MCH-401:Application of Spectroscopy (Organic)

UNIT- 4th: Carbon-13 NMR Spectroscopy

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C. NMR Spectroscopy

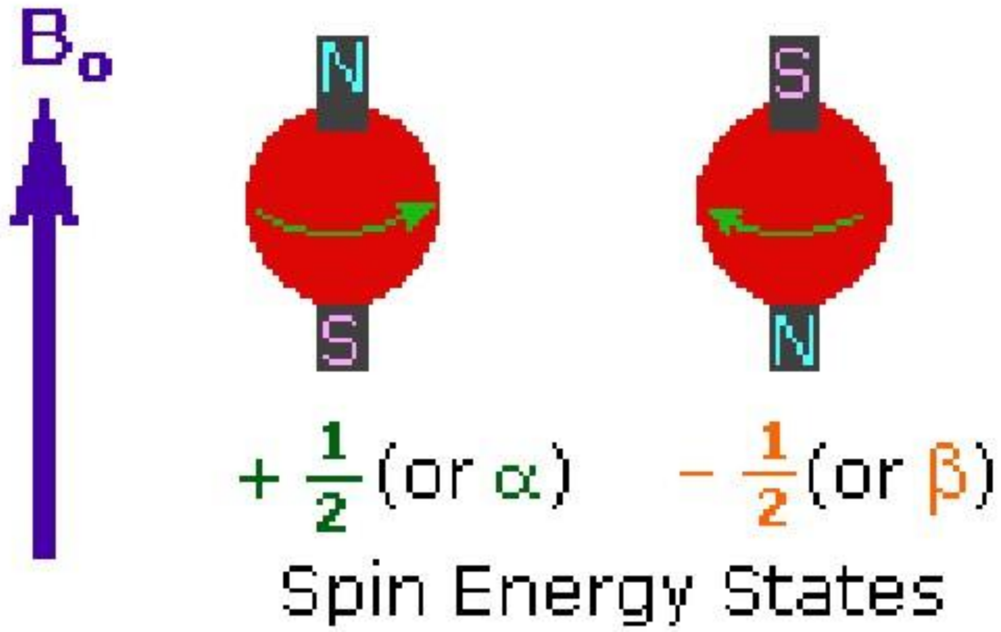
1. General Theory
2. ^{13}C NMR
3. ^{1}H NMR

1. General Theory of NMR

A magnetic field is generated by a spinning charge

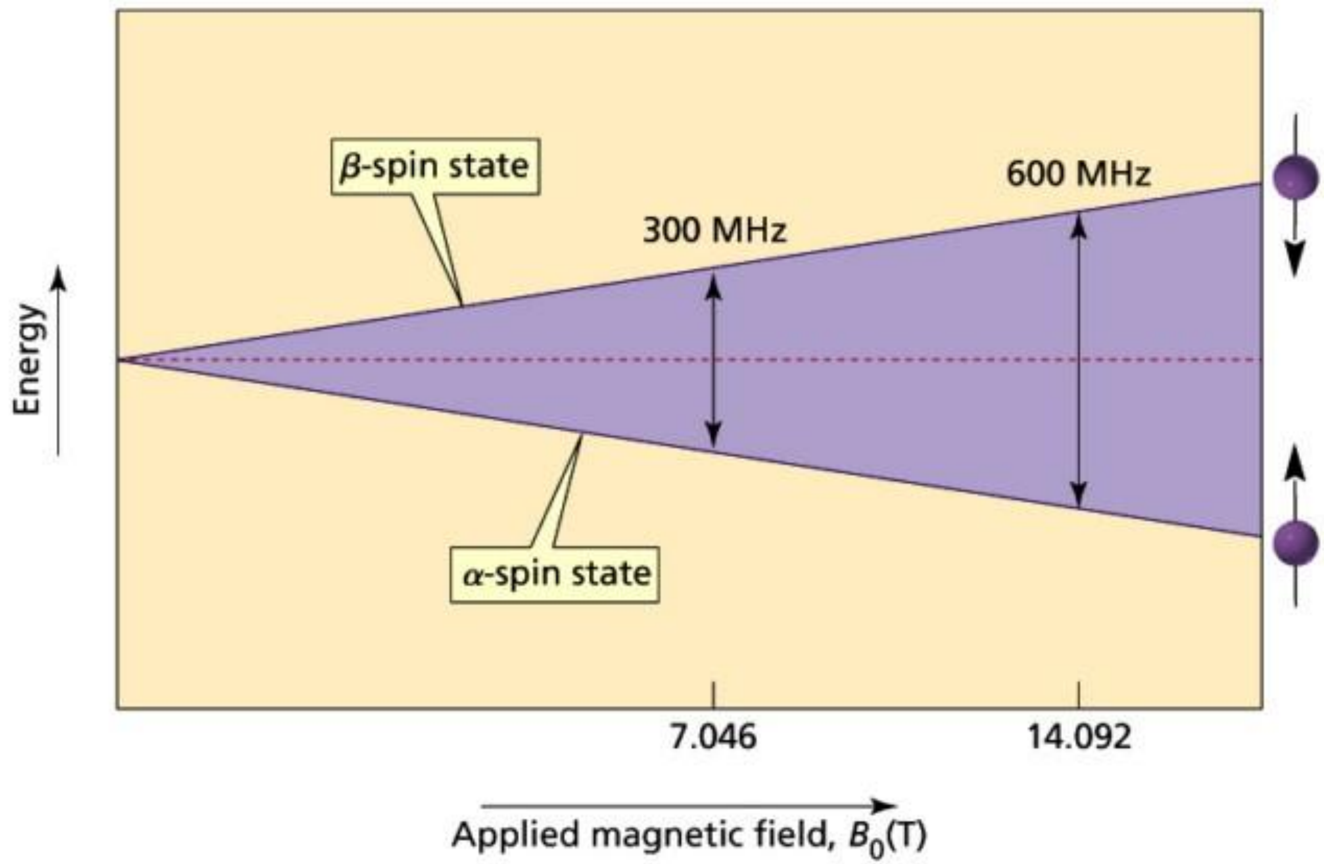
The nucleus of many atoms is a spinning charge.

For many nuclei, an external magnetic field will cause the spinning charge to either line up **with** the external magnetic field or **against it**



The β spin state is slightly greater in energy.

The difference in energy between α and β increases with increasing magnetic field strength.



Nuclei can absorb energy.

When nuclei in the α state absorb radiation equal in E to the difference between the α and β spin states, the α spin state is promoted to the β spin state.

The radiation required for “**spin flipping”** has a frequency in the radio wave range

Nuclei can emit energy.

As nuclei move from

the β spin state to the α spin state,

energy is emitted and the frequency of that energy can be detected.

resonance = nuclei flipping back and forth between the α and β spin state.

Resonance is the "Song of the Nuclei."

Every molecule sings its own song

as a result of its structure.

Analysis of an NMR spectrum

may involve analyzing:

a) The **number of signals** a molecule emits

b) The **frequencies** at which signals occur

c) The **intensity** of signals

d) The **splitting** of signals

2. ^{13}C NMR

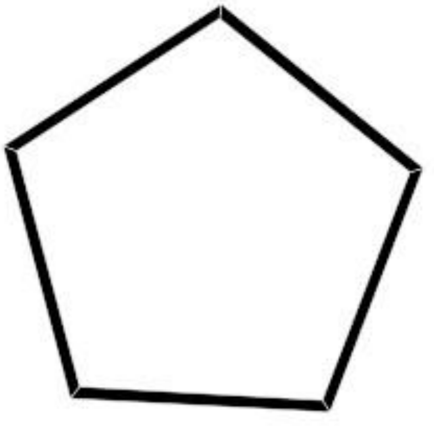
a) Number of signals

b) Position of signals

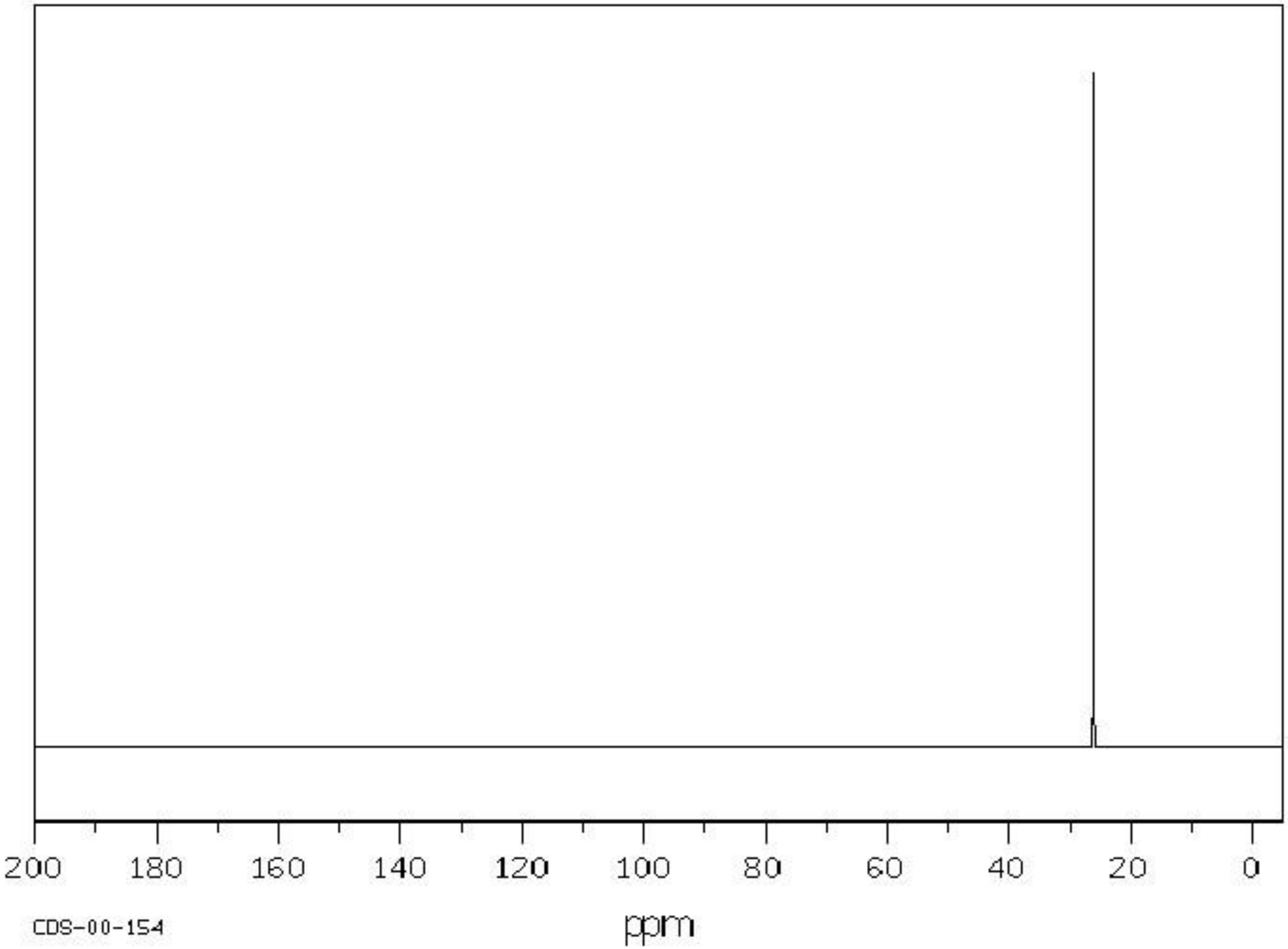
c) DEPT data

a) The number of signals correlates with the number **types of carbon** in a molecule

