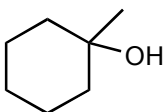


HOMEWORK PROBLEMS: IR SPECTROSCOPY AND ^{13}C NMR

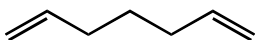
1. You find a bottle on the shelf only labeled $\text{C}_3\text{H}_6\text{O}$. You take an IR spectrum of the compound and find major peaks at 2950 , 1720 , and 1400 cm^{-1} . Draw a molecule that might be the compound in the bottle.

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.

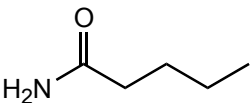
a.



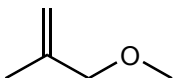
b.



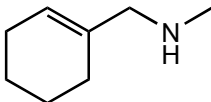
c.



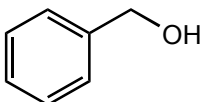
d.



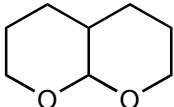
e.



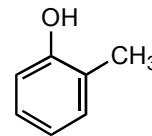
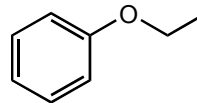
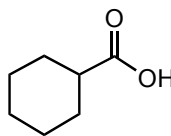
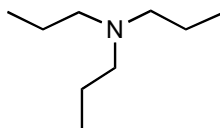
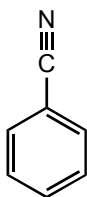
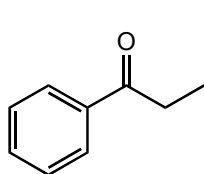
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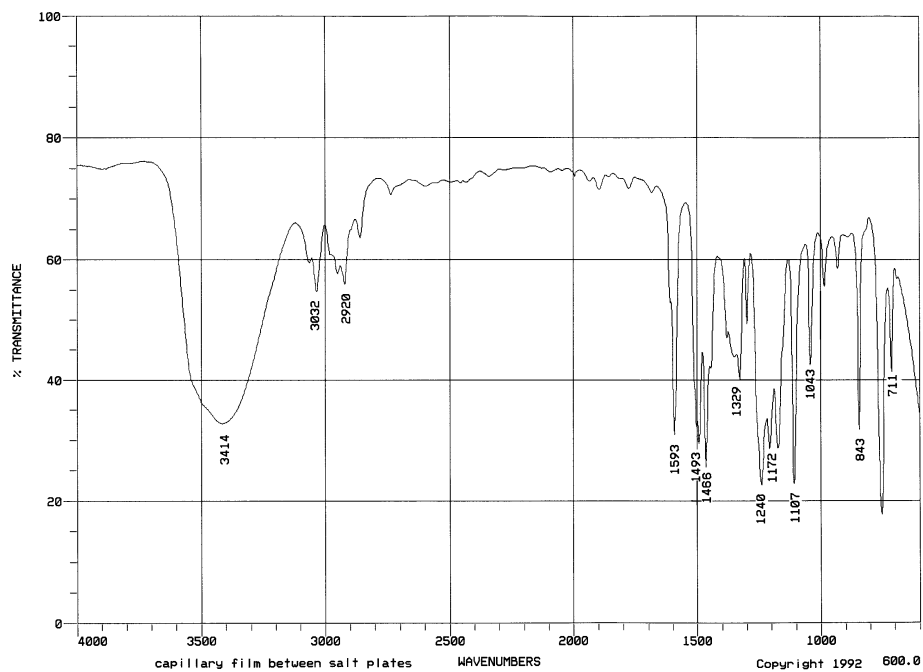
g.



