

C1403

NMR Homework

The IR and proton (^1H NMR) and carbon (^{13}C 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 ^{13}C NMR spectra of the same compounds. Correlation Tables for the IR, ^1H NMR and ^{13}C NMR are given. In this homework exercise you should try to make sense out of the ^1H NMR and ^{13}C 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 ^{13}C 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.

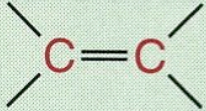
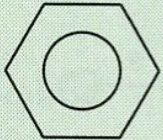
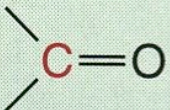
TABLE 13.1

Chemical Shifts of Representative Types of Protons

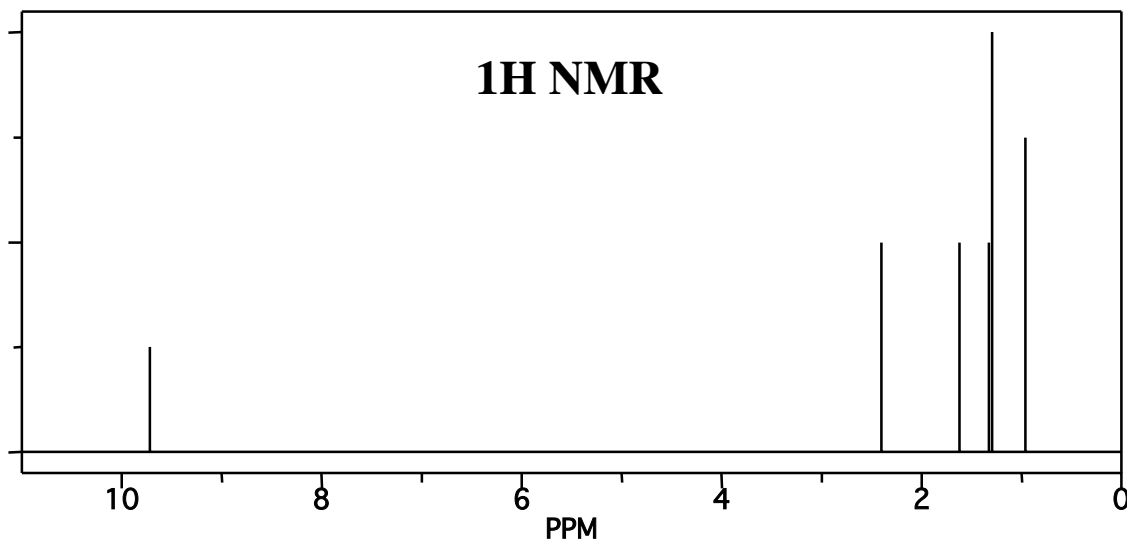
Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
$\text{H}-\text{C}-\text{R}$	0.9–1.8	$\text{H}-\text{C}-\text{NR}$	2.2–2.9
$\text{H}-\text{C}-\text{C}=\text{C}$	1.6–2.6	$\text{H}-\text{C}-\text{Cl}$	3.1–4.1
$\text{H}-\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$	2.1–2.5	$\text{H}-\text{C}-\text{Br}$	2.7–4.1
$\text{H}-\text{C}\equiv\text{C}-$	2.5	$\text{H}-\text{C}-\text{O}$	3.3–3.7
$\text{H}-\text{C}-\text{Ar}$	2.3–2.8	$\text{H}-\text{NR}$	1–3†
$\text{H}-\text{C}=\overset{\diagup}{\text{C}}\diagdown$	4.5–6.5	$\text{H}-\text{OR}$	0.5–5†
$\text{H}-\text{Ar}$	6.5–8.5	$\text{H}-\text{OAr}$	6–8†
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-$	9–10	$\text{H}-\overset{\text{O}}{\parallel}{\text{O}}\text{C}-$	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

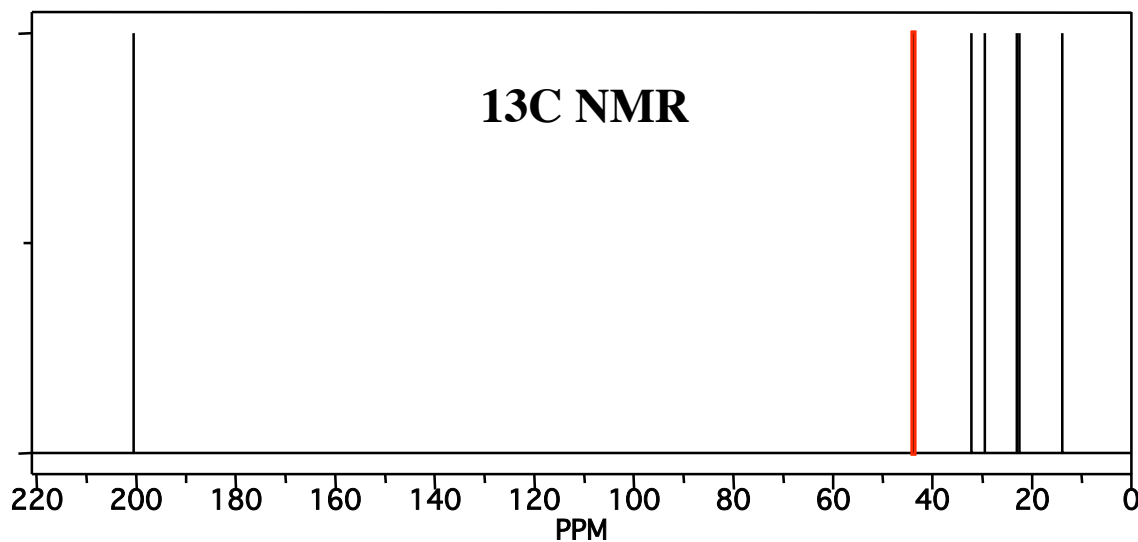
Type of carbon	Chemical shift (δ) ppm*	Type of carbon	Chemical shift (δ) ppm*
RCH ₃	0–35		100–150
R ₂ CH ₂	15–40		110–175
RCH ₂ Br	20–40		190–220
R ₃ CH	25–50		
RCH ₂ Cl	25–50		
RCH ₂ NH ₂	35–50		
RCH ₂ OH	50–65		
—C≡C—	65–90		

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.



¹H range = 0 to
~ 10 ppm

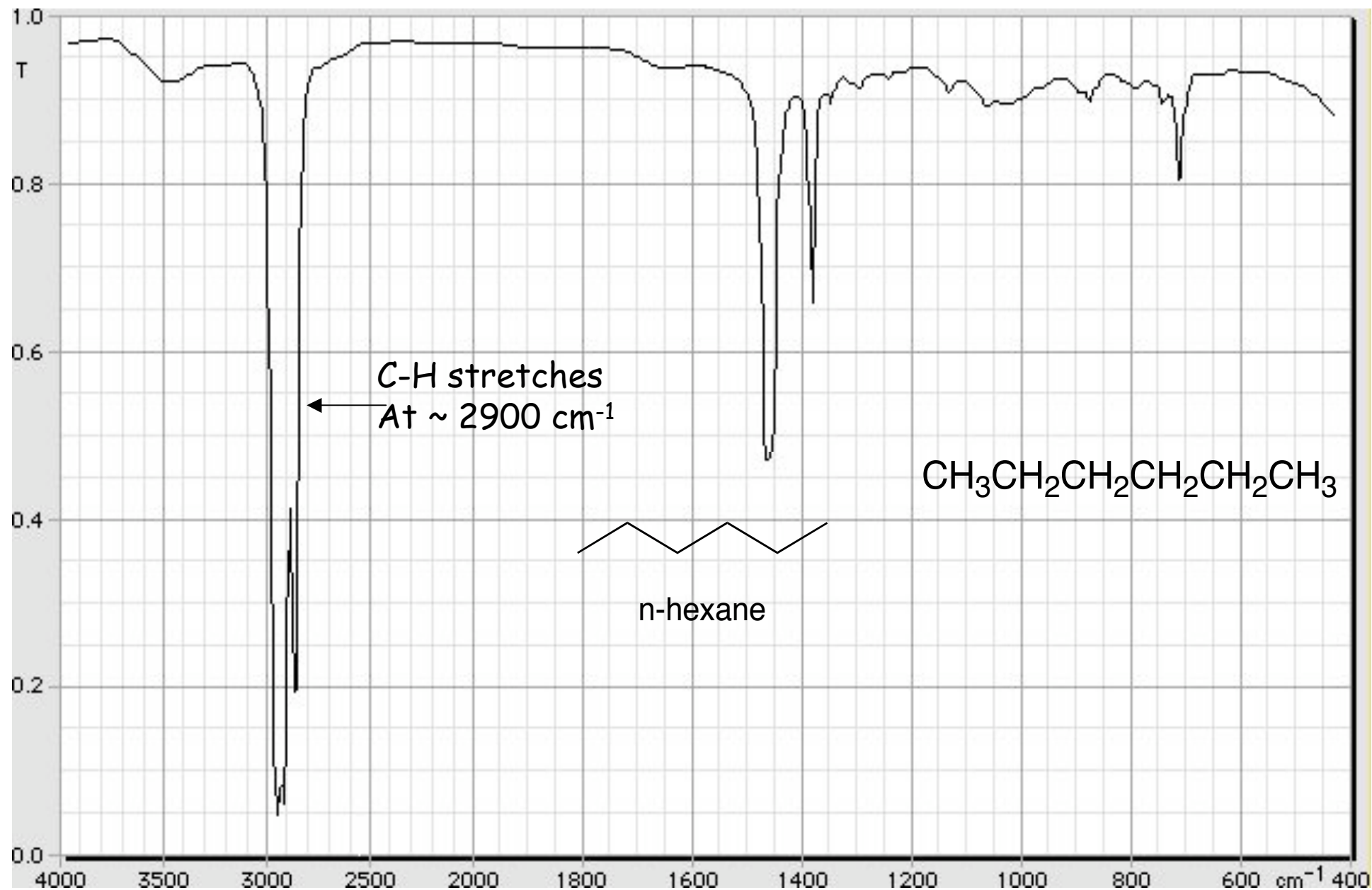
Increasing magnetic field, H_0 →



¹³C range = 0 to
~ 200 ppm

Use the correlation tables and note scale of x-axis

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

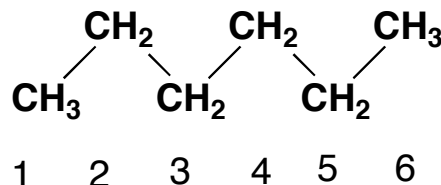


Now let's consider the ^1H (proton) and ^{13}C (carbon) NMR spectra of n-hexane (next slide).

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 ^{13}C 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?

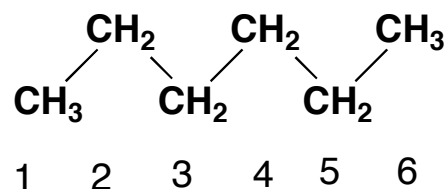


First consider the protons: there are three different kinds of protons: the CH₃ protons on C₁, the CH₂ protons on C₂ and the CH₂ protons on C₃. We note that C₁ is equivalent to C₆, C₂ is equivalent to C₅ and C₃ is equivalent to C₄.

We expect to see three signals in the ¹H NMR of n-hexane (next slide) 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.

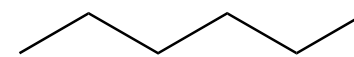
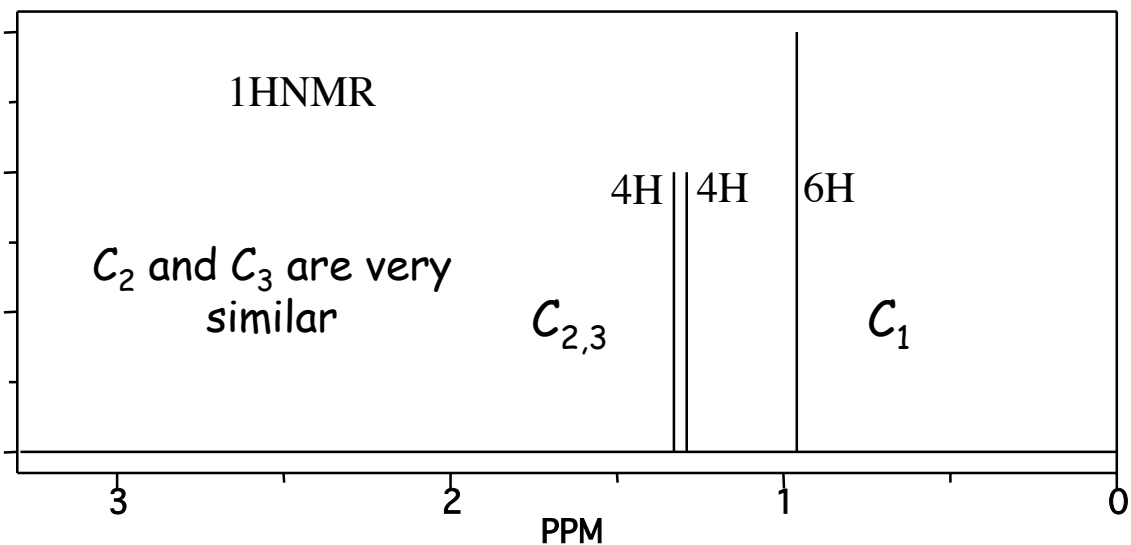
Next let's consider the *carbon* atoms of n-hexane



