Stereoselective, Dual-Mode Ruthenium-Catalyzed Ring-Expansion of Alkynylcyclopropanols

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Supporting Information

Materials and Methods:

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Reaction solvents were dried using J. C. Meyer's Solvent Purification System passing through activated alumina prior to use. Dry acetone was distilled over drierite. All other reagents were purchase from commercial sources and used without further purification, unless otherwise indicated.
Flash Chromatography was performed using SiliCycle SilicaFlash F 60 40-60 μm 60 Å silica gel. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (E. Merck, DC-Glasfolien, Kieselgel 60 F254) and visualized with UV light and potassium permanganate stain. Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Varian Gemini 300 (300 MHz), Mercury 400 (400 MHz), Varian 400 (400 MHz), or on a Varian Unity Inova-500 (500 MHz) spectrometer. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired at 100 MHz on a Mercury 400 or at 125 MHz on a Varian Unity Inova 500 spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to deuterochloroform (7.26 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C). Infrared (IR) data were recorded as films on potassium bromide (KBr) pellets on a Thermo Scientific Nicolet IR 100 FT-IR spectrometer. High resolution mass spectra were obtained from Stanford University on a Micromass Q-Tof API US Mass Spectrometer using positive electrospray ionization (+ESI). Elemental analyses were conducted by M-H-W Laboratories, Phoenix, Az.

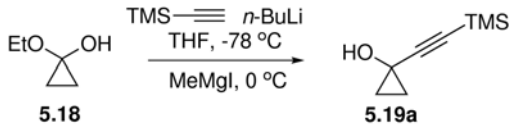
Abbreviations:
Me = methyl
Et = ethyl
Ph = phenyl
Ind = indenyl
EA = ethyl acetate
PE = petroleum ether

Experimental procedures

General procedure for the preparation of 1-alkynylcyclopropanols

Silyl- and alkyl-substituted cyclopropanols (4a-f, 10a-f)

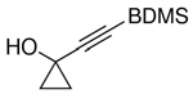
1-((Trimethylsilyl)ethynyl)cyclopropanol (4a)



To a solution of 1-ethoxycyclopropanol **5.18** (562 mg, 5.5 mmol) in THF (15 ml) was added a 2.75 M solution of methylmagnesium iodide in THF (2.0 ml, 5.5 mmol) at 0 °C. The suspension was stirred for 30 min at 0 °C. Meanwhile, to another solution of ethynyltrimethylsilane (594 mg, 6.05 mmol) in THF (15 ml) was added dropwise a 2.30 M solution of *n*-butyllithium in THF (2.63 ml, 6.05 mmol) at -78 °C. The solution was stirred for 1h at -78 °C and then cannulated into the suspension of magnesium salt at 0 °C. The mixture was slowly warmed to room temperature with continued stirring overnight. The reaction was quenched with saturated aqueous NH_4Cl (10 ml) and extracted with ether (3 *times* 10 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 ml) and brine (10 ml), dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue by flash chromatography (10% diethyl ether in petroleum ether, silica gel) gave **4a** (Yield: 750 mg, 88%) as a colorless liquid.

R*f* = 0.50 (25% ether in pet. ether) IR (neat): 3332, 2961, 2161, 1251, 843 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.18 (s, 1H), 1.07 – 1.04 (m, 2H), 0.98 – 0.94 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 107.5, 86.6, 45.7, 17.5, -0.15. Spectral data matched that reported in the literature. [1]

1-((Benzyldimethylsilyl)ethynyl)cyclopropanol (4b)

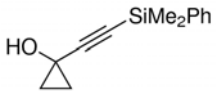


Cyclopropanol **4b** was prepared according to the general procedure using benzyl(ethynyl)dimethylsilane (526.4 mg, 3.02 mmol), 1-ethoxycyclopropanol (281 mg, 2.75 mmol), a 2.50 M solution of *n*-butyllithium in hexane (1.21 ml, 3.02 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.0 ml, 2.75 mmol). Reaction was conducted in THF (15

ml) for 12 h. Purification by flash chromatograph (10% ether in petroleum ether, silica gel) afforded **4b** (Yield: 350 mg, 55%) as a colorless oil.

R*f* = 0.27 (10% ether in pet. ether). IR (neat): 3478, 2934, 2859, 2193, 1714, 1673, 1514, 1248, 1096, 1036, 822 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 – 7.20 (m, 2H), 7.10 – 7.04 (m, 3H), 2.85 (s, 1H), 2.18 (s, 2H), 1.07 – 1.04 (m, 2H), 0.99 – 0.96 (m, 2H), 0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.9, 128.3, 128.1, 124.3, 108.7, 85.1, 45.8, 26.1, 17.6, -2.2. HRMS (EI) Calc'd for $C_{14}H_{18}OSi$: 230.1127, found: 230.1126.

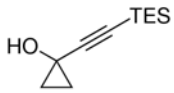
1-((Dimethylphenylsilyl)ethynyl)cyclopropanol (4c)



Cyclopropanol **4c** was prepared according to the general procedure using ethynyldimethylphenylsilane (705.3 mg, 4.40 mmol), 1-ethoxycyclopropanol (408.5 mg, 4.00 mmol), a 2.50 M solution of *n*-butyllithium in hexane (1.76 ml, 4.40 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.45 ml, 4.00 mmol). Reaction was conducted in THF (20 ml) for 12 h. Purification by flash chromatograph (15% ether in petroleum ether, silica gel) afforded **4c** (Yield: 600 mg, 70%) as a colorless oil.

R*f* = 0.47 (25% ether in pet. ether). IR (neat): 3336, 2961, 2160, 1428, 1234, 1117, 821cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.62 (m, 2H), 7.41 – 7.38 (m, 3H), 2.76 (s, 1H), 1.13 – 1.10 (m, 2H), 1.08 – 1.04 (m, 2H), 0.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.8, 133.6, 129.4, 127.8, 109.0, 84.8, 46.0, 17.7, -0.93. Elemental Analysis Calc'd for $C_{13}H_{16}OSi$: C, 72.17; H, 7.45; Found: C, 71.96; H, 7.22.

1-((Triethylsilyl)ethynyl)cyclopropanol (4d)

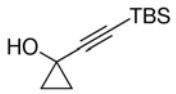


Cyclopropanol **4d** was prepared according to the general procedure using triethyl(ethynyl)silane (617.3 mg, 4.40 mmol), 1-ethoxycyclopropanol (408.5 mg, 4.00 mmol), a 2.50 M solution of *n*-butyllithium in hexane (1.76 ml, 4.40 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.45 ml, 4.00 mmol). Reaction was conducted in THF (20 ml) for 12 h. Purification by flash chromatograph (10% ether in petroleum ether, silica gel) afforded **4d** (Yield: 660 mg, 84%) as a colorless oil.

R*f* = 0.56 (25% ether in pet. ether). IR (neat): 3346, 2956, 2877, 2159, 1459, 1235, 1020, 736 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.78 (b, 1H), 1.09 – 1.06 (m, 2H), 1.00 – 0.97 (m, 2H),

0.96 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 108.6, 84.0, 46.0, 17.8, 7.4, 4.3. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$: 196.1283, found: 196.1278.

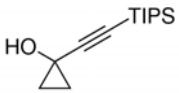
1-((*tert*-Butyldimethylsilyl)ethynyl)cyclopropanol (4e)



Cyclopropanol **4e** was prepared according to the general procedure using *tert*-butylethynldimethylsilane (594.2 mg, 4.24 mmol), 1-ethoxycyclopropanol (393.2 mg, 3.85 mmol), a 2.50 M solution of *n*-butyllithium in hexane (1.70 ml, 4.24 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.40 ml, 3.85 mmol). Reaction was conducted in THF (20 ml) for 12 h. Purification by flash chromatograph (10% ether in petroleum ether, silica gel) afforded **4e** (Yield: 600 mg, 80%) as a colorless oil.

Rf = 0.50 (25% ether in pet. ether). IR (neat): 3320, 2955, 2858, 2160, 1472, 1250, 937, 838, 776 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.46 (s, 1H), 1.05 (dd, J_1 = 8.3 Hz, J_2 = 5.4 Hz, 2H), 0.94 (dd, J_1 = 8.3 Hz, J_2 = 5.4 Hz, 2H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 108.3, 84.5, 45.7, 26.0, 17.6, 16.4, -4.7. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$: 196.1283, found: 196.1289.

1-((Triisopropylsilyl)ethynyl)cyclopropanol (4f)

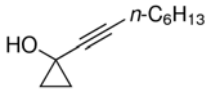


Cyclopropanol **4f** was prepared according to the general procedure using ethynltriisopropylsilane (662.0 mg, 3.63 mmol), 1-ethoxycyclopropanol (337.0 mg, 3.30 mmol), a 2.50 M solution of *n*-butyllithium in hexane (1.45 ml, 3.63 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.20 ml, 3.30 mmol). Reaction was conducted in THF (15 ml) for 12 h. Purification by flash chromatograph (10% ether in petroleum ether, silica gel) afforded **4f** (Yield: 660 mg, 84%) as a colorless oil.

Rf = 0.55 (25% ether in pet. ether). IR (neat): 3320, 2955, 2858, 2160, 1472, 1250, 937, 838, 776cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88 (s, 1H), 1.09 – 1.03 (m, 21H), 0.99 – 0.96 (m, 2H), 0.88 – 0.85 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 109.5, 82.5, 46.0, 18.5, 17.8, 11.1. Spectral data matched that reported in the literature. [1]

Alkyl derivatives

1-(Oct-1-ynyl)cyclopropanol (10a)



Cyclopropanol **10a** was prepared according to the general procedure using 1-octyne (770 mg, 7.00 mmol), 1-ethoxycyclopropanol (650 mg, 6.36 mmol), a 2.50 M solution of *n*-butyllithium in hexane (2.80 ml, 7.00 mmol), a 2.75 M solution of methylmagnesium iodide in THF (2.31 ml, 6.36 mmol). Reaction was conducted in THF (30 ml) for 12 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10a** (Yield: 850 mg, 80%) as a colorless oil.

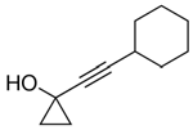
R*f* = 0.70 (50% ether / pet. ether): 0.70. IR (neat): 3332, 2932, 2859, 2360, 1458, 1237, 1019, 969, 882 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88 (b, 1H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.46 (quint, *J* = 7.2 Hz, 2H), 1.38 – 1.23 (m, 6H), 1.05 – 0.98 (m, 2H), 0.89 – 0.85 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 82.8, 81.7, 45.6, 31.3, 28.6, 28.5, 22.5, 18.7, 17.0, 14.0. Spectral data matched that reported in the literature. [1]

1-(3-Phenylprop-1-ynyl)cyclopropanol (10b)

Cyclopropanol **10b** was prepared according to the general procedure using prop-2-ynylbenzene (348.5 mg, 3.02 mmol), 1-ethoxycyclopropanol (281mg, 2.75 mmol), a 2.40 M solution of *n*-butyllithium in hexane (1.25 ml, 3.02 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.0 ml, 2.75 mmol). Reaction was conducted in THF (20 ml) for 20 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10b** (Yield: 320 mg, 68%) as a colorless oil.

R*f* = 0.37 (25% ether in pet. ether). IR (neat): 3383, 3030, 2887, 2240, 1604, 1495, 1454, 1235, 1019, 967, 731, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.22 – 7.19 (m, 1H), 3.58 (s, 2H), 3.17 (s, 1H), 1.04 (m, 2H), 0.93 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.5, 128.4, 127.7, 126.5, 83.9, 80.0, 45.5, 25.0, 17.0. HRMS (EI) Calc'd for $C_{12}H_{12}O$: 172.0888, found: 172.0880.

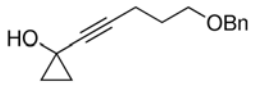
1-(Cyclohexylethynyl)cyclopropanol (10c)



Cyclopropanol **10c** was prepared according to the general procedure using ethynylcyclohexane (458 mg, 4.24 mmol), 1-ethoxycyclopropanol (393 mg, 3.85 mmol), a 2.30 M solution of *n*-butyllithium in hexane (1.84 ml, 4.24 mmol), a 2.75 M solution of methylmagnesium iodide in THF (1.40 ml, 3.85 mmol). Reaction was conducted in THF (20 ml) for 12 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10c** (Yield: 520 mg, 82%) as a colorless oil.

R*f* = 0.43 (25% ether in pet. ether). IR (neat): 3406, 2931, 2854, 1645, 1449, 1237, 1020, 967, 887 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.55 (b, 1H), 2.35 (m, 1H), 1.78 – 1.75 (m, 2H), 1.69 – 1.63 (m, 2H), 1.52 – 1.47 (m, 1H), 1.43 – 1.35 (m, 2H), 1.30 – 1.23 (m, 3H), 1.03 – 1.01 (m, 2H), 0.91 – 0.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 87.0, 81.6, 45.8, 32.6, 29.0, 25.8, 24.9, 17.2. Elemental Analysis Calc'd for $C_{11}H_{16}O$: C, 80.44; H, 9.82; Found: C, 80.22; H, 9.66.

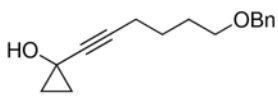
1-(5-(Benzyloxy)pent-1-ynyl)cyclopropanol (10d)



Cyclopropanol **10d** was prepared according to the general procedure using ((pent-4-ynyloxy)methyl)benzene (417 mg, 2.38 mmol), 1-ethoxycyclopropanol (290 mg, 2.84 mmol), a 2.50 M solution of *n*-butyllithium in hexane (0.96 ml, 2.40 mmol), a 2.75 M solution of methylmagnesium iodide in THF (0.80 ml, 2.20 mmol). Reaction was conducted in THF (15 ml) for 12 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10d** (Yield: 180 mg, 39%) as a colorless oil.

R*f* = 0.30 (25% ether in pet. ether). IR (neat): 3392, 2925, 2857, 1461, 1239, 1102 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 5H), 4.51 (s, 2H), 3.55 (t, *J* = 7.8 Hz, 2H), 2.34 (t, *J* = 8.8 Hz, 2H), 2.26 (s, 1H), 1.80 (quint, *J* = 8.2 Hz, 2H), 1.01 (dd, J_1 = 8.5 Hz, J_2 = 6.0 Hz, 2H), 0.89 (dd, J_1 = 8.5 Hz, J_2 = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.4, 128.3, 127.6, 127.5, 82.2, 81.9, 72.9, 68.7, 45.9, 28.8, 17.1, 15.6. HRMS (ESI) Calc'd for $C_{15}H_{18}O_2$ + Na: 253.1204, found: 253.1207.

1-(6-(Benzyloxy)hex-1-ynyl)cyclopropanol (10e)

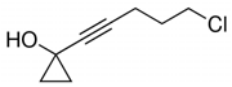


Cyclopropanol **10e** was prepared according to the general procedure using ((hexen-5-ynyloxy)methyl)benzene (414 mg, 2.20 mmol), 1-ethoxycyclopropanol (290 mg, 2.84 mmol), a 2.50 M solution of *n*-butyllithium in hexane (0.95 ml, 2.38 mmol), a 2.75 M solution of methylmagnesium iodide in THF (0.87 ml, 2.39 mmol). Reaction was conducted in THF (15

ml) for 12 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10e** (Yield: 276 mg, 51%) as a colorless oil.

R*f* = 0.33 (25% ether in pet. ether). IR (neat): 3392, 2937, 2855, 2114, 1636, 1460, 1234, 1090 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 5H), 4.53 (s, 2H), 3.51 (t, *J* = 7.0 Hz, 2H), 2.82 (b, 1H), 2.53 (t, *J* = 7.0 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.65 – 1.59 (m, 2H), 1.03 (dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, 2H), 0.92 (dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.4, 128.3, 127.6, 127.5, 82.4, 82.0, 72.8, 69.7, 45.6, 28.8, 25.3, 18.5, 17.0. HRMS (ESI) Calc'd for $C_{16}H_{20}O_2$ + Na: 267.1361, found: 267.1364.

1-(5-chloropent-1-ynyl)cyclopropanol (10f)

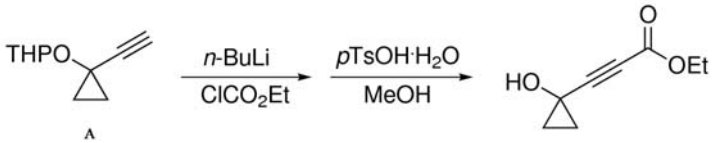


Cyclopropanol **10f** was prepared according to the general procedure using 5-chloropent-1-yne (205 mg, 2.00 mmol), 1-ethoxycyclopropanol (291 mg, 2.84 mmol), a 2.50 M solution of *n*-butyllithium in hexane (0.87 ml, 2.18 mmol), a 2.75 M solution of methylmagnesium iodide in THF (0.87 ml, 2.39 mmol). Reaction was conducted in THF (15 ml) for 12 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded **10f** (Yield: 125 mg, 39%) as a colorless oil.

R*f* = 0.38 (25% ether in pet. ether). IR (neat): 3359, 2959, 2929, 1467, 1231, 1061, 970 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63 (t, *J* = 7.8 Hz, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 2.35 (b, 1H), 1.95 (quint, *J* = 8.0 Hz, 2H) 1.05 – 1.02 (m, 2H), 0.94 – 0.90 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 82.7, 80.9, 45.8, 45.7, 31.3, 17.2, 16.2. HRMS (ESI) Calc'd for $C_8H_{11}ClO$ + Na: 214.1208, found: 214.1213.

<u>EWG-substituted cyclopropanes</u>

Ethyl 3-(1-hydroxycyclopropyl)propiolate (7b)



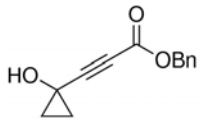
A

To a solution of the starting acetylene **A** (283 mg, 1.70 mmol) in THF (15 ml) was added a 2.30 M solution of *n*-butyllithium in hexane (0.74 ml, 1.70 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h followed by addition of ethyl chloroformate (0.18 ml, 1.87 mmol) at -

78 °C, and the reaction mixture was warmed to room temperature overnight during stirring. The reaction was quenched with saturated aqueous NH_4Cl (5 ml) and extracted with ether with ether (3 *times* 5 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 ml) and brine (10 ml), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was dissolved in MeOH (5 ml) followed by addition of *p*TsOH•H_2O (5 mg). The mixture was stirred for 30 min followed by concentrated in vacuo. The residue was then purified by flash chromatography (25% diethyl ether in petroleum ether, silica gel) to give **7b** as a colorless liquid (180 mg, 69%).

R*f* = 0.19 (25% ether in pet. ether). IR (neat): 3402, 2986, 2225, 1712, 1312, 1228, 1036 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.18 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.18 – 1.15 (m, 2H), 1.12 – 1.08 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.8, 90.5, 74.3, 62.0, 44.5, 18.0, 13.8. Spectral data matched that reported in the literature. [1]

Benzyl 3-(1-hydroxycyclopropyl)propiolate (7c)

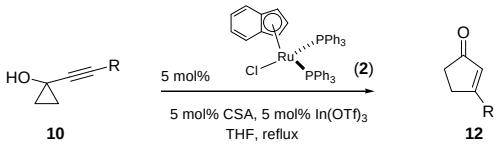


Cyclopropanol **7c** was prepared according to the general procedure using **A** (499 mg, 3.0 mmol), chlorobenzylformate (0.47 ml, 3.3 mmol), a 2.30 M solution of *n*-butyllithiumin hexane (1.30 ml, 3.0 mmol) and *p*TsOH•H_2O (5 mg). Reaction was conducted in THF (20 ml) for 15 h. Purification by flash chromatography (25% ether in petroleum ether) afforded **7c** (Yield: 480 mg, 74%) as a colorless oil.

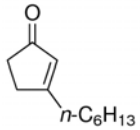
R*f* = 0.25 (25% ether in pet. ether). IR (neat): 3398, 3034, 2226, 1709, 1456, 1308, 1271, 1010, 748, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.25 (m, 5H), 4 (s, 2H), 3.67 (br s, 1H), 1.21 – 1.17 (m, 2H), 1.15 – 1.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.5, 134.6, 128.6, 128.5, 128.4, 127.0, 74.4, 67.6, 44.8, 18.2. HRMS (EI) Calc'd for $C_{13}H_{12}O_3$: 216.0786, found: 216.0784.

General procedure for the ruthenium-catalyzed ring expansion reactions

3-Hexylcyclopent-2-enone (12a)

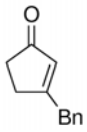


To a flame-dried flask charged with ruthenium catalyst **2** (23.3 mg, 0.03 mmol), $In(OTf)_3$ (16.9 mg, 0.03 mmol) and CSA (7.0 mg, 0.03 mmol) was added THF (2.0 ml). After the mixture was stirred for 10 min at room temperature, a solution of cyclopropanol **10a** (100 mg, 0.60 mmol) in THF (1.0 ml) was added. The solution was heated to reflux. After stirring for 4h at reflux, the solution was cooled to room temperature and concentrated in vacuo. Purification of the residue by flash chromatography (5 – 15% diethyl ether in petroleum ether, silica gel) gave **12a** as a liquid (78 mg, 78%).



R*f* = 0.45 (50% ether in pet. ether). IR (neat): 2929, 2858, 1710, 1616, 1438, 1183, 840 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.95 (quint, *J* = 1.5 Hz, 1H), 2.60 – 2.57 (m, 2H), 2.43 – 2.40 (m, 4H), 1.59 (m, 2H), 1.36 – 1.28 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.2, 183.3, 35.2, 33.4, 31.5, 31.4, 28.9, 27.0, 22.4, 14.0. Spectral data matched that reported in the literature.[1]

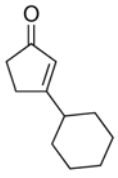
3-Benzylcyclopent-2-enone (12b)



Cyclopentenone **12b** was prepared according to the general procedure using ruthenium catalyst **2** (31.1 mg, 0.040 mol), $In(OTf)_3$ (22.5 mg, 0.040 mol), CSA (9.3 mg, 0.040 mmol) and **10b** (138 mg, 0.80 mmol). Reaction was conducted in THF (16 ml) at reflux for 6 h. Purification by flash chromatograph (50% ether in petroleum ether, silica gel) afforded **12b** (112 mg, 81%) as a colorless oil.

R*f* = 0.22 (50% ether in pet. ether). IR (neat): 3028, 2918, 1706, 1616, 1496, 1183, 758, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 7.19 – 7.16 (m, 2H), 5.89 (m, 1H), 3.71 (s, 2H), 2.57 – 2.54 (m, 2H), 2.40 – 2.38 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 209.8, 181.0, 136.7, 130.5, 128.8, 128.6, 126.8, 39.9, 35.4, 30.9. Spectral data matched that reported in the literature.[2]

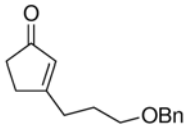
3-Cyclohexylcyclopent-2-enone (12c)



Cyclopentenone **12c** was prepared according to the general procedure using ruthenium catalyst **2** (31.1 mg, 0.040 mol), $In(OTf)_3$ (22.5 mg, 0.040 mol), CSA (9.3 mg, 0.040 mmol) and **10c** (134 mg, 0.80 mmol). Reaction was conducted in THF (16 ml) at reflux for 4 h. Purification by flash chromatograph (50% ether in petroleum ether, silica gel) afforded **12c** (115 mg, 88%) as a colorless oil.

R*f* = 0.25 (50% ether in pet. ether). IR (neat): 2927, 2854, 1712, 1609, 1449, 1185 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.87 (m, 1H), 2.56 (m, 2H), 2.34 (m, 2H), 2.29 – 2.23 (m, 1H), 1.88 – 1.83 (m, 2H), 1.79 – 1.75 (m, 2H), 1.70 – 1.66 (m, 1H), 1.34 – 1.14 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.4, 187.6, 127.8, 41.8, 34.9, 31.1, 29.5, 25.9, 25.8. Spectral data matched that reported in the literature.[2]

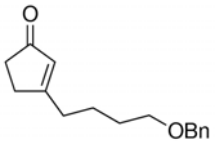
3-(3-(Benzyloxy)propyl)cyclopent-2-enone (12d)



Cyclopentenone **12d** was prepared according to the general procedure using ruthenium catalyst **2** (7.8 mg, 0.010 mol), $In(OTf)_3$ (5.6 mg, 0.010 mol), CSA (2.3 mg, 0.010 mmol) and **10d** (46 mg, 0.050 mmol). Reaction was conducted in THF (2 ml) at reflux for 2 h. Purification by flash chromatograph (50% ether in petroleum ether, silica gel) afforded **12d** (35 mg, 76%) as a colorless oil.

R*f* = 0.24 (50% ether in pet. ether). IR (neat): 2928, 2858, 1704, 1654, 1611, 1124 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.26 (m, 5H), 5.95 – 5.93 (m, 1H), 4.50 (s, 2H), 3.52 (t, *J* = 7.8 Hz, 2H), 2.59 – 2.56 (m, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.40 – 2.38 (m, 2H), 1.93 – 1.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.1, 182.5, 138.2, 129.4, 128.4, 127.7, 127.6, 73.0, 69.2, 35.2, 31.5, 30.3, 27.2. HRMS (ESI) Calc'd for $C_{15}H_{18}O_2$ + Na: 253.1204; found: 253.1206.

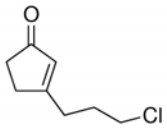
3-(4-(Benzyloxy)butyl)cyclopent-2-enone (12e)



Cyclopentenone **12e** was prepared according to the general procedure using ruthenium catalyst **2** (2.2 mg, 0.0028 mol), $In(OTf)_3$ (1.6 mg, 0.0028 mol), CSA (1.7 mg, 0.0073 mmol) and **10e** (35 mg, 0.014 mmol). Reaction was conducted in THF (2 ml) at reflux for 2 h. Purification by flash chromatograph (40% ether in petroleum ether, silica gel) afforded **12e** (23 mg, 68%) as a colorless oil.

R*f* = 0.28 (50% ether in pet. ether). IR (neat): 2931, 2858, 1708, 1671, 1616, 1279, 1114 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 5H), 5.96 – 5.94 (m, 1H), 4.50 (s, 2H), 3.50 (t, *J* = 7.5 Hz, 2H), 2.58 – 2.55 (m, 2H), 2.44 – 2.38 (m, 4H), 1.71 – 1.64 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.2, 182.8, 138.4, 129.5, 128.4, 127.6(2), 73.0, 69.7, 35.3, 33.3, 31.5, 29.4, 23.8. Spectra matched that reported in the literature.[3]

3-(3-Chloropropyl)cyclopent-2-enone (12f)

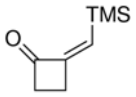


Cyclopentenone **12f** was prepared according to the general procedure using ruthenium catalyst **2** (12.2 mg, 0.0157 mol), $In(OTf)_3$ (8.9 mg, 0.0158 mol), CSA (3.7 mg, 0.0159 mmol) and **10f** (50 mg, 0.315 mmol). Reaction was conducted in THF (3 ml) at reflux for 2 h. Purification by flash chromatograph (50% ether in petroleum ether, silica gel) afforded **12f** (34 mg, 74%) as a colorless volatile oil.

R*f* = 0.30 (50% ether in pet. ether). IR (neat): 2947, 2918, 1710, 1681, 1617, 1441, 1185 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.96 (quint, *J* = 2.0 Hz, 1H), 3.58 (t, *J* = 8.0 Hz, 2H), 2.61 – 2.55 (m, 4H), 2.42 – 2.39 (m, 2H), 2.09 – 2.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 209.7, 180.8, 129.8, 44.0, 35.2, 31.6, 30.5, 29.7. Spectra matched that reported in the literature. [4]

Silyl substituted cyclobutanones

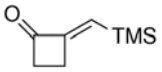
(*Z*)-2-((Trimethylsilyl)methylene)cyclobutanone (5a)



Cyclobutanone **5a** was prepared according to the general procedure using ruthenium catalyst **2** (31.0 mg, 0.040 mol), $In(OTf)_3$ (22.5 mg, 0.040 mol), CSA (9.3 mg, 0.040 mmol) and **4a** (123.4 mg, 0.80 mmol). Reaction was conducted in THF (16 ml) at reflux for 2 h, giving *Z*-**5a** (Yield: 102.4 mg, 83%) and *E*-**6a** (Yield: 18.5 mg, 15%) with a 5.7:1 *Z*/*E* ratio (Yield and *Z*/*E* ratio were determined by ^{1}H NMR of protons of the vinyl group on the cyclobutanone using mesitylene (12.2 mg, 0.10 mmol) as the internal standard). Purification by flash chromatograph (4% ether in petroleum ether, silica gel) afforded *Z*-**5a** and *E*-**6a** as colorless oils.

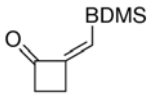
R*f* = 0.39 (5% ether in pet. ether). IR (neat): 2956, 1754, 1622, 1248, 1067, 850 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (t, *J* = 2.4 Hz, 1H), 2.89 – 2.86 (m, 2H), 2.62 – 2.58 (m, 2H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.3, 162.0, 138.0, 42.8, 24.3, -1.1. Spectral data matched that reported in the literature. [5]

(*E*)-2-((Trimethylsilyl)methylene)cyclobutanone (6a)



R*f* = 0.25 (5% ether in pet. ether). IR (neat): 2957, 1766, 1628, 1250, 1077, 853 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.37 (t, *J* = 2.9 Hz, 1H), 2.99 (m, 2H), 2.71 (m, 2H), 0.17 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.6, 161.4, 130.4, 44.6, 24.0, -1.2. Spectral data matched that reported in the literature. [5]

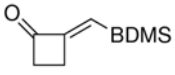
(*Z*)-2-((Benzyldimethylsilyl)methylene)cyclobutanone (5b)



Cyclobutanone **5b** was prepared according to the general procedure using ruthenium catalyst **2** (17.5 mg, 0.0225 mol), $In(OTf)_3$ (12.6 mg, 0.0225 mol), CSA (5.2 mg, 0.0225 mmol) and **4b** (104 mg, 0.45 mmol). Reaction was conducted in THF (9 ml) at reflux for 4 h, giving *Z*-**5b** (Yield: 80 mg, 77%) and *E*-**6b** (Yield: 13 mg, 12.5%) with a 6.0:1 *Z*/*E* ratio (Yield and *Z*/*E* ratio were determined by ^{1}H NMR of protons of the vinyl group on the cyclobutanone using mesitylene (15.2 mg, 0.182 mmol) as the internal standard). Purification by flash chromatography (5% ether in petroleum ether, silica gel) afforded *Z*-**5b** and *E*-**6b** as colorless oils.

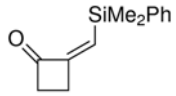
R*f* = 0.61 (10% ether in pet. ether). IR (neat): 2956, 1751, 1600, 1493, 1248, 1057, 846, 670 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 – 7.20 (m, 2H), 7.10 – 7.06 (m, 1H), 7.03 – 7.01 (m, 2H), 5.92 (t, *J* = 2.5 Hz, 1H), 2.93 – 2.89 (m, 2H), 2.64 – 2.60 (m, 2H), 2.28 (s, 2H), 0.16 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.3, 162.8, 139.6, 135.8, 128.2, 128.1, 124.1, 42.9, 25.3, 24.4, -3.1. HRMS (EI) Calc'd for $C_{14}H_{18}OSi$: 203.1127, found: 230.1131.

(*E*)-2-((benzyldimethylsilyl)methylene)cyclobutanone (6b)



R*f* = 0.46 (10% ether in pet. ether). IR (neat): 2957, 1762, 1600, 1493, 1250, 1078, 847, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 – 7.20 (m, 2H), 7.11 – 7.07 (m, 1H), 7.00 – 6.98 (m, 2H), 6.34 (t, *J* = 2.9 Hz, 1H), 2.96 – 2.92 (m, 2H), 2.50 – 2.46 (m, 2H), 2.20 (s, 2H), 0.15 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.3, 162.7, 138.8, 128.3, 128.2, 124.4, 44.6, 25.6, 24.0, -3.2. HRMS (EI) Calc'd for $C_{14}H_{18}OSi$: 203.1127, found: 230.1128.

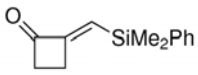
(*Z*)-2-((Dimethyl(phenyl)silyl)methylene)cyclobutanone (5c)



Cyclobutanone **5c** was prepared according to the general procedure using ruthenium catalyst **2** (50.4 mg, 0.065 mol), $In(OTf)_3$ (36.5 mg, 0.065 mol), CSA (15.1 mg, 0.065 mmol) and **4c** (281 mg, 1.30 mmol). Reaction was conducted in THF (26 ml) at reflux for 2 h, giving *Z*-**5c** (Yield: 230 mg, 82%) and *E*-**6c** (Yield: 40 mg, 14%) with a 6.0:1 *Z*/*E* ratio (Yield and *Z*/*E* ratio were determined by ^{1}H NMR of protons of the vinyl group on the cyclobutanone using mesitylene (14.5 mg, 0.121 mmol) as the internal standard). Purification by flash chromatography (5–10% ether in petroleum ether, silica gel) afforded *Z*-**5c** and *E*-**6c** as colorless oils.

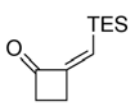
R*f* = 0.29 (5% ether in pet. ether). IR (neat): 2958, 1753, 1622, 1428, 1271, 1062, 843 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 2H), 7.39 – 7.37 (m, 3H), 6.09 (t, *J* = 2.5 Hz, 1H), 2.93 – 2.90 (m, 2H), 2.68 – 2.64 (m, 2H), 0.51 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.0, 163.0, 138.1, 135.6, 133.6, 129.1, 127.8, 42.9, 24.5, -2.5. HRMS (EI) Calc'd for $C_{13}H_{16}OSi$ - H: 215.0892, found: 215.0899.

(*E*)-2-((dimethyl(phenyl)silyl)methylene)cyclobutanone (6c)



R*f* = 0.13 (5% ether in pet. ether). IR (neat): 3070, 2958, 1763, 1627, 1428, 1250, 1082, 843, 733, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.52 (m, 2H), 7.40 – 7.37 (m, 3H), 6.50 (t, *J* = 2.8 Hz, 1H), 2.97 (t, *J* = 8.2 Hz, 2H), 2.56 (t, J_1 = 8.2 Hz, J_2 = 2.8 Hz, 2H), 0.45 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.4, 162.7, 136.8, 133.7, 129.5, 128.1, 128.0, 44.7, 24.1, -2.5. HRMS (EI) Calc'd for $C_{13}H_{16}OSi$ - H: 215.0892, found $[M-H]^+$: 215.0899.

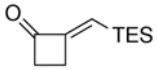
(*Z*)-2-(Triethylsilylmethylene)cyclobutanone (5d)



5d was prepared according to the general procedure of the ruthenium-catalyzed ring expansion reaction starting from **4d** (196.4 mg, 1.00 mmol). *Z*/*E* = 10 : 1 (crude NMR). NMR yield: *Z*-**5d**: 172.8 mg (88%), *E*-**6d**: 17.7 mg (9%). Isolated yield of *Z*-**5d**: 150 mg (76%).

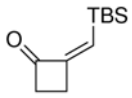
R*f* = 0.50 (5% ether in pet. ether). IR (neat): 2954, 2875, 1756, 1273, 1062, 742 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (t, *J* = 2.4 Hz, 1H), 2.88 – 2.84 (m, 2H), 2.63 – 2.59 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.69 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.2, 163.1, 135.0, 42.7, 24.5, 7.4, 3.5. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$ - C_2H_5 (Et): 167.0892, found: 167.0891.

(*E*)-2-(triethylsilylmethylene)cyclobutanone (6d)



R*f* = 0.33 (5% ether in pet. ether). IR (neat): 2955, 1762, 1646, 1078 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (t, *J* = 2.8 Hz, 1H), 3.01 – 2.98 (m, 2H), 2.73 – 2.69 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.3, 162.5, 128.3, 44.5, 24.3, 7.3, 3.4. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$: 196.1283, found: 196.1287.

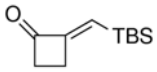
(*Z*)-2-((*tert*-Butyldimethylsilyl)methylene)cyclobutanone (5e)



Cyclobutanone **5e** was prepared according to the general procedure using ruthenium catalyst **2** (31.1 mg, 0.040 mol), $In(OTf)_3$ (22.5 mg, 0.040 mol), CSA (9.3 mg, 0.040 mmol) and **4e** (157 mg, 0.80 mmol). Reaction was conducted in THF (16 ml) at reflux for 2 h, giving *Z*-**5e** (Yield: 141.3 mg, 90%) and *E*-**6e** (Yield: 12.6 mg, 8%) with a 11.4:1 *Z*/*E* ratio (Yield and *Z*/*E* ratio were determined by ^{1}H NMR of protons of the vinyl group on the cyclobutanone using mesitylene (14.0 mg, 0.117 mmol) as the internal standard). Purification by flash chromatography (5% ether in petroleum ether, silica gel) afforded *Z*-**5e** and *E*-**6e** as colorless oils.

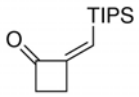
R*f* = 0.31 (5% ether in pet. ether). IR (neat): 2953, 2857, 1755, 1470, 1249, 1061, 845 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (t, *J* = 2.4 Hz, 1H), 2.87 – 2.83 (m, 2H), 2.63 – 2.59 (m, 2H), 0.88 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.0, 163.2, 135.6, 42.7, 26.2, 24.5, 16.9, -5.7. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$ - C_4H_9 (*t*-Bu): 139.0579, found: 139.0565.

(*E*)-2-((*tert*-butyldimethylsilyl)methylene)cyclobutanone (6e)



R*f* = 0.19 (5% ether in pet. ether). IR (neat): 2953, 2857, 1764, 1471, 1250, 1078, 842 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.42 (t, *J* = 2.9 Hz, 1H), 3.01 – 2.98 (m, 2H), 2.74 – 2.70 (m, 2H), 0.91 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.4, 162.6, 128.6, 44.6, 26.2, 24.4, 17.2, -5.7. HRMS (EI) Calc'd for $C_{11}H_{20}OSi$: 196.1283, found: 196.1280.

(*Z*)-2-((Triisopropylsilyl)methylene)cyclobutanone (5f)



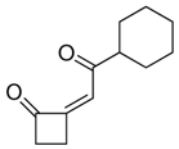
Cyclobutanone **5f** was prepared according to the general procedure using ruthenium catalyst **2** (15.5 mg, 0.020 mol), $In(OTf)_3$ (11.3 mg, 0.020 mol), CSA (4.7 mg, 0.020 mmol) and **4f** (95.4 mg, 0.40 mmol). Reaction was conducted in THF (8 ml) at reflux for 2 h, giving *Z*-**5f** (Yield: 85.9 mg, 90%) only (determined by ^{1}H NMR of protons of the vinyl group on the cyclobutanone using mesitylene (12.6 mg, 0.105 mmol) as the internal standard). Purification by flash chromatograph (3% ether in petroleum ether, silica gel) afforded *Z*-**5f** (83 mg, 87%) as a colorless oil.

R*f* = 0.50 (5% ether in pet. ether). IR (neat): 2940, 2869, 1752, 1624, 1463, 1274, 1058, 882 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86 (t, *J* = 2.5 Hz, 1H), 2.88 – 2.84 (m, 2H), 2.67 – 2.63 (m, 2H), 1.33 (quint, *J* = 7.5 Hz, 3H), 1.02 (d, *J* = 7.5 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.0, 163.9, 133.8, 42.6, 24.9, 18.7, 11.5. HRMS (EI) Calc'd for $C_{14}H_{26}OSi$: 238.1753, found: 238.1753.

EWG-substituted cyclobutanones

NB: Only one olefin geometry was observed in these reactions, and it was assigned based on the chemical shift of the vinyl proton by comparing with analogous silyl and alkyl substituted cyclobutanones.

(*Z*)-2-(2-Cyclohexyl-2-oxoethylidene)cyclobutanone (8a)

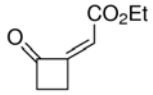


Cyclobutanone **8a** was prepared according to the general procedure using ruthenium catalyst **2** (15.5 mg, 0.020 mmol), $In(OTf)_3$ (11.2 mg, 0.020 mmol), CSA (4.6 mg, 0.020 mmol) and **7a** (76.9 mg, 0.40 mmol). Reaction was conducted in THF (8 ml) at reflux for 12 h. Purification

by flash chromatograph (20% ether in petroleum ether, silica gel) afforded *Z*-**8a** (Yield: 68 mg, 88%) as a colorless oil (The configuration was assigned based on ^{1}H NMR of protons of the vinyl group).

R*f* = 0.75 (50% ether in pet. Ether). IR (neat): 2931, 2855, 1764, 1693, 1450, 1336, 1109, 1012 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (t, *J* = 3.0 Hz, 1H), 3.16 – 3.11 (m, 2H), 3.05 – 2.99 (m, 2H), 2.51 – 2.44 (m, 1H), 1.86 – 1.82 (m, 2H), 1.79 – 1.74 (m, 2H), 1.68 – 1.64 (m, 1H), 1.36 – 1.15 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 203.9, 200.5, 159.4, 117.7, 51.6, 46.7, 27.9, 25.7, 25.4, 24.7. HRMS (EI) Calc'd for $C_{12}H_{16}O_2$: 192.1150, found: 192.1155.

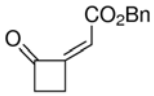
(*Z*)-Ethyl 2-(2-oxocyclobutylidene)acetate (8b)



Cyclobutanone **8b** was prepared according to the general procedure using ruthenium catalyst **2** (27.2 mg, 0.035 mmol), $In(OTf)_3$ (19.7 mg, 0.035 mmol), CSA (8.1 mg, 0.035 mmol) and **7b** (108 mg, 0.70 mmol). Reaction was conducted in THF (14 ml) at reflux for 8 h. Purification by flash chromatograph (15% ether in petroleum ether, silica gel) afforded *Z*-**8b** (Yield: 73 mg, 68%) as a colorless oil (The configuration was assigned based on ^{1}H NMR of protons of the vinyl group).

R*f* = 0.48 (25% ether in pet. ether). IR (neat): 2984, 1769, 1716, 1659, 1330, 1201, 1096, 875 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.19 (t, *J* = 3.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.14 – 3.10 (m, 2H), 3.06 – 3.02 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8, 165.2, 161.9, 114.4, 61.0, 45.9, 24.3 14.1. HRMS (EI) Calc'd for $C_8H_{10}O_3$: 154.0630, found: 154.0635.

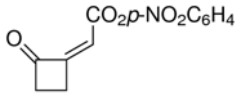
(*Z*)-Benzyl 2-(2-oxocyclobutylidene)acetate (8c)



Cyclobutanone **8c** was prepared according to the general procedure using ruthenium catalyst **2** (19.4 mg, 0.025 mmol), $In(OTf)_3$ (14.1 mg, 0.025 mmol), CSA (5.8 mg, 0.025 mmol) and **7c** (108 mg, 0.50 mmol). Reaction was conducted in THF (10 ml) at reflux for 6 h. Purification by flash chromatograph (20% ether in petroleum ether, silica gel) afforded *Z*-**8c** (Yield: 88 mg, 81%) as a colorless oil (The configuration was assigned based on ^{1}H NMR of protons of the vinyl group).

R*f* = 0.43 (25% ether in pet. Ether). IR (neat): 3034, 2945, 1767, 1715, 1660, 1455, 1329, 1269, 1168, 1095, 1017, 876, 746, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.35 (m, 5H), 6.26 (t, *J* = 2.8 Hz, 1H), 7 (s, 2H), 3.16 – 3.11 (m, 2H), 3.08 – 3.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.6, 165.0, 162.4, 135.3, 128.6, 128.4, 128.3, 114.1, 66.8, 45.9, 24.4. HRMS (EI) Calc'd for $C_{13}H_{12}O_3$: 216. 0786, found: 216.0792.

(*Z*)-4-Nitrophenyl 2-(2-oxocyclobutylidene)acetate (8d)



Cyclobutanone **8d** was prepared according to the general procedure using ruthenium catalyst **2** (15.5 mg, 0.020 mmol), $In(OTf)_3$ (11.2 mg, 0.020 mmol), CSA (4.6 mg, 0.020 mmol) and **7d** (98.9 mg, 0.40 mmol). Reaction was conducted in THF (8 ml) at reflux for 12 h. Purification by flash chromatograph (25% ether in petroleum ether, silica gel) afforded *Z*-**8d** (Yield: 84 mg, 85%) as a white solid (The configuration was assigned based on ^{1}H NMR of protons of the vinyl group).

Isolated yield: 84 mg (85%). M.P.: 95 – 97 °C.

R*f* = 0.62 (50% ether in pet. Ether). IR (neat): 1764, 1732, 1612, 1520, 1349, 1148, 858, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (m, 2H), 7.36 (m, 2H), 6.45 (t, *J* = 3.0 Hz, 1H), 3.28 – 3.23 (m, 2H), 3.20 – 3.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.8, 165.4, 162.5, 154.8, 145.5, 125.3, 122.2, 112.6, 46.3, 24.8. Elemental Analysis Calc'd for $C_{12}H_9NO_5$: C, 58.30; H, 3.67; N, 5.67; found: C, 58.50; H, 4.00; N, 5.84. HRMS(EI) Calc'd for $C_{12}H_9NO_5$: 247.0481; found: 247.0484.

References

1. Iwasawa, N.; Matsuo, T.; Iwamoto, M.; Ikeno, T. *J. Am. Chem. Soc.* **1998**, *120*, 3903-3914.
2. Collins, S.; Hong, Y.; Kataoka, M. *J. Org. Chem.* **1990**, *55*, 3395-3398.
3. Moritani, Y.; Yasunori, A.; Appella, D. H.; Jurkauskas, V.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 6797-6798.
4. Laroche, C.; Bertus, P.; Szymoniak, J. *Chem. Commun.* **2005**, *24*, 3030-3032.
5. Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708-9709.

