Supporting Information

Synthesis of Lactams by Radical Substitution Reaction of α,β-Unsaturated Acyl Radicals at Amine Nitrogen

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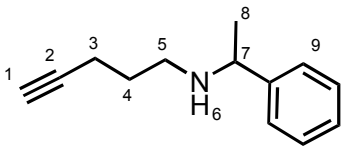
General information. ^{1}H NMR spectra were recorded with a JEOL JMN-ECP500 (500 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN-ECP500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. For ^{1}H-Sn or ^{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-4100 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 inc. 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.

Typical procedure for stannylcarbonylation of *N*-phenylethyl-pentynylamine (1b).

A magnetic stirring bar, AIBN (16.5 mg, 0.1 mmol), benzene (50 mL), Bu_3SnH (194.6 mg, 0.67 mmol), and *N*-(4-pentynyl)-N-(1-phenylethyl)amine (**1b**) (93.1 mg, 0.50 mmol) were placed in a 100-mL stainless autoclave. The autoclave was closed, purged three times with

carbon monoxide, pressurized with 78 atm of CO and then heated 90 °C for 4 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc = 1/1) to give **(Z)-2a** (141.8 mg, 71%, R_f = 0.63) and **(E)-2a** (6.7 mg, 3%, Rf = 0.075) R_f values were with hexane/EtOAc = 2/1.

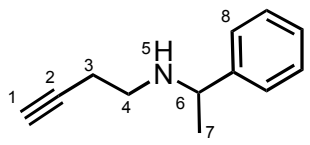
Preparation of *N*-(4-Pentynyl)-*N*-(1-phenylethyl)amine (1b).



A mixture of 4-pent-1-yl methansulfonate (20 mmol, 3.5 g) and (R)-(+)-1-phenylethylamine (60 mmol, 7.3 g) in acetonitrile (20mL) was stirred for 7.5 h under reflux. After cooling to room temperature, saturated Na_2CO_3 aqueous solution and AcOEt were added to the mixture. The layers were separated and the aqueous layer was extracted with AcOEt (3 x 30 mL). The combined AcOEt extracts were washed with brine. The organic layer was dried over K_2CO_3, filtered, and concentrated. The crude product was flash chromatographed on SiO_2 (AcOEt) and distilled under reduce pressure (bp = 50-52 °C/0.5 mmHg) to give 2.2 g (59%) of *N*-4-pentynyl-*N*-(1-phenylethyl)amine (**1b**) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (bs, 1H, H-6), 1.34 (d, *J* = 6.9 Hz, 3H, H-8), 1.66 (quint, *J* = 6.9 Hz, 2H, H-4), 1.91 (t, *J* = 2.3 Hz, 1H, H-1), 2.14-2.30 (m, 2H, H-3), 2.46-2.55 (m, 1H, H-5), 2.57-2.66 (m, 1H, H-5), 3.76 (q, *J* = 6.4 Hz, 1H, H-7), 7.20-7.35 (m, 5H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) 16.44, 24.59, 29.07, 46.66, 58.34, 68.69, 84.25, 126.63, 126.94, 128.50, 145.90; IR (neat) 1369, 1450, 1492, 1602, 2116, 2840, 2863, 2960, 3026, 3061, 3300; MS (EI) m/z (rel intensity) 186 (M^+-H, 15), 172 (98), 134 (13), 105 (100), 77 (19); HRMS (EI) m/z calcd for $C_{13}H_{18}N$ (M^+-H) 186.1283, found 186.1283.

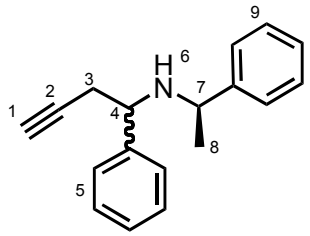
N-Phenylethyl-ω-alkynylamines **1a**, **1c**, **1d**, **1e**, **1j**, **1k**, **1m**, **1n** were prepared by a similar procedure from the racemic phenylethyl amine and the corresponding methansulfonate.

_N_-(3-Butynyl)-_N_-(1-phenylethyl)amine (1e).



Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, *J* = 7.4 Hz, 3H, H-7), 1.59 (bs, 1H, H-5), 1.98 (t, *J* = 2.3 Hz, 1H, H-1), 2.27-2.40 (m, 2H, H-3), 2.56-2.70 (m, 2H, H-4), 3.80 (q, *J* = 6.4 Hz, 1H, H-6), 7.20-7.36 (m, 5H, H-8); ^{13}C NMR (125 MHz, $CDCl_3$) 19.74, 24.62, 45.83, 57.81, 69.70, 82.68, 126.67, 126.69, 128.56, 145.56; IR (neat) 1451, 1492, 1602, 2116, 2840, 2925, 2962, 3025, 3061, 3300; MS (EI) m/z (rel intensity) 173 (M^+, 4), 158 (21), 134 (100), 129 (52), 105 (100), 77 (36); HRMS (EI) m/z calcd for $C_{12}H_{18}N$ (M^+) 173.1205, found 173.1196.

Preparation of _N_-(1-Phenyl-3-butynyl)-_N_-(1-phenylethyl)amine (1f, 1g).



Benzaldehyde (50 mmol, 5.1 mL) was cooled to 0 °C and (R)-(+)-1-phenylethylamine (50 mmol, 6.3 mL) was added dropwise. The mixture was then allowed to warm to room temperature and stirred for 1 h. Alumina Activated 200 (5 g) was added to the mixture. This was then filtered. The alumina was washed with THF, and the filtrate was concentrated to afford benzylidene-(1-phenyl-ethyl)-amine quantitatively. Zinc powder (150 mmol, 9.8 g) was subsequently washed with 2 N HCl, H_2O, MeOH, and THF (x2). The zinc was then suspended in THF and a THF solution of benzylidene-(1-phenyl-ethyl)-amine was added. 3-Bromo-propyne was added dropwise to this mixture at 0 °C and stirred for 30 min. Then the mixture was allowed to warm to room

temperature and stirred for 12 h. Water and Et_2O were added, and the reaction mixture was filtered through Celite. The aqueous phase was extracted with AcOEt (30 mL x 3) and the combined organic layers were washed with brine, dried over K_2CO_3, and concentrated under vacuum. The crude product was purified by vacuum distillation (bp = 118 °C/0.5 mmHg) to give 10.1g (81%) of the **1f** and **1g** as a diastereomeric mixture (dr = 51/49). To a ether solution of the diastereomeric mixture (5.5 g) was added 2 N HCl (30 mL) and the mixture was then cooled to 0 °C for 4 h. The white solid was afforded. This solid was filtered, then treated with NaOHaq. The mixture was extracted with ether and the combined organic phase was washed with water and brine, dried over K_2CO_3, and concentrated under vacuum to afford (S,R)- *N*-(1-phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1f**) in 53% yield, (93.8% de). The filtrate from the recrystallization process was treated with NaOHaq and extracted with Et_2O. The organic phase was washed with water and brine and then dried over K_2CO_3, filtered, and evaporated under vacuum to afford (R,R)-*N*-(1-phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1g**) in 43% yield, (90%de). This acid/base treatment was repeated two times to afford (R,R)-*N*-(1-phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1g**) in 99.8%de. Diastereomeric excess was determined by HPLC. HPLC conditions; Chiracel OD-H; hexane/2-propanol 99.9/0.1; flow rate 1.0 mL/min; column temperature 20 °C; UV detector 254 nm; retention time for (R,R)- *N*-(1-phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1g**) 10.6 min, retention time for (S,R)- *N*-(1-phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1f**) 14.2 min.

(S,R)- *N*-(1-Phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1f**) [5]

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.4 Hz, 3H, H-8), 1.87 (bs, 1H, H-6), 1.99 (t, *J* = 2.3 Hz, 1H, H-1), 2.57 (ddd, *J* = 8.7, 6.0, 2.3 Hz, 1H, H-3), 2.64 (ddd, *J* = 9.2, 6.4, 2.3 Hz, 1H, H-3), 3.79 (q, *J* = 6.4 Hz, 1H, H-7), 3.89 (t, *J* = 6.0 Hz, 1H, H-4), 7.20-7.40 (m,

10H, H-5,9); ^{13}C NMR (125 MHz, $CDCl_3$) 23.15, 27.09, 54.90, 58.30, 70.88, 81.57, 126.74, 127.10. 127.22, 127.47, 128.50, 128.56, 143.00, 145.85; IR (neat) 1453, 1492, 1602, 1738, 2117, 2863, 2923, 2962, 3026, 3061, 3002, 3025, 3061, 3083, 3300; MS (EI) m/z (rel intensity) 249 (M^+, 0.40), 210 (81), 128 (14), 105 (100), 77 (20); HRMS (EI) m/z calcd for $C_{18}H_{19}N$ (M^+) 249.1518, found 249.1516.

(R,R)- *N*-(1-Phenyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1g**)

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (d, *J* = 6.4 Hz, 3H, H-8), 2.02 (t, *J* = 2.8 Hz, 1H, H-1), 2.10 (bs, 1H, H-6), 2.41-2.49 (m, 2H, H-3), 3.51 (q, *J* = 6.9 Hz, 1H, H-7), 3.55 (t, *J* = 6.4 Hz, 1H, H-4), 7.17-7.36 (m, 10H, H-5,9); ^{13}C NMR (125 MHz, $CDCl_3$) 25.03, 28.52, 55.00, 58.30, 70.49, 81.73, 126.72, 126.95, 127.24, 127.50, 128.53(b), 142.82, 145.40. IR (neat) 1453, 1492, 1602, 1737, 2117, 2862, 2925, 2965, 3026, 3061, 3082, 3300; MS (EI) m/z (rel intensity) 249 (M^+, 0.35), 210 (93), 128 (14), 105 (100), 77 (19); HRMS (EI) m/z calcd for $C_{18}H_{19}N$ (M^+) 249.1518, found 249.1510.

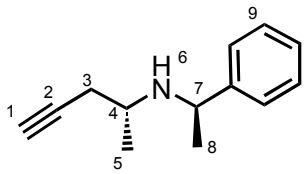
The structure of **1g** was determined as a HCl salt by X-ray analysis. To ether solution of **1g** was added 2 N HCl and filtered. The obtained white solid was recrystallized with acetonitrile.

***N*-(1-Methyl-3-butynyl)-*N*-(1-phenylethyl)amine (1h, 1i).**

A similar procedure was used for *N*-(1-methyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1h**, **1i**), in which acetaldehyde was used in place of benzaldehyde. The reaction mixture obtained was distilled under reduced pressure (bp = 65-67 °C/0.5 mmHg). Two diastereomers were separated by flash chromatography on SiO_2 (Hexane/AcOEt =10/1). HPLC conditions: Chiracel OD-H; hexane/2-propanol 99.9/0.1; flow rate 0.8 mL/min; column temperature

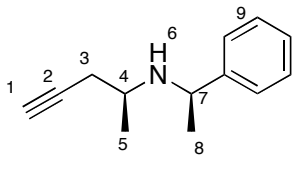
20 °C; UV detector 254 nm; retention time for (R,R)-*N*-(1-methyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1h**) 11.7 min in 99.9% dr, and retention time for retention time for (S,R)-*N*-(1-methyl-3-butynyl)-*N*-(1-phenylethyl)amine (**1i**) 13.8 min in 99.3% dr.

(R,R)-*N*-(1-Methyl-3-butynyl)-*N*-(1-phenylethyl)amine (1h)



Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (d, *J* = 6.4 Hz, 3H, H-5), 1.34 (d, *J* = 6.4 Hz, 3H, H-8), 1.48-1.58 (bs, 1H, H-6), 2.00 (t, *J* = 2.7 Hz, 1H, H-1), 2.19 (ddd, *J* = 8.7, 6.4, 2.7 Hz, 1H, H-3), 2.23 (ddd, *J* = 8.2, 6.0, 2.7 Hz, 1H, H-3), 2.68 (sext, *J* = 6.4 Hz, 1H, H-4), 3.90 (q, *J* = 6.4 Hz, 1H, H-7), 7.20-7.35 (m, 5H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) 19.70, 24.95, 27.11, 48.68, 54.99, 70.33, 81.95, 126.62, 126.97, 128.53, 145.69; IR (neat) 1375, 1451, 1493, 1603, 2116, 2866, 2926, 2963, 3025, 3062, 3302; MS (EI) m/z (rel intensity) 186 (M^+-H, 8), 148 (45), 105 (100), 77 (15); HRMS (EI) m/z calcd for $C_{13}H_{16}N$ (M^+-H) 186.1283, found 186.1277.

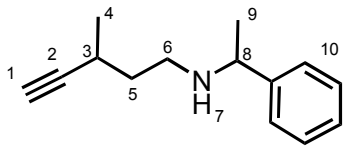
(S,R)-*N*-(1-Methyl-3-butynyl)-*N*-(1-phenylethyl)amine (1i)



Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (d, *J* = 6.4 Hz, 3H, H-5), 1.32 (d, *J* = 6.4 Hz, 3H, H-8), 1.36-1.44 (bs, 1H, H-6), 1.99 (t, *J* = 2.8 Hz, 1H, H-1), 2.16-2.26 (m, 1H, H-3), 2.39 (ddd, *J* = 8.7, 6.4, 2.7 Hz, 1H, H-3), 2.65-2.74 (m, 1H, H-4), 3.89 (q, *J* = 6.5 Hz, 1H, H-7), 7.20-7.36 (m, 5H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) 21.21, 24.93, 25.28, 48.49, 55.04, 70.48, 81.50, 126.68, 126.98, 128.55, 145.89; IR (neat) 1374, 1452, 1492, 1603, 1810, 1878, 1952, 2116, 2865, 2926, 2965, 3025, 3062, 3303; MS (EI) m/z (rel intensity) 186 (M^+-H, 4), 148 (50), 105 (100),

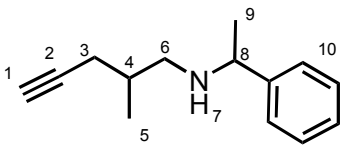
77 (16); HRMS (EI) m/z calcd for $C_{13}H_{16}N$ (M^+-H) 186.1283, found 186.1275. The structure of **1i** was determined as a HCl salt by X-ray analysis. To ether solution of **1i** was added 2 N HCl and filtered. The obtained white solid was recrystallized with $CHCl_3$.

***N*-(3-Methyl-4-pentyny)-*N*-(1-phenylethyl)amine (1j)** [5]



Colorless oil. bp = 60-64 °C/0.5 mmHg. dr = 50/50: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (d, *J* = 6.9 Hz, 3H, H-4), 1.16 (d, *J* = 6.9 Hz, 3H, H-4), 1.24 (bs, 2H, H-7), 1.34 (d, *J* = 6.4 Hz, 6H, H-9), 1.58 (q, *J* = 7.3 Hz, 4H, H-5), 1.99 (t, *J* = 1.8 Hz, 1H, H-1), 2.00 (t, *J* = 1.8 Hz, 1H, H-1), 2.44-2.70 (m, 6H, H-3,6), 3.76 (q, *J* = 6.9 Hz, 2H, H-8), 7.20-7.35 (m, 10H, H-10); ^{13}C NMR (125 MHz, $CDCl_3$) 21.01, 21.25, 23.71, 23.82, 24.50, 24.57, 37.16, 37.22, 45.53, 45.70, 58.42 (b), 68.54, 68.65, 88.63, 88.82, 126.63 (b), 126.90 (b), 128.46 (b), 145.86, 145.98, IR (neat) 1372, 1452, 1493, 1603, 1810, 1949, 2111, 2967, 3026, 3061, 3303; MS (EI) m/z (rel intensity) 200 (M^+-H, 16), 186 (98), 158 (9), 105 (100), 97 (16), 77 (19); HRMS (EI) m/z calcd for $C_{14}H_{18}N$ (M^+-H) 200.1440, found 200.1441.

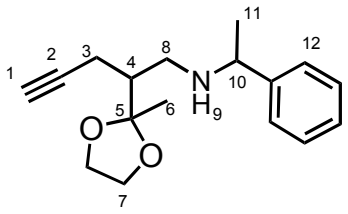
***N*-(2-Methyl-4-pentynyl)-*N*-(1-phenylethyl)amine (1k)** [5]



Colorless oil. bp = 107-110 °C/3 mmHg. dr = 51/49: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (d, *J* = 6.5 Hz, 3H, H-5), 0.98 (d, *J* = 6.9 Hz, 3H, H-5), 1.24 (bs, 2H, H-7), 1.33 (d, *J* = 6.4 Hz, 3H, H-9), 1.34 (d, *J* = 6.5 Hz, 3H, H-9), 1.73 (m, 2H, H-4), 1.92 (t, *J* = 2.8 Hz, 1H, H-1), 1.93 (t, *J* = 2.8 Hz, 1H, H-1), 2.06-2.56 (m, 8H, H-3,6), 3.735 (q, *J* = 6.4 Hz, 1H, H-8), 3.7340 (q, *J* = 6.4 Hz, 1H, H-8), 7.20-7.35 (m, 10H, H-10); ^{13}C NMR (125 MHz, $CDCl_3$) 17.92, 17.94, 23.71, 23.91, 24.69, 24.72, 58.37, 58.52, 69.42 (b), 83.13, 83.16, 126.67 (b), 126.88 (b), 128.46 (b), 146.04, 146.14, IR (neat) 1452, 1493, 1541, 1602, 1646, 1947, 2116, 2310, 2348, 2370,

2832, 2925, 2960, 3026, 3061, 3083, 3304; MS (EI) m/z (rel intensity) 200 (M^+-H, 22), 186 (100), 105 (35), 77 (10); HRMS (EI) m/z calcd for $C_{14}H_{18}N$ (M^+-H) 200.1440, found 200.1431.

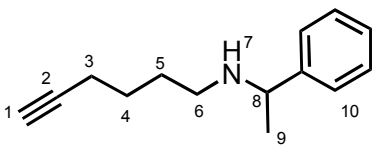
{2-(2-Methyl-[1,3]dioxolan-2-yl)-4-pentynyl}-(1-phenylethyl)amine (1l) [5]



2-(2-Methyl-[1,3]dioxolan-2-yl)-pent-4-ynal was prepared from ethyl-3-oxobutanoate in 4 steps by propargylation of ethyl 3-oxobutanate, acetal protection of ketone, reduction with lithium aluminum hydride, and oxidation with PCC in 35% over four steps. The obtained aldehyde (7.7 mmol) was treated with (R)-(+)-1-phenylethylamine (7.7 mmol) at 0 °C for 10 min and then stirred for 1 h at room temperature to give the corresponding imine. After the addition of Et_2O and water to the mixture, the aqueous layer was extracted with Et_2O (30 mL x 3), the combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. To a MeOH (10 mL) solution of the imine was added $NaBH_4$ (23.1 mmol) portionwise at 0 °C and stirred for 12 h at room temperature. Water and Et_2O were added to the mixture. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined Et_2O extracts were washed with brine. The organic layer was dried over K_2CO_3, filtered, and concentrated. The crude product was flash chromatographed on SiO_2 (hexane/AcOEt = 1/1) and distilled under reduce pressure (bp = 103-105 °C/0.5 mmHg) to give 1.3 g (62%) of the desired amine (**1l**) as a colorless oil. dr = 50/50: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 3H, H-6), 1.21 (s, 3H, H-6), 1.339 (d, *J* = 6.9 Hz, 3H, H-11), 1.344 (d, *J* = 6.9 Hz, 3H, H-11), 1.86-2.06 (m, 6H, H-1,4,9), 2.12-2.30 (m, 2H, H-3 or 8), 2.42-2.53 (m, 2H, H-3 or 8), 2.56-2.76 (m, 4H, H-3 or 8), 3.65-3.80 (m, 2H, H-10), 3.84-4.00

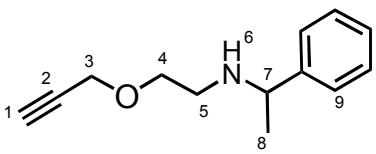
(m, 8H, H-7), 7.17-7.50 (m, 10H, H-12); ^{13}C NMR (125 MHz, $CDCl_3$) 18.09, 18.28, 20.97, 21.16, 24.57, 24.63, 45.64, 45.88, 47.71, 47.81, 58.45, 58.56, 64.52, 64.64, 69.34(b), 83.37, 83.50, 111.16, 111.32, 126.66(b), 126.71(b), 126.78(b), 128.38(b), 145.93, 146.07, IR (neat) 1375, 1450, 1493, 1603, 2116, 2883, 2924, 2979, 3025, 3060, 3294; MS (EI) m/z (rel intensity) 272 (M^+-H, 20), 258 (58), 228 (28), 186 (28), 134 (23), 118 (38), 105 (100), 77 (17); HRMS (EI) m/z calcd for $C_{17}H_{22}N_1O_2$ (M^+-H) 272.1650, found 272.1653.

***N*-(5-Hexynyl)-*N*-(1-phenylethyl)amine (1m).**



Colorless oil. bp = 62-63 °C/0.5 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (bs, 1H, H-7), 1.34 (d, *J* = 6.4 Hz, 3H, H-9), 1.47-1.62 (m, 4H, H-4,5), 1.92 (t, *J* = 2.3 Hz, 1H, H-1), 2.10-2.22 (m, 2H, H-3), 2.38-2.46 (m, 1H, H-6), 2.47-2.55 (m, 1H, H-6), 3.74 (q, *J* = 6.9 Hz, 1H, H-8), 7.20-7.35 (m, 5H, H-10); ^{13}C NMR (125 MHz, $CDCl_3$) 18.41, 24.59, 26.35, 29.47, 47.32, 58.44, 68.55, 84.43, 126.60, 126.99, 128.47, 145.96, IR (neat) 1369, 1451, 1493, 1603, 2116, 2862, 2935, 3025, 3061, 3303; MS (EI) m/z (rel intensity) 200 (M^+-H, 5), 186 (55), 148 (12), 134 (11), 105 (100), 79 (16), 77 (15); HRMS (EI) m/z calcd for $C_{14}H_{18}N$ (M^+-H) 200.1440, found 200.1436.

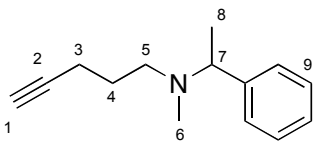
***N*-(3-Butyloxyethyl)-*N*-(1-phenylethyl)amine (1n).**



Colorless oil. bp = 78-80 °C/0.5 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (d, *J* = 6.9 Hz, 3H, H-8), 1.70 (bs, 1H, H-6), 2.41 (t, *J* = 2.3 Hz, 1H, H-1), 2.62 (ddd, *J* = 10.1, 6.4, 3.7 Hz, 1H, H-5), 2.70 (ddd, *J* = 10.5, 6.4, 3.7 Hz, 1H, H-5), 3.56 (ddd, *J* = 9.6, 6.9, 3.7 Hz, 1H, H-4), 3.62 (ddd, *J* = 9.2, 6.4, 3.7 Hz, 1H, H-4), 3.77 (q, *J* = 6.4 Hz, 1H, H-7), 4.12 (dd, *J* =

15.6, 2.3 Hz, 1H, H-3), 4.16 (dd, *J* = 15.6, 2.3 Hz, 1H, H-3), 7.20-7.34 (m, 5H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) 24.55, 47.15, 58.30, 69.61, 74.59, 74.63, 79.86, 126.71, 126.97, 128.51, 145.62, IR (neat) 1351, 1451, 1493, 1603, 2116, 2862, 2926, 3026, 3061, 3290; MS (EI) m/z (rel intensity) 203 (M^+, 7), 188 (37), 149 (16), 134 (100), 105 (100), 77 (21); HRMS (EI) m/z calcd for $C_{13}H_{16}N$ (M^+) 203.1310, found 203.1302.

***N*-Methyl-*N*-(1-phenylethyl)-4-pentynyl-1-amine** (**1o**).



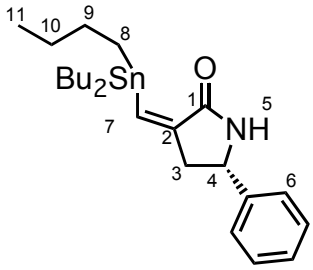
Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (d, *J* = 6.9 Hz, 3H, H-8), 1.67 (quint, *J* = 7.3 Hz, 2H, H-4), 1.90 (t, *J* = 2.3 Hz, 1H, H-1), 2.11-2.25 (m, 5H, H-3, 6), 2.36 (dt, *J* = 12.8, 6.9 Hz, 1H, H-5), 2.49 (dt, *J* = 12.4, 7.4 Hz, 1H, H-5), 3.56 (q, *J* = 6.9 Hz, 1H, H-7), 7.20-7.35 (m, 5H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) 16.28, 18.36, 26.44, 38.41, 53.04, 63.49, 68.25, 84.65, 126.76, 127.75, 128.17, 144.12, IR (neat) 1452, 1492, 1602, 2117, 2791, 2841, 2972, 3027, 3060, 3305; MS (EI) m/z (rel intensity) 200 (M^+-H, 6), 186 (74), 172 (25), 148 (20), 105 (100), 77 (15); HRMS (EI) m/z calcd for $C_{14}H_{18}N$ (M^+-H) 200.1440, found 200.1436.

Typical procedure for stannylcarbonylation of *N*-phenylethyl-pentynylamine (1b).

A magnetic stirring bar, AIBN (16.5 mg, 0.1 mmol), benzene (50 mL), Bu_3SnH (194.6 mg, 0.67 mmol), and *N*-(4-pentynyl)-N-(1-phenylethyl)amine (**1b**) (93.1 mg, 0.50 mmol) were placed in a 100-mL stainless autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 78 atm of CO and then heated 90 °C for 4 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc = 1/1) to give **(Z)-2a** (141.8 mg, 71%, R_f = 0.63) and **(E)-2a** (6.7 mg, 3%, Rf =

0.075) R_f values were with hexane/EtOAc = 2/1. The spectral data of these compounds, as well as those of 3-[(tributylstannanyl)methylene]pyrrolidin-2-one (**2e**) and 3-[(tributylstannanyl)methylene]azepan-2-one (**2l**), were identical with the data we previously reported.[4]

(*S*)-5-Phenyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (2f).

