Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Radical Carbonylation Reactions of ω-Alkynylamines Leading to α-Methylene Lactams. Synthetic Scope and the Mechanistic Insights

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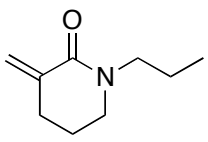
General information. ^{1}H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) or JEOL JMN AL-400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) or JEOL JMN AL-400 (100 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. For ^{1}H-Sn and ^{13}C-Sn coupling constants, the central signals are normally associated with two close pairs of satellites corresponding to both ^{117}Sn and ^{119}Sn isotopes, and average values of the two different coupling constants are reported. Infrared spectra were obtained on a JASCO FT/IR-5300 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. Products were purificated by flash chromatography on silica gel (nacalai tesque int. Silica Gel 60, 230-400 mesh). Optical rotations were obtained on JASCO DIP-370 Digital Polarimeter at a wavelength of 589 nm (sodium D line). A single crystal suitable for X-ray crystallography was sealed in glass capillary. All measurements were performed on a Rigaku RAXIS Rapid diffractometer equipped with an imaging plate detector. The frame data were processed using the Rigaku PROCESS-AUTO program,[1] and the reflection data were corrected for absorption with an ABSCOR program.[2] The structure were solved by direct method and refined on F^2 by full-matrix least-squares method by using SHELX97.[3] Anisotropic refinement was applied to all non hydrogen atoms. Hydrogen atoms were found in the final difference Fourier map and have been isotropically refined. Alkynylamines **1a**-**1j**, **1n**, and **1o** were prepared as previously described.[4] Alkynylamines **1k**, **1l**, and **1m** were prepared from the corresponding *N*-ω-alkynyl-*N*-(1-phenylethyl) amines.

1. PROCESS-AUTO. *Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer*, Rigaku Corporation: Tokyo, Japan, 1998.
2. T. Higashi, *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation*; Rigaku Corporation: Tokyo, Japan, 1998.
3. G. M. Sheldrick, *SHELX97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.
4. a) M. Tojino, Y. Uenoyama, T. Fukuyama, and I. Ryu, *Chem. Comm.* **2004**, 2482. b) Y. Uenoyama, T. Fukuyama, and I. Ryu, *Org. Lett.*, 2007, **9**, 935.

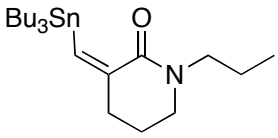
Typical procedure for stannylcarbonylation of alkynylamine 1 (Protocol A); A magnetic stirring bar, AIBN (2,2'-azobisisobutyronitrile, 16.2 mg, 0.1 mmol), benzene (50 mL), Bu_3SnH (170.2 mg, 0.58 mmol), and 4-pentynylpropylamine **1a** (65 mg, 0.52 mmol) were placed in a 100-mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 75 atm of CO and then heated 90 °C for 3 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was dissolved into MeOH and TMSCl (5.2 mmol) was added. The reaction mixture was stirred at room temperature for 10 min. After evaporation, the resulting mixture was purified by flash chromatography on SiO_2 to give **2a** (R_f = 0.2, EtOAc/MeOH = 5/1, 71%, 56.5 mg).

1-Propyl-3-methylene-2-piperidinone (2a).



Colorless oil, (R_f = 0.2, hexane/EtOAc = 5/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.87 (sext, *J* = 7.3 Hz, 2H), 1.83 (quint, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.2 Hz, 2H), 3.30-3.38 (m, 4H), 5.21 (s, 1H), 6.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.29, 20.25, 23.19, 30.06, 48.36, 49.26, 121.16, 137.79, 163.91; IR (neat) 1659, 1615 cm^{-1}; MS (EI) *m/z* (rel intensity) 153 (M^+, 22), 139 (36), 124 (61), 110 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 153.1153, found 153.1159.

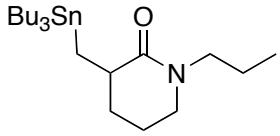
1-Propyl-3-tributylstannylmethylene-2-piperidinone (3a).



E isomer: Colorless oil, (R_f = 0.33, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-1.03 (m, 18H), 1.22-1.39 (m, 6H), 1.40-1.68 (m, 6H), 1.82-1.94 (m, 2H), 2.49-2.58 (m, 2H), 3.31-3.42 (m, 4H), 7.40 (s, *J* ^{1}H-Sn = 65.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.09, 11.49, 13.73, 20.45, 23.80, 27.37, 29.22, 32.67, 48.58, 49.78, 139.71, 144.77, 163.46; IR (neat) 1642, 1586 cm^{-1}; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity) 386 (M^+-C_4H_9, 100), 272 (46); HRMS (EI) *m/z* calcd for $C_{17}H_{32}NO^{120}Sn$ (M^+-C_4H_9) 386.1506, found 386.1509.

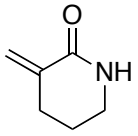
Z isomer: Colorless oil, (R_f = 0.3, hexane/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78-0.92 (m, 18H), 1.23-1.30 (sext, *J* = 7.3 Hz, 6H), 1.37-1.60 (m, 6H), 1.82-1.87 (m, 2H), 2.61-2.63 (m, 2H), 3.32-3.36 (m, 4H), 6.33 (s, *J* ^{1}H-Sn = 71.0 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 11.9, 13.9, 20.42, 23.83, 27.57, 29.45, 33.85, 48.68, 49.27, 143.87, 144.22, 165.09; IR (neat) 1636, 1584; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity); 386 (M^+-C_4H_9, 100), 272 (48); HRMS (EI) *m/z* calcd for $C_{17}H_{32}NO^{120}Sn$ (M^+-C_4H_9) 386.1506, found 386.1513.

1-Propyl-3-tributylstannylmethyl-2-piperidinone (4a).



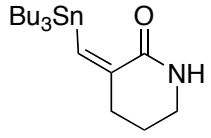
Colorless oil, (R_f = 0.3, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76-1.11 (m, 19H), 1.24-1.32 (m, 7H), 1.35-1.56 (m, 9H), 1.68-1.78 (m, 1H), 1.82-1.98 (m, 2H), 2.38-2.57 (m, 1H), 3.18-3.30 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.85, 11.38, 13.67, 13.78, 20.38, 21.85, 27.53, 29.32, 31.36, 40.00, 48.21, 49.00, 173.85; IR (neat) 1634 cm^{-1}; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity); 388 (M^+-C_4H_9, 67), 350 (100); HRMS (EI) *m/z* calcd for $C_{17}H_{34}NO^{120}Sn$ (M^+-C_4H_9) 388.1662, found 388.1664.

3-Methylene-2-piperidinone (2b).



Colorless oil, (R_f = 0.18, EtOAc/MeOH = 19/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.87 (quint, *J* = 6.0 Hz, 2H), 2.57-2.60 (m, 2H), 3.39-3.41 (m, 2H), 5.32 (d, *J* = 1.4 Hz, 1H), 6.21 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.08, 29.75, 42.63, 122.07, 137.51, 166.04; IR (neat) 1668, 1618 cm^{-1}; This product is a known compound and was identified by NMR with comparison of literature data (S. Klutchko *et al*. *J*. *Med*. *Chem*. **1981**, *24*, 104.).

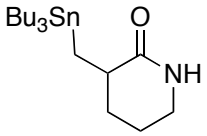
3-Tributylstannylmethylene-2-piperidinone (3b).



E isomer: Colorless oil, (R_f = 0.38, EtOAc), ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.90 (m, 15H), 1.23-1.46 (m, 6H), 1.61 (quint, *J* = 7.6 Hz, 6H), 1.92-1.98 (m, 2H), 2.69-2.72 (m, 2H), 3.45-3.52 (m, 2H), 6.54 (bs, 1H), 7.05 (s, *J* ^{1}H-Sn = 90.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.61, 20.23, 22.85, 26.63, 27.98, 30.22, 42.92, 140.55, 154.86, 169.19; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 344 (M^+-C_4H_9, 19), 322, (100), 230 (76), 149 (20); IR (neat) 1641, 1575 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{15}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 344.1037, found 344.1037.

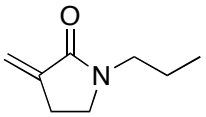
Z isomer: Colorless oil, (R_f = 0.20, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77-0.92 (m, 15H), 1.28 (sext, *J* = 7.3 Hz), 1.40-1.49 (m, 6H), 1.66-1.95 (m, 2H), 2.63 (m, 2H), 3.35-3.38 (m, 2H), 6.45 (s, *J* ^{1}H-Sn = 69.2 Hz, 1H), 6.85 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.83, 13.78, 23.63, 27.46, 29.33, 33.29, 42.80, 142.85, 146.17, 166.81; IR (neat) 1663, 1586 cm^{-1}; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 344 (M^+-C_4H_9, 100), 230 (45); HRMS (EI) *m/z* calcd for $C_{14}H_{26}NO^{120}Sn$ (M^+-C_4H_9) 344.1037, found 344.1039.

3-Tributhylstannylmethyl-2-piperidione (4b).



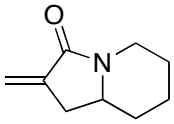
Colorless oil, (R_f = 0.13, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0,78-0.89 (m, 15H), 1.14-1.32 (m, 8H), 1.35-1.50 (m, 7H), 1.63-1.73 (m, 1H), 1.81-1.85 (m, 1H), 1.91-1.97 (m, 1H), 2.42 (quint, *J* = 7.8 Hz, 1H), 3.24-3.26 (m, 2H), 6.70 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.83, 12.93, 13.65, 21.67, 27.40, 29.23, 31.27, 39.49, 42.50, 176.71; IR (neat) 1659 cm^{-1}; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 346 (M^+- C_4H_9, 27), 324 (100), 230 (33), 198 (22), 151 (52); HRMS (EI) *m/z* calcd for $C_{14}H_{28}NO^{120}Sn$ (M^+-C_4H_9) 346.1193, found 346.1195.

1-Propyl-3-methylene-2-pyrrolidinone (2c).



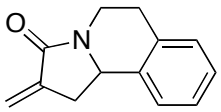
Colorless oil, (R_f= 0.10, hexane/EtOAc = 2/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H), 1.57 (sext, *J* = 7.5 Hz, 2H), 2.73 (m, 2H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.37 (t, *J* = 6.6 Hz, 2H), 5.28 (s, 1H), 5.94 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.28, 20.43, 24.01, 43.94, 44.77, 114.94, 139.89, 167.92; IR (neat) 1686, 1659 cm^{-1}; MS (EI), *m/z* (rel intensity) 139 (M^+, 36), 124 (61), 110 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 139.0997, found 139.0982.

1-Oxo-2-methyleneoctahydroindolizine (2d).



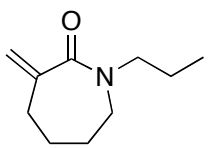
Colorless oil, (R_f = 0.18, Hexane/EtOAc = 1/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.20 (m, 1H), 1.30-1.47 (m, 2H), 1.66-1.69 (m, 1H), 1.84-1.90 (m, 2H), 2.27-2.30 (m, 1H), 2.68-2.73 (m, 1H), 2.86-2.90 (m, 1H), 3,41-4.44 (m, 1H), 4.18-4.20 (m, 1H), 5.21-5.28 (m, 1H), 5.88-5.91 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.90, 24.67, 31.84, 33.74, 40.69, 54.50, 115.05, 139.60, 166.84; IR (neat) 1685, 1658 cm^{-1}; MS (EI) *m/z* (rel intensity) 151 (M^+, 100), 122 (34), 110 (19), 95 (21); HRMS (EI) *m/z* calcd for $C_9H_{13}NO$ (M^+) 151.0997, found 151.0985.

Pyrrolo[2,1-a]isoquinolin-3(2H)-one (2e).



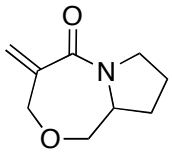
Carbonylation with tributyltin hydride was carried out with V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)) as a radical initiator. Colorless oil, (R_f = 0.18, Hexane/EtOAc = 1/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68-2.83 (m, 2H), 2.98-3.06 (m, 1H), 3.16-3.23 (m, 1H), 3.40 (ddd, *J* = 16.6, 7.8, 2.0 Hz, 1H), 4.39 (ddd, *J* = 12.9, 6.1, 2.2 Hz, 1H), 5.36-5.37 (m, 1H), 5.98-6.02 (m, 1H), 7.11-7.26 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.35, 33.43, 37.69, 54.05, 115.17, 124.92, 126.80, 126.98, 129.07, 133.64, 137.22, 139.61, 166.33; IR (neat) 1686 cm^{-1}; MS (EI) *m/z* (rel intensity) 199 (M^+, 77), 198 (100), 149 (26), 130 (20); HRMS (EI) *m/z* calcd for $C_{13}H_{13}NO$ (M^+) 199.0997, found 199.0996.

1-Propyl-3-methylene-2-azacycloheptanone (2f).



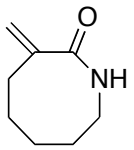
Colorless oil, (R_f= 0.18, hexane/EtOAc = 1/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.3 Hz, 3H), 1.50 (sext, *J* = 7.5 Hz, 2H), 1.56-1.72 (m, 4H), 2.23-2.29 (m, 2H), 3.19-3.24 (m, 2H), 3.26-3.32 (m, 2H), 5.12 (s, 1H), 5.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.35, 21.28, 27.82, 28.87, 32.36, 48.97, 49.48, 117.99, 147.78, 172.95; IR (neat) 1644 cm^{-1}; MS (EI) *m/z* (relative intensity), 167 (M^+, 52), 138 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 167.1311, found 167.1305.

Hexahydro-4-methylene-(9a-S)-1H,5H-pyrrolo[2,1-c][1,4]oxazepine-5-one (2g).



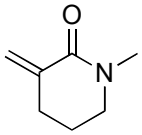
Colorless oil, (R_f = 0.16, hexane/EtOAc = 1/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44-1.58 (m, 1H), 1.70-1.81 (m, 1H), 1.82-1.92 (m, 1H), 2.25-2.42 (m, 1H), 3.34 (dd, *J* = 11.9, 9.2 Hz, 1H), 3.40 (ddd, *J* = 15.6, 8.7, 6.8, 1H), 3.81 (ddd, *J* = 11.9, 7.8, 3.7, 1H), 3.82-3.89 (m, 1H), 3.90 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.01 (d, *J* = 12.8 Hz, 1H), 4.30 (d, *J* = 12.8 Hz, 1H), 5.50 (s, 1H), 5.90 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.81, 29.67, 47.29, 60.01, 70.54, 73.80, 125.51, 144.22, 169.27; IR (neat) 1647 cm^{-1}; MS (EI) *m/z* (rel intensity) 167 (M^+, 12), 149 (11), 137 (21), 109 (28), 83 (100); HRMS (EI) *m/z* calcd for $C_9H_{13}NO$ (M^+) 167.0946, found 167.0946.

3-Methylene-2-azacyclooctanone (2h).



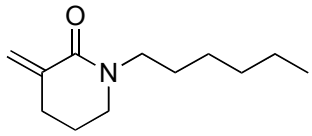
Colorless oil, (R_f = 0.2, EtOAc/MeOH = 19/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52-1.61 (m, 6H), 2.37-2.40 (m, 2H), 3.26-3.30 (m, 2H), 4.98-5.13 (m, 1H), 5.14-5.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.53, 26.22, 31.59, 37.36, 41.54, 114.34, 145.75, 176.31; IR (neat) 1738, 1640 cm^{-1}; MS (EI) *m/z* (rel intensity) 139 (M^+, 14), 111 (100), 67 (62); HRMS (EI) *m/z* calcd for $C_{15}H_{30}N$ (M^+) 415.1901, found 415.1910.

1-Methyl-3-methylene-2-piperidinone (**2j**).



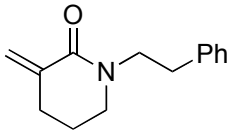
Colorless oil, (R_f = 0.2, Hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.88 (quint, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 6.4 Hz, 2H), 3.01 (s, 3H), 3.37 (t, *J* = 6.0 Hz, 2H), 5.24 (s, 1H), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.07, 30.11, 35.09, 50.30, 120.90, 137.82, 164.35; IR (neat) 1657, 1613 cm^{-1}; EIMS, *m/z* (rel intensity) 125 (M^+, 100), 96 (17), 82 (18), 69 (24), 54 (100); HRMS (EI) *m/z* calcd for $C_7H_{11}NO$ (M^+) 125.0841, found 125.0848.

1-Hexyl-3-methylene-2-piperidinone (**2k**).



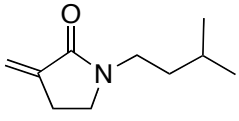
Colorless oil, (R_f = 0.24, Hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86-0.88 (m, 3H), 1.25-1.34 (m, 6H), 1.54-1.57 (m, 2H), 1.87 (quint, *J* = 6.0 Hz, 2H), 2.53-2.58 (m, 2H), 3.35-3.44 (m, 4H), 5.25 (s, 1H), 6.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.98, 22.47, 23.23, 26.58, 27.00, 30.08, 31.56, 47.79, 48.36, 121.21, 137.81, 163.85; IR (neat) 1659, 1633 cm^{-1}; EIMS, *m/z* (rel intensity) 195 (M^+, 33), 138 (26), 124 (100), 69 (24), 54 (100); HRMS (EI) *m/z* calcd for $C_{12}H_{21}NO$ (M^+) 195.1623, found 195.1630.

1-(2-Phenylethyl)-3-methylene-2-piperidinone (**2l**) .



Colorless oil, (R_f = 0.24, Hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.74-1.80 (m, 2H), 2.50-2.55 (m, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 3.20 (t, *J* = 5.9 Hz, 2H), 3.62 (t, *J* = 7.5 Hz, 2H), 5.26 (s, 1H), 6.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.10, 29.94, 33.50, 49.33, 50.14, 121.28, 126.24, 128.41, 128.80, 164.02; IR (neat) 1631 cm^{-1}; EIMS, *m/z* (rel intensity) 215 (M^+, 39), 124 (100), 91 (20); HRMS (EI) *m/z* calcd for $C_{14}H_{17}NO$ (M^+) 215.1310, found 215.1319.

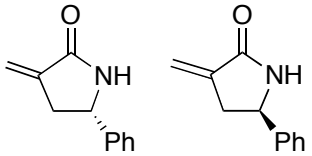
1-(3-Methylbutyl)-3-methylene-2-pyrrolidinone (**2m**) .



Colorless oil. (R_f = 0.24, Hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94 (d, *J* = 6.4 Hz, 6H), 1.42-1.48 (m, 2H), 1.52-1.65 (m, 1H), 2.74-2.76 (m, 2H), 3.35-3.40 (m, 4H), 5.29 (s, 1H), 5.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.44, 24.08, 25.87, 35.88, 41.47, 43.82, 114.79, 139.90,

167.71; IR (neat) 1691, 1659 cm^{-1}; EIMS, *m/z* (rel intensity) 167 (M^+, 15), 111 (81), 110 (100), 55 (17); HRMS calcd for $C_{10}H_{17}NO$ (M^+) 167.1310, found 167.1311.

3-Methylene-5-phenyl-2-pyrrolidinone (**2n and 2o**)

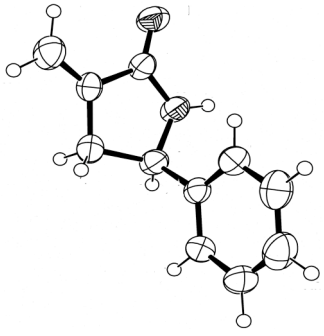


2n: white solid mp = 169-170 °C,: (R_f = 0.15, hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.60-2.69 (m, 1H), 3.22-3.34 (m, 1H), 4.74 (m, 1H), 5.34 (s, 1H), 6.00 (s, 1H), 7.22-7.38 (m, 5H), 7.49 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.89, 54.96, 116.48, 125.76, 128.00, 129.01, 139.05, 142.85, 171.19; IR (KBr) 1656, 1591 cm^{-1}; EIMS, *m/z* (rel intensity) 173 (M^+, 100), 144 (27), 104 (37); HRMS calcd for $C_{11}H_{11}NO$ (M^+) 173.0840, found 173.0843.

2o: white solid, mp = 169-170 °C, ^{1}H-NMR, ^{13}C-NMR, IR and EIMS were identical with those of **2n**. HRMS calcd for $C_{11}H_{11}NO$ (M^+) 173.0840, found 173.0845.

The optical yields were determined by HPLC analysis using a chiral column. HPLC conditions; Chiralcel OD-H; hexane/2-propanol 95/5; flow rate 1.0 mL/min; column temperature 20 °C; UV detector 254 nm; retention time for racemate 26.5 and 31.4 min, retention time for (*R*)-isomer (**2o**) 26.5 min in 99% ee, $[\alpha]^{18}_D$ = -10.0 (c = 0.50, $CHCl_3$), retention time for (*S*)-isomer (**2n**) 31.4 min in 98% ee, $[\alpha]^{18}_D$ =10.0 (c = 0.50 $CHCl_3$). It should be noted that R isomer has been already known. ((a) Dembele, Y. A.; Belaud, C.; Villieras, J. *Tetrahedron Asymmetry*, **1992**, *3*, 511. (b) Frenandes, R. A.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 3562.) However, there is discrepancy in spectral and physical data between their data and our data. This led us to examine X-ray analysis of **2o**, which well supported the structure of **2o**. Crystallographic data: $C_{11}H_{11}N_1O_1$; M = 173.21, orthorhombic, space group $P2_12_12_1$, a = 8.179(4) Å, b = 9.368(5) Å, c = 12.062(7) Å, α = 90°, β = 90°, γ = 90°, V = 924.2(7) $Å^3$, Z = 4, D_{calcd} = 1.245 g/cm^3, T = 296 K, μ(Mo Kα) = 0.080 mm^{-1}, 9103 reflections measured, 2118 unique (R_{int} = 0.0299), R1 = 0.0342, wR2 = 0.0900, GOF = 1.023.

ORTEP drawing of **2o**.



DFT Calculations DFT calculations were carried out using the Gaussian 03 programs.[5] Geometry optimizations were performed using standard gradient techniques at the BHandHLYP level of theory using restricted (RBHandHLYP) and unrestricted (UBHandHLYP) methods for closed- and open-shell systems respectively.[6] All ground and transition states were verified by vibrational frequency analysis. Standard basis sets were used, as well as the (valence) double-ζ pseudo potential basis sets of Hay and Wadt[7] supplemented with a single set of *d*-type polarization functions for the tin (exponent $d(\zeta)_{Sn}$ = 0.200),[8] together with the double-ζ all-electron basis sets of Dunning[9] with an additional set of polarization functions (exponents $d(\zeta)_C = 0.75$, $d(\zeta)_N = 0.80$, $d(\zeta)_O = 0.85$ and $p(\zeta)_H = 1.00$) for C, N, O and H were used in this study. We refer to this basis set as DZP throughout this work.

