# Highly Efficient Trapping of the Nazarov Intermediate with Substituted Arenes

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## Supporting Information

**General** Reactions were conducted in oven-dried (120 °C) or flame-dried glassware under a positive nitrogen atmosphere unless otherwise stated. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes or cannulae. Solvents were distilled before use: dichloromethane from calcium hydride; diethyl ether and tetrahydrofuran from sodium benzophenone ketyl. Thin layer chromatography (TLC) was performed on plates of silica precoated with 0.25 mm Kieselgel 60 $F_{254}$. Flash chromatography columns were packed with 230-400 mesh silica gel. Column dimensions include outer diameters. Radial chromatography was performed on plates of silica precoated with 1, 2 or 4 mm silica gel 60 $PF_{254}$ containing gypsum. Barium manganate was purchased from Aldrich and was used without any prior activation or purification.

Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a 500 MHz Varian VXR NMR unless otherwise stated, and the chemical shifts are reported on the δ scale (ppm) downfield from tetramethylsilane. Coupling constants (*J*) are reported in Hz. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets, etc. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) were obtained at 125 MHz and are reported (ppm) relative to the center line of a triplet at 77.23 ppm for deuterochloroform. Infrared (IR) spectra were measured with a Mattson Galaxy 3000 FT-IR or a Mattson Polaris FT-IR infrared spectrophotometer. Mass spectra were determined on a VG Micromass 7050E mass spectrometer equipped with a VG 2000 Data system. Elemental analyses were obtained from Altantic Microlabs Inc., Norcross, GA.

**Representative Synthesis of Aldehydes 2: (*E*)-2-Methyl-5-phenyl-2-pentenal 2a.** *General procedure for Horner-Emmons olefination.* In a dry 250 mL round bottomed flask equipped with a rubber septum, nitrogen inlet, and magnetic stir bar, ethyl 2-diethylphosphopropionate (2.097 g, 8.801 mmol), $CH_3CN$ (60 mL) and LiCl (0.377 g, 8.90 mmol) were combined. 1,8-Diaza-bicyclo[5.4.0]undec-7-ene (DBU) (1.32 mL, 8.79 mmol) was added via syringe. The reaction mixture was allowed to stir at rt for 15 min, then cooled to 0 °C. Dihydrocinnamaldehyde (0.77 mL, 5.9 mmol) in $CH_3CN$ (5 mL) was then added dropwise via cannula and the reaction mixture was monitored by TLC. The reaction was complete within 30 min and was then quenched with sat'd $NH_4Cl$ (50 mL) and extracted with $Et_2O$ (3 x 20 mL). Radial chromatography (silica gel, 4 mm plate, 1:9 EtOAc/Hex) provided ethyl (*E*)-2-methyl-5-phenyl-2-pentenoate (1.132 g, 89%) as a clear, colorless oil. $^1$H and $^{13}$C NMR and IR were in accordance with previously published data.[1] $R_f$ 0.53 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.37-

7.27 (m, 2H), 7.23-7.18 (m, 3H), 6.80 (tq, $J$ = 7.4, 1.5 Hz, 1H), 4.18 (q, $J$ = 7.1 Hz, 2H), 2.75 (t, $J$ = 7.8 Hz, 2H), 2.49 (dt, $J$ = 7.8, 7.8 Hz, 2H), 1.78 (s, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 168.4, 141.5, 141.1, 128.6, 128.5, 126.3, 60.7, 35.0, 30.8, 14.5, 12.5 (2 $sp^2$ carbon resonances are overlapping); IR (thin film) 3087, 3061, 3035, 3016, 1709 $cm^{-1}$.

*General procedure for DIBALH reduction.* Ethyl (*E*)-2-methyl-5-phenyl-2-pentenoate (1.049 g, 4.803 mmol) was dissolved in $CH_2Cl_2$ (48 mL) in a dry 100 mL round-bottomed flask fitted with rubber septum, nitrogen inlet, and magnetic stirbar. The solution was cooled to –78 °C and diisobutylaluminum hydride (DIBALH) (6.5 mL of a 1.5 M solution, 9.8 mmol) was added dropwise via syringe. TLC indicated that the reaction was complete after 15 min. The reaction was quenched with saturated aqueous potassium sodium tartrate (10 mL) and stirred 5 h. The layers were separated and the aqueous layer extracted with $CH_2Cl_2$ (3 x 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Column chromatography (silica gel, 185 x 35 mm, 1:4 EtOAc/Hex and increased concentration to 1:1 EtOAc/Hex) provided (*E*)-2-methyl-5-phenyl-2-pentenol (0.792 g, 94%) as a clear, colorless oil. $^1$H and $^{13}$C NMR and IR are consistent with previously published data.[2] $R_f$ 0.42 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.30-7.27 (m, 2H), 7.2-7.15 (m, 3H), 5.47 (tq, $J$ = 7.1, 1.4 Hz, 1H), 4.00 (d, $J$ = 5.2 Hz, 2H), 2.68 (t, $J$ = 7.9 Hz, 2H), 2.37 (dt, $J$ = 7.9, 7.9 Hz, 2H) overlapping with 2.36 (br s, 1H), 1.62 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 142.2, 135.6, 128.6, 128.5, 126.0, 125.4, 69.0, 35.9, 29.7, 13.8; IR (thin film) 3336 (br), 2923, 2855 $cm^{-1}$.

*General procedure for TPAP oxidation.* (*E*)-2-Methyl-5-phenyl-2-pentenol (0.761 g, 4.32 mmol) was dissolved in $CH_2Cl_2$ (33 mL) in a dry 100 mL round-bottomed flask fitted with rubber septum, nitrogen inlet, and magnetic stirbar. Crushed 4Å molecular sieves (0.984 g) and 4-methylmorpholine-N-oxide (NMO) (0.597 g, 5.18 mmol) were added and stirred 5 min. Tetrapropylammonium perruthenate (TPAP) (0.074 g, 0.21 mmol, 3.5 mol %) was added slowly. TLC showed the reaction was complete after 30 min. The slurry was concentrated and eluted over silica with $CH_2Cl_2$ and EtOAc. The crude product was carried on without further purification, providing (*E*)-2-methyl-5-phenyl-2-pentenal **2a** (0.652 g, 87%) as a brown oil. $R_f$ 0.40 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 9.39 (s, 1H), 7.33-7.28 (m, 2H), 7.25-7.18 (m, 3H), 6.51 (dq, $J$ = 7.3, 1.4 Hz, 1H), 2.83 (t, $J$ = 7.7 Hz, 2H), 2.69 (dt, $J$ = 7.7, 7.7 Hz, 2H), 1.69 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 195.4, 153.4, 140.8, 140.1, 128.8, 128.6, 126.5, 34.6, 30.9, 9.4; IR (thin film) 2915, 2857, 2823, 2760, 2713, 1683, 1646 $cm^{-1}$.

**(*E*)- 5-(3-Methoxyphenyl)-2-methyl-2-pentenal 2b.** The procedures described above for **2a** were carried out using 3-methoxydihydrocinnamaldehyde in the initial Horner-Emmons step.

Ethyl (*E*)-5-(3-methoxyphenyl)-2-methyl-2-pentenoate: colorless oil; $R_f$ 0.65 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.21 (t, $J$ = 7.6 Hz, 1H), 6.83-6.74 (m, 4H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.80 (s, 3H), 2.73 (t, $J$ = 7.8 Hz, 2H), 2.48 (dt, $J$ = 7.8, 7.8 Hz, 2H), 1.80-1.79 (d, $J$ = 1.3 Hz, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 168.4, 159.9, 143.1, 141.1, 129.7, 128.7, 121.0, 114.4, 111.6, 60.7, 55.4, 35.0, 30.7, 14.5, 12.5; IR (thin film) 2980, 2936, 1706 $cm^{-1}$; Anal. calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.42; H, 8.12.

(*E*)-5-(3-Methoxyphenyl)-2-methyl-2-pentenol: pale yellow oil; $R_f$ 0.74 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.23-7.19 (m, 1H), 6.81-6.78 (m, 1H), 6.76-6.73 (m, 2H), 5.47 (tq, $J$ = 7.1, 1.3 Hz, 1H), 4.00 (s, 2H), 3.81 (s, 3H), 2.66 (t, $J$ = 7.6 Hz, 2H), 2.36 (dt, $J$ = 7.6, 7.6 Hz, 2H), 1.64 (s, 3H), 1.39 (br s, 1H); $^{13}$C NMR ($CDCl_3$) δ 159.8, 143.9, 135.7, 129.5, 125.5, 121.1, 114.5, 111.2, 69.1, 55.3, 35.9, 29.6, 13.9; IR (thin film) 3358 (br), 2935, 2922, 2857, 2835 $cm^{-1}$.

(*E*)-5-(3-Methoxyphenyl)-2-methyl-2-pentenal **2b**: pale yellow oil; $R_f$ 0.67 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 9.39 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.81-6.74 (m, 3H), 6.51 (tq, *J* = 7.2, 1.4 Hz, 1H), 3.81 (s, 3H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.68 (dt, *J* = 7.6, 7.6 Hz, 2H), 1.71 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 195.4, 160.0, 153.4, 142.4, 140.1, 129.8, 120.9, 114.5, 111.6, 55.4, 34.6, 30.7, 9.4; IR (thin film) 2927, 2835, 2763, 2713, 1684 cm$^{-1}$.

**(*E*)- 5-(3,4-Methylenedioxyphenyl)-2-methyl-2-pentenal 2c.** The procedures described above for **2a** were carried out using 3,4-methylenedioxydihydrocinnamaldehyde in the initial Horner-Emmons step.

(*E*)-5-(3,4-Methylenedioxyphenyl)-2-methyl-2-pentenoate: pale yellow oil; $R_f$ 0.69 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.77 (tq, *J* = 7.4, 1.4 Hz, 1H ), 6.73 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.44 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.79 (d, *J* = 1.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 168.4, 147.8, 146.0, 141.0, 135.3, 128.7, 121.3, 109.0, 108.4, 101.0, 60.7, 34.7, 31.1, 14.5, 12.6; IR (thin film) 2978, 2924, 2900, 1706 cm$^{-1}$; Anal. calcd for $C_{15}H_{18}O_2$: C, 68.68; H, 6.92. Found C, 68.85; H, 6.86.

(*E*)-5-(3,4-Methylenedioxyphenyl)-2-methyl-2-pentenol: pale yellow oil; $R_f$ 0.45 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 5.44 (tq, *J* = 7.0, 1.4 Hz, 1H), 3.99 (s, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.31 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.63 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 147.7, 145.8, 136.1, 135.7, 125.3, 121.3, 109.1, 108.3, 101.0, 69.1, 35.6, 30.0, 13.9; IR (thin film) 3226 (br), 2937, 2922 cm$^{-1}$.

(*E*)-5-(3,4-methylenedioxyphenyl)-2-methyl-2-pentenal **2c**: pale yellow oil; $R_f$ 0.67 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 9.38 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.7 Hz, 1H)), 6.48 (tq, *J* = 7.2, 1.3 Hz, 1H), 5.94 (s, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.63 (dt, *J* = 7.6, 7.6 Hz, 2H), 1.69 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 195.4, 153.3, 147.9, 146.2, 140.1, 134.6, 121.4, 108.9, 108.5, 101.1, 34.4, 31.1, 9.4; IR (thin film) 2924, 2857, 2777, 2715, 1683 cm$^{-1}$.

**Representative Synthesis of Dienones 3: (*E*)-2,4-Dimethyl-7-phenyl-1,4-heptadien-3-one 3a.** *General procedure for Grignard reaction.* In a dry 10 mL round bottomed flask equipped with a magnetic stir bar, nitrogen inlet, reflux condenser, and rubber septum, magnesium powder (0.031 g, 1.3 mmol) was stirred with THF(2.0 mL). 2-Bromopropene (0.088 mL, 0.99 mmol) was added dropwise until exothermic reaction began, and then one drop at a time allowing the flask to cool between drops. When all of the bromide had been added, the Grignard reagent was cooled to 0 °C. (*E*)-2-Methyl-5-phenyl-2-pentenal **2a** (0.132 g, 0.760 mmol) was added to the Grignard reagent via cannula, and the reaction was monitored by TLC. The reaction was was complete within five minutes and was quenched with saturatedd $NH_4Cl$ (5 mL) and extracted with $Et_2O$ (3 x 5 mL). The combined $Et_2O$ layers were then dried ($MgSO_4$) and concentrated. Radial chromatography (silica gel, 2 mm plate, 1:4 EtOAc/Hex) provided (*E*)-2,4-dimethyl-7-phenyl-1,4-heptadien-3-ol (0.116 g, 71%) as a clear, pale yellow oil. $R_f$ 0.32 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 5.55 (tdq, *J* = 7.1, 1.1, 1.1 Hz, 1H), 5.05 (br s, 1H), 4.91 (dq, *J* = 1.5, 1.1 Hz, 1H), 4.19 (s, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.39 (dt, *J* = 7.7, 7.7 Hz, 2H), 1.57 (br s, 3H), 1.47 (br s, 3H); $^{13}$C NMR ($CDCl_3$) δ 145.5, 142.2, 135.8, 128.6, 128.5, 127.0, 126.0, 110.9, 80.9, 35.9, 29.8, 18.9, 11.6; IR (thin film) 3406 (br), 3027, 2856 cm$^{-1}$; Anal. calcd for $C_{15}H_{20}O$: C, 83.22; H, 9.32. Found C, 83.29; H, 9.34.

*General procedure for barium manganate oxidation.* In a dry 10 mL round-bottomed flask equipped with a magnetic stir bar, nitrogen inlet, and rubber septum, (*E*)-2,4-dimethyl-7-phenyl-1,4-heptadien-3-ol (0.111 g, 0.514 mmol) was dissolved in $CH_2Cl_2$ (5 mL) and combined with barium manganate (0.647 g, 2.69 mmol). After 5 days, TLC indicated that the dienol was consumed. The reaction mixture was concentrated, and the slurry was filtered over a pad of celite on silica in $CH_2Cl_2$, followed by washing with EtOAc. The eluent was concentrated and radial chromatography (silica gel, 2 mm plate, 1:9 EtOAc/Hex) provided (*E*)-2,4-dimethyl-7-phenyl-1,4-heptadien-3-one **3a** (0.075 g, 68%) as a clear, pale yellow oil: $R_f$ 0.50 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.32-7.28 (m, 2H), 7.23-7.18 (m, 3H), 6.39 (tq, *J* = 7.2, 1.3 Hz, 1H), 5.54 (dq, *J* = 1.6, 1.0 Hz, 1H), 5.33-5.32 (m, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.56 (dt, *J* = 7.6, 7.6 Hz, 2H), 1.92 (br s, 3H), 1.79 (br s, 3H); $^{13}$C NMR ($CDCl_3$) δ 200.8, 144.0, 143.2, 141.3, 136.6, 128.7, 128.6, 126.4, 123.1, 35.0, 30.9, 19.4, 12.5; IR (thin film) 2924, 2857, 1650 cm$^{-1}$.