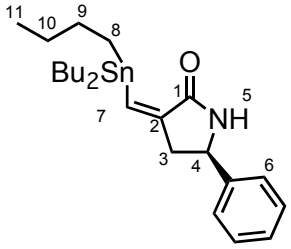


E isomer: (R_f = 0.55, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.75-1.00 (m, 15H, H-8, 11), 1.20-1.34 (m, 6H, H-10), 1.38-1.52 (m, 6H, H-9), 2.58-2.68 (m, 1H, H-3), 3.20-3.30 (m, 1H, H-3), 4.72 (q, *J* = 3.7 Hz 1H, H-4), 5.96 (bs, 1H, H-5), 7.20 (s, H-7), 7.23-7.40 (m, 5H, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.69 (C-8), 13.60 (C-11), 27.22 (C-10), 29.07 (C-9), 39.20 (C-3), 54.32 (C-4), 125.78 (C-6), 127.98 (C-6), 128.94 (C-6), 134.84 (C-7), 142.9 (C-6), 146.23 (C-2), 169.12 (C-1); IR (neat) 1685, 1623, EIMS, *m/z* (rel intensity) 406 (M^+-C_4H_9, 100), 292 (59); HRMS calcd for $C_{19}H_{28}NOSn$ (M^+-C_4H_9) 406.1193, found 406.1195.

Z isomer: (R_f = 0.80, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78-0.96 (m, 15H, H-8, 11), 1.18-1.34 (m, 6H, H-10), 1.34-1.54 (m, 6H, H-9), 2.70 (ddd, *J* = 17.0, 4.6, 2.3 Hz, 1H, H-3), 3.32 (ddd, *J* = 17.0, 4.6, 2.3 Hz, 1H, H-3), 4.74 (q, *J* = 3.7 Hz, 1H, H-4), 6.56 (s, *J* ^{1}H-Sn = 60.5 Hz, 1H, H-7), 7.22-7.40 (m, 5H, H-6), 8.00 (bs, 1H, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.49 (*J* ^{13}C-Sn = 354.1 Hz, C-8), 13.75 (C-11), 27.31 (*J* ^{13}C-Sn = 56.6 Hz, C-10), 29.20 (*J* ^{13}C-Sn = 20.2 Hz, C-9), 39.52 (C-3), 54.53 (C-4), 125.63 (C-2 or 6 or 7), 127.62 (C-2 or 6 or 7), 128.74 (C-2 or 6 or 7), 138.56 (C-2 or 6 or 7), 143.16 (C-2 or 6 or 7), 144.31 (C-2 or 6 or 7), 171.96 (C-1); IR (neat) 1689, 1621; EIMS, *m/z* (rel intensity) 406 (M^+-C_4H_9, 100), 292 (59); HRMS calcd for $C_{19}H_{28}NOSn$ (M^+-C_4H_9) 406.1193, found

406.1195.

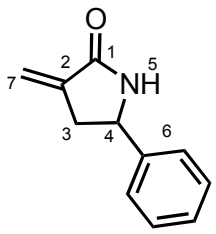
(*R*)-5-Phenyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (2g).



E isomer: colorless oil. ^{1}H-NMR, ^{13}C-NMR, IR and EIMS were identical with those of (*S*)-5-phenyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (**2f**); HRMS calcd for $C_{19}H_{28}NOSn$ (M^{+}-C_4H_9) 406.1193, found 406.1196.

Z isomer: colorless oil. ^{1}H-NMR, ^{13}C-NMR, IR and EIMS were identical with those of (*S*)-5-phenyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (**2f**); HRMS calcd for $C_{19}H_{28}NOSn$ (M^{+}-C_4H_9) 406.1193, found 406.1197.

3-Methylene-5-phenyl-2-pyrrolidine (3g)

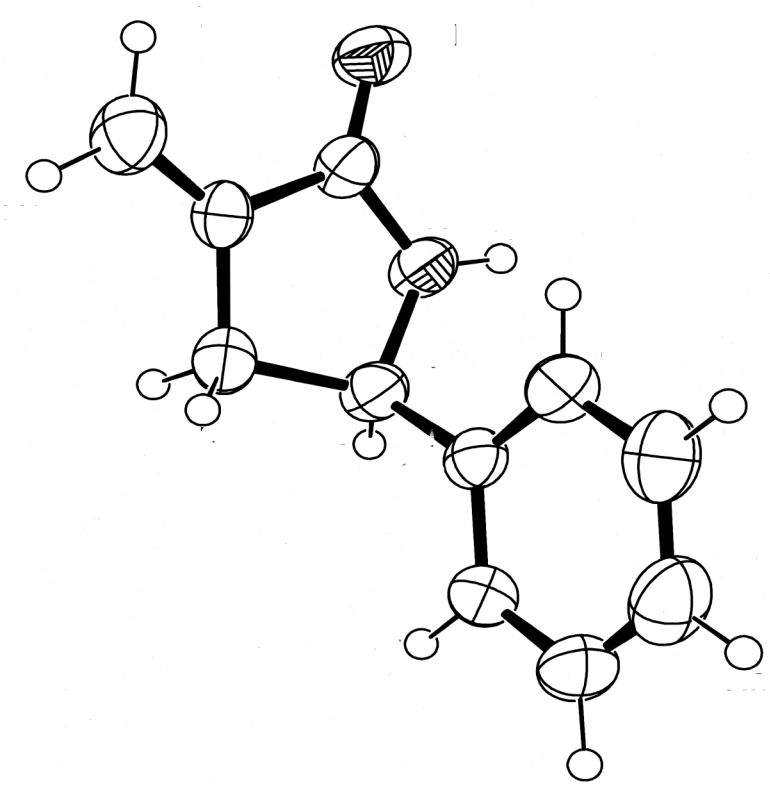


Protodestannylation of **2g** leading to 3-methylene-5-phenyl-2-pyrrolidine (**3g**) was carried out. The optical yield was estimated by HPLC analysis using a chiral column.

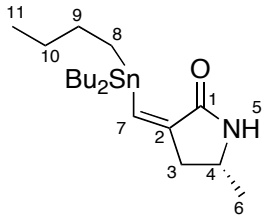
(R_f = 0.15, hexane/EtOAc = 1/1), white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.60-2.69 (m, 1H, H-3), 3.22-3.34 (m, 1H, H-3), 4.73 (m, 1H, H-4), 5.34 (s, 1H, H-7), 6.00 (s, 1H, H-7), 7.22-7.38 (m, 5H, H-6), 7.49 (bs, 1H, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.71 (C-3), 54.78 (C-4), 116.32 (C-2 or 6or 7), 125.58 (C-2 or 6 or 7), 127.82 (C-2 or 6 or 7), 128.83 (C-2 or 6 or 7), 138.87 (C-2 or 6 or 7), 142.67 (C-2 or 6or 7), 171.01 (C-1); IR (KBr) 1656, 1591; 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; 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, 31.4 min, retention time for (R)-isomer (**3g**) 26.5 min in 95% ee, retention time for (S)-isomer (**3f**) 31.4 min in 98% ee. m.p. 169-170 °C, $[\alpha]^{18}_{D}$ -10.0 (c 0.88, $CHCl_3$). It should be noted that R isomer has been already known.[6] However, there is discrepancy in spectral and physical data between their data and our data. This led us to examine X-ray analysis of **3g**, which well supported the structure of **3g**. 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, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, 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 **3g**.



(R)-5-Methyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (2h).

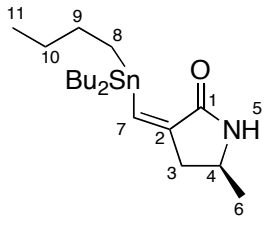


E isomer: (R_f = 0.13, hexane/EtOAc = 2/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80-1.08 (m, 15H, H-8, 11), 1.24 (d, J = 6.4 Hz,

3H, H-6), 1.25-1.40 (m, 6H, H-10), 1.41-1.60 (m, 6H, H-9), 2.32 (ddd, *J* = 16.5, 4.1, 2.7 Hz, 1H, H-3), 2.95 (ddd, J = 16.5, 7.3, 2.3 Hz, 1H, H-3), 3.72-3.84 (m, 1H, H-4), 6.82 (bs, 1H, H-5), 7.09 (s, *J* ^{1}H-Sn = 61.9 Hz, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.78 (*J* ^{13}C-Sn = 361.8 Hz, C-8), 13.73 (C-11), 23.21 (C-6), 27.36 (*J* ^{13}C-Sn = 57.6 Hz, C-10), 29.20 (*J* ^{13}C-Sn = 20.2 Hz, C-9), 37.21 (C-3), 46.33 (C-4), 133.71 (C-7), 147.34 (C-2), 168.92 (C-1); IR (neat) 1691, 1622, EIMS, *m/z* (rel intensity) 344 (M^+-C_4H_9, 100), 230 (53), 148 (9); 105 (10); HRMS calcd for $C_{14}H_{26}ONSn$ (M^+-C_4H_9) 344.1037, found 344.1034.

Z isomer: (R_f = 0.31, hexane/EtOAc = 2/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82-0.99 (m, 15H, H-8, 11), 1.23 (d, *J* = 6.4 Hz, 3H, H-6), 1.24-1.33 (m, 6H, H-10), 1.39-1.57 (m, 6H, H-9), 2.33 (ddd, *J* = 17.0, 4.1, 2.3 Hz, 1H, H-3), 3.00 (ddd, J = 17.0, 7.8, 2.3 Hz, 1H, H-3), 3.68-3.80 (m, 1H, H-4), 6.47 (s, *J* ^{1}H-Sn = 61.9 Hz, H-7), 7.64 (bs, 1H, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.54 (C-8), 13.74 (C-11), 23.02 (C-6), 27.38 (C-10), 29.27 (C-9), 37.64 (C-3), 46.52 (C-4), 137.22 (C-7), 145.46 (C-2), 171.52 (C-1); IR (neat) 1693, 1624, EIMS, *m/z* (rel intensity) 344 (M^+-C_4H_9, 29), 288 (14), 230 (44), 149 (17); HRMS calcd for $C_{14}H_{26}ONSn$ (M^+-C_4H_9) 344.1037, found 344.1038.

(S)-5-Methyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (2i).

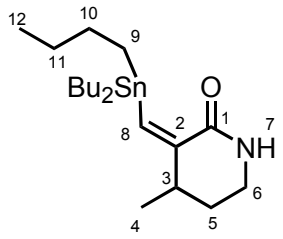


E isomer: colorless oil. ^{1}H-NMR, ^{13}C-NMR, IR and EIMS were identical with those of (R)-5-methyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (**2h**); HRMS calcd for $C_{14}H_{26}ONSn$ (M^+-C_4H_9) 344.1037, found 344.1037.

Z isomer: colorless oil. ^{1}H-NMR, ^{13}C-NMR, IR and EIMS were identical with those of (R)-5-methyl-3-[(tributylstannanyl)methylene]-2-pyrrolidinone (**2h**); HRMS calcd for

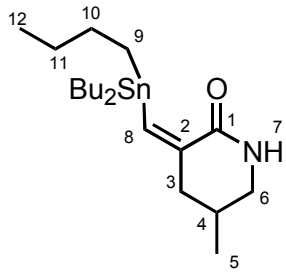
$C_{14}H_{26}ONSn$ (M^+-C_4H_9) 344.1037, found 344.1037.

4-Methyl-3-[t(ributylstannanyl)methylene]-2-piperidinone (2j).



(R_f = 0.75, hexane/EtOAc = 2/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76-0.94 (m, 15H, H-9,12), 1.18 (d, *J* = 6.9 Hz, 3H, H-4), 1.22-1.33 (m, 6H, H-11), 1.40-1.51 (m, 6H, H-10), 1.56-1.64 (m, 1H, H-5), 1.87-1.95 (m, 1H, H-5), 2.61-2.71 (m, 1H, H-3), 3.30-3.44 (m, 1H, H-6), 6.52 (s, *J* ^{1}H-Sn = 70.1 Hz, 1H, H-8), 7.65 (bs, 1H, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.10 (*J* ^{13}C-Sn = 359.9 Hz, C-9), 13.90 (C-12), 19.71 (C-4), 27.56 (*J* ^{13}C-Sn = 31.7 Hz, C-11), 29.43 (C-10), 30.72 (C-3or5), 35.87 (C-3or5), 40.05 (C-6), 143.84 (C-8), 148.37 (C-2), 167.15 (C-1); IR (neat) 1661, 1582; EIMS, *m/z* (rel intensity) 358 (M^+- C_4H_9, 65), 269 (44), 203 (22); HRMS calcd for $C_{15}H_{28}NOSn$ (M^+-C_4H_9) 358.1192, found 358.1194.

5-Methyl-3-[(tributylstannanyl)methylene]-2-piperidinone (2k).

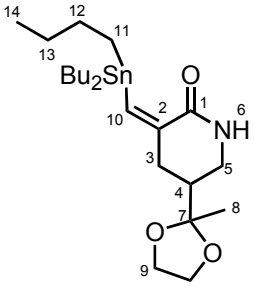


E isomer: (R_f = 0.10, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82-0.98 (m, 15H, H-9,12), 1.02 (d, *J* = 6.5 Hz, 3H, H-5), 1.22-1.36 (m, 6H, H-11), 1.40-1.56 (m, 6H, H-10), 2.02-2.14 (m, 1H, H-3), 2.22-2.34 (m, 1H, H-3), 2.50-2.62 (m, 1H, H-4), 3.00-3.10 (m, 1H, H-6), 3.30-3.40 (m, 1H, H-6), 5.93 (bs, 1H, H-7), 7.44 (s, *J* ^{1}H-Sn = 60.5 Hz, 1H, H-8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.20 (C-9), 13.73 (C-12), 18.38 (C-5), 27.38 (C-11), 29.23 (C-10), 29.67 (C-4), 40.52 (C-3), 49.46 (C-6), 141.83 (C-8), 143.56 (C-2), 164.72 (C-1); IR (neat) 1661, 1588; EIMS, *m/z* (rel intensity) 358 (M^+- C_4H_9, 30), 244 (14); HRMS calcd for $C_{15}H_{28}NOSn$

(M^+-C_4H_9) 358.1193, found 358.1192.

Z isomer: (R_f = 0.55, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76-0.93 (m, 15H, H-9,12), 0.99 (d, *J* = 6.9 Hz, 3H, H-5), 1.21-1.34 (m, 6H, H-11), 1.38-1.54 (m, 6H, H-10), 1.98-2.12 (m, 1H, H-3), 2.26-2.38 (m, 1H, H-3), 2.63-2.74 (m, 1H, H-4), 2.95-3.06 (m, 1H, H-6), 3.26-3.37 (m, 1H, H-6), 6.45 (s, *J* ^{1}H-Sn =70.1 Hz, 1H, H-8), 7.50 (bs, 1H, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.98 (*J* ^{13}C-Sn = 352.2 Hz, C-9), 13.88 (C-12), 18.22 (C-5), 27.56 (C-11), 29.38 (C-4or10), 29.45 (C-4or10), 41.47 (C-3), 49.37 (C-6), 142.36 (C-8), 146.34 (C-2), 166.97 (C-1); IR (neat) 1661, 1588; EIMS, *m/z* (rel intensity) 358 (M^+-Bu, 45), 244 (19); HRMS calcd for $C_{15}H_{28}NOSn$ (M^+-C_4H_9) 358.1193, found 358.1193.

5-(2-Methyl-[1,3]dioxolan-2-yl)-3-[(tributylstannanyl)methylene]-2-piperidinone (2l).

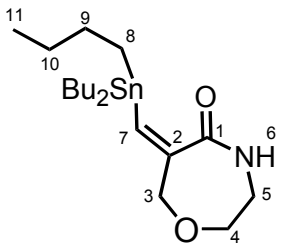


E isomer: (R_f = 0.08, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84-1.00 (m, 15H, H-11,14), 1.25-1.35 (m, 9H, H-8,13), 1.45-1.54 (m, 6H, H-12), 2.10-2.26 (m, 1H, H-4), 2.40-2.52 (m, 1H, H-3), 2.66-2.76 (m, 1H, H-3), 3.26-3.34 (m, 1H, H-5), 3.40-3.47 (m, 1H, H-5), 3.85-4.02 (m, 4H, H-9), 5.83 (bs, 1H, H-6), 7.44 (s, *J* ^{1}H-Sn = 59.1 Hz, 1H, H-10); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.17 (C-11), 13.77 (C-14), 21.80 (C-8), 29.23 (C-12), 33.53 (C-3), 43.32 (C-4or5), 43.41 (C-4or5), 65.02 (C-9), 109.56 (C-7), 142.14 (C-10), 143.36 (C-2), 164.65 (C-1); IR (neat) 1663, 1592; EIMS, *m/z* (rel intensity) 430 (M^+-C_4H_9, 9), 386 (14); HRMS calcd for $C_{18}H_{32}NO_3Sn$ (M^+-C_4H_9) 430.1405, found 430.1407.

Z isomer: (R_f = 0.73, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76-0.92 (m, 15H, H-11,14), 1.22-1.34 (m, 9H, H-8,13), 1.38-1.52 (m, 6H, H-12), 2.12-2.22 (m, 1H, H-4), 2.47-2.58 (m, 1H, H-3), 2.76-2.84 (m, 1H, H-3), 3.22-3.30 (m, 1H, H-5),

3.38-3.46 (m, 1H, H-5), 3.84-4.00 (m, 4H, H-9), 6.50 (s, J ^{1}H-Sn = 68.7 Hz, 1H, H-10) 7.40 (bs, 1H, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.94 (J ^{13}C-Sn = 360.4 Hz, C-11), 13.89 (C-14), 21.72 (C-8), 27.55 (J ^{13}C-Sn = 56.6 Hz, C-12), 29.43 (J ^{13}C-Sn = 19.2 Hz, C-13), 34.44 (C-3), 42.98 (C-4or5), 43.27 (C-4or5), 64.95 (C-9), 109.65 (C-10), 141.89 (C-7), 146.83 (C-2), 166.85 (C-1); IR (neat) 1662, 1588; EIMS, *m/z* (rel intensity) 430 (M^+-C_4H_9, 15), 272 (4); HRMS calcd for $C_{18}H_{32}NO_3Sn$ (M^+-C_4H_9) 430.1405, found 430.1404.

6-[(Tributylstannanyl)methylene]-[1,4]oxazepan-5-one (2n).



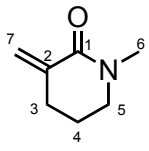
E isomer: (R_f = 0.15, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82-1.08 (m, 15H, H-8,11), 1.20-1.34 (m, 6H, H-10), 1.40-1.56 (m, 6H, H-9), 3.31 (q, J = 4.0 Hz, 2H, H-5), 3.78 (t, J = 4.6 Hz, 2H, H-4), 4.14 (s, 2H, H-3), 6.48 (bs, 1H, H-6), 7.12 (s, J ^{1}H-Sn = 52.7 Hz, 1H, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.53 (C-8), 13.74 (C-11), 27.33 (C-10), 29.11 (C-9), 44.20 (C-3), 70.15 (C-5), 71.31 (C-4), 145.84 (C-7), 150.96 (C-2), 174.63 (C-1); IR (neat) 1653, 1579; EIMS, *m/z* (rel intensity) 360 (M^+-C_4H_9, 8), 246 (4); HRMS calcd for $C_{12}H_{26}NO_2Sn$ (M^+-C_4H_9) 360.0985, found 360.0986.

Z isomer: (R_f = 0.58, hexane/EtOAc = 1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80-0.92 (m, 15H, H-8,11), 1.20-1.32 (m, 6H, H-10), 1.38-1.54 (m, 6H, H-9), 3.32 (q, J = 4.6 Hz, 2H, H-5), 3.79 (t, J = 4.6 Hz, 2H, H-4), 4.25 (s, 2H, H-3), 6.73 (s, J = ^{1}H-Sn = 60.1 Hz, 1H, H-7), 7.47 (bs, 1H, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.28 (J ^{13}C-Sn = 353.7 Hz, C-8), 13.84 (C-11), 27.45 (J ^{13}C-Sn = 58.5 Hz, C-10), 29.26 (J ^{13}C-Sn = 20.2 Hz, C-9), 43.80 (C-3), 70.06 (C-5), 72.74 (C-4), 149.64 (C-7), 150.13 (C-2), 174.58 (C-1); IR (neat) 1650, 1591; EIMS, *m/z* (rel intensity) 360 (M^+-C_4H_9, 8), 246 (3); HRMS calcd for $C_{14}H_{26}NO_2Sn$ (M^+-C_4H_9) 360.0985, found 360.0985.

Procedure for the carbonylative S_Hi reaction coupled with the subsequent protodestannylation of *N*-methyl-*N*-(1-phenylethyl)-4-pentynyl-1-amine (1o).

A magnetic stirring bar, AIBN (31.6 mg, 0.19 mmol), benzene (100 mL), Bu_3SnH (457.1 mg, 1.57 mmol), and *N*-methyl-*N*-(1-phenylethyl)-4-pentyn-1-amine (**1o**) (225.4 mg, 1.12 mmol) were placed in a 200-mL stainless autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 93 atm of CO and then heated 90 °C for 4 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. To the residue dissolved in methanol (7 mL) was added dropwise TMSCl (1.5 mL) at room temperatuere and the reaction mixture was stirred for 10 min. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give 1-methyl-3-methylene-piperidin-2-one (**2o**) (120.9 mg, 86%).

1-Methyl-3-methylene-piperidin-2-one (**2o**)



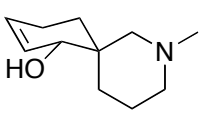
Colorless oil. (R_f = 0.2, Hexane/EtOAc = 1/1), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.88 (quint, *J* = 6.0 Hz, 2H, H-4), 2.55 (t, *J* = 6.4 Hz, 2H, H-3), 3.01 (s, 3H, H-6), 3.37 (t, *J* = 6.0 Hz, 2H, H-5), 5.24 (s, 1H, H-7), 6.17 (s, 1H, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.07 (C-4), 30.11 (C-3), 35.09(C-5), 50.30 (C-6), 120.90 (C-2), 137.82 (C-7), 164.35 (C-1); IR (neat) 1657, 1613; EIMS, *m/z* (rel intensity) 125 (M^+, 100), 96 (17), 82 (18), 69 (24), 54 (100); HRMS calcd for $C_7H_{11}NO$ (M^+) 125.0841, found 125.0848

Procedure for the synthesis of (±)-sibirine from 1-methyl-3-methylene-piperidin-2-one (2o)

A mixture of 1-methyl-3-methylene-piperidin-2-one (130 mg, 1 mmol) and 1-(trimethylsilyloxy)-1,3-butadiene (4 mL, *E*/*Z* = 94/6) was stirred for 24 h at reflux. After the

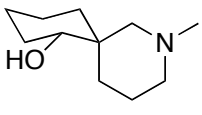
remained diene was removed, the residue was purified by flash chromatography on silica gel (hexane/EtOAc = 2/1) to give **4** (303.1 mg, R_f = 0.3). Further purification using preparative HPLC gave the desired spirocyclic compound **4** (132.6 mg, 0.5 mmol, 50%). The spirocyclic compound **4** (0.5 mmol) was added to a suspension of $LiAlH_4$ (19 mg, 1.0 equiv) in ether (5 mL). The mixture was stirred for 1 h. The reaction was then quenched with water and the resulting mixture extracted with ether. The organic layer was treated with acid/base workup and the desired compound **5** was obtained. (60.8 mg, 0.34 mmol, 68%). The compound **5** (60.8 mg, 0.34 mmol) was added to the suspension of $Pd(OH)_2/C$ (3 mg) in methanol (3 mL). The mixture was stirred for 20 h at room temperature under hydrogen atmosphere. The reaction mixture was filtered through Celite. After removal of the solvent, the residue was dissolved with ether. The ethereal solution of the mixture was treated with acid/base workup to give the desired alkaloid (±)-sibirine (37.4 mg, 60%).

7-Hydroxy-2-azaspiro[5,5]undec-8-ene (5)



Colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96-1.10 (m, 1H), 1.20-1.40 (m, 3H), 1.48-1.62 (m, 1H), 1.85-2.20 (m, 6H), 2.20-2.30 (m, 3H), 2.45-2.60 (m, 1H), 2.60-2.80 (m, 1H), 4.15-4.30 (m, 1H), 5.60-5.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.07, 22.78, 27.34, 30.76, 35.79, 46.73, 56.57, 67.83, 75.82, 126.88, 129.67; IR (neat) 1451, 1650, 2789, 2849, 2936, 3402; EIMS, *m/z* (rel intensity) 181 (M^+, 46), 138 (20), 112 (33), 91 (17), 70 (17), 58 (100); HRMS calcd for $C_{11}H_{19}NO$ (M^+) 181.1467, found 181.1464.

(±)-Sibirine (6)



Colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80-1.00 (m, 2H), 1.10-1.28 (m, 2H), 1.32-1.40 (m, 2H), 1.46-1.55 (m, 2H), 1.66-1.76 (m, 2H), 1.82-1.92 (m, 2H), 2.08-2.16 (m, 2H), 2.10 (s, 3H), 2.57 (d, *J* = 11.0 Hz, 1H), 2.74-2.84 (m, 1H), 3.59 (dd, *J* = 3.7, 11.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.33, 23.08, 24.35, 27.66, 29.44, 37.05, 37.15, 46.46, 56.36, 69.95, 80.51; IR (neat) 1450, 2788, 2859, 2931, 3406; EIMS, *m/z* (rel intensity) 183 (M^+, 19), 155 (9), 140 (25), 98 (22), 71 (28), 57 (100); HRMS calcd for $C_{11}H_{21}NO$ (M^+) 183.1623, found 183.1623.

