

Supporting Information for *Organic Letters*

Lewis Acid-Catalyzed Nucleophilic Reactions of Enol Silyl Ethers with Propargyl Silyl Ethers

Teruhiko Ishikawa*, Toshiaki Aikawa, Yumiko Mori, and Seiki Saito*

Department of Bioscience and Biotechnology, School of Engineering, Okayama University, Tsushima,
Okayama, 700-8530 (Japan)

E-mail: seisaito@biotech.okayama-u.ac.jp

Experimental Section

Instrumentation. IR spectra were recorded on a Horiba Fourier transform infrared spectrophotometer Model FT-210 instrument. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury-300 (300 MHz for proton and 75 MHz for carbon-13) instrument. The chemical shifts are given in δ unit relative to internal CHCl₃ (7.26 ppm for ¹H) or CDCl₃ (77 ppm for ¹³C). All NMR experiments were performed using deuteriochloroform as a solvent. Mass spectra were obtained on a JEOL JMS-DX303 instrument relying on a JMA-DA5000 mass data system. Elemental analyses were made with a Perkin-Elmer 2400 CHN Elemental Analyzer.

Analytical Procedure and Data Presentation. Analytical thin layer chromatography was performed on Merck pre-coated silica gel 60 F-254 (0.25 mm thickness). ¹H-NMR spectral data were indicated in the form: δ -value of signal (peak multiplicity, integrated number of protons and coupling constant (if any)). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

General Reaction Procedure. All reactions were conducted under a nitrogen or an argon atmosphere. Liquid reagents were transferred via a dry hypodermic syringe from sure seal bottles to a reaction flask through a rubber septa wired on to the reaction flask. The septa can also serve to permit evacuation to eliminate air and introduce the inert gas by means of a steady stream of inert gas flowing system. Organic extracts were concentrated by evaporation with a rotary evaporator evacuated at around 60 mmHg. Column chromatography was performed with an open column packed with Merck silica gel 60 7734 using an appropriate ratio of ethyl acetate-hexane mixed solvent.

Synthesis of 3a-d, 4a-b, 5a-i, 6a-i. The following procedure for the synthesis of **3a** is representative. To a solution of **1a** (61 mg, 0.23 mmol) and **2a** (74 mg, 0.21 mmol) in CH₂Cl₂ was added BF₃·Et₂O (0.0025 mL, 0.02 mmol) at -30 °C. The reaction was stirred at -30 °C for 15 min and quenched by the addition of saturated aqueous solution of NaHCO₃ (1 mL). The mixture was diluted with water and extracted with ethyl acetate-hexane mixed solvent. The organic layers were dried over Na₂SO₄ and concentrated by a rotary evaporator. Purification by column chromatography (hexane/EtOAc = 100/1) provided **3a** (69 mg, 80 %): for spectral data for **3a**, see ref. 3.

2-(3,3-Diphenyl-1,2-propadienyl)-2-methylcyclohexanone (3b). ¹H NMR δ 0.19 (s, 9H), 1.35 (s, 3H), 1.55–1.72 (m, 4H), 1.76–1.87 (m, 1H), 2.20–2.33 (m, 2H), 2.37–2.49 (m, 1H), 7.20–7.38 (m, 10H); ¹³C NMR δ 1.1, 22.2, 25.3, 27.8, 39.5, 40.5, 54.0, 105.5, 106.9, 126.68, 126.72, 127.7, 128.1, 128.39, 128.41, 136.7 (2C), 206.5, 213.7; IR (neat) 2935, 1907, 1707 cm⁻¹; exact mass, m/z 374.2068 (calcd for C₂₅H₃₀OSi m/z 374.2066). Anal. Calcd for C₂₅H₃₀OSi: C, 80.16; H, 8.07. Found: C, 80.30; H, 8.28.

4,4-Dimethyl-1,1,5-triphenyl-3-propyl-1,2-pentadien-5-one (3c). ¹H NMR δ 0.84 (t, 3H, *J* = 6.4 Hz),

1.50–1.66 (m, 2H), 1.55 (s, 6H), 2.01 (t, 2H, J = 7.1 Hz), 7.10–7.18 (m, 2H), 7.30–7.45 (m, 11H), 7.88–7.94 (m, 2H); ^{13}C NMR δ 14.1, 21.5, 26.5, 31.7, 51.4, 114.1, 114.8, 127.1, 127.9, 128.1, 128.4, 128.9, 132.0, 136.1, 136.8, 201.2, 203.4; IR (neat) 2961, 1910, 1675 cm^{-1} ; exact mass, m/z 380.2138 (calcd for $\text{C}_{28}\text{H}_{28}\text{O}$ m/z 380.2140). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}$: C, 88.38; H, 7.42. Found: C, 88.07; H, 7.22.

1,3-Diphenyl-2,2,3-trimethyl-5-trimethylsilyl-4-pentyn-1-one (4a). ^1H NMR δ 0.20 (s, 9H), 1.30 (s, 3H), 1.43 (s, 3H), 1.93 (s, 3H), 6.76–6.80 (m, 2H), 7.14–7.20 (m, 2H), 7.26–7.36 (m, 4H), 7.57–7.60 (m, 2H); ^{13}C NMR δ 0.3, 24.8, 24.9, 25.8, 48.1, 53.9, 89.0, 111.0, 127.3, 127.4, 127.6, 128.1, 128.9, 130.2, 141.5, 142.6, 210.9; IR (neat) 2167, 1670 cm^{-1} ; exact mass, m/z 348.1908 (calcd for $\text{C}_{28}\text{H}_{28}\text{O}$ m/z 348.1909). Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{OSi}$: C, 79.26; H, 8.10. Found: C, 79.44; H, 8.01.

4,4-Dimethyl-3-trimethylsilyl-1,1,7-triphenyl-1,2,(6E)-heptatrien-5-one (3d) and **4,4-Dimethyl-7-trimethylsilyl-1,5,5-triphenyl-(1E)-hepten-6-yn-3-one (4b)**. Data for **3d**: ^1H NMR δ 0.17 (s, 9H), 1.47 (s, 6H), 7.20–7.58 (m, 17 H); Data for **4b**: ^1H NMR δ 0.30 (s, 9H), 1.43 (s, 6H), 6.93–7.04 (m b, 2H), 7.20–7.58 (m, 15 H); ^{13}C NMR δ 0.0, 24.8, 53.9, 57.1, 91.8, 111.5, 124.4, 126.8, 127.7, 128.3, 128.5, 129.7, 135.2, 141.3, 142.6, 203.2; IR (neat) 3002, 2207, 1750 cm^{-1} ; exact mass, m/z 374.2061 (calcd for $\text{C}_{25}\text{H}_{30}\text{OSi}$ m/z 374.2066). Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{OSi}$: C, 80.16; H, 8.07. Found: C, 79.91; H, 8.22.

Ethyl 4,7,7-trimethyl-8-oxo-6,8-diphenyl-4-octen-2-ynoate (5a). Data for Z-isomer: ^1H NMR δ 1.29 (s, 3H), 1.35 (t, 3H, J = 7.1 Hz), 1.36 (s, 3H), 1.92 (d, 3H, J = 1.4 Hz), 4.28 (q, 2H, J = 7.1 Hz), 4.59 (d, 1H, J = 10.7 Hz), 6.50 (dq, 1H, J = 1.4, 10.7 Hz), 7.08–7.58 (m, 10H); ^{13}C NMR δ 14.1, 22.2, 24.0, 24.4, 52.0, 53.8, 61.9, 84.8, 84.9, 117.9, 126.9, 127.8, 128.05, 128.13, 129.4, 130.8, 139.1, 139.5, 142.5, 153.8, 208.0; IR (neat) 2212, 1709, 1674 cm^{-1} ; exact mass, m/z 374.1879 (calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3$ m/z 374.1882). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3$: C, 80.18; H, 7.00. Found: C, 79.95; H, 6.88.

1,5-Diphenyl-4,4,7-trimethyl-9-trimethylsilyl-6-nonene-1,8-diyn-3-one (5b). Data for Z-isomer: ^1H NMR δ 0.11 (s, 9H), 1.26 (s, 3H), 1.28 (s, 3H), 1.88 (d, 3H, J = 1.4 Hz), 4.39 (d, 1H, J = 10.4 Hz), 6.16 (dq, 1H, J = 1.4, 10.4 Hz), 7.17–7.60 (m, 10H); ^{13}C NMR δ -0.1, 22.1, 22.3, 23.1, 52.4, 53.5, 86.8, 92.7, 99.0, 104.2, 120.3, 121.0, 126.6, 127.9, 128.5, 129.5, 130.5, 132.9, 136.4, 140.1, 192.9; IR (neat) 2964, 2199, 2143, 1664 cm^{-1} ; exact mass, m/z 398.2056 (calcd for $\text{C}_{27}\text{H}_{30}\text{OSi}$ m/z 398.2066). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{OSi}$: C, 81.35; H, 7.59. Found: C, 81.15; H, 7.44.

1,5-Diphenyl-4,4,7-trimethyl-9-trimethylsilyl-(1E),6-nonadien-8-yn-3-one (5c). Data for Z-isomer: ^1H NMR δ 0.23 (s, 9H), 1.21 (s, 3H), 1.22 (s, 3H), 1.85 (d, 3H, J = 1.4 Hz), 4.35 (d, 1H, J = 10.4 Hz), 6.13 (dq, 1H, J = 1.4, 10.4 Hz), 7.11 (d, 1H, J = 15.7 Hz), 7.12–7.58 (m, 10H), 7.62 (d, 1H, J = 15.7 Hz); ^{13}C NMR δ 0.1, 22.1, 22.5, 23.0, 50.9, 53.4, 98.8, 104.4, 120.7, 121.9, 126.6, 127.9, 128.3, 128.8, 129.4, 130.1, 135.1, 136.7, 140.2, 142.4, 202.8; IR (neat) 2964, 2204, 1608 cm^{-1} . exact mass, m/z 400.2221 (calcd for $\text{C}_{27}\text{H}_{32}\text{OSi}$ m/z 400.2222). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{OSi}$: C, 80.95; H, 8.05. Found: C, 80.88; H, 8.01.

2,5-Dimethyl-1,3-diphenyl-7-trimethylsilyl-4-hepten-6-yn-1-one (5d). Data for major isomer: ^1H NMR δ 0.25 (s, 9H), 1.28 (d, 3H, J = 7.2 Hz), 1.87 (d, 3H, J = 1.7 Hz), 3.84–4.00 (m, 1H), 4.45 (t, 1H, J = 10.2 Hz), 5.88 (dq, 1H, J = 1.4, 10.4 Hz), 7.16–7.60 (m, 10H); ^{13}C NMR δ 0.0, 16.4, 23.0, 45.8, 49.5, 98.5, 104.4, 119.7, 126.2, 127.7, 128.0, 128.2, 128.4, 132.7, 137.0, 139.1, 142.8, 202.9; IR (neat) 2964, 2180, 1716 cm^{-1} . exact mass, m/z 360.1907 (calcd for $\text{C}_{24}\text{H}_{28}\text{OSi}$ m/z 360.1909). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{OSi}$: C, 79.95; H, 7.83. Found: C, 79.79; H, 7.68.

2-Methyl-2-(3-methyl-5-trimethylsilyl-1-phenyl-2-penten-4-ynyl)cyclohexanone (5e). Data for major isomer: ^1H NMR δ 0.22 (s, 9H), 0.95 (s, 3H), 1.20–1.34 (m, 1H), 1.60–1.80 (m, 3H), 1.78 (d, 3H, J = 1.4 Hz), 1.92–2.40 (m, 3H), 2.86 (dt, 1H, J = 6.0, 13.7 Hz), 4.66 (d, 1H, J = 10.7 Hz), 6.05 (dq, 1H, J =

1.4, 10.7 Hz), 7.10–7.36 (m, 5H); ^{13}C NMR δ 0.0, 19.2, 21.1, 22.7, 27.9, 37.5, 39.1, 48.1, 52.4, 98.6, 104.3, 119.9, 126.7, 127.9, 129.8, 136.3, 139.5, 215.3; IR (neat) 2935, 2143, 1707 cm^{-1} . exact mass, m/z 338.2052 (calcd for $\text{C}_{22}\text{H}_{30}\text{OSi}$ m/z 338.2066). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{OSi}$: C, 78.05; H, 8.93. Found: C, 78.23; H, 901.

(6E)-Benzylidene-2-methyl-2-(3-methyl-5-trimethylsilyl-1-phenyl-2-penten-4-ynyl)cyclohexanone (5f). Data for major isomer: ^1H NMR δ 0.14 (s, 9H), 1.17 (s, 3H), 1.21 (s, 3H), 1.58–2.20 (m, 4H), 1.87 (d, 3H, J = 1.4 Hz), 2.62–2.82 (m b, 2H), 4.22 (d, 1H, J = 10.4 Hz), 6.32 (dq, 1H, J = 1.4, 10.4 Hz), 7.10–7.40 (m, 11H); ^{13}C NMR δ –0.1, 19.7, 22.6, 23.0, 29.2, 35.4, 51.5, 53.3, 98.5, 104.6, 119.9, 126.5, 127.9, 128.1, 129.5, 129.7, 130.0, 135.6, 136.1, 137.8, 140.7, 206.1; IR (neat) 2935, 2180, 1628 cm^{-1} . exact mass, m/z 426.2382 (calcd for $\text{C}_{29}\text{H}_{34}\text{OSi}$ m/z 426.2379). Anal. Calcd for $\text{C}_{29}\text{H}_{34}\text{OSi}$: C, 81.64; H, 8.03. Found: C, 81.71; H, 7.91.

2-Methyl-2-(3-methyl-5-trimethylsilyl-1-phenyl-2-penten-4-ynyl)cyclopentanone (5g). Data for diastereomer pair: ^1H NMR δ (0.20, 0.22) (s, 9H for each), (1.05, 1.06) (s, 3H for each), 1.58–1.80 (m, 8/2H), (1.85, 1.87) (d, 3H, J = 1.4 Hz for each), 2.10–2.22 (m, 4/2H), [3.95 (d, 1H, J = 10.4 Hz), 4.25 (d, 1H, J = 10.7 Hz)], [6.06 (dq, 1H, J = 1.4, 10.7 Hz), 6.40 (dq, 1H, J = 1.4, 10.4 Hz)], 7.10–7.30 (m, 10/2H); ^{13}C NMR δ (0.06, 0.17), (18.5, 18.7), (21.6, 22.4), (18.8, 22.9), (32.6, 35.0), (38.3, 39.4), (50.6, 53.5), (52.3, 52.9), (98.4, 98.7), (104.1, 104.6), (119.7, 120.7), (126.4, 126.5), (127.3, 128.1), (129.0, 129.6), (136.7, 137.7), (140.4, 141.2), (222.0, 222.8); IR (neat) 2958, 2143, 1737 cm^{-1} . exact mass, m/z 324.1915 (calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$ m/z 324.1909). Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70. Found: C, 77.90; H, 8.91.

2-*tert*-Butyldimethylsilyloxy-4,4,7-trimethyl-9-trimethylsilyl-6-non-en-8-yn-3-one (5h). Data for major isomer: ^1H NMR δ –0.02 (s, 3H), 0.04 (s, 3H), 0.20 (s, 9H), 0.86 (s, 9H), 1.13 (d, 3H, J = 6.6 Hz), 1.21 (s, 3H), 1.22 (s, 3H), 1.84 (d, 3H, J = 1.7 Hz), 4.26 (d, 1H, J = 10.4 Hz), 4.48 (q, 1H, J = 6.6 Hz), 6.19 (dq, 1H, J = 1.7, 10.4 Hz), 7.10–7.26 (m, 5H); ^{13}C NMR δ –4.5, –4.4, 0.0, 18.2, 20.8, 23.0, 23.2, 25.8, 51.0, 53.7, 71.3, 98.8, 104.3, 120.3, 126.4, 127.9, 129.8, 137.7, 140.8, 213.7; IR (neat) 2935, 2143, 1707 cm^{-1} . exact mass, m/z 456.28775 (calcd for $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Si}_2$ m/z 456.28798). Anal. Calcd for $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Si}_2$: C, 70.99; H, 9.71. Found: C, 70.71; H, 9.60.

2-*tert*-Butyldimethylsilyloxy-4,7-dimethyl-9-trimethylsilyl-6-non-en-8-yn-3-one (5i). Data for major isomer: ^1H NMR δ –0.05 (s, 3H), 0.01 (s, 3H), 0.25 (s, 9H), 0.76 (d, 3H, J = 6.9 Hz), 0.90 (s, 9H), 1.10 (d, 3H, J = 6.9 Hz), 1.84 (d, 3H, J = 1.4 Hz), 3.56 (dq, 1H, J = 6.9, 10.3 Hz), 3.96 (q, 1H, J = 6.9 Hz), 4.02–4.26 (m, 1H), 5.80 (dq, 1H, J = 1.4, 10.3 Hz), 7.10–7.26 (m, 5H); ^{13}C NMR δ –4.8, –4.5, 0.0, 16.0, 18.0, 19.6, 25.8, 22.9, 45.0, 49.2, 74.7, 98.5, 104.2, 119.8, 126.3, 128.0, 128.4, 139.3, 142.9, 215.8; IR (neat) 2979, 2138, 1714 cm^{-1} . exact mass, m/z 442.27248 (calcd for $\text{C}_{26}\text{H}_{42}\text{O}_2\text{Si}_2$ m/z 442.27233). Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_2\text{Si}_2$: C, 70.53; H, 9.56. Found: C, 70.31; H, 9.68.

3-(1-Benzoyl-1-methylethyl)-1-(phenylethynyl)cyclohexene (6a): for spectral data and copies of NMR spectra (^1H and ^{13}C) of **6a**, see supporting information accompanied to ref. 3.

3-(1-Phenylpropioloyl-1-methylethyl)-1-(phenylethynyl)cyclohexene (6b). ^1H NMR δ 1.23 (s, 3H), 1.27 (s, 3H), 1.26–1.38 (m, 1H), 1.54–1.70 (m, 1H), 1.76–1.96 (m, 2H), 2.18–2.26 (m b, 2H), 2.81–2.91 (m b, 1H), 6.09 (s b, 1H), 7.25–7.62 (m, 10H); ^{13}C -NMR δ 20.8, 21.2, 22.3, 23.3, 29.3, 43.0, 51.3, 86.3, 87.6, 90.9, 92.5, 120.1, 123.0, 123.5, 127.8, 128.2, 128.6, 130.6, 131.4, 133.0, 134.7, 193.5; IR (neat) 2935, 2197, 1662 cm^{-1} . exact mass, m/z 352.18262 (calcd for $\text{C}_{26}\text{H}_{24}\text{O}$ m/z 352.18271). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}$: C, 88.60; H, 6.86. Found: C, 88.81; H, 6.71.

3-(1-Cinnamoyl-1-methylethyl)-1-(phenylethynyl)cyclohexene (6c). ^1H NMR δ 1.18 (s, 3H), 1.23 (s,

3H), 1.20–1.35 (m, 1H), 1.50–1.90 (m, 3H), 2.16–2.24 (m b, 2H), 2.68–2.80 (m, 1H), 6.06 (s b, 1H), 7.14 (d, 1H, J = 15.4 Hz), 7.26–7.46 (m, 8H), 7.57–7.63 (m, 2H), 7.73 (d, 1H, J = 15.4 Hz); ^{13}C -NMR δ 20.8, 21.4, 22.3, 23.4, 29.3, 42.8, 49.6, 87.5, 90.9, 120.9, 122.9, 123.5, 127.8, 128.2, 128.3, 128.8, 130.3, 131.4, 134.9, 135.0, 143.3, 203.4; IR (neat) 2964, 2213, 1618 cm^{-1} ; exact mass, m/z 354.19829 (calcd for $\text{C}_{26}\text{H}_{26}\text{O}$ m/z 354.19836). Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_2\text{Si}_2$: C, 88.09; H, 7.39. Found: C, 88.33; H, 7.40.

Ethyl [3-(1-benzoyl-1-methylethyl)cyclohexenyl]propiolate (6d) and **Ethyl (3-Hydroxycyclohexenyl)propiolate (7a)**. Data for **6d**: ^1H NMR δ 1.23 (s, 3H), 1.31 (t, 3H, J = 7.1 Hz), 1.32 (s, 3H), 1.40–1.92 (m, 4H), 2.10–2.20 (m b, 2H), 2.92–3.02 (m b, 1H), 4.24 (q, 2H, J = 7.1), 6.30 (s b, 1H), 7.34–7.66 (m, 5H); ^{13}C -NMR δ 14.1, 21.9, 22.6, 23.1, 28.2, 43.5, 50.6, 61.9, 79.1, 87.7, 120.4, 127.6, 128.2, 131.0, 138.8, 142.0, 154.2, 208.3; IR (neat) 2980, 2937, 2212, 1707, 1674 cm^{-1} ; exact mass, m/z 324.17248 (calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$ m/z 324.17254). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.33.

Data for **7a**: ^1H NMR δ 1.31 (t, 3H J = 7.1 Hz), 1.50–1.96 (m, 4H), 2.06–2.22 (m, 2H), 4.25 (q, 2H, J = 7.1 Hz), 4.24–4.30 (m b, 1H), 6.35–6.40 (m b, 1H); ^{13}C -NMR δ 14.0, 18.8, 28.2, 30.7, 62.0, 65.3, 79.9, 86.4, 121.3, 141.7, 154.0; IR (neat) 3450, 2942, 2214, 1711 cm^{-1} .

3-(1-Benzoyl-1-methylethyl)-1-(trimethylsilylethynyl)cyclohexene (6e) and **3-Hydroxy-1-(trimethylsilylethynyl)cyclohexene (7b)**. Data for **6e**: ^1H NMR δ 0.17 (s, 9H), 1.22 (s, 3H), 1.23–1.28 (m, 1H), 1.30 (s, 3H), 1.38–1.85 (m, 3H), 2.06–2.14 (m b, 2H), 2.86–2.98 (m, 1H), 6.01 (s b, 1H), 7.37–7.50 (m, 3H), 7.61–7.67 (m, 2H); ^{13}C -NMR δ 0.0, 22.2, 22.5, 23.0, 23.4, 29.2, 43.1, 50.7, 91.7, 106.8, 122.8, 127.6, 128.1, 130.8, 135.9, 139.0, 208.8; IR (neat) 2939, 2242, 1674 cm^{-1} ; exact mass, m/z 324.19090 (calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$ m/z 324.19094). Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70. Found: C, 77.61; H, 8.66.

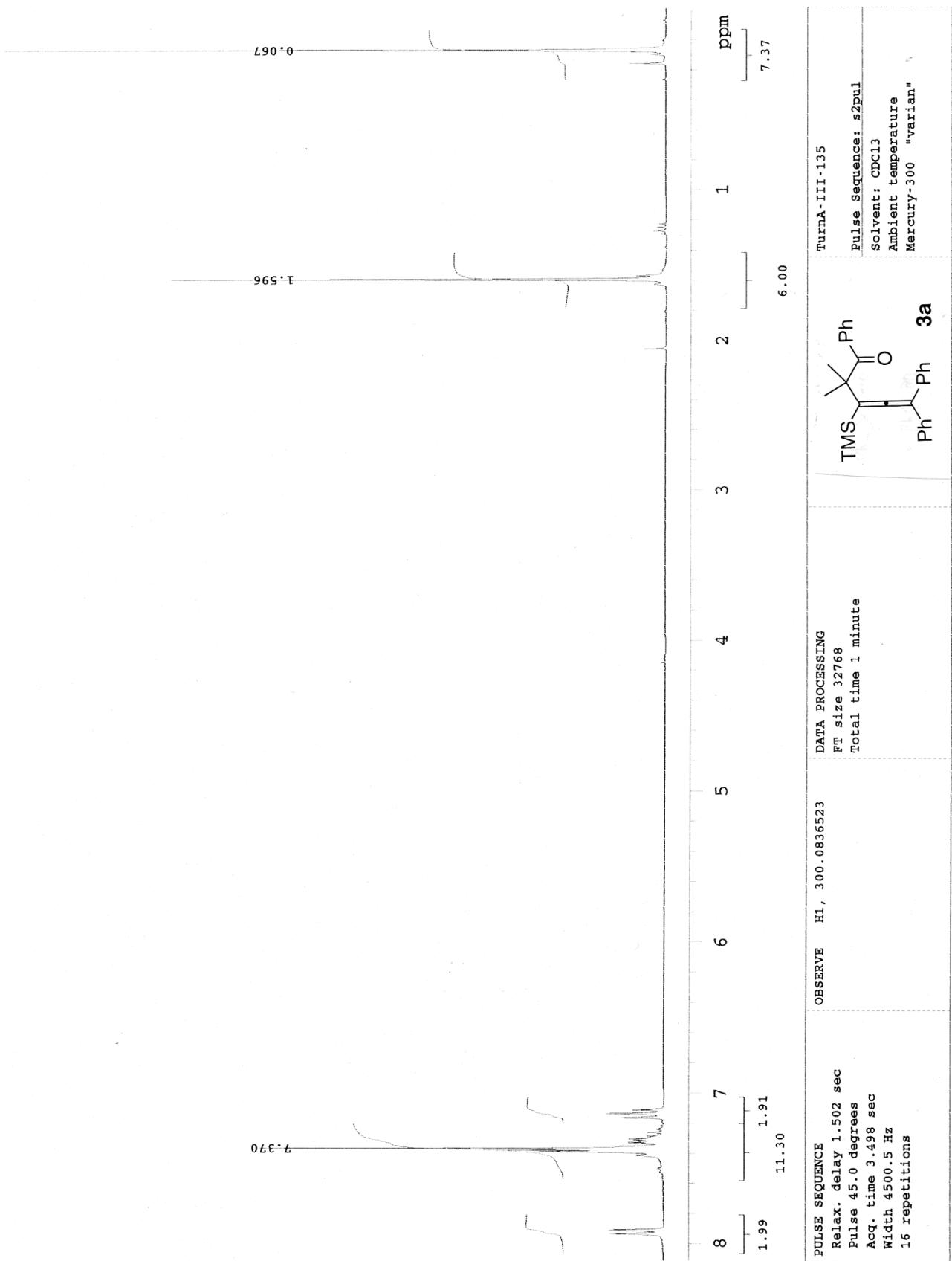
Data for **7e**: ^1H NMR δ 0.17 (s, 9H), 1.50–1.90 (m, 4H), 2.05–2.18 (m, 2H), 4.18–4.28 (m b, 1H), 6.11–6.16 (m, 1H); ^{13}C -NMR δ –0.1, 18.8, 29.2, 31.0, 65.4, 93.5, 105.7, 124.0, 136.6; IR (neat) 3450, 2939, 2240 cm^{-1} .

