HOMEWORK PROBLEMS: IR SPECTROSCOPY AND 13C NMR

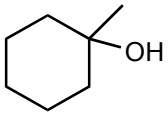
1. You find a bottle on the shelf only labeled C_3H_6O. You take an IR spectrum of the compound and find major peaks at 2950, 1720, and 1400 cm^{-1}. Draw a molecule that might be the compound in the bottle.

The peak at 1720 indicates a C=O bond (carbonyl). One possibility is acetone: 

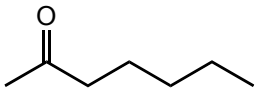
2. For each of the following compounds, draw an isomer that changes the functional groups in the molecule. Name all the functional groups. Indicate the major absorbances you would expect to find in the IR spectrum for each isomer, and highlight how you could use IR to tell them apart.

In each case I have shown just one possibility. Others will exist. Remember to check the molecular formulas to make sure you have created isomers.

a.

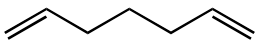


alcohol O-H at 3500

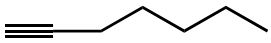


ketone C=O at 1720

b.

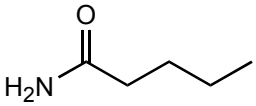


alkene C=C bands near 1600

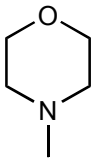


terminal alkyne C≡C band near 2200
alkyne C-H near 3300

c.

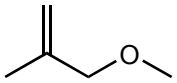


amide N-H bands near 3300
C=O band near 1680

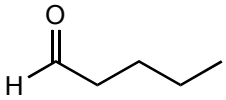


amine and ether
C-N and C-O bands in the fingerprint region

d.

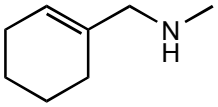


alkene and ether
C=C bands near 1650
C-O bands in the fingerprint region

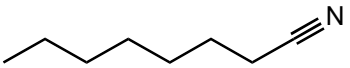


aldehyde C-H at 2700, 2900
C=O at 1730

e.

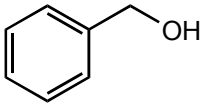


amine and alkene
C-N bands in the fingerprint region
C=C bands near 1650

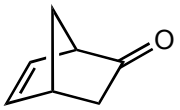


nitrile C≡N at 2250

f.



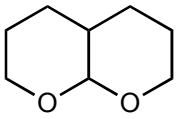
alcohol (and aromatic ring)
O-H at 3500



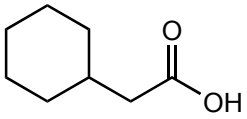
ketone (and alkene)
C=O at 1720

I got a little crazy on this one. Note that it would not be easy to identify the difference between C=C bonds of the aromatic ring in the first compound and the alkene in the second.

g.

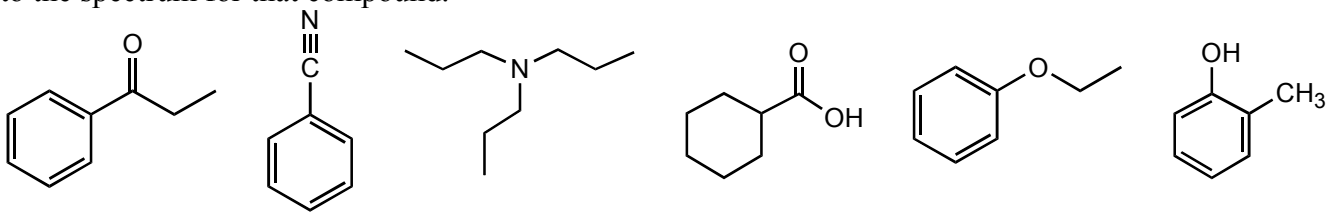


ether C-O bands in the fingerprint region
(actually a special kind of ether-like functionalgroup called an acetal)

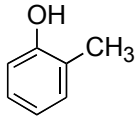


carboxylic acid
O-H at 2500-3200
C=O at 1720

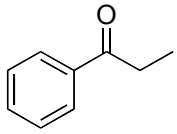
3. For the three infrared spectra below, pick out the molecule from the list that would correspond to the spectrum for that compound.



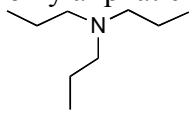
a. With O-H stretch at 3414 cm^{-1}, aliphatic C-H, and aromatic/vinyl C-H (below and above 3000 cm^{-1}), must be:



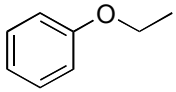
b. With C=O peak at 1687cm^{-1} (C=O in conjugation), aliphatic C-H, and aromatic/vinyl C-H (below and above 3000 cm^{-1}), must be:



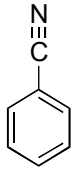
c. With only aliphatic C-H, must be:



because no aromatic/vinyl C-H (above 3000cm^{-1}), can't be:

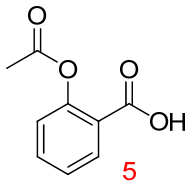


because no C≡N at about 2200 cm^{-1}, can't be:

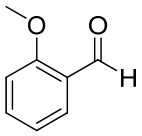


4. For the infrared spectra below (numbers 1-6; and letters A-G), pick out the molecule from the list that would correspond to the spectrum for that compound. (note D and E very similar)

