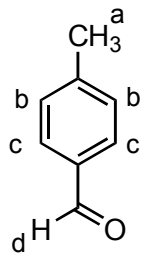
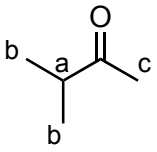
In-Class NMR Exercises

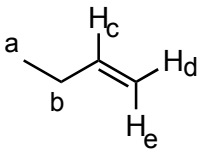
1. For each of the following molecules, determine the number of equivalent hydrogens. Indicate each type of equivalent hydrogen with a letter (see the example).



4 unique hydrogens

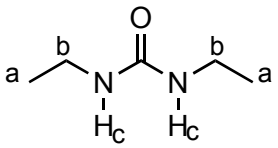


3 unique hydrogens



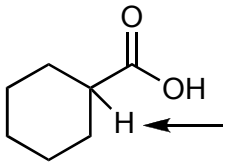
5 unique hydrogens

Remember that since there is no free rotation about a double bond, those hydrogens are different!

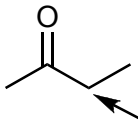


3 unique hydrogens

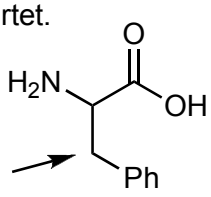
2. For the indicated hydrogen atom in each molecule, specify the integration and splitting pattern.



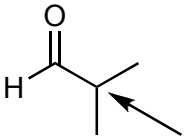
The integration would be 1H. The proton has 4 H's on neighboring carbons, so the splitting pattern would be a pentet.



The integration would be 2H. The proton has 3H's on the neighboring carbon, so the splitting pattern would be a quartet.

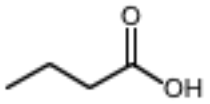


The integration would be 2H. There is only one neighboring H, so the peak would be a doublet.

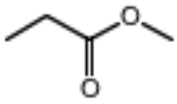


The integration would be 1H. There are 6 neighboring H's, so the peak would be a septet (or a multiplet).

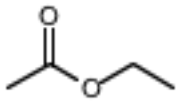
3. Explain how you would distinguish the three isomers below using NMR spectroscopy. Give specific examples of peaks, chemical shifts and splitting patterns that would illustrate the differences.