**(*E*)-2,4-Dimethyl-7-(3-methoxyphenyl)-1,4-heptadien-3-one 3b.** The general procedures described above for **3a** were followed using **2b** in place of **2a**.

(*E*)-7-(3-Methoxyphenyl)-2,4-dimethyl-1,4-heptadiene-3-ol: colorless oil; $R_f$ 0.66 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.20 (td, *J* = 7.7, 1.3 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.75-6.72 (m, 2H), 5.54 (tdd, *J* = 7.1, 1.2, 1.2 Hz, 1H), 5.05 (s, 1H), 4.92-4.90 (m, 1H), 4.39 (s, 1H), 3.80 (s, 3H), 2.68 (t, *J* = 7.4, Hz, 2H), 2.38 (dt, *J* = 7.4, 7.4 Hz, 2H), 1.57 (s, 3H), 1.48 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 159.8, 145.5, 143.8, 135.8, 129.5, 127.0, 121.1, 114.5, 111.2, 110.9, 80.8, 55.4, 35.9, 29.7, 18.9, 11.6; IR (thin film) 3451 (br), 2937, 2921, 2856, 2830 cm$^{-1}$.

(*E*)-7-(3-Methoxyphenyl)-2,4-dimethyl-1,4-heptadiene-3-one **3b**: pale yellow oil; $R_f$ 0.47 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.80-6.73 (m, 3H), 6.39 (tq, *J* = 7.2, 1.3 Hz, 1H), 5.54 (dq, *J* = 1.5, 1.5 Hz, 1H), 5.33 (s, 1H), 3.80 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.56 (dt, *J* = 7.6, 7.6 Hz, 2H), 1.92 (br s, 3H), 1.80 (br s, 3H); $^{13}$C NMR ($CDCl_3$) δ 200.8, 159.9, 144.0, 143.2, 142.9, 136.6, 129.7, 123.1, 120.9, 114.4, 111.5, 55.4, 35.0, 30.8, 19.4, 12.5; IR (thin film) 2924, 2836, 1643 cm$^{-1}$; Anal. calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.60;H, 8.23.

**(*E,E'*)-8-(3-Methoxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-one 3c.** *General procedure for Shapiro reaction.* 3-Pentanone trisyl hydrazone (0.489 g, 1.34 mmol) was dissolved in tetrahydrofuran (13 mL) and cooled to -78 °C in a dry 50 mL round bottomed flask fitted with rubber septum, nitrogen inlet, and magnetic stir bar. *Sec*-BuLi (1.23 M in hexane, 2.2 mL, 2.7 mmol) was added dropwise by syringe and the mixture was allowed to stir at –78 °C for 1.5 h. Following this period, the reaction was placed in a 0 °C bath for 30 min or until nitrogen evolution ceased. After recooling to -78 °C, (*E*)-5-(3-methoxyphenyl)-2-methyl-2-pentenal **2b** (0.245 g, 1.28 mmol) was added via cannula in a soultion with THF (2 mL). The reaction was monitored by TLC and quenched with saturated $NH_4Cl$ (10 mL) upon consumption of aldehyde. The crude product was extracted with $Et_2O$ (3 x 10 mL), dried ($MgSO_4$), concentrated, and purified by radial chromatography (silica gel, 2 mm plate, 1:10 to 1:4 EtOAc/Hex) to yield 0.165 g (47%) (*E,E'*)-8-(3-methoxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-ol as a clear, pale yellow oil: $R_f$ 0.64 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.76-6.73 (m, 2H), 5.57 (tdq, *J* = 7.1, 1.2, 1.2 Hz, 1H), 5.53 (q, *J* = 6.8 Hz, 1H), 4.40 (s, 1H), 3.81 (s, 3H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.38 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.04-1.97 (m, 1H), 1.91-1.83 (m, 1H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.57 (br s, 1H), 1.46 (s, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 159.8, 144.0, 142.0, 136.4, 129.5, 125.8, 121.1, 120.3, 114.5, 111.2,

80.6, 55.4, 36.0, 29.8, 20.5, 13.7, 13.1, 12.4; IR (thin film) 3453 (br), 2961, 2929, 2871, 2857 $cm^{-1}$.

This material was oxidized with barium manganate per the procedure described above for **3a** to give (*E,E'*)-8-(3-methoxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-one **3c** as a pale yellow oil: $R_f$ 0.69 (1:1 EtOAc/Hex); $^1H$ NMR ($CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 1H), 6.79-6.73 (m, 3H), 6.12 (tq, *J* = 7.2, 1.5 Hz, 1H), 6.00 (q, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.53 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 1.79 (br s, 3H), 1.76 (d, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) δ 201.5, 159.9, 143.4, 143.1, 140.8, 137.6, 135.8, 129.6, 121.0, 114.6, 111.4, 55.4, 35.1, 30.4, 20.2, 14.1, 13.2, 13.1; IR (thin film) 2962, 2931, 2836, 1634 $cm^{-1}$.

**(*E*)-1-Cyclohexenyl-5-(3-methoxyphenyl)-2-methyl-2-penten-1-one 3d.** The general procedures described above for **3c** were followed using cyclohexanone trisyl hydrazone in place of 3-pentanone trisyl hydrazone.

(*E*)-1-Cyclohexenyl-5-(3-methoxyphenyl)-2-methyl-2-penten-1-ol: pale yellow oil; $R_f$ 0.26 (1:4 EtOAc/Hex); $^1H$ NMR ($CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.76-6.72 (m, 2H), 5.73 (dddd, *J* = 3.4, 3.4, 1.8, 1.8 Hz, 1H), 5.51 (tqd, *J* = 7.1, 1.2, 1.2 Hz, 1H), 4.30 (s, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.38 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.07-2.02 (m, 2H), 1.80-1.67 (m, 2H), 1.62-1.51 (m, 5H), 1.46 (s, 3H); $^{13}C$ NMR ($CDCl_3$) δ 159.8, 143.9, 138.0, 136.2, 129.4, 125.7, 122.8, 121.1, 114.5, 111.2, 80.9, 55.3, 36.0, 29.7, 25.2, 24.6, 22.9, 22.8, 12.3; IR (thin film) 3418 (br), 2924, 2855, 2835 $cm^{-1}$. Anal. calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found C, 79.41; H, 9.12.

(*E*)-1-Cyclohexenyl-5-(3-methoxyphenyl)-2-methyl-2-penten-1-one **3d**: pale yellow oil; $R_f$ 0.38 (1:4 EtOAc/Hex); $^1H$ NMR ($CDCl_3$) δ 7.22 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 6.81-6.74 (m, 3H), 6.31 (ddd, *J* = 3.9, 2.2, 1.7 Hz, 1H), 6.12 (tq, *J* = 7.2, 1.5 Hz, 1H), 3.81 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.54 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.27-2.23 (m, 2H), 2.19-2.14 (m, 2H), 1.80 (d, *J* = 1.4 Hz, 3H), 1.69-1.57 (m, 4H); $^{13}C$ NMR ($CDCl_3$) δ 200.9, 159.9, 143.2, 140.2, 140.0, 138.4, 136.6, 129.6, 121.0, 114.5, 111.4, 55.4, 35.1, 30.4, 25.9, 24.5, 22.3, 21.9, 13.2; IR (thin film) 2933, 2858, 2836, 1632 $cm^{-1}$.

**(*E*)-7-(3,4-Methylenedioxyphenyl)-2,4-dimethyl-1,4-heptadien-3-one 3e.** The general procedures described above for **3a** were followed using **2c** in place of **2a**.

(*E*)-7-(3,4-Methylenedioxyphenyl)-2,4-dimethyl-1,4-heptadien-3-ol: colorless oil; $R_f$ 0.27 (1:4 EtOAc/Hex); $^1H$ NMR ($CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 5.52 (tqd, *J* = 7.1, 1.2, 1.2 Hz, 1H), 5.05 (br s, 1H), 4.91 (br s, 1H), 4.39 (br s, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.34 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.58 (br s, 1H) overlapping with 1.57 (br s, 3H), 1.48 (br s, 3H); $^{13}C$ NMR ($CDCl_3$) δ 147.7, 145.8, 145.5, 136.0, 135.8, 126.8, 121.3, 110.9, 109.1, 108.3, 100.9, 80.8, 35.6, 30.1, 18.9, 11.6. Anal. calcd for $C_{16}H_{20}O_3$: C, 73.52; H, 7.74. Found C, 73.59; H, 7.81.

(*E*)-7-(3,4-Methylenedioxyphenyl)-2,4-dimethyl-1,4-heptadien-3-one **3e**: colorless oil; $R_f$ 0.38 (1:4 EtOAc/Hex); $^1H$ NMR ($CDCl_3$) δ 6.73 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.37 (tq, *J* = 7.2, 1.3 Hz, 1H), 5.93 (s, 2H), 5.55 (dq, *J* = 1.5, 1.5 Hz, 1H), 5.34 (br s, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.51 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.93 (br s, 3H), 1.79 (br s, 3H), $^{13}C$ NMR ($CDCl_3$) δ 200.8, 147.9, 146.1, 144.0, 143.0, 136.6, 135.2, 123.0, 121.3, 108.9, 108.4, 101.1, 34.7, 31.1, 19.4, 12.5; IR (thin film) 2922, 2863, 1652 $cm^{-1}$.

**(*E,E'*)-8-(3,4-Methylenedioxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-one 3f.** The general procedures described above for **3c** were followed using **2c** in place of **2b**.

(*E,E'*)-8-(3,4-Methylenedioxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-ol: pale yellow oil; $R_f$ 0.25 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 5.58-5.48 (m, 2H), 4.39 (br s, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.33 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.06 (dq, *J* = 13.6, 7.4 Hz, 1H), 1.87 (dq, *J* = 13.0, 7.4 Hz, 1H), 1.65 (d, *J* = 6.7 Hz, 3H), 1.59 (br s, 1H), 1.45 (br s, 3H), 0.91 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 147.7, 145.7, 141.9, 136.4, 136.2, 125.6, 121.3, 120.3, 109.1, 108.3, 100.9, 80.6, 35.7, 30.2, 20.6, 13.7, 13.2, 12.5; IR (thin film) 3438 (br), 2962, 2927, 2872 cm$^{-1}$.

(*E,E'*)-8-(3,4-Methylenedioxyphenyl)-3-ethyl-5-methyl-2,5-octadien-4-one **3f**: colorless oil; $R_f$ 0.40 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.74 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 1.5 Hz, 1H), 6.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.11 (tq, *J* = 7.1, 1.3 Hz, 1H), 6.01 (q, *J* = 7.0 Hz, 1H), 5.93 (s, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.48 (dt, *J* = 7.4, 7.4 Hz, 2H), 2.34 (q, *J* = 7.5 Hz, 2H), 1.79 (d, *J* = 7.0 Hz, 3H),1.78 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 201.5, 147.8, 146.0, 143.2, 140.8, 137.6, 135.7, 135.3, 121.4, 109.0, 108.3, 101.0, 34.8, 30.9, 20.2, 14.1, 13.2, 13.1; Anal. calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found C, 75.52; H, 7.73.

**(*E*)-1-Cyclohexenyl-5-(3,4-methylendioxyphenyl)-2-methyl-2-penten-1-one 3g.** The general procedures described above for **3d** were followed using **2c** in place of **2b**.

(*E*)-1-Cyclohexenyl-5-(3,4-methylendioxyphenyl)-2-methyl-2-penten-1-ol: pale yellow oil; $R_f$ 0.25 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 1H), 5.91 (s, 1H), 5.72 (dddd, *J* = 3.7, 3.7, 1.8, 1.5 Hz, 1H), 5.48 (tdq, *J* = 7.2, 1.2, 1.2 Hz, 1H), 4.29 (br s, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.33 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.07-2.02 (m, 2H), 1.81-1.67 (m, 2H), 1.61-1.52 (m, 4H), 1.50 (br s, 1H), 1.45 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 147.7, 145.8, 138.0, 136.3, 136.2, 125.6, 122.9, 121.4, 109.1, 108.3, 100.9, 80.9, 35.7, 30.0, 25.2, 24.6, 22.9, 22.8, 12.3; IR (thin film) 3360 (br), 2960, 2927, 2872 cm$^{-1}$.

(*E*)-1-Cyclohexenyl-5-(3,4-methylendioxyphenyl)-2-methyl-2-penten-1-one **3g**: pale yellow oil; $R_f$ 0.39 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 6.73 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.31 (dddd, *J* = 3.7, 3.7, 2.2, 1.6 Hz, 1H), 6.10 (tq, *J* = 7.2, 1.4 Hz, 1H), 5.92 (s, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.48 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.26-2.22 (m, 2H), 2.19-2.15 (m, 2H), 1.78 (d , *J* = 0.8 Hz, 3H), 1.68-1.58 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ 200.9, 147.9, 146.0, 140.1, 139.9, 138.5, 136.7, 135.5, 121.4, 109.0, 108.4, 101.1, 34.9, 30.8, 25.9, 24.5, 22.3, 21.9, 13.2.

**(*E*)-5-(3'-Furyl)-2-methyl-2-pentenal (perillenal) 2d.** The Horner-Emmons/reduction/oxidation procedure described above for **2a** was followed using 3-(3'-furyl)propanal.[3]

Ethyl (*E*)-5-(3'-furyl)-2-methyl-2-pentenoate: pale yellow oil; $R_f$ 0.67 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.36-7.34 (m, 1H), 7.26-7.24 (m, 1H), 6.77 (tq, *J* = 7.2, 1.4 Hz, 1H), 6.29-6.27 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.43 (dt, *J* = 7.4, 7.4 Hz, 2H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 168.3, 143.1, 141.1, 139.2, 128.7, 124.3, 111.1, 60.7, 29.4, 24.1, 14.5, 12.6; IR (thin film) 2984, 2930, 2860, 1705 cm$^{-1}$.

(*E*)-5-(3'-Furyl)-2-methyl-2-pentenol: yellow oil; $^1$H NMR consistent with previously published data;[4] $R_f$ 0.43 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.36-7.34 (m, 1H), 7.23-7.21 (m, 1H), 6.28-6.26 (m, 1H), 5.45 (tq, *J* = 7.0, 1.3 Hz, 1H), 4.00 (s, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.30

(dt, $J$ = 7.6, 7.6 Hz, 2H), 1.66 (br s, 3H), 1.58 (br s, 1H); $^{13}$C NMR ($CDCl_3$) δ 142.9, 139.1, 135.7, 125.5, 124.9, 111.2, 69.1, 28.3, 24.9, 13.9.

(*E*)-5-(3-Furyl)-2-methyl-2-pentenal **2d**: yellow oil; $^1$H NMR consistent with previously published data;[6,5] $R_f$ 0.60 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 9.39 (s, 1H), 7.36-7.37 (m, 1H), 7.25-7.24 (m, 1H), 6.49 (tq, $J$ = 7.1, 1.3 Hz, 1H), 6.29-6.28 (m, 1H), 2.67-2.60 (m, 4H), 1.72 (br s, 3H); $^{13}$C NMR ($CDCl_3$) δ 195.3, 153.4, 143.3, 140.1, 139.3, 123.8, 110.9, 29.5, 23.8, 9.5.

