42.1
33	2527.195	25.140	61.0
34	2272.365	22.605	69.4
35	1683.358	16.745	51.7
36	1410.980	14.036	61.1
37	1192.773	11.865	44.6
38	903.610	8.989	44.9



33
400 MHz ($CDCl_3$)



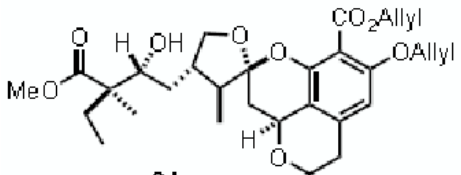

wzk-11-13-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: wzk-11-13-2COSY
INOVA-500 "gamble"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D width 5000.0 Hz
single scan
128 increments
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 57 sec
MeO
O
H
OH
O
H
O
O
CO2Allyl
OAllyl
C5H11
33
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)
7
6
5
4
3
2
1

wxx-11-13-3

Pulse Sequence: s2pul

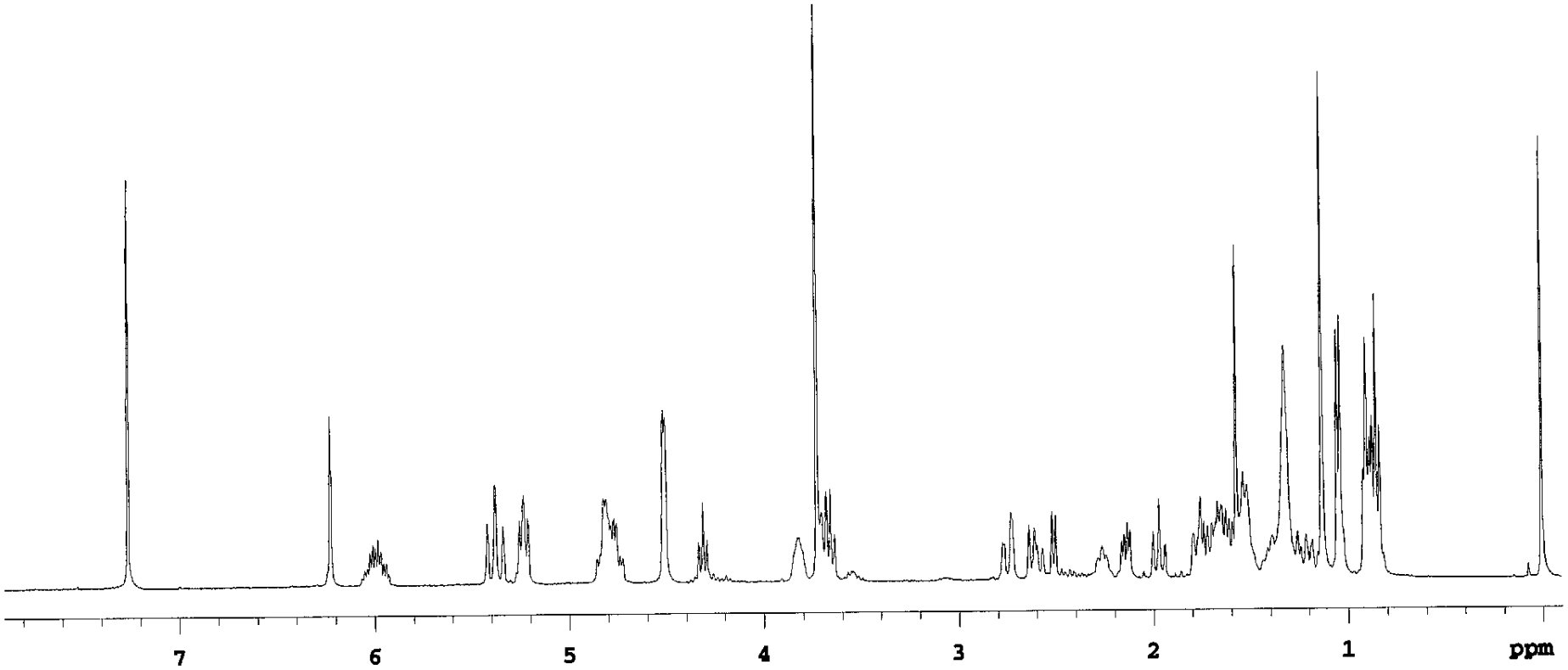
Solvent: CDCl3
Ambient temperature
File: wxx-11-13-3
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
42 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec



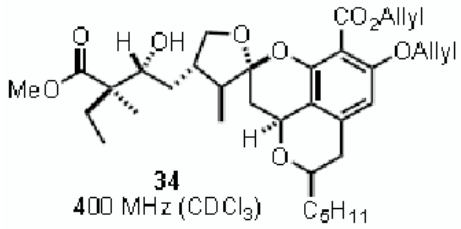
34

400 MHz ($CDCl_3$)



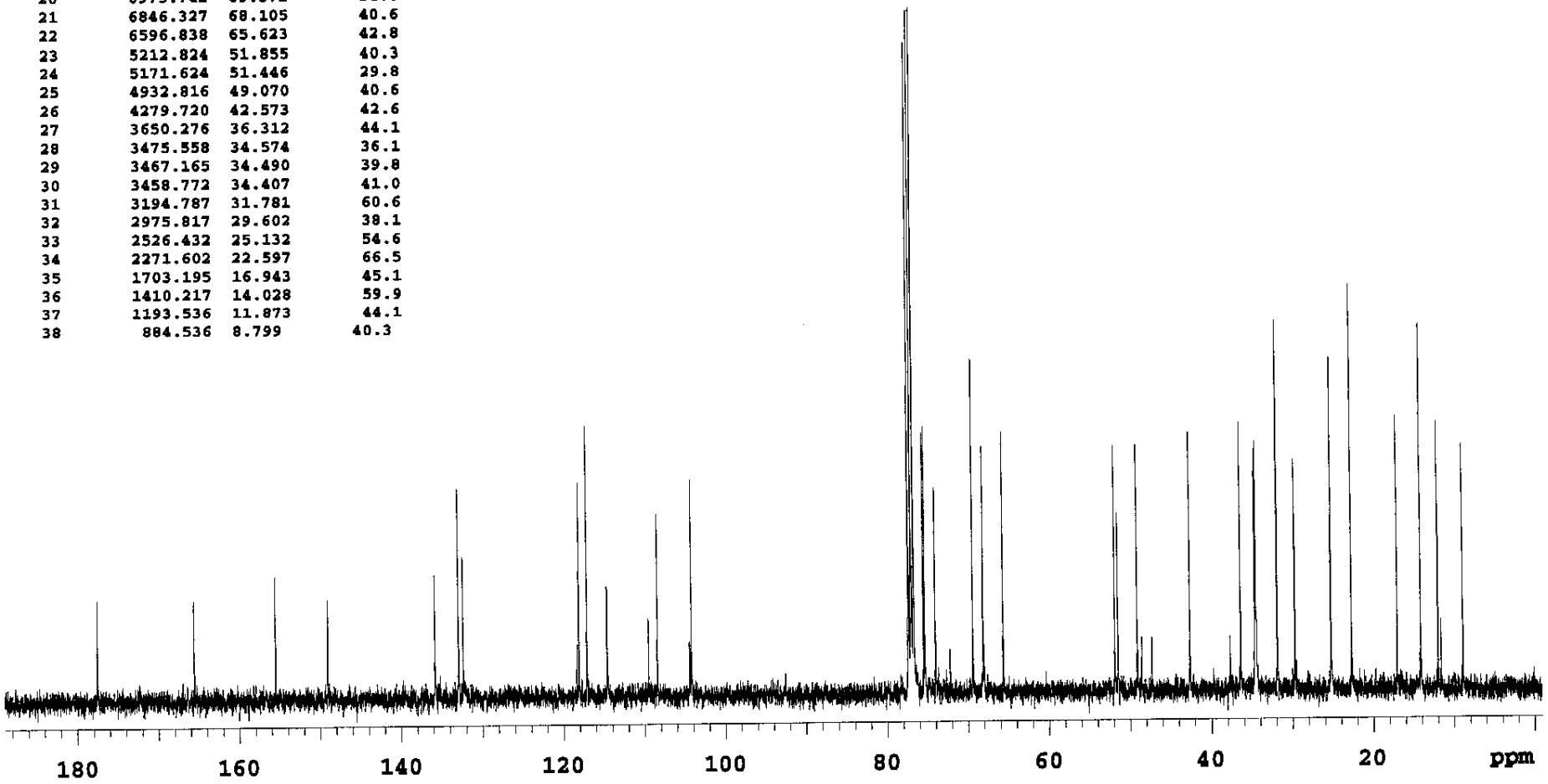
WXX-11-19-3C

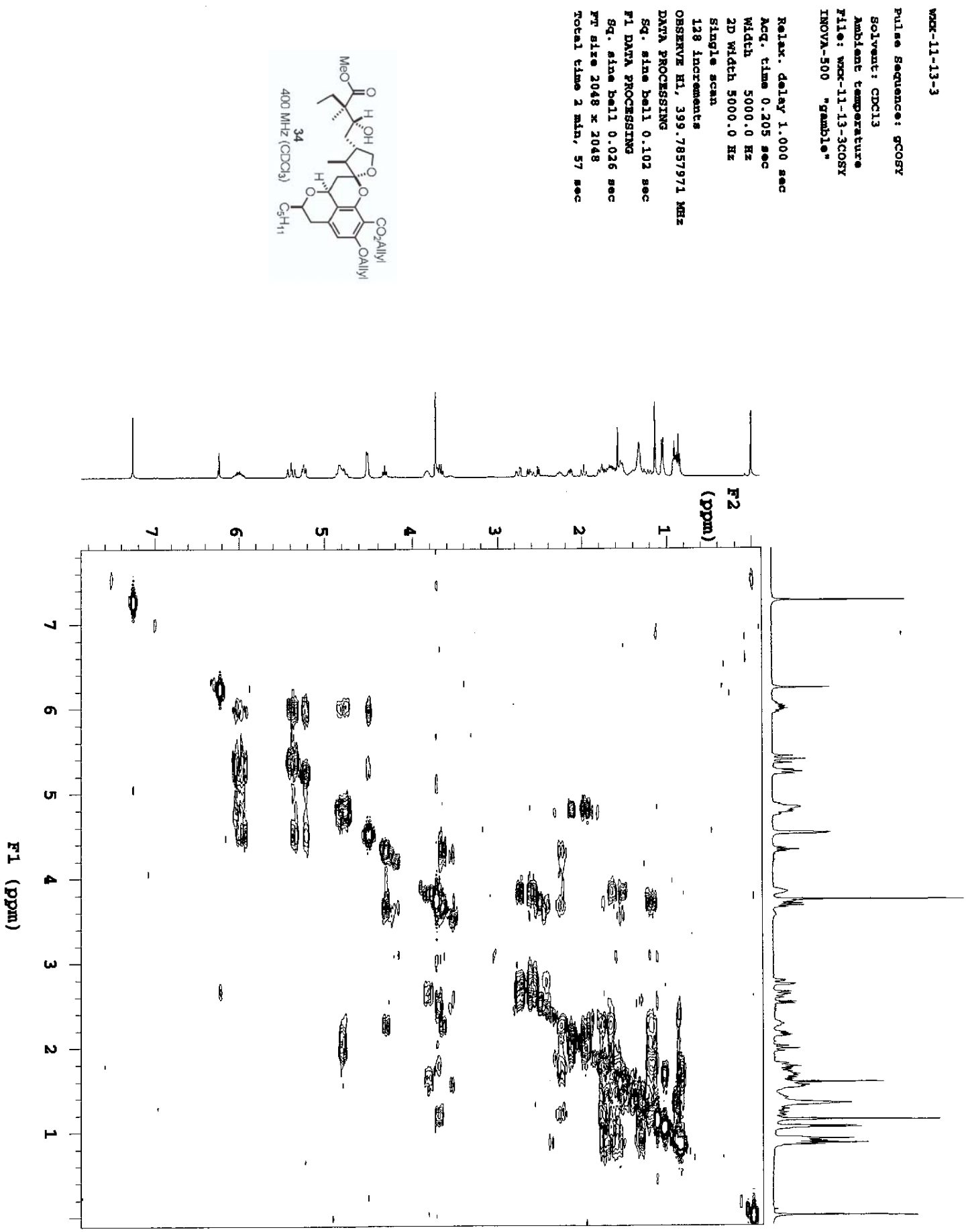
INDEX	FREQUENCY	PPM	HEIGHT
1	17851.301	177.579	16.6
2	16650.398	165.632	16.4
3	15637.946	155.561	20.2
4	14988.665	149.102	16.4
5	13658.821	135.873	20.4
6	13365.844	132.959	34.3
7	13308.621	132.390	23.3
8	11873.488	118.113	35.3
9	11773.540	117.119	44.2
10	11524.052	114.637	18.3
11	11009.052	109.514	13.0
12	10899.948	108.429	30.1
13	10477.267	104.224	35.6
14	7772.563	77.319	105.9
15	7740.519	77.000	110.8
16	7708.475	76.681	111.3
17	7588.689	75.490	42.8
18	7569.616	75.300	43.8
19	7439.149	74.002	34.0
20	6973.742	69.372	54.6
21	6846.327	68.105	40.6
22	6596.838	65.623	42.8
23	5212.824	51.855	40.3
24	5171.624	51.446	29.8
25	4932.816	49.070	40.6
26	4279.720	42.573	42.6
27	3650.276	36.312	44.1
28	3475.558	34.574	36.1
29	3467.165	34.490	39.8
30	3458.772	34.407	41.0
31	3194.787	31.781	60.6
32	2975.817	29.602	38.1
33	2526.432	25.132	54.6
34	2271.602	22.597	66.5
35	1703.195	16.943	45.1
36	1410.217	14.028	59.9
37	1193.536	11.873	44.1
38	884.536	8.799	40.3

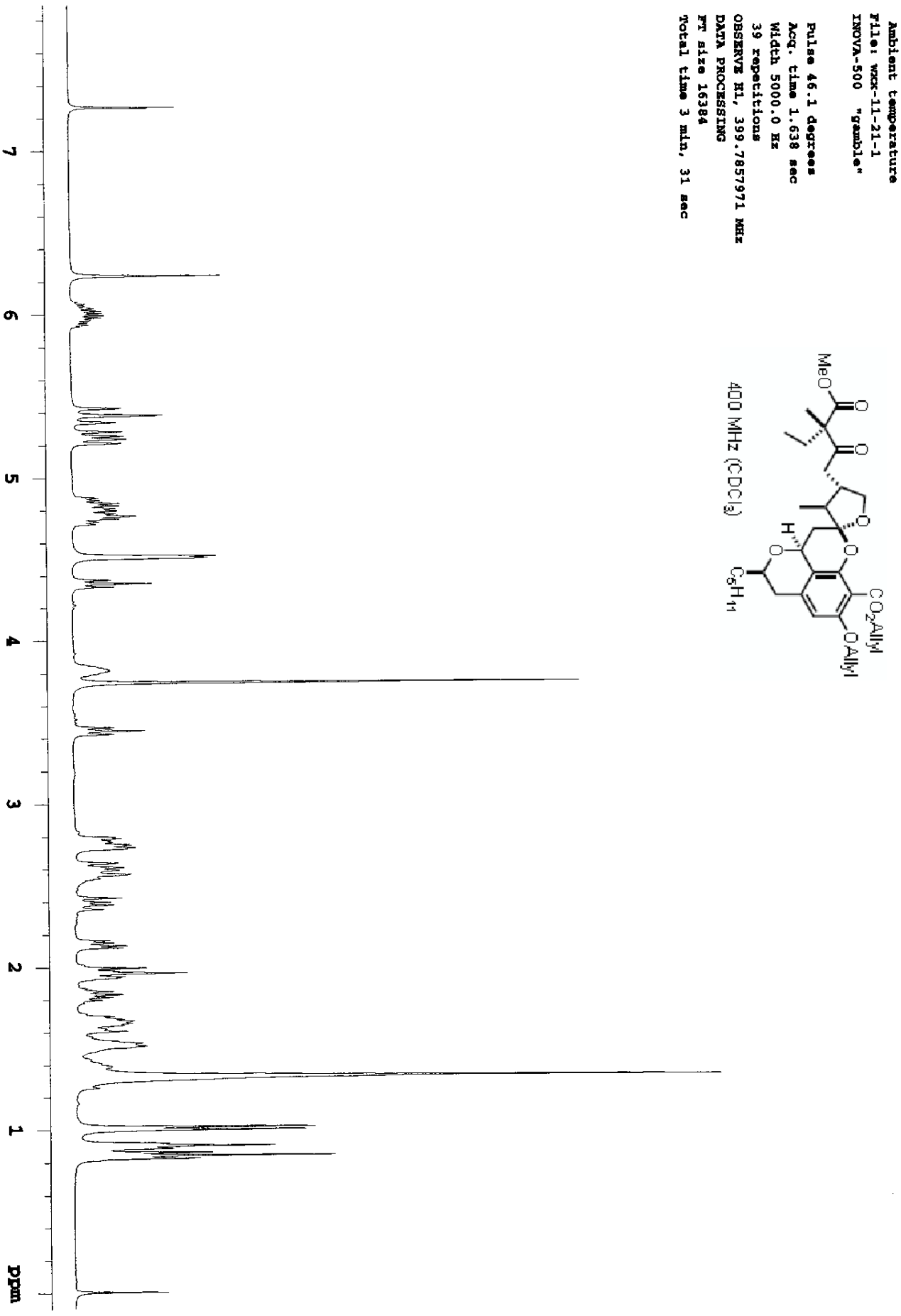


34

400 MHz ($CDCl_3$)




wzk-11-13-3
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: wzk-11-13-3COSY
INOVA-500 "gamble"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
single scan
128 increments
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 57 sec
MeO
OH
H
CO2Allyl
OAllyl
C5H11
34
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)


wsx-11-21-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wsx-11-21-1
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
39 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
400 MHz (CDCl3)
MeO
O
O
O
H
O
O
C5H11
CO2Allyl
OAllyl
7
6
5
4
3
2
1
ppm

