Experimental

General. ^{1}H NMR (at 300 MHz) and ^{13}C NMR (at 300 MHz) spectra were obtained as solutions in deuteriochloroform ($CDCl_3$). The infrared (IR) spectra were determined as neat oils. Mass spectra (MS) were obtained using FTMS at an ionizing potential of 70 eV. Substances for which C, H analysis are not reported were purified as specified, and gave spectroscopic data consistent with being > 95% the assigned structure. R_f values indicated refer to thin layer chromatography (TLC) on 5.0 x 10 cm, 250 μm analytical plates coated with silica gel 60, F_{254}, developed in the solvent system indicated. Materials were visualized using 5% phosphomolybdic acid in ethanol as stain. Elemental analysis was carried out by Quantitative Technologies Inc., P.O. Box 470, Salem Industrial Park, Bldg. 5, Whitehouse, NJ 08888. Column chromatography was carried out on an Isco MPLC using silica gel 60 particle size 0.015 – 0.040 mm. The solvent mixtures reported are volume/volume mixtures. All glassware was oven dried and reactions were carried out under a flow of dry nitrogen. Potassium bis(trimethylsilyl)amide (KHMDS) 0.50 M in toluene was from Aldrich Sure-Seal® bottles kept under dry nitrogen. All reactions were stirred magnetically, under dry N_2, unless otherwise noted.

1,6-Dibromo-2-methoxy-naphthalene (9). To a stirring suspension of 1,6-dibromo-2-naphthol **8** (100 g, 331 mmol), K_2CO_3 (114 g, 828 mmol), and anhydrous DMF (80 mL), was added iodomethane (94.0 g, 662 mmol) dropwise over a 20 min period. An ice bath was periodically used to maintain the internal temperature below 30

°C. The mixture was stirred at ambient temperature for 3 h during which time the suspension solidified to a thick cake. The mixture was partitioned between H_2O and CH_2Cl_2. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to give **9** (101 g, 305 mmol, 97% yield) as a light tan solid: Mp = 97-98 °C; Lit.[7a] Mp = 100 °C; TLC R_f = 0.60 (30% EtOAc/hexane); ^{1}H NMR δ 4.03 (s, 3H), 7.26 (d, 1H, *J* = 11.1 Hz), 7.61(dd, 1H, *J* = 9.3 Hz, *J* = 2.1 Hz), 7.73 (d, 1H, *J* = 9.3 Hz), 7.94 (d, 1H, *J* = 1.8 Hz), 8.09 (d, 1H, *J* = 9.3 Hz); ^{13}C NMR δ C: 152.4, 130.2, 129.0, 116.6, 107.1 CH: 129.4, 128.3, 126.5, 126.4, 112.9 CH_3: 55.5; IR cm^{-1} 2964 (m), 1588(s), 1598 (m), 1490 (s), 1271 (s); Anal. calcd for $C_{11}H_8Br_2O$: C, 41.81; H, 2.55, found C, 41.79; H, 2.25.

1,2,6-Trimethoxynaphthalene (10). To a mechanically stirred solution of sodium methoxide (5.4 M in MeOH, 390 ml, 2100 mmol) and MeOH (330 mL) was added **9** (100 g, 316 mmol), 2,4,6-collidine (345 mL), and copper(I)iodide (64.8 g, 340 mmol). The mixture was heated at reflux for 19 h. The mixture was filtered and the filtrate was evaporated to remove the bulk of the 2,4,6-collidine. This slurry was diluted with H_2O (1.5 L) and carefully acidified to pH = 2 with concentrated aqueous HCl. The resulting mixture was partitioned between EtOAc and, sequentially, 1 N aqueous HCl, brine, and H_2O. The combined organic extract was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was filtered through a bed of silica gel (~400 g) using 1-chlorobutane (3 L). The filtrate was concentrated to give **10** (61.0 g, 281 mmol, 89% yield) as a white solid: Mp = 55-56 °C; Lit.[7b] Mp = 54-55 °C; TLC R_f = 0.36 (10% EtOAc/hexane); ^{1}H NMR δ 3.89 (s, 3H, CH_3), 3.96 (s, 3H, CH_3), 3.98 (s, 3H, CH_3), 7.07 (d, 1H, *J* = 2.7 Hz), 7.14 (dd, 1H, *J* = 9.3 Hz, *J* = 2.7 Hz), 7.24 (d, 1H, *J* = 9.0 Hz), 7.46 (d, 1H, *J* = 9.0 Hz), 8.01 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR δ C: 155.1, 145.3, 142.0, 129.3, 123.0 CH: 121.5,

121.2, 177.6, 114.7, 104.4 CH_3: 59.7, 55.6, 53.7; IR cm^{-1} 2962 (s), 1602(m), 1507 (m), 1455 (s), 1271 (s); Anal. calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47, found C, 71.51; H, 6.09.

β-Tetralone methyl ester (11). To a mechanically stirred solution of **10** (60.0 g, 275 mmol) and EtOH (175 mL), heated at reflux, was carefully added sodium metal (45.0 g, 1.96 mol) portionwise over a period of 1h. The solution was cooled to 25 °C, carefully quenched with EtOH (100 mL) followed by H_2O (100 mL), and then partitioned between H_2O and CH_2Cl_2. The combined organic extract was evaporated to dryness and the residue was diluted with 1 N aqueous HCl (500 mL). The mixture was heated at reflux, for 20 min. The cooled solution was partitioned between H_2O and CH_2Cl_2. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo.* The residue was distilled under reduced pressure to give **5** (51.0 g) as a clear oil (Bp = 155-165 °C, 1.0 mm Hg). The oil **5** (51.0 g) was immediately treated with sodium methoxide (5.4 M in MeOH, 55.0 ml, 295 mmol), dimethyl carbonate (750 mL), and MeOH (100 mL). The solution was heated at reflux for 2 h. Aqueous hydrochloric acid (1N, 850 mL) was added dropwise over a 30 min period at 0 °C and the mixture was stirred for 5 min. The solution was partitioned between H_2O and EtOAc. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was diluted with a solution of hexane/ Et_2O - 1/1 (100 mL) and cooled to 0 °C. The formed solid was filtered and vacuum dried to give **11** (39.0 g, 148 mmol, 61%) as a white solid: Mp = 86-87 °C; TLC R_f = 0.27 (10% EtOAc/hexane); ^{1}H NMR δ 2.47 (t, 2H, J = 7.8 Hz), 2.89 (t, 2H, J = 7.8 Hz), 3.78 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 6.76 (d, 1H, J = 9.3 Hz), 7.39 (d, 1H, J = 9.3 Hz), 13.11 (s, 1H); ^{13}C NMR δ C: 175.6, 170.8, 148.8, 143.8, 126.2, 123.3, 98.0 CH:

120.2, 108.2 CH_2: 27.4, 18.7 CH_3: 59.0, 54.2, 50.16; IR cm^{-1} 2924 (s), 1646(m), 1594 (s), 1449 (s), 1312 (s); HRMS calcd for $C_{13}H_{15}O_3$ (M^+) 219.1021, found 219.1017.

(*Z*)-Alkenyl bromide (12). A stirring solution of 1,3-dibromo-2-methylpropene (10.0 g, 46.7 mmol), potassium carbonate (7.20 g, 52.4 mmol), and H_2O (80 mL) was heated at reflux for 19 h. The cooled solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to obtain the alcohol (6.50 g, 43.0 mmol, 92% yield) as an *E* and *Z* mixture. The pure *Z*-isomer was obtained by distillation through a spinning band column; bp = 72 °C at 16 mm Hg. A solution of the pure *Z*-alcohol (1.60 g, 10.6 mmol), dibromotriphenylphosphorane (6.7 g, 15.9 mmol), and chloroform (2 mL) was stirred at 25 °C for 1 h. The solution was distilled to obtain **12** (1.97 g, 9.20 mmol, 87% yield from alcohol) as a clear oil: bp = 42 °C at 1.0 mm Hg; ^1H NMR δ 1.95 (s, 3H), 4.10 (s, 2H), 6.11 (s, 1H); ^{13}C NMR δ C: 137.6 CH: 106.0 CH_2: 32.8 CH_3: 21.0; IR cm^{-1} 3070 (m), 1624(s), 1432 (s), 1298 (s), 1212 (s); Anal. calcd for $C_4H_6Br_2$: C, 22.46; H, 2.83, found C, 22.31; H, 2.97.

Bromoalkene-β-tetralone (13). To a stirring solution of diisopropylamine (18.3 g, 181 mmol) and anhydrous THF (400 mL), at 0 °C, was added n-butyllithium (2.5 M in hexanes, 66.8 ml, 167 mmol) dropwise over a 10 min period. The solution was stirred at 0 °C for 30 min and a solution of **11** (20.0 g, 75.8 mmol) in THF (100 mL) was added dropwise over a 5 min period. The solution was stirred at 0 °C for 1 h and cis-1,3-dibromo-2-methyl-1-propene (25.8 g, 121 mmol)was then added dropwise over a 10 min period. The solution was stirred at ambient temperature for 1 h. The mixture was partitioned between 1 N aqueous HCl and Et_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to

obtain a yellow oil (22.8 g): TLC R_f = 0.18 (10% EtOAc/hexane). A stirring solution of the yellow oil (22.8 g), lithium chloride (956 mg, 22.5 mmol), DMSO (13.0 ml), and H_2O (1.3 mL) was heated at 150 °C for 20 min. The cooled solution was partitioned between EtOAc and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **13** (6.80 g, 20.0 mmol, 80% yield) as a clear oil: TLC R_f = 0.39 (30% EtOAc/hexane); ^{1}H NMR δ 1.80 (s, 3H), 2.14 (dd, 1H, J = 13.9 Hz, J = 9.0 Hz), 2.48-2.61 (m, 1H), 2.62-2.68 (m, 1H), 2.70 (d, 1H, , J = 9.3 Hz), 3.21 (dd, 1H, J = 15.9 Hz, J = 5.1 Hz), 3.55 (d, 2H, J = 6.9 Hz), 3.82, (s, 3H), 3.86 (s, 3H), 5.96 (s, 1H), 6.81 (d, 2H, J = 1.8 Hz); ^{13}C NMR δ C: 209.5, 149.8, 144.7, 137.4, 127.8, 124.5 CH: 121.7, 109.6, 101.9, 43.2 CH_2: 42.7, 36.8, 24.9 CH_3: 59.4, 54.3, 17.2; IR cm^{-1} 2938 (m), 1714 (s), 1492 (s), 1276 (s); HRMS calcd for $C_{16}H_{20}BrO_3$ (M+1) 339.0596, found 339.0591.

β-Tetralone ketals (4 and 14). A solution of **13** (3.00 g, 8.84 mmol), (S,S)-hydrobenzoin (2.30 g, 10.6 mol), p-toluenesulfonic acid monohydrate (20 mg, 0.10 mmol), triethyl orthoformate (1.30 g, 8.80 mmol), and CH_2Cl_2 (7.5 mL) was stirred at 25 °C for 19 h. The solution was concentrated *in vacuo* and the residue was purified by chromatography to obtain **4** (2.04 g, 3.80 mmol, 43% yield) as a white semi-solid and **14** (2.04 g, 3.80 mmol, 43% yield) as a white semi-solid: **4**: TLC R_f = 0.28 (10% EtOAc/hexane); $[\alpha]^{20}_D$ = -101.7° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.88 (s, 3H), 2.11 (t, J = 13.2 Hz, J = 11.4 Hz), 2.39-2.48 (m, 1H), 2.73 (d, 1H, J = 13.5 Hz), 2.92 (dd, 1H, J = 17.1 Hz, J = 5.4 Hz), 3.09 (dd, 1H, J = 17.1 Hz, J = 5.4 Hz), 3.14 (d, 1H, J = 17.1 Hz), 3.29 (d, 1H, J = 17.1 Hz), 3.81 (s, 3H), 3.84 (s, 1H), 4.79 (d, 1H, J = 8.4 Hz), 4.87 (d, 1H, J = 8.4 Hz), 5.90 (s, 1H), 6.79 (d, 1H, J = 8.4 Hz), 6.85 (d, 1H, J = 8.4 Hz), 7.19-7.35 (m,

10H); ^{13}C NMR δ C: 150.8, 146.9, 139.6, 136.7, 136.1, 127.1, 110.1 CH: 128.4, 128.3, 126.7, 126.6, 124.1, 110.8, 102.6, 85.7, 85.3, 38.8 CH_2: 37.8, 37.7, 26.0 CH_3: 60.0, 55.8, 19.0; IR cm^{-1} 2935 (m), 1493 (s), 1456 (m), 1279 (s); Anal. calcd for $C_{30}H_{31}BrO_4$: C, 67.29; H, 5.84, found C, 67.42; H, 5.69. **14**: TLC R_f = 0.27 (10% EtOAc/hexane); $[\alpha]^{20}_D$ = -30.9° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.88 (s, 3H), 2.35-2.41 (m, 2H), 2.72 (dd, 1H, *J* = 16.8 Hz, *J* = 9.0 Hz), 2.84 (d, 1H, *J* = 9.9 Hz), 3.11 (dd, 1H, *J* = 16.8 Hz, *J* = 4.2 Hz), 3.29 (d, 2H, *J* = 4.2 Hz), 3.80 (s, 3H), 3.83 (s, 3H), 4.75 (d, 1H, *J* = 8.7), 4.85 (d, 1H, *J* = 8.7), 6.08 (s, 1H), 6.78 (d, 1H, *J* = 8.4), 6.84 (d, 1H, *J* = 8.4), 7.19-7.37 (m, 10H); ^{13}C NMR δ C: 149.3, 145.2, 138.3, 135.4, 134.5, 127.6, 126.0, 108.6 CH: 127.1, 127.0, 126.9, 125.2, 122.6, 109.6, 101.0, 84.9, 83.4, 38.0 CH_2: 38.0, 36.2, 25.9 CH_3: 58.5, 54.5, 17.5; IR cm^{-1} 2936 (m), 1493 (s), 1455 (m), 1279 (s); HRMS calcd for $C_{30}H_{32}BrO_4$ (M+1) 535.1484, found 535.1498.

β-Tetralone cyclopentene ketal (3). To a stirring solution of **4** (5.00 g, 9.34 mmol) in Et_2O (300 mL) was added KHMDS (0.5 M in toluene, 37.2 mL, 18.6 mmol), at room temperature over a period of 10 min. The mixture was stirred at room temperature for 2 h. Water (50 mL) was added dropwise over a 20 min period at 0 °C. The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **3** (3.27 g, 7.19 mmol, 77% yield) as a white semi-solid: TLC R_f = 0.44 (20% EtOAc/hexane); $[\alpha]^{20}_D$ = +38.6° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.68 (s, 3H), 2.52 (s, 1H), 2.55 (s, 1H), 2.97 (dd, 1H, *J* = 15.6 Hz, *J* = 2.0 Hz), 3.29 (dq, 1H, *J* = 13.8 Hz, *J* = 2.0 Hz), 3.41 (d, 1H, *J* = 15.6 Hz), 3.78 (s, 3H), 3.88 (s, 3H), 4.42 (d, 1H, *J* = 9.3 Hz), 4.81 (q, 2H, *J* = 12.3 Hz), 5.68 (s, 1H), 6.73 (d, 1H, *J* = 8.7 Hz), 6.83 (d, 1H, *J* = 8.7 Hz), 7.16-7.36 (m, 10H);); ^{13}C NMR δ C: 149.6, 144.9, 136.8, 135.6, 131.0, 127.0

110.7 CH: 126.9, 126.8, 126.7, 126.6, 125.6, 125.3, 125.2, 122.9, 122.7, 109.2, 84.3, 84.2, 44.8, 44.1 CH_2: 38.3, 34.6 CH_3: 58.7, 54.3, 15.1; IR cm^{-1} 2933 (m), 1491 (s), 1453 (m), 1278 (s); HRMS calcd for $C_{30}H_{31}O_4$ (M+1) 455.2222, found 455.2235.

β-Tetralone cyclopentene (15). A stirring solution of **3** (3.00 g, 6.61 mmol), AcOH (150 mL), and H_2O (75 mL) was heated at reflux for 4 h. The cooled solution was partitioned between Et_2O and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to recover (*S*,S)-hydrobenzoin (1.30 g, 6.08 mmol, 92% recovered yield) and to obtain **15** (1.36 g, 5.29 mmol, 80% yield) as a clear oil: TLC R_f = 0.54 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = -51.0° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.74 (s, 3H), 2.58 (d, 1H, J = 16.5 Hz), 2.75-2.87 (m 1H), 3.05-3.13 (m, 1H), 3.36 (dd, 1H, J = 16.5 Hz, J = 1.6 Hz), 3.66 (dd, 1H, J = 16.5 Hz, J = 0.8 Hz), 3.86 (s, 3H), 3.88 (s, 3H), 4.61-4.69 (m, 1H), 5.30 (s, 1H), 6.75 (d, 1H, J = 8.7 Hz), 6.79 (d, 1H, J = 8.7 Hz); ^{13}C NMR δ C: 210.6, 149.9, 144.8, 137.9, 129.3, 124.5 CH: 125.2, 122.0, 109.8, 46.9, 45.2 CH_2: 41.5, 39.6 CH_3: 59.1, 54.3, 14.6; IR cm^{-1} 2937 (m), 1715 (s), 1491 (m), 1276 (s); HRMS calcd for $C_{16}H_{18}O_3$ (M^+) 258.1256, found 258.1249.

Cyclopentene alcohol (16). To a stirring solution of **15** (1.20 g, 4.65 mmol) and THF (20 mL) at 0 °C was added dropwise L-Selectride® (1.0 M in THF, 5.1 mL, 5.1 mmol) over a 10 min period. The solution was stirred at 0 °C for 17 h. To this solution was added 1.0 N aqueous NaOH (10 mL) dropwise at 0 °C followed by 30% H_2O_2 (5 mL). The solution was stirred at ambient temperature for 1 h. The cooled solution was partitioned between EtOAc and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to recover

15 (310 mg, 1.16 mmol, 25% recovered yield) and to obtain **16** (870 mg, 3.35 mmol, 97% yield) as a clear oil: TLC R_f = 0.20 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = +260.0° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.74 (s, 3H), 2.59 (d, 1H, J = 16.8 Hz), 2.75-2.87 (m, 1H), 3.09, (t, 1H, J = 8.1 Hz), 3.36 (dd, 1H, J = 16.5 Hz, J = 1.5 Hz), 3.66 (dd, 1H, J = 16.5 Hz, J = 1.0 Hz), 3.86 (s, 3H), 3,87 (s, 3H), 4.62-4.70 (m, 1H), 5.30 (s, 1H), 6.75 (d, 1H, J = 8.4 Hz), 6.79 (d, 1H, J = 8.4 Hz); ^{13}C NMR δ C: 149.6, 145.0, 130.7, 125.7 CH: 126.7, 122.8, 109.0, 68.4, 43.7, 39.6 CH_2: 35.6, 32.7 CH_3: 58.6, 54.3, 15.0; IR cm^{-1} 3406 (b), 2926 (m), 1490 (s), 1276 (s); HRMS calcd for $C_{16}H_{20}O_3$ (M^+) 260.1412, found 260.1402.

Sulfonamide (17). To a stirring solution of **16** (800 mg, 3.08 mmol), diphenylphosphoryl azide (1.71 g, 6.20 mmol), triphenylphosphine (1.63 g, 6.20 mmol), and THF (35 mL) at 0 °C was added diethyl azodicarboxylate (1.08 g, 6.20 mmol) dropwise over a 5 min period. The solution was stirred at ambient temperature for 17 h. The solution was partitioned between EtOAc and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain the azide: TLC R_f = 0.48 (10% EtOAc/hexane). The azide was immediately dissolved in THF (50 mL), cooled to 0 °C, and treated dropwise with a preformed solution of $LiAlH_4$ (1.0 M in THF, 6.20 ml, 6.20 mmol), EtOH (286 mg, 6.20 mmol), and THF (15 mL) over a 5 min period. The solution was stirred at ambient temperature for 2 h. Saturated aqueous Na_2SO_4 solution (0.6 mL) was added followed by Na_2SO_4 (1.0 g). The mixture was filtered and the filtrate was concentrated *in vacuo*. The residual oil was dissolved in a solution of CH_2Cl_2 (25 mL), Et_3N (627 mg, 6.20 mmol), and DMAP (757 mg, 0.620 mmol) followed by the dropwise addition of benzenesulfonyl chloride (653 mg, 3.70 mmol) over a 2 min period. The mixture was stirred at ambient

temperature for 17 h. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **17** (528 mg, 1.32 mmol, 43% yield) as a white solid: Mp = 151-152 °C; TLC R_f = 0.49 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = +122.8° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.53 (s, 3H), 1.98 (d, 1H, J = 15.9 Hz), 2.36 (dd, 1H, J = 15.3 Hz , J = 6.9 Hz), 2.41-2.60 (m, 2H), 2.77 (dd, 1H, J = 15.3 Hz, J = 3.3 Hz), 3.45-3.56 (m, 1H), 3.84 (s, 3H), 3.85 (s, 3H), 4.08-4.14 (m, 1H), 4.37 (d, 1H, J = 9.0 Hz), 6.59 (d, 1H, J = 8.4 Hz), 6.70 (d, 1H, J = 8.4 Hz), 7.48-7.63 (m, 3H), 7.81-7.86 (m, 2H); ^{13}C NMR δ C: 151.1, 146.5, 141.1, 137.7, 125.8 CH: 132.4, 129.0, 127.8, 126.9, 124.3, 110.6, 52.2, 43.6, 42.3 CH_2: 40.6, 33.4 CH_3: 60.2, 55.7, 16.2; IR cm^{-1} 3253 (m), 2926 (s), 1492 (m), 1279 (s); Anal. calcd for $C_{22}H_{25}NO_4S$: C, 66.14; H, 6.31, found C, 66.05; H, 6.25.

