C1403 NMR Homework

The IR and proton (1H NMR) and carbon (13C NMR) spectra of the molecules of IR Tutor are given along with correlation tables.

This assignment will challenge you to interpret NMR spectra by correlating spectra data with molecular structure.

The following IR spectra that appear in IR Tutor are shown on the following slides together with the 1H NMR and the 13C NMR spectra of the same compounds. Correlation Tables for the IR, 1H NMR and 13C NMR are given. In this homework exercise you should try to make sense out of the 1H NMR and 13C NMR spectra based on the empirical approach that we used for the interpretation of IR spectra.

The different signals in the 1H NMR spectra correspond to signals for chemically different protons. The intensity of the signal is roughly proportional to the number of protons in the structure.

The different signals in the 13C NMR spectra correspond to signals for chemically different carbon atoms. The intensity of the signal is roughly proportional to the number of carbons in the structure.

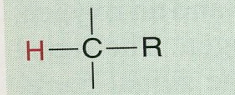
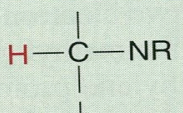
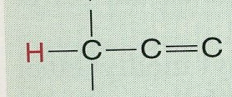
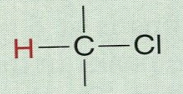
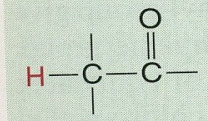
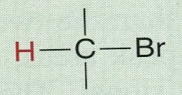
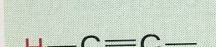
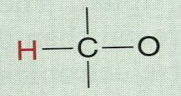
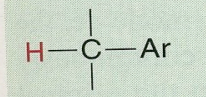
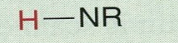
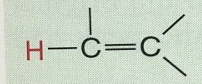
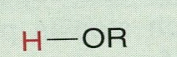
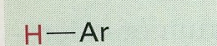
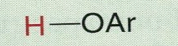
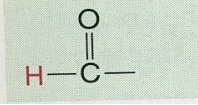
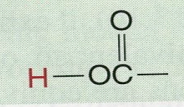
Some Important and Characteristic Infrared Absorption Frequencies and Wavelengths for Some Common Stretching Motions

Atom Group	Typical of	Frequency (cm^{-1})	Wavelength (μ)
O-H (free)	Alcohols (dilute)	3550-3650 cm^{-1}	2.8 μ
O-H (H bonded)	Alcohols (concentrated) Carboxylic acids	3200-3400 cm^{-1}	3.0 μ
C≡C—H	Acetylene (CH)	3300 cm^{-1}	3.0 μ
C=C—H	Benzene (CH), Ethylene (CH)	3010-3100 cm^{-1}	3.3 μ
C—C—H	Ethane (CH)	2950-3000 cm^{-1}	3.5 μ
C≡C	Acetylene	2100-2260 cm^{-1}	4.5 μ
C≡N	Nitriles	2000-2300 cm^{-1}	4.5 μ
C=O	Carbonyl	1650-1750 cm^{-1}	5.5- 6.0 μ
C=C	Alkene	1620-1680 cm^{-1}	6.0 μ
C—C	Alkane	600-1500 cm^{-1}	6.7-17 μ
C—O	Alcohols, Ethers	1000-1300 cm^{-1}	10-7.7 μ

In general we will only be using the data in an IR spectrum for stretching vibrations which have energies higher than 1620 cm^{-1}. Although the bands at lower energy are known and assigned, the region below 1620 cm^{-1} is very congested with single bond stretches of two heavy atoms (see C-C and C-O in table) and C-H bends and are beyond the scope of what we want to do.

NMR units are ppm (parts per million). We discuss where this ppm unit comes from in class.

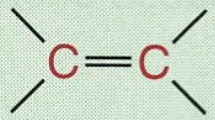
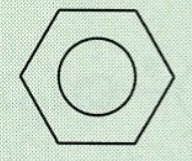
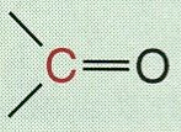
TABLE 13.1
Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
	0.9–1.8		2.2–2.9
	1.6–2.6		3.1–4.1
	2.1–2.5		2.7–4.1
	2.5		3.3–3.7
	2.3–2.8		1–3†
	4.5–6.5		0.5–5†
	6.5–8.5		6–8†
	9–10		10–13†

These are the signals of protons (1H NMR). We think of the position (in ppm) of the NMR signals in the same way we viewed the frequency of IR signals. The 1H NMR signals are characteristic of certain types of protons in molecules

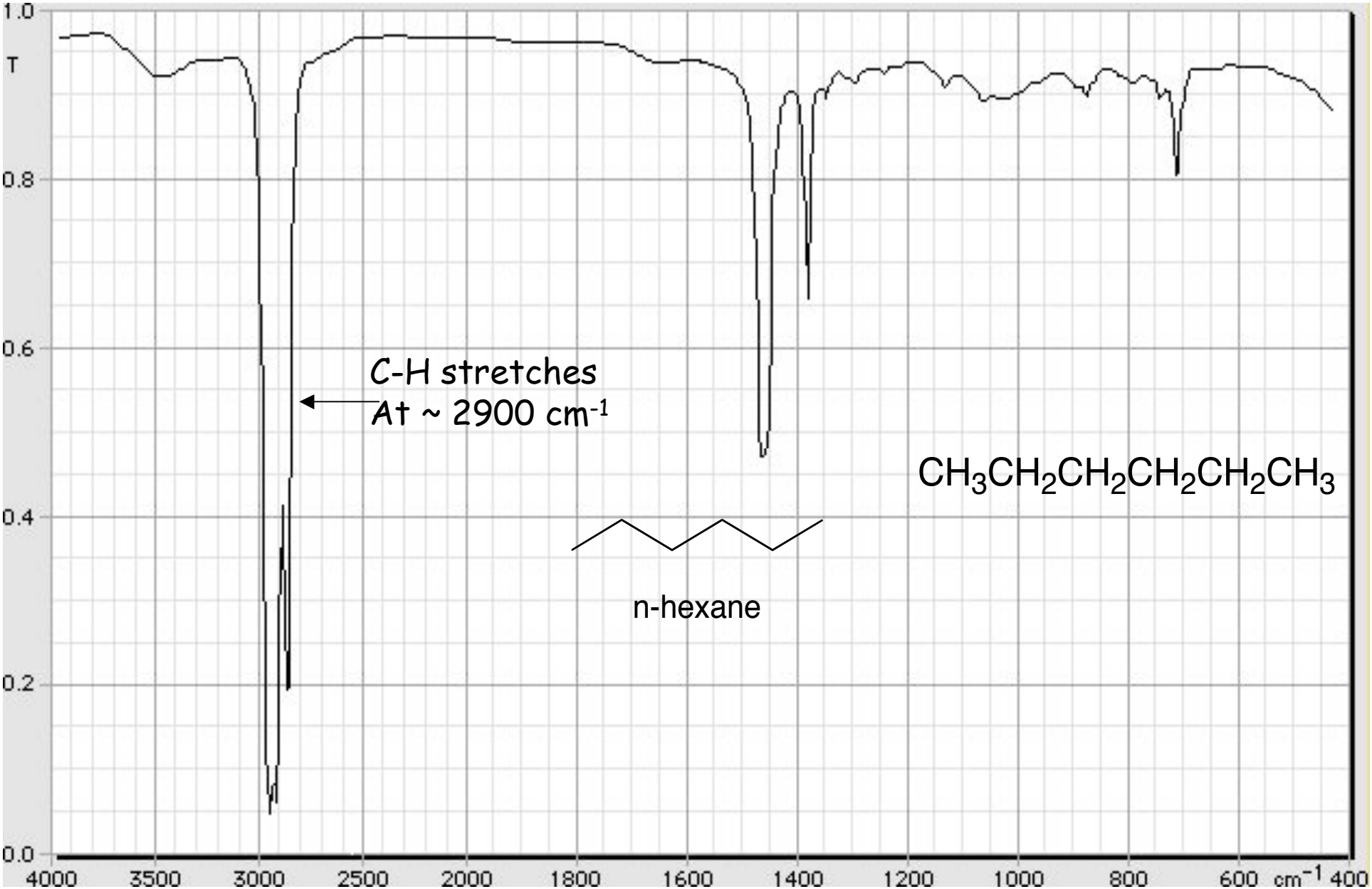
TABLE 13.3

Chemical Shifts of Representative Carbons

Type of carbon	Chemical shift (δ) ppm*	Type of carbon	Chemical shift (δ) ppm*
RCH_3	0–35		100–150
R_2CH_2	15–40		
RCH_2Br	20–40		110–175
R_3CH	25–50		
RCH_2Cl	25–50		
RCH_2NH_2	35–50		190–220
RCH_2OH	50–65		
$-C\equiv C-$	65–90		

These are the position of the signals of carbon atoms (13C) in ppm. We think of the position of a NMR signal in ppm in the same way we viewed the frequency of IR signals. The 13C NMR signals are characteristic of certain types of carbon atoms in molecules.

Example: n-hexane. You've seen the IR and have considered the C-H strecthes

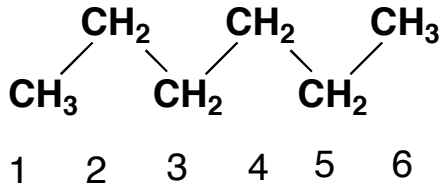


Now let's consider the 1H (proton) and 13C (carbon) NMR spectra of n-hexane (slide 9) .

The 1H NMR shows the signals of ALL of the protons of which a molecular structure is composed. The position of the signal depends on the chemical environments of the electrons so 1H NMR provides information on molecular structure of any molecules containing X-H bonds.

The 13 C NMR shows the signals of ALL of the carbons of which a molecular structure is composed. The position of the signal depends on the chemical environments of the carbon atoms so 13C NMR provides information on organic molecules.

Now consider the structure of n-hexane below. How many different kinds of protons and carbon atoms does the structure suggest?

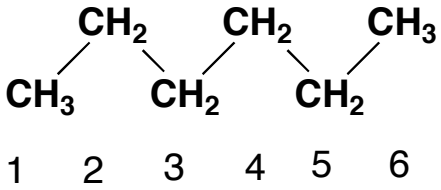


First consider the protons: there are three different kinds of protons: the CH_3 protons on C_1, the CH_2 protons on C_2 and the CH_2 protons on C_3. We note that C_1 is equivalent to C_6, C_2 is equivalent to C_5 and C_3 is equivalent to C_4.

We expect to see three signals in the 1H NMR of n-hexane (slide 9) for the three different types of protons. We can't predict where they will be but we will empirically try to correlate them with the structure of n-hexane.

The intensity of the signals in a 1H NMR are proportional to the relative number of protons in a structure. This will make the assignments easier.

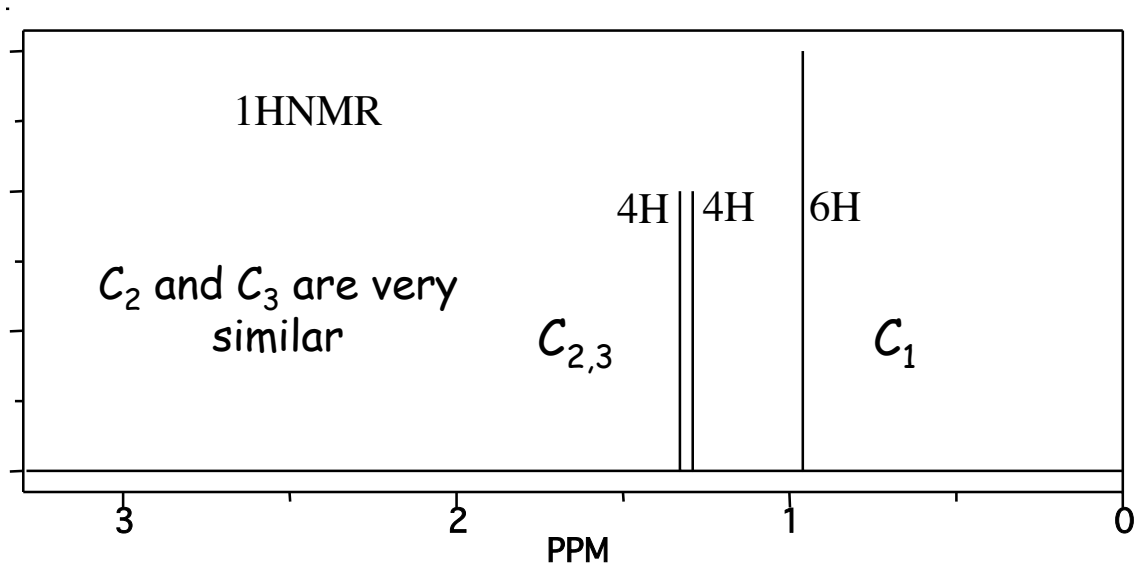
Next let's consider the carbon atoms of n-hexane

