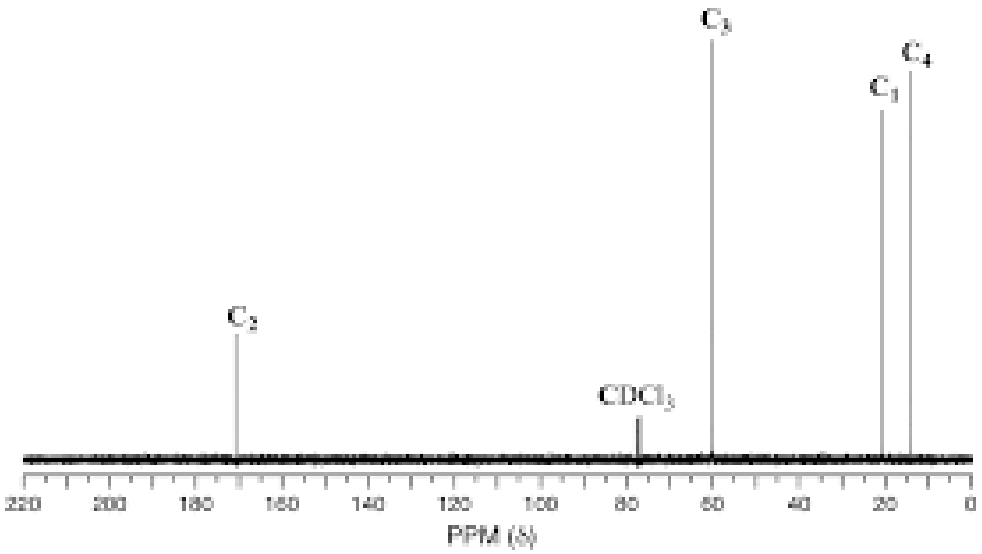
^{13}C NMR Spectroscopy

Gives structural and functional details of a compound
Very useful for determining the structure of unknown compounds
Shows the different magnetic environments of carbon atoms in a compound

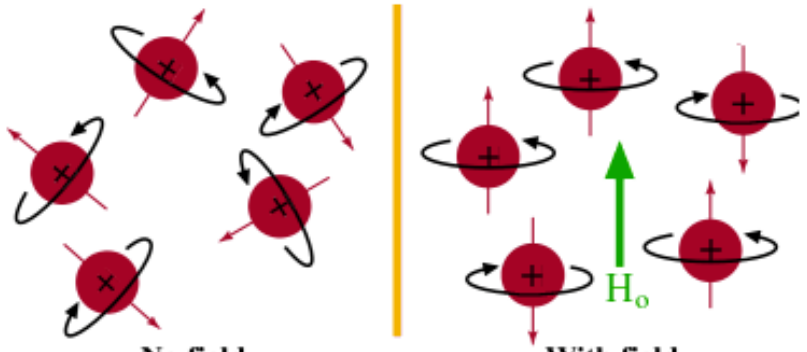


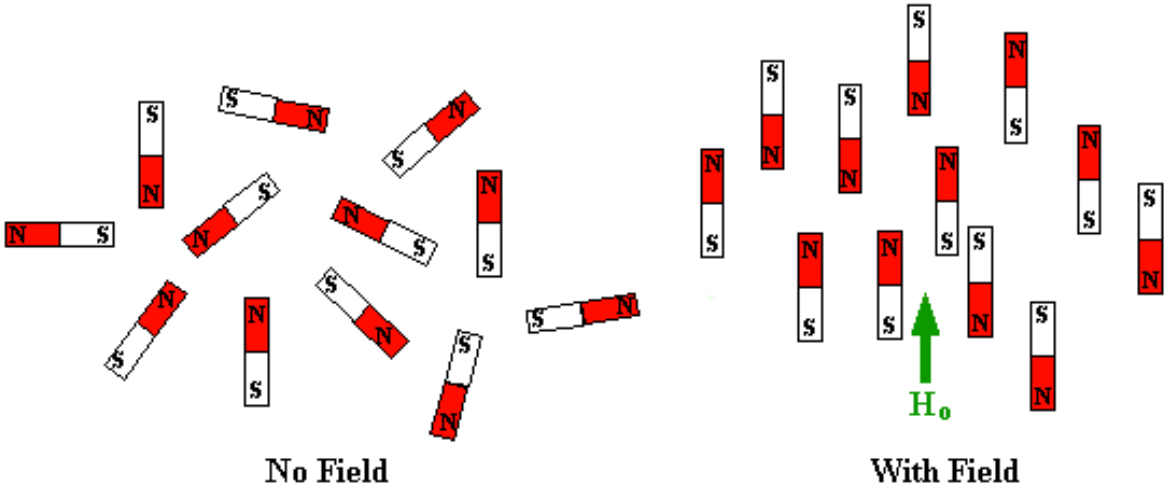
NMR

N	M	R
u	a	e
c	g	s
l	n	o
e	e	n
a	t	a
r	i	n
	c	c
		e

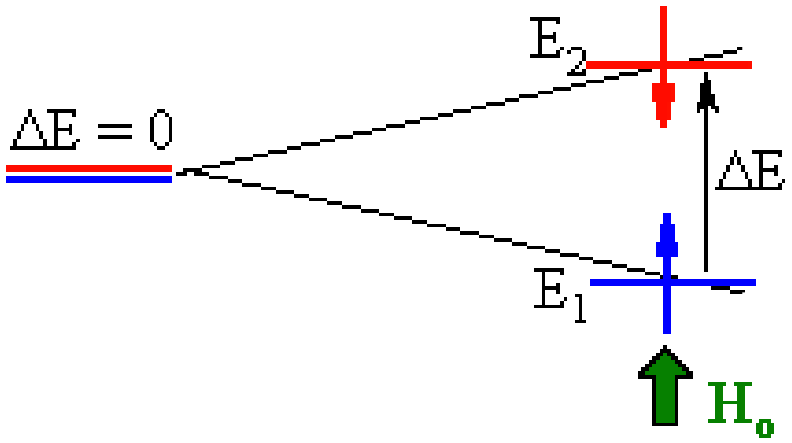
MRI (magnetic resonance imaging)

^{13}C NMR spectroscopy





^{13}C NMR spectroscopy



^{13}C NMR spectroscopy measures the difference in energy between the aligned spin state and unaligned spin state

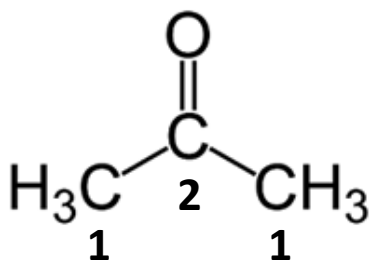
The difference in energy is measured in ppm (parts per million).

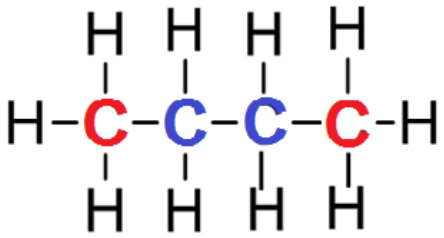
The lower the energy gap the easier it is to flip from one state to another

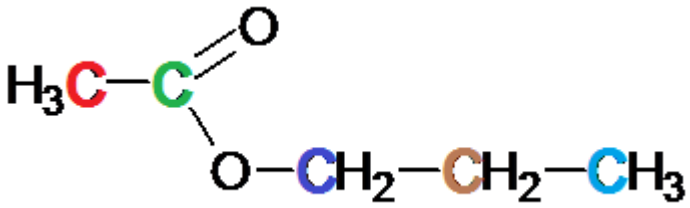
Chemical Environments

^{13}C NMR spectroscopy shows peaks for each of the different chemical environments of the carbon atom in a molecule.

The environment of a carbon atom can be determined by looking at the sequence of bonds the carbon atom has to other atoms. If two carbon atoms have the same bond sequence they will have the same environment.





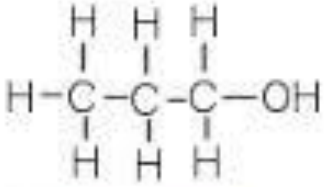


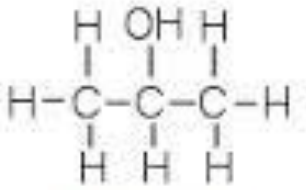
Chemical Environments

The number of chemical environment a molecule has is the number of peaks in the ^{13}C NMR spectrum.

For example: IR has told you that you have an alcohol functional group, but you don't know if the alcohol is propan-1-ol or propan-2-ol. The ^{13}C NMR will allow you to tell the difference.

Number of carbon chemical environments in propan-1-ol:
Number of carbon chemical environments in propan-2-ol:





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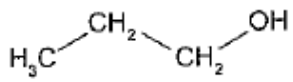
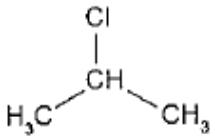
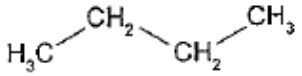
1. Identify the number of chemical environments in the following:

a. 

3

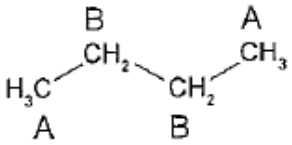
b. 

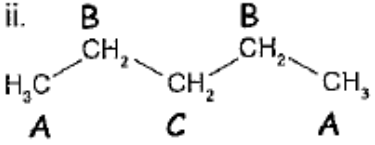
2

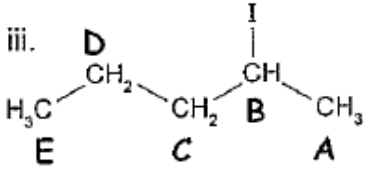
c. 