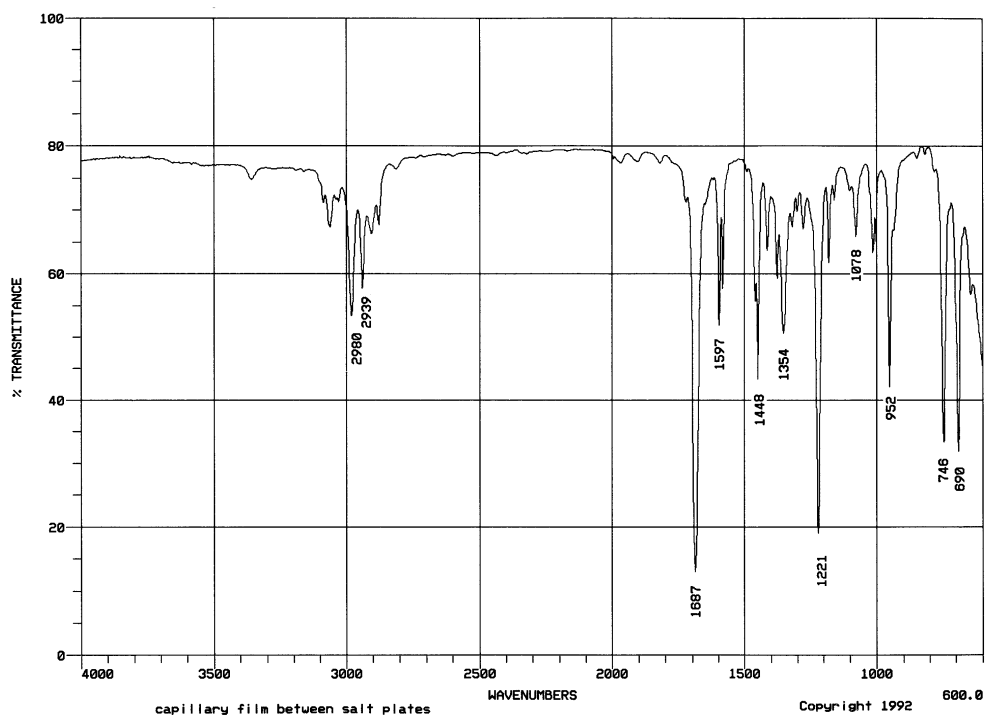
3. For the three infrared spectra below, pick out the molecule from the list that would correspond to the spectrum for that compound.



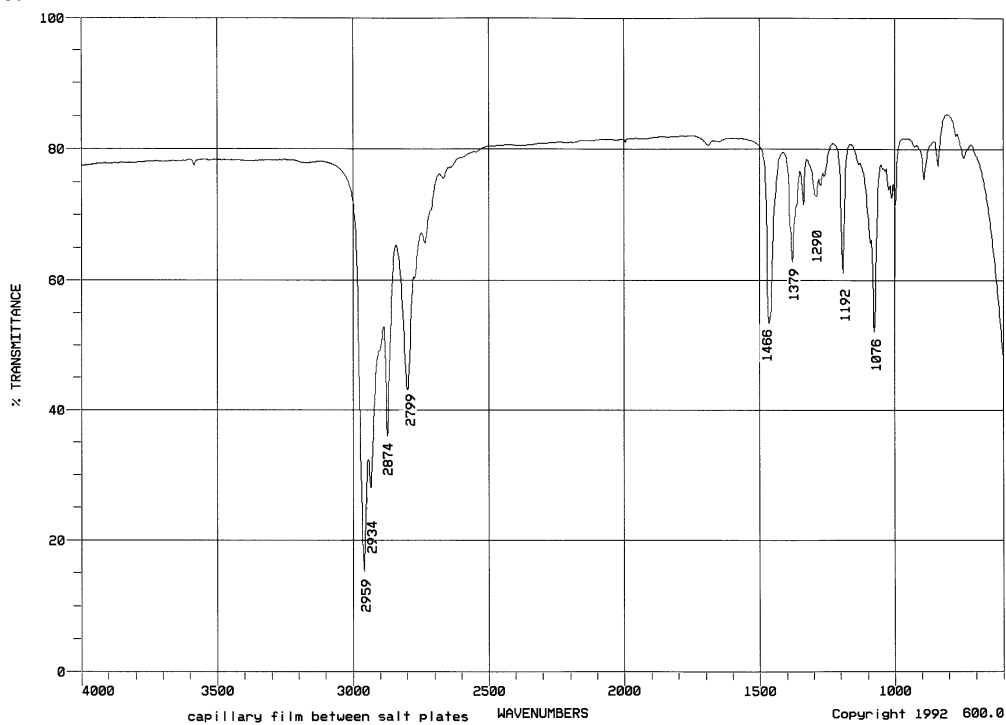
3a.



