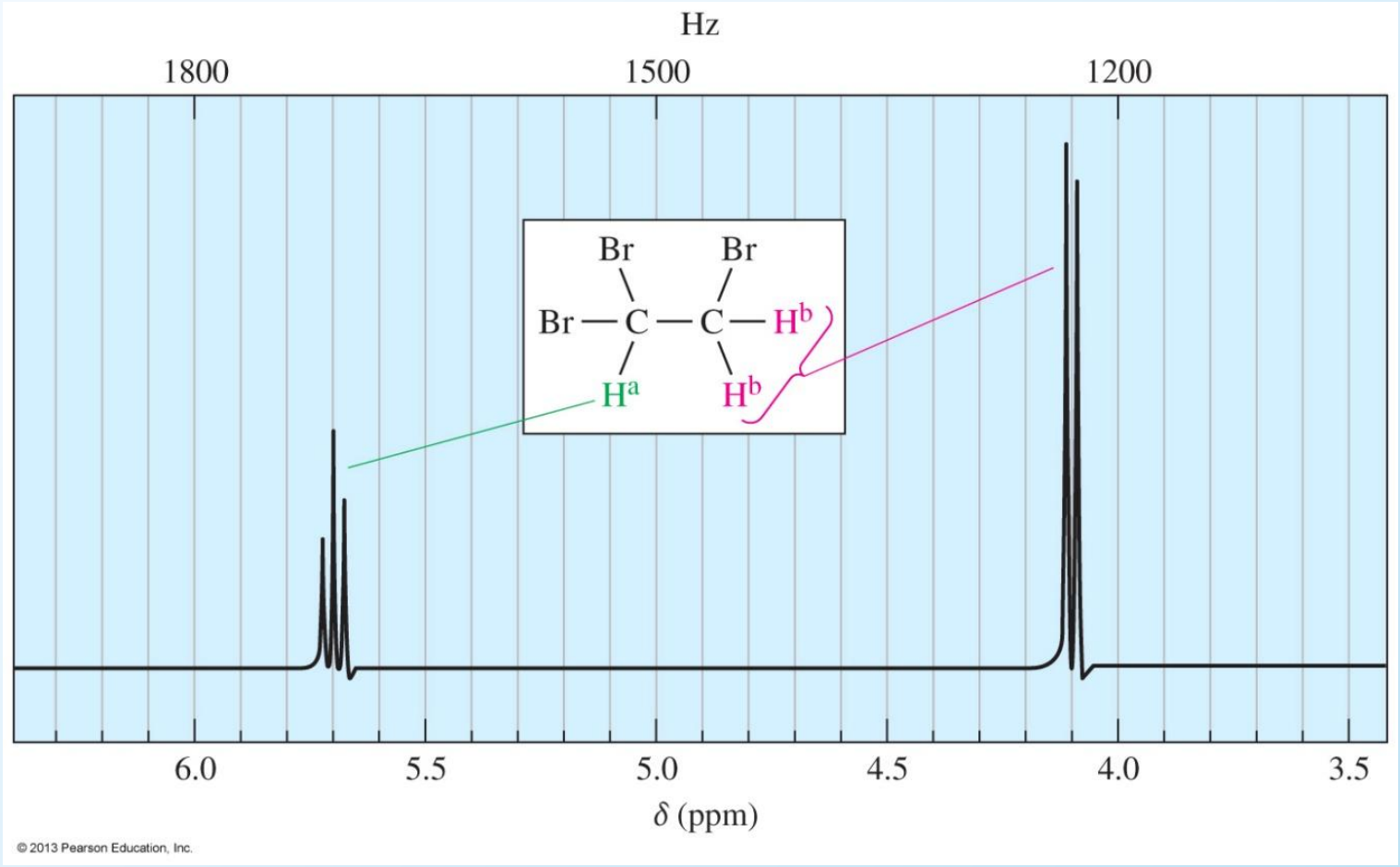
Nuclear Magnetic Resonance
2 - Proton NMR
Number of Signals, Chemical Shift, Integration and Coupling

Dr. Sapna Gupta

The NMR Graph - First Look



Aspects to Study in NMR

NMR spectrum has four main aspects to be studied.

- The ***number*** of signals shows the different kinds of protons present.
- The *location* (**chemical shift**) of the signals shows how shielded or deshielded the proton is.
- The *intensity* (**integration**) of the signal shows the number of protons under a signal.
- Signal ***splitting*** (**coupling**) shows the number of protons on adjacent atoms.

Number of Signals

The number of signals from a compound depends on how many unique hydrogens on the compound.

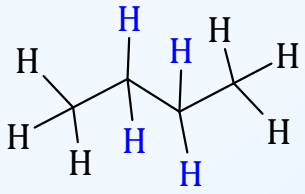
Equivalent hydrogens would be that they exist in the same environment. The best way to identify equivalent protons is:

- If they are on the same sp^3 carbon (unless it is chiral).
- There is symmetry in the molecule (shown below by the red curve).

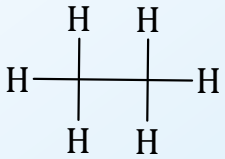
Number of Signals

Here are some examples of the number of signals to expect.

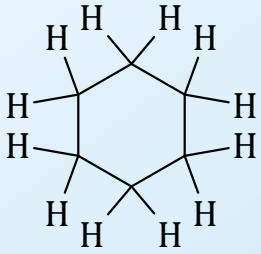
I have the marked the equivalent hydrogens with the same color. The symmetry in the molecule is shown by the red curve.



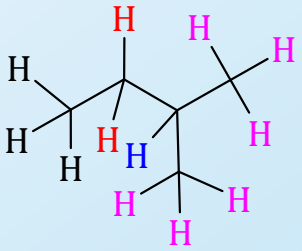
2 signals



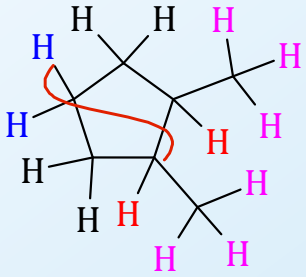
1 signal



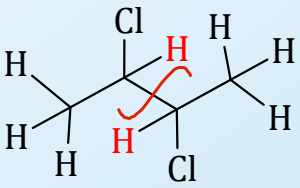
1 signal



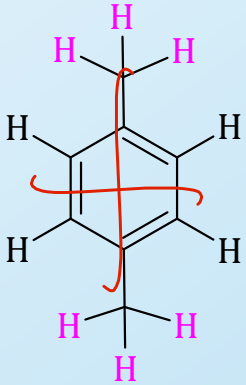
4 signals



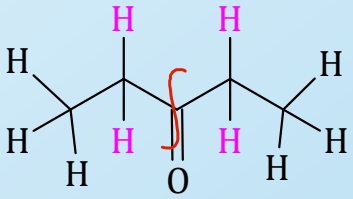
3 signals



2 signals



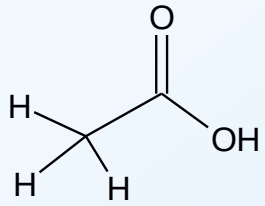
2 signals



2 signals

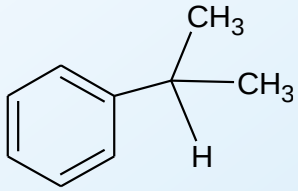
Worked Example: How many signals will you see for the following compounds?

a CH_3COOH



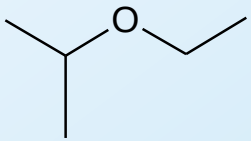
Two different Hs

b $C_6H_5CH(CH_3)_2$



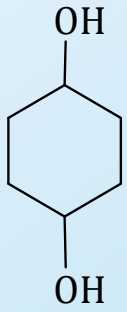
Three different Hs

c $(CH_3)_2CHOCH_2CH_3$



Four different Hs

d Cyclohexane-1,4-diol



Four different Hs

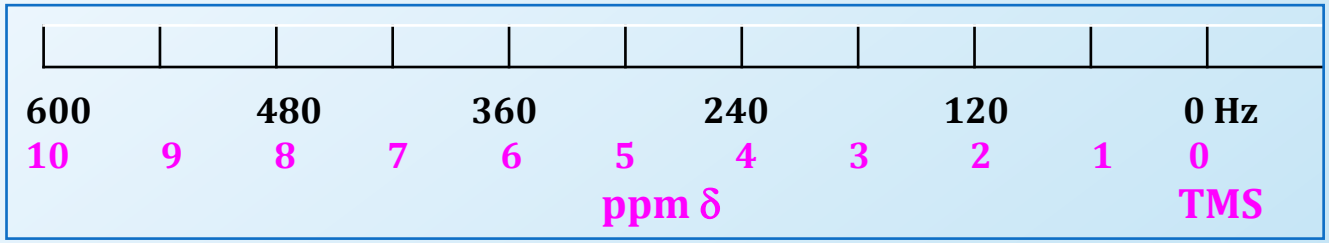
Chemical Shift

Chemical shift is the ratio of shift downfield from TMS (Hz) to total spectrometer frequency (MHz). This is the x-axis.

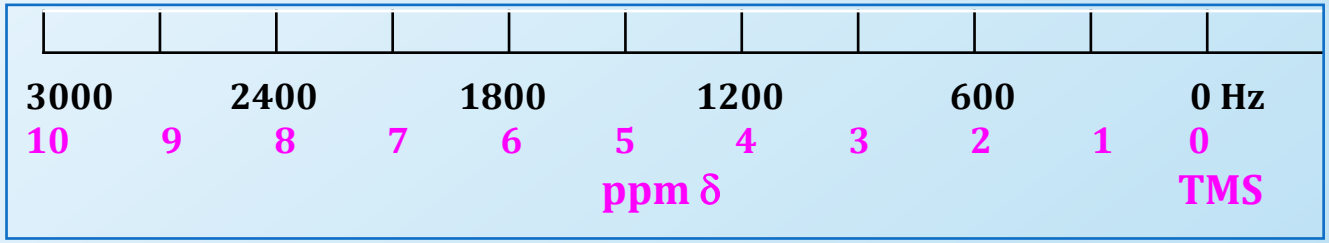
- The spectrum is referenced with TMS at 0 Hz. The x-axis is labeled as parts per million (ppm) or the delta (δ) scale.
- In calculating for ppm the frequency of the instrument does not matter since the Hz to MHz ratio is always the same no matter what MHz machine is used. Same value for 60, 100, or 300 MHz machine.

$$\text{chemical shift} = \frac{\text{shift downfiled from TMS in Hz}}{\text{Spectrophotometer frequency MHz}}$$

60 MHz



300 MHz



Magnetic Shielding

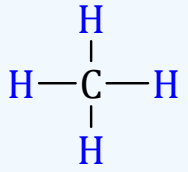
- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield or deshield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.
- Magnetic field strength must be increased for a shielded proton to flip at the same frequency.

Chemical Shift - Typical Values

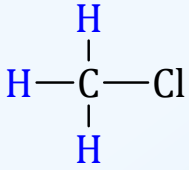
These are approximate values as chemical shifts can change according to what groups are around the proton.

