Quinone Approaches Toward the Synthesis of Aflatoxin B$_2$: Supporting Information

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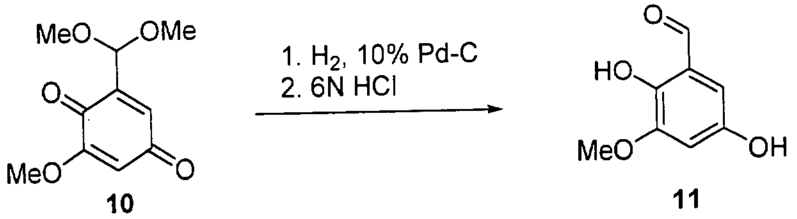
Experimental Section

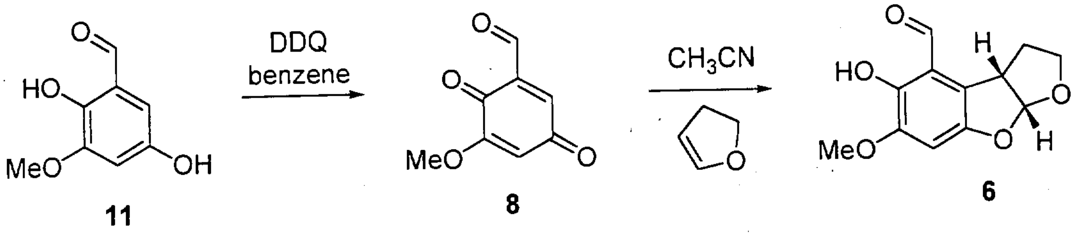
General Methods. Benzene, DMF, pyridine, CH_3CN, and CH_2Cl_2 were dried by distillation from CaH_2; tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone. Reagents were purchased from Aldrich Chemical Co. and were used as received, unless otherwise noted. Brine refers to saturated aqueous NaCl solution. Reactions were monitored by TLC on precoated silica gel plates (POLYGRAM® SIL G/UV$_{254}$). Column chromatography was performed with silica gel (E. Merck 60, 230-400 mesh), unless otherwise noted. Solvent ratios used in TLC and column chromatography are reported by volume. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, unless otherwise noted. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ.

Preparation of 2,5-Dihydroxy-3-methoxybenzaldehyde (11).



Quinone-acetal **10** (21.220 g, 100.0 mmol) was dissolved in EtOAc (500 mL), 10% Pd-C (0.50 g) was added, and the reaction mixture was maintained under H_2 (balloon), with vigorous stirring for 18 h. The reaction mixture was filtered through a bed of Celite and the solvent removed under reduced pressure, giving a viscous yellow oil. The oil was dissolved in ether (350 mL), 6 N HCl (350 mL) was added, and the mixture was stirred for 24 h. The layers were separated and the aqueous layer extracted with ether (10 x 100 mL) followed by EtOAc (3 x 100 mL). The combined organic layers were washed with brine (2 x 200 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure, giving a yellow-black solid. This solid was dissolved in a minimum amount of EtOAc and purified by flashing through a short plug of silica gel (1:1 hexane/EtOAc) to remove a purple impurity, giving a dark yellow solid, which was recrystallized from benzene, giving **11** as golden needles in 3 crops (11.481 g, 68%): mp 148-149 °C (lit. mp 142-143 °C); the ^{1}H NMR spectrum was identical to the published spectrum.[9]

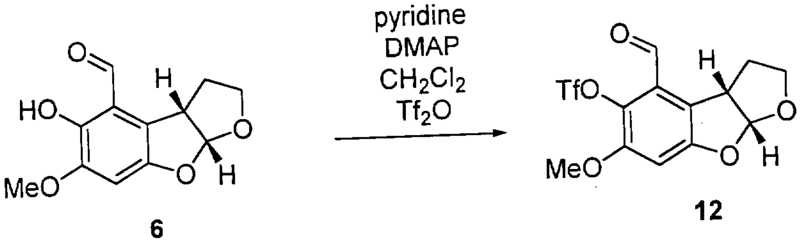
Preparation of (±)-*cis*-2,3,3a,8a-Tetrahydro-5-hydroxy-6-methoxy[2,3-*d*]-benzo[*b*]furan-4-carboxaldehyde (6) from 11 via 8.



Hydroquinone **11** (1.000 g, 5.95 mmol) was combined with DDQ (1.360 g, 5.99 mmol), and benzene (200 mL), and the resulting mixture was stirred in the dark for 12 h. The mixture was then filtered through a bed of Celite to remove reduced DDQ, and the solvent was removed under reduced pressure at room temperature, giving **8** as a red-brown oil which solidified. This solid was dissolved in CH_3CN (100 mL) under N_2, the solution cooled to 0 °C, and dihydrofuran (1.38 mL, 18.3 mmol) was added, with stirring. The solution was stirred at 0 °C for 2 h, then warmed to room temperature and stirred for an additional 2 h. Volatile components were removed under reduced pressure, leaving a yellow-brown residue, which was dissolved in a minimum amount of EtOAc and purified by flash chromatography on silica gel (33:33:1 hexane/EtOAc/AcOH), giving **6** as a yellow microcrystalline solid (0.829 g, 59% from **11**): TLC R_f 0.54 (33:33:1 hexane/EtOAc/AcOH); mp 151-153 °C; IR (KBr, cm^{-1}) 3197, 2975, 2936, 2877, 2845, 1665, 1455, 1269, 1204, 1079, 953; ^1H NMR ($CDCl_3$, δ ppm) 10.22 (s, 1 H), 10.05 (s, 1 H), 6.68 (s, 1 H), 6.40 (d, J = 5.7 Hz, 1 H), 4.29 (dd, J = 9.0, 6.0 Hz, 1 H), 4.12 (ddd, J = 9.0, 7.8, 1.2 Hz, 1 H), 3.88 (s, 3 H), 3.68 (ddd, J = 12.3, 9.0, 5.1 Hz, 1 H), 2.41 (ddt, J = 12.3, 12.3, 8.7, 7.8 Hz, 1 H), 2.03 (ddd, J = 12.6, 5.1, 0.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, δ ppm) 193.0, 152.1, 148.8, 146.8, 117.6, 115.8, 112.0, 101.4, 67.1, 56.5, 45.5, 34.2; EI

HRMS *m/z* (M^+) calcd 236.0685, found 236.0684. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 60.83; H, 5.38.

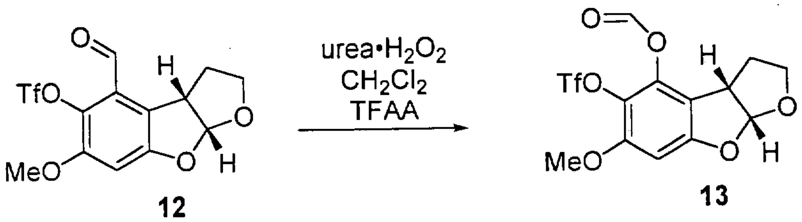
Preparation of (±)-*cis*-5-Trifluoromethanesulfonyloxy-2,3,3a,8a-tetrahydro-6-methoxy[2,3-*d*]benzo[*b*]furan-4-carboxaldehyde (12).



The phenol **6** (1.000 g, 4.23 mmol) was mixed with DMAP (26.0 mg, 0.21 mmol, 5 mol%), CH_2Cl_2 (10 mL), pyridine (10 mL), and the resulting solution was cooled to 0 °C under N_2. Triflic anhydride (1.42 mL, 8.44 mmol) was added dropwise, with stirring, and the solution was stirred for 1.5 h at 0 °C, during which time it developed a dark green tint. Water (40 mL) was then added and the resulting mixture was extracted with ether (4 x 30 mL). The combined ether fractions were washed successively with 1 N HCl (3 x 30 mL) and brine (2 x 30 mL), dried over Na_2SO_4, filtered, and solvent removed under reduced pressure, giving a yellow oil. Purification by flash chromatography (silica gel, 2:1 petroleum ether (30-60 °C)/ether) gave **12** as a white microcrystalline solid (1.247 g, 80%): TLC R_f 0.41 (3:1 hexane/EtOAc); mp 102.5-103.5 °C; IR (KBr, cm^{-1}) 3004, 2963, 2921, 1693, 1446, 1419, 1359, 1225, 1210, 1128, 915; ^1H NMR ($CDCl_3$, δ ppm) 10.34 (s, 1 H), 6.74 (s, 1 H), 6.43 (d, J = 5.7 Hz, 1 H), 4.34 (ddd, J = 9.3, 5.7, 1.5 Hz, 1 H), 4.11 (ddd, J = 9.0, 7.8, 1.2 Hz, 1 H), 3.92 (s, 3 H), 3.63 (ddd, J = 12.3, 9.0. 5.1 Hz, 1 H), 2.43 (dddd, J = 12.9, 12.3, 9.3, 7.8 Hz, 1 H), 1.93 (dd, J = 12.9, 5.7 Hz, 1 H); ^{13}C NMR

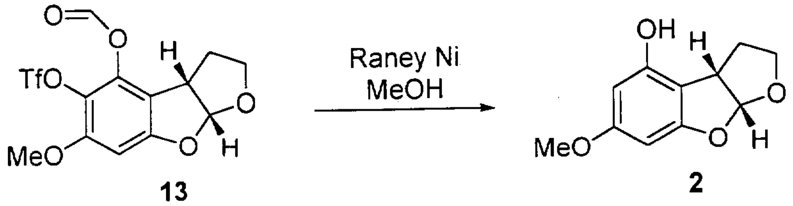
(CDCl$_3$, δ ppm) 187.1, 159.7, 152.5, 134.4, 125.2, 120.6, 118.7 (q, J_{C-F} = 321 Hz), 113.3, 99.9, 67.3, 56.8, 46.8, 33.3; ^{19}F NMR (CDCl$_3$, δ ppm) –73.06 (s); FAB HRMS *m/z* (M + H)$^+$ calcd 369.0256, found 369.0257. Anal. Calcd for $C_{13}H_{11}F_3SO_7$: C, 42.40; H, 3.01; S, 8.71. Found: C, 42.21; H, 3.16; S, 8.66.

Preparation of (±)-*cis*-2,3,3a,8a-Tetrahydro-6-methoxy[2,3-*d*]benzo[*b*]furan-4-*O*-formate (13).



Urea•H$_2$O$_2$ complex (UHP) (2.56 g, 27.2 mmol) was mixed with CH$_2$Cl$_2$ (60 mL), and TFAA (0.96 mL, 6.78 mmol) was added dropwise, with stirring. The mixture was stirred for 1 h at room temperature and aldehyde **12** (1.0000 g, 2.715 mmol) was added in one portion, with stirring. After 15 h, another portion of TFAA (0.96 mL, 6.78 mmol) was added dropwise, with stirring. After an additional 30 h, the reaction was complete. The organic solution was decanted from the semisolid peroxide layer, and the peroxide layer was extracted with CH$_2$Cl$_2$ (60 mL, 30 mL). The combined CH$_2$Cl$_2$ layers were washed with aqueous 5% Na$_2$SO$_3$/5% Na$_2$HPO$_4$ (60 mL), and were determined to be free of peroxides by starch/iodine paper. The combined CH$_2$Cl$_2$ layers were further washed with brine (60 mL), dried over Na$_2$SO$_4$, filtered, and the solvent removed under reduced pressure. The resulting light yellow oil was extracted with CH$_2$Cl$_2$ (3 x 4 mL), and the combined CH$_2$Cl$_2$ layers were evaporated and dried under high vacuum, giving **13** as a sticky yellow oil (287.1 mg, 28%): TLC R_f 0.27 (3:1 hexane/EtOAc); IR (CCl_4, cm^{-1}) 2954, 1758, 1633, 1494, 1453, 1424, 1215, 1139, 957, 916; ^1H NMR ($CDCl_3$, δ ppm) 8.27 (s, 1 H), 6.44 (s, 1 H), 6.38 (d, $J = 5.7$ Hz, 1 H), 4.12 (t, $J = 8.1$ Hz, 1 H), 3.95 (dd, $J = 8.4, 6.0$ Hz, 1 H), 3.87 (s, 3 H), 3.67 (ddd, $J = 12.3, 9.3, 5.1$ Hz, 1 H), 2.16 (tt, $J = 12.3, 12.3, 8.1, 8.1$ Hz, 1 H), 1.99 (dd, $J = 12.3, 4.8$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, δ ppm) 159.6, 156.6, 153.4, 138.8, 124.6, 118.5 (q, $J_{C\text{-}F} = 319$ Hz), 112.8, 112.6, 92.9, 67.6, 56.7, 45.2, 31.3; ^{19}F NMR ($CDCl_3$, δ ppm) –74.09 (s); FAB HRMS m/z (M^+) calcd 384.0127, found 384.0133.

