Supporting Information

CO-Trapping Reaction under Thermolysis of Alkoxyamines.

Application to the Synthesis of 3,4-Cyclopenta-1-Tetralones

Yoshitaka Uenoyama, † Masaaki Tsukida, † Takashi Doi, † Ilhyong Ryu,*, † and

Armido Studer* ‡

† Department of Chemistry, Graduate School of Science, Osaka Prefecture University,

Sakai, Osaka 599-8531, Japan

‡ Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,

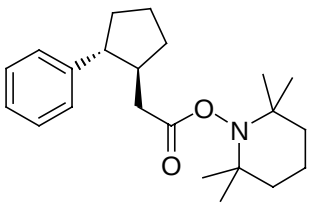
Corrensstrasse 40, 48149 Münster, Germany

General information. ^{1}H NMR spectra were recorded with a JEOL JMN ECP-500 (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 ECP-500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. 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. GPC was performed on a JAI LC-908 chromatograph with JAIGEL-1H + JAIGEL-2H columns. Alkoxyamines **1a-1h** were prepared from the corresponding benzyl bromides and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) according the procedure described in reference 2. Alkoxyamine **1i** was prepared from 6-bromo-6-phenyl-1-hexene[1] and the corresponding nitroxide according to the similar procedure. Products were purified by flash chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N, 70-230 mesh).

Experimental procedure for carbonylation of 1a (entry 1 of Table 1).

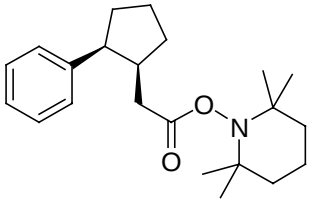
A magnetic stirring bar, 2,2,6,6-tetramethyl-1-(1-phenylhex-5-enoyloxy)piperidine **1a** (157.7 mg, 0.50 mmol) and ^{t}BuOH (50 mL) were placed in a 100 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized to 85 atm of CO and then heated at 130 ^{o}C. After 12 h, excess CO was discharged at room temperature. And the solvent was removed under reduced pressure. After adding ether (5 mL) and 1%-NaOHaq (5 mL) to the residue, the aqueous phase was then separated, washed twice with ether, and acidified with 2M-HCl. This solution was extracted with ether twice. The ether phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*, to give carboxylic acid **4a** as the product (14.2 mg, 14%), which was essentially pure by NMR that there was no need for further purification. On the other hand, the organic phase was washed with brine, dried over Na_2SO_4 and then filtrated. After evaporation, tetrachloroethane (0.121 mmol) was added to the residue as a standard and the yield of **2a** was determined to be 7% by NMR. After determining the NMR yield, the crude mixture was purified by column chromatography on slica gel (eluent: hexane/EtOAc = 10/1) to give **3a** (41.5 mg, 24%). The separation of the cis- and trans-isomers of **3a** was achieved using a preparative HPLC.

trans-1-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy-carbonylmethyl)cyclopentane (trans-3a)



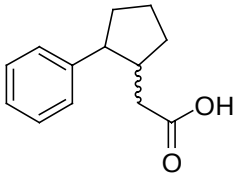
IR (neat) 1763 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (s, 3.00H, C*H*$_3$), 1.01 (s, 3.00H, C*H*$_3$),1.10 (s, 3.00H, C*H*$_3$), 1.11 (s, 3.00H, C*H*$_3$), 1.32-1.82 (m, 10.00H, C*H*$_2$), 2.04-2.22 (m, 3.00H, C*H*$_2$CO, C*H*$_2$), 2.32-2.41 (m, 1.00H, C*H*CH$_2$CO), 2.45 (dd, *J* = 15.12, 3.67 Hz, 1.00H, C*H*$_2$CO), 2.53-2.59 (m, 1.00H, PhC*H*), 7.19-7.32 (m, 5.00H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.03, 20.60, 23.79, 32.05, 32.32, 35.19, 37.17, 39.03, 44.30, 52.86, 59.96, 126.36, 127.64, 128.57, 144.02, 172.81; HRMS (EI) *m/z* calcd for $C_{22}H_{33}NO_2$ (M^+) 343.2511, found 343.2513.

cis-1-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy-carbonylmethyl)cyclopentane (cis-3a)



^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 3.00H, C*H*$_3$), 1.00 (s, 3.00H, C*H*$_3$),1.08 (s, 3.00H, C*H*$_3$), 1.10 (s, 3.00H, C*H*$_3$), 1.35-2.03 (m, 13.00H, C*H*$_2$CO, C*H*$_2$), 2.05-2.22 (m, 1.00H, C*H*$_2$CO), 2.64-2.72 (m, 1.00H, C*H*CH$_2$CO), 3.30-3.45 (m, 1.00H, PhC*H*), 7.17-7.32 (m, 5.00H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.03, 20.60, 23.55, 30.38, 31.45, 34.64, 39.04, 40.54, 44.30, 48.32, 59.97, 126.12, 128.27, 128.53, 142.94, 173.28.

2-Phenylcyclopentylacetic acid (4a)

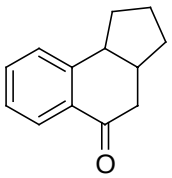


IR (neat) 1707, 2400-3600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17-2.15 (m, 7.32H, C*H*$_2$CO, trans, C*H*$_2$CO, cis, C*H*$_2$), 2.20-2.32 (m, 0.68H, C*H*CH$_2$CO, trans), 2.41 (dd, *J* = 15.12, 4.12 Hz, 0.68H, C*H*$_2$CO, trans), 2.48-2.66 (m, 1.00H, PhC*H*, trans, C*H*CH$_2$CO, cis), 3.26-3.32 (m, 0.32H, PhC*H*, cis), 7.10-7.38 (m, 5.00H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.50 (cis), 23.76 (trans), 30.05 (cis), 31.08 (cis), 32.16 (trans), 35.01 (trans), 35.88 (cis), 38.36 (trans), 40.42 (cis), 44.42 (trans), 48.18 (cis), 52.54 (trans), 126.24 (cis), 126.40 (trans), 127.61 (trans), 128.30 (cis), 128.45 (cis), 128.55 (trans), 142.59 (cis), 143.95 (trans), 179.64 (trans), 180.01 (cis); HRMS (EI) *m/z* calcd for $C_{13}H_{16}O_2$ (M^+) 204.1150, found 204.1146.

Typical Procedure for 3,4-Cyclopenta-1-tetralones 2. A magnetic stirring bar, 2,2,6,6-tetramethyl-1-(1-phenylhex-5-enoyloxy)piperidine **1a** (156.8 mg, 0.5 mmol) and ^{t}BuOH (50 mL) were placed in a 100 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized to 75 atm of CO, then

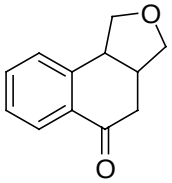
heated 130 ^{o}C (bath temp.) for 20 h. Excess CO was then discharged at room temperature. The solvent was removed under reduced pressure. CF_3SO_3H (3 mL) was added to the residue, followed by stirring for 2 h at 50°C (bath temp). After quenching with ice, the solution was extracted with ether three times, the organic layer was washed with brine and then dried over Na_2SO_4. After evaporation, the residue was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 30/1) to give **2a** (46.6 mg, 51%).

1,2,3,3a,4,9b-Hexahydro-cyclopenta[*a*]naphthalen-5-one (2a)



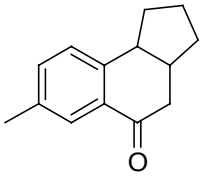
Obtained as a diastereomer mixture. mp 89-90 ^{o}C; IR (neat) 1682 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-2.08 (m, 5.65H, C*H*$_2$), 2.15-2.26 (m, 0.35H, C*H*$_2$, cis), 2.31-2.46 (m, 1.30H, C*H*$_2$CO, C*H*CH$_2$CO, trans), 2.53-2.80 (m, 1.70H, C*H*$_2$CO, cis, C*H*CH$_2$CO, cis, C*H*Ph, trans), 3.00 (dd, *J* = 16.96, 3.67 Hz, 0.65H, C*H*$_2$CO, trans), 3.23-3.30 (m, 0.35H, C*H*Ph, cis), 7.20-7.38 (m, 3.00H, Ar*H*), 7.96 (d, *J* = 7.33 Hz, 0.35H, Ar*H*, cis), 8.03 (d, *J* = 7.79 Hz, 0.65H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.21 (trans), 23.75 (cis), 28.41 (trans), 31.00 (trans), 31.41 (cis), 33.18 (cis), 38.61 (cis), 40.85 (cis), 42.86 (cis), 44.24 (trans), 45.51 (trans), 46.59 (trans), 126.24 (trans), 126.37 (cis), 126.50 (trans), 126.66 (cis), 127.64 (trans), 129.23 (cis), 131.61 (cis), 132.33 (trans), 133.54 (trans), 133.74 (cis), 146.34 (cis), 146.96 (trans), 199.03 (cis), 199.22 (trans); HRMS (EI) *m/z* calcd for $C_{13}H_{14}O$ (M^+) 186.1045, found 186.1044;

1,3,3a,9b-Tetrahydronaphtho[1,2-c]furan-5(4H)-one (2b)[3]



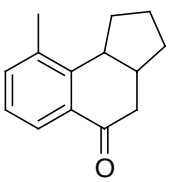
Obtained as a diastereomer mixture. IR (neat) 1686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.72-2.79 (m, 1.18H, C*H*$_2$CO, cis), 2.99-3.08 (m, 0.59H, C*H*CH$_2$CO, cis), 3.00-3.04 (m, 0.82H, C*H*$_2$CO, trans), 3.15-3.20 (m, 0.41H, C*H*CH$_2$CO, trans), 3.62-3.70 (m, 1.00H, PhC*H*), 3.72-3.92 (m, 2.00H, C*H*$_2$O), 4.10 (dd, J = 8.71, 5.96 Hz, 0.59 H, C*H*$_2$O, cis), 4.18 (t, *J* = 7.33 Hz, 0.41H, C*H*$_2$O, trans), 4.33 (t, *J* = 8.25 Hz, 0.59H, C*H*$_2$O, cis), 4.56 (t, *J* = 7.33 Hz, 0.41H, C*H*$_2$O,trans), 7.07 (d, *J* = 7.79 Hz, 0.41H, Ar*H*, trans), 7.26 (d, *J* = 7.79 Hz, 0.59H, Ar*H*, cis), 7.36 (t, *J* = 7.79 Hz, 0.59H, Ar*H*, cis), 7.40 (d, *J* = 7.79 Hz, 0.41H, Ar*H*, trans), 7.52-7.57 (m, 1.00H, Ar*H*), 8.00 (d, *J* = 7.79 Hz, 0.59H, Ar*H*, cis), 8.07 (d, *J* = 7.79, 0.41H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.47, 38.74, 41.39, 41.91, 43.40, 45.57, 70.06, 71.76, 73.39, 73.71, 125.74, 127.06, 127.36, 127.47, 128.21, 129.38, 131.60 (cis), 132.27 (trans), 133.84 (trans), 134.13 (cis), 141.63 (cis), 142.24 (trans), 197.16 (trans), 197.38 (cis); HRMS (EI) *m/z* calcd for $C_{12}H_{12}O_2$ (M^+) 188.0837, found 188.0830.

7-Methyl-1,2,3,3a,4,9b-hexahydro-cyclopenta[*a*]naphthalen-5-one (2c)



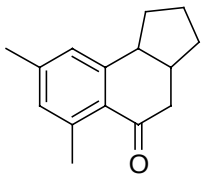
Obtained as a diastereomer mixture. mp 81-82 °C; IR (neat) 1682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.18-2.05 (m, 5.67H, C*H*$_2$), 2.11-2.23 (m, 0.33H, C*H*$_2$, cis), 2.25-2.41 (m, 1.34H, C*H*$_2$CO, C*H*CH$_2$CO, trans), 2.35 (s, 2.01H, PhC*H*$_3$, cis), 2.37 (s, 0.99H, PhC*H*$_3$, trans), 2.50-2.80 (m, 1.66H, C*H*$_2$CO, cis, C*H*CH$_2$CO, cis, C*H*Ph, trans), 2.96 (dd, *J* = 16.96, 3.67 Hz, 0.67H, C*H*$_2$CO, trans), 3.18-3.27 (m, 0.33H, C*H*Ph, cis), 7.12-7.38 (m, 2.00H, Ar*H*), 7.77 (s, 0.33H, Ar*H*, cis), 7.84 (s, 0.67H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.09 (cis), 21.10 (trans), 22.23 (trans), 23.76 (cis), 28.51 (trans), 30.95 (trans), 31.23 (cis), 33.21 (cis), 38.72 (cis), 40.92 (cis), 42.51 (cis), 44.39 (trans), 45.53 (trans), 46.30 (trans), 126.17 (trans), 126.73 (cis), 127.86 (trans), 129.15 (cis), 131.40 (cis), 132.11 (trans), 134.37 (trans), 134.77 (cis), 136.02 (cis), 136.14 (trans), 143.44 (cis), 144.17 (trans), 199.26 (cis), 199.46 (trans); HRMS (EI) *m/z* calcd for $C_{14}H_{16}O$ (M^+) 200.1201, found 200.1194;

9-Methyl-1,2,3,3a,4,9b-hexahydro-cyclopenta[*a*]naphthalen-5-one (2d)



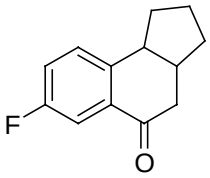
Obtained as a diastereomer mixture. mp 105-107 °C; IR (neat) 1682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.18-2.05 (m, 5.53H, C*H*$_2$), 2.22-2.58 (m, 1.53H, C*H*$_2$, cis, C*H*$_2$CO, trans, C*H*CH$_2$CO, trans), 2.36 (s, 1.41H, PhC*H*$_3$, cis), 2.43 (s, 1.59H, PhC*H*$_3$, trans), 2.60-2.82 (m, 1.94H, C*H*$_2$CO, cis, C*H*CH$_2$CO, cis, C*H*Ph, trans), 2.95 (dd, *J* = 16.04, 3.21 Hz, 0.53H, C*H*$_2$CO, trans), 3.20-3.24 (m, 0.47H, C*H*Ph, cis), 7.17-7.40 (m, 2.00H, Ar*H*), 7.87 (d, *J* = 7.79 Hz, 0.47H, Ar*H*, cis), 7.97 (s, *J* = 7.79 Hz 0.53H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.35 (cis), 21.78 (trans), 22.43 (trans), 23.27 (cis), 29.39 (cis), 30.17 (trans), 30.88 (trans), 31.65 (cis), 39.34 (cis), 40.09 (cis), 40.76 (cis), 44.02 (trans), 44.41 (trans), 46.81 (trans), 124.73 (cis), 126.01 (cis), 126.08 (trans), 126.27 (trans), 131.50 (cis), 133.59 (trans), 135.45 (cis), 136.14 (trans), 136.80 (cis), 136.84 (trans), 144.78 (cis), 145.03 (trans), 199.11 (cis), 199.36 (trans); HRMS (EI) *m/z* calcd for $C_{14}H_{16}O$ (M^+) 200.1201, found 200.1199;

6,8-Dimethyl-1,2,3,3a,4,9b-hexahydro-cyclopenta[*a*]naphthalen-5-one (2e)



