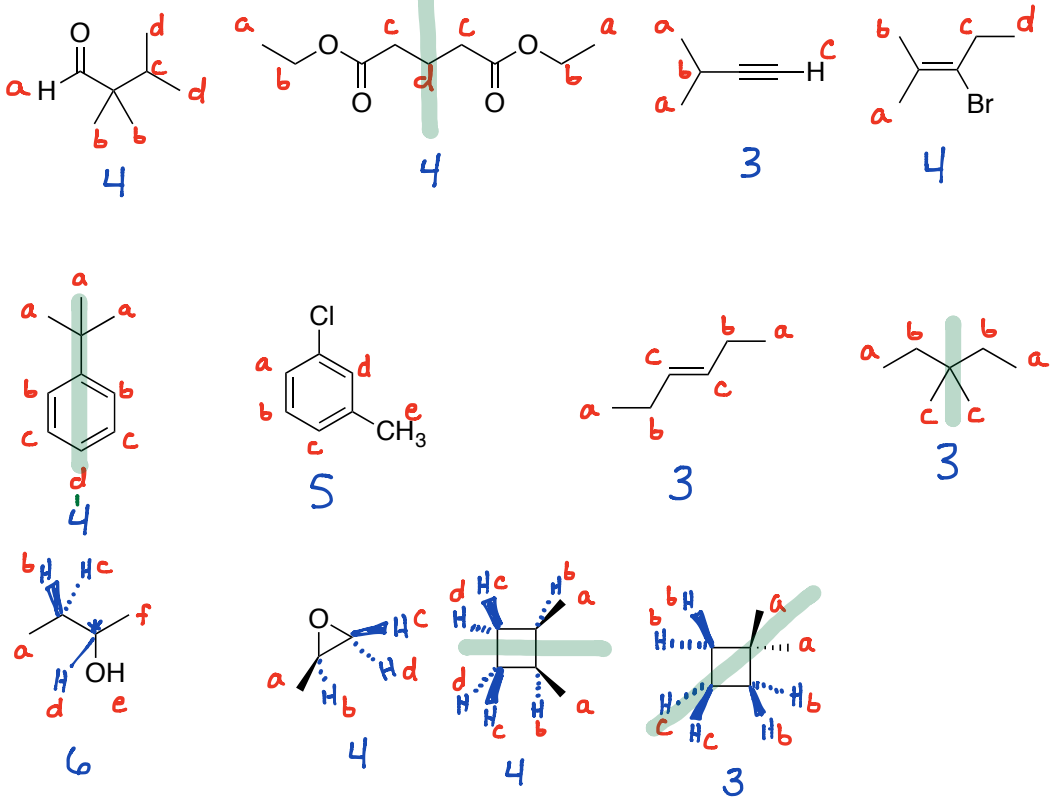
# Answer Key

**Chemistry 233**

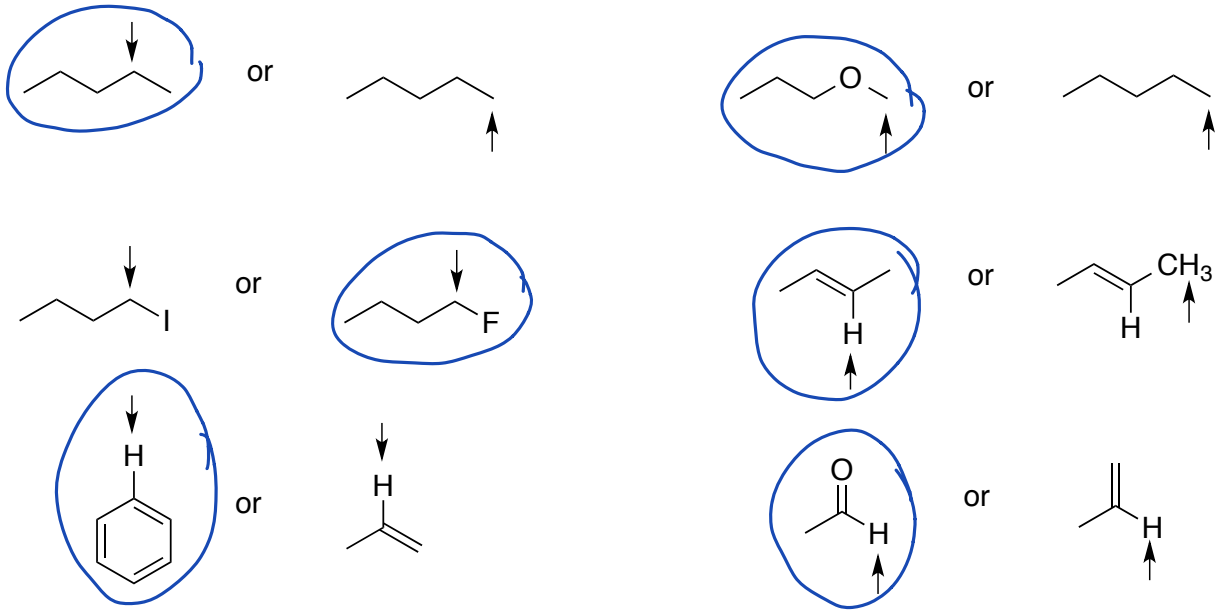
**Chapter 13: NMR Spectroscopy Problem Set**

1) For each compound below, identify each chemically distinct type of hydrogen. Specify the number of $^1$H NMR signals you would expect to see.

