NMR SPECTROSCOPY

Part 02

^{13}CNMR

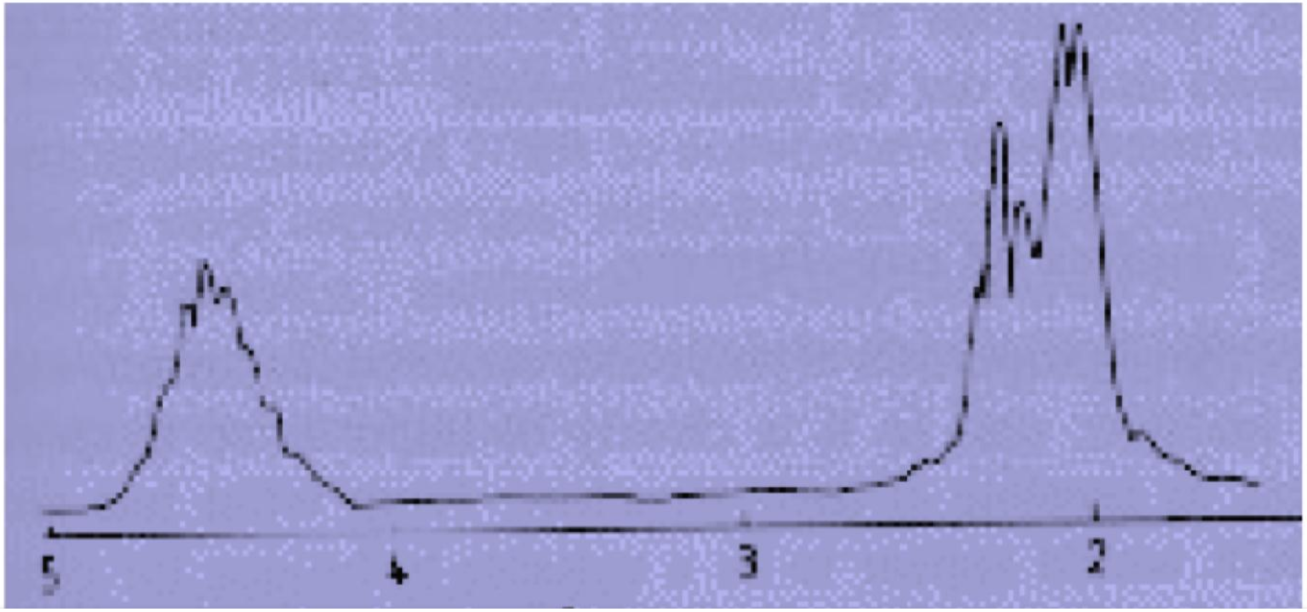
Features of ^{13}CNMR

1) **Low Natural Abundance: Since most polymers are composed of hydrogen and carbon, the natural alternative nucleus for NMR is ^{13}C. There are a number of major differences between proton and carbon 13 NMR. First, the natural abundance of ^{13}C is much lower than ^{1}H (12C does not display spin since the number of protons and neutrons are both even). The natural abundance of ^{13}C is about 1.1 % while that of 1H is close to 100%. Since only nuclei of similar magnetic resonance can lead to coupling and splitting of the absorption peaks, the low natural abundance of 13C leads to no splitting of the absorption peaks. The sensitivity of absorption of a RF pulse and the associated decay are also much lower for 13C.**

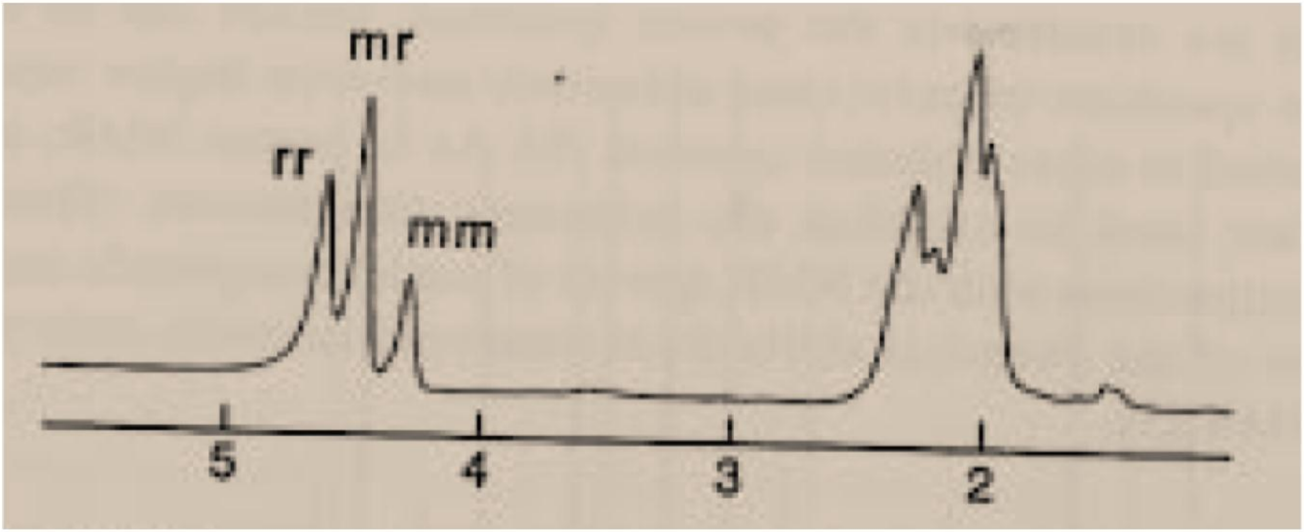
Features of ^{13}CNMR

2) Large Chemical Shifts: The range of proton absorptions are on the order of 10ppm relative to TMS. For ^{13}C the range of absorptions are on the order of 200ppm relative to TMS. The ^{13}C spectrum has more than an order higher resolution when compared to ^{1}H spectra as can be seen in the PVC spectra, for example.

1H and 13CNMR for PVC



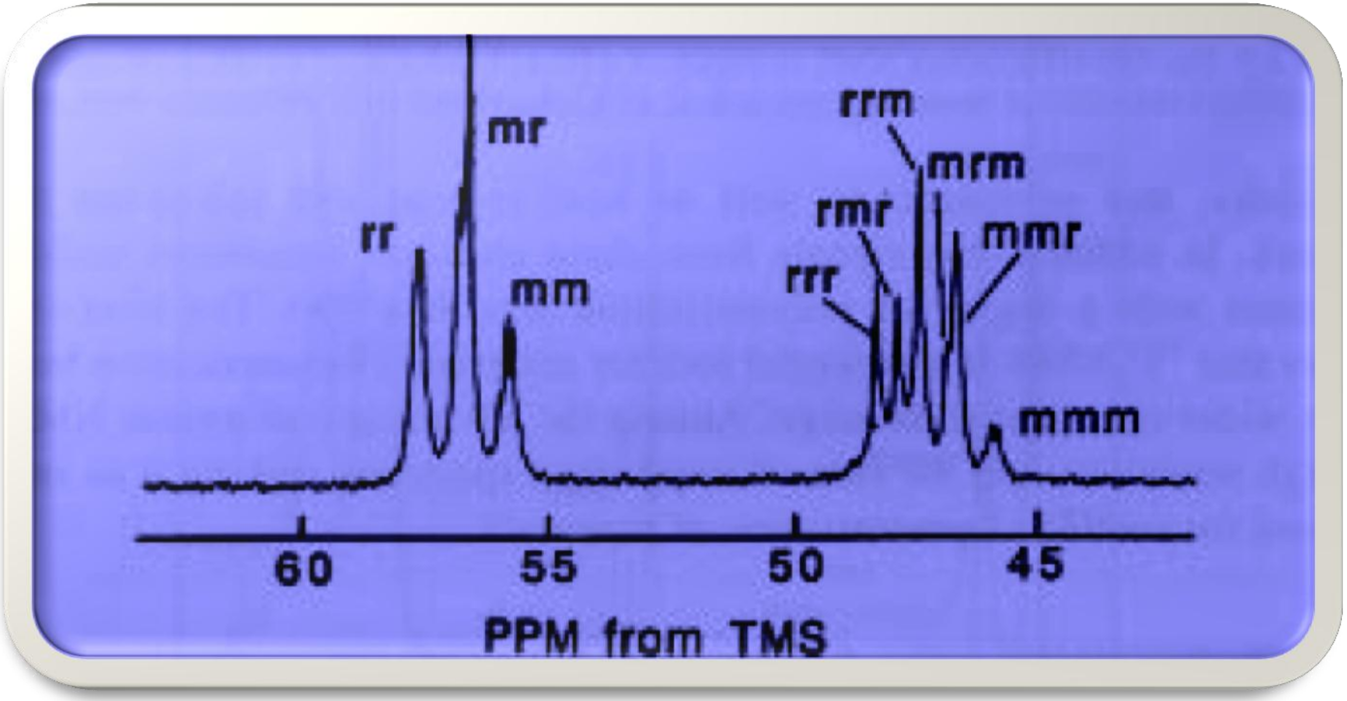
100 MHZ HNMR spectrum of PVC.



500 MHZ HNMR spectrum of PVC in benzen -D.

Using ^{13}CNMR

The splittings of the tactic peaks in the proton NMR spectrum of PVC, shown above, are not resolvable on typical NMR spectrometers. Use of a different nucleus, ^{13}C, can overcome problems with resolution of this type. The 125 MHz, ^{13}C spectra for PVC is shown below. Notice the higher resolution even compared to the 500 MHz proton spectra shown above. (Note that spectrometer magnetic field strength is in reference to the proton resonance frequency even if a different nuclei is probed.)



Features of ^{13}CNMR

3)The large abundance of ^{1}H nuclei compared with ^{13}C leads to loss of ^{13}C resolution and signal due to weak coupling of ^{13}C and ^{1}H resonances. This problem is amplified in solid samples, so called solid state ^{13}C NMR.

Features of ^{13}CNMR

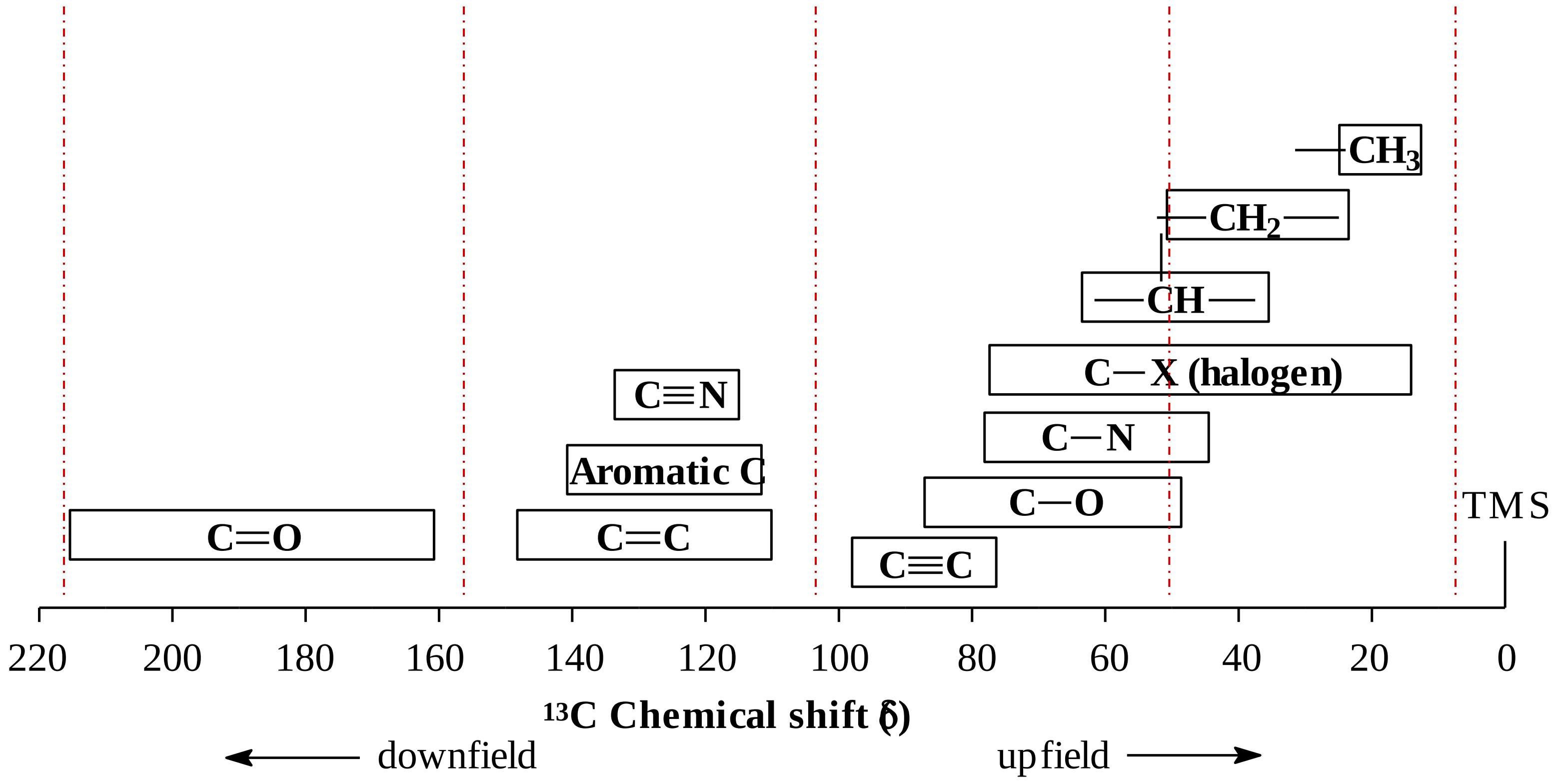
4) Each unique C in a structure gives a <u>single peak</u> in the spectrum; there is rarely any overlap.

