Supporting Information for
"Facile Preparation of Allenic Hydroxyketones via Rearrangement of Propargylic Alcohols" Michael E. Jung and Joseph Pontillo

General Procedures. All reactions were conducted under an argon atmosphere. THF was distilled over sodium/benzophenone, benzene over calcium hydride and methanol over magnesium methoxide. Commercially available propargyl alcohol, 3-butyn-2-ol, 2-butyn-1-ol, 3-methyl-1-pentyn-3-ol, and 1-phenyl-2-propyn-1-ol (Aldrich Chemical Co.) were distilled prior to use. All other chemicals were used as received from Aldrich Chemical Co. Thin layer chromatography (TLC) was done on silica gel (0.25 mm thickness) aluminum plates. Plates were viewed under UV light (254 nm) and with *p*-anisaldehyde dip. Column chromatography was performed on 230-400 mesh silica gel. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra were recorded on a Bruker ARX-400 spectrometer, while infrared spectra were recorded on a Nicolet Fourier transform spectrometer. High resolution mass spectra were performed by the UCLA Mass Spectrometry Laboratory.

2-Methyl-1-phenoxy-3-butyn-2-ol (5): To (trimethylsilyl)acetylene (0.051 g, 0.52 mmol) in 2 mL THF at -78 °C was added *n*-BuLi (1.88 M in pentane, 0.26 mL, 0.48 mmol) dropwise, and stirring was continued for 20 min. 1-Phenoxyacetone (**8**, 0.060 g, 0.40 mmol) in 0.5 mL THF was then added dropwise *via* cannula. This was followed by 2 x 0.25 mL THF rinses, and stirring was continued at -78 °C for 1 h. Ammonium chloride (0.100 g, 1.87 mmol) was then added in one portion, and the mixture was warmed to room temperature. After diluting with 15 mL of Et_2O, the mixture was successively washed with 5 mL saturated aqueous NH_4Cl and 2 x 5 mL brine. Drying over $MgSO_4$ and concentrating at reduced pressure gave a yellow oil (0.098 g), which was then dissolved in 3 mL MeOH. To this solution was added K_2CO_3 (0.061 g, 0.44 mmol) in one portion, and the resulting suspension was stirred for 2 h. The mixture was quenched with 2 mL sat. aqueous NH_4Cl, then extracted with 4 x 5 mL Et_2O. The combined extracts were washed with 2 x 10 mL brine, dried over $MgSO_4$, and concentrated to give a yellow oil. Subjection of the crude to flash column chromatography (20% Et_2O/pentane) gave propargyl alcohol **5** as a pale yellow oil (0.067 g, 95%): ^{1}H NMR ($CDCl_3$) δ 7.33-7.21 (m, 2H), 7.01-6.88 (m, 3H), 4.06 (d, *J*=8.9 Hz, 1H), 3.95 (d, *J*=8.9 Hz, 1H), 3.12 (s, 1H), 2.51 (s, 1H), 1.63 (s, 3H); ^{13}C NMR ($CDCl_3$) 158.4, 129.6, 121.5, 114.9, 85.4, 75.2, 72.2, 67.0, 25.9; IR (neat) 3411, 3291, 3000, 2929, 1599, 1496, 1246, 1051, 754, 693 cm^{-1}.

2-Methyl-1-phenoxy-3-buten-2-ol (15): A mixture of 2-methyl-1-phenoxy-3-butyn-2-ol (**5**) (0.096 g, 0.54 mmol), quinoline (0.055 g, 0.42 mmol) and 5% Pd on $BaSO_4$ (0.016 g, 0.0075 mmol) in 5 mL absolute EtOH was hydrogenated (balloon) for 10 min. Following filtration through a pipette column of Celite (3 cm) and elution with a further 3 x 2 mL Et_2O, concentration at reduced pressure gave a yellow oil, which was

subjected to flash column chromatography (20% Et_2O/pentane). 2-Methyl-1-phenoxy-3-buten-2-ol (**15**) was isolated as a colorless oil (0.091 g, 94%): ^{1}H NMR ($CDCl_3$) δ 7.31-7.28 (m, 2H), 7.00-6.93 (m, 3H), 6.03 (dd, *J*=10.8, 6.5 Hz, 1H), 5.41 (d, *J*=17 Hz, 1H), 5.20 (d, *J*=10.8 Hz, 1H), 3.89 (d, *J*=8.9 Hz, 1H), 3.84 (d, *J*=8.9 Hz, 1H), 2.95 (s, 1H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$) 158.6, 141.8, 129.5, 121.2, 114.7, 114.0, 74.8, 72.5, 24.5; IR (neat) 3413, 2936, 2929, 1599, 1497, 1246, 1049, 754, 691 cm^{-1}.

General Procedure: Allenic Hydroxyketones via Rearrangement of Propargylic Alcohols. To a mixture of 0.26 mmol of the propargylic alcohol and 0.013 mmol $Rh_2(OAc)_4$ in 2 mL benzene at room temperature was added, dropwise over 5 min, a solution of 0.52 mmol 3-diazo-2-butanone (**6**) in 2 mL benzene. The yellow solution was then immediately filtered through a pipette column of Celite (3 cm), eluted with a further 3 x 2 mL Et_2O, and carefully concentrated under reduced pressure (5 °C stillpot bath, 12 mm Hg) to give crude yellow oils, which were subjected to flash column chromatography (Et_2O/pentane).

3-Hydroxy-3,6-dimethyl-7-phenyloxyhepta-4,5-dien-2-ones, (9) and (10): Employment of the general procedure with 2-methyl-1-phenoxy-3-butyn-2-ol (**5**) gave 0.037 g of a pale yellow liquid (58%, 76% based on 0.011 g recovered starting material) as an inseparable 9:1 mixture of diastereomers. Major diastereomer **9**: ^{1}H NMR ($CDCl_3$) δ 7.31-7.26 (m, 2H), 6.98-6.90 (m, 3H), 5.28-5.27 (m, 1H), 4.54 (m, 2H), 3.93 (s, 1H), 2.23 (s, 3H), 1.86 (d, *J*=2.9 Hz, 3H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.7, 201.3, 158.3, 129.5, 121.2, 115.0, 101.3, 97.1, 77.6, 69.0, 24.2, 23.4, 15.7. Minor diastereomer **10**: ^{1}H NMR ($CDCl_3$) δ 7.31-7.26 (m, 2H), 6.98-6.90 (m, 3H), 5.24 Hz (m, 1 H), 4.54 (m, 2H), 3.96 (s, 1H), 2.20 (s, 3H), 1.86 (d, *J*=2.9 Hz, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.7, 201.3, 158.3, 129.1, 121.2, 114.8, 101.3, 97.1, 77.4, 69.0, 24.2, 23.4, 15.7. IR (mixture, neat) 3467, 3000, 2928, 1969, 1713, 1599, 1496, 1356, 1238, 756, 693 cm^{-1}; HRMS (CI) *m/e* ($M+NH_4^+$) calcd for $C_{15}H_{22}NO_3$ 264.1600, found 264.1593.

3-Hydroxy-3-methyl-6-phenylhexa-4,5-dien-2-ones (14a): Employment of the general procedure with 1-phenyl-2-propyn-1-ol (**13a**) gave 0.039 g of a pale yellow liquid (75%) as an inseparable 3:1 mixture of diastereomers. Major diastereomer **14a**: ^{1}H NMR ($CDCl_3$) δ 7.35-7.22 (m, 5H), 6.45 (d, *J*=6.4 Hz, 1H), 5.66 (d, *J*=6.4 Hz, 1H), 4.13 (s, 1H), 2.31 (s, 3H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.4, 204.7, 133.0, 128.8, 127.7, 126.9, 99.9, 98.7, 78.0, 24.2, 23.7. Minor diastereomer **14a**: ^{1}H NMR ($CDCl_3$) δ 7.35-7.22 (m, 5H), 6.43 (d, *J*=6.4 Hz, 1H), 5.65 (d, *J*=6.4 Hz, 1H), 4.19 (s, 1H), 2.29 (s, 3H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.4, 204.5, 133.0, 128.8, 127.7, 126.9, 100.3, 98.7, 77.6, 24.2, 23.6. IR (mixture, neat) 3459, 3033, 2988, 1950, 1713, 1458, 1356, 1129, 783, 693 cm^{-1}.

3-Hydroxy-3-methylhexa-4,5-dien-2-ones (14b): Employment of the general procedure with propargyl alcohol (**13b**) gave 0.022 g of **14b** as a colorless liquid (68%): ^{1}H NMR ($CDCl_3$) δ 5.19 (t, *J*=6.7 Hz, 1H), 4.96 (dd, *J*=4.0, 1.6 Hz, 2H), 4.03

(s, 1H), 2.22 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.6, 207.5, 95.3, 79.0, 51.6, 24.0, 23.5; IR (neat) 3467, 2988, 2853, 1956, 1714, 1358, 1128, 858, 615 cm^{-1}.