Proton	Approximate ppm	Proton	Approximate ppm
Alkane (-CH_3)	0.9-1.4	Ph-CH_3	2.3
-COCH_3	2.1	R-CHO	9-10
-C C-H	2.5	R-COOH	10-12
R-CH_2-X	3-4	R-OH	2-5
=CH_2	5-6	Ar-OH	4-7
Ph-H	7.2	R-NH_2	1.5-4

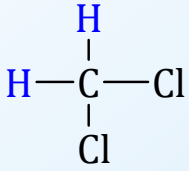
Chemical Shift – Shielding/Deshielding



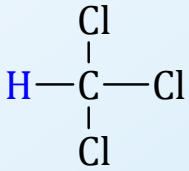
δ 0.2 ppm



δ 3.0 ppm



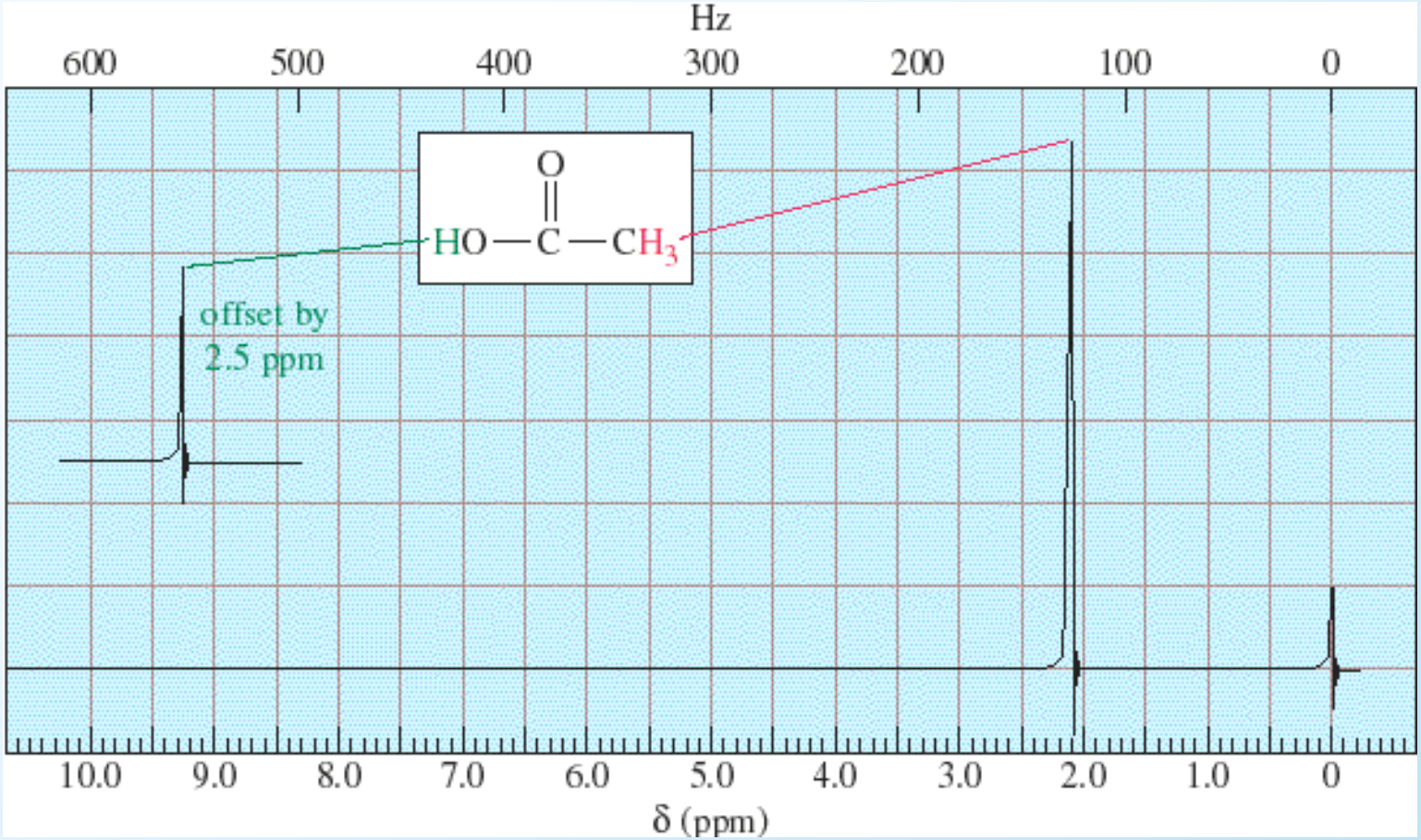
δ 5.3 ppm



δ 7.2 ppm

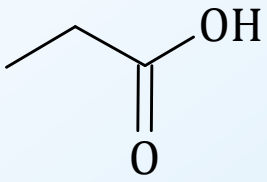
- More electronegative atoms deshield more and give larger shift values (left side of spectrum).
- Each chlorine shifts the H ppm by about 2 ppm.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

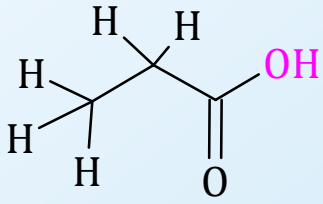
Carboxylic Acid Proton, δ10+



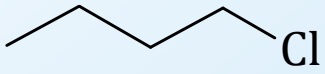
Worked Example: Identify the most downfield proton in the following compounds.

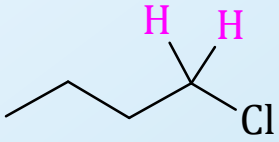
a CH_3COOH



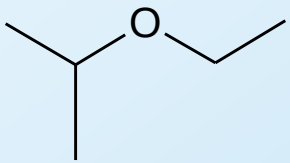


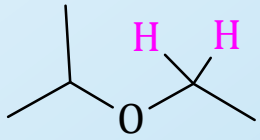
b $CH_3CH_2CH_2CH_2Cl$



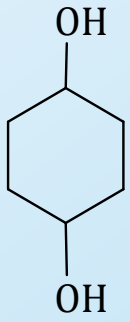


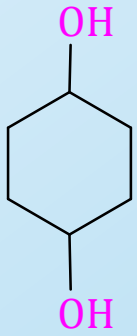
c $(CH_3)_2CHOCH_2CH_3$





d Cyclohexane-1,4-diol

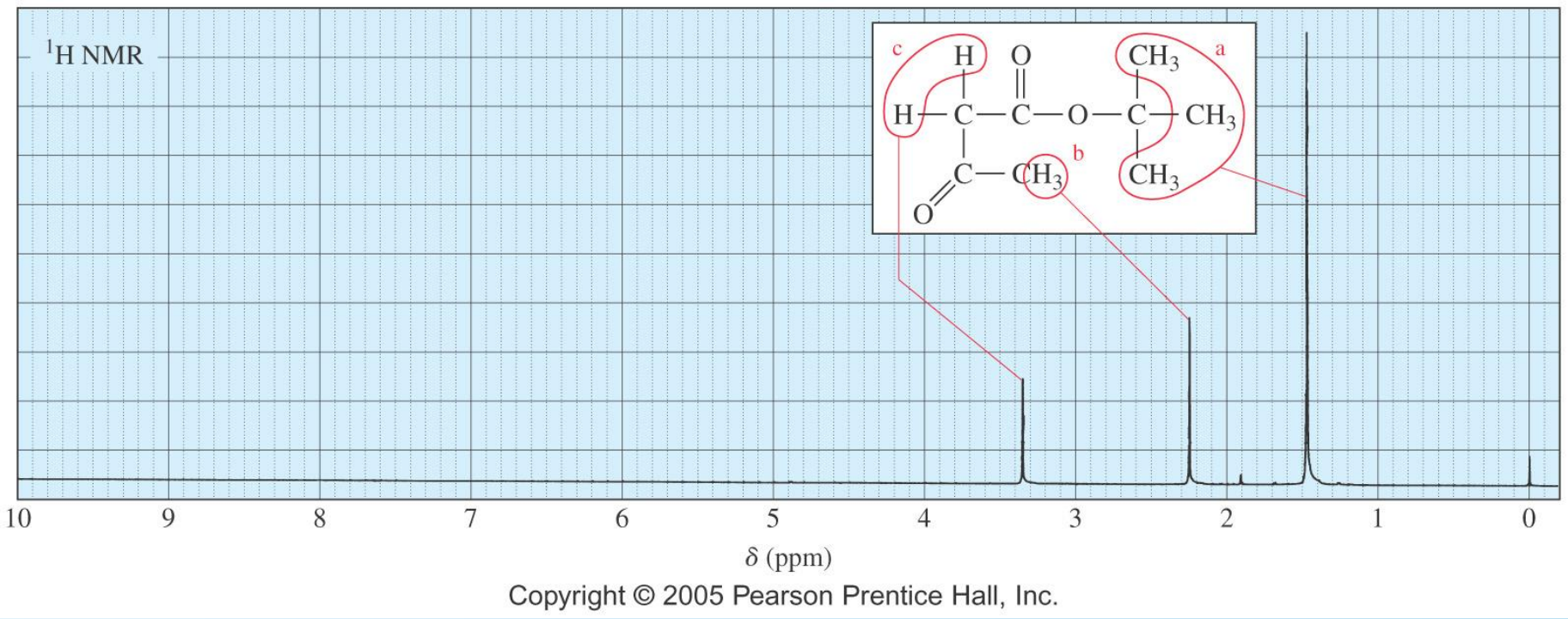




Number of Signals and Chemical Shift

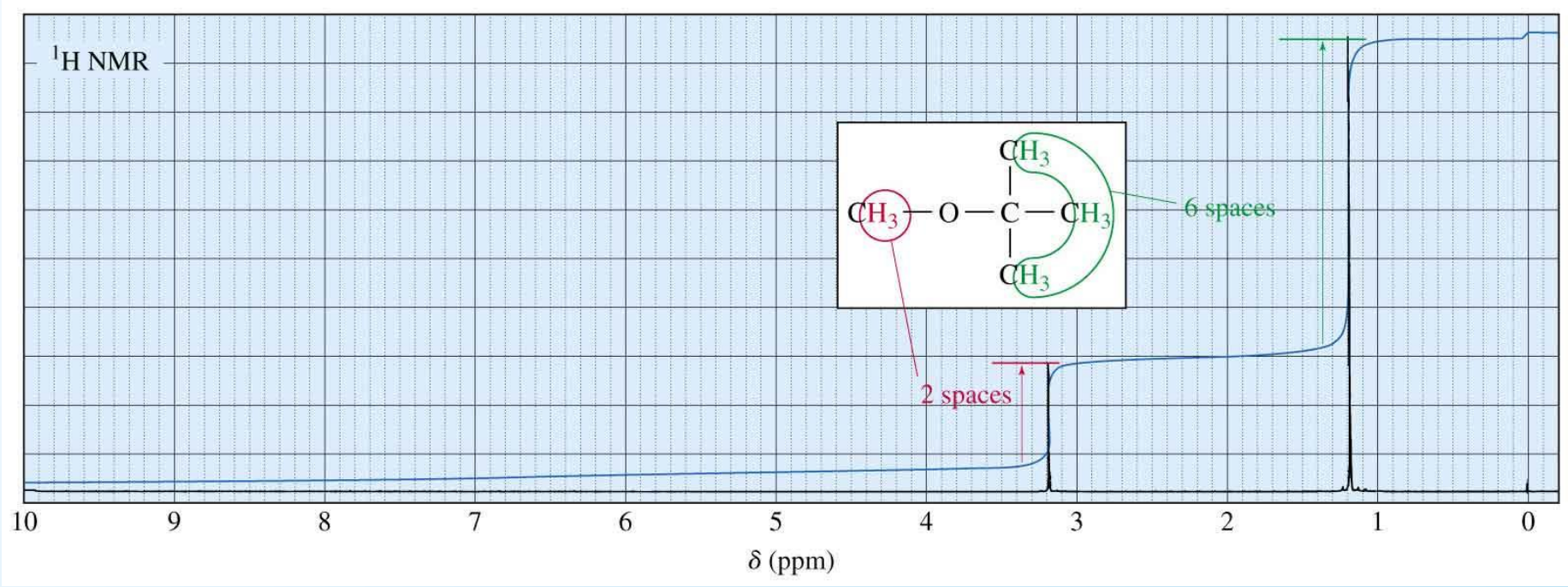
Equivalent hydrogens have the same chemical shift.