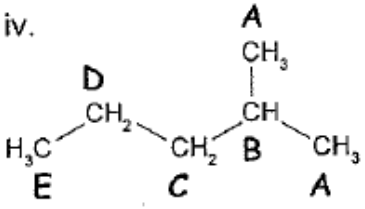
2

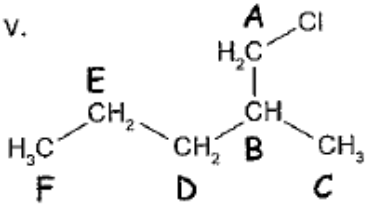
a. Label each carbon with a capital letter (A, B, C…). Any carbons in the same environment should be given the same letter. The first example is done for you.

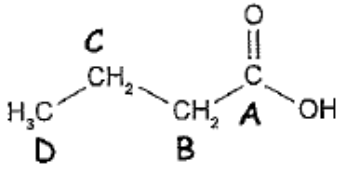
i. 

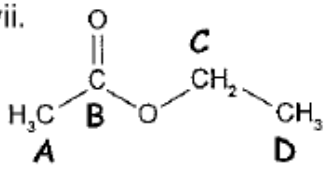
ii. 

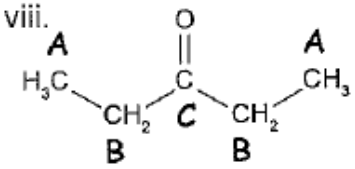
iii. 

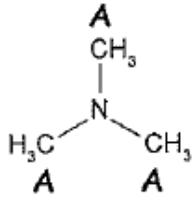
iv. 

v. 

vi. 

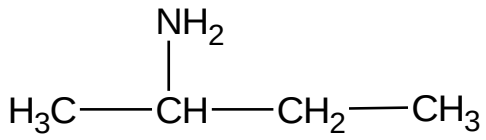
vii. 

viii. 

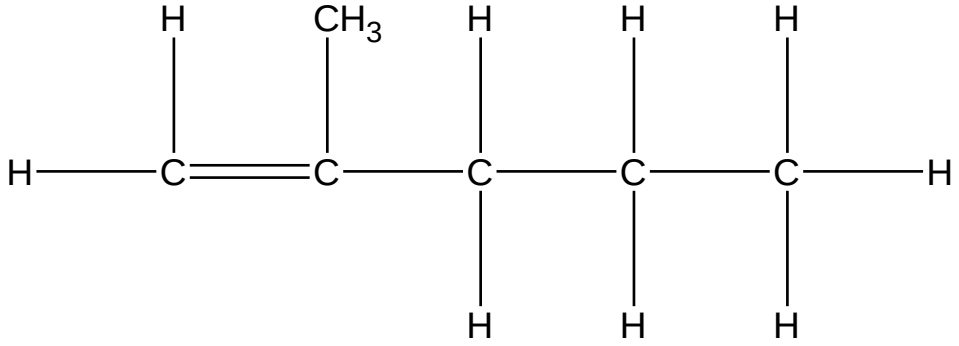
ix. 

Do now:

How many carbon environments will the following compounds have?



3-methylbutanal



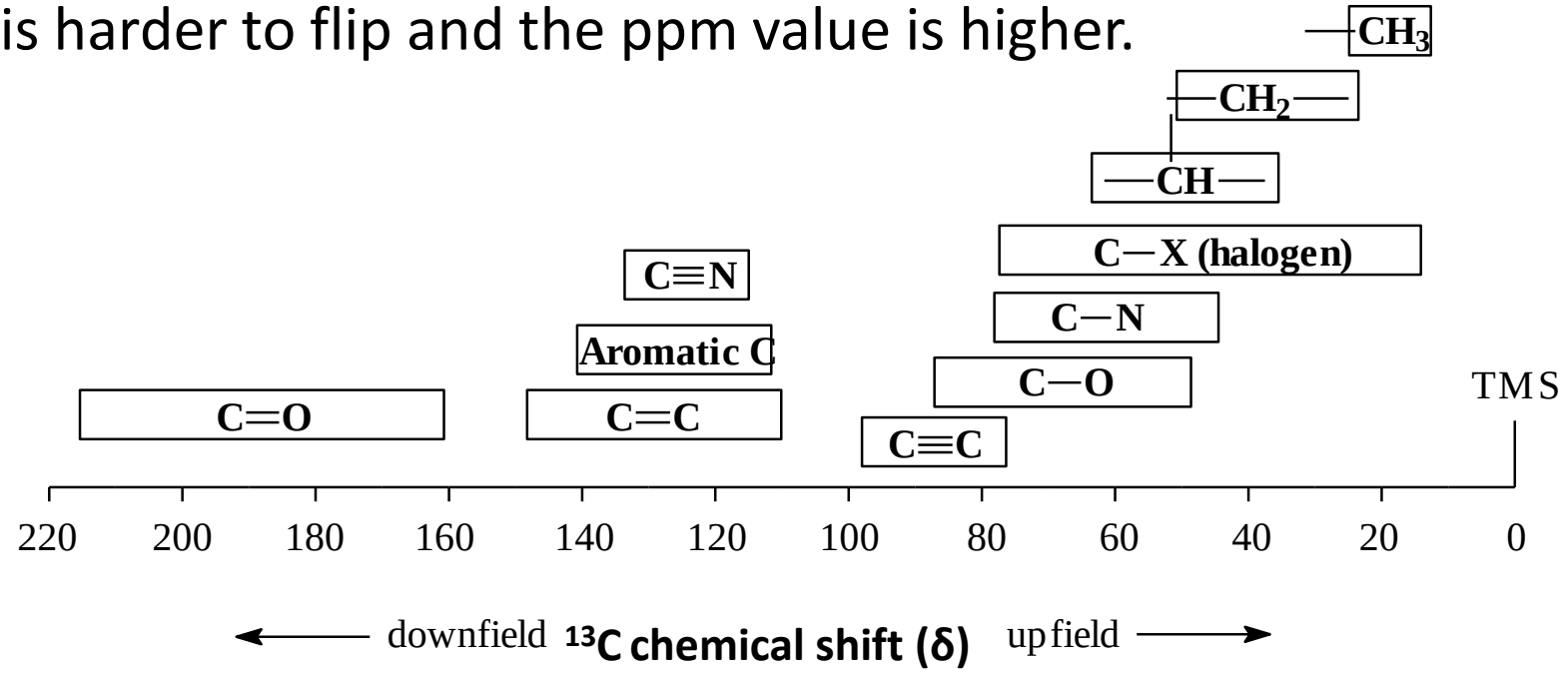
2,4-dichloropentane

pentan-2-one

^{13}C NMR spectroscopy

The position of the peak in a ^{13}C NMR spectrum is determined by the shielding or deshielding effects of other atoms around it.

The less electrons (ie the more electronegative atoms around the carbon) the higher magnetic field the nucleus is exposed to, hence it is harder to flip and the ppm value is higher.



^{13}C NMR spectroscopy

Shielding and deshielding

Shielding and deshielding effects explain the chemical shifts that we observe in the NMR. The closer the ^{13}C nucleus is to an electronegative atom the more deshielded it will be.

Electronegative atoms (like O, Cl, Br etc) or multiple bonds (C=C, C≡C) partially remove electrons from the ^{13}C nucleus. This leaves it exposed to more of a magnetic field and it takes more energy to flip, resulting in a higher chemical shift.

It is not possible to predict the exact position of ^{13}C peaks as they are influenced by the environment around them but we can predict the approximate location.

^{13}C NMR spectroscopy

δ (ppm)	Carbons Associated With This Region
0-15	**C**H_3CH_2-
15-30	**C**H_3-
20-35	-**C**H_2-
30-60	**C**-N, **C**-Cl, **C**-Br, **C**-C=O
50-70	**C**-O
60-90	**C**≡**C**
100-150	**C**=**C**
160-185	**C**=O present in carboxylic acids, esters, acyl chlorides and amides
180-220	**C**=O present in aldehydes and ketones

Using this information could ^{13}C NMR distinguish between the following functional groups?

Acid chlorides and aldehydes

Ketones and amides

^{13}C NMR spectroscopy

δ (ppm)	Carbons Associated With This Region
0-15	**C**H_3CH_2-
15-30	**C**H_3-
20-35	-**C**H_2-
30-60	**C**-N, **C**-Cl, **C**-Br, **C**-C=O
50-70	**C**-O
60-90	**C**≡**C**
100-150	**C**=**C**
160-185	**C**=O present in carboxylic acids, esters, acyl chlorides and amides
180-220	**C**=O present in aldehydes and ketones

This information is only a guide. It is extremely difficult to predict exactly the chemical shift of carbon atoms in a compound.

Carbon atoms in the same environment will always have the same chemical shift.

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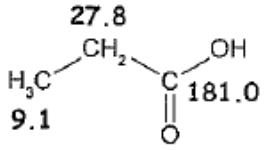
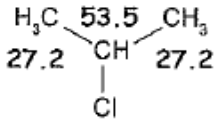
1. Use the data tables and what you have learnt about chemical environments to assign the chemical shifts supplied to the carbons of the following substances.