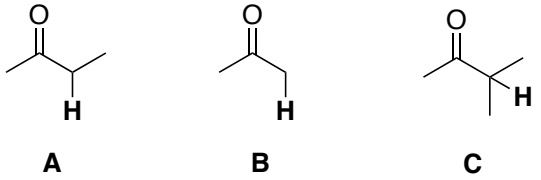



2) Which of the indicated protons in each pair shows up farther downfield?

**Tips:** For H-C-Z, H moves further downfield as Z becomes more electronegative
For $C_{sp^3}$-H, H moves further downfield as C becomes more substituted (3°>2°>1°)



3) Consider the indicated protons in each of the three compounds below. Arrange in order of increasing chemical shift of the indicated proton. *See tips in Q2.*

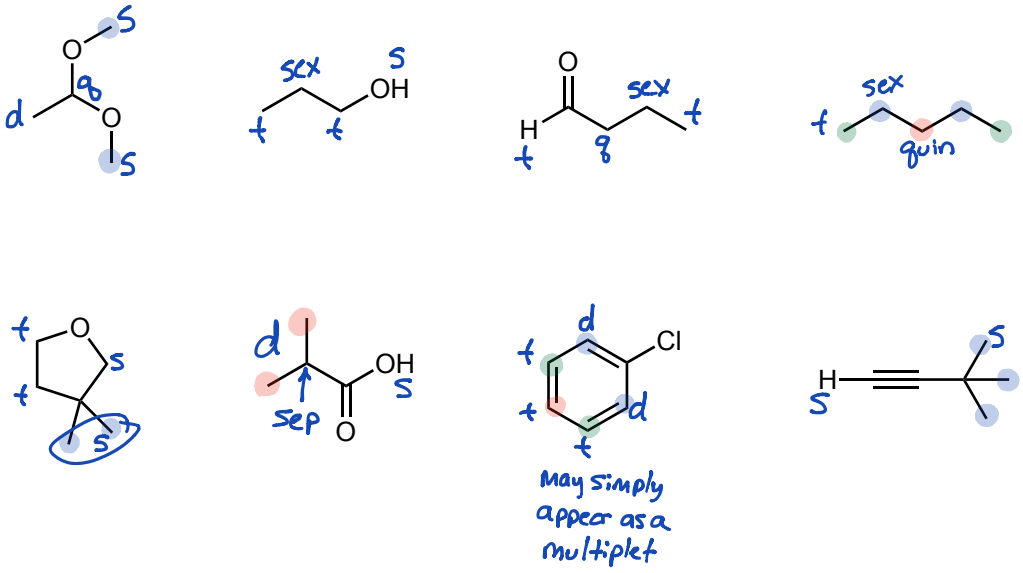



lowest δ highest δ

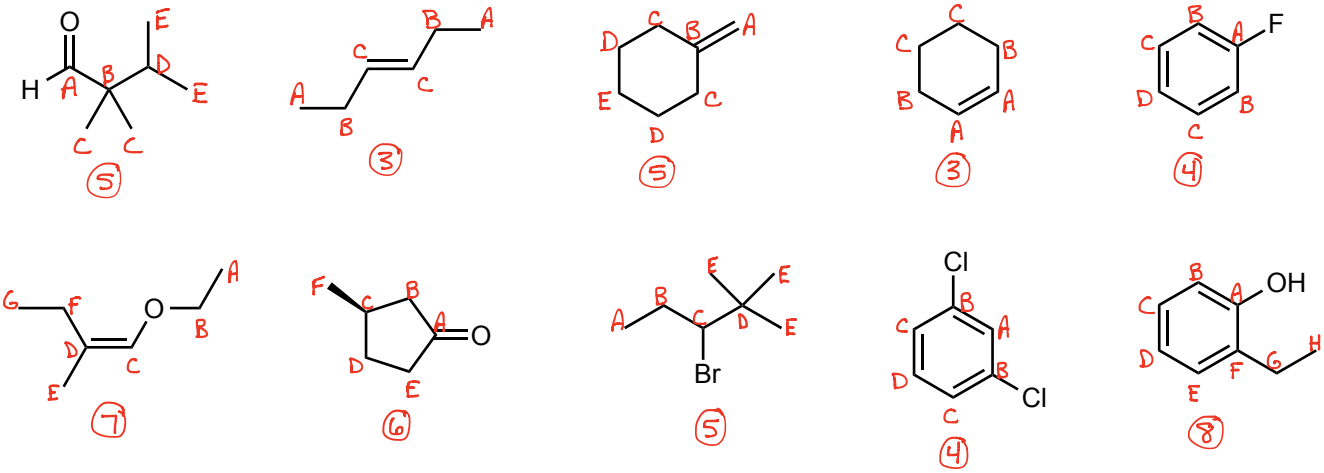
B < A < C

4) For each of the compounds below, determine the expected splitting for all protons.