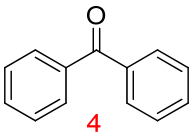
Spetra 1-6



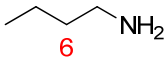
5



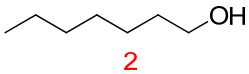
3



4

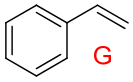


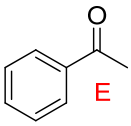
6



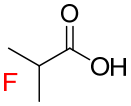
2


1

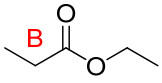

G



E

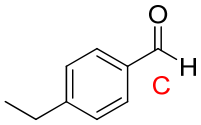


F

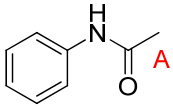


B

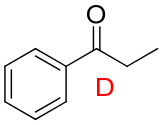
Spetra A-G



C

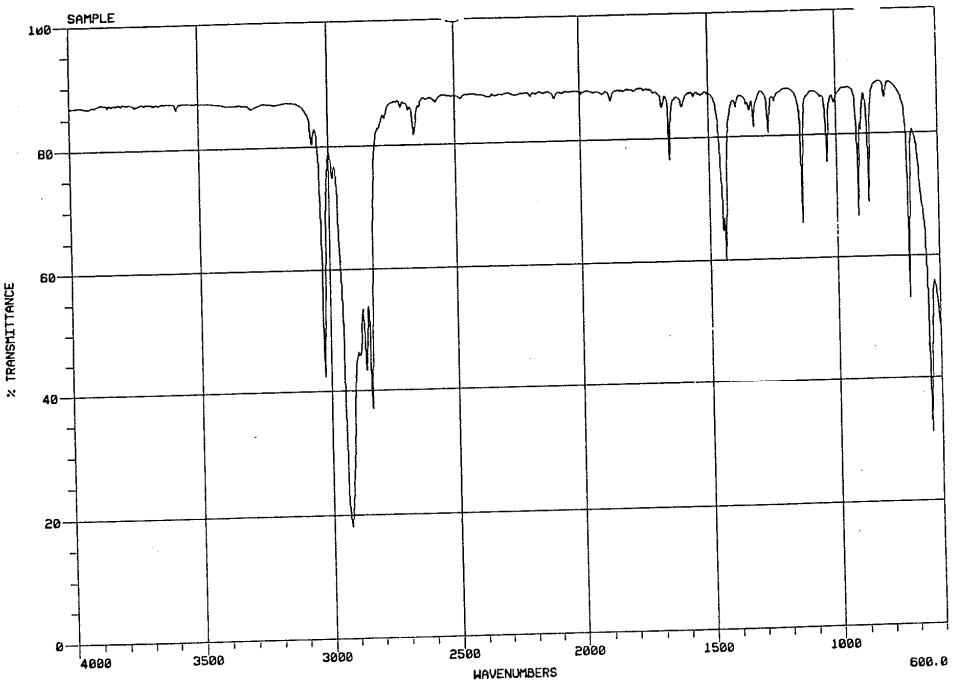


A

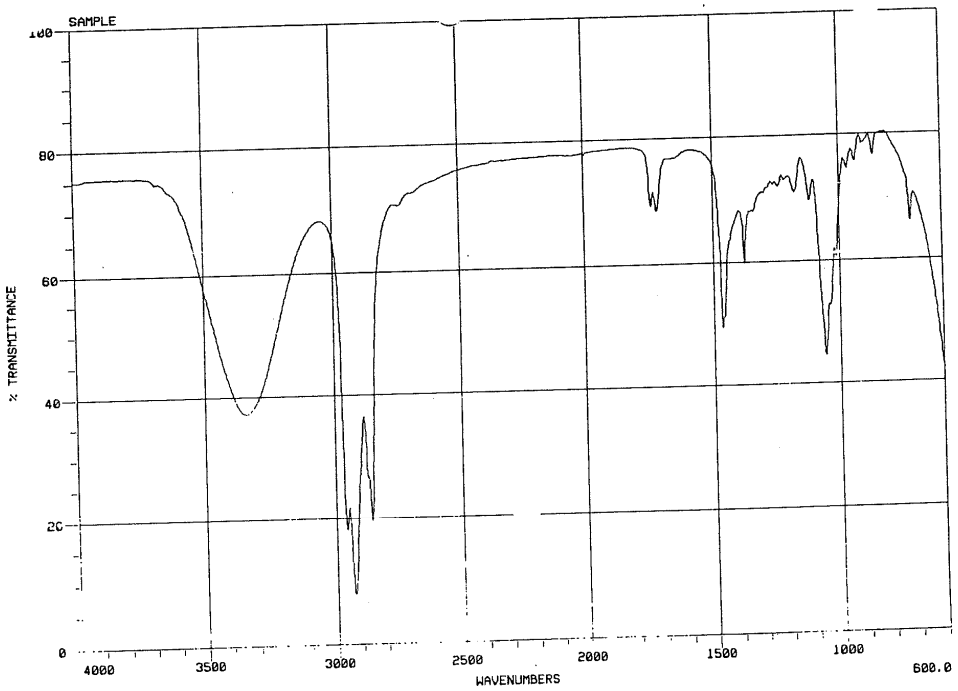


D

1.



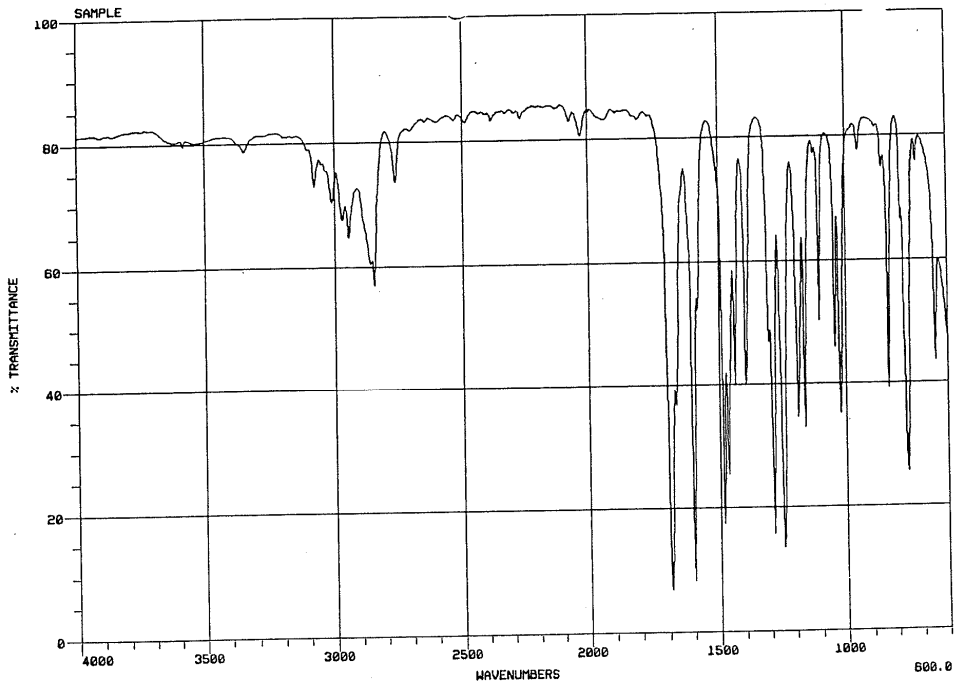
2.



