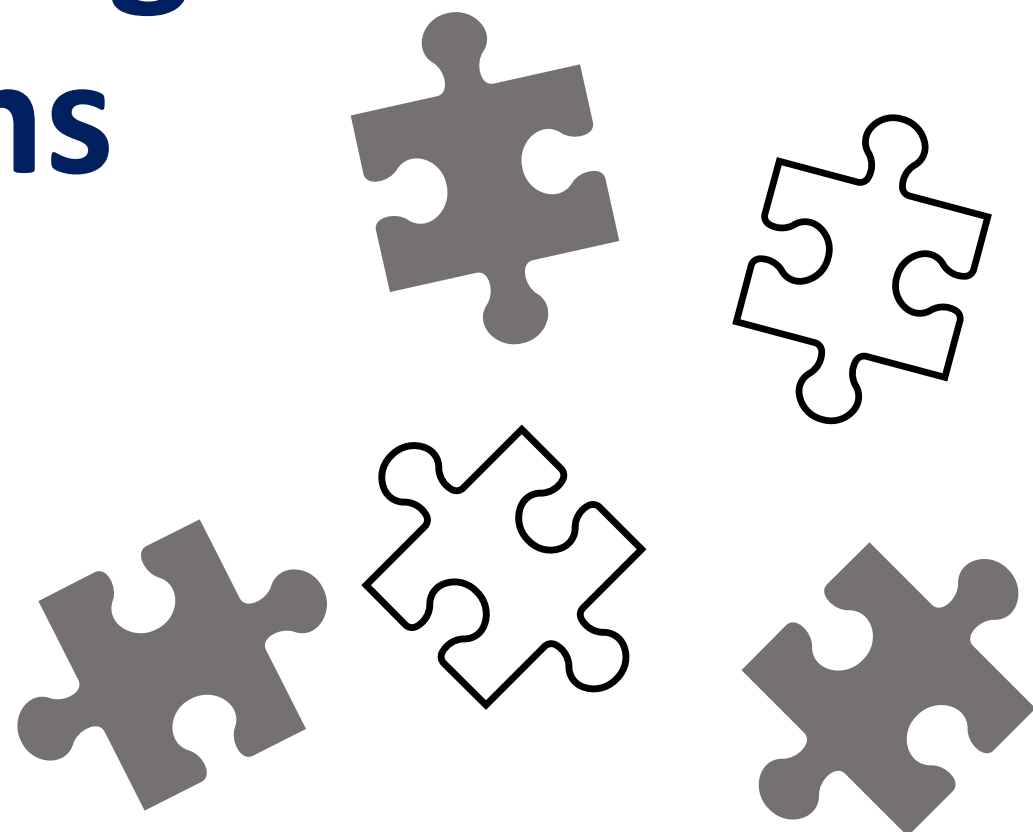
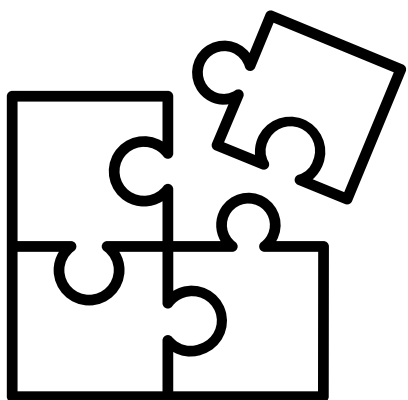
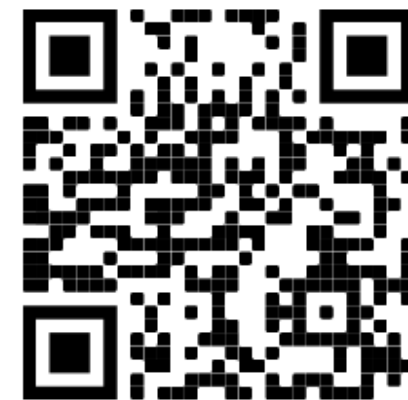


Putting the Puzzle Pieces Together: A Systematic Approach to Solving ^1H NMR Problems

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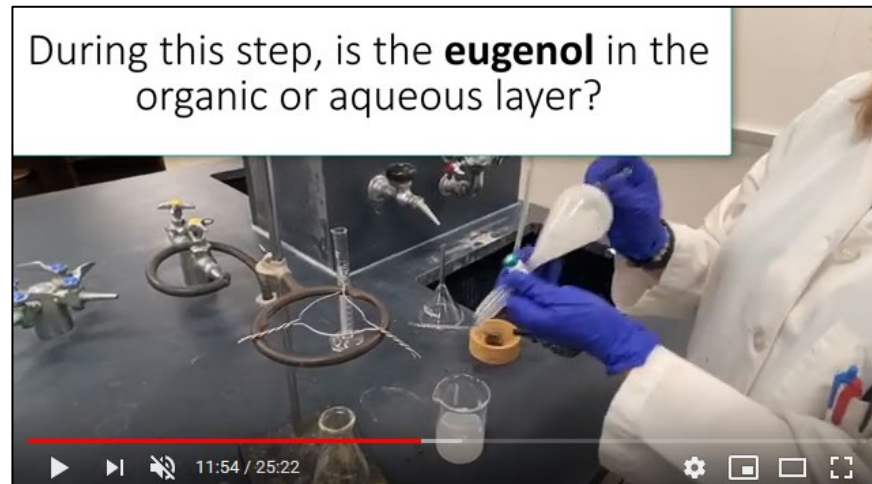