Hydrogens/protons in different environments will show different chemical shifts. In the NMR below: “a” protons are most shielded and “c” protons are most deshielded)

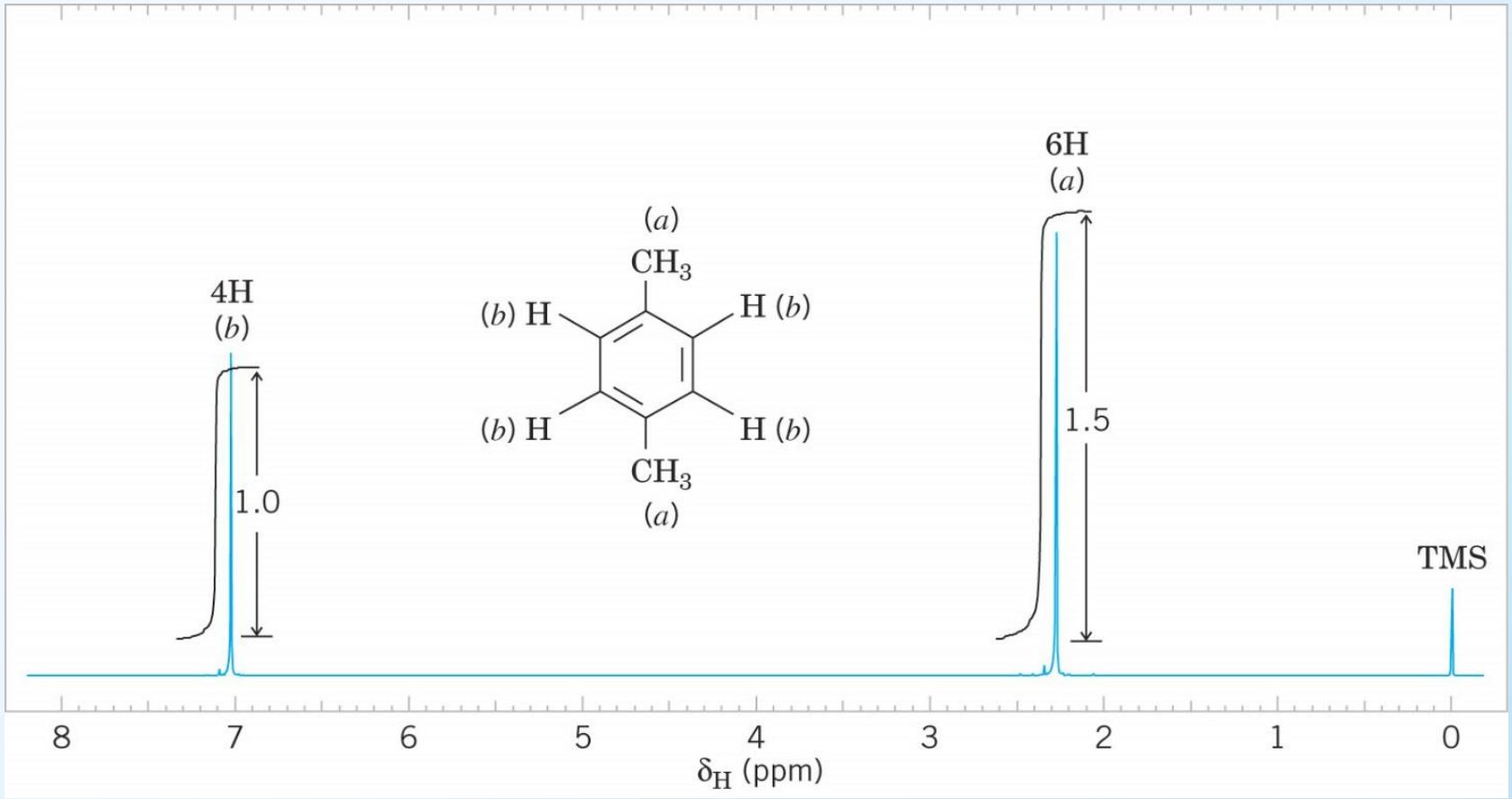


Intensity of Signals – Integration - 1

- The area under each peak is proportional to the number of protons.
- Shown by integral trace.

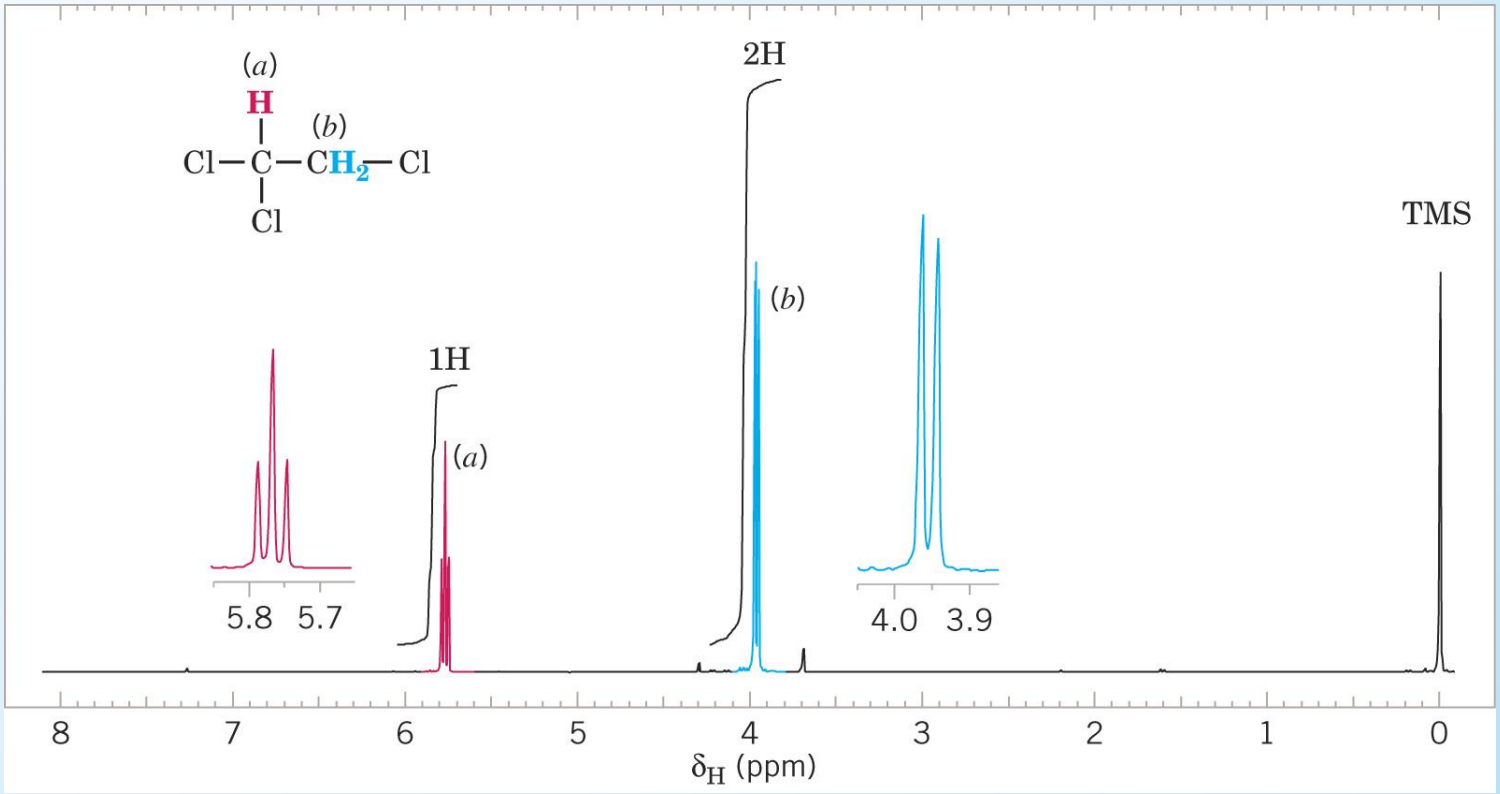


Intensity of Signals – Integration - 2

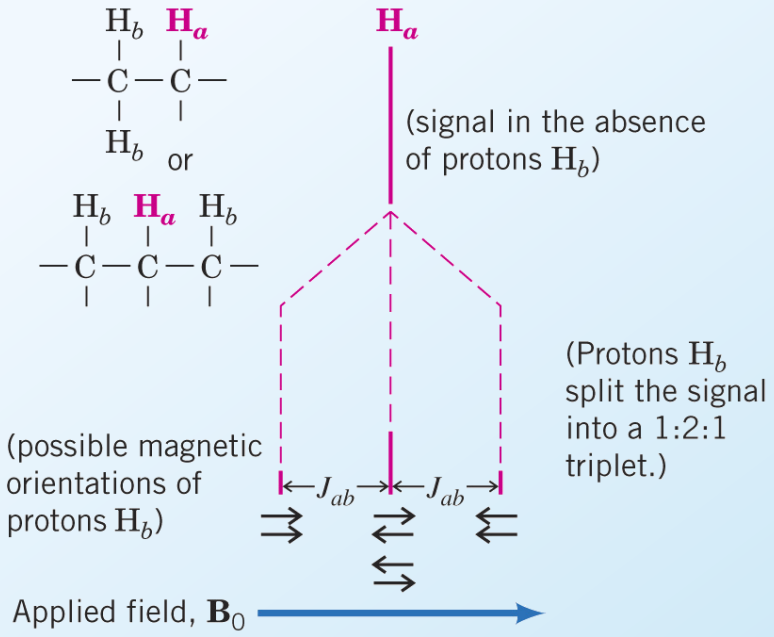


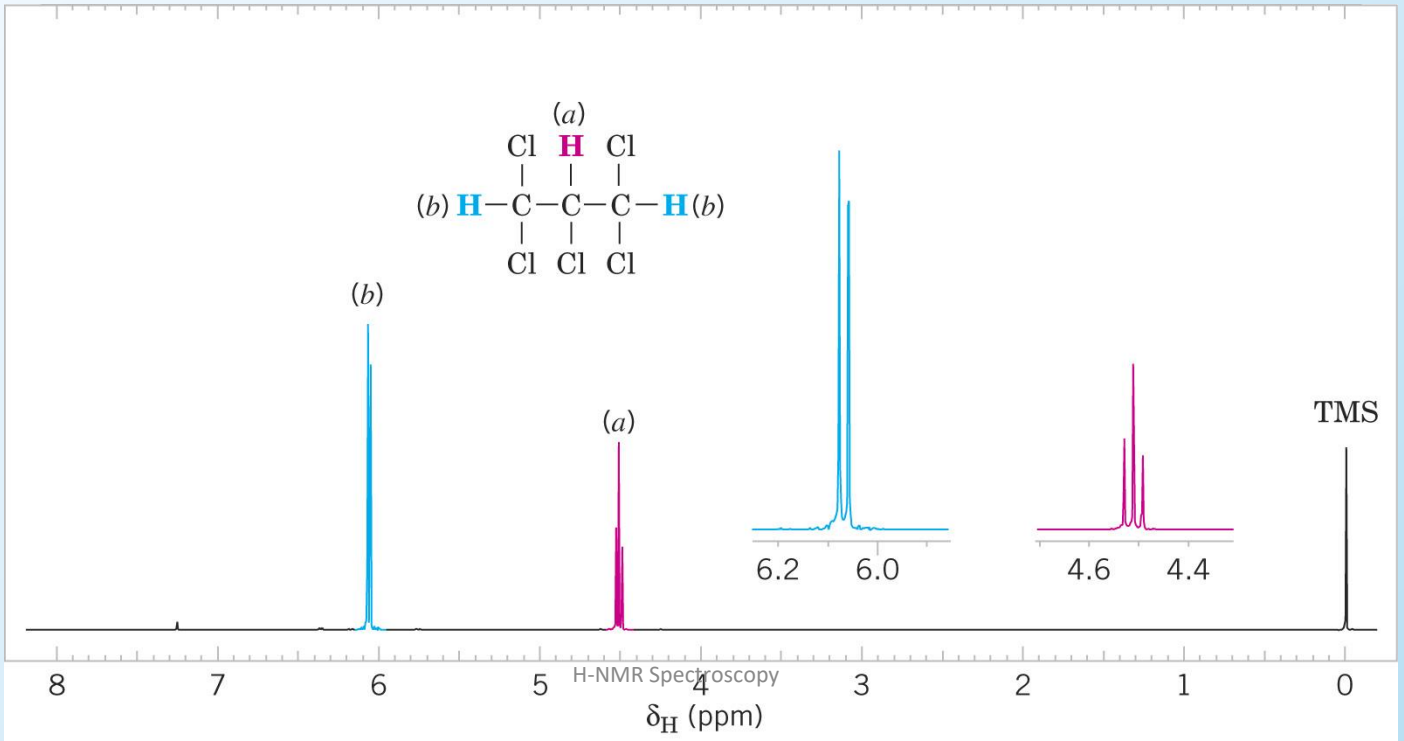
Spin-Spin Splitting (Coupling)

- Signal splitting occurs when there are unequivalent protons (therefore have a different chemical shift) on the neighboring carbons.
- Signal splitting for a proton is neighboring proton +1.
- This has to do with the alignment of the protons to the magnetic field.