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

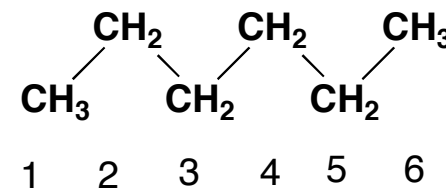
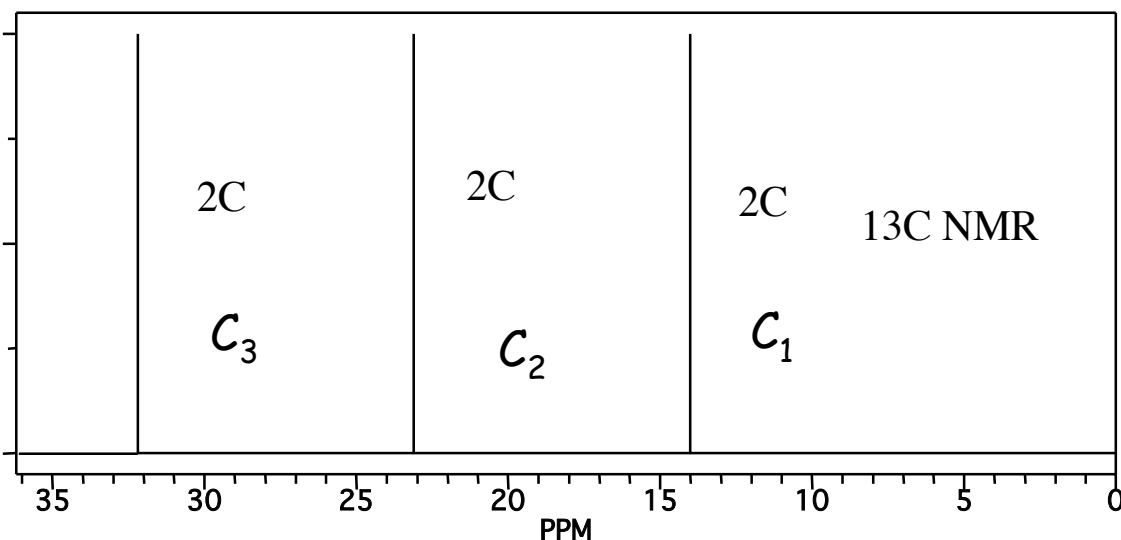
We therefore expect three signals for the three different carbon atoms

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



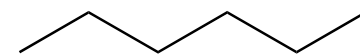
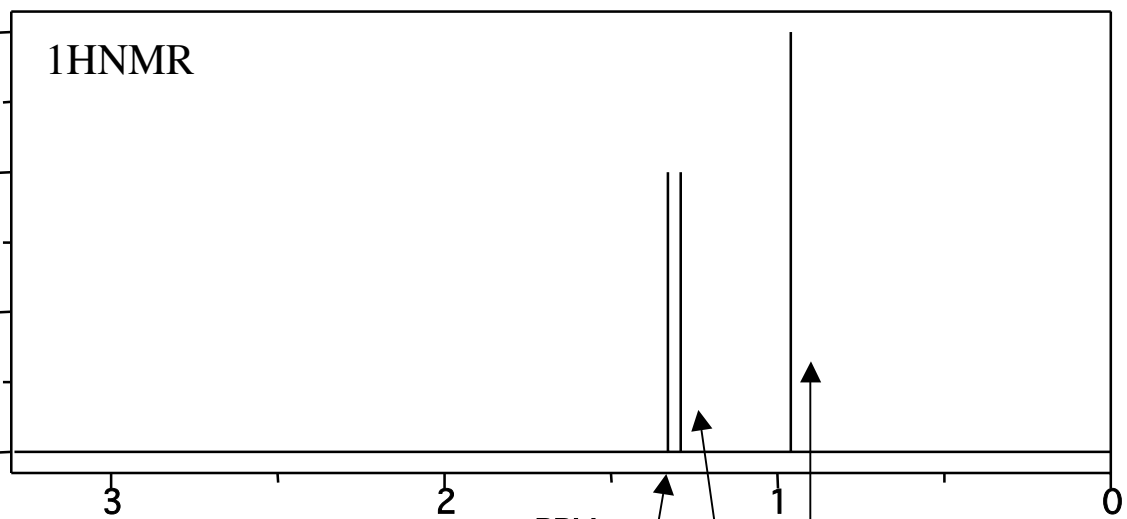
n-hexane

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



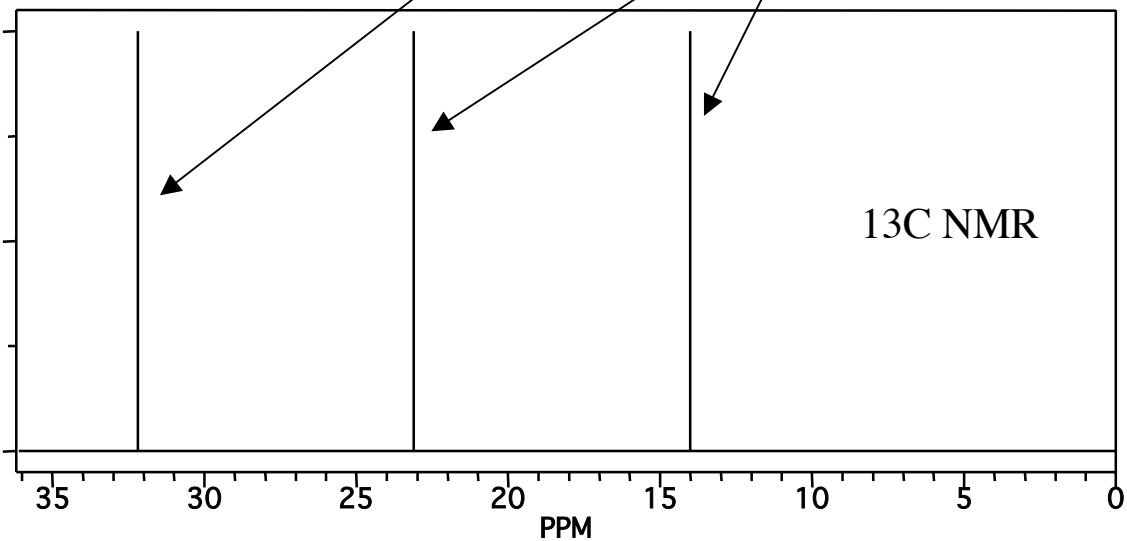
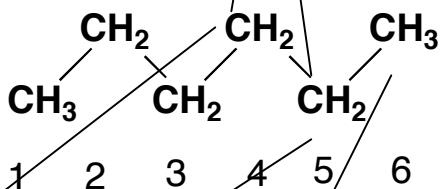
Task: Assign the 13C signals to the carbon atoms of n-hexane

Use the correlation tables and note scale of x-axis

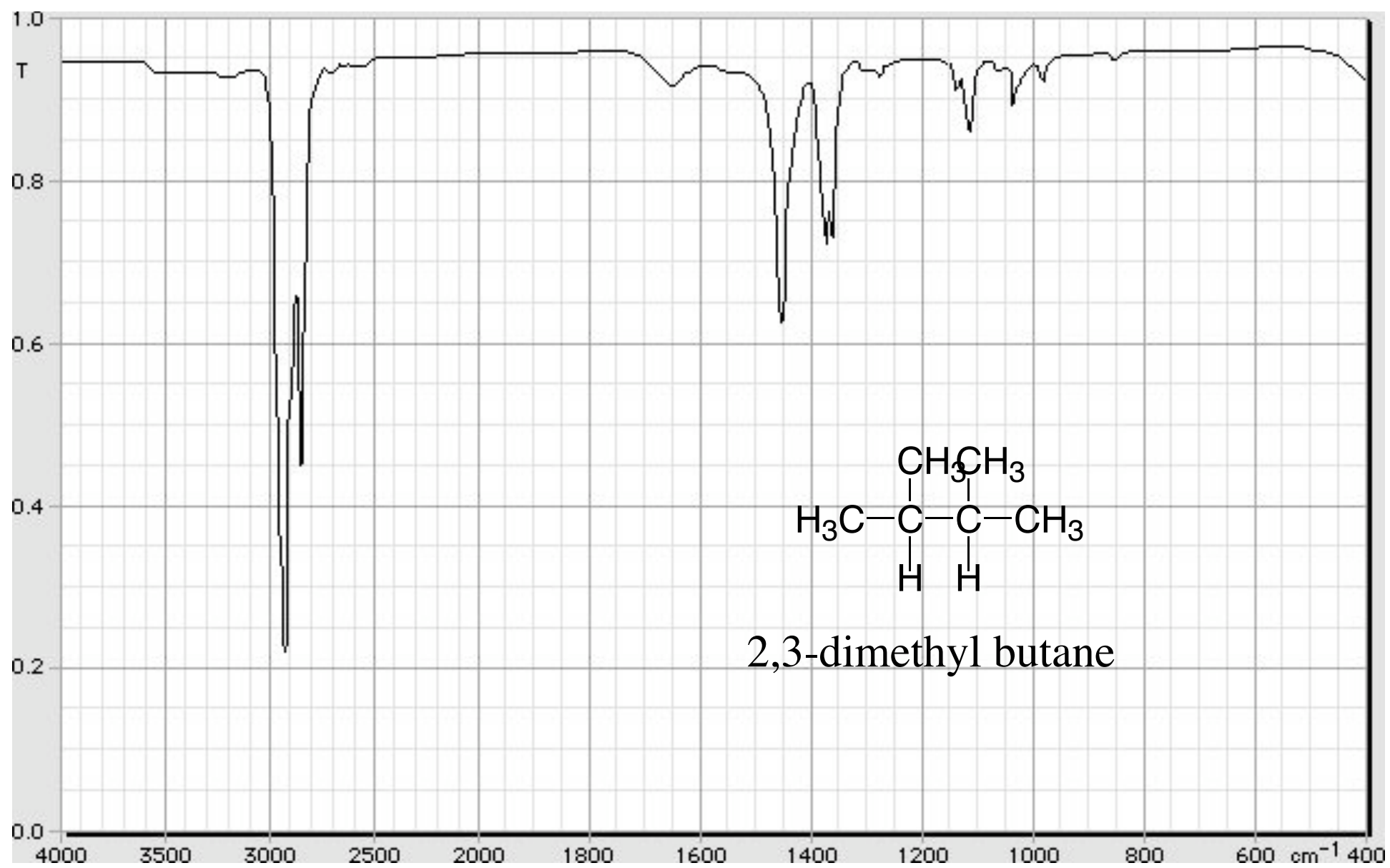


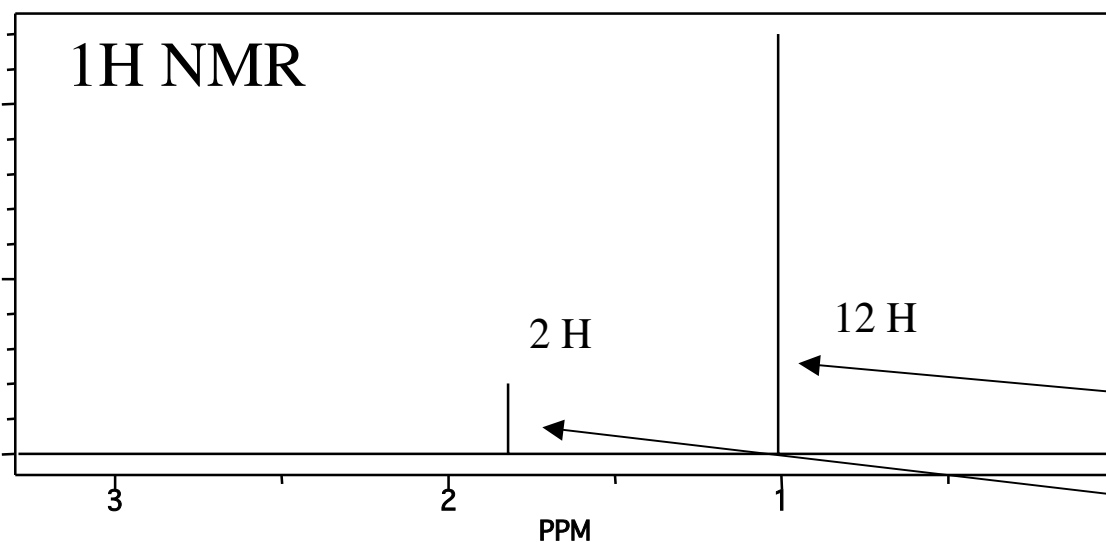
n-hexane

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

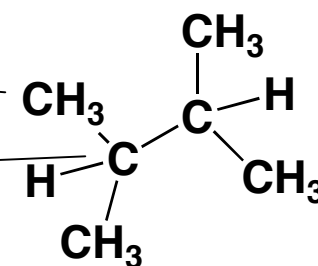
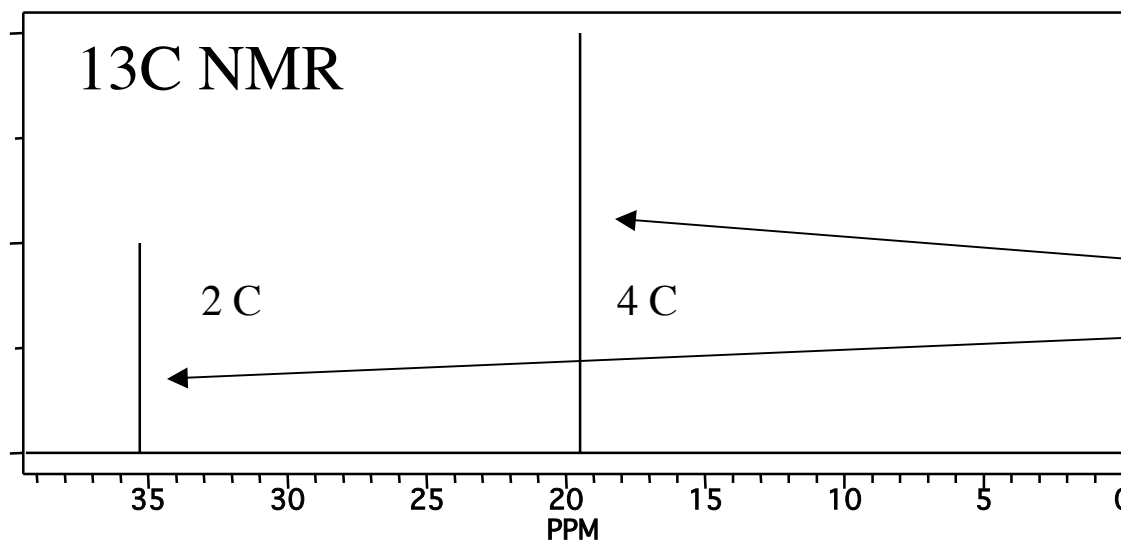
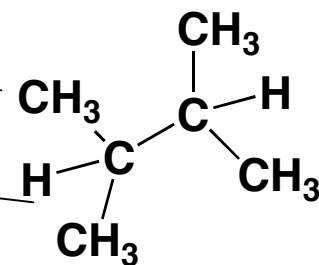