References

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BHandHLYP/DZP Gaussian Archive entries for the optimized structures involved in the 1,4-hydrogen shift reactions

Substrate of the 1,4-hydrogen shift involving 5-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C5H10N1O1Sn1(2)\MATSU\22-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYM M GEOM=CHECK GUESS=READ\\Enol for 1,4-hydrogen transfer in 5-ring\\0,2\O\H,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\N,3,r5,1,a4,2,d3,0\C,4,r6,3,a5,1,d4,0\Sn,5,r7,4,a6,3,d5,0\H,5,r8,4,a7,3,d6,0\C,6,r9,3,a8,4,d7,0\H,6,r10,3,a9,4,d8,0\H,7,r11,4,a10,3,d9,0\H,7,r12,4,a11,3,d10,0\H,10,r13,6,a12,3,d11,0\H,10,r14,6,a13,3,d12,0\H,8,r15,5,a14,4,d13,0\H,8,r16,5,a15,4,d14,0\H,8,r17,5,a16,4,d15,0\\r1=0.9589722\r2=1.35310722\r3=1.38136762\r4=1.38675018\r5=1.39240727\r6=1.5186447\r7=2.10930348\r8=1.08149062\r9=1.47172017\r10=1.00772612\r11=1.08879772\r12=1.08638901\r13=1.09021622\r14=1.08579618\a1=109.73826385\a2=125.6252607\a3=127.39252422\a4=119.61557032\a5=105.71424303\a6=125.60334247\a7=116.41437684\a8=106.04537969\a9=113.75124132\a10=109.56217419\a11=112.98691104\a12=110.21555545\a13=110.77701043\d1=-128.59115735\d2=1.22564912\d3=-312.43803171\d4=-182.40826154\d5=-0.70452585\d6=179.14467131\d7=-15.51091708\d8=218.22399439\d9=-105.91299219\d10=134.04621087\d11=-95.8991929\d12=144.12533027\r15=1.70726772\r16=1.70400184\r17=1.71

100563\a14=112.82196463\a15=113.10096183\a16=106.59344187\d13=60.97438042\d14=-62.94664649\d15=178.6821175\\Version=x86-Linux-G03RevB.05\HF=-329.64989\S2=0.79768\S2-1=0.\S2A=0.750463\RMSD=4.420e-09\RMSF=2.822e-05\Dipole=0.909499,-1.0012927,0.5632342\PG=C01 [X(C5H10N1O1Sn1)]\\@

Transition state of the 1,4-hydrogen shift involving 5-membered ring

1\1\GINC-DUAL1\FTS\UBHandHLYP\Gen\C5H10N1O1Sn1(2)\MATSU\20-Mar-2009\0\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(TS,NOEIGENTEST,READFC,MAXCYCLE=100) NOSYMM\\TS for 1,4-hydrogen transfer in 5-ring\\0,2\O,-0.0083839243,0.057740758,0.0708157253\H,0.0523914405,0.0263553524,1.2493258694\C,1.2631974363,0.0301512384,-0.0460302355\C,2.0281003008,0.0813006113,1.1397998756\C,1.1908592874,0.214513061,2.2853681936\N,2.0170318235,-0.1516047926,-1.1360104473\C,3.4441681286,-0.2712778558,0.77489966\Sn,0.5652122012,2.1769896324,2.8614396719\H,1.516886647,-0.3138666816,3.1764246551\C,3.4383286138,-0.1554947599,-0.7763186397\H,1.6629396537,-0.1819391762,-2.0710157885\H,3.6968798257,-1.2856011379,1.0867690636\H,4.1812585254,0.3950339641,1.2157168073\H,3.9130082053,0.7690747074,-1.1001001022\H,3.9439713148,-0.9879627268,-1.2567097151\H,0.0593894098,3.0519195735,1.4883890544\H,1.8213611101,3.0652301766,3.617894287\H,-0.7247957863,2.0586935677,3.9726300688\\Version=x86-Linux-G03RevB.05\HF=-329.6096299\S2=0.755634\S2-1=0.\S2A=0.750026\RMSD=7.409e-09\RMSF=2.654e-06\Dipole=1.4238009,-0.4356629,-1.1192199\PG=C01 [X(C5H10N1O1Sn1)]\\@

Product of the 1,4-hydrogen shift involving 5-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C5H10N1O1Sn1(2)\MATSU\23-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\product for 1,4-hydrogen transfer in 5-ring\\0,2\O\C,1,r2\C,2,r3,1,a2\C,3,r4,2,a3,1,d2,0\N,2,r5,3,a4,4,d3,0\C,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\Sn,4,r81,3,a71,2,d61,0\C,5,r9,2,a8,3,d7,0\H,5,r10,2,a9,3,d8,0\H,6,r11,3,a10,2,d9,0\H,6,r12,3,a11,2,d10,0\H,10,r13,5,a12,2,d11,0\H,10,r14,5,a13,2,d12,0\H,9,r15,4,a14,3,d13,0\H,9,r16,4,a15,3,d14,0\H,9,r17,4,a16,3,d15,0\\r2=1.22621207\r3=1.45288414\r4=1.47378691\r5=1.36405291\r6=1.49440617\r7=1.09436935\r8=1.08802958\r81=2.17218497\r9=1.45289923\r10=1.00199263\r11=1.09188027\r12=1.08882288\r13=1.0896896\r14=1.08679397\r15=1.69546399\r16=1.69783186\r17=1.72321212\a2=125.65997372\a3=121.92694973\a4=107.81204895\a5=109.00807223\a6=110.45257001\a7=111.39732853\a71=113.62762743\a8=113.25361678\a9=119.77750585\a10=110.49906791\a11=112.77758457\a12=110.96938337\a13=111.08559097\a14=113.78817062\a15=112.76007676\a16=102.46410645\d2=6.1120908\d3=-174.14653663\d4=-179.0363155\d5=91.23712047\d6=-150.98837212\d61=-26.77908539\d7=-10.44022772\d8=192.00681958\d9=-111.13380694\d10=129.62768484\d11=-103.81406539\d12=135.89555525\d13=87.10788983\d14=-45.11903296\d15=201.04483841\\Version=x86-Linux-G03RevB.05\HF=-329.6861872\S2=0.758398\S2-1=0.\S2A=0.750054\RMSD=7.235e-09\RMSF=3.994e-05\Dipole=-0.5484046,-0.0154413,1.9324678\PG=C01 [X(C5H10N1O1Sn1)]\\@

Substrate of the 1,4-hydrogen shift involving 6-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C6H12N1O1Sn1(2)\MATSU\23-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\Enol for 1,4-hydrogen transfer in 6-ring\\0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4,d5,0\H,7,r71,1,a61,2,d51,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\Sn,16,r15,6,a14,1,d13,0\H,16,r16,6,a15,1,d14,0\H,17,r17,16,a16,6,d15,0\H,17,r18,16,a17,6,d16,0\H,17,r19,16,a18,6,d17,0\\r1=1.38746581\r2=1.45689612\r3=1.52001092\r4=1.52578651\r5=1.38453977\r6=1.36636749\r7=1.00700307\r71=0.95915233\r8=1.09351079\r9=1.08775126\r10=1.08818688\r11=1.08884055\r12=1.09061596\r13=1.08722727\r14=1.39528112\r15=2.10782753\r16=1.08212926\r17=1.70391816\r18=1.70859932\r19=1.71504247\a1=117.69964328\a2=109.84661139\a3=110.2565321\a4=125.98693837\a5=113.56224032\a6=113.23923321\a61=109.27456582\a7=110.97353226\a8=108.3609311\a9=109.07008704\a10=109.20602567\a11=109.58546528\a12=110.13322597\a13=120.68048023\a14=127.6095296\a15=115.31875695\a16=113.94805774\a17=113.54530357\a18=105.89211136\d1=-39.0443693\d2=58.6101139\d3=13.20406644\d4=-170.48907704\d5=-171.66557394\d51=-51.10075643\d6=81.65415293\d7=-160.15801401\d8=180.27401723\d9=-62.37360004\d10=69.63084717\d11=186.66296799\d12=-154.08178271\d13=1.08810596\d14=180.58422089\d15=64.6585792\d16=-60.90072878\d17=182.30812321\\Version=x86-Linux-G03RevB.05\HF=-368.9515584\S2=0.798957\S2-1=0.\S2A=0.750477\RMSD=7.074e-09\RMSF=2.785e-05\Dipole=0.2813389,-0.0478948,1.6772283\PG=C01 [X(C6H12N1O1Sn1)]\\@

Transition state of the 1,4-hydrogen shift involving 6-membered ring

1\1\GINC-DUAL1\FTS\UBHandHLYP\Gen\C6H12N1O1Sn1(2)\MATSU\23-Mar-2009\0\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(TS,NOEIGENTEST,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\TS for 1,4-hydrogen transfer in 6-ring\\0,2\O,-0.0050603752,0.03974673

15,0.0749126956\H,0.0603361836,0.0132696552,1.2522074598\C,1.2730912071,0.029066355,-0.0744998341\C,2.0244216164,0.085979978,1.1298224424\C,1.1480516767,0.2556742498,2.2460952143\N,1.8292899906,-0.0468026219,-1.2951367783\C,3.4977617719,-0.1892126705,1.073650788\H,1.4874982161,-0.2126304377,3.1655395304\Sn,0.4531322853,2.2238394488,2.7254448349\C,3.2477682729,-0.3406118619,-1.4416584815\C,4.0472539363,0.2538829141,-0.2868048047\H,1.2072131634,-0.2612469677,-2.0521686997\H,4.012319456,0.3397840989,1.8725983453\H,3.6981305034,-1.2528754589,1.2248640093\H,3.5892317584,0.076257211,-2.3859222528\H,3.4039537938,-1.4207482766,-1.4796960981\H,5.0866015253,-0.0483986335,-0.3972658801\H,4.0126555481,1.3397689847,-0.3540387994\H,1.6276359405,3.1028531223,3.6117302118\H,-0.9493342506,2.1236410272,3.6929923258\H,0.1051631419,3.0884761574,1.2992056245\\Version=x86-Linux-G03RevB.05\HF=-368.9185236\S2=0.755097\S2-1=0.\S2A=0.750022\RMSD=6.876e-09\RMSF=6.985e-06\Dipole=1.4183268,-0.5425081,-1.0735448\PG=C01 [X(C6H12N1O1Sn1)]\\@

Product of the 1,4-hydrogen shift involving 6-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C6H12N1O1Sn1(2)\MATSU\23-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\product for 1,4-hydrogen transfer in 6-ring\\0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4,d5,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,15,r15,6,a14,1,d13,0\H,15,r16,6,a15,1,d14,0\Sn,15,r17,6,a16,1,d15,0\H,18,r18,15,a17,6,d16,0\H,18,r19,15,a18,6,d17,0\H,18,r20,15,a19,6,d18,0\\r1=1.36160122\r2=1.45056984\r3=1.52041544\r4=1.52784083\r5=1.45590123\r6=1.23527914\r7=1.00348575\r8=1.09305893\r9=1.0873662\r10=1.08781049\r11=1.08837893\r12=1.09519239\r13=1.08868327\r14=1.47575676\r15=1.08578621\r16=1.09262063\r17=2.17275049\r18=1.7253115\r19=1.69982478\r20=1.69581699\a1=123.6688418\a2=110.07478008\a3=110.57471485\a4=118.24265362\a5=121.06103351\a6=118.78967076\a7=110.90694211\a8=108.38917506\a9=109.34802607\a10=109.04513277\a11=109.45201619\a12=110.44849713\a13=122.5576972\a14=111.57463587\a15=110.48230912\a16=112.74397064\a17=103.92685434\a18=112.2589407\a19=113.65908572\d1=-38.30615592\d2=55.11805733\d3=13.95068201\d4=-166.376639\d5=-195.51350316\d6=83.31169656\d7=-158.93579681\d8=176.86866145\d9=-65.53268863\d10=71.22178218\d11=187.55692703\d12=-156.21172335\d13=166.64840124\d14=286.36418912\d15=40.78493806\d16=144.86287571\d17=30.76377436\d18=-100.52892291\\Version=x86-Linux-G03RevB.05\HF=-368.9859447\S2=0.758406\S2-1=0.\S2A=0.750052\RMSD=9.706e-09\RMSF=2.113e-05\Dipole=1.2928615,-0.4243473,1.4765586\PG=C01 [X(C6H12N1O1Sn1)]\\@

Substrate of the 1,4-hydrogen shift involving 7-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C7H14N1O1Sn1(2)\MATSU\24-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\Enol for 1,4-hydrogen transfer in 7-ring\\0,2\O\H,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\N,3,r5,1,a4,2,d3,0\C,6,r6,3,a5,4,d4,0\C,7,r7,6,a6,3,d5,0\C,4,r8,3,a7,1,d6,0\C,9,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\Sn,5,r11,4,a10,3,d9,0\H,6,r12,3,a11,1,d10,0\H,7,r13,6,a12,3,d11,0\H,7,r14,6,a13,3,d12,0\H,8,r15,7,a14,6,d13,0\H,8,r16,7,a15,6,d14,0\H,9,r17,4,a16,3,d15,0\H,9,r18,4,a17,3,d16,0\H,10,r19,9,a18,4,d17,0\H,10,r20,9,a19,4,d18,0\H,12,r21,5,a20,4,d19,0\H,12,r22,5,a21,4,d20,0\H,12,r23,5,a22,4,d21,0\\r1=0.95775296\r2=1.36545037\r3=1.3902539\r4=1.40250309\r5=1.37337052\r6=1.45264544\r7=1.52691603\r8=1.52596425\r9=1.52953814\r10=1.0822601\r11=2.10779843\r12=1.00230808\r13=1.08689144\r14=1.0907262\r15=1.0889161\r16=1.09026978\r17=1.08790686\r18=1.09133359\r19=1.08790452\r20=1.08901666\r21=1.70726519\r22=1.70531696\r23=1.71364236\a1=109.12716896\a2=121.66385682\a3=121.56359613\a4=111.24614985\a5=120.08941116\a6=111.84428611\a7=120.74177763\a8=116.62752775\a9=114.581863\a10=130.08162604\a11=112.17172874\a12=108.09093039\a13=109.52133067\a14=109.77673579\a15=108.26822641\a16=106.30613703\a17=109.60127973\a18=108.98809144\a19=108.83917542\a20=107.02818632\a21=113.31285505\a22=112.11867283\d1=45.19741846\d2=10.52613811\d3=-136.35742286\d4=29.42307786\d5=-84.4009193\d6=-167.8666586\d7=23.3497146\d8=-173.68193877\d9=18.93617317\d10=-5.9059236\d11=154.2904173\d12=37.84071898\d13=-79.99915024\d14=163.48452686\d15=144.29754674\d16=-101.95943992\d17=44.35604753\d18=160.17408868\d19=170.40440196\d20=50.5251793\d21=-71.79485326\\Version=x86-Linux-G03RevB.05\HF=-408.2362625\S2=0.790137\S2-1=0.\S2A=0.750342\RMSD=8.908e-09\RMSF=5.238e-05\Dipole=0.5544239,0.7537982,-0.6462539\PG=C01 [X(C7H14N1O1Sn1)]\\@

Transition state of the 1,4-hydrogen shift involving 7-membered ring

1\1\GINC-DUAL1\FTS\UBHandHLYP\Gen\C7H14N1O1Sn1(2)\MATSU\24-Mar-2009\0\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(TS,NOEIGENTEST,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\TS for 1,4-hydrogen transfer in 7-ring\\0,2\O,-0.0073132192,-0.0439474001,0.0649846163\H,0.0479435243,-0.0225255593,1.2461254034\C,1.273481788,-0.0075343763,-0.0793244955\C,2.0113896863,-0.0087250493,1.1404085129\C,1.1173980324,-0.2570795999,2.233896375\N,1.7979872713,0.047

4786608,-1.3171133073\C,3.1846914935,-0.3074119079,-1.5701545651\C,4.1716524099,0.7953101141,-1.1914948689\C,3.4315085266,0.4787021007,1.2623995704\C,3.8774467003,1.4483261039,0.1632318099\H,1.3980251015,0.2312136885,3.161894814\Sn,0.4989181308,-2.2605245849,2.6556146992\H,1.1338373933,-0.0031516499,-2.0658894056\H,3.2784953586,-0.5400202759,-2.62708815\H,3.4210336533,-1.2188353136,-1.0228258575\H,4.1758904696,1.5653842688,-1.9612706923\H,5.1670859141,0.3509661612,-1.1832055903\H,3.511532422,0.9786902878,2.2266126085\H,4.1233222222,-0.3664766511,1.3182240554\H,3.1069534202,2.2070509039,0.0402825568\H,4.7738873289,1.9715283511,0.4920635048\H,-1.0083697153,-2.2631422468,3.4563254429\H,1.6224699757,-3.0580464616,3.6736196947\H,0.3718967787,-3.1458260246,1.2038818681\\Version=x86-Linux-G03RevB.05\HF=-408.208489\S2=0.755388\S2-1=0.\S2A=0.750024\RMSD=9.543e-09\RMSF=3.046e-06\Dipole=1.3424321,0.3070738,-1.0682489\PG=C01 [X(C7H14N1O1Sn1)]\\@

Product of the 1,4-hydrogen shift involving 7-membered ring

1\1\GINC-DUAL1\FOpt\UBHandHLYP\Gen\C7H14N1O1Sn1(2)\MATSU\27-Mar-2009\1\\#BHANDHLYP/GEN SCF=DIRECT PSEUDO=READ FREQ=NORAMAN OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ\\product for 1,4-hydrogen transfer in 7-ring\\0,2\O\C,1,r2\C,2,r3,1,a2\C,3,r4,2,a3,1,d2,0\N,2,r5,3,a4,4,d3,0\C,5,r6,2,a5,3,d4,0\C,6,r7,5,a6,2,d5,0\C,3,r8,2,a7,1,d6,0\C,8,r9,3,a8,2,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\Sn,4,r1,3,a1,2,d1,0\H,5,r12,2,a11,1,d10,0\H,6,r13,5,a12,2,d11,0\H,6,r14,5,a13,2,d12,0\H,7,r15,6,a14,5,d13,0\H,7,r16,6,a15,5,d14,0\H,8,r17,3,a16,2,d15,0\H,8,r18,3,a17,2,d16,0\H,9,r19,8,a18,3,d17,0\H,9,r20,8,a19,3,d18,0\H,12,r21,4,a20,3,d19,0\H,12,r22,4,a21,3,d20,0\H,12,r23,4,a22,3,d21,0\\r2=1.23630759\r3=1.46223923\r4=1.4745267\r5=1.36078869\r6=1.45051406\r7=1.52701479\r8=1.50464391\r9=1.53025575\r10=1.0901237\r11=1.08482444\r1=2.18149753\r12=1.00270422\r13=1.08647863\r14=1.08922946\r15=1.08868829\r16=1.09023214\r17=1.09089293\r18=1.09489825\r19=1.08793207\r20=1.08844558\r21=1.72633715\r22=1.69626167\r23=1.699277 1\a2=119.76702294\a3=115.02251812\a4=119.70981465\a5=123.60587831\a6=112.9839756\a7=124.51028406\a8=116.09702736\a9=111.71824039\a10=112.18826554\a1=110.73411255\a11=113.59546224\a12=107.88298546\a13=109.34245361\a14=109.97034572\a15=108.00424039\a16=106.78580946\a17=109.79385377\a18=108.74695549\a19=108.87080084\a20=104.15115685\a21=113.46969502\a22=112.11136885\d2=18.75269113\d3=-161.75604139\d4=18.61381722\d5=-82.28673401\d6=-151.55341819\d7=14.06677609\d8=62.08053679\d9=-175.58924493\d1=-51.47229163\d10=-3.89246376\d11=155.78006189\d12=40.22583188\d13=-77.86948156\d14=165.65669927\d15=135.34437822\d16=-111.35427024\d17=47.91222108\d18=163.50772553\d19=218.66224752\d20=104.0188635\d21=-27.19519048\\Version=x86-Linux-G03RevB.05\HF=-408.2733403\S2=0.758547\S2-1=0.\S2A=0.750054\RMSD=8.421e-09\RMSF=2.818e-05\Dipole=-0.6330105,0.2518418,1.8453656\PG=C01 [X(C7H14N1O1Sn1)]\\@

Substrate of the 1,4-hydrogen shift involving 8-membered ring

1\1\GINC-I7\FOpt\UBHandHLYP\Gen\C8H16N1O1Sn1(2)\HIROSHI\13-Nov-2010\1\\#BHandHLYP/gen pseudo=read freq=NOraman geom=check guess=read OPT=(Z-matrix,ReadFC,Maxcycle=100) Nosymm\\c8 subst\\0,2\O\C,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\H,1,r4,2,a3,3,d2,0\N,2,r5,1,a4,3,d3,0\C,6,r6,2,a5,1,d4,0\C,7,r7,6,a6,2,d5,0\C,3,r8,2,a7,6,d6,0\C,9,r9,3,a8,2,d7,0\C,10,r10,9,a9,3,d8,0\H,4,r11,3,a10,2,d9,0\Sn,4,r12,3,a11,2,d10,0\H,6,r13,2,a12,1,d11,0\H,7,r14,6,a13,2,d12,0\H,7,r15,6,a14,2,d13,0\H,8,r16,7,a15,6,d14,0\H,8,r17,7,a16,6,d15,0\H,9,r18,3,a17,2,d16,0\H,9,r19,3,a18,2,d17,0\H,10,r20,9,a19,3,d18,0\H,10,r21,9,a20,3,d19,0\H,11,r22,10,a21,9,d20,0\H,11,r23,10,a22,9,d21,0\H,13,r24,4,a23,3,d22,0\H,13,r25,4,a24,3,d23,0\H,13,r26,4,a25,3,d24,0\\r1=1.36728572\r2=1.38968679\r3=1.40401676\r4=0.95797863\r5=1.36444467\r6=1.45123859\r7=1.52717719\r8=1.52216467\r9=1.54414076\r10=1.53272942\r11=1.08185713\r12=2.1086434\r13=1.0017124\r14=1.08669521\r15=1.08945896\r16=1.09005197\r17=1.09052804\r18=1.09074207\r19=1.08674375\r20=1.08849635\r21=1.08790399\r22=1.08990394\r23=1.09135411\r24=1.70532702\r25=1.71323201\r26=1.70724474\a1=121.17655902\a2=121.04724357\a3=108.66332474\a4=110.85765811\a5=125.78653936\a6=112.95441306\a7=121.13786812\a8=118.86737795\a9=114.93168857\a10=114.75431662\a11=129.84884552\a12=113.06686266\a13=109.05262185\a14=107.78560324\a15=107.54847929\a16=108.64575226\a17=109.59041097\a18=105.38770474\a19=107.33057071\a20=110.54657919\a21=108.91233283\a22=108.13684599\a23=113.05858997\a24=112.26432686\a25=107.04192628\d1=14.48870767\d2=38.27074779\d3=-179.91636157\d4=215.7050934\d5=-110.77586474\d6=15.06077193\d7=35.45761823\d8=-107.70122297\d9=-172.71024812\d10=20.97266076\d11=10.19355819\d12=13.45244767\d13=-231.24141913\d14=-45.32840934\d1 5=-160.34099713\d16=-90.77217231\d17=-203.10563122\d18=133.47522305\d19=18.15069855\d20=201.55605299\d21=-43.7824022\d22=46.99012182\d23=-75.22100417\d24=166.88572667\\Version=EM64L-G03RevE.01\HF=-447.5224662\S2=0.788248\S2-1=0.\S2A=0.75032\RMSD=5.966e-09\RMSF=1.637e-05\Thermal=0.\Dipole=-0.9127766,-0.3713922,0.7659367\PG=C01 [X(C8H16N1O1Sn1)]\\@

Transition state of the 1,4-hydrogen shift involving 8-membered ring

1\1\GINC-I7\FTS\UBHandHLYP\Gen\C8H16N1O1Sn1(2)\HIROSHI\13-Nov-2010\1\\#BHandHLYP/gen pseudo=read geom=check guess=read OPT=(TS,Z-matrix,NoEigenTest,ReadFC,Maxcycle=100) Nosymm\\c8 TS another\\0,

2\O\H,1,r1\C,1,r2,2,a1\C,2,r3,1,a2,3,d1,0\C,3,r4,1,a3,2,d2,0\N,3,r5,1,a4,2,d3,0\C,6,r6,3,a5,1,d4,0\C,7,r7,6,a6,3,d5,0\C,5,r8,3,a7,6,d6,0\C,9,r9,5,a8,3,d7,0\C,10,r10,9,a9,5,d8,0\H,4,r11,5,a10,3,d9,0\Sn,4,r12,5,a11,3,d10,0\H,6,r13,3,a12,1,d11,0\H,7,r14,6,a13,3,d12,0\H,7,r15,6,a14,3,d13,0\H,8,r16,7,a15,6,d14,0\H,8,r17,7,a16,6,d15,0\H,9,r18,5,a17,3,d16,0\H,9,r19,5,a18,3,d17,0\H,10,r20,9,a19,5,d18,0\H,10,r21,9,a20,5,d19,0\H,11,r22,10,a21,9,d20,0\H,11,r23,10,a22,9,d21,0\H,13,r24,4,a23,5,d22,0\H,13,r25,4,a24,5,d23,0\H,13,r26,4,a25,5,d24,0\\r1=1.18355526\r2=1.29246335\r3=1.46214443\r4=1.42619215\r5=1.34262218\r6=1.45178479\r7=1.5285342\r8=1.50562178\r9=1.54433794\r10=1.53147937\r11=1.08526138\r12=2.13862557\r13=1.00264638\r14=1.08700997\r15=1.08750386\r16=1.08970318\r17=1.09009177\r18=1.09332512\r19=1.08756404\r20=1.08848442\r21=1.08916233\r22=1.08981976\r23=1.09151836\r24=1.71330649\r25=1.70520761\r26=1.70696215\a1=93.99704897\a2=134.38351684\a3=114.30364455\a4=117.57627556\a5=126.7784953\a6=114.2075321\a7=125.95015753\a8=118.17422782\a9=115.89380004\a10=114.26376449\a11=119.722648\a12=113.75889172\a13=109.07786083\a14=106.59493222\a15=108.06457221\a16=108.23194762\a17=110.48900436\a18=105.30155773\a19=107.07563478\a20=110.09061703\a21=108.50956642\a22=108.37394134\a23=111.38131083\a24=109.97085248\a25=110.437288\d1=-15.04113238\d2=0.50366164\d3=-178.53498121\d4=199.60691963\d5=-100.08614764\d6=21.91119366\d7=34.13332956\d8=-101.11700628\d9=-148.43386114\d10=79.2605039\d11=2.98382119\d12=24.62467285\d13=-220.71505237\d14=-38.08875957\d15=-153.16880722\d16=-92.32156038\d17=-204.76767471\d18=139.86547479\d19=25.06887592\d20=200.71036394\d21=-44.66869372\d22=85.84341334\d23=-34.09112896\d24=205.07707711\\Version=EM64L-G03RevE.01\HF=-447.4953658\S2=0.755602\S2-1=0.\S2A=0.750026\RMSD=8.378e-09\RMSF=6.668e-05\Thermal=0.\Dipole=1.4122355,0.3615347,-1.063535\PG=C01 [X(C8H16N1O1Sn1)]\\@

