

# <sup>1</sup>H NMR

Protons (nucleus of a hydrogen atom) also have a net spin and can be observed in the NMR.

- Hydrogen atoms are more than 99% <sup>1</sup>H.

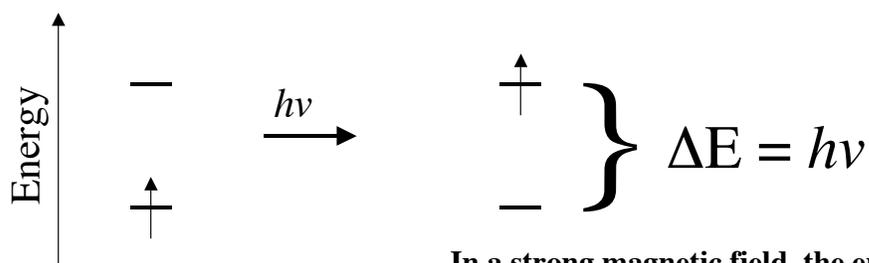
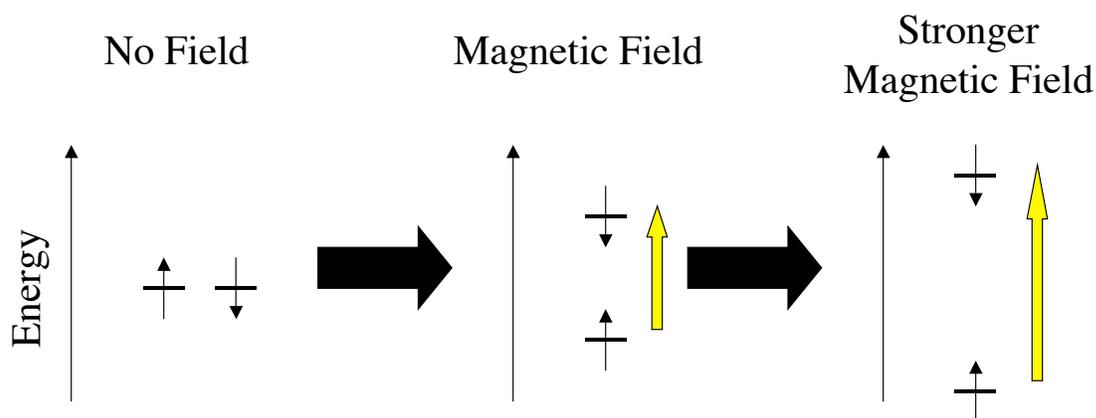
Other isotopes have special names

<sup>2</sup>H = deuterium

<sup>3</sup>H = Tritium (radioactive)

- Remember <sup>13</sup>C is only 1% of carbon; <sup>1</sup>H NMR is much more sensitive.

–Practically speaking for a typical lab molecule, you can obtain a <sup>1</sup>H-NMR with 1-2 mg of compound in a matter of minutes but the same sample may require a few hours to obtain a <sup>13</sup>C spectrum.



In a strong magnetic field, the energy level difference corresponds to the energy of radio waves

## FYI: Q&A

### How strong is a magnetic field in a typical NMR?

300 MHz NMR = 7.0459 tesla

600 MHz NMR = 14.0918 tesla

### What other nuclei are commonly observed by NMR?

$^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$

#### What type of NMR is used in MRI?

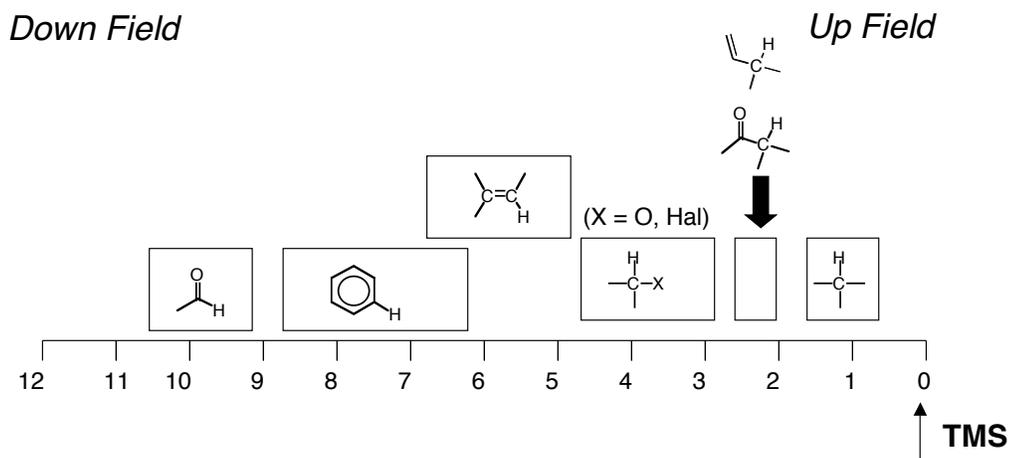
MRI methods typically look at  $^1\text{H}$ -NMR of water in the different environments of the body.



Protons resonate at a different frequency than  $^{13}\text{C}$ 's. Typical compounds lie within a smaller range of frequencies than  $^{13}\text{C}$ .

PROTONS ON TYPICAL ORGANIC COMPOUNDS **1-12 ppm**

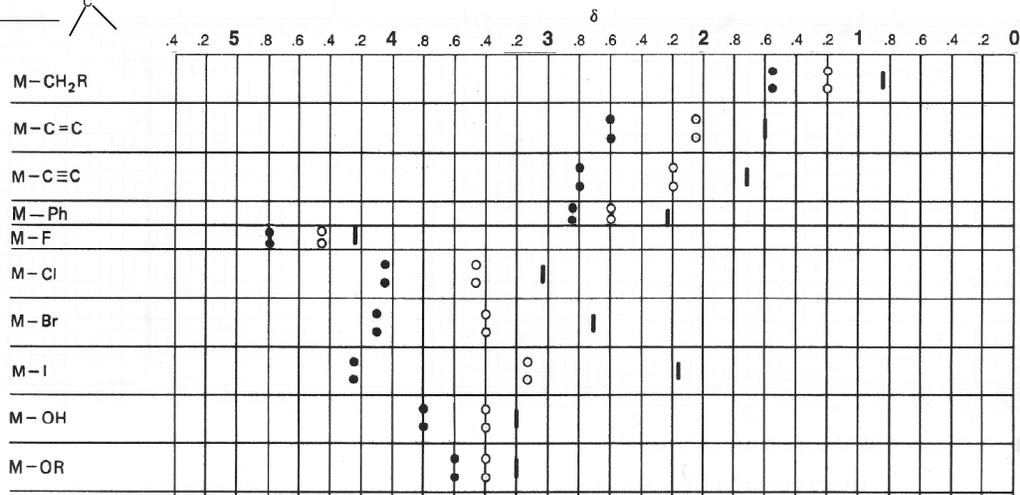
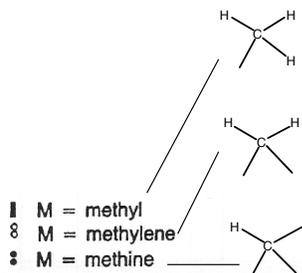
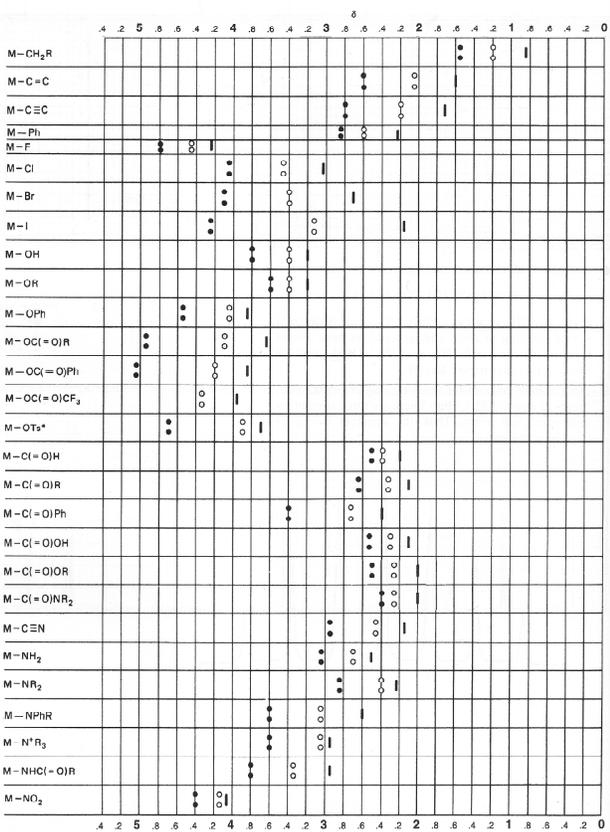
Typical locations of  $^1\text{H}$ -NMR resonances.



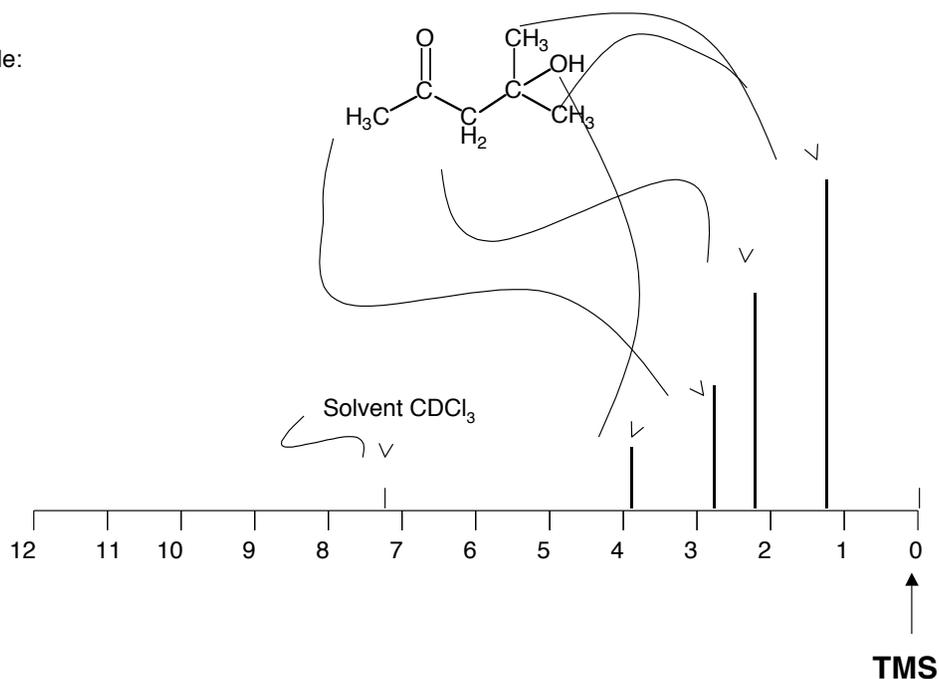
**Appendix A CHART A.1 Chemical Shifts of Protons on a Carbon Atom Adjacent ( $\alpha$  Position) to a Functional Group in Aliphatic Compounds (M—Y)**

| M = methyl  
 8 M = methylene  
 : M = methine

See Table 13.1 in your text.



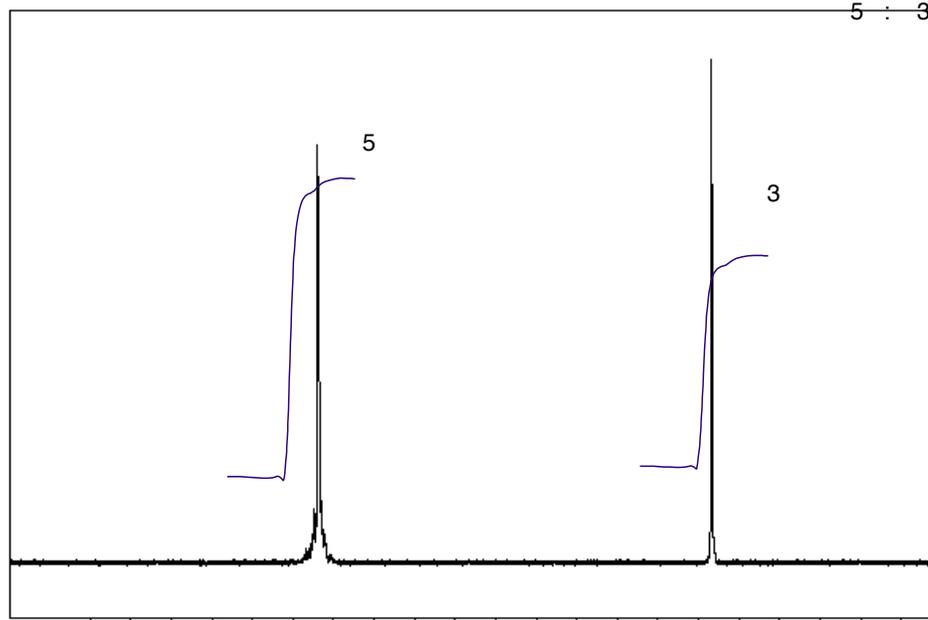
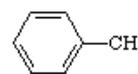
Example:



## WHAT IS SO SPECIAL ABOUT PROTON NMR?

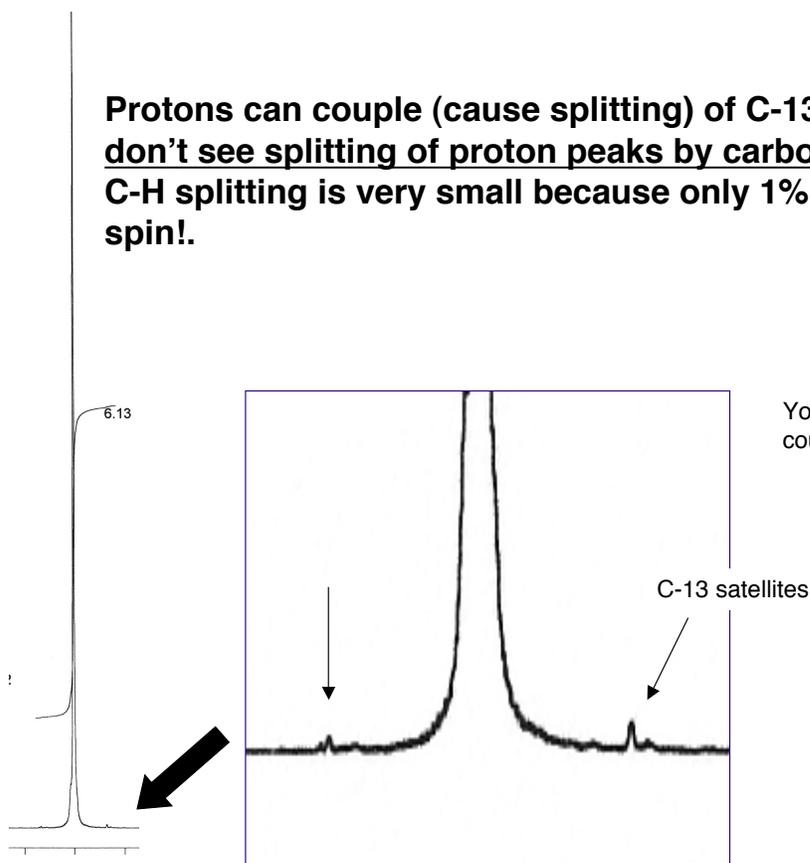
- You can accurately integrate your spectra to know how many of each proton type you have.
- Through bond coupling tells us about what is adjacent to the protons of a particular resonance.