Features of ^{13}CNMR

5) The intensity (size) of each peak is NOT directly related to the number of that type of carbon. Other factors contribute to the size of a peak:

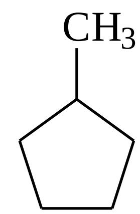
- Peaks from carbon atoms that have attached hydrogen atoms are bigger than those that don't have hydrogens attached.

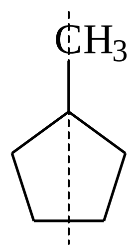
^{13}C Chemical Shifts

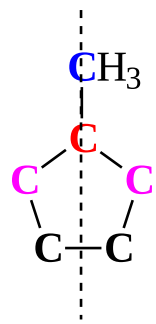


Predicting ^{13}C Spectra

- Problem 13.6 Predict the <u>number</u> of carbon resonance lines in the ^{13}C spectra of the following:

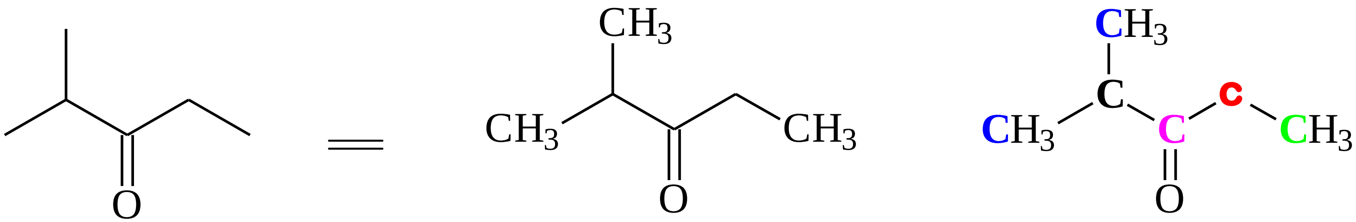




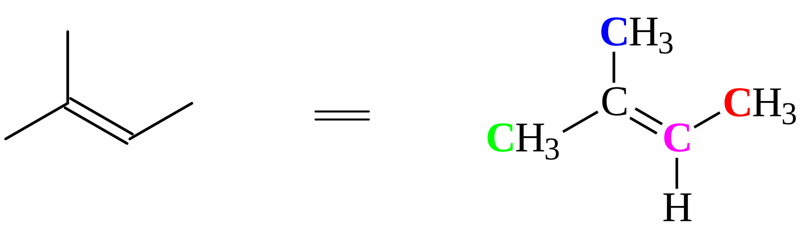


plane of symmetry

4 lines



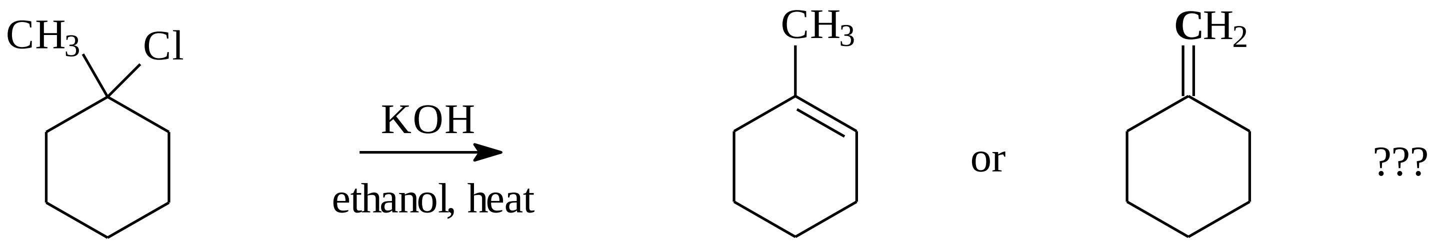
5 lines

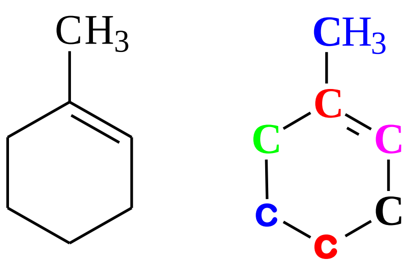


5 lines

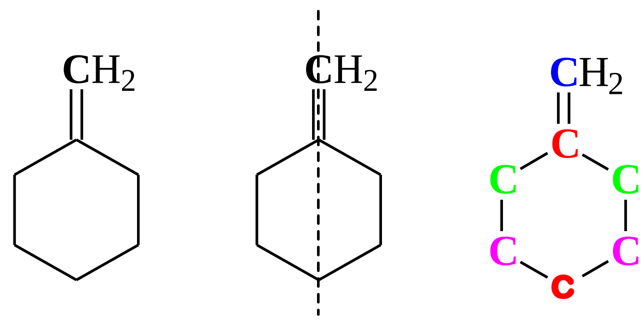
Predicting ^{13}C Spectra

- Predicted the number of carbon resonance lines in the ^{13}C spectra of the products of the following reaction:





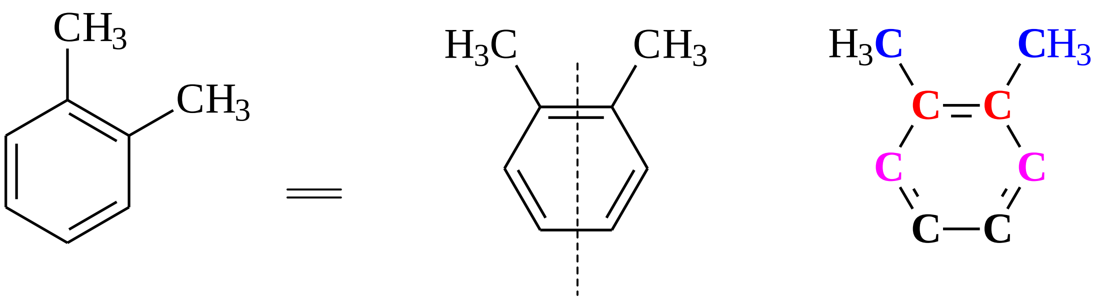
7 lines



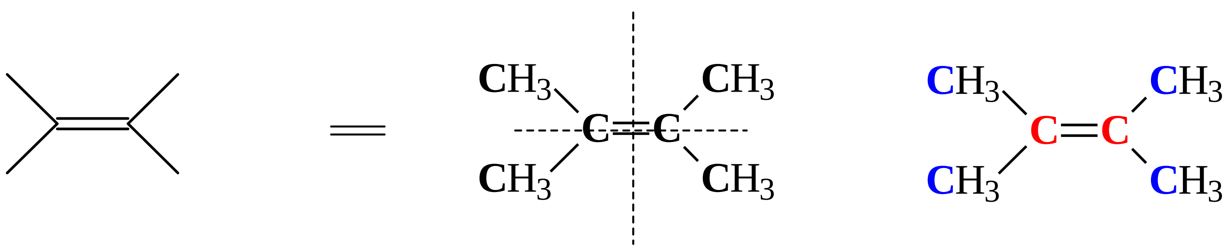
5 lines

plane of symmetry

Predicting ^{13}C Spectra

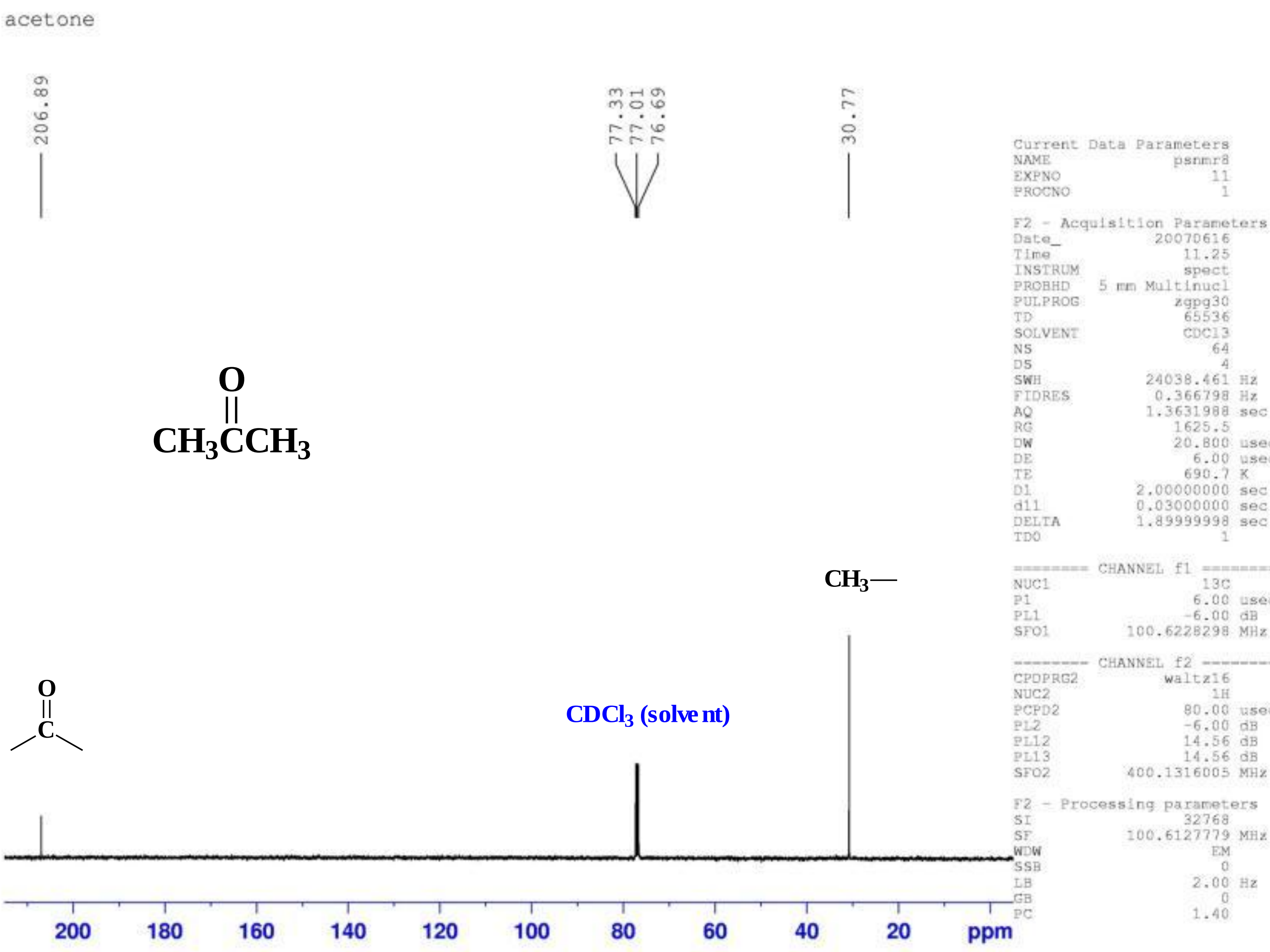


4 lines



2 lines

Symmetry Simplifies Spectra!!!