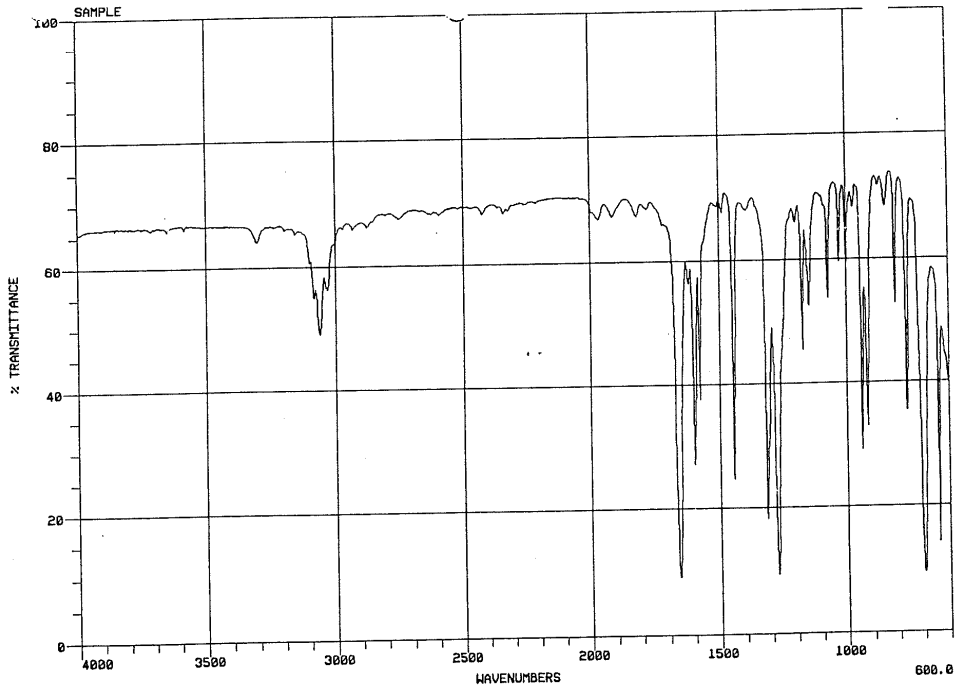
Spectra 1: alkene C-H stretch above 3000cm^{-1}, alkane C-H stretch below 3000cm^{-1}, weak C=C near 1650cm^{-1}

Spectra 2: O-H stretch near 3350cm^{-1}, alkane C-H below 3000cm^{-1}

3.



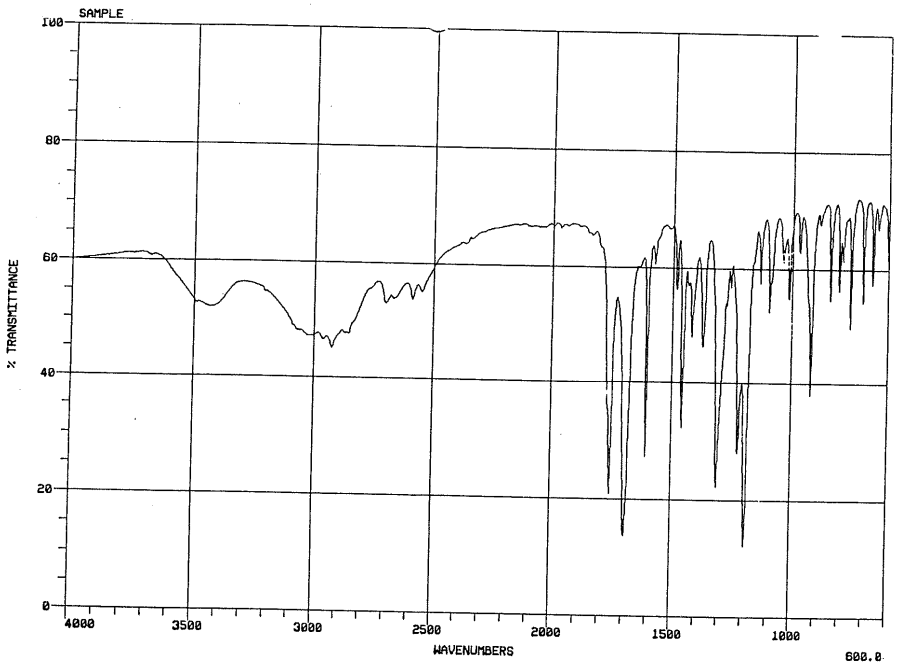
4.



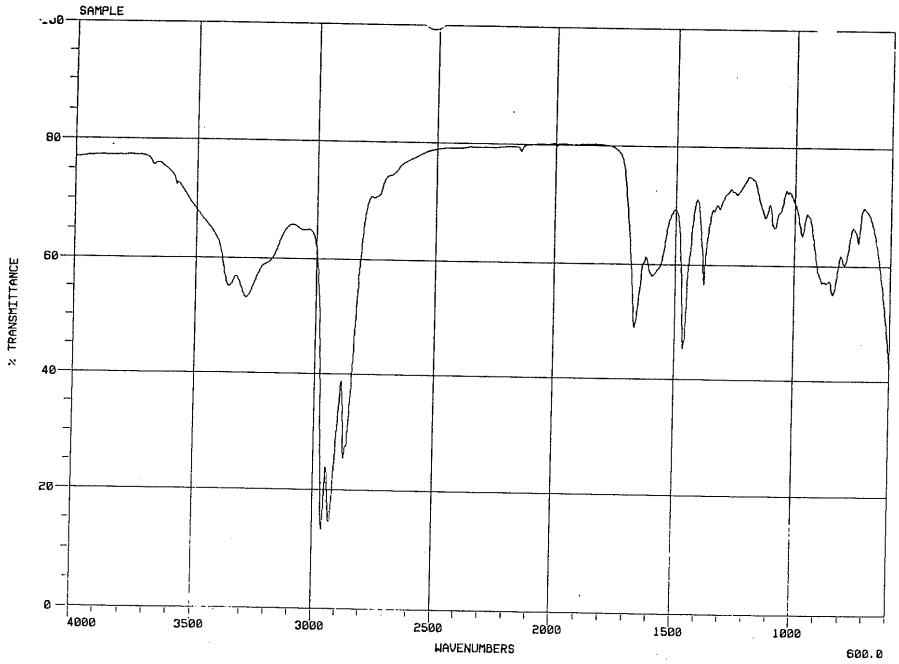
Spectra 3: alkene C-H stretch above 3000cm^{-1}, alkane C-H stretch below 3000cm^{-1}, aldehyde C-H stretch near 2700cm^{-1}, C=O 1700cm^{-1}, weak C=C near 1600 and 1500cm^{-1}

Spectra 4: alkene C-H above 3000cm^{-1}, C=O just below 1700cm^{-1} (conjugated)

5.