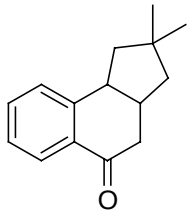
Obtained as a diastereomer mixture. mp 82-84 °C; IR (neat) 1673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.20-2.02 (m, 5.74H, C*H*$_2$), 2.12-2.24 (m, 0.26H, C*H*$_2$, cis), 2.26-2.40 (m, 1.48H, C*H*$_2$CO, C*H*CH$_2$CO, trans), 2.31 (s, 0.78H, PhC*H*$_3$, cis), 2.34 (s, 2.22H, PhC*H*$_3$, trans), 2.50-2.73 (m, 1.52H, C*H*$_2$CO, cis, C*H*CH$_2$CO, cis, C*H*Ph, trans), 2.56 (s, 0.78H, PhC*H*$_3$, cis), 2.61 (s, 2.22H, PhC*H*$_3$, trans), 2.93 (dd, *J* = 17.41, 4.58 Hz, 0.74H, C*H*$_2$CO, trans), 3.17-3.22 (m, 0.26H, C*H*Ph, cis), 6.68-6.92 (m, 2.00H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.53, 21.66, 22.44, 22.85, 23.15, 23.89, 28.97, 31.05, 31.88, 33.97, 38.15, 43.39, 43.66, 44.71, 47.00, 47.12, 124.66 (trans), 127.85 (cis), 128.14 (cis), 128.51 (trans), 130.96 (cis), 131.33 (trans), 140.18 (cis), 141.64 (trans), 142.87 (trans), 143.30 (cis), 147.65 (cis), 148.13 (trans), 200.68 (trans), 200.90 (cis); HRMS (EI) *m/z* calcd for $C_{15}H_{18}O$ (M^+) 214.1358, found 214.1358;

7-Fluoro-1,2,3,3a,4,9b-hexahydro-cyclopenta[*a*]naphthalen-5-one (2f)



Obtained as a diastereomer mixture. mp 54-56 ^{o}C; IR (neat) 1690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35-2.08 (m, 5.59H, C*H*$_2$), 2.10-2.23 (m, 0.41H, C*H*$_2$, cis), 2.28-2.43 (m, 1.18H, C*H*$_2$CO, C*H*CH$_2$CO, trans), 2.51-2.78 (m, 1.82H, C*H*$_2$CO, cis, C*H*CH$_2$CO, cis, C*H*Ph, trans), 3.00 (dd, *J* = 17.41, 3.67 Hz, 0.59H, C*H*$_2$CO, trans), 3.18-3.26 (m, 0.41H, C*H*Ph, cis), 7.17-7.32 (m, 2.00H, Ar*H*), 7.61 (dd, *J* = 9.17, 2.75 Hz, 0.41H, Ar*H*, cis), 7.68 (dd, *J* = 9.17, 2.75 Hz, 0.59H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.12 (trans), 23.69 (cis), 28.61 (trans), 30.84 (trans), 31.24 (cis), 33.19 (cis), 38.64 (cis), 40.52 (cis), 42.27 (cis), 44.35 (trans), 45.20 (trans), 46.07 (trans), 112.52 (d, $^{2}J_{C\text{-}F}$ = 22.07 Hz, cis), 113.79 (d, $^{2}J_{C\text{-}F}$ = 22.07 Hz, trans), 120.53 (d, $^{2}J_{C\text{-}F}$ = 22.07 Hz, trans), 121.03 (d, $^{2}J_{C\text{-}F}$ = 22.07 Hz, cis), 128.12 (d, $^{3}J_{C\text{-}F}$ = 7.68 Hz, trans), 131.07 (d, $^{3}J_{C\text{-}F}$ = 7.68 Hz, cis), 133.19 (d, $^{3}J_{C\text{-}F}$ = 6.72 Hz, cis), 134.06 (d, $^{3}J_{C\text{-}F}$ = 5.76 Hz, trans), 142.00 (d, $^{4}J_{C\text{-}F}$ = 2.88 Hz, cis), 142.75 (d, $^{4}J_{C\text{-}F}$ = 2.88 Hz, trans), 161.56 (d, $^{1}J_{C\text{-}F}$ = 245.68 Hz, trans), 161.77 (d, $^{1}J_{C\text{-}F}$ = 246.64 Hz, cis), 197.92 (cis), 198.12 (trans); HRMS (EI) *m/z* calcd for $C_{13}H_{13}FO$ (M^{+}) 204.0950, found 204.0947

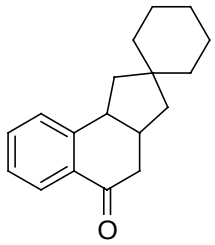
2,2-Dimethyl-1,2,3,3a,4,9b-hexahydro-cyclopenta[*a*]naphthalen-5-one (2g)



Obtained as a diastereomer mixture. IR (neat) 1684 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, C*H*$_3$), 1.12 (s, C*H*$_3$), 1.13 (s, C*H*$_3$), 1.20 (s, C*H*$_3$), 1.34-1.43 (m, C*H*$_2$), 1.52 (dd, *J* = 11.91, 11.91 Hz, C*H*$_2$), 1.79-1.85 (m, C*H*$_2$), 2.00 (dd, *J* = 12.83, 7.33 Hz, C*H*$_2$), 2.10-2.23 (m, 0.54H, C*H*CH$_2$CO, trans), 2.20 (dd, *J* = 11.91, 6.87 Hz, C*H*$_2$), 2.36 (dd, *J* = 16.96, 13.29 Hz, 0.54H, C*H*$_2$CO, trans), 2.60-2.69 (m, 0.92H, C*H*$_2$CO, cis), 2.80-2.89 (m, 1.00H, C*H*CH$_2$CO, cis, PhC*H*, trans), 2.92 (dd, *J* = 16.96, 3.67 Hz, 0.54H, C*H*$_2$CO, trans), 3.43-3.48 (m, 0.46H, PhC*H*, cis), 7.18-7.50 (m, 3.00H, Ar*H*), 7.93 (d, *J* = 7.79 Hz, 0.46H,

Ar*H*, cis), 8.02 (d, *J* = 7.79 Hz, 0.54H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.33, 31.46, 32.08, 32.21, 37.26, 38.08, 38.79, 41.77, 42.05, 43.73, 44.93, 45.43, 46.07, 47.09, 47.58, 48.99, 126.08 (trans), 126.26 (cis), 126.50 (trans), 126.58 (cis), 127.64 (trans), 129.14 (cis), 131.80 (cis), 132.37 (trans), 133.51 (trans), 133.69 (cis), 146.30 (cis), 147.07 (trans), 198.98 (cis), 199.02 (trans); HRMS (EI) *m/z* calcd for $C_{15}H_{18}O$ (M^+) 214.1358, found 214.1357.

Spiro[cyclohexane-1,2'-(1',2',3',3a',4',9b'-hexahydro-cyclopenta[*a*]naphthalen-5'-one)] (2h)



Obtained as a diastereomer mixture. IR (neat) 1684 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-1.62 (m, C*H*$_2$), 1.73-1.94 (m, C*H*$_2$), 2.02-2.14(m, 0.42H, C*H*CH_2CO,trans), 2.08 (dd, *J* = 13.29, 7.79 Hz, C*H*$_2$), 2.29 (dd, *J* = 13.27, 6.87 Hz, C*H*$_2$), 2.33 (dd, *J* = 16.96, 13.29 Hz, 0.42H, C*H*$_2$CO, trans), 2.58-2.68 (m, 1.16H, C*H*$_2$CO, cis), 2.74-2.84 (m, 1.00H, PhC*H*, trans, C*H*CH_2CO,cis), 2.93 (dd, *J* = 16.96, 3.67 Hz, 0.42H, C*H*$_2$CO, trans), 3.35-3.39 (m, 0.58H, PhC*H*, cis), 7.23-7.56 (m, 3.00H, Ar*H*), 7.95 (d, *J* = 7.79 Hz, 0.58H, Ar*H*, cis), 8.02 (d, *J* = 7.79 Hz, 0.42H, Ar*H*, trans); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.44, 23.63, 23.73, 24.78, 26.03, 26.06, 37.80, 39.69, 40.48, 40.73, 41.08, 41.50, 41.60, 41.76, 42.83, 42.88, 45.12, 45.51, 126.09 (trans), 126.30 (cis), 126.46 (trans), 126.67 (cis), 127.63 (trans), 129.15 (cis), 131.73 (cis), 132.39 (trans), 133.49 (trans), 133.68 (cis), 146.33 (cis), 147.21 (trans), 199.01 (cis), 199.09 (trans); HRMS (EI) *m/z* calcd for $C_{18}H_{22}O$ (M^+) 254.1671, found 254.1672.

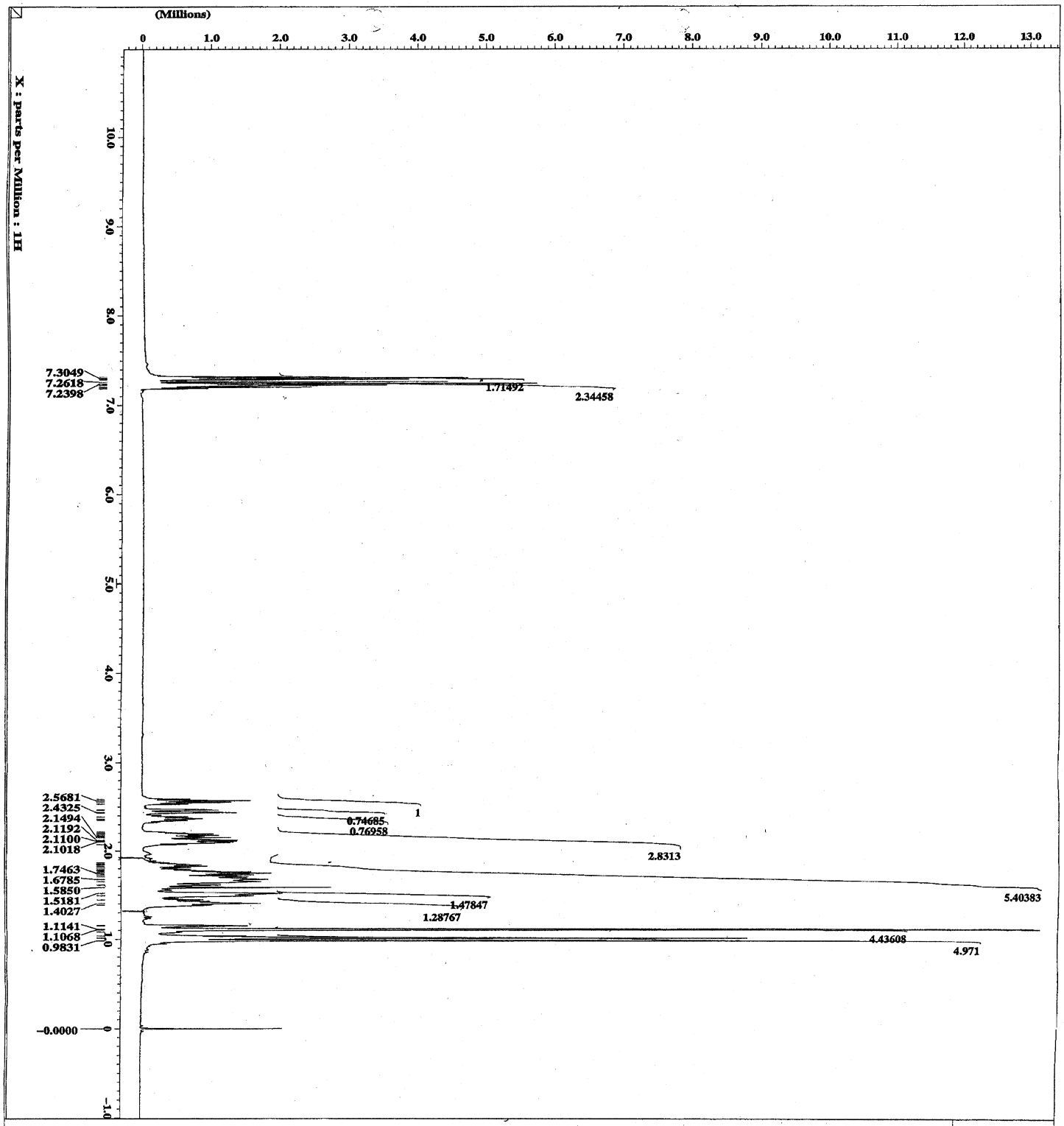
References.

(1) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545.

(2) (a) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W.

Macromolecules **1996**, *29*, 5245. (b) Marque, S.; Fischer, H.; Baier, E.; Studer, A. *J. Org. Chem*, **2001**, *66*, 1146.

(3) Oh, S.-H; Sato, T. *J. Org. Chem.*, **1994**, *59*, 3744.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7.2398
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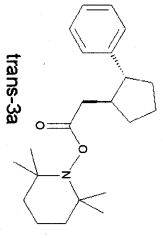
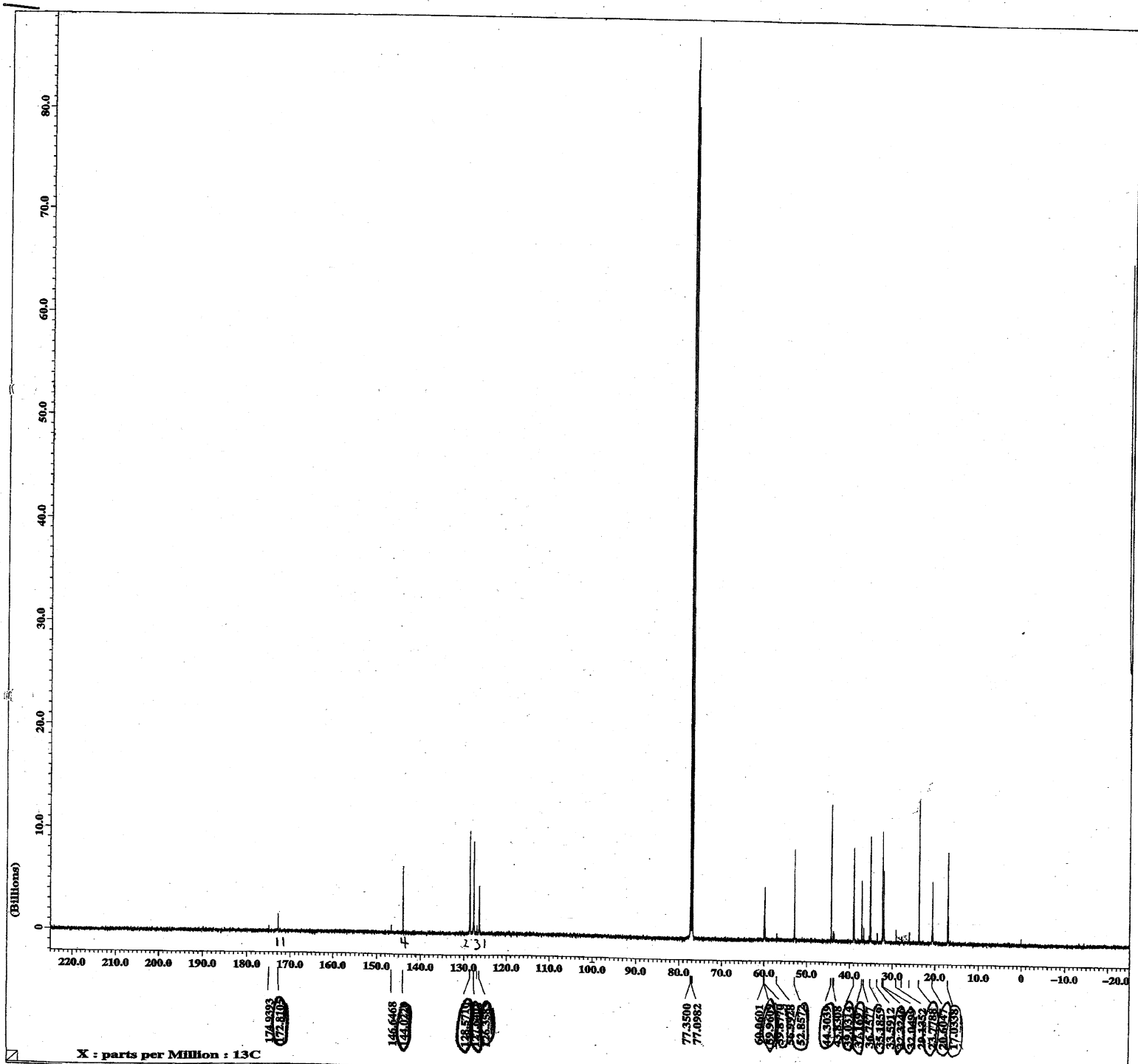
2.34458
2.5681
2.4325
2.1494
2.1192
2.1100
2.1018
1
0.74685
0.76958
2.8313
1.7463
1.6785
1.5850
1.5181
1.4027
1.47847
1.28767
5.40383
1.1141
1.1068
0.9831
4.43608
4.971
-0.0000


trans-3a



JEOL

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---- ACQUISITION PARAMETERS ----
File Name       = 1d_13c_spectrum_copy.9
Author          =
Sample ID       = MAS-TEMPO-017 HPLC-C
Content         = Single Pulse with Broad
Creation Date   = 31-AUG-2004 09:28:17

