

# Preparation of $\alpha$ -Haloacrylate Derivatives via Dimethyl Sulfoxide-Mediated Selective Dehydrohalogenation

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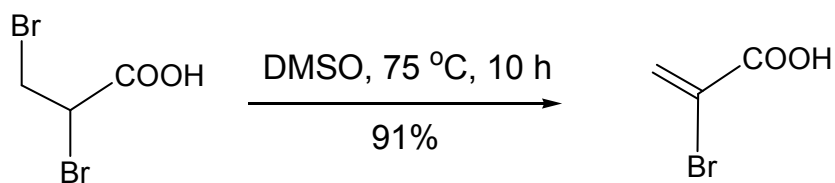
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**1. General experimental:** All reagents and solvents were purchased from commercial sources and used as received. The  $\alpha,\beta$ -dihalo substrates were purchased or prepared from the corresponding acrylate precursors through known olefin halogenation reactions.<sup>1</sup> All products were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and MS if ionization was detectable. Mass spectrometers used were the Micromass LCT (ESI or APCI) with an Agilent 1100 LC Pump (for LCMS). All the reactions in Tables 1, 2 and 3 were carried out in either pure DMSO or wet DMSO containing up to 10% water. Gilson reversed-phase preparatory HPLC (pump models of 331 and 332 and UV detector wave length: 230 nm) was used for separation with a Phenomenex Gemini column (5u C18 110A, 150 X 30mm) gradient solvent program (solvent A:  $\text{H}_2\text{O}$ , solvent B: acetonitrile) from 10% to 50% solvent B for 10 min. at 40mL/min. flow rate. NMR experiments were performed on a Bruker AVANCE 400 MHz spectrometer equipped with a 5 mm broadband probe.

The following abbreviations are used to designate the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

### Preparation of $\alpha$ -Bromoacrylate Derivatives and $\alpha$ -Bromo Vinylketones



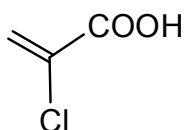
General DMSO dehydrohalogenation procedures: A solution of 2,3-dibromopropanoic acid (0.696 g, 3.0 mmol) in 9 mL of DMSO with 1.0 mL of water was heated at 75 °C for 10 hours. The reaction mixture was loaded onto prep HPLC and purified (Gilson gradient of water and acetonitrile, see general experimental). The pH of the combined

<sup>1</sup> a) Johnson, J. R.; McEwen, W. L. *Org. Synth. Coll Vol. I*, **1941**, 521. b) Snyder, H. R.; Brooks, L. A. *Org. Synth. Coll Vol. II*, **1943**, 171.

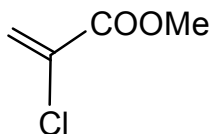
fractions was adjusted to pH = 8 using aqueous NaOH (2 N). Lyophilization of the fractions gave 0.47 g (91%) of the  $\alpha$ -bromoacrylic acid sodium salt as a white solid.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  5.93 (d,  $J$  = 1.8 Hz, 1H), 6.41 (d,  $J$  = 1.8 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  123.4, 127.2, 166.1. LC-ESMS  $[\text{M-H}]^-$ : 148.9.

Similar procedure was used for the preparation of  $\alpha$ -bromoacrylic esters and  $\alpha$ -bromo vinylketones. The water content of DMSO in these reactions was reduced to 3-5%.

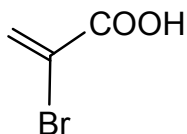
The following a-haloacrylate derivatives and the  $\alpha$ -bromo vinylketones were prepared following the corresponding procedures described above.



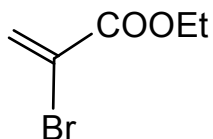
**2-Chloroacrylic acid (entry 1 of table 1):**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  6.16 (d,  $J$  = 1.8 Hz, 1H) 6.50 (d,  $J$  = 1.8 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  126.12, 131.50, 162.48. LC-ESMS:  $[\text{M-H}]^-$ : 105.0.



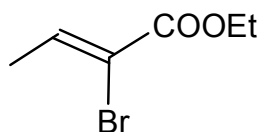
**Methyl 2-chloroacrylate (entry 2 of table 1):**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  3.79 (s, 3H) 6.25 (d,  $J$  = 2.0 Hz, 1H) 6.56 (d,  $J$  = 2.0 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  53.40, 127.23, 129.94, 161.73. LC-ESMS  $[\text{M-H}]^-$ : 119.0.



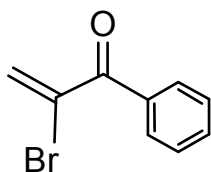
**2-Bromoacrylic acid (entry 3 of table 1):**  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  5.93 (d,  $J$  = 1.8 Hz, 1H), 6.41 (d,  $J$  = 1.8 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  123.4, 127.2, 166.1. LC-ESMS  $[\text{M-H}]^-$ : 148.9.



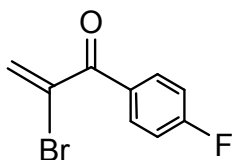
**Ethyl 2-bromoacrylate<sup>2</sup> (entry 4 of table 1):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.23 (t, *J* = 7.2 Hz, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 13.9, 62.6, 120.5, 131.7, 161.3. LC-ESMS [M-H]<sup>-</sup>: 177.0.



**(Z)-Ethyl 2-bromobut-2-enoate<sup>2</sup> (entry 5 of table 1):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.30 (t, *J* = 7.1 Hz, 3H) 1.96 (d, *J* = 6.8 Hz, 3H) 4.26 (q, *J* = 7.1 Hz, 2H) 7.45 (q, *J* = 6.8 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 14.0, 17.8, 62.1, 116.7, 142.1, 161.6. LC-ESMS [M-H]<sup>-</sup>: 191.0.



**2-Bromo-1-phenylprop-2-en-1-one<sup>3</sup> (entry 6 of table 1):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 6.57 (d, *J* = 3.3 Hz, 1H), 6.75 (d, *J* = 3.3 Hz, 1H), 7.53 - 7.62 (m, 2H), 7.68 - 7.76 (m, 1H), 7.78 - 7.83 (m, 2H).

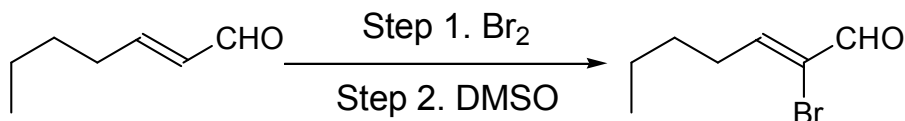


**2-Bromo-1-(4-fluorophenyl)prop-2-en-1-one (entry 7 of table 1):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 6.56 (d, *J* = 3.4 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 7.22 - 7.48 (m, 2H), 7.83 - 7.93 (m, 2H).

<sup>2</sup> Chang, M.; Hsu, R.; Tseng, T.; Sun, P.; Chang, N. *Tetrahedron* **2004**, 60, 5545.

<sup>3</sup> Nield, C. H. *J. Am. Chem. Soc.* **1945**, 67, 1145.

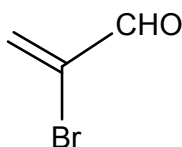
## Preparation of 2-Bromoacrylaldehyde Analogues



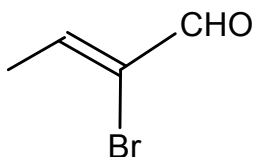
Step 1: To a solution of (E)-hept-2-enal (0.610 g, 5 mmol) in methylene chloride (10 mL) was added bromine (0.84 g, 5.25 mmol). The resulting solution was stirred at 0 °C for 10 min. after which saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 mL) was added. After stirring for an additional 10 min. at room temperature, the product was extracted into methylene chloride (2 x 20 mL). The organic layers were combined and dried over MgSO<sub>4</sub>. After filtration, the organic solution was concentrated under reduced pressure to give the desired 2,3-dibromohexanal (1.28 g), which was used in the next step without purification.

Step 2: The crude 2,3-dibromopentanal intermediate (1.28 g) was dissolved in DMSO (20 mL). The solution was heated to 60 °C for 2 h before the addition of pentane (20 mL, 25 °C). The resulting mixture was washed with water (2 x 10 mL) and brine (2 x 10 mL). The organic layer was dried over MgSO<sub>4</sub> and concentrated to give the desired product (920 mg, 96.3%) as a colorless liquid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 0.78 (t, *J* = 7.2 Hz, 3H), 1.15 - 1.29 (m, 2H), 1.30 - 1.48 (m, 2H), 2.37 (q, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H) 9.14 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 188.1, 158.7, 128.0, 31.7, 29.1, 22.0, 13.9.

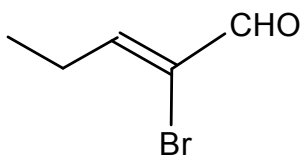
The following α-haloacrylaldehyde and α-haloacrylonitrile analogs were prepared following similar procedures described above.



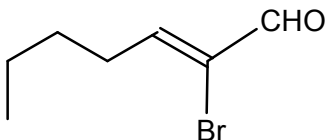
**2-Bromoacrylaldehyde (entry 1 of table 2):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.11 (d, *J* = 2.4 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 9.26 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 188.0, 140.5, 131.8.



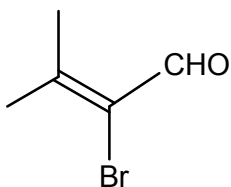
**(Z)-2-Bromobut-2-enal<sup>4</sup> (entry 2 of table 2):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 2.04 (d, *J* = 6.7 Hz, 3H), 7.57 (q, *J* = 6.7 Hz, 1H), 9.23 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 187.8, 154.1, 129.3, 18.3.



**(Z)-2-Bromopent-2-enal<sup>5</sup> (entry 3 of table 2):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.06 (t, *J* = 7.6 Hz, 3H), 2.38 - 2.47 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 9.23 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 187.9, 159.5, 127.5, 25.6, 11.9.



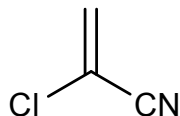
**(Z)-2-Bromohept-2-enal (entry 4 of table 2):** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 0.78 (t, *J* = 7.2 Hz, 3H), 1.15 - 1.29 (m, 2H), 1.30 - 1.48 (m, 2H), 2.37 (q, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 9.14 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 188.1, 158.7, 128.0, 31.7, 29.1, 22.0, 13.9.



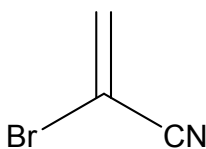
<sup>4</sup> Dai, W.; Wu, J.; Chiu, K.; Fong, K. C.; Lee, M. Y. H.; Lau, C. W. *J. Org. Chem.* **1999**, *64*, 5062.

<sup>5</sup> Henning Lutjens, H.; Wahl, G.; Moller, F.; Knochel, P.; Sundermeyer, J. *Organometallics* **1997**, *16*, 5869.

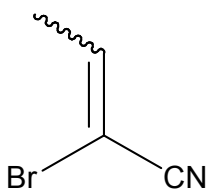
**2-Bromo-3-methylbut-2-enal (entry 5 of table 2):**  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  2.10 (s, 3H), 2.28 (s, 3H), 9.65 (s, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  184.4, 161.8, 122.8, 28.2, 21.5.



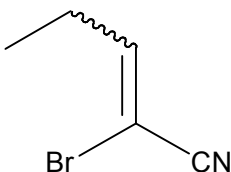
**2-Chloroacrylonitrile (entry 1 of table 3):**  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  6.79 (d,  $J$  = 3.3 Hz, 1H), 6.61 (d,  $J$  = 3.3 Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  135.2, 114.7, 108.0.



**2-Bromoacrylonitrile (entry 2 of table 3):**  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  6.81 (d,  $J$  = 3.1 Hz, 1H), 7.19 (d,  $J$  = 3.1 Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  139.8, 116.0, 93.5.



**2-Bromobut-2-enenitrile<sup>6</sup> (entry 3 of table 3):**  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  1.89 (d,  $J$  = 6.8 Hz, 3H), 1.96 (d,  $J$  = 7.2 Hz, 3H), 7.18 (q,  $J$  = 7.2 Hz, 1H), 7.38 (q,  $J$  = 6.8 Hz, 1H).



**2-Bromopent-2-enenitrile<sup>7</sup> (entry 4 of table 3):**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  1.06 - 1.15 (m, 6H), 2.29 - 2.43 (m, 4H), 7.27 (t,  $J$  = 8.0 Hz, 1H), 7.45 (t,  $J$  = 7.2 Hz, 1H).

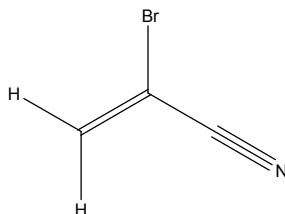
<sup>6</sup> Madsen, J. O.; Lawesson, S. O. *Tetrahedron* **1974**, 30, 3481.

<sup>7</sup> Ishizaki, M.; Osada, S.; Kato, T. *Jpn. Kokai Tokkyo Koho* **1993**, JP05117263A.

## 2. Structural Determinations

Structural determinations were carried out on Bruker 500MHz NMR instrument equipped with an inverse broadband probe at room temperature (25 °C). Proton direct observe experiments are typically acquired in eight scans using a 45 degree observe pulse and approximately five second recycle delay (this includes the acquisition time). Carbon direct observe experiments are typically acquired using a 45 degree pulse and a 1 second recycle delay (again, this includes the acquisition time). Proton decoupling is applied during acquisition. We obtained good S/N for most types of carbon atoms under these conditions, although the line intensities could vary by up to two-fold relative to the carbon integral. NOE experiments were run as double pulsed field gradient spin echo NOEs (DPFGSE-NOE) at 800ms build-up time. The carrier is placed on the resonance to be perturbed, and the selective excitation pulse is in the range of 20-160ms, depending on the extent of chemical shift overlap. Homonuclear correlation experiments (COSY) are run using pulsed field gradients, typically acquiring 2048 (direct dimension) by 256 (indirect dimension) points. We linearly predict 2x in the indirect dimension and zero fill another 2x to give a final data matrix of 1024 x 1024. Heteronuclear correlation experiments (HSQC or HMBC) are also run as pulsed field gradient experiments with the same acquisition and processing parameters. Carbon-proton HSQC is run using a  $^1\text{H}$ - $^{13}\text{C}$  coupling of 145 Hz; carbon-proton HMBC is generally run optimized for eight Hz couplings, with a one-bond filter. All pulse sequences were Bruker library standard. Any significant deviations from these conditions are described if needed.

### 2-Bromoacrylonitrile (entry 2 of Table 3)

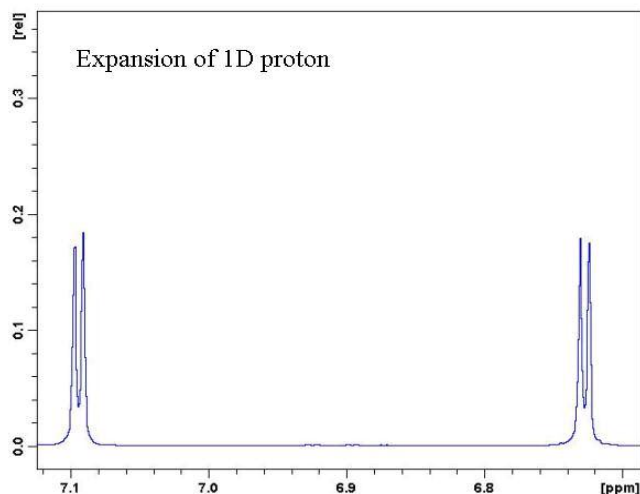


The proof of this structure is made primarily from the observation that both protons are connected to the same carbon, and that there is only one protonated carbon in the

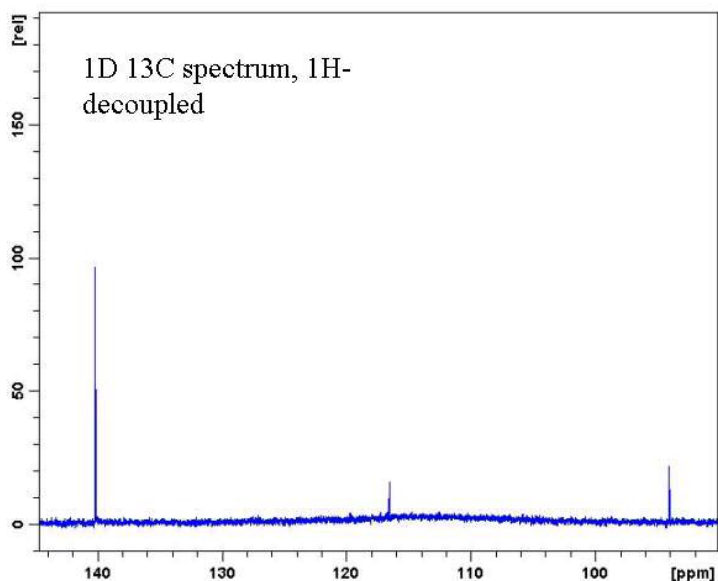


molecule. The HSQC experiment correlates protons to their attached carbons as long as the 1-bond  $^{13}\text{C}$ - $^1\text{H}$  coupling used for measurement is approximately correct. If the coupling constant is incorrect it is typically not possible to observe a correlation.

