Electronic Supplementary Information

Iron-catalyzed decarbonylation reaction of aliphatic carboxylic acids leading to α-olefins

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1. General information.

^{1}H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) spectrometer in $CDCl_3$ and are referenced at 7.26 ppm for $CHCl_3$. Chemical shifts are reported in parts per million (δ). ^{13}C NMR spectra were recorded with a JEOL JMN-500 (125 MHz) spectrometer in $CDCl_3$ and are referenced at 77.00 ppm for $CDCl_3$. Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer. Melting point was measured by BÜCHI Melting Point B-540. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with an FID detector using a J&W Scientific DB-5 column, and a VARIAN Micro GC CP4900 instrument equipped with a TCD detector using a Molsieve 5A column and PoraPLOT Q column. The products were purified by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40－50 μm)). Anhydrous $FeCl_2$ (powder, purity of 98%) was purchased from Sigma-Aldrich, Co. Potassium Iodide (granular powder, purity of 99.5%) was purchased from Wako Pure Chemical Industries, Ltd. Acetic anhydride (purity of 97%) was purchased from Nacalai Tesque, Inc. Other reagents were received from commercial sources and used without further purification.

2. Experimental procedure.

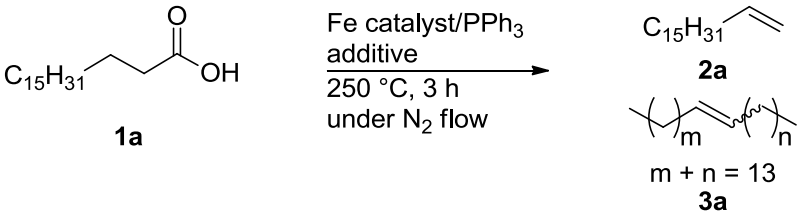
Typical procedure for iron-catalyzed decarbonylation reaction of carboxylic acids (Table 1, Entry 10):

To a 30-mL stainless steel autoclave were added stearic acid **1a** (285.0 mg, 1.0 mmol), $FeCl_2$ (13.0 mg, 0.10 mmol), DPPPent (88.4 mg, 0.20 mmol), KI (167.2 mg, 1.0 mmol), Ac_2O (103.4 mg, 1.0 mmol) and a magnetic stirring bar. The autoclave was closed, purged three times with carbon monoxide, pressurized with 20 atm of CO. The reaction mixture was heated at 240 °C by a salt bath (eutectic mixture of inorganic salts: potassium nitrate 53%, sodium nitrite 40%, and sodium nitrate 7%) for 3 h. After cooling, excess CO was discharged. The reaction mixture was diluted with ether, passed through a pad of Celite, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give heptadecenes (176.6 mg, 74%, **2a**/**3a** = 97/3).

Large-scale procedure (Table 1, Entry 11):

To a 100-mL stainless steel autoclave were added stearic acid **1a** (2.9 g, 10 mmol), $FeCl_2$ (128.8 mg, 1 mmol), DPPPent (883.0 mg, 2 mmol), KI (1.7 g, 10 mmol), Ac_2O (1.2 g, 10 mmol) and a magnetic stirring bar. The autoclave was closed, purged three times with carbon monoxide, pressurized with 20 atm of CO. The reaction mixture was heated at 240 °C by a salt bath for 3 h. After cooling, excess CO was discharged. The reaction mixture was diluted with ether, passed through a pad of Celite, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give heptadecenes (1.6 g, 69%, **2a**/**3a** = 96/4).

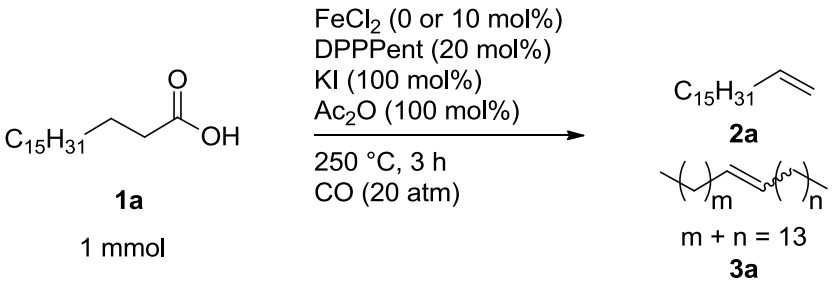
Table S1 Decarbonylation of stearic acid with different Fe catalyst.



Entry	Catalyst (mol%)	Additive (mol%)	Yield (%)[b] (**2a**/**3a**)[c]
1	$FeCl_2$ (10)	none	<1
2	$FeCl_2$ (10)	KI (100), Ac_2O (100)	79 (19/81)
3	$FeCl_2$ (10)	HI[d] (100)	<1
4	$FeCl_2$ (10)	HOAc (100)	<1
5	FeI_2 (10)	Ac_2O (100)	73 (9/91)
6	FeI_2 (10)	KI (100), Ac_2O (100)	77 (13/87)
7	$Fe_2(CO)_9$ (5)	KI (100), Ac_2O (100)	<1
8	$Fe_3(CO)_{12}$ (3.3)	KI (100), Ac_2O (100)	<1
9	$[Fe(CO)_2Cp]_2$ (5)	KI (100), Ac_2O (100)	<1
10	$FeI(CO)_2Cp$ (10)	Ac_2O (100)	40[e] (14/86)
11	$FeI(CO)_2Cp$ (10)	KI (100), Ac_2O (100)	37[e] (14/86)

[a] Reaction conditions: **1a** (1.0 mmol), Fe catalyst, PPh_3 (40 mol%), additive, 250 °C, 3 h under N_2. [b] Total yield of isomers after silica gel chromatography. [c] Selectivity was determined by ^1H NMR analysis. [d] 55 w/w aq. solution. [e] Yield based on ^1H NMR analysis relative to anisole as an internal standard.

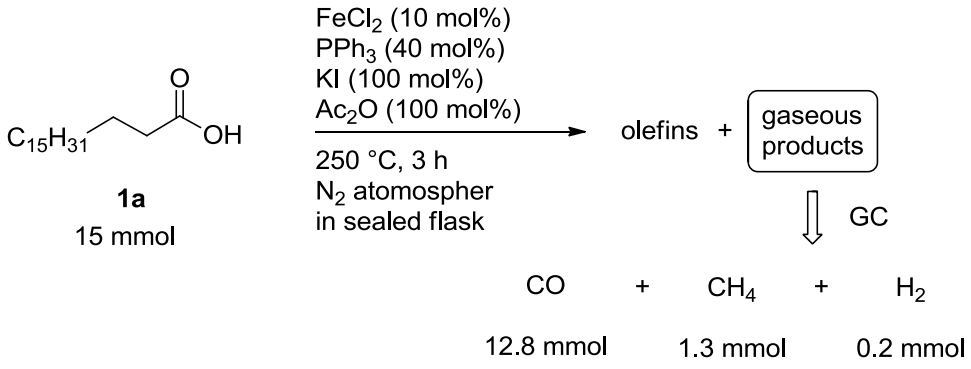
Effect of $FeCl_2$ purity:



$FeCl_2$ purity	Yield[a] (%) (**2a**/**3a**)
no catalyst	<1
98% (Aldrich)	91 (92/8)
99.998% (Aldrich)	89 (93/7)

[a] Total yield of isomers after silica gel chromatography.

Analysis of the gaseous products by GC-TCD:

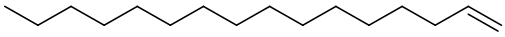


Spectral data of products.

1-Heptadecene (**2a**)[1]

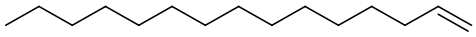
Obtained as an inseparable mixture (**2a**/**3a** = 97/3); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.92－5.01 (m, 2H), 2.02－2.06 (m, 2H), 1.25－1.39 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.19, 114.08, 33.90, 32.01, 29.78, 29.60, 29.46, 29.24, 29.03, 22.76, 14.14.

1-Hexadecene (**2b**)



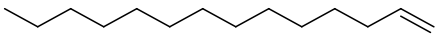
Obtained as an inseparable mixture (**2b**/**3b** = 98/2); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.91－5.01 (m, 2H), 2.01－2.08 (m, 2H), 1.26－1.39 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ139.24, 114.06, 33.84, 31.95, 29.70, 29.53, 29.38, 29.18, 28.97, 22.71, 14.12. The NMR data were identical with those of a commercial sample of 1-hexadecene.

1-Pentadecene (**2c**)[2]



Obtained as an inseparable mixture (**2c**/**3c** = 97/3); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78－5.86 (m, 1H), 4.92－5.01 (m, 2H), 2.02－2.06 (m, 2H), 1.26－1.39 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.25, 114.06, 33.85, 31.95, 29.70, 29.53, 29.38, 29.18, 28.97, 22.71, 14.12.

1-Tetradecene (**2d**)[2]

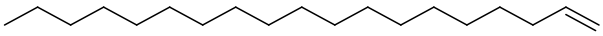


Obtained as an inseparable mixture (**2d**/**3d** = 97/3); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78－5.86 (m, 1H), 4.92－5.01 (m, 2H), 2.01－2.06 (m, 2H), 1.26－1.39 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.15, 114.08, 33.91, 32.03, 29.77, 29.63, 29.47, 29.27, 29.05, 22.77. 14.12.

1-Tridecene (**2e**)[3]

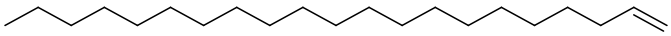
Obtained as an inseparable mixture (**2e**/**3e** = 97/3); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.91－5.01 (m, 2H), 2.02－2.06 (m, 2H), 1.26－1.39 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.23, 114.07, 33.87, 31.97, 29.69, 29.57, 29.40, 29.21, 29.01, 22.73, 14.12.

1-Nonadecene (**2f**)[4]



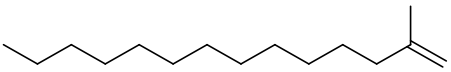
Obtained as an inseparable mixture (**2f**/**3f** = 98/2); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.91－5.01 (m, 2H), 2.01－2.06 (m, 2H), 1.25－1.39 (m, 30H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.20, 114.07, 33.87, 31.98, 29.57, 29.42, 29.21, 29.01, 14.13.

1-Henicosene (**2g**)[5]



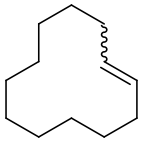
Obtained as an inseparable mixture (**2g**/**3g** = 98/2); white solid. mp 32.3 °C (lit.[6] mp 35.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.91－5.01 (m, 2H), 2.01－2.06 (m, 2H), 1.25－1.39 (m, 34H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.23, 114.07, 33.86, 31.96, 29.73, 29.55, 29.41, 29.20, 28.99, 22.72, 14.13.

2-Methyl-l-tetradecene (**2j**)[7]



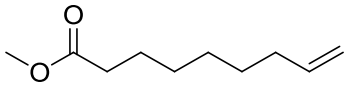
Obtained as an inseparable mixture (**2j**/**3j** = 92/8); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77－5.86 (m, 1H), 4.91－5.01 (m, 2H), 2.02－2.06 (m, 2H), 1.26－1.39 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.23, 114.07, 33.87, 31.97, 29.69, 29.57, 29.40, 29.21, 29.01, 22.73, 14.12.