$^1\text{H-NMR}$  peaks can be integrated!!



Tells you the ratio of the number of protons that compose each resonance. This is particularly helpful when you have symmetry.

**Protons can couple (cause splitting) of C-13 peaks but we don't see splitting of proton peaks by carbon!!**  
**C-H splitting is very small because only 1% of Carbon has a spin!**

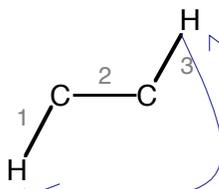


You can see carbon-proton coupling if you look very closely!

## Protons can split other protons by through bond J-coupling.

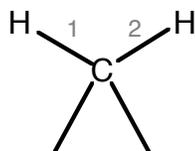
Coupling can be observed between two protons.

The coupling originates because in a magnetic field, the nuclear spin will perturb the local distribution of electrons.



Protons on adjacent carbons are said to be **Vicinal** protons

Are coupled over three bonds.



**Splitting over two bonds is usually not observed.**

Geminal coupling is only observed when the two protons are in different "chemical environments", this happens when the protons are diastereotopic (more on this later).

Protons on the same carbons are said to be **geminal** protons

Proton NMR signals are also split following the N+1 rule but for proton NMR N typically represents the number of adjacent protons.

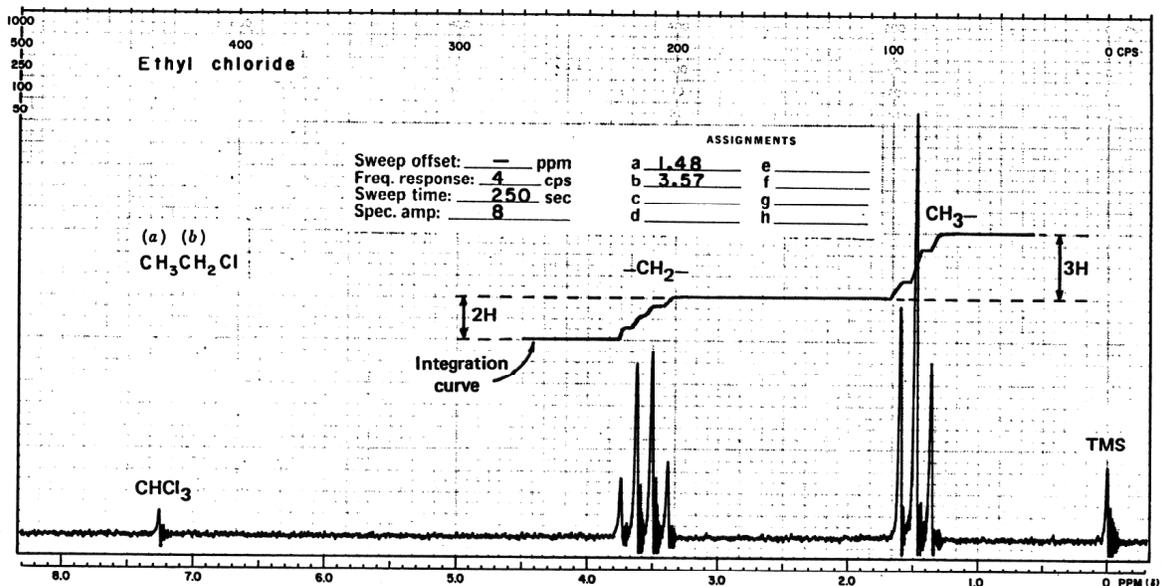
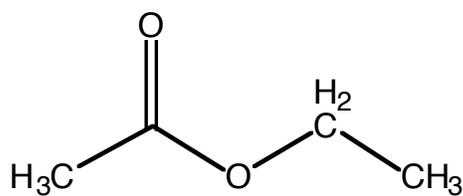
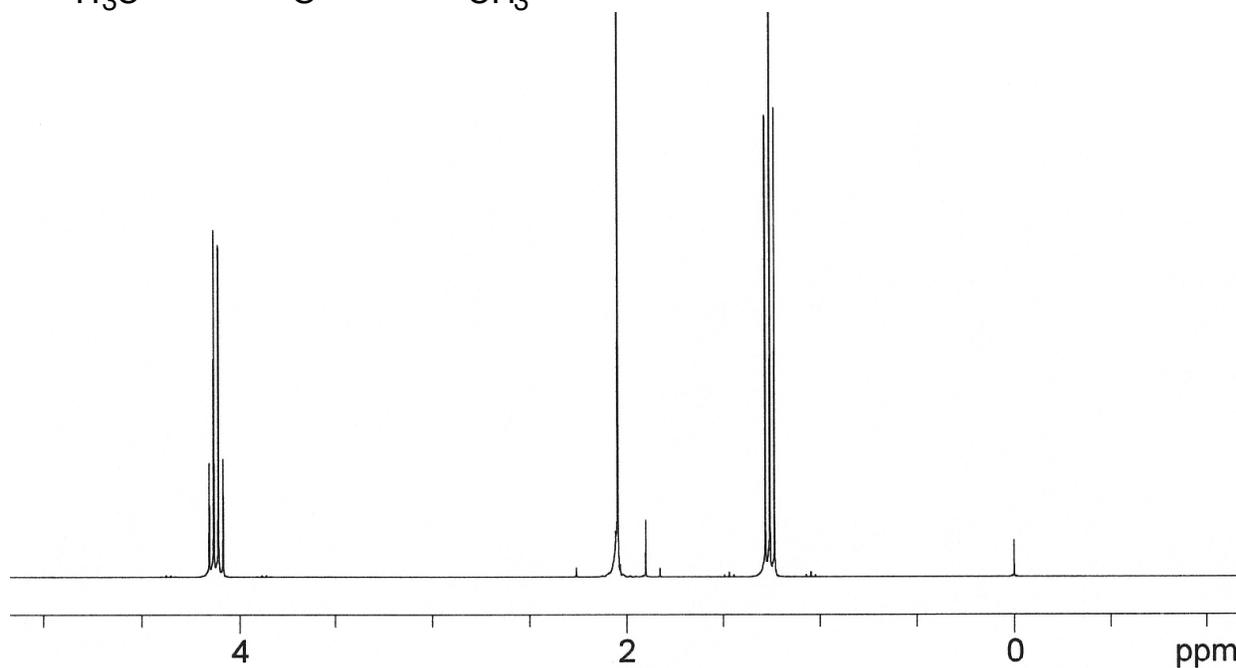


FIGURE 4.29. Ethyl chloride in  $\text{CDCl}_3$  at 60 MHz. (Courtesy of Varian Associates, Palo Alto, CA.)

Old NMR with Small wimpy magnet!



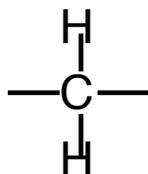
N+1 RULE STILL APPLIES  
(but it can get more complicated)



## PAY ATTENTION!:

### <sup>13</sup>C-NMR

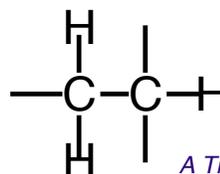
Splitting pattern reflects how many protons are directly attached to the carbon atom



*A Triplet*

### <sup>1</sup>H-NMR

Splitting pattern reflects how many protons are connected to adjacent carbon atom(s)



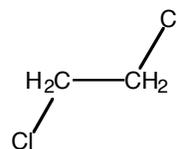
*A doublet*

*A Triplet*

## Rules for J-coupling

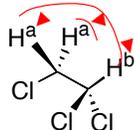
•Nuclei must be chemical shift NON-EQUIVALENT to show (obvious) coupling to each other:

•1,2-dichloroethane is a singlet



•The coupling is mutual: A splits B the same amount as B splits A

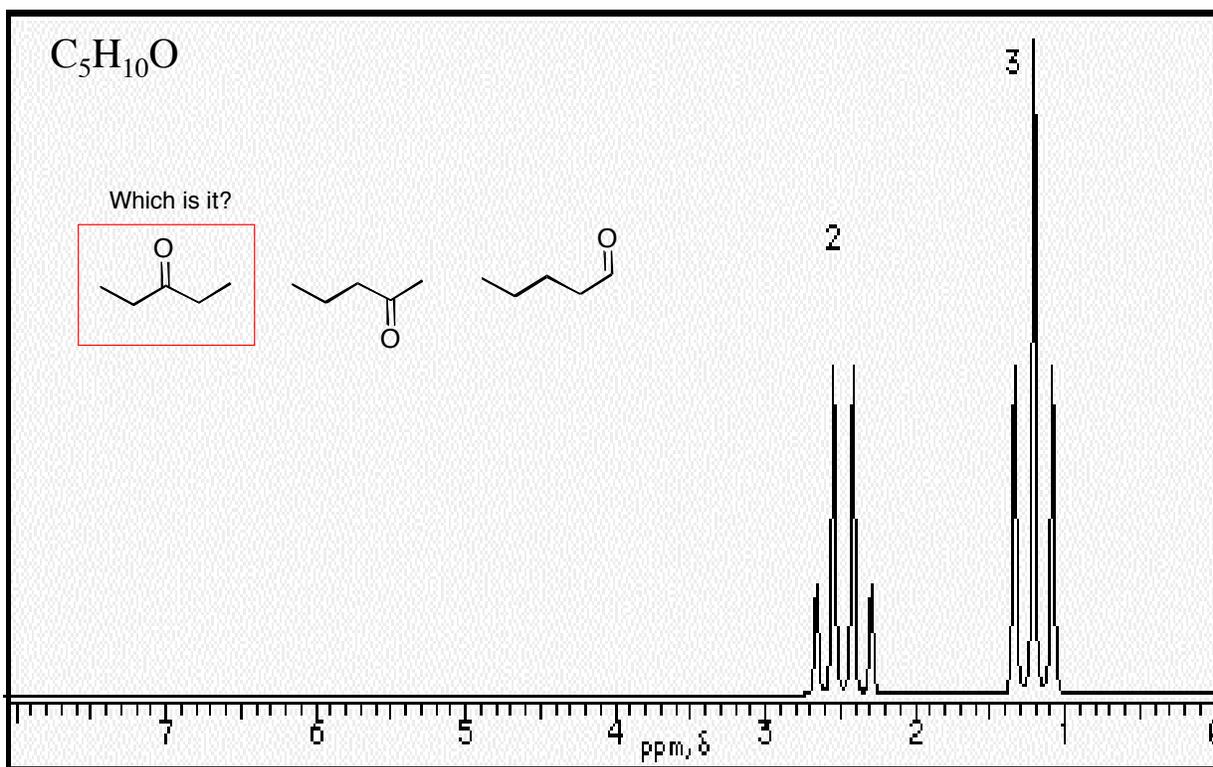
$$J_{AB} = J_{BA}$$

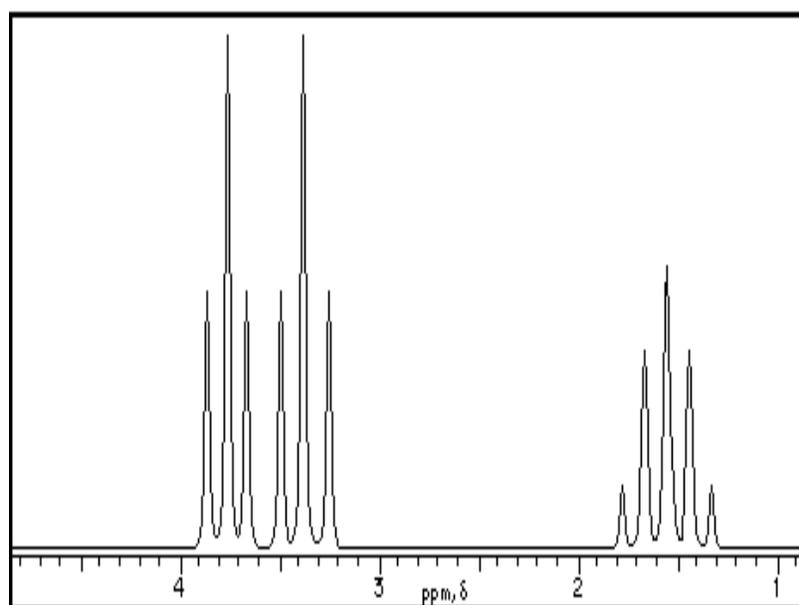
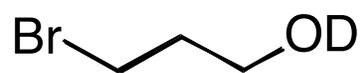
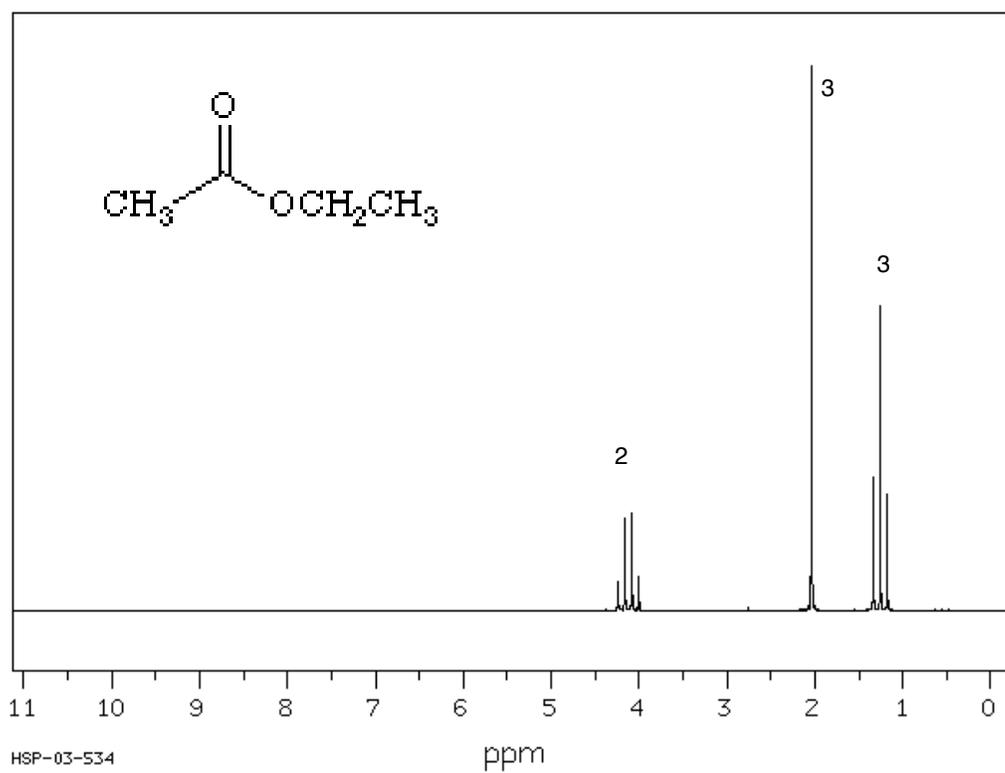