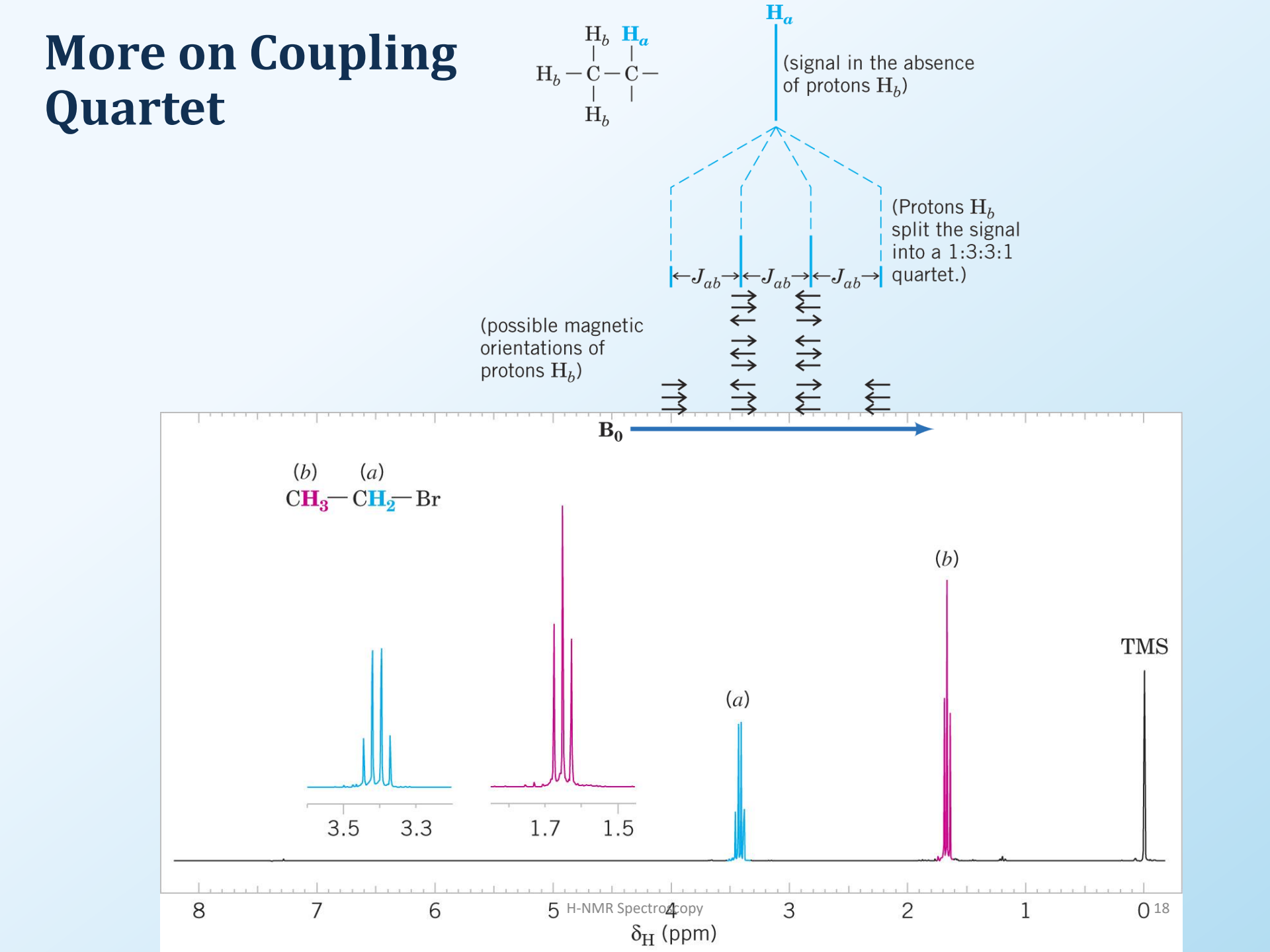


More on Coupling Triplet





More on Coupling Quartet



The *N* + 1 Rule

If a signal is split by *N* equivalent protons, it is split into *N* + 1 peaks.

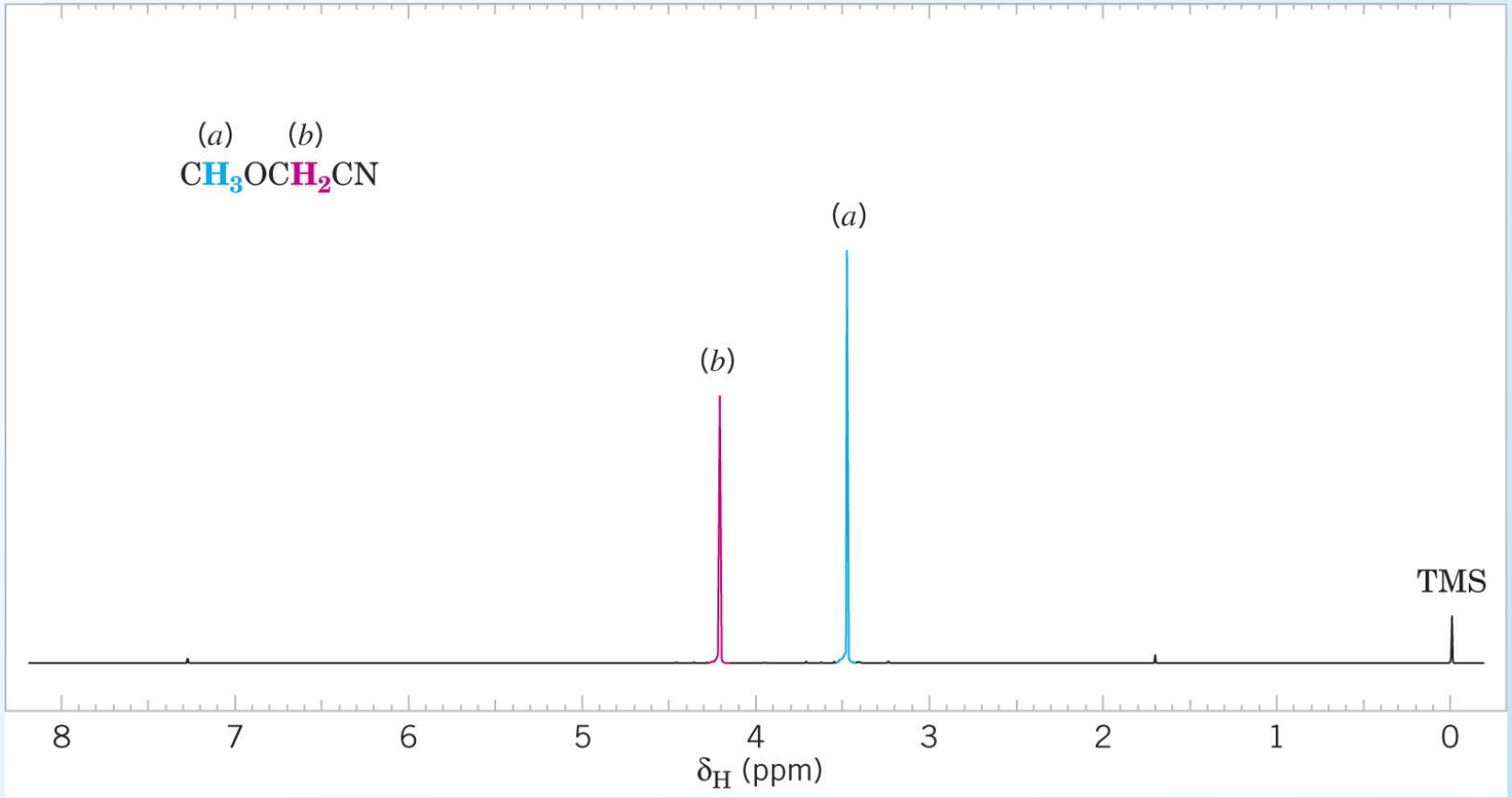
Number of Equivalent Protons	Splitting	Area Ratios Pascal's Triangle
0	1 – singlet - s	1
1	2 – doublet - d	1 1
2	3 – triplet - t	1 2 1
3	4 – quartet - q	1 3 3 1
4	5 – quintet	1 4 6 4 1
5	6 – sextet	1 5 10 10 5 1
6	7 - septet	1 6 15 20 15 6 1

Range of Magnetic Coupling

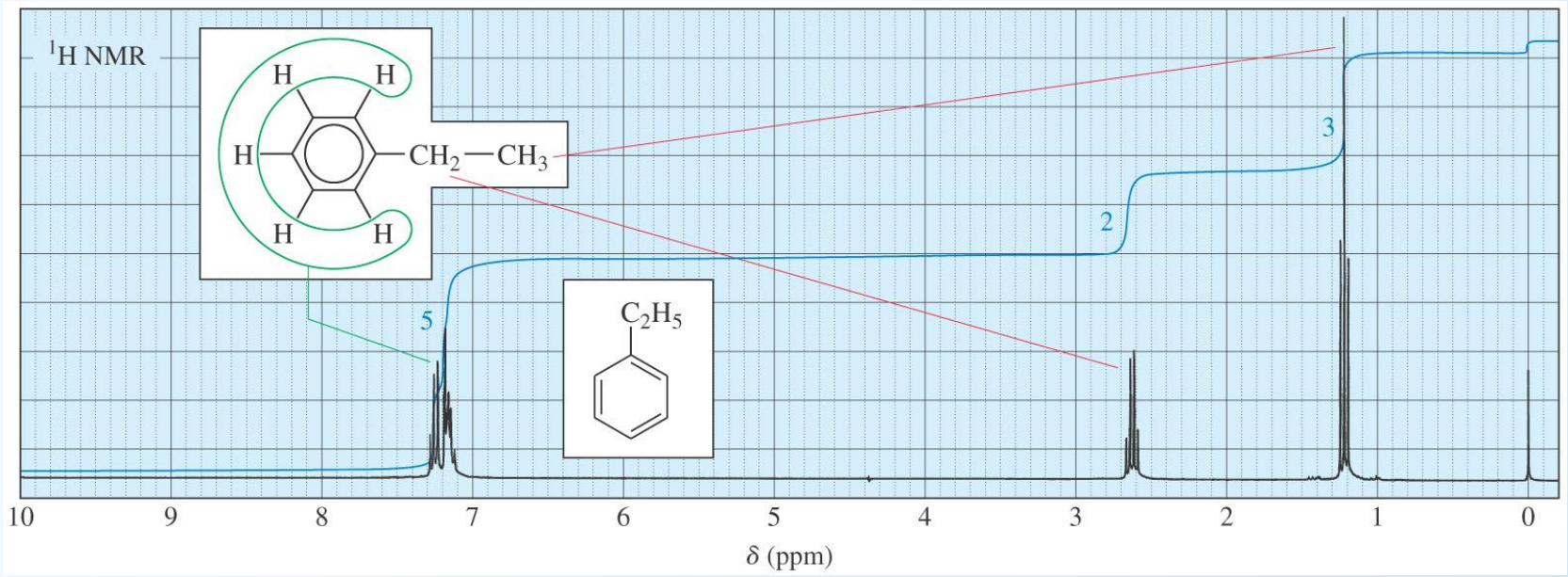
- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other only if they are not equivalent.
- Protons on adjacent carbons normally will couple.
- Protons separated by four or more bonds will not couple.

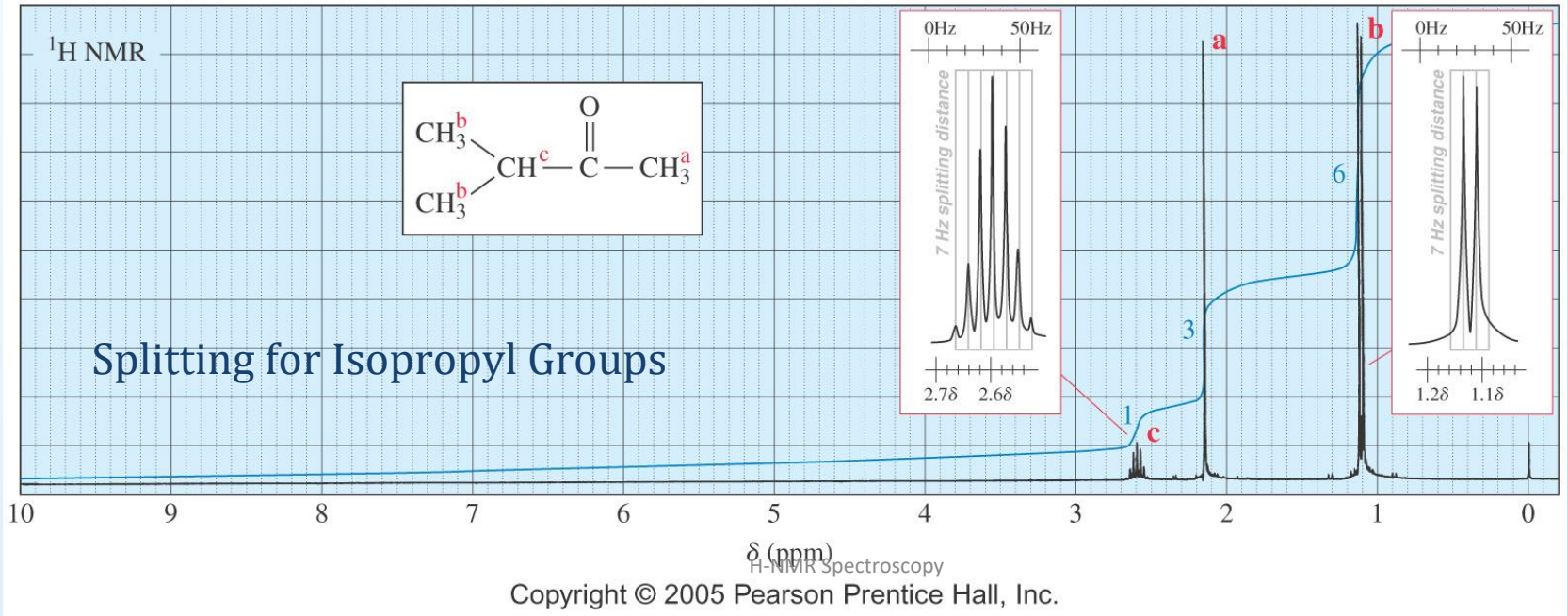
More on Coupling – No Coupling

No coupling between Hs because of electronegative oxygen in the middle.



