

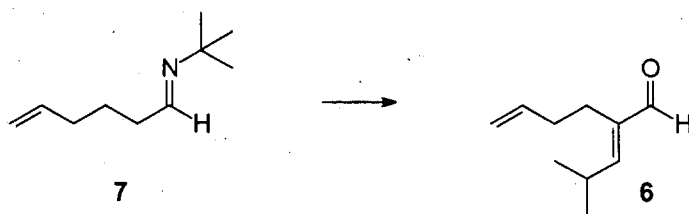
### Experimental

General:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on either a General Electric QE-300 spectrometer operating at either 300 MHz ( $^1\text{H}$ ) or 75 MHz ( $^{13}\text{C}$ ) or on a Varian Unity Inova 400 WB operating at either 400 MHz ( $^1\text{H}$ ) or 101 MHz ( $^{13}\text{C}$ ). Chemical shifts are reported in  $\delta$  units and are referenced to the solvent, i.e., 7.26/77.0 for  $\text{CDCl}_3$ , 7.15/128.0 for benzene- $d_6$ , 3.58/67.4 for THF- $d_8$  and 5.32/53.8 for methylene chloride- $d_2$ . Multiplicities are indicated as: br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet) or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). Infrared spectra were recorded on a Perkin-Elmer IR 1430 spectrometer. Electron impact mass spectra were performed on a VG-70SE mass spectrometer. Thin-layer chromatography (TLC) was performed on Sigma-Aldrich TLC plates, 250  $\mu\text{m}$ , particle size 5 to 17  $\mu\text{m}$ , pore size 60  $\text{\AA}$ . Flash column chromatography was performed on ICN silica gel, 32-63, 60  $\text{\AA}$ . Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Triethylamine, diisopropylamine, morpholine, and benzylamine were distilled from calcium hydride and stored over potassium hydroxide. 1,4-Dioxane was distilled from calcium hydride and stored over activated 4 $\text{\AA}$  molecular sieves. Methylene chloride and trimethylsilyl chloride were distilled from calcium hydride immediately before use. Propionic acid and isobutyraldehyde were distilled before use. Other reagents were used as received. All moisture sensitive reactions were performed under a static nitrogen or argon atmosphere in oven-dried or flame-dried glassware.



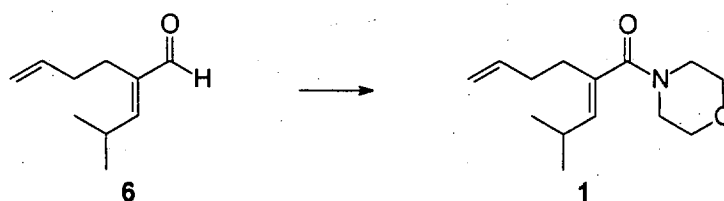
To 5-hexenal **8** (1.371 g, 13.97 mmol) at  $0^\circ\text{C}$  was added *tert*-butylamine (1.60 mL, 1.11 g, 15.2 mmol). The reaction mixture was warmed to room temperature, stirred for 21 h, and potassium hydroxide pellets were added. Purification by distillation on a Kugelrohr (oven temperature  $125^\circ\text{C}$ ) under reduced pressure (water aspirator, ca. 25

mmHg) gave the imine **7** (2.011 g, 94%) as a colorless liquid: IR (neat) 2980, 2880, 1675, 1650, 1460, 1370, 1220, 995, 915  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.40 (t,  $J = 4.4$  Hz, 1H), 5.72 (ddt,  $J = 16.9, 10.4, 6.6$  Hz, 1H), 5.02-4.93 (m, 2H), 2.11 (td,  $J = 7.4, 4.4$  Hz, 2H), 1.96 (q br,  $J = 7.2$  Hz, 2H), 1.52 (quint,  $J = 7.4$  Hz, 2H), 1.14 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  156.7, 138.7, 114.9, 56.5, 35.9, 33.7, 29.9, 25.6.



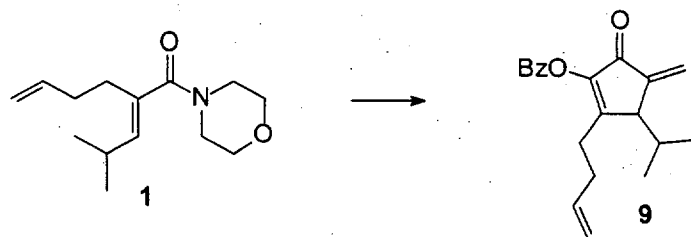
To a solution of diisopropylamine (2.90 mL, 2.09 g, 20.7 mmol) in THF (55 mL) at  $-78^\circ\text{C}$  was added *n*-BuLi (7.50 mL, 20.9 mmol, 2.78 M in hexanes). After 30 min, a solution of the imine **7** (2.899 g, 18.91 mmol) in THF (20 mL) was added via cannula. The solution was warmed from  $-78^\circ\text{C}$  to  $-20^\circ\text{C}$  over 3 h, cooled to  $-78^\circ\text{C}$ , and trimethylsilyl chloride (2.70 mL, 2.31 g, 21.5 mmol) was added. The reaction mixture was warmed from  $-78^\circ\text{C}$  to  $10^\circ\text{C}$  over 14 h, concentrated, and diluted with petroleum ether, saturated  $\text{NaHCO}_3$ , and water. The aqueous phase was extracted with petroleum ether (3 x) and the combined organic extracts were washed with brine (1 x), dried over  $\text{K}_2\text{CO}_3$ , and concentrated to give the crude  $\alpha$ -TMS imine. The crude  $\alpha$ -TMS imine was dissolved in THF (20 mL), cooled to  $-78^\circ\text{C}$ , and added via cannula to a solution of LDA generated from diisopropylamine (2.90 mL, 2.09 g, 20.7 mmol) and *n*-BuLi (7.50 mL, 20.9 mmol, 2.78 M in hexanes) in THF (60 mL) at  $-78^\circ\text{C}$ . The solution was warmed from  $-78^\circ\text{C}$  to  $0^\circ\text{C}$  over 3 h, cooled to  $-78^\circ\text{C}$ , and isobutyraldehyde (1.90 mL, 1.51 g, 20.9 mmol) was added. The reaction mixture was warmed from  $-78^\circ\text{C}$  to  $10^\circ\text{C}$  over 5 h, concentrated, and diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with water (1 x), brine (1 x), dried over  $\text{MgSO}_4$ , and concentrated to give the crude  $\alpha,\beta$ -unsaturated imine. The crude  $\alpha,\beta$ -unsaturated imine was dissolved in THF (15 mL) and water (15 mL) and oxalic acid dihydrate (5.388 g, 42.74 mmol) were added. The reaction mixture was stirred at room

temperature for 12 h and diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x) and dried over  $\text{MgSO}_4$ . Purification by flash column chromatography on silica gel (1.25% to 2.5% to 5% EtOAc in hexanes) gave the aldehyde **6** (2.058 g, 71%) as a colorless oil and a single isomer by  $^1\text{H}$  NMR:  $R_f = 0.40$  (5% EtOAc in hexanes); IR (neat) 2980, 2945, 2885, 2830, 1690, 1645, 915  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.33 (s, 1H), 6.25 (d,  $J = 10.3$  Hz, 1H), 5.75 (ddt,  $J = 16.9, 10.3, 6.6$  Hz, 1H), 5.01-4.92 (m, 2H), 2.81 (d sept,  $J = 10.0, 6.6$  Hz, 1H), 2.32 (t,  $J = 7.7$  Hz, 2H), 2.10 (q br,  $J = 7.4$  Hz, 2H), 1.07 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 161.6, 140.4, 137.7, 115.0, 33.1, 28.2, 23.8, 22.1.



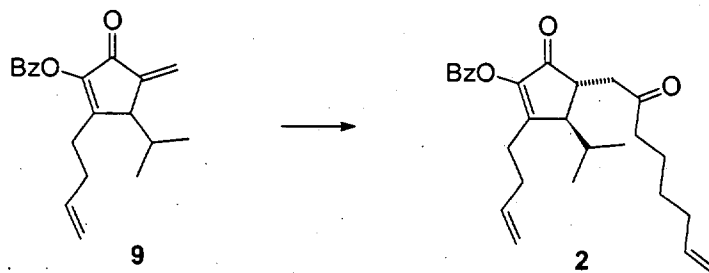
To a solution of the aldehyde **6** (1.061 g, 6.969 mmol) in 2-methyl-2-butene (30.0 mL, 19.9 g, 283 mmol) and *tert*-butyl alcohol (84 mL) at  $0^\circ\text{C}$  was added a solution of  $\text{NaClO}_2$  (4.905 g, 54.23 mmol) and  $\text{KH}_2\text{PO}_4$  (7.418 g, 54.51 mmol) in water (48 mL) at  $0^\circ\text{C}$ . The reaction mixture was warmed to room temperature, stirred for 7 h, and diluted with EtOAc and water. The aqueous phase was extracted with EtOAc (3 x) and the combined organic extracts were washed with brine (1 x), dried over  $\text{MgSO}_4$ , and concentrated to give the crude acid. To a solution of the crude acid and carbon tetrabromide (2.593 g, 7.818 mmol) in  $\text{CH}_2\text{Cl}_2$  (14 mL) was added at  $0^\circ\text{C}$ , triethylamine (1.10 mL, 799 mg, 7.89 mmol), morpholine (690  $\mu\text{L}$ , 689 mg, 7.19 mmol), and a solution of triphenylphosphine (2.189 g, 8.346 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL). After 30 min, the reaction mixture was partially concentrated under a stream of argon to a volume of approximately 15 mL and loaded directly onto a silica gel flash column. Purification by chromatography (10% to 20% to 30% to 50% EtOAc in hexanes) gave the amide **1** (1.449 g, 88%) as a colorless oil:  $R_f = 0.26$  (30% EtOAc in hexanes); IR (neat) 2975, 2940, 2870, 1640, 1430, 1280, 1260, 1120, 1030, 920  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

$\delta$  5.73 (ddt,  $J = 16.9, 10.3, 6.6$  Hz, 1H), 5.23 (d,  $J = 9.5$  Hz, 1H), 5.00-4.89 (m, 2H), 3.62-3.40 (m, 8H), 2.56 (d sept,  $J = 9.8, 6.4$  Hz, 1H), 2.36 (t,  $J = 7.6$  Hz, 2H), 2.08 (q br,  $J = 7.3$  Hz, 2H), 0.93 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 171.5, 139.0, 137.7, 131.6, 114.9, 66.7, 44.9 (br), 32.4, 27.9, 26.9, 22.5; mass spectrum  $m/z$  196 (39), 194 (31), 151 (33), 109 (44), 81 (100), 69 (44), 67 (62); exact mass calcd for  $\text{C}_{14}\text{H}_{23}\text{NO}_2$  237.1729, found 237.1733.

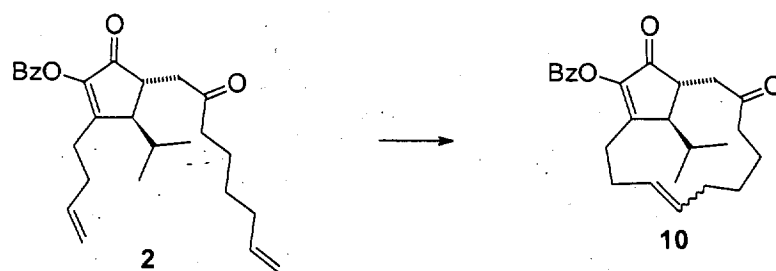


To a solution of methyloxymethyl allenyl ether (170  $\mu\text{L}$ , 157 mg, 1.57 mmol) in THF (4 mL) at  $-78^\circ\text{C}$  was added  $n\text{-BuLi}$  (630  $\mu\text{L}$ , 1.52 mmol, 2.41 M in hexanes). After 30 min, a solution of the amide 1 (302 mg, 1.27 mmol) in THF (9 mL) at  $-78^\circ\text{C}$  was added. After 30 min, the reaction mixture was quenched with AcOH (610  $\mu\text{L}$ , 1.52 mmol, 2.49 M in THF), warmed to room temperature, and diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x), dried over  $\text{MgSO}_4$ , and concentrated to give the crude cyclopentenone. To a solution of the crude cyclopentenone in  $\text{CH}_2\text{Cl}_2$  (10 mL) at  $0^\circ\text{C}$  was added triethylamine (210  $\mu\text{L}$ , 152 mg, 1.51 mmol) and benzoyl chloride (170  $\mu\text{L}$ , 206 mg, 1.46 mmol). After 30 min, the reaction mixture was diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x) and dried over  $\text{MgSO}_4$ . Purification by flash column chromatography on silica gel (2.5% to 5% EtOAc in hexanes) gave the protected cyclopentenone 9 (192 mg, 49%) as a colorless oil:  $R_f = 0.20$  (10% EtOAc in hexanes); IR (neat) 2980, 1750, 1715, 1670, 1635, 1455, 1260, 1180, 1090, 1070, 1025, 710  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.14 (dm,  $J = 7.8$  Hz, 2H), 7.07 (tt,  $J = 7.4, 1.3$  Hz, 1H), 6.97 (tm,  $J = 7.6$  Hz, 2H), 6.18 (s, 1H), 5.58 (m, 1H), 5.01 (s, 1H), 4.95-4.88 (m, 2H), 3.00 (s br, 1H), 2.45 (m, 1H), 2.15-1.95 (m, 3H), 1.78 (sept d,  $J = 6.9, 2.9$  Hz, 1H), 0.84

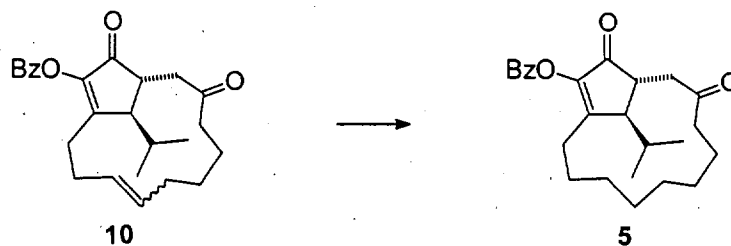
(d,  $J = 6.8$  Hz, 3H), 0.67 (d,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  186.8, 163.4, 158.8, 149.1, 142.0, 137.1, 133.5, 130.5, 129.3, 128.7, 117.1, 115.7, 47.8, 30.8, 29.3, 26.5, 21.6, 16.3; mass spectrum  $m/z$  122 (7), 106 (8), 105 (100), 77 (30), 76 (14); exact mass calcd for  $\text{C}_{20}\text{H}_{22}\text{O}_3$  310.1569, found 310.1593.



To a mixture of the cyclopentenone **9** (150 mg, 0.483 mmol) and 6-heptenal (120 mg, 1.07 mmol) was added 1.0 mL of a solution of 3-benzyl-5-(hydroxyethyl)-4-methylthiazolium chloride (42 mg, 0.16 mmol) and triethylamine (100  $\mu\text{L}$ , 72.6 mg, 0.717 mmol) in 1,4-dioxane (2.9 mL). The reaction mixture was heated to 70°C in a sealed tube. After 18 h, the reaction mixture was diluted with  $\text{Et}_2\text{O}$  and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x) and dried over  $\text{MgSO}_4$ . Purification by flash column chromatography on silica gel (2.5% to 5% to 10% to 20%  $\text{EtOAc}$  in hexanes) gave the *trans*-diene **2** (123 mg, 60%) as a colorless oil:  $R_f = 0.16$  (10%  $\text{EtOAc}$  in hexanes); IR (neat) 2975, 2945, 1750, 1725, 1665, 1265, 1100, 1070, 715  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (dm,  $J = 7.1$  Hz, 2H), 7.62 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 2H), 5.87-5.72 (m, 2H), 5.09-4.92 (m, 4H), 2.80-2.73 (m, 2H), 2.69-2.57 (m, 3H), 2.43 (t,  $J = 7.3$  Hz, 2H), 2.38-2.18 (m, 4H), 2.05 (q br,  $J = 7.2$  Hz, 2H), 1.59 (quint br,  $J = 7.6$  Hz, 2H), 1.43-1.33 (m, 2H), 1.06 (d,  $J = 6.8$  Hz, 3H), 0.85 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  208.0, 200.8, 164.2, 163.3, 145.6, 138.4, 136.8, 133.6, 130.3, 128.6, 128.5, 115.8, 114.6, 49.7, 44.3, 43.0, 40.7, 33.5, 30.6, 28.44, 28.41, 26.7, 23.2, 21.1, 16.3; mass spectrum  $m/z$  190 (20), 106 (15), 105 (100), 77 (45); exact mass calcd for  $\text{C}_{27}\text{H}_{34}\text{O}_4$  422.2457, found 422.2467.

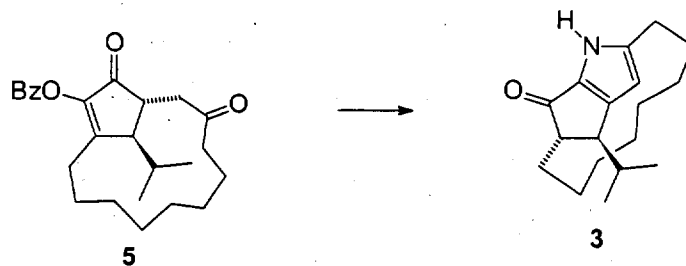


To a solution of Grubbs' catalyst (62 mg, 0.075 mmol) in  $\text{CH}_2\text{Cl}_2$  (460 mL) was added a solution of the *trans*-diene **2** (103 mg, 0.244 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL). The solution was degassed for 15 min, heated to  $40^\circ\text{C}$  for 30 h, partially concentrated, and filtered through silica gel (eluted with 30% EtOAc in hexanes). Purification by flash column chromatography on silica gel (5% to 10% to 20% to 30% EtOAc in hexanes) gave the *E, Z* mixture **10** (87 mg, 90%) as a low melting solid.