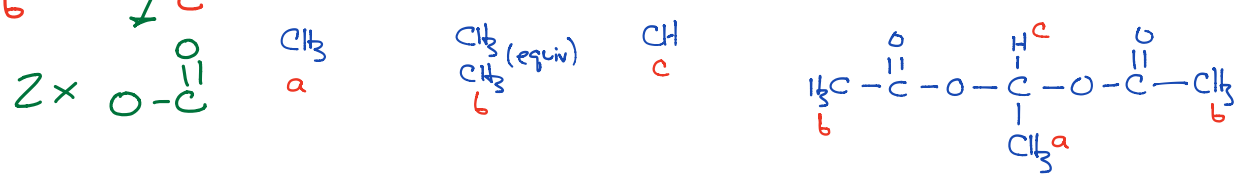
2 doublet (d)
3 triplet (t)
4 quartet (q)
5 quintet (quin)
6 sextet (sex)
7 septet (sep)



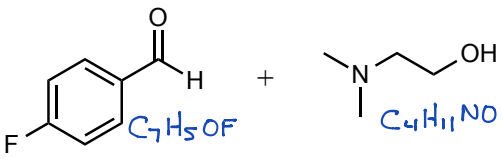

5) How many $^{13}C$ signals would you expect each compound below to exhibit? (i.e. How many chemically distinct C atoms are present in each molecule?)

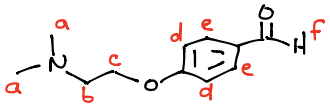



6) A symmetric diester has the formula $\mathbf{C_6H_{10}O_4}$ and the following $^1H$ NMR spectral data: 1.47 (d, 3H), 2.07 (s, 6H), 6.84 (q, 1H). Propose a structure for this compound.



7) The reaction shown below was carried out in a laboratory to give a compound with the indicated spectral data. Determine the structure of this compound.




$C_{11}H_{15}NO_2$ – lost H and F

IR stretch at 1730 $cm^{-1}$ – retain aldehyde

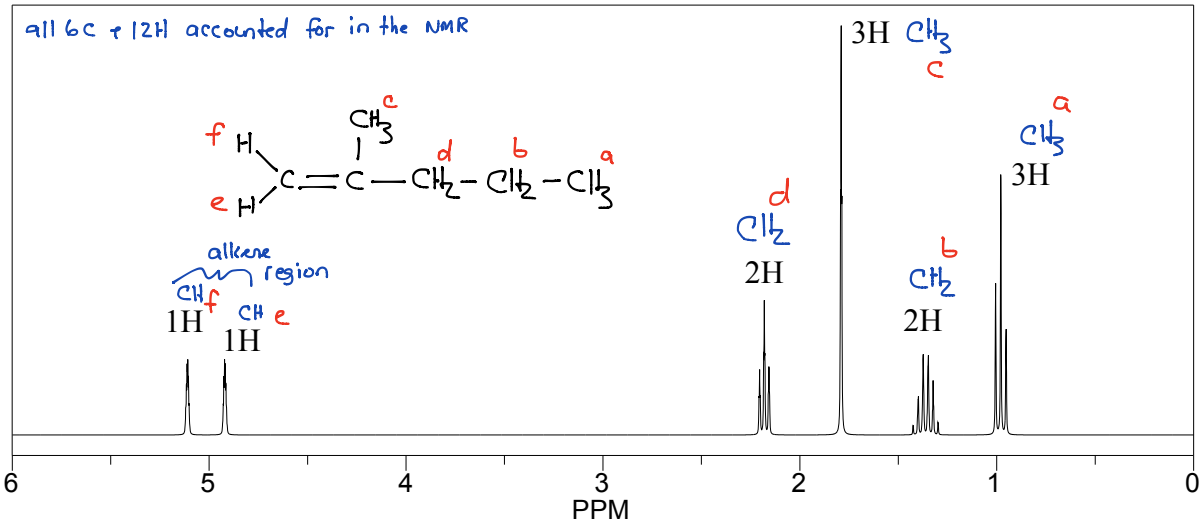
Eight signals in the $^{13}C$ NMR

$^1H$ NMR Data: 2.32 (s, 6H), 3.05 (t, 2H), 4.20 (t, 2H), 6.97 (d, 2H), 7.82 (d, 2H), 9.97 (s, 1H)