These data are identical with those reported for (-)-sibirine.[6]

References

1 PROCESS-AUTO. *Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer*, Rigaku Corporation: Tokyo, Japan, 1998.

2 Higashi, T. *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation*; Rigaku Corporation: Tokyo, Japan, 1998.

3 Sheldrick, G. M. *SHELX97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

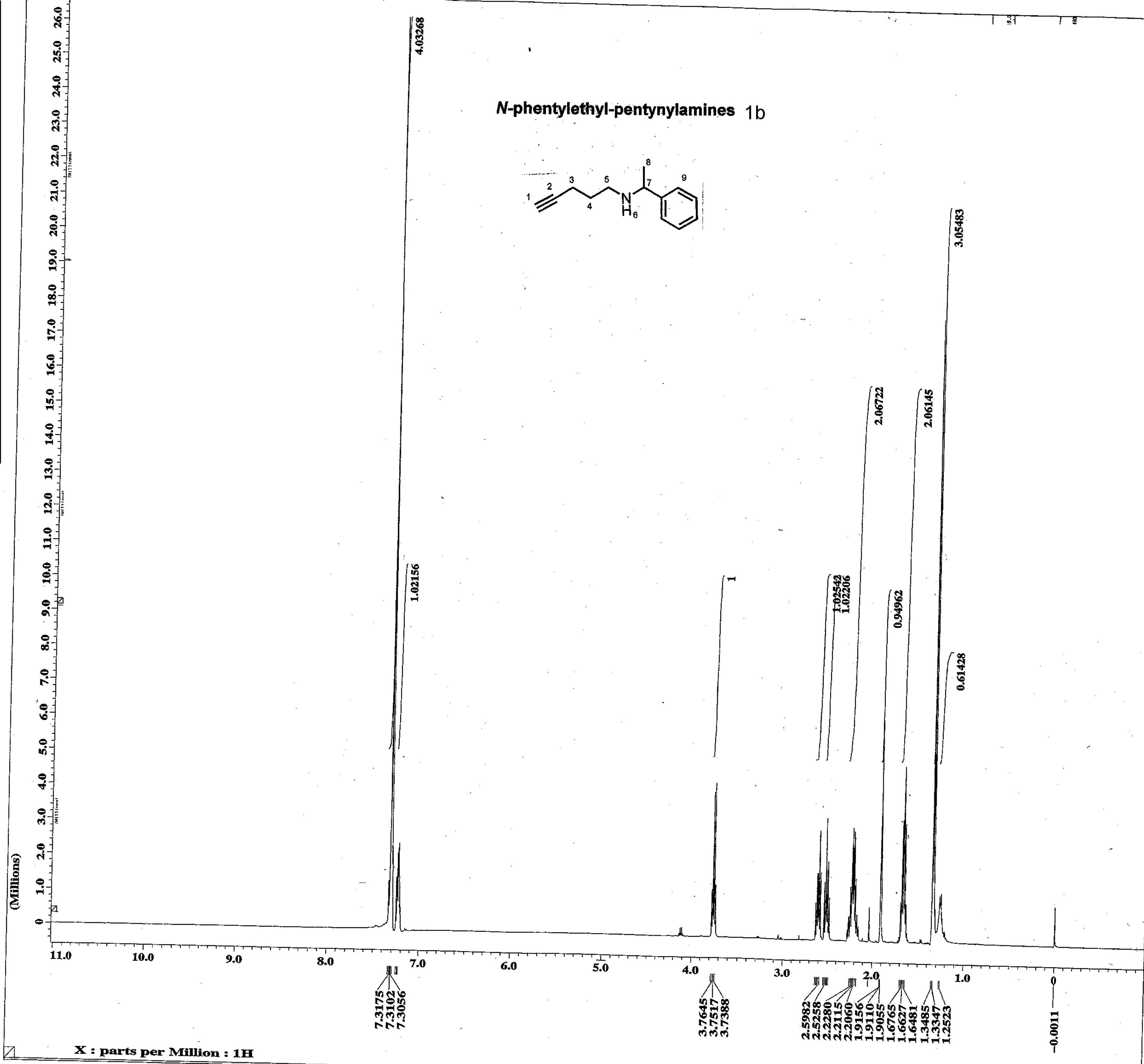
4 Tojino, M.; Uenoyama, Y.; Fukuyama, T.; Ryu, I. *Chem. Commun*. **2004**, 2482.

5 For these compounds, some ^{13}C-NMR signal corresponding to the respective diastereomers are not well resolved due to overlapping.

6 (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.

7 Koreeda, M.; Wang, Y.; Zhang, L. *Org. Lett*. **2002**, *4*, 3329.

N-phentylethyl-pentynylamines 1b



JEOL

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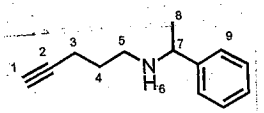
N-phentylethyl-pentynylamines 1b

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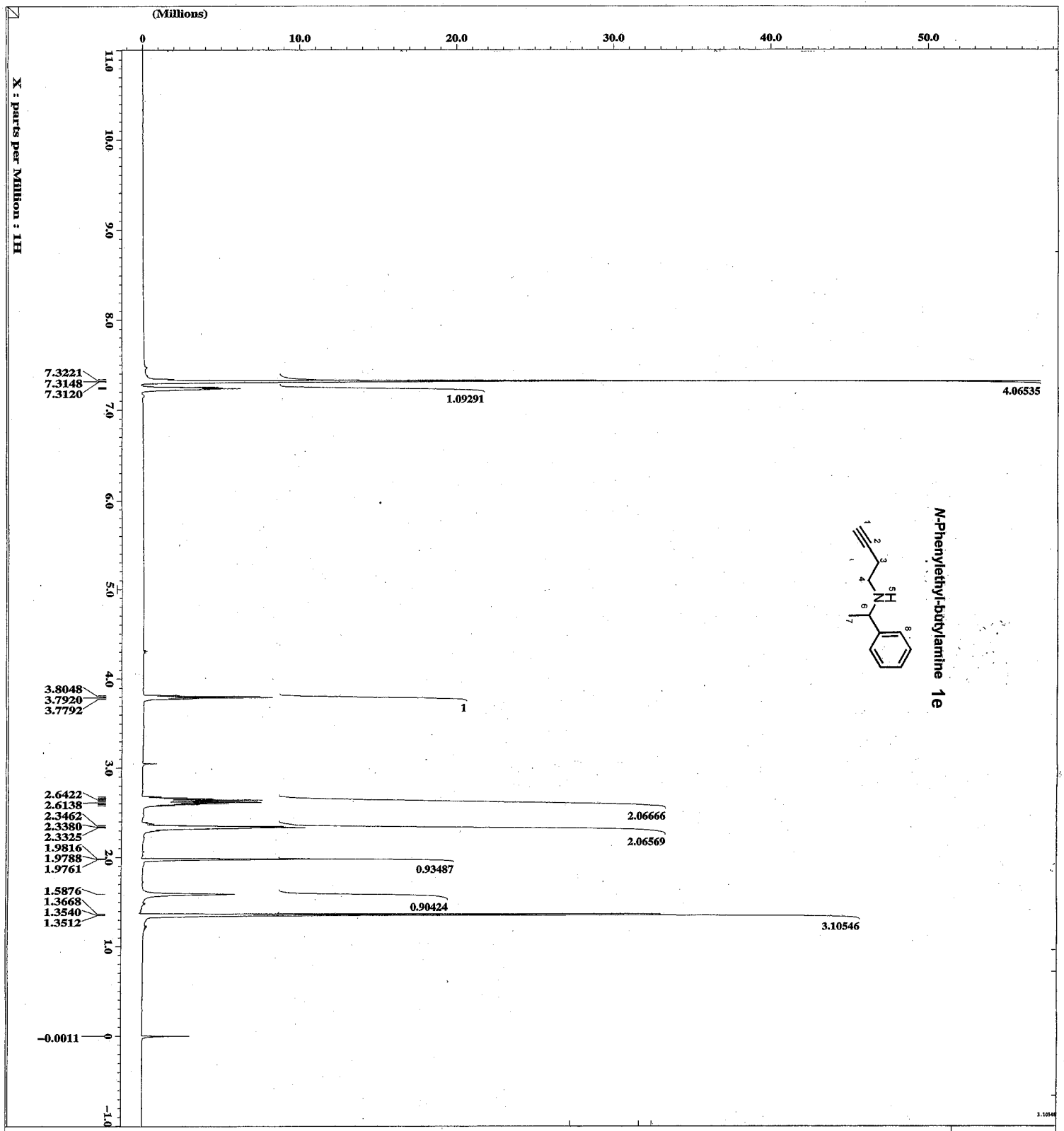


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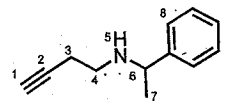
N-Phenylethyl-butylamine **1e**

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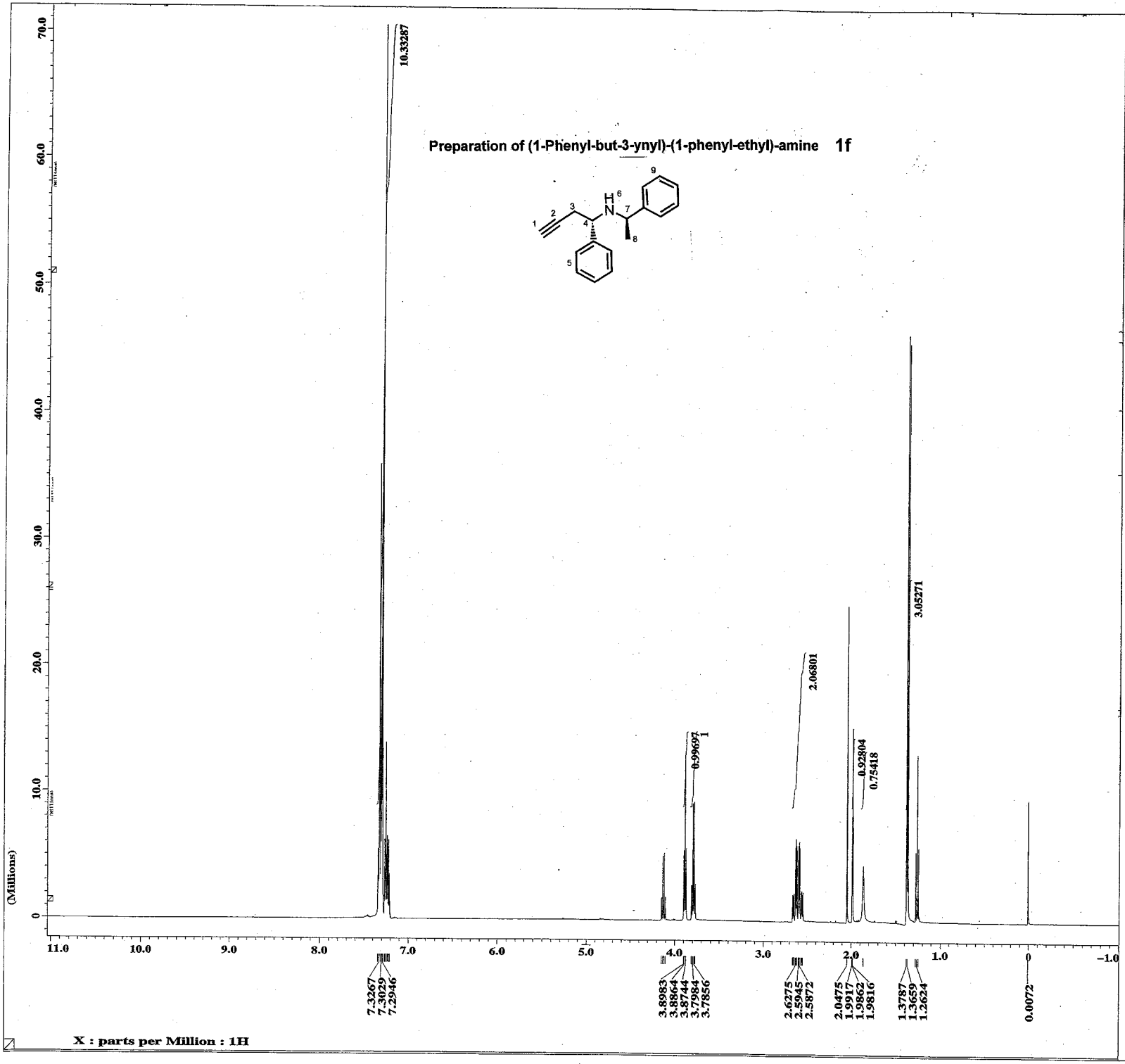

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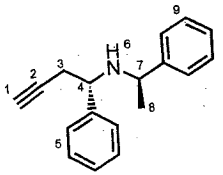
Preparation of (1-Phenyl-but-3-ynyl)-(1-phenyl-ethyl)-amine **1f**

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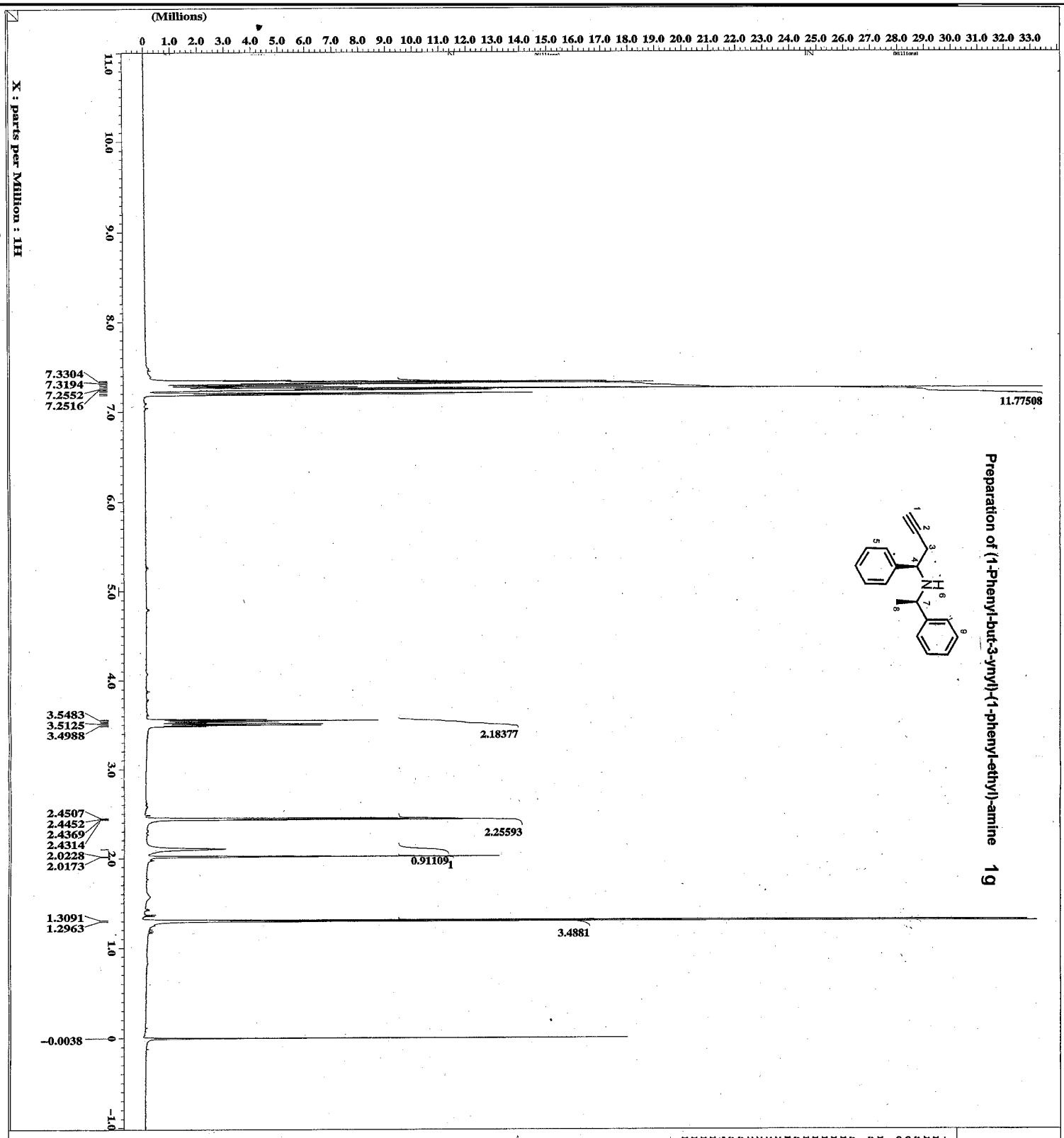

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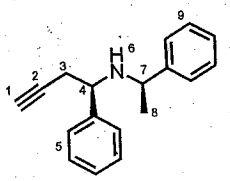
Preparation of (1-Phenyl-but-3-ynyl)-(1-phenyl-ethyl)-amine 1g



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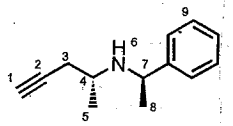
(1-Methyl-but-3-ynyl)-(1-phenyl-ethyl)-amine 1h



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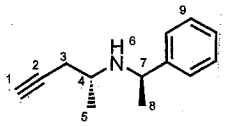
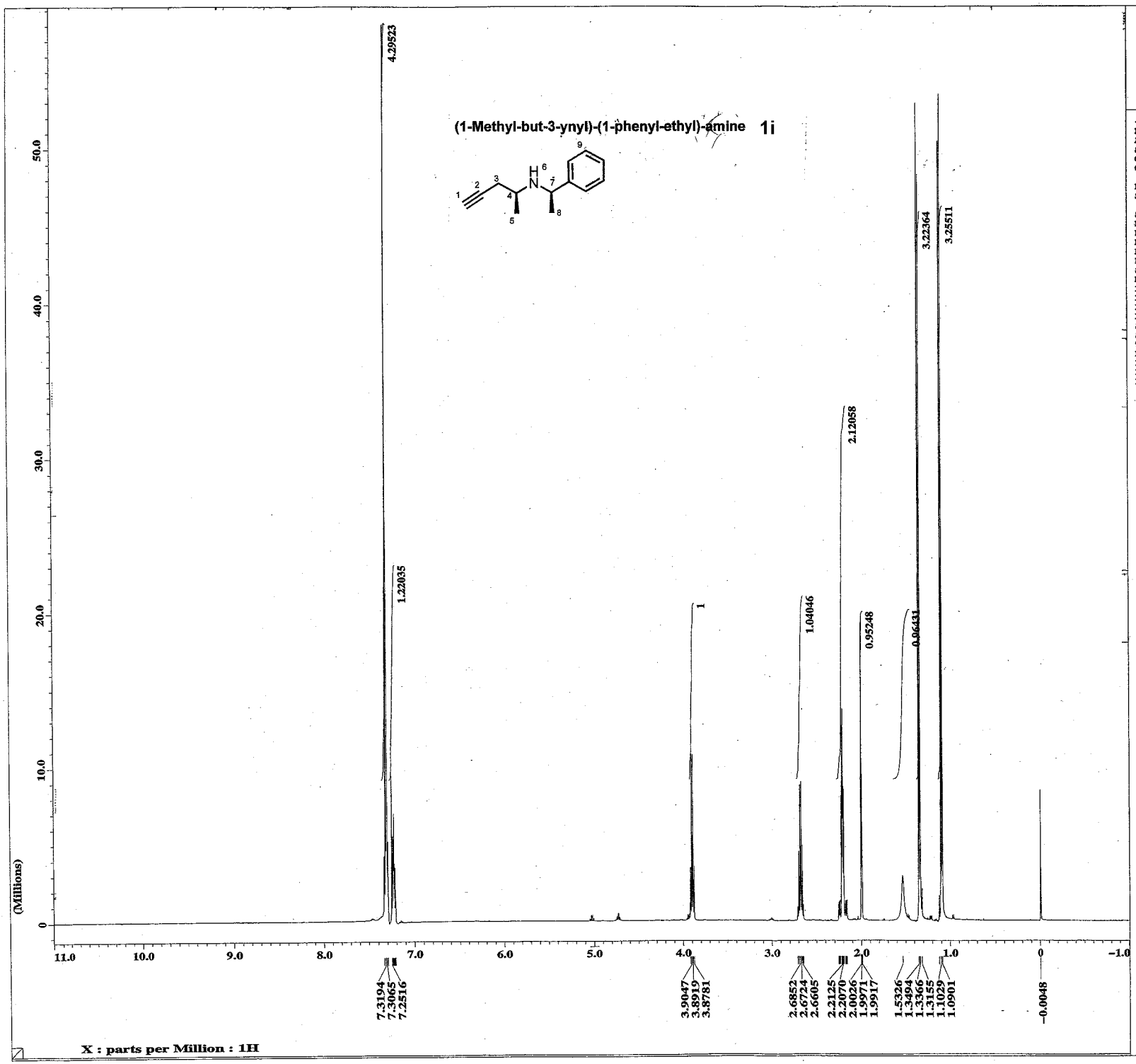
Creation Date	= 13-APR-2005 14:01:08
Revision Date	= 14-APR-2005 15:46:28
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 0[Hz]
Temp_get	= 22.7[dC]
Recvr_gain	= 24
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]

(1-Methyl-but-3-ynyl)-(1-phenyl-ethyl)-amine 1h



JEOL

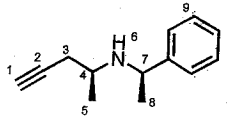
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.109
Author          =
Sample ID       = dai
Content         = Single Pulse with Broad
Creation Date   = 11-NOV-2004 18:09:49

Revision Date   = 12-NOV-2004 17:04:57
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 35
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        = 14[Hz]
Temp_set        = 22.9[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```



---- ACQUISITION PARAMETERS ----

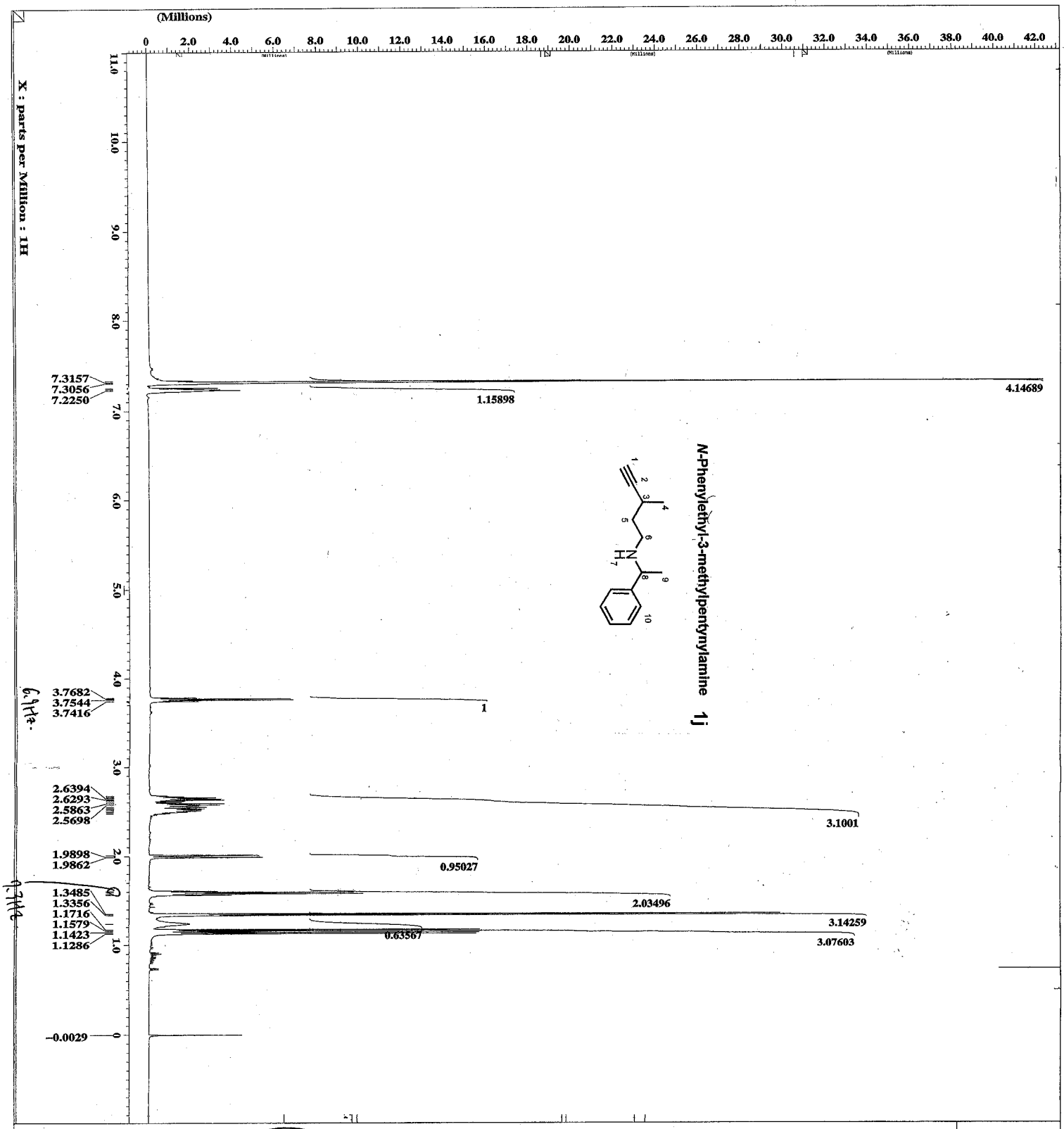
File Name	= 1d_spectrum.4618
Author	=
Sample ID	= 11
Content	= Single Pulse Experiment
Creation Date	= 13-APR-2005 13:56:28
Revision Date	= 14-APR-2005 15:40:50
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 14[Hz]
Temp_get	= 22.3[dC]
Recvr_gain	= 23
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]