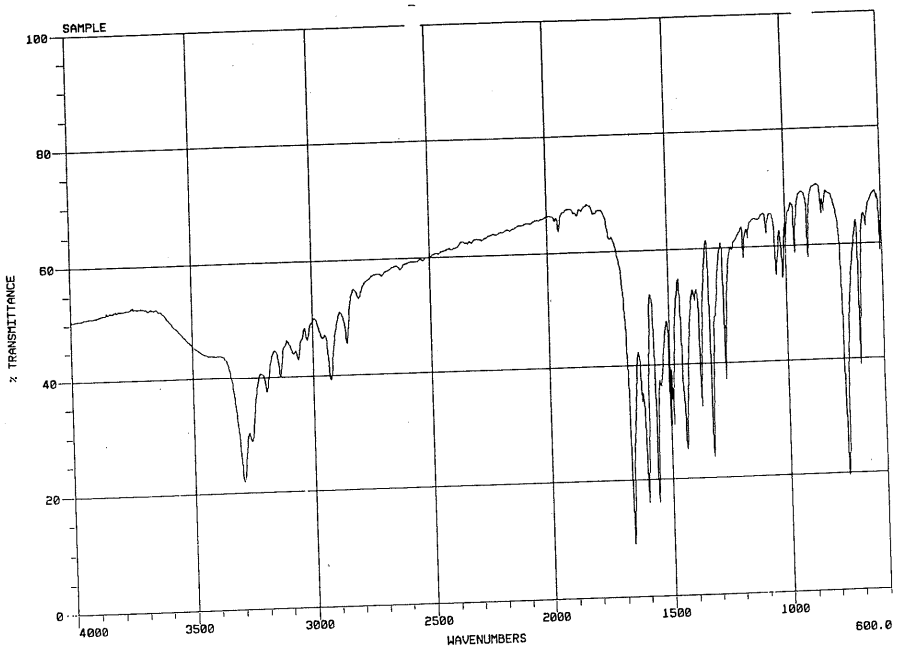
6.



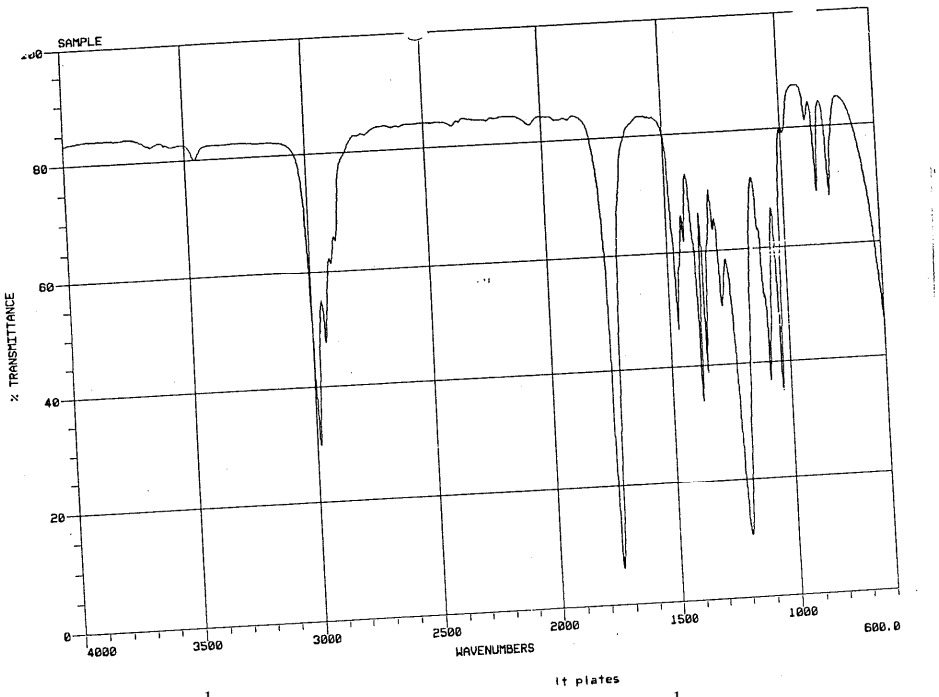
Spectra 5: very broad O-H of acid 3500-2500cm^{-1}, alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1} harder to see with broad acid O-H, two C=O stretches 1750cm^{-1} and 1700cm^{-1}, weak C=C near 1600 and 1450cm^{-1}

Spectra 6: primary amine has 2 N-H stretches near 3300cm^{-1}, alkane C-H below 3000cm^{-1}

A.



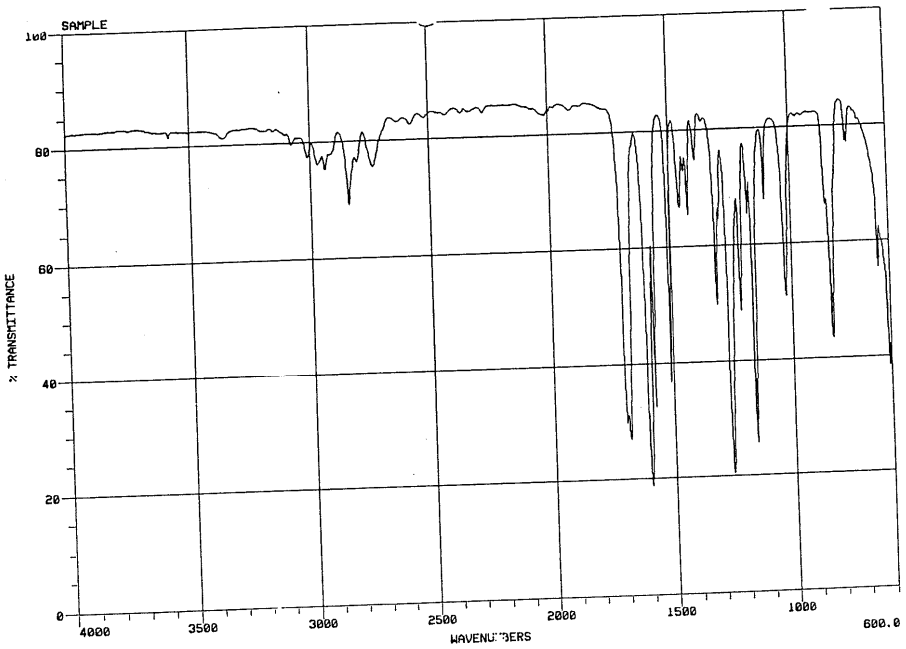
B.