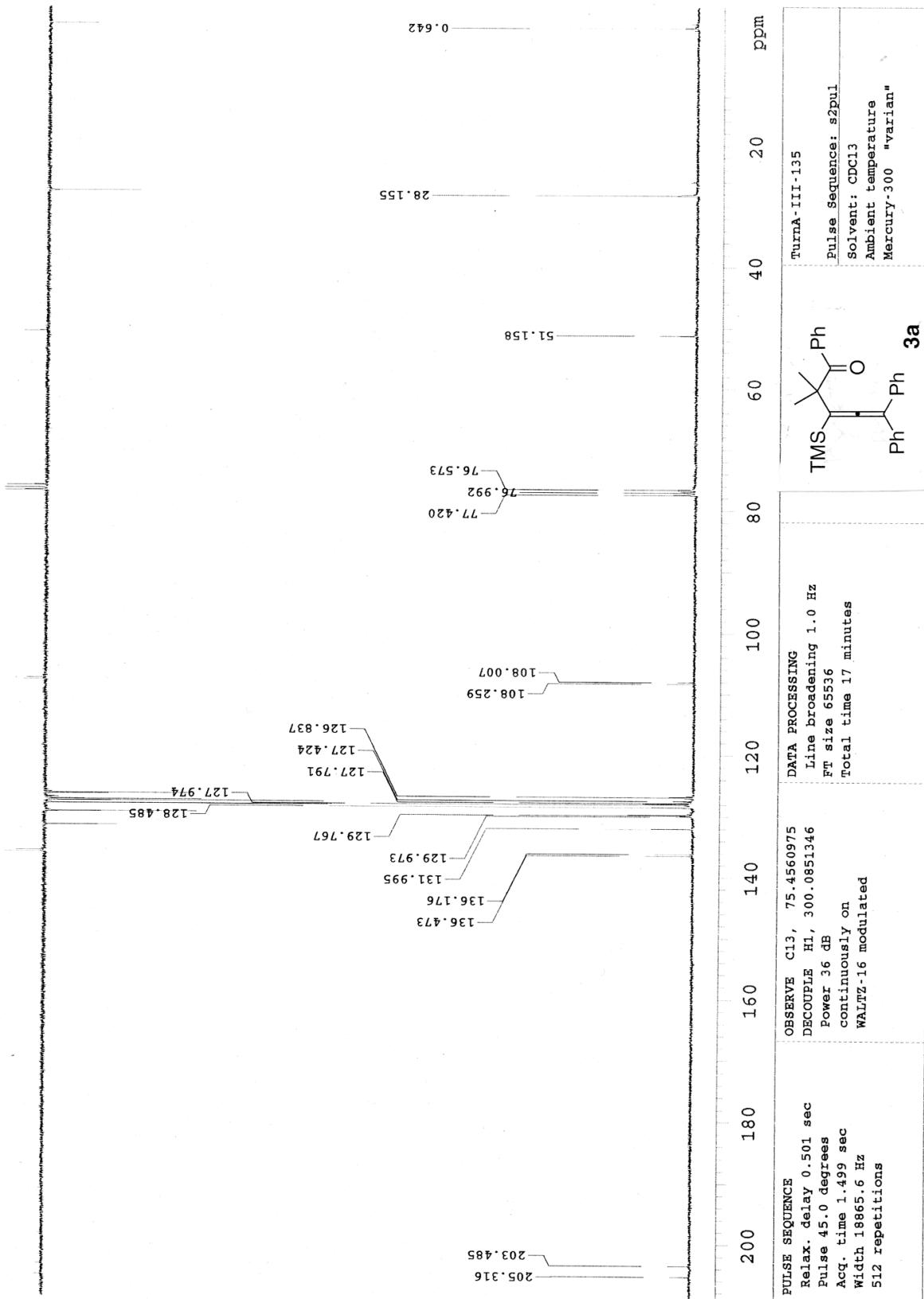
2-Methyl-2-[3-(phenylethynyl)-2-cyclohexen-1-yl]cyclohexanone (6f). Data for diastereomer pair: ^1H NMR δ 0.97 (s, 6/2H), 1.16–1.28 (m, 2/2H), 1.38–2.10 (m, 18/2H), 2.14–2.24 (m, 4/2H), 2.32–2.58 (m, 4/2H), 2.80–2.96 (m, 2/2H), (5.80, 6.04) (s b, 1H for each), 7.24–7.45 (m, 10/2H); ^{13}C -NMR δ (18.8, 19.5), (20.6, 20.7), (22.0, 22.6), (22.36, 22.39), (27.2, 27.5), 29.2, (35.5, 36.5), (38.6, 39.1), (39.2, 39.8), (51.5, 51.7), 87.4, (90.7, 90.9), (122.6, 122.7), 123.5, (127.76, 127.83), (128.17, 128.20), 131.4, (134.8, 135.4), (215.2, 215.8); IR (neat) 2935, 2204, 1705 cm^{-1} ; exact mass, m/z 292.18271 (calcd for $\text{C}_{21}\text{H}_{24}\text{O}$ m/z 292.18271). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}$: C, 86.26; H, 8.27. Found: C, 86.20; H, 8.20.

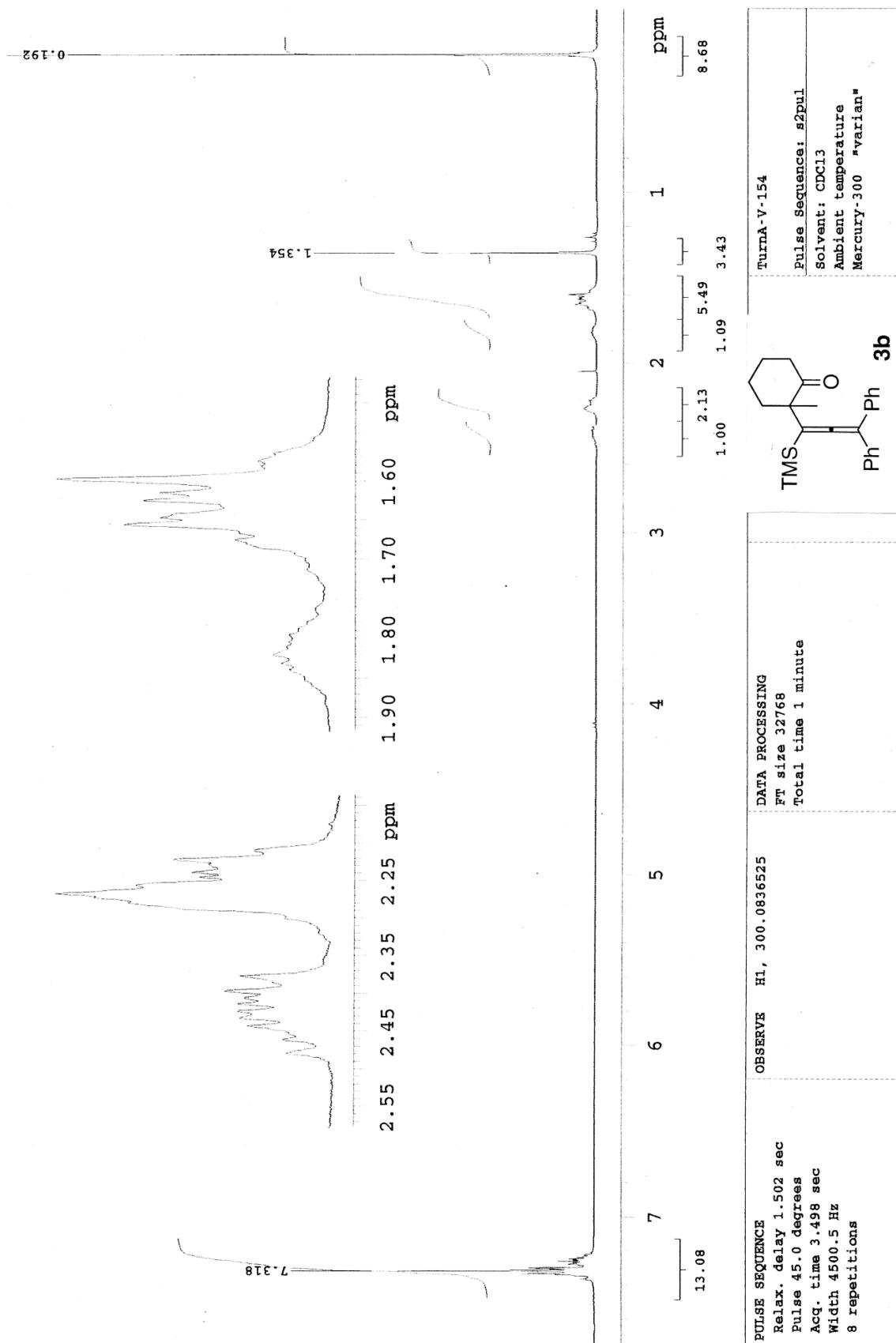
(6E)-Benzilidene-2-methyl-2-[3-(phenylethynyl)-2-cyclohexen-1-yl]cyclohexanone (6g). Data for major isomer: ^1H NMR δ 1.19 (s, 3H), 1.20–1.34 (m, 1H), 1.50–2.00 (m, 7H), 2.17–2.26 (m, 2H), 2.68–2.86 (m b, 3H), 6.10 (s b, 1H), 7.25–7.46 (m, 11H); ^{13}C -NMR δ 19.6, 22.0, 22.3, 22.9, 29.1, 29.4, 32.6, 42.0, 49.9, 87.3, 91.1, 122.7, 123.6, 128.2, 128.3, 130.2, 131.4, 135.2, 135.7, 135.8, 135.9, 136.4, 137.2, 206.6; IR (neat) 2935, 2204, 1631 cm^{-1} ; exact mass, m/z 380.21411 (calcd for $\text{C}_{28}\text{H}_{28}\text{O}$ m/z 380.21402). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}$: C, 88.38; H, 7.42. Found: C, 88.45; H, 7.40.

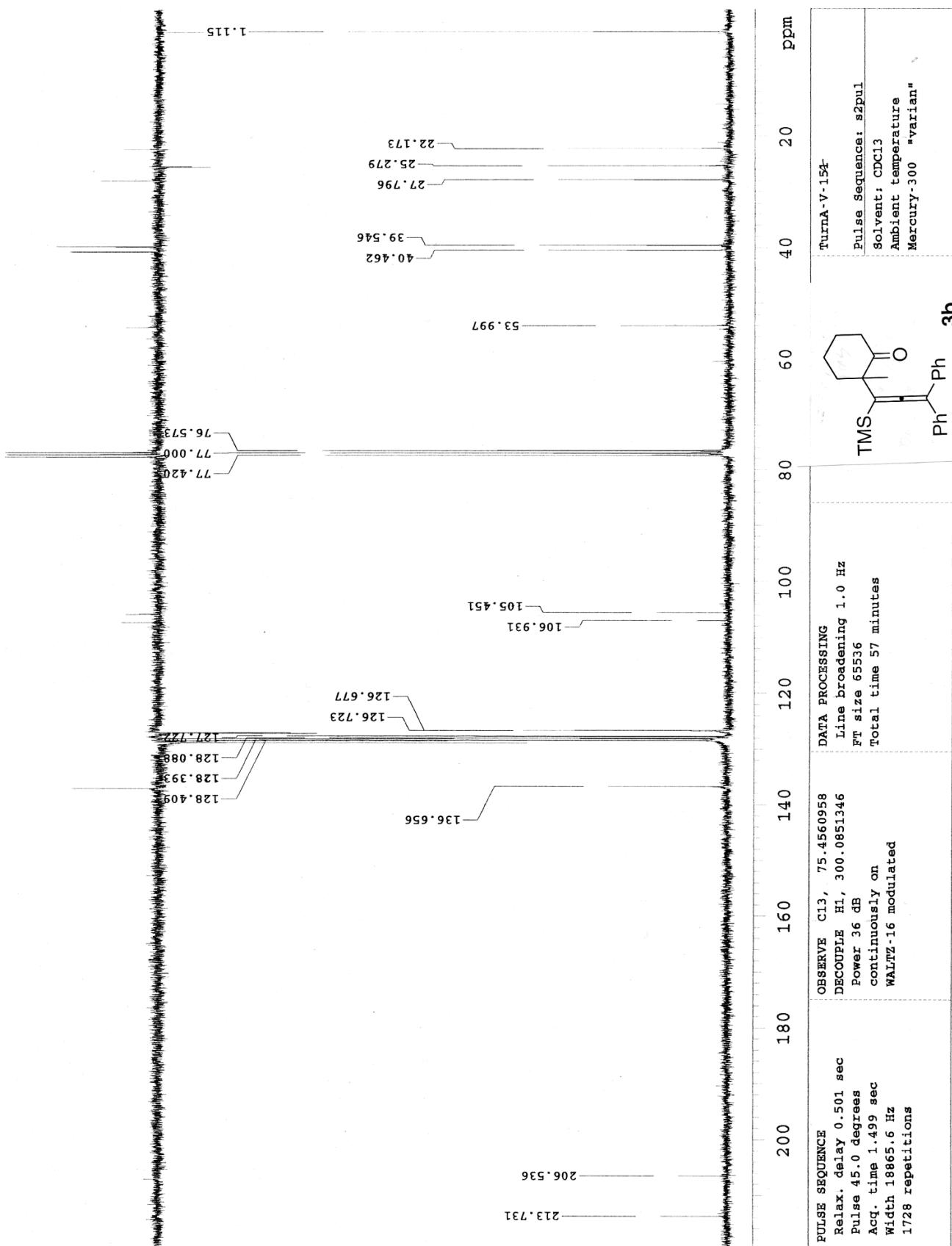
2-Methyl-2-[3-(phenylethynyl)-2-cyclohexen-1-yl]cyclopentanone (6h). Data for major isomer: ^1H NMR δ 1.08 (s, 3H), 1.14–1.28 (m, 3H), 1.46–2.00 (m, 8H), 2.10–2.24 (m, 3H), 2.28–2.64 (m, 2H), 6.23 (s b, 1H), 7.25–7.44 (m, 5H); ^{13}C -NMR δ 18.7, 20.8, 22.1, 23.5, 38.6, 41.6, 50.8, 87.3, 90.8, 123.1, 123.5, 127.8, 128.2, 131.4, 134.9, 222.9; IR (neat) 2958, 2204, 1735 cm^{-1} ; exact mass, m/z 278.16695 (calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ m/z 278.16706). Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29; H, 7.97. Found: C, 85.98; H, 7.90.

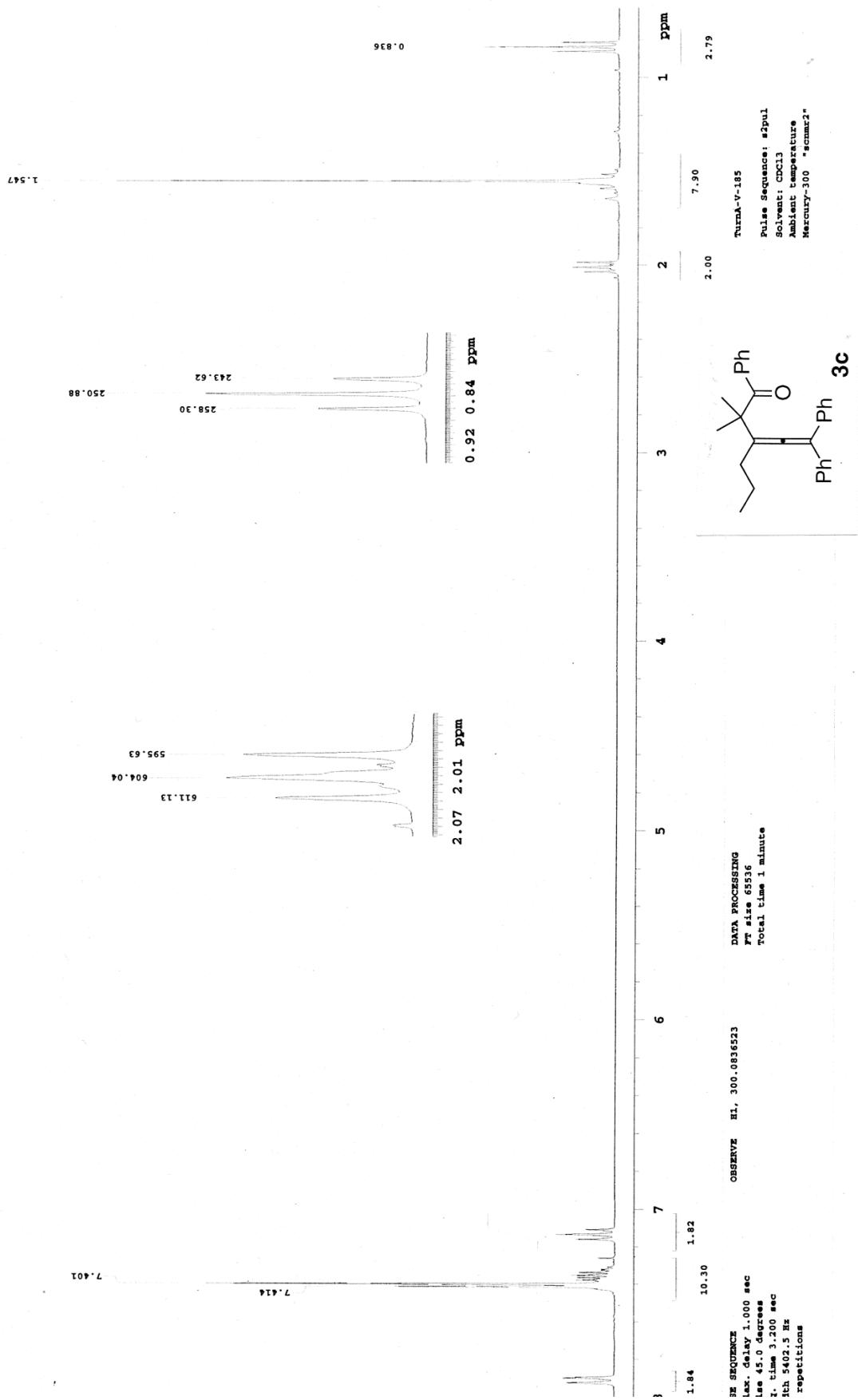
4-*tert*-Butyldimethylsiloxy-2-methyl-2-[3-(phenylethynyl)-2-cyclohexen-1-yl]-3-pentanone (6i). Data for major isomer: ^1H NMR δ 0.10 (s, 3H), 0.11(s, 3H), 0.91 (s, 9H), 1.11 (s, 3H), 1.23 (s, 3H), 1.20–1.28 (m, 1H), 1.34 (d, 3H, J = 6.9 Hz), 1.58–1.74 (m, 2H), 1.80–1.92 (m, 1H), 2.14–2.24 (m b, 2H), 2.90–3.00 (m, 1H), 4.59 (q, 1H, J = 6.9 Hz), 5.97 (s b, 1H), 7.25–7.43 (m, 5H); ^{13}C -NMR δ –4.6, –4.2, 18.0, 21.0, 21.1, 21.3, 22.3, 23.4, 25.8, 29.2, 41.8, 50.4, 72.2, 87.2, 91.0, 122.3, 123.5, 128.2, 131.4, 131.5, 135.5, 214.9; IR (neat) 2933, 2206, 1716 cm^{-1} ; exact mass, m/z 410.26418 (calcd for $\text{C}_{26}\text{H}_{38}\text{O}_2\text{Si}$ m/z 410.26411). Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{O}_2\text{Si}$: C, 76.04; H, 9.33. Found: C, 76.22; H, 9.31.

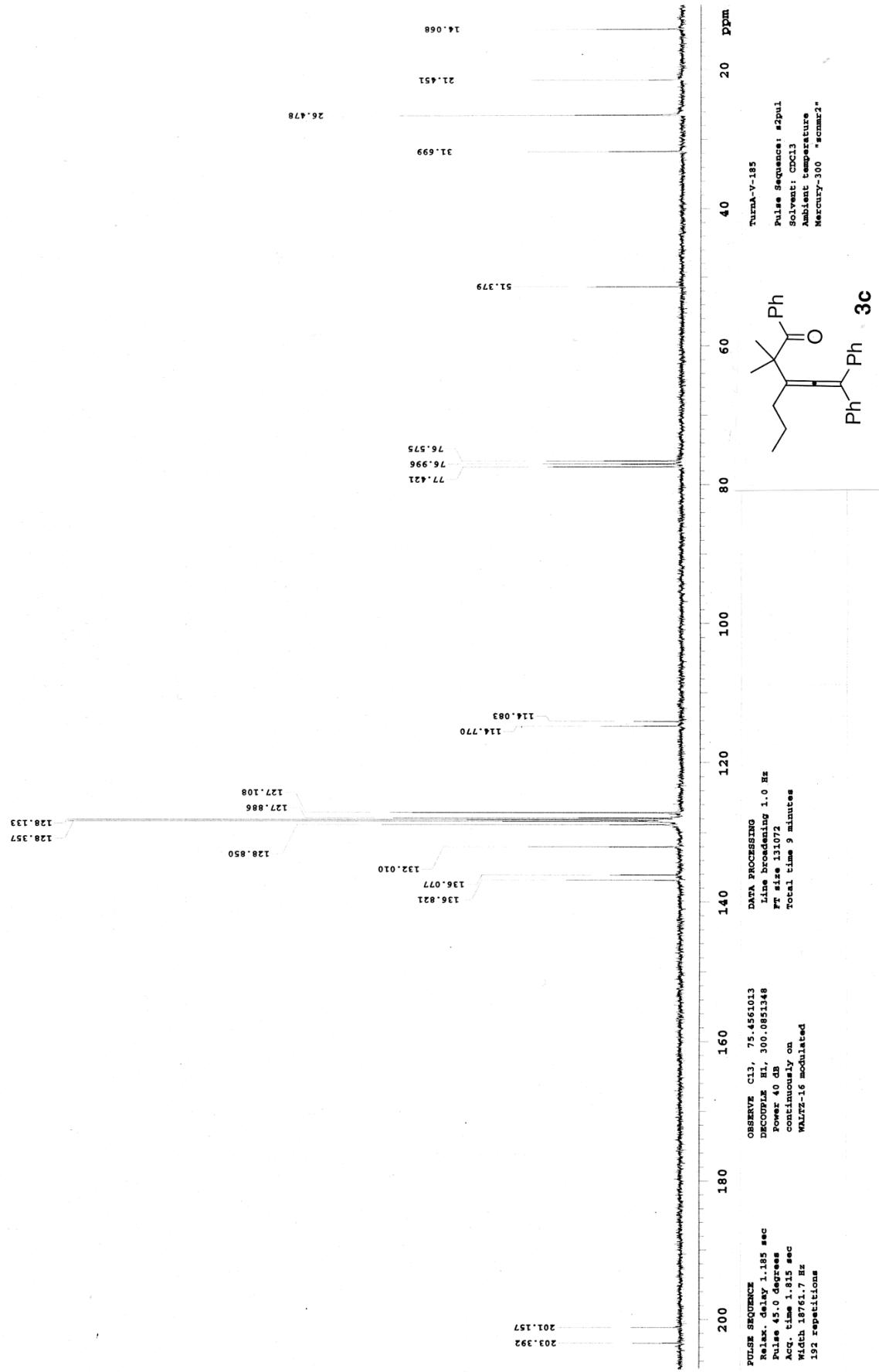


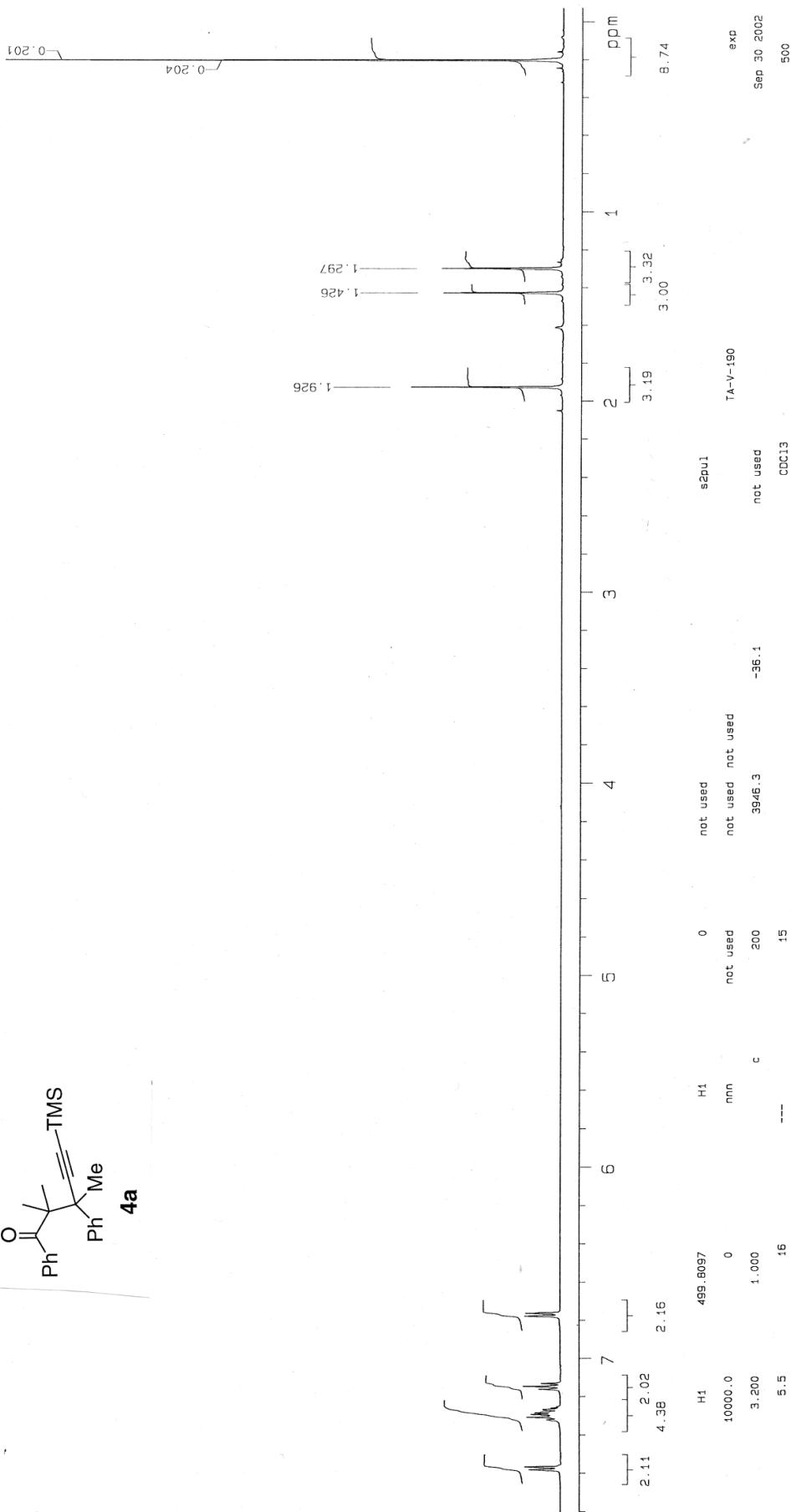
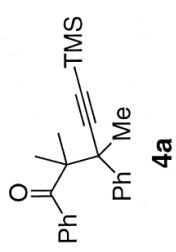