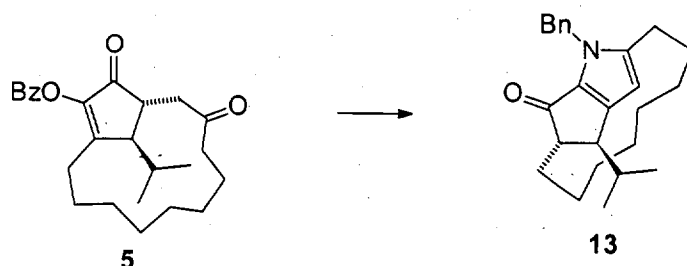


To the *E, Z* mixture **10** (84 mg, 0.21 mmol) was added 10% palladium on carbon (35 mg) and THF (10 mL). The nitrogen atmosphere was replaced by hydrogen from a double balloon, stirred at room temperature for 4 h, filtered through cotton, and concentrated. Purification by flash column chromatography on silica gel (5% to 10% to 20% EtOAc in hexanes) gave the macrocycle **5** (78 mg, 92%) as a white solid: mp  $94\text{--}96^\circ\text{C}$ ;  $R_f = 0.17$  (10% EtOAc in hexanes); IR (neat) 2940, 2880, 1745, 1725, 1660, 1455, 1260, 1215, 1100, 1065, 1025,  $710\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (dm,  $J = 7.4$  Hz, 2H), 7.62 (tm,  $J = 7.4$  Hz, 1H), 7.48 (tm,  $J = 7.8$  Hz, 2H), 3.08 (dd,  $J = 14.9, 6.8$  Hz, 1H), 2.70–2.61 (m, 3H), 2.53 (ddd,  $J = 14.5, 10.9, 3.4$  Hz, 1H), 2.44 (ddd,  $J = 15.5, 7.8, 3.8$  Hz, 1H), 2.37 (ddd,  $J = 15.5, 8.7, 3.8$  Hz, 1H), 2.24 (ddd,  $J = 14.5, 6.4, 3.0$  Hz, 1H), 2.18 (sept d,  $J = 7.0, 3.2$  Hz, 1H), 1.75–1.16 (m, 12H), 1.13 (d,  $J = 7.0$  Hz, 3H), 0.82 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.7, 201.2, 165.5, 163.5, 146.5, 133.7,

130.4, 128.53, 128.51, 48.0, 44.4, 42.7, 41.9, 29.1, 26.3, 26.14, 26.12, 25.5, 25.4, 24.2, 23.1, 21.1, 16.2; mass spectrum  $m/z$  396 ( $M^+$ , 3), 291 (5), 106 (8), 105 (100), 77 (24); exact mass calcd for  $C_{25}H_{32}O_4$  396.2301, found 396.2282.



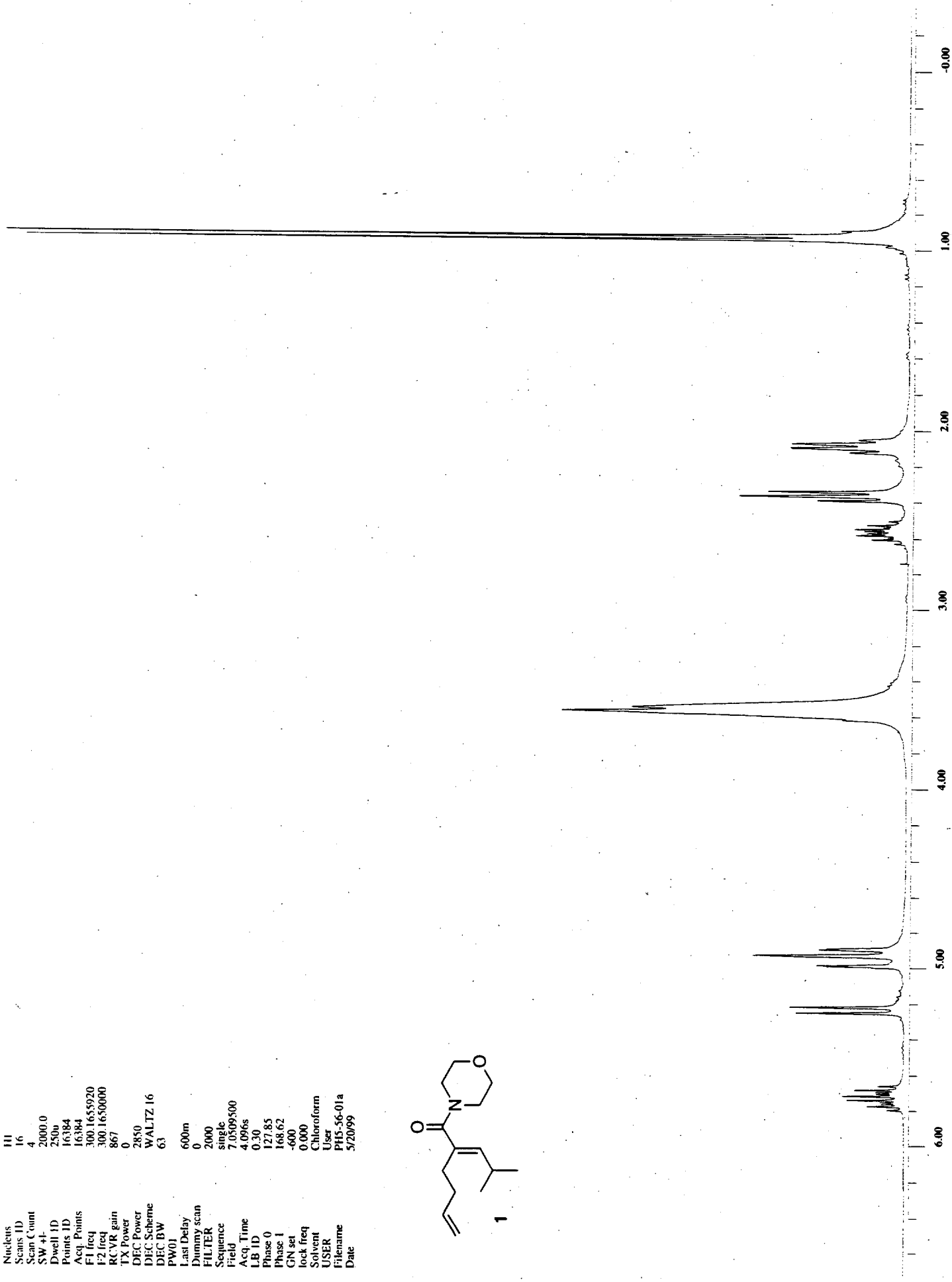
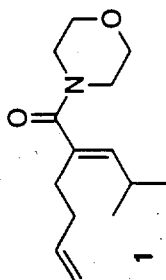
A degassed solution of the diketone **5** (31.7 mg, 0.0799 mmol) and ammonium carbonate (270 mg, 2.81 mmol) in propionic acid (2.2 mL) was heated to 140°C for 10 h. After 10 h, the reaction mixture was diluted with Et<sub>2</sub>O and saturated NaHCO<sub>3</sub>. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x) and dried over MgSO<sub>4</sub>. Purification by flash column chromatography on silica gel (5% to 10% to 20% EtOAc in hexanes) gave the ketopyrrole **3** (11.4 mg, 52%) as a white solid:  $R_f$  = 0.34 (20% EtOAc in hexanes); IR (neat) 3180, 2940, 1675, 1475, 1380, 1340, 1295, 1275, 830, 740, 640  $cm^{-1}$ ; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 11.36 (s br, 1H), 5.99 (d,  $J$  = 1.5 Hz, 1H), 2.86 (dt,  $J$  = 13.7, 4.9 Hz, 1H), 2.74 (t,  $J$  = 4.3 Hz, 1H), 2.65 (ddd,  $J$  = 13.4, 10.8, 5.9 Hz, 1H), 2.63 (d,  $J$  = 6.6 Hz, 1H), 1.90-1.70 (m, 4H), 1.39-0.75 (m, 9H), 1.00 (d,  $J$  = 6.8 Hz, 3H), 0.88 (d,  $J$  = 6.6 Hz, 3H), 0.47-0.35 (m, 2H); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.36 (s br, 1H), 5.97 (d,  $J$  = 1.5 Hz, 1H), 2.86 (dt,  $J$  = 12.7, 4.8 Hz, 1H), 2.79 (t br,  $J$  = 4.2 Hz, 1H), 2.69 (ddd,  $J$  = 13.7, 10.5, 5.6 Hz, 1H), 2.62 (d,  $J$  = 6.6 Hz, 1H), 1.98-1.72 (m, 4H), 1.37-0.76 (m, 9H), 1.00 (d,  $J$  = 6.6 Hz, 3H), 0.88 (d,  $J$  = 6.6 Hz, 3H), 0.47-0.34 (m, 2H); <sup>13</sup>C NMR (75 MHz, THF-*d*<sub>8</sub>) δ 192.5, 154.9, 147.7, 135.6, 107.1, 59.6, 49.1, 34.2, 32.7, 29.3, 29.2, 28.7, 28.5, 28.2, 26.6, 26.0, 21.9, 20.3; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.0, 156.9, 149.9, 133.6, 106.9, 58.8, 48.2, 33.1, 32.0, 28.3, 28.2, 28.1, 27.44, 27.35, 25.6, 24.9, 21.5, 20.0; mass spectrum  $m/z$  273 ( $M^+$ , 14), 258 (15), 205 (39), 145 (11), 115 (11), 105 (15), 91 (24), 81 (10), 79 (17), 78 (100); exact mass calcd for  $C_{18}H_{27}NO$  273.2093, found 273.2086.



A solution of the diketone **5** (29 mg, 0.073 mmol) and benzylamine (500  $\mu$ L, 491 mg, 4.58 mmol) in propionic acid (5 mL) was heated to 200°C for 10 d. After 10 d, the reaction mixture was diluted with Et<sub>2</sub>O, 1 M HCl, and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with saturated NaHCO<sub>3</sub> (2 x), brine (1 x), and dried over MgSO<sub>4</sub>. Purification by flash column chromatography on silica gel (1.25% to 2.5% to 5% to 10% to 20% to 30% to 50% EtOAc in hexanes) gave the *N*-benzylpyrrole **13** (9.1 mg, 34%) as a low melting solid: *R*<sub>f</sub> = 0.36 (10% EtOAc in hexanes); IR (neat) 2920, 2855, 1685, 1670, 1500, 1475, 1460, 1395, 1255, 800, 725, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.31 (tm, *J* = 7.2 Hz, 2H), 7.25 (tm, *J* = 7.2 Hz, 1H), 7.19 (dm, *J* = 7.8 Hz, 2H), 6.00 (s, 1H), 5.67 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 2.71-2.61 (m, 3H), 2.58 (ddd, *J* = 14.4, 7.2, 6.0 Hz, 1H), 1.95 (m, 1H), 1.81-1.67 (m, 3H), 1.50 (m, 1H), 1.24 (m, 1H), 1.15-0.84 (m, 6H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.76-0.67 (m, 2H), 0.57 (m, 1H); <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  193.7, 154.1, 147.0, 138.7, 135.1, 129.0, 127.8, 127.2, 109.4, 59.7, 48.6, 47.9, 33.5, 32.1, 28.4, 28.0, 27.7, 27.4, 25.7, 25.4, 25.3, 21.5, 19.9; mass spectrum *m/z* 363 (M<sup>+</sup>, 19), 321 (13), 320 (21), 106 (13), 92 (9), 91 (100); exact mass calcd for C<sub>25</sub>H<sub>33</sub>NO 363.2562, found 363.2574.



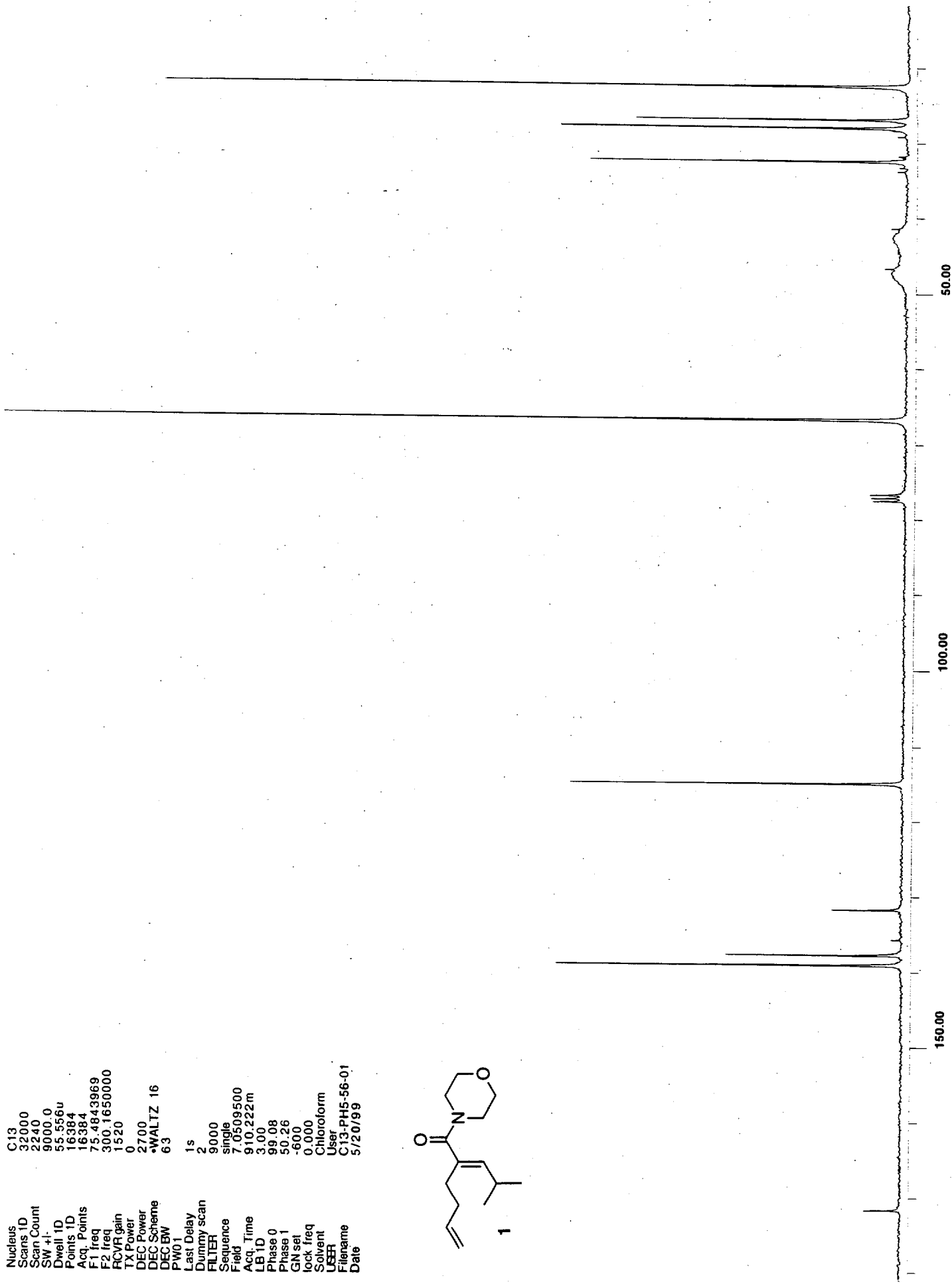
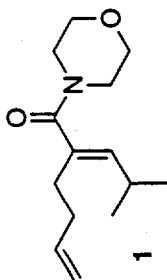
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 RCVR gain 867  
 TX Power 0  
 DEC Power 2850  
 DEC Scheme WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 FILTER 2000  
 Sequence single  
 Field 7.0509500  
 Acq Time 4.096s  
 LB 1D 0.30  
 Phase 0 127.85  
 Phase 1 168.62  
 GN set -600  
 lock freq 0.000  
 Solvent Chloroform  
 USER User  
 Filename PMS-56-01a  
 Date 3/20/99