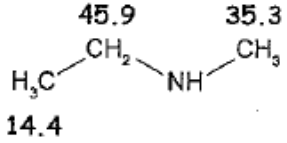
a. 9.1, 27.8, 181.0



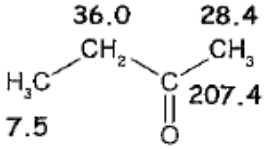
b. 27.2, 53.5



c. 14.4, 35.3, 45.9



d. 7.5, 28.4, 36.0, 207.4



2. A student has four samples (a-d), that are either: an **aldehyde**, an **ester**, a **chloroalkane** or an **alkene**. Use the characteristic (distinct) shifts given for a-d to work out which is which.

a. 170.0 **ester**

b. 55.8 **chloroalkane**

c. 143.1 **alkene**

d. 202.8 **aldehyde**

3. A student analyses four samples and gets the following characteristic peaks:

206.7 **172.2** **47.4** **90.1**

Which peak is likely to belong to the following compounds?

a. bromoalkane **47.4**

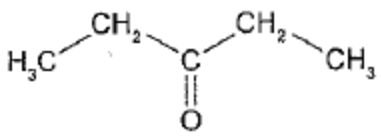
b. alkyne **90.1**

c. ketone **206.7**

d. amide **172.7**

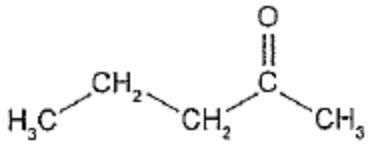
Use your knowledge to evaluate which set of shifts goes with which compound. Justify your answer.

a. pentan-3-one



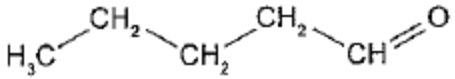
iii. 8.0, 35.5, 210.9

b. pentan-2-one



ii. 13.5, 17.5, 29.3, 45.2, 206.6

c. pentanal



i. 13.8, 22.4, 24.3, 43.6, 201.3

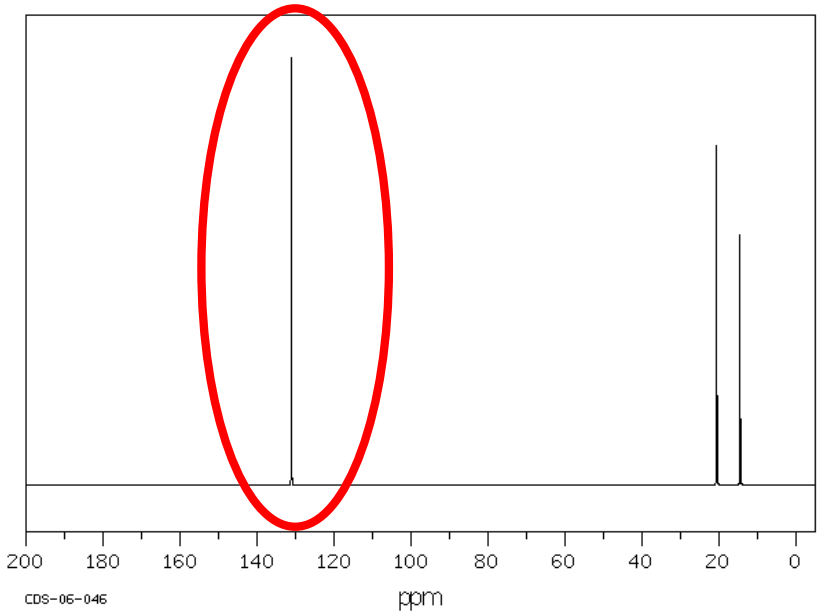
Explanation:

Pentan-3-one is symmetric and therefore has three chemical environments. This means it is the set iii. In addition to the C=O (180-220), pentan-2-one will have two deshielded peaks (CH_2 and CH_3 attached to C=O), one CH_2 and one CH_3. Conversely pentanal will have one deshielded peak, aside from C=O, two CH_2's and one CH_3. In addition to a C=O signal, set ii has two peaks with high chemical shift and two with low chemical shift whereas set i has one high chemical shift two mediums and a low chemical shift. Therefore set ii fits pentan-2-one and set i fits pentanal.

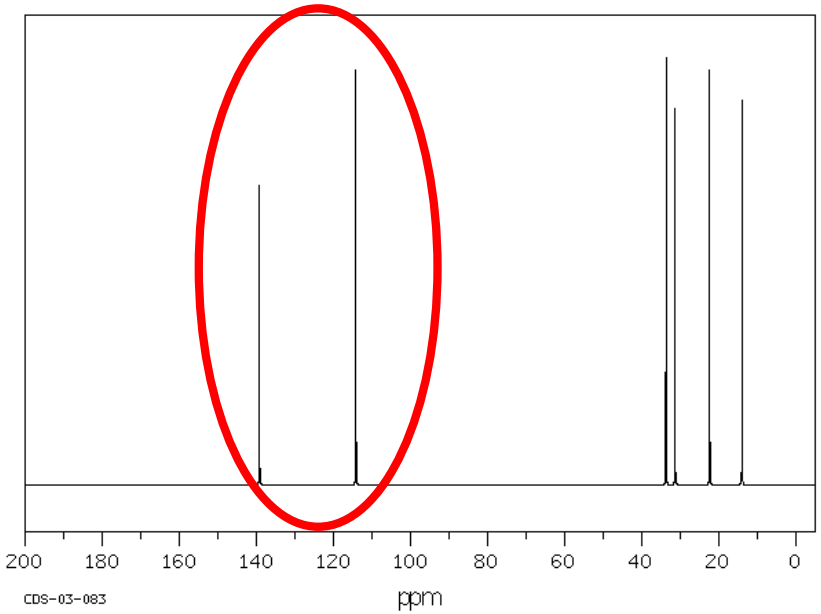
^{13}C NMR spectroscopy

Comparing hex-1-ene to hex-3-ene.

How many peaks would you expect to see in the ^{13}C NMR spectra of the above compounds? Why?



hex-3-ene

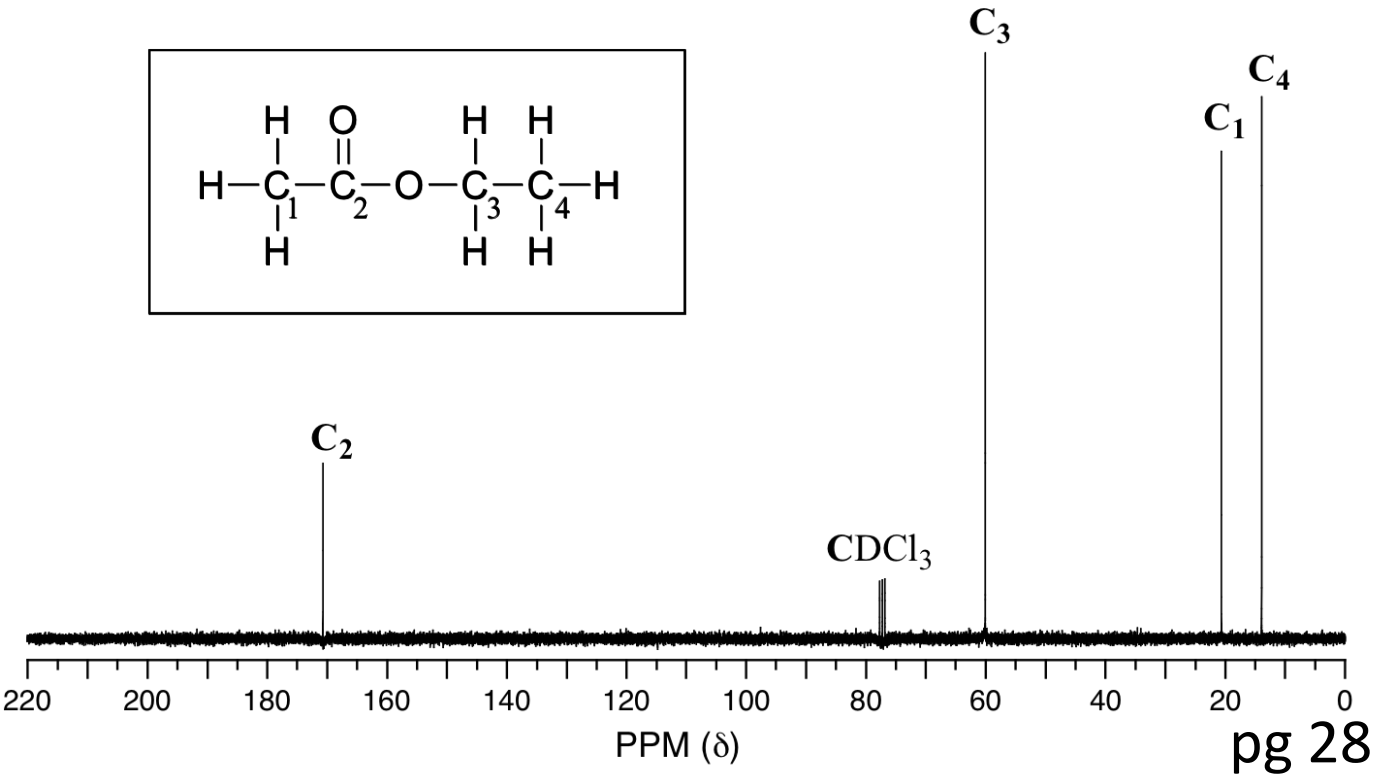


hex-1-ene

^{13}C NMR spectroscopy

How many different carbon environments would ethyl ethanoate have?

Where would you expect the peaks to be in the spectrum?