3-Hydroxy-3-methylhepta-4,5-dien-2-ones (14c): Employment of the general procedure with 3-butyn-2-ol (**13c**) gave 0.023 g of a pale yellow liquid (62%) as an inseparable 3:2 mixture of diastereomers. Major diastereomer **14c**: ^{1}H NMR ($CDCl_3$) δ 5.41-5.35 (m, 1H), 5.14-5.12 (m, 1H), 4.00 (s, 1H), 2.22 (s, 3H), 1.72 (d, *J*=3.2 Hz, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.4, 204.0, 129.1, 95.6, 90.2, 24.0, 23.5, 13.9. Minor diastereomer **14c**: ^{1}H NMR ($CDCl_3$) δ 5.41-5.35 (m, 1H), 5.14-5.12 (m, 1H), 3.98 (s, 1H), 2.24 (s, 3H), 1.70 (d, *J*=3.2 Hz, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.4, 204.0, 129.1, 95.6, 90.2, 24.0, 23.4, 13.8. IR (mixture, neat) 3465, 2990, 2930, 1950, 1714, 1356, 1130, 1086, 872, 629 cm^{-1}.

3-Hydroxy-3,6-dimethylocta-4,5-dien-2-ones (14d): Employment of the general procedure with 3-methyl-1-pentyn-3-ol (**13d**) gave 0.020 g of a pale yellow liquid (45%) as an inseparable 3:2 mixture of diastereomers. Major diastereomer **14d**: ^{1}H NMR ($CDCl_3$) δ 5.14-5.10 (m, 1H), 3.97 (s, 1H), 2.23 (s, 3H), 2.03-2.01 (m, 2H), 1.75 (s, 3H), 1.43 (s, 3H), 1.03 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 210.4, 200.4, 106.6, 96.3, 77.7, 27.0, 23.9, 23.4, 18.6, 12.2. Minor diastereomer **14d**: ^{1}H NMR ($CDCl_3$) 5.14-5.10 (m, 1H), 3.90 (s, 1H), 2.23 (s, 3H), 2.03-2.01 (m, 2H), 1.74 (s, 3H), 1.43 (s, 3H), 1.03 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 210.3, 200.4, 106.7, 95.9, 77.8, 26.9, 24.1, 23.6, 18.8, 12.3. IR (mixture, neat) 3465, 2990, 2930, 1950, 1714, 1356, 1130, 1086, 872, 629 cm^{-1}.

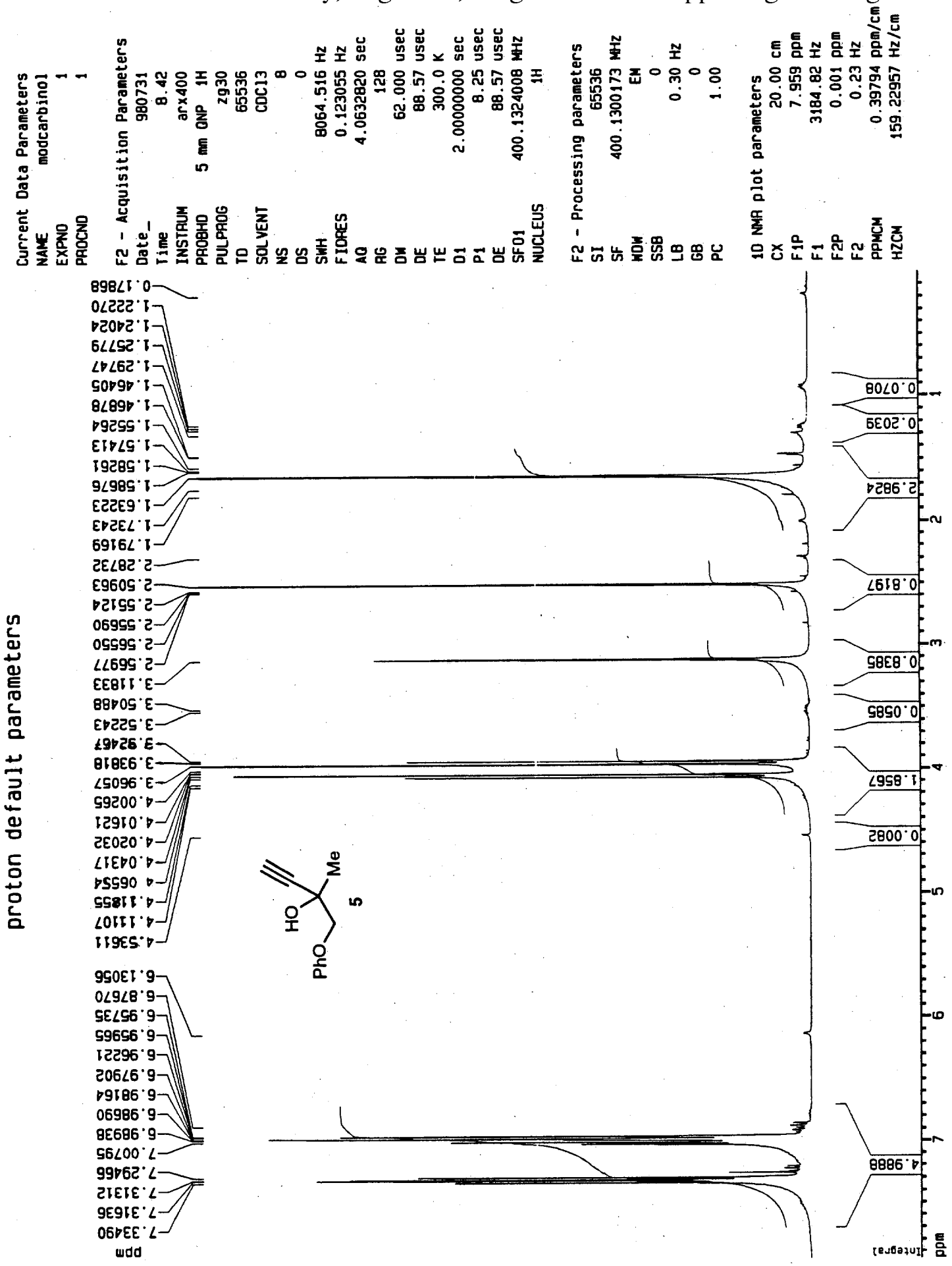
3-Hydroxy-3,4-dimethylhexa-4,5-dien-2-ones (14e): Employment of the general procedure with 2-butyn-1-ol (**13e**) gave 0.016 g of **14e** as a pale yellow liquid (44%): ^{1}H NMR ($CDCl_3$) δ 4.90-4.83 (m, 2H), 4.09 (s, 1H), 2.20 (s, 3H), 1.56 (t, *J*=3.1 Hz, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 210.5, 206.5, 101.4, 77.4, 57.7, 23.6, 23.1, 13.8; IR (neat) 3463, 2986, 2924, 2857, 1958, 1713, 1358, 1129, 855, 617 cm^{-1}.