Product of the 1,4-hydrogen shift involving 8-membered ring

1\1\GINC-I7\FOpt\UBHandHLYP\Gen\C8H16N1O1Sn1(2)\HIROSHI\13-Nov-2010\1\\#BHandHLYP/gen pseudo=read freq=NOraman geom=check guess=read OPT=(Z-matrix,calcFC,Maxcycle=100,Maxstep=15) SCF=NoVarAcc Nosymm\\c8 product\\0,2\O\C,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\H,4,r4,3,a3,2,d2,0\N,2,r5,1,a4,3,d3,0\C,6,r6,2,a5,1,d4,0\C,7,r7,6,a6,2,d5,0\C,3,r8,2,a7,6,d6,0\C,9,r9,3,a8,2,d7,0\C,10,r10,9,a9,3,d8,0\Sn,4,r11,3,a10,2,d9,0\H,4,r12,3,a11,2,d10,0\H,6,r13,2,a12,1,d11,0\H,7,r14,6,a13,2,d12,0\H,7,r15,6,a14,2,d13,0\H,8,r16,7,a15,6,d14,0\H,8,r17,7,a16,6,d15,0\H,9,r18,3,a17,2,d16,0\H,9,r19,3,a18,2,d17,0\H,10,r20,9,a19,3,d18,0\H,10,r21,9,a20,3,d19,0\H,11,r22,10,a21,9,d20,0\H,11,r23,10,a22,9,d21,0\H,12,r24,4,a23,3,d22,0\H,12,r25,4,a24,3,d23,0\H,12,r26,4,a25,3,d24,0\\r1=1.23747493\r2=1.46255653\r3=1.47601327\r4=1.08945055\r5=1.35694961\r6=1.45194071\r7=1.52545891\r8=1.50488412\r9=1.53928163\r10=1.53280938\r11=2.18309085\r12=1.08491266\r13=1.00377215\r14=1.08770354\r15=1.08840035\r16=1.08973624\r17=1.09025731\r18=1.09476424\r19=1.09150895\r20=1.08845508\r21=1.08850797\r22=1.08957066\r23=1.09140181\r24=1.69637509\r25=1.69941541\r26=1.72749069\a1=119.2390411\a2=114.24890593\a3=111.98836546\a4=119.92831389\a5=126.7452075\a6=113.67208609\a7=126.00168285\a8=120.34375535\a9=115.95104308\a10=110.27687425\a11=112.24929636\a12=112.33153904\a13=109.06003938\a14=107.32882394\a15=108.06195011\a16=108.66123789\a17=109.3882137\a18=105.00268353\a19=106.29382428\a20=110.53990676\a21=108.52529351\a22=108.31089803\a23=113.63594098\a24=112.0997475\a25=104.13322168\d1=25.01246761\d2=59.98374736\d3=-179.49139239\d4=203.3247013\d5=-108.62817222\d6=39.32269869\d7=9.64724241\d8=-94.08265575\d9=-54.0029968\d10=182.64656953\d11=0.30426828\d12=15.35778235\d13=-229.68593634\d14=-41.81804535\d15=-157.19161976\d16=-117.63320032\d17=-229.06257253\d18=147.37803809\d19=32.75613681\d20=204.75904128\d21=-40.6745246\d22=103.60122402\d23=-27.89397006\d24=218.14971169\\Version=EM64L-G03RevE.01\HF=-447.5590166\S2=0.758675\S2-1=0.\S2A=0.750056\RMSD=9.485e-09\RMSF=5.803e-05\Thermal=0.\Dipole=-0.7072549,0.1629213,1.8605772\PG=C01 [X(C8H16N1O1Sn1)]\\@

BHandHLYP/6-31G* Gaussian Archive entries for the optimized structures involved in the radical substitution reaction on nitrogen and higher-level calculated single-point energies

N-phenethyl-5-amino-2-methylenepentanoyl radical (K)

BHandHLYP/6-31G*

1\1\GINC-QUAD\POpt\UBHandHLYP\6-31G(d)\C14H18N1O1(2)\HIROSHI\12-Jan-2011\1\\#BHandHLYP/6-31G* SCF=direct OPT=(Z-matrix,CalcFC,Maxcycle=100) Nosymm\\subst for cyclization with phenethylamine\\0,2\C\X,1,1.\O,1,r1,2,90.\C,1,r2,2,a1,3,d1,0\C,4,r3,1,a2,3,d2,0\C,4,r4,1,a3,3,d3,0\C,6,r5,4,a4,1,d4,0\C,7,r6,6,a5,4,d5,0\N,8,r7,7,a6,6,d6,0\H,9,r8,8,a7,7,d7,0\C,9,r81,8,a71,7,d71,0\H,5,r9,4,a8,1,d8,0\H,5,r10,4,a9,1,d9,0\H,6,r11,4,a10,1,d10,0\H,6,r12,4,a11,1,d11,0\H,7,r13,6,a12,4,d12,0\H,7,r14,6,a13,4,d13,0\H,8,r15,7,a14,6,d14,0\H,8,r16,7,a15,6,d15,0\C,11,r17,9,a16,8,d16,0\C,11,r18,9,a17,8,d17,0\H,11,r19,9,a18,8,d18,0\H,20,r20,11,a19,9,d19,0\H,20,r21,11,a20,9,d20,0\H,20,r22,11,a21,9,d20c,0\X,21,1.4,11,90.,20,180.,0\X,21,1.4,26,90.,11,180.,0\C,27,r23,21,a22,20,d21,0\C,27,r24,28,a23,21,d22,0\C,27,r25,29,a24,28,d23,0\C,27,r26,30,a25,29,d24,0\C,27,r27,31,a26,30,d25,0\H,28,r28,21,a27,11,d26,0\H,29,r29,28,a28,21,d27,0\H,30,r30,29,a29,28,d28,0\H,31,r31,30,a30,29,d29,0\H,32,r32,31,a31,30,d30,0\\r1=1.17821566\r2=1.49157859\r3=1.32829694\r4=1.49923957\r5=1.5282239\r6=1.51987634\r7=1.44893843\r8=1.00905549

\r81=1.4577249\r9=1.07740623\r10=1.07912442\r11=1.08815316\r12=1.09059172\r13=1.0910414\r14=1.08797819
\r15=1.0878176\r16=1.09905303\r17=1.52821282\r18=1.51269236\r19=1.09788514\r20=1.0866846\r21=1.0869023
4\r22=1.0864481\r23=1.37763167\r24=1.37867577\r25=1.39349871\r26=1.39169565\r27=1.38531133\r28=1.07738
225\r29=1.07842165\r30=1.07813593\r31=1.07830911\r32=1.07948389\a1=40.77825619\a2=118.03465557\a3=11
6.63706906\a4=112.74511384\a5=112.48725885\a6=110.63571346\a7=108.79469425\a71=115.22220503\a8=120.9
2519175\a9=121.58521856\a10=109.2167985\a11=108.94342712\a12=109.01341124\a13=109.91469936\a14=108.
9440585\a15=109.48106862\a16=110.76791567\a17=109.6273699\a18=110.8931866\a19=110.056503\a20=111.74
291586\a21=110.17460863\a22=60.13267274\a23=60.34160423\a24=60.01709223\a25=59.65680223\a26=59.8838
9125\a27=119.04162771\a28=119.71301392\a29=120.2348963\a30=120.13950383\a31=119.67712545\d1=196.565
43402\d2=-0.25238179\d3=179.57172148\d4=-66.15105127\d5=176.87209295\d6=177.80883188\d7=52.59692906\
d71=-185.69434838\d8=0.23184187\d9=180.38187434\d10=-188.59255015\d11=55.05875749\d12=55.20806614\d
13=-61.46662344\d14=58.22391397\d15=-57.79443995\d16=70.11601281\d17=192.26414279\d18=-49.14338249\
d19=57.10866479\d20=-63.46466727\d20c=176.75062866\d21=80.50089168\d22=178.38195568\d23=178.221664
23\d24=178.38794061\d25=178.44348939\d26=2.19156522\d27=180.16953692\d28=180.05566838\d29=180.3736
1092\d30=180.45309446\\Version=EM64L-G03RevE.01\HF=-673.8044076\S2=0.755527\S2-1=0.\S2A=0.750022\
RMSD=5.075e-09\RMSF=1.501e-05\Thermal=0.\Dipole=-0.8512308,-0.0885551,0.4879445\Polar=139.0371571,-1.
6799544,133.5095373,32.7520943,-18.9076914,163.836409\PG=C01 [X(C14H18N1O1)]\\@

BHandHLYP/6-31+G*//BHandHLYP/6-31G*
HF=-673.8269034

Transition state for the ring-closure reaction L

BHandHLYP/6-31G*

1\1\GINC-QUAD\FTS\UBHandHLYP\6-31G(d)\C14H18N1O1(2)\HIROSHI\12-Jan-2011\1\\#BHandHLYP/6-31G
* SCF=direct OPT=(TS,NoEigenTest,Z-matrix,CalcFC,Maxcycle=100) Nosymm\\TS for cyclization with phenetyla
mine\\0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a
6,4,d5,0\C,2,r71,3,a61,4,d51,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r1
2,4,a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,16,r15,6,a14,1,d13,0\H,16,r16,6,a15,1,d14,0\C,9,r17,
2,a16,1,d15,0\C,9,r18,2,a17,1,d16,0\H,9,r19,2,a18,1,d17,0\H,19,r20,9,a19,2,d18,0\H,19,r21,9,a20,2,d19,0\H,19,r22,
9,a21,2,d20,0\X,20,1.4,9,90.,19,180.,0\X,20,1.4,25,90.,9,180.,0\C,26,r23,20,a22,19,d21,0\C,26,r24,27,a23,20,d22,0\
C,26,r25,28,a24,27,d23,0\C,26,r26,29,a25,28,d24,0\C,26,r27,30,a26,29,d25,0\H,27,r28,20,a27,9,d26,0\H,28,r29,27,a
28,20,d27,0\H,29,r30,28,a29,27,d28,0\H,30,r31,29,a30,28,d29,0\H,31,r32,30,a31,29,d30,0\\r1=2.25823542\r2=1.457
50671\r3=1.51610784\r4=1.52170597\r5=1.35398962\r6=1.17655291\r7=1.0064264\r71=1.4856871\r8=1.08837862
\r9=1.09276315\r10=1.08924538\r11=1.08867688\r12=1.09199982\r13=1.08711828\r14=1.41053201\r15=1.075107
5\r16=1.07589564\r17=1.52712529\r18=1.51360394\r19=1.08987058\r20=1.08589986\r21=1.08401829\r22=1.0871
5316\r23=1.38450229\r24=1.39029069\r25=1.39191861\r26=1.37882615\r27=1.38038285\r28=1.07923994\r29=1.0
7821059\r30=1.07804654\r31=1.07818188\r32=1.07880275\a1=111.3255863\a2=110.23276427\a3=112.33700206\
a4=104.3507508\a5=100.10969251\a6=109.80633908\a61=115.03221246\a7=107.96015789\a8=111.44000049\a9=
108.92042417\a10=109.88377012\a11=108.08455497\a12=108.3987436\a13=117.92270779\a14=121.92194961\a1
5=119.72725829\a16=112.61253418\a17=110.68798282\a18=107.09944769\a19=111.02601341\a20=111.09155138
\a21=109.56295493\a22=59.85289574\a23=59.96531437\a24=59.69224618\a25=60.07168362\a26=60.25701084\a2
7=119.5607808\a28=119.79371747\a29=120.21045187\a30=120.03775779\a31=119.85921051\d1=-43.94256677\d
2=66.53667314\d3=20.31065918\d4=-163.66325101\d5=-149.74517227\d51=87.7880645\d6=75.11719901\d7=-16
7.57332216\d8=186.58892308\d9=-56.937815\d10=62.44456511\d11=176.57679522\d12=-150.84970867\d13=-3.4
2213965\d14=173.32389072\d15=20.13662452\d16=-105.25748838\d17=138.13525147\d18=55.77823781\d19=-64
.58799624\d20=175.58925139\d21=112.66051077\d22=179.67797507\d23=179.92031281\d24=179.7522167\d25=
179.62221433\d26=0.23188859\d27=179.9647264\d28=180.16558141\d29=179.89761497\d30=179.72071453\\Ver
sion=EM64L-G03RevE.01\HF=-673.7940561\S2=0.787945\S2-1=0.\S2A=0.750311\RMSD=2.694e-09\RMSF=3.6
78e-05\Thermal=0.\Dipole=0.4898516,-0.0074923,1.313475\Polar=170.6256992,-30.5005285,102.4055788,-30.611
4054,1.7996495,172.2301087\PG=C01 [X(C14H18N1O1)]\\@

BHandHLYP/6-31+G*//BHandHLYP/6-31G*
HF=-673.8139062

Intermediate M

BHandHLYP/6-31G*

1\1\GINC-QUAD\FOpt\UBHandHLYP\6-31G(d)\C14H18N1O1(2)\HIROSHI\12-Jan-2011\1\\#BHandHLYP/6-31G
* SCF=direct OPT=(Z-matrix,CalcFC,Maxcycle=100) Nosymm\\intermediate for cyclization with phenethylamine\\
0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4,d5,
0\C,2,r71,3,a61,4,d51,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,a11
,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,16,r15,6,a14,1,d13,0\H,16,r16,6,a15,1,d14,0\C,9,r17,2,a16,1
,d15,0\C,9,r18,2,a17,1,d16,0\H,9,r19,2,a18,1,d17,0\H,19,r20,9,a19,2,d18,0\H,19,r21,9,a20,2,d19,0\H,19,r22,9,a21,2,
d20,0\X,20,1.4,9,90.,19,180.,0\X,20,1.4,25,90.,9,180.,0\C,26,r23,20,a22,19,d21,0\C,26,r24,27,a23,20,d22,0\C,26,r25
,28,a24,27,d23,0\C,26,r26,29,a25,28,d24,0\C,26,r27,30,a26,29,d25,0\H,27,r28,20,a27,9,d26,0\H,28,r29,27,a28,20,d2
7,0\H,29,r30,28,a29,27,d28,0\H,30,r31,29,a30,28,d29,0\H,31,r32,30,a31,29,d30,0\\r1=1.55422306\r2=1.48324604\r
3=1.51205484\r4=1.52134688\r5=1.39544363\r6=1.24134983\r7=1.01342093\r71=1.53786224\r8=1.08604538\r9=
1.08653645\r10=1.08759604\r11=1.08917578\r12=1.09225243\r13=1.08798901\r14=1.38399329\r15=1.07475454\r
16=1.0773759\r17=1.52067855\r18=1.50922339\r19=1.08494036\r20=1.08496564\r21=1.0825194\r22=1.08644314
\r23=1.39264993\r24=1.39238039\r25=1.38410301\r26=1.37368913\r27=1.38476992\r28=1.07950799\r29=1.07797
802\r30=1.0779839\r31=1.07792923\r32=1.08010714\a1=114.54259915\a2=109.25972372\a3=109.77441759\a4=1
17.02099581\a5=110.61123445\a6=108.00030515\a61=112.71344846\a7=107.00479617\a8=108.36182175\a9=108.
99519958\a10=109.64508602\a11=108.21910225\a12=109.44000382\a13=118.43014723\a14=120.76912332\a15=1
20.85903073\a16=112.5708813\a17=109.3675683\a18=104.94343119\a19=111.21195738\a20=111.00823724\a21=
108.0220433\a22=59.65580852\a23=59.70648001\a24=59.8459113\a25=60.39374791\a26=60.27449121\a27=119.7
8240344\a28=119.84220376\a29=120.07590699\a30=120.04353899\a31=120.8653326\d1=-54.12693299\d2=63.47
349176\d3=27.00137625\d4=-156.47114348\d5=-165.1581484\d51=79.47620265\d6=65.4342007\d7=-177.878731
72\d8=184.98193341\d9=-58.58964945\d10=76.29190833\d11=191.17652632\d12=-165.24861701\d13=-1.316086
05\d14=177.50029179\d15=13.42048833\d16=-112.9962064\d17=131.0602276\d18=58.79941503\d19=-61.770148
04\d20=178.17875664\d21=111.18211229\d22=178.7430566\d23=179.13159597\d24=178.98114912\d25=178.754
06932\d26=0.94644699\d27=179.87971181\d28=180.25015626\d29=180.03189357\d30=180.27934473\\Version=E
M64L-G03RevE.01\HF=-673.8049731\S2=0.799627\S2-1=0.\S2A=0.750444\RMSD=6.178e-09\RMSF=2.227e-05\
Thermal=0.\Dipole=0.485537,-0.2931342,2.6229333\Polar=163.3788942,-34.235024,107.8529044,-36.9584904,4.8
211945,178.6980242\PG=C01 [X(C14H18N1O1)]\\@

BHandHLYP/6-31+G*//BHandHLYP/6-31G*

HF=-673.8271981

Transition state for the expulsion of phenethyl radical N

BHandHLYP/6-31G*

1\1\GINC-QUAD\FTS\UBHandHLYP\6-31G(d)\C14H18N1O1(2)\HIROSHI\12-Jan-2011\1\\#BHandHLYP/6-31G
* SCF=direct OPT=(TS,NoEigenTest,Z-matrix,CalcFC,Maxcycle=100) Nosymm\\TS for expulsion of phenetyl radi
cal\\0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4
,d5,0\C,2,r71,3,a61,4,d51,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,
a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,16,r15,6,a14,1,d13,0\H,16,r16,6,a15,1,d14,0\C,9,r17,2,a1
6,1,d15,0\C,9,r18,2,a17,1,d16,0\H,9,r19,2,a18,1,d17,0\H,19,r20,9,a19,2,d18,0\H,19,r21,9,a20,2,d19,0\H,19,r22,9,a2
1,2,d20,0\X,20,1.4,9,90.,19,180.,0\X,20,1.4,25,90.,9,180.,0\C,26,r23,20,a22,19,d21,0\C,26,r24,27,a23,20,d22,0\C,26
,r25,28,a24,27,d23,0\C,26,r26,29,a25,28,d24,0\C,26,r27,30,a26,29,d25,0\H,27,r28,20,a27,9,d26,0\H,28,r29,27,a28,2
0,d27,0\H,29,r30,28,a29,27,d28,0\H,30,r31,29,a30,28,d29,0\H,31,r32,30,a31,29,d30,0\\r1=1.43351864\r2=1.471318
2\r3=1.51376507\r4=1.52161678\r5=1.44451509\r6=1.2406231\r7=1.01145878\r71=1.85999713\r8=1.08802047\r9
=1.08629715\r10=1.08755076\r11=1.08905353\r12=1.09198744\r13=1.08724911\r14=1.34930859\r15=1.07543943
\r16=1.07799259\r17=1.49894239\r18=1.46840938\r19=1.08227836\r20=1.08710574\r21=1.08219629\r22=1.08901
534\r23=1.38950604\r24=1.39885529\r25=1.39726426\r26=1.37913139\r27=1.3791073\r28=1.07951504\r29=1.078
17615\r30=1.07785176\r31=1.07808627\r32=1.07846212\a1=118.27942864\a2=109.43457762\a3=109.72066286\a
4=117.8551395\a5=114.99794462\a6=111.08994473\a61=108.98892227\a7=108.73606181\a8=107.88344789\a9=1
09.23730079\a10=109.49787346\a11=108.24758658\a12=110.20835218\a13=120.78391261\a14=120.40686212\a1
5=121.36131846\a16=105.63794739\a17=104.89613871\a18=100.29169186\a19=110.74415089\a20=112.18797084
\a21=109.05623579\a22=60.12101024\a23=59.48435723\a24=59.49914714\a25=59.97374402\a26=60.21670725\a2
7=119.38981688\a28=119.79324461\a29=120.16750757\a30=119.97853989\a31=120.28092749\d1=-50.82048249\
d2=60.60061998\d3=27.51583677\d4=-159.4730523\d5=-173.22748887\d51=82.46422619\d6=69.91985227\d7=-1
73.36243545\d8=182.23193773\d9=-60.85241297\d10=71.97084523\d11=187.72448033\d12=-158.95305724\d13
=-2.20837429\d14=176.88114389\d15=10.10212905\d16=-116.78276854\d17=126.79118069\d18=49.6309805\d19
=-70.64285773\d20=168.45833473\d21=132.43972577\d22=181.25924372\d23=182.09809082\d24=182.45826889\

d25=181.84979721\d26=-2.60014261\d27=179.09563077\d28=180.12616604\d29=180.96414414\d30=182.46944795\\Version=EM64L-G03RevE.01\HF=-673.7906466\S2=0.804471\S2-1=0.\S2A=0.751982\RMSD=8.418e-09\RMSF=3.351e-05\Thermal=0.\Dipole=0.7972611,-0.3398403,1.9256248\Polar=220.7297507,-29.977484,109.75202,-112.1532882,8.7198168,298.2214059\PG=C01 [X(C14H18N1O1)]\\@

BHandHLYP/6-31+G*//BHandHLYP/6-31G*
HF=-673.8125744

Product lactam O

BHandHLYP/6-31G*

1\1\GINC-DUAL1\FOpt\RBHandHLYP\6-31G(d)\C6H9N1O1\MATSU\12-Jan-2011\1\\#BHANDHLYP/6-31G* OPT=(Z-MATRIX,CALCFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN\\exomethylene delta valerolactam\\0,1\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4,d5,0\H,3,r8,2,a7,1,d6,0\H,3,r9,2,a8,1,d7,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,15,r15,6,a14,1,d13,0\H,15,r16,6,a15,1,d14,0\\r1=1.35898604\r2=1.44834363\r3=1.51800781\r4=1.52338934\r5=1.49799524\r6=1.21332358\r7=1.00270476\r8=1.09230206\r9=1.08706067\r10=1.08723788\r11=1.08861417\r12=1.09222823\r13=1.08687338\r14=1.32421982\r15=1.07641503\r16=1.07849255\a1=127.52445555\a2=110.58851821\a3=109.59116445\a4=116.15442652\a5=121.09611904\a6=118.72587178\a7=110.60273599\a8=108.3822992\a9=109.33400389\a10=109.54901155\a11=108.58740235\a12=111.19355149\a13=124.22139328\a14=120.1611797\a15=121.6267745\d1=-25.86405675\d2=51.77882769\d3=3.81456565\d4=-177.48683155\d5=-199.26737554\d6=95.64548342\d7=-147.17662795\d8=173.48949486\d9=-68.77472795\d10=62.1020876\d11=179.2205648\d12=-142.29886108\d13=1.34453269\d14=181.02346701\\Version=x86-Linux-G03RevB.05\HF=-363.8124503\RMSD=4.601e-09\RMSF=3.347e-05\Dipole=1.2269046,-0.0483746,1.0361948\PG=C01 [X(C6H9N1O1)]\\@

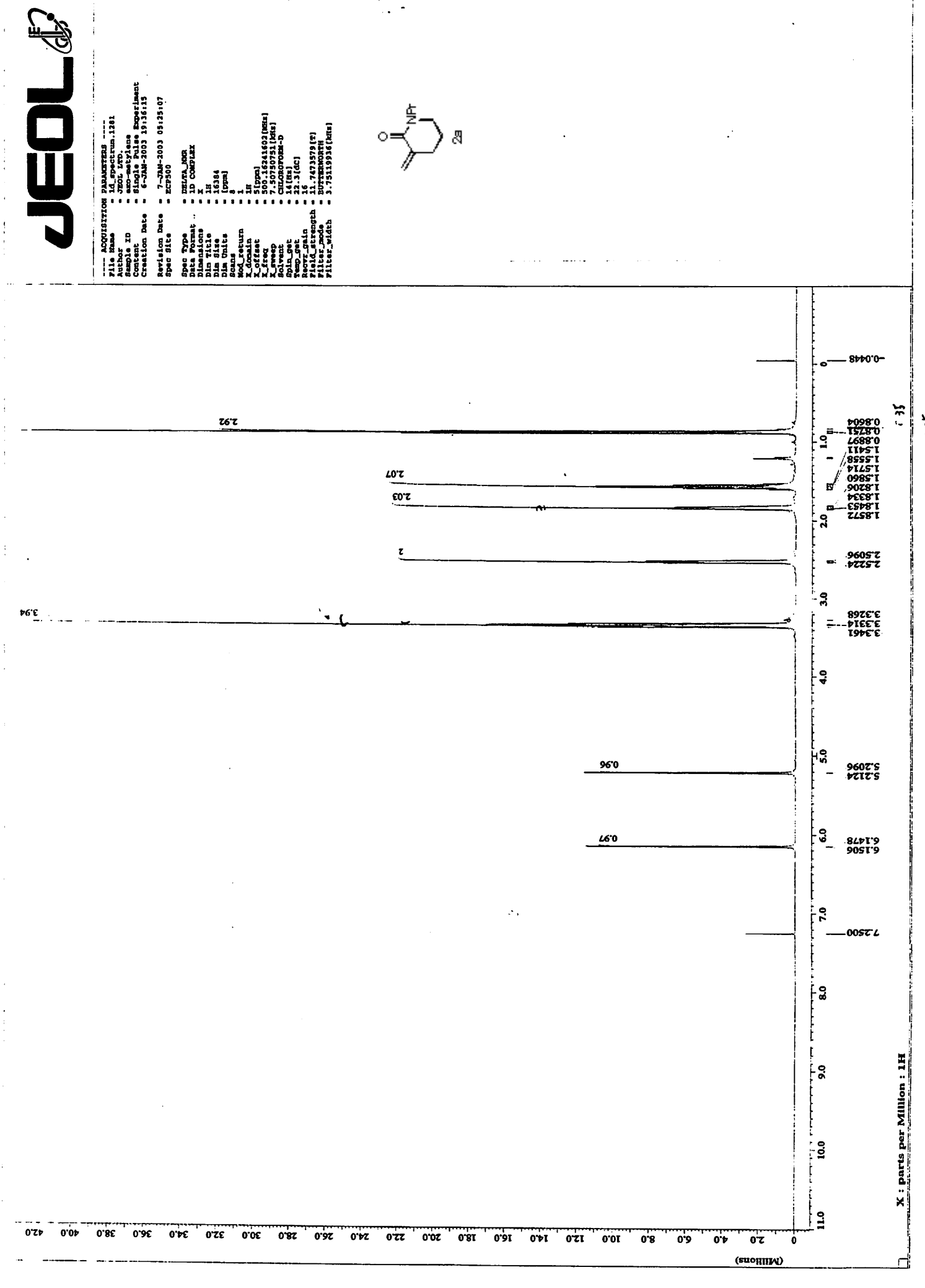
BHandHLYP/6-31+G*//BHandHLYP/6-31G*
HF=-363.8252594