Resources for Organic Chemistry

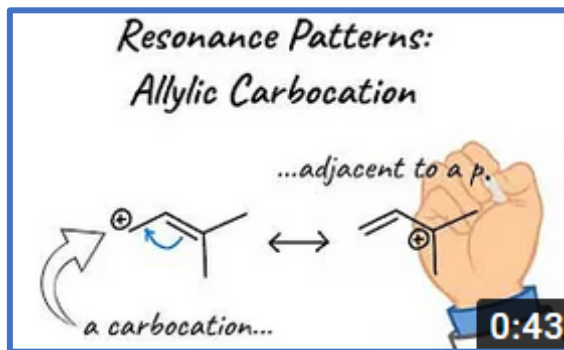
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Clicker Questions, Worksheets,
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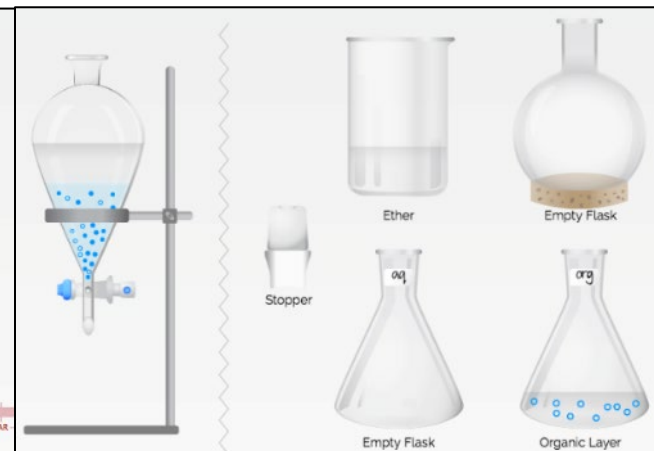
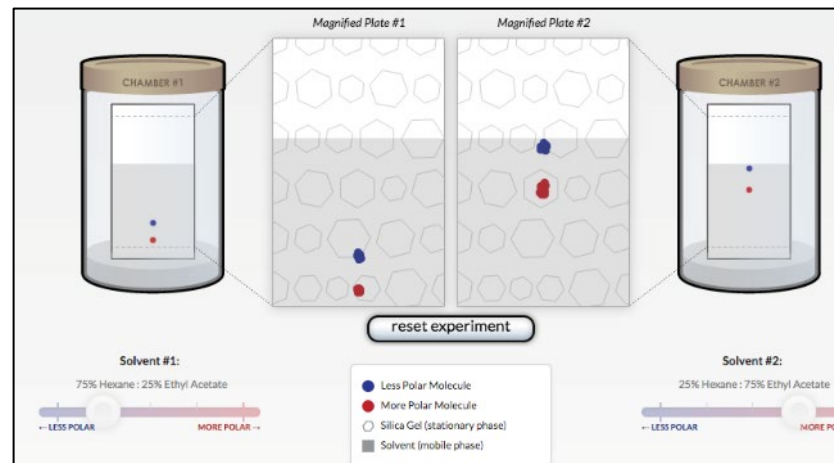
<https://chemistryconnected.com/local>



“Inquisitive” lab demos
eugenol video has almost
15,000 views since March 2020



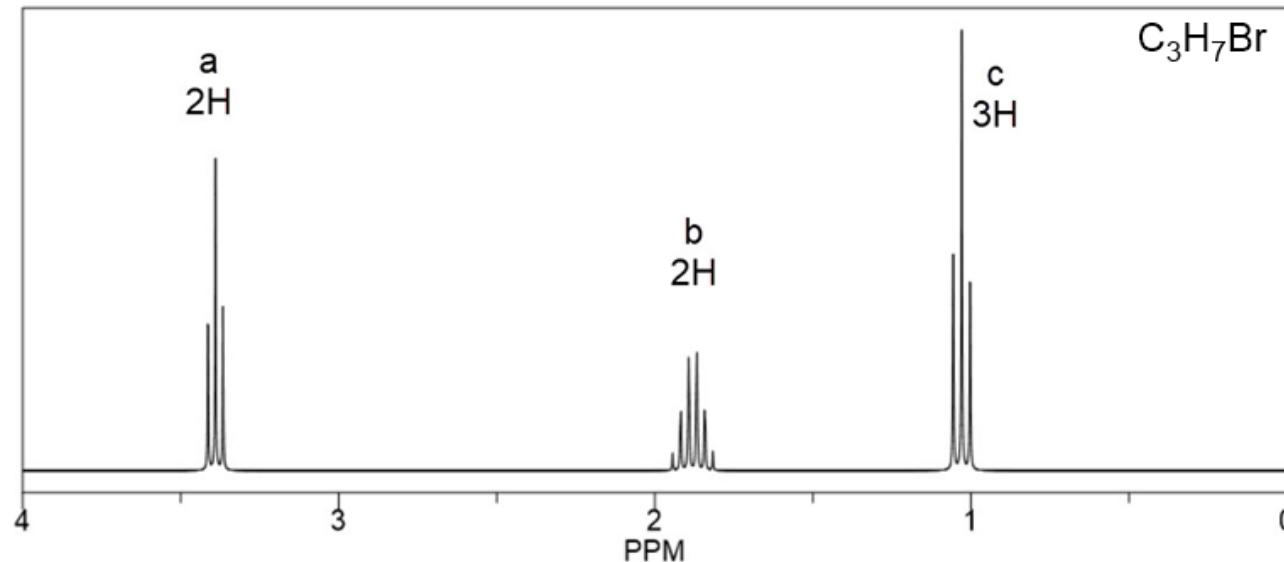
Animations
TLC &
Extraction



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The Challenge of ^1H NMR? **T.M.I.**

- 1) **# of signals** indicates the number of different types of hydrogens (chemical equivalence).
- 2) **Integration** or peak area indicates how many hydrogens are in each signal. It is given as a ratio.
- 3) **Chemical shifts** are given as δ (delta) values, in ppm. The chemical shift indicates the electronic environment of the hydrogens (electron-rich/shielded or electron-poor/deshielded).
- 4) **Splitting patterns** indicate the # of neighboring hydrogens. The magnitude of the coupling constants (given as J values) depend on the spatial relationship (dihedral angle) of the two H atoms.