(1-Methyl-but-3-ynyl)-(1-phenyl-ethyl)-amine 1i

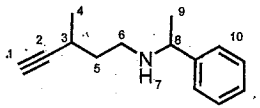


---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.111
Author	=
Sample ID	= syou
Content	= Single Pulse with Broad
Creation Date	= 11-NOV-2004 18:14:57
Revision Date	= 12-NOV-2004 17:09:26
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 45
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	= 22.8[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]

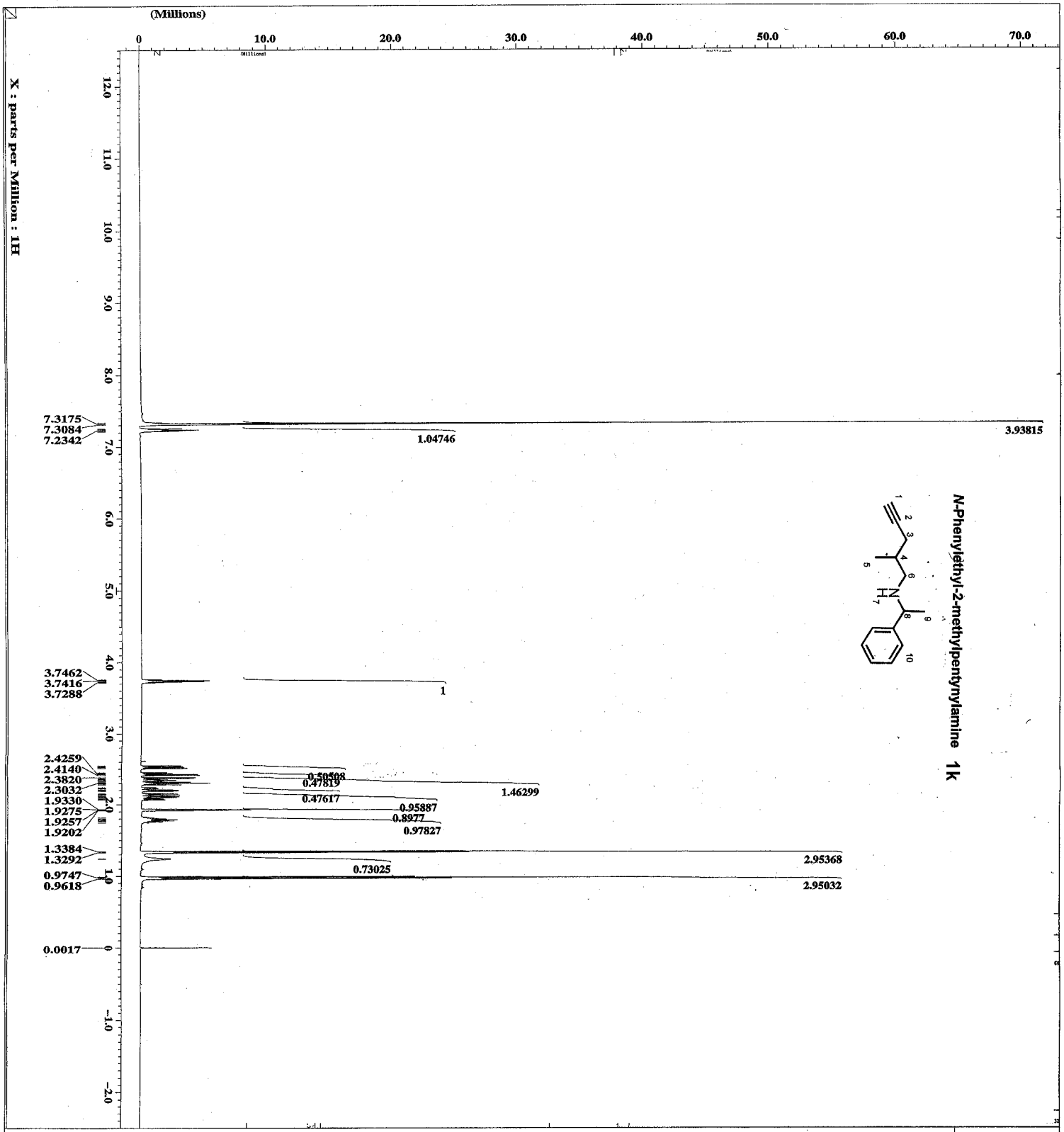

(Millions)
X : parts per Million : 1H
7.3157
7.3056
7.2250
1.15898
4.14689
N-Phenylethyl-3-methylpentynylamine 1j
3.7682
3.7544
3.7416
1
2.6394
2.6293
2.5863
2.5698
3.1001
1.9898
1.9862
0.95027
1.3485
1.3356
1.1716
1.1579
1.1423
1.1286
2.03496
3.14259
0.63567
3.07603
-0.0029
---- ACQUISITION PARAMETERS ----
File Name = id_spectrum.4631
Author =
Sample ID = a
Content = Single Pulse Experiment
Creation Date = 13-APR-2005 17:07:41
Revision Date = 14-APR-2005 18:52:19
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = ID COMPLEX
Dimensions = 2
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[KHz]
Solvent = CHLOROFORM-D
Spin_set = 17[Hz]
Temp_set = 22.4[dc]
Recvr_gain = 21.7473579[%]
Field_strength = 11.74[T]
Filter_mode = BOXCAR1H
Filter_width = 3.75139936[KHz]

N-Phenylethyl-3-methylpentynylamine **1j**

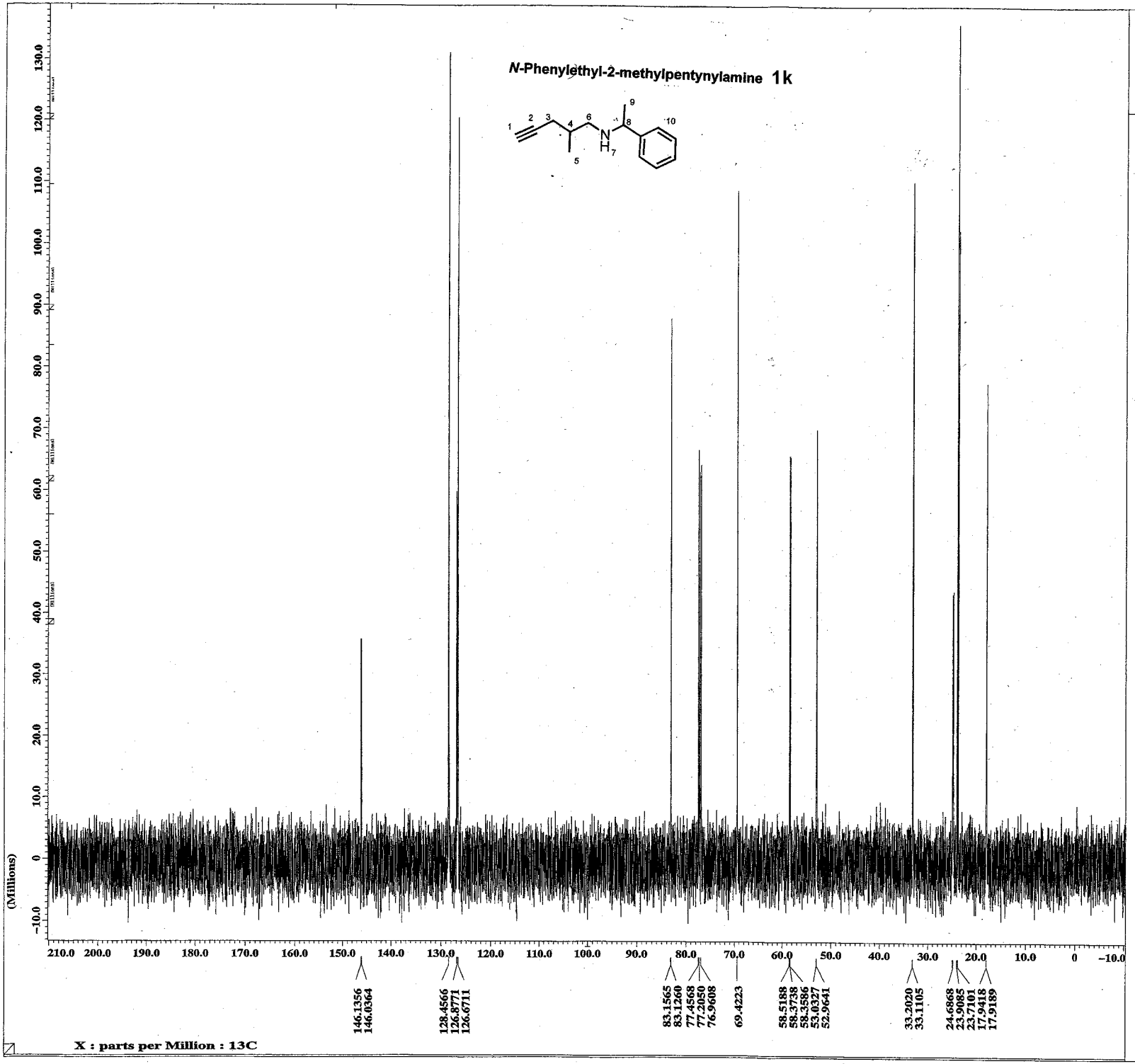


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_13c_spectrum.1283
Author           =
Sample ID        = a
Content          = Single Pulse with Broad
Creation Date    = 13-APR-2005 17:27:46

Revision Date    = 14-APR-2005 19:11:22
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 13C
Dim Size         = 32768
Dim Units        = [ppm]
Scans            = 67
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         = 16[Hz]
Temp_set         = 23.1[dC]
Recvr_gain       = 30
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 15.72066221[kHz]
```

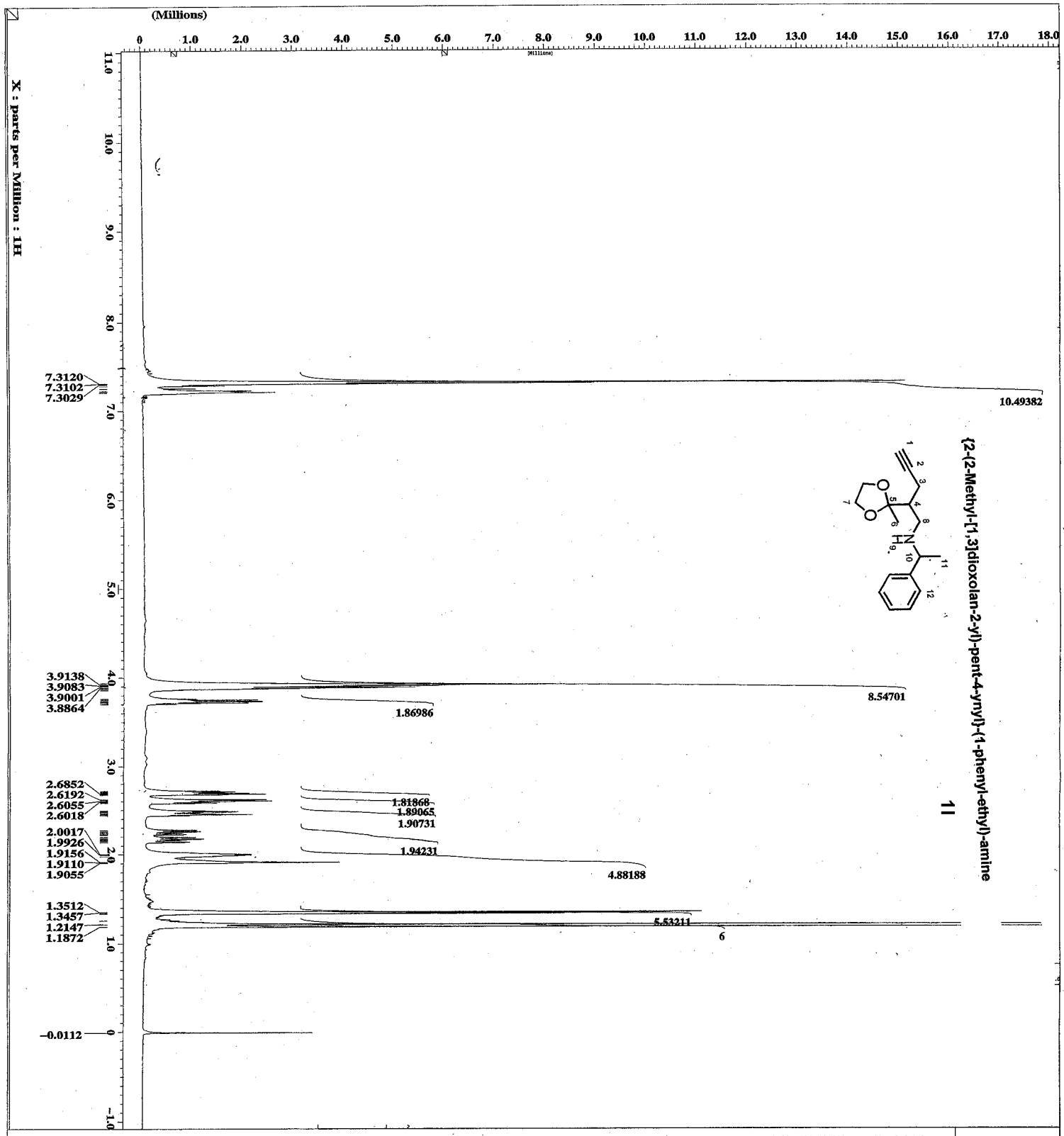



```
---- ACQUISITION PARAMETERS ----
File Name          = id_spectrum.4634
Author             =
Sample ID          = a
Content            = Single Pulse Experiment
Creation Date      = 13-APR-2005 17:37:56
Revision Date      = 14-APR-2005 19:20:34
Spec Site          = ECP500

Spec Type          = DELTA NMR
Data Format        = 1D COMPLEX
Dimensions         = 2
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Scans              = 8
Mod_return         = 1
X_domain           = 1H
X_offset           = 5[ppm]
X_freq             = 500.162416O2[MHz]
X_sweep            = 7.507507S1[kHz]
Solvent            = CHLOROFORM-D
Spin_set           = 16[Hz]
Temp_set           = 22.3[dC]
Recvr_gain         = 19
Field_strength     = 11.74735791[T]
Filter_mode        = BOTTOMWIDTH
Filter_width       = 3.751139336[kHz]
```



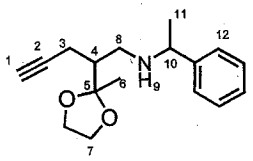
---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.1284
Author	=
Sample ID	= a
Content	= Single Pulse with Broad
Creation Date	= 13-APR-2005 17:45:14
Revision Date	= 14-APR-2005 19:26:53
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 41
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	= 17[Hz]
Temp_get	= 23.2[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]




```
---- ACQUISITION PARAMETERS ----
File Name          = id_spectrum.4635
Author             =
Sample ID          = a
Comment            = Single Pulse Experiment
Creation Date      = 13-APR-2005 18:05:20
Revision Date      = 14-APR-2005 19:50:06
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 2D COMPLEX
Dimensions         = 2
Dim Titles         = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Scans              = 8
Mod_return         = 1
X_domain           = 1H
X_offset           = 5[ppm]
X_freq             = 500.16241602[MHz]
X_sweep            = 7.50750751[kHz]
Solvent            = CHLOROFORM-D
Spin_set           = 13[Hz]
Temp_set           = 22.5[dC]
Recvr_gain         = 11
Field_strength     = 11.74735579[T]
Filter_mode        = SUPERGAUSS
Filter_width       = 3.75119936[MHz]
```

{2-(2-Methyl-[1,3]dioxolan-2-yl)-pent-4-ynyl}-(1-phenyl-ethyl)-amine 1l



JEOL

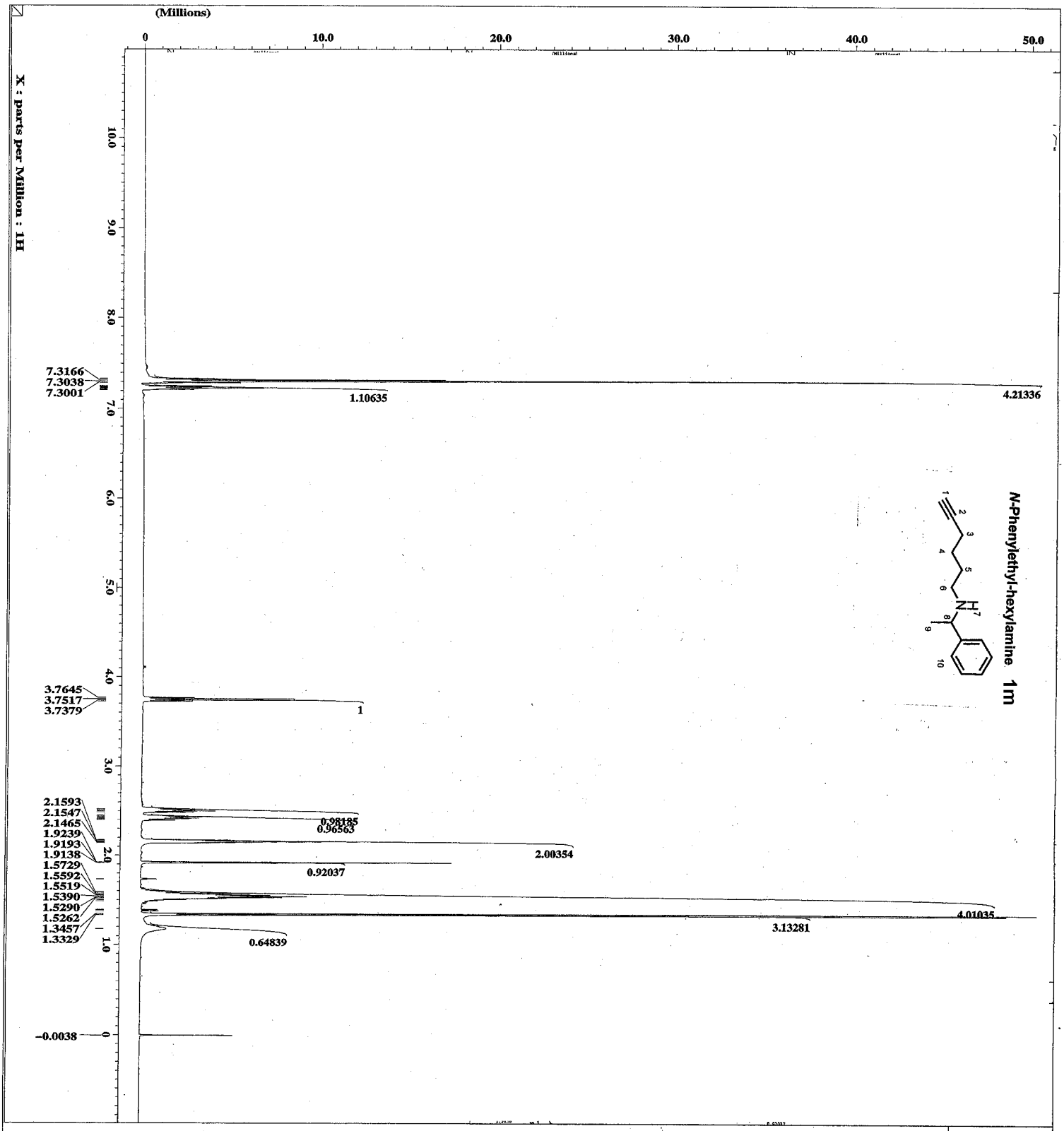
```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_13c_spectrum.1285
Author          =
Sample ID       = S#713071
Content         = Single Pulse with Broad
Creation Date   = 13-APR-2005 18:11:50

Revision Date   = 14-APR-2005 19:53:34
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 87
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        = 22.9[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

(Millions)

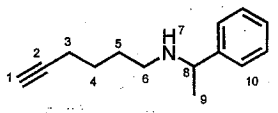
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

146.0745
145.9296
128.3803
126.7093
126.6559
111.3193
111.1591
83.4998
83.3701
77.4873
77.2202
76.9761
69.3383
64.6763
64.6382
64.6076
64.5237
58.5646
58.4501
47.8061
45.8757
45.6391
24.6258
24.6029
24.5723
18.2775
18.0944

X : parts per Million : 13C

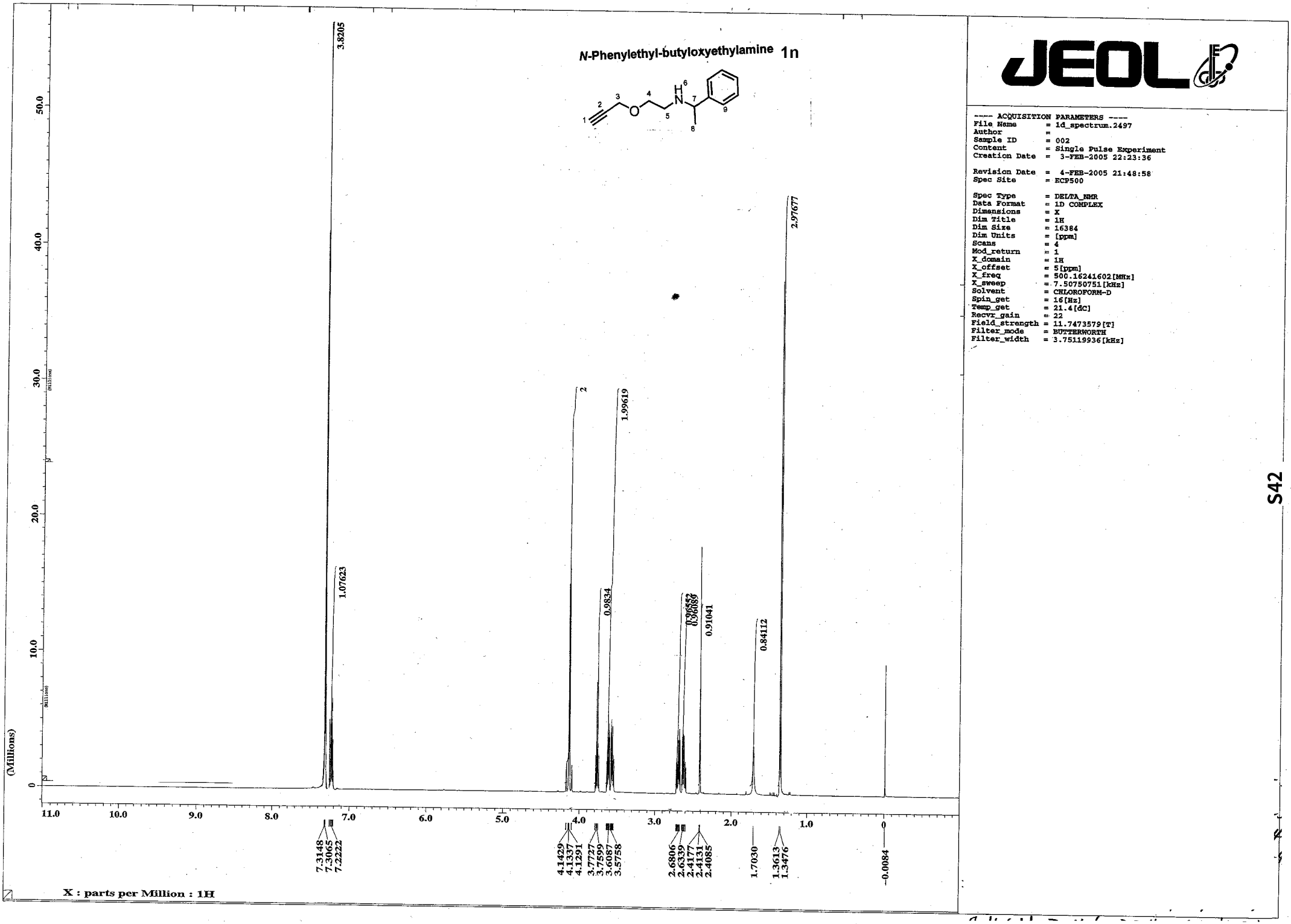

(Millions)
0
10.0
20.0
30.0
40.0
50.0
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3166
7.3038
7.3001
1.10635
4.21336
3.7645
3.7517
3.7379
1
2.1593
2.1547
2.1465
1.9239
1.9193
1.9138
1.5729
1.5592
1.5519
1.5390
1.5290
1.5262
1.3457
1.3329
0.98185
0.96563
2.00354
0.92037
4.01035
3.13281
0.64839
-0.0038
N-Phenylethyl-hexylamine 1m
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.4626
Author =
Sample ID = 1
Content = Single Pulse Experiment
Creation Date = 13-APR-2005 14:20:08
Revision Date = 14-APR-2005 16:02:16
Spec Site = RCP500
Spec Type = DELTA NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
Solvent = CHLOROFORM-D
Spin_gpt = 17[Hz]
Temp_gpt = 22.6[dC]
Recvr_gain = 19.6[dC]
Field_strength = 11.74735791[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75115936[kHz]