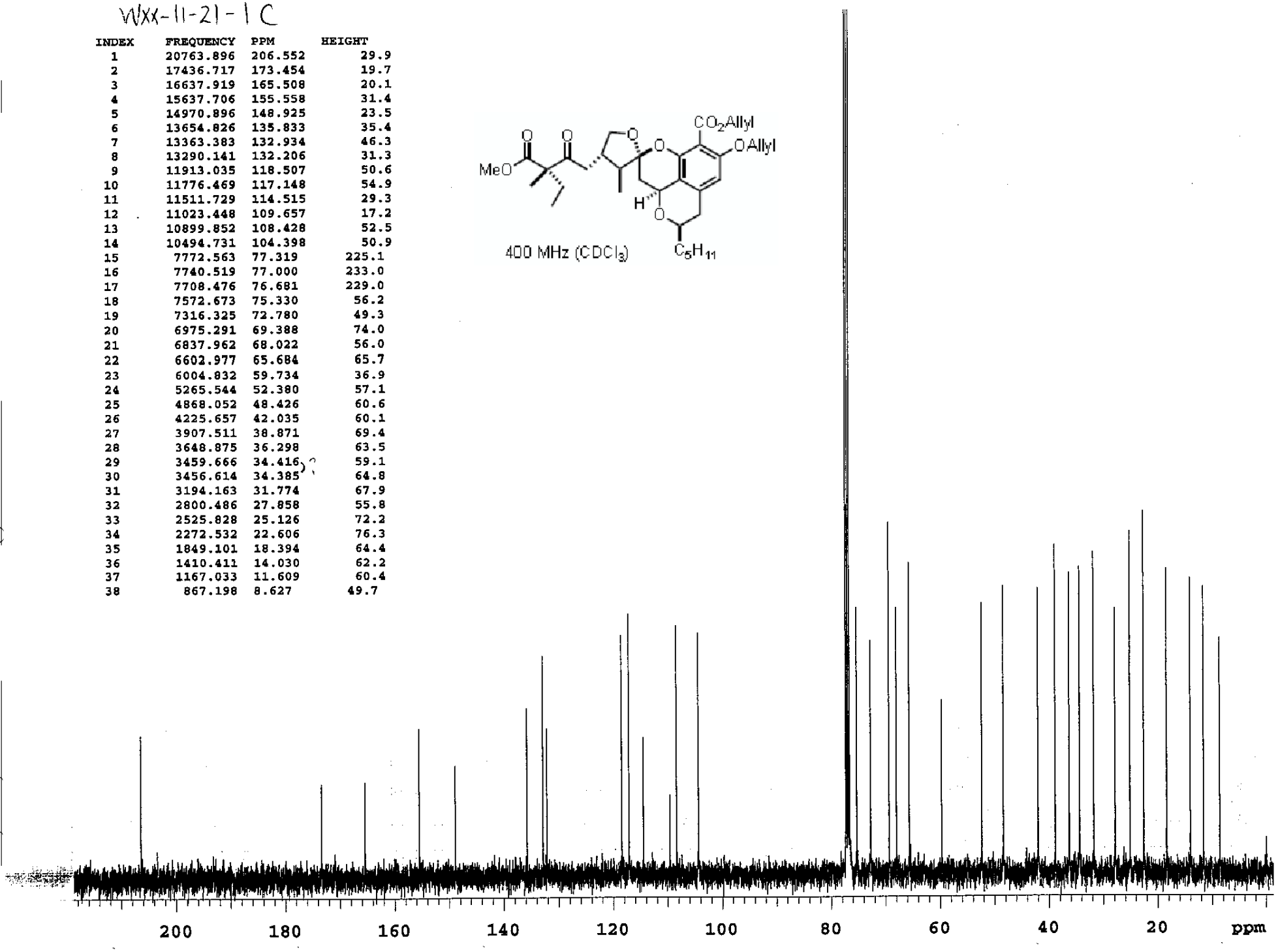
(-)-Berkelic Acid

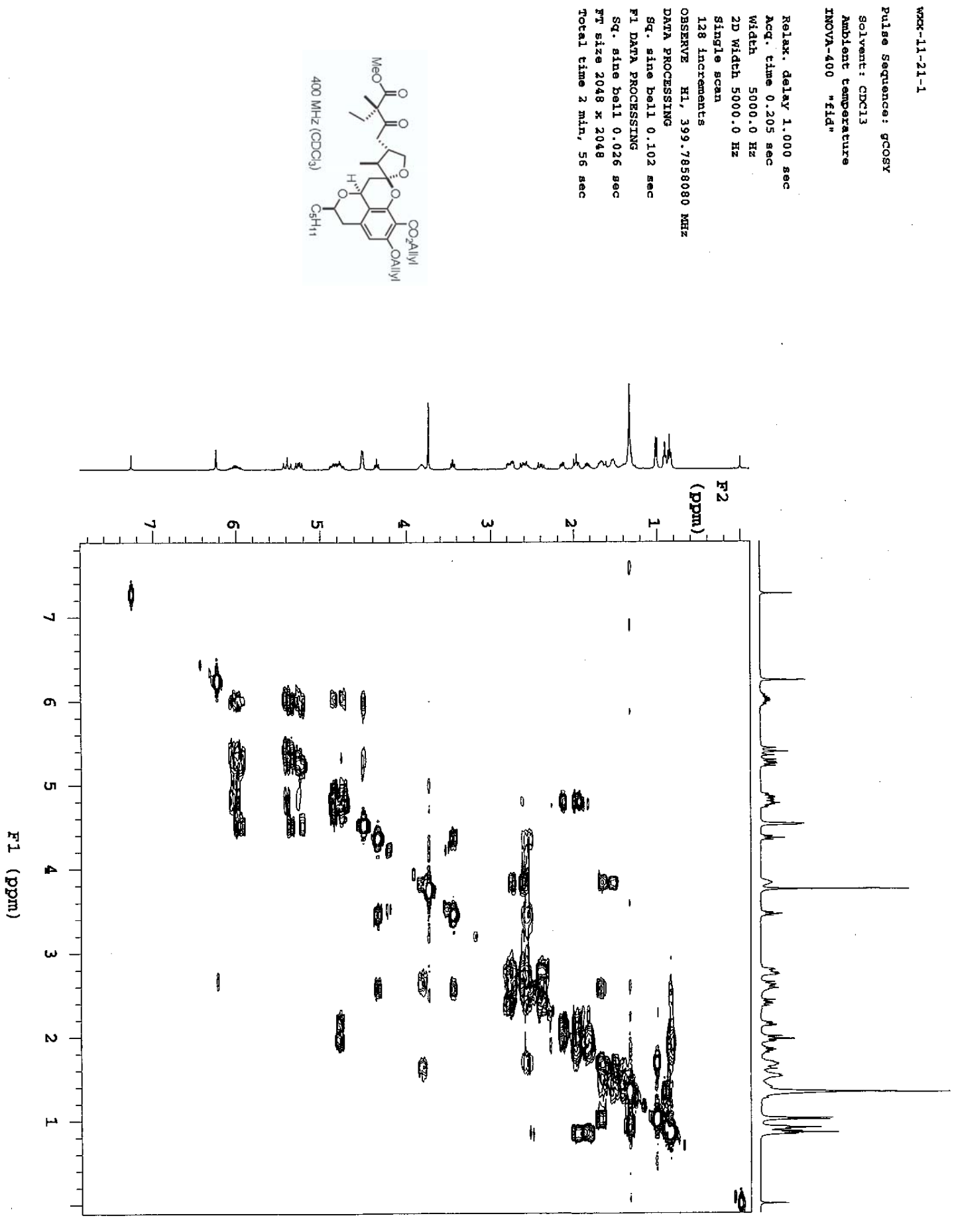
Wu, Zhou, and Snider

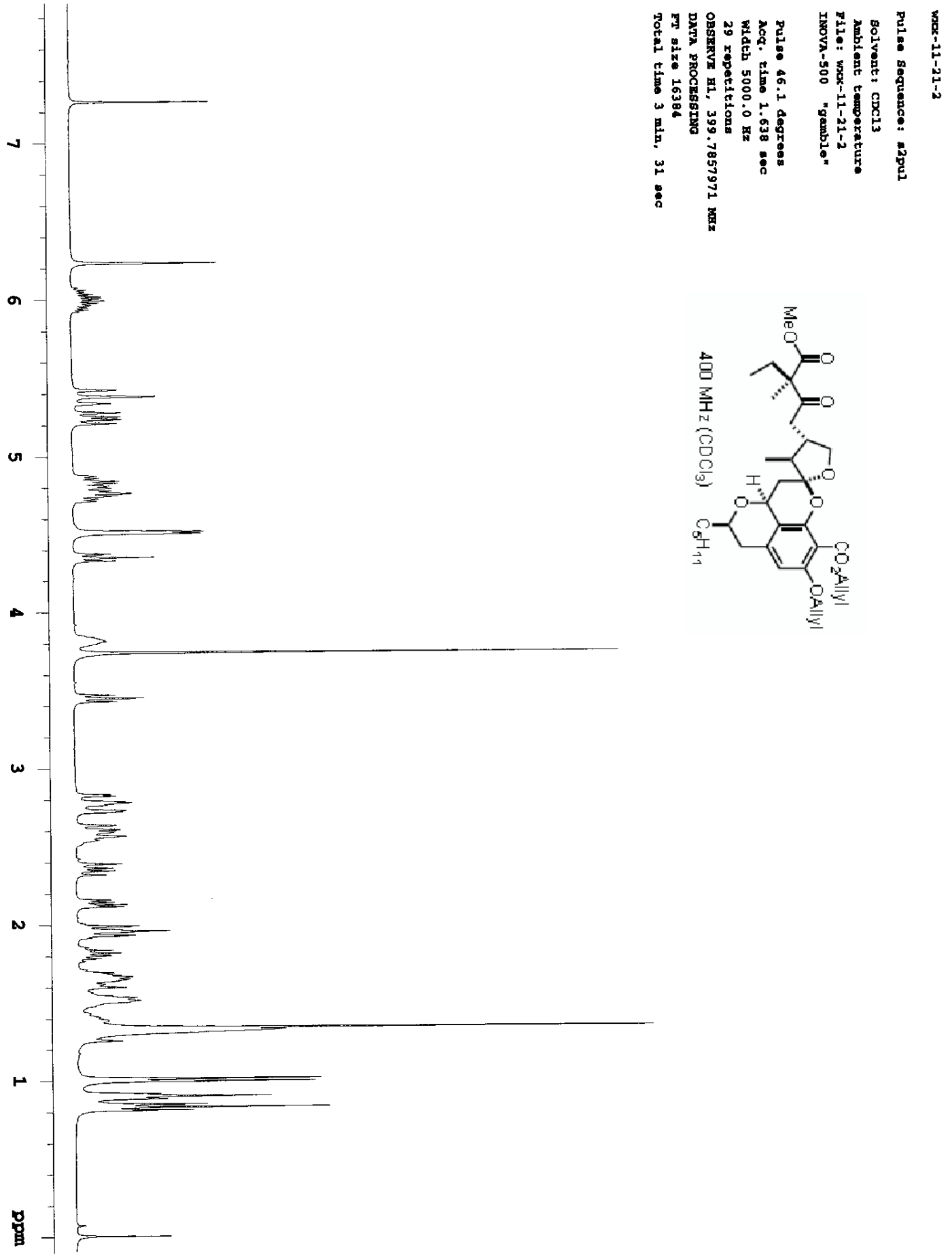
WXX-11-21-1C

INDEX	FREQUENCY	PPM	HEIGHT
1	20763.896	206.552	29.9
2	17436.717	173.454	19.7
3	16637.919	165.508	20.1
4	15637.706	155.558	31.4
5	14970.896	148.925	23.5
6	13654.826	135.833	35.4
7	13363.383	132.934	46.3
8	13290.141	132.206	31.3
9	11913.035	118.507	50.6
10	11776.469	117.148	54.9
11	11511.729	114.515	29.3
12	11023.448	109.657	17.2
13	10899.852	108.428	52.5
14	10494.731	104.398	50.9
15	7772.563	77.319	225.1
16	7740.519	77.000	233.0
17	7708.476	76.681	229.0
18	7572.673	75.330	56.2
19	7316.325	72.780	49.3
20	6975.291	69.388	74.0
21	6837.962	68.022	56.0
22	6602.977	65.684	65.7
23	6004.832	59.734	36.9
24	5265.544	52.380	57.1
25	4868.052	48.426	60.6
26	4225.657	42.035	60.1
27	3907.511	38.871	69.4
28	3648.875	36.298	63.5
29	3459.666	34.416	59.1
30	3456.614	34.385	64.8
31	3194.163	31.774	67.9
32	2800.486	27.858	55.8
33	2525.828	25.126	72.2
34	2272.532	22.606	76.3
35	1849.101	18.394	64.4
36	1410.411	14.030	62.2
37	1167.033	11.609	60.4
38	867.198	8.627	49.7

400 MHz ($CDCl_3$)




WZK-11-21-1
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858080 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
CO2Allyl
OAllyl
C5H11
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)


wxk-11-21-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wxk-11-21-2
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
29 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
MeO
O
O
O
H
O
C5H11
CO2Allyl
OAllyl
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm

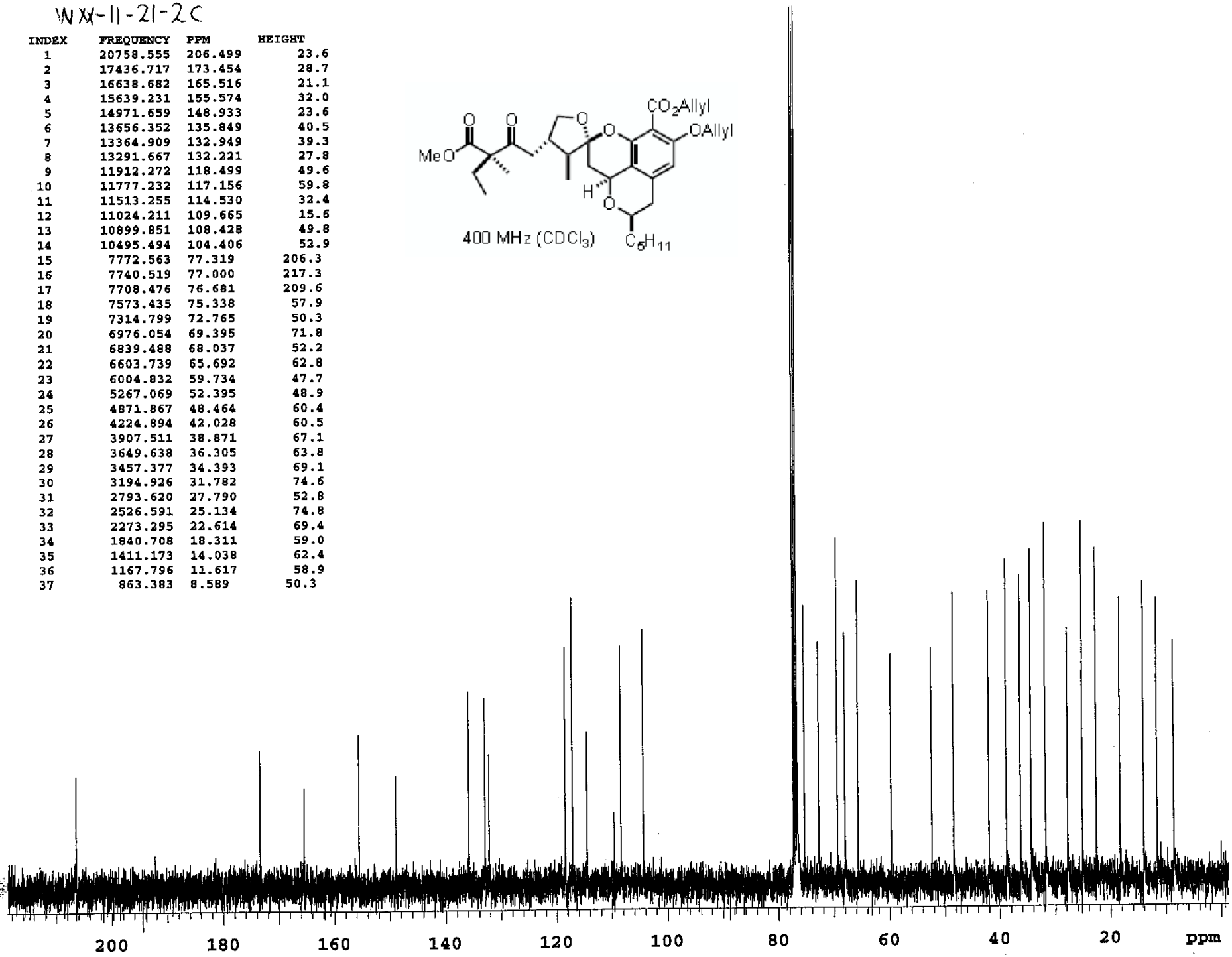
(-)-Berkelic Acid

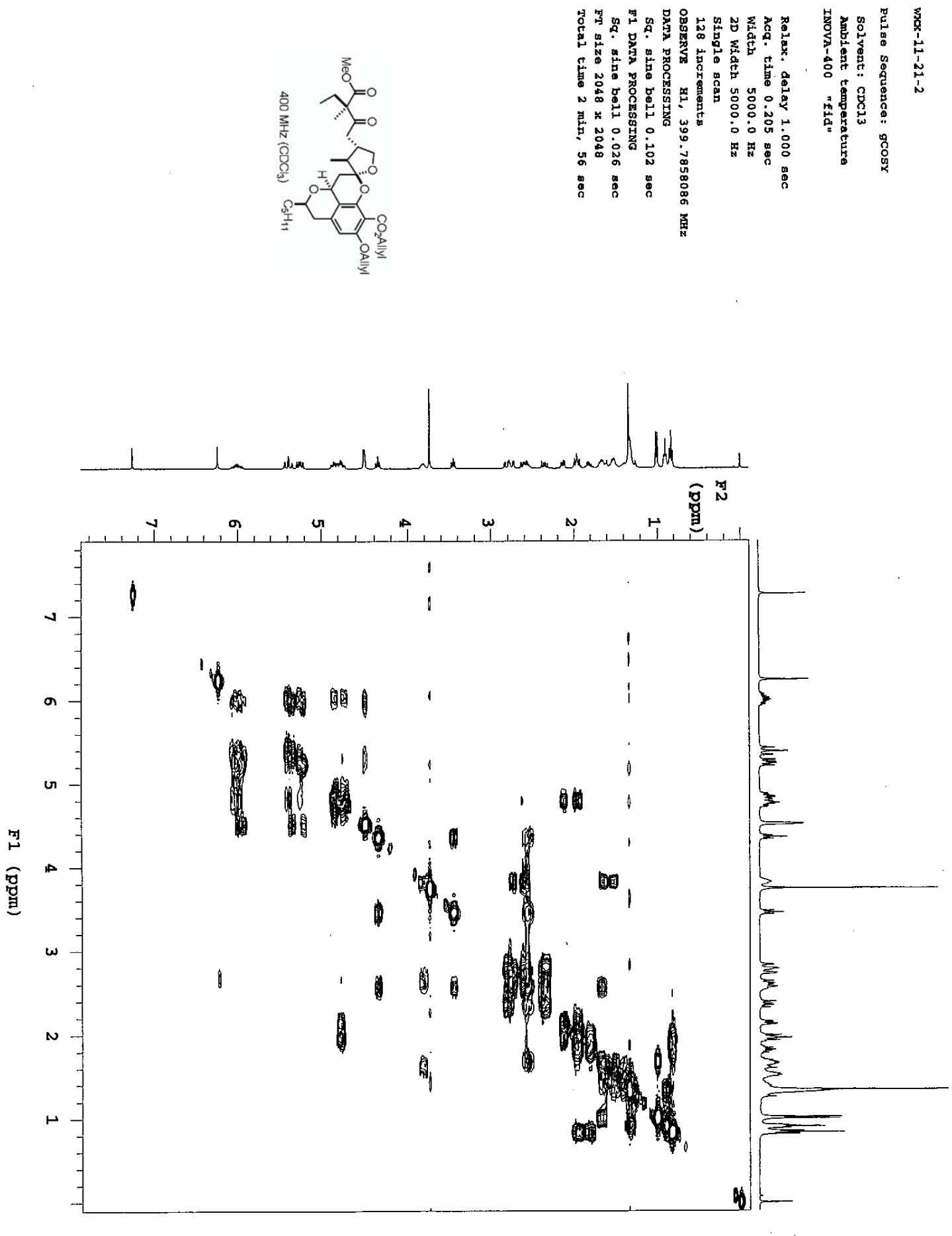
Wu, Zhou, and Snider

WX-11-21-2C

INDEX	FREQUENCY	PPM	HEIGHT
1	20758.555	206.499	23.6
2	17436.717	173.454	28.7
3	16638.682	165.516	21.1
4	15639.231	155.574	32.0
5	14971.659	148.933	23.6
6	13656.352	135.849	40.5
7	13364.909	132.949	39.3
8	13291.667	132.221	27.8
9	11912.272	118.499	49.6
10	11777.232	117.156	59.8
11	11513.255	114.530	32.4
12	11024.211	109.665	15.6
13	10899.851	108.428	49.8
14	10495.494	104.406	52.9
15	7772.563	77.319	206.3
16	7740.519	77.000	217.3
17	7708.476	76.681	209.6
18	7573.435	75.338	57.9
19	7314.799	72.765	50.3
20	6976.054	69.395	71.8
21	6839.488	68.037	52.2
22	6603.739	65.692	62.8
23	6004.832	59.734	47.7
24	5267.069	52.395	48.9
25	4871.867	48.464	60.4
26	4224.894	42.028	60.5
27	3907.511	38.871	67.1
28	3649.638	36.305	63.8
29	3457.377	34.393	69.1
30	3194.926	31.782	74.6
31	2793.620	27.790	52.8
32	2526.591	25.134	74.8
33	2273.295	22.614	69.4
34	1840.708	18.311	59.0
35	1411.173	14.038	62.4
36	1167.796	11.617	58.9
37	863.383	8.589	50.3

400 MHz ($CDCl_3$)



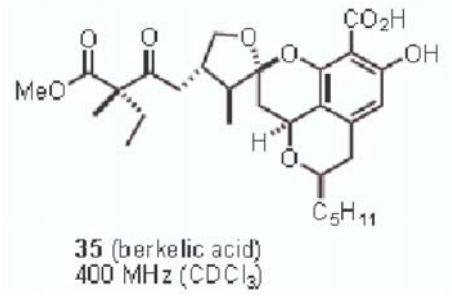

WSK-11-21-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858086 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
CO2Allyl
OAllyl
C5H11
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-11-23-5

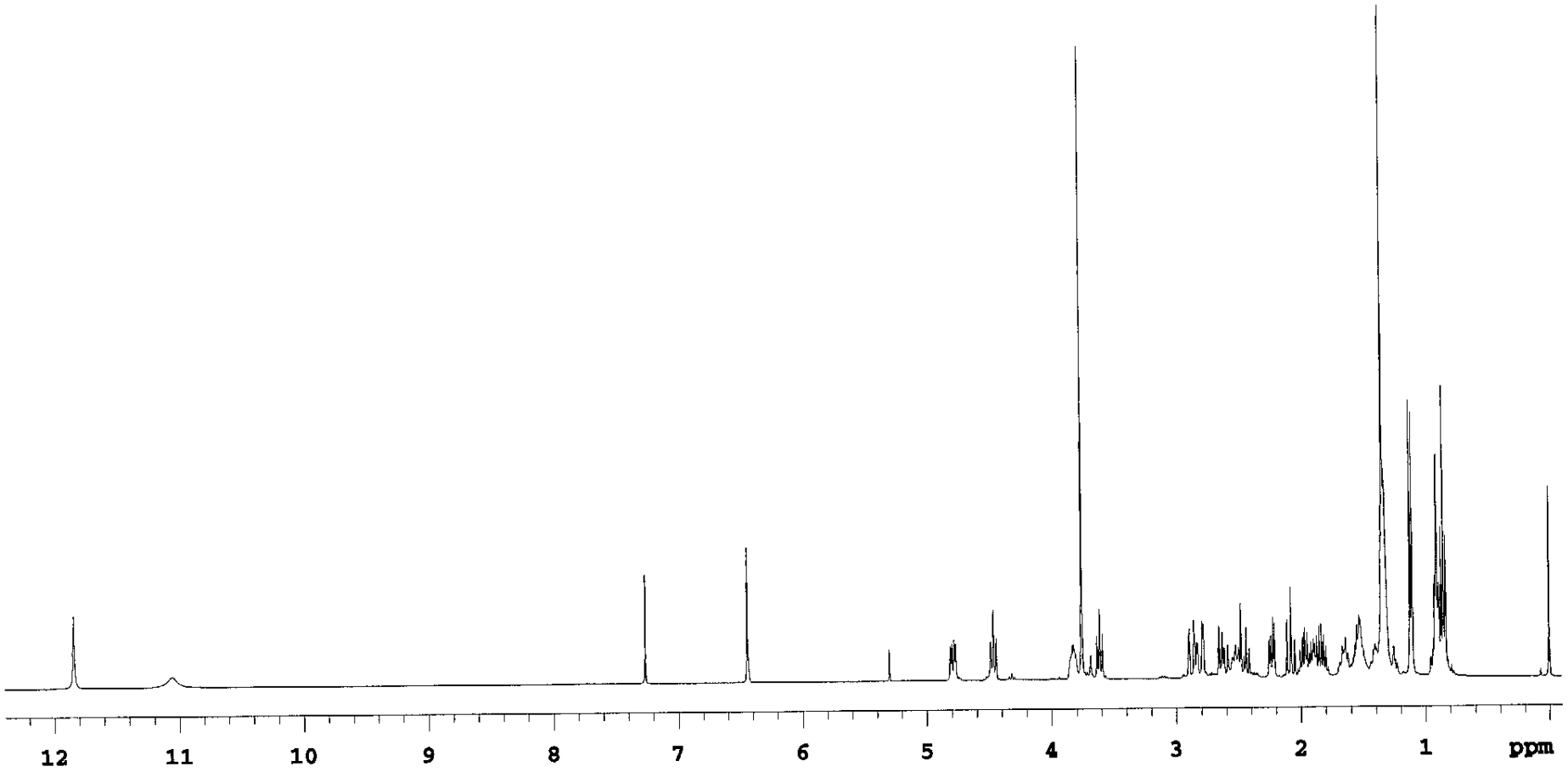
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-11-23-5
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 8000.0 Hz
31 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 31 sec



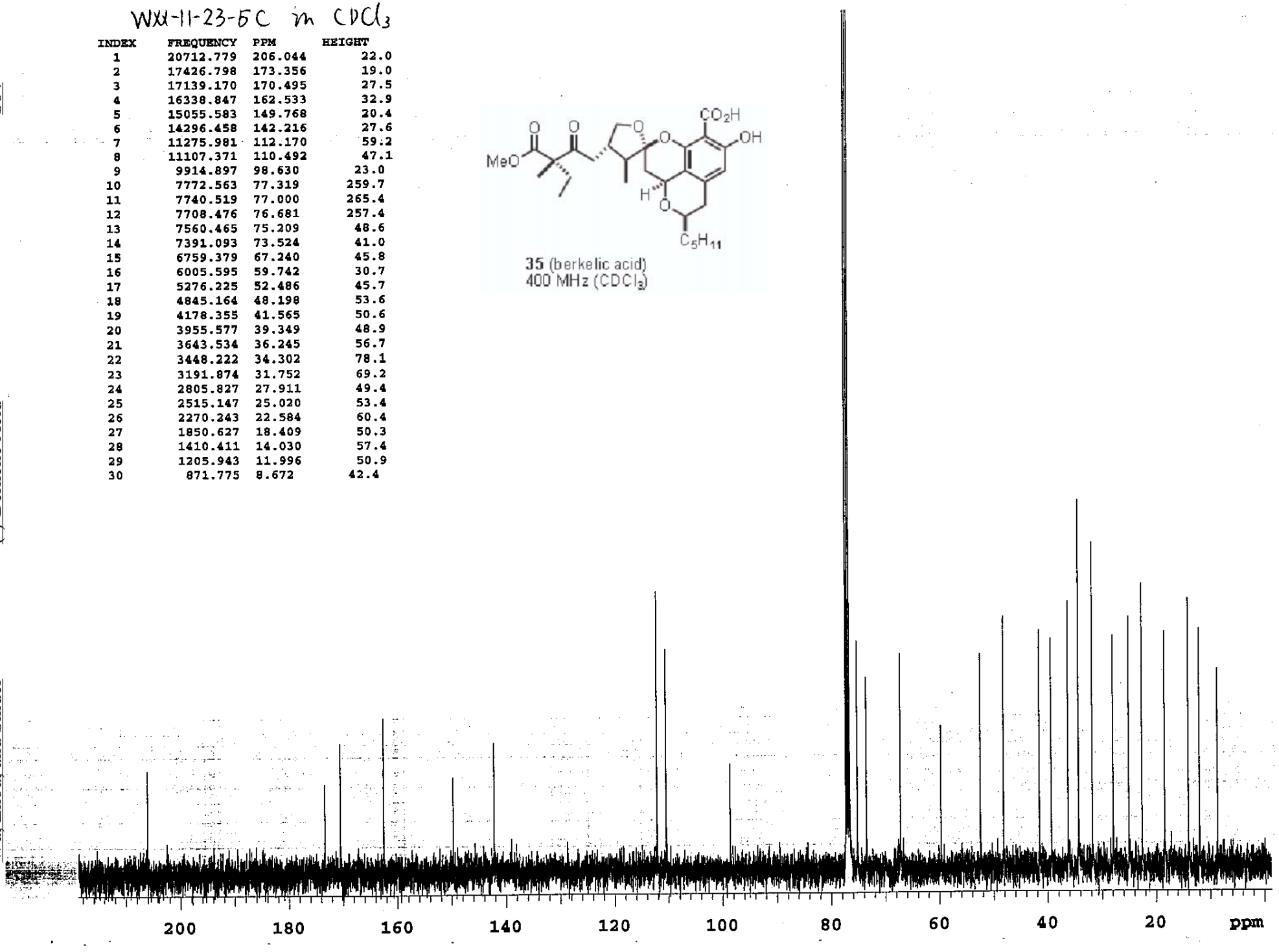
35 (berkelic acid)
400 MHz ($CDCl_3$)