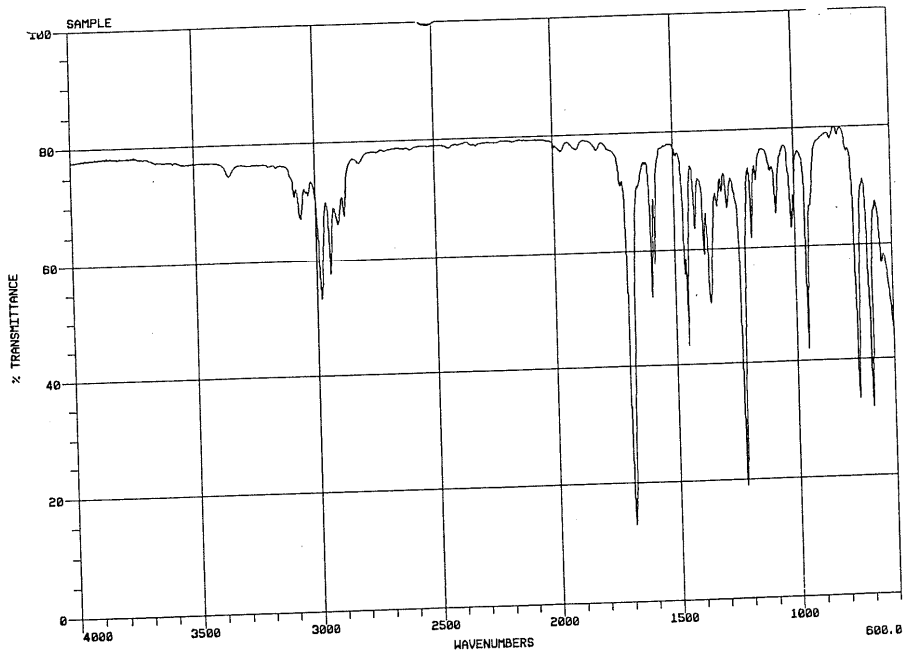
Spectra A: N-H of amide 3300cm^{-1}, alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1}, C=O stretch below 1700cm^{-1}, C=C near 1600 and 1550cm^{-1}

Spectra B: alkane C-H below 3000cm^{-1}, C=O stretch above 1700cm^{-1}, C-O stretch near 1200cm^{-1}

C.



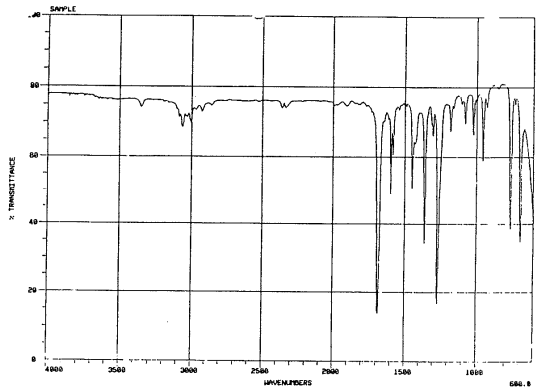
D.



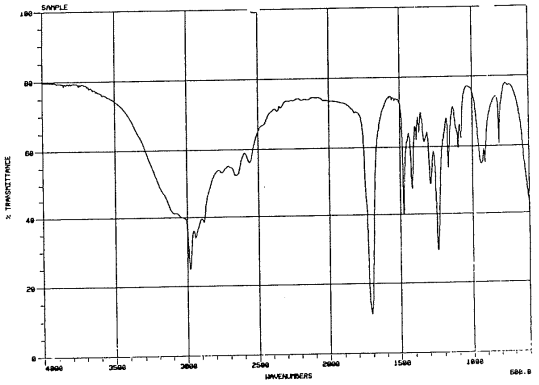
Spectra C: weak alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1}, aldehyde C-H stretch near 2750cm^{-1}, C=O stretch at 1700cm^{-1}, C=C near 1600 and 1500cm^{-1}

Spectra D: alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1}, C=O stretch just below 1700cm^{-1}, C=C near 1600 and 1450cm^{-1}

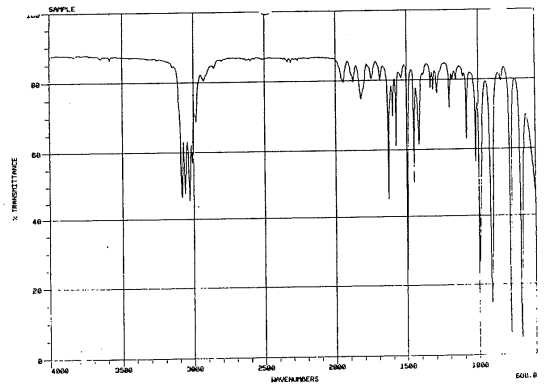
E.



F.



G.



