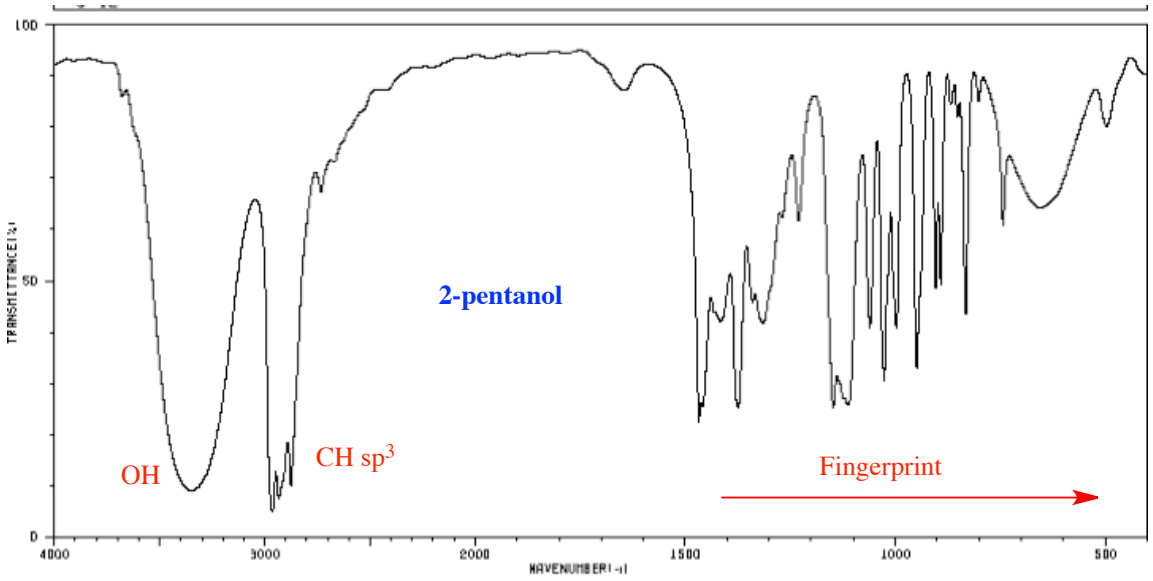
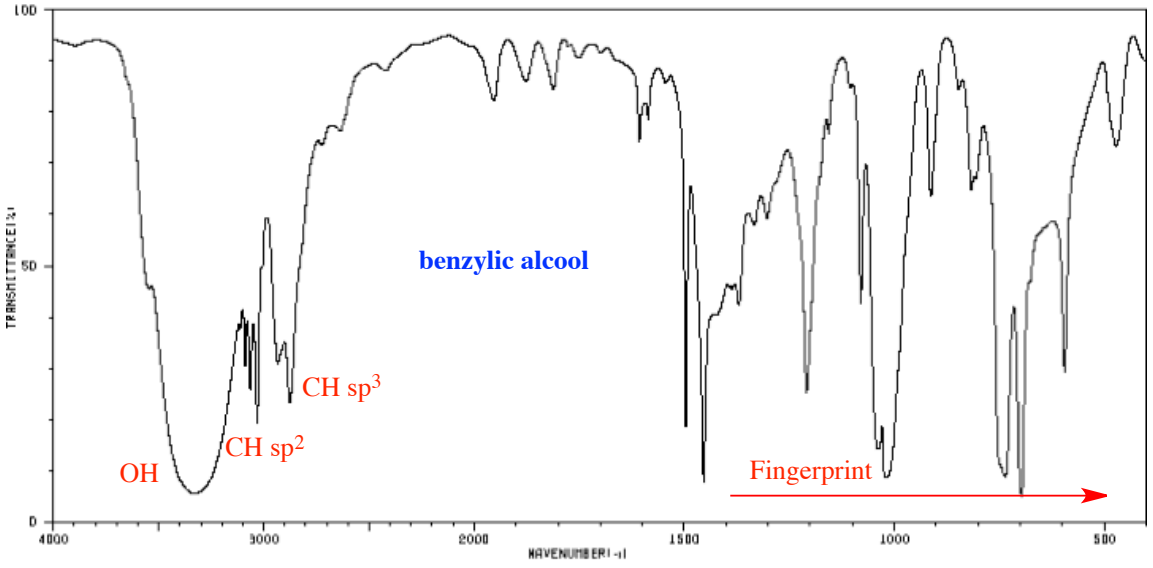
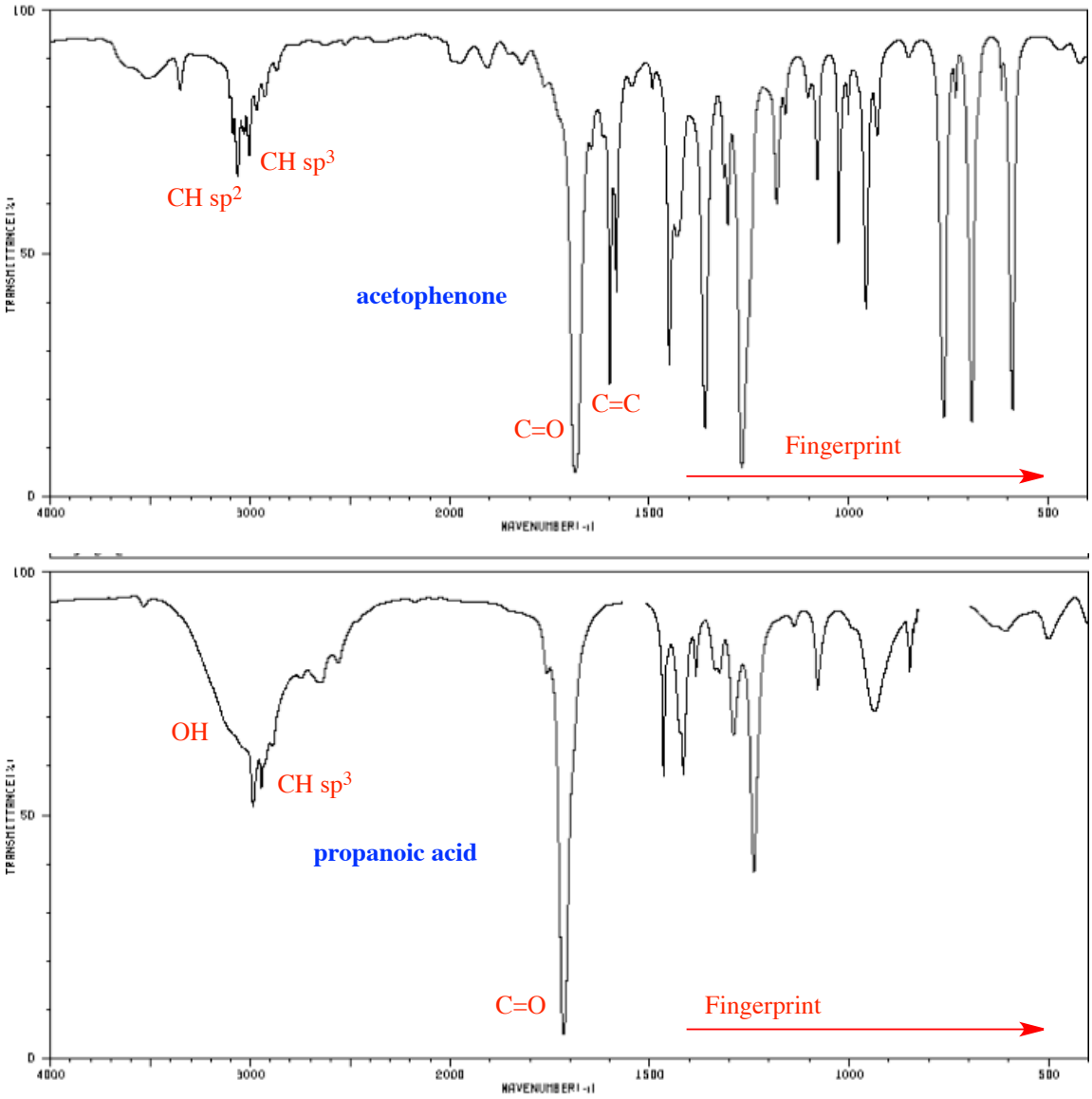
Assignment 5 - Spectroscopy