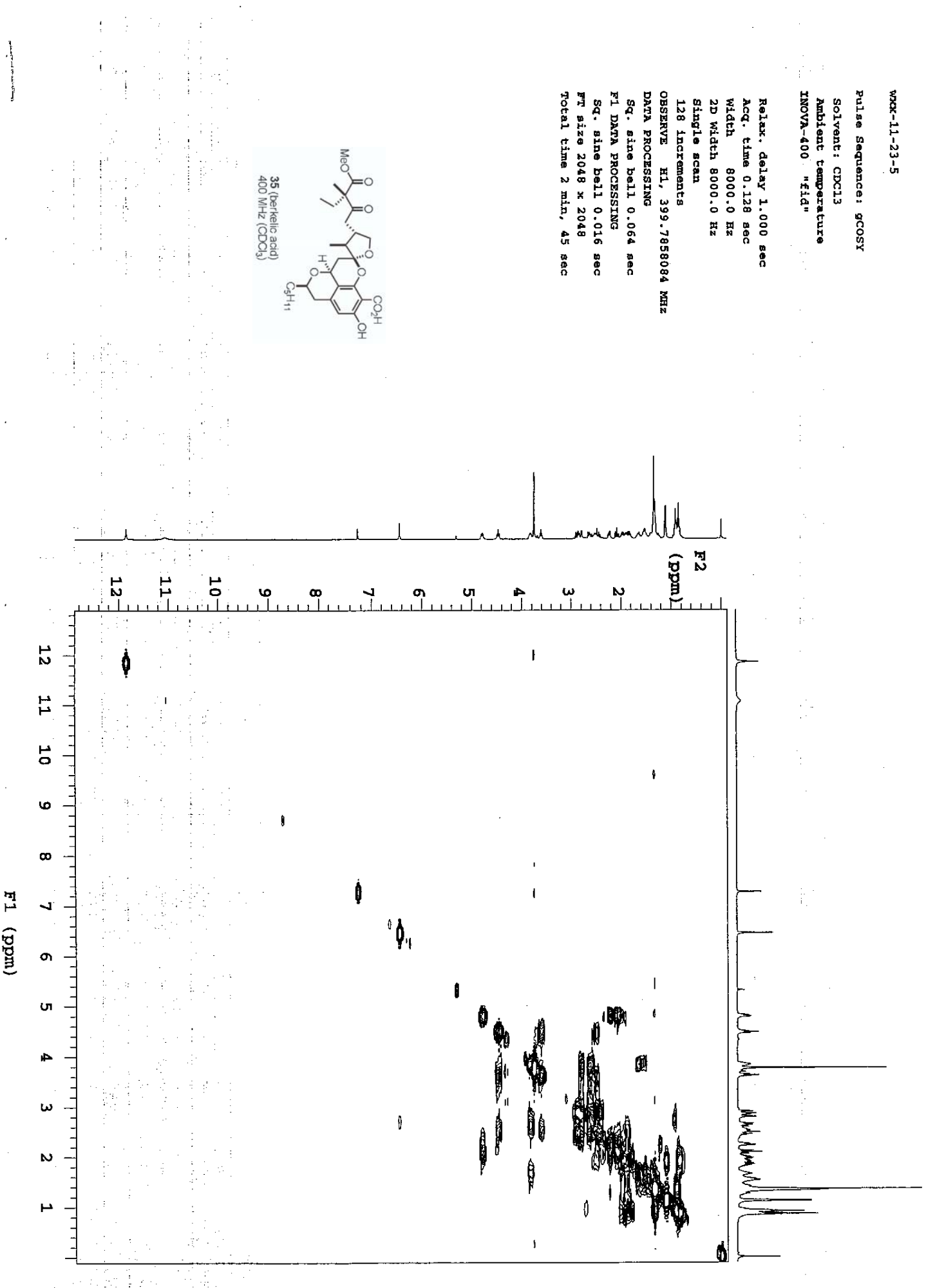


WXL-11-23-5C in $CDCl_3$

INDEX	FREQUENCY	PPM	HEIGHT
1	20712.779	206.044	22.0
2	17426.798	173.356	19.0
3	17139.170	170.495	27.5
4	16338.847	162.533	32.9
5	15055.583	149.768	20.4
6	14296.458	142.216	27.6
7	11275.981	112.170	59.2
8	11107.371	110.492	47.1
9	9914.897	98.630	23.0
10	7772.563	77.319	259.7
11	7740.519	77.000	265.4
12	7708.476	76.681	257.4
13	7560.465	75.209	48.6
14	7391.093	73.524	41.0
15	6759.379	67.240	45.8
16	6005.595	59.742	30.7
17	5276.225	52.486	45.7
18	4845.164	48.198	53.6
19	4178.355	41.565	50.6
20	3955.577	39.349	48.9
21	3643.534	36.245	56.7
22	3448.222	34.302	78.1
23	3191.874	31.752	69.2
24	2805.827	27.911	49.4
25	2515.147	25.020	53.4
26	2270.243	22.584	60.4
27	1850.627	18.409	50.3
28	1410.411	14.030	57.4
29	1205.943	11.996	50.9
30	871.775	8.672	42.4

35 (berkelic acid)
400 MHz ($CDCl_3$)



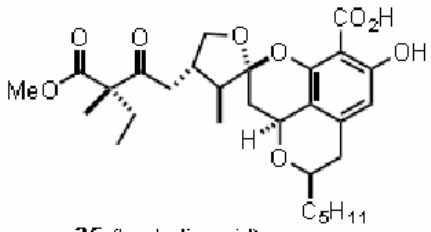

wzk-11-23-5
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858084 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
35 (berkelic acid)
400 MHz (CDCl3)
MeO
CO2H
OH
C5H11
F2 (ppm)
F1 (ppm)

wox-11-23-5-CD3OD – 500 M

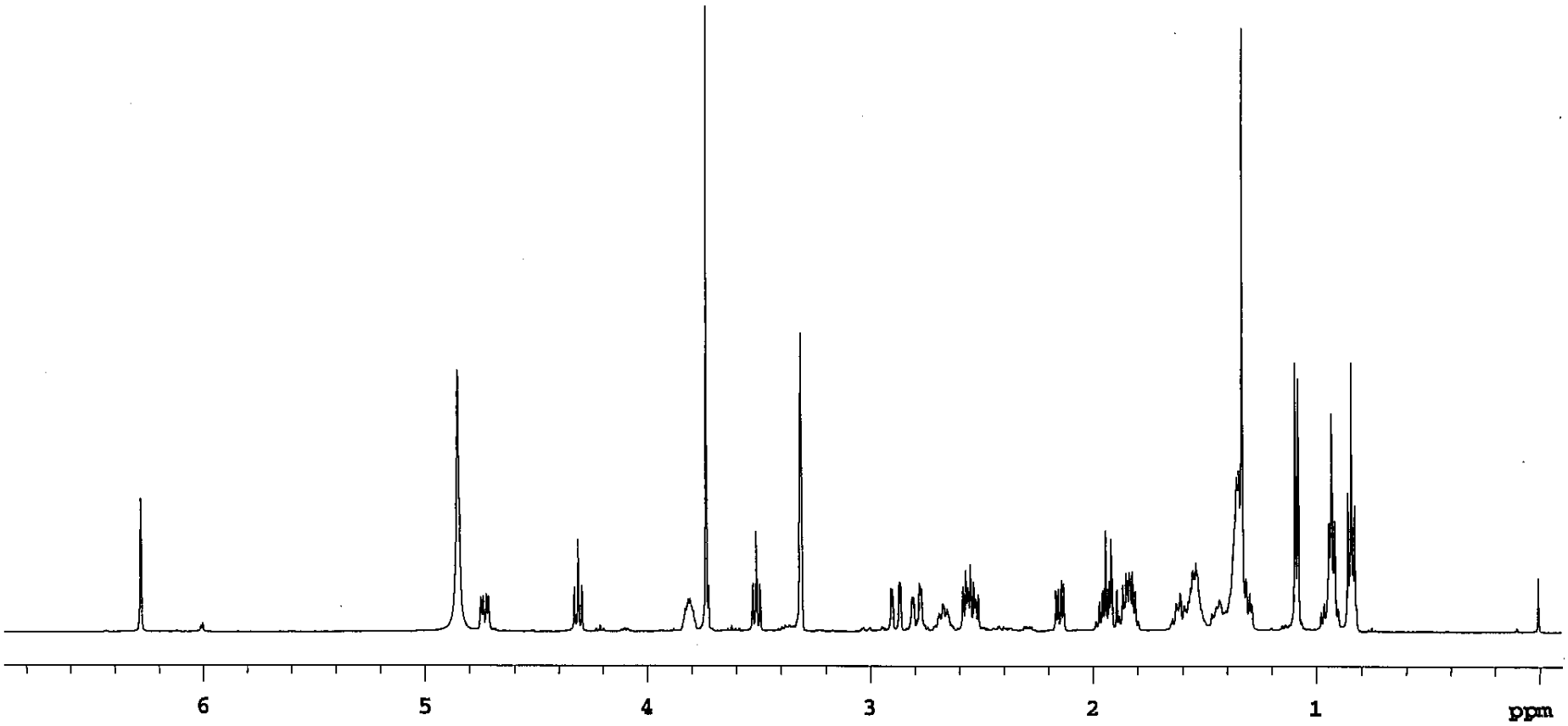
Pulse Sequence: s2pul

Solvent: CD3OD
Temp. 25.0 C / 298.1 K
File: wox-11-23-5-CD3OD
INOVA-500 "echo"

Pulse 47.4 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
66 repetitions
OBSERVE H1, 499.8040886 MHz
DATA PROCESSING
FT size 32768
Total time 4 min, 3 sec

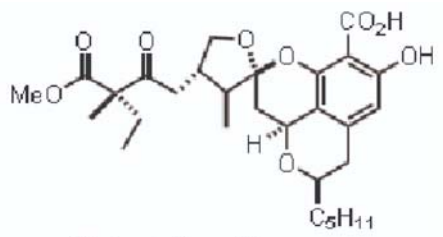


35 (berkelic acid)
500 MHz (CD_3OD)

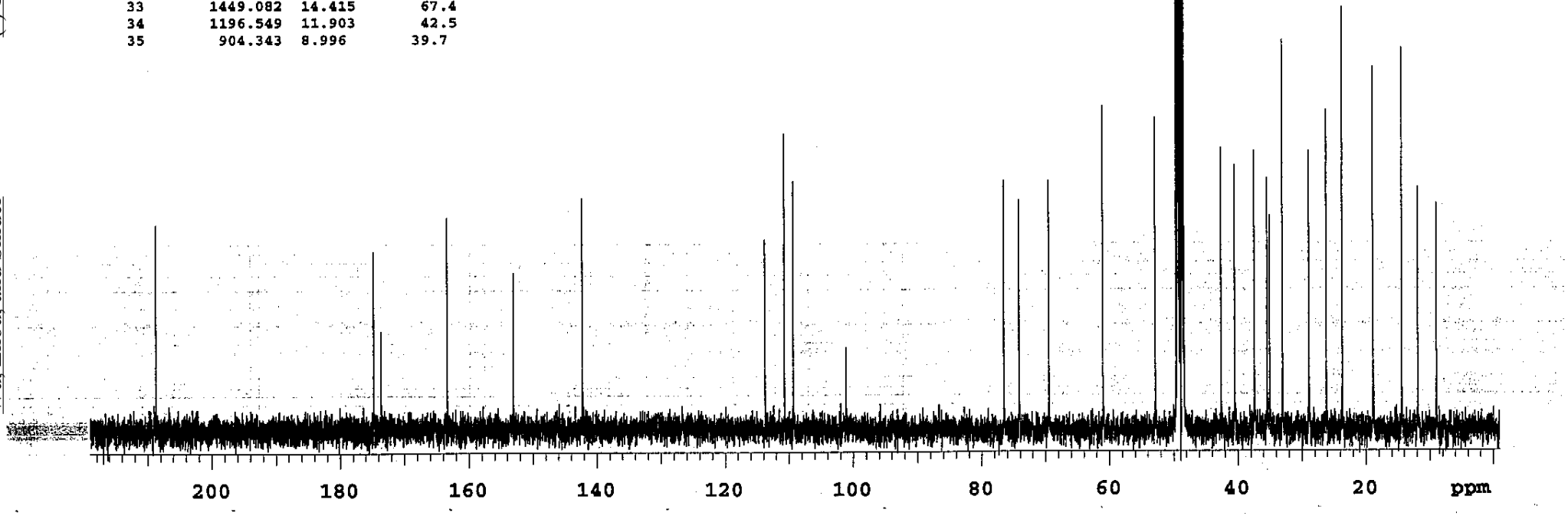


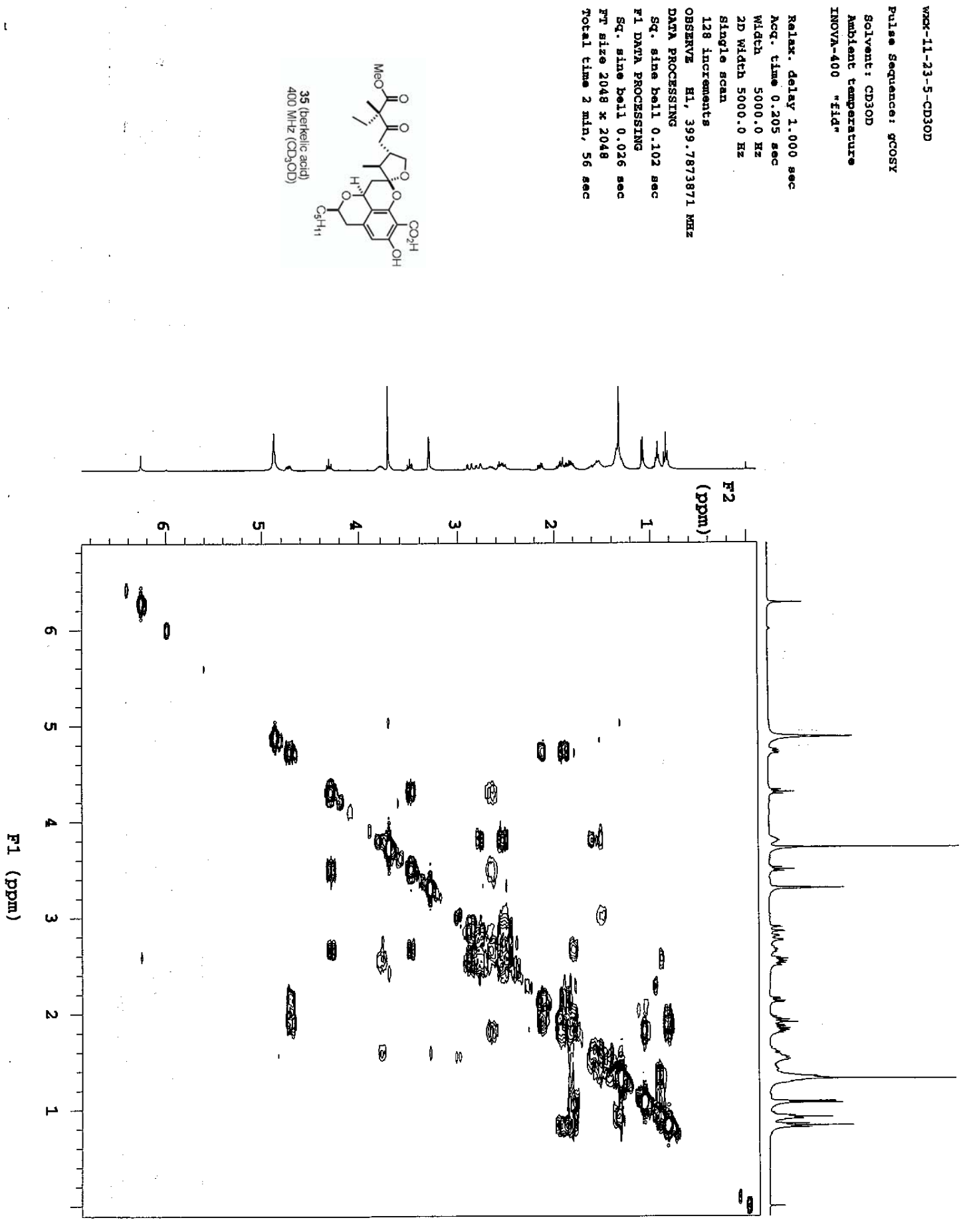
WXX-11-23-5- CD_3OD-C

INDEX	FREQUENCY	PPM	HEIGHT
1	20989.487	208.796	36.3
2	17575.333	174.833	31.6
3	17457.078	173.657	17.4
4	16424.058	163.380	37.6
5	15387.986	153.074	27.7
6	14303.086	142.282	40.9
7	11435.960	113.761	33.6
8	11131.547	110.732	52.2
9	10993.455	109.359	43.8
10	10167.954	101.147	14.3
11	7695.267	76.550	43.8
12	7455.705	74.167	40.4
13	6985.734	69.491	43.8
14	6135.056	61.029	57.1
15	5313.371	52.855	55.0
16	4989.884	49.638	349.0
17	4968.522	49.425	1186.2
18	4947.160	49.213	2434.1
19	4925.797	49.000	2529.8
20	4904.435	48.787	2206.7
21	4883.073	48.575	1207.1
22	4861.710	48.362	362.7
23	4284.165	42.617	49.7
24	4069.016	40.477	46.6
25	3762.315	37.426	49.0
26	3562.424	35.438	44.2
27	3521.226	35.028	37.7
28	3321.336	33.039	68.9
29	2904.771	28.896	49.1
30	2631.638	26.179	56.3
31	2382.920	23.704	74.7
32	1899.979	18.900	64.0
33	1449.082	14.415	67.4
34	1196.549	11.903	42.5
35	904.343	8.996	39.7

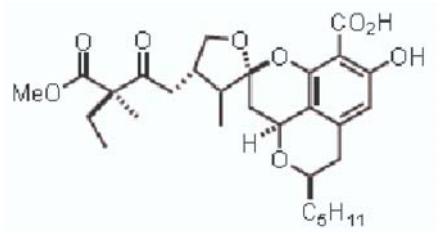


35 (berkelic acid)
400 MHz (CD_3OD)

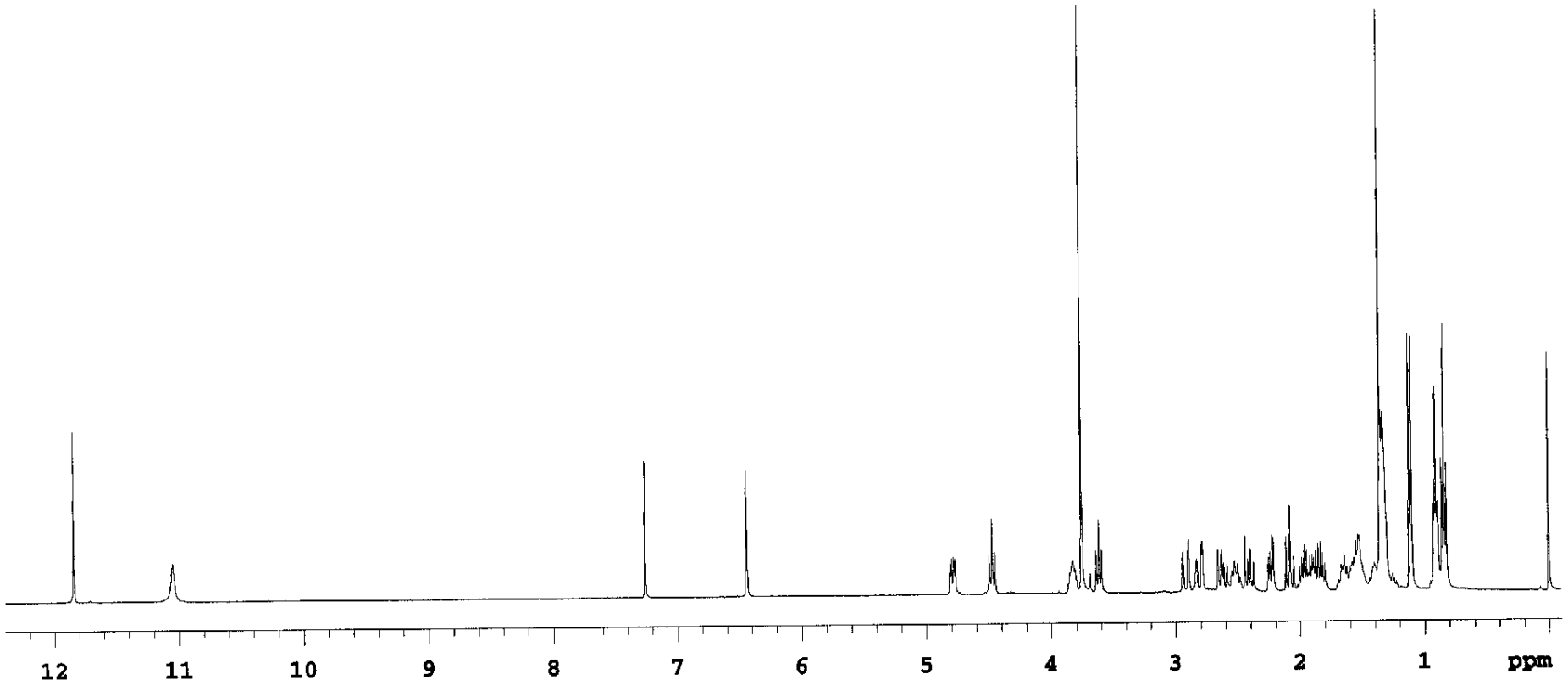



wzk-11-23-5-CD3OD
Pulse Sequence: gCOSY
Solvent: CD3OD
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
single scan
128 increments
OBSERVE H1, 399.7873871 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
35 (berkelic acid)
400 MHz (CD3OD)
F2 (ppm)
F1 (ppm)

```
wxx-11-23-6

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
File: wxx-11-23-6
INOVA-500  "gamble"

 Pulse 46.1 degrees
 Acq. time 1.638 sec
 Width 8000.0 Hz
 18 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 31 sec
```