Cyclododecene (**2k**)[8]



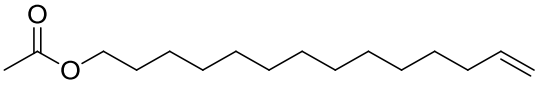
Obtained as an inseparable mixture (*E*/*Z* = 78/22); colorless oil. *E* isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25－1.36 (m, 12H), 1.40－1.47 (m, 4H), 2.05－2.06 (m, 4H), 5.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.40, 32.13, 26.24, 25.60, 24.95, 24.60. *Z* isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25－1.39 (m, 12H), 1.40－1.49 (m, 4H), 2.09－2.13 (m, 4H), 5.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.34, 26.95. 24.35, 23.93, 22.05.

Methyl 8-nonenate (**2l**)[9]



Obtained as an inseparable mixture (**2l**/**3l** = 95/5); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.76－5.84 (m, 1H), 4.92－5.01 (m, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.01－2.06 (m, 2H), 1.57－1.65 (m, 2H), 1.31－1.41 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.24, 138.96, 114.24, 51.41, 34.04, 33.66, 28.94, 28.66, 24.86.

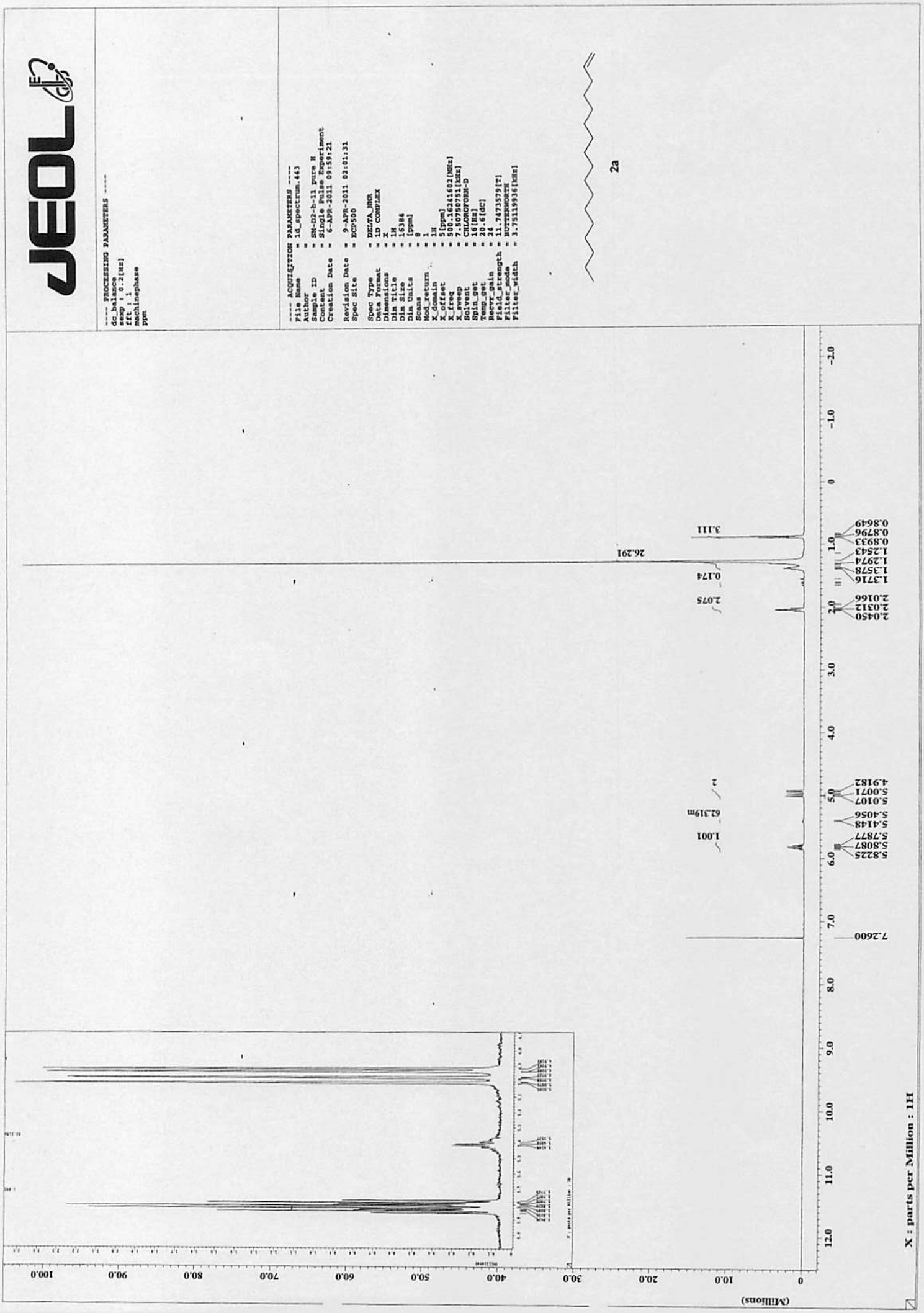
13-Tetradecenyl acetate (**2m**)[10]



Obtained as an inseparable mixture (**2m**/**3m** = 96/4); colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.76－5.84 (m, 1H), 4.91－5.01 (m, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.01－2.08 (m, 2H), 1.59－1.65 (m, 2H), 1.31－1.41 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 171.18, 139.19, 114.05, 64.62, 33.96, 29.57, 29.48, 29.23, 29.12, 28.92, 28.58, 25.88, 21.11.

References.

1. D. H. R. Barton, J. Boivin, E. Crepon, J. Sarma, H. Togo and S. Z. Zard, *Tetrahedron*, 1991, **47**, 7091.
2. D. H. Burns, J. D. Miller, H.-K. Chan and M. O. Delaney, *J. Am. Chem. Soc*., 1997, **119**, 2125.
3. G. Rojas and K. B. Wagener, *J. Org. Chem*., 2008, **73**, 4962.
4. J.-F. Biellmann, H. d'Orchymont and J.-L. Schmitt, *J. Am. Chem. Soc*., 1979, **101**, 3283.
5. M. Feldhues and H. J. Schafer, *Tetrahedron*, 1985, **41**, 4213.
6. A. W. Schmidt, V. Schoeller and K. Eberlein, *Chem. Ber*., 1941, **74**, 1313.
7. B. A. Pearlaman, S. R. Putt and J. A. Fleming, *J. Org. Chem*., 1985, **50**, 3625.
8. A. Maercker and U. Girreser, *Tetrahedron*, 1994, **50**, 8019.
9. H. Zhu, J. G. Wickenden, N. E. Campbell, J. C. T. Leung, K. M. Johnson and G. M. Sammis, *Org. Lett*., 2009, **11**, 2019.
10. J. Lin, F. Liu, Y. Wang and M. Liu, *Synth. Commun*., 1995, **25**, 3457.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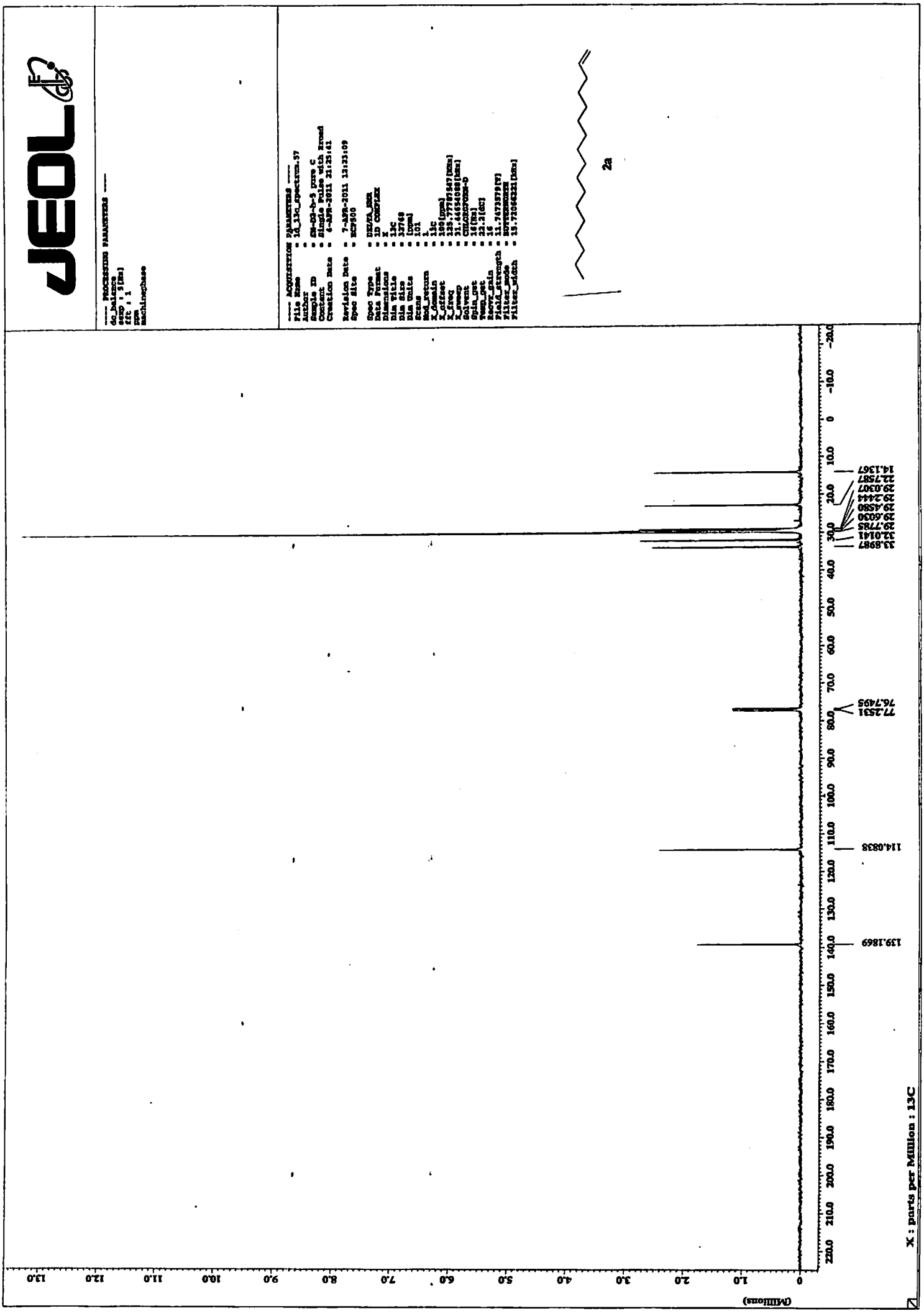