1. Associate each of the following IR spectra with one of the following compounds and justify your answer.
    a. Propanoic acid
    b. 2-Pentanol
    c. Benzyl alcohol
    d. Acetophenone



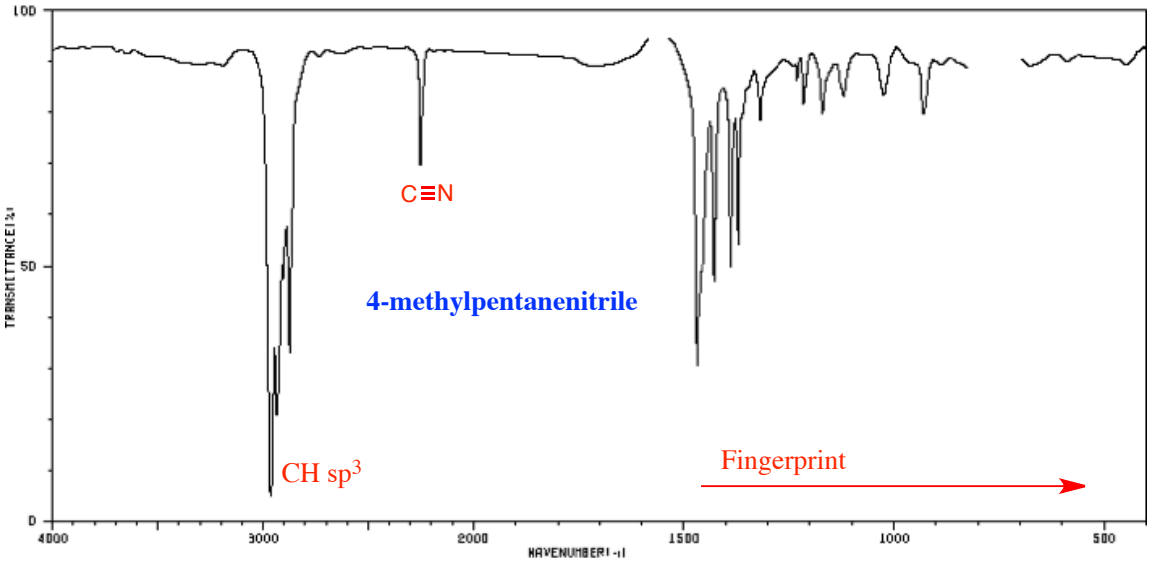


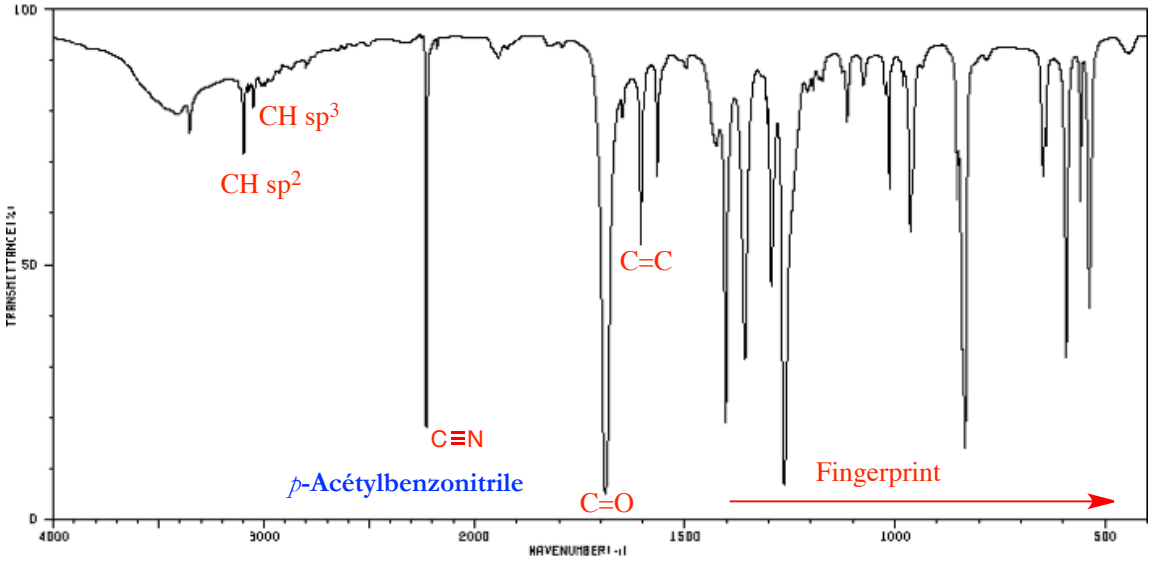
1. cont.