Splitting for Ethyl Groups

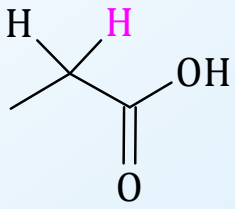




Splitting for Isopropyl Groups

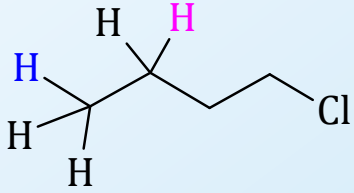
Worked Example: What kind of splitting will you see for the proton coloured blue and pink in the following compounds.

a CH_3COOH



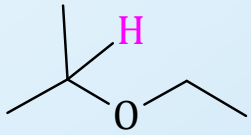
H will be quartet (q)

b $CH_3CH_2CH_2CH_2Cl$



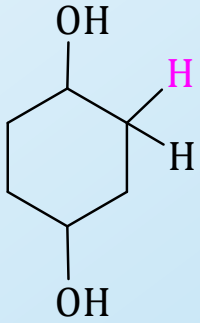
H will be triplet (t)
H will be sextet

c $(CH_3)_2CHOCH_2CH_3$



H will be septet

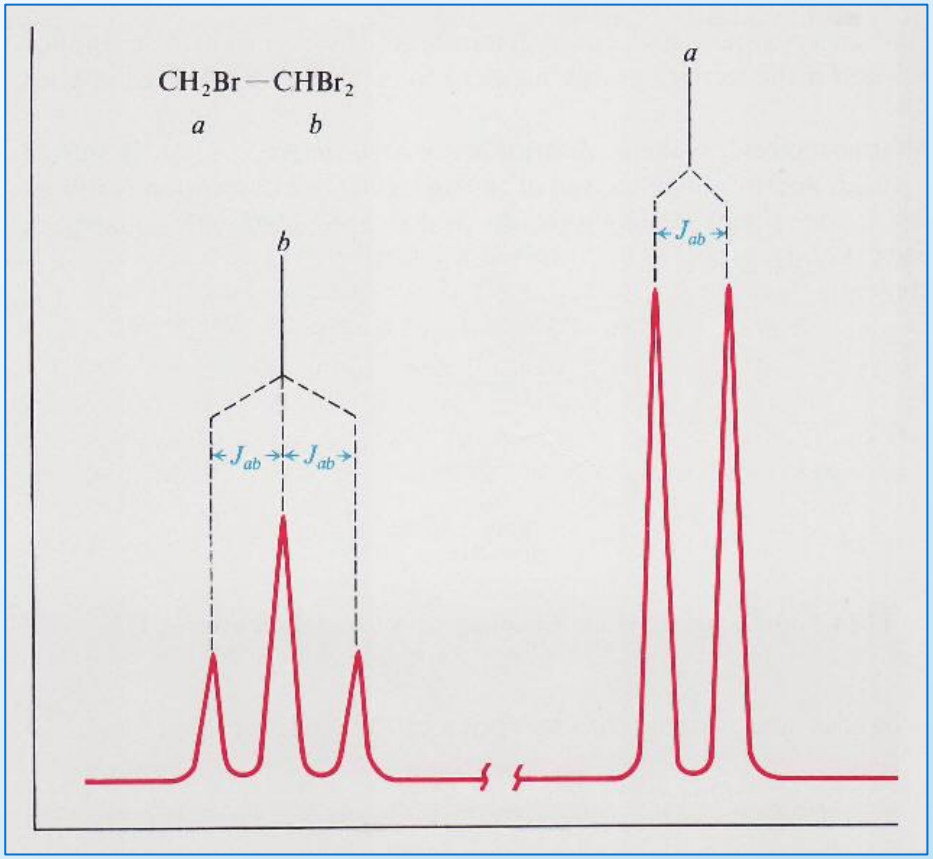
d Cyclohexane-1,4-diol



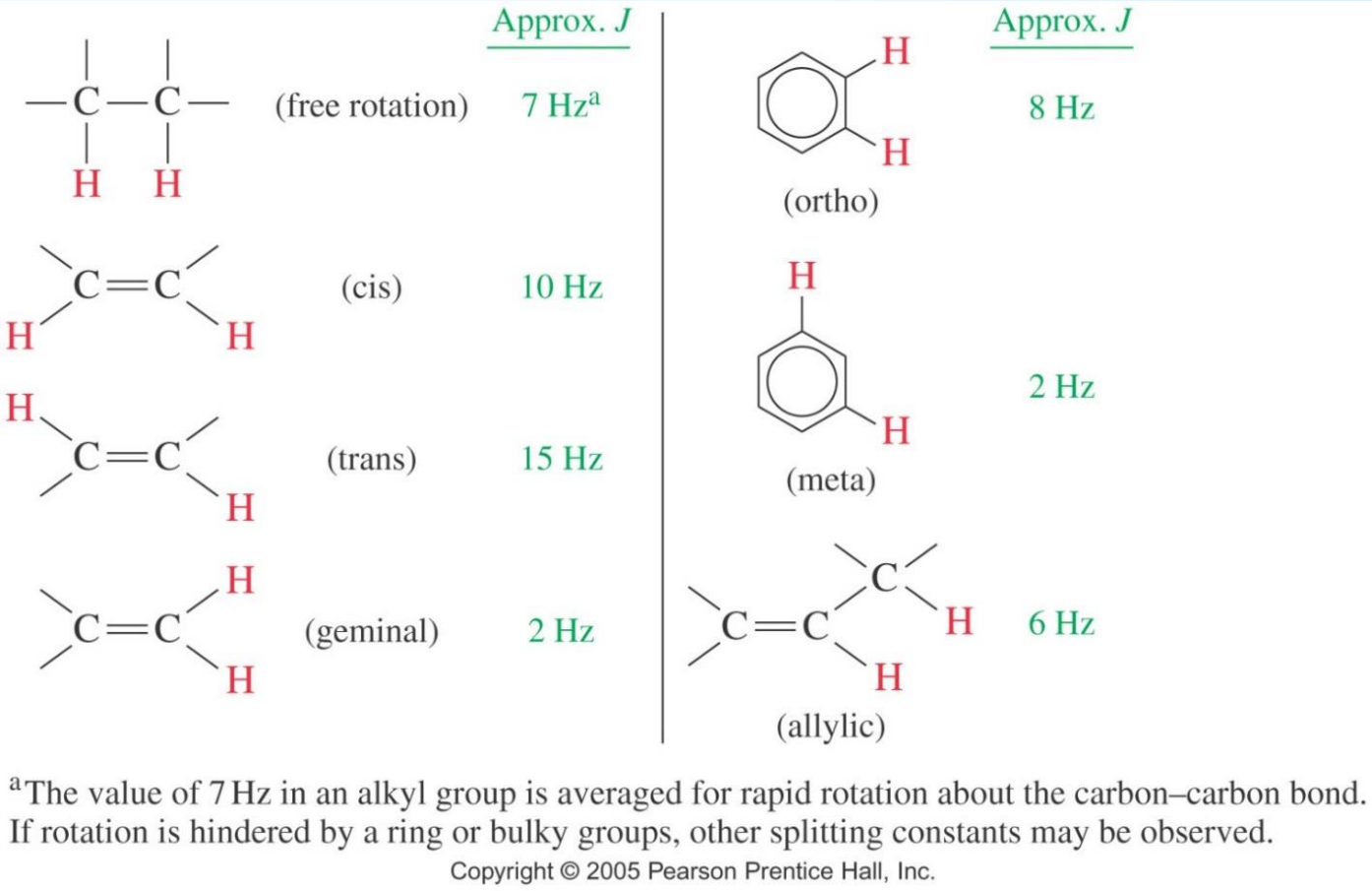
H will be a quartet (q)

Coupling Constants and Values

- Distance between the peaks of multiplet.
- Measured in Hz.
- Not dependent on strength of the external field.
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

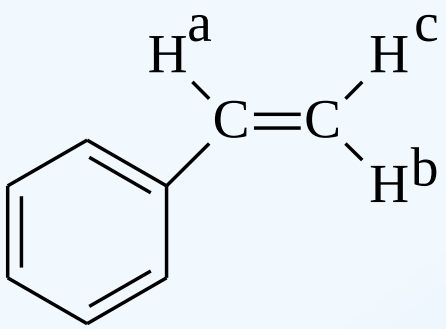


Coupling Constant Values

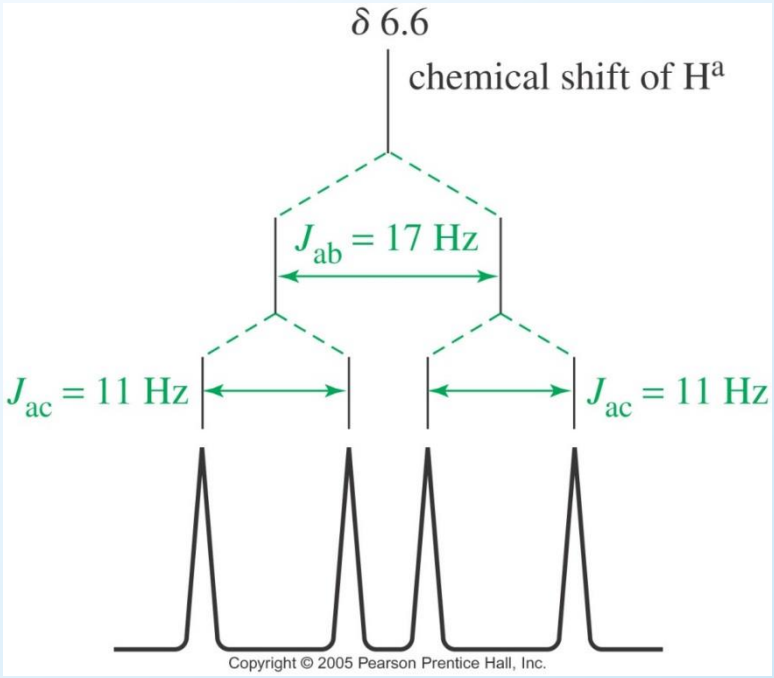


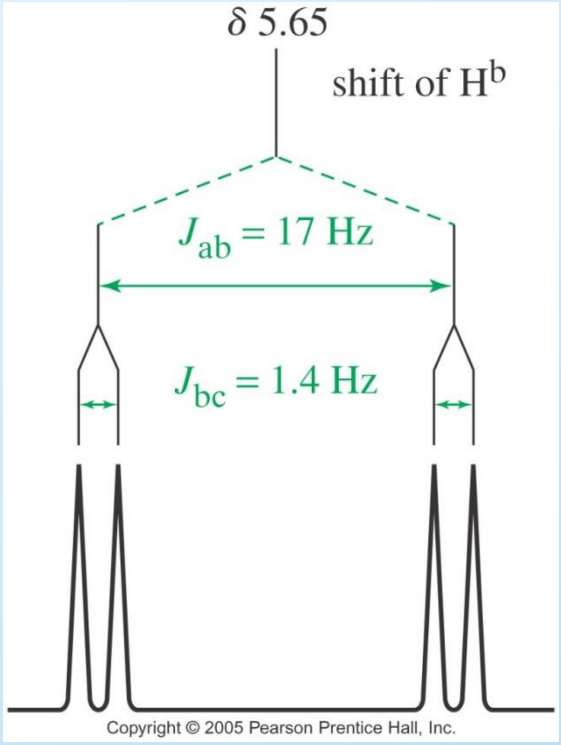
[a]The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