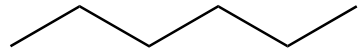


There are only three different kinds of carbon atoms in n-hexane: $C_1 = C_6$, $C_2 = C_5$, and $C_3 = C_4$

We therefore expect three signals for the three different carbon atoms

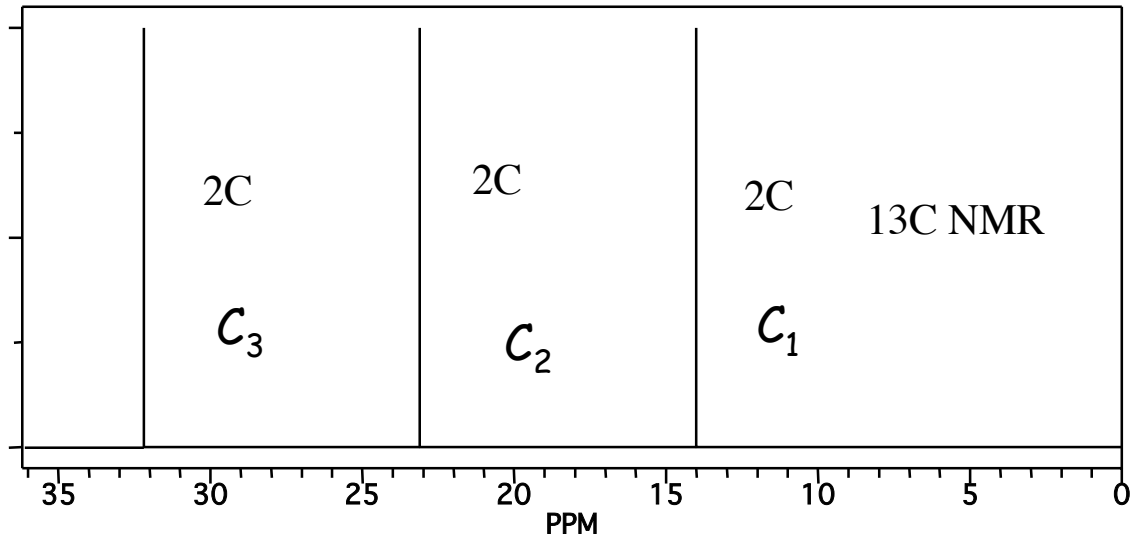
The signals in a 13C NMR are proportional to the relative number of carbon atoms in a structure. This will make the assignments easier.

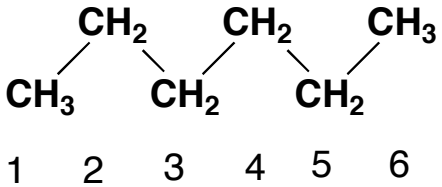




n-hexane

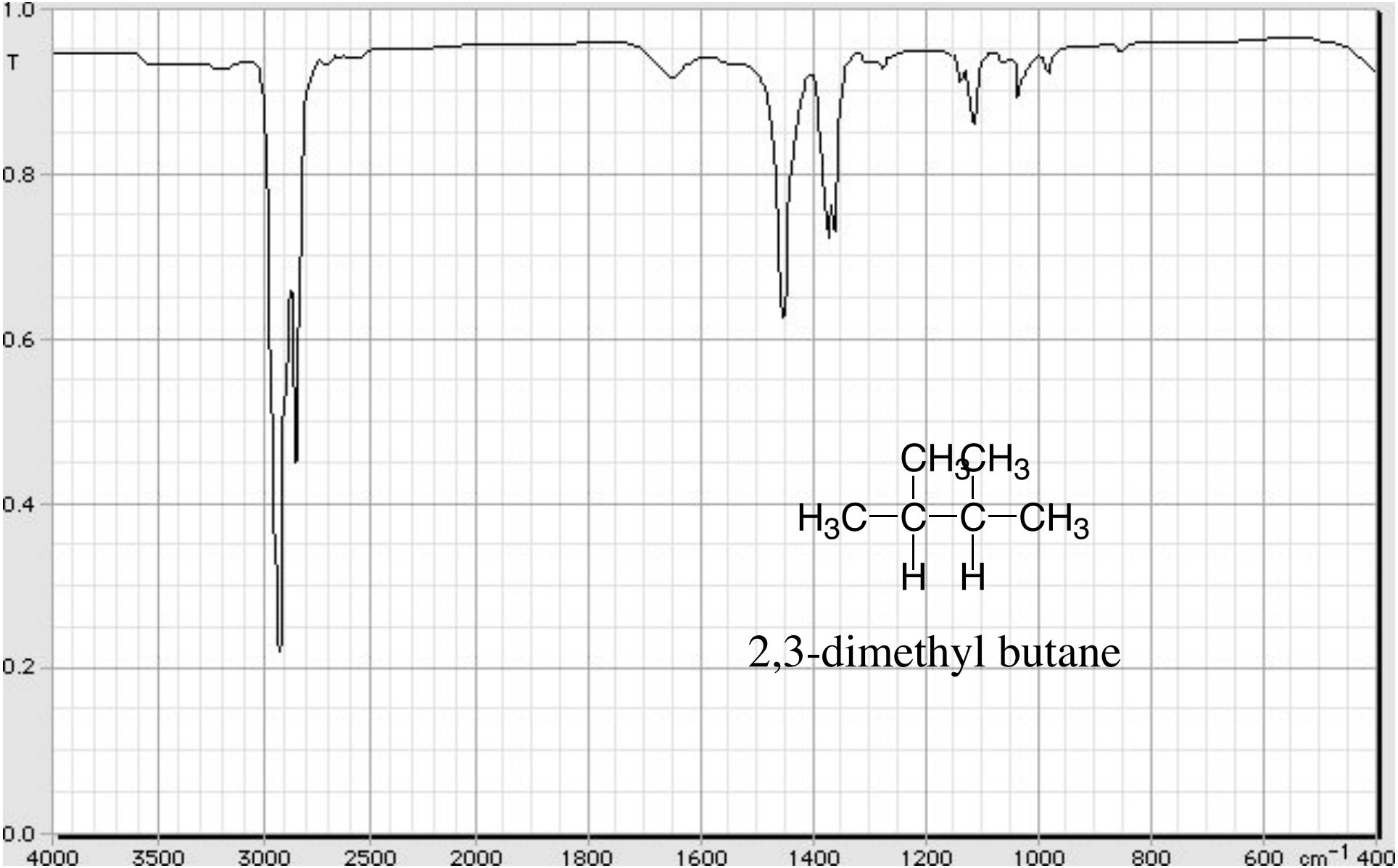
Assign the 1H signals to the protons of n-hexane





Assign the 13C signals to the carbon atoms of n-hexane

Use the correlation tables and note scale of x-axis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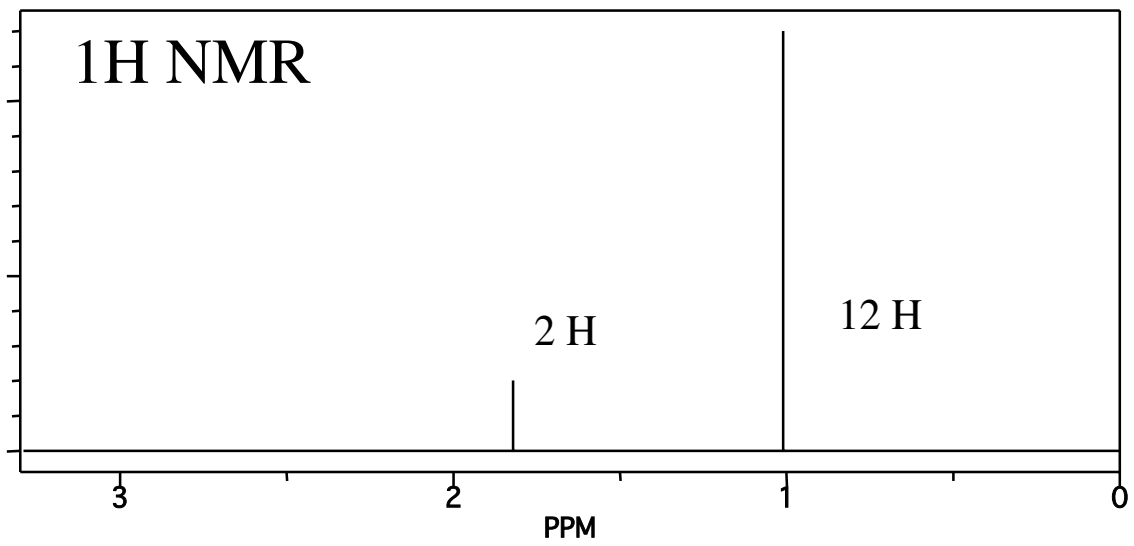
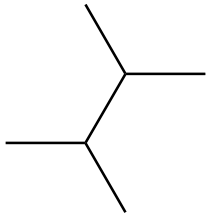
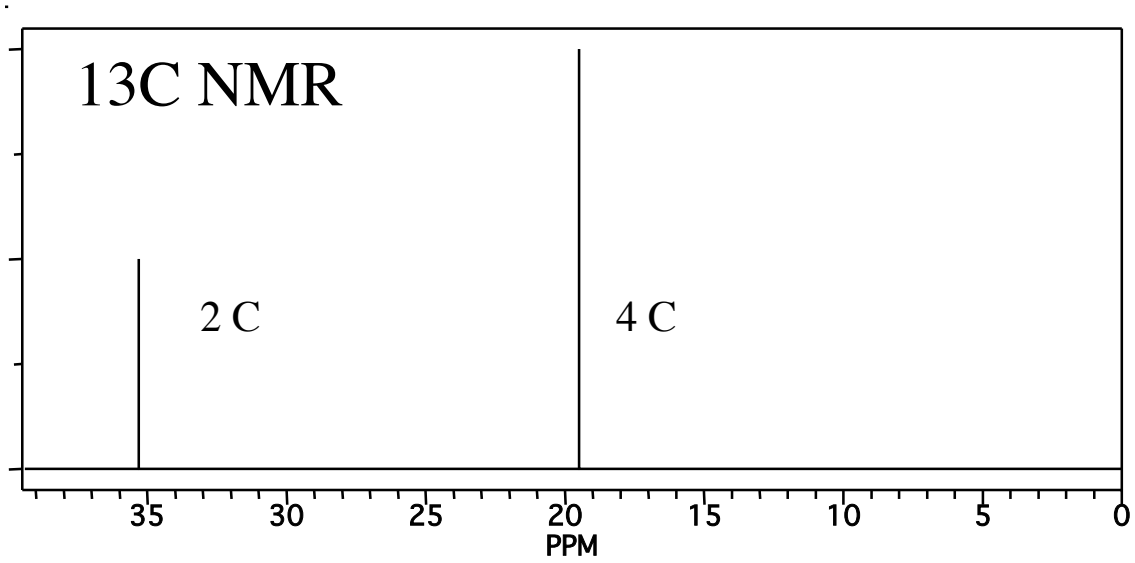
2,3-dimethyl butane