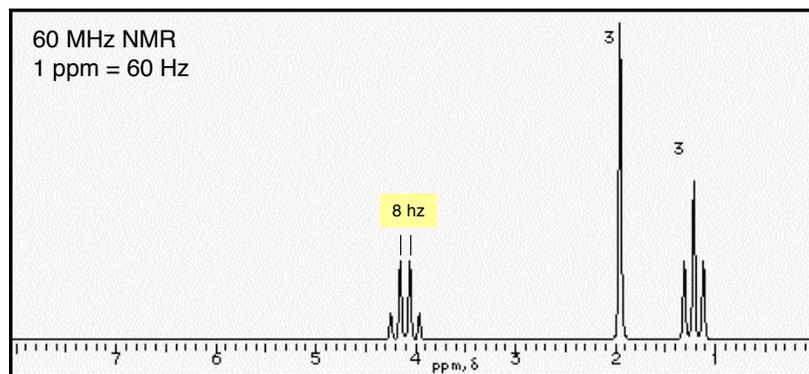
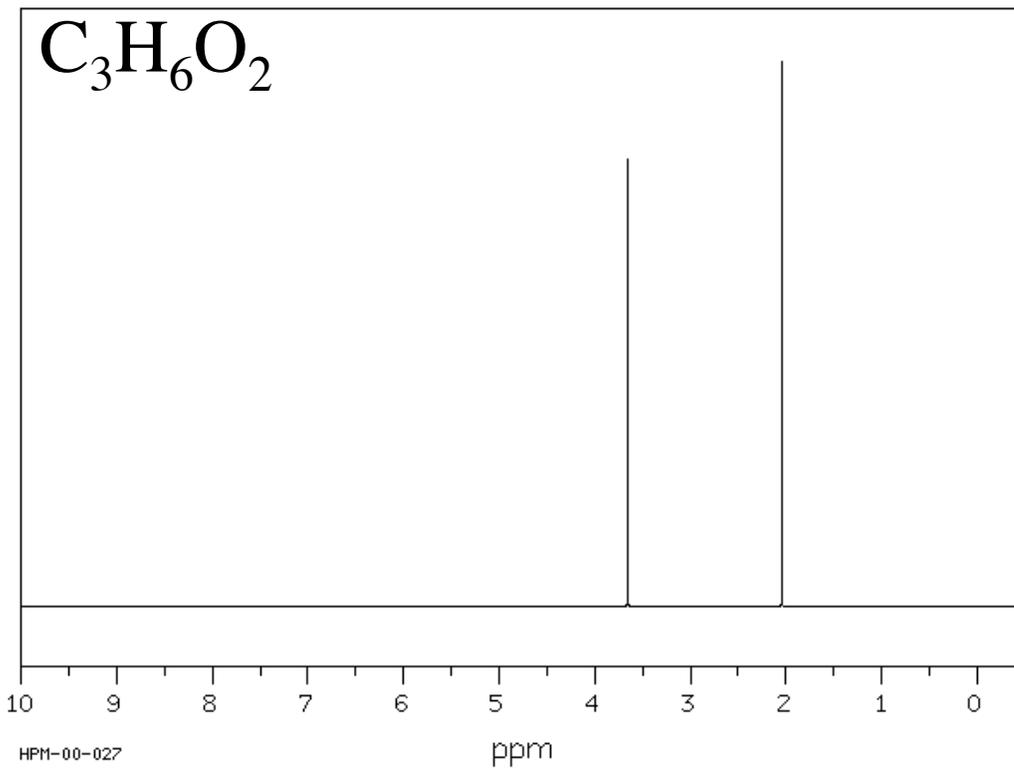
H<sup>a</sup>: 3.90 ppm, d (J = 7.1 Hz)

H<sup>b</sup>: 5.77 ppm, t (J = 7.1 Hz)

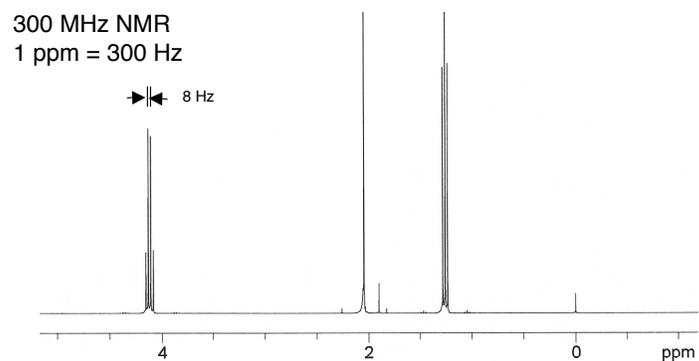
•Coupling constants are reported in Hz and will have the same value on different instruments.





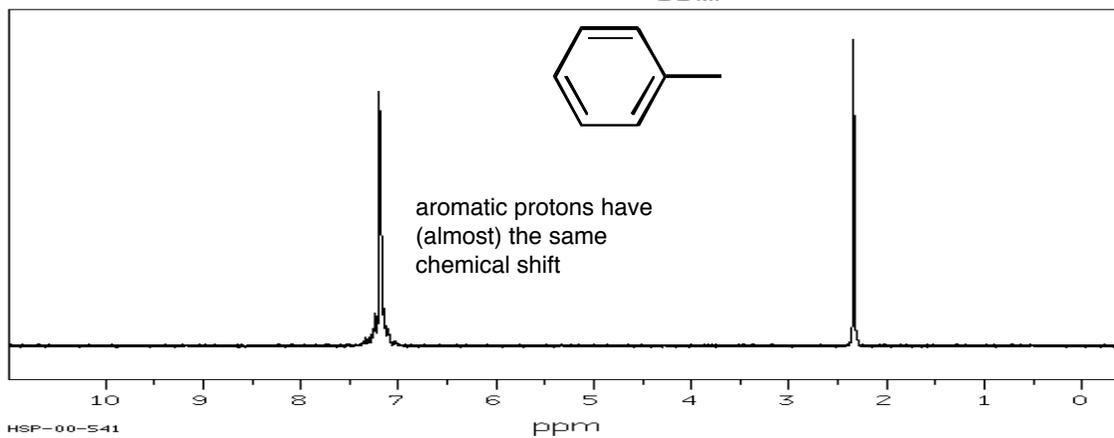
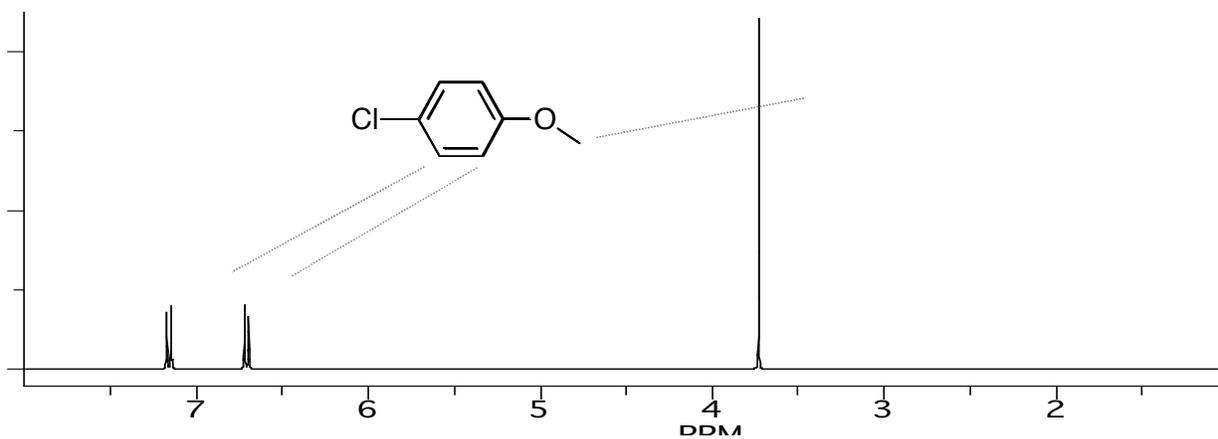
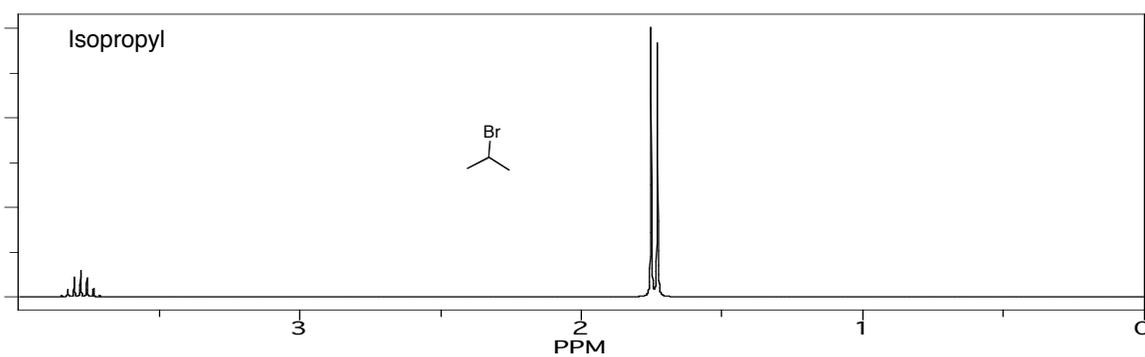
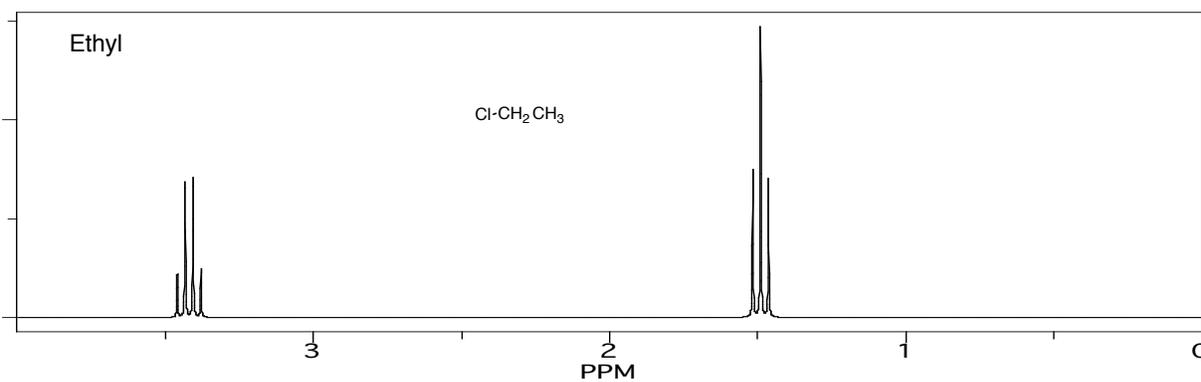


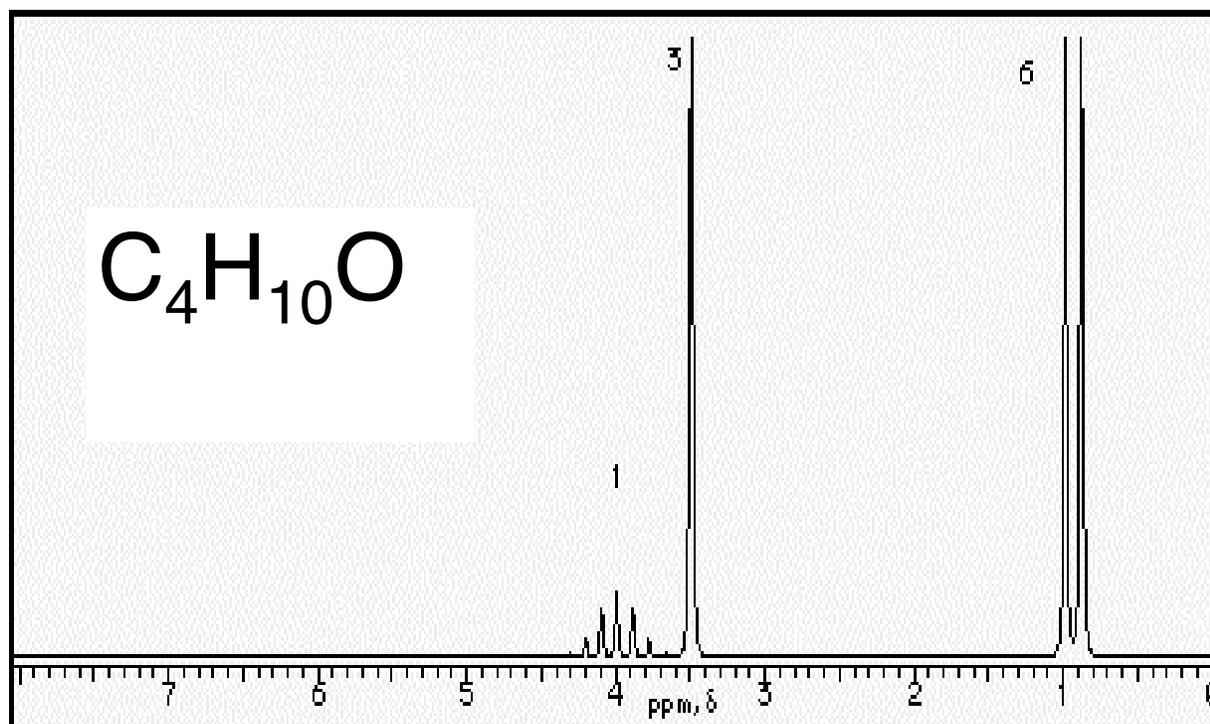
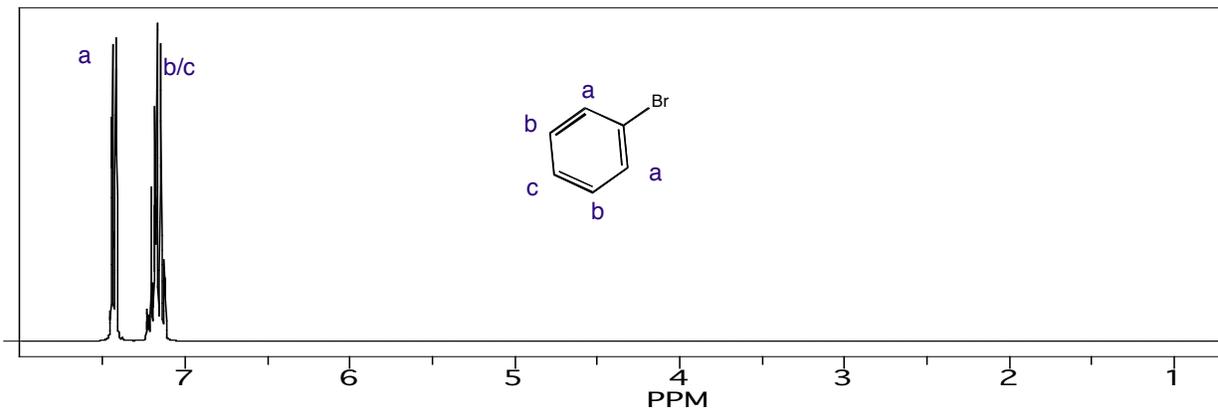
Same  
compound run  
on a 60 MHz  
and a 300 MHz  
spectrum