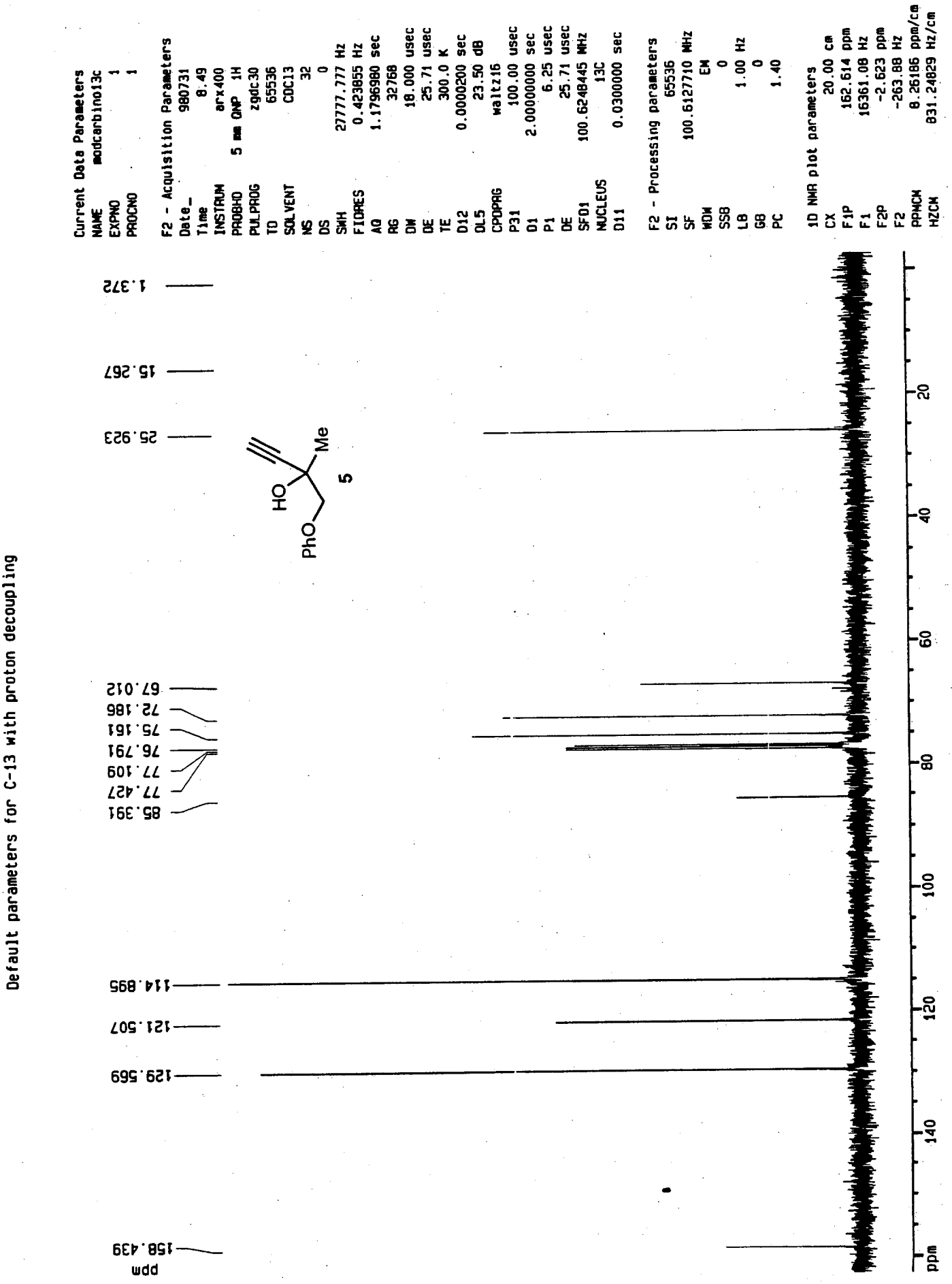
(*E*) and (*Z*) 3-Hydroxy-3,6-dimethyl-7-phenoxyhept-5-en-2-ones (16) and (17): Employment of the general procedure with 2-methyl-1-phenoxy-3-buten-2-ol (**15**) gave 0.043 g of a colorless liquid (67%, 92% based on 0.013 g recovered starting material) as an inseparable 7:1 mixture of diastereomers. Major diastereomer **16**: ^{1}H NMR ($CDCl_3$) δ 7.29-7.25 (m, 2H), 6.93-6.87 (m, 3H), 5.49 (t, *J*=4.6 Hz, 1H), 4.43 (s, 2H), 3.76 (s, 1H), 2.50 (d, *J*=6.6 Hz, 2H), 2.17 (s, 3H), 1.75 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 221.8, 158.6, 135.0, 129.4, 121.7, 120.8, 114.9, 78.7, 73.5, 37.6, 25.1, 23.8, 14.2. Minor diastereomer **17**: ^{1}H NMR ($CDCl_3$) δ 7.29-7.25 (m, 2H), 6.93-6.87 (m, 3H), 5.35 (t, *J*=4.6 Hz, 1H), 4.40 (s, 2H), 3.84 (s, 1H), 2.50 (d, *J*=6.6 Hz, 2H), 2.19 (s, 3H), 1.85 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 221.8, 158.6, 135.0, 129.4, 121.7, 120.8, 114.6, 78.7, 73.5, 37.6, 25.1, 23.8, 14.2. IR (mixture, neat) 3476, 2983, 2926, 1709, 1599, 1495, 1356, 1242, 1172, 1008, 756, 693 cm^{-1}.

2-Hydroxy-2,5-dimethyl-1-phenyl-6-phenoxyhepta-3,4-dien-1-ones 19: Employment of the general procedure with 2-methyl-1-phenoxy-3-butyn-2-ol (**5**) and

α-diazopropiophenone (**18**) gave 0.044 g of a pale yellow liquid (55%, 81% based on 0.015 g recovered starting material) as an inseparable (>15:1) mixture of diastereomers. Major diastereomer **19**: ^{1}H NMR ($CDCl_3$) δ 8.09 (d, *J*=7.8 Hz, 2H), 7.24-7.45 (m, 5 H), 6.95-6.86 (m, 3H), 5.58-5.56 (m, 1H), 4.47 (s, 1H), 4.46 (s, 3H), 1.86 (s, 3H), 1.65 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 201.9, 201.7, 158.3, 133.3, 133.2, 130.2, 129.4, 128.4, 128.3, 121.1, 115.0, 101.6, 98.3, 68.8, 26.4, 15.2. IR (neat) 3444, 2984, 2932, 1970, 1676, 1599, 1495, 1448, 1238, 754, 693 cm^{-1}.

3-Hydroxy-6-methyl-3-phenyl-7-phenoxyhepta-4,5-dien-2-ones 20: Employment of a modification of the general procedure (addition of $Rh_2(OAc)_4$ in one portion to a mixture of 2-methyl-1-phenoxy-3-butyn-2-ol (**5**) and α-diazopropiophenone (**18**) in 4 mL benzene at room temperature, and stirring 15 min) gave 0.042 g of a pale yellow liquid (52%, 75% based on 0.014 g recovered starting material) as an inseparable (>15:1) mixture of isomers. Major diastereomer **20**: ^{1}H NMR ($CDCl_3$) δ 7.52-7.26 (m, 7 H), 6.96-6.87 (m, 3H), 5.84-5.81 (m, 1H), 4.55 (s, 3H), 4.41 (s, 1H), 2.09 (s, 3H), 1.87 (d, *J*=3.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 207.1, 201.2, 158.2, 140.3, 129.6, 129.5, 128.6, 126.7, 121.1, 114.9, 101.5, 95.5, 82.0, 68.7, 24.7, 15.7. IR (neat) 3449, 3100, 2950, 2932, 1970, 1713, 1599, 1495, 1449, 1238, 1172, 756, 693 cm^{-1}.

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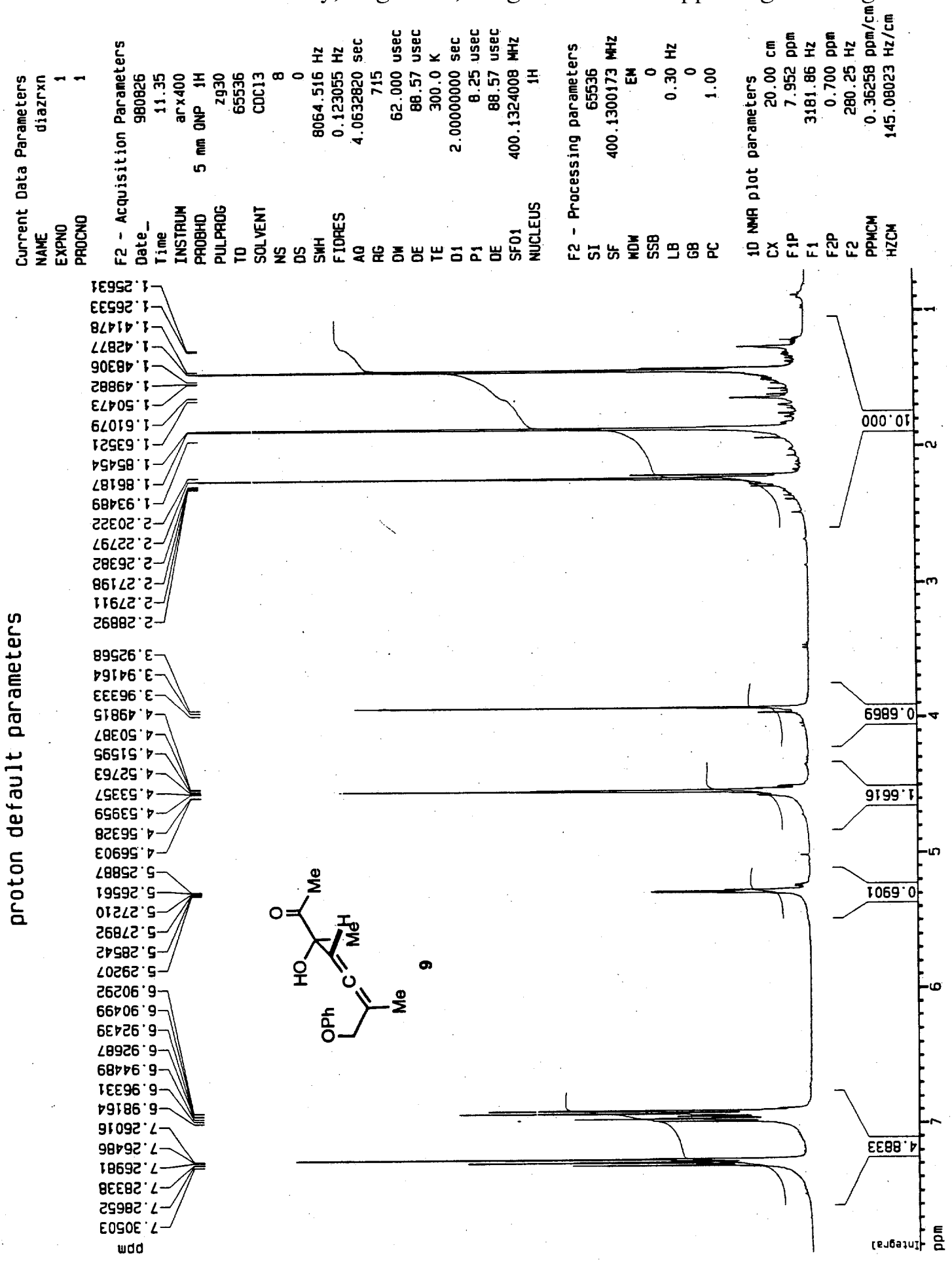