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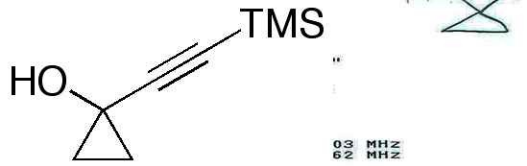

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62 MHz

5.19a

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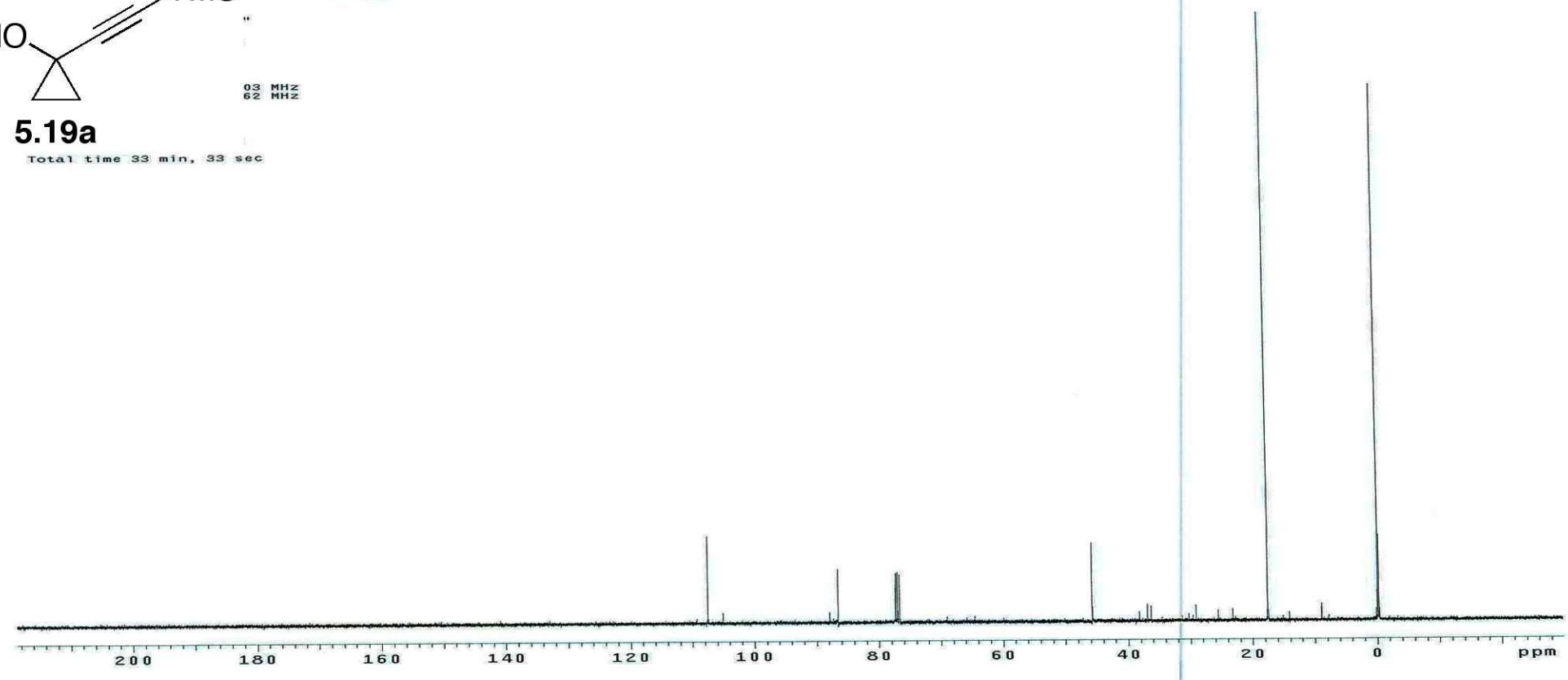

JX-XV-05

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Ambient temperature
Mercury-400BB "merc400"

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8 repetitions
OBSERVE H1, 400.1115370 MHz
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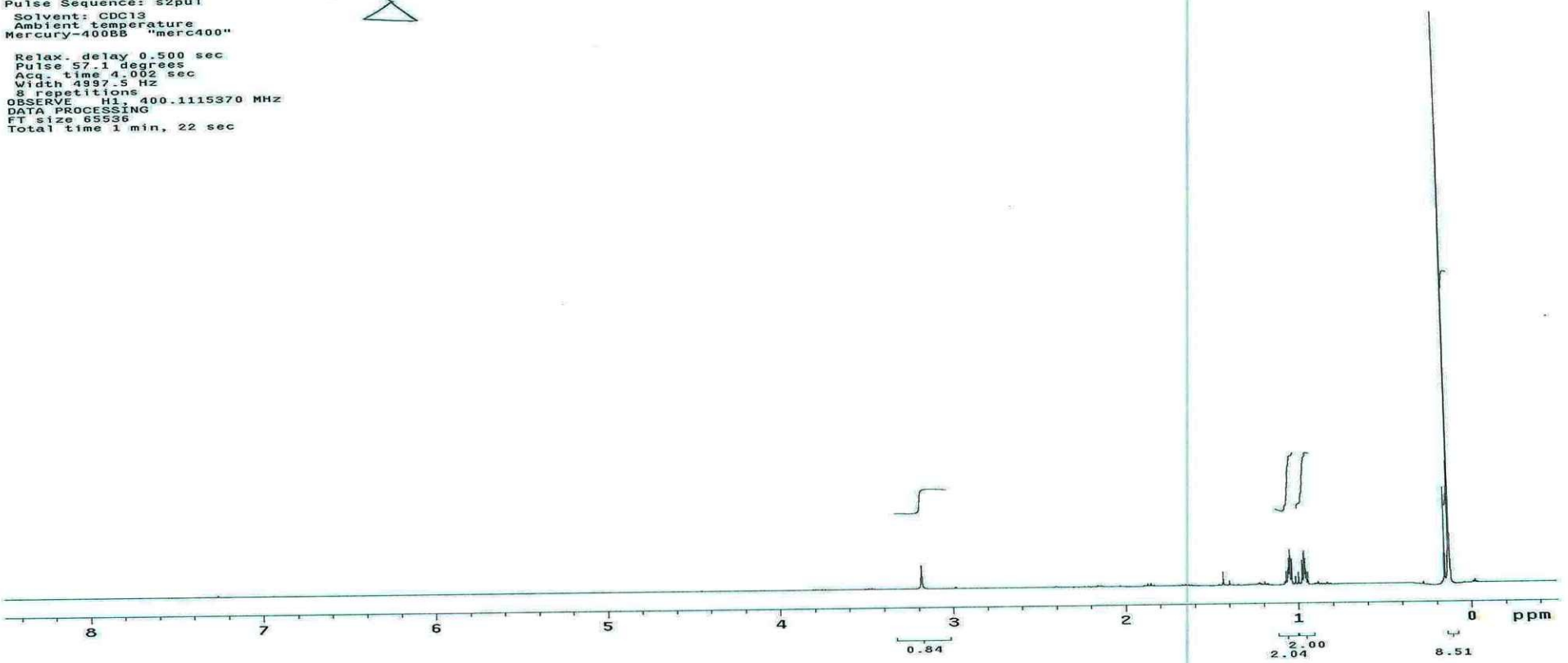
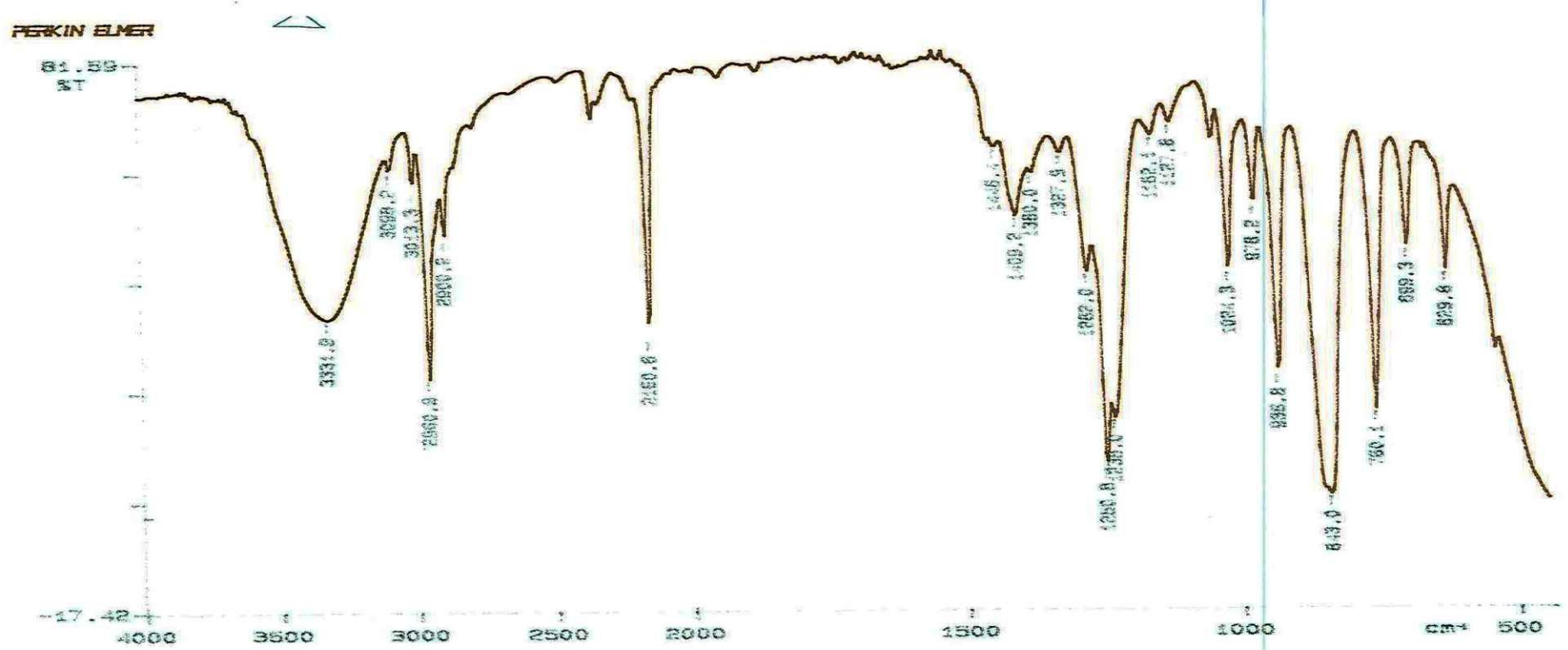
Total time 1 min, 22 sec





06/07/31 07:28
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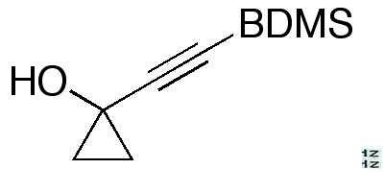
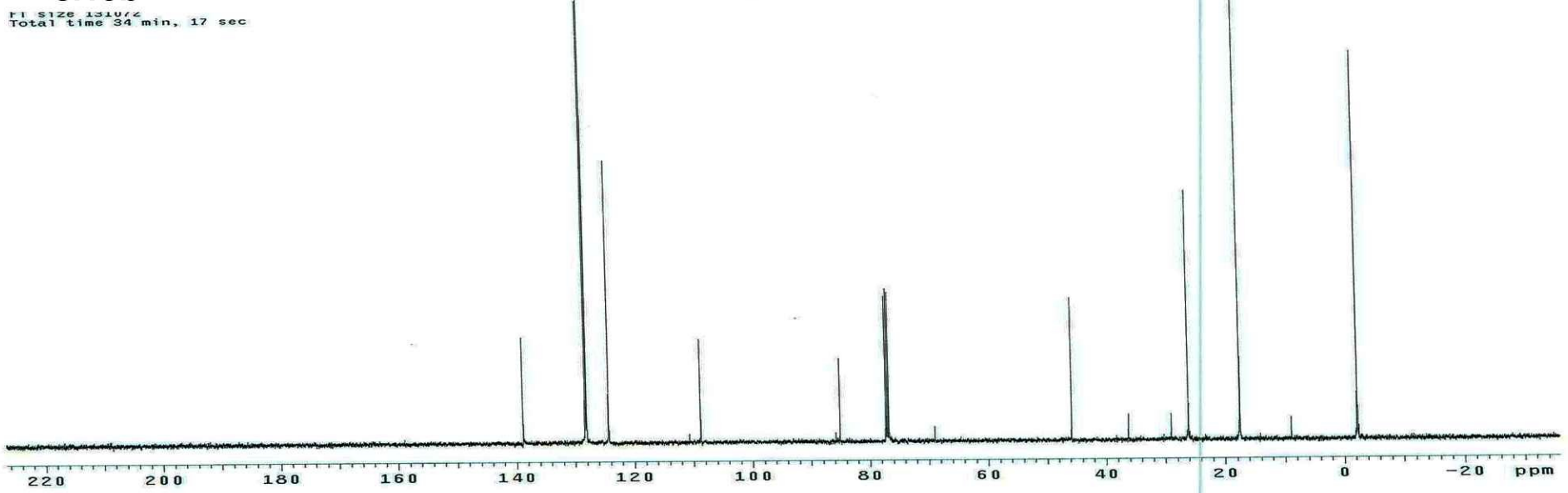


5.19b



JX-XV-78

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
12 repetitions
OBSERVE H1, 499.7485939 MHz
DATA PROCESSING
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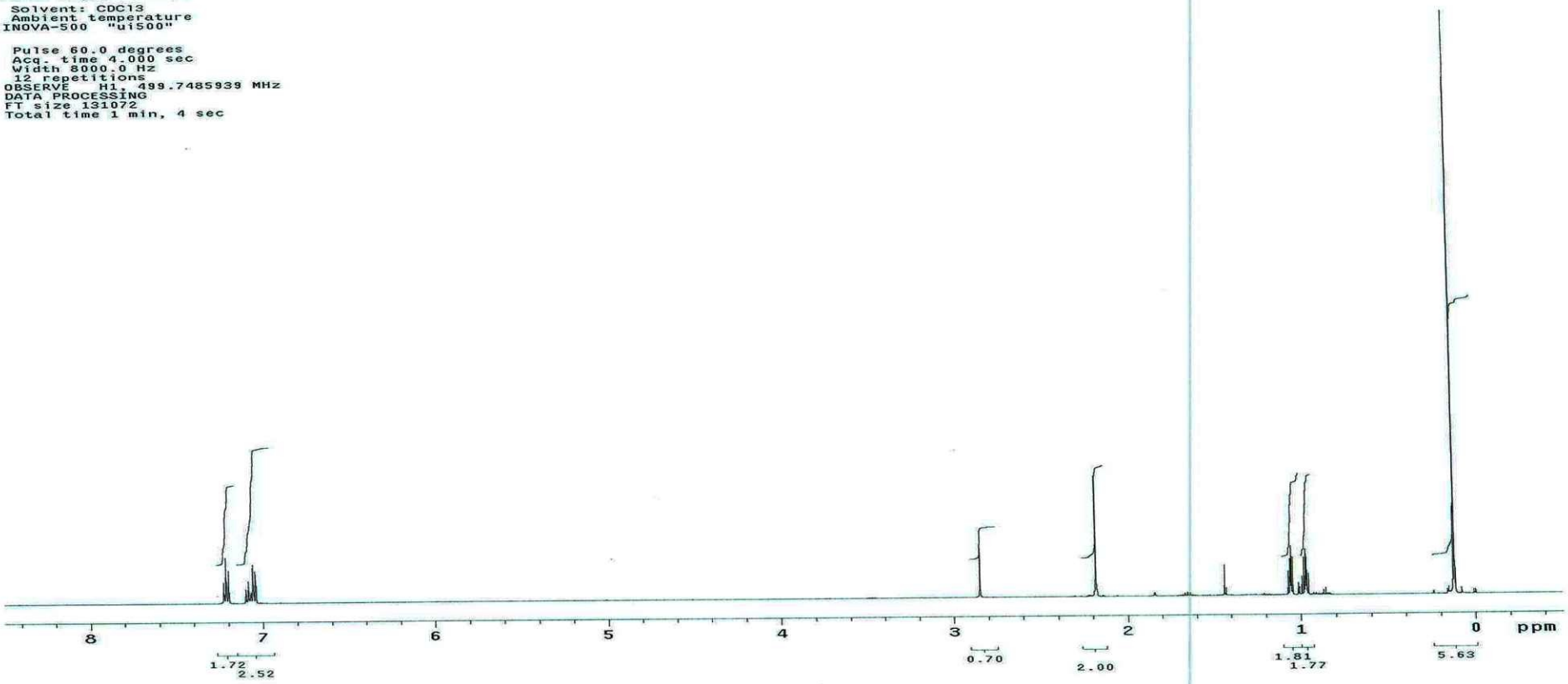
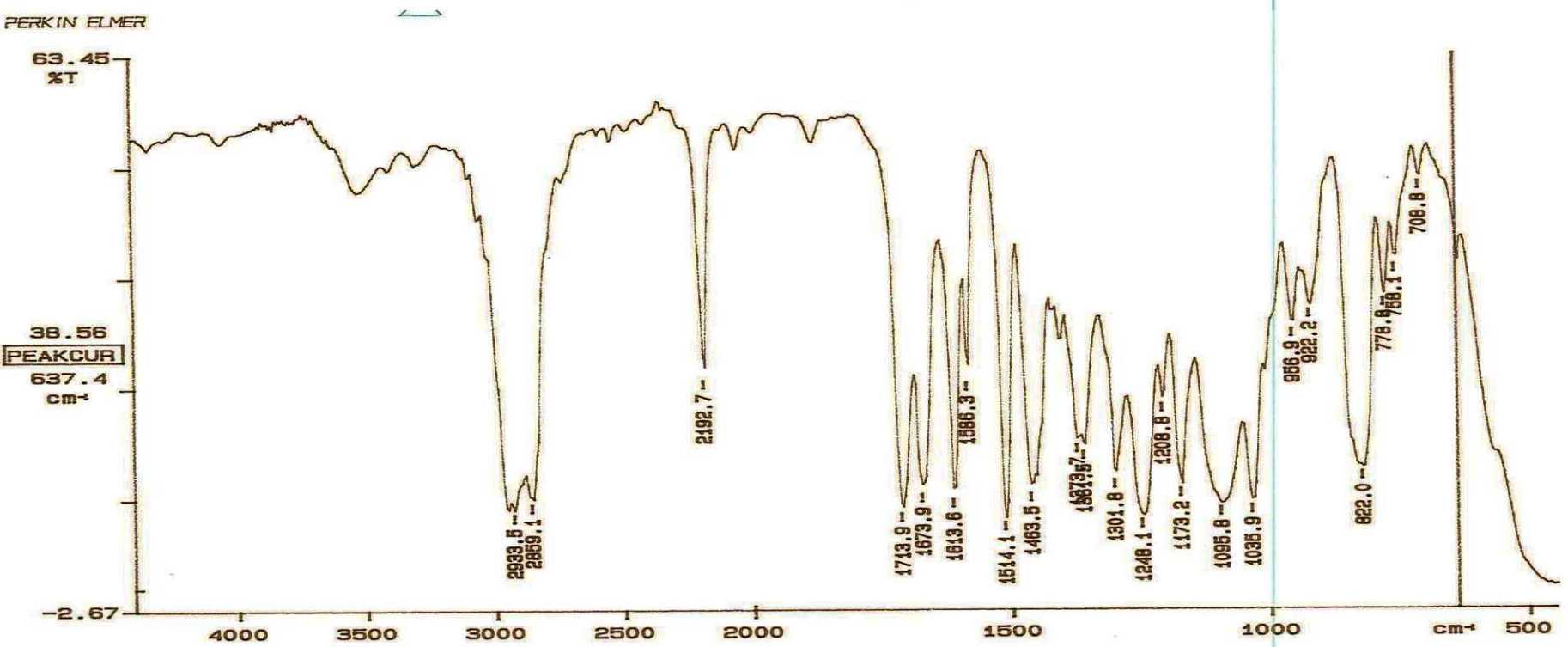
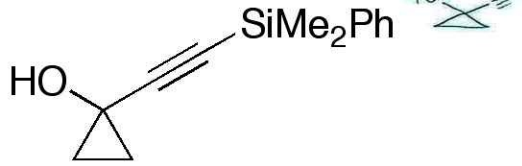
Total time 1 min, 4 sec



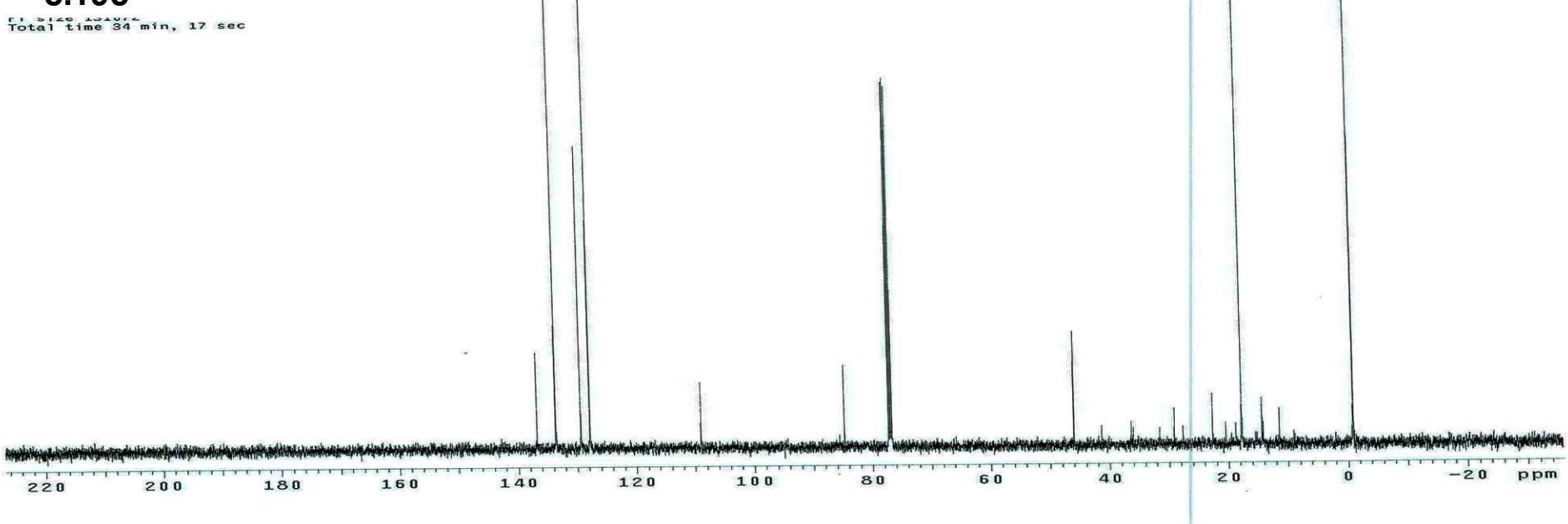


06/10/10 16:07
X: 4 scans, 4.0cm-1, flat



5.19c

Total time 34 min, 17 sec



JX-XV-11

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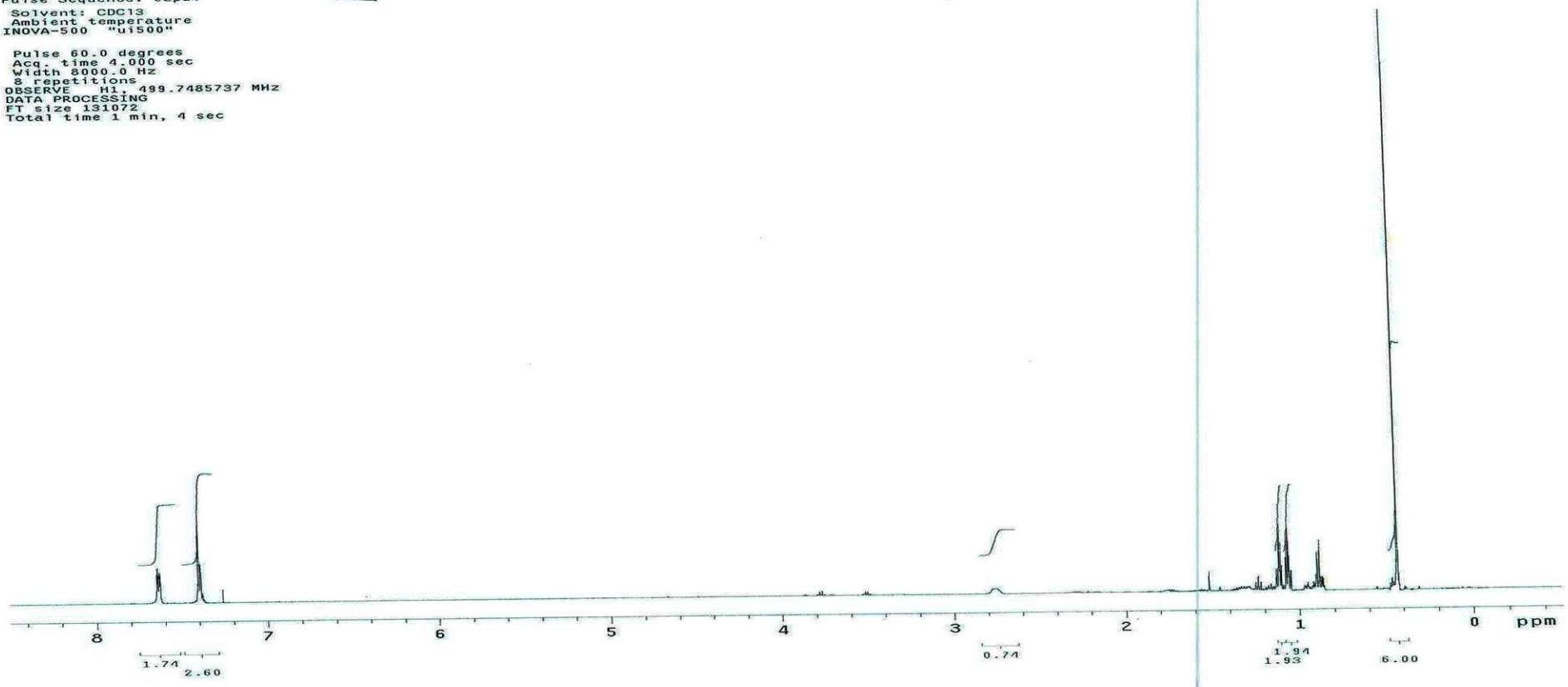
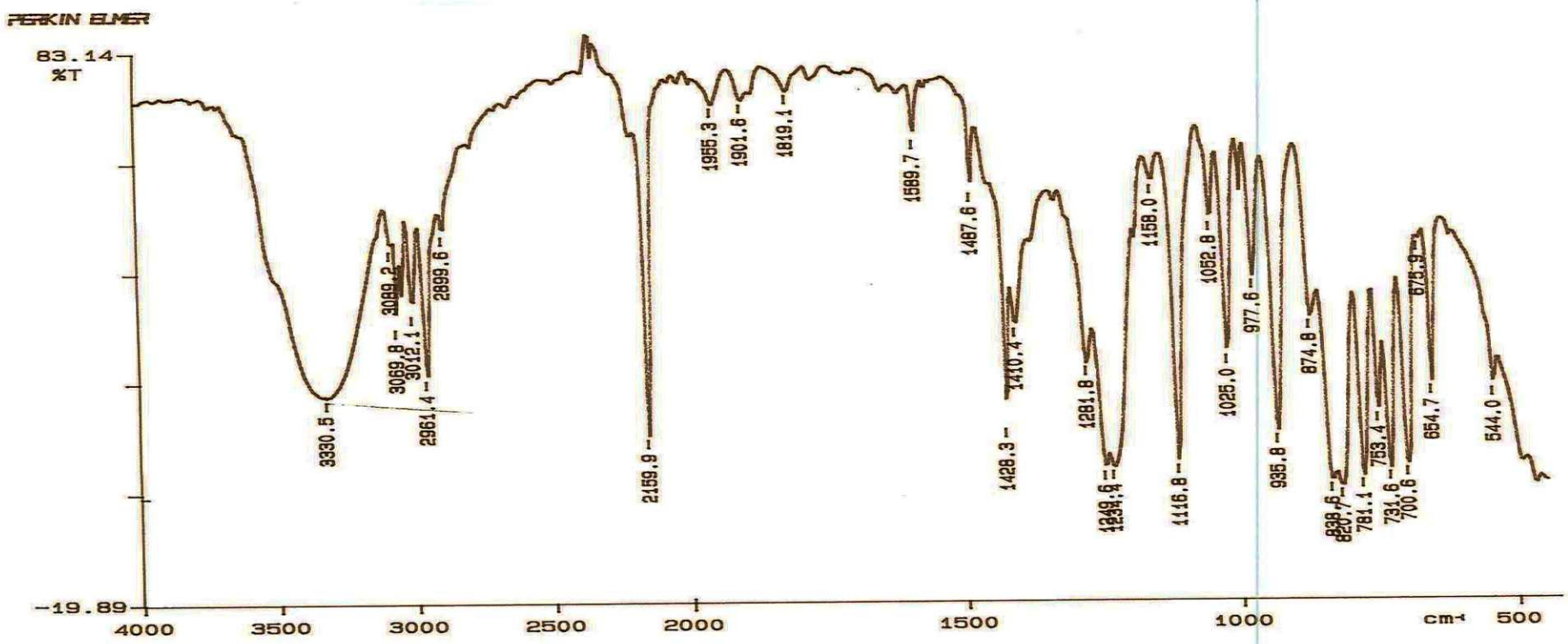
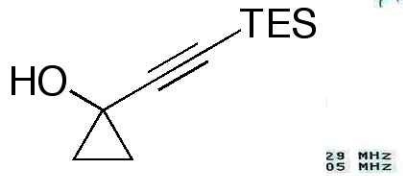
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec





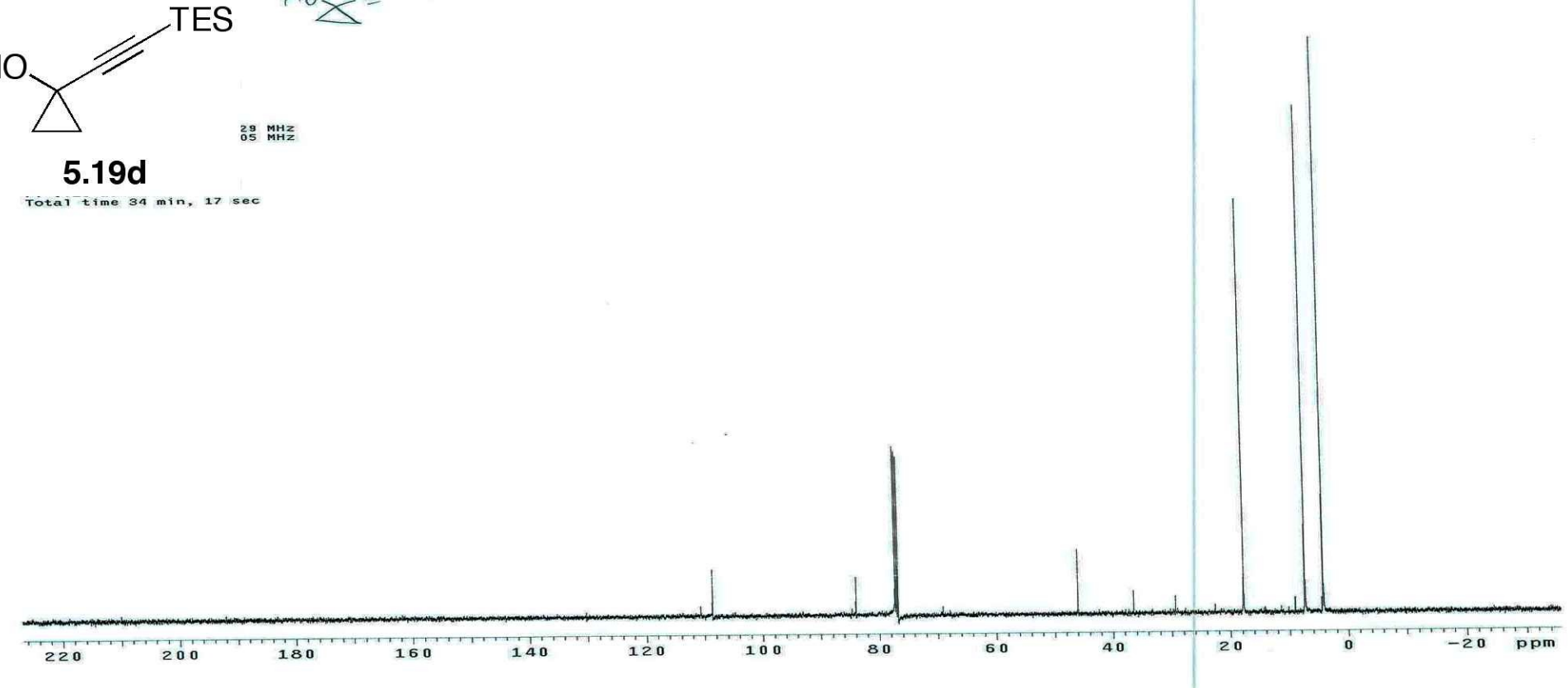
06/08/01 09:02
X: 4 scans. 4.0cm-1



29 MHz
05 MHz

5.19d

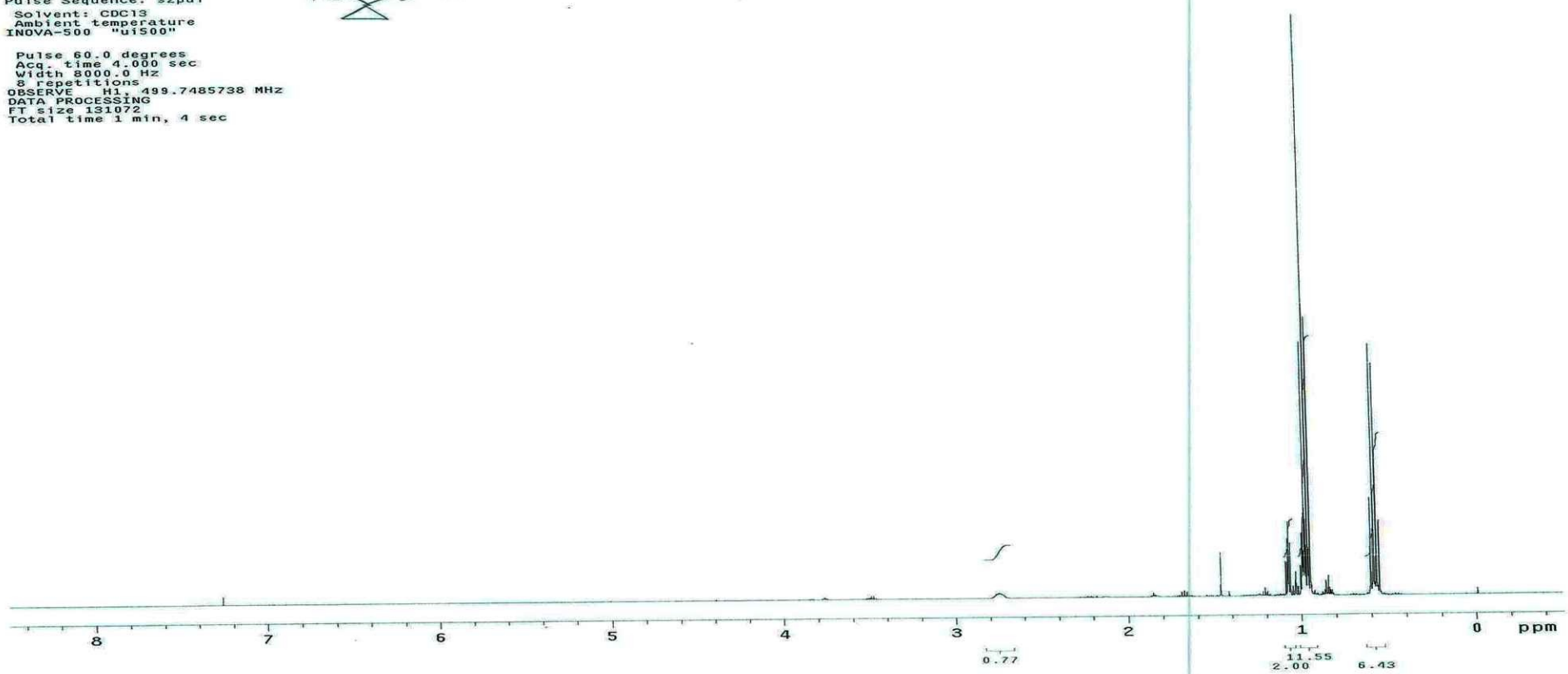
Total time 34 min, 17 sec

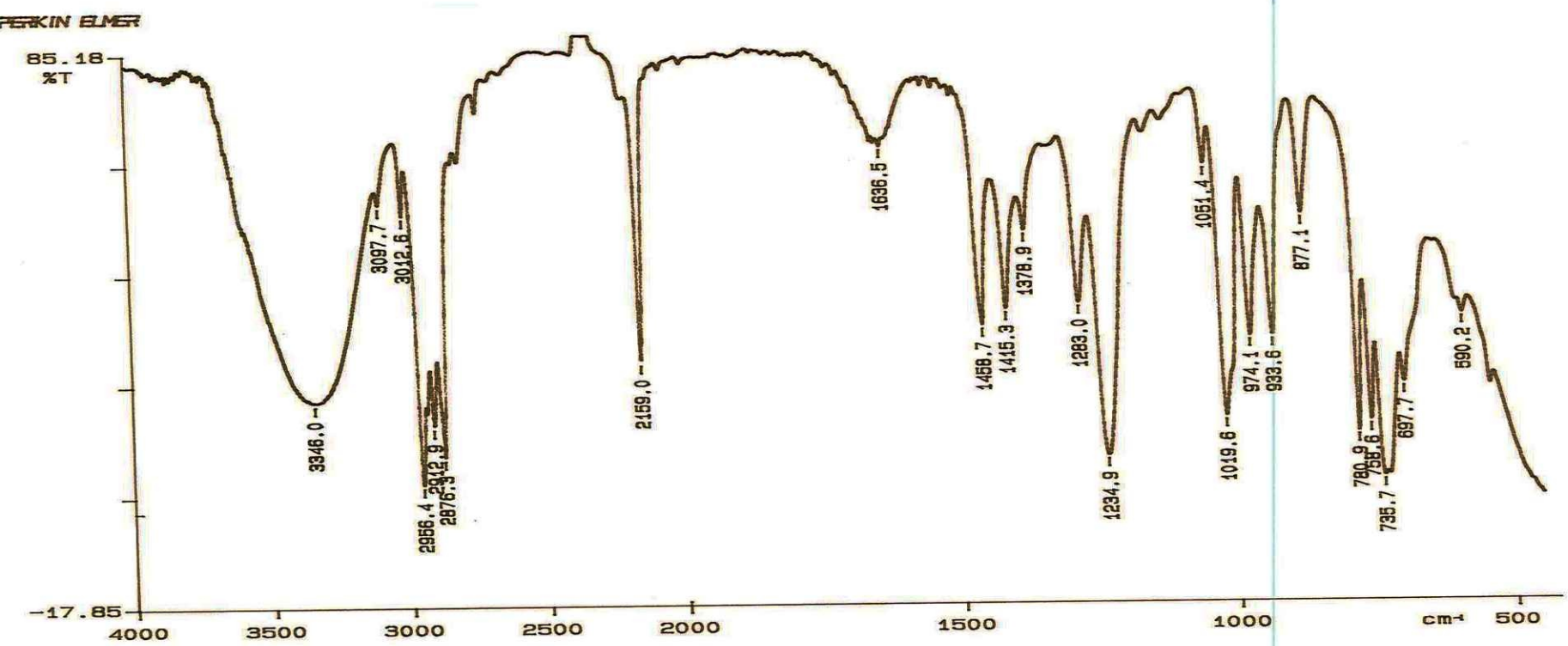


JX-XV-10

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec





06/08/01 08:54
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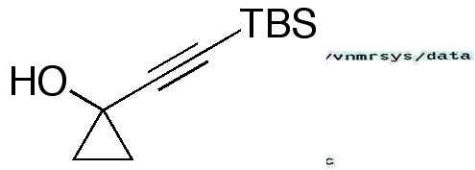

/vnmrsys/data

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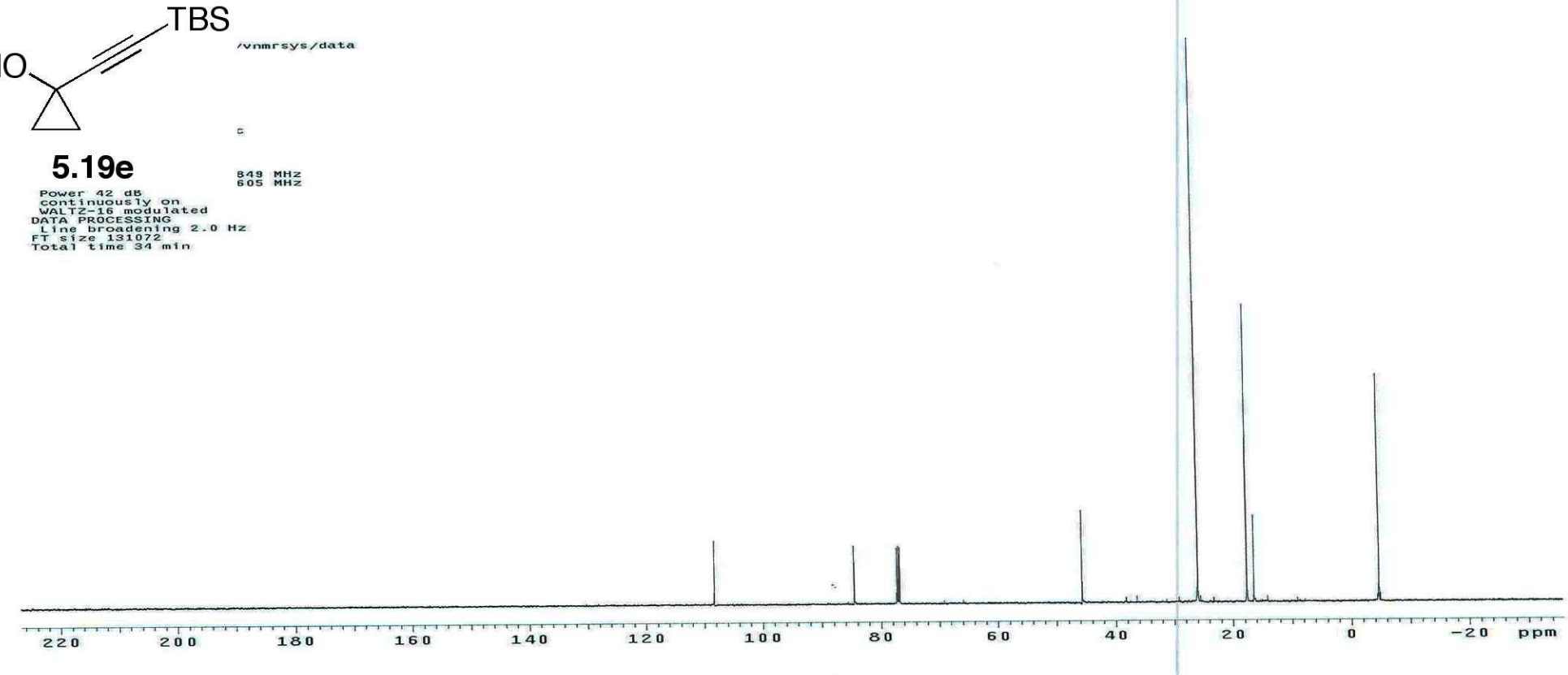
5.19e

849 MHz
605 MHz

Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min



JX-XV-24

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Sample directory:

File: JX-XV-24-H

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
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Width 8000.0 Hz
4 repetitions
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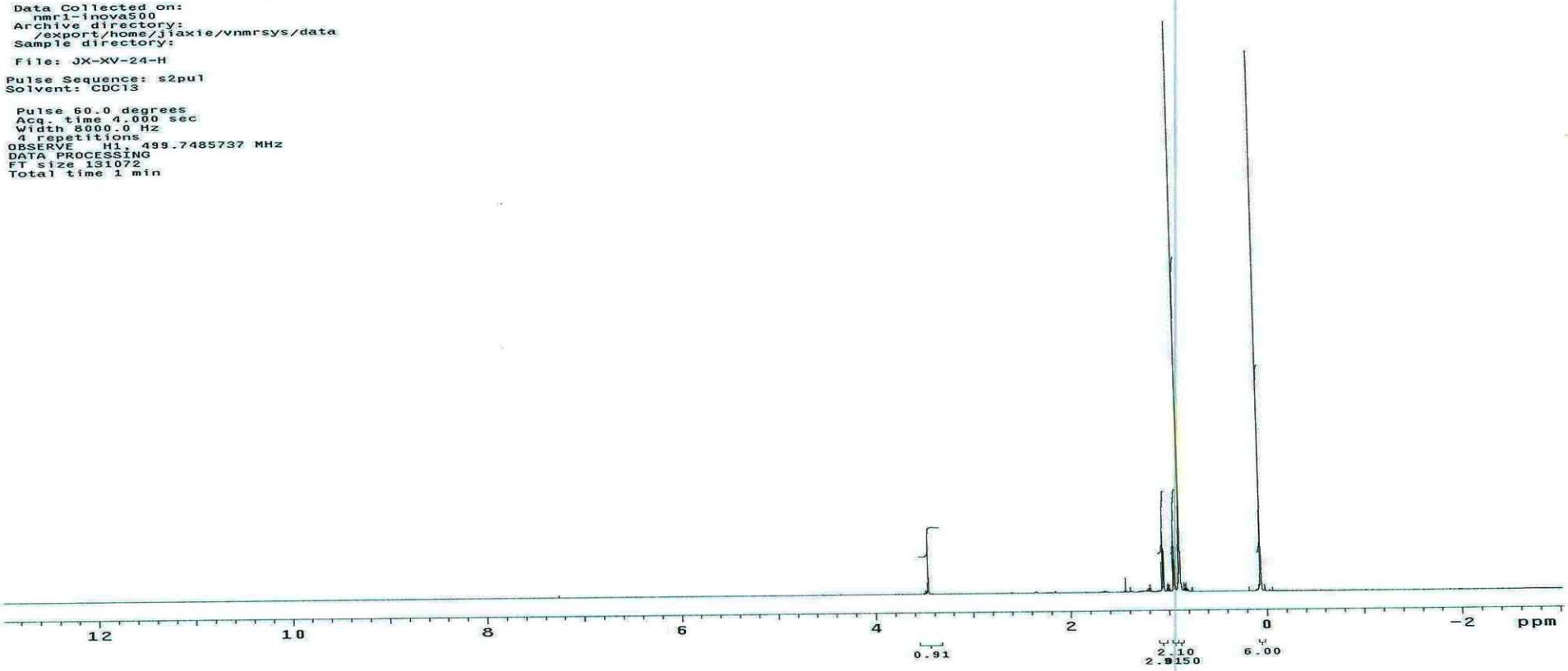
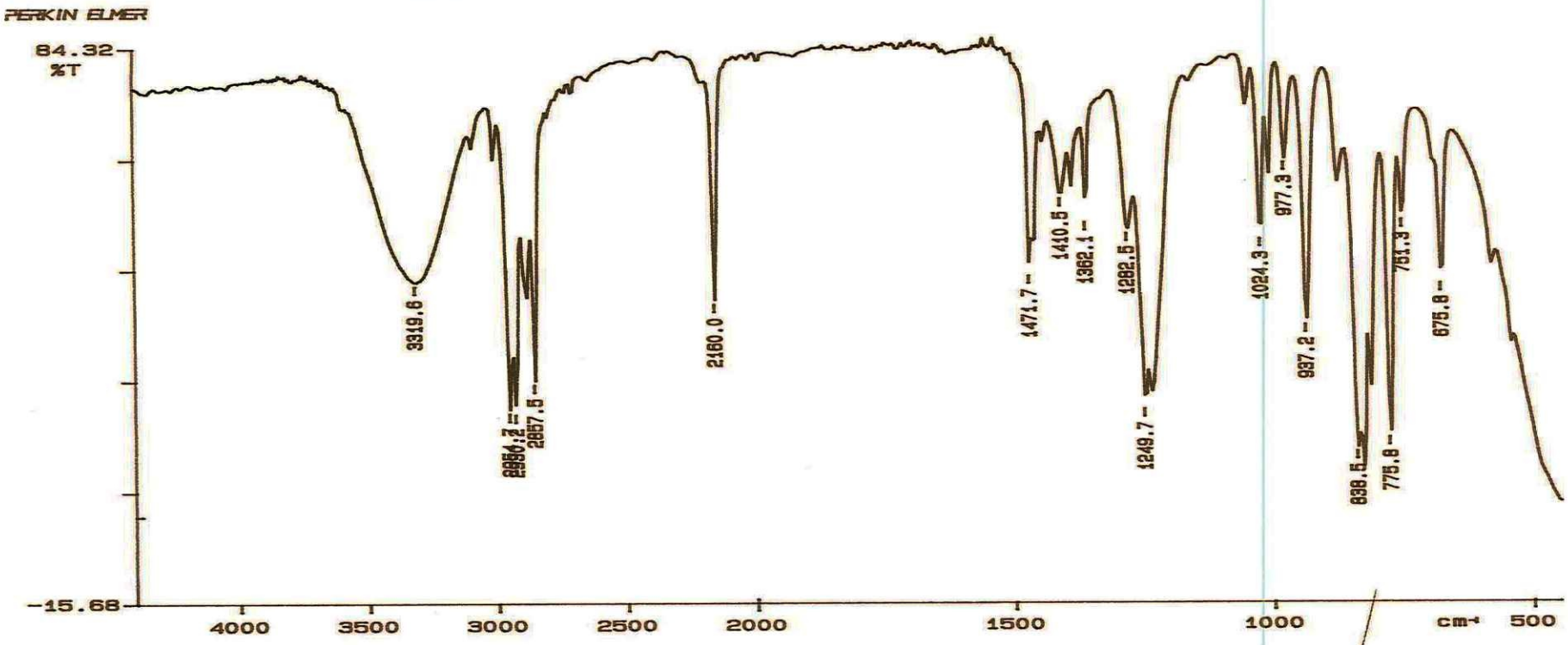
DATA PROCESSING
FT size 131072
Total time 1 min





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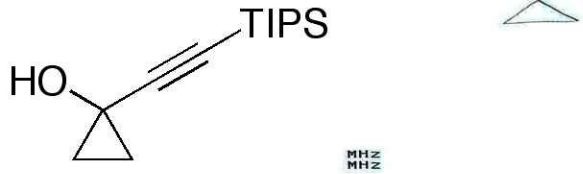
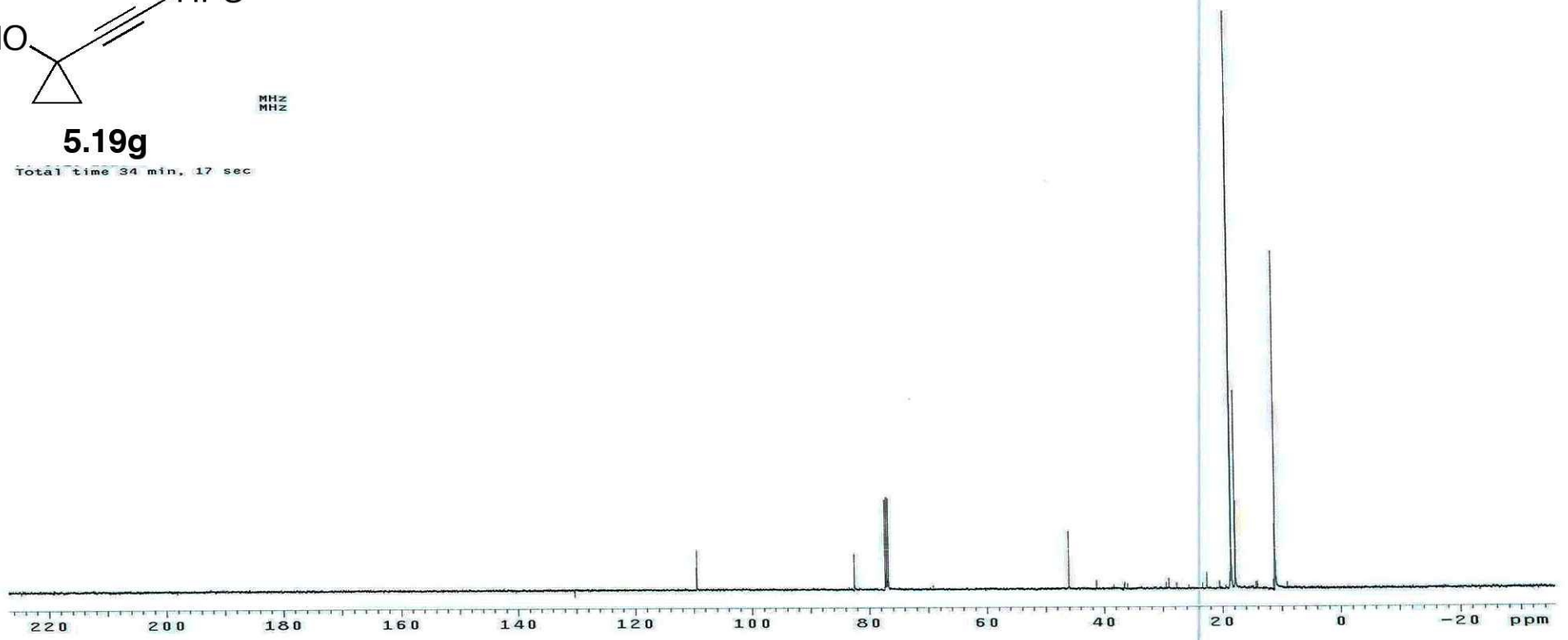