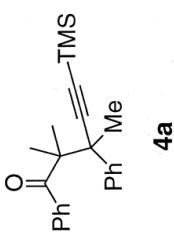
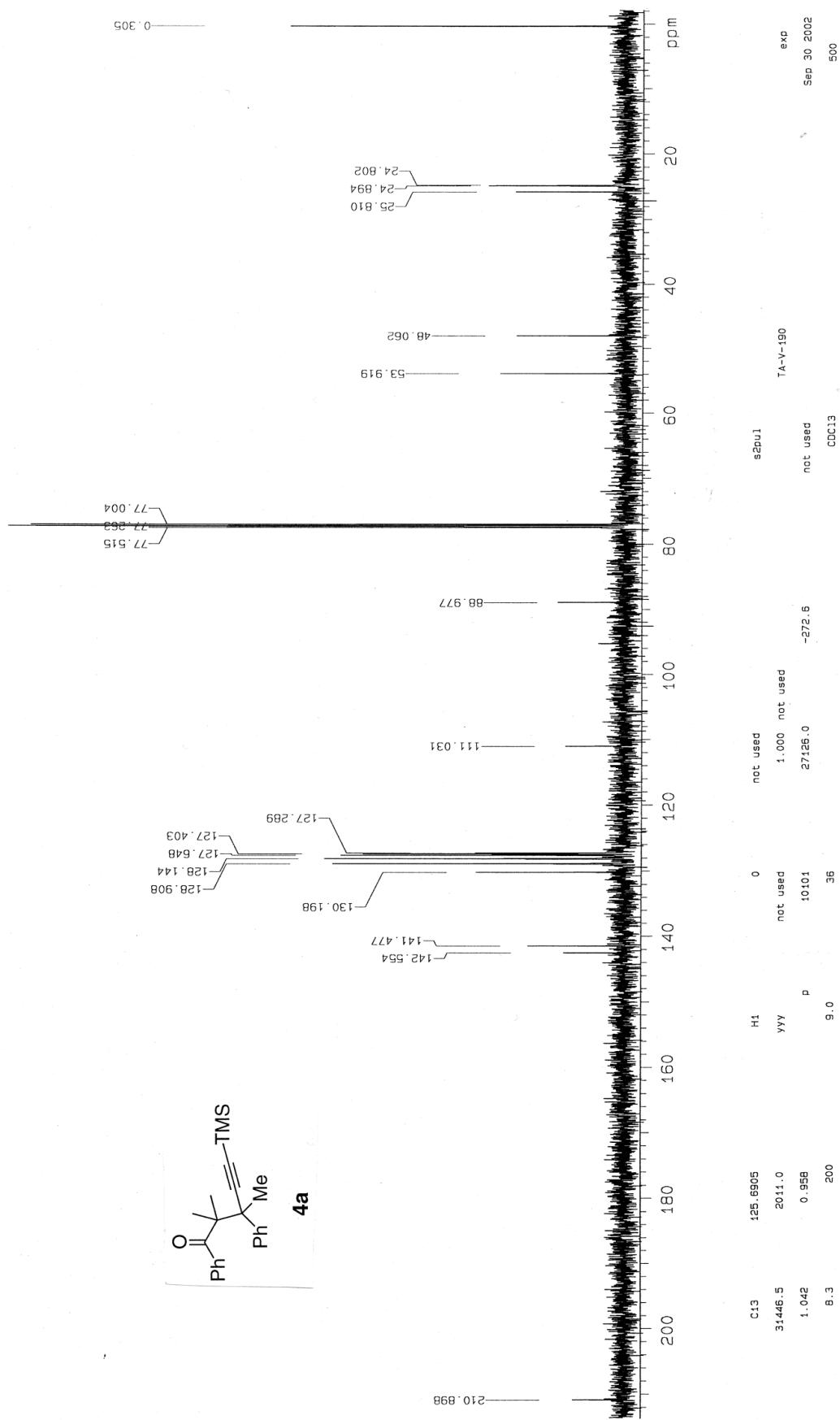


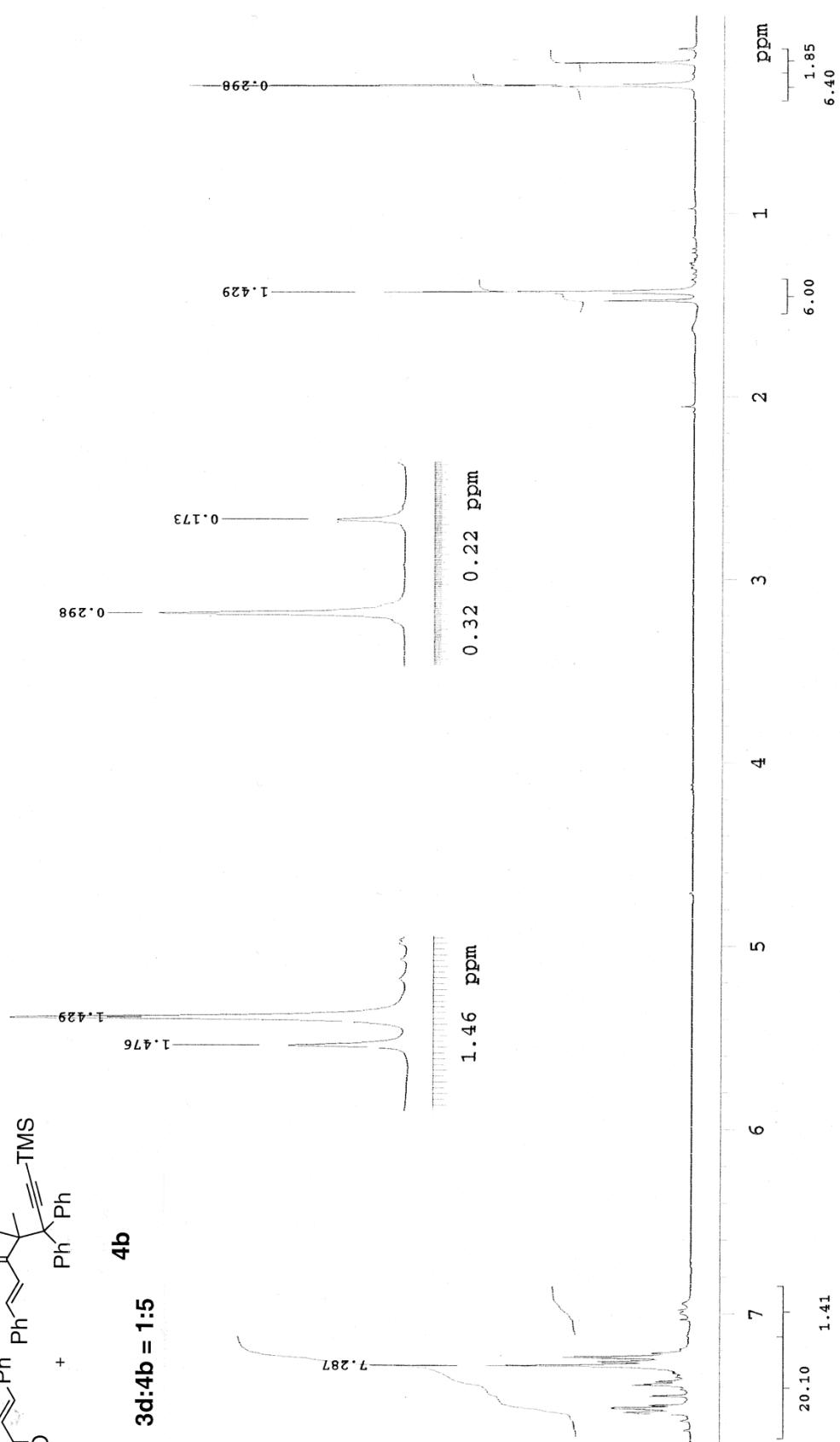
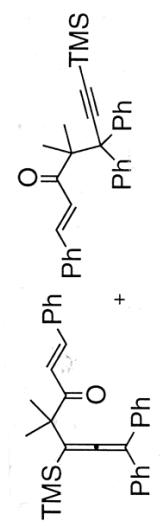




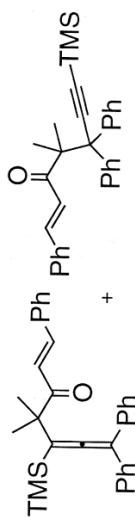




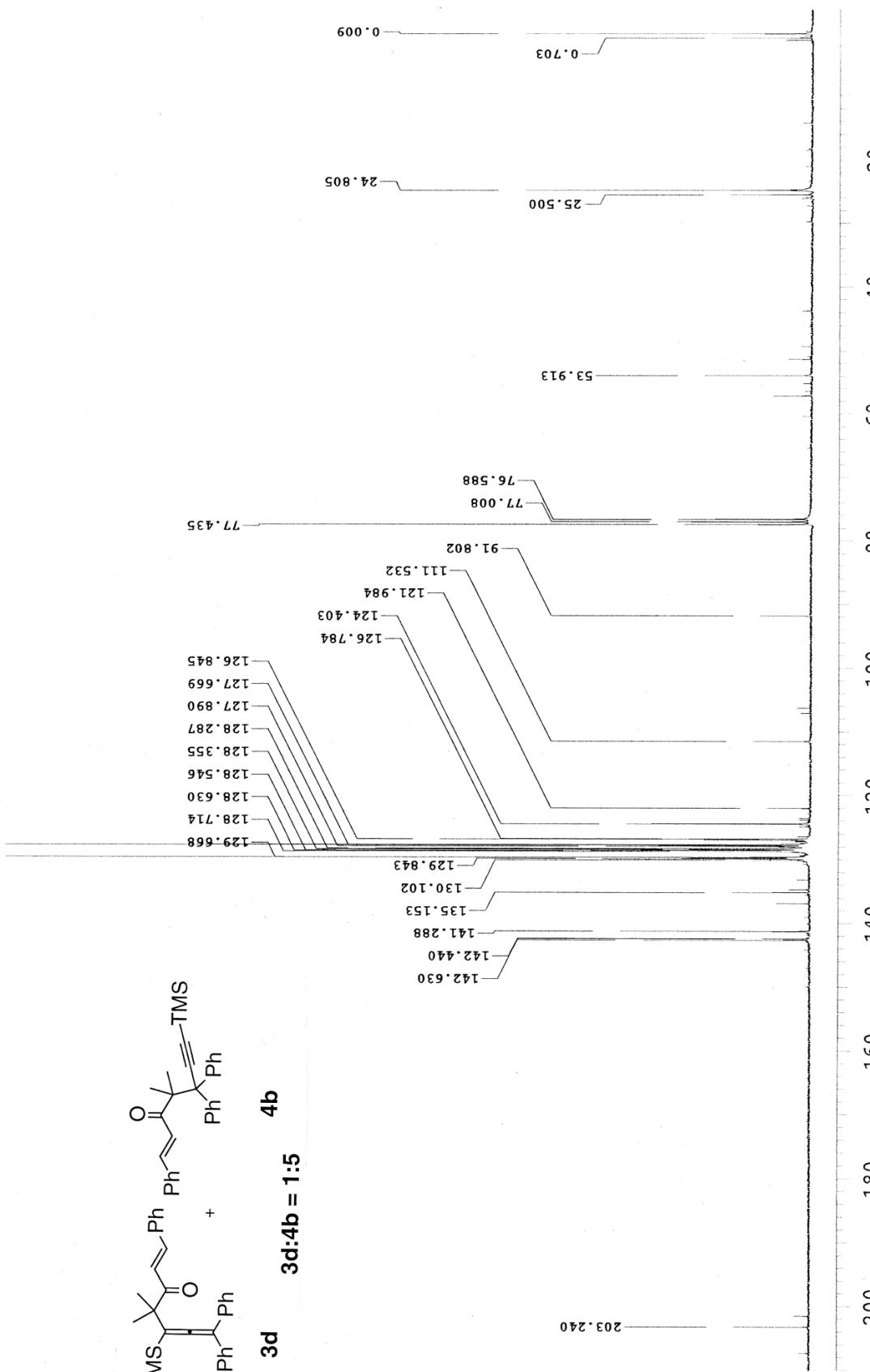




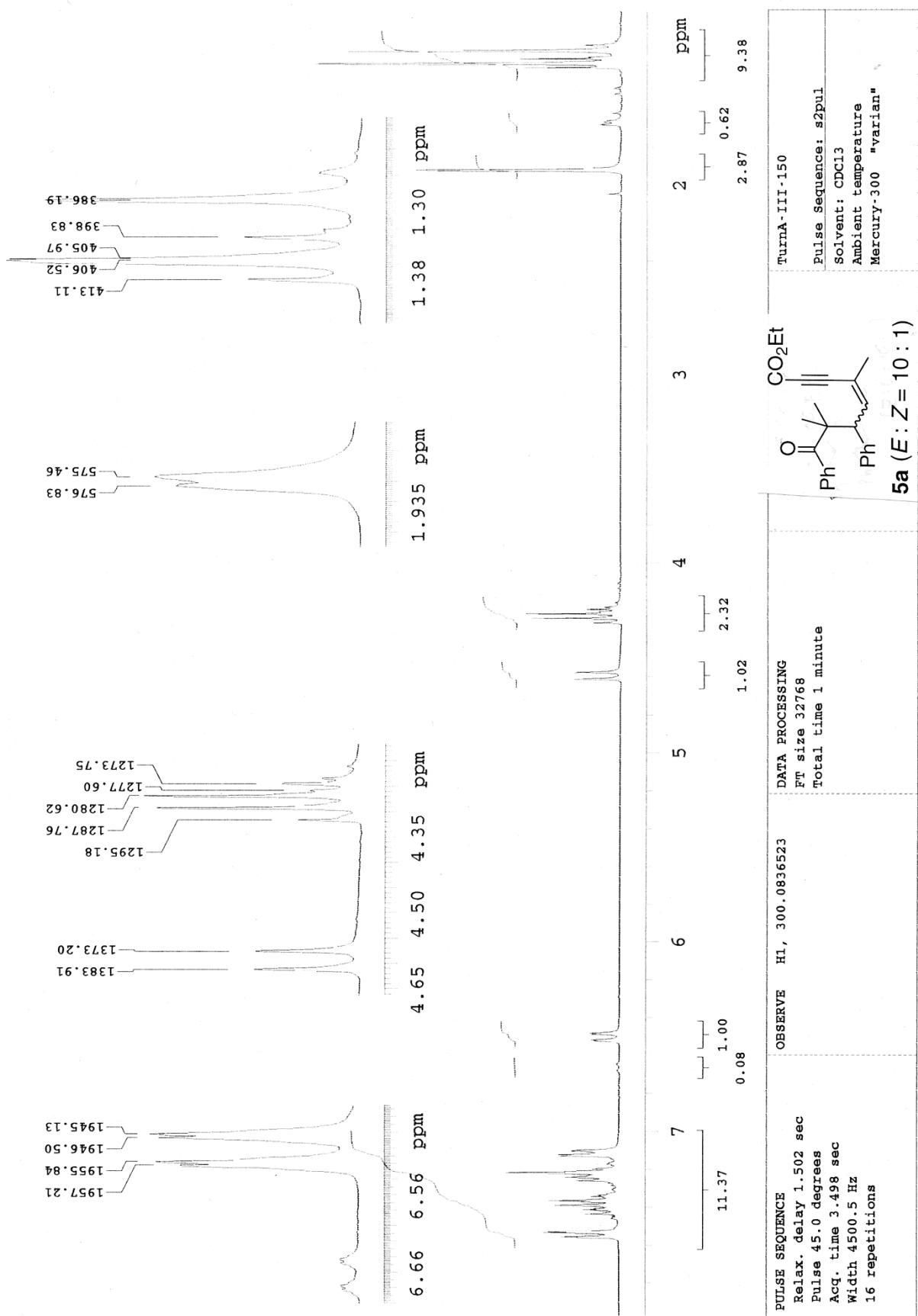
PULSE SEQUENCE	OBSERVE	H1, 300.0836523	DATA PROCESSING
Relax. delay 1.502 sec		FT size 32768	
Pulse 45.0 degrees		Total time 1 minute	
Acq. time 3.498 sec			
Width 4500.5 Hz			
16 repetitions			
<hr/>			
TurnA-III-72			
Pulse Sequence: s2pul1			
Solvent: CDCl3			
Ambient temperature			
Mercury-300 "varian"			

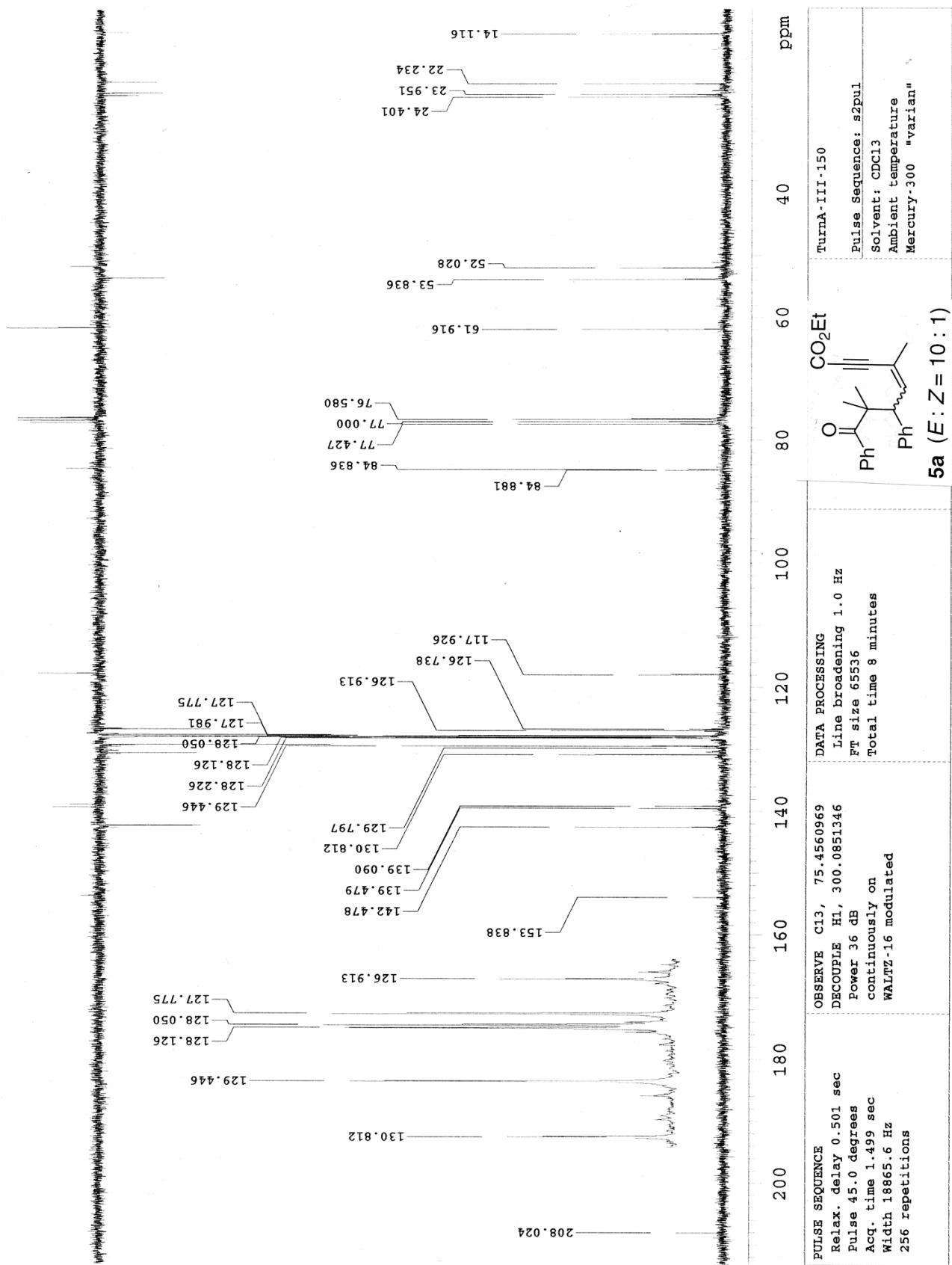


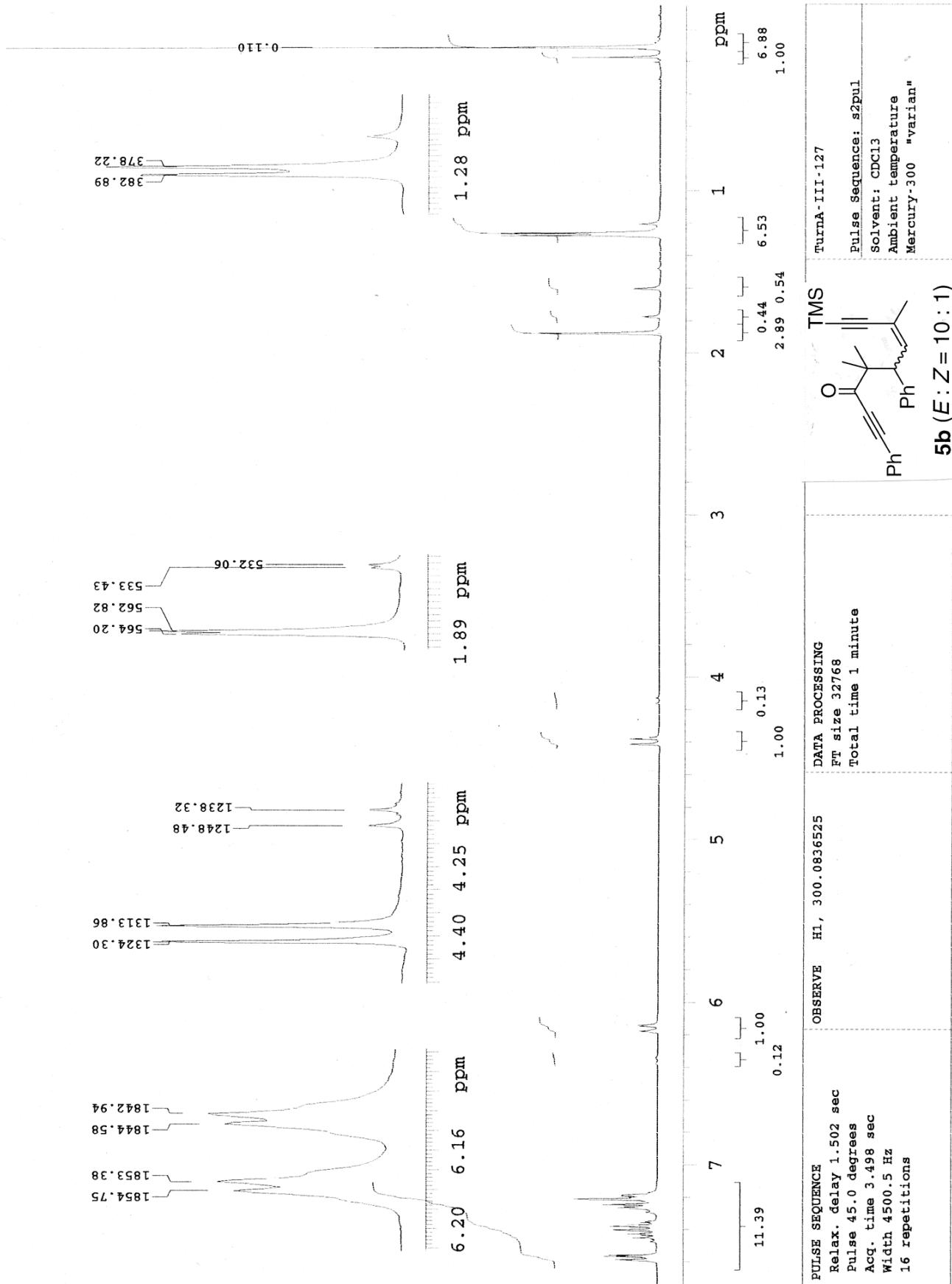
$$3d:4b = 1:5$$

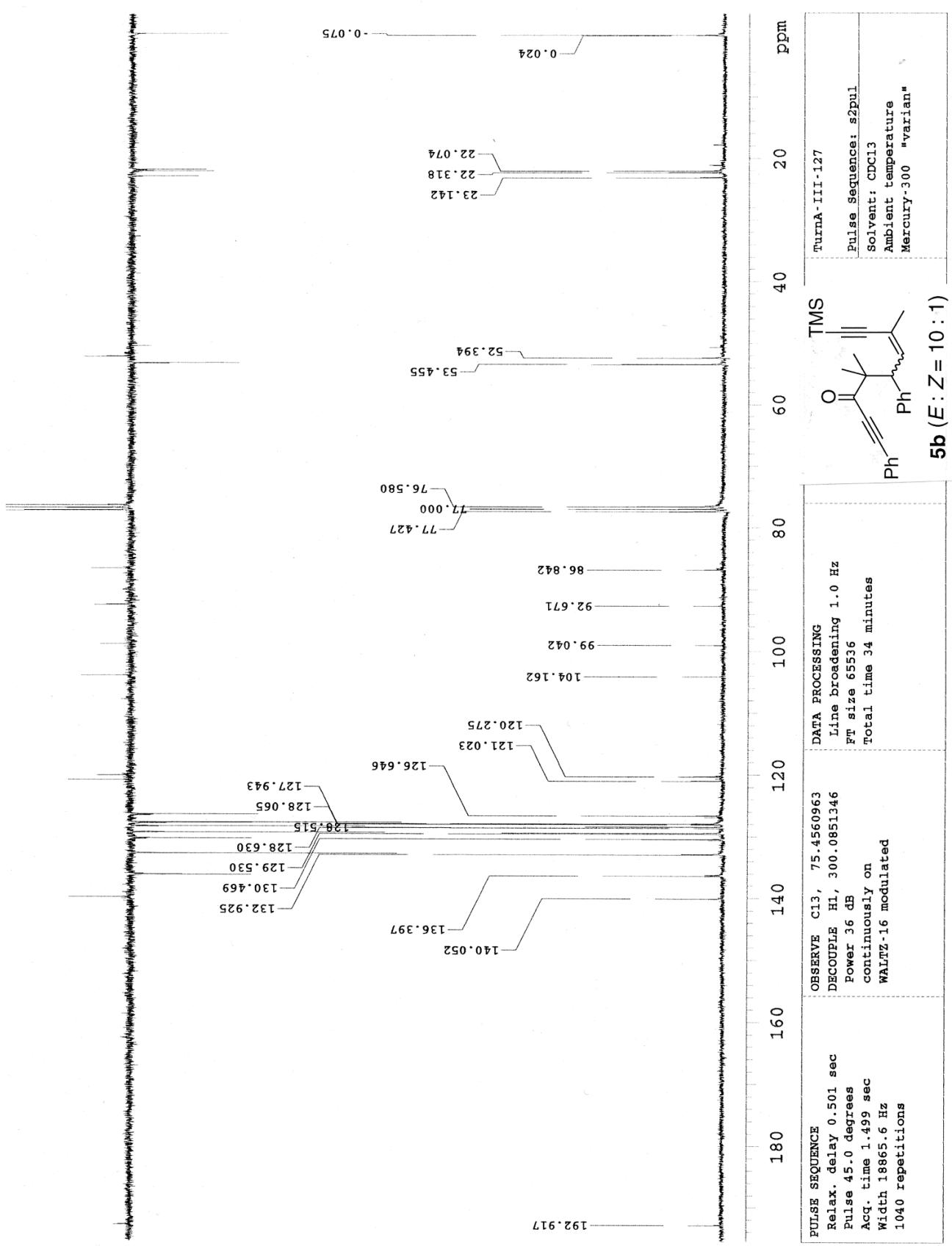


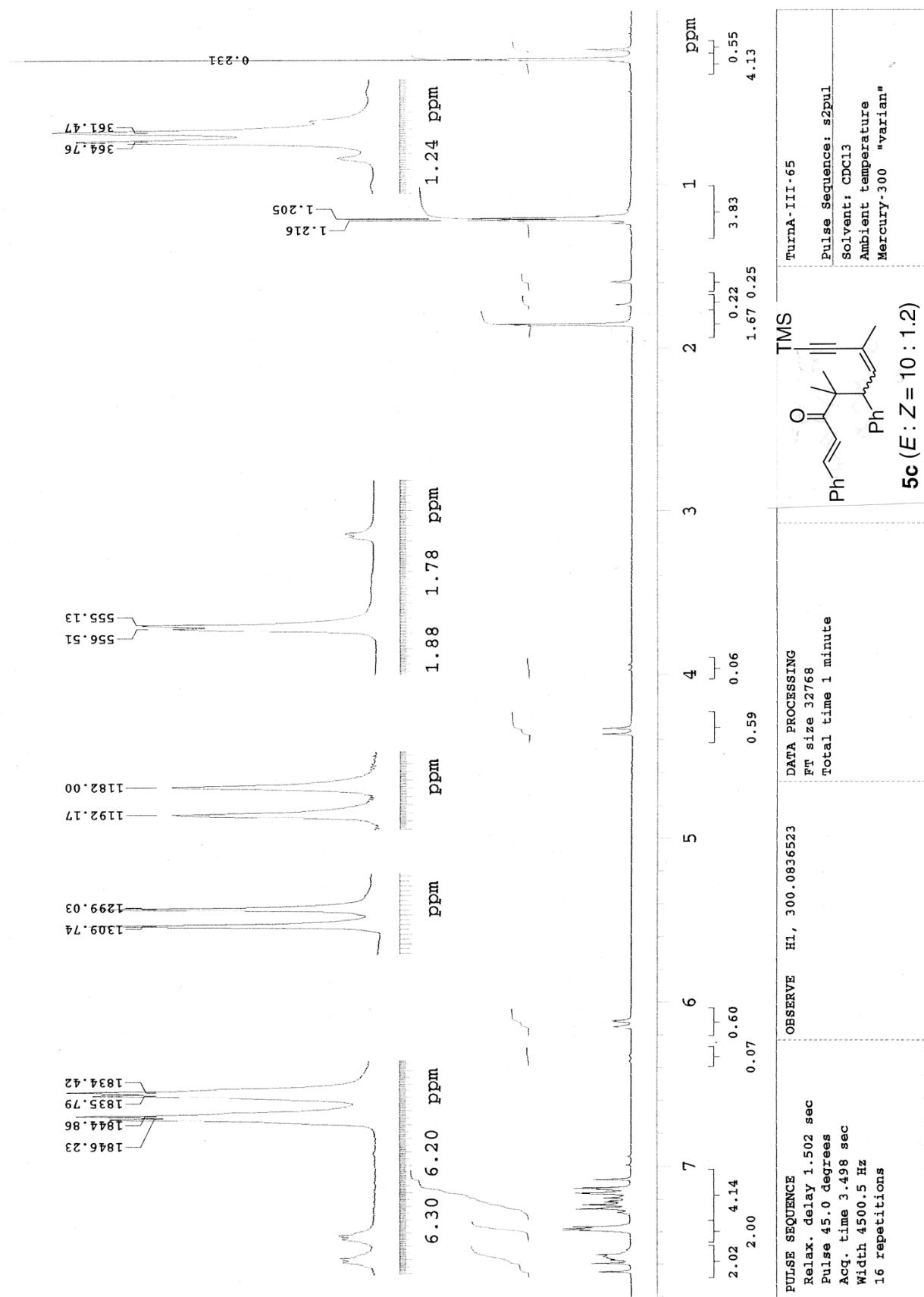
PULSE SEQUENCE
 Relax. delay 0.501 sec
 Pulse 45.0 degrees
 Accq. time 1.499 sec
 Width 18665.6 Hz
 14848 repetitions
 OBSERVE C13, 75.4560940
 DECOUPLE H1, 300.0851346
 Power 36 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 8.2 hours
 TURIA-III-72
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-300 "varian"