Revision Date   =  1-SEP-2004 07:03:50
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 22441
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        = 24[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
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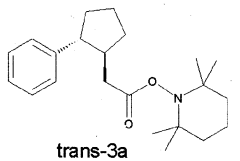
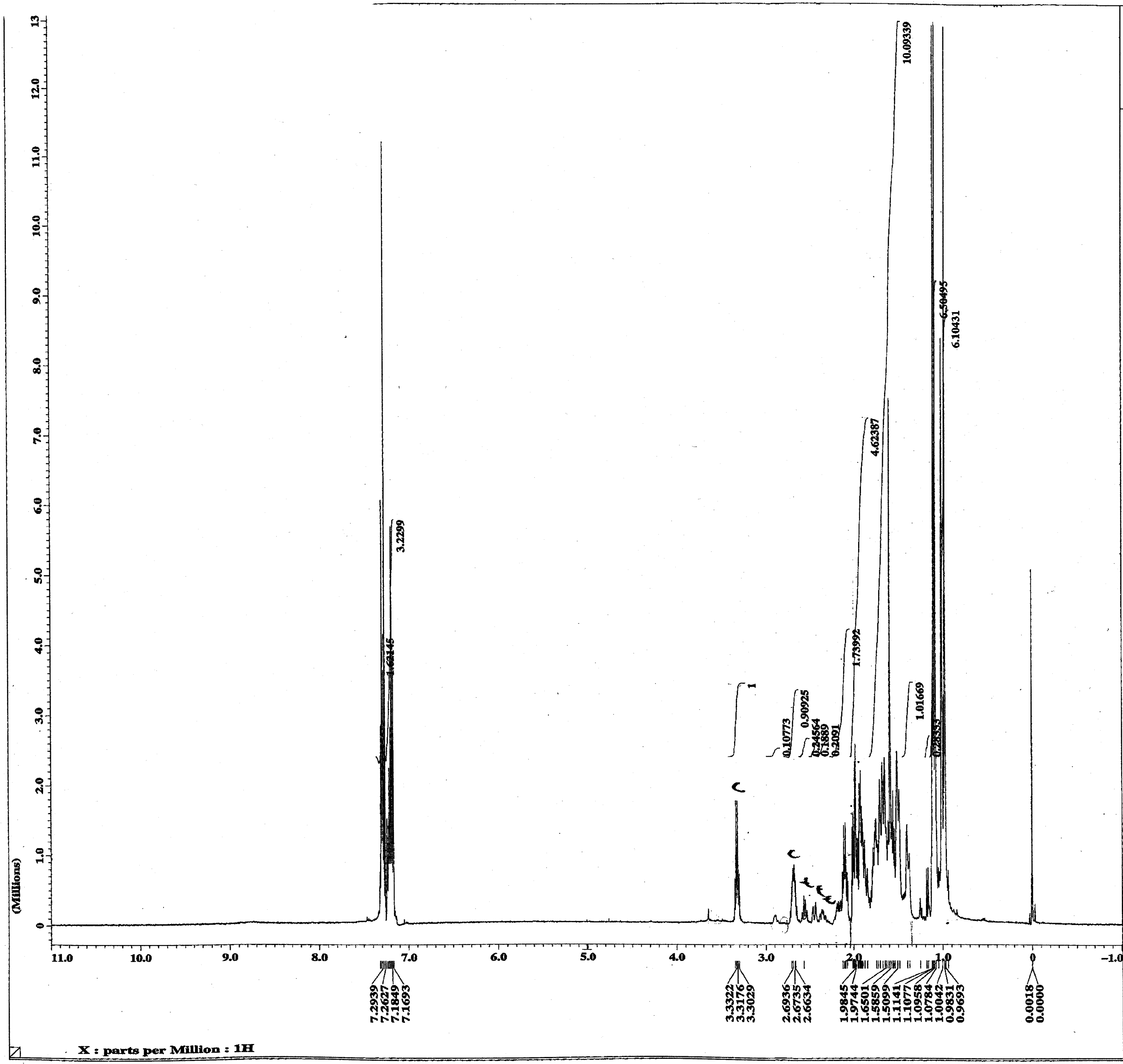


trans-3a



JEOL

---- ACQUISITION PARAMETERS ----

File Name	= 1d_spectrum.550
Author	=
Sample ID	= MAS-TEMPO-017 HPLC-F
Content	= Single Pulse Experiment
Creation Date	= 30-AUG-2004 11:49:56
Revision Date	= 31-AUG-2004 09:24:33
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
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Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
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X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 15[Hz]
Temp_get	= 21.8[dC]
Recvr_gain	= 22
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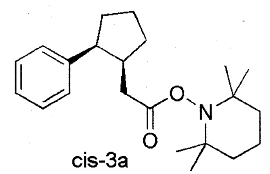
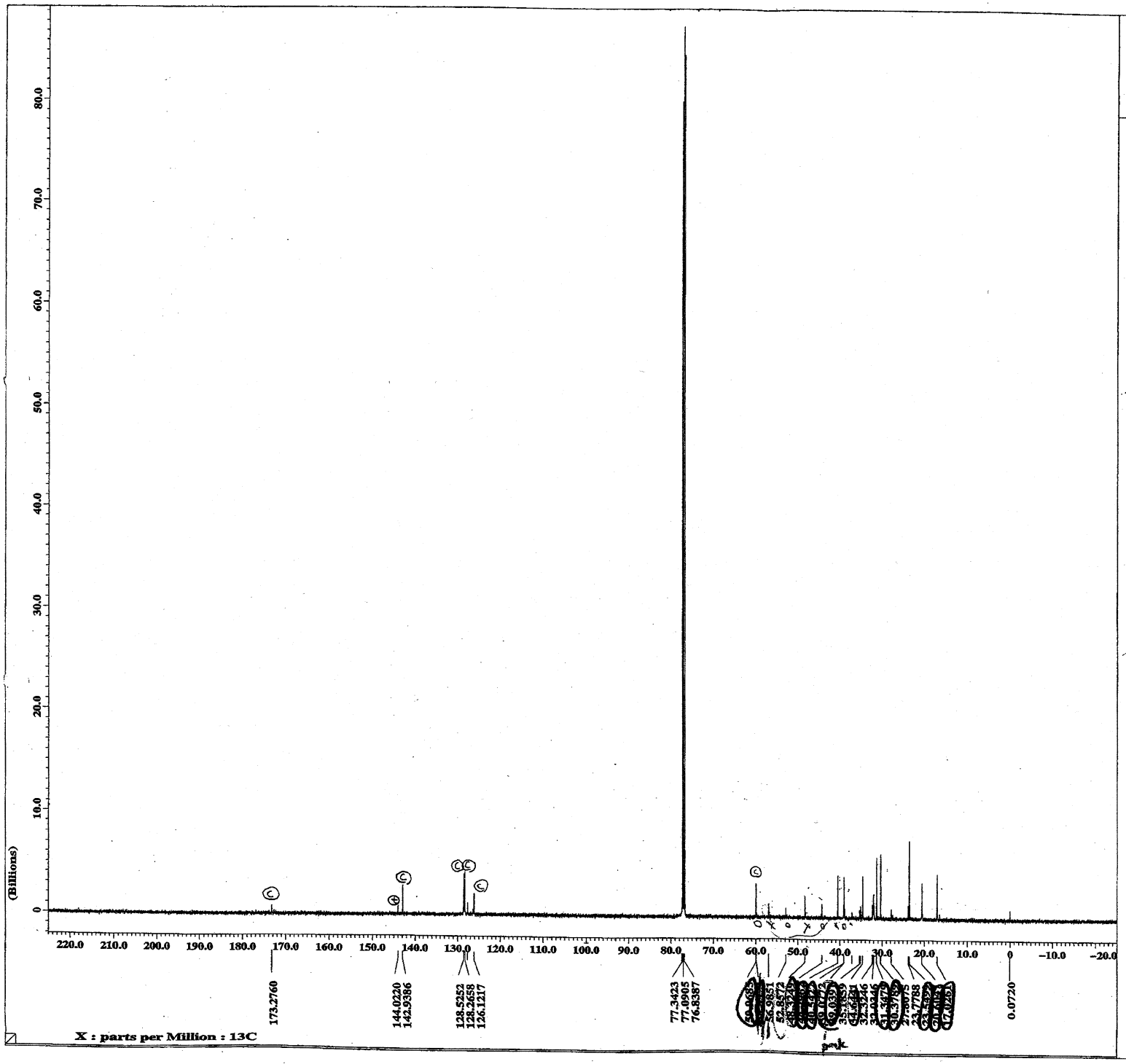


cis-3a



JEOL

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Author          =
Sample ID       = MAS-TEMPO-017 HPLC-F
Content         = Single Pulse with Broad
Creation Date   =  1-SEP-2004 09:21:01

Revision Date   =  2-SEP-2004 06:57:58
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 13C
Dim Size        = 32768
Dim Units       = [ppm]
Scans           = 20849
Mod_prtorn      = 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        = 23.5[dC]
Recvr_gain      = 30
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221[kHz]
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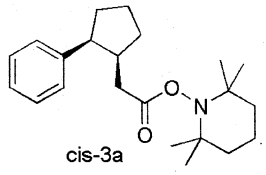
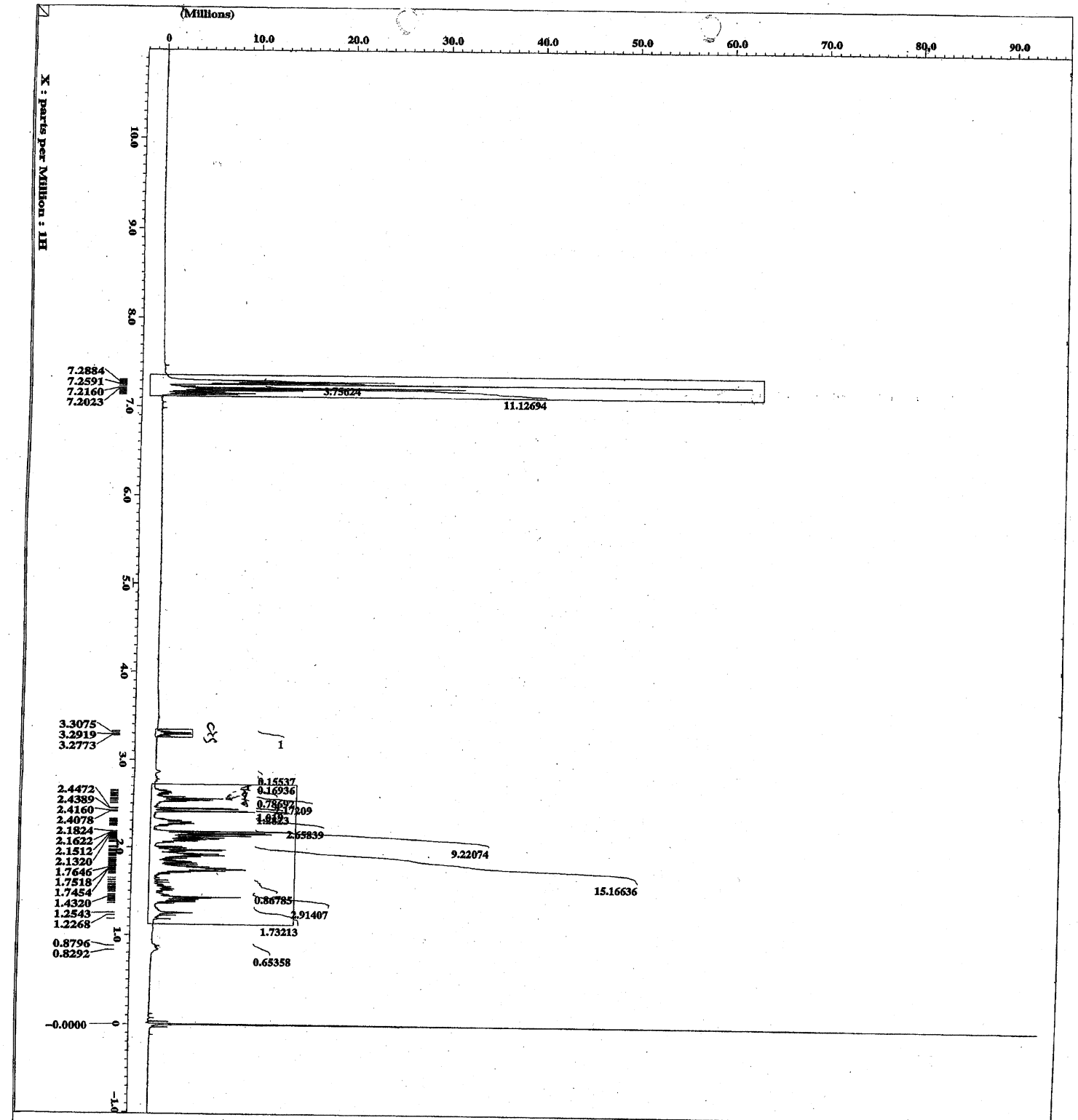