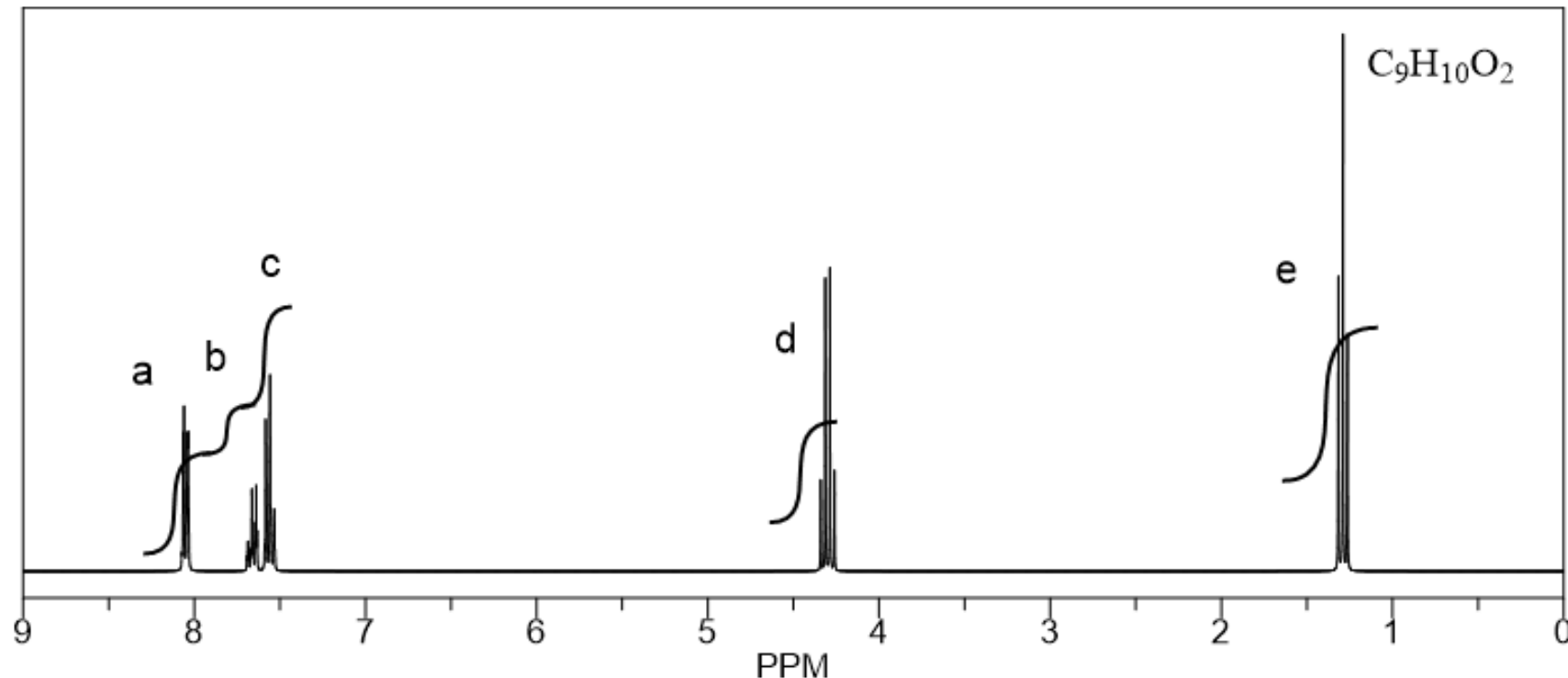


Solution: Applying a Systematic Approach

^1H NMR Problem-Solving Strategies

Dr. Laurie S. Starkey, Cal Poly Pomona

The goal of solving a ^1H NMR spectrum is to determine the structure that is consistent with ALL given data. Since the NMR provides a lot of information, we must develop a systematic approach. First, we determine what pieces are present. Next, we figure out how those pieces fit together. Finally, we confirm that our structure matches the spectral data given. Be sure to label every proton a/b/c/etc. to match NMR peaks a/b/c.



Step 1: Identify Functional Groups in IR

1) If given an IR spectrum, what functional groups (FG) are present? These are pieces to your puzzle. e.g.

~1700 cm^{-1} strong absorption indicates a carbonyl (C=O stretch)

~3300 cm^{-1} broad signal indicates an alcohol (O—H stretch)

absorptions *just above* $>3000 \text{ cm}^{-1}$ indicate $\text{sp}^2 \text{ C—H}$, and *just below* $<3000 \text{ cm}^{-1}$ indicate $\text{sp}^3 \text{ C—H}$

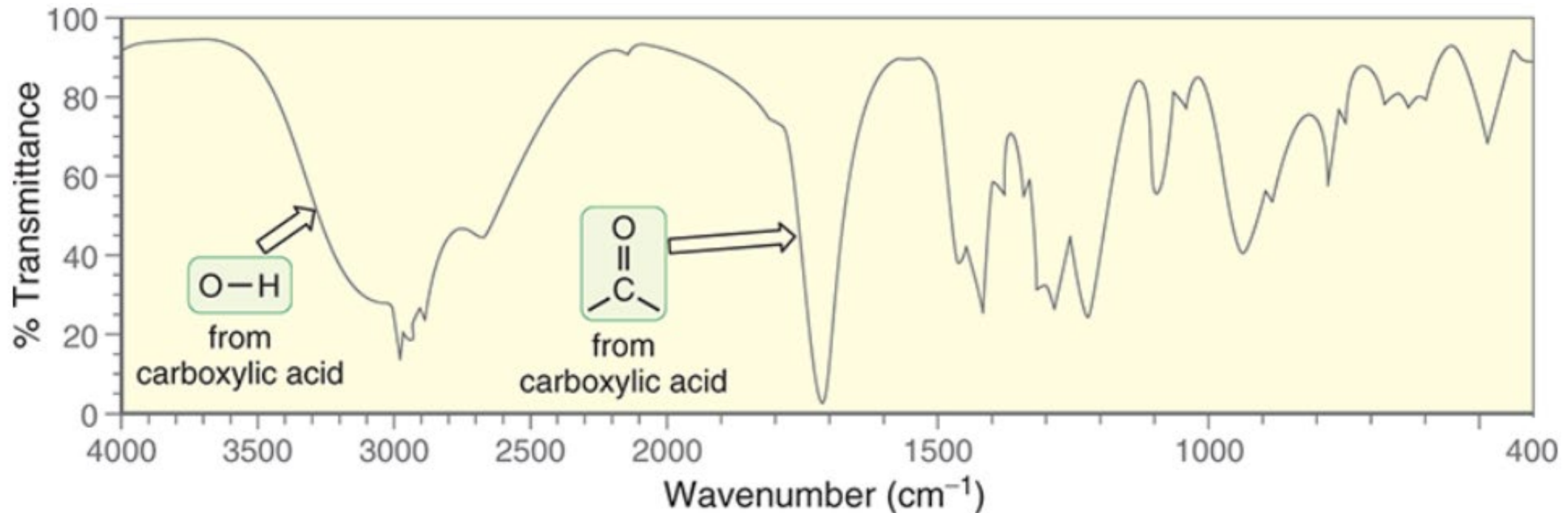


FIGURE 14.18 An IR spectrum of butyric acid.

FYI: Systematic Approach to IR Spectra...

Other peaks to look for:

$\equiv\text{C}-\text{H}$ sp C-H stretch is sharp peak around 3300 (s)

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$ aldehyde C-H stretch appears as two sharp peaks 2900–2800 and 2800–2700 (w)

C=C stretches occur 1680–1630 with variable intensity (v) and will disappear if symmetrical.

C-O stretches occur 1150–1050 and are typically sharp (s)

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$ Carboxylic acids should be obvious because the H-bonded dimer has a HUGE O-H stretch (3400–2400) that overlaps with the C-H stretch bands. Acids will also have a C=O stretch (1725–1700) and a C-O stretch (1320–1210).

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \end{array}$ Since esters have two C-O bonds, they typically have two C-O stretches. Together with the C=O stretch, it's known as the "rule of 3" (~1700, 1200, 1100).

alkene C-H bend	1000–700	} gives excellent information on substitution patterns (o,m,p, etc)
benzene C-H bend	850–700 (+ overtone 2000–1700)	

C=N is not a common FG and C-N stretches are typically not useful.

DO NOT try to interpret every little peak in the spectrum but **DO** recognize which ones are significant and are giving you clues to the sample's structure. It takes practice!