Assign the 13C signals to the carbon atoms of n-hexane

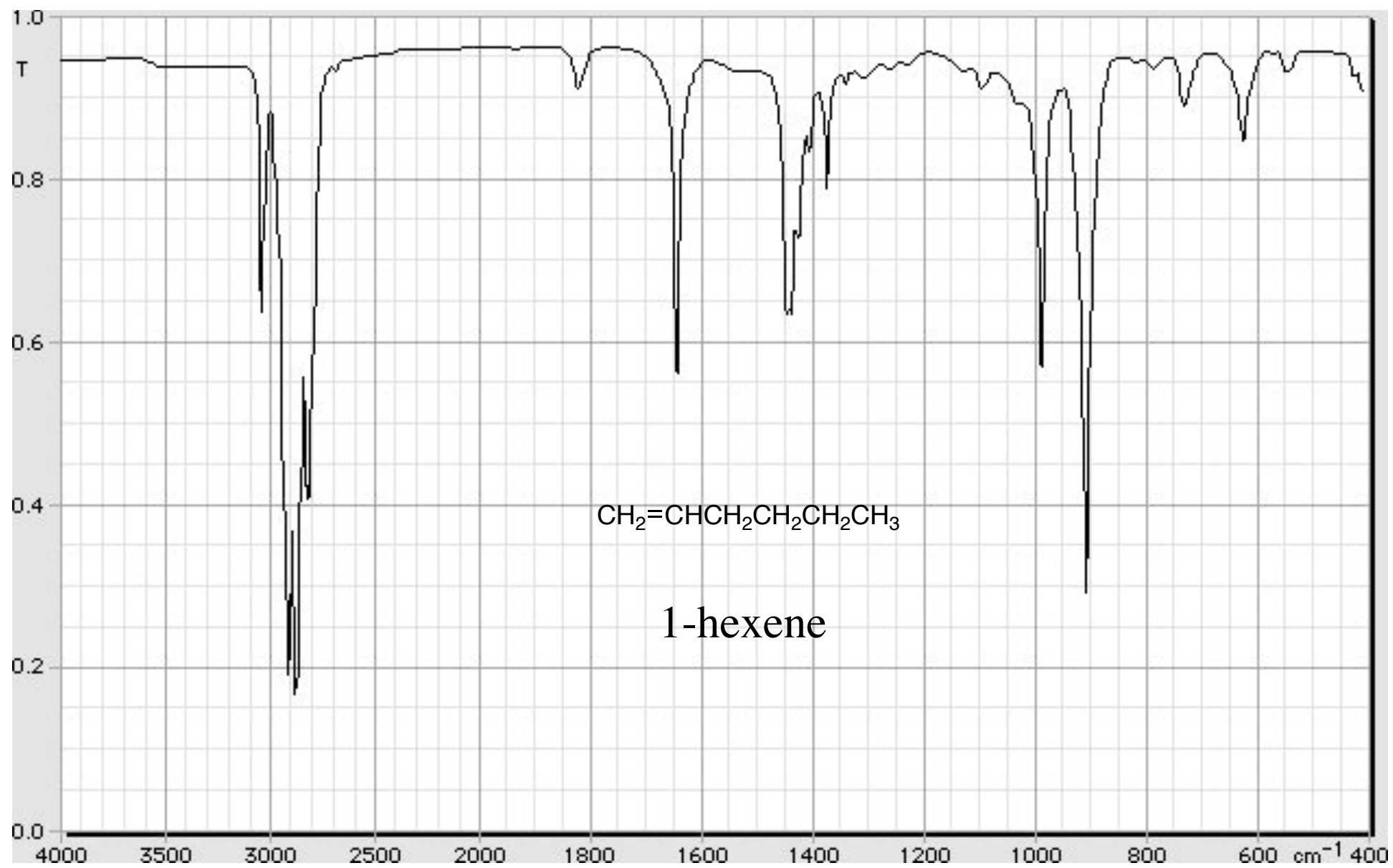


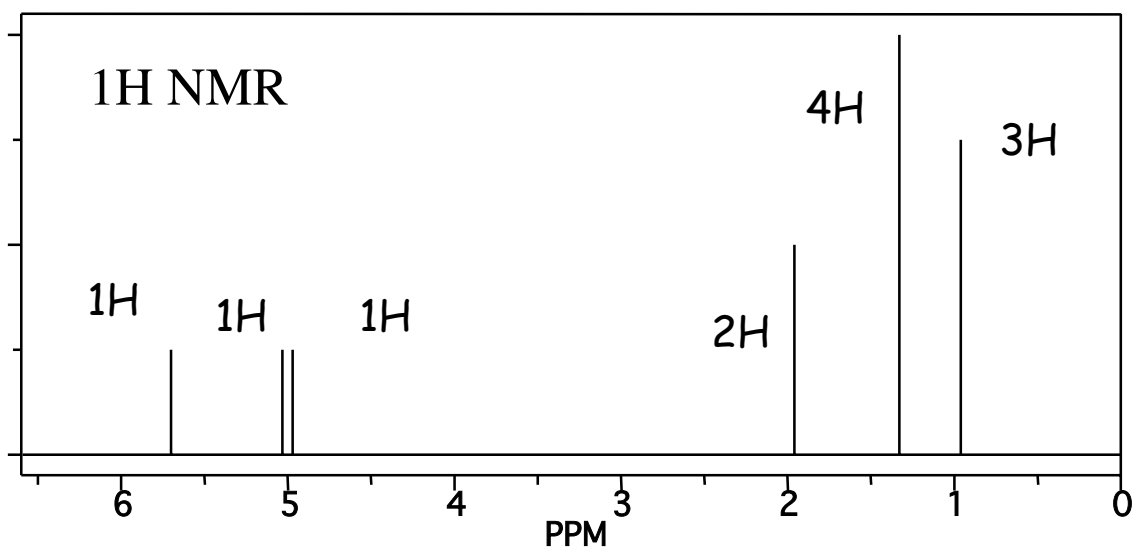


Assign the signals in the NMR spectra to the H and C in the structures

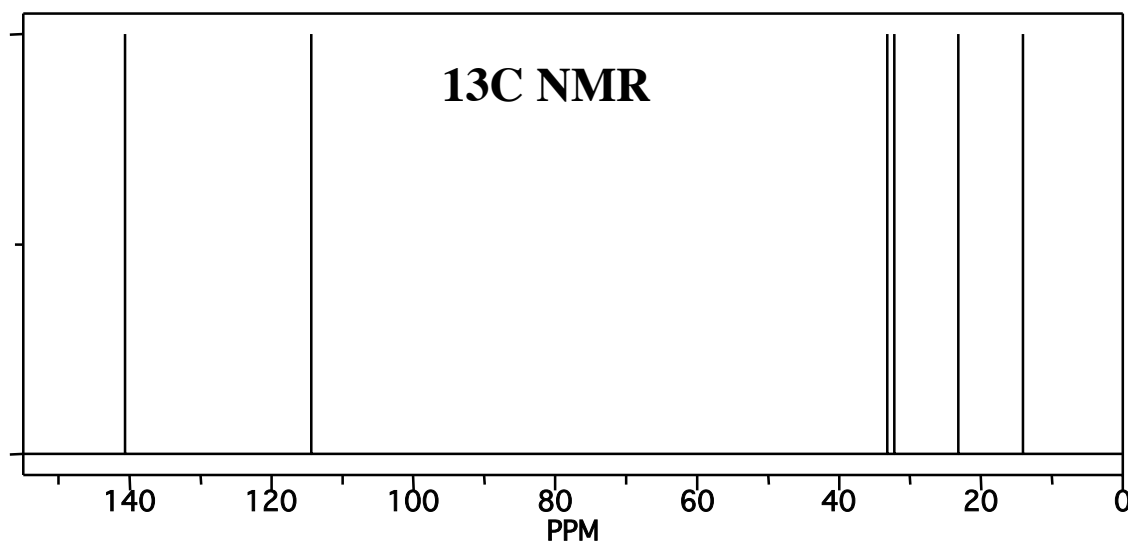
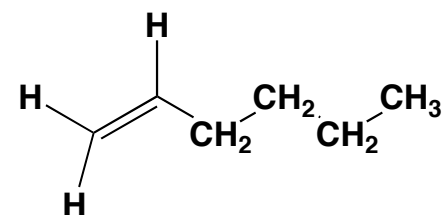


Use the correlation tables and note scale of x-axis

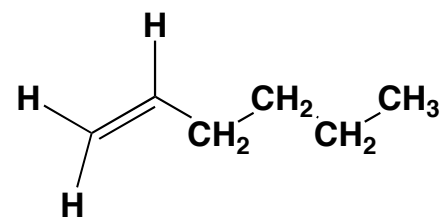




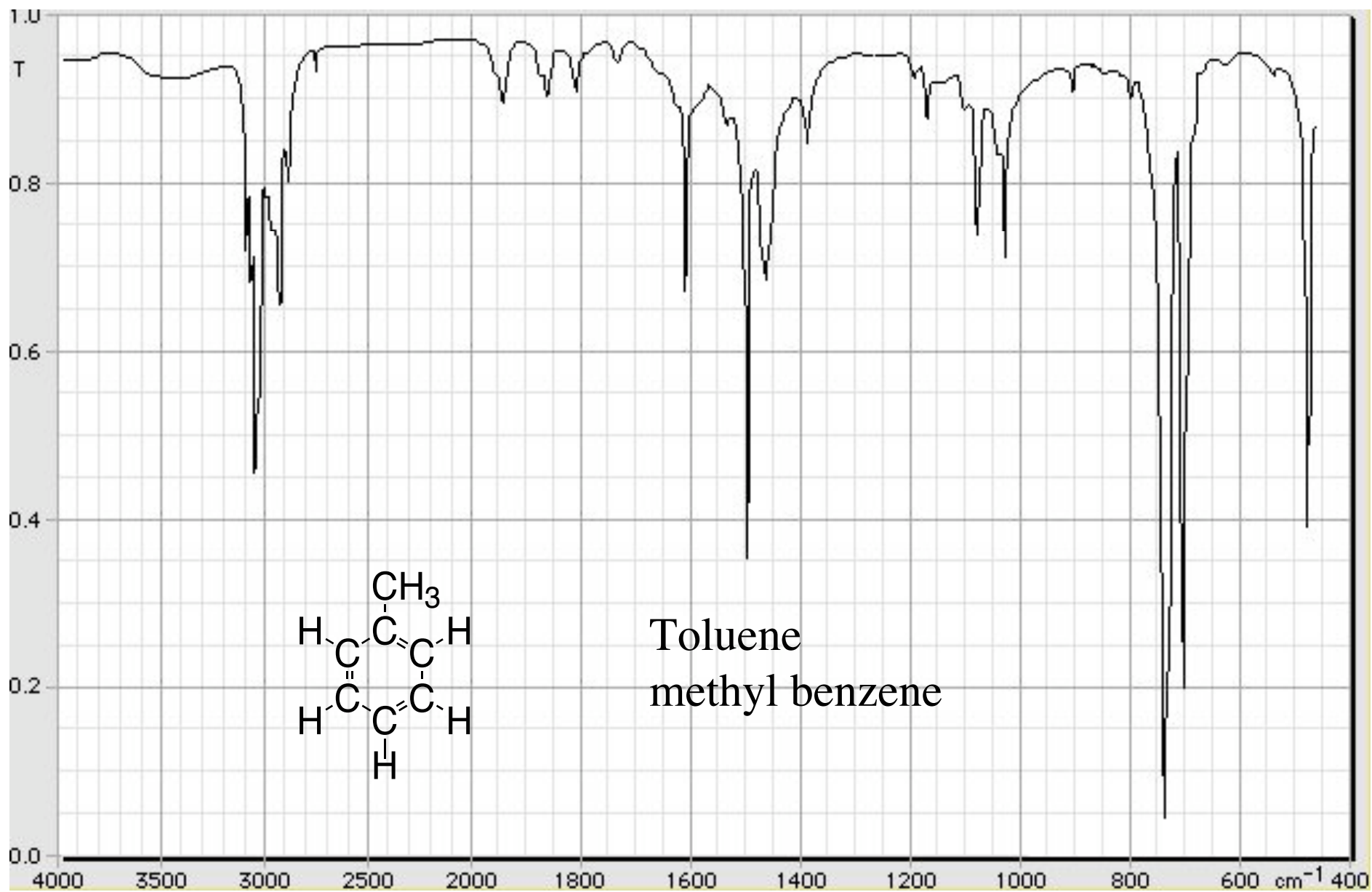
Assign the signals at ~ 5 ppm and ~ 5.7.