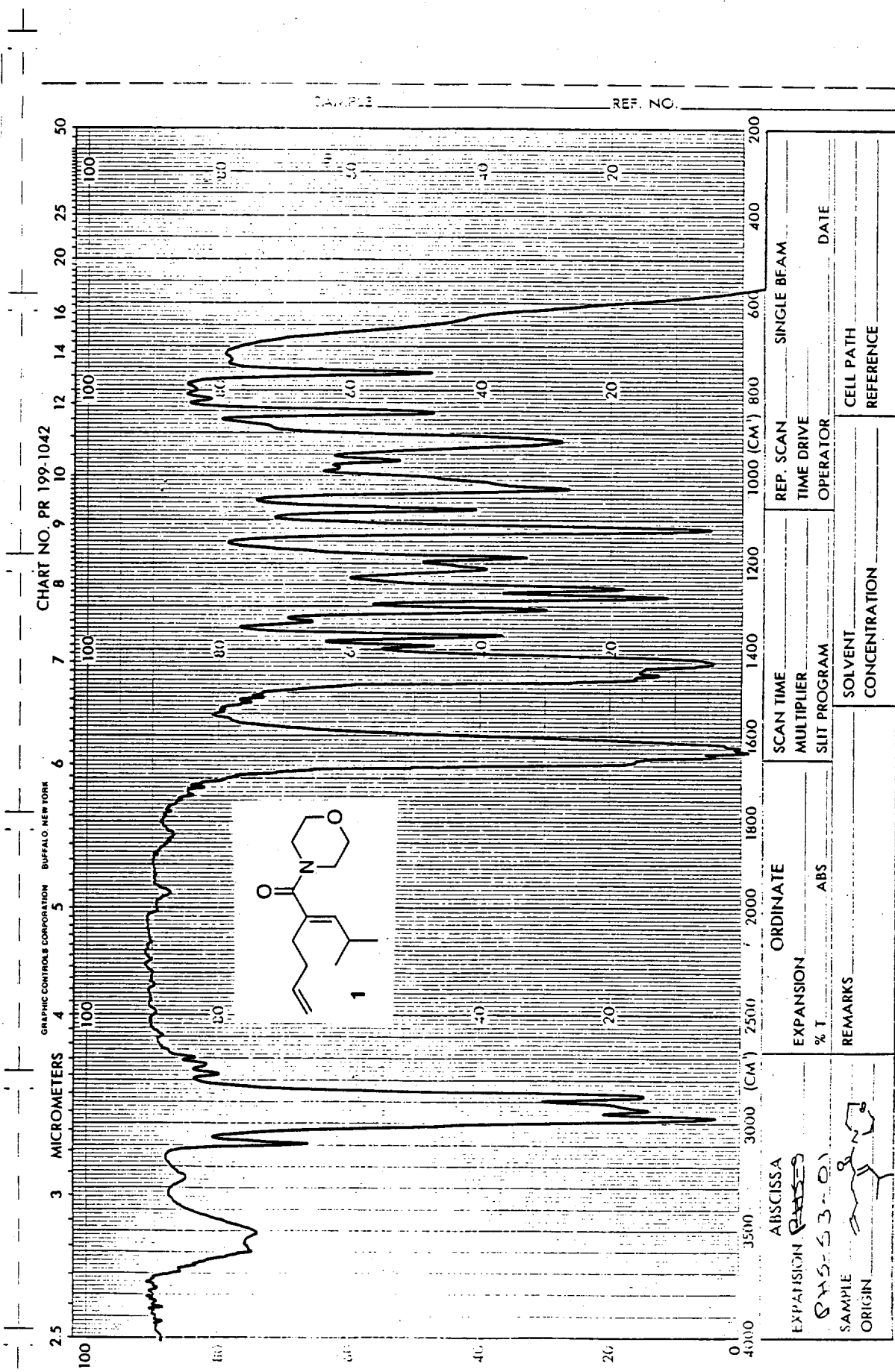


ppm

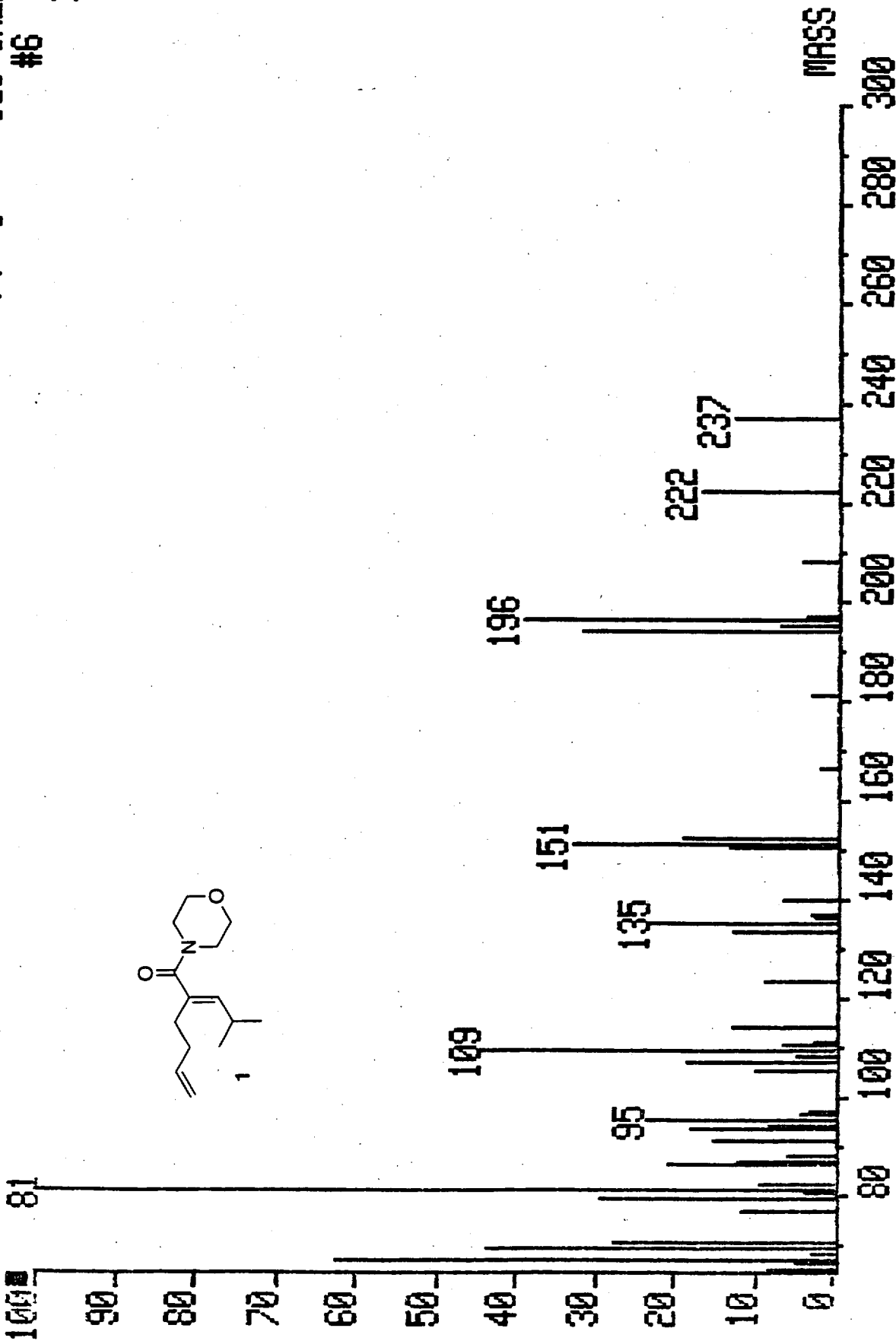
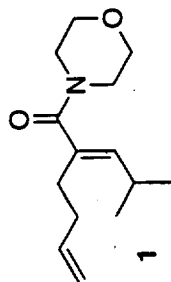
4 2

Nucleus C13  
 Scans ID 32000  
 Scan Count 2240  
 SW +/- 9000.0  
 Dwell ID 55.556u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 75.4843969  
 F2 freq 300.1650000  
 RCV gain 1520  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 1s  
 Dummy scan 2  
 FILTER single  
 Sequence 9000  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB ID 3.00  
 Phase 0 99.08  
 Phase 1 50.26  
 GN set -600  
 lock freq 0.000  
 Solvent Chloroform  
 User USER  
 Filename C13-PH5-56-01  
 Date 5/20/99



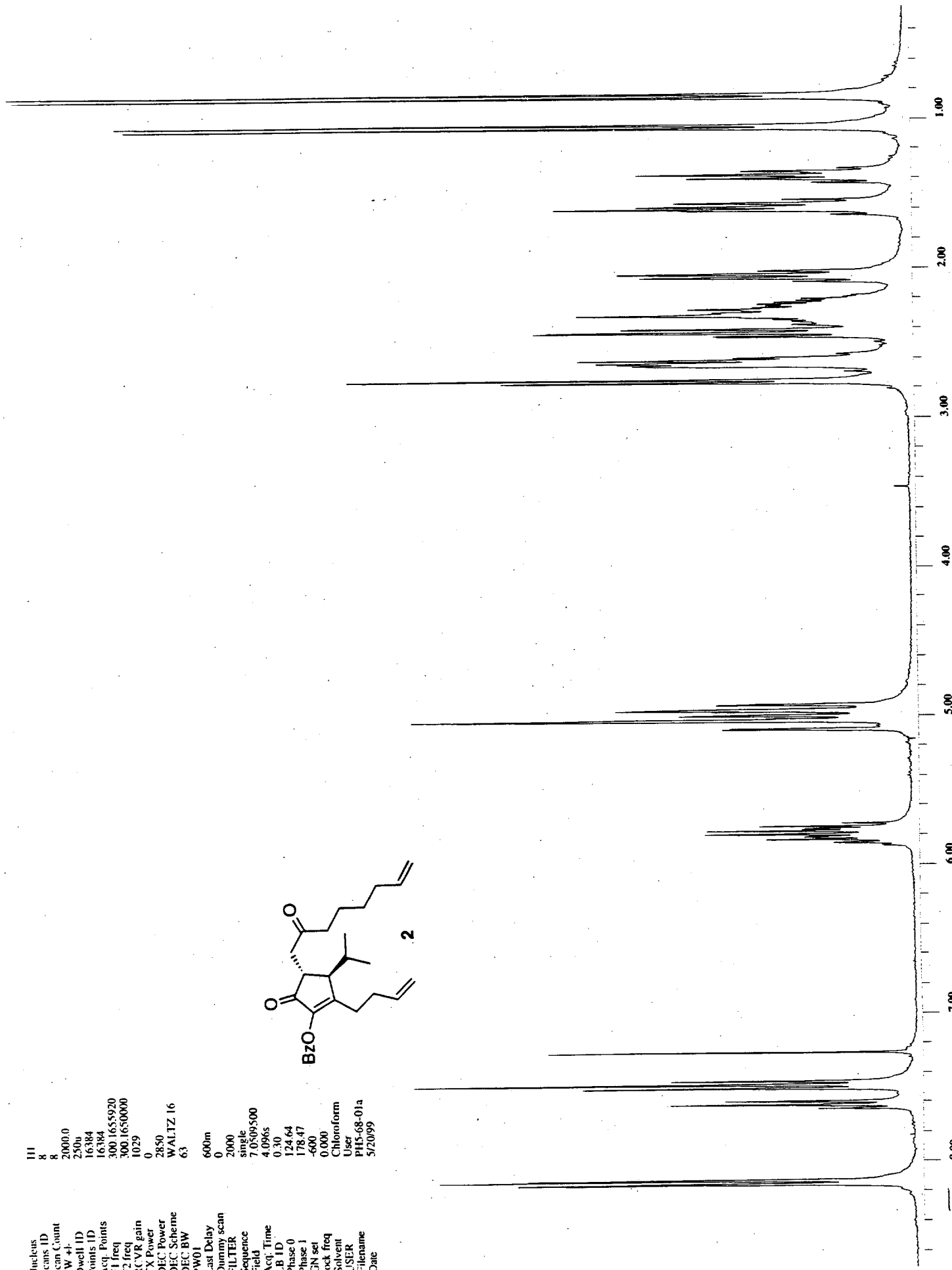
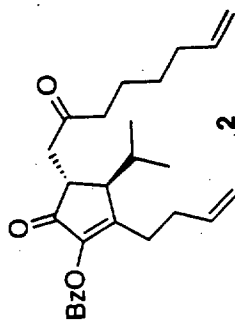


M1051/1#6 X1 Bgd=1 17-MAR-99 10:12+0:01:47 70-SE EI+  
BpM=91 I=276mV Hm=238 TIC=13607000 Agnt: UNCHEM Sys: EI700  
PAUL PHS-53-01 C14H23NO2 237 PT= 0° Cal: CAL700  
#6 1.0  
1814000



2

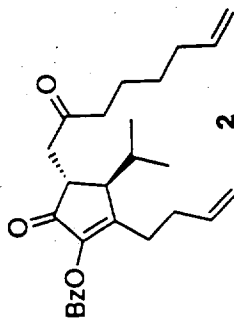
Nucleus 1H  
 Scans 8  
 Count 2000.0  
 SW +/- 250u  
 Dwell 16384  
 Points 16384  
 Acq. Points 3001655920  
 F1 freq 3001650000  
 F2 freq 1029  
 RCVR gain 0  
 TX Power 2850  
 DEC Power WALTZ 16  
 DEC Scheme 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 2000  
 FILTER single  
 Sequence 7.0509500  
 Field 4.096s  
 Acq. Time 0.30  
 LB ID 124.64  
 Phase 0 178.47  
 GN set -600  
 Lock freq 0.000  
 Solvent Chloroform  
 USER PHS-68-01a  
 Filename 572099  
 Date



13

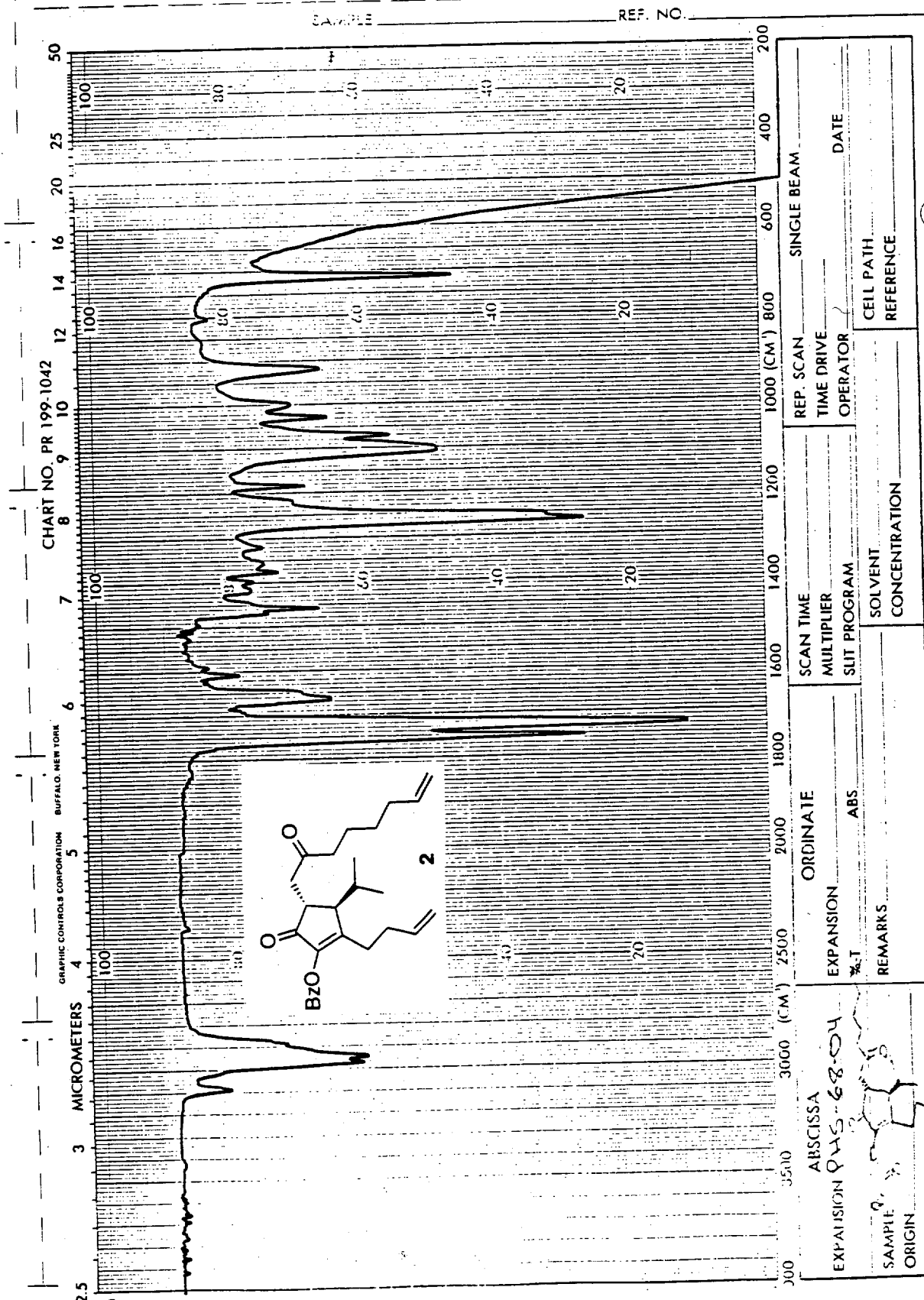
4 ppm

Nucleus C13  
 Scans ID 10000  
 Scan Count 6312  
 SW +/- 9000.0  
 Dwell ID 55.556u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 75.4843969  
 F2 freq 300.1650000  
 RCVR gain 1584  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme -WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 1s  
 Dummy scan 2  
 FILTER 9000  
 Sequence Single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB ID 0.50  
 Phase 0 116.63  
 Phase 1 35.04  
 GN sel -600  
 lock freq 0.000  
 Solvent Chloroform  
 USER User  
 Filename CT3-PH5-68-04  
 Date 3/7/99



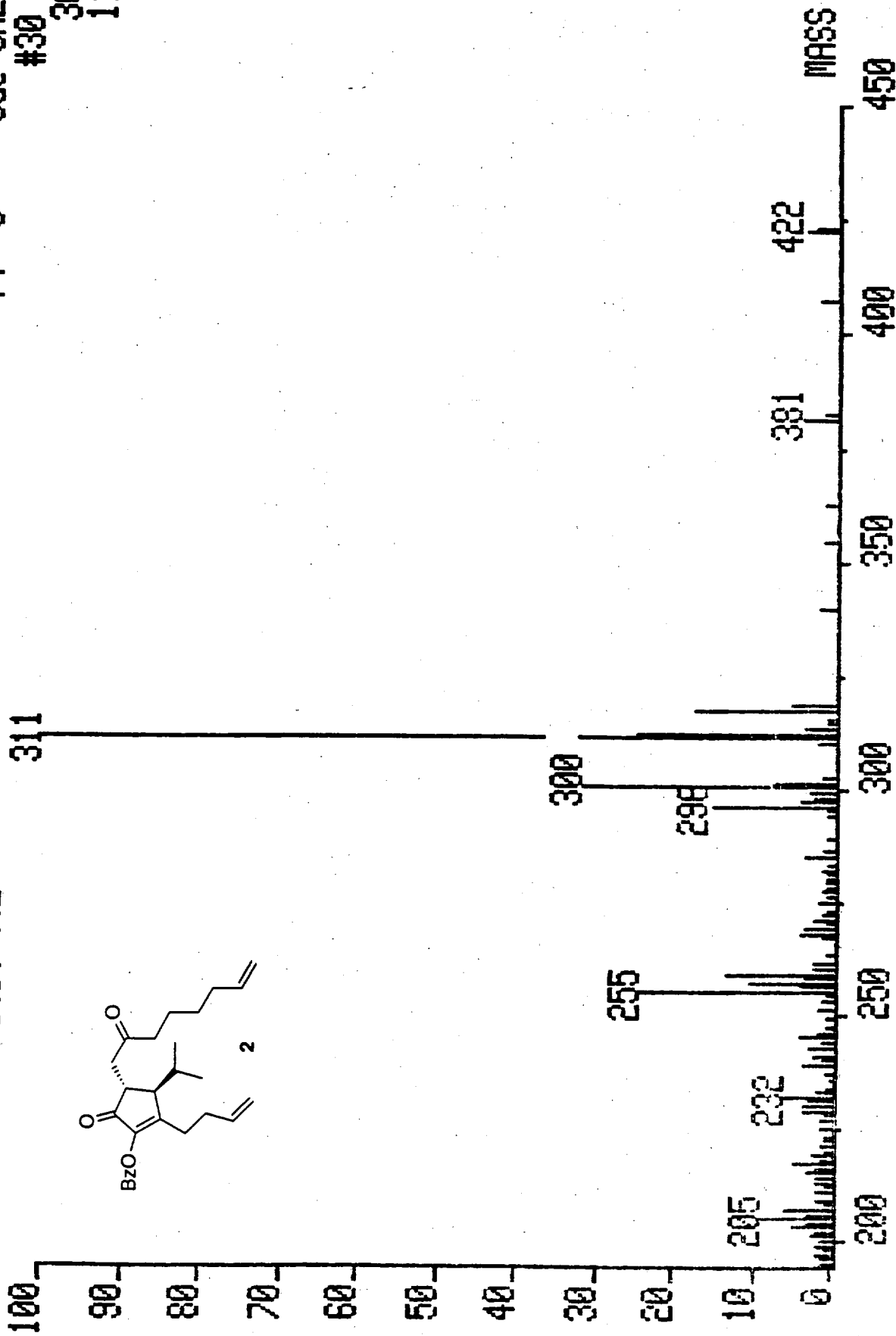
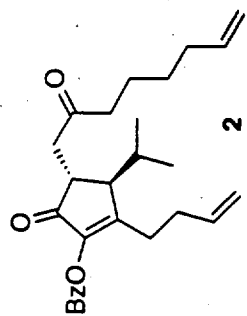
Ppm

14



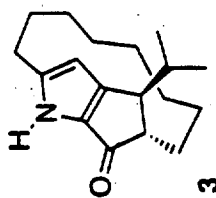
ABSCISSA EXPANSION 0.45-68.04 SAMPLE ORIGIN	ORDINATE EXPANSION %T REMARKS	SCAN TIME MULTIPLIER SLIT PROGRAM SOLVENT CONCENTRATION	REP. SCAN TIME DRIVE OPERATOR CELL PATH REFERENCE	SINGLE BEAM DATE
---	-------------------------------------	---	---	---------------------

MT05173#30 x1 Bgd=22 17-MAR-99 10:59+0:08:07 70-SE EI+  
BpM=77 I=10v Hm=424 TIC=1042659008 Rept:UHCHEM Sys:EI700  
PAUL PHS-68-04 C27H34O4 442 PT=0° Cal:CAL700 #30 1.0  
36627000  
11520000