Alkyl bromide (18). A stirring mixture of **17** (500 mg, 1.25 mmol), 1,2-dibromoethane (1.30 mL, 2.84 g, 15.1 mmol), tetrabutylammonium bromide (52 mg, 0.16 mmol), sodium hydroxide (50% aqueous, 1.3 mL), and toluene (5 mL) was heated at 100 °C for 40 min. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **18** (526 mg, 1.04 mmol, 83% yield) as a white semi-solid: TLC R_f = 0.60 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = +86.2° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.59 (s, 3H), 2.13 (d, 1H, J = 14.4 Hz), 2.30-2.47 (m, 3H), 2.65 (dd, 1H, J = 15.0 Hz, J = 12.3 Hz), 3.34-3.68 (m, 4H), 3.75-3.83 (m, 1H), 3.83 (s, 3H), 3.85 (s, 3H), 4.19 (s, 1H), 5.44 (s, 1H), 6.56 (d, 1H, J = 8.4 Hz), 6.71 (d, 1H, J = 8.4 Hz), 7.49-7.64 (m, 3H), 7.81-7.85 (m, 1H); IR cm^{-1} 2934 (m) 1491 (s), 1446 (m), 1342 (s); ^{13}C NMR δ C: 149.5, 145.4, 138.7, 136.3, 129.0, 125.7 CH: 131.2, 127.7, 125.5, 122.0, 109.4, 54.1,

43.7, 39.6, CH_2: 44.5, 38.2, 31.1, 29.0 CH_3: 58.6, 54.3, 14.8; IR cm^{-1} 3406 (b), 2926 (m), 1490 (s), 1276 (s); HRMS calcd for $C_{24}H_{29}BrNO_3S$ (M+1) 506.1000, found 506.0997.

Enone 20. To a stirring solution of **18** (500 mg, 0.99 mmol) and CH_2Cl_2 (30 mL) at –78 °C was bubbled O_3 until **18** was consumed (TLC). Triphenylphosphine (259 mg, 0.99 mmol) was added and the mixture was allowed to warm to room temperature over a 9 h period. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **2** (453 mg, 0.84 mmol, 85% yield) as a white semi-solid: TLC R_f = 0.28 (30% EtOAc/hexane). Ketoaldehyde **2** was immediately dissolved in toluene (15 mL). Tetrabutylammonium bromide (52 mg, 0.16 mmol) and potassium carbonate (636 mg, 4.60 mmol) were added and the mixture was heated at reflux for 2 h. The mixture was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **20** (340 mg, 0.77 mmol, 92% yield from **2**) as a white semi-solid: TLC R_f = 0.38 (50% EtOAc/hexane); $[\alpha]^{20}_D$ = -87.6° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.72 (td, 1H, J = 12.6 Hz, J = 5.1 Hz), 1.95 (d, 1H, J = 12.6 Hz), 2.23-2.41 (m, 3H), 2.59 (d, 1H, J = 18.9 Hz), 2.77 (td, 1H, J = 12.6 Hz, J = 3.3 Hz), 3.01 (dd, 1H, J = 18.3 Hz, J = 5.7 Hz), 3.69-3.73 (m, 1H), 3.74 (s, 3H), 3.81 (s, 3H), 4.24 (s, 1H), 5.91 (d, 1H, J = 9.6 Hz), 6.67 (d, 1H, J = 8.4 Hz), 6.77 (d, 1H, J = 8.4 Hz), 7.48-7.62 (m, 3H), 7.79-7.84 (m, 2H); ^{13}C NMR δ C: 196.4, 150.3, 145.6, 139.0, 129.0, 125.7, 36.7 CH: 157.1, 131.1, 127.7, 125.4, 124.4, 121.8, 110.3, 49.0, 42.2 CH_2: 37.9, 37.2, 34.8, 28.3 CH_3:

58.7, 54.2; IR cm^{-1} 2939 (m), 1679 (s), 1486 (s), 1280 (s); HRMS calcd for $C_{24}H_{26}NO_5S$ (M+1) 440.1531, found 440.1525.

Pentacycle 22. To a stirring solution of **20** (250 mg, 0.57 mmol) and EtOH (20 mL) at 0 °C was added sodium borohydride (49 mg, 1.30 mmol) portionwise over a 5 min period. The solution was stirred at 0 °C for 1 h. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to obtain alcohol **21** (232 mg, 0.52 mmol, 92% yield) as a white semi-solid: TLC R_f = 0.19 (50% EtOAc/hexane). Alcohol **21** (232 mg, 0.52mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to –40 °C. Boron tribromide (1.0 M in CH_2Cl_2, 5.20 ml, 5.20 mmol) was added dropwise over a 10 min period at –40 °C. The solution was stirred at –40 °C for 1 h. The solution was poured into saturated aqueous $NaHCO_3$ solution (50 mL). The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **22** (149 mg, 0.36 mmol, 70% yield from alcohol **21**) as a clear oil: TLC R_f = 0.48 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = -173.9° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.35-1.48 (m, 1H), 1.82-1.88 (m, 2H), 1.98 (dt, 1H, J = 17.4 Hz, J = 5.7 Hz), 2.33-2.41 (m, 1H), 2.42 (d, 1H, J = 18.3 Hz), 2.81 (dd, 1H, J = 19.2 Hz, J = 6.6 Hz), 2.86-2.93 (m, 1H), 3.75 (d, 1H, J = 12.9 Hz), 3.83 (s, 3H), 4.43 (dd, 1H, J = 6.3 Hz, J = 3.3 Hz), 4.92 (s, 1H), 5.69 (dt, 1H, J = 10.2 Hz, J = 3.3 Hz), 5.82 (dd, 1H, J = 10.2 Hz, J = 5.4 H), 6.48 (d, 1H, J = 8.4 Hz), 6.67 (d, 1H, J = 8.4 Hz), 7.50-7.63 (m, 3H), 7.82-7.86 (m, 2H); ^{13}C NMR δ C: 145.0, 143.7, 140.7, 128.2, 125.4, 41.1 CH: 132.7, 131.6, 129.4, 127.1, 124.6, 119.0, 113.7, 87.4, 52.6, 38.6, 35.1, 27.5, 24.0 CH_2: 39.5, 35.1, 27.5, 24.0 CH_3:

56.4; IR cm^{-1} 2931 (m), 1501 (m), 1446 (m), 1161 (s); HRMS calcd for $C_{23}H_{24}NO_4S$ (M+1) 410.1426, found 410.1423.

Carbamate 23. A stirring solution of **22** (125 mg, 0.29 mmol), Red-Al® (30% in toluene, 0.91 mL, 2.90 mmol), and toluene (1 mL) was heated at reflux for 30 min. The solution was cooled to 0 °C and saturated Na_2SO_4 aqueous solution (0.50 mL) was added followed by Na_2SO_4 (2.0 g). The mixture was filtered and the filtrate was concentrated. The residual oil was dissolved in a solution of CH_2Cl_2 (10 mL) and Et_3N (0.10 mL, 0.72 mmol). Ethyl chloroformate (0.46 mL, 53 mg, 0.48 mmol) was added dropwise over a 2 min period. The solution was stirred at 25 °C for 1 h. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **23** (77 mg, 0.23 mmol, 78% yield) as a clear oil: TLC R_f = 0.48 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = -191.5° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.27 (t, 3H, J = 7.2 Hz), 1.41-1.54 (m, 1H), 1.72-1.87 (m, 1H), 2.00 (dt, 1H, , J = 17.6 Hz, J = 5.6 Hz), 2.24-2.33 (m, 1H), 2.69 (d, 1H, J = 18.4 Hz), 2.80-3.07 (m, 2H), 3.86 (s, 3H), 3.90-4.11 (m, 1H), 4.15(q, 2H, J = 7.2 Hz), 4.57 (minor amide rotamer), (s, 1H), 4.70 (major amide rotamer), (s, 1H), 4.94 (s, 1H), 5.71 (d, 1H, J = 10.2 Hz) 5.85 (dd, 1H, J = 10.2 Hz, J = 5.6 Hz), 6.62 (d, 1H, J = 8.4 Hz), 6.73 (d, 1H, J = 8.4 Hz); ^{13}C NMR δ (major amide rotamer) C: 155.3, 144.8, 143 4, 128.5, 125.8, 41.1 CH: 131.8, 124.4, 118.9, 113.3, 87.3, 50.1, 37.7 CH_2: 61.3, 37.8, 35.0, 28.8, 24.0 CH_3: 56.2, 14.6; (minor amide rotamer) C: 155.0, 144.8, 143 4, 128.5, 125.6, 41.1 CH: 131.5, 124.6, 118.9, 113.3, 87.3, 50.4, 37.7 CH_2: 61.3, 37.8, 34.7, 29.0, 24.1 CH_3: 56.2, 14.7; IR cm^{-1} 2909 (m), 1693 (s), 1503 (m), 1427 (m); HRMS calcd for $C_{20}H_{22}NO_4$ (M+1) 342.1705, found 342.1703.

Epoxide 24. A stirring solution of **22** (77 mg, 0.23 mmol), hydrogen peroxide (30% in H_2O, 0.15 mL, 0.72 mmol), $[(C_8H_{17})_3NCH_3]^+_3[PO_4[W(O)(O_2)_2]_4^{3-}$ (0.026 M in dichloroethane, 1.90 mL, 0.05 mmol), dichloroethane (12.5 ml), and H_2O (1.25 mL) was heated at reflux for 2 h. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was purified by chromatography to obtain **23** (62 mg, 0.17 mmol, 75% yield) as a clear oil: TLC R_f = 0.21 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = -220.1° (c = 1.0, CH_2Cl_2);); ^{1}H NMR δ 1.16 (dd, 1H, J = 14.7 Hz, J = 12.0 Hz), 1.26 (t, 3H, J = 7.2 Hz), 1.68-1.81 (m, 2H), 2.03 (d, 1H, J = 13.2 Hz), 2.18 (dt, 1H, J = 11.7 Hz, J = 4.5 Hz), 2.69 (d, 1H, J = 18.9 Hz), 2.76-3.00 (m, 2H), 3.08 (t, 1H, J = 3.3 Hz), 3.16 (d, 1H, J = 3.3 Hz), 3.89 (s, 3H), 3.91-4.07 (m, 1H), 4.10-4.21 (m, 2H), 4.49 (minor amide rotamer), (bs, 1H), 4.63 (major amide rotamer), (bs, 1H), 4.76 (s, 1H), 6.66 (d, 1H, J = 8.4 Hz) , 6.78 (d, 1H, J = 8.4 Hz); ^{13}C NMR (major amide rotamer) δ C: 155.3, 145.4, 142.7, 127.1, 125.8, 40.8 CH: 119.6, 113.6, 85.4, 52.4, 51.3, 49.9, 32.3 CH_2: 61.4, 37.6, 35.9, 28.9, 23.2 CH_3: 56.3, 14.6; (minor amide rotamer) δ C: 154.9, 145.4, 142.7, 127.1, 125.6, 40.8 CH: 119.6, 113.6, 85.4, 52.4, 51.3, 50.3, 32.4 CH_2: 61.4, 37.4, 35.6, 29.1, 23.3 CH_3: 56.3, 14.7; IR cm^{-1} 2933 (m), 1693 (s), 1504 (m), 1428 (m); HRMS calcd for $C_{20}H_{24}NO_5$ (M+1) 358.1654, found 358.1663.

Phenylselenide 25. To a stirring solution of **23** (62 mg, 0.17 mmol) and EtOH (6 mL) was added a preformed solution of sodium borohydride (114 mg, 3.00 mmol), diphenyldiselenide (468 mg, 1.50 mmol) and EtOH (6 mL) dropwise over a 2 min period. The solution was heated at reflux for 2 h. The solution was partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*.

The residual oil was purified by chromatography to obtain **23** (66 mg, 0.13 mmol, 75% yield) as a white solid: Mp = 78-80 °C; TLC R_f = 0.26 (30% EtOAc/hexane); $[\alpha]^{20}_D$ = -110.0° (c = 1.0, CH_2Cl_2);); ^{1}H NMR δ 1.15 (t, 1H, *J* = 12.6 Hz), 1.23 (t, 3H, *J* = 6.9 Hz), 1.62-1.79 (m, 2H), 1.96 (d, 1H, *J* = 14.1 Hz), 2.04 (d, 1H, *J* = 12.0 Hz), 2.60-2.86 (m, 3H), 3.09 (t, 1H, *J* = 11.7 Hz) 3.39 (dd, 1H, *J* = 11.7, *J* = 6.3 Hz), 3.88 (s, 3H), 3.92-4.03 (m, 1H), 4.11 (q, 2H, *J* = 6.9 Hz), 4.45 (s, 1H), 4.47 (minor amide rotamer), (s, 1H), 4.62 (major amide rotamer), (s, 1H), 6.62 (d, 1H, *J* = 8.1 Hz), 6.74 (d, 1H, *J* = 8.1 Hz), 7.22-7.31 (m, 3H), 7.49-7.56 (m, 2H); ^{13}C NMR (major amide rotamer) δ C: 55.4, 144.1, 143.8, 128.8, 127.7, 124.9, 43.7 CH: 135.2, 129.2, 128.1, 119.7, 114.3, 95.3, 76.1, 50.3, 46.7, 41.8 CH_2: 61.4, 37.8, 34.8, 32.1, 28.4 CH_3: 56.6, 14.6; (minor amide rotamer) δ C: 55.1, 144.1, 143.8, 128.8, 127.7, 124.7, 43.5 CH: 135.2, 129.2, 128.1, 119.7, 114.3, 95.3, 76.1, 50.6, 46.7, 41.8 CH_2: 61.4, 37.8, 34.4, 32.1, 28.7 CH_3: 56.6, 14.7; IR cm^{-1} 3419 (b), 2926 (m) 1686 (s), 1500 (m), 1438 (s); Anal. calcd for $C_{26}H_{29}NO_5Se$: C, 60.70; H, 5.68, found C, 60.52; H, 5.33.

Allylic alcohol 26. To a stirring solution of **25** (10.0 mg, 0.019 mmol), saturated aqueous $NaHCO_3$ solution (2.0 mL) and THF (2.0 mL) at 25 °C was added a solution of sodium periodate (100 mg, 0.47 mmol) and H_2O (0.50 mL) in a single portion. The mixture was stirred at 25 °C for 30 min. The solution was filtered through a bed of Celite® and the filtrate was extracted with CH_2Cl_2 (3 x 50 ml). The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was added to a mixture of benzene (2.0 mL) and saturated aqueous $NaHCO_3$ solution (2.0 mL). The mixture was heated at reflux for 45 min, then partitioned between CH_2Cl_2 and H_2O. The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil

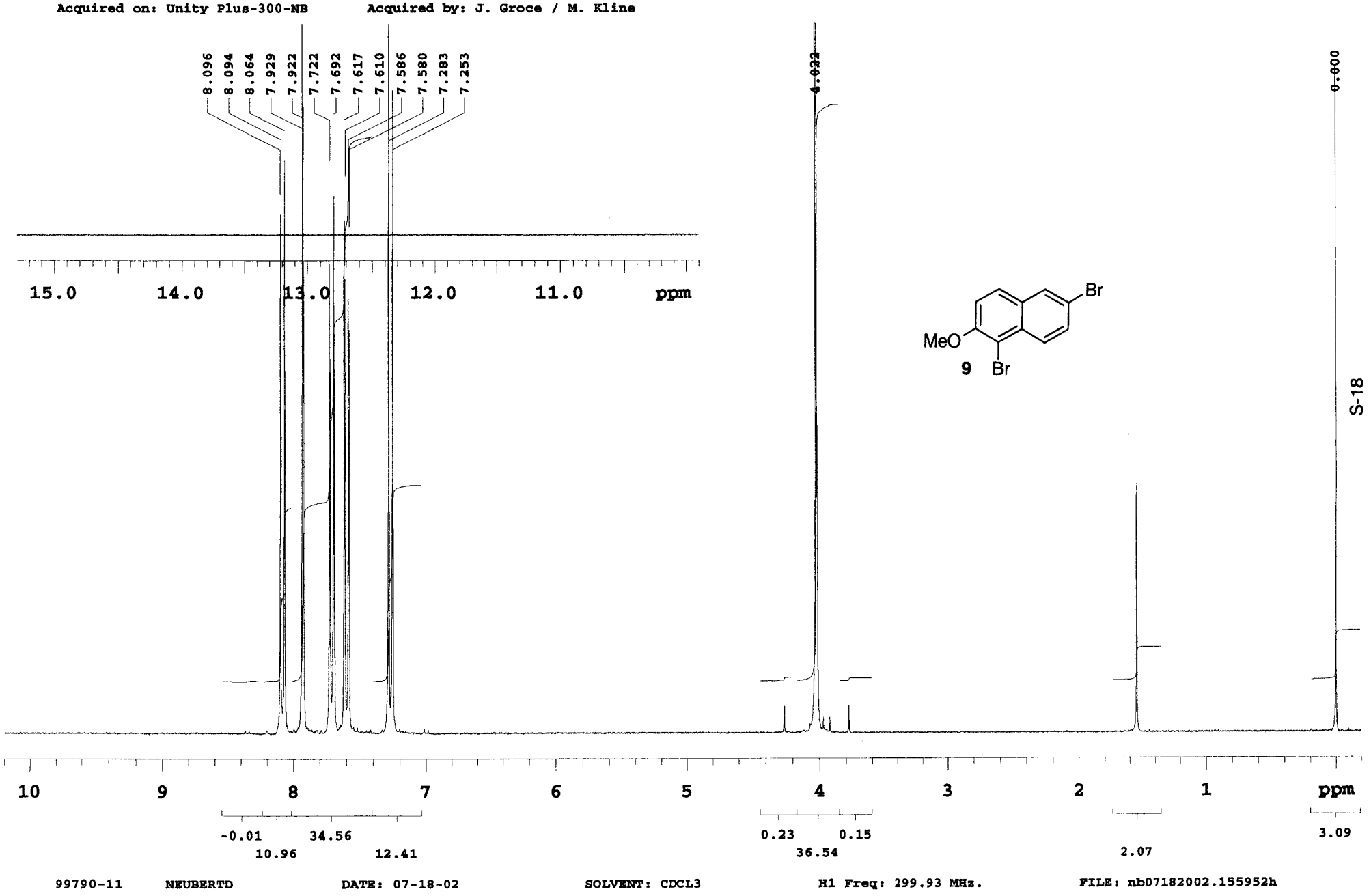
was purified by chromatography to obtain **23** (3.9 mg, 0.011 mmol, 58% yield) as a clear oil; TLC R_f = 0.31 (50% EtOAc/hexane); $[\alpha]^{20}_D$ = -208° (c = 1.0, CH_2Cl_2); ^{1}H NMR δ 1.23-1.34 (t, 3H, *J* = 6.9 Hz), 1.70 (s, 1H), 1.83-2.04 (m, 2H), 2.30-2.48 (m, 1H), 2.67-3.01 (m, 1H), 3.85 (major amide rotamer) (s, 3H), 3.91 (minor amide rotamer), (s, 3H), 3.92-4.30 (m, 3H), 4.66 (minor amide rotamer), (s, 1H), 4.77 (major amide rotamer), (s, 1H), 4. 62 (minor amide rotamer), (bs, 1H), 4.93 (major amide rotamer), (s, 1H), 5.65 (d, 1H, *J* = 9.9 Hz), 5.98-6.06 (m, 1H), 6.54-6.75 (m, 2H, Ar); ^{13}C NMR (major amide rotamer) δ 155.8, 146.0, 143.4, 132.4, 131.9, 129.7, 126.2, 119.5, 113.6, 94.3, 68.1, 56.6, 50.4, 47.5, 41.7, 39.3, 38.3, 35.7, 29.3, 14.9; (minor amide rotamer) δ 155.5, 145.7, 142.6, 132.2, 132.0, 129.7, 126.0, 120.5, 115.3, 91.4, 61.8, 56.9, 50.8, 47.5, 40.0, 39.4, 38.1, 35.4, 29.5, 15.0; IR cm^{-1} 3428 (b), 2931 (m), 1689 (s), 1503 (m), 1438 (s); HRMS calcd for $C_{20}H_{24}NO_5$ (M+1) 358.1654, found 358.1639.