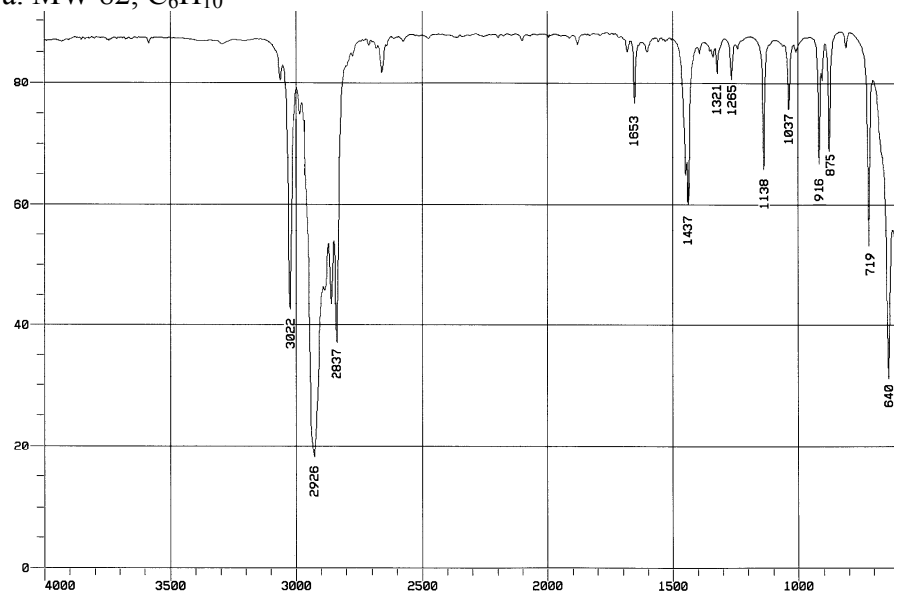
Spectra E: alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1}, C=O stretch just below 1700cm^{-1}, C=C near 1600 and 1450cm^{-1}

Spectra F: very broad O-H of acid 3500-2000cm^{-1}, alkane C-H overlapping with OH just below 3000cm^{-1}, C=O just above 1700cm^{-1}

Spectra G: alkene C-H stretch above 3000cm^{-1} (no alkane C-H stretch below 3000cm^{-1}), C=C stretches near 1650, 1600 and 1450cm^{-1}

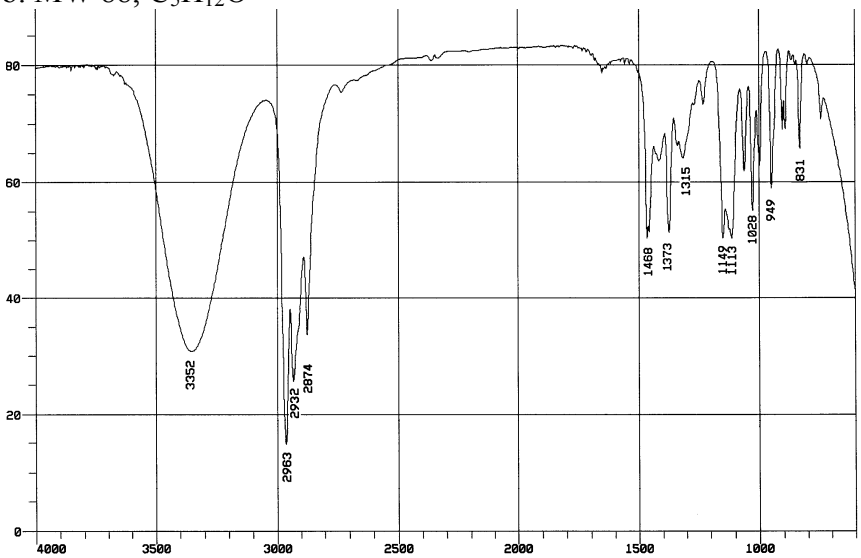
5. For each case, draw at least one possible isomer that is consistent with the molecular formula and the IR spectrum. MULTIPLE CORRECT ANSWERS, I PROVIDED ACTUAL COMPOUND IN THE ANSWER KEY.

a. MW 82, C_6H_{10}

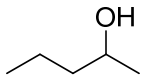


Peak at 3022 indicates C-H of alkene. no other major functional groups. Actual compound is cyclohexene.

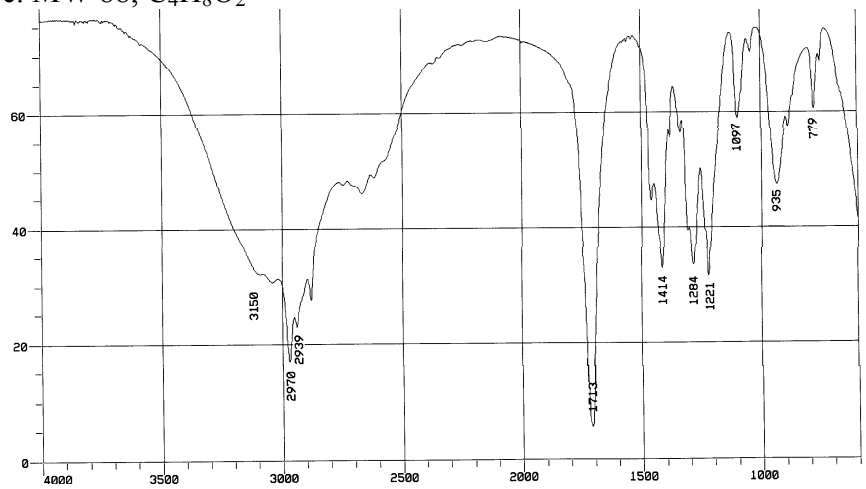
b. MW 88, $C_5H_{12}O$



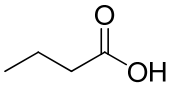
IR shows an alcohol (and not much else). Actual compound is 2-pentanol.



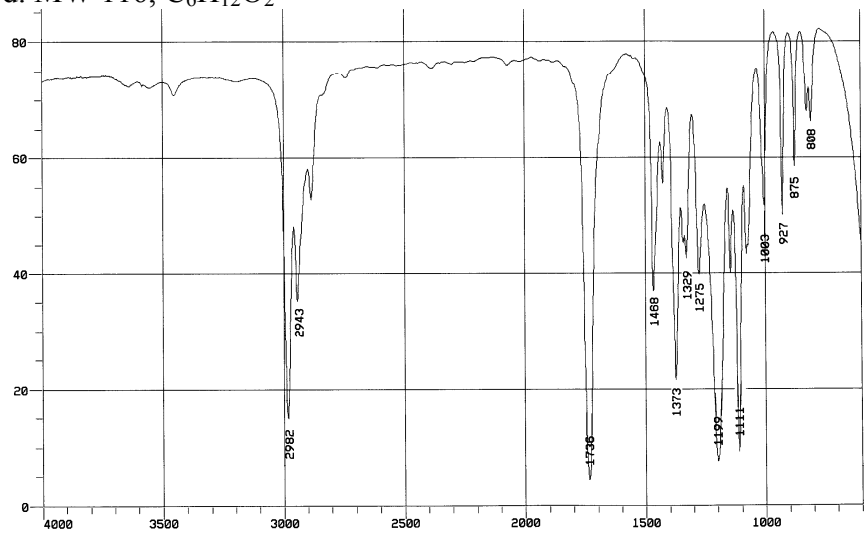
c. MW 88, $C_4H_8O_2$



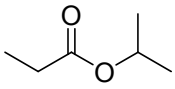
IR shows the characteristic signature of a carboxylic acid (carbonyl at 1713, broad lower energy O-H). There are only two isomers possible, the actual one is butanoic acid.