cyclopentane



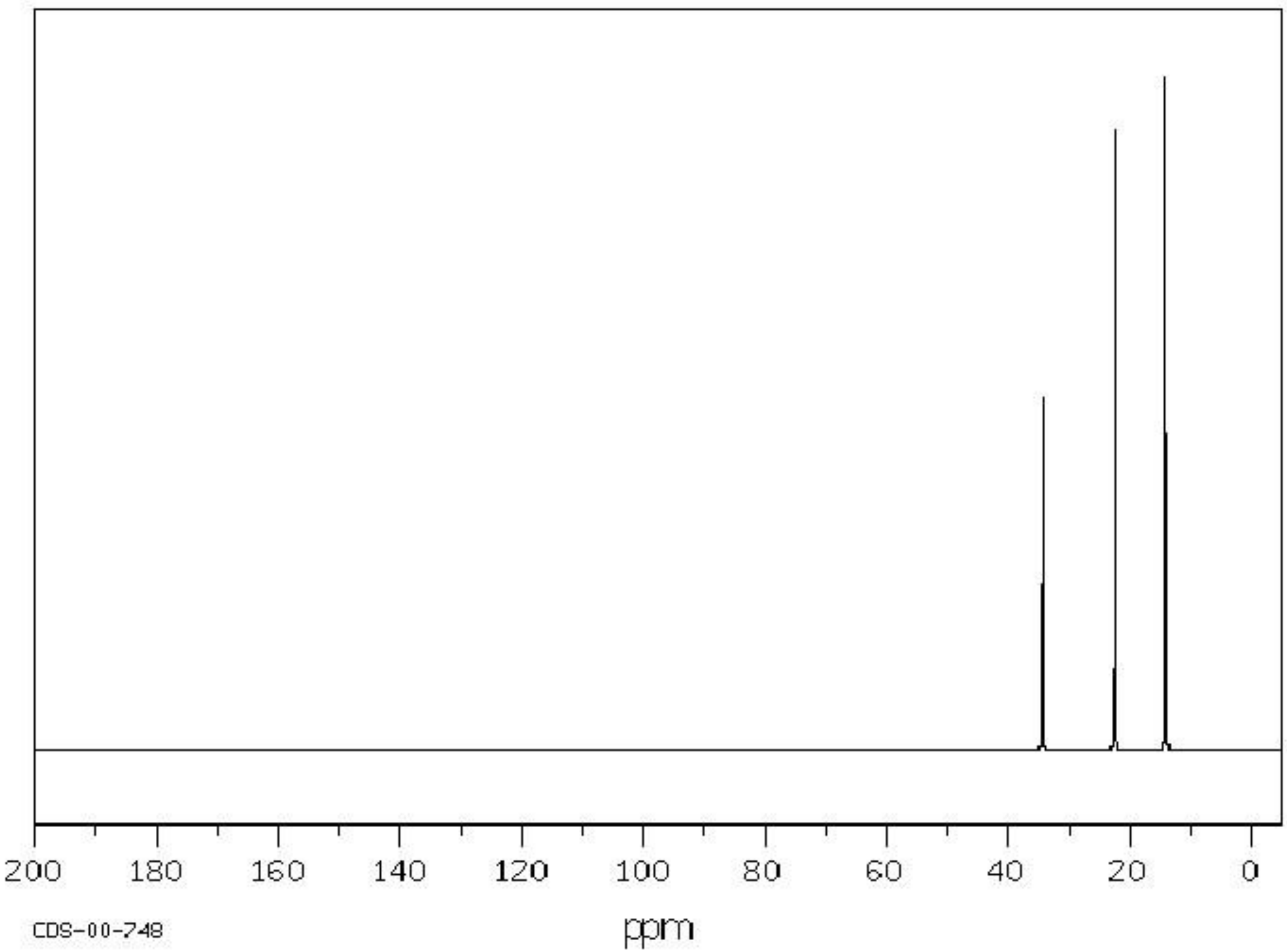
13C-NMR cyclopentane



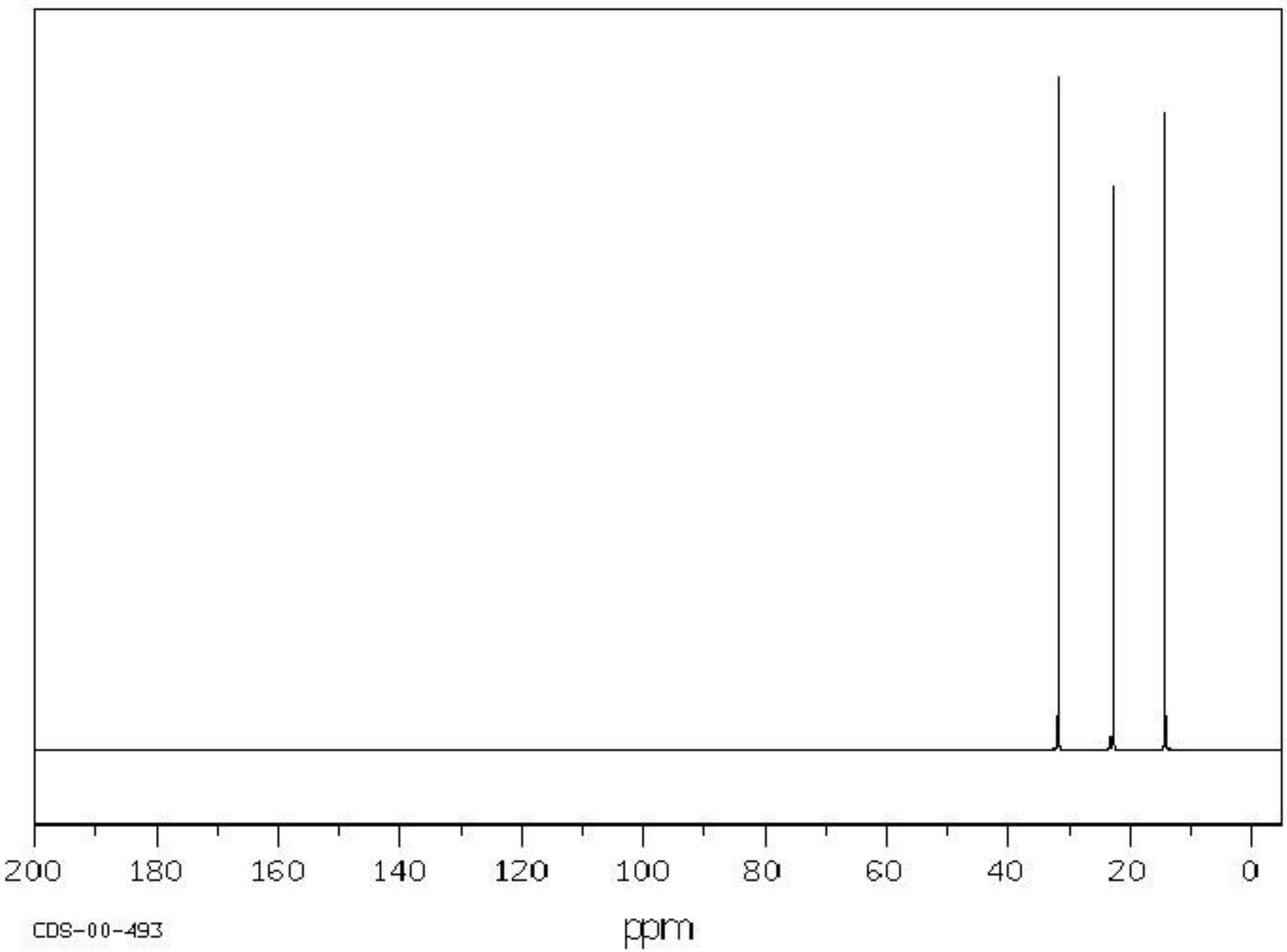
Pentane

$CH_3CH_2CH_2CH_2CH_3$

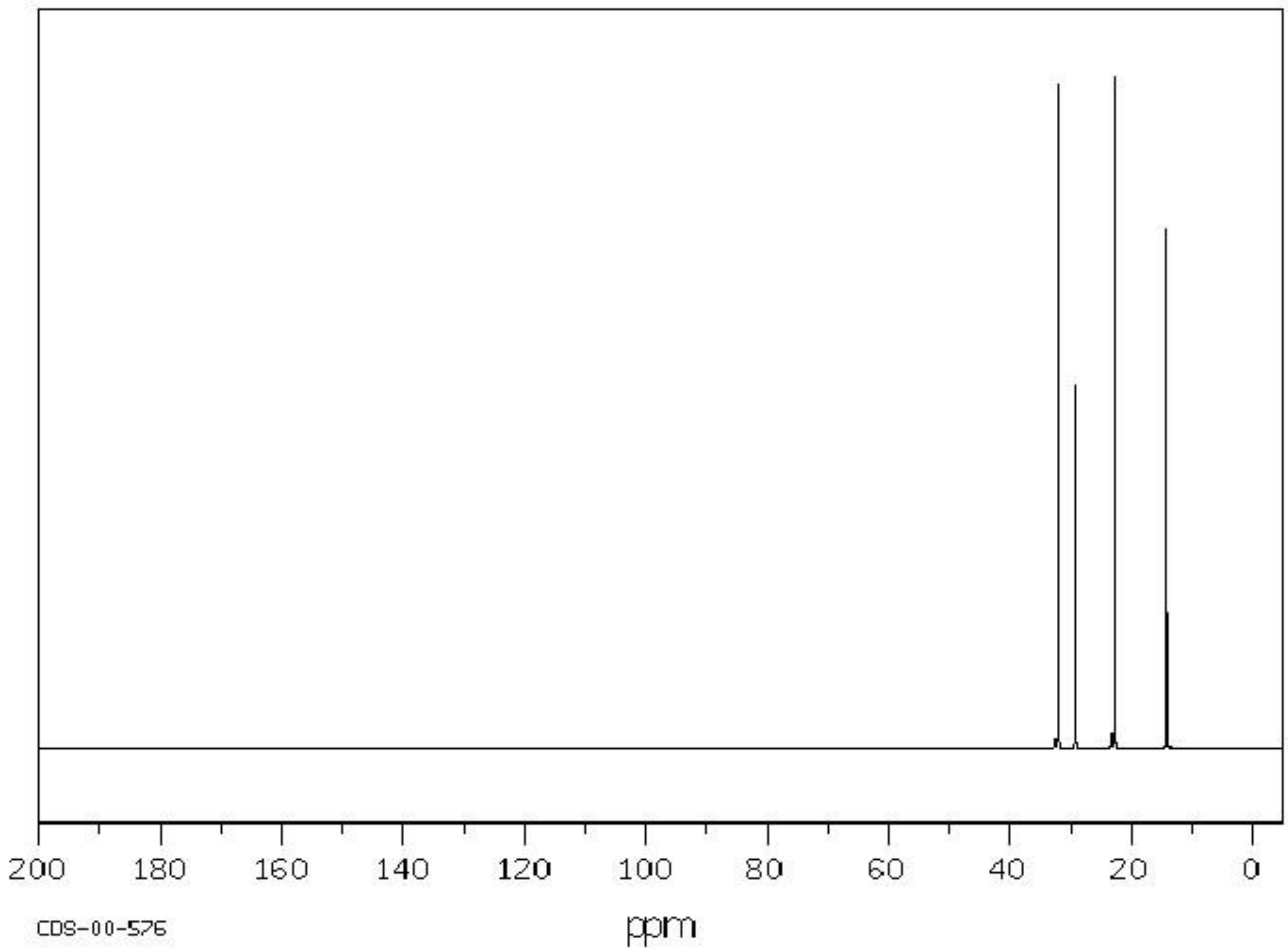
^{13}C-NMR pentane



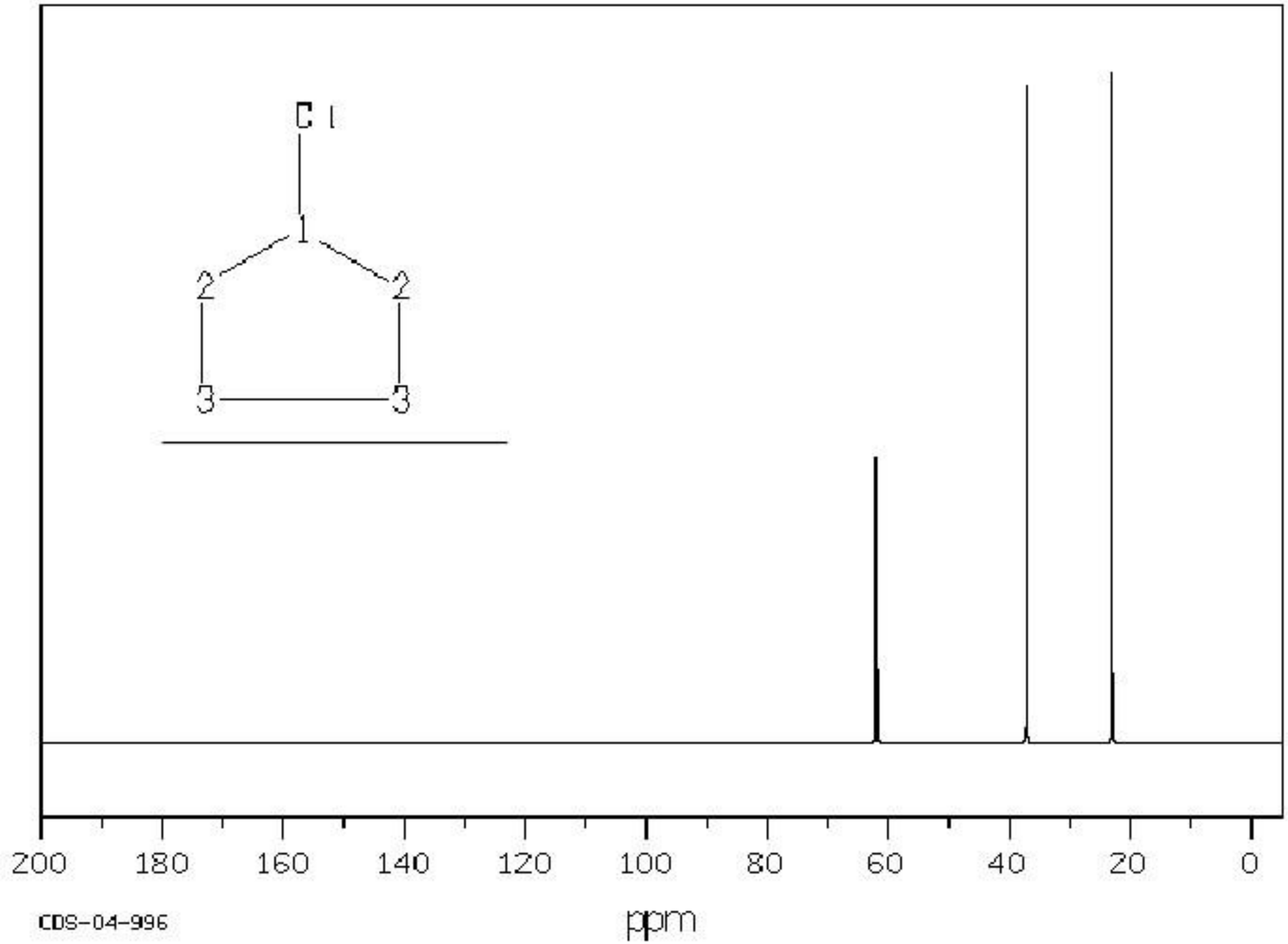
^{13}C-NMR hexane



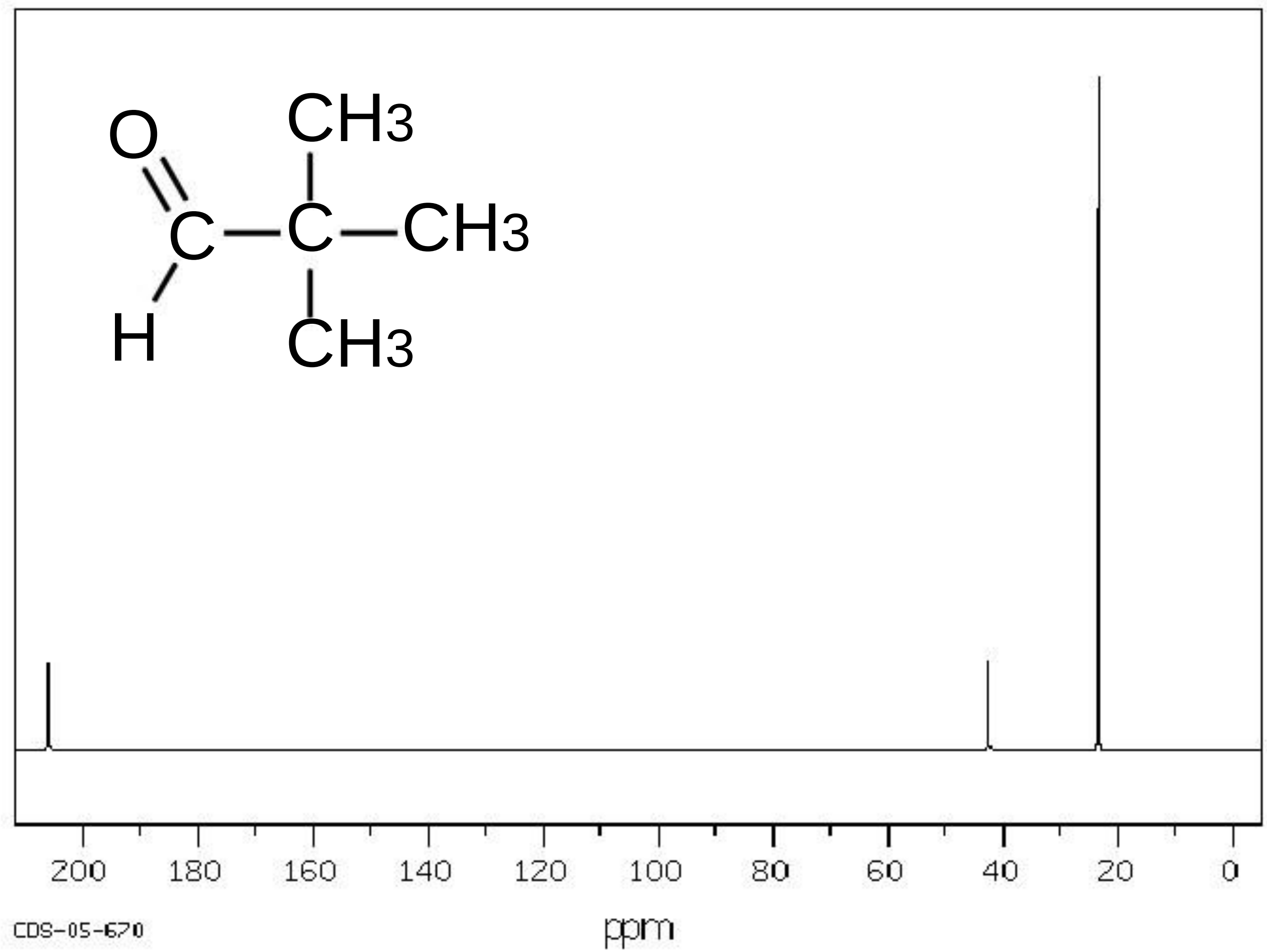
^{13}C-heptane



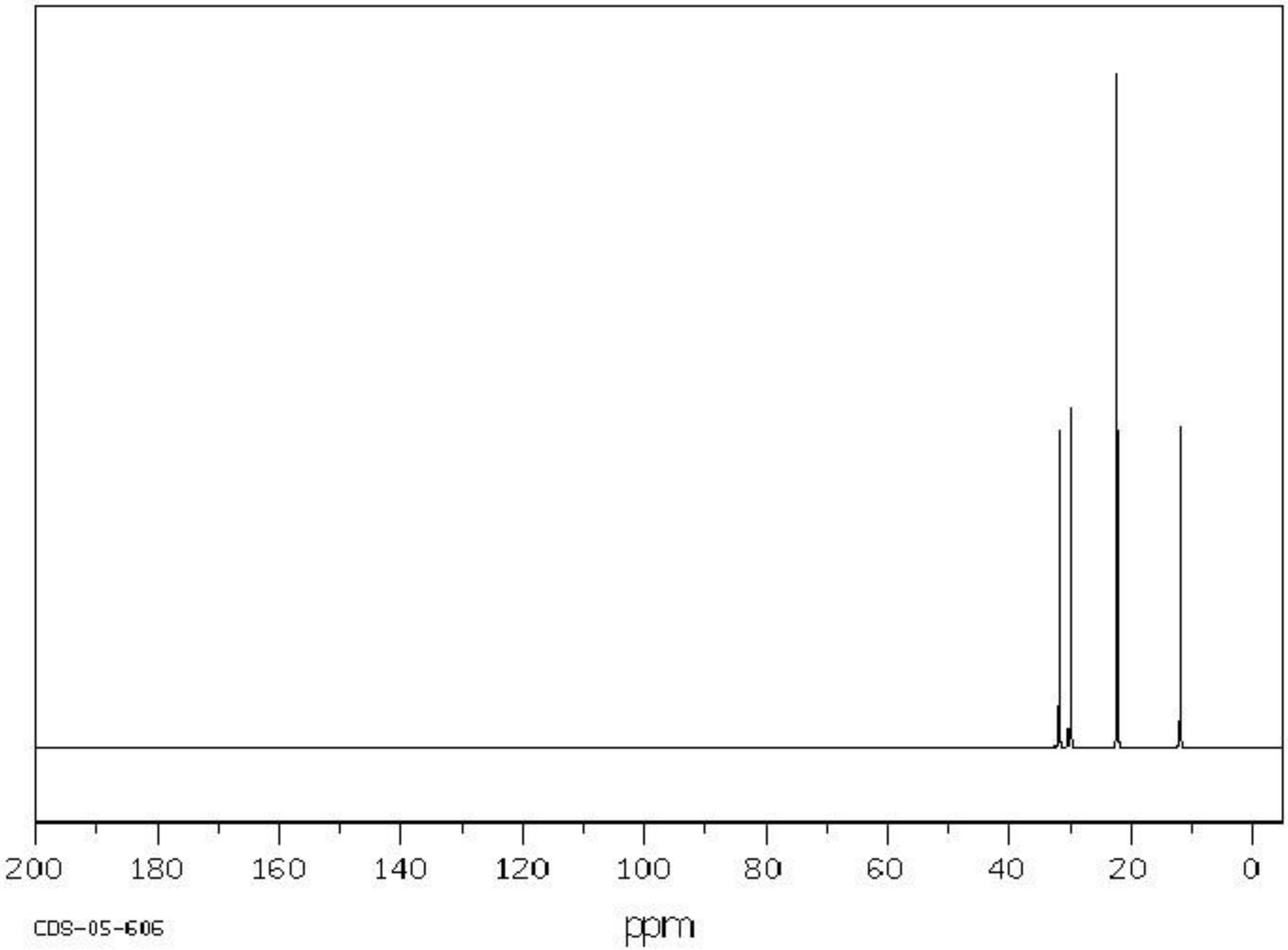
^{13}C-NMR chlorocyclopentane



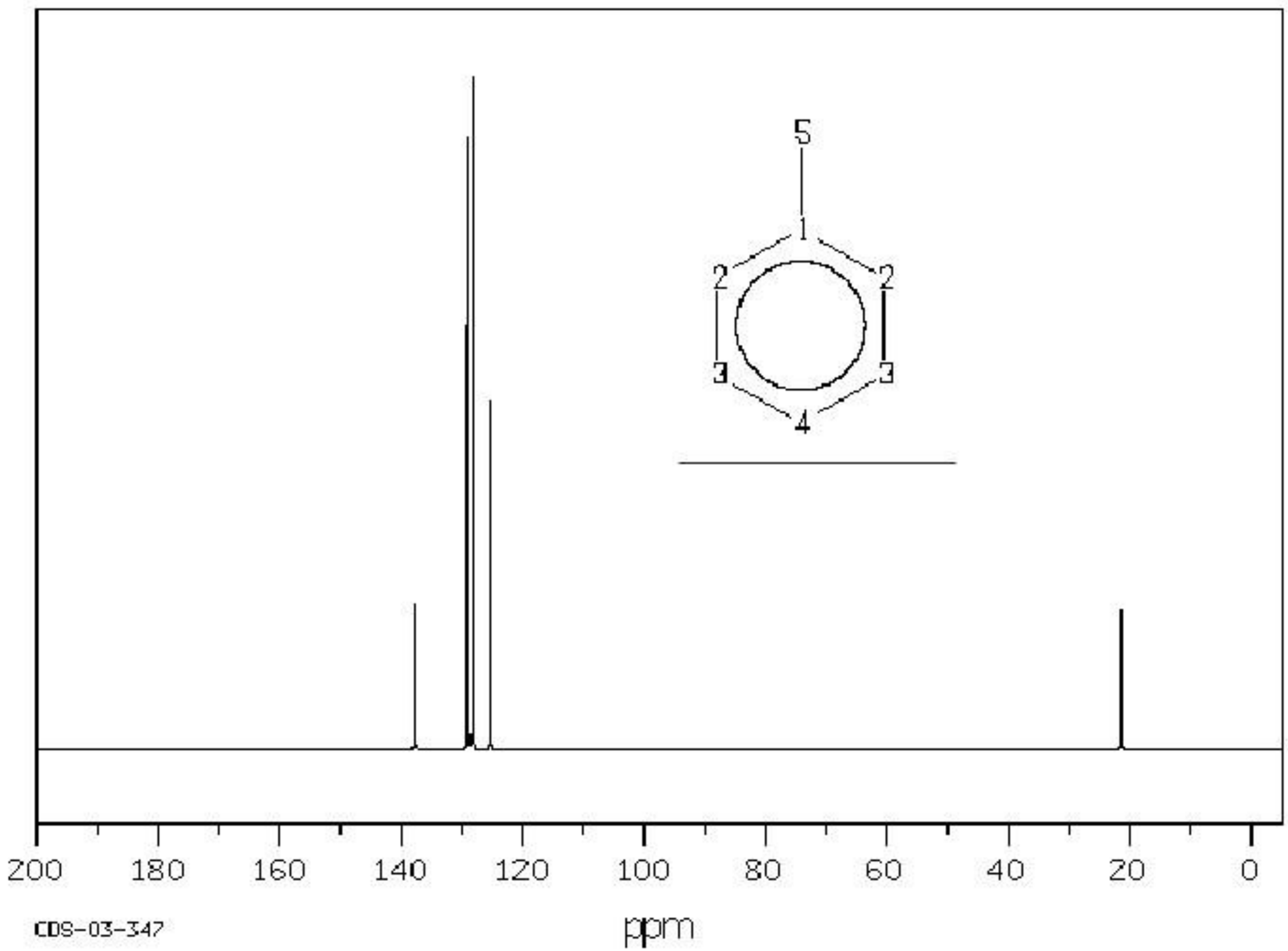
^{13}C-NMR 2,2-dimethylpropanal



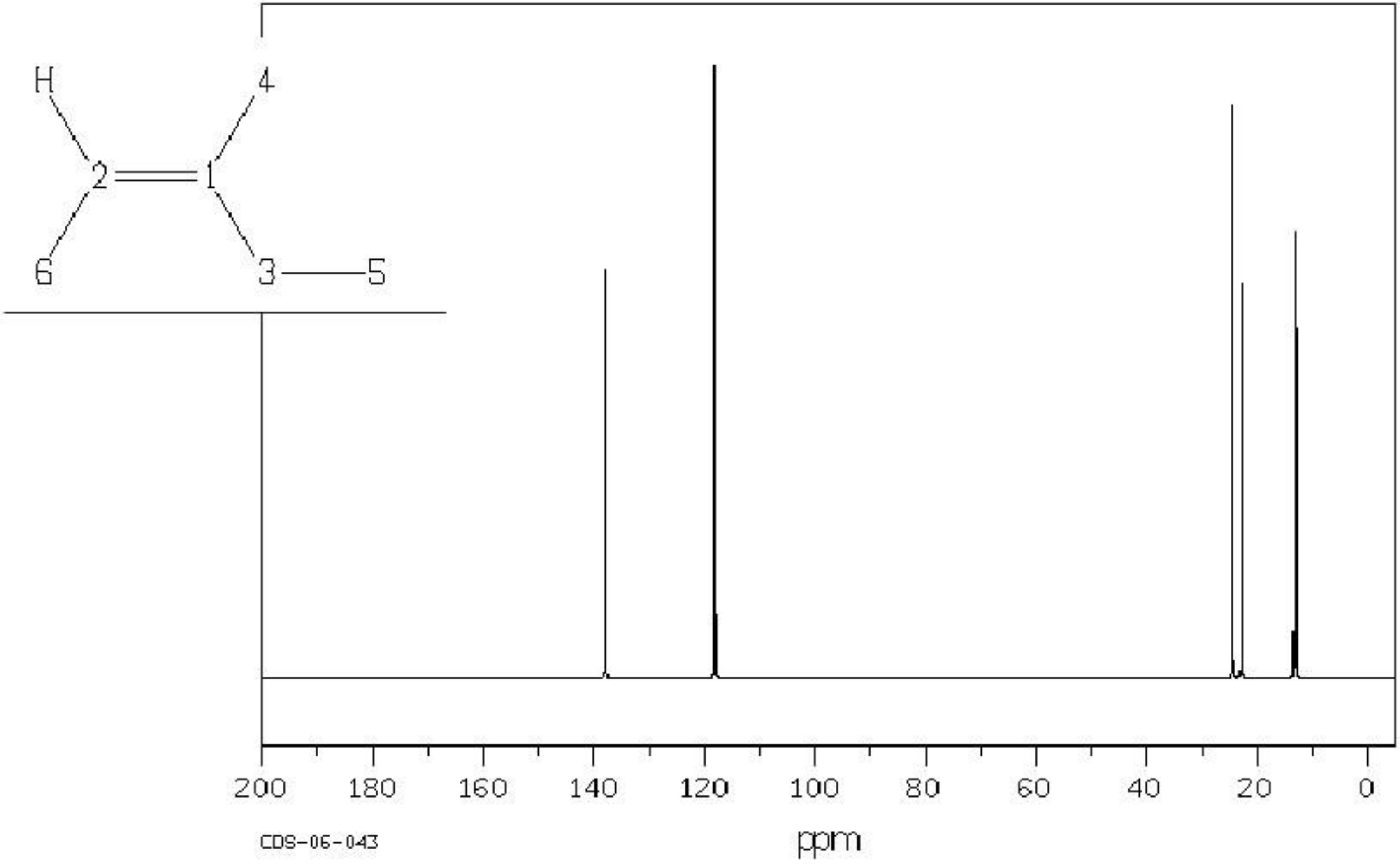
^{13}C-NMR 2-methylbutane



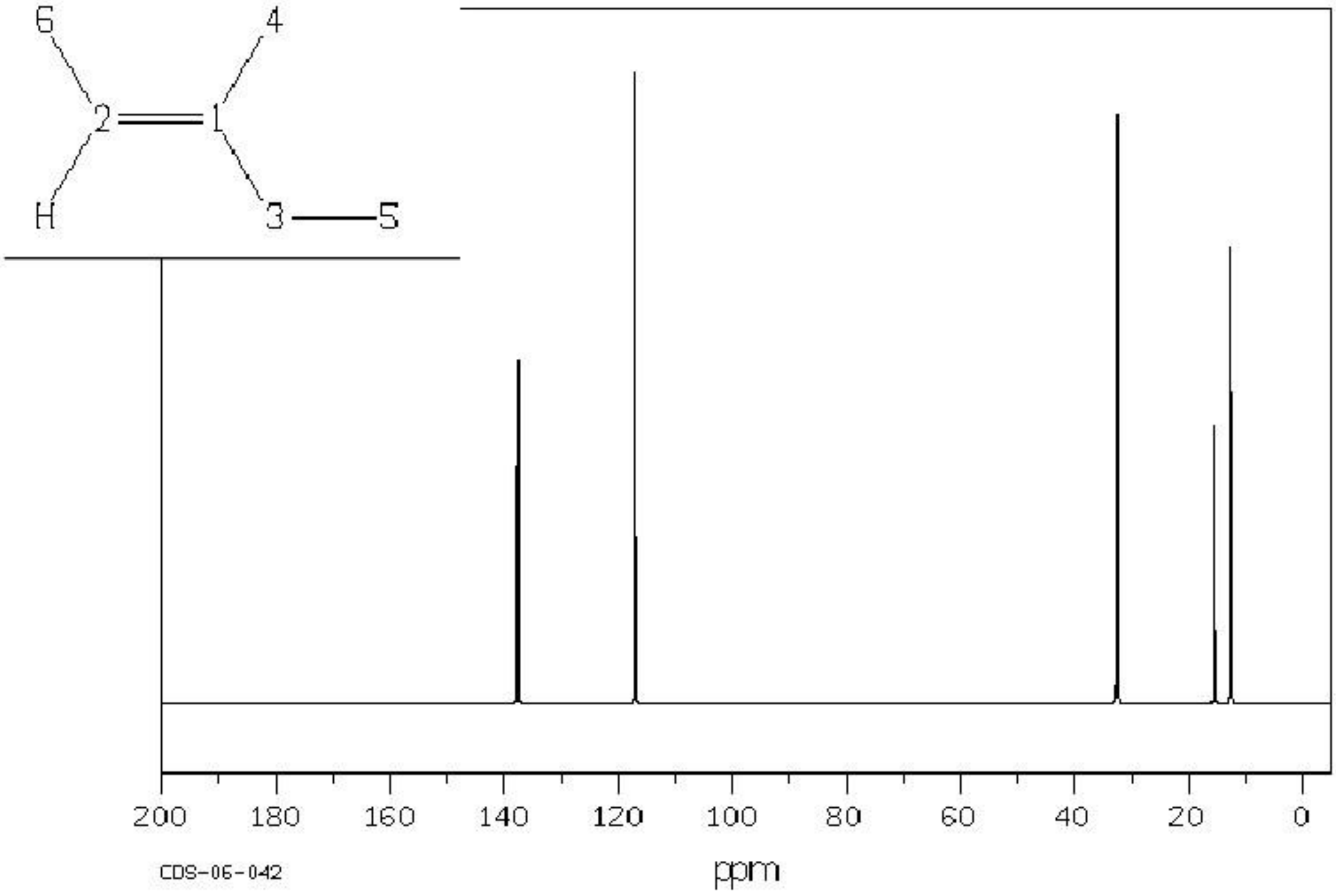
^{13}C-NMR toluene



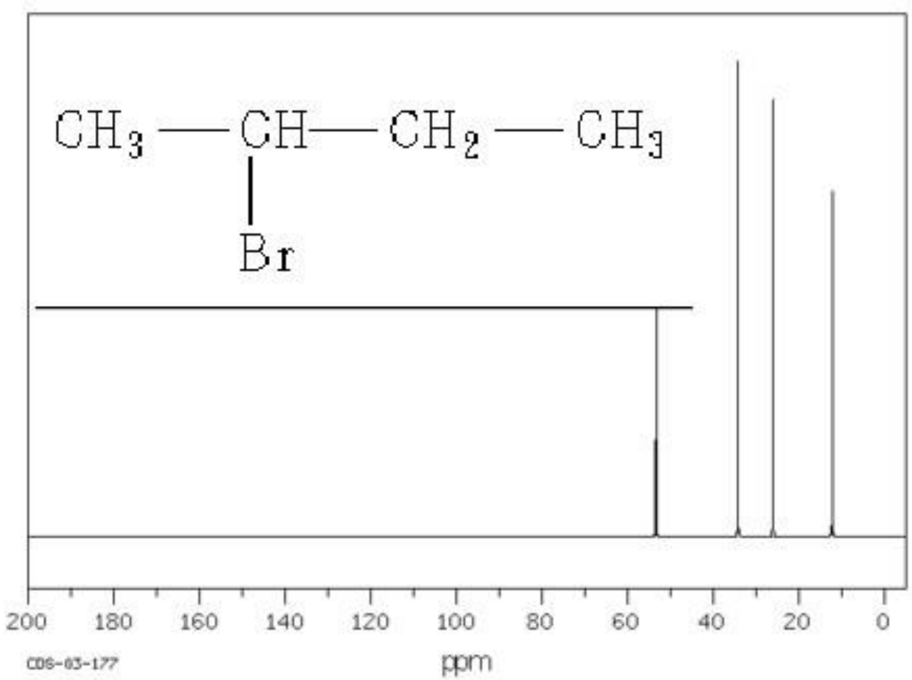
(Z)-3-methyl-2-pentene

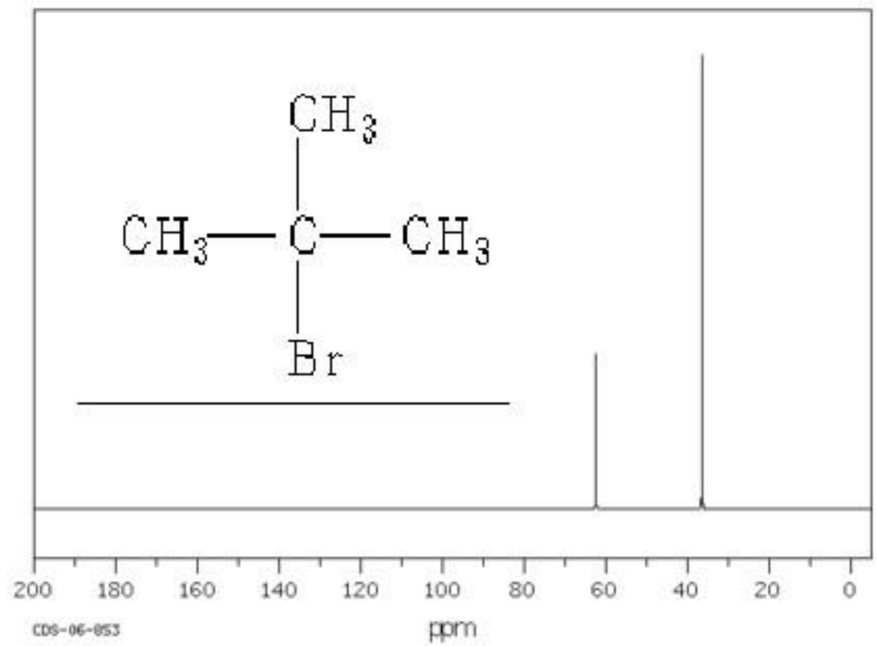


(E)-3-methyl-2-pentene



Consider C_4H_9Br

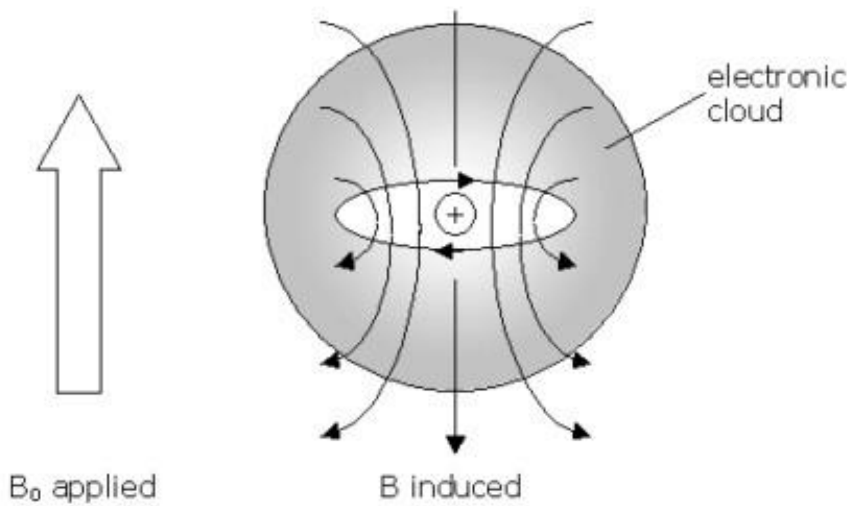




Which isomers are represented by these spectra?

b) The positions of signals correlate with the extent of **shielding and deshielding** by electrons experienced by each C nucleus

Diamagnetic Shielding



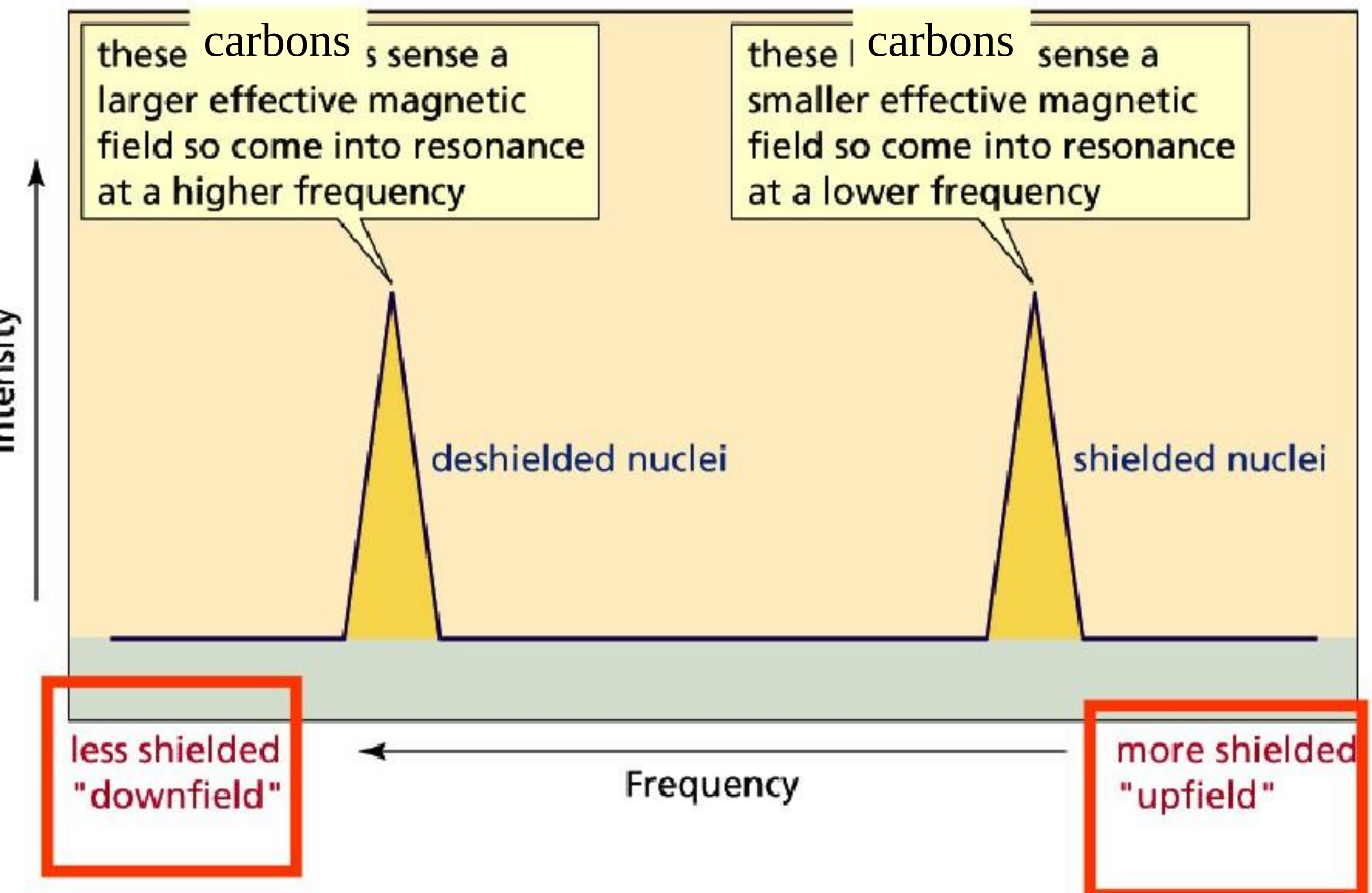
The greater the electron density around a C nucleus, the lower the effective magnetic field around that C nucleus.

Needs lower frequency for resonance

The carbon nucleus is "shielded"

Carbon nuclei adjacent to electronegative atoms experience a lower e^- cloud density

These carbons are "deshielded" and require greater frequencies for resonance.


these carbons sense a larger effective magnetic field so come into resonance at a higher frequency
these carbons sense a smaller effective magnetic field so come into resonance at a lower frequency
Intensity
deshielded nuclei
shielded nuclei
less shielded
"downfield"
Frequency
more shielded
"upfield"

Chemical Shift

The frequency at which a nucleus will resonate is dependent on the magnetic field strength.