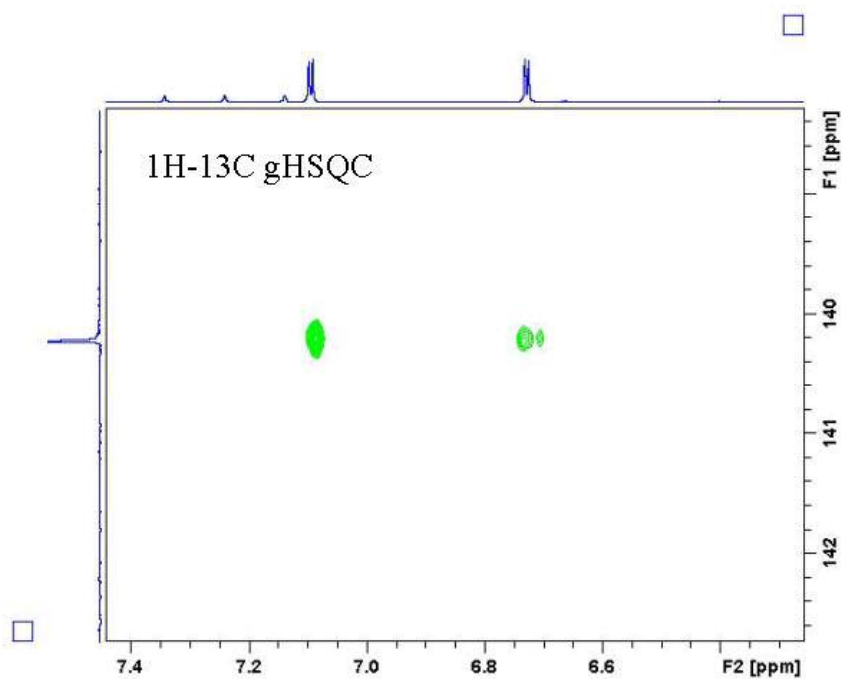
The proton 1D NMR spectrum consists of two doublets at 7.10 and 6.73 ppm, each with a 3.2 Hz coupling. This is pretty typical for terminal methylenes.



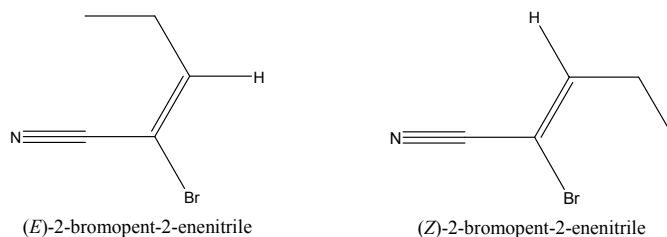
The 1D  $^{13}\text{C}$  spectrum shows the expected three carbons, one of which is protonated. The observed chemical shifts match chemical shift predicted values reasonably well.



The gHSQC experiment shows that both protons are connected to this protonated carbon, establishing the structure.



### Determination of the E/Z configuration (entry 4, Table 3)



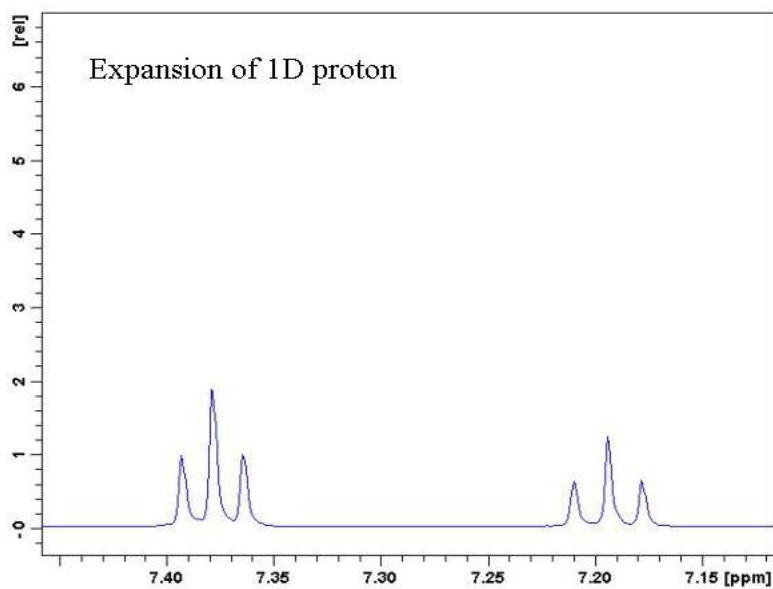
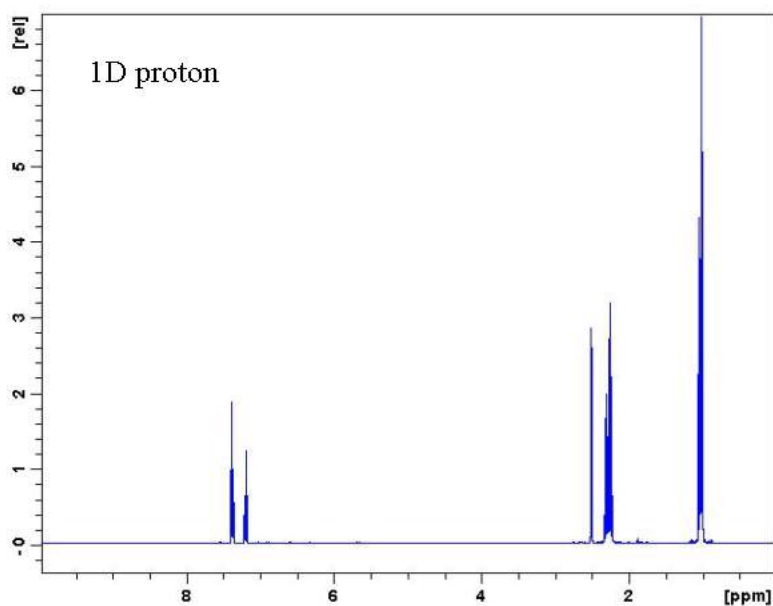
In the analysis that follows, we looked at a mixture of these two double bond isomers to identify the vinyl proton chemical shift for each compound. This allowed us to determine which compound was formed in subsequent reactions. The simplest way to discriminate between these isomers is to measure the three bond heteronuclear coupling constant between the vinyl proton and the nitrile carbon; in the compound on the left these are *trans* and so we would expect a coupling constant of greater than 10 Hz, whereas in the compound on the right these are *cis* and we would expect a coupling constant of approximately 5 Hz. A coupled carbon spectrum was used to make this determination, and since the two isomers are at somewhat different concentrations, we can relate this measurement back to the proton spectrum through the HSQC (not shown), or simply from the difference in intensity in the proton spectrum.

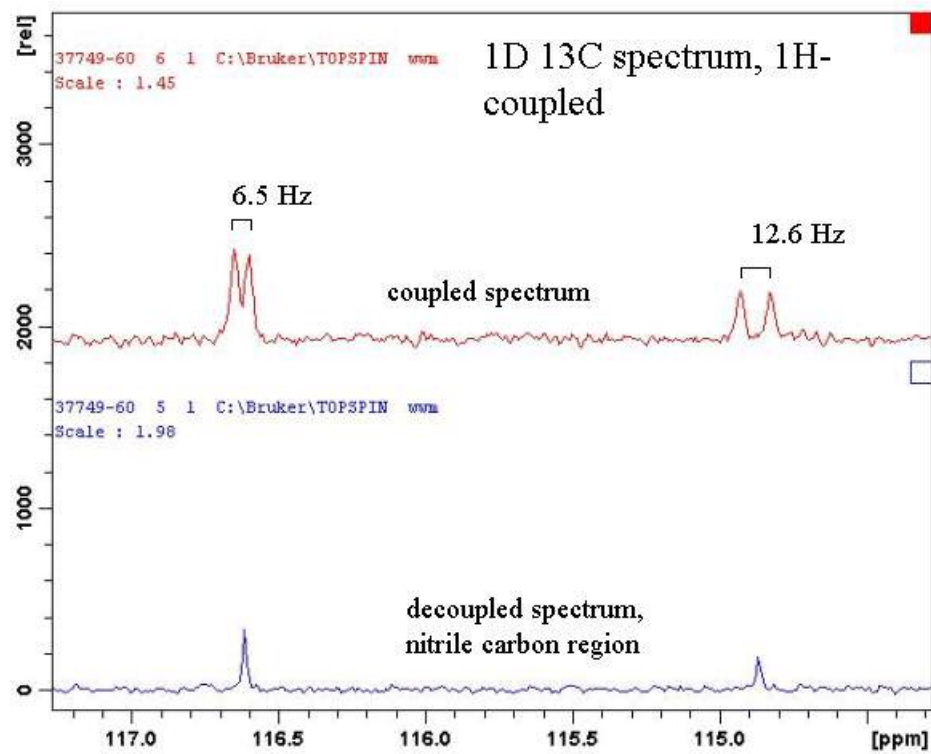
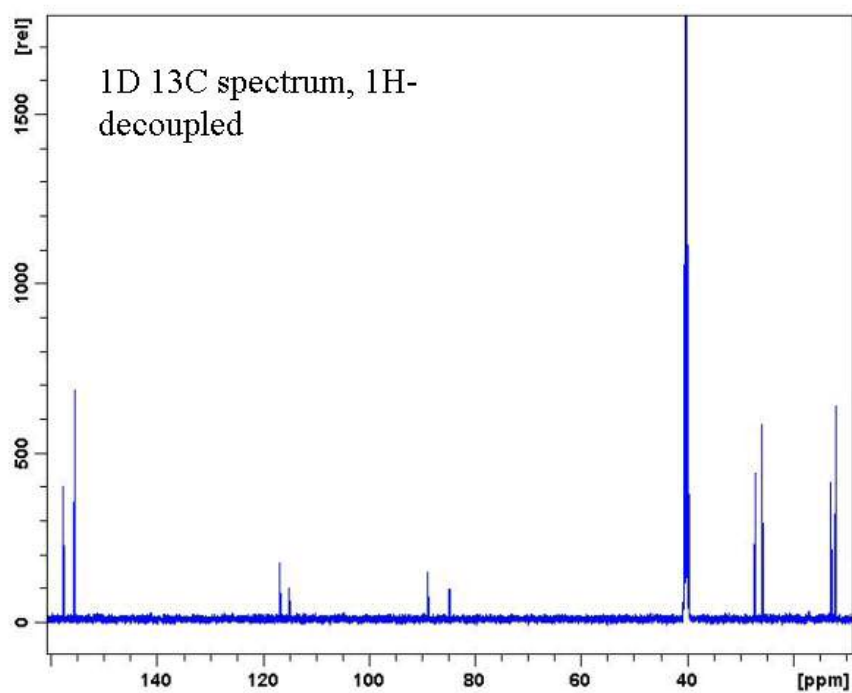
Table of chemical shifts and important coupling constants

	(E)-2-bromopent-2-enitrile	(Z)-3-bromohex-3-en-1-yne
vinyl 1H	7.195 ppm	7.379 ppm
3JHH	7.9 Hz	7.1 Hz
13C	157.47 ppm	155.40 ppm
	114.89	116.64
	84.66	88.74
	27.00	25.63
	12.69	11.73
3JCH	<b>12.6 Hz</b>	<b>6.5 Hz</b>

The proton spectrum of the mixture shows that each isomer has a typical three-bond proton-proton coupling between the vinyl proton and the methylene of the ethyl. This shows that the vinyl proton and ethyl are on the same carbon.

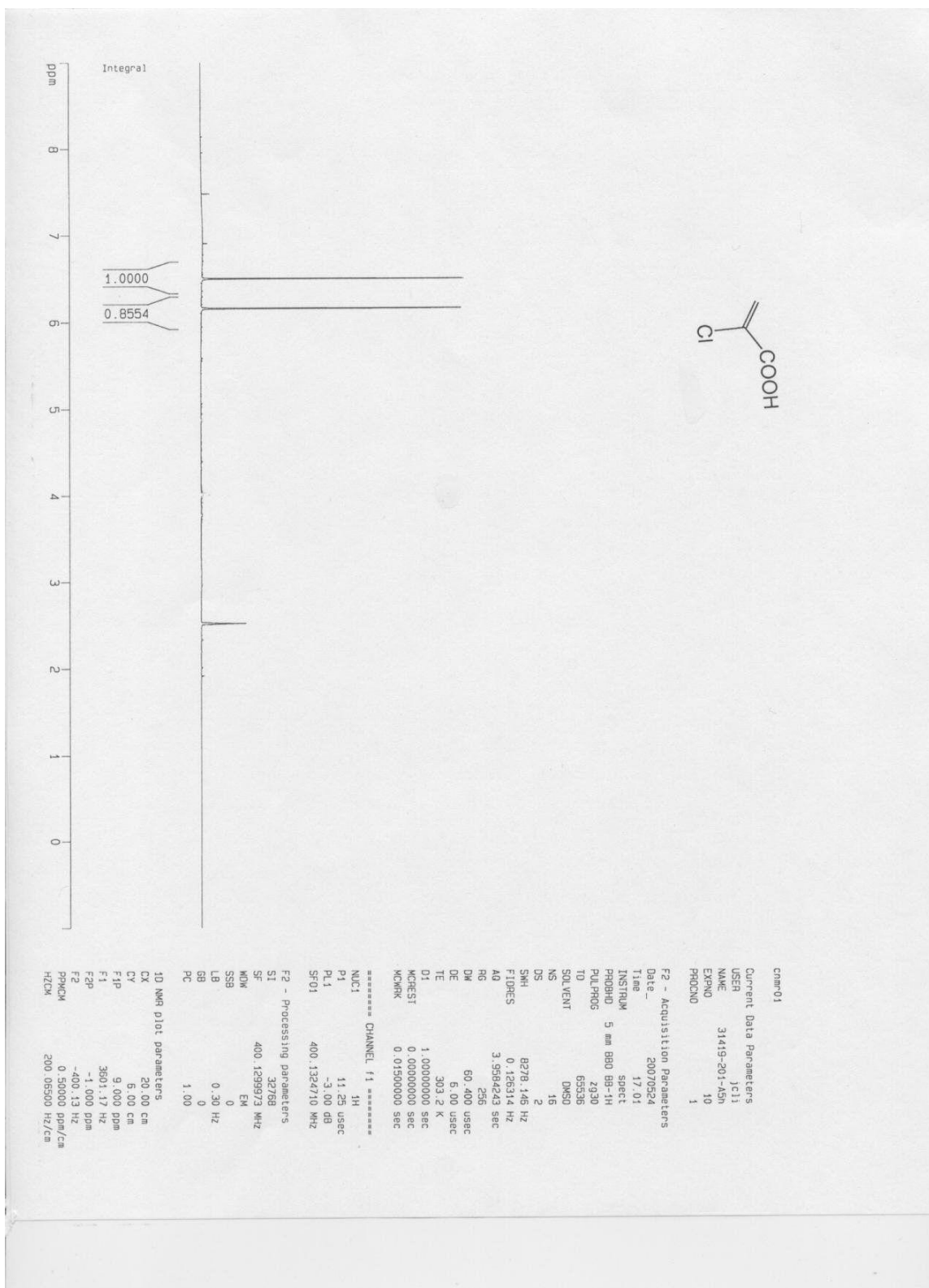
The carbon spectrum shows five pairs of chemical shifts, one pair for each carbon, with no significant overlaps. The coupled carbon spectrum clearly shows the difference in vinyl proton to nitrile carbon coupling, allowing us to make the assignments as given in the table.