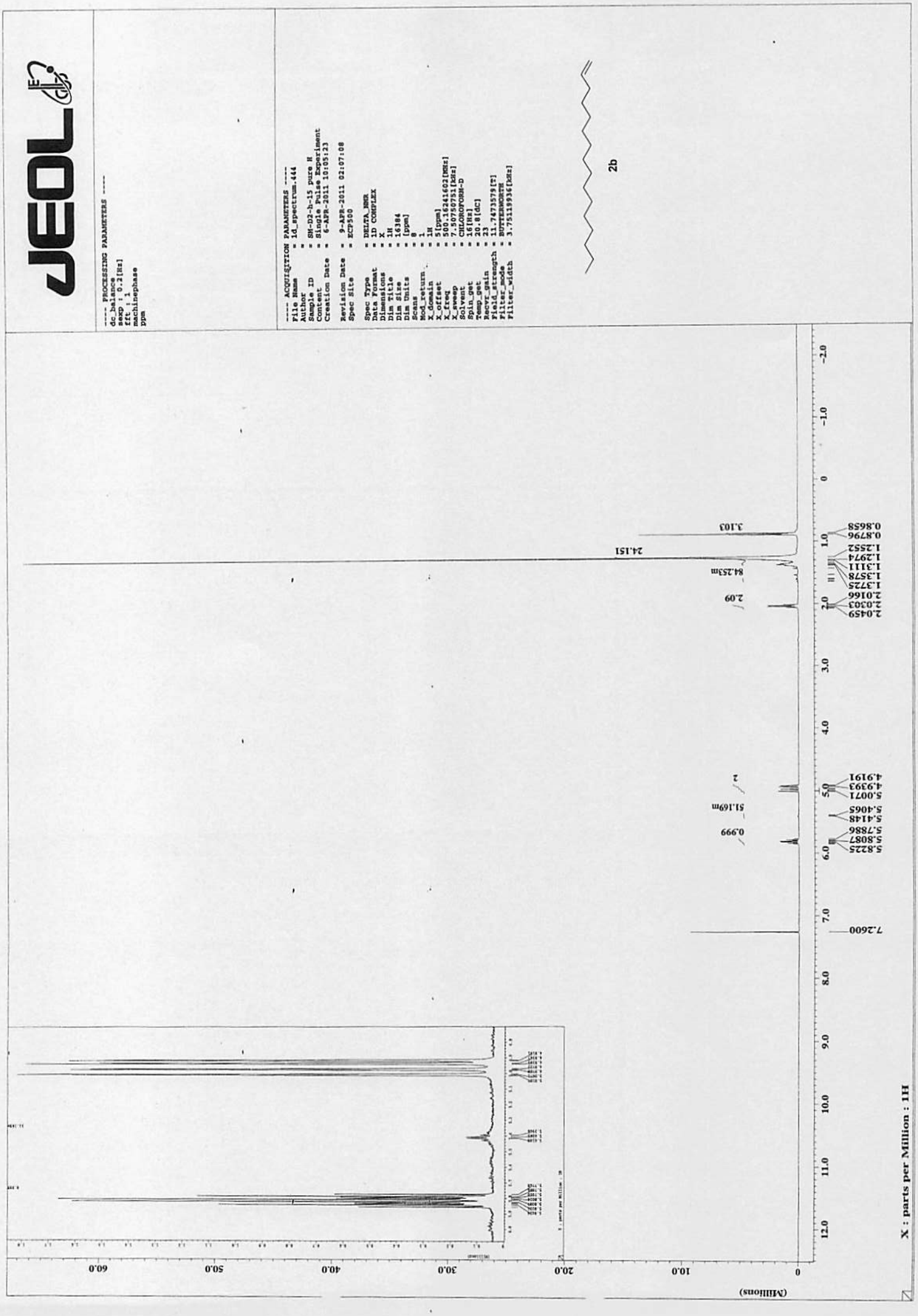

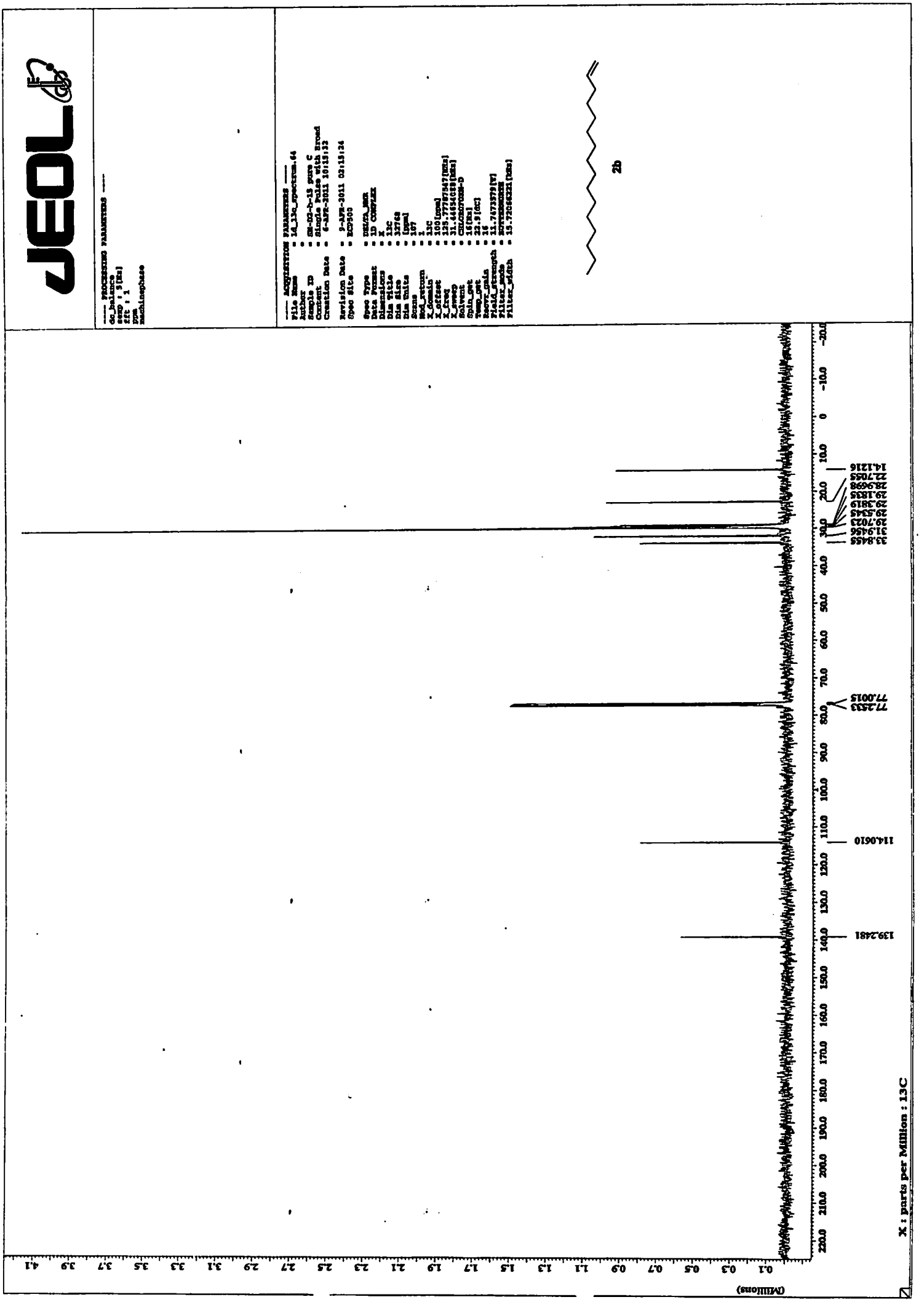
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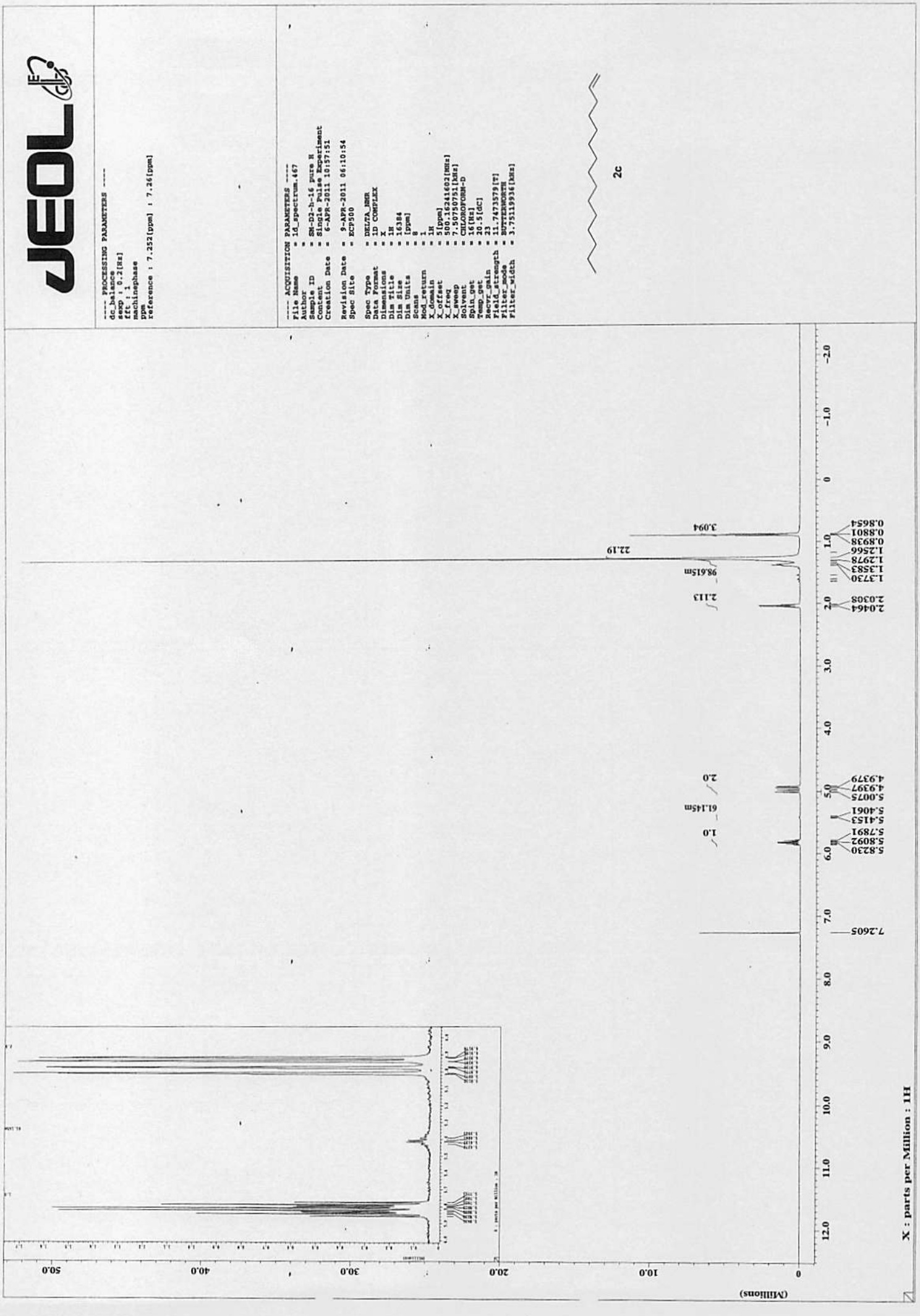