Because this can vary from instrument to instrument, frequency is expressed relative to magnetic field strength, "chemical shift"

$$\textbf{Chemical Shift} = \frac{\textbf{frequency of resonance (Hz)}}{\textbf{frequency of instrument(MHz)}}$$

units = parts per million = ppm

13C Chemical Shift Correlation Chart

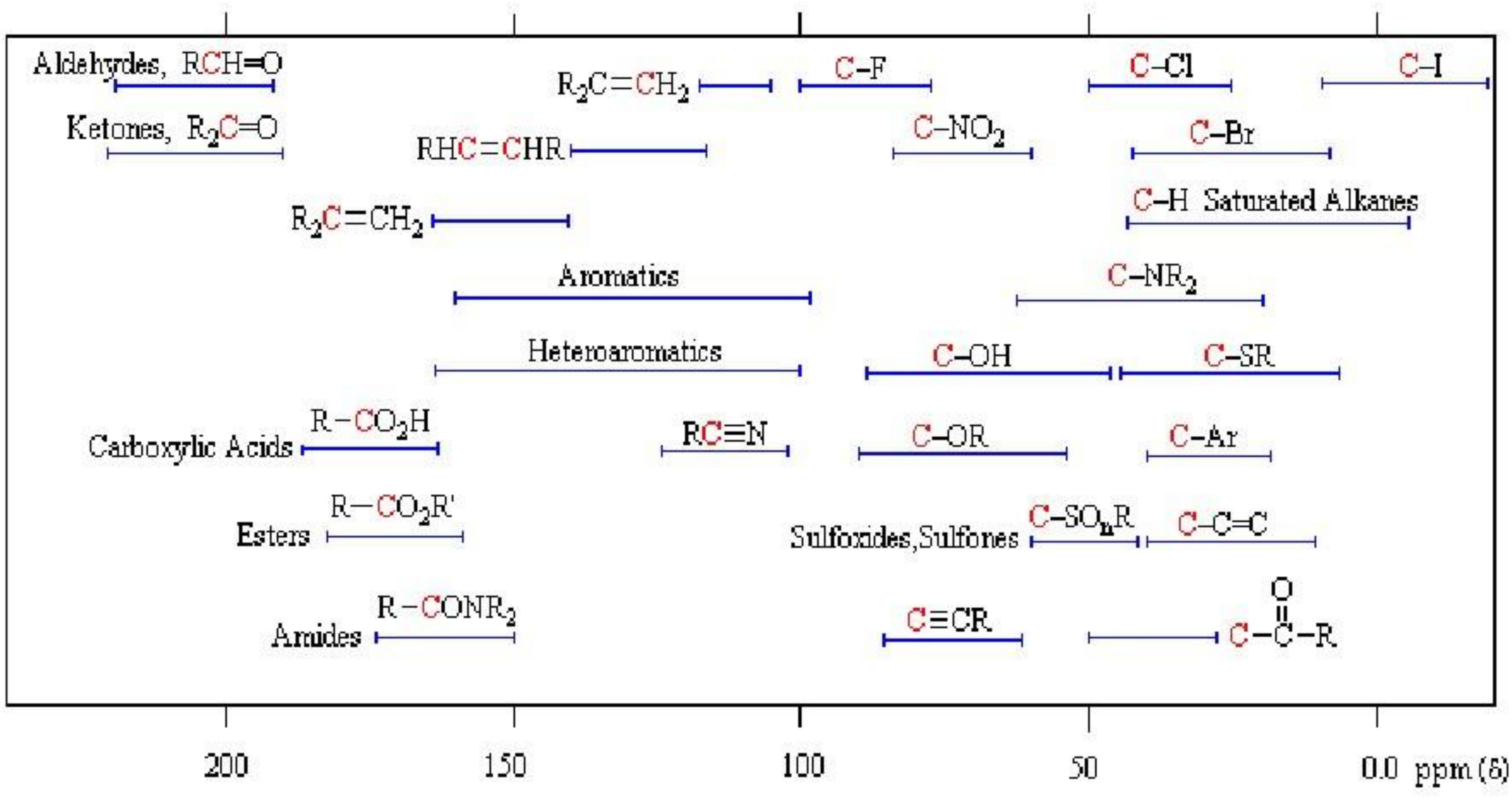
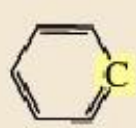
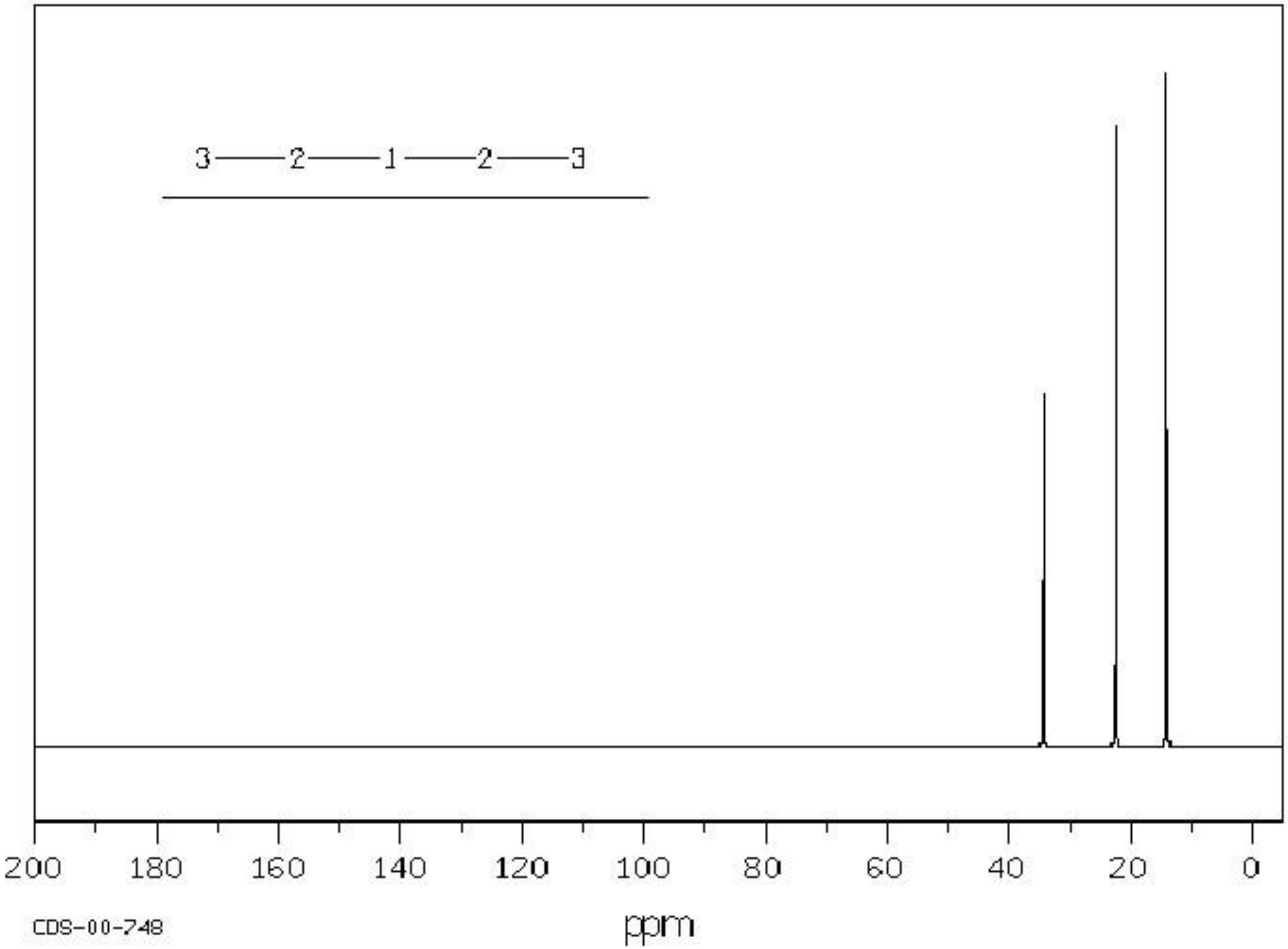


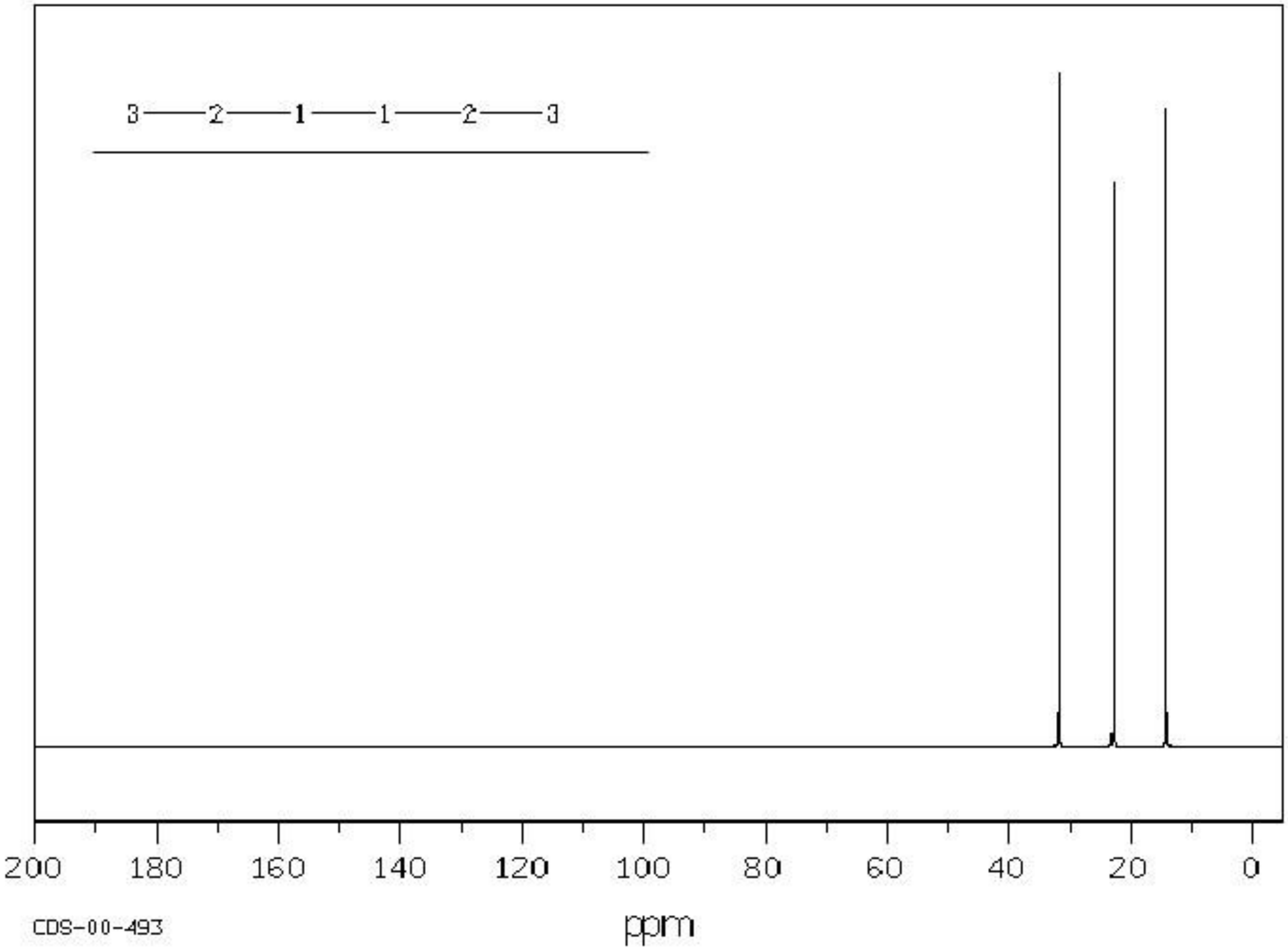
TABLE 13.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
R_2CH-R	20–60	$R-C(=O)-N<$	165–175
R_3C-R	30–40	$R-C(=O)-OR$	165–175
$\equiv C$	65–85	$R-C(=O)-OH$	175–185
$=C$	100–150	$R-C(=O)-H$	190–200
	110–170	$R-C(=O)-R$	205–220