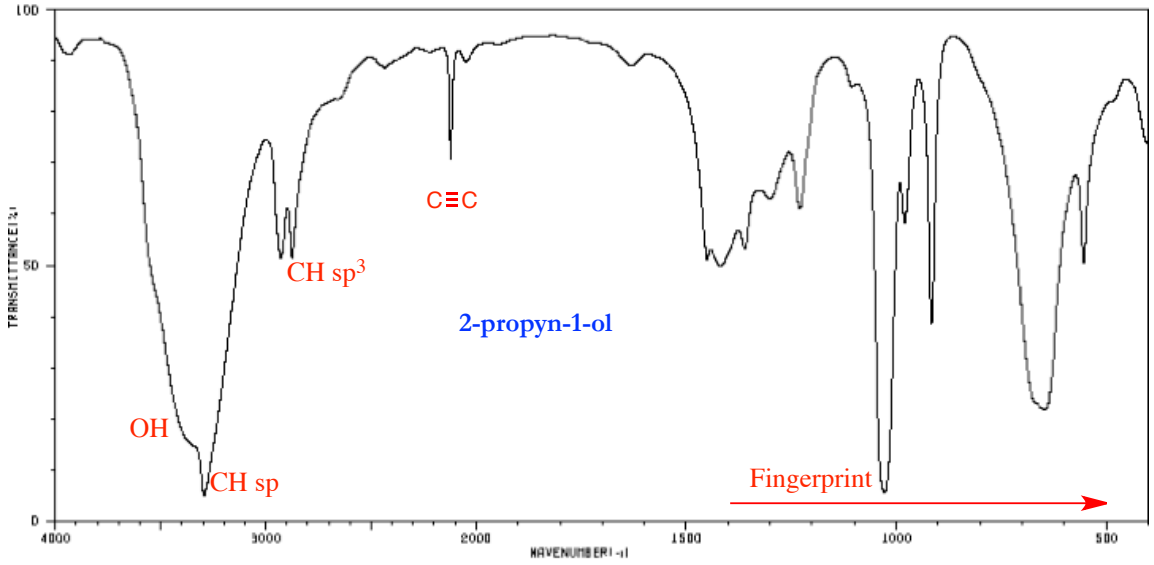
note: the OH peak for a carboxylic acid is generally smaller than the OH peak for an alcool.

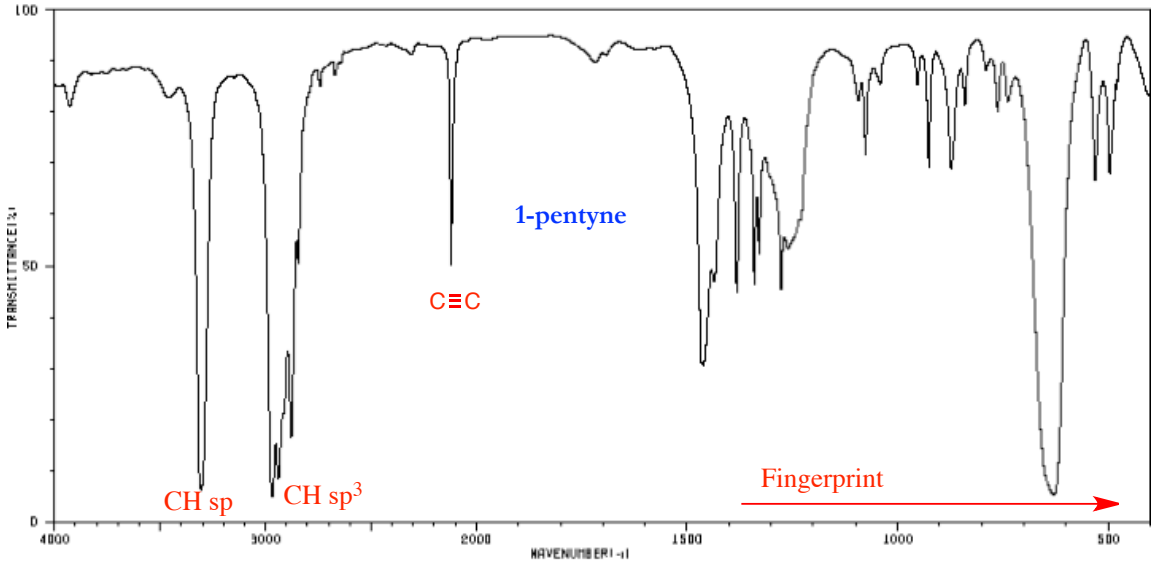
2. Associate each of the following IR spectra with one of the following compounds and justify your answer.
    a. 2-Propyn-1-ol
    b. 1-Pentyne
    c. 4-Méthylpentanenitrile
    d. *p*-Acétylbenzonitrile





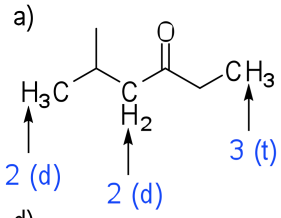
2. Cont.