acetone
206.89
77.33
77.01
76.69
30.77
O
||
CH_3CCH_3
CH_3—
O
C
$CDCl_3$ (solvent)
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME psnmr8
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070616
Time 11.25
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1625.5
DW 20.800 usec
DE 6.00 usec
TE 690.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
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WDW EM
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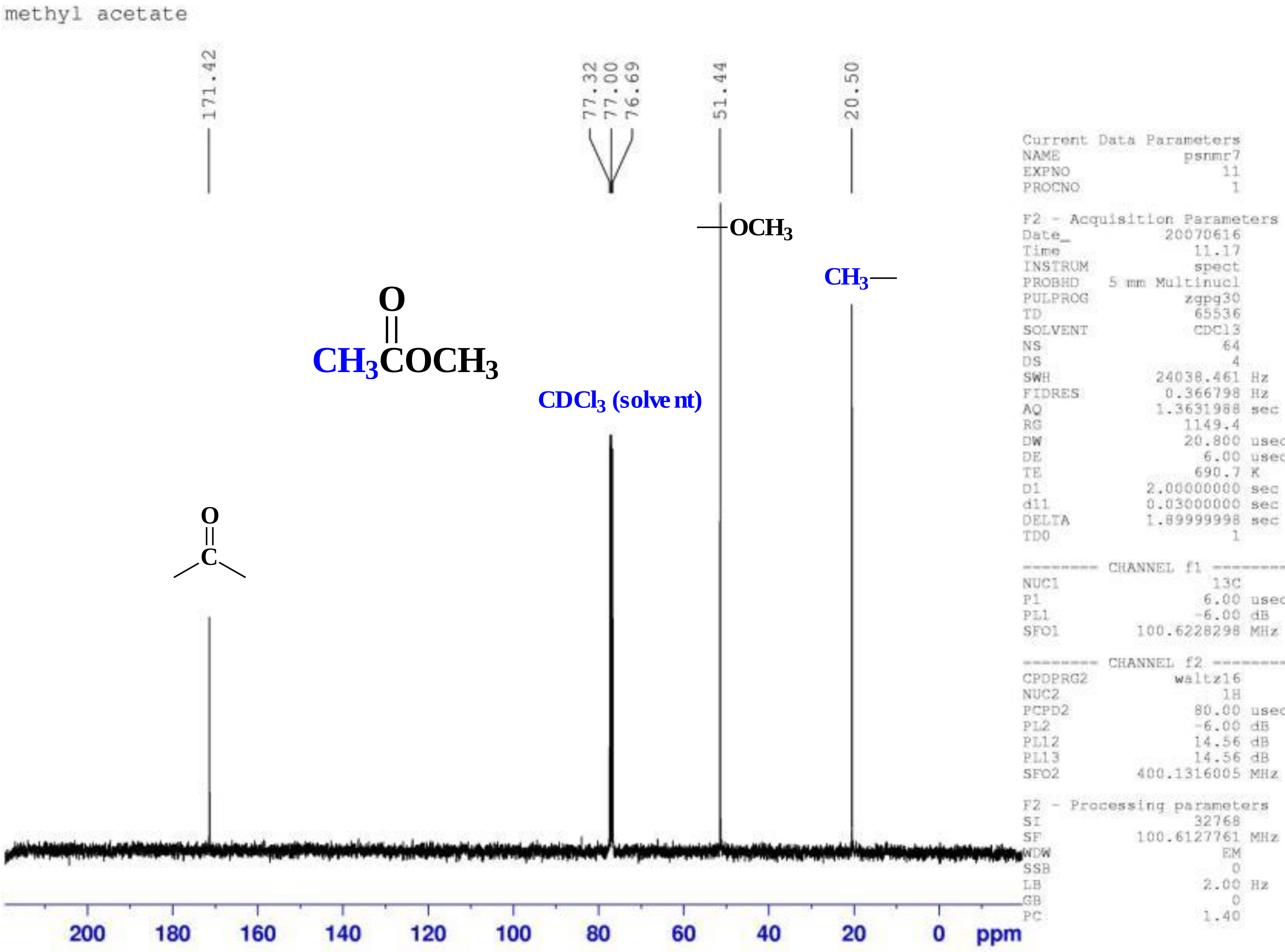
LB 2.00 Hz
GB 0
PC 1.40


methyl acetate
171.42
77.32
77.00
76.69
51.44
20.50
O
C
CH3COCH3
CDCl3 (solvent)
—OCH3
CH3—
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME psnmr7
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070616
Time 11.17
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1149.4
DW 20.800 usec
DE 6.00 usec
TE 690.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
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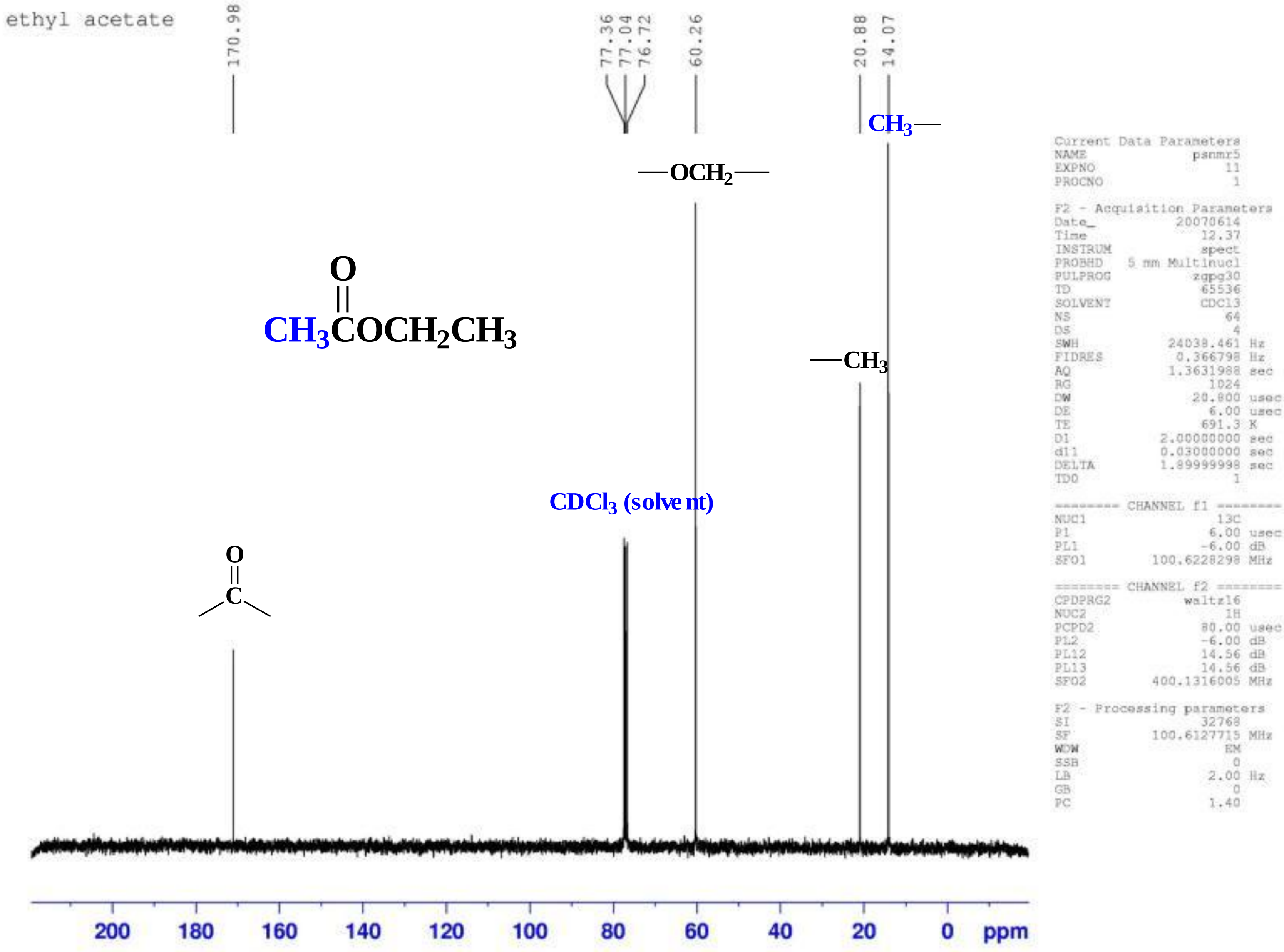
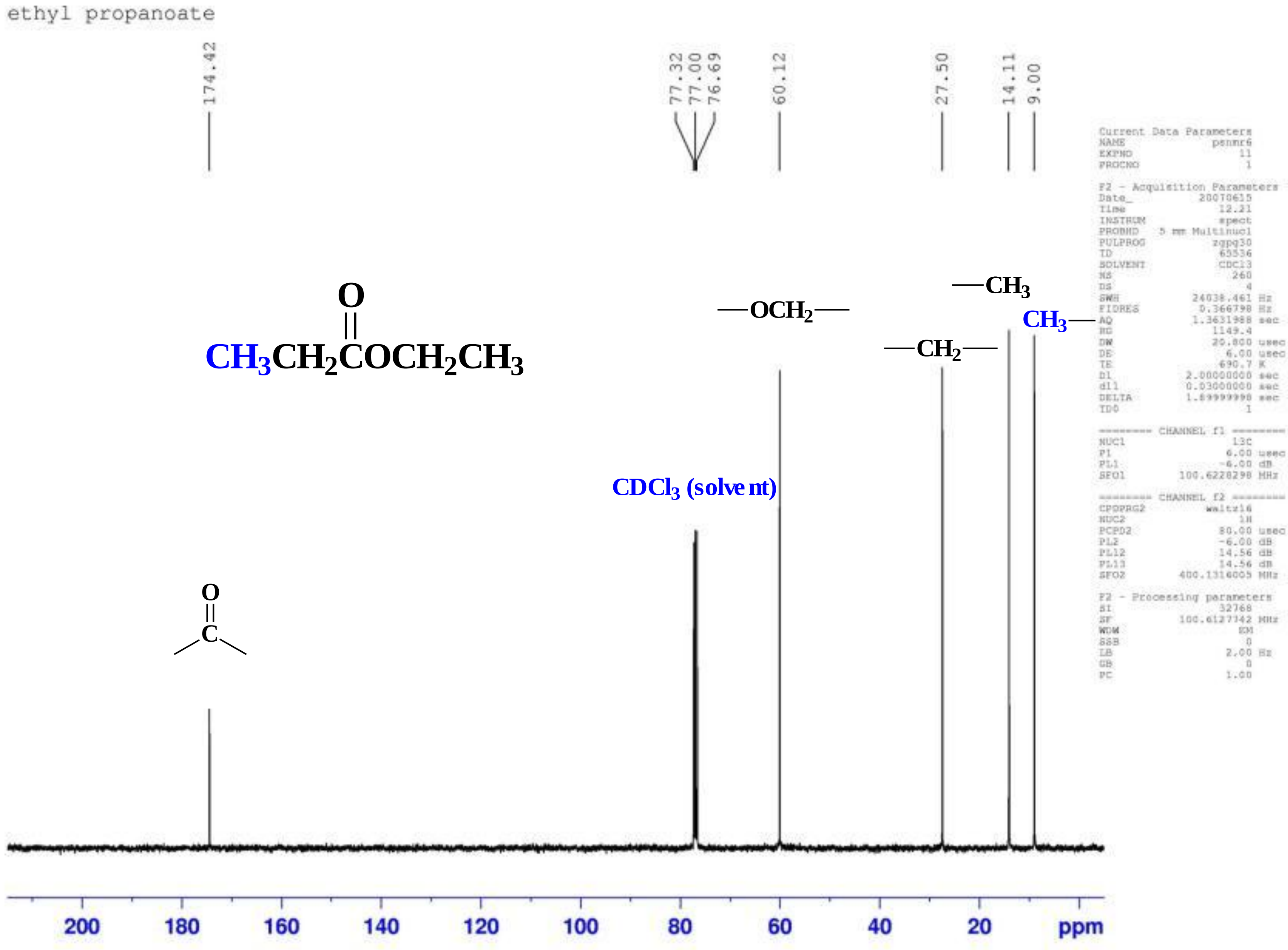
SF 100.6127761 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



