

## NMR Spectroscopy II

**Reading:** Wade chapter 13, sections 13-7- 13-13

**Study Problems:** 13-36, 13-38, 13-45, 13-47, 13-48

### **Key Concepts and Skills:**

- Use proton spin-spin splitting patterns to determine the structure of alkyl and other groups in a molecule
- Predict which protons in a structure will be magnetically coupled, and predict the number of peaks and approximate coupling constants of their multiplets.
- Predict the approximate chemical shifts of carbon atoms in a given compound. Given the chemical shifts of  $^{13}\text{C}$  absorptions, suggest likely types of carbons.

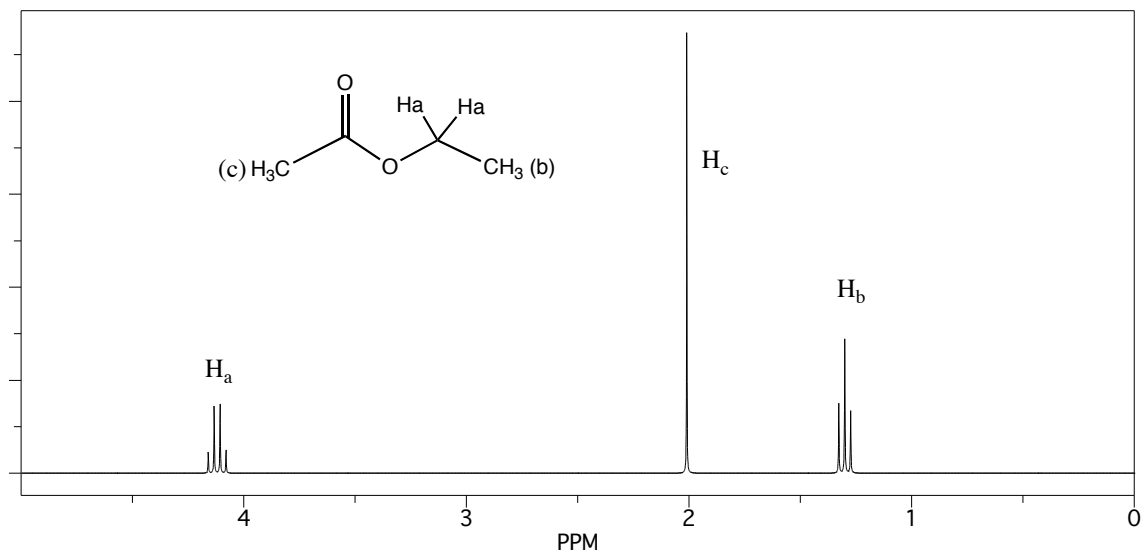
### **Lecture Topics:**

#### **I. Splitting of absorptions in NMR spectra**

For protons on adjacent carbon atoms, the local magnetic field of one proton effects the absorption frequency of the neighboring proton, and vice-versa. This leads to a splitting of the signal for each given proton. Thus, splitting of signals into multiplets results when two different types of protons are close enough that their magnetic fields influence each other – such protons are said to be **magnetically coupled**.

#### **N+1 rule**

In general, if a signal is split by N equivalent protons, it is split into N+1 peaks  
Consider the  $^1\text{H}$ NMR spectrum of ethyl acetate:

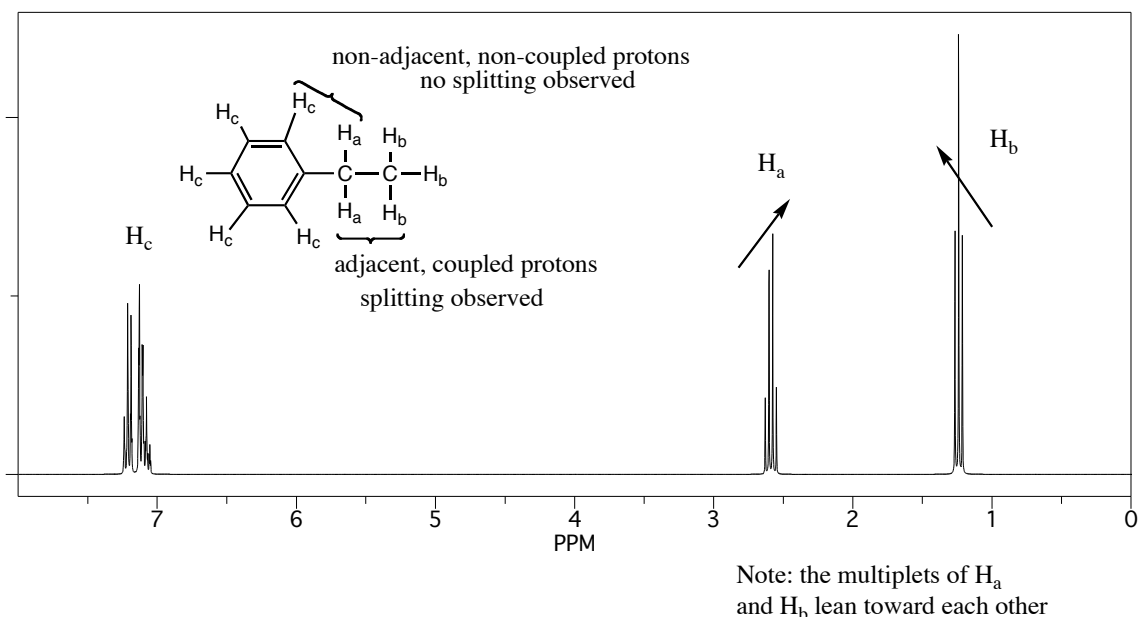


The  $\text{H}_a$  protons are split by three protons on the adjacent methyl group, producing  $3+1=4$  peaks or a quartet pattern for its absorption. The adjacent methyl group has three equivalent protons  $\text{H}_b$  which are split by the two equivalent protons  $\text{H}_a$ , producing  $2+1=3$  peaks or a triplet pattern for its absorption. The methyl group protons  $\text{H}_c$  on the

other side of the ketone isn't split by any protons, so it shows up as a simple singlet. The relative areas of the N+1 multiplets are given by Pascal's triangle:

#equivalent protons	# peaks	area ratios
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

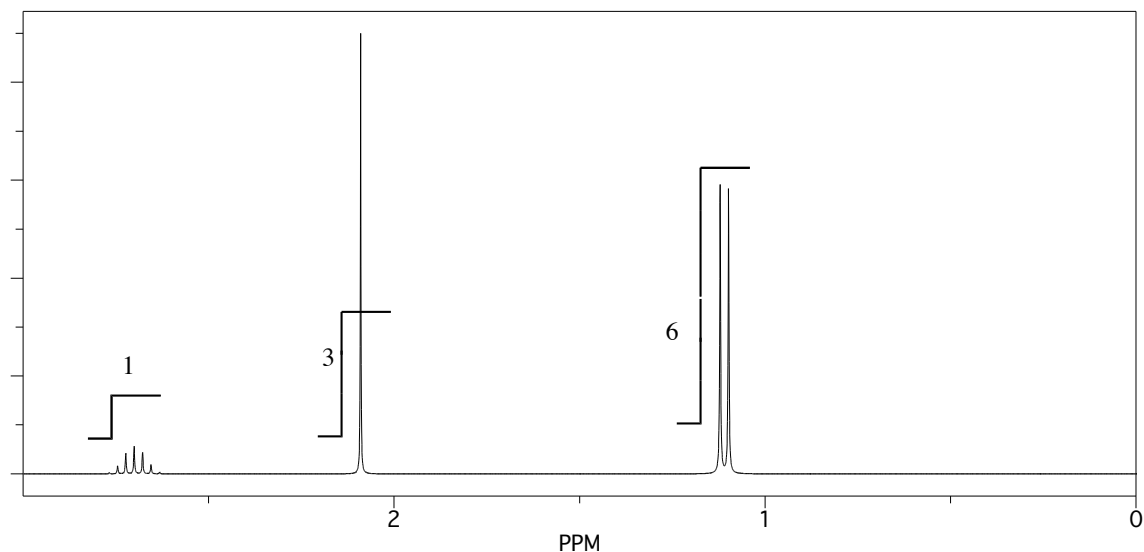
Most spin-spin splitting is between protons on adjacent carbon atoms. Protons on the **same** carbon atom can split each other only if they are non-equivalent (see below). The absorptions of spin-coupled protons often "lean" toward each other in their spectra:



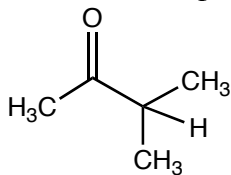
### Useful information for NMR problem solving:

1. Determine how many different types of protons present in a molecule and their proportions from the integrals
2. The splitting pattern for each absorption tell you the number of adjacent protons
3. The chemical shift of each absorption tells you the environment of each proton by the relative degree of shielding or deshielding.

Consider the following spectrum, which apparently contains three different types of protons in a ratio of 6:3:1 :



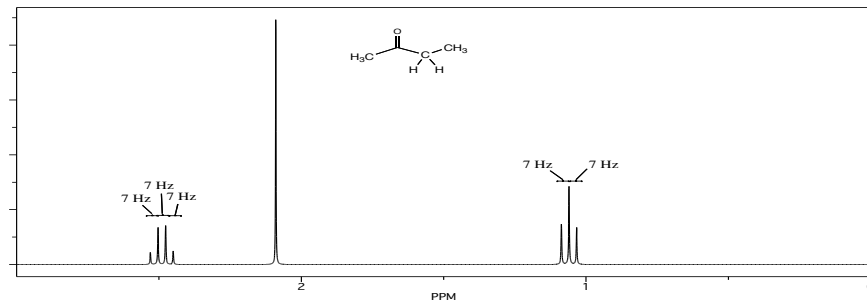
The absorption just above 1 ppm is likely to be due to an alkane group, specifically, two methyl groups ( $2 \times \text{CH}_3$  a total of 6 protons) which are chemically equivalent and are each split by a single proton, giving rise to the observed doublet. The absorption at 2.1 ppm is likely due to a group adjacent to a carbonyl ( $\text{C}=\text{O}$ ), and since three protons are indicated, it must be a methyl group that is split by no other protons. The last absorption at 2.6 ppm shows a septet, or seven peaks, indicating a single proton that is split by 6 nearby protons. This can only arise when there are two equivalent methyl groups (a total of 6 protons) attached to the carbon bearing this proton. The structure is given below. Be sure to match up each proton in the structure with an absorption in the spectrum:



## II. Coupling constants

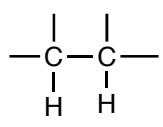
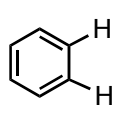
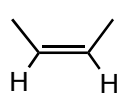
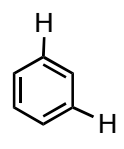
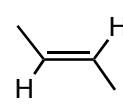
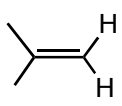
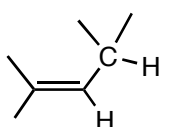
Structural information can be gleaned from examination of the distances between peaks in the splitting pattern of a multiplet..

The distance between the peaks of a multiplet is called the **coupling constant** and is represented by  $J_{a,b}$  for spin-spin coupled protons  $\text{H}_a$  and  $\text{H}_b$ . Multiplets that have the same coupling constant arise from adjacent groups of protons that split each other. Any two magnetically coupled protons must have equal magnitude effects on each other.