MHz
MHz

5.19g

Total time 34 min, 17 sec



JA-XV-14

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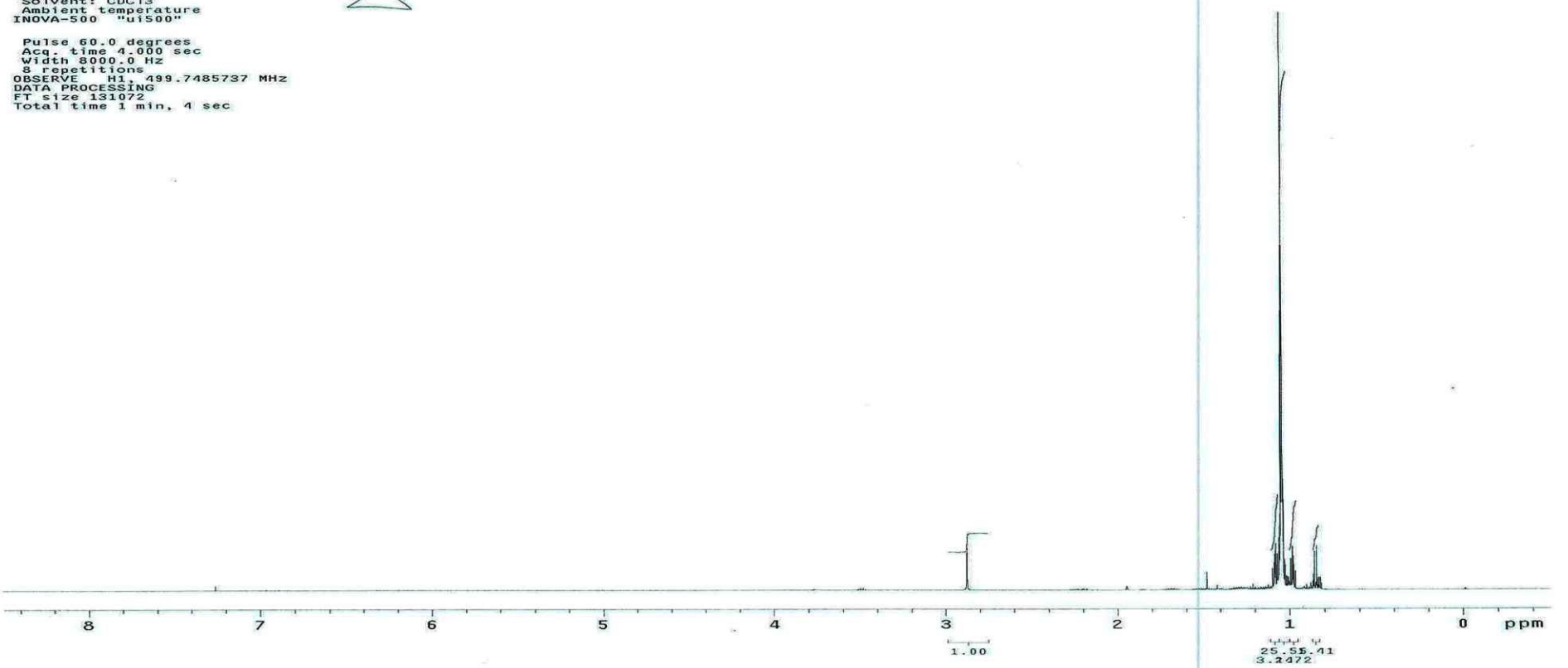
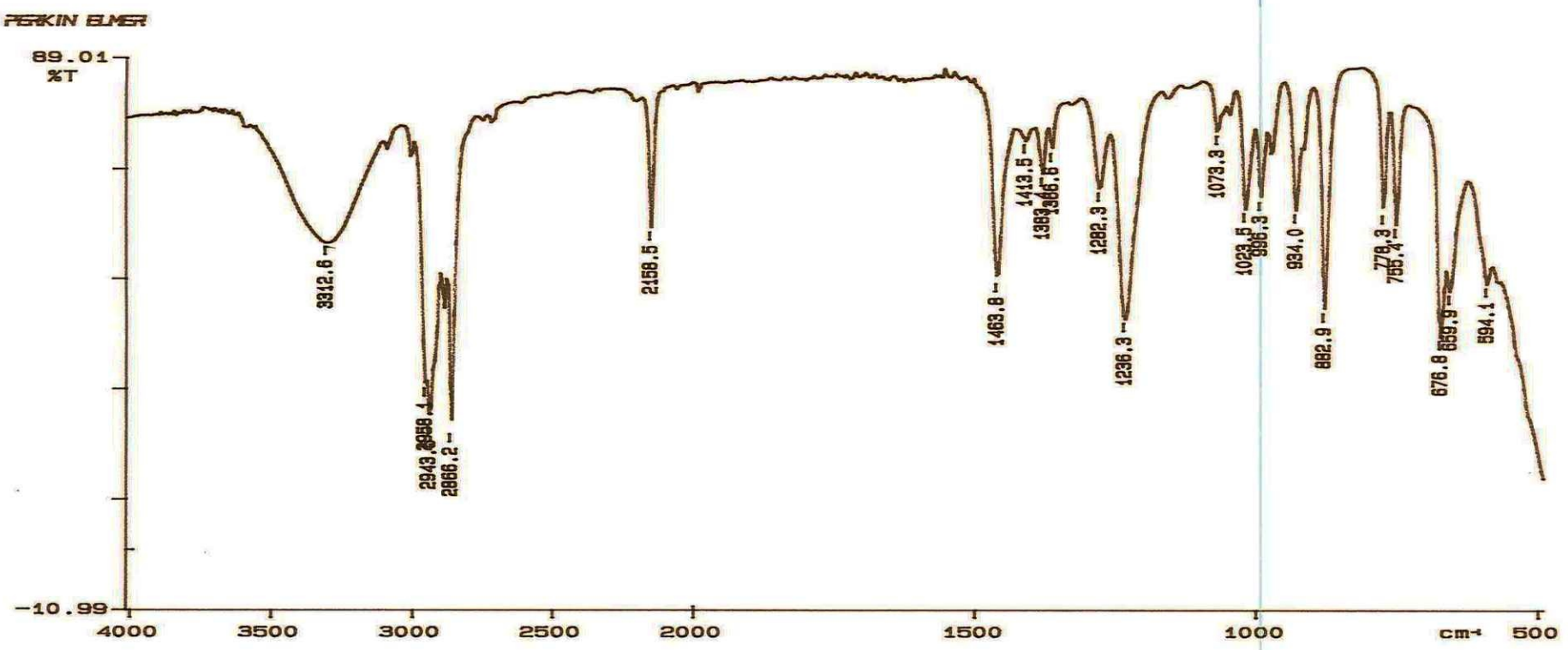
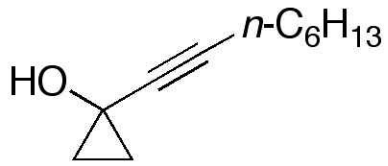
Total time 1 min, 4 sec

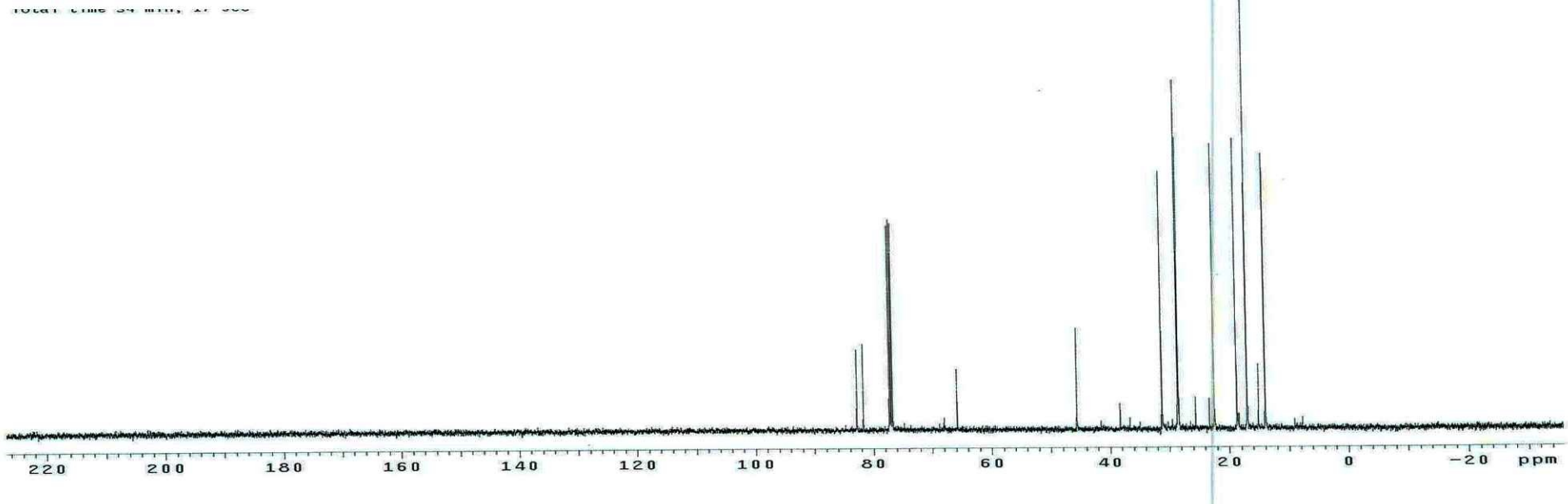




06/08/03 16:53
X: 4 scans, 4.0cm-1

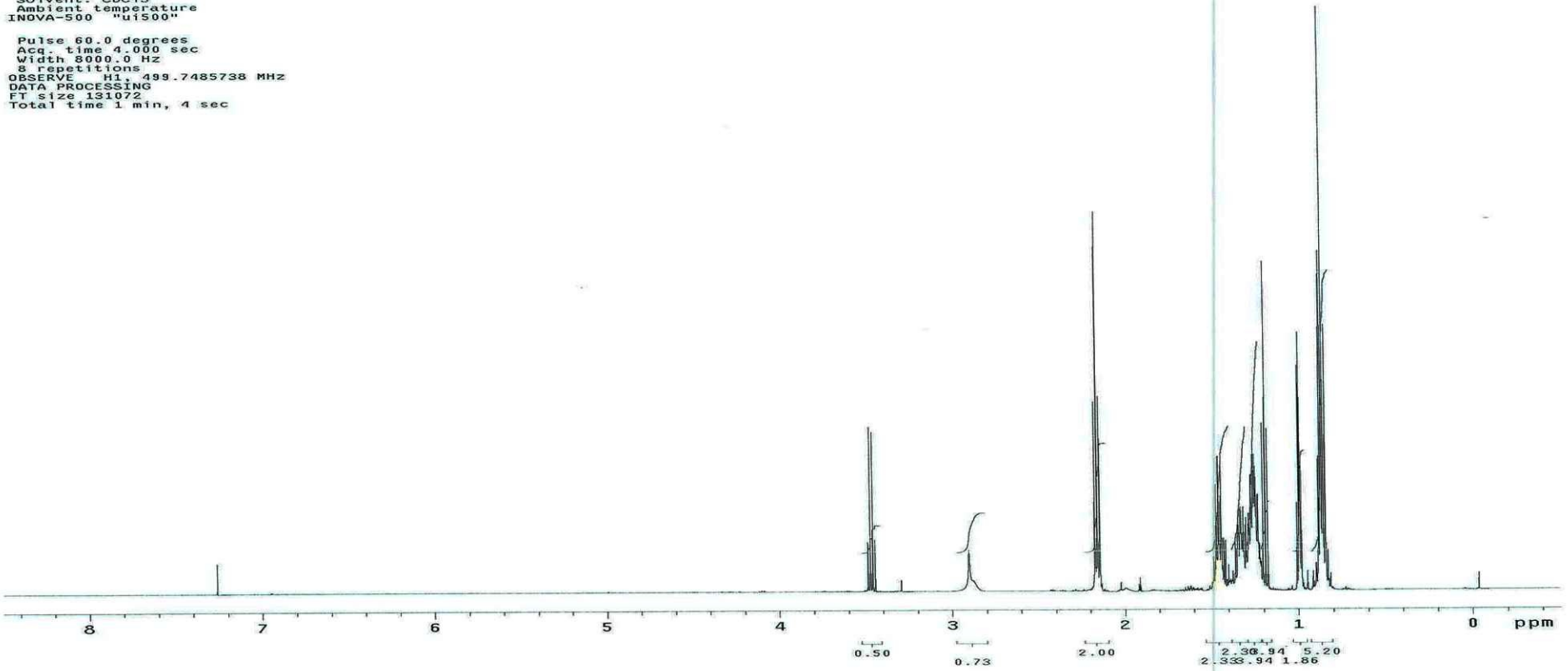


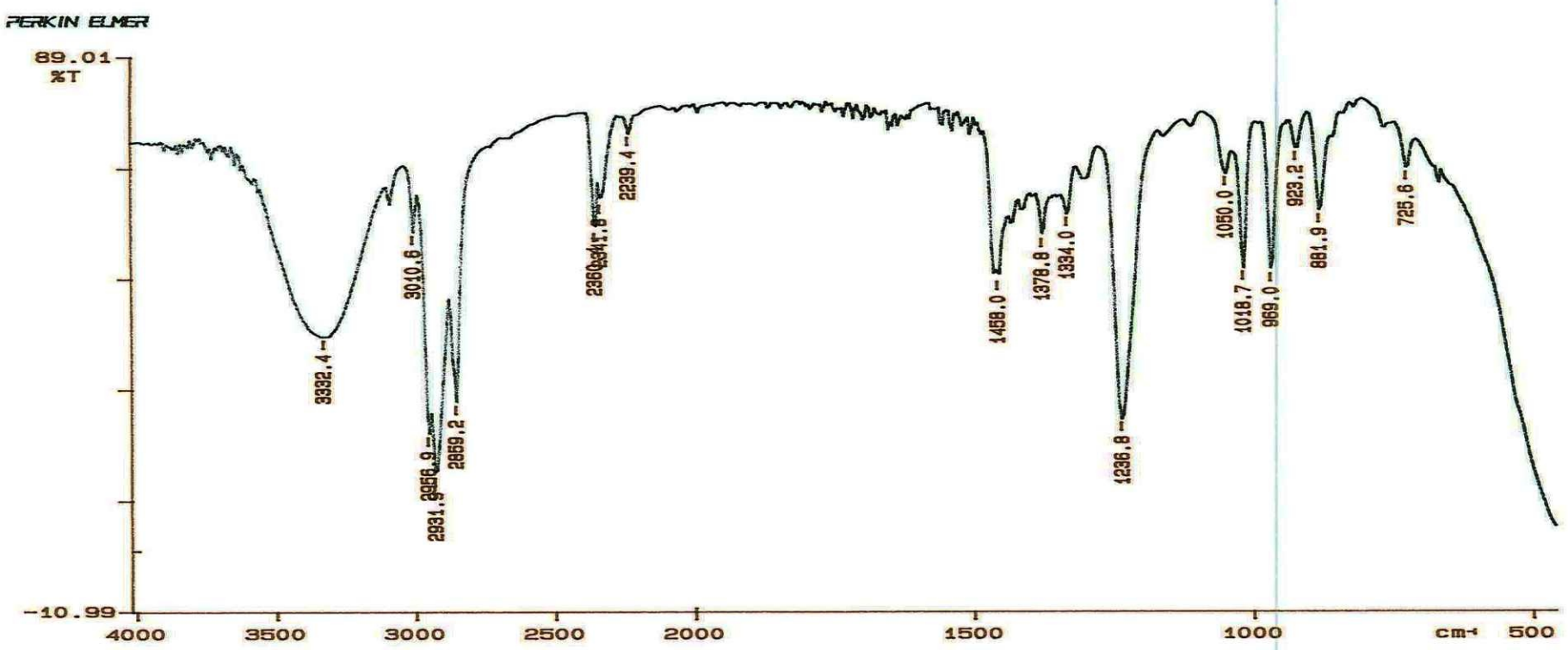
5.20a



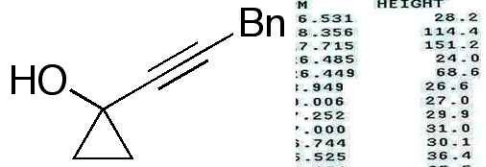
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



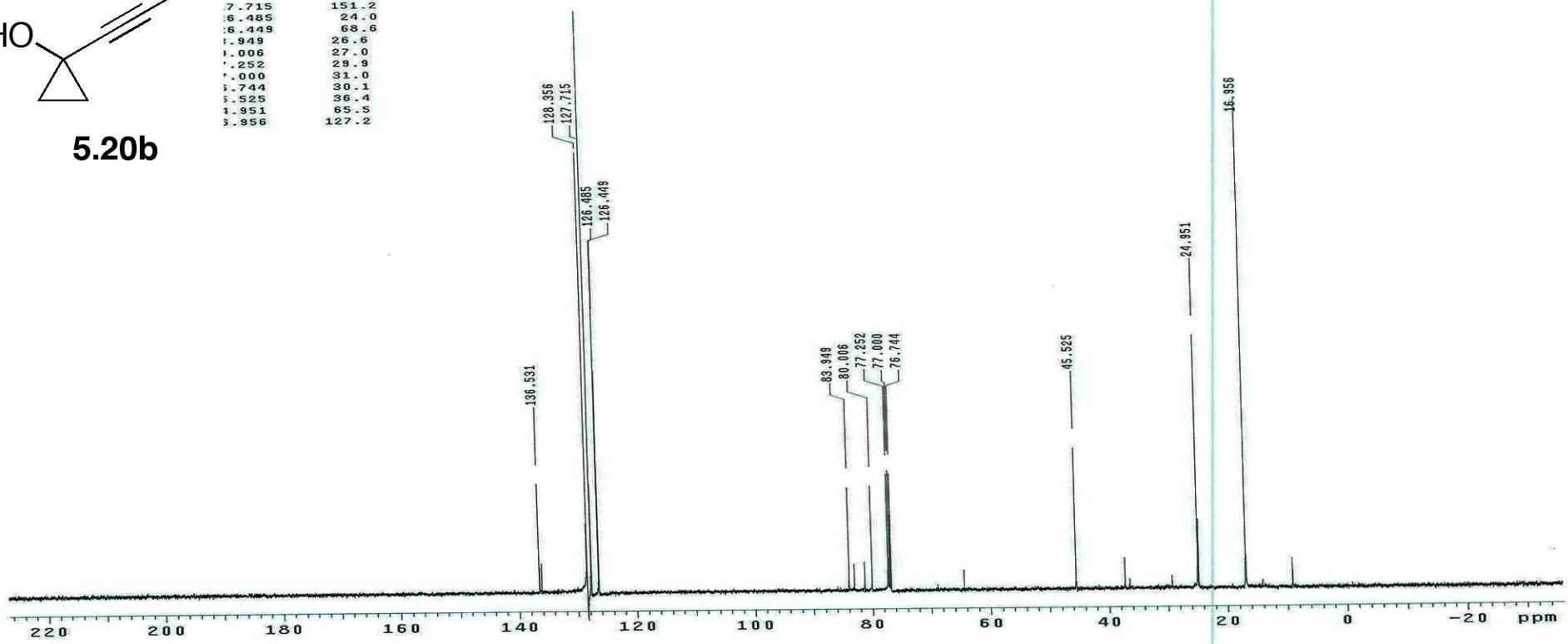


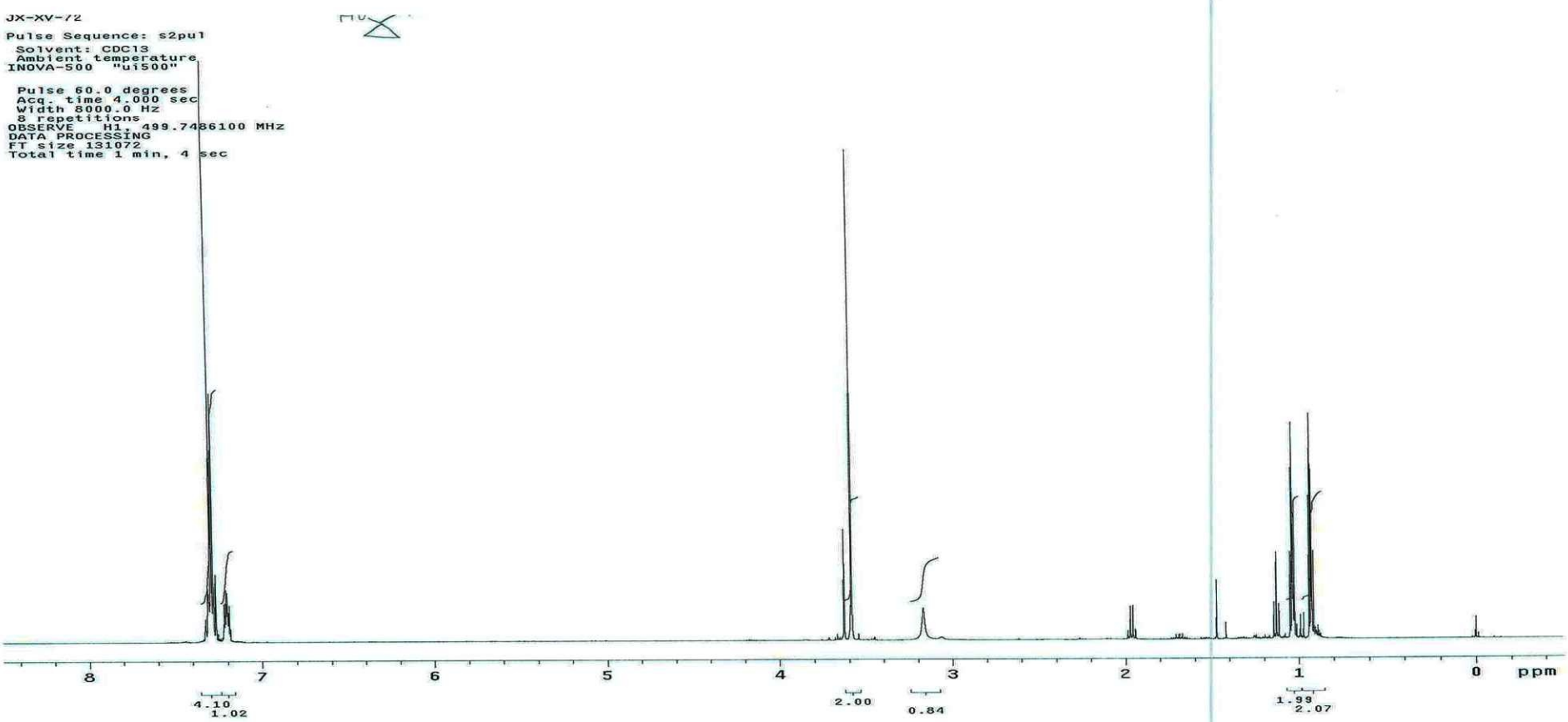
06/07/07 14:10
X: 4 scans, 4.0cm-1

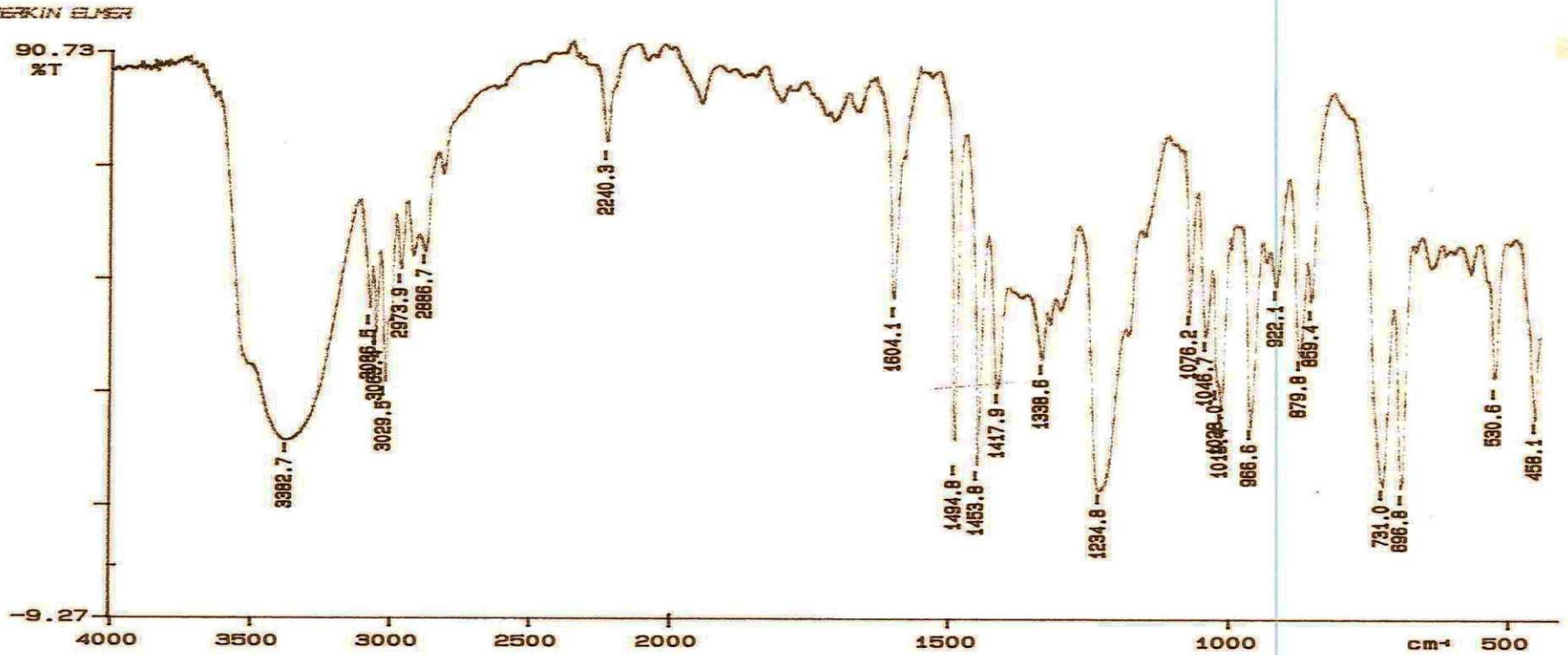


5.20b

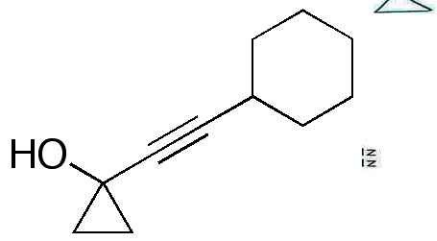
M	HEIGHT
6.531	28.2
8.356	114.4
7.715	151.2
6.485	24.0
6.449	68.6
1.949	26.6
1.006	27.0
7.252	29.9
7.000	31.0
6.744	30.1
5.525	36.4
1.951	65.5
6.956	127.2



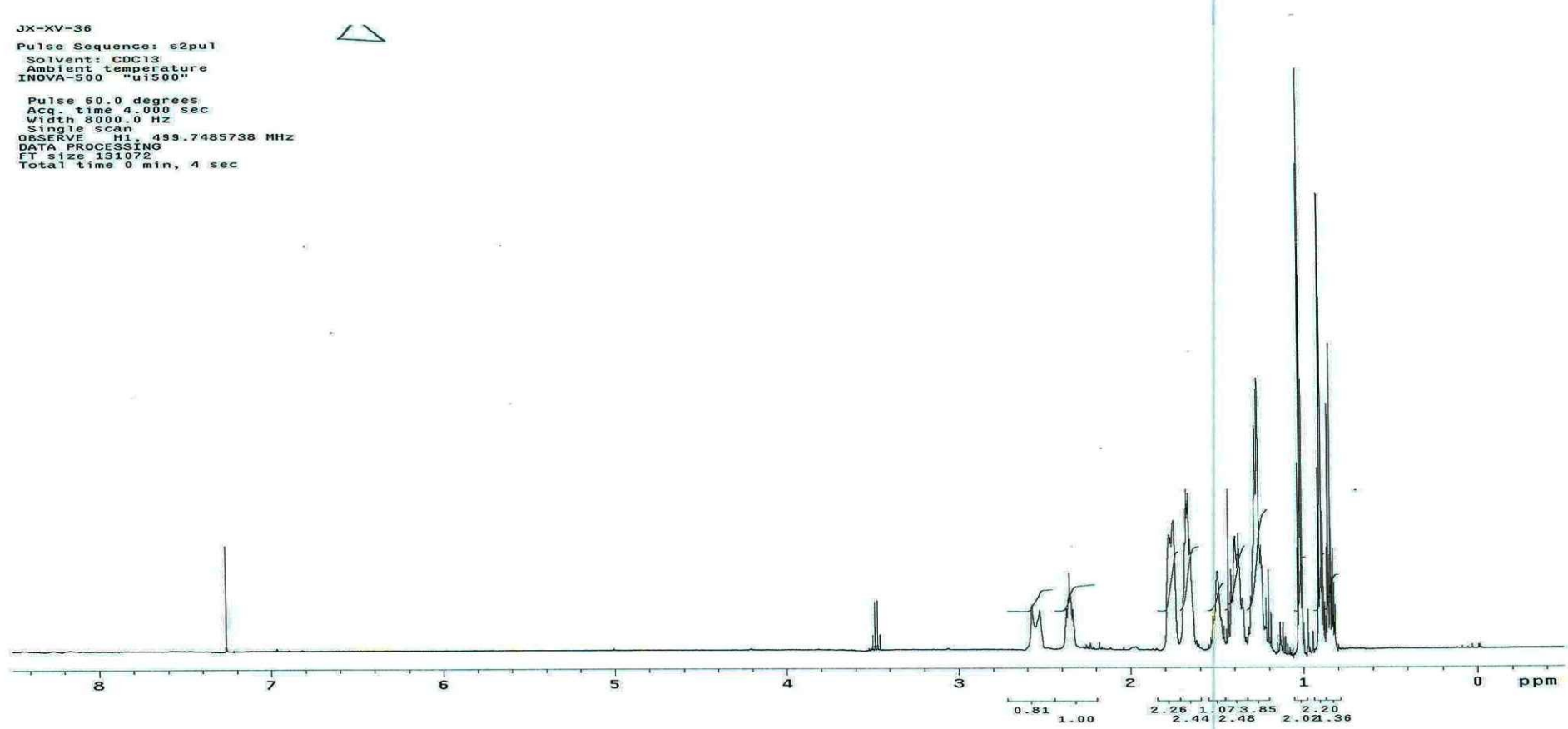




06/10/06 16:43
X: 4 scans, 4.0cm-1



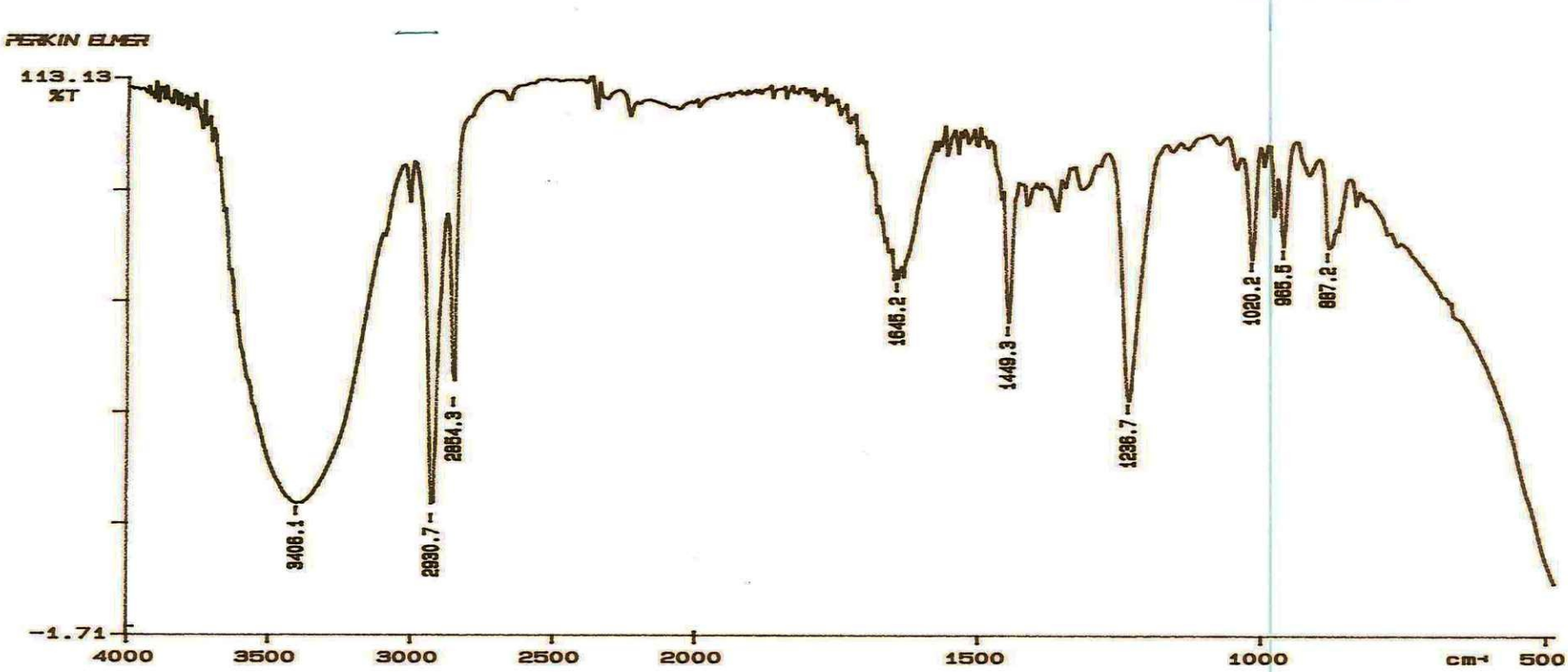
5.20c



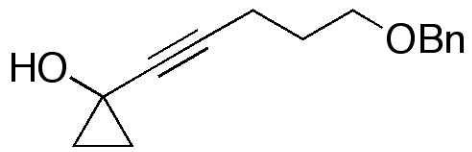
JX-XV-36

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

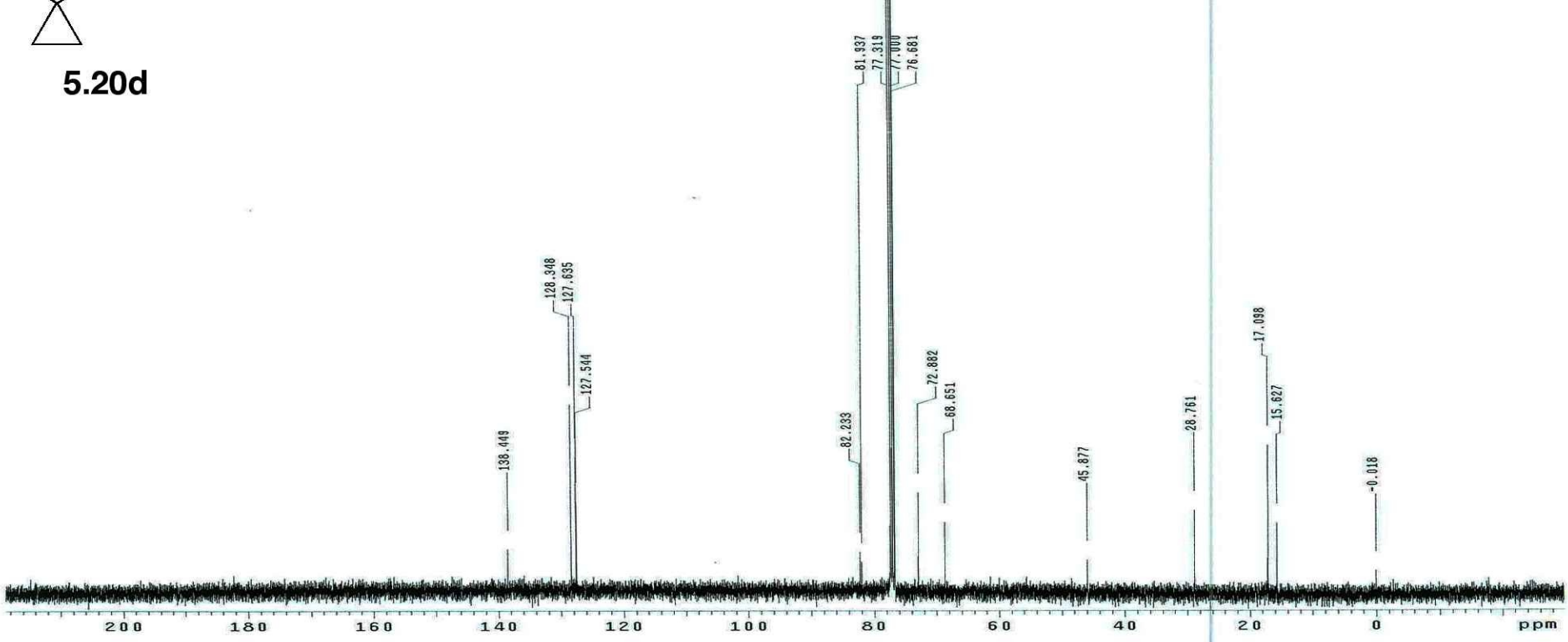
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
Single scan
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 0 min, 4 sec

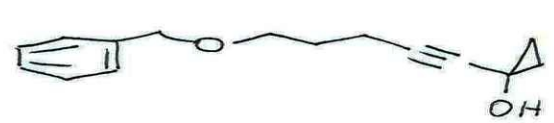


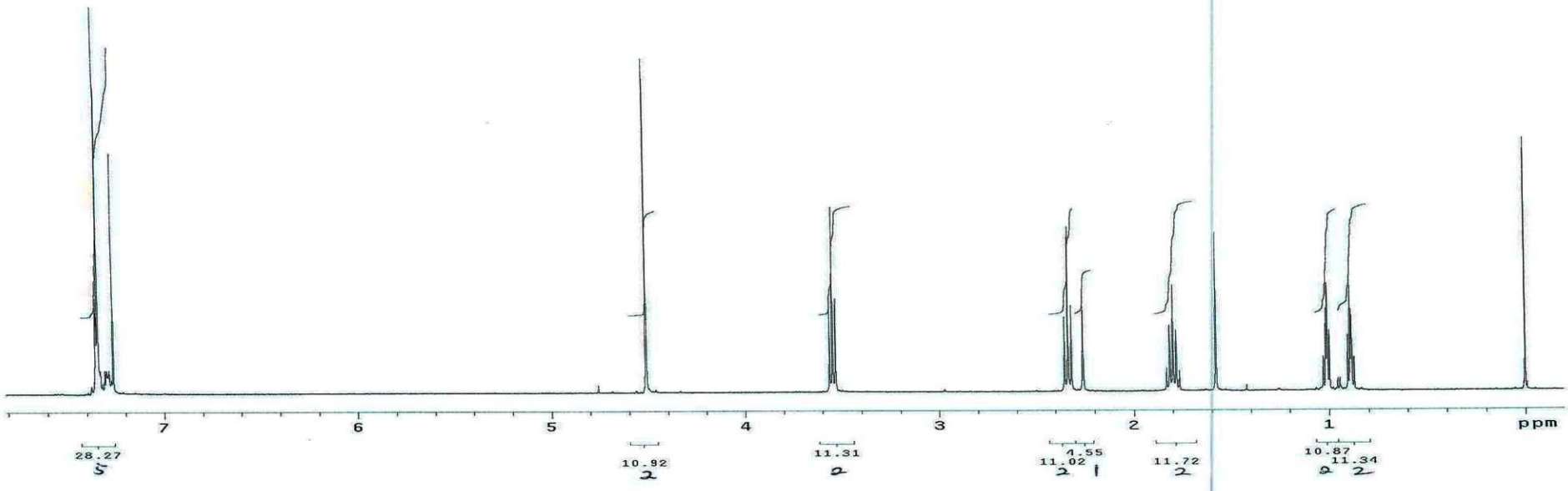
06/08/21 11:26
X: 4 scans, 4.0cm-1

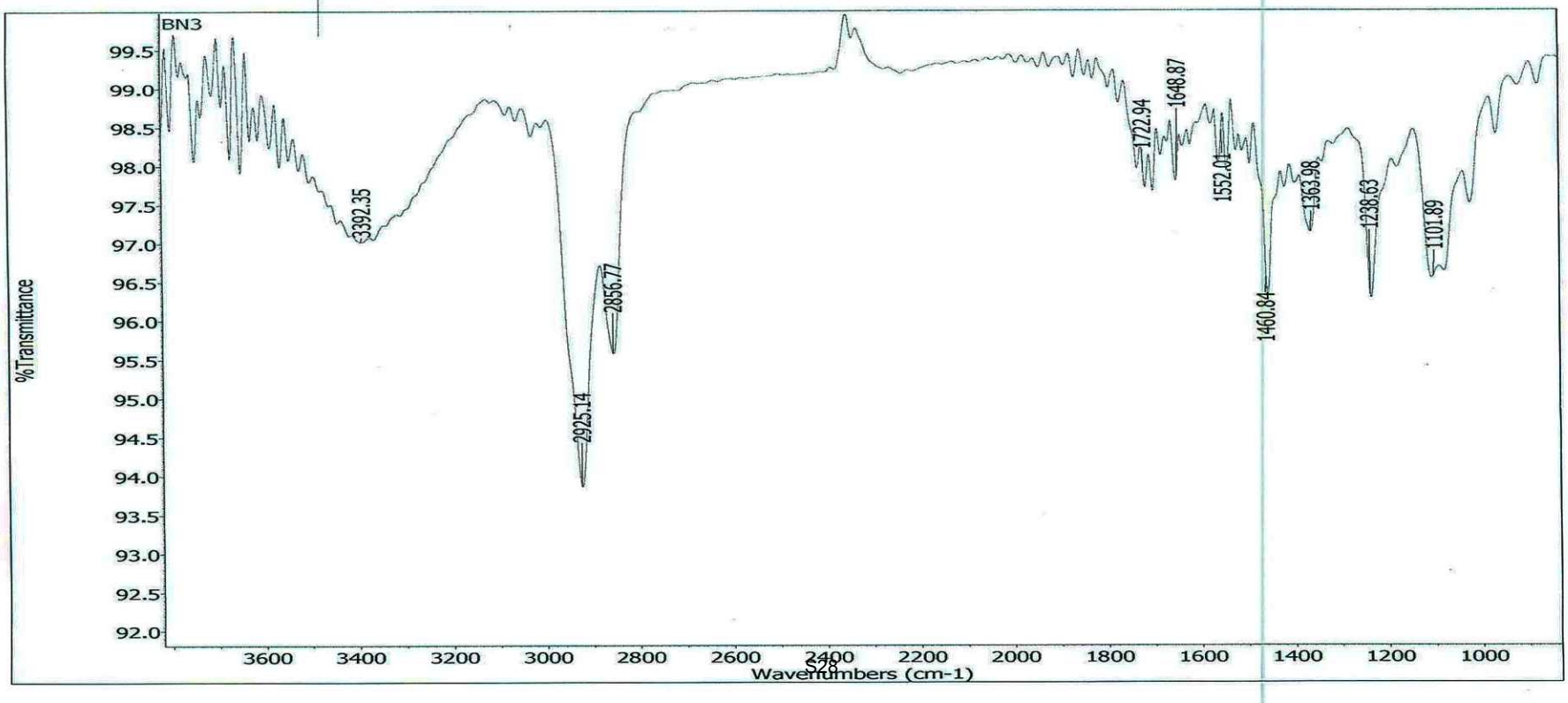

HO
OBn

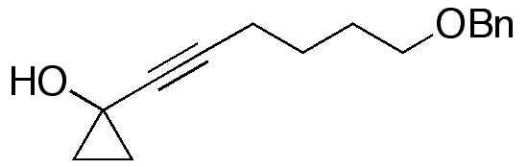
5.20d


138.449
128.348
127.635
127.544
82.233
81.937
77.319
76.681
72.882
68.651
45.877
28.761
17.098
15.627
-0.018
200
180
160
140
120
100
80
60
40
20
0
ppm

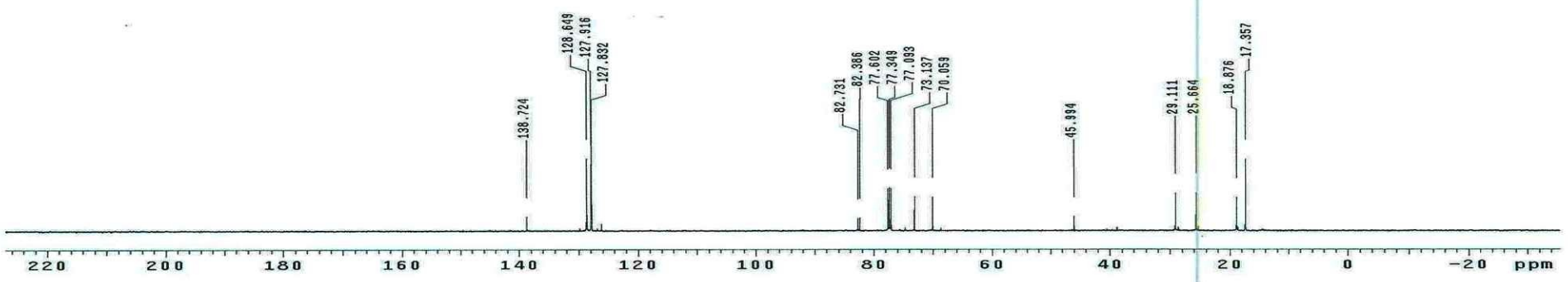

OH

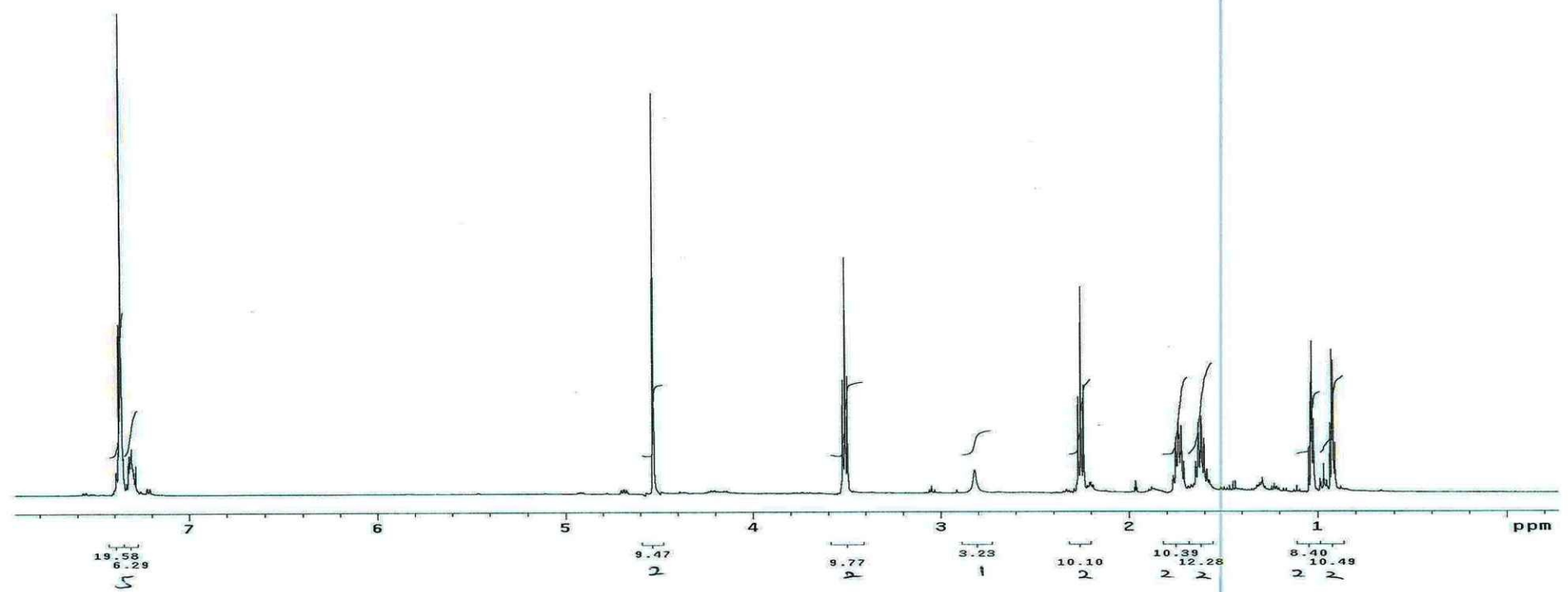

7
6
5
4
3
2
1
ppm
28.27
10.92
11.31
4.55
11.02
11.72
10.87
11.34

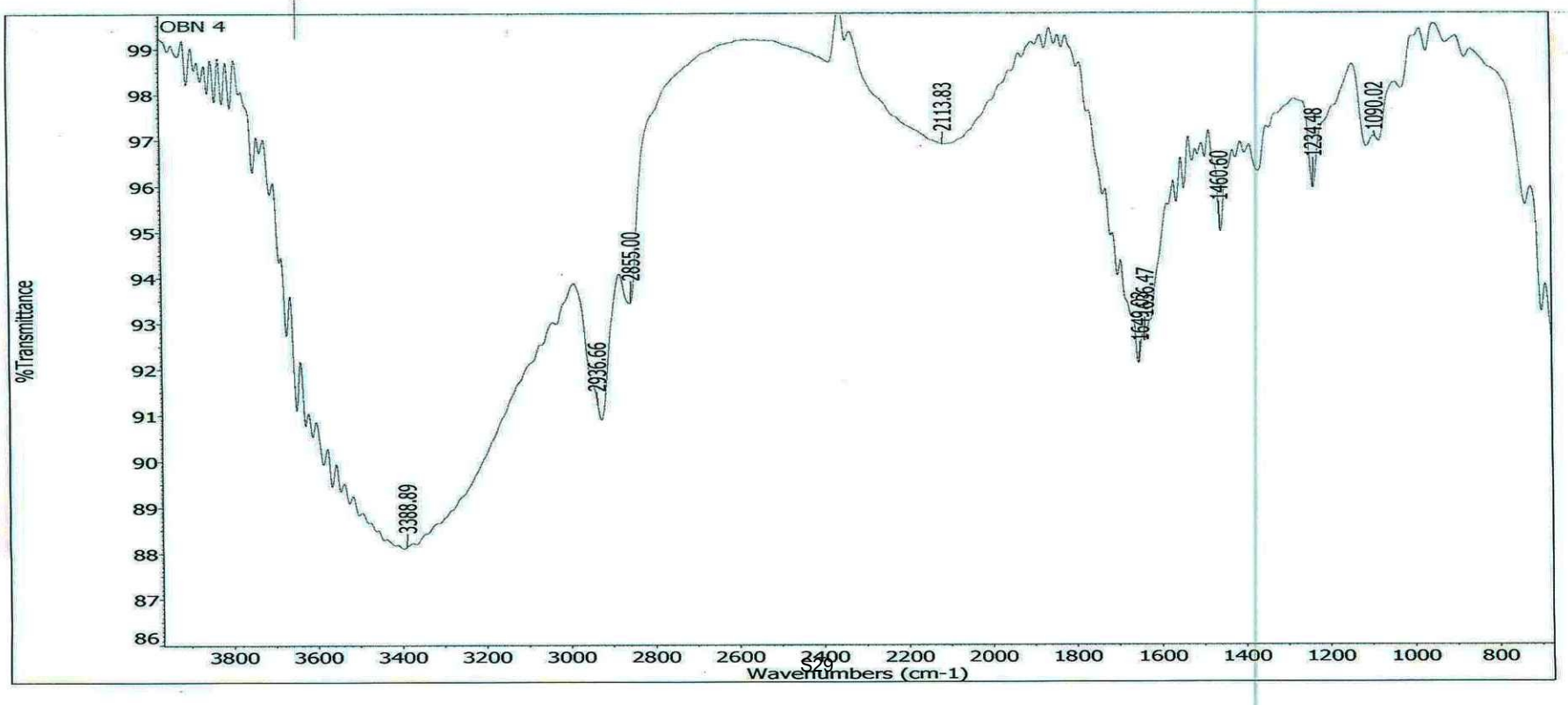

BN3
%Transmittance
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
3392.35
2925.14
2856.77
1722.94
1648.87
1552.01
1460.84
1363.98
1238.63
1101.89
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
Wavenumbers (cm-1)