ethyl acetate
170.98
77.36
77.04
76.72
60.26
20.88
14.07
CH3—
—OCH2—
O
CH3COCH2CH3
—CH3
CDCl3 (solvent)
O
C
Current Data Parameters
NAME psnmr5
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070614
Time 12.37
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1024
DW 20.800 usec
DE 6.00 usec
TE 691.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


ethyl propanoate
174.42
77.32
77.00
76.69
60.12
27.50
14.11
9.00
$CH_3CH_2COCH_2CH_3$
O
—OCH₂—
—CH₃
CH₃—
—CH₂—
CDCl₃ (solvent)
O
C
200
180
160
140
120
100
80
60
40
20
ppm

exersices

Styrene

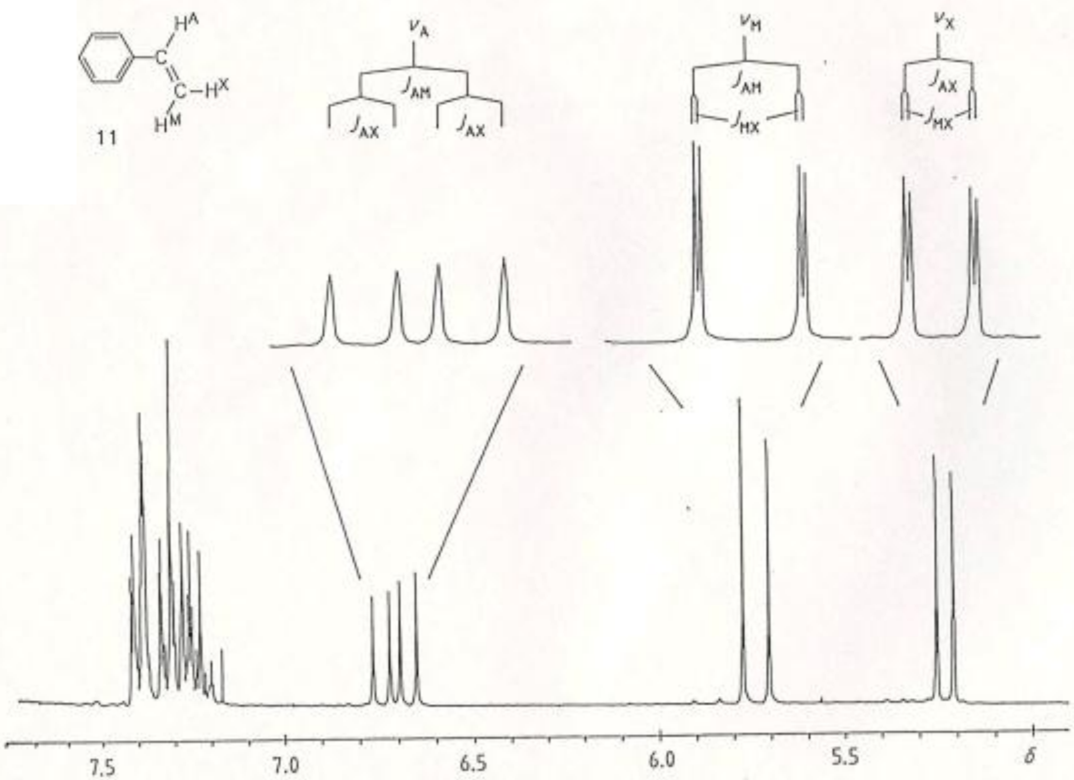
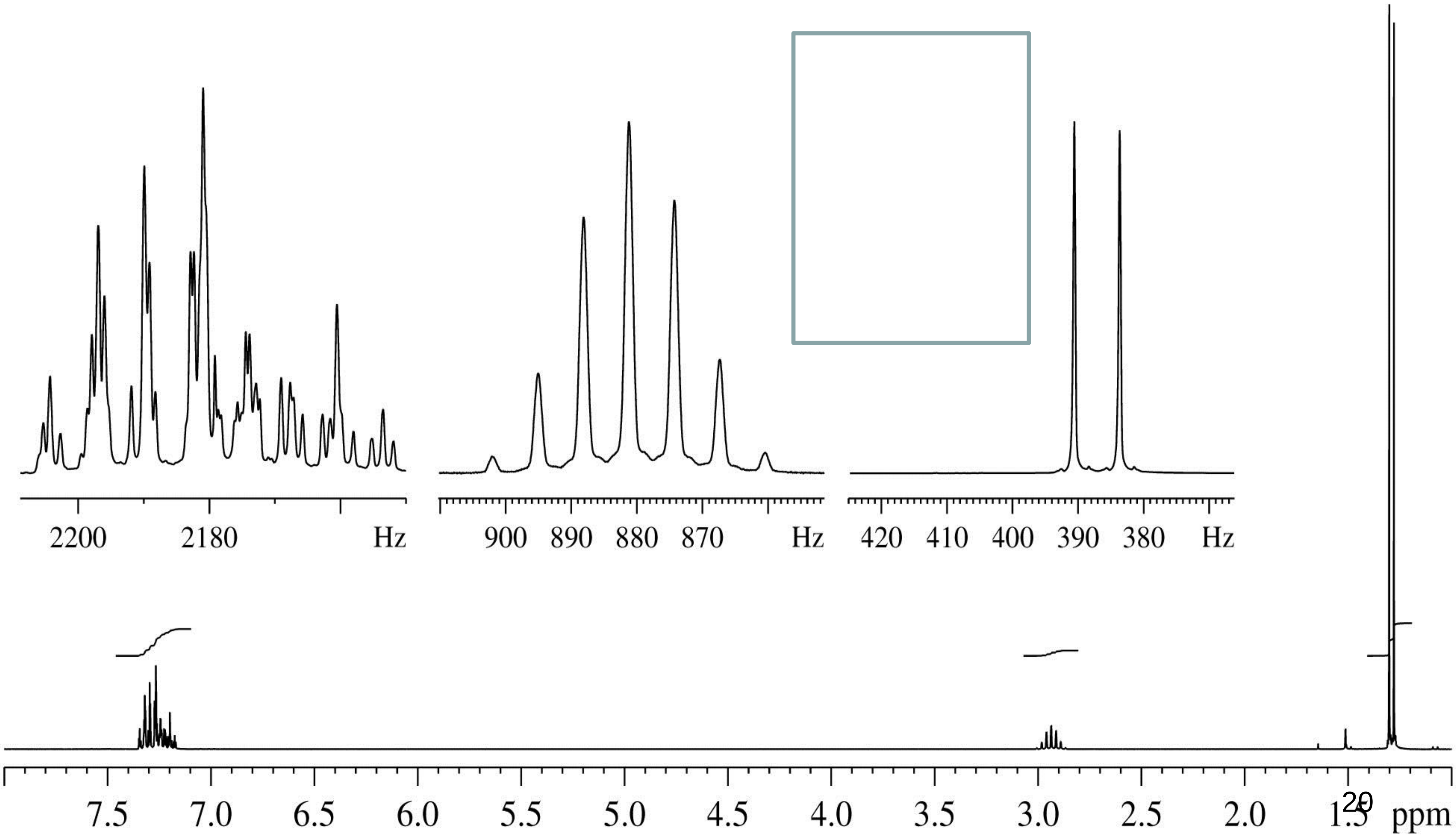


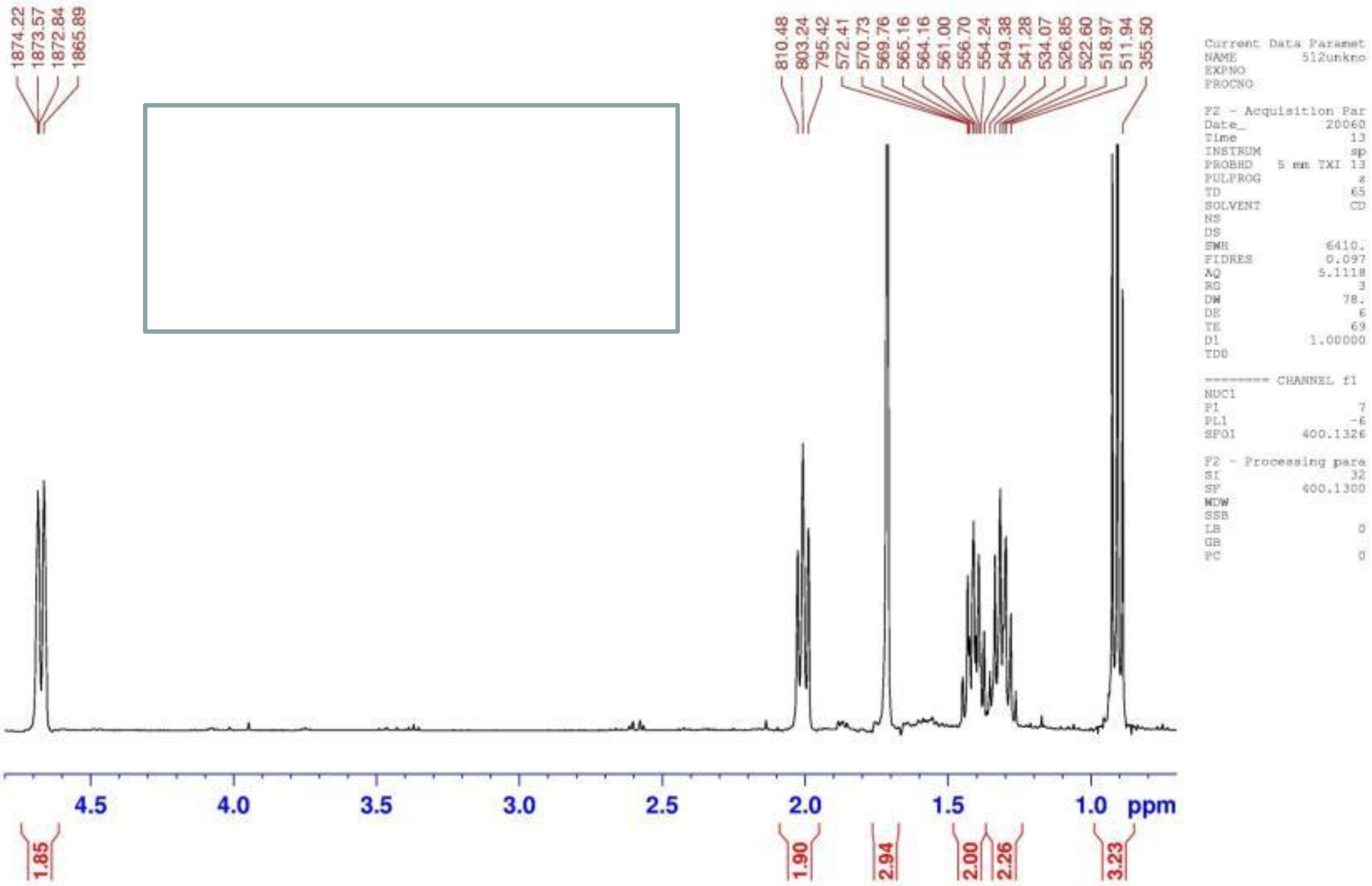
Figure 1-24.
250 MHz ^{1}H NMR spectrum of styrene (**11**) in $CDCl_3$. The protons H^A, H^M and H^X each give a doublet