butanoic acid



methyl propanoate

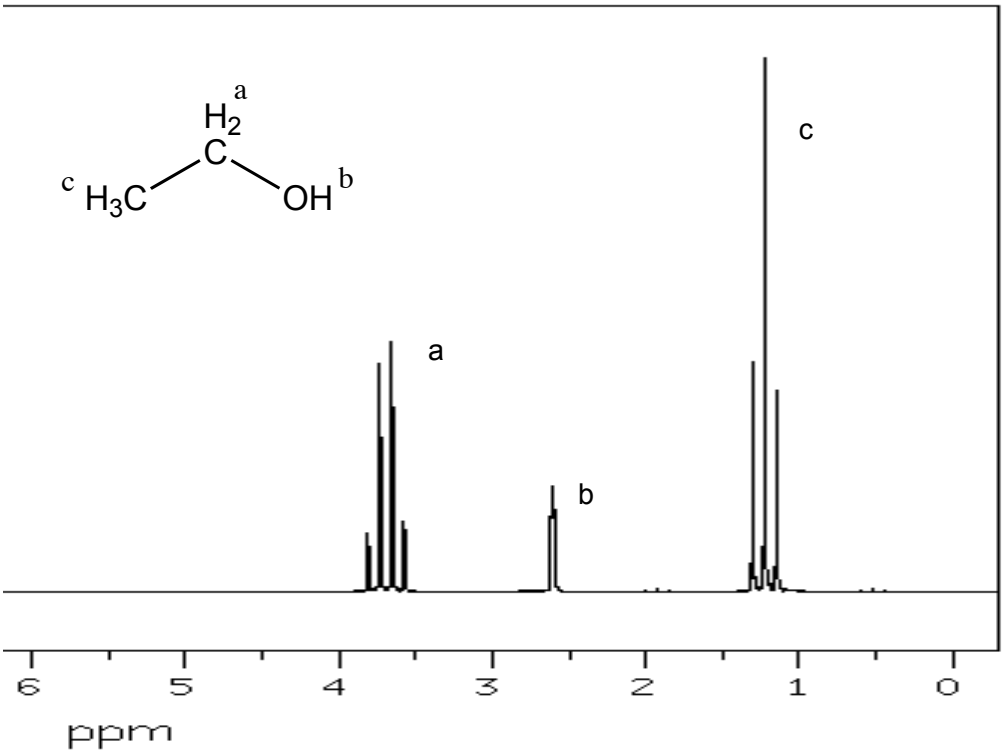


ethyl ethanoate

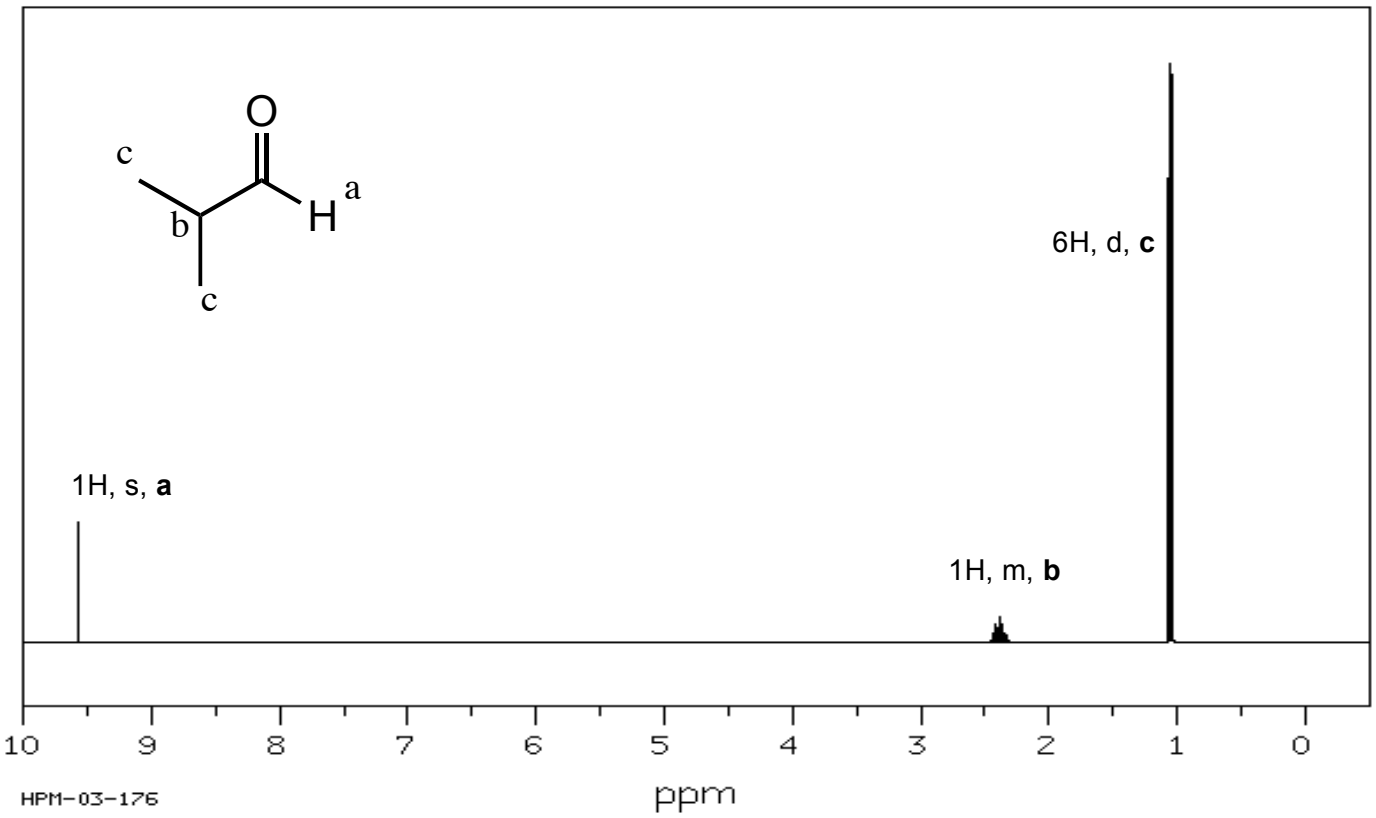
Butanoic acid would be the easiest to differentiate. We would see 4 peaks for the acid, but only three for the other two. The most diagnostic peak would be the carboxylic acid peak, which would be a singlet around 10-13 ppm. To differentiate the two esters, the most diagnostic peak would be the ester peak around 4 ppm. For methyl propanoate, the ester peak would be a singlet that integrated for 3 hydrogens, and be slightly below 4 ppm. For ethyl ethanoate, that peak would be a quartet and integrate for 2 hydrogens, and be found just above 4 ppm.