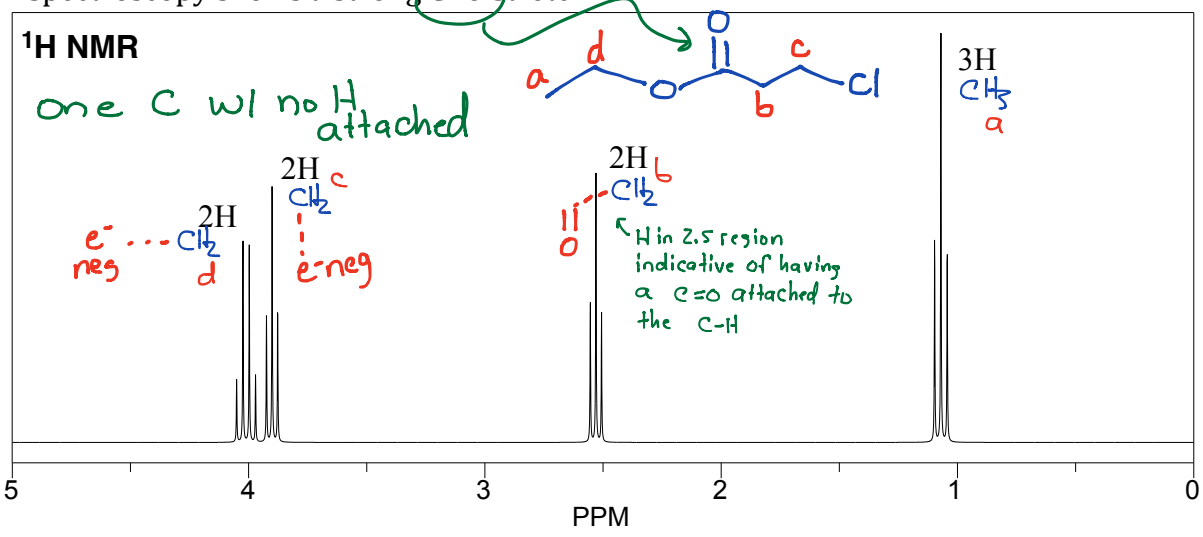
aromatic region

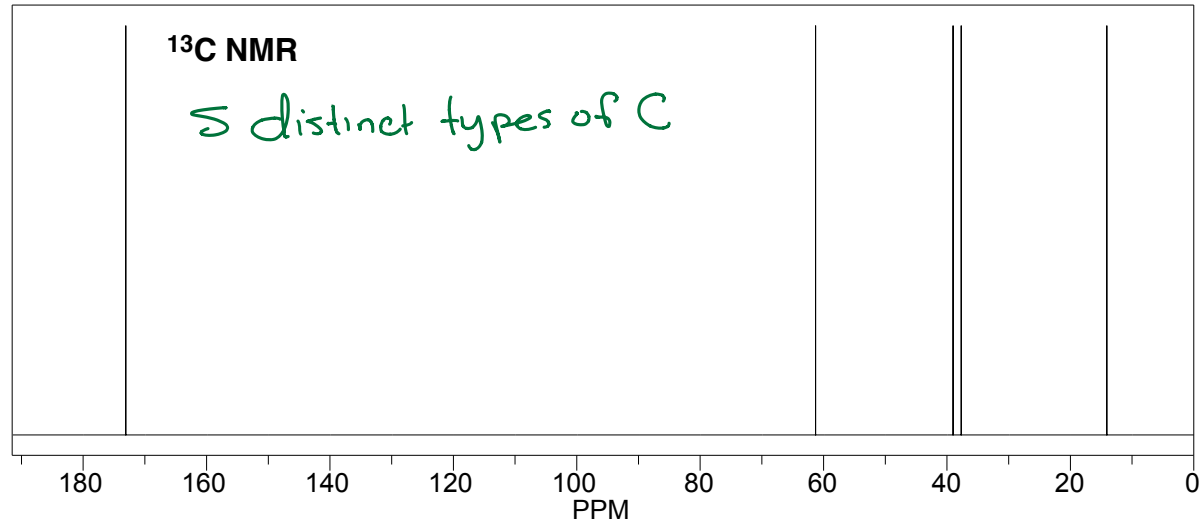
8) For each of the following, use the data provided to deduce an appropriate structure.

**A. $C_6H_{12}$** → 1 unsat

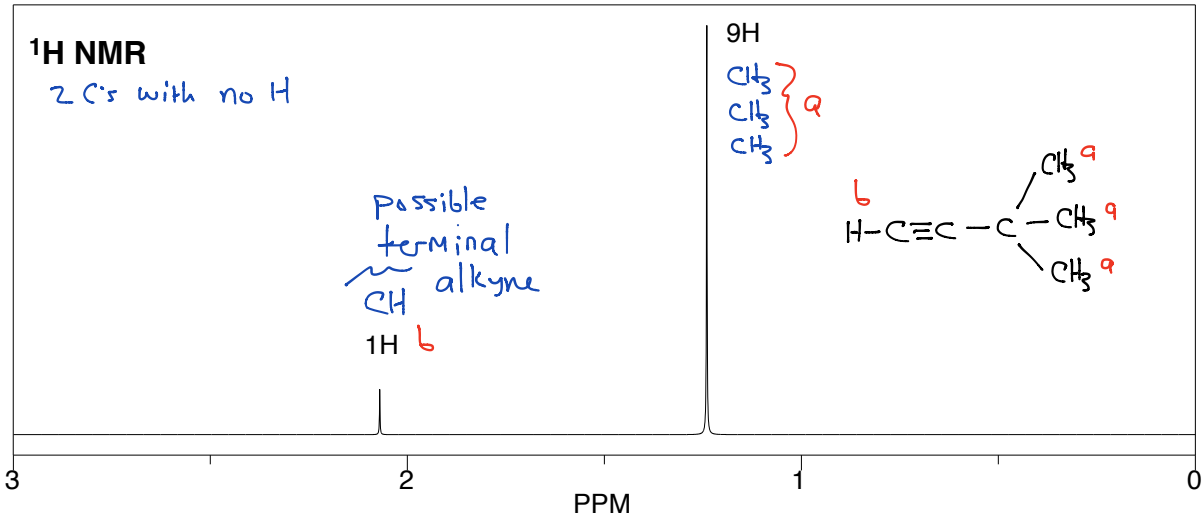


**B.** $C_5H_9ClO_2$ *Use the $^{13}C$ NMR to determine the number of distinct C atoms.*
IR spectroscopy shows a strong C=O stretch.