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Match the following six compounds to the following six ^{13}C NMR spectra.

propanoic acid

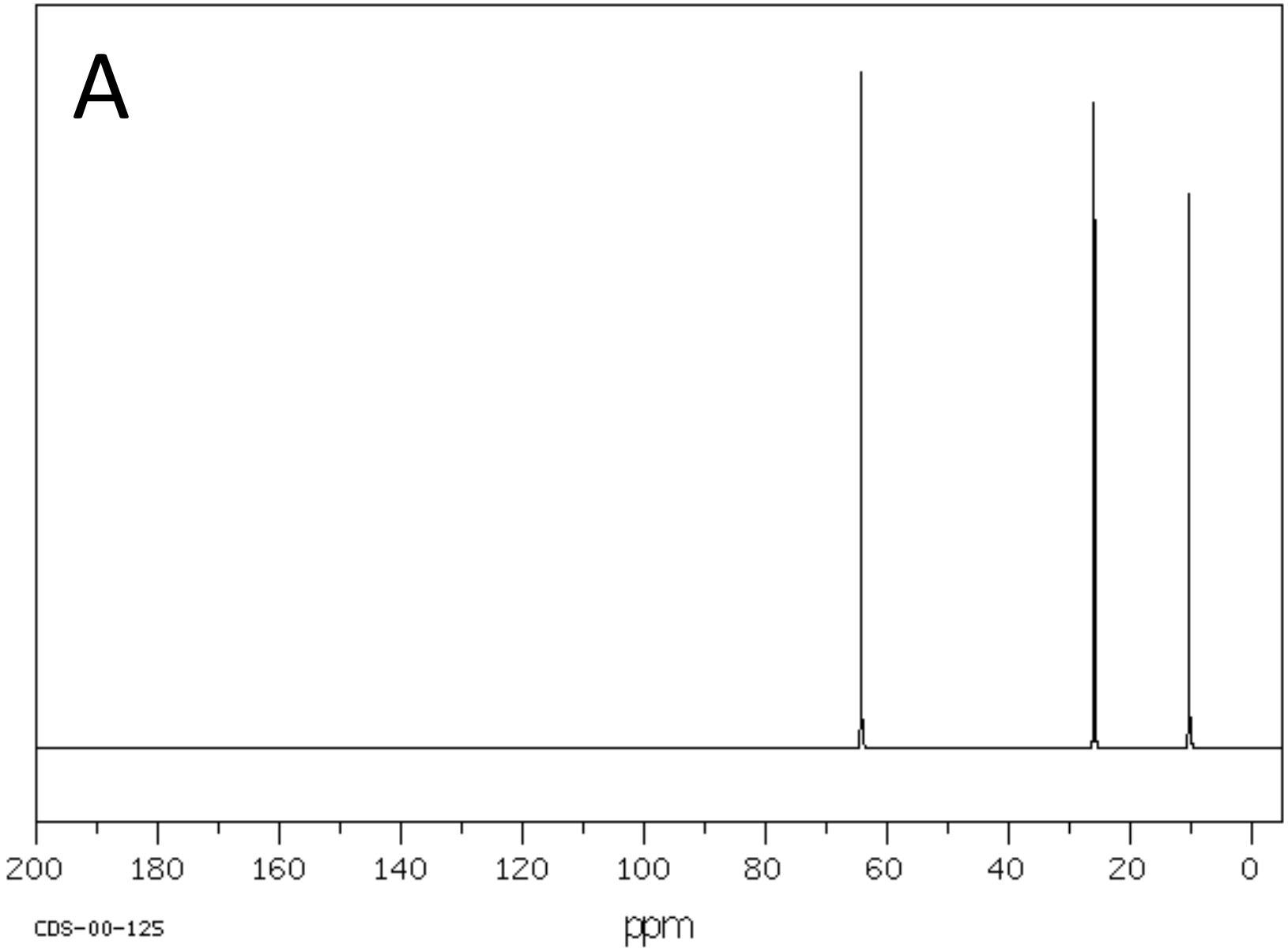
propanone

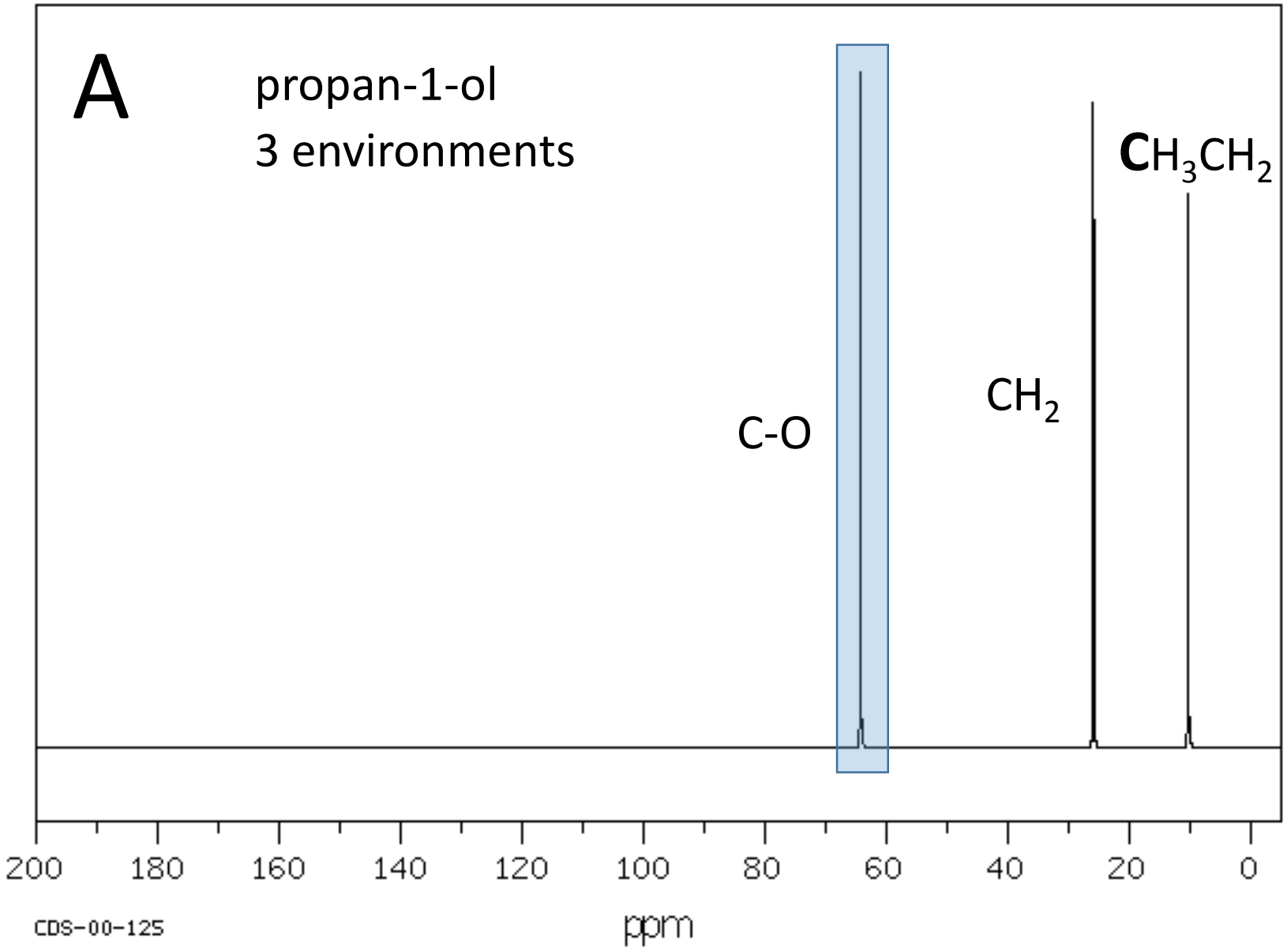