4. Assign the peaks for the following spectra.

Ethanol



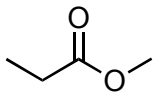
2-methylpropanal



5. Two different compounds (A and B) have the formula $C_4H_8O_2$.
   a. What is the isomer term for this? **These are structural, or constitutional, isomers**
   b. What is the index of hydrogen deficiency? **One**
   c. Both compounds show a strong peak at 1745 cm^{-1} in the IR, but no OH peak (alc or acid) by IR. Use the NMR data provided to determine the structures of the two isomers.
   The IR shows a carbonyl (C=O) group. If there is no OH, it can't be a carboxylic acid.

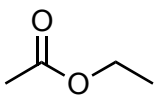
Compound A:

3.7 ppm, s, 3H **An ester peak! C(O)O-CH, 3H, singlet means it is a methyl group.**
2.4 ppm, q, 2H **An alpha $-CH_2-$, next to a $-CH_3$ (quartet).**
1.2 ppm, t, 3H **The $-CH_3$ group.**

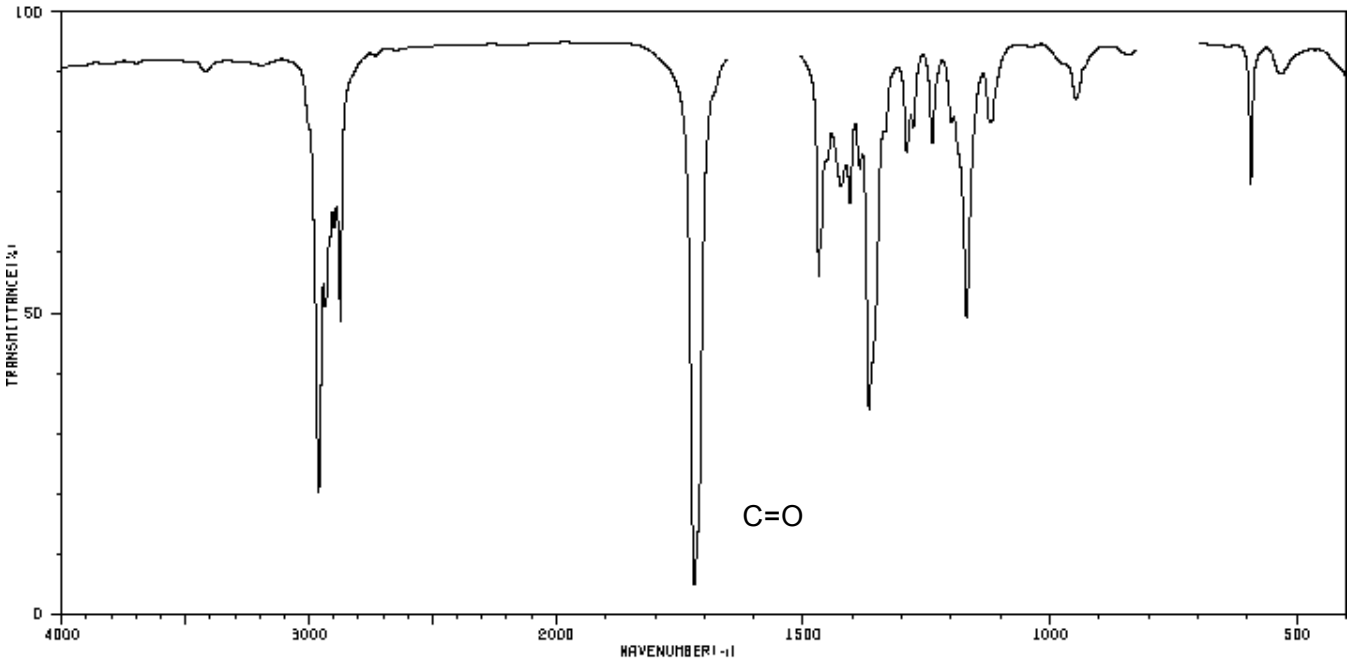


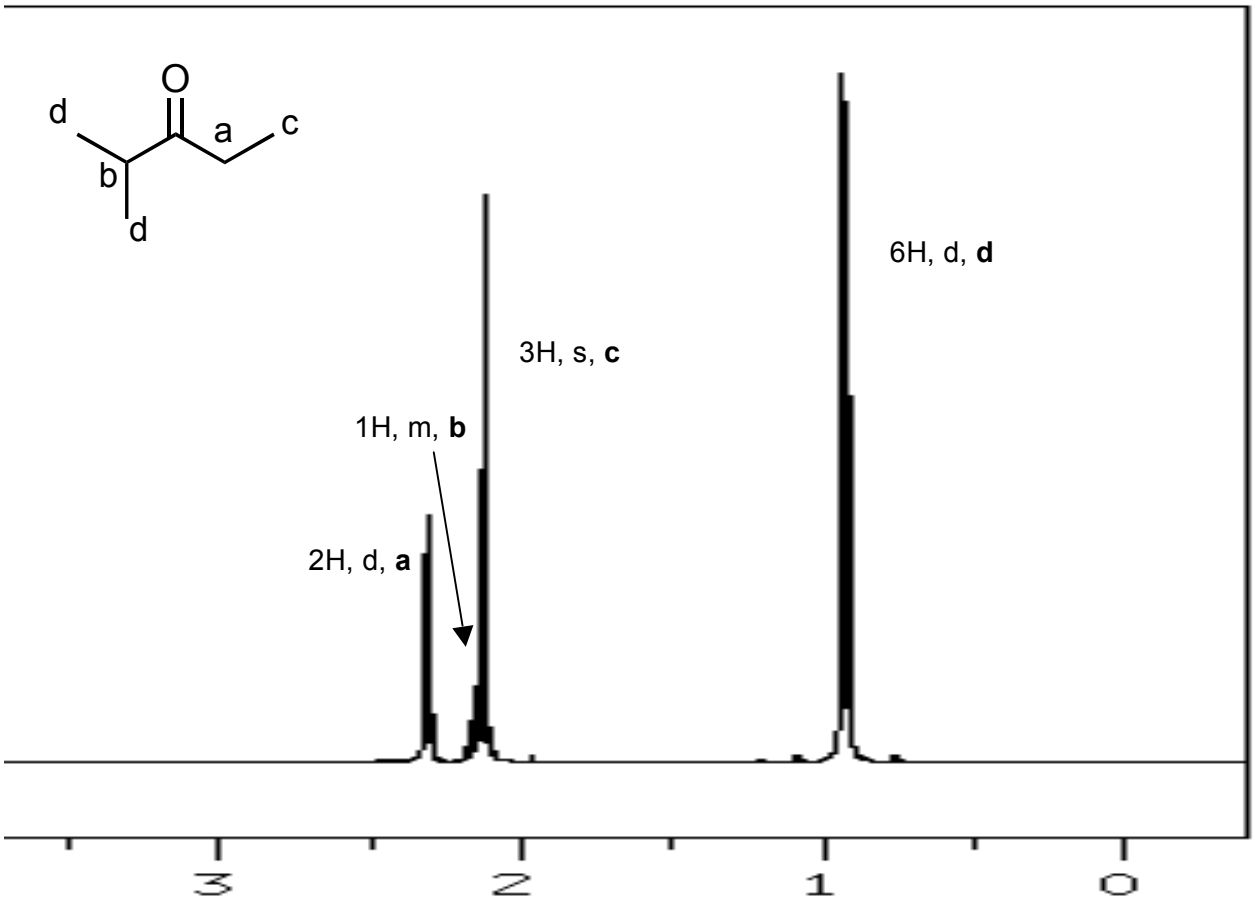
Compound B:

4.1 ppm, q, 2H **The ethyl group is now on the oxygen side of the ester.**
2.0 ppm, s, 3H **The methyl is on the carbonyl side of the ester.**
1.3 ppm, t, 3H

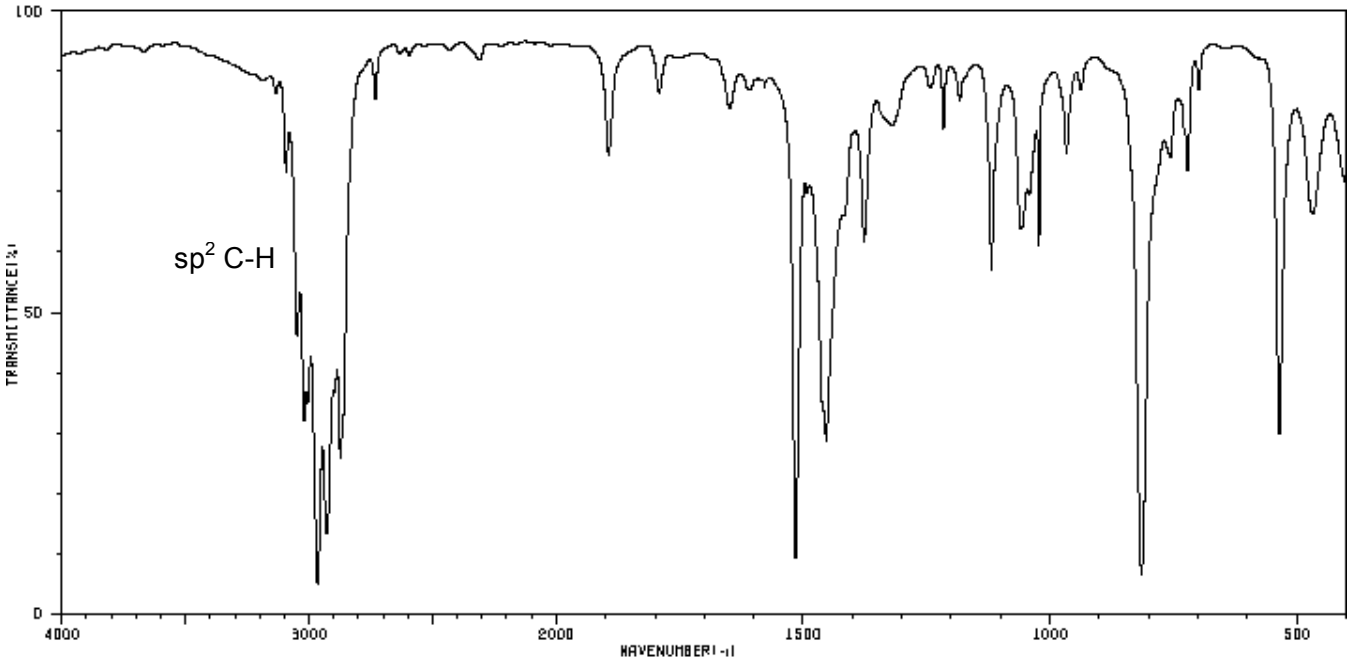


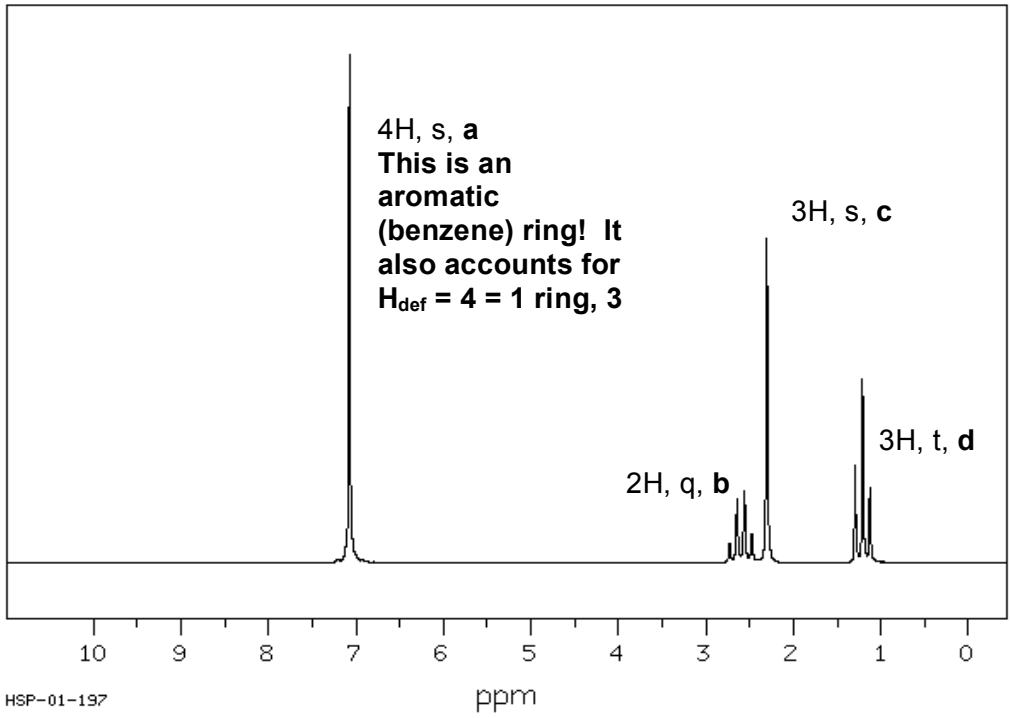
6. Use the IR and NMR data provided to determine the structure of the molecule.
$C_6H_{12}O$ **H_{def} = 1, IR shows a C=O, it must be an aldehyde or ketone. Neither the IR (2700 cm^{-1}) nor the NMR show an aldehyde peak (around 9.5 – 10 ppm)**