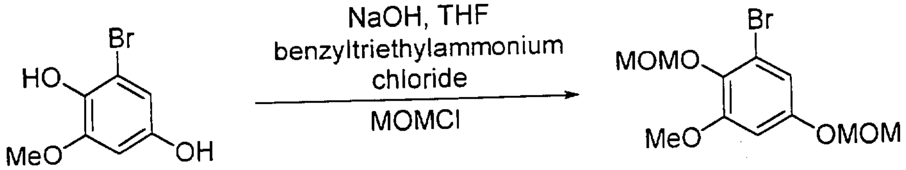
Preparation of (±)-*cis*-2,3,3a,8a-Tetrahydro-4-hydroxy-6-methoxy[2,3-*d*]benzo[*b*]furan (2).



The formate ester **13** (19.0 mg, 0.049 mmol) was dissolved in MeOH (1.6 mL). Raney nickel (50% slurry in water, pore size ~50 µ, surface area 80-100 m^2/g) was rinsed with MeOH (3 x 0.2 mL) and added as a slurry in MeOH (0.4 mL settled volume), and the mixture was stirred vigorously for 3 h at room temperature. The mixture was vacuum-filtered through Celite, rinsing with MeOH, gravity filtered, and the cloudy filtrate was evaporated to a white residue. This residue was suspended in EtOAc (1 mL) and eluted through a plug of silica gel with 1:1 hexane/EtOAc. The solvent was evaporated, giving a light yellow-brown oil, which crystallized upon standing.

Purification by vacuum sublimation (100-115 °C, 0.1 torr), followed by washing with a small amount of ether, gave **2** as a white solid (6.3 mg, 61%): TLC R_f 0.20 (3:1 hexane/EtOAc); mp 151-152 °C (lit. mp 152-153 °C); IR (KBr, cm^{-1}) 3348, 2925, 1630, 1515, 1445, 1248, 1194, 1137, 1054, 961, 920, 818; ^{1}H NMR (CDCl$_3$, δ ppm) 6.32 (d, *J* = 5.7 Hz, 1 H), 6.04 (d, *J* = 2.1 Hz, 1 H), 5.91 (d, *J* = 2.1 Hz, 1 H), 4.11-4.06 (m, 1 H), 4.01-3.96 (m, 1 H), 3.84 (s, 1 H), 3.73 (s, 3 H), 3.73-3.63 (m, 1 H), 2.10-2.20 (m, 2 H); the ^{1}H NMR spectrum matches reported values for **2**.[5j,n] CI HRMS *m/z* (M+H$^+$) calcd 209.0814, found 209.0829.

Preparation of 1-Bromo-3-methoxy-2,5-bis(methoxymethoxy)benzene (15).

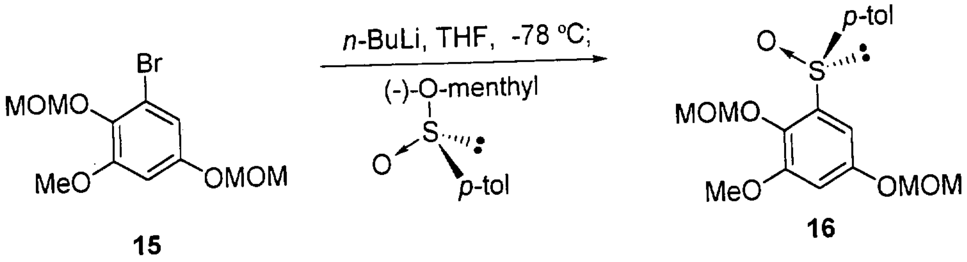


14

15

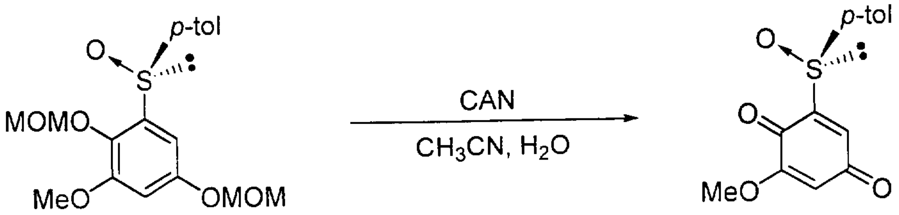
The hydroquinone **14** (1.095g, 5.00 mmol) was combined with benzyltriethylammonium chloride (0.114 g, 0.500 mmol), dissolved in THF (7 mL), placed under an atmosphere of dry N_2, and cooled to 0 °C. Freshly ground NaOH powder (1.20 g, 30.0 mmol) was added, with stirring and N_2 flushing, giving an emerald green solution above the solid NaOH. A solution of MOMCl (1.51 mL, 20.0 mmol) in THF (1.5 mL) was added dropwise over 15 min., causing a color change to off-white. The mixture was stirred for an additional hour at 0 °C, then warmed to room temperature and stirred for another hour and then H_2O (5 mL) was added. Stirring this mixture for 20 min gave two clear tan-colored phases. The organic layer was separated, washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure, giving a brown oil. Flash chromatography (basic alumina activity 1, 3:1 hexane/EtOAc) gave **15** as a clear, light yellow-tinted oil (1.353 g, 88%): the FTIR (neat) and ^1H NMR ($CDCl_3$) spectra matched the published spectra.[4c,j,k,n]

Preparation of (*S*)-(-)-4-Methylbenzenesulfinyl-3-methoxy-2,5-bis-methoxymethoxybenzene (16).



THF (37 mL) was cooled to –78 °C under an atmosphere of dry N_2 in a flame-dried 200 mL point bottom flask. A 2.3 M solution of *n*-BuLi in hexanes (8.90 mL, 20.4 mmol) was added via syringe, with stirring, followed by dropwise addition of a solution of the aryl bromide **15** (5.688 g, 18.5 mmol) in THF (82 mL), with stirring. This solution was stirred at –78 °C for 1 h and transferred rapidly via a short cannula into a –78 °C solution of (-)-menthyl (*S*)-*p*-toluenesulfinate (6.543 g, 22.2 mmol) in THF (278 mL) under N_2, with rapid stirring. The light yellow solution was stirred at –78 °C for 2 h, then allowed to warm to room temperature, and stirred for an additional 2 h. The solution was hydrolyzed by addition of H_2O (350 mL), with stirring, and this mixture was extracted with CH_2Cl_2 (3 x 250 mL). The combined CH_2Cl_2 layers were washed with brine (250 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure, giving a clear light yellow oil. This mixture was dissolved in a minimum amount of CH_2Cl_2 and separated by flash chromatography (silica gel, 2:1 hexane/EtOAc), giving the desired product as a clear colorless oil which crystallized upon standing. The product was recrystallized as follows: low boiling (30-60 °C) petroleum ether (50 mL) was added and the solid was crushed to a fine powder. This mixture was heated to reflux, with stirring, and EtOAc was added dropwise until the solid just dissolved. The solution was cooled and seeded, giving **16** as white needles. The filtrate was concentrated and the process repeated on the resulting oil, giving an additional crop of crystals (5.124 g, 76%): TLC R_f 0.16 (2:1 hexane/EtOAc); mp 80-81 °C; $[\alpha]^{24}_D = -16.8$ (c 1.00, $CHCl_3$); IR (KBr, cm^{-1}) 3024, 2934, 2832, 1594, 1578, 1481, 1449, 1303, 1152, 1074, 998; ^{1}H NMR ($CDCl_3$, δ ppm) 7.62 (AA'BB' system, $J = 8.4$ Hz, 2 H), 7.22 (AA'BB' system, $J = 8.4$ Hz, 2 H), 7.11 (d, $J = 2.7$ Hz, 1 H), 6.66 (d, $J = 2.7$ Hz, 1 H), 5.22 (d, J = 5.7 Hz, 1 H), 5.17 (AB system d, $J = 6.9$ Hz, 1 H), 5.14 (AB system d, $J = 6.9$ Hz, 1 H), 5.05 (d, $J = 5.7$ Hz, 1 H), 3.80 (s, 3 H), 3.65 (s, 3 H), 3.46 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ ppm) 154.8, 152.6, 142.5, 141.2, 140.4, 136.2, 129.8, 124.9, 104.2, 101.8, 98.8, 94.6, 58.1, 56.2, 56.0, 21.3; EI HRMS m/z (M^+) calcd 366.1137, found 366.1129. Anal. Calcd for $C_{18}H_{22}SO_6$: C, 59.00; H, 6.05; S, 8.75. Found: C, 59.08; H, 6.17; S, 8.66.

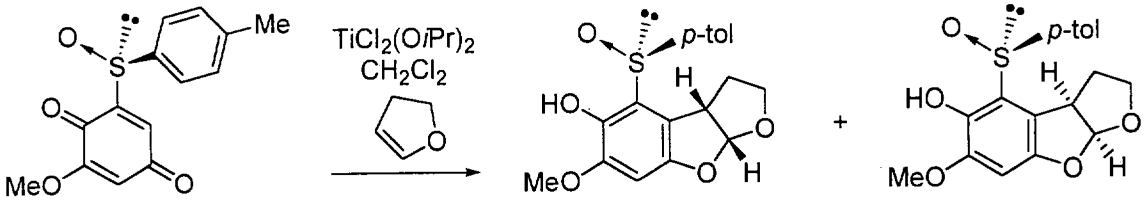
Preparation of (*S*)-(+)-2-Methoxy-6-(4-methylbenzenesulfinyl)-1,4-benzoquinone (9).



16 **9**

The MOM-protected sulfoxide **16** (1.833 g, 5.00 mmol) was dissolved in CH_3CN (60 mL) and to this stirred solution was added dropwise a solution of ceric ammonium nitrate (CAN; 6.033 g, 11.0 mmol) in H_2O (25 mL). A color change to orange occurred and a small quantity of gas was evolved. The solution was stirred for 30 min, and brine (125 mL) was added. The mixture was extracted with $CHCl_3$ (3 x 125 mL), and the combined $CHCl_3$ fractions were dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure, giving an orange oil which crystallized upon standing. The product was dissolved in a minimum amount of $CHCl_3$ and rapidly flashed through a short silica gel column (1:1 hexane/EtOAc) to remove a dark impurity of low R_f. Concentration of the product solution gave an orange oil, which was crystallized from acetone, giving **9** as orange-red needles (1.227 g, 89%): TLC R_f 0.40 (1:1 hexane/EtOAc); mp of material recrystallized from ether 152-153 °C; $[\alpha]^{25}{}_D = +375.8$ (*c* 1.00, $CHCl_3$); IR (KBr, cm^{-1}) 3058, 2979, 2941, 1682, 1641, 1596, 1302, 1236, 1129, 1081, 1060, 997, 910; ^1H NMR ($CDCl_3$, δ ppm) 7.66 (AA'BB' system, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 2.7 Hz, 1 H), 7.28 (AA'BB' system, *J* = 8.4 Hz, 2 H), 5.94 (d, *J* = 2.7 Hz, 1 H), 3.78 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ ppm) 184.6, 178.3, 158.8, 153.5, 143.0, 138.2, 132.6, 130.3, 125.8, 108.4, 56.7, 21.5; EI HRMS *m/z* (M^+) calcd 276.0456, found 276.0453. Anal. Calcd for $C_{14}H_{12}SO_4$: C, 60.68; H, 4.38; S, 11.60. Found: C, 60.75; H, 4.50; S, 11.45.

Preparation of (-)-(S_s)-2,3,3a*S*,8a*R*-Tetrahydro-5-hydroxy-6-methoxy-4-methylbenzenesulfinyl-[2,3-*d*]-benzo[*b*]furan (7a) and (+)-(S_s)-2,3,3a*R*,8a*S*-Tetrahydro-5-hydroxy-6-methoxy-4-methylbenzenesulfinyl-[2,3-*d*]-benzo[*b*]furan (7b).