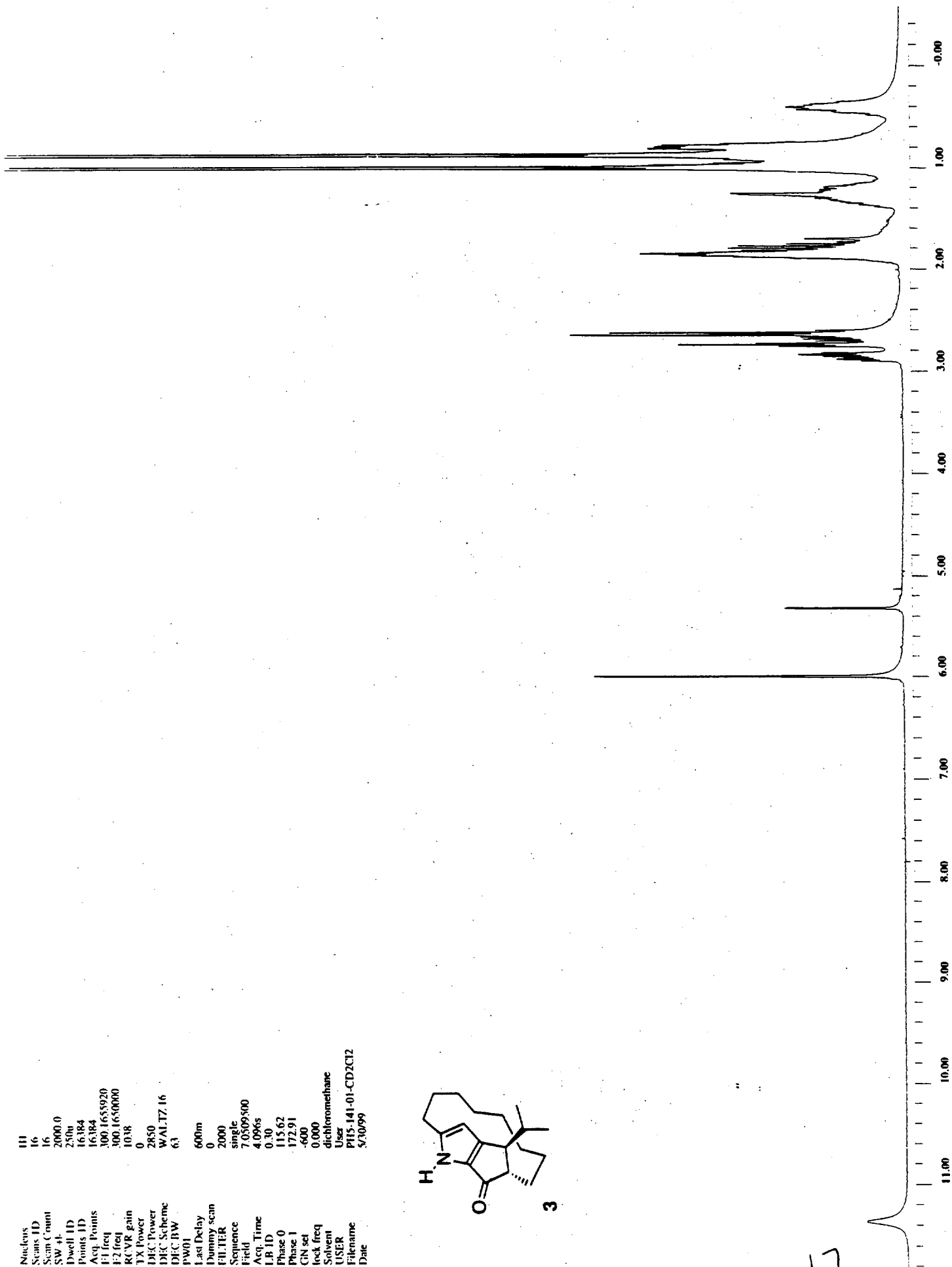




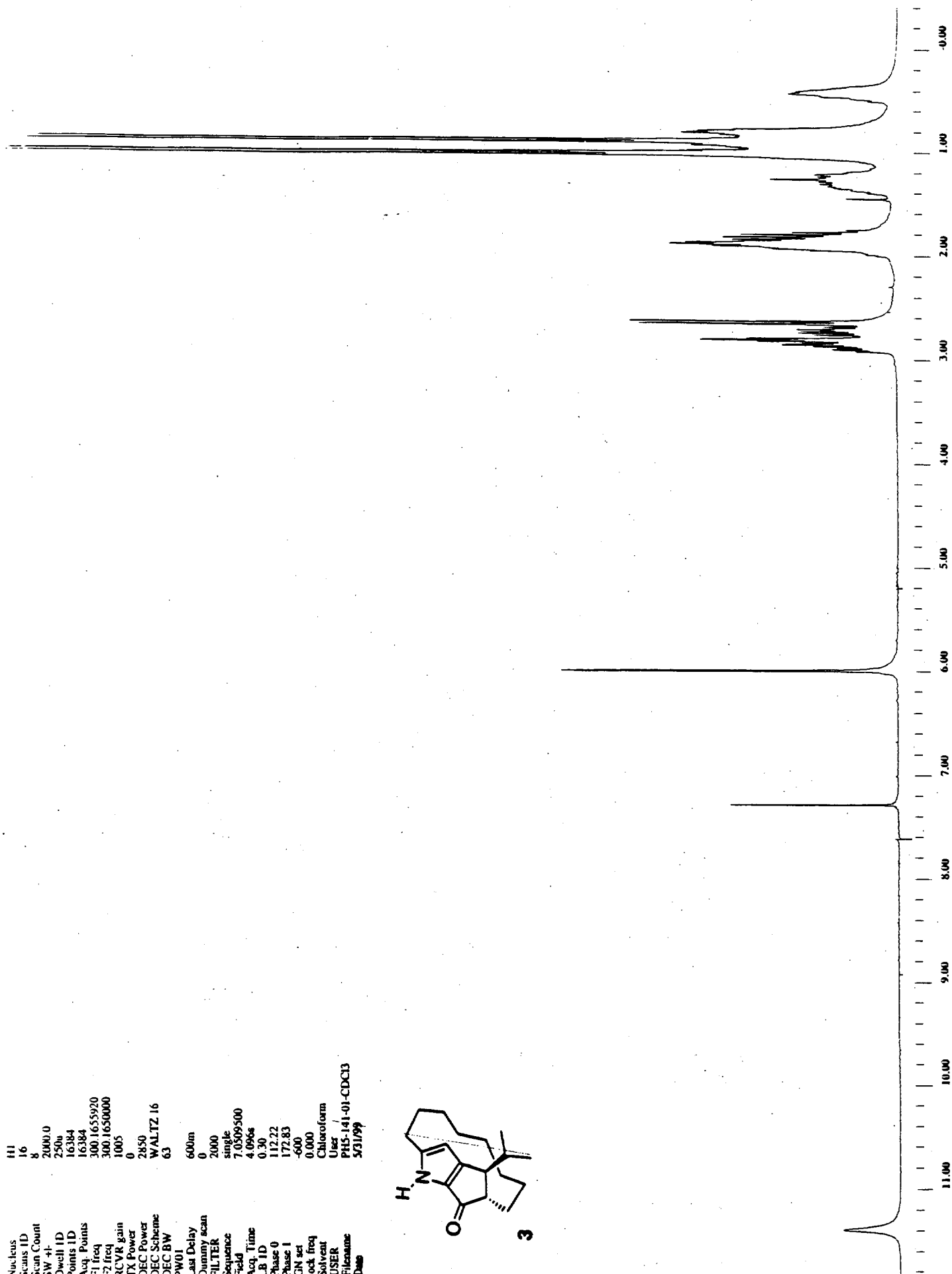
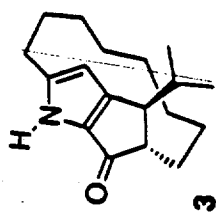
Nucleus 1H  
 Scans 1D 16  
 SW 4F 2000.0  
 Dwell 1D 2.500  
 Points 1D 16384  
 Acq. Points 16384  
 F1 freq 300.1655920  
 F2 freq 300.1650000  
 RCVR gain 1038  
 TX Power 0  
 DEC Power 2850  
 DEC Scheme WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 FILTER 2000  
 Sequence single  
 Field 70509500  
 Acq. Time 4.0965  
 LB 1D 0.30  
 Phase 0 115.62  
 Phase 1 172.91  
 GN sel -600  
 Lock freq 0.000  
 Solvent dichloromethane  
 USER Usez  
 Filename PHS-141-01-CD2C12  
 Date 5/30/99



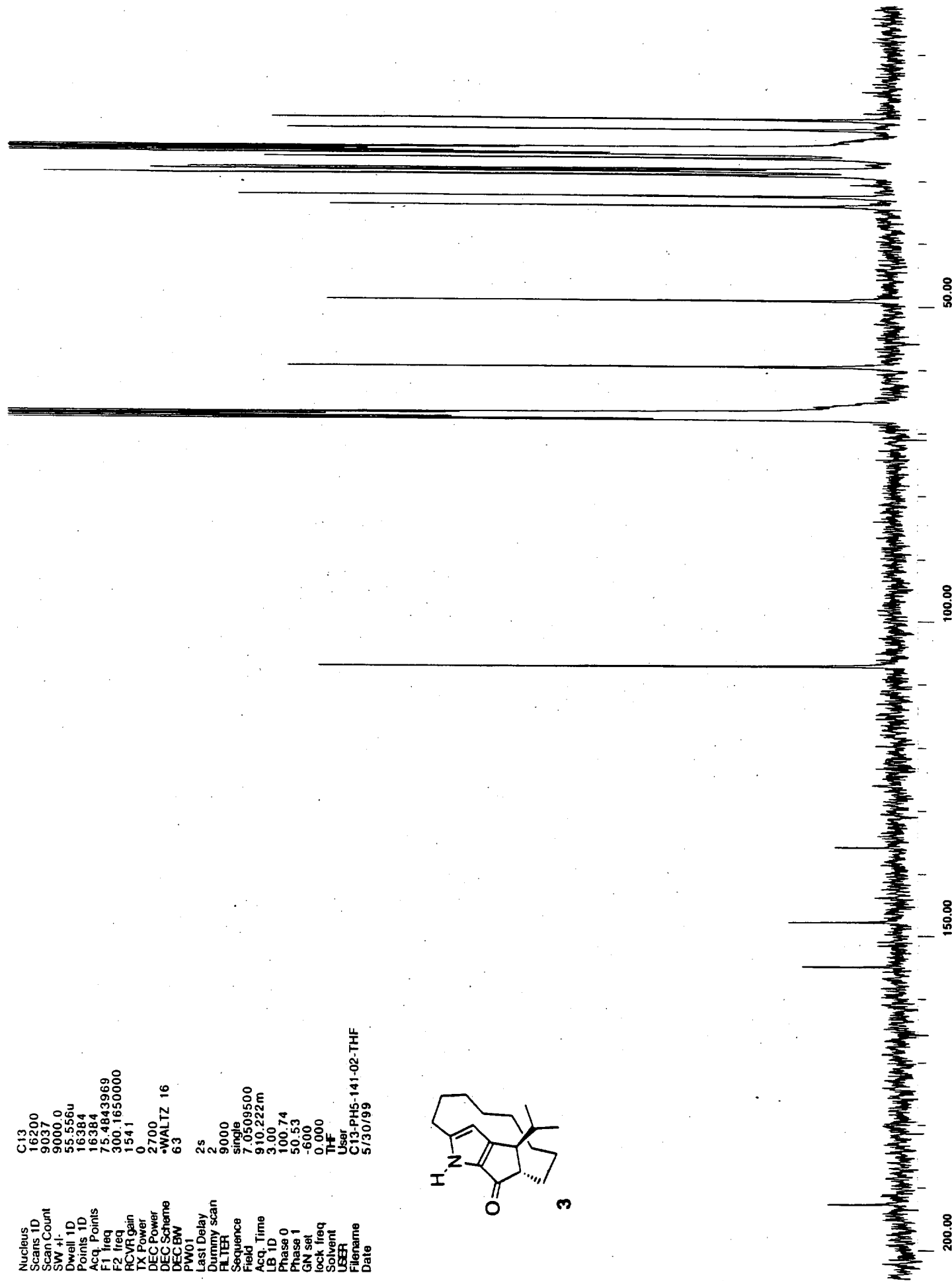
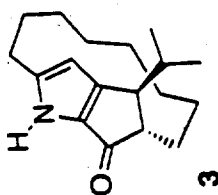
17



Nucleus 1H  
 Scans 16  
 Scan Count 8  
 SW +/- 2000.0  
 Dwell ID 250u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 300.165920  
 F2 freq 300.165000  
 1005  
 RCVR gain 2850  
 TX Power 0  
 DEC Power WALTZ 16  
 DEC Scheme 63  
 DEC BW  
 PW01  
 Last Delay 600um  
 Dummy scan 0  
 FILTER 2000  
 Sequence single  
 Field 7.0509500  
 Field 4.096s  
 Acq. Time 0.30  
 LB ID 112.22  
 Phase 0 172.83  
 Phase 1 -600  
 lock freq 0.000  
 GN set Chloroform  
 lock lock Solvent  
 lock lock USER  
 File name PHS-141-01-CDCl3  
 Date 5/31/99



Nucleus C13  
 Scans ID 16200  
 Scan Count 9037  
 SW +/- 9000.0  
 Dwell ID 55.556u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 75.4843969  
 F2 freq 300.1650000  
 RCVR gain 1.541  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme -WALTZ 16  
 DECBW 63  
 PW01  
 Last Delay 2s  
 Dummy scan 2  
 FILTER 9000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB ID 3.00  
 Phase 0 100.74  
 Phase 1 50.53  
 GN set -600  
 lock freq 0.000  
 Solvent THF  
 User C13-PHS-141-02-THF  
 Date 5/30/99



Nucleus C13  
 Scans 6200  
 Scan Count 1908  
 SW +/- 9000.0  
 Dwell 1D 55.556u  
 Points 1D 16384  
 Acq. Points 16384  
 F1 freq 78.4843969  
 F2 freq 300.1650000  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme -WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 2s  
 Dummy scan 2  
 FILTER 9000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB 1D 3.00  
 Phase 1 107.12  
 Phase 0 53.15  
 GN set -600  
 lock freq 0.000  
 Solvent Chloroform  
 User User  
 Filename C13-PH5-141-01-CDC13-ibd3.0  
 Date 5/31/89

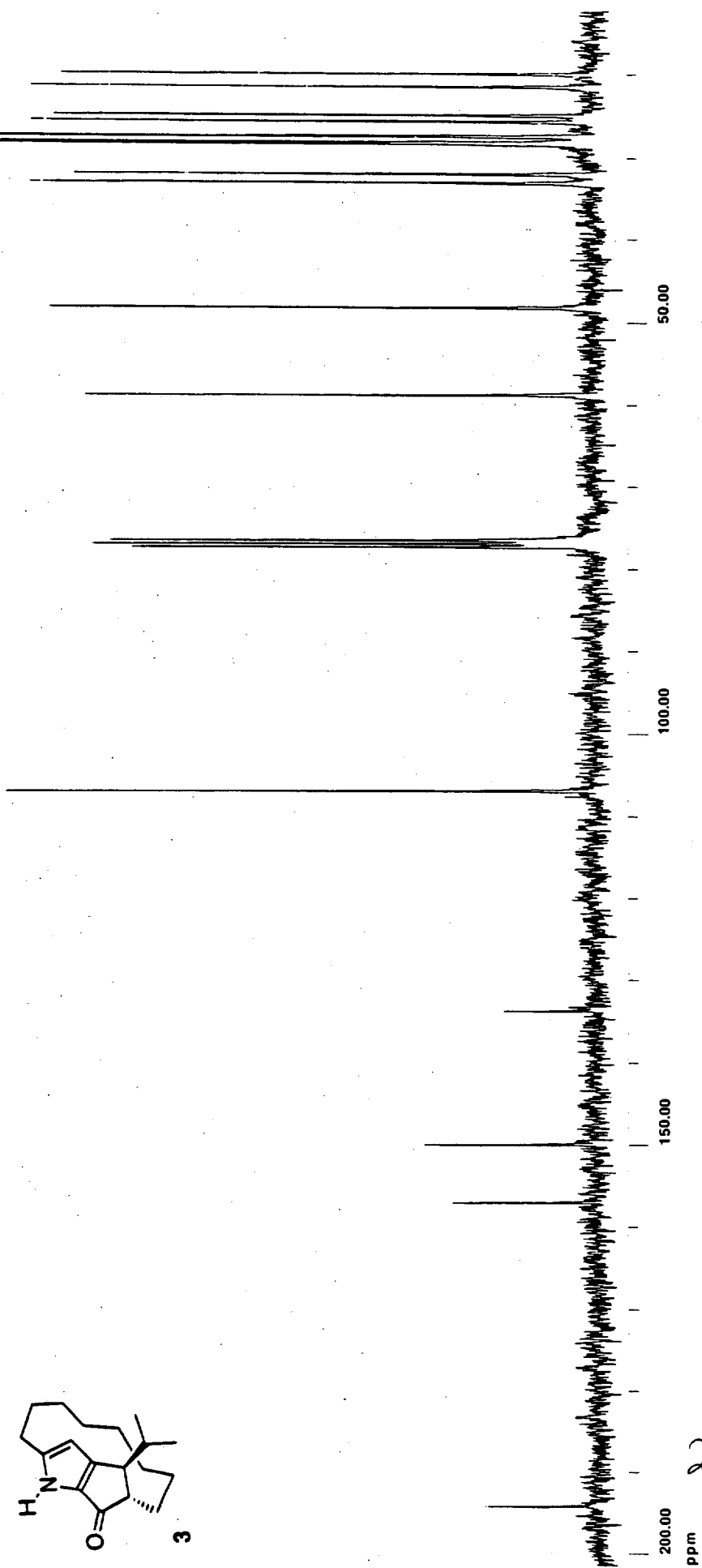
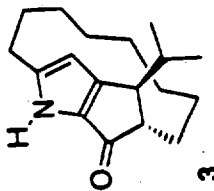
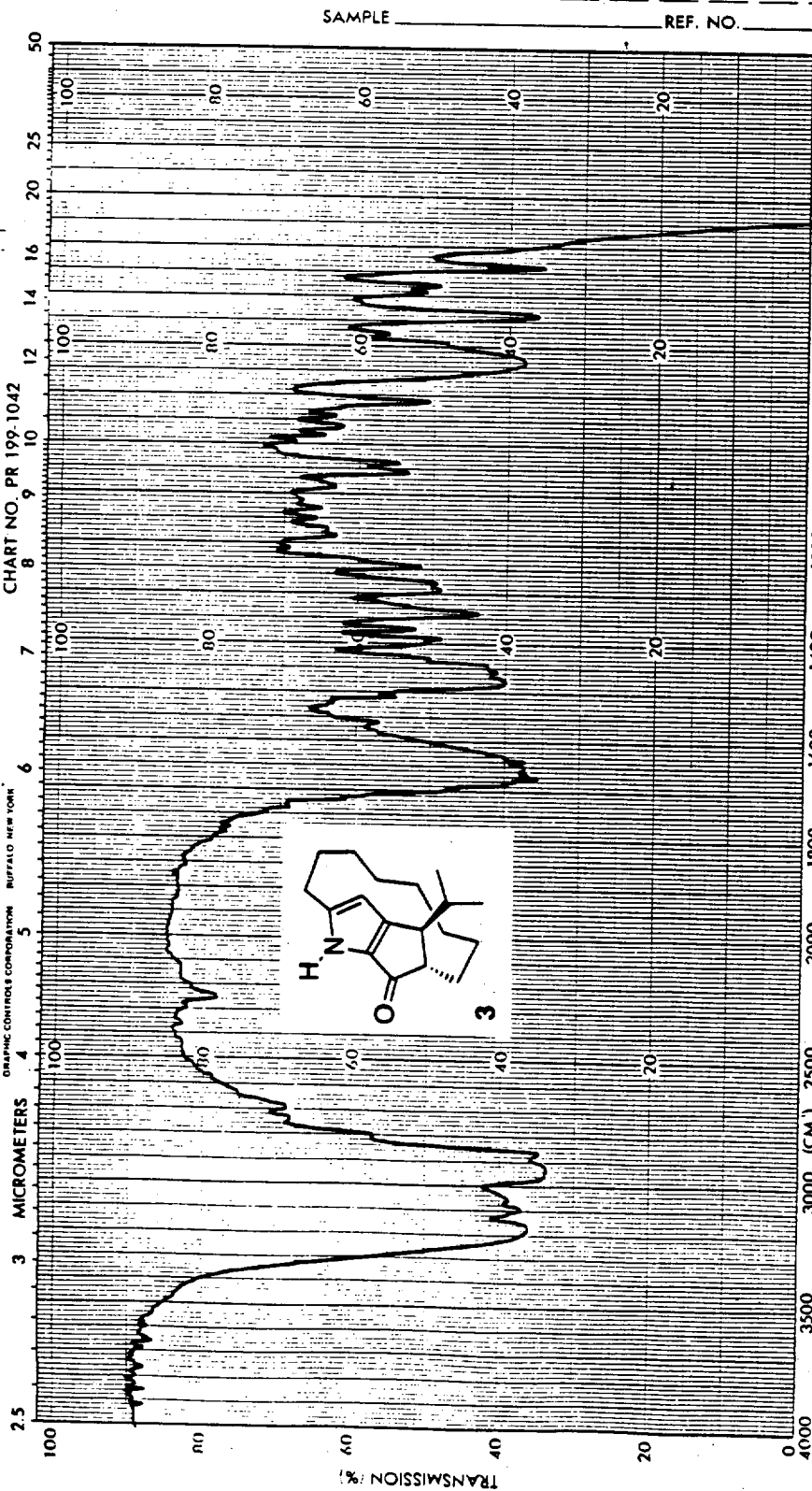