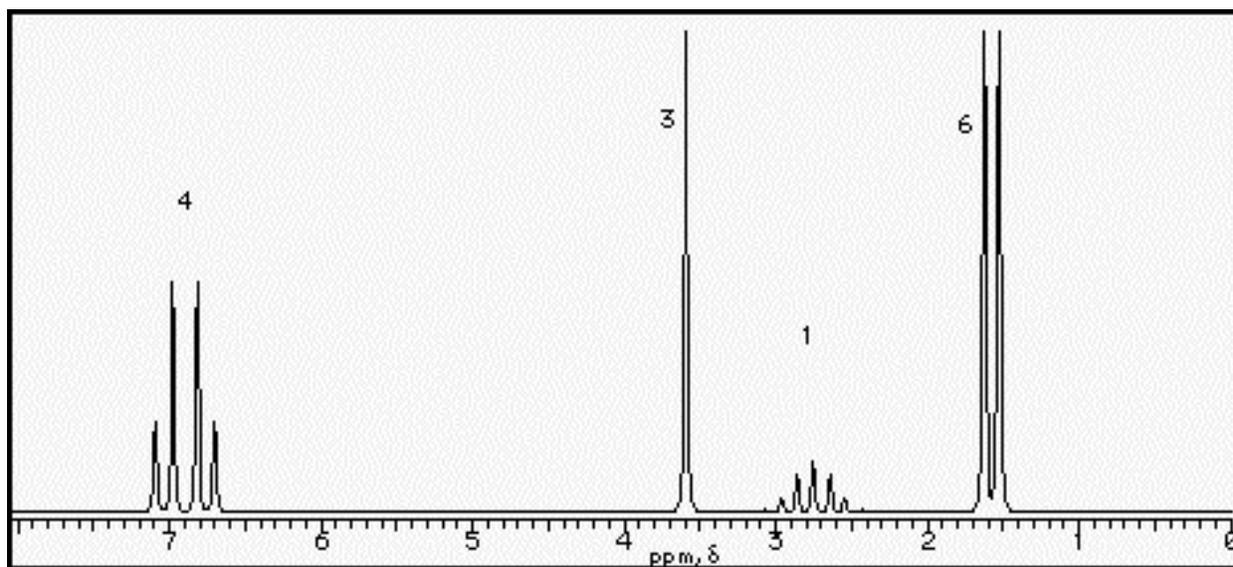
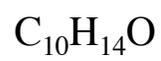
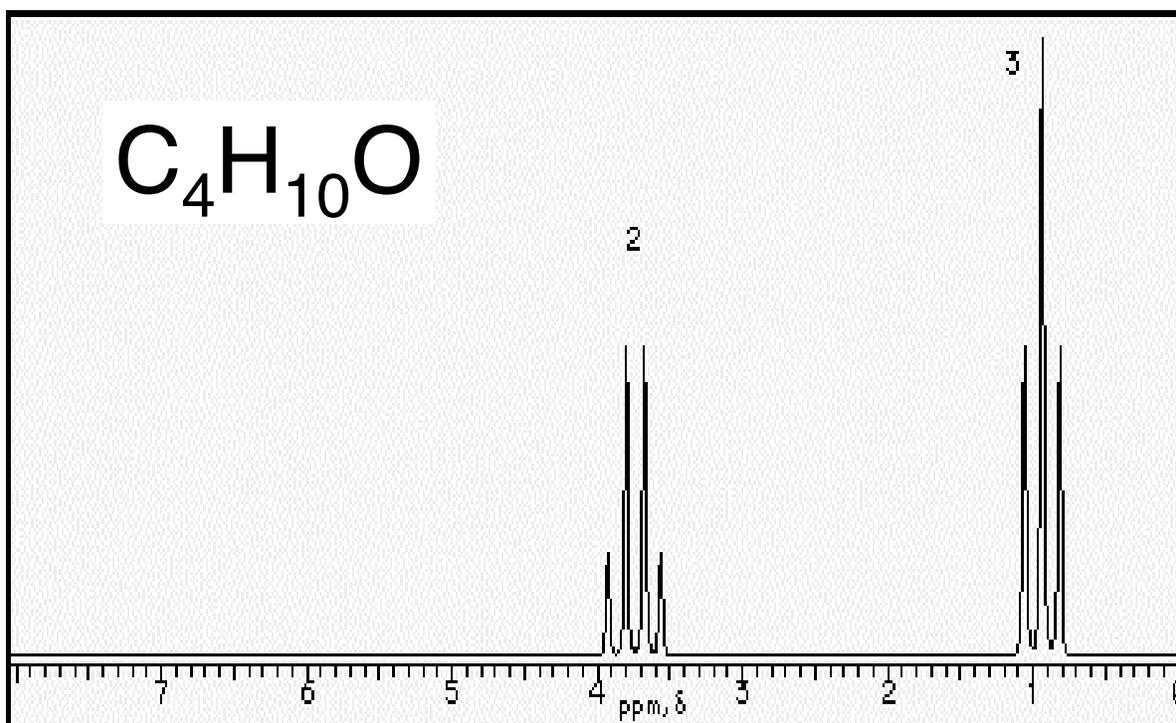


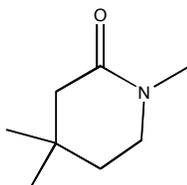
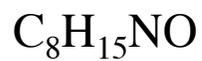
Coupling constant is measured by taking the difference between peaks (in ppm) within a multiplet and multiplying by the field strength in Hz.

# Common Splitting Patterns







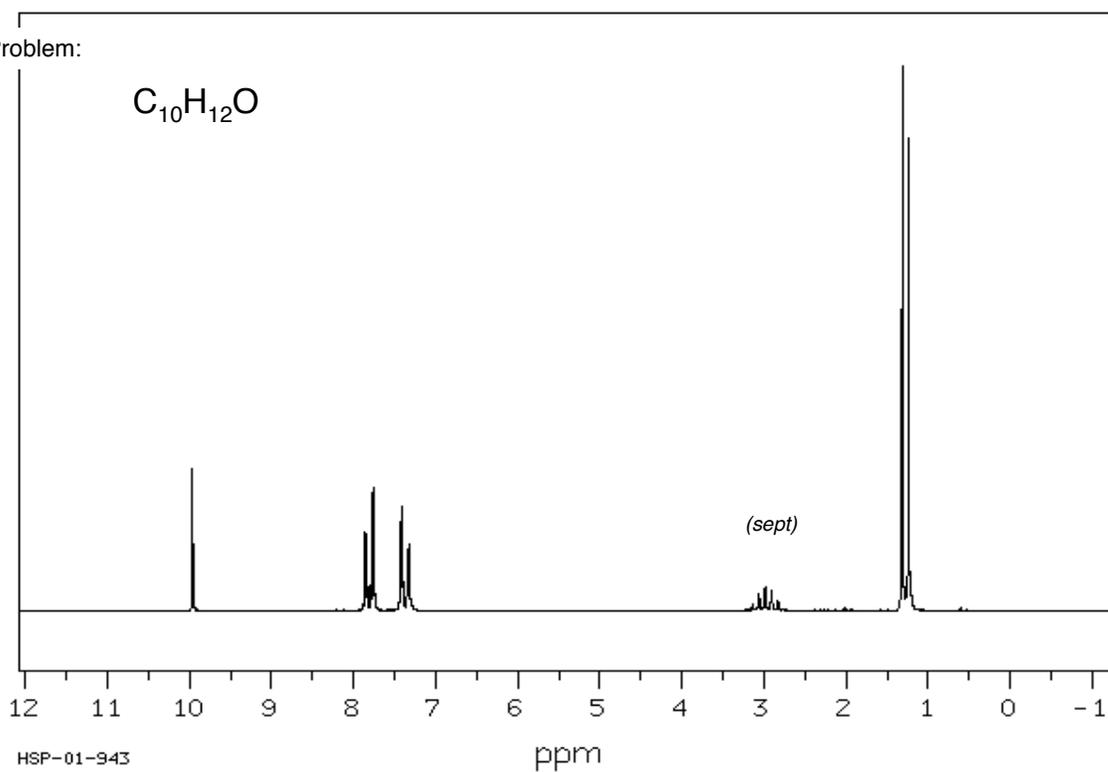
**C-13**

173.2	s
46.9	t
46.5	t
44.2	t
32.6	q
27.4	s
25.9	q (2)

**H-1 (first order)**

2.90	s	3H
3.2	t	2H
2.10	s	2H
1.47	t	2H
1.11	s	6H

Problem:

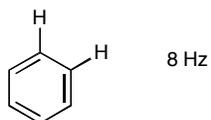
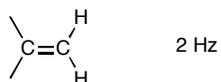
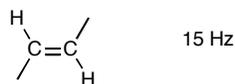
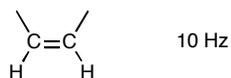
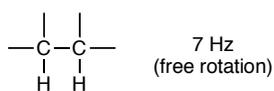


# Protons in different chemical structures have different amounts of splitting or “coupling constants”.

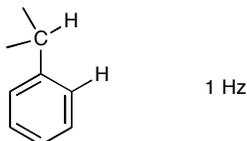
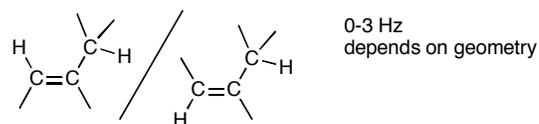
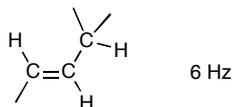
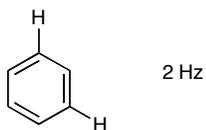
- Bad News: Life gets more complicated
- Good News: Splitting tells us more about the chemical structure.

## Coupling Constants Depends on Structure and Geometry

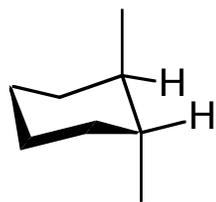
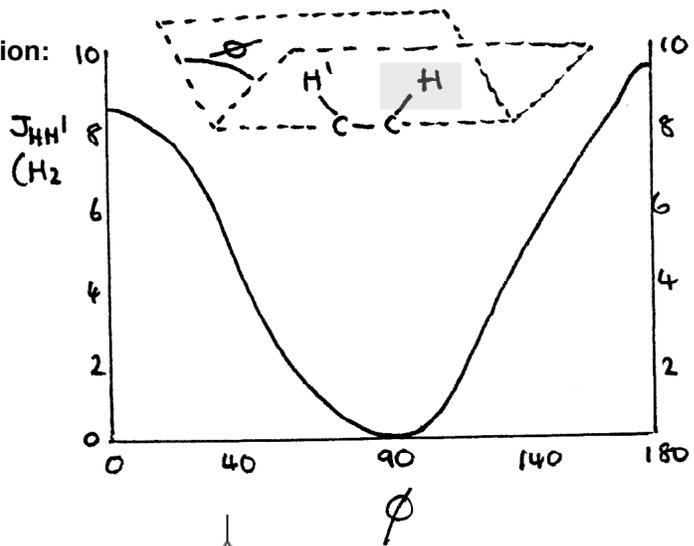
Approximate Coupling Constants.



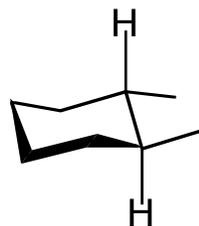
### Special Couplings over more than 3 bonds



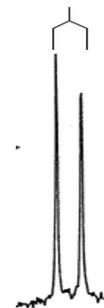
Karplus Equation:



$J = 2-3$  Hz



$J = 8-10$  Hz



C

Aldrich M7,970-0

CAS [108-27-0]

$C_5H_9NO$

60 MHz: 1, 661D

178.56

5-Methyl-2-pyrrolidinone, 98%

FW 99.13

FT-IR: 1, 789B

50.22

mp 42°C

VP-FT-IR: 3, 788C

30.77

bp 248°C

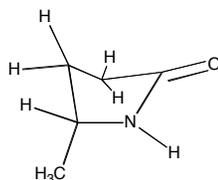
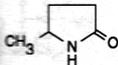
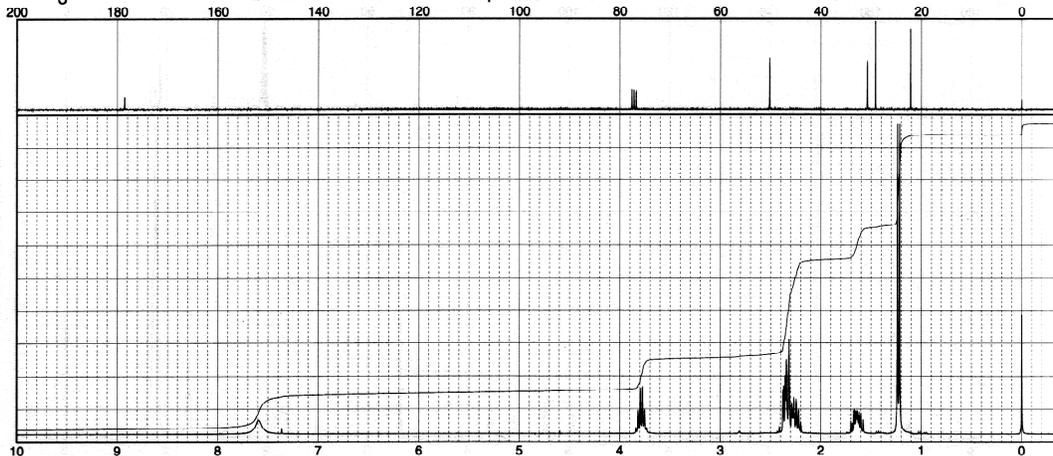
29.17