Step 2: Identify Degrees of Unsaturation

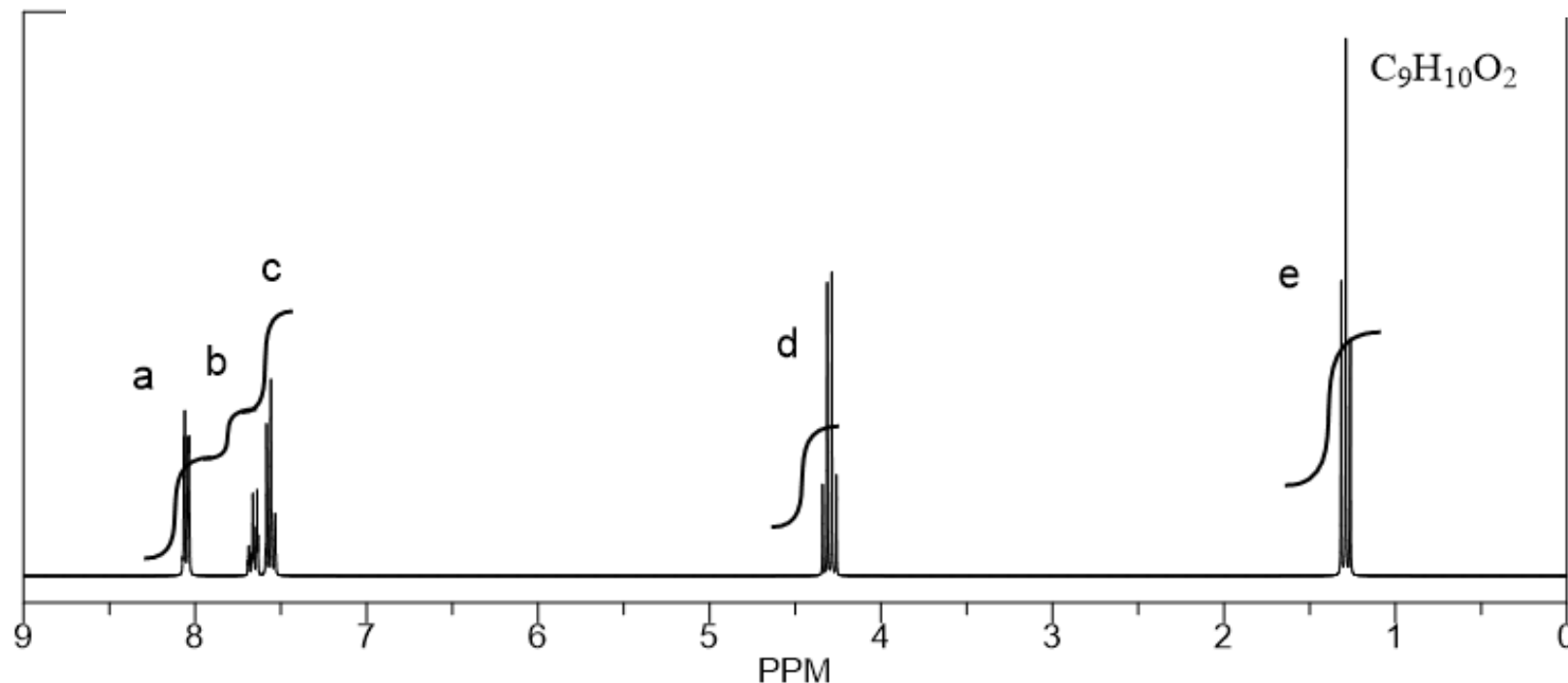
2) If given molecular formula: **check for sites/degrees of unsaturation (DU).**

If saturated, maximum # of H's = $C_nH_{2n+2+\#N}$

every 2 missing H's = 1 DU

each DU = a π bond or a ring

4 DU = a possible benzene ring (3 π bonds, plus 1 ring)



Formula $\text{C}_9\text{H}_{10}\text{O}_2$

If saturated: C_9H_{20}

Compare: C_9H_{10}

➔ 10 missing H's

➔ 5 DU

Step 3: Peak Integration = Puzzle Pieces

Using the peak integration, determine the pieces of your molecule. *Ignore δ value for now, unless ~ 7 ppm!*

3H signal = $-\text{CH}_3$

2H signal = $-\text{CH}_2-$

1H signal = CH or OH or NH (Note: OH and NH typically appear as broad singlets)

6H signal = two equivalent $-\text{CH}_3$ groups

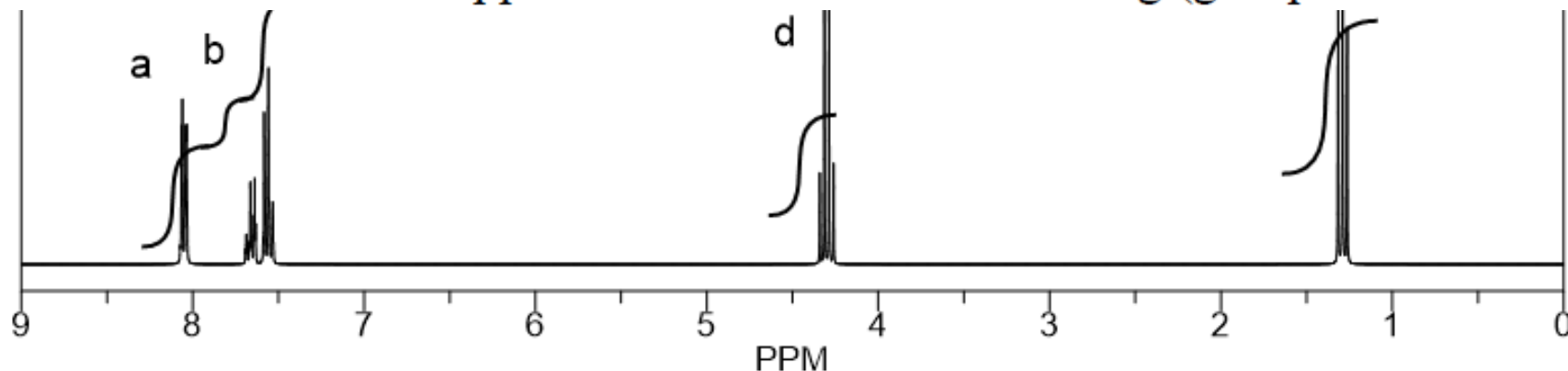
4H signal = two CH_2 's or a $\text{CH}_3 + \text{CH}$ (overlapping signals are possible!)

peaks around 7 ppm = aromatic H's (indicates presence of a benzene ring)