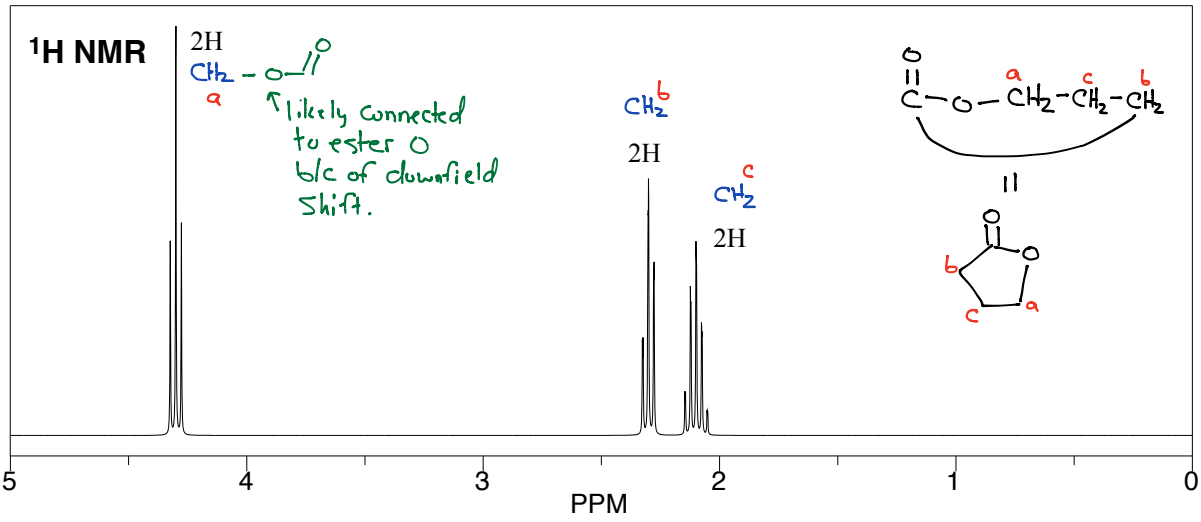




**C.** $C_6H_{10}$ – 2 unsat

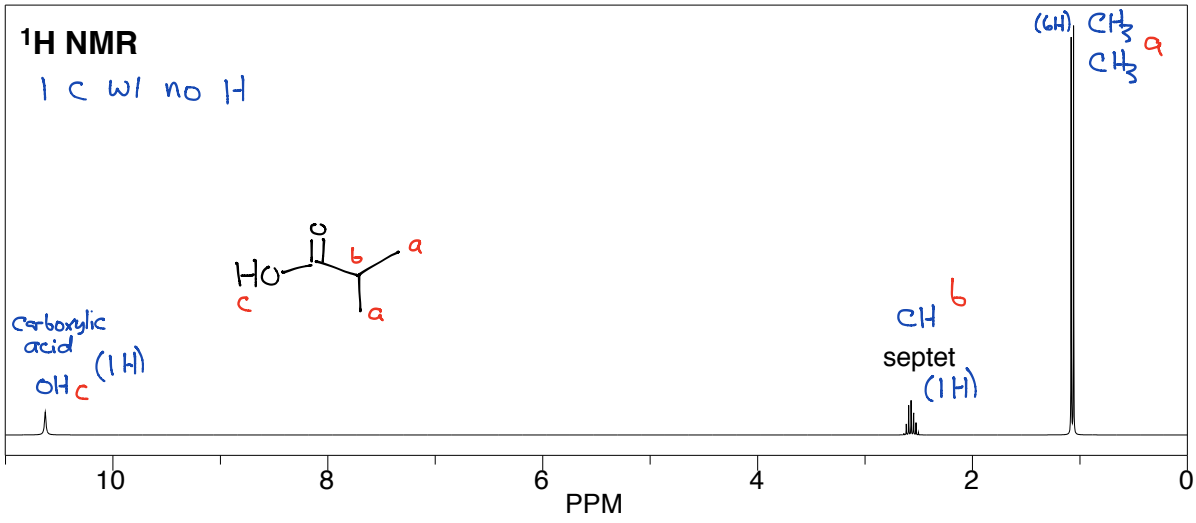


**D.** $C_4H_6O_2$ - 2 unsat → ester  No indications of C=C so other unsat is likely a ring.

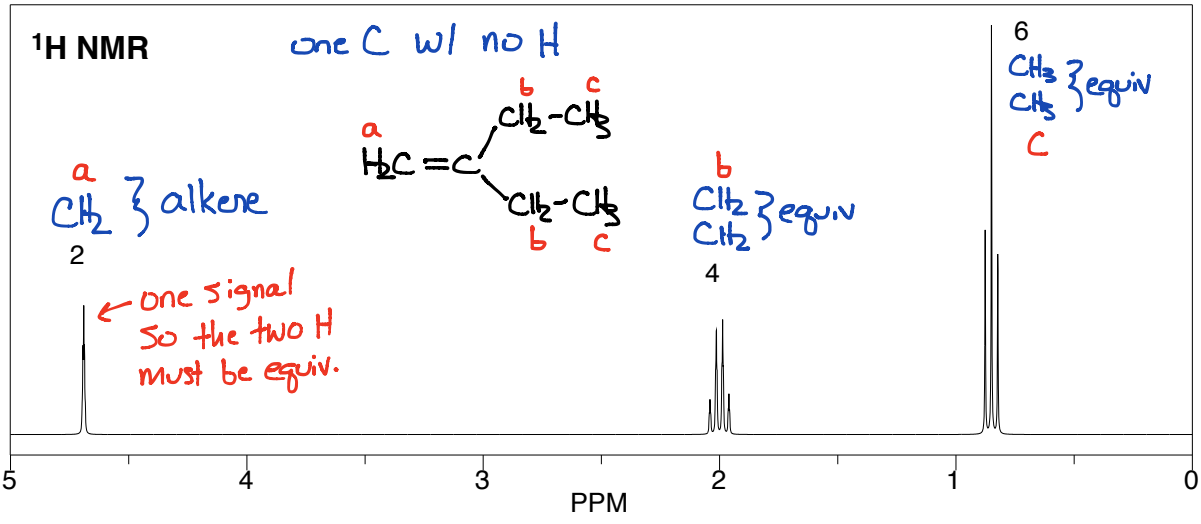
IR shows a strong stretch at 1740 $cm^{-1}$