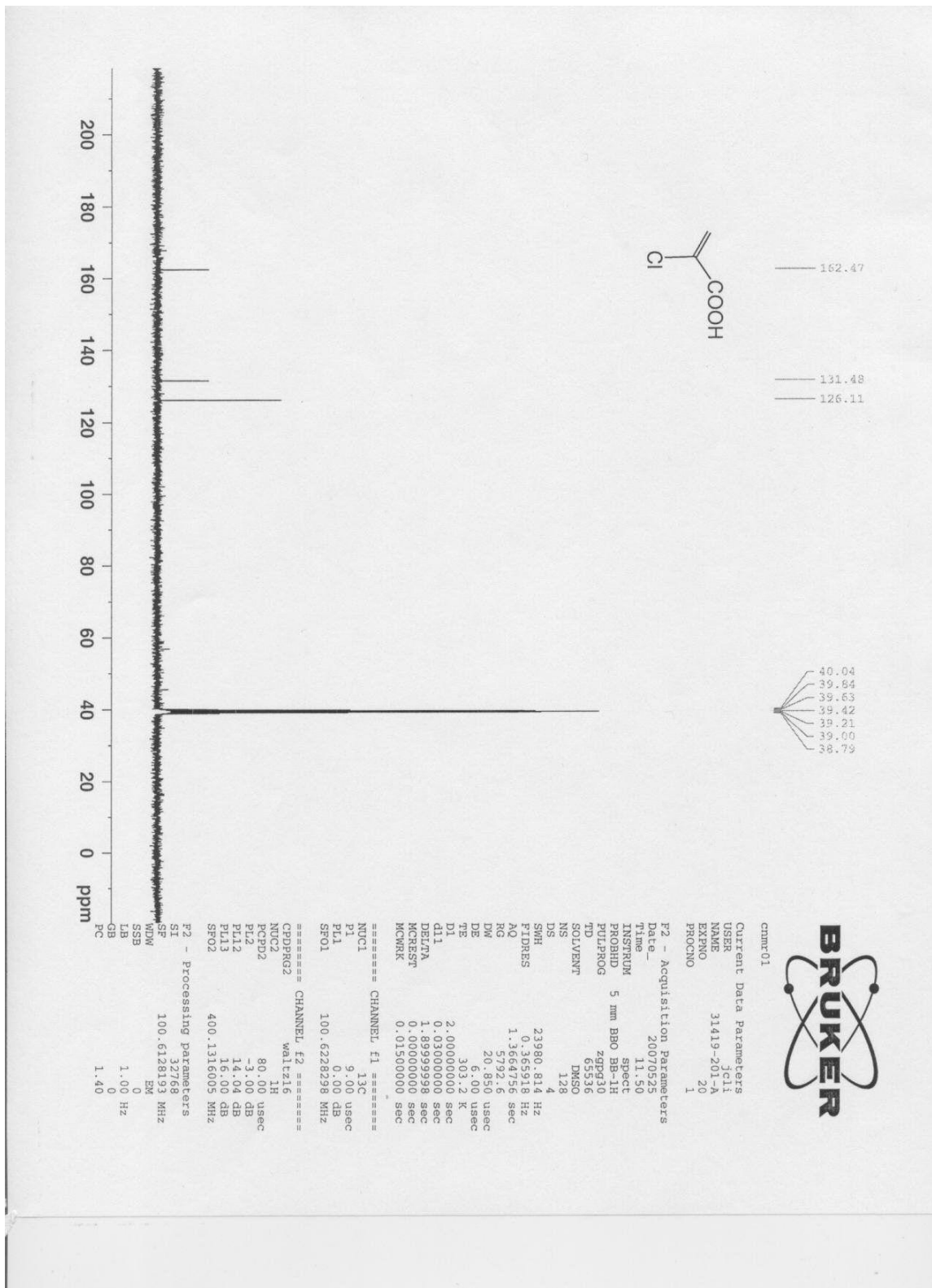


### 3. $^1\text{H}$ , $^{13}\text{C}$ NMR spectra

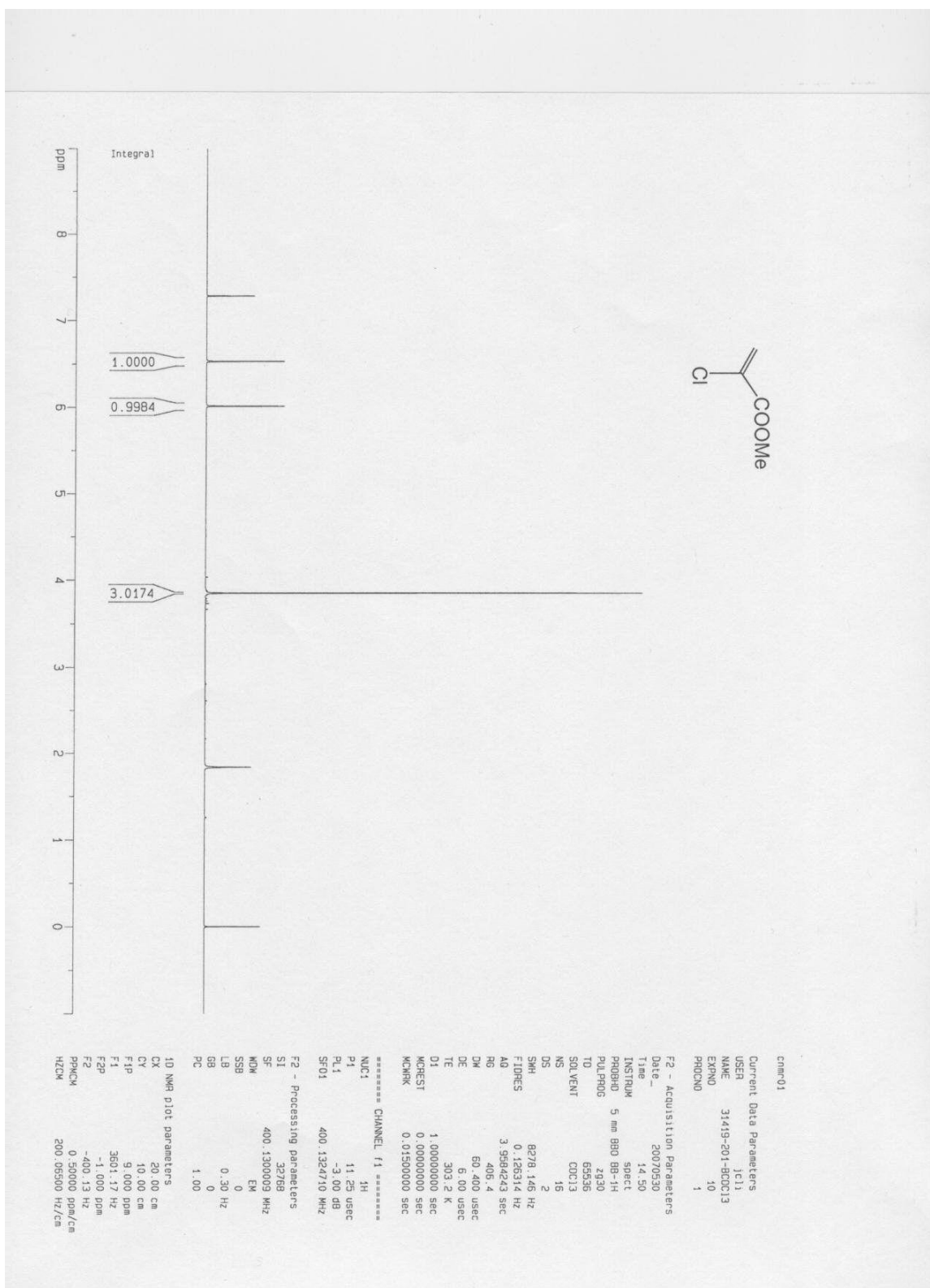
#### 2-Chloroacrylic acid (entry 1 of Table 1): $^1\text{H}$ NMR



# 2-Chloroacrylic acid (entry 1 of Table 1): <sup>13</sup>C NMR

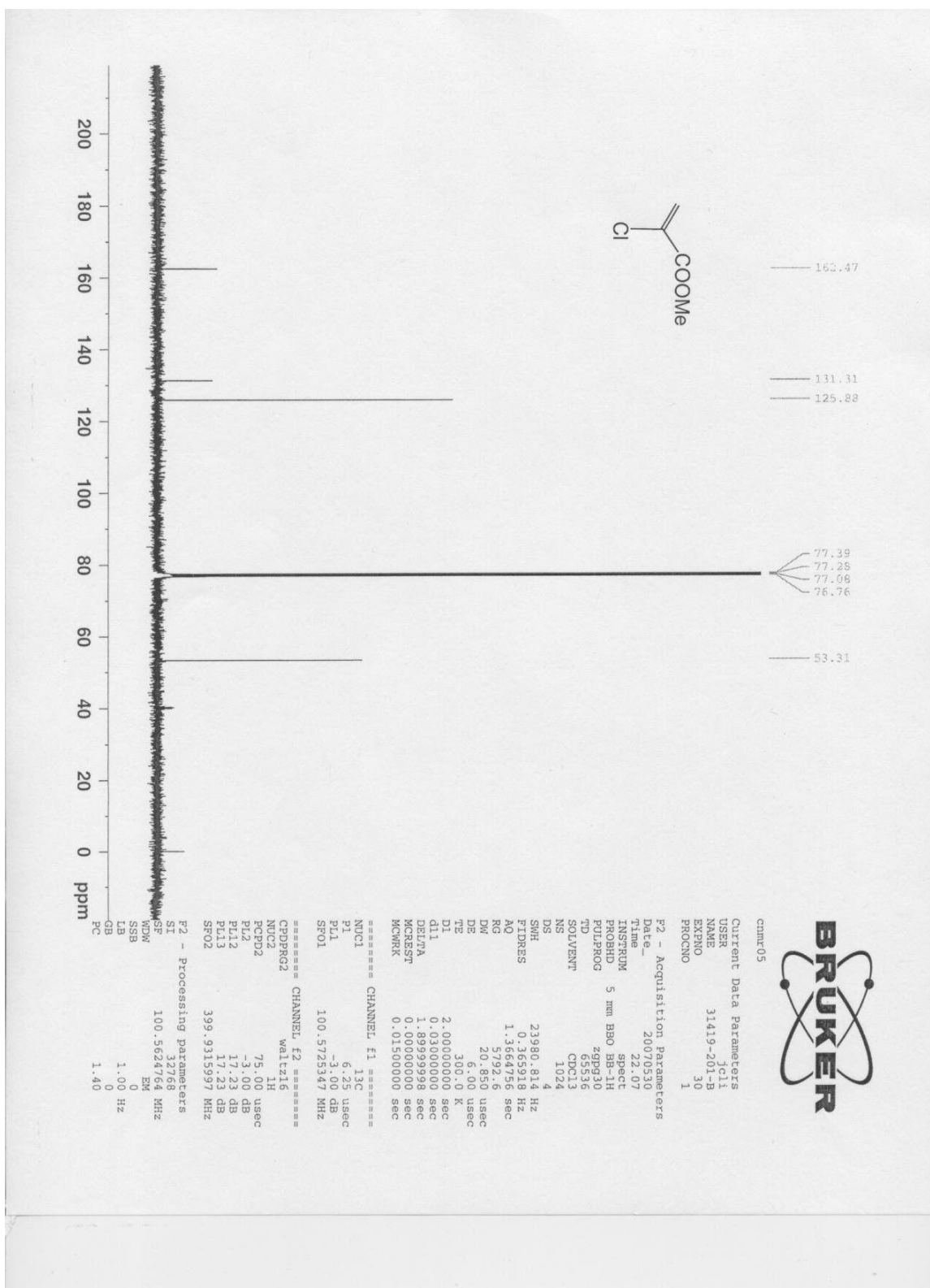


# Methyl 2-chloroacrylate (entry 2 of Table 1): <sup>1</sup>H NMR

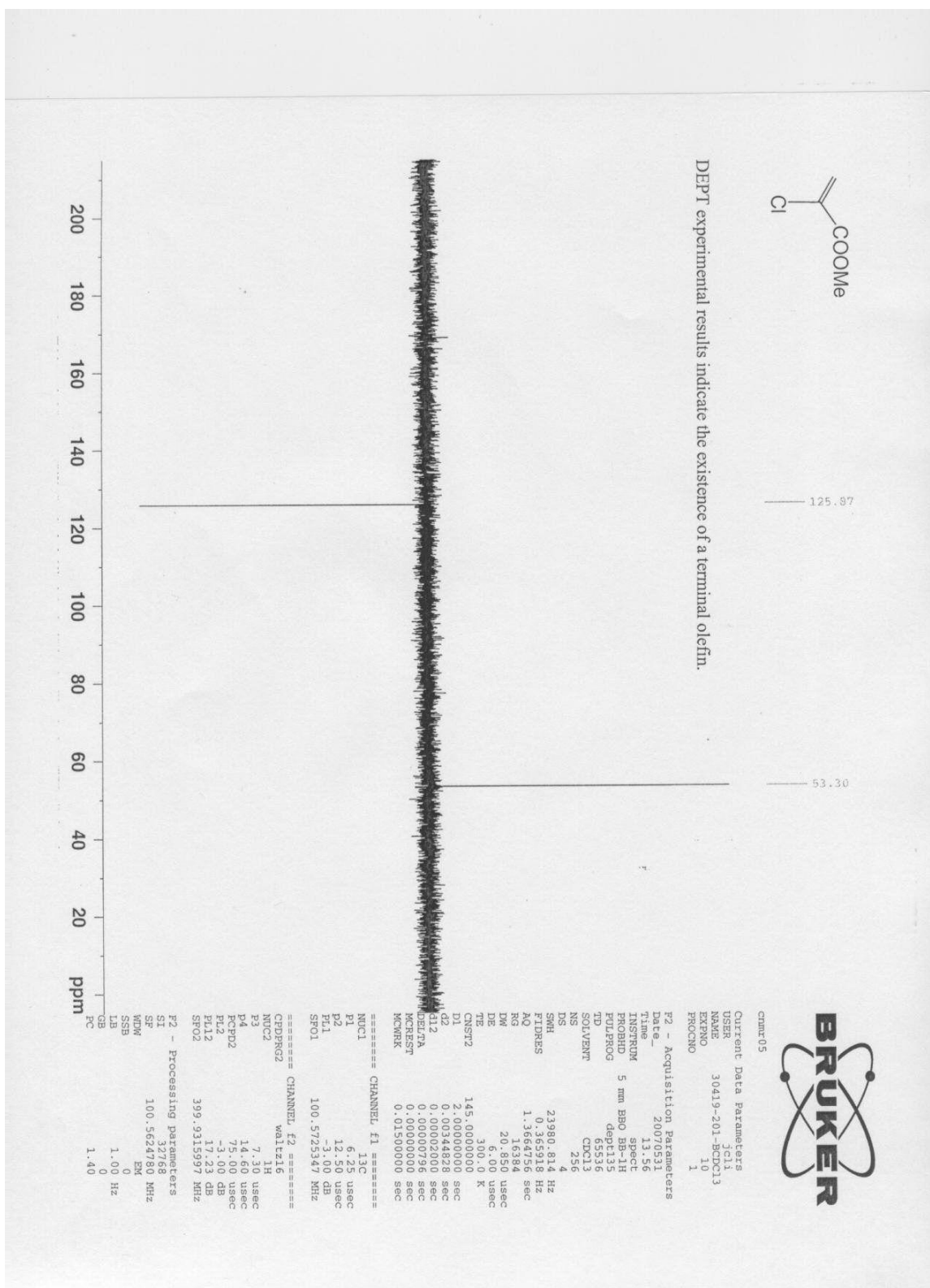




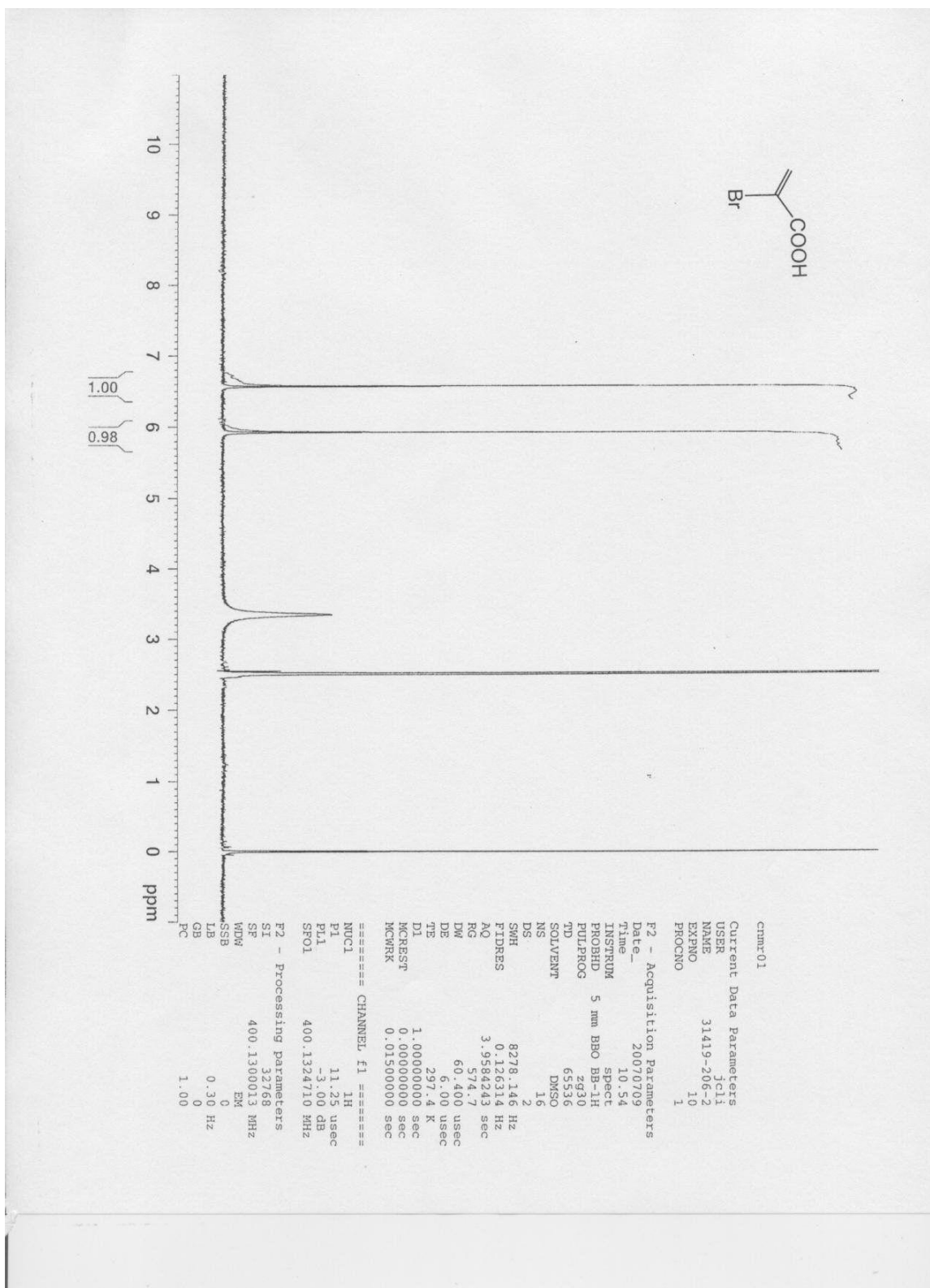
Methyl 2-chloroacrylate (entry 2 of Table 1):  $^{13}\text{C}$  NMR