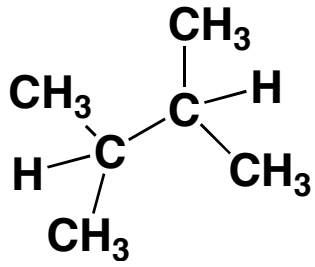


Assign the signals in the NMR spectra to the H and C in the structures

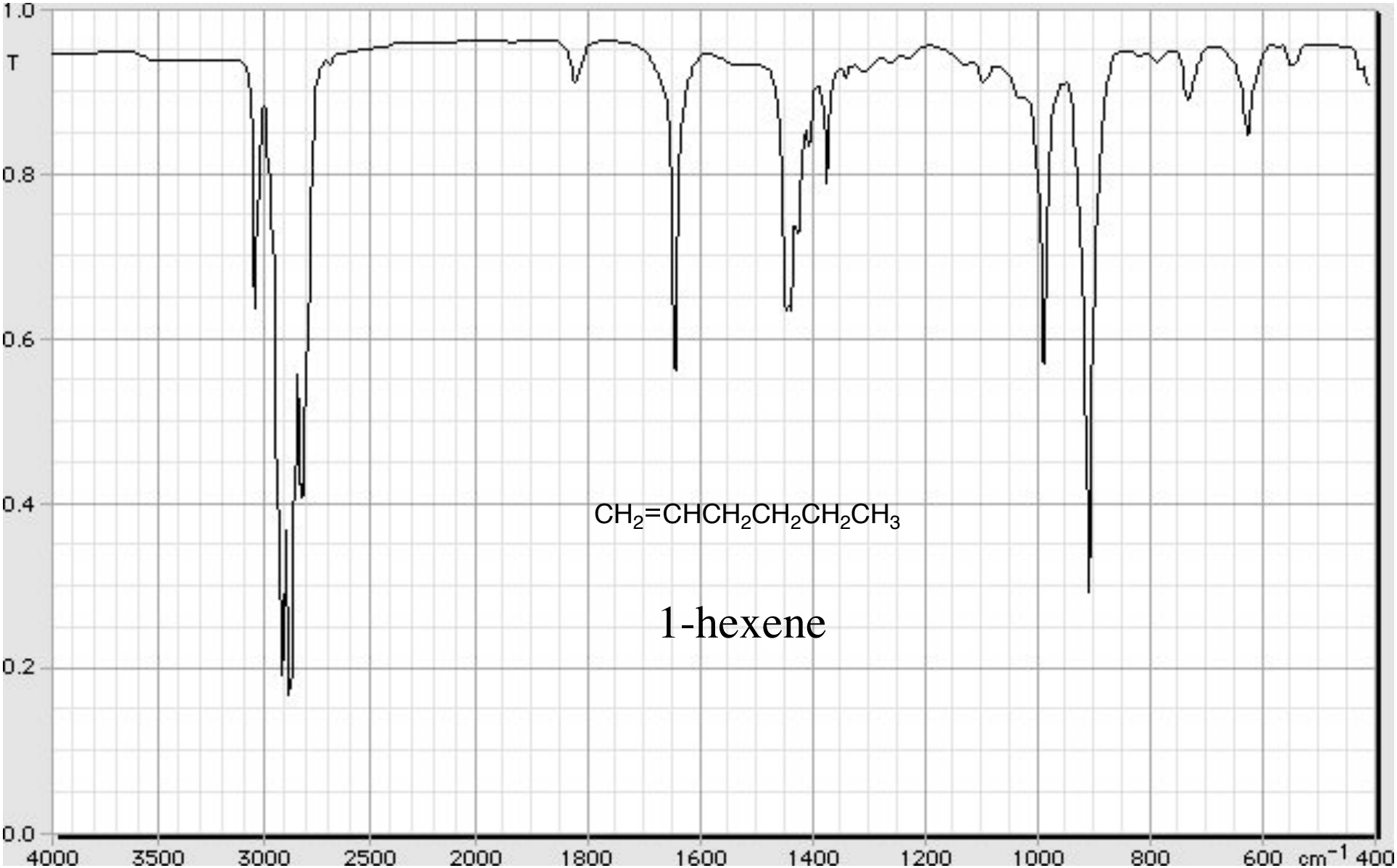


2,3-dimethylbutane





Use the correlation tables and note scale of x-axis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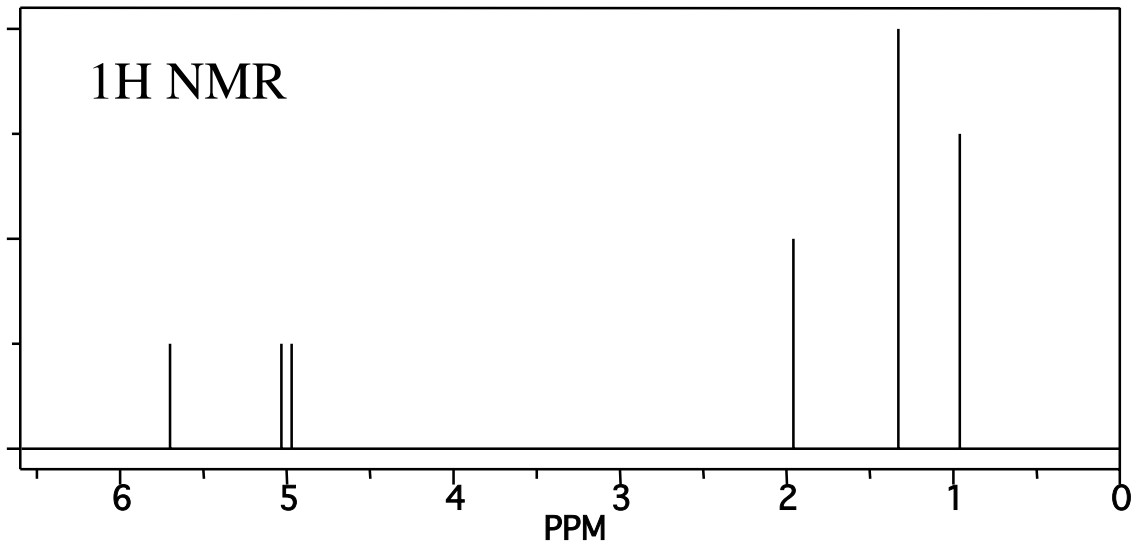
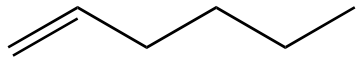
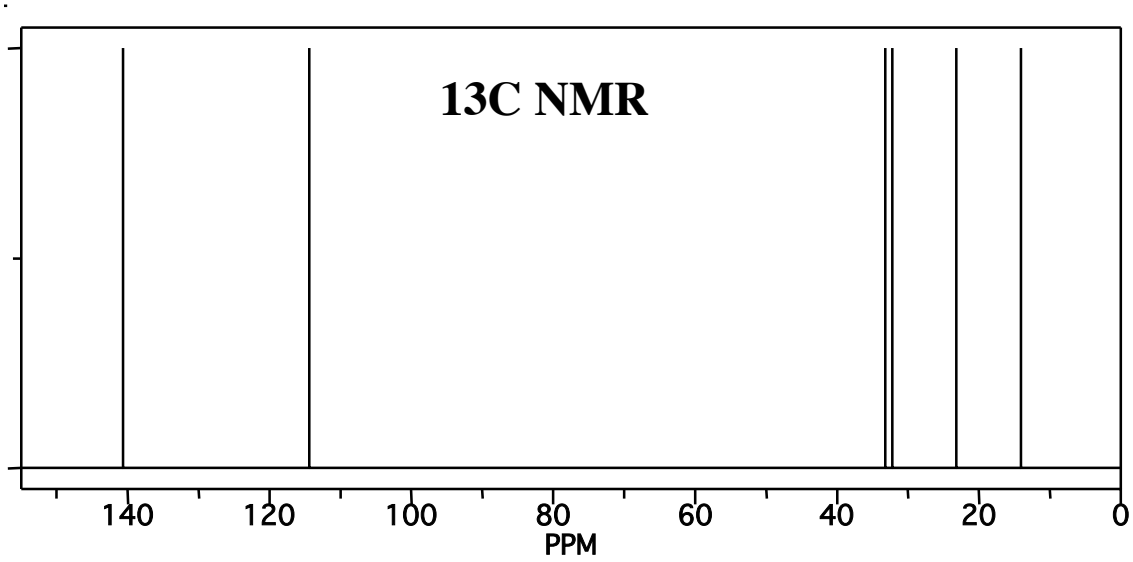
CH2=CHCH2CH2CH2CH3
1-hexene



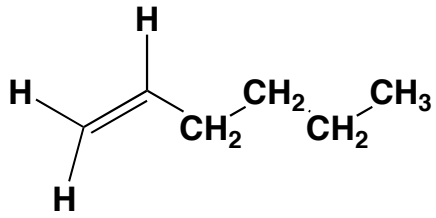
Assign the signals at ~ 5 ppm and ~ 5.7.



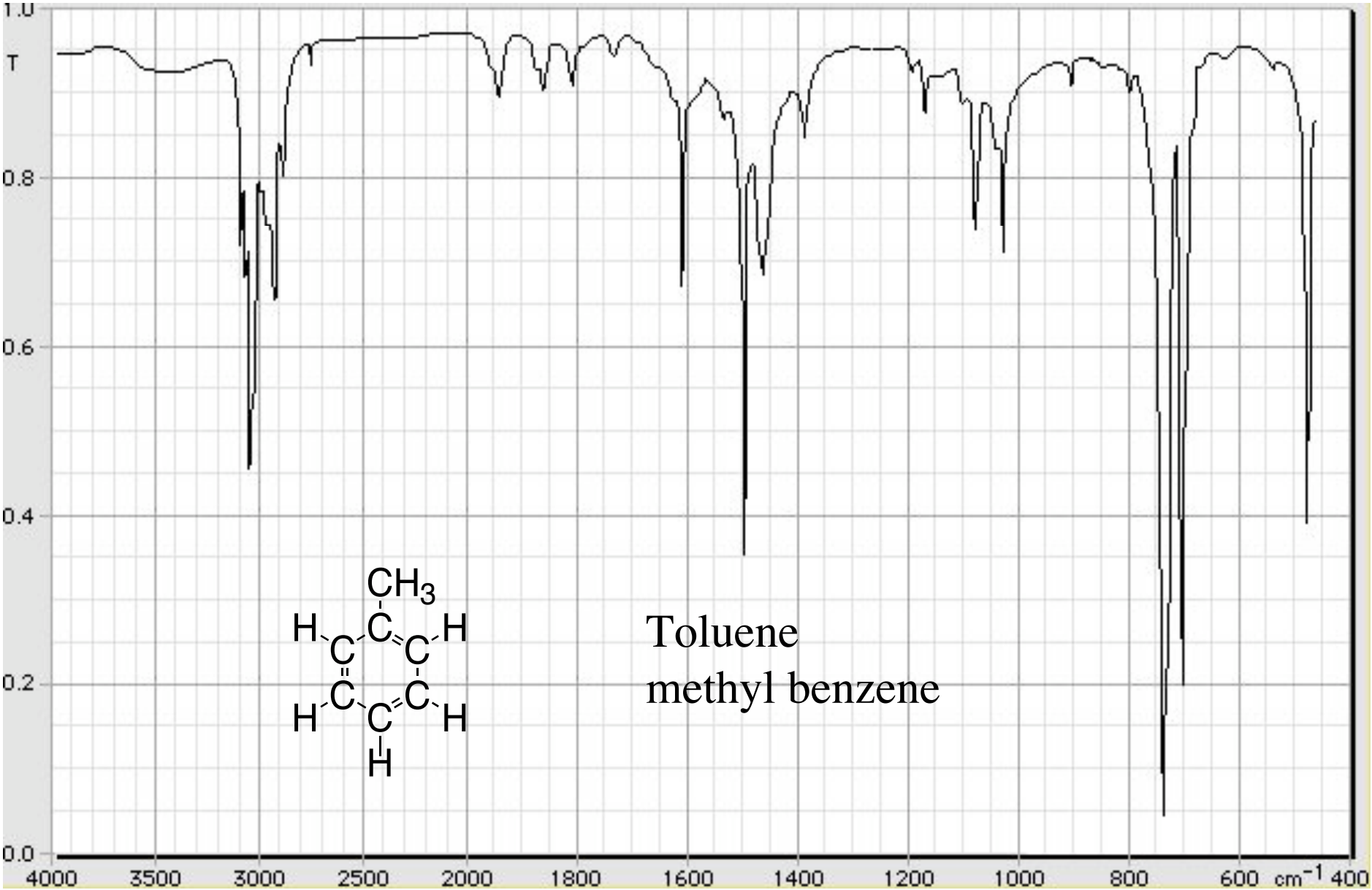
1-hexene



Assign the signals at ~ 115 ppm and ~ 140 ppm.