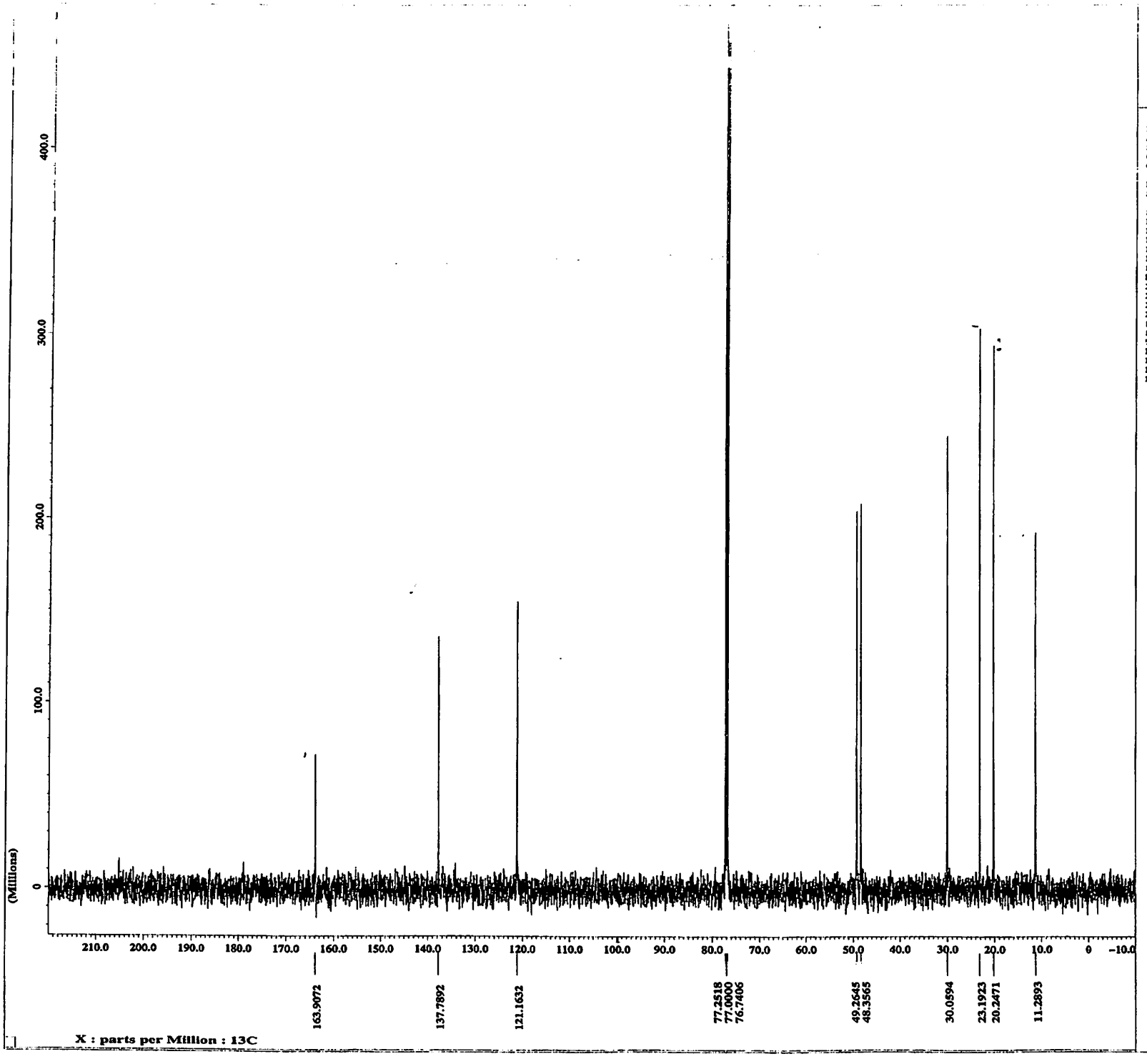
Phenethyl radical (P)

BHandHLYP/6-31G*

1\1\GINC-DUAL1\POpt\UBHandHLYP\6-31G(d)\C8H9(2)\MATSU\12-Jan-2011\1\\#BHANDHLYP/6-31G* SCF=DIRECT FREQ=NORAMAN OPT=(Z-MATRIX,CALCFC,MAXCYCLE=100) NOSYMM\\phenethyl radical\\0,2\X\C,1,r1\C,1,r2,2,a1\C,1,r3,3,a2,2,d1,0\C,1,r4,4,a3,3,d2,0\C,1,r5,5,a4,4,d3,0\C,1,r6,6,a5,5,d4,0\C,2,r7,3,a6,4,d5,0\C,8,r8,2,a7,3,d6,0\H,3,r9,2,a8,8,d7,0\H,4,r10,3,a9,2,d8,0\H,5,r11,4,a10,3,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,8,r14,2,a13,3,d12,0\H,9,r15,8,a14,2,d13,0\H,9,r16,8,a15,2,d14,0\H,9,r17,8,a16,2,d15,0\\r1=1.43974015\r2=1.38729361\r3=1.37202934\r4=1.37792863\r5=1.38659885\r6=1.4072121\r7=1.40910089\r8=1.49117026\r9=1.07894534\r10=1.07837674\r11=1.07765809\r12=1.07847546\r13=1.07741222\r14=1.0786105\r15=1.09119672\r16=1.09119697\r17=1.08532101\a1=60.05880089\a2=59.86524497\a3=60.88284012\a4=60.45234266\a5=59.15579347\a6=120.36280514\a7=124.51399624\a8=118.69086161\a9=119.73081379\a10=120.28726367\a11=119.79206735\a12=119.5587893\a13=117.42601843\a14=111.94114338\a15=111.94115112\a16=111.01902712\d1=180.00416704\d2=180.00398324\d3=180.00388729\d4=180.00390295\d5=180.00003091\d6=180.00001753\d7=0.00002545\d8=180.00000065\d9=179.9999809\d10=179.99998779\d11=179.99995581\d12=0.00019764\d13=59.84965428\d14=-59.85160093\d15=-180.0009531\\Version=x86-Linux-G03RevB.05\HF=-310.0360481\S2=0.843335\S2-1=0.\S2A=0.756159\RMSD=3.302e-09\RMSF=3.280e-06\Dipole=-0.0491113,0.0000089,0.1235134\PG=C01 [X(C8H9)]\\@