Complex Splitting

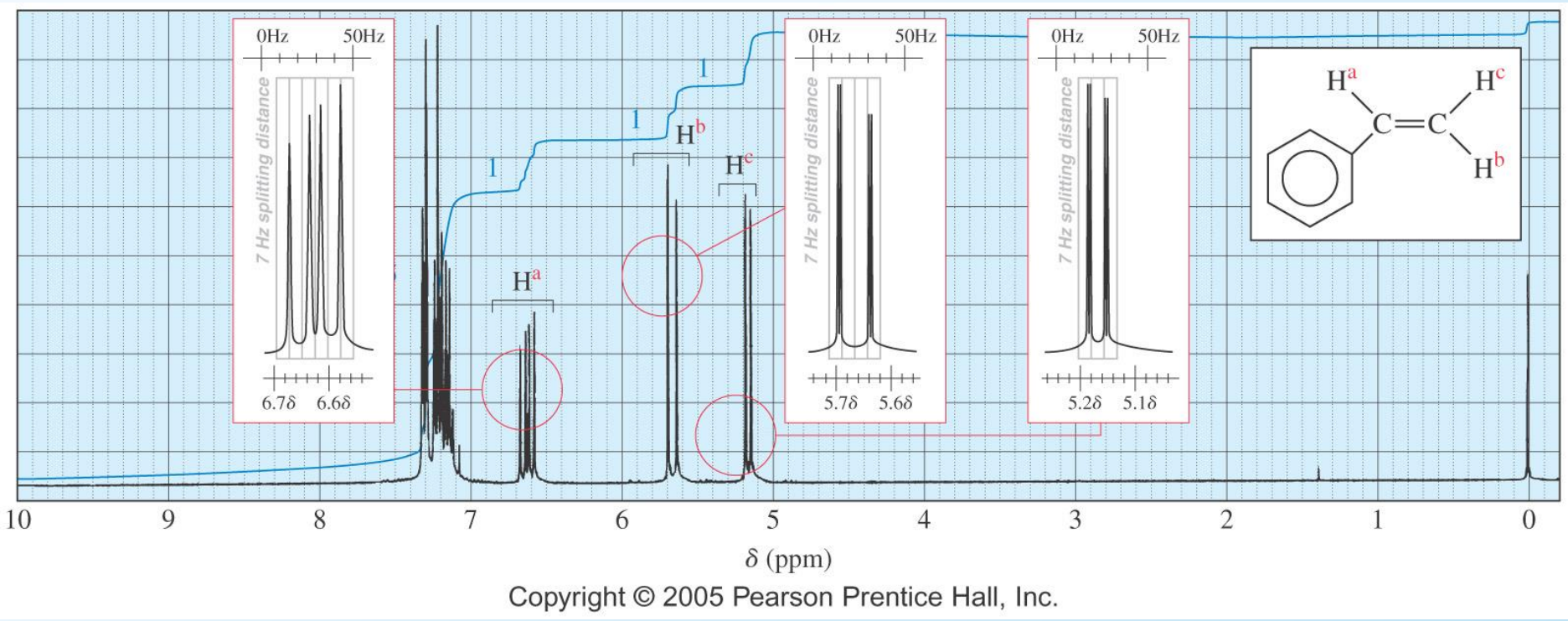


- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).



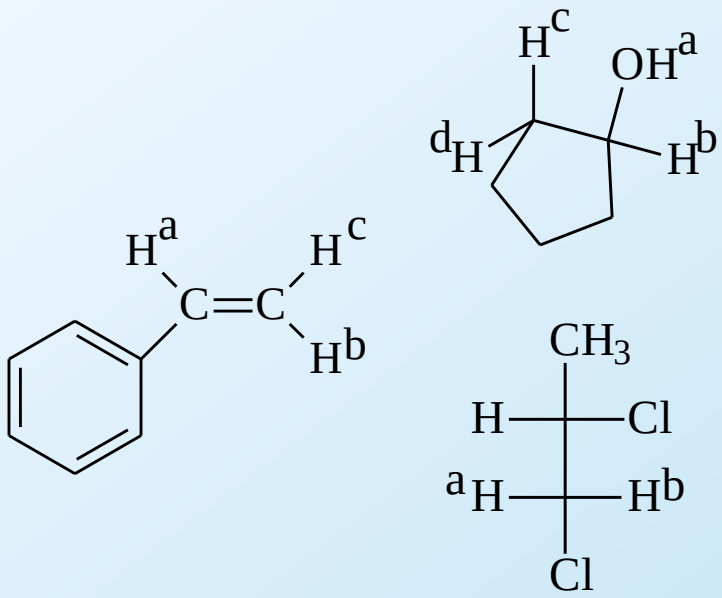


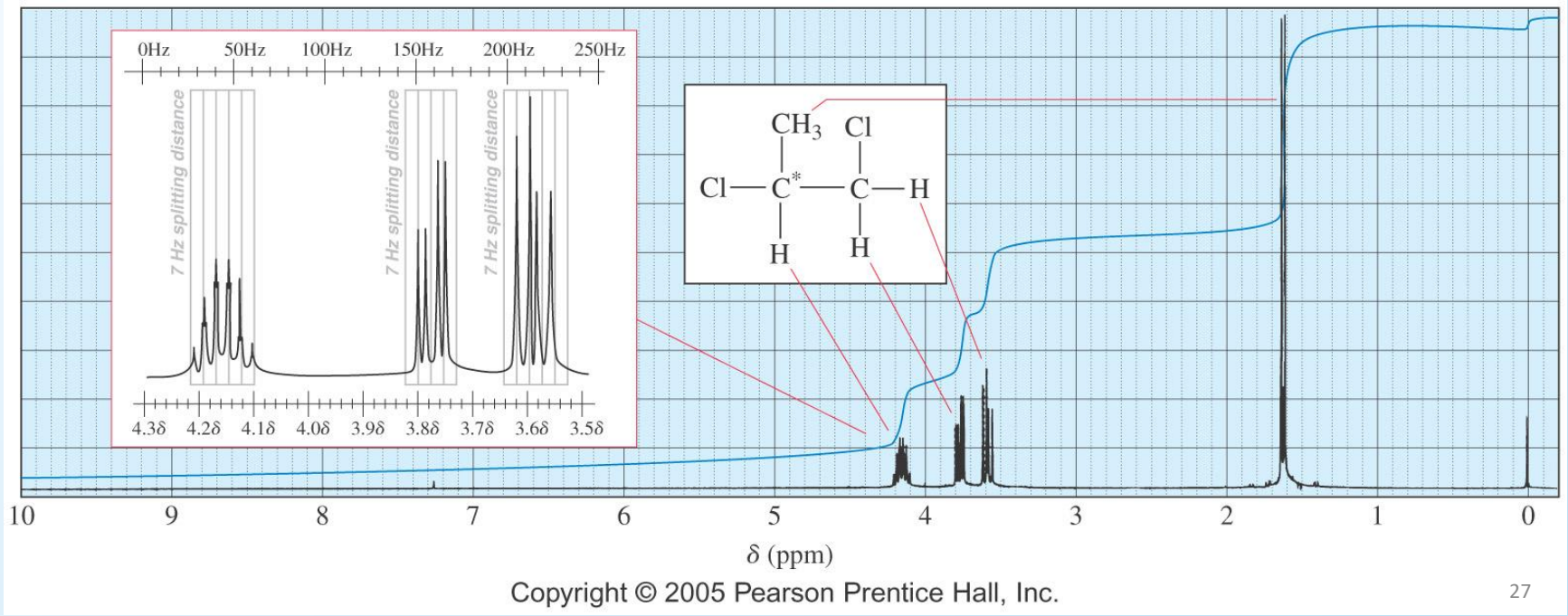
Spectrum for Styrene



Some Nonequivalent Protons

- Usually, two protons on the same C are equivalent and do not split each other.
- If the replacement of each of the protons of a -CH_2 group with an imaginary "Z" gives stereoisomers, then the protons are non-equivalent and will split each other.



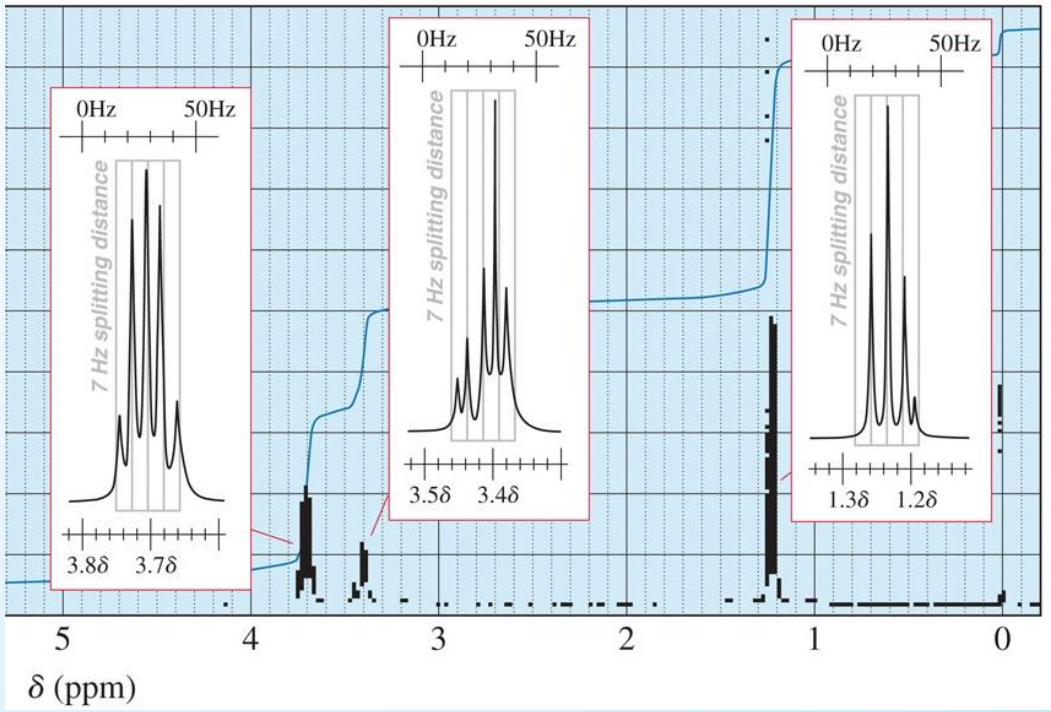


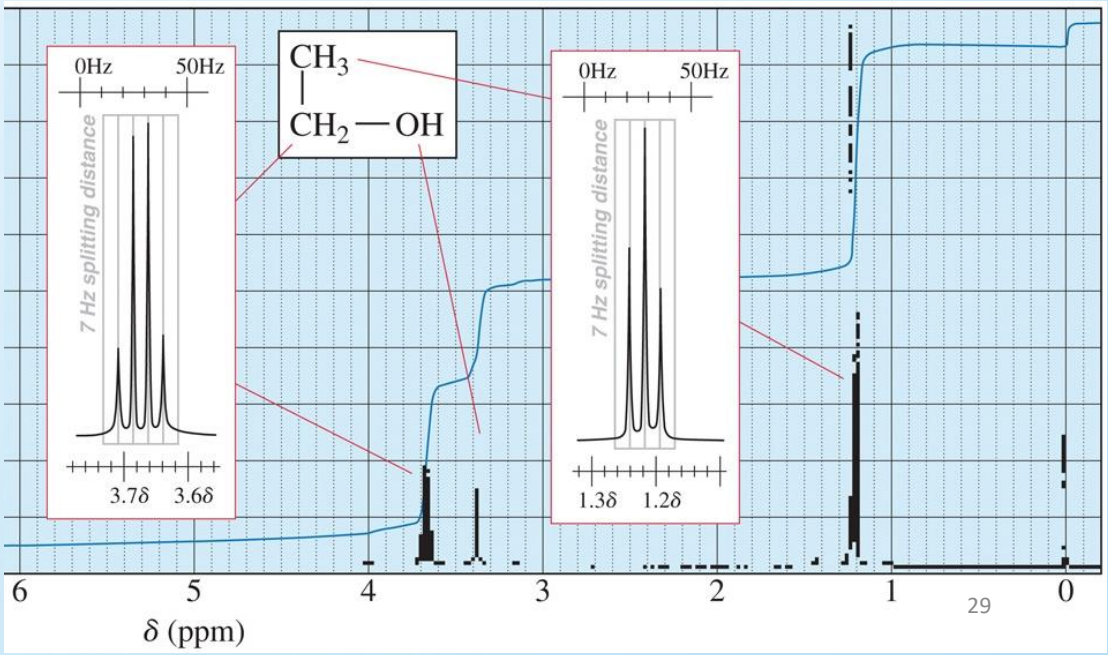
Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.
- Hydrogen bonding in concentrated solutions deshield the protons, so signal is around δ3.5 for N-H and δ4.5 for O-H.
- Proton exchanges between the molecules broaden the peak.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O.
- Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