CHART NO. PR 199-1042

DRAWING CONTROLS CORPORATION BUFFALO, NEW YORK



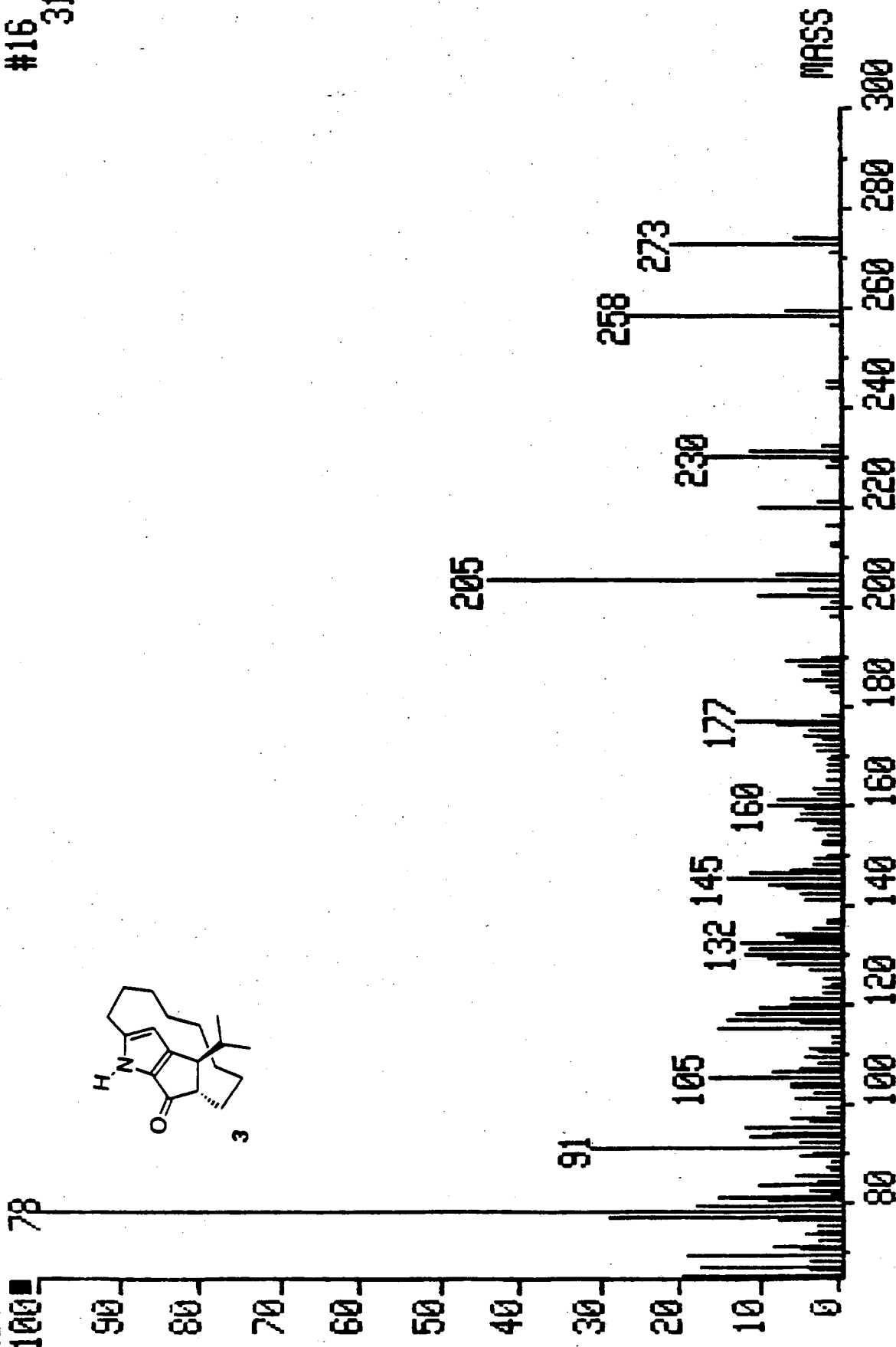
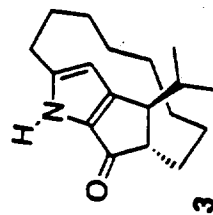
SAMPLE \_\_\_\_\_ REF. NO. \_\_\_\_\_

ABSCISSA EXPANSION	ORDINATE	SCAN TIME	REP. SCAN	SINGLE BEAM
EXPANSION % T	EXPANSION ABS	MULTIPLIER	TIME DRIVE	DATE
SAMPLE ORIGIN	REMARKS	SPLIT PROGRAM	OPERATOR	CELL PATH REFERENCE
		SOLVENT CONCENTRATION		

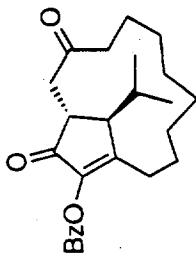
21

MT060031#16 x1 Bgd=12 3-JUN-99 13:26+0:04:31 70-SE EI+  
BpM=78 I=4.7v Hm=275 TIC=324472992  
PAUL PSH-141-01 C18H27NO 273

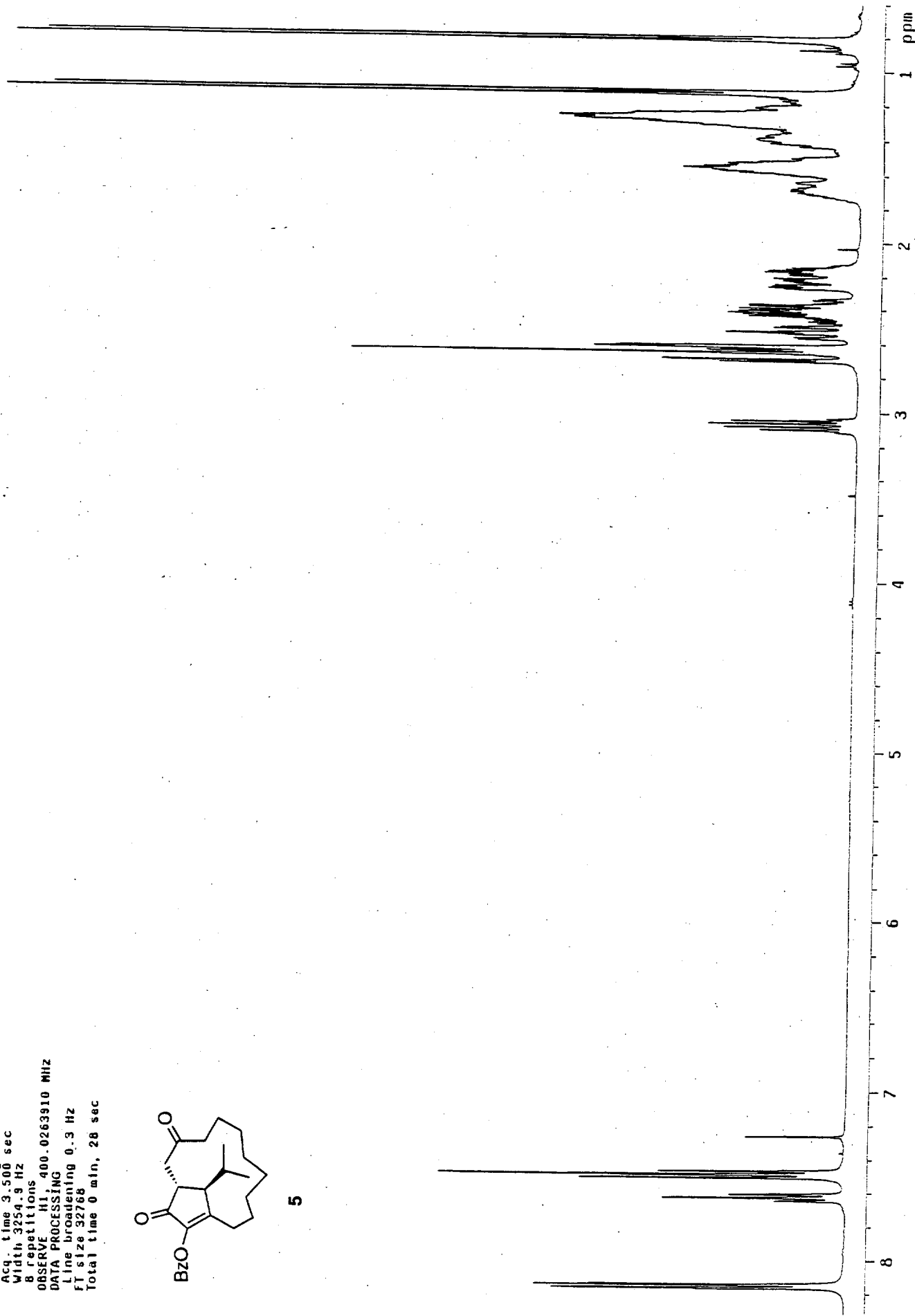
Acnt:UHCHEM Sys:EI700  
PT=0° Cal:PFK770  
#16 1.0  
31029000



Pulse Sequence: s2pul  
Solvent: cuc13  
Temp: 25.0 C / 298.1 K  
File: ph-5-22-99-lh  
INOVA-400 "carbon"  
PULSE SEQUENCE  
Pulse 450.0 degrees  
Acq. time 3.500 sec  
Width 3254.9 Hz  
8 repetitions  
OBSERVE H1, 400.0263910 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 0 min, 28 sec



5



Varian Unity Inova 400 WB

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

File: ph-5-22-99-13c

INOVA-400 "carbon"

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 36.0 degrees

Acq. time 0.857 sec

Width 21367.5 Hz

448 repetitions

OBSERVE C13, 100.5867159 MHz

DECOUPLE H1, 400.0283950 MHz

Power 42 dB

continuously on

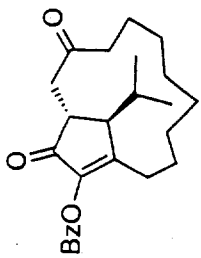
WALTZ-16 modulated

DATA PROCESSING

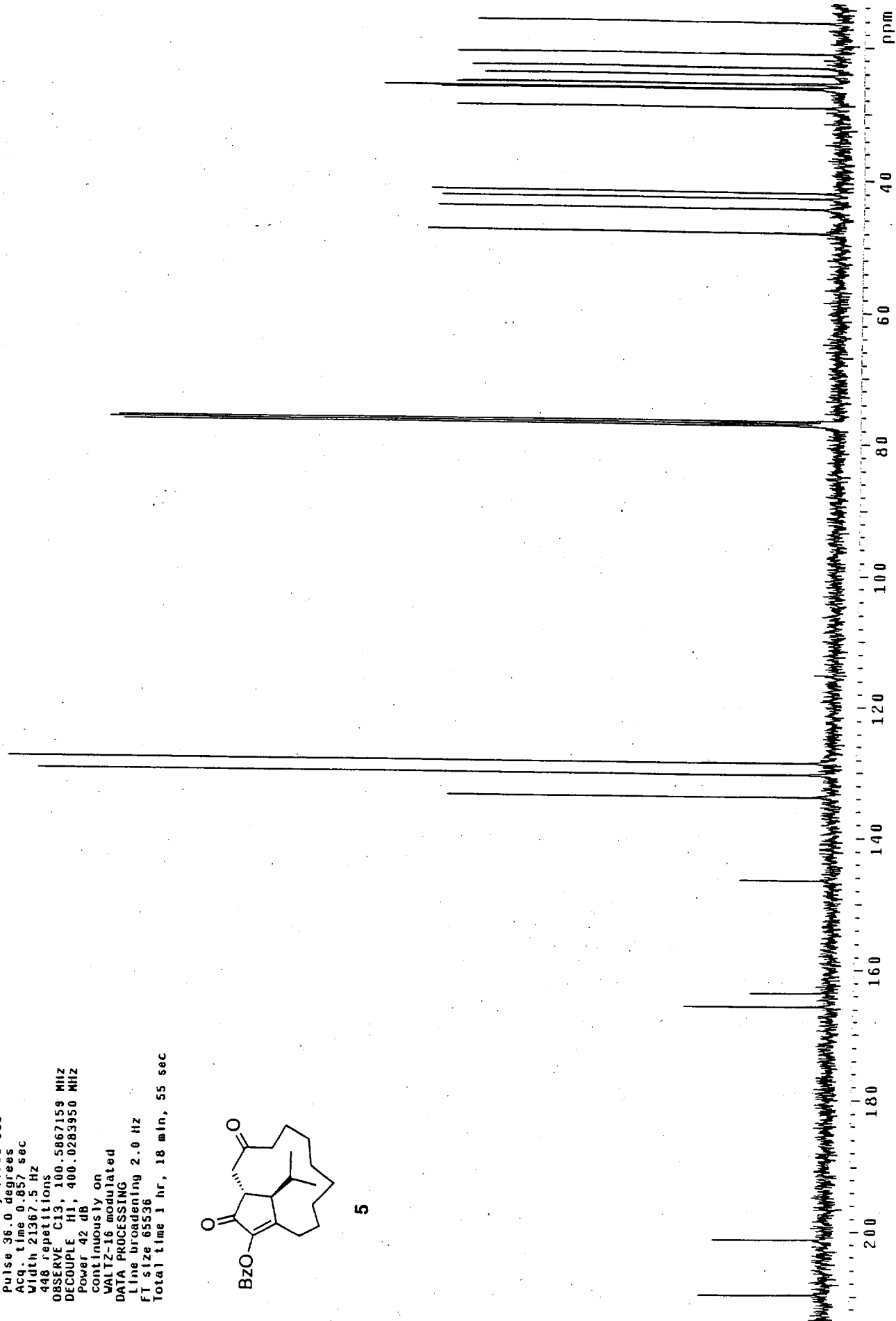
Line broadening 2.0 Hz

FT size 65536

Total time 1 hr, 18 min, 55 sec



5



24



CHART NO. PR 199-1042

GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK

MICROMETERS

2.5 3 4 5 6 7 8 9 10 12 14 16 20 25 51

100

80

60

40

20

0

4000

3500

3000

2500

2000

1800

1600

1400

1200

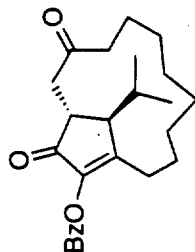
1000

800

600

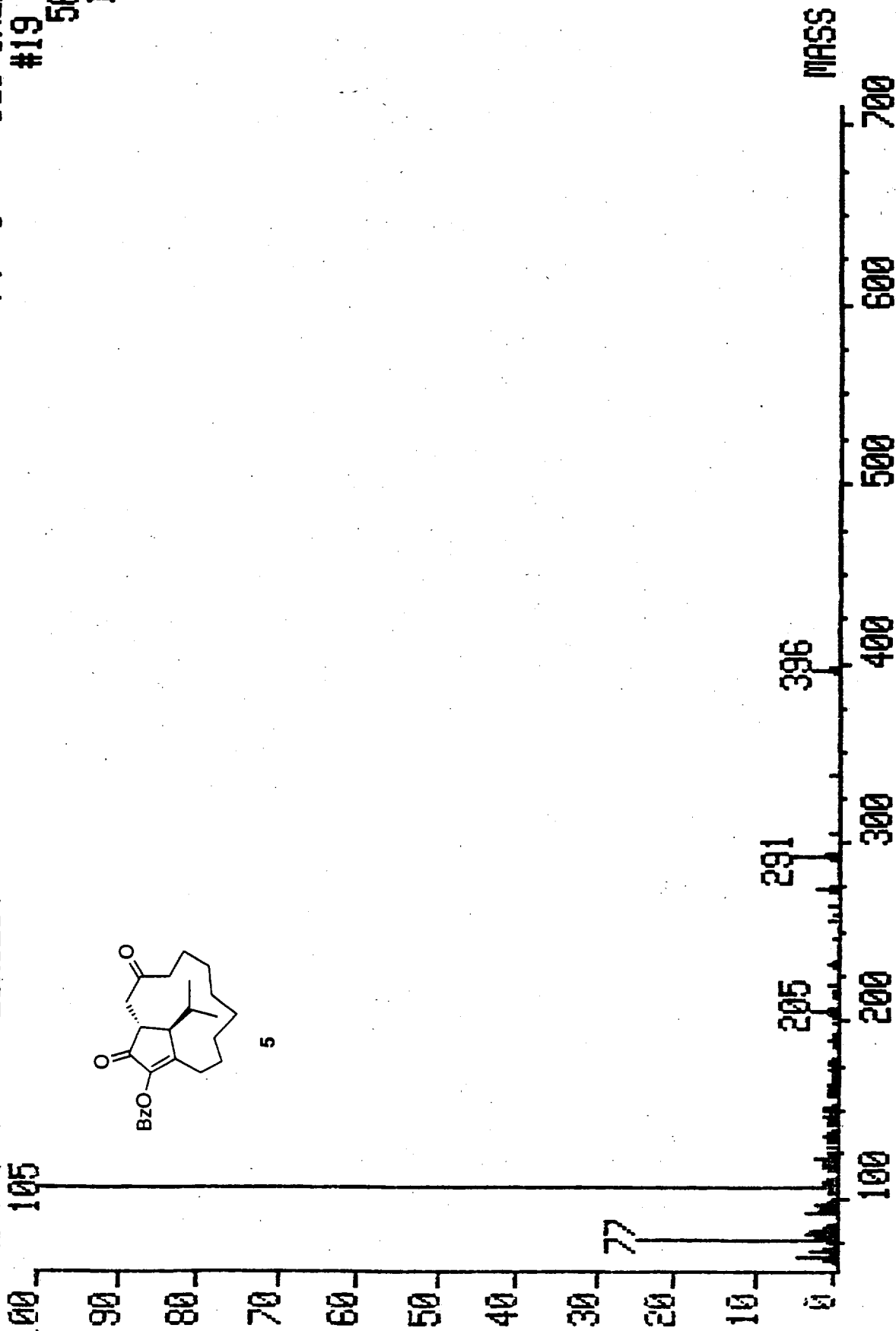
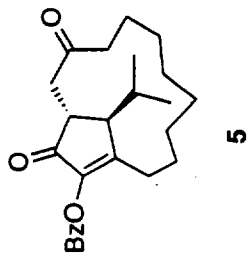
400