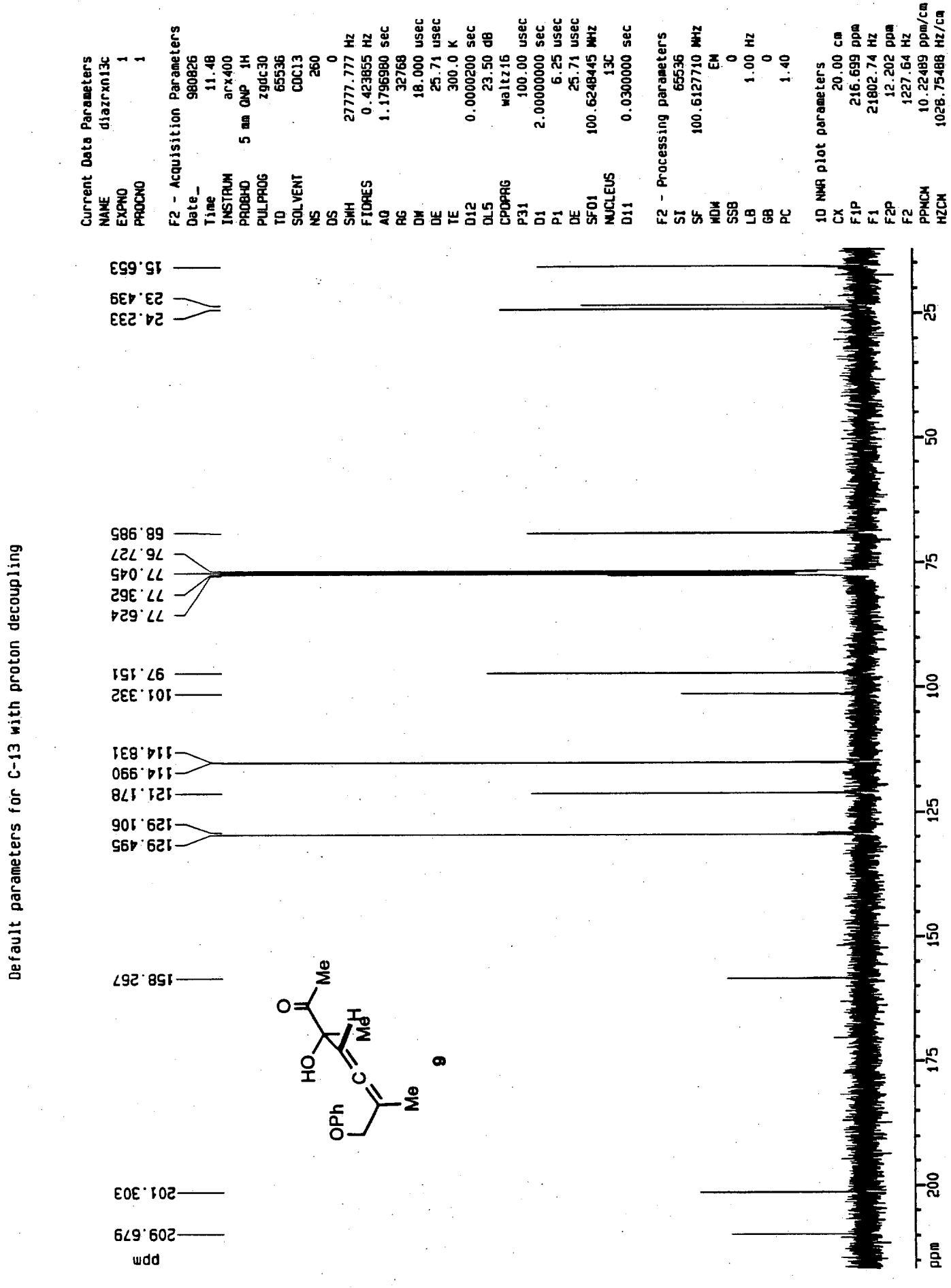
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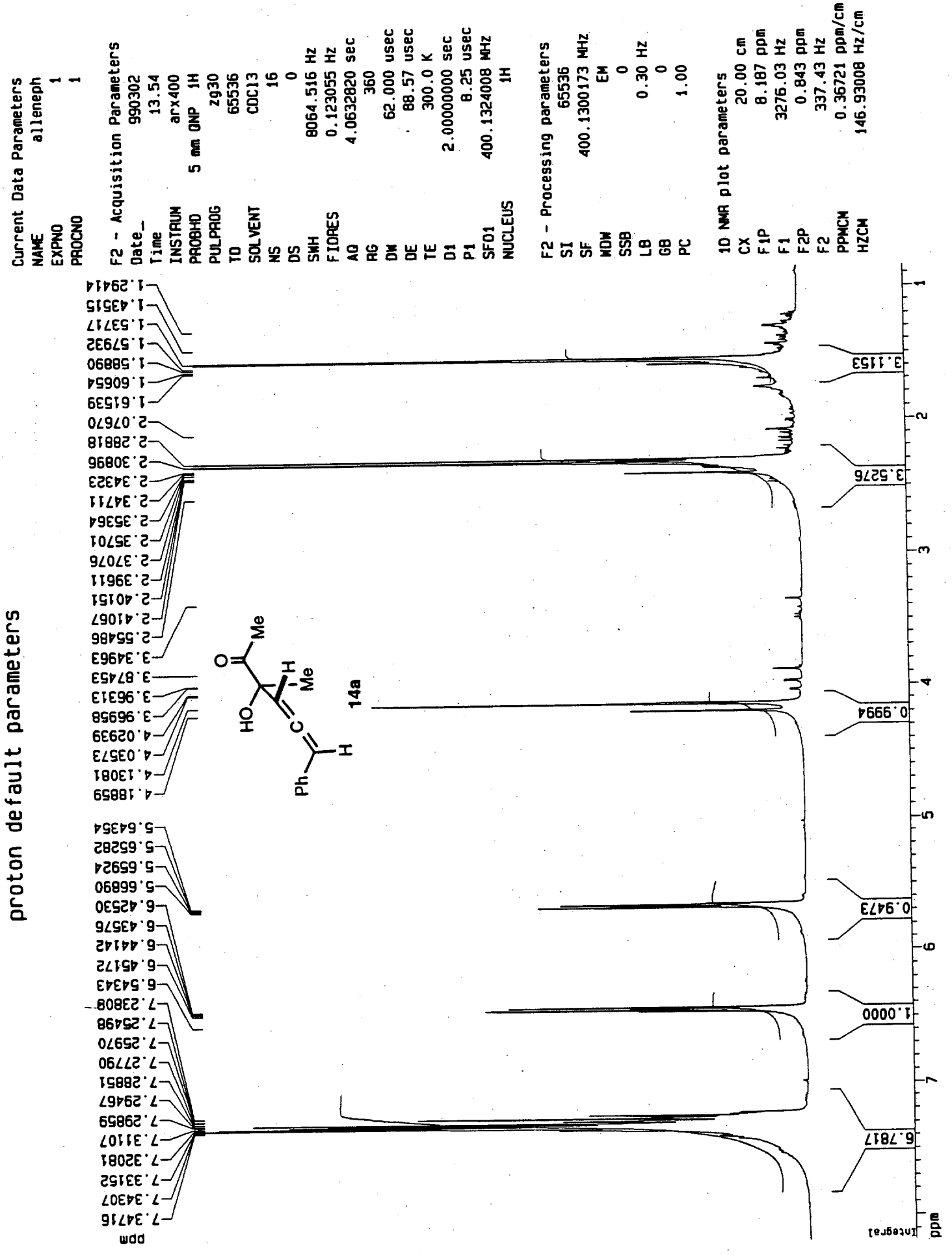