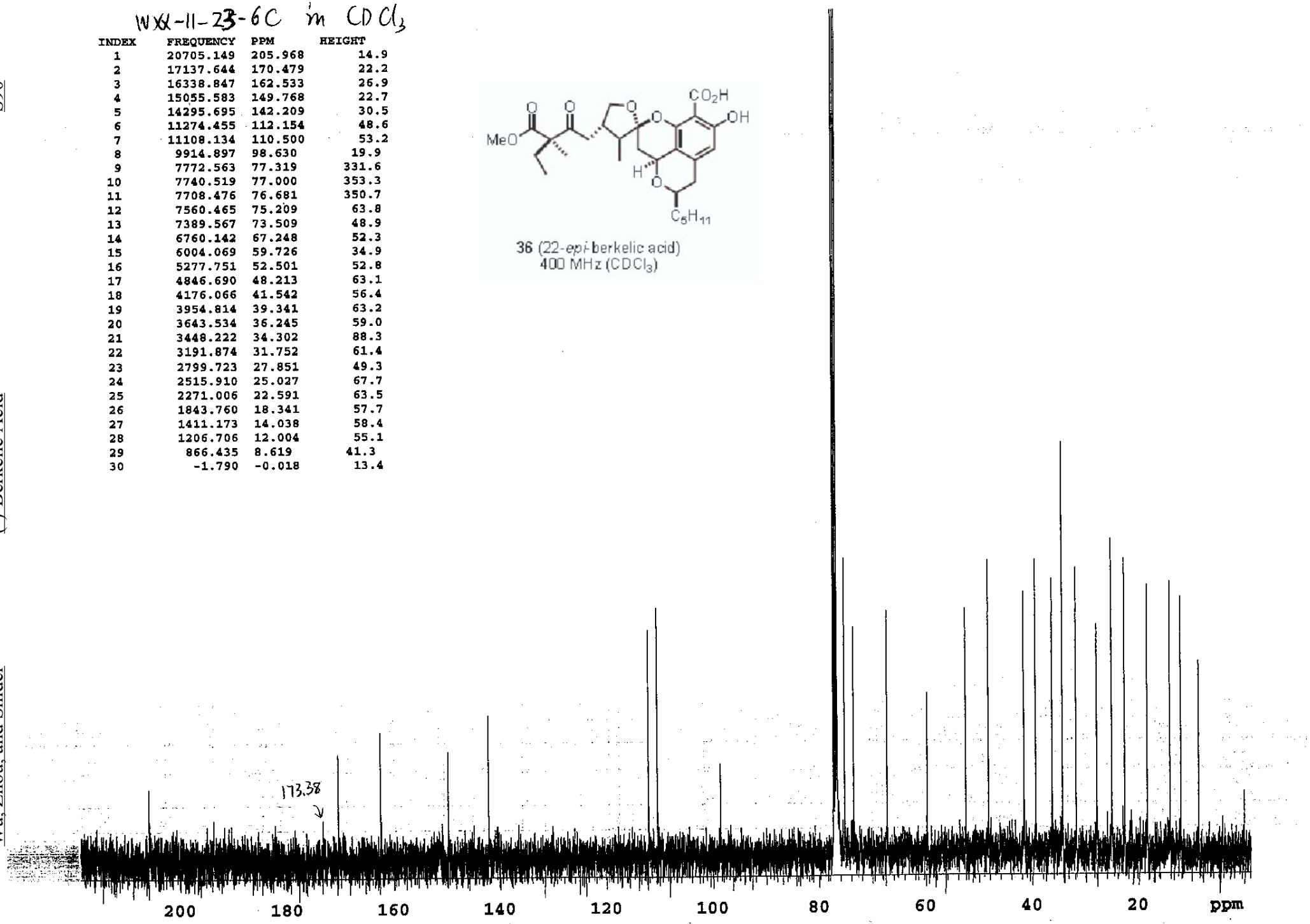
36 (22-*epi*-berkelic acid)
400 MHz ($CDCl_3$)

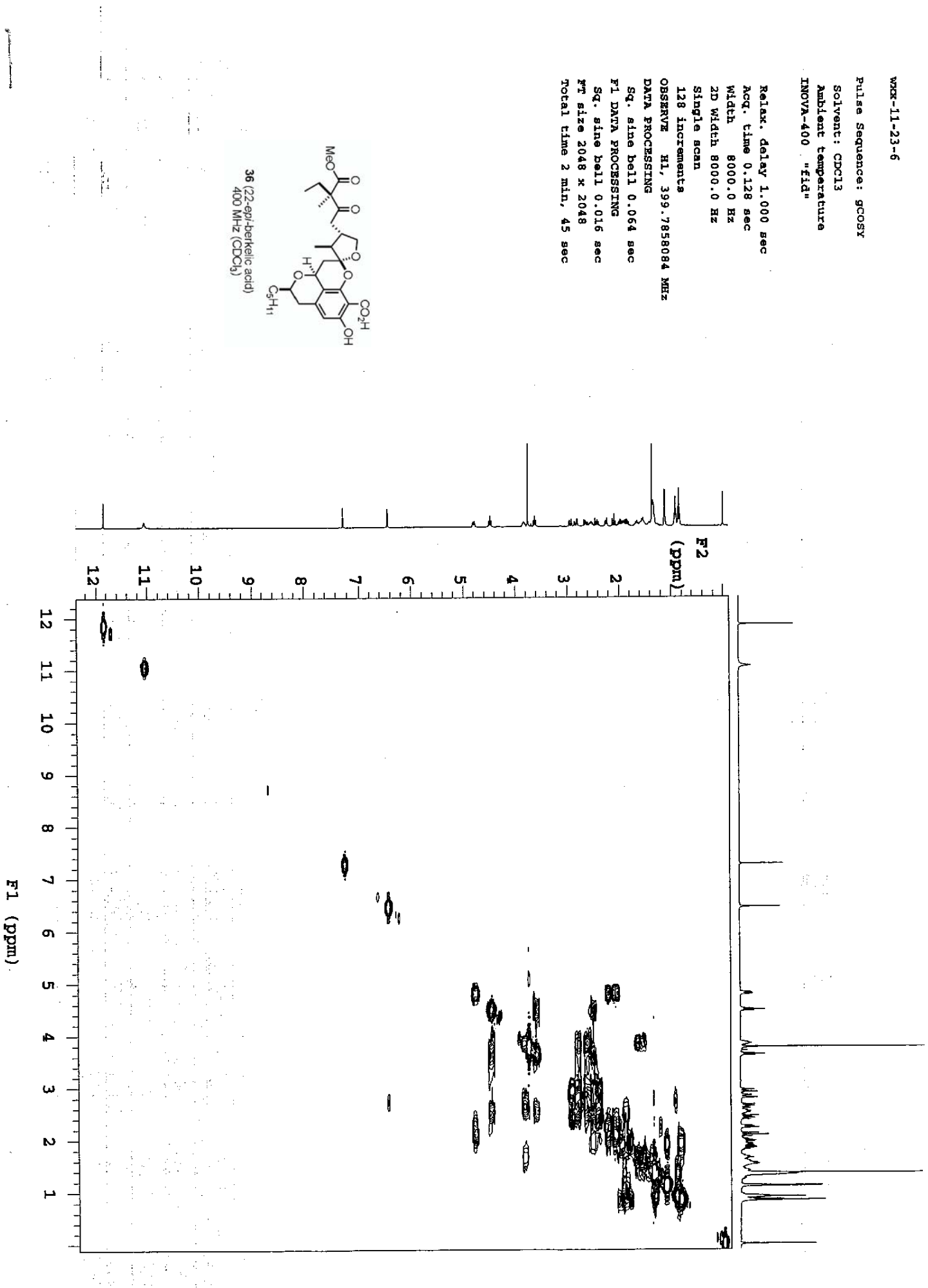


WXX-11-23-6C in $CDCl_3$

INDEX	FREQUENCY	PPM	HEIGHT
1	20705.149	205.968	14.9
2	17137.644	170.479	22.2
3	16338.847	162.533	26.9
4	15055.583	149.768	22.7
5	14295.695	142.209	30.5
6	11274.455	112.154	48.6
7	11108.134	110.500	53.2
8	9914.897	98.630	19.9
9	7772.563	77.319	331.6
10	7740.519	77.000	353.3
11	7708.476	76.681	350.7
12	7560.465	75.209	63.8
13	7389.567	73.509	48.9
14	6760.142	67.248	52.3
15	6004.069	59.726	34.9
16	5277.751	52.501	52.8
17	4846.690	48.213	63.1
18	4176.066	41.542	56.4
19	3954.814	39.341	63.2
20	3643.534	36.245	59.0
21	3448.222	34.302	88.3
22	3191.874	31.752	61.4
23	2799.723	27.851	49.3
24	2515.910	25.027	67.7
25	2271.006	22.591	63.5
26	1843.760	18.341	57.7
27	1411.173	14.038	58.4
28	1206.706	12.004	55.1
29	866.435	8.619	41.3
30	-1.790	-0.018	13.4

36 (22-*epi*-berkelic acid)
400 MHz ($CDCl_3$)



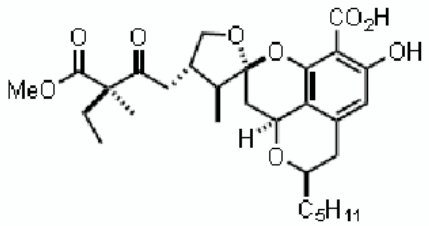

WXK-11-23-6
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 8000.0 Hz
2D width 8000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858084 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
36 (22-epi-berkelic acid)
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-11-23-6-CD3OD – 500M

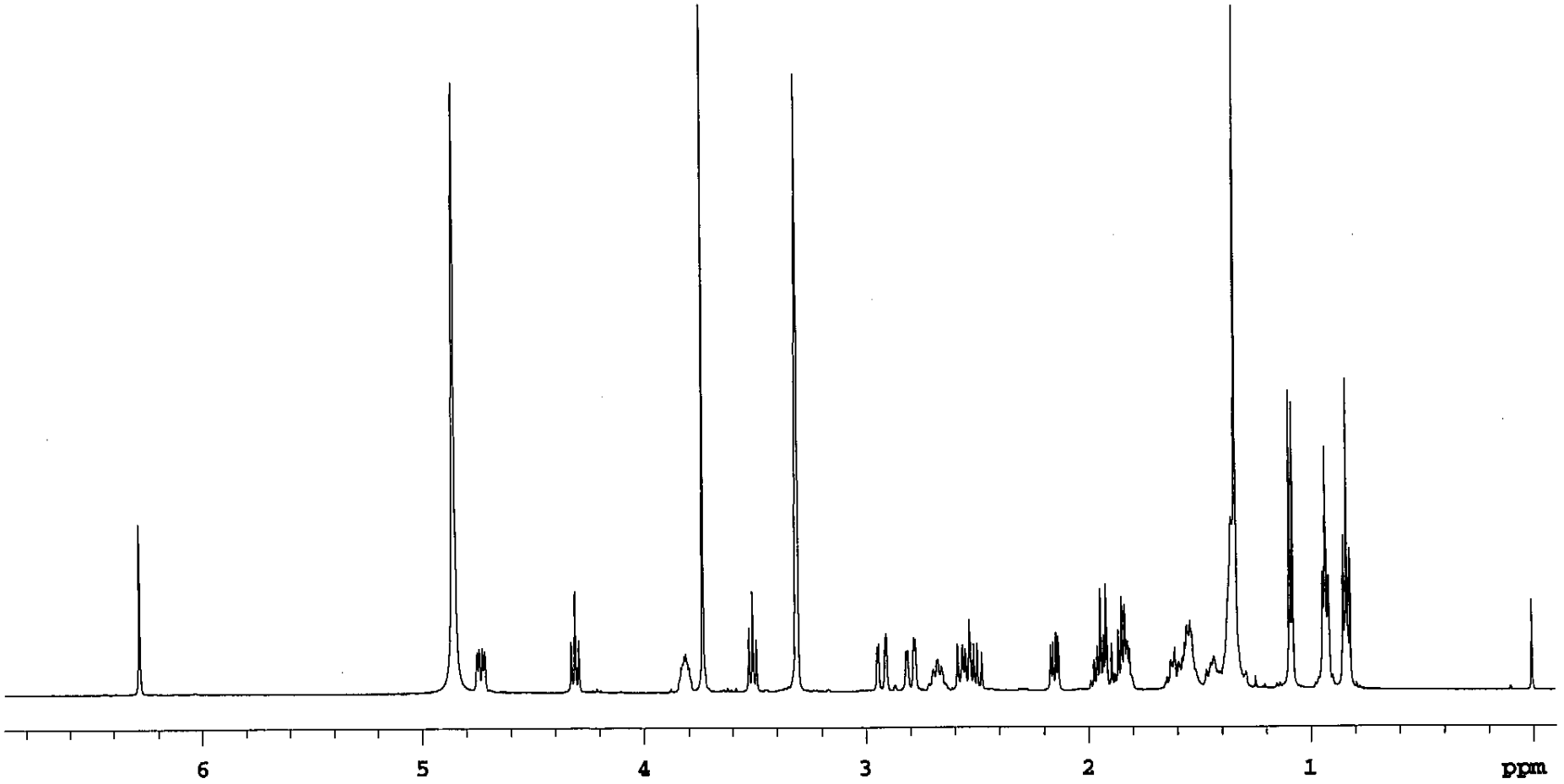
Pulse Sequence: s2pul

Solvent: CD3OD
Temp. 25.0 C / 298.1 K
INOVA-500 "echo"

Pulse 47.4 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
28 repetitions
OBSERVE H1, 499.8040901 MHz
DATA PROCESSING
FT size 32768
Total time 4 min, 3 sec



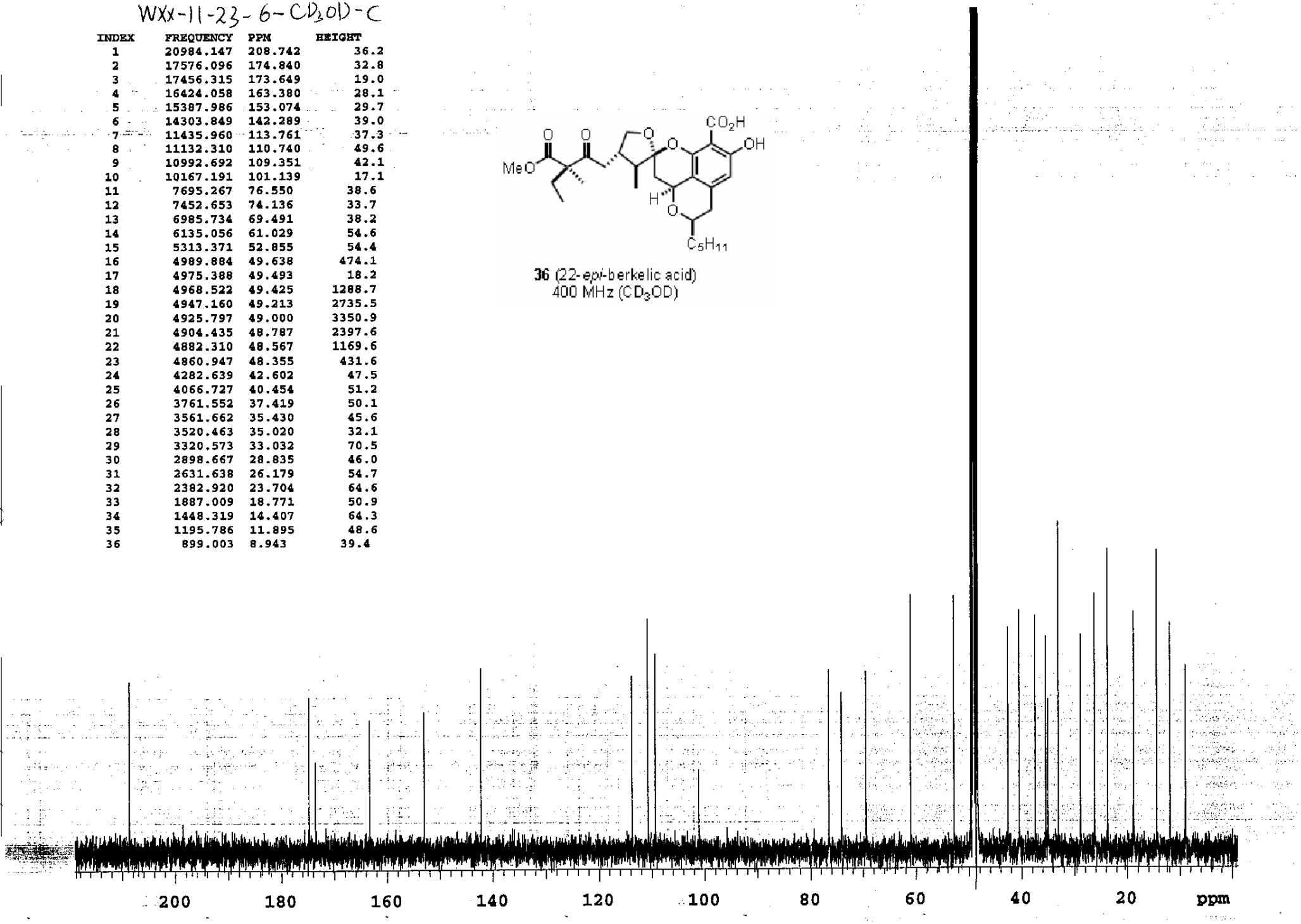
36 (22-*epi*-berkelic acid)
500 MHz (CD_3OD)



WXx-11-23-6-CD_3OD-C

INDEX	FREQUENCY	PPM	HEIGHT
1	20984.147	208.742	36.2
2	17576.096	174.840	32.8
3	17456.315	173.649	19.0
4	16424.058	163.380	28.1
5	15387.986	153.074	29.7
6	14303.849	142.289	39.0
7	11435.960	113.761	37.3
8	11132.310	110.740	49.6
9	10992.692	109.351	42.1
10	10167.191	101.139	17.1
11	7695.267	76.550	38.6
12	7452.653	74.136	33.7
13	6985.734	69.491	38.2
14	6135.056	61.029	54.6
15	5313.371	52.855	54.4
16	4989.884	49.638	474.1
17	4975.388	49.493	18.2
18	4968.522	49.425	1288.7
19	4947.160	49.213	2735.5
20	4925.797	49.000	3350.9
21	4904.435	48.787	2397.6
22	4882.310	48.567	1169.6
23	4860.947	48.355	431.6
24	4282.639	42.602	47.5
25	4066.727	40.454	51.2
26	3761.552	37.419	50.1
27	3561.662	35.430	45.6
28	3520.463	35.020	32.1
29	3320.573	33.032	70.5
30	2898.667	28.835	46.0
31	2631.638	26.179	54.7
32	2382.920	23.704	64.6
33	1887.009	18.771	50.9
34	1448.319	14.407	64.3
35	1195.786	11.895	48.6
36	899.003	8.943	39.4

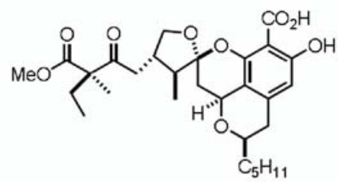
36 (22-*epi*-berkelic acid)
400 MHz (CD_3OD)



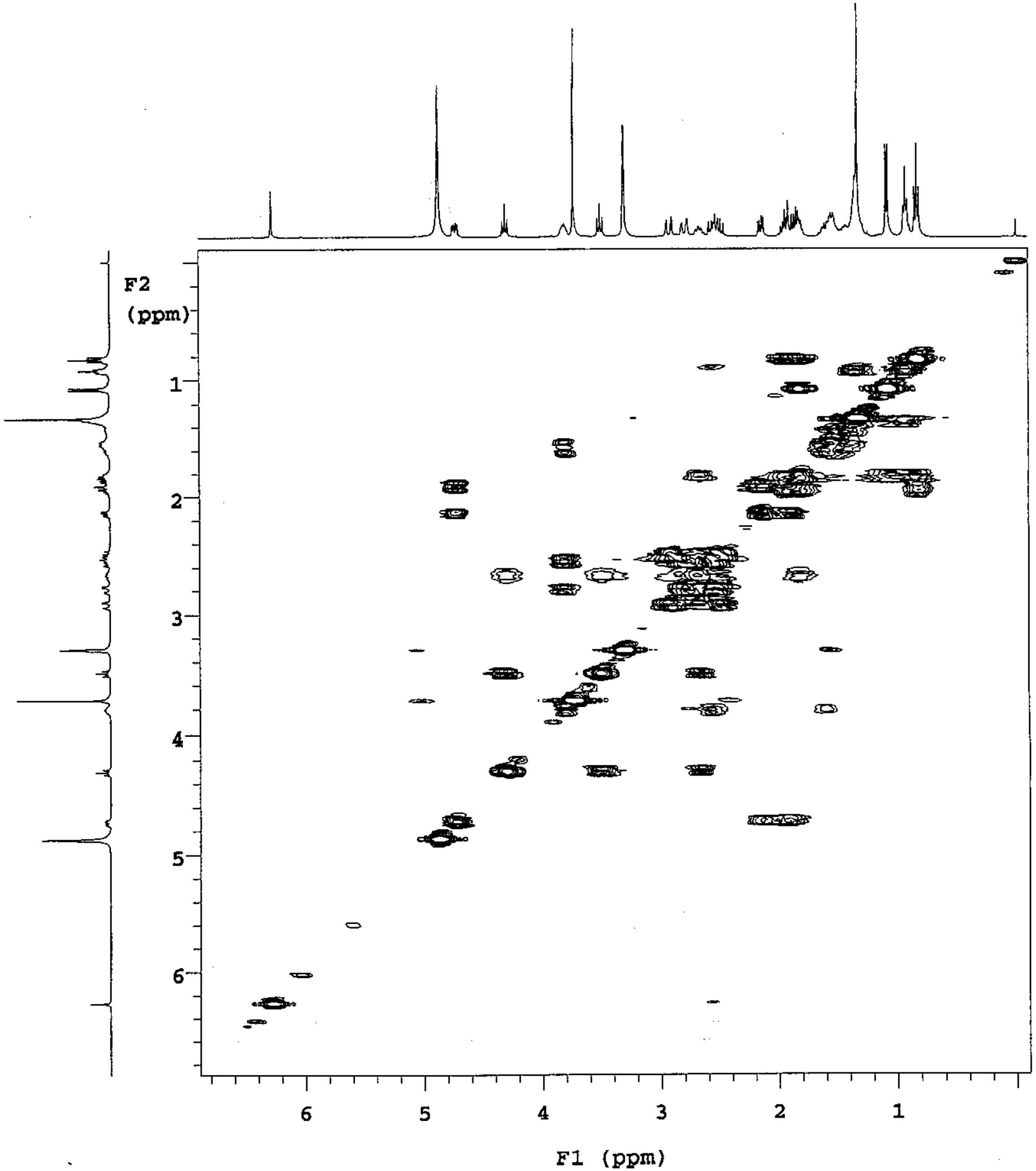
wxx-11-23-6-CD3OD

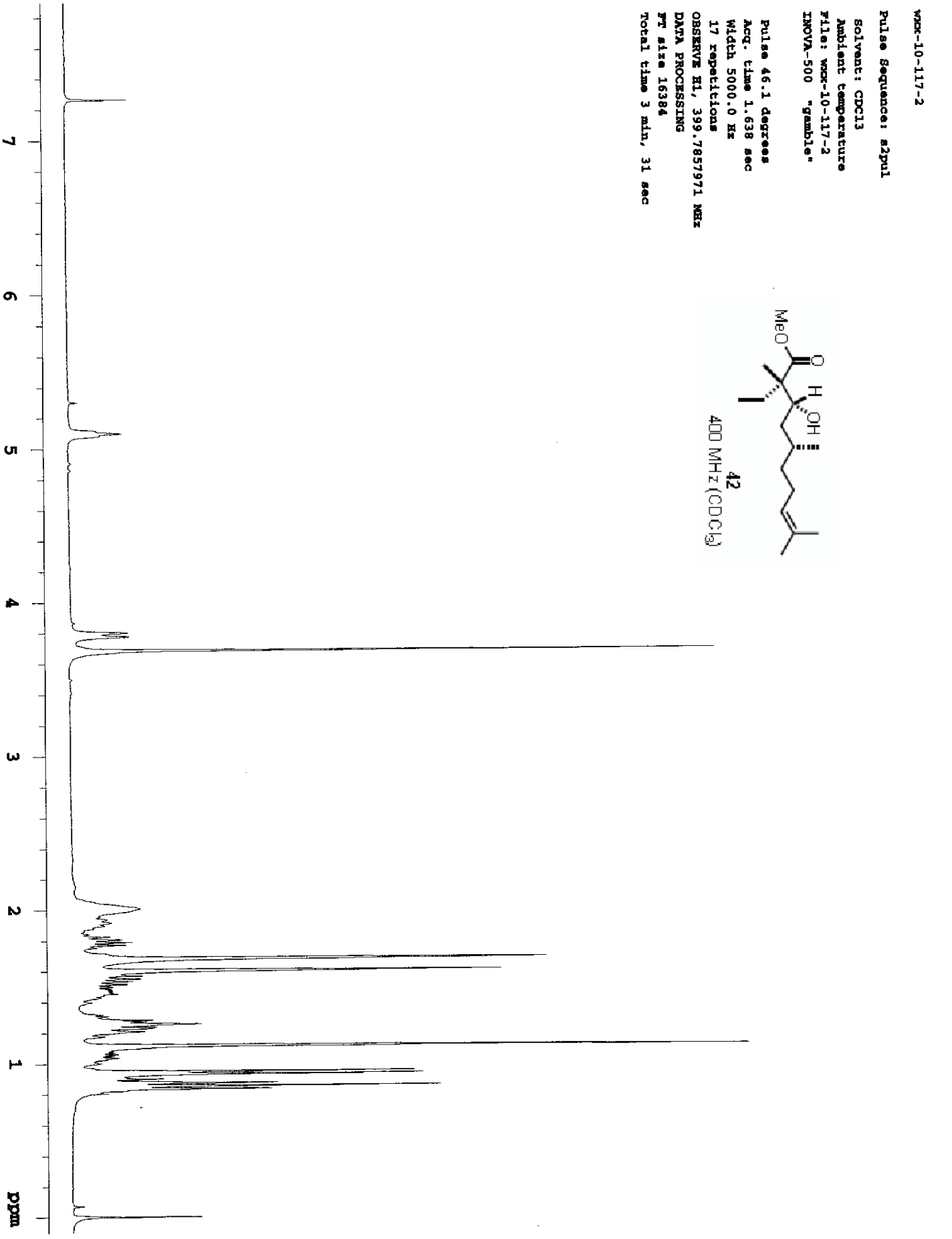
Pulse Sequence: gCOSY
Solvent: CD3OD
Ambient temperature
INOVA-400 "fid"