Use the correlation tables and note scale of x-axis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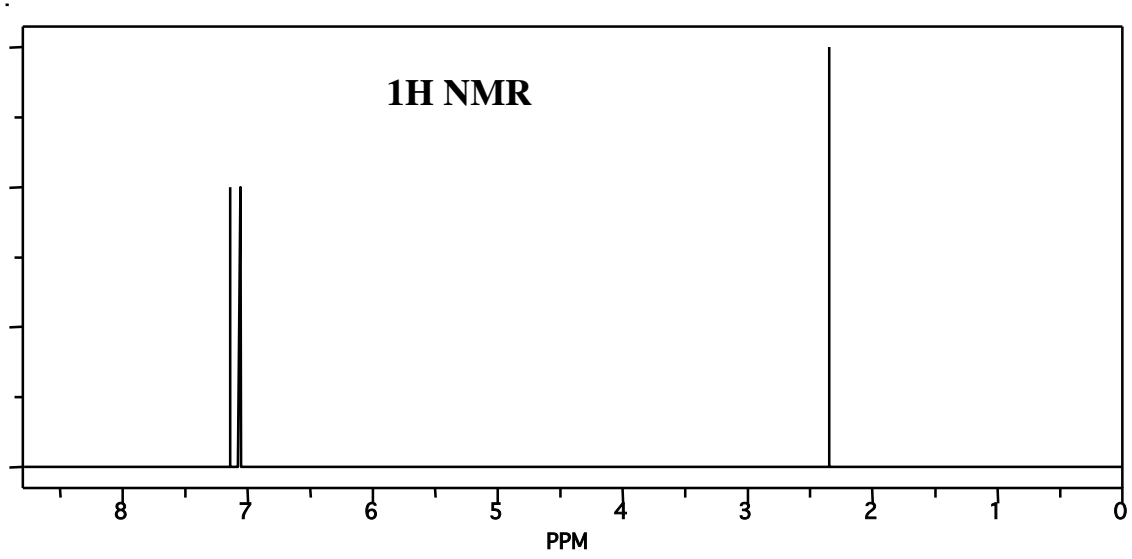
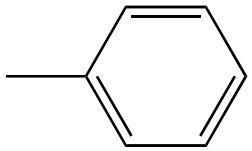
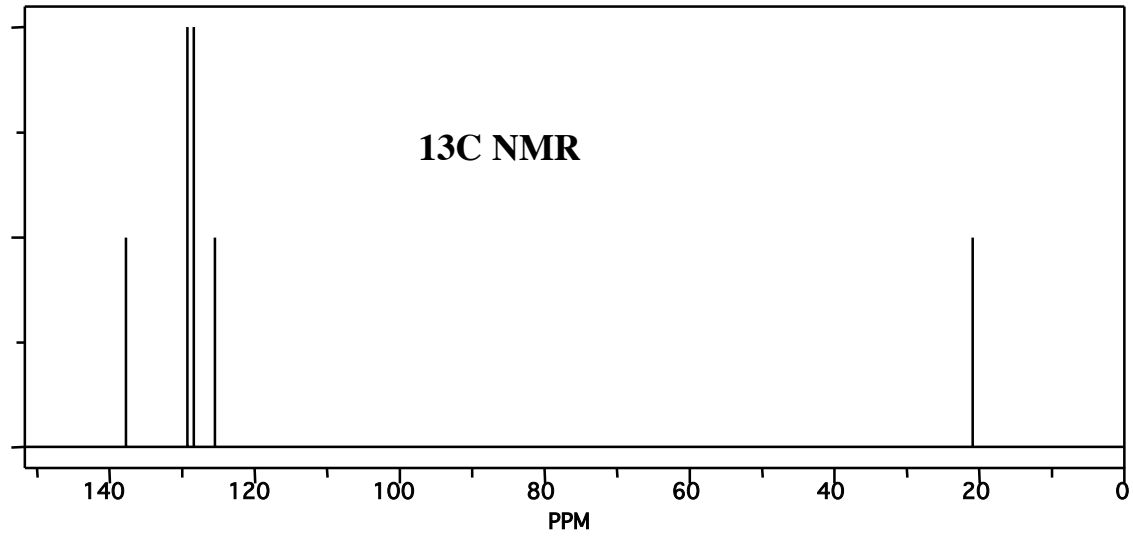
methyl benzene



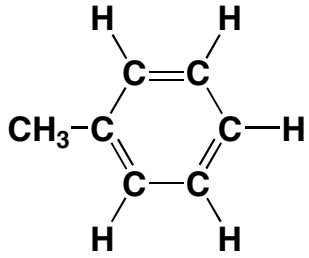
Assign the signal at ~ 2.3 ppm.



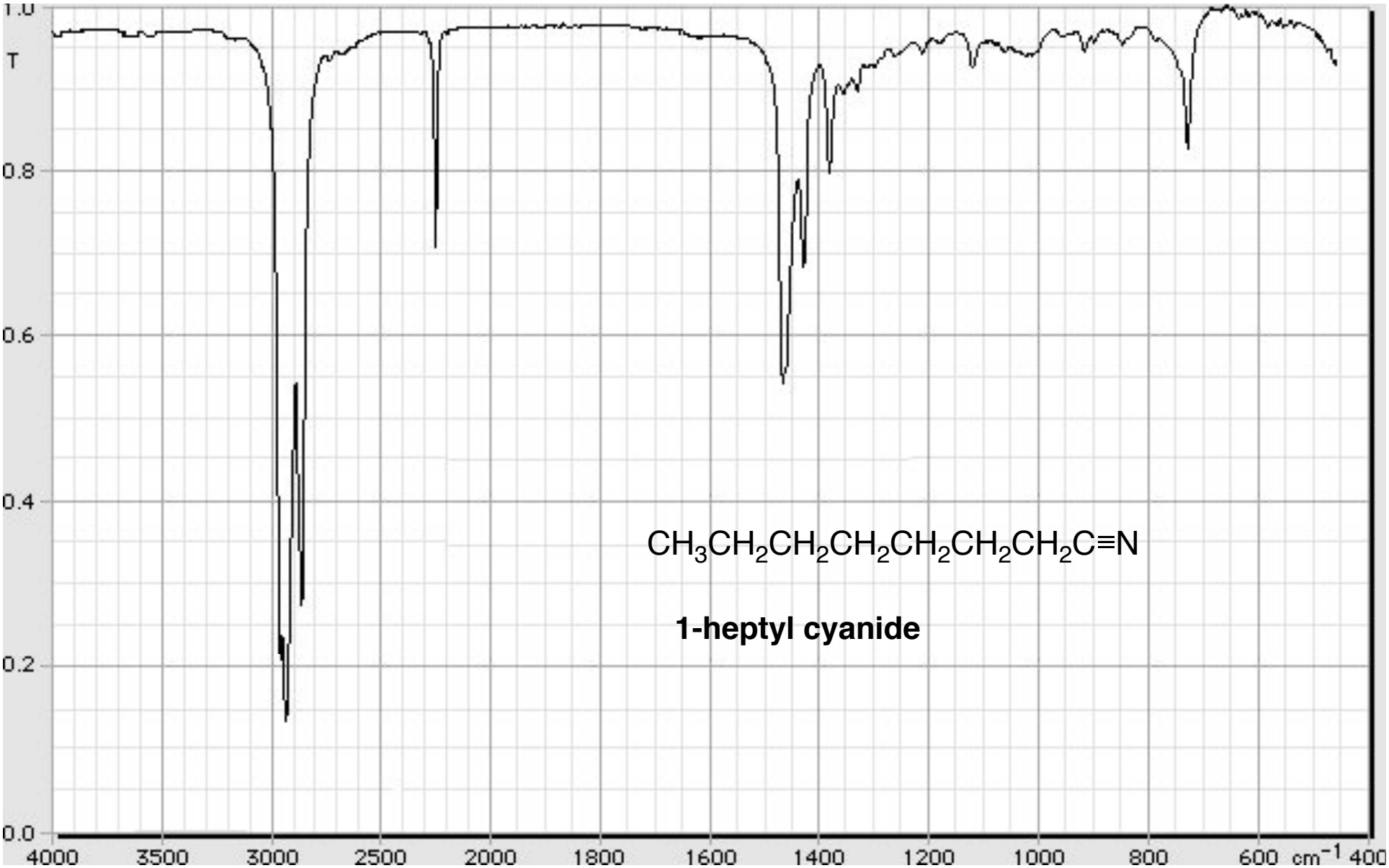
toluene



Assign the signal at ~ 20 ppm.



Use the correlation tables and note scale of x-axis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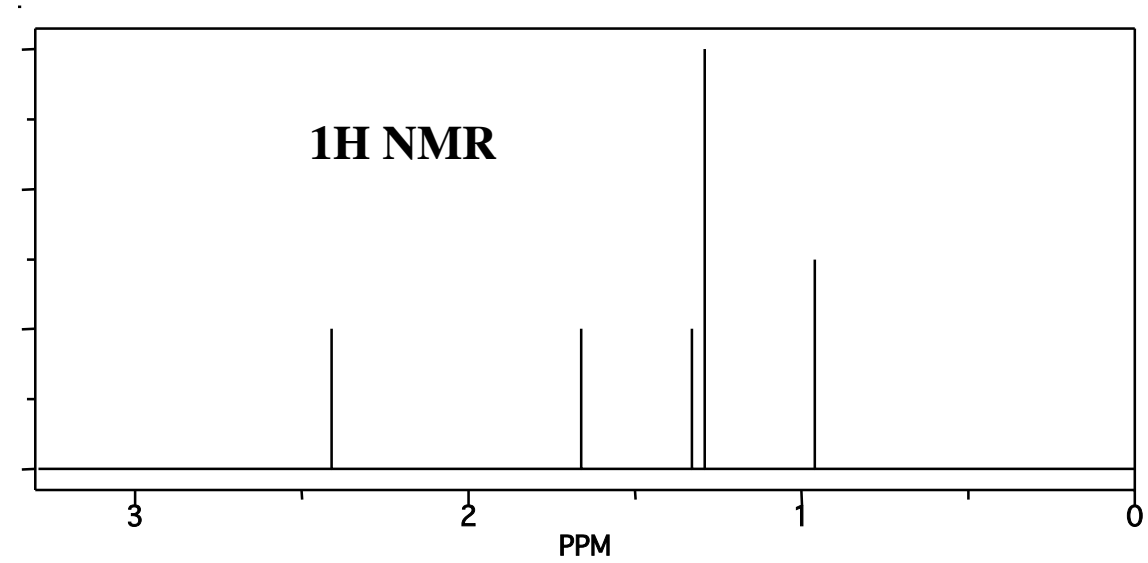
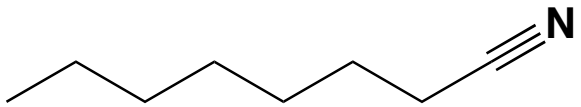
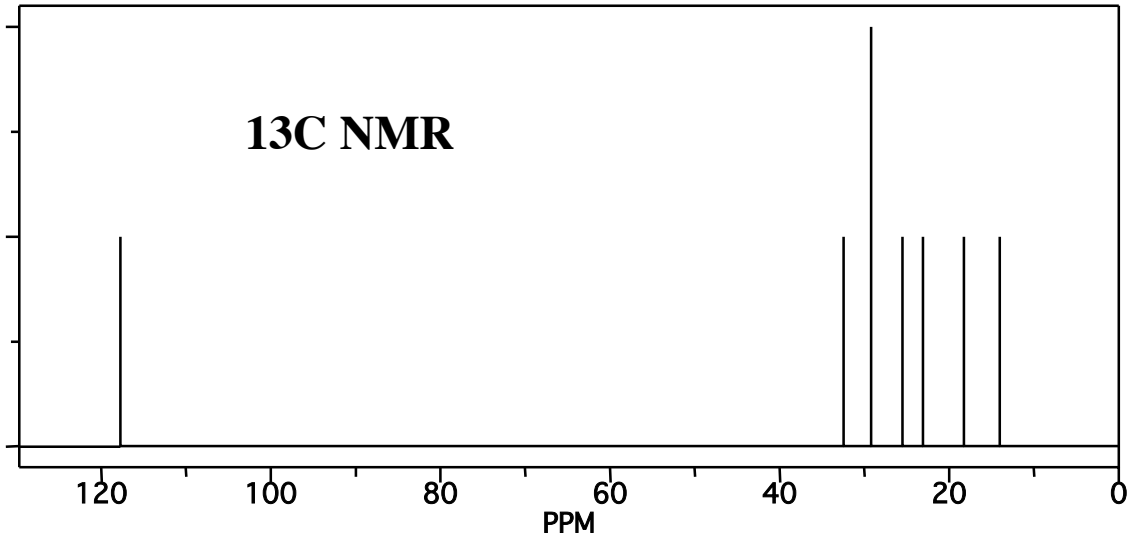
1-heptyl cyanide



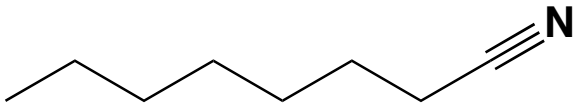
Assign the signals at ~ 2.4 ppm and 1.3 ppm.