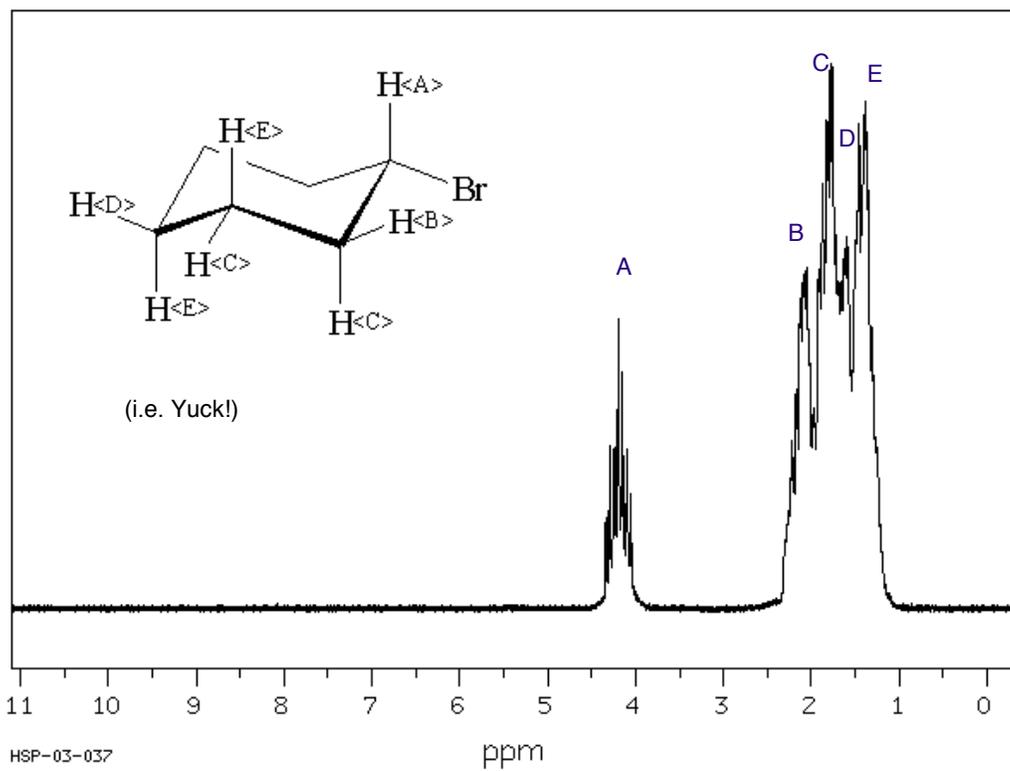
Fp >230°F

22.17

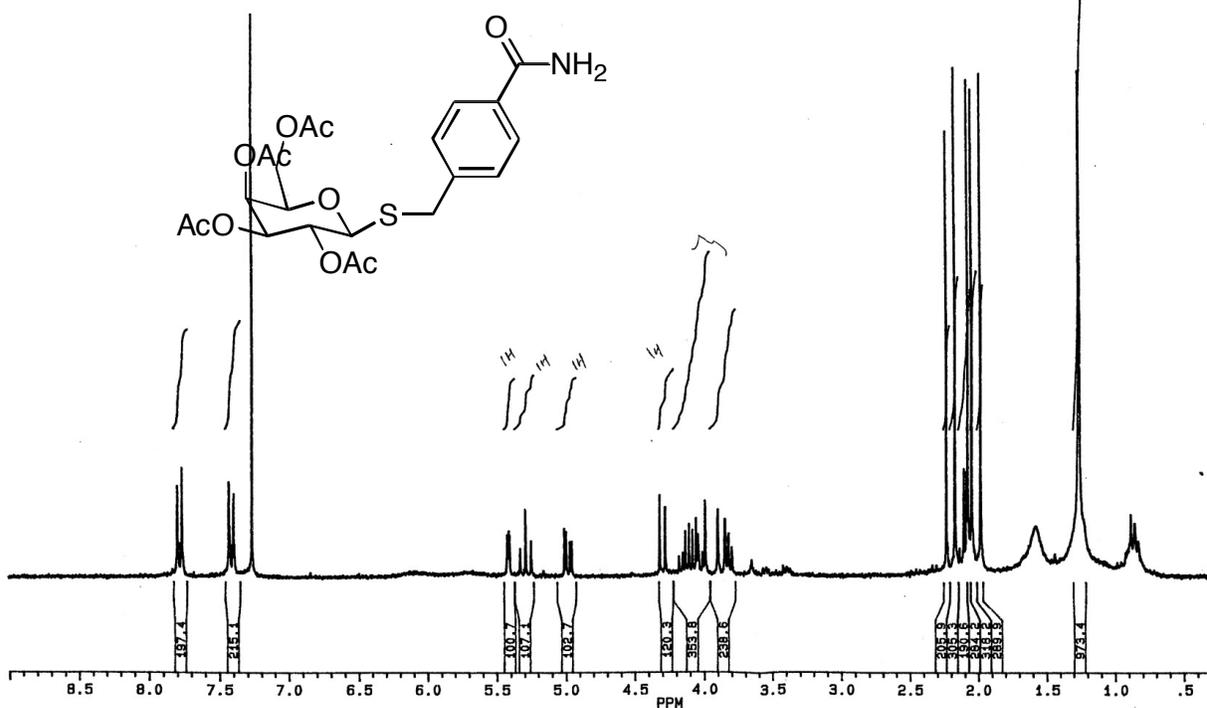
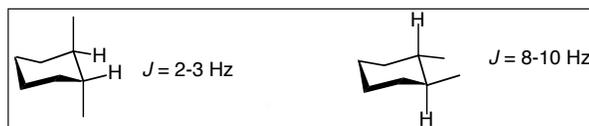
$CDCl_3$

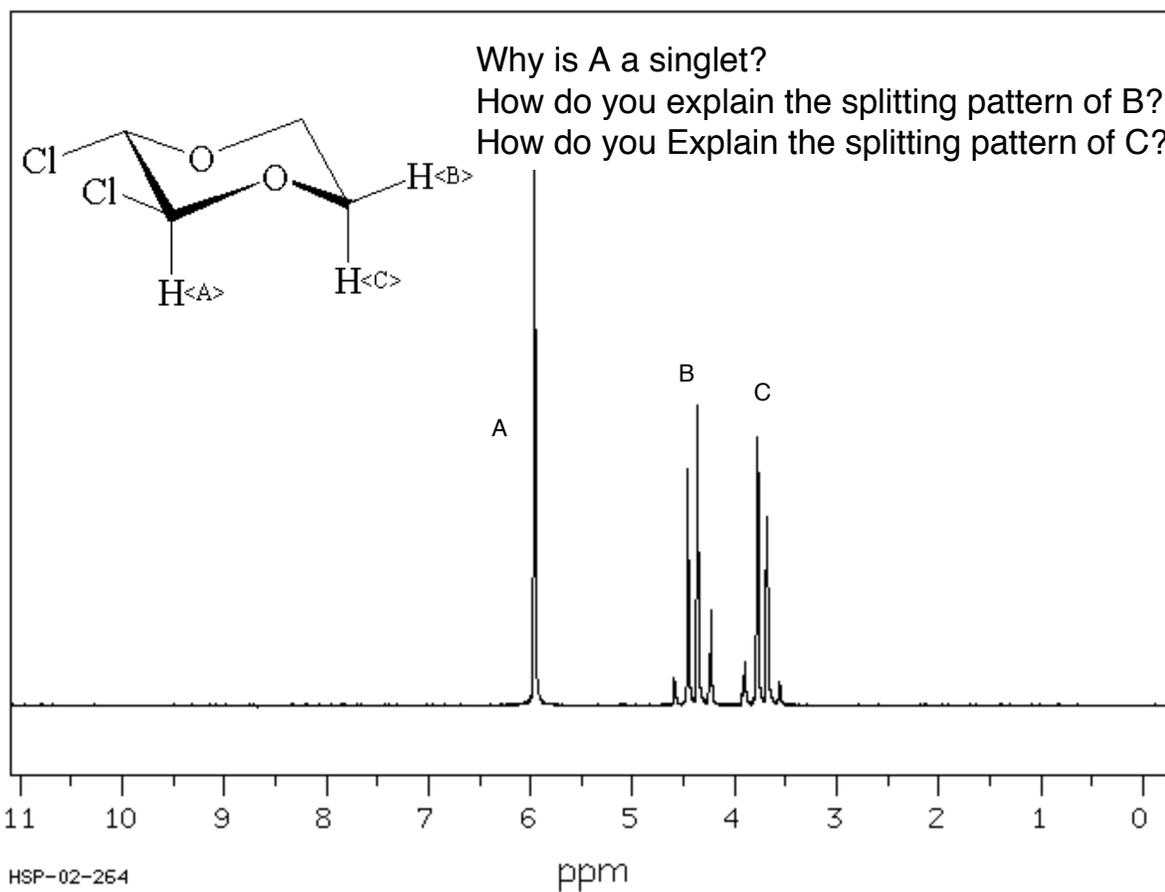
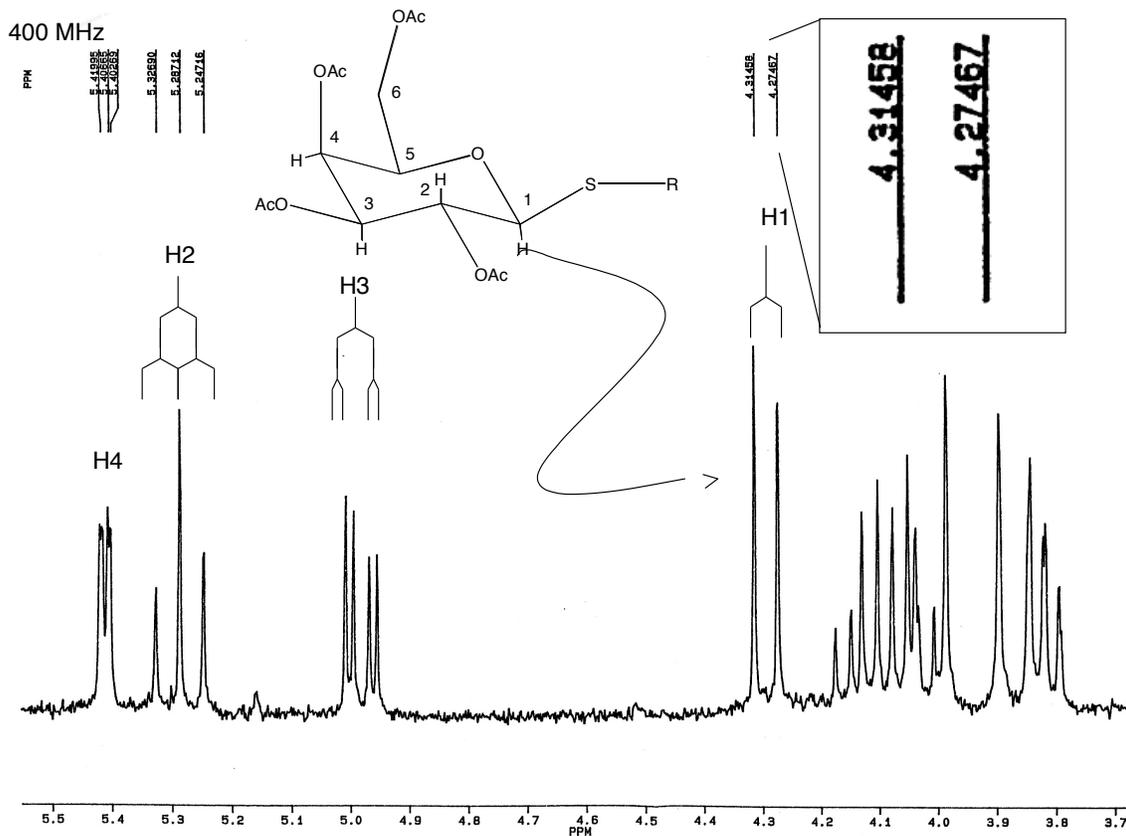
QE-300



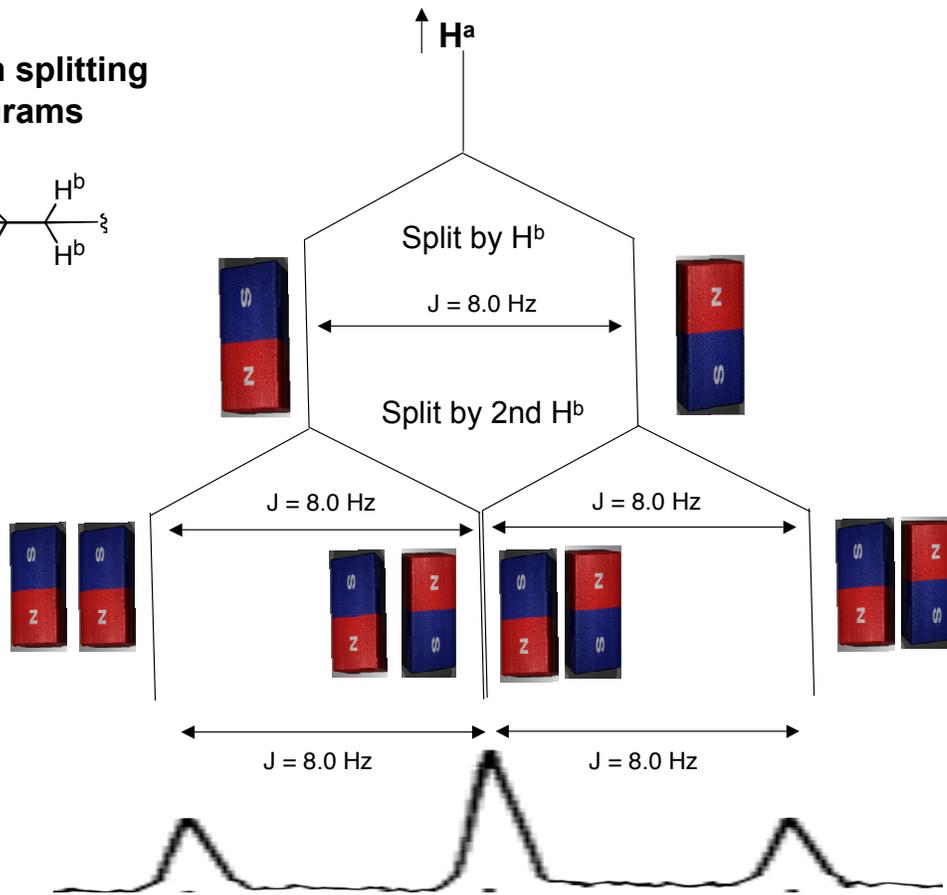
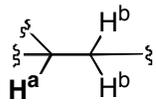