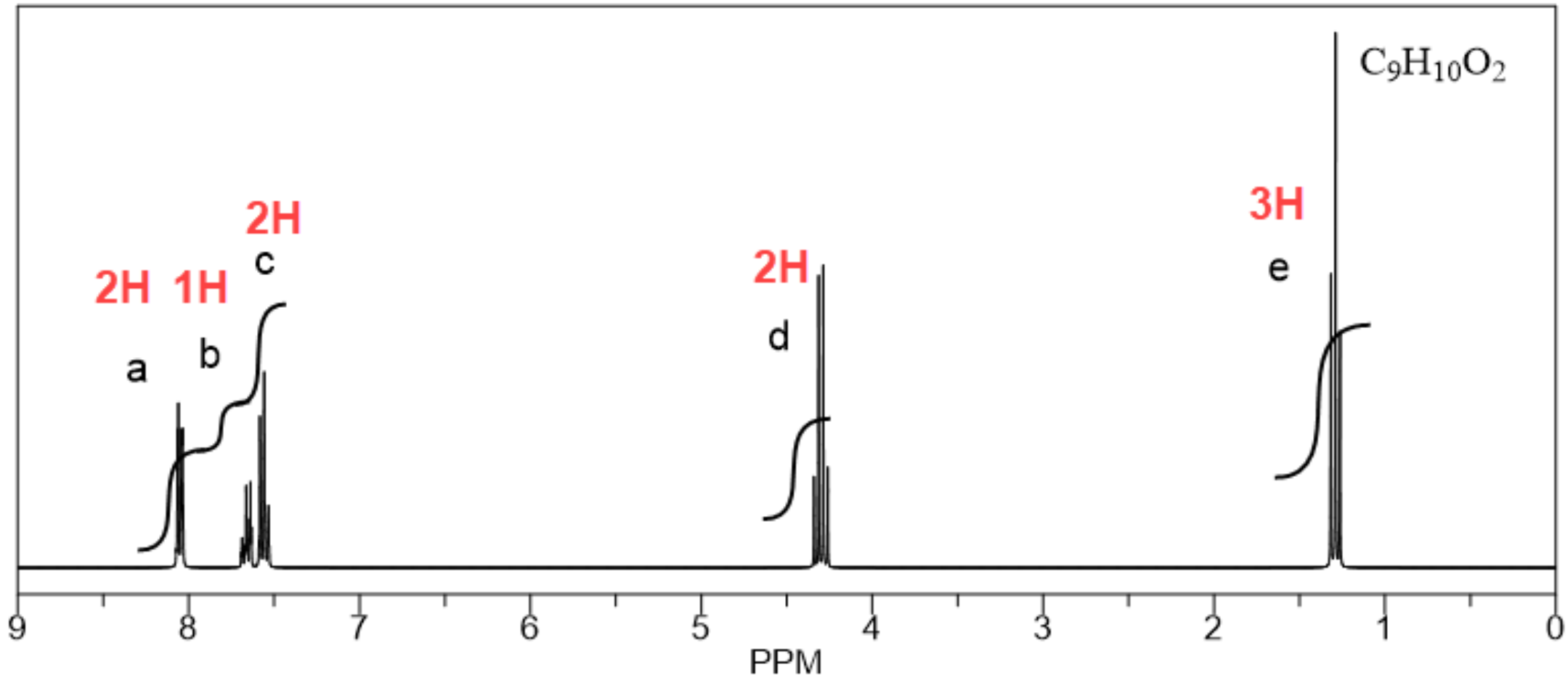
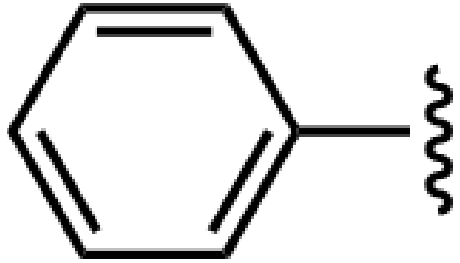
may be grouped closely together (as a singlet or multiplet) or may be several signals in the region:

a total of 5 H's around 7 ppm = monosubstituted benzene ring

a total of 4 H's around 7 ppm = disubstituted benzene ring (groups can be *ortho*, *meta* or *para*)



Step 3: Peak Integration = Puzzle Pieces

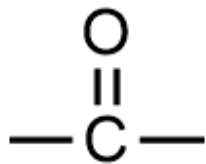
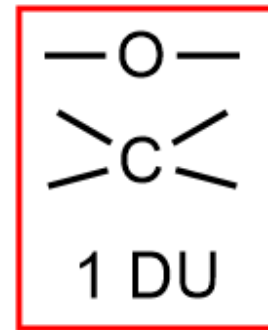
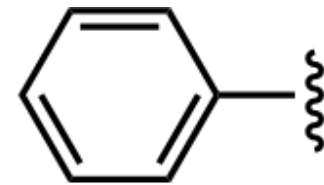
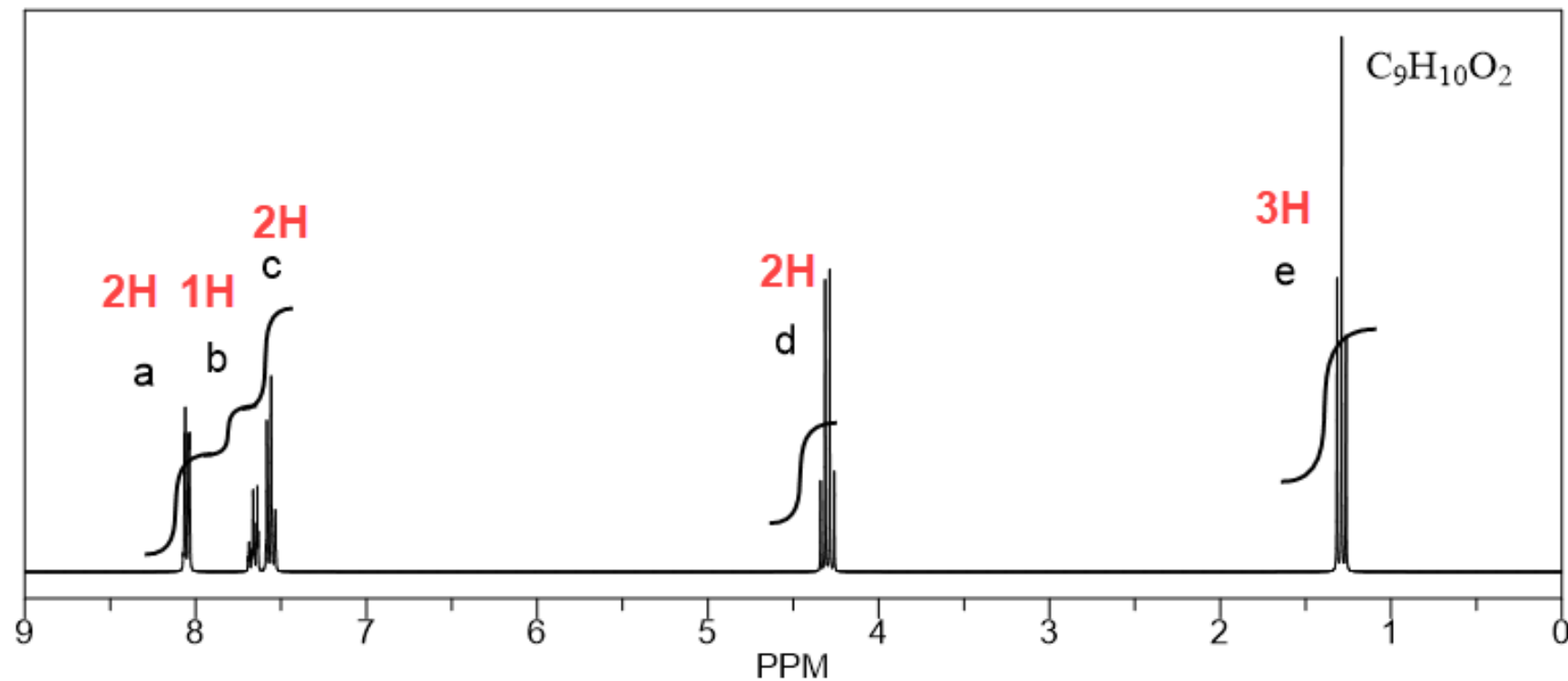