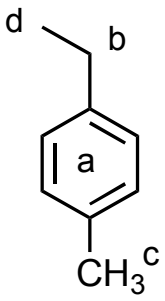




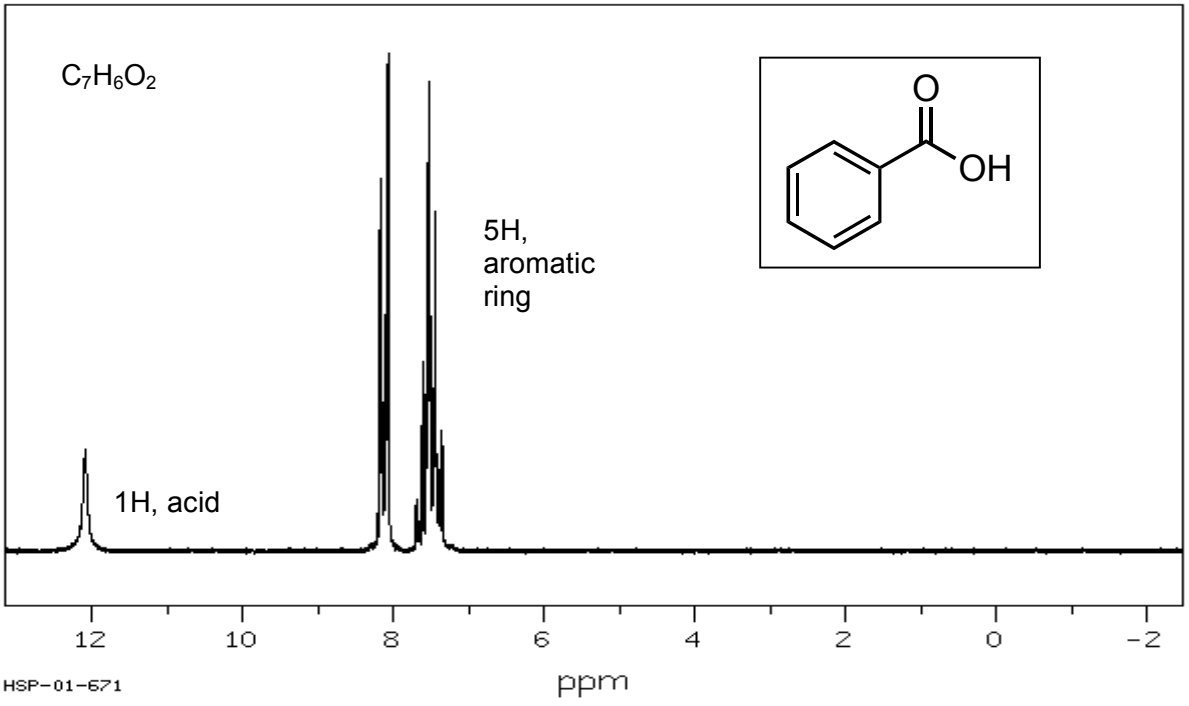
C_9H_{12}, **H_{def} = 4**

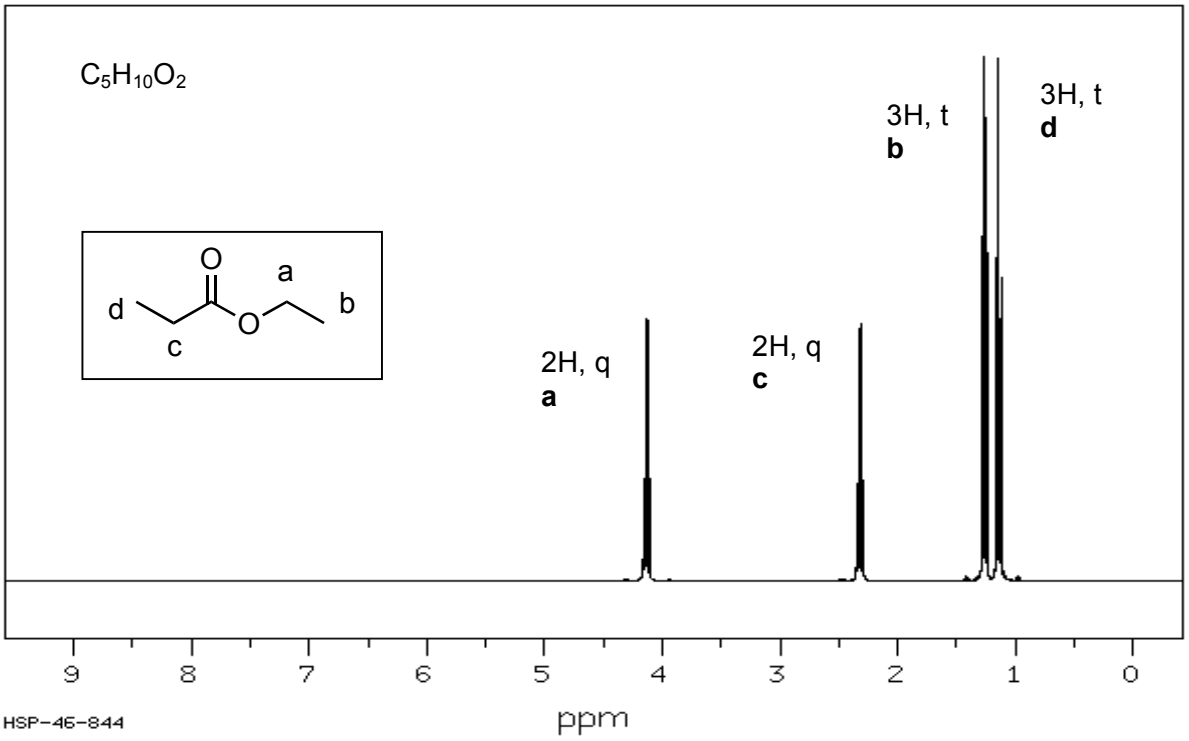

100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
sp2 C-H


4H, s, a
This is an aromatic (benzene) ring! It also accounts for Hdef = 4 = 1 ring, 3
3H, s, c
3H, t, d
2H, q, b
10
9
8
7
6
5
4
3
2
1
0
HSP-01-197
ppm


d
b
a
CH3
c

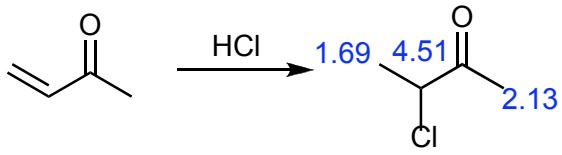
7. Propose a structure based on the chemical formula and NMR spectra given.





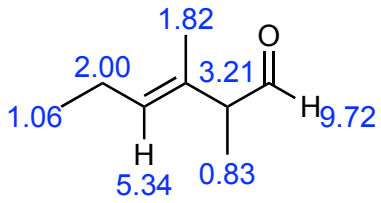
Some challenges…

8. Treatment of but-3-en-2-one with one equivalent of HCl forms compound A. Compound A exhibits the following NMR spectrum: 1.69 ppm, 3H, d; 2.13 ppm, 3H, s; 4.51 ppm, 1H, q. What is the structure of compound A?



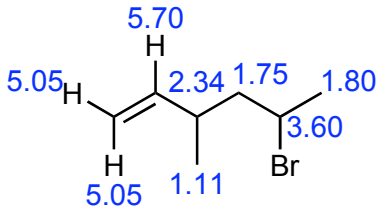