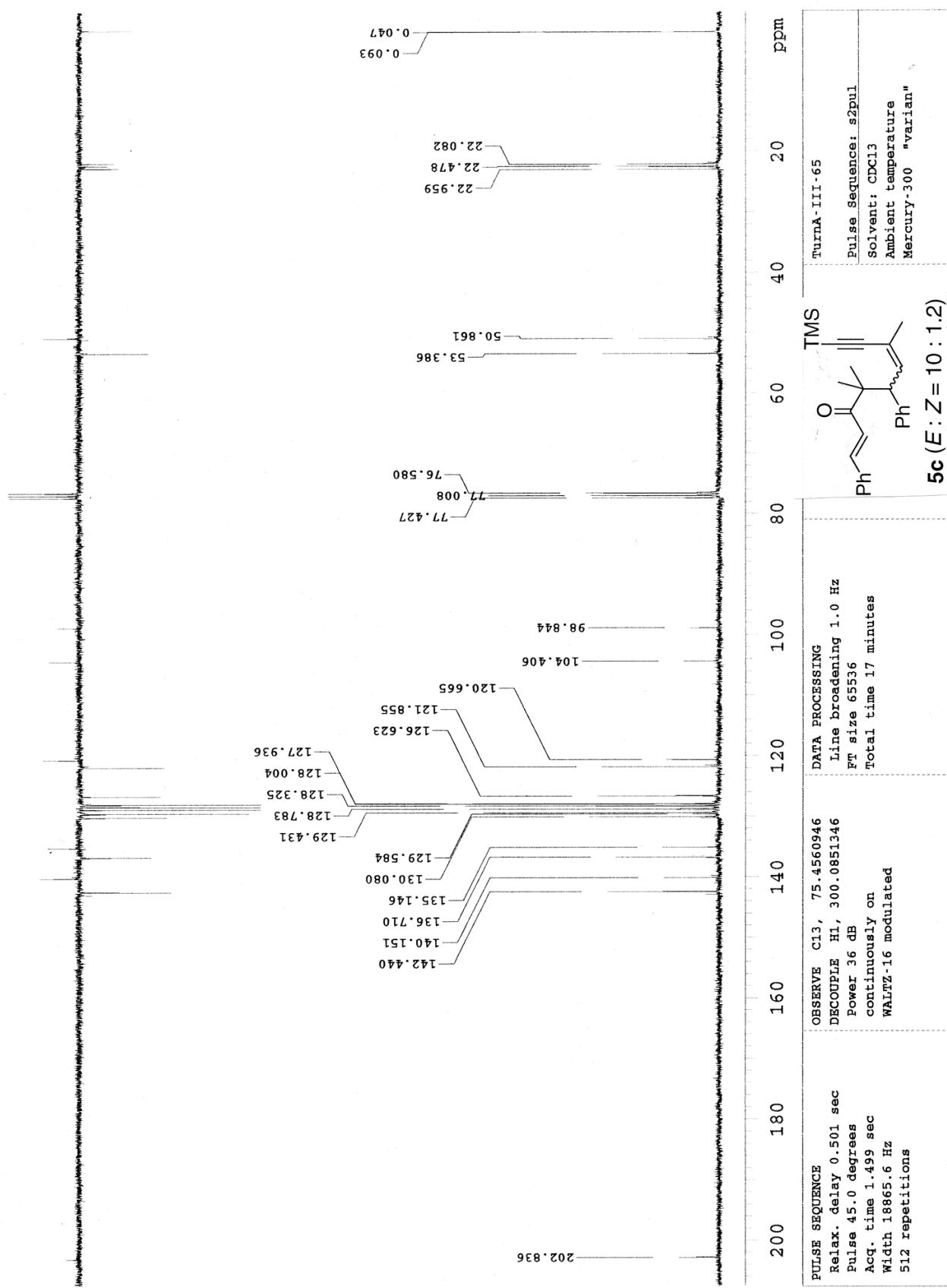


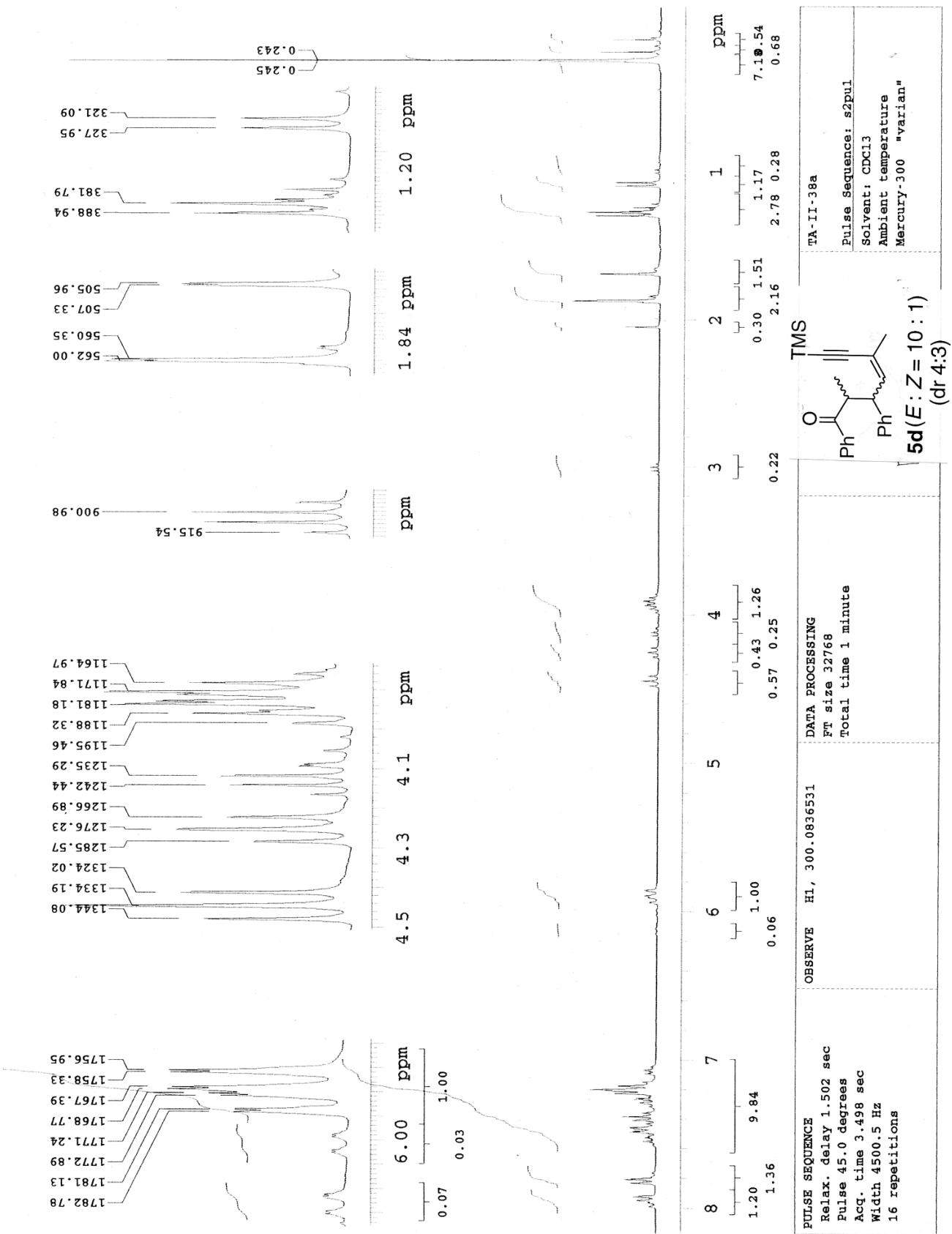


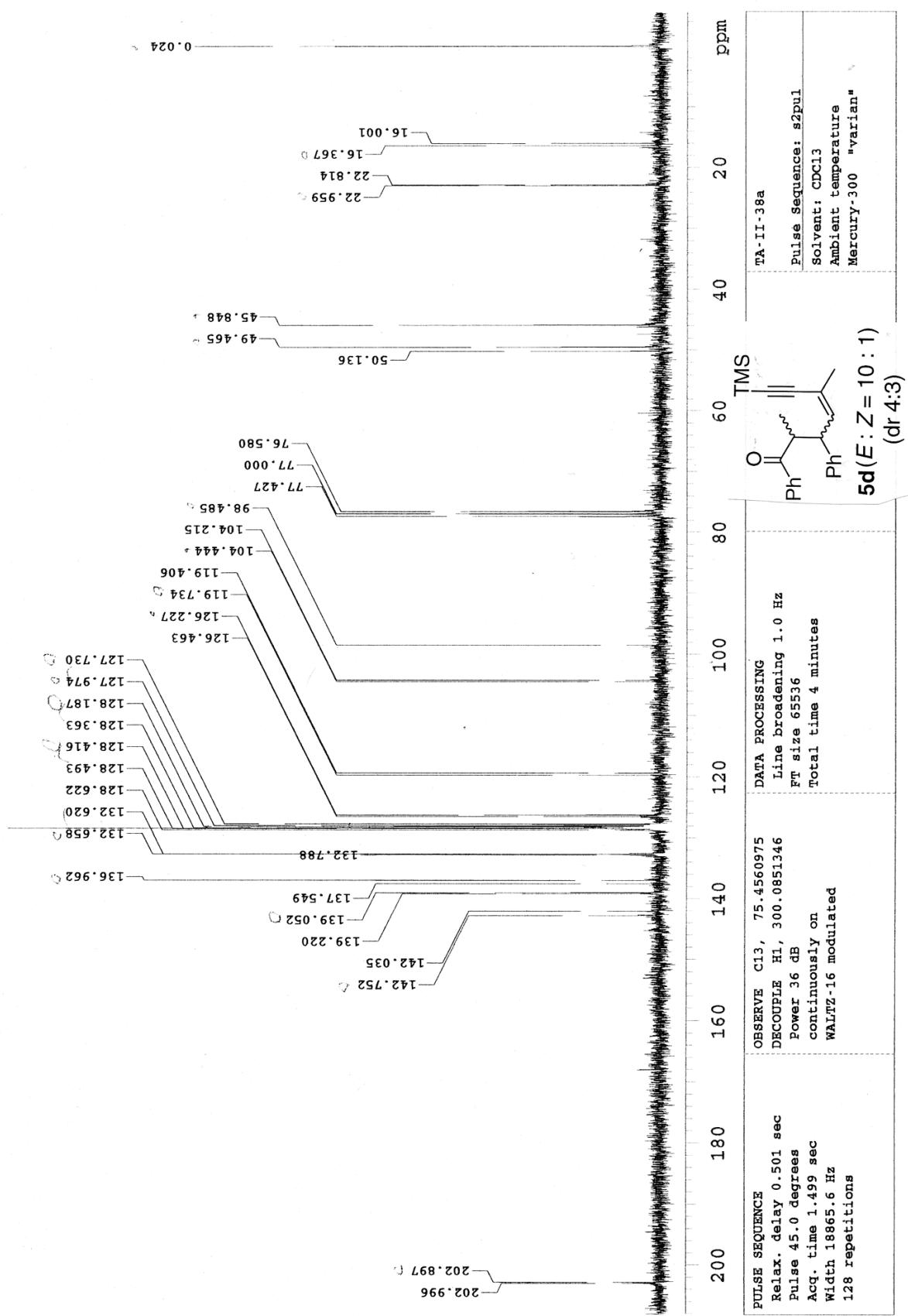


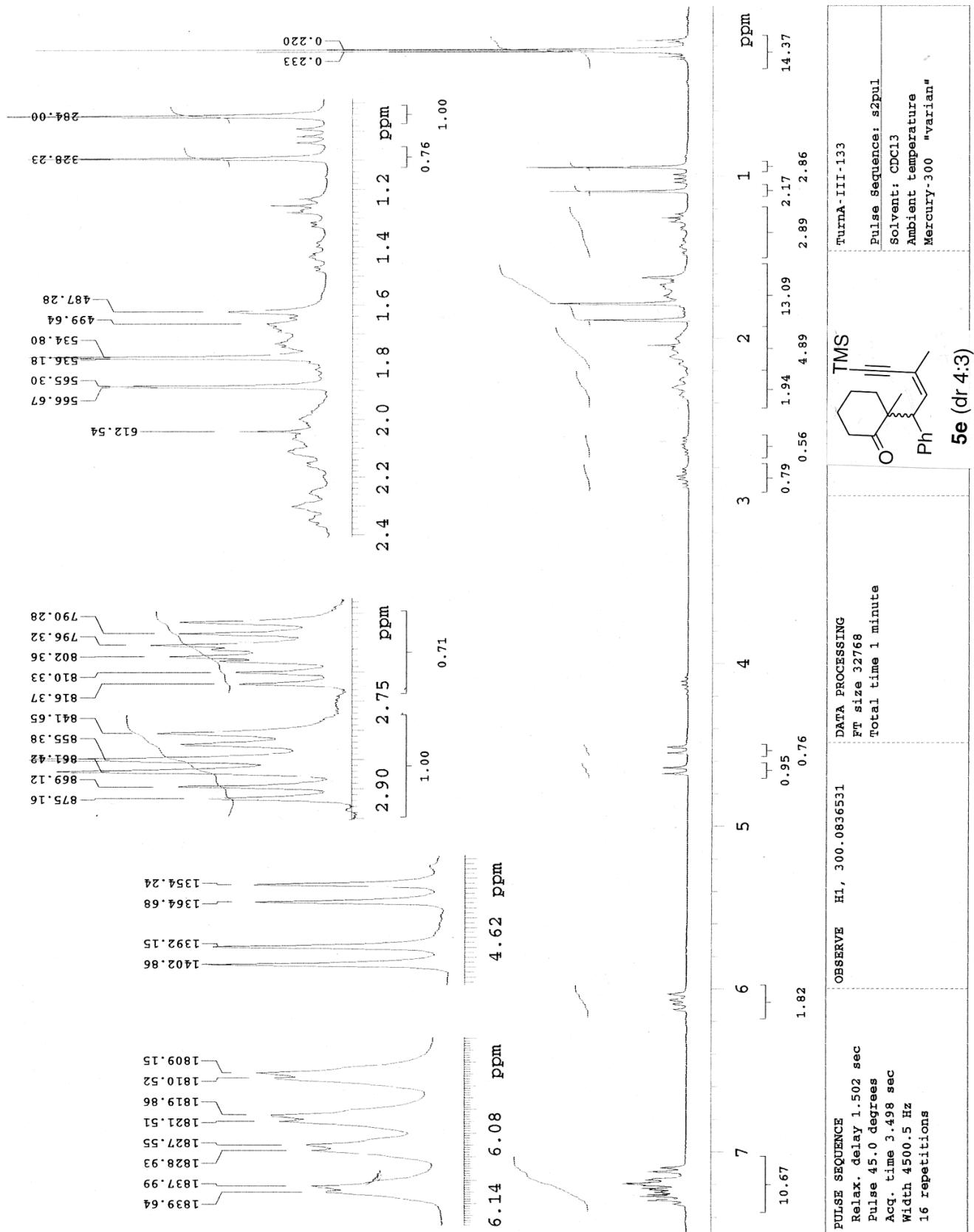


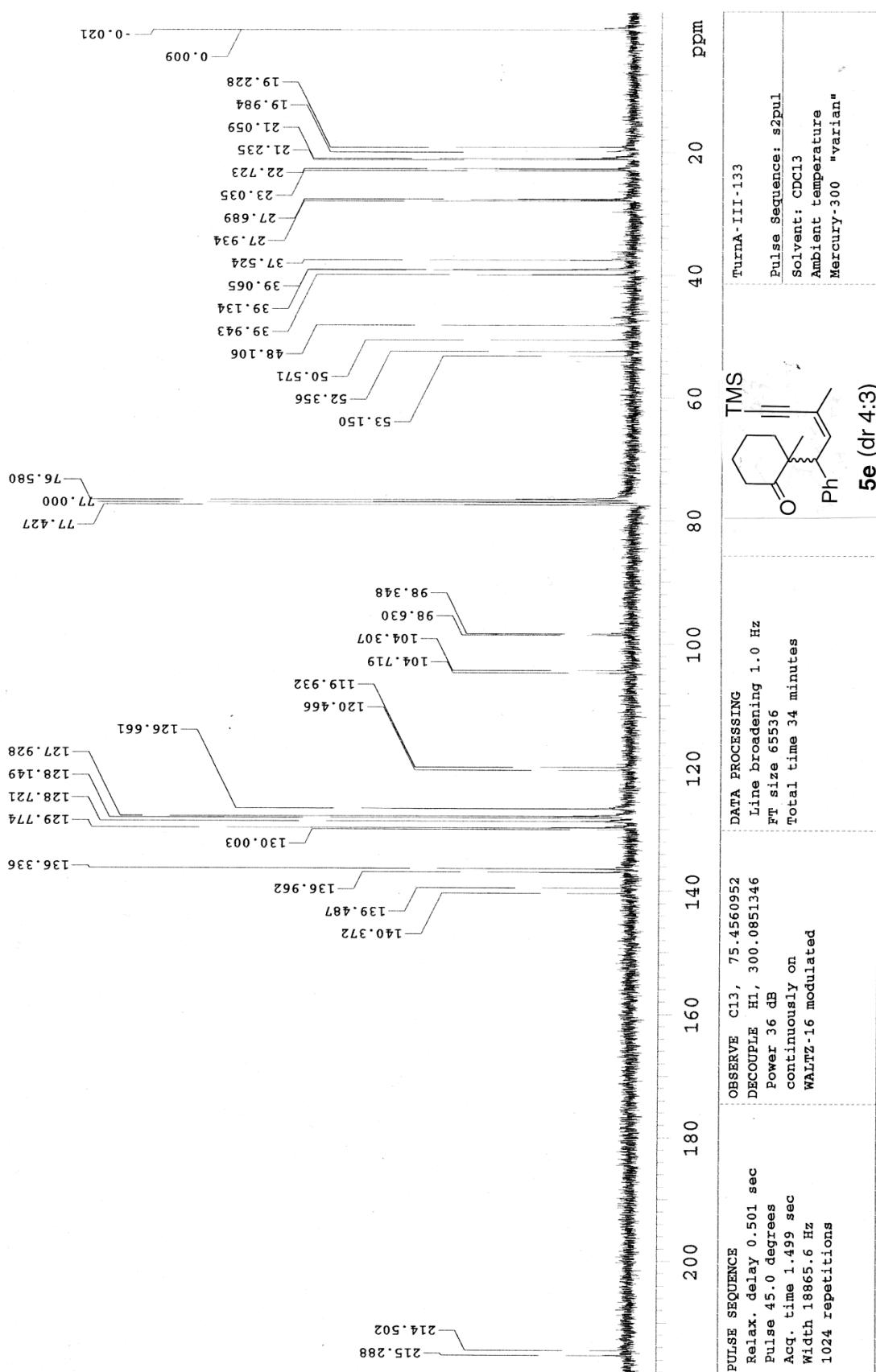


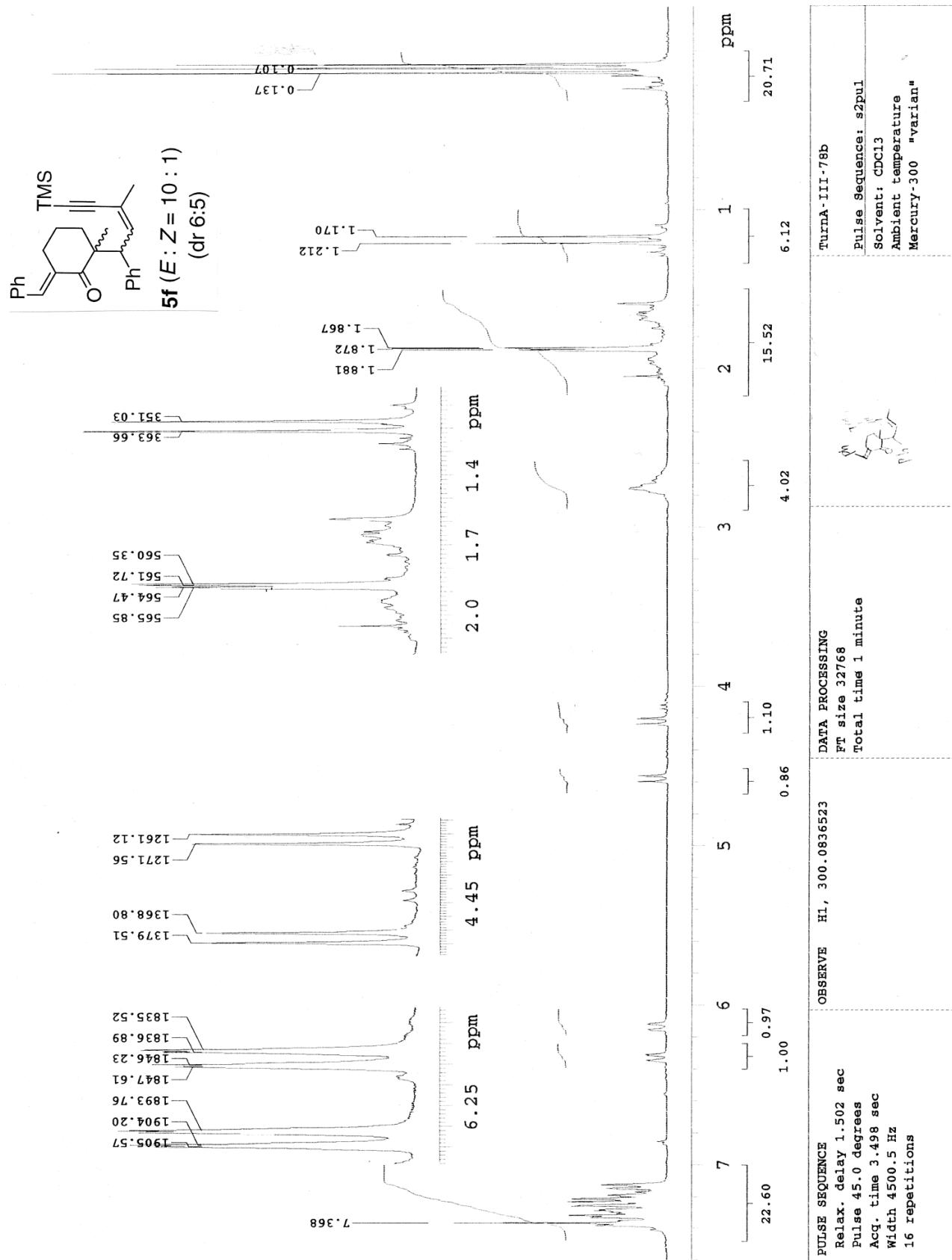


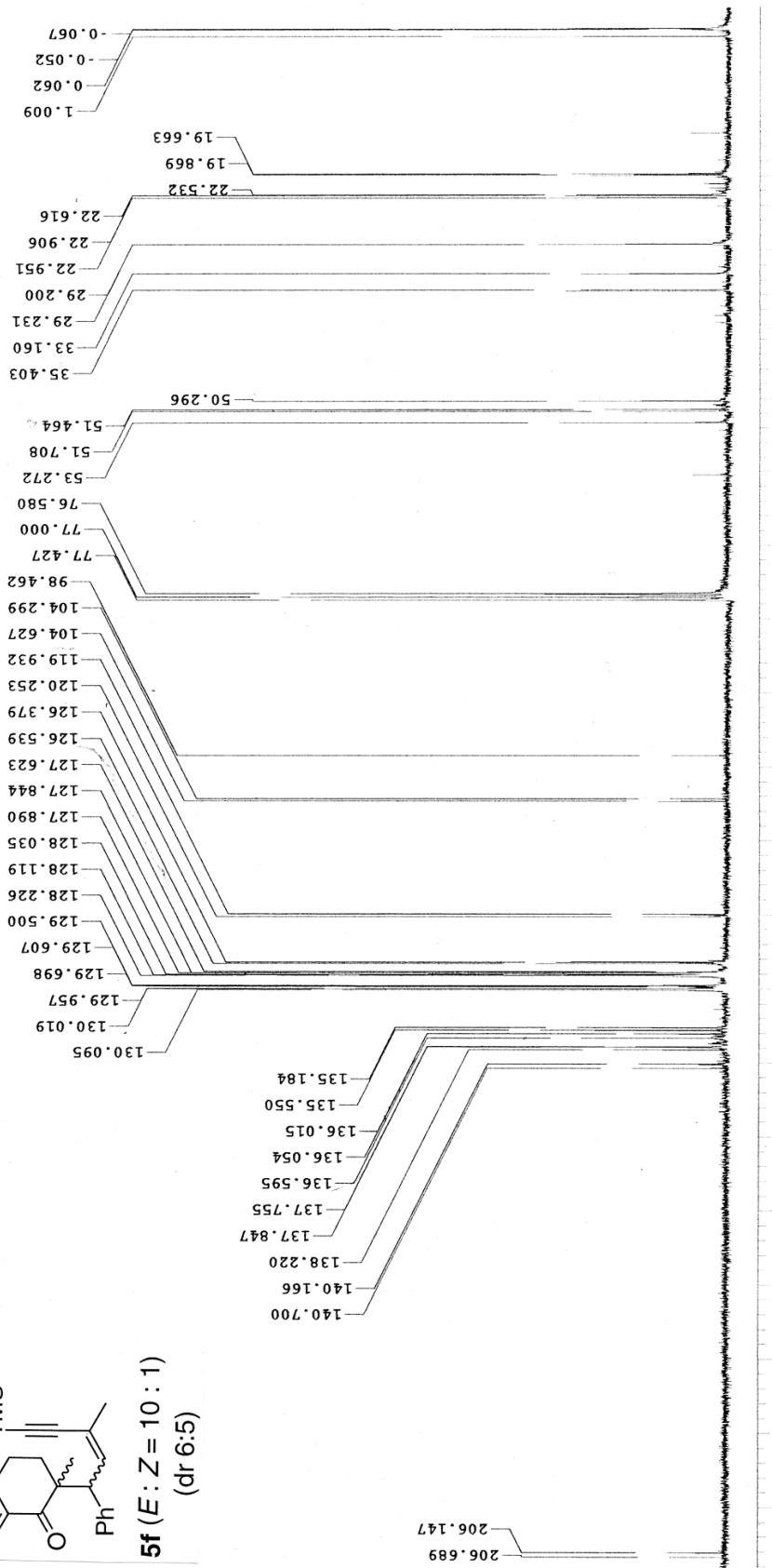
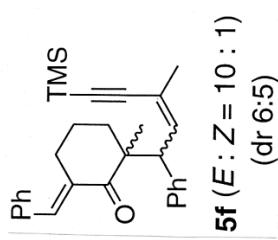