N-Phenylethyl-hexylamine 1m

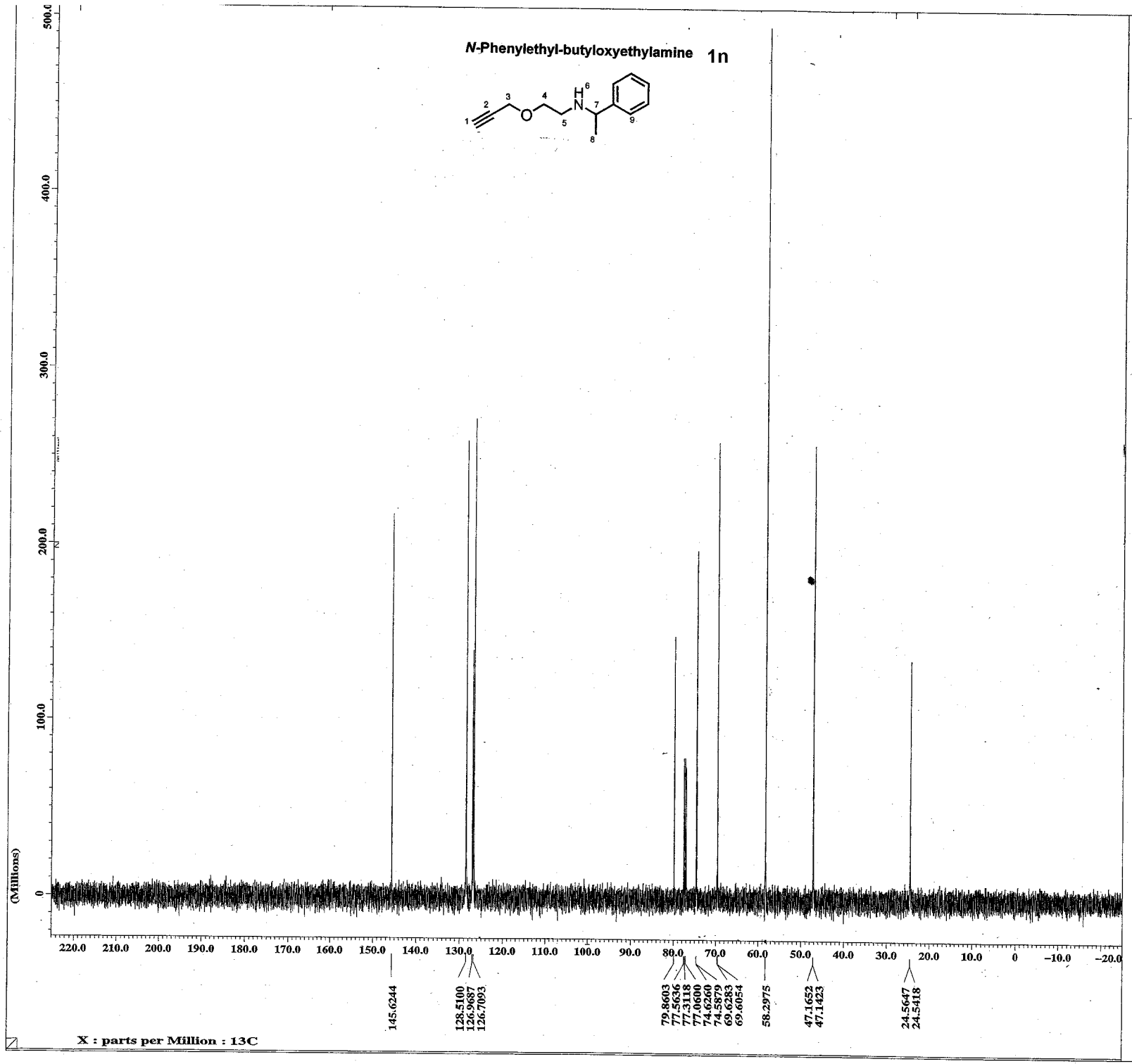


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.1280
Author          =
Sample ID       = 1
Content         = Single Pulse with Broad
Creation Date   = 13-APR-2005 14:24:13

Revision Date   = 14-APR-2005 16:07:32
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 37
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        = 17[Hz]
Temp_get        = 23.1[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```




```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_spectrum.2497
Author           =
Sample ID        = 002
Content          = Single Pulse Experiment
Creation Date    =  3-FEB-2005 22:23:36

Revision Date    =  4-FEB-2005 21:48:58
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 1H
Dim Size         = 16384
Dim Units        = [ppm]
Scans            = 4
Mod_return       = 1
X_domain         = 1H
X_offset         = 5[ppm]
X_freq           = 500.16241602[MHz]
X_sweep          = 7.50750751[kHz]
Solvent          = CHLOROFORM-D
Spin_get         = 16[Hz]
Temp_get         = 21.4[dC]
Recvr_gain       = 22
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 3.75119936[kHz]
```

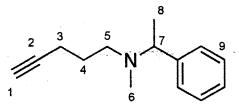


---- ACQUISITION PARAMETERS ----
File Name = 1d_13c_spectrum.828
Author =
Sample ID = 002
Content = Single Pulse with Broad
Creation Date = 3-FEB-2005 22:36:01

Revision Date = 4-FEB-2005 22:07:47
Spec Site = ECP500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 43
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 = 22.2[dC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.72066221[kHz]

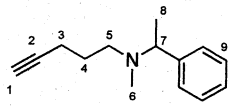
N-Methyl-*N*-(1-phenylethyl)-4-pentynyl-1-amine (1o)



JEOL

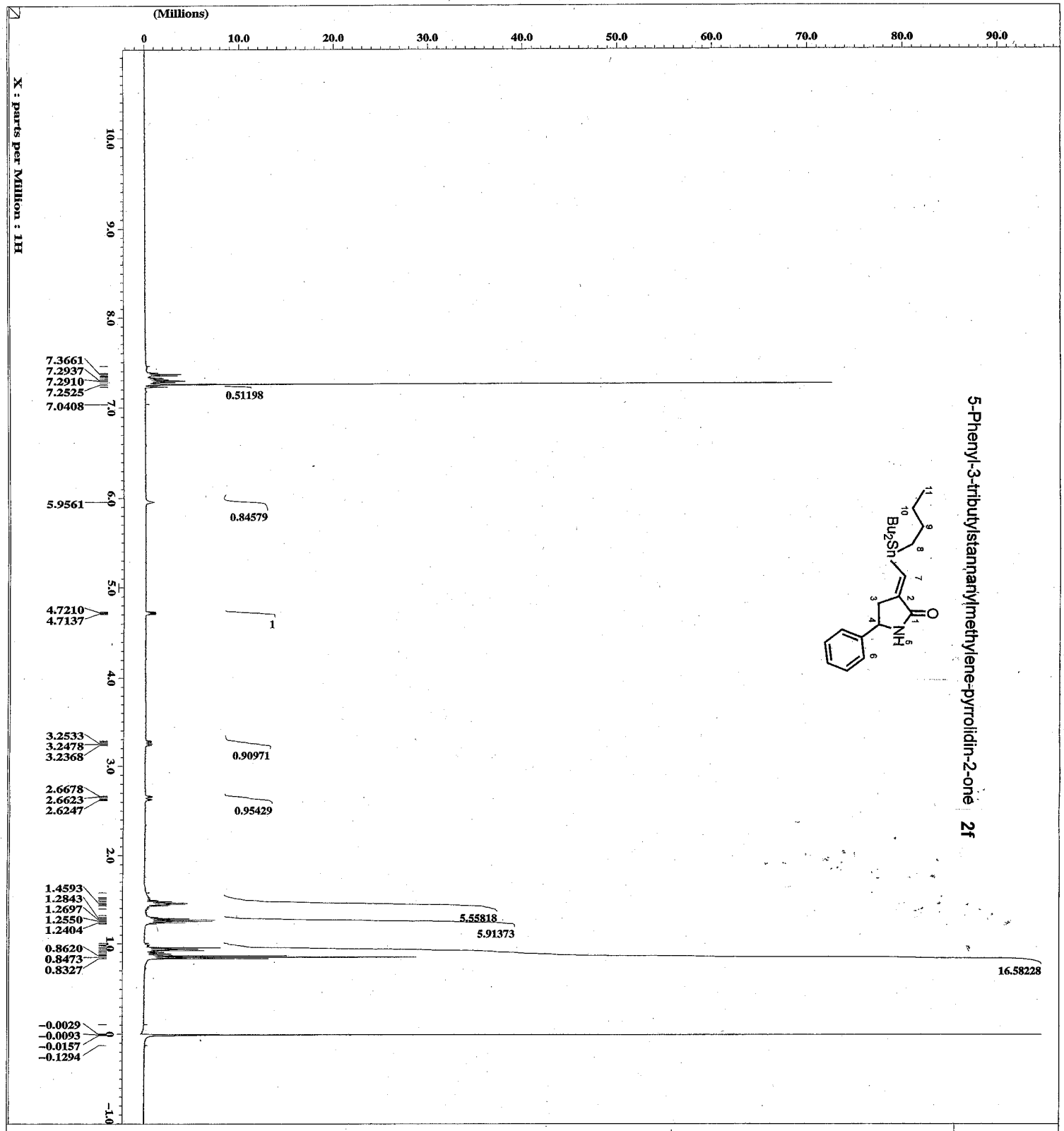
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.369
Author          =
Sample ID       = phenylethyl-methyl
Content         = Single Pulse Experiment
Creation Date   = 21-JUN-2006 10:57:18

Revision Date   = 22-JUN-2006 20:38:21
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 4
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 17[Hz]
Temp_get        = 23.8[dC]
Recvr_gain      = 22
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```

N-Methyl-*N*-(1-phenylethyl)-4-pentynyl-1-amine (1o)



JEOL

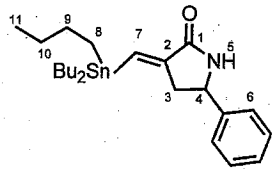
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.306
Author          =
Sample ID       = phenylethyl-methyl
Content         = Single Pulse with Broad
Creation Date   = 21-JUN-2006 11:05:06

Revision Date   = 22-JUN-2006 20:44:58
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 87
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        = 23.4[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```



---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.4285
Author =
Sample ID = fr14-17
Content = Single Pulse Experiment
Creation Date = 18-MAR-2005 10:41:42
Revision Date = 19-MAR-2005 10:53:54
Spec Site = ECP500

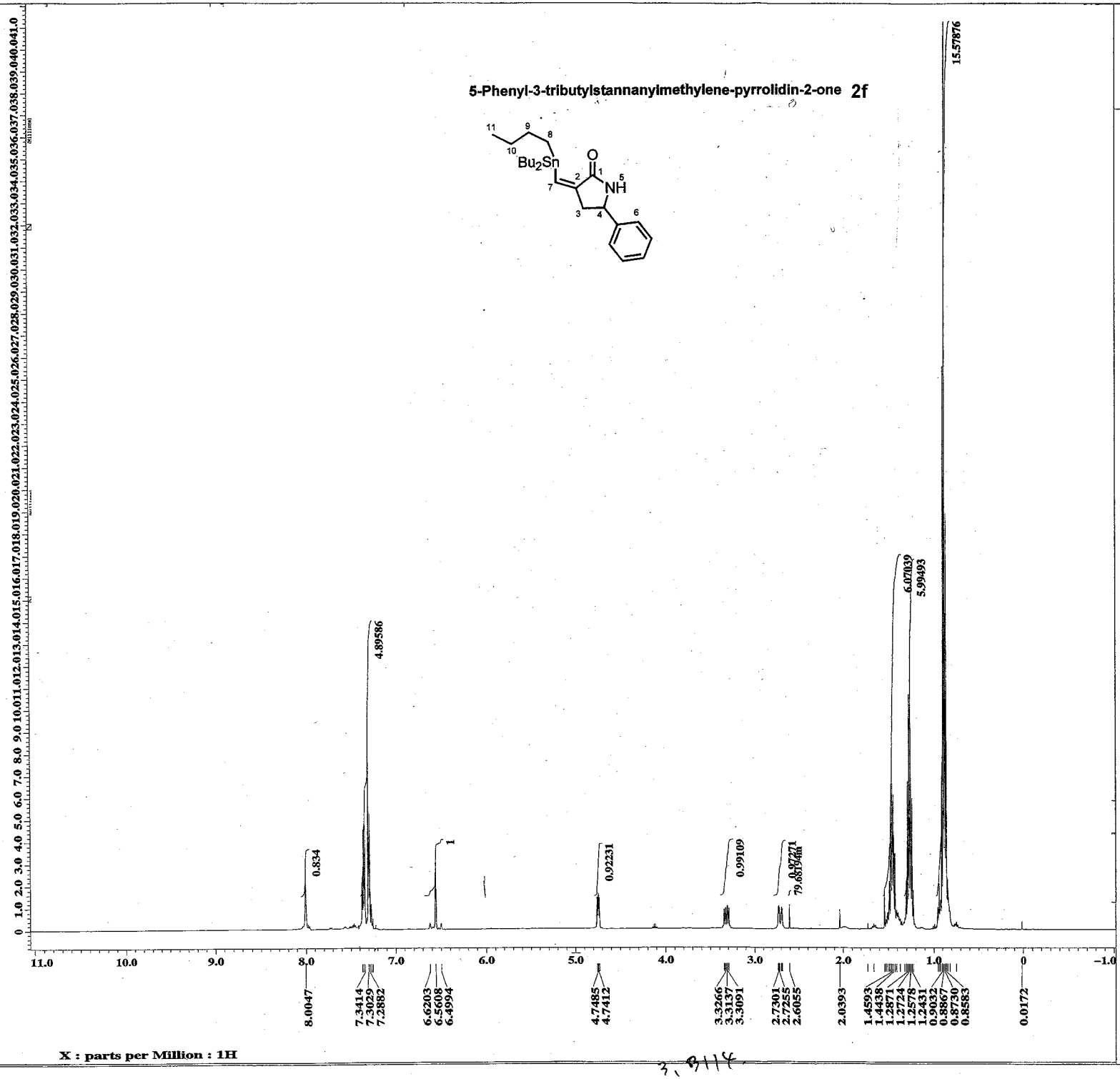
Spec Type = DELTA_NMR
Data Format = 2D COMPLEX
Dimensions = 2
X_points = 1K
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
Solvent = CHLOROFORM-D
Spin_get = 16[Hz]
Temp_get = 21.8[dC]
Recvr_gain = 29
Field_strength = 11.7473579[T]
Filter_mode = BOTTENWORTH
Filter_width = 3.75115936[kHz]

5-Phenyl-3-tributylstannanylmethylene-pyrrolidin-2-one **2f**



---- ACQUISITION PARAMETERS ----

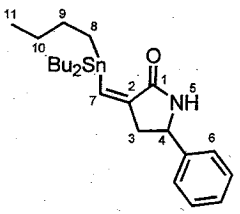
File Name	= 1d_13c_spectrum.64
Author	=
Sample ID	= RD1-019 fr18-22
Content	= Single Pulse with Broad
Creation Date	= 29-JUN-2004 00:48:16
Revision Date	= 29-JUN-2004 21:13:48
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 316
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	= 23.6[dC]
Recvr_gain	= 19
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



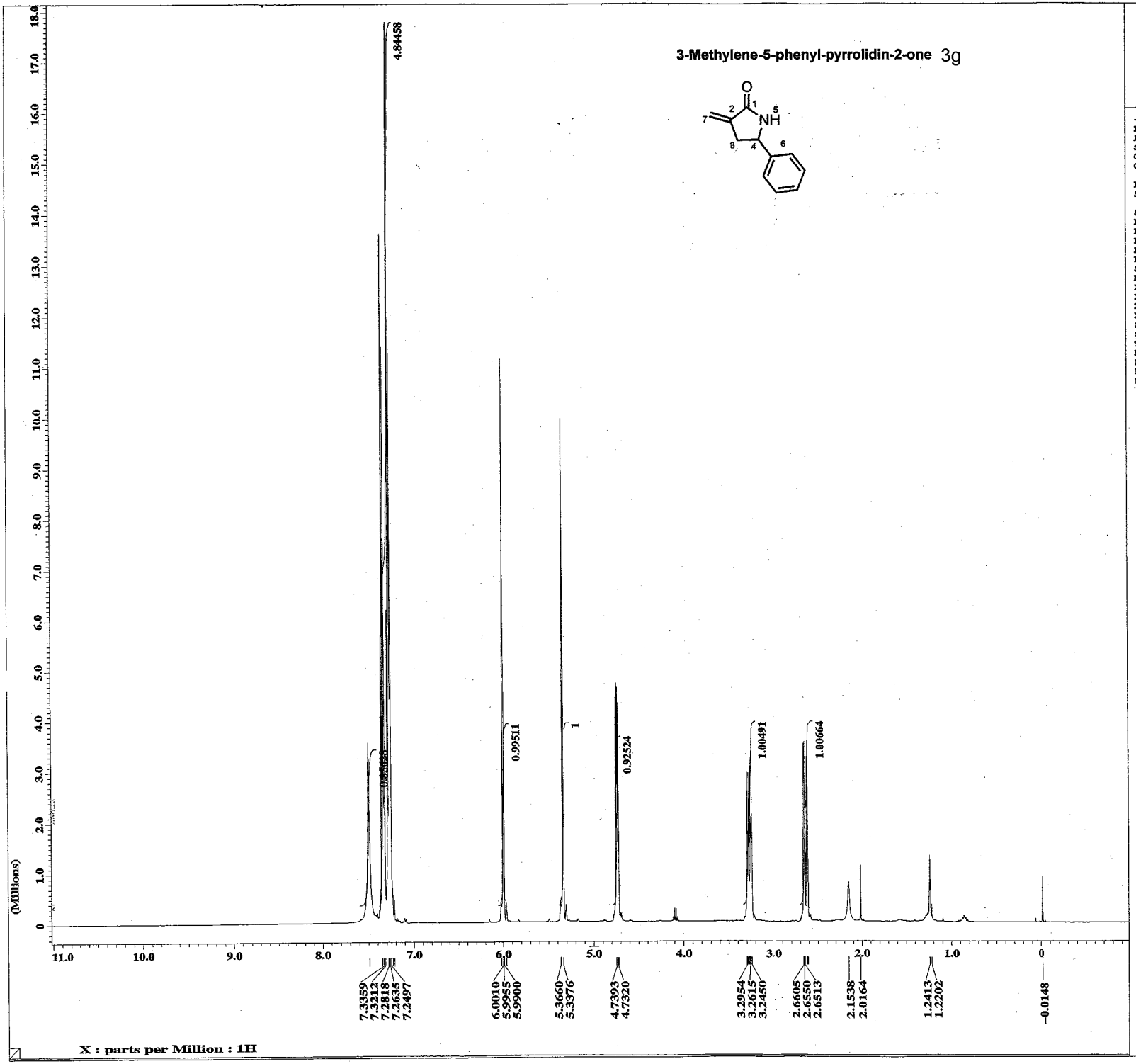
JEOL

```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_spectrum.308
Author          =
Sample ID       = RD1-019  fr3-10
Content         = Single Pulse Experiment
Creation Date   = 29-JUN-2004 00:23:28

Revision Date   = 29-JUN-2004 21:08:13
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_set        = 16[Hz]
Temp_set        = 22.8[dC]
Recvr_gain      = 13
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```

5-Phenyl-3-tributylstannanylmethylene-pyrrolidin-2-one **2f**



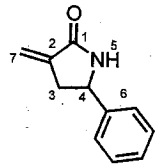
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.63
Author          =
Sample ID       = RD1-019  fr3-10
Content         = Single Pulse with Broad
Creation Date   = 29-JUN-2004 00:28:56

Revision Date   = 29-JUN-2004 21:09:40
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 150
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        = 23.5[dC]
Recvr_gain      = 14
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```



---- ACQUISITION PARAMETERS ----

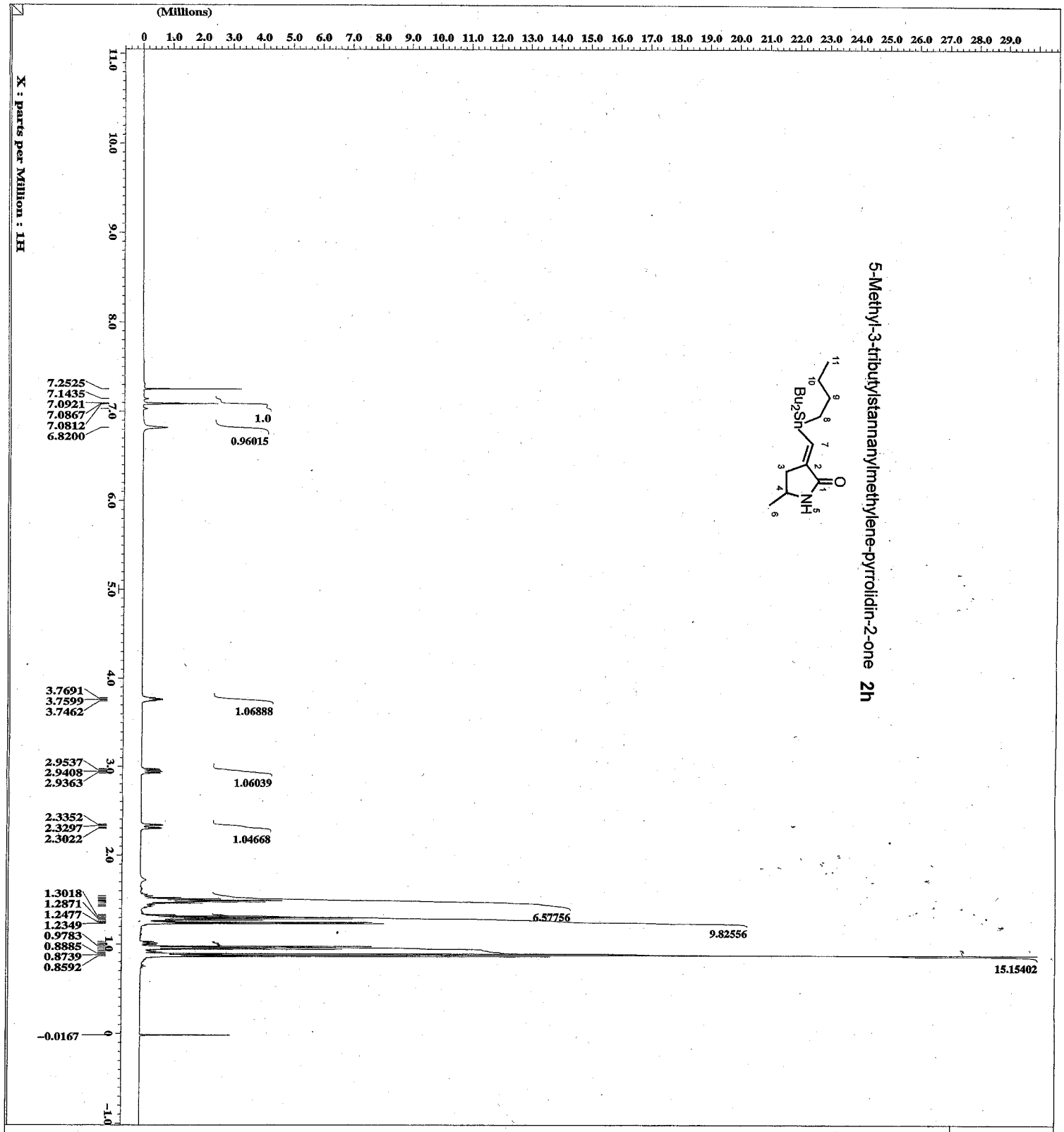
File Name	= 1d_spectrum.386
Author	=
Sample ID	= RD1-020 Z fr9-12
Content	= Single Pulse Experiment
Creation Date	= 30-JUN-2004 22:12:38
Revision Date	= 1-JUL-2004 18:42:06
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 15[Hz]
Temp_get	= 22.3[dC]
Recvr_gain	= 17
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]

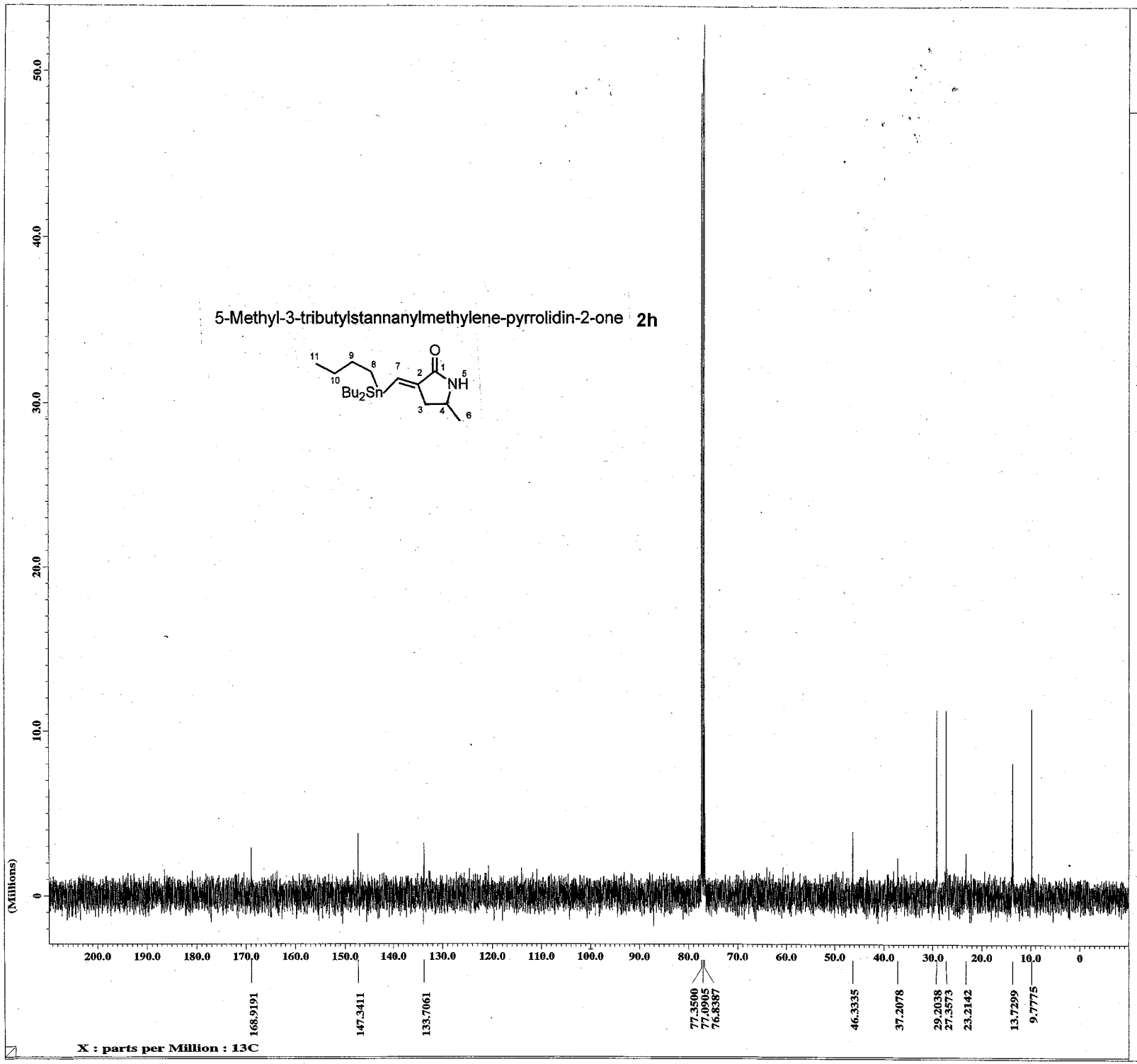
3-Methylene-5-phenyl-pyrrolidin-2-one 3g



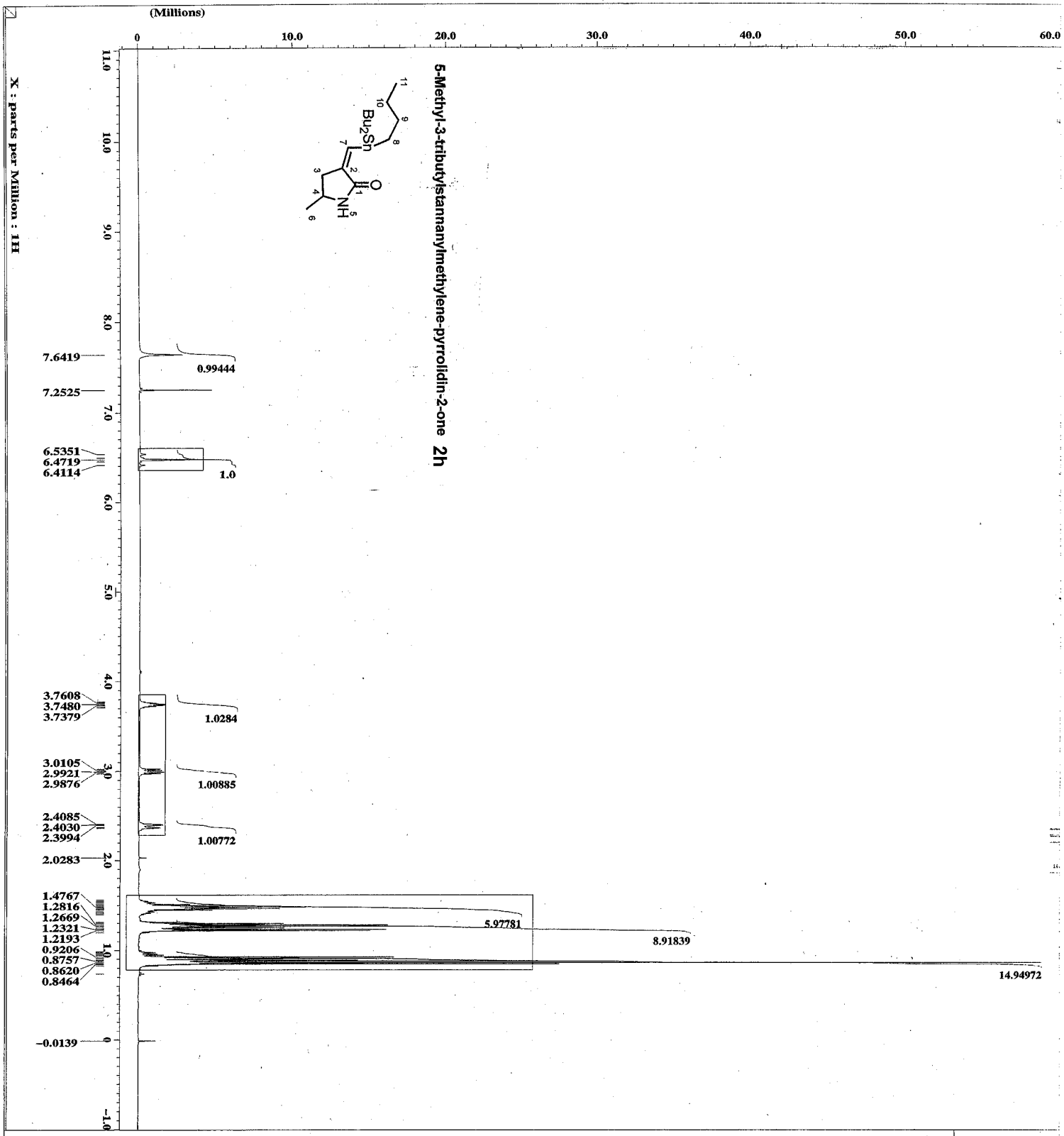
JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.80
Author          =
Sample ID       = RD1-020 Z fr9-12
Content         = Single Pulse with Broad
Creation Date   = 30-JUN-2004 22:16:51

Revision Date   =  1-JUL-2004 18:44:15
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 113.0
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        = 23[dC]
Recvr_gain      = 18
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

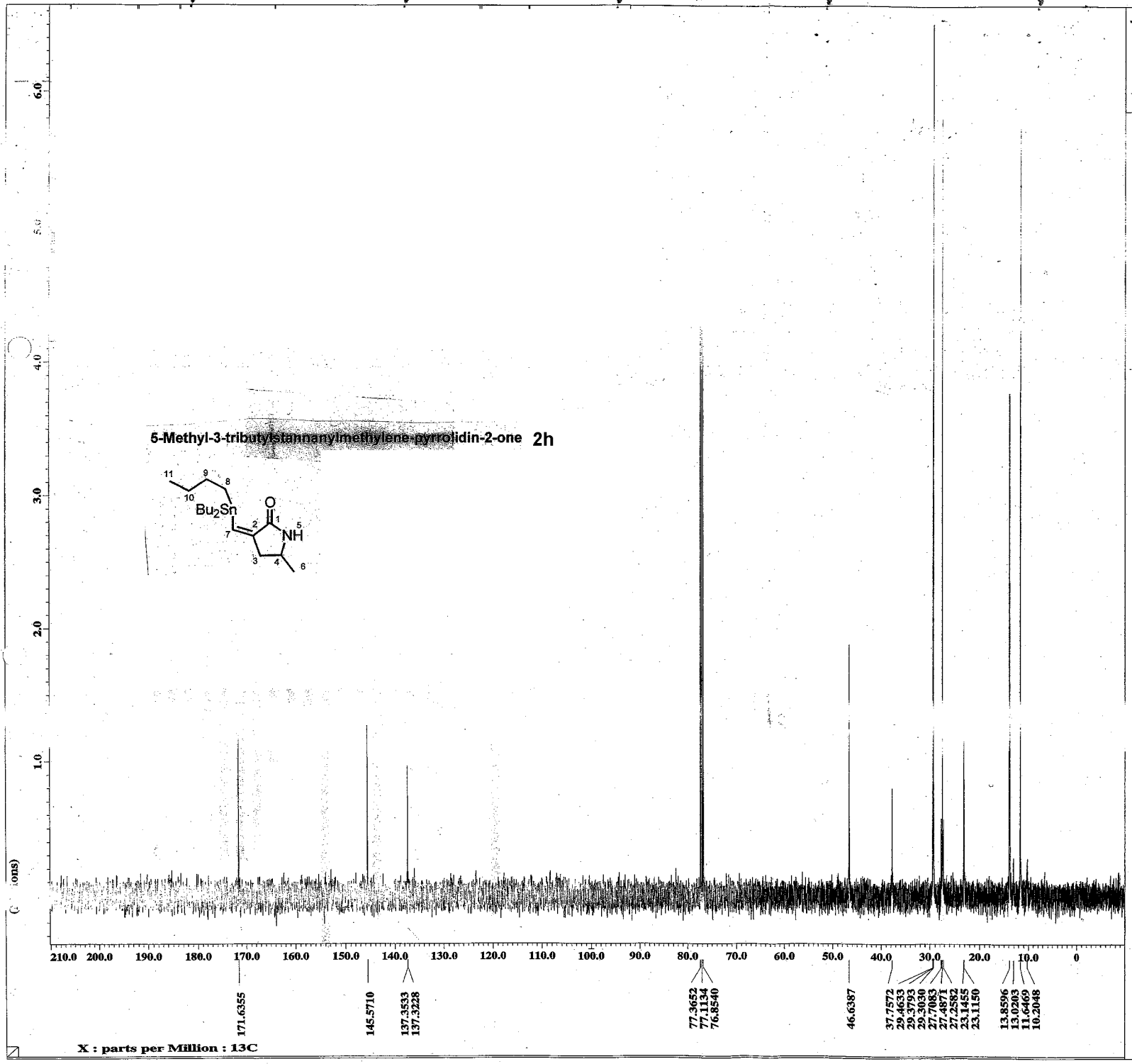

5-Methyl-3-tributylstannanylmethylene-pyrrolidin-2-one 2h
X : parts per Million : 1H
(Millions)
7.2525
7.1435
7.0921
7.0867
7.0812
6.8200
1.0
0.96015
3.7691
3.7599
3.7462
1.06888
2.9537
2.9408
2.9363
1.06039
2.3352
2.3297
2.3022
1.04668
1.3018
1.2871
1.2477
1.2349
0.9783
0.8885
0.8739
0.8592
6.57756
9.82556
15.15402
-0.0167
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.4805
Author = GoGo
Sample ID = Single Pulse Experiment
Content = 19-APR-2005 16:55:38
Creation Date = 20-APR-2005 18:44:08
Revision Date = ECP500
Spec Site = DELTA_NMR
Spec Type = 1D COMPLEX
Data Format = X
Dimensions = 1H
Dim Title = 16384
Dim Size = [ppm]
Dim Units = 1
Scans = 1H
Nucleus = 1
X_domain = 5[ppm]
X_offset = 500.16241602[MHz]
X_freq = 7.50750751[kHz]
X_sweep = CHCL3FORM-D
Solvent = 14[Hz]
Spin_set = 22.2[dC]
Temp_set = 21
Recvr_gain = 11.7473579[P]
Field_strength = BUTTERWORTH
Filter_mode = 3.75119936[kHz]
Filter_width