BHandHLYP/6-31+G*//BHandHLYP/6-31G*
HF=-310.0455823





JEOL

```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_13c_spectrum.419
Author           = JEOL LTD.
Sample ID        = exo-metylene
Content          = Single Pulse with Broad
Creation Date    =  6-JAN-2003 19:43:52

Revision Date    =  7-JAN-2003 05:30:01
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 13C
Dim Size         = 32768
Dim Units        = [ppm]
Scans            = 122
Mod_return       = 1
X_domain         = 13C
X_offset         = 100[ppm]
X_freq           = 125.77787567[MHz]
X_sweep          = 31.44654088[kHz]
Solvent          = CHLOROFORM-D
Spin_set         = 16[Hz]
Temp_set         = 22.9[dC]
Recvr_gain       = 30
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 15.72066221[kHz]
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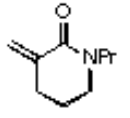
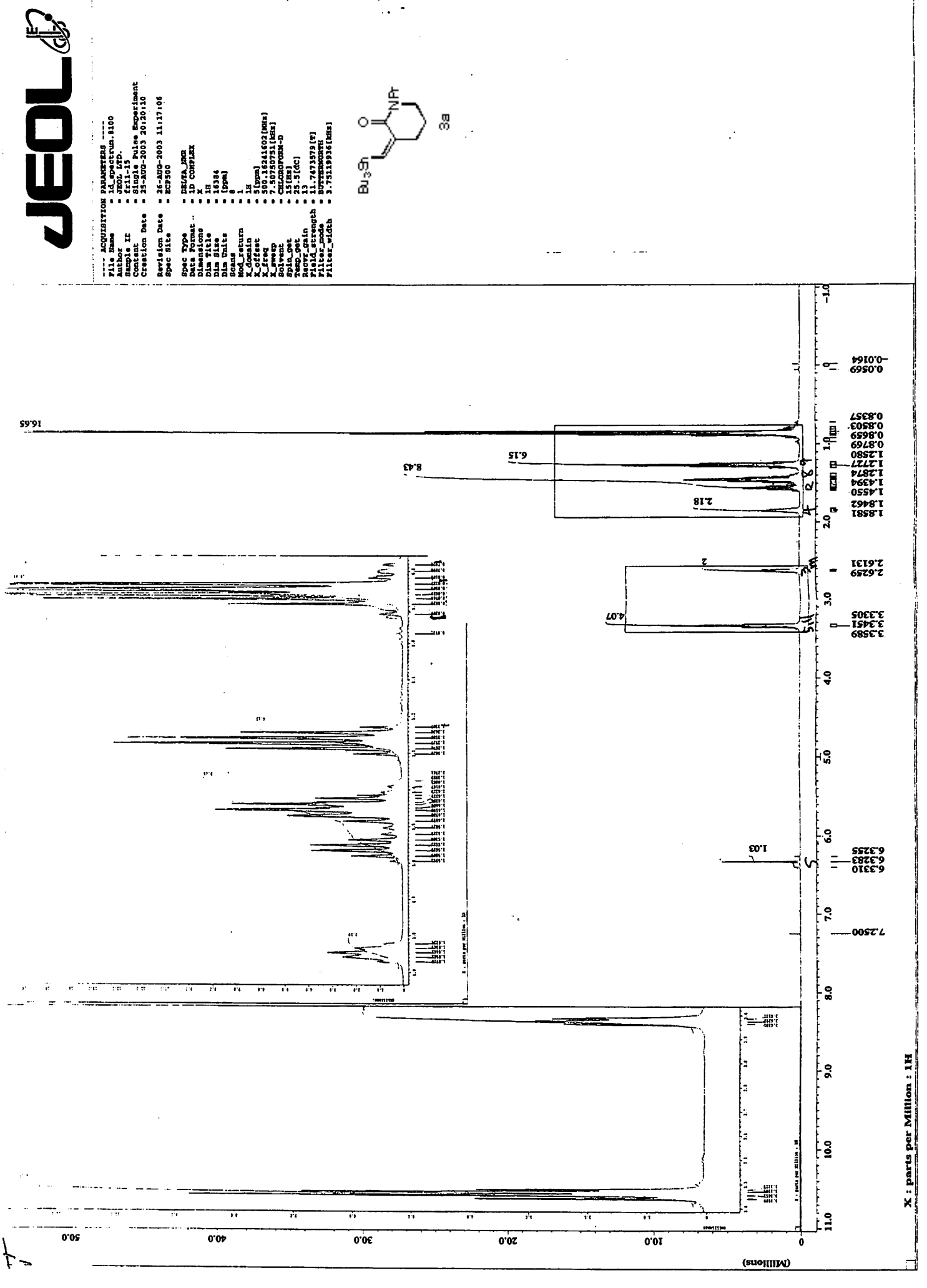
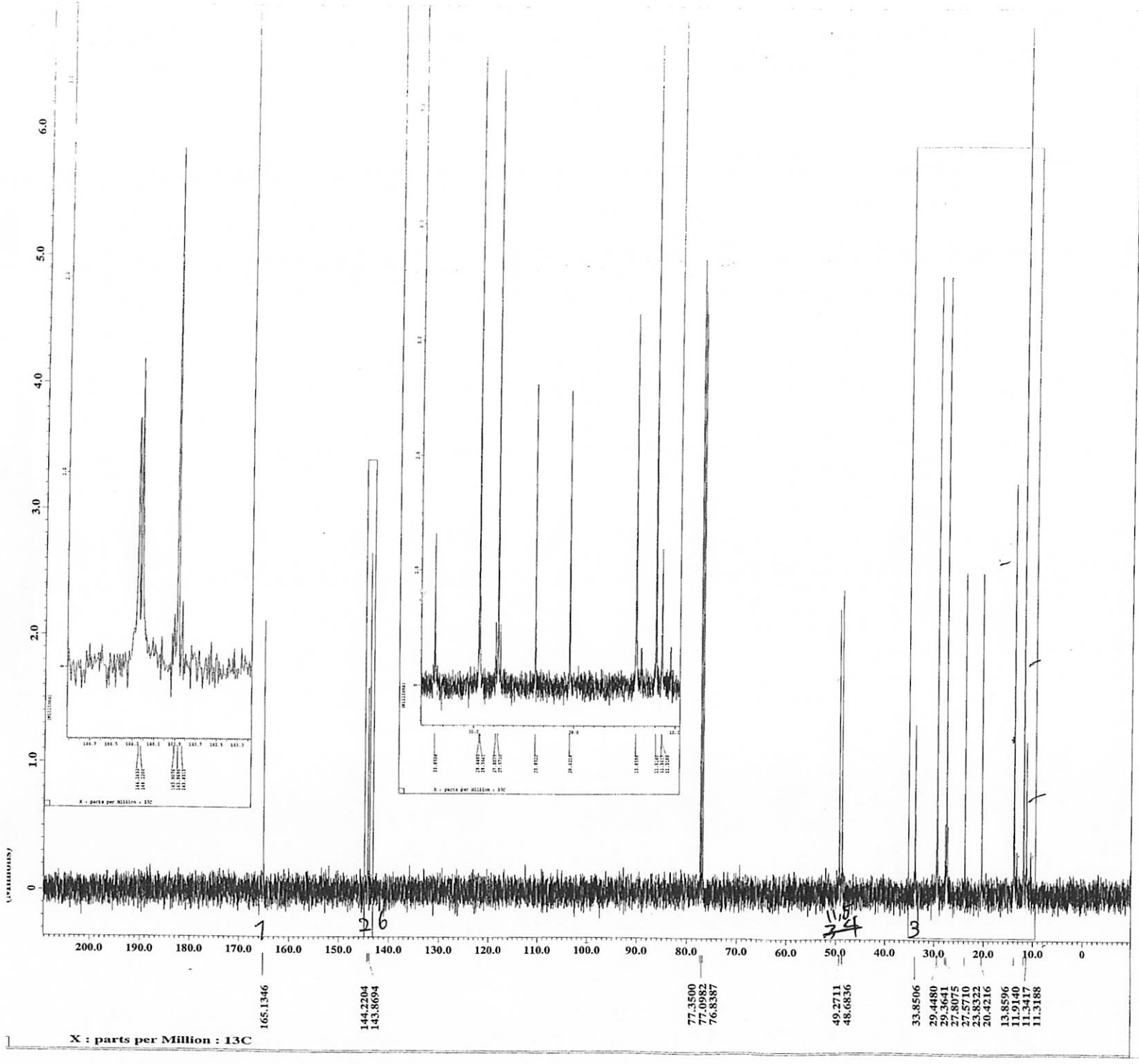
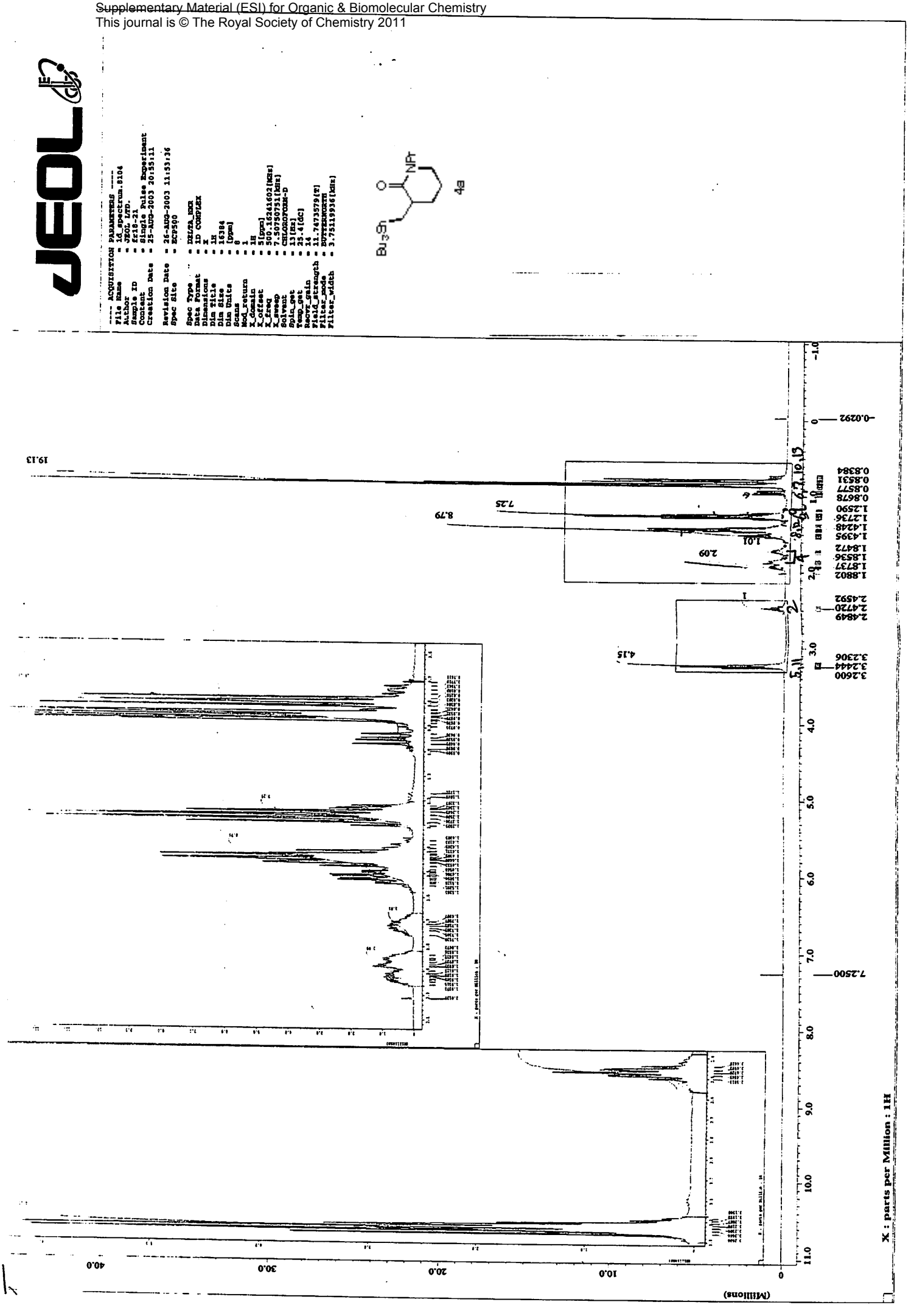
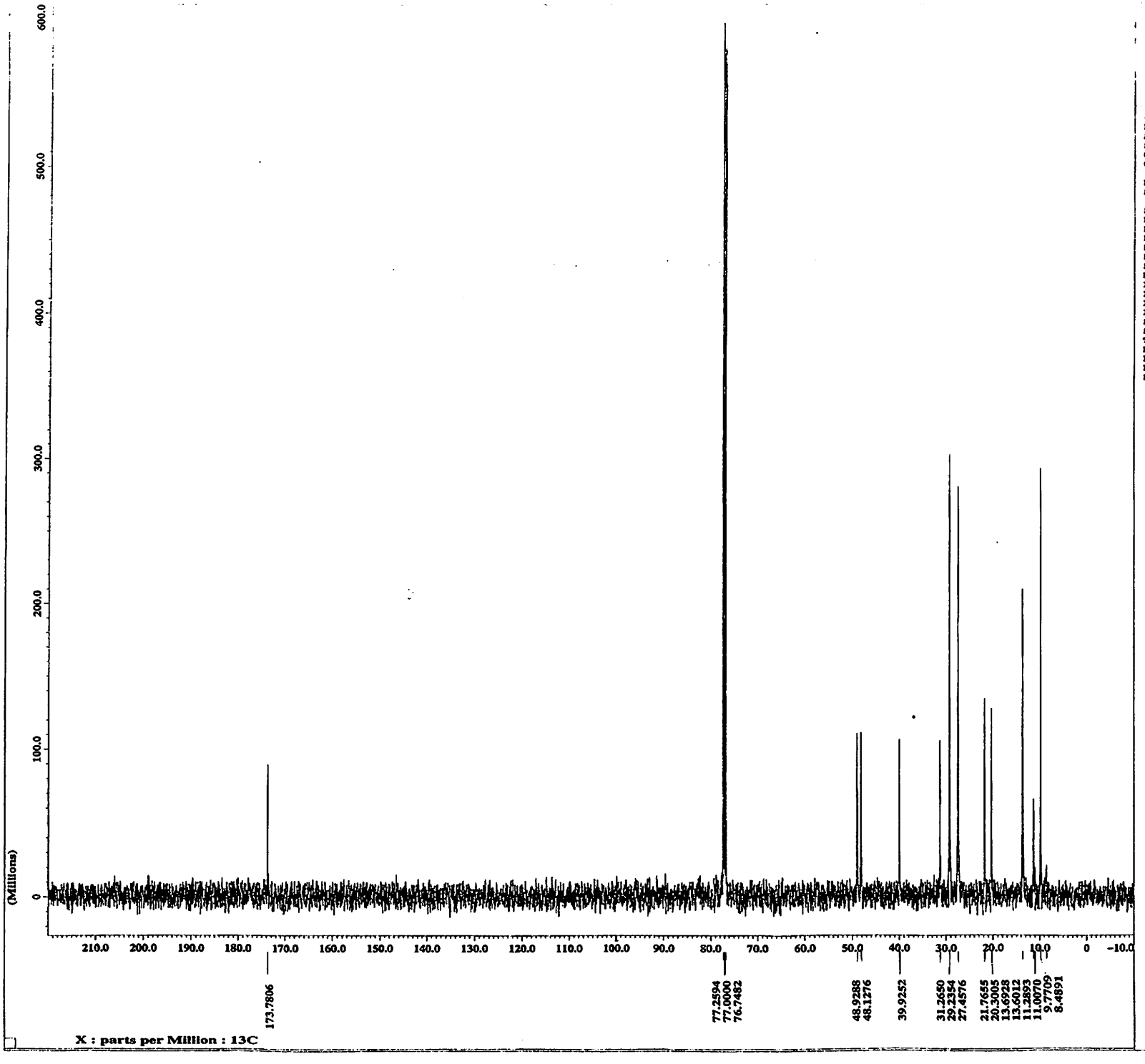


2a



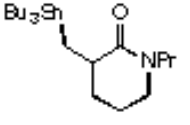




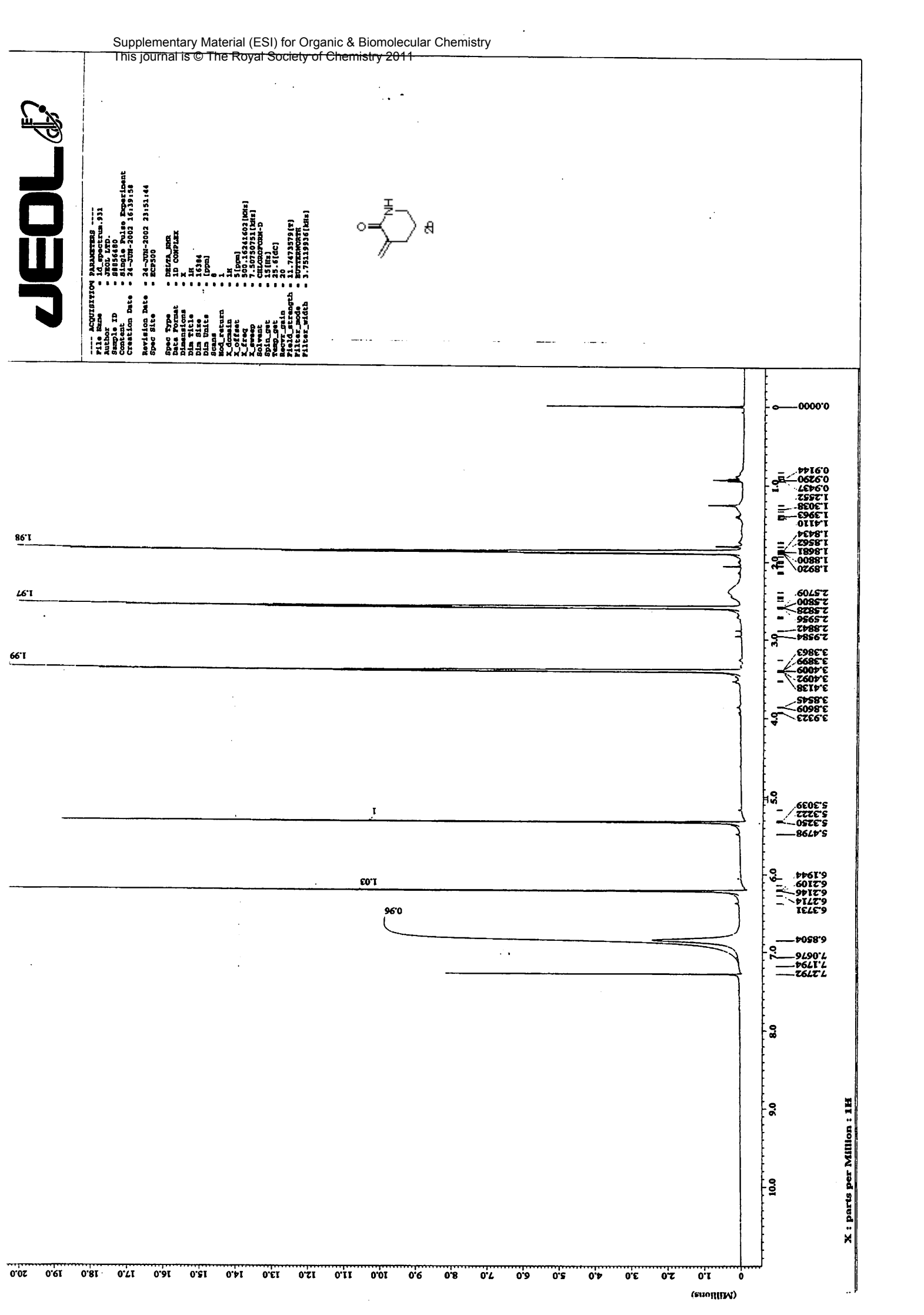


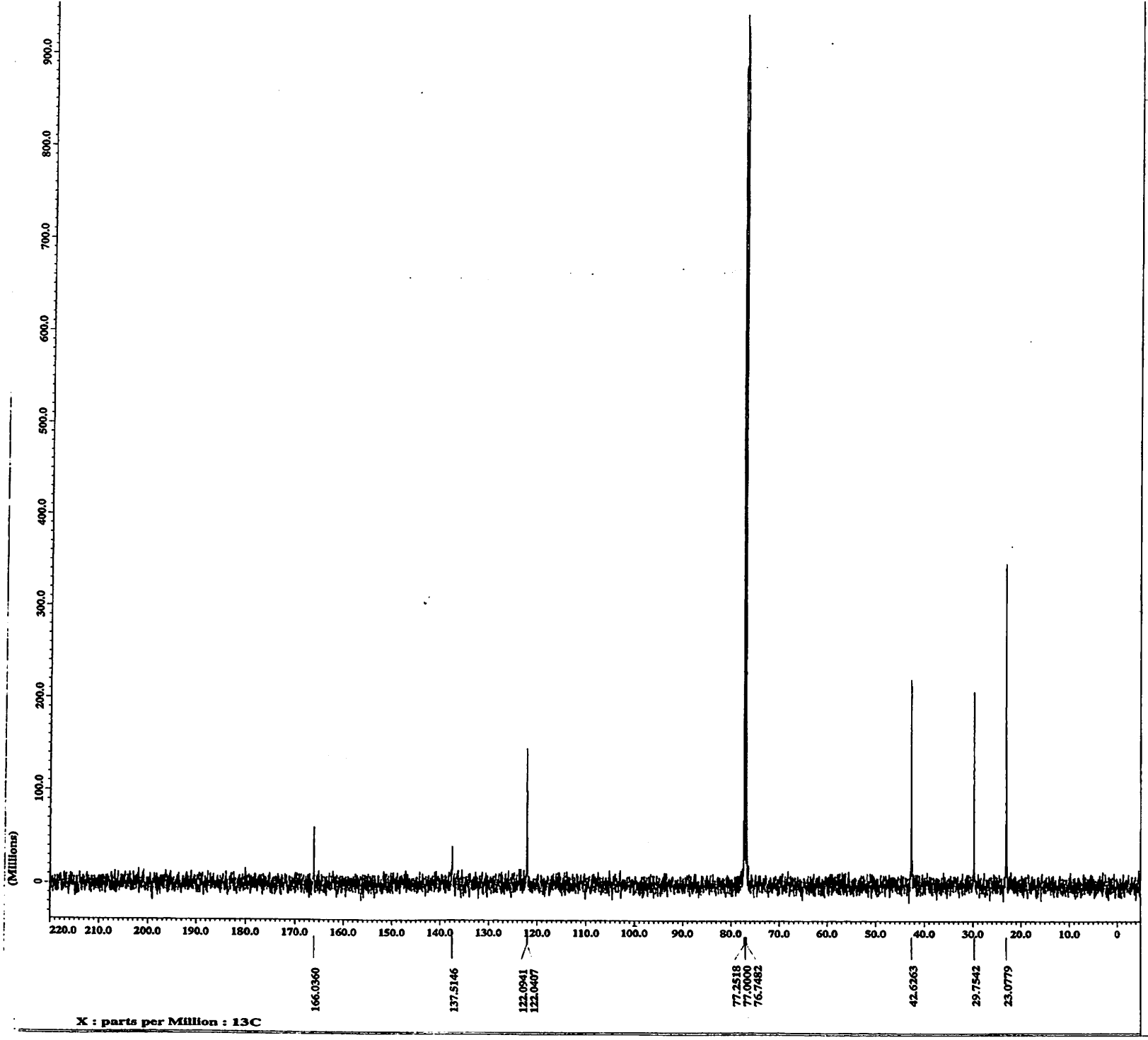
---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.1172
Author	= JEOL LTD.
Sample ID	= Bu3Sn-Houwa
Content	= Single Pulse with Broad
Creation Date	= 11-APR-2003 17:03:38
Revision Date	= 12-APR-2003 05:30:07
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 262
Mod_return	= 1
X_domain	= 13C
X_offset	= 100[ppm]
X_freq	= 125.77787547[MHz]
X_sweep	= 31.44654088[KHz]
Solvent	= CHLOROFORM-D
Spin_get	= 13[Hz]
Temp_get	= 27.4[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[KHz]



4a

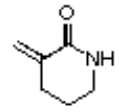




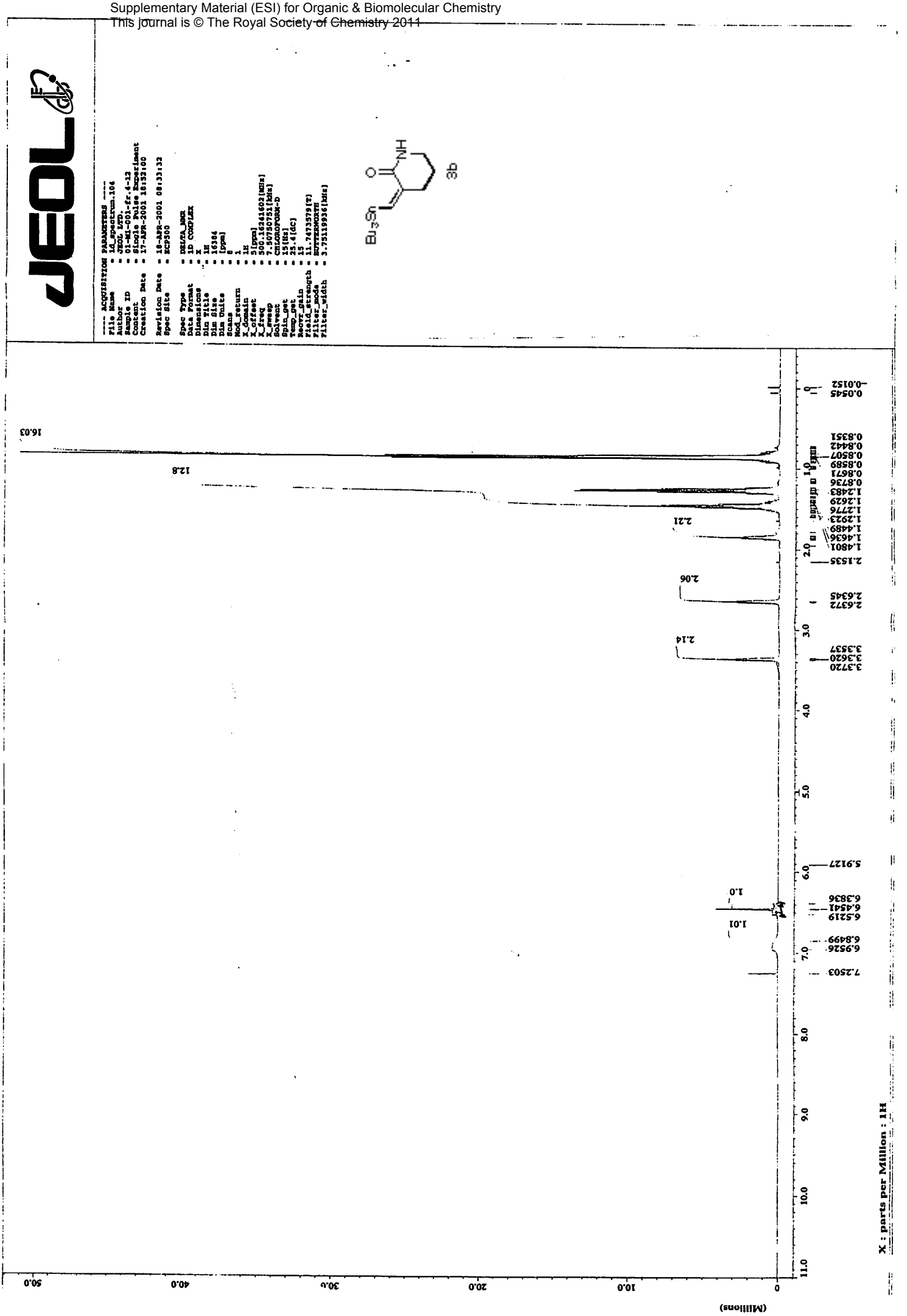
JEOL

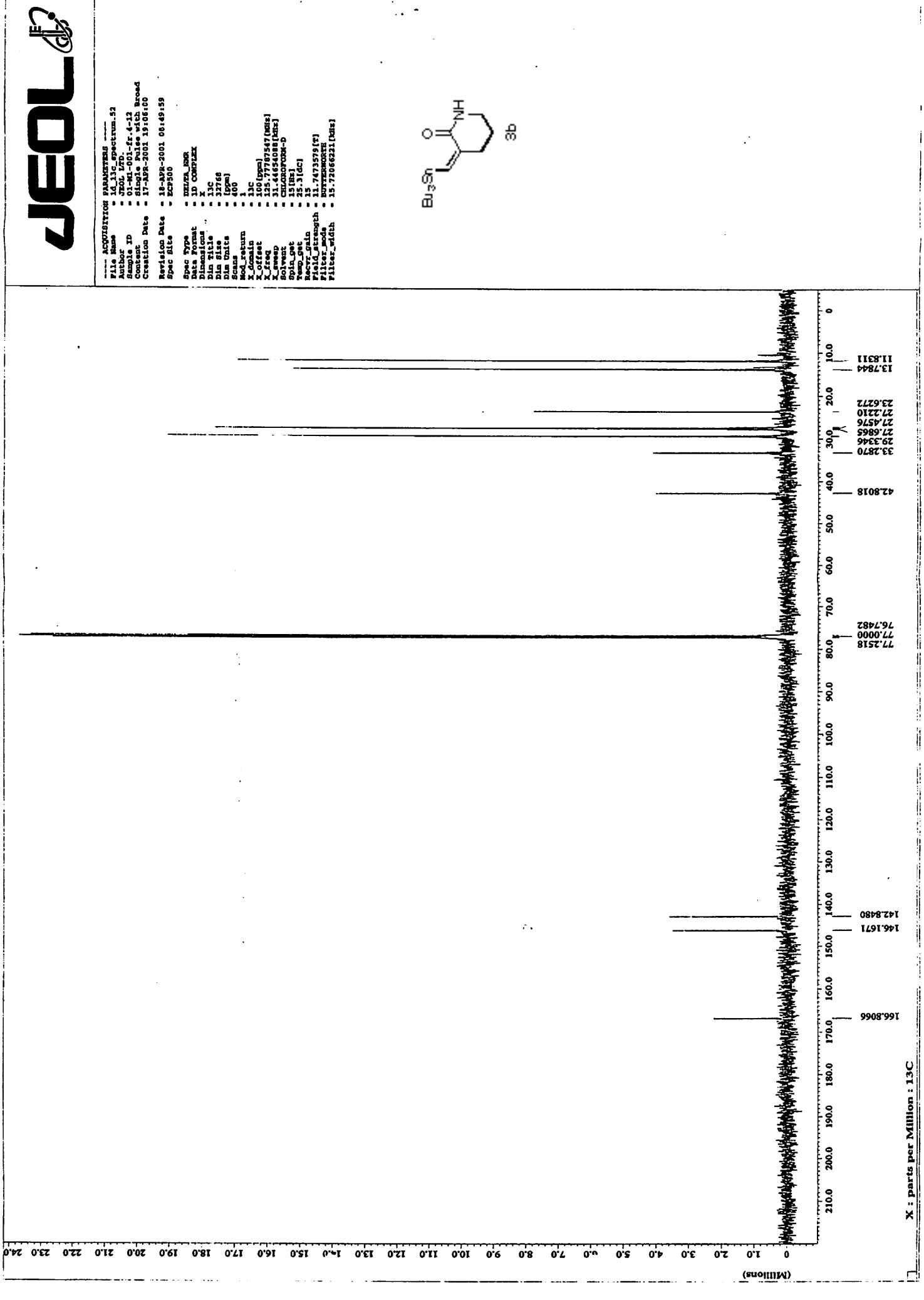
---- ACQUISITION PARAMETERS ----

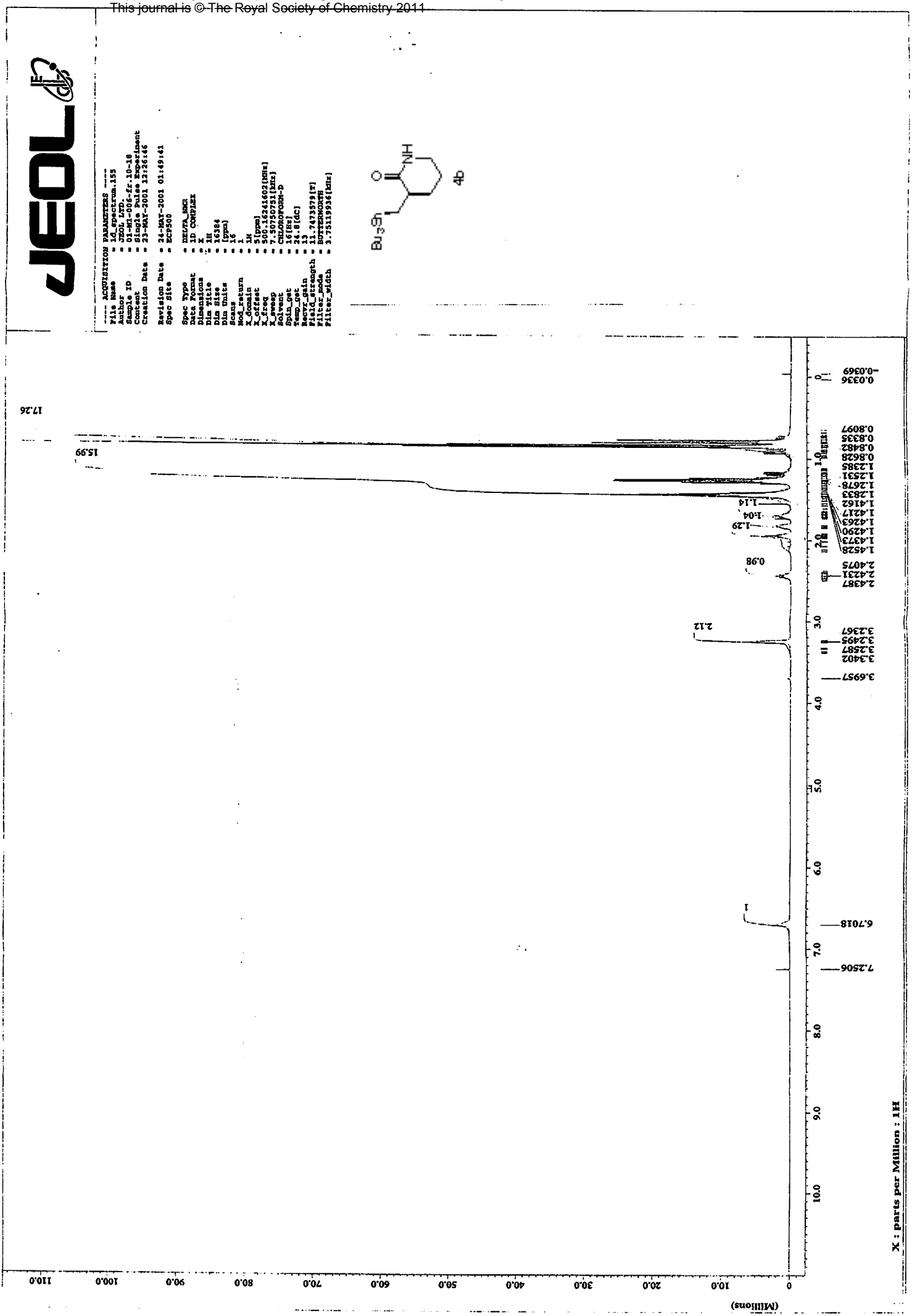
File Name	= 1d_13c_spectrum.331
Author	= JEOL LTD.
Sample ID	= 88858126
Content	= Single Pulse with Broad
Creation Date	= 24-JUN-2002 16:55:06
Revision Date	= 25-JUN-2002 00:19:03