Codeine 27. A solution of **26** (5.0 mg, 0.014 mmol), MnO_2 (20.0 mg, 0.23 mmol) and CH_2Cl_2 (2.0 mL) was stirred at 25 °C for 15 min. The mixture was filtered through a bed of Celite® and the filtrate was concentrated. The residual oil was immediately dissolved in THF (1.0 mL) and $LiAlH_4$ (1.0M in THF, 0.50 ml, 0.50 mmol) was added dropwise over a period of 1 min. The solution was heated at reflux for 15 min. The solution was cooled to 0 °C and saturated Na_2SO_4 aqueous solution (0.50 mL) was added followed by Na_2SO_4 (2.0 g). The mixture was filtered and the filtrate was concentrated. The residual oil was purified by chromatography to obtain **27** (3.1 mg, 0.011 mmol, 75% yield) as a white solid: Mp = 151-153 °C; TLC R_f = 0.21 (10% MeOH/CH_2Cl_2); $[\alpha]^{20}_D$ = -134° (c = 0.1, EtOH); ^{1}H NMR δ 1.88 (d, 1H, *J* = 12.8 Hz), 2.03-2.12 (m, 1H), 2.31 (dd, 1H, *J* = 18.4 Hz, *J* = 6.0 Hz), 2.40 (dd, 1H, *J* = 12.4 Hz, *J* =

3.5 Hz), 2.45 (s, 3H), 2.60 (dd, 1H, J = 12.0 Hz, J = 4.4 Hz), 2.69 (s, 1H), 3.05 (d, 1H, J = 18.4 Hz), 3.36 (dd, 1H, J = 3.2 Hz), 3.85 (s, 3H), 4.16-4.20 (m, 1H), 4.89 (dd, 1H, J = 6.8 Hz, J = 1.1 Hz), 5.29 (dt, , J = 10.0 Hz, J = 2.7 Hz), 5.71 (d, 1H, J = 10.0 Hz), 6.57 (d, 1H, J = 8.4 Hz), 6.66 (d, 1H, J = 8.4 Hz); ^{13}C NMR δ C: 146.2, 142.0, 130.8, 126.8, 56.1 CH: 133.3, 127.9, 119.3, 112.7, 91.2, 66.3, 58.7, 40.4 CH_2: 46.3, 35.5, 20.3 CH_3: 58.8, 42.8; IR cm^{-1} 3400 (b), 2925 (s), 1501 (s), 1451 (s); HRMS calcd for $C_{18}H_{22}NO_3$ (M+1) 300.1599, found 300.1601.

Morphine (1). To a stirring solution of **27** (6.0 mg, 0.020 mmol) and $CHCl_3$ (2.0 mL) was added boron tribromide (1.0 M in CH_2Cl_2, 0.140 mL, 0.140 mmol) dropwise over a 1 min period. The mixture was stirred at 25 °C for 15 minutes. A solution of 10% aqueous ammonium hydroxide (2 mL) was added dropwise at 0 °C over a 2 min period. The aqueous portion was extracted with a 9:1 mixture of CH_2Cl_2/EtOH (4 x 80 mL). The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was crystallized from MeOH/$CHCl_3$/Et_2O to obtain **1** (4.9 mg, 0.017 mmol, 86% yield) as a white solid: Mp = 251-255 °C; TLC R_f = 0.06 (10% MeOH/CH_2Cl_2); $[\alpha]^{20}_D$ = -127.1° (c = 0.1, MeOH); ^{1}H NMR ($CDCl_3$/CD_3OD-5/1) δ 1.90 (d, 1H, J = 12.9 Hz), 2.06 (td, 1H, J = 12.9 Hz, J = 5.1 Hz), 2.34 (dd, 1H, J = 18.9 Hz, J = 6.3 Hz), 2.46 (s, 3H), 2.47 (dd, 1H, J = 24.3, J = 3.6 Hz), 2.60 (d, 1H, J = 4.5 Hz), 2.62-2.68 (m, 1H), 3.03, (d, 1H, J = 18.6 Hz), 3.35-3.39 (m, 1H), 4.16-4.21 (m, 1H), 4.84 (dd, 1H, J = 6.3 Hz, J = 1.3 Hz), 5.27 (td, 1H, J = 9.9 Hz, J = 2.6 Hz), 5.67 (d, 1H, J = 9.9 Hz), 6.48 (d, 1H, J = 8.1 Hz), 6.62 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ C: 145.6, 138.1, 130.4, 125.5, 42.7 CH: 132.7, 127.9, 119.5, 116.8, 91.1, 66.2, 58.7, 40.0 CH_2: 46.2, 34.8, 20.4 CH_3: 42.4 ;

IR cm^{-1} 3352 (b), 2924 (s), 1459 (m), 1249 (m); HRMS calcd for $C_{17}H_{20}NO_3$ (M+1) 286.1443, found 286.1445.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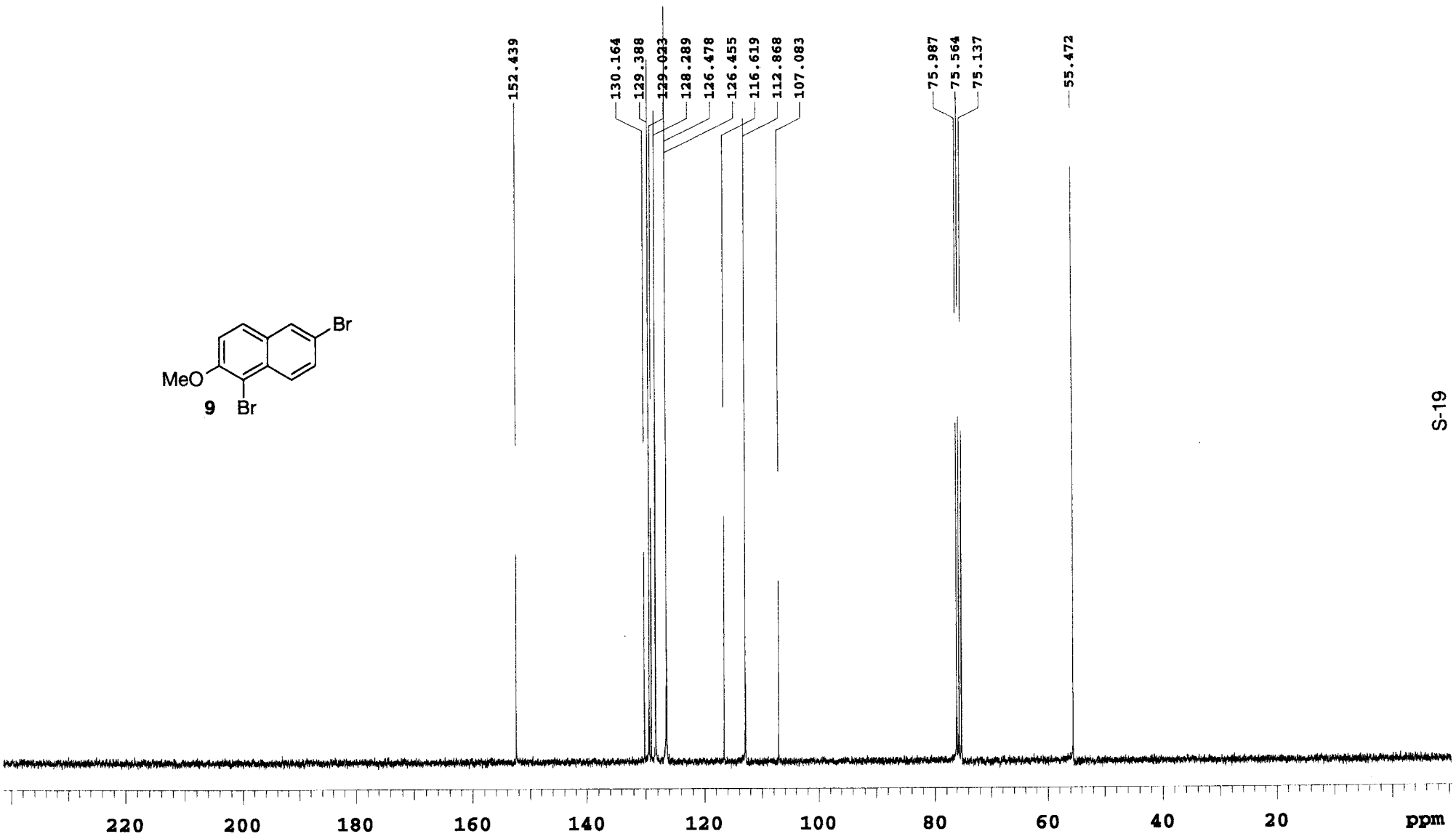

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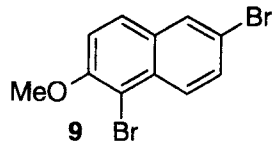

CH2 carbons

CH carbons

all protonated carbons

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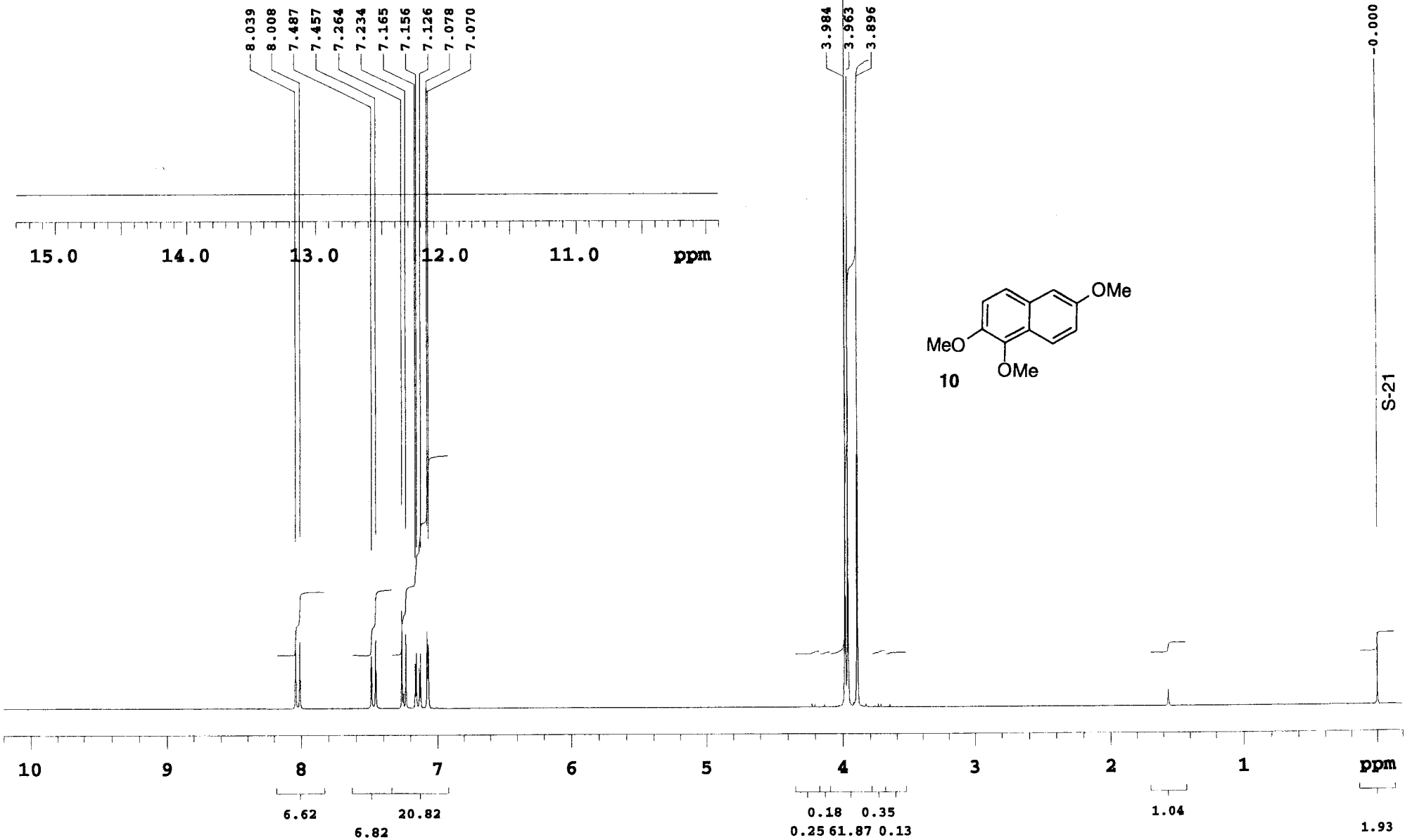

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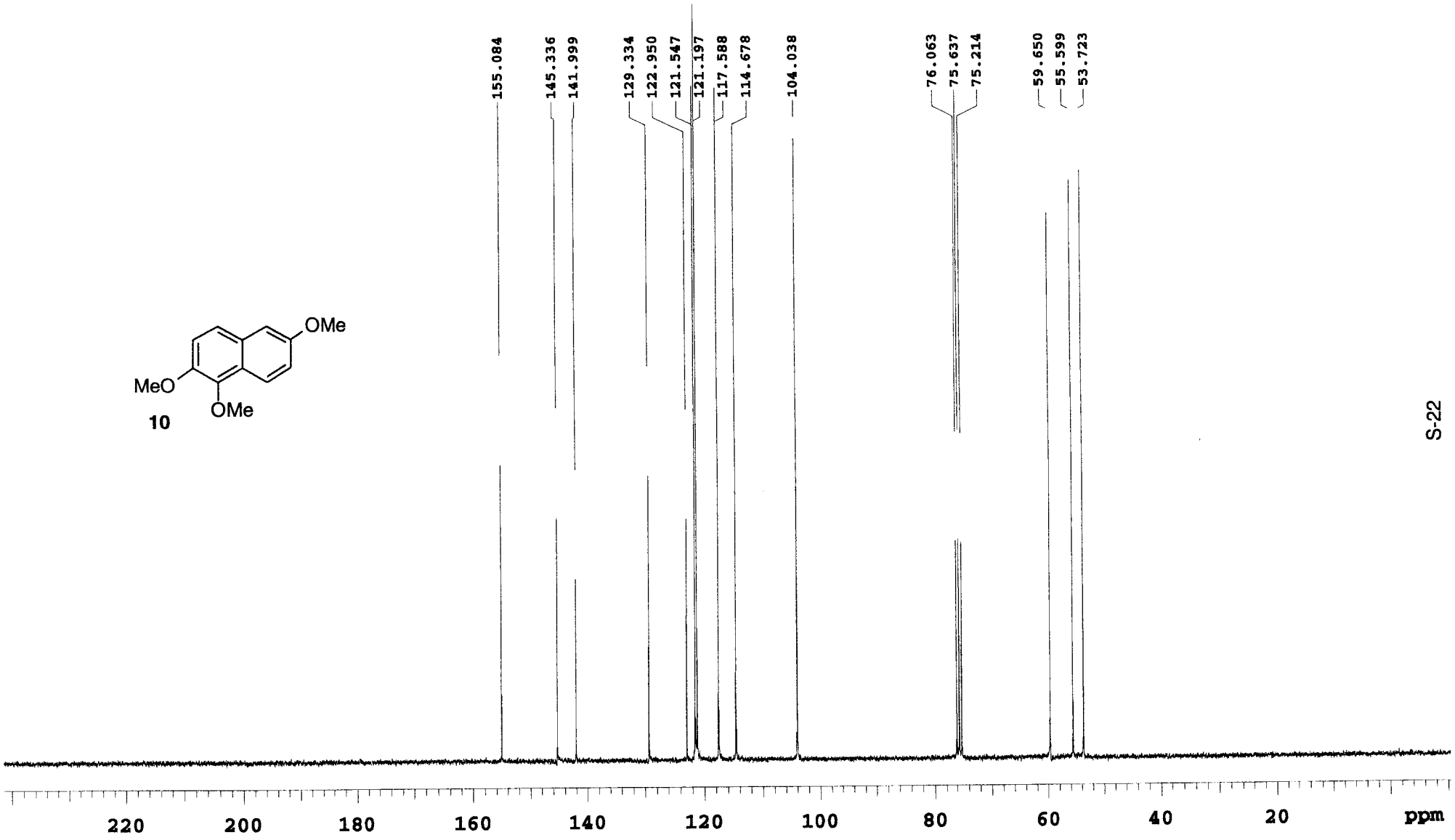
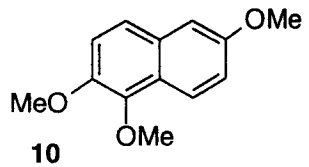


S-22

99790-12 NEUBERTD DATE: 05-23-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na05232002.185248c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



10

CH2 carbons

CH carbons

all protonated carbons

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99790-12 NEUBERTD DATE: 05-23-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na05232002.194048c

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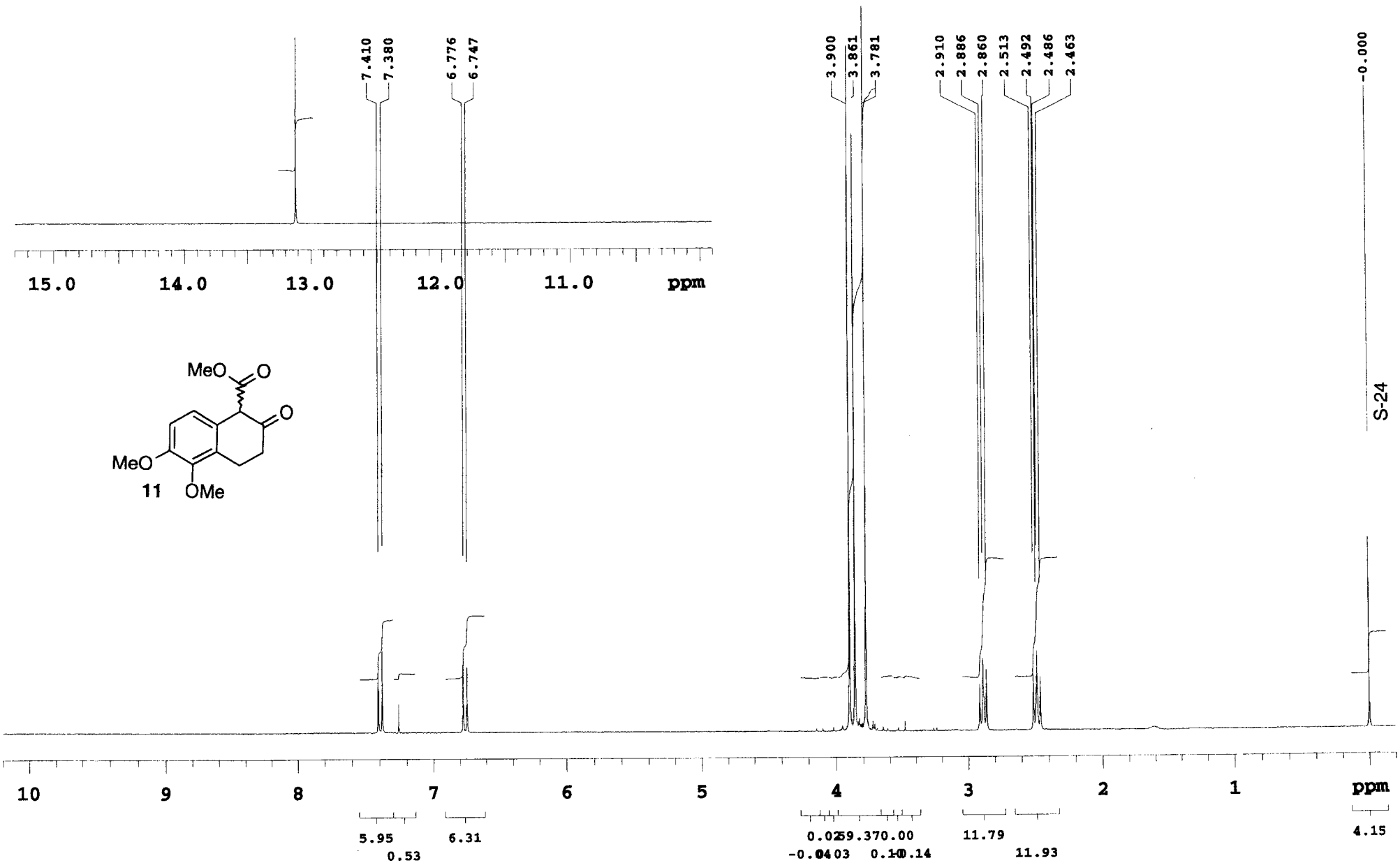

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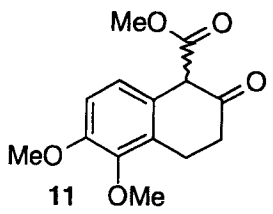

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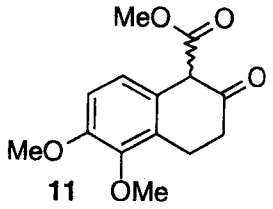
220 200 180 160 140 120 100 80 60 40 20 ppm

S-25

99790-14 NEUBERTD DATE: 10-03-00 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb10032000.185452c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / G. Blankenship