**(*E*)-7-(3'-Furyl)-2,4-dimethyl-1,4-heptadien-3-one 3h.** The general procedures described above for **3a** were followed using **2d** in place of **2a**.

(*E*)-7-(3'-Furyl)-2,4-dimethyl-1,4-heptadien-3-ol: colorless oil; $R_f$ 0.70 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.35 (t, $J$ = 1.6 Hz, 1H), 7.23-7.22 (m, 1H), 6.30-6.28 (m, 1H), 5.54 (tdq, $J$ = 7.1, 1.2, 1.2 Hz, 1H), 5.07 (br s, 1H), 4.93 (dq, $J$ = 4.0, 1.5 Hz, 1H), 4.41 (br s, 1H), 2.51 (t, $J$ = 7.6 Hz, 2H), 2.33 (dt, $J$ = 7.6, 7.6 Hz, 2H), 1.59 (br s, 3H), 1.57 (br s, 1H), 1.52 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 145.6, 142.9, 139.1, 135.8, 127.0, 124.9, 111.2, 111.0, 80.8, 28.4, 24.9, 28.8, 11.7.

(*E*)-7-(3'-Furyl)-2,4-dimethyl-1,4-heptadien-3-one **3h**: colorless oil; $R_f$ 0.63 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.36 (t, $J$ = 1.5 Hz, 1H), 7.23-7.22 (m, 1H), 6.37 (tq, $J$ = 7.0, 1.3 Hz, 1H), 6.28-6.27 (m, 1H), 5.56 (dq, $J$ = 1.5, 1.5 Hz, 1H), 5.36-5.35 (m, 1H), 2.59 (t, $J$ = 7.0 Hz, 2H), 2.50 (dt, $J$ = 7.0, 7.0 Hz, 2H), 1.93 (dd, $J$ = 1.5, 1.0 Hz, 3H), 1.84-1.82 (m, 3H); $^{13}$C NMR ($CDCl_3$) δ 200.8, 144.1, 143.2, 143.1, 139.2, 136.7, 124.2, 123.1, 111.0, 29.5, 24.1, 19.4, 12.6; Anal. calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found C, 76.15; H, 7.92.

**Cyclization of 3a. 2,5-Dimethyl-3-(2-phenylethyl)cyclopent-2-en-1-one 4a.** A solution of **3a** (0.073 g, 0.34 mmol) in $CH_2Cl_2$ (35 mL) in a 100 mL round-bottomed flask fitted with magnetic stirbar, nitrogen inlet, and rubber septum, was cooled to –78 °C. $BF_3$•$OEt_2$ (0.180 mL, 1.42 mmol) was added dropwise. The reaction was then allowed to warm slowly to rt, after which TLC indicated **3a** was consumed. The reaction was quenched with $H_2O$ (20 mL), the layers separated, and the aqeous layer extracted with $CH_2Cl_2$. The combined organic layers were dried ($MgSO_4$), concentrated, and subjected to radial chromatography (silica gel, 2 mm plate, 1:4 EtOAc/Hex) to provide **4a** (0.036 g, 69%) as a clear, colorless oil: $R_f$ 0.55 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.30-7.26 (m, 2H), 7.23-7.15 (m, 3H), 2.83 (t, $J$ = 7.4 Hz, 2H), 2.75-2.68 (m, 3H), 2.34 (qdd, $J$ = 7.2, 7.2, 2.4 Hz, 1H), 2.06 (br d, $J$ = 18.4 Hz, 1H), 1.57 (t, $J$ = 2.0 Hz, 3H), 1.14 (d, $J$ = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 212.7, 170.7, 140.9, 135.7, 128.7, 128.4, 126.5, 39.6, 38.8, 33.5, 33.1, 16.8, 8.2; IR (thin film) 2962, 2924, 2861, 1697, 1649 cm$^{-1}$.

**Cyclization of Dienones 3b-e and g.** The representative procedure described in reference 10 of the text for the formation of **5f** was followed to give **5b-e** and **5g**.

Benzohydrindenone **5b**: pale yellow oil; single regio- and diastereoisomer by $^1$H and $^{13}$C NMR analysis; $R_f$ 0.39 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.42 (d, $J$ = 8.8 Hz, 1H), 6.71 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.58 (d, $J$ = 2.8 Hz, 1H), 3.76 (s, 3H), 2.88 (ddd, $J$ = 17.4, 12.0, 6.0 Hz, 1H), 2.72 (ddd, $J$ = 17.4, 6.0, 2.0 Hz, 1H), 2.28 (ddq, $J$ = 11.3, 8.2, 7.1 Hz, 1H), 2.19 (ddt, $J$ = 12.0, 6.0, 3.5 Hz, 1H), 2.07 (ddd, $J$ = 12.5, 8.3, 6.1 Hz, 1H), 2.00 (dddd, $J$ = 12.5, 9.8, 6.1, 3.8 Hz, 1H), 1.92-1.85 (m, 2H), 1.36 (s, 3H), 0.99 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 222.6, 158.1, 136.9, 130.3, 127.7, 113.9, 112.8, 55.3, 50.7, 42.9, 41.5, 31.7, 27.2, 25.4, 21.3, 16.0; IR (thin film) 2958, 2926, 2870, 1732 cm$^{-1}$.

Benzohydrindenone **5c**: colorless oil; single regio- and stereoisomer by $^1$H and $^{13}$C NMR analysis; $R_f$ 0.70 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.37 (d, $J$ = 8.7 Hz, 1H), 6.70 (dd, $J$ = 8.6, 2.8 Hz, 1H), 6.57 (d, $J$ = 2.8 Hz, 1H), 3.75 (s, 3H), 2.84 (ddd, $J$ = 17.7, 13.0, 6.5 Hz, 1H), 2.71 (dd, $J$ = 17.5, 5.0 Hz, 1H), 2.04 (dddd, $J$ = 14.0, 5.1, 3.3, 1.8 Hz, 1H), 1.91 (dqd, $J$ = 13.5, 6.2, 3.5 Hz, 1H), 1.83-1.75 (m, 2H), 1.73-1.68 (m, 1H), 1.54-1.42 (m, 2H), 1.35 (s, 3H), 1.12 (d, $J$ = 6.1 Hz, 3H), 0.61 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 221.6, 158.0, 137.0, 130.1, 127.5, 113.9, 112.7, 56.6, 55.3, 51.4, 48.9, 33.2, 27.1, 25.1, 21.9, 18.3, 17.7, 11.1; IR (thin film) 2958, 2923, 2865, 1730 cm$^{-1}$.

Benzohydrindenone **5d**: colorless solid; single regio- and stereoisomer by $^1$H and $^{13}$C NMR analysis; mp 86-88 °C; $R_f$ 0.40 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.66 (d, $J$ = 8.8 Hz, 1H), 6.76 (dd, $J$ = 8.8, 2.4 Hz, 1H), 6.57 (d, $J$ = 2.8 Hz, 1H), 3.77 (s, 3H), 2.79 (ddd, $J$ = 17.5, 13.2, 5.8 Hz, 1H), 2.67 (ddd, $J$ = 17.5, 5.9, 2.4 Hz, 1H), 2.10-2.00 (m, 3H), 1.92-1.80 (m, 4H), 1.76 (ddd, $J$ = 13.1, 11.4, 3.4 Hz, 1H), 1.49-1.40 (m, 1H), 1.42 (s, 3H), 1.29-1.08 (m, 3H), 1.04-0.96 (m, 1H); $^{13}$C NMR ($CDCl_3$) δ 219.6, 157.9, 137.1, 130.7, 128.9, 113.6, 112.8, 55.3, 54.3, 50.7, 48.2, 41.0, 30.6, 28.5, 26.4, 26.1, 25.8, 25.7, 19.1; IR (thin film) 2924, 2855, 1734 cm$^{-1}$.

Benzohydrindenone **5e**: pale yellow oil; single regio- and diastereoisomer by $^1$H and $^{13}$C NMR analysis; $R_f$ 0.39 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.01 (s, 1H), 6.50 (s, 1H), 5.88 (d, $J$ = 1.5 Hz, 1H), 5.86 (d, $J$ = 1.5 Hz, 1H), 2.80 (ddd, $J$ = 17.0, 12.3, 5.9 Hz, 1H), 2.64 (ddd, $J$ = 17.0, 5.9, 2.2 Hz, 1H), 2.28 (ddq, $J$ = 15.4, 11.2, 7.2 Hz, 1H), 2.20-2.14 (m, 1H), 2.06 (ddd, $J$ = 12.5, 8.3, 6.0 Hz, 1H), 1.96 (dddd, $J$ = 12.5, 12.5, 6.0, 3.8, Hz, 1H), 1.90 (dd, $J$ = 1.4, 1.4 Hz, 1H), 1.89-1.83 (m, 1H), 1.35 (s, 3H), 1.01 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 146.4, 129.0, 128.5, 108.7, 100.9, 51.1, 42.8, 41.4, 31.6, 27.2, 25.4, 21.4, 16.0; IR (thin film) 2959, 2925, 2872, 1732 cm$^{-1}$.

Benzohydrindenone **5g**: pale yellow solid; single regio- and stereoisomer by $^1$H and $^{13}$C NMR analysis; mp 124-126 °C; $R_f$ 0.32 (1:4 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.25 (s, 1H), 6.48 (s, 1H), 5.88 (d, $J$ = 1.5 Hz, 1H), 5.84 (d, $J$ = 1.5 Hz, 1H), 2.75-2.66 (m, 1H), 2.62-2.54 (m, 1H), 2.09-2.03 (m, 2H), 2.03-1.97 (m, 1H), 1.85-1.78 (m, 4H), 1.74 (ddd, $J$ = 13.1, 11.2, 3.4 Hz, 1H), 1.47-1.39 (m, 1H), 1.39 (s, 3H), 1.24-1.07 (m, 3H), 1.05-0.97 (m, 1H); $^{13}$C NMR ($CDCl_3$) δ 219.4, 146.4, 146.2, 129.7, 129.1, 109.2, 108.5, 100.9, 54.2, 51.2, 48.1, 41.0, 30.6, 28.5, 26.4, 26.1, 25.7, 25.7, 19.2; IR (thin film) 2924, 2856, 1735 cm$^{-1}$.

**Cyclization of 3h. Furohydrindenone 5h.** (*E*)-7-(3-furyl)-2,4-dimethyl-1,4-heptadien-3-one **3h** (0.042 g, 0.21 mmol) was dissolved in $CH_2Cl_2$ (20 mL) and cooled to –78 °C. $TiCl_4$ (0.060 mL of a 3.51 M solution in $CH_2Cl_2$, 0.21 mmol) was added, and the reaction was allowed to warm to rt; after 15 min at rt, the reaction was quenched with $H_2O$ (10 mL), and stirred overnight. The layers were separated, the aqueous layer was extracted with $CH_2Cl_2$ (3 x 10 mL), dried ($MgSO_4$), and concentrated. Radial chromatography (silica gel, 1 mm plate, 1:4 EtOAc/Hex) provided 0.024 g (56%) of the tricyclic ketone **5h** as a colorless oil and a single regio- and stereoisomer by $^1$H and $^{13}$C NMR analysis: $R_f$ 0.70 (1:1 EtOAc/Hex); $^1$H NMR ($CDCl_3$) δ 7.30 (d, $J$ = 1.9 Hz, 1H), 6.15 (d, $J$ = 1.9 Hz, 1H), 2.51-2.48 (m, 2H), 2.35-2.25 (m, 3H), 2.07 (ddd, $J$ = 8.5, 6.3, 6.3 Hz, 1H), 1.91-1.86 (m, 2H), 1.39 (s, 3H), 1.05 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 218.8, 147.9, 142.8, 117.4, 110.3, 49.8, 43.1, 42.8, 31.7, 29.9, 22.4, 18.8, 15.2; IR (thin film) 2960, 2924, 2853, 1739, 1456 cm$^{-1}$.

**Table 1. Crystal data and structure refinement for 5f.**

| | | |
|---|---|---|
| Identification code | shelxl | |
| Empirical formula | $C_{18}H_{22}O_3$ | |
| Formula weight | 286.36 | |
| Temperature | 200(0.1) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P\,2_1/a$ | |
| Unit cell dimensions | a = 14.8521(3) Å | α= 90°. |
| | b = 13.1882(4) Å | β= 98.9157(17)°. |
| | c = 15.7055(5) Å | γ = 90°. |
| Volume | 3039.11(15) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.252 $Mg/m^3$ | |
| Absorption coefficient | 0.084 $mm^{-1}$ | |
| F(000) | 1232 | |
| Crystal size | 0.30 x 0.21 x 0.13 $mm^3$ | |
| Theta range for data collection | 2.34 to 32.60°. | |
| Index ranges | -19<=h<=19 | |
| | -18<=k<=19 | |
| | -23<=l<=23 | |
| Reflections collected | 16494 | |
| Independent reflections | 9581 [R(int) = 0.0354] | |
| Completeness to theta = 32.60° | 86.4 % | |
| Absorption correction | SCALEPACK | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9581 / 0 / 556 | |
| Goodness-of-fit on $F^2$ | 1.017 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0548, wR2 = 0.1110 | |
| R indices (all data) | R1 = 0.1068, wR2 = 0.1297 | |
| Extinction coefficient | 0.0034(9) | |
| Largest diff. peak and hole | 0.252 and -0.171 $e.Å^{-3}$ | |

**Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 5f.**

| | x | y | z | U(eq)[a] |
|---|---|---|---|---|
| O(1) | 3848(1) | 2621(1) | 4906(1) | 37(1) |
| O(2) | 5103(1) | -753(1) | 6254(1) | 42(1) |
| O(3) | 4182(1) | -1734(1) | 6985(1) | 42(1) |
| C(1) | 3143(1) | 2413(1) | 5170(1) | 28(1) |
| C(2) | 2554(1) | 1475(1) | 4910(1) | 27(1) |
| C(3) | 2935(1) | 595(1) | 5495(1) | 25(1) |
| C(4) | 3874(1) | 373(1) | 5559(1) | 29(1) |
| C(5) | 4211(1) | -416(1) | 6071(1) | 30(1) |
| C(6) | 5056(1) | -1691(1) | 6703(1) | 39(1) |
| C(7) | 3666(1) | -998(1) | 6517(1) | 30(1) |
| C(8) | 2756(1) | -807(1) | 6461(1) | 31(1) |
| C(9) | 2380(1) | 5(1) | 5944(1) | 28(1) |
| C(10) | 1368(1) | 203(1) | 5897(1) | 34(1) |
| C(11) | 982(1) | 930(1) | 5184(1) | 35(1) |
| C(12) | 1624(1) | 1821(1) | 5127(1) | 30(1) |
| C(13) | 1864(1) | 2459(1) | 5950(1) | 32(1) |
| C(14) | 2700(1) | 3071(1) | 5786(1) | 31(1) |
| C(15) | 3369(1) | 3421(1) | 6568(1) | 39(1) |
| C(16) | 3823(1) | 2566(1) | 7121(1) | 42(1) |
| C(17) | 2547(1) | 1209(1) | 3960(1) | 35(1) |
| C(18) | 1081(1) | 3118(2) | 6153(2) | 52(1) |
| O(1') | 10(1) | 1279(1) | 301(1) | 56(1) |
| O(2') | -129(1) | 5016(1) | 1085(1) | 67(1) |
| O(3') | -1284(1) | 5532(1) | 1814(1) | 68(1) |
| C(1') | -732(1) | 1098(1) | 496(1) | 41(1) |
| C(2') | -1604(1) | 1703(1) | 182(1) | 39(1) |
| C(3') | -1566(1) | 2715(1) | 669(1) | 36(1) |
| C(4') | -811(1) | 3351(1) | 635(1) | 42(1) |
| C(5') | -783(1) | 4262(1) | 1048(1) | 46(1) |
| C(6') | -366(2) | 5728(2) | 1694(2) | 72(1) |
| C(7') | -1467(1) | 4569(1) | 1488(1) | 48(1) |

| | | | | |
|---|---|---|---|---|
| C(8') | -2209(1) | 3977(1) | 1529(1) | 49(1) |
| C(9') | -2265(1) | 3025(1) | 1115(1) | 40(1) |
| C(10') | -3087(1) | 2369(2) | 1171(1) | 53(1) |
| C(11') | -3231(1) | 1551(2) | 490(1) | 55(1) |
| C(12') | -2351(1) | 997(1) | 425(1) | 42(1) |
| C(13') | -1900(1) | 448(1) | 1246(1) | 40(1) |
| C(14') | -943(1) | 222(1) | 1056(1) | 43(1) |
| C(15') | -195(1) | 10(2) | 1818(1) | 58(1) |
| C(16') | 14(1) | 892(2) | 2424(1) | 58(1) |
| C(17') | -1696(2) | 1886(2) | -790(1) | 53(1) |
| C(18') | -2426(2) | -482(2) | 1463(2) | 64(1) |

Key: (a) U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

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[2] (a) Daub, G. W.; *et al J. Org. Chem.* **1997**, *62,* 1976-1985. (b) Jung, M. E.; D'Amico, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 7379-7388.