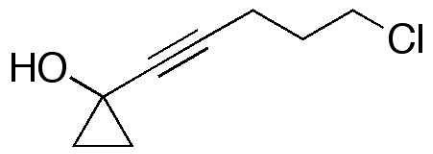

HO
OBn

5.20e

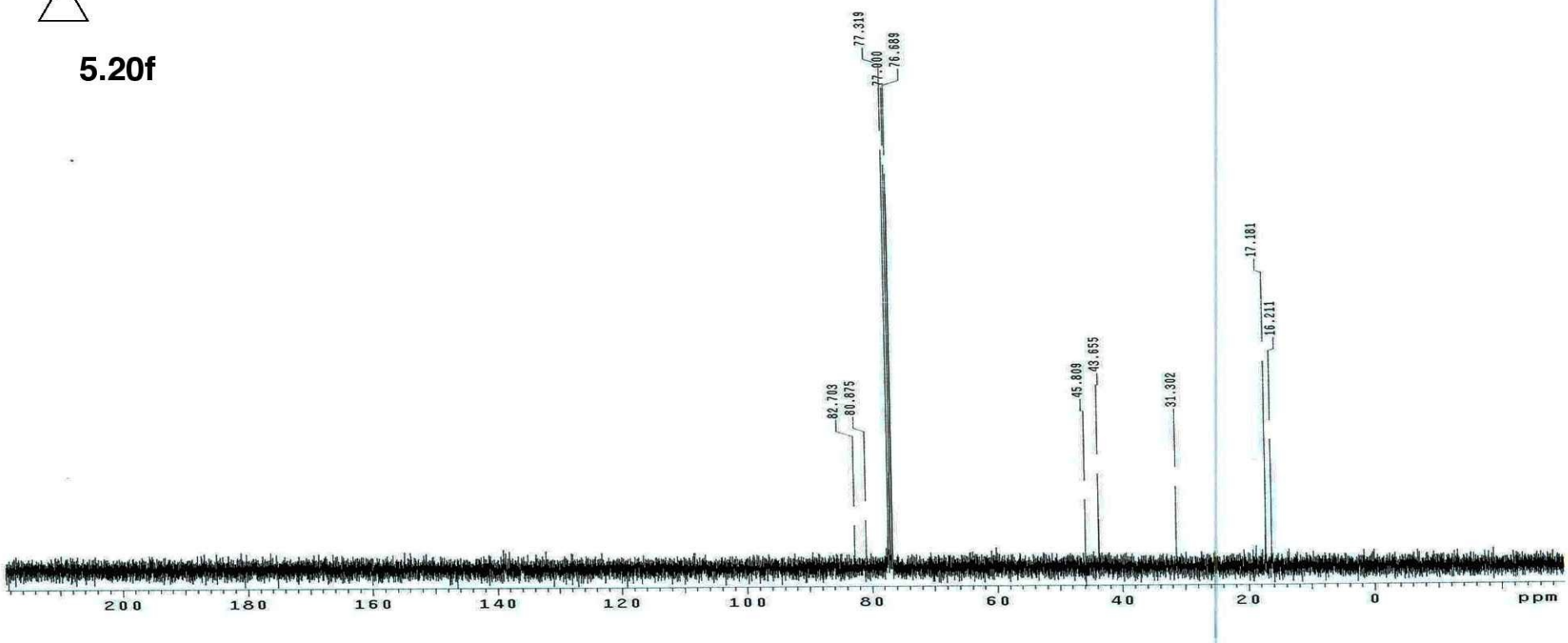

138.724
128.649
127.916
127.832
82.731
82.386
77.602
77.349
77.093
73.137
70.059
45.994
29.111
25.664
18.876
17.357
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm


7
6
5
4
3
2
1
ppm
19.58
6.29
9.47
9.77
3.23
10.10
10.39
12.28
8.40
10.49

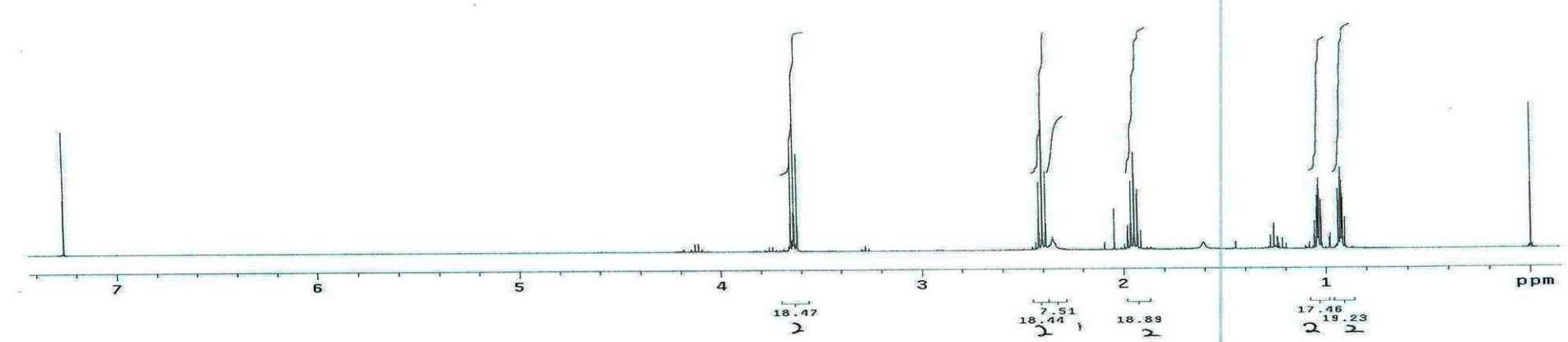

OBN 4
%Transmittance
3388.89
2936.66
2855.00
2113.83
1650.47
1460.60
1234.48
1090.02
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumbers (cm-1)

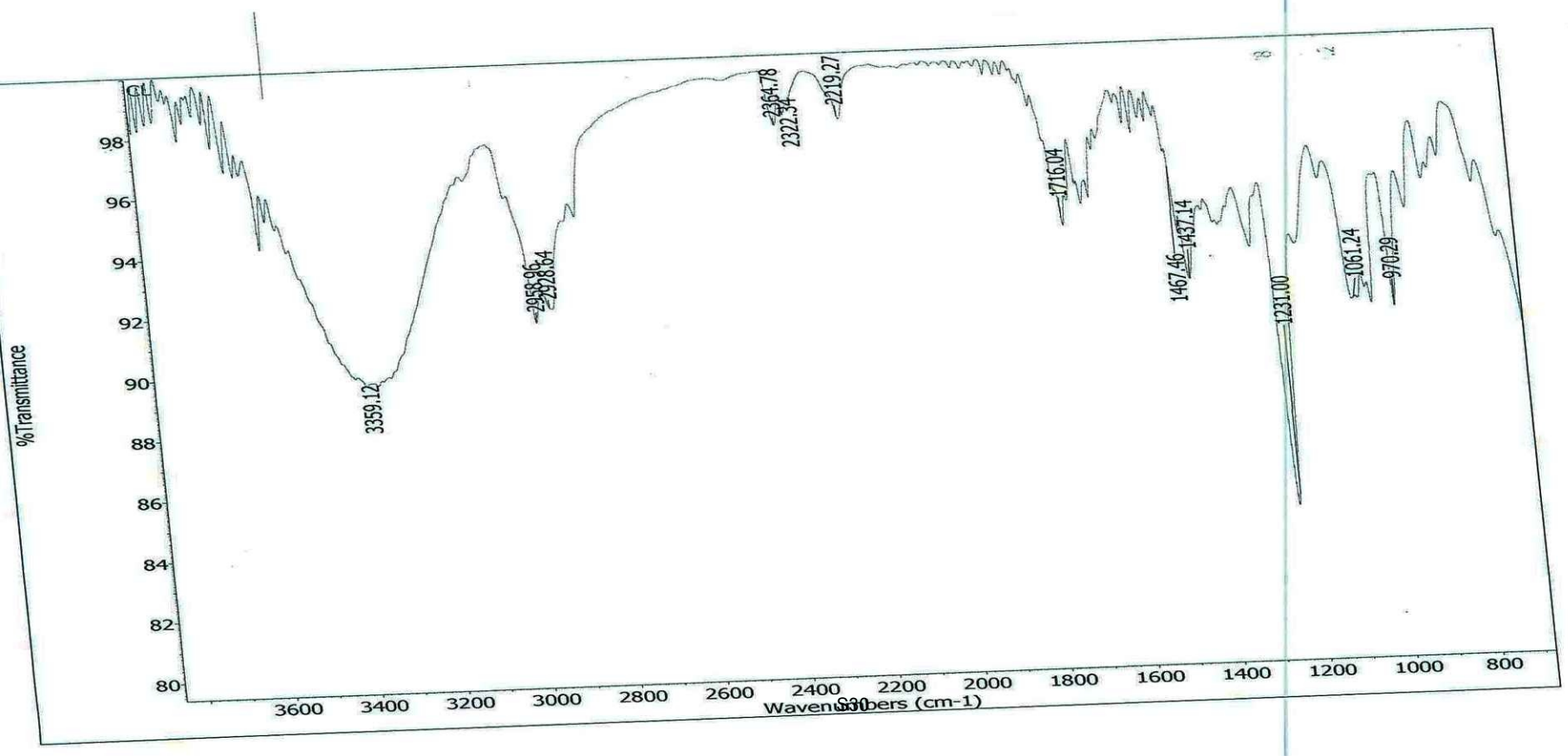

HO
Cl

5.20f

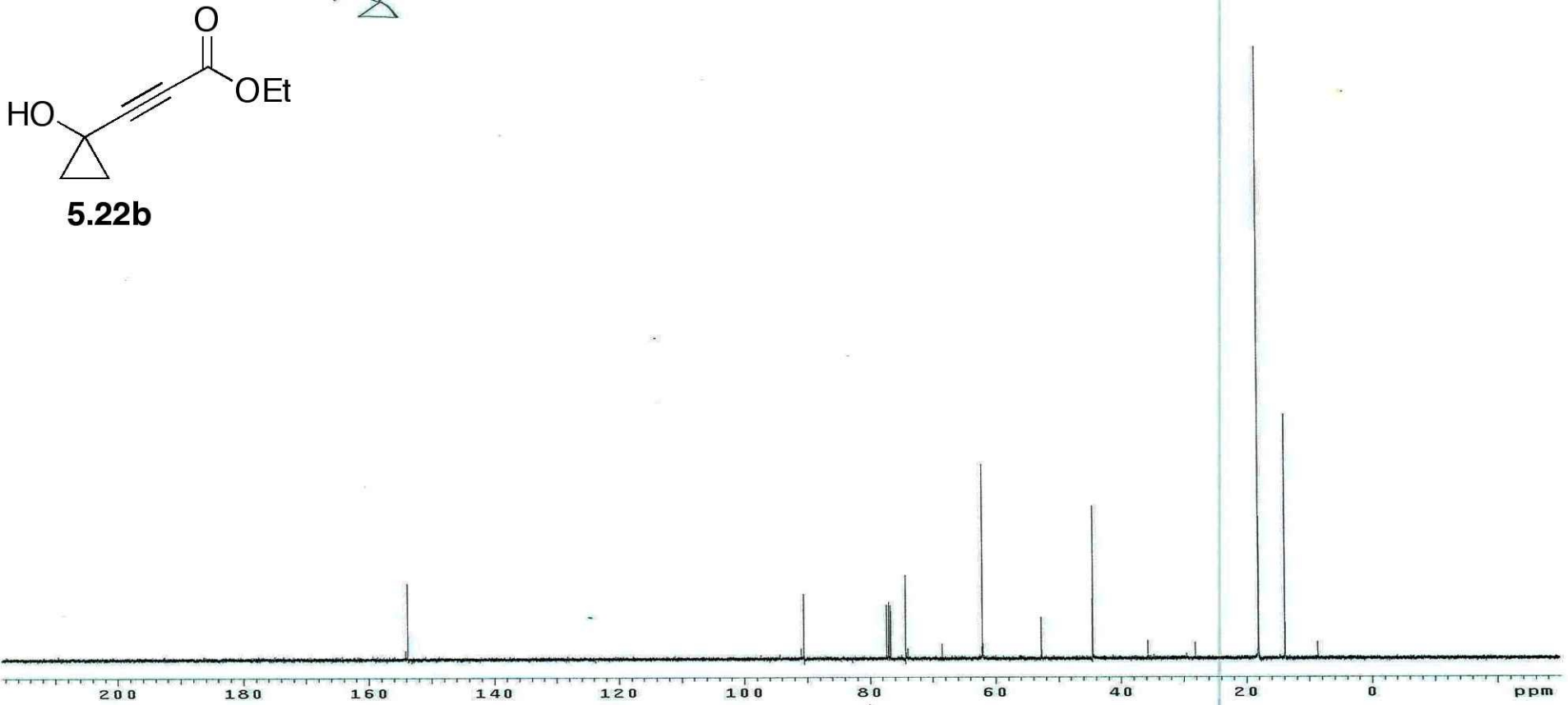

77.319
77.000
76.689
82.703
80.875
45.809
43.655
31.302
17.181
16.211
200
180
160
140
120
100
80
60
40
20
0
ppm


OH


7
6
5
4
3
2
1
ppm
18.47
7.51
18.44
18.89
17.46
19.23


%Transmittance
98
96
94
92
90
88
86
84
82
80
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumbers (cm-1)
3359.12
2958.96
2928.04
2364.78
2322.54
2219.27
1716.04
1467.46
1437.14
1231.00
1061.24
970.29

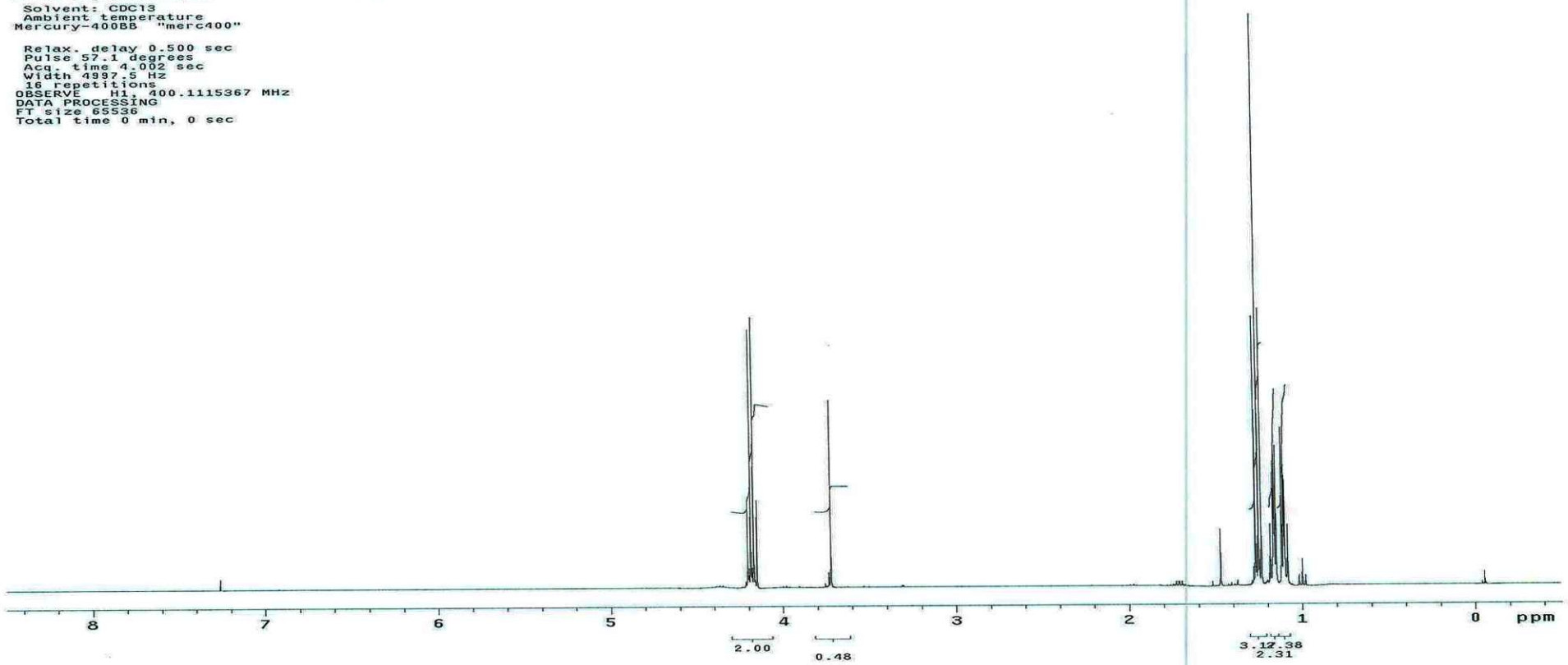
5.22b



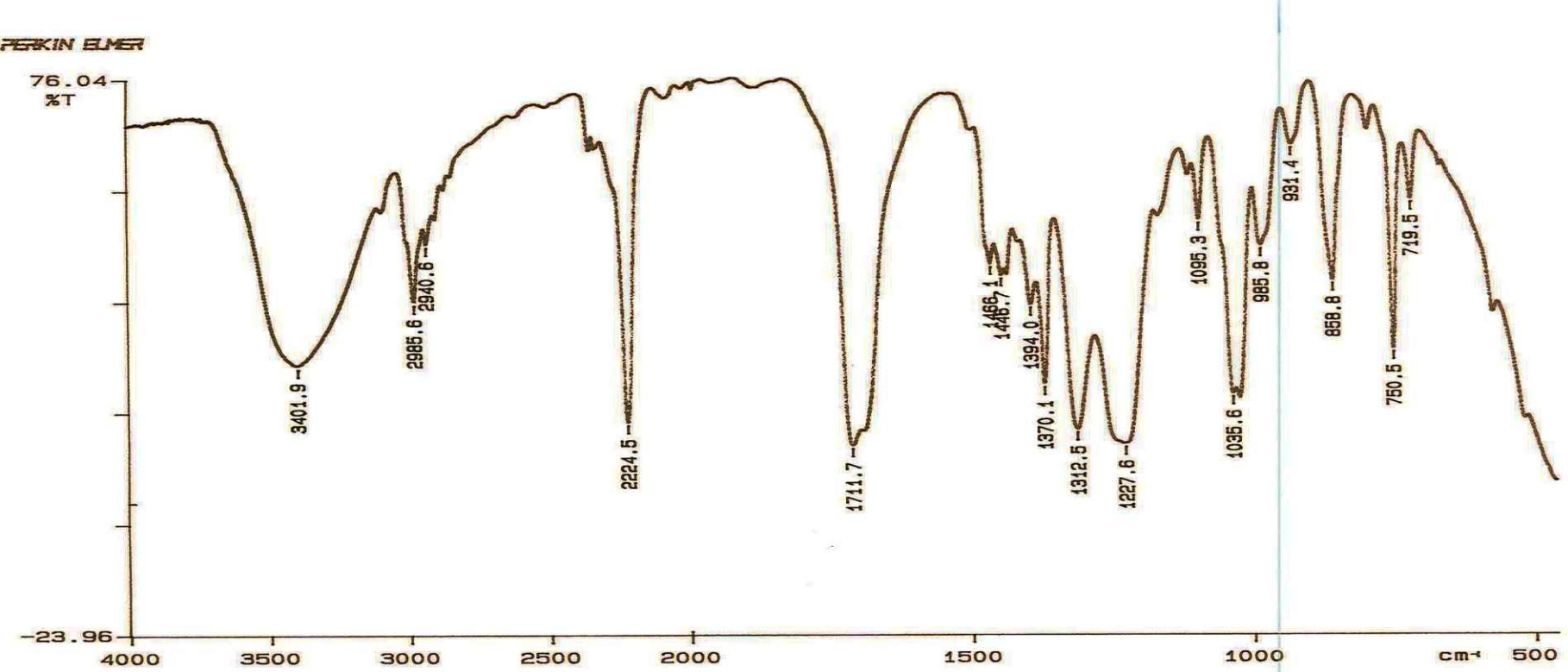
JX-XV-54

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"

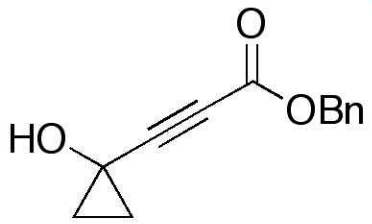
Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115367 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec



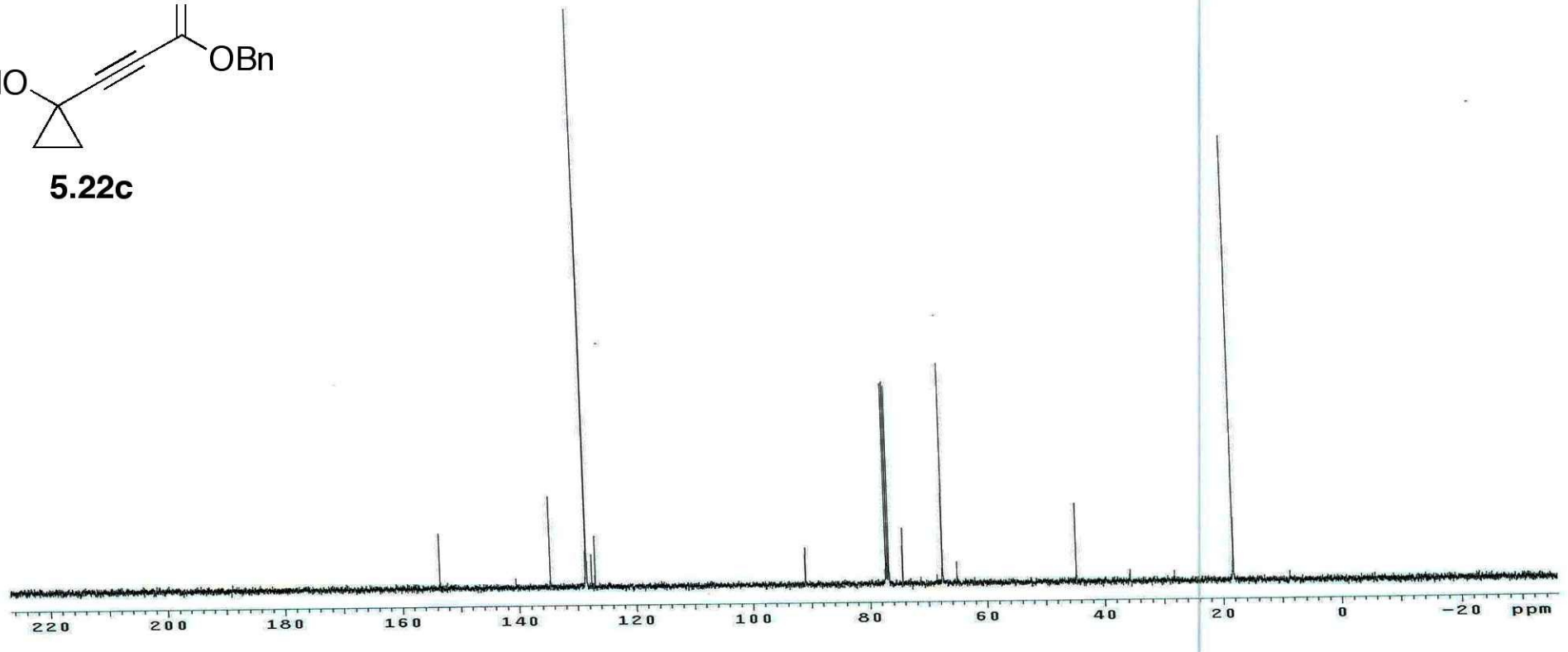
PERKIN ELMER

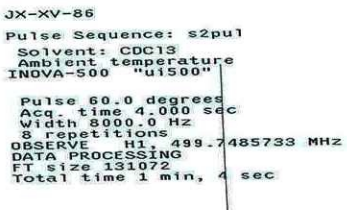


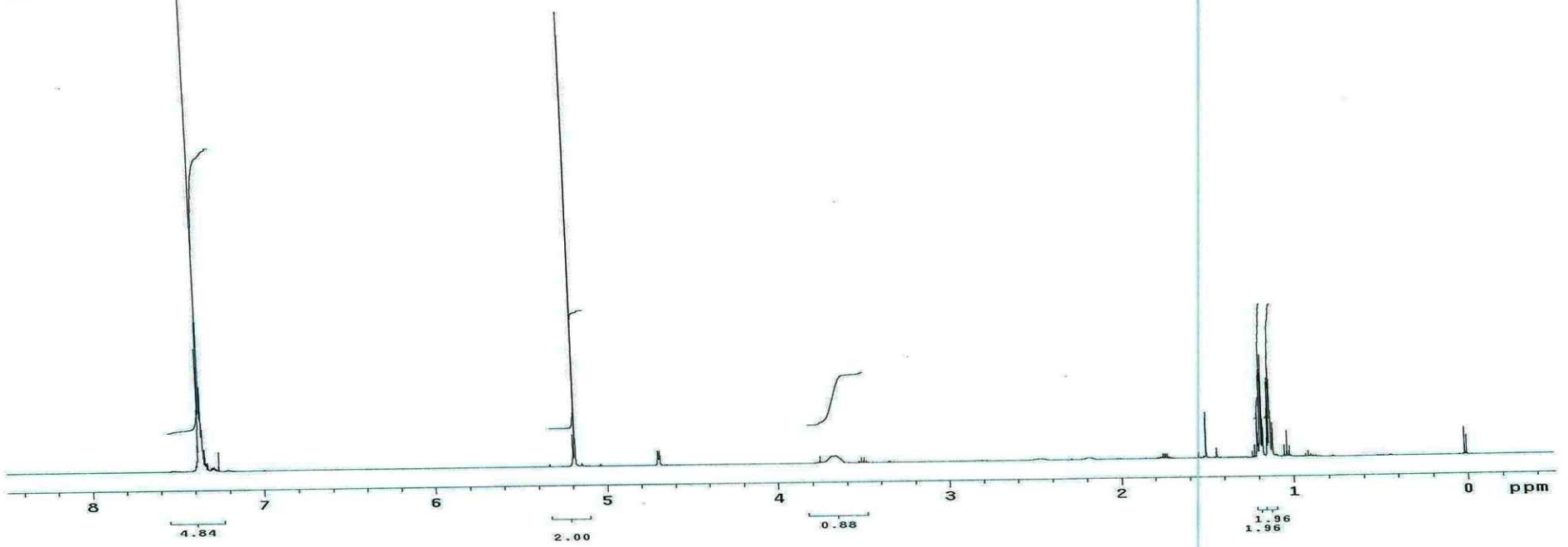
06/09/25 11:10
X: 4 scans, 4.0cm-1

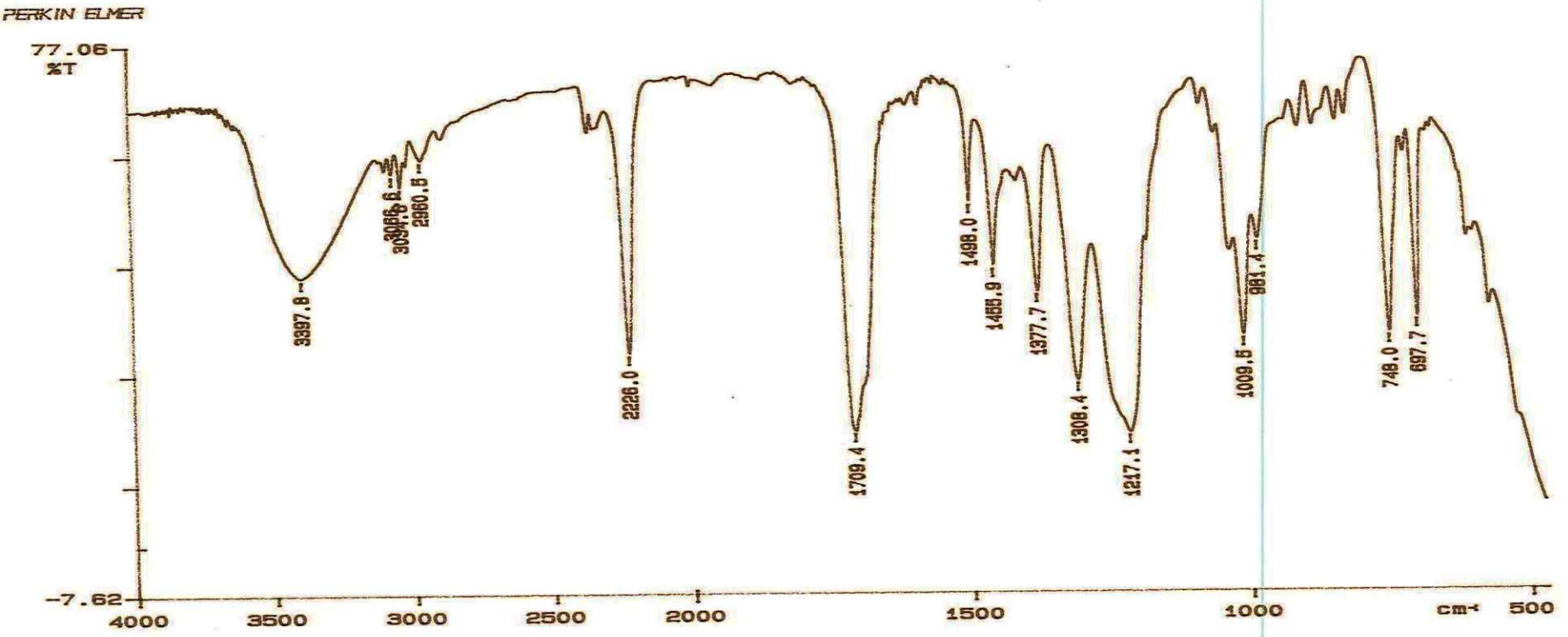

O
OBn
HO

5.22c


220
200
180
160
140
120
100
80
60
40
20
0
−20
ppm


JX-XV-86
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485733 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec

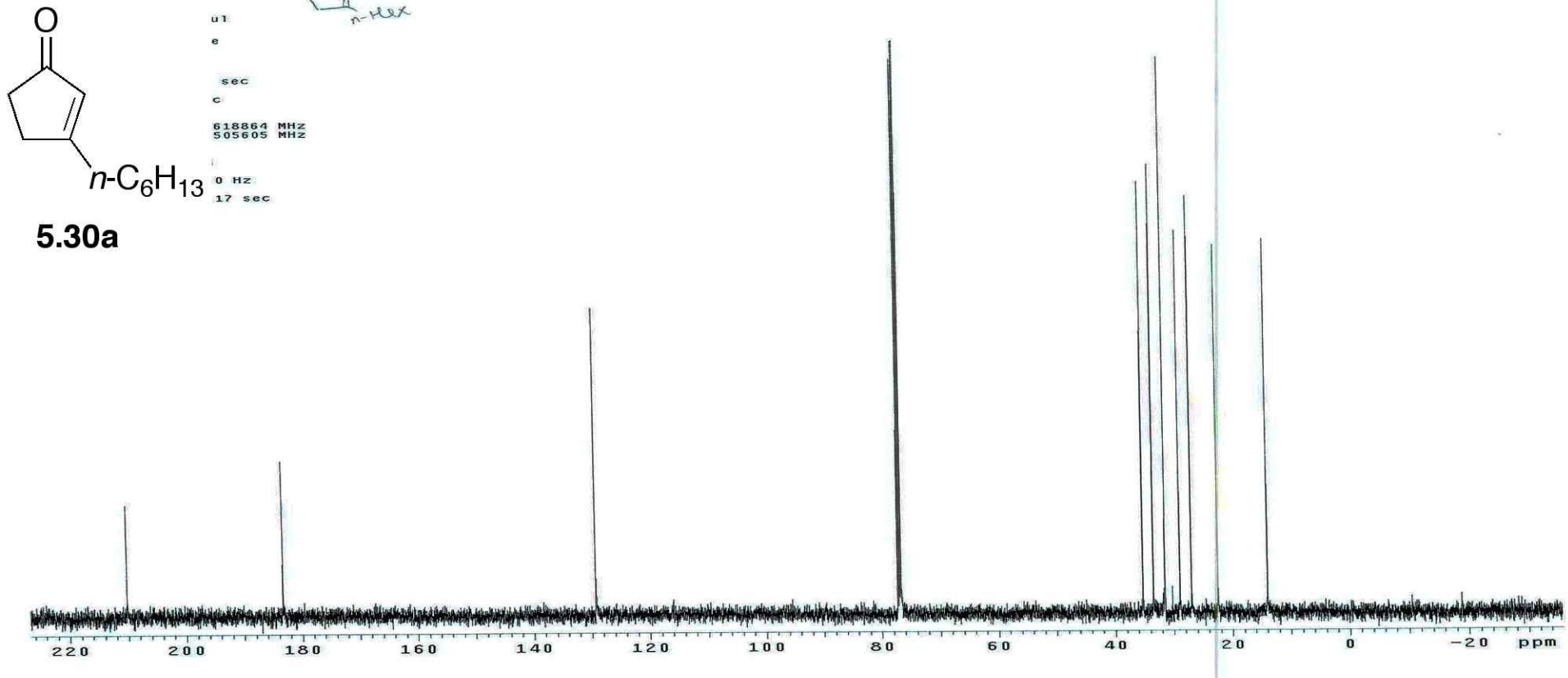

8
7
6
5
4
3
2
1
0
ppm
4.84
2.00
0.88
1.96
1.96

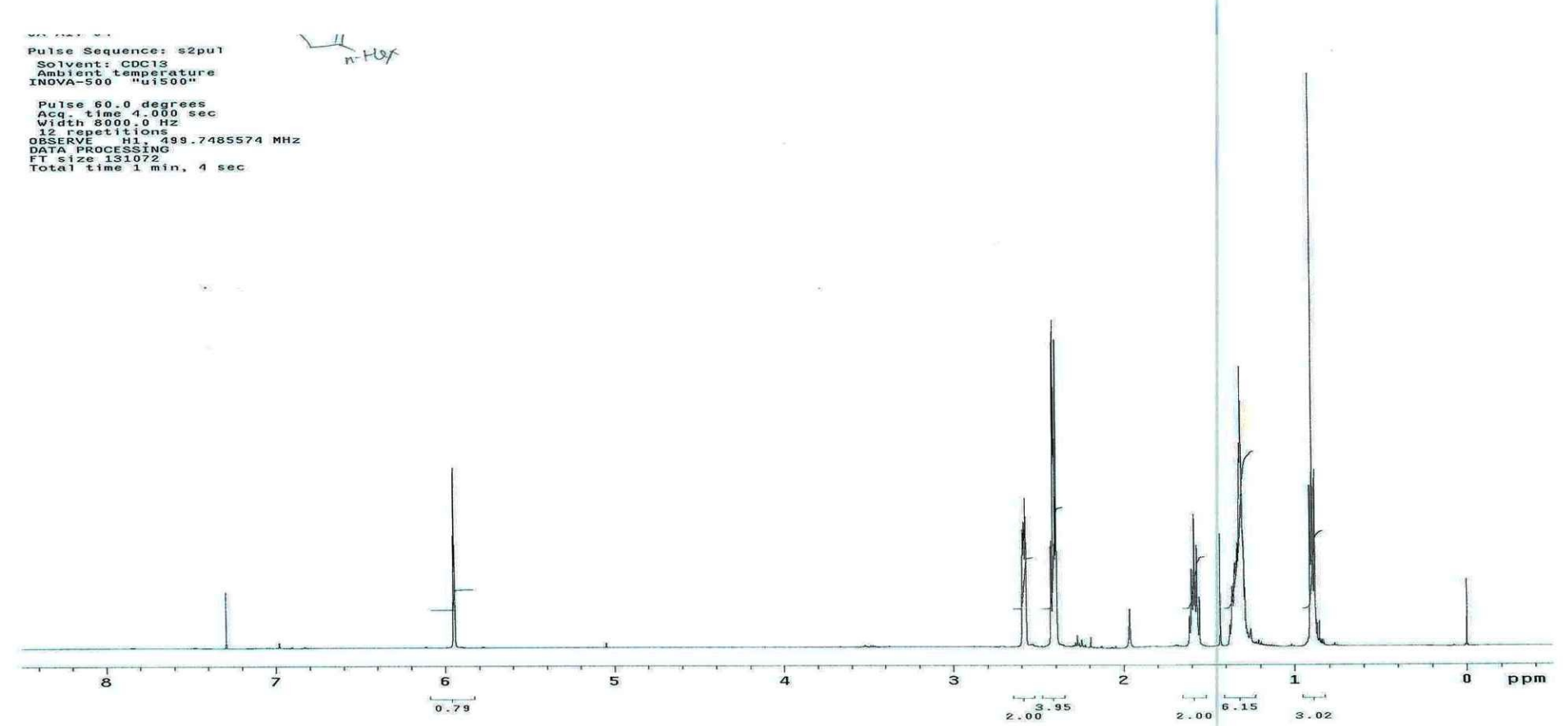

PERKIN ELMER
77.06
%T
−7.62
3397.8
3066.6
3030.9
2980.5
2226.0
1709.4
1498.0
1488.9
1377.7
1308.4
1217.1
1009.5
981.4
748.0
697.7
4000
3500
3000
2500
2000
1500
1000
cm-1
500

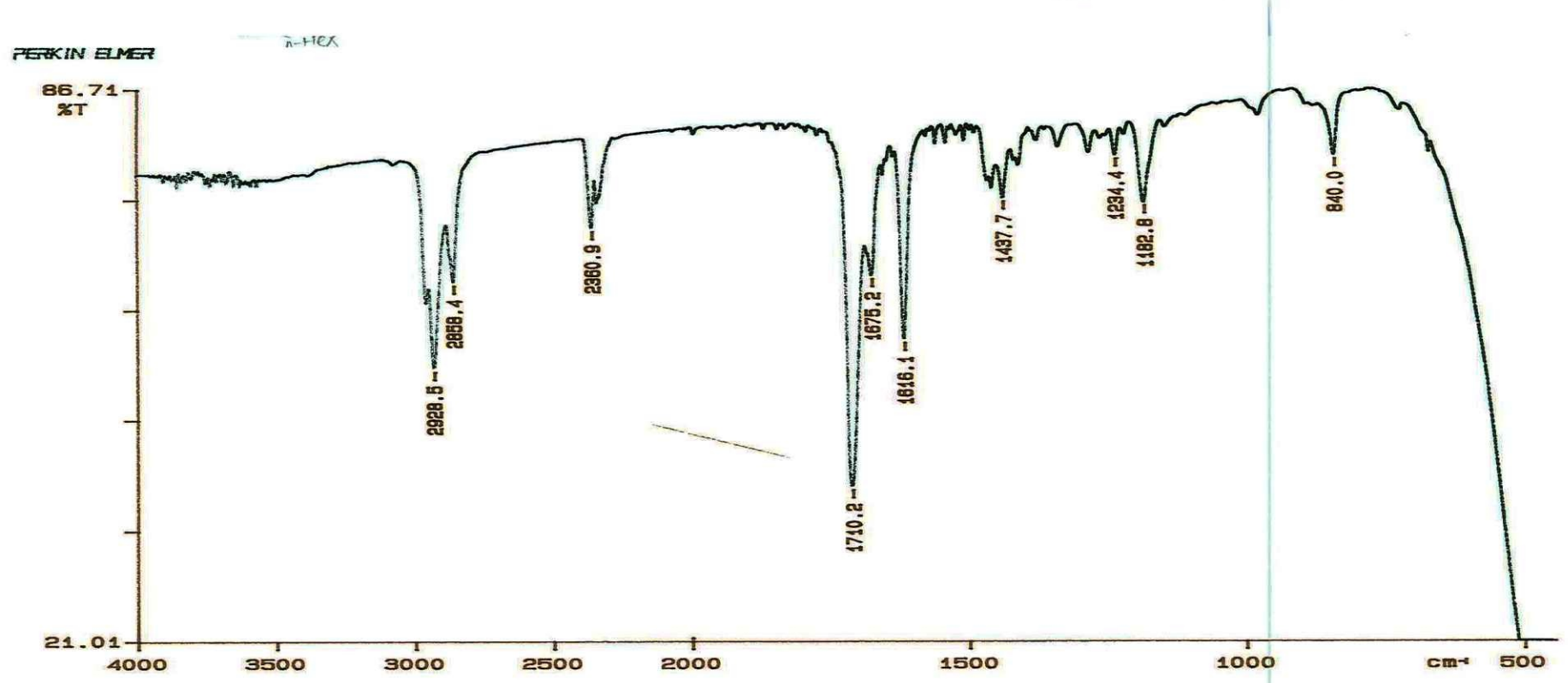

06/10/17 12:23
X: 4 scans, 4.0cm-1

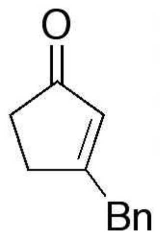
O
n-C6H13

5.30a

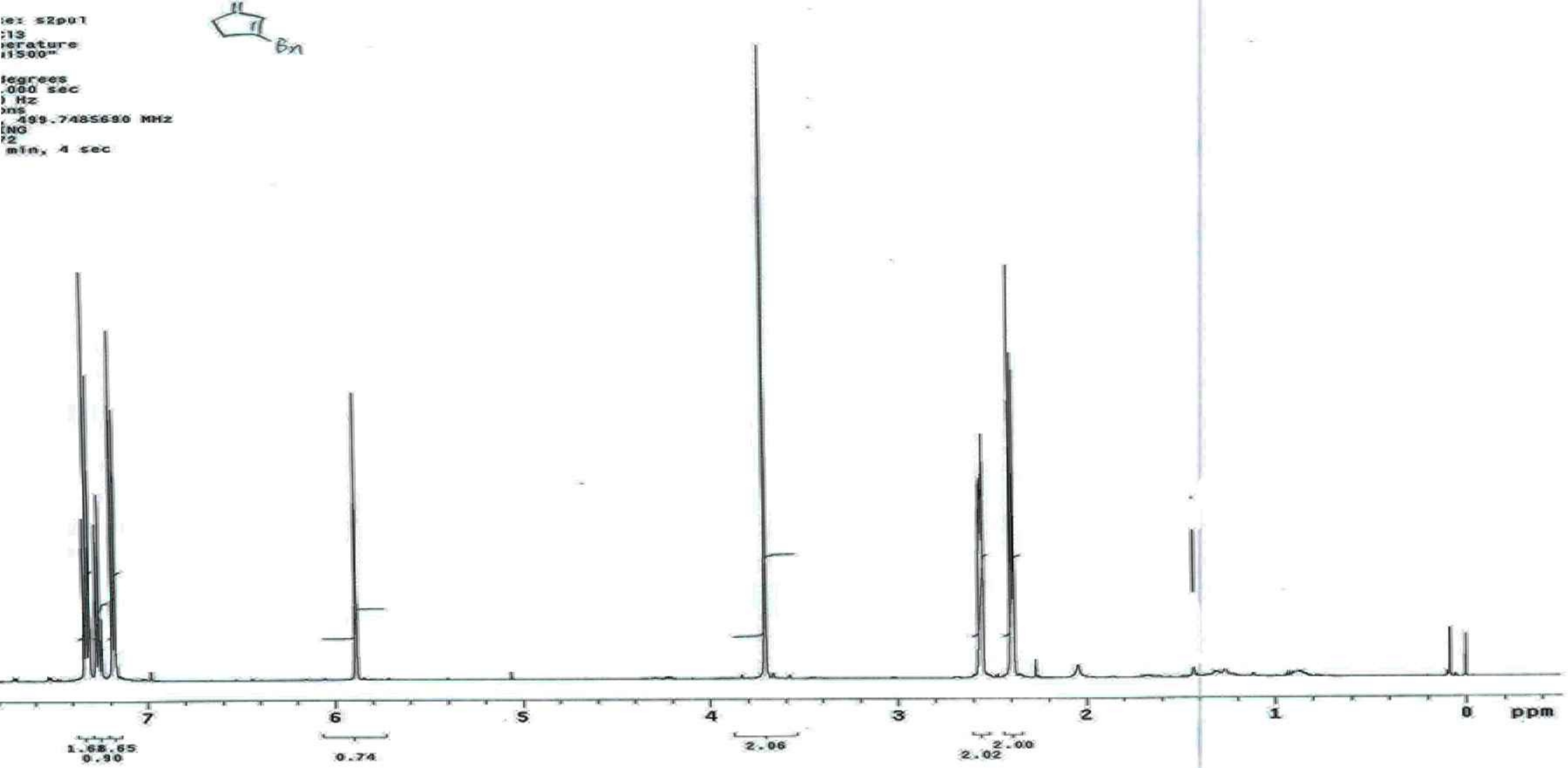

n-Hex
sec
618864 MHz
505605 MHz
0 Hz
17 sec
220
200
180
160
140
120
100
80
60
40
20
0
−20
ppm


n-Hex
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
12 repetitions
OBSERVE H1, 499.7485574 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
8
7
6
5
4
3
2
1
0
ppm
0.79
2.00
3.95
2.00
6.15
3.02