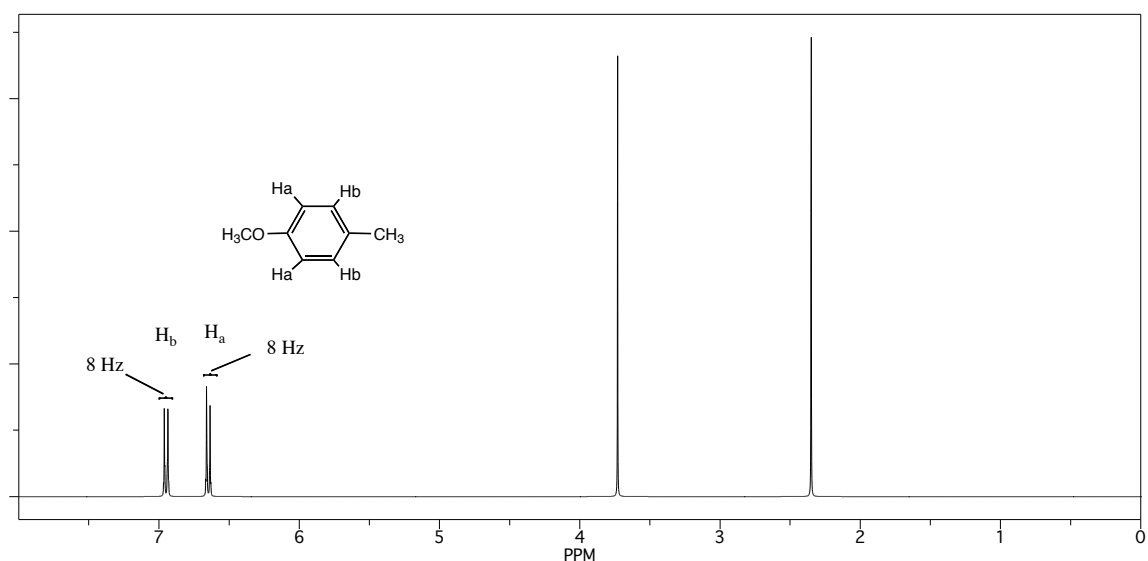


Coupling constants allow us to distinguish among the possible isomers of a compound.

Consult the following table for typical  $J_{\text{Hz}}$  values:

free rotation:	$J_{\text{Hz}}$		$J_{\text{Hz}}$
	7 Hz		8 Hz
	10 Hz		2 Hz
	15 Hz		
	2 Hz		
	6 Hz		

Consider the following examples:

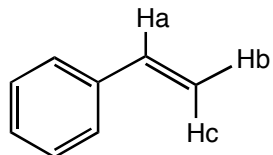


For the methoxy benzene shown above, notice that both Ha and Hb are split into doublets with 8 Hz coupling constant. Both doublets lean toward each other. This pattern for aromatic protons is indicative of 1,4 substitution on the benzene ring (why?). Notice also that Ha is shielded relative to Hb; this is because the methoxy group is a resonance donor

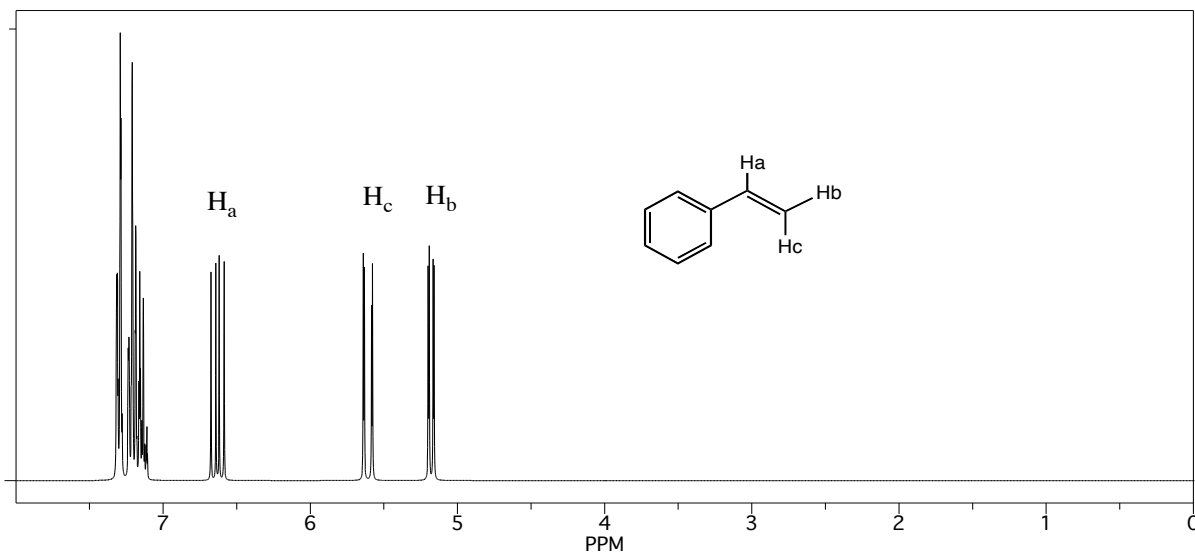
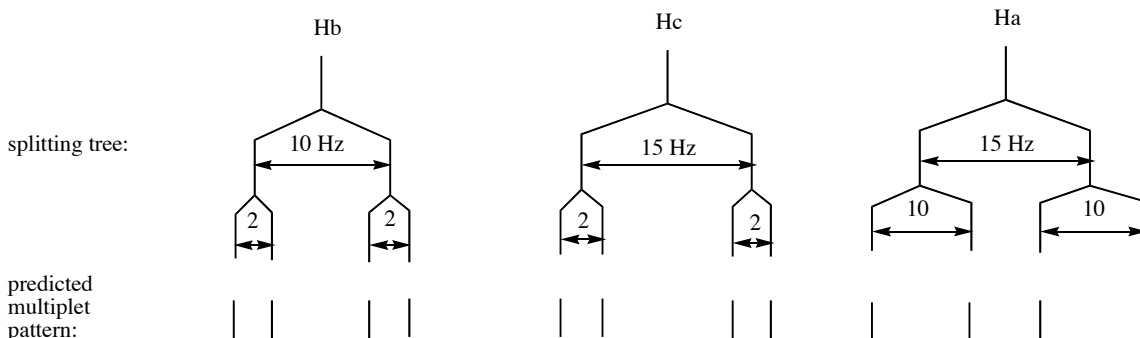
through the pi bonds of the aromatic ring; a resonance form of the methoxy benzene places a negative charge on the carbons bearing Ha, leading to shielding of these protons relative to Hb.