9 **7a** **7b**

In a flame dried 200 mL round-bottom flask under N_2 was placed CH_2Cl_2 (7 mL), neat Ti(O*i*Pr)$_4$ (3.0 mL, 10 mmol), and a 1 M solution of $TiCl_4$ in CH_2Cl_2 (10.0 mL, 10 mmol), with stirring. After stirring for 30 min, this solution was cooled to –78 °C, causing some of the Lewis acid to precipitate, forming a white suspension. A solution of **9** (0.552 g, 2.00 mmol) in CH_2Cl_2 (20 mL) under N_2 was cooled to –78 °C and transferred to the Lewis acid solution by cannula at –78 °C, with rapid stirring. The opaque orange mixture was stirred for 30 min, and dihydrofuran (0.170 mL, 2.25 mmol) was added as rapidly as possible, with vigorous stirring, giving a rapid color change to dark red. Stirring was continued at –78 °C for 75 min, and then the reaction was diluted with CH_2Cl_2 (40 mL) and warmed to 0 °C. Solid $NaHCO_3$ (20 g) was added, followed by *i*PrOH (60 mL), and the mixture was stirred vigorously for 15 min resulting in a color change to orange. Next, H_2O (20 mL) was added, with stirring, causing a color change to yellow and considerable thickening of the reaction mixture. After being stirred for 5 min, the mixture was vacuum filtered through a sintered glass funnel and the solid material was rinsed successively with CH_2Cl_2 (100 mL), H_2O (100 mL), CH_2Cl_2 (100 mL), H_2O

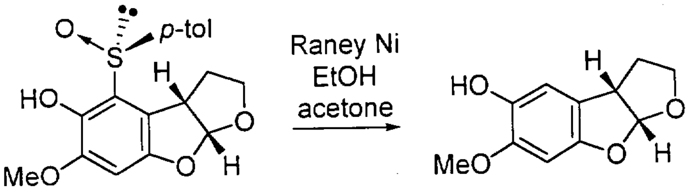
(100 mL), and CH_2Cl_2 (100 mL). The combined filtrate and washings gave a two-phase mixture, which was separated, and the CH_2Cl_2 layer was dried over Na_2SO_4. Filtration and concentration under reduced pressure gave an off-white foam (3.3:1 **7b**:**7a**). Separation of the diastereomers by column chromatography on silica gel (10:1 CH_2Cl_2/acetone) gave **7a** and **7b** as oils which crystallized upon addition of ether (0.446 g, 64%).

7a: TLC R_f 0.59 (10:1 CH_2Cl_2/acetone); mp 179-180 °C; $[\alpha]^{24}{}_D = -153.1$ ° (*c* 1.29, $CHCl_3$); IR (KBr, cm^{-1}) 2975, 1611, 1480, 1441, 1313, 1198, 1083, 1005, 962, 816; ^1H NMR ($CDCl_3$, 500 MHz, δ ppm) 9.90 (s, 1 H), 7.67 (AA'BB' system, *J* = 8.0 Hz, 2 H), 7.32 (AA'BB' system, *J* = 8.0 Hz, 2 H), 6.49 (s, 1 H), 6.24 (d, *J* = 6.0 Hz, 1 H), 4.12 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1 H), 3.84 (s, 3 H), 3.78 (ddd, *J* = 8.0, 5.5, 2.0 Hz, 1 H), 3.69 (ddd, *J* = 12.0, 9.0, 5.5 Hz, 1 H), 2.41 (s, 3 H), 2.31-2.21 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm) 152.4, 149.7, 143.3, 143.1, 140.0, 130.5, 126.0, 119.2, 113.7, 111.9, 97.4, 67.4, 56.4, 45.8, 32.8, 21.6; EI HRMS *m/z* (M^+) calcd 346.0875, found 346.0870. Anal. Calcd for $C_{18}H_{18}SO_5$: C, 62.41; H, 5.24; S, 9.26. Found: C, 62.60; H, 5.44; S, 9.09.

7b: TLC R_f 0.51 (10:1 CH_2Cl_2/acetone); mp 185 °C; $[\alpha]^{25}{}_D = +62.8$ ° (*c* 1.29, $CHCl_3$); IR (KBr, cm^{-1}) 2958, 1608, 1479, 1439, 1309, 1223, 1082, 1011, 959, 821; ^1H NMR ($CDCl_3$, 500 MHz, δ ppm) 8.71 (s, 1 H), 7.66 (AA'BB' system, *J* = 8.0 Hz, 2 H), 7.29 (AA'BB' system, *J* = 8.0 Hz, 2 H), 6.52 (s, 1 H), 6.31 (d, *J* = 5.5 Hz, 1 H), 4.01 (ddd, *J* = 9.0, 6.0, 1.5 Hz, 1 H), 3.94 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1 H), 3.86 (s, 3 H), 3.55 (ddd, *J* = 11.5, 8.5, 5.0 Hz, 1 H), 2.40 (s, 3 H), 2.05 (dddd, *J* = 12.5, 11.5, 9.0, 8.0 Hz, 1 H), 1.63 (dd, *J* = 12.5, 5.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm) 152.6, 149.1, 142.8, 142.0, 140.6, 130.4, 126.7, 120.6, 115.5, 112.2, 97.4, 67.1, 56.4, 45.8, 33.6, 21.5;

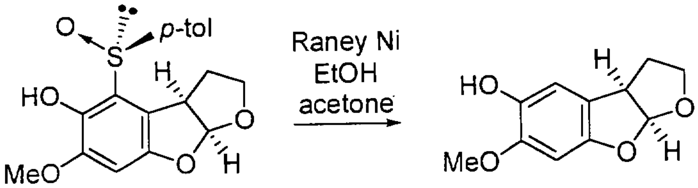
EI HRMS *m/z* (M^+) calcd 346.0875, found 346.0878. Anal. Calcd for $C_{18}H_{18}SO_5$: C, 62.41; H, 5.24; S, 9.26. Found: C, 62.65; H, 5.42; S, 9.11.

Preparation of (-)-2,3,3a*S*,8a*R*-Tetrahydro-5-hydroxy-6-methoxy[2,3-*d*]-benzo[*b*]furan (-)-(17) and (+)-2,3,3a*R*,8a*S*-Tetrahydro-5-hydroxy-6-methoxy[2,3-*d*]-benzo[*b*]furan (+)-(17).



7a

(-)-17



7b

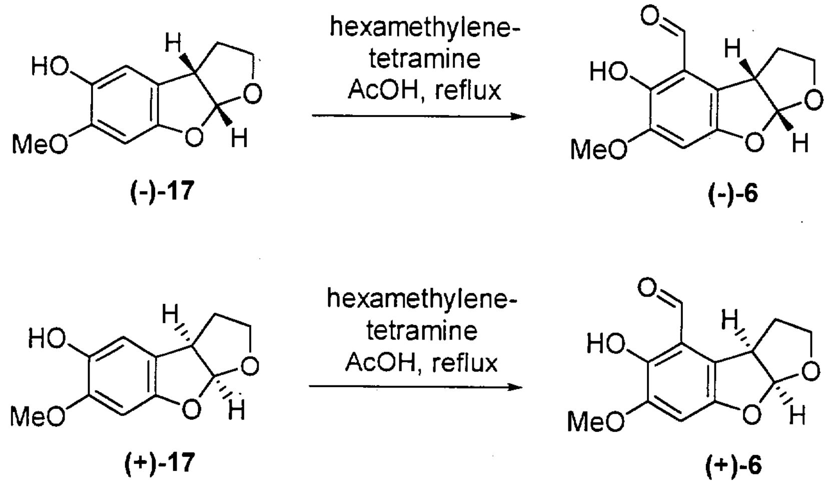
(+)-17

Phenol **7a** (62.5 mg, 0.18 mmol) was dissolved in EtOH (5.2 mL) and acetone (1.3 mL). Raney nickel (50% slurry in water, pore size ~50 μ, surface area 80-100 m^2/g) was rinsed with EtOH (3 x 1 mL) and added as a slurry in EtOH (0.55 mL settled volume), and the mixture was stirred for 3 h at room temperature. The mixture was filtered through Celite, rinsing with EtOH. This solution was gravity-filtered, and the solvent removed under reduced pressure. giving (-)-**17** as a white microcrystalline solid (37.6 mg, 100%): TLC R_f 0.25 (3:1 hexane/EtOAc); mp 152-153 °C; $[\alpha]^{26}_D = -97.8$ ° (*c* 1.41, $CHCl_3$); IR (KBr, cm^{-1}) 3394, 2970. 2874, 1498, 1344, 1321, 1245, 1216, 1156, 1078, 953; ^1H NMR ($CDCl_3$, δ ppm) 6.74 (d, $J = 0.9$ Hz, 1 H), 6.42 (s, 1 H), 6.26 (d, $J =$

5.4 Hz), 5.23 (bs, 1 H), 4.05 (t, J = 8.1 Hz, 1 H), 3.95 (dd, J = 7.8, 5.7 Hz, 1 H), 3.84 (s, 3 H), 3.60 (ddd, J = 12.0, 8.4, 4.8 Hz, 1 H); 2.23 (tt, J = 12.0, 12.0, 7.8, 7.8 Hz, 1 H), 2.01 (dd, J = 12.0, 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, δ ppm) 152.8, 146.7, 140.2, 118.2, 111.3, 110.0, 93.7, 67.3, 56.2, 46.8, 33.5; EI HRMS *m/z* (M^+) calcd 208.0736, found 208.0737. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.38; H, 5.68.

Phenol **7b** (126.0 mg, 0.364 mmol) was dissolved in EtOH (10.9 mL) and acetone (2.7 mL). Raney nickel (50% slurry in water, pore size ~50 μ, surface area 80-100 m^2/g) was rinsed with EtOH (3 x 2 mL) and added as a slurry in EtOH (1.10 mL settled volume), and the mixture was stirred for 3 h at room temperature. The mixture was filtered through Celite, rinsing with EtOH. This solution was gravity-filtered, and the solvent removed under reduced pressure, giving (+)-**17** as a white microcrystalline solid (75.5 mg, 100%): TLC R_f 0.25 (3:1 hexane/EtOAc); mp 152-153 °C; $[\alpha]^{26}_D = +98.6^\circ$ (*c* 1.41, $CHCl_3$); the IR, ^{1}H NMR, and ^{13}C NMR spectra were identical to those obtained for the enantiomer (-)-**17**; FAB HRMS *m/z* (M^+) calcd 208.0736, found 208.0740. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.50; H, 5.64.

Preparation of (-)- and (+)-2,3,3a,8a-Tetrahydro-5-hydroxy-6-methoxy[2,3-*d*]-benzo[*b*]furan-4-carboxaldehyde (6) from 17.