1-heptylcyanide

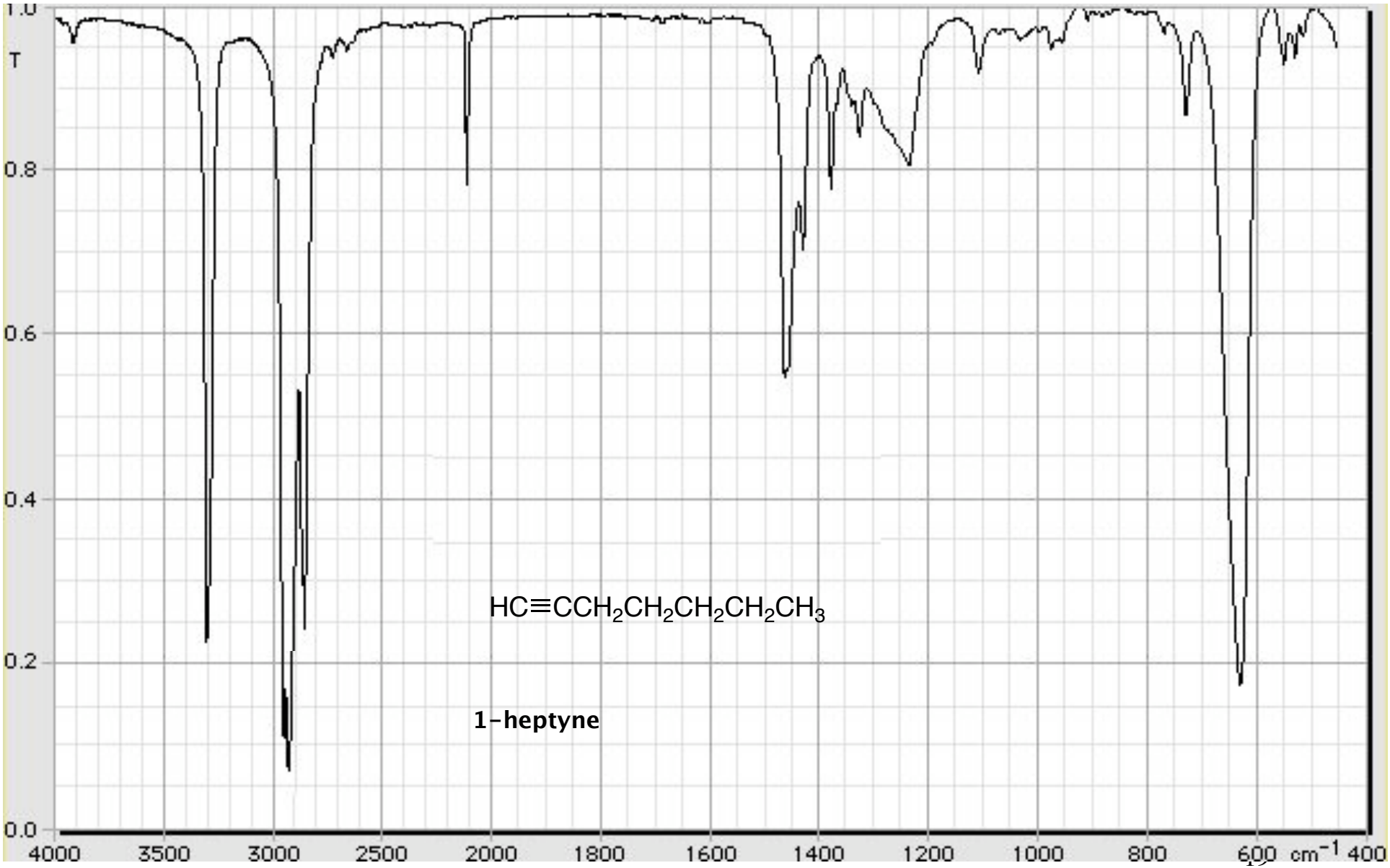


Assign the signal at ~ 120 ppm.



1-heptylcyanide

Use the correlation tables and note scale of x-axis


T
1.0
0.8
0.6
0.4
0.2
0.0
4000
3500
3000
2500
2000
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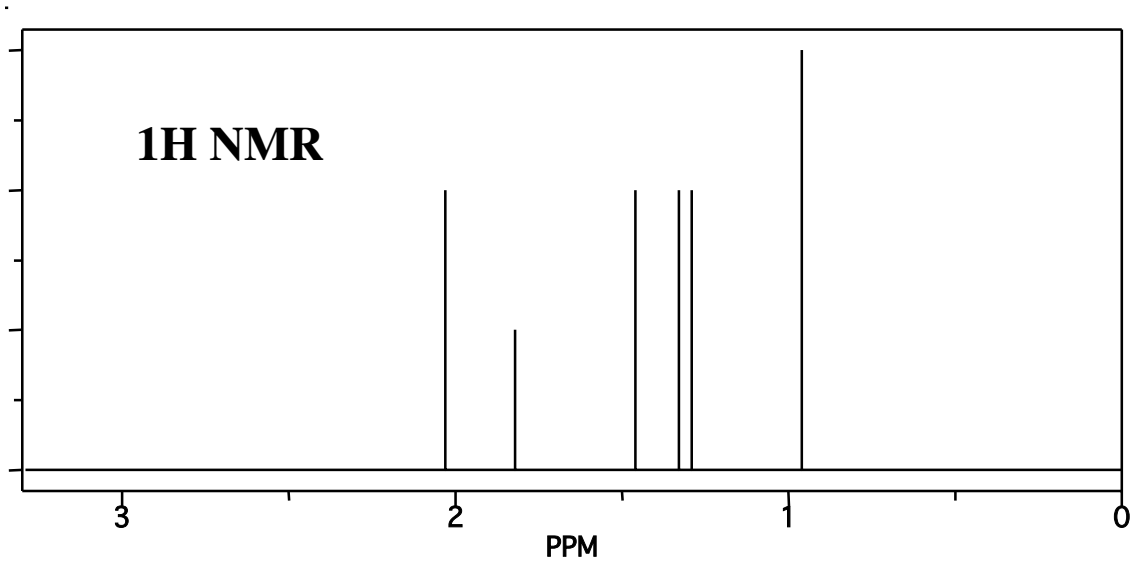
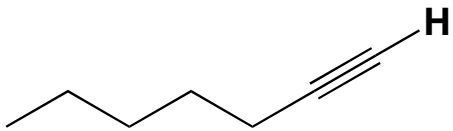
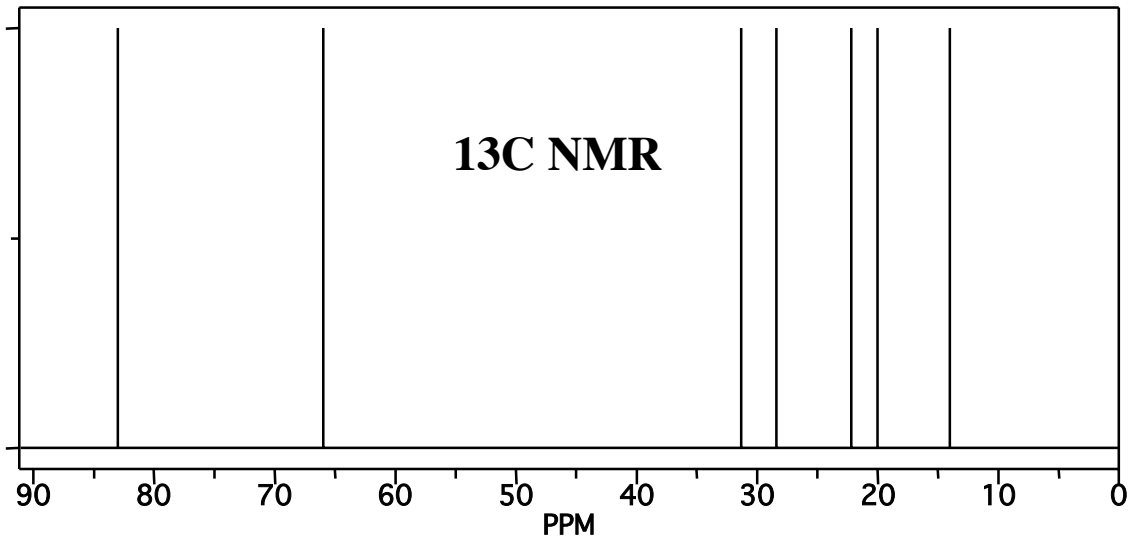
1600
1400
1200
1000
800
600
cm-1
400
HC≡CCH2CH2CH2CH2CH3
1-heptyne



Can you find the C-H signal associated with the triple bond?



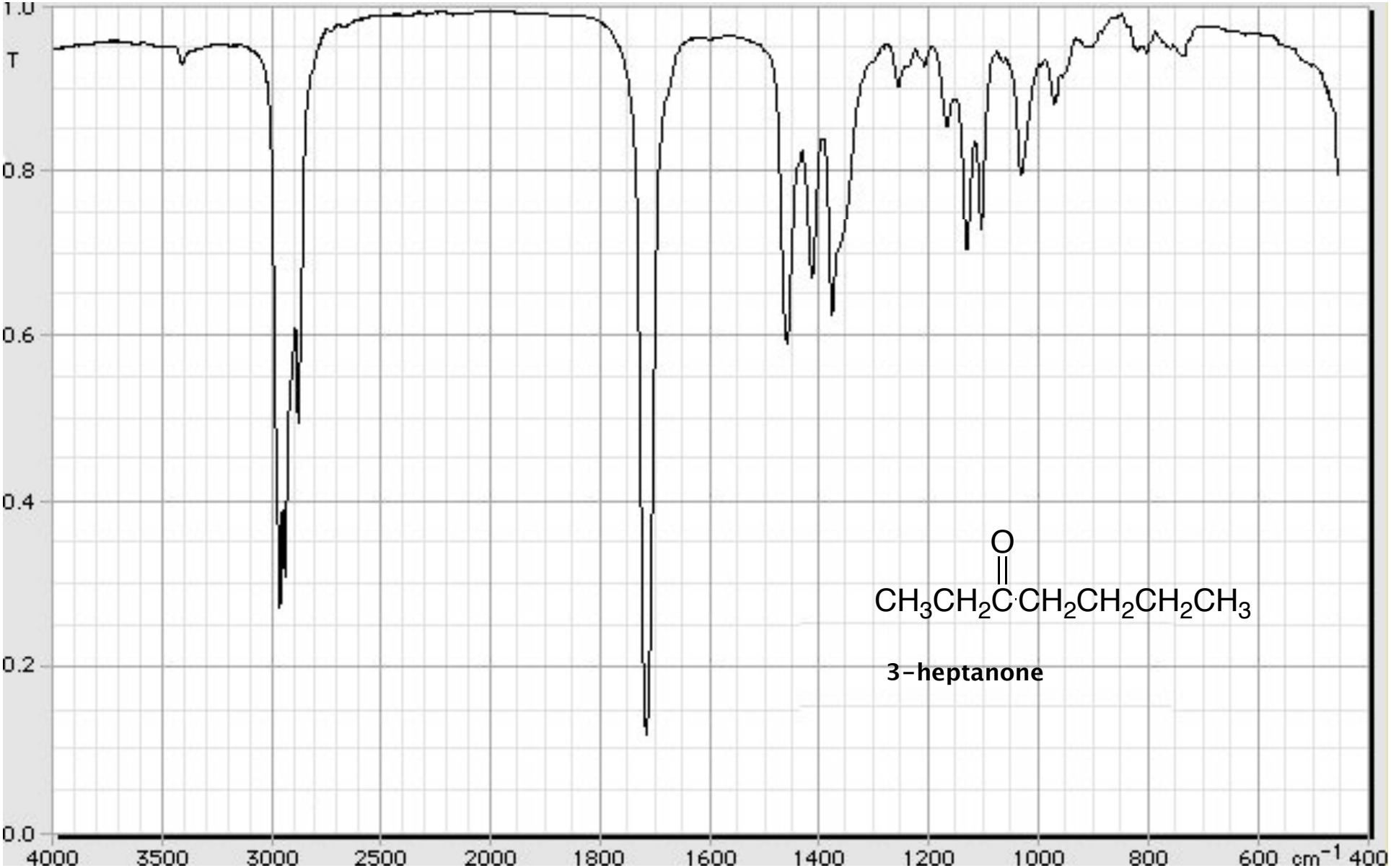
1-heptyne



Which signals are due to the triple bond carbons?