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 400
Mod_return	= 1
X_domain	= 13C
X_offset	= 100[ppm]
X_freq	= 125.77787547[MHz]
X_sweep	= 31.44654088[kHz]
Solvent	= CHLOROFORM-D
Spin_set	= 15[Hz]
Temp_set	= 26.1[dC]
Recvr_gain	= 29
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]

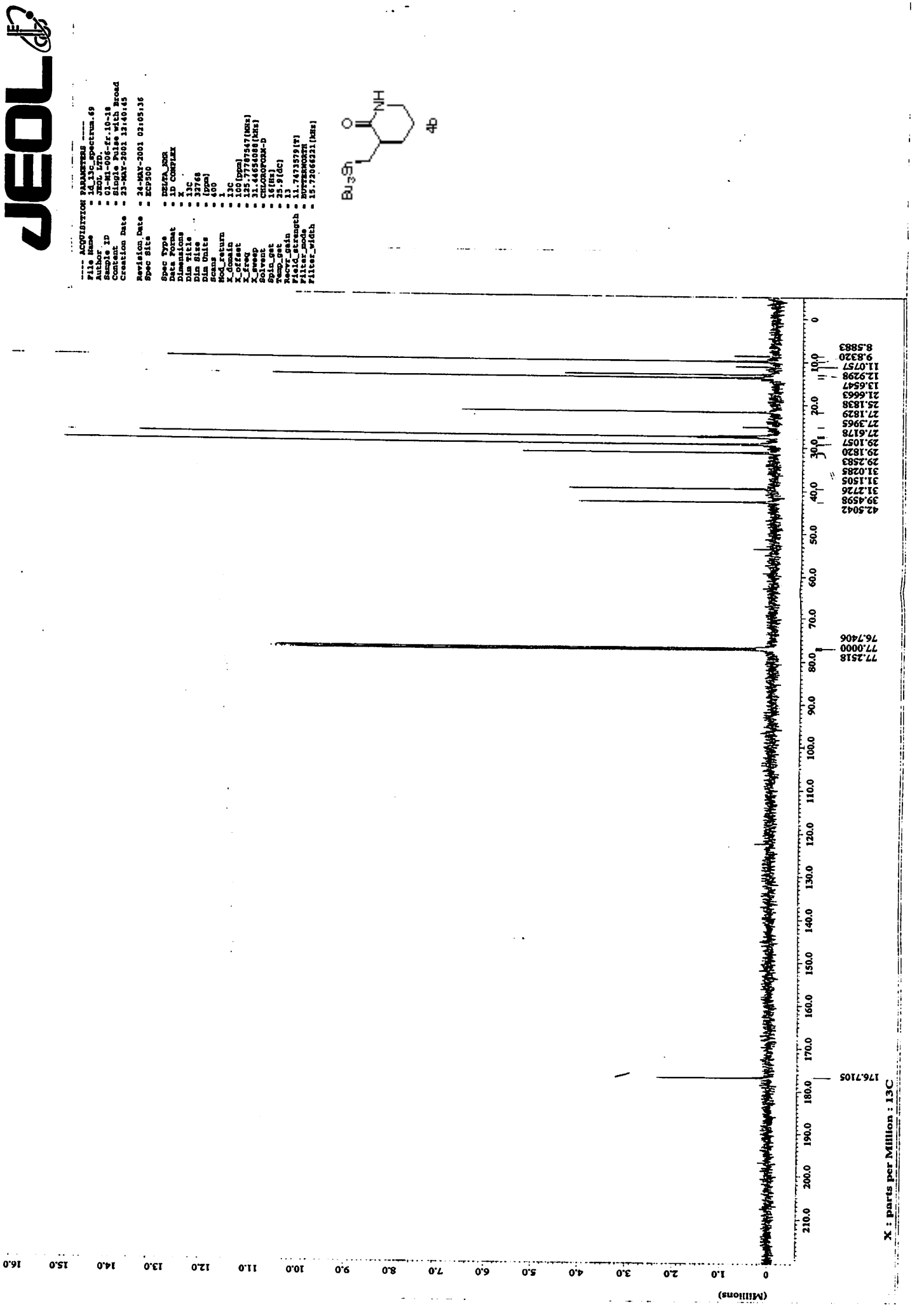


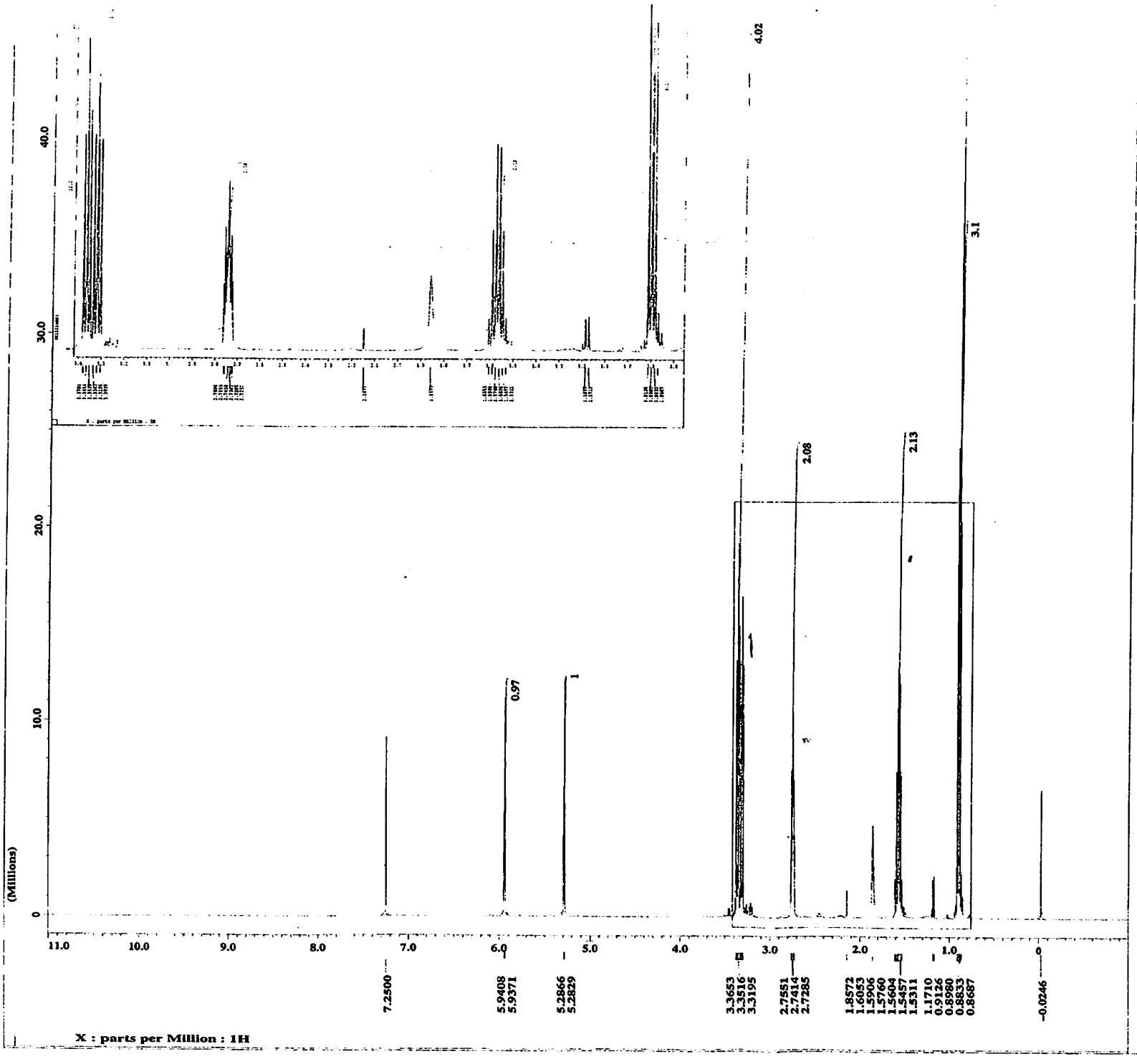
2b

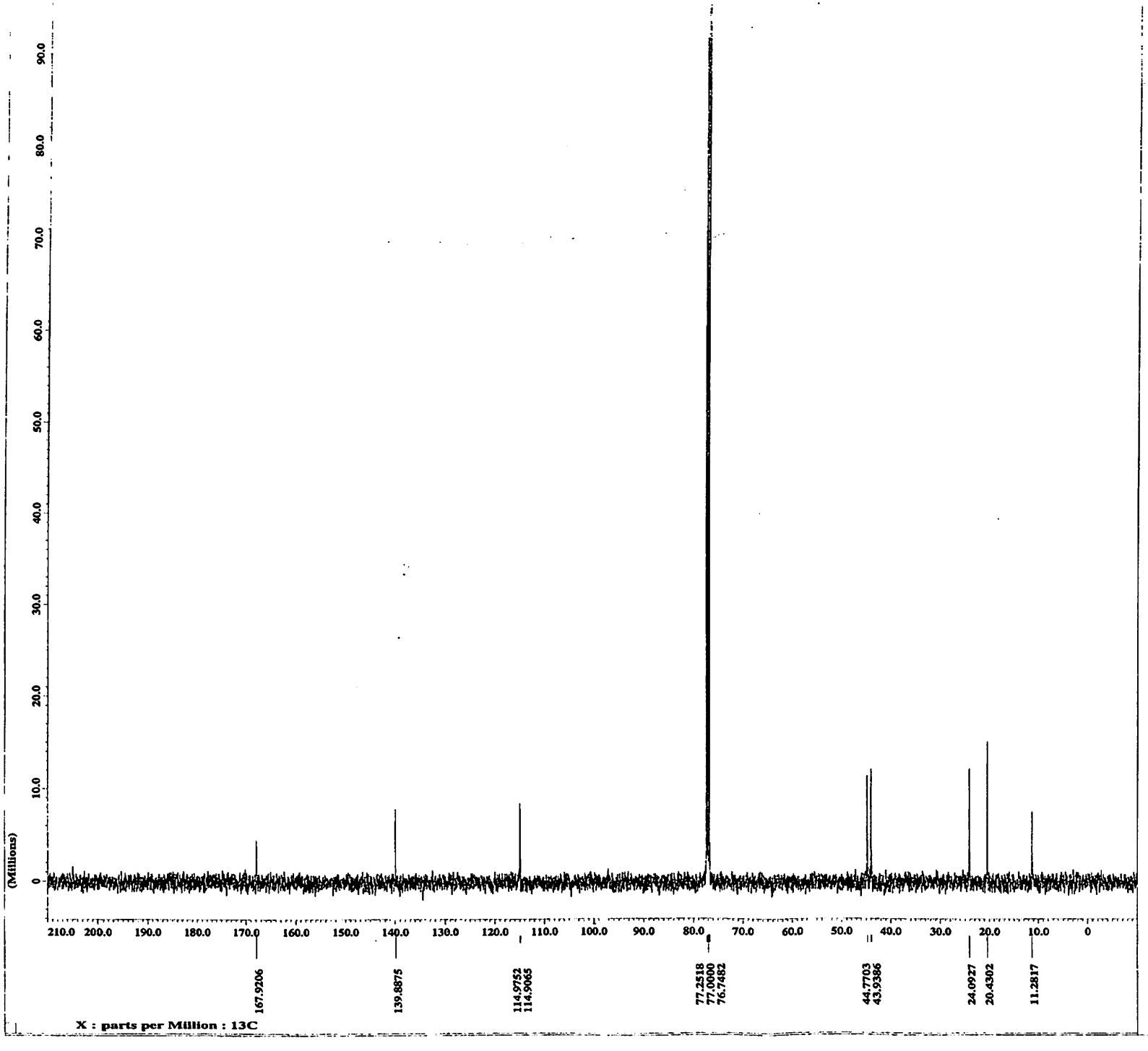












JEOL

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---- ACQUISITION PARAMETERS ----
File Name          = 1d_13c_spectrum.1630
Author             = JEOL LTD.
Sample ID          = RM2-019  fr  exomethyle
Content            = Single Pulse with Broad
Creation Date      = 28-MAY-2003 21:37:42

Revision Date      = 29-MAY-2003 10:54:07
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Scans              = 495
Mod_return         = 1
X_domain           = 13C
X_offset           = 100[ppm]
X_freq             = 125.77787547[MHz]
X_sweep            = 31.44654088[kHz]
Solvent            = CHLOROFORM-D
Spin_get           = 14[Hz]
Temp_get           = 25.8[dC]
Recvr_gain         = 21
Field_strength     = 11.7473579[T]
Filter_mode        = BUTTERWORTH
Filter_width       = 15.72066221[kHz]
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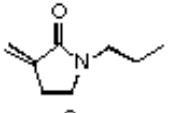
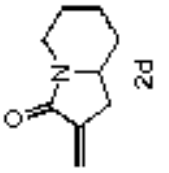
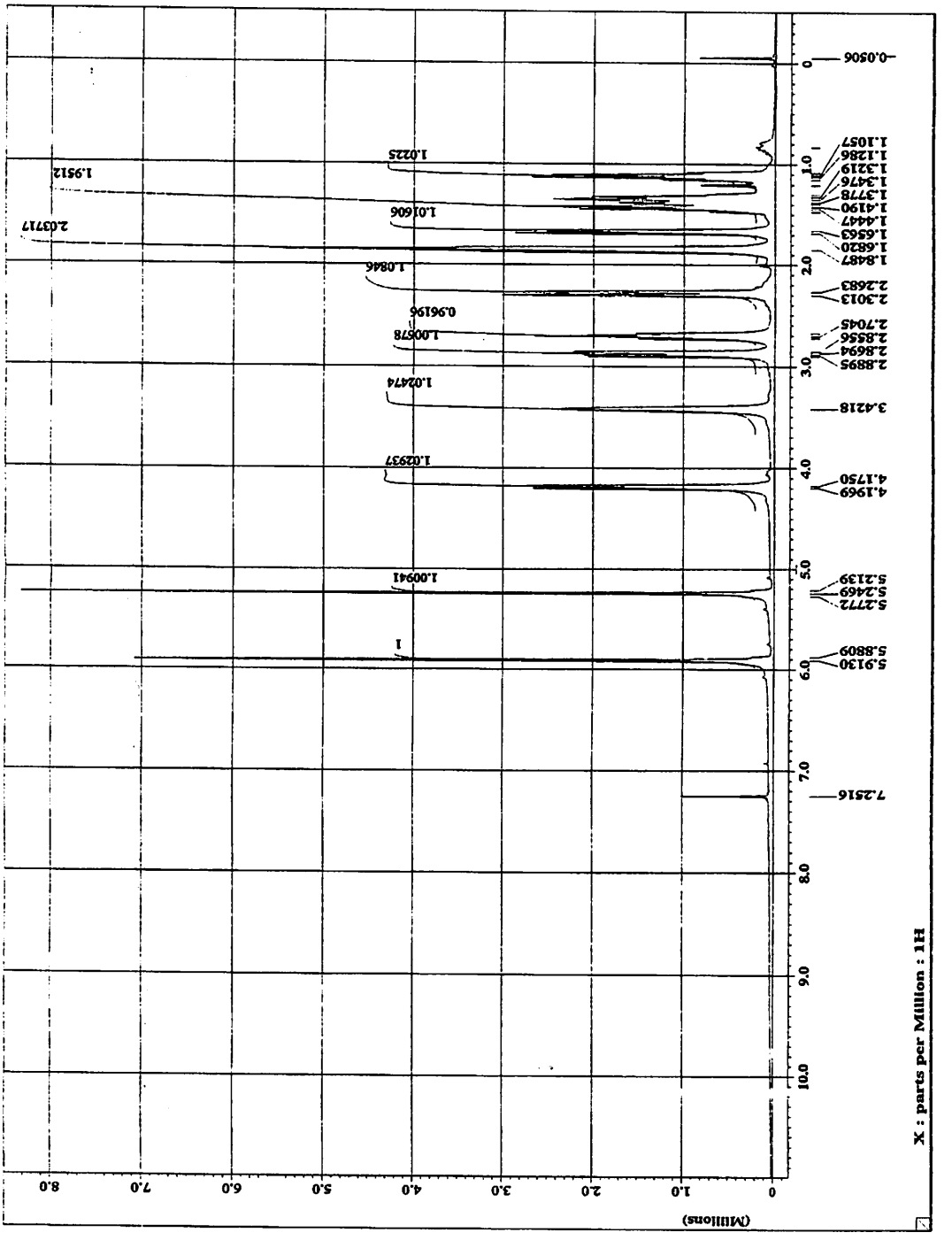
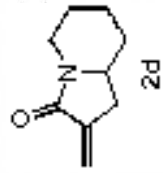
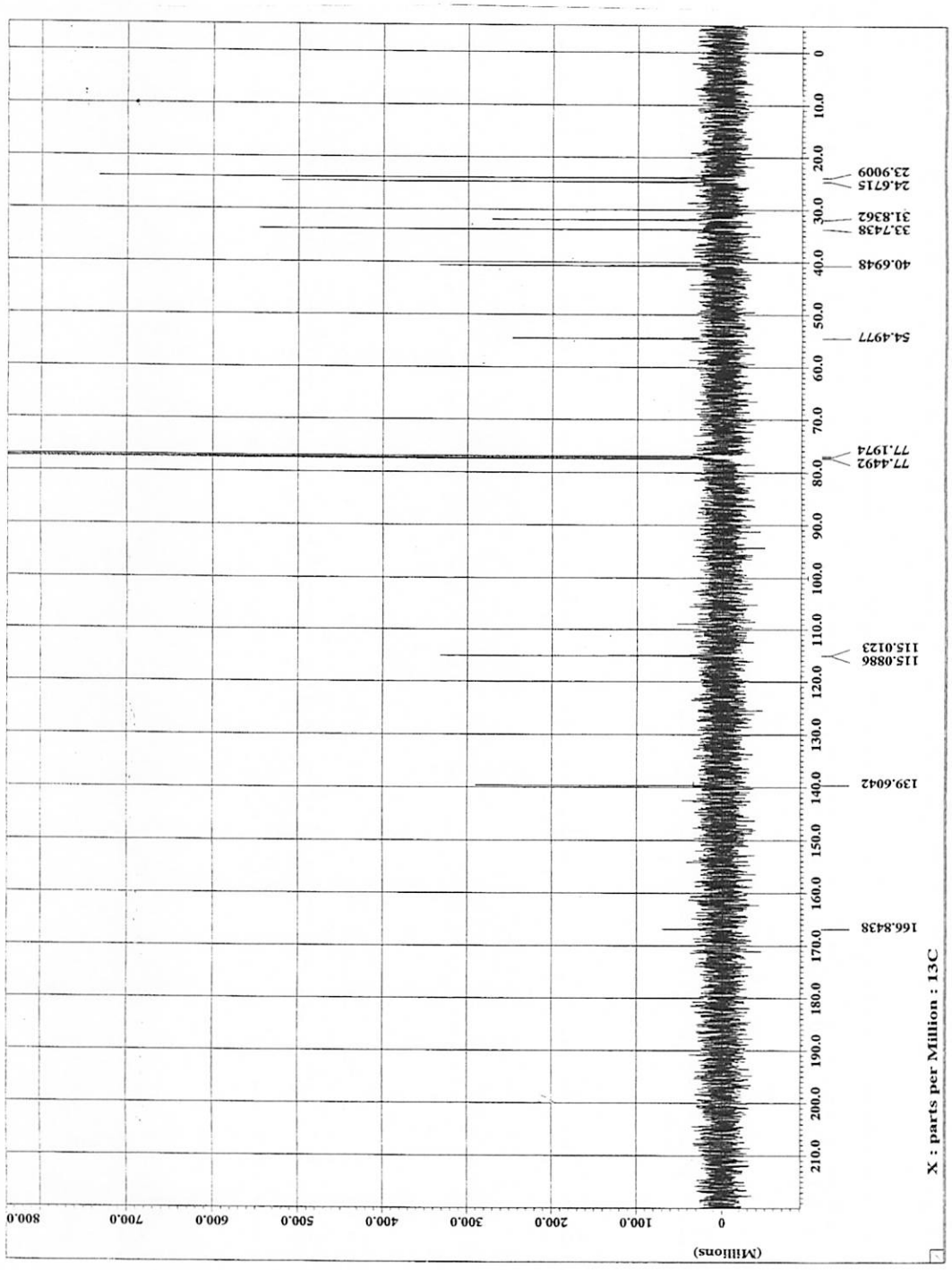


2c

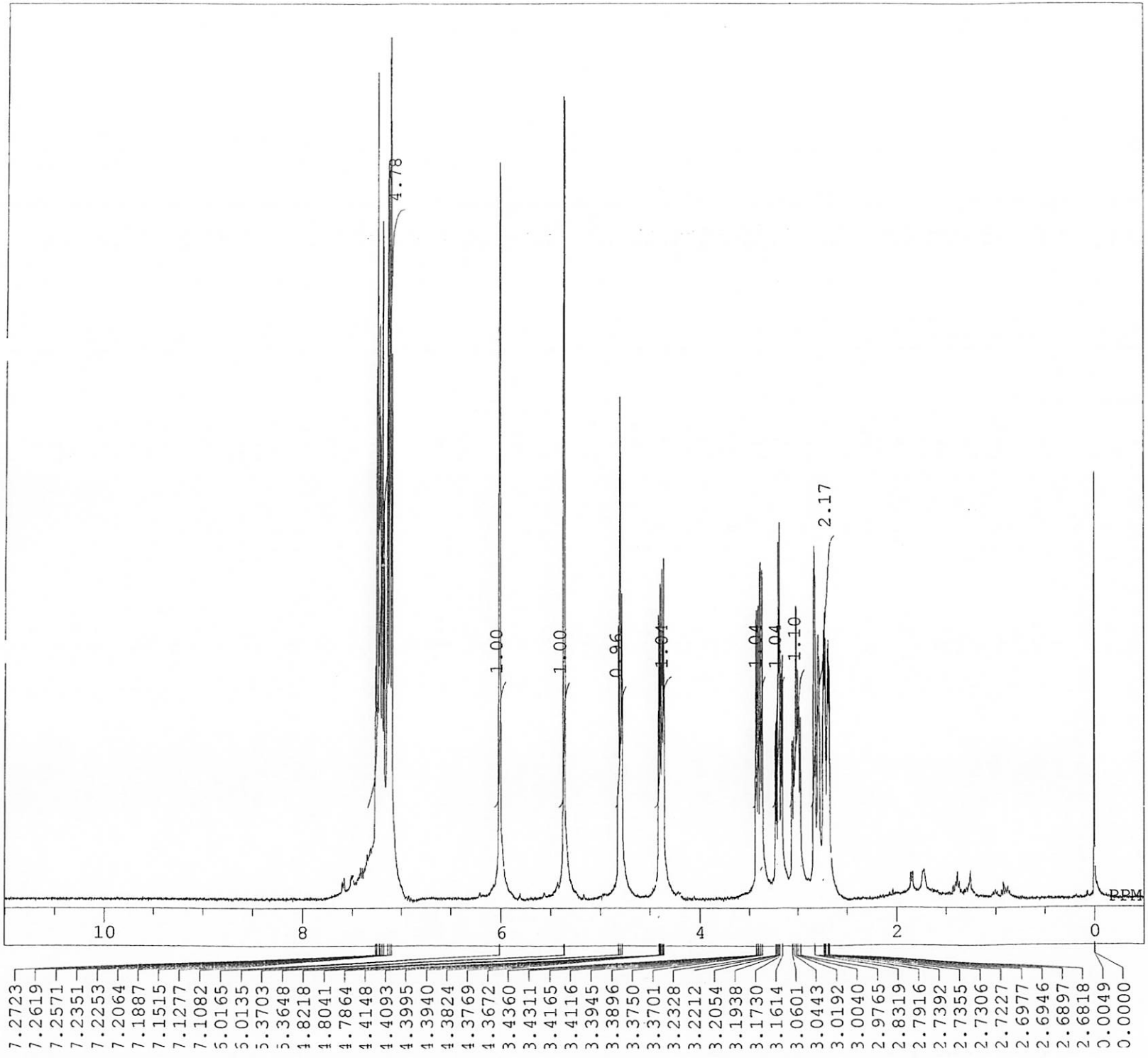




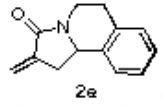




C:\WINNMR98\COMMON_DEFAULT.ALS
04-D1-115-HPLC

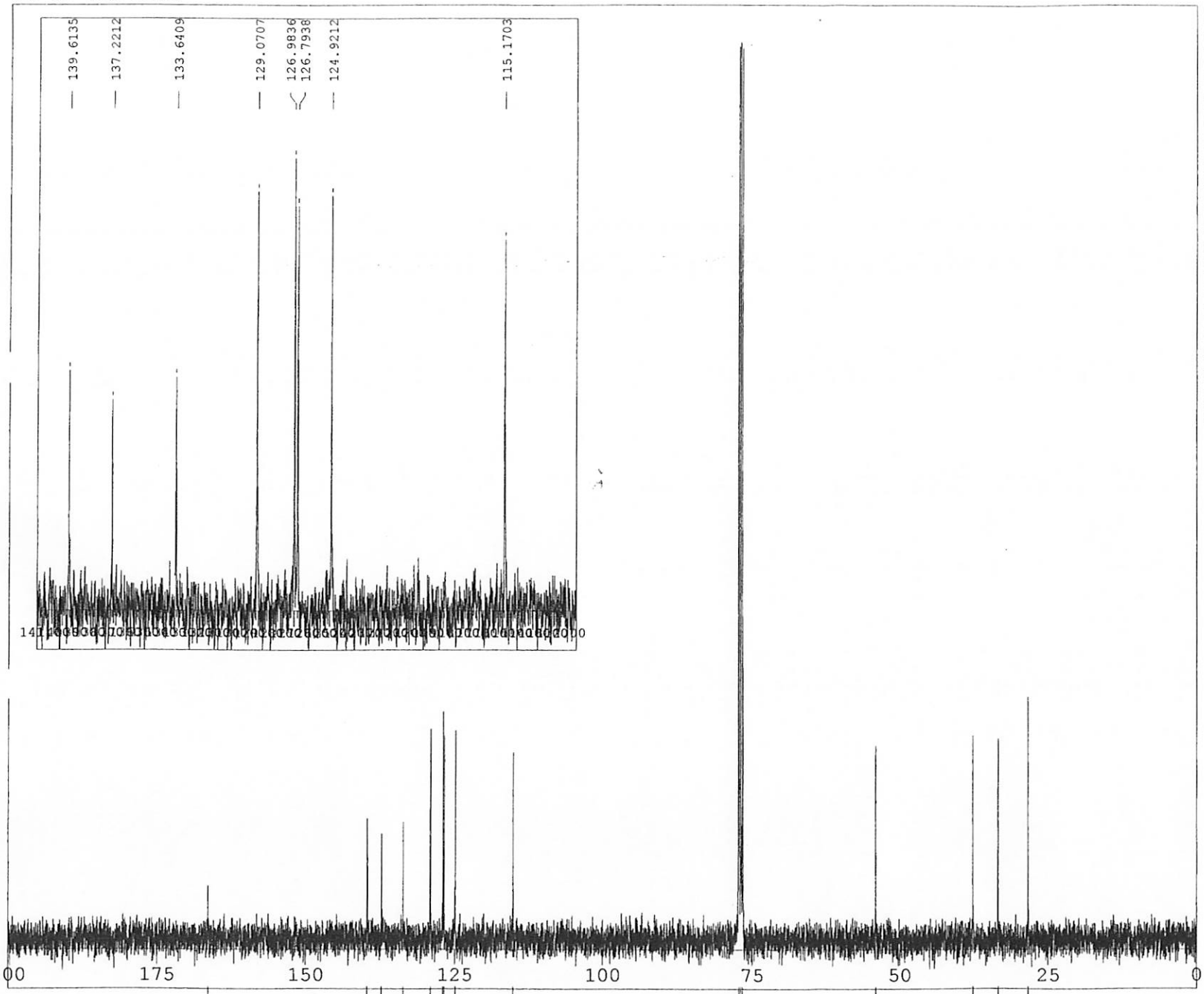


DFILE	C:\WINNMR98\COMMON_DEF
COMNT	04-D1-115-HPLC
DATIM	Sat Mar 20 17:22:14 200
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7993.6 Hz
SCANS	8
ACQTM	4.099 sec
PD	2.901 sec
PW1	5.8 us
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	13

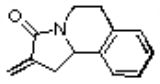


2a

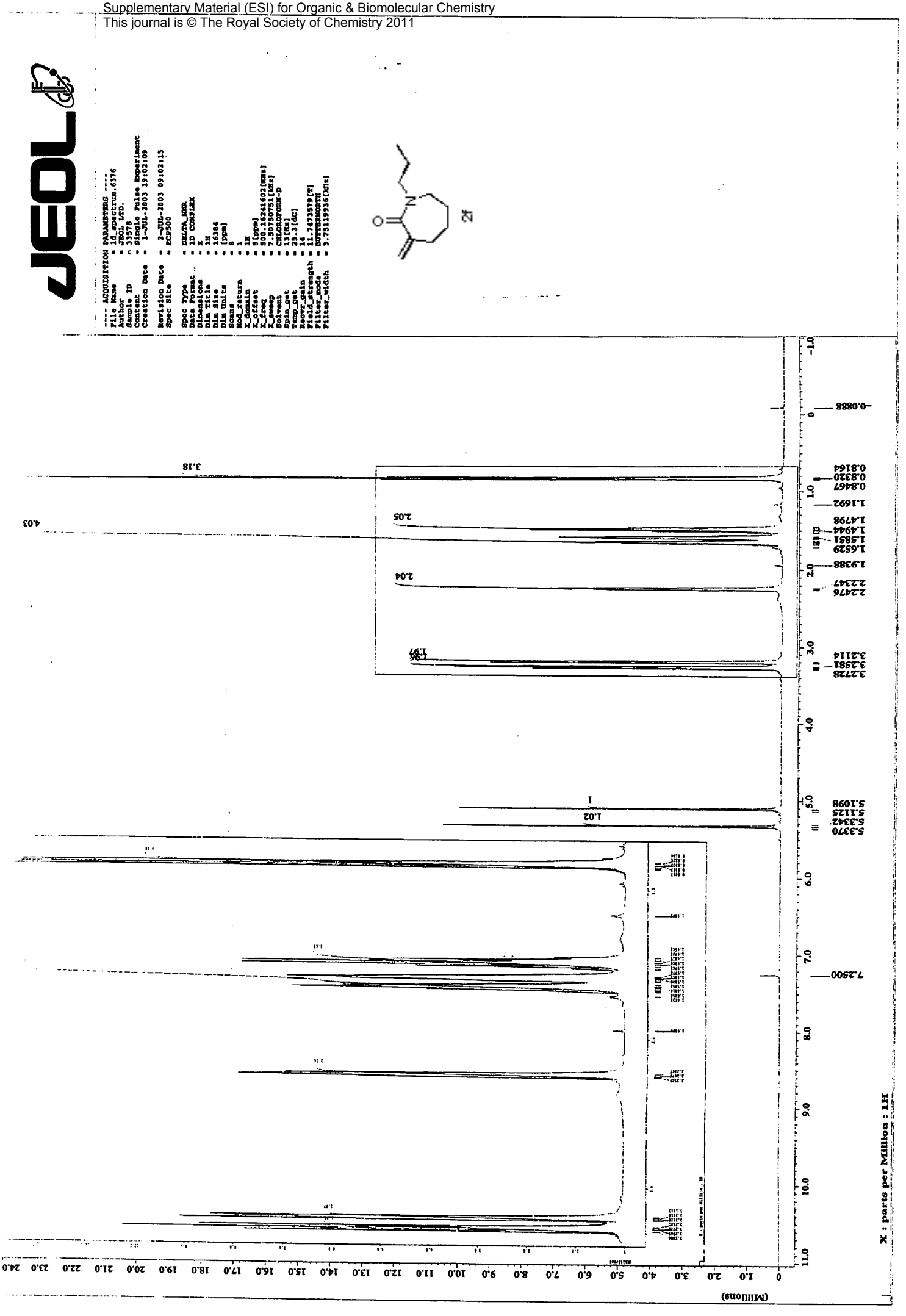
C:\WINNMR98\COMMON_DEFAULT.ALS