General Procedure. Phenol **17** (10.0 mg, 0.048 mmol) was combined with hexamethylenetetramine (13.5 mg, 0.096 mmol) and dissolved in glacial AcOH (1 mL) in a screw-top culture tube. The solution was heated, with stirring, at 110 °C for 42 h, during which a dark red color developed. An aqueous 33% H_2SO_4 solution was added (1 mL), and the reaction solution was heated at 110 °C for 1h, and then cooled to room temperature and diluted with H_2O (2 mL). This solution was extracted with CH_2Cl_2 (3 x 2 mL), and the combined CH_2Cl_2 extracts were washed with brine (2 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The resulting oil was purified by column chromatography on silica gel (33:33:1, hexane/EtOAc/AcOH), giving **6** as a yellow oil, which crystallized upon standing, and was vacuum dried (4.1 mg, 36%): TLC R_f 0.54 (33:33:1 hexane/EtOAc/AcOH); mp 151-153 °C; (-)-**6**: $[\alpha]^{23}_D = -74.5$ ° (*c* 0.68, $CHCl_3$); (+)-**6**: $[\alpha]^{23}_D = +70.8$ ° (*c* 0.76, $CHCl_3$); the ^1H NMR spectrum was identical to that obtained previously for (±)- **6** .

```
100mg-BV

Pulse Sequence: s2pul

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Date:      Jan. 29, 2000
Solvent: CDCl3
File:      100mg-BV
Starting Time:      19:17:50
Completion Time: 19:18:55
Total acq. time 1 minute

UNITYplus-500   "fid"
Ambient temperature

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 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.999 sec
 Width 6003.3 Hz
 16 repetitions
OBSERVE    H1, 300.1683396 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 131072
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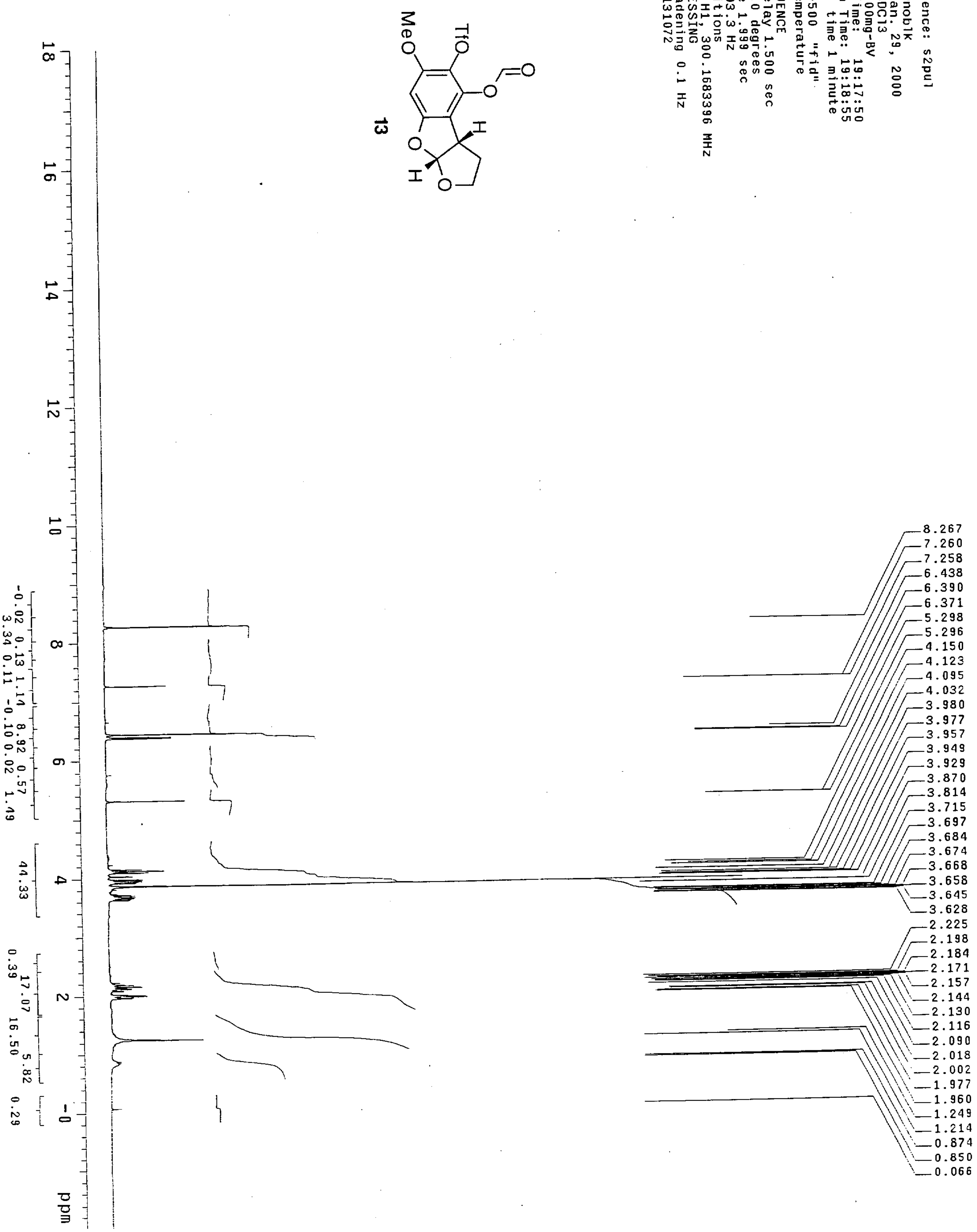
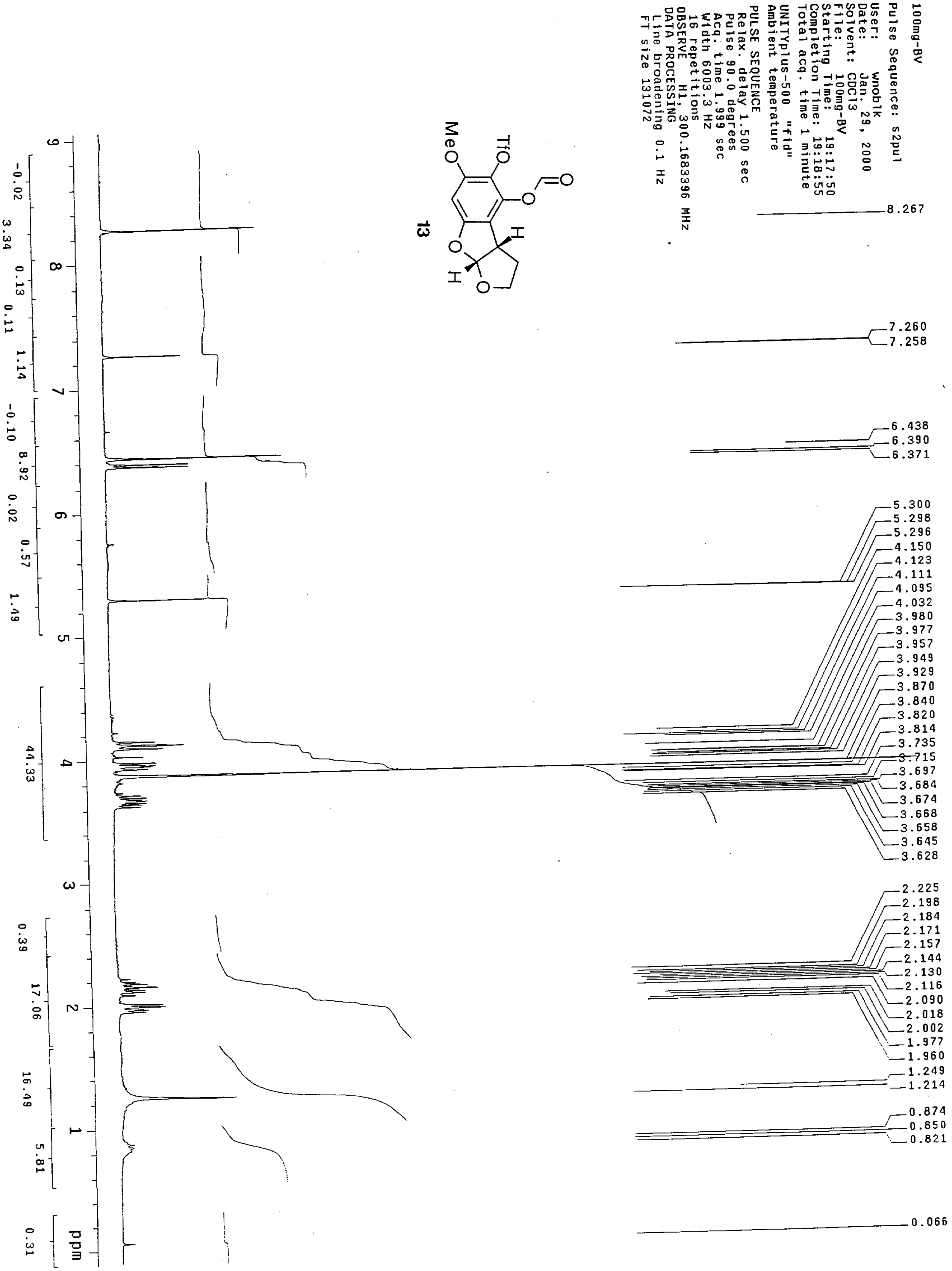


13



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Solvent: CDCl3
File: 100mg-BV
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Completion Time: 19:18:55
Total acq. time 1 minute
UNITYplus-500 "fid"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
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16 repetitions
OBSERVE H1, 300.1683396 MHz
DATA PROCESSING
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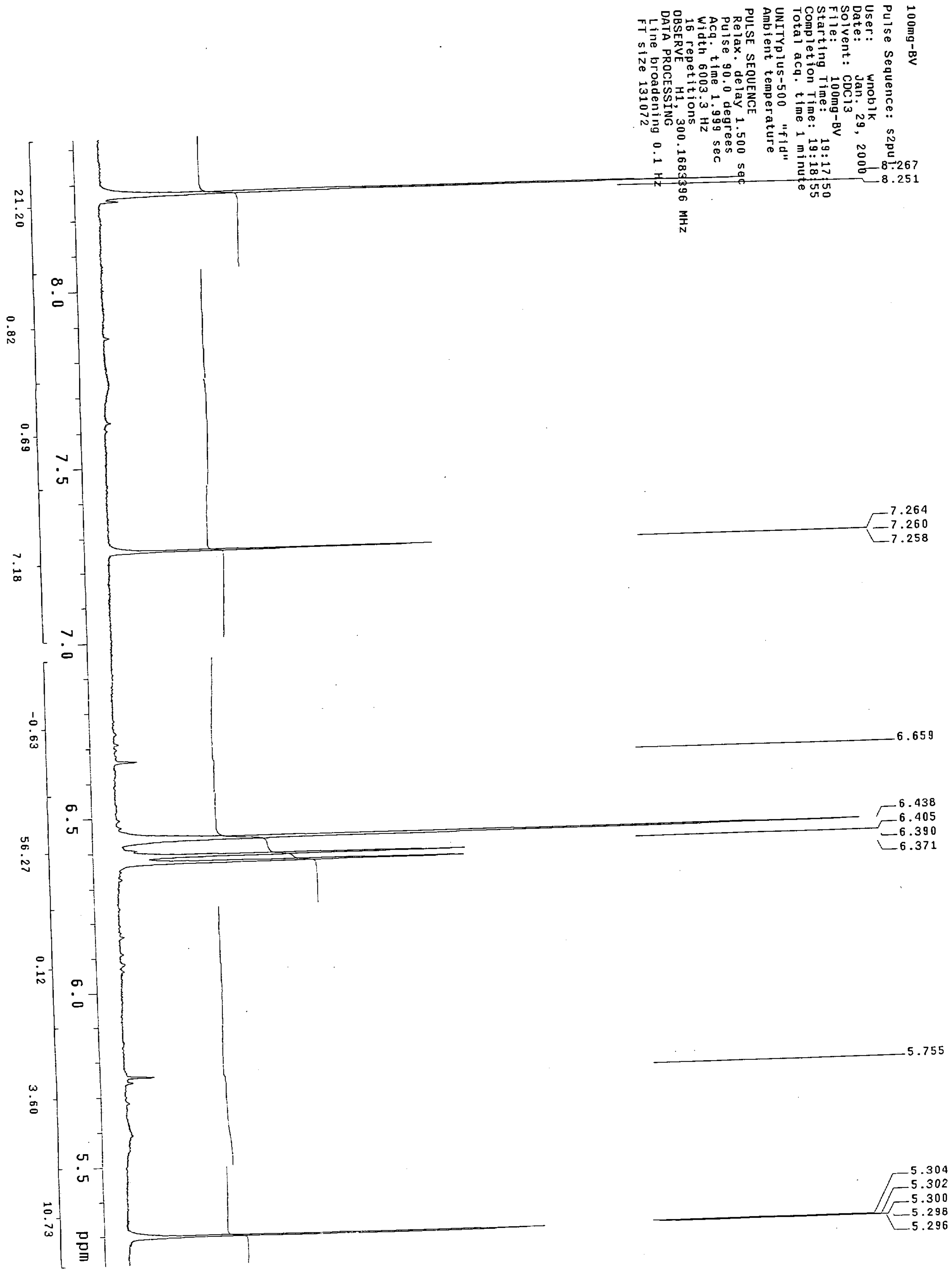
FT size 131072

13



100mg-BV

Pulse Sequence: s2pul

User: wnoblk
Date: Jan. 29, 2000
Solvent: CDCl3
File: 100mg-BV
Starting Time: 19:17:50
Completion Time: 19:18:55
Total acq. time 1 minute
UNITYplus-500 "fid"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 6003.3 Hz
16 repetitions
OBSERVE H1, 300.1683396 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072

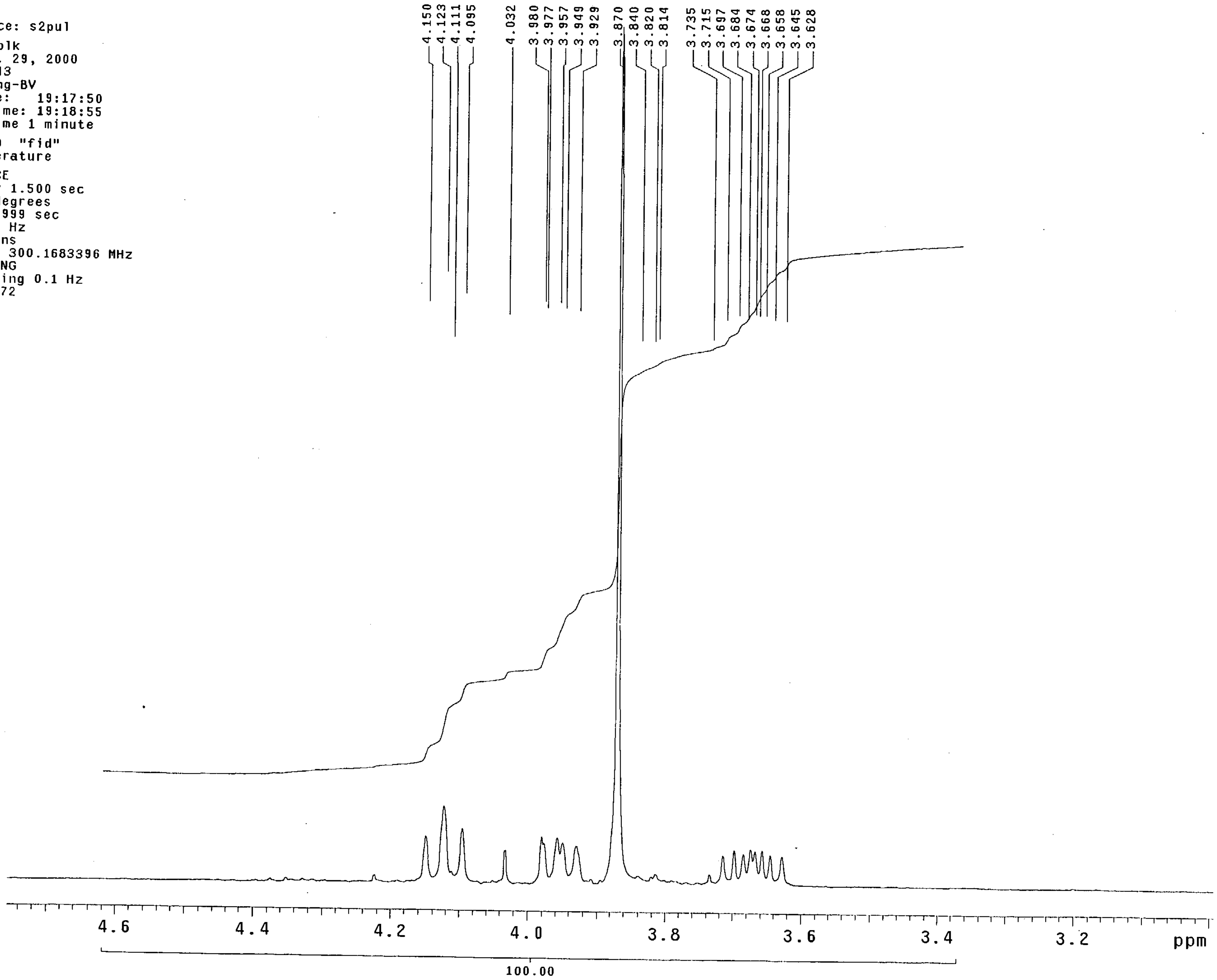
100mg-BV

Pulse Sequence: s2pul

User: wnoblk
Date: Jan. 29, 2000
Solvent: CDCl3
File: 100mg-BV
Starting Time: 19:17:50
Completion Time: 19:18:55
Total acq. time 1 minute

UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 6003.3 Hz
16 repetitions
OBSERVE H1, 300.1683396 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072



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100mg-BV

Pulse Sequence: s2pul

User:     wnoblk
Date:     Jan. 29, 2000
Solvent: CDCl3
File:      100mg-BV
Starting Time:    19:17:50