Cumene



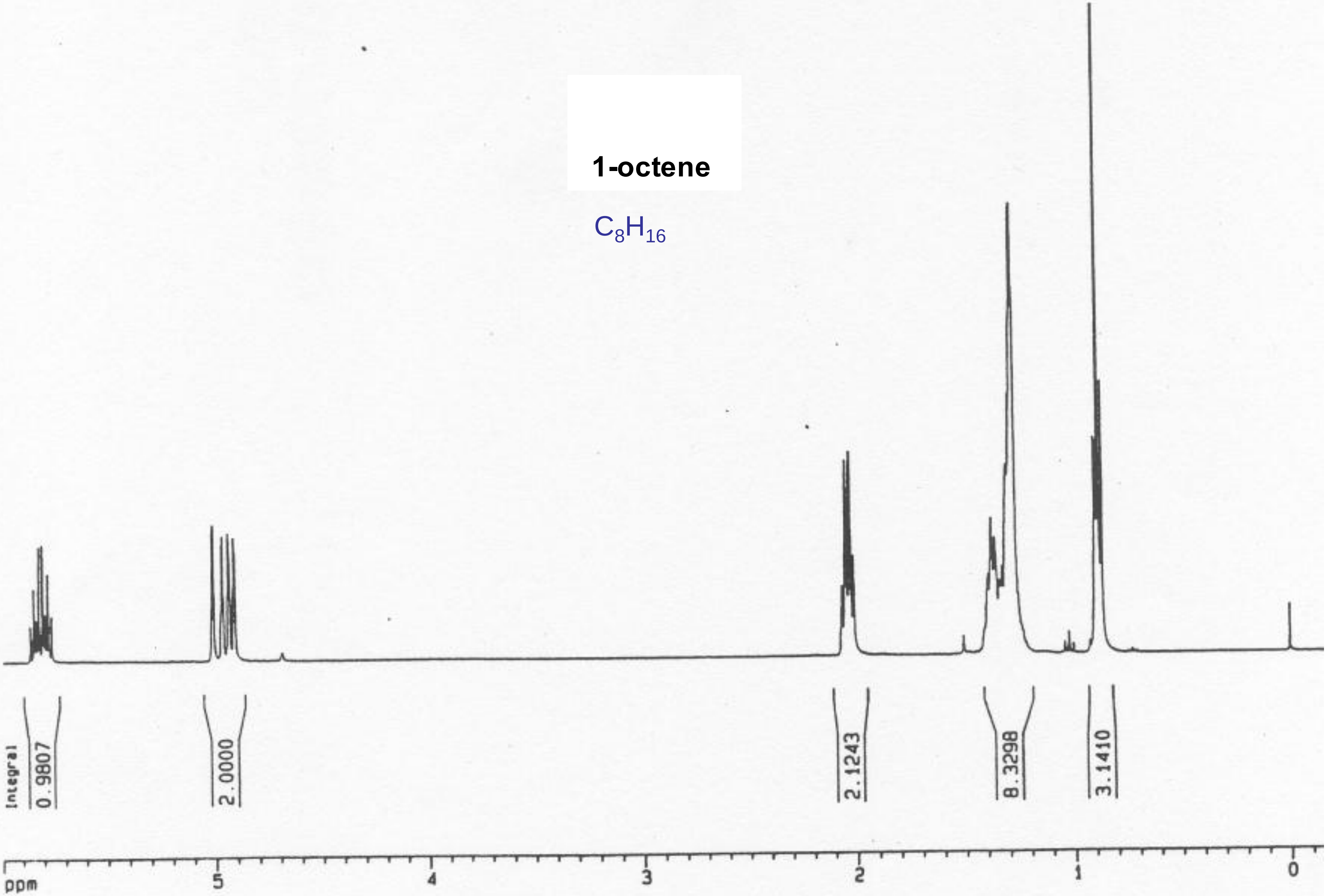
2200
2180
Hz
900
890
880
870
Hz
420
410
400
390
380
Hz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

2-methyl-1-hexene

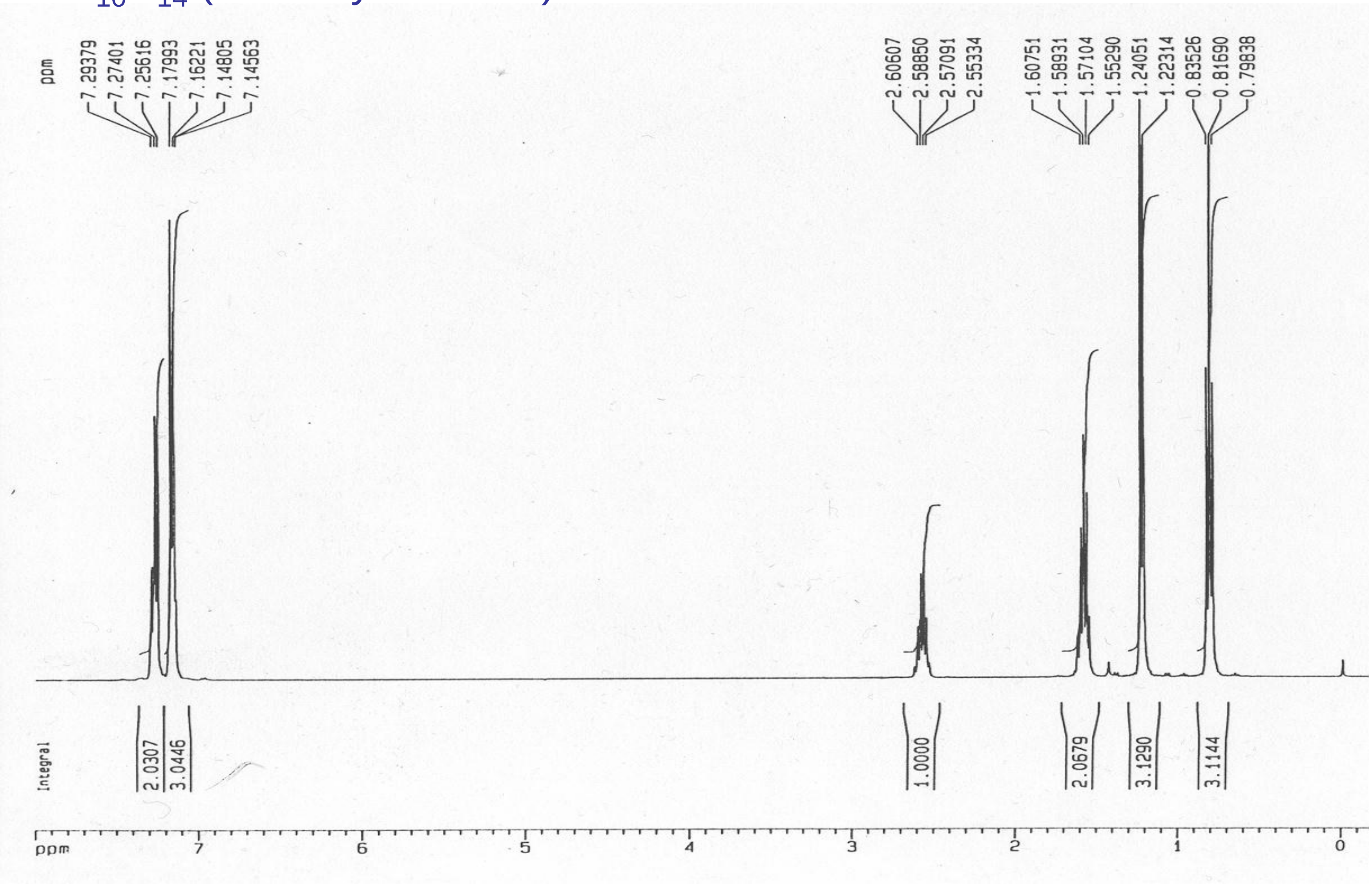


1-octene

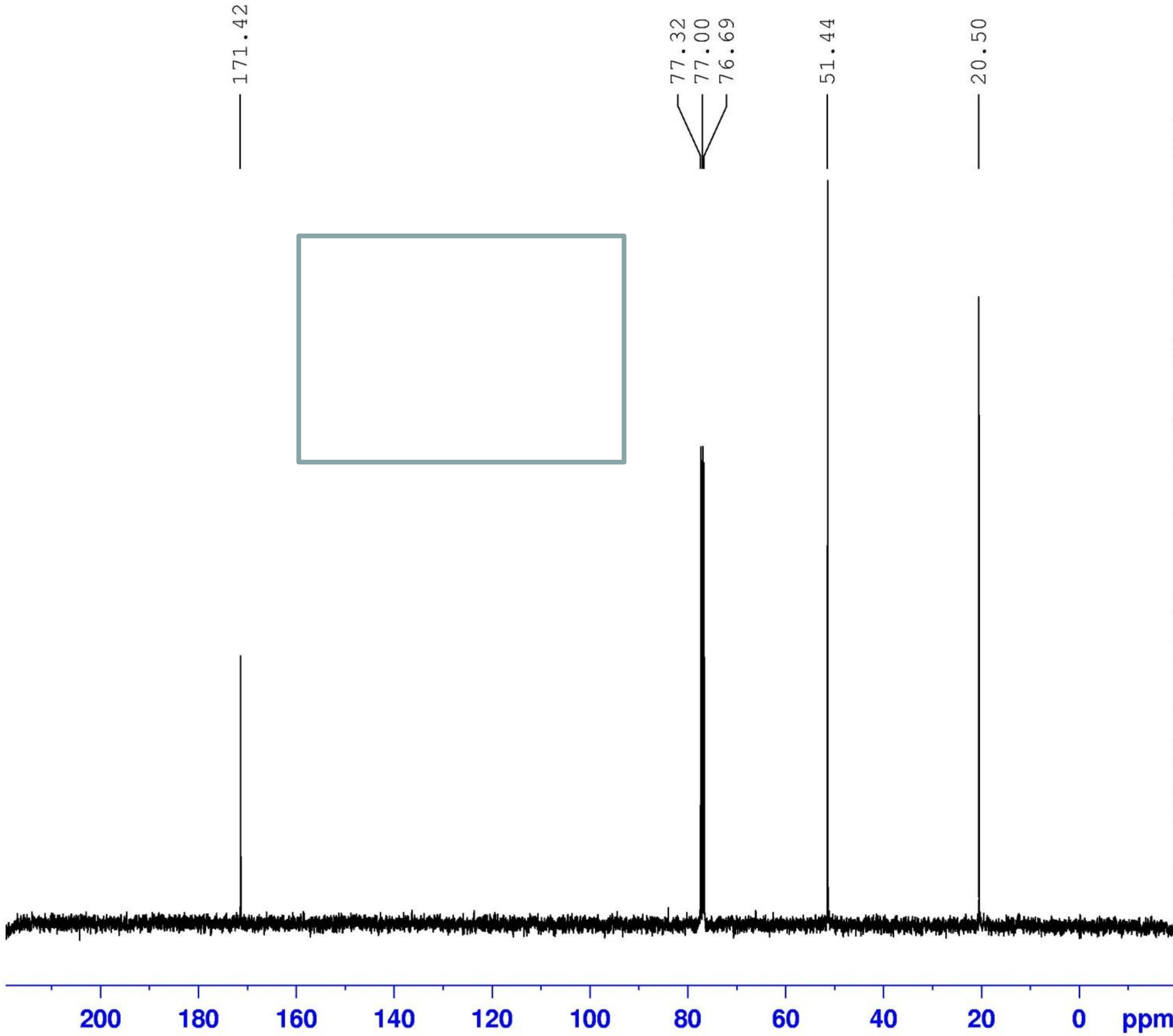
C_8H_{16}



$C_{10}H_{14}$ (*sec*-butylbenzene)