11

CH3 carbons

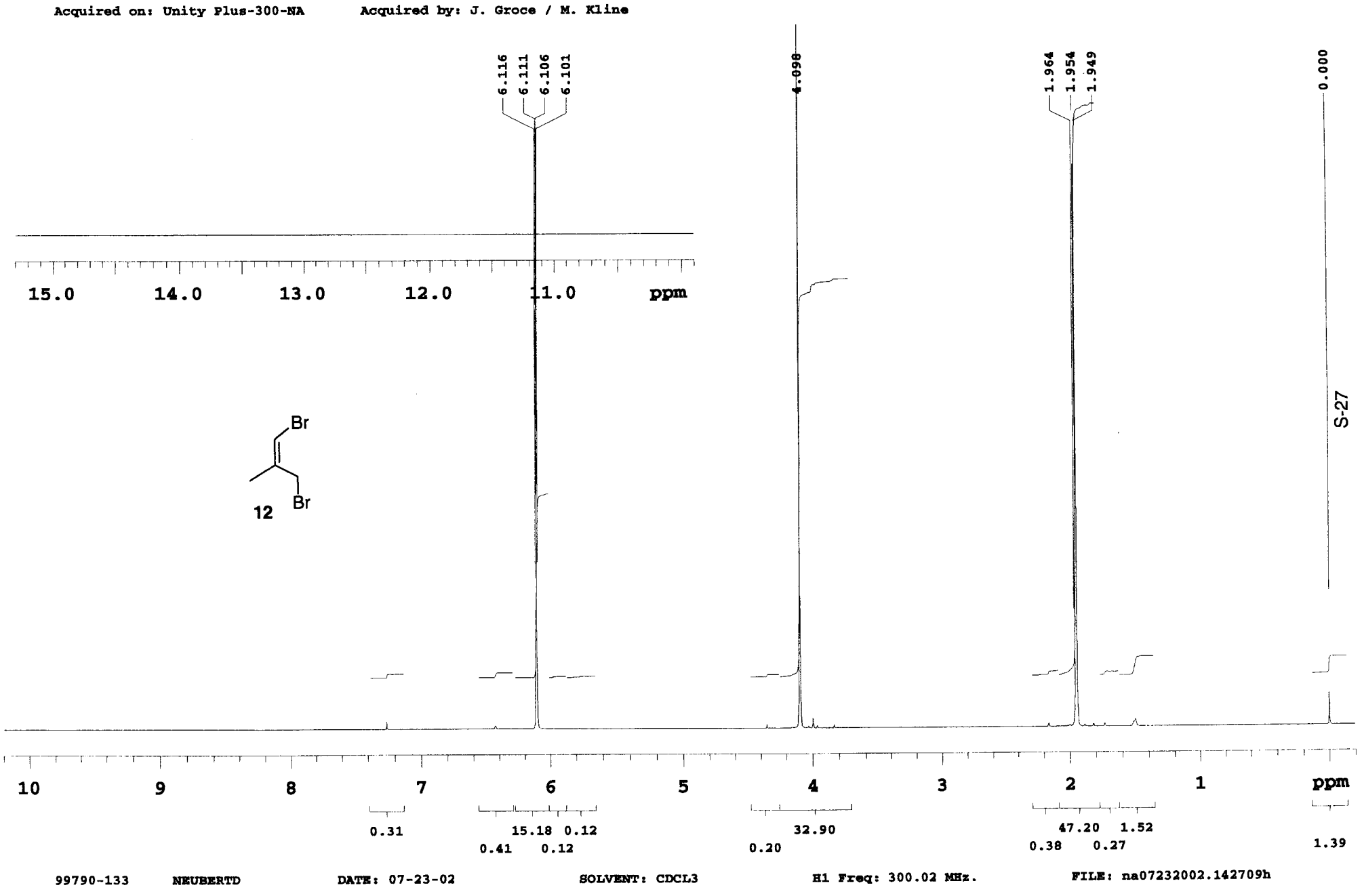
CH2 carbons

CH carbons

all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-14 NEUBERTD DATE: 10-03-00 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb10032000.194540c


Acquired on: Unity Plus-300-NA
Acquired by: J. Groce / M. Kline
6.116
6.111
6.106
6.101
4.098
1.964
1.954
1.949
0.000
15.0
14.0
13.0
12.0
11.0
ppm
Br
Br
12
S-27
10
9
8
7
6
5
4
3
2
1
ppm
0.31
15.18
0.12
0.41
0.12
32.90
0.20
47.20
1.52
0.38
0.27
1.39
99790-133
NEUBERTD
DATE: 07-23-02
SOLVENT: CDCL3
H1 Freq: 300.02 MHz.
FILE: na07232002.142709h

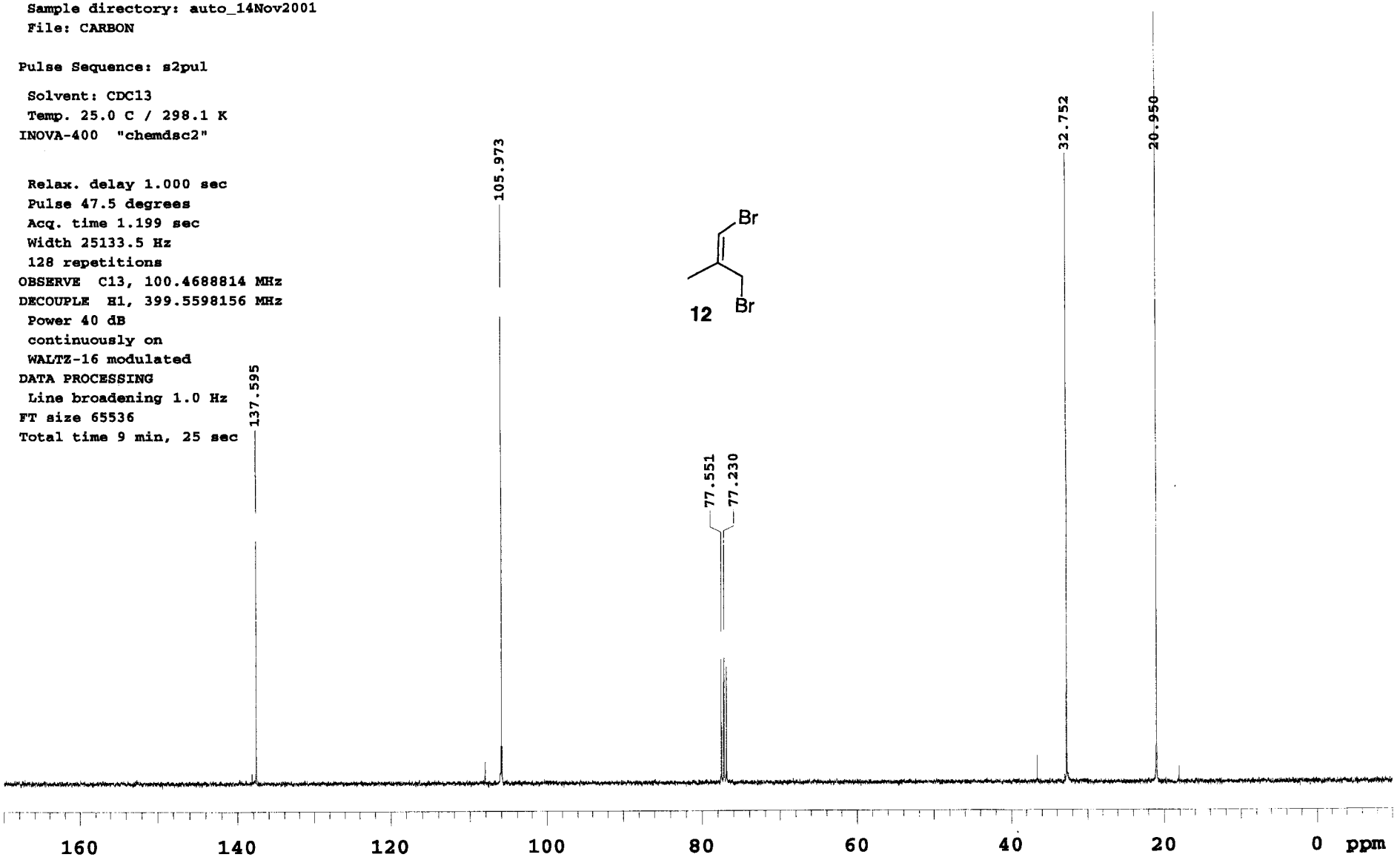
99790-133 NEUBERTD

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

Pulse Sequence: s2pul

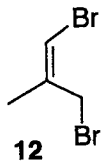
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
128 repetitions
OBSERVE C13, 100.4688814 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 9 min, 25 sec



Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



12

CH2 carbons

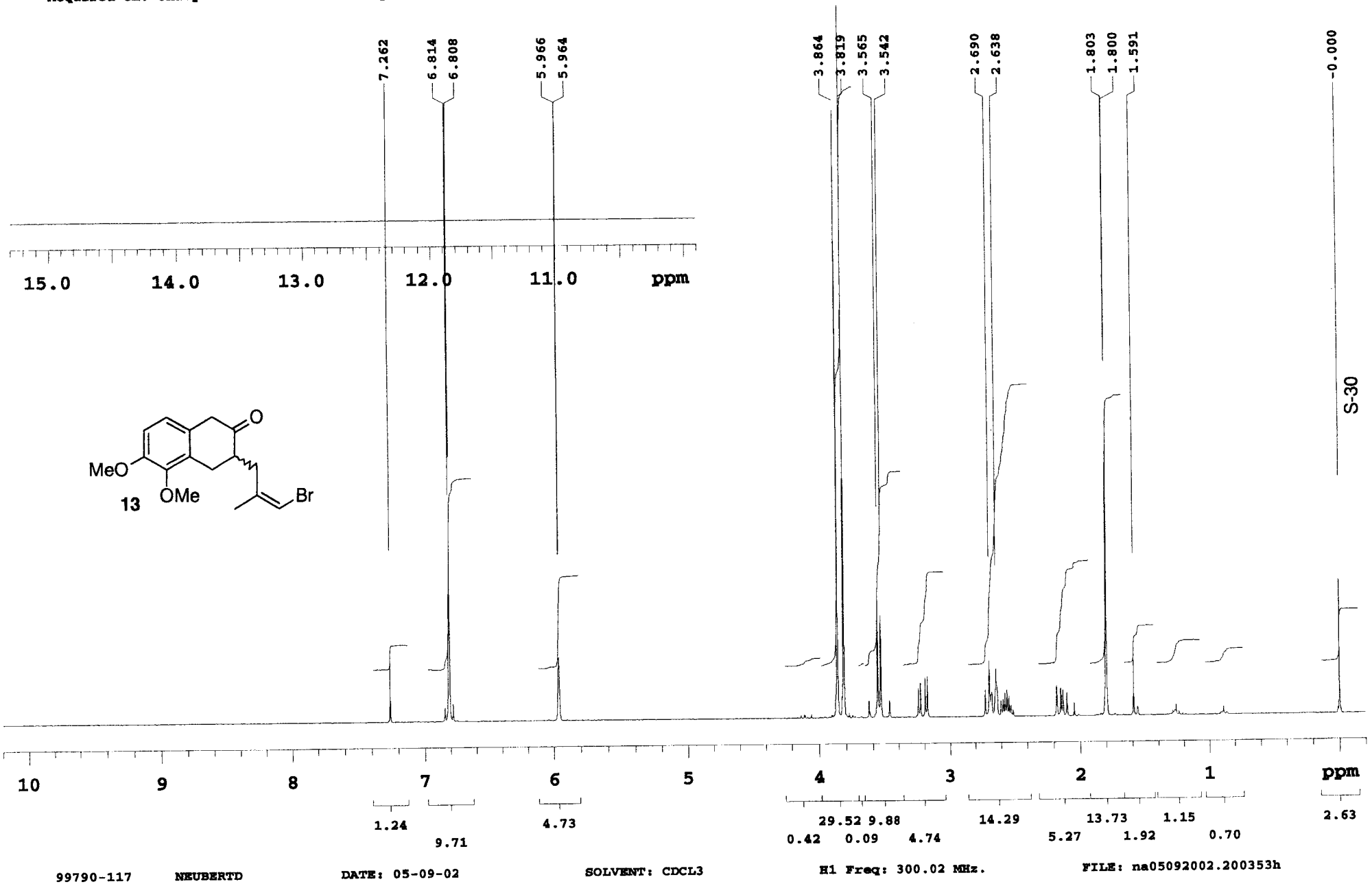
CH carbons

all protonated carbons

140 120 100 80 60 40 20 0 ppm

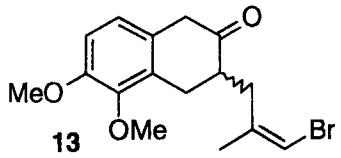
99790-133 NEUBERTD DATE: 07-23-02 SOLVENT: cdcl3 C13 Freq: 100.48 MHz. FILE: nd07232002.151957c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



99790-117 NEUBERTD DATE: 05-09-02 SOLVENT: CDCL3 H1 Freq: 300.02 MHz. FILE: na05092002.200353h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



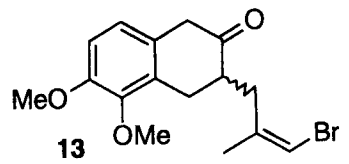
13

index	freq(ppm)	freq(Hz)
1	209.515	15807.5
2	190.127	14344.7
3	176.345	13304.9
4	149.827	11304.2
5	144.743	10920.6
6	138.851	10476.1
7	137.406	10367.1
8	137.226	10353.4
9	136.488	10297.8
10	133.533	10074.8
11	129.443	9766.3
12	127.776	9640.4
13	126.538	9547.1
14	124.505	9393.7
15	121.703	9182.3
16	115.193	8691.1
17	113.406	8556.3
18	112.764	8507.9
19	109.559	8266.0
20	108.733	8203.7
21	101.946	7691.6
22	101.850	7684.4
23	76.009	5734.7
24	75.586	5702.8
25	75.159	5670.6
26	59.564	4494.0
27	59.249	4470.2
28	59.137	4461.8
29	55.540	4190.4
30	54.318	4098.2
31	43.177	3257.6
32	42.681	3220.2
33	42.320	3192.9
34	38.192	2881.5
35	36.751	2772.8
36	24.895	1878.3
37	17.896	1350.3
38	17.312	1306.2
39	17.235	1300.4

99790-117 NEUBERTD DATE: 05-14-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na05142002.212029c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



13

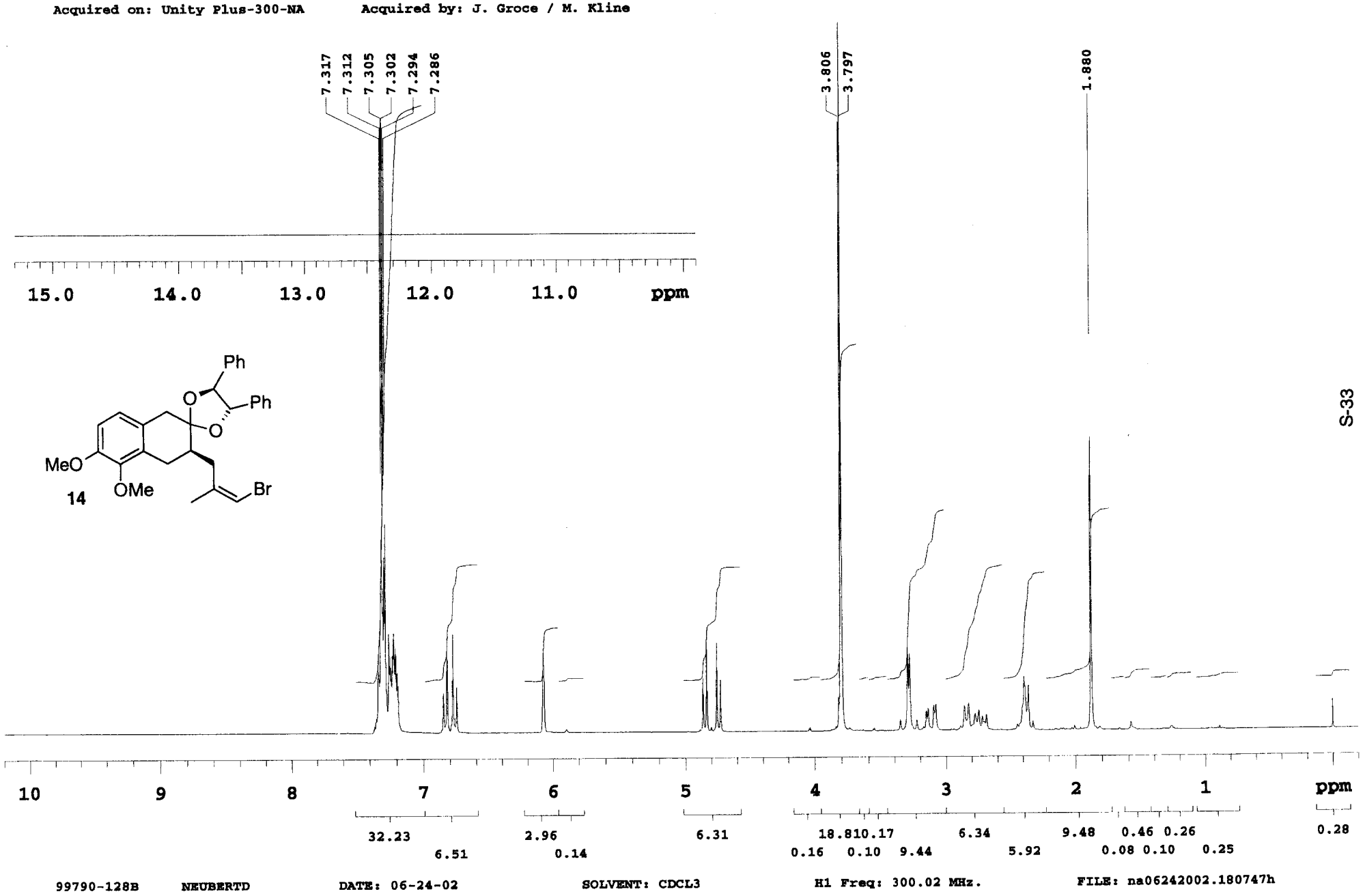
CH2 carbons

CH carbons

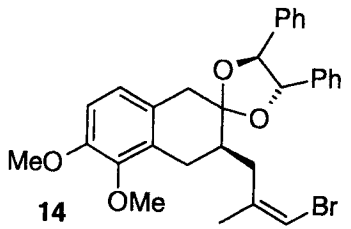
all protonated carbons

180 160 140 120 100 80 60 40 20 0 ppm

99790-117 NEUBERTD DATE: 05-11-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na05112002.185338c


Acquired on: Unity Plus-300-NA
Acquired by: J. Groce / M. Kline
7.317
7.312
7.305
7.302
7.294
7.286
3.806
3.797
1.880
15.0
14.0
13.0
12.0
11.0
ppm
Ph
Ph
O
O
MeO
OMe
Br
14
S-33
10
9
8
7
6
5
4
3
2
1
ppm
32.23
6.51
2.96
0.14
6.31
18.81
0.17
0.16
0.10
9.44
6.34
5.92
9.48
0.08
0.46
0.10
0.26
0.25
0.28
99790-128B
NEUBERTD
DATE: 06-24-02
SOLVENT: CDCL3
H1 Freq: 300.02 MHz.
FILE: na06242002.180747h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



14

149.280 145.163 138.283 135.404 134.519 127.662 127.063 126.993 126.936 126.032 125.237 122.600 109.550 108.632 101.033 84.846 83.374 76.025 75.602 75.179 58.540 54.465 37.956 36.203 25.964 17.461

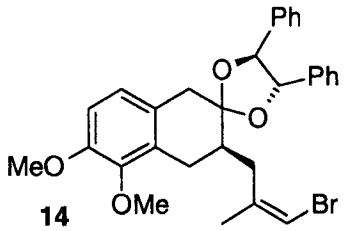
220 200 180 160 140 120 100 80 60 40 20 ppm

S-34

99790-128B NEUBERTD DATE: 06-24-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06242002.185534c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