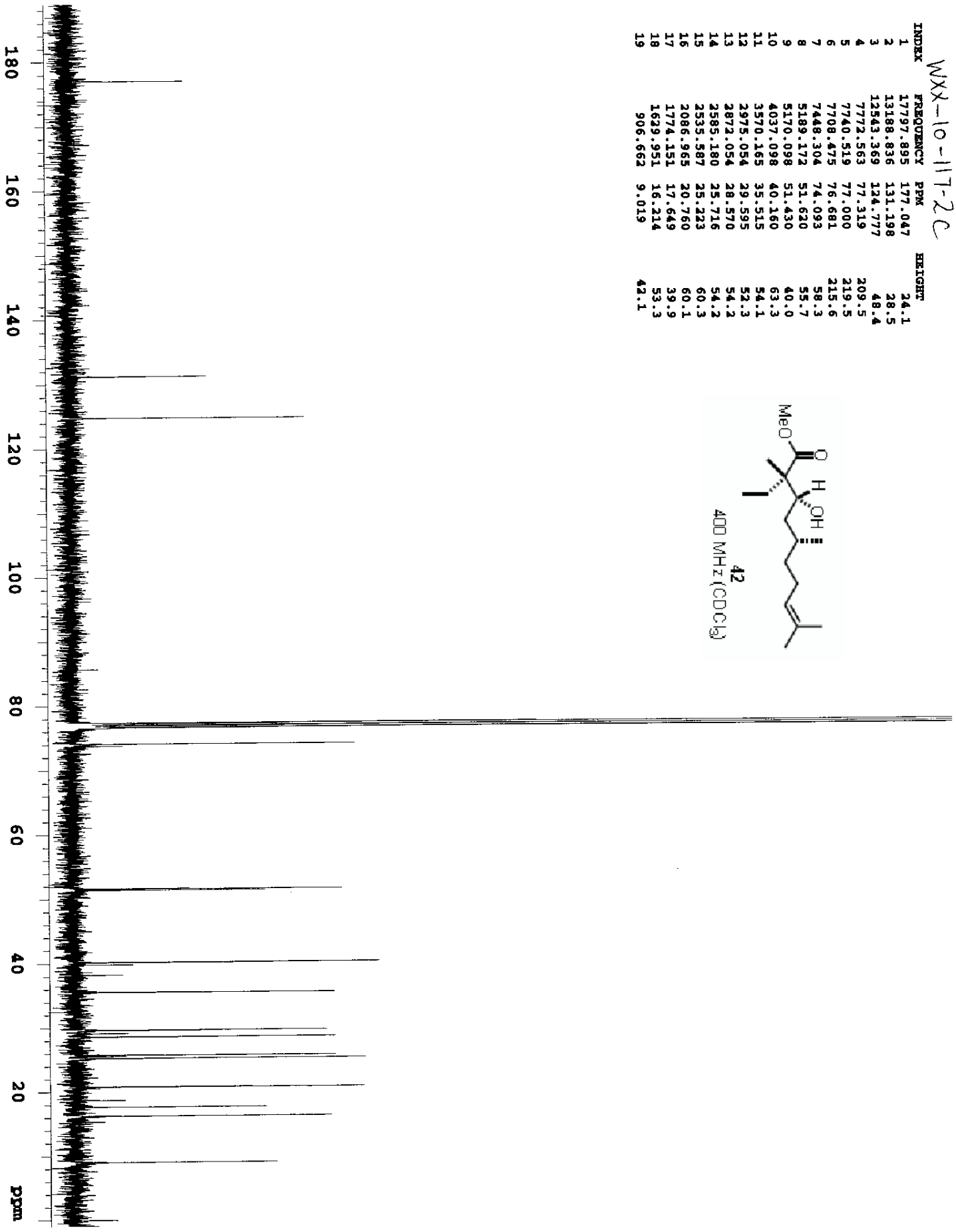
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7873871 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec

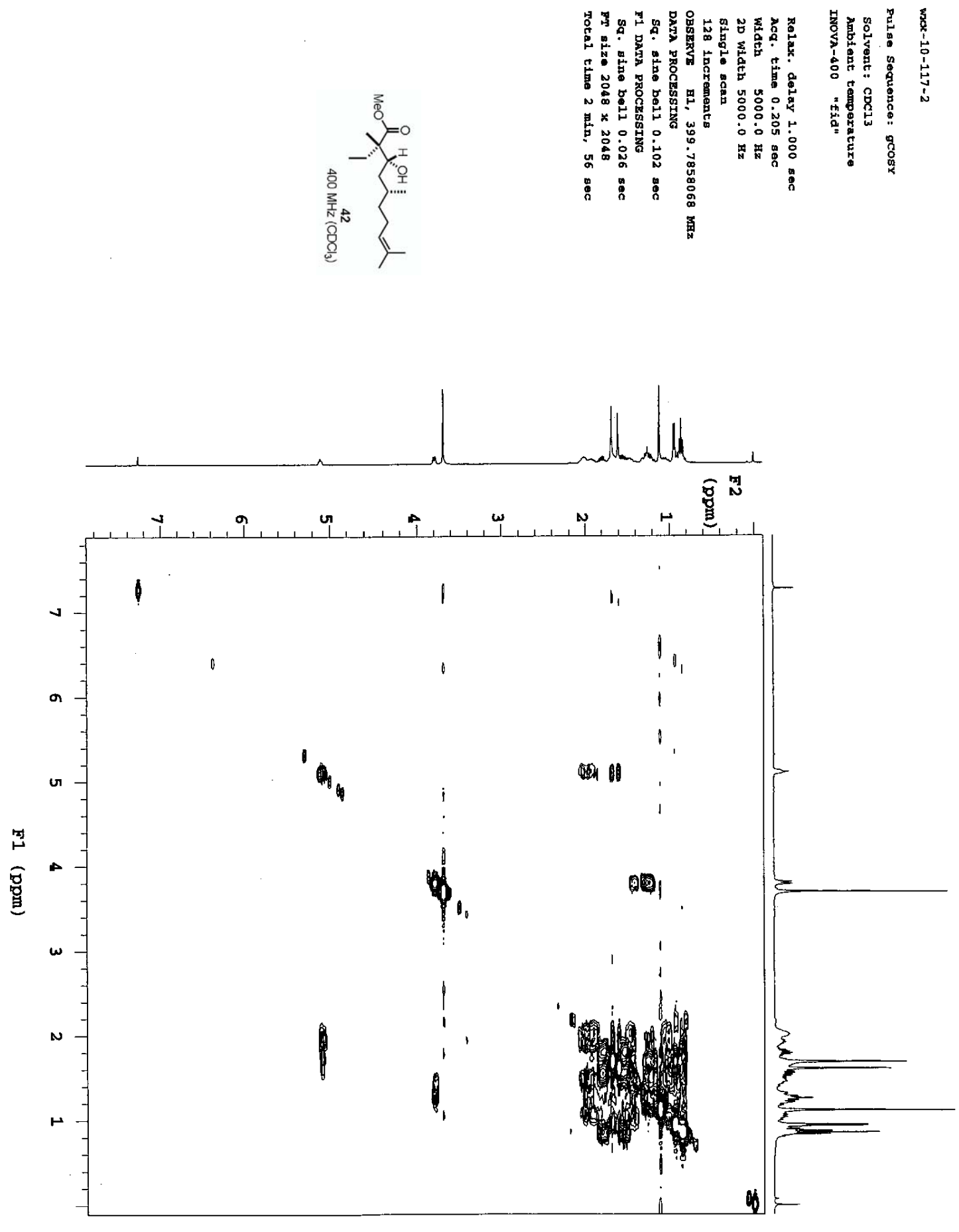


36 (22-*epi*-berkelic acid)
400 MHz (CD_3OD)




wzk-10-117-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-10-117-2
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
17 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
MeO
O
H
OH
42
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm


WXX-10-117-2C
INDEX FREQUENCY PPM HEIGHT
1 17797.895 177.047 24.1
2 13188.836 131.198 28.5
3 12543.369 124.777 48.4
4 7772.563 77.319 209.5
5 7740.519 77.000 219.5
6 7708.475 76.681 215.6
7 7448.304 74.093 58.3
8 5189.172 51.620 55.7
9 5170.098 51.430 40.0
10 4037.098 40.160 63.3
11 3570.165 35.515 54.1
12 2975.054 29.595 52.3
13 2872.054 28.570 54.2
14 2585.180 25.716 54.2
15 2535.587 25.223 60.3
16 2086.965 20.760 60.1
17 1774.151 17.649 39.9
18 1629.951 16.214 53.3
19 906.662 9.019 42.1
MeO
O
H
OH
42
400 MHz (CDCl3)
180
160
140
120
100
80
60
40
20
ppm

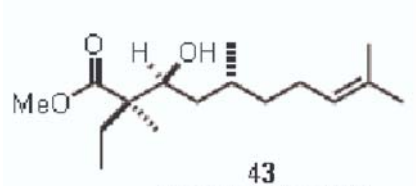

wsx-10-117-2
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858068 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
O
H
OH
42
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-10-129-6

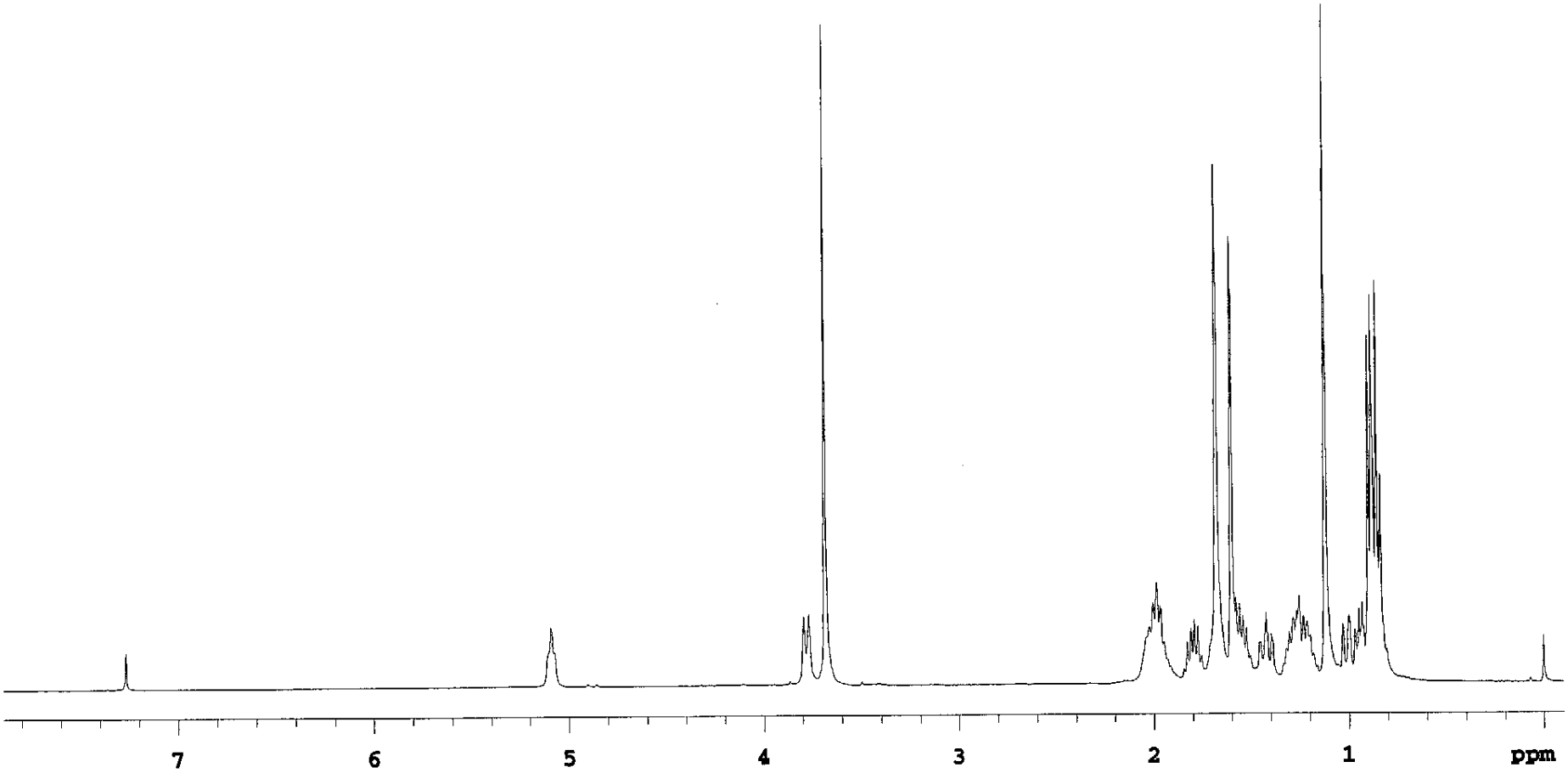
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-10-129-6
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
22 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

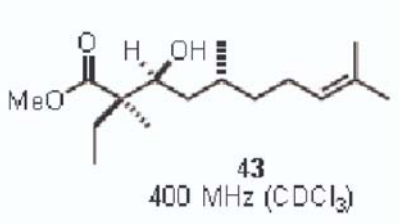


43
400 MHz ($CDCl_3$)

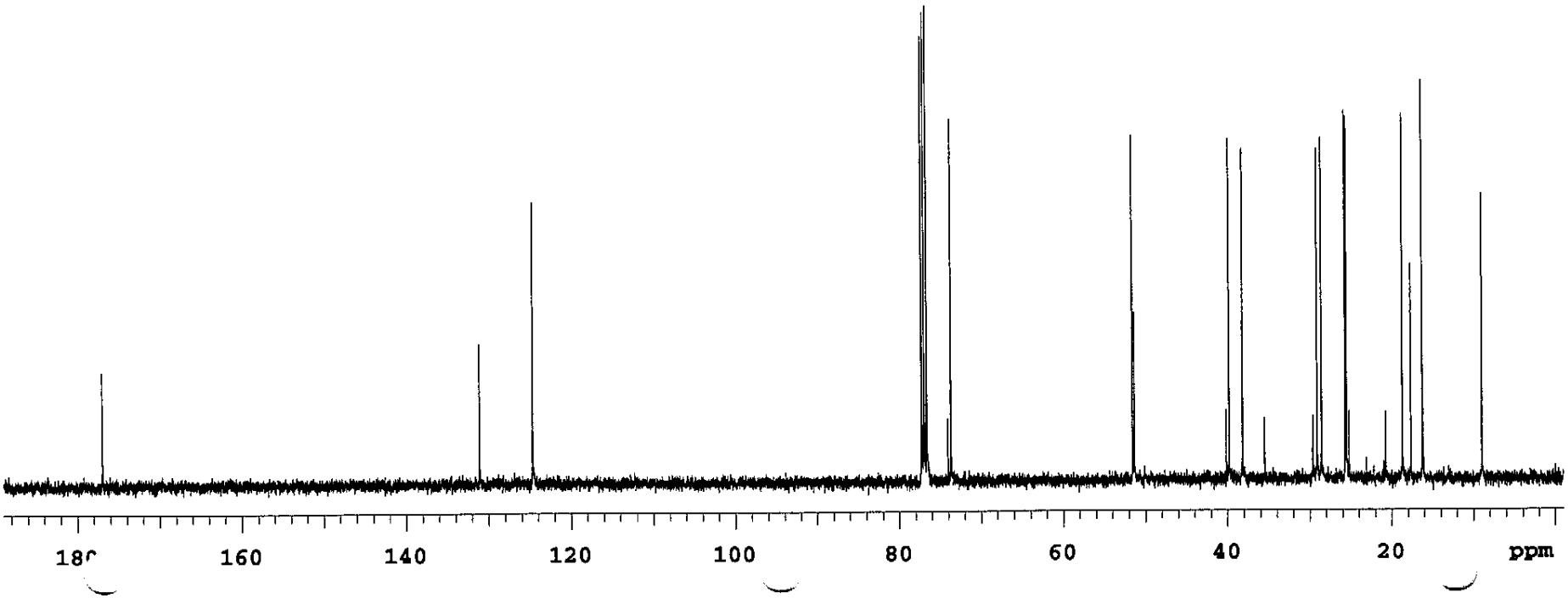


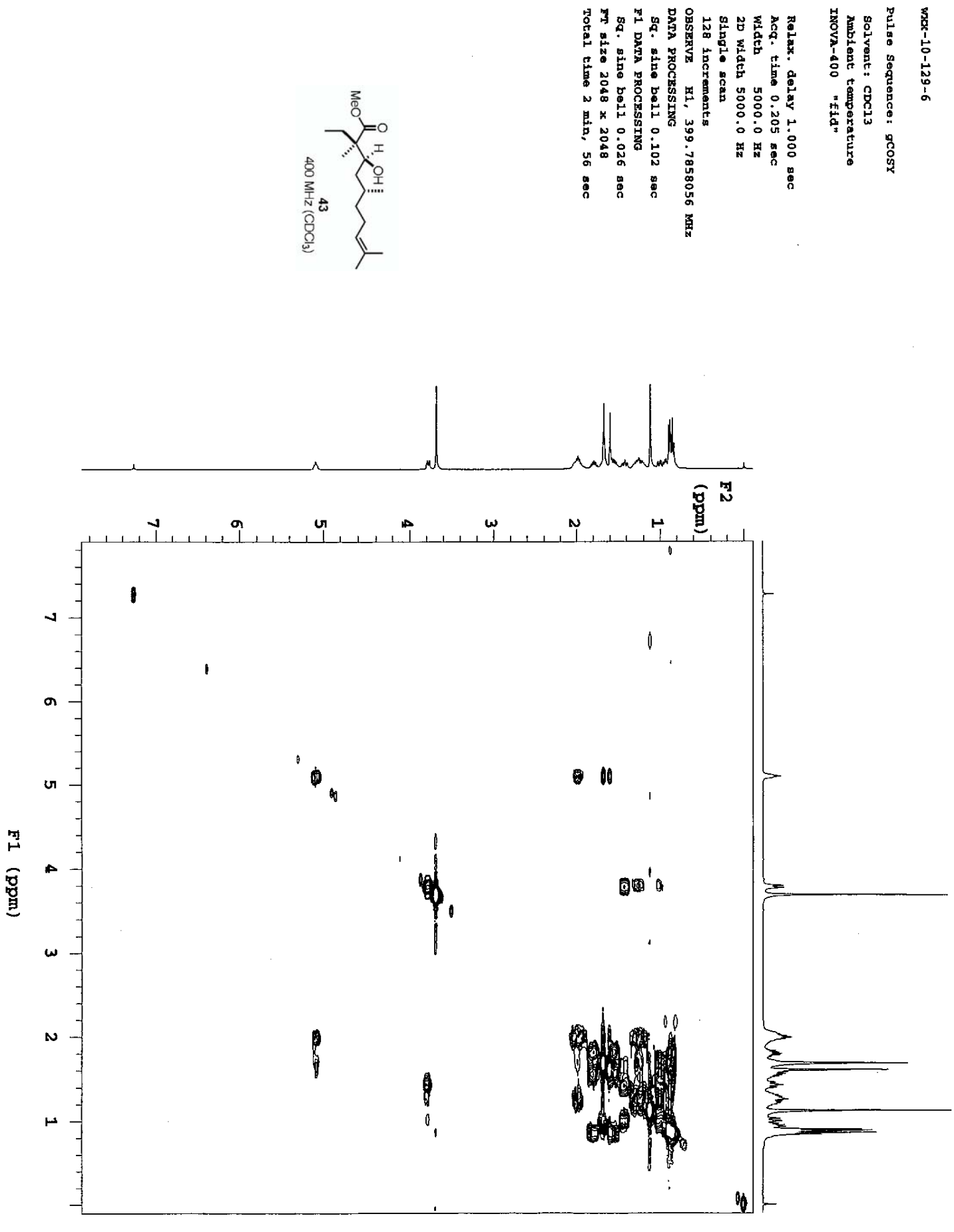
WXX-10-129-6C

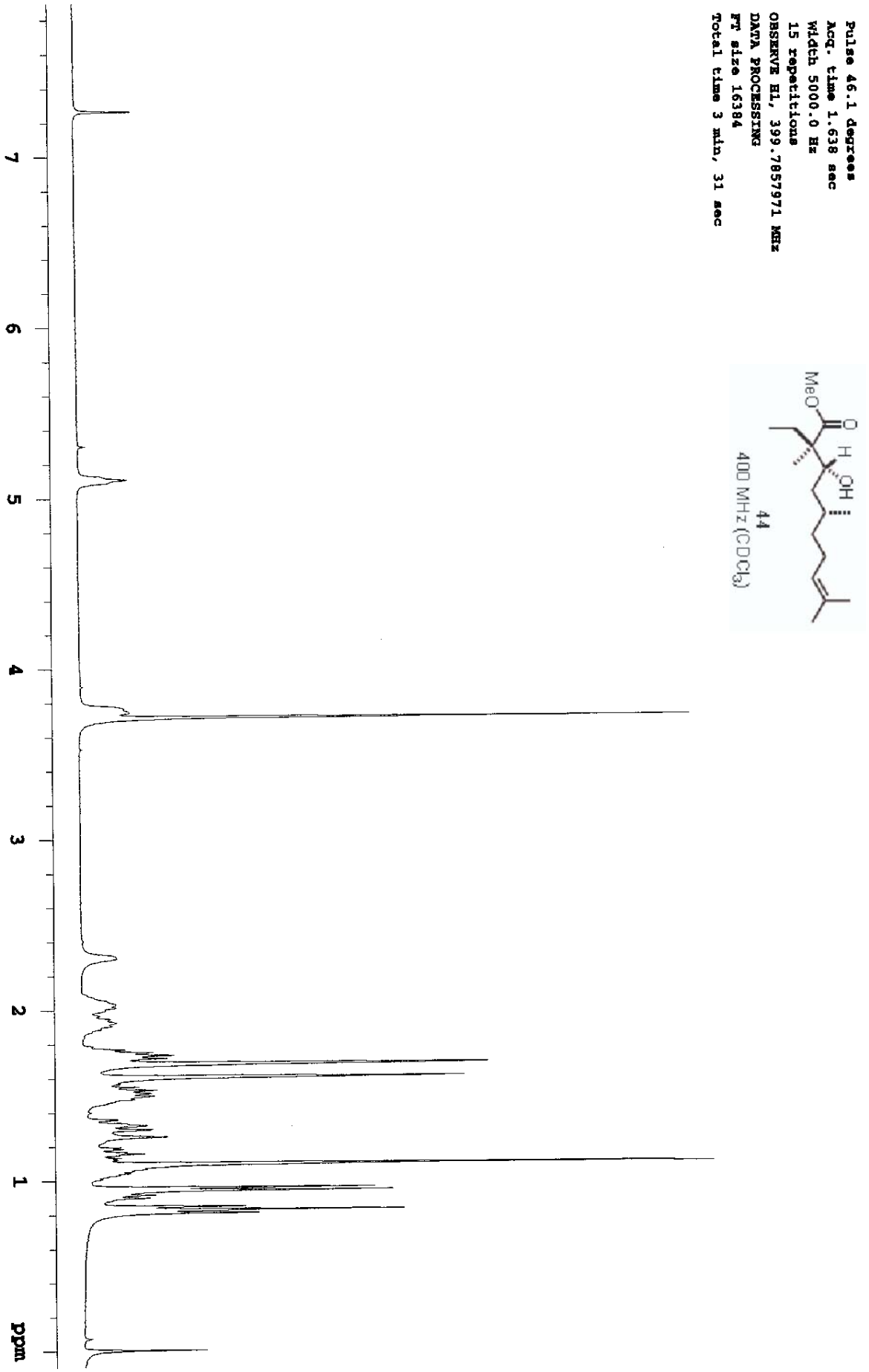
INDEX	FREQUENCY	PPM	HEIGHT
1	17799.876	177.067	18.6
2	13184.092	131.151	23.0
3	12535.594	124.700	45.6
4	7771.800	77.311	72.0
5	7740.519	77.000	75.8
6	7708.476	76.681	76.8
7	7411.692	73.729	58.6
8	5186.961	51.598	55.9
9	5162.547	51.355	27.6
10	4002.879	39.819	55.3
11	3838.847	38.188	53.8
12	2925.608	29.103	53.7
13	2870.677	28.556	55.4
14	2583.049	25.695	59.7
15	2564.738	25.513	58.7
16	1878.092	18.683	59.2
17	1772.807	17.635	35.3
18	1633.952	16.254	64.7
19	901.530	8.968	46.5