methyl acetate

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PROCNO                1

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PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               1149.4
DW               20.800 usec
DE                 6.00 usec
TE                690.7 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.00 usec
PL1               -6.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              14.56 dB
PL13              14.56 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
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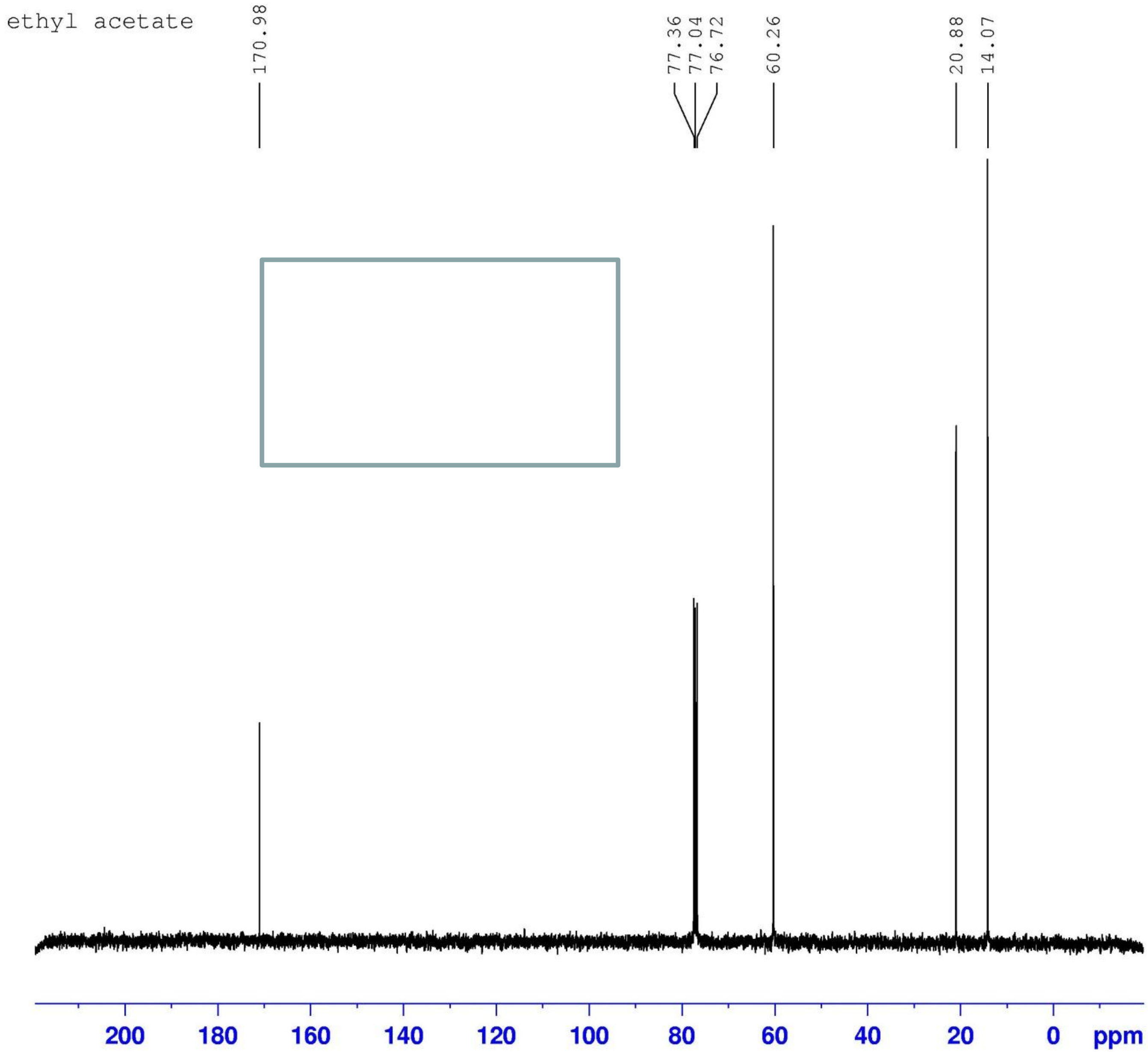
SF          100.6127761 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.40
```

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Current Data Parameters
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EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
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INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 1024
DW               20.800 usec
DE                 6.00 usec
TE                691.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.00 usec
PL1               -6.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              14.56 dB
PL13              14.56 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127715 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.40
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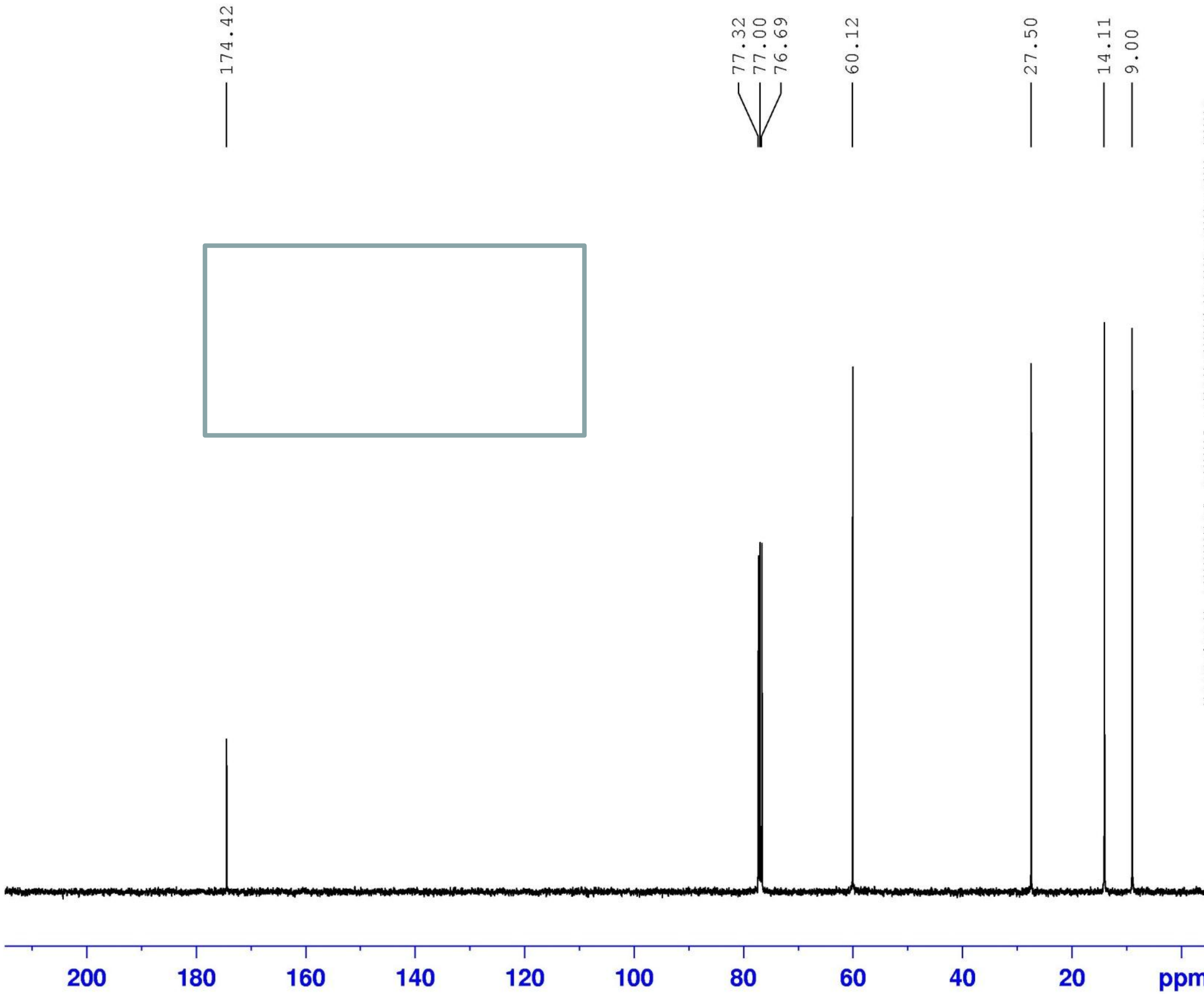
ethyl propanoate



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PROCNO 1

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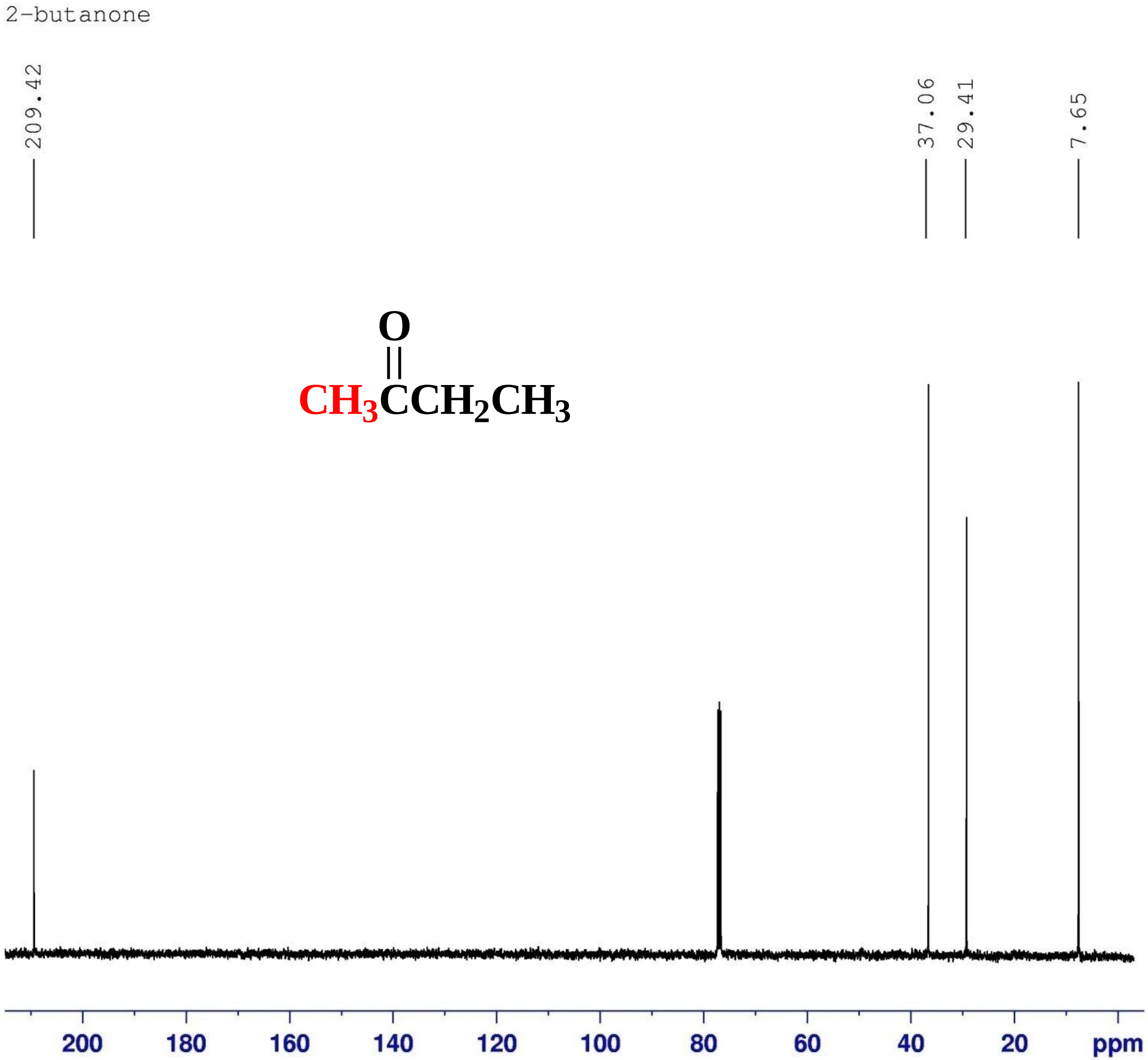
Time 12.21
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 260
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1149.4
DW 20.800 usec
DE 6.00 usec
TE 690.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127742 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00



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PROCNO 1

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Time 11.41
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 1448.2