14

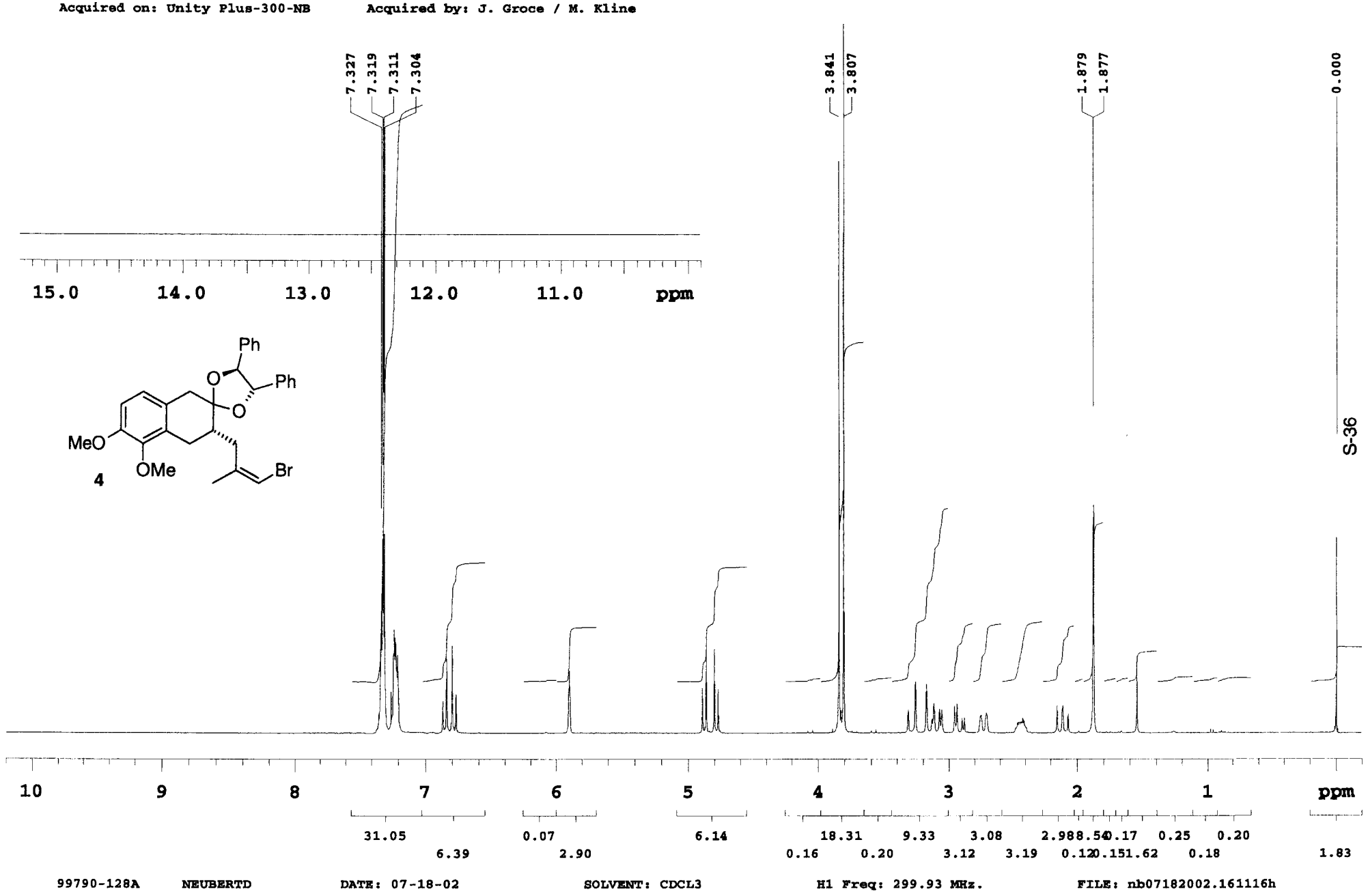
CH2 carbons

CH carbons

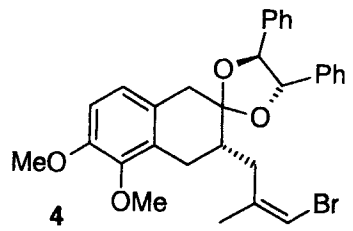
all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-128B NEUBERTD DATE: 06-24-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06242002.194331c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.327
7.319
7.311
7.304
3.841
3.807
1.879
1.877
0.000
15.0
14.0
13.0
12.0
11.0
ppm
Ph
Ph
O
O
MeO
OMe
Br
4
S-36
10
9
8
7
6
5
4
3
2
1
ppm
31.05
6.39
0.07
2.90
6.14
18.31
9.33
3.08
2.98
8.54
0.17
0.25
0.20
0.16
0.20
3.12
3.19
0.12
0.15
1.62
0.18
1.83
99790-128A
NEUBERTD
DATE: 07-18-02
SOLVENT: CDCL3
H1 Freq: 299.93 MHz.
FILE: nb07182002.161116h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

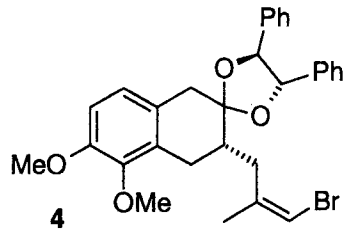


4

99790-128A NEUBERTD DATE: 06-10-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06102002.124720c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



4

CH2 carbons

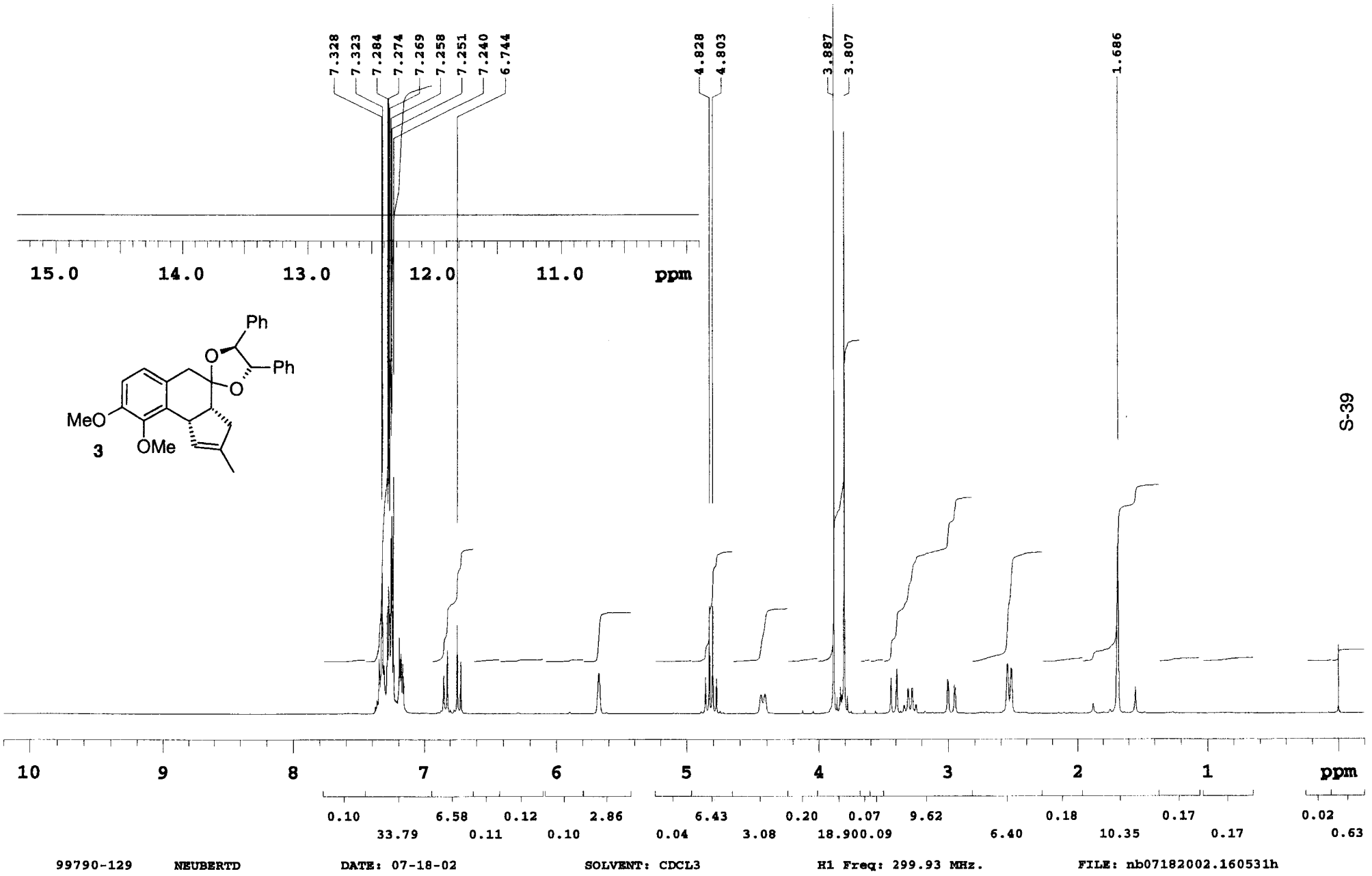
CH carbons

all protonated carbons

160 140 120 100 80 60 40 20 ppm

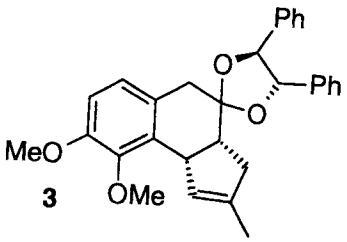
99790-128A NEUBERTD DATE: 06-10-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06102002.125014c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



99790-129 NEUBERTD DATE: 07-18-02 SOLVENT: CDCL3 H1 Freq: 299.93 MHz. FILE: nb07182002.160531h

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



3

149.574 144.934 136.765 135.615 135.569 130.987 127.020 126.858 126.816 126.662 126.616 126.574 125.663 125.351 125.213 122.868 122.687 110.697 109.243 84.290 84.194 76.071 75.644 75.221 58.713 54.323 44.801 44.059 38.339 34.598 15.076

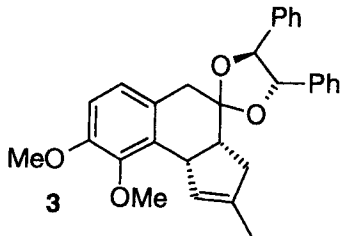
220 200 180 160 140 120 100 80 60 40 20 ppm

S-40

99790-129 NEUBERTD DATE: 06-19-02 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb06192002.185508c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline

CH3 carbons



3

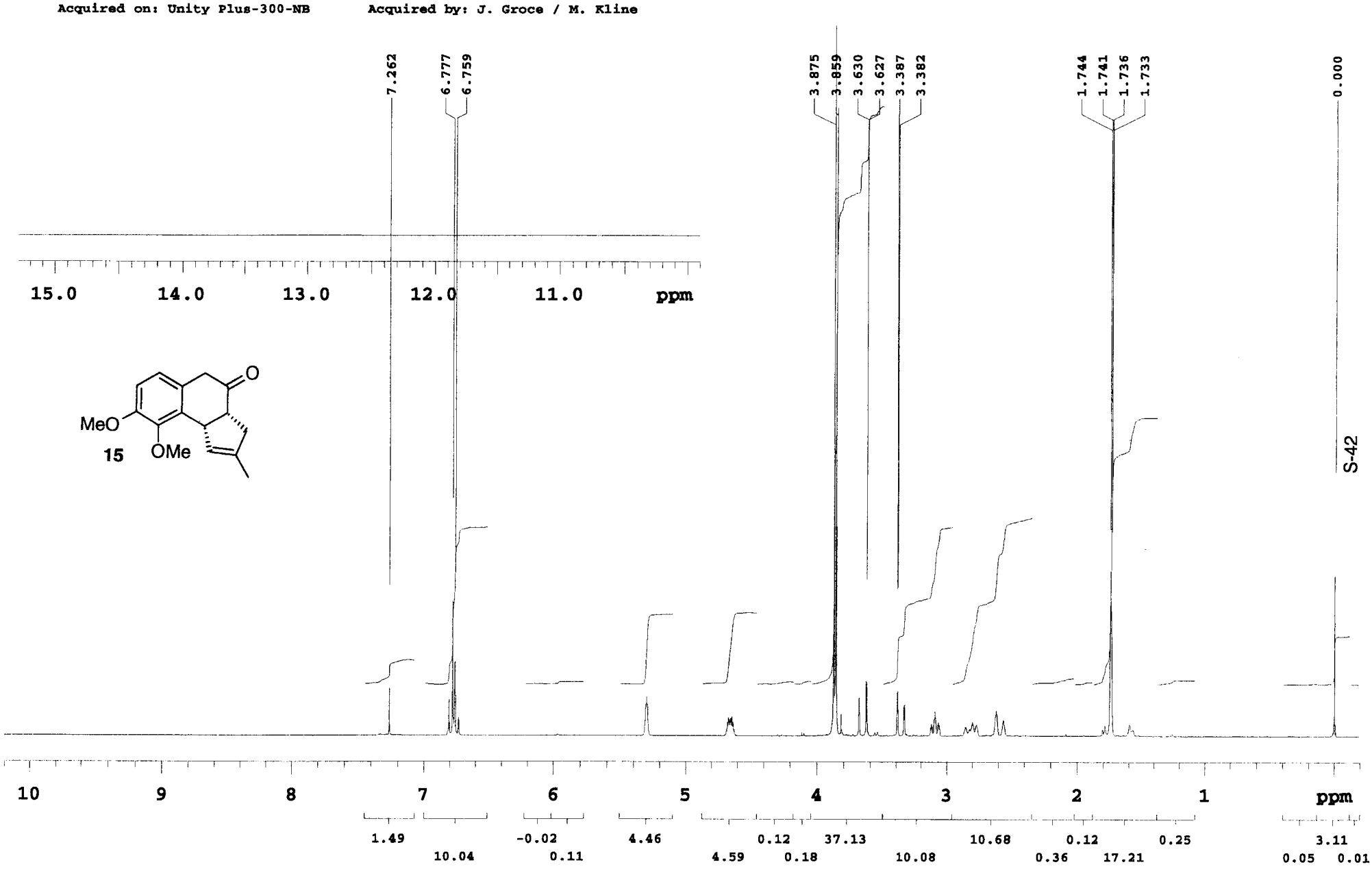
CH2 carbons

CH carbons

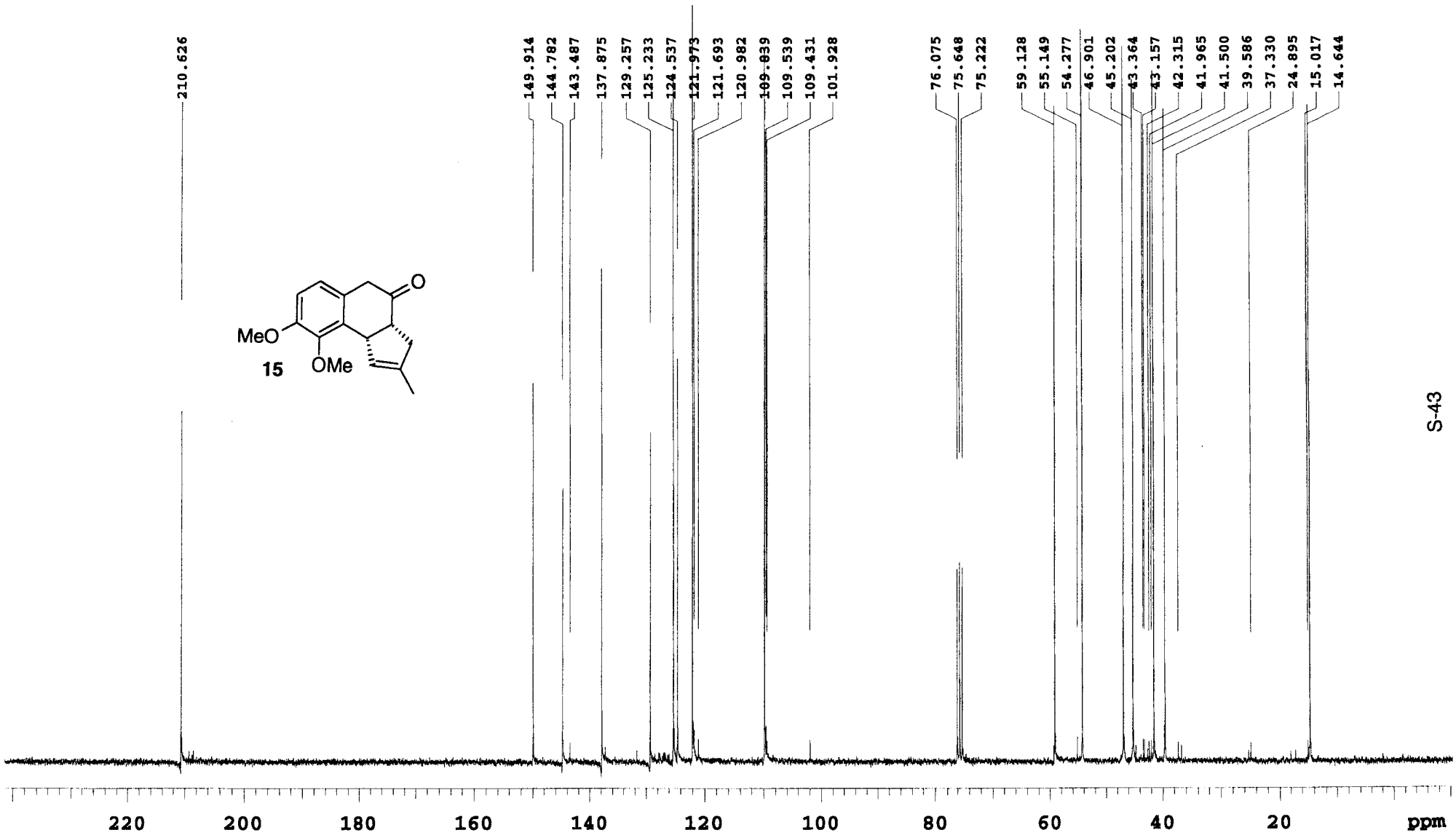
all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-129 NEUBERTD DATE: 06-19-02 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb06192002.194608c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.262
6.777
6.759
3.875
3.859
3.630
3.627
3.387
3.382
1.744
1.741
1.736
1.733
0.000
15.0
14.0
13.0
12.0
11.0
ppm
MeO
OMe
O
15
S-42
10
9
8
7
6
5
4
3
2
1
ppm
1.49
10.04
-0.02
0.11
4.46
4.59
0.12
0.18
37.13
10.08
10.68
0.36
0.12
17.21
0.25
3.11
0.05
0.01
99790-130
NEUBERTD
DATE: 06-24-02
SOLVENT: CDCL3
H1 Freq: 299.93 MHz.
FILE: nb06242002.213647h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

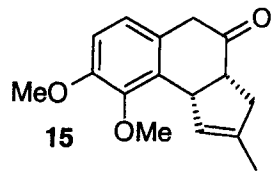


S-43

99790-130 NEUBERTD DATE: 06-25-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06252002.185309c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



15

CH2 carbons

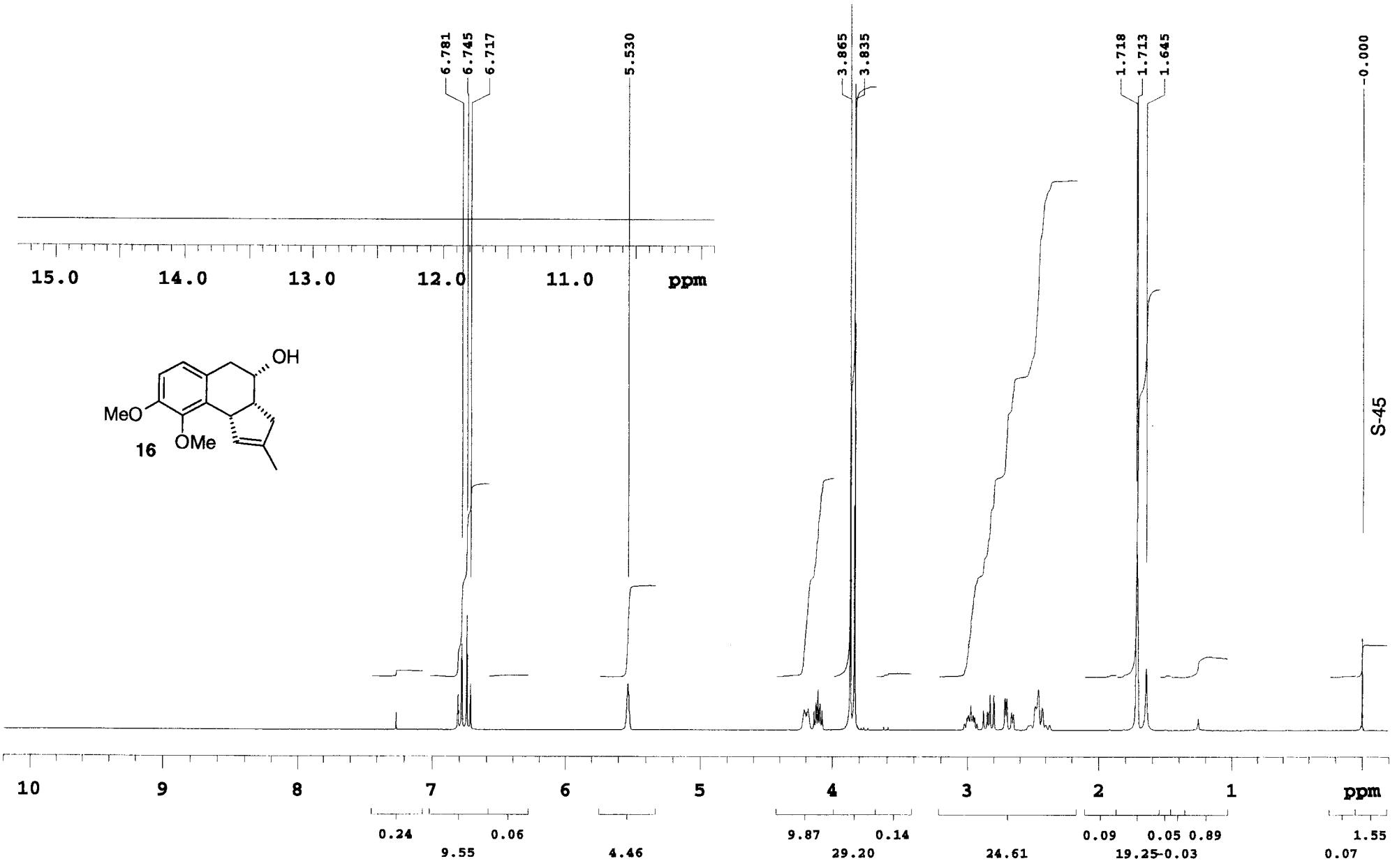
CH carbons

all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

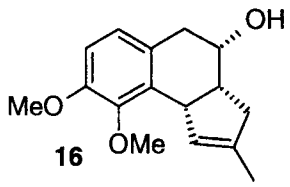
99790-130 NEUBERTD DATE: 06-25-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06252002.194108c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



99790-131 NEUBERTD DATE: 07-12-02 SOLVENT: CDCL3 H1 Freq: 299.93 MHz. FILE: nb07122002.094135h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



16

149.560
149.456
145.117
144.963
137.817
136.203
130.645
130.422
126.867
126.694
125.733
125.133
123.330
122.992
122.834
109.151
109.070
75.998
75.571
75.149
68.387
67.769
58.636
54.285
43.672
42.884
42.684
39.590
38.710
35.623
34.205
32.733
15.009