20

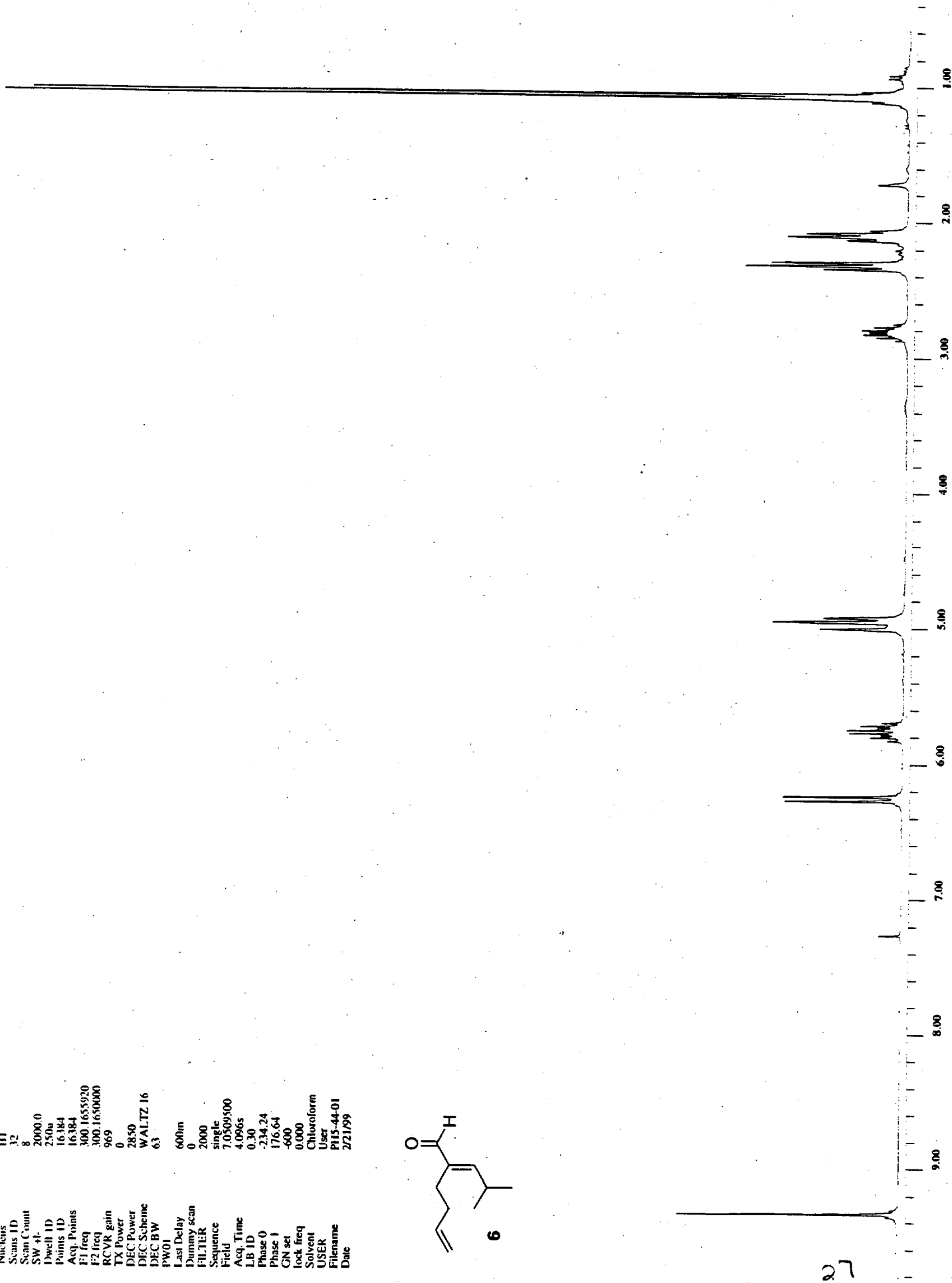
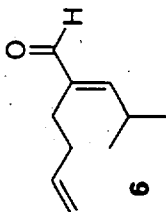


ABSCISSA	ORDINATE	REP. SCAN	SINGLE BEAM
EXPANSION 5x5-72-01	EXPANSION % T	TIME DRIVE	DATE
SAMPLE ORIGIN	REMARKS	OPERATOR	CELL PATH
		SLIT PROGRAM	REFERENCE
		SOLVENT CONCENTRATION	

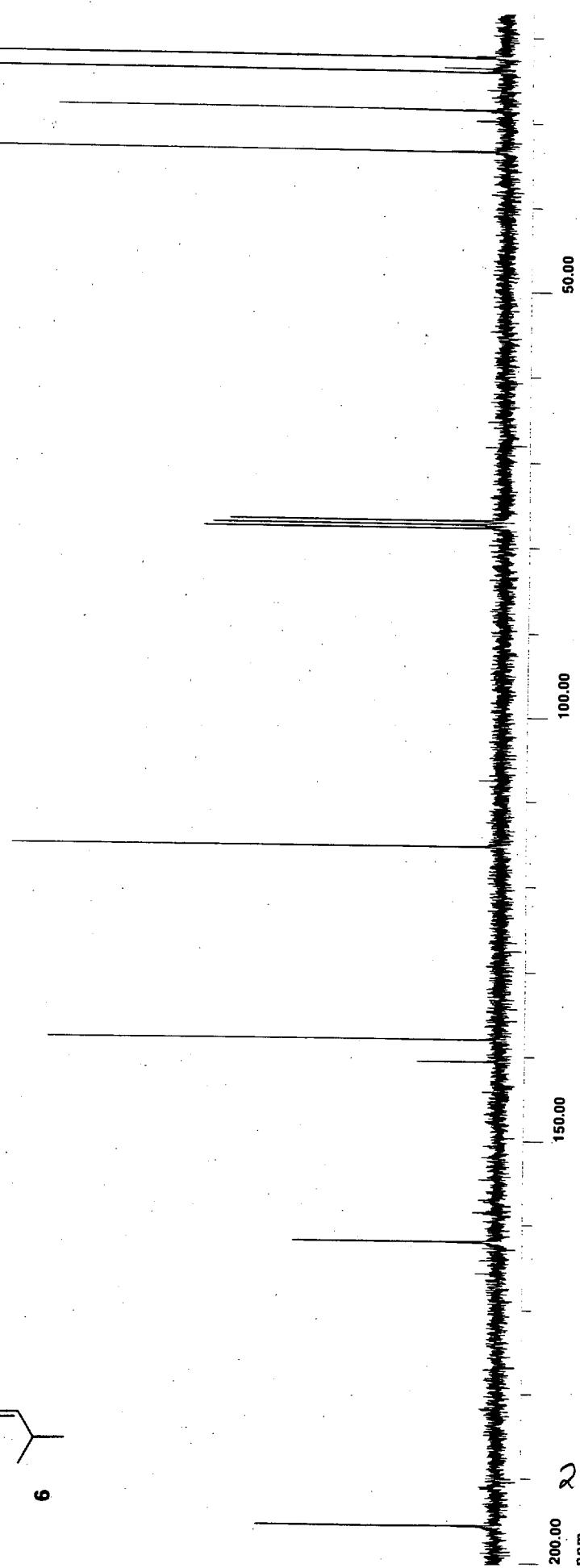
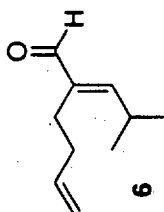
MT03101#19 x1 Bgd=17 10-MAR-99 12:22+0:05:10 70-SE EI+  
BpM=105 I=8.7v Hm=398 TIC=131702000 Acnt:UHCHEM Sys:EI700  
PAUL PHS-72-01 396 C25H32O4 PT= 0° Cal:CAL700  
#19 1.0  
56844000  
14750000

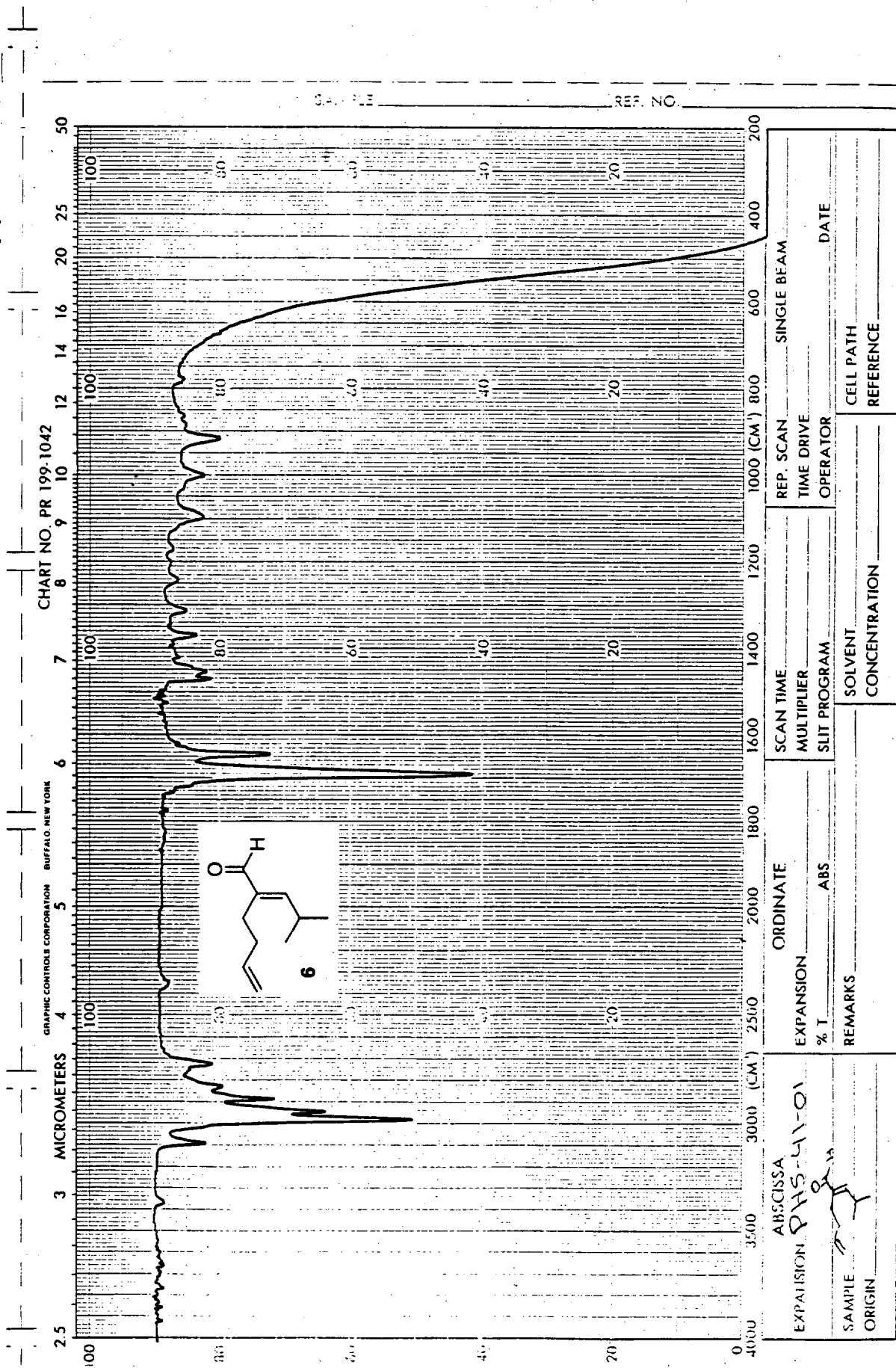


Nucleus 1H  
 Scans 32  
 Scan Count 8  
 SW 4.0 20000.0  
 Dwell ID 250u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 300.1655920  
 F2 freq 300.1650000  
 RCVR gain 969  
 TX Power 0  
 DEC Power 2850  
 DEC Scheme WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 FILTER 2000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 4.096s  
 LB ID 0.30  
 Phase 0 -234.24  
 Phase 1 176.64  
 CN set -600  
 lock freq  
 Solvent Chloroform  
 USER  
 P115-44-01  
 Filename  
 Date 2/21/99

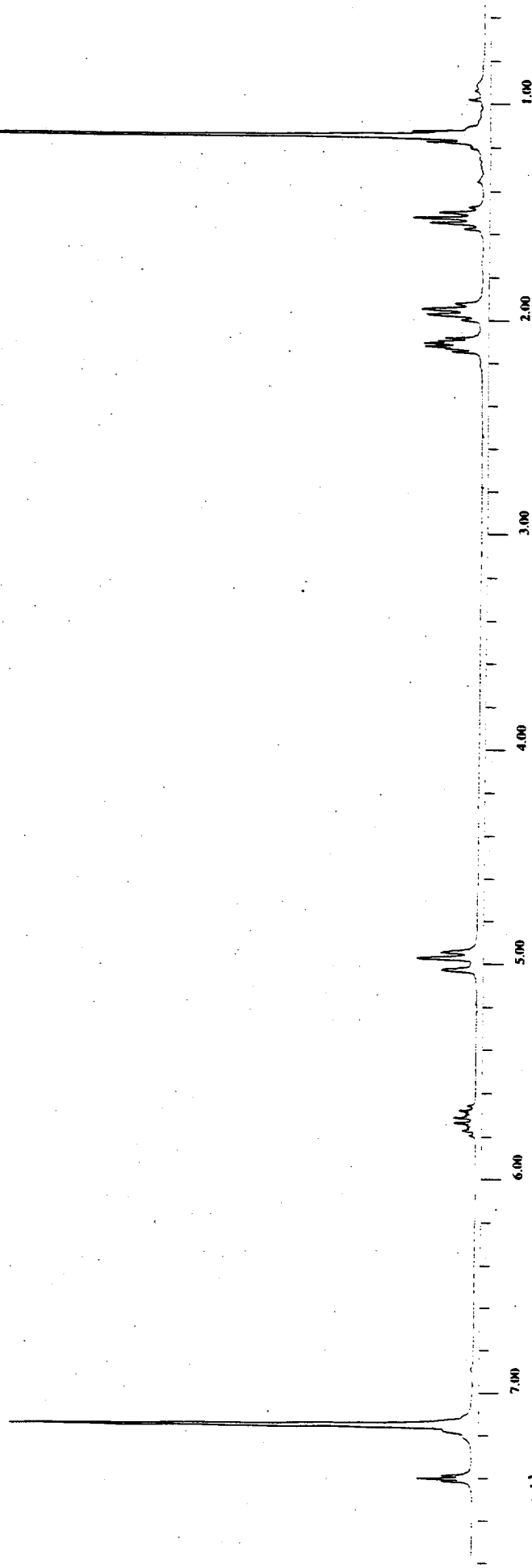
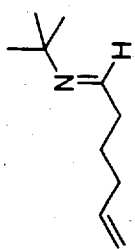


Nucleus C13  
 Scans 1D 3200  
 Scan Count 964  
 SW +/- 9000.0  
 Dwell 1D 55.556u  
 Points 1D 16384  
 Acq. Points 16384  
 F1 freq 75.4843869  
 F2 freq 300.1650000  
 RCVR gain 1607  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme \*WALTZ 16  
 DEC BW 6.3  
 PW01  
 Last Delay 1s  
 Dummy scan 2  
 FILTER 9000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB 1D 0.50  
 Phase 0 -240.38  
 Phase 1 69.97  
 GN set -600  
 lock freq 0.000  
 Solvent Chloroform  
 USER User  
 Filename C13-PH5-44-01  
 Date 2/21/99