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
C≡C
CH sp3
2-propyn-1-ol
OH
CH sp
Fingerprint

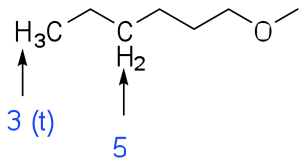

100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
1-pentyne
C≡C
CH sp
CH sp3
Fingerprint

3. Give the number of peaks (splitting) expected in the ^{1}H NMR for the indicated protons in each of the following structures.

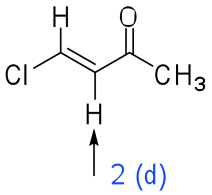
a)



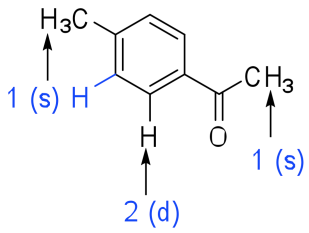
b)



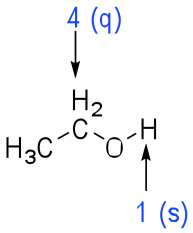
c)



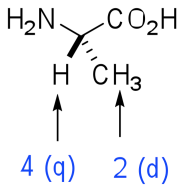
d)



e)



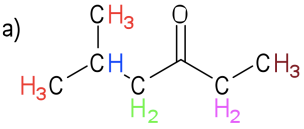
f)



#peaks = n+1 (s)=singlet, (d)=doublet, (t)=triplet, (q)=quartet

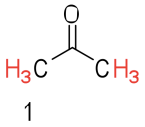
4. How many signals would be expected in the ^{1}H NMR of the following molecules?

a)



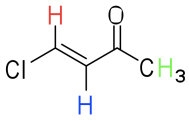
5

b)



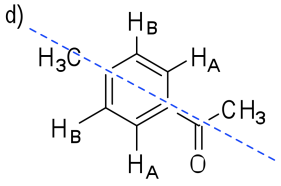
1

c)



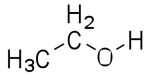
3

d)



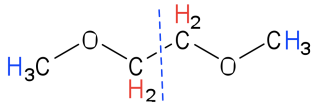
4

e)



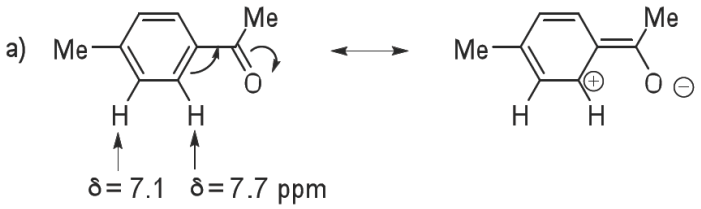
3

f)

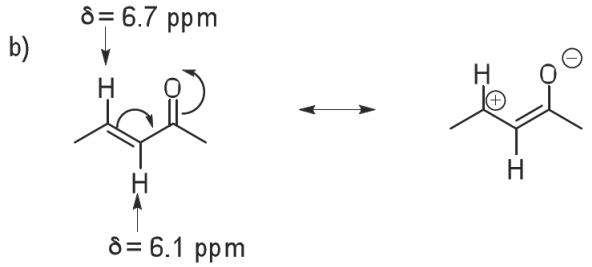


2

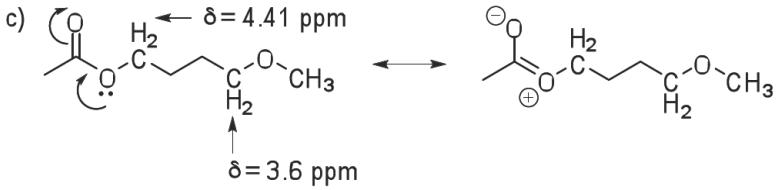
5. Explain the following differences in chemical shift.

a) 

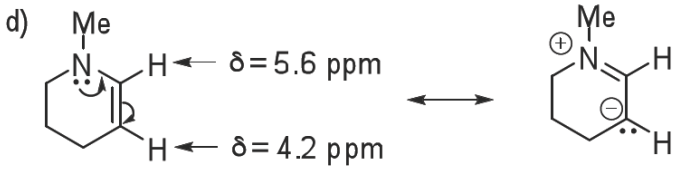
The proton at 7.7 ppm is on a carbon with a partial positive charge δ+ due to the presence of a full positive charge on this carbon in the resonance structure. Therefore, there is less electron density around that carbon = it is deshielded and as such will come out at a higher ppm.

b) 

The proton at 6.7 ppm is on a carbon with a partial positive charge δ+ due to the presence of a full positive charge on this carbon in the resonance structure. Therefore there is less electron density around that carbon = it is deshielded and as such will come out at a higher ppm.

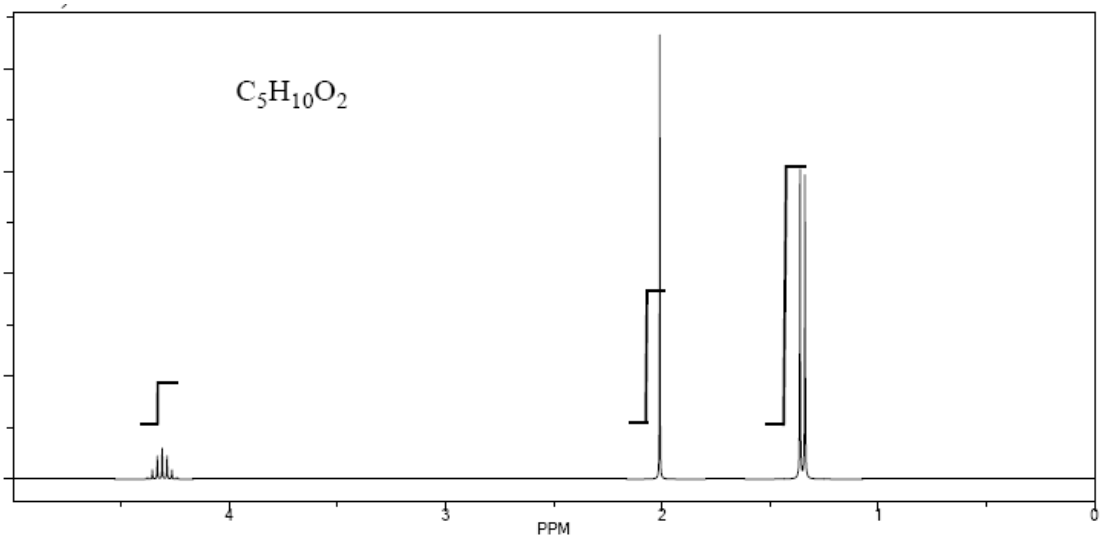
c) 