9. Determine the structure of $C_8H_{14}O$ from the NMR data below.

9.72 ppm, 1H, s
5.34 ppm, 1H, t
3.21 ppm, 1H, q
2.00 ppm, 2H, m
1.82 ppm, 3H, s
1.06 ppm, 3H, t
0.83 ppm, 3H, s



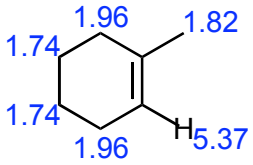
10. Determine the structure of $C_7H_{13}Br$ from the spectral data given below.

5.70 ppm, 1H, m
5.05 ppm, 2H, d
3.60 ppm, 1H, m
2.34 ppm, 1H, m
1.80 ppm, 3H, d
1.75 ppm, 2H, t
1.11 ppm, 3H, d

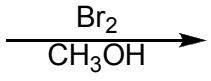


11. Use the following spectroscopic and reaction data to determine the structures of Compounds B and C.

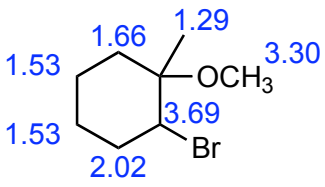
Compound B, C_7H_{12}



IR: 1643 cm^{-1} **C=C**
NMR: 5.37 ppm, 1H, t
1.96 ppm, 4H, m
1.82 ppm, 3H, s
1.74 ppm, 4H, m



Compound C, $C_8H_{15}OBr$



NMR: 3.69 ppm, 1H, t
3.30ppm, 3H, s
2.02 ppm, 2H, q
1.66 ppm, 2H, t
1.53 ppm, 4H, m
1.29 ppm, 3H, s