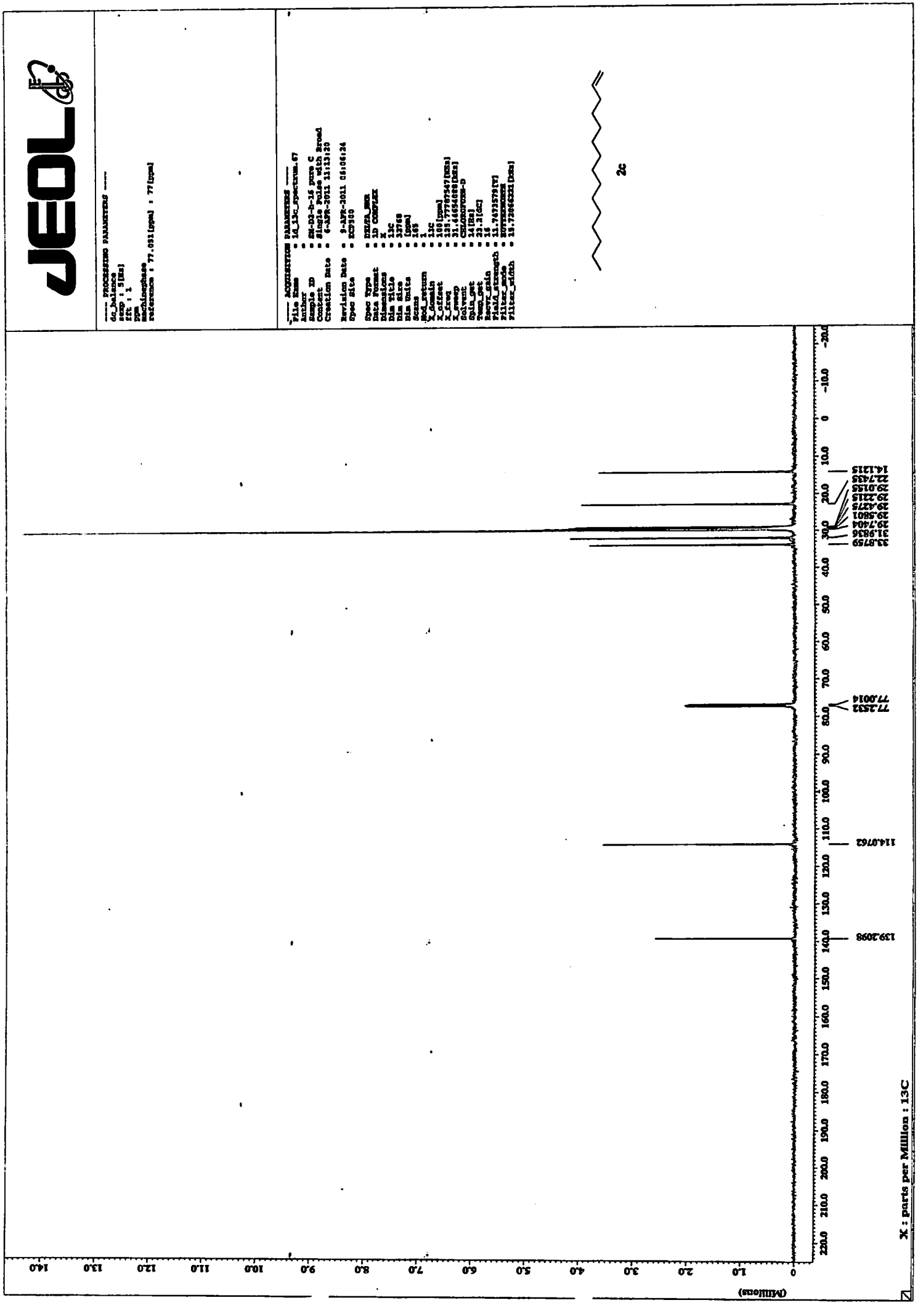

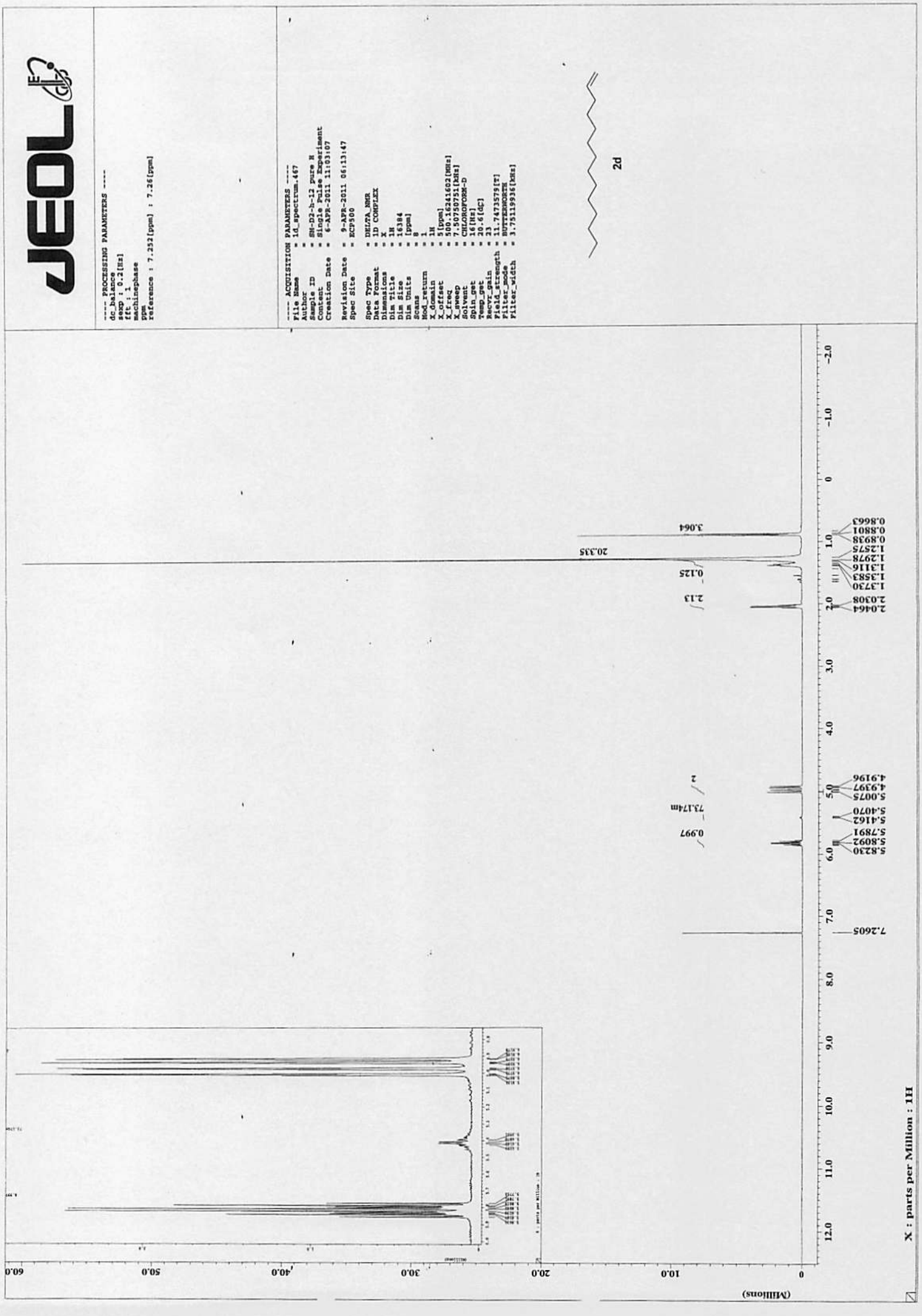

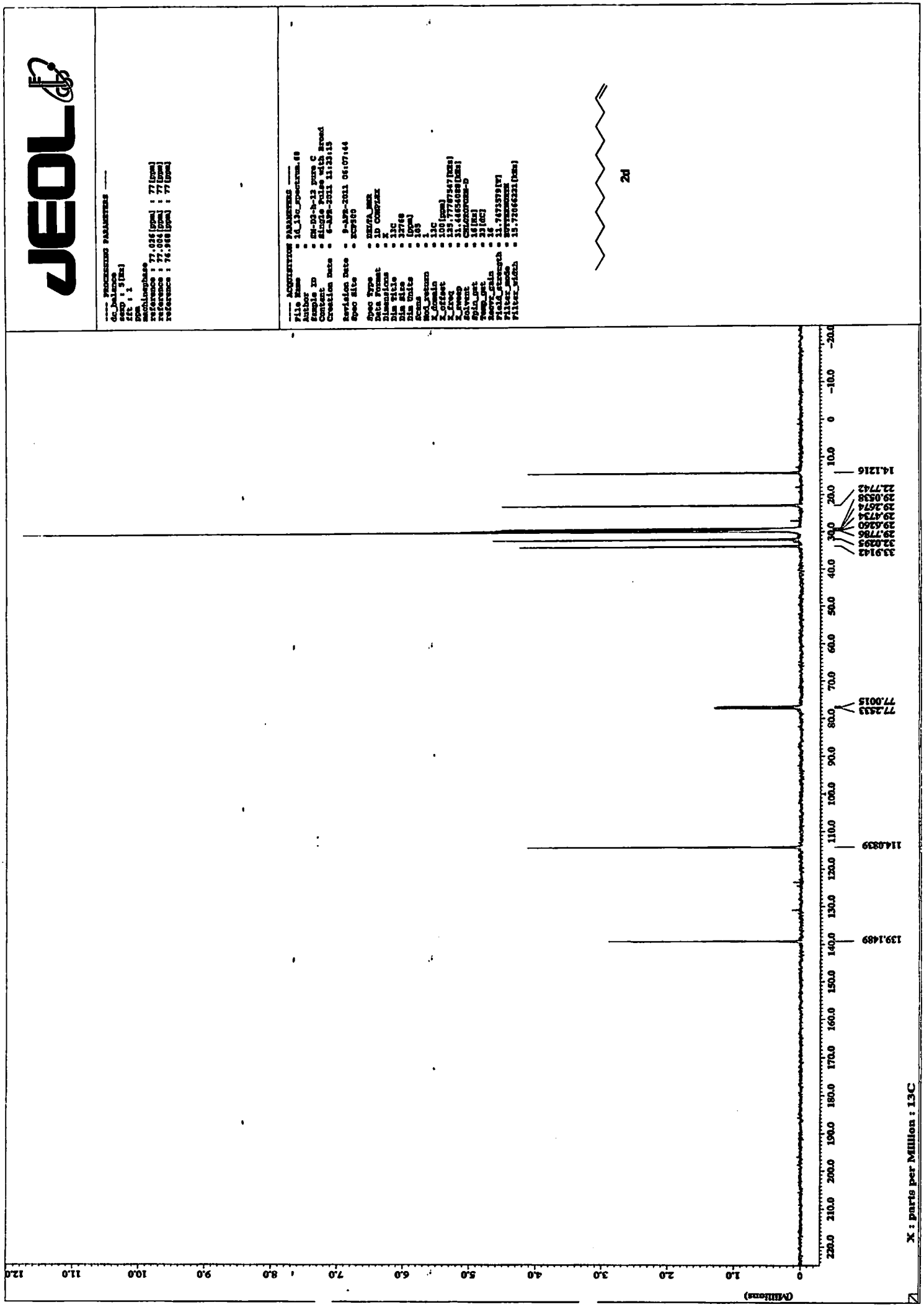

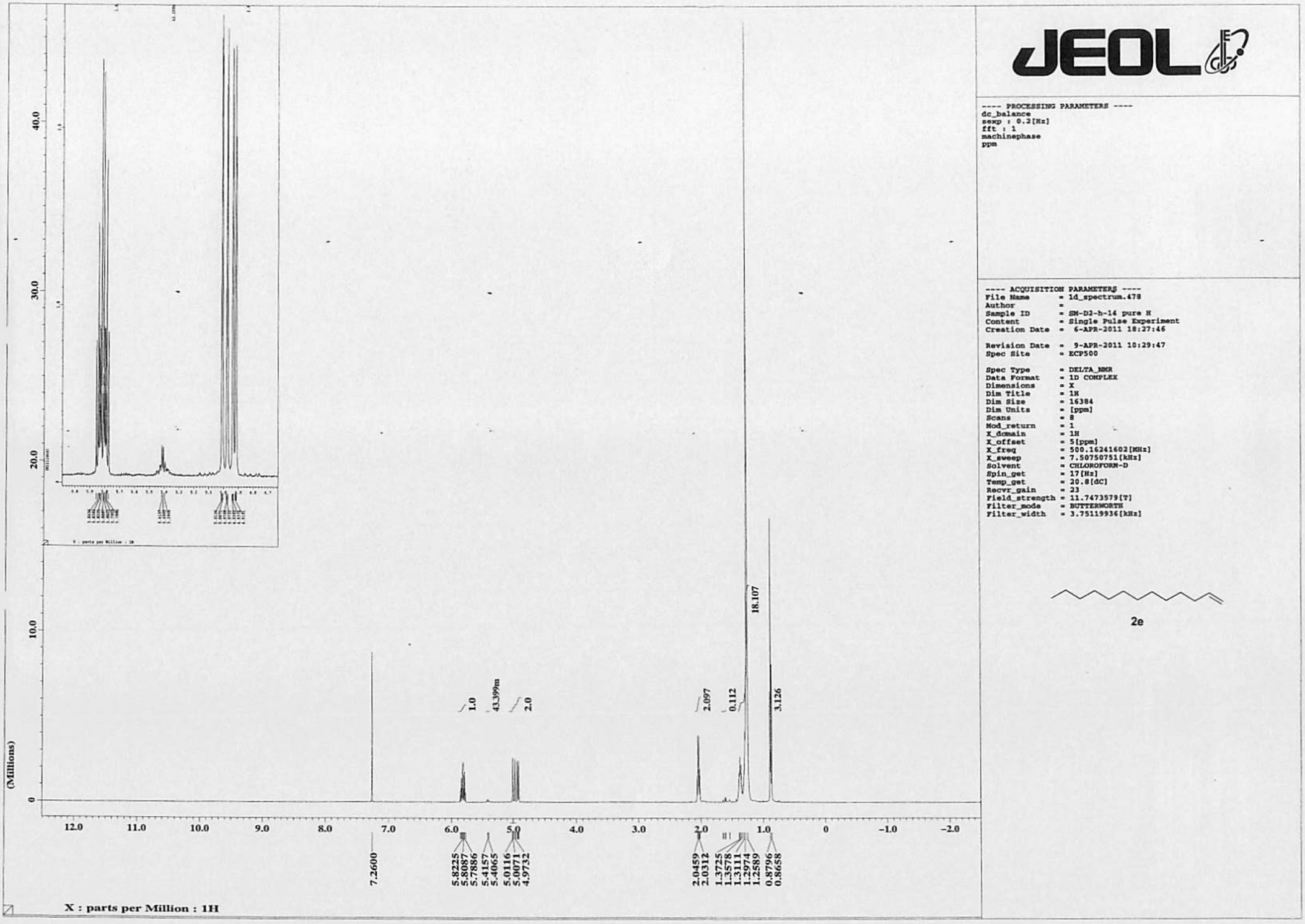