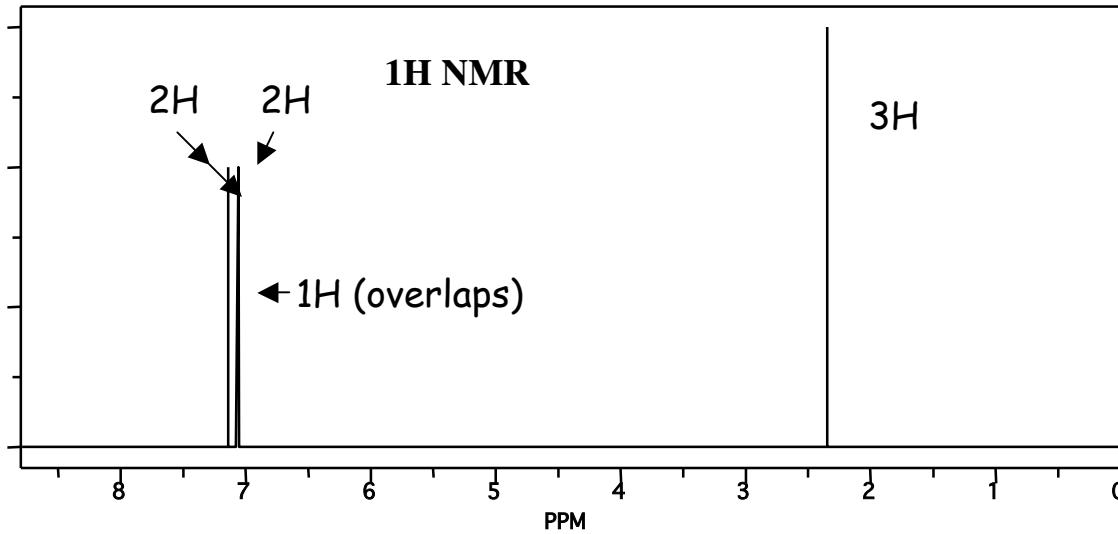


Assign the signals at ~ 115 ppm and ~ 140 ppm.

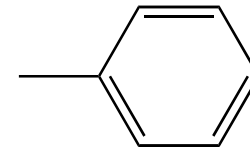


Use the correlation tables and note scale of x-axis

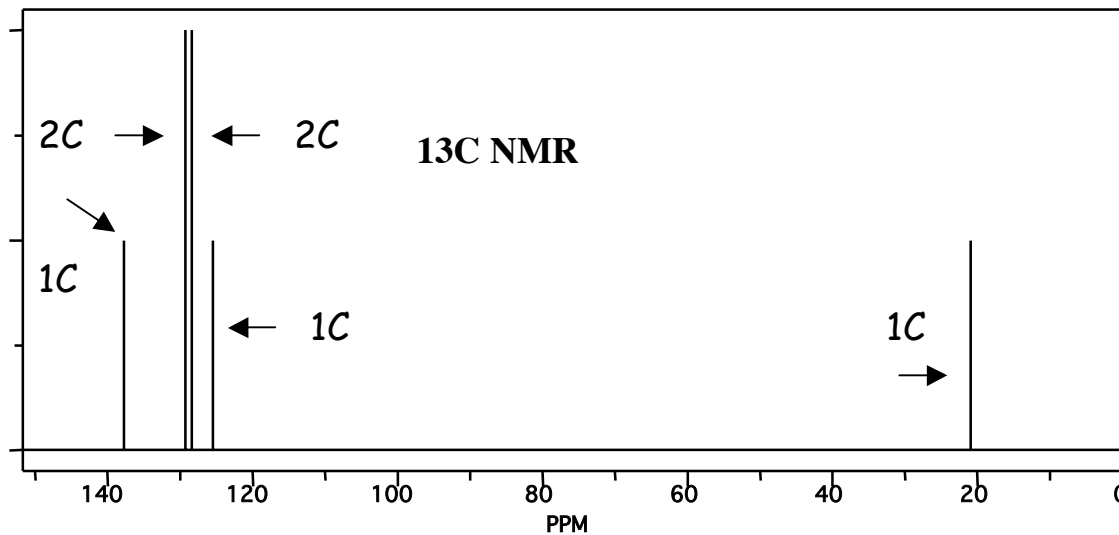




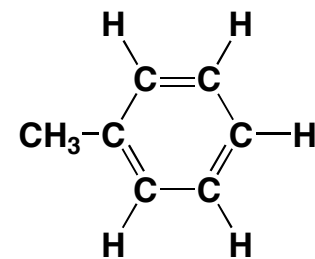
Assign the signal at
~ 2.3 ppm.



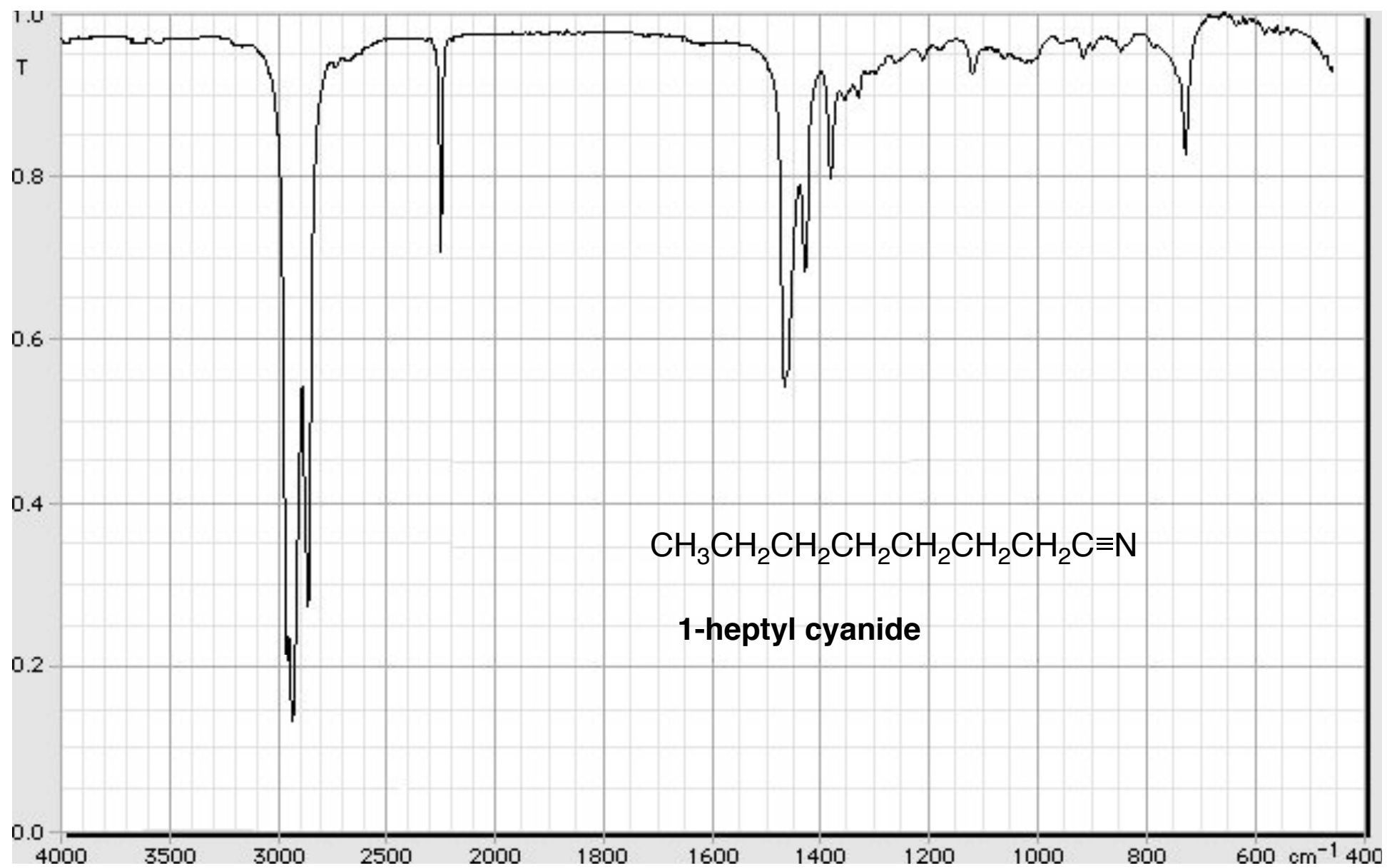
toluene

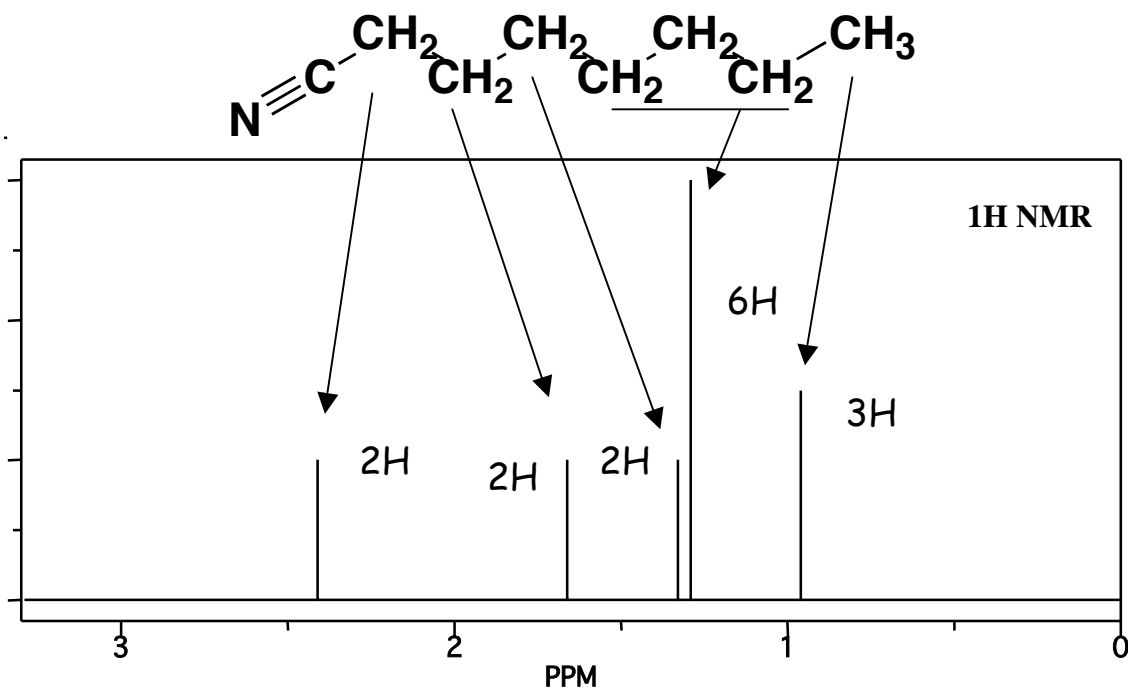


Assign the signal at
~ 20 ppm.