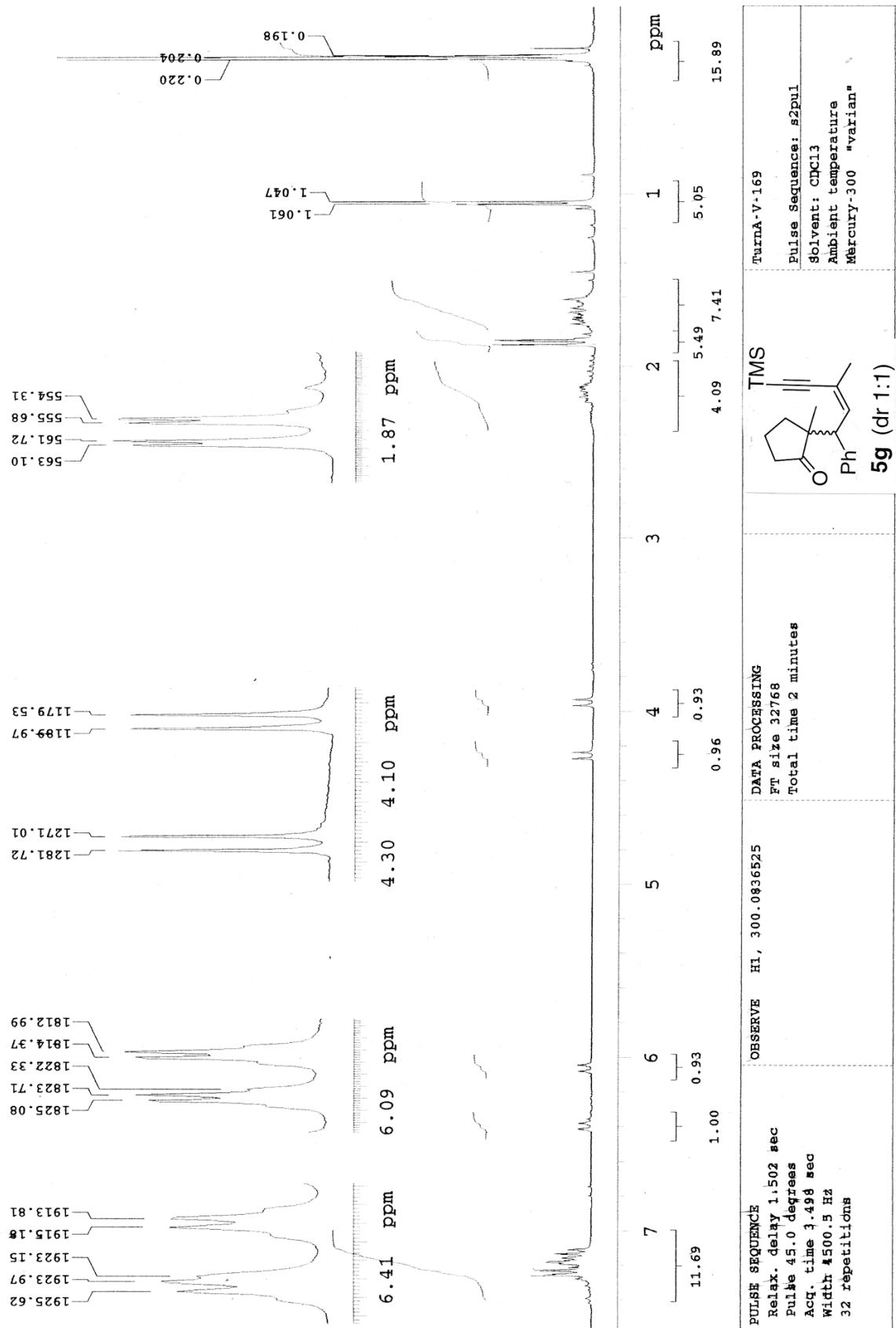


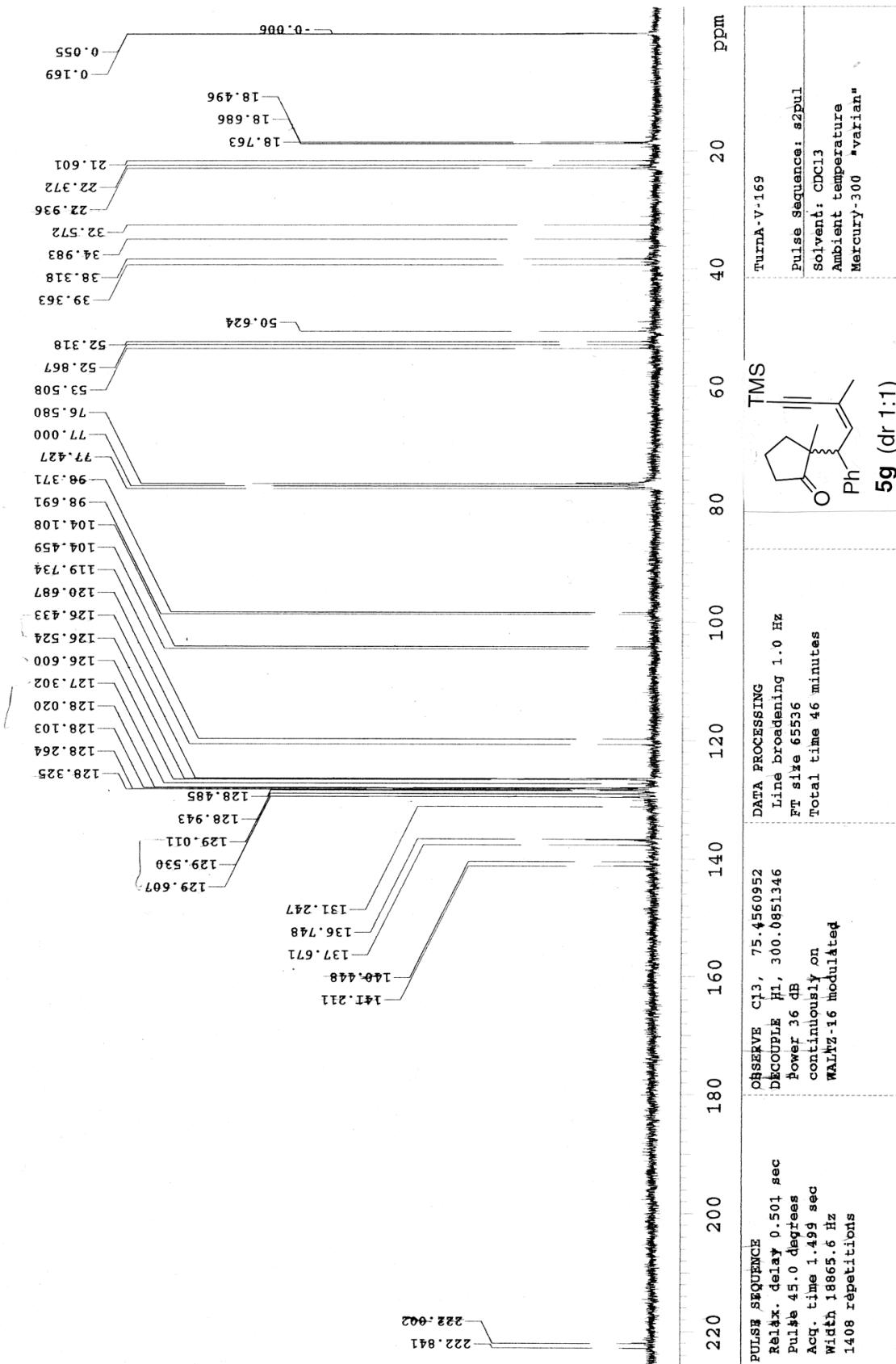


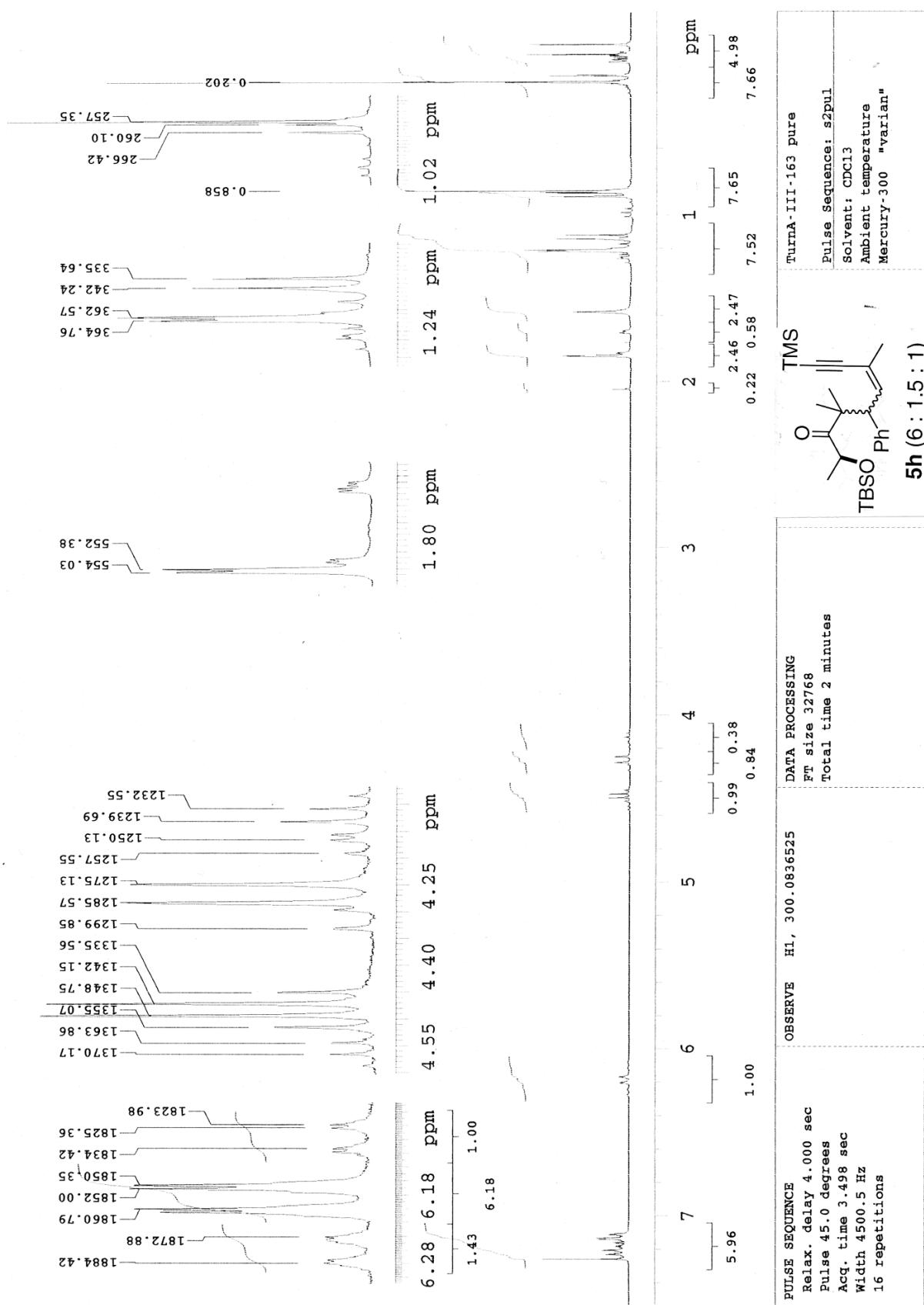


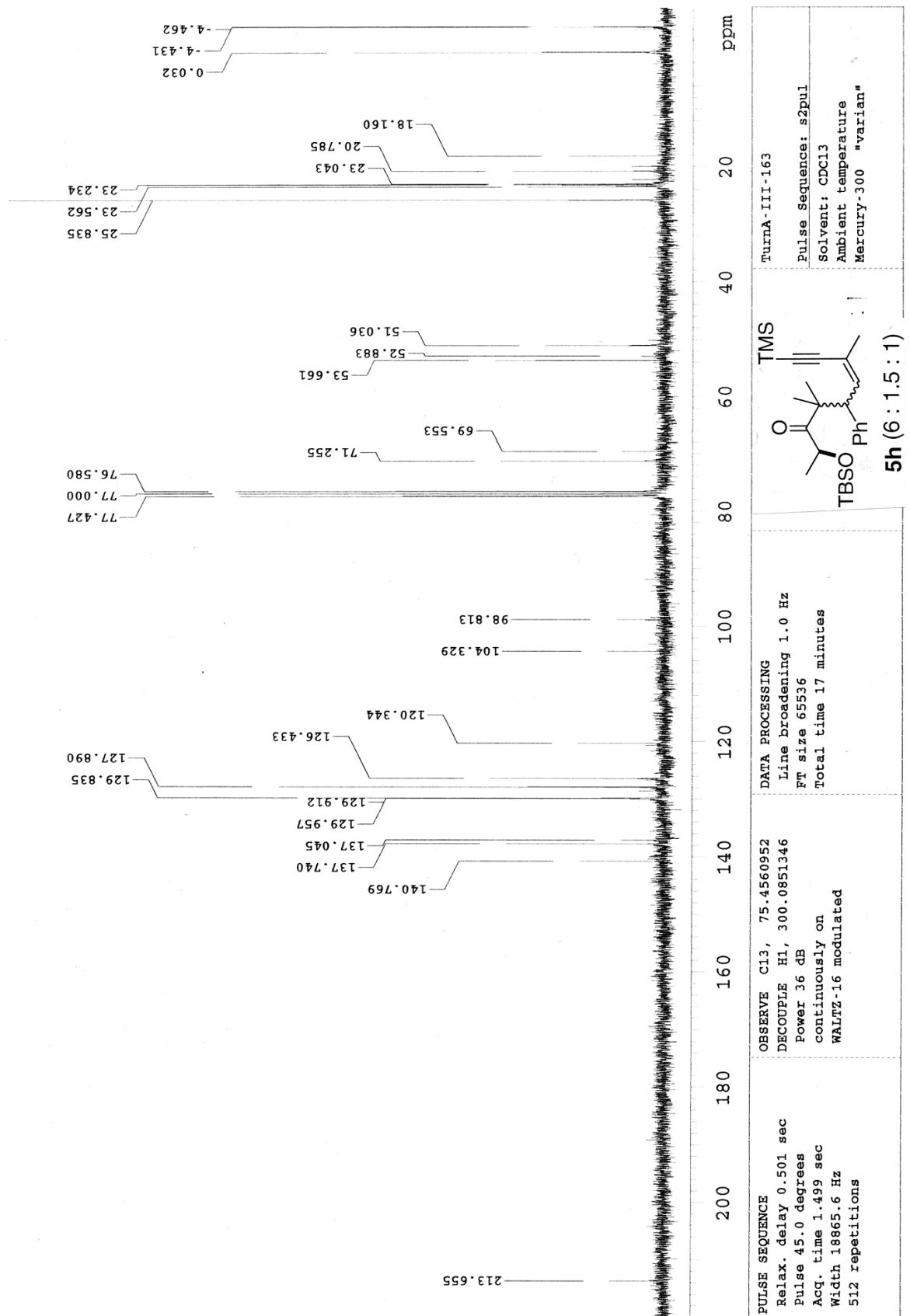


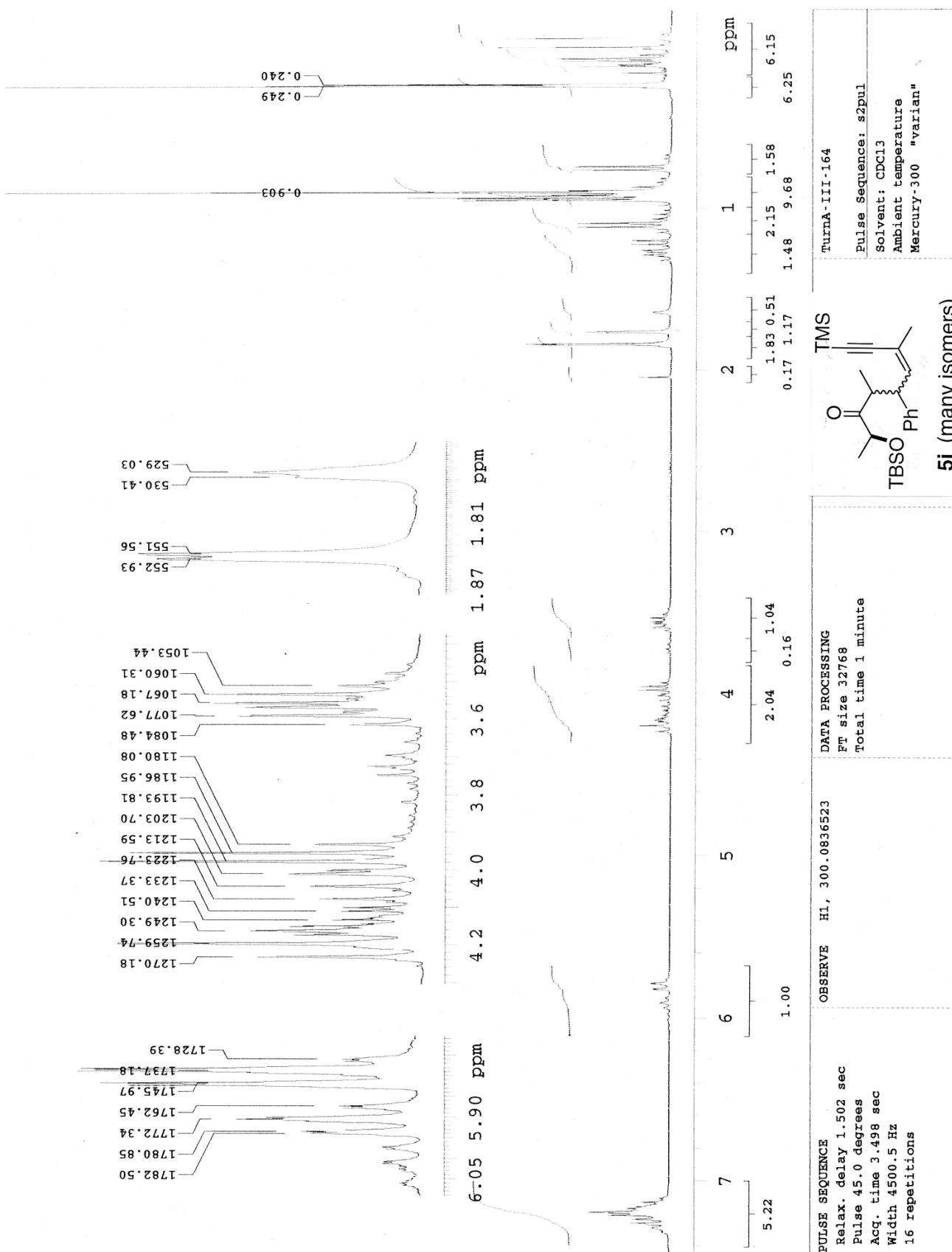
PULSE SEQUENCE	OBSERVE C13, 75.4560946	DATA PROCESSING
Relax. delay 0.501 sec	DECOPPLE H1, 300.0851346	Line broadening 1.0 Hz
Pulse 45.0 degrees	Power 36 dB	FT size 65536
Acc. time 1.49 sec	continuously on	Total time 2.4 hours
Width 18865.6 Hz		
4368 repetitions		
		Turna-II-78B
		Pulse sequence: s2pul
		Solvent: CDCl3
		Ambient temperature
		Mercury-300 "varian"