**E.** $C_4H_8O_2$ – 1 unsat

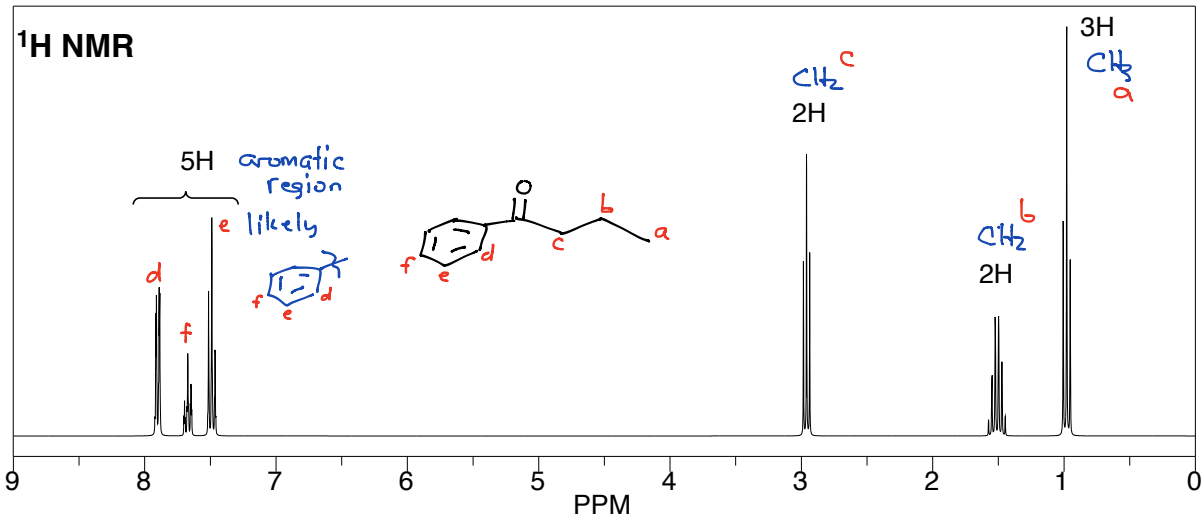



**F.** $C_6H_{12}$ – 1 unsat.

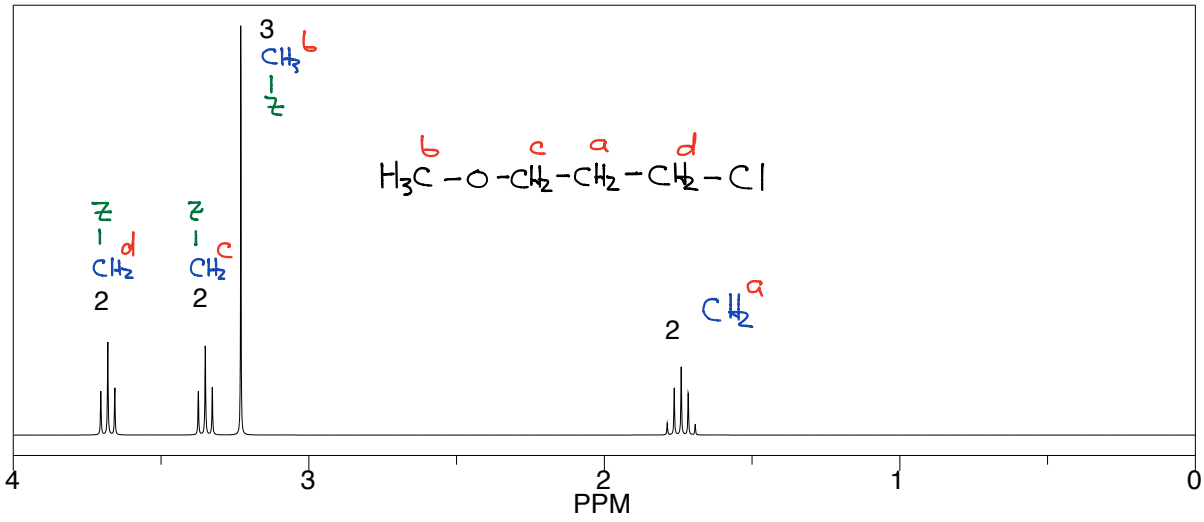


↳ Conjugated C=O

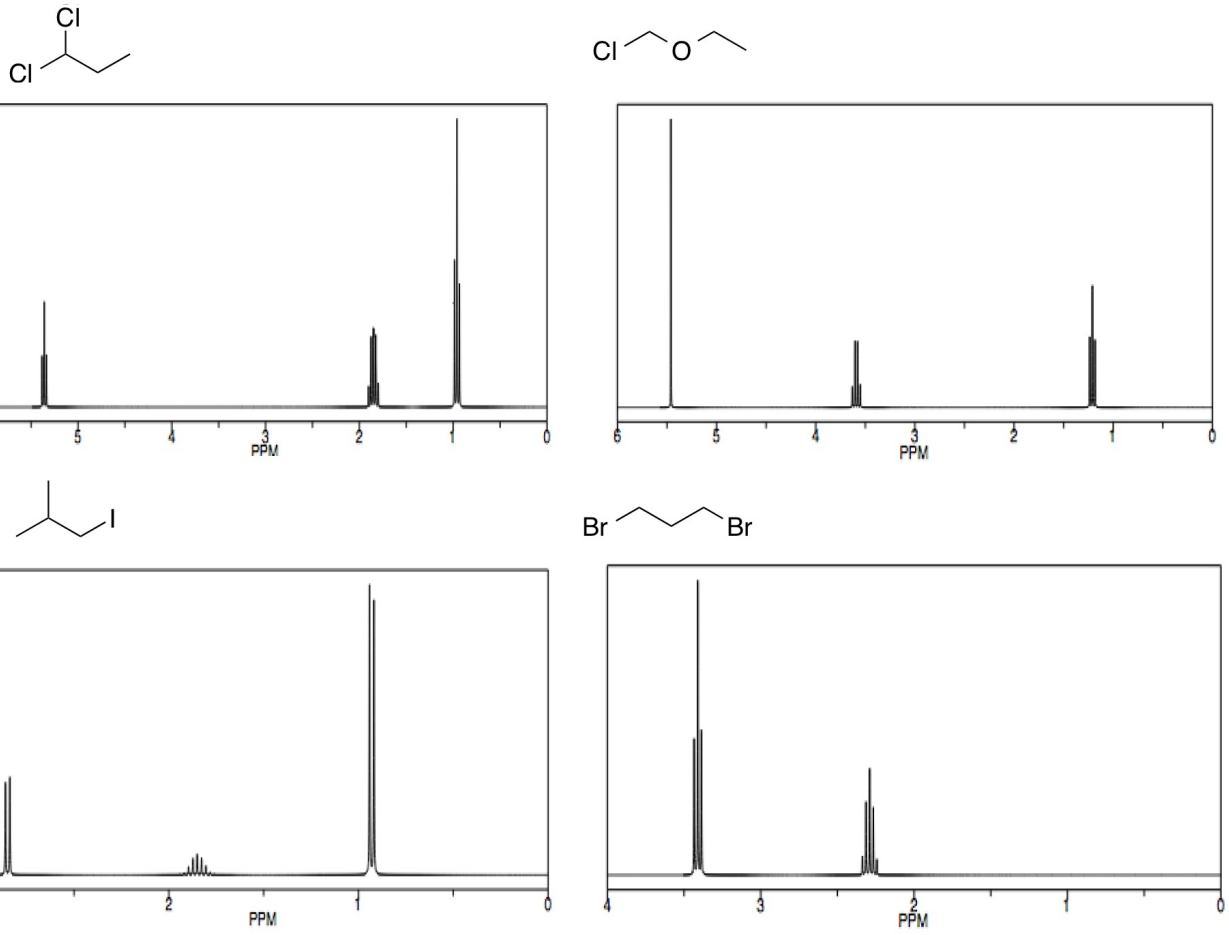
**G. Compound contains 10C and IR shows a strong stretch around 1690 cm$^{-1}$**




**H. $C_4H_9OCl$** – no unsat.

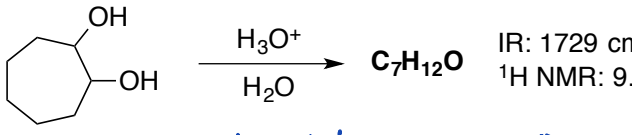


9) For each of the compounds below, draw a rough estimation of its expected $^1$H NMR spectrum.