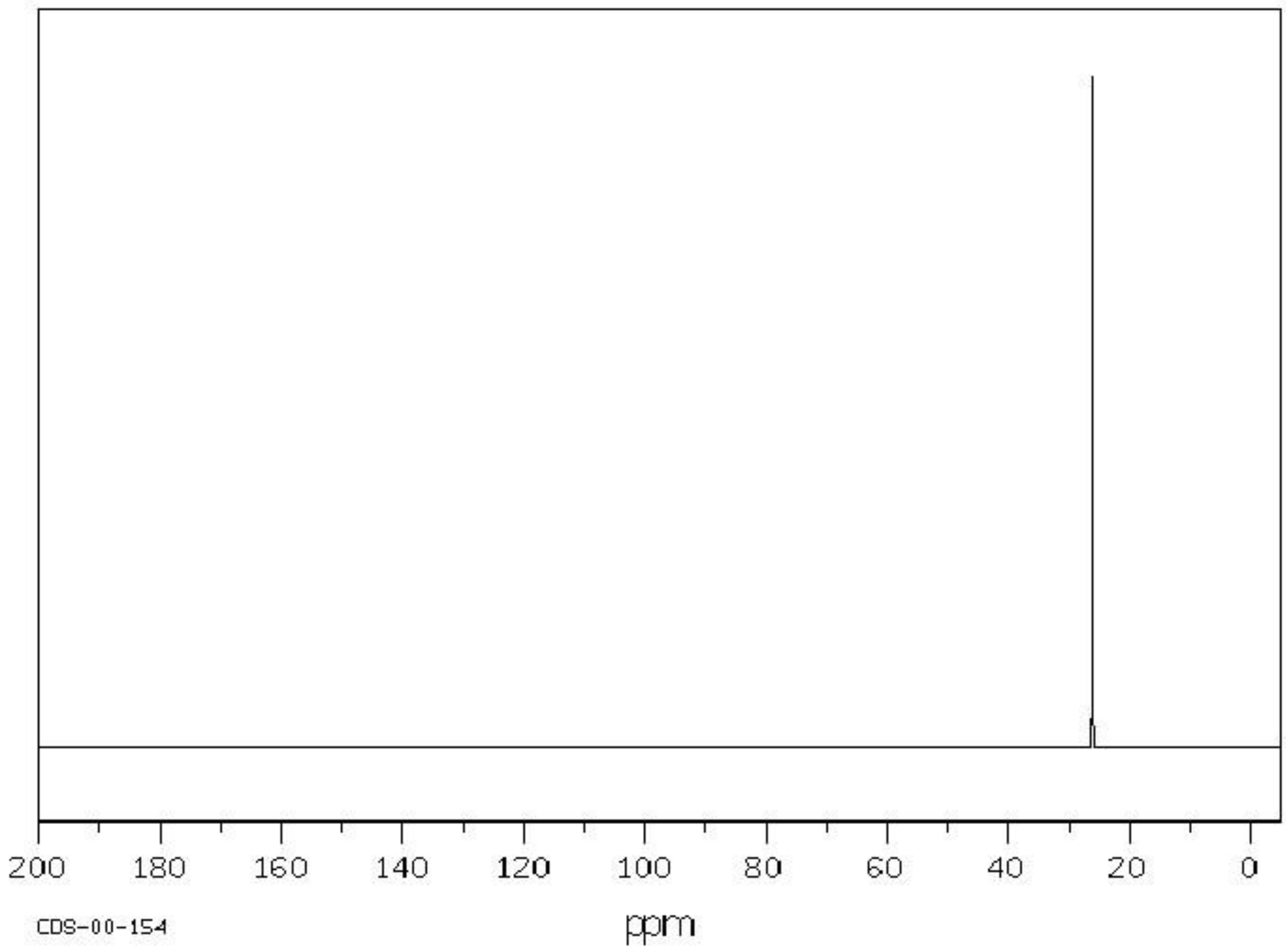
pentane



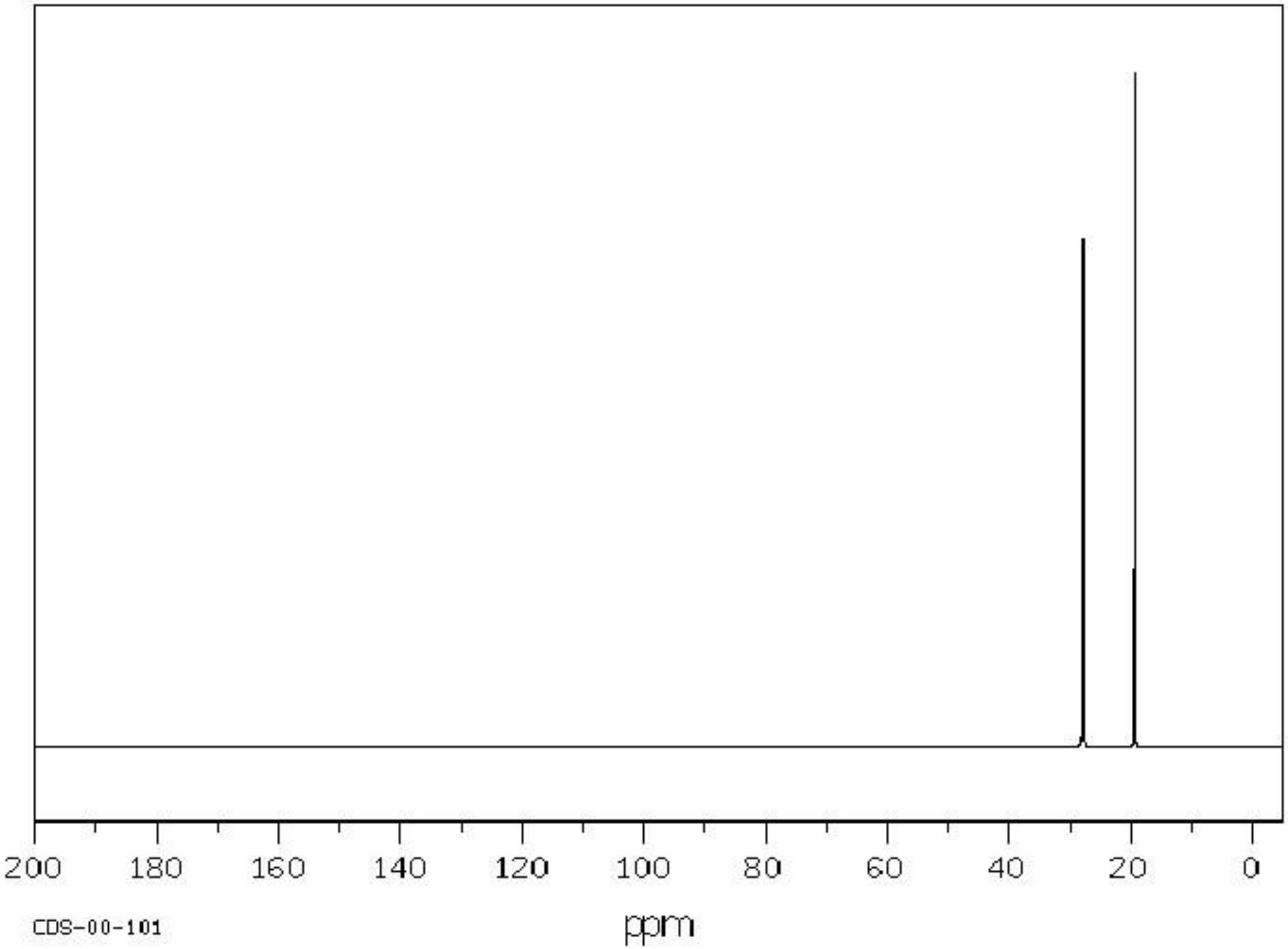
hexane



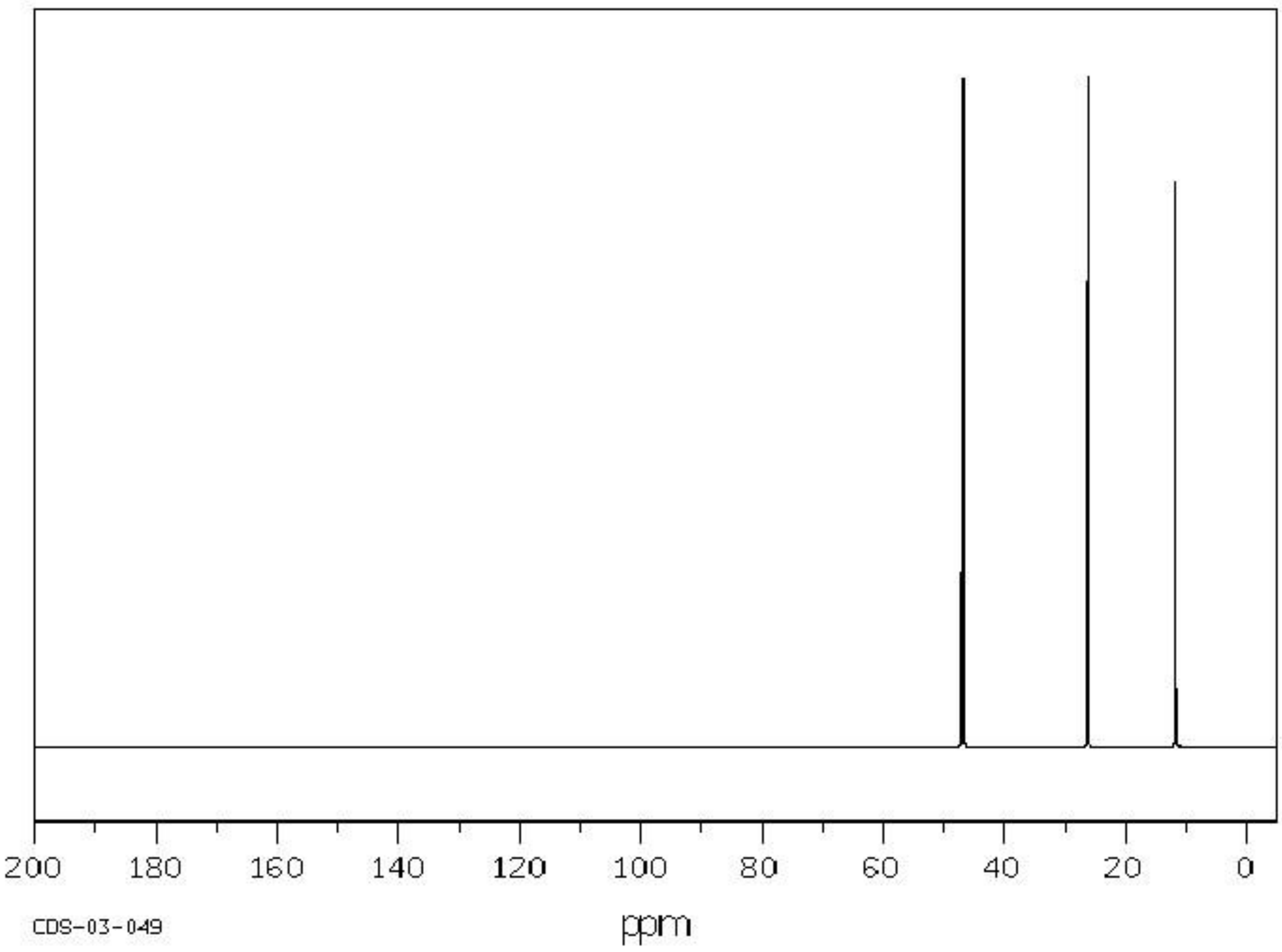
cyclopentane



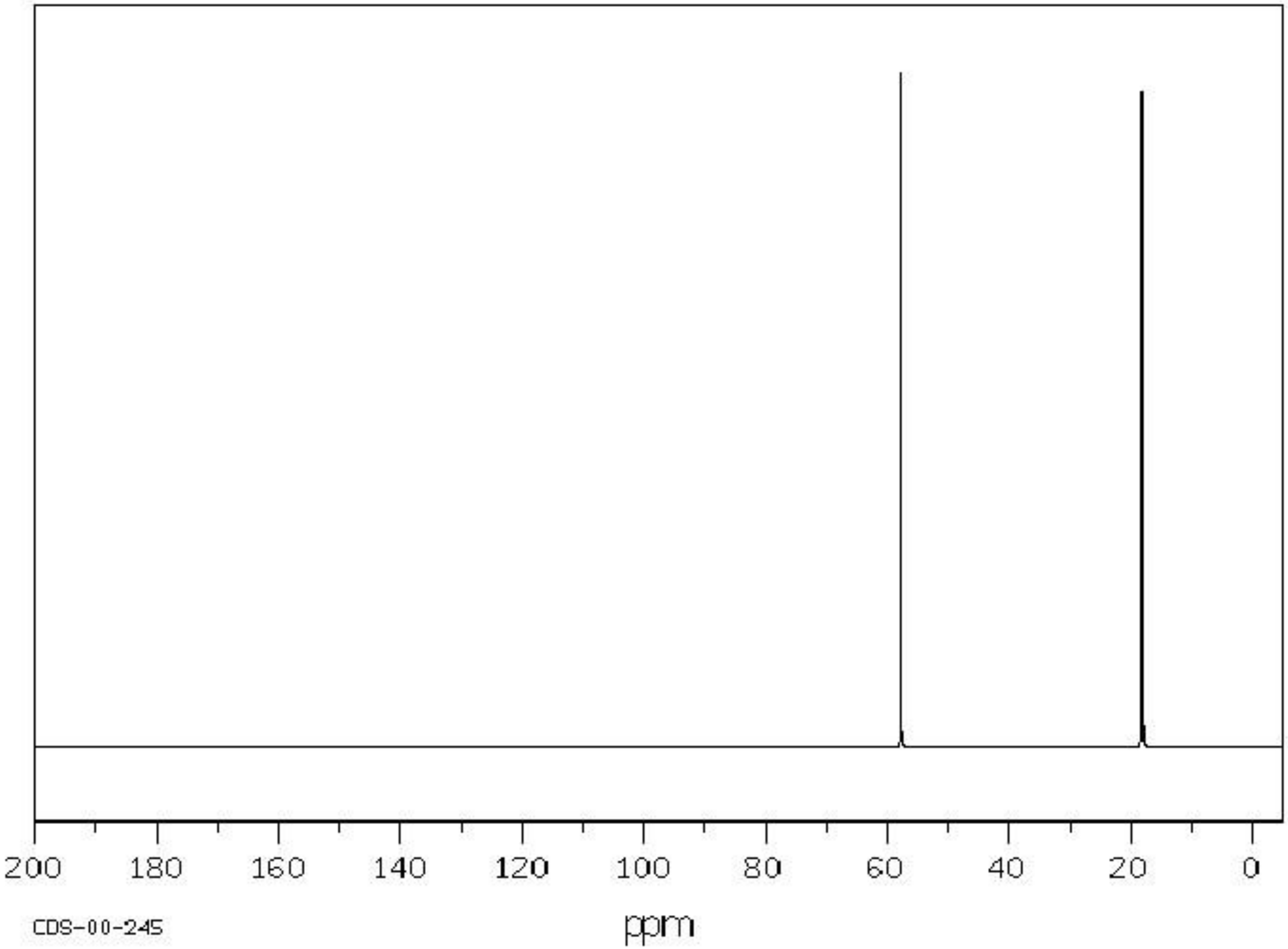
ethyl bromide



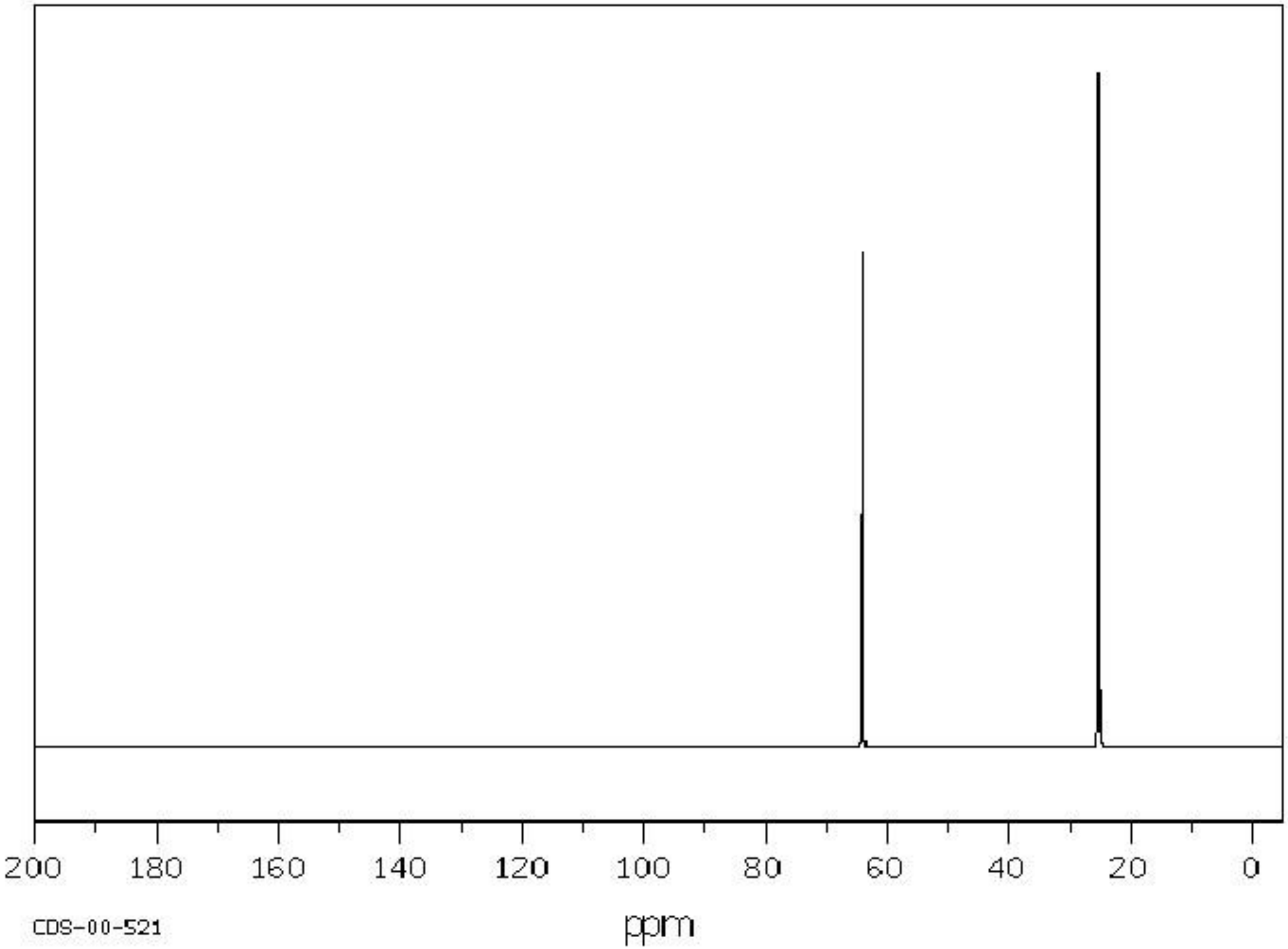
n-propyl chloride

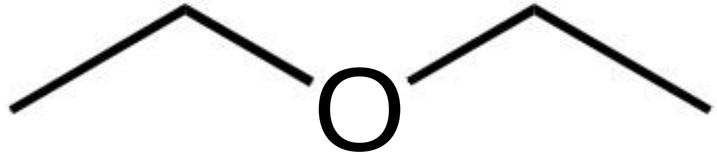


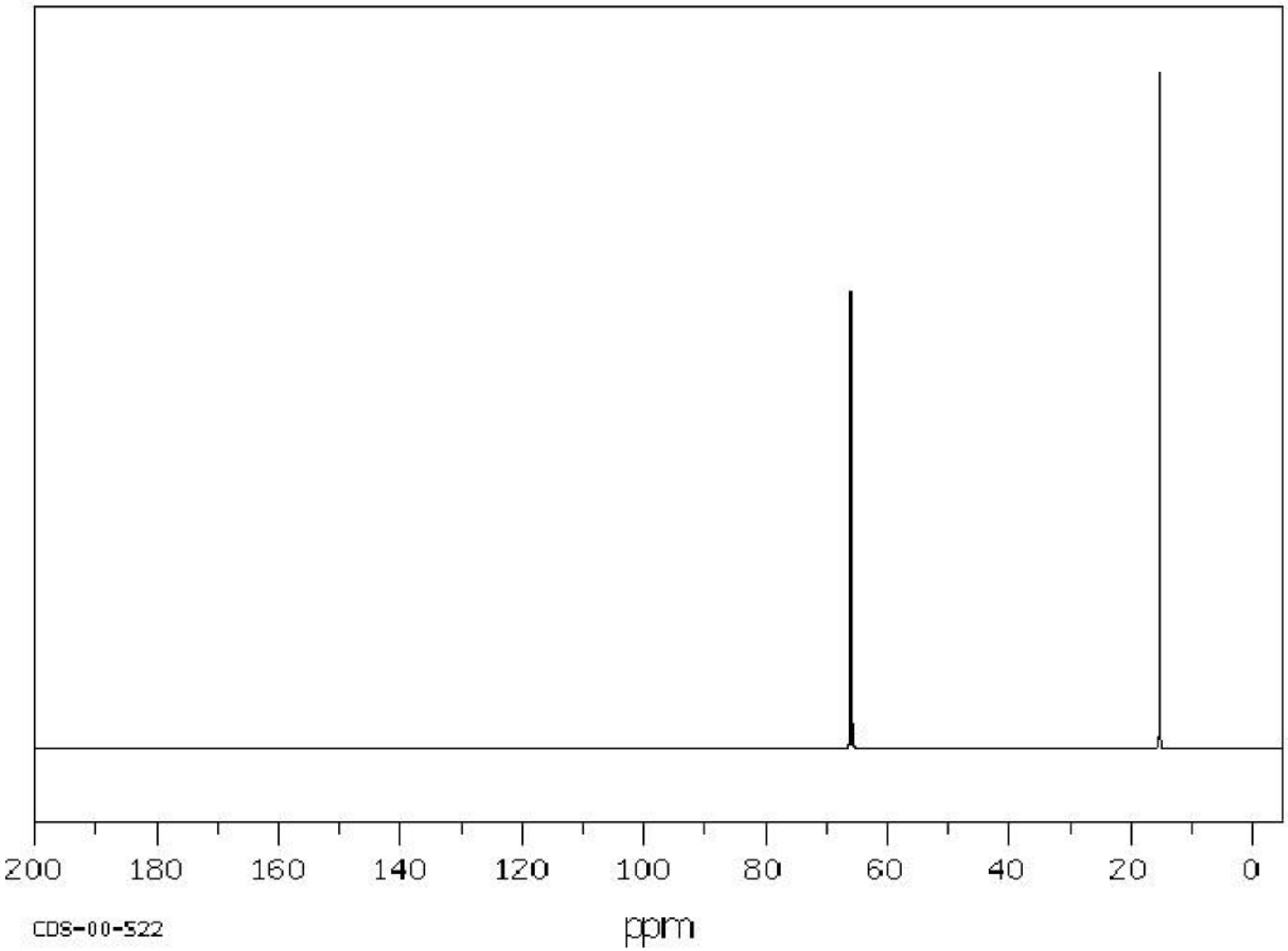
ethanol



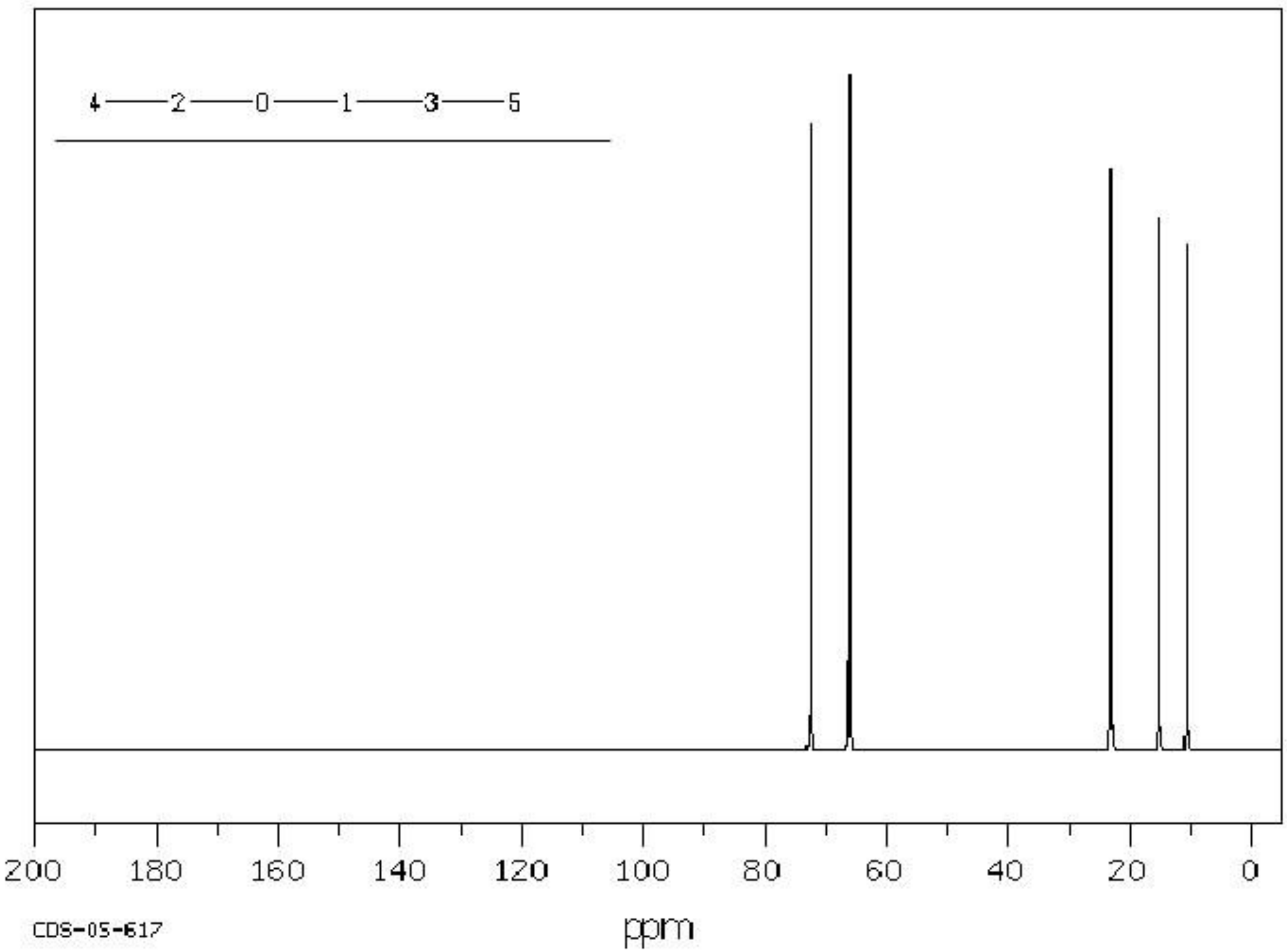
2-propanol



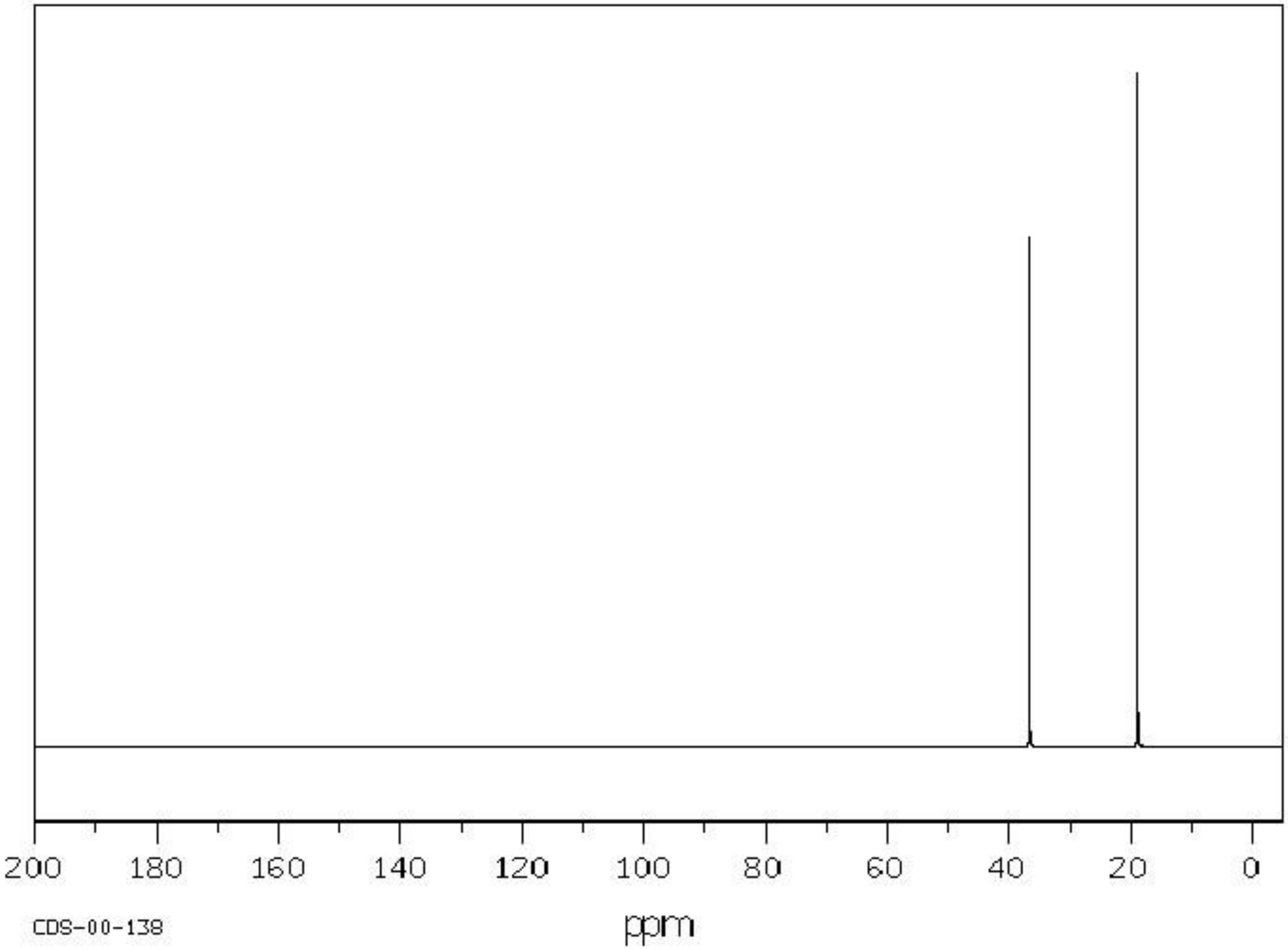



200 180 160 140 120 100 80 60 40 20 0
ppm
CDS-00-522

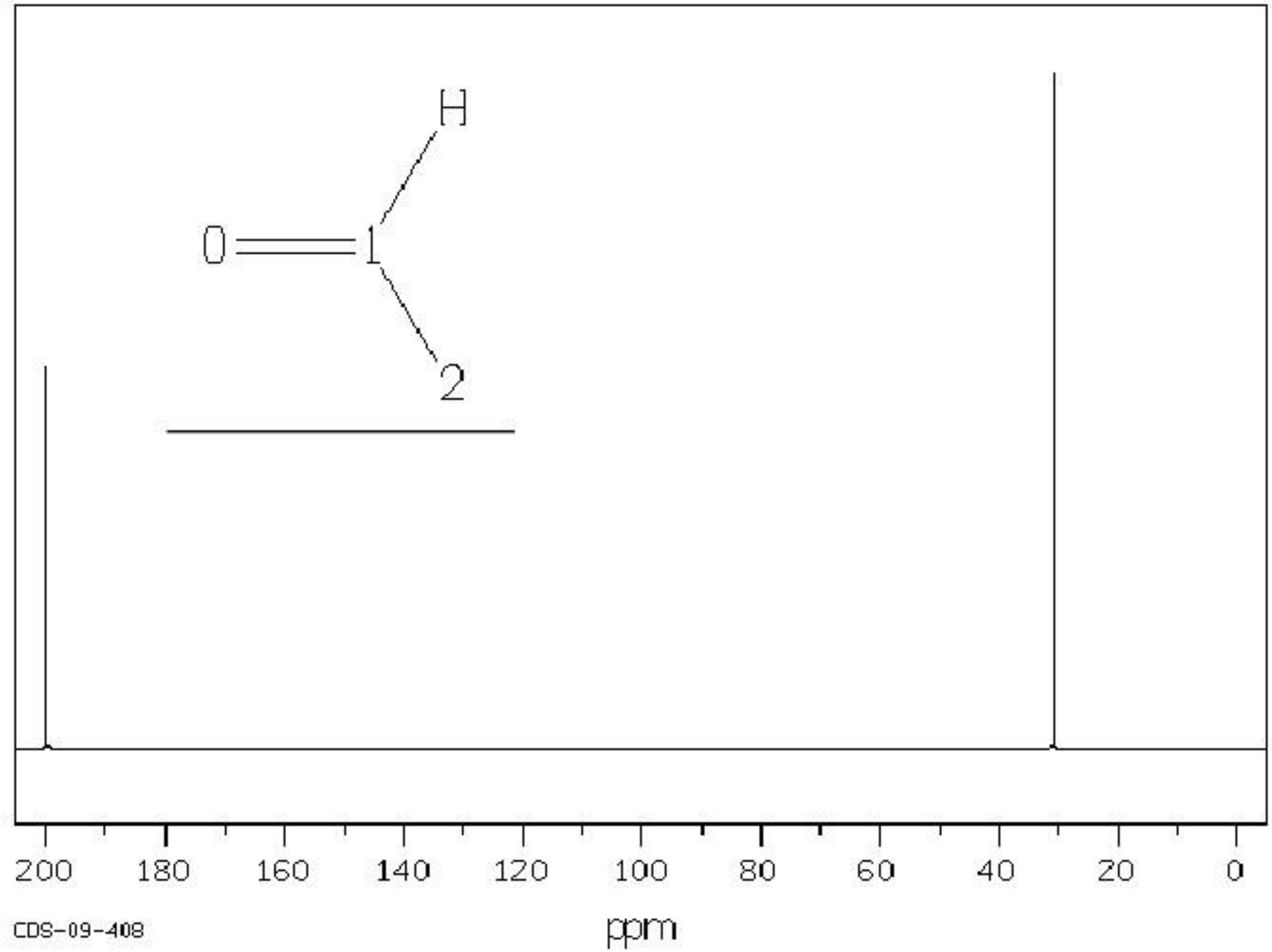
ethyl propyl ether



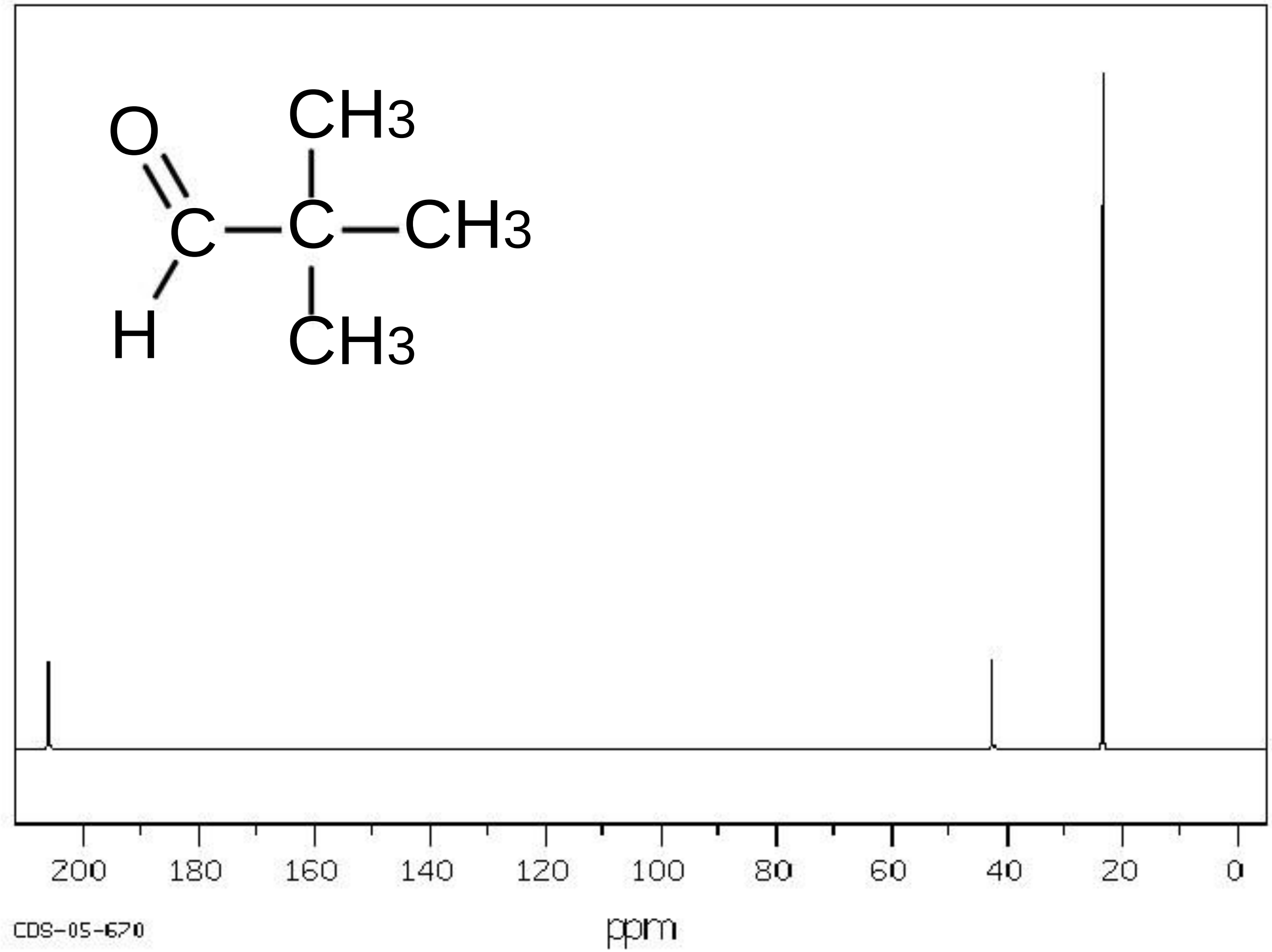