Step 4: Confirm pieces ✓ formula ✓ DU ✓ IR

Do you have all your pieces? “Add up” your pieces and compare to your molecular formula.

have you accounted for the calculated DU?

have you accounted for the functional groups in the IR?



Step 5: Assemble pieces (start with $-\text{CH}_3$)

Put the pieces together! Start with an end piece, such as a methyl ($-\text{CH}_3$).

consider chemical shift (refer to a provided table <https://www.chemistryconnected.com/NMR>)

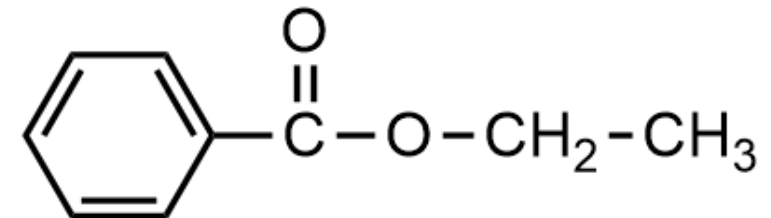
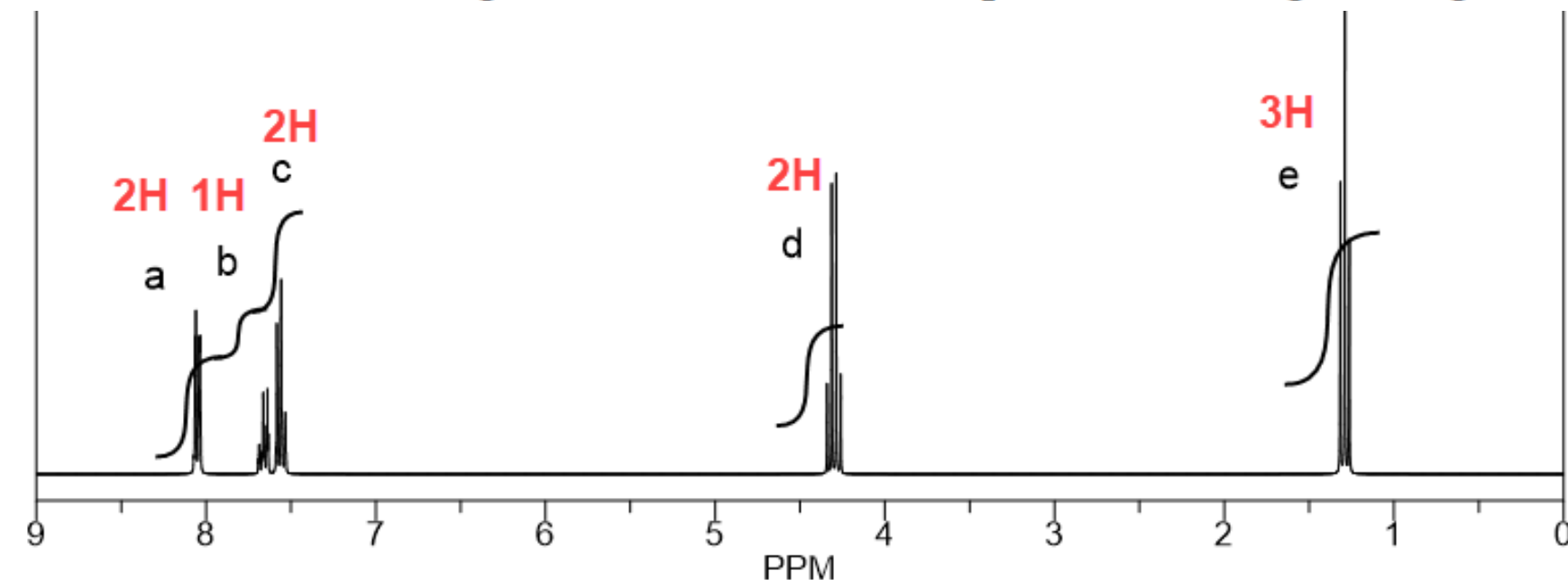
is it next to an oxygen? (~ 3.8 ppm)

is it next to a $\text{C}=\text{O}$ or a benzene ring? (~ 2.2 ppm)

consider splitting patterns ($n+1$ rule, where $n = \#$ of nonequivalent neighbors)

is it a triplet? It might be attached to a CH_2 (2 neighbors \rightarrow 3 peaks)

is it a singlet? There must be no protons on neighboring carbon atoms (0 neighbors \rightarrow 1 peak).