The oxygen on the ester is more electron-withdrawing than the oxygen on the ether due to the possibility of resonance in the ester leaving a positive charge on is oxygen. The protons next to the ester oxygen will therefore be deshielded as their electron density is pulled towards that oxygen = their signal comes out at a higher ppm (4.41 vs 3.6 ppm).

d) 

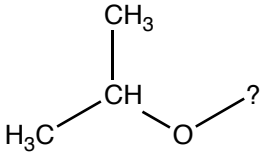
The proton at 4.2 ppm is on a carbon with a partial positive charge δ- due to the presence of a full negative charge on this carbon in the resonance structure. Therefore there is more electron density around that carbon = it is shielded and as such will come out at a lower ppm.

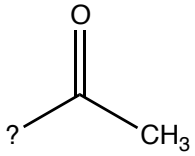
6. Determine the structure of the following unknowns using the table to fill in your answers.
    a. D.U. = (2x5+2+0-10-0)/2 = 1 --> 1 double bond or 1 ring



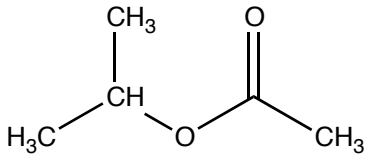
Signal	δ	Integration	Multiplicity	Comments
A	~4.3	1H	septet n=6	CH next to O (based on δ) and next to 6 H
B	~2.0	3H	singlet n=0	CH_3 next to no other CH_x next to carbonyl (based on δ)
C	~1.3	6H	doublet n=1	2 x CH_3 next to a CH

Fragments:





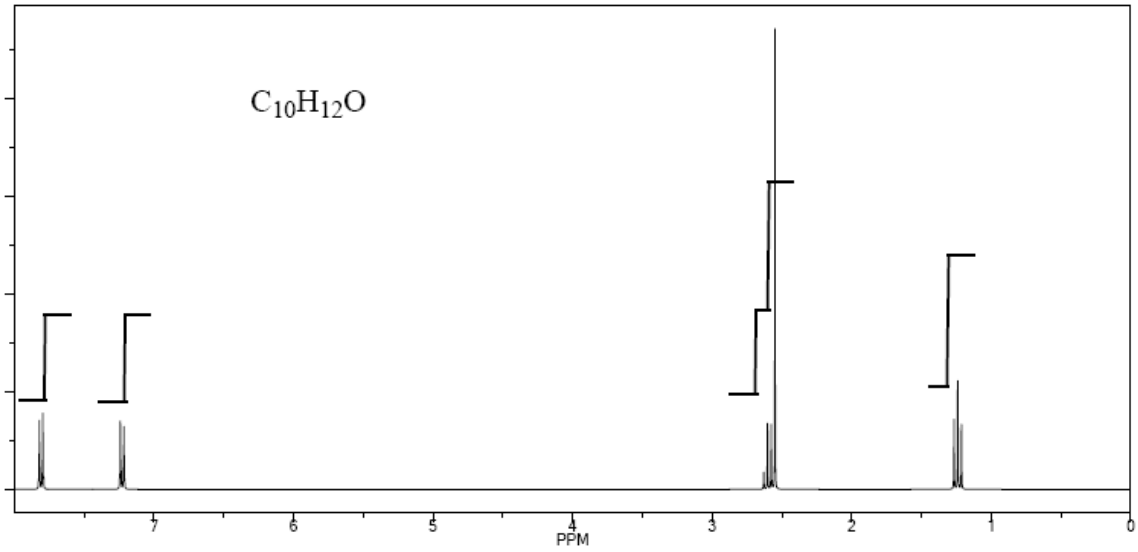
Molecule:



CH next to Oxygen. CH_3 next to carbonyl

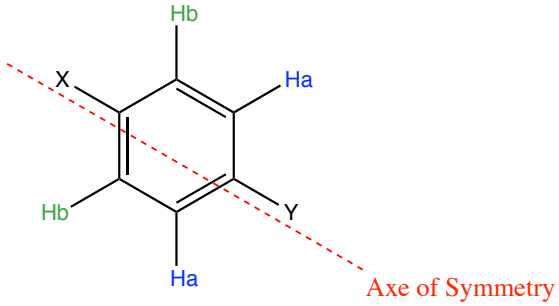
total of $C_5H_{10}O_2$: all atoms accounted for. C=O is the unsaturation

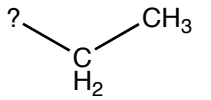
b. D.U. = (2x10+2+0-12-0)/2 = 5 --> aromatic ring = 4 unsaturations
possibility of benzene + 1 double bond
or + 1 ring

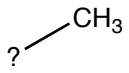


Signal	δ	Integration	Multiplicity	Comments
A	~7.8	2H	doublet n=1	aromatic area = 2 x CH next to another CH
B	~7.2	2H	doublet n=1	aromatic area = 2 x CH next to another CH
C	~2.7	2H	quartet n=3	CH_2 next to CH_3 small deshielding: next to C=O or aromatic ring?
D	~2.6	3H	singlet n=0	CH_3 next to no other CH_x. small deshielding: next to C=O or aromatic ring?
E	~1.2	3H	triplet n=2	CH_3 next to CH_2