Ethyl amine



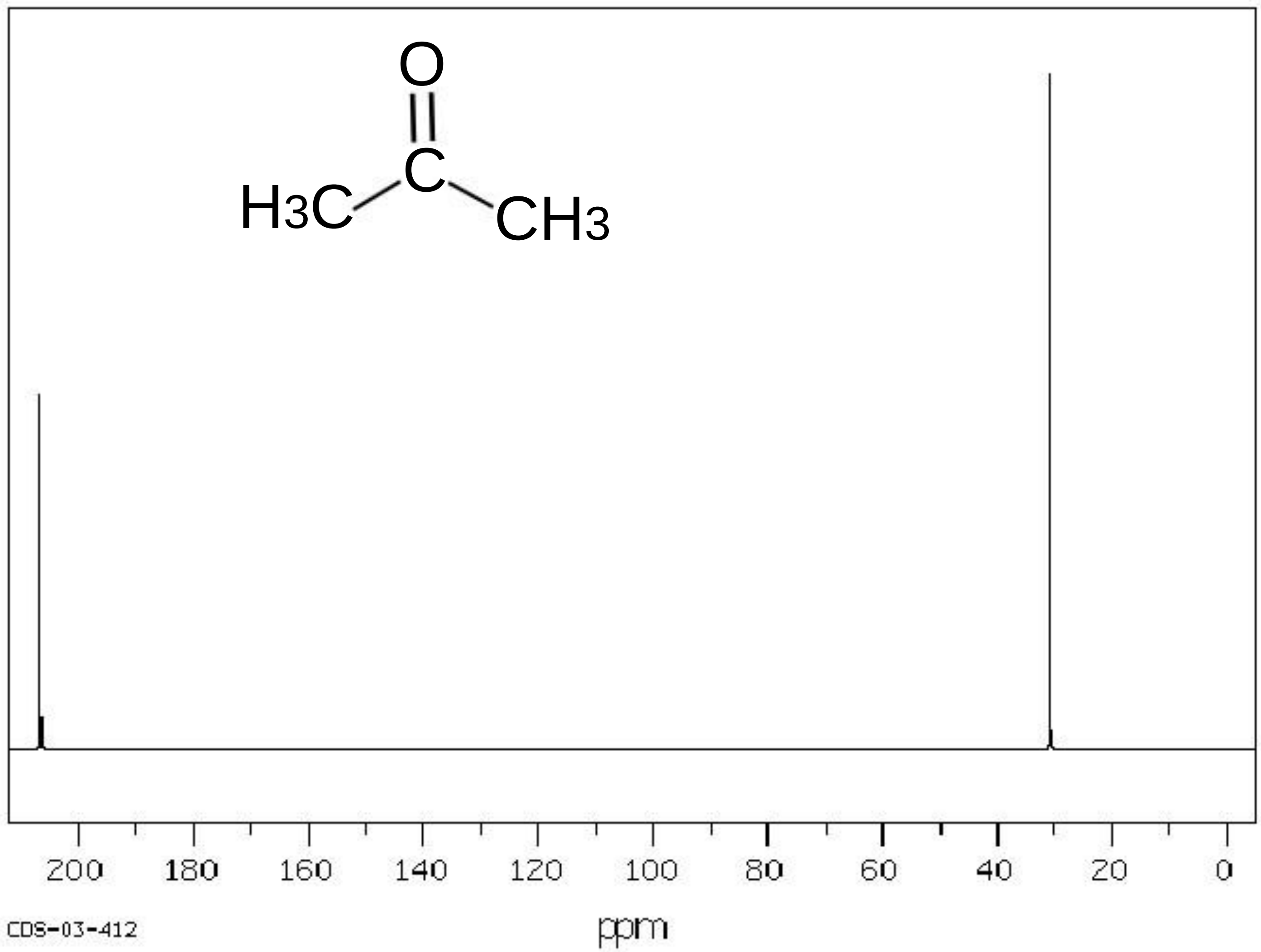
Acetaldehyde



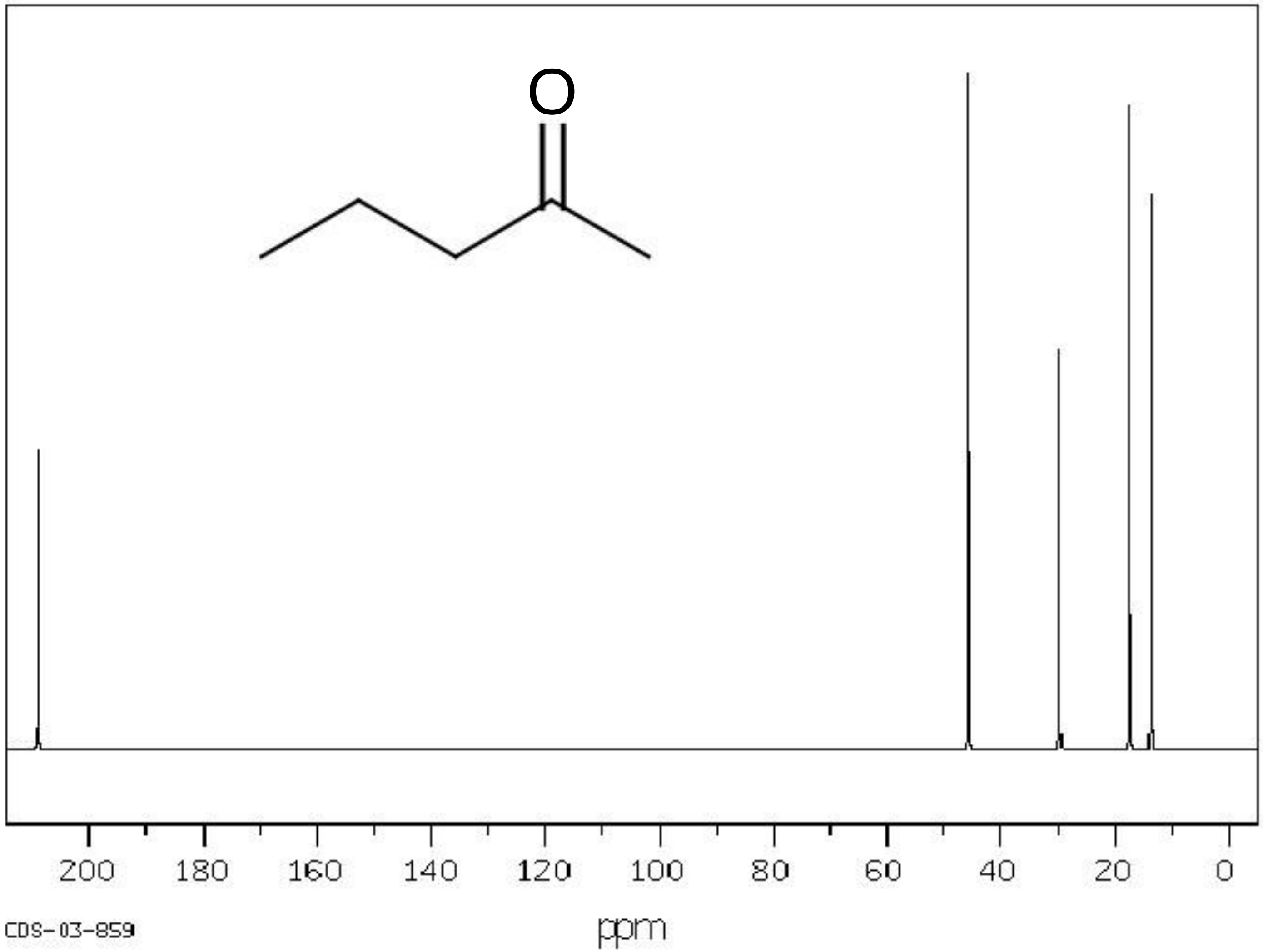
2,2-dimethylpropanal



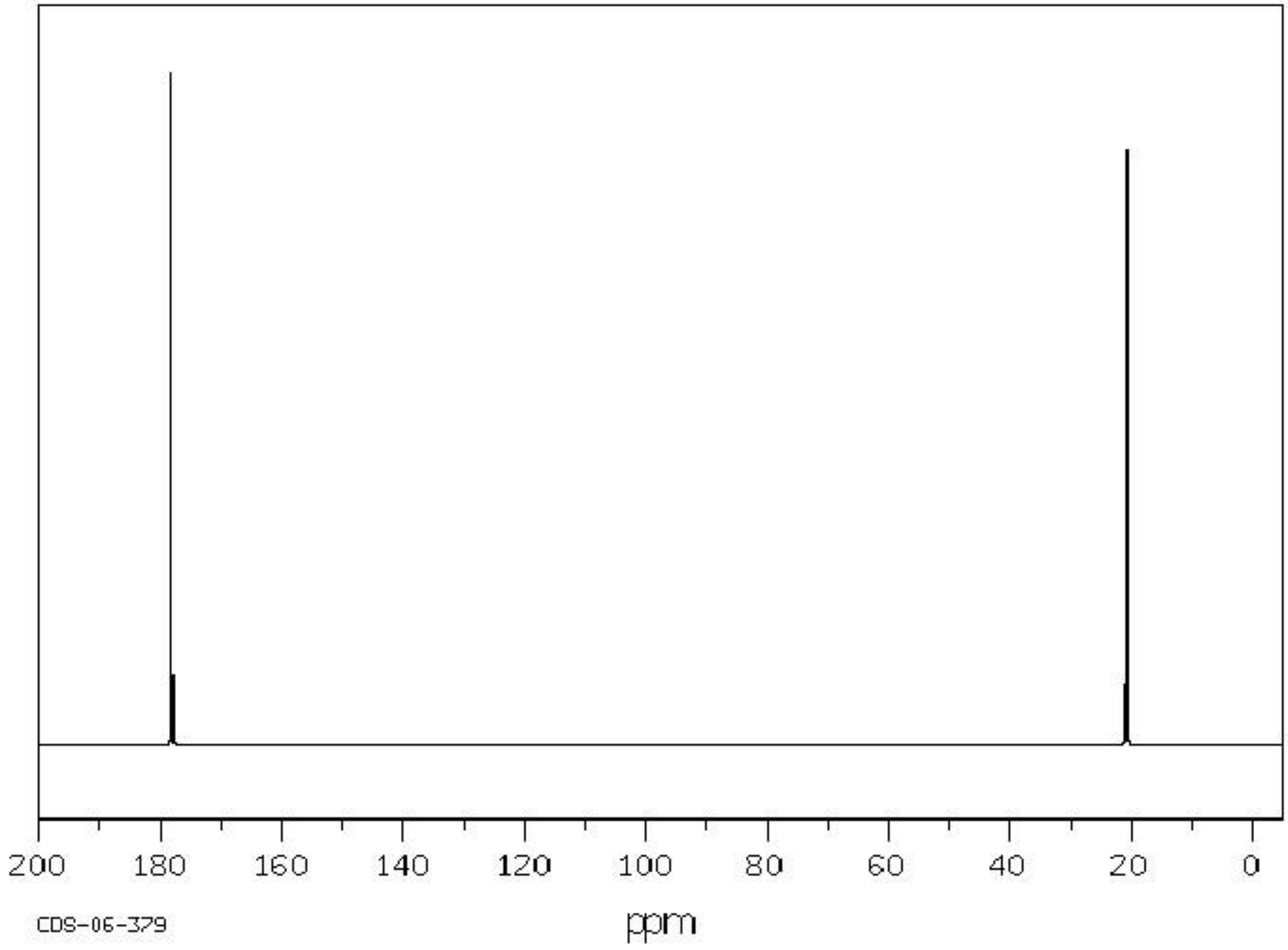
Acetone



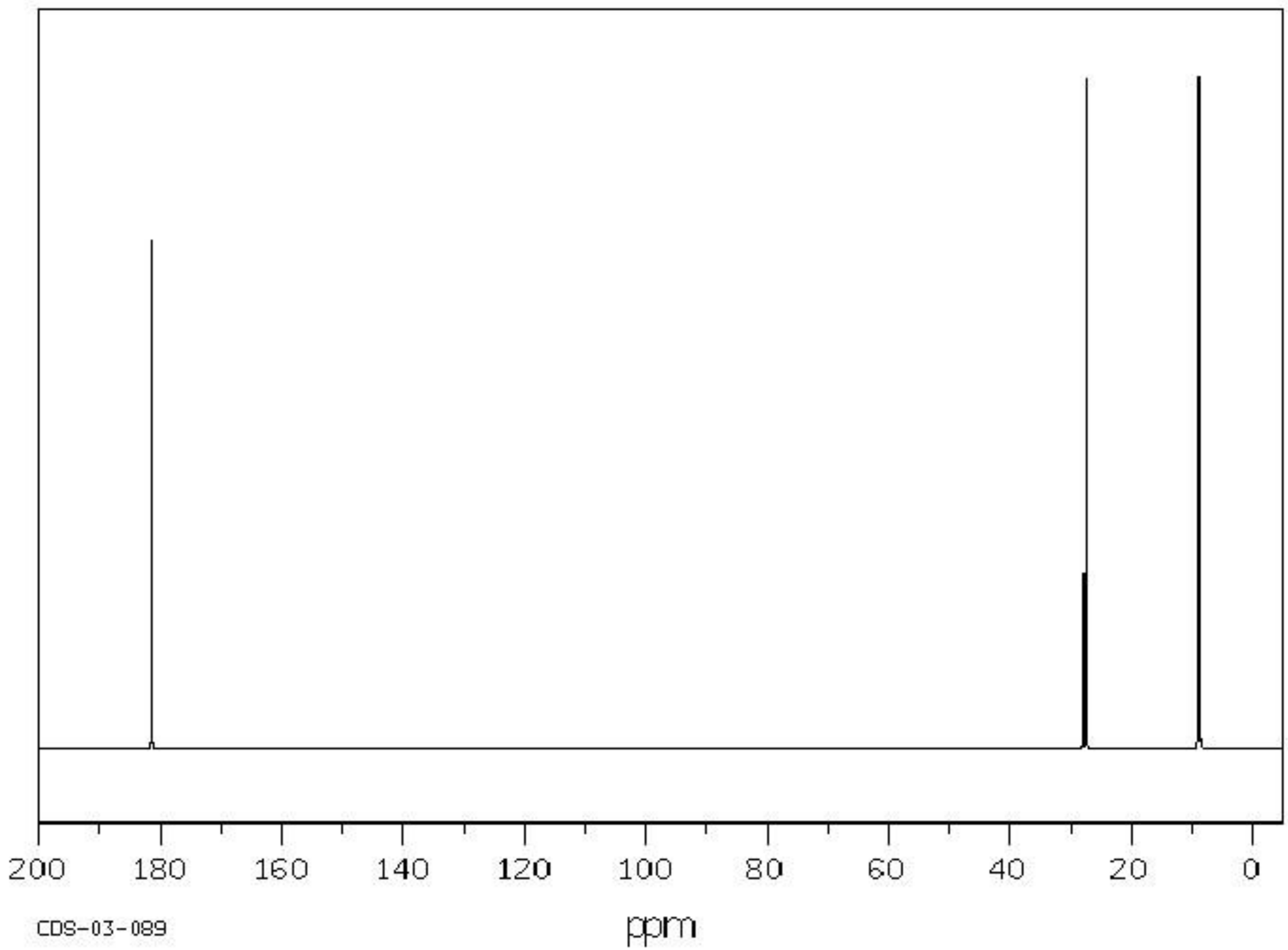
2-pentanone



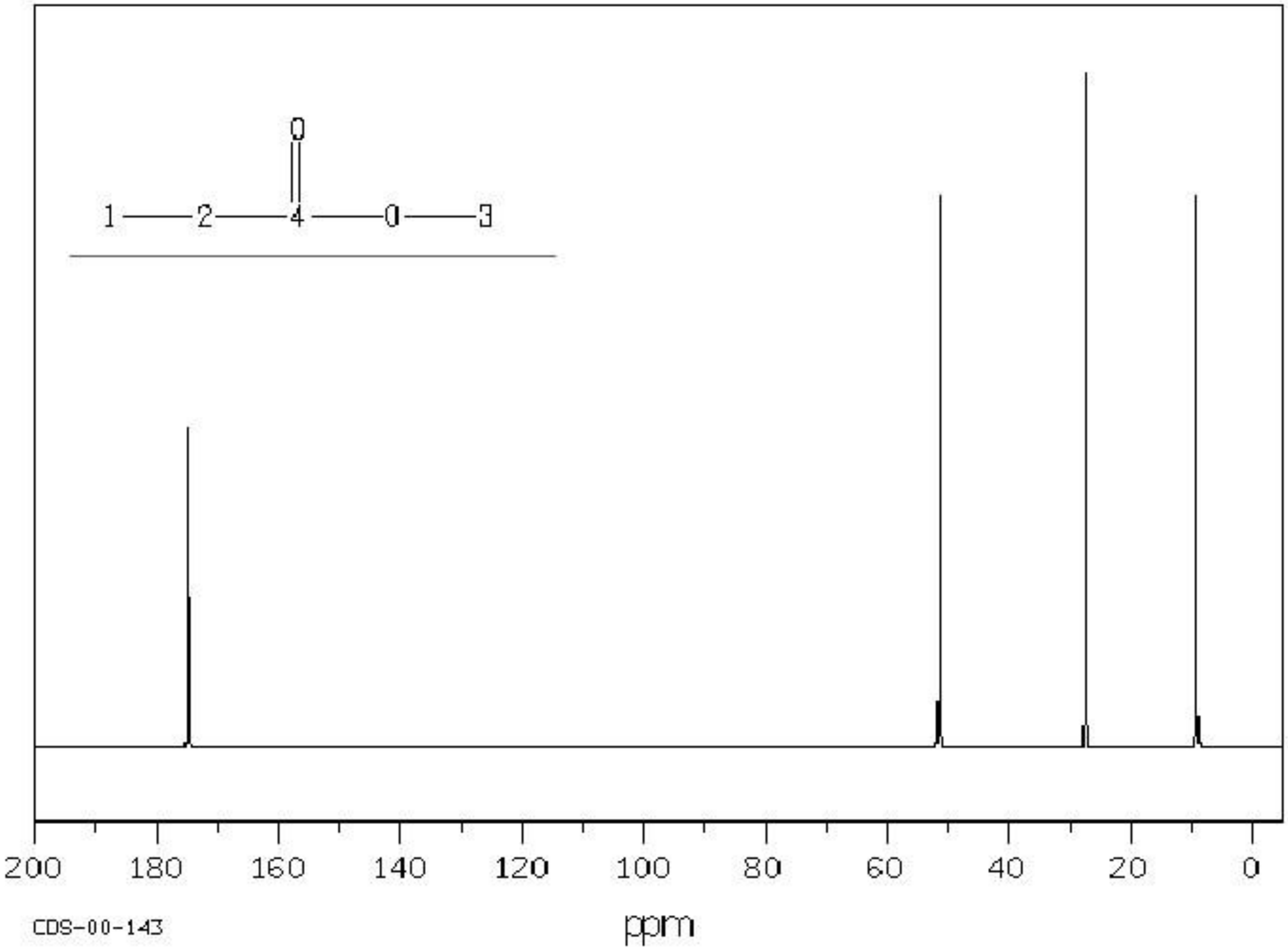
acetic acid



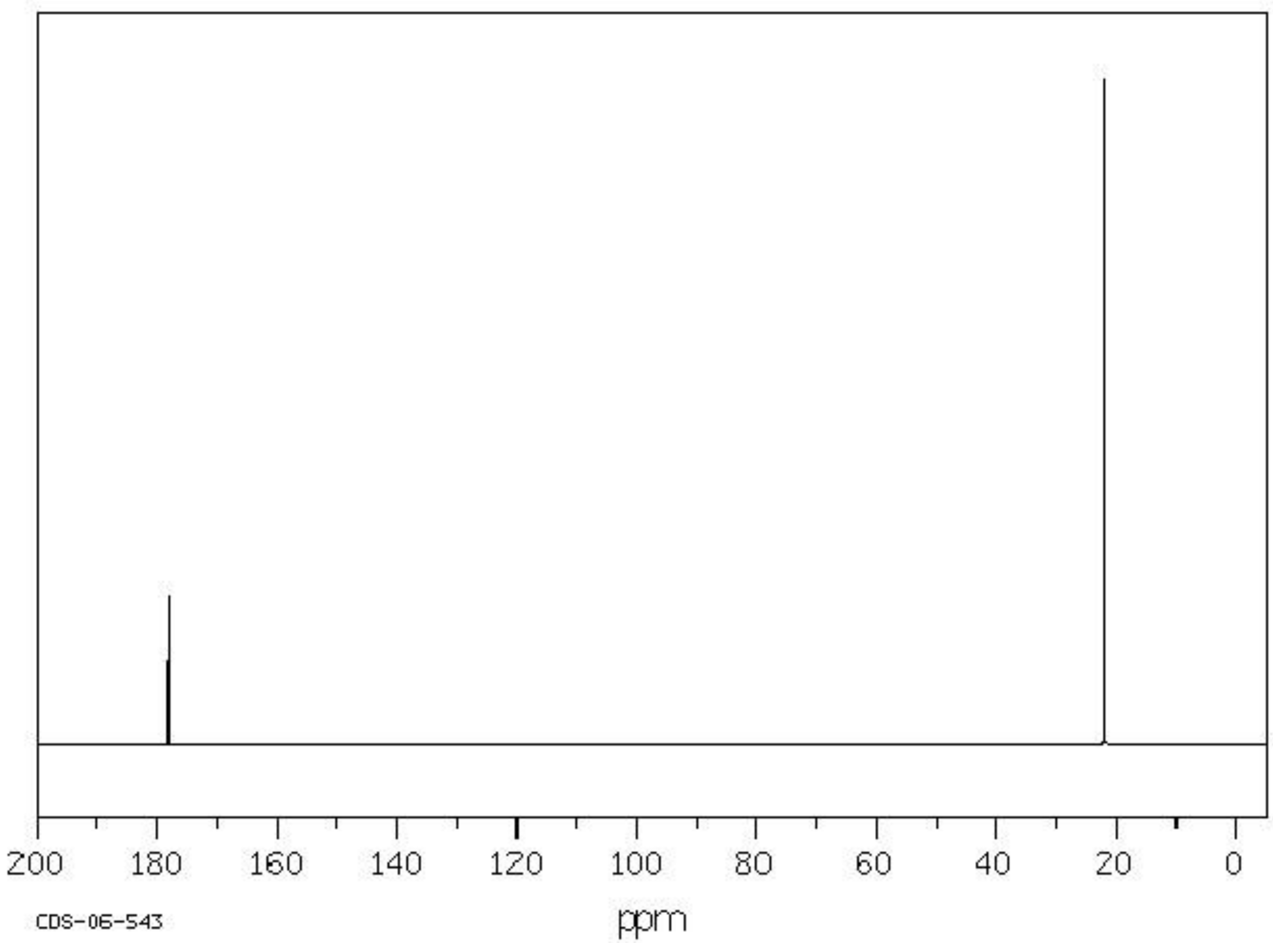
Propionic acid



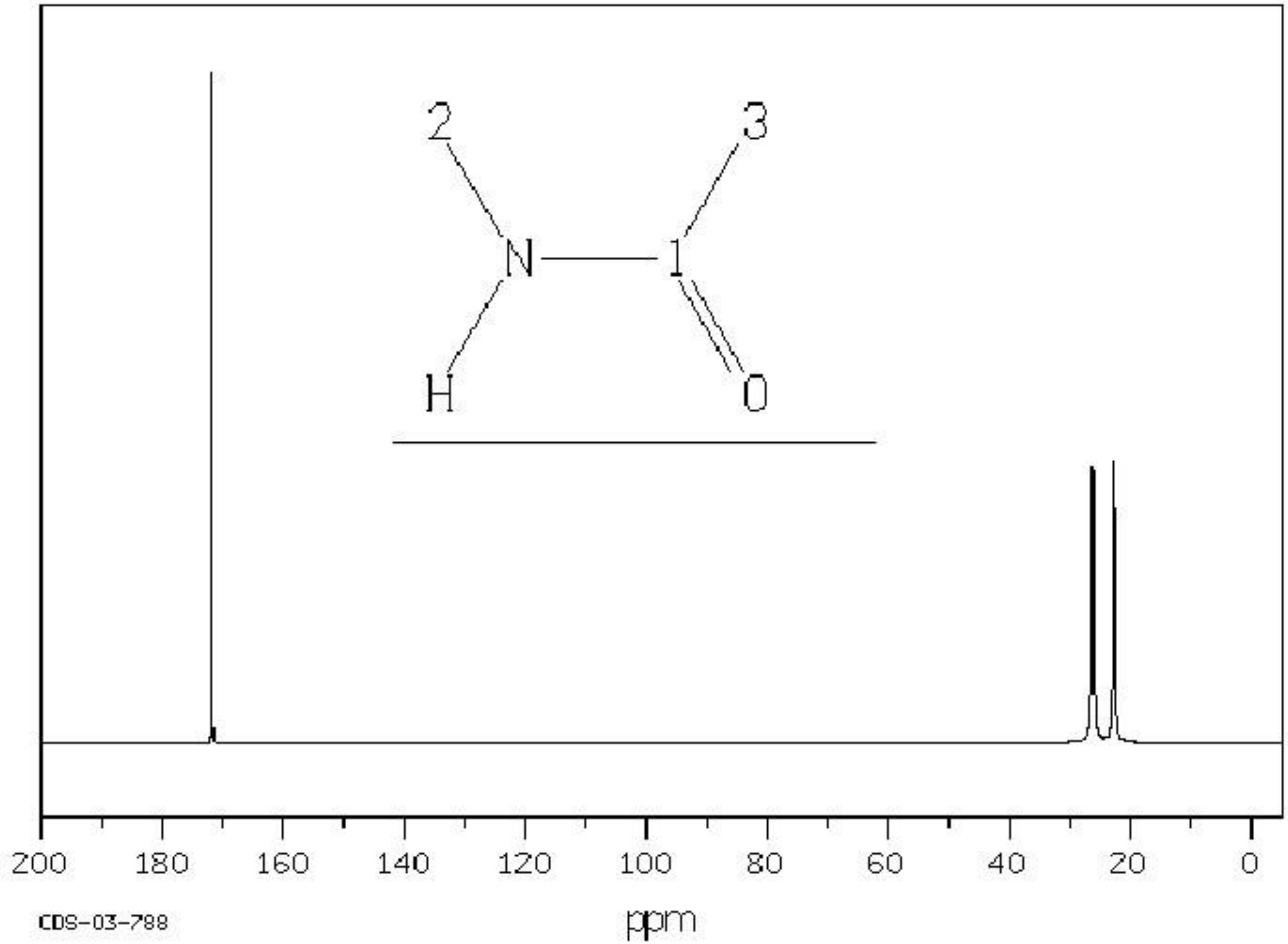
methyl propionate



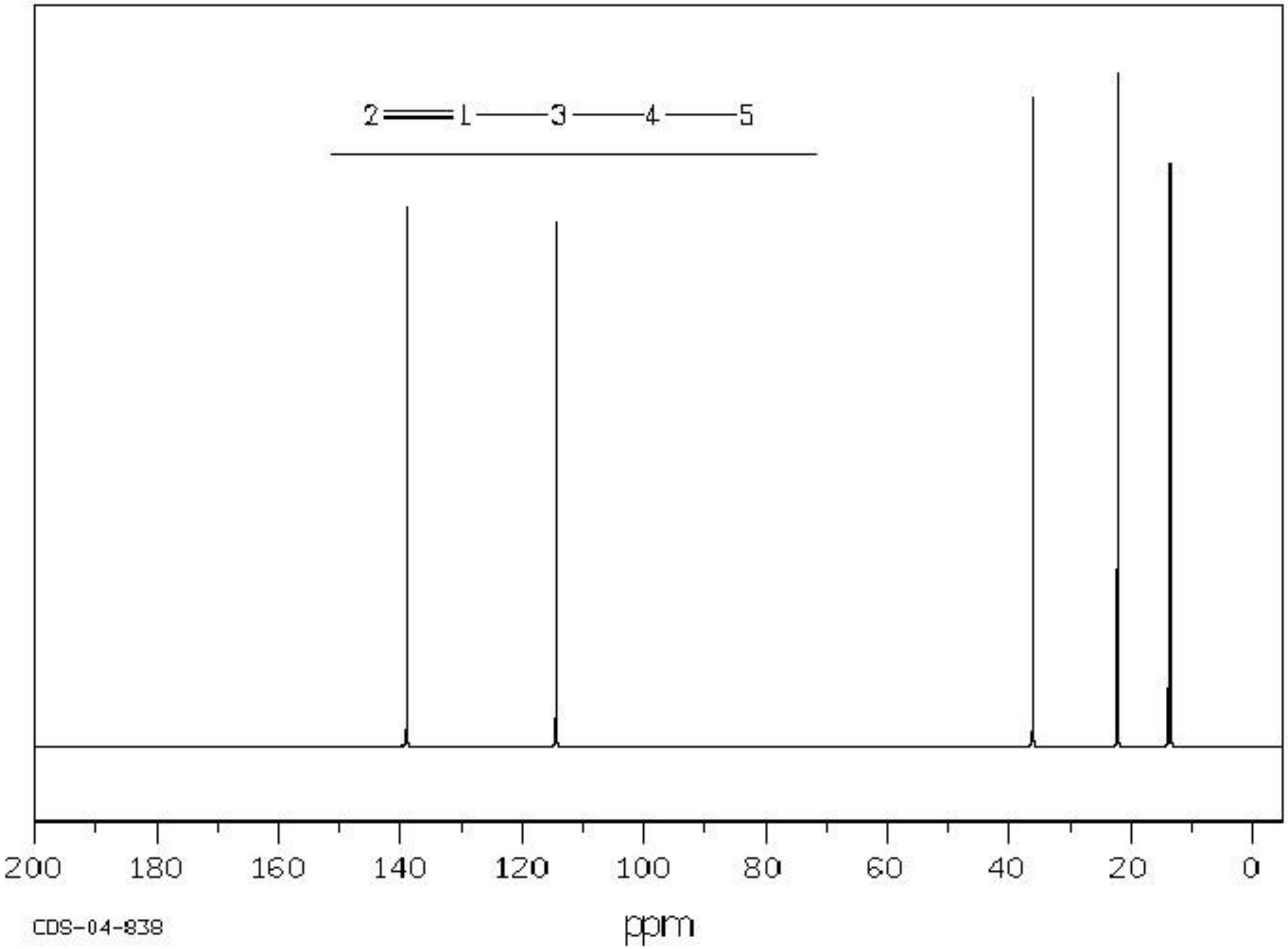
Acetamide



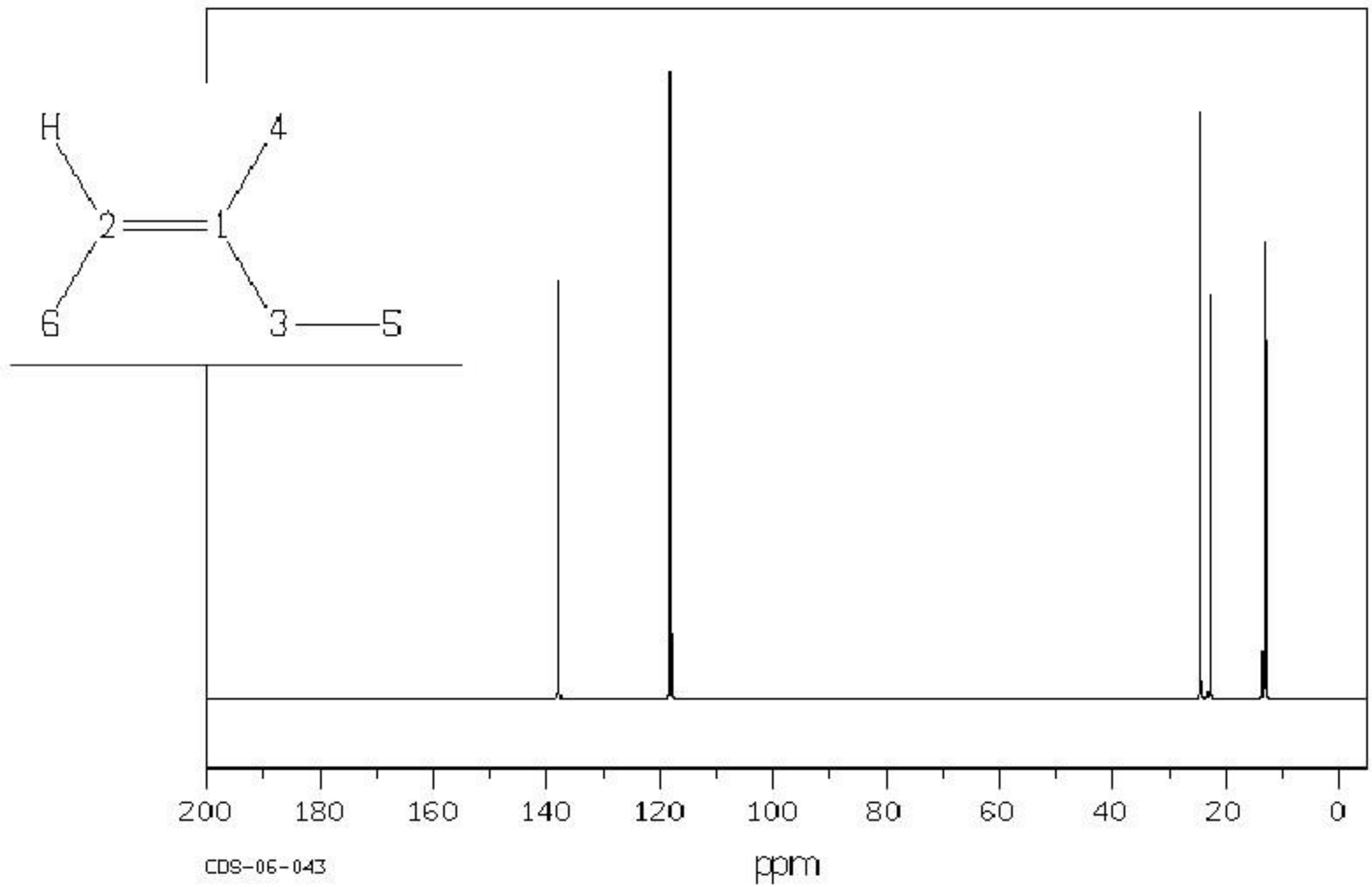
N-methyl acetamide



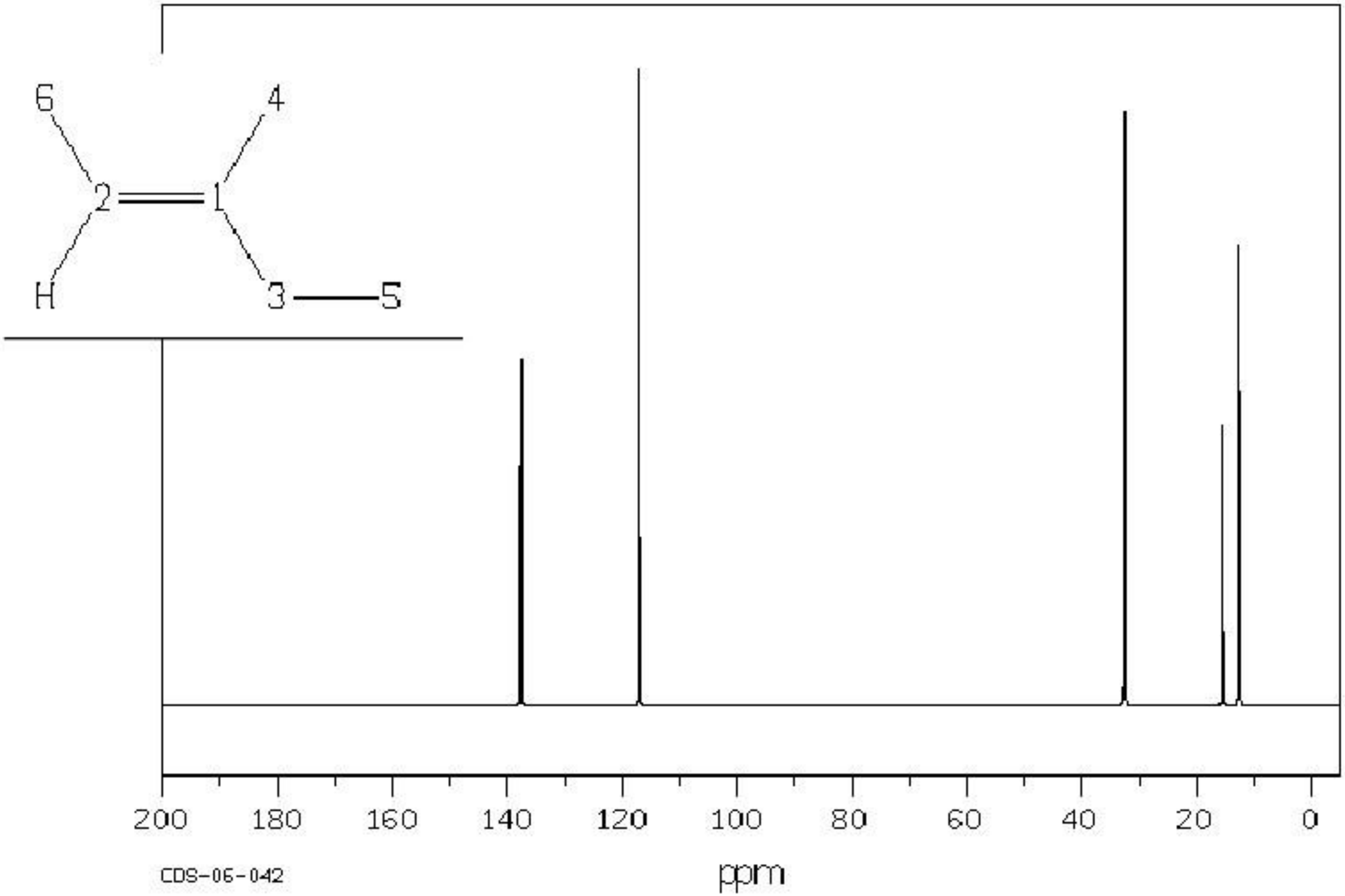
1-pentene