Completion Time: 19:18:55
Total acq. time 1 minute

UNITYplus-500   "fid"
Ambient temperature

PULSE SEQUENCE
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  Pulse 90.0 degrees
  Acq. time 1.999 sec
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  16 repetitions
OBSERVE    H1, 300.1683396 MHZ
DATA PROCESSING
  Line broadening 0.1 Hz
  FT size 131072
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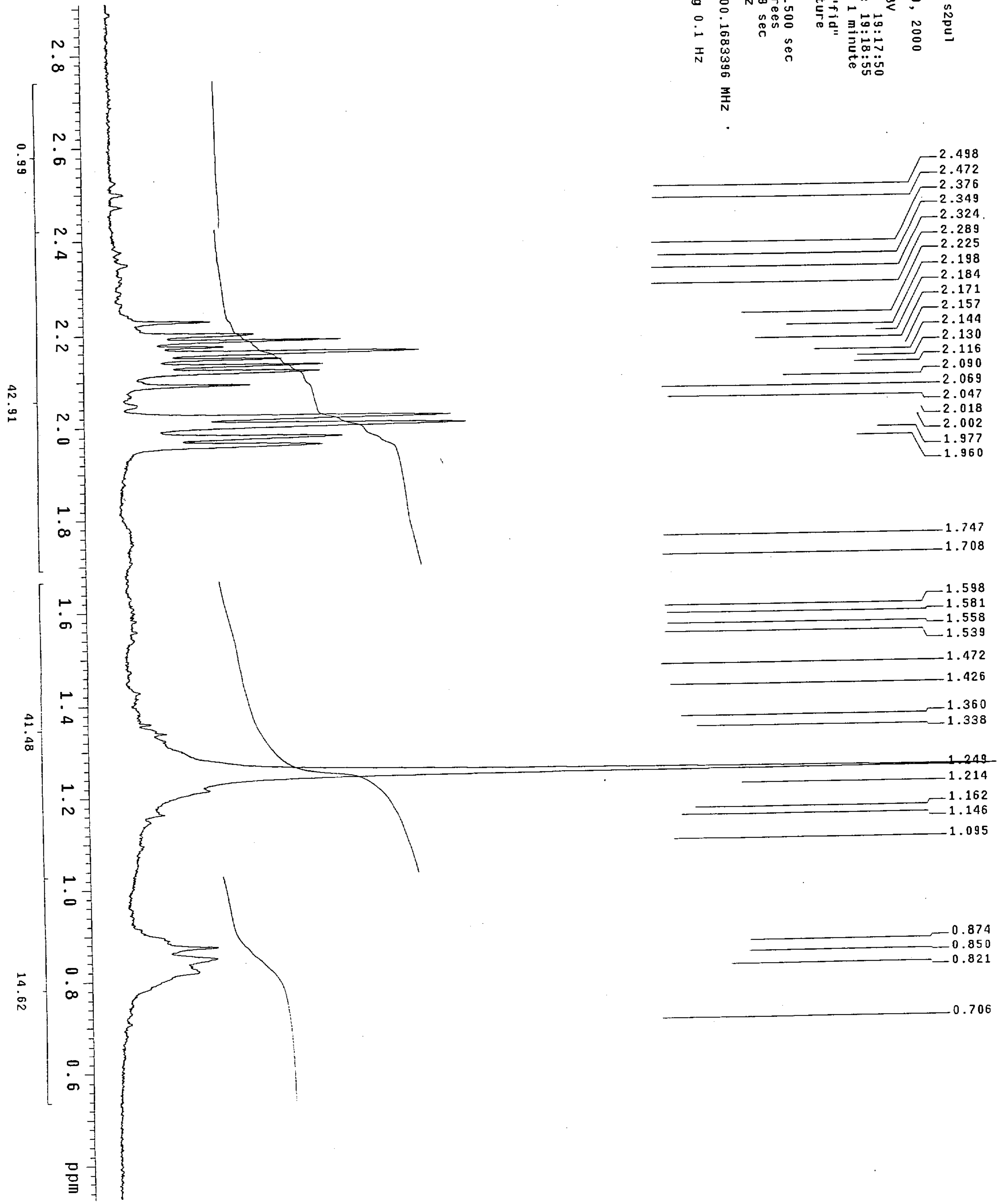

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sublimed

Pulse Sequence: s2pul
User:    wnoblk
Date:    Feb. 10, 2000
Solvent: CDCl3
File:    sublimed
Starting Time:   19:57:29
Completion Time: 19:58:34
Total acq. time 1 minute

UNITYplus-500  "fid"
Ambient temperature

PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 2.000 sec
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 16 repetitions
OBSERVE   H1, 299.8827589 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 131072
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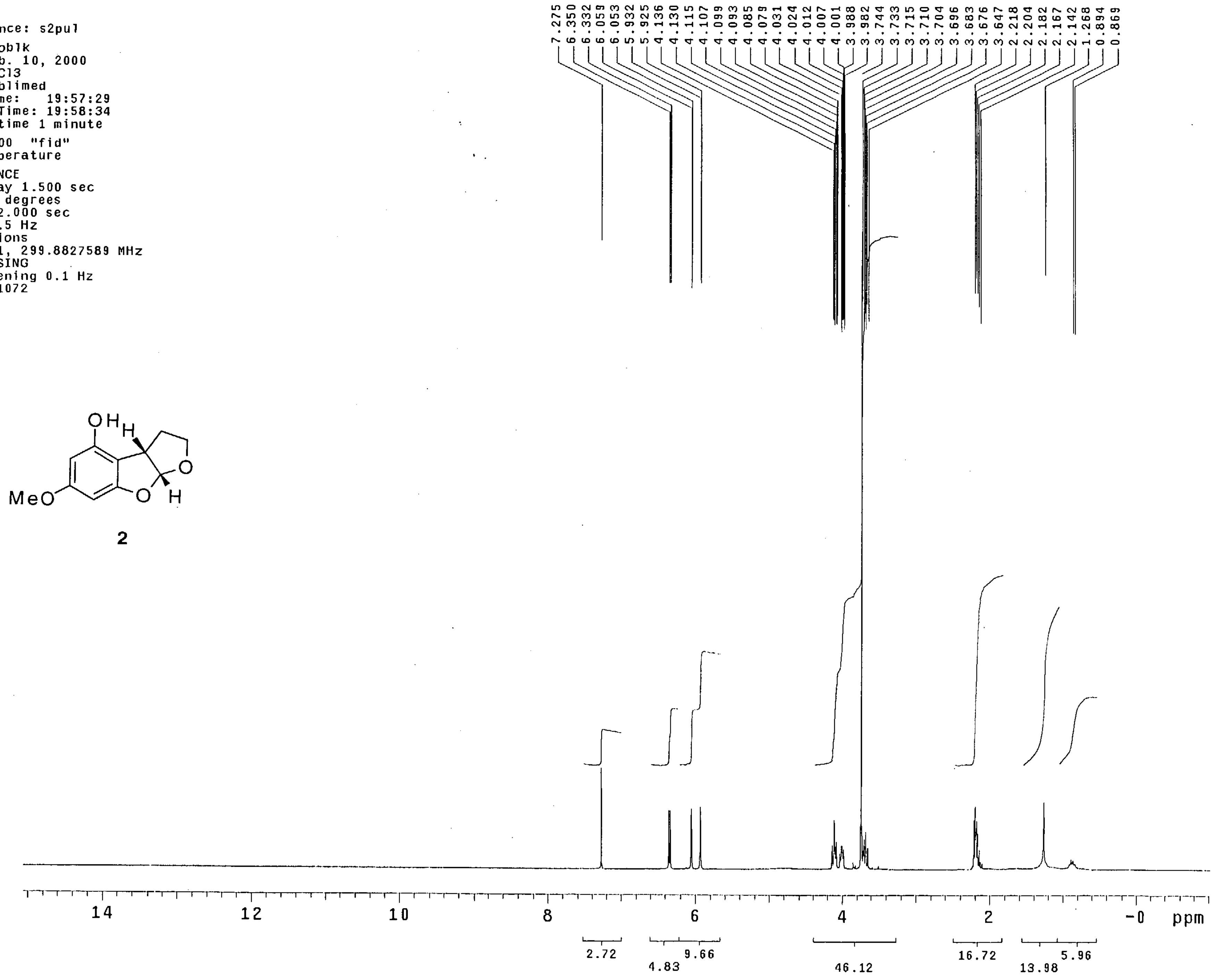
2



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sublimed

Pulse Sequence: s2pul

User:     wnoblk
Date:     Feb. 10, 2000
Solvent: CDCl3
File:     sublimed
Starting Time:    19:57:29
Completion Time: 19:58:34
Total acq. time 1 minute

UNITYplus-500  "fid"
Ambient temperature

PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 2.000 sec
 Width 6001.5 Hz
 16 repetitions
OBSERVE   H1, 299.8827589 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 131072
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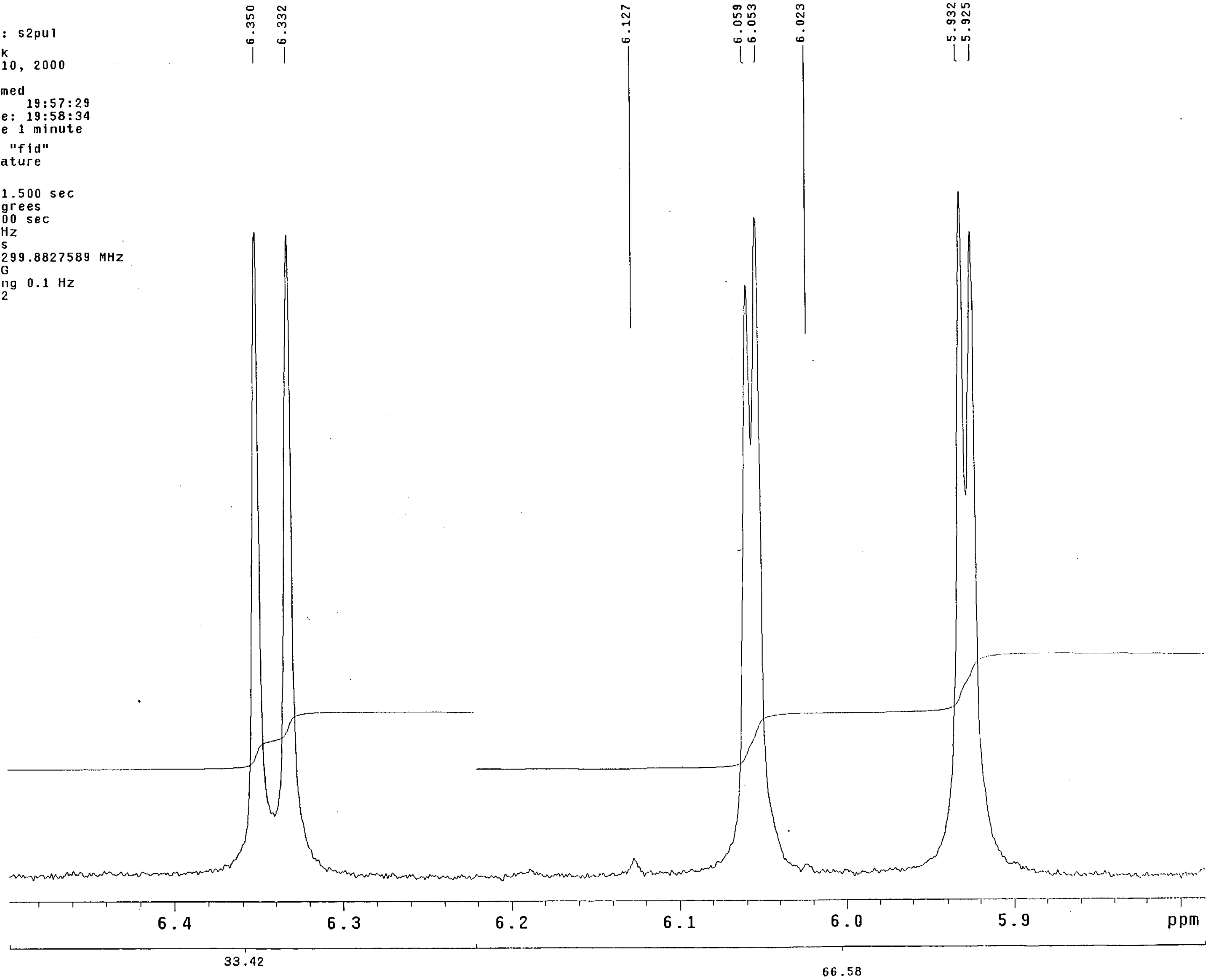

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sublimed

Pulse Sequence: s2pul
User:     wnoblk
Date:     Feb. 10, 2000
Solvent: CDCl3
File:     sublimed
Starting Time:    19:57:29
Completion Time: 19:58:34
Total acq. time 1 minute
UNITYplus-500  "fid"
Ambient temperature
PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 2.000 sec
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 16 repetitions
OBSERVE   H1, 299.8827589 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 131072
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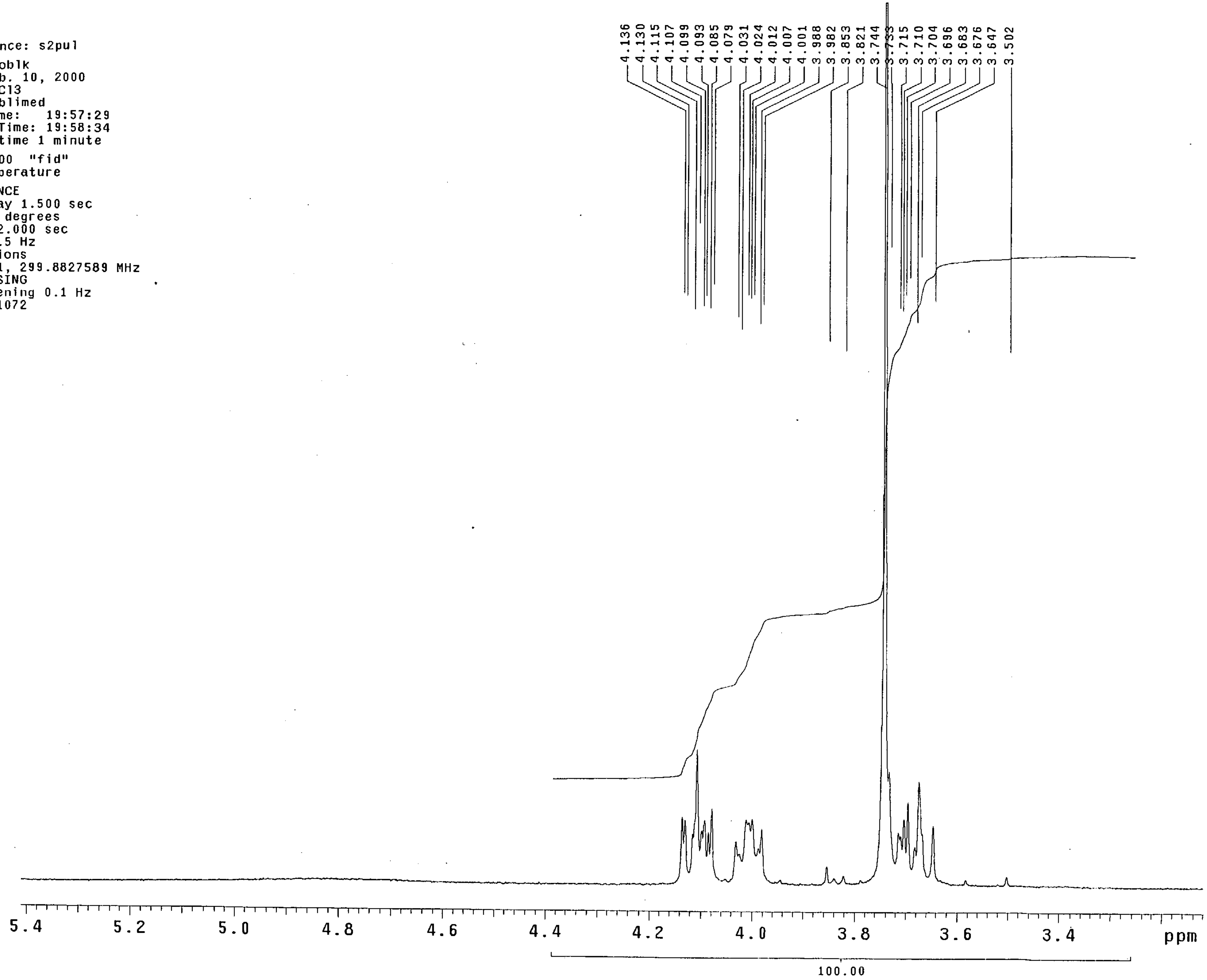

sublimed

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Date: Feb. 10, 2000
Solvent: CDCl3
File: sublimed
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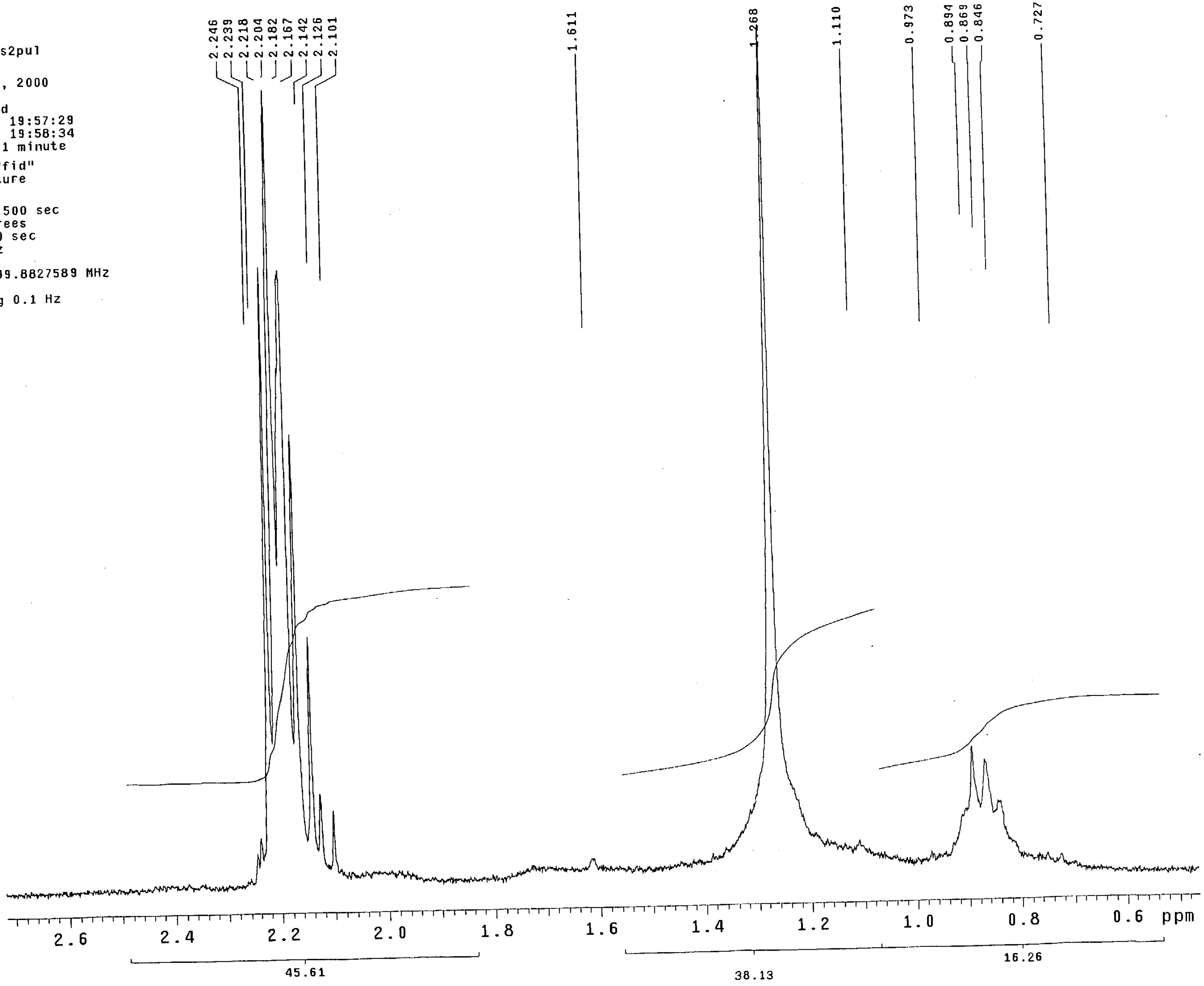
Completion Time: 19:58:34
Total acq. time 1 minute

UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 6001.5 Hz
16 repetitions
OBSERVE H1, 299.8827589 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072



CRYSTAL STRUCTURE REPORT

$C_{18}H_{18}O_5S$

Report prepared for:
B. Kedrowski / Prof. W. Noland

18 August 1999

Carrie E. Buss
X-Ray Crystallographic Laboratory
160 Kolthoff Hall
Chemistry Department
207 Pleasant St. S.E.
The University of Minnesota
Minneapolis, MN 55455

DATA COLLECTION

A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from 59 reflections. Final cell constants are calculated from a set of 6608 strong reflections from the actual data collection. Final cell constants reported in this manner usually are about one order of magnetude better in precision than reported from four-circle diffractometers. Please refer to Table 1 for additional crystal and refinement information.