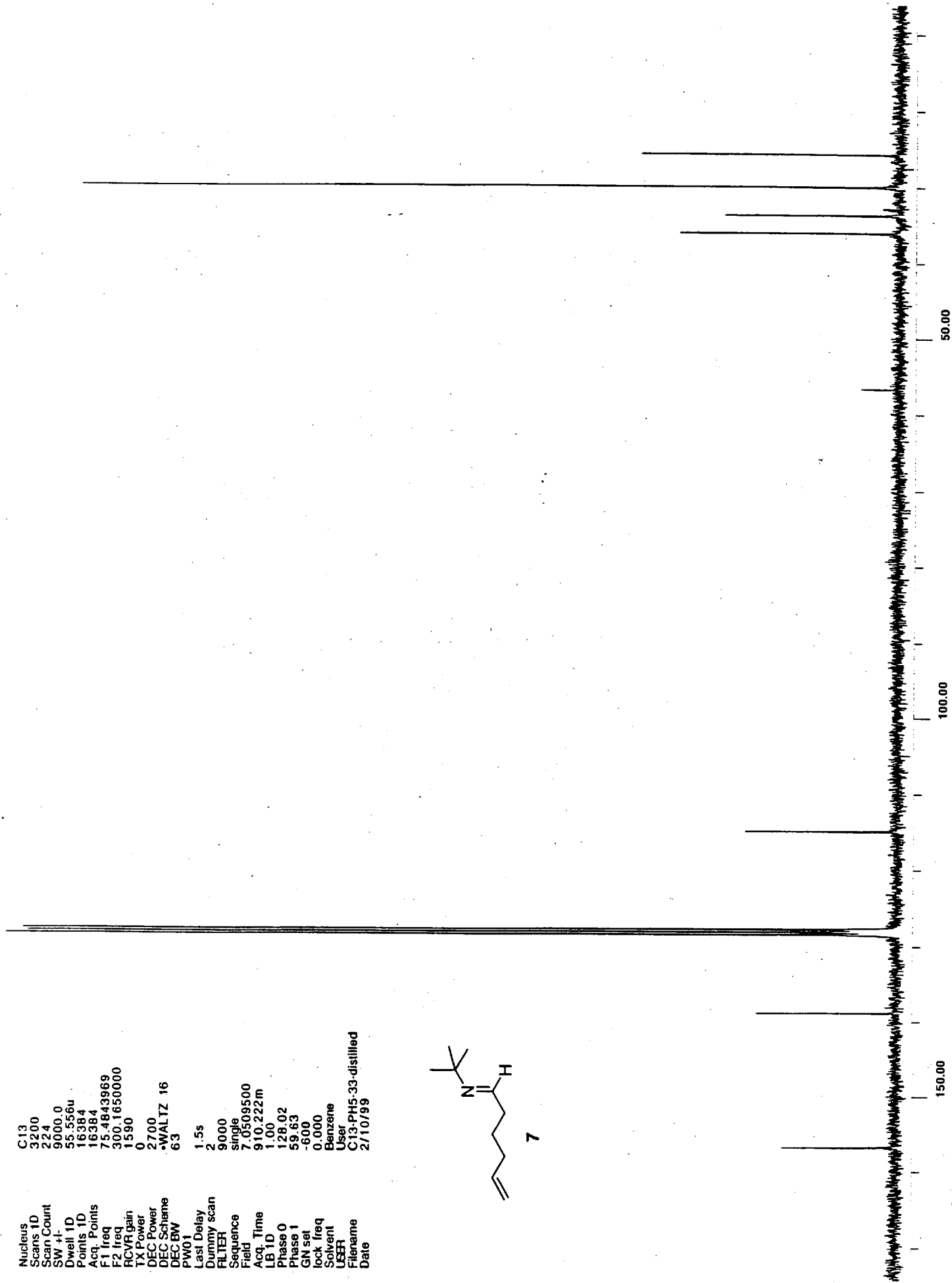
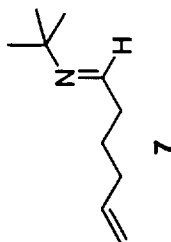


Nucleus H1  
 Scans ID 32  
 Scan Count 4  
 SW-H 2000.0  
 Z30h  
 Dwell ID 16384  
 Points ID 16384  
 Acq. Points 300.1655920  
 F1 freq 300.1650000  
 F2 freq 1037  
 RCVR gain 0  
 TX power 2850  
 DEC Power WALTZ 16  
 DEC Scheme 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 FILTER single  
 Sequence 7.0509500  
 Field 4.0906  
 Acq. Time 0.30  
 LB ID 135.02  
 Phase 0 172.89  
 Phase 1  
 GN set -600  
 lock freq 0.000  
 Solvent Benzene  
 User P115-33-distilled  
 Filename 2/10/99  
 Date

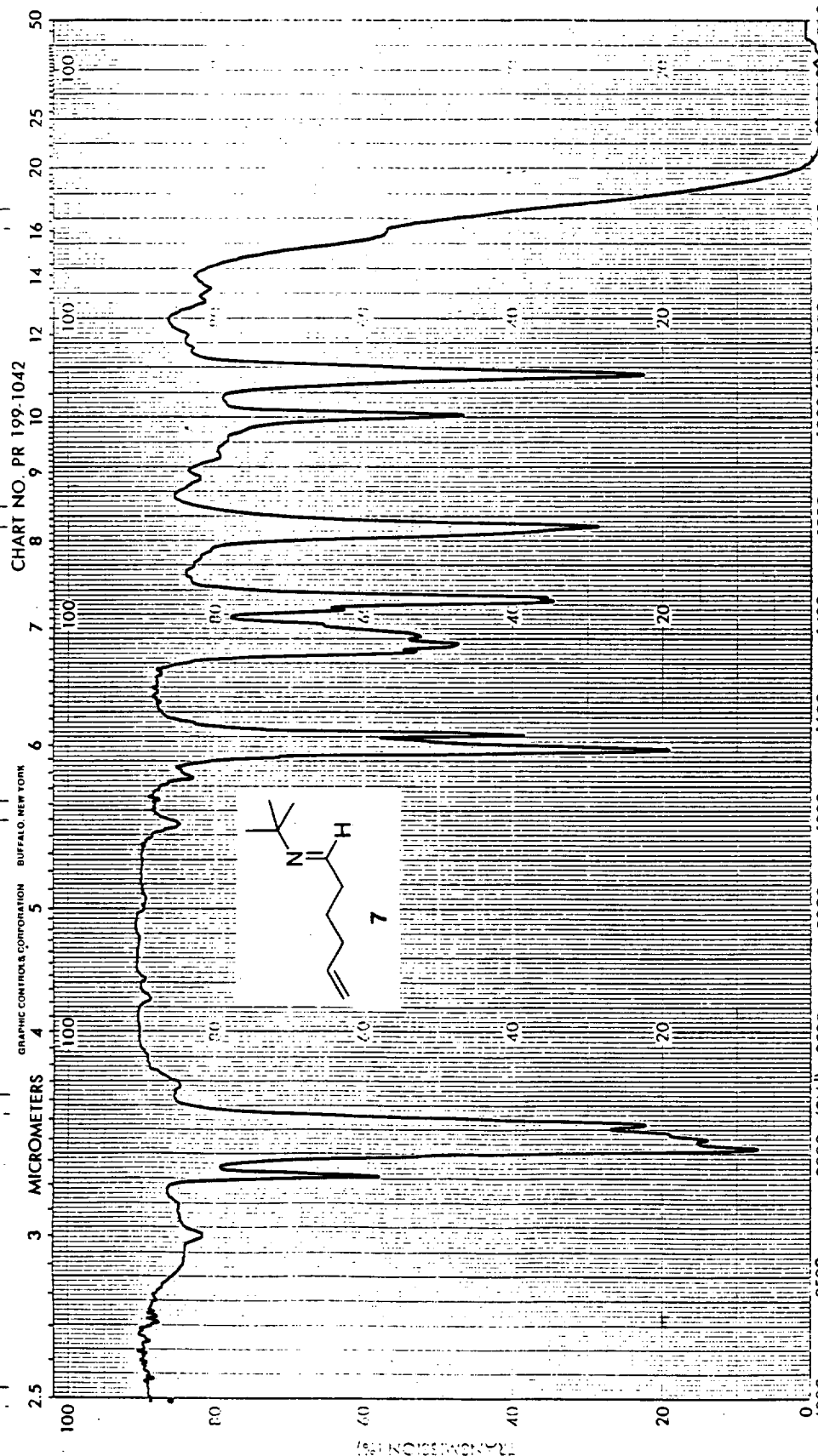


30

Nucleus C13  
 Scans 1D 3200  
 Scan Count 224  
 SW +/- 9000.0  
 Dwell 1D 55.556u  
 Points 1D 16384  
 Acq. Points 16384  
 F1 freq 75.4843969  
 F2 freq 300.1650000  
 RCVR gain 1590  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 1.5s  
 Dummy scan 2  
 FILTER 9000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB 1D 1.00  
 Phase 0 128.02  
 Phase 1 59.63  
 GN set -600  
 lock freq 0.000  
 Solvent Benzene  
 User  
 Filename C13-PH5-33-distilled  
 Date 2/10/99



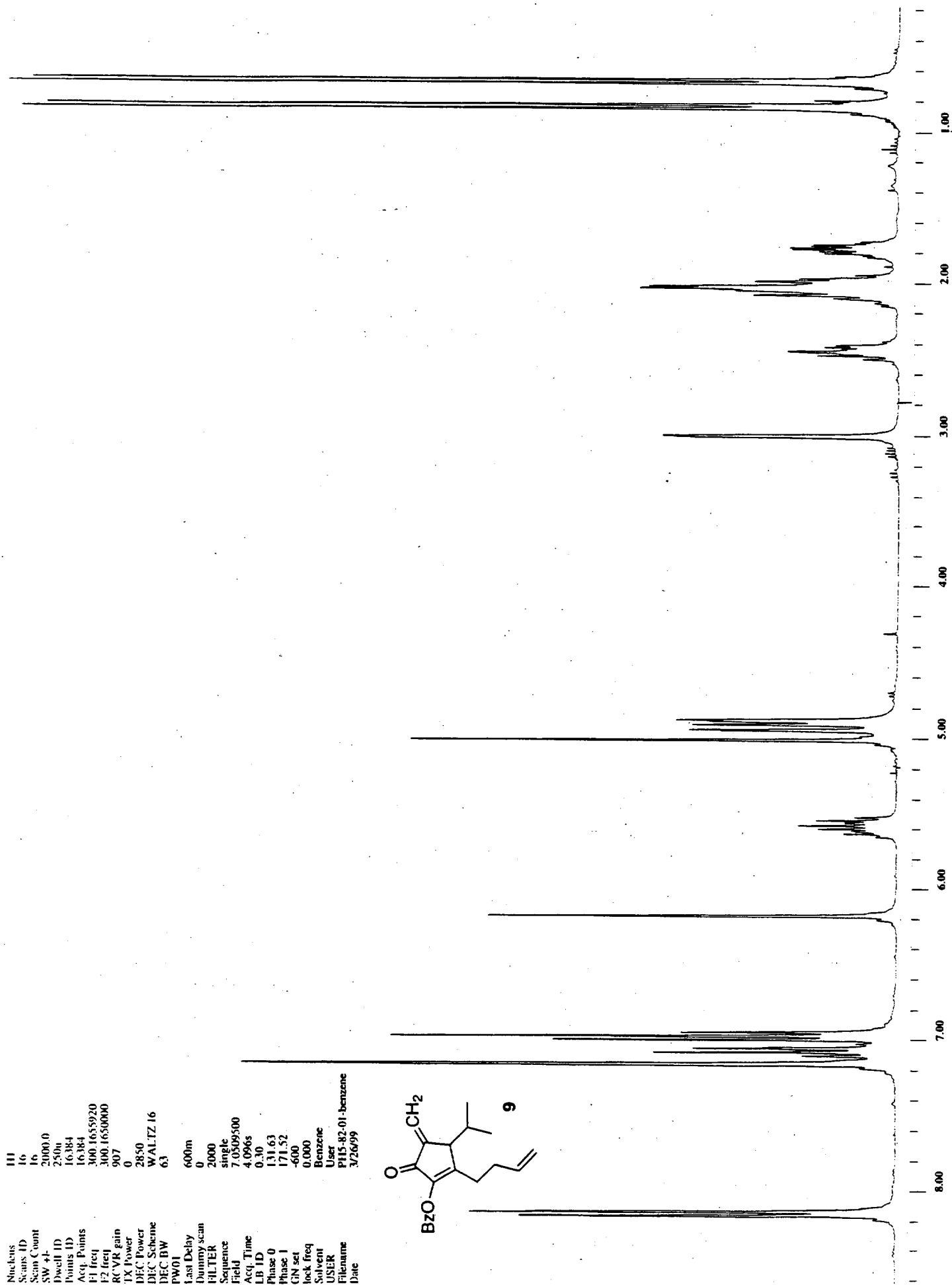
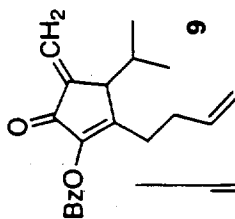
ppm 3



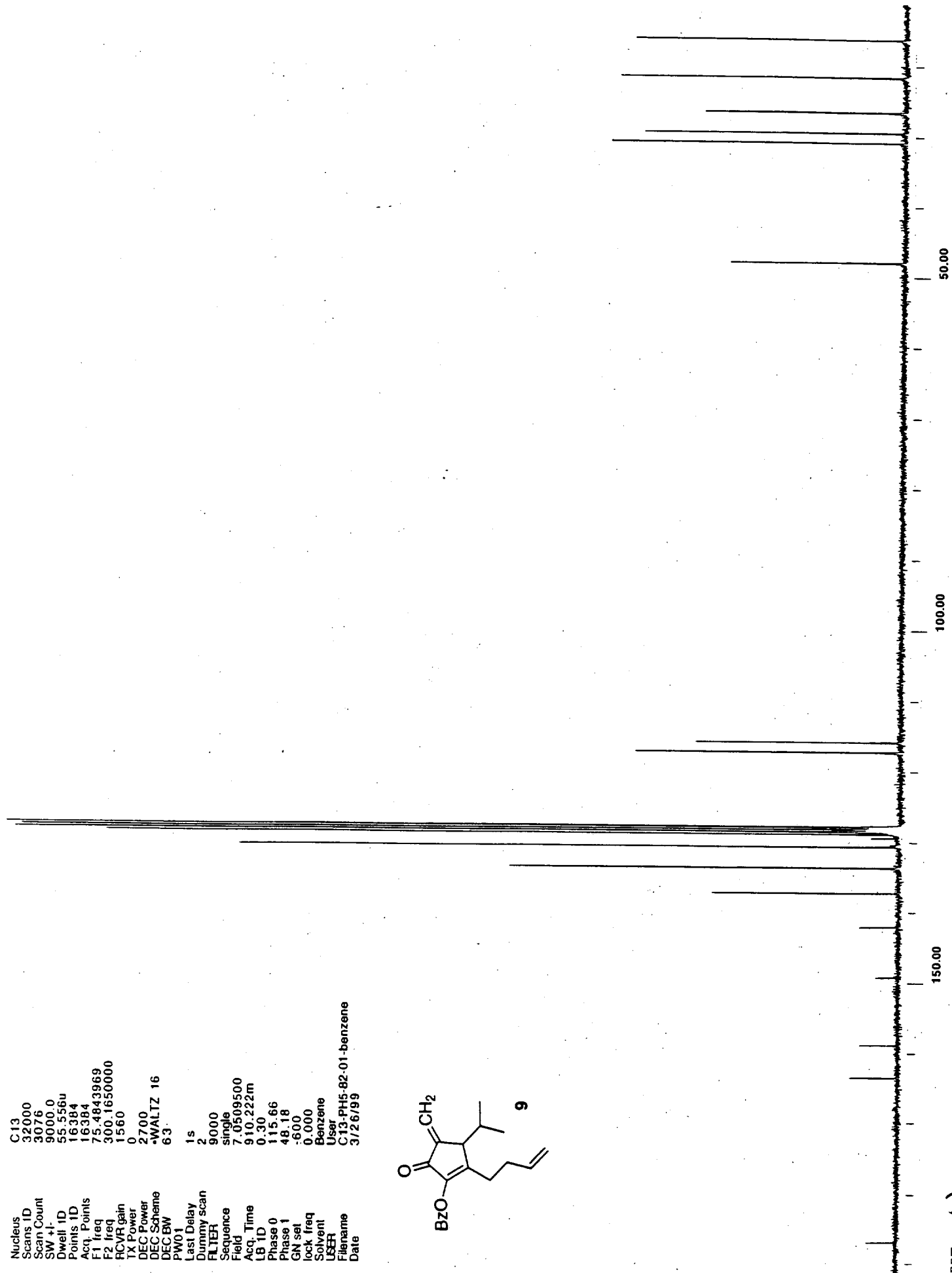
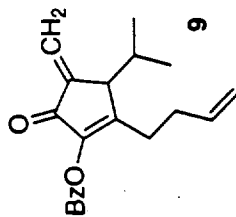
ABSCISSA	ORDINATE	SCAN TIME	REP. SCAN	SINGLE BEAM
EXPANSION <u>PHS-33-3.5x1.0</u>	EXPANSION	MULTIPLIER	TIME DRIVE	
	% T	SLIT PROGRAM	OPERATOR	DATE
SAMPLE	REMARKS	SOLVENT	CELL PATH	REFERENCE
ORIGIN		CONCENTRATION		

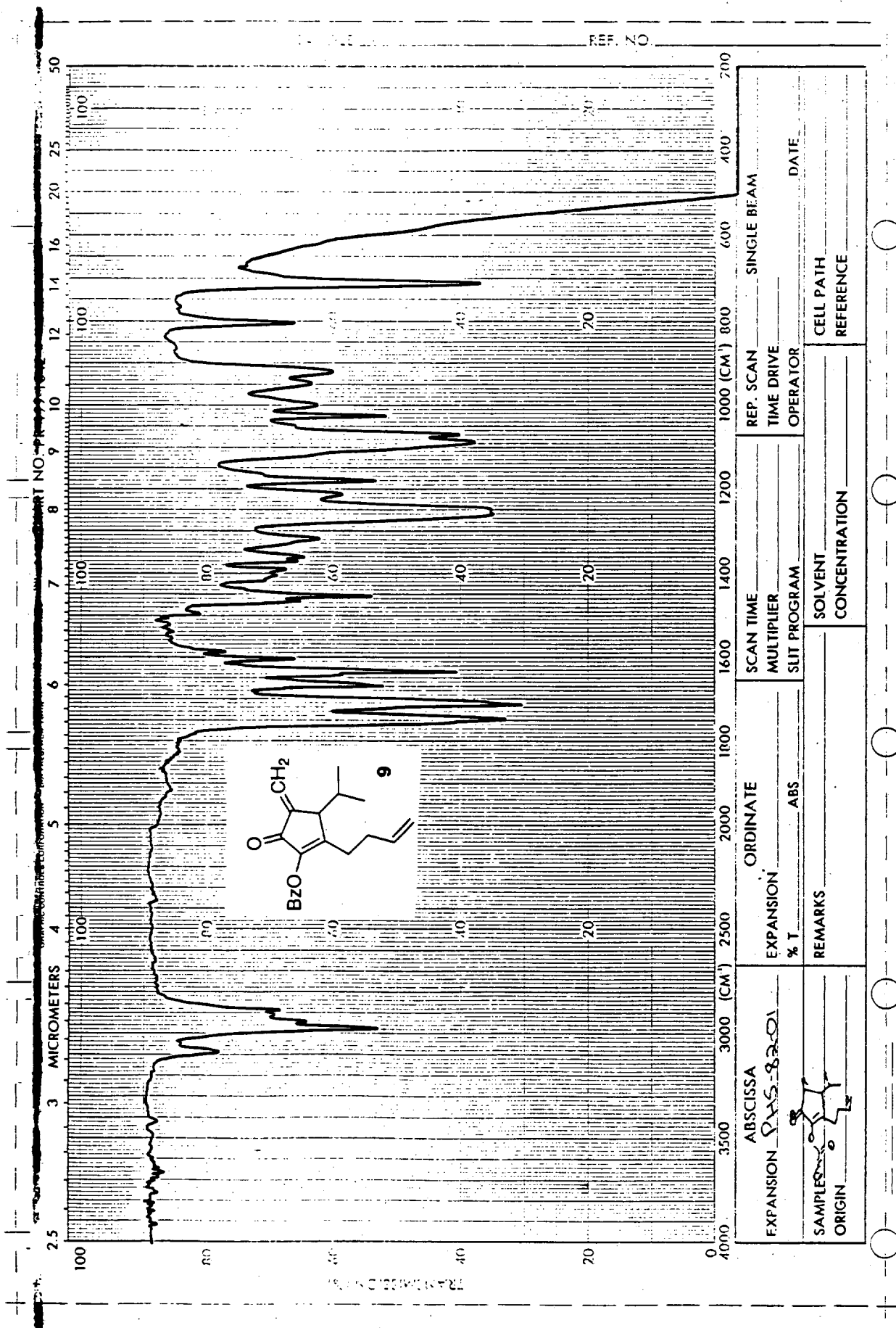


Nucleus III  
 Scans ID 16  
 Scan Count 2000.0  
 SW +/- 250u  
 Dwell ID 16.384  
 Points ID 16.384  
 Acq. Points 300.1655920  
 F1 freq 300.1650000  
 F2 freq 907  
 RCVR gain 0  
 TX Power 2850  
 DEC Power W/ALTZ 16  
 DEC Scheme 63  
 PW01  
 Last Delay 600m  
 Dummy scan 0  
 FILTER 2000  
 Sequence single  
 Field 7.0509500  
 Field 4.0965  
 Acq. Time 0.30  
 LR ID 131.63  
 Phase 0 171.52  
 CNV set -600  
 lock freq 0.000  
 Solvent Benzene  
 USER PFI5-82-01-benzene  
 Filename 3/26/99  
 Date