```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_13c_spectrum.265
Author          =
Sample ID       = RM2-084  fr39-44
Content         = Single Pulse with Broad
Creation Date   = 10-MAR-2004 22:21:53

Revision Date   = 11-MAR-2004 15:49:13
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 270
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        = 10[Hz]
Temp_get        = 24.1[dC]
Recvr_gain      = 19
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

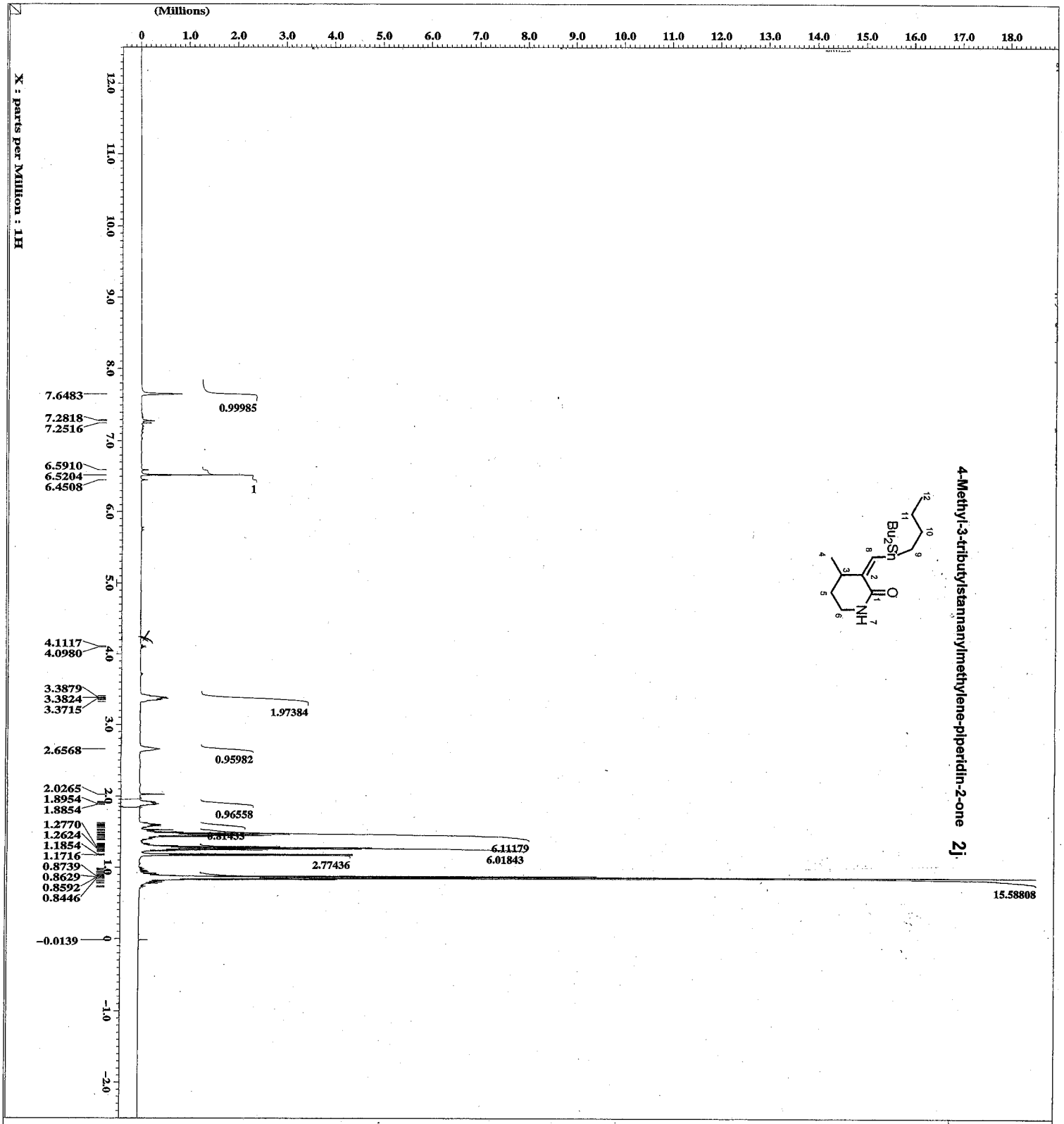



```
---- ACQUISITION PARAMETERS ----
File Name          = id_spectrum.1075
Author             =
Sample ID          = RM2-084  fr15-27 HPLC
Content            = Single Pulse Experiment
Creation Date      = 24-MAR-2004 14:53:17

Revision Date      = 25-MAR-2004 08:37:16
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Scans              = 8
Mod_return         = 1
X_domain           = 1H
X_offset           = 5[ppm]
X_freq             = 500.1624160Z[MHz]
X_sweep            = 7.5075075l[kHz]
Solvent            = CHLOROFORM-D
Spin_set           = 10[Hz]
Temp_set           = 23.2[dC]
Recvr_gain         = 15
Field_strength     = 11.7473579[T]
Filter_mode        = NUTHERWORTH
Filter_width       = 3.75l.l9936[kHz]
```



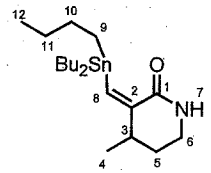
---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.172
Author	=
Sample ID	= RD1-016 fr7-17
Content	= Single Pulse with Broad
Creation Date	= 25-MAY-2004 21:13:15
Revision Date	= 26-MAY-2004 17:07:10
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 119
Mod_return	= 1
X_domain	= 13C
X_offset	= 100[ppm]
X_freq	= [illegible] 77787547[MHz]
X_sweep	= [illegible]4654088[kHz]
Solvent	= CHLOROFORM-D
Spin_set	= 14[Hz]
Temp_set	= 23.2[AC]
Recvr_gain	= 13
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.3373
Author =
Sample ID = frt4-11
Content = Single Pulse Experiment
Creation Date = 21-FEB-2005 21:58:08
Revision Date = 22-FEB-2005 21:44:26
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 4
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.1624602[MHz]
X_sweep = 7.5075075[kHz]
Solvent = CHLOROFORM-D
Spin_set = 13[Hz]
Temp_set = 21.3[dC]
Receiver_gain = 11.7472579[r]
Field_strength = EXPERIMENTAL
Filter_mode = 3.7511993e[kHz]
Filter_width

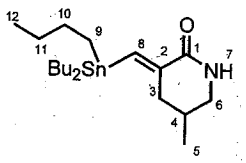
4-Methyl-3-tributylstannanylmethylene-piperidin-2-one **2j**



JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.1011
Author          =
Sample ID       = fr4-11
Content         = Single Pulse with Broad
Creation Date   = 21-FEB-2005 22:02:02

Revision Date   = 22-FEB-2005 21:49:24
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 103
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        = 21.9[dC]
Recvr_gain      = 14
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

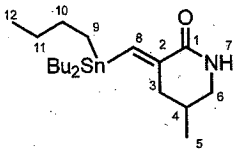
5-Methyl-3-tributylstannanylmethylene-piperidin-2-one **2k**



---- ACQUISITION PARAMETERS ----

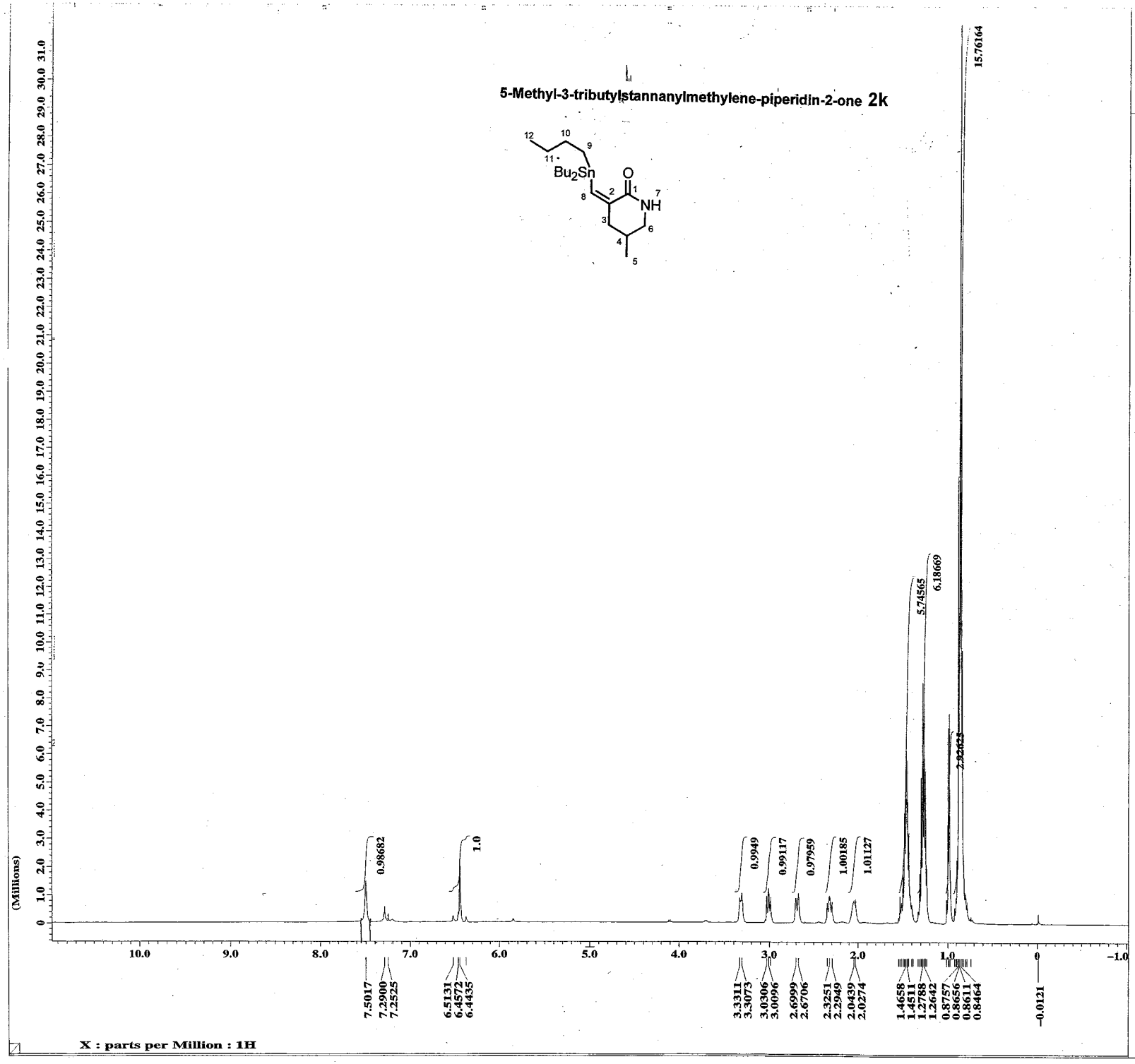
File Name	= 1d_spectrum.1200
Author	=
Sample ID	= RD1~001 fr27-33 HPLC
Content	= Single Pulse Experiment
Creation Date	= 9-APR-2004 10:08:59
Revision Date	= 10-APR-2004 05:14:52
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 10[Hz]
Temp_get	= 23.1[dC]
Recvr_gain	= 23
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]

5-Methyl-3-tributylstannanylmethylene-piperidin-2-one **2k**



JEOL

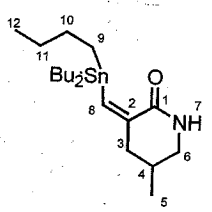
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.362
Author          =
Sample ID       = RD1-001 HPLC
Content         = Single Pulse with Broad
Creation Date   = 10-APR-2004 06:58:50

Revision Date   = 11-APR-2004 04:34:36
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 15000
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        = 10[Hz]
Temp_get        = 24[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```



---- ACQUISITION PARAMETERS ----

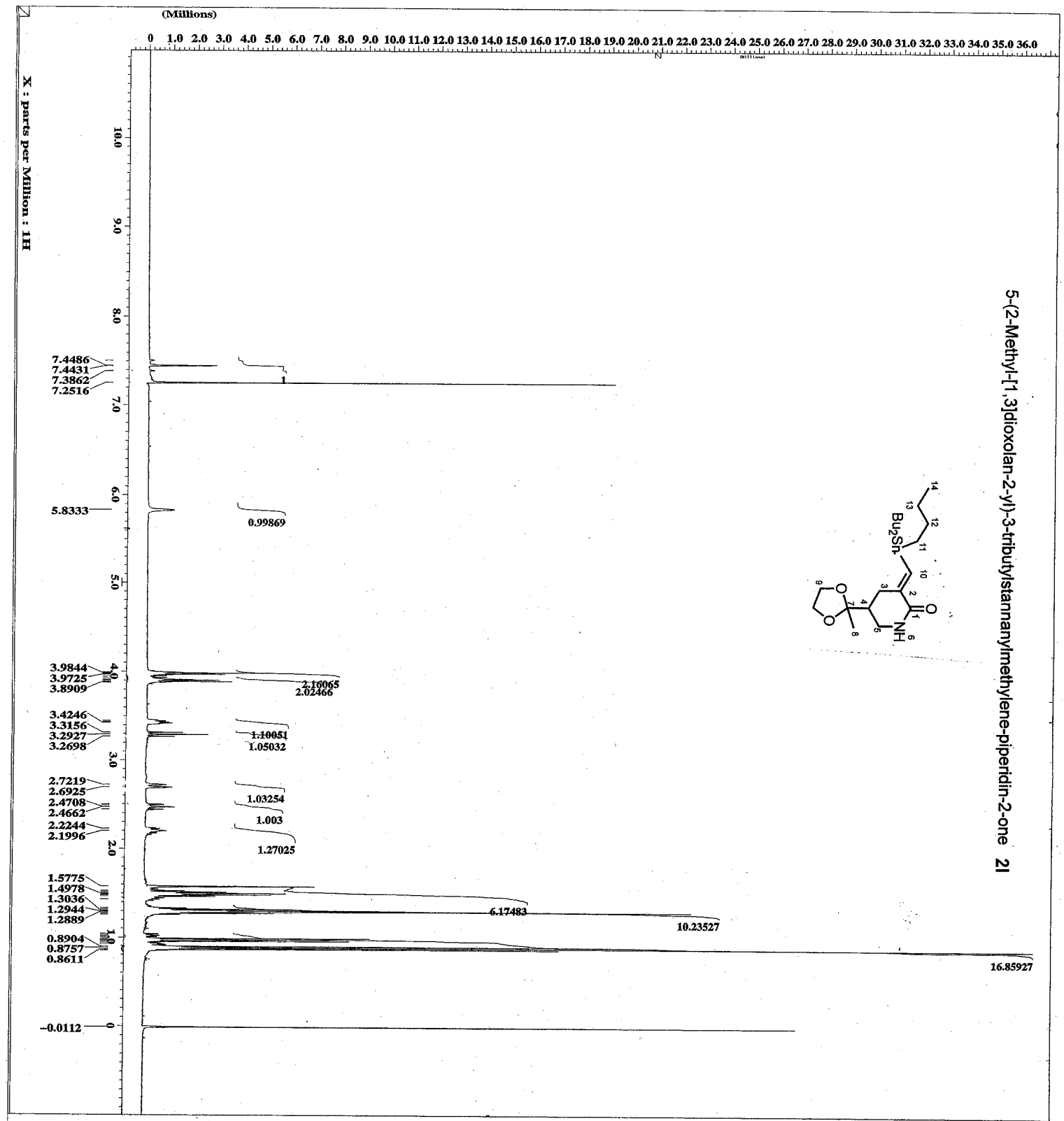
File Name	= 1d_spectrum.1165
Author	=
Sample ID	= RD1-001 fr5-12
Content	= Single Pulse Experiment
Creation Date	= 7-APR-2004 19:06:46
Revision Date	= 8-APR-2004 14:07:17
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 7[Hz]
Temp_get	= 22.7[dC]
Recvr_gain	= 13
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]