cis-3a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X : parts per Million : 1H
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7.2591
7.2160
7.2023
3.75624
11.12694
3.3075
3.2919
3.2773
1
2.4472
2.4389
2.4160
2.4078
2.1824
2.1622
2.1512
2.1320
1.7646
1.7518
1.7454
1.4320
1.2543
1.2268
0.8796
0.8292
0.15537
0.16936
0.78697
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1.0423
2.65839
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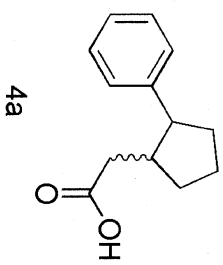
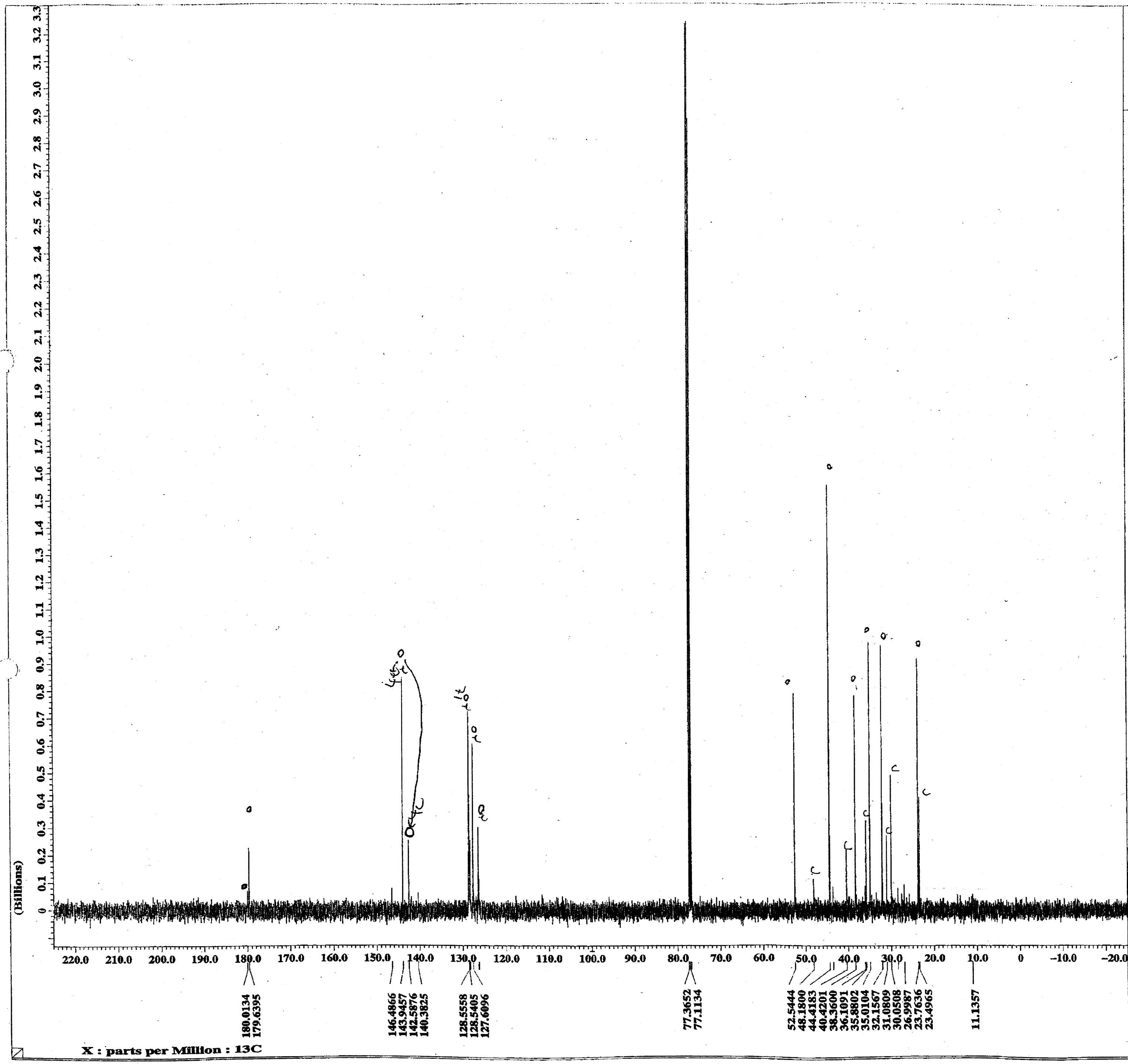

O
OH

4a



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Author =
Sample ID = fr4-10
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Creation Date = 22-MAY-2004 11:02:48

Revision Date = 23-MAY-2004 06:52:44
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Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
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X_offset = 100[ppm]
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X_sweep = 31.44654088[kHz]
Solvent = CHLOROFORM-D
Spin_get = 17[Hz]
Temp_get = 25[dC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
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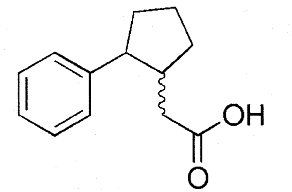
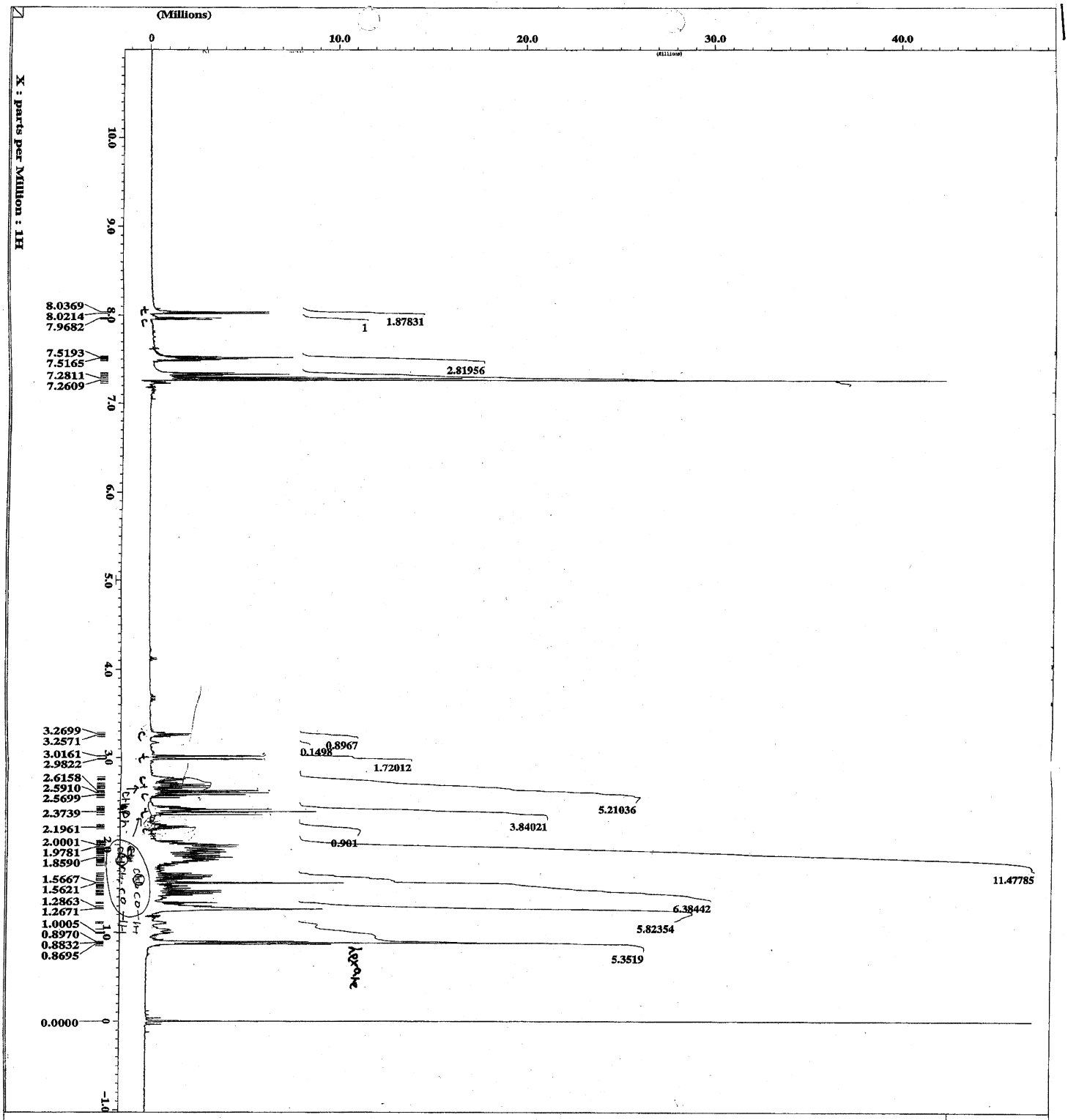
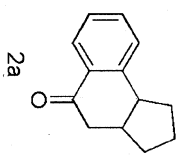


4a





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File Name = 1d_spectrum.1514
Author = mas-MEMPO-029 ft-11
Comment = Single Pulse Experiment
Creation Date = 28-SEP-2004 16:25:41
Revision Date = 29-SEP-2004 14:34:54
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
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Dim Size = 16384
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X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
X_scans = CHLOROFORM-D
Spin_get = 15[Hz]
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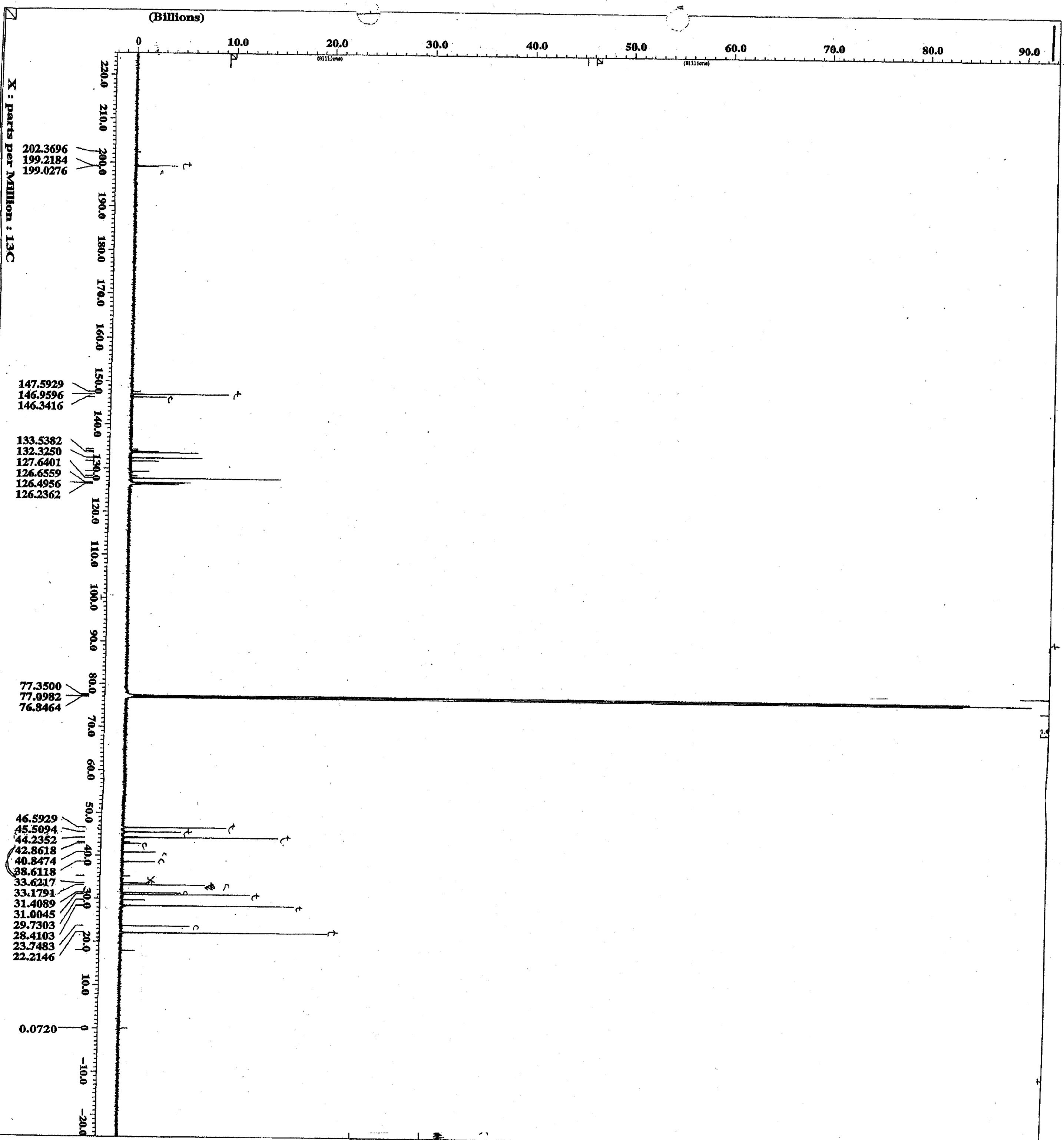
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126.6559
126.4956
126.2362
77.3500
77.0982
76.8464
46.5929
45.5094
44.2352
42.8618
40.8474
38.6118
33.6217
33.1791
31.4089
31.0045
29.7303
28.4103
23.7483
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Sample ID = MAS-TEMPO-022 fr4-7
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Creation Date = 7-SEP-2004 09:27:43
Revision Date = 8-SEP-2004 07:09:34
Spec Site = ECP500
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Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
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Solvent = CHLOROFORM-D
Spin_get = 17[Hz]
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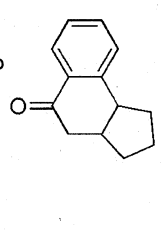

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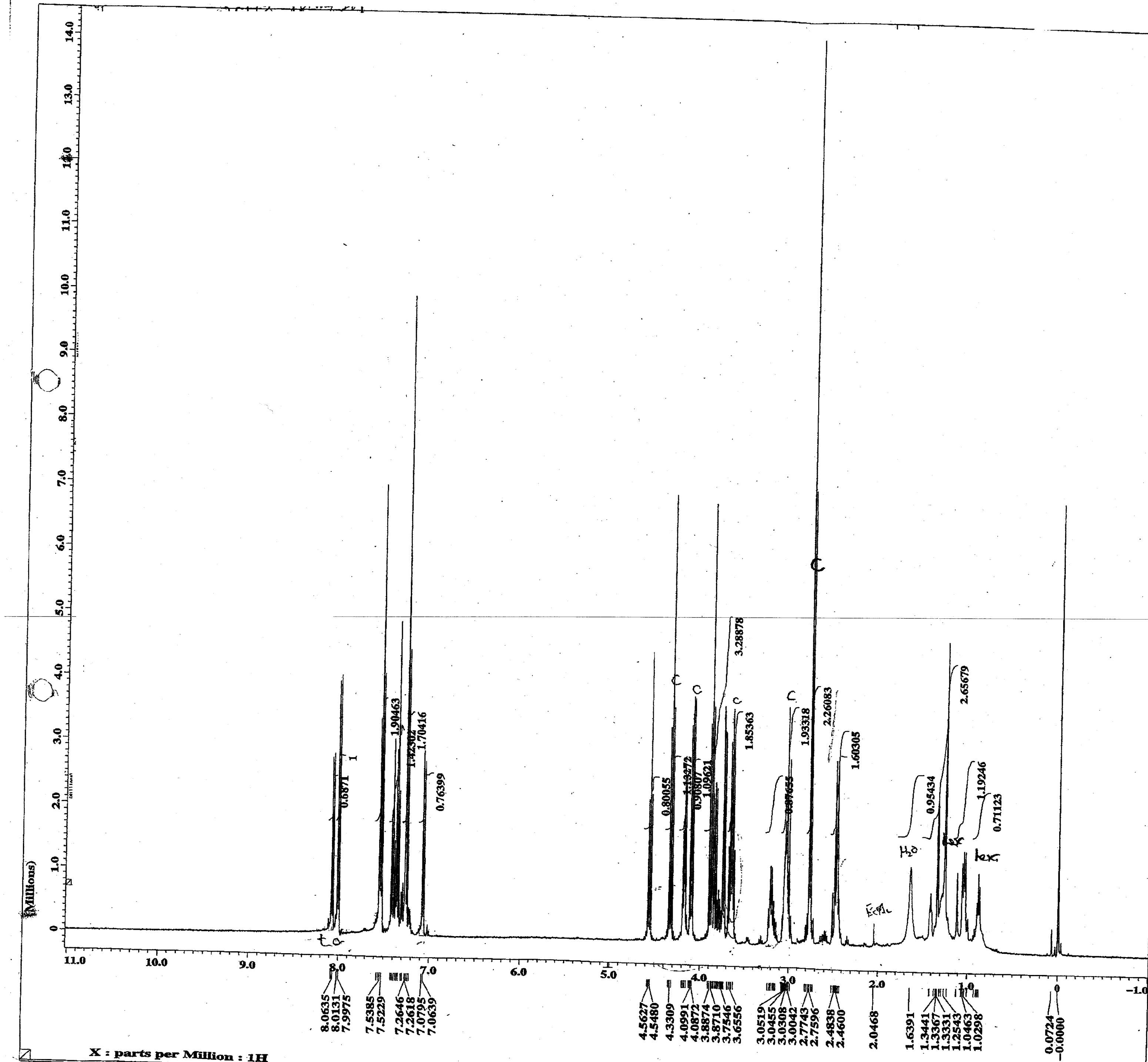