### III. Complex Splitting Patterns

Signals for individual protons may be split by adjacent protons of more than one type. A splitting tree analysis is often helpful in deconvoluting a given multiplet:

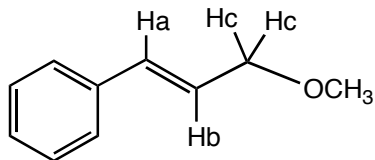


Ha-Hb      10 Hz  
 Ha-Hc      15 Hz  
 Hb-Hc      2 Hz



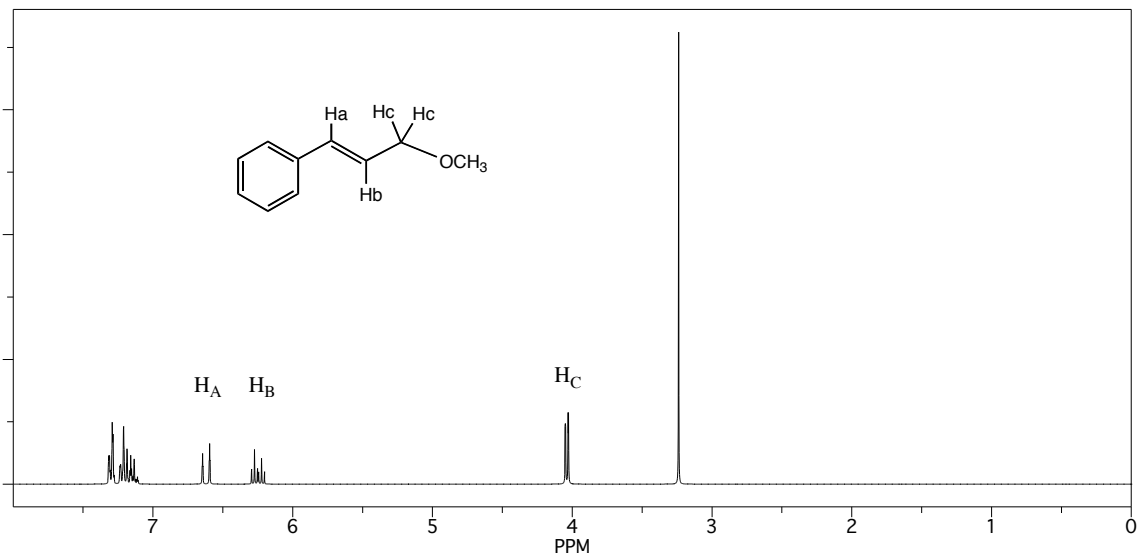
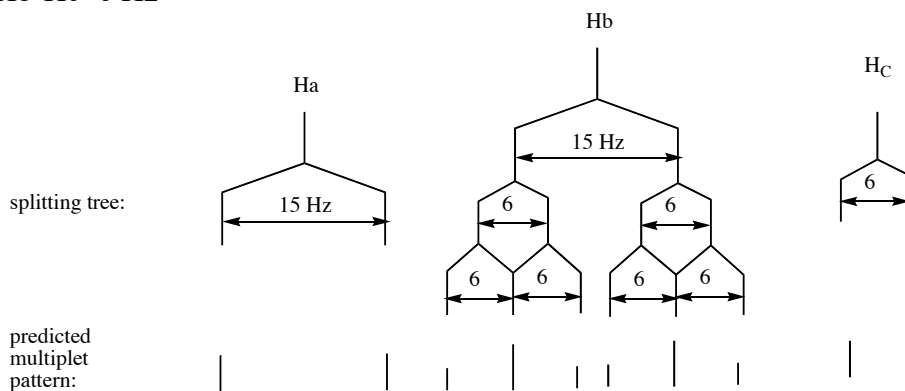
The absorptions for Ha, Hb, and Hc in the above spectrum are called “doublet of doublets”.

Example #2:



Ha-Hb 15 Hz

Hb-Hc 6 Hz



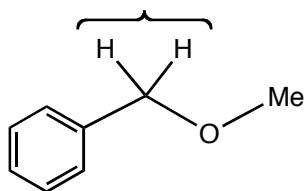
The absorption for  $H_b$  in the above spectrum is called a doublet of triplets; both  $H_c$  and  $H_a$  are doublets.

#### IV. Diastereotopic protons

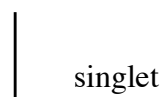
Diastereotopic protons are non-equivalent protons on the **same** carbon atom that split each other. This results when the protons are in different chemical environments.