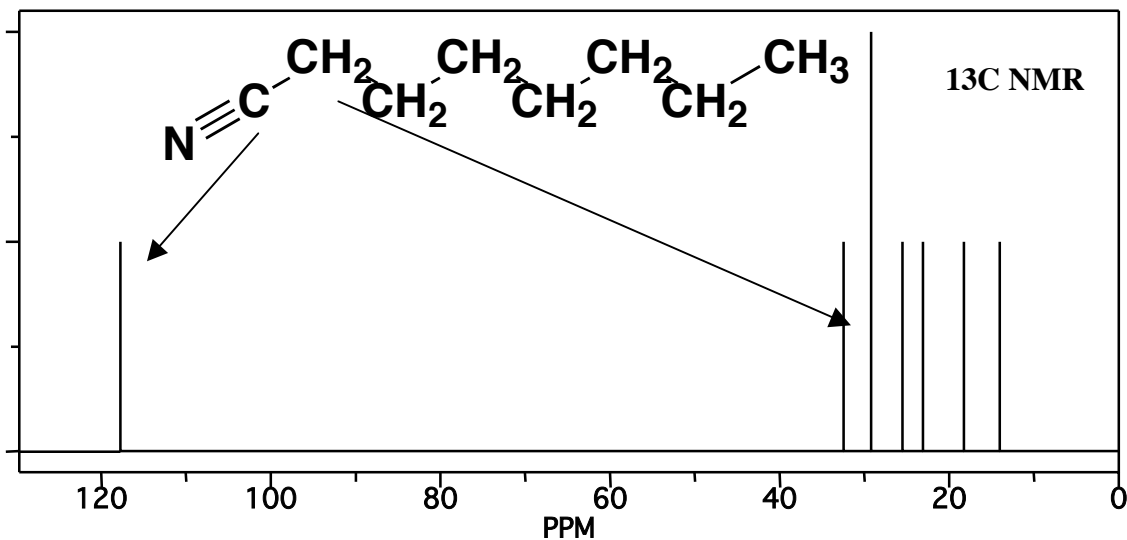


Use the correlation tables and note scale of x-axis

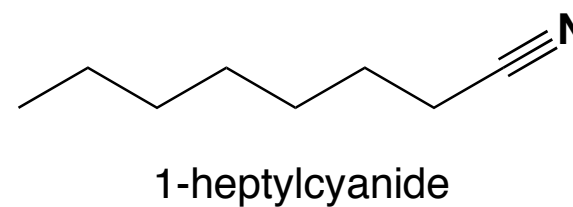




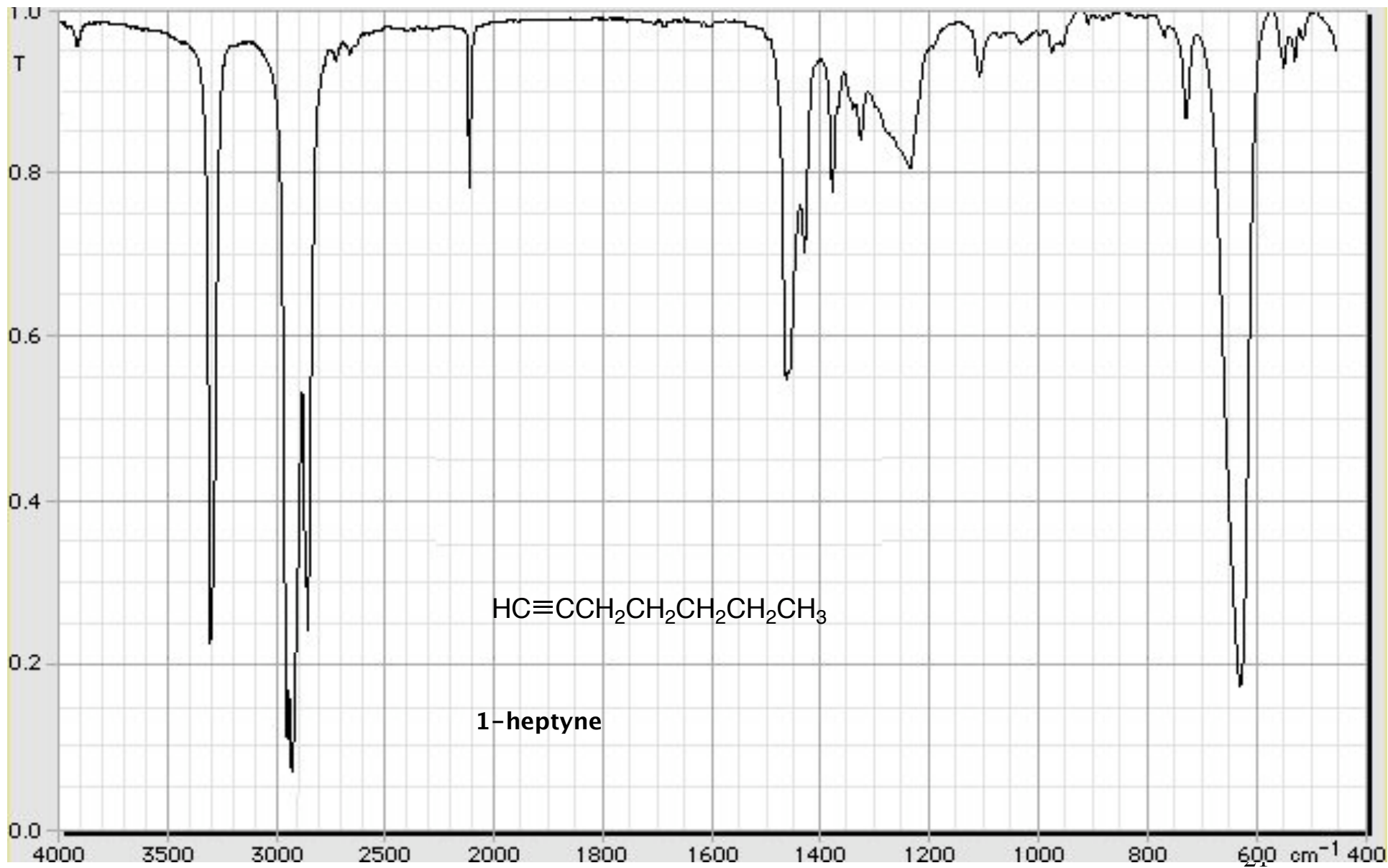
Assign the 1H signals

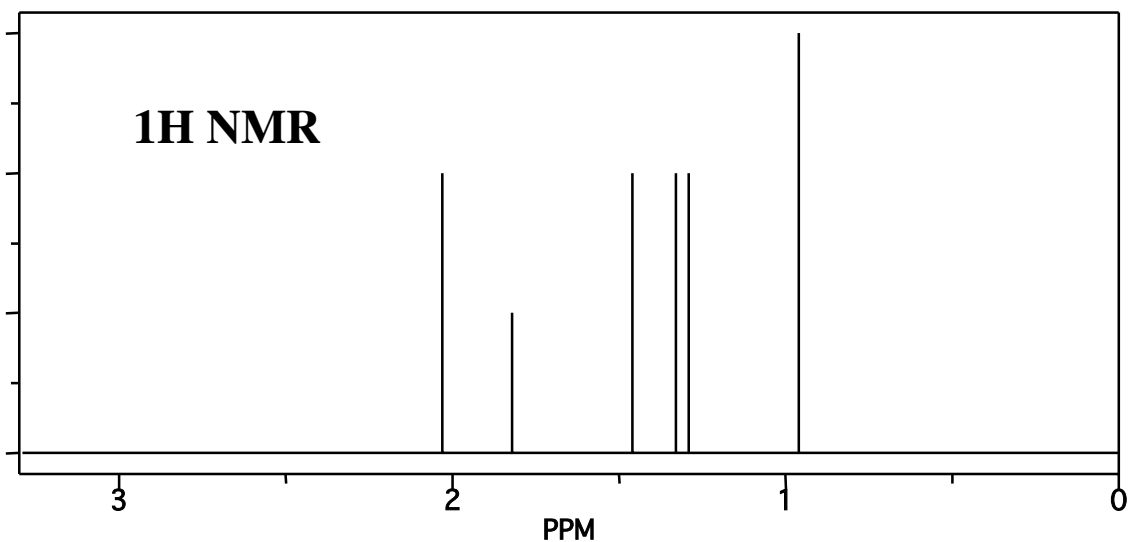


Assign the 13C signals

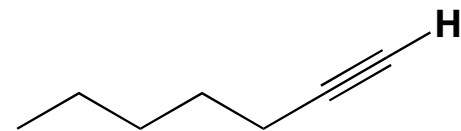


Use the correlation tables and note scale of x-axis

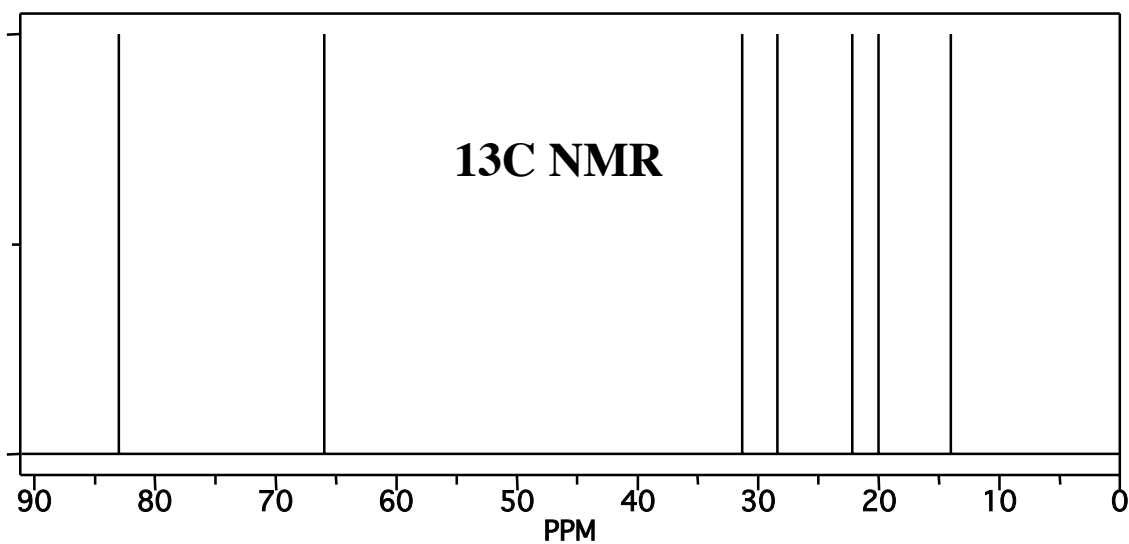




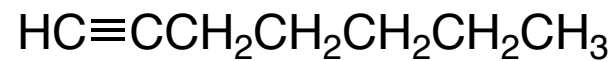
Can you find the C-H signal associated with the triple bond?



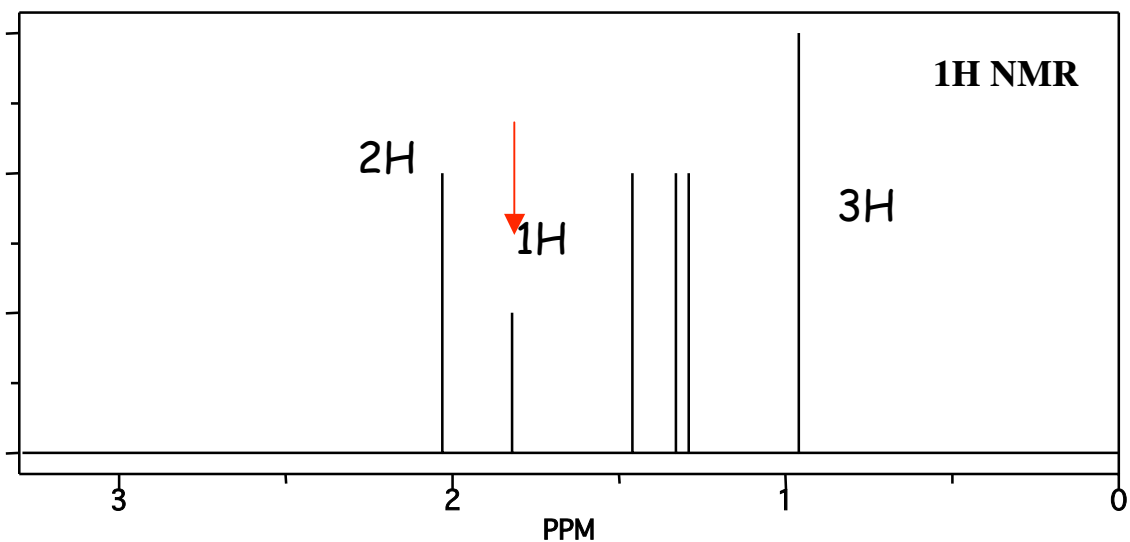
1-heptyne



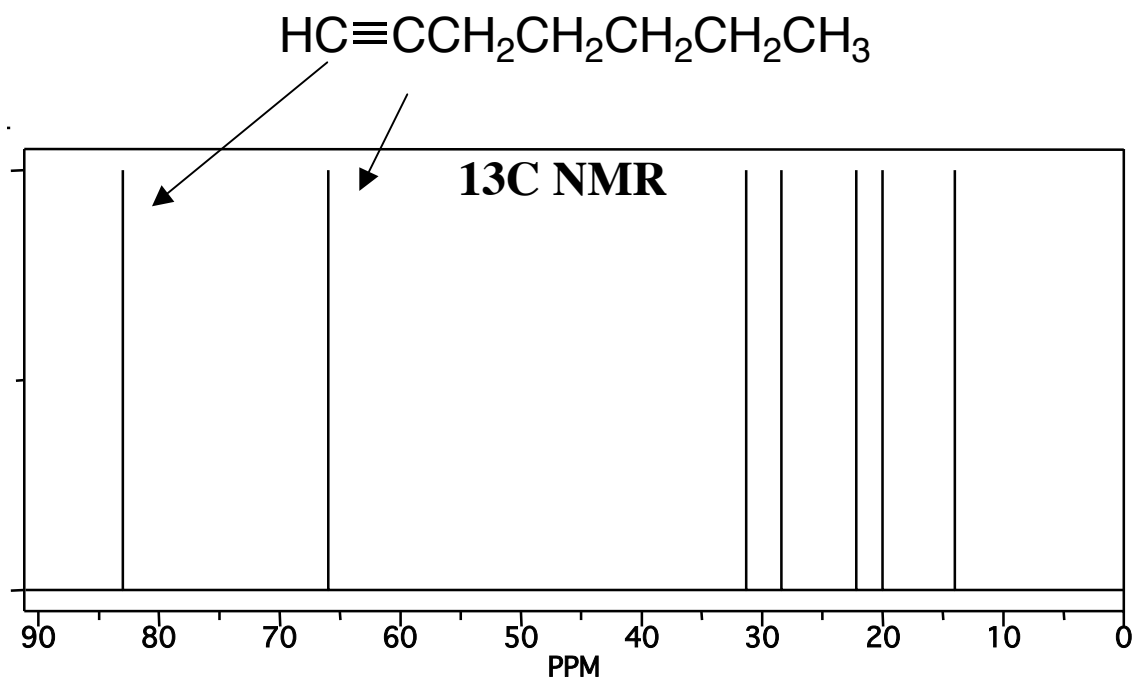
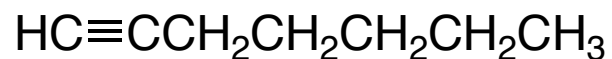
Which signals are due to the triple bond carbons?