JEOL

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Sample ID = MAS-TEMPO-028 fr21-40
Content = Single Pulse Experiment
Creation Date = 21-SEP-2004 13:26:36

Revision Date = 22-SEP-2004 11:27:03
Spec Site = ECP500

Spec Type = DELTA_NMR
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Dim Title = 1H
Dim Size = 16384
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Solvent = CHLOROFORM-D
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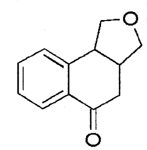
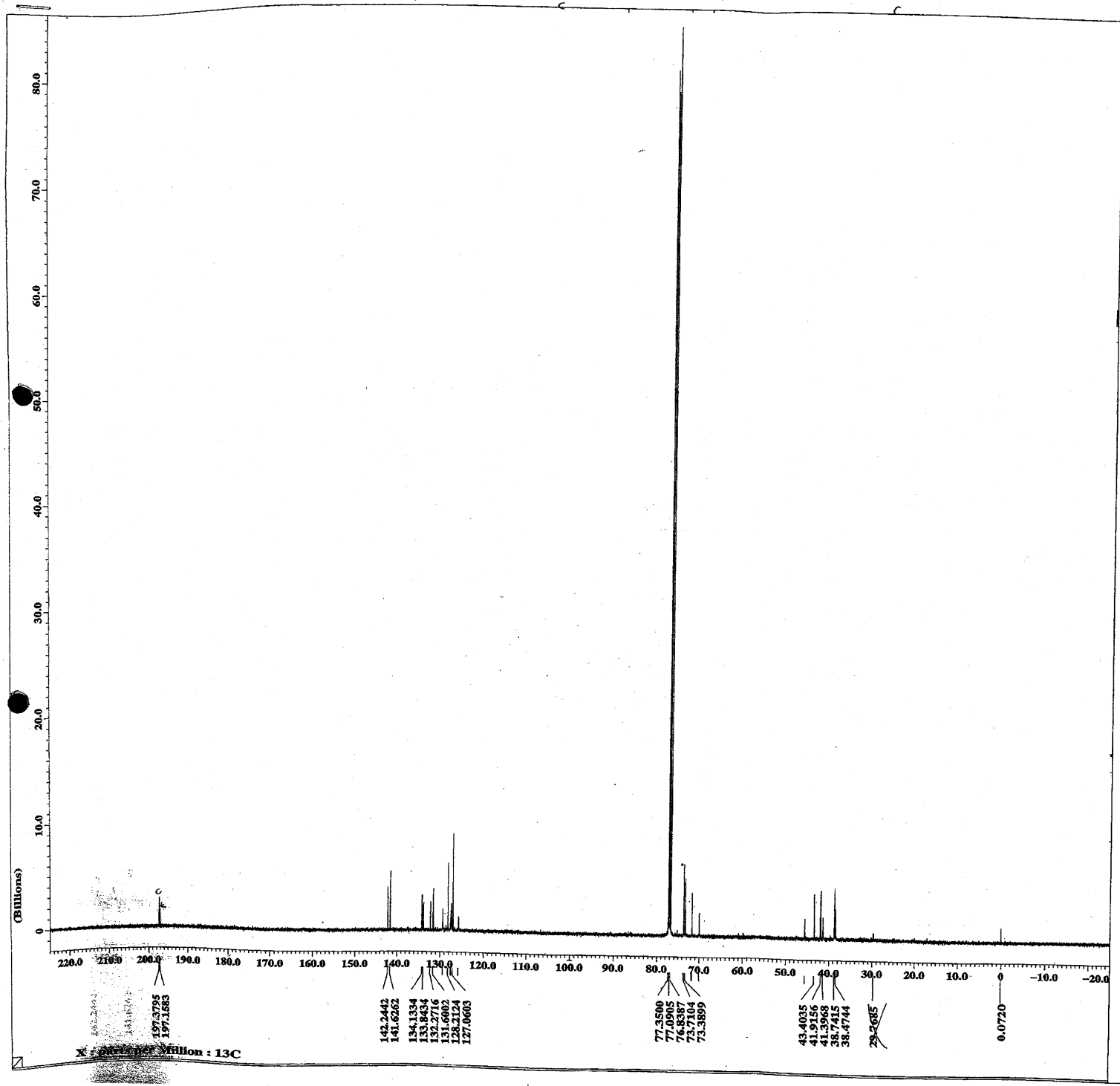


2b



JEOL

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Sample ID          = MAS-TEMPO-028 fr22-40
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Creation Date      = 22-SEP-2004 09:22:58

Revision Date      = 23-SEP-2004 07:23:08
Spec Site          = ECP500

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Data Format        = 1D COMPLEX
Dimensions         = X
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X_sweep            = 31.44654088[kHz]
Solvent            = CHLOROFORM-D
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Temp_get           = 24.8[dC]
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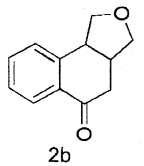
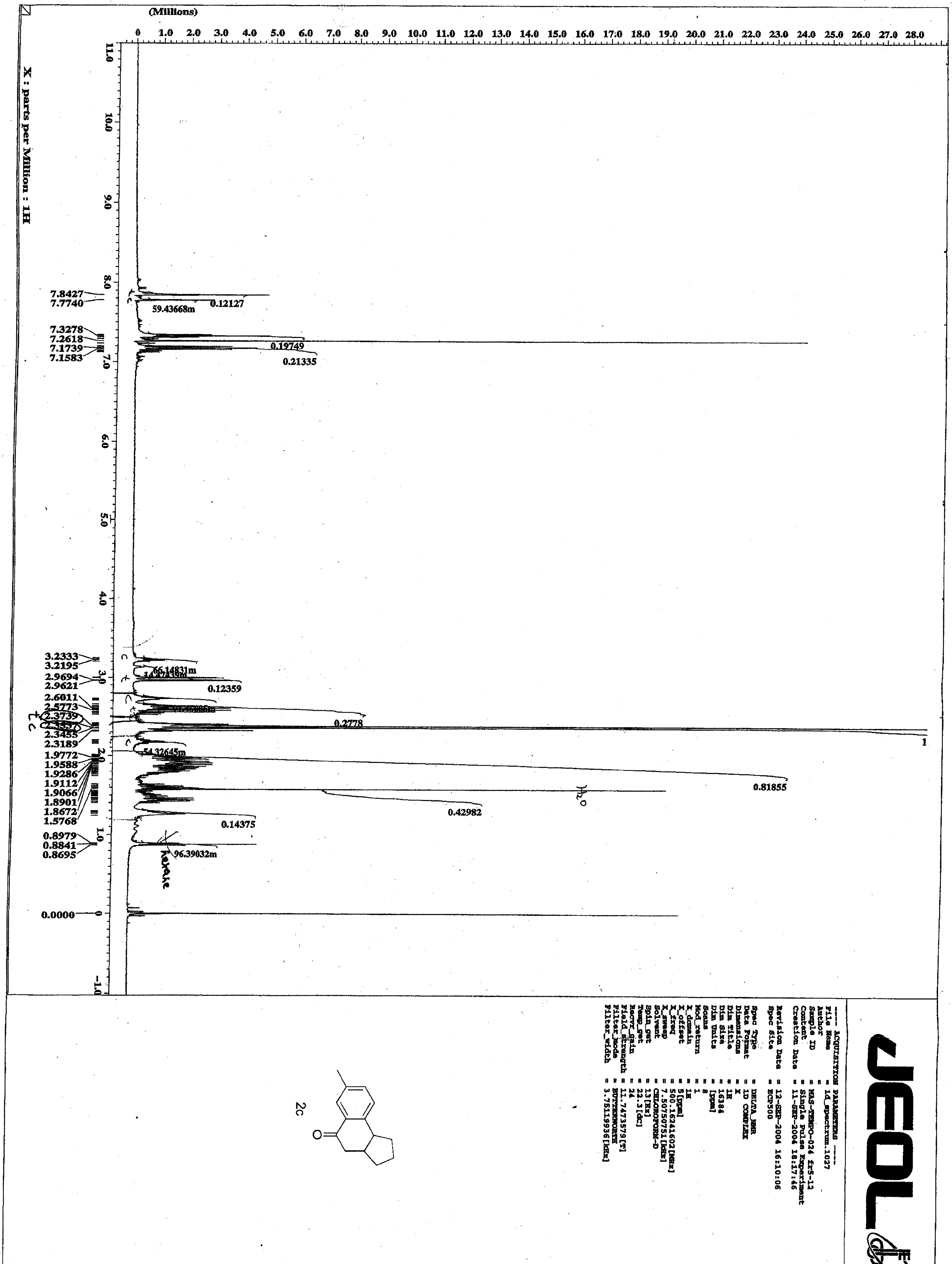


2b



(Millions)
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7.1739
7.1583
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0.21335
3.2333
3.2195
2.9694
2.9621
2.6011
2.5773
2.3739
2.3455
2.3189
1.9772
1.9588
1.9286
1.9112
1.9066
1.8901
1.8672
1.5768
0.8979
0.8841
0.8695
0.0000
66.14831m
0.12359
0.2778
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0.81855
0.42982
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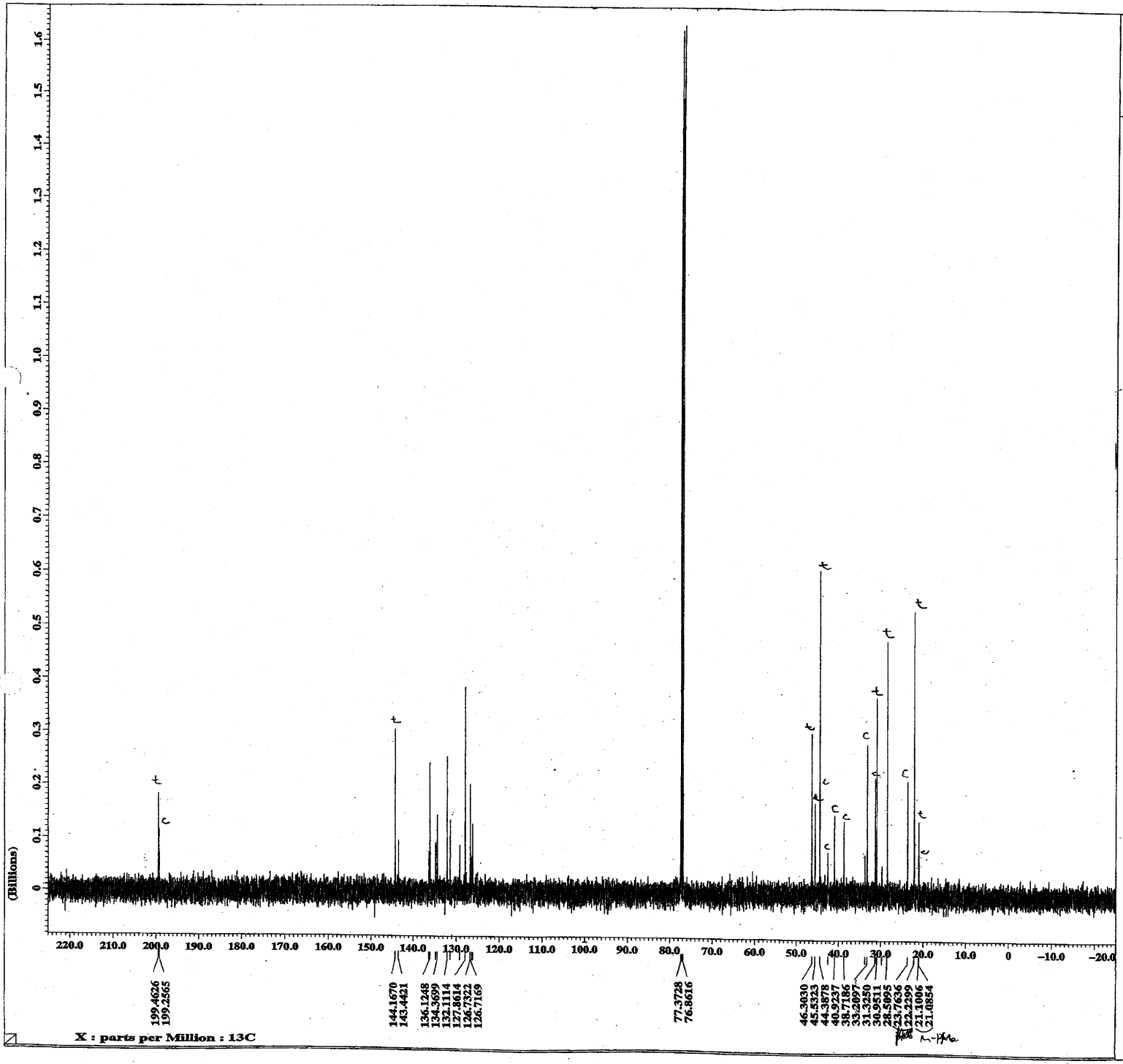
96.39032m
---- ACQUISITION PARAMETERS ----
JEOL
2c



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Content	= Single Pulse with Broad
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Revision Date	= 12-SEP-2004 17:59:27
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
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X_domain	= 13C
X_offset	= 100[ppm]
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X_sweep	= 31.44654088[kHz]
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Spin_set	= 17[Hz]
Temp_set	= 24.1[dC]
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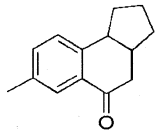
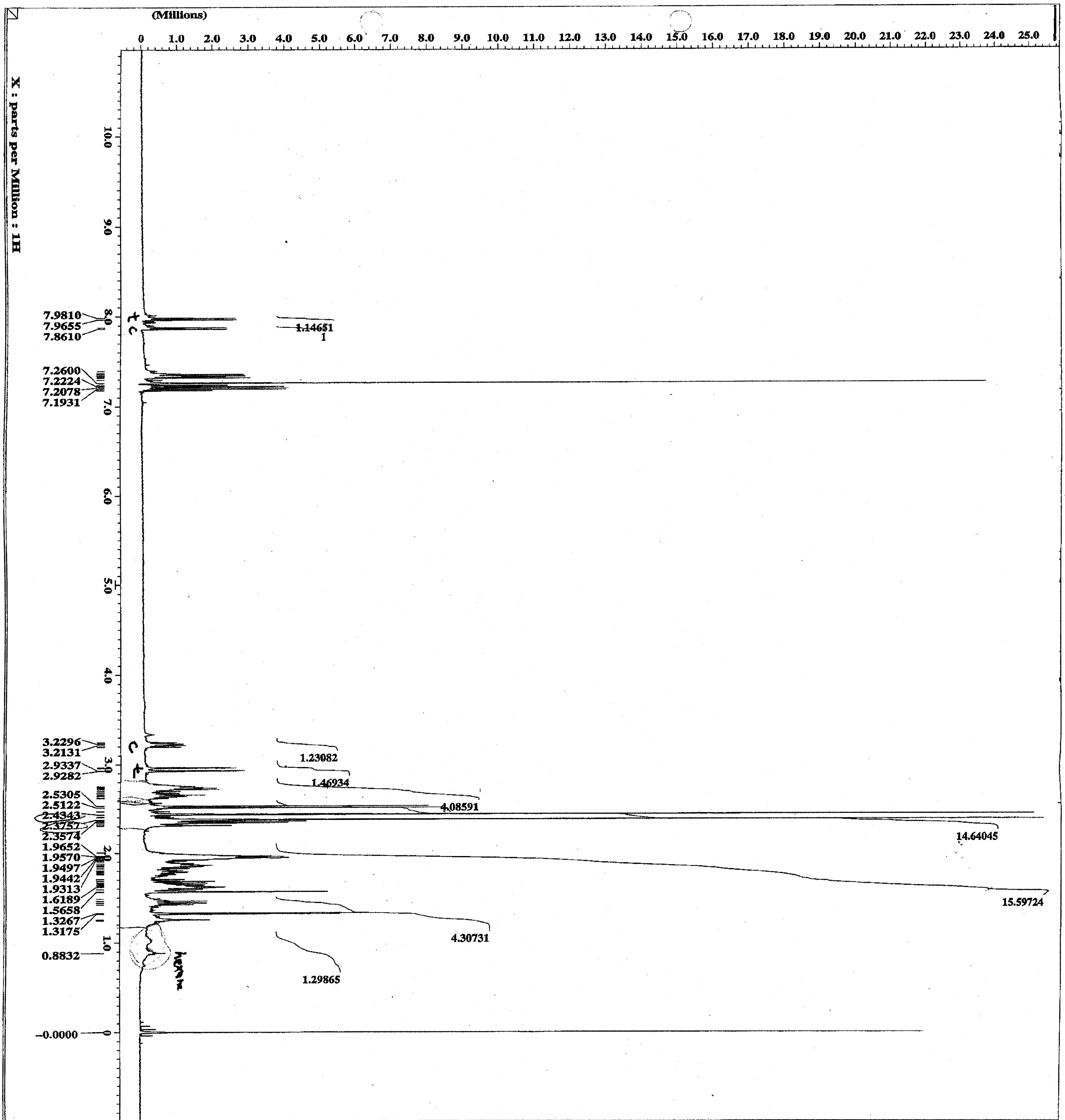