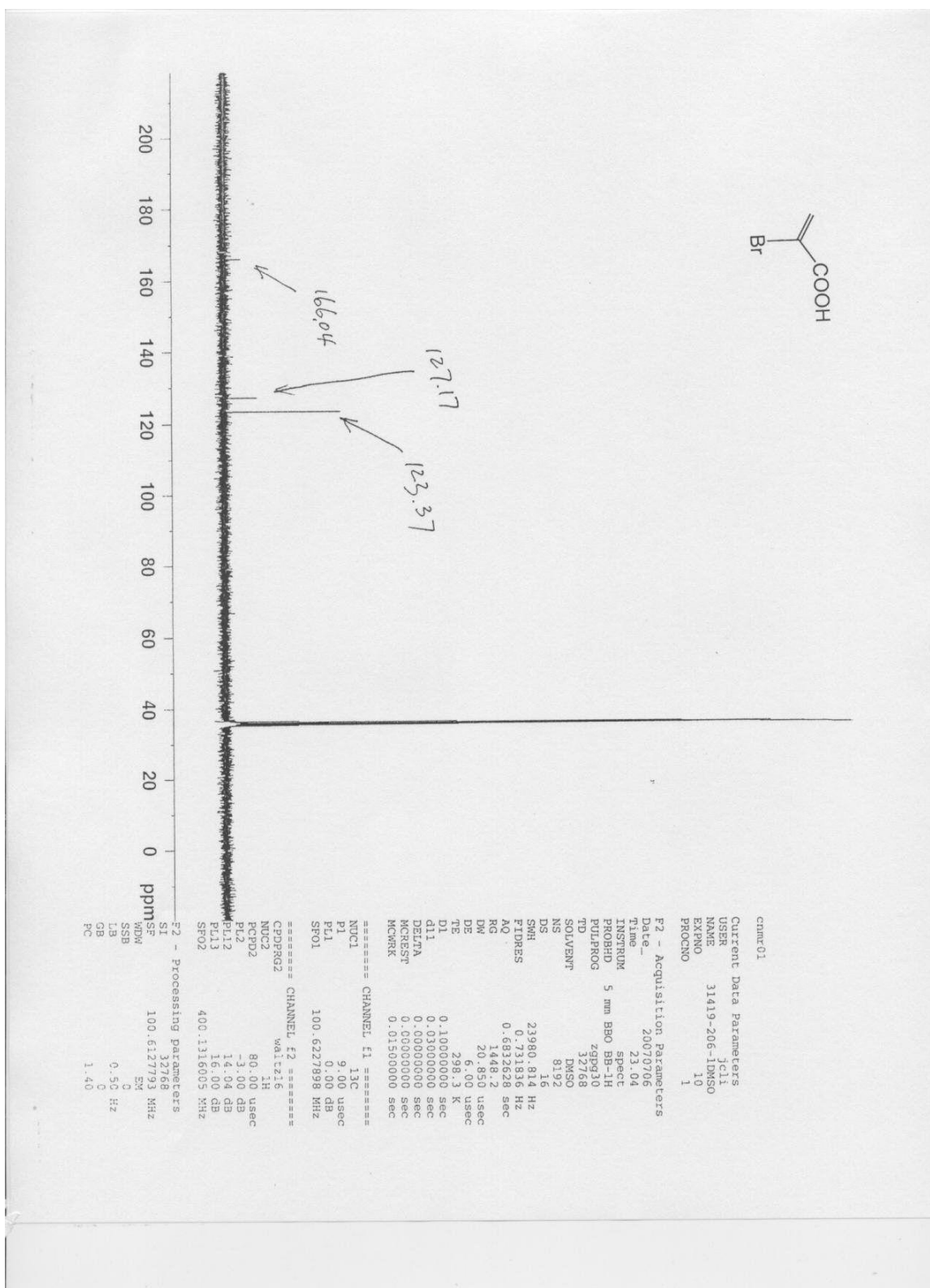
# Methyl 2-chloroacrylate (entry 2 of Table 1): DEPT



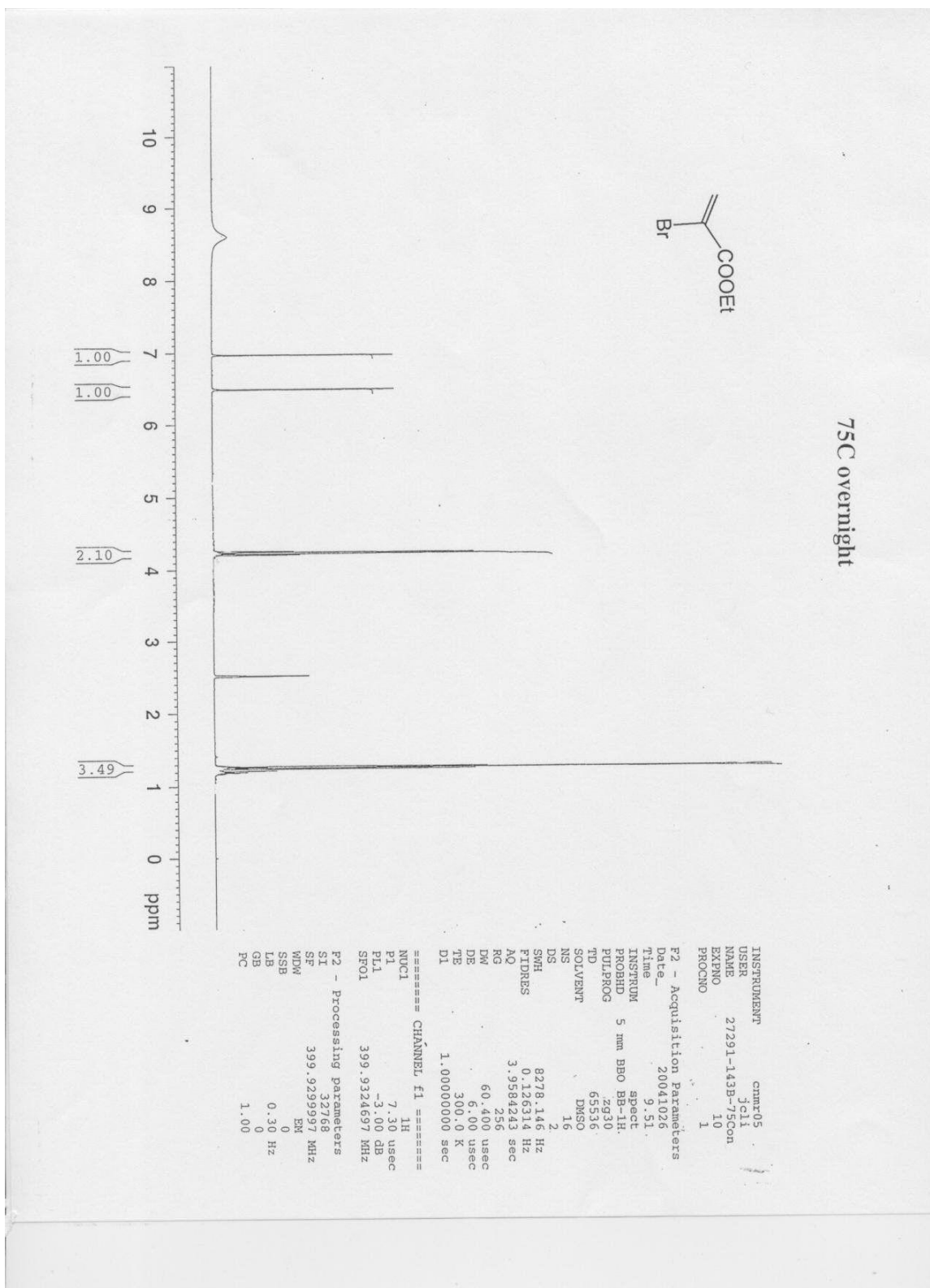
2-Bromoacrylic acid (entry 3 of Table 1):  $^1\text{H}$  NMR



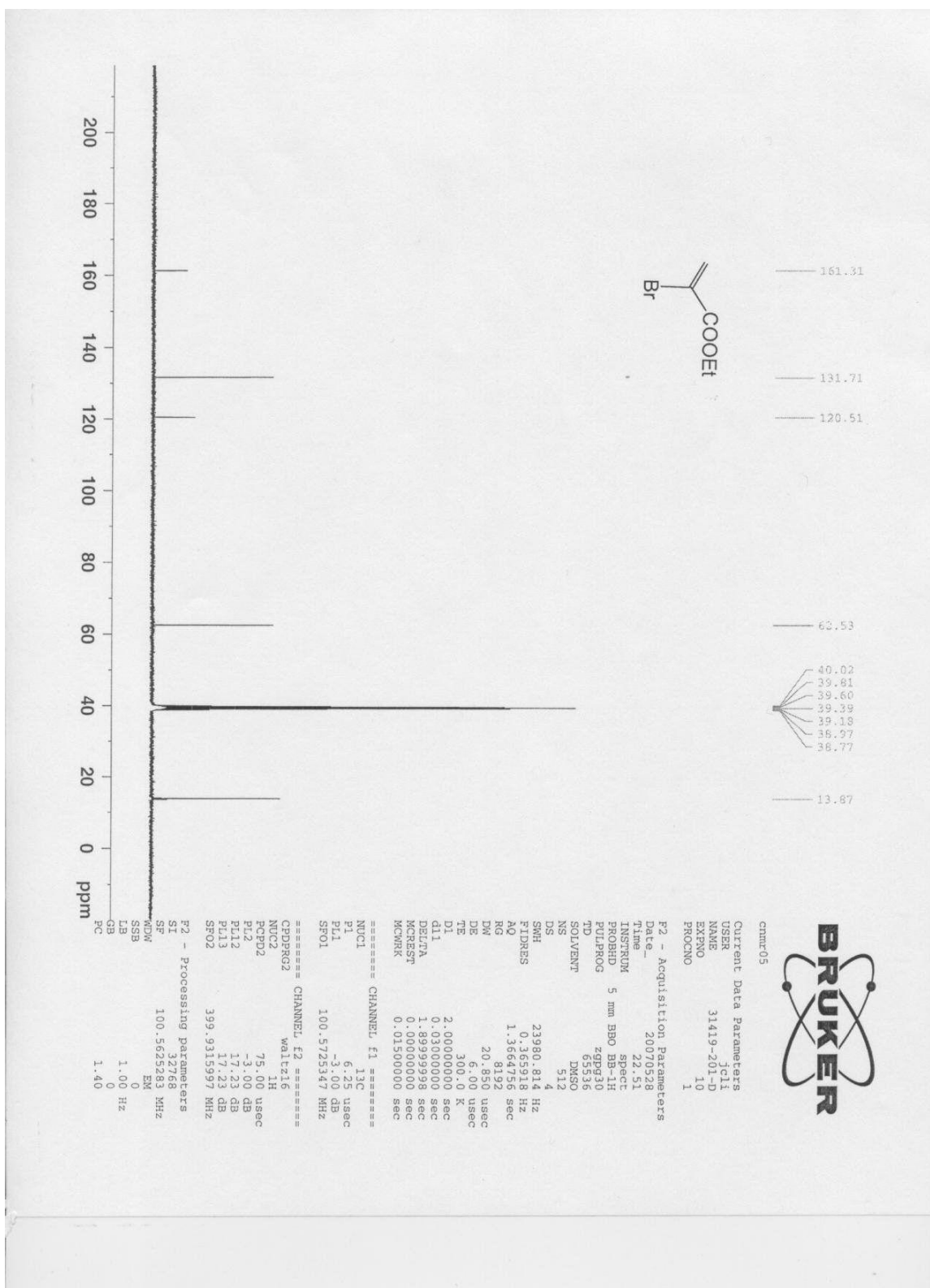
2-Bromoacrylic acid (entry 3 of Table 1):  $^{13}\text{C}$  NMR