Hydroxyl Proton

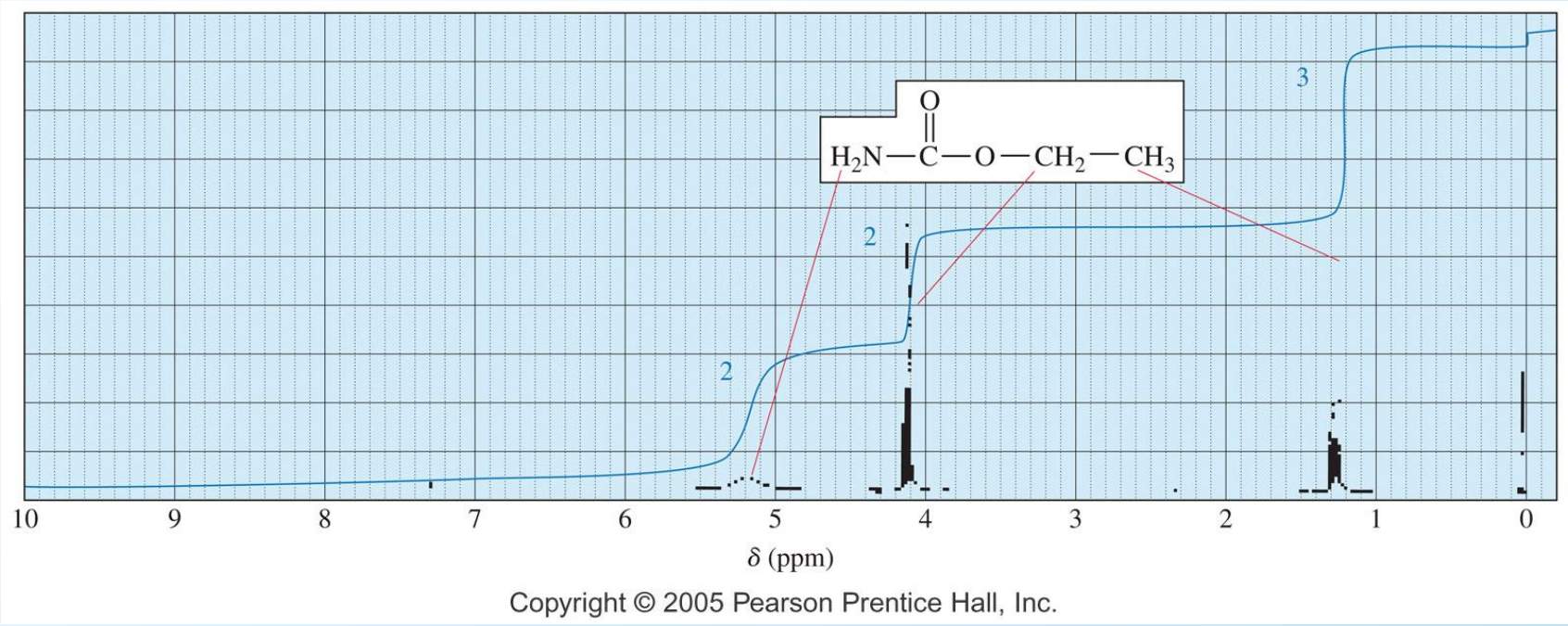
- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.





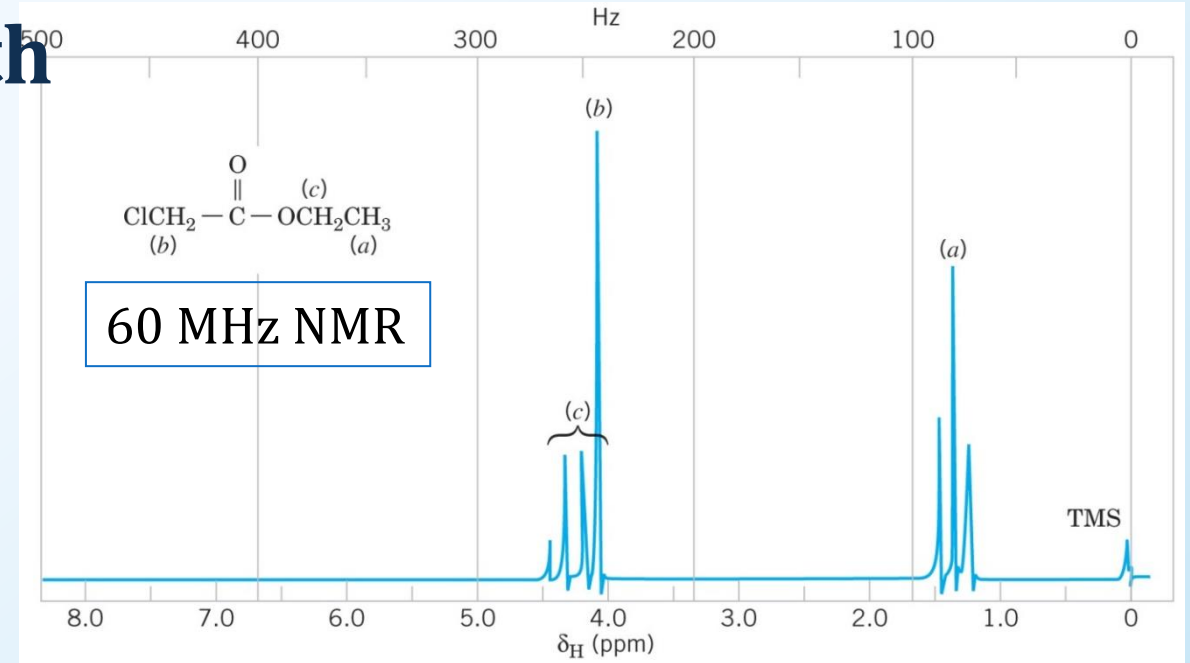
N-H Proton

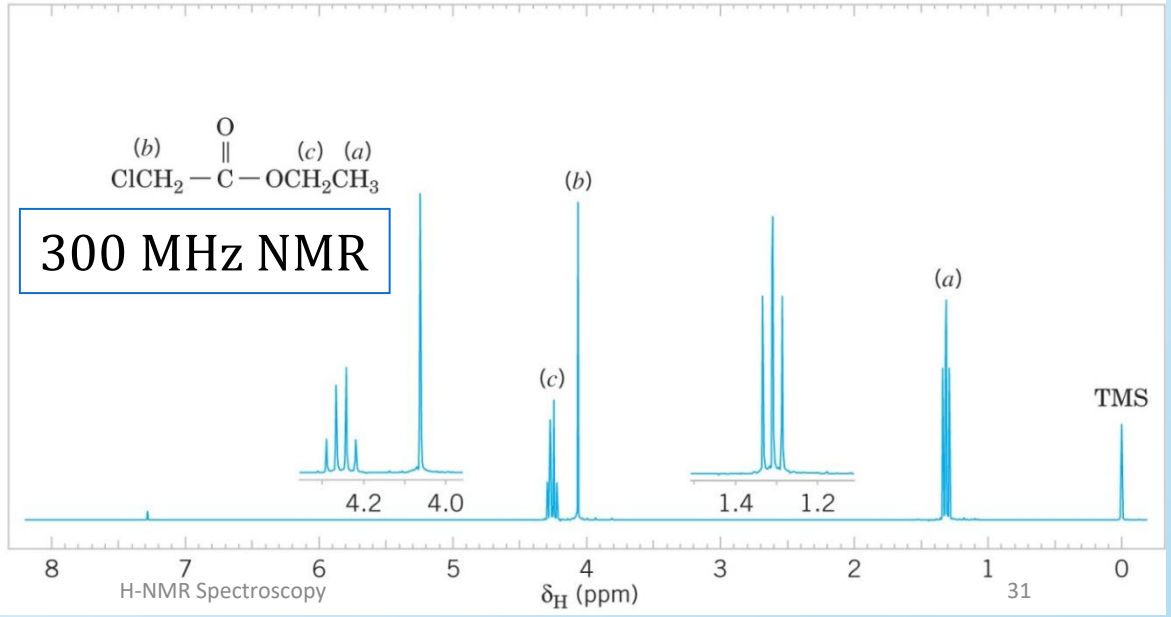
- Moderate rate of exchange with deuterium.
- Peak may be broad due to H-bonding.



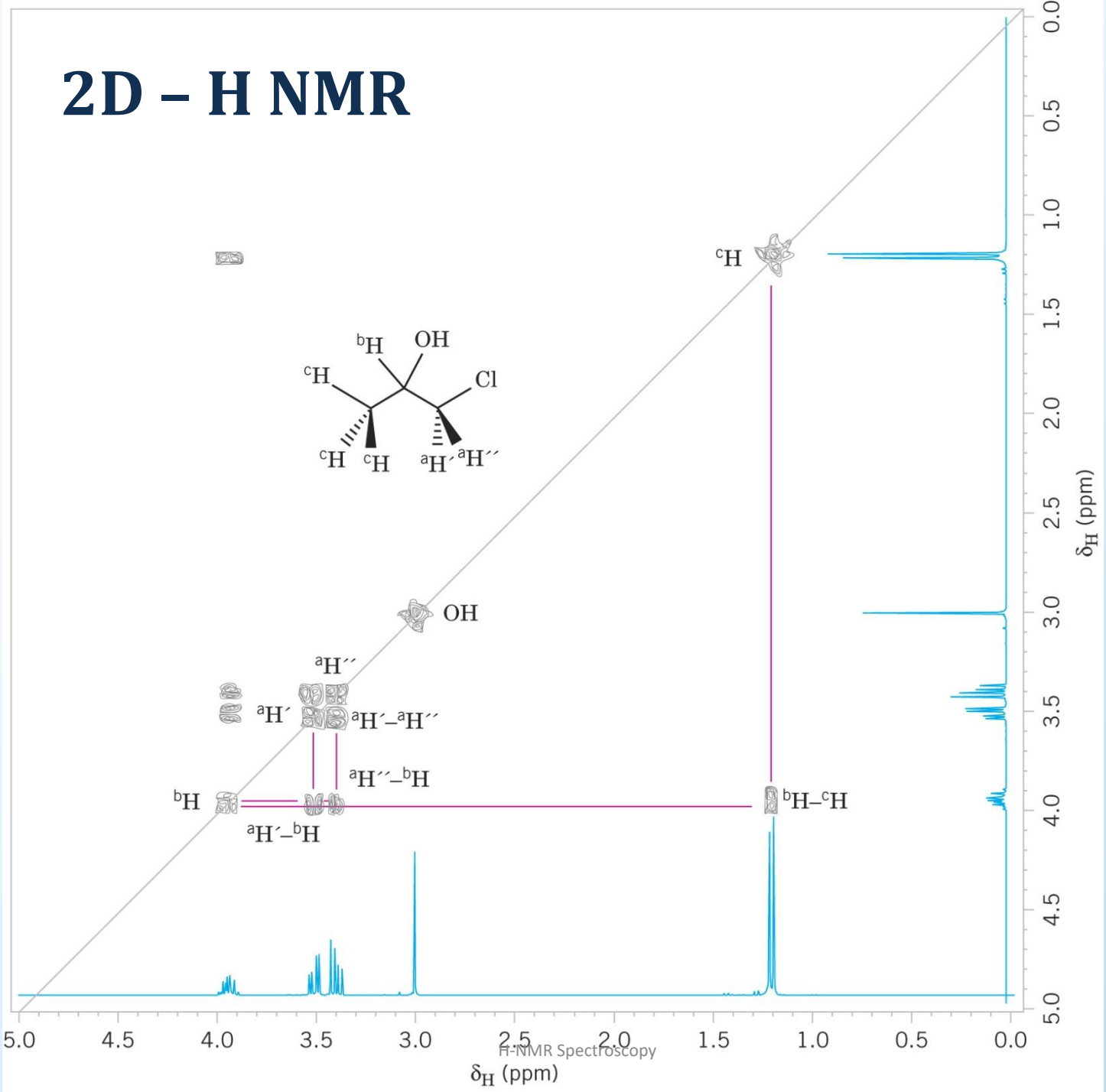
Magnetic Strength and Frequency

- Higher frequency of instrument can give a clearer resolution of peaks.
- Usually when the frequency is higher, the magnet is also stronger, which causes the protons to spin farther in energy from each other.