2c



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Revision Date = 17-SEP-2006 10:33:42
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Spec Type = DELTA_NMR
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Dim Size = 16384
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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 = 24[dC]
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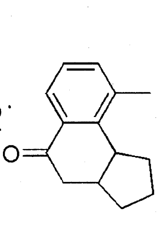
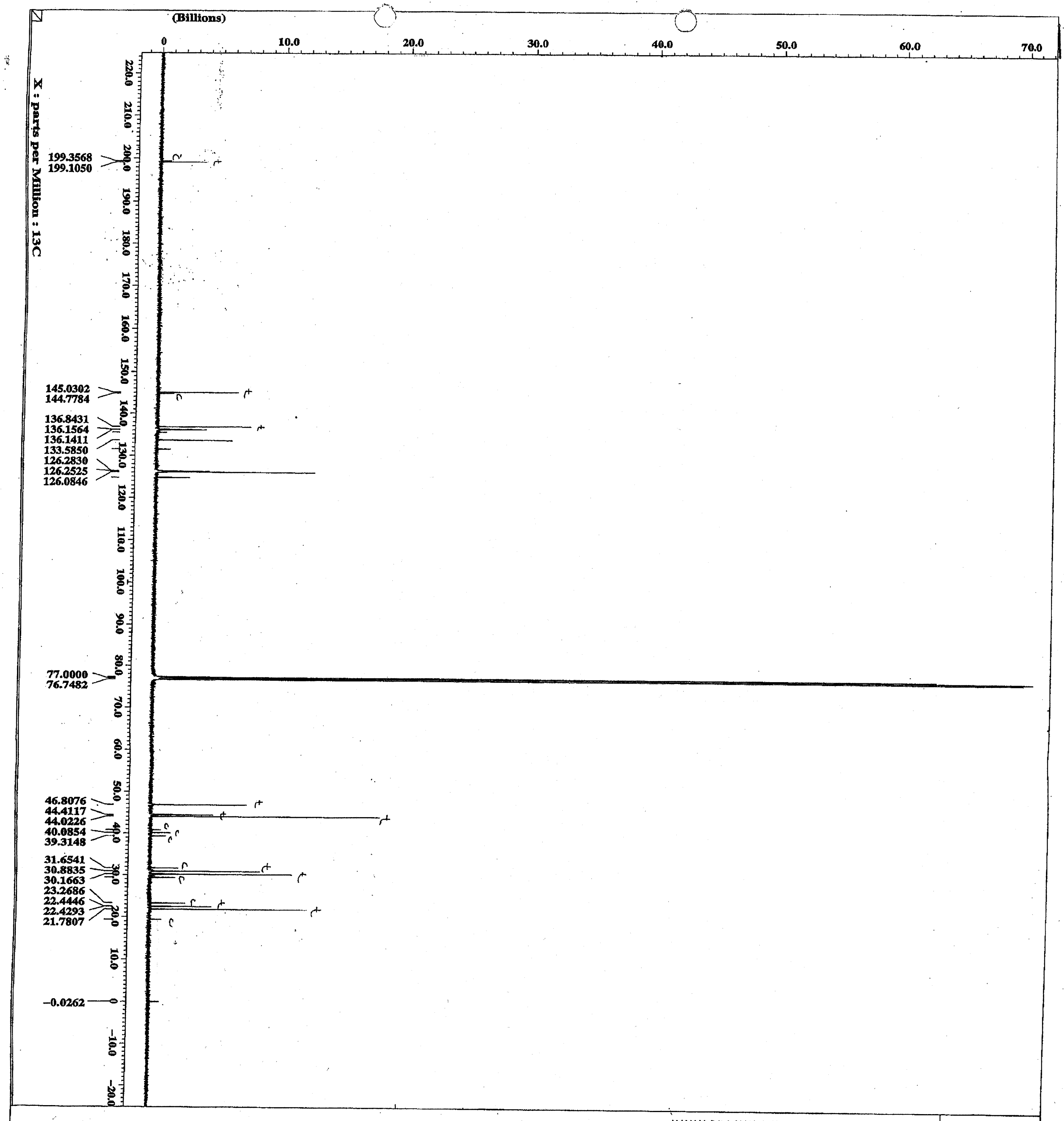
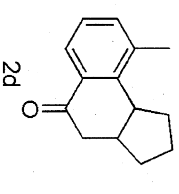
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[kHz]

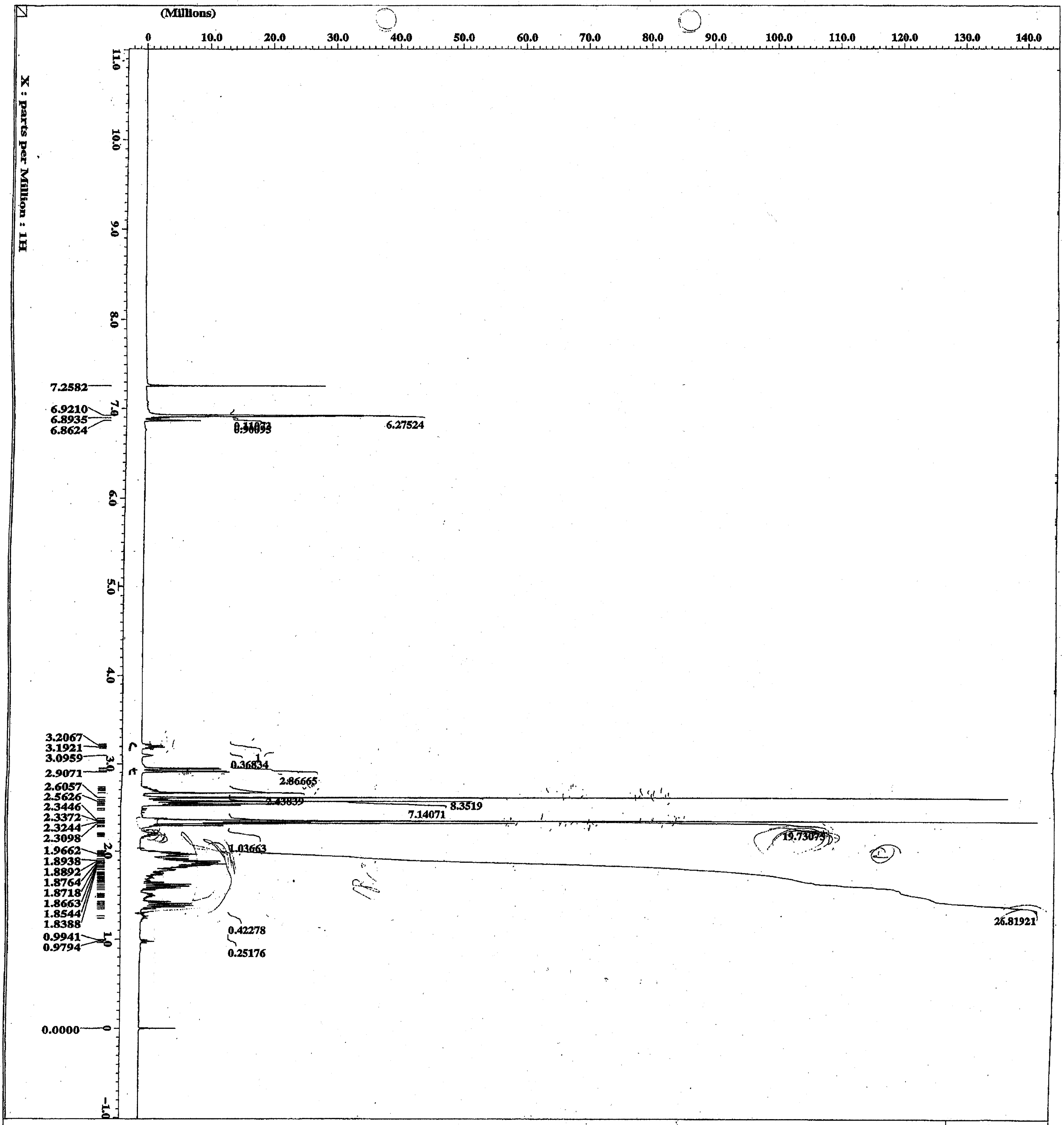

2d



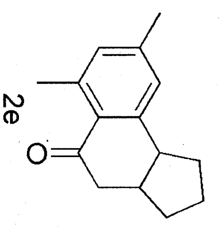
---- ACQUISITION PARAMETERS ----
File Name = 1d_13c_spectrum_copy-4
Author
Sample ID = MAS-TEMPO-027 fr9-21 re
Content = Single Pulse with Broad
Creation Date = 18-SEP-2004 09:45:24
Revision Date = 19-SEP-2004 07:42:25
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 18397
Mod_return = 1
X_domain = 13C
X_offset = 100[ppm]
X_freq = 125.77387547[MHz]
X_sweep = 31.44654088[kHz]
Solvent = CHLOROFORM-D
Spin_get = 16[Hz]
Temp_get = 24.4[dC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.7206621[kHz]