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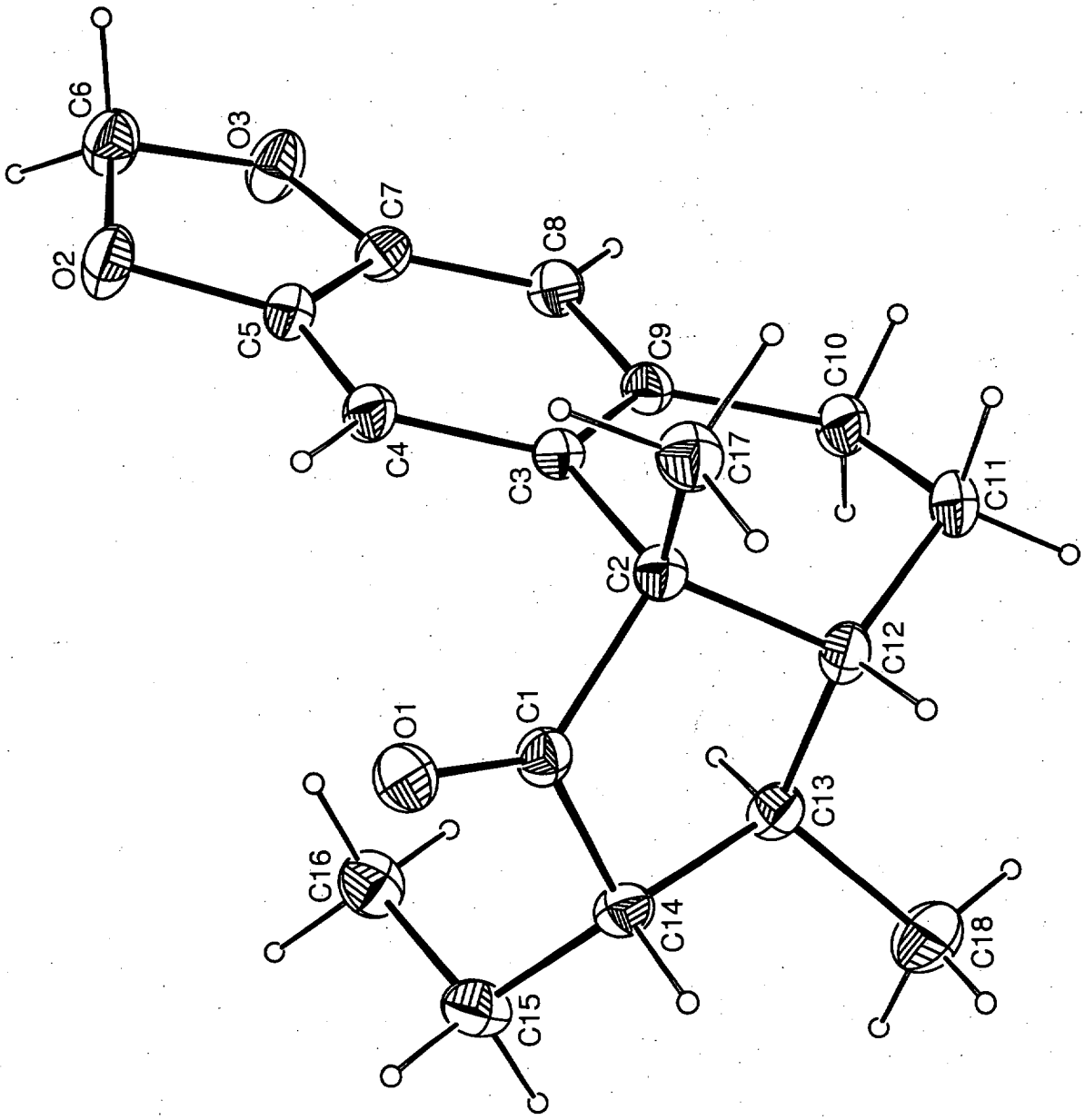
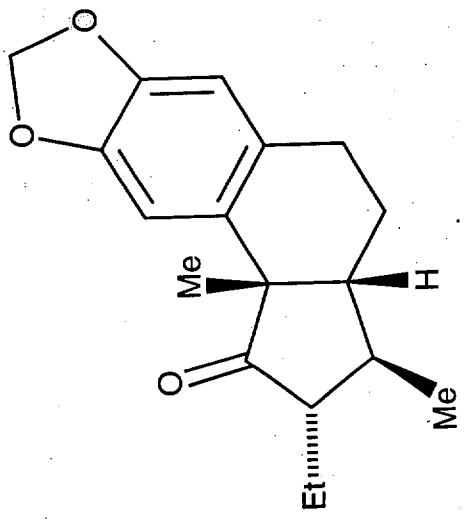
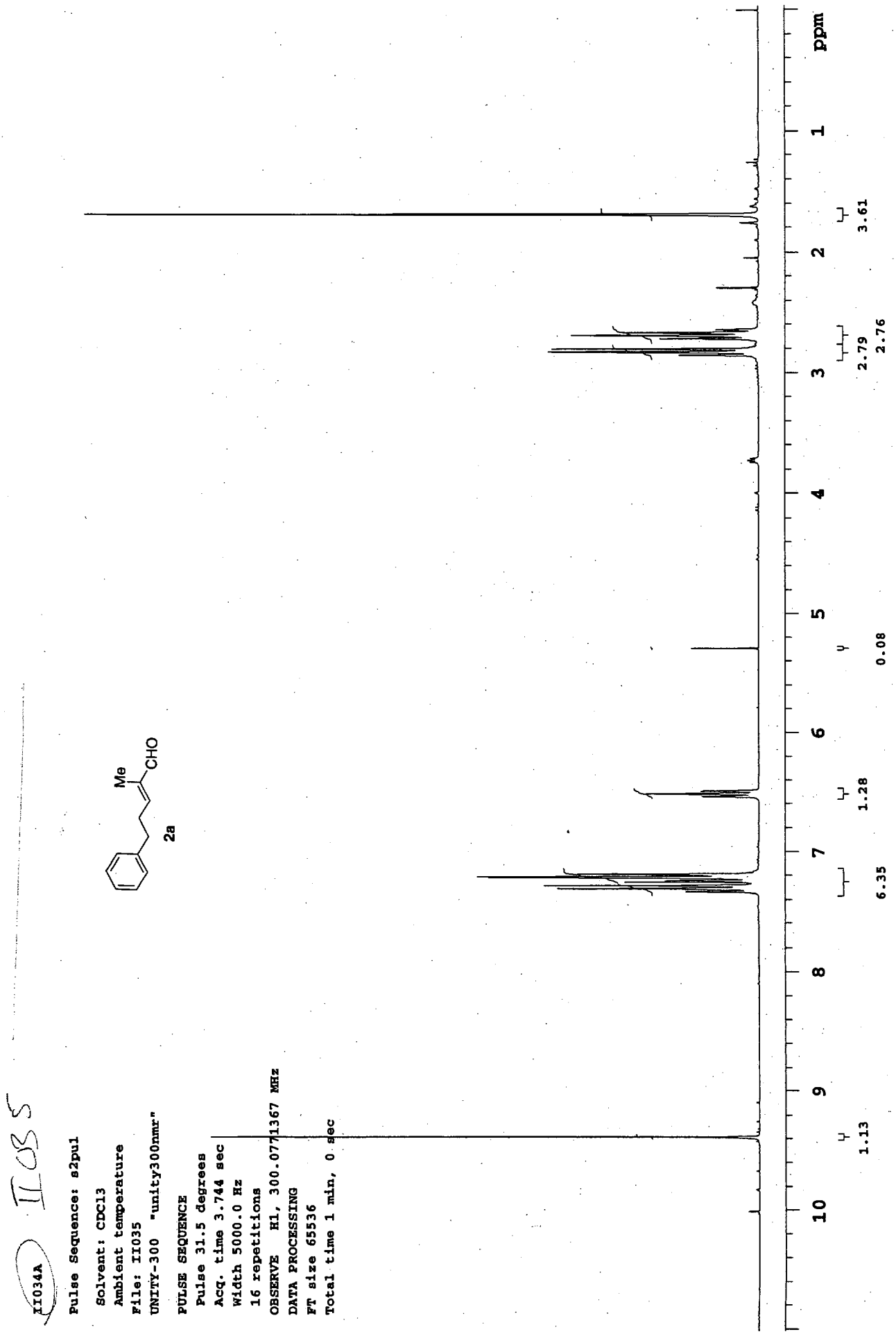
[4] Bock, I.; Bornowski, H.; Ranft, A.; Theis, H. *Tetrahedron* **1990**, *46*, 1199-1210.

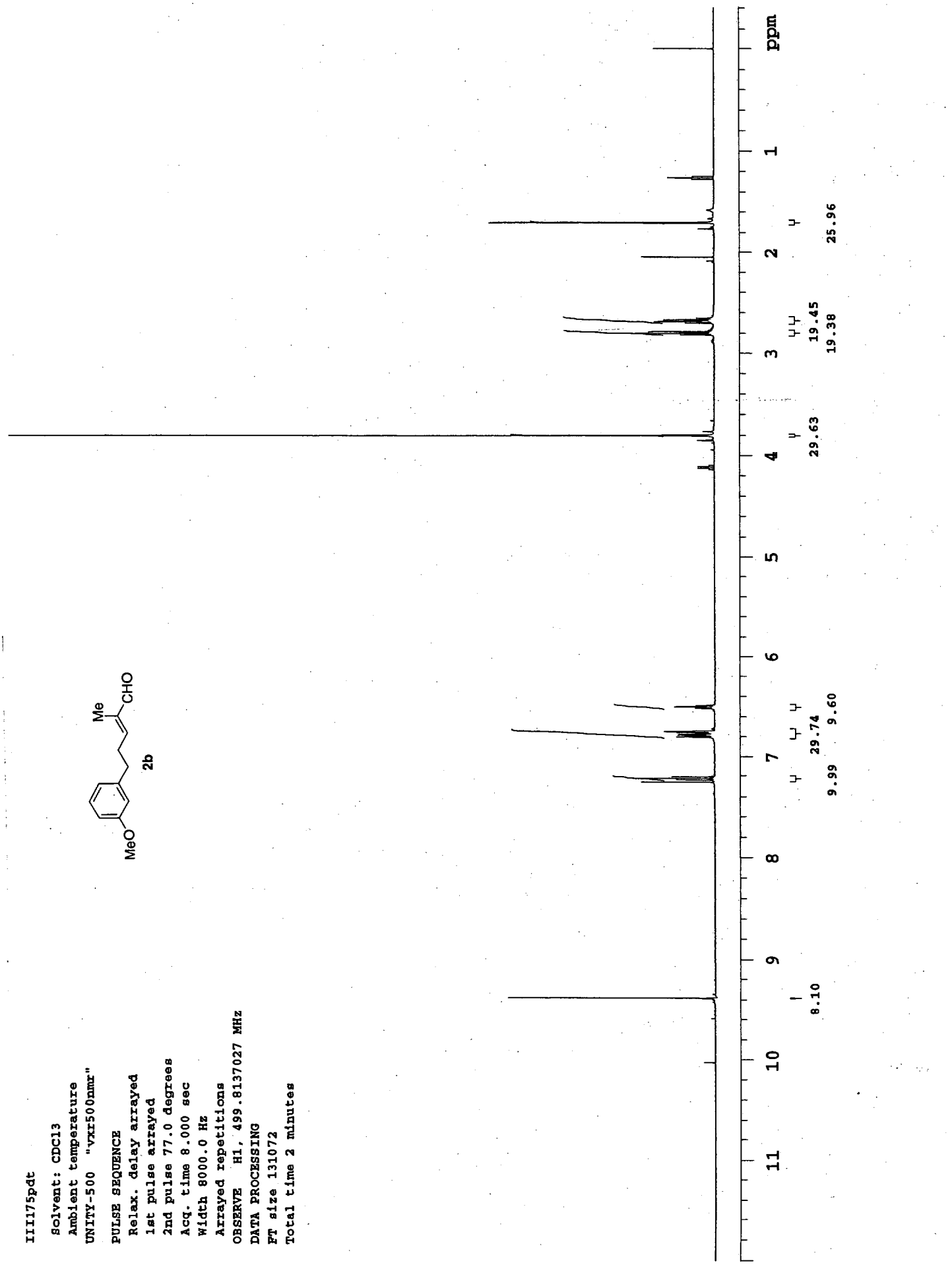
[5] Bernasconi, S.; Colombo, M.; Jommi, G.; Sisti, M. *Gazzetta Chimica Italiana* **1986**, *116*, 69-71.