DW 22.000 usec
DE 6.00 usec
TE 690.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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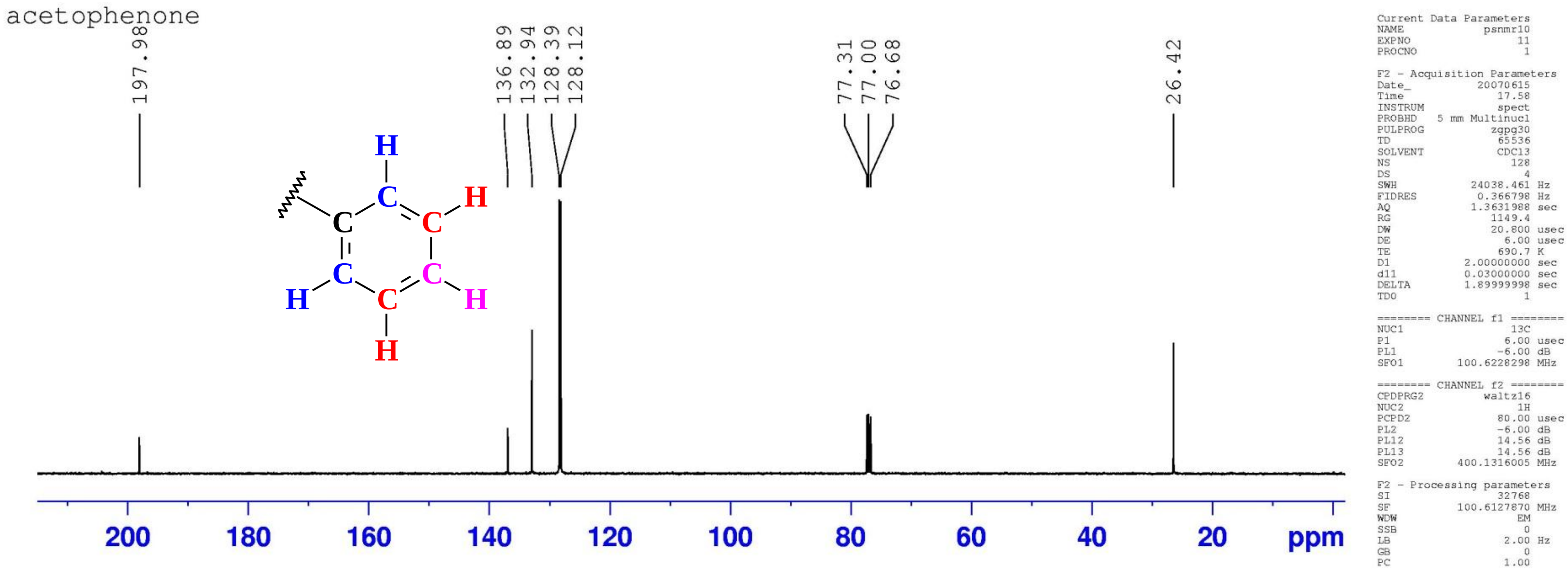
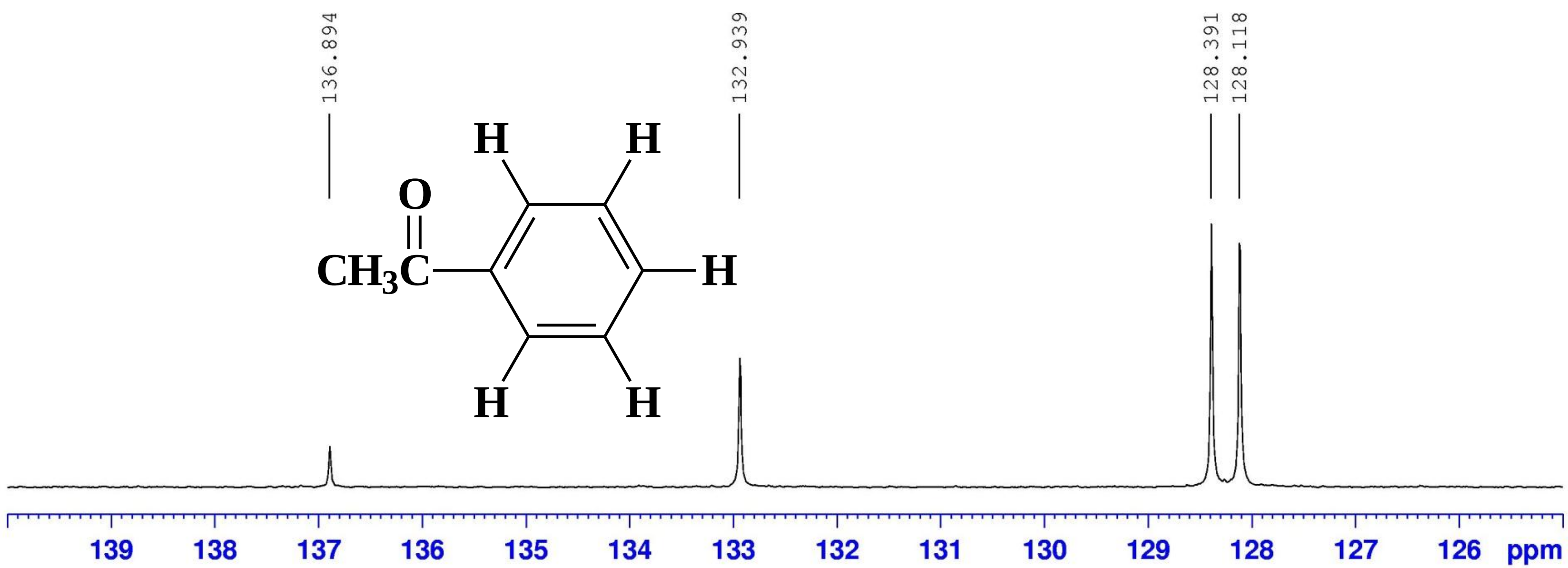
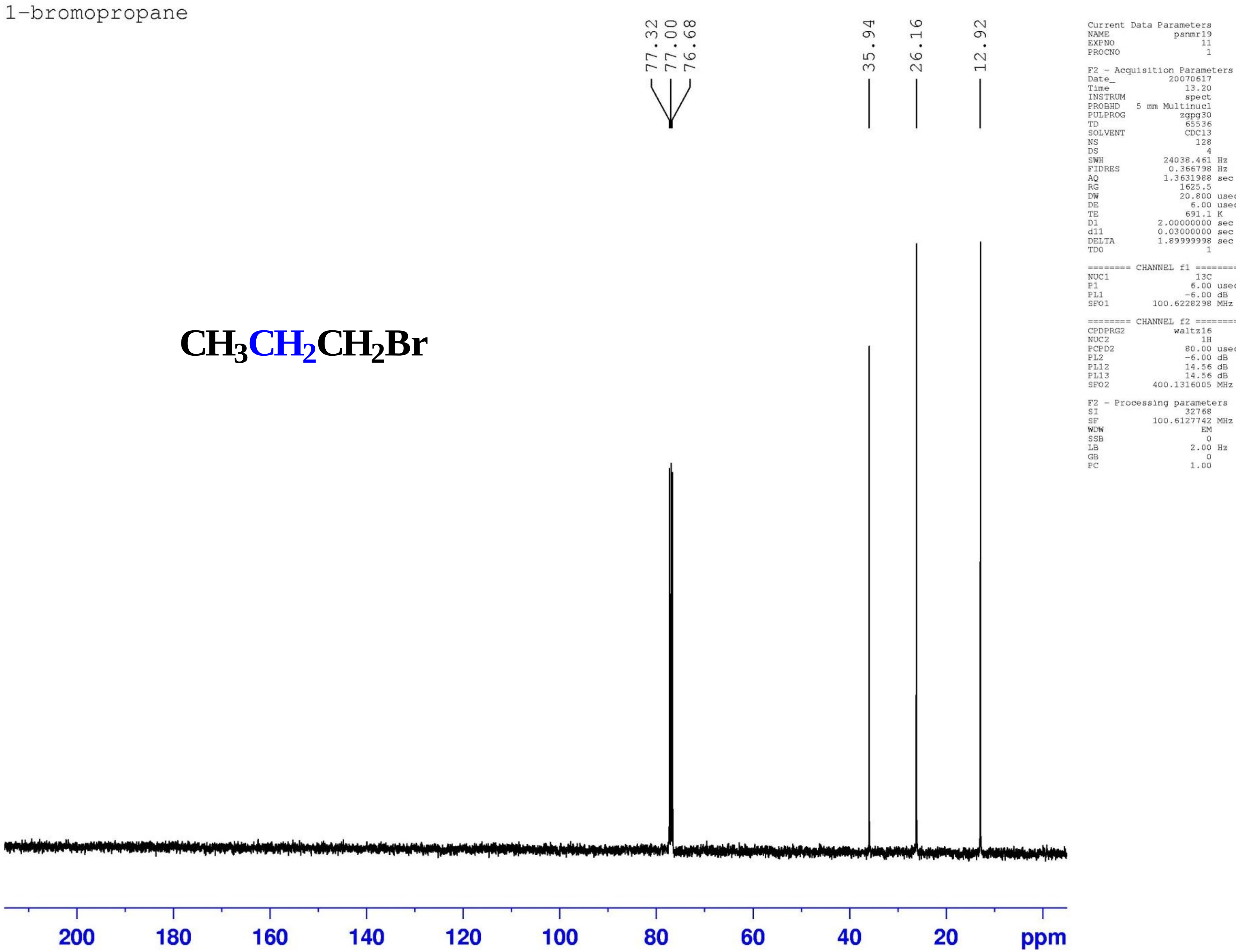
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

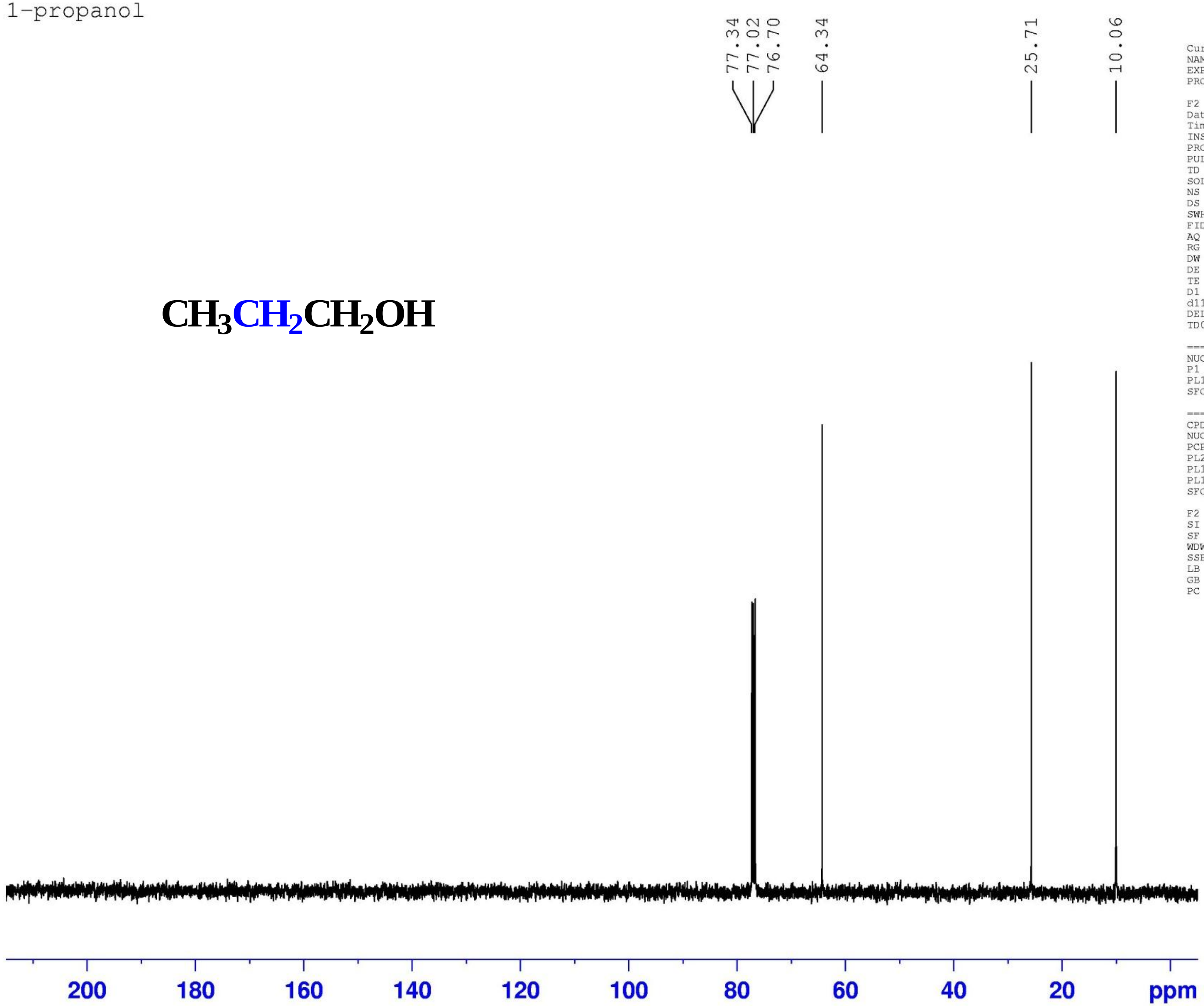

acetophenone
197.98
136.89
132.94
128.39
128.12
77.31
77.00
76.68
26.42
H
C
H
C
C
C
H
C
C
H
H
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME psnmr10
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070615
Time 17.58
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1149.4
DW 20.800 usec
DE 6.00 usec
TE 690.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127870 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00


136.894
132.939
128.391
128.118
O
CH3C
H
H
H
H
H
139
138
137
136
135
134
133
132
131
130
129
128
127
126
ppm


1-bromopropane
77.32
77.00
76.68
35.94
26.16
12.92
CH3CH2CH2Br
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME psnmr19
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070617
Time 13.20
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1625.5
DW 20.800 usec
DE 6.00 usec
TE 691.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 14.56 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127742 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1-propanol

$CH_3CH_2CH_2OH$

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Current Data Parameters
NAME              psnmr11
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070616
Time                13.47
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 3649.1
DW                 20.800 usec
DE                   6.00 usec
TE                  690.8 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.00 usec
PL1                 -6.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                14.56 dB
PL13                14.56 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127742 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.00
```
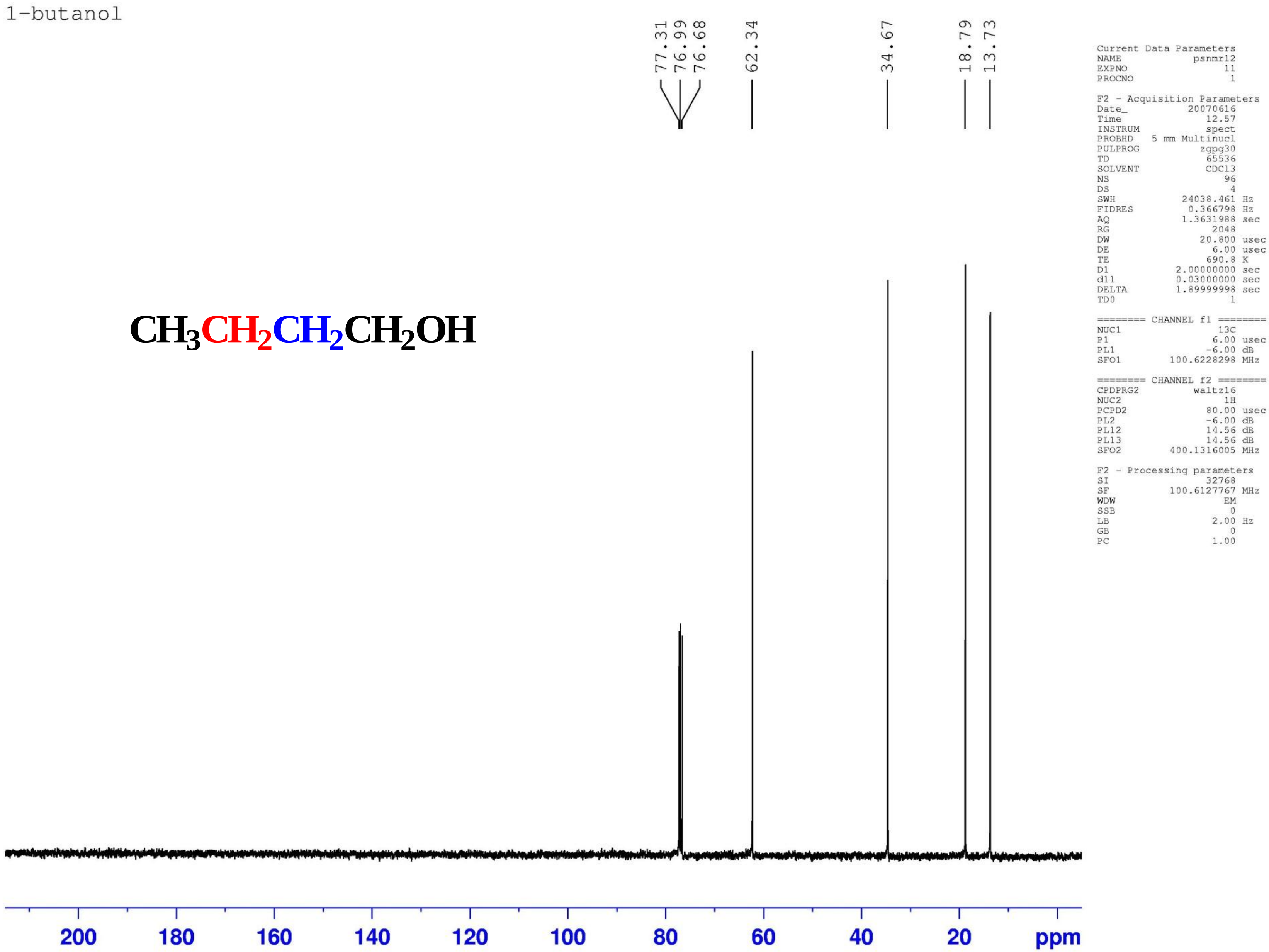
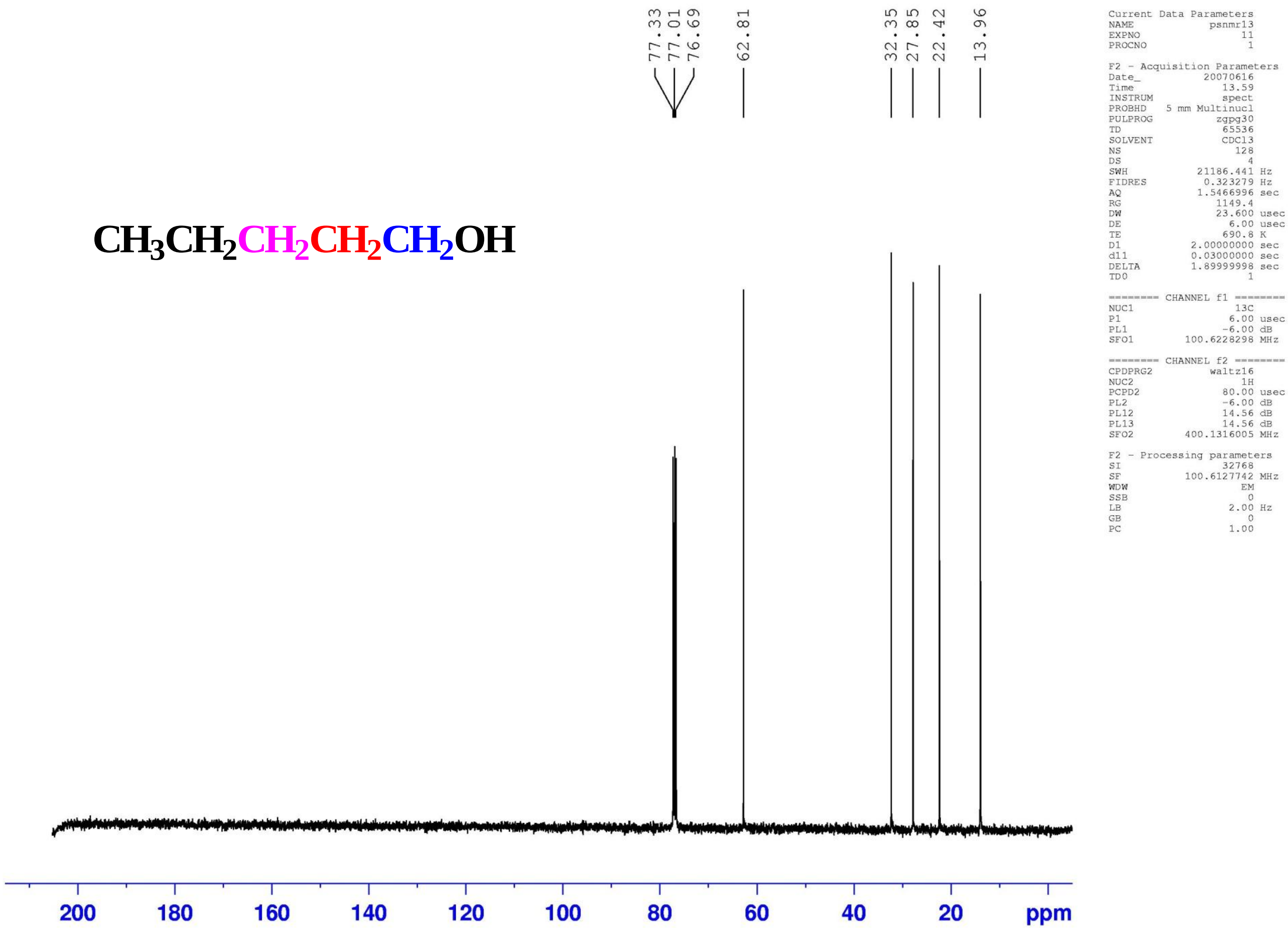