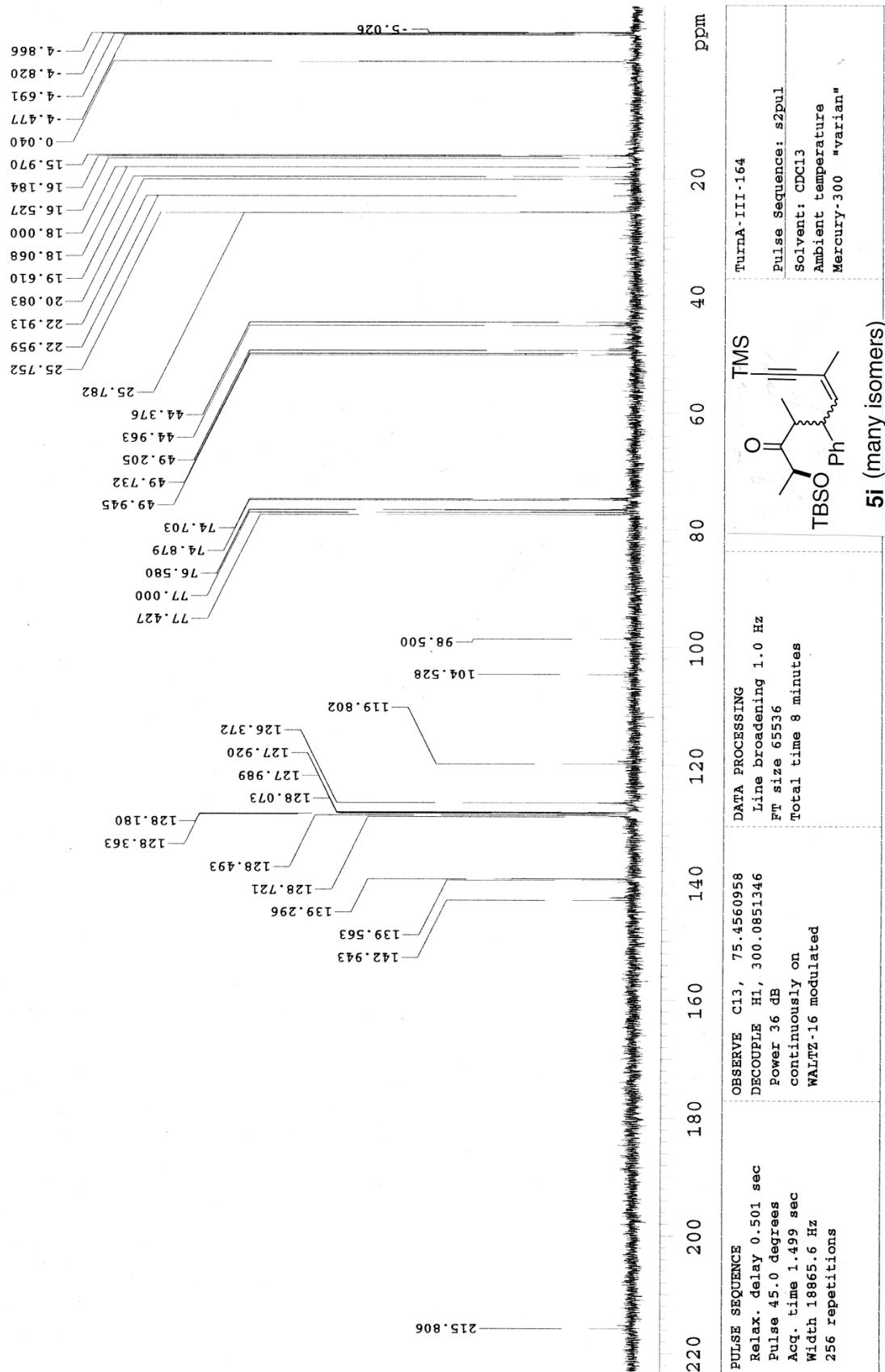


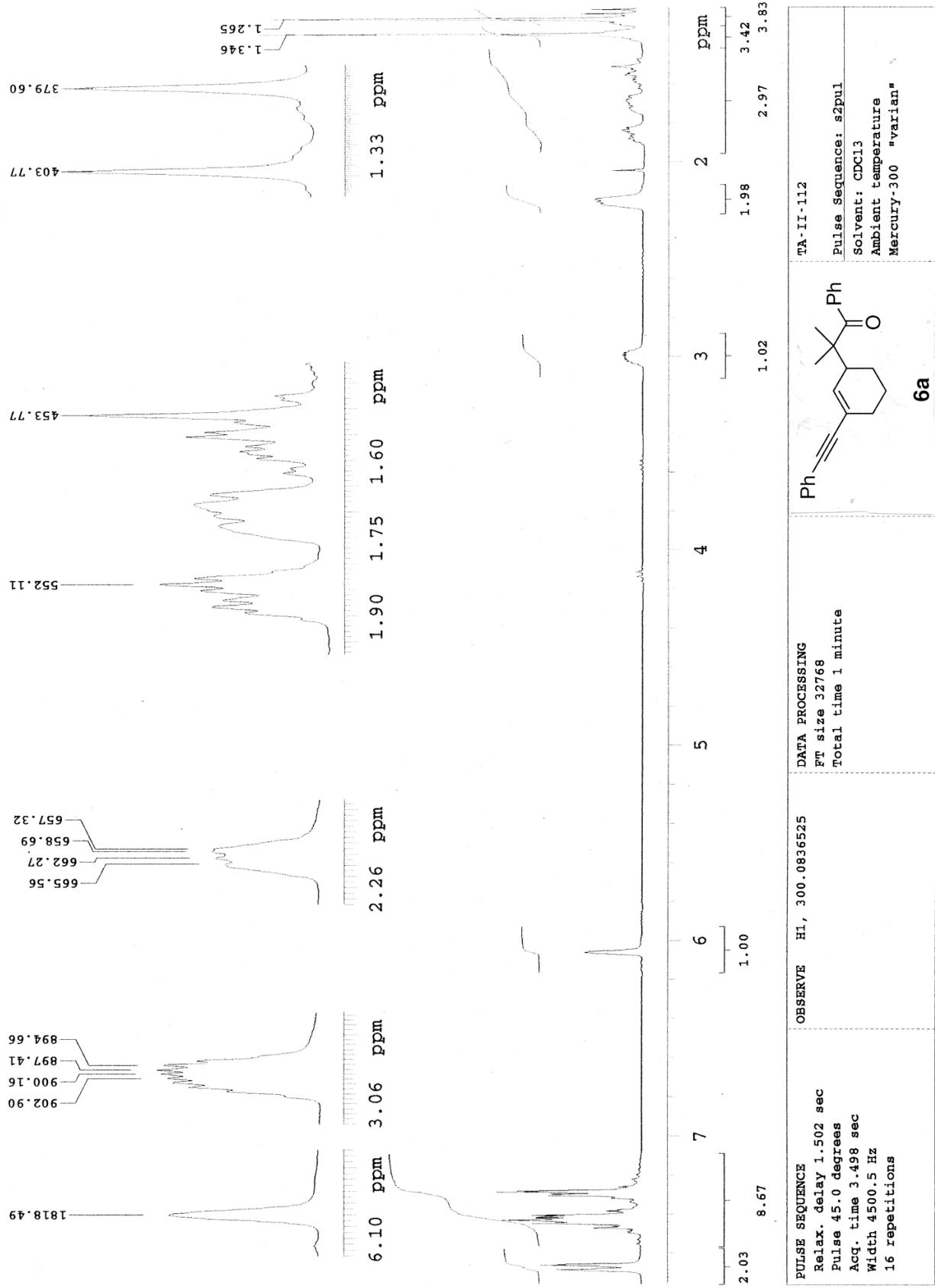


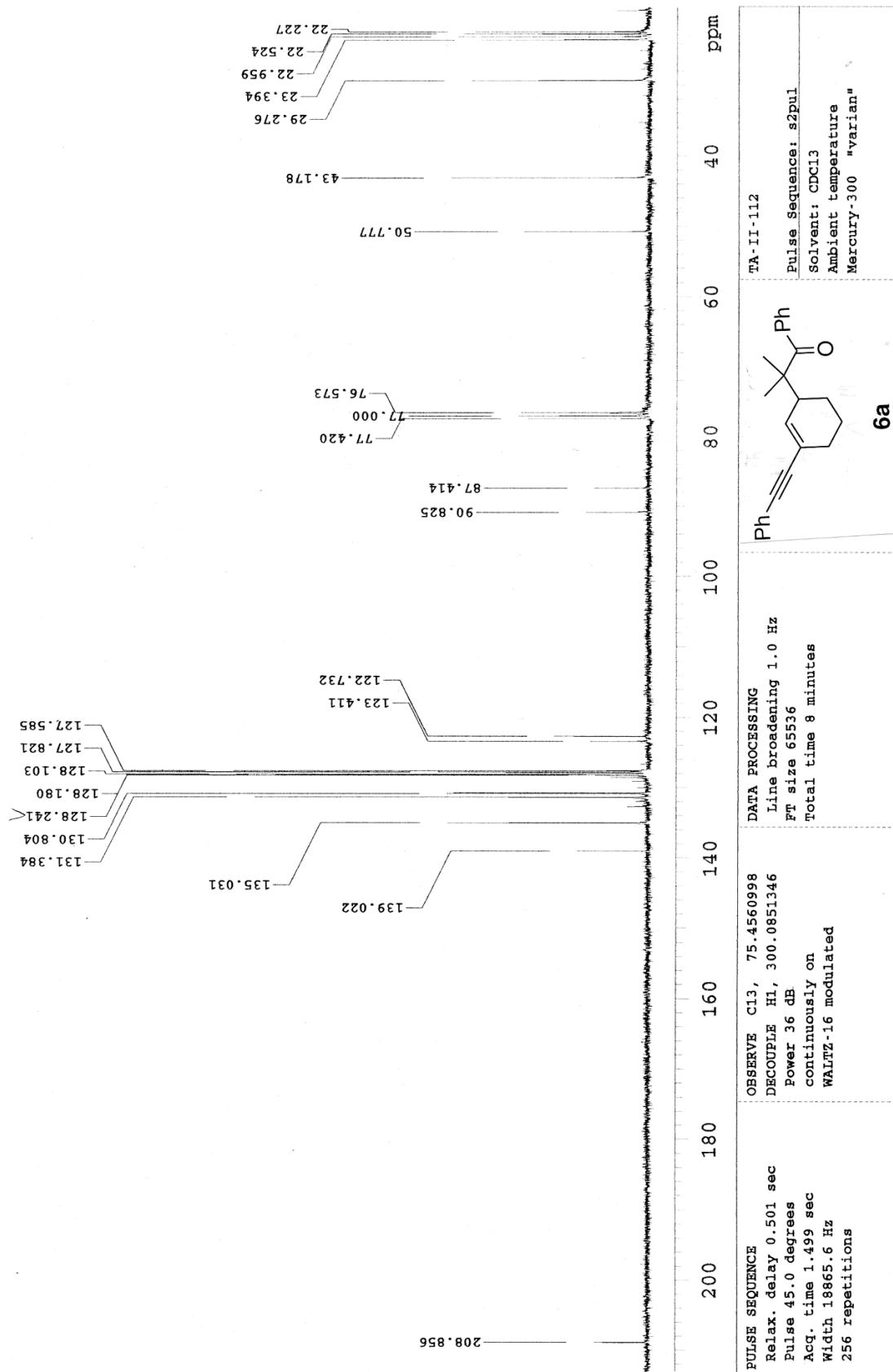


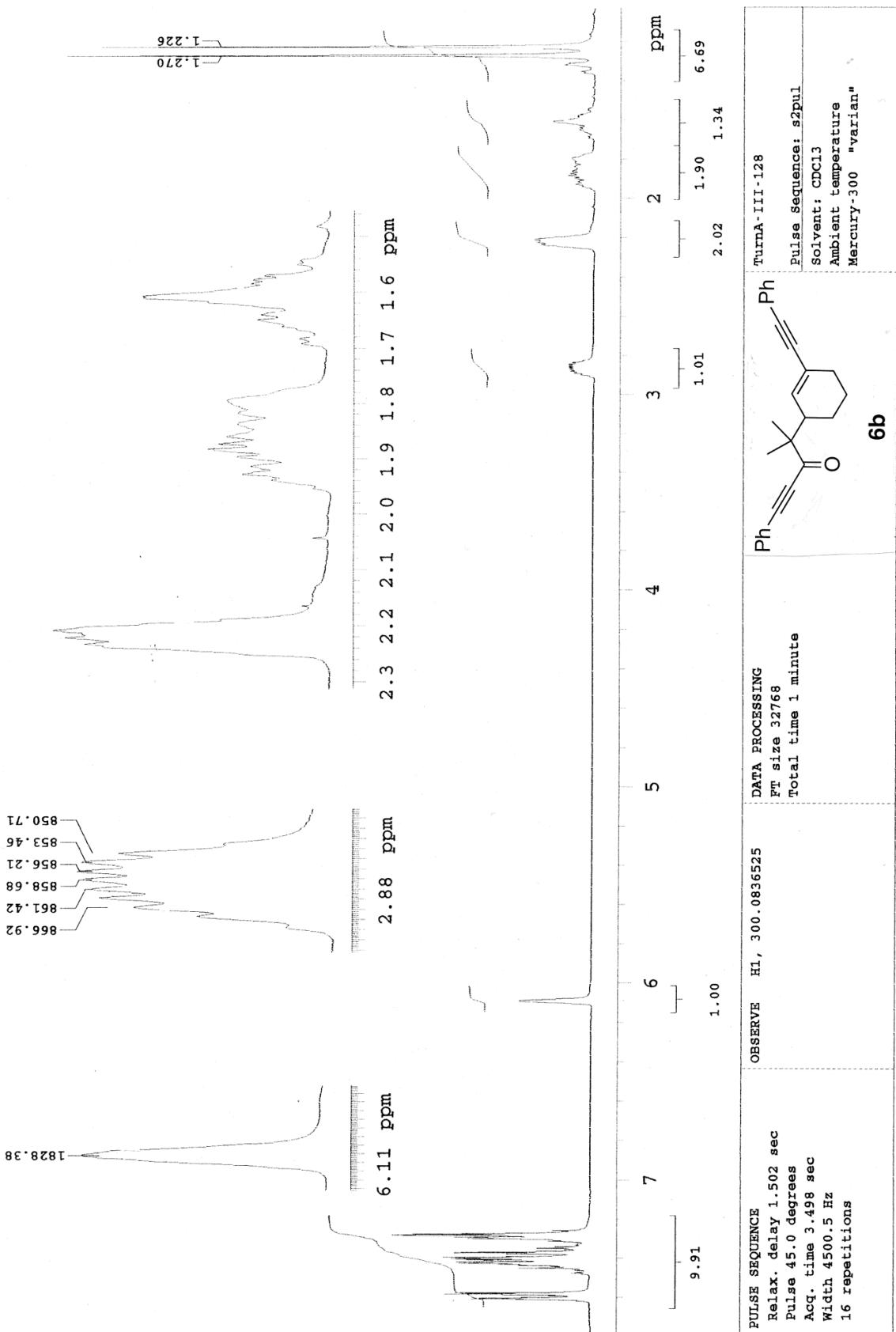


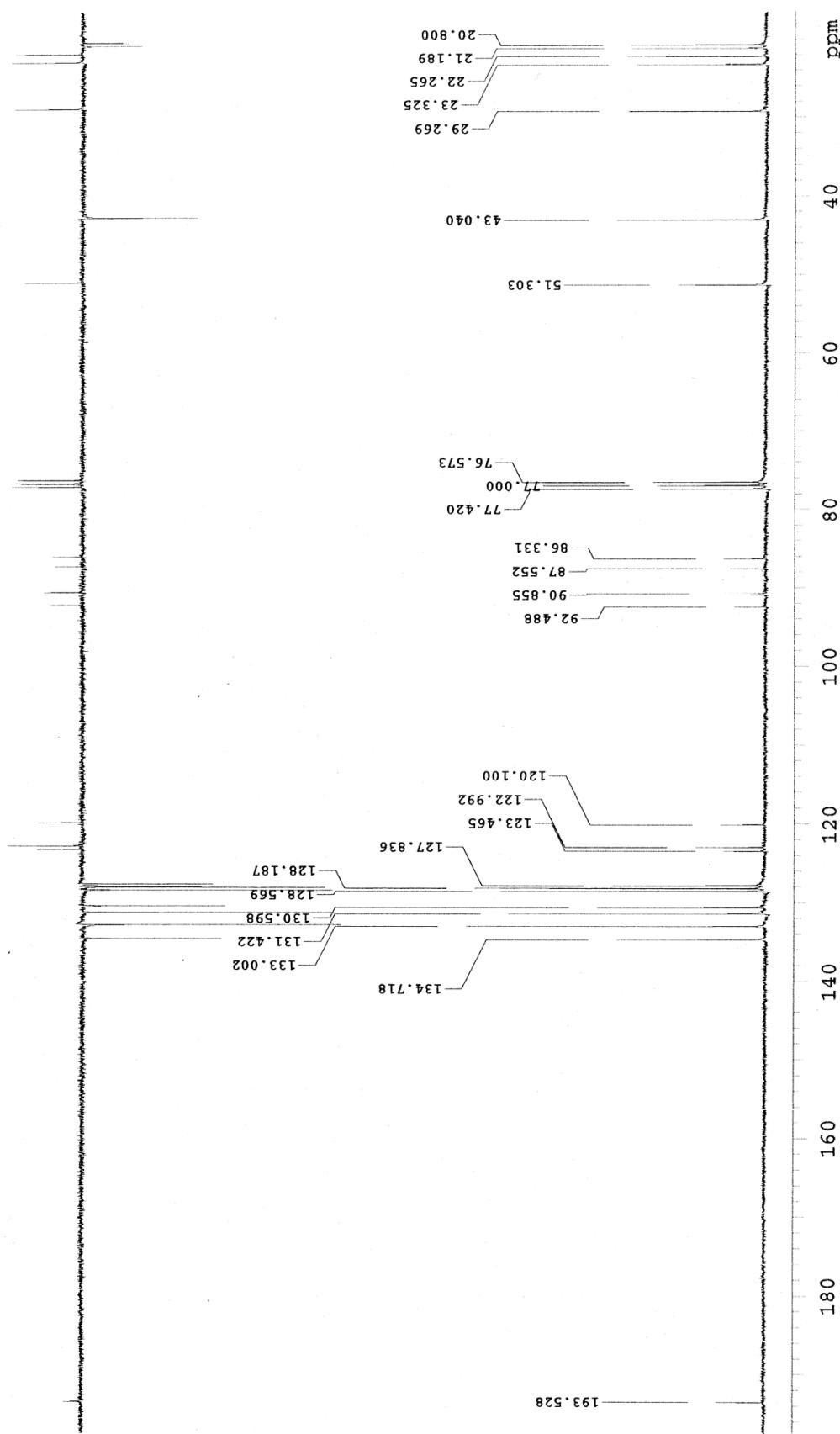








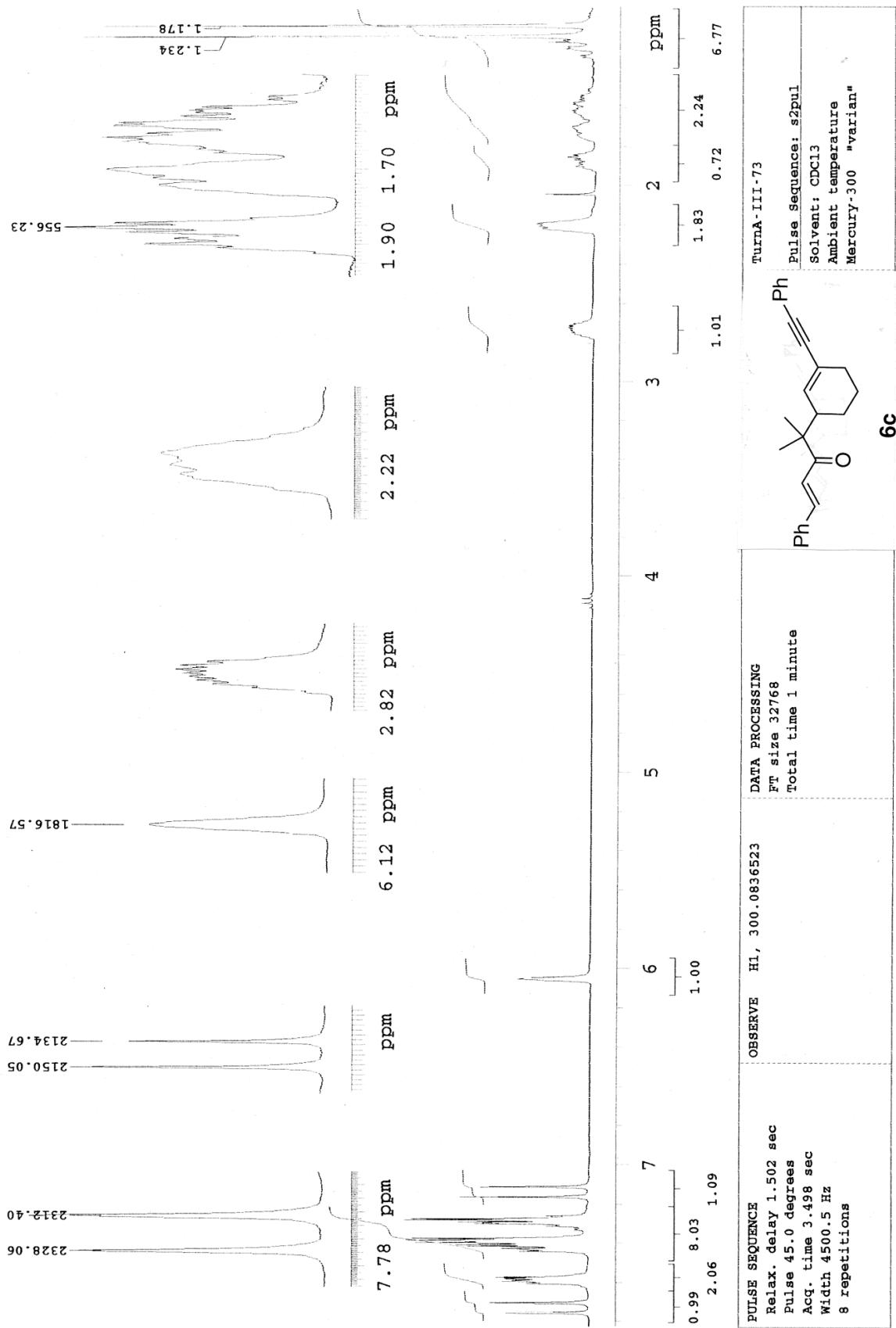


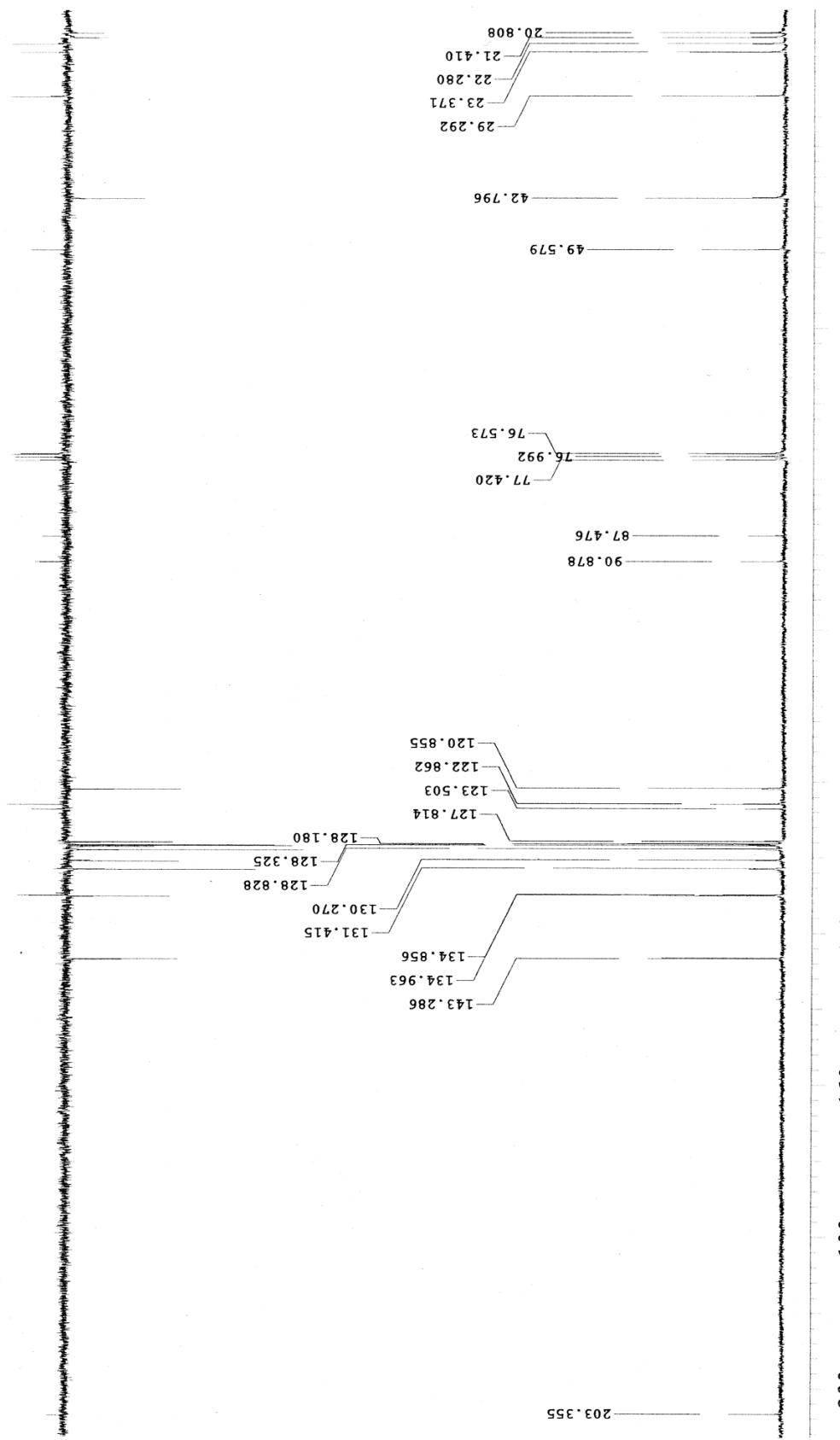


PULSE SEQUENCE	OBSERVE C13, 75.4560963 DECOUPLE H1, 300.0851346	DATA PROCESSING	TunaA-III-128
Relax. delay 0.501 sec	Line broadening 1.0 Hz	Pulse Sequence: s2pul	
Pulse 45.0 degrees	FT size 65536	Solvent: CDCl3	
Acq. time 1.499 sec	Total time 34 minutes	Ambient temperature	
Width 18865.6 Hz	WALTZ-16 modulated	Mercury-300 "varian"	
1024 repetitions			

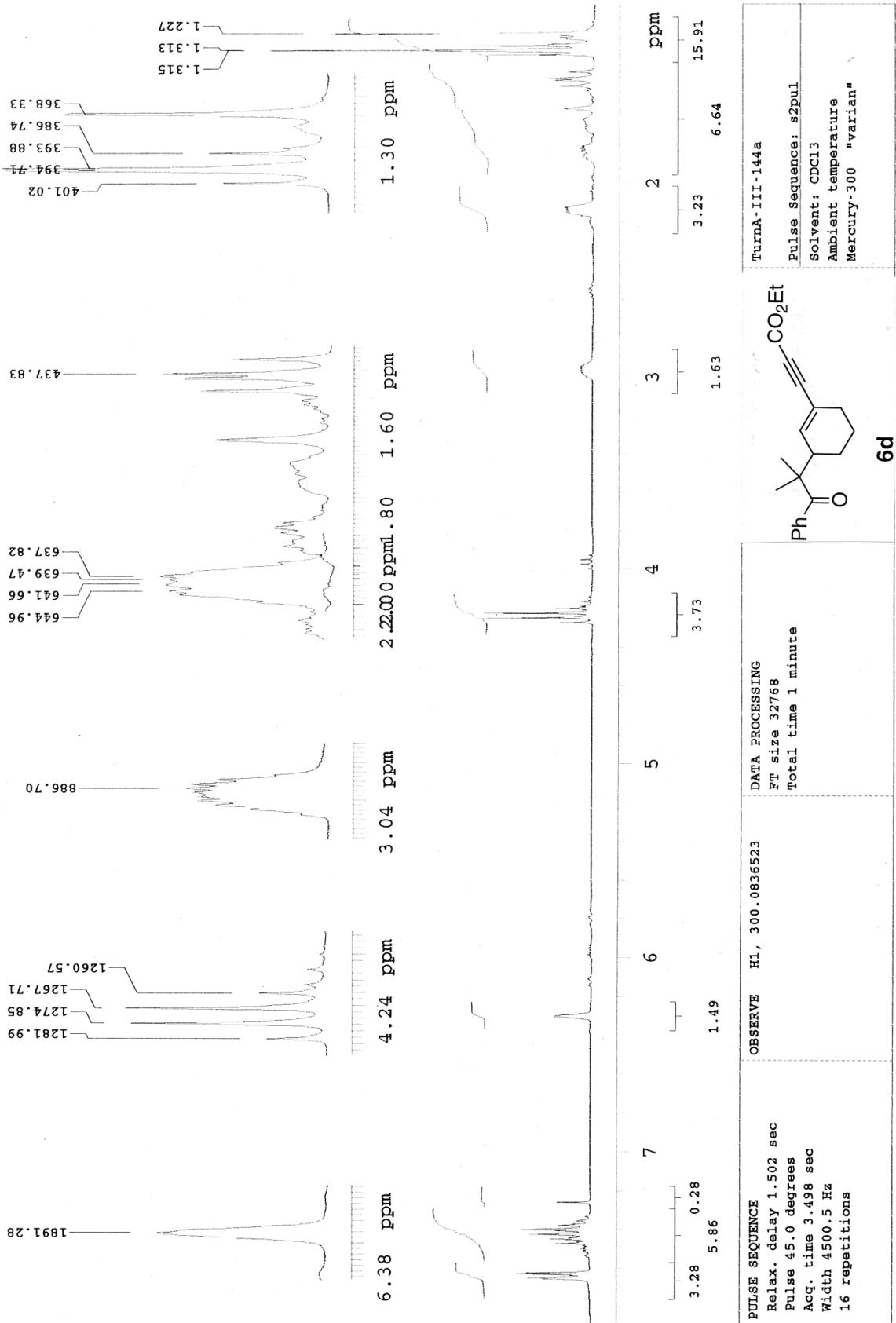
6b

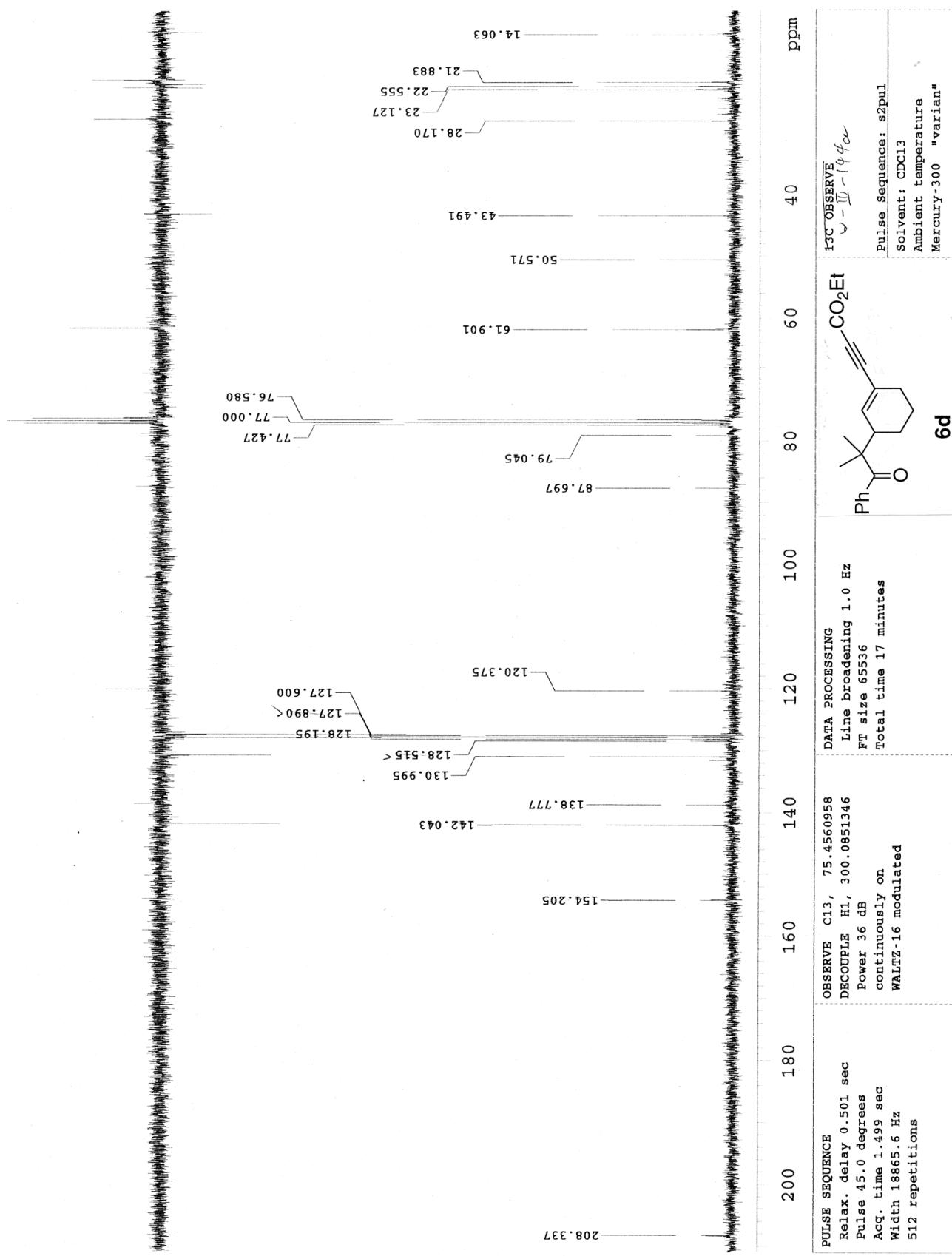
CC(C)(C)c1ccccc1C#Cc2ccccc2C(=O)C3CCCCC3