Ethyl 2-Bromoacrylate (7entry 4 in Table 1):  $^1\text{H}$  NMR

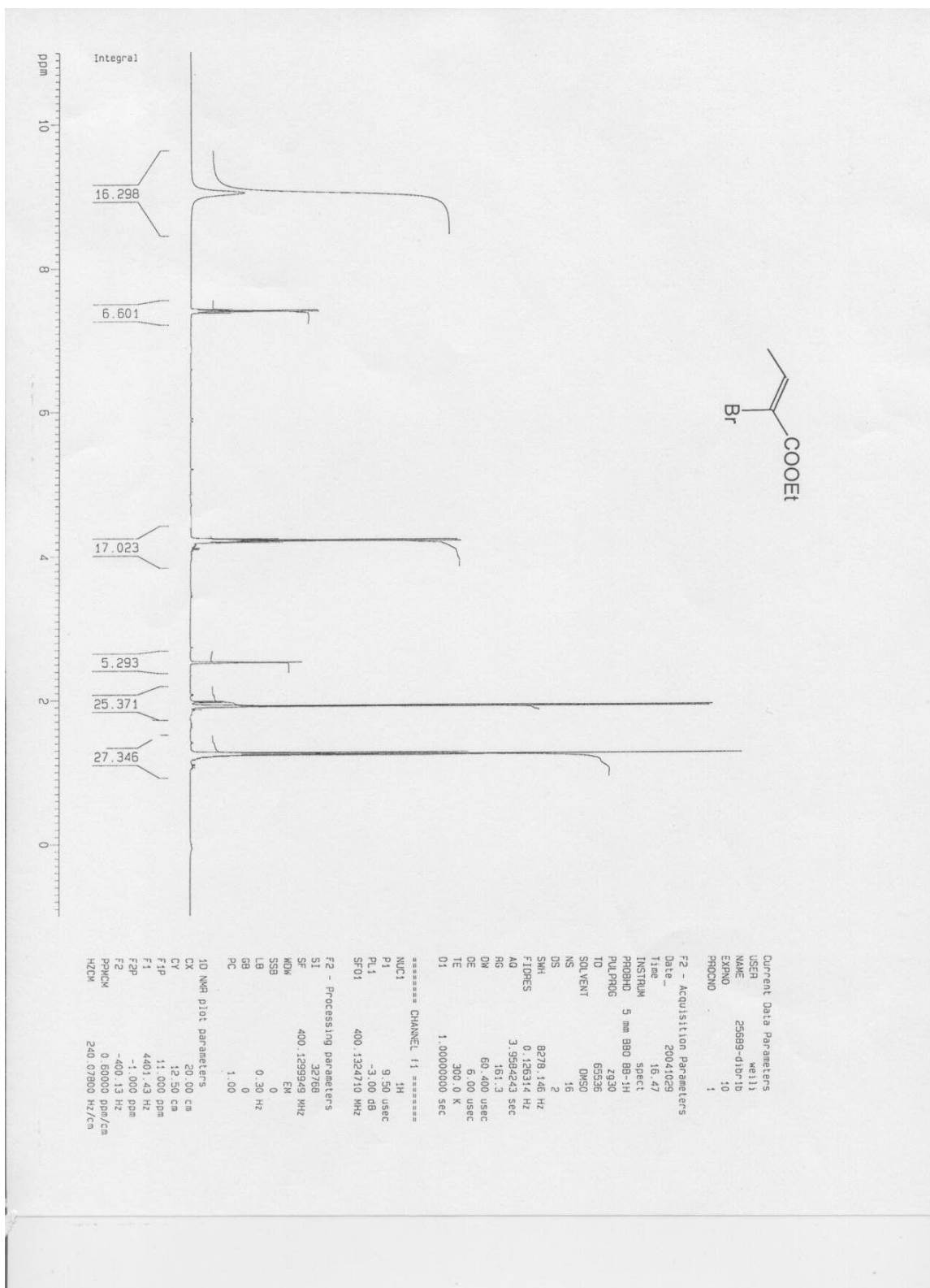


# Ethyl 2-bromoacrylate (entry 4 of Table 1): $^{13}\text{C}$ NMR

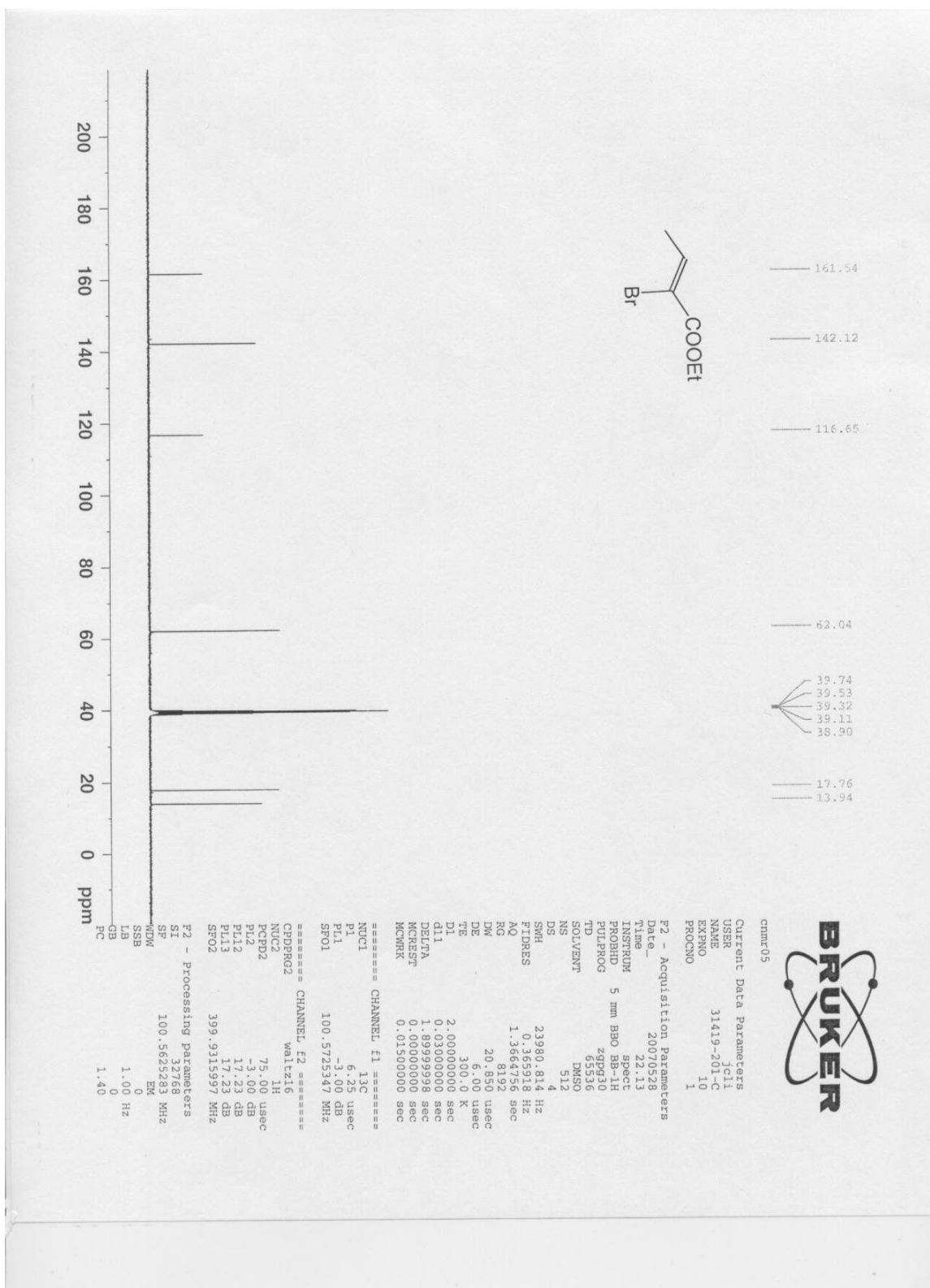




**(Z)-Ethyl 2-bromobut-2-enoate (entry 5 of Table 1):  $^1\text{H}$  NMR**

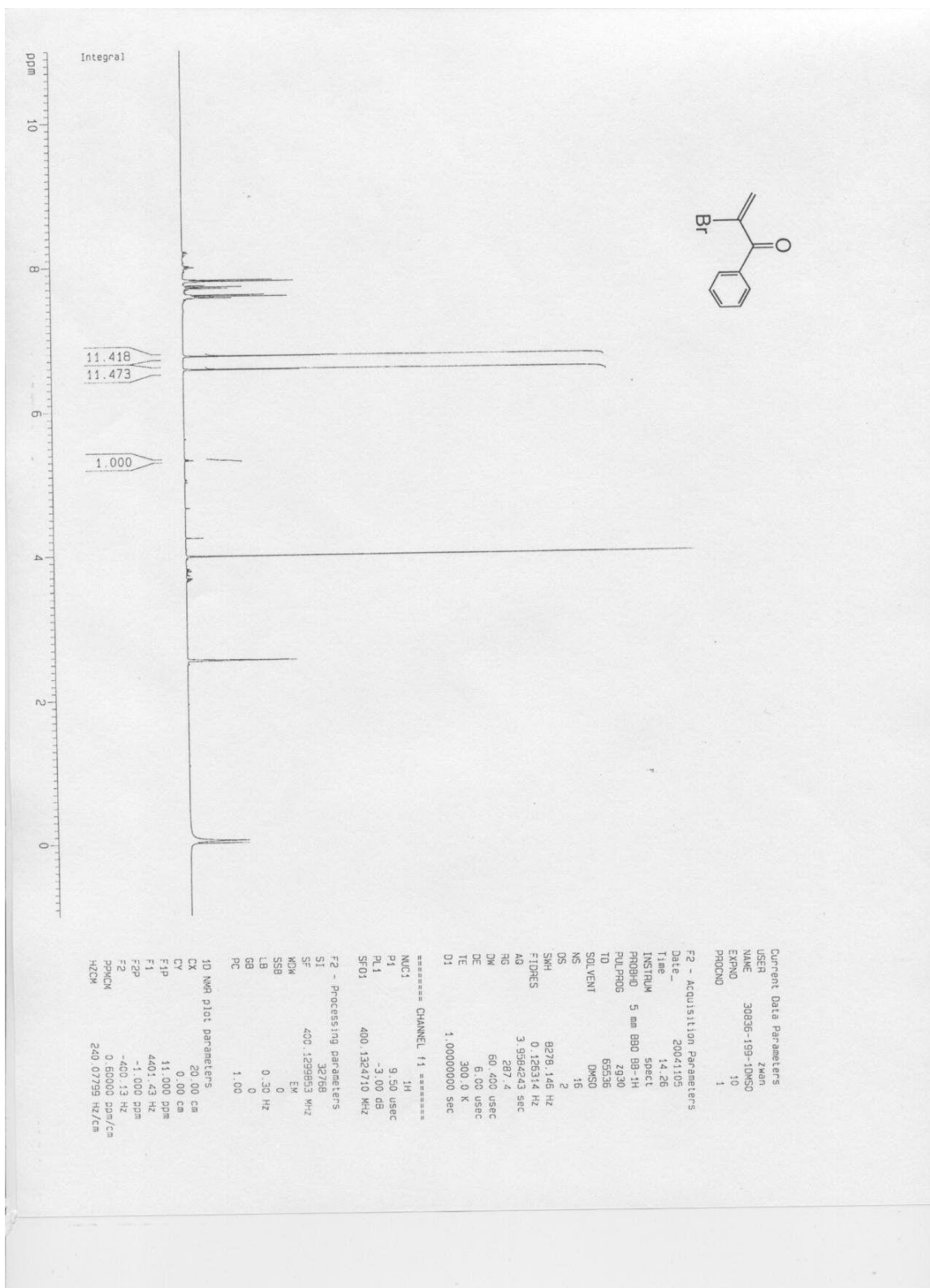


(Z)-Ethyl 2-bromobut-2-enoate (entry 5 of Table 1):  $^{13}\text{C}$  NMR

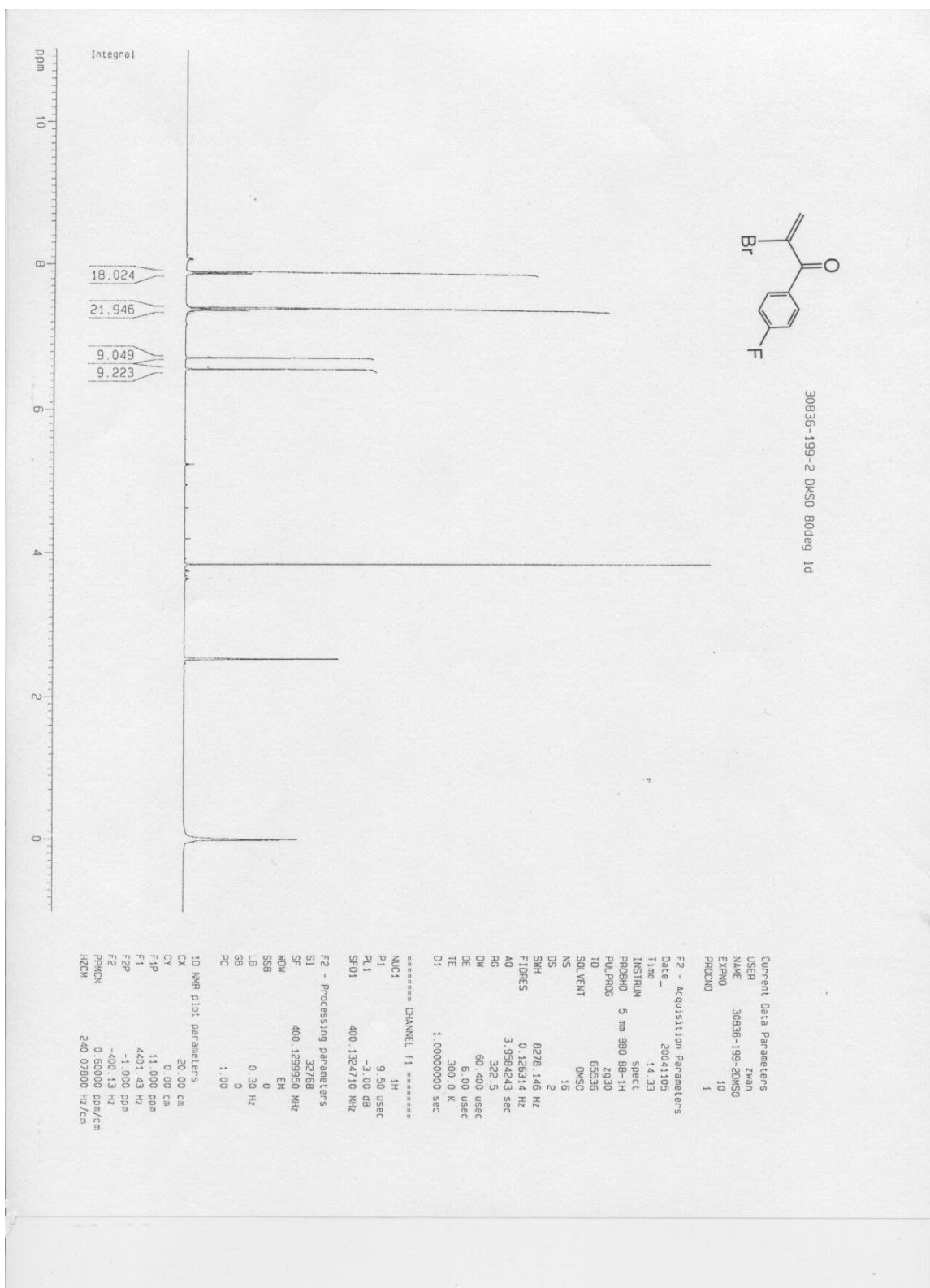




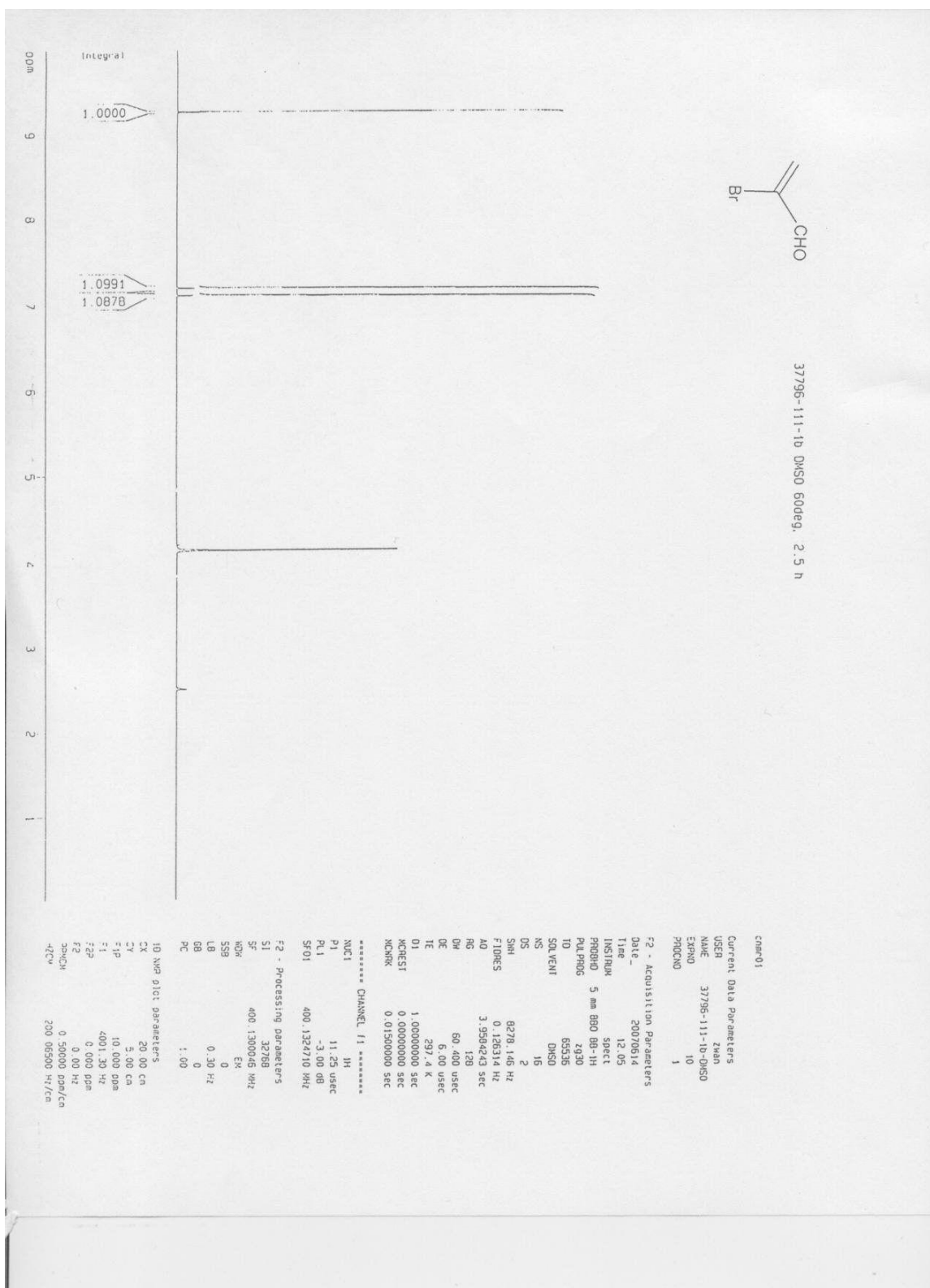
**2-Bromo-1-phenylprop-2-en-1-one (entry 6 of Table 1):  $^1\text{H}$  NMR**



**2-Bromo-1-(4-fluorophenyl)prop-2-en-1-one (entry 7 of Table 1):  $^1\text{H}$  NMR**



# 2-Bromoacrylaldehyde (entry 1 of Table 2): <sup>1</sup>H NMR



37796-111-1b DMSO 60deg. 2.5h

Chemical structure: CC(Br)C=O

10 NMR Data Parameters

NAME	37796-111-1b-DMSO
EXPNO	10
F2 - Acquisition Parameters	
Date_	20070615
Time	3.59
INSTRUM	SPECT
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMSO
NS	4096
DS	16
SWH	23000 Hz
FIDRES	0.731036 Hz
AQ	0.6030528 sec
RG	1149.4
DW	20.850 usec
DE	6.00 usec
TE	298.4 K
OT	1.00000000 sec
d11	0.03000000 sec
DELTA	0.69999999 sec
MDRES	0.00000000 sec
RCNCR	0.01000000 sec
***** CHANNEL f1 *****	
NUC1	<sup>13</sup> C
P1	9.00 usec
PL1	0.00 dB
SFO1	100.6227050 MHz
***** CHANNEL f2 *****	
CPDPRG2	waltz16
NUC2	<sup>1</sup> H
PCPD2	80.00 usec
PL2	-3.00 dB
SFO2	400.1315005 MHz
F2 - Processing parameters	
SF	32768
SP	100.6127793 MHz
NUC	<sup>1</sup> H
SSB	0
LB	1.00 Hz
ZF	1.00

10 NMR Data Parameters

NAME	37796-111-1b-DMSO
EXPNO	10
F2 - Acquisition Parameters	
Date_	20070615
Time	3.59
INSTRUM	SPECT
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMSO
NS	4096
DS	16
SWH	23000 Hz
FIDRES	0.731036 Hz
AQ	0.6030528 sec
RG	1149.4
DW	20.850 usec
DE	6.00 usec
TE	298.4 K
OT	1.00000000 sec
d11	0.03000000 sec
DELTA	0.69999999 sec
MDRES	0.00000000 sec
RCNCR	0.01000000 sec
***** CHANNEL f1 *****	
NUC1	<sup>13</sup> C
P1	9.00 usec
PL1	0.00 dB
SFO1	100.6227050 MHz
***** CHANNEL f2 *****	
CPDPRG2	waltz16
NUC2	<sup>1</sup> H
PCPD2	80.00 usec
PL2	-3.00 dB
SFO2	400.1315005 MHz
F2 - Processing parameters	
SF	32768
SP	100.6127793 MHz
NUC	<sup>1</sup> H
SSB	0
LB	1.00 Hz
ZF	1.00