Use the correlation tables and note scale of x-axis

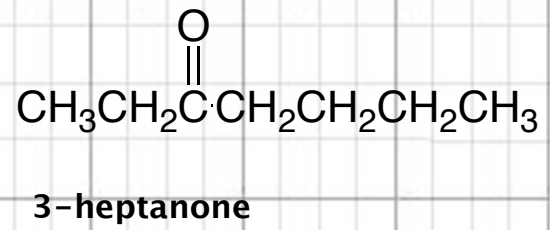
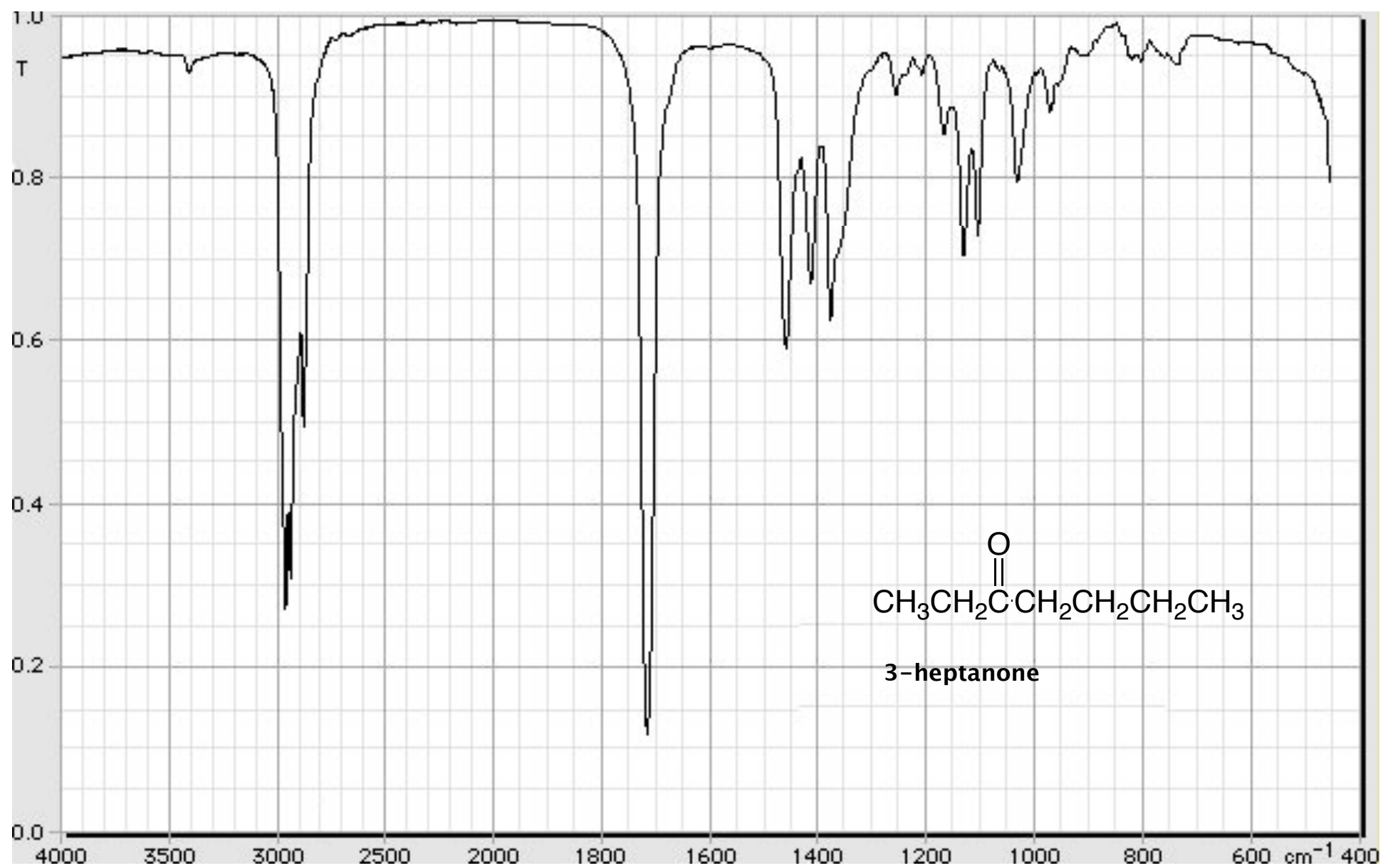


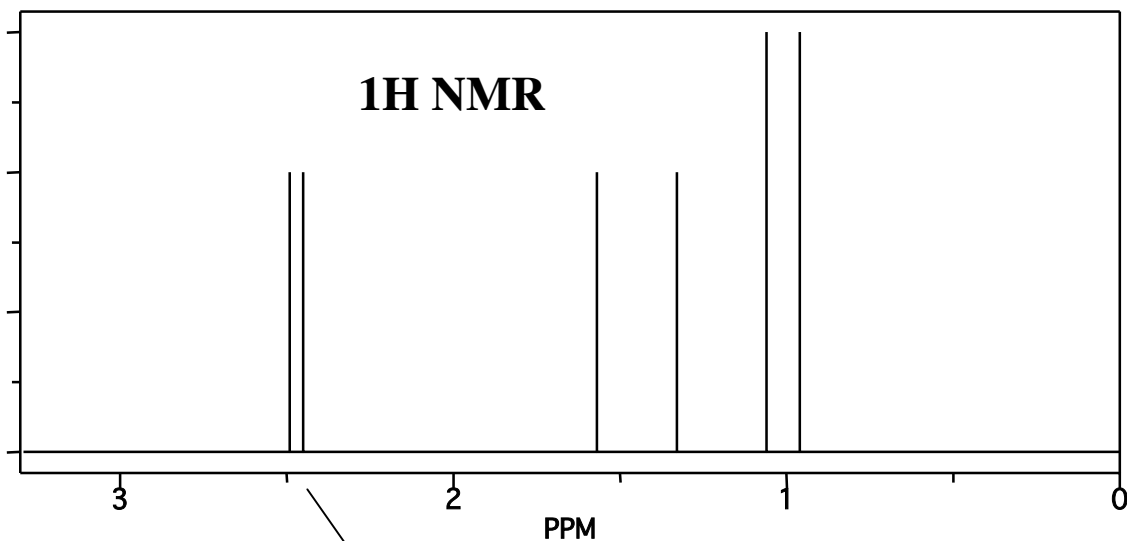
Can you find the C-H signal associated with the triple bond?



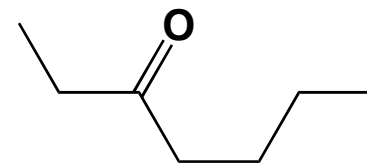
Which signals are due to the triple bond carbons?

Use the correlation tables and note scale of x-axis

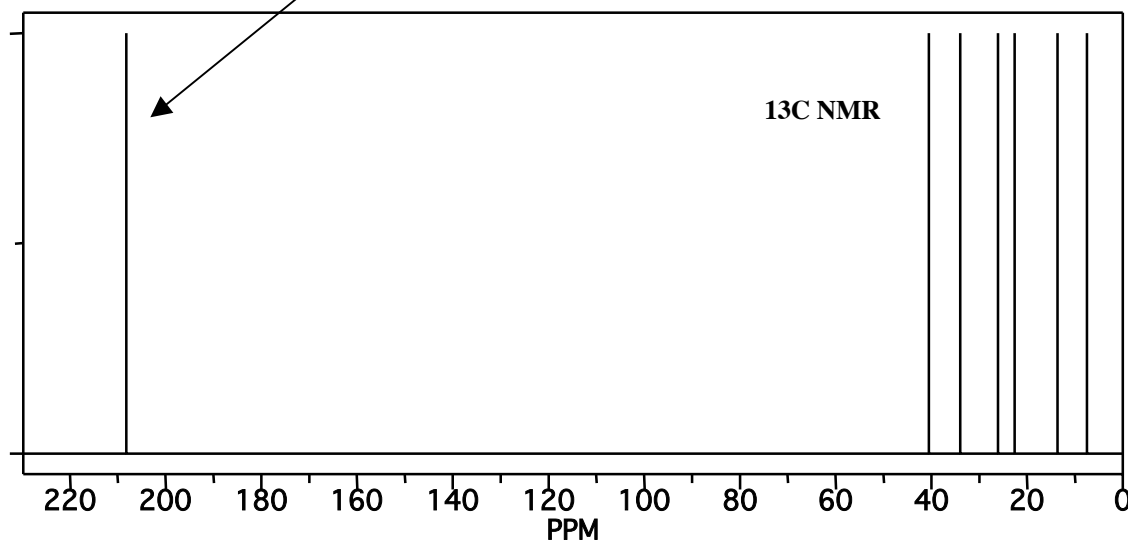
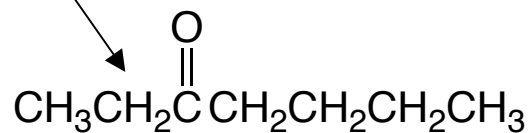




¹H: How many signals can you assign?

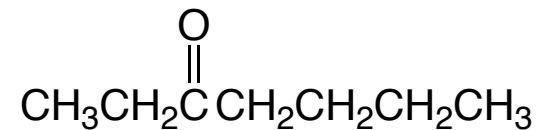


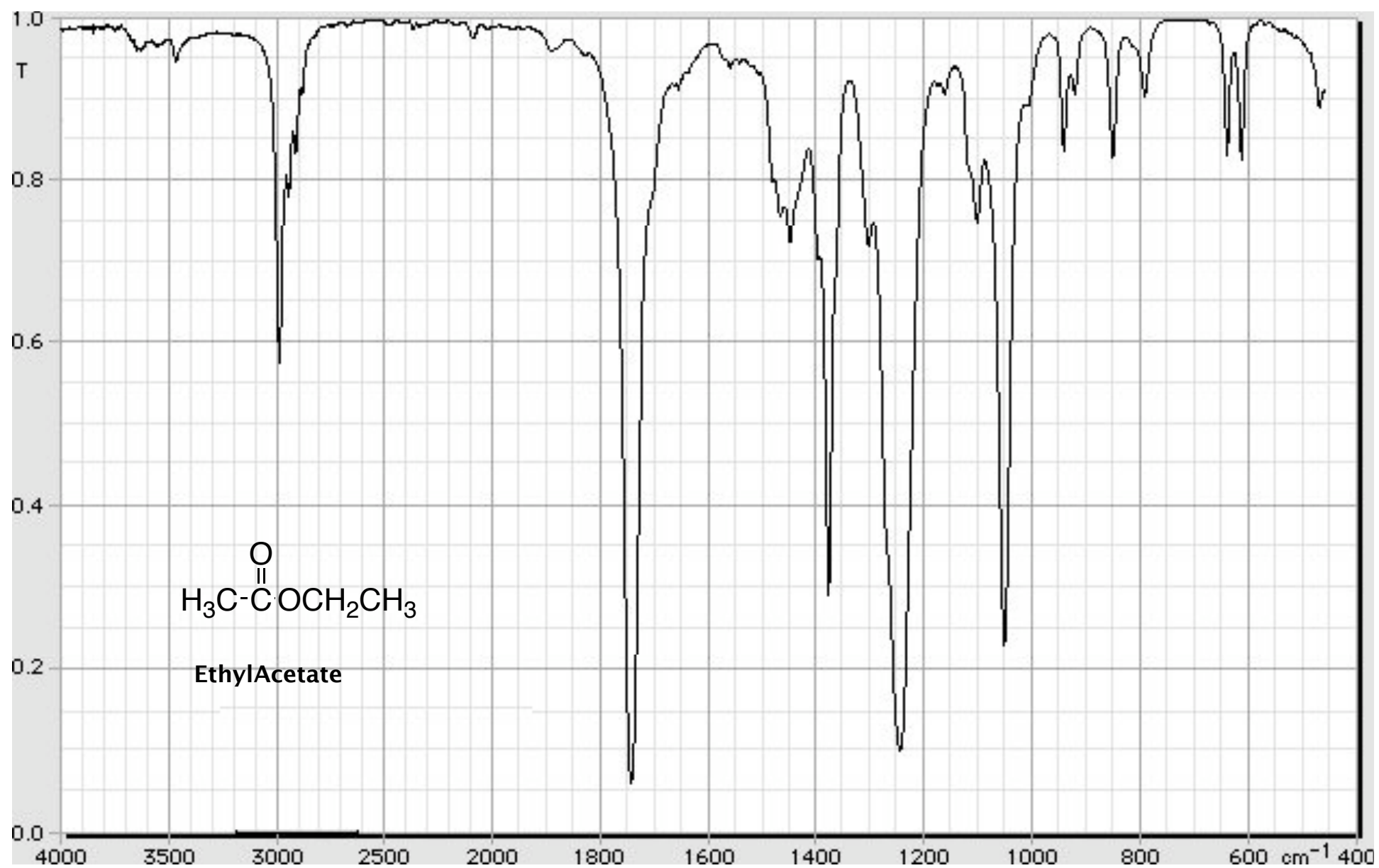
3-heptanone

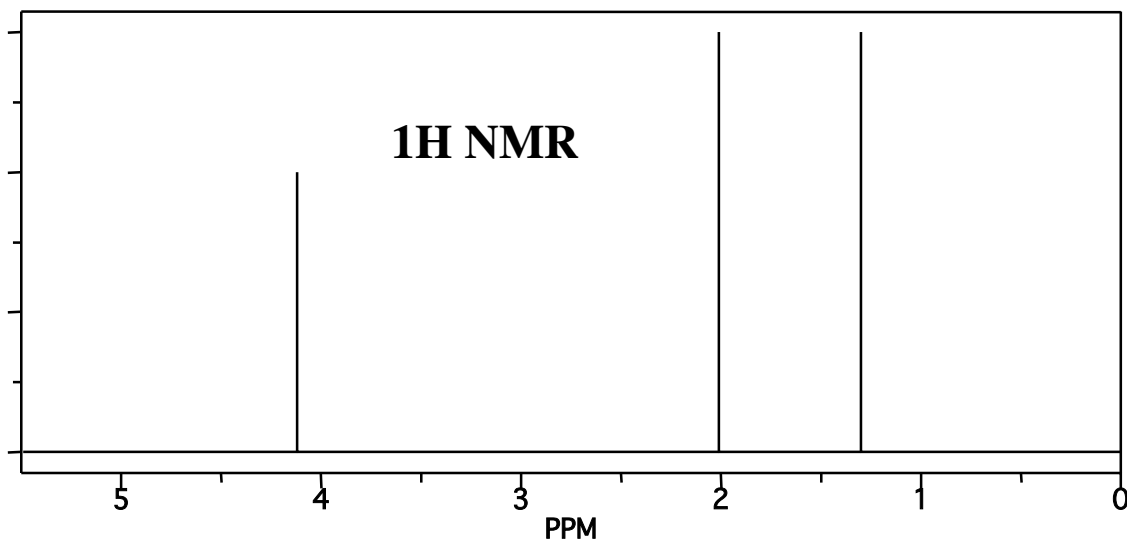


¹³C: What is the signal at ~ 210 ppm due to?

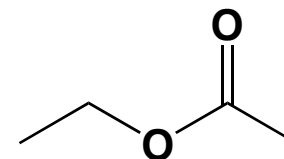
Which signal is associated with this signal in the IR of 3-heptanone?