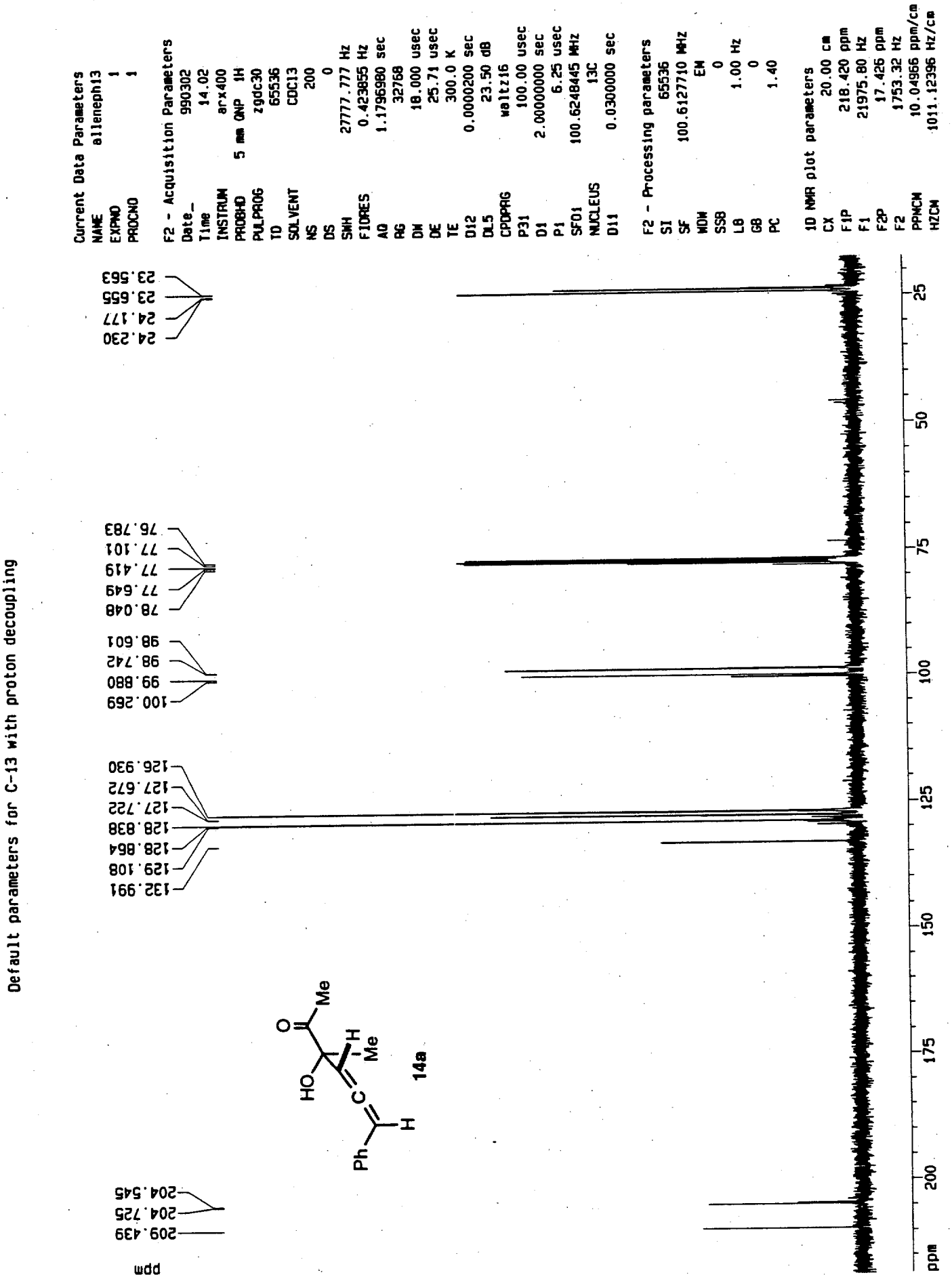

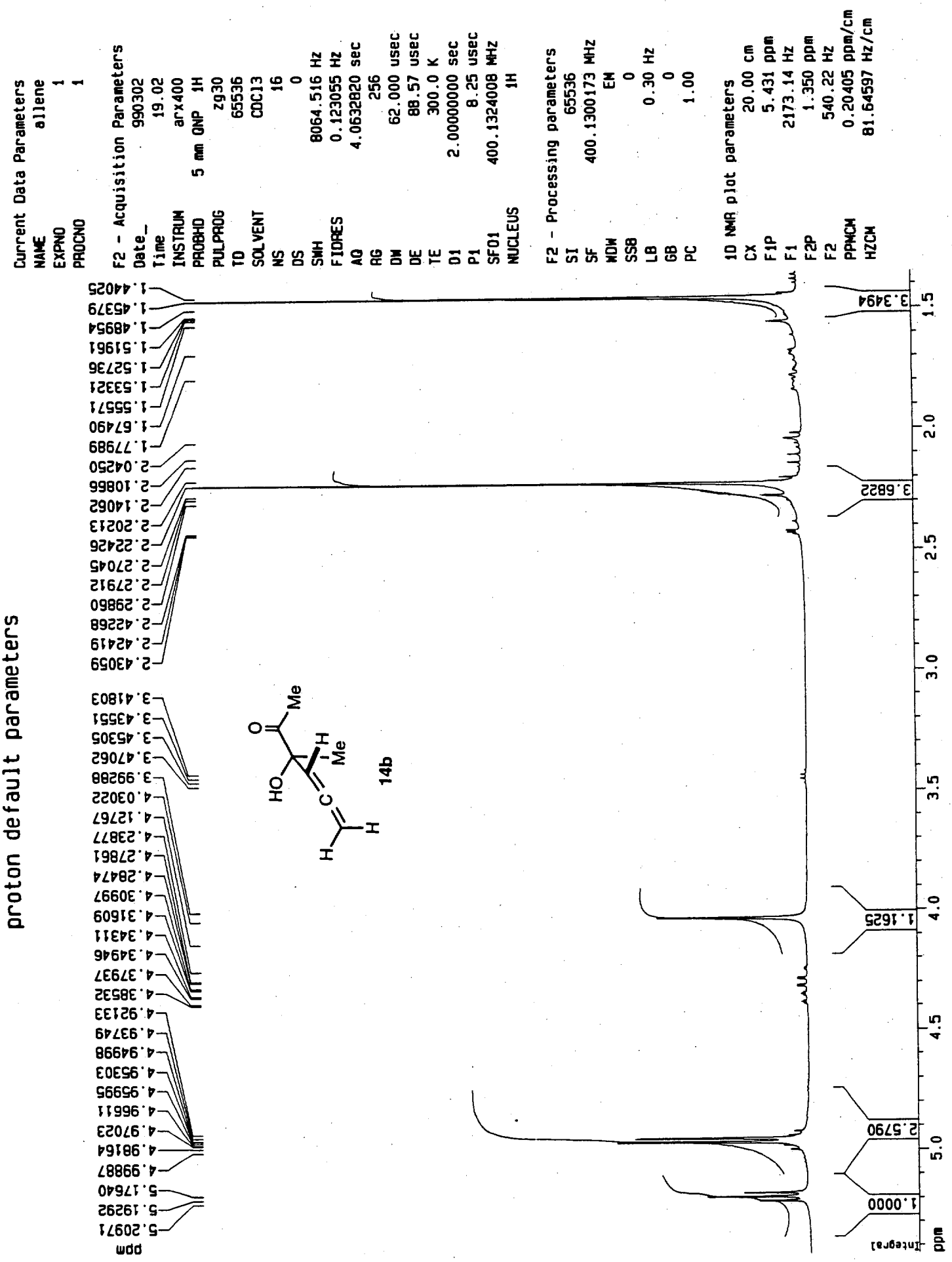

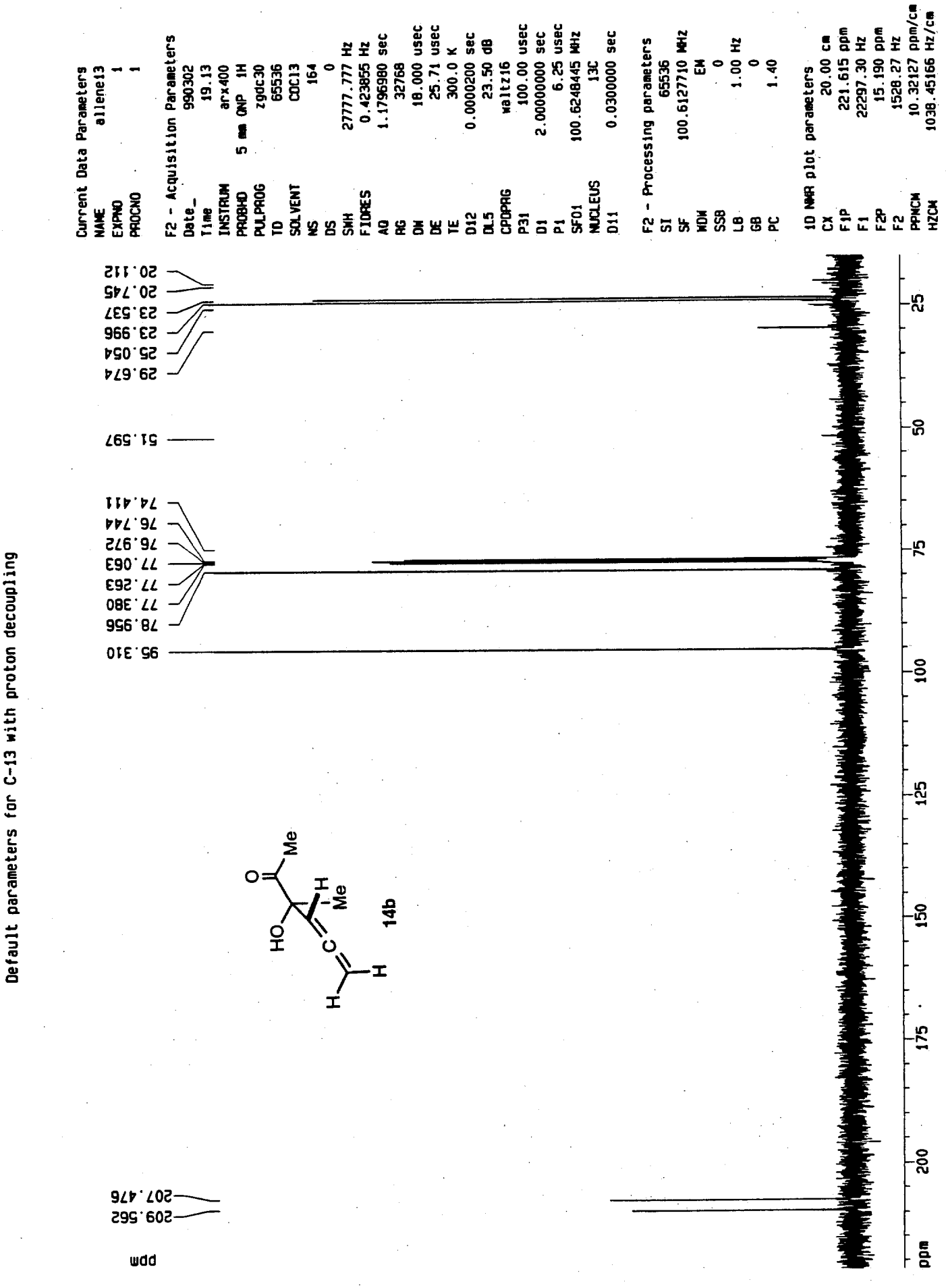

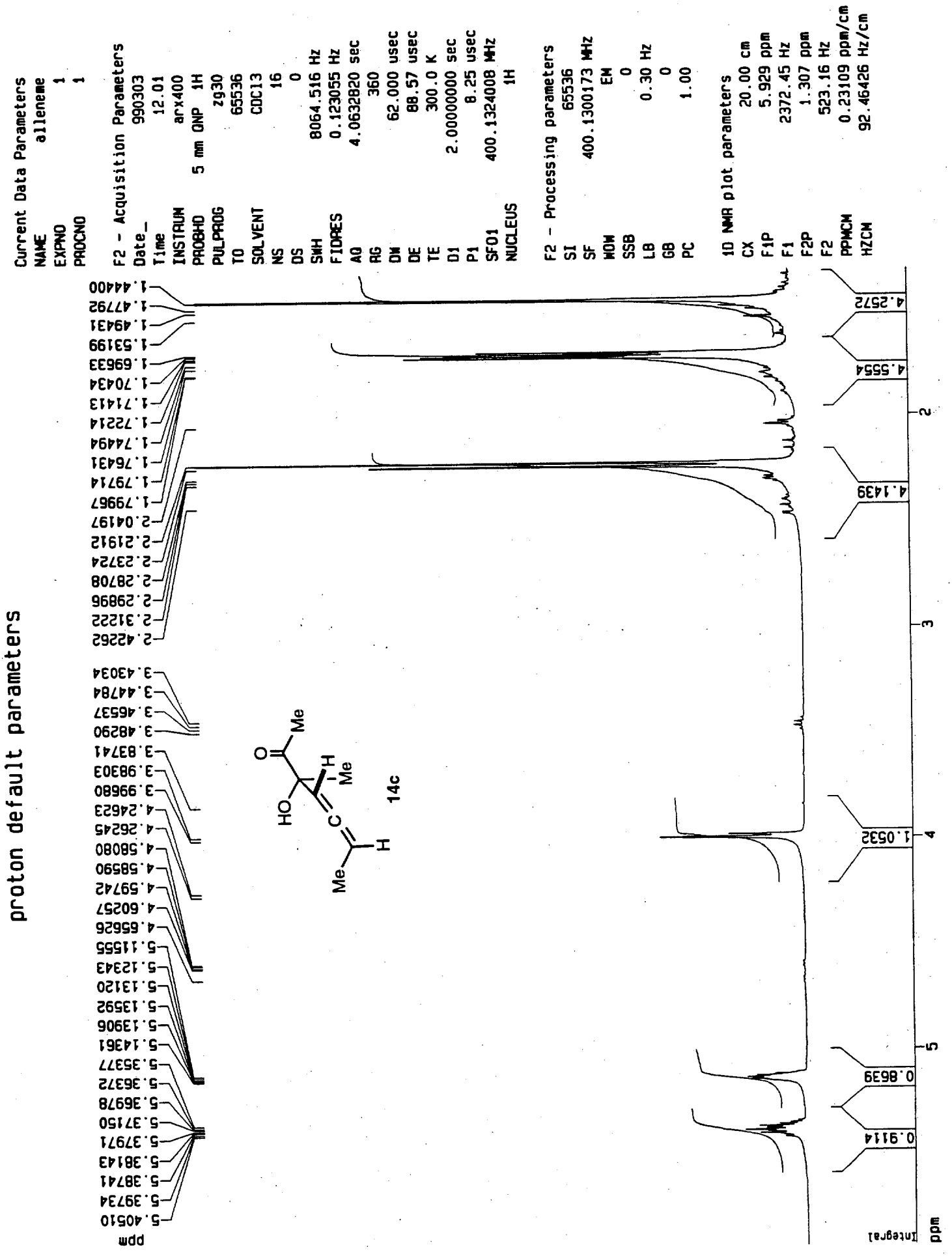