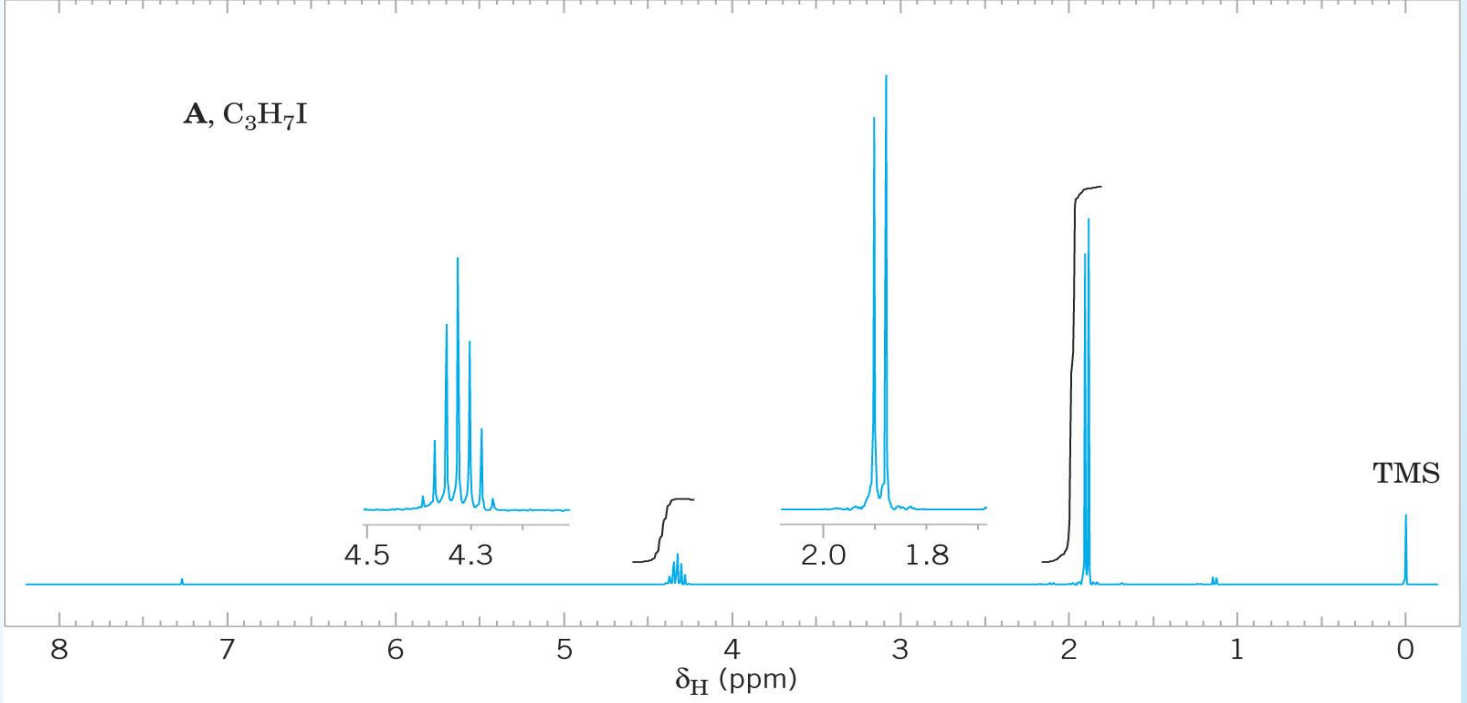


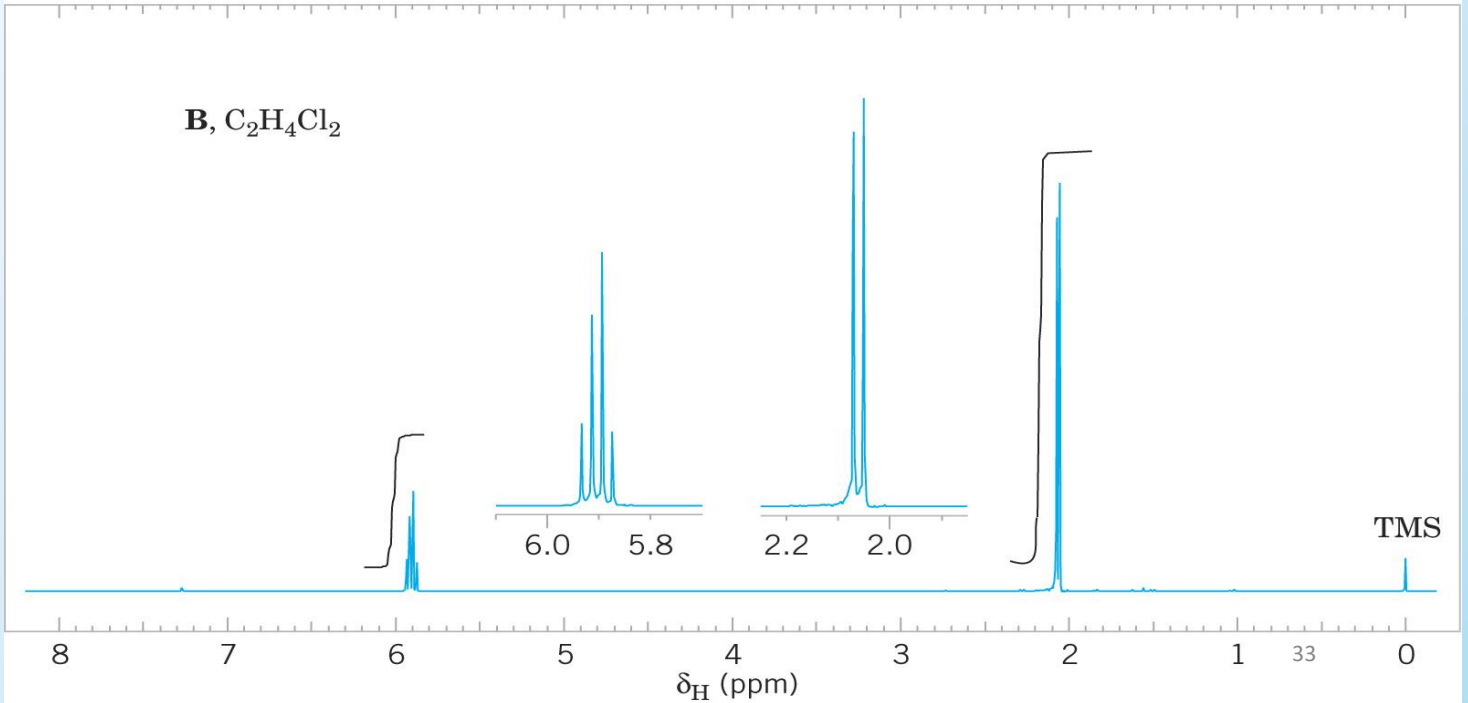
2D – H NMR


bH
OH
cH
Cl
cH
cH
aH´aH´´
cH
OH
aH´´
aH´
aH´–aH´´
aH´´–bH
bH
aH´–bH
bH–cH
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δH (ppm)

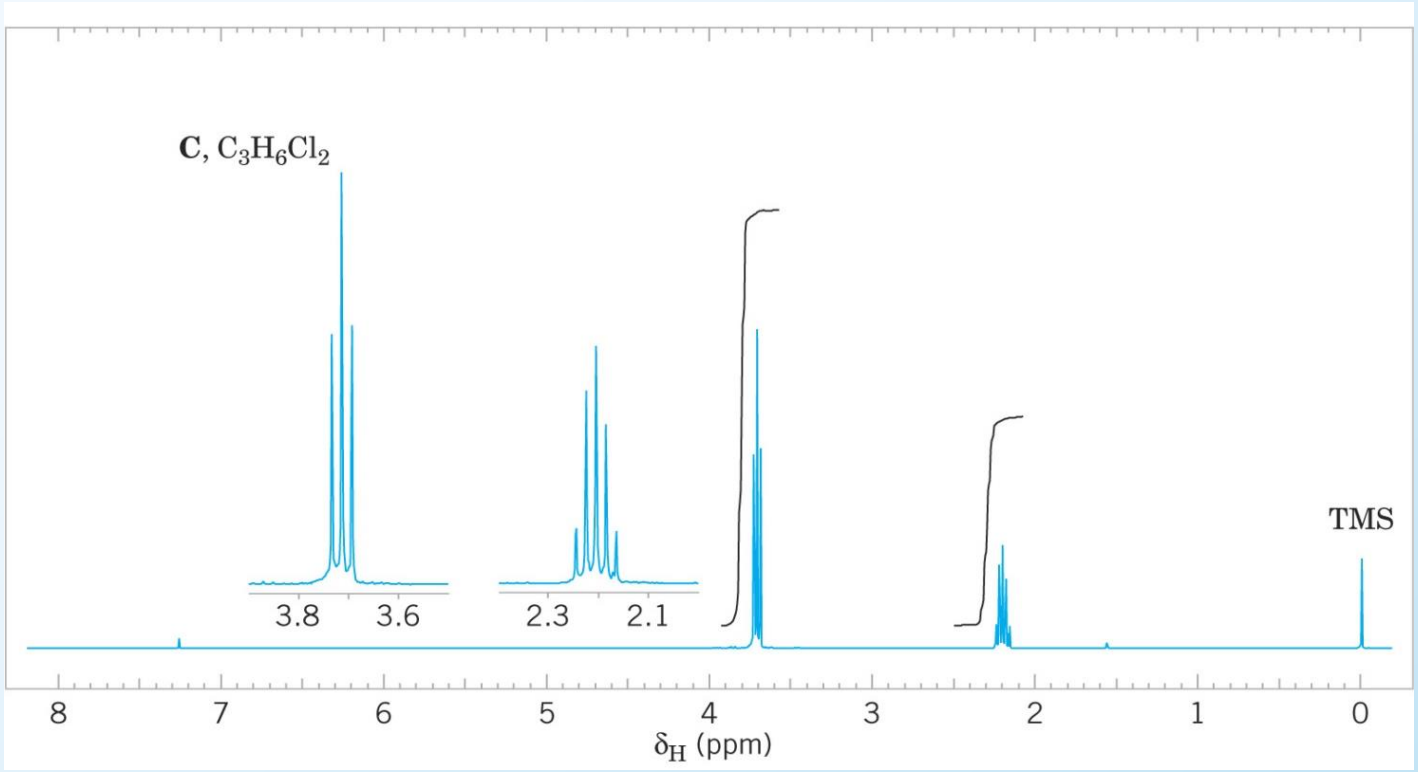
Problem

Determine the structures for the following H-NMR given the molecular formula.



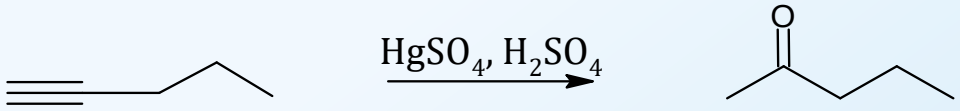


Problem



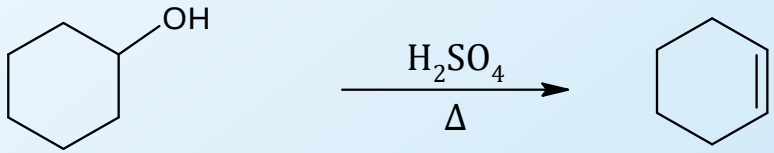
Worked Example: What changes in NMR will you see in the following reaction?

a



There will be 5 peaks in the alkyne and four in the ketone. The alkyne proton at 2.5 ppm will disappear.

b



OH peak around 3-5 ppm will disappear with only alkyl peaks remaining.

Key Concepts

- Chemical shifts
- Integration
- Coupling
- Interpret a NMR
- Predict NMR for a compound