5-Methyl-3-tributylstannanylmethylene-piperidin-2-one 2k



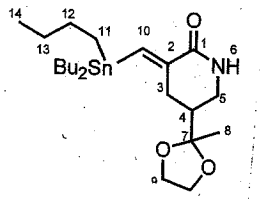
JEOL

```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_13c_spectrum.347
Author           =
Sample ID        = RD1-001 fr5-12
Content          = Single Pulse with Broad
Creation Date    =  7-APR-2004 19:11:01

Revision Date    =  8-APR-2004 14:09:29
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 13C
Dim Size         = 32768
Dim Units        = [ppm]
Scans            = 110
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         = 7[Hz]
Temp_set         = 23.1[dC]
Recvr_gain       = 13
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 15.72066221[kHz]
```



---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.4555
Author =
Sample_ID = sns
Comment = Single Pulse Experiment
Creation Date = 9-NOV-2005 17:19:54
Revision Date = 10-APR-2005 19:02:13
Spec Site = ECP500
Spec Type = NMR/FA NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Rcd_return = 1
X_domain = 1H
X_offset = 5.00152441402[MHz]
X_sweep = 7.50150755[KHz]
Solvent = CHLOROFORM-D
Spin_set = 17[Hz]
Temp_set = 22.2[dC]
Recvr_gain = 25
Field_strength = 11.74735797[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[KHz]

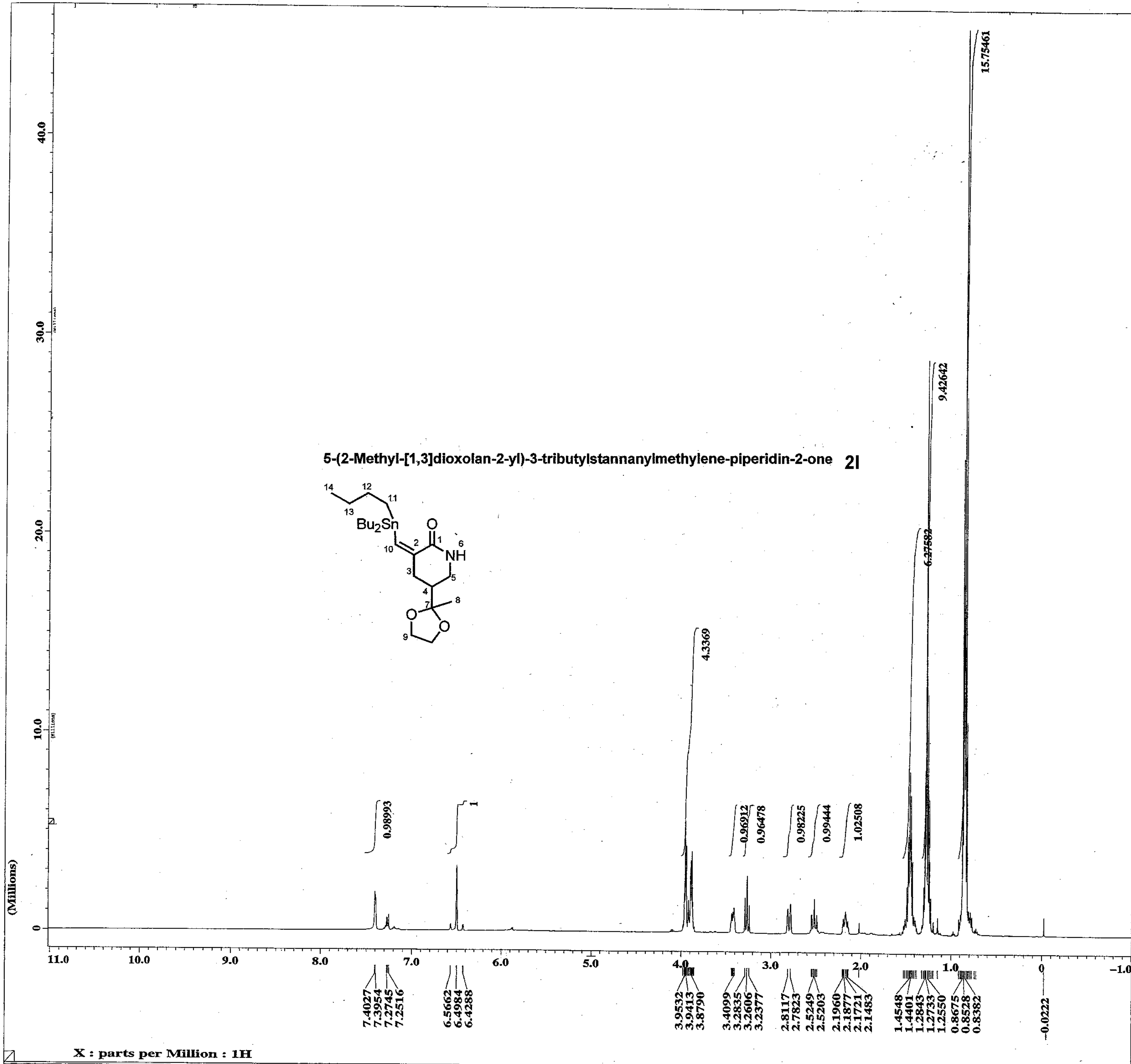
5-(2-Methyl-[1,3]dioxolan-2-yl)-3-tributylstannanylmethylene-piperidin-2-one **2l**



JEOL

```
---- ACQUISITION PARAMETERS ----
File Name          = id_13c_spectrum.1262
Author             =
Sample ID          = 6-cetal-E-
Content            = Single Pulse with Broad
Creation Date      = 11-APR-2005 10:02:08

Revision Date      = 12-APR-2005 11:40:39
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Scans              = 59034
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           = 15[Hz]
Temp_get           = 23.6[dC]
Recvr_gain         = 30
Field_strength     = 11.7473579[T]
Filter_mode        = BUTTERWORTH
Filter_width       = 15.72066221[kHz]
```

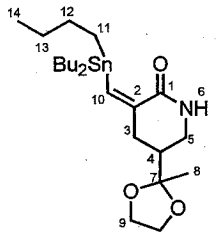
5-(2-Methyl-[1,3]dioxolan-2-yl)-3-tributylstannanylmethylene-piperidin-2-one **2l**



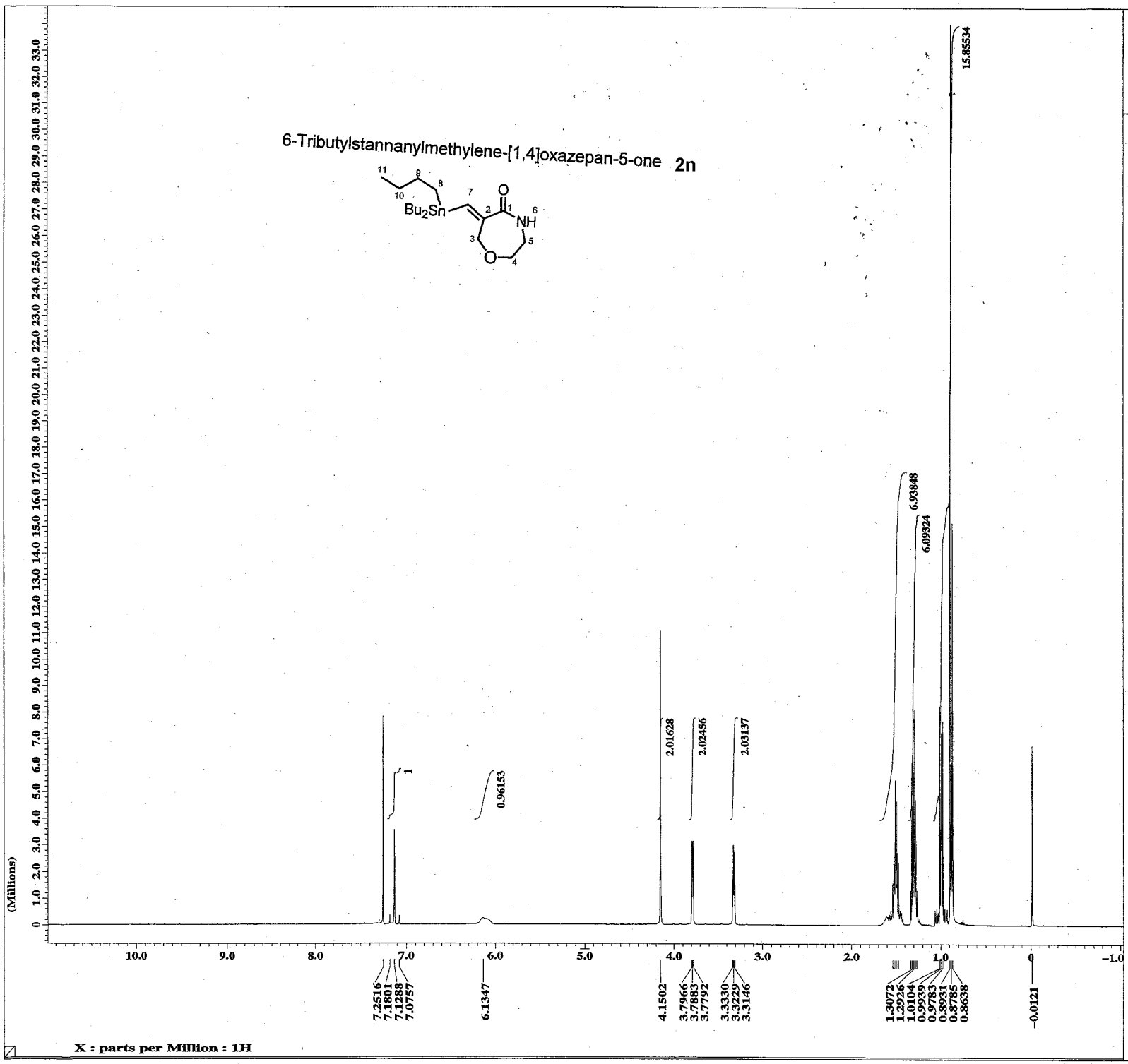
JEOL

```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_spectrum.2871
Author           =
Sample ID        = fr6-16
Content          = Single Pulse Experiment
Creation Date    = 10-FEB-2005 15:04:28

Revision Date    = 11-FEB-2005 14:37:08
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 1H
Dim Size         = 16384
Dim Units        = [ppm]
Scans            = 8
Mod_return       = 1
X_domain         = 1H
X_offset         = 5[ppm]
X_freq           = 500.16241602[MHz]
X_sweep          = 7.50750751[kHz]
Solvent          = CHLOROFORM-D
Spin_get         = 18[Hz]
Temp_get         = 22.1[dC]
Recvr_gain       = 15
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 3.75119936[kHz]
```

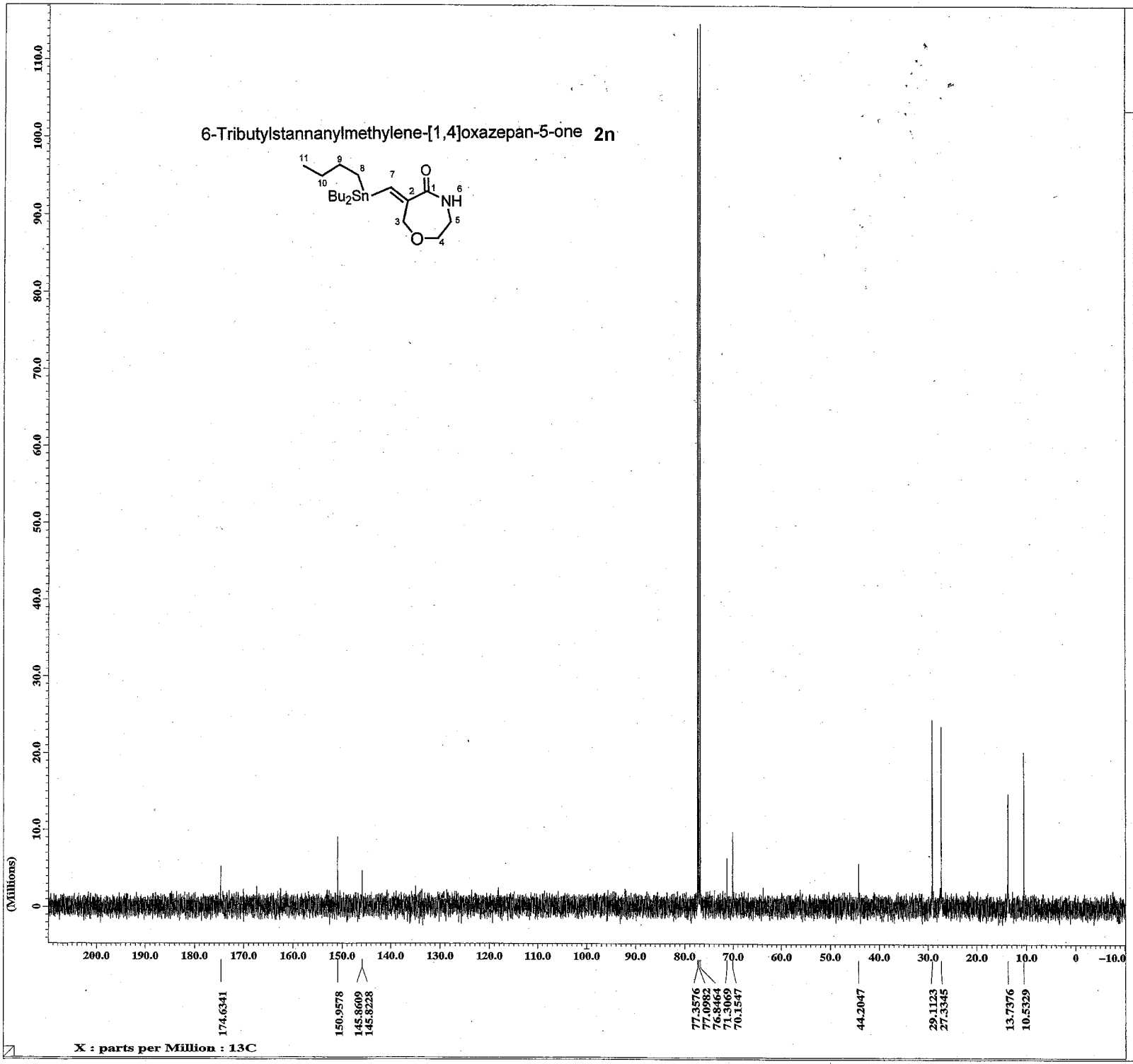
5-(2-Methyl-[1,3]dioxolan-2-yl)-3-tributylstannanylmethylene-piperidin-2-one **2l**




```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.942
Author          =
Sample ID       = fr6-16
Content         = Single Pulse with Broad
Creation Date   = 10-FEB-2005 15:09:21

Revision Date   = 11-FEB-2005 14:41:45
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 132
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        = 18[Hz]
Temp_get        = 22[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

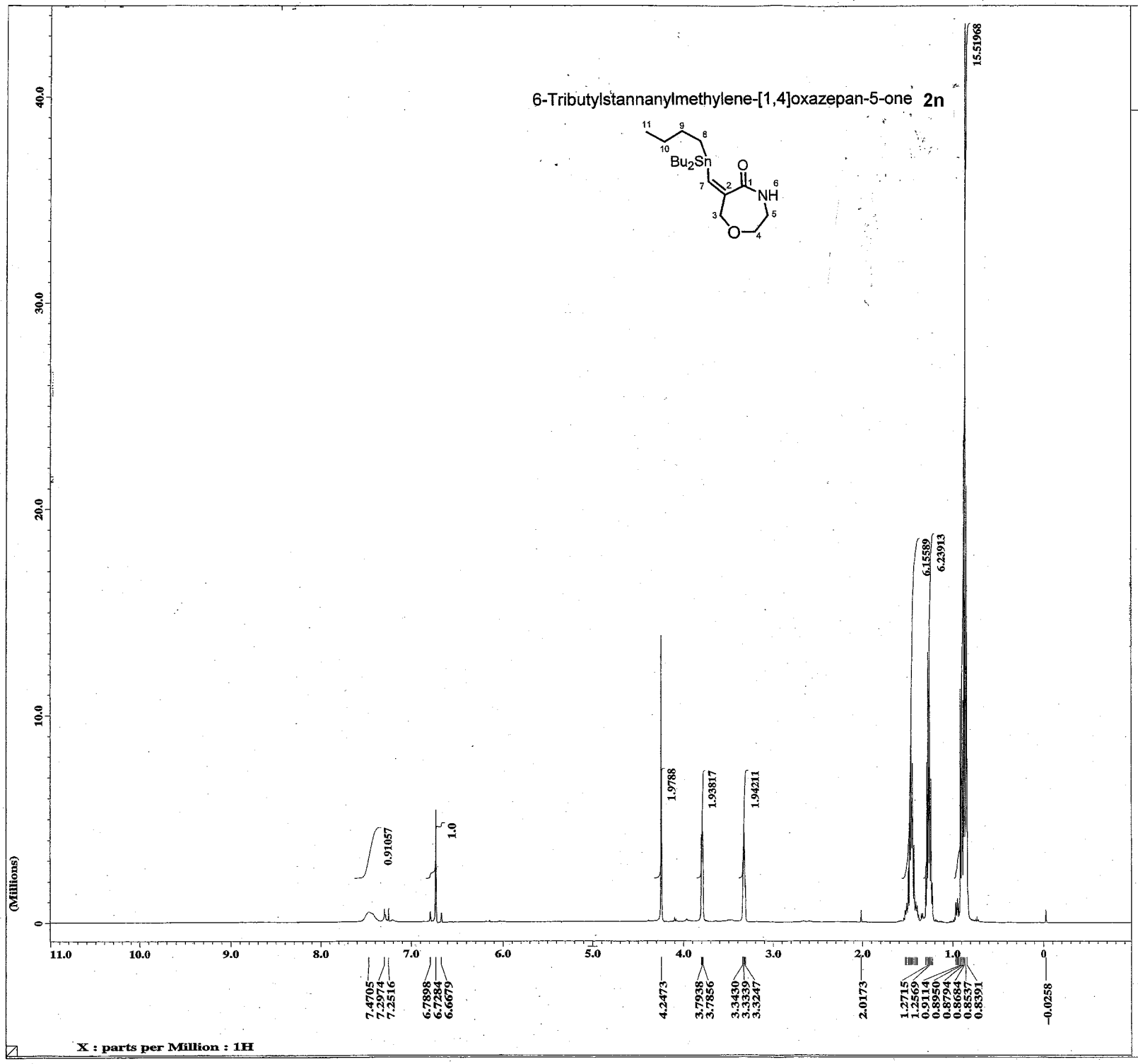



```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.4810
Author          =
Sample ID       = a
Content         = Single Pulse Experiment
Creation Date   = 19-APR-2005 18:57:47

Revision Date   = 20-APR-2005 20:46:34
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 4
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 13[Hz]
Temp_get        = 22.9[dC]
Recvr_gain      = 24
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



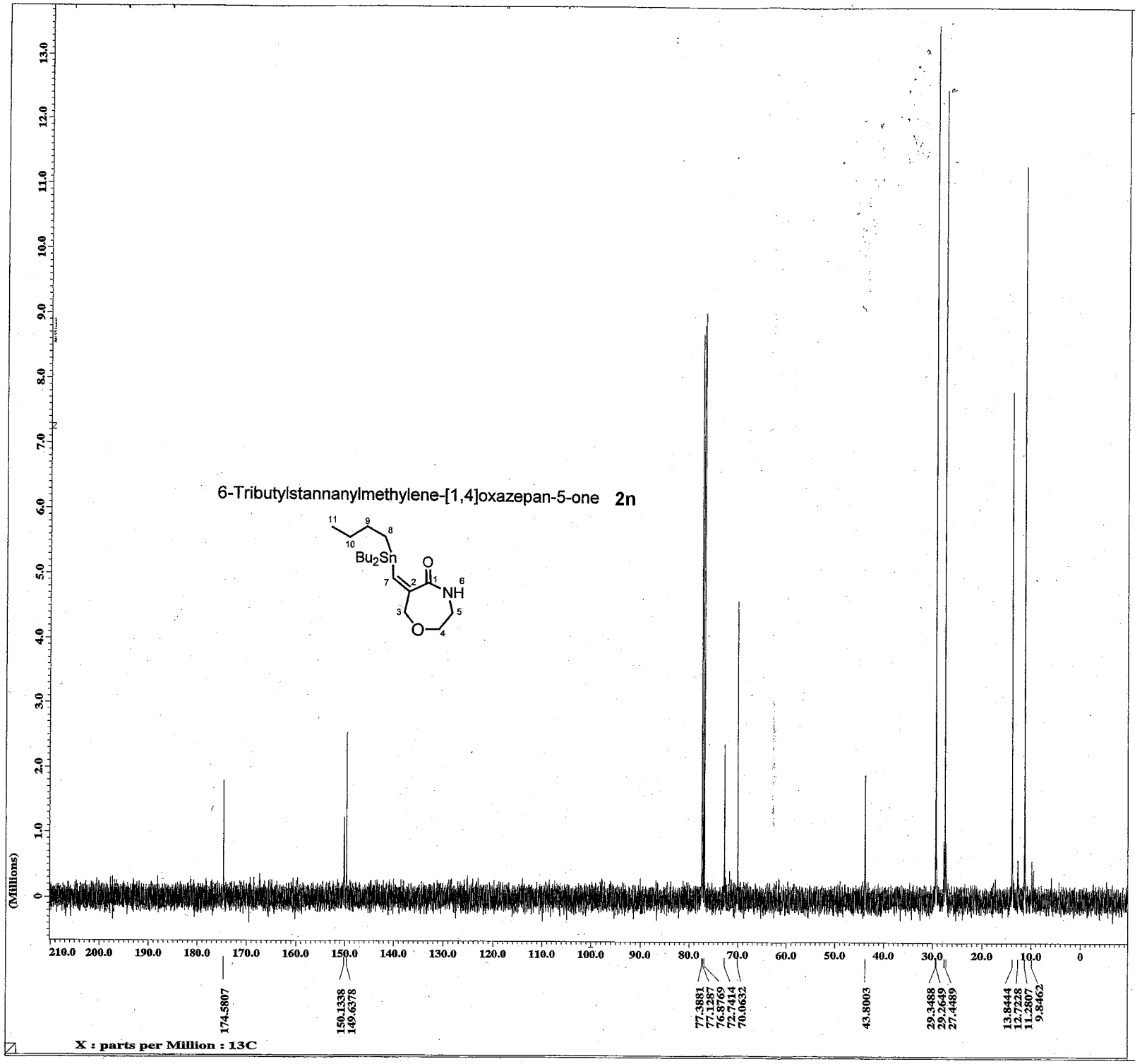
JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.893
Author          =
Sample ID       = fr27-34
Content         = Single Pulse with Broad
Creation Date   =  7-FEB-2005 21:33:01

Revision Date   =  8-FEB-2005 21:02:39
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_get        = 13[Hz]
Temp_get        = 21.8[dC]
Recvr_gain      = 21
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```