propanal

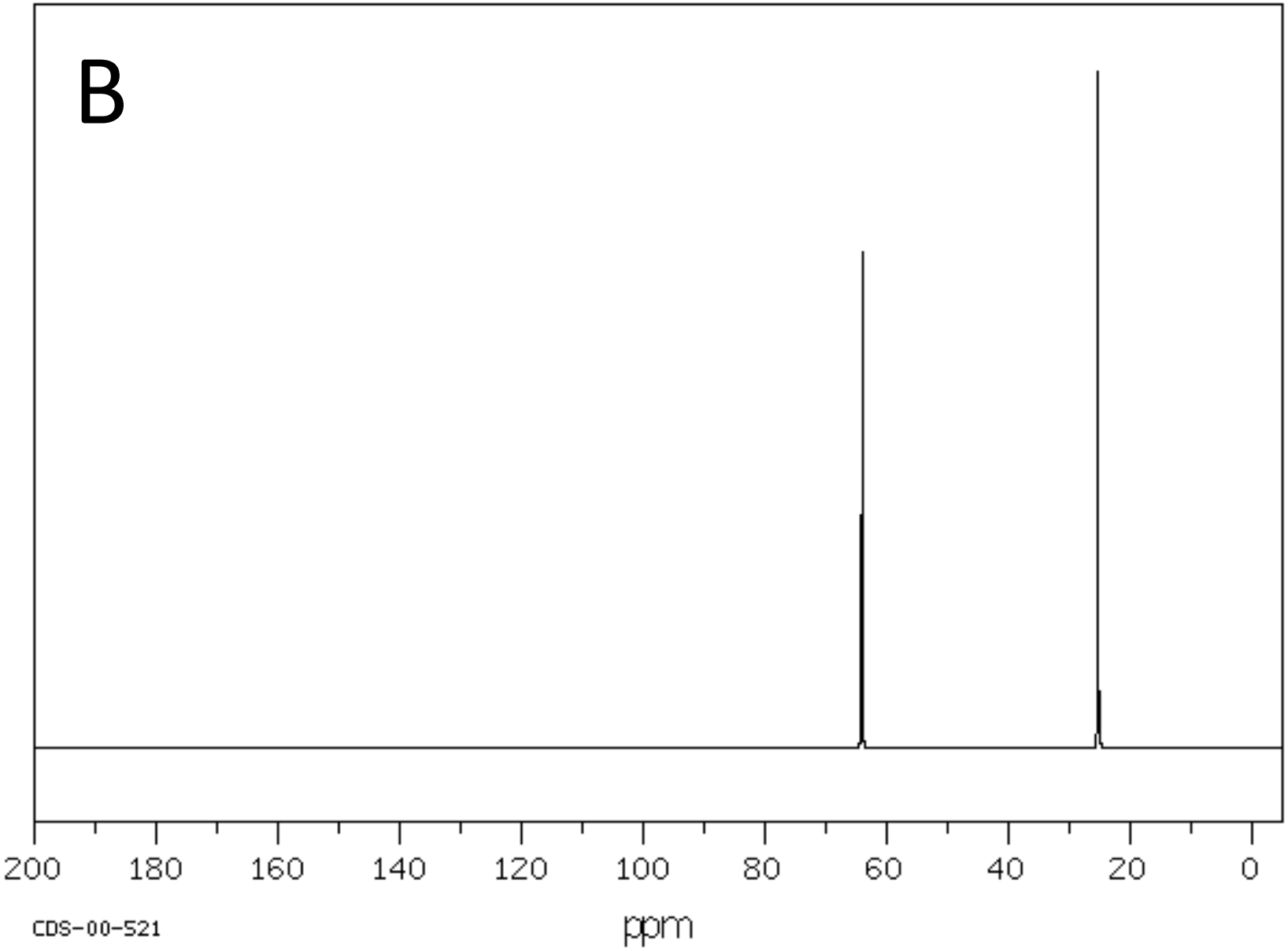
propan-1-ol

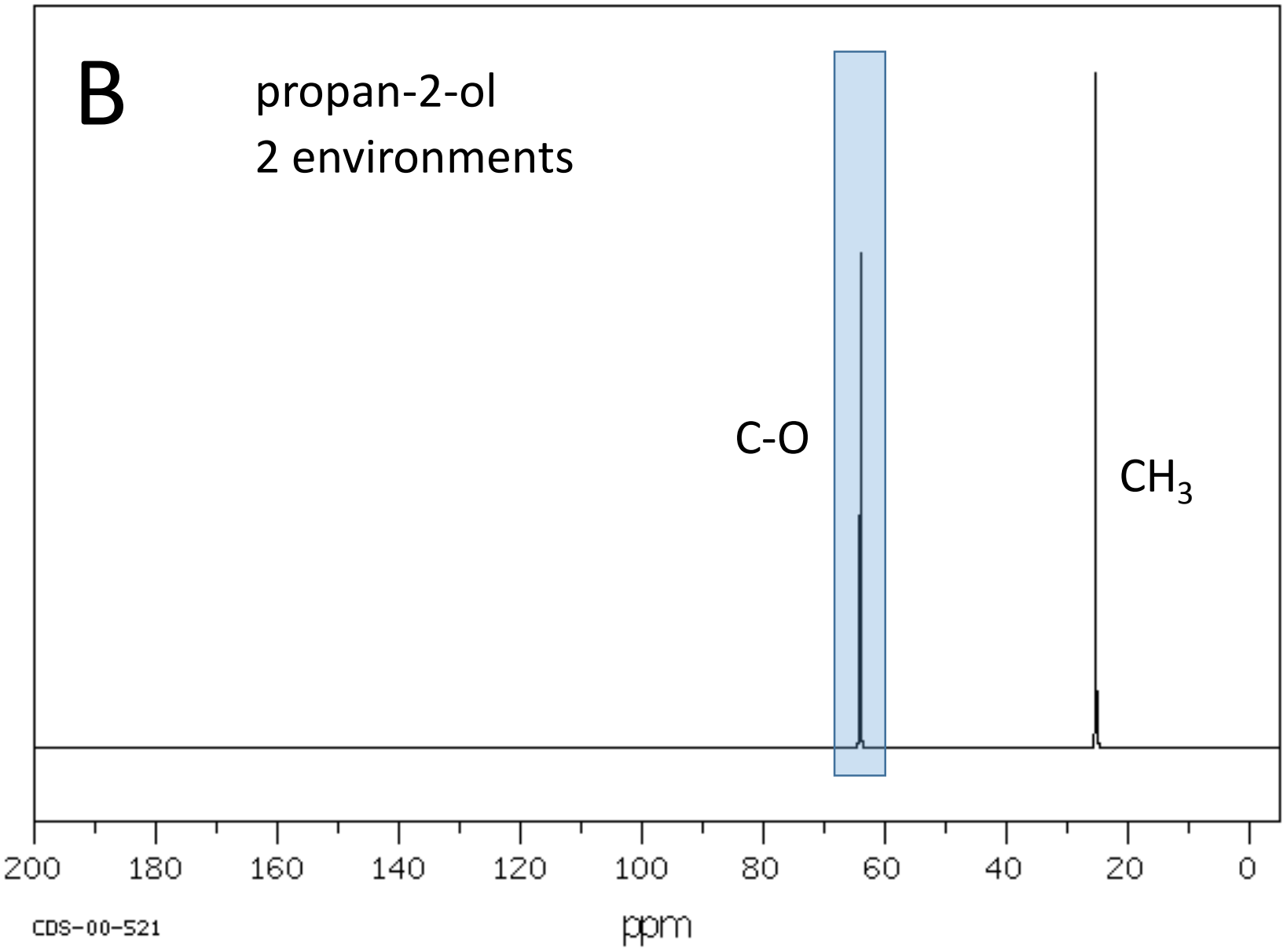
propan-2-ol

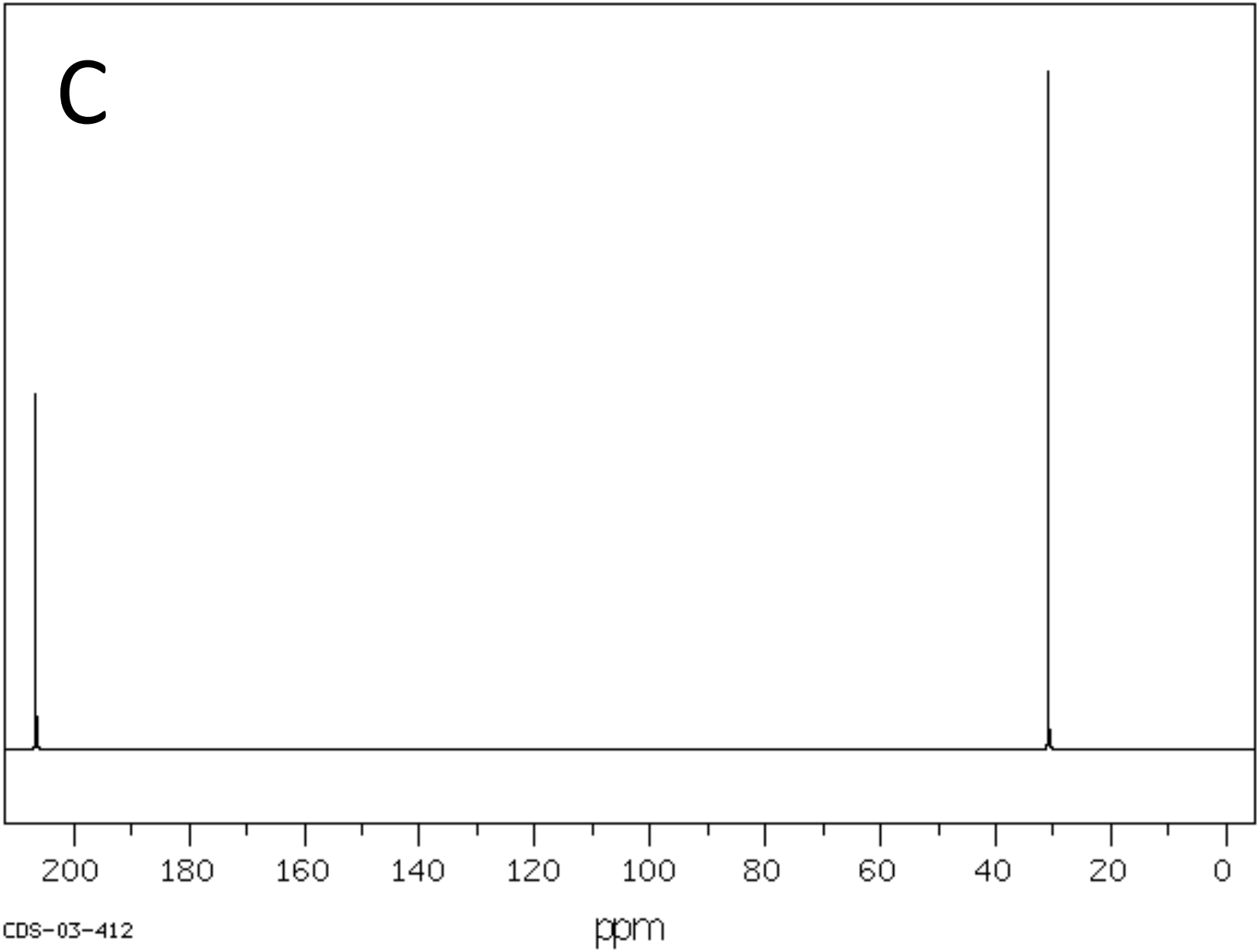
methyl ethanoate