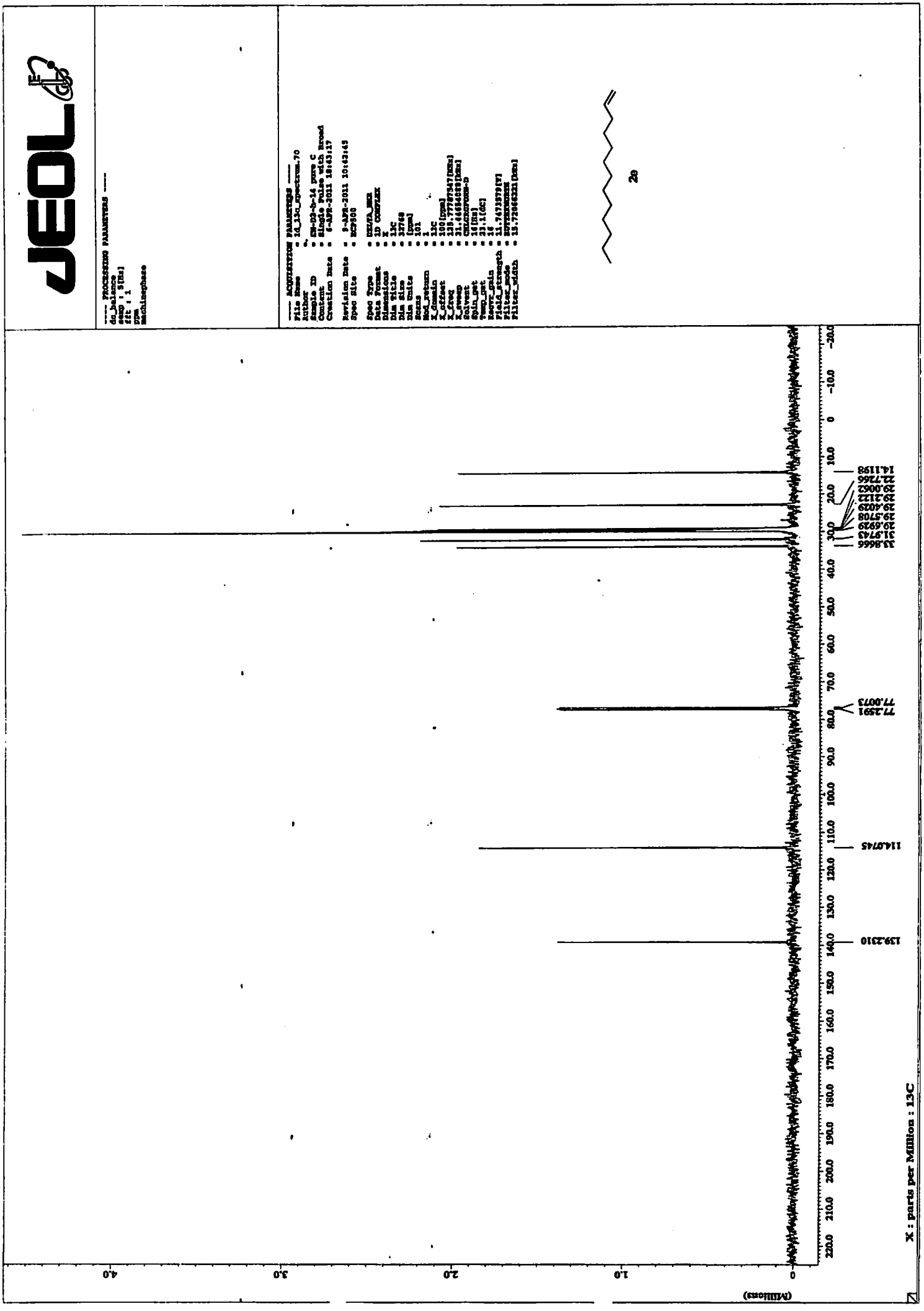

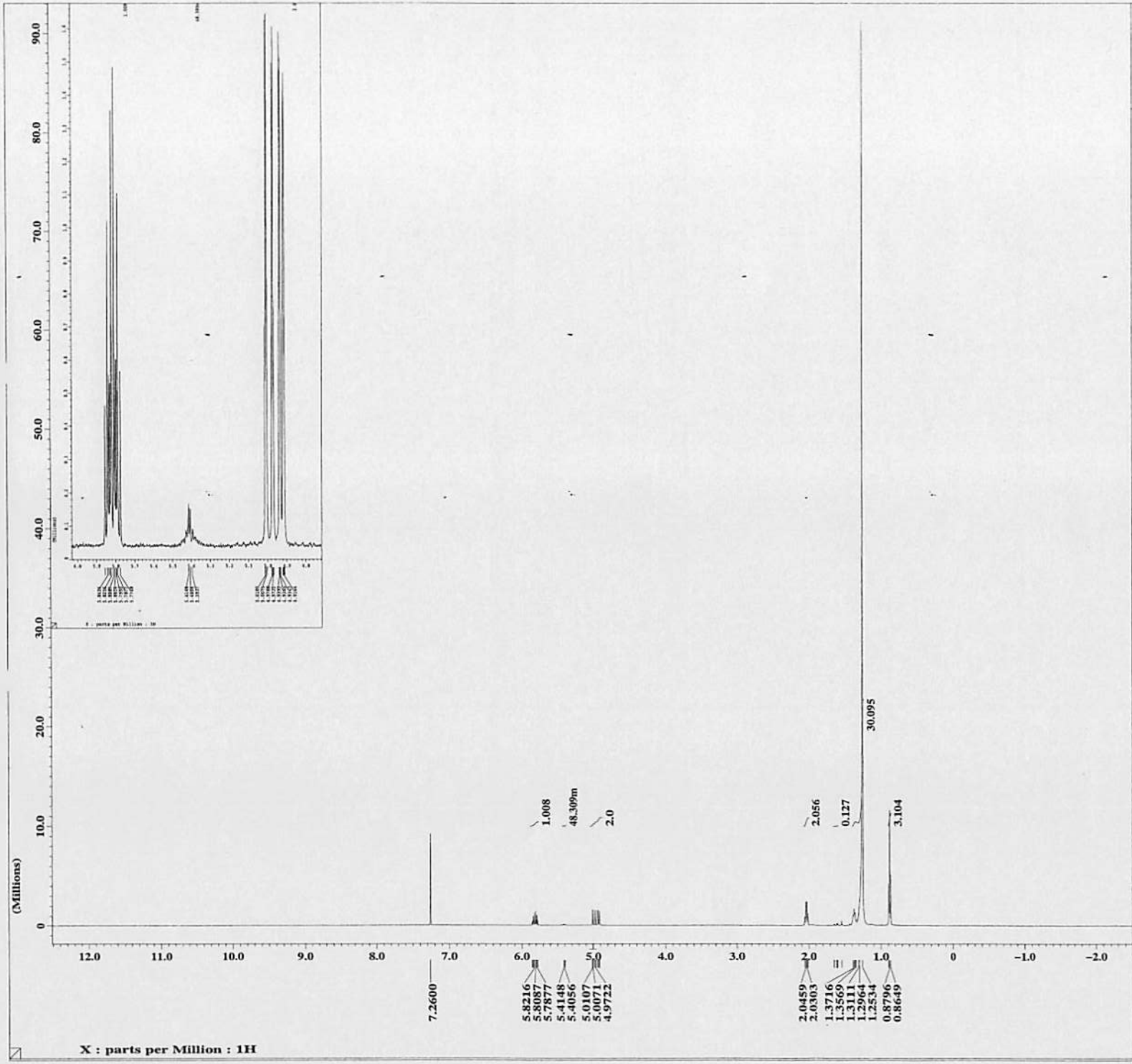

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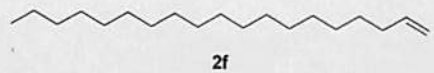