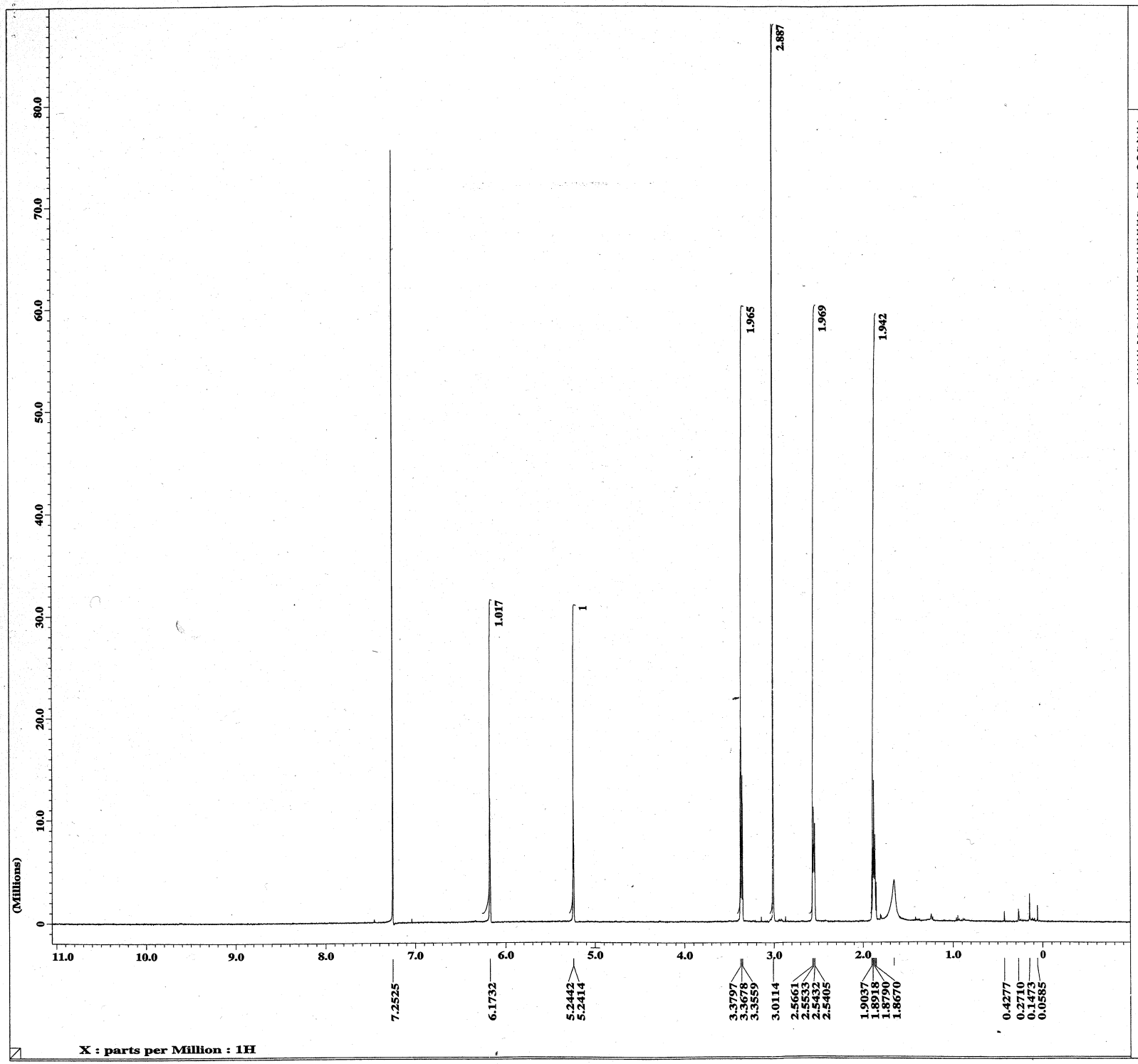
---- ACQUISITION PARAMETERS ----

File Name	= 1d_spectrum.2644
Author	=
Sample ID	= fr14-18
Content	= Single Pulse Experiment
Creation Date	= 5-FEB-2005 20:15:02
Revision Date	= 6-FEB-2005 19:41:53
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 0[Hz]
Temp_get	= 21.2[dC]
Recvr_gain	= 15
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]



JEOL

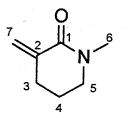
```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_13c_spectrum.865
Author          =
Sample ID       = fr14-18
Content         = Single Pulse with Broad
Creation Date   =  5-FEB-2005 20:20:27

Revision Date   =  6-FEB-2005 19:49:09
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 148
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        = 0[Hz]
Temp_get        = 22.3[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

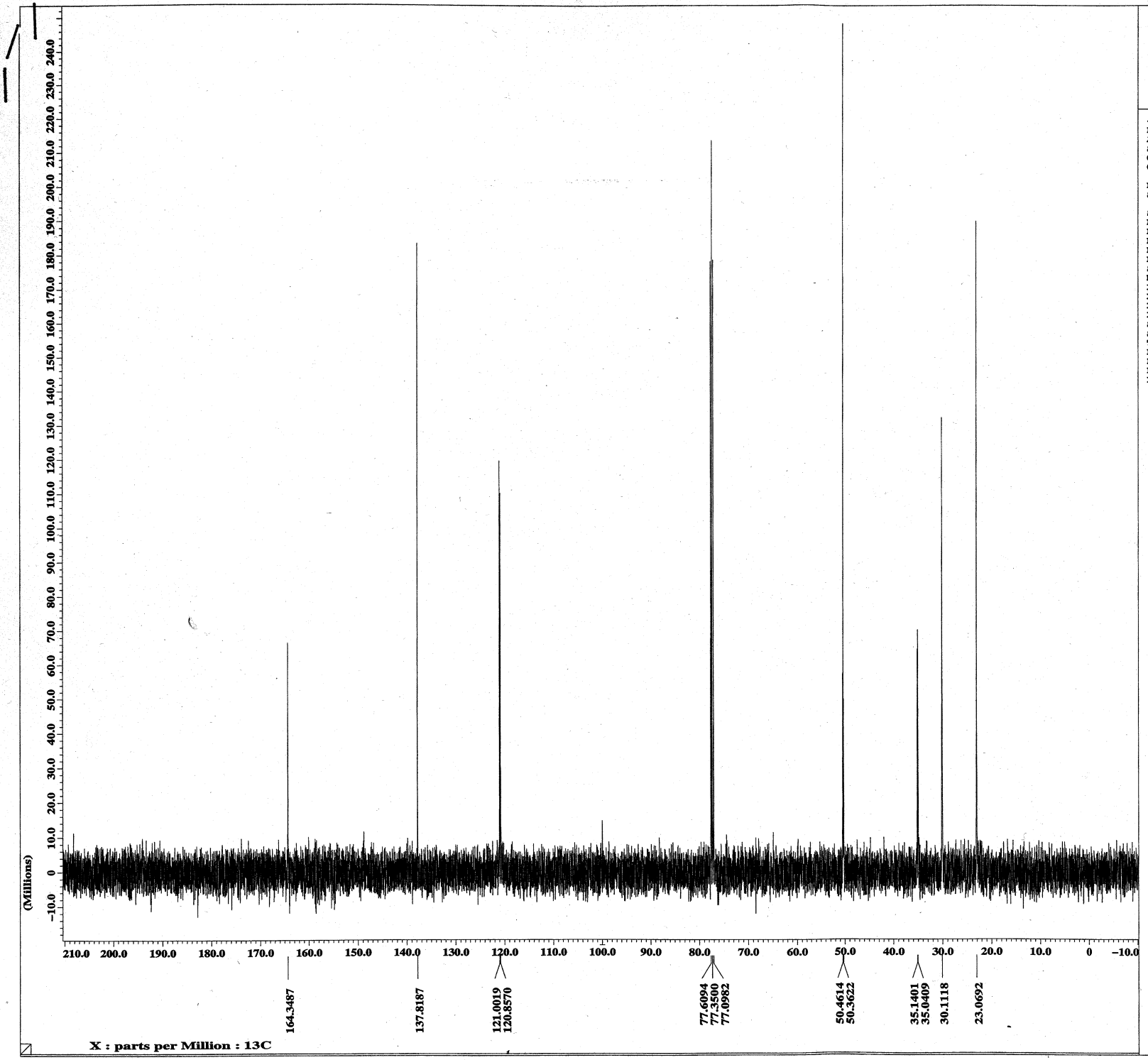


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name        = 1d_spectrum.483
Author           =
Sample ID        = GoGo
Content          = Single Pulse Experiment
Creation Date    = 26-JUN-2006 18:56:40

Revision Date    = 28-JUN-2006 04:42:37
Spec Site        = ECP500

Spec Type        = DELTA_NMR
Data Format      = 1D COMPLEX
Dimensions       = X
Dim Title        = 1H
Dim Size         = 16384
Dim Units        = [ppm]
Scans            = 8
Mod_return       = 1
X_domain         = 1H
X_offset         = 5[ppm]
X_freq           = 500.16241602[MHz]
X_sweep          = 7.50750751[kHz]
Solvent          = CHLOROFORM-D
Spin_get         = 15[Hz]
Temp_get         = 23.3[dC]
Recvr_gain       = 30
Field_strength   = 11.7473579[T]
Filter_mode      = BUTTERWORTH
Filter_width     = 3.75119936[kHz]
```

1-Methyl-3-methylene-piperidin-2-one (2o)

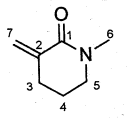


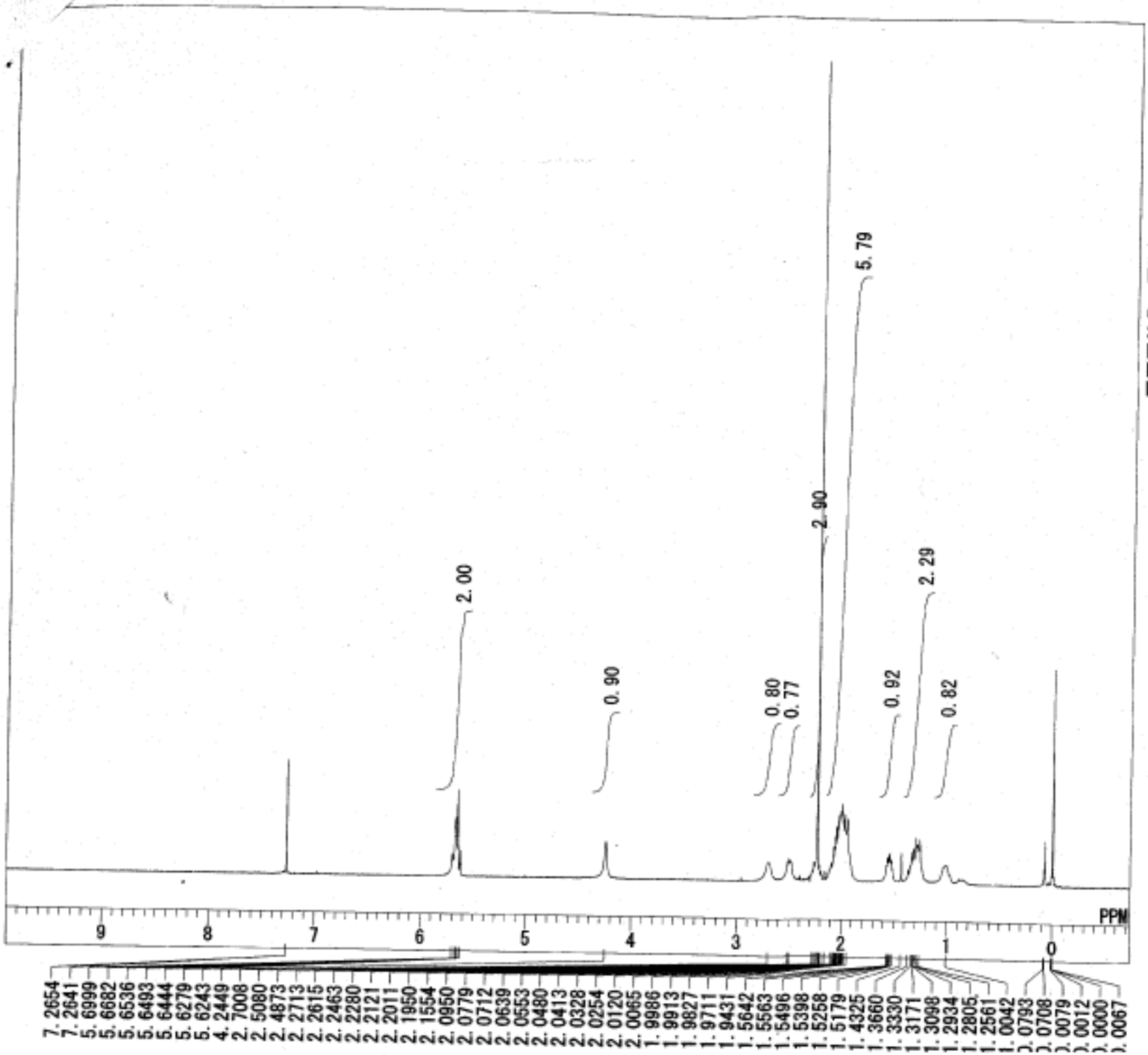


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum.561
Author          =
Sample ID       = S#851148
Content         = Single Pulse with Broad
Creation Date   =  7-AUG-2006 13:12:43

Revision Date   =  8-AUG-2006 23:41:59
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 59
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        = 24.3[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
```

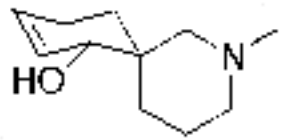
1-Methyl-3-methylene-piperidin-2-one (2o)

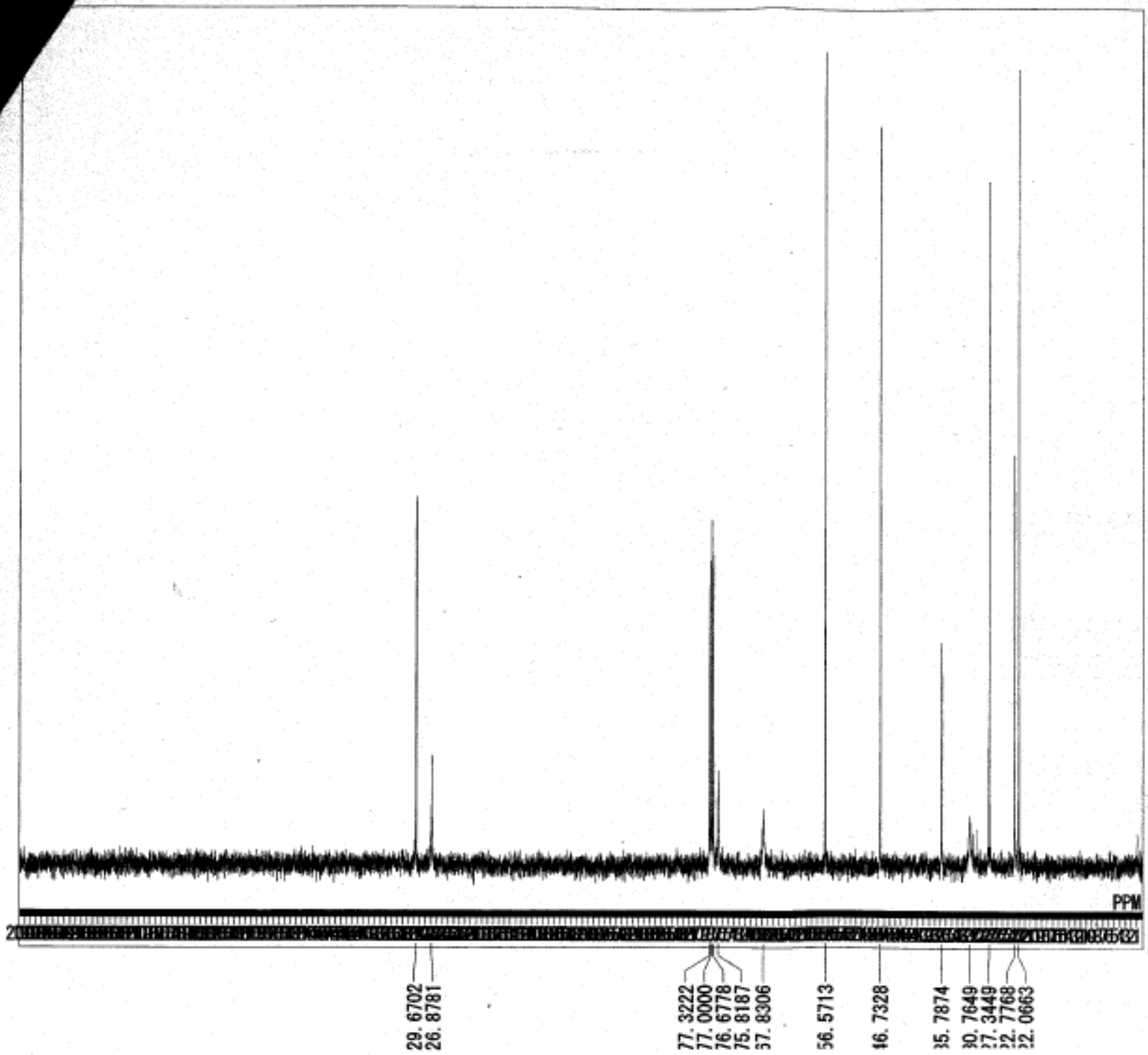




DFILE	C:¥WINNMR98¥COMMON¥_DEFAULT.AL	
COMNT		
DATIM	Sat Sep 02 16:39:55 2006	
OBNUC	1H	
EXMOD	NON	
OBFRQ	399.65	MHz
OBSET	124.00	KHz
OBFIN	10500.00	Hz
POINT	32768	
FREQU	7992.01	Hz
SCANS	8	
ACQTM	4.1001	sec
PD	2.9010	sec
PW1	5.80	usec
IRNUC	1H	
CTEMP	21.8	c
SLVNT	CDCL3	
EXREF	0.00	ppm
BF	0.12	Hz
RGAIN	15	

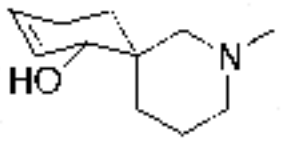
7-Hydroxy-2-azaspiro[5,5]undec-8-ene (5)

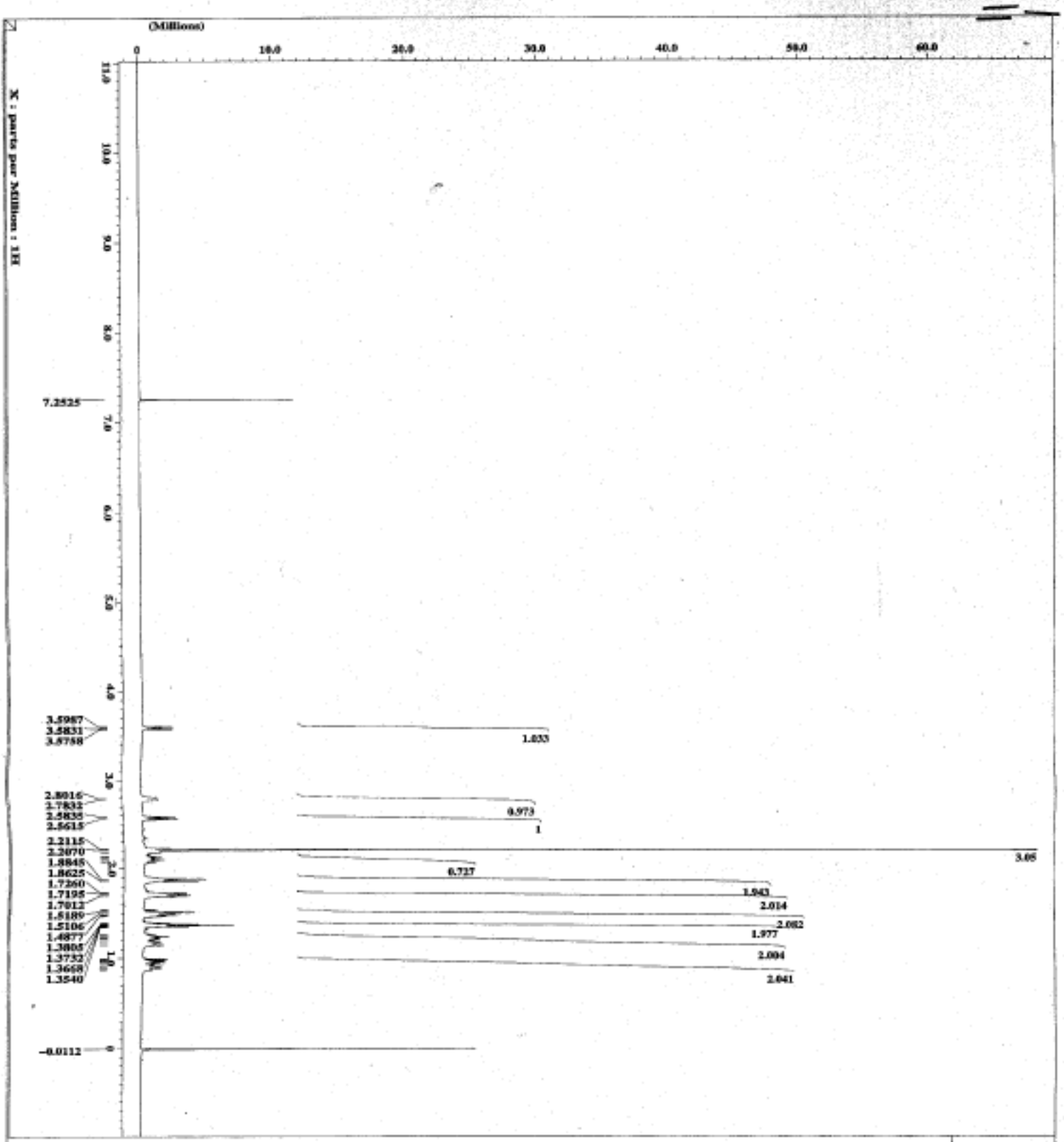


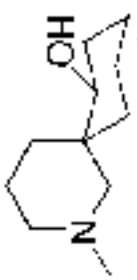


DFILE	C:¥WINNMR98¥COMMON¥_DEFAULT.AL	
COMNT		
DATIM	Sat Sep 02 16:49:18 2006	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	100.40	MHz
OBSET	125.00	KHz
OBFIN	10500.00	Hz
POINT	32768	
FREQU	27210.88	Hz
SCANS	73	
ACQTM	1.2042	sec
PD	1.7940	sec
PW1	5.50	usec
IRNUC	1H	
CTEMP	22.3	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	1.20	Hz
RGAIN	23	

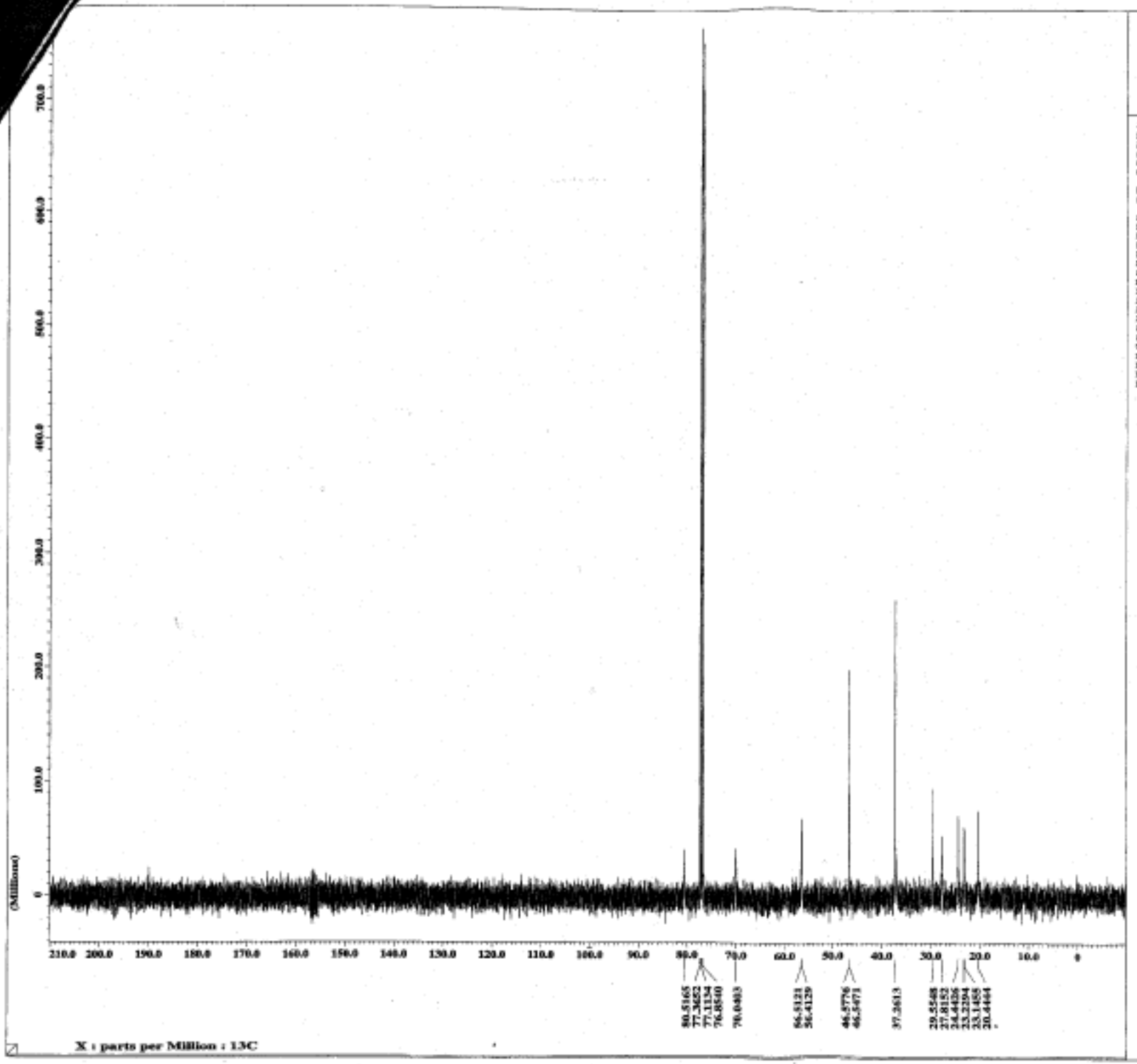
7-Hydroxy-2-azaspiro[5,5]undec-8-ene (5)




(Millions)
X : parts per Million : 1H
7.2525
3.5987
3.5831
3.5758
2.8016
2.7832
2.5835
2.5615
2.2115
2.2070
1.8845
1.8625
1.7260
1.7195
1.7012
1.5189
1.5106
1.4877
1.3805
1.3732
1.3658
1.3540
-0.0112
1.833
0.973
1
3.68
0.727
1.943
2.014
2.082
1.977
2.004
2.041


OH
N

(±)-Sibirine



JEOL

```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_13c_spectrum.fid
Author          = 
Sample ID       = F.P.
Content         = Single Pulse with Broad
Creation Date   =  5-SEP-2006 19:14:26

Revision Date   =  7-SEP-2006 06:17:35
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = 1
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Nuclei          = 400
Mod_return      = 1
X_domain        = 13C
X_offset        = 100[ppm]
X_freq          = 125.77787547[MHz]
X_sweep         = 31.44656988[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 15[Hz]
Temp_get        = 26.1[DC]
Recvr_gain      = 22
Field_strength  = 11.7473579[T]
Filter_mode     = NOTHROUGH
Filter_width    = 15.72066221[kHz]
```

(±)-Sibirine