43
400 MHz ($CDCl_3$)



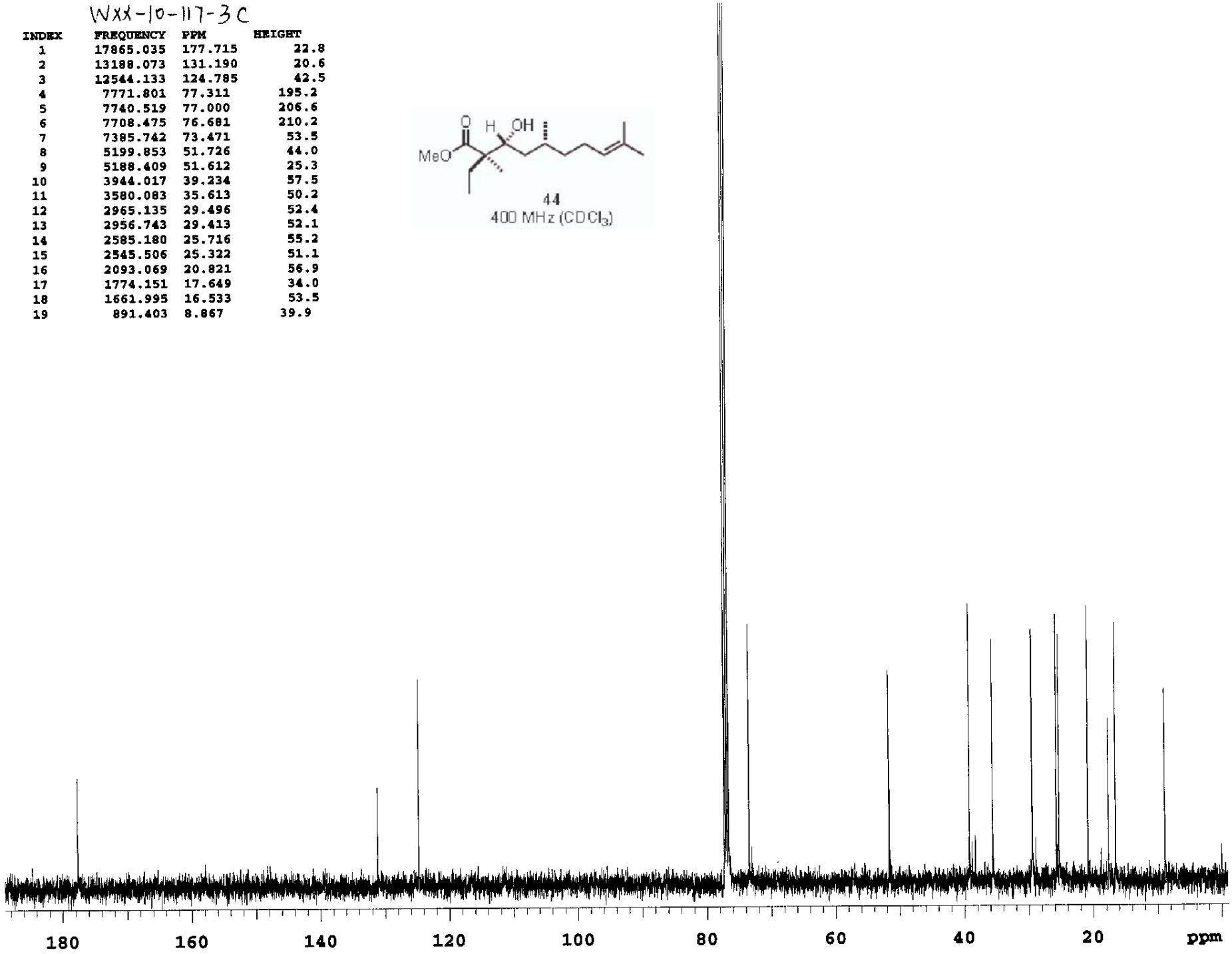

WSK-10-129-6
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858056 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
O
H
OH
43
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)


wzx-10-117-3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzx-10-117-3
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
15 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
MeO
O
H
OH
44
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm

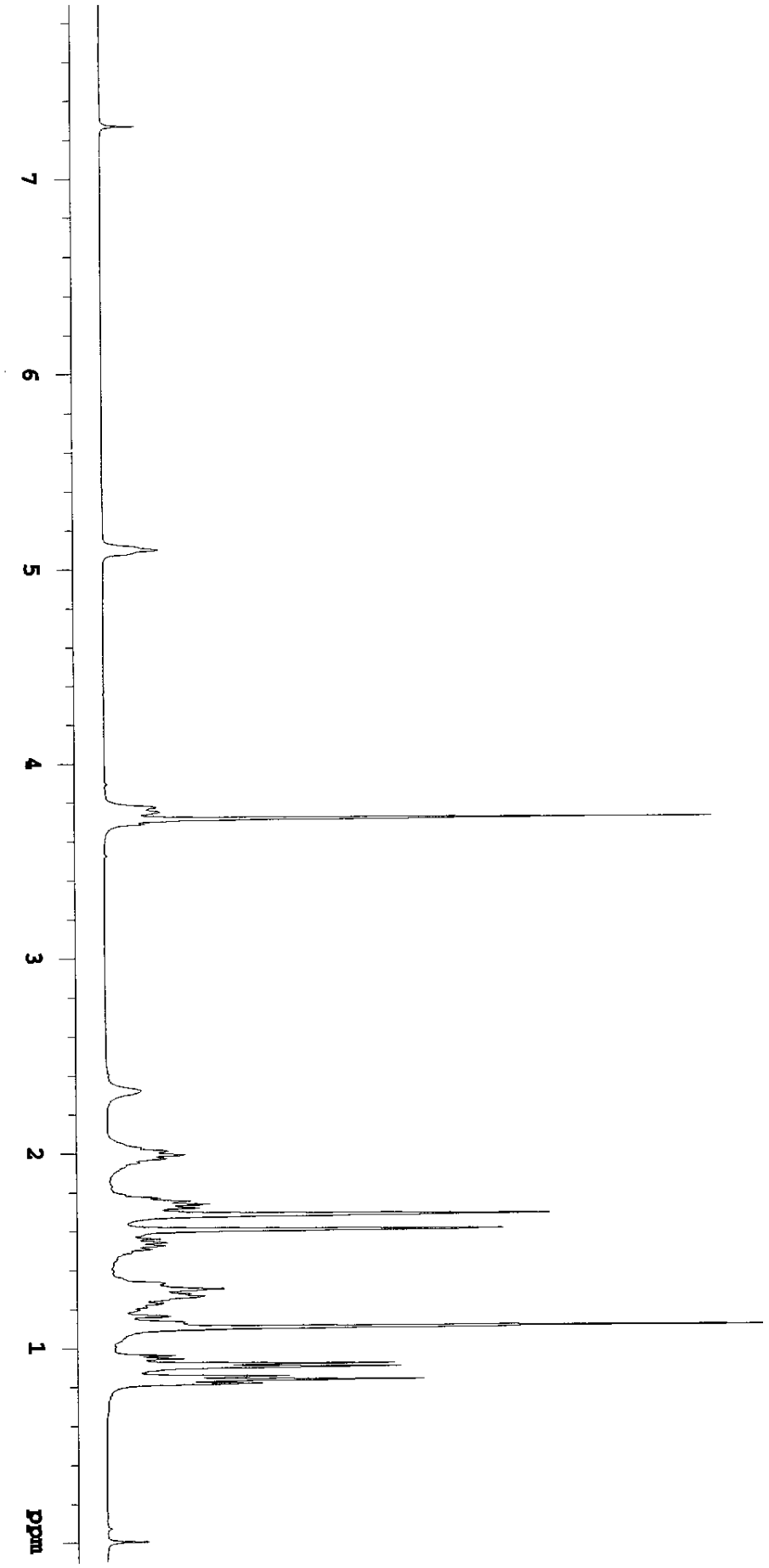
WXX-10-117-3C

INDEX	FREQUENCY	PPM	HEIGHT
1	17865.035	177.715	22.8
2	13188.073	131.190	20.6
3	12544.133	124.785	42.5
4	7771.801	77.311	195.2
5	7740.519	77.000	206.6
6	7708.475	76.681	210.2
7	7385.742	73.471	53.5
8	5199.853	51.726	44.0
9	5188.409	51.612	25.3
10	3944.017	39.234	57.5
11	3580.083	35.613	50.2
12	2965.135	29.496	52.4
13	2956.743	29.413	52.1
14	2585.180	25.716	55.2
15	2545.506	25.322	51.1
16	2093.069	20.821	56.9
17	1774.151	17.649	34.0
18	1661.995	16.533	53.5
19	891.403	8.867	39.9

44
400 MHz ($CDCl_3$)

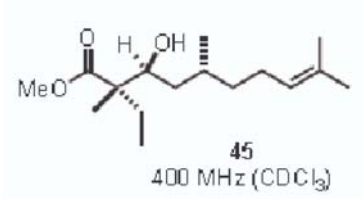



wxx-10-117-3
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858074 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
O
H
OH
44
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

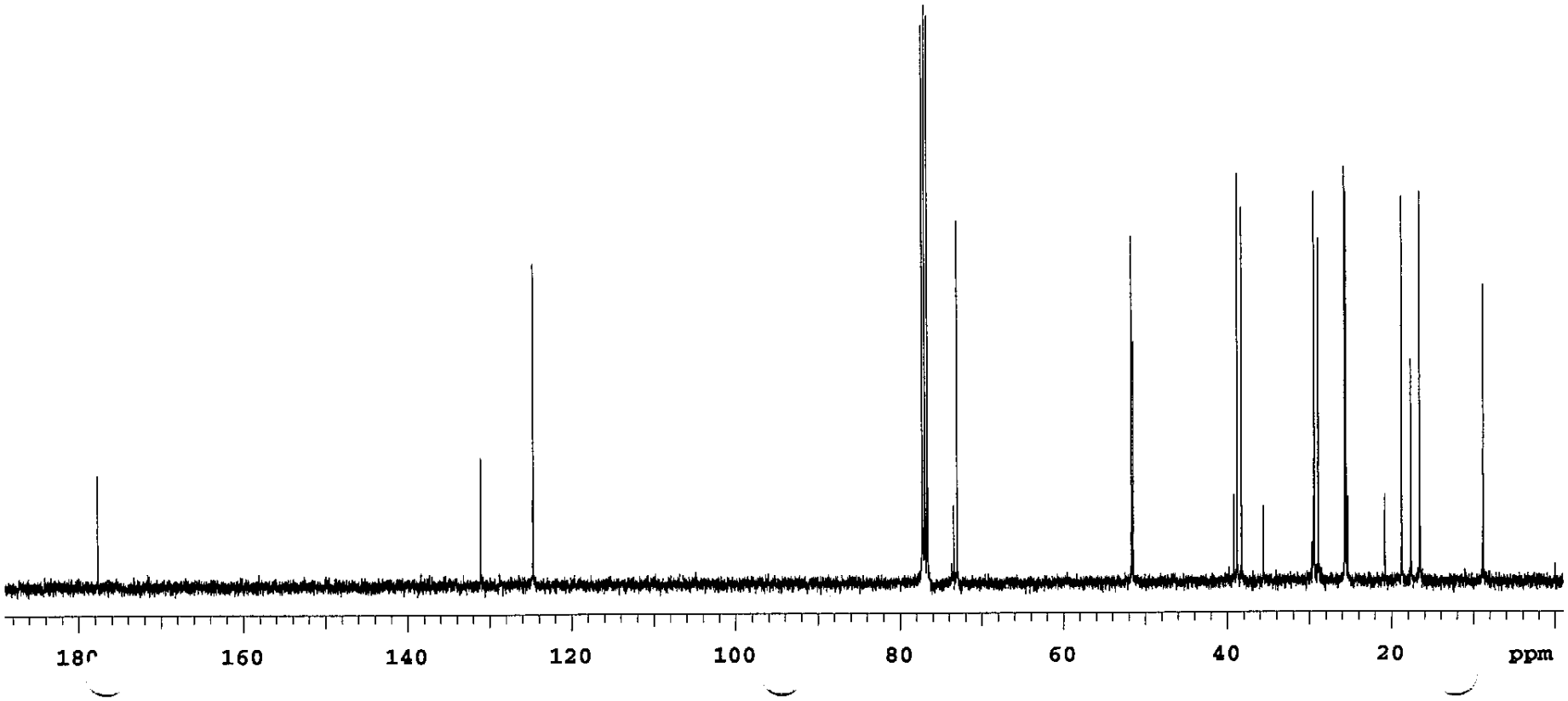

wzx-10-129-7
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzx-10-129-7
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
16 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
MeO
O
H
OH
45
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm

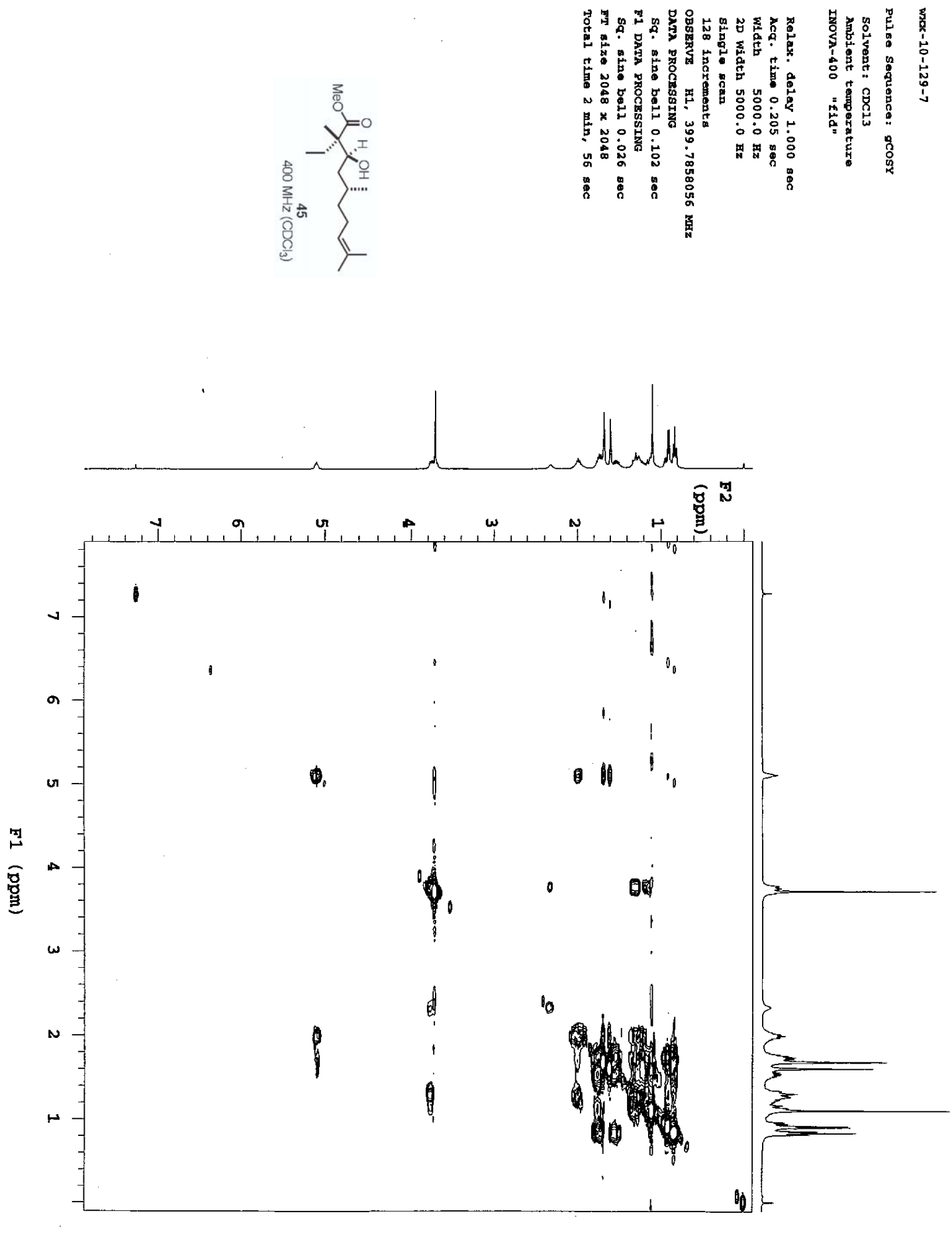
WXX-10-129-7C

INDEX	FREQUENCY	PPM	HEIGHT
1	17867.778	177.742	18.3
2	13182.566	131.136	21.0
3	12537.883	124.723	51.9
4	7772.563	77.319	90.1
5	7740.519	77.000	93.4
6	7708.476	76.681	91.7
7	7343.791	73.053	58.6
8	5197.642	51.704	56.1
9	5176.280	51.492	39.1
10	3900.645	38.802	66.3
11	3848.765	38.286	60.8
12	2956.889	29.414	63.3
13	2907.298	28.921	55.7
14	2583.811	25.703	67.5
15	2567.027	25.536	63.3
16	1884.959	18.751	62.4
17	1772.807	17.635	36.4
18	1666.758	16.580	63.4
19	887.034	8.824	48.2



45
400 MHz ($CDCl_3$)



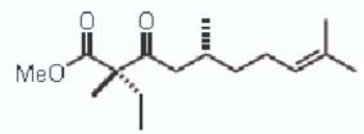

wzk-10-129-7
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D width 5000.0 Hz
single scan
128 increments
OBSERVE H1, 399.7858056 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
MeO
O
H
OH
45
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-11-35-4

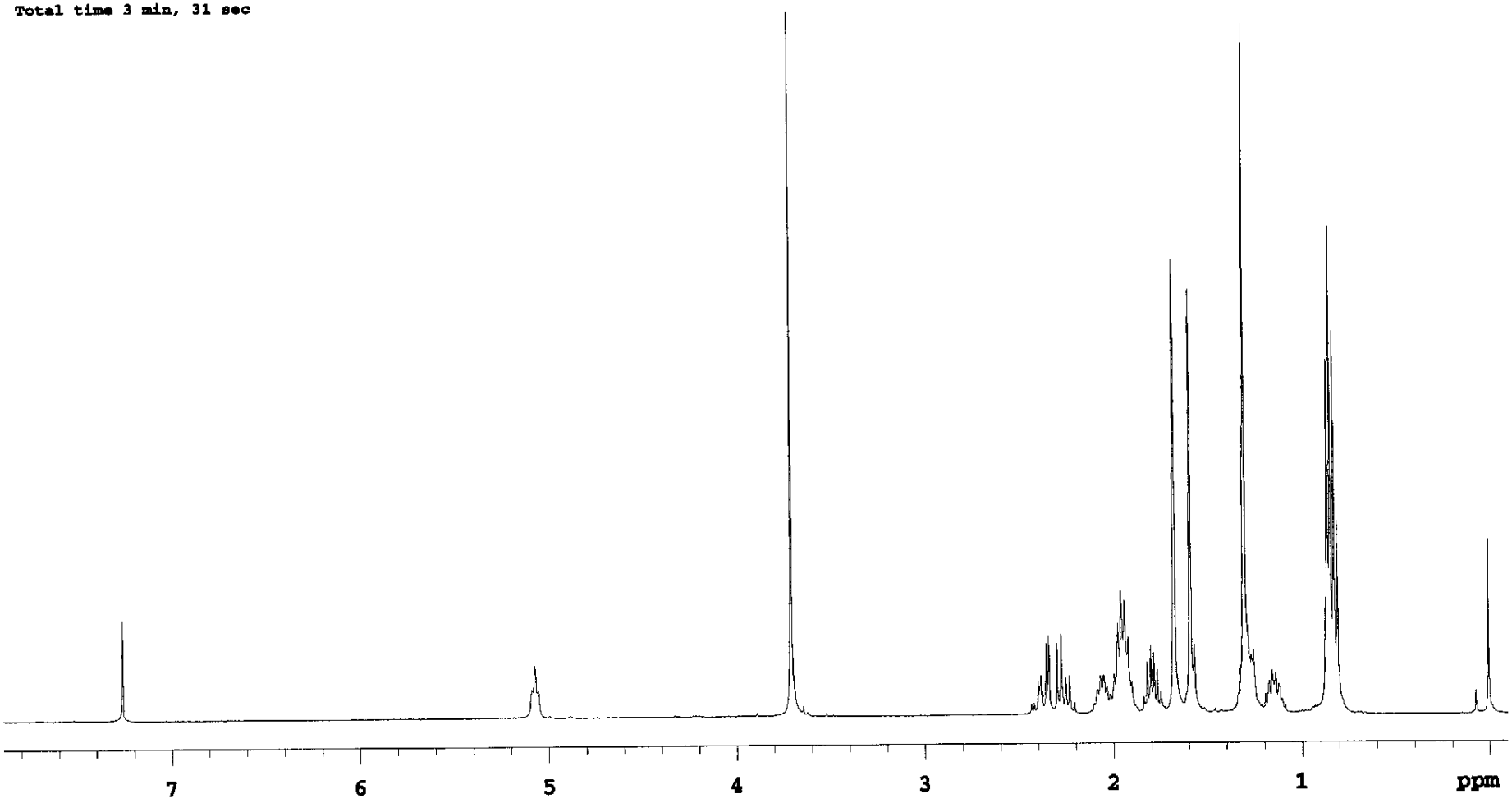
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-11-35-4
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
20 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

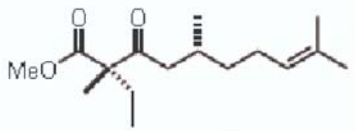


46
400 MHz ($CDCl_3$)