10 NMR Data Parameters

NAME	37796-111-1b-DMSO
EXPNO	10
F2 - Acquisition Parameters	
Date_	20070615
Time	3.59
INSTRUM	SPECT
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMSO
NS	4096
DS	16
SWH	23000 Hz
FIDRES	0.731036 Hz
AQ	0.6030528 sec
RG	1149.4
DW	20.850 usec
DE	6.00 usec
TE	298.4 K
OT	1.00000000 sec
d11	0.03000000 sec
DELTA	0.69999999 sec
MDRES	0.00000000 sec
RCNCR	0.01000000 sec
***** CHANNEL f1 *****	
NUC1	<sup>13</sup> C
P1	9.00 usec
PL1	0.00 dB
SFO1	100.6227050 MHz
***** CHANNEL f2 *****	
CPDPRG2	waltz16
NUC2	<sup>1</sup> H
PCPD2	80.00 usec
PL2	-3.00 dB
SFO2	400.1315005 MHz
F2 - Processing parameters	
SF	32768
SP	100.6127793 MHz
NUC	<sup>1</sup> H
SSB	0
LB	1.00 Hz
ZF	1.00

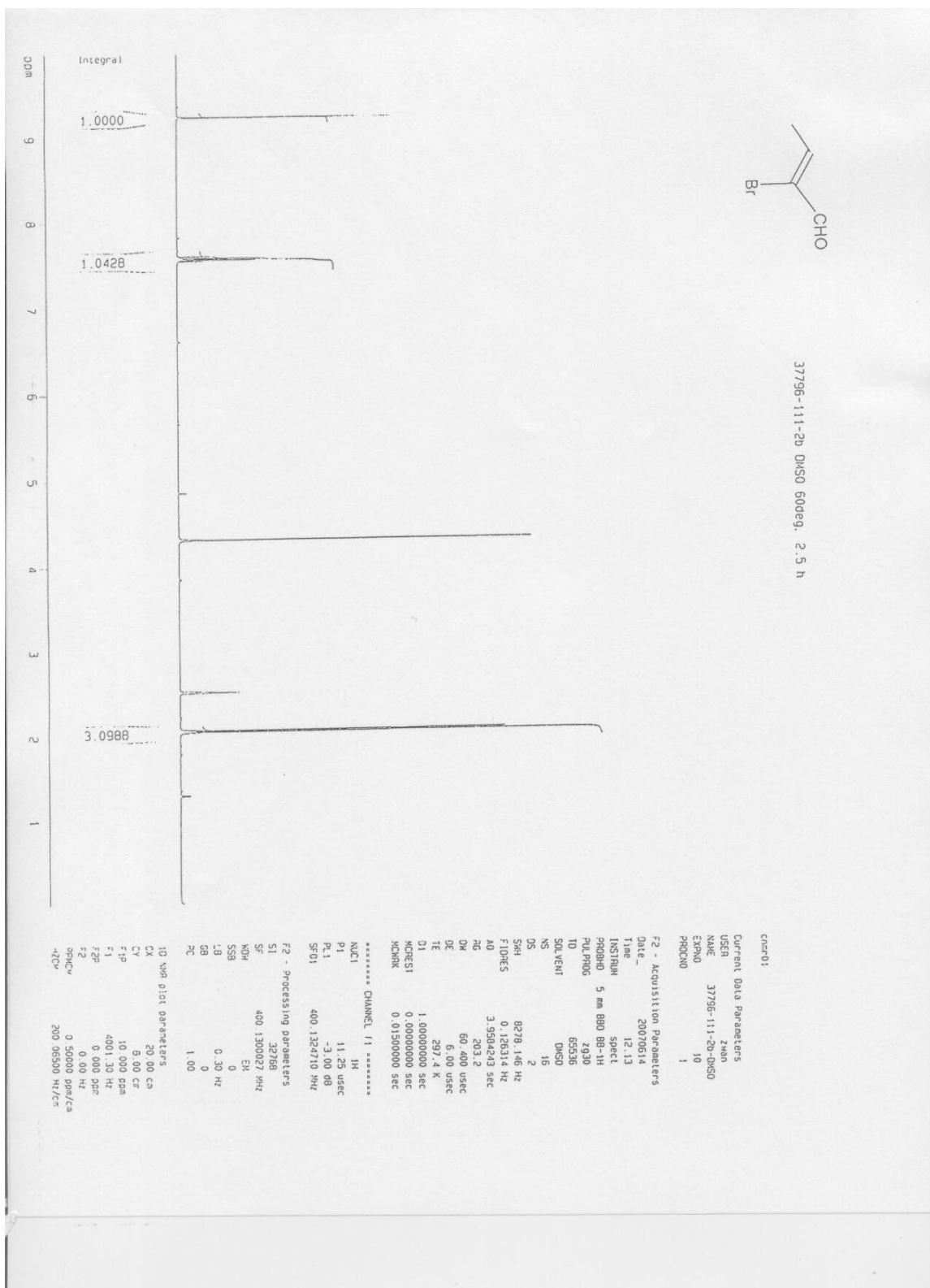
10 NMR Data Parameters

NAME	37796-111-1b-DMSO
EXPNO	10
F2 - Acquisition Parameters	
Date_	20070615
Time	3.59
INSTRUM	SPECT
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMSO
NS	4096
DS	16
SWH	23000 Hz
FIDRES	0.731036 Hz
AQ	0.6030528 sec
RG	1149.4
DW	20.850 usec
DE	6.00 usec
TE	298.4 K
OT	1.00000000 sec
d11	0.03000000 sec
DELTA	0.69999999 sec
MDRES	0.00000000 sec
RCNCR	0.01000000 sec
***** CHANNEL f1 *****	
NUC1	<sup>13</sup> C
P1	9.00 usec
PL1	0.00 dB
SFO1	100.6227050 MHz
***** CHANNEL f2 *****	
CPDPRG2	waltz16
NUC2	<sup>1</sup> H
PCPD2	80.00 usec
PL2	-3.00 dB
SFO2	400.1315005 MHz
F2 - Processing parameters	
SF	32768
SP	100.6127793 MHz
NUC	<sup>1</sup> H
SSB	0
LB	1.00 Hz
ZF	1.00

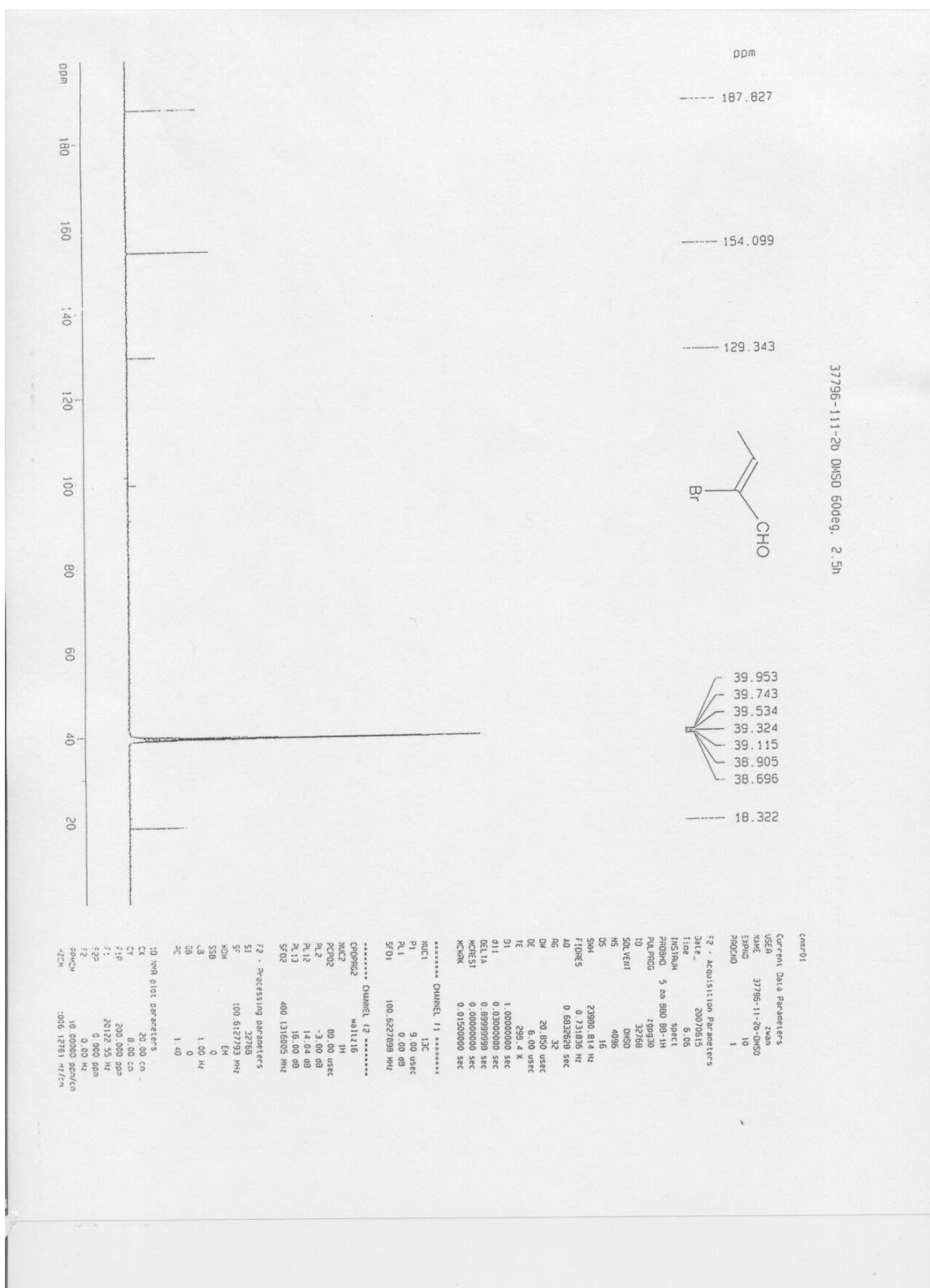
10 NMR Data Parameters

NAME	37796-111-1b-DMSO
EXPNO	10
F2 - Acquisition Parameters	
Date_	20070615
Time	3.59
INSTRUM	SPECT
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMS

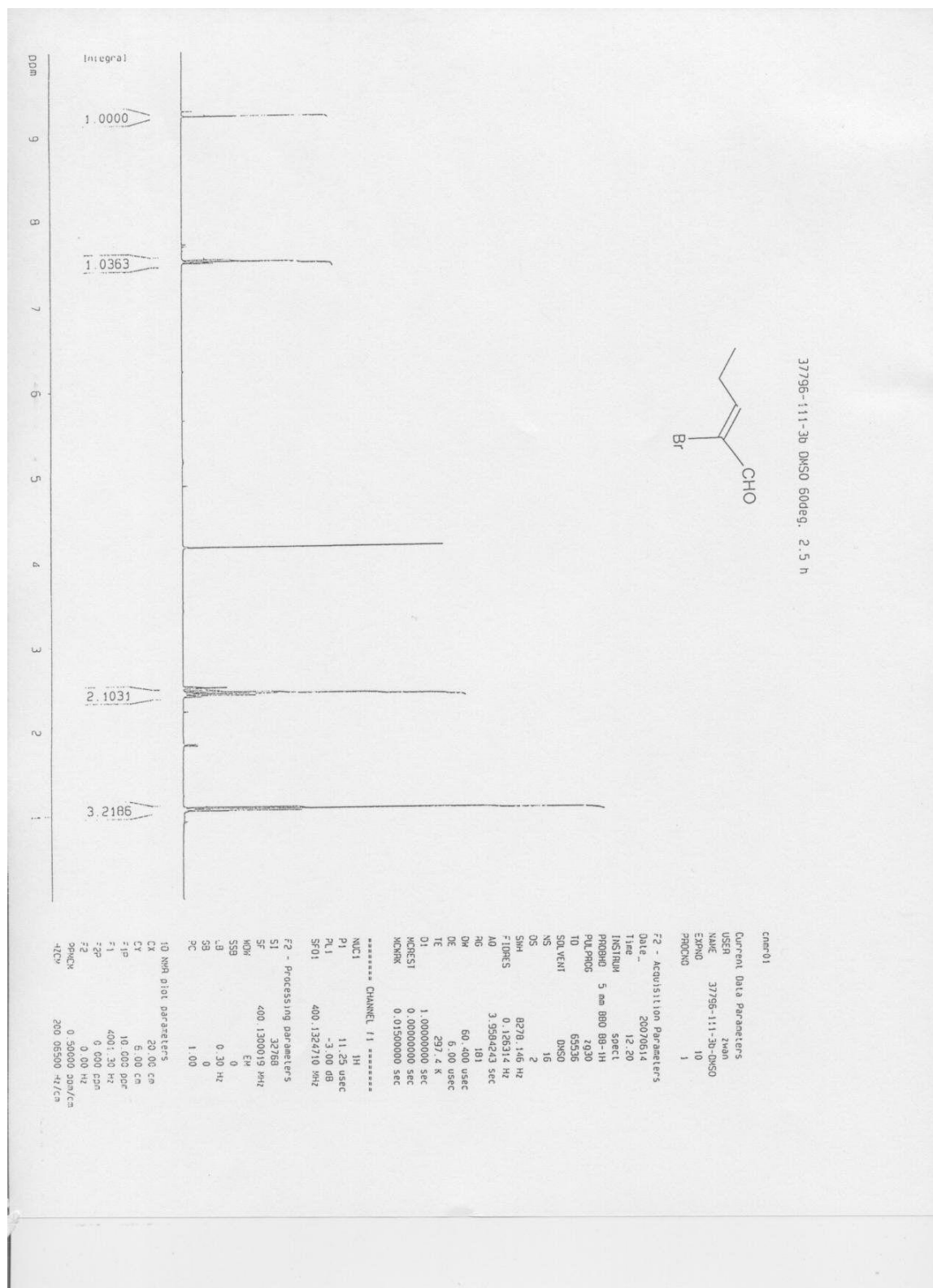
**(Z)-2-Bromobut-2-enal (entry 2 in Table 2):  $^1\text{H}$  NMR**



**(Z)-2-Bromobut-2-enal (entry 2 in Table 2):  $^{13}\text{C}$  NMR**



**(Z)-2-Bromopent-2-enal (entry 3 of Table 2):  $^1\text{H}$  NMR**





37796-111-3b DMSO 60deg. 2.5h

ppm

187.947

159.509

139.929

127.639

39.967

39.758

39.548

39.339

39.129

38.920

38.711

25.618

11.894

0.00

20

40

50

80

100

120

140

160

180

200

Chemical structure: CC/C=C/C(=O)Br

Current Data Parameters

NAME	37796-11-3b-0650
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20070615
Time	8.13
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	DMSO
NS	4096
DS	16
SWH	23090.841 Hz
FIDRES	0.271036 Hz
AQ	0.6633628 sec
RG	912.3
DE	20.050 usec
TE	298.1 K
Q1	1.00000000 sec
Q11	0.03000000 sec
DELTA	0.65959598 sec
ACQRES	0.65000000 sec
ACQNR	0.01500000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*

NUC1	<sup>13</sup> C
P1	9.00 usec
PL1	0.00 dB
SFO1	100.627099 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*

CPDPRG2	waltz16
NUC2	<sup>1</sup> H
PCPD2	89.00 usec
PL2	0.00 dB
PL12	1.4.00 dB
PL13	16.00 dB
SFO2	400.1316005 MHz