400 MHz

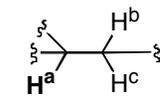




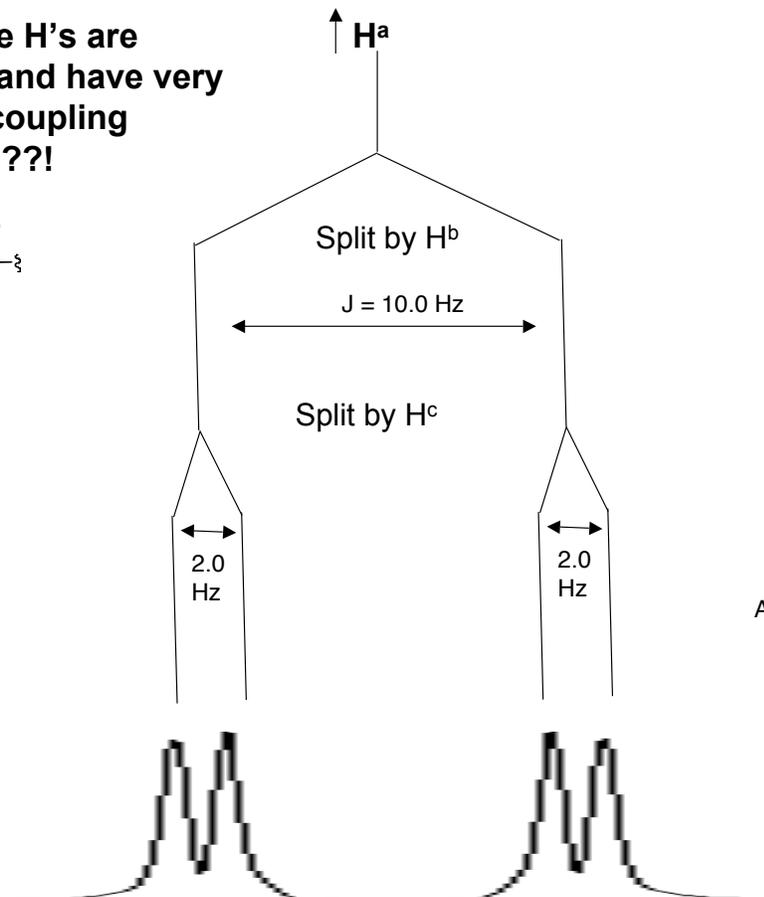
### Spin splitting diagrams



### What if the H's are different, and have very different coupling constants??!

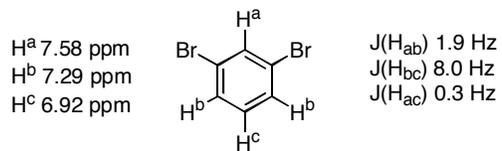


$J_{AB}$  10 Hz  
 $J_{AC}$  2 Hz

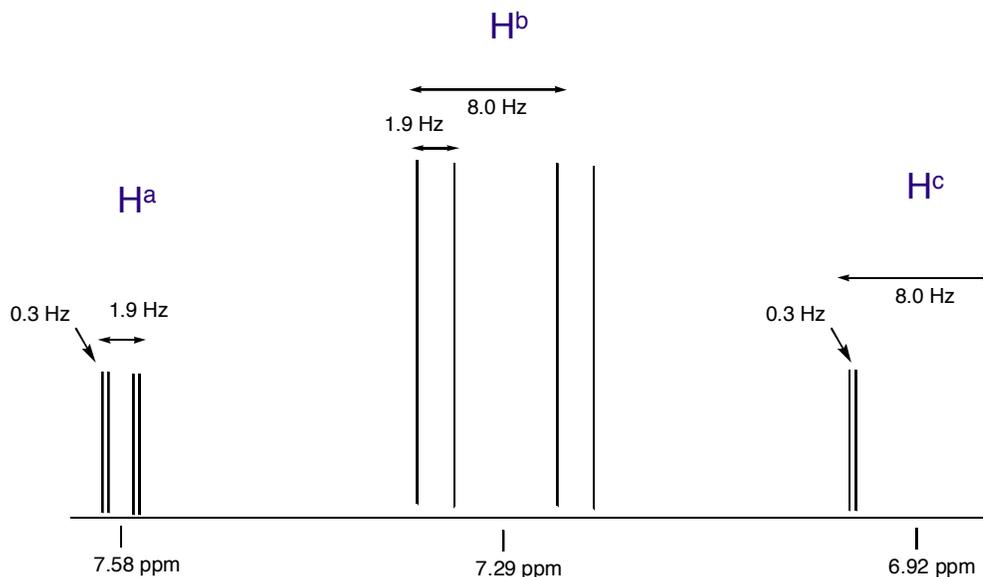


A doublet of doublets

# Aromatic (o,m,p) coupling constants

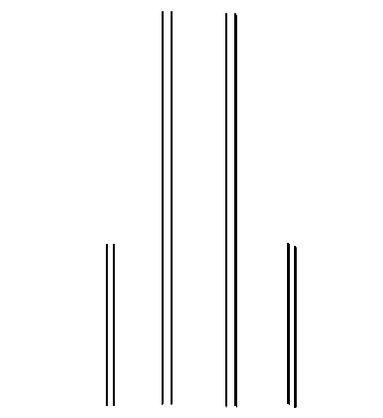
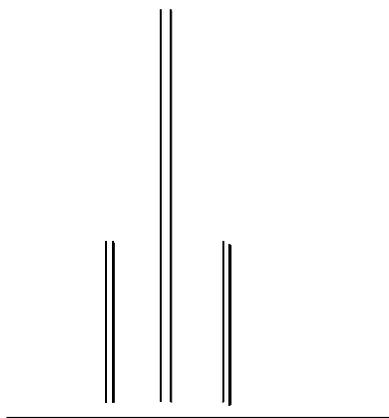
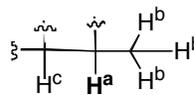
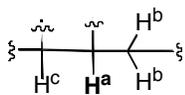


3 doublets of doublets

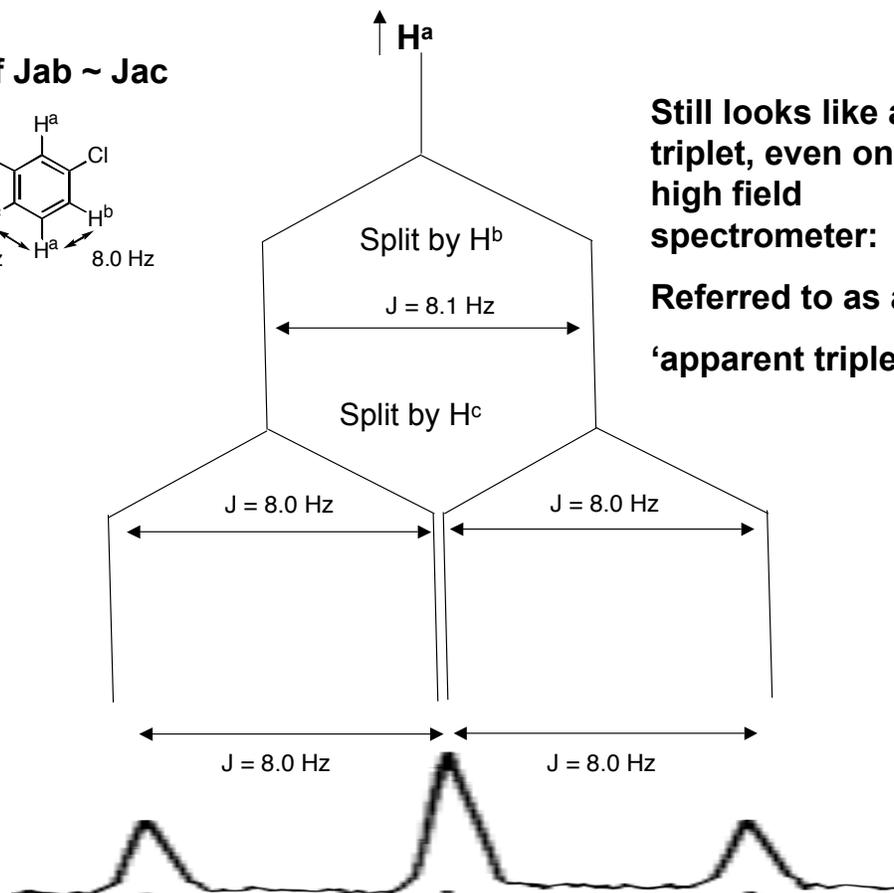
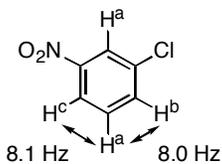


## 'Doublets of triplets' and 'doublets of quartets'

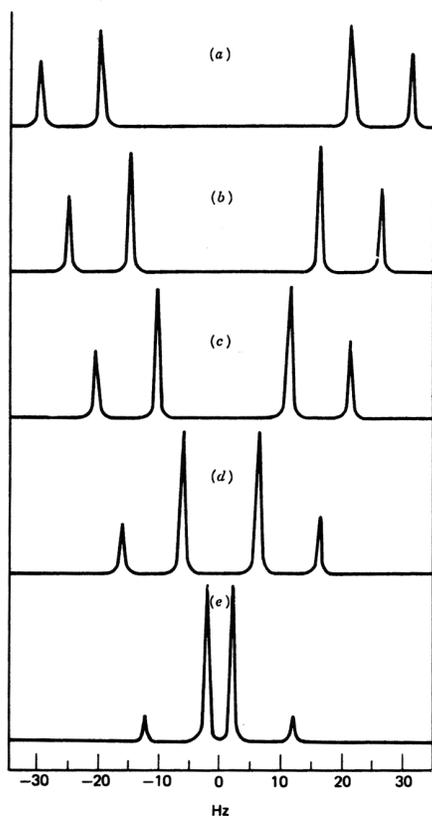
where  $J_{ab} \neq J_{ac}$



### What if $J_{ab} \sim J_{ac}$



Still looks like a triplet, even on a high field spectrometer:  
Referred to as an 'apparent triplet'



### WHEN PROTONS DON'T SPLIT!!

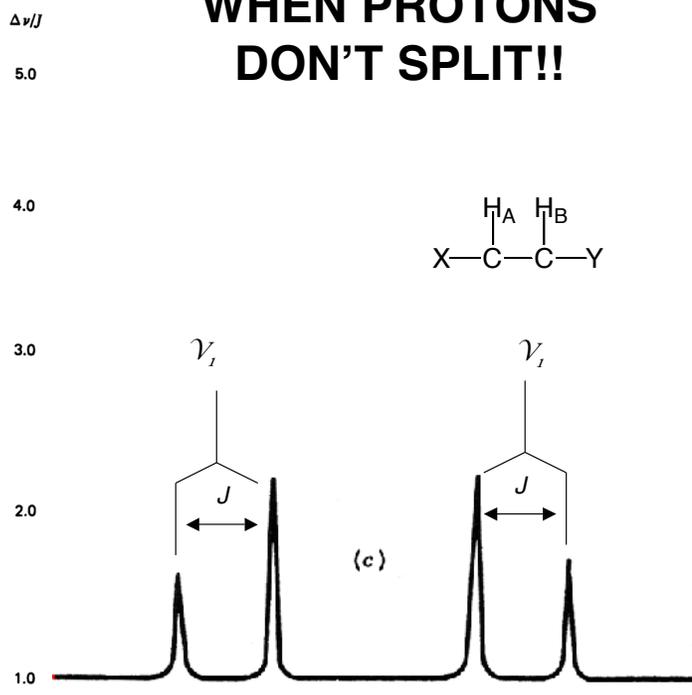
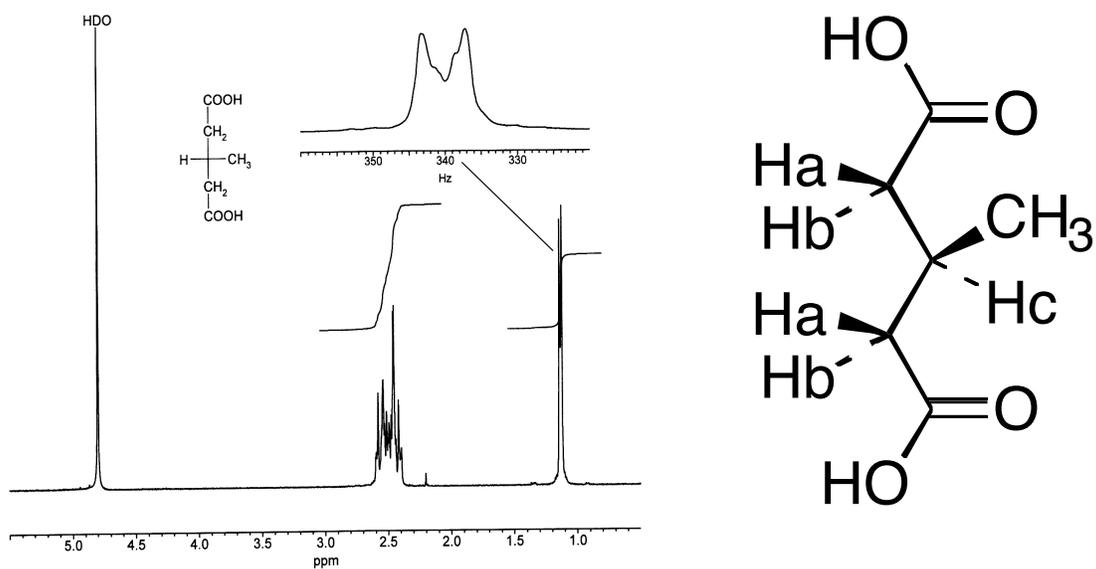


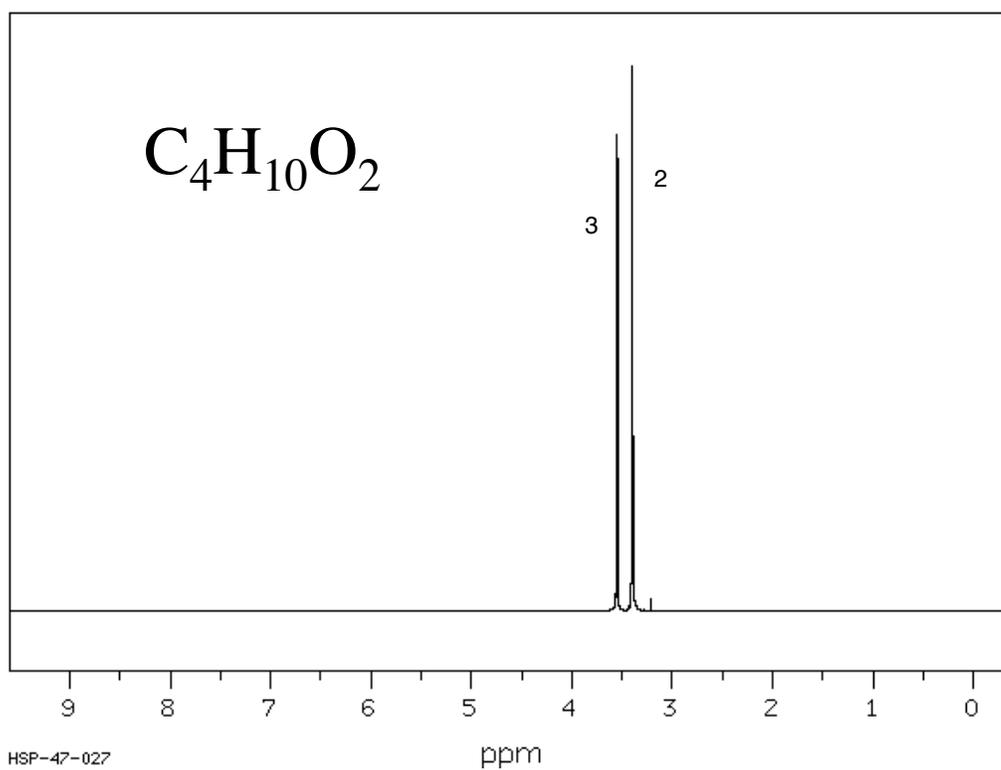
FIGURE 4.23. A two-proton system spin coupling with a decreasing difference in chemical shifts and a large  $J$  value (10 Hz); the difference between  $AB$  and  $AX$  notation is explained in the text (p. 179).