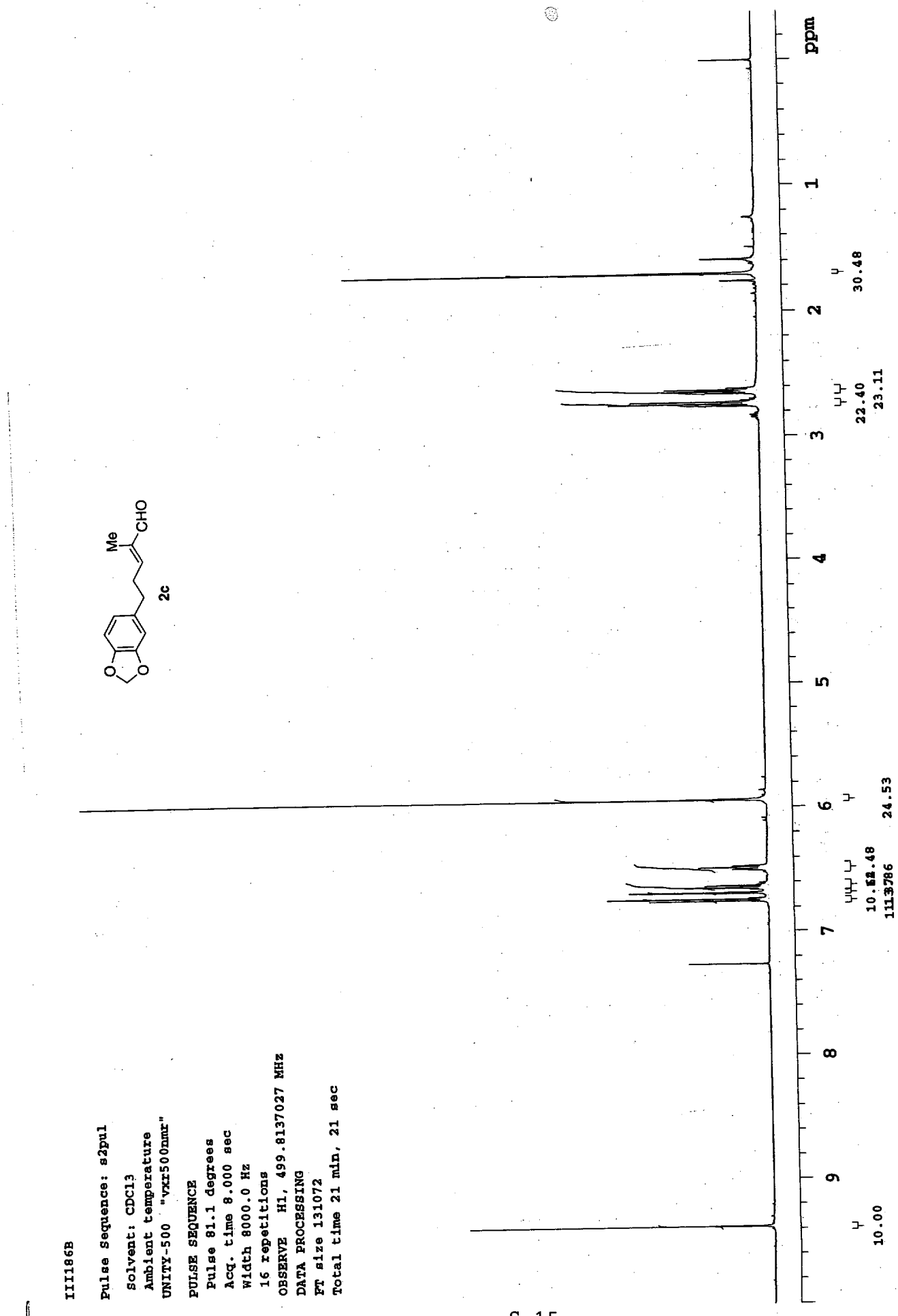

C6
O3
C7
C8
O2
C5
C9
C10
C4
C3
C17
C11
C2
C12
O1
C1
C13
C16
C14
C18
C15

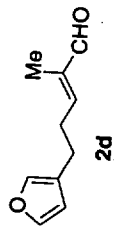

Me
H
Me
Et

**5f**

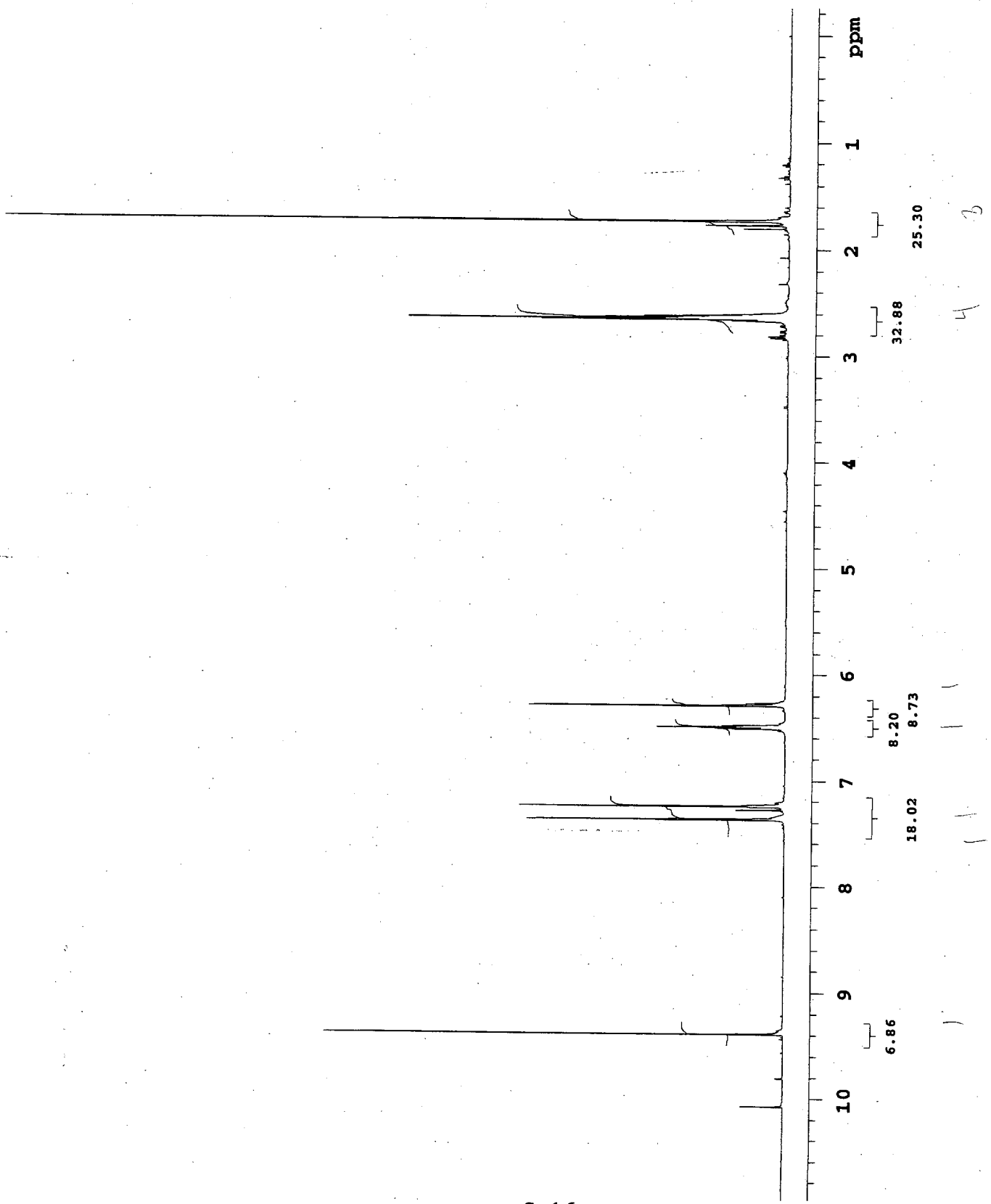


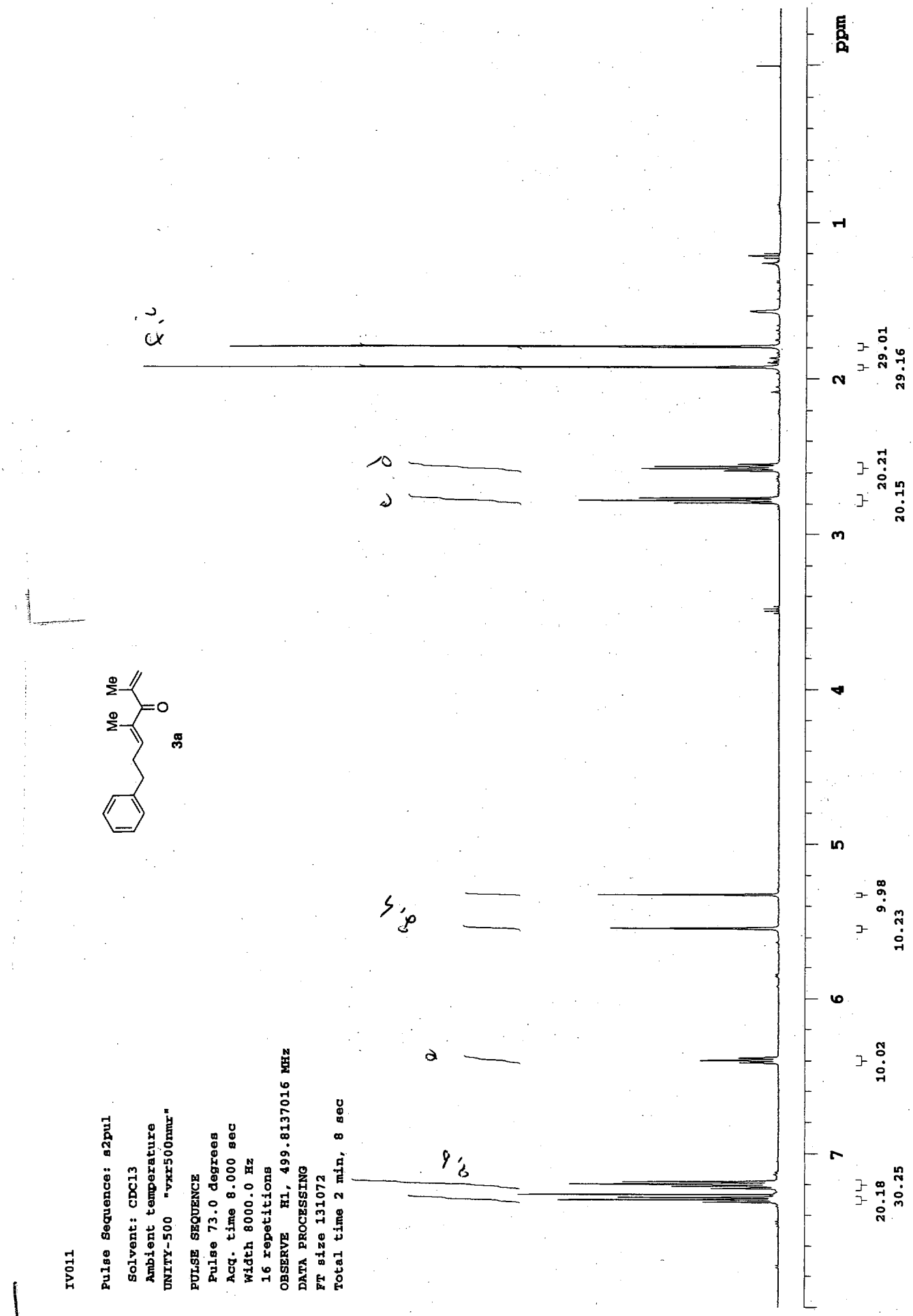

III175pdt
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Relax. delay arrayed
1st pulse arrayed
2nd pulse 77.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
Arrayed repetitions
OBSERVE H1, 499.8137027 MHz
DATA PROCESSING
FT size 131072
Total time 2 minutes
Me
CHO
MeO
2b
ppm
1
2
3
4
5
6
7
8
9
10
11
8.10
9.99
29.74
9.60
29.63
19.45
19.38
25.96

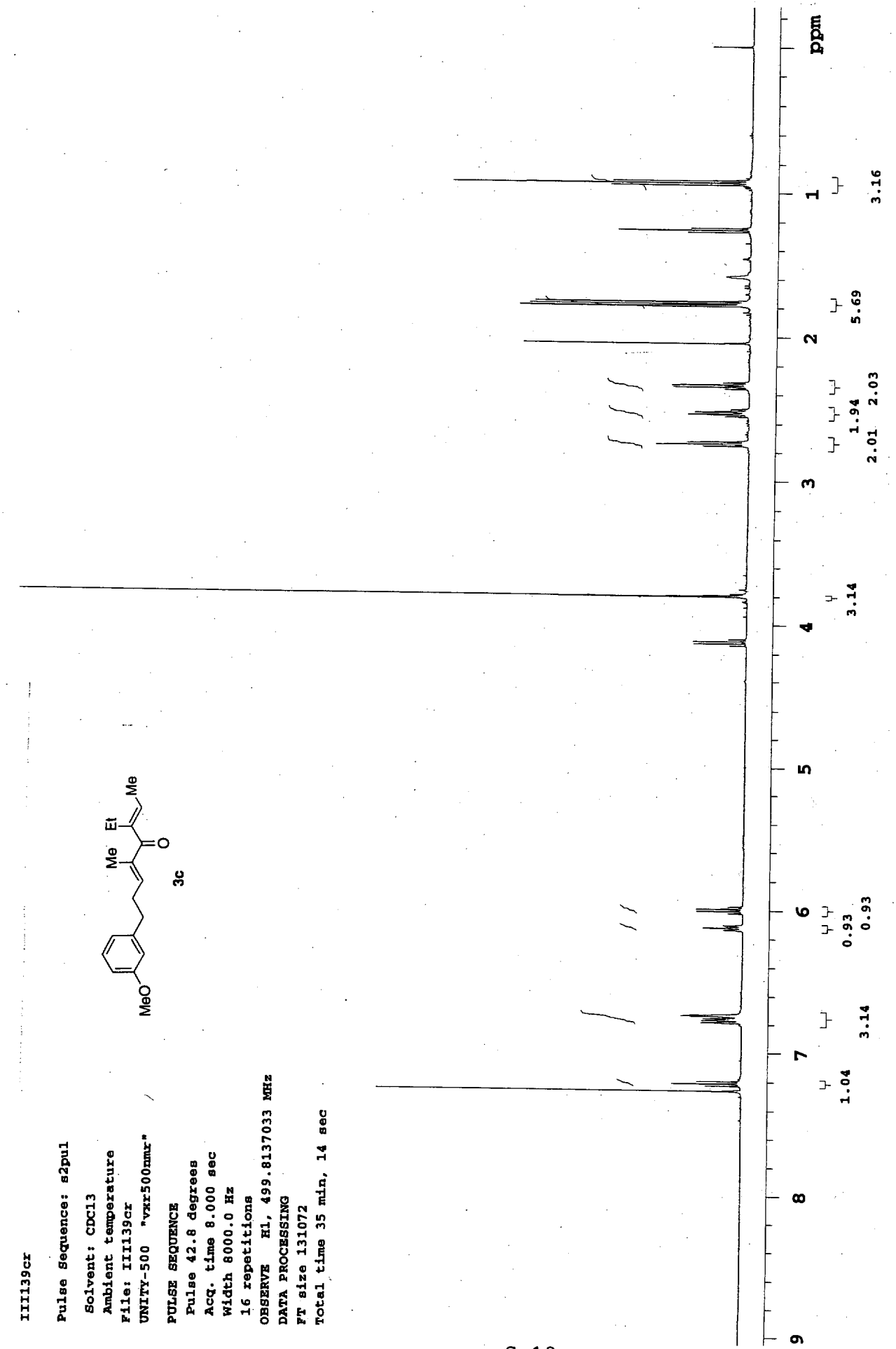

III186B
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 81.1 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137027 MHz
DATA PROCESSING
FT size 131072
Total time 21 min, 21 sec
Me
CHO
2c
ppm
10.00
30.48
22.40
23.11
10.48
24.53