$HC{\equiv}CCH_2CH_2CH_2CH_2CH_3$

Use the correlation tables and note scale of x-axis


1.0
T
0.8
0.6
0.4
0.2
0.0
4000
3500
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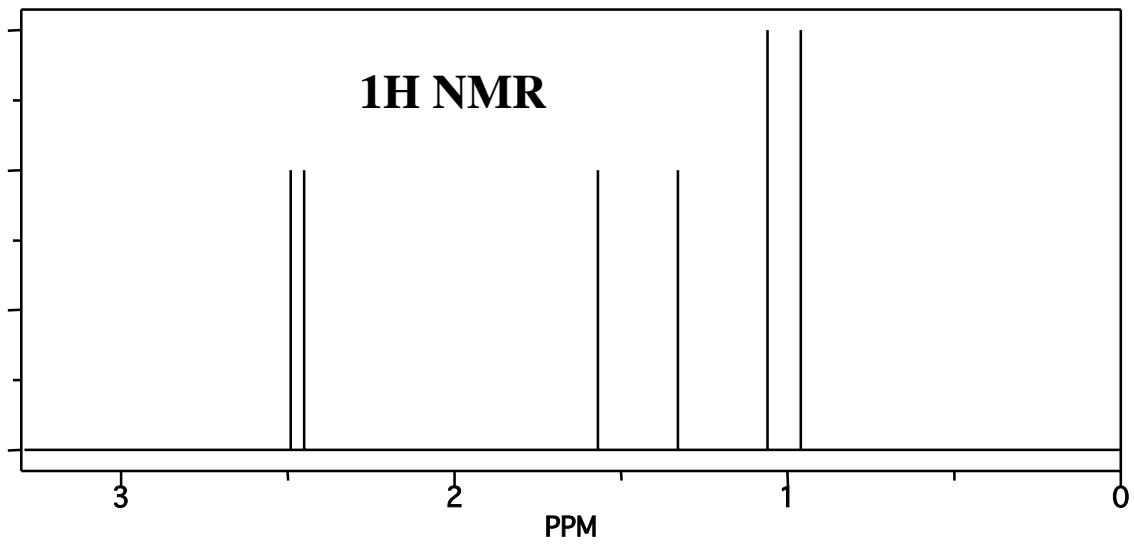
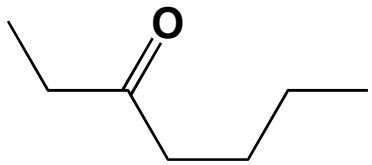
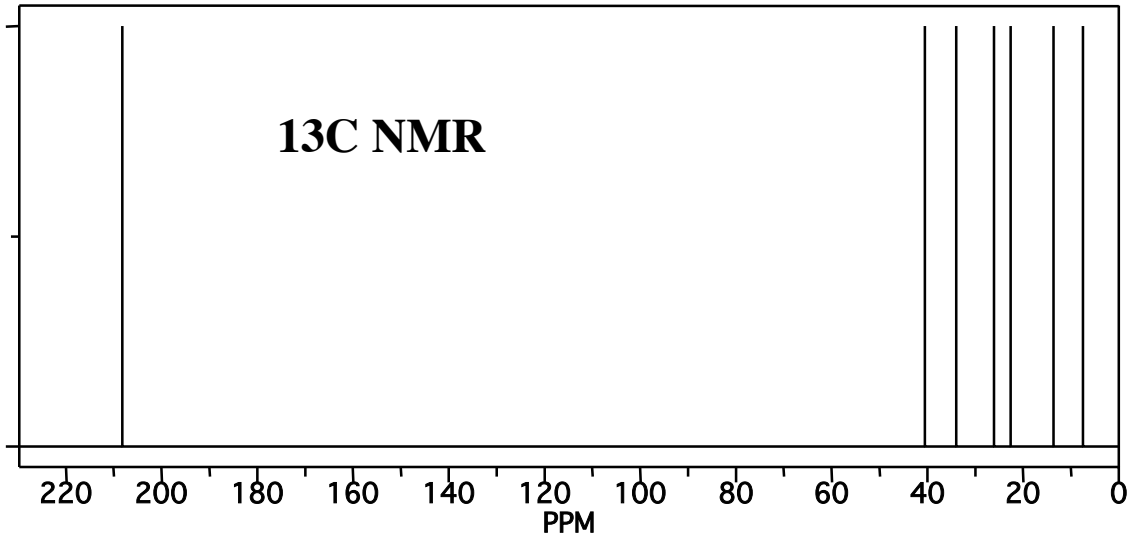
2500
2000
1800
1600
1400
1200
1000
800
600
cm-1
400
O
CH3CH2CCH2CH2CH2CH3
3-heptanone



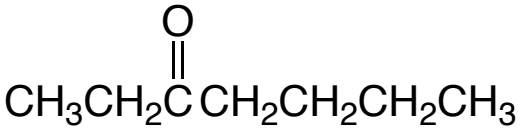
How many signal can you assign?



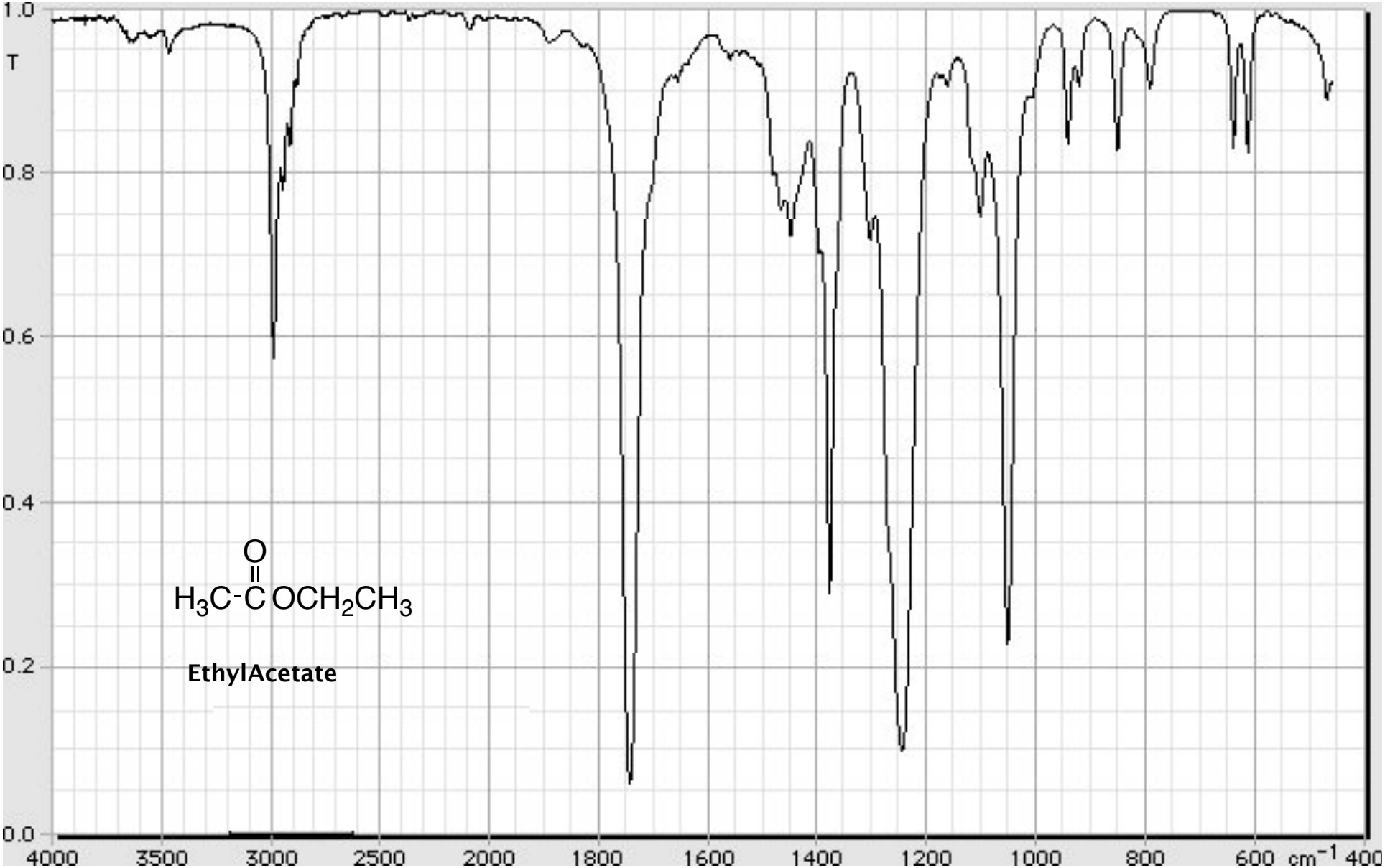
3-heptanone



What is the signal at ~ 210 ppm due to? What signal is associated with this signal in the IR of 3-heptanone?



Use the correlation tables and note scale of x-axis


1.0
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0.4
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1600
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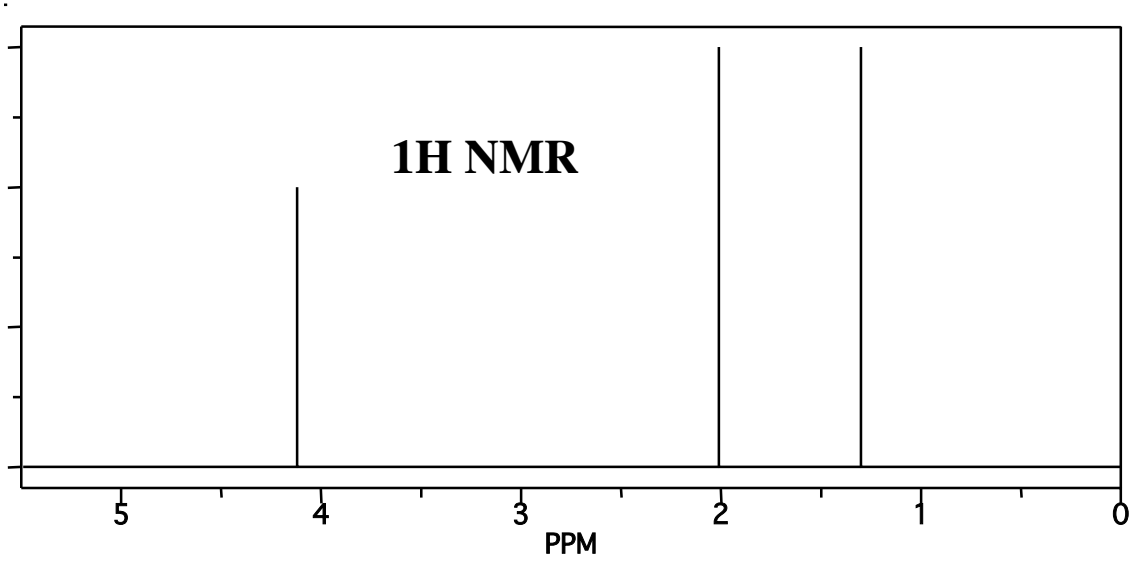
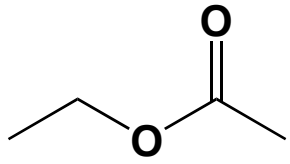
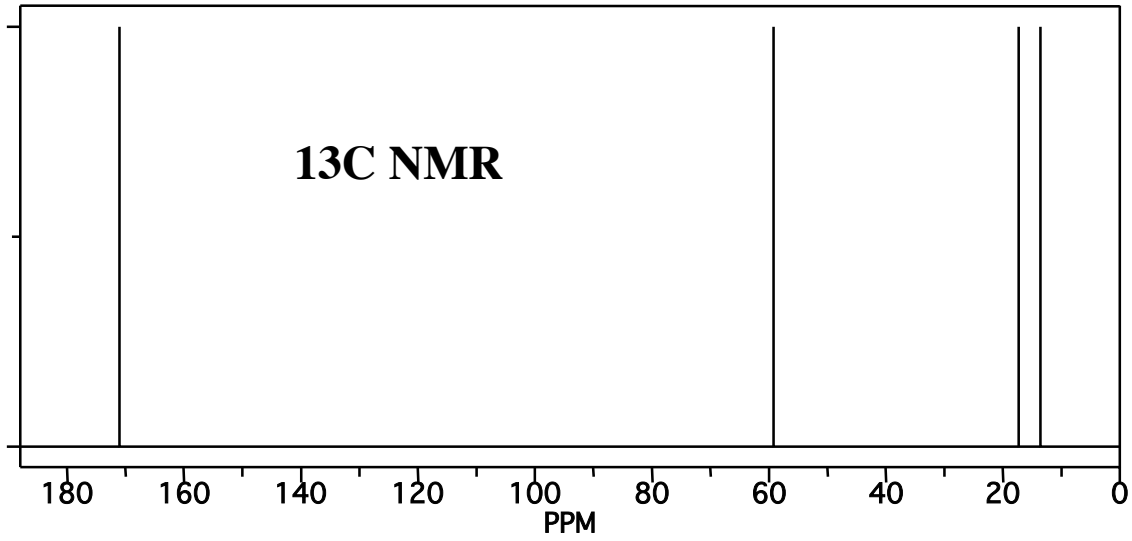
1200
1000
800
600
cm-1
400
O
H3C-C-OCH2CH3
EthylAcetate



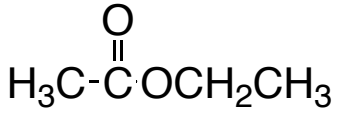
What is the signal at ~ 4.2 ppm due to? The signal at ~ 2.0 ppm?