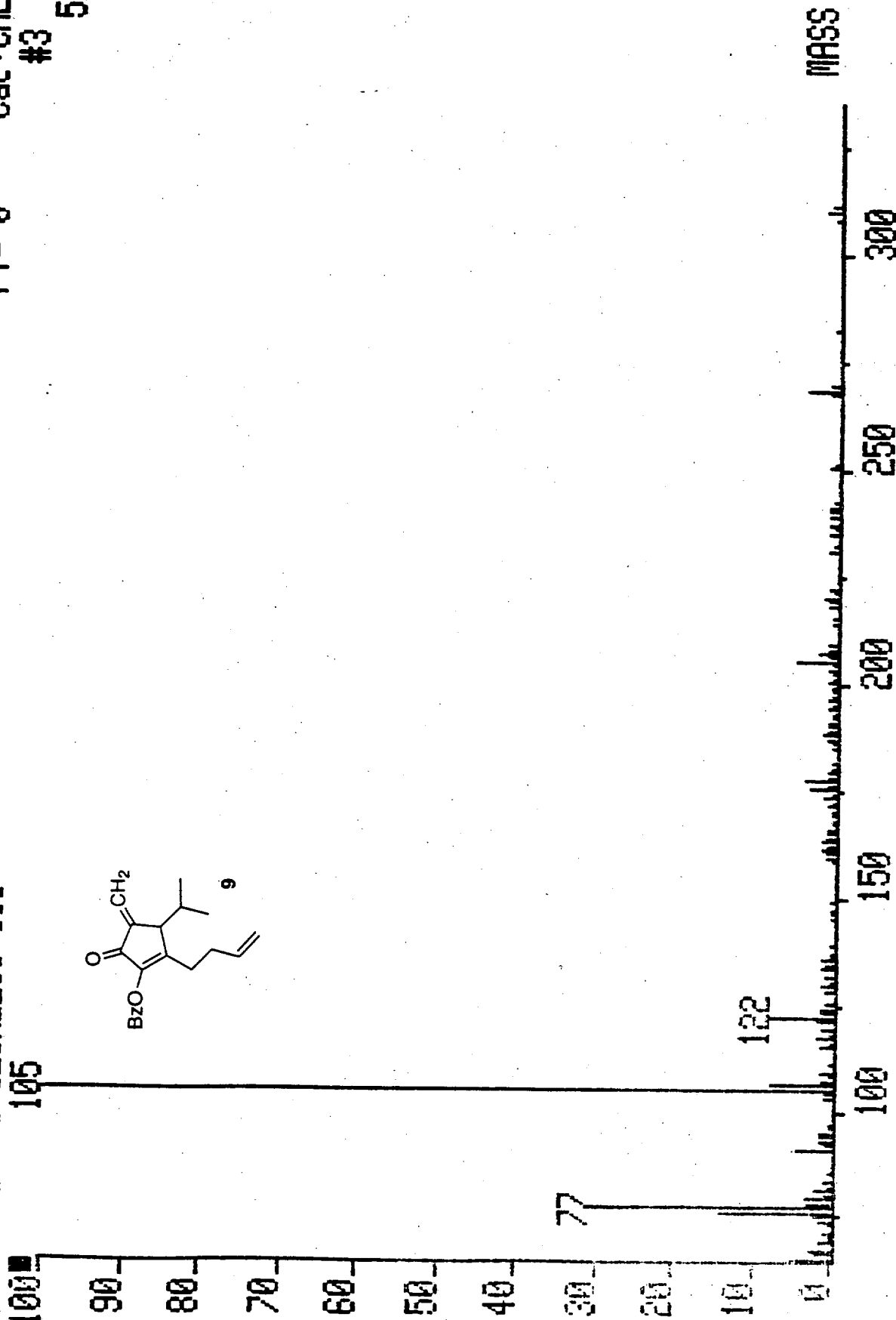
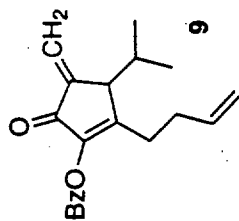
Nucleus C13  
 Scans ID 32000  
 Scan Count 3076  
 SW +/- 9000.0  
 Dwell ID 55.556u  
 Points ID 16384  
 Acq. Points 16384  
 F1 freq 75.4843969  
 F2 freq 300.1650000  
 RCVR gain 1560  
 TX Power 0  
 DEC Power 2700  
 DEC Scheme -WALTZ 16  
 DEC BW 63  
 PW01  
 Last Delay 1s  
 Dummy scan 2  
 FILTER 9000  
 Sequence single  
 Field 7.0509500  
 Acq. Time 910.222m  
 LB ID 0.30  
 Phase 0 115.66  
 Phase 1 48.18  
 GN set -600  
 lock freq 0.000  
 Solvent Benzene  
 User C13-PH5-82-01-benzene  
 Filename 3/26/99  
 Date



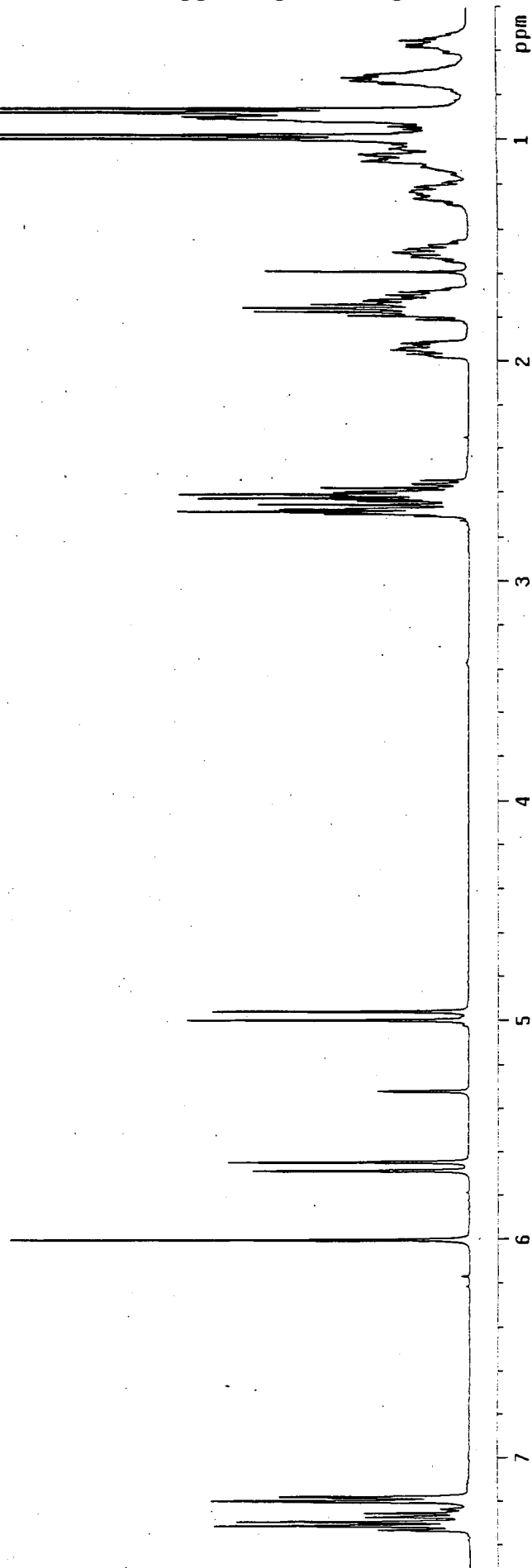
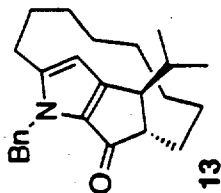


ABSCISSA EXPANSION <u>0.45-8.201</u>	ORDINATE EXPANSION % T _____ ABS _____	SCAN TIME _____ MULTIPLIER _____ SLIT PROGRAM _____	REP. SCAN _____ TIME DRIVE _____ OPERATOR _____
SAMPLES <u>1</u> ORIGIN _____	REMARKS _____	SOLVENT _____ CONCENTRATION _____	CELL PATH _____ REFERENCE _____
		SINGLE BEAM _____ DATE _____	

HT051/2H3 X1 Bgd=1 17-11HK-99 10:41+0:00:59 /0-SE EI+  
BPM=105 I=8.8V Hm=312 TIC=150197008 Acnt:UHCHEM Sys:EI700  
PAUL PHS-38-01 C20H22O3 310 PT=0° Cal:CAL700 #3 1.0  
57896000



Pulse Sequence: s2pu1  
Solvent: cd2cl2  
Ambient temperature  
File: ph-5-16-99-1h  
INOVA-400 "carbon"  
PULSE SEQUENCE  
Pulse 450.0 degrees  
Acq. time 3.504 sec  
Width 3096.0 Hz  
8 repetitions  
OBSERVE H1 400.0271650 MHZ  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 0 min, 28 sec



Varian Unity Inova 400 WB

Pulse Sequence: s2pul

Solvent: cd2cl2  
Ambient temperature  
File: ph-5-16-99-13c  
INOVA-400 "carbon"

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 36.0 degrees

Acq. time 0.858 sec

Width 21265.3 Hz

1072 repetitions

OBSERVE C13, 100.5868700 MHz

DECOUPLE H1, 400.9291631 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 2 hr, 37 min, 51 sec

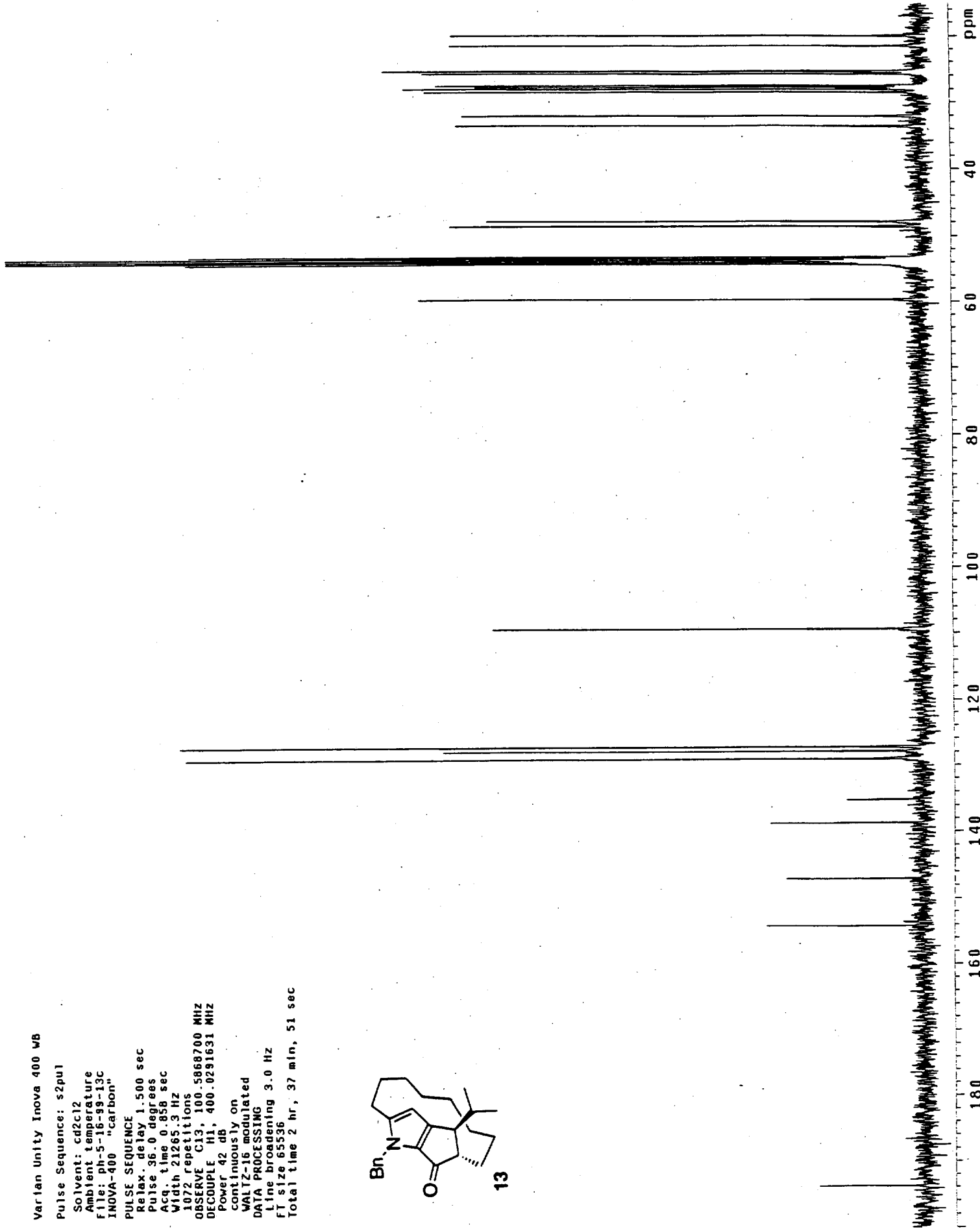
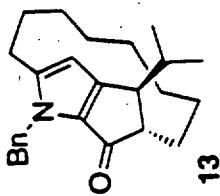
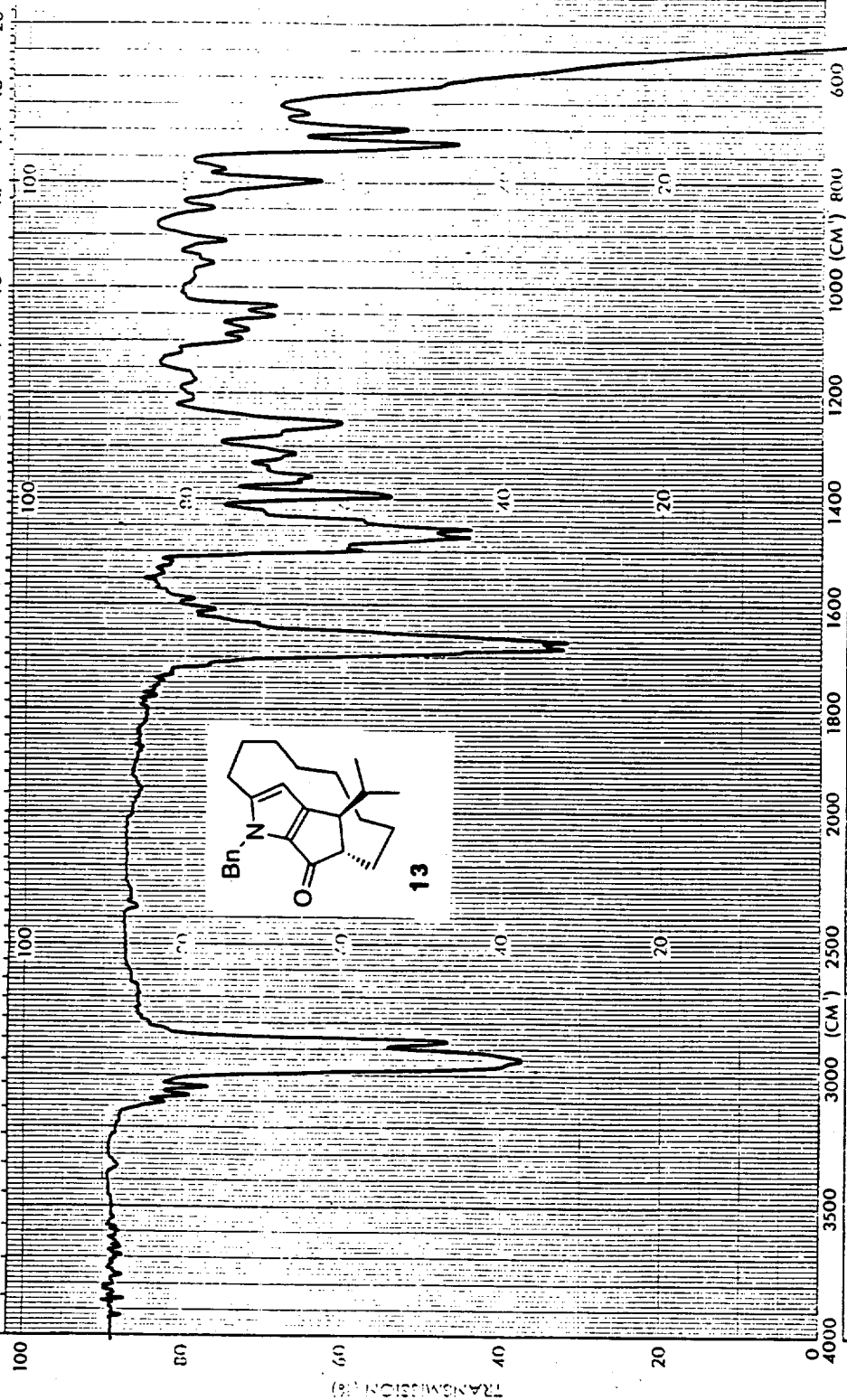


CHART NO. PR 199-1042

GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK

MICROMETERS

2.5



ABSCISSA		ORDINATE		SCAN TIME		REP. SCAN		SINGLE BEAM	
EXPANSION 10x		EXPANSION		MULTIPLIER		TIME DRIVE		TIME DRIVE	
SAMPLE		REMARKS		SLIT PROGRAM		OPERATOR		OPERATOR	
ORIGIN				SOLVENT		CONCENTRATION		CELL PATH	
								REFERENCE	

MT05241#19 x1 Bgd=10 24-MAY-99 13:57+0:05:50 70-SE EI+  
BpM=0 I=6.5v Hm=0 TIC=187121008 Acnt:UHCHEM Sys:EI700  
PAUL PHS-119-01 C25H33NO 363 PT=0° Cal:CAL700 #19 1.0  
42388000