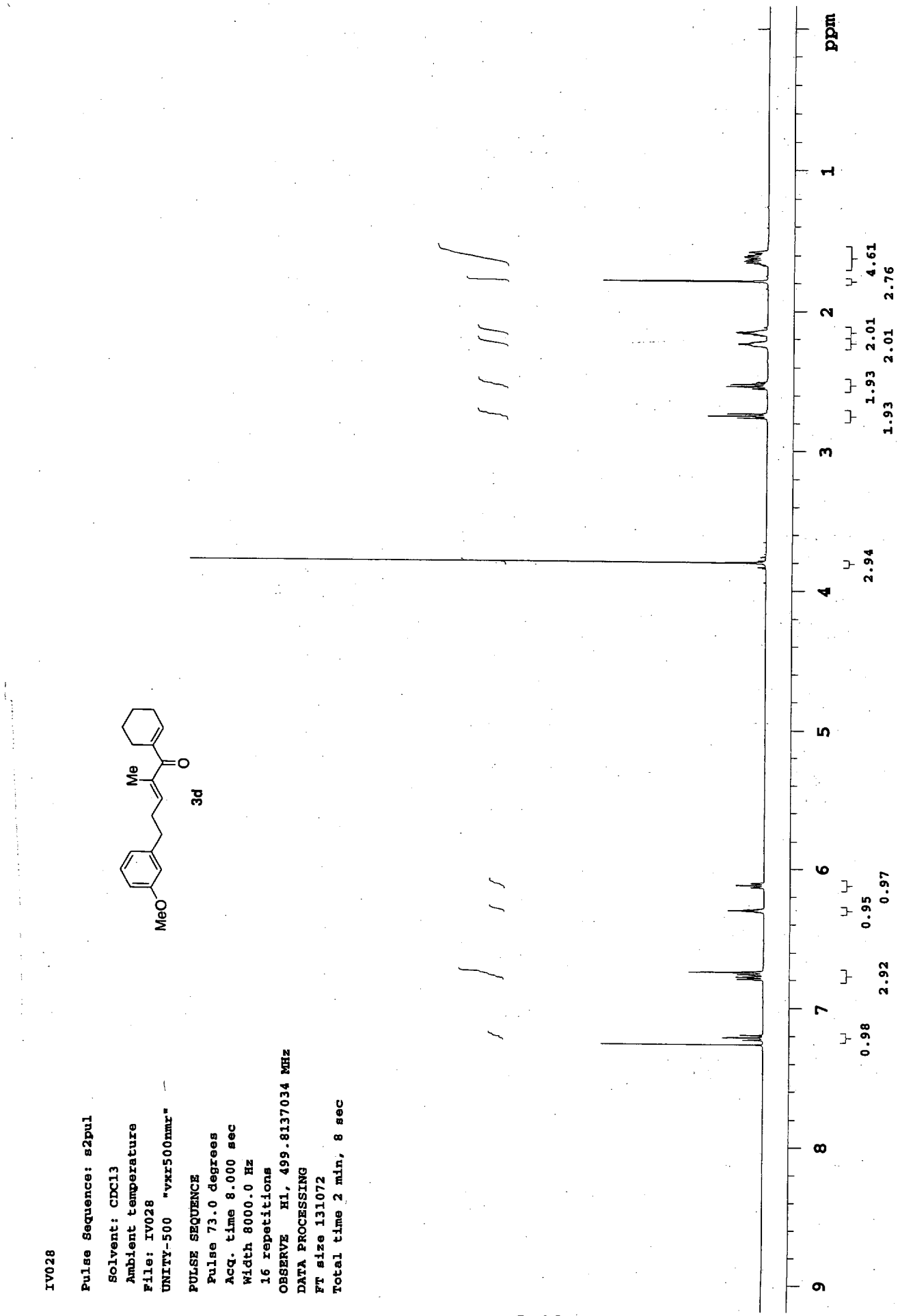


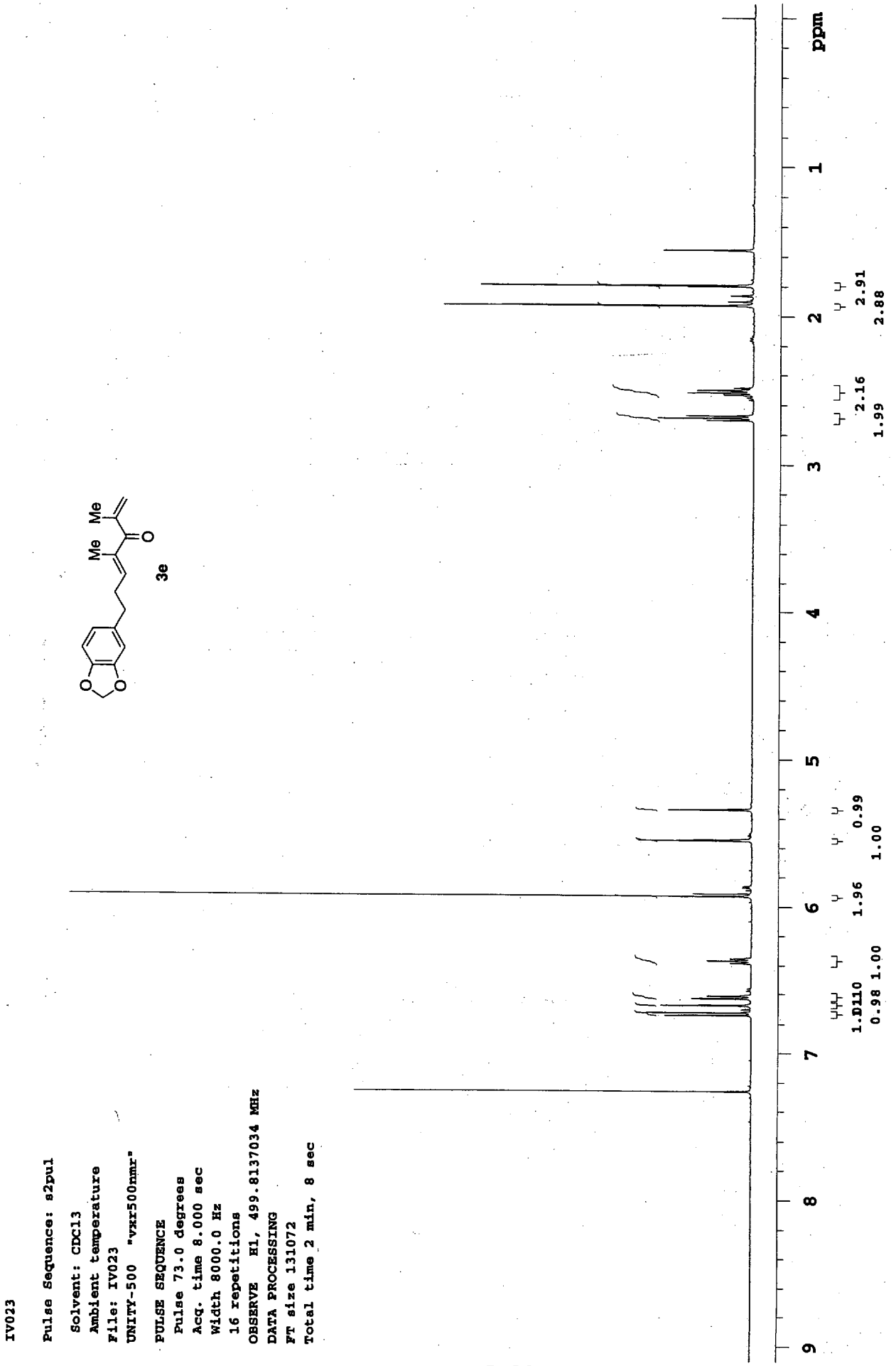

2d

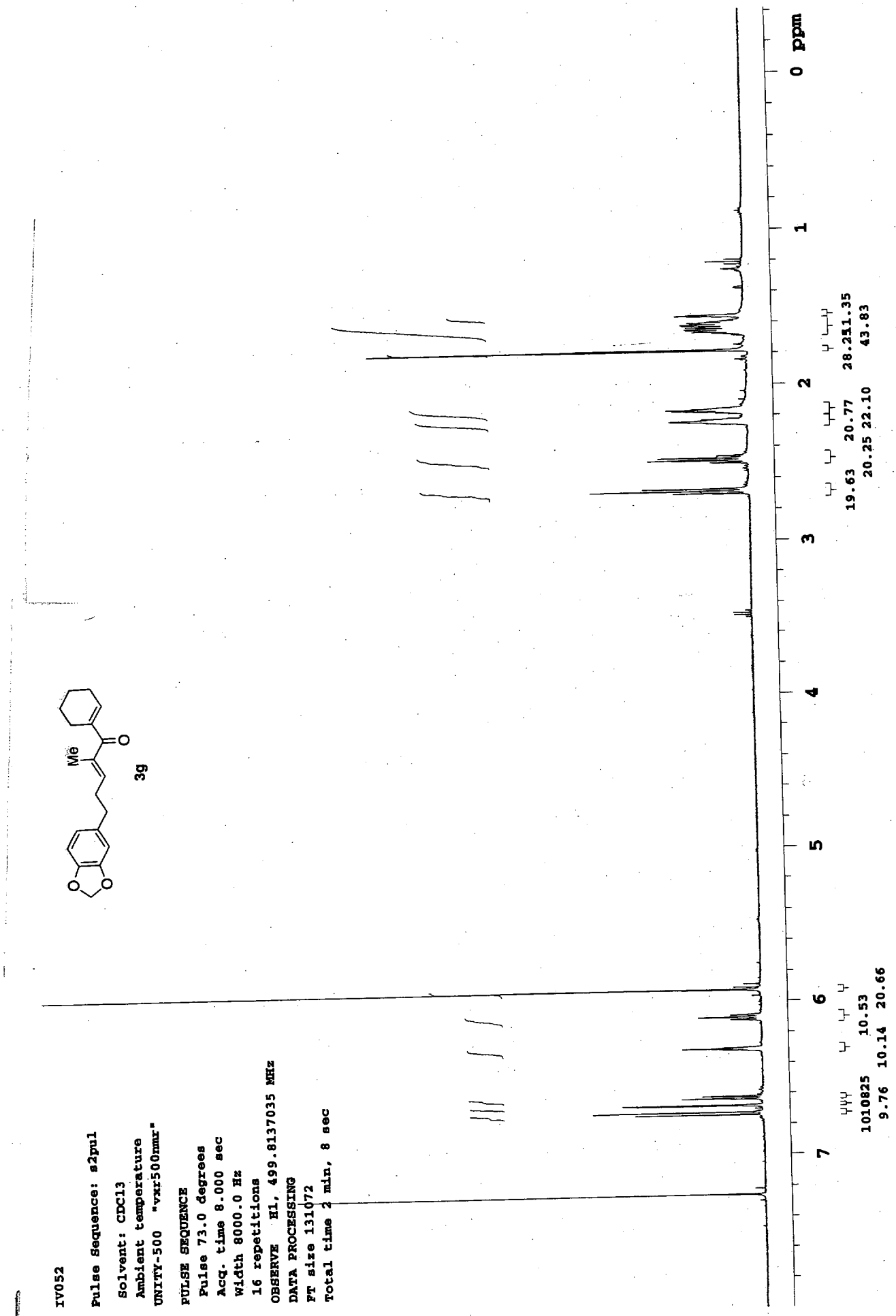


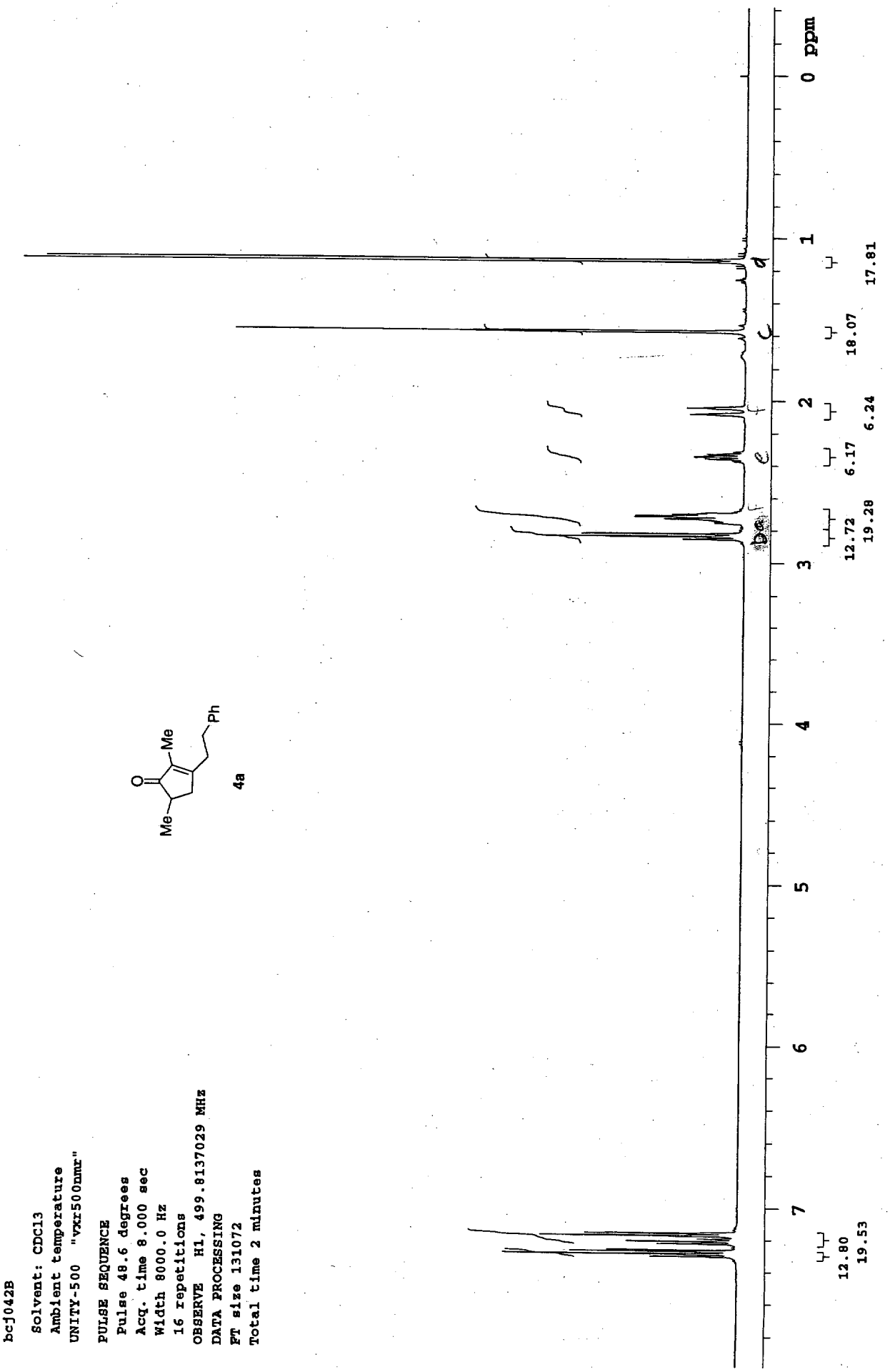

IV011
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137016 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
Me
Me
O
3a
ppm
1
2
3
4
5
6
7
20.18
30.25
10.02
9.98
10.23
20.21
20.15
29.01
29.16