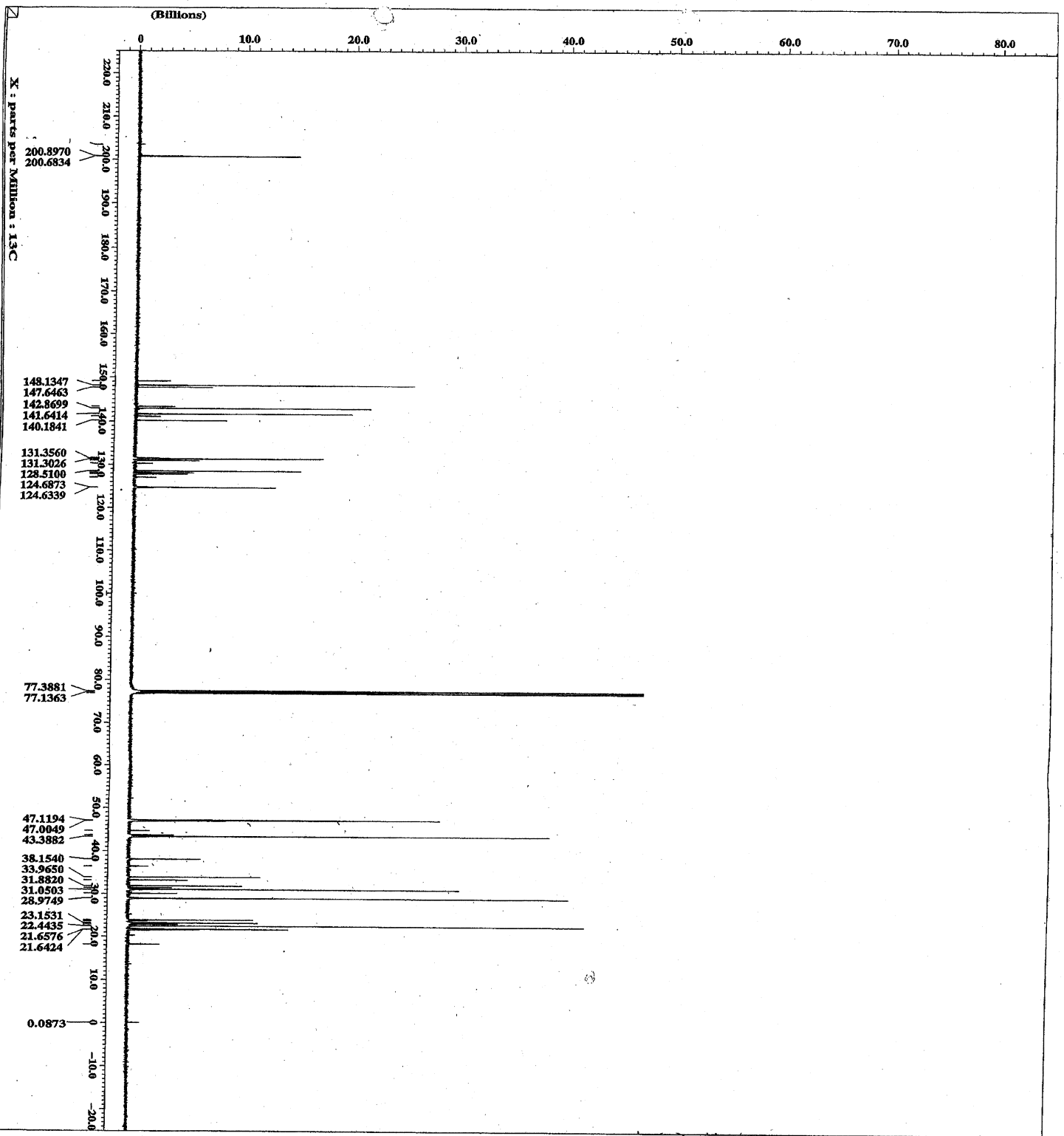
2d

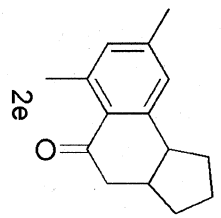


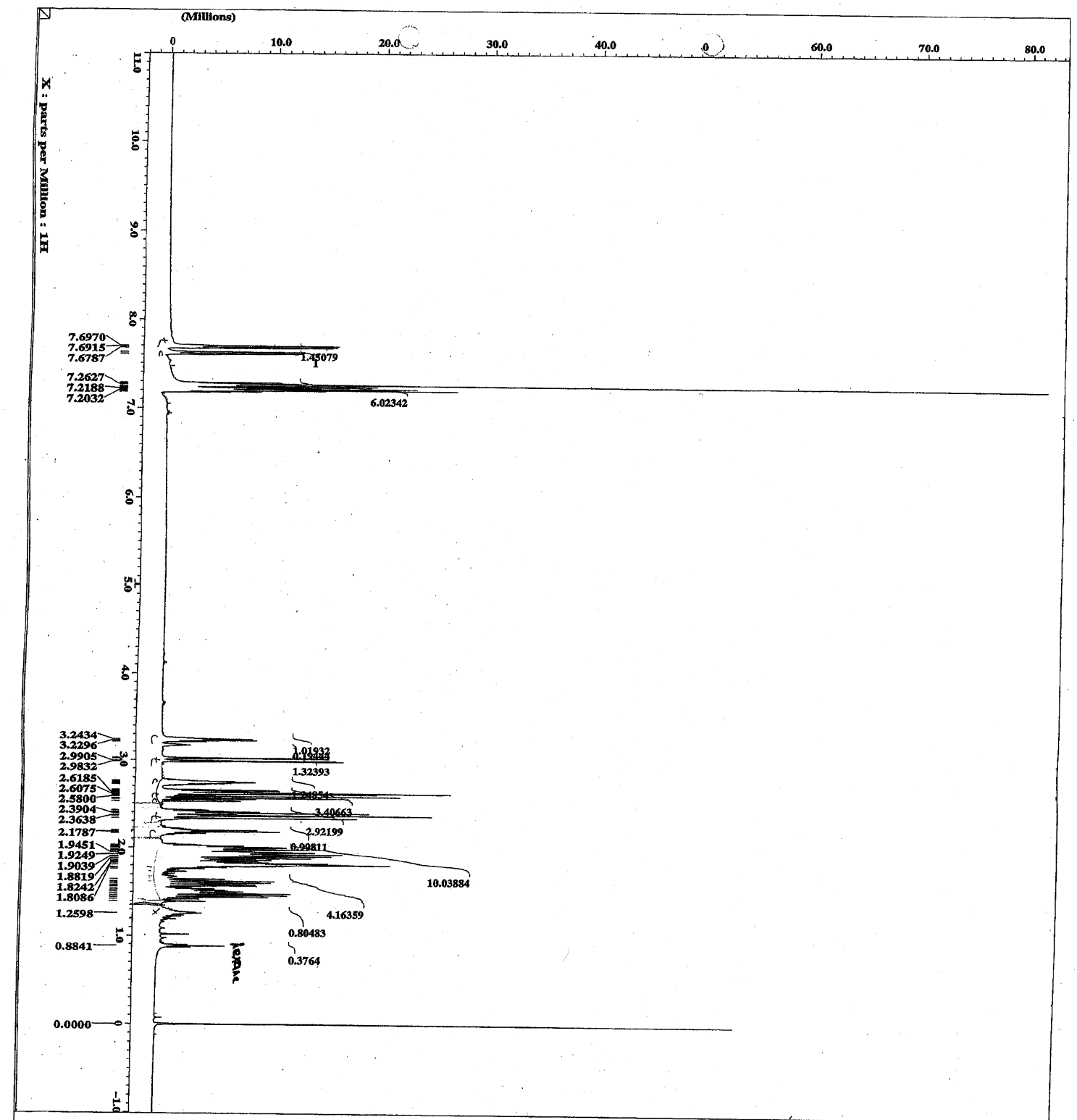
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.958
Author =
Sample ID = MAS-TEMPO-033 HPLC-B
Content = Single Pulse Experiment
Creation Date = 24-NOV-2004 17:09:55
Revision Date = 25-NOV-2004 16:21:08
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 32
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 = 22.2[dC]
Recvr_gain = 17
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[kHz]

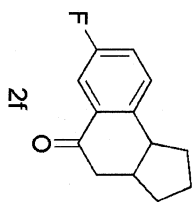


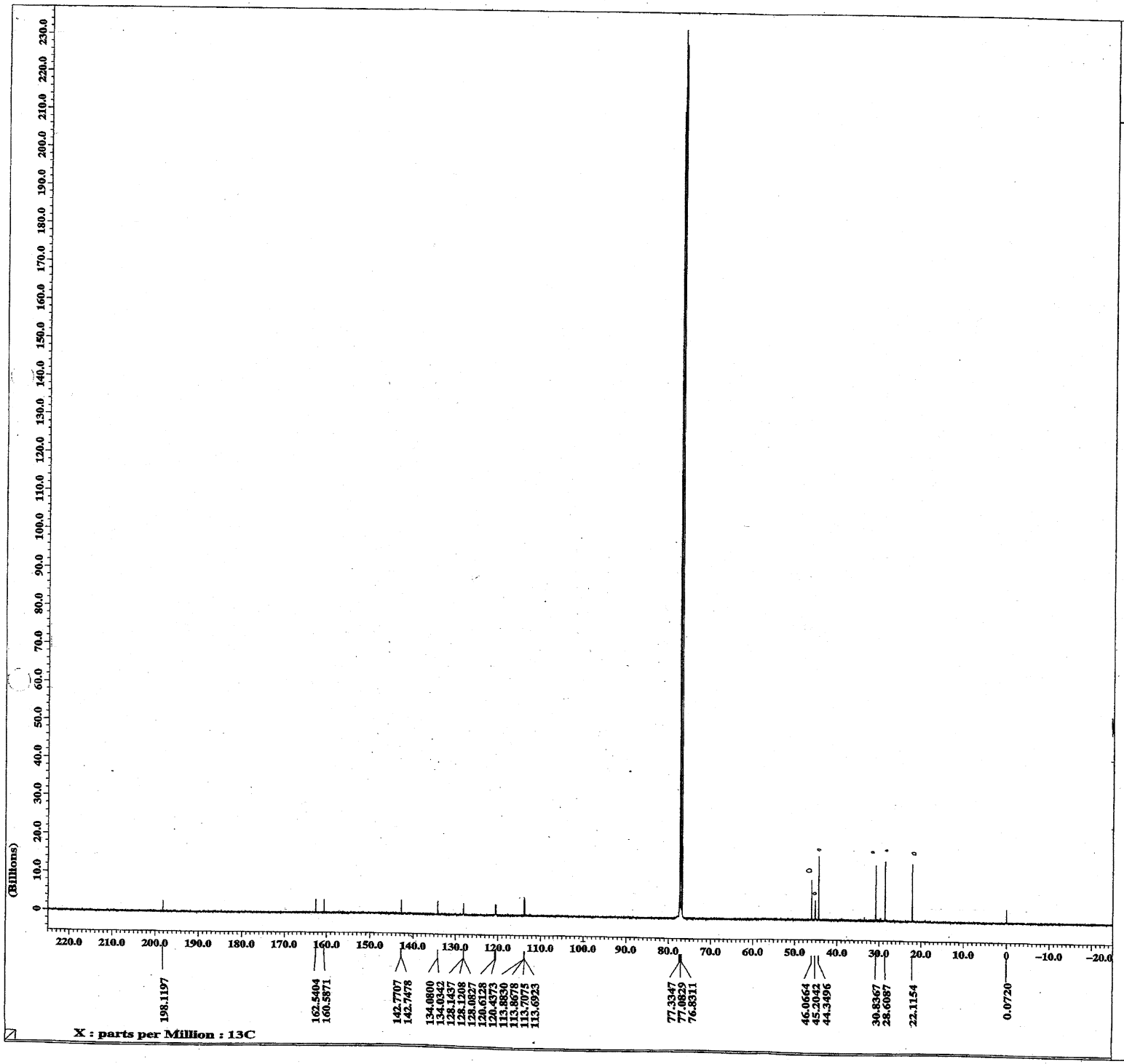
2e


(Billions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
X : parts per Million : 13C
200.8970
200.6834
148.1347
147.6463
142.8699
141.6414
140.1841
131.3560
131.3026
128.5100
124.6873
124.6339
77.3881
77.1363
47.1194
47.0049
43.3882
38.1540
33.9650
31.8820
31.0503
28.9749
23.1531
22.4435
21.6576
21.6424
0.0873


2e
O

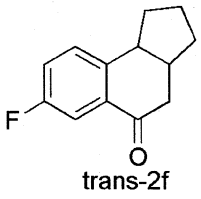

(Millions)
X : parts per Million : 1H
7.6970
7.6915
7.6787
7.2627
7.2188
7.2032
1.45079
6.02342
3.2434
3.2296
2.9905
2.9832
2.6185
2.6075
2.5800
2.3904
2.3638
2.1787
1.9451
1.9249
1.9039
1.8819
1.8242
1.8086
1.2598
0.8841
0.0000
1.01932
1.32393
3.40663
2.92199
0.99811
10.03884
4.16359
0.80483
0.3764
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.654
Author =
Sample ID = MAS-TEMPO-037 frs-10
Content = Single Pulse Experiment
Creation Date = 13-DEC-2004 14:25:38
Revision Date = 14-DEC-2004 12:54:37
Spec Site = ECP500
Spec Type = NMR_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Observe = 1H
Nucleus = 1H
X_domain = 1H
X_offset = 5.[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.5075075[kHz]
Solvent = CHLOROFORM-D
Spin_set = 17[Hz]
Temp_set = 25.4[dC]
Recvr_gain = 24
Pulse_Strength = 11.7473579[U]
Pulse_Mode = EXPERIMENTS
Filter_Width = 3.7511993[kHz]


F
2f
O

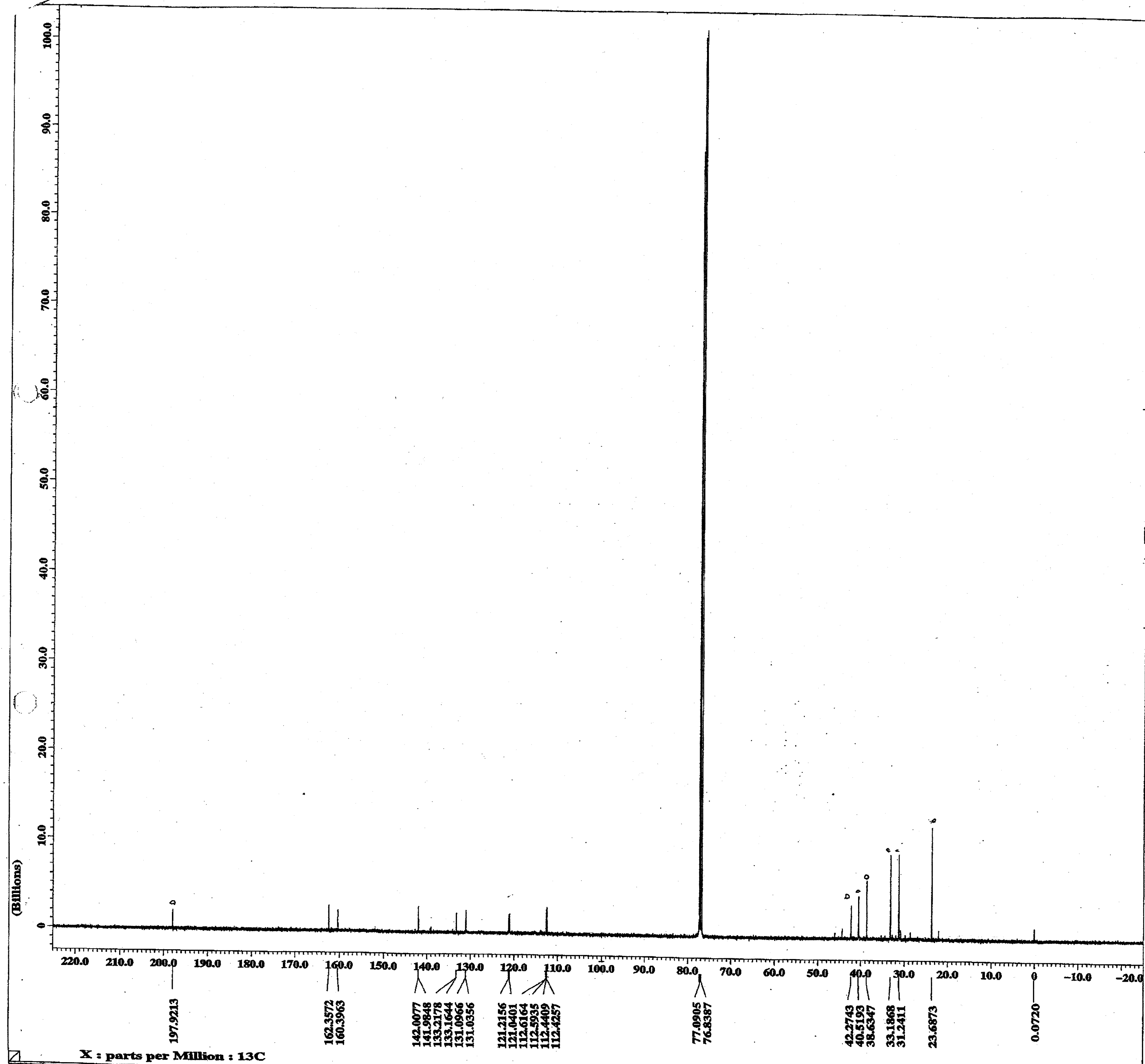


---- ACQUISITION PARAMETERS ----

File Name	= 1d_13c_spectrum.308
Author	=
Sample ID	= MAS-TEMPO-026-2 fri-5
Content	= Single Pulse with Broad
Creation Date	= 13-SEP-2004 09:18:56
Revision Date	= 14-SEP-2004 07:08:18
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 61863
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	= 24.6[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



trans-2f

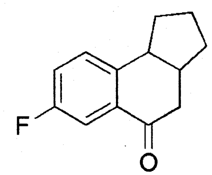


JEOL

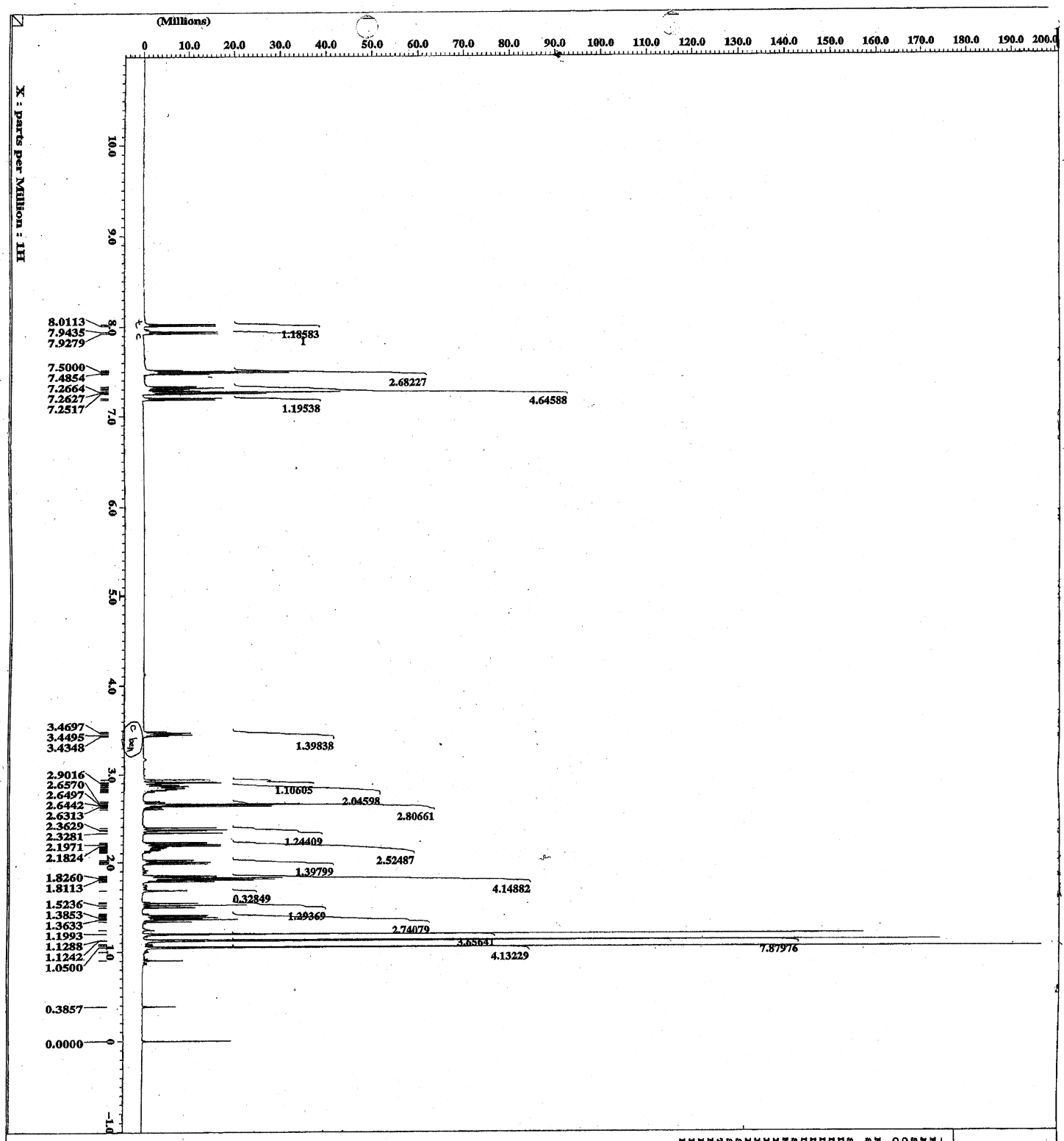
---- ACQUISITION PARAMETERS ----
File Name = 1d_13c_spectrum.138
Author =
Sample ID = MAS-TEMPO-013 HPLC-C
Content = Single Pulse with Broad
Creation Date = 16-JUL-2004 08:52:01