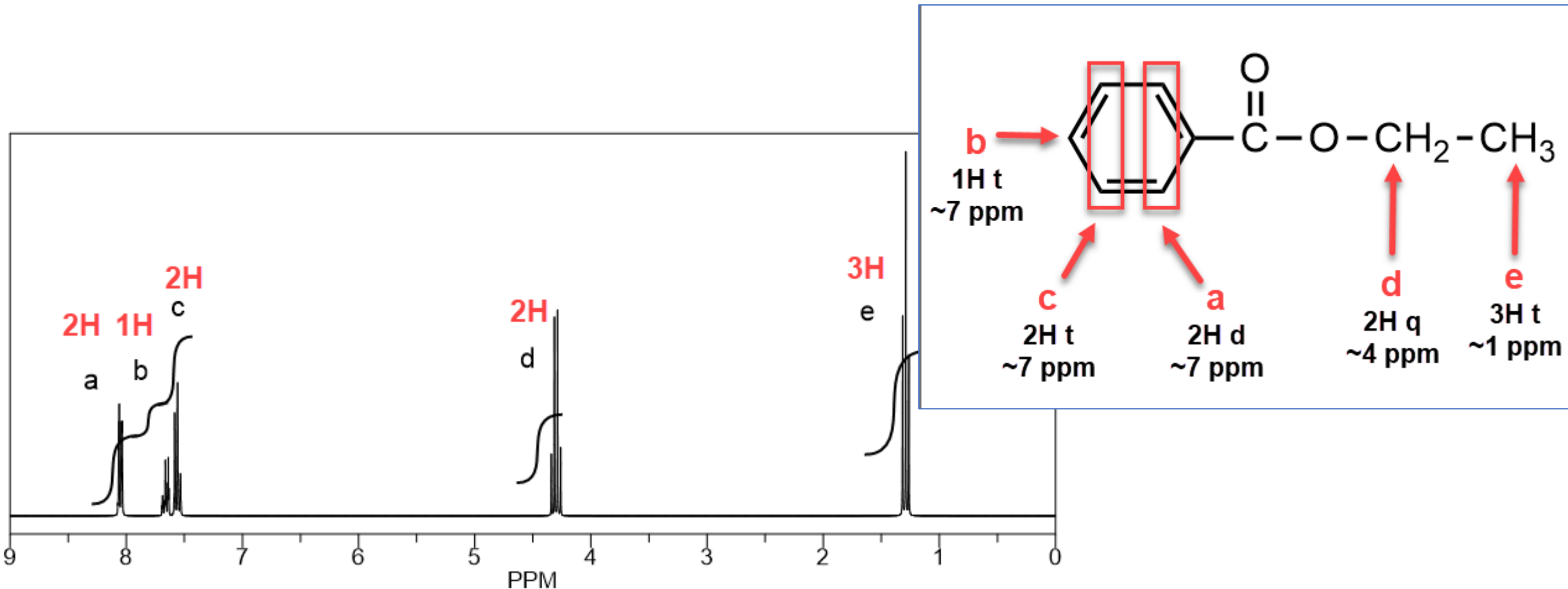


Step 6: Assemble pieces (start with $-\text{CH}_3$)

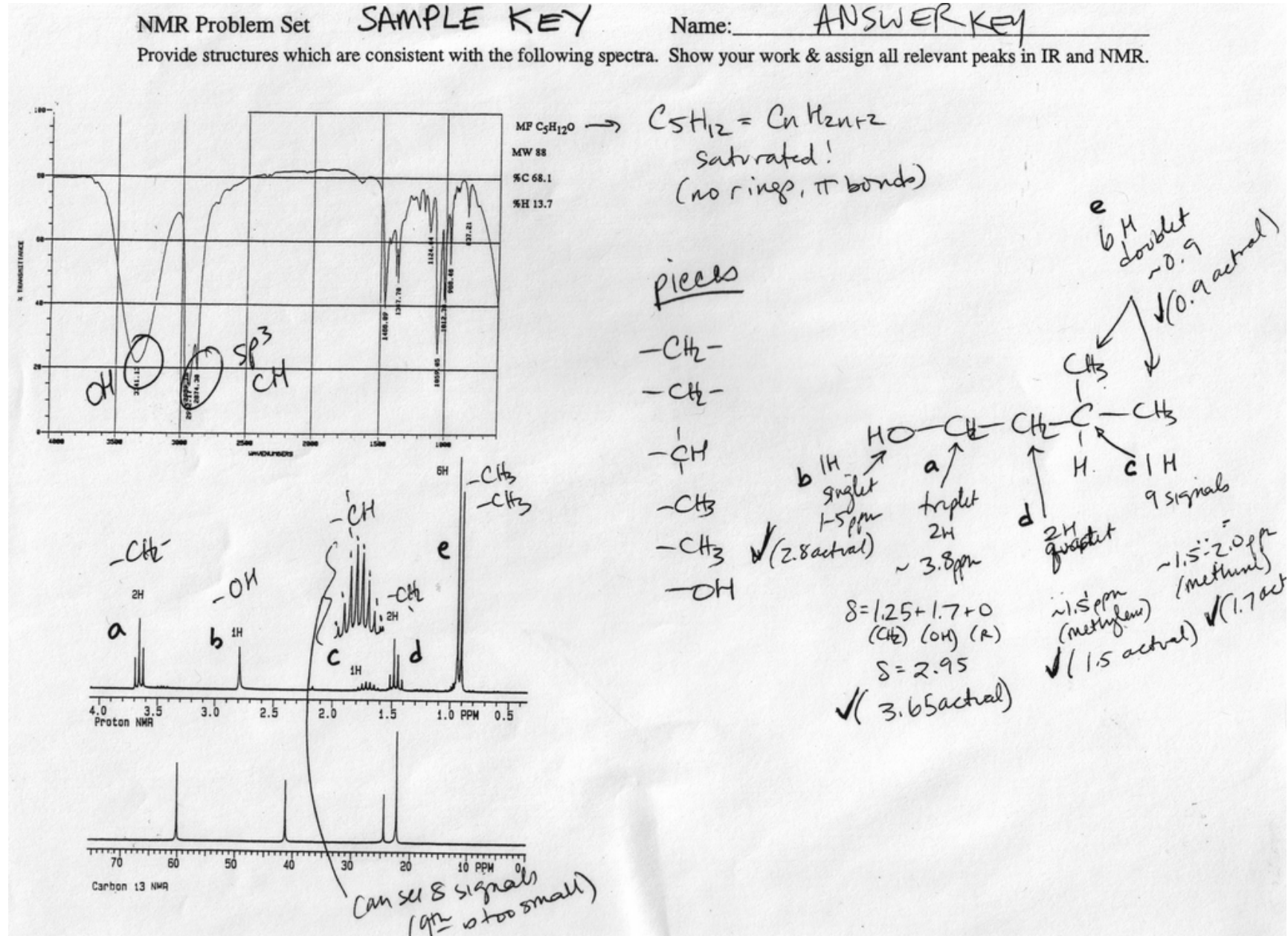
Check your answer! Final structure must match molecular formula, and IR and NMR spectra.

Look for symmetry...how many peaks should be in the NMR? What would integration be for each?