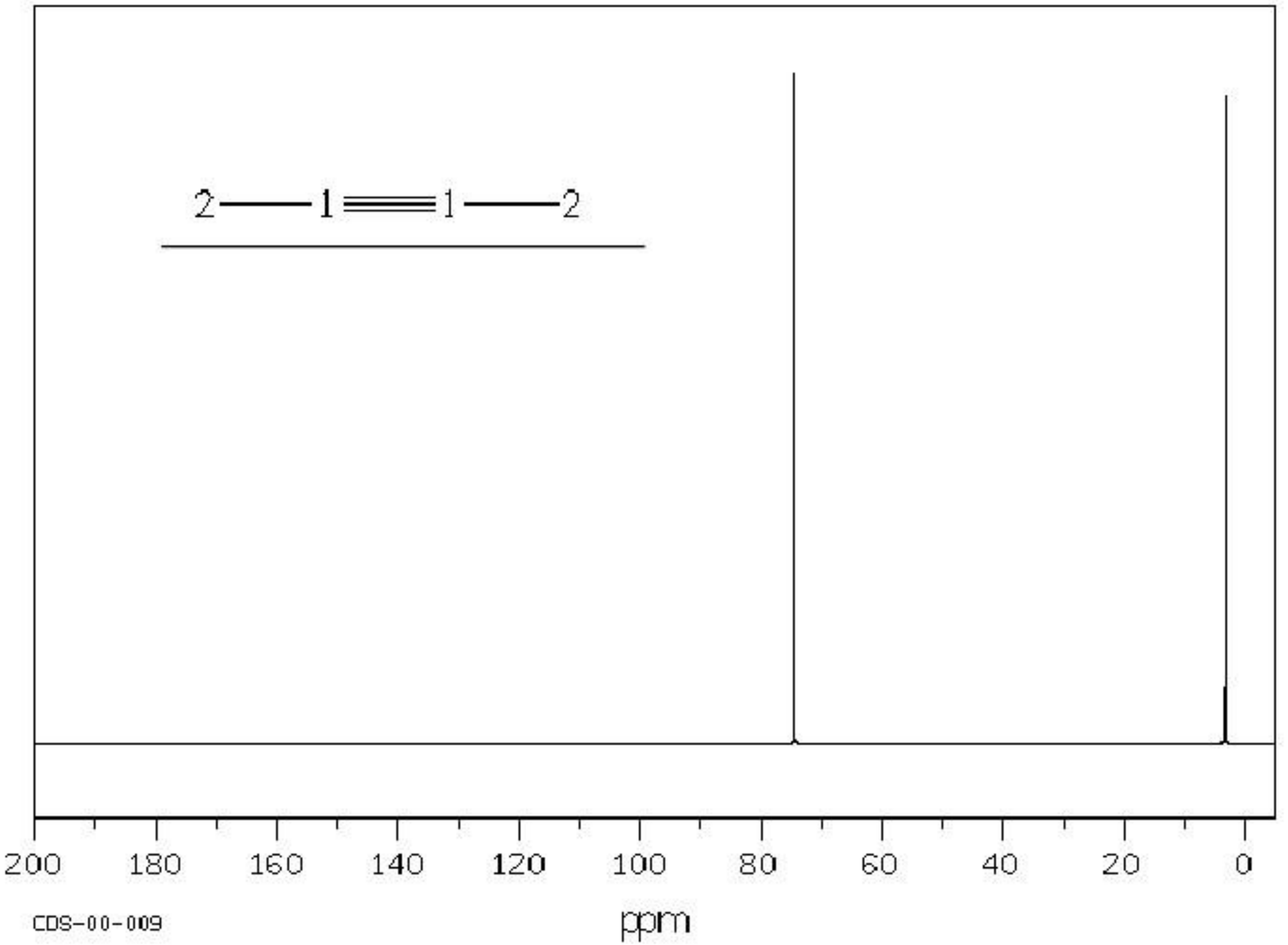
(Z)-3-methyl-2-pentene



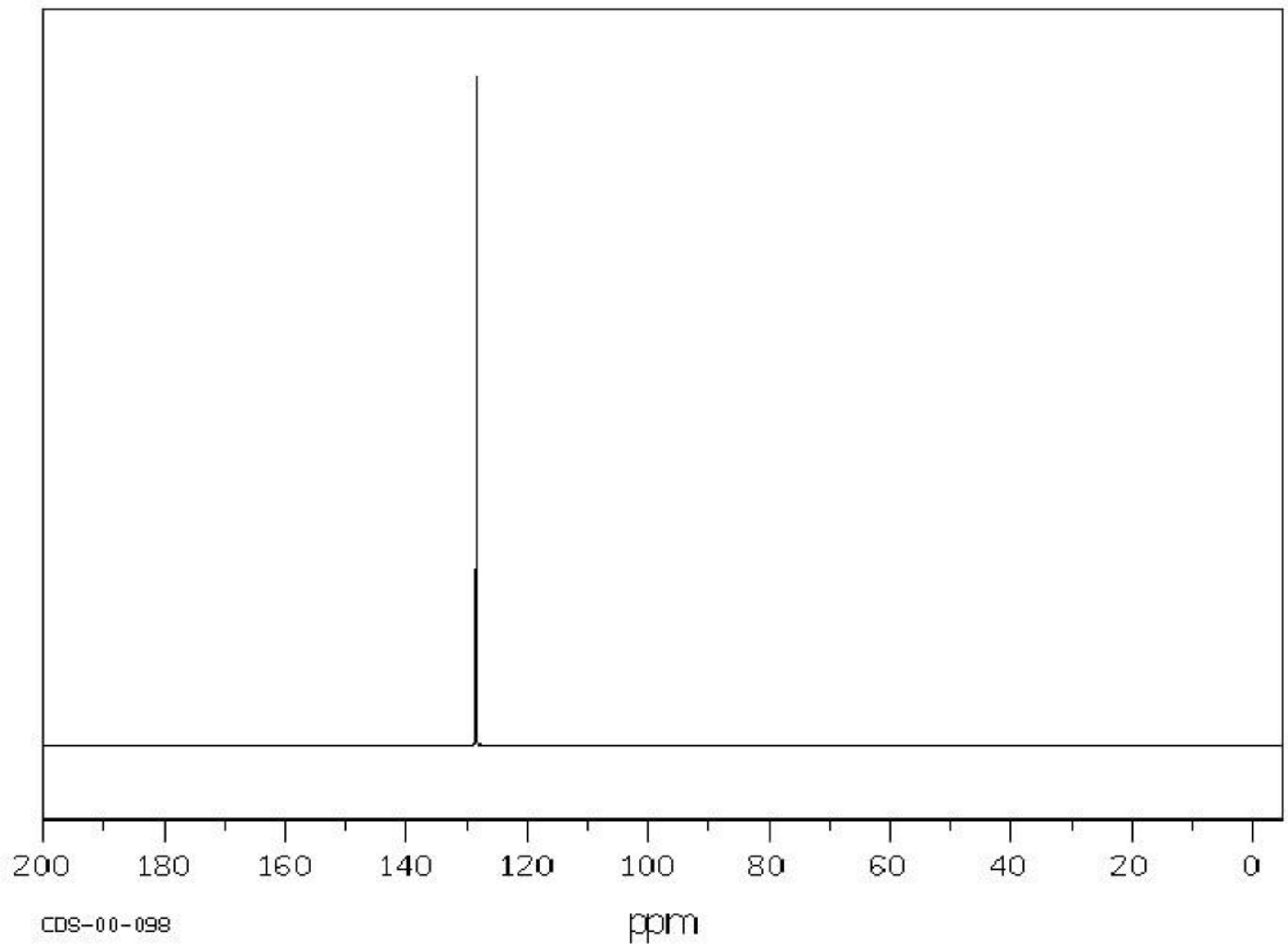
(E)-3-methyl-2-pentene



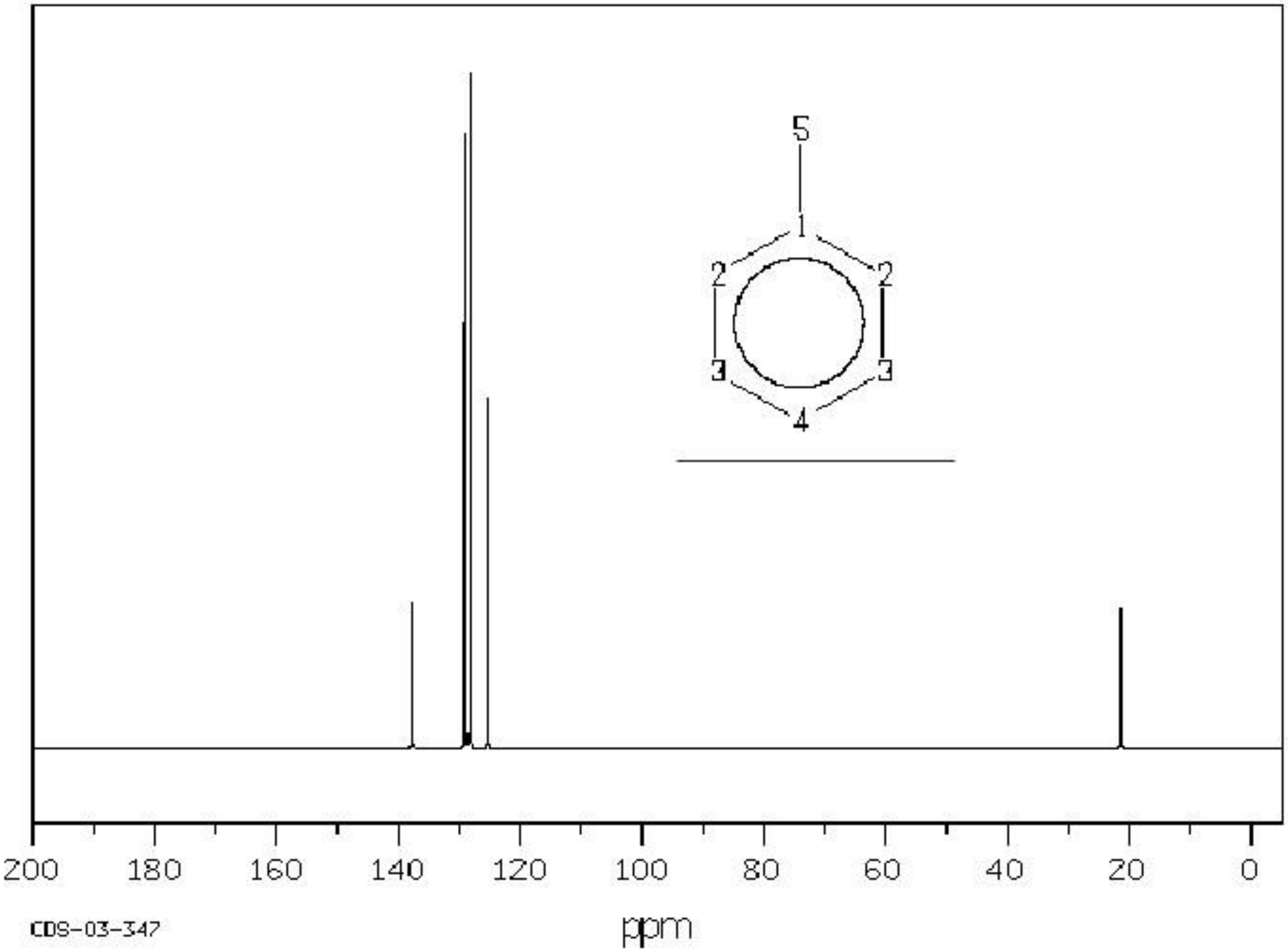
2-butyne



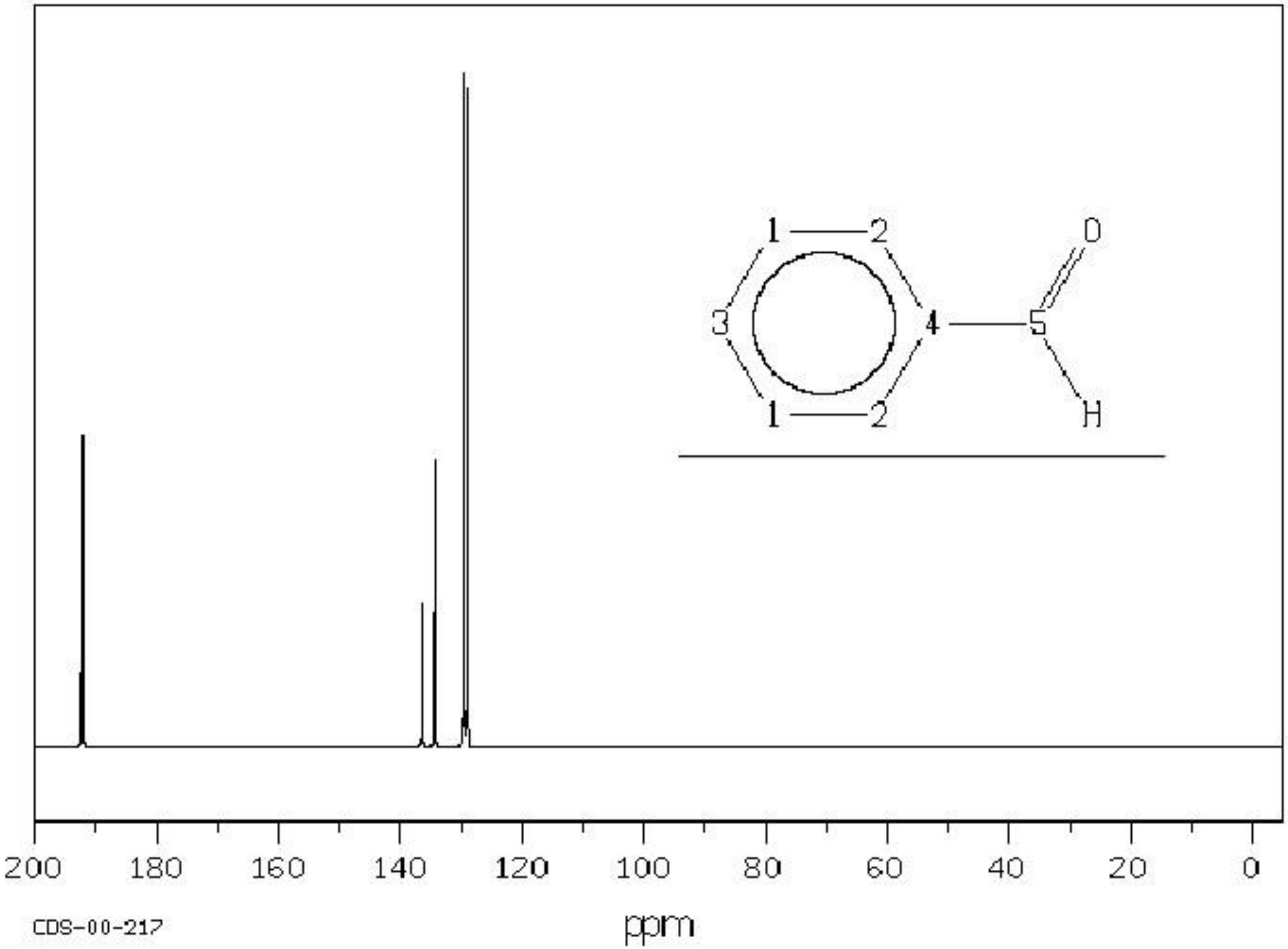
Benzene



toluene



Benzaldehyde



c) DEPT data

DEPT = distortionless enhancement by polarization

Distinguishes:

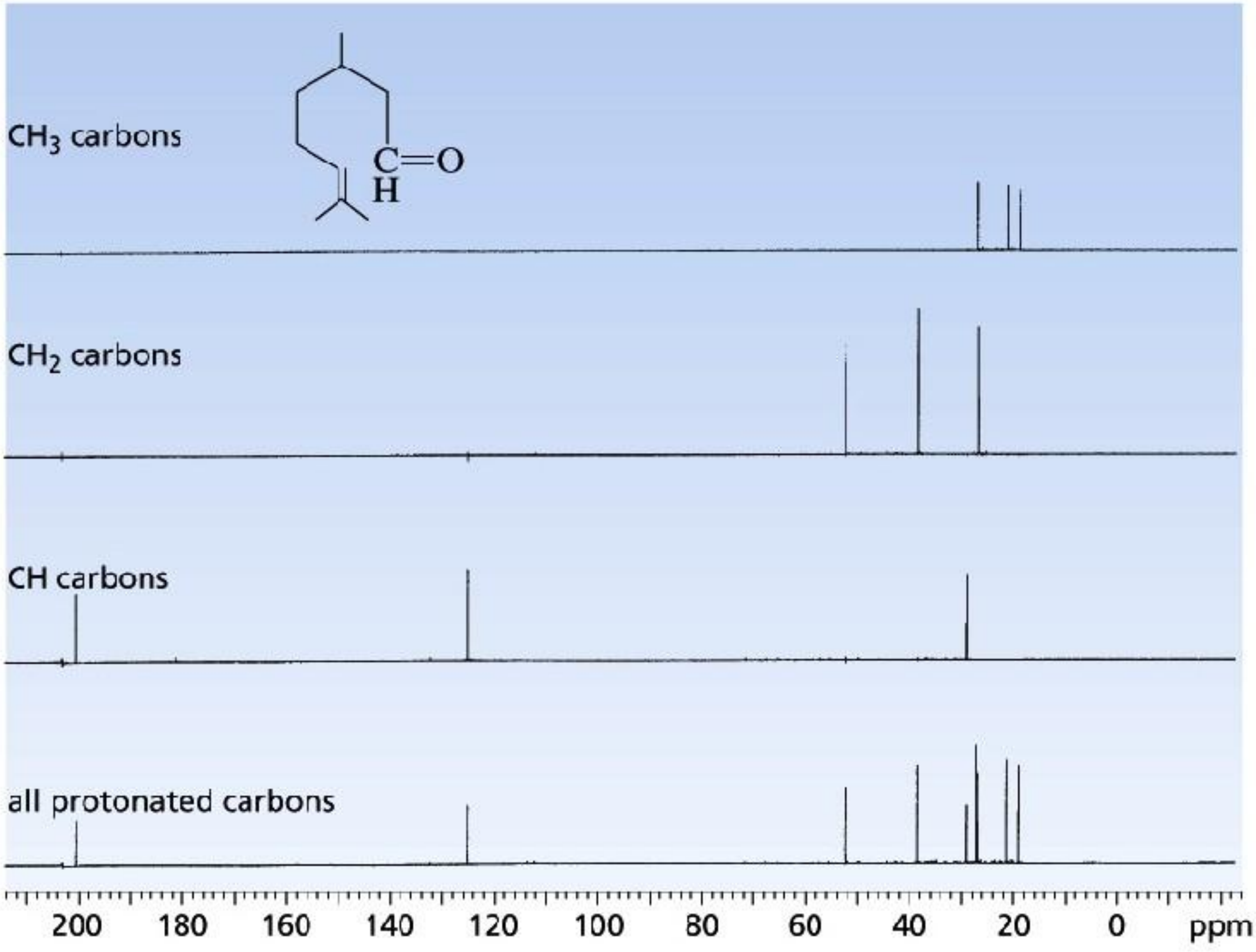
CH_3 - methyl groups

$-CH_2-$ methylene groups

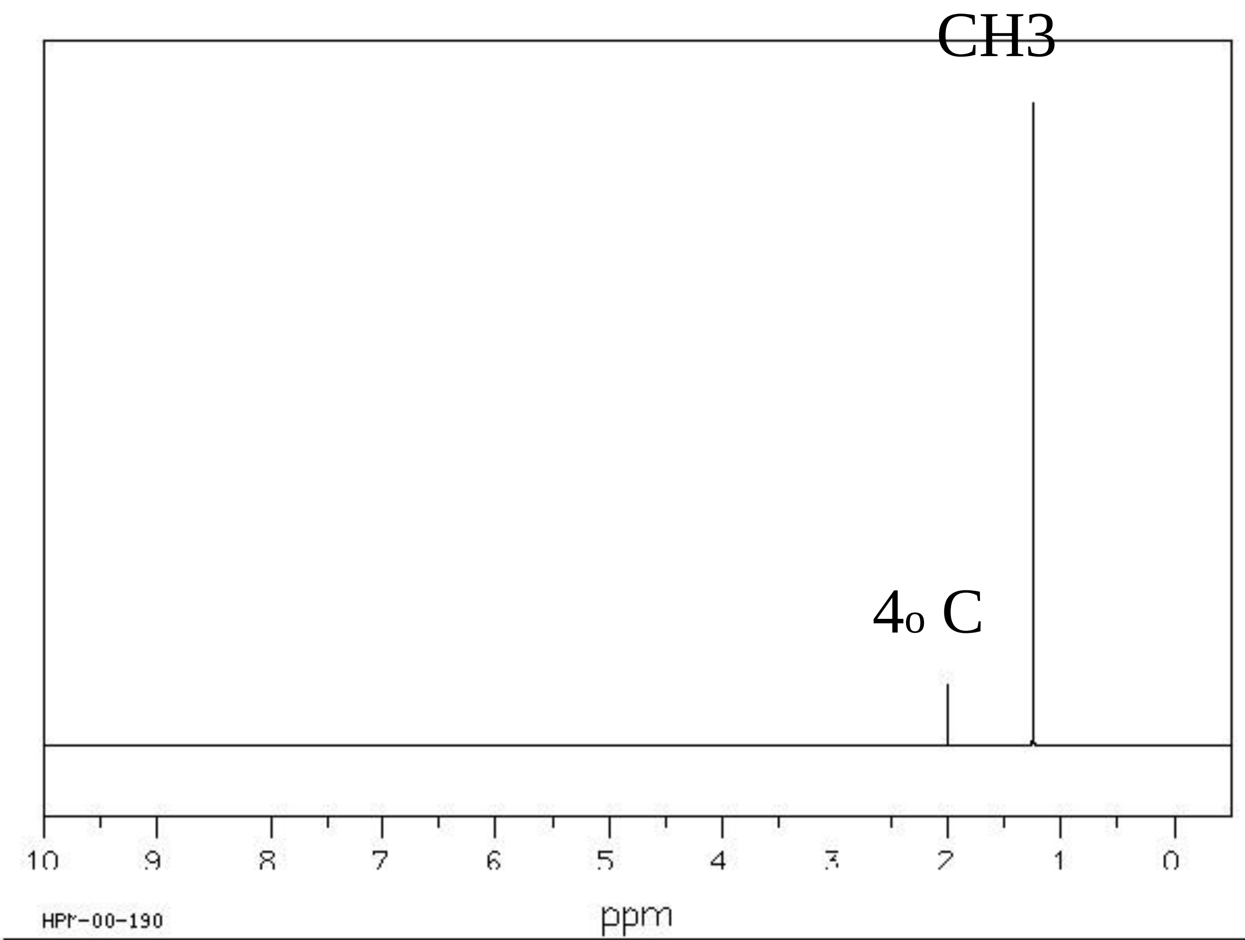
I
-CH- methine groups

I
-C- 4^o carbons (not detected by DEPT)
I

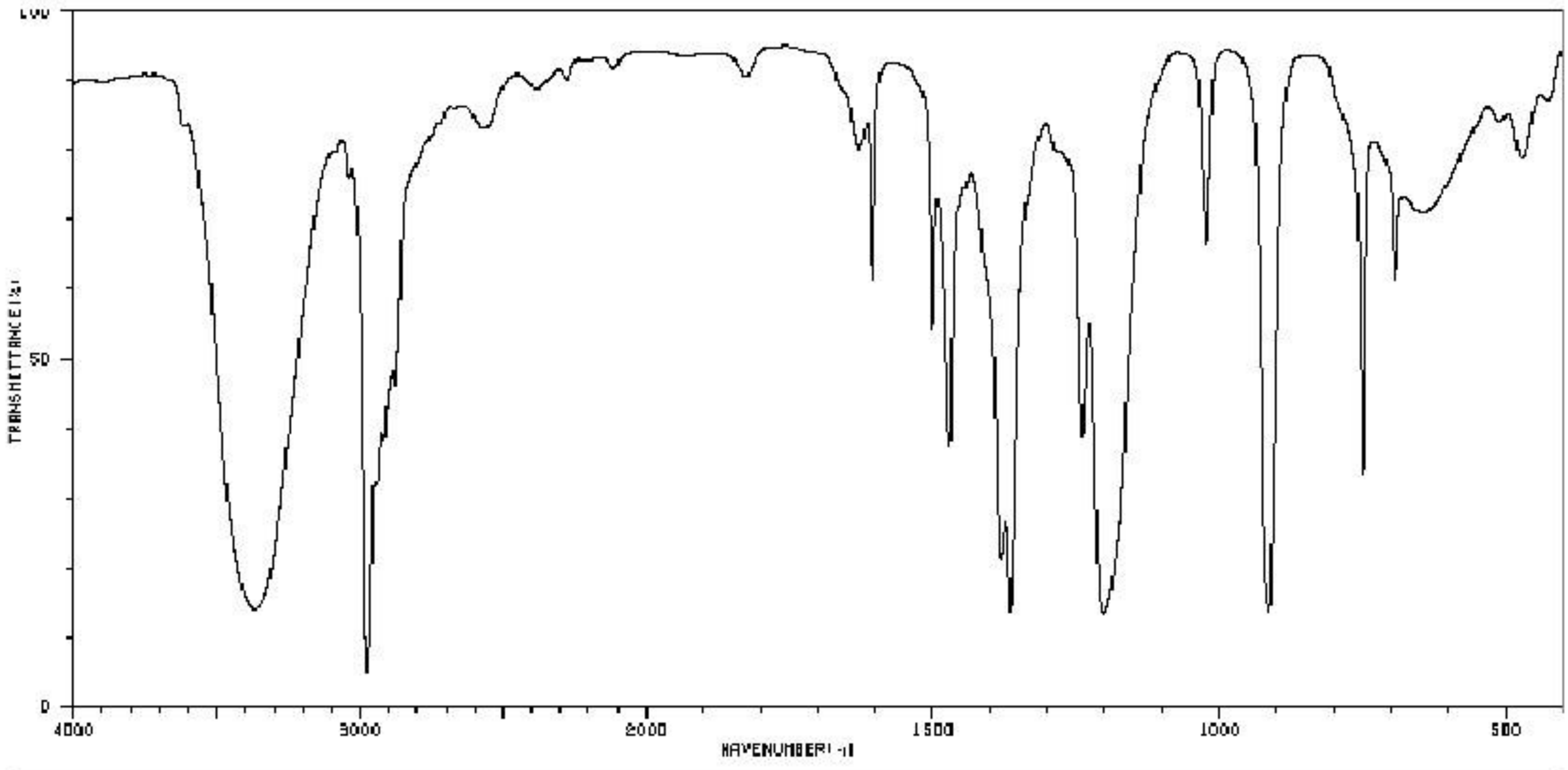
DEPT ^{13}C spectrum of citronella $C_{10}H_{16}O$