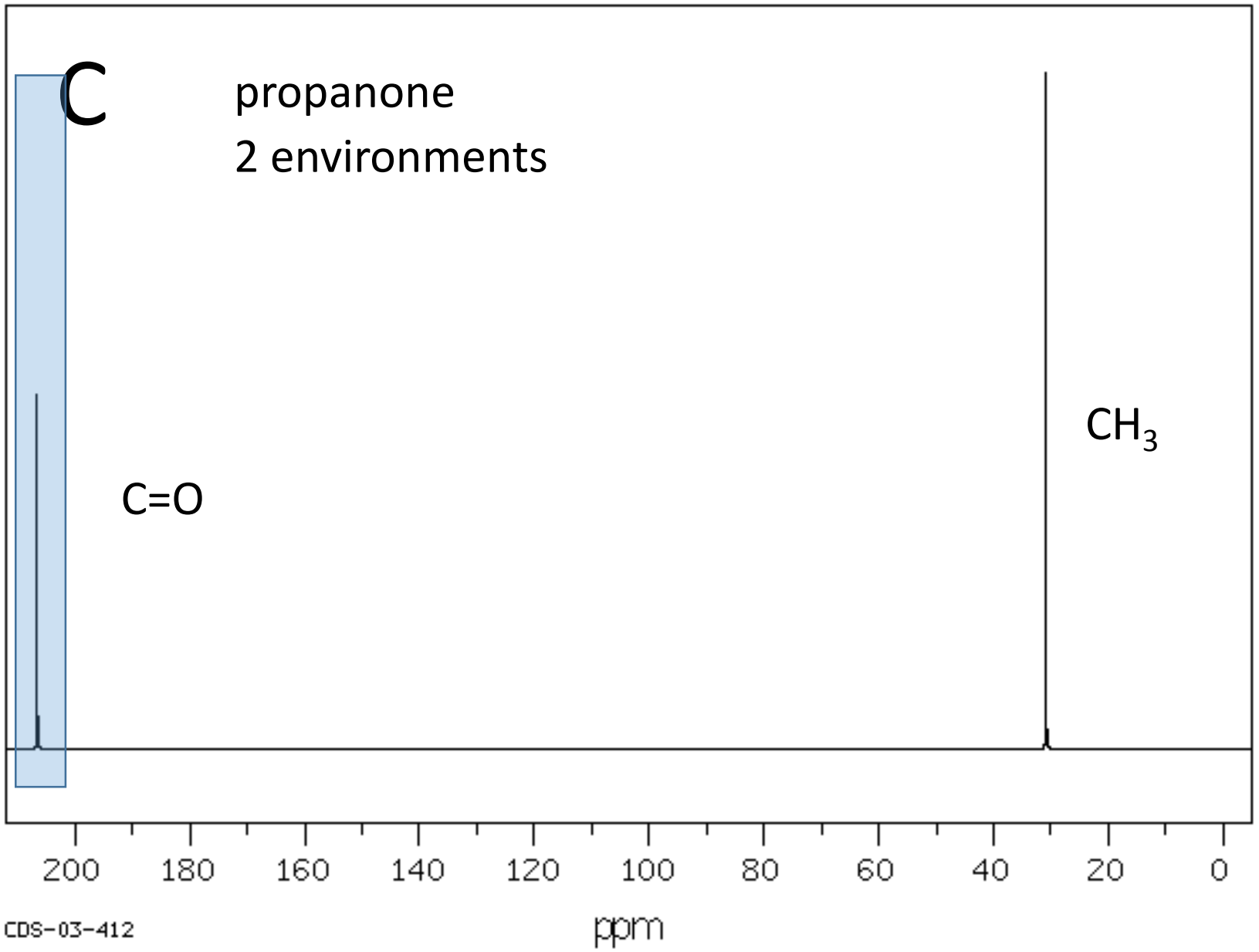

A
200
180
160
140
120
100
80
60
40
20
0
CDS-00-125
ppm

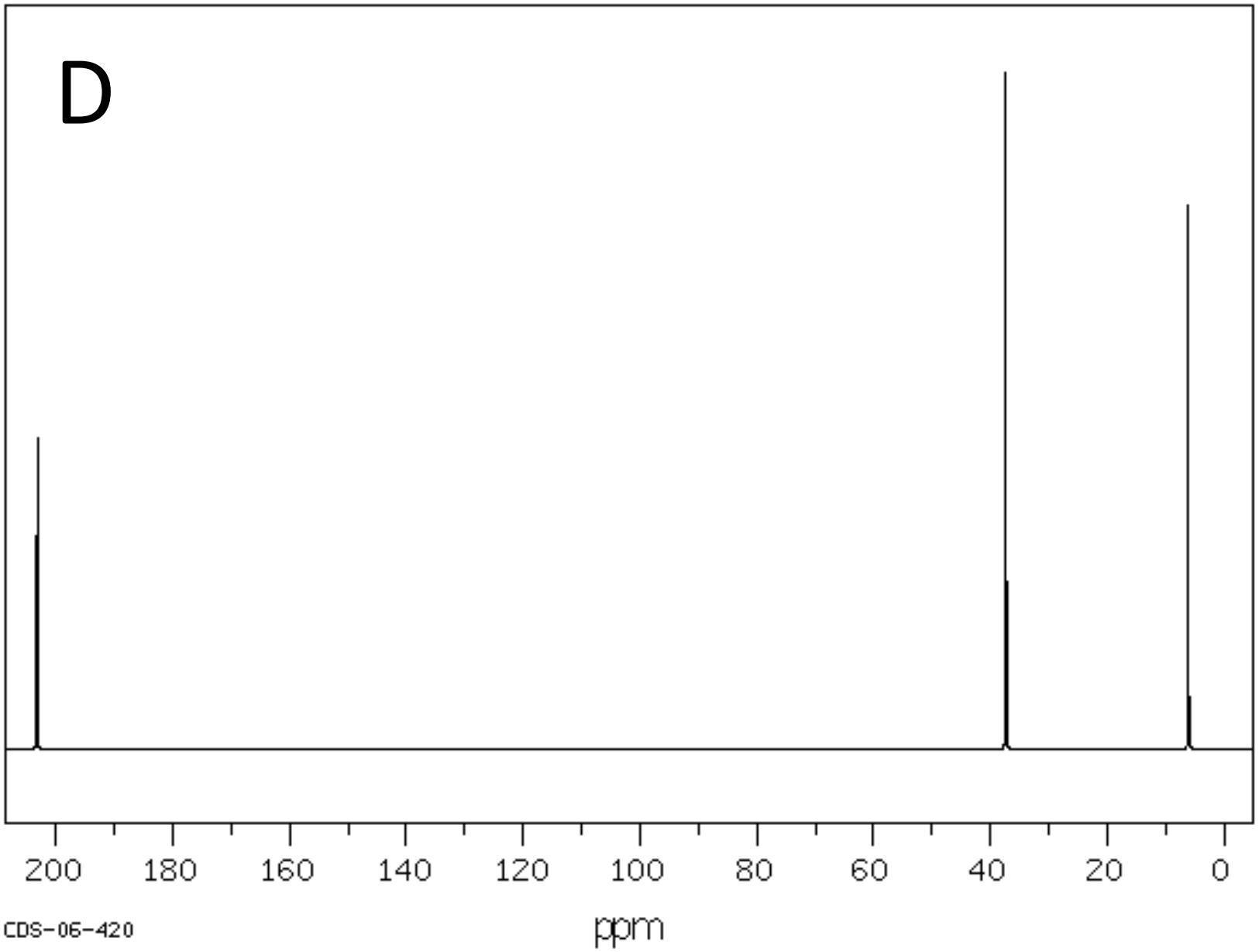

A
propan-1-ol
3 environments
C-O
CH2
CH3CH2
200
180
160
140
120
100
80
60
40
20
0
CDS-00-125
ppm