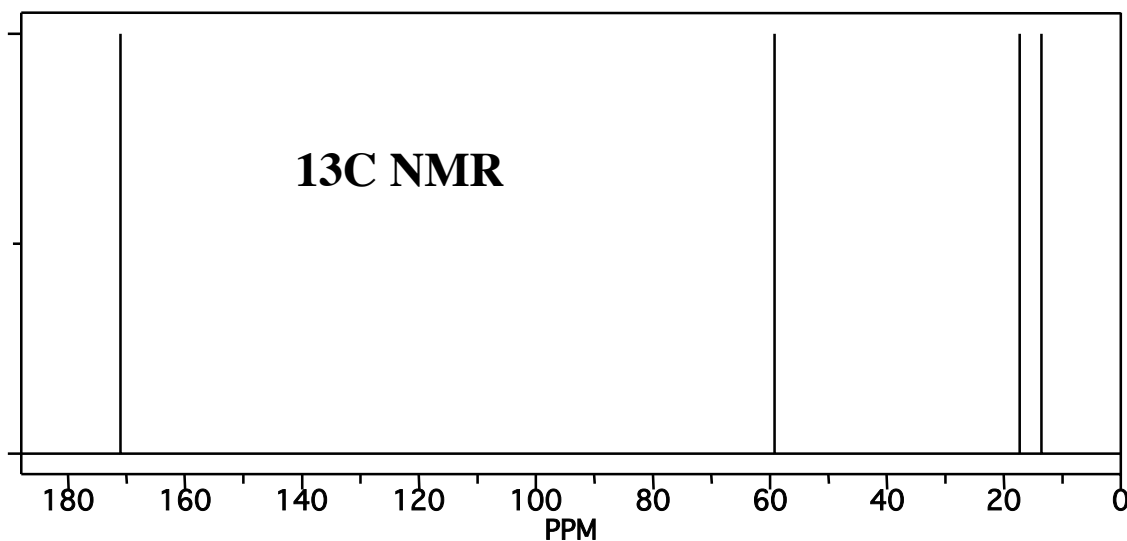




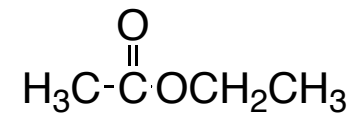
What is the signal at ~ 4.2 ppm due to? The signal at ~ 2.0 ppm?



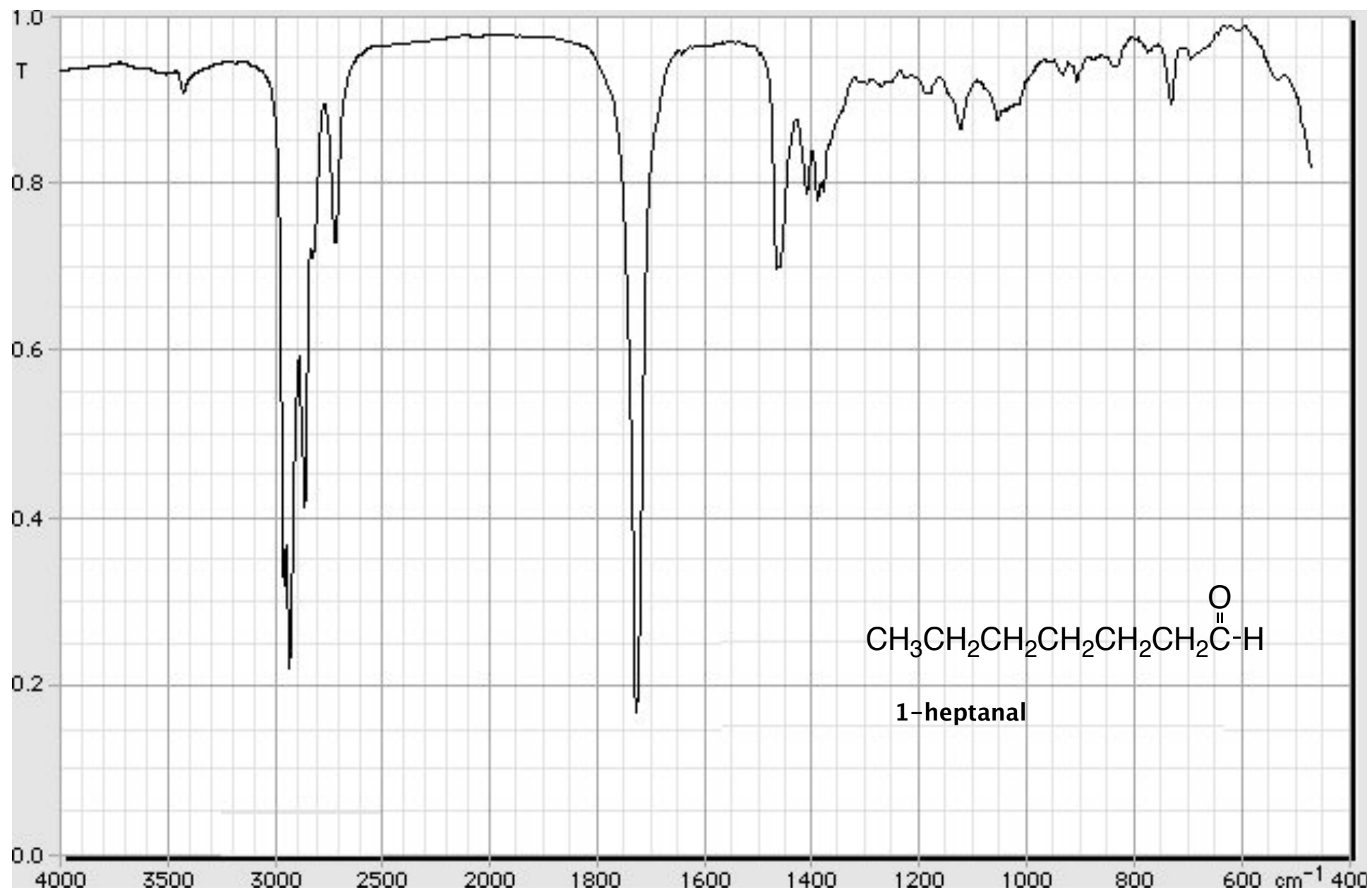
ethyl acetate

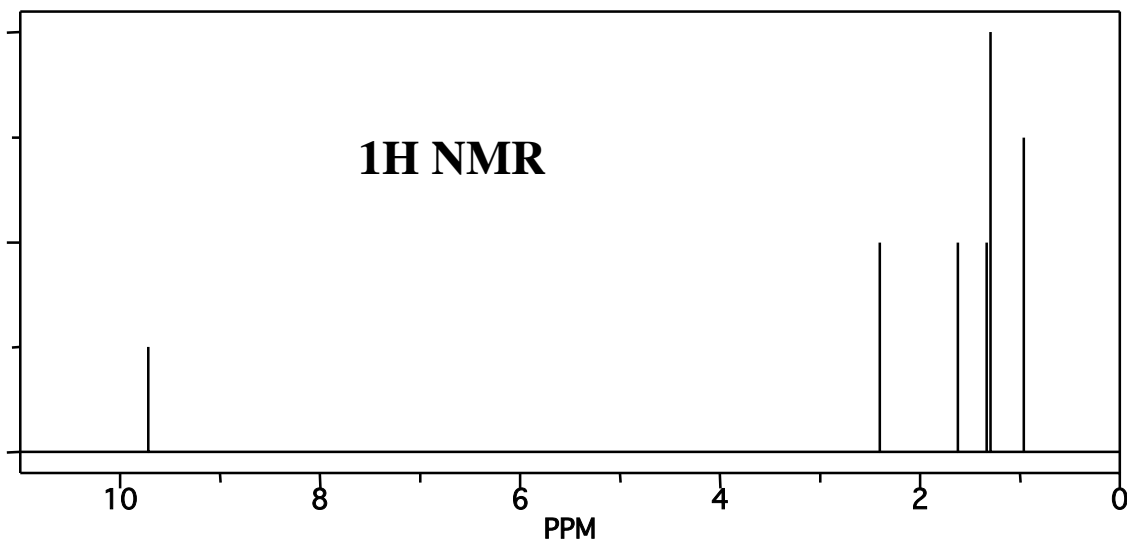


What are the peaks at ~ 170 ppm and ~60 ppm due to?

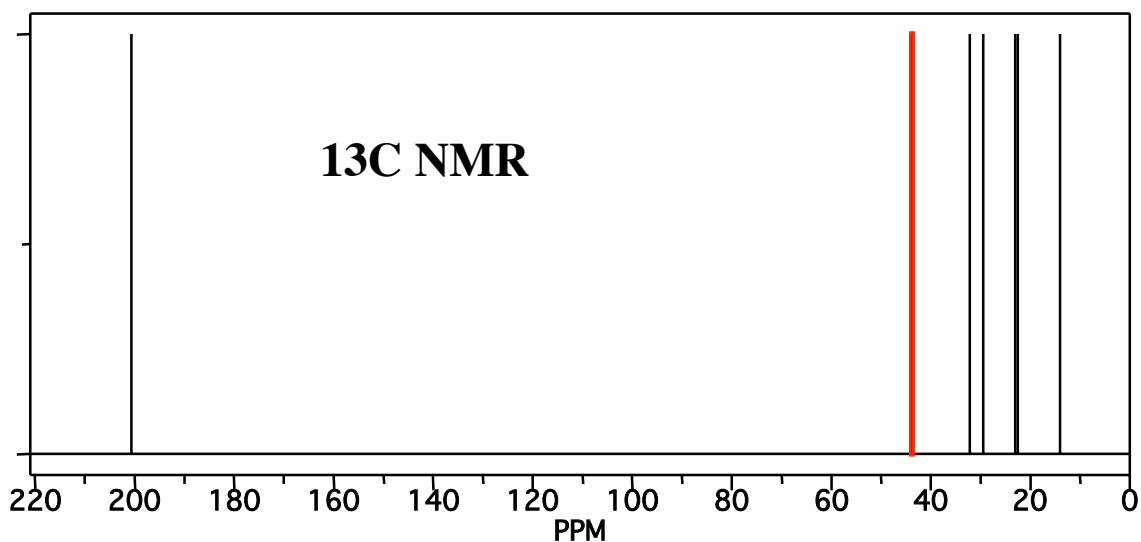
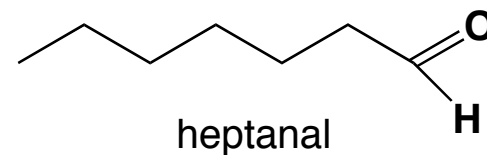


Use the correlation tables and note scale of x-axis

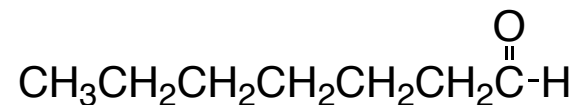




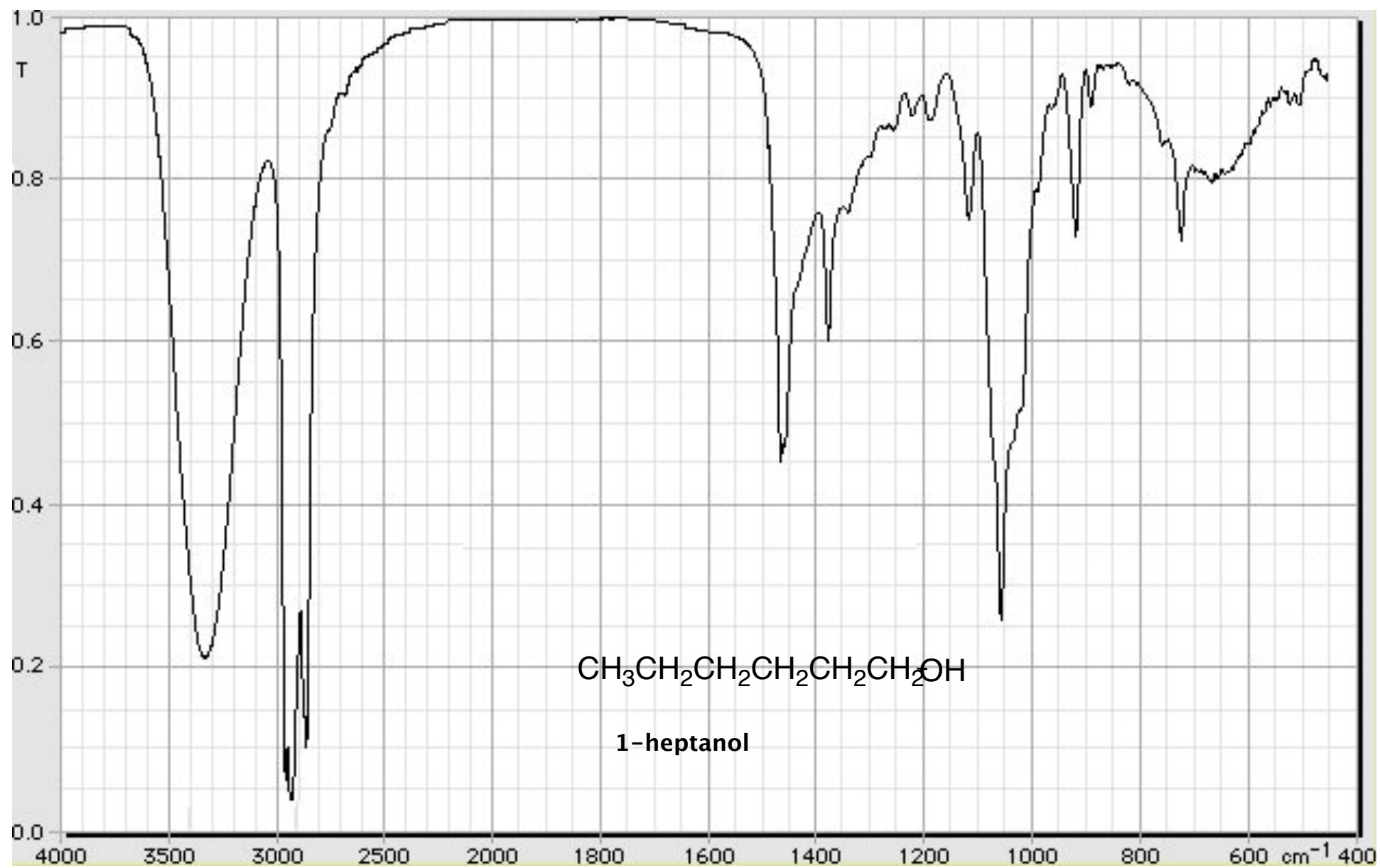
What is the signal at ~ 10 ppm due to? Can you find the analogous signal in the IR?