Fragments:



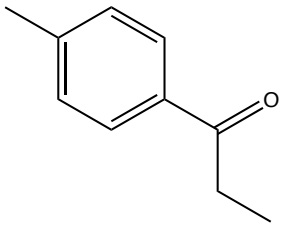




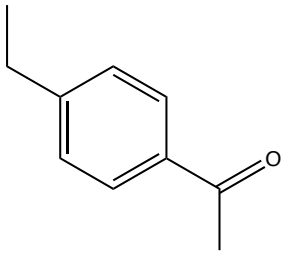
explains aromatic pattern

compare with molecular formula: $C_{10}H_{12}O$
we currently have: 9C, 12H and 4 unsaturations (aromatic ring).
missing: 1C, 1O and 1 unsaturation. C=O

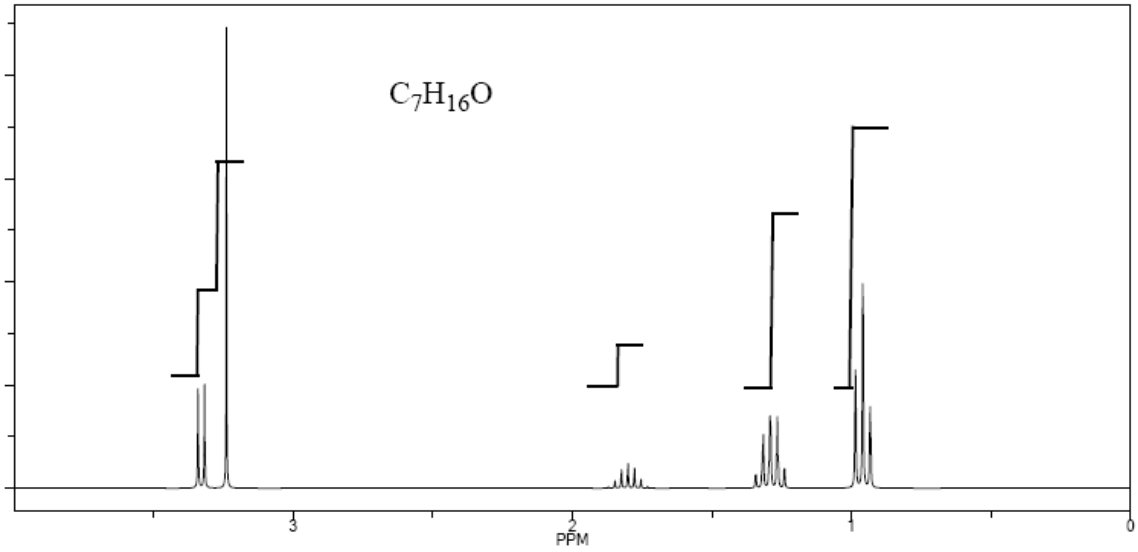
Molecule:



or

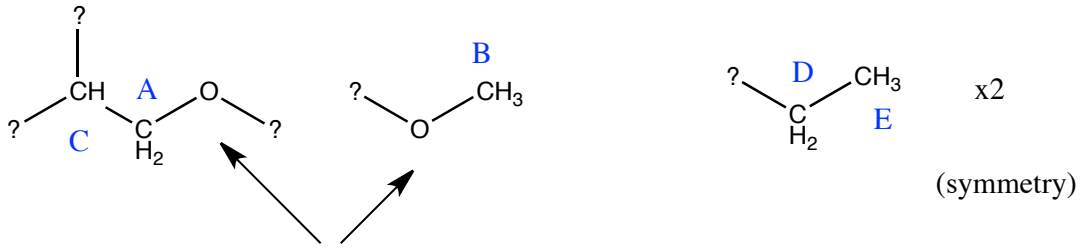


c. D.U. = (2x7+2+0-16-0)/2 = 0 --> no ring or double or triple bond



Signal	δ	Integration	Multiplicity	Comments
A	3.4	2H	doublet n=1	CH_2 next to CH deshielded, next to Oxygen?
B	3.3	3H	singlet n=0	CH_3 next to no other CH_x. deshielded, next to Oxygen?
C	1.8	1H	septet n=6	CH next to 6 H next to 2x CH_3 or 3x CH_2
D	1.3	4H	pentet n=4	4H = 2x CH_2 = symmetry in molecule next to 4 H = next to multiple CH_x
E	0.9	6H	triplet n= 2	6H 2x CH_3 = symmetry in molecule next to 2 H = Next to CH_2?

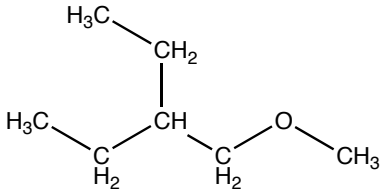
Fragments:



(symmetry)

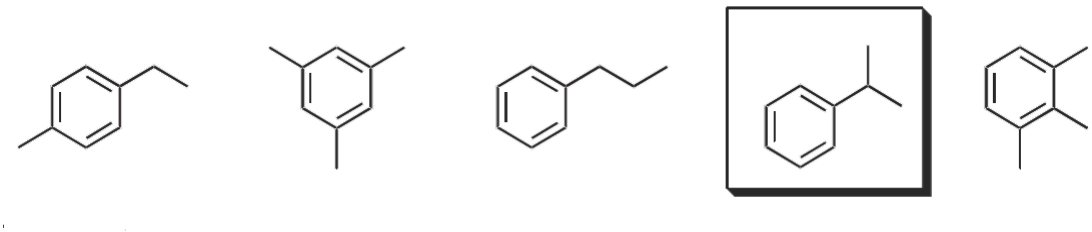
same oxygen (only one O in molecule)

Molecule:

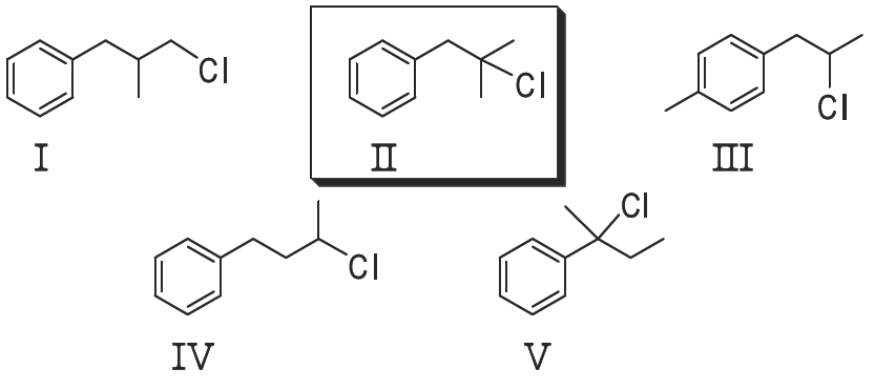


CH next to 3xCH_2. Symmetry in 2 ethyl substituents.
molecular formula: $C_7H_{16}O$ all atoms and (non)unsaturations accounted for.

7. Determine the most likely structure of a compound, with the molecular formula C_9H_{12}, which gave a ^{1}H NMR spectrum consisting of:
   a doublet at δ 1.25 ppm
   a septet at δ 2.90 ppm
   a multiplet at δ 7.25 ppm

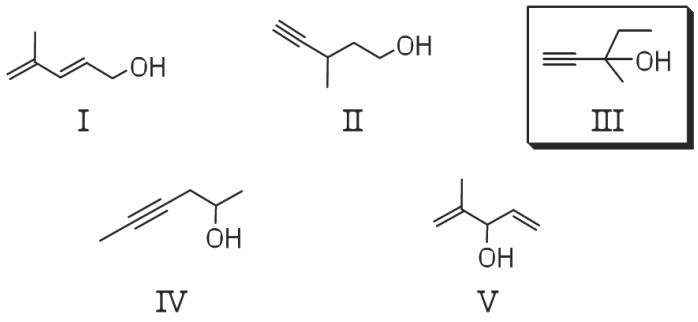


8. Determine the most likely structure of a compound with the molecular formula $C_{10}H_{13}Cl$, which gave the following ^{1}H NMR spectrum:
   singlet at δ 1.6 ppm
   singlet at δ 3.1 ppm
   multiplet at δ 7.2 (5H) ppm



9. Determine the likely structure for a compound A ($C_6H_{10}O$). Its spectral data is as follows:

^{1}H NMR		IR
triplet, δ 1.0 ppm	singlet, δ 2.4 ppm	2200 cm^{-1} (sharp)
singlet, δ 1.4 ppm	singlet, δ 3.4 ppm	3300 cm^{-1} (sharp)
quartet, δ 1.6 ppm		3500 cm^{-1} (broad)

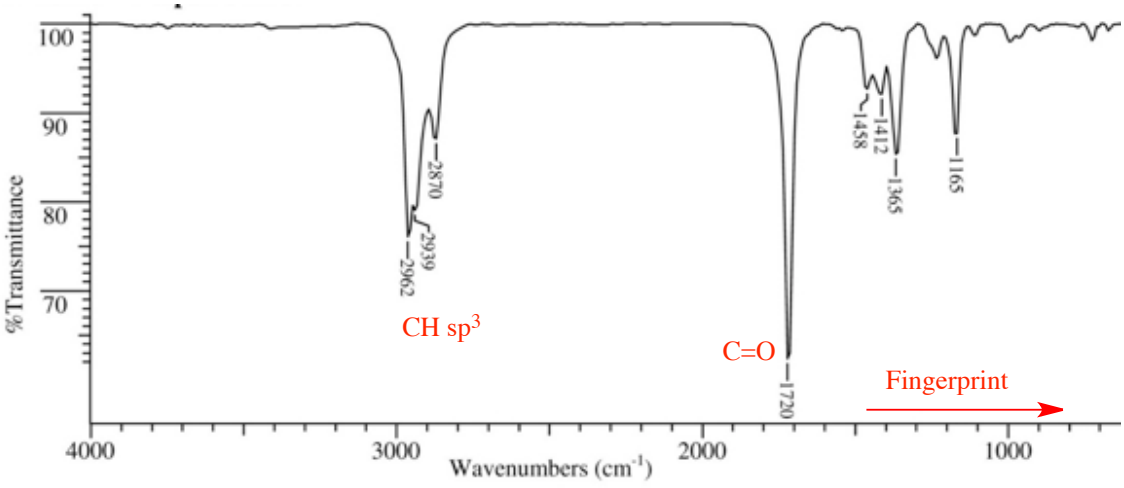


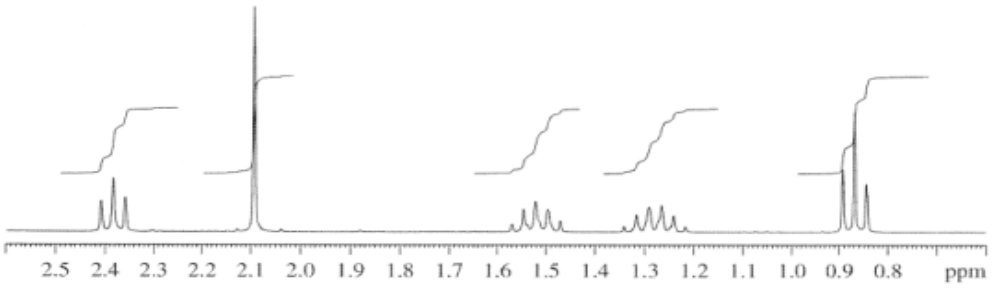
10. Briefly explain how you might distinguish between the following substances by comparing their ^{1}H-NMR spectra?