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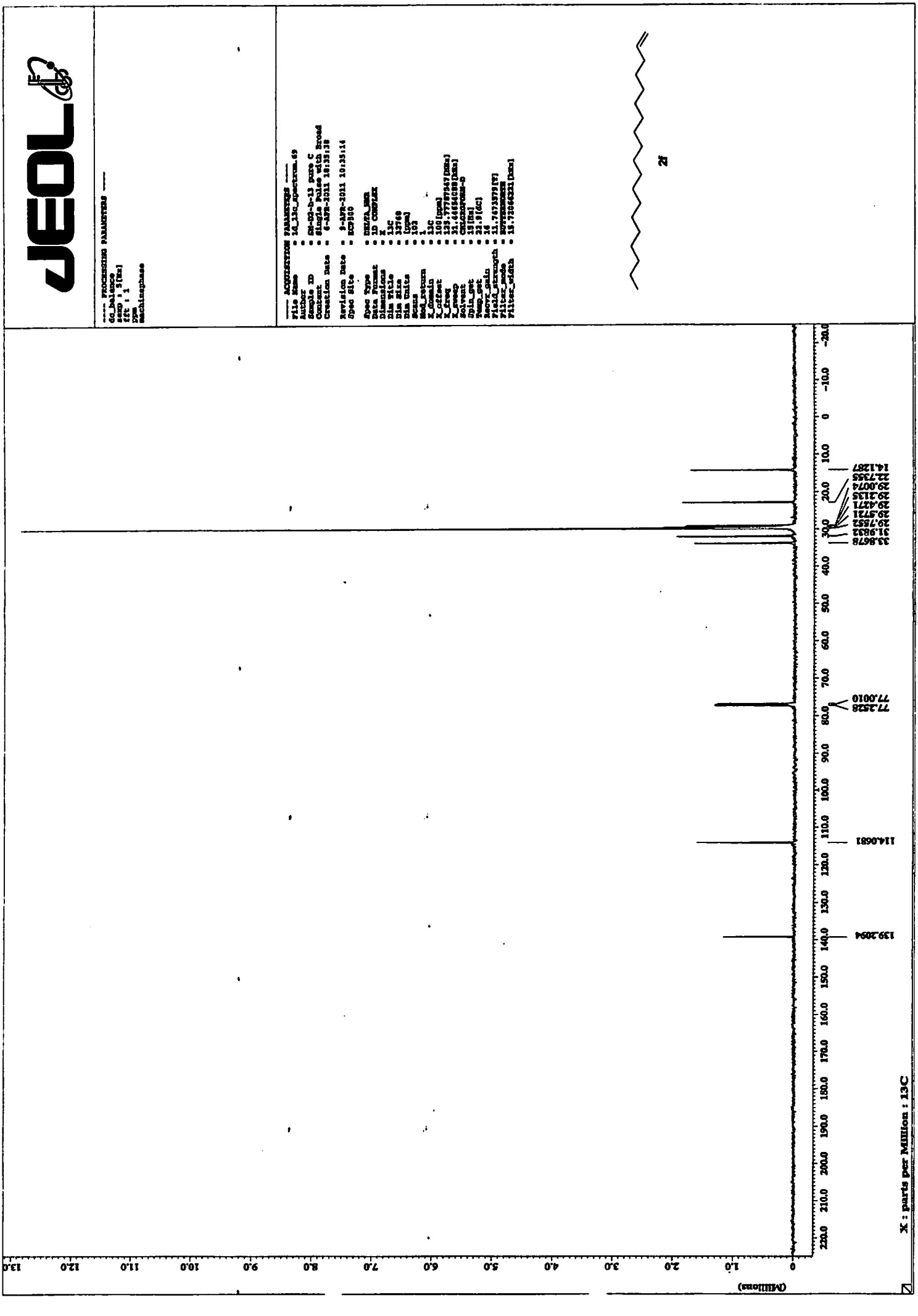