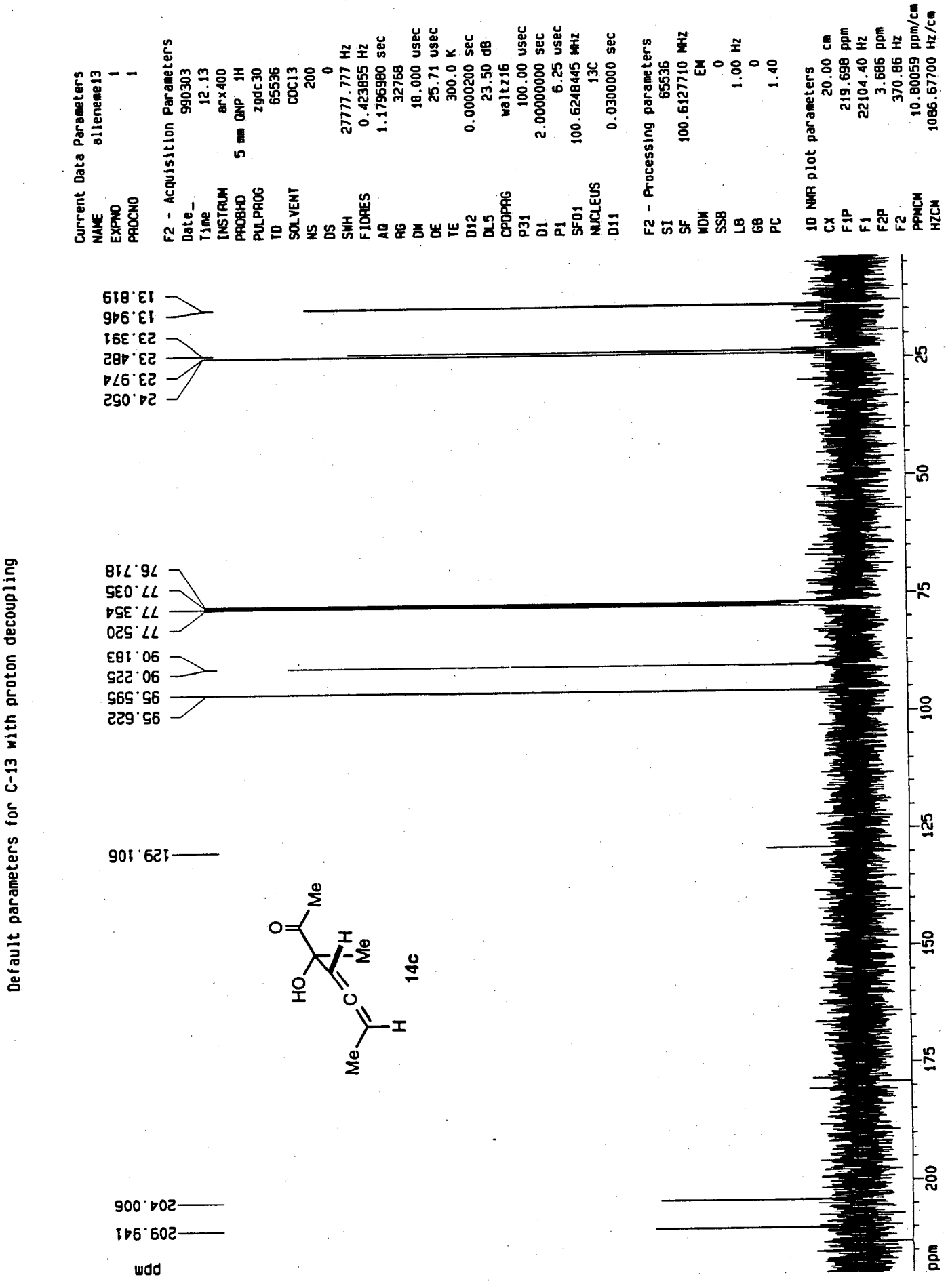

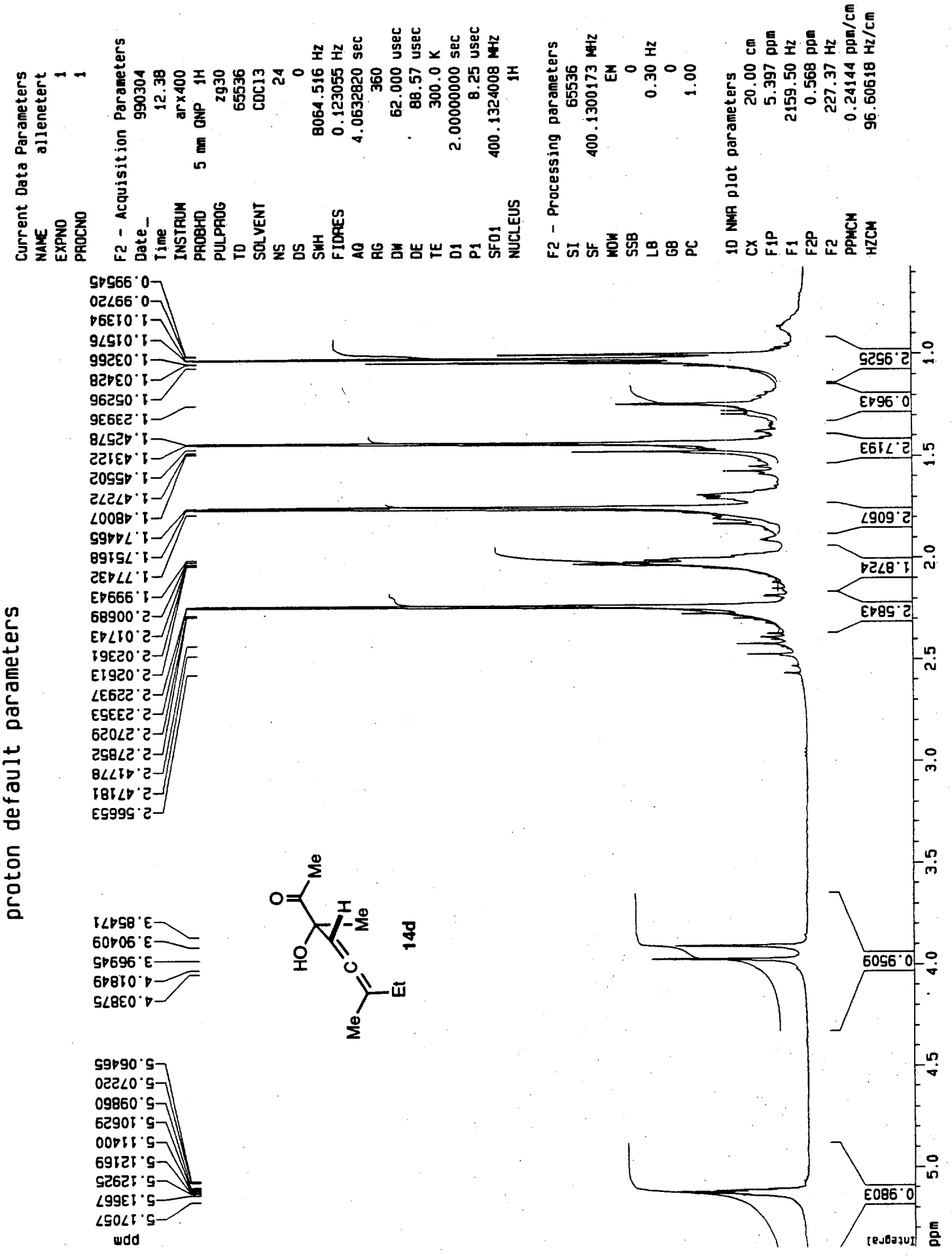

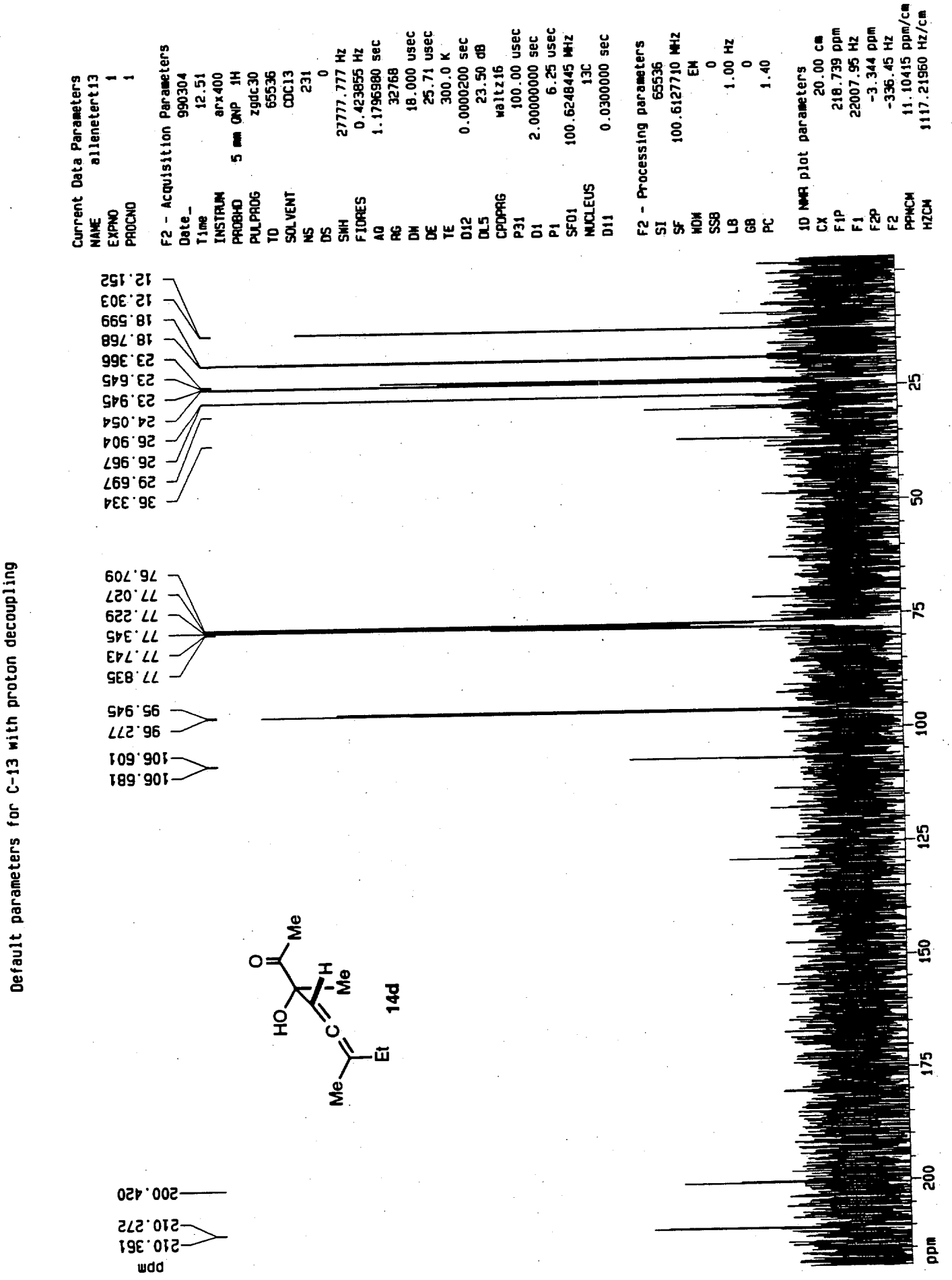

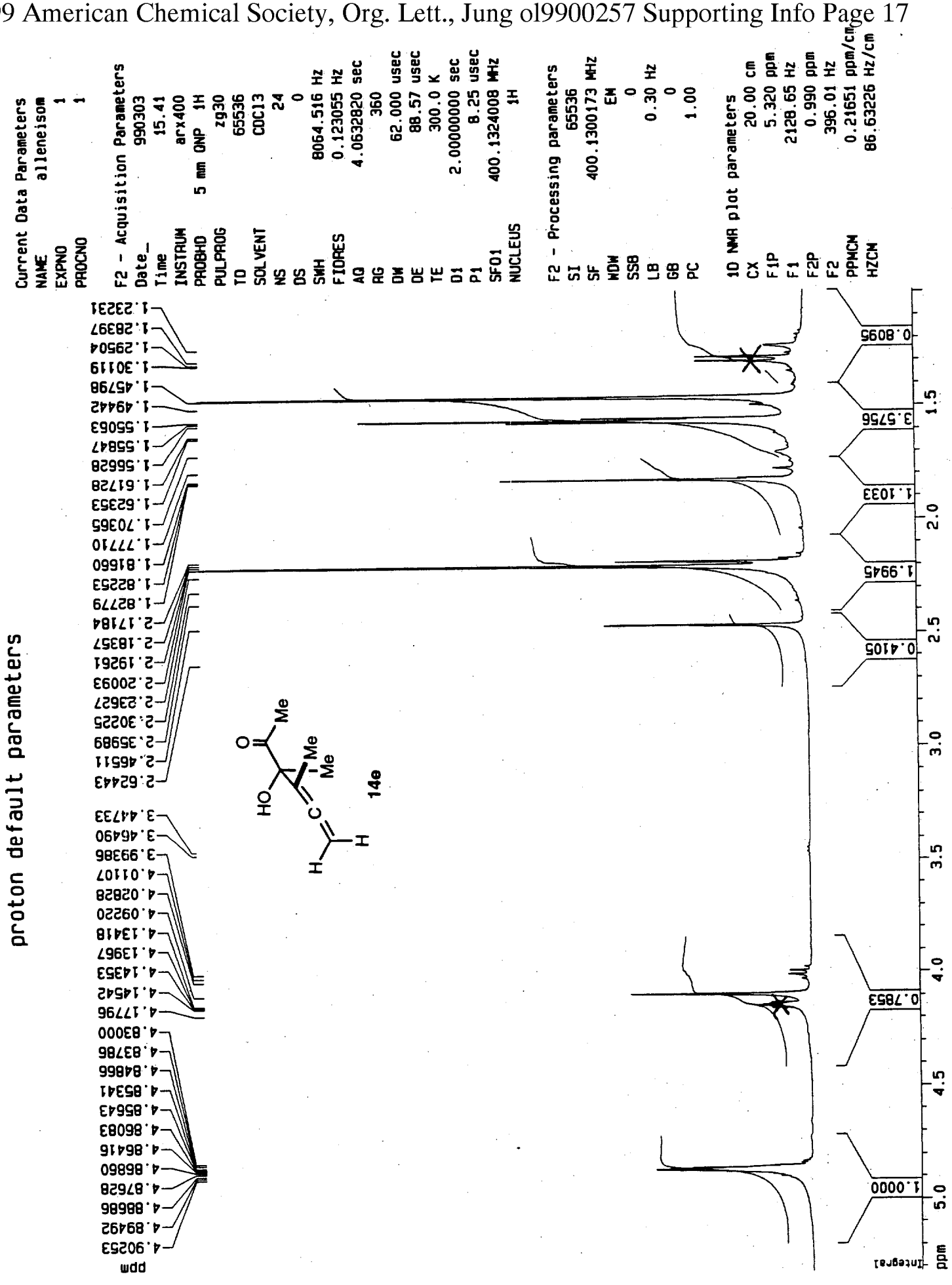