04-D1-115-HPLC

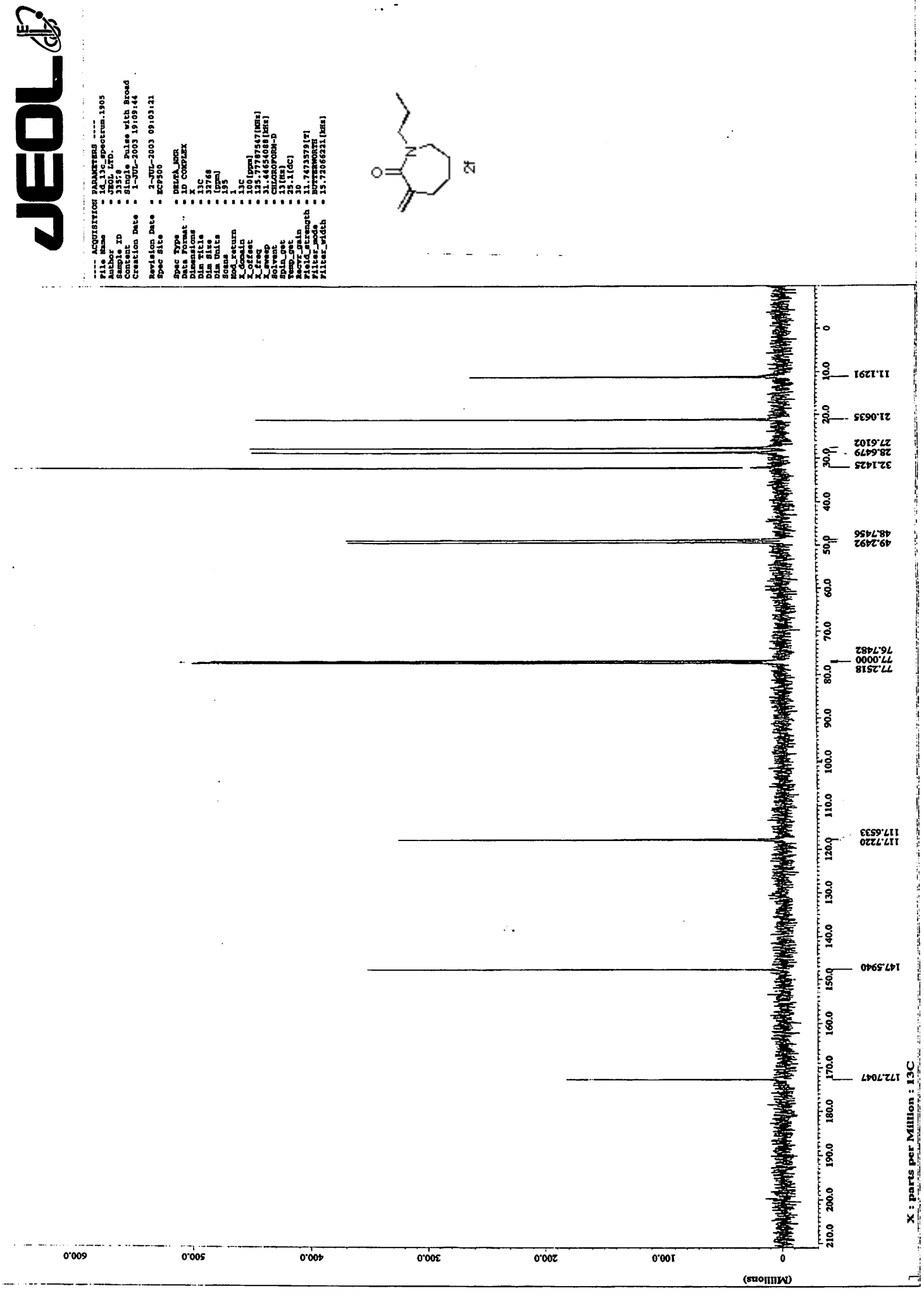


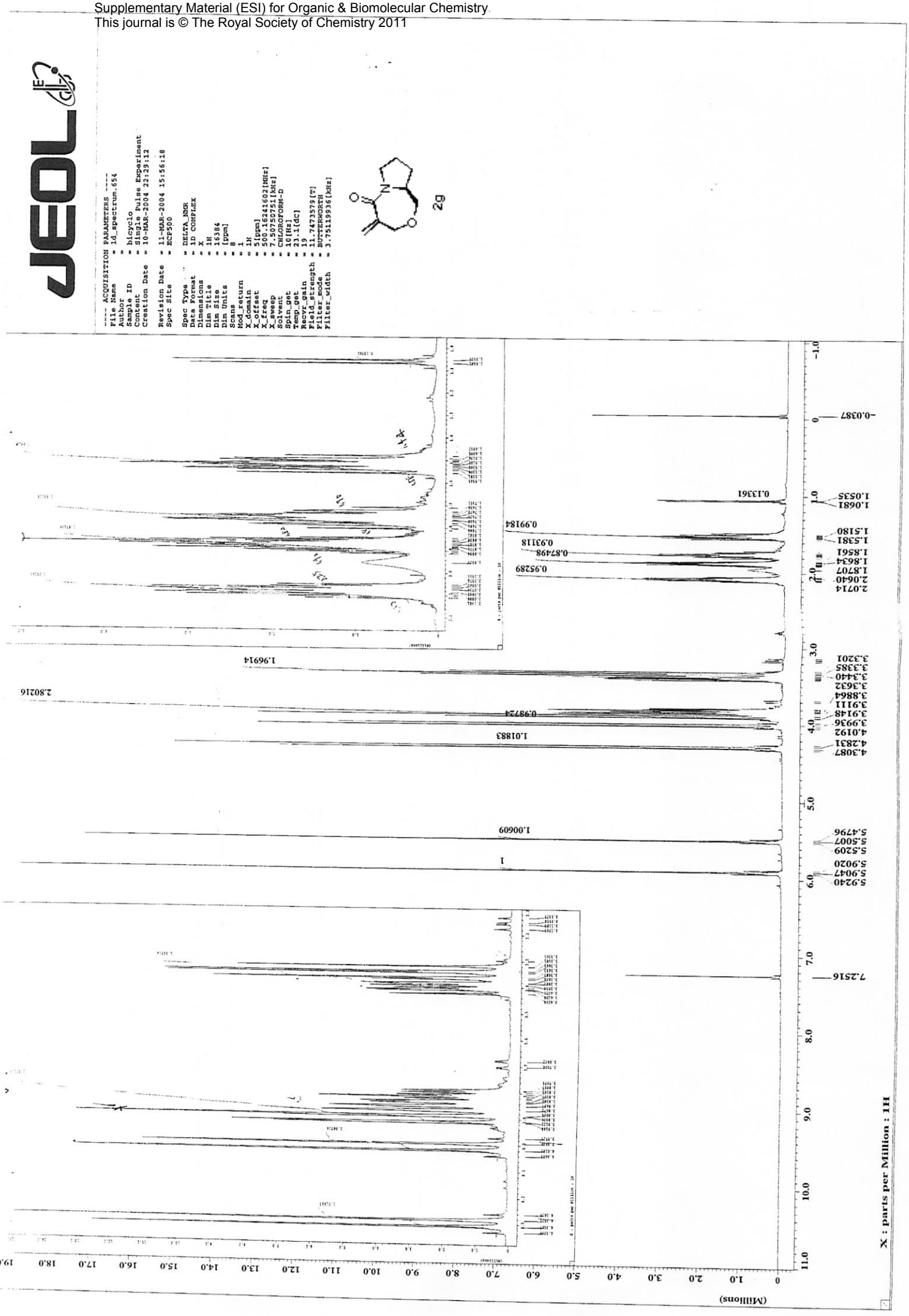
DFILE C:\WINNMR98\COMMON_DEF
COMNT 04-D1-115-HPLC
DATIM Sat Mar 20 17:46:25 200
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 400
ACQTM 1.206 sec
PD 1.794 sec
PW1 5.5 us
IRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24

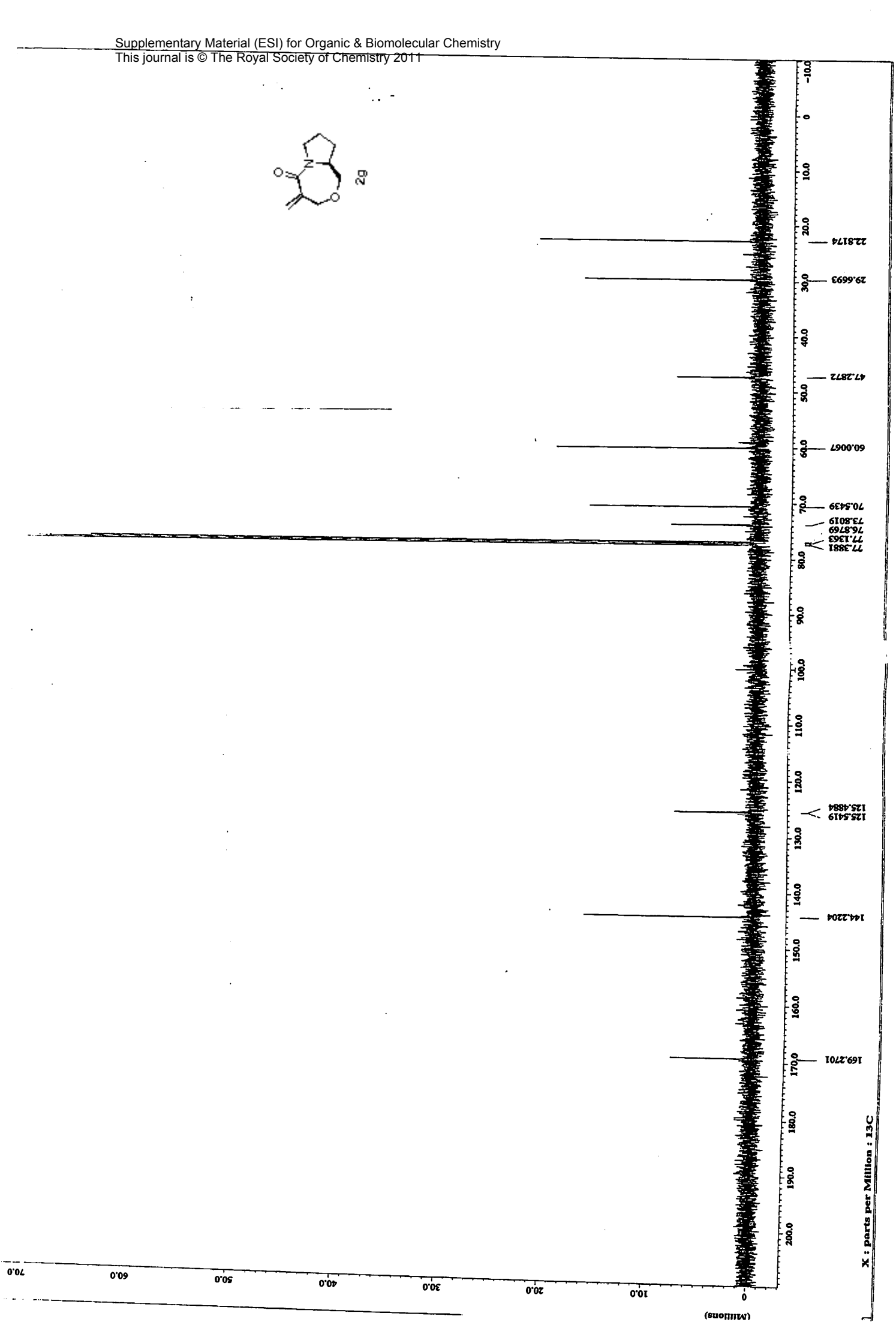


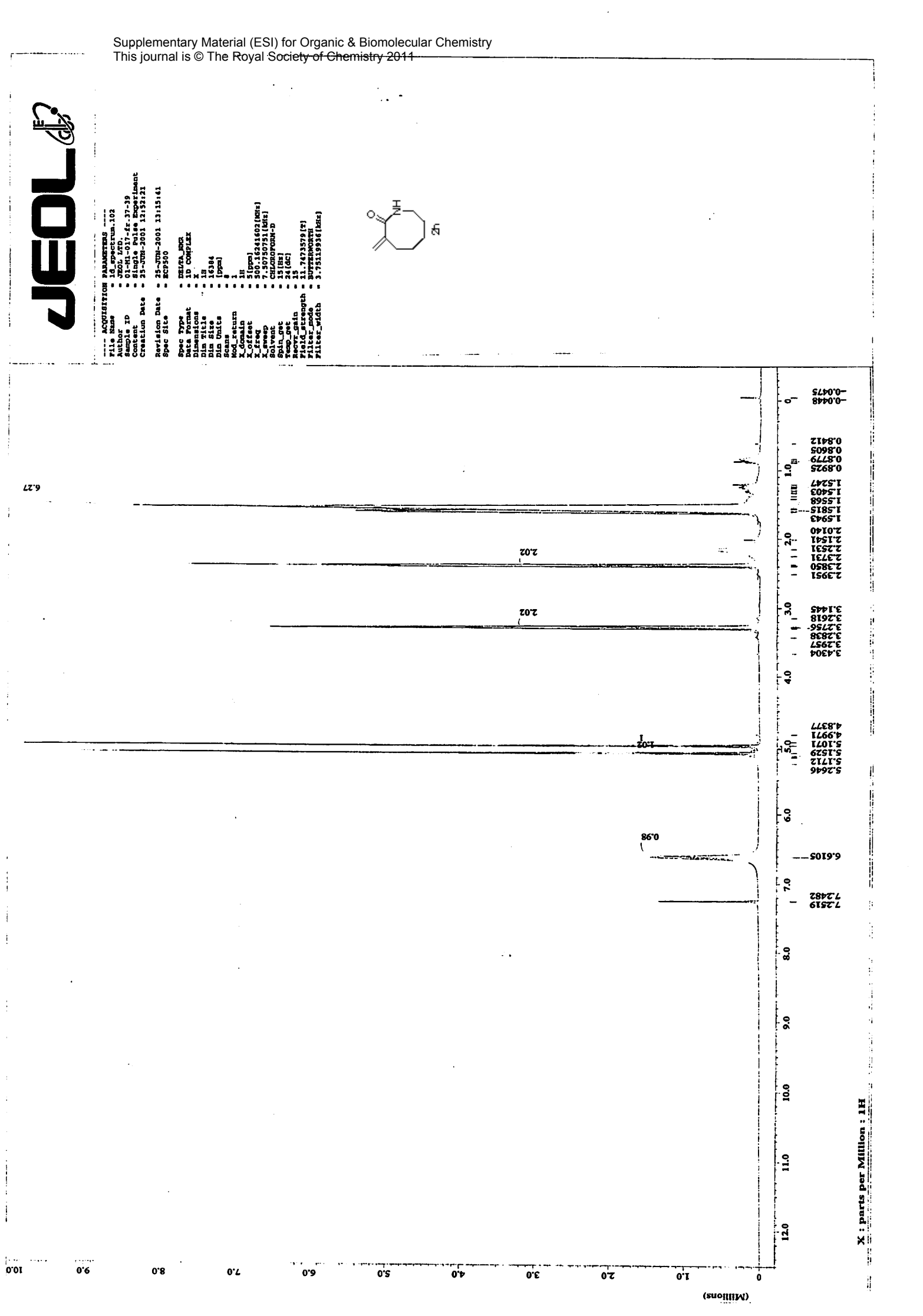
2e

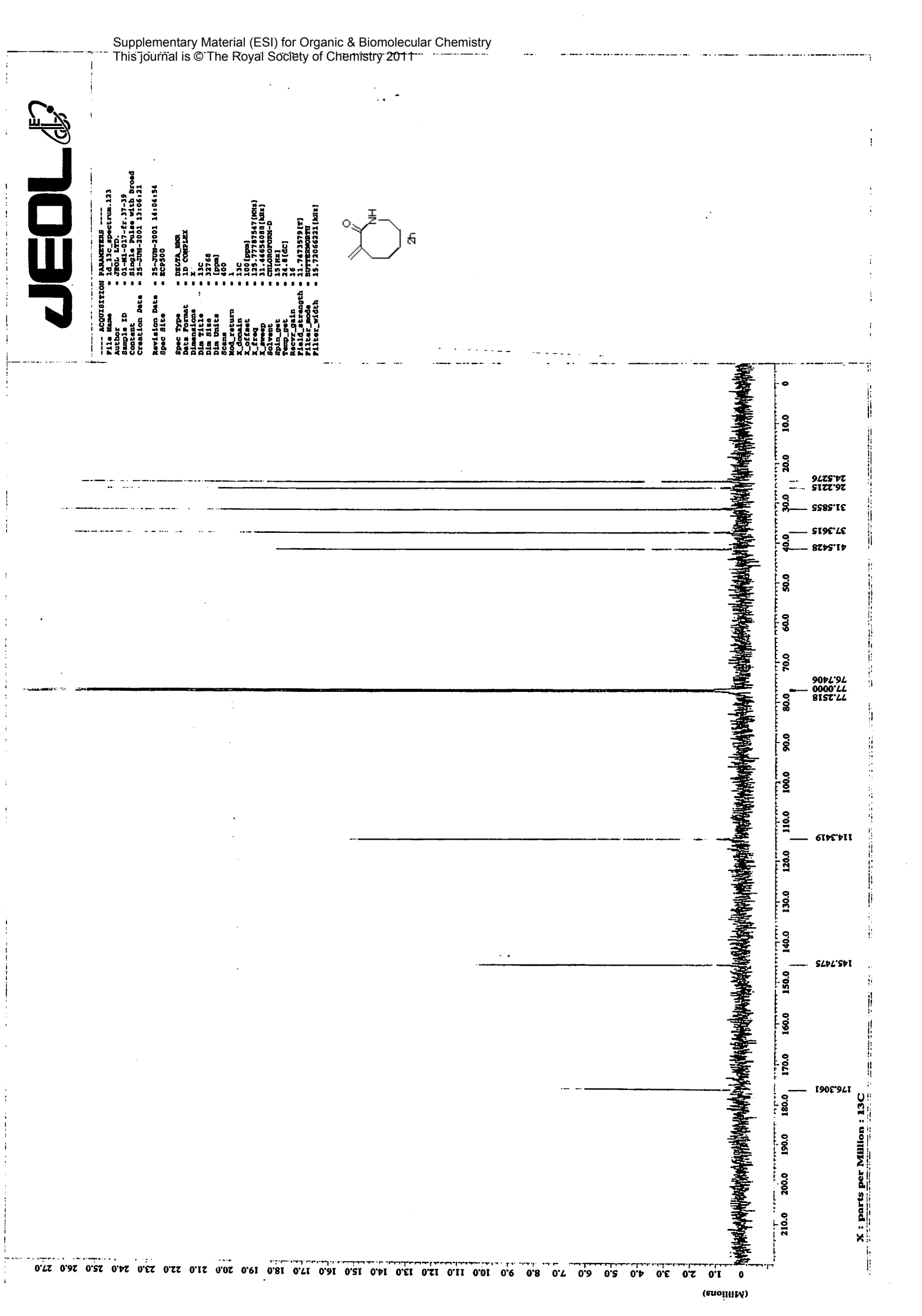


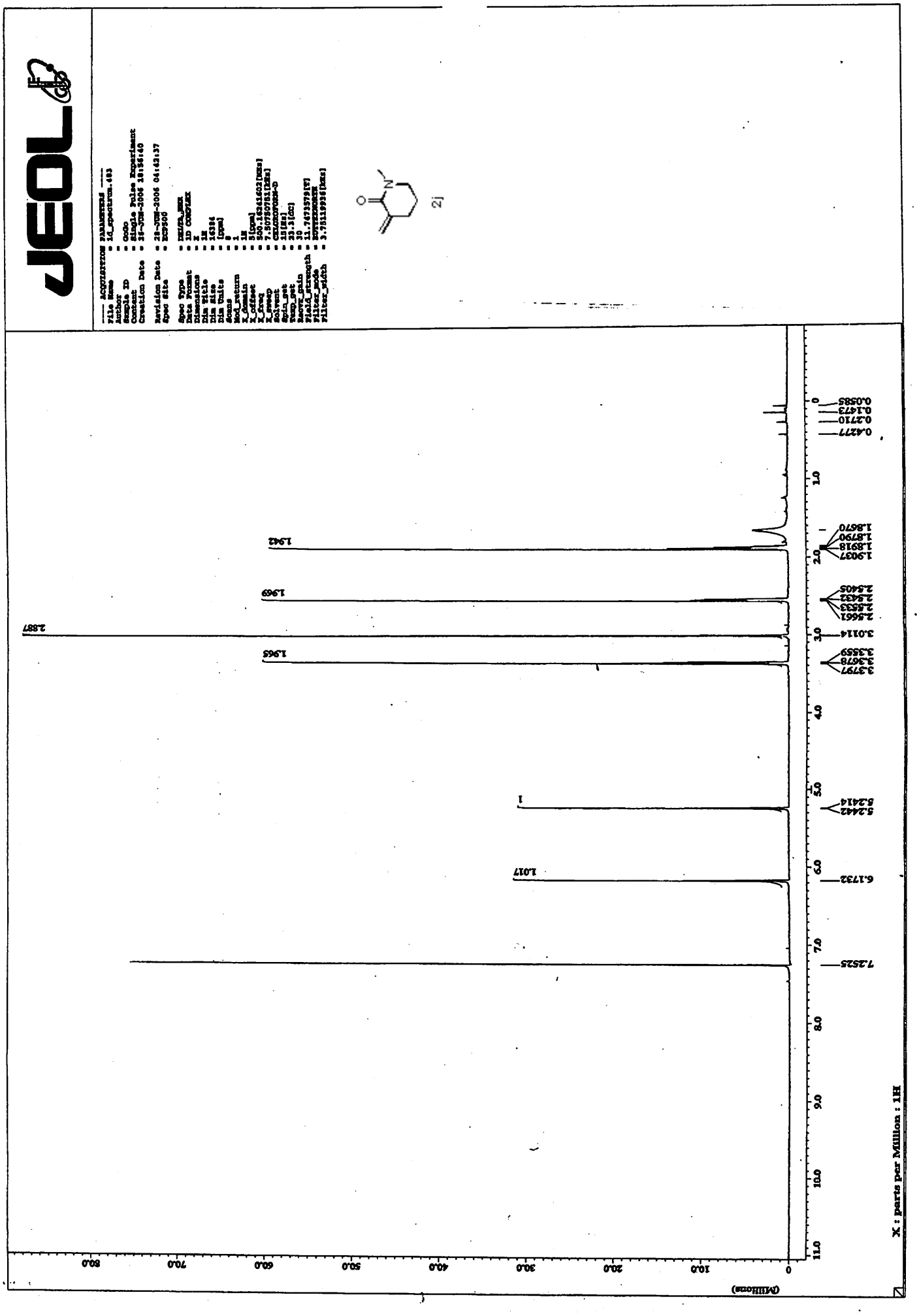


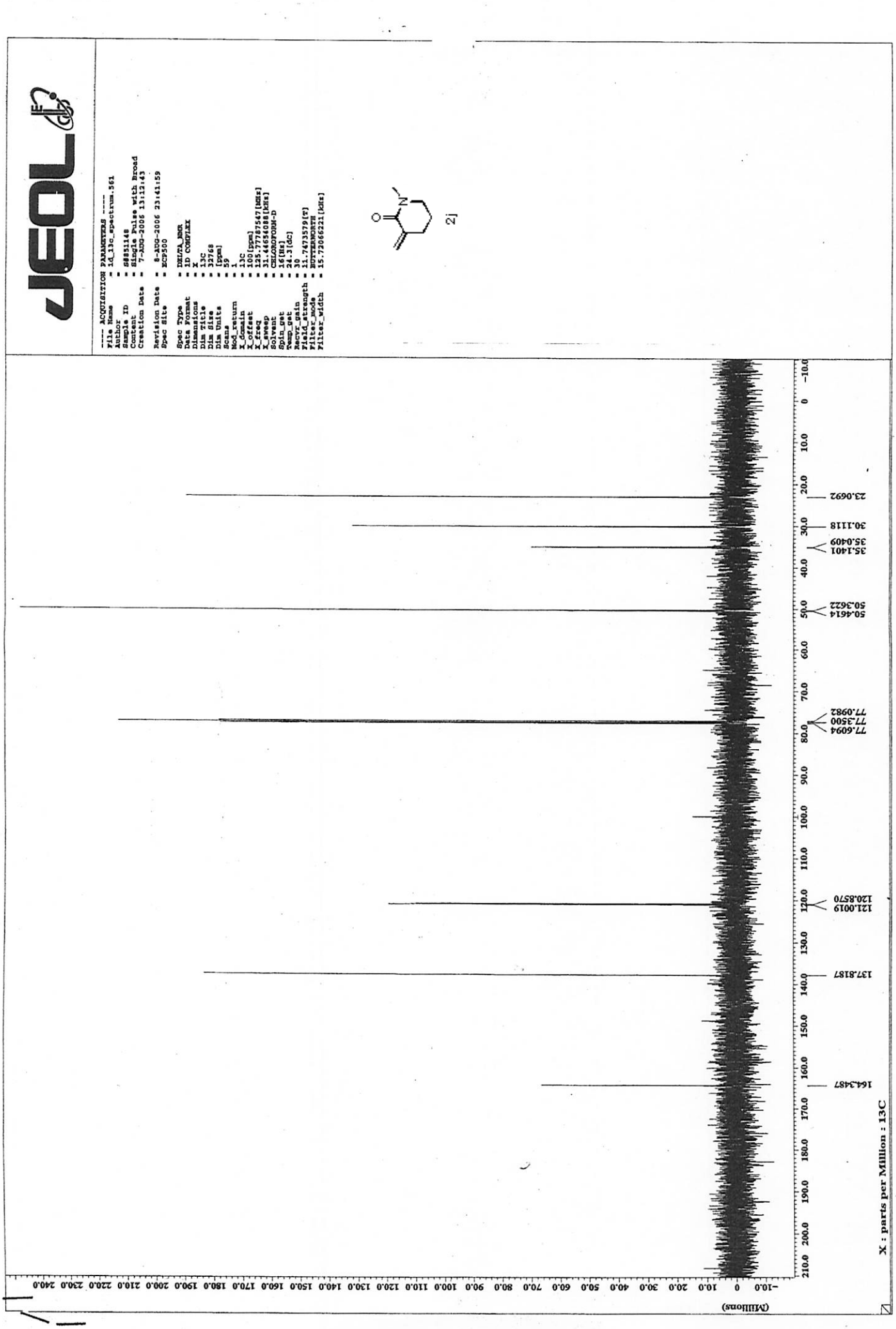




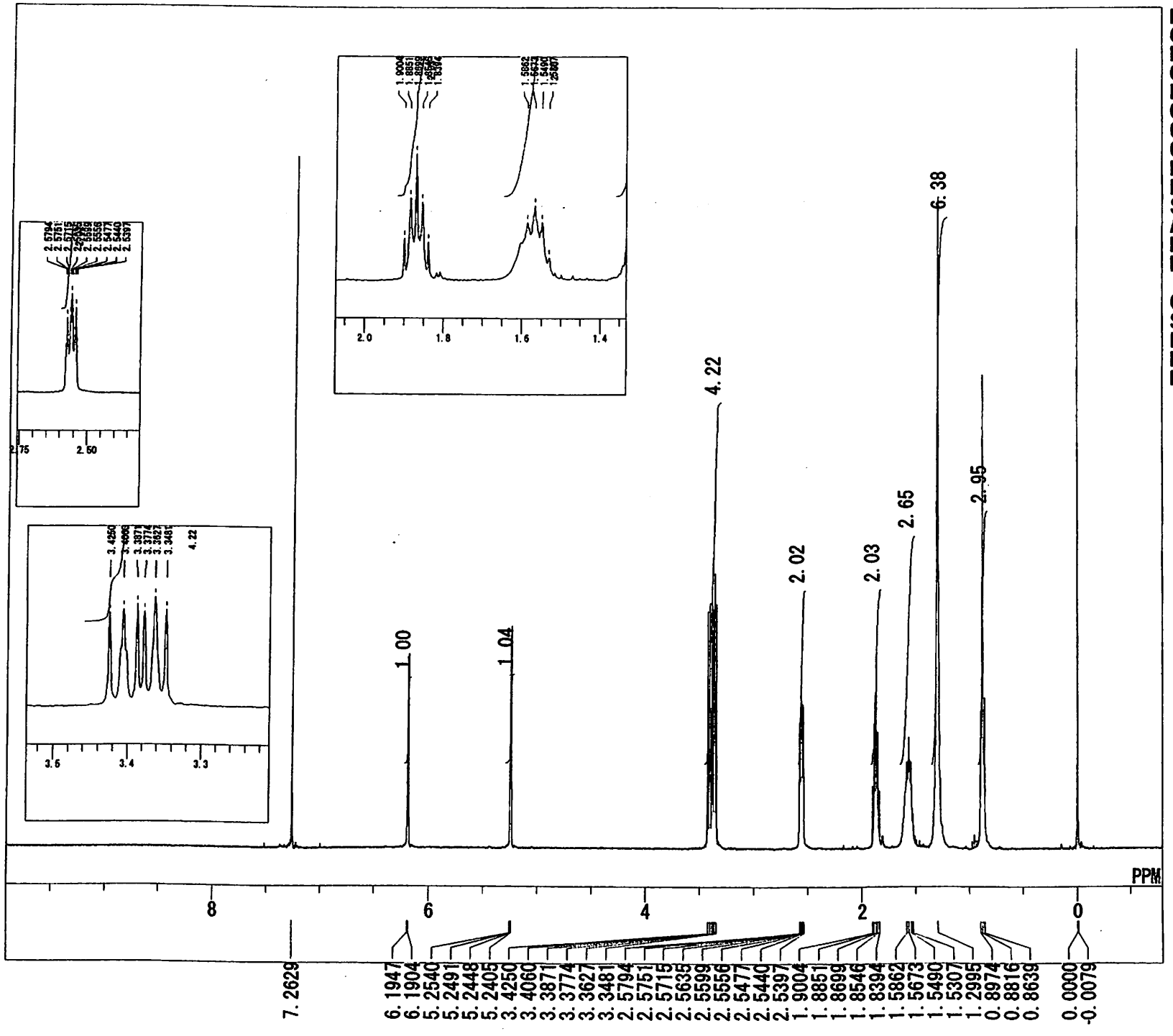




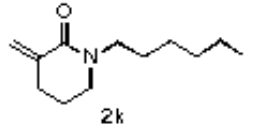




C:¥WINNMR98¥COMMON¥_DEFAULT.ALS

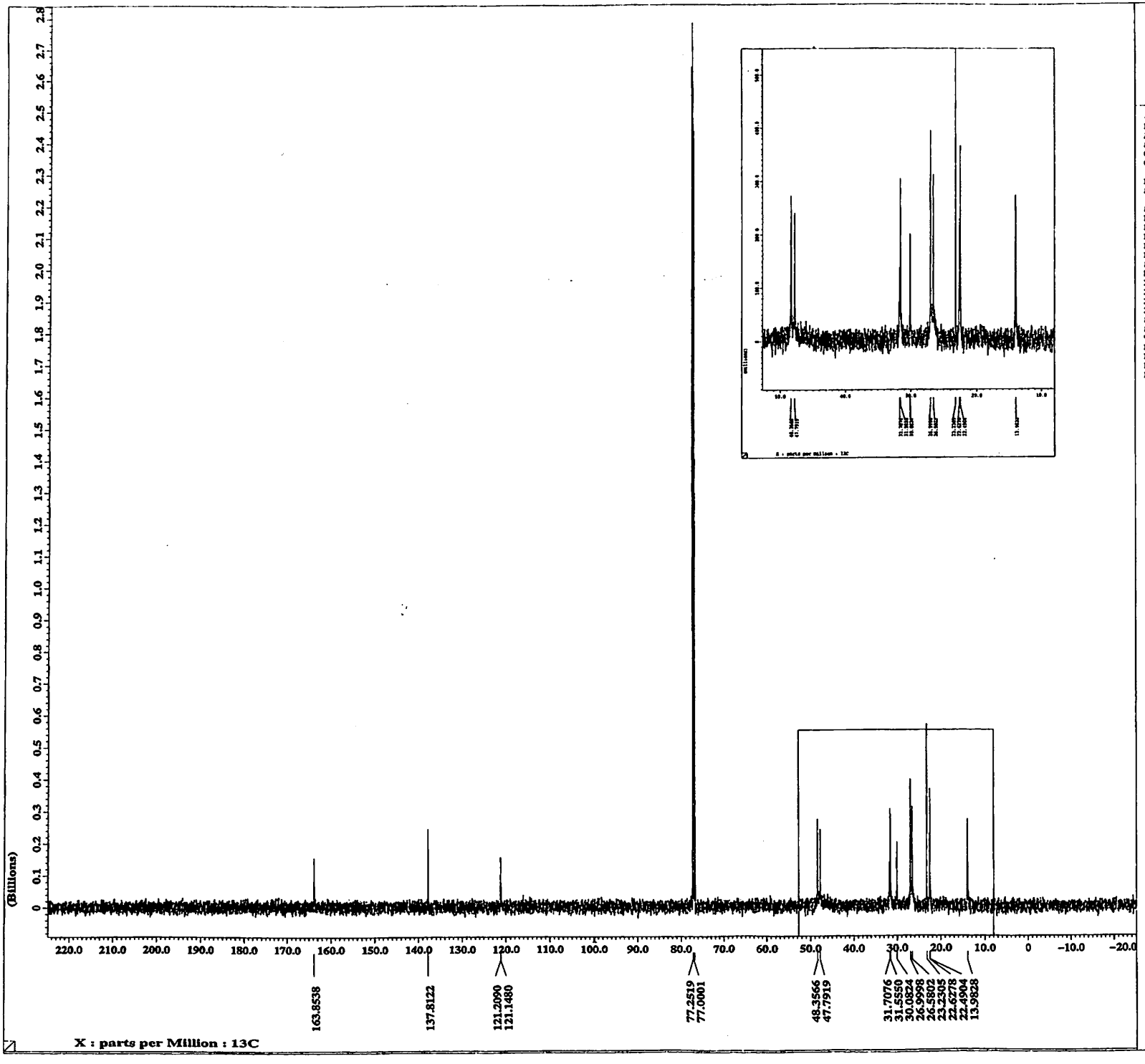


DFILE	C:¥WINNMR98¥COMMON¥_DEFAULT.AL
COMNT	
DATIM	Tue Mar 20 17:32:01 2007
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	7992.01 Hz
SCANS	8
ACQTM	4.1001 sec
PD	2.9010 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	17



2k

6.1947 6.1904 5.2540 5.2491 5.2448 5.2405 3.4250 3.4060 3.3871 3.3774 3.3627 3.3481 2.5794 2.5751 2.5715 2.5635 2.5599 2.5556 2.5477 2.5440 2.5397 1.9004 1.8851 1.8699 1.8546 1.8394 1.5862 1.5673 1.5490 1.5307 1.2995 0.8974 0.8816 0.8639 0.0000 -0.0079

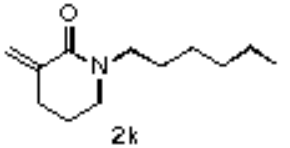


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name          = 1d_13c_spectrum.398
Author             =
Sample ID          = S8694615
Content            = Single Pulse with Broad
Creation Date      = 23-MAR-2008 23:27:06

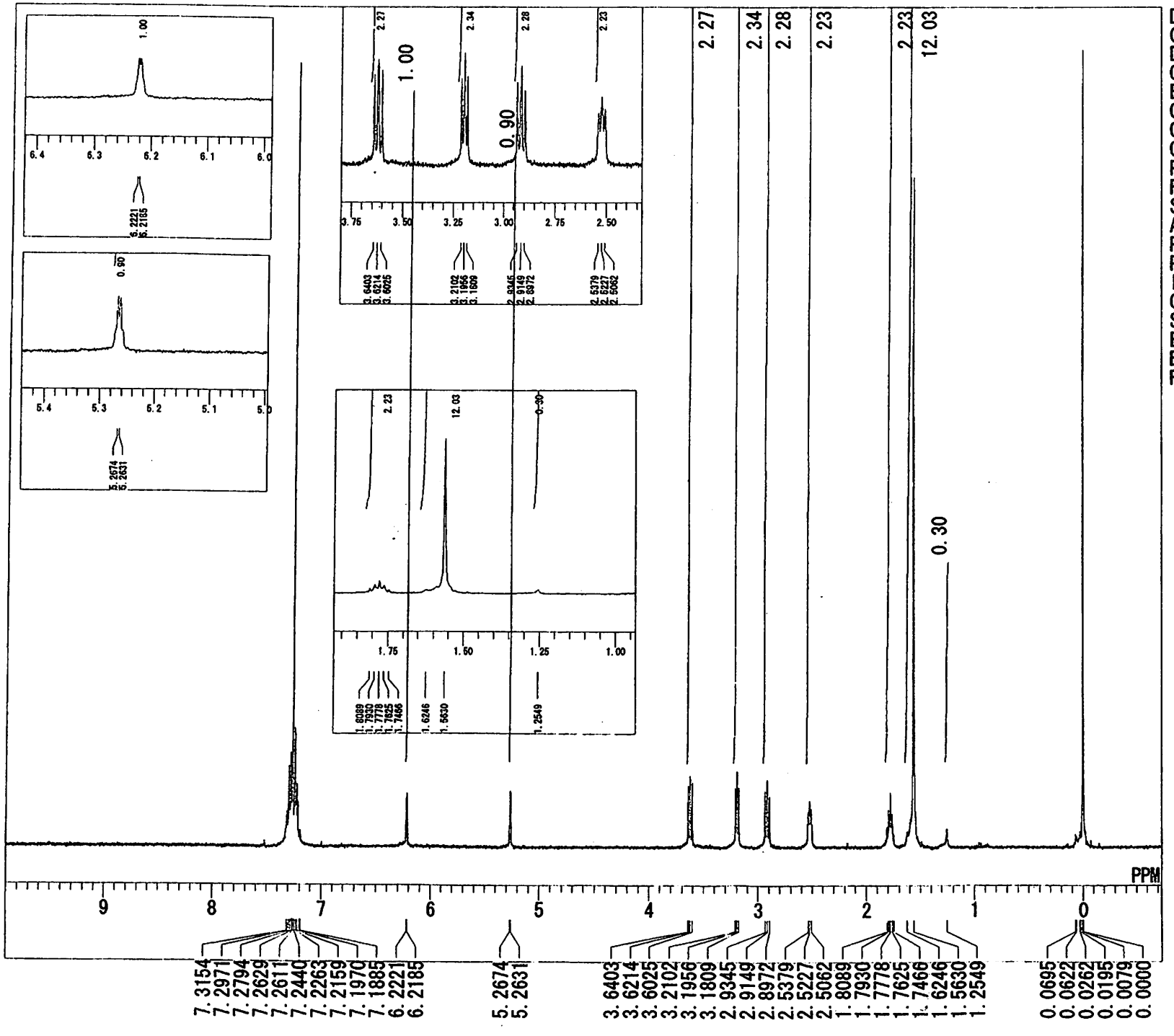
Revision Date      = 25-MAR-2008 20:07:49
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Scans              = 1000
Mod_return         = 1
X_domain           = 13C
X_offset           = 100[ppm]
X_freq             = 125.77787547[MHz]
X_sweep            = 31.44654088[kHz]
Solvent            = CHLOROFORM-D
Spin_get           = 16[Hz]
Temp_get           = 22.1[dC]
Recvr_gain         = 30
Field_strength     = 11.7473579[T]
Filter_mode        = BUTTERWORTH
Filter_width       = 15.72066221[kHz]
```