F2 - Processing Parameters

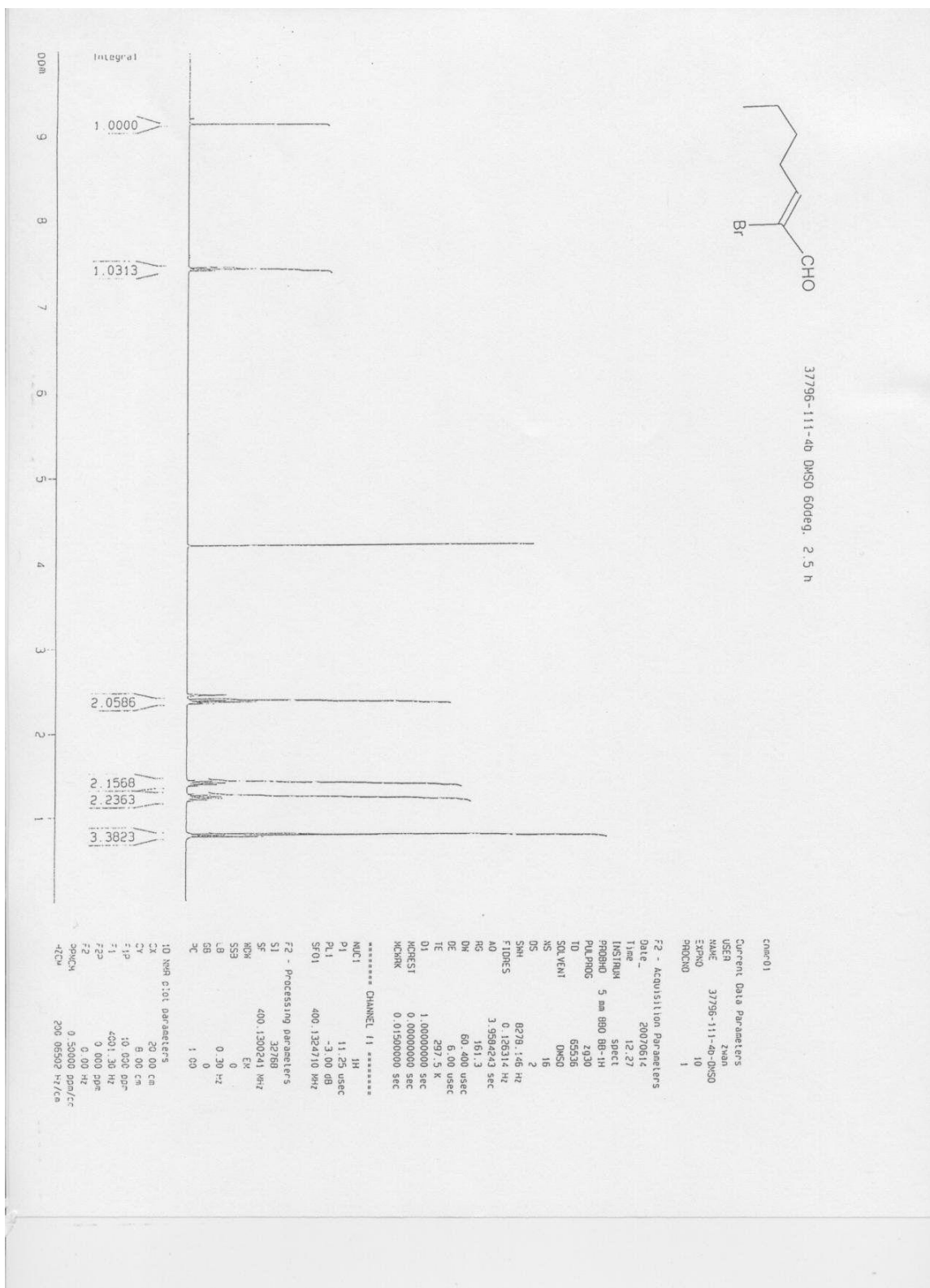
SI	32768
SF	100.6127793 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR Data Parameters

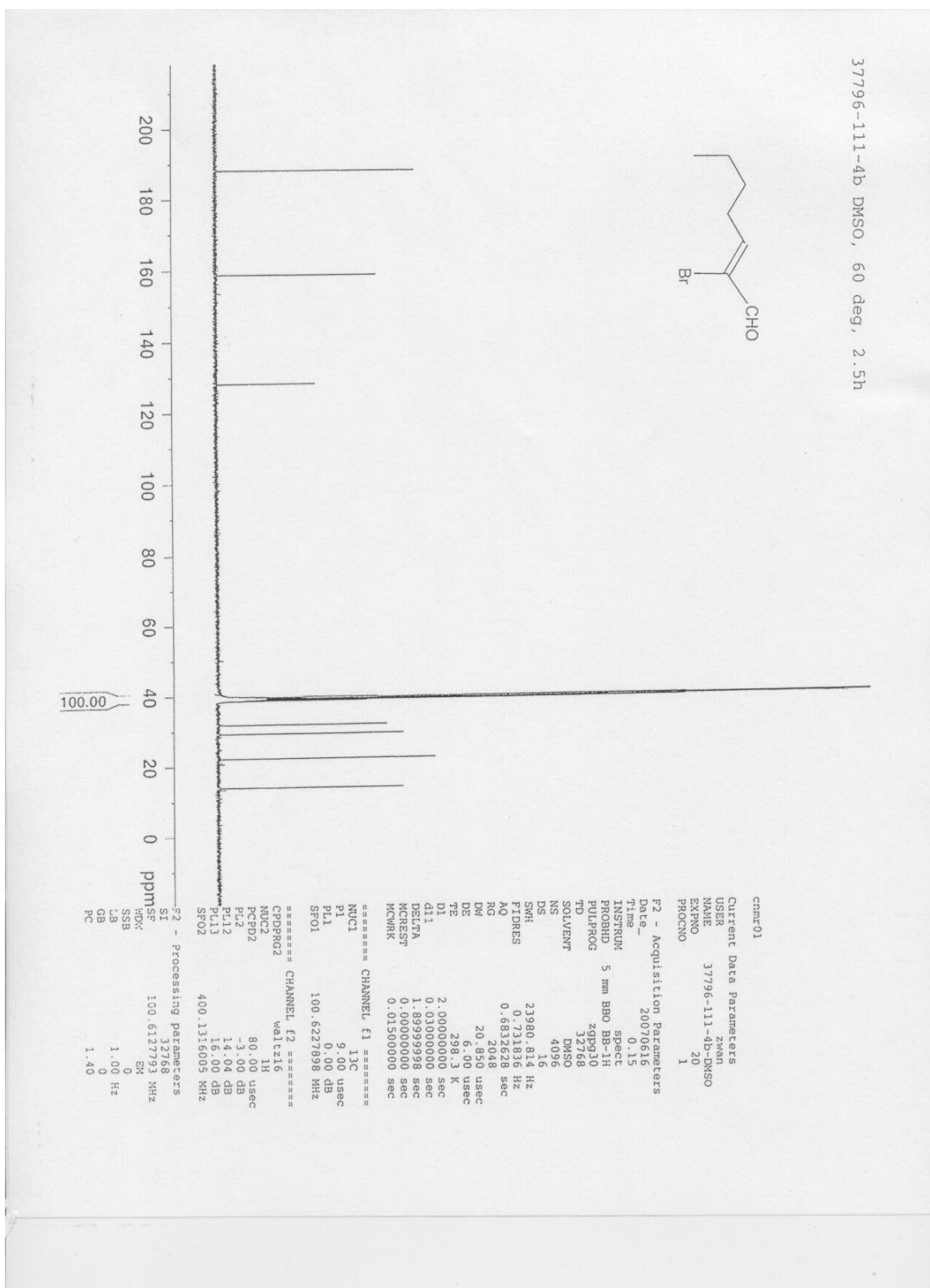
EX	20.00 cm
CV	6.00 cm
FLP	200.000 dB
F1	20127.55 Hz
PCP	0.000 dB
PC	0.00 Hz
PCPD	30.00 Hz
PCPD	1005.12781 MHz



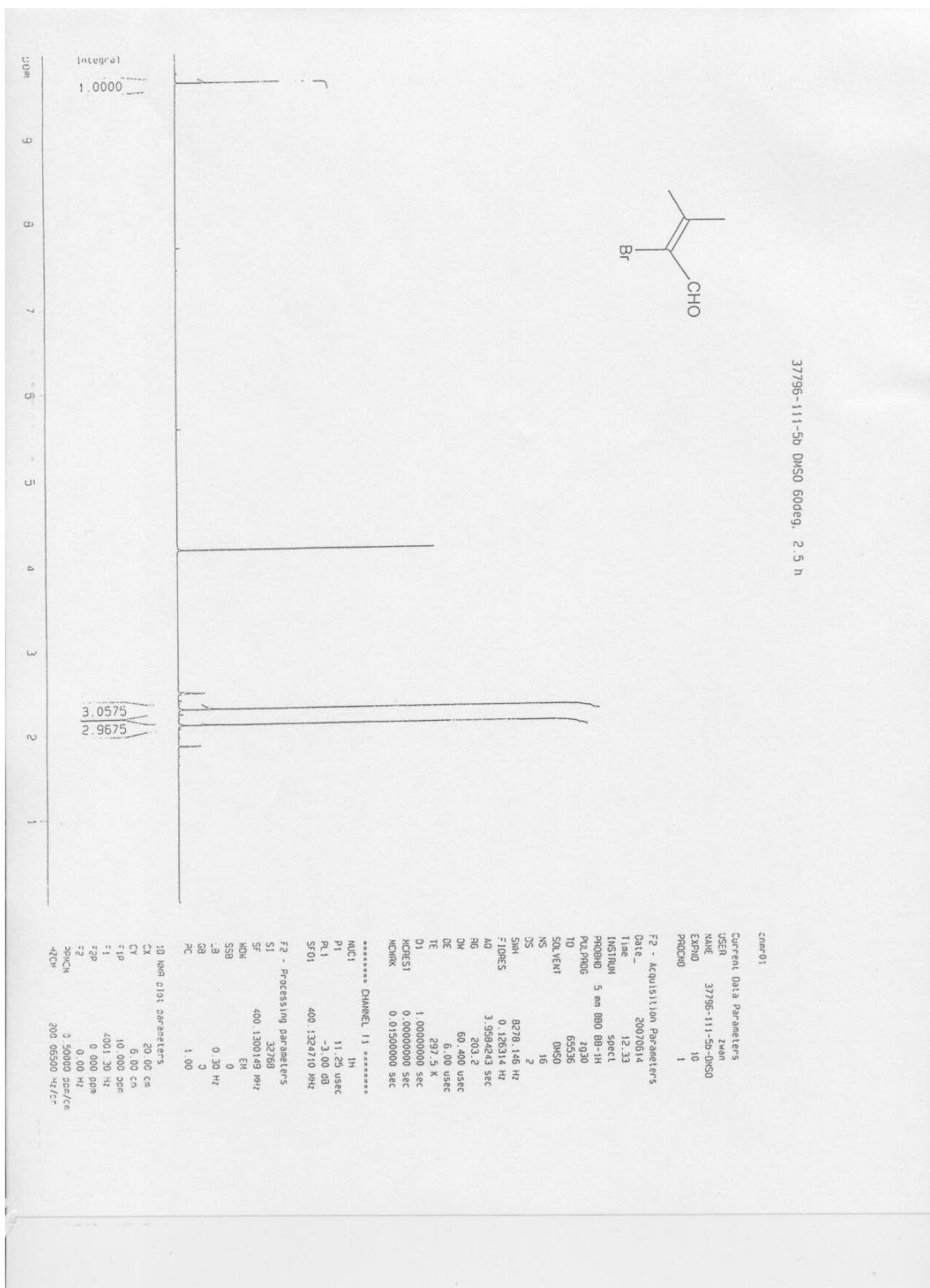
**(Z)-2-Bromohept-2-enal (1entry 4 of Table 2):  $^1\text{H}$  NMR**



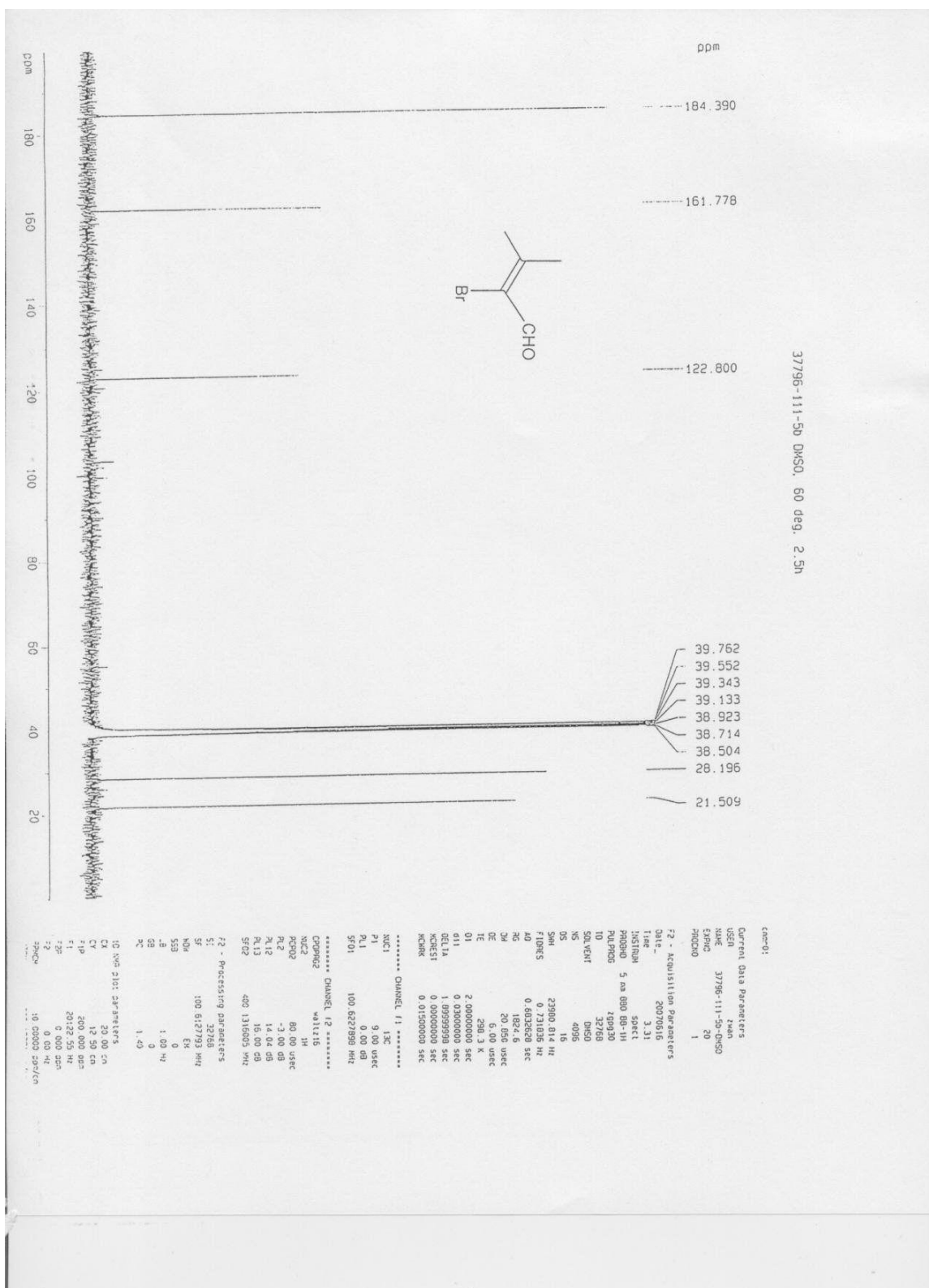
(Z)-2-Bromohept-2-enal (1entry 4 of Table 2):  $^{13}\text{C}$  NMR



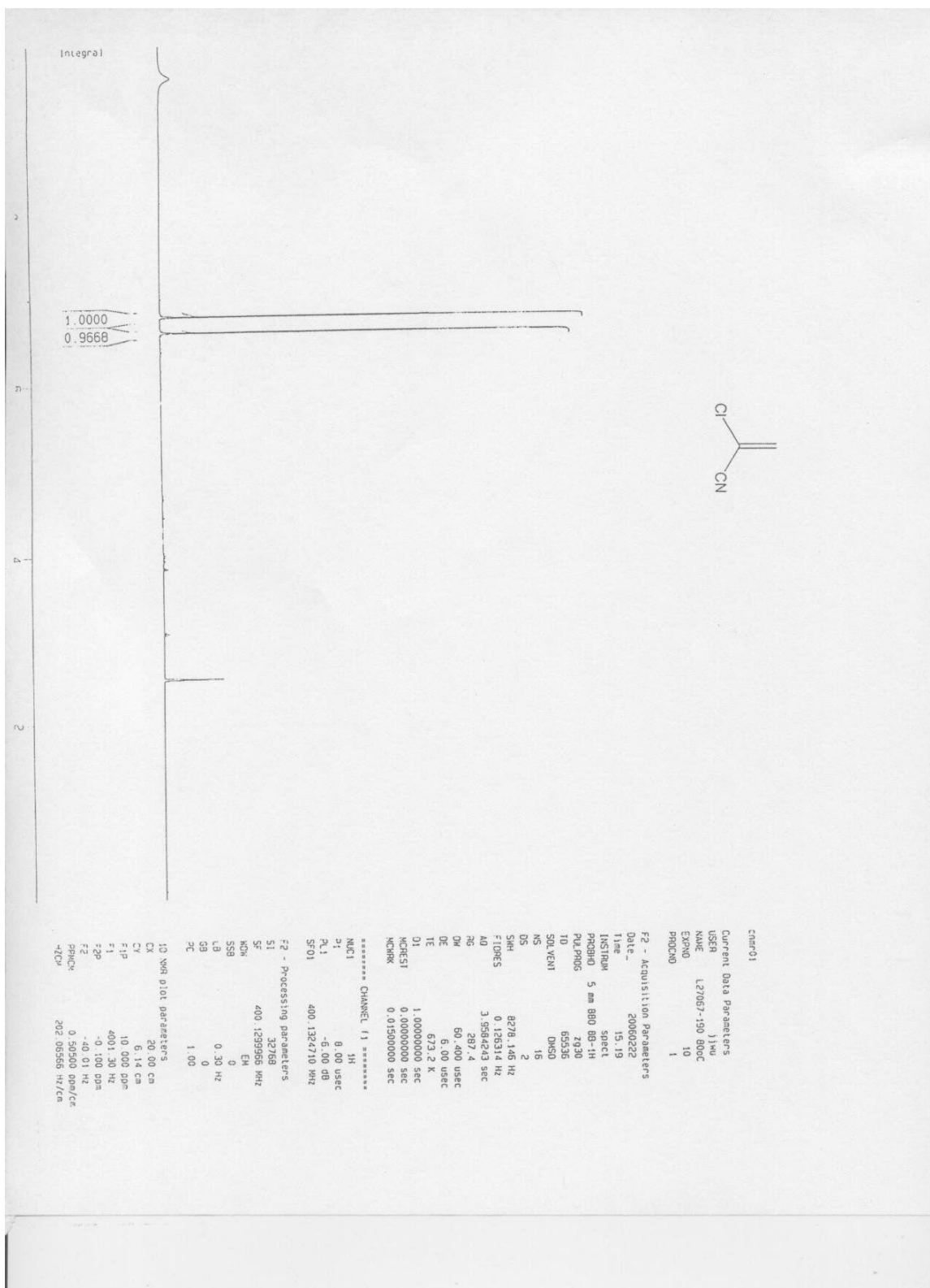
# 2-Bromo-3-methylbut-2-enal (entry 5 of Table 2): <sup>1</sup>H NMR