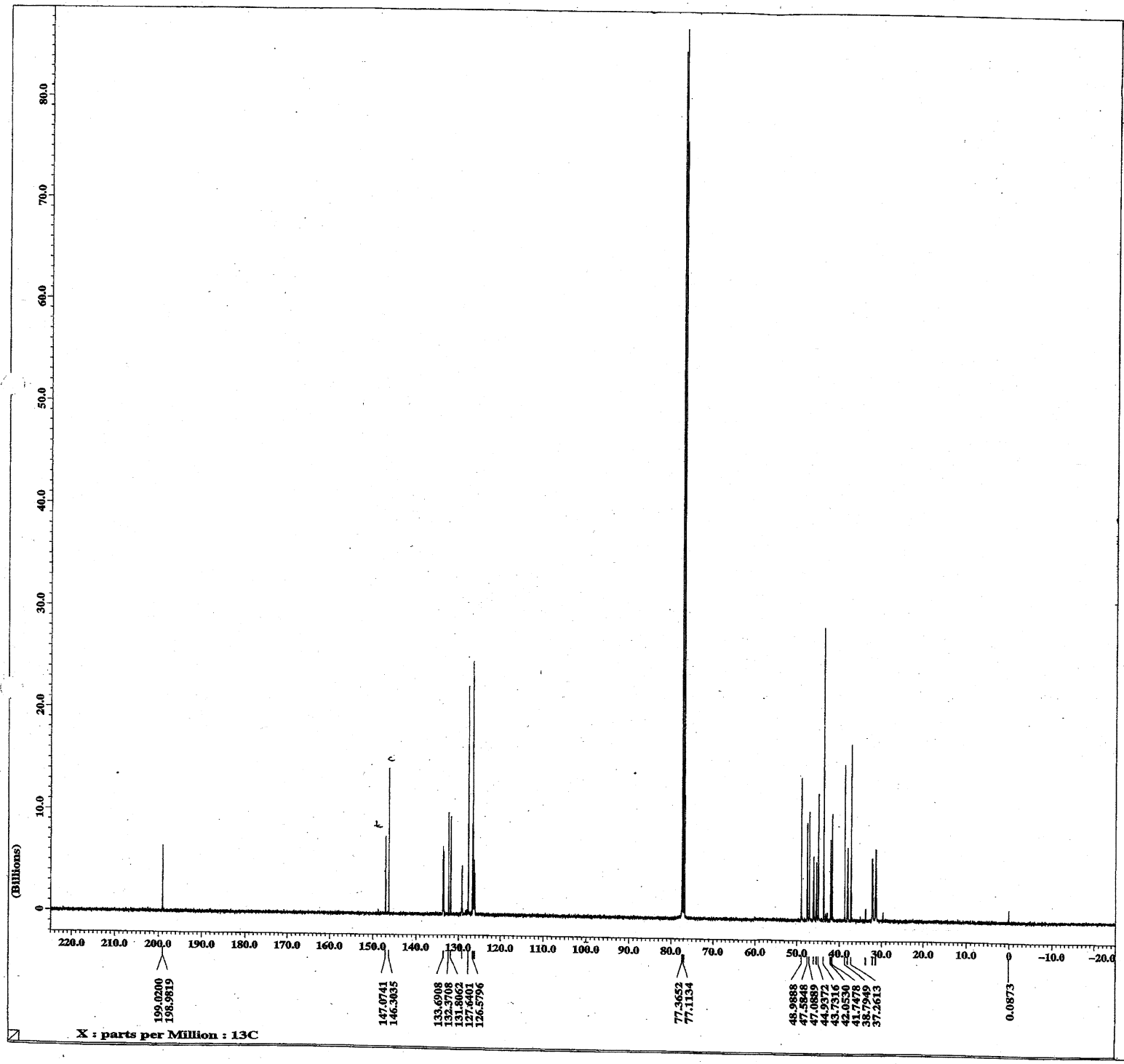
Revision Date = 17-JUL-2004 06:12:16
Spec Site = ECP500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 20000
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 = 30
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.72066221[kHz]



cis-2f

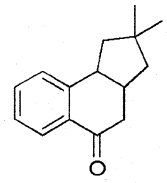

X : parts per Million : 1H
(Millions)
8.0113
7.9435
7.9279
7.5000
7.4854
7.2664
7.2627
7.2517
3.4697
3.4495
3.4348
2.9016
2.6570
2.6497
2.6442
2.6313
2.3629
2.3281
2.1971
2.1824
1.8260
1.8113
1.5236
1.3853
1.3633
1.1993
1.1288
1.1242
1.0500
0.3857
0.0000
1.18583
2.68227
4.64588
1.19538
1.39838
1.10605
2.04598
2.80661
1.24409
2.52487
1.39799
4.14882
0.32849
1.29369
2.74079
3.65641
4.13229
7.87976
JEOL
2g



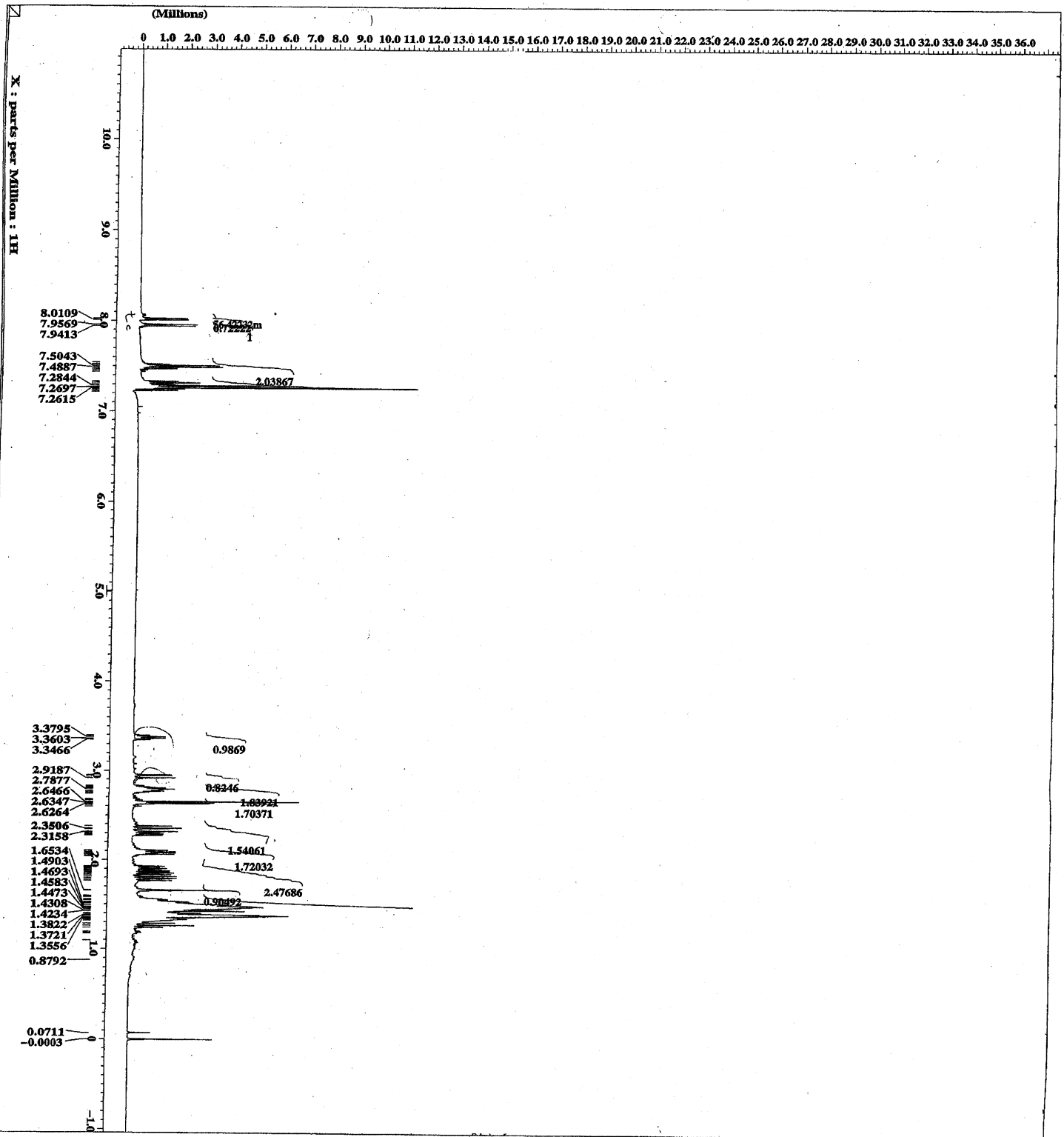
JEOL

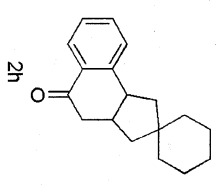
---- ACQUISITION PARAMETERS ----

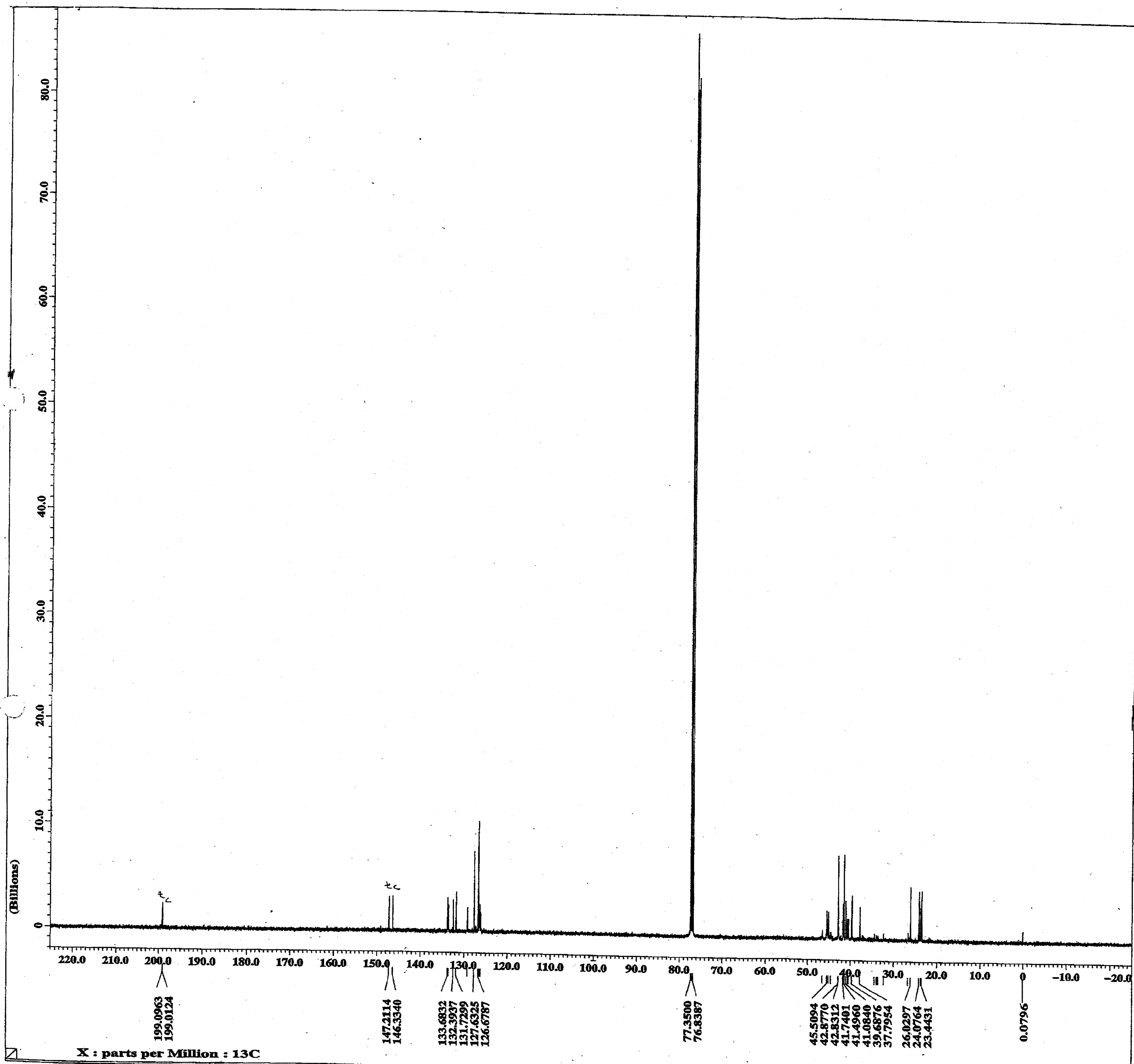
File Name	= 1d_13c_spectrum.326
Author	=
Sample ID	= MAS-TEMPO-035 HPLC-B
Content	= Single Pulse with Broad
Creation Date	= 3-DEC-2004 09:13:55
Revision Date	= 4-DEC-2004 07:33:01
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Scans	= 20705
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	= 24[dC]
Recvr_gain	= 30
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 15.72066221[kHz]



2g


(Millions)
X : parts per Million : 1H
8.0109
7.9569
7.9413
7.5043
7.4887
7.2844
7.2697
7.2615
2.03867
3.3795
3.3603
3.3466
0.9869
2.9187
2.7877
2.6466
2.6347
2.6264
0.8246
1.83921
1.70371
2.3506
2.3158
1.54061
1.6534
1.4903
1.4693
1.4583
1.4473
1.4308
1.4234
1.3822
1.3721
1.3556
1.72032
2.47686
0.90492
0.8792
0.0711
-0.0003

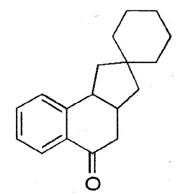

2h
O



---- ACQUISITION PARAMETERS ----
File Name = 1d_13c_spectrum.114
Author =
Sample ID = MAS-TEMPO-032 HPLC-B
Content = Single Pulse with Broad
Creation Date = 12-NOV-2004 08:24:15

Revision Date = 13-NOV-2004 07:23:35
Spec Site = ECP500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 21368
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 = 23.6[dC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.72066221[kHz]



2h