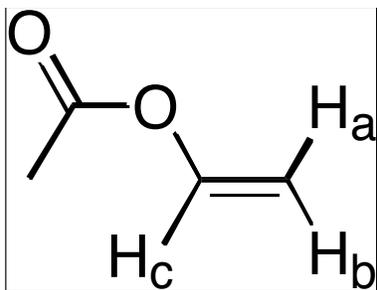
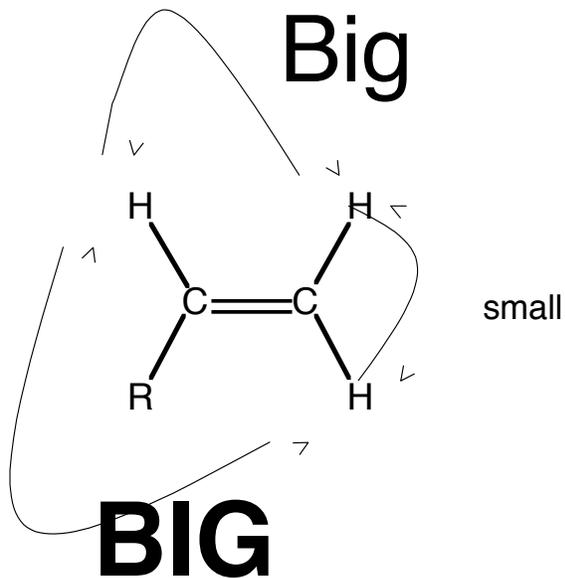
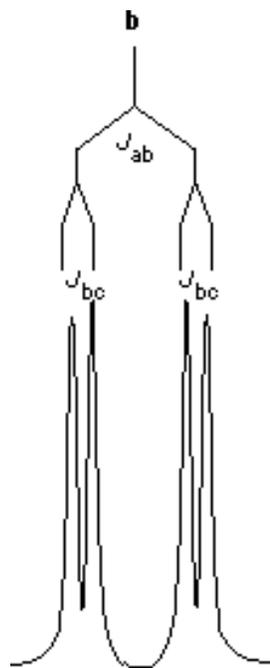
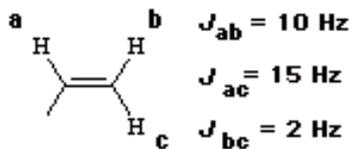
### EXAMPLE: Diastereotopic protons

Diastereotopic protons are in non-chemically equivalent environments.

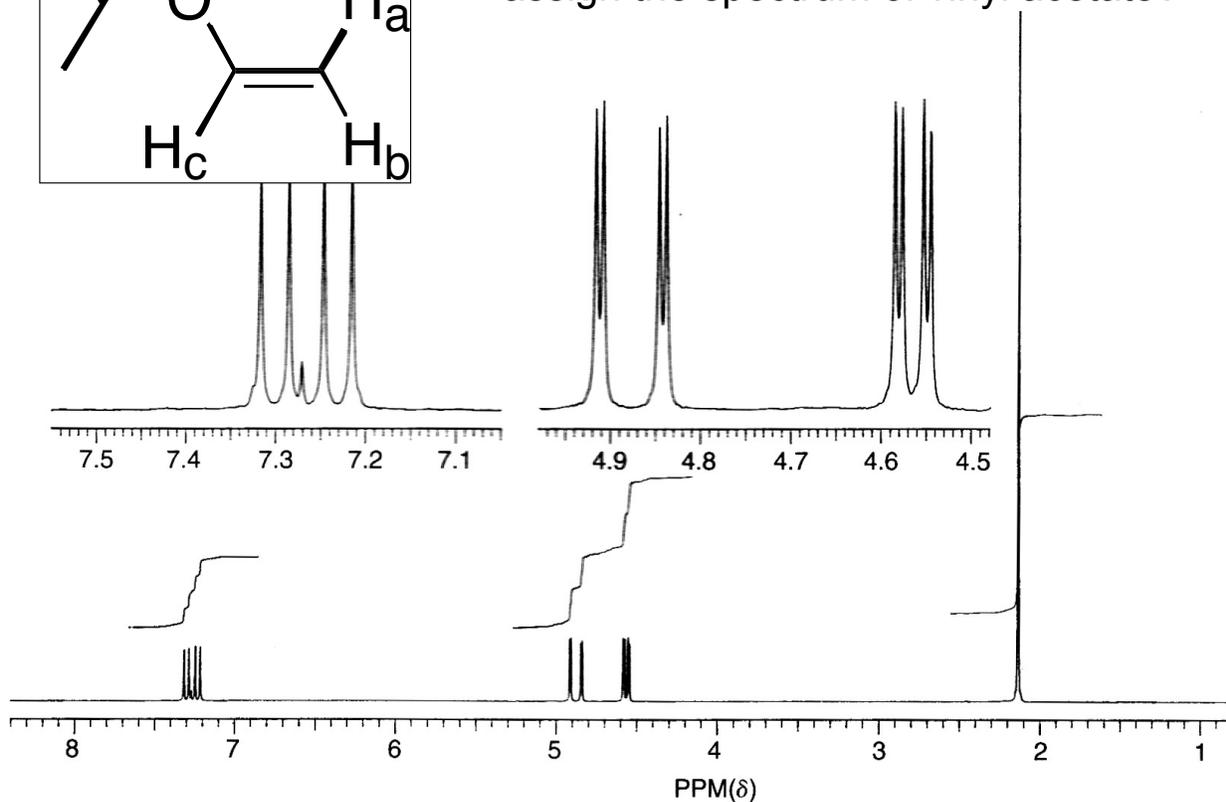


**FIGURE 4.48.** 3-Methylglutaric acid in D<sub>2</sub>O at 300 MHz. The COOH protons have exchanged with D<sub>2</sub>O and appear in the HDO peak. The CH<sub>3</sub> peak is broadened and “filled in.”

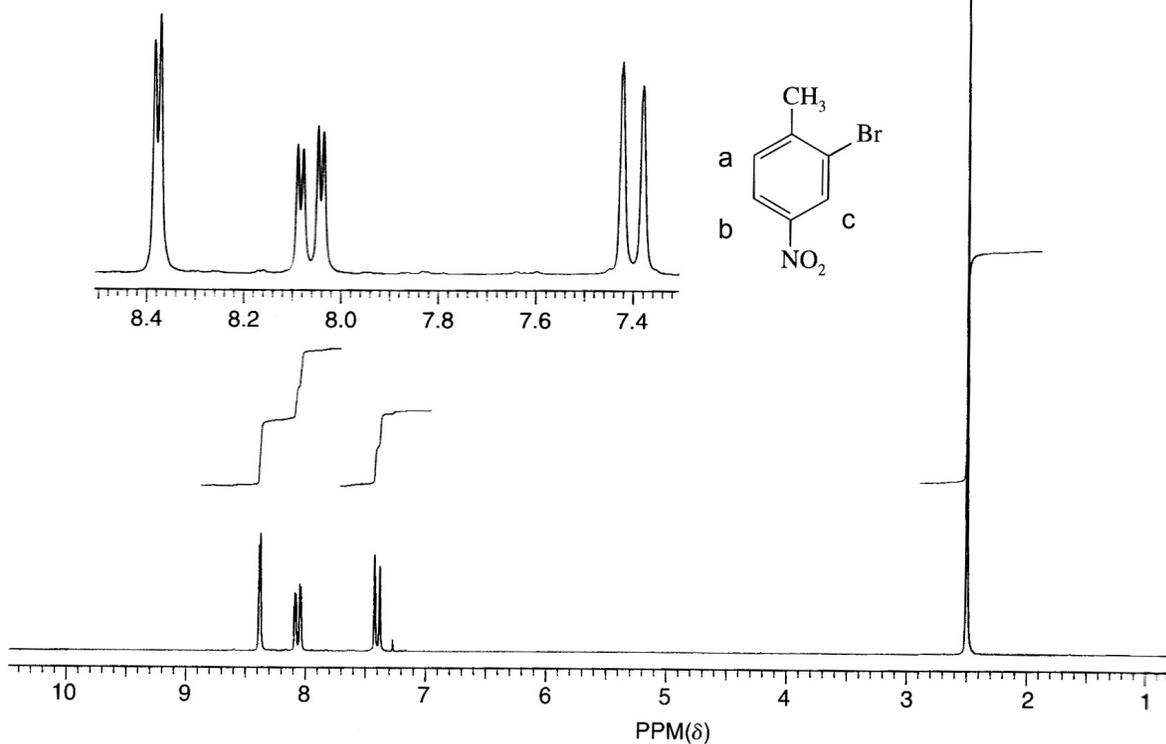
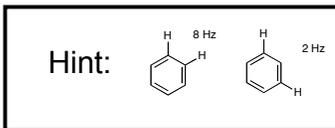




How can coupling constants help you assign the spectrum of vinyl acetate?



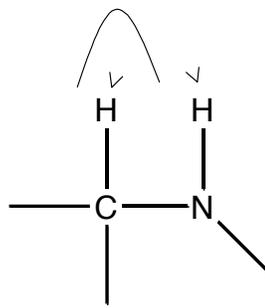
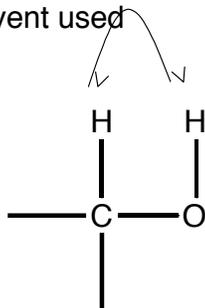
Assign the aromatic protons:



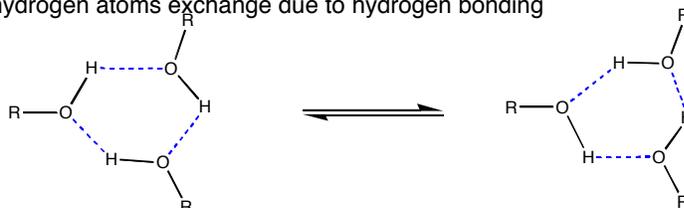
## Coupling to Hetero Atoms

Observed Only Sometimes  
Depends on Concentration  
Solvent used

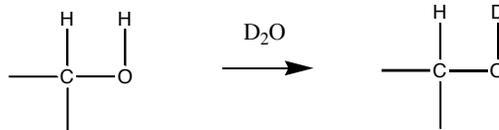
Rarely Observed



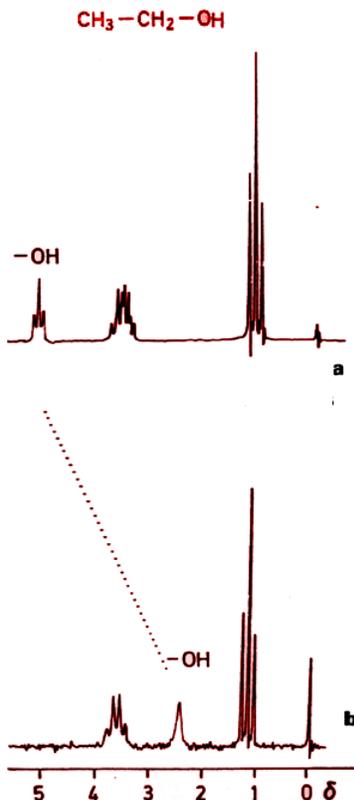
WHY: hydrogen atoms exchange due to hydrogen bonding



Easy Test



The hydrogen isotope deuterium (<sup>2</sup>H) has no spin and cannot couple



from M. Denk [http://131.104.156.23/Lectures/CHEM\\_207/CHM\\_207\\_NMR.htm](http://131.104.156.23/Lectures/CHEM_207/CHM_207_NMR.htm)

## Assembling Structures Using $^1\text{H}$ and $^{13}\text{C}$ NMR.

1. Determine and Assign IHD (Mol formula/C13)
2. Identify symmetry (C13)
3. Identify Functional Groups (C13 or other techniques).
4. Explore around functional groups  
Identify or “map” groups in H-NMR and infer adjacent groups
5. Assemble fragments.