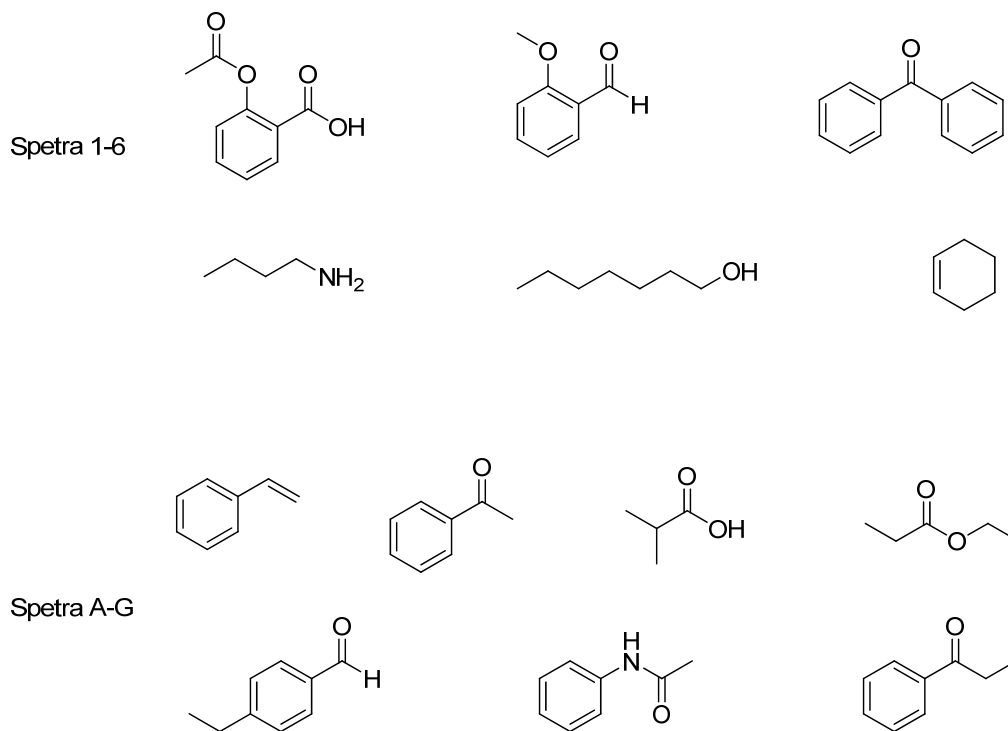
3b.



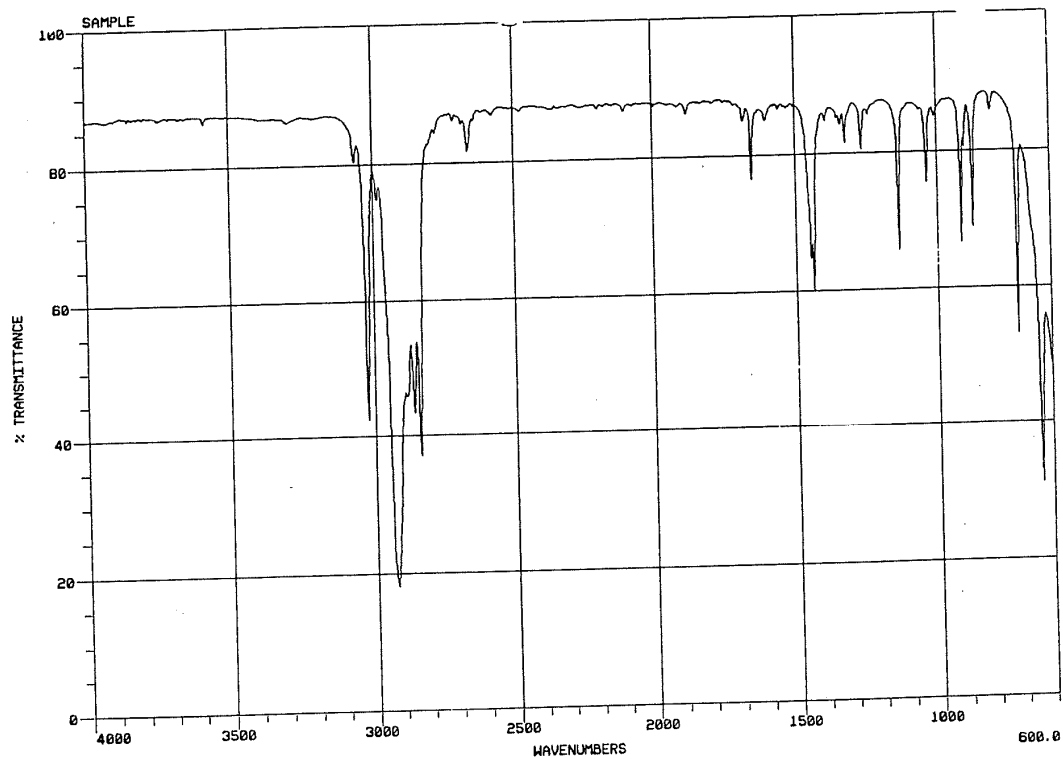
3c.