In the following structures, note that  $H_a$  and  $H_b$  are non-equivalent and thus split each other to varying amounts. Some complex patterns may emerge in this analysis through the use of splitting trees:

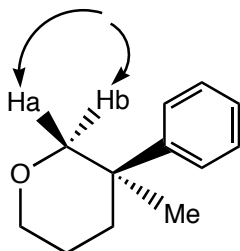
chemically equivalent



Absorption

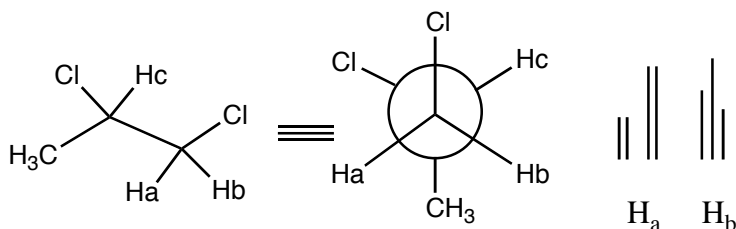


diastereotopic protons



"ABx"

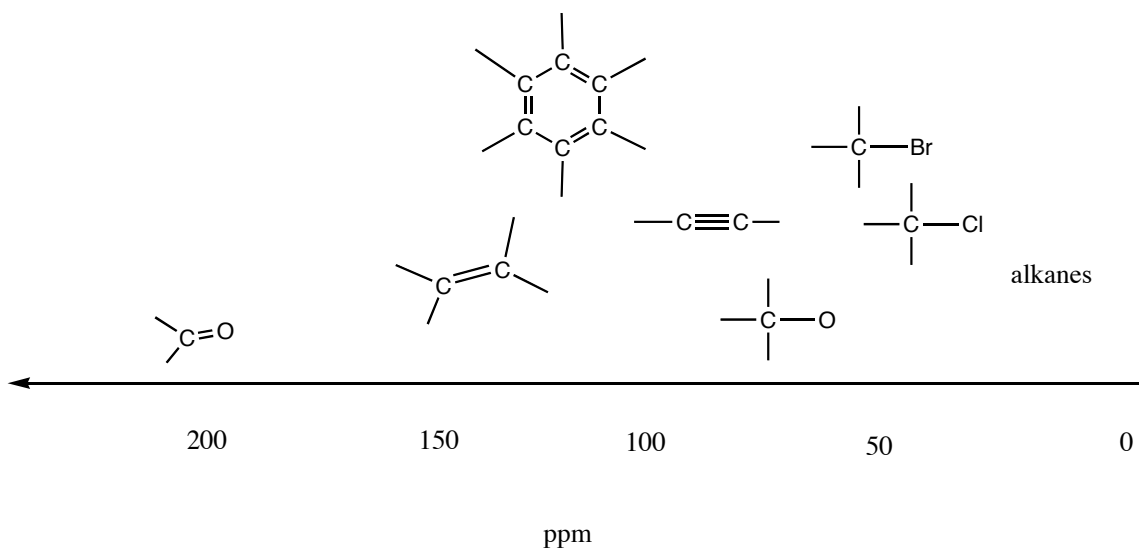
staggered



$$\begin{aligned} H_a-H_b & 7 \text{ Hz} \\ H_a-H_c & 10 \text{ Hz} \\ H_b-H_c & 7 \text{ Hz} \end{aligned}$$

## V. Carbon-13 NMR spectroscopy

Carbon 13 ( $^{13}\text{C}$ ) NMR allows us to gain important information about the backbone of organic structures. Note that the naturally occurring isotope of carbon is  $^{12}\text{C}$  (99%); the  $^{13}\text{C}$  isotope has only 1% natural abundance, so typically more compound is required for this analysis. Note also that the gyromagnetic ratio for  $^{13}\text{C}$  is 1/4 that of  $^1\text{H}$ , thus a 300MHz instrument must also have a 75.6 MHz transmitter to observe carbon. Because of the decreased sensitivity this implies, averaging of multiple scans (using a computer to **Fourier Transform** the acquisition data obtained) is employed to obtain a spectrum. Below are typical ranges where carbons absorb in the  $^{13}\text{C}$  spectrum. Note that the range of the spectrum is extended from 0ppm to 200ppm. For a proton on carbon absorbing at a certain ppm, the corresponding carbon resonance is at 15-20 times this frequency; thus the aldehyde carbonyl carbon absorbs at around 200 ppm, where the aldehyde proton absorbs at around 10 ppm.