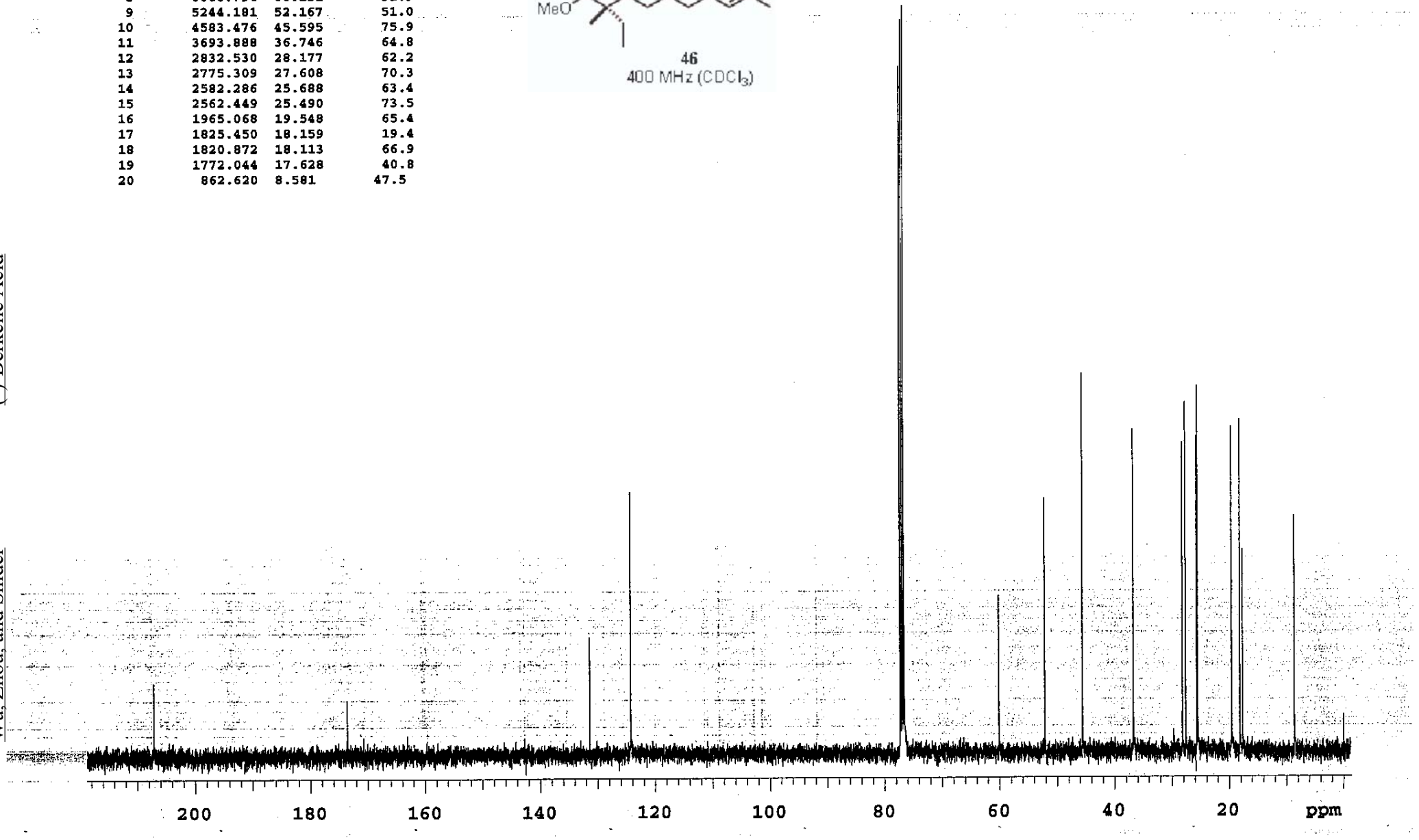
WXX-11-35-5C

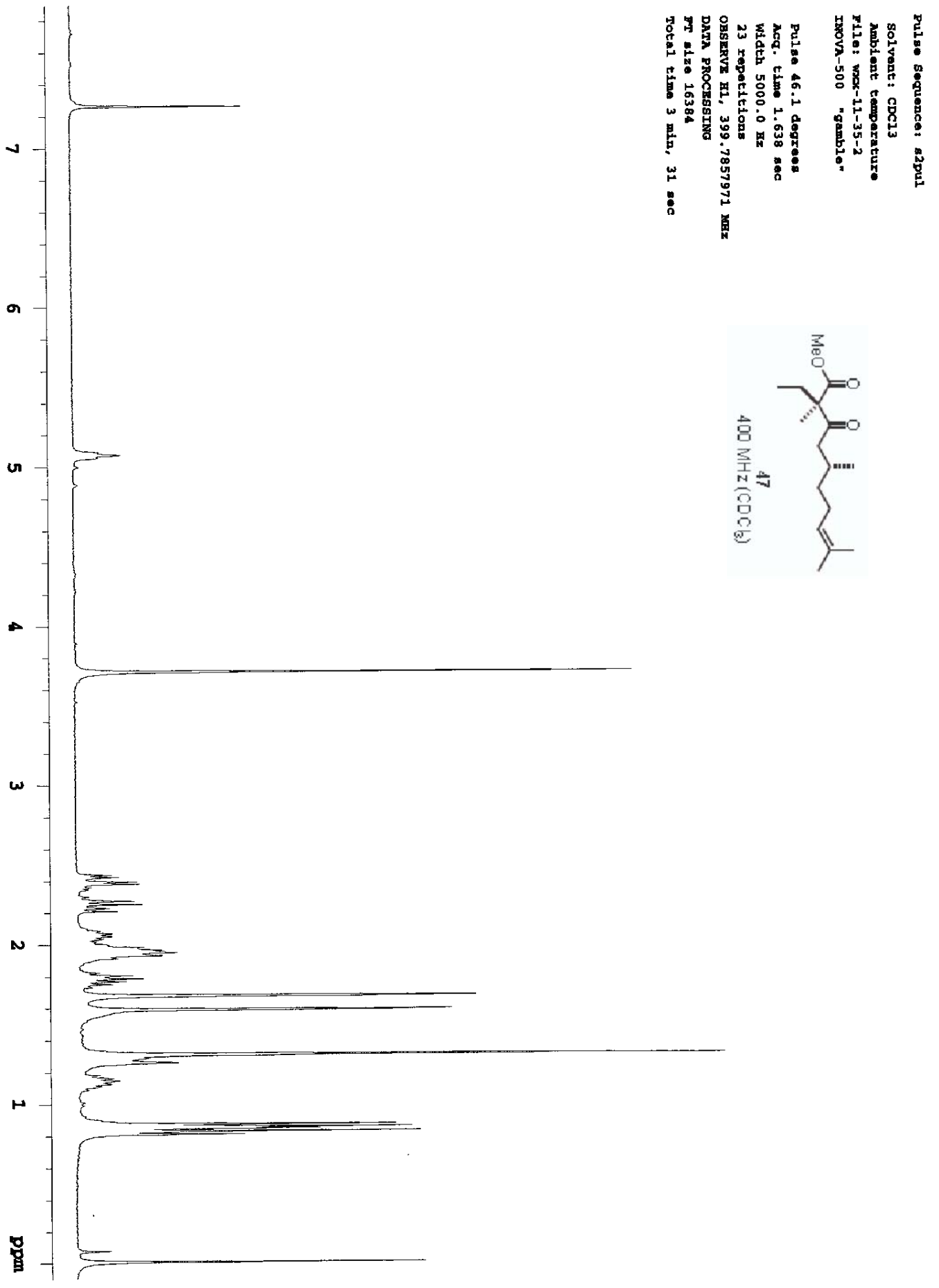
INDEX	FREQUENCY	PPM	HEIGHT
1	20831.797	207.227	14.7
2	17455.027	173.637	11.2
3	13212.321	131.432	23.8
4	12497.447	124.320	52.4
5	7772.563	77.319	135.8
6	7740.519	77.000	145.0
7	7708.476	76.681	147.8
8	6046.794	60.151	31.9
9	5244.181	52.167	51.0
10	4583.476	45.595	75.9
11	3693.888	36.746	64.8
12	2832.530	28.177	62.2
13	2775.309	27.608	70.3
14	2582.286	25.688	63.4
15	2562.449	25.490	73.5
16	1965.068	19.548	65.4
17	1825.450	18.159	19.4
18	1820.872	18.113	66.9
19	1772.044	17.628	40.8
20	862.620	8.581	47.5



46

400 MHz ($CDCl_3$)

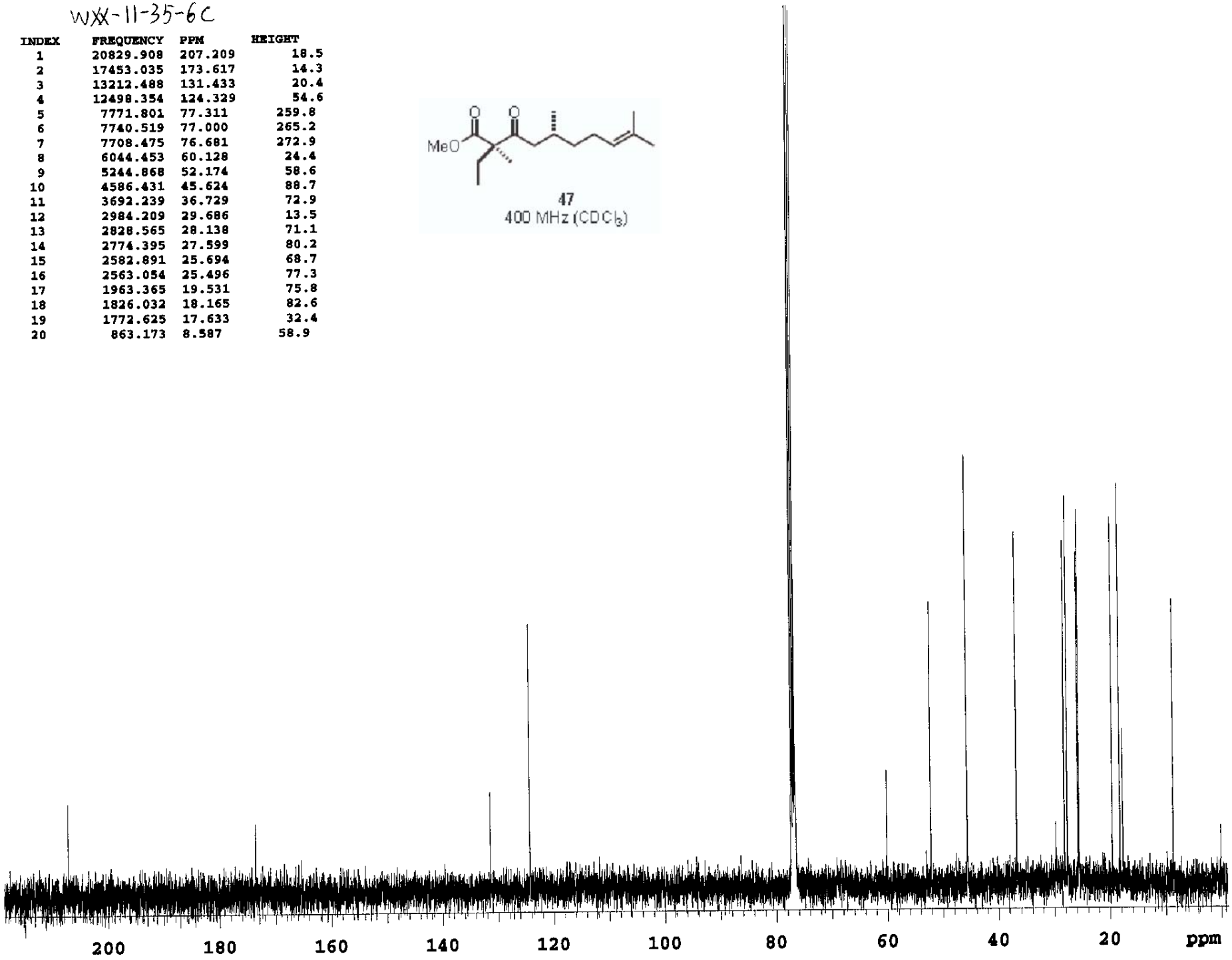



wzk-11-35-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: wzk-11-35-2
INOVA-500 "gamble"
Pulse 46.1 degrees
Acq. time 1.638 sec
width 5000.0 Hz
23 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
MeO
O
O
47
400 MHz (CDCl3)
7
6
5
4
3
2
1
ppm

WXX-11-35-6C

INDEX	FREQUENCY	PPM	HEIGHT
1	20829.908	207.209	18.5
2	17453.035	173.617	14.3
3	13212.488	131.433	20.4
4	12498.354	124.329	54.6
5	7771.801	77.311	259.8
6	7740.519	77.000	265.2
7	7708.475	76.681	272.9
8	6044.453	60.128	24.4
9	5244.868	52.174	58.6
10	4586.431	45.624	88.7
11	3692.239	36.729	72.9
12	2984.209	29.686	13.5
13	2828.565	28.138	71.1
14	2774.395	27.599	80.2
15	2582.891	25.694	68.7
16	2563.054	25.496	77.3
17	1963.365	19.531	75.8
18	1826.032	18.165	82.6
19	1772.625	17.633	32.4
20	863.173	8.587	58.9

47
400 MHz ($CDCl_3$)

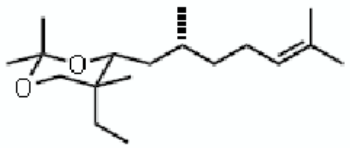


wxx-11-33-1

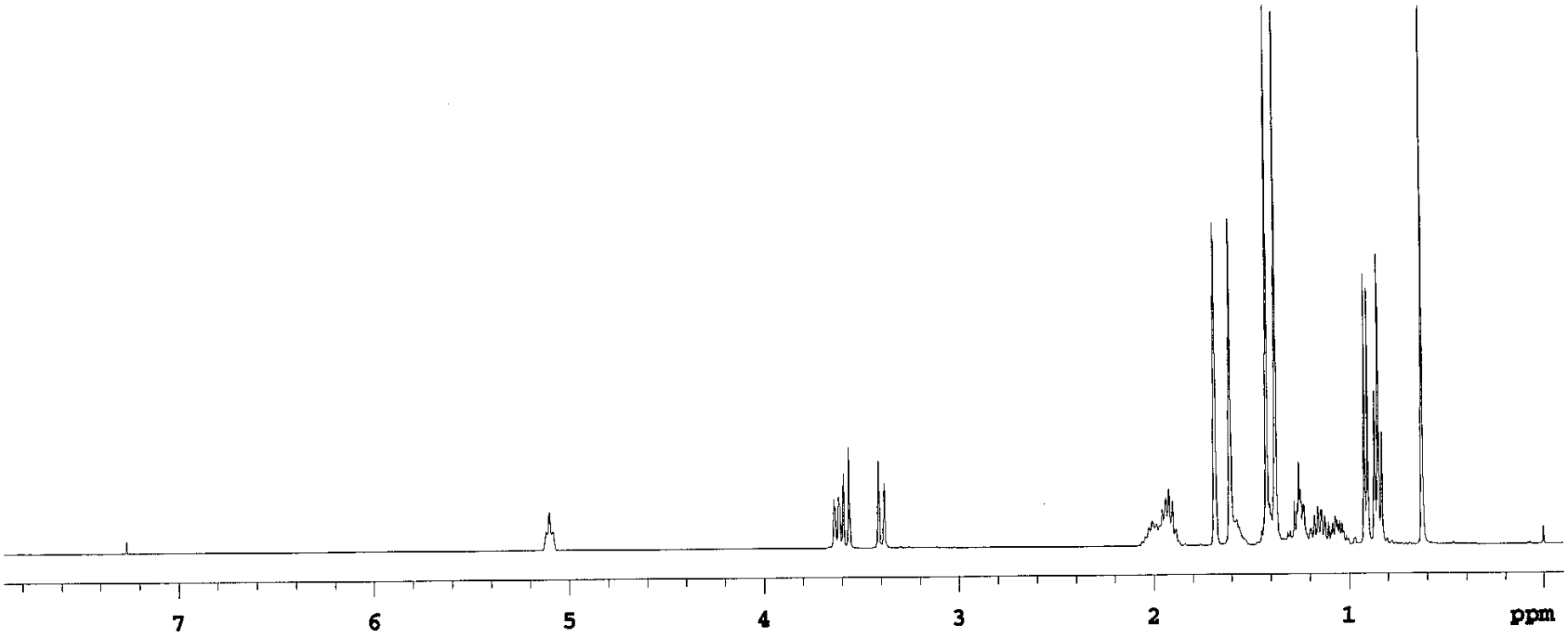
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wxx-11-33-1
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
20 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

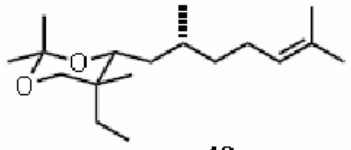


48
400 MHz ($CDCl_3$)

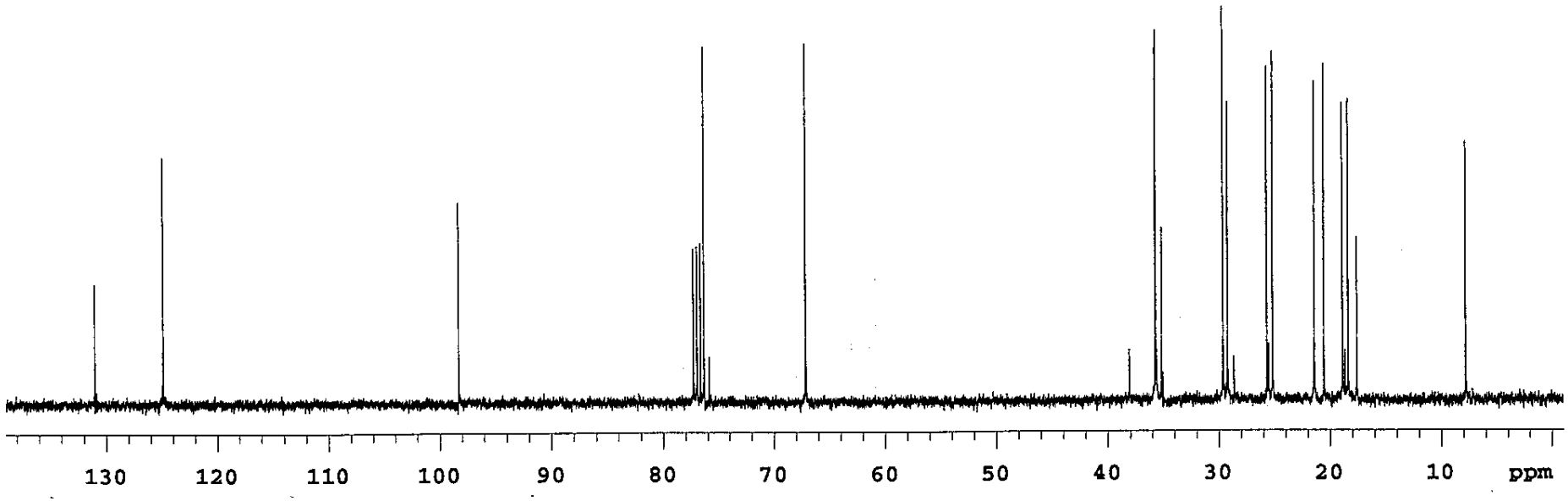


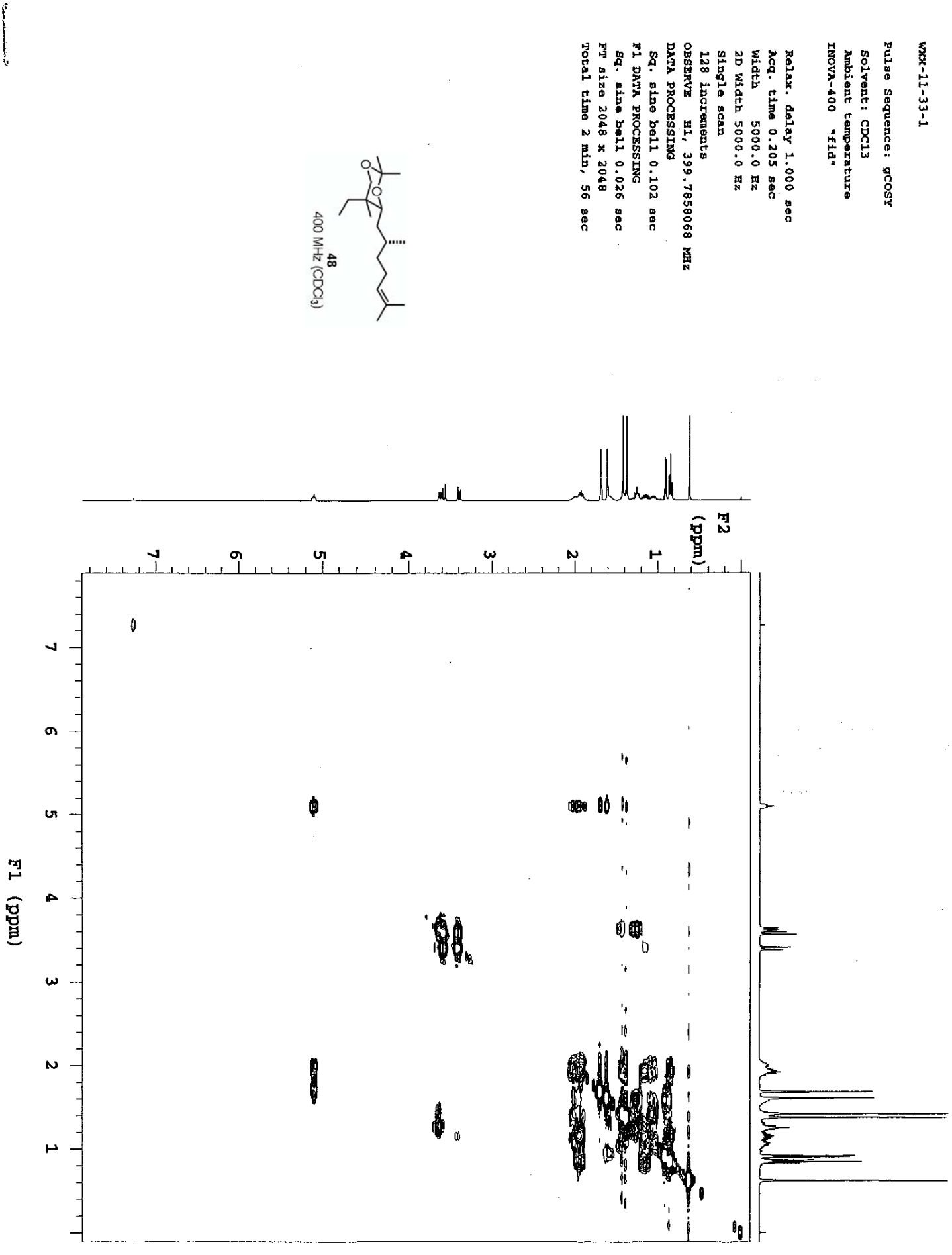
WXX-11-33-1C

INDEX	FREQUENCY	PPM	HEIGHT
1	13177.226	131.082	19.8
2	12559.245	124.935	40.1
3	9886.668	98.349	32.7
4	7772.563	77.319	25.2
5	7740.519	77.000	25.6
6	7708.476	76.681	26.1
7	7675.669	76.355	57.5
8	6753.276	67.179	58.0
9	3595.469	35.766	57.2
10	3591.654	35.729	60.0
11	3536.723	35.182	28.4
12	2979.777	29.642	63.8
13	2938.578	29.232	48.5
14	2583.811	25.703	54.2
15	2530.406	25.172	56.6
16	2152.751	21.415	51.8
17	2067.301	20.565	54.7
18	1899.455	18.895	48.3
19	1847.575	18.379	48.9
20	1769.755	17.605	26.8
21	784.800	7.807	42.1



48
400 MHz ($CDCl_3$)