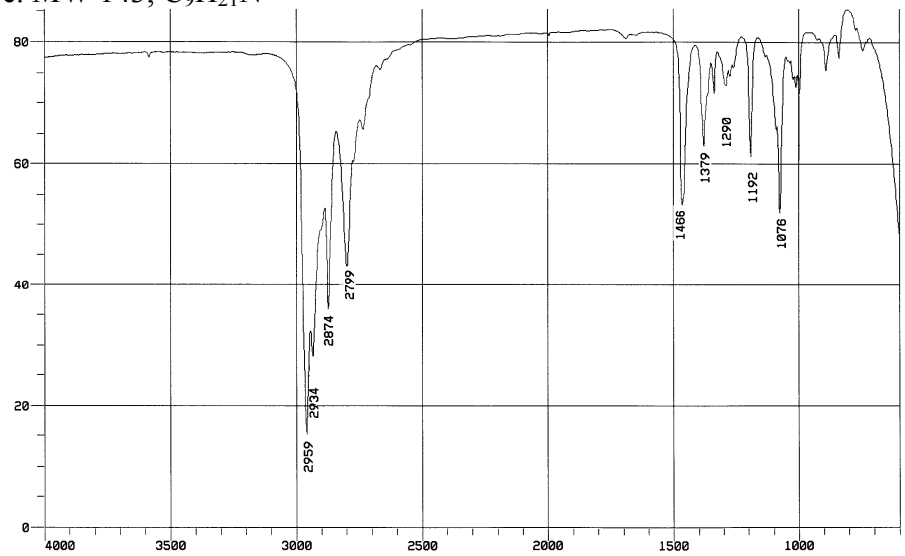
d. MW 116, $C_6H_{12}O_2$



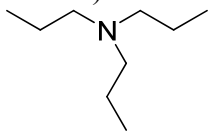
IR shows the characteristic signature of an ester (carbonyl at 1736, C-O at 1199). Many isomers possible. The actual one is isopropyl propanoate.



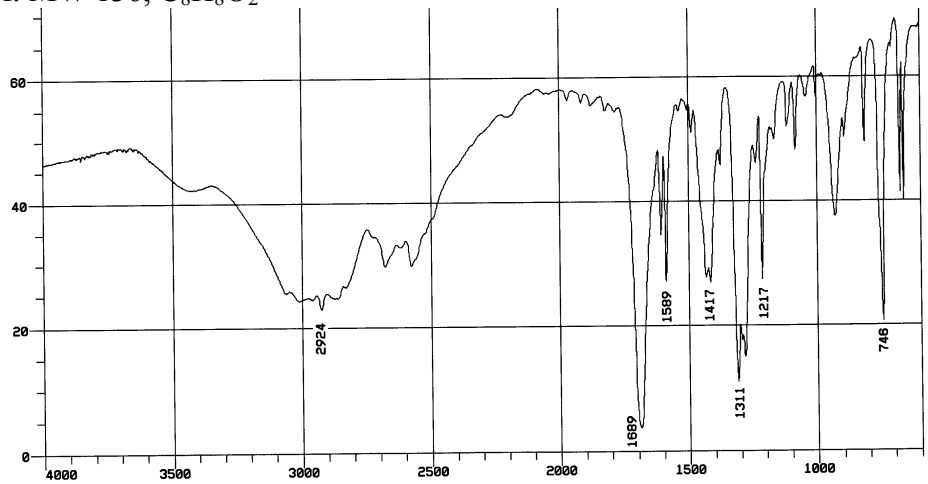
e. MW 143, $C_9H_{21}N$



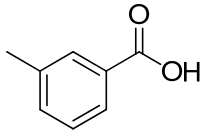
IR shows not much of anything. What do we do? This structure must be completely saturated (no multiple bonds in IR), and contain any amine isomers that have no N-H bonds (only tertiary amines). The actual compound is tripropylamine.



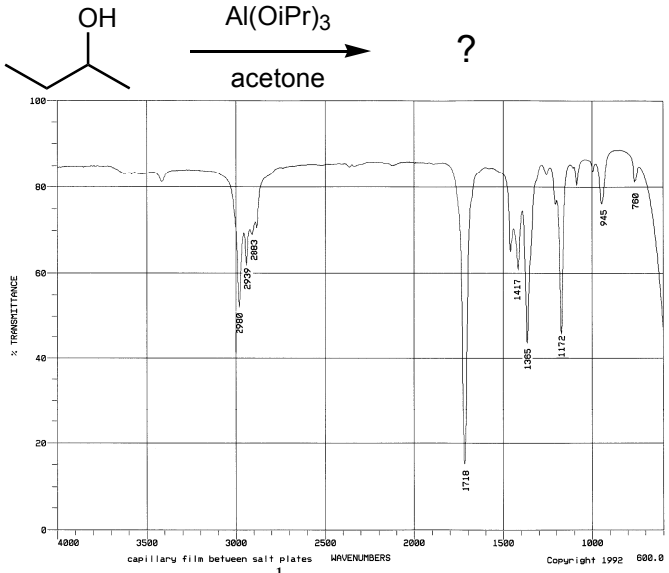
f. MW 136, $C_8H_8O_2$



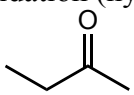
IR looks like a carboxylic acid (carbonyl plus broad, low energy O-H). However, the value for the carbonyl (1689) is lower than expected, which leads one to suspect conjugation. Thinking conjugation and five degrees of unsaturation, I jump to a benzene ring. The best isomers are all benzoic acids, and the actual one is 3-methyl benzoic acid.