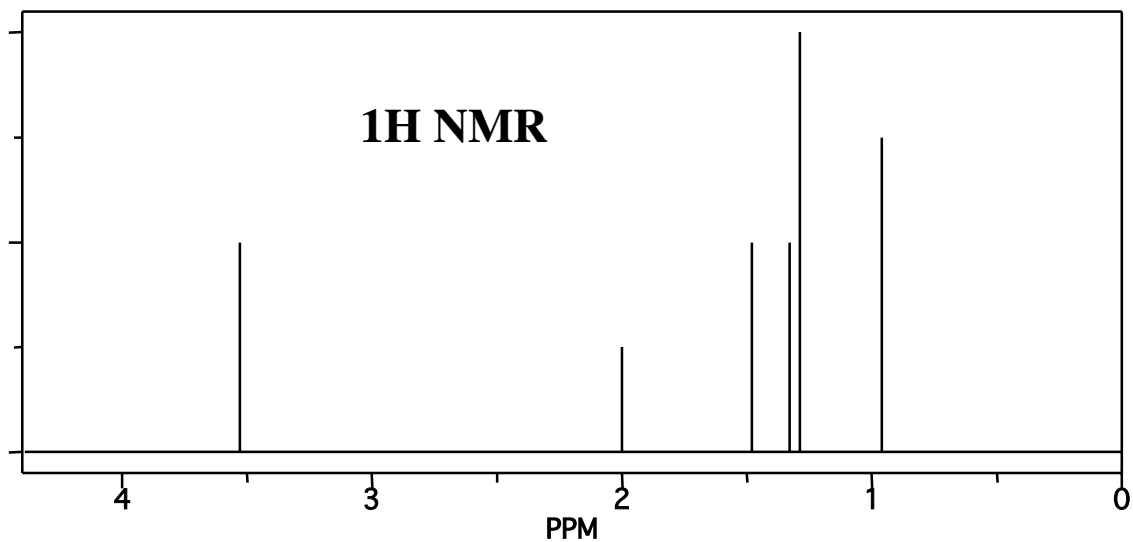


What is the signal at ~ 200 ppm due to?

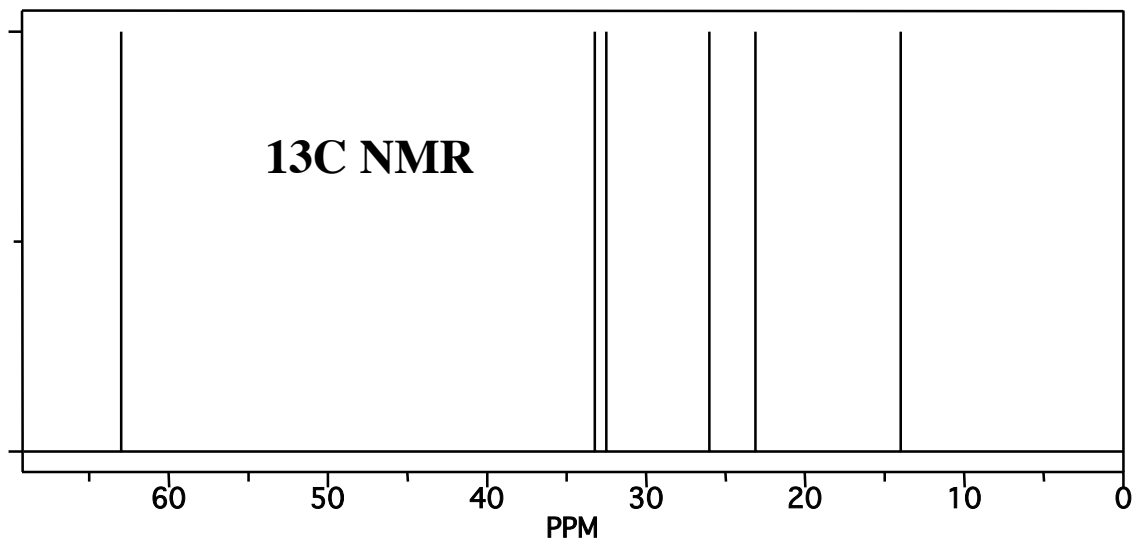
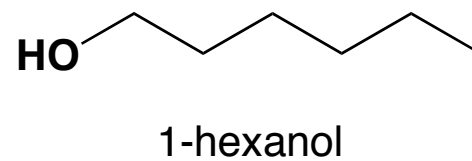


Use the correlation tables and note scale of x-axis

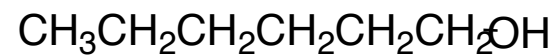




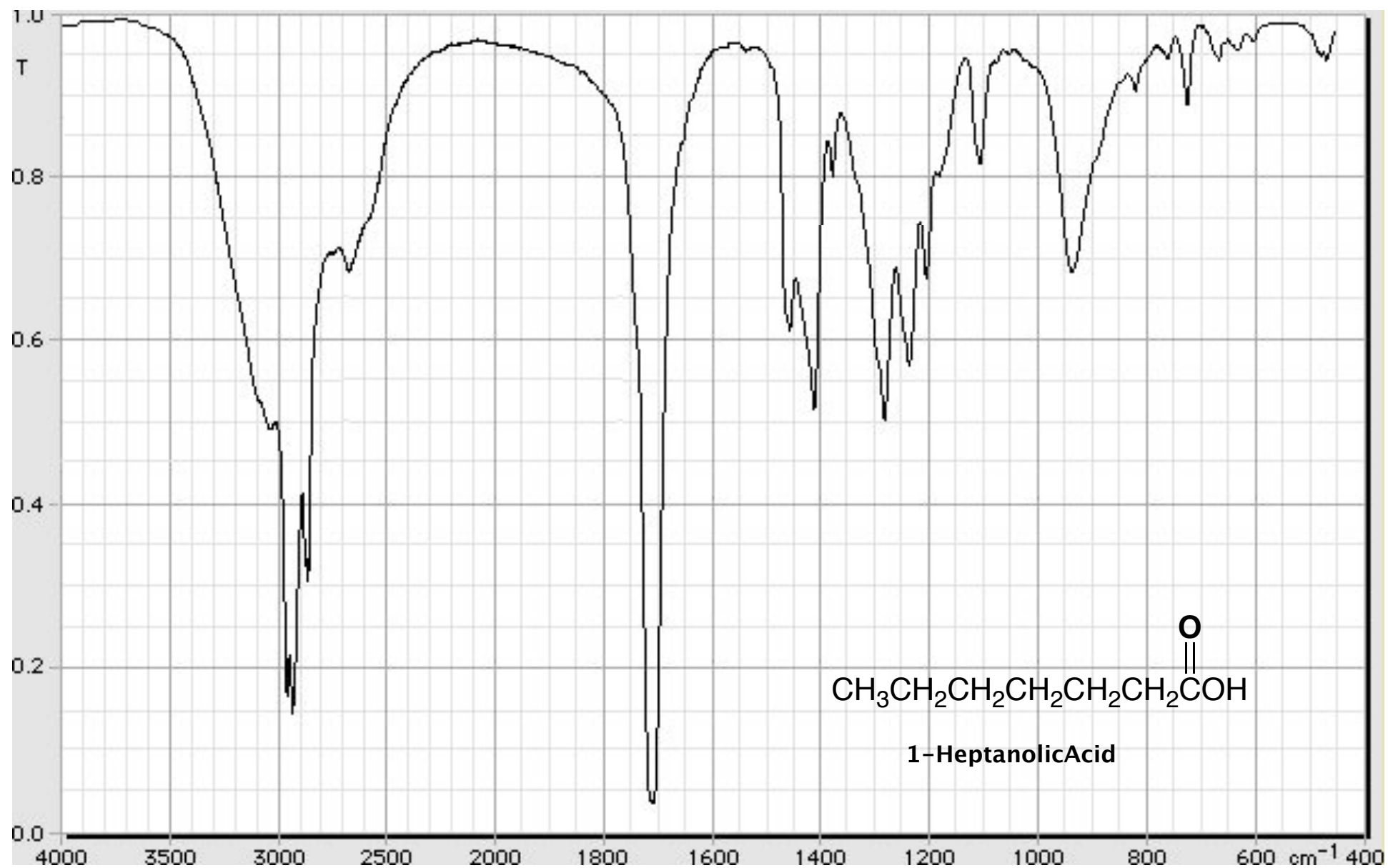
What is the signal at
~ 3.5 ppm due to?

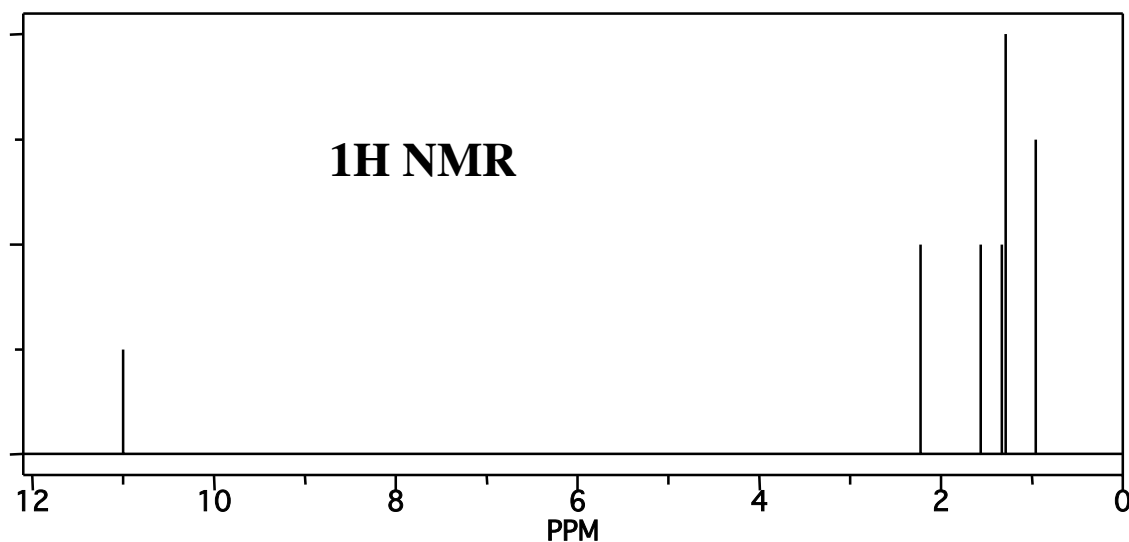


What is the signal ~63
ppm due to?

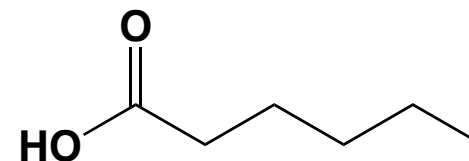


Use the correlation tables and note scale of x-axis

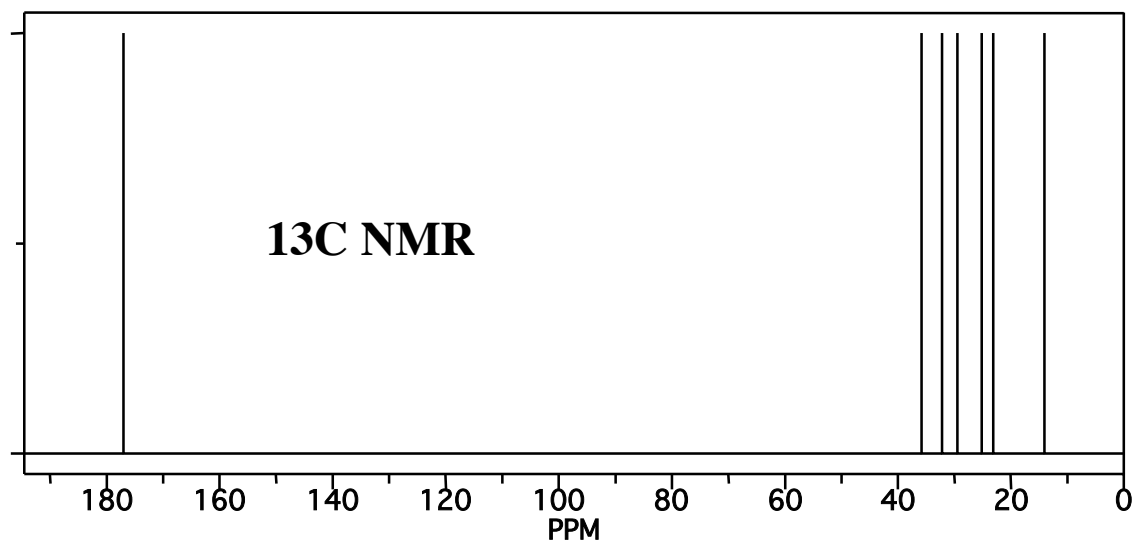




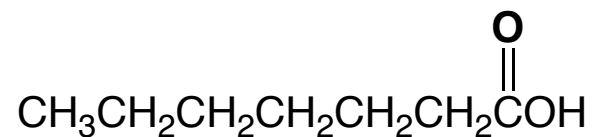
What is the signal at ~ 11 ppm due to?



1-heptanoic acid



What is the signal at ~180 ppm due to?



Use the correlation tables and note scale of x-axis