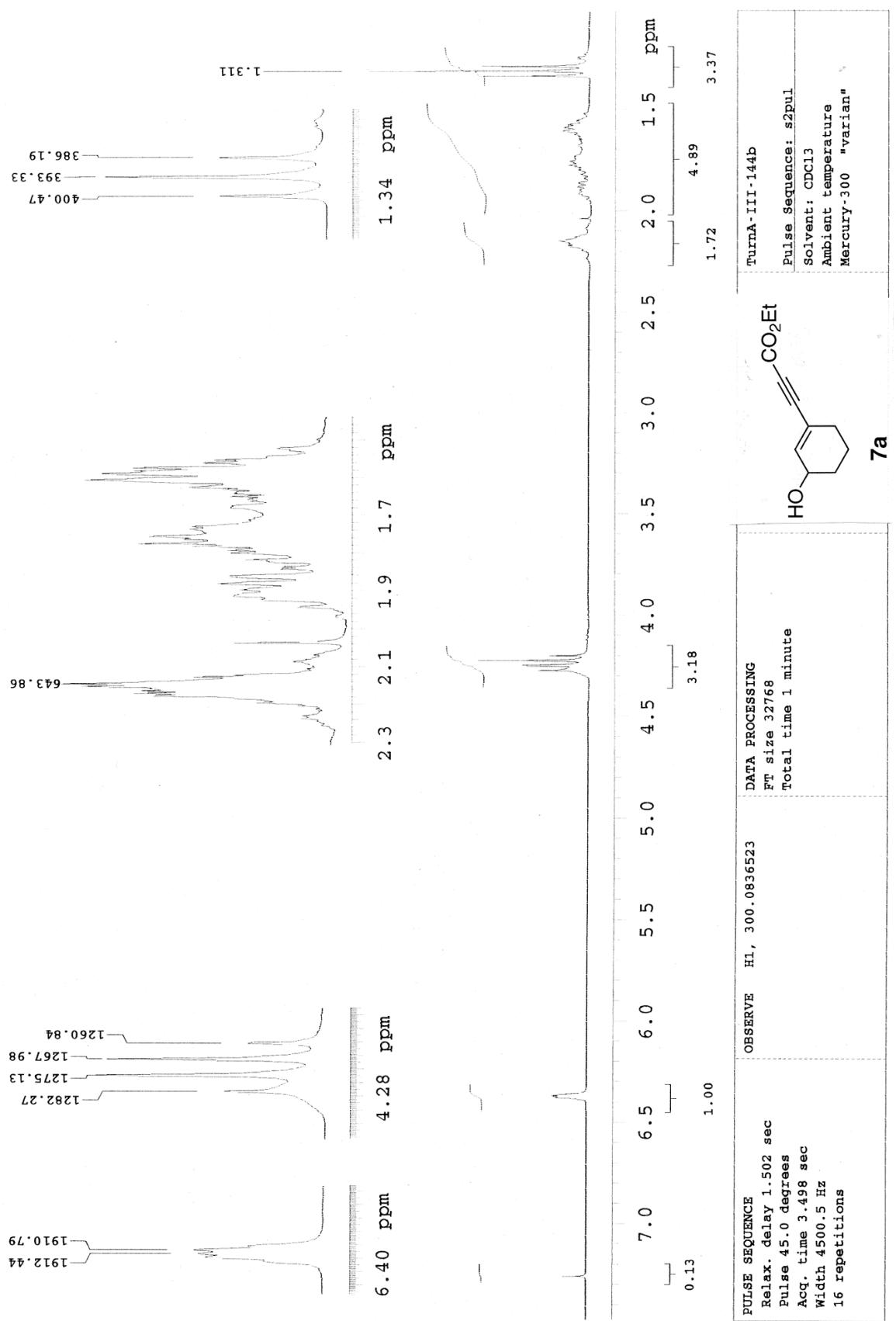


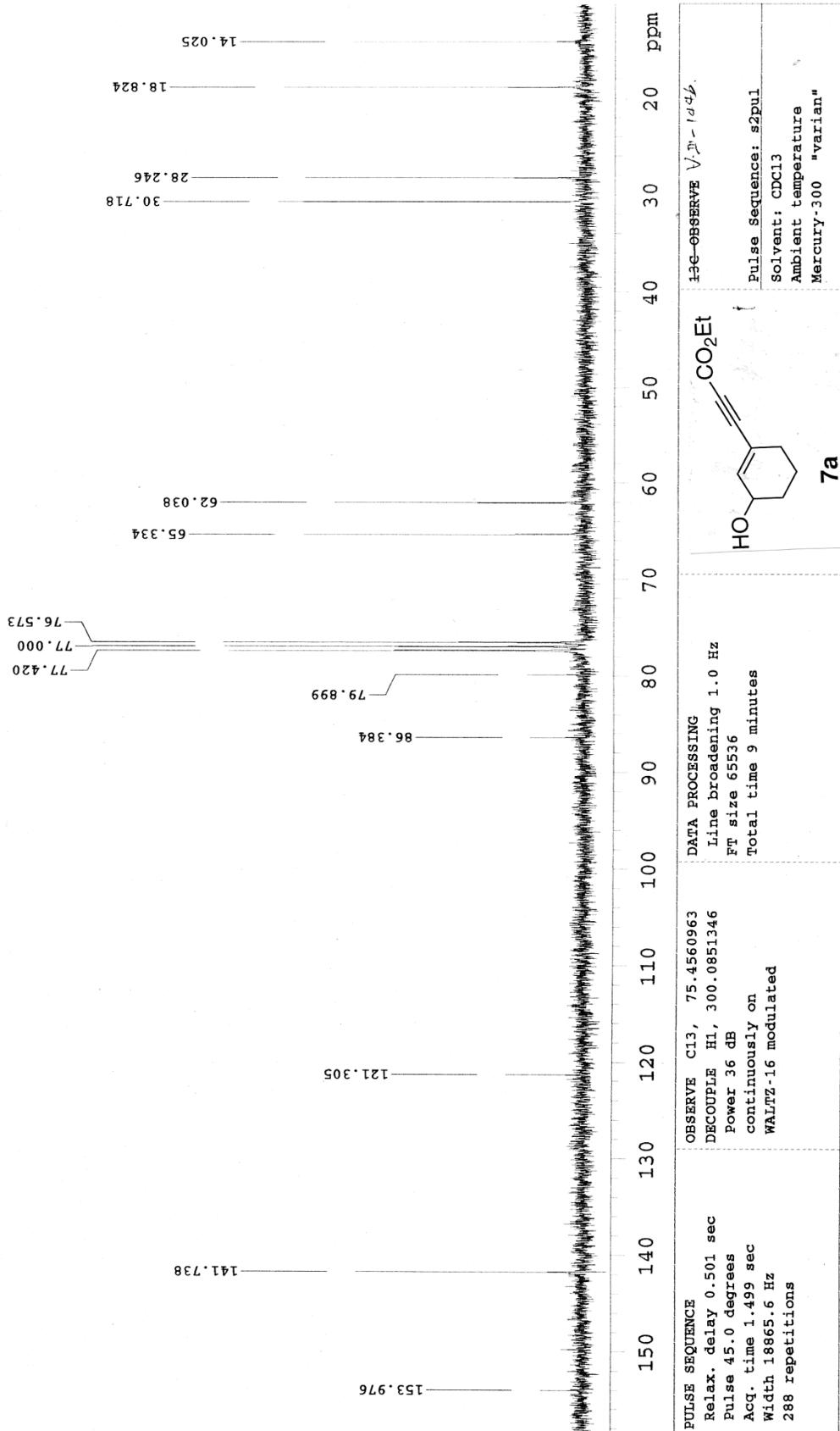


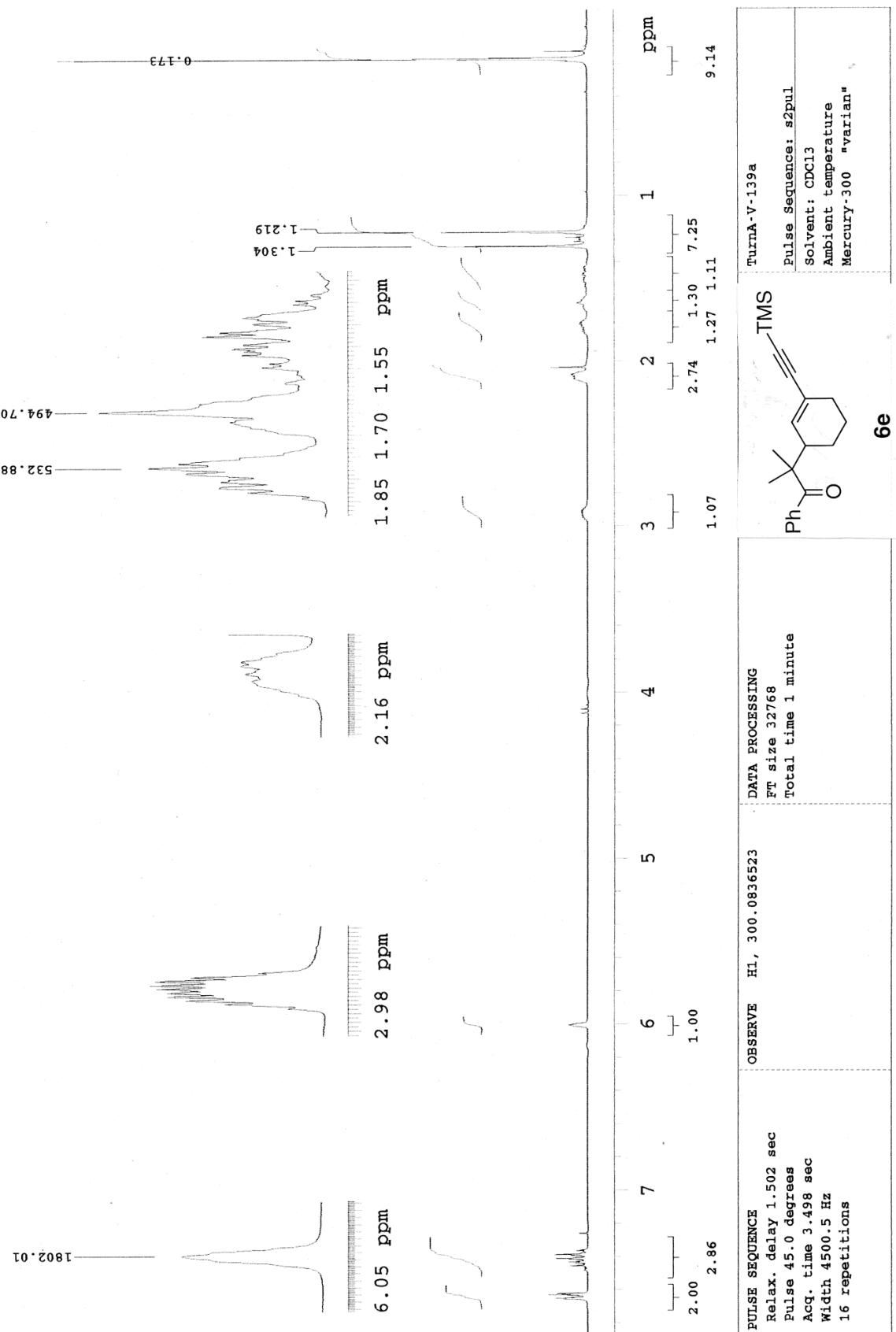
PULSE SEQUENCE	OBSERVE C13, 75.4560963 DECOPPLE H1, 300.0851346 Power 36 dB continuously on	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 17 minutes	TurnA-III-73 Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian" 6c
Relax. delay 0.501 sec			
Pulse 45.0 degrees			
Acq. time 1.499 sec			
Width 18865.6 Hz			
512 repetitions			