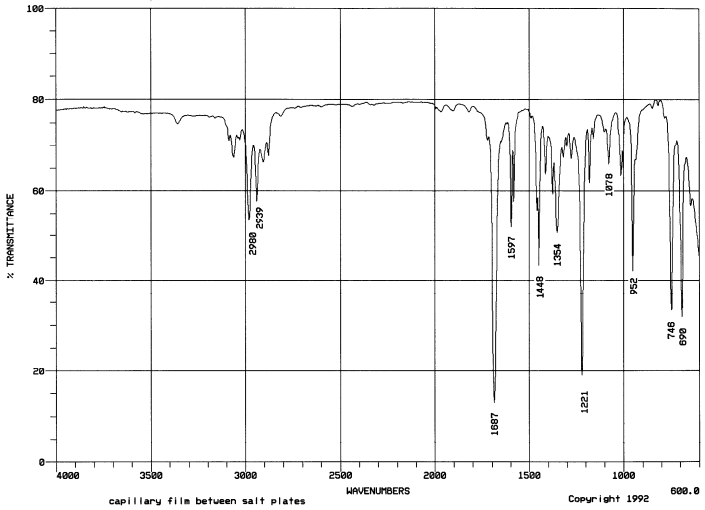
6. The product of the reaction below gives the IR spectrum shown. Although you are unfamiliar with the reaction, use your knowledge of IR spectroscopy to predict a likely product. (Note: the number of carbon atoms remained the same.)



Carbonyl at 1718 cm^{-1}, ketone or aldehyde, but no aldehyde C-H stretch at 2750 and 2850 cm^{-1}. This oxidation (hydrogen content is reduced) must be yielding:



7. Is the following compound an aldehyde, ketone, ester, or carboxylic acid? Explain the location of the cabonyl in the spectrum.

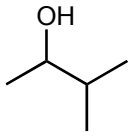


No O-H strectch, so not a carboxylic acid; no aldehyde C-H stretches; carbonyl value of 1687 cm^{-1} much too low for an ester. Must be a ketone, but the value is still low, so must be a ketone with conjugation.

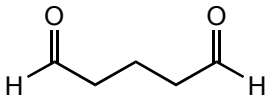
8. When a ketone is in conjugation with a π-bond, the C=O peak in its IR spectrum comes at a lower frequency: the peak that usually comes at 1720 cm^{-1} moves to about 1690 cm^{-1}. Where would you expect the C=O peak of an ester with conjugation to come in the IR spectrum?

Assuming a loss of 25-30 cm^{-1}, the drop would be from about 1740 cm^{-1} to maybe 1710 cm^{-1}. Note that the carbonyl stretch for an ester with conjugation appears in the same range as a ketone/aldehyde without conjugation.

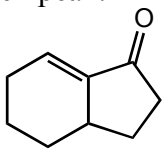
9. For each of the following compounds, indicate how many peaks you would expect in its ^{13}C NMR spectrum and the approximate location of each peak.



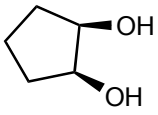
4 peaks
all in 0-100 ppm



3 peaks
2 in 0-100 ppm
1 in 160-220 ppm

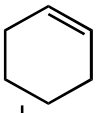
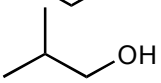
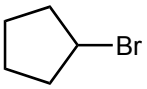
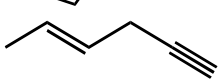
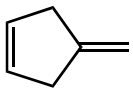


9 peaks
6 in 0-100 ppm
2 in 100-160 ppm
1 in 160-220 ppm

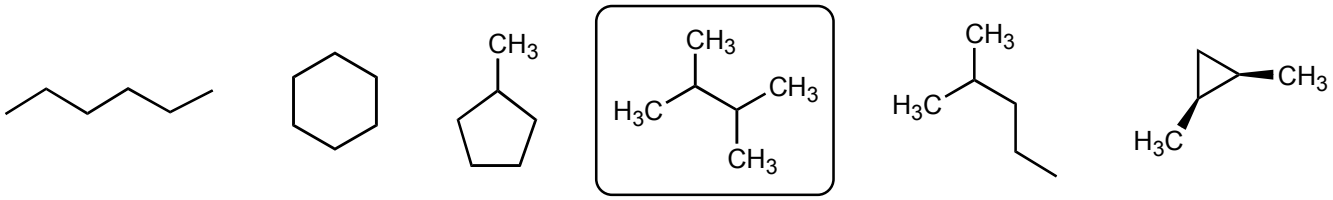


3 peaks
all in 0-100 ppm

10. For each set below, draw an isomer of the given formula that would show the given number of peaks in its ^{13}C NMR spectrum.
I have given one possibility for each case -- there are often others.

formula	^{13}C NMR peaks	
C_3H_6	1	
C_6H_{10}	3	
$C_4H_{10}O$	3	
C_5H_9Br	3	
C_6H_8	6	
C_6H_8	4	

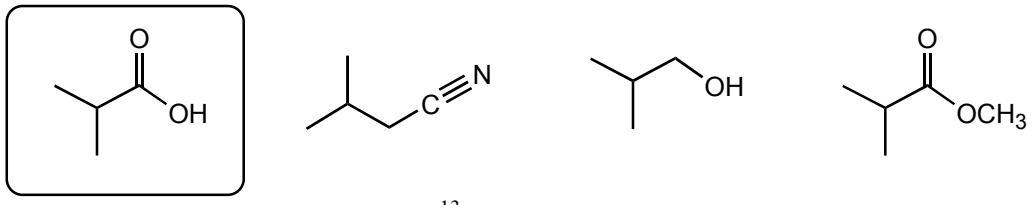
11. You have been given a sample of one of the C6 compounds shown below. You take the ^{13}CNMR and find 2 peaks in the spectrum. Which compound do you have?



3 peaks 1 peak 4 peaks **2 peaks!!** 5 peaks 3 peaks

12. You have an unknown that you are told is one of the four compounds below, and it exhibits the following spectral data. Which compound do you have?
^{13}C NMR: 3 peaks
IR major peaks:

- 1710cm^{-1} Large and Sharp
- 3300cm^{-1} Large and Broad
- 3000cm^{-1} C-H Aliphatic (mostly obscured by 3300cm^{-1} broad peak).



C=O, O-H peaks for acid in IR; 3 peaks in ^{13}C NMR
note: even if the O-H confused you, just the C=O plus 3 NMR peaks is enough for the identification