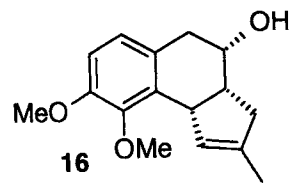
220 200 180 160 140 120 100 80 60 40 20 ppm

S-46

99790-131 NEUBERTD DATE: 06-25-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06252002.203359c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



16

CH2 carbons

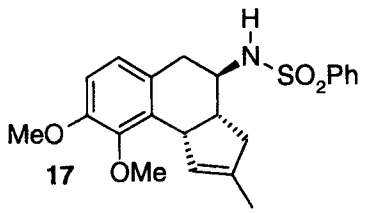
CH carbons

all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-131 NEUBERTD DATE: 06-25-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na06252002.212203c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



7.854 7.851 7.828 7.823 7.540 7.514 7.260 6.719 6.691 6.603

3.851 3.840

1.549 1.529

-0.000

S-48

15.0 14.0 13.0 12.0 11.0 ppm

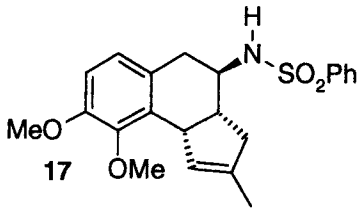
10 9 8 7 6 5 4 3 2 1 ppm

7.22 1.02 3.75 3.44 3.13 22.52 3.71 3.18 0.27

11.31 3.63 3.81 4.07 10.65 12.77 5.50

99790-50 NEUBERTD DATE: 07-01-02 SOLVENT: CDCL3 H1 Freq: 300.02 MHz. FILE: na07012002.101955h

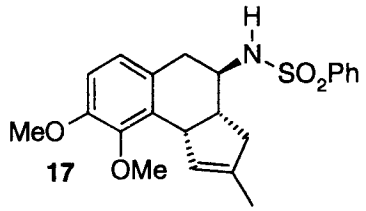
Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



99790-50 NEUBERTD DATE: 07-02-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na07022002.074027c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



CH2 carbons

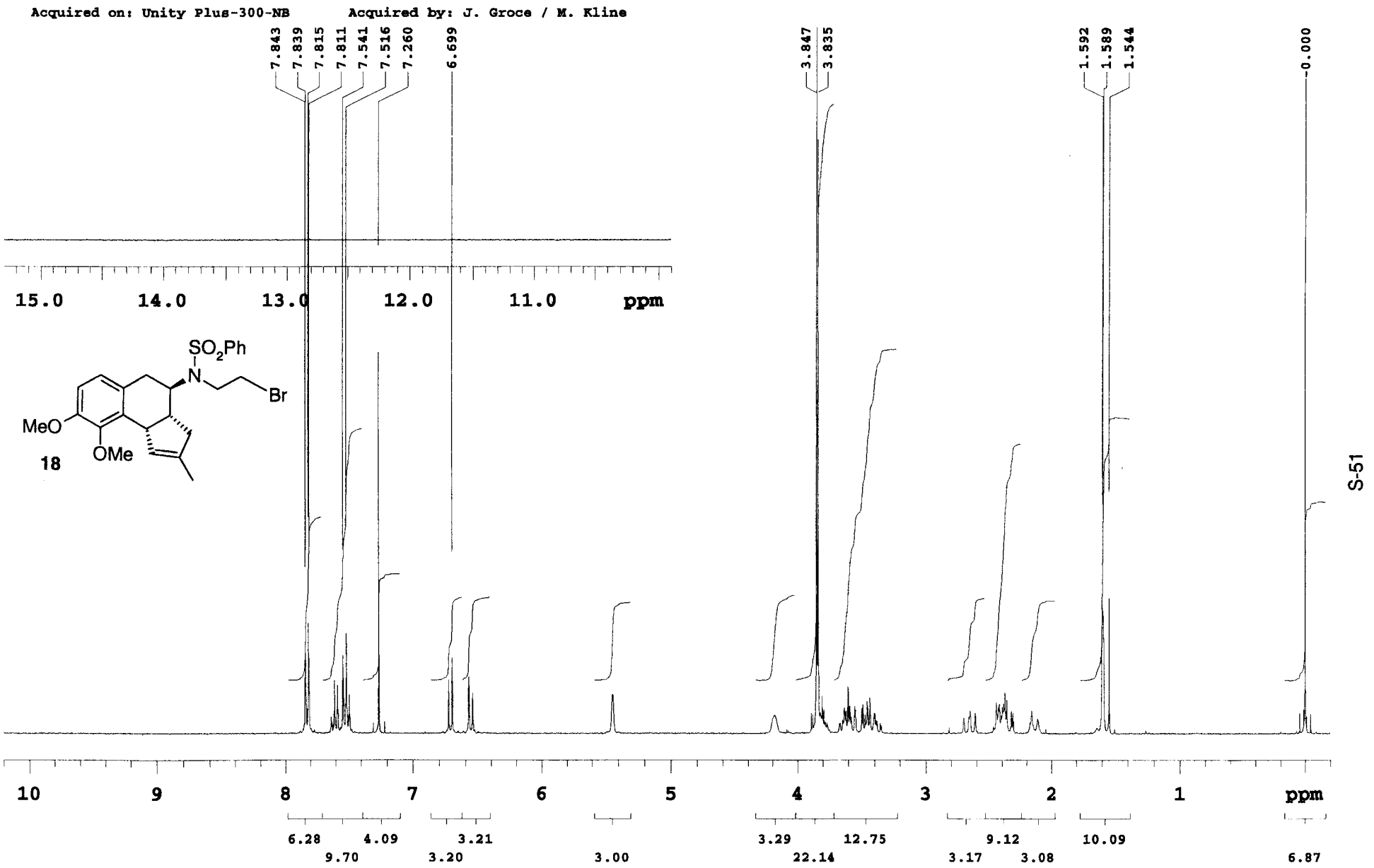
CH carbons

all protonated carbons

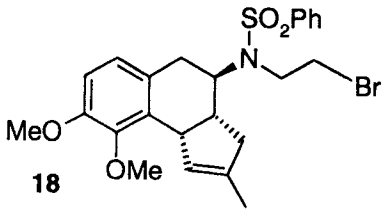
S-50

160 140 120 100 80 60 40 20 ppm

99790-50 NEUBERTD DATE: 07-02-02 SOLVENT: CDCL3 C13 Freq: 75.45 MHz. FILE: na07022002.074057c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.843
7.839
7.815
7.811
7.541
7.516
7.260
6.699
3.847
3.835
1.592
1.589
1.544
0.000
15.0
14.0
13.0
12.0
11.0
ppm
SO2Ph
N
Br
MeO
OMe
18
10
9
8
7
6
5
4
3
2
1
ppm
6.28
4.09
3.21
3.29
12.75
9.12
10.09
9.70
3.20
3.00
22.14
3.17
3.08
6.87
99790-58
NEUBERTD
DATE: 11-06-01
SOLVENT: CDCL3
H1 Freq: 299.93 MHz.
FILE: nb11062001.101424h

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



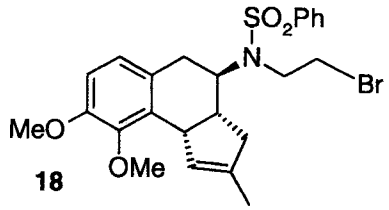
18

index	freq(ppm)	freq(Hz)
1	149.494	11275.8
2	145.369	10964.7
3	138.773	10467.1
4	136.362	10285.3
5	131.219	9897.3
6	129.016	9731.2
7	127.728	9634.1
8	127.555	9621.0
9	126.502	9541.6
10	125.695	9480.7
11	125.537	9468.8
12	125.437	9461.2
13	122.969	9275.1
14	122.031	9204.3
15	109.399	8251.5
16	75.938	5727.7
17	75.516	5695.9
18	75.093	5664.0
19	58.766	4432.5
20	58.559	4416.8
21	54.557	4115.0
22	54.330	4097.9
23	54.088	4079.6
24	44.535	3359.1
25	43.658	3293.0
26	39.637	2989.7
27	38.195	2880.9
28	31.053	2342.2
29	28.965	2184.8
30	14.826	1118.3

99790-58 NEUBERTD DATE: 09-21-01 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb09212001.190229c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline

CH3 carbons



18

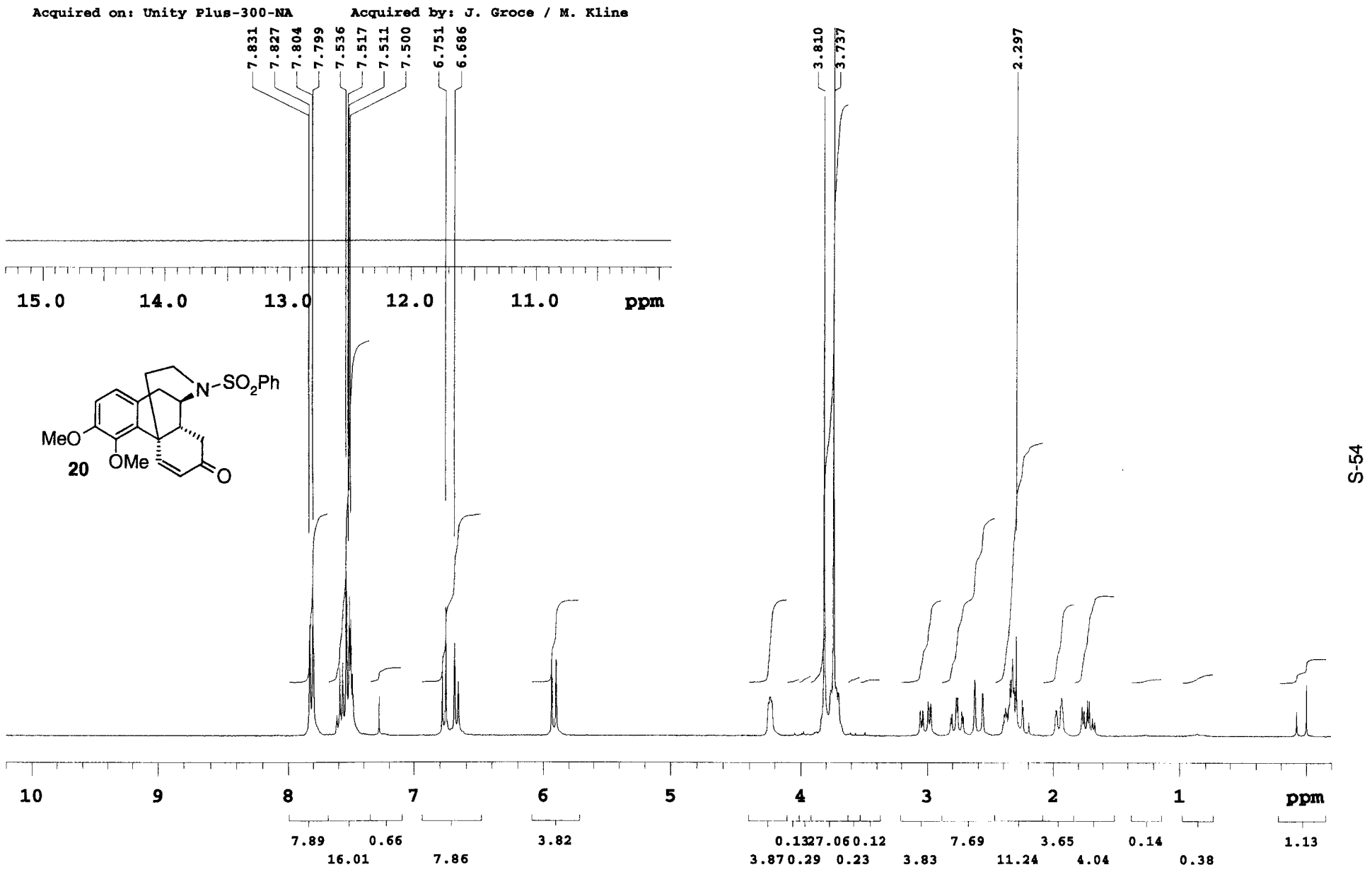
CH2 carbons

CH carbons

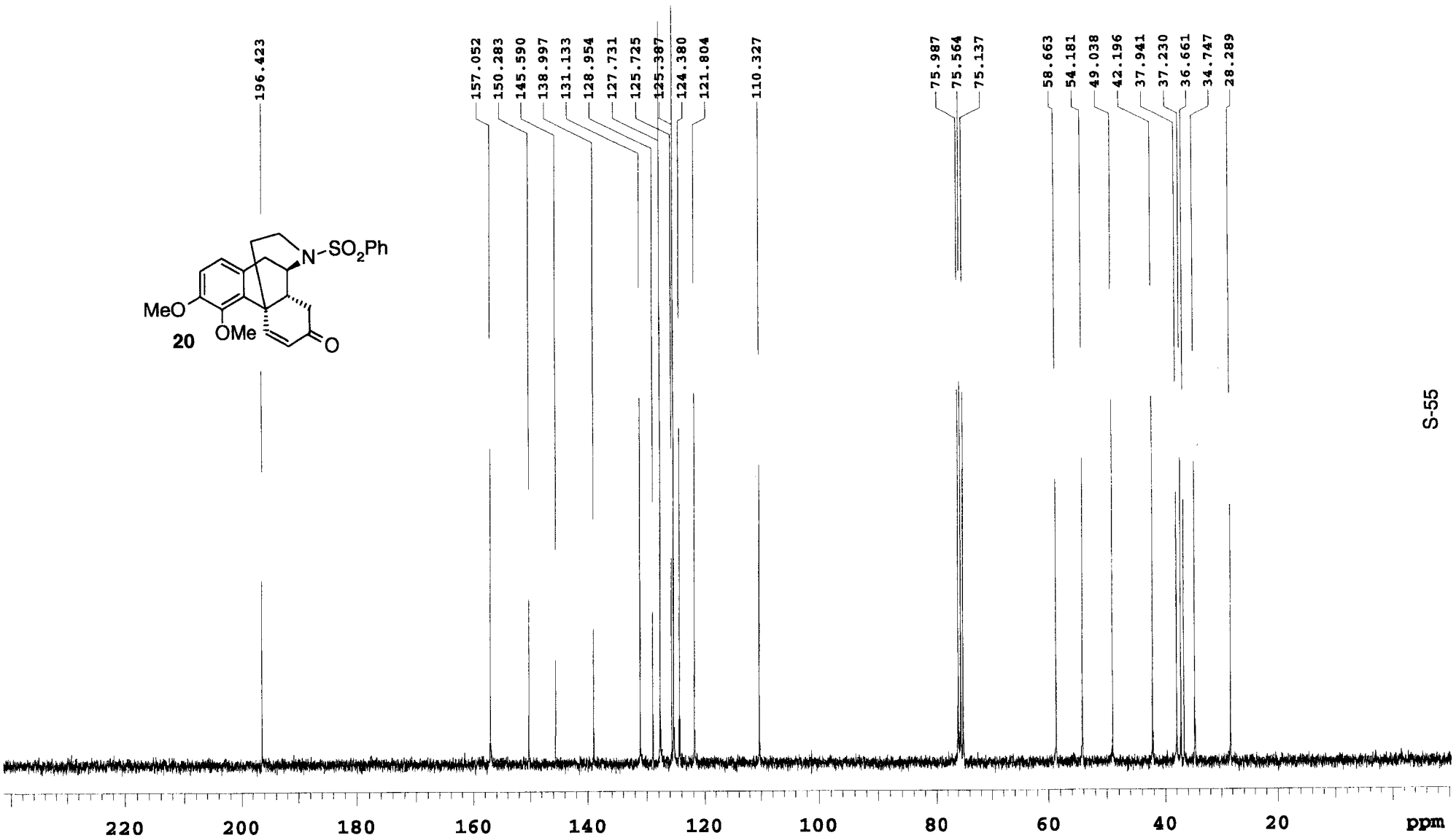
all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-58 NEUBERTD DATE: 09-21-01 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb09212001.195327c


Acquired on: Unity Plus-300-NA
Acquired by: J. Groce / M. Kline
7.831
7.827
7.804
7.799
7.536
7.517
7.511
7.500
6.751
6.686
3.810
3.737
2.297
15.0
14.0
13.0
12.0
11.0
ppm
N-SO2Ph
MeO
OMe
O
20
10
9
8
7
6
5
4
3
2
1
ppm
7.89
0.66
16.01
7.86
3.82
0.13
27.06
0.12
3.87
0.29
0.23
3.83
7.69
11.24
3.65
4.04
0.14
0.38
1.13
99790-63
NEUBERTD
DATE: 11-08-01
SOLVENT: CDCL3
H1 Freq: 299.98 MHz.
FILE: na11082001.180537h

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline



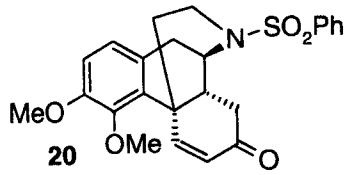
20

S-55

99790-63 NEUBERTD DATE: 11-08-01 SOLVENT: CDCL3 C13 Freq: 75.44 MHz. FILE: na11082001.185326c

Acquired on: Unity Plus-300-NA Acquired by: J. Groce / M. Kline

CH3 carbons



20

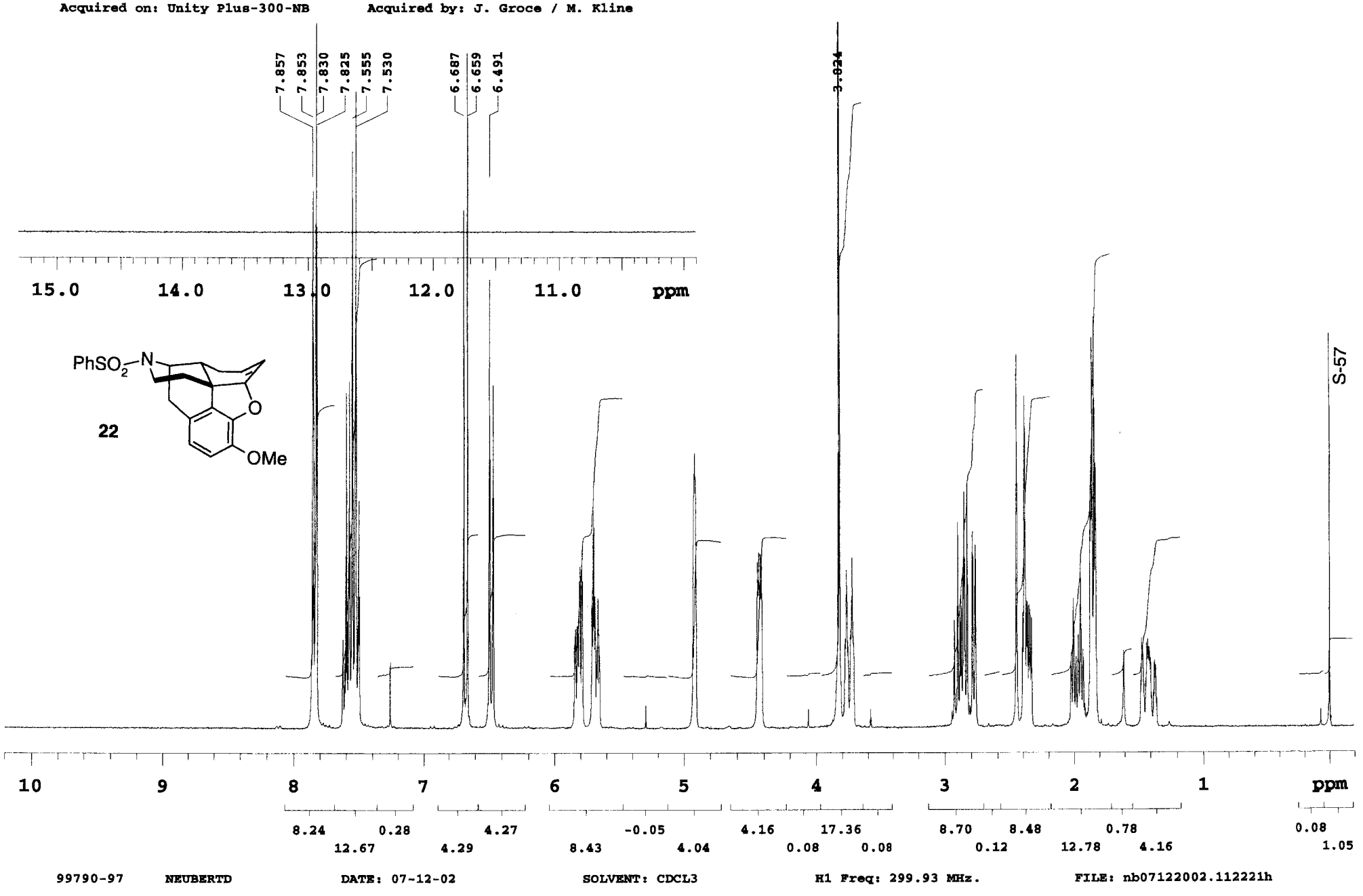
CH2 carbons

CH carbons

all protonated carbons

220 200 180 160 140 120 100 80 60 40 20 ppm

99790-63 NEUBERTD DATE: 11-08-01 SOLVENT: CDCL3 C13 Freq: 75.44 MHz. FILE: na11082001.194121c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.857
7.853
7.830
7.825
7.555
7.530
6.687
6.659
6.491
3.824
15.0
14.0
13.0
12.0
11.0
ppm
PhSO2–N
O
OMe
22
S-57
10
9
8
7
6
5
4
3
2
1
ppm
8.24
0.28
4.27
-0.05
4.16
17.36
8.70
8.48
0.78
0.08
12.67
4.29
8.43
4.04
0.08
0.08
0.12
12.78
4.16
1.05
99790-97
NEUBERTD
DATE: 07-12-02
SOLVENT: CDCL3
H1 Freq: 299.93 MHz.
FILE: nb07122002.112221h