$C_4H_{10}O$

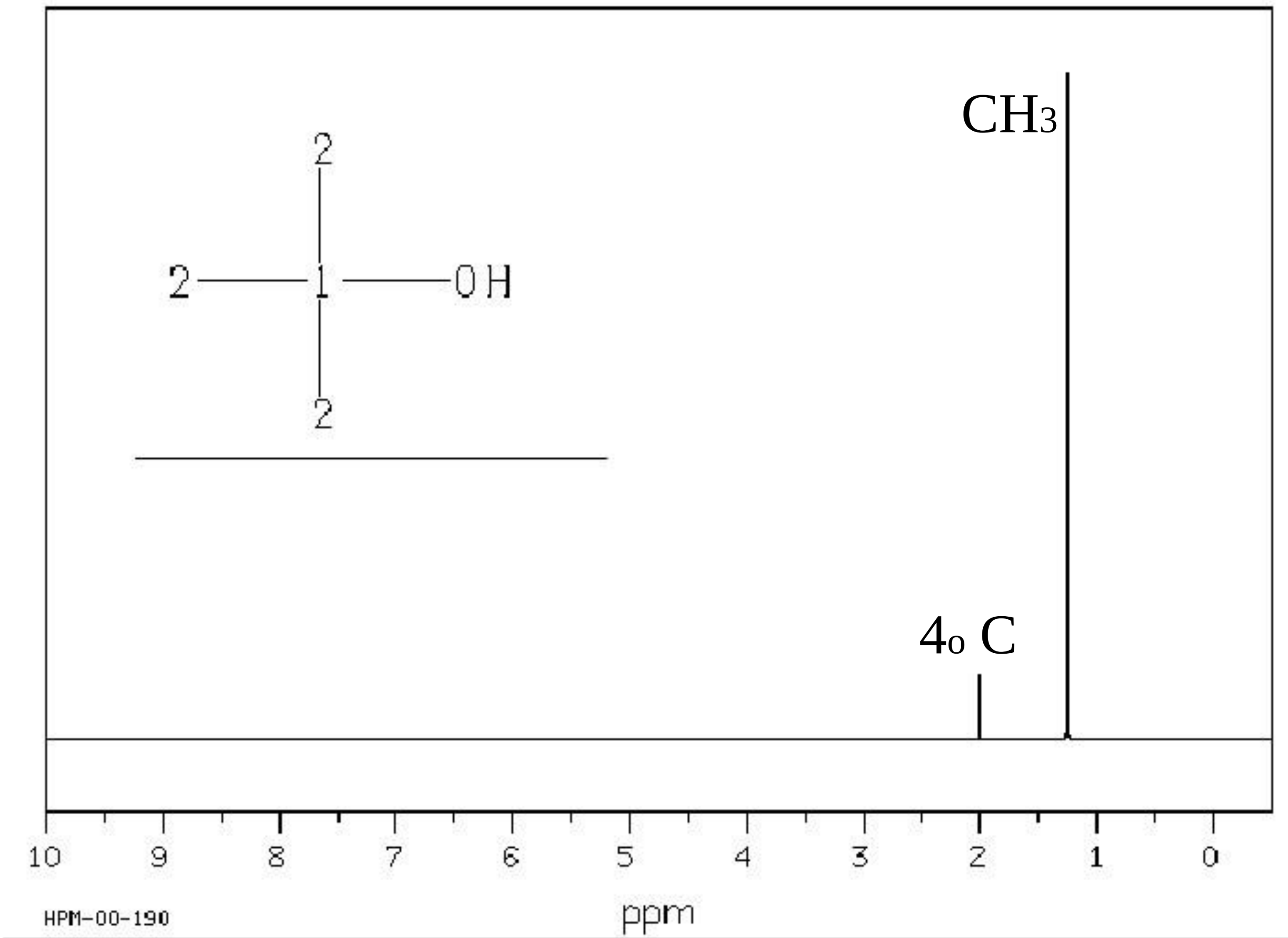


$C_4H_{10}O$

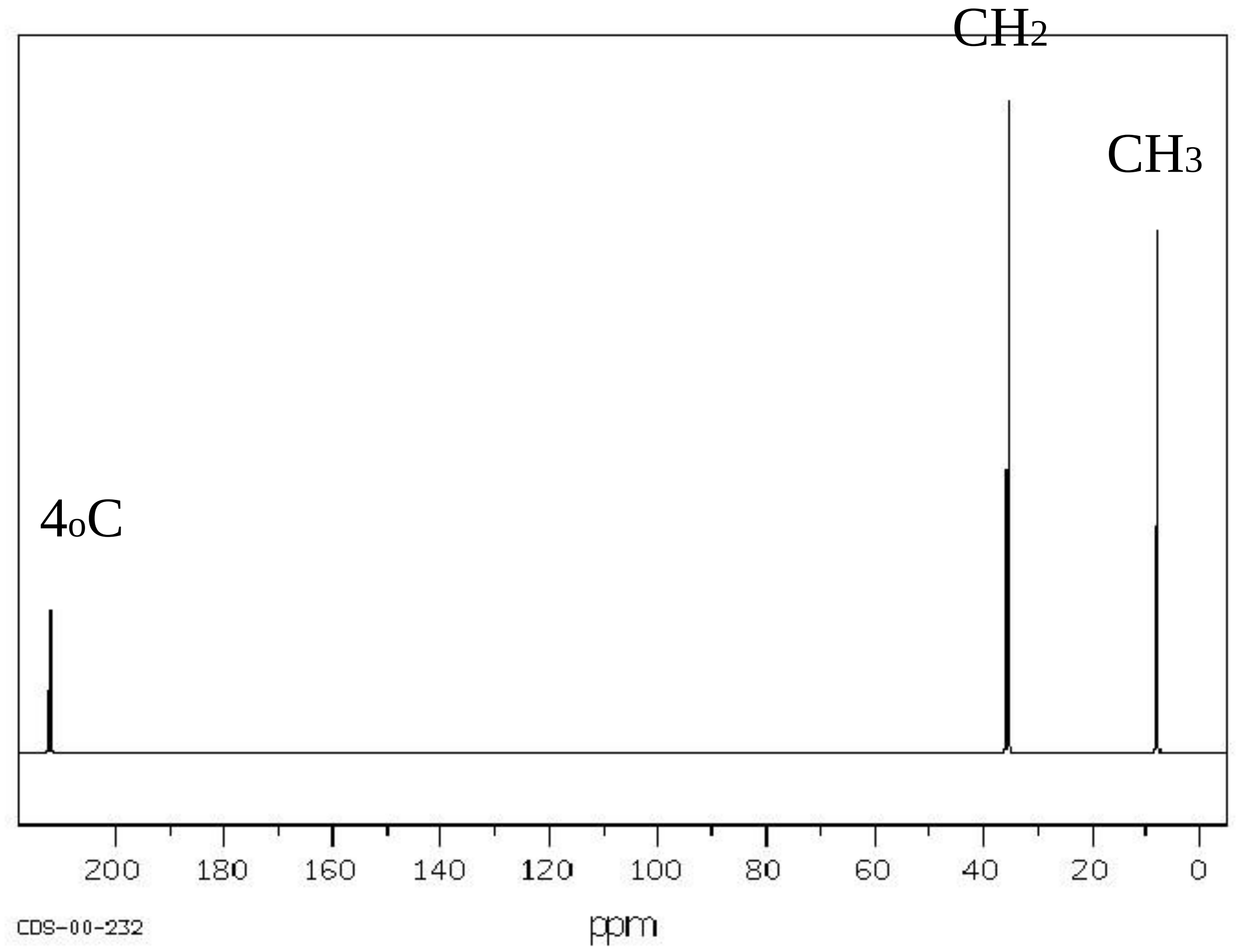


TRANSMITTANCE(%)
WAVENUMBER(-1)
4000
3000
2000
1500
1000
500
50
0

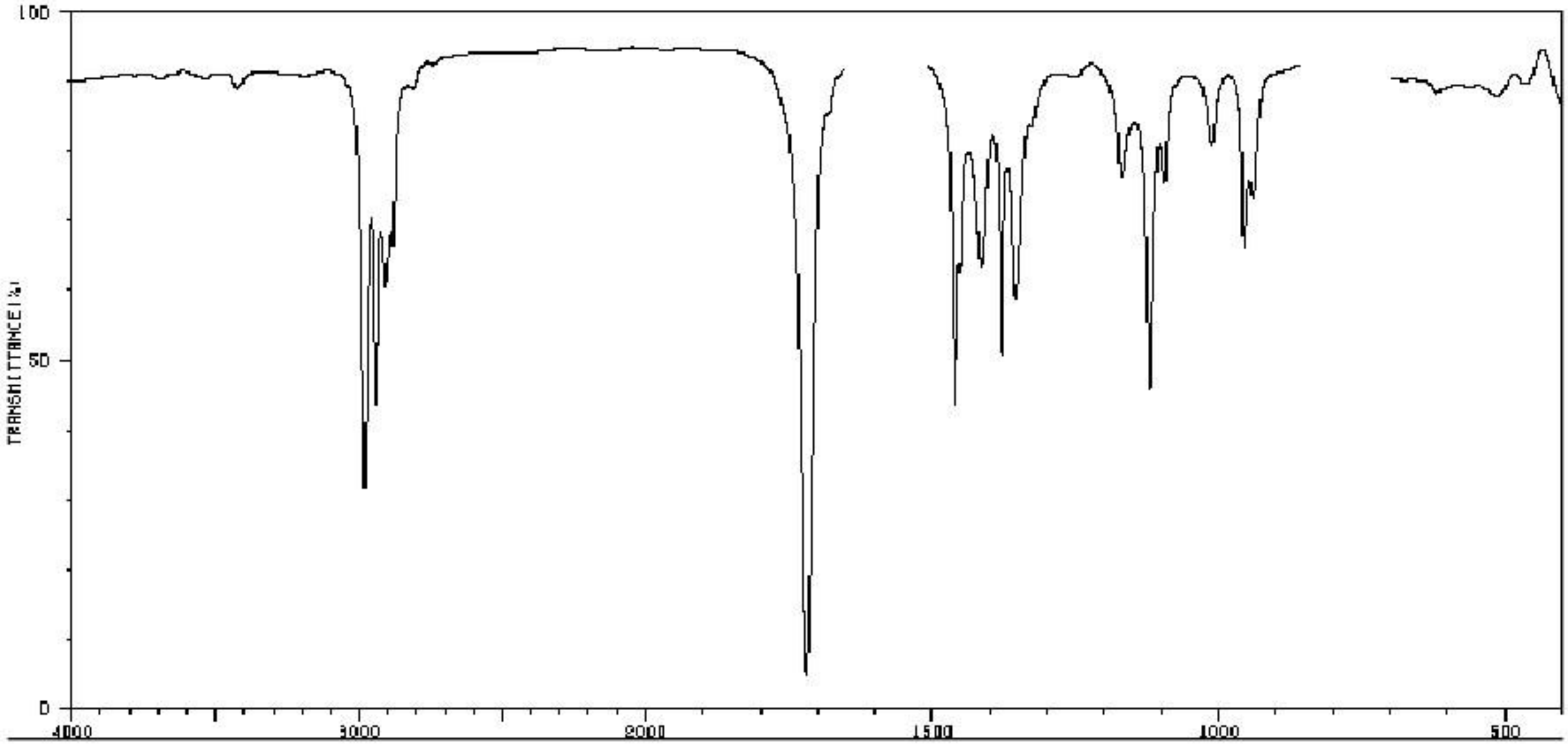
$C_4H_{10}O$



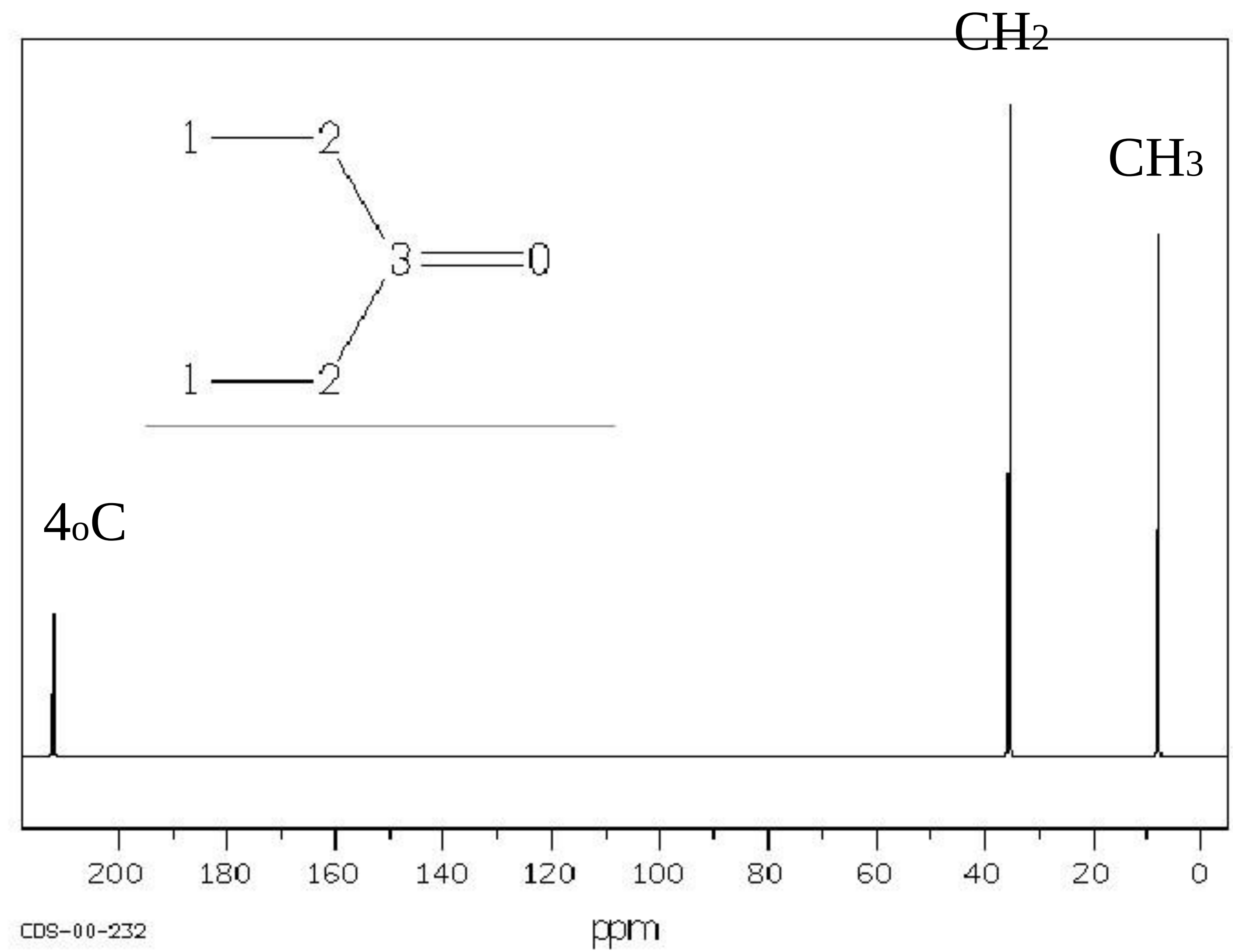
$C_5H_{10}O$



$C_5H_{10}O$

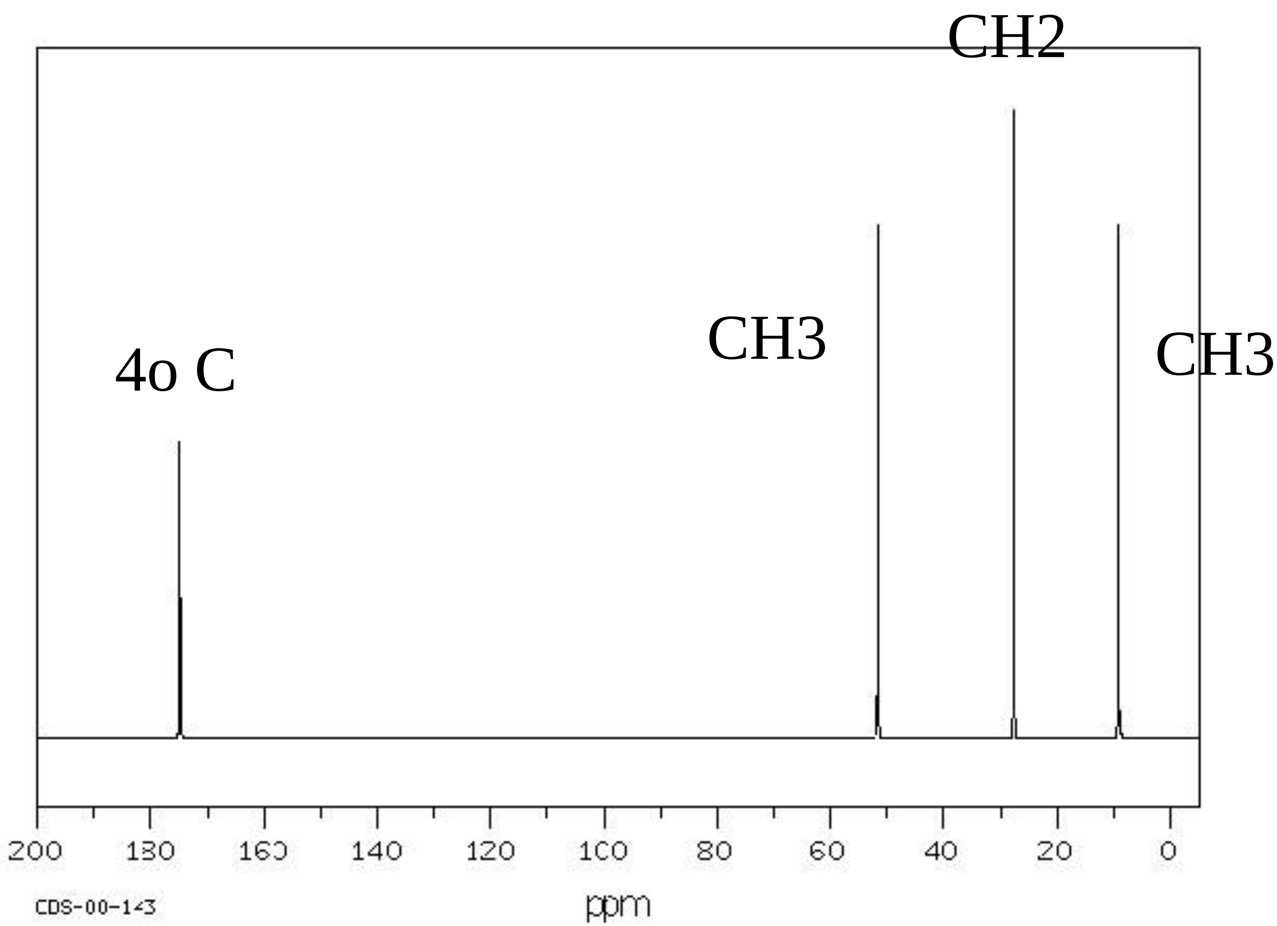


$C_5H_{10}O$

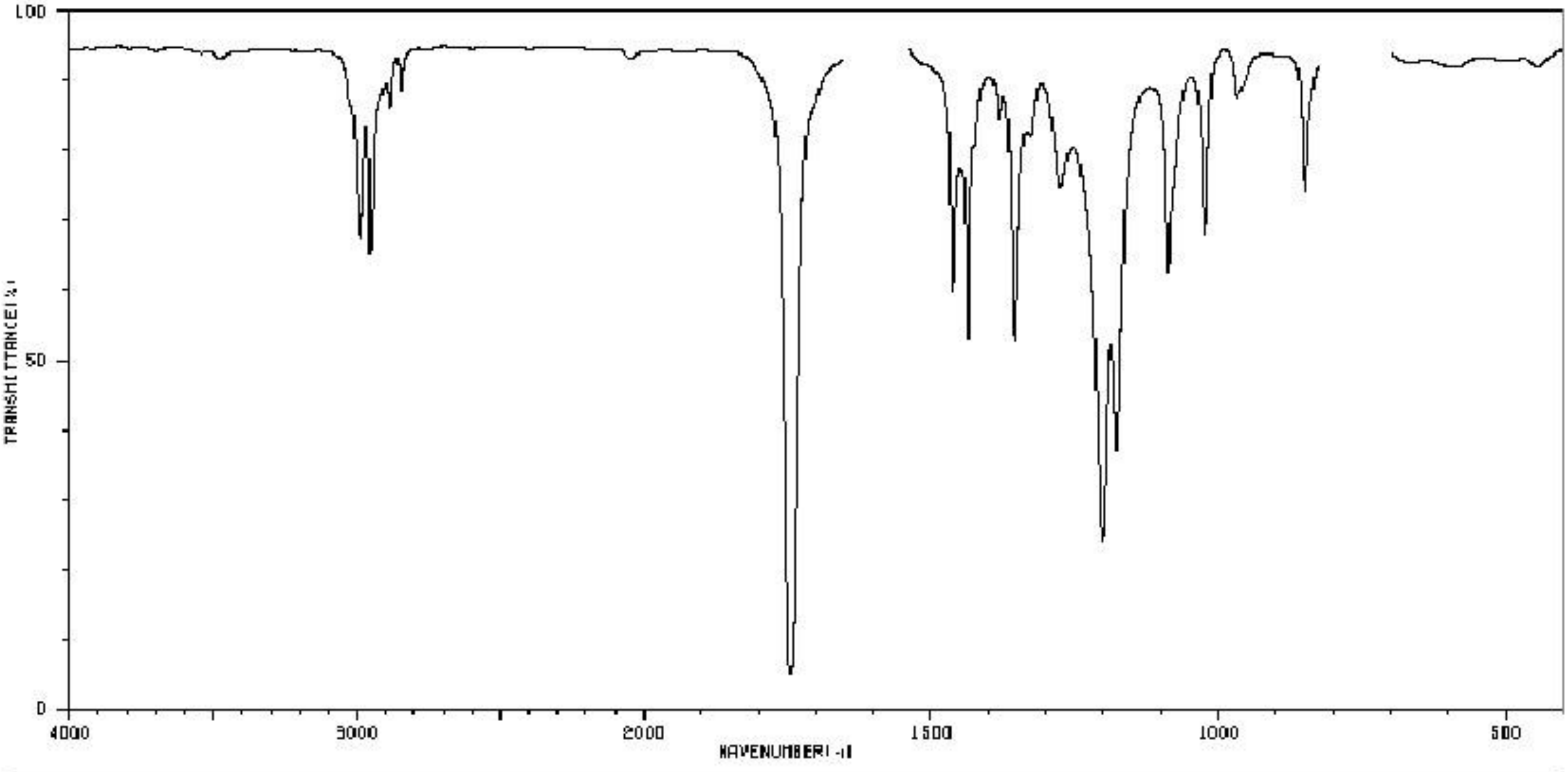


CH_2
CH_3
1
2
3
O
1
2
4_oC
200
180
160
140
120
100
80
60
40
20
0
CDS-00-232
ppm

$C_4H_8O_2$

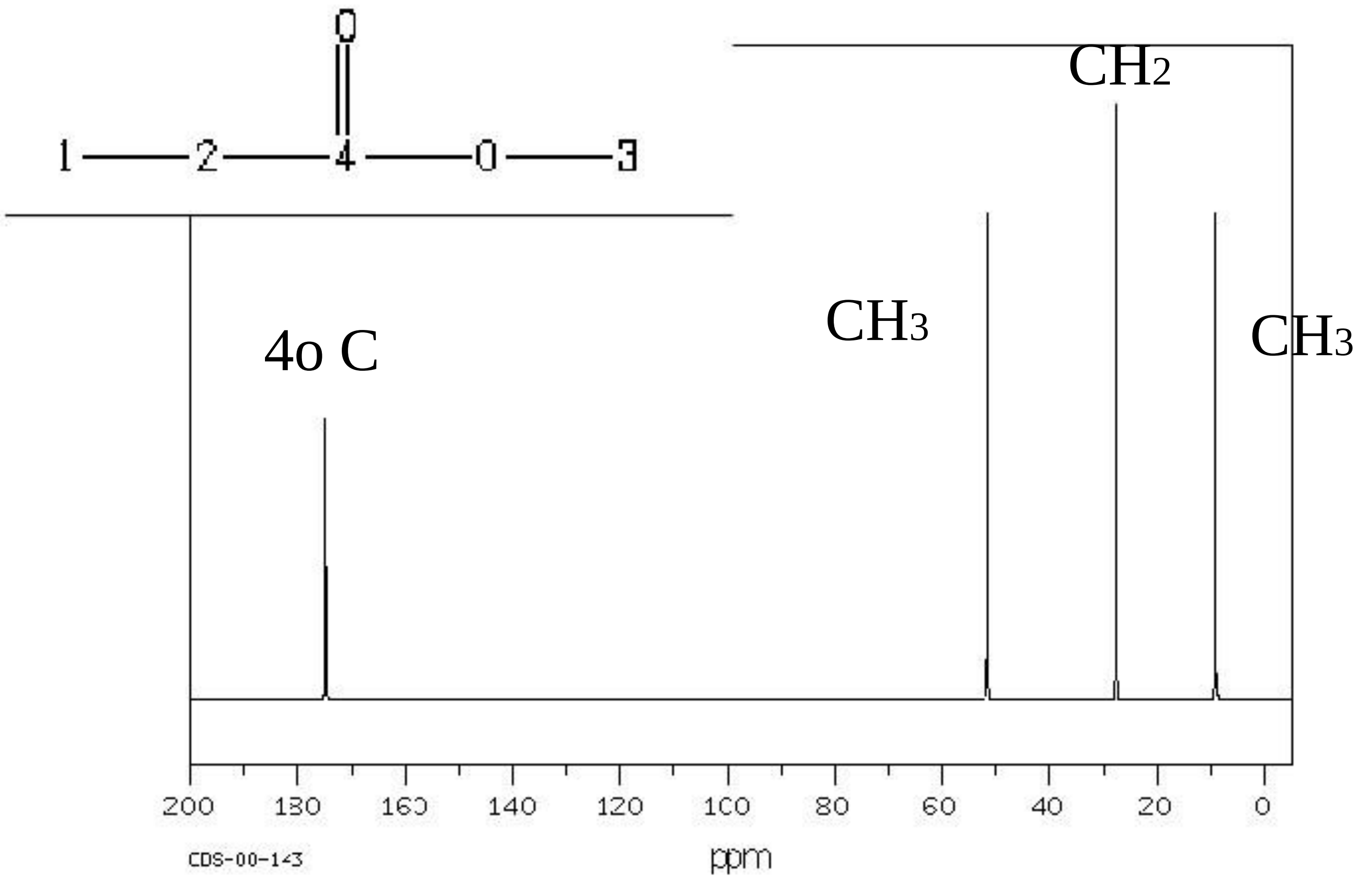

CH2
CH3
CH3
4o C
200
180
160
140
120
100
80
60
40
20
0
CDS-00-143
ppm

$C_4H_8O_2$

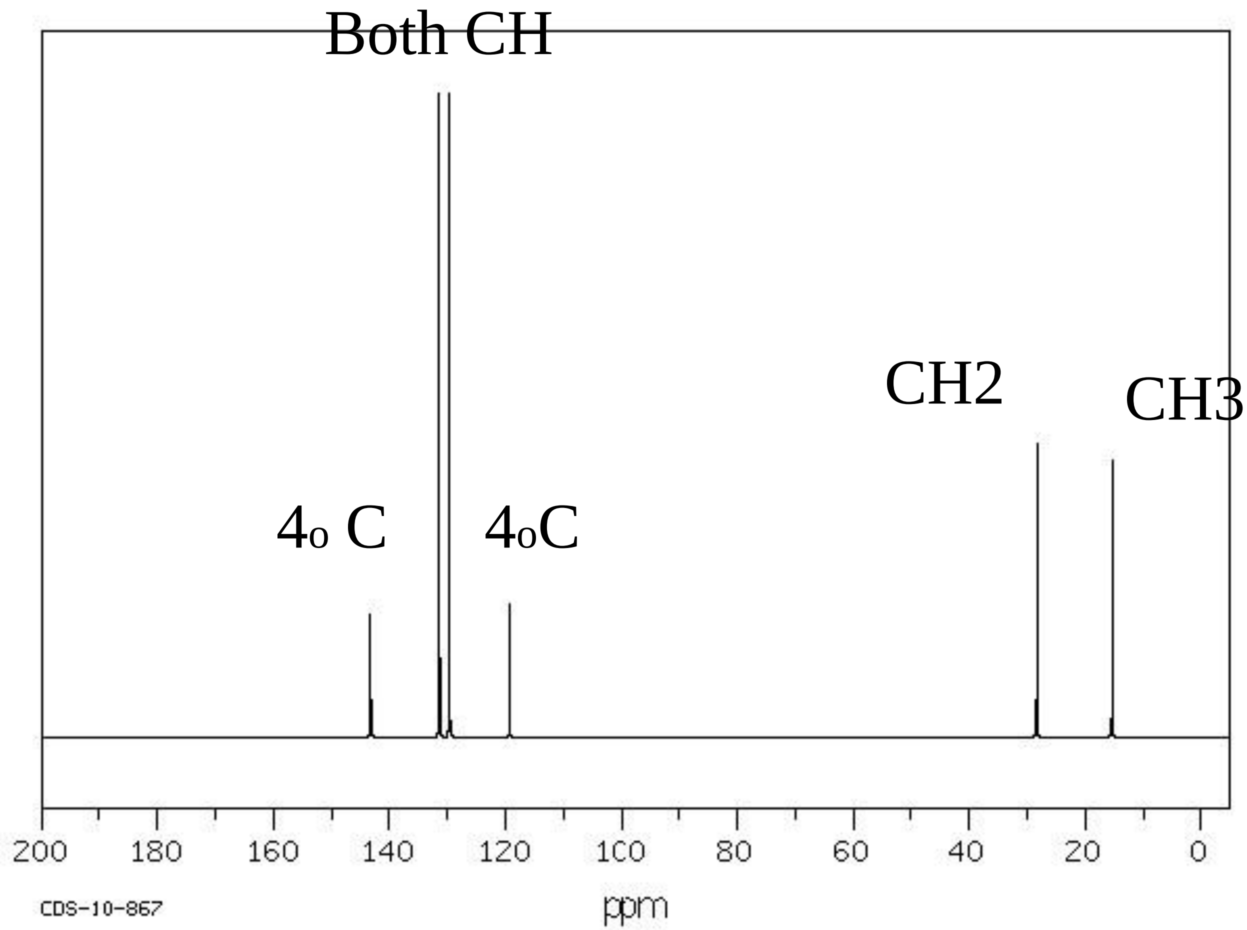


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]