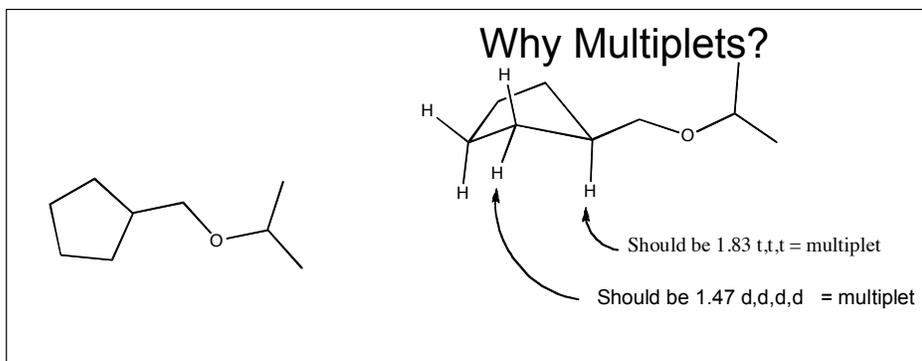
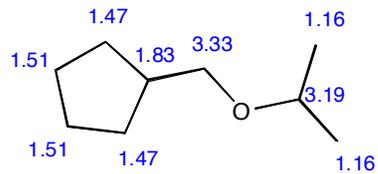
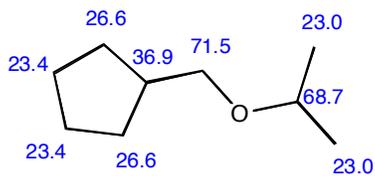
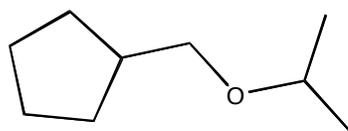


**C-13**

71.5	t
68.7	d
36.9	d
26.6	t (2)
23.4	t (2)
23.0	q (2)

**H-1**

3.33	d	2H
3.19	sept	1H
1.83	m	1H
1.47	m	4H
1.51	m	4H
1.16	d	6H



13.3



**$^{13}\text{C}$ -NMR:**

173.6, s

51.3, q

42.0, t

34.9, d

33.1, t (2)

26.2, t (2)

26.1, t

**$^1\text{H}$ -NMR:**

3.67, s, 3H

2.19, d, J = 6.4 Hz, 2H

1.70, m, 6H

0.9-1.3, m, 5H

13.4



127.1, s

126.3, d

117.7, s

28.0, t

25.8, t

25.1, t

22.5, t

21.8, t

5.79, t, J = 6.2 Hz, 1H

2.97, s, 2H

2.02, m, 4H

1.70, m, 4H

 **$^1\text{H}$  NMR**

214.9, s

173.5, s

73.6, d

61.7, t

55.1, d

44.1, t

29.9, t

29.2, t

28.1, t

24.0, t

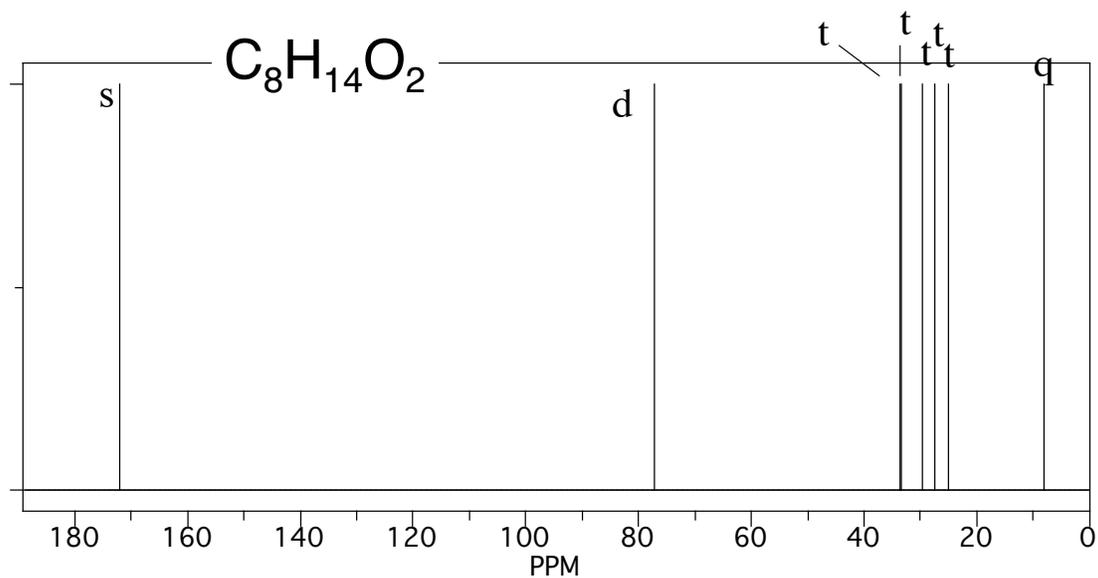
14.1, q

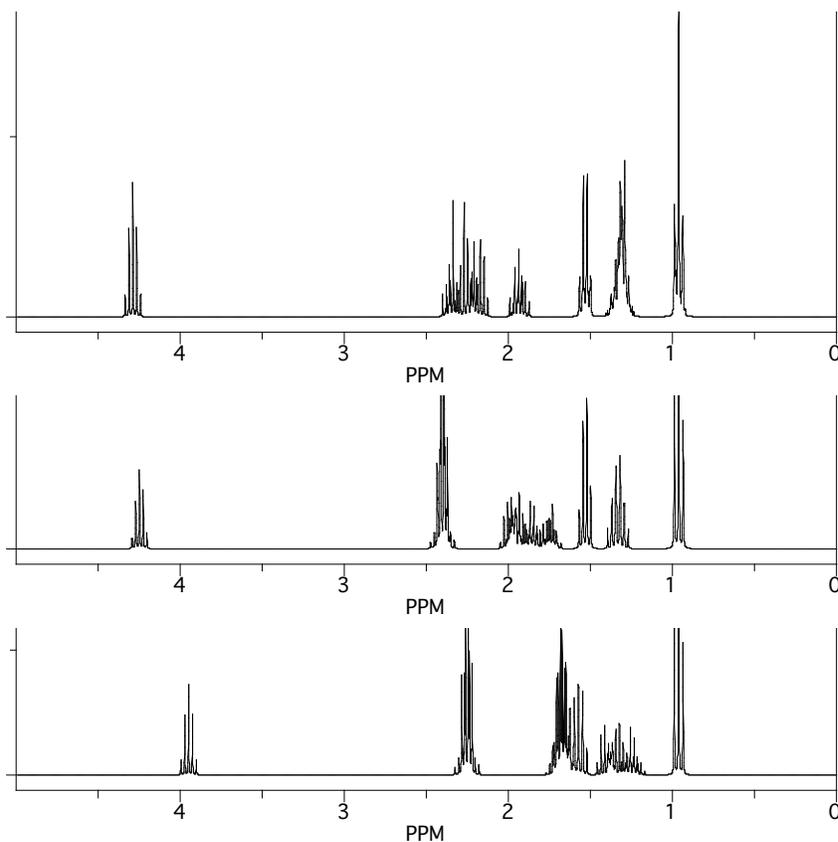
 **$^{13}\text{C}$ -NMR**4.20, q,  $J = 6.0$  Hz, 2H4.00, d,  $J = 3.5$ , 1H

2.9, d, bs, 1H (exchanges)

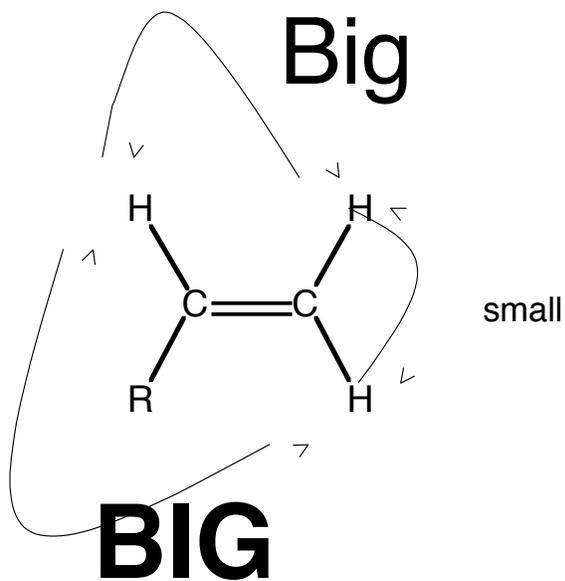
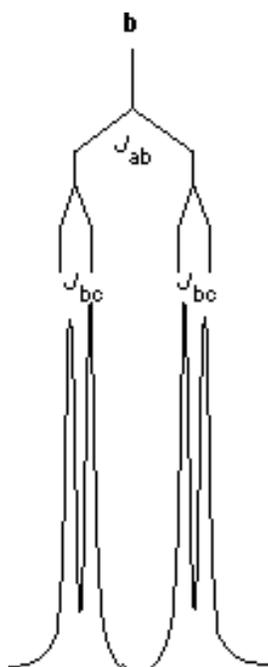
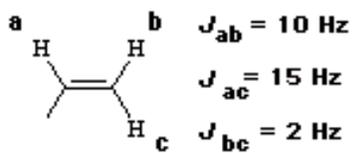
2.3-2.7, m, 3H

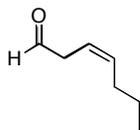
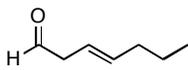
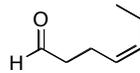
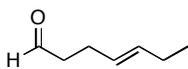
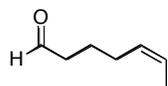
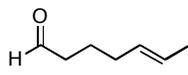
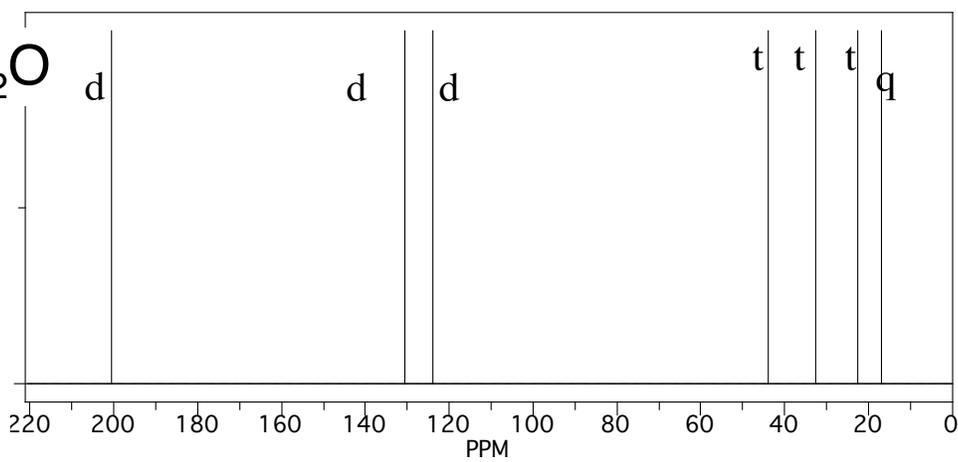
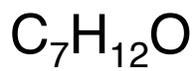
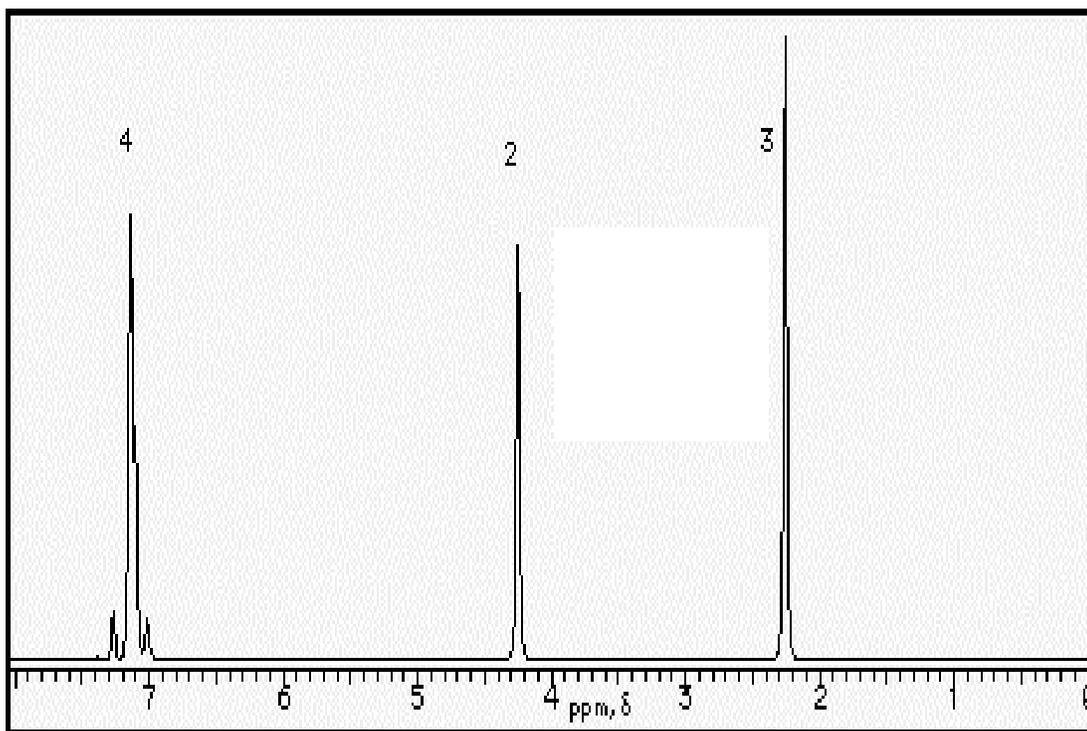
1.2-1.9, m, 8H

1.30, t,  $J = 3$ H



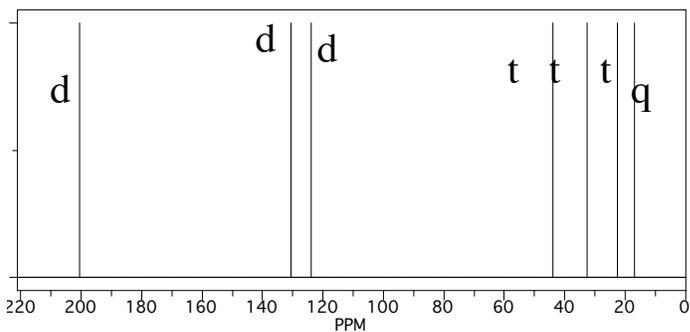
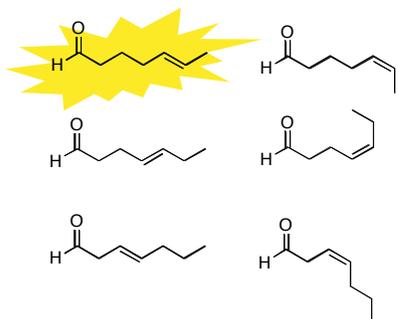
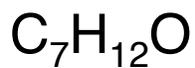
Difficult to determine structure by  $^1\text{H}$  and  $^{13}\text{C}$  NMR only.





Where is the double bond?

Is the double bond cis or trans?



**$^1H$ -NMR**

9.72 t J = 8.1 Hz, 1H

5.48 dq, J = 15.9, 6.2 Hz, 1H

5.20, dt, J = 15.9, 5.9, 1H

2.40 dt, J = 8.1, 7.4 Hz, 2H

1.96, td, J = 7.9, 5.9 Hz, 2H

1.66, quint, J = 8.0 Hz, 2H

1.71, d, J = 6.2 Hz, 3H

Question:

Would you be able to solve the structure of this compound by  $^1H$  and  $^{13}C$  NMR?