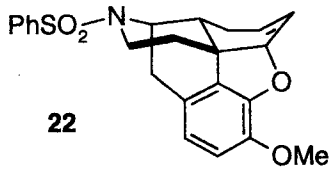
99790-97 NEUBERTD

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

Pulse Sequence: s2pul

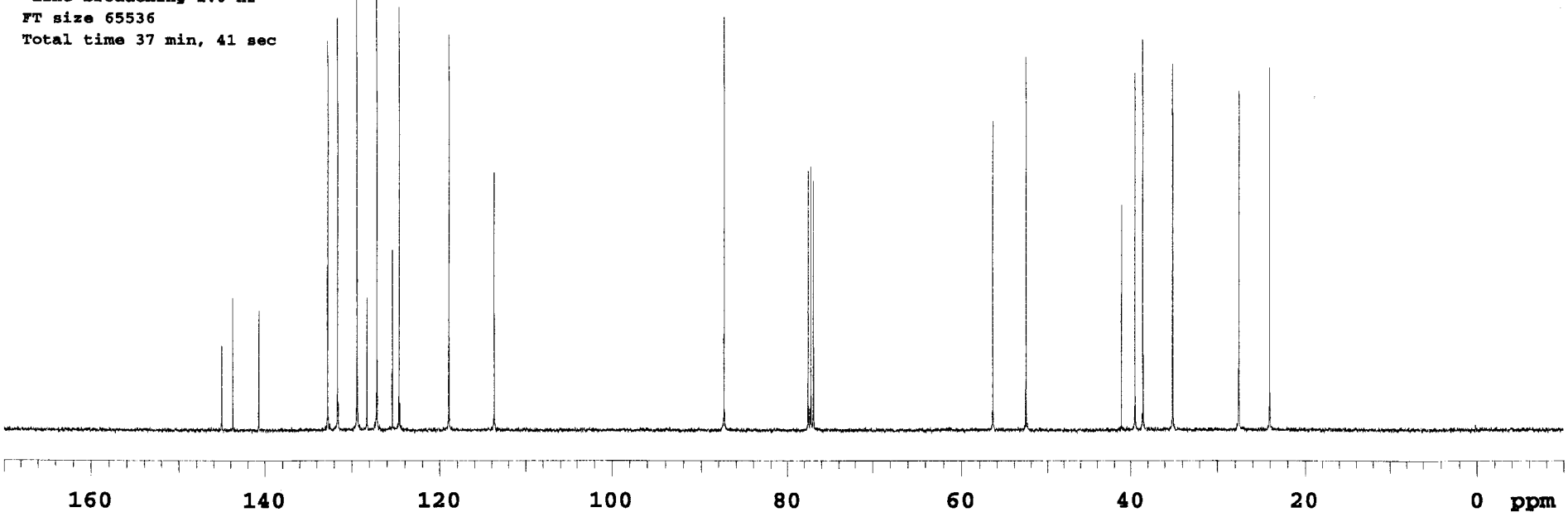
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
1024 repetitions
OBSERVE C13, 100.4688783 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 37 min, 41 sec



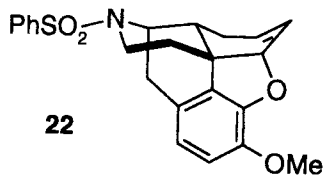
22

INDEX	FREQUENCY	PPM	HEIGHT
1	14571.065	145.031	13.4
2	14439.905	143.725	21.0
3	14136.168	140.702	19.0
4	13333.871	132.716	62.2
5	13221.120	131.594	66.1
6	12997.919	129.373	138.8
7	12884.400	128.243	20.9
8	12771.649	127.120	126.8
9	12596.770	125.380	28.6
10	12521.603	124.632	67.7
11	11953.245	118.975	63.3
12	11421.704	113.684	41.0
13	8780.107	87.391	66.2
14	7791.426	77.551	41.3
15	7759.211	77.230	42.1
16	7726.997	76.909	39.7
17	5672.933	56.465	49.5
18	5287.125	52.625	59.8
19	4129.700	41.104	35.8
20	3967.093	39.486	57.2
21	3874.284	38.562	62.6
22	3522.992	35.066	58.7
23	2765.949	27.530	54.3
24	2414.656	24.034	58.1



Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



22

CH2 carbons

CH carbons

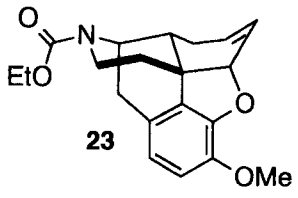
all protonated carbons

140 120 100 80 60 40 20 0 ppm

99790-97 NEUBERTD DATE: 07-11-02 SOLVENT: cdcl3 C13 Freq: 100.48 MHz. FILE: nd07112002.151443c

99790-110 NEUBERTD

Pulse Sequence: s2pul
E. I. Dupont - Crop Protection Products
Global Technology - Lead Discovery
Acquired on: Unity Inova-400-ND
Acquired by: vnmr1
File: nd07152002.085534h



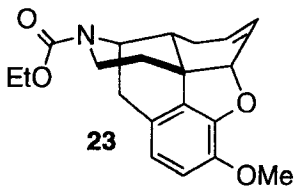
23

99790-110 NEUBERTD

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

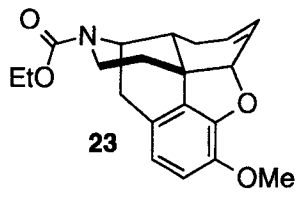


23

Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
4197 repetitions
OBSERVE C13, 100.4689014 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 1 min, 29 sec

Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



23

CH2 carbons

CH carbons

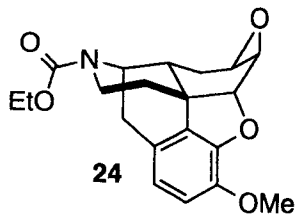
all protonated carbons

160 140 120 100 80 60 40 20 ppm

99790-110 NEUBERTD DATE: 07-15-02 SOLVENT: cdcl3 C13 Freq: 100.48 MHz. FILE: nd07152002.143135c

99790-111 NEUBERTD

Pulse Sequence: s2pul
E. I. Dupont - Crop Protection Products
Global Technology - Lead Discovery
Acquired on: Unity Inova-400-ND
Acquired by: vnmr1
File: nd07162002.090624h



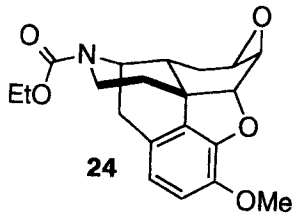
24

99790-111 NEUBERTD

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

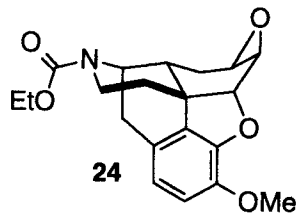


24

Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
3330 repetitions
OBSERVE C13, 100.4688961 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 1 min, 29 sec

Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



24

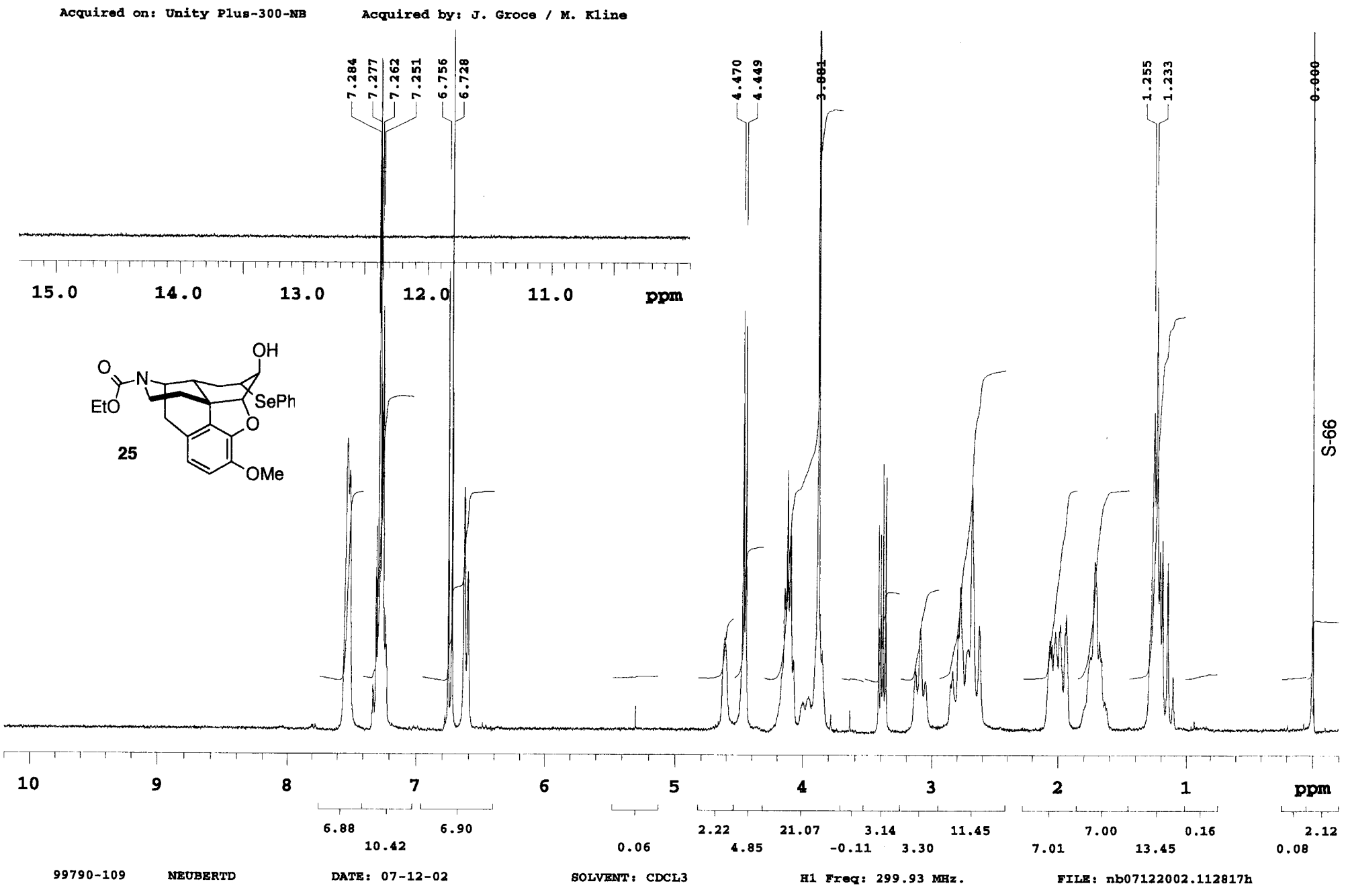
CH2 carbons

CH carbons

all protonated carbons

160 140 120 100 80 60 40 20 ppm

99790-111 NEUBERTD DATE: 07-16-02 SOLVENT: cdcl3 C13 Freq: 100.48 MHz. FILE: nd07162002.142405c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.284
7.277
7.262
7.251
6.756
6.728
4.470
4.449
3.001
1.255
1.233
0.000
15.0
14.0
13.0
12.0
11.0
ppm
OH
O
N
EtO
SePh
O
OMe
25
S-66
10
9
8
7
6
5
4
3
2
1
ppm
6.88
10.42
6.90
0.06
2.22
4.85
21.07
3.14
-0.11
3.30
11.45
7.00
7.01
0.16
13.45
2.12
0.08
99790-109
NEUBERTD
DATE: 07-12-02
SOLVENT: CDCL3
H1 Freq: 299.93 MHz.
FILE: nb07122002.112817h

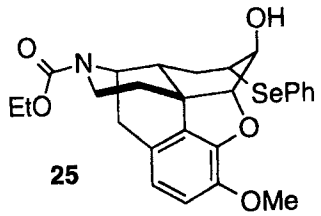
99790-109 NEUBERTD

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

Pulse Sequence: s2pul

Solvent: CDC13
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

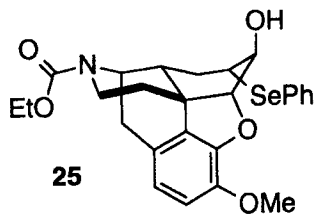
Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
10240 repetitions
OBSERVE C13, 100.4688945 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 16 min, 51 sec



25

Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



25

CH2 carbons

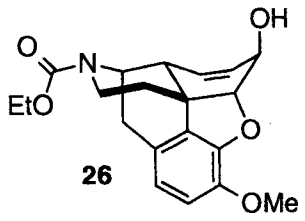
CH carbons

all protonated carbons

140 120 100 80 60 40 20 ppm

99790-109 NEUBERTD DATE: 07-12-02 SOLVENT: cdcl3 C13 Freq: 100.48 MHz. FILE: nd07122002.033638c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



26

6.714 6.687 6.578 4.767 4.173 4.149 3.912 3.854 2.905 2.769 1.702 1.299 1.275 1.253 -0.000

15.0 14.0 13.0 12.0 11.0 ppm

10 9 8 7 6 5 4 3 2 1 ppm

0.27 8.07 3.05 3.07 -0.04 8.13 27.94 0.04 0.07 15.55 2.96 15.06 0.21 13.16 0.28 2.19

S-69

99790-115 NEUBERTD DATE: 07-18-02 SOLVENT: CDCL3 H1 Freq: 299.93 MHz. FILE: nb07182002.135449h

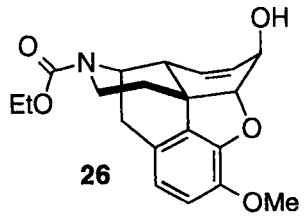
99790-115 neubertd

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: auto_14Nov2001
File: CARBON

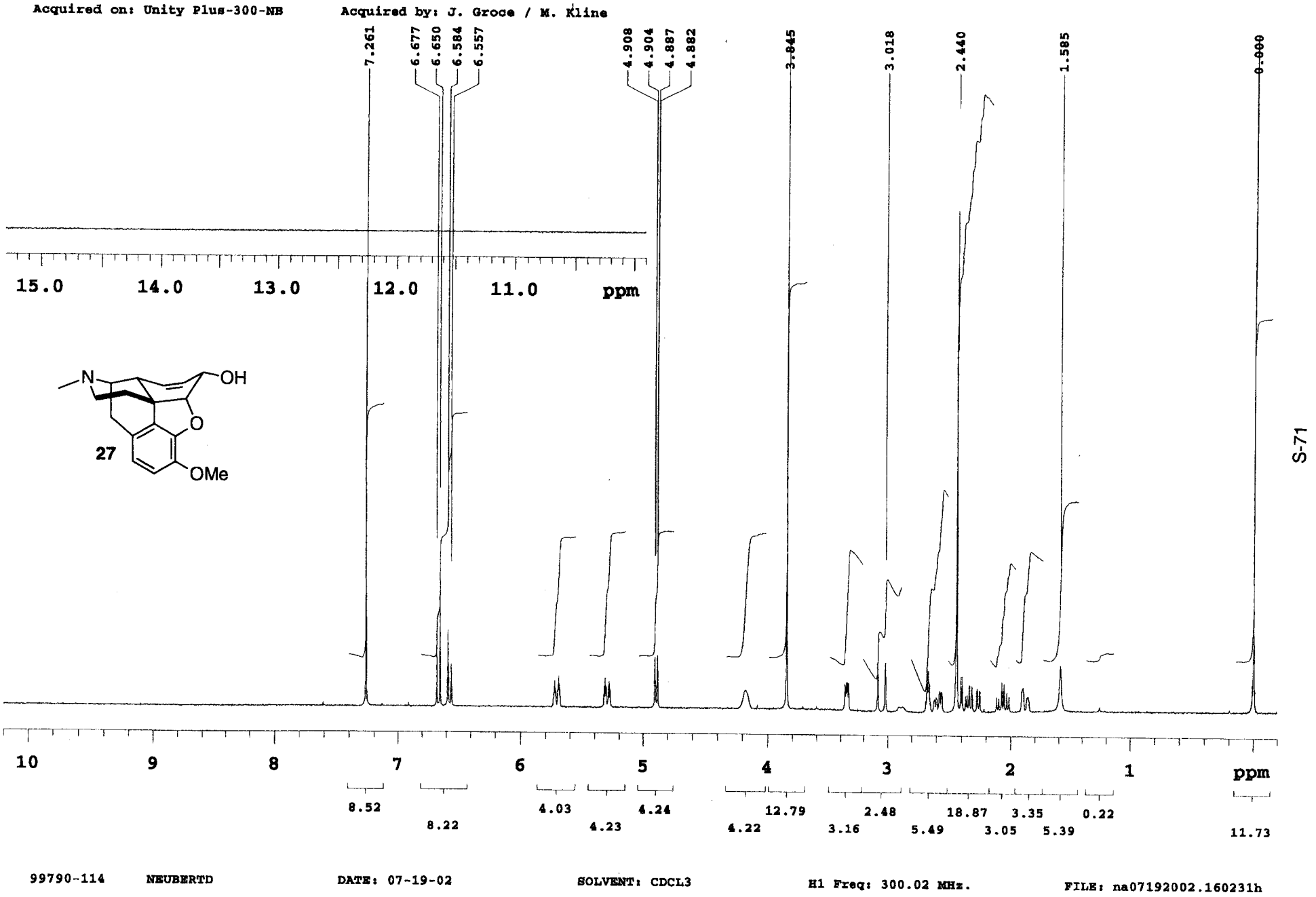
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "chemdsc2"

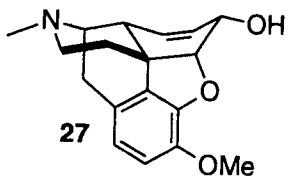
Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 1.199 sec
Width 25133.5 Hz
25792 repetitions
OBSERVE C13, 100.4688691 MHz
DECOUPLE H1, 399.5598156 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 18 hr, 24 min, 6 sec



26


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.261
6.677
6.650
6.584
6.557
4.908
4.904
4.887
4.882
3.845
3.018
2.440
1.585
0.000
15.0
14.0
13.0
12.0
11.0
ppm
N
OH
O
27
OMe
10
9
8
7
6
5
4
3
2
1
ppm
8.52
8.22
4.03
4.23
4.24
4.22
12.79
3.16
2.48
5.49
18.87
3.05
3.35
5.39
0.22
11.73
99790-114
NEUBERTD
DATE: 07-19-02
SOLVENT: CDCL3
H1 Freq: 300.02 MHz.
FILE: na07192002.160231h

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline



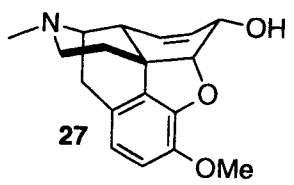
27

S-72

99790-114 NEUBERTD DATE: 07-21-02 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb07212002.185623c

Acquired on: Unity Plus-300-NB Acquired by: J. Groce / M. Kline

CH3 carbons



27

CH2 carbons

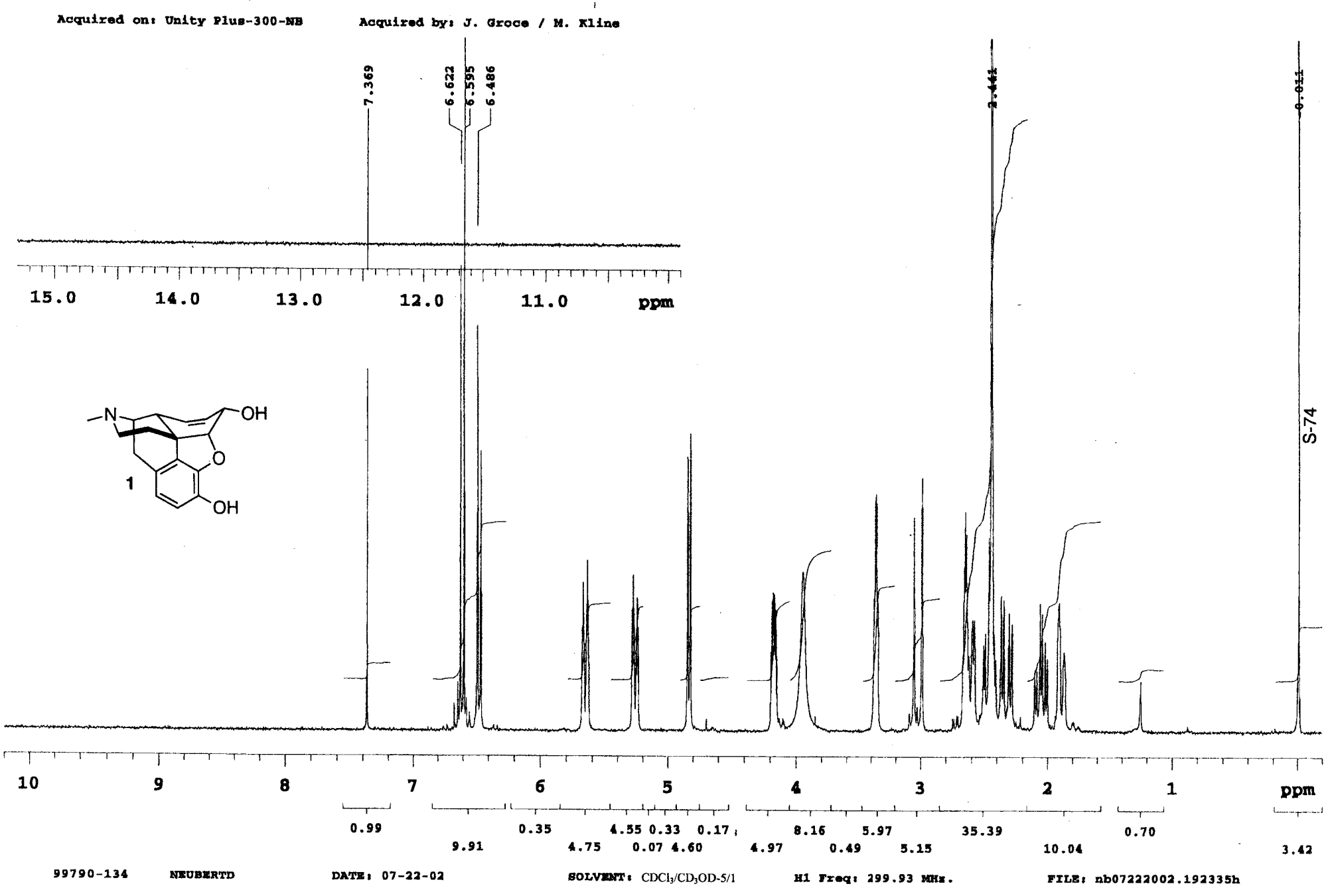
CH carbons

all protonated carbons

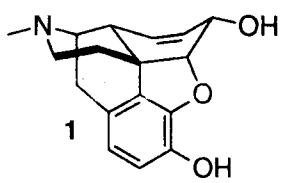
220 200 180 160 140 120 100 80 60 40 20 ppm