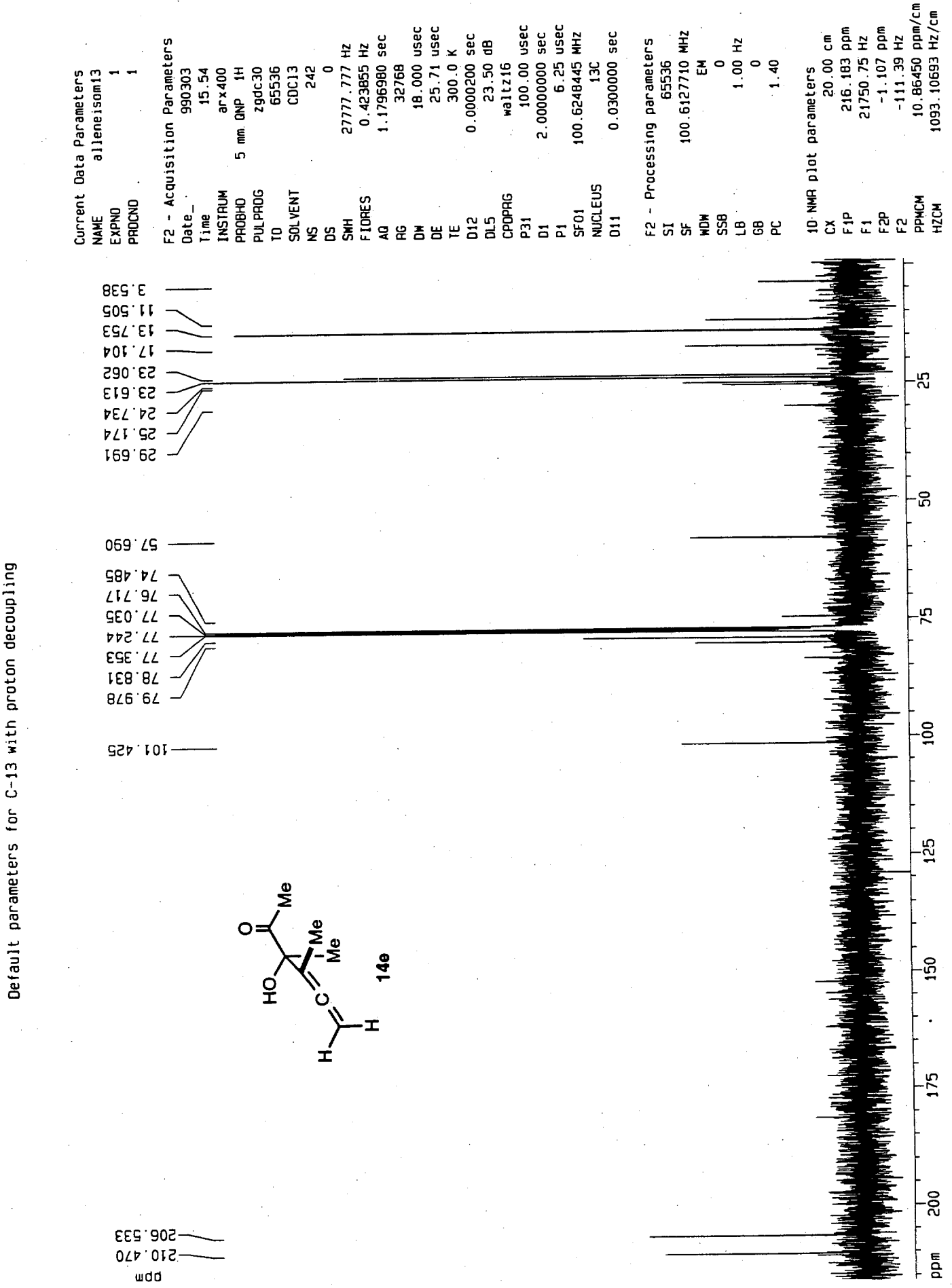

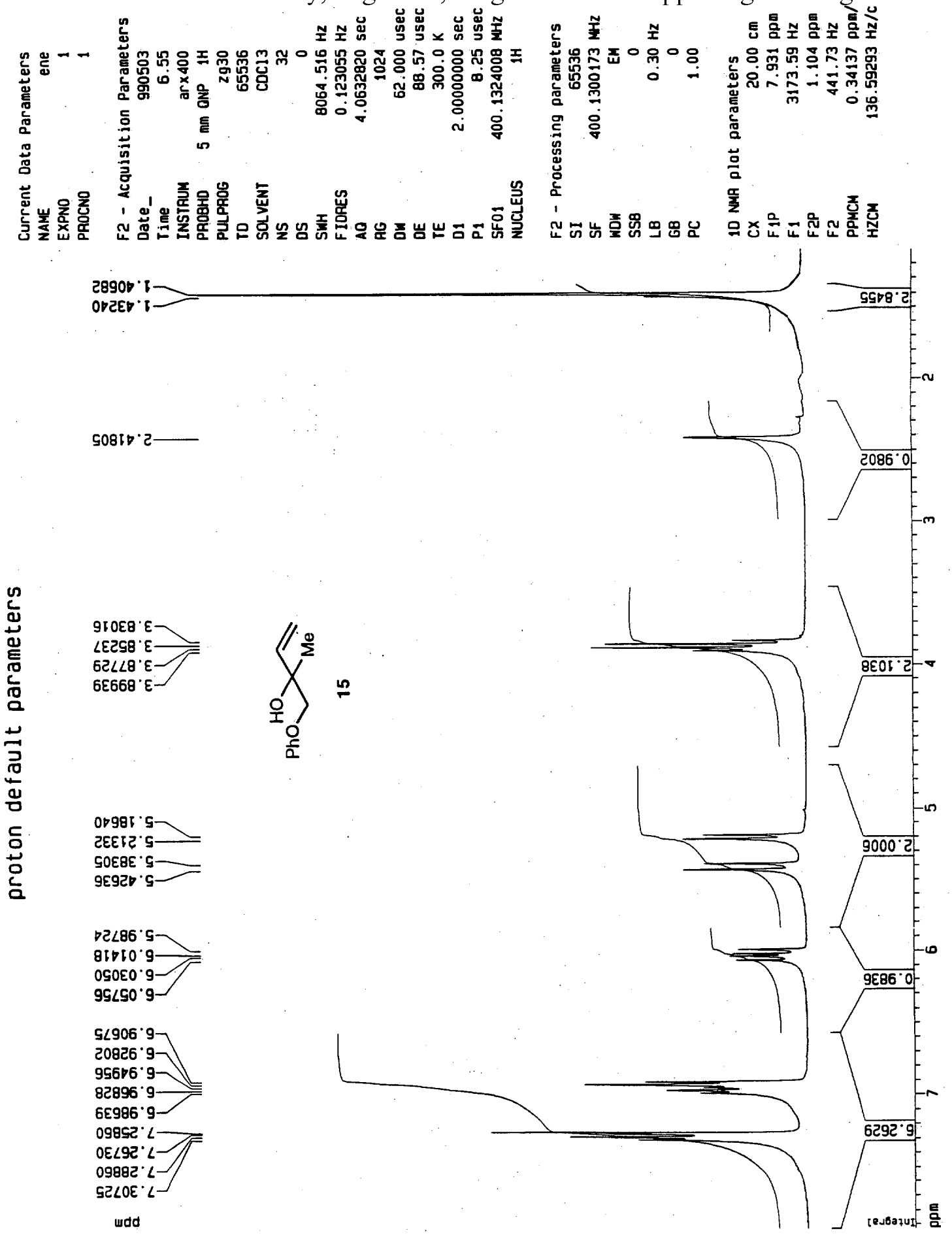
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5.21332
5.38305
5.42636
5.98724
6.01418
6.03050
6.05756
6.90675
6.92802
6.94956
6.96828
6.98639
7.25860
7.26730
7.28860
7.30725
ppm
HO
PhO
Me
15
2.8455
0.9802
2.1038
2.0006
0.9836
6.2629
Integral
ppm