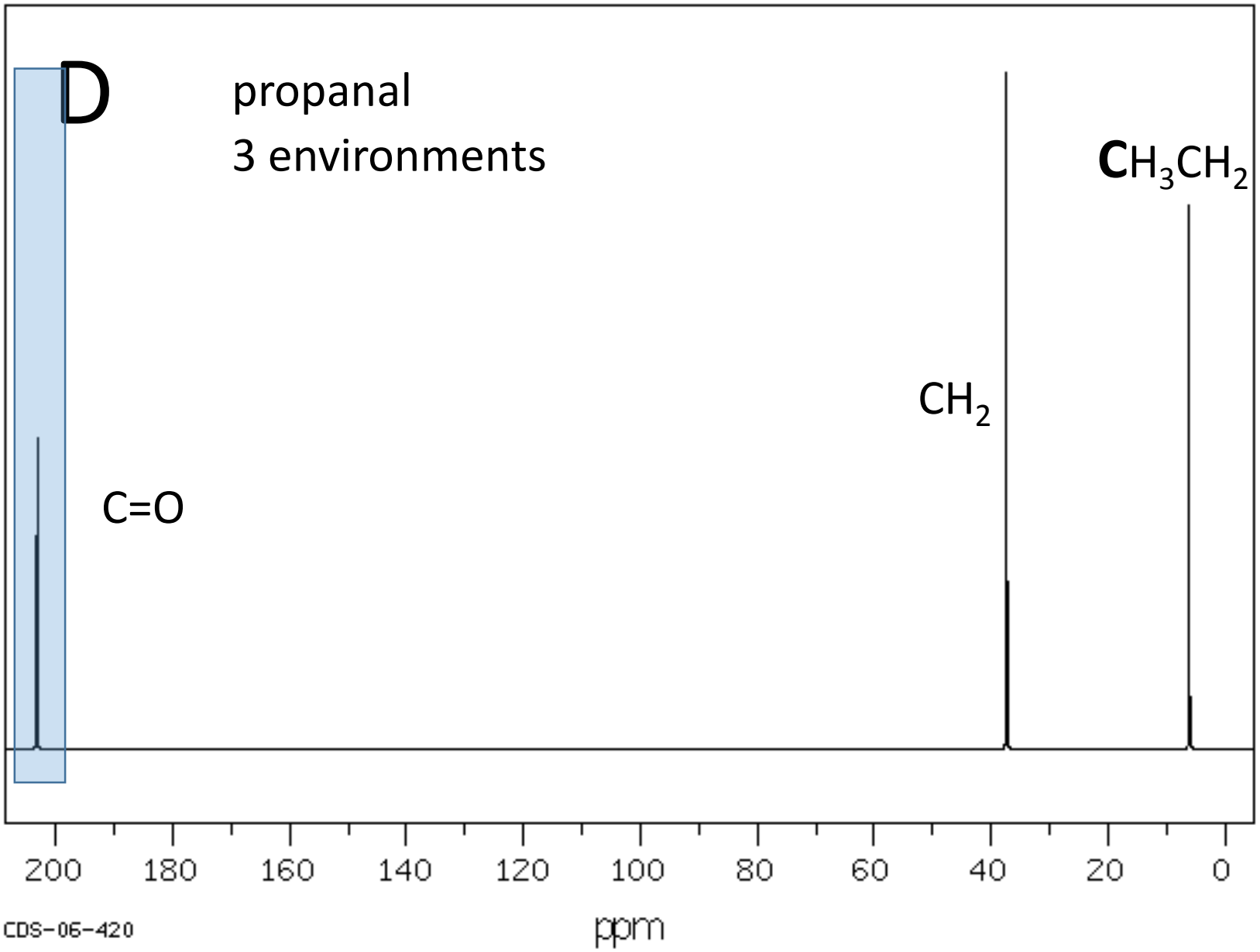

B
200
180
160
140
120
100
80
60
40
20
0
CDS-00-521
ppm

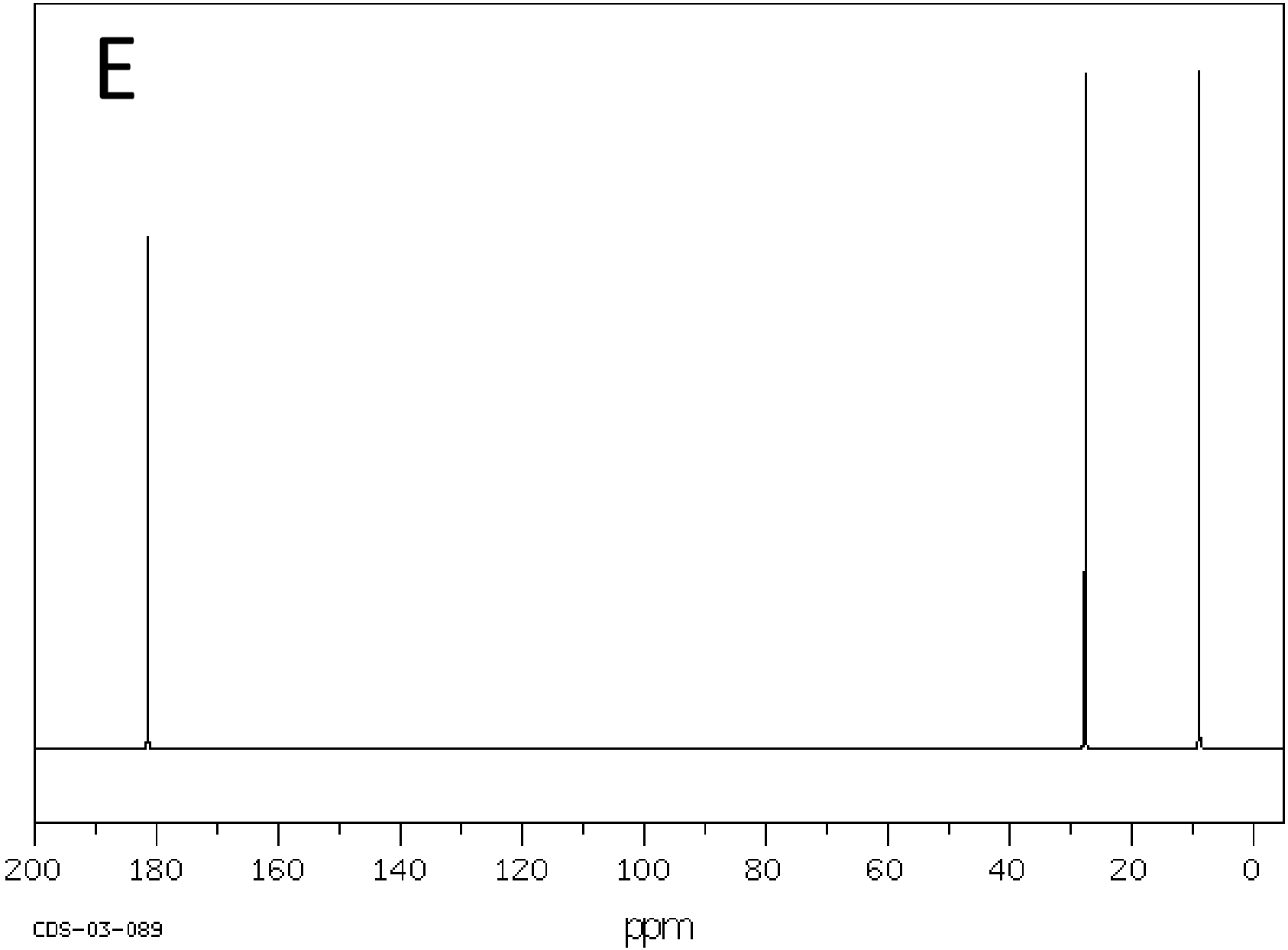

B
propan-2-ol
2 environments
C-O
CH3
200
180
160
140
120
100
80
60
40
20
0
CDS-00-521
ppm