**Challenge Problems:**

10) Use the spectral data provided to predict the product of the reaction shown below.



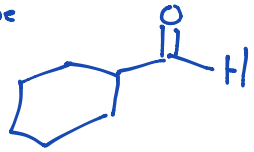

**$C_7H_{12}O$**

IR: 1729 cm$^{-1}$

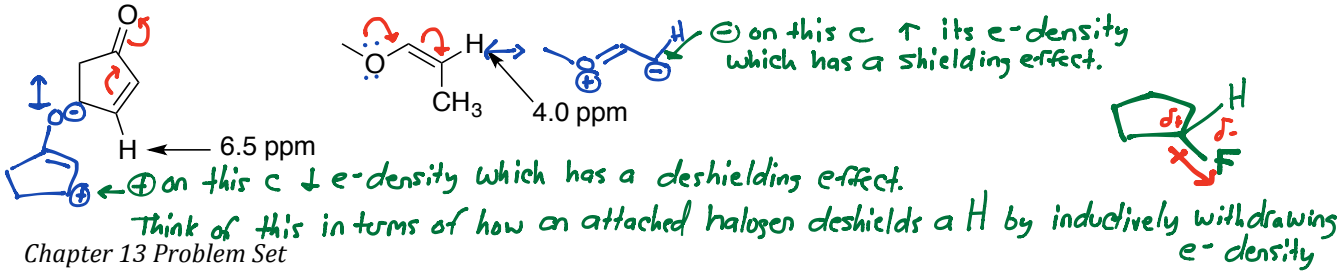
$^1$H NMR: 9.72 (d, 1H), 2.30 (sex, 1H), 1.4-18 (m, 10H)

signals for 10 H overlapping in this region. Some are and some are not equivalent.