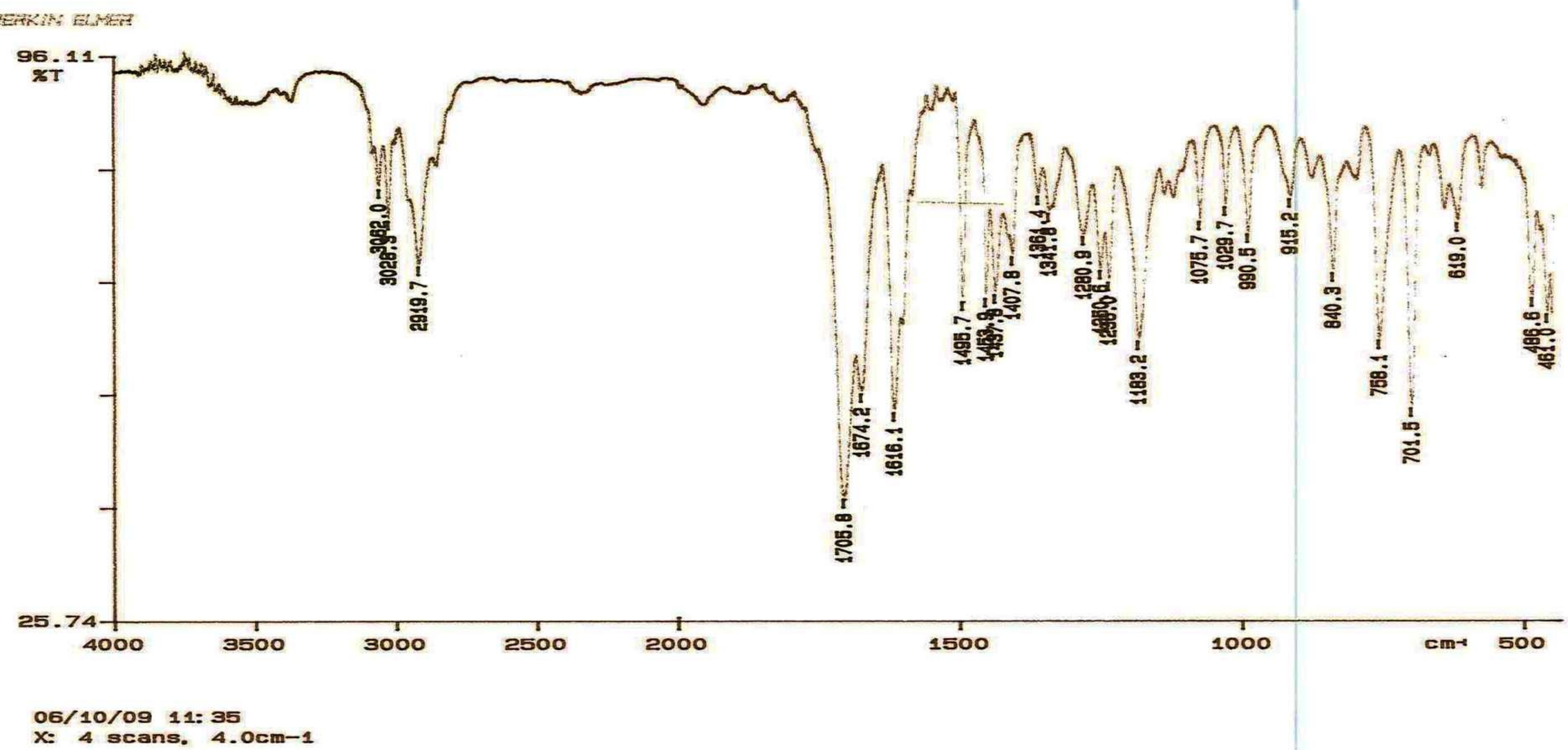

n-Hex
PERKIN ELMER
86.71
%T
21.01
2928.5
2858.4
2360.9
1710.2
1675.2
1616.1
1437.7
1234.4
1182.8
840.0
4000
3500
3000
2500
2000
1500
1000
cm-1
500
06/07/10 11:20
X: 4 scans, 4.0cm-1



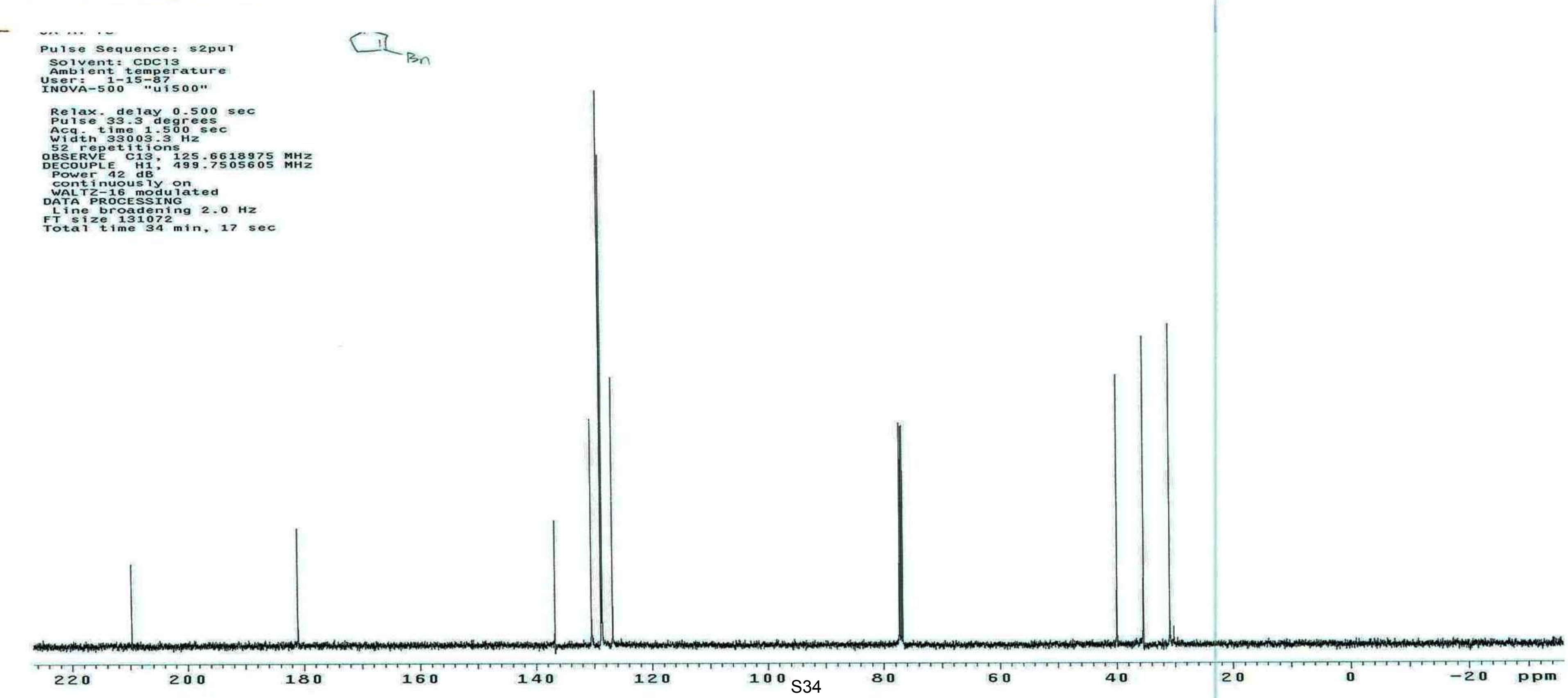
5.30b



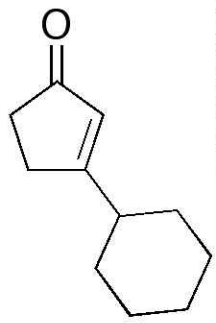
e: s2pul
:13
erature
ui500"
legrees
000 sec
) Hz
ns
499.7485680 MHz
NG
72
min, 4 sec
ppm
1.68.65
0.90
0.74
2.06
2.02
2.00



ERKIN ELMER
96.11
%T
25.74
3062.0
3028.9
2919.7
1705.8
1674.2
1616.1
1495.7
1453.8
1437.9
1407.8
1364.4
1341.8
1280.9
1256.0
1183.2
1075.7
1029.7
990.5
915.2
840.3
758.1
701.5
619.0
486.6
461.0
4000
3500
3000
2500
2000
1500
1000
cm-1
500
06/10/09 11:35
X: 4 scans, 4.0cm-1

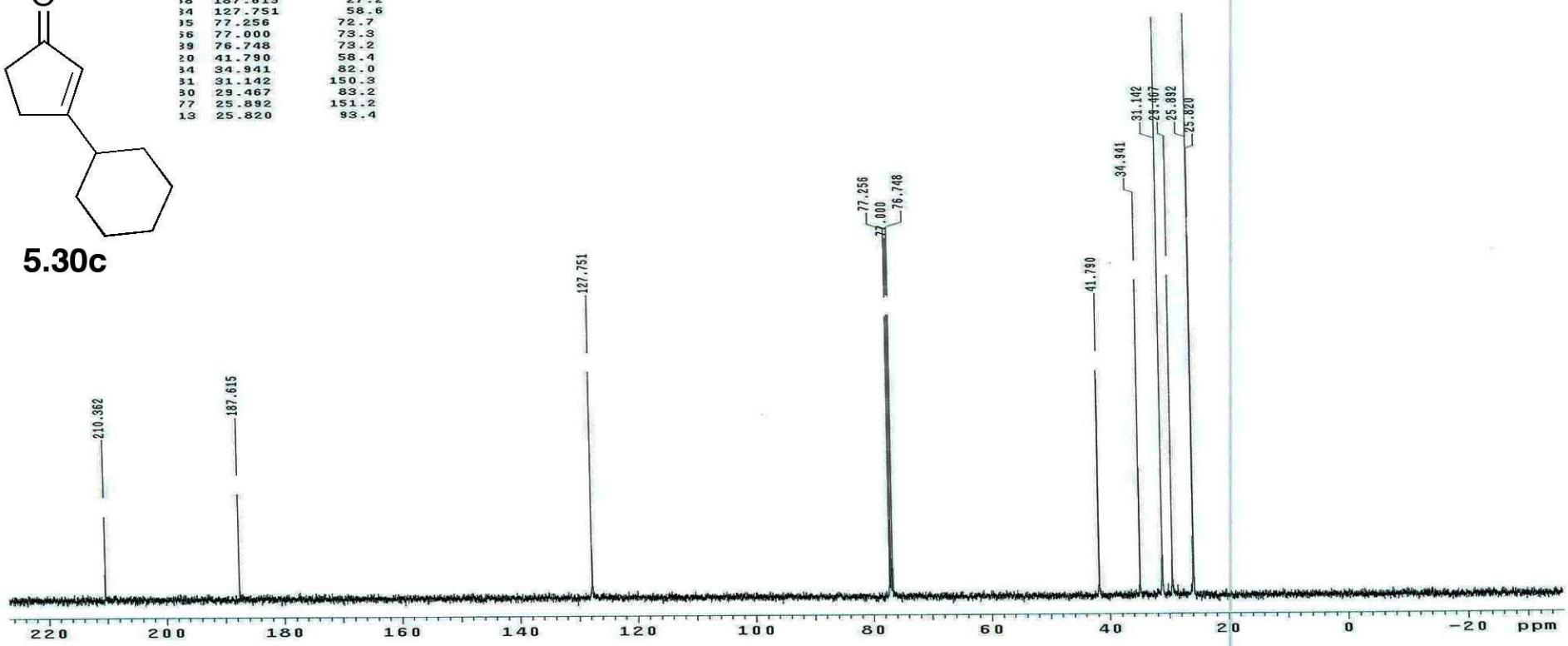


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"
Relax. delay 0.500 sec
Pulse 33.3 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
52 repetitions
OBSERVE C13, 125.6618975 MHz
DECOUPLE H1, 499.7505605 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec
ppm



5.30c

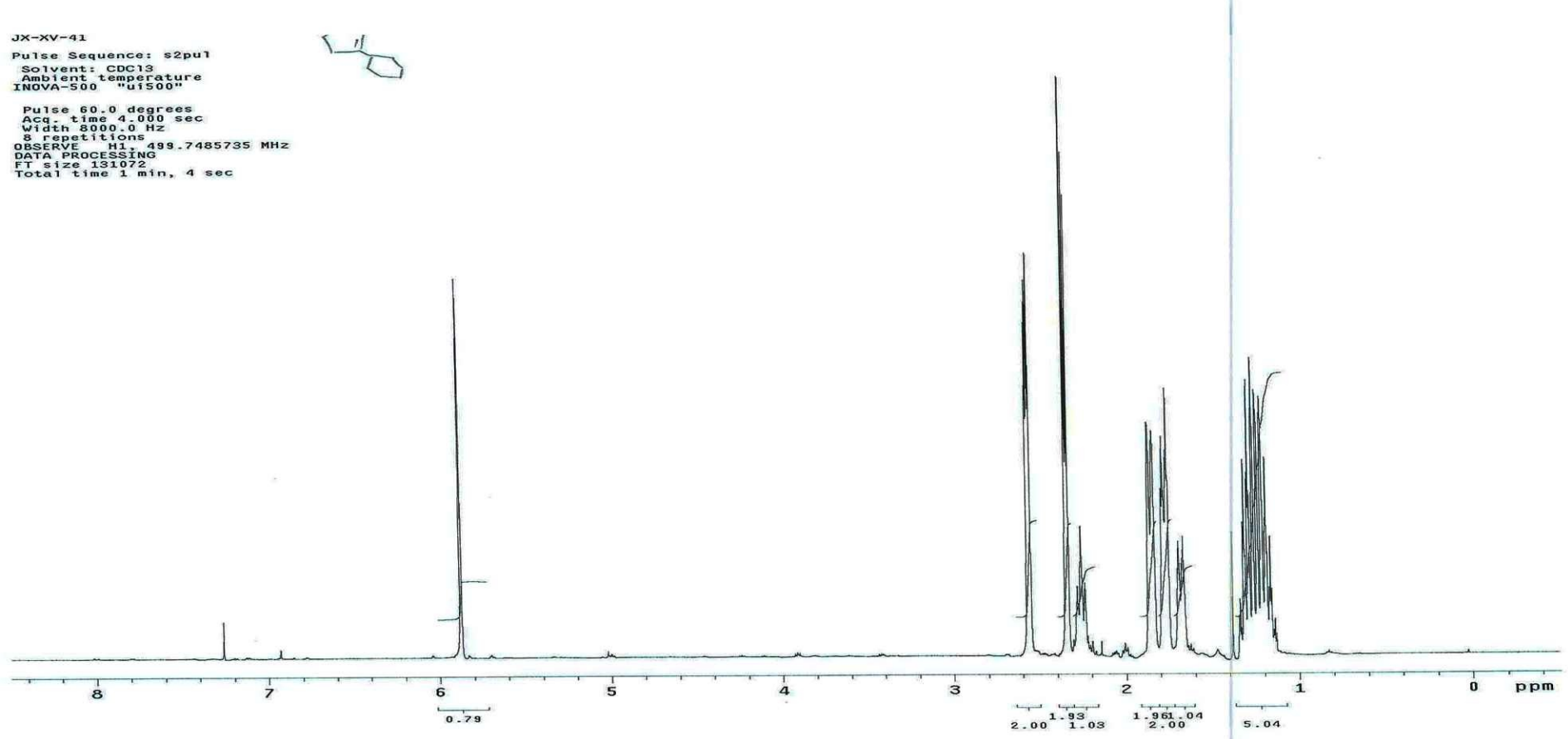
Y	PPM	HEIGHT
17	210.362	21.6
18	187.615	27.2
34	127.751	58.6
35	77.256	72.7
56	77.000	73.3
39	76.748	73.2
20	41.790	58.4
34	34.941	82.0
31	31.142	150.3
50	29.467	83.2
77	25.892	151.2
13	25.820	93.4



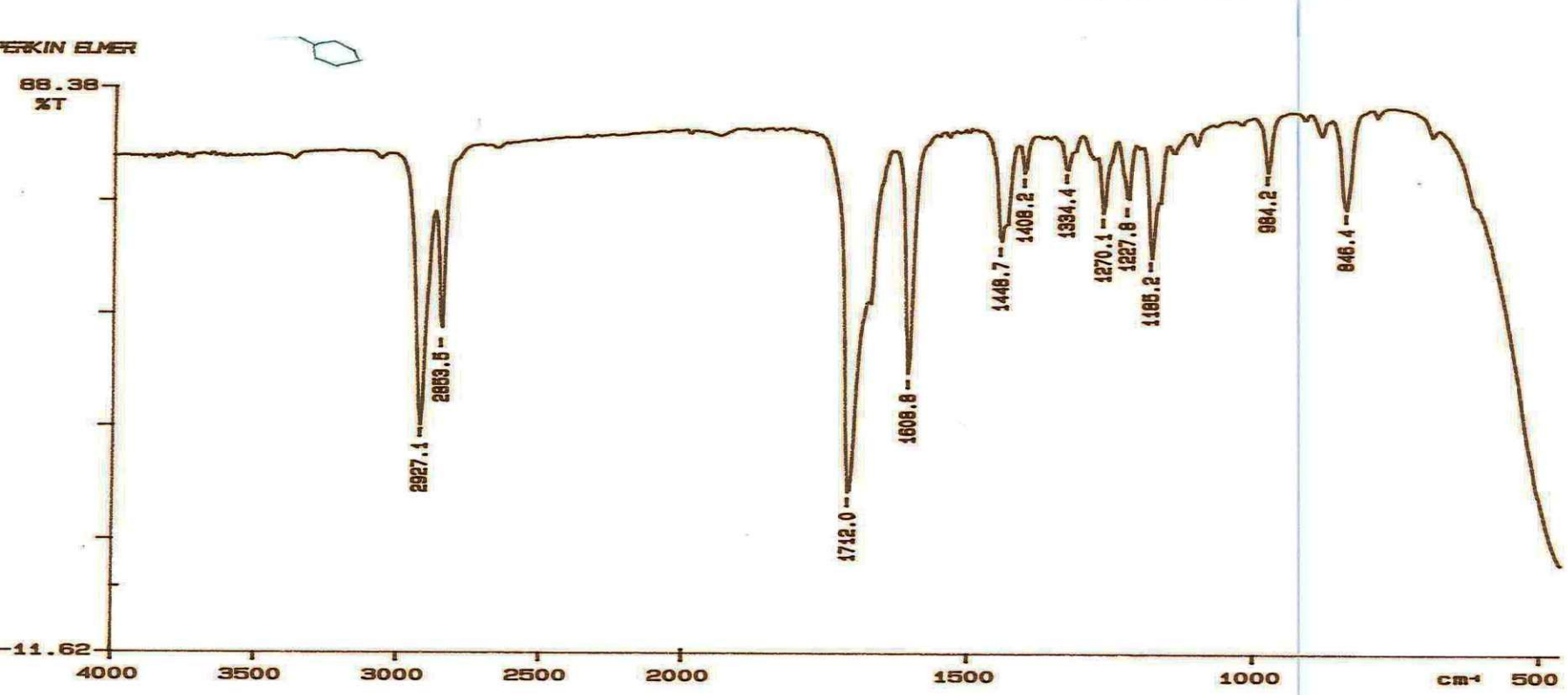
JX-XV-41

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "u1500"

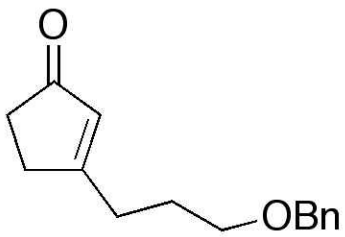
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



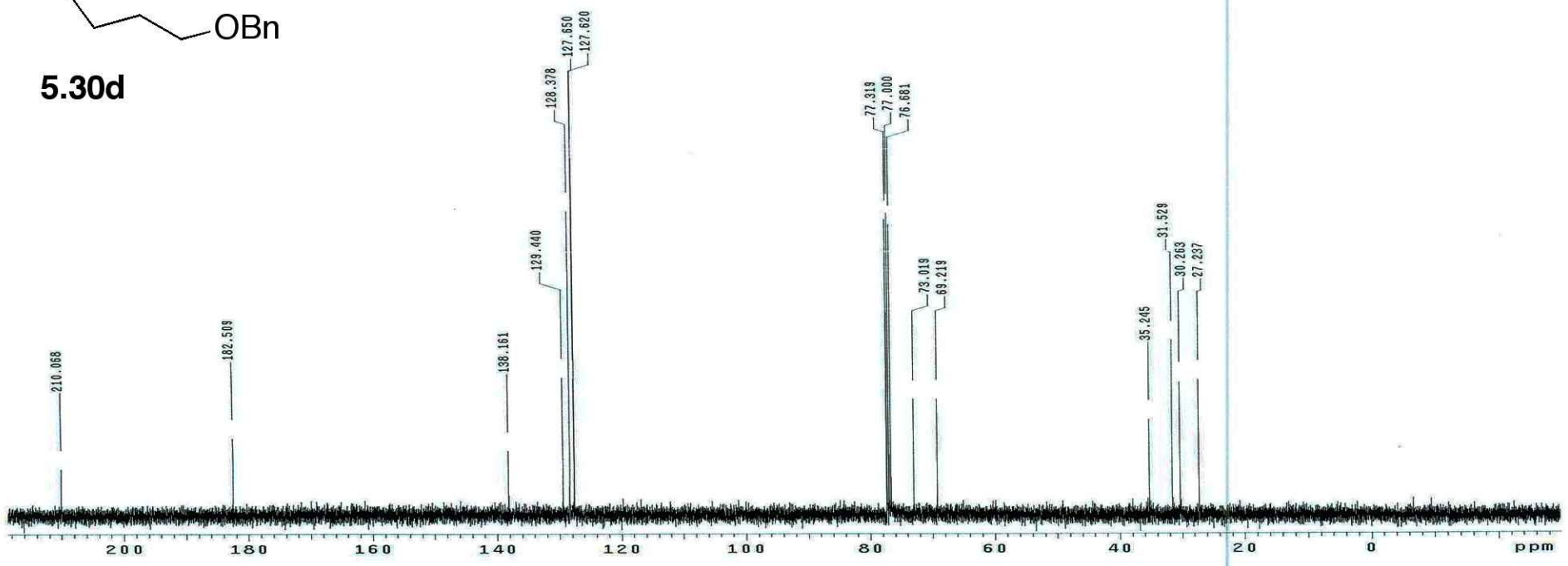
PERKIN ELMER

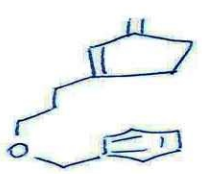


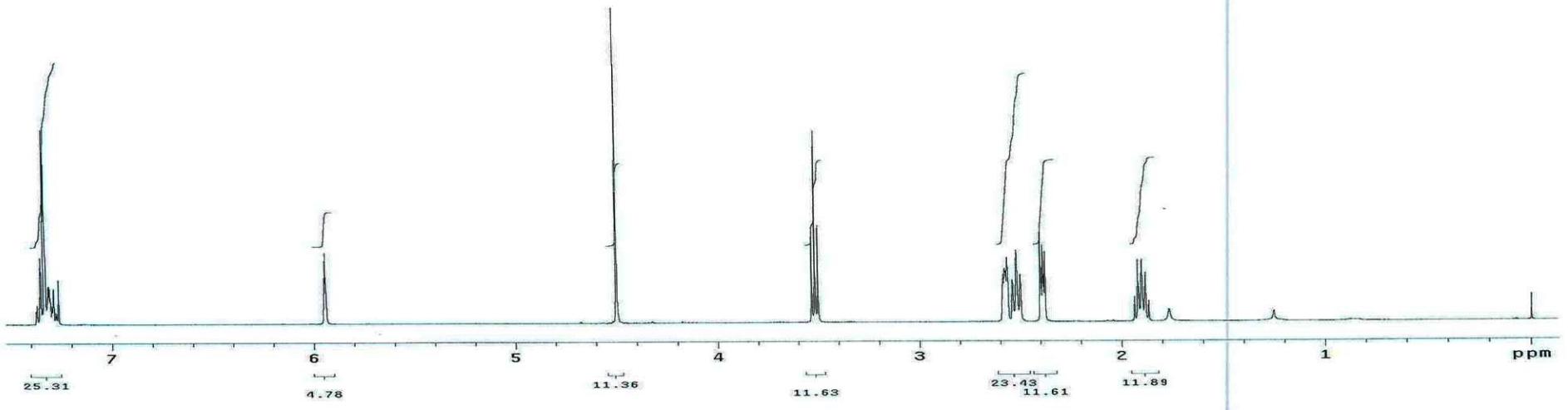
06/08/22 16:50
X: 4 scans, 4.0cm-1

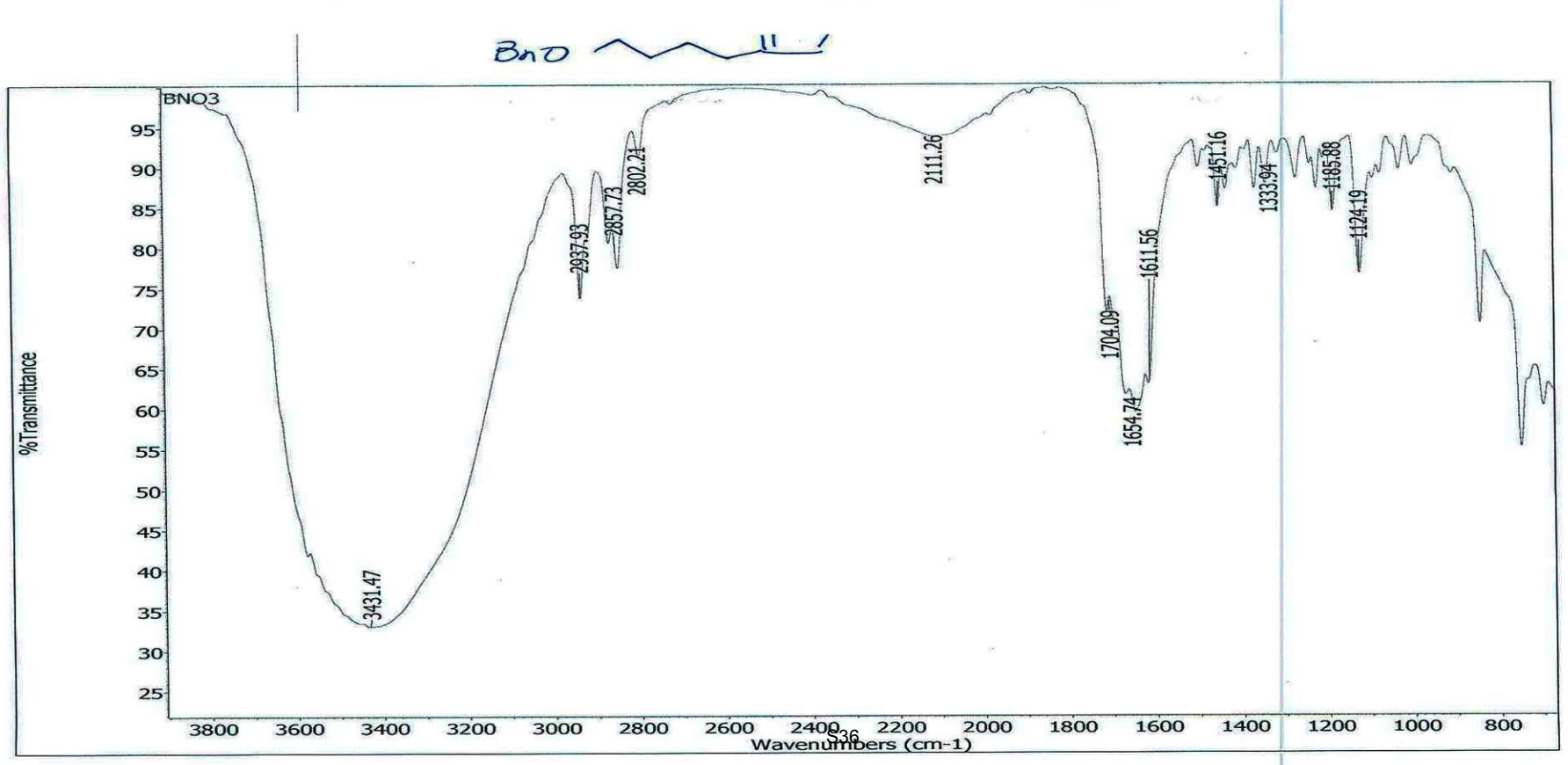

O
OBn

5.30d


210.068
182.509
138.161
129.440
128.378
127.650
127.620
77.319
77.000
76.681
73.019
69.219
35.245
31.529
30.263
27.237
200
180
160
140
120
100
80
60
40
20
0
ppm

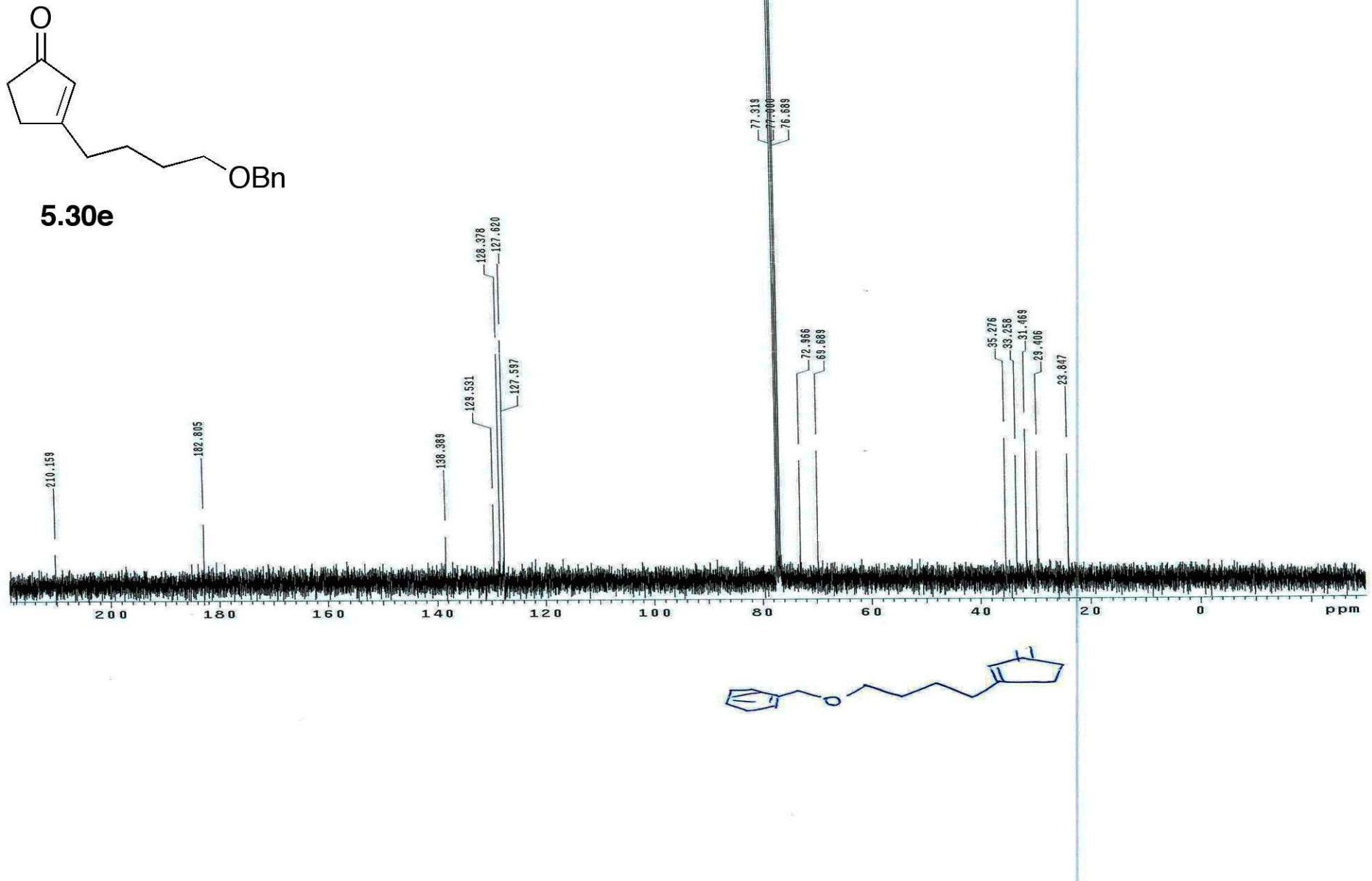


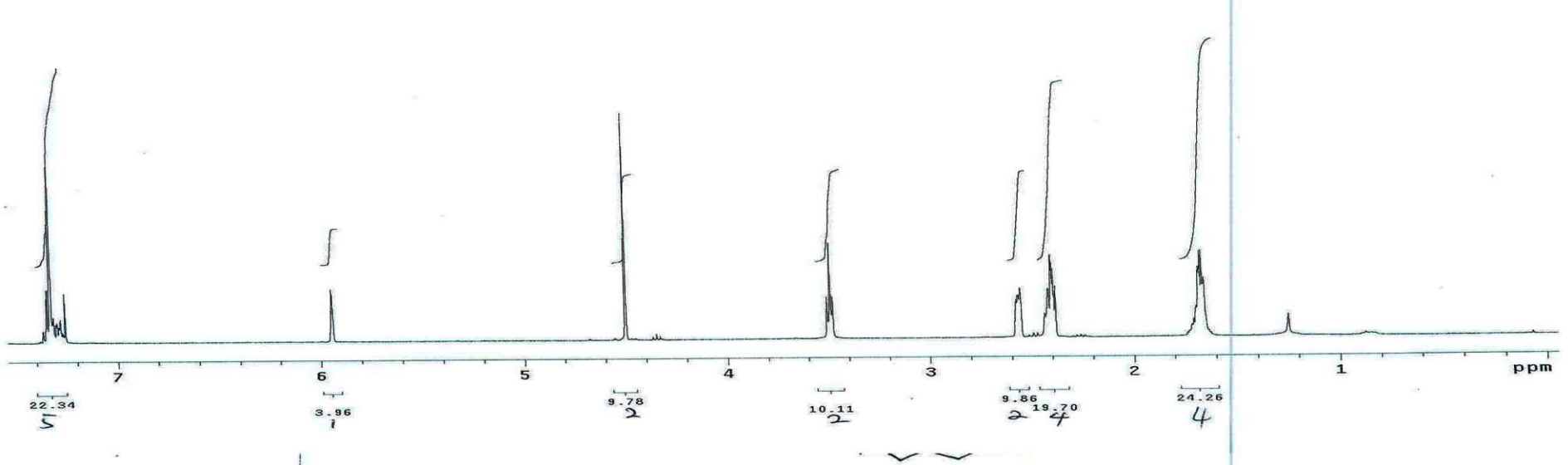

7
6
5
4
3
2
1
ppm
25.31
4.78
11.36
11.63
23.43
11.61
11.89

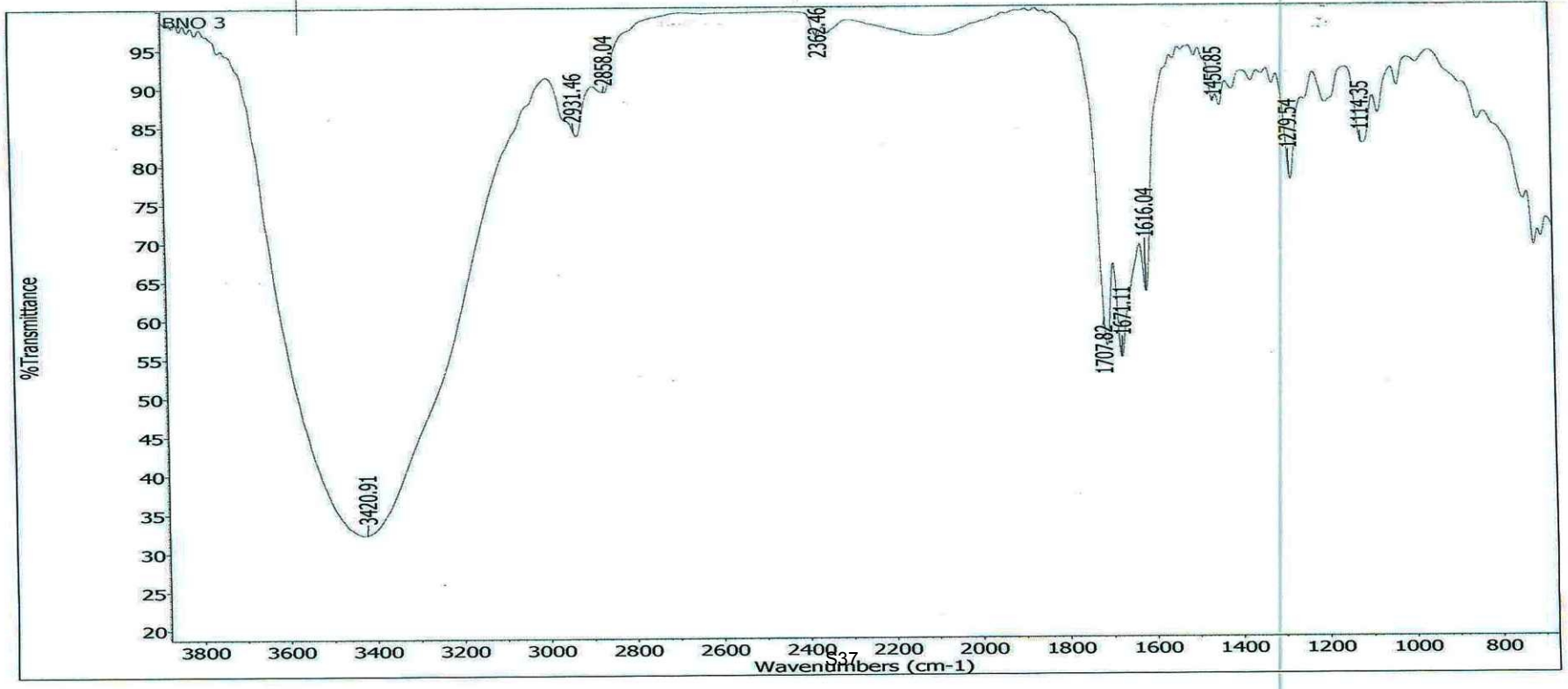

BnO
BNQ3
%Transmittance
3431.47
2937.93
2857.73
2802.21
2111.26
1704.09
1654.74
1611.56
1451.16
1333.94
1185.88
1124.19
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumbers (cm-1)

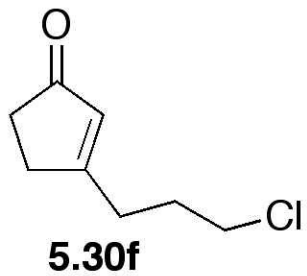
O
OBn

5.30e

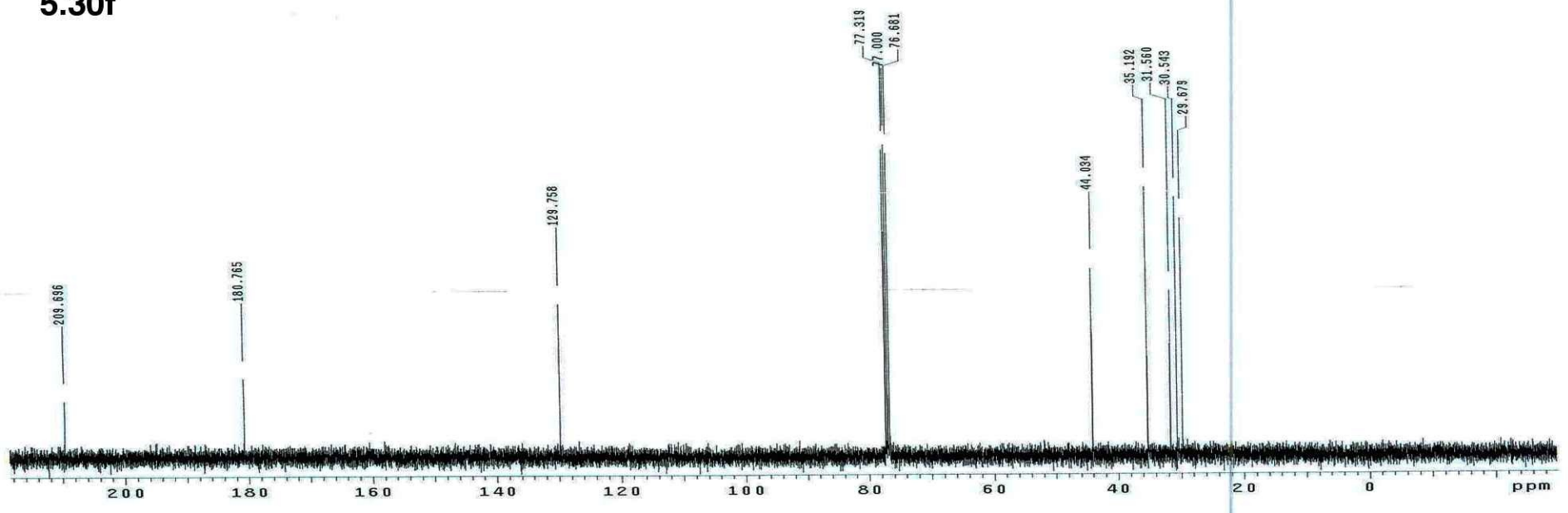

210.159
182.805
138.389
129.531
128.378
127.620
127.597
77.319
77.000
76.689
72.966
69.688
35.276
33.258
31.468
29.406
23.847
200
180
160
140
120
100
80
60
40
20
0
ppm


7
6
5
4
3
2
1
ppm
22.34
3.96
9.78
10.11
9.86
19.70
24.26

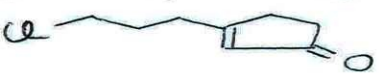

BNO 3
%Transmittance
3420.91
2931.46
2858.04
2362.46
1707.82
1671.11
1616.04
1450.85
1279.54
1114.35
Wavenumbers (cm-1)



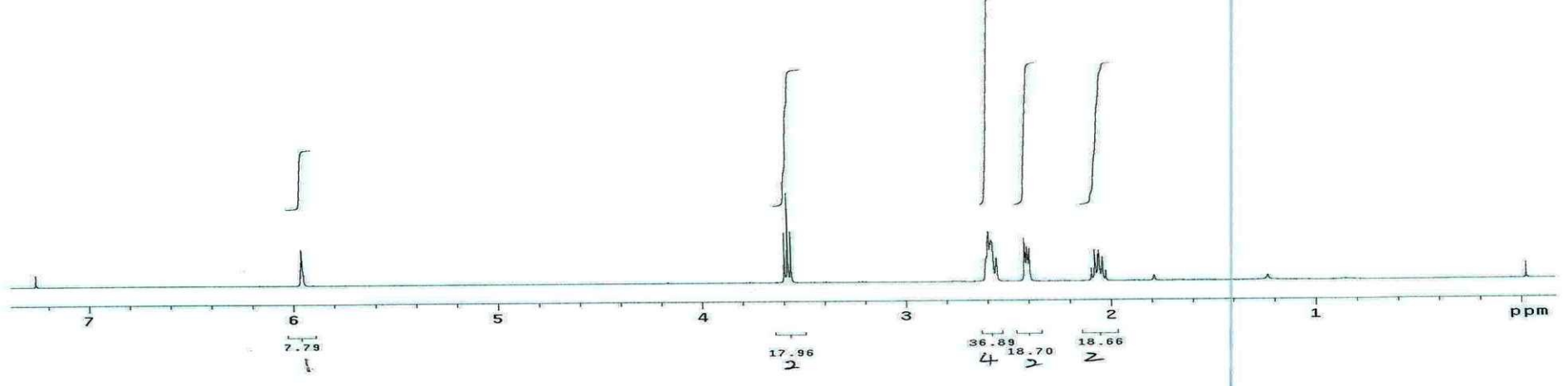
5.30f

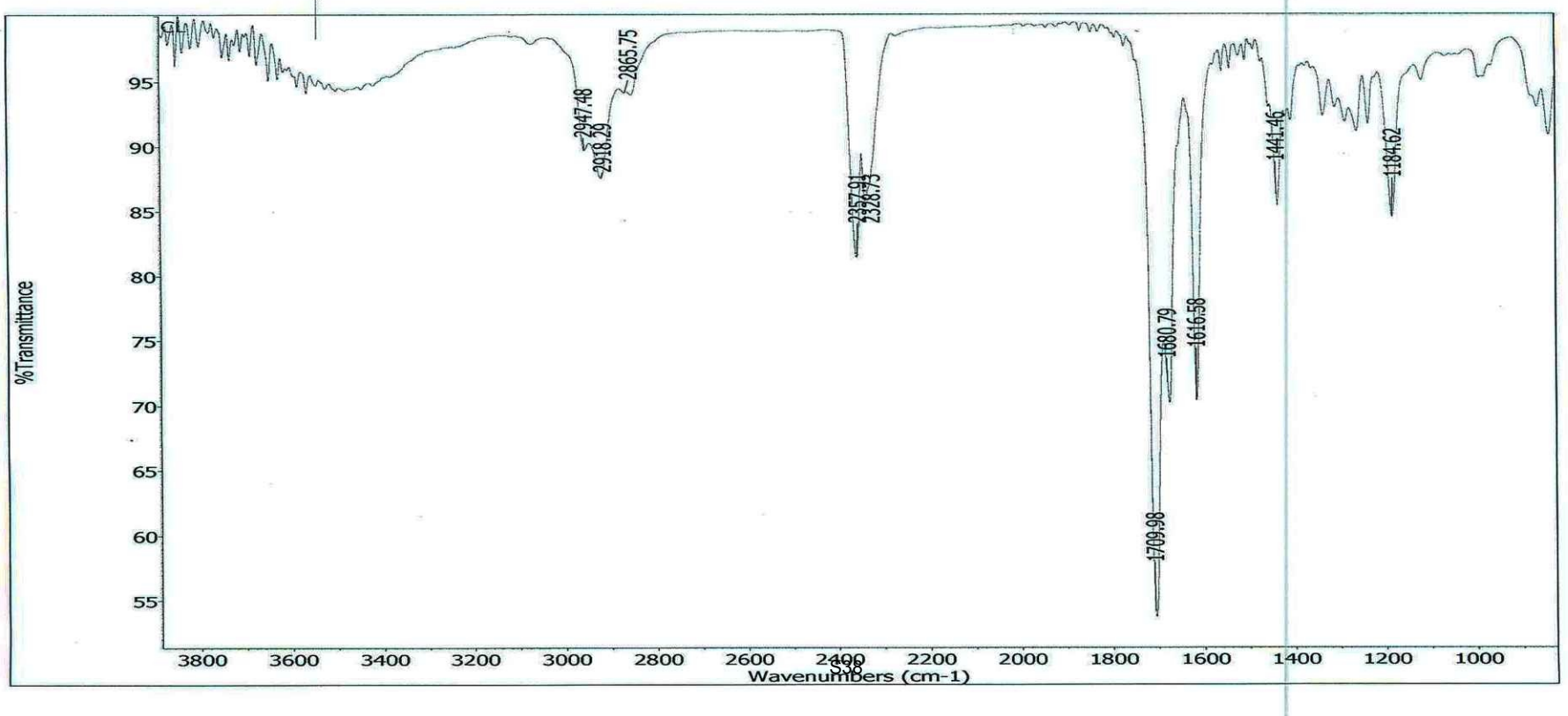


[CC 2005, 3030-3032]