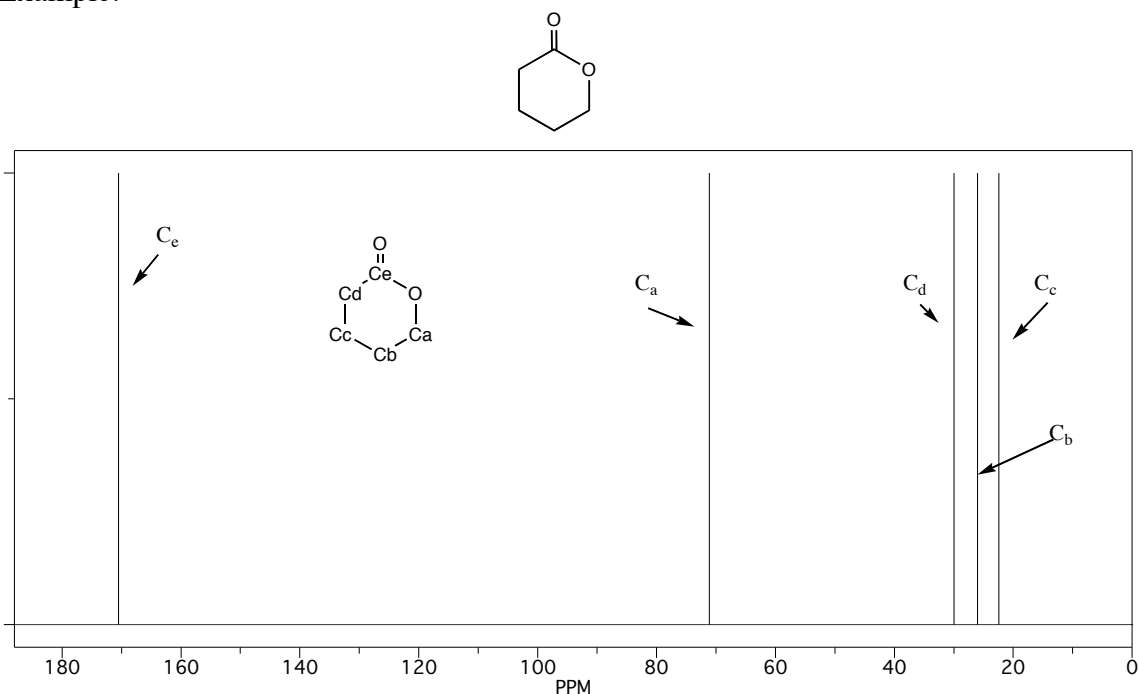
### Features of $^{13}\text{C}$ NMR

- The areas of the peaks do not correspond to the number of carbon atoms
- C-C splitting can be ignored (unlikely to have two  $^{13}\text{C}$ 's next to each other)
- C-H coupling is common, but often complicated and difficult to interpret
- proton spin decoupling is often performed so that each carbon atom shows up as a single unsplit peak.

• Thus, in proton decoupling mode, the number of signals implies the number of different carbon atoms present in sample.

• The chemical shifts of those signals suggest the types of functional groups present in a molecule.

Example:





Additional Problems for practice.

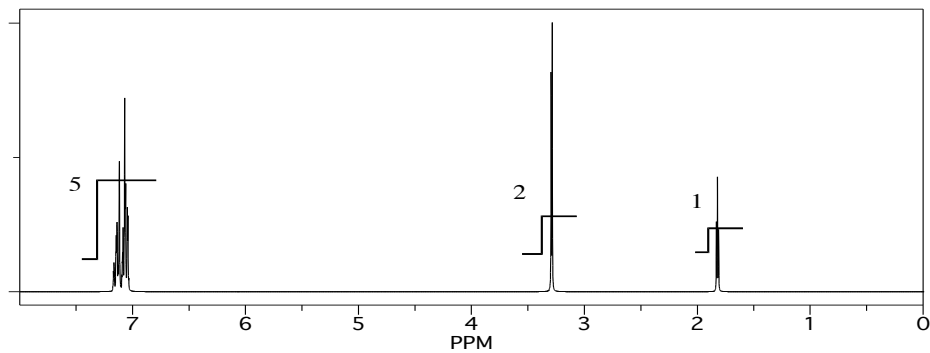
1. Predict the structure of the molecules given by the following spectral data:

a

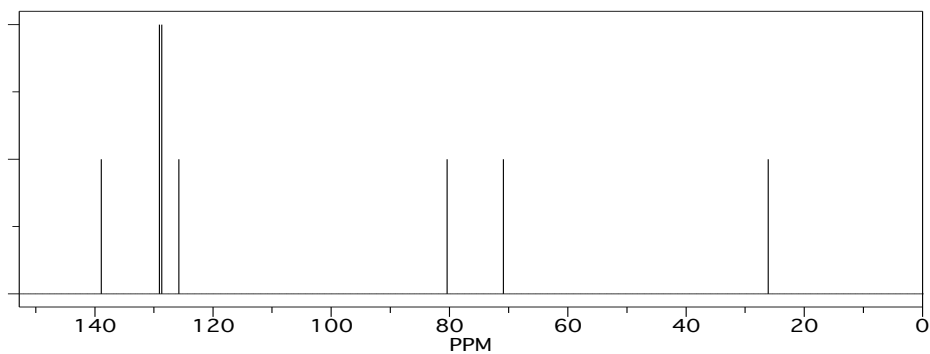
Mass spectrum:  $M^+ = 116$

IR: weak absorption at  $2190\text{ cm}^{-1}$   
medium absorption at  $1600\text{ cm}^{-1}$