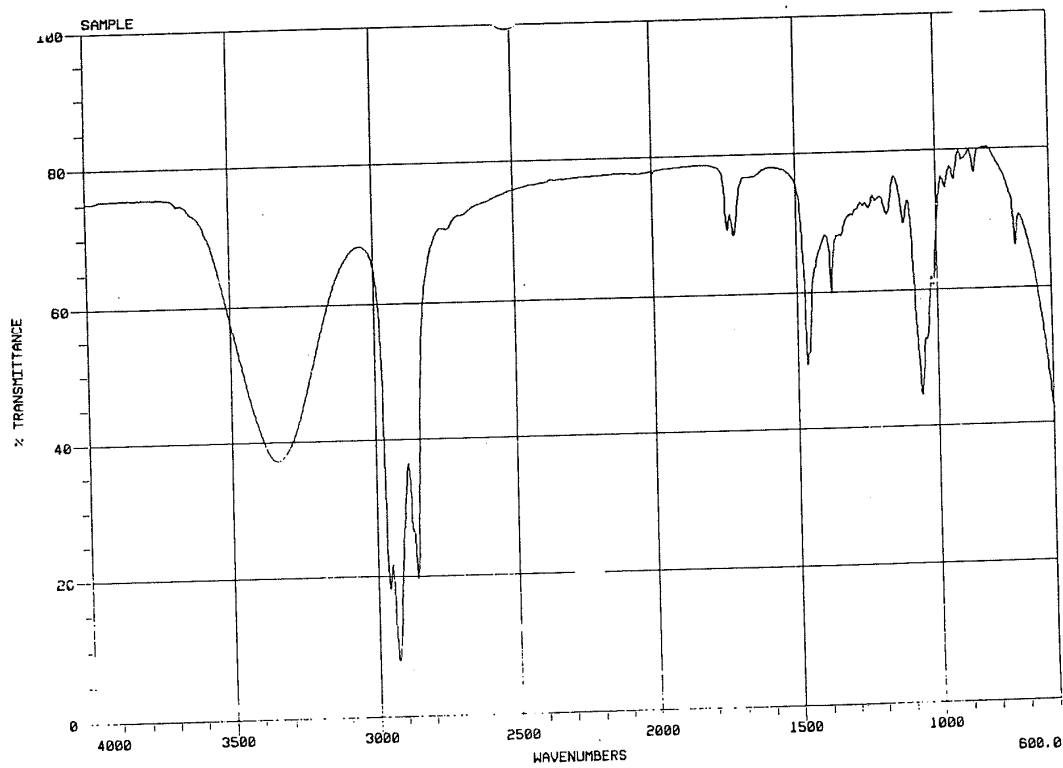
4. For the infrared spectra below (numbers 1-6; and letters A-G), pick out the molecule from the list that would correspond to the spectrum for that compound.