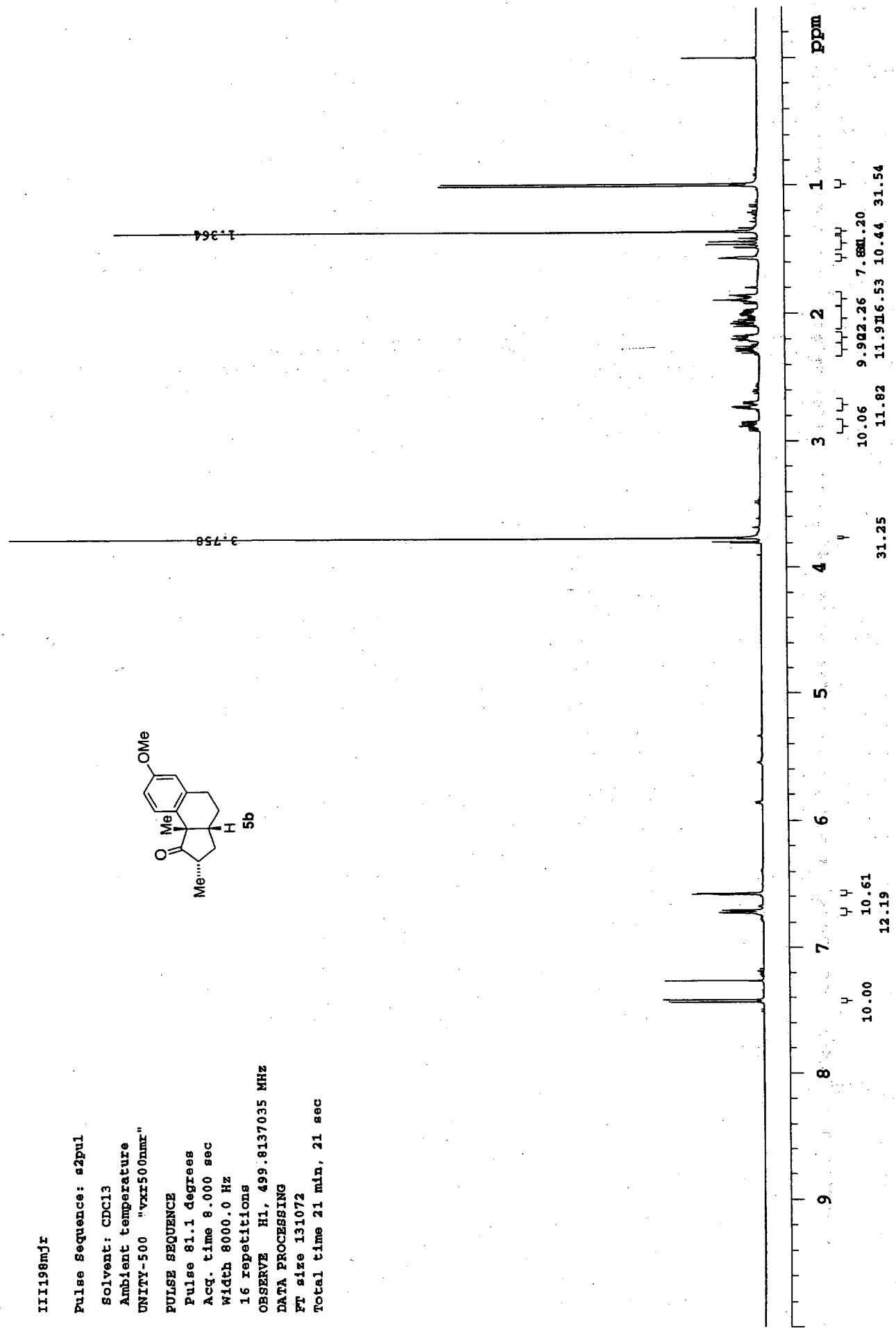


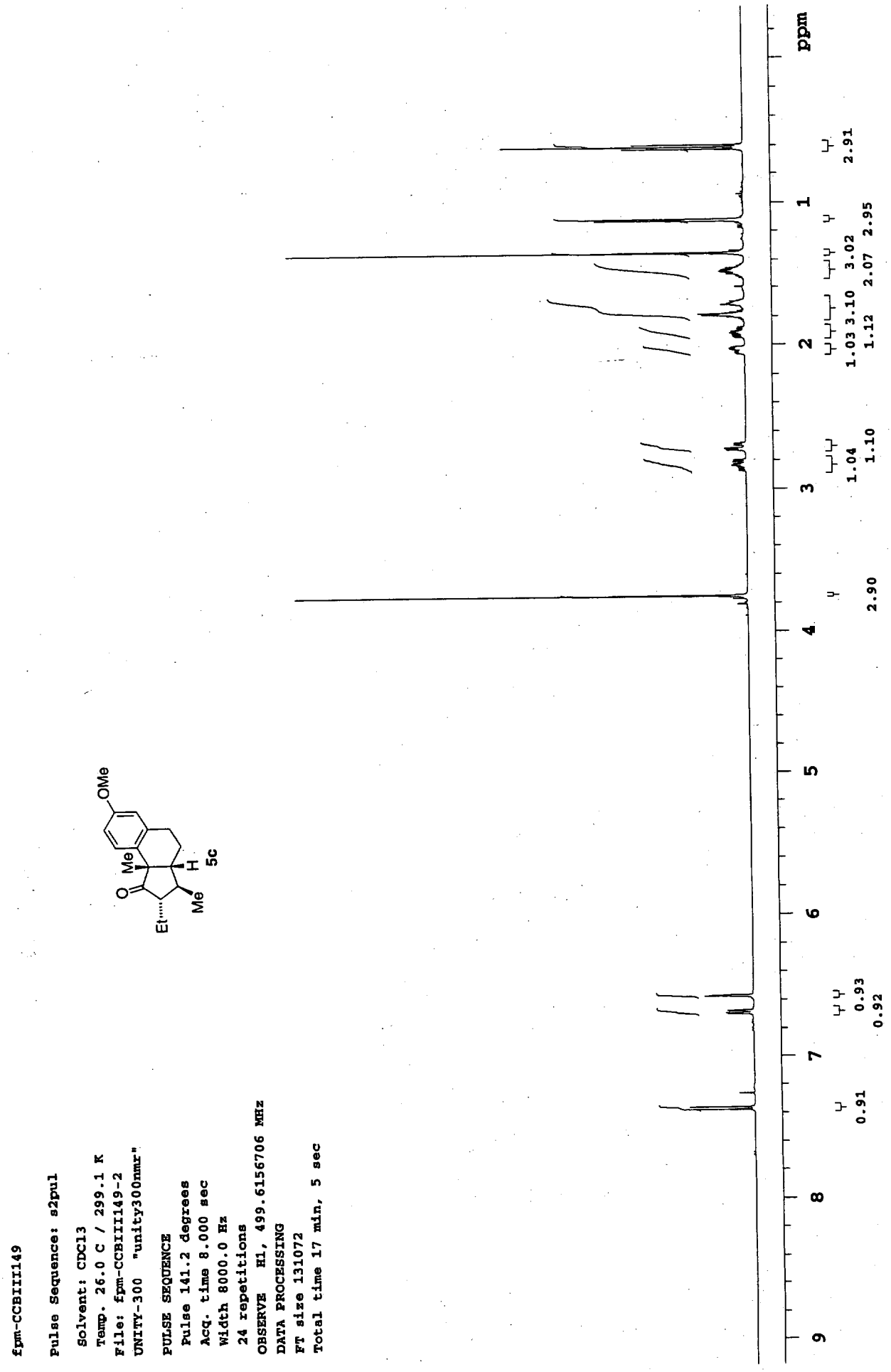

IV028
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: IV028
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137034 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
Me
O
MeO
3d
ppm
9
8
7
6
5
4
3
2
1
0.98
2.92
0.95
0.97
2.94
1.93
2.01
1.93
2.01
4.61
2.76

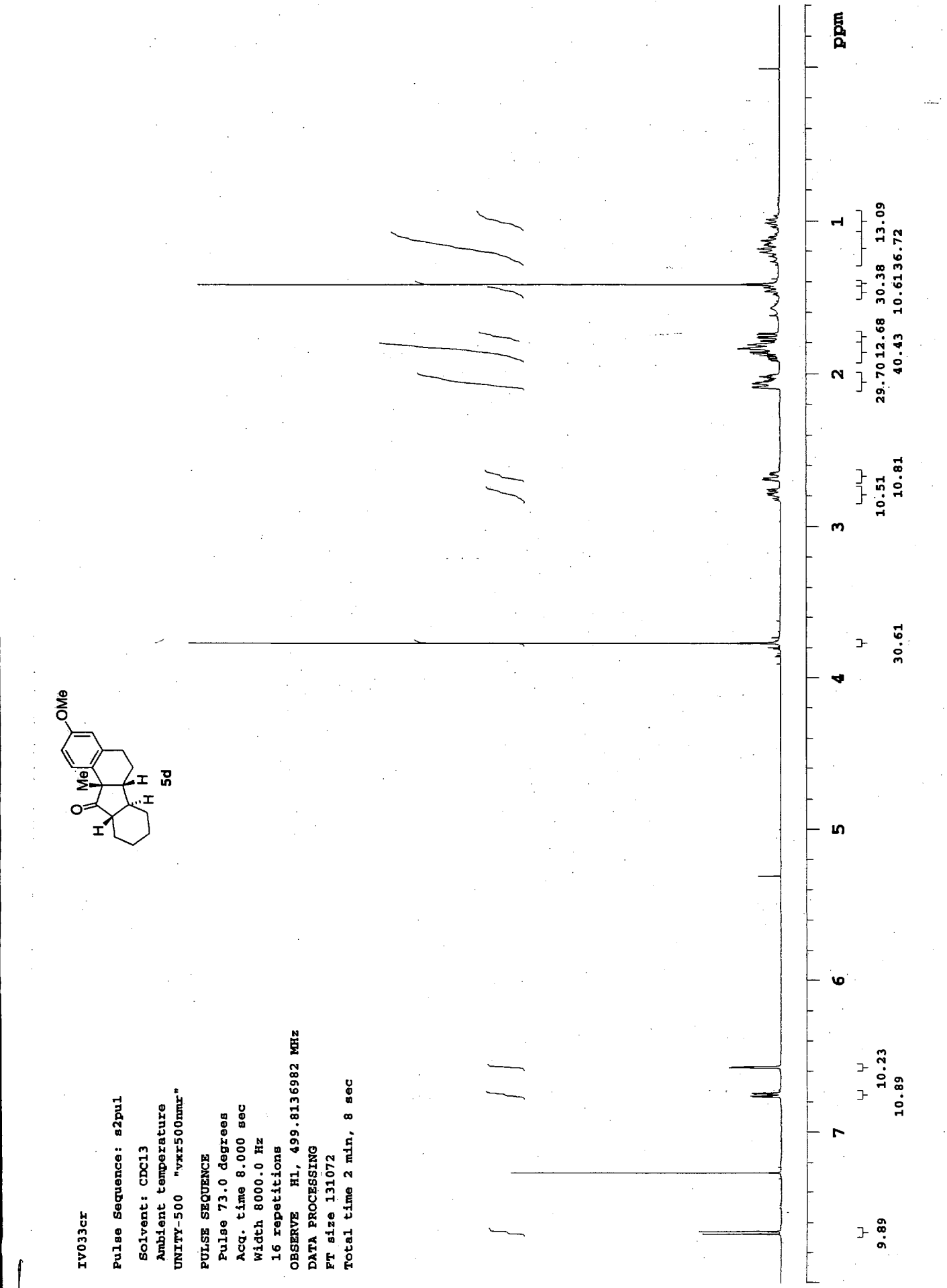

IV023
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: IV023
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137034 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
Me
Me
O
O
O
3e
ppm
1
2
3
4
5
6
7
8
9
1.0110
0.98
1.00
1.96
0.99
1.00
2.16
1.99
2.91
2.88