The main difference would be the chemical displacement of the CH of the isopropyl (sp^3 hybridized). When next to the O (I), it would be more deshielded, showing up on the spectrum at a higher δ of 3.0 to 5.0 ppm. When next to the carbonyl (II), it would be less deshielded (carbon of carbonyl is less electron-withdrawing than the O) and would show up in a more shielded area of the spectrum (more to the right, lower δ 2.1-2.5 ppm).

11. An unknown compound has the formula $C_6H_{12}O$. Elucidate the structure of the molecule by analyzing its IR and ^1H NMR spectra, shown below.

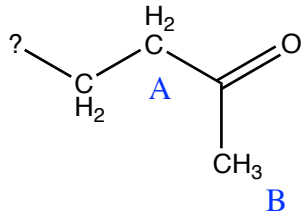
D.U. = (2x6+2+0-12-0)/2 = 1 --> 1 ring or one double bond

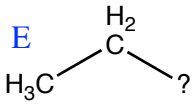




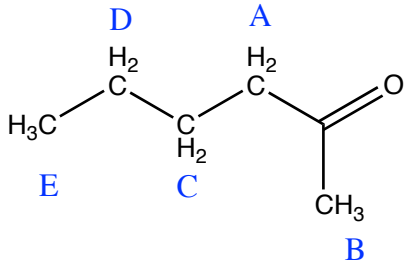
Signal	δ	Integration	Multiplicity	Comments
A	2.4	2H	triplet n=2	CH_2 next to another CH_2 small deshielding: next to carbonyl (see IR)
B	2.1	3H	singlet n=0	CH_3 next to no other CH_x. small deshielding: next to carbonyl (see IR)
C	1.6	2H	pentet n=4	CH_2 next to 4H (2x CH_2?)
D	1.3	2H	sextet n=5	CH_2 next to 5H
E	0.9	3H	triplet n=2	CH_3 next to CH_2

Fragments:





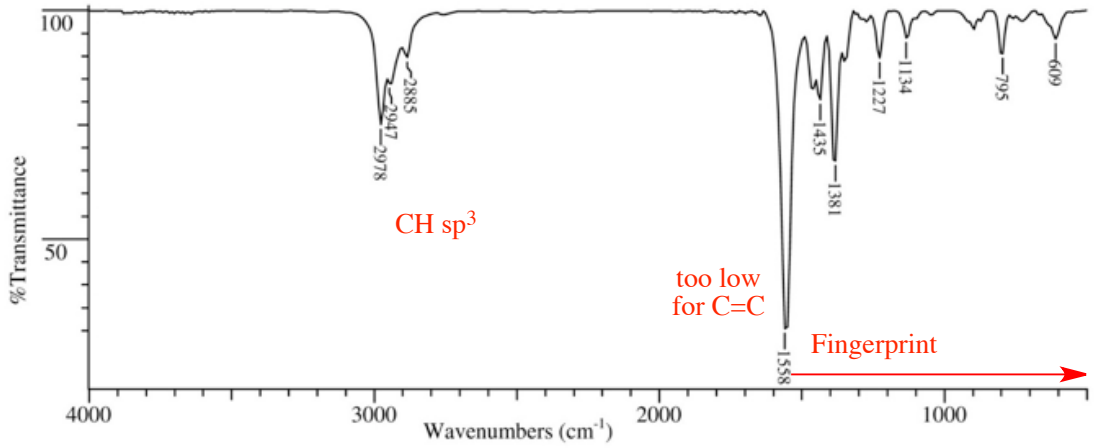
Molecule:

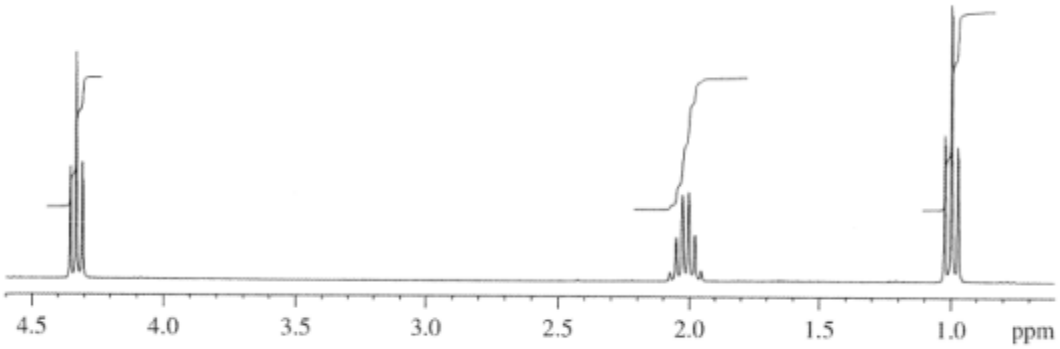


molecular formula: $C_6H_{12}O$ = all atoms and the 1 unsaturation accounted for.

12. An unknown compound, **I**, has the formula $C_3H_7NO_2$. Elucidate the structure of **I** by analyzing its IR and ^1H NMR spectra, shown below.

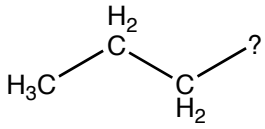
D.U. = (2x3+2+0-7-0)/2 = 1 --> 1 ring or one double bond (not a C=O or C=C).





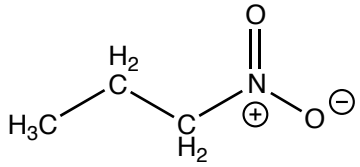
Signal	δ	Integration	Multiplicity	Comments
A	4.4	2H	triplet n=2	CH_2 next to another CH_2 next to very strong é-withdrawing group. N or O
B	2.0	2H	sextuplet n=5	CH_2 next to 5 H. slightly deshielded.
C	1.0	3H	triplet n=2	CH_3 next to CH_2

Fragments:



what is left? 1 unsaturation, 1 N and 2 O : NO_2

Molecule:



positive charge accounts for the chemical displacement of CH_2 (A).