$CH_3CH_2CH_2CH_2OH$



1-pentanol

$CH_3CH_2CH_2CH_2CH_2OH$



NMR Magnet Safety

- **NMR magnets are always charged!**
  - NMR magnets may interfere with medical devices (i.e. pacemakers, metallic implants)
  - NMR magnets and RF consoles may interfere with electronic and mechanical devices and may damage them (cell phones, pagers, watches, etc.)
  - NMR magnets will erase credit cards, ID cards, floppy disks, hard disks (I-pods and some other mp3 players).
  - NMR magnets will attract ferromagnetic objects of any size (i.e. paper clips, coins, keys, pens, scissors, screw drivers, wrenches, metallic chairs, gas cylinders, etc.) and spectrometer and people may sustain severe damage or injury, if handled carelessly.

- **NMR magnets contain Cryogens (liquid Helium and Nitrogen)**
  - Cryogens can cause severe burns if handled improperly (use eye protection and gloves).
  - Cryogens evaporate and may cause asphyxiation if a lab is not properly ventilated.
  - During a magnet quench up to 100 liters of liquid Helium are vaporized in a matter of minutes (2600 cu ft, 70,000 liters gas) and may cause asphyxiation, even if the lab is well ventilated. If a magnet quenches, leave the lab immediately. Don’t panic, helium gas will rise to the ceiling.
  - During a refill the refill tubing may shatter. Frozen rubber cuts like glass!!