The data collection technique used for this specimen is generally known as a hemisphere collection. Here a randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames are collected with 0.30° steps in ω. In the event the lattice is triclinic some additional sets of frames are collected to better model the absorption correction.

STRUCTURE SOLUTION AND REFINEMENT

The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics.[1] A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares / difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the E-map and refined with isotropic displacement parameters.

The structure was found as expected with the exception of the relative stereochemistry.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 160 Kolthoff Hall, Chemistry Department, The University of Minnesota. All calculations were preformed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs. All publications arising from this report MUST either 1)include Carrie E. Buss as a coauthor or 2)acknowledge both Carrie E. Buss and the X-Ray Crystallographic Laboratory.

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[1] SHELXTL-Plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.

Some equations of interest:

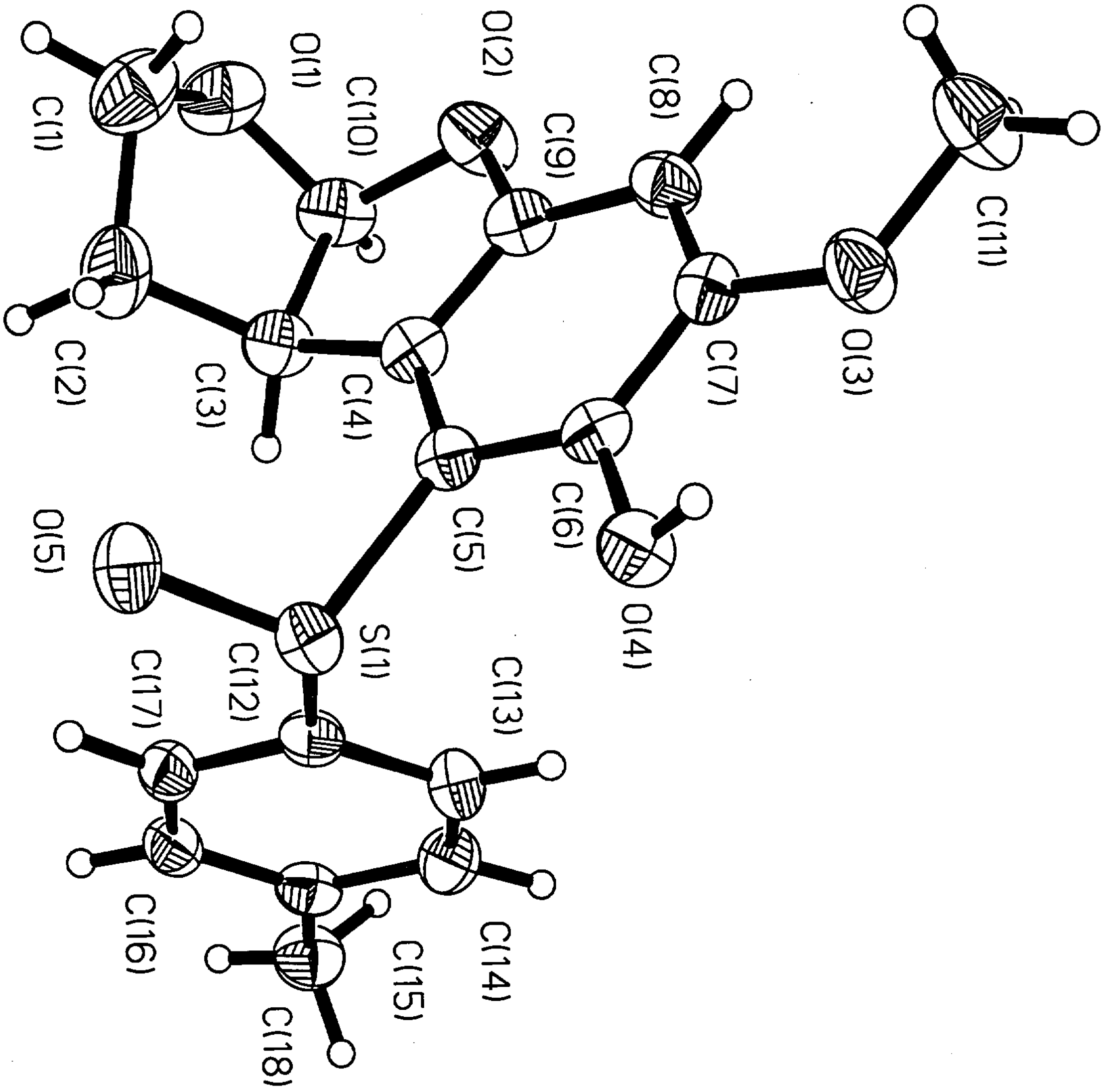
$$R_{int}=\sum|F_o^2-<F_o^2>|/\sum|F_o^2|$$

$$R1=\sum||F_o|-|F_c||/\sum|F_o|$$

$$wR2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2},$$

$$\text{where } w=q/\sigma^2(F_o^2)+(a*P)^2+b*P$$

$$GooF=S= [\sum[w(F_o^2-F_c^2)^2]/(n-p)^{1/2}$$


C(1)
O(1)
C(10)
O(2)
C(9)
C(8)
C(11)
O(3)
C(7)
C(2)
C(3)
C(4)
C(5)
C(6)
O(4)
O(5)
S(1)
C(12)
C(17)
C(13)
C(14)
C(15)
C(16)
C(18)

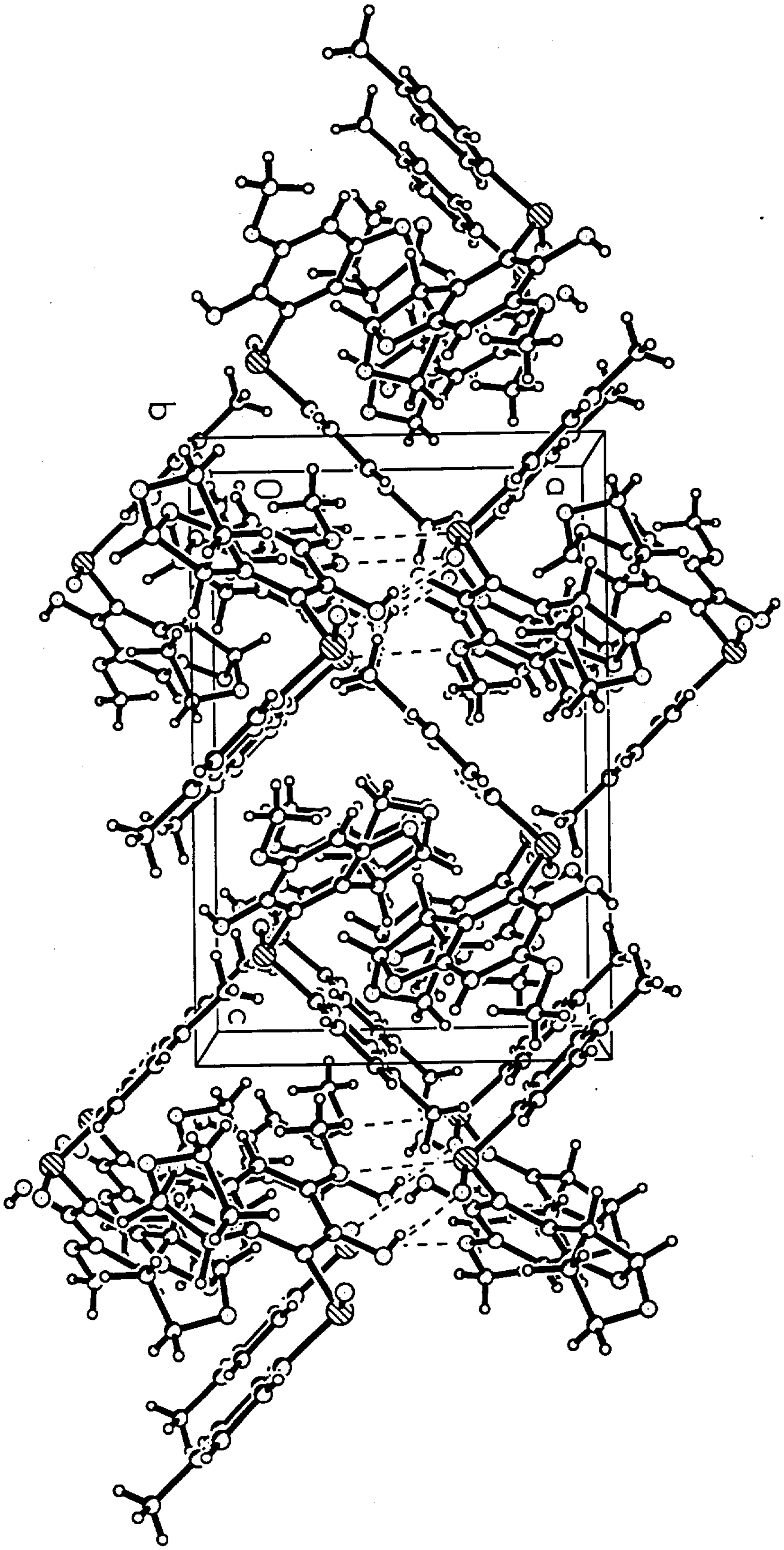

b
0
a
c

Table 1. Crystal data, data collection, and solution and refinement for 99210.

Crystal Data	
Empirical formula	$C_{18}H_{18}O_5S$
Crystal Habit, color	Block, Colorless
Crystal size	0.40 x 0.35 x 0.35 mm
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
	a = 10.2178(7) Å α = 90°
	b = 10.4776(8) Å β = 90°
	c = 15.071(1) Å γ = 90°
Volume	1613.5(2) $Å^3$
Z	4
Formula weight	346.38
Density (calculated)	1.426 Mg/m^3
Absorption coefficient	0.226 mm^{-1}
F(000)	728
Data Collection	
Diffractometer	Siemens SMART Platform CCD
Wavelength	0.71073 Å
Temperature	173(2) K
θ range for data collection	2.37 to 25.06°
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-17 \le \ell \le 17$
Reflections collected	12175
Independent reflections	2858 (R_{int} = 0.0338)
Solution and Refinement	
System used	SHELXTL-V5.0
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(F_o^2)+(AP)^2+(BP)]^{-1}$, where $P = (Fo^2+2Fc^2))/3$, A = 0.0558, and B = 0.0000
Absorption correction	SADABS (Sheldrick, 1996)
Max. and min. transmission	1.000000 and 0.784822
Absolute structure parameter	0.01(6)
Data / restraints / parameters	2858 / 0 / 289
R indices ($I>2\sigma(I)$ = 2668)	R1 = 0.0292, wR2 = 0.0748
R indices (all data)	R1 = 0.0323, wR2 = 0.0764
Goodness-of-fit on F^2	1.009