$^1\text{H}$  NMR



$^{13}\text{C}$  NMR

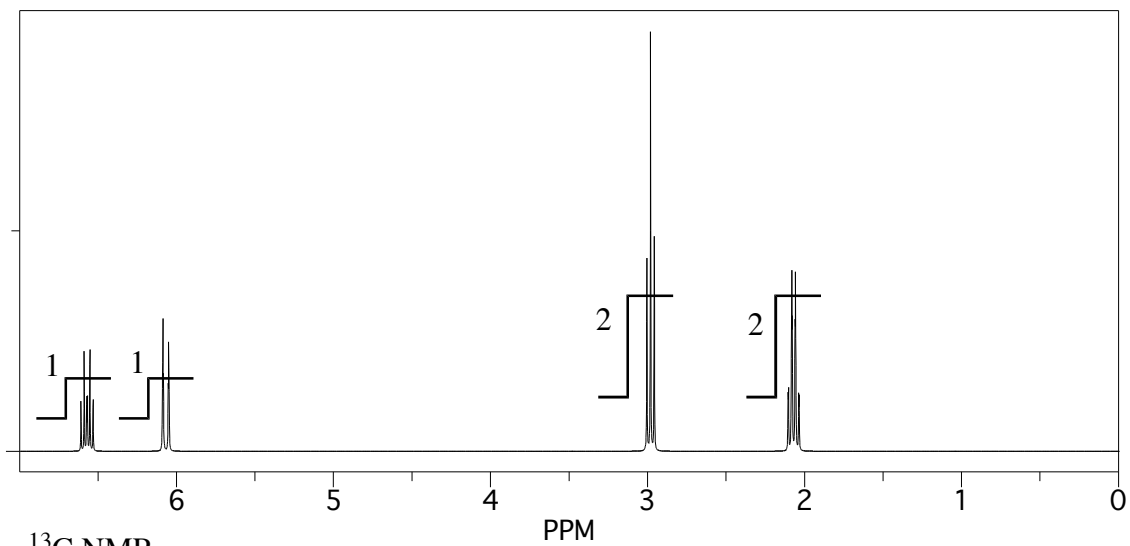


b

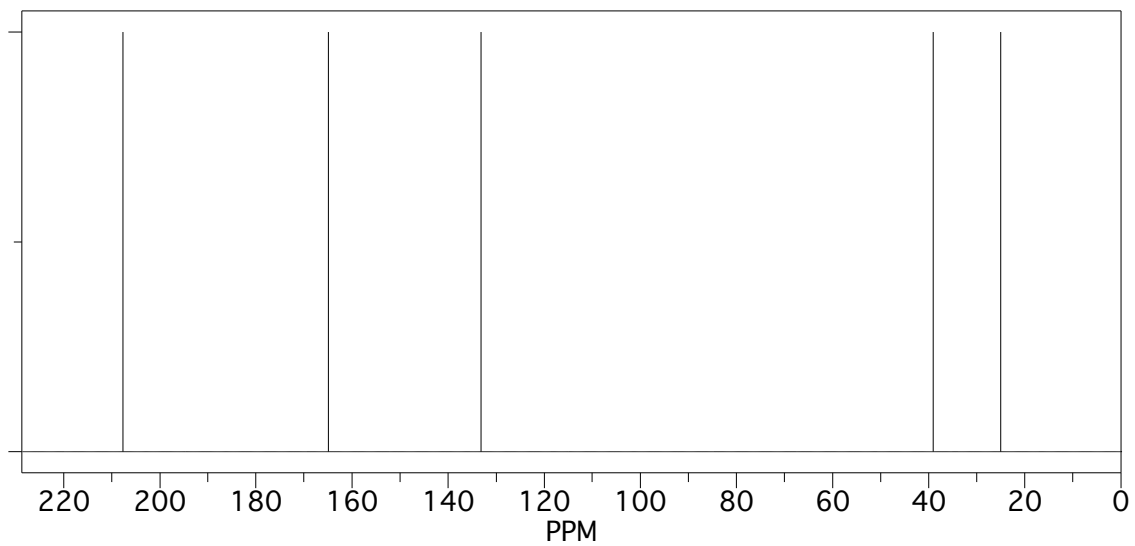
Mass spectrum:  $M^+ = 82$   
molecular formula:  $C_5H_6O$

IR:  $1690\text{ cm}^{-1}$  (strong) with a shoulder at  $1626\text{ cm}^{-1}$

$^1\text{H}$  NMR



$^{13}\text{C}$  NMR

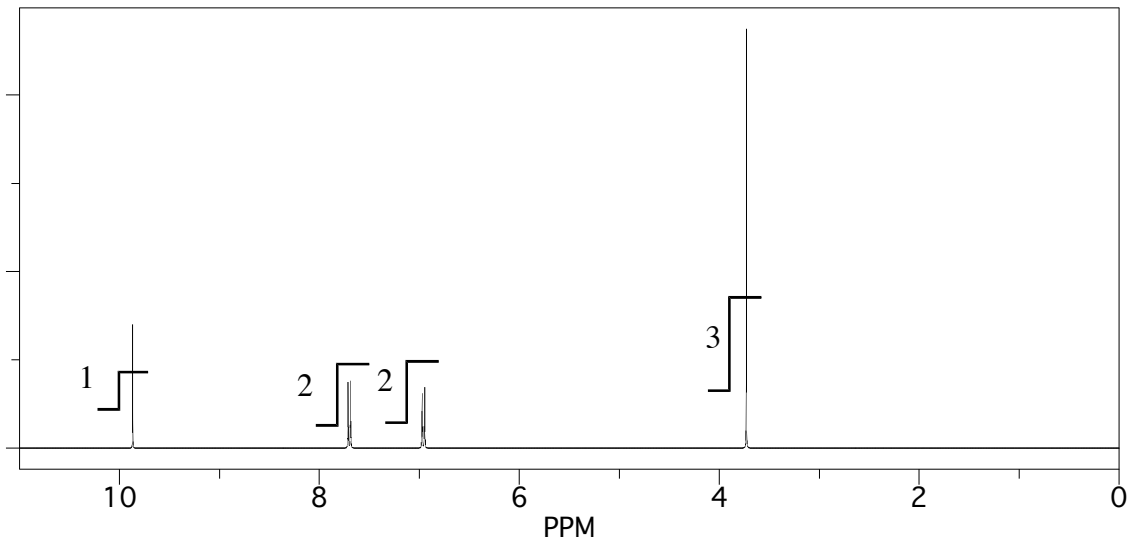


c.

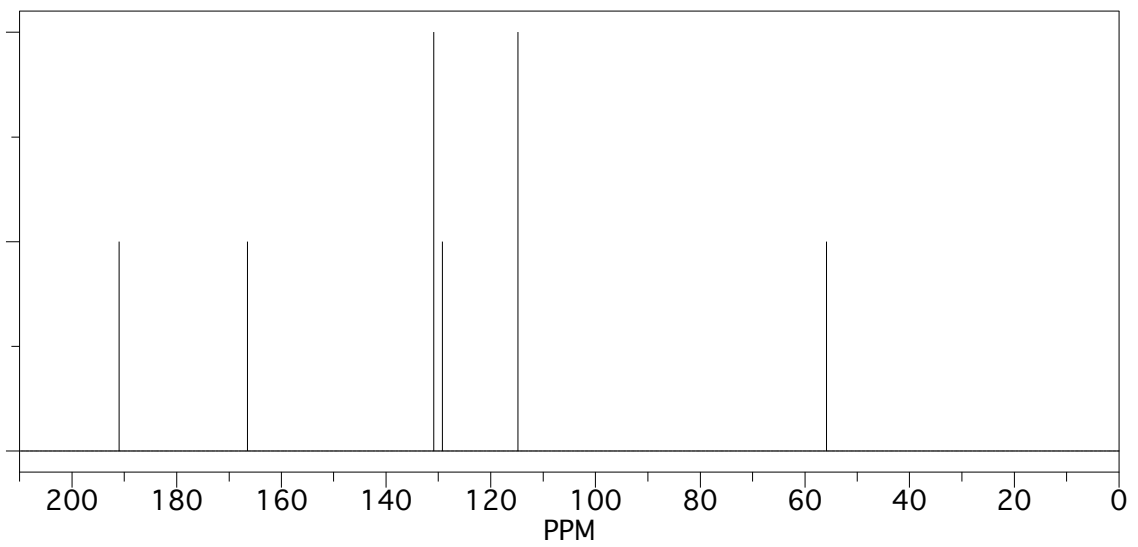
mass spectrum:  $M^+ = 136$ ,  $C_8H_8O_2$