741.0





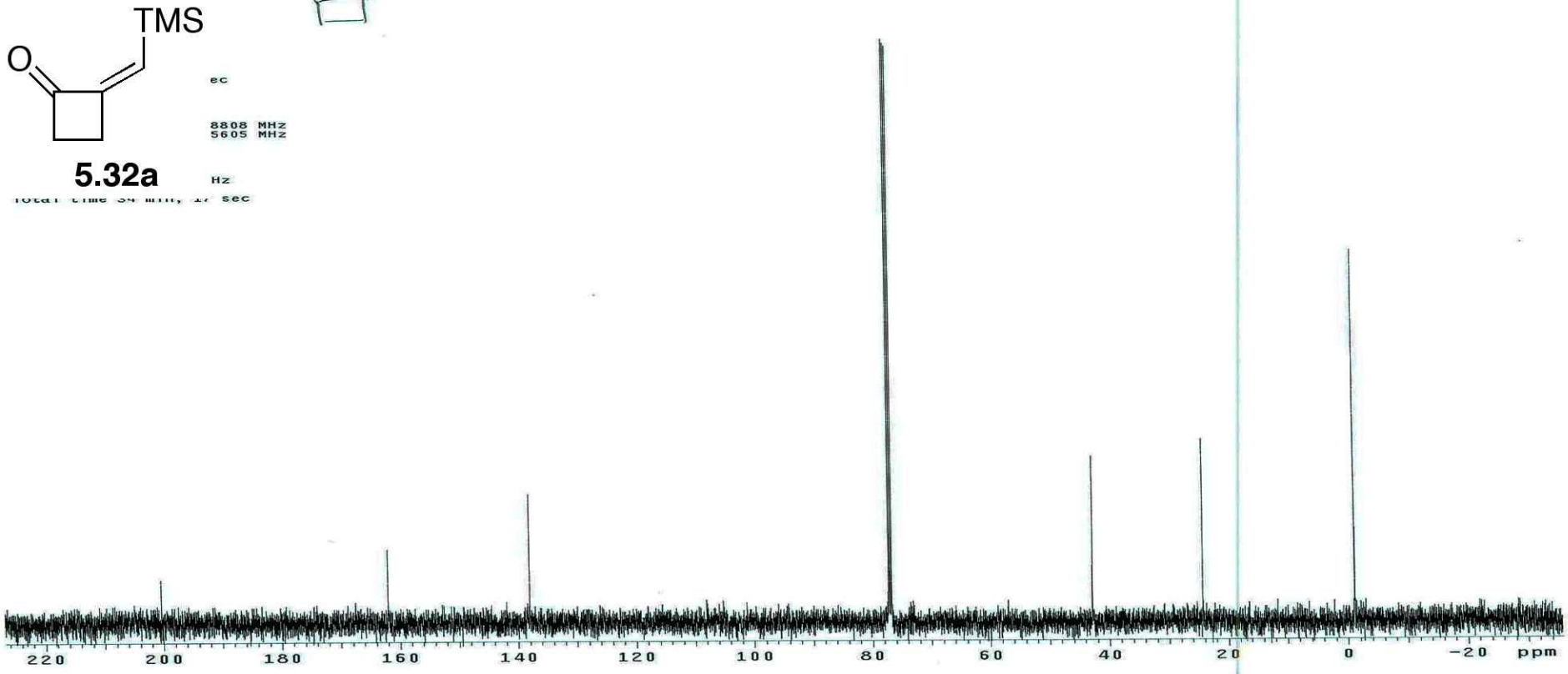
ec

8808 MHz
5605 MHz

5.32a

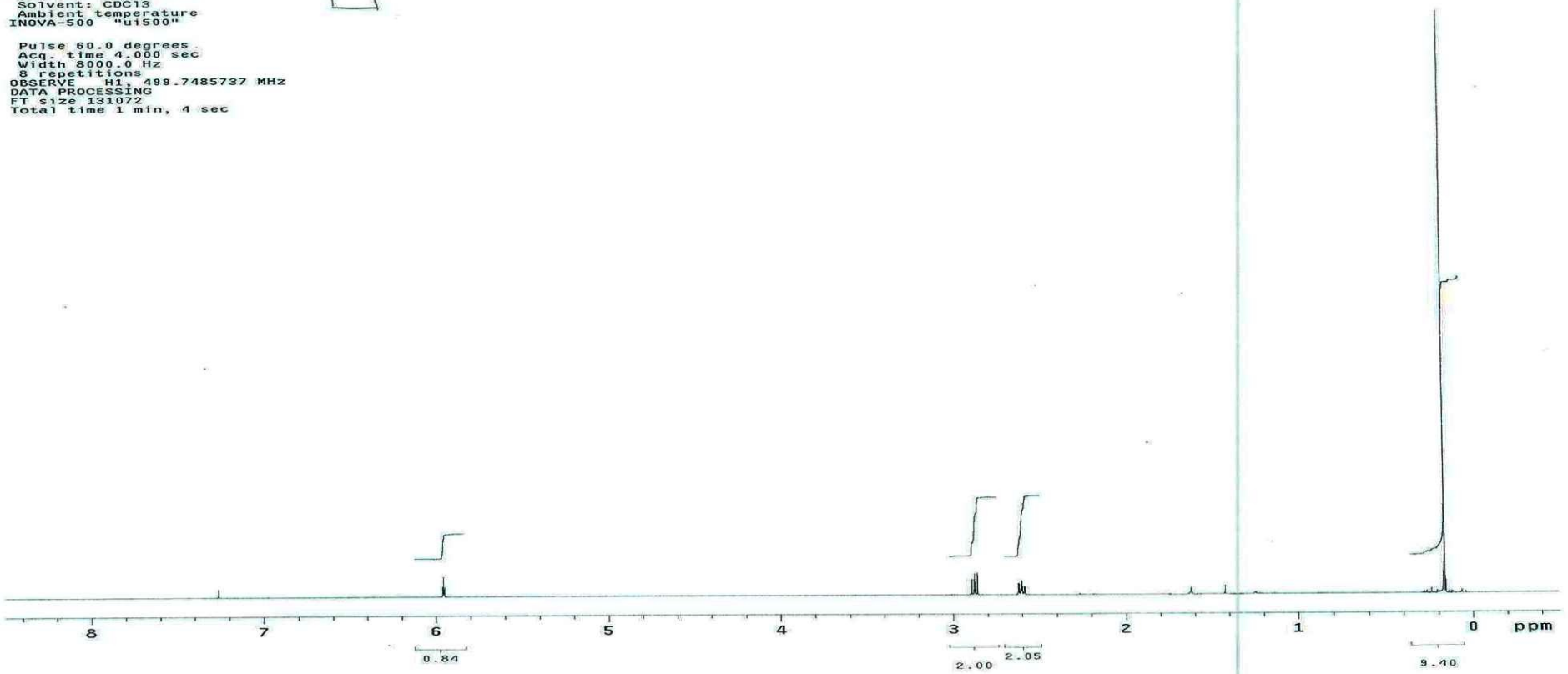
Hz

Total time 34 min, 17 sec

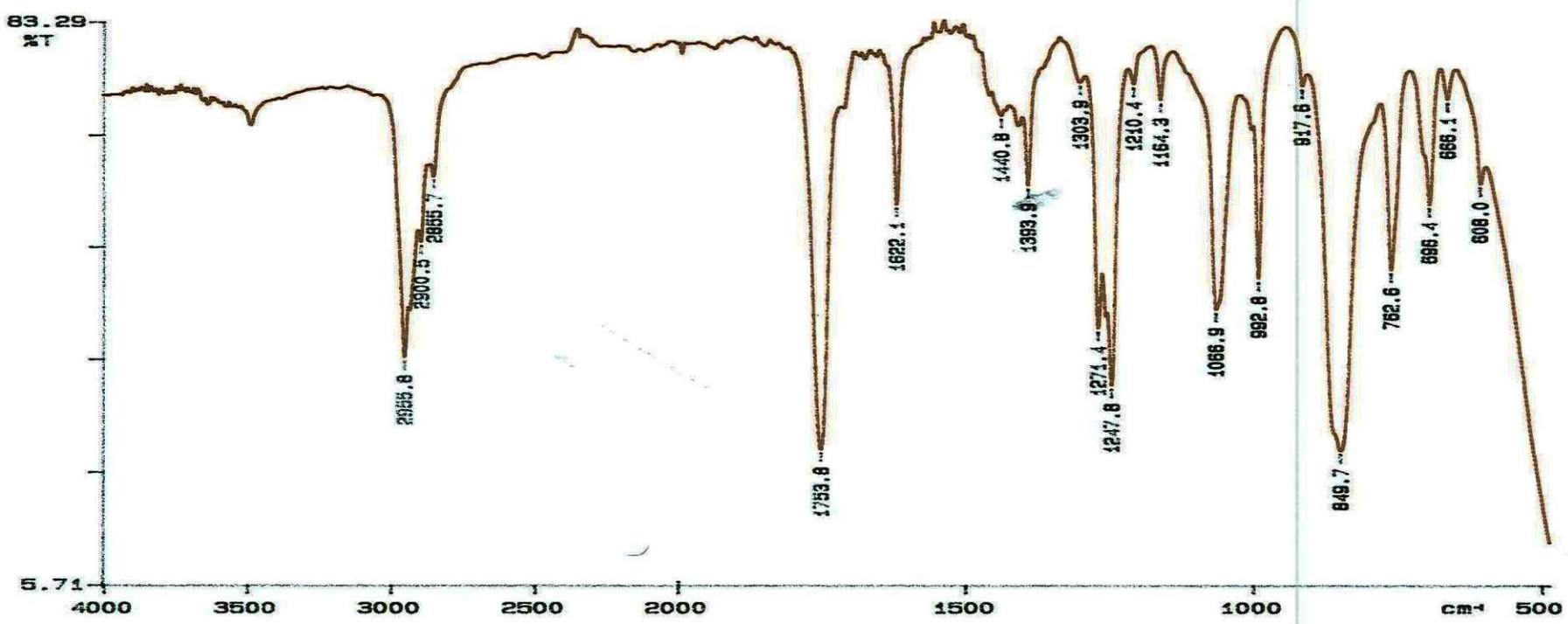


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "u1500"

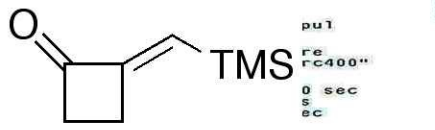
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



PERKIN ELMER



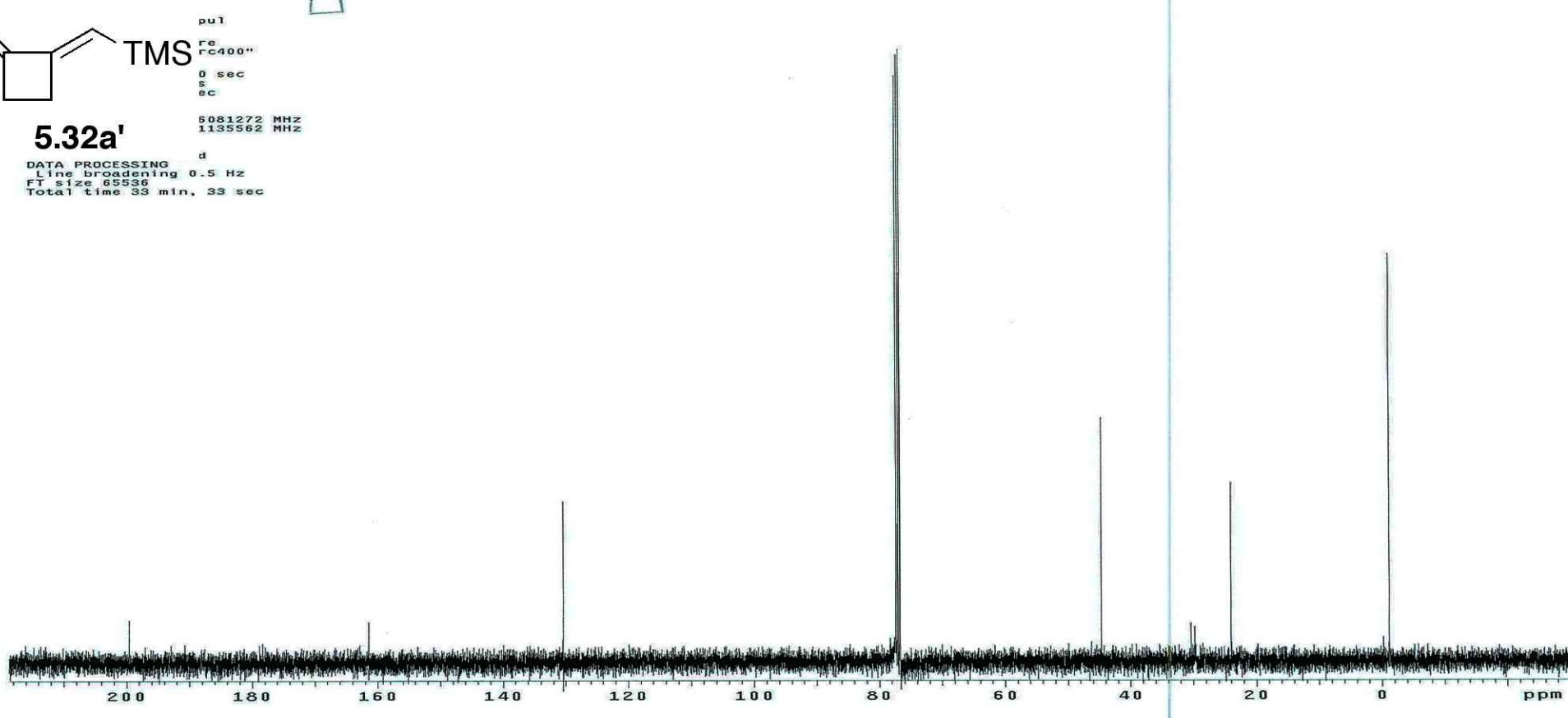
06/07/27 12:17
X: 4 scans, 4.0cm-1



5.32a'

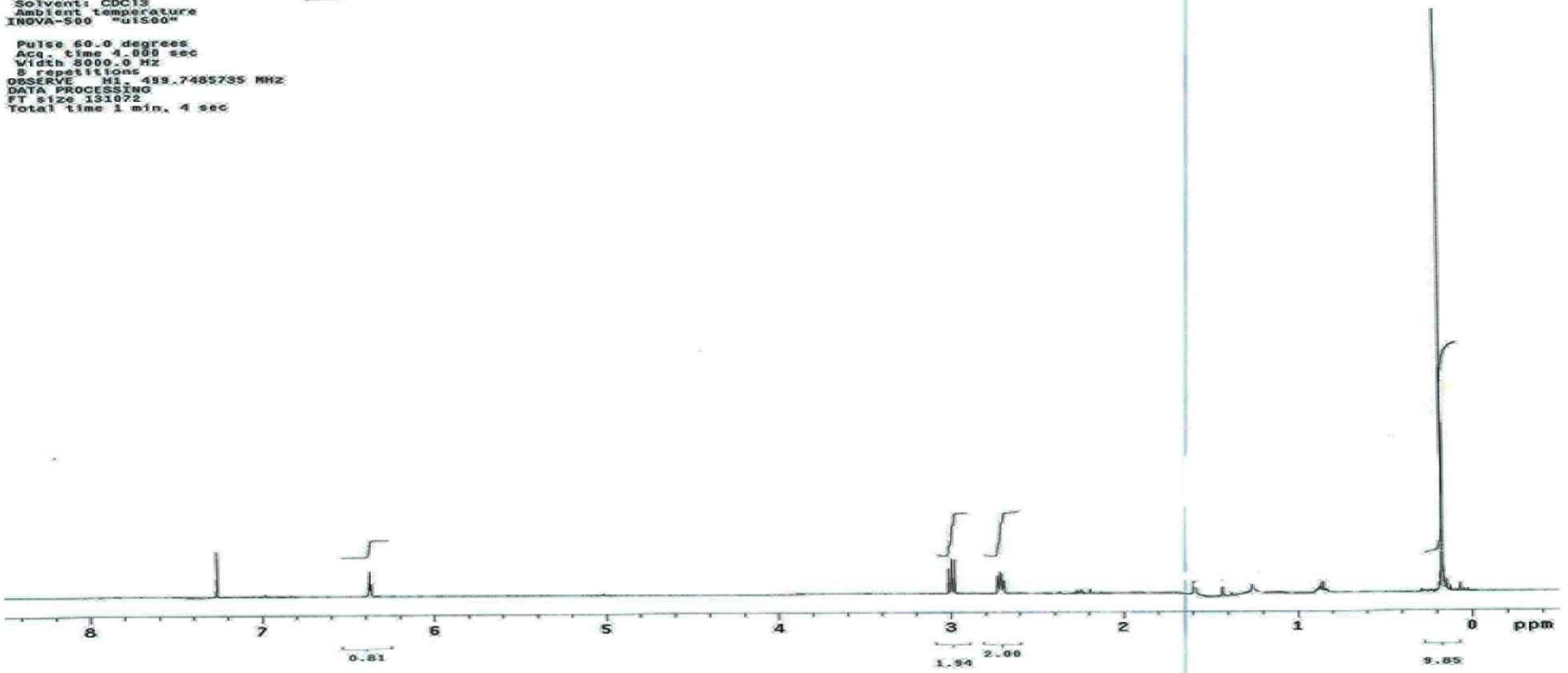
pul
re
rc400"
0 sec
s
ec
6081272 MHz
1135562 MHz
d

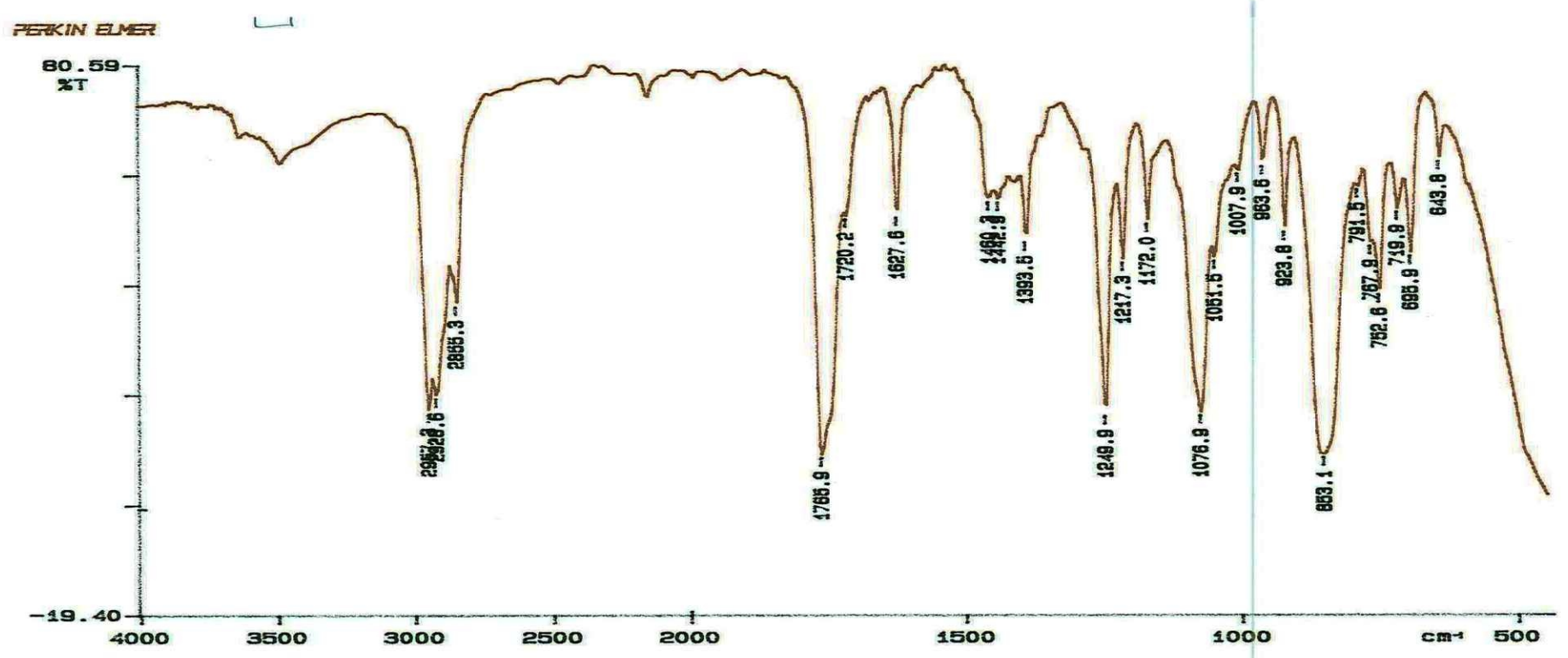
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec



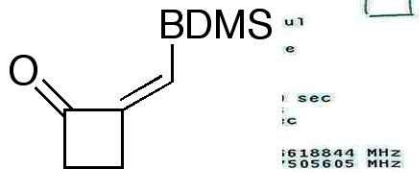
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "uis00"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



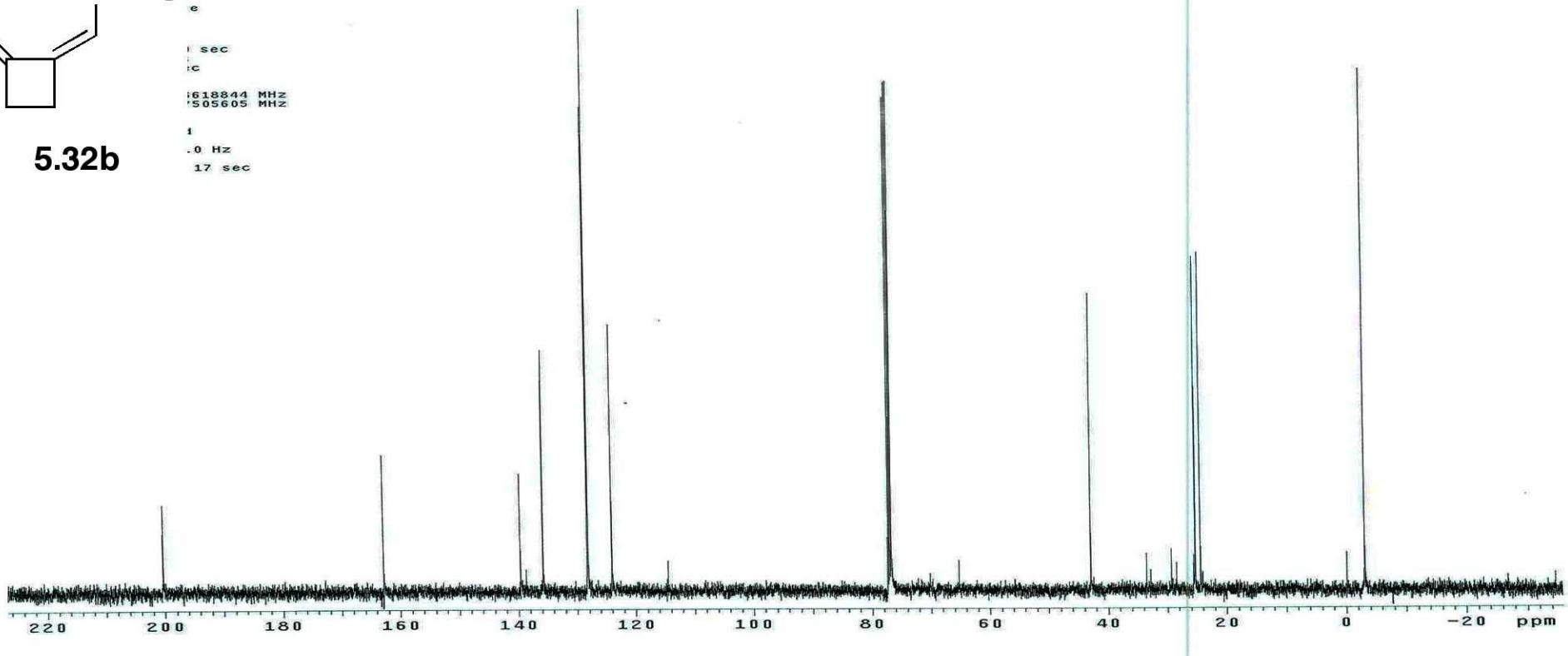


06/07/27 12:22
X: 4 scans, 4.0cm-1



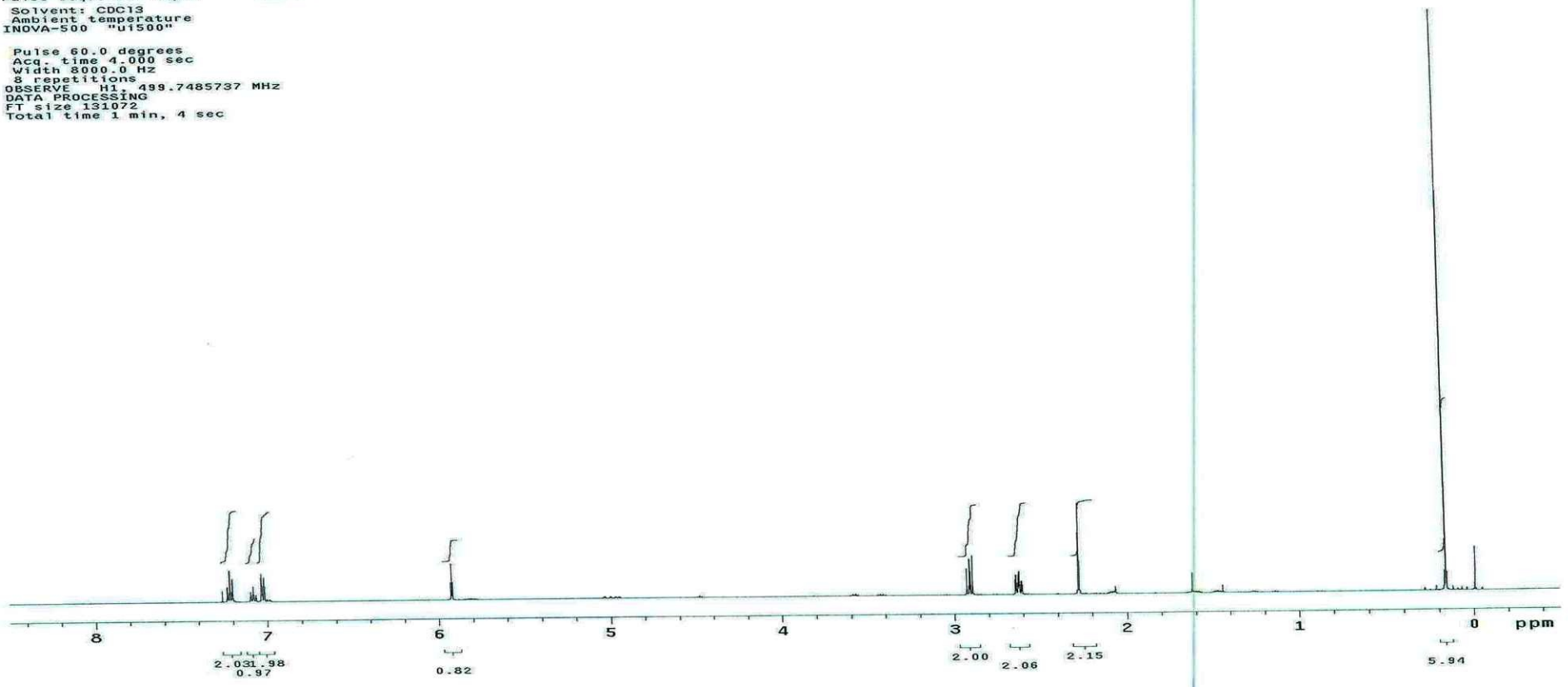
5.32b

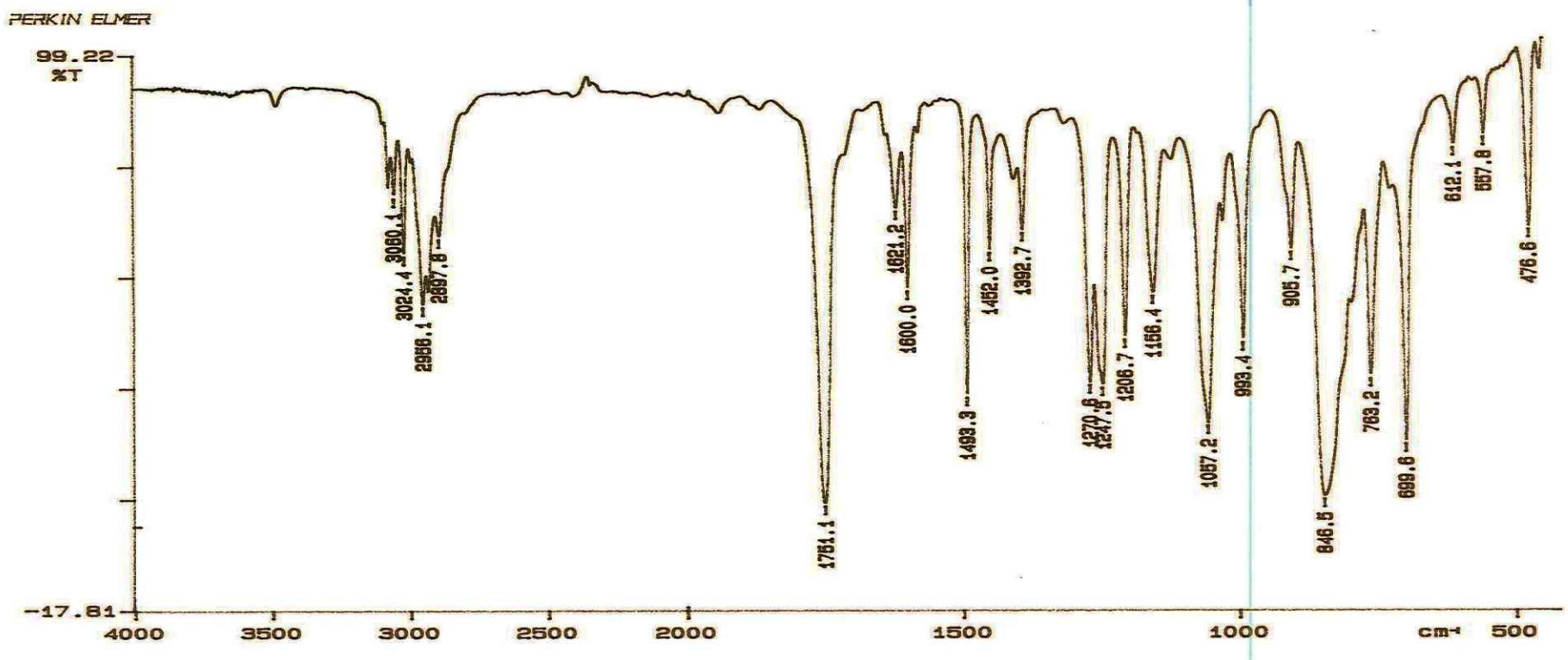
sec
618844 MHz
505605 MHz
.0 Hz
17 sec



JX-XV-83-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



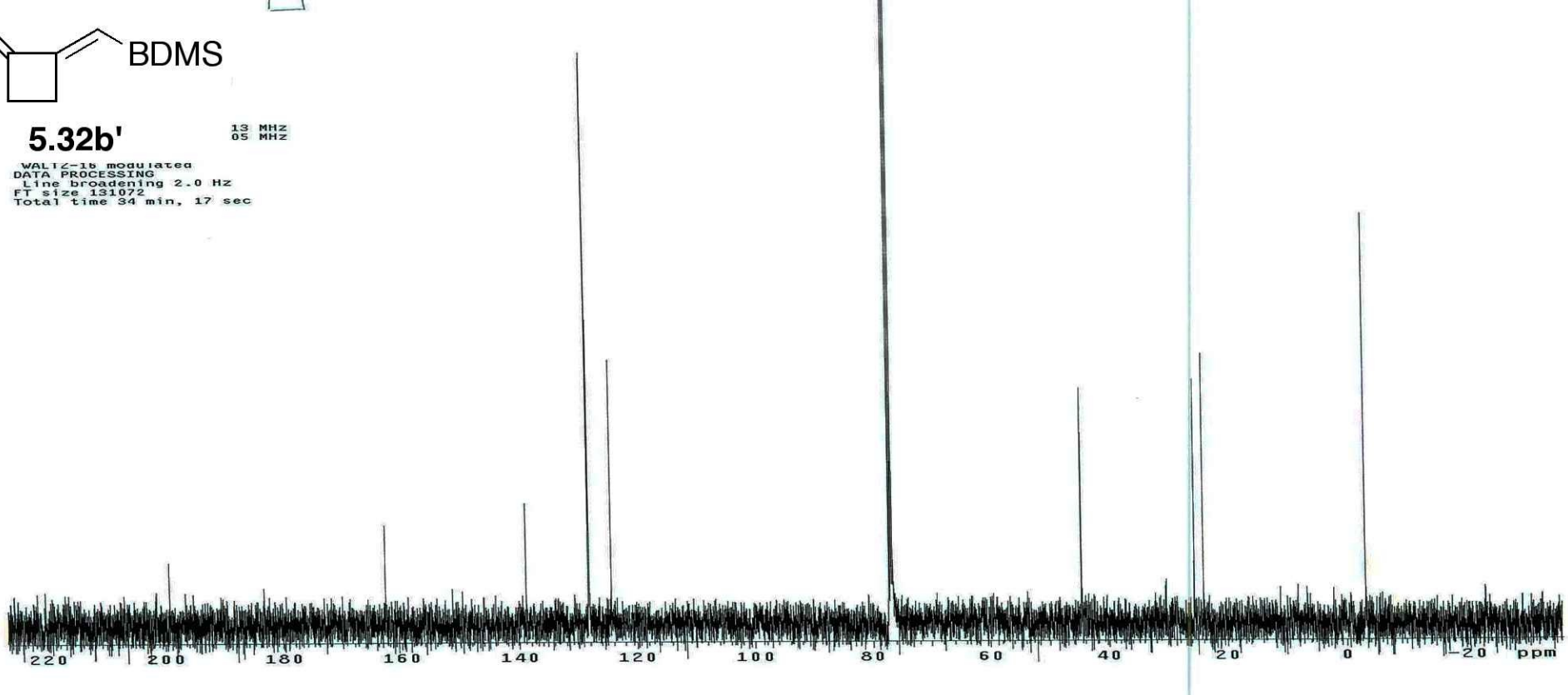


06/10/17 07:01
X: 4 scans, 4.0cm-1

5.32b'

13 MHz
05 MHz

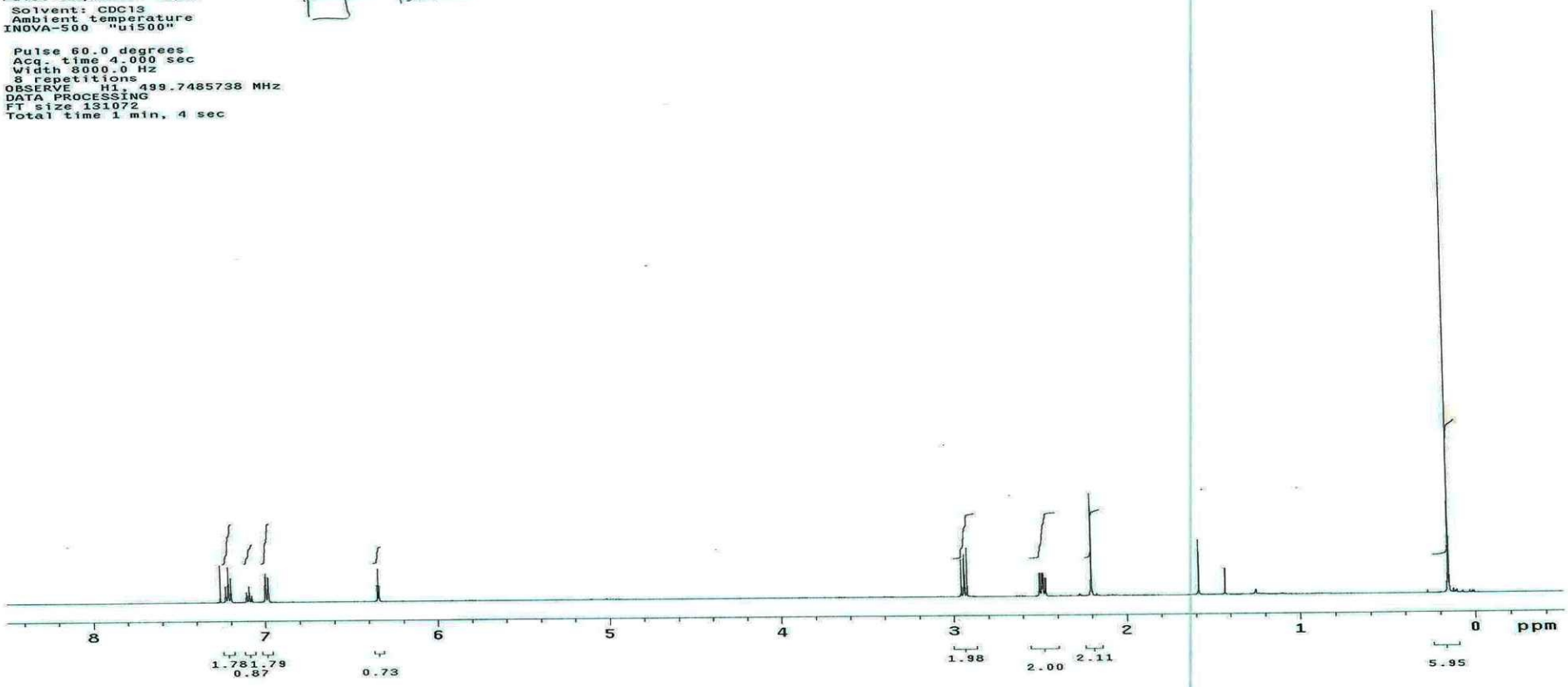
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec

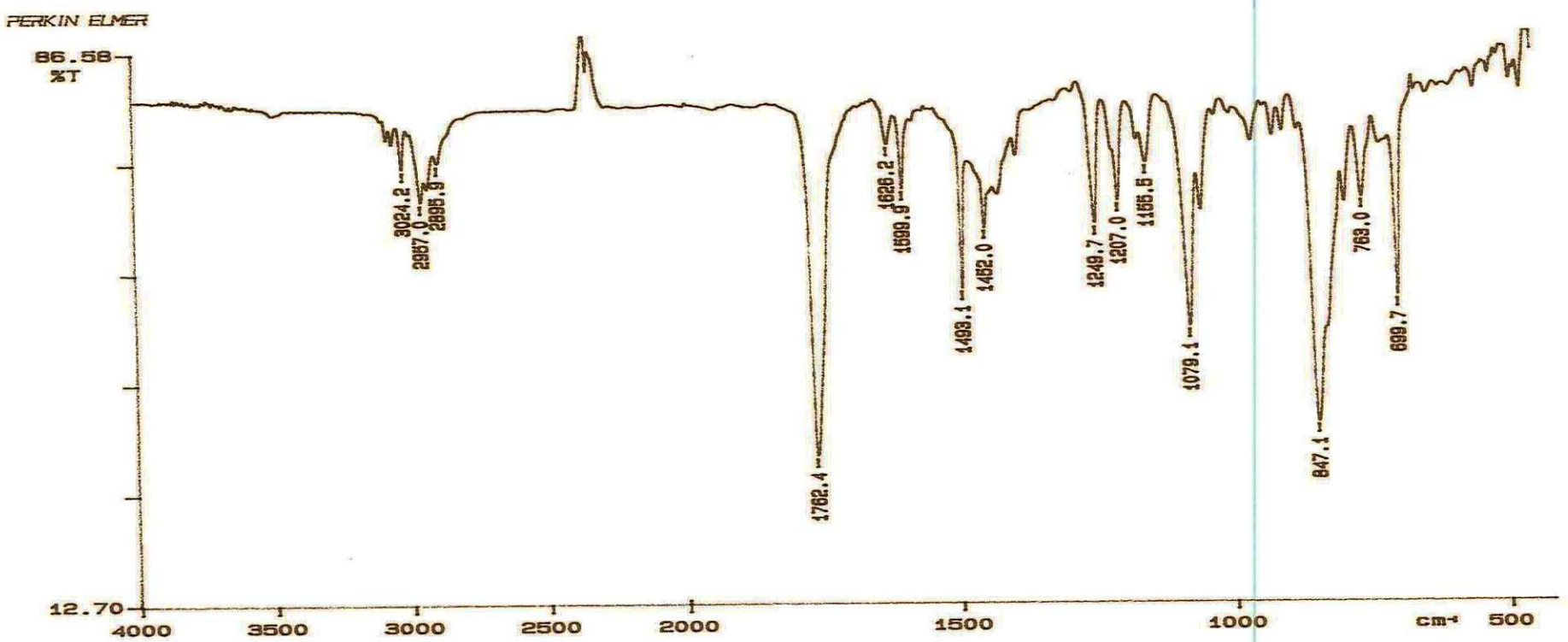


JX-XV-83-2

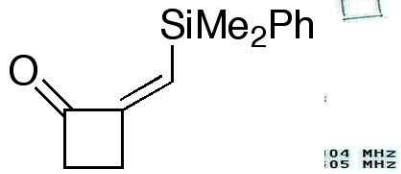
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "u1500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



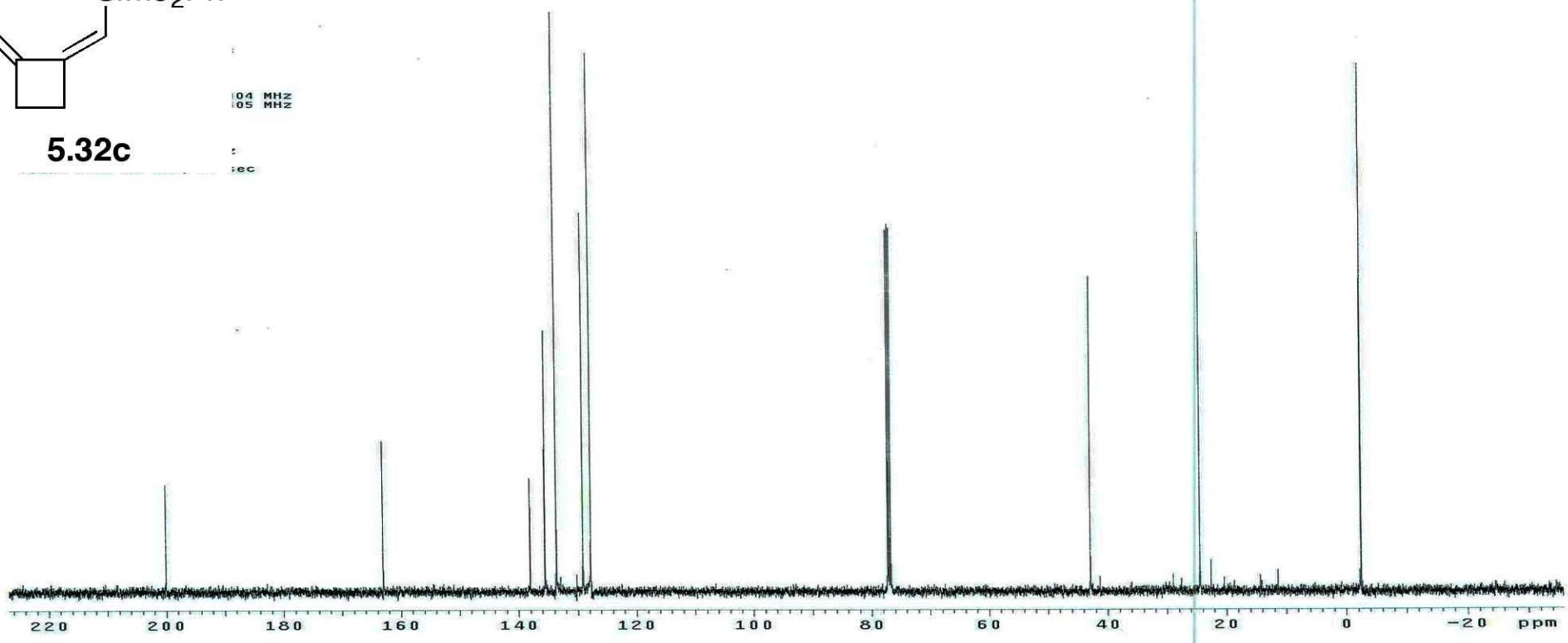


06/10/17 07:05
Y: 4 scans. 4.0cm-1. flat



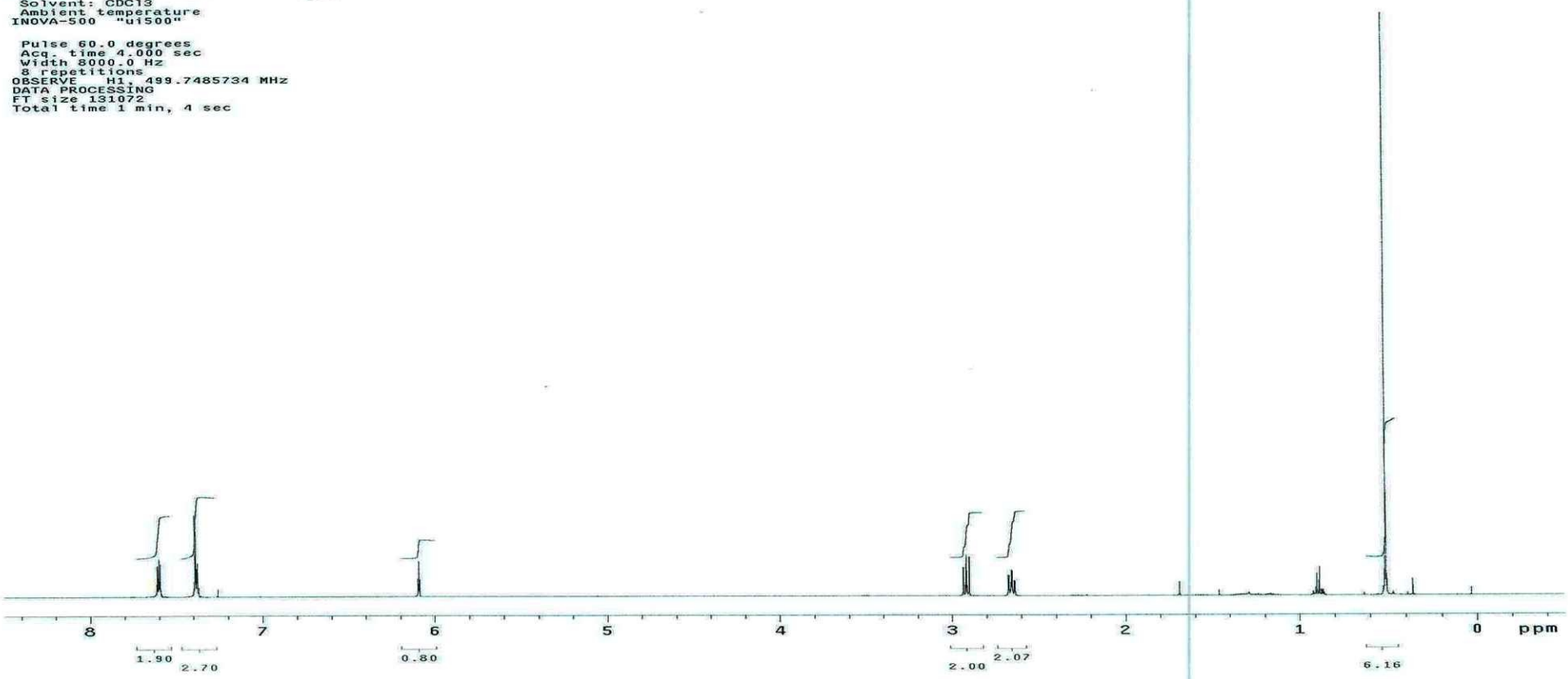
5.32c

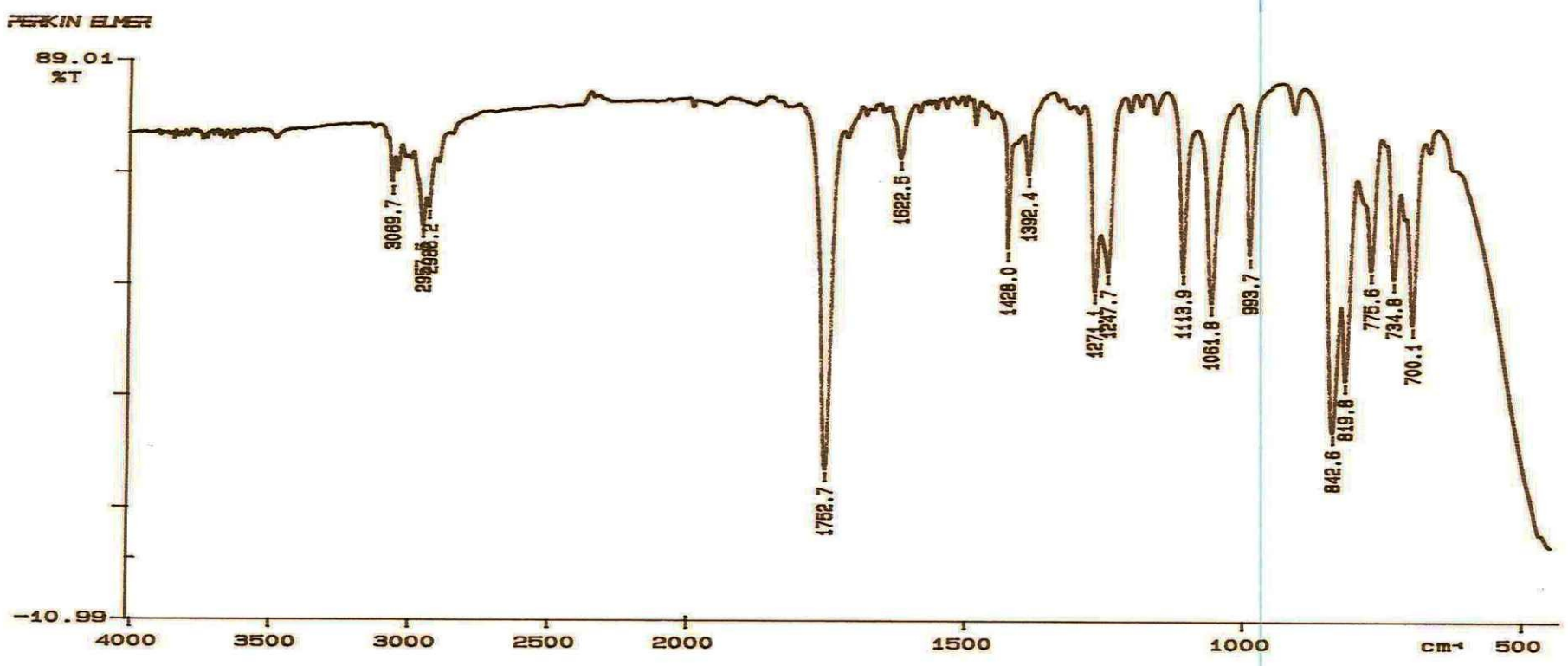
04 MHz
05 MHz
ec



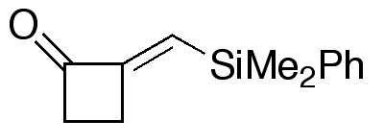
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485734 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec





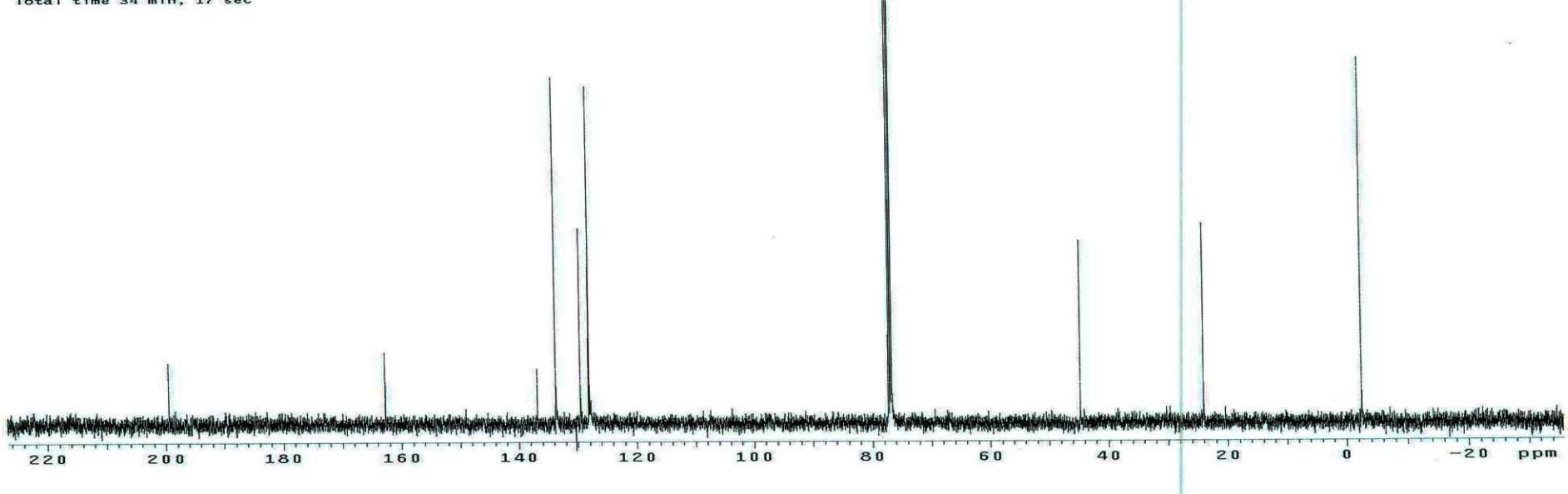
06/08/04 13:39
X: 4 scans, 4.0cm-1



5.32c'

MHz
MHz

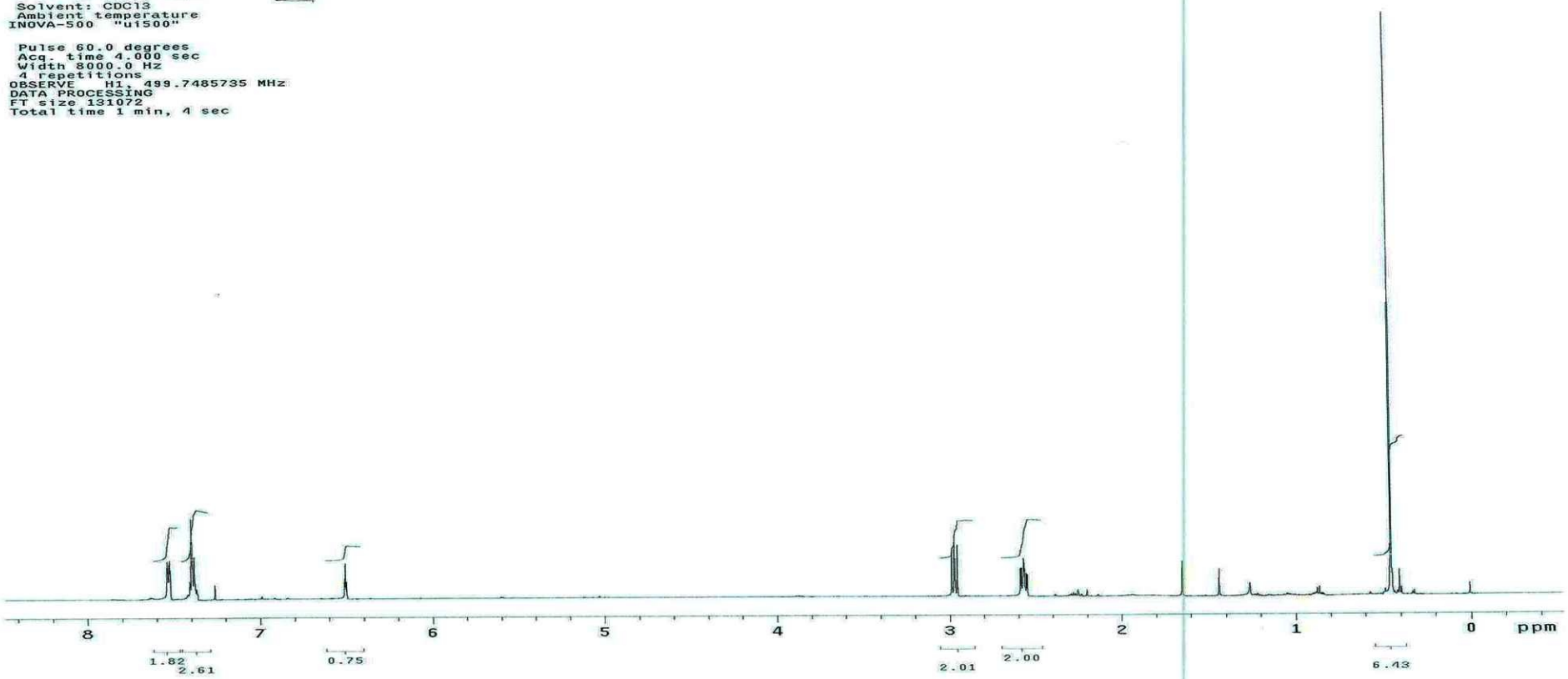
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec



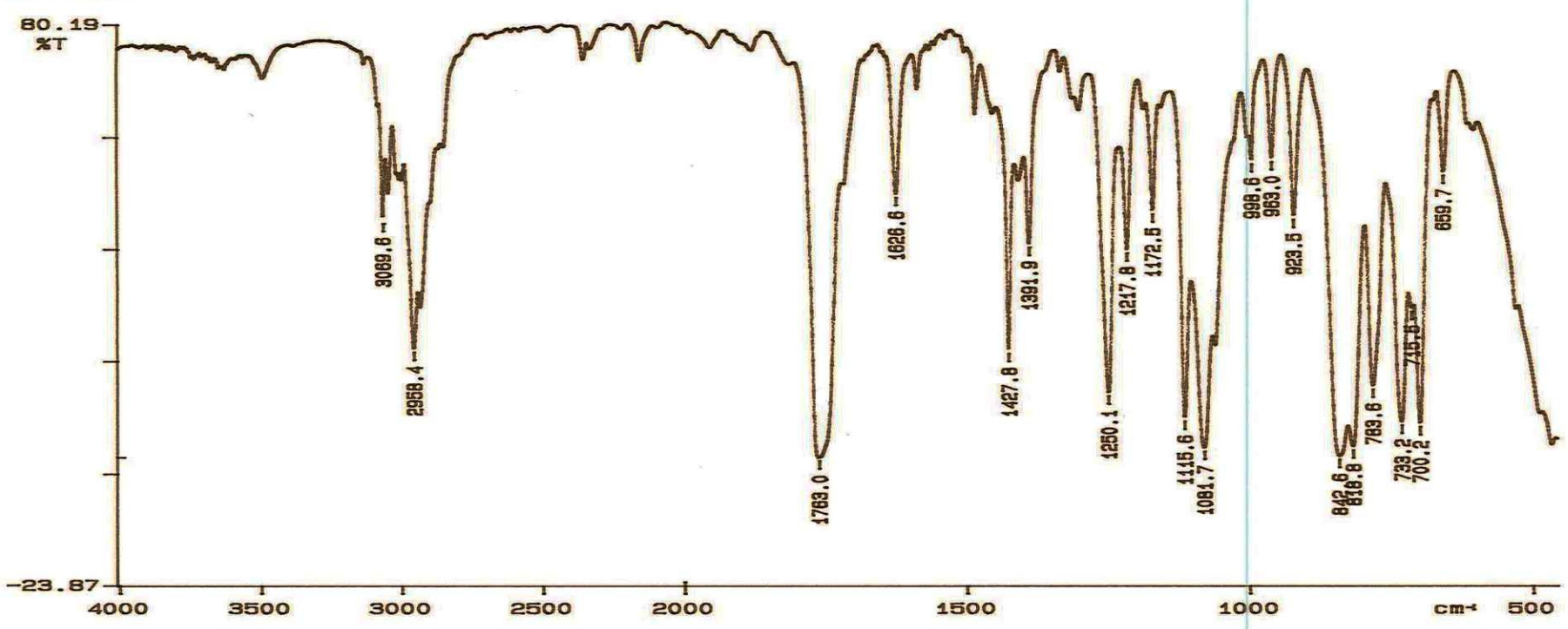
JX-XV-13-2

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

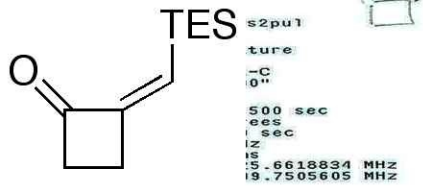
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec



PERKIN ELMER



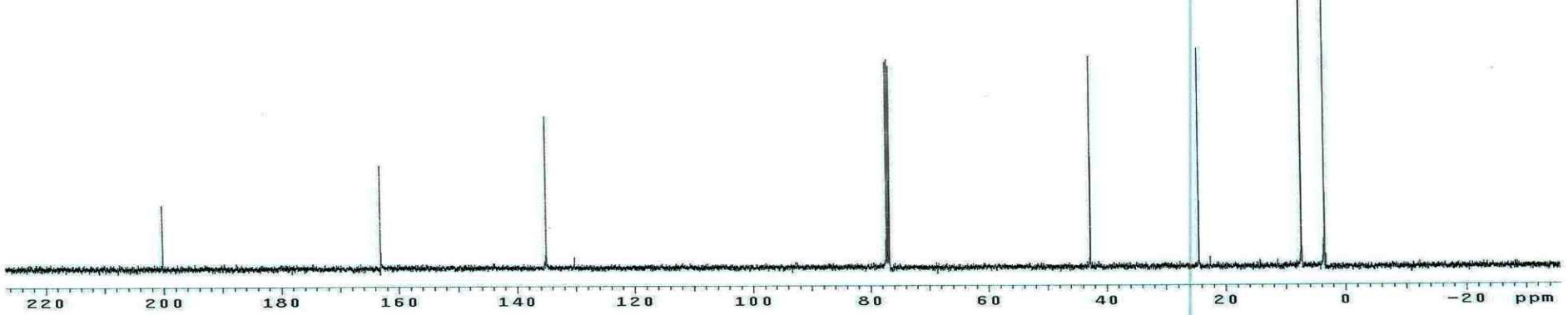
06/08/04 16:34
X: 4 scans, 4.0cm−1



s2pul
ture
-C
0"
500 sec
ees
sec
z
s
5.6618834 MHz
9.7505605 MHz
ted
2.0 Hz

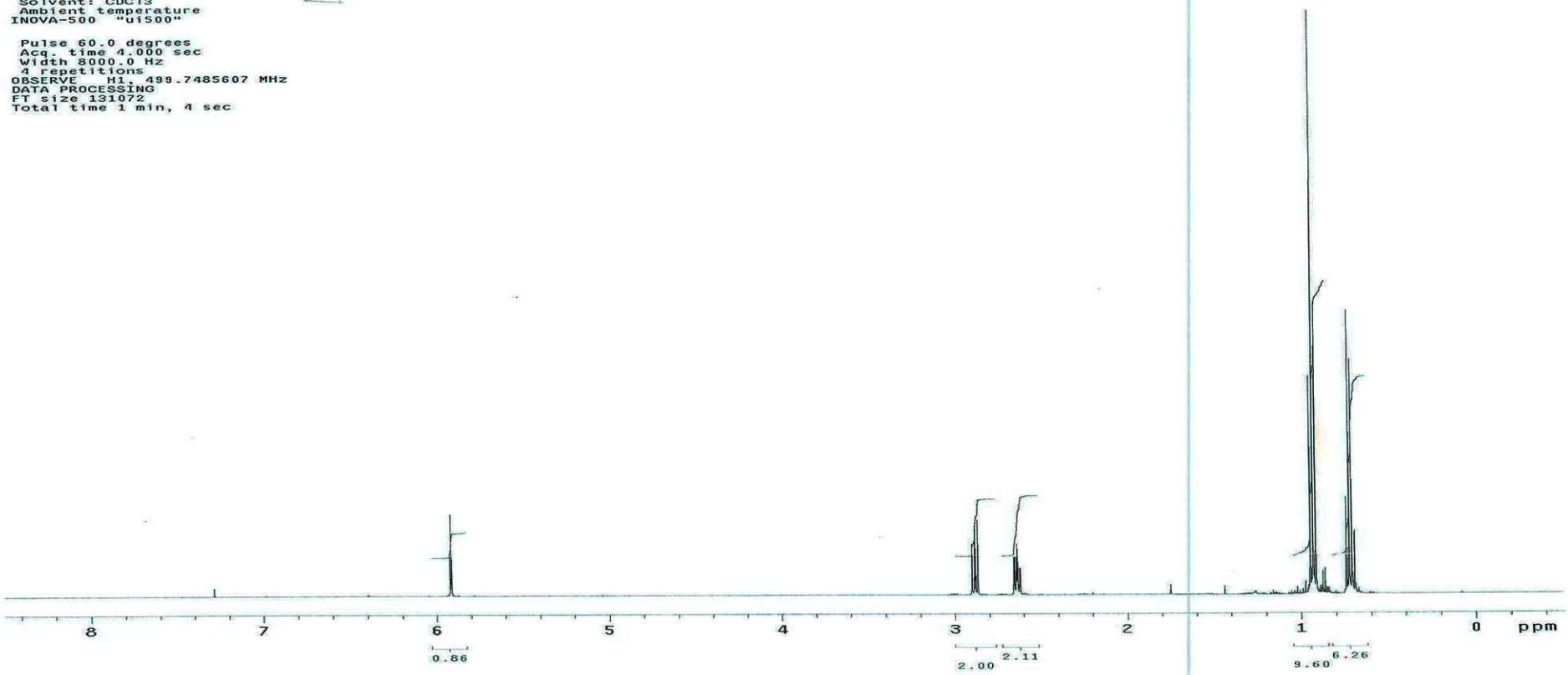
5.32d

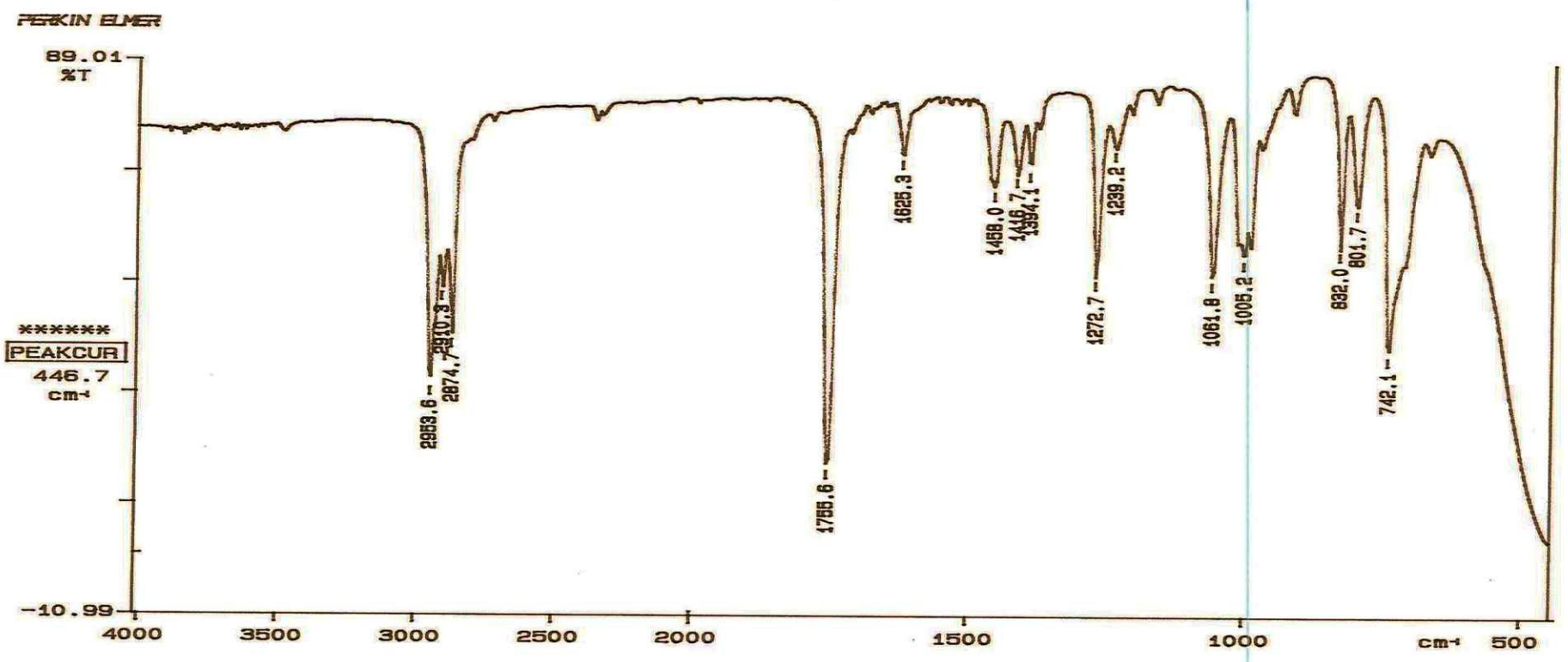
Total time 34 min, 17 sec



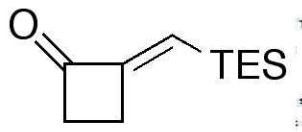
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.7485607 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec





06/08/04 13:11
X: 4 scans, 4.0cm-1

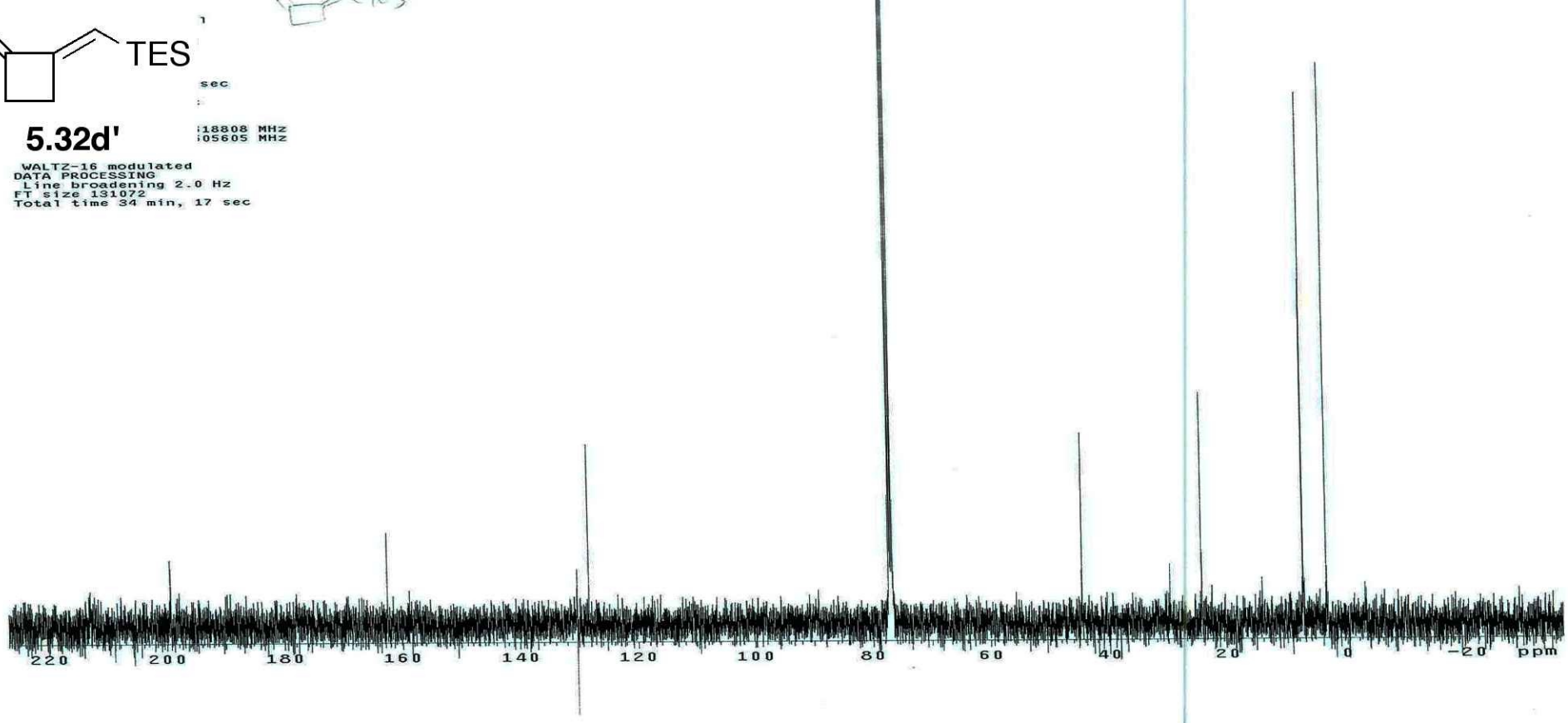


5.32d'

sec

:18808 MHz
:05605 MHz

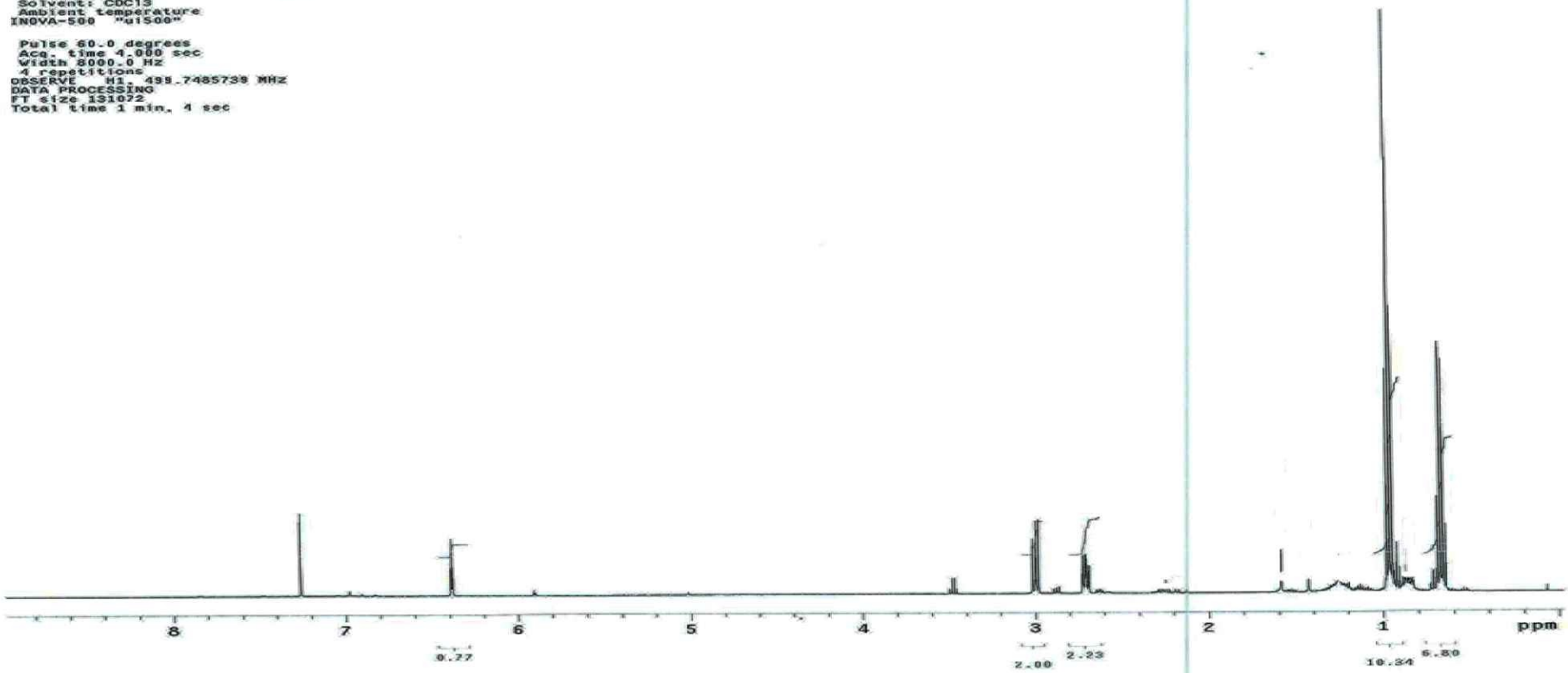
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec

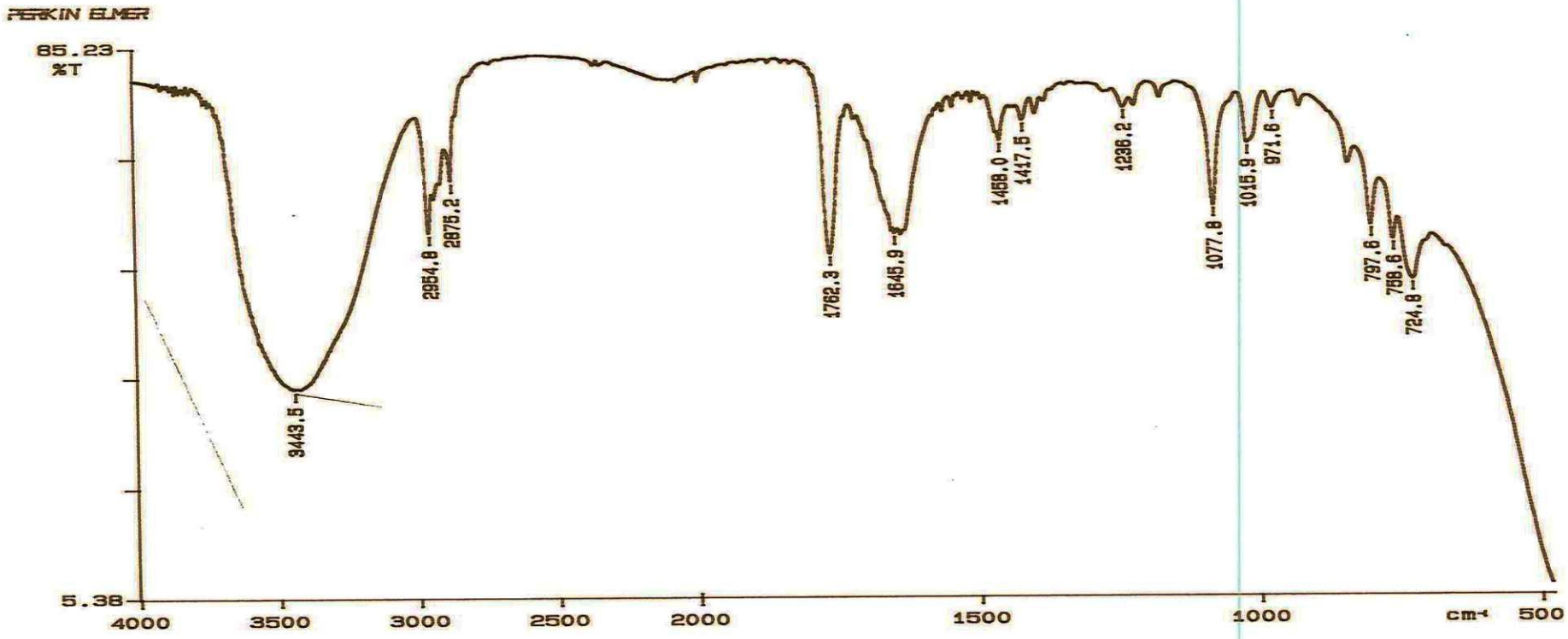


JX-XV-1Z-2

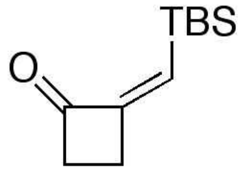
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.7485739 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec

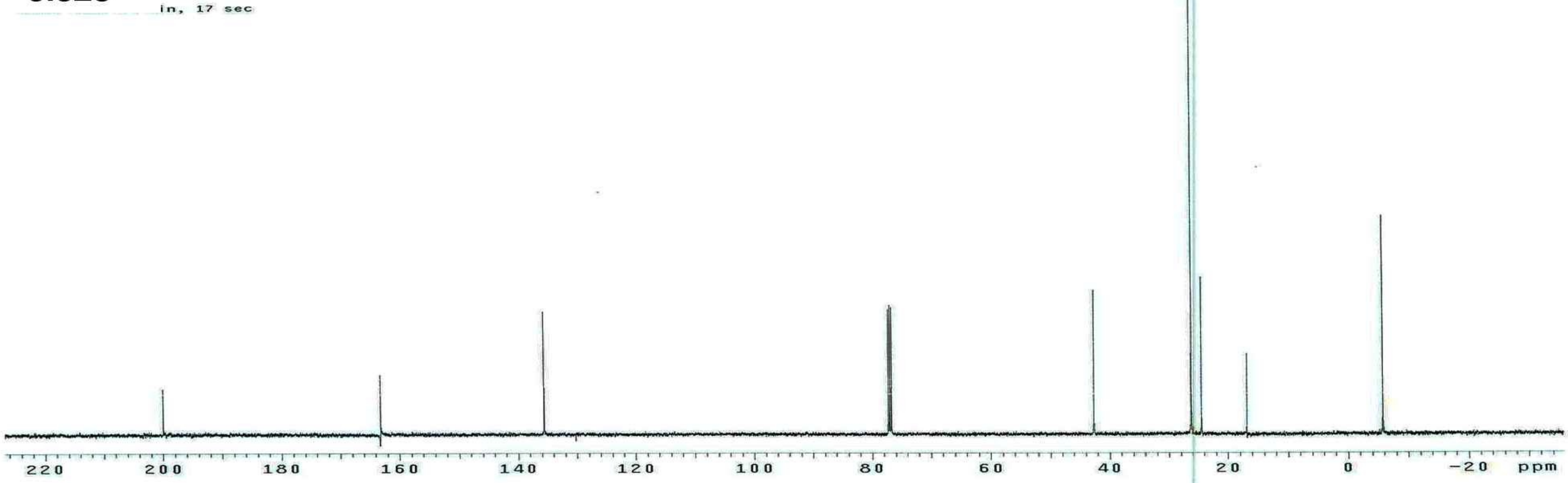


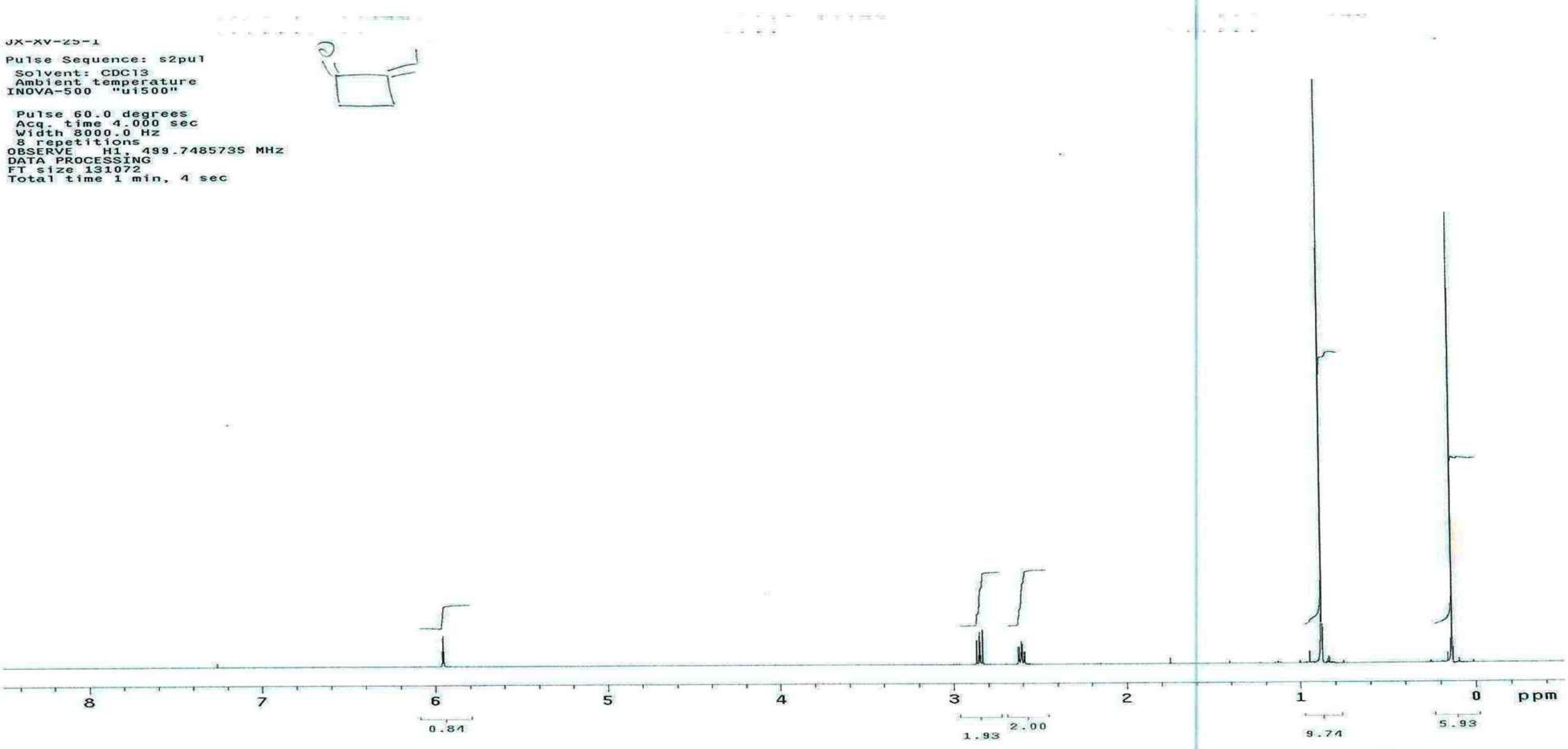


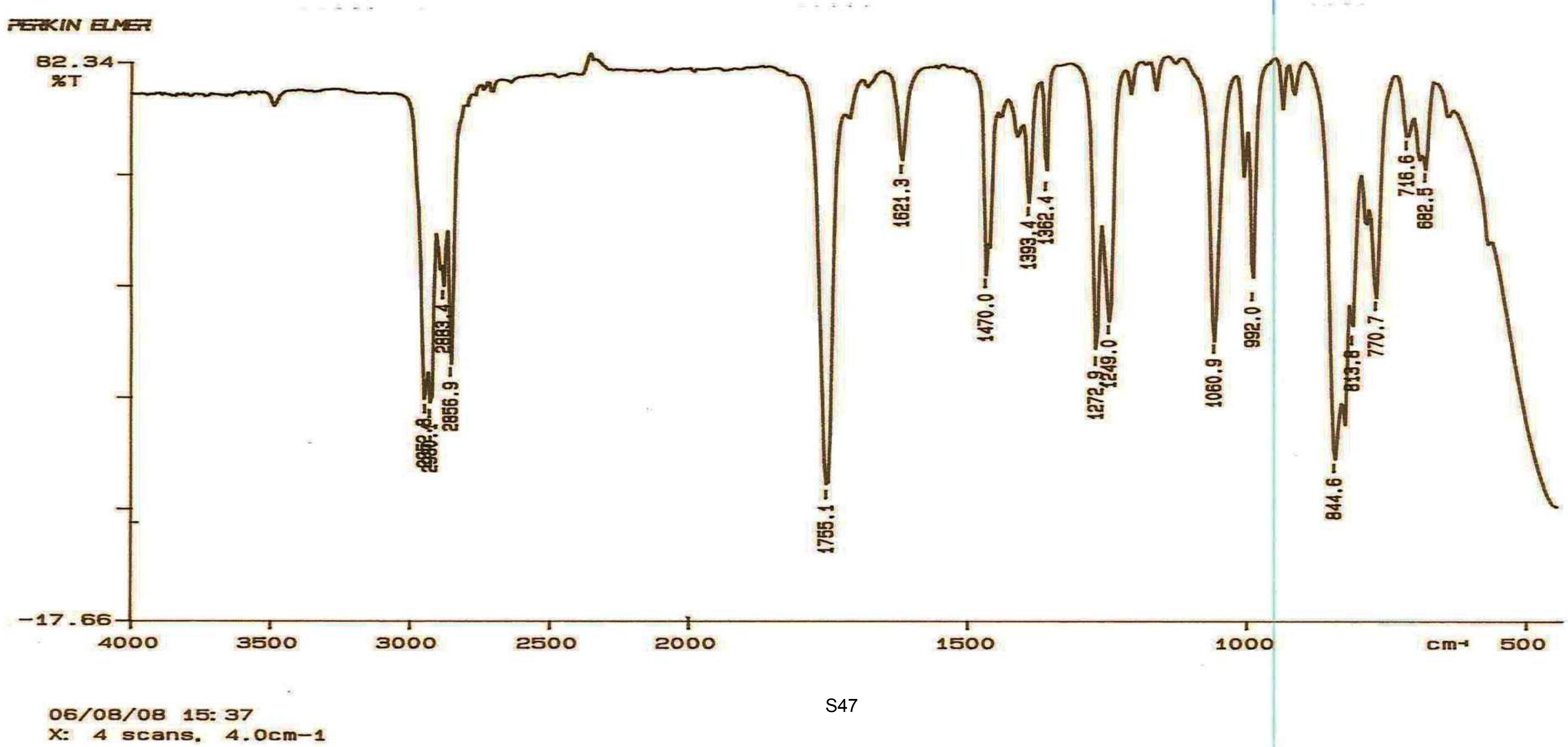
06/08/04 16:25
X: 4 scans, 4.0cm-1

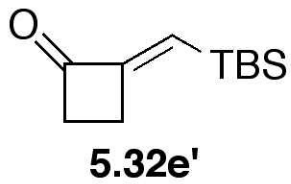

TBS
O

5.32e


s2pul
ture
500 sec
sec
5.6618834 MHz
9.7505605 MHz
ted
2.0 Hz
in, 17 sec
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

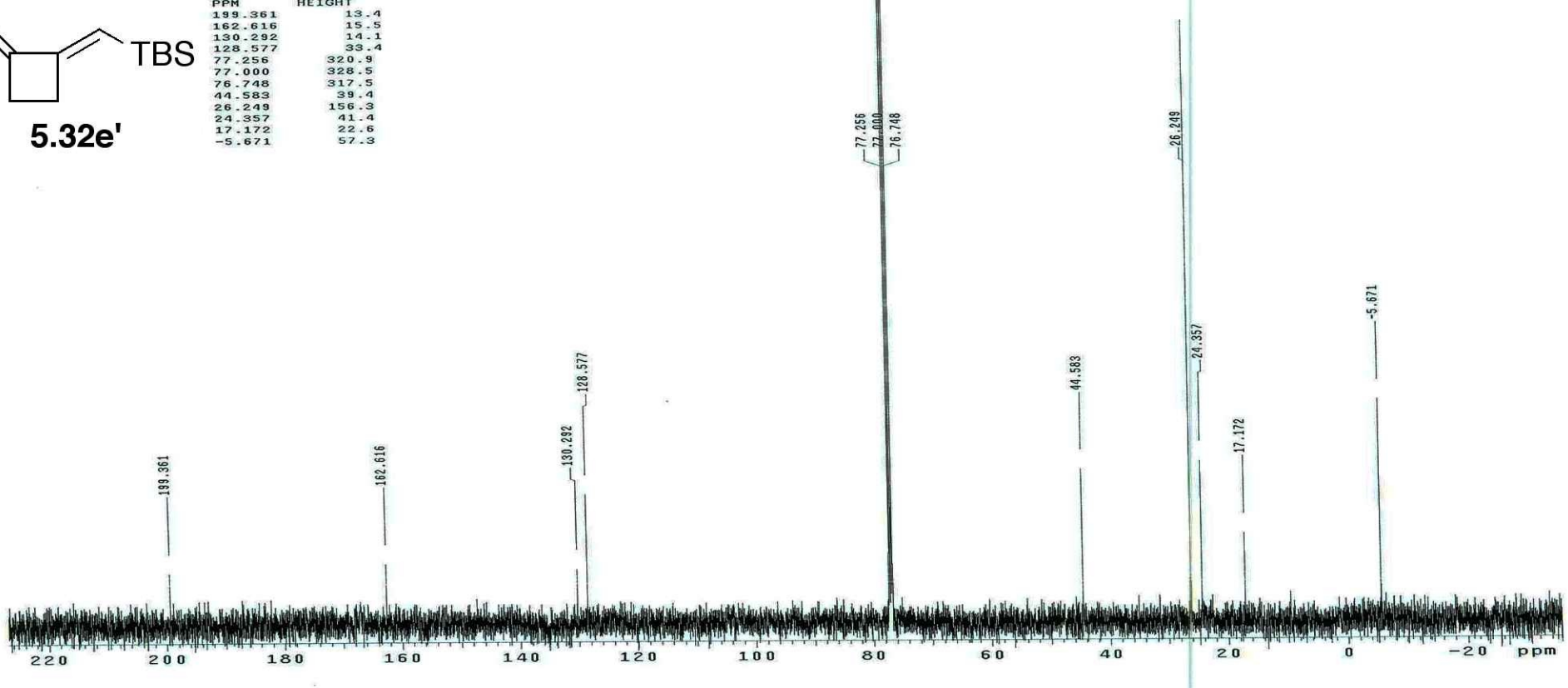

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
8
7
6
5
4
3
2
1
0
ppm
0.84
1.93
2.00
9.74
5.93


PERKIN ELMER
82.34
%T
-17.66
4000
3500
3000
2500
2000
1500
1000
cm-1
500
1755.1
1621.3
1470.0
1393.4
1362.4
1272.9
1249.0
1060.9
992.0
844.6
813.8
770.7
716.6
682.5
2856.9
06/08/08 15:37
X: 4 scans, 4.0cm-1



5.32e'

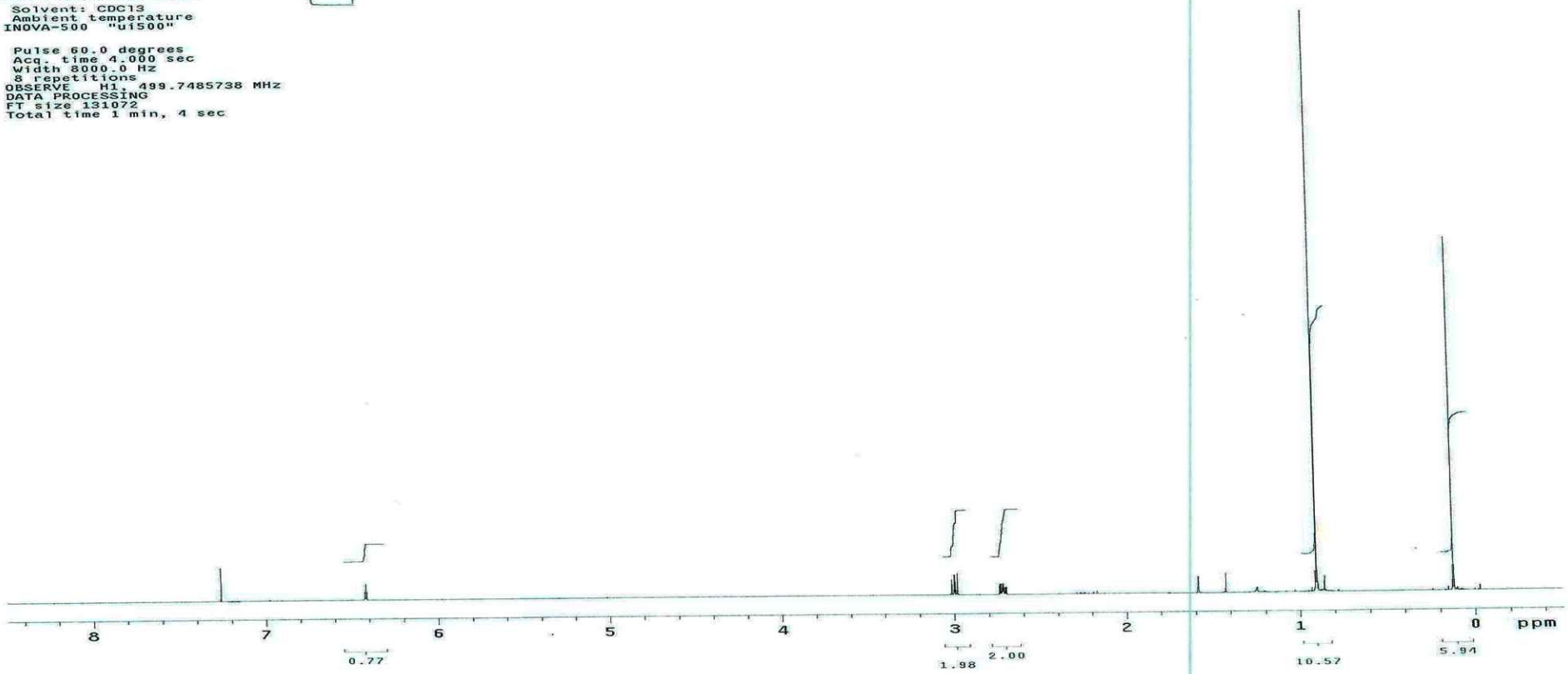
PPM	HEIGHT
199.361	13.4
162.616	15.5
130.292	14.1
128.577	33.4
77.256	320.9
77.000	328.5
76.748	317.5
44.583	39.4
26.249	156.3
24.357	41.4
17.172	22.6
-5.671	57.3

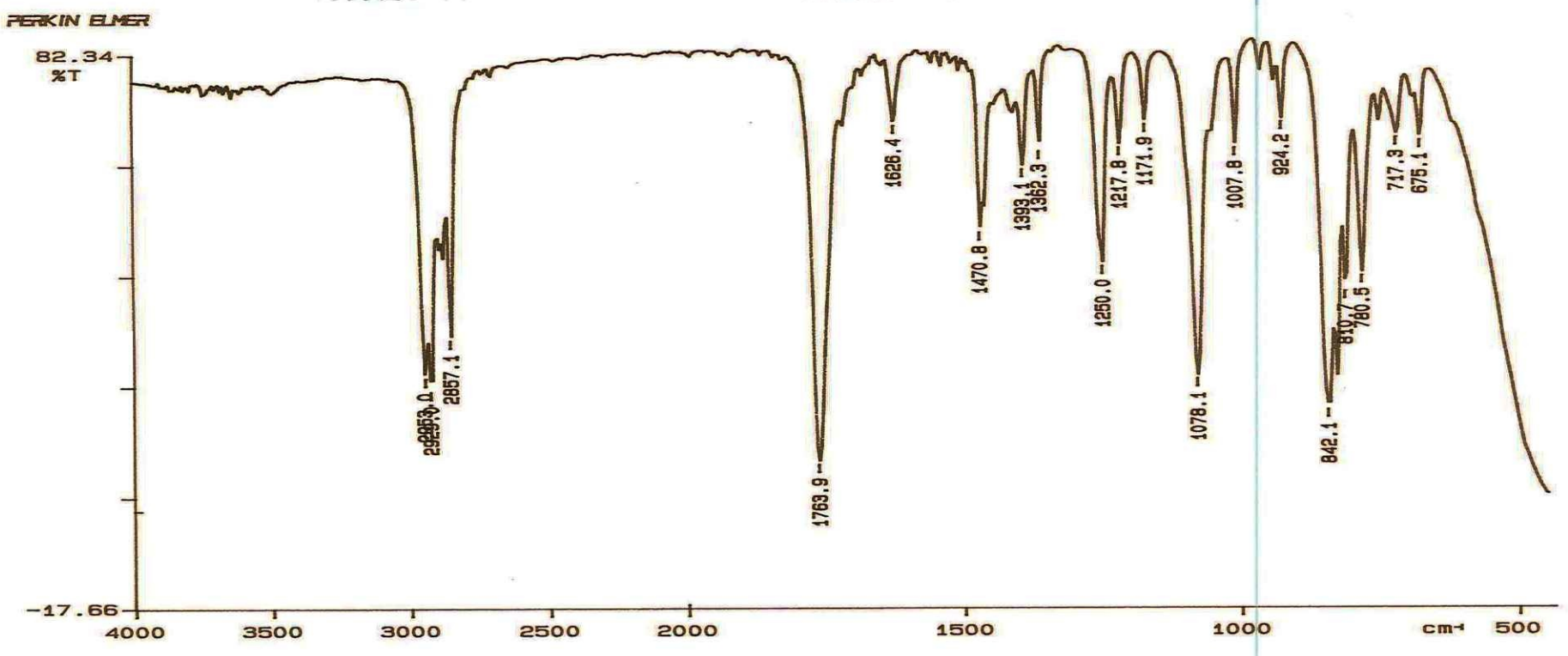


JX-XV-25-2

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "u1500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec

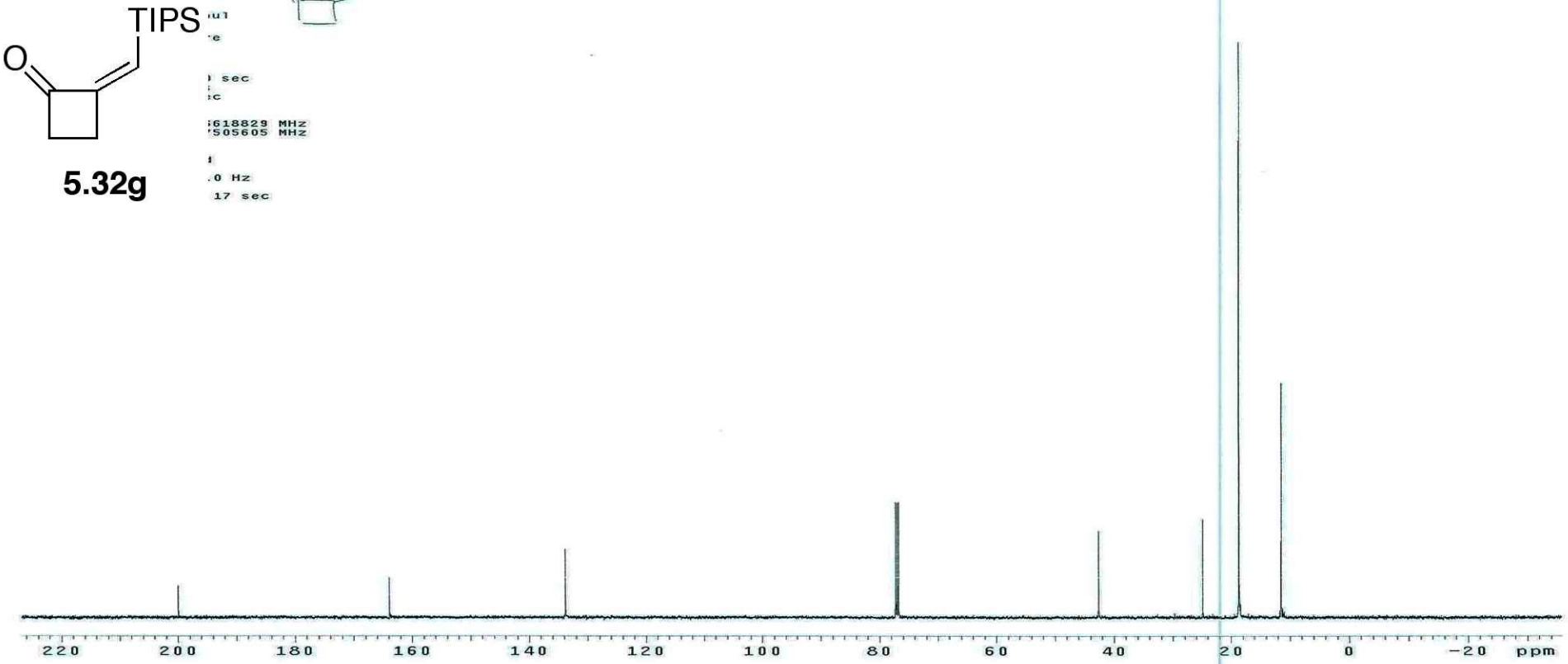




06/08/09 07:14
X: 4 scans, 4.0cm-1

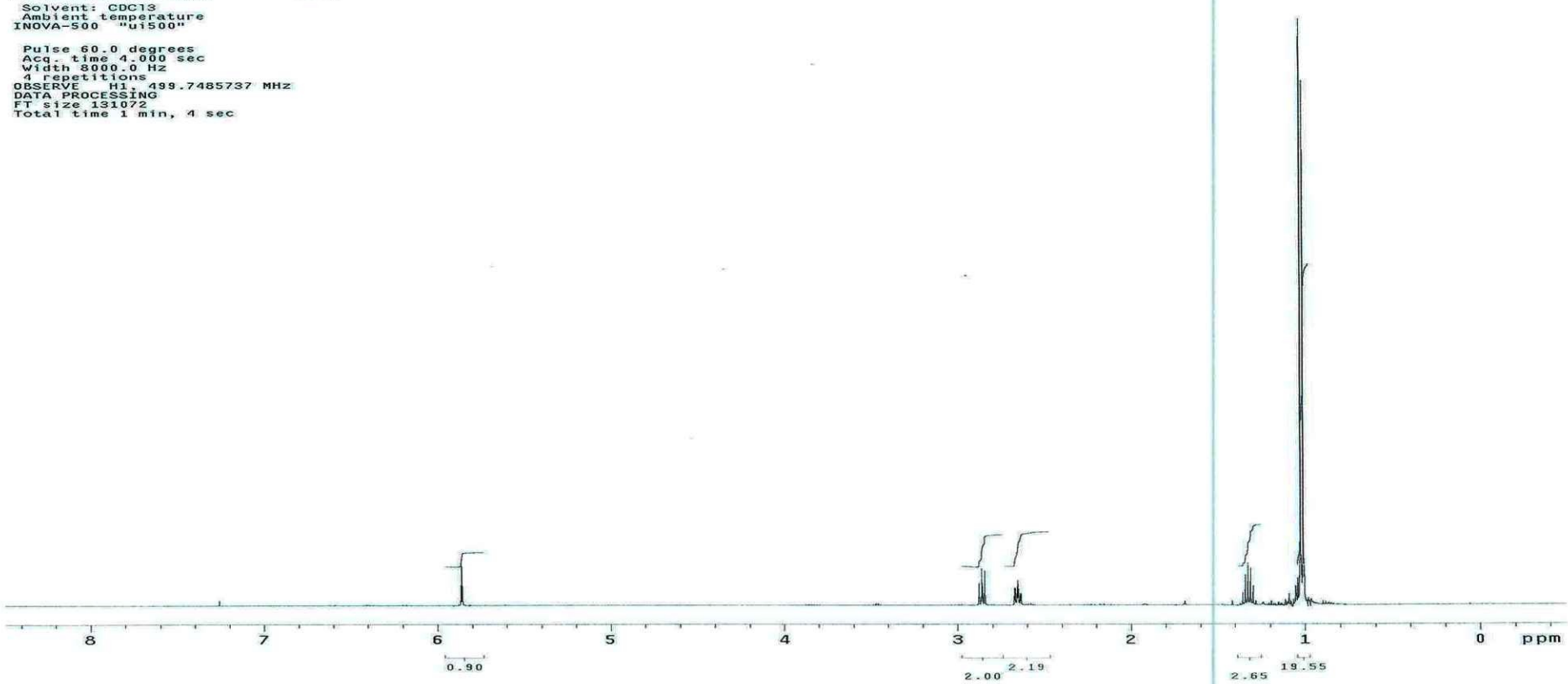
5.32g

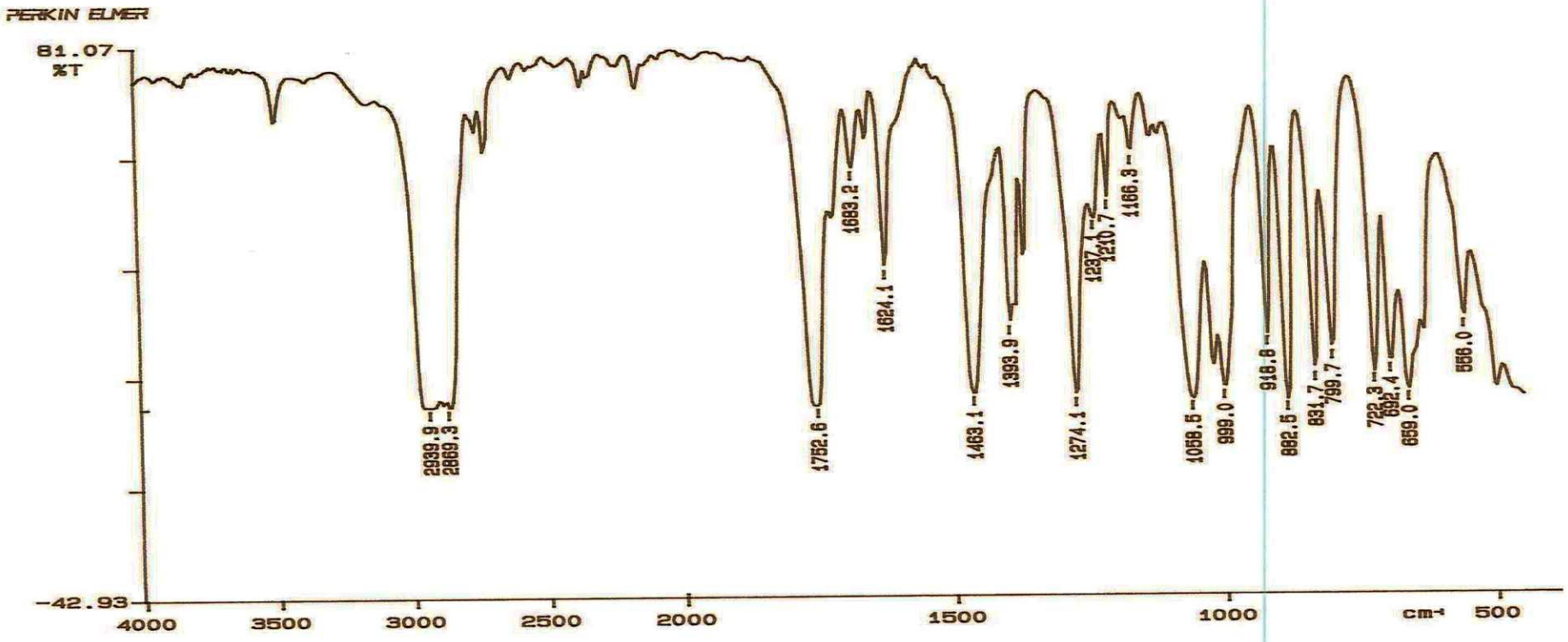
sec
c
618829 MHz
505605 MHz
.0 Hz
17 sec



Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

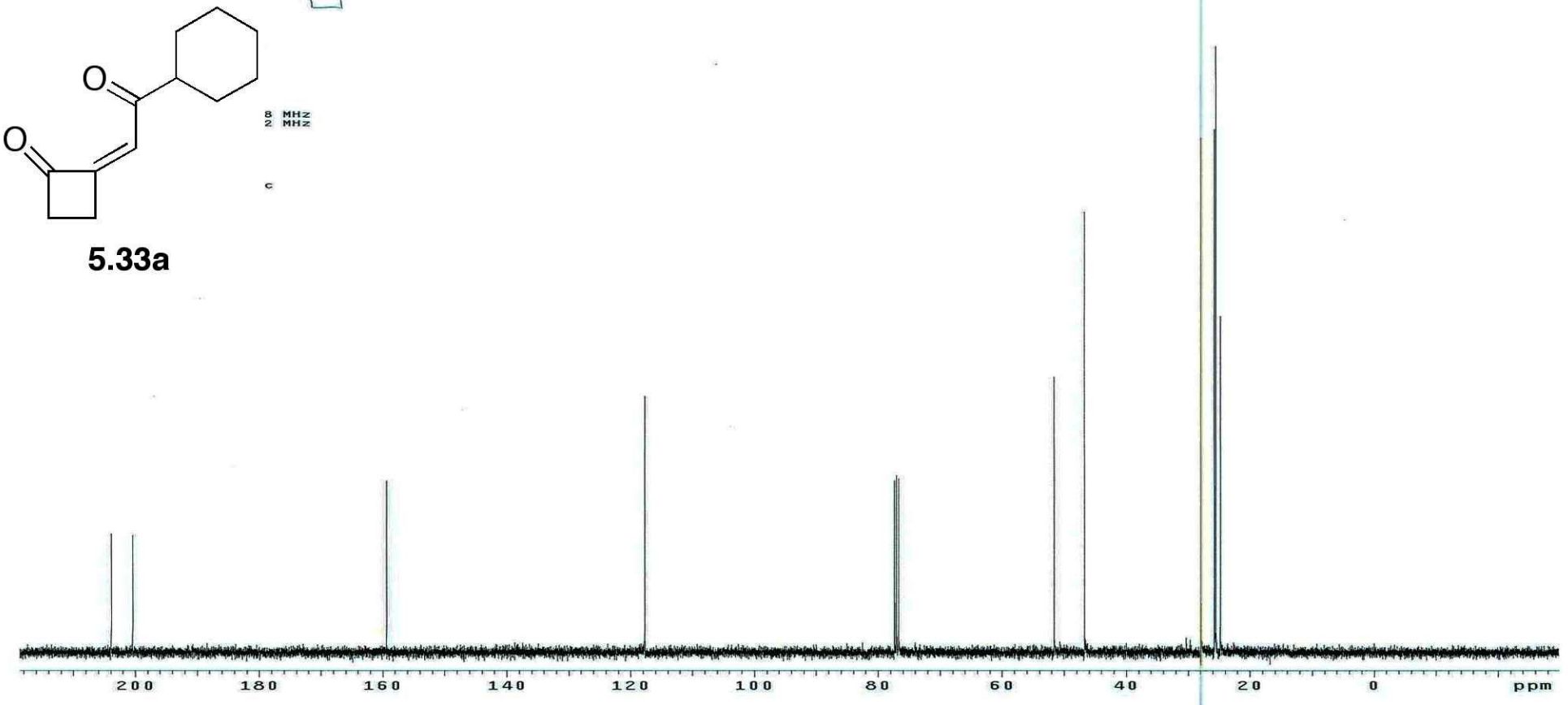
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec

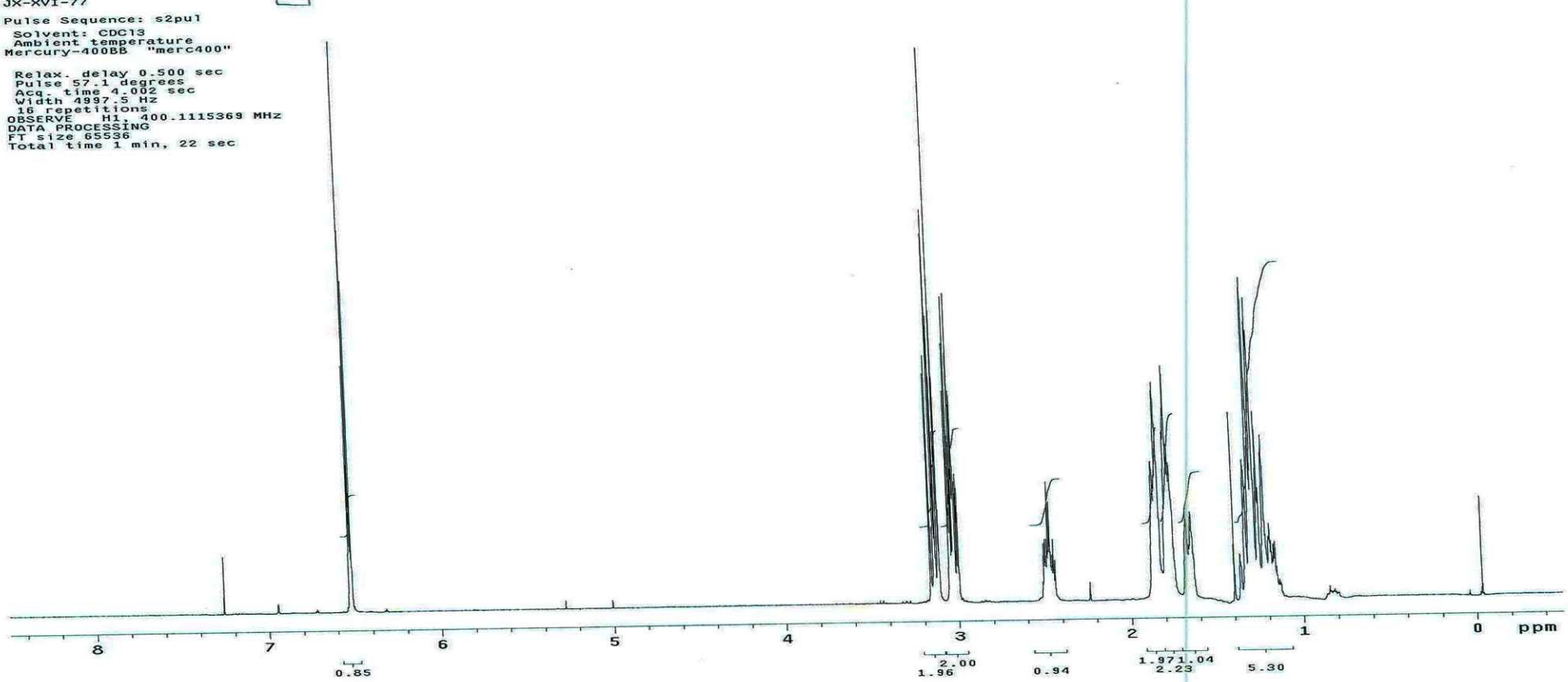


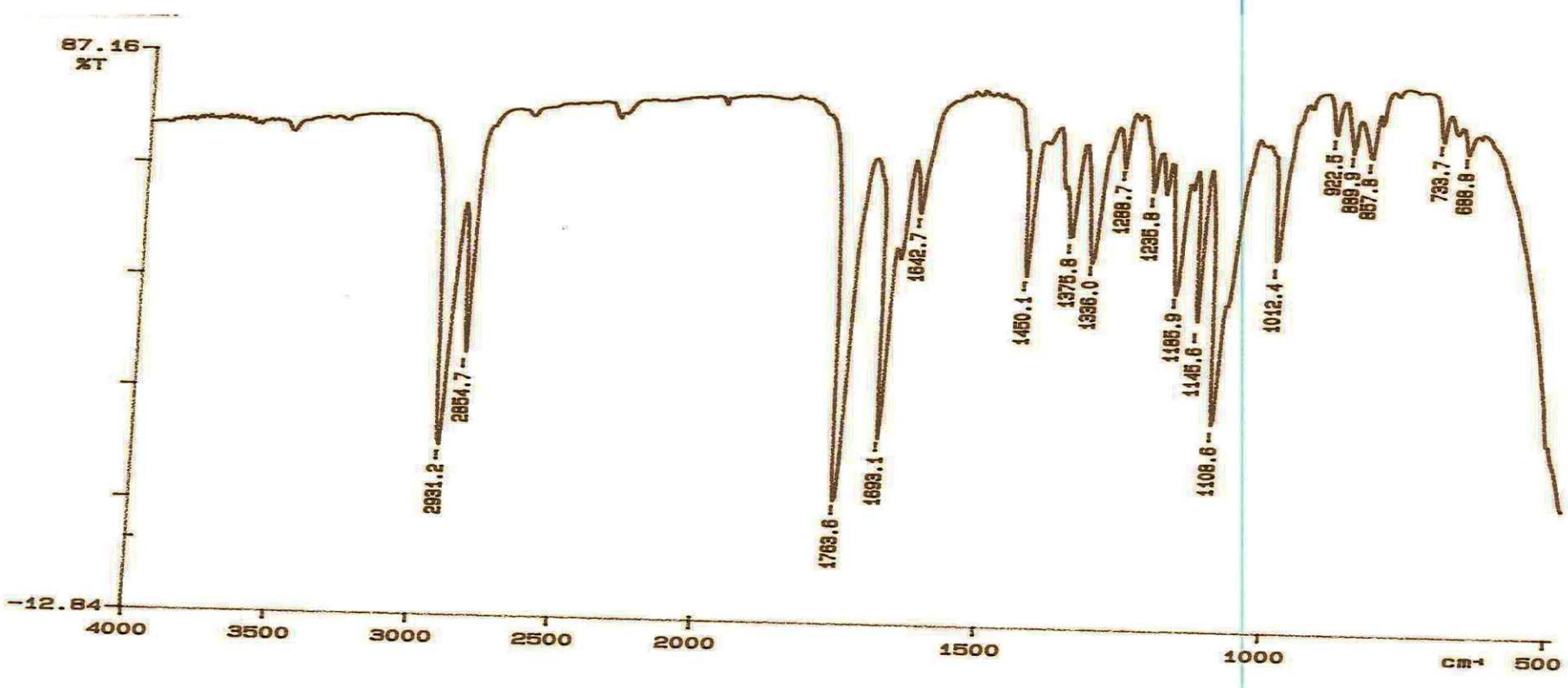


06/08/07 13:02
Y: 4 scans, 4.0cm-1

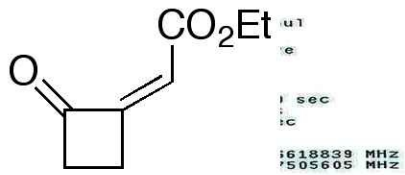
5.33a





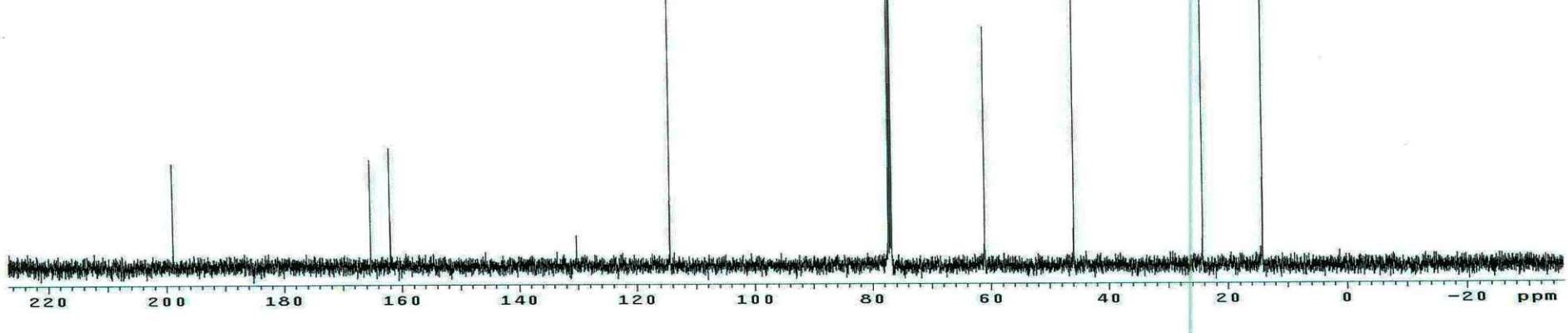


06/12/08 15:38
X: 4 scans, 4.0cm-1



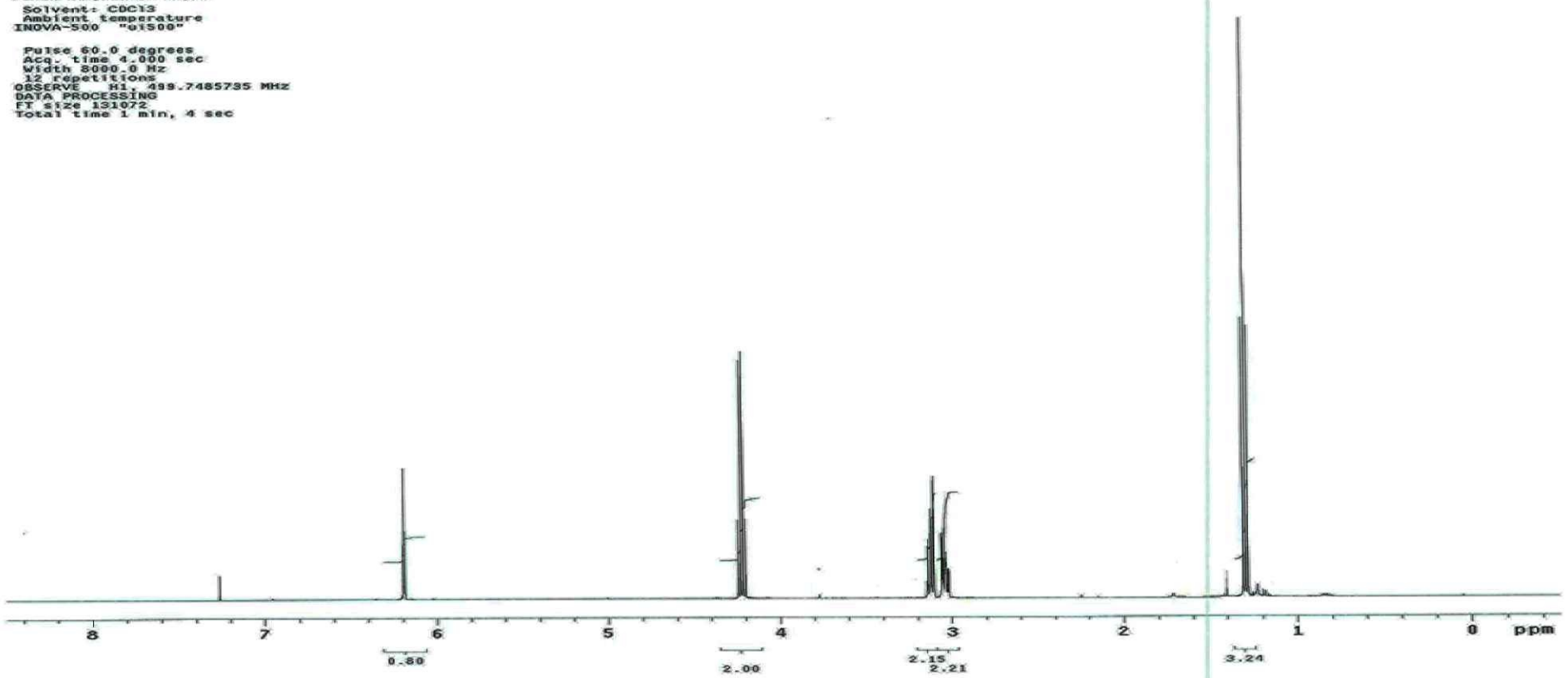
5.33b

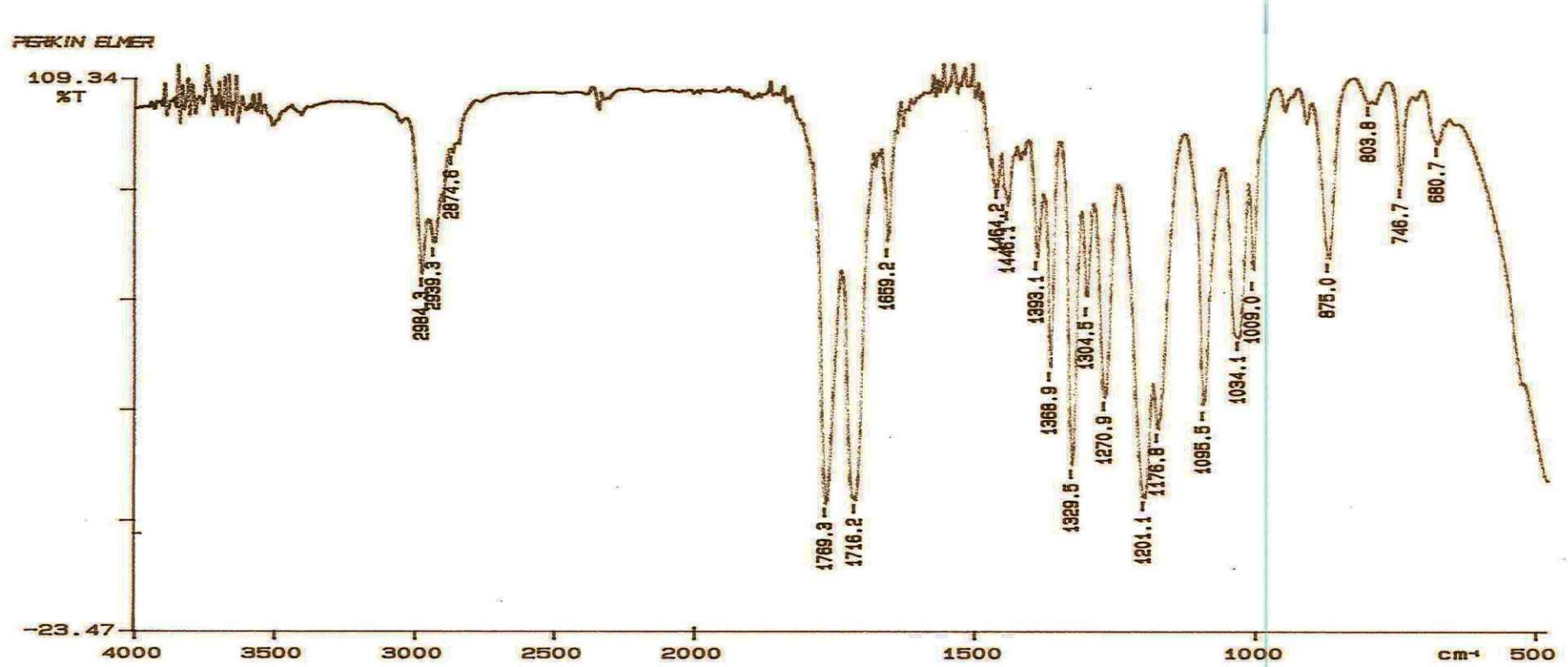
Total time 34 min, 17 sec



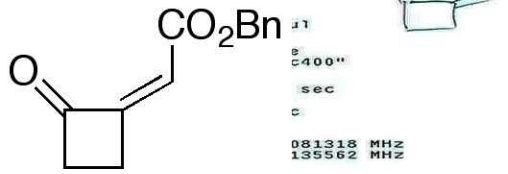
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
12 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec





06/10/02 09:39
X: 4 scans, 4.0cm-1

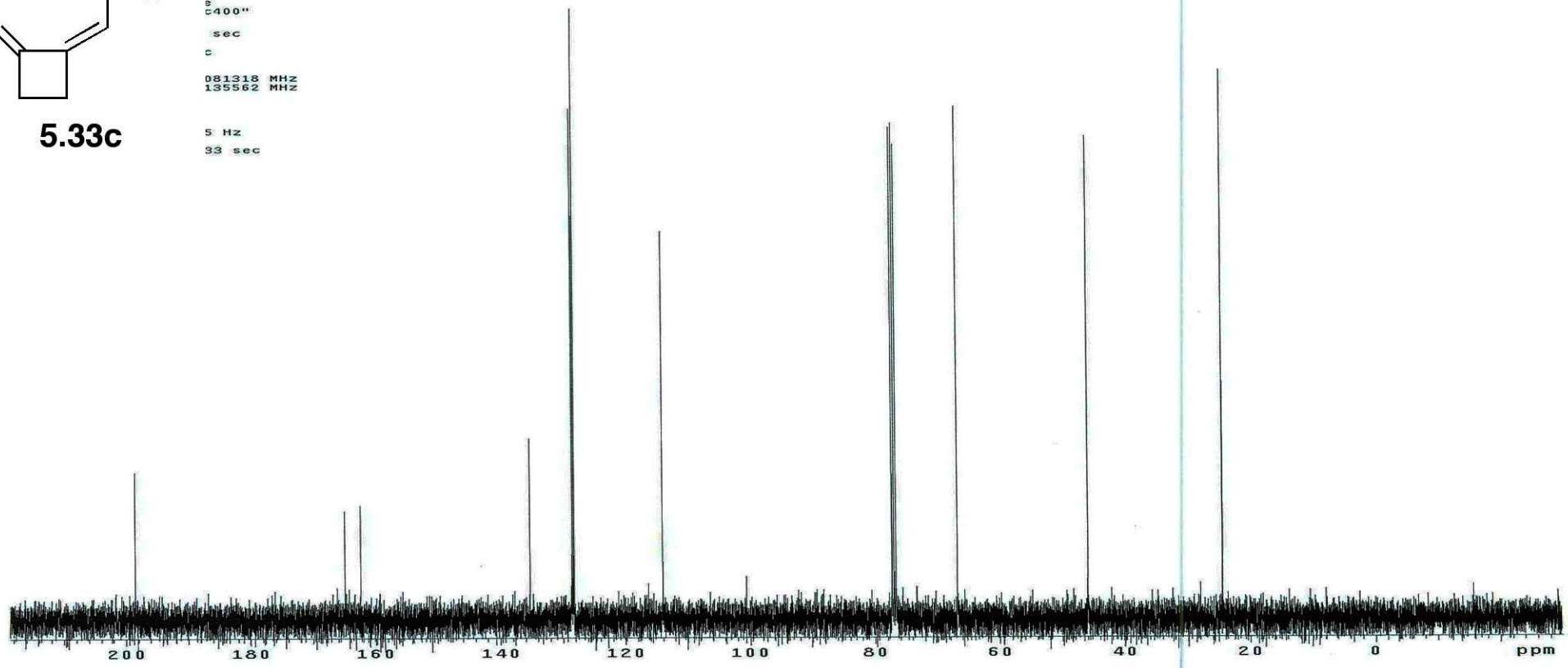


5.33c

c400"
sec
c

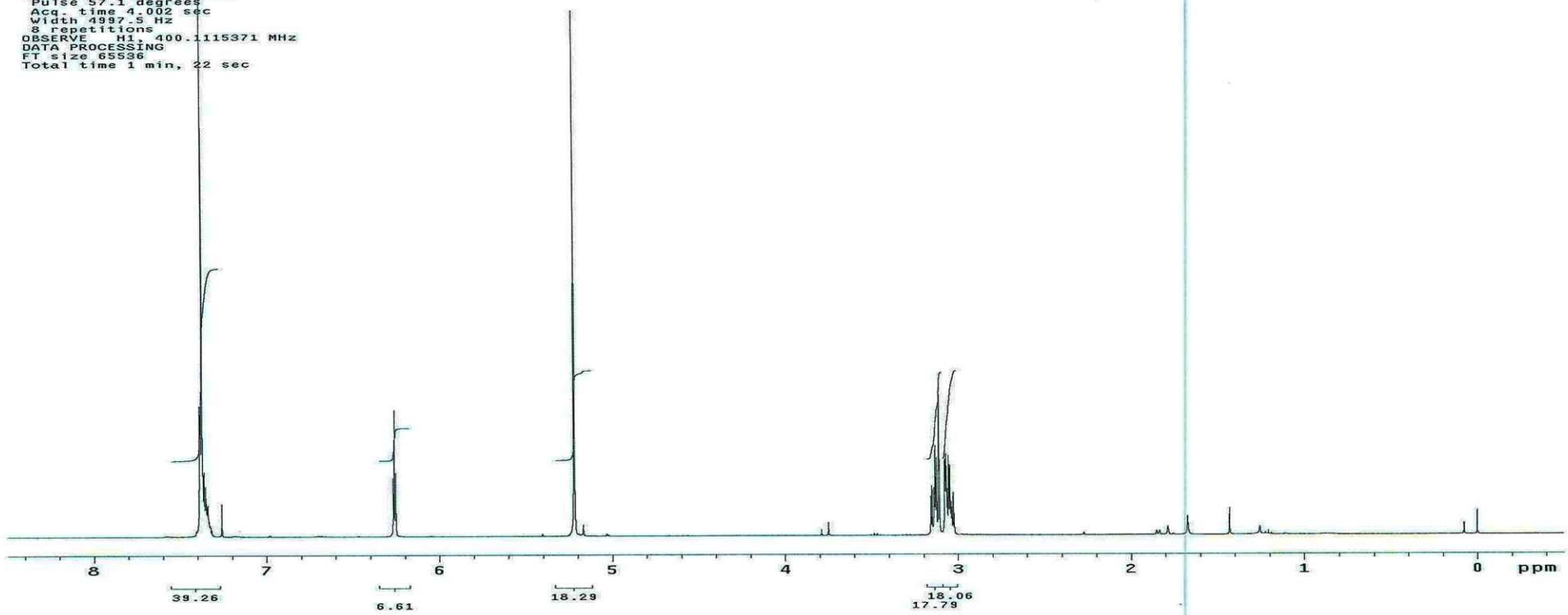
081318 MHz
135562 MHz

5 Hz
33 sec

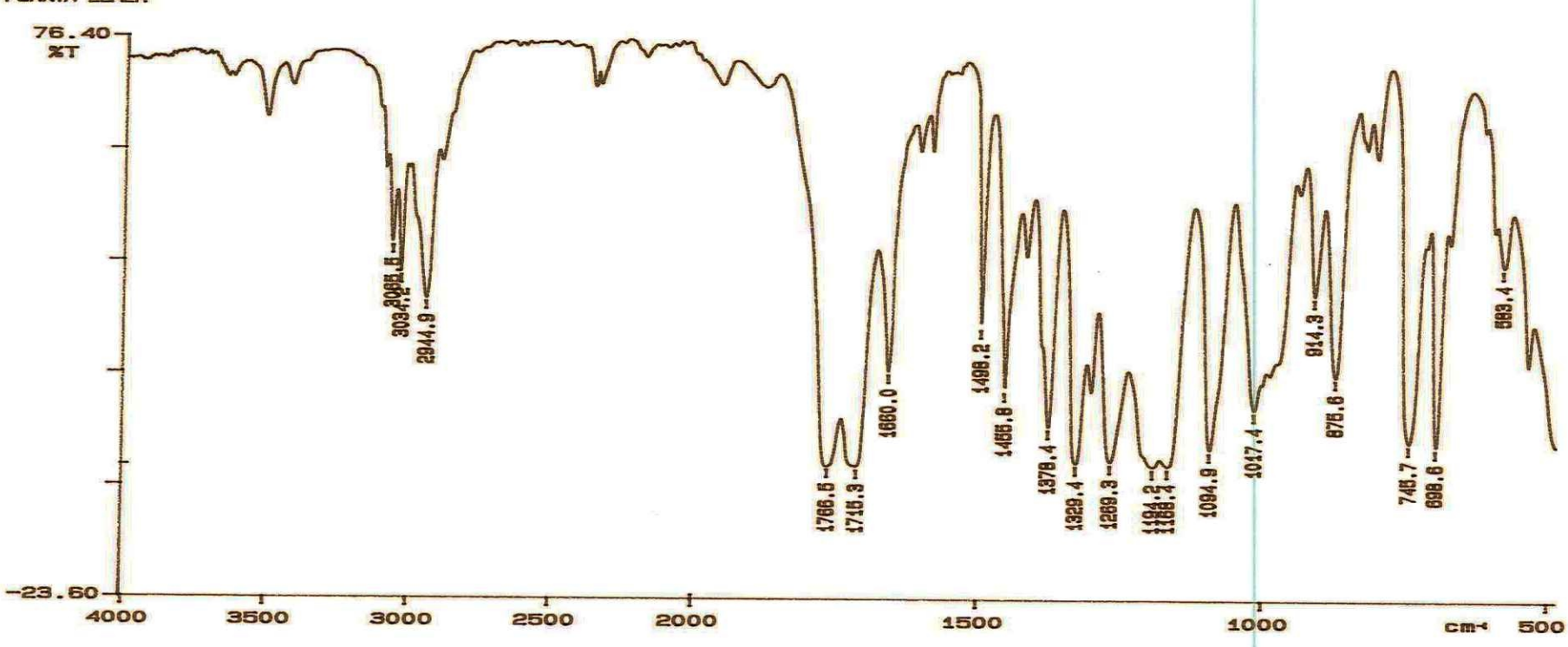


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"

Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
8 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec



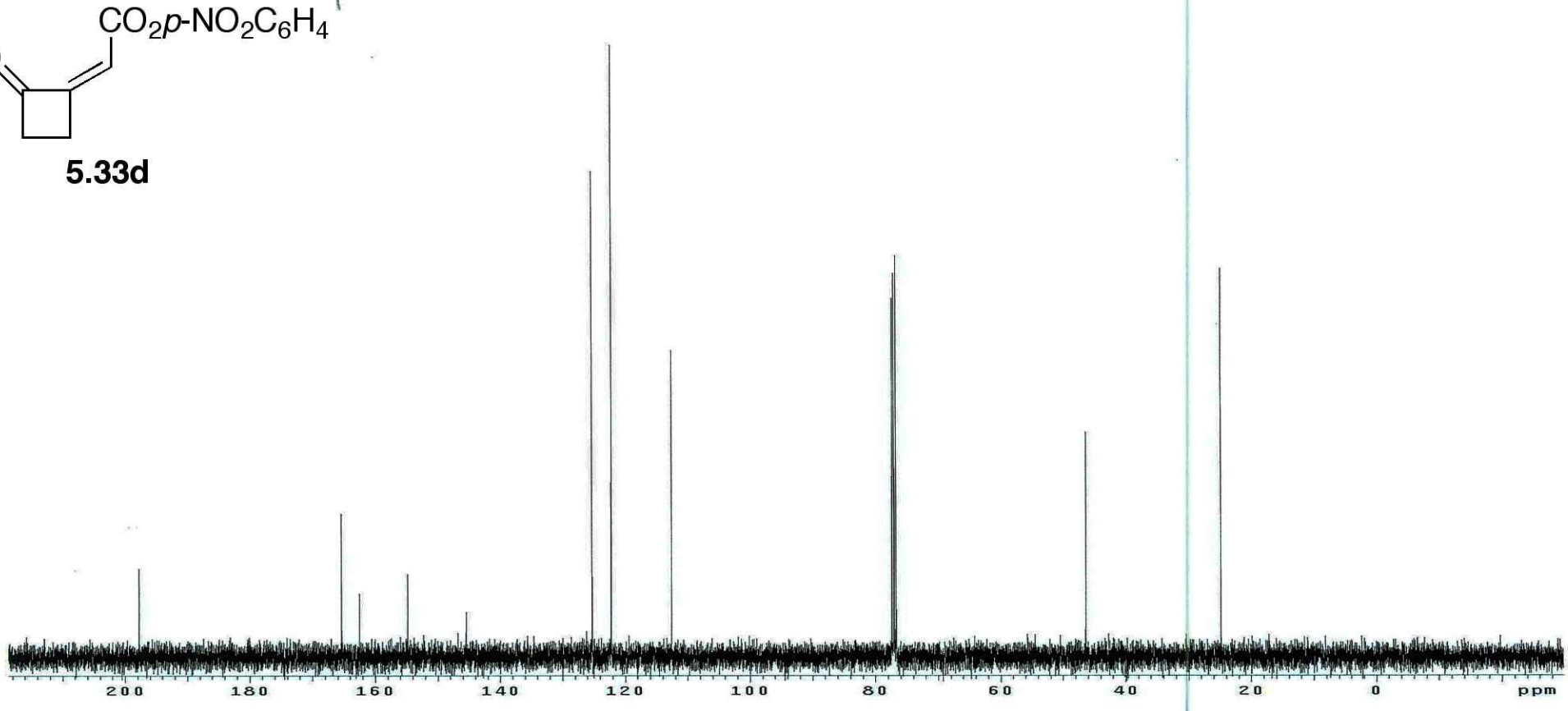
PERKIN ELMER



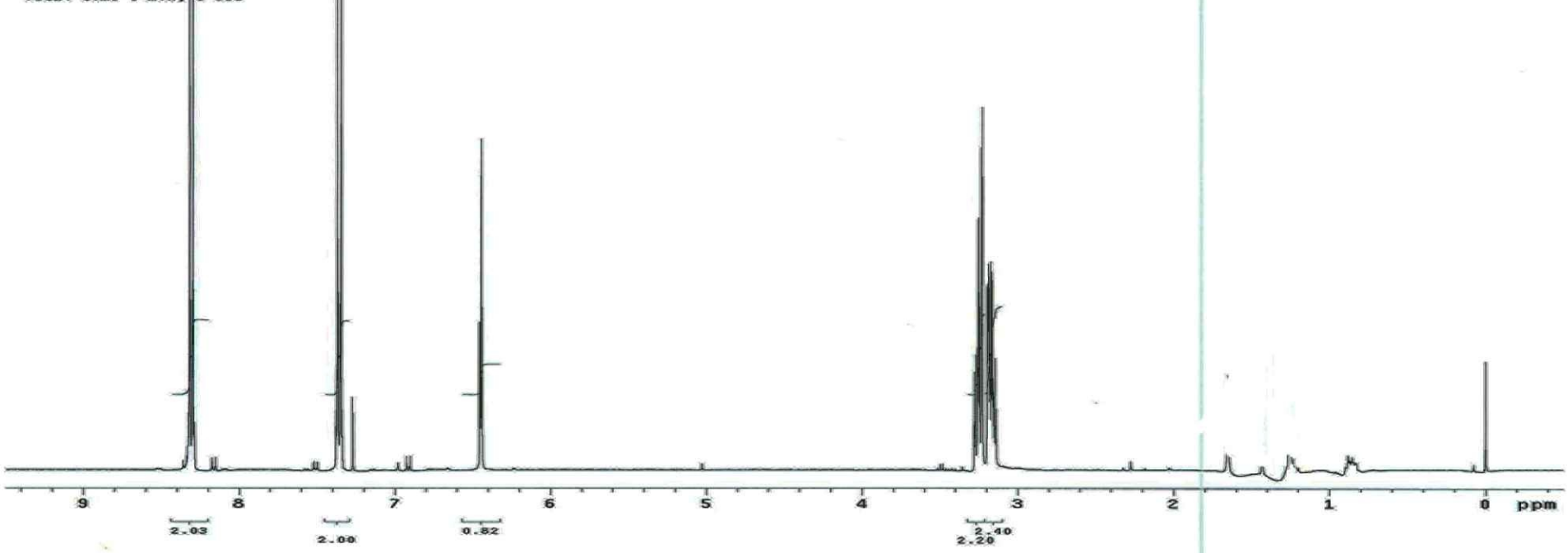
06/10/18 20:38
X: 4 scans, 4.0cm-1

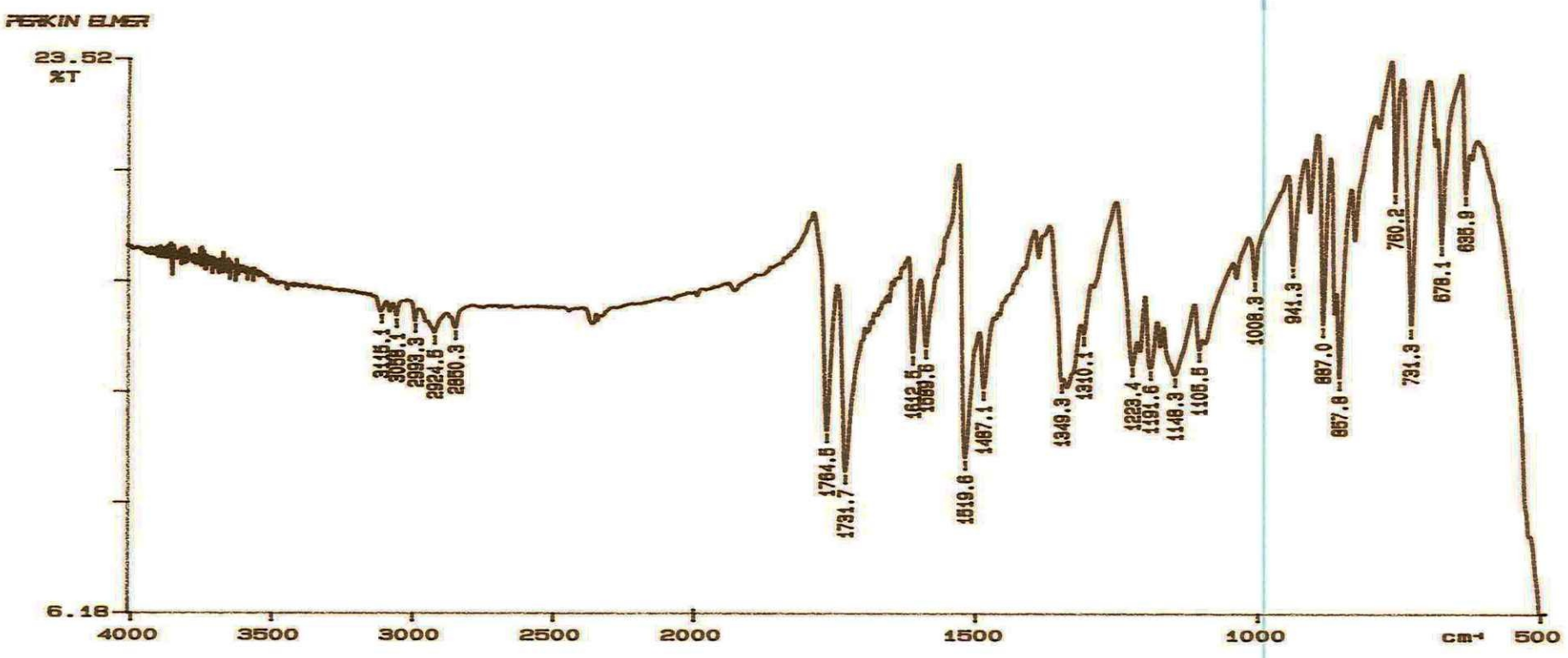
CO_2p-$NO_2C_6H_4$
O

5.33d


200
180
160
140
120
100
80
60
40
20
0
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115321 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec


9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.00
0.82
2.40
2.20


PERKIN ELMER
23.52
%T
6.18
3119.1
3068.1
2993.3
2924.6
2860.3
1784.8
1731.7
1612.5
1580.6
1519.6
1487.1
1349.3
1310.1
1223.4
1191.6
1148.3
1106.8
1008.3
941.3
887.0
857.8
780.2
731.3
678.1
635.9
4000
3500
3000
2500
2000
1500
1000
cm-1
500
06/12/08 15:31
X: 4 scans, 4.0cm-1, flat