a pinacol type rearrangement



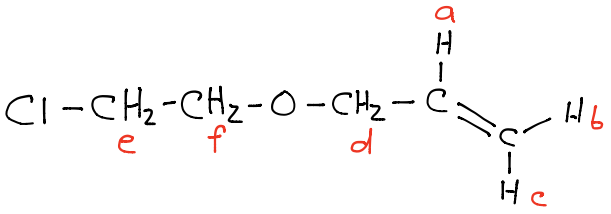
11) The vinyl proton chemical shift in the two compounds shown below is substantially different. Explain why the shift in these two compounds is so different. *Hint: think about resonance.*



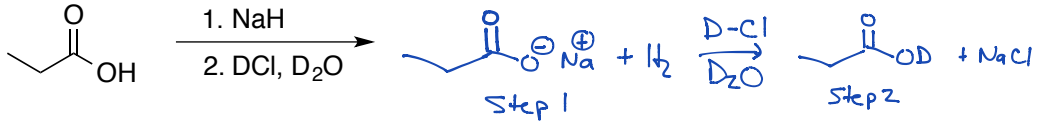

Think of this in terms of how an attached halogen deshields a H by inductively withdrawing e- density

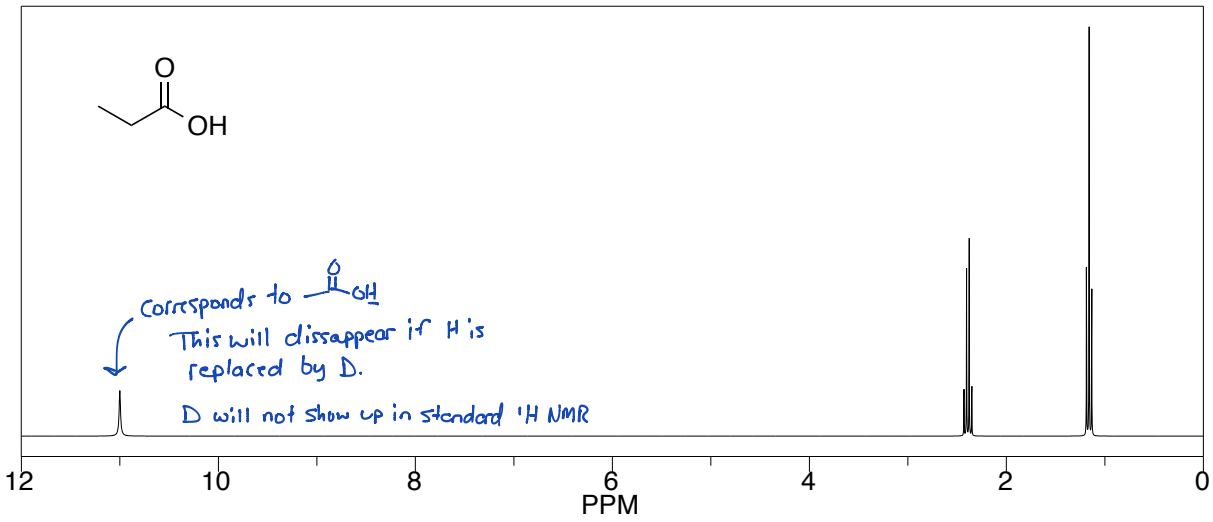
12)Propose a structure for a compound with the formula **$C_5H_9ClO$**.

$^1$H NMR Data: a δ 6.07 (1H, multiplet) *alkene H*
b or c δ 5.43 (1H, d) *alkene H*
δ 5.31 (1H, d) *alkene H*
d δ 4.04 (2H, d)
e δ 3.83 (2H, t)
f δ 3.65 (2H, t)

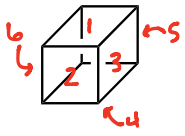



13)A student ran the reaction shown below. What would you expect the structure of the product to be? Given the $^1$H NMR of the starting materials, how would you expect it to change following the reaction? *Note: D is a heavy isotope of H. It reacts almost identically to H (ie. DCl reacts like HCl).*




14) The structure of cubane is shown below. What is the molecular formula for cubane? Using the unsaturation calculation, determine the degrees of unsaturation. Now, using visual inspection, determine the degrees of unsaturation. You should find that there is a discrepancy. Which number is correct? Can you use an alternate method to confirm your unsaturation count?

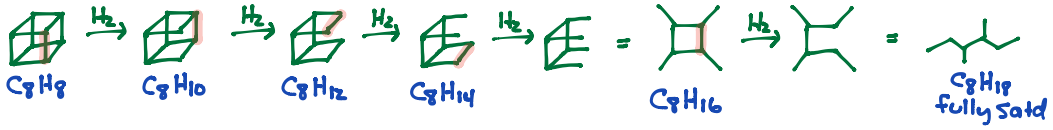



$C_8H_8$ #unsat = $\frac{18-8}{2} = \frac{10}{2} = 5$ unsaturations

Satd F: $C_8H_{18}$

6 sides to a cube, appears to be 6 rings = 6 unsaturations

Theoretical Hydrogenation:




Flattened view of Cubane:


Really only 5 rings.

Took 5 molecules of $H_2$ (10 H) to fully saturate
So there must only be ≤ unsaturations