Largest diff. peak and hole	0.234 and -0.163 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for 99210. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
O(1)	5760(2)	4162(2)	6087(1)	45(1)	1
C(1)	4480(3)	3636(3)	5912(2)	51(1)	1
C(2)	3874(2)	3482(2)	6814(2)	44(1)	1
C(3)	4377(2)	4669(2)	7309(1)	32(1)	1
C(4)	3498(2)	5824(2)	7251(1)	27(1)	1
C(5)	2303(2)	6134(2)	7656(1)	24(1)	1
C(6)	1676(2)	7272(2)	7445(1)	24(1)	1
C(7)	2252(2)	8112(2)	6831(1)	26(1)	1
C(8)	3429(2)	7813(2)	6427(1)	29(1)	1
C(9)	4021(2)	6664(2)	6660(1)	29(1)	1
O(2)	5222(1)	6290(2)	6327(1)	39(1)	1
C(10)	5563(2)	5078(2)	6738(1)	36(1)	1
O(4)	525(1)	7563(2)	7852(1)	31(1)	1
O(3)	1564(1)	9205(1)	6684(1)	36(1)	1
C(11)	2040(3)	10078(3)	6030(2)	48(1)	1
S(1)	1493(1)	5104(1)	8429(1)	27(1)	1
O(5)	1363(1)	3810(1)	8006(1)	35(1)	1
C(12)	2789(2)	4933(2)	9228(1)	25(1)	1
C(13)	3335(2)	5998(2)	9634(1)	30(1)	1
C(14)	4266(2)	5835(2)	10283(1)	33(1)	1
C(15)	4698(2)	4609(2)	10535(1)	29(1)	1
C(16)	4118(2)	3571(2)	10121(1)	30(1)	1
C(17)	3171(2)	3722(2)	9475(1)	28(1)	1
C(18)	5760(2)	4451(3)	11211(2)	38(1)	1

Table 3. Bond lengths [Å] and angles [°] for 99210.

O(1)-C(10)	1.388(2)	O(1)-C(1)	1.443(3)
C(1)-C(2)	1.503(4)	C(2)-C(3)	1.539(3)
C(3)-C(4)	1.509(3)	C(3)-C(10)	1.546(3)
C(4)-C(9)	1.362(3)	C(4)-C(5)	1.403(3)
C(5)-C(6)	1.390(3)	C(5)-S(1)	1.791(2)
C(6)-O(4)	1.360(2)	C(6)-C(7)	1.406(3)
C(7)-O(3)	1.362(2)	C(7)-C(8)	1.384(3)
C(8)-C(9)	1.392(3)	C(9)-O(2)	1.382(2)
O(2)-C(10)	1.456(2)	O(3)-C(11)	1.430(3)
S(1)-O(5)	1.5040(14)	S(1)-C(12)	1.799(2)
C(12)-C(17)	1.378(3)	C(12)-C(13)	1.390(3)
C(13)-C(14)	1.375(3)	C(14)-C(15)	1.410(3)
C(15)-C(16)	1.387(3)	C(15)-C(18)	1.498(3)
C(16)-C(17)	1.383(3)		
C(10)-O(1)-C(1)	105.1(2)	O(1)-C(1)-C(2)	104.5(2)
C(1)-C(2)-C(3)	102.3(2)	C(4)-C(3)-C(2)	114.9(2)
C(4)-C(3)-C(10)	102.3(2)	C(2)-C(3)-C(10)	102.5(2)
C(9)-C(4)-C(5)	118.4(2)	C(9)-C(4)-C(3)	108.8(2)
C(5)-C(4)-C(3)	132.8(2)	C(6)-C(5)-C(4)	120.0(2)
C(6)-C(5)-S(1)	116.92(14)	C(4)-C(5)-S(1)	123.03(14)
O(4)-C(6)-C(5)	119.2(2)	O(4)-C(6)-C(7)	121.2(2)
C(5)-C(6)-C(7)	119.6(2)	O(3)-C(7)-C(8)	124.5(2)
O(3)-C(7)-C(6)	114.6(2)	C(8)-C(7)-C(6)	120.8(2)
C(7)-C(8)-C(9)	117.5(2)	C(4)-C(9)-O(2)	113.8(2)
C(4)-C(9)-C(8)	123.6(2)	O(2)-C(9)-C(8)	122.6(2)
C(9)-O(2)-C(10)	107.7(2)	O(1)-C(10)-O(2)	109.7(2)
O(1)-C(10)-C(3)	108.4(2)	O(2)-C(10)-C(3)	106.9(2)
C(7)-O(3)-C(11)	118.3(2)	O(5)-S(1)-C(5)	107.95(8)
O(5)-S(1)-C(12)	105.02(9)	C(5)-S(1)-C(12)	98.95(8)
C(17)-C(12)-C(13)	120.5(2)	C(17)-C(12)-S(1)	118.7(2)
C(13)-C(12)-S(1)	120.7(2)	C(14)-C(13)-C(12)	119.4(2)
C(13)-C(14)-C(15)	121.4(2)	C(16)-C(15)-C(14)	117.4(2)
C(16)-C(15)-C(18)	121.9(2)	C(14)-C(15)-C(18)	120.7(2)
C(17)-C(16)-C(15)	121.7(2)	C(12)-C(17)-C(16)	119.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 99210. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
O(1)	37(1)	56(1)	42(1)	-5(1)	6(1)	18(1)
C(1)	49(2)	54(2)	50(1)	-12(1)	-4(1)	14(1)
C(2)	38(1)	32(1)	61(2)	-3(1)	4(1)	9(1)
C(3)	30(1)	36(1)	31(1)	3(1)	2(1)	9(1)
C(4)	23(1)	30(1)	27(1)	-2(1)	-2(1)	2(1)
C(5)	19(1)	26(1)	25(1)	-2(1)	-2(1)	-4(1)
C(6)	19(1)	31(1)	23(1)	-4(1)	-3(1)	1(1)
C(7)	25(1)	26(1)	29(1)	-2(1)	-4(1)	1(1)
C(8)	27(1)	33(1)	28(1)	3(1)	1(1)	-4(1)
C(9)	21(1)	36(1)	30(1)	-2(1)	1(1)	0(1)