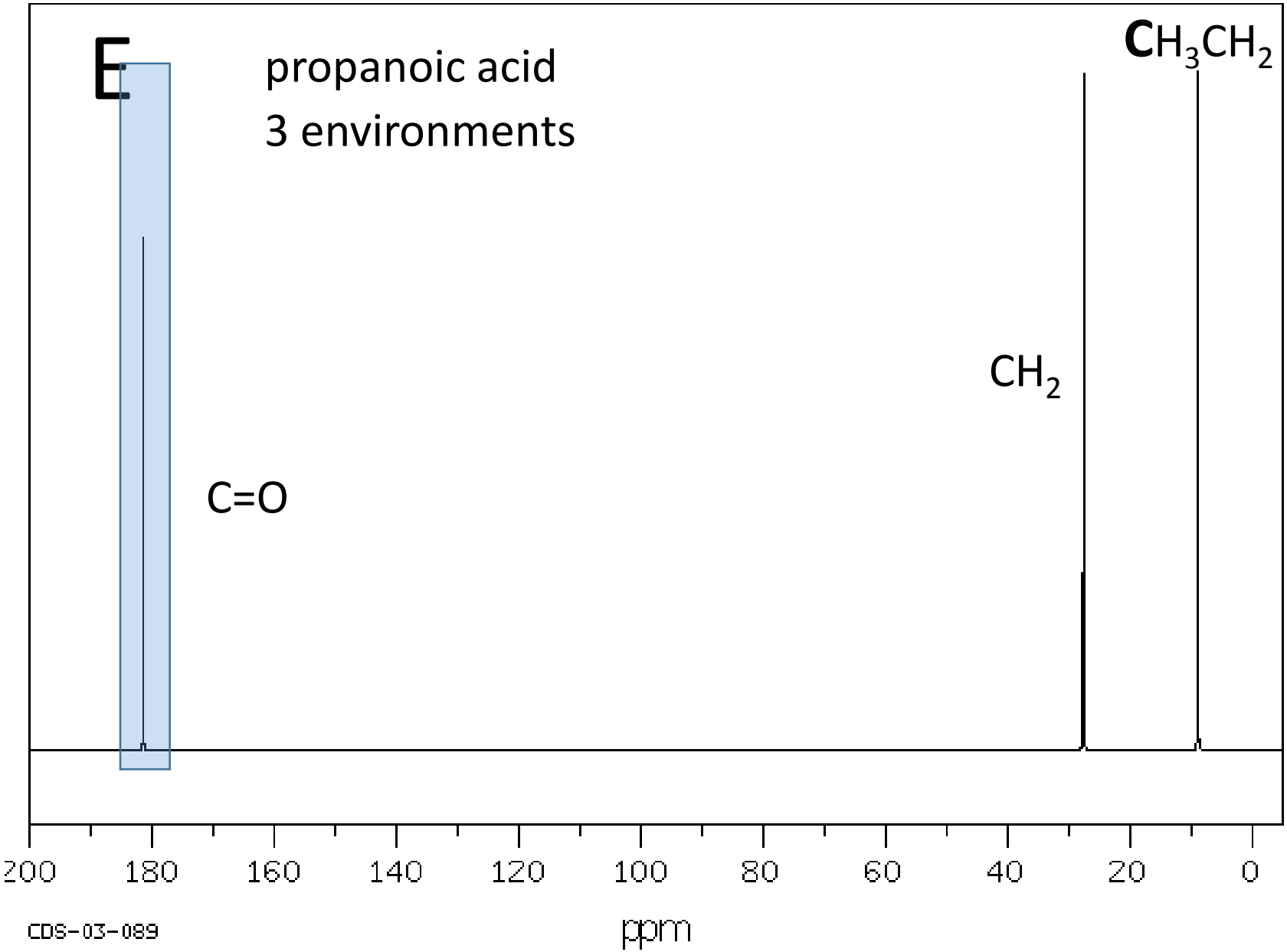

C
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-03-412

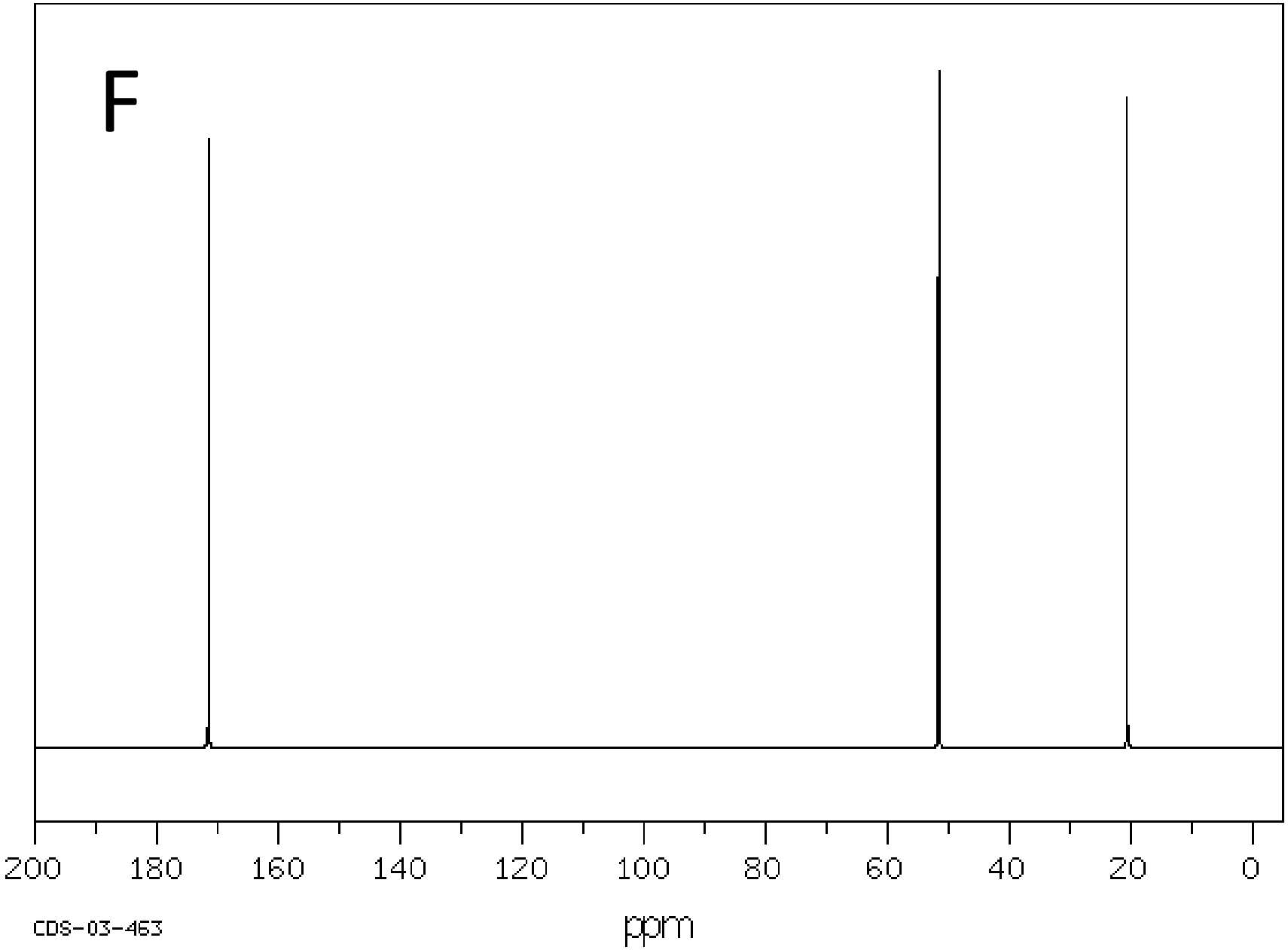

C
propanone
2 environments
C=O
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-03-412

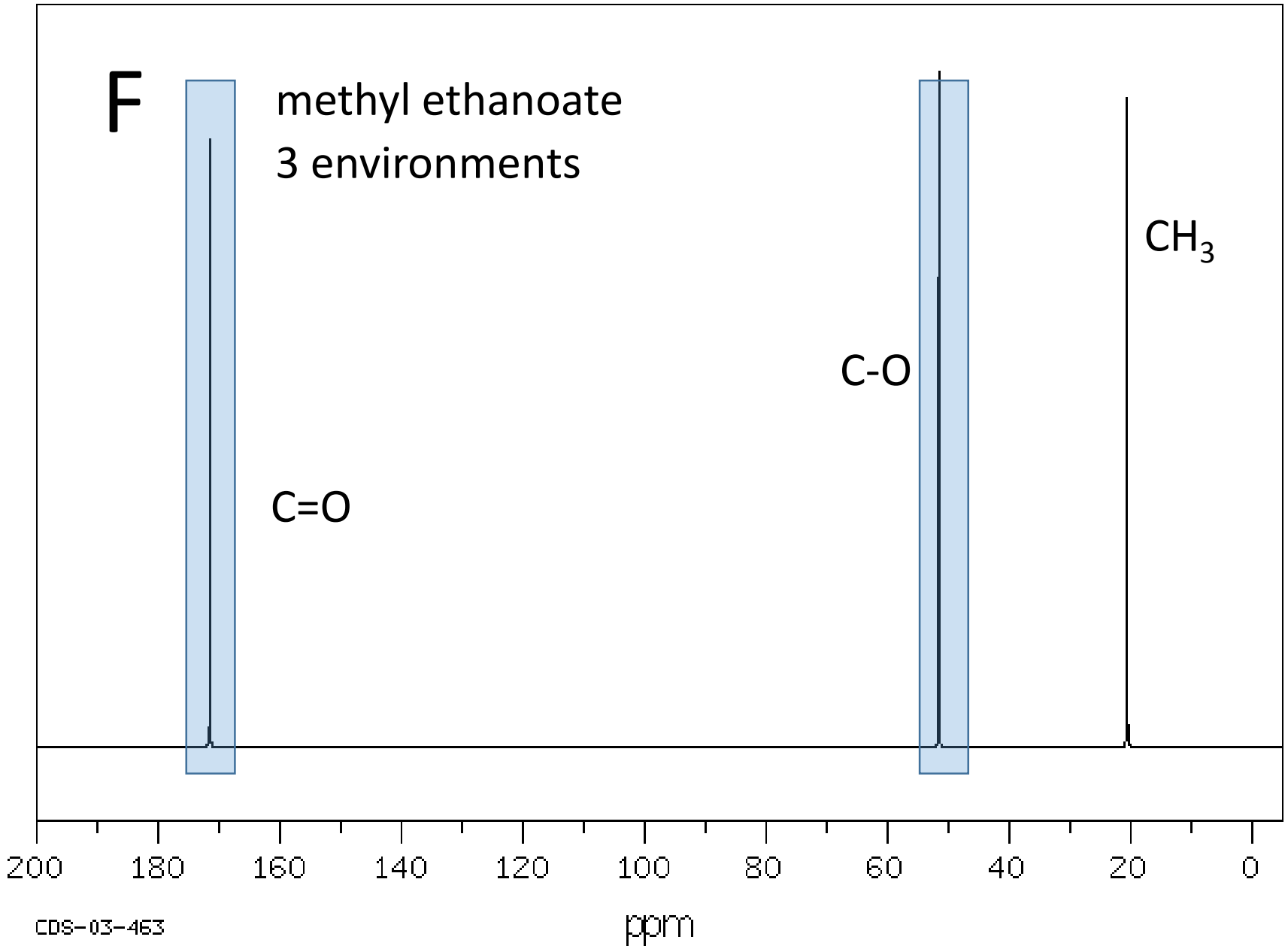

D
200
180
160
140
120
100
80
60
40
20
0
ppm
CDS-06-420


D
propanal
3 environments
CH3CH2
CH2
C=O
200
180
160
140
120
100
80
60
40
20
0
CDS-06-420
ppm


E
200
180
160
140
120
100
80
60
40
20
0
CDS-03-089
ppm


E
propanoic acid
3 environments
CH3CH2
CH2
C=O
200
180
160
140
120
100
80
60
40
20
0
CDS-03-089
ppm


F
200
180
160
140
120
100
80
60
40
20
0
CDS-03-463
ppm


F
methyl ethanoate
3 environments
C=O
C-O
CH3
200
180
160
140
120
100
80
60
40
20
0
CDS-03-463
ppm