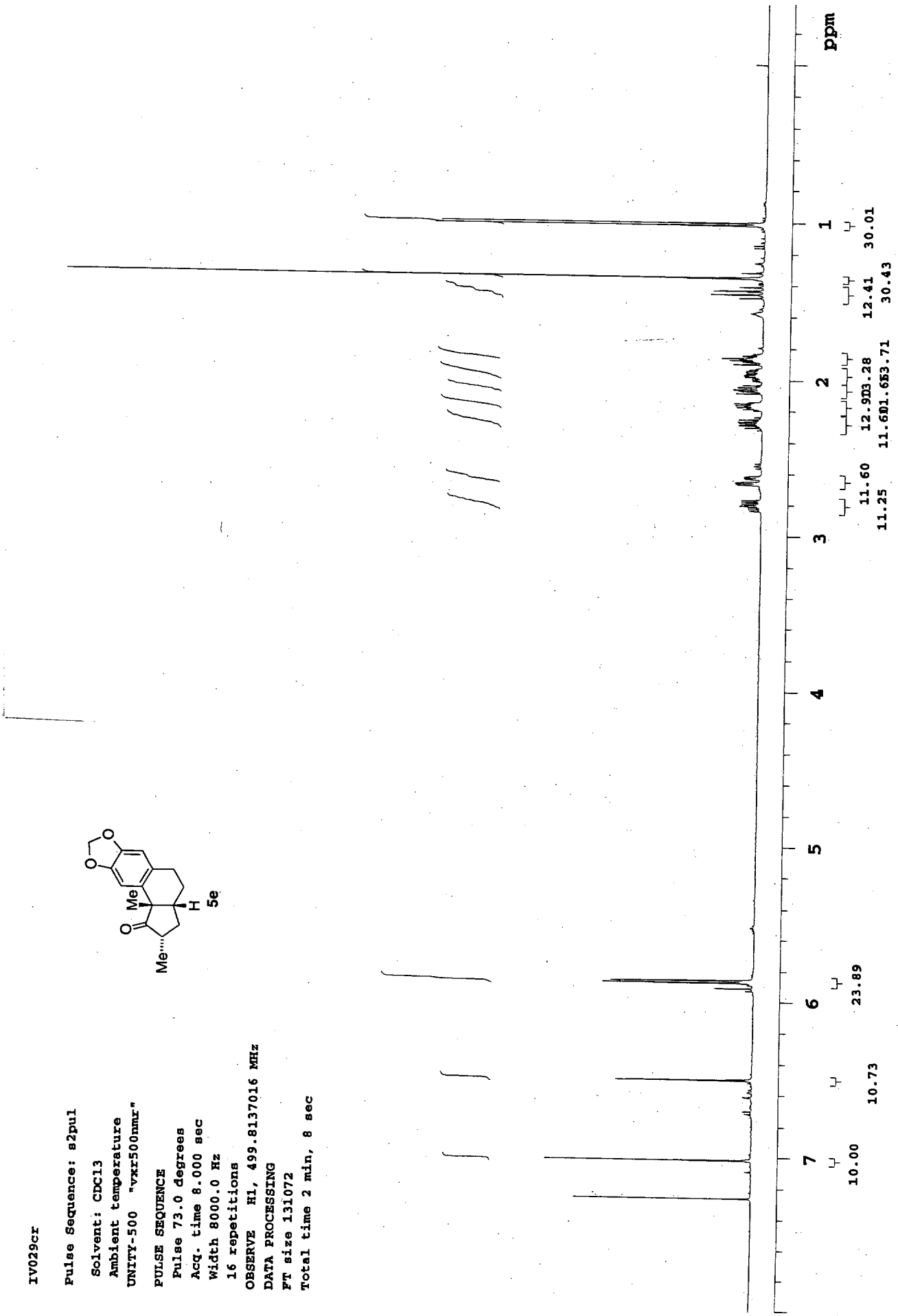


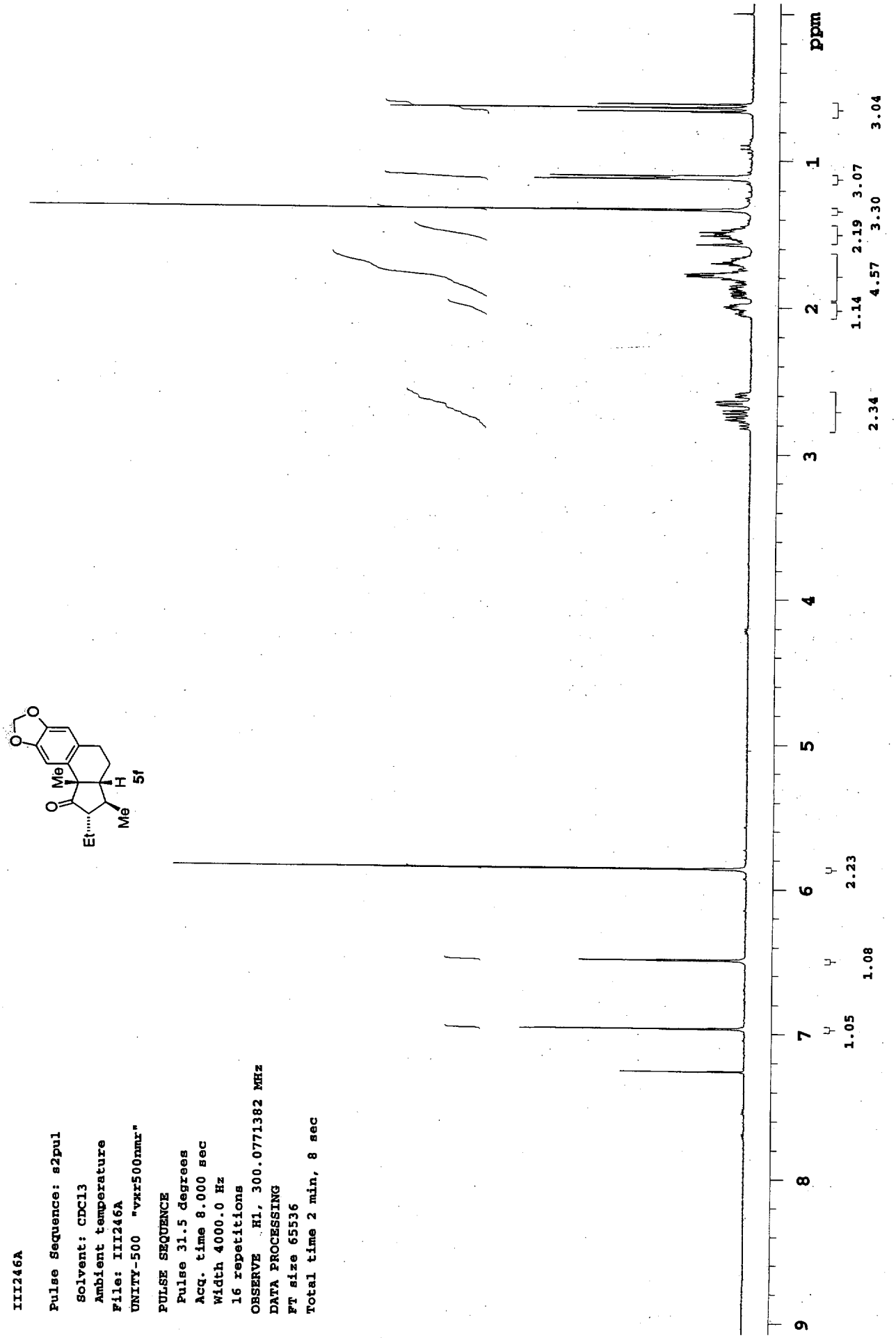

bcj042B
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 48.6 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137029 MHz
DATA PROCESSING
FT size 131072
Total time 2 minutes
Me
Ph
Me
O
4a
0 ppm
1
2
3
4
5
6
7
12.80
19.53
12.72
19.28
6.17
6.24
18.07
17.81

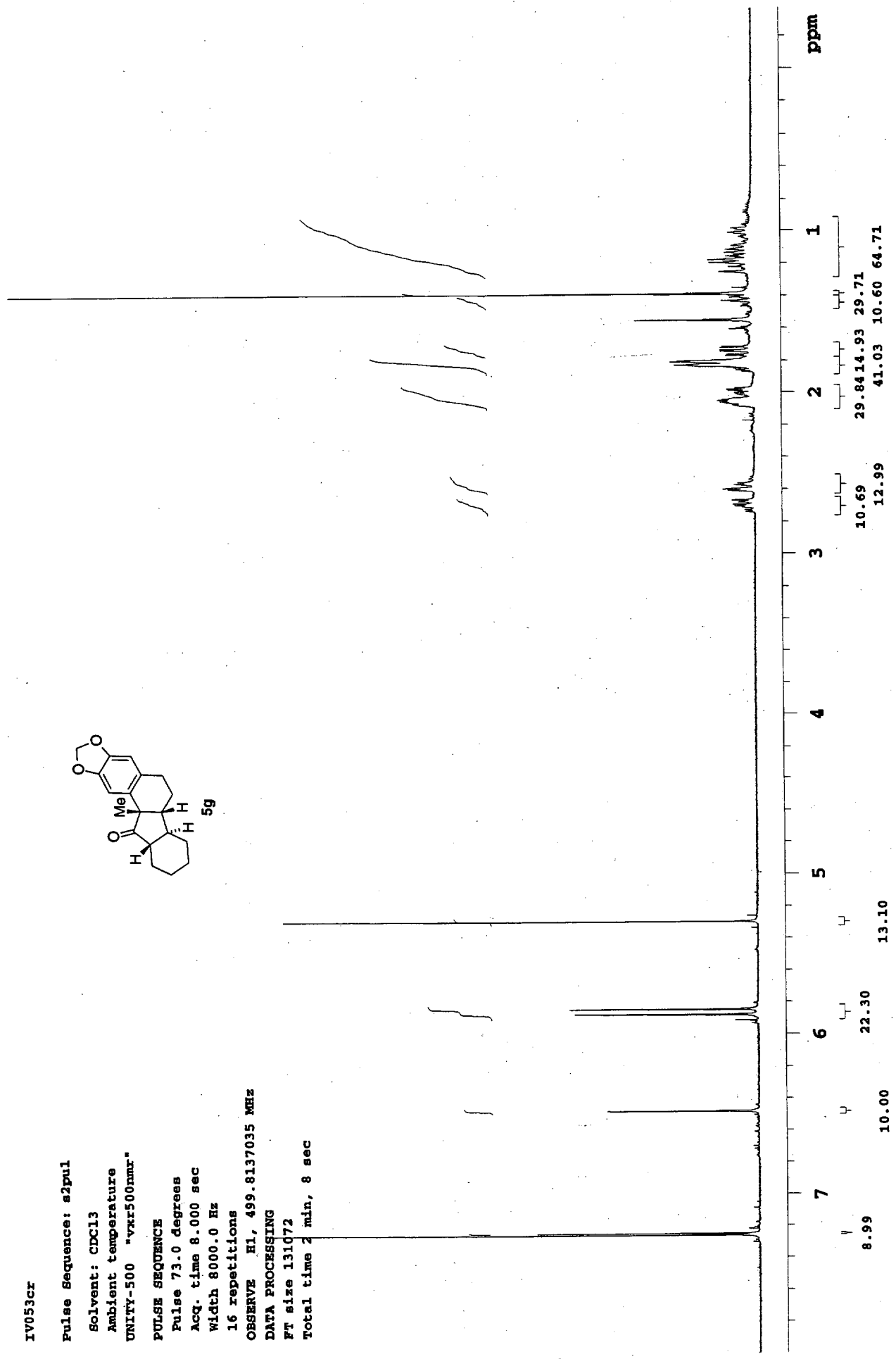

III198mjr
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 81.1 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137035 MHz
DATA PROCESSING
FT size 131072
Total time 21 min, 21 sec
3.758
1.364
OMe
Me
H
O
Me
5b
ppm
10.00
10.61
12.19
10.06
11.82
31.25
9.902.26
11.916.53
10.44
31.54

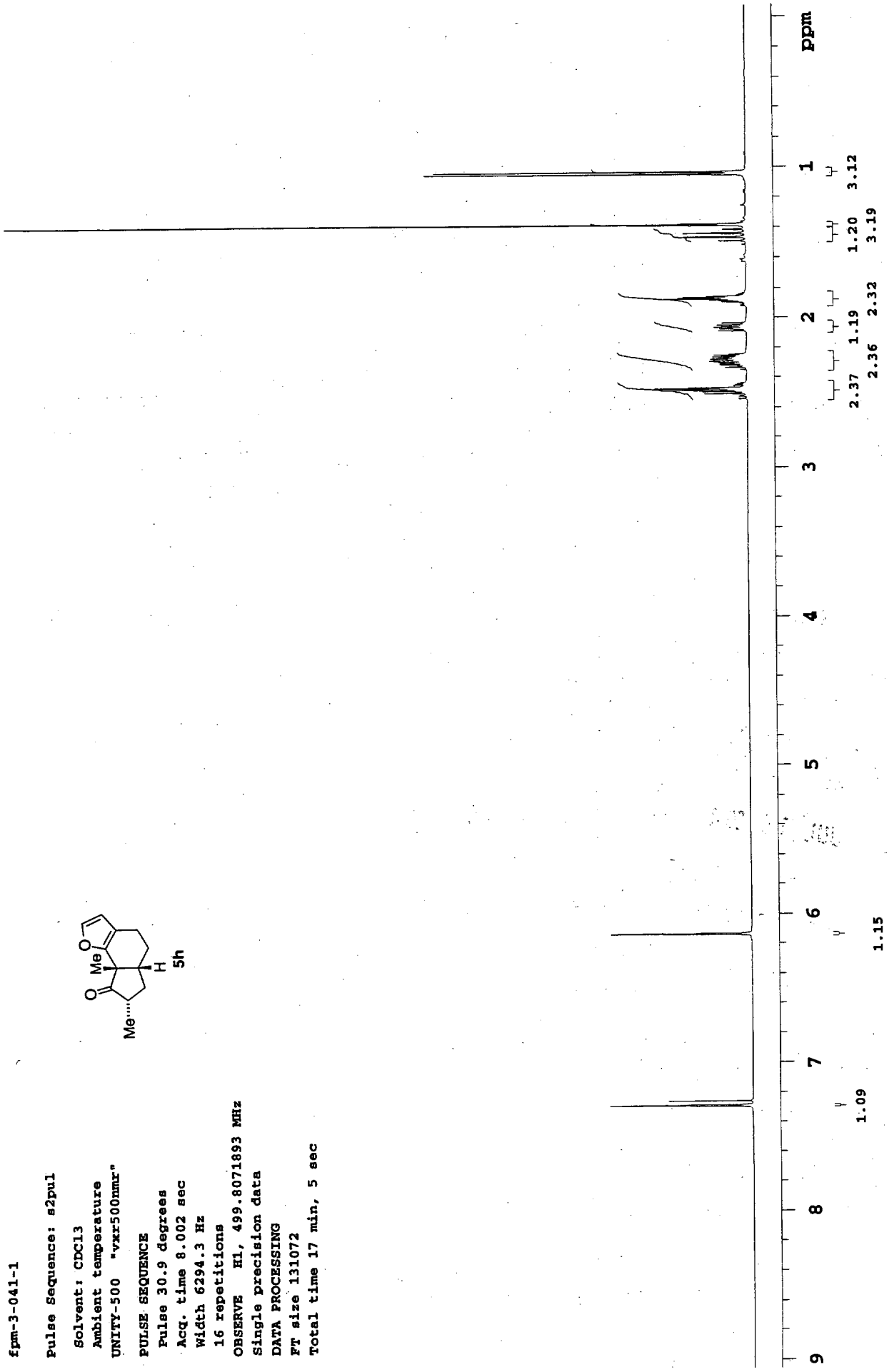



IV033cr
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8136982 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
OMe
Me
H
H
H
O
5d
ppm
9.89
10.23
10.89
30.61
10.51
10.81
29.70
12.68
30.38
13.09
40.43
10.61
36.72


IV029cr
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137016 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
Me
H
Me
5e
ppm
10.00
23.89
10.73
11.60
11.25
12.90
11.65
3.28
1.71
12.41
30.43
30.01




IV053cr
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 73.0 degrees
Acq. time 8.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8137035 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec
Me
H
H
H
O
O
O
5g
ppm
8.99
10.00
22.30
13.10
10.69
12.99
29.84
14.93
29.71
41.03
10.60
64.71


fpm-3-041-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "vxr500nmr"
PULSE SEQUENCE
Pulse 30.9 degrees
Acq. time 8.002 sec
Width 6294.3 Hz
16 repetitions
OBSERVE H1, 499.8071893 MHz
Single precision data
DATA PROCESSING
FT size 131072
Total time 17 min, 5 sec
Me
O
O
H
Me
5h
ppm
1
2
3
4
5
6
7
8
9
2.37
1.19
2.36
2.32
1.20
3.19
3.12
1.15
1.09