$C_4H_8O_2$

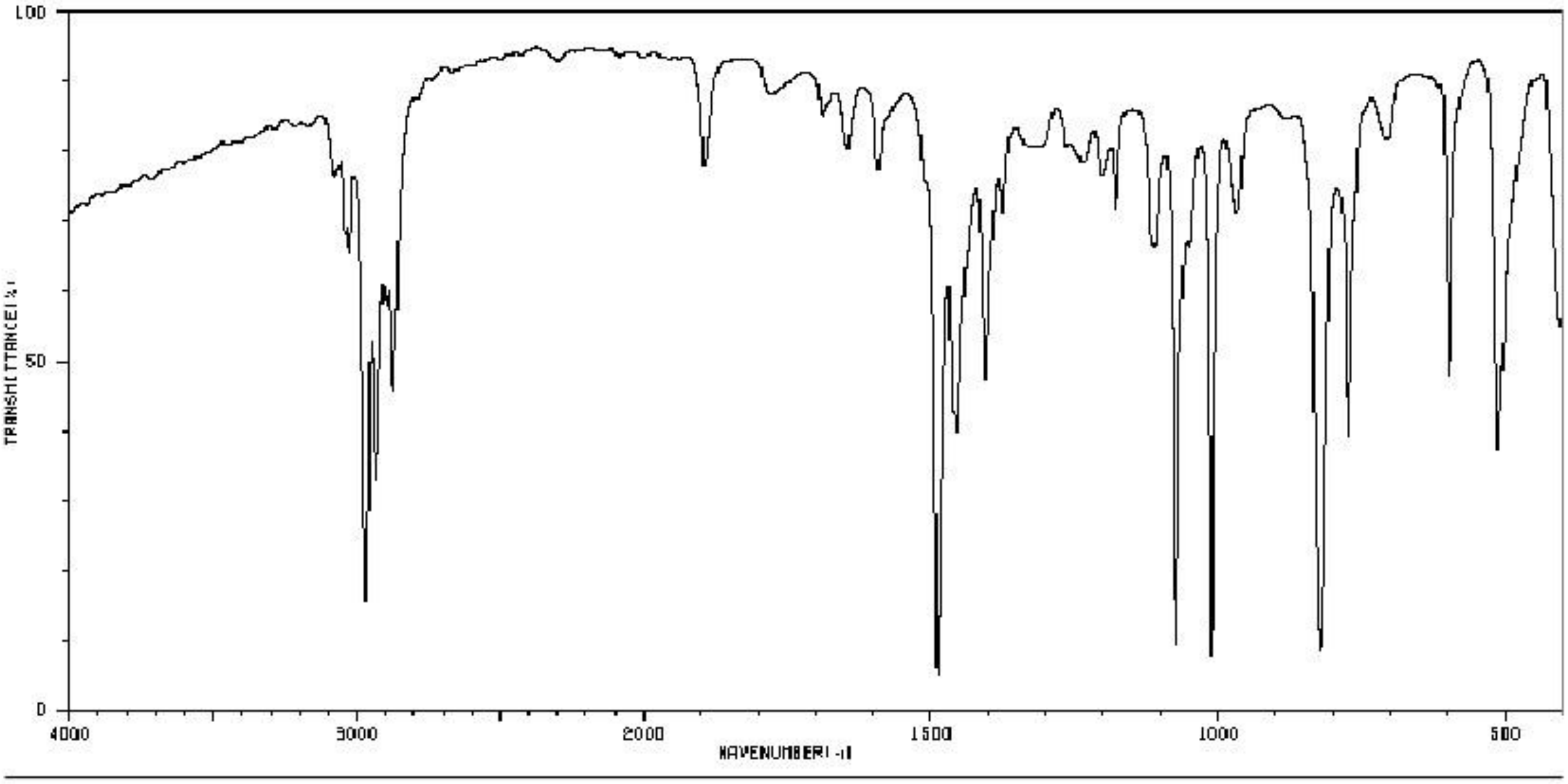

O
1 — 2 — 4 — O — 3
CH_2
CH_3
4o C
CH_3
200 180 160 140 120 100 80 60 40 20 0
CDS-00-143
ppm

C_8H_9Br



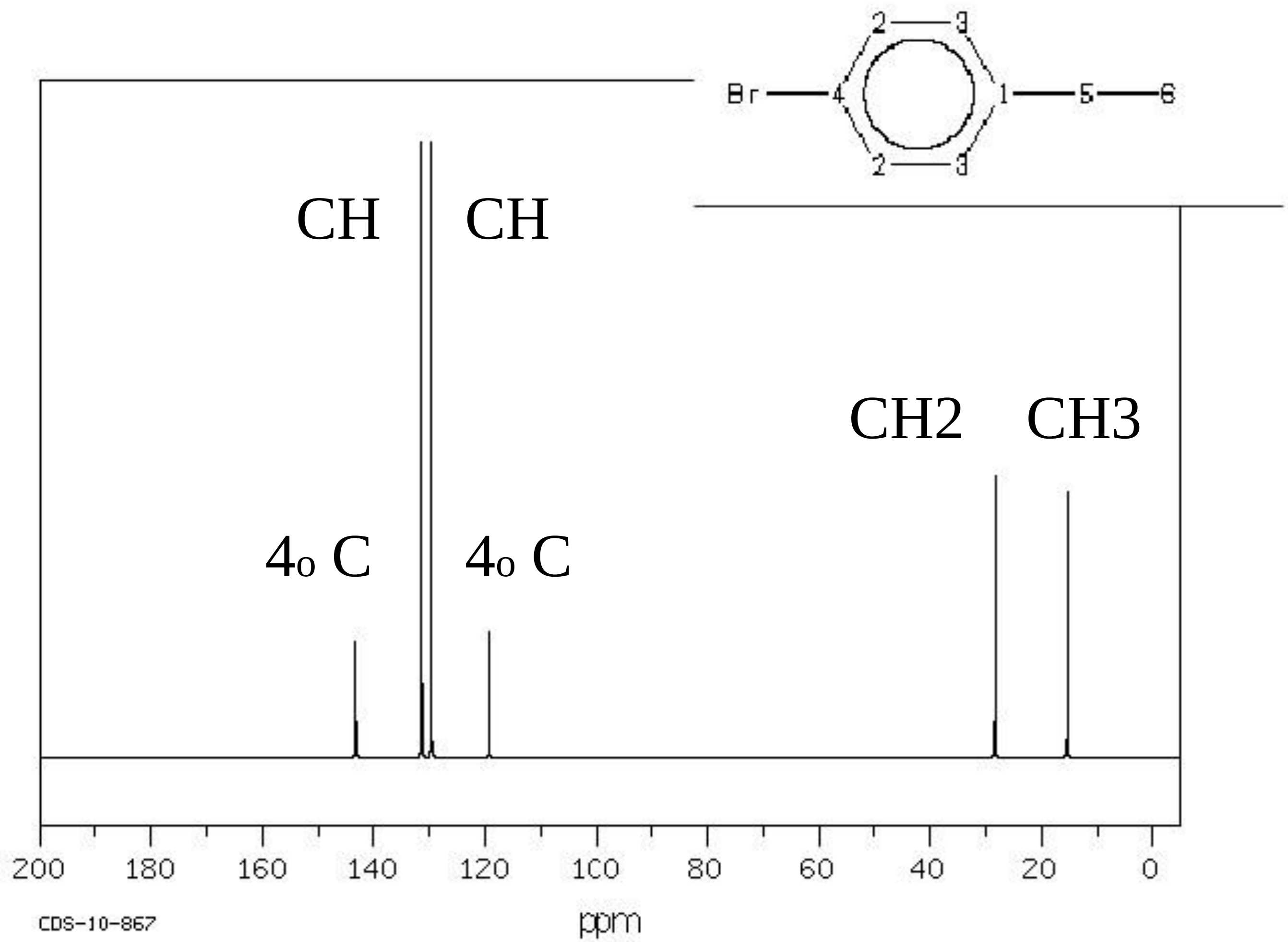
Both CH
CH2
CH3
4o C
4oC
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-10-867

C_8H_9Br



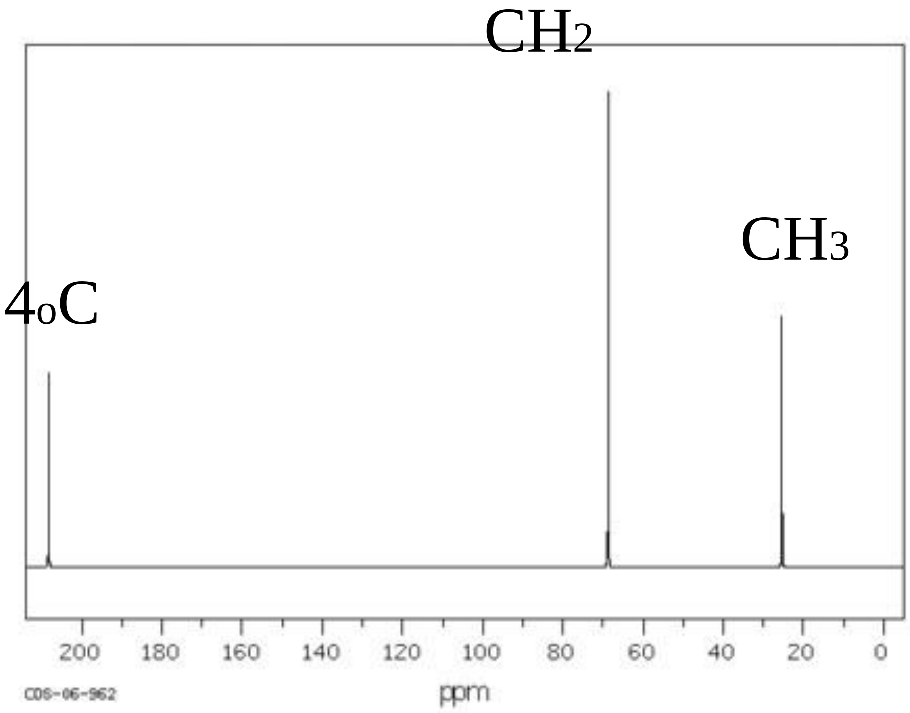
100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]

C_8H_9Br

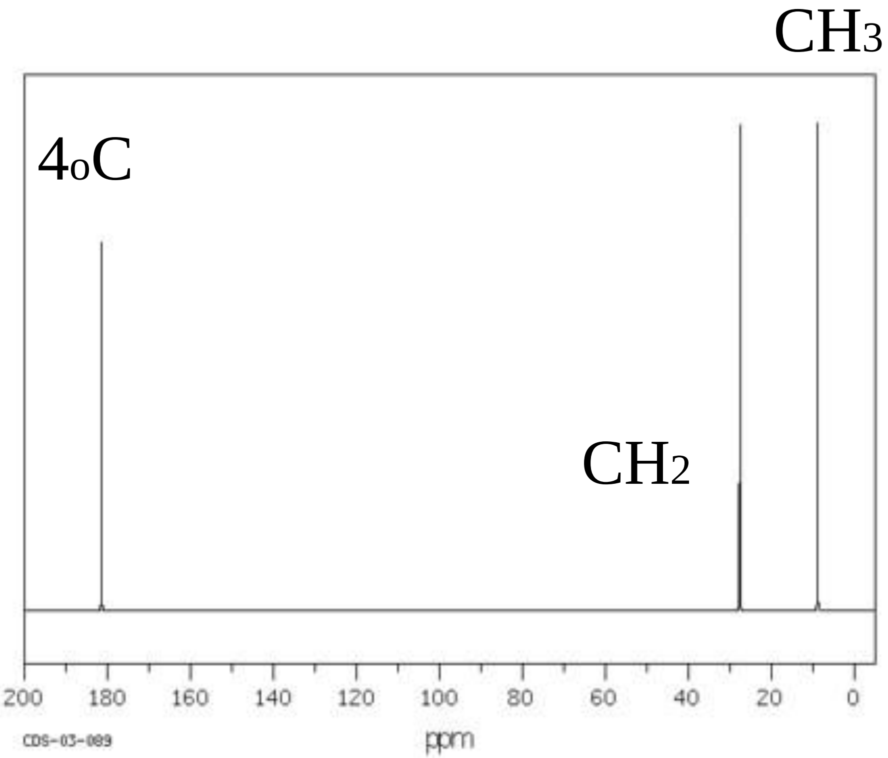


Br
4
2
3
1
5
6
CH
CH
CH2
CH3
4o C
4o C
200
180
160
140
120
100
80
60
40
20
0
CDS-10-867
ppm

Both $C_3H_6O_2$

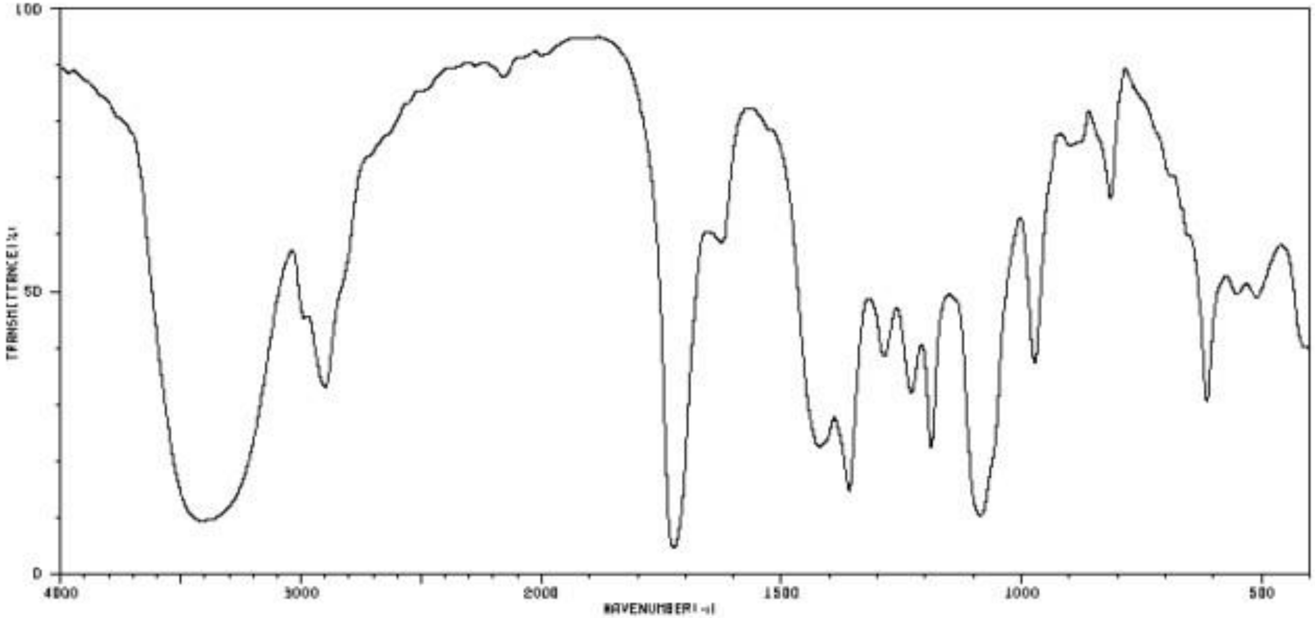


A

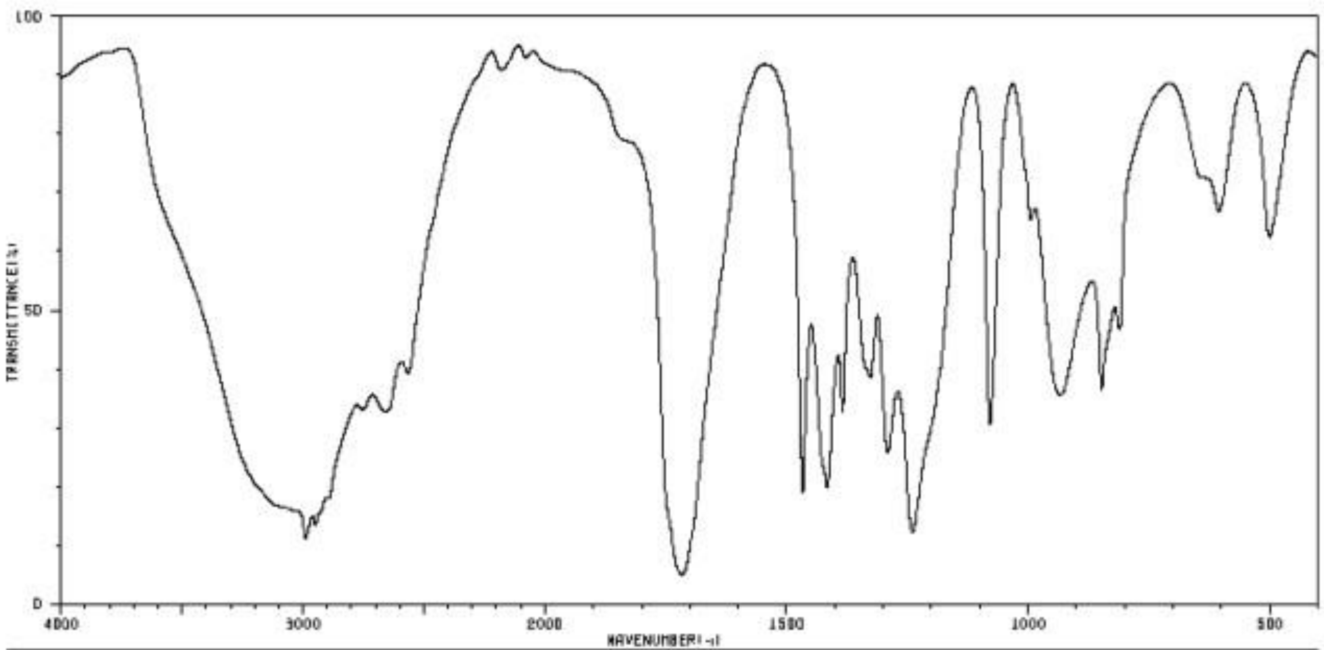


B

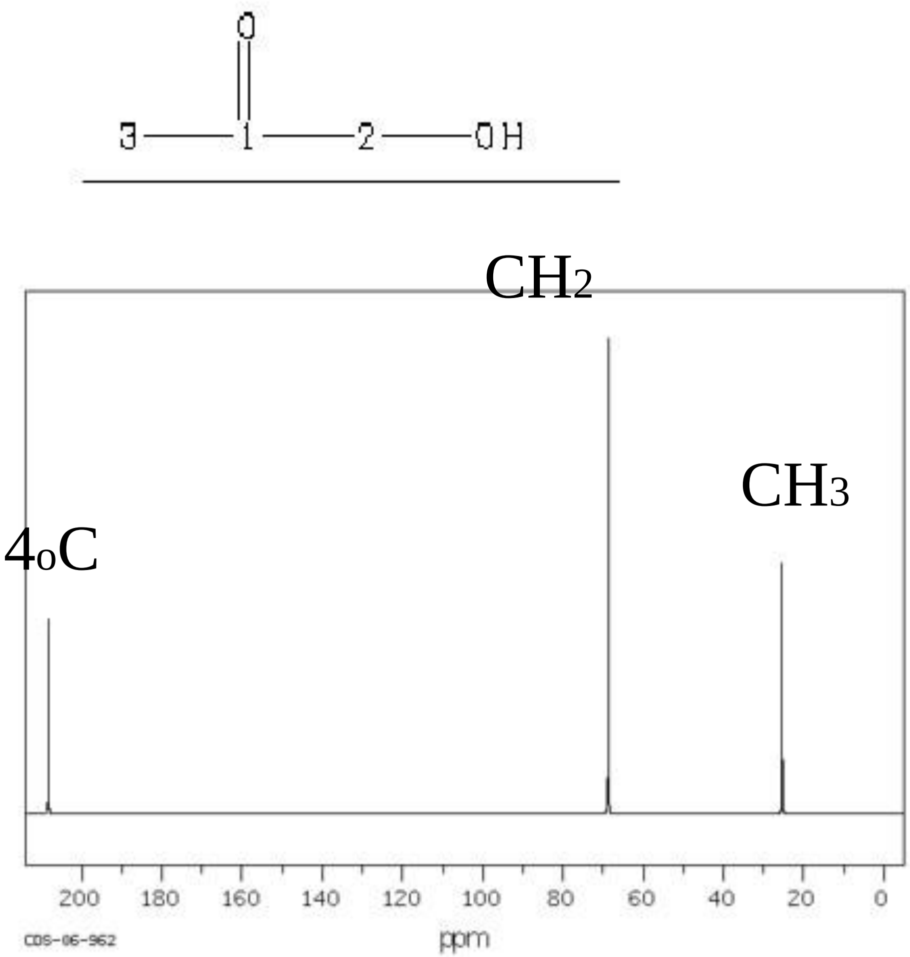
A


100
50
0
TRANSMITTANCE
4000
3000
2000
1500
1000
500
WAVENUMBER

B

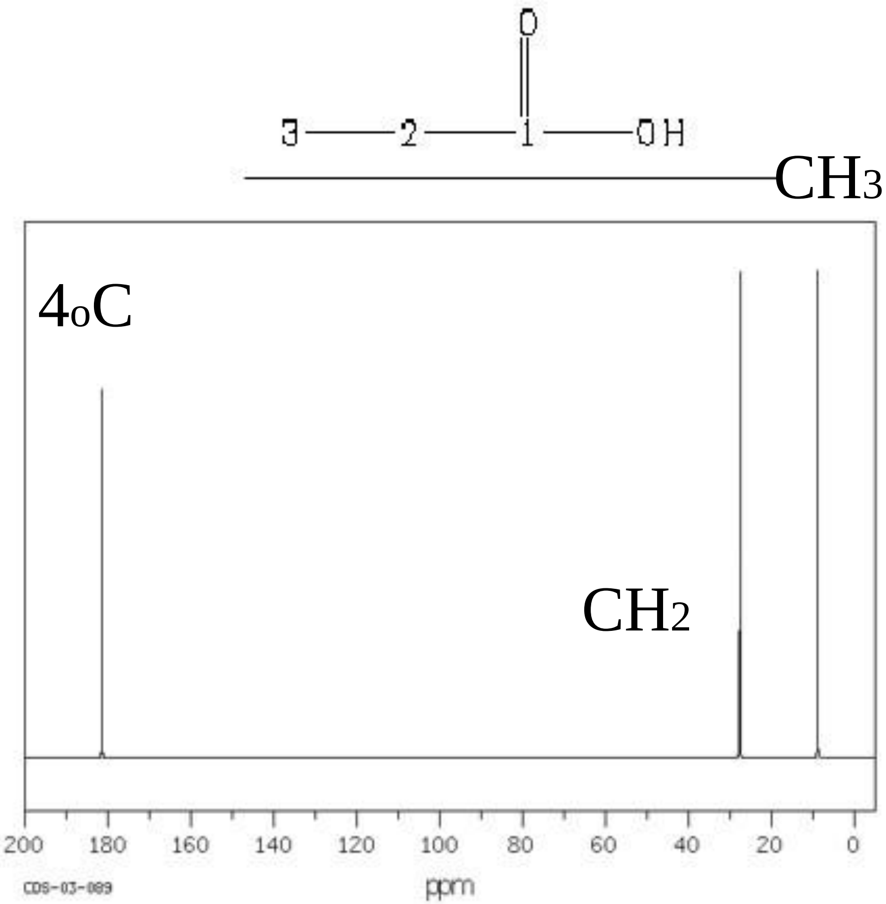

100
50
0
TRANSMITTANCE
4000
3000
2000
1500
1000
500
WAVENUMBER

$C_3H_6O_2$



O
3
1
2
OH
CH2
CH3
4oC
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-06-962

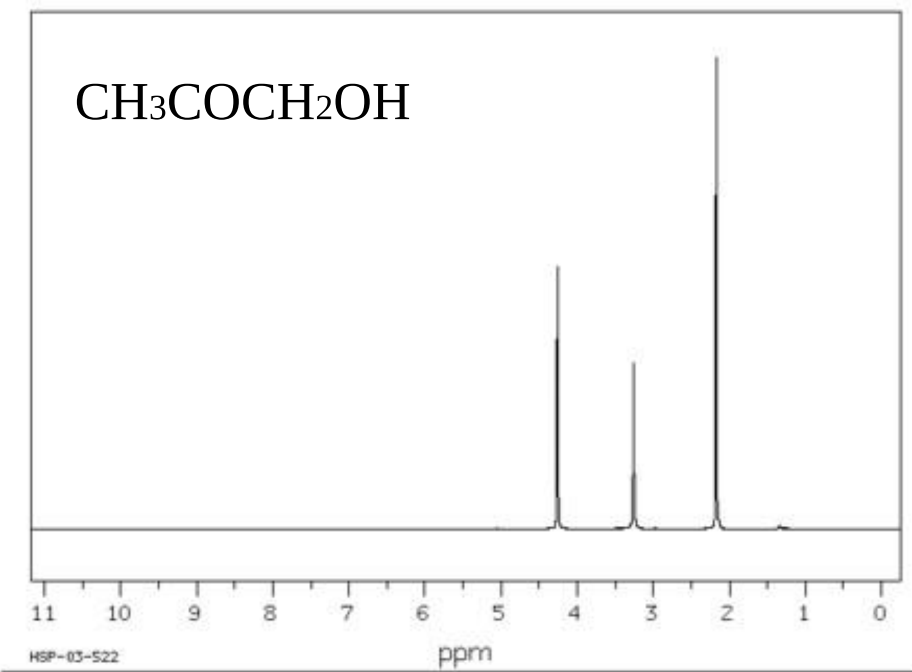
A



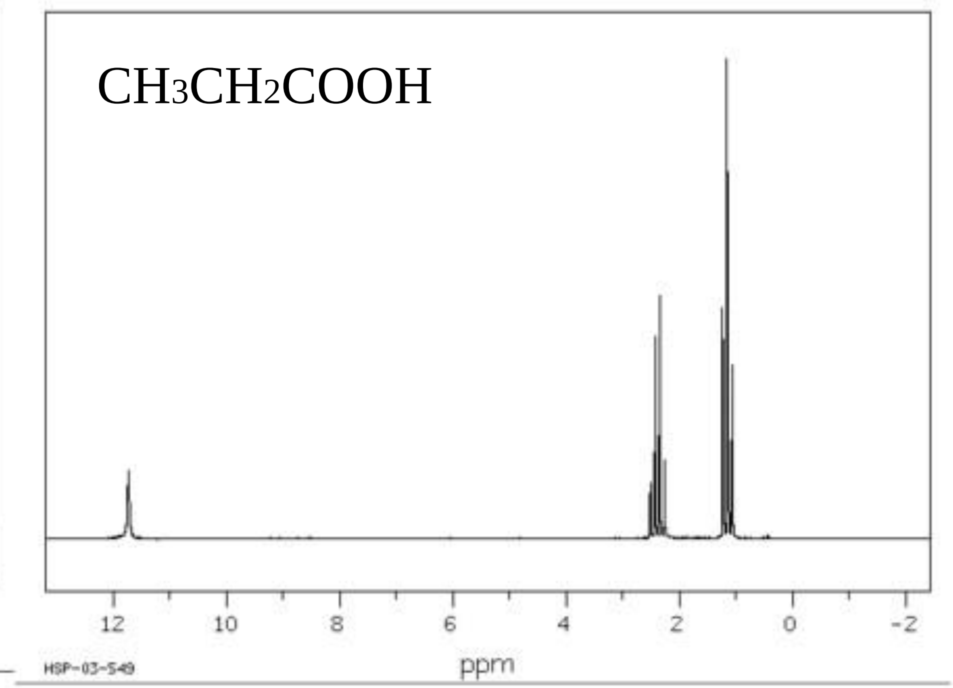
O
3
2
1
OH
CH3
4oC
CH2
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-03-089

B

^{1}H NMR



CH_3COCH_2OH
11 10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-03-522



CH_3CH_2COOH
12 10 8 6 4 2 0 -2
ppm
HSP-03-549