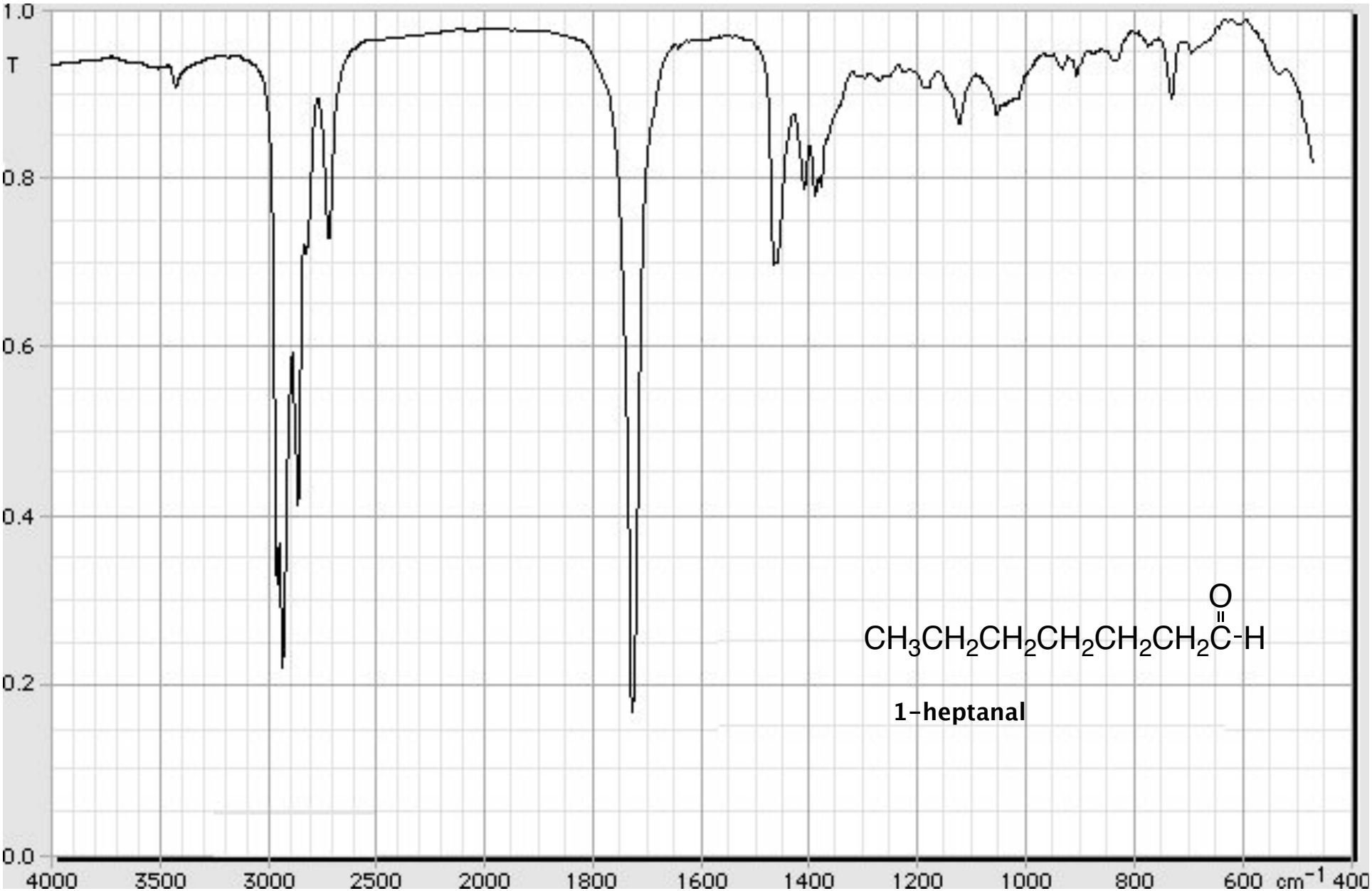
ethyl acetate



What are the peaks at ~ 170 ppm and ~60 ppm due to?



Use the correlation tables and note scale of x-axis


1.0
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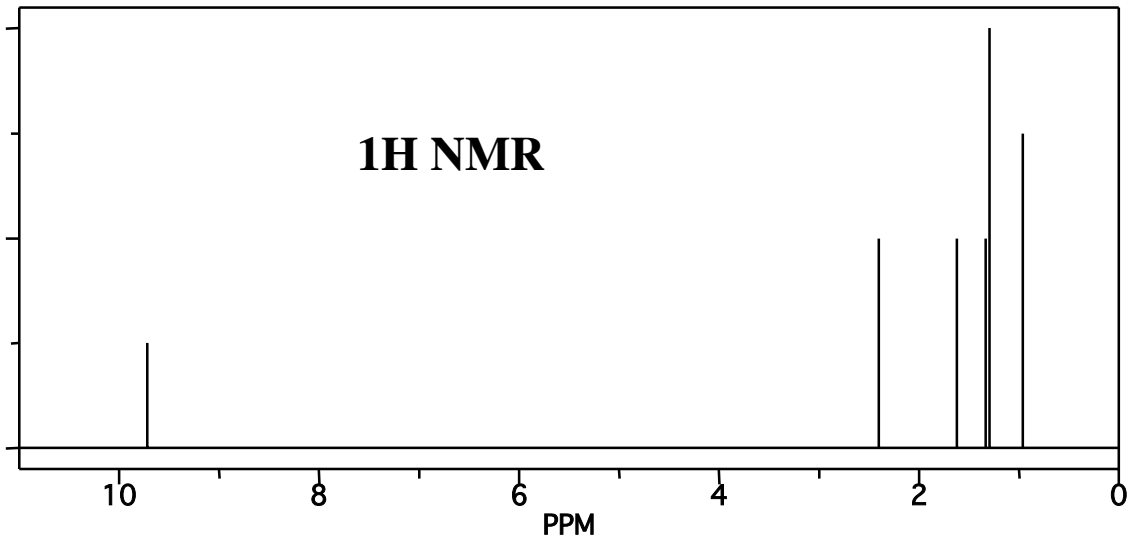
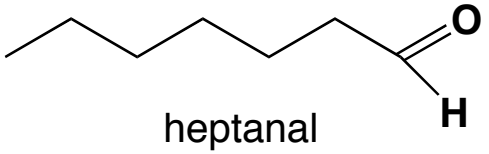
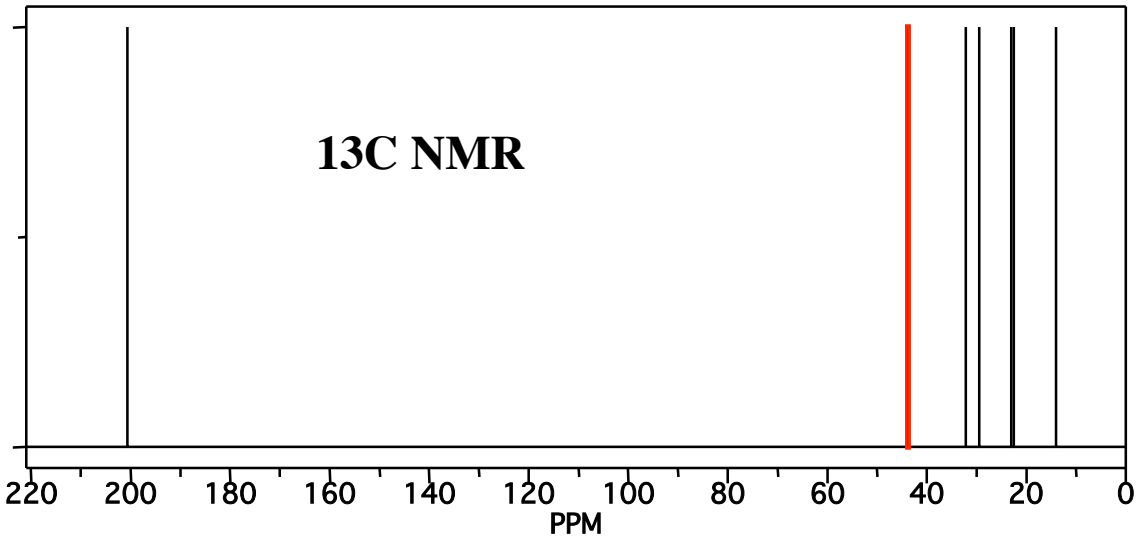
0.4
0.2
0.0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
cm-1
400
O
CH3CH2CH2CH2CH2CH2C-H
1-heptanal

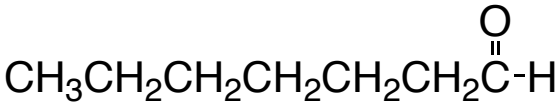


What is the signal at ~ 10 ppm due to? Can you find the analogous signal in the IR?

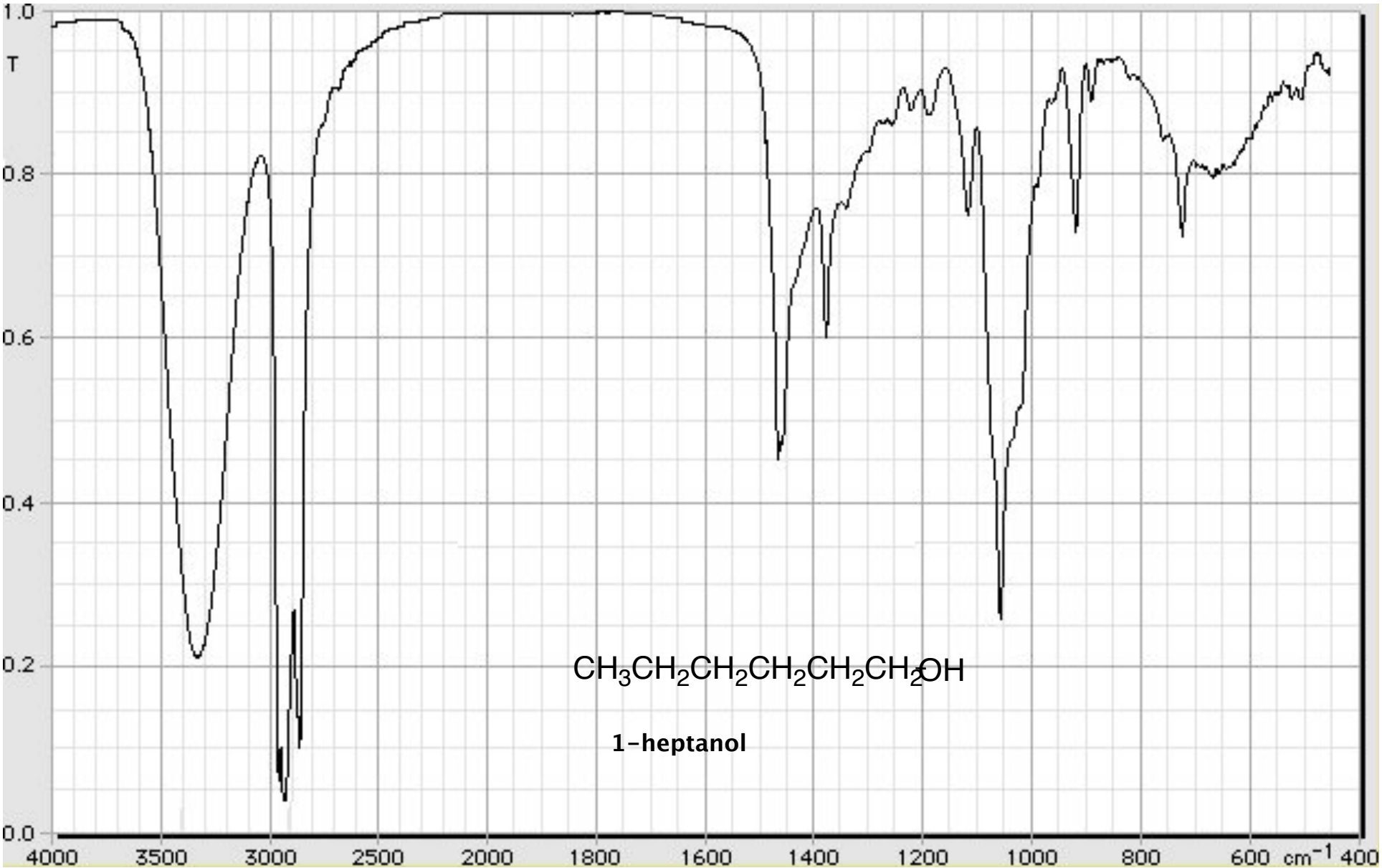




What is the signal at ~ 200 ppm due to?