IR:  $1691\text{ cm}^{-1}$  (strong);  $1600\text{ cm}^{-1}$  (medium)

$^1\text{H}$  NMR



$^{13}\text{C}$  NMR



d.

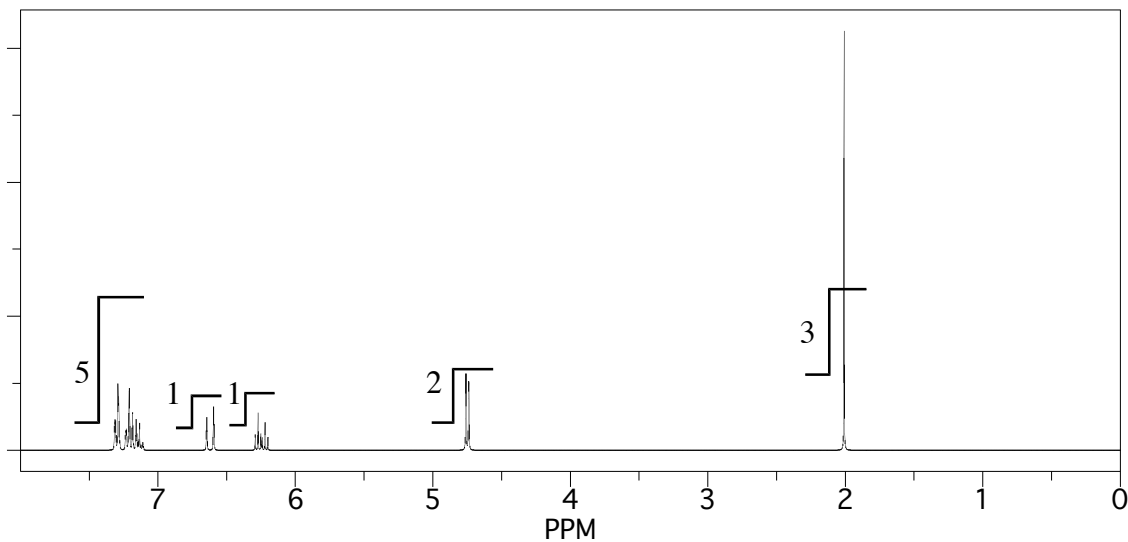
Mass spectrum:  $M^+ = 176$

molecular formula:  $C_{11}H_{12}O_2$

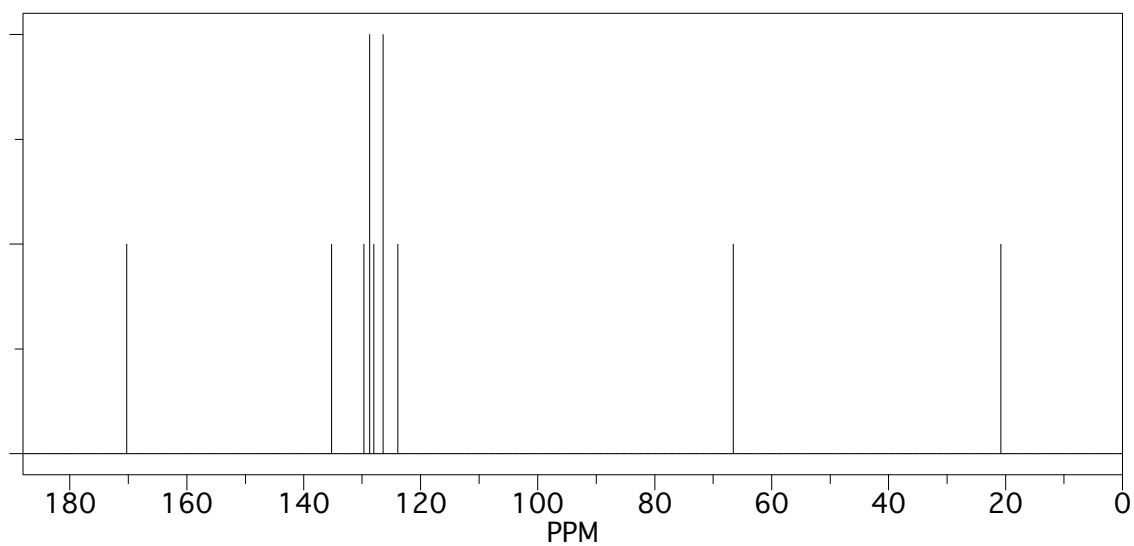
IR:  $1735\text{ cm}^{-1}$  (strong);  $1660\text{ cm}^{-1}$  (medium)

$1600\text{ cm}^{-1}$  (medium)

$^1\text{H}$ NMR



$^{13}\text{C}$ NMR



2. Show a splitting tree for the  $H_a$ ,  $H_b$ , and  $H_c$  protons in the following compound, and match your predicted multiplet patterns with the spectrum shown below. Indicate rough values for coupling constants on your diagram.