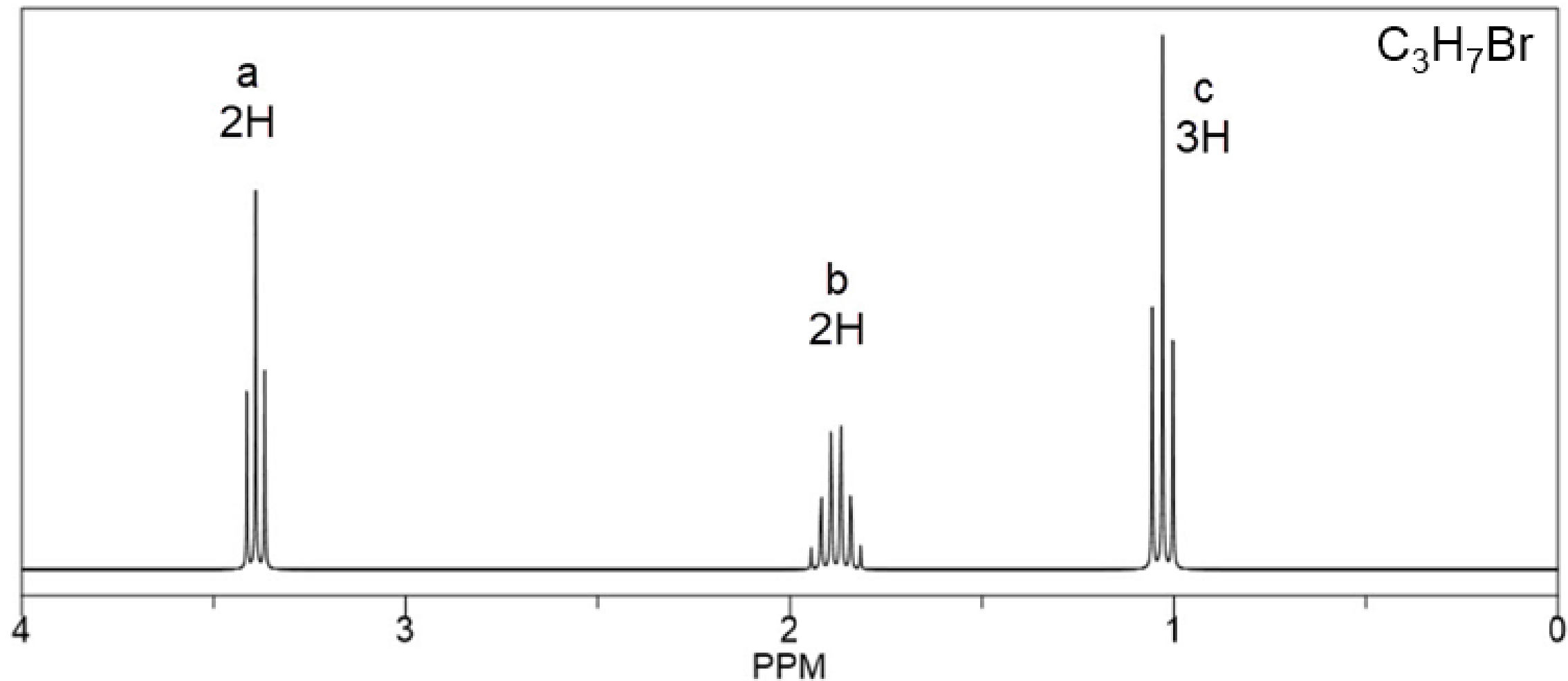
Calculate/estimate chemical shifts, predict splitting patterns, compare to NMR spectrum, label H's a/b/c.



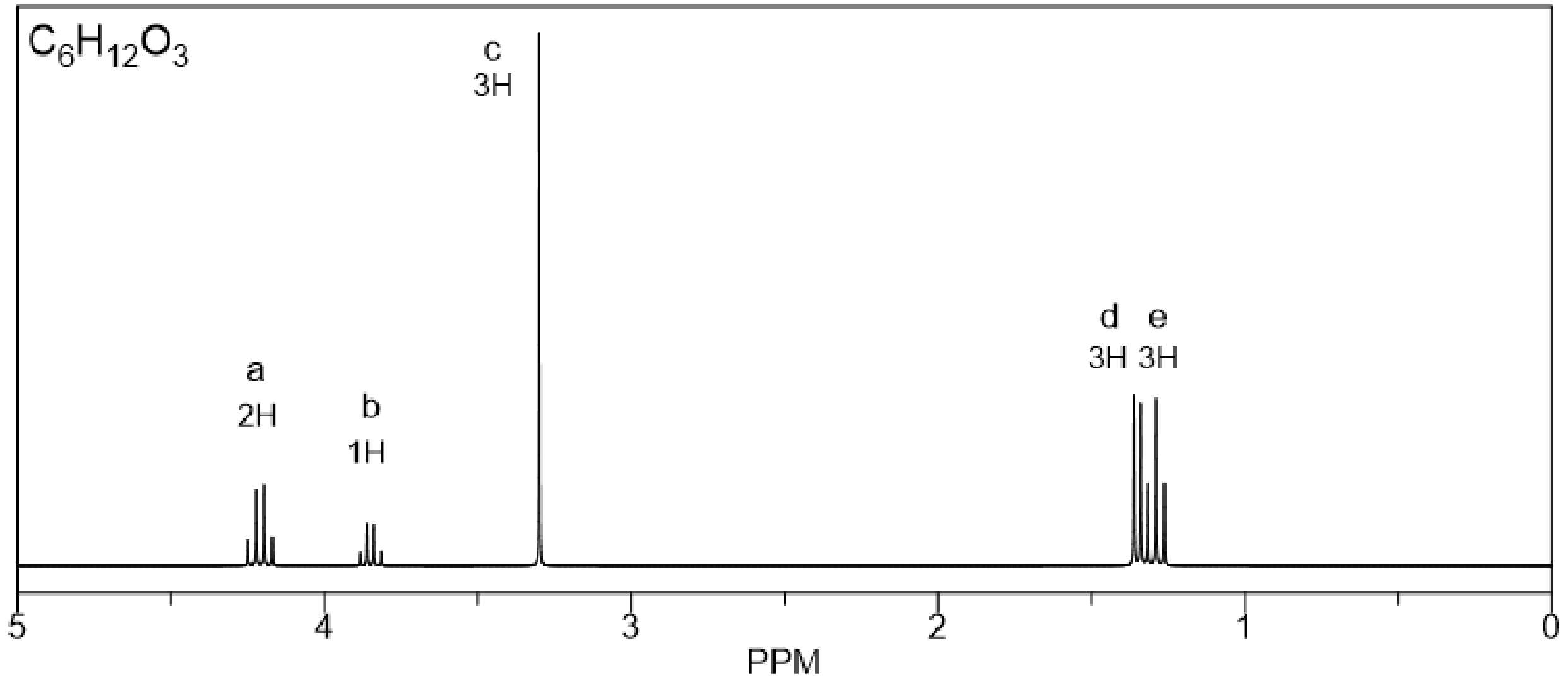
Work through lots of examples together...



Quickly interpret simple spectra...



...and efficiently solve challenging spectra!





Thank you!
Any Questions?

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