Use the correlation tables and note scale of x-axis


1.0
T
0.8
0.6
0.4
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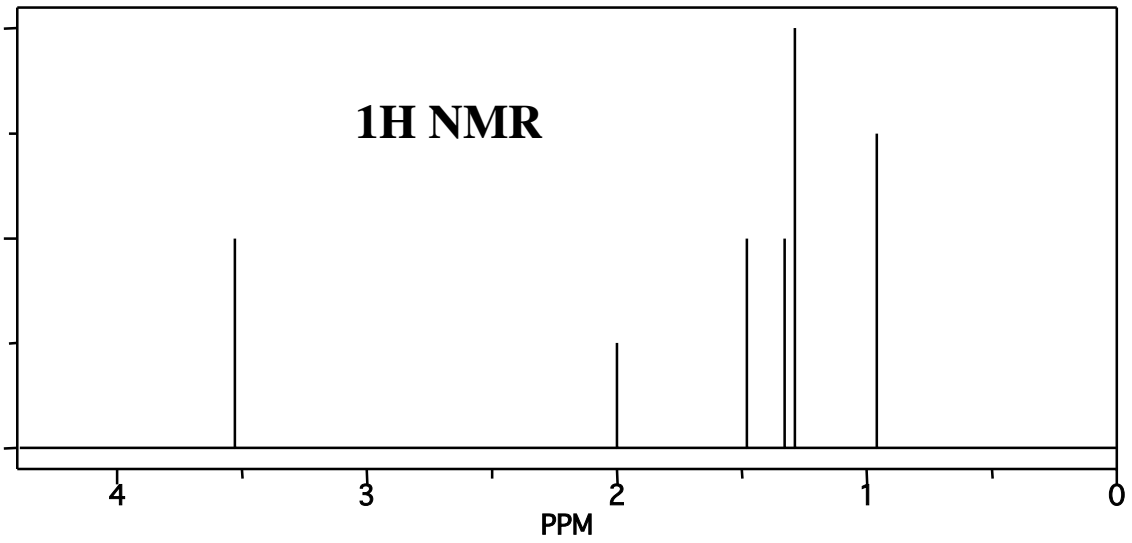
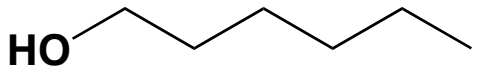
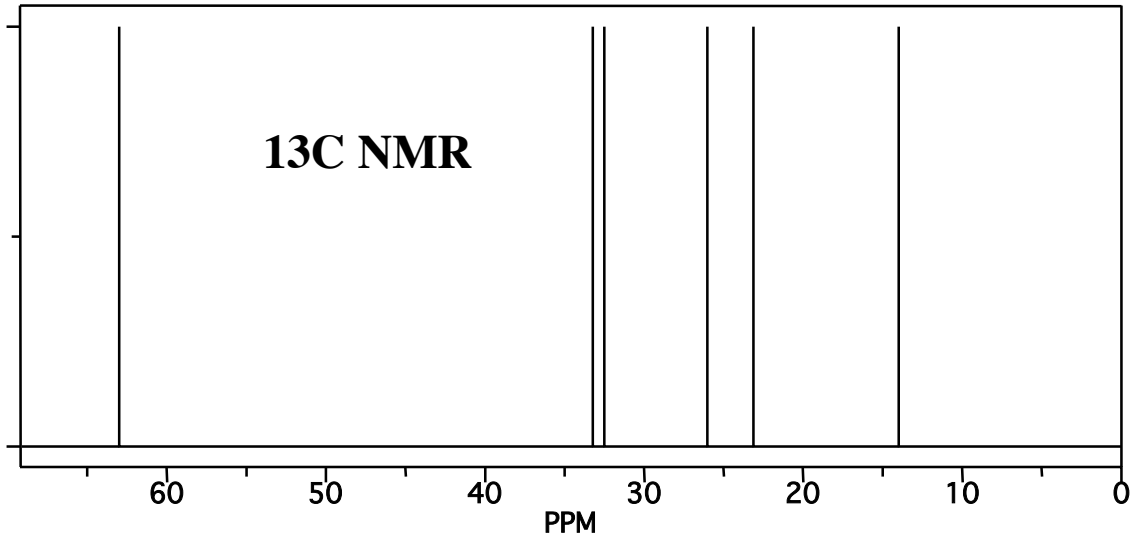
2500
2000
1800
1600
1400
1200
1000
800
600
cm-1
400
CH3CH2CH2CH2CH2CH2OH
1-heptanol



What is the signal at ~ 3.5 ppm due to?



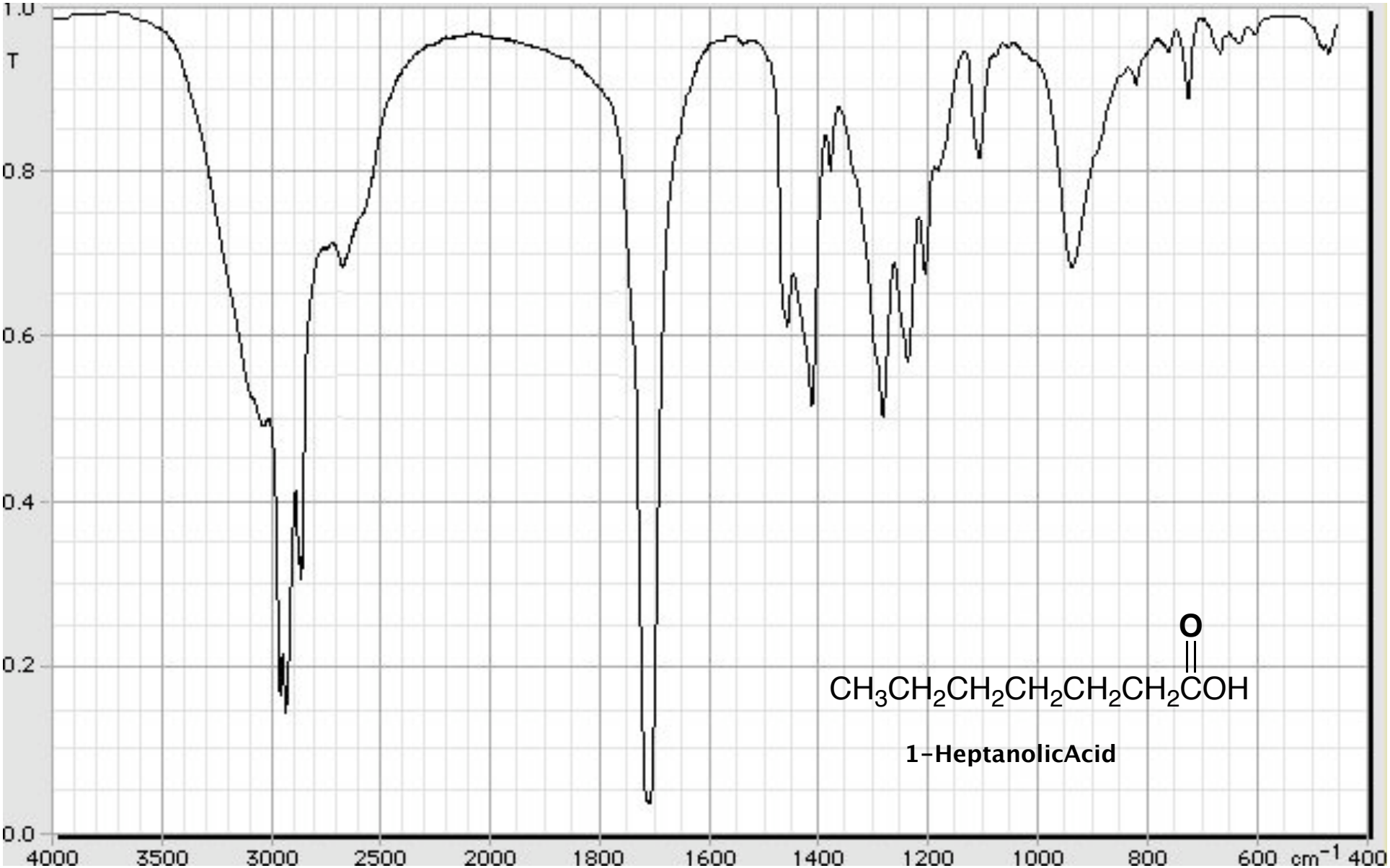
1-hexanol

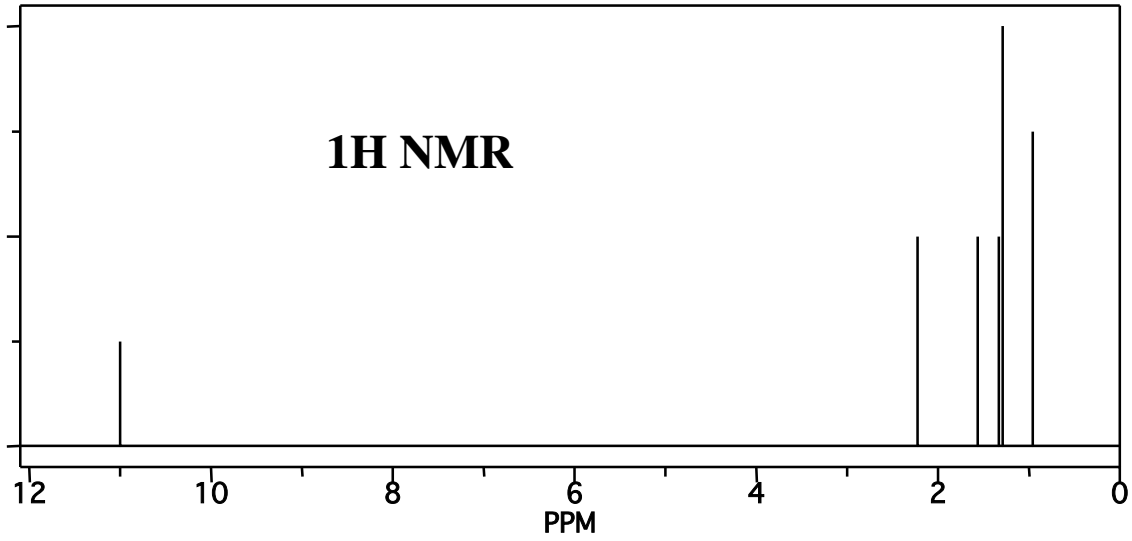


What is the signal ~63 ppm due to?

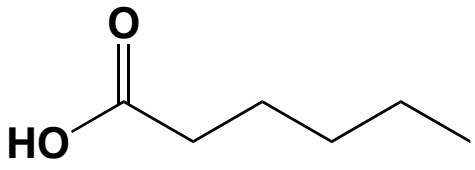
$CH_3CH_2CH_2CH_2CH_2CH_2OH$

Use the correlation tables and note scale of x-axis

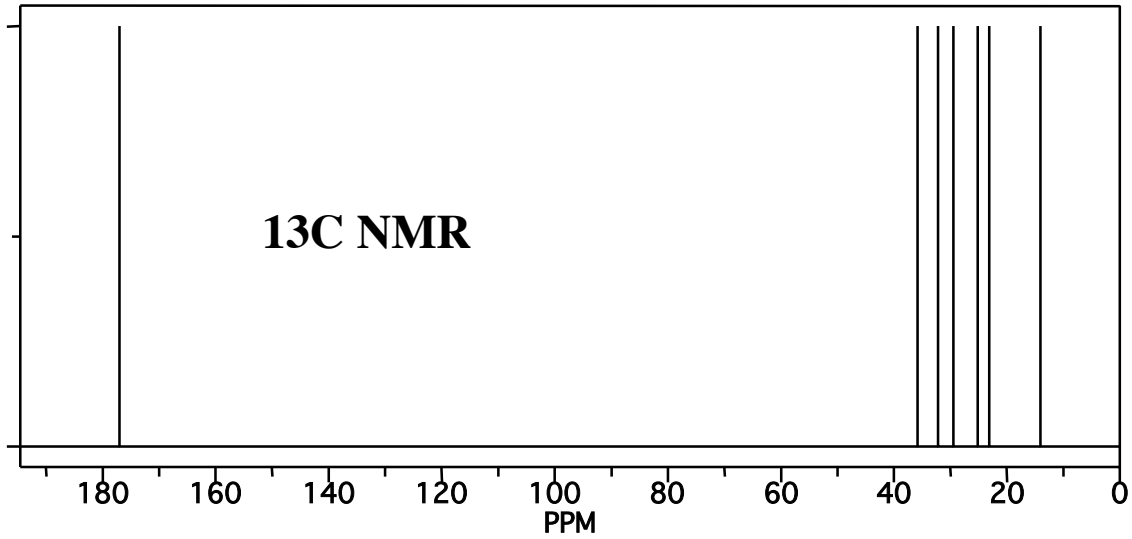

T
1.0
0.8
0.6
0.4
0.2
0.0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
cm-1
400
O
CH3CH2CH2CH2CH2CH2COH
1-HeptanolicAcid



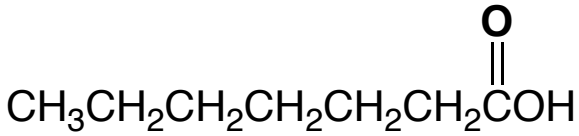
What is the signal at ~ 11 ppm due to?



1-heptanoic acid



What is the signal at ~180 ppm due to?



Use the correlation tables and note scale of x-axis