O(2)	28(1)	44(1)	44(1)	12(1)	12(1)	10(1)
C(10)	27(1)	47(1)	34(1)	3(1)	2(1)	10(1)
O(4)	24(1)	34(1)	36(1)	6(1)	3(1)	10(1)
O(3)	34(1)	31(1)	43(1)	10(1)	5(1)	8(1)
C(11)	42(1)	44(2)	57(2)	22(1)	6(1)	8(1)
S(1)	19(1)	29(1)	33(1)	2(1)	0(1)	-2(1)
O(5)	27(1)	31(1)	47(1)	-2(1)	-7(1)	-9(1)
C(12)	20(1)	30(1)	26(1)	1(1)	5(1)	-1(1)
C(13)	33(1)	23(1)	35(1)	3(1)	-1(1)	1(1)
C(14)	35(1)	31(1)	33(1)	-4(1)	-3(1)	-6(1)
C(15)	26(1)	35(1)	24(1)	3(1)	5(1)	2(1)
C(16)	31(1)	27(1)	32(1)	4(1)	6(1)	2(1)
C(17)	27(1)	26(1)	30(1)	0(1)	5(1)	-2(1)
C(18)	37(1)	43(1)	33(1)	4(1)	-4(1)	4(1)

Table 5. Torsion angles [°] for 99210.

C(10)-O(1)-C(1)-C(2)	-42.4(2)	O(1)-C(1)-C(2)-C(3)	37.3(2)
C(1)-C(2)-C(3)-C(4)	91.2(2)	C(1)-C(2)-C(3)-C(10)	-18.9(2)
C(2)-C(3)-C(4)-C(9)	-103.6(2)	C(10)-C(3)-C(4)-C(9)	6.7(2)
C(2)-C(3)-C(4)-C(5)	74.4(3)	C(10)-C(3)-C(4)-C(5)	-175.4(2)
C(9)-C(4)-C(5)-C(6)	0.4(3)	C(3)-C(4)-C(5)-C(6)	-177.3(2)
C(9)-C(4)-C(5)-S(1)	178.79(14)	C(3)-C(4)-C(5)-S(1)	1.0(3)
C(4)-C(5)-C(6)-O(4)	-179.3(2)	S(1)-C(5)-C(6)-O(4)	2.3(2)
C(4)-C(5)-C(6)-C(7)	-0.5(3)	S(1)-C(5)-C(6)-C(7)	-178.96(13)
O(4)-C(6)-C(7)-O(3)	-0.4(2)	C(5)-C(6)-C(7)-O(3)	-179.1(2)
O(4)-C(6)-C(7)-C(8)	179.4(2)	C(5)-C(6)-C(7)-C(8)	0.7(3)
O(3)-C(7)-C(8)-C(9)	179.0(2)	C(6)-C(7)-C(8)-C(9)	-0.7(3)
C(5)-C(4)-C(9)-O(2)	177.6(2)	C(3)-C(4)-C(9)-O(2)	-4.2(2)
C(5)-C(4)-C(9)-C(8)	-0.5(3)	C(3)-C(4)-C(9)-C(8)	177.7(2)
C(7)-C(8)-C(9)-C(4)	0.7(3)	C(7)-C(8)-C(9)-O(2)	-177.3(2)
C(4)-C(9)-O(2)-C(10)	-0.6(2)	C(8)-C(9)-O(2)-C(10)	177.5(2)
C(1)-O(1)-C(10)-O(2)	-86.9(2)	C(1)-O(1)-C(10)-C(3)	29.5(2)
C(9)-O(2)-C(10)-O(1)	122.3(2)	C(9)-O(2)-C(10)-C(3)	4.9(2)
C(4)-C(3)-C(10)-O(1)	-125.1(2)	C(2)-C(3)-C(10)-O(1)	-5.8(2)
C(4)-C(3)-C(10)-O(2)	-6.9(2)	C(2)-C(3)-C(10)-O(2)	112.4(2)
C(8)-C(7)-O(3)-C(11)	3.9(3)	C(6)-C(7)-O(3)-C(11)	-176.3(2)
C(6)-C(5)-S(1)-O(5)	125.81(14)	C(4)-C(5)-S(1)-O(5)	-52.6(2)
C(6)-C(5)-S(1)-C(12)	-125.11(14)	C(4)-C(5)-S(1)-C(12)	56.5(2)
O(5)-S(1)-C(12)-C(17)	-15.8(2)	C(5)-S(1)-C(12)-C(17)	-127.24(14)
O(5)-S(1)-C(12)-C(13)	168.4(2)	C(5)-S(1)-C(12)-C(13)	57.0(2)
C(17)-C(12)-C(13)-C(14)	0.2(3)	S(1)-C(12)-C(13)-C(14)	175.9(2)
C(12)-C(13)-C(14)-C(15)	1.3(3)	C(13)-C(14)-C(15)-C(16)	-2.1(3)
C(13)-C(14)-C(15)-C(18)	177.0(2)	C(14)-C(15)-C(16)-C(17)	1.3(3)
C(18)-C(15)-C(16)-C(17)	-177.7(2)	C(13)-C(12)-C(17)-C(16)	-0.9(3)
S(1)-C(12)-C(17)-C(16)	-176.68(14)	C(15)-C(16)-C(17)-C(12)	0.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 99210.

	x	y	z	U(eq)	SOF
H(1A)	3979(25)	4167(26)	5540(16)	49(7)	1
H(1B)	4662(25)	2863(24)	5611(17)	54(7)	1
H(2A)	2895(28)	3418(24)	6800(17)	53(7)	1
H(2B)	4159(25)	2640(25)	7090(16)	49(7)	1
H(3A)	4600(20)	4495(19)	7916(13)	25(5)	1
H(4A)	131(27)	7988(23)	7567(16)	34(7)	1
H(8A)	3797(20)	8375(21)	6012(14)	31(6)	1
H(10A)	6410(23)	5268(21)	7047(14)	40(6)	1
H(11A)	2975(30)	10346(27)	6088(17)	66(8)	1
H(11B)	2009(25)	9690(24)	5526(17)	49(8)	1
H(11C)	1399(26)	10758(26)	6016(16)	54(7)	1
H(13A)	3062(19)	6768(20)	9488(12)	21(5)	1
H(14A)	4689(21)	6564(21)	10549(13)	31(5)	1
H(16A)	4401(21)	2750(23)	10273(14)	38(6)	1
H(17A)	2811(22)	3026(22)	9184(15)	40(6)	1
H(18A)	5535(27)	4712(25)	11773(18)	60(8)	1
H(18B)	5998(27)	3619(31)	11271(19)	67(9)	1
H(18C)	6524(31)	4998(30)	11072(20)	86(10)	1