S-73

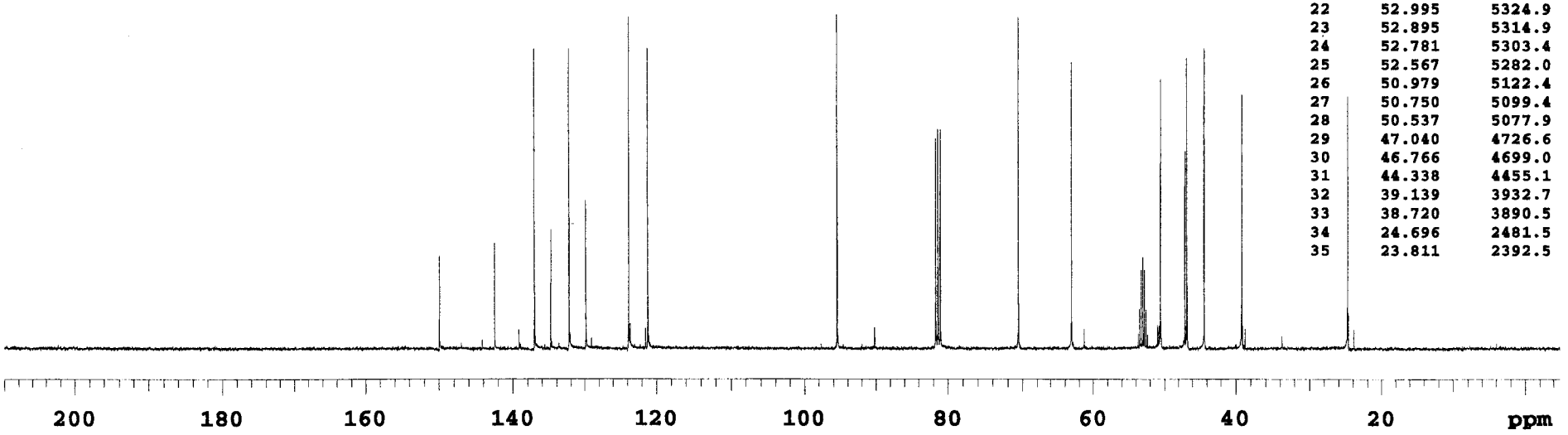
99790-114 NEUBERTD DATE: 07-21-02 SOLVENT: CDCL3 C13 Freq: 75.43 MHz. FILE: nb07212002.194708c


Acquired on: Unity Plus-300-NB
Acquired by: J. Groce / M. Kline
7.369
6.622
6.595
6.486
2.441
0.011
15.0
14.0
13.0
12.0
11.0
ppm
N
OH
O
1
OH
S-74
10
9
8
7
6
5
4
3
2
1
ppm
0.99
9.91
0.35
4.75
4.55
0.07
0.33
4.60
0.17
4.97
8.16
0.49
5.97
5.15
35.39
10.04
0.70
3.42
99790-134
NEUBERTD
DATE: 07-22-02
SOLVENT: CDCl3/CD3OD-5/1
H1 Freq: 299.93 MHz.
FILE: nb07222002.192335h

Acquired on: Unity Inova-400-ND Acquired by: vnmr1



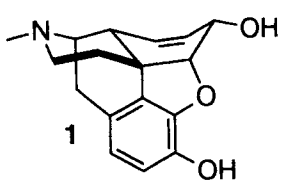
index	freq(ppm)	freq(Hz)
1	149.913	15063.2
2	142.447	14313.1
3	139.134	13980.2
4	137.027	13768.5
5	134.744	13539.1
6	132.202	13283.7
7	129.805	13042.8
8	123.790	12438.4
9	123.553	12414.6
10	121.446	12202.9
11	121.133	12171.5
12	95.454	9591.2
13	90.133	9056.5
14	81.652	8204.4
15	81.331	8172.1
16	81.011	8139.9
17	70.537	7087.6
18	63.041	6334.3
19	61.270	6156.4
20	53.422	5367.9
21	53.208	5346.4
22	52.995	5324.9
23	52.895	5314.9
24	52.781	5303.4
25	52.567	5282.0
26	50.979	5122.4
27	50.750	5099.4
28	50.537	5077.9
29	47.040	4726.6
30	46.766	4699.0
31	44.338	4455.1
32	39.139	3932.7
33	38.720	3890.5
34	24.696	2481.5
35	23.811	2392.5



99790-134 NEUBERTD DATE: 07-23-02 SOLVENT: $CDCl_3/CD_3OD$-5/1 C13 Freq: 100.48 MHz. FILE: nd07232002.112046c

Acquired on: Unity Inova-400-ND Acquired by: vnmr1

CH3 carbons



1

CH2 carbons

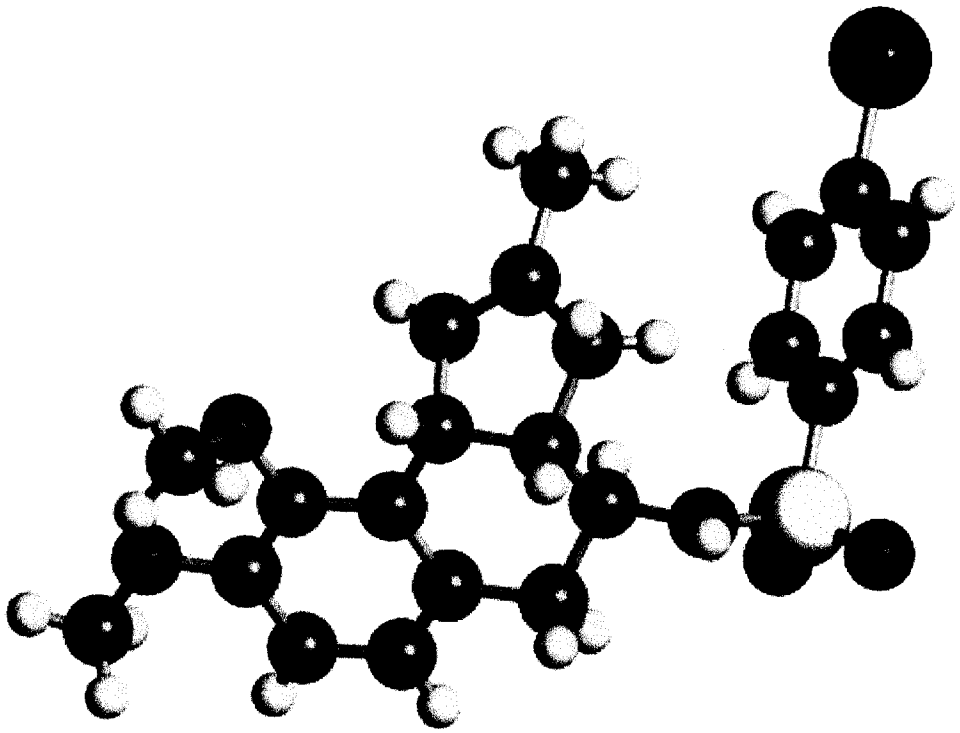
CH carbons

all protonated carbons

140 120 100 80 60 40 20 ppm

99790-134 NEUBERTD DATE: 07-23-02 SOLVENT: $CDCl_3/CD_3OD$-5/1 C13 Freq: 100.48 MHz. FILE: nd07232002.140824c

Crystal structure for ***i***.



i

Table 1. Crystal data and structure refinement for *i*.

Identification code	*i*	
Empirical formula	C26 H34 Br N O5 S	
Formula weight	552.51	
Temperature	219(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.6075(5) Å	α= 90°.
	b = 12.7948(9) Å	β= 104.8680(10)°.
	c = 13.7654(9) Å	γ= 90°.
Volume	1295.02(15) Å^3	
Z	2	
Density (calculated)	1.417 Mg/m^3	
Absorption coefficient	1.704 mm^{-1}	
F(000)	576	
Crystal size	0.40 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.80 to 25.99°.	
Index ranges	-9<=h<=8, -15<=k<=15, -16<=l<=15	
Reflections collected	8253	
Independent reflections	4955 [R(int) = 0.0203]	
Completeness to theta = 25.99°	98.9 %	
Absorption correction	None	
Max. and min. transmission	0.8481 and 0.5489	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4955 / 1 / 307	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0898	
R indices (all data)	R1 = 0.0431, wR2 = 0.0917	
Absolute structure parameter	0.033(8)	
Largest diff. peak and hole	0.439 and -0.385 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for tab22. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7582(1)	1970(1)	3369(1)	59(1)
S(1)	6072(1)	6186(1)	787(1)	34(1)
O(1)	419(3)	8482(2)	4241(2)	40(1)
O(2)	1621(4)	10409(2)	4768(2)	49(1)
O(3)	5873(3)	5920(2)	-246(2)	45(1)
O(4)	7431(3)	6917(2)	1277(2)	45(1)
O(5)	1001(4)	6383(3)	-817(2)	71(1)
N(1)	4135(3)	6604(2)	866(2)	33(1)
C(1)	3848(3)	7091(3)	1781(2)	32(1)
C(2)	3936(4)	8269(3)	1714(3)	37(1)
C(3)	3462(4)	8812(3)	2580(2)	33(1)
C(4)	4095(4)	9805(3)	2863(3)	36(1)
C(5)	3562(4)	10364(3)	3595(3)	40(1)
C(6)	2310(4)	9924(3)	4057(3)	37(1)
C(7)	1672(4)	8918(3)	3788(2)	34(1)
C(8)	2248(4)	8344(3)	3074(3)	32(1)
C(9)	1564(4)	7246(3)	2836(2)	32(1)
C(10)	2261(4)	6456(3)	3661(3)	36(1)
C(11)	2517(4)	5524(3)	3295(3)	36(1)
C(12)	2062(4)	5554(3)	2174(3)	35(1)
C(13)	1994(3)	6724(2)	1913(2)	32(1)
C(14)	3133(6)	4547(3)	3870(3)	52(1)
C(15)	-1397(5)	8853(3)	3832(3)	54(1)
C(16)	2228(6)	11436(3)	5042(3)	57(1)
C(17)	5861(4)	4083(3)	1055(3)	39(1)
C(18)	6182(4)	3159(3)	1616(3)	41(1)
C(19)	7118(4)	3223(3)	2607(3)	38(1)
C(20)	7760(4)	4149(3)	3060(3)	39(1)
C(21)	7467(4)	5054(3)	2500(3)	36(1)
C(22)	6512(4)	5023(3)	1498(2)	32(1)
C(23)	-1290(13)	7593(7)	-1648(11)	194(6)

C(24)	-381(7)	7164(10)	-956(6)	175(6)
C(25)	427(19)	5401(8)	-1142(8)	216(7)
C(26)	1264(9)	4583(6)	-892(7)	140(3)

Table 3. Bond lengths [Å] and angles [°] for tab22.

Br(1)-C(19)	1.899(3)
S(1)-O(4)	1.429(3)
S(1)-O(3)	1.432(2)
S(1)-N(1)	1.598(2)
S(1)-C(22)	1.764(4)
O(1)-C(7)	1.384(4)
O(1)-C(15)	1.432(4)
O(2)-C(6)	1.372(4)
O(2)-C(16)	1.412(5)
O(5)-C(25)	1.367(9)
O(5)-C(24)	1.428(9)
N(1)-C(1)	1.471(4)
C(1)-C(2)	1.513(5)
C(1)-C(13)	1.540(3)
C(2)-C(3)	1.501(5)
C(3)-C(4)	1.378(5)
C(3)-C(8)	1.414(4)
C(4)-C(5)	1.380(5)
C(5)-C(6)	1.393(5)
C(6)-C(7)	1.391(5)
C(7)-C(8)	1.385(5)
C(8)-C(9)	1.504(5)
C(9)-C(10)	1.512(5)
C(9)-C(13)	1.542(4)
C(10)-C(11)	1.328(5)
C(11)-C(14)	1.490(6)
C(11)-C(12)	1.493(5)
C(12)-C(13)	1.537(5)

C(17)-C(22)	1.383(5)
C(17)-C(18)	1.399(5)
C(18)-C(19)	1.370(5)
C(19)-C(20)	1.368(5)
C(20)-C(21)	1.378(5)
C(21)-C(22)	1.385(5)
C(23)-C(24)	1.162(12)
C(25)-C(26)	1.228(11)

O(4)-S(1)-O(3)	120.20(14)
O(4)-S(1)-N(1)	108.46(15)
O(3)-S(1)-N(1)	106.44(14)
O(4)-S(1)-C(22)	106.20(16)
O(3)-S(1)-C(22)	107.91(15)
N(1)-S(1)-C(22)	106.98(13)
C(7)-O(1)-C(15)	113.3(2)
C(6)-O(2)-C(16)	116.9(3)
C(25)-O(5)-C(24)	115.9(8)
C(1)-N(1)-S(1)	122.88(19)
N(1)-C(1)-C(2)	110.5(3)
N(1)-C(1)-C(13)	108.3(2)
C(2)-C(1)-C(13)	111.5(2)
C(3)-C(2)-C(1)	112.9(3)
C(4)-C(3)-C(8)	118.6(3)
C(4)-C(3)-C(2)	120.9(3)
C(8)-C(3)-C(2)	120.4(3)
C(3)-C(4)-C(5)	122.5(3)
C(4)-C(5)-C(6)	119.2(3)
O(2)-C(6)-C(7)	116.0(3)
O(2)-C(6)-C(5)	125.0(3)
C(7)-C(6)-C(5)	119.0(3)
O(1)-C(7)-C(8)	119.1(3)
O(1)-C(7)-C(6)	119.1(3)
C(8)-C(7)-C(6)	121.9(3)
C(7)-C(8)-C(3)	118.8(3)
C(7)-C(8)-C(9)	119.7(3)

C(3)-C(8)-C(9)	121.5(3)
C(8)-C(9)-C(10)	115.2(3)
C(8)-C(9)-C(13)	116.7(2)
C(10)-C(9)-C(13)	102.8(3)
C(11)-C(10)-C(9)	111.9(3)
C(10)-C(11)-C(14)	127.5(3)
C(10)-C(11)-C(12)	110.6(3)
C(14)-C(11)-C(12)	121.9(3)
C(11)-C(12)-C(13)	104.6(3)
C(12)-C(13)-C(1)	110.3(3)
C(12)-C(13)-C(9)	103.4(2)
C(1)-C(13)-C(9)	111.0(2)
C(22)-C(17)-C(18)	120.0(3)
C(19)-C(18)-C(17)	118.1(3)
C(20)-C(19)-C(18)	122.6(3)
C(20)-C(19)-Br(1)	119.0(3)
C(18)-C(19)-Br(1)	118.3(3)
C(19)-C(20)-C(21)	119.0(3)
C(20)-C(21)-C(22)	120.1(3)
C(17)-C(22)-C(21)	120.1(3)
C(17)-C(22)-S(1)	119.6(3)
C(21)-C(22)-S(1)	120.3(3)
C(23)-C(24)-O(5)	134.7(10)
C(26)-C(25)-O(5)	126.3(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for tab22. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	76(1)	46(1)	53(1)	12(1)	11(1)	-7(1)
S(1)	30(1)	39(1)	35(1)	2(1)	13(1)	1(1)
O(1)	50(1)	35(1)	39(1)	7(1)	21(1)	6(1)
O(2)	76(2)	33(1)	40(1)	-1(1)	21(1)	5(1)

O(3)	48(1)	58(2)	36(1)	6(1)	21(1)	7(1)
O(4)	35(1)	44(1)	56(1)	6(2)	11(1)	-6(1)
O(5)	63(2)	52(2)	77(2)	-14(2)	-21(1)	5(2)
N(1)	26(1)	44(2)	27(1)	-6(1)	4(1)	1(1)
C(1)	32(1)	38(2)	26(1)	-1(2)	8(1)	2(1)
C(2)	37(1)	41(2)	37(2)	2(2)	12(1)	-5(2)
C(3)	29(1)	37(2)	33(2)	1(1)	5(1)	2(1)
C(4)	35(2)	36(2)	40(2)	3(2)	11(1)	-3(1)
C(5)	46(2)	33(2)	39(2)	-2(2)	6(2)	-4(2)
C(6)	45(2)	31(2)	33(2)	4(2)	6(2)	12(2)
C(7)	36(1)	34(2)	32(2)	5(1)	5(1)	6(1)
C(8)	31(1)	34(2)	29(2)	1(2)	3(1)	6(1)
C(9)	30(1)	38(2)	30(2)	-1(1)	9(1)	0(1)
C(10)	35(1)	40(2)	33(2)	2(2)	10(1)	-7(1)
C(11)	36(2)	34(2)	38(2)	1(2)	11(2)	-3(1)
C(12)	38(2)	32(2)	37(2)	-5(2)	13(1)	-6(1)
C(13)	26(1)	40(2)	29(2)	-5(1)	7(1)	-3(1)
C(14)	65(2)	43(2)	51(2)	8(2)	20(2)	4(2)
C(15)	47(2)	51(2)	75(3)	16(2)	34(2)	13(2)
C(16)	79(2)	42(2)	49(2)	-9(2)	16(2)	4(2)
C(17)	36(2)	48(2)	31(2)	-9(2)	4(1)	0(2)
C(18)	42(2)	39(2)	41(2)	-8(2)	8(2)	-3(2)
C(19)	40(2)	32(2)	41(2)	4(2)	11(2)	0(2)
C(20)	39(2)	44(2)	33(2)	1(2)	4(1)	-3(2)
C(21)	34(1)	37(2)	35(2)	-6(2)	7(1)	-4(1)
C(22)	26(1)	38(2)	34(2)	-2(2)	13(1)	3(1)
C(23)	129(6)	112(7)	380(19)	101(9)	135(10)	41(5)
C(24)	45(3)	323(15)	159(6)	155(9)	30(3)	46(5)
C(25)	297(14)	80(6)	184(10)	-15(6)	-97(10)	-57(9)
C(26)	111(4)	74(5)	178(8)	-39(5)	-67(5)	29(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for tab22.

	x	y	z	U(eq)
H(1B)	3210	6542	345	40
H(1A)	4815	6851	2366	38
H(2A)	5168	8473	1694	45
H(2B)	3097	8500	1086	45
H(4B)	4921	10112	2544	44
H(5A)	4038	11034	3781	48
H(9A)	224	7267	2711	39
H(10A)	2487	6606	4350	43
H(12A)	884	5221	1883	42
H(12B)	2997	5197	1922	42
H(13A)	1016	6868	1298	38
H(14A)	3334	4684	4584	78
H(14B)	4258	4310	3735	78
H(14C)	2209	4012	3667	78
H(15A)	-2209	8520	4179	82
H(15B)	-1780	8685	3122	82
H(15C)	-1431	9604	3920	82
H(16A)	1644	11699	5542	85
H(16B)	1922	11883	4453	85
H(16C)	3537	11433	5318	85
H(17A)	5202	4064	376	47
H(18A)	5769	2512	1321	49
H(20A)	8392	4166	3743	47
H(21A)	7917	5694	2798	43
H(23A)	-1976	8140	-1422	291
H(23B)	-2124	7098	-2060	291
H(23C)	-530	7900	-2040	291
H(24A)	-1260	6867	-622	210
H(24B)	211	7736	-519	210
H(25A)	-748	5309	-984	259

H(25B)	165	5426	-1877	259
H(26A)	472	3994	-1136	210
H(26B)	1677	4551	-165	210
H(26C)	2305	4558	-1176	210