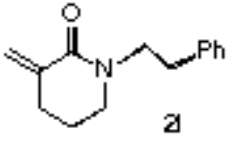


2k

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS



DFILE	C:¥WINNMR98¥COMMON¥_DEFAULT.AL
COMNT	
DATIM	Fri Apr 27 17:12:13 2007
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	7992.01 Hz
SCANS	8
ACQTM	4.1001 sec
PD	2.9010 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	21



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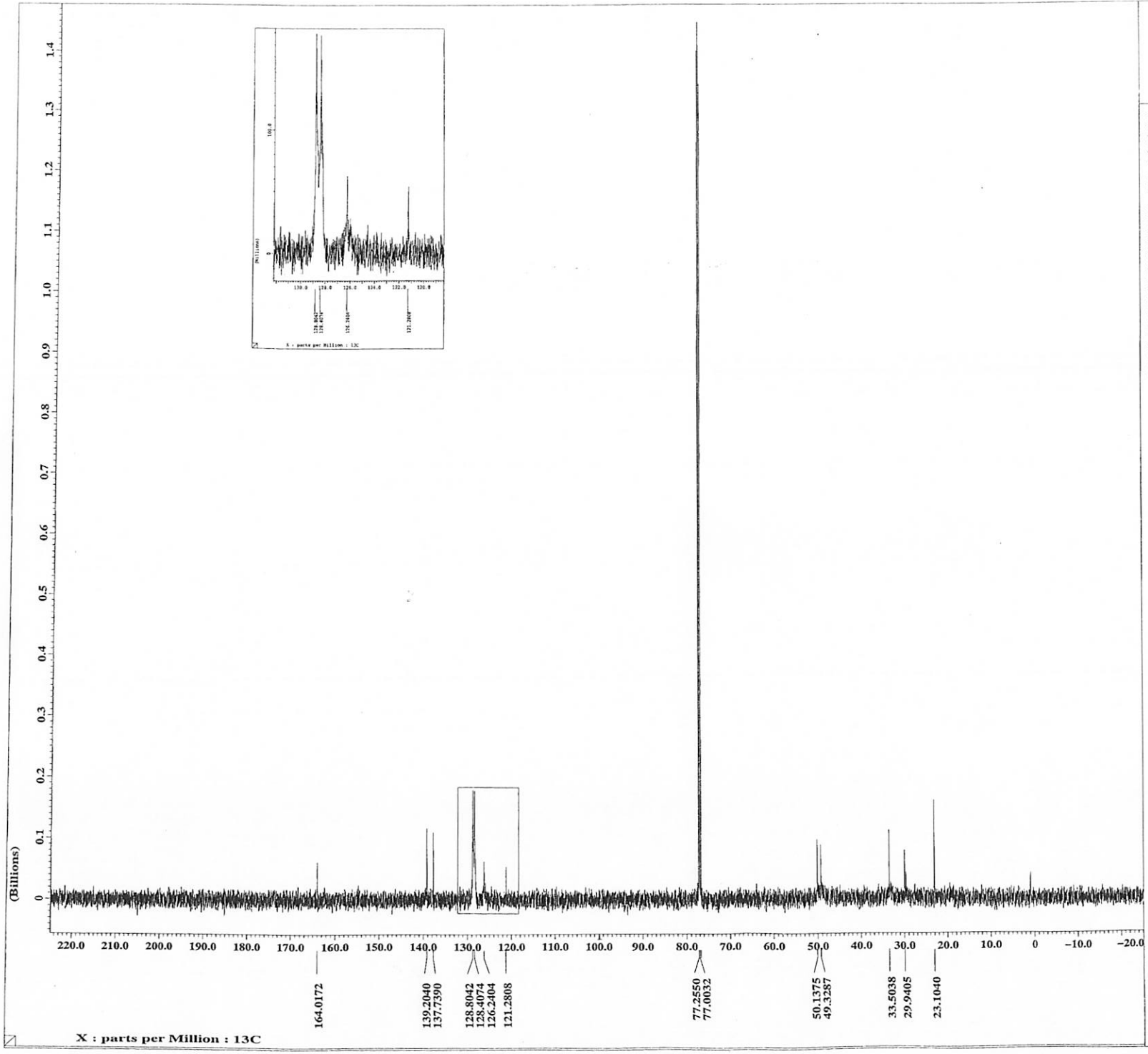
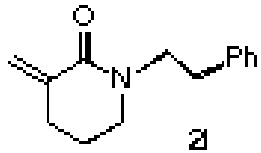
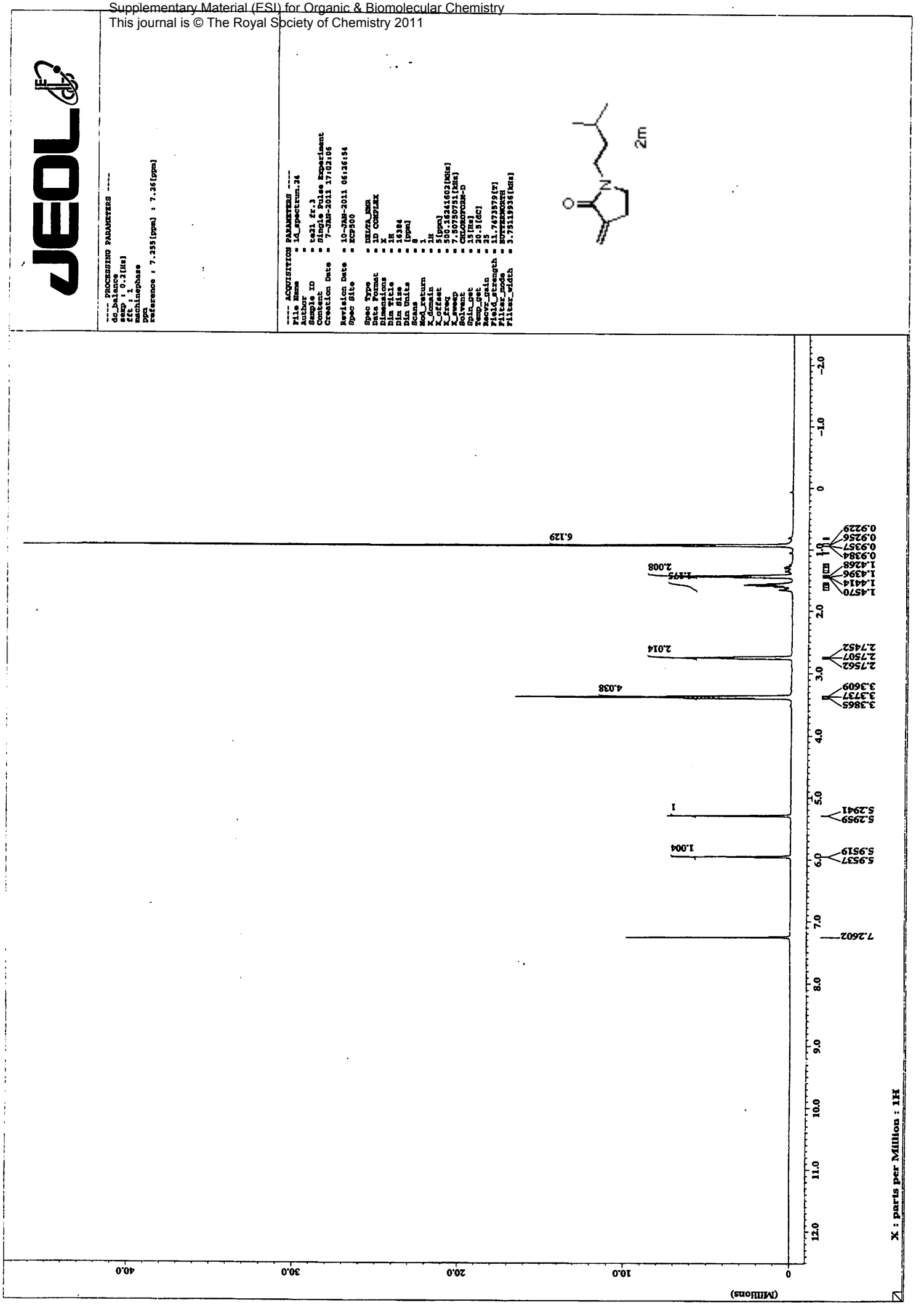


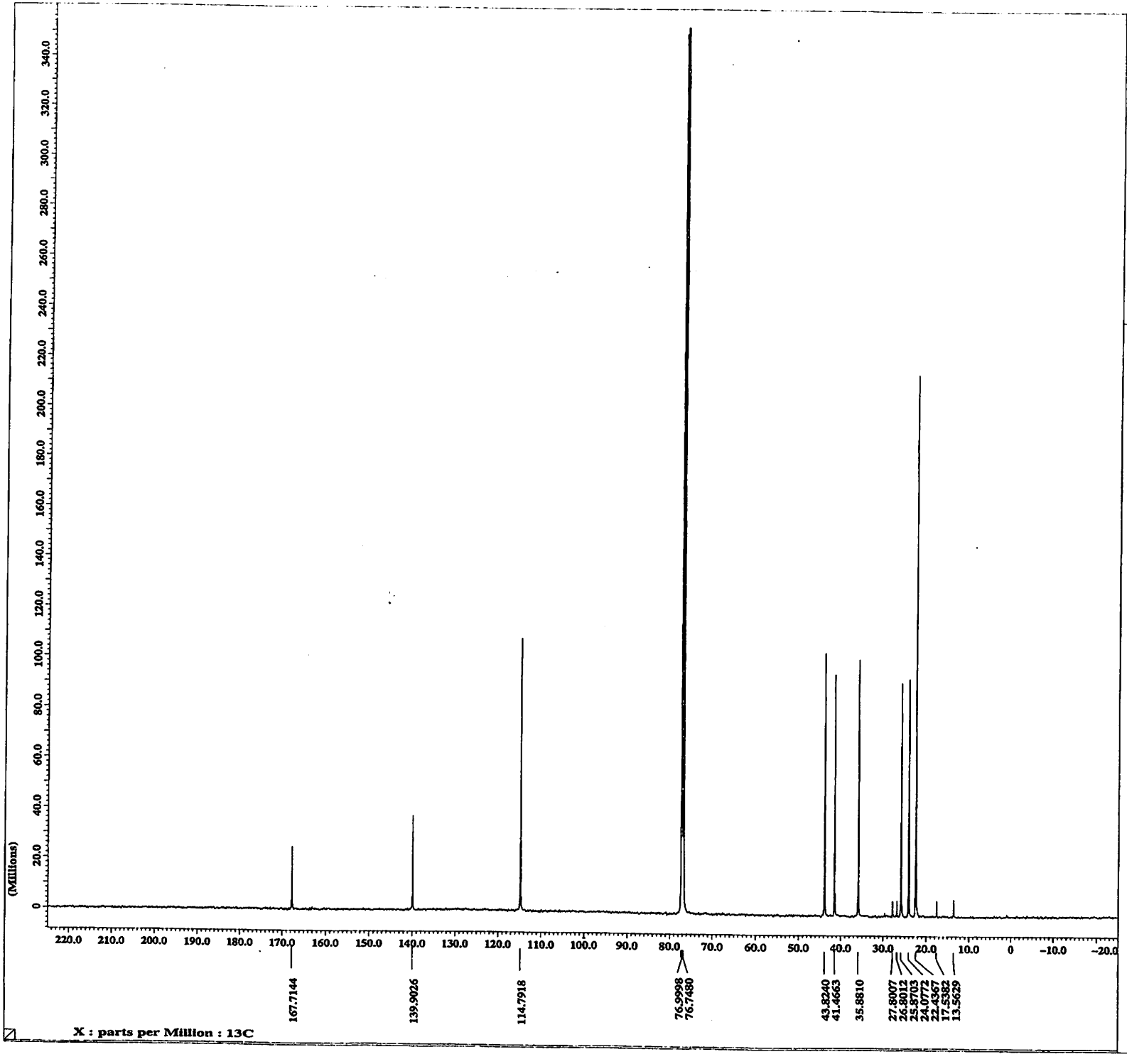
---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.345
Author	=
Sample ID	= yonamine-phenethyl
Content	= Single Pulse wich Broad
Creation Date	= 18-MAR-2008 14:57:29
Revision Date	= 20-MAR-2008 11:18:46
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 489.0
Mod_return	= 1
X_domain	= 13C
X_offset	= 100[ppm]
X_freq	= 125.77787547[MHz]
X_sweep	= 31.44654088[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 14[Hz]
Temp_get	= 22.9[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



2a



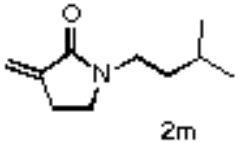


JEOL

---- PROCESSING PARAMETERS ----
dc_balance
exp : 5[Hz]
fft : 1
ppm
zachinephase
reference : 77.106[ppm] : 77[ppm]

---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.4
Author	=
Sample ID	= te21 fr.3 C
Content	= Single Pulse with Broad
Creation Date	= 8-JAN-2011 09:22:40
Revision Date	= 10-JAN-2011 22:46:15
Spec Site	= ECP500
Spec Type	= DEL/FA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 19500
Mod_return	= 1
X_domain	= 13C
X_offset	= 100[ppm]
X_freq	= 125.77787547[MHz]
X_sweep	= 31.44654088[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 13[Hz]
Temp_get	= 23.1[dC]
Recvr_gain	= 16
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



2m