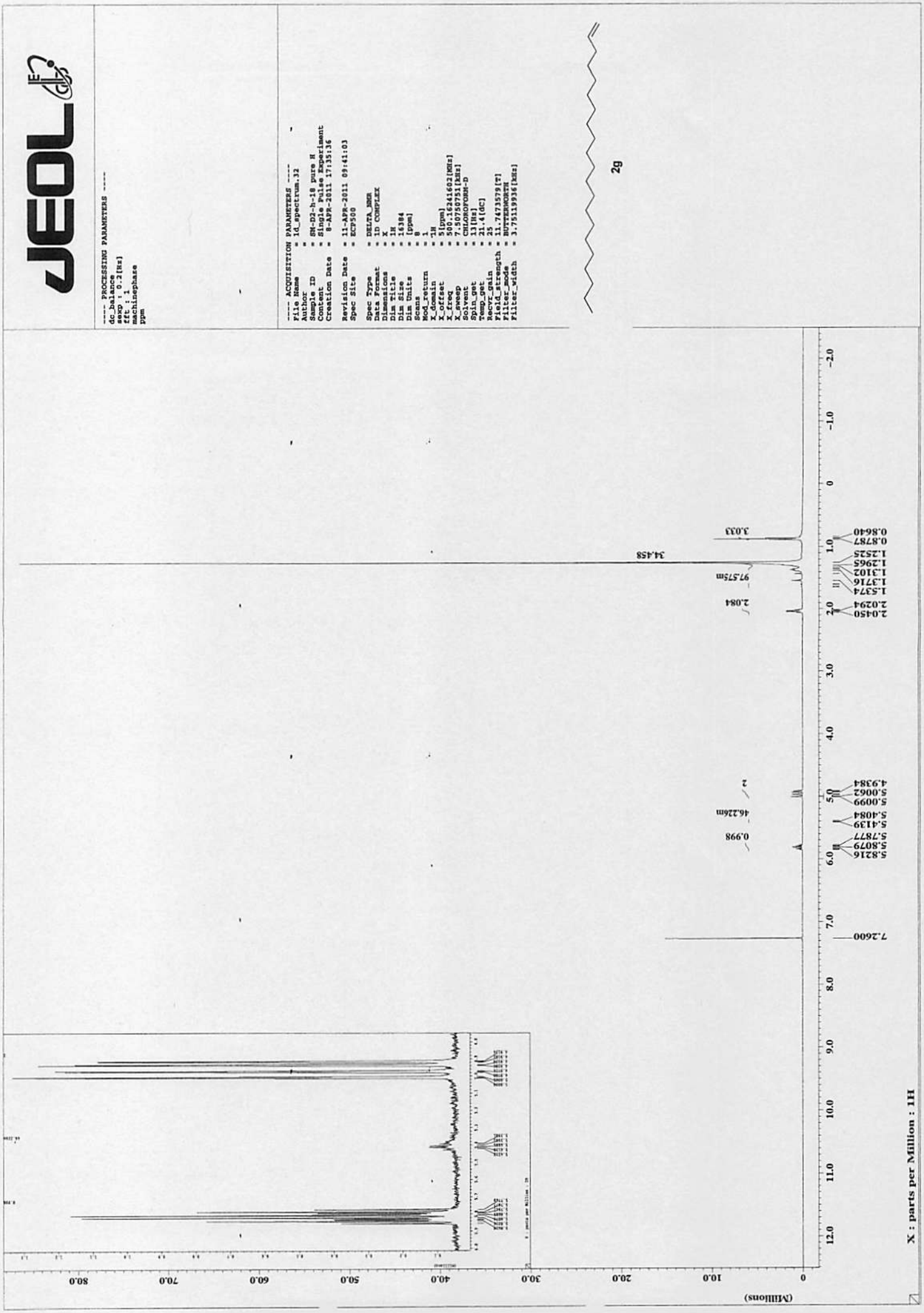

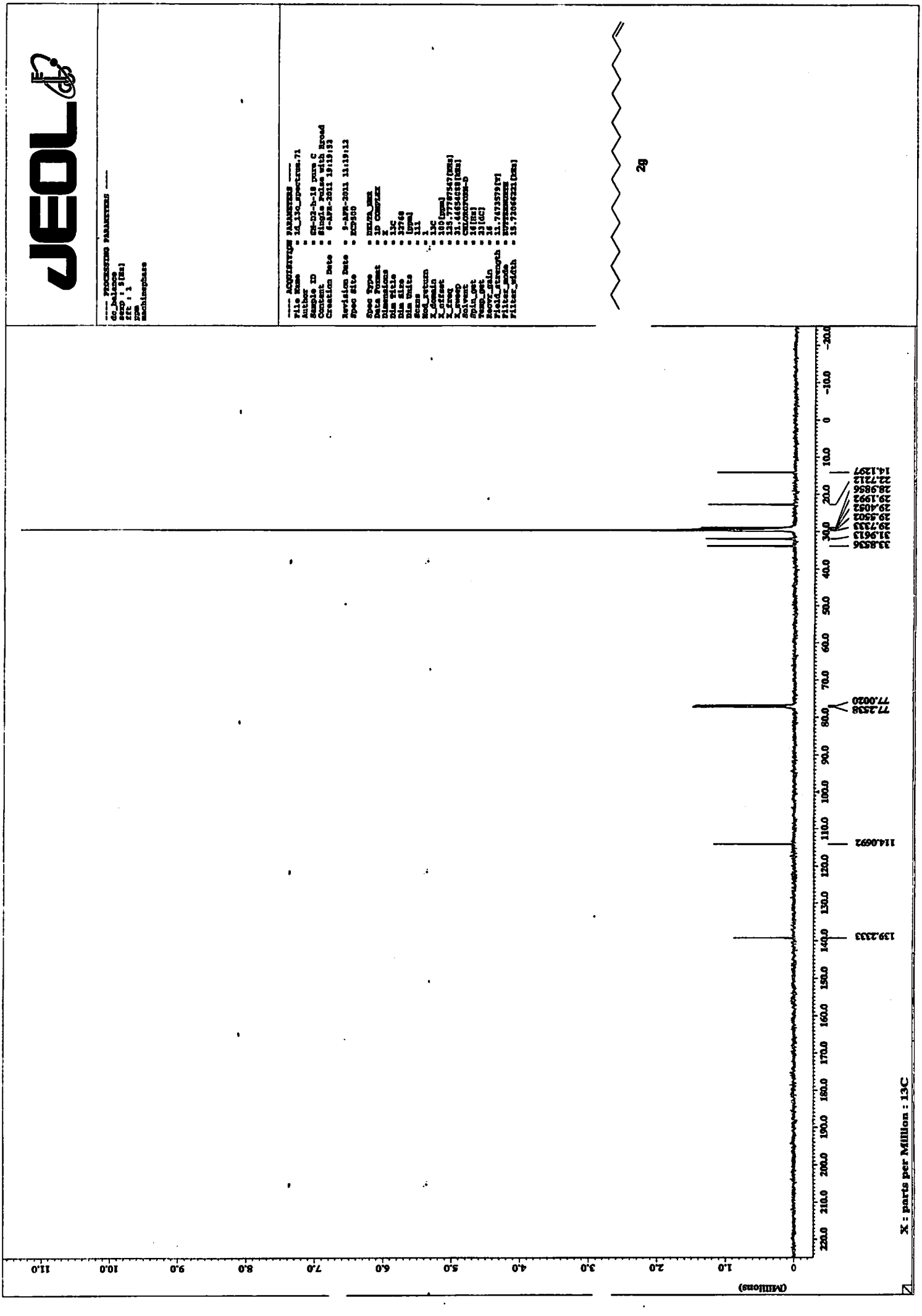

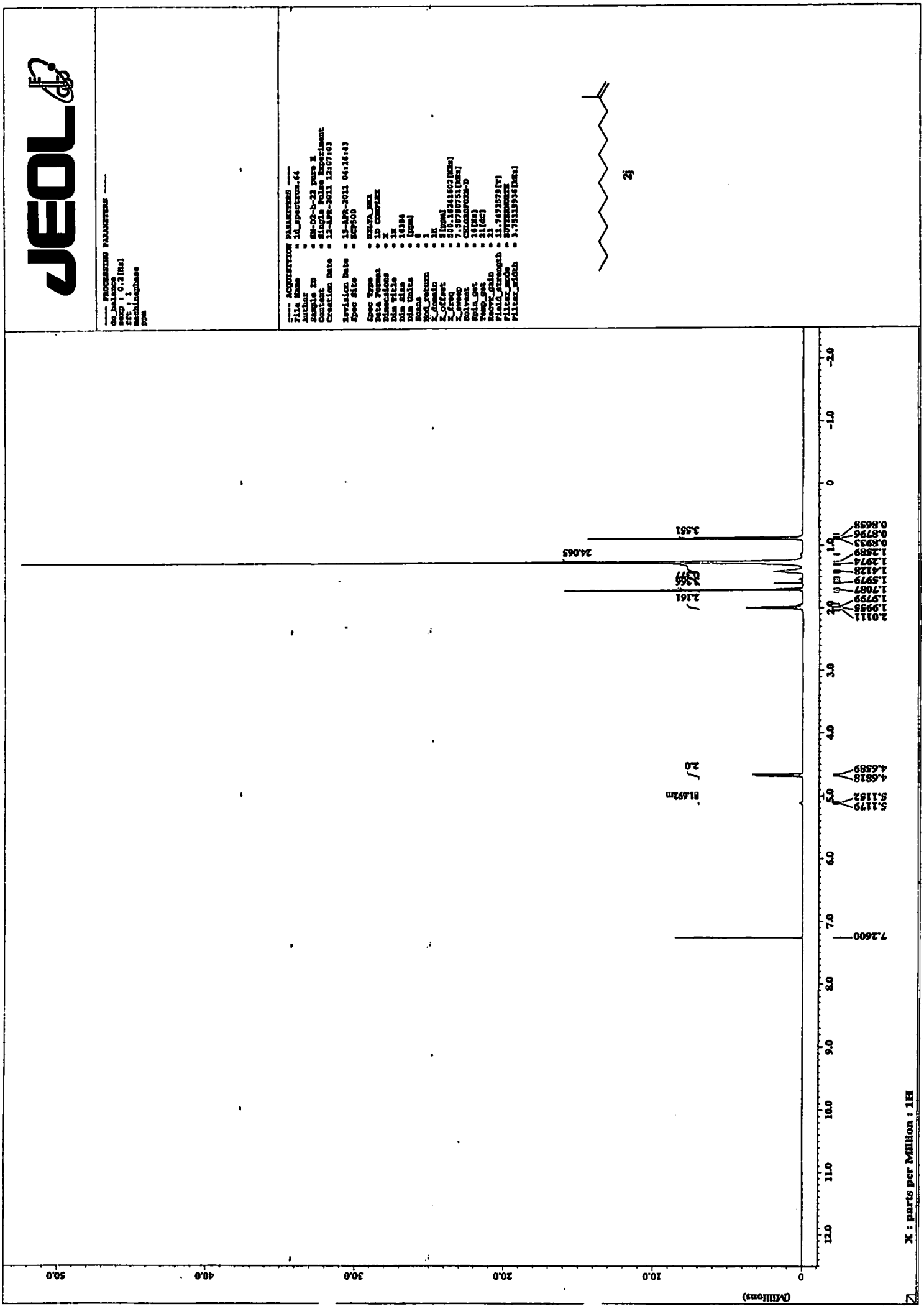

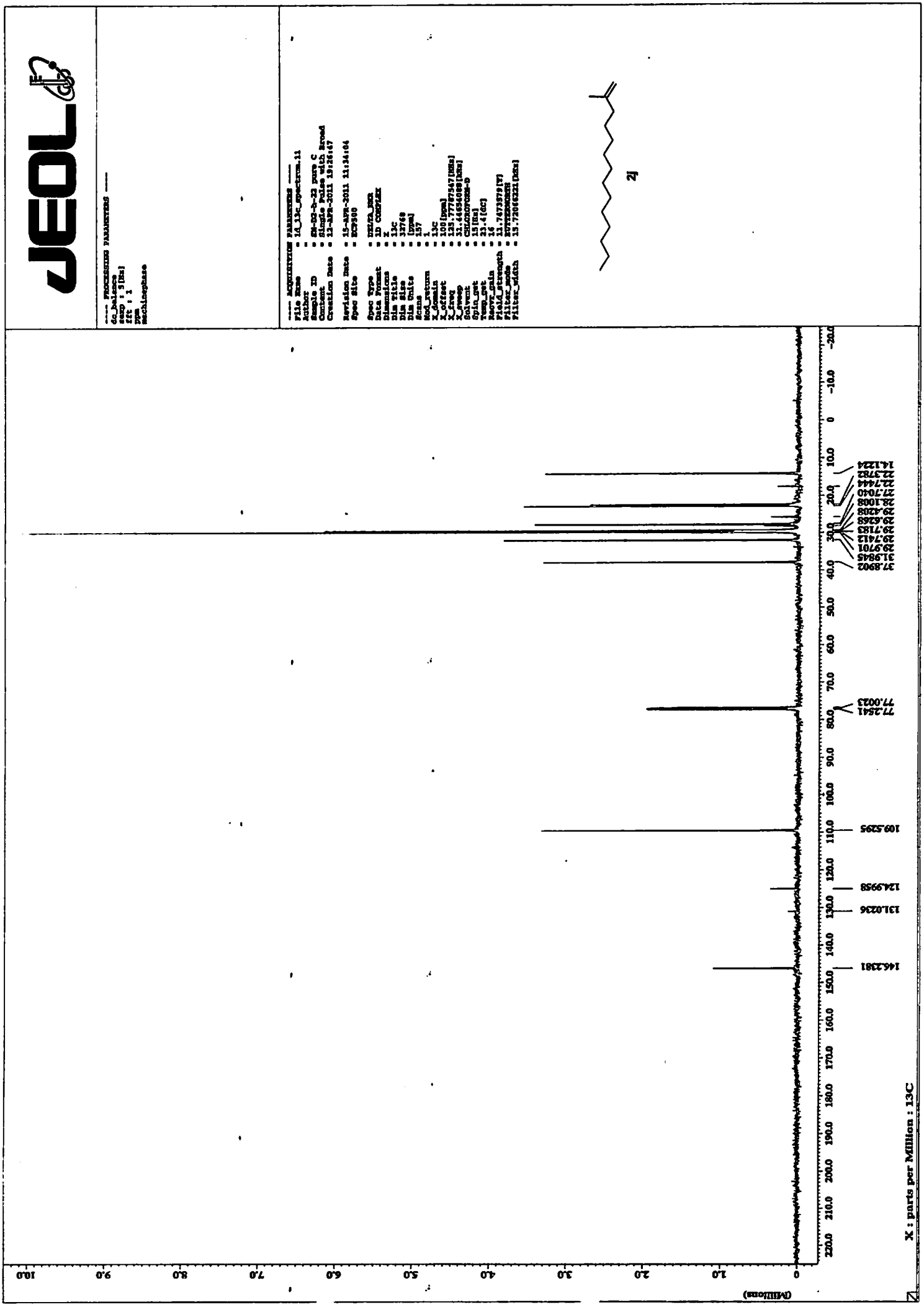

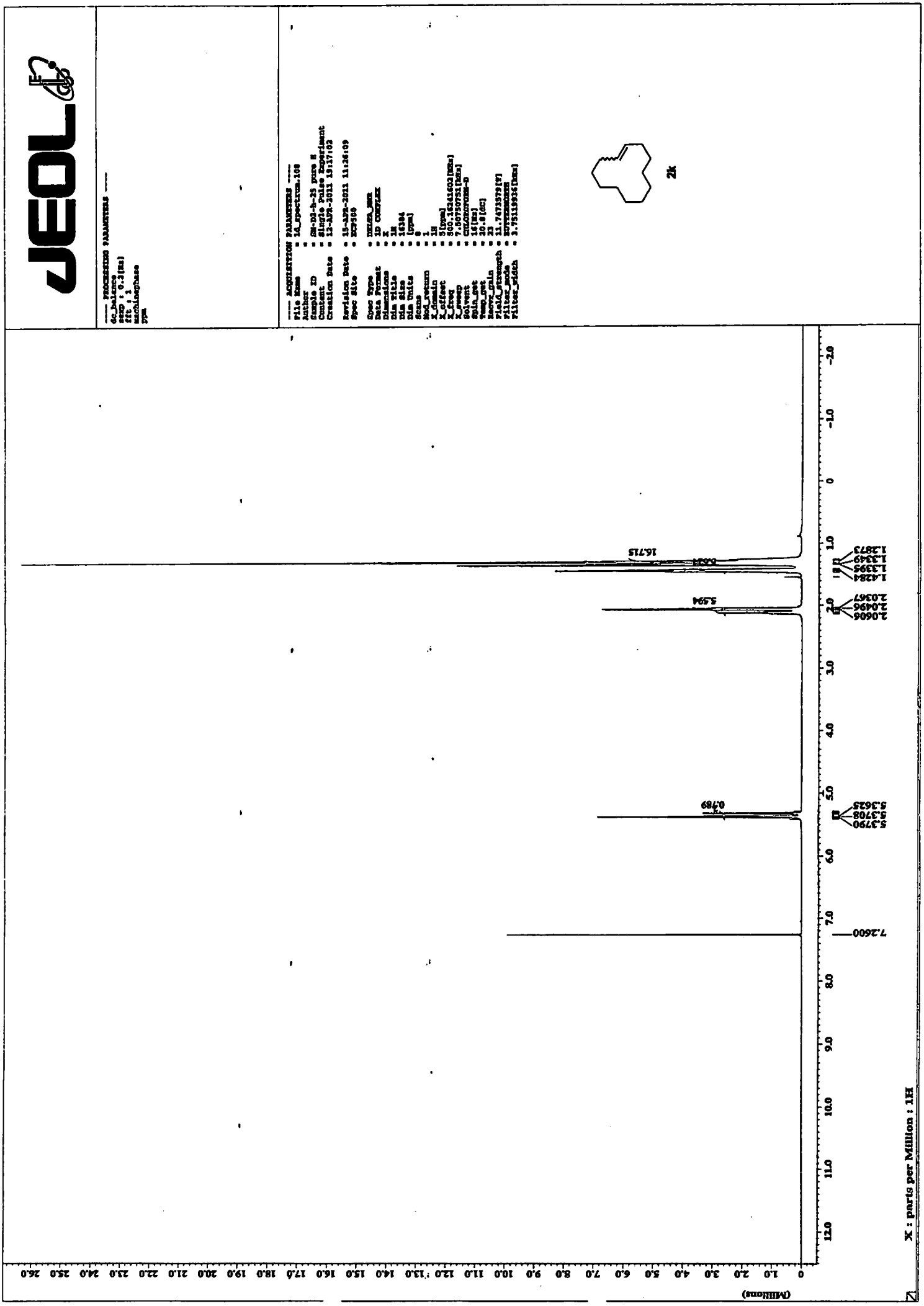

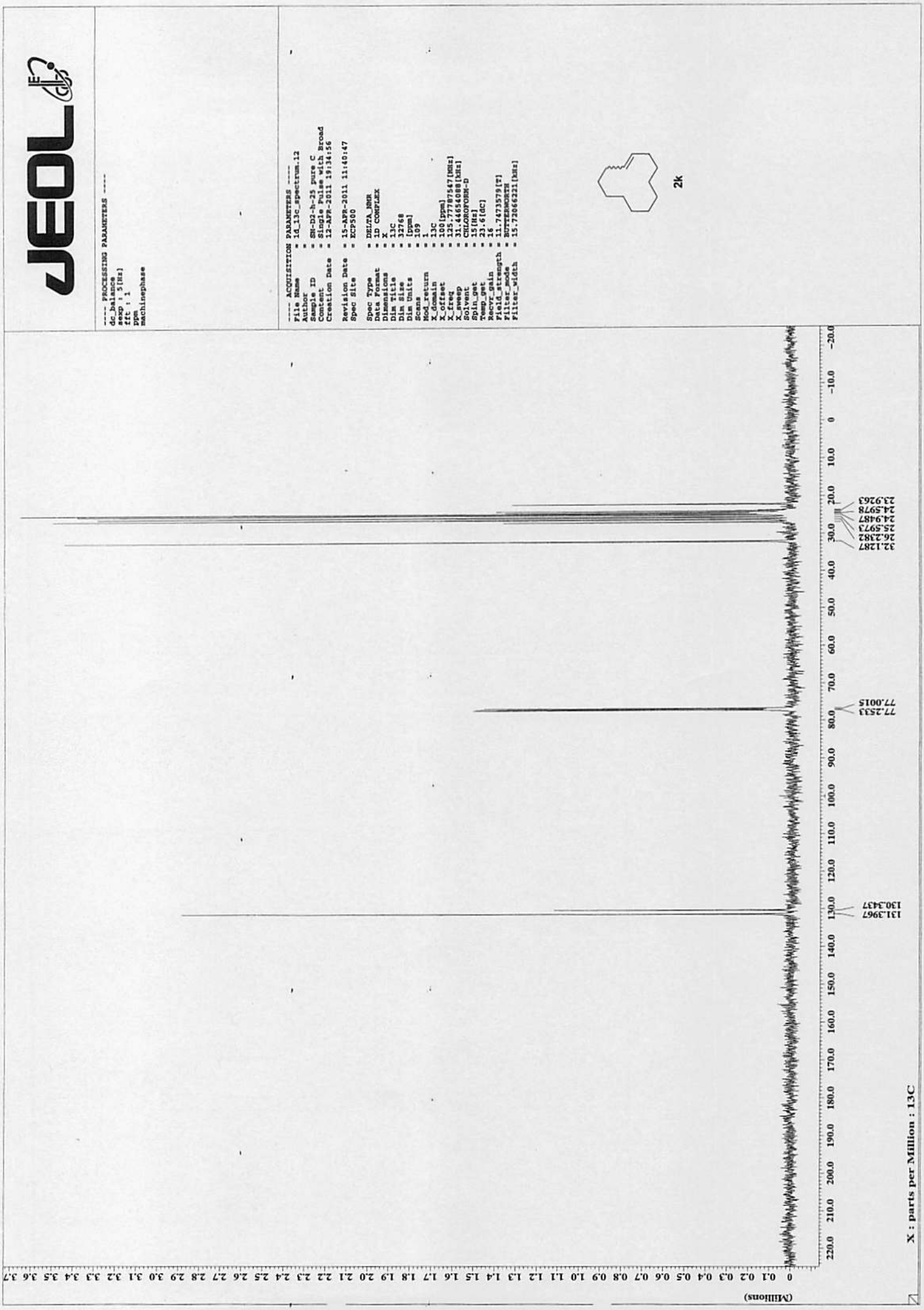

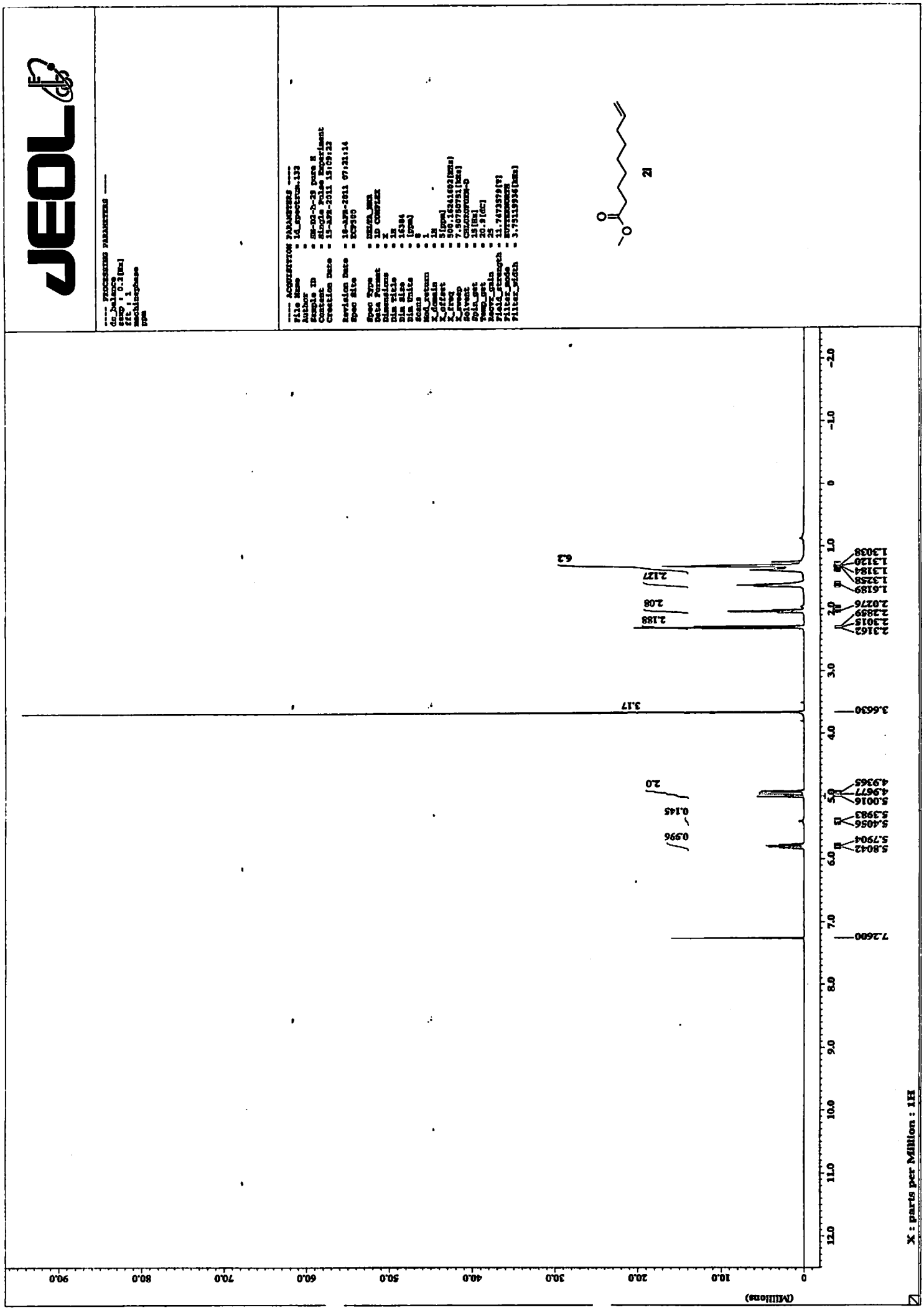

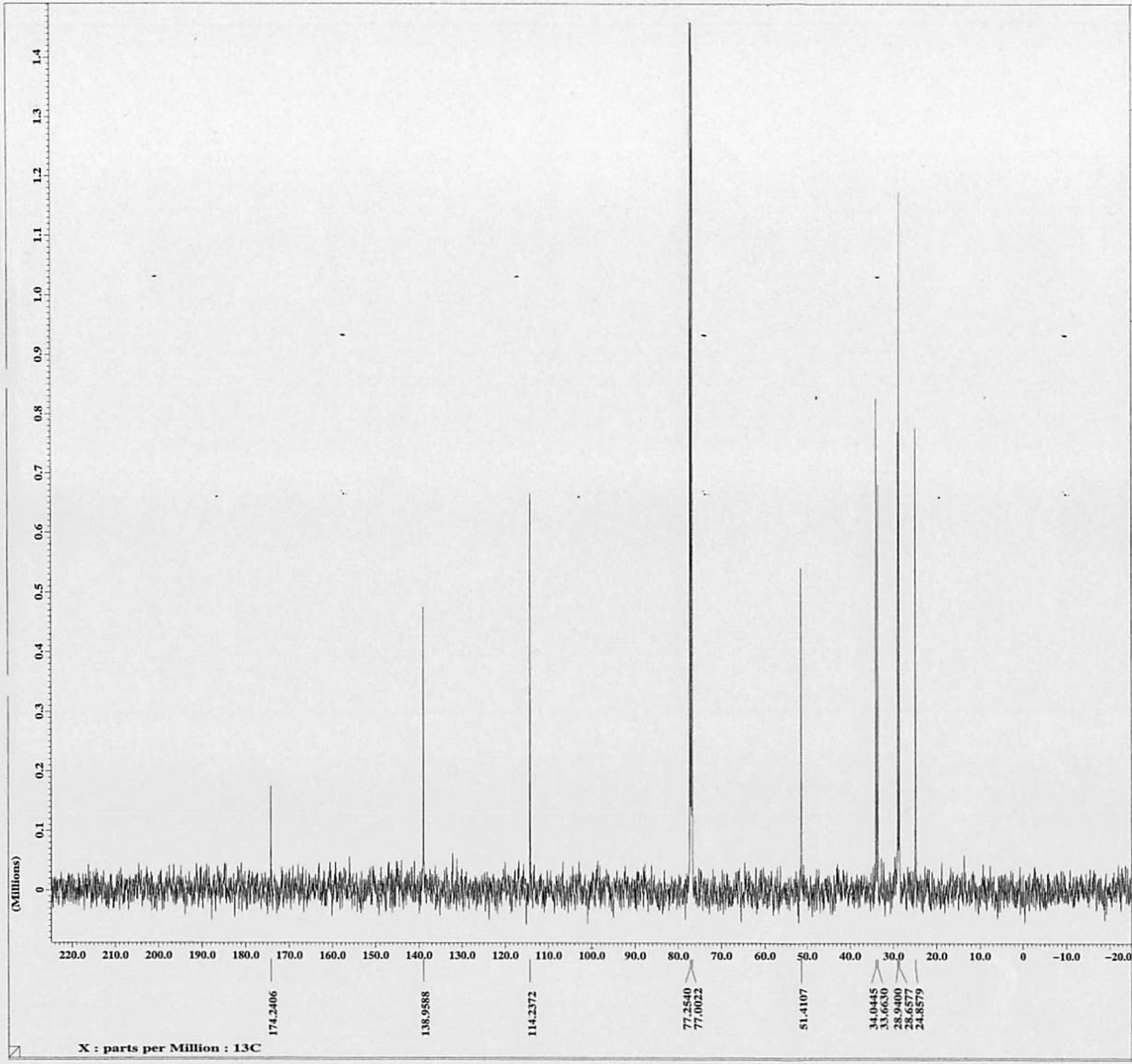

JEOL

---- PROCESSING PARAMETERS ----
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sexp : 5[Hz]
fft : 1
ppm
machinephase

---- ACQUISITION PARAMETERS ----
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Author =
Sample ID = SM-D2-h-29 pure C
Content = Single Pulse with Broad
Creation Date = 15-APR-2011 15:19:20

Revision Date = 18-APR-2011 07:28:15
Spec Site = ECP500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 101
Mod_return = 1
X_domain = 13C
X_offset = 100[ppm]
X_freq = 125.77787547[MHz]
X_sweep = 31.44654088[kHz]
Solvent = CHLOROFORM-D
Spin_get = 14[Hz]
Temp_get = 22.8[dC]
Recvr_gain = 16
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
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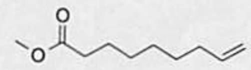

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