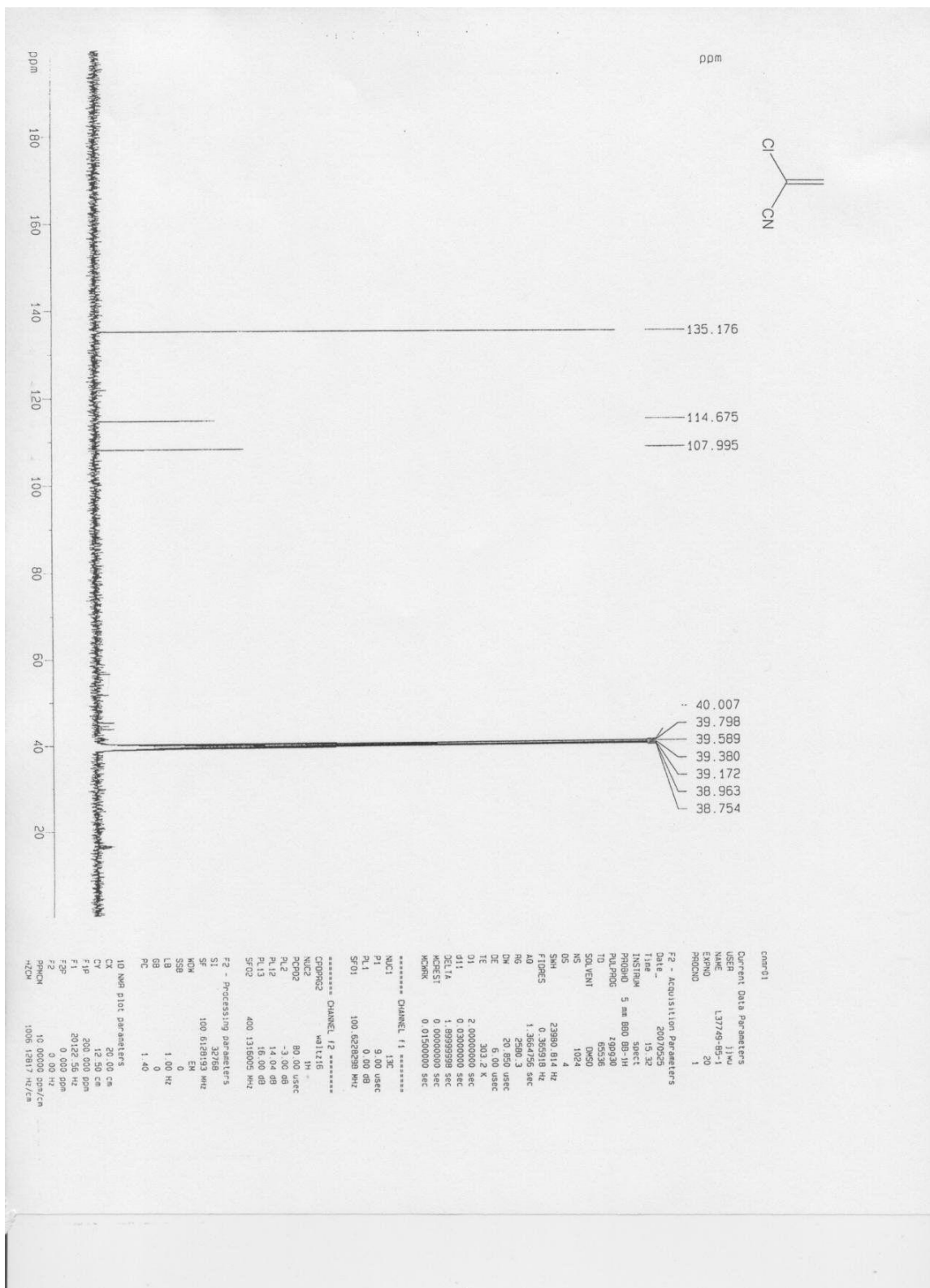
## 2-Bromo-3-methylbut-2-enal (entry 5 of Table 2): $^{13}\text{C}$ NMR



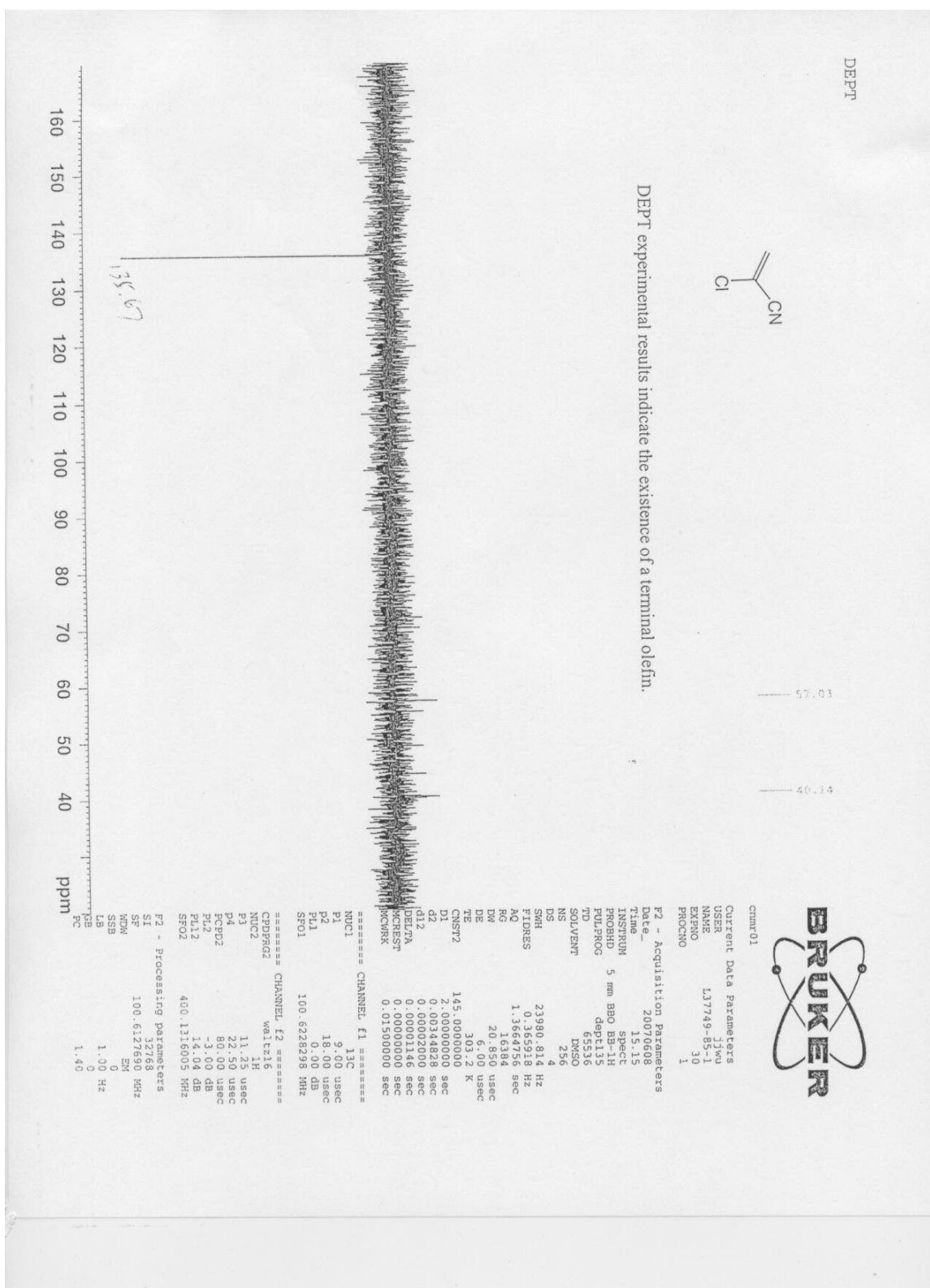
# 2-chloroacrylonitrile: <sup>1</sup>H NMR



# 2-Chloroacrylonitrile: <sup>13</sup>C NMR

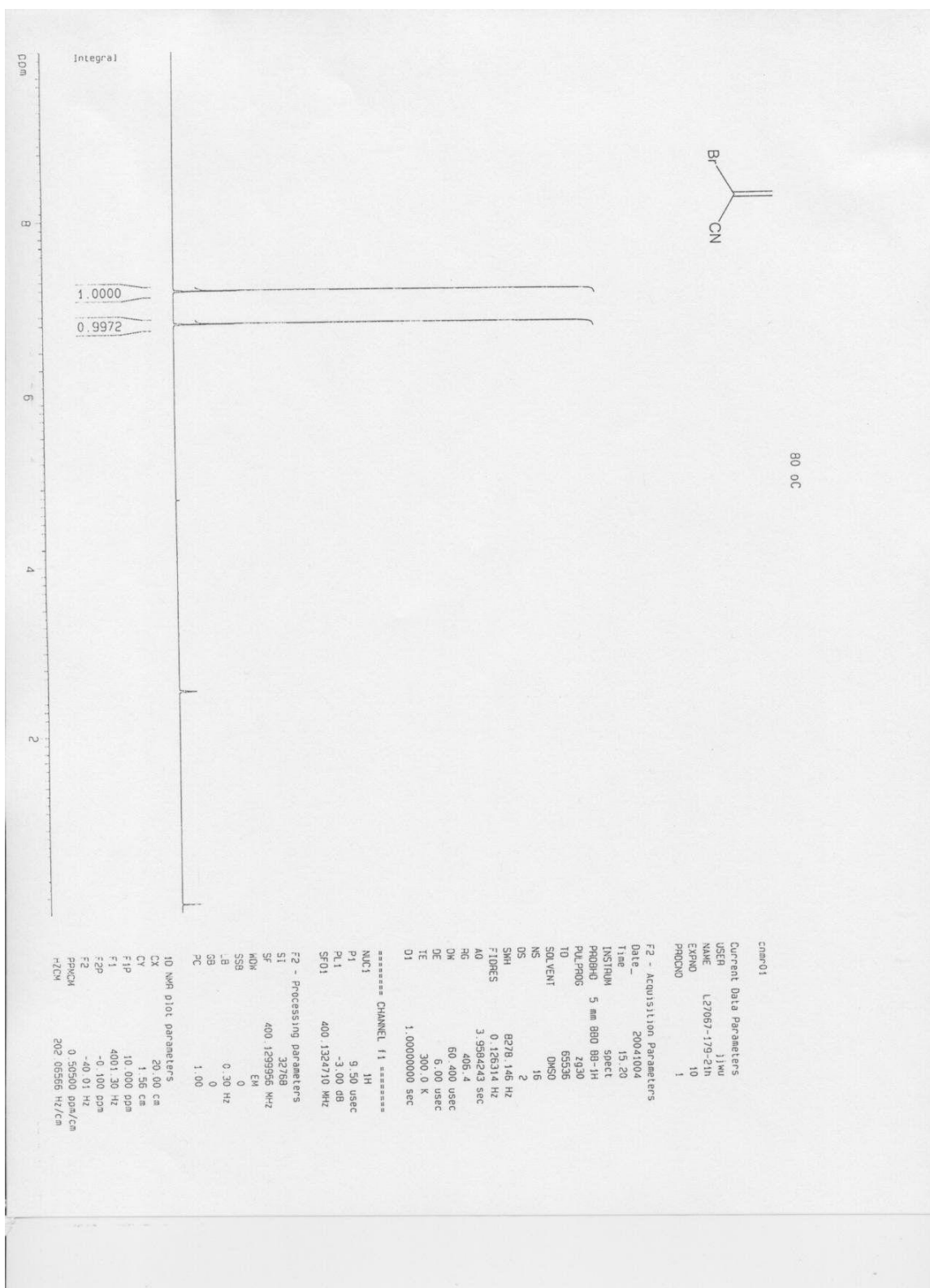


# 2-Chloroacrylonitrile: DEPT



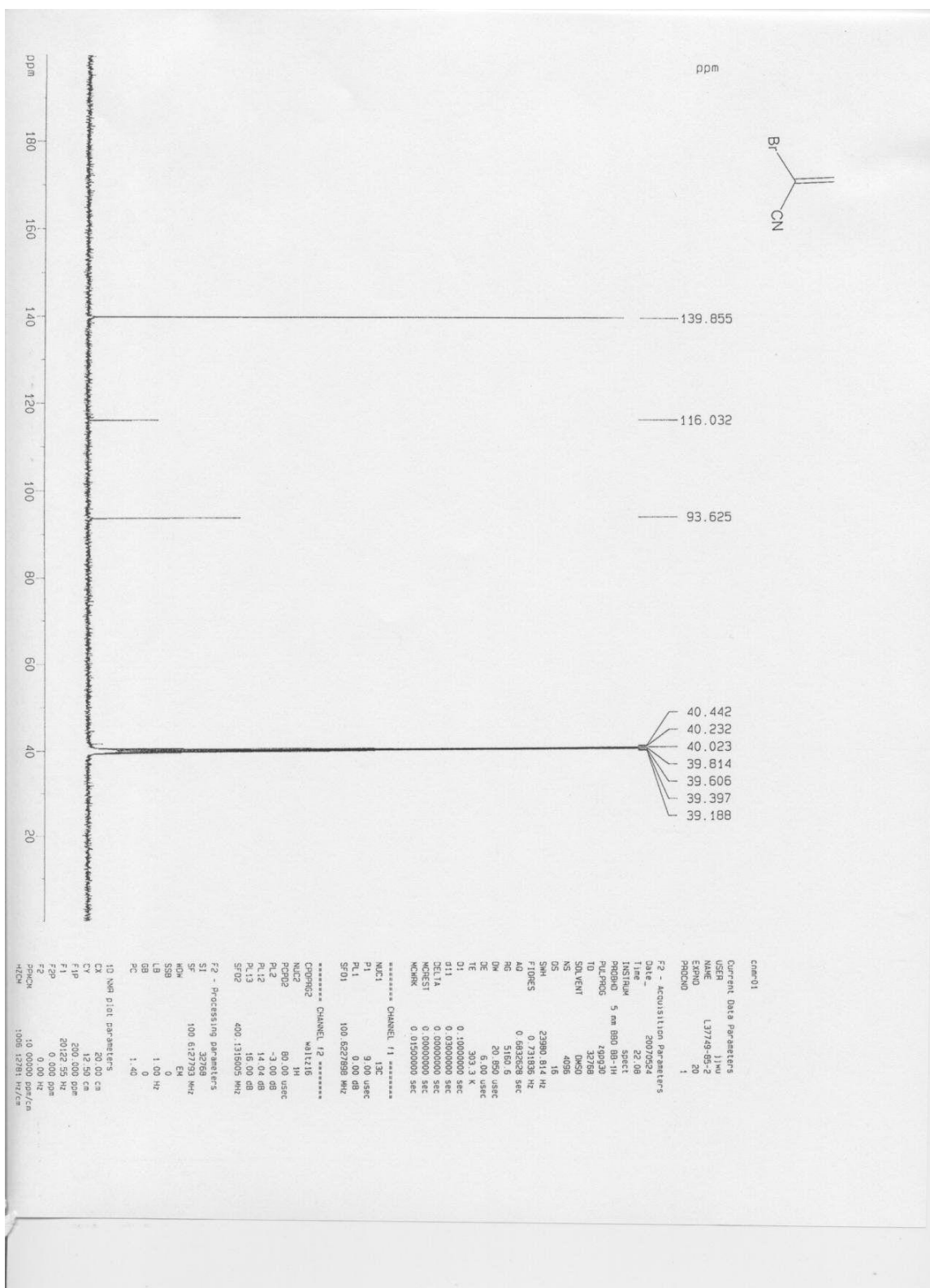


# 2-Bromoacrylonitrile: <sup>1</sup>H NMR





## 2-Bromoacrylonitrile: $^{13}\text{C}$ NMR



## 2-Bromoacrylonitrile: DEPT