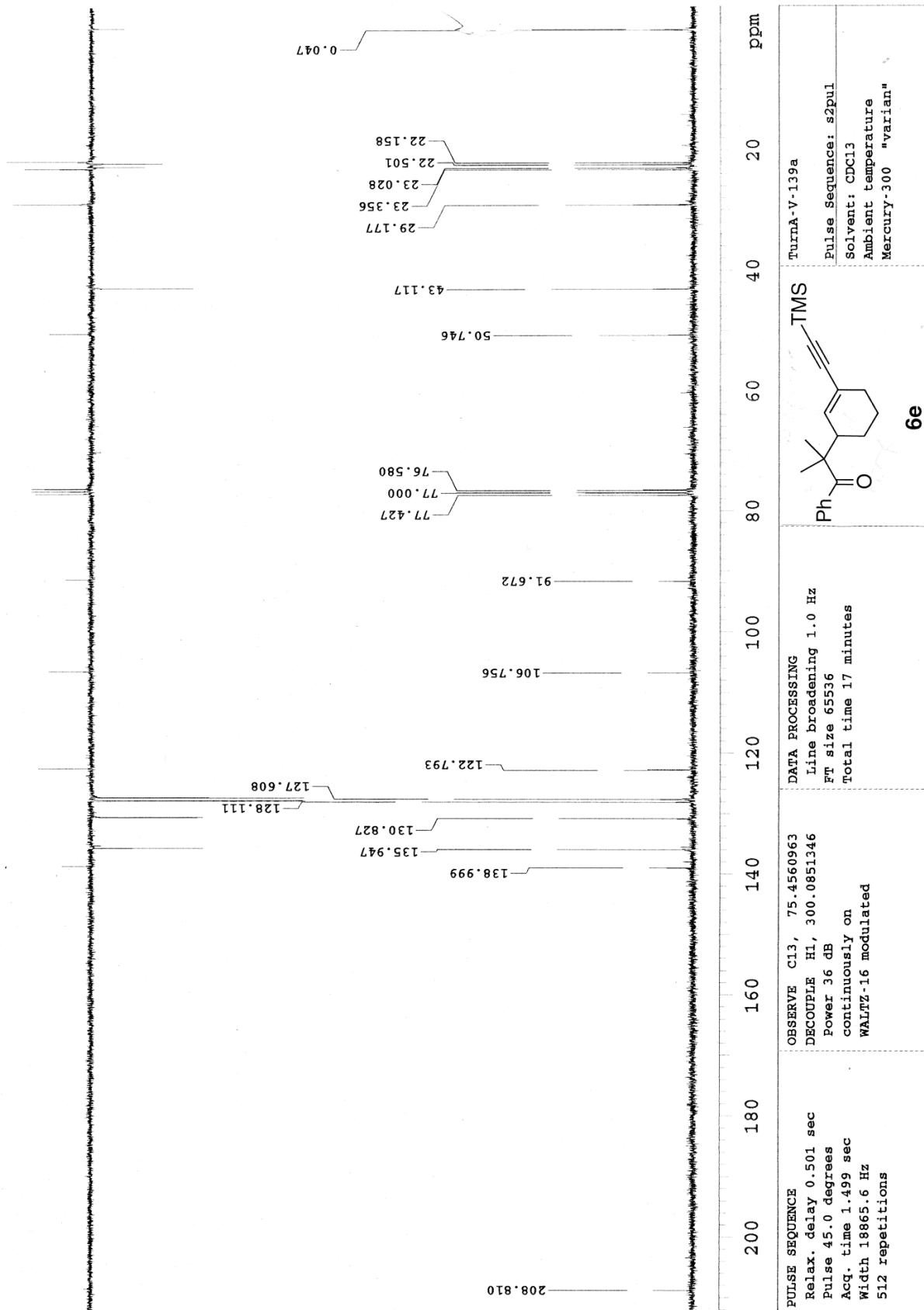


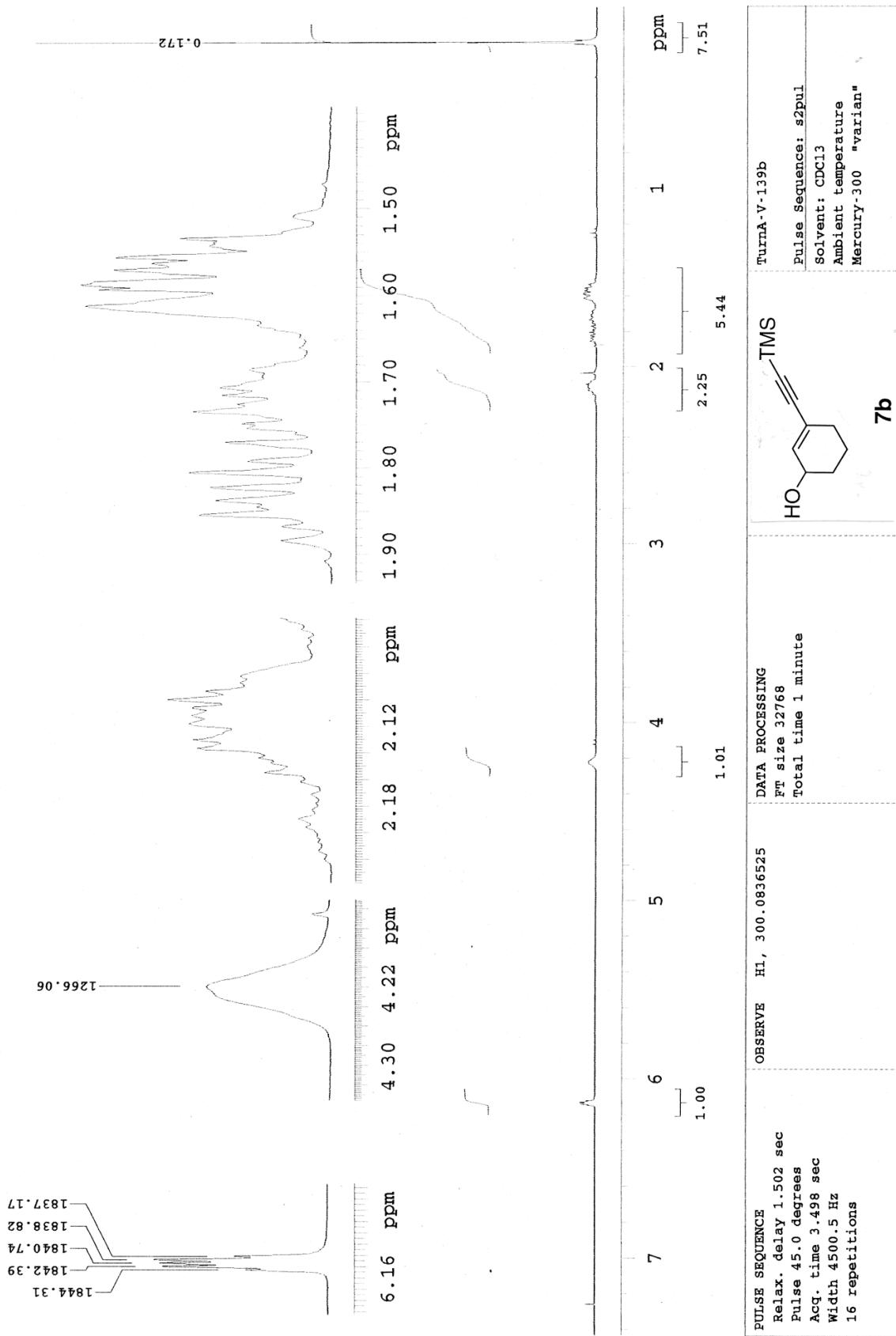


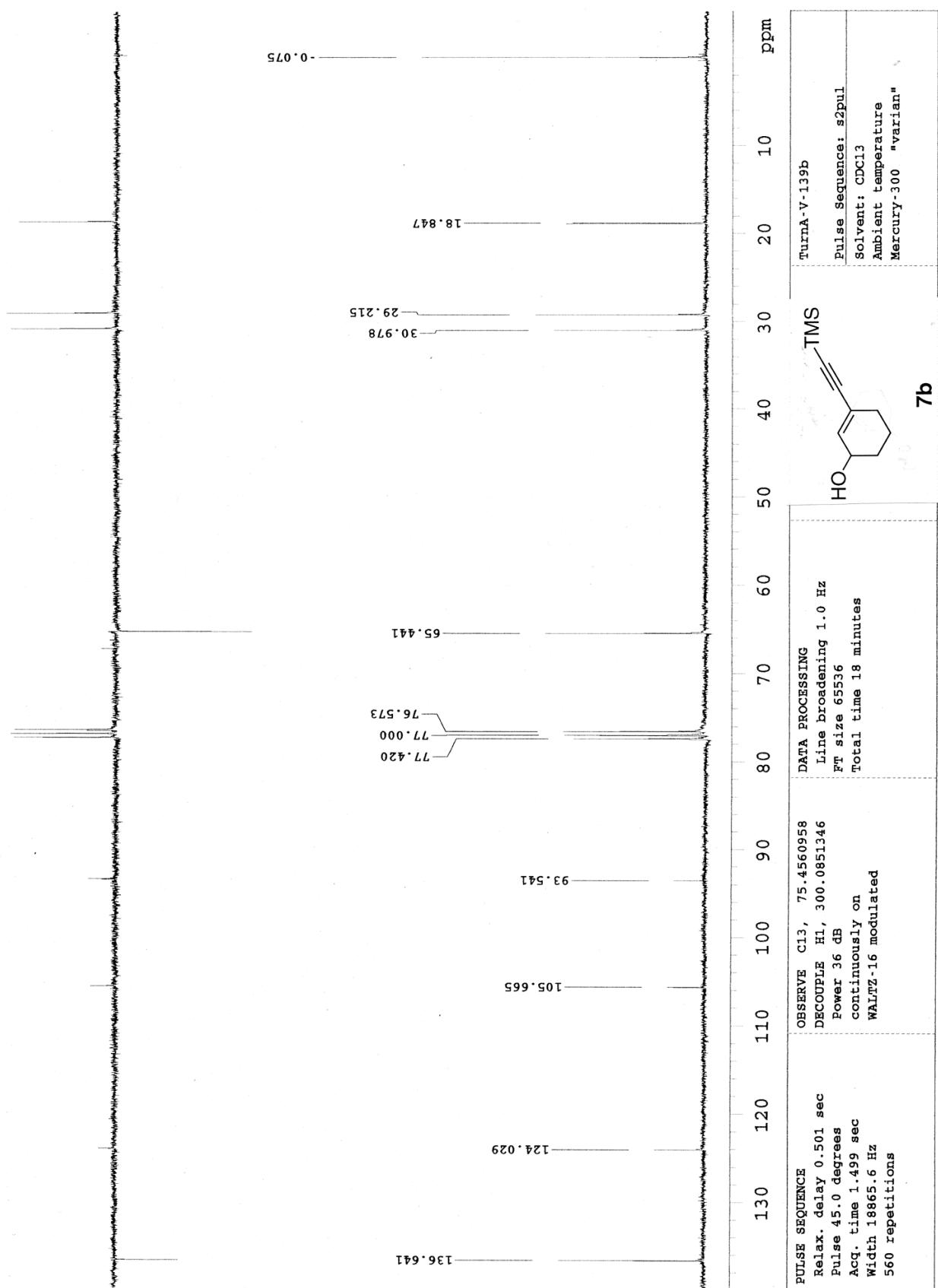


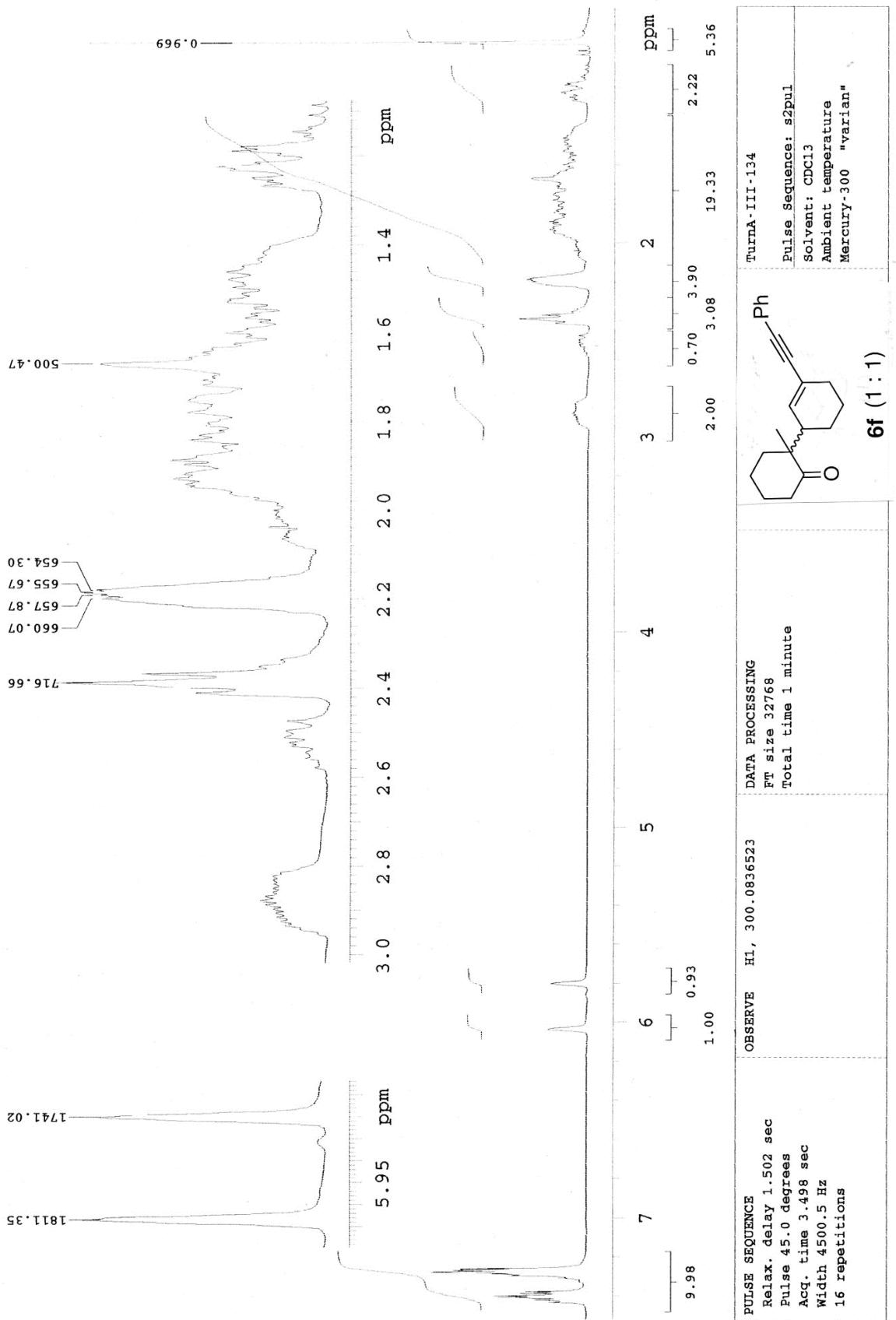


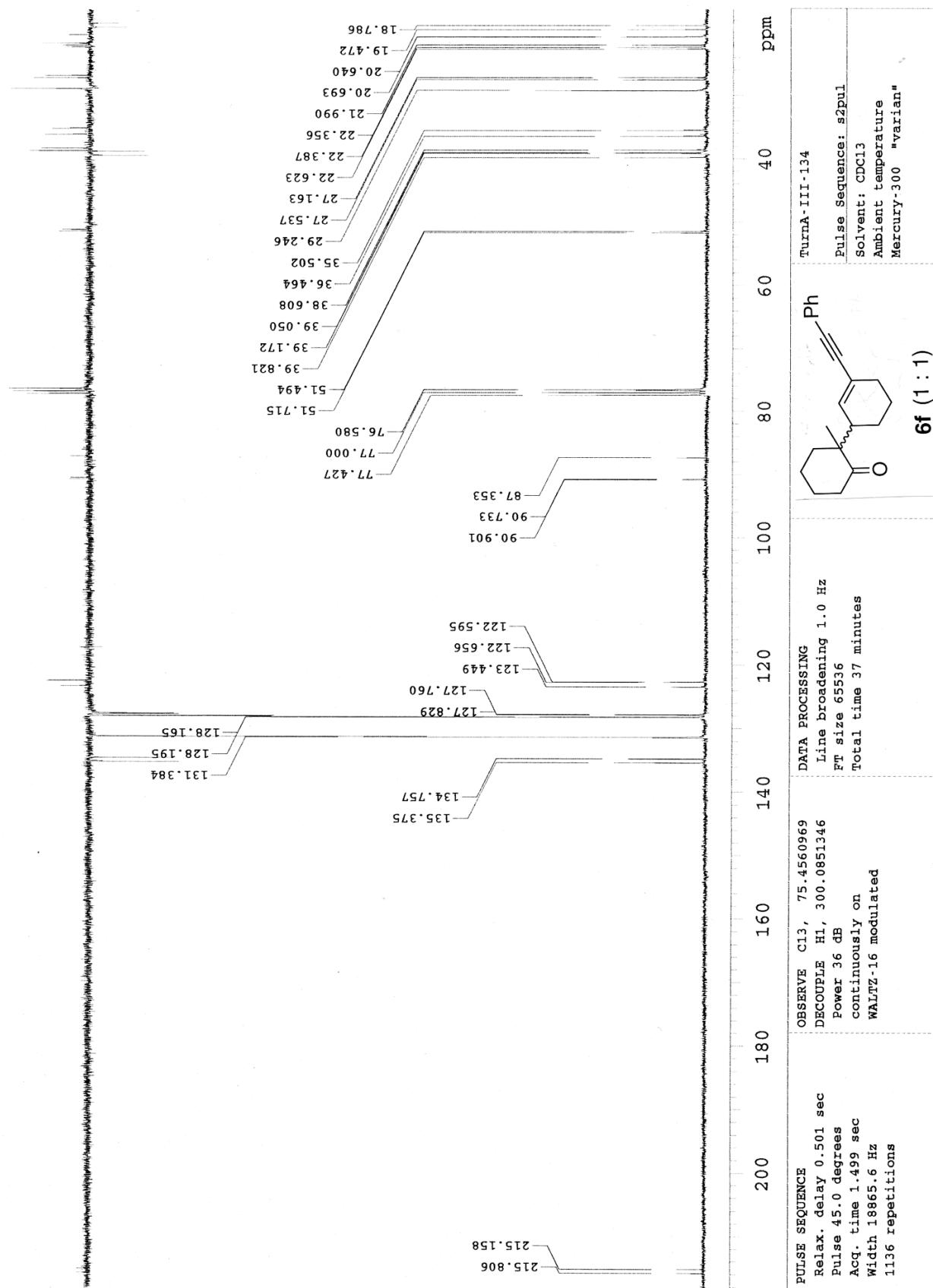


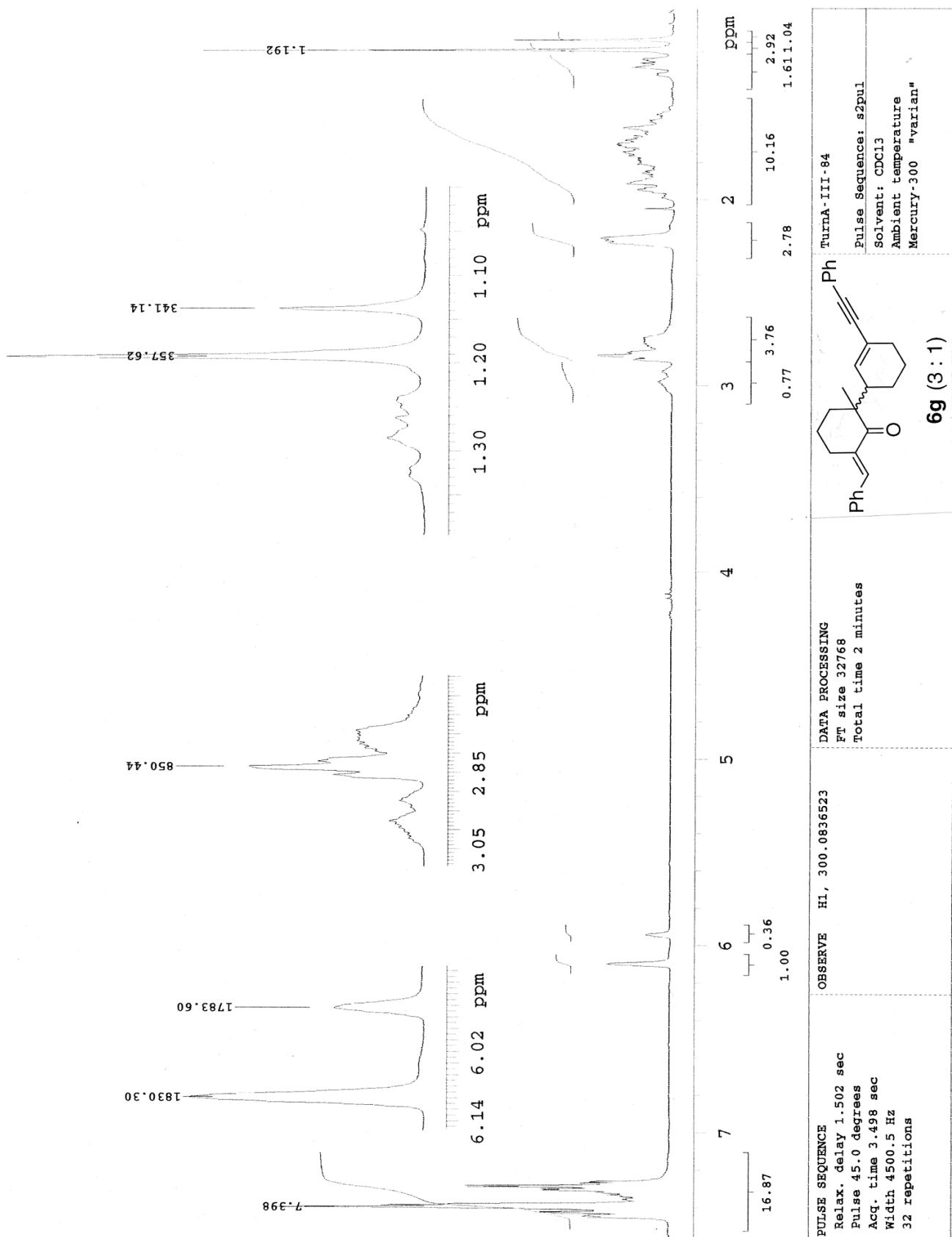


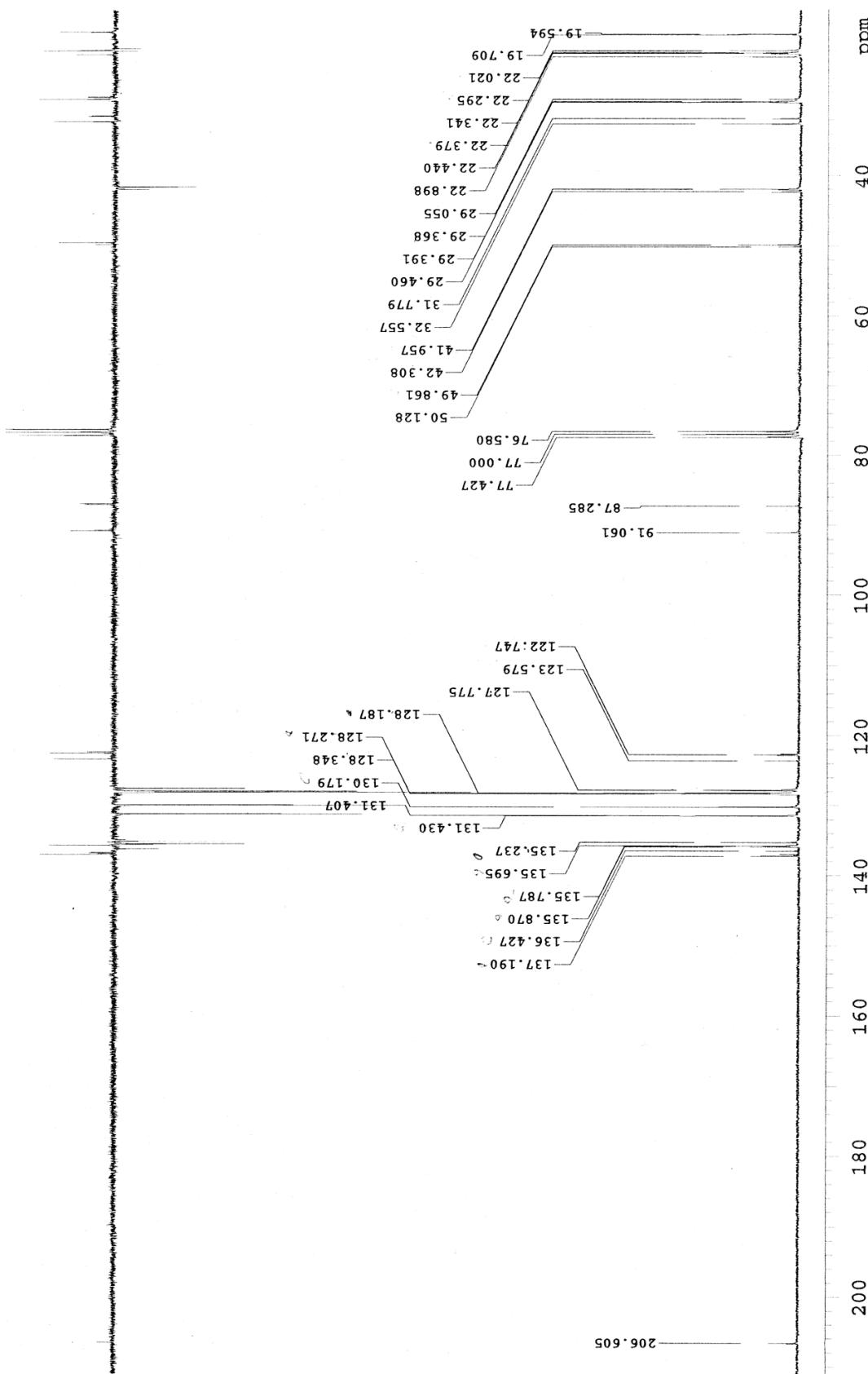




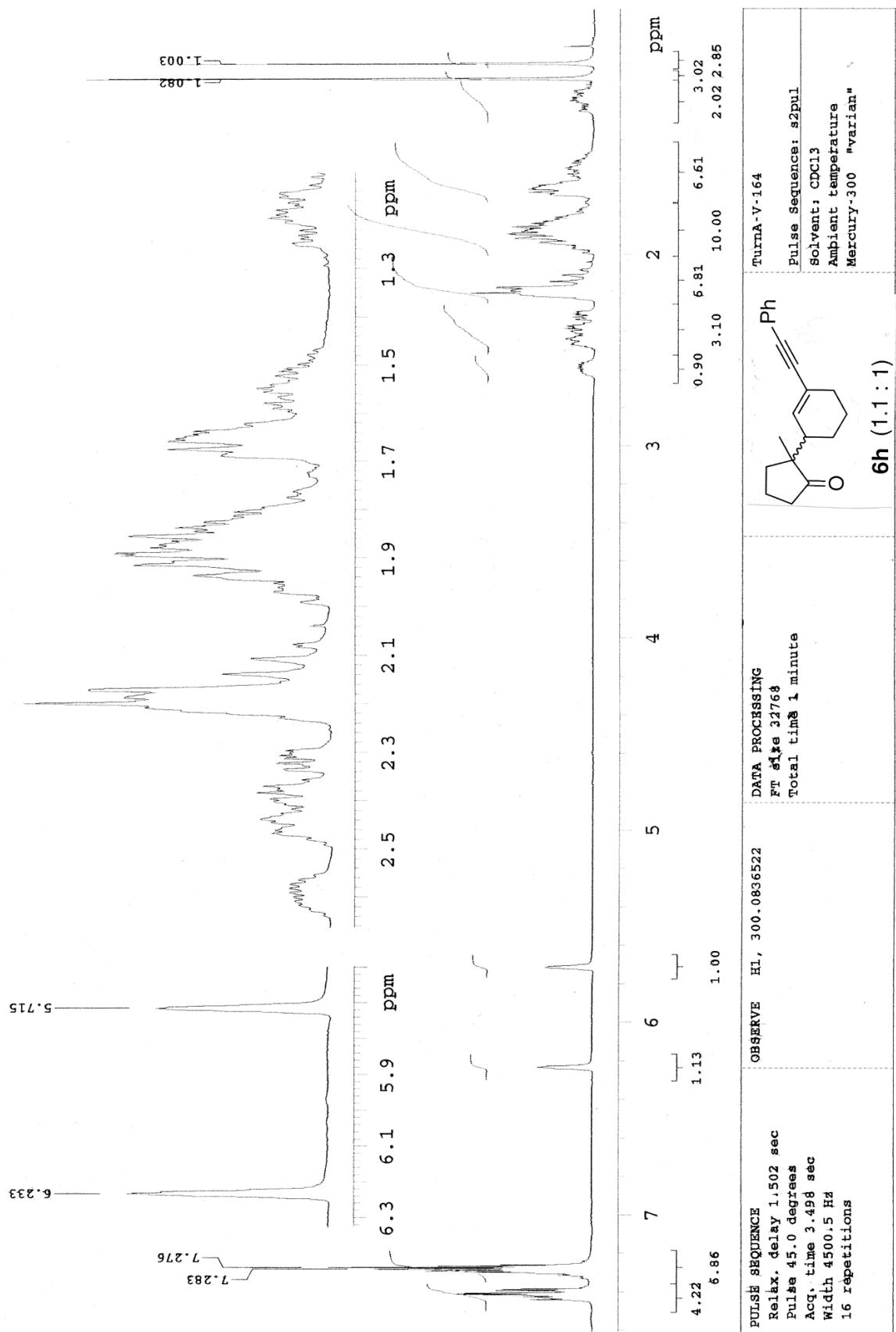


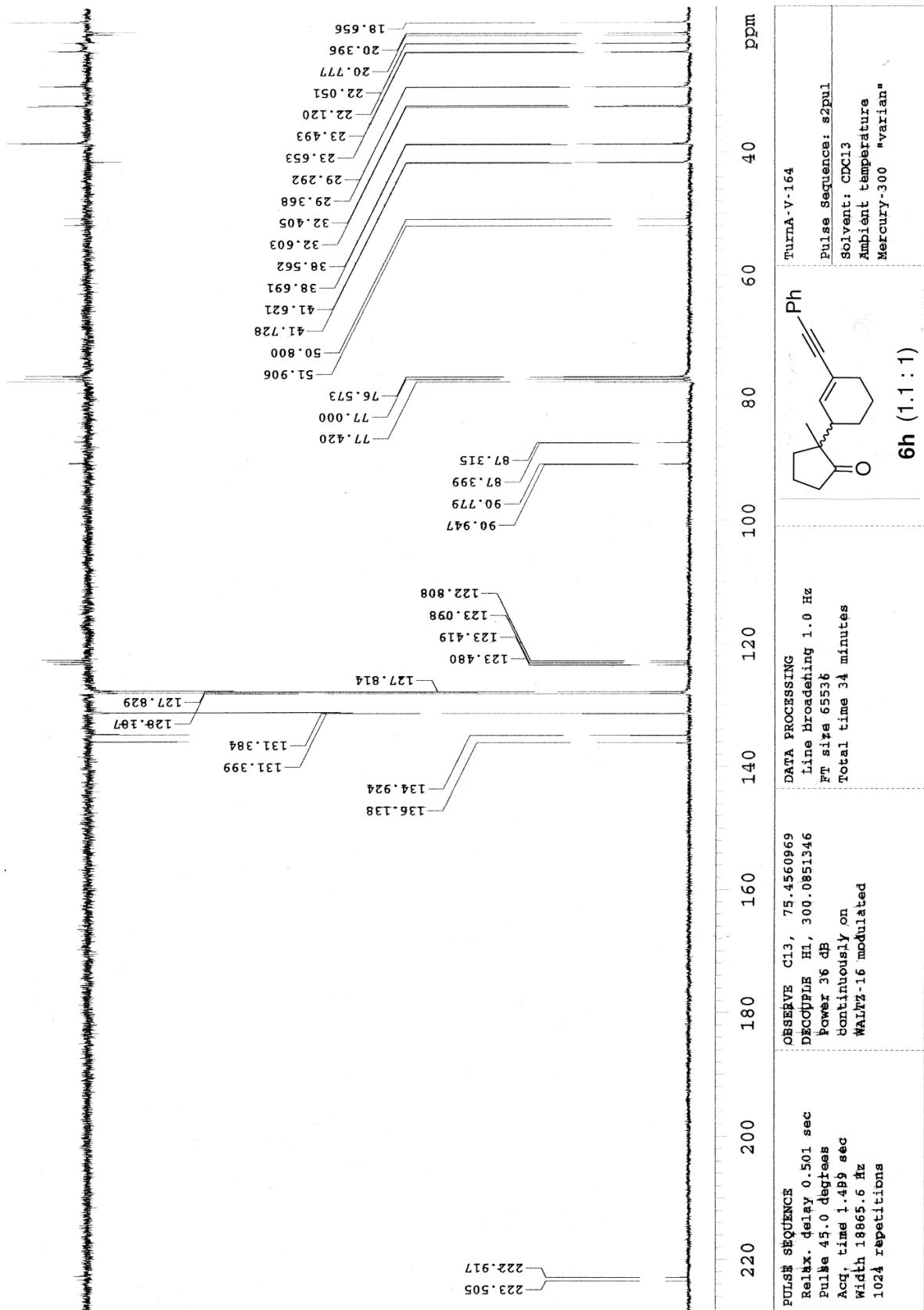


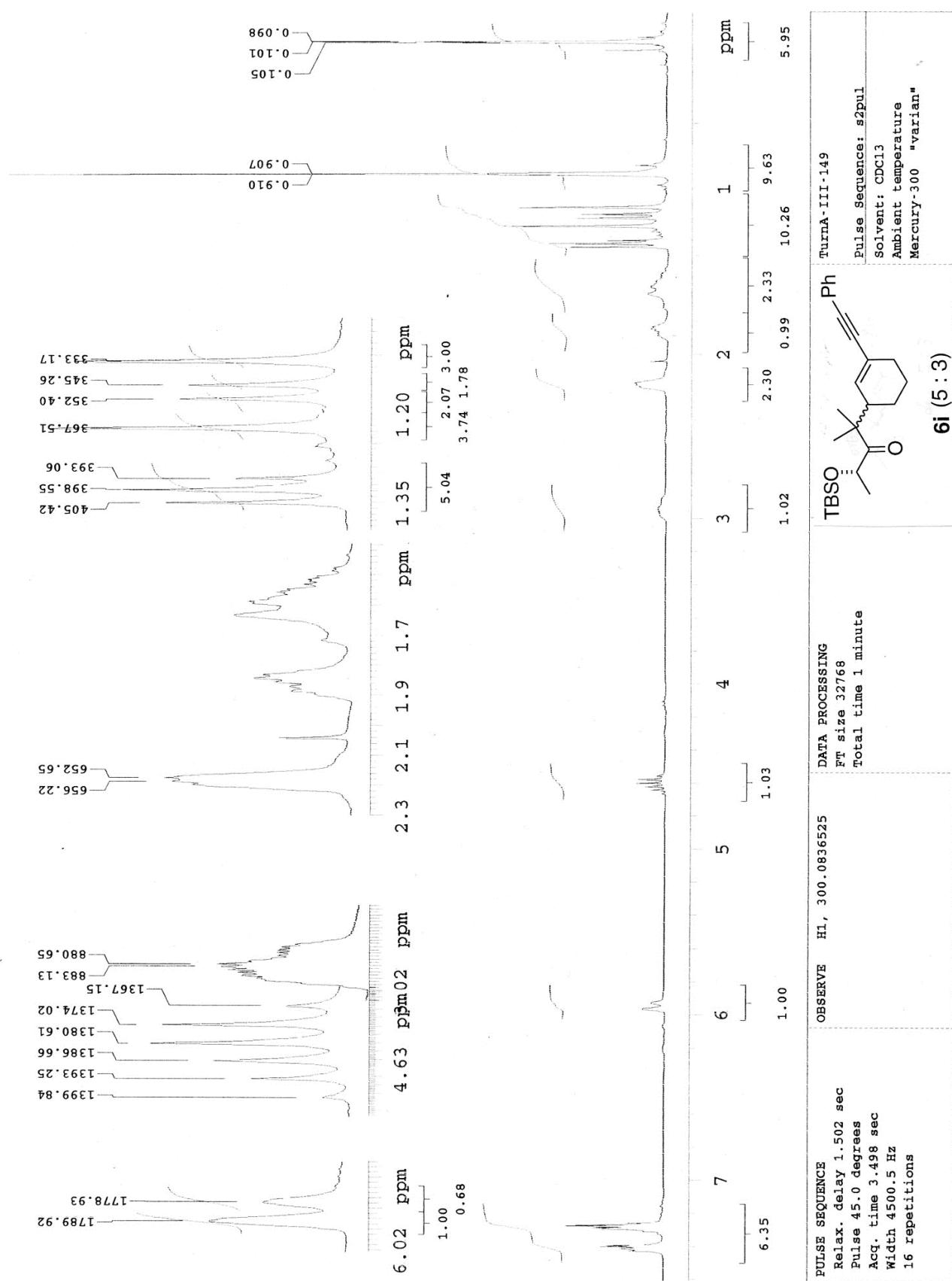


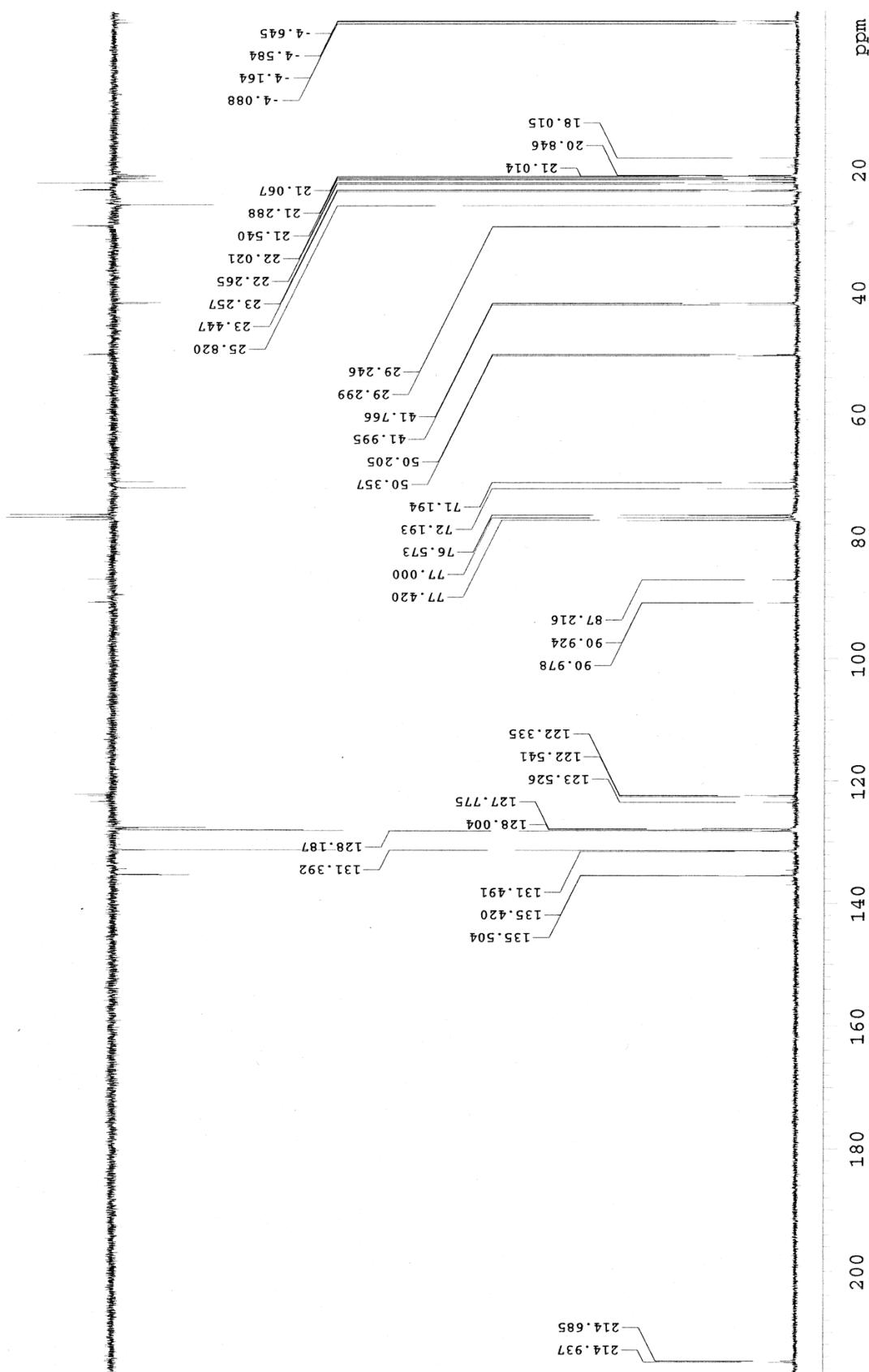


PULSE SEQUENCE	OBSERVE C13, 75.4560958	DATA PROCESSING
Relax. delay 0.501 sec	DECOPPLE H1, 300.0851346	Line broadening 1.0 Hz
Pulse 45.0 degrees	Power 36 dB	FT size 65536
Acq. time 1.499 sec	continuously on	Total time 68 minutes
Width 18865.6 Hz		
2048 repetitions		
		Turna-III-94
		Pulse Sequence: s2pal
		Solvent: CDCl3
		Ambient temperature
		Mercury-300 "Varian"
		6g (3 : 1)









PULSE SEQUENCE	OBSERVE C13 , 75.4560363	DATA PROCESSING
Relax. delay 0.501 sec	DECOPPLE H1 , 300.0851346	Line broadening 1.0 Hz
Pulse 45.0 degrees	Power 36 dB	FT size 65536
Acc. time 1.499 sec	continuously on	Total time 34 minutes
Width 18865.6 Hz		
1024 repetitions		
Ph Turna-III-149		
Pulse Sequence: s2pul		
Solvent: CDCl3		
Ambient temperature		
Mercury-300 "varian"		
6i (5:3)		