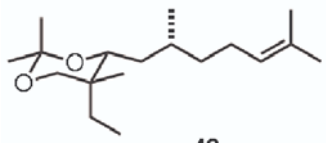

WXK-11-33-1
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "fid"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858068 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
48
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

wxx-11-33-1-2DNOE
STANDARD 1H OBSERVE

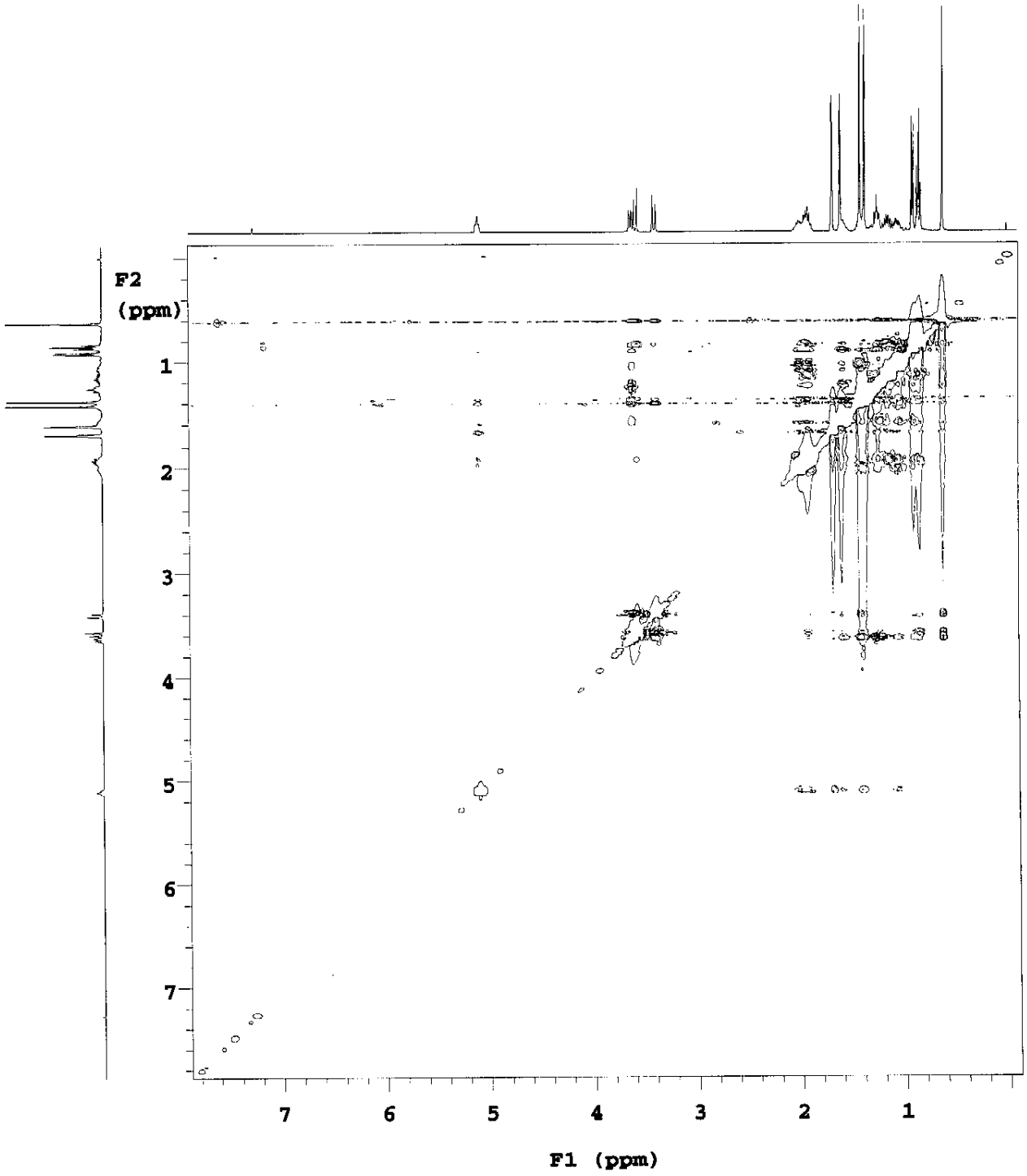
Pulse Sequence: NOESY

Solvent: CDCl3
Ambient temperature
File: wxx-11-33-1_2DNOE
INOVA-500 "gamble"

Relax. delay 1.000 sec
Mixing 0.400 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
44 repetitions
2 x 200 increments
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 8 hr, 48 sec



48
400 MHz ($CDCl_3$)

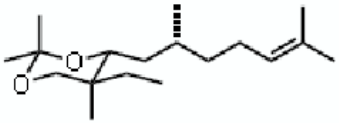


wux-11-37-1

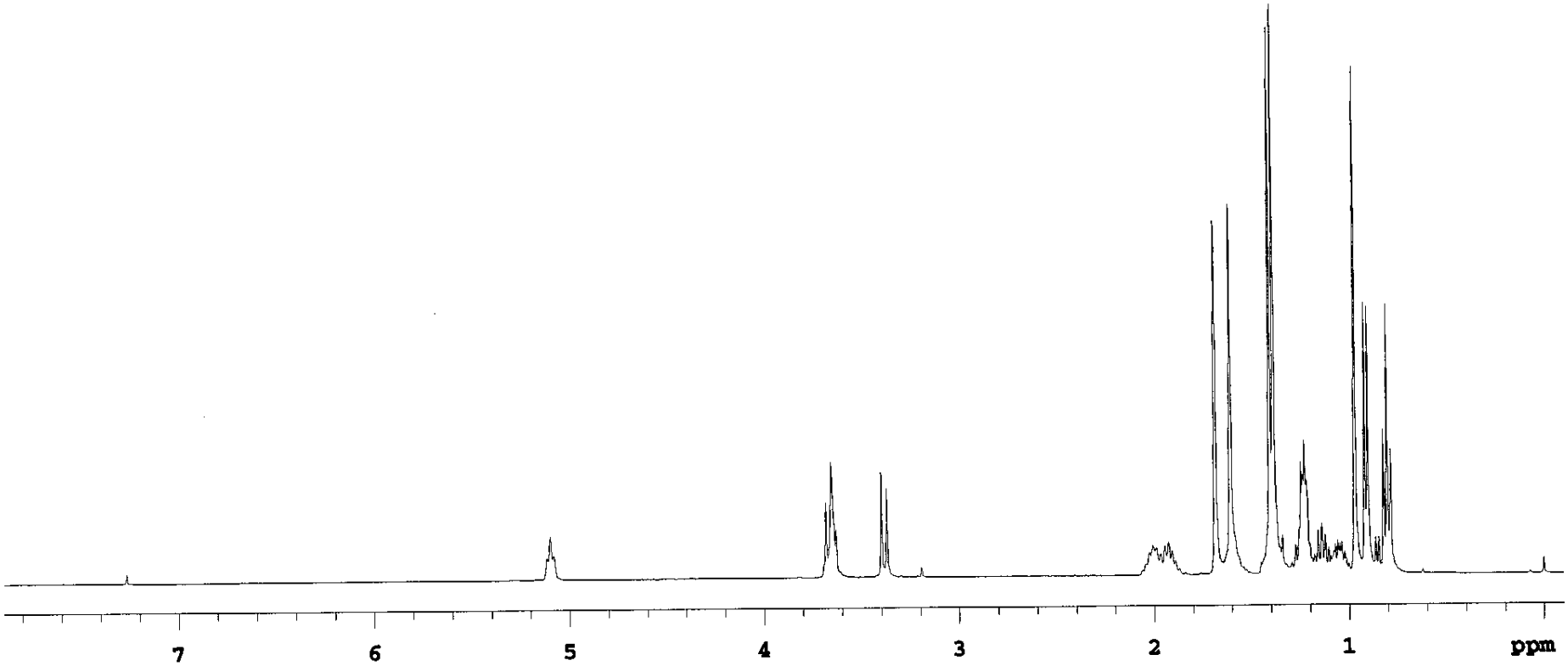
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: wux-11-37-1
INOVA-500 "gamble"

Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
19 repetitions
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec

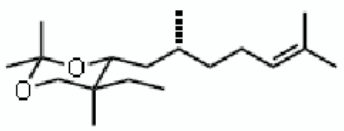


49
400 MHz ($CDCl_3$)



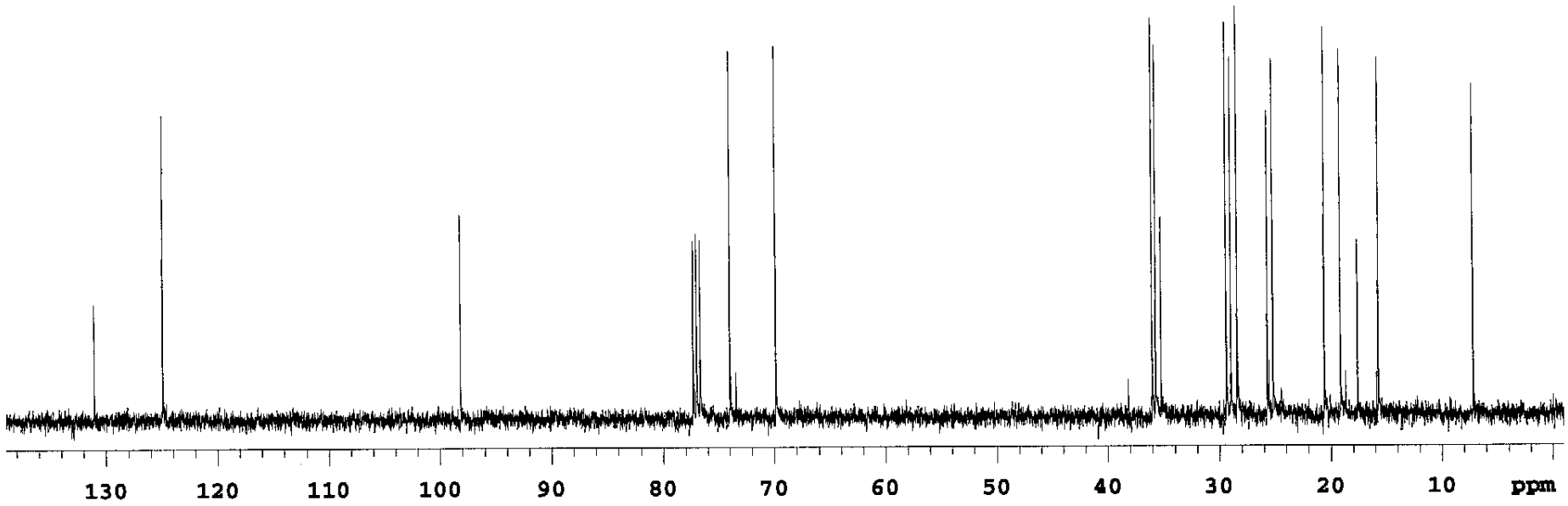
WXX-11-37-1C

INDEX	FREQUENCY	PPM	HEIGHT
1	13176.629	131.077	18.9
2	12559.392	124.936	49.2
3	9871.474	98.198	33.2
4	7772.563	77.319	29.0
5	7740.519	77.000	30.1
6	7708.475	76.681	29.0
7	7438.386	73.994	59.1
8	7024.097	69.873	59.9
9	3623.572	36.046	64.4
10	3590.765	35.720	59.8
11	3541.935	35.234	32.4
12	2953.691	29.382	63.7
13	2912.491	28.972	57.9
14	2856.032	28.411	66.2
15	2584.417	25.709	49.4
16	2532.535	25.193	57.6
17	2069.417	20.586	62.7
18	1923.691	19.136	59.1
19	1769.573	17.603	28.7
20	1581.884	15.736	57.8
21	725.077	7.213	53.6



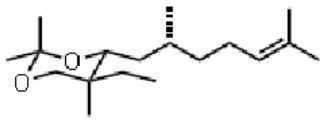
49

400 MHz ($CDCl_3$)



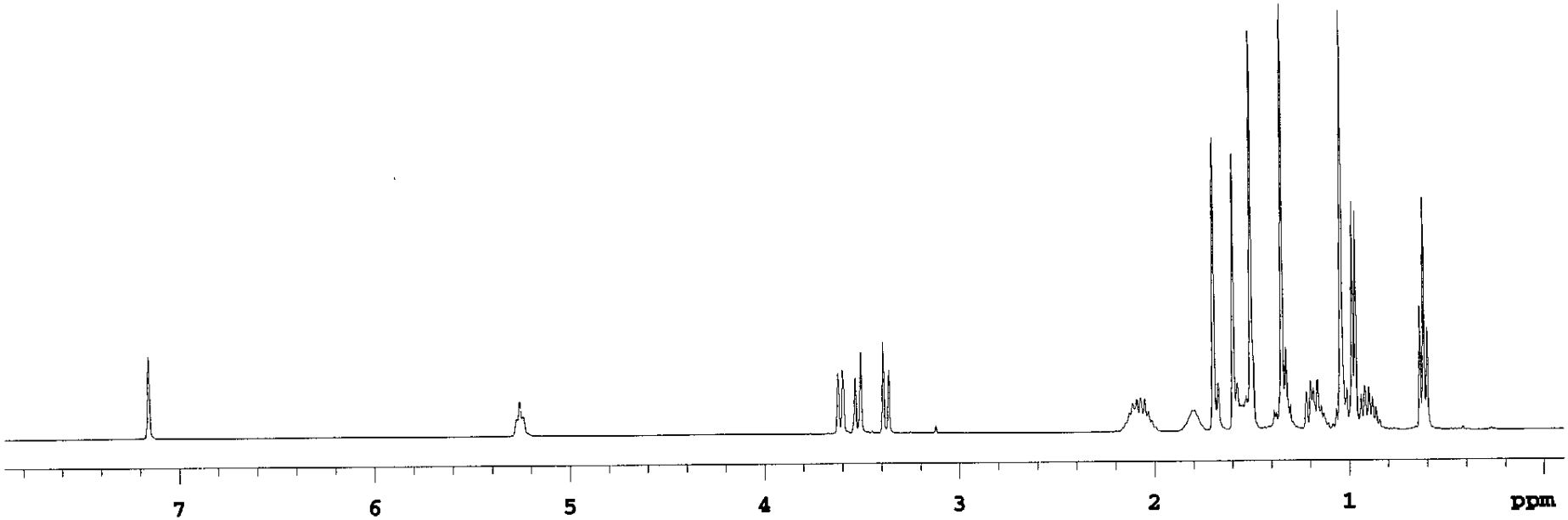

wzx-11-37-1
Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
File: wzx-11-37-1COSY
INOVA-500 "gamble"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7857971 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 57 sec
49
400 MHz (CDCl3)
F2 (ppm)
F1 (ppm)

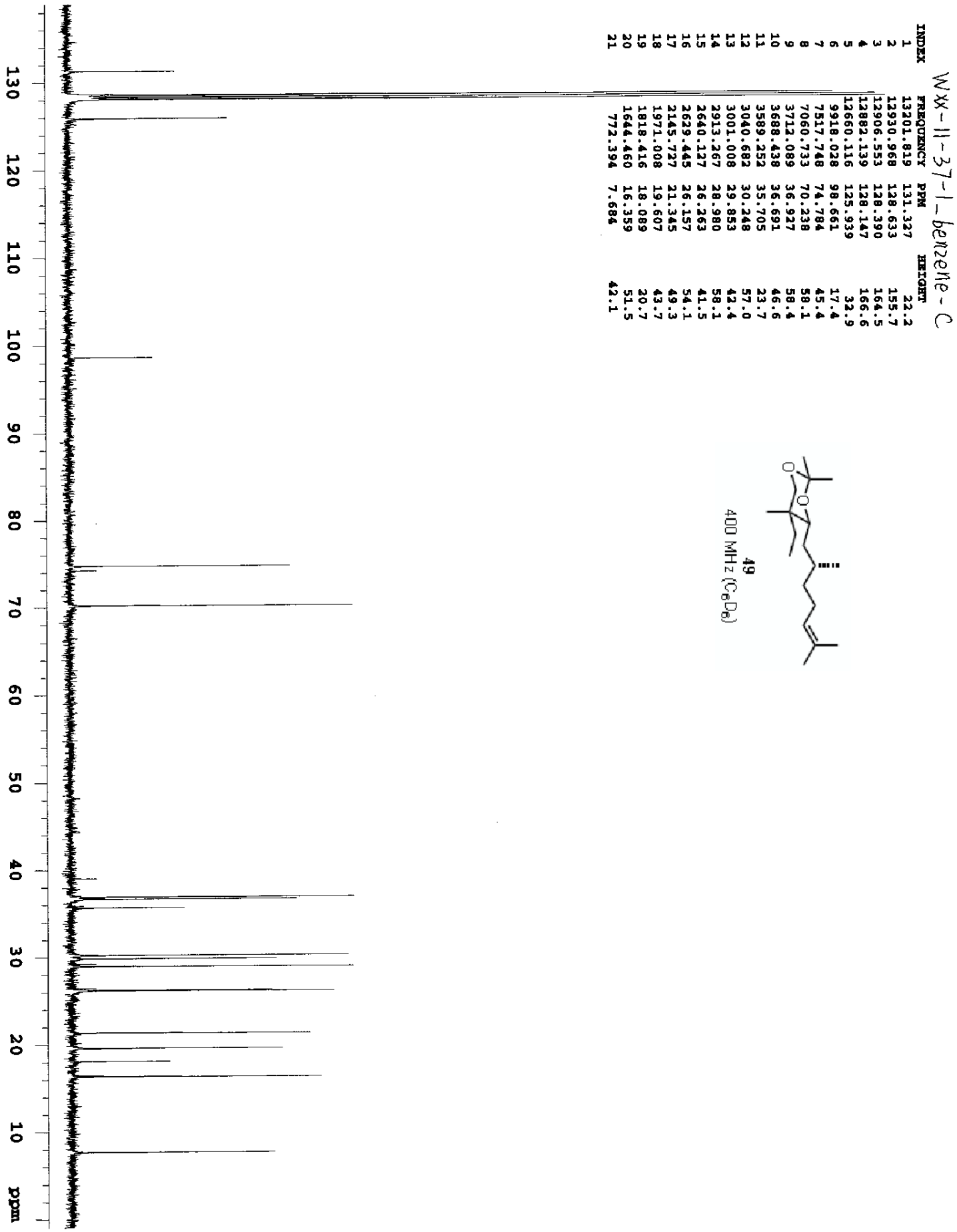
```
wux-11-37-1_benzene

Pulse Sequence: s2pul

 Solvent: Benzene
 Ambient temperature
File: wux-11-37-1_benzene
INOVA-500  "gamble"

 Pulse 46.1 degrees
 Acq. time 1.638 sec
 Width 5000.0 Hz
 76 repetitions
OBSERVE H1, 399.7858276 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 31 sec
```

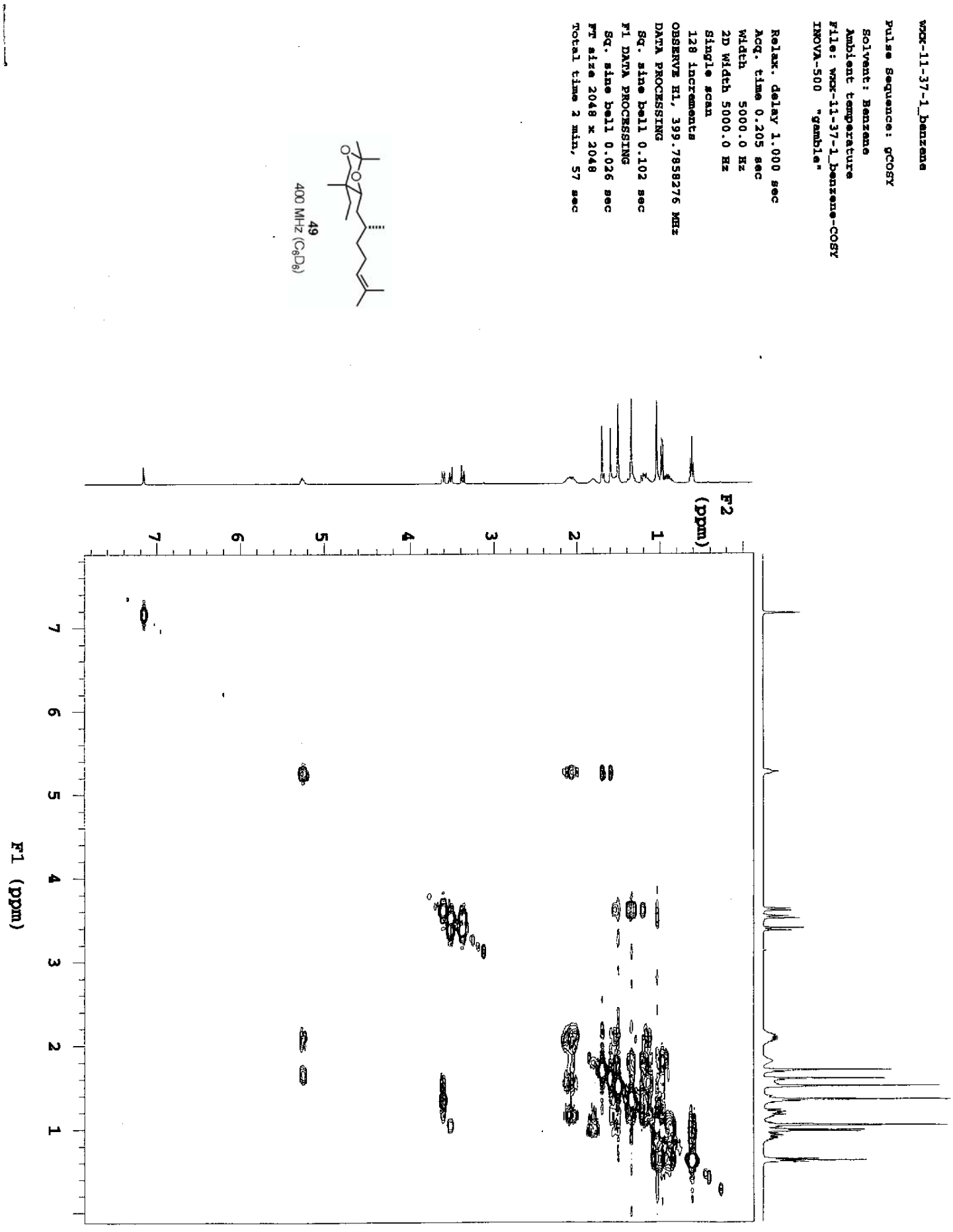


49

400 MHz (C_6D_6)




WX-11-37-1_benzene-C
INDEX FREQUENCY PPM HEIGHT
1 13201.819 131.327 22.2
2 12930.968 128.633 155.7
3 12906.553 128.390 164.5
4 12882.139 128.147 166.6
5 12660.116 125.939 32.9
6 9918.028 98.661 17.4
7 7517.748 74.784 45.4
8 7060.733 70.238 58.1
9 3712.089 36.927 58.4
10 3688.438 36.691 46.6
11 3589.252 35.705 23.7
12 3040.682 30.248 57.0
13 3001.008 29.853 42.4
14 2913.267 28.980 58.1
15 2640.127 26.263 41.5
16 2629.445 26.157 54.1
17 2145.727 21.345 49.3
18 1971.008 19.607 43.7
19 1818.416 18.089 20.7
20 1644.460 16.359 51.5
21 772.394 7.684 42.1
O
O
49
400 MHz (C_6D_6)
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


wxk-11-37-1_benzene
Pulse Sequence: gCOSY
Solvent: Benzene
Ambient temperature
File: wxk-11-37-1_benzene-COSY
INOVA-500 "gamble"
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
128 increments
OBSERVE H1, 399.7858276 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 57 sec
49
400 MHz (C6D6)
F2 (ppm)
F1 (ppm)


WXX-11-37-1_benzene-2DNOE
STANDARD 1H OBSERVE
Pulse Sequence: NOESY
Solvent: Benzene
Ambient temperature
File: wxx-11-37-1_benzene-2DNOE
INOVA-500 "gamble"
Relax. delay 1.000 sec
Mixing 0.400 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D width 5000.0 Hz
60 repetitions
2 x 200 increments
OBSERVE H1, 399.7858276 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 10 hr, 55 min, 19 sec
F2 (ppm)
F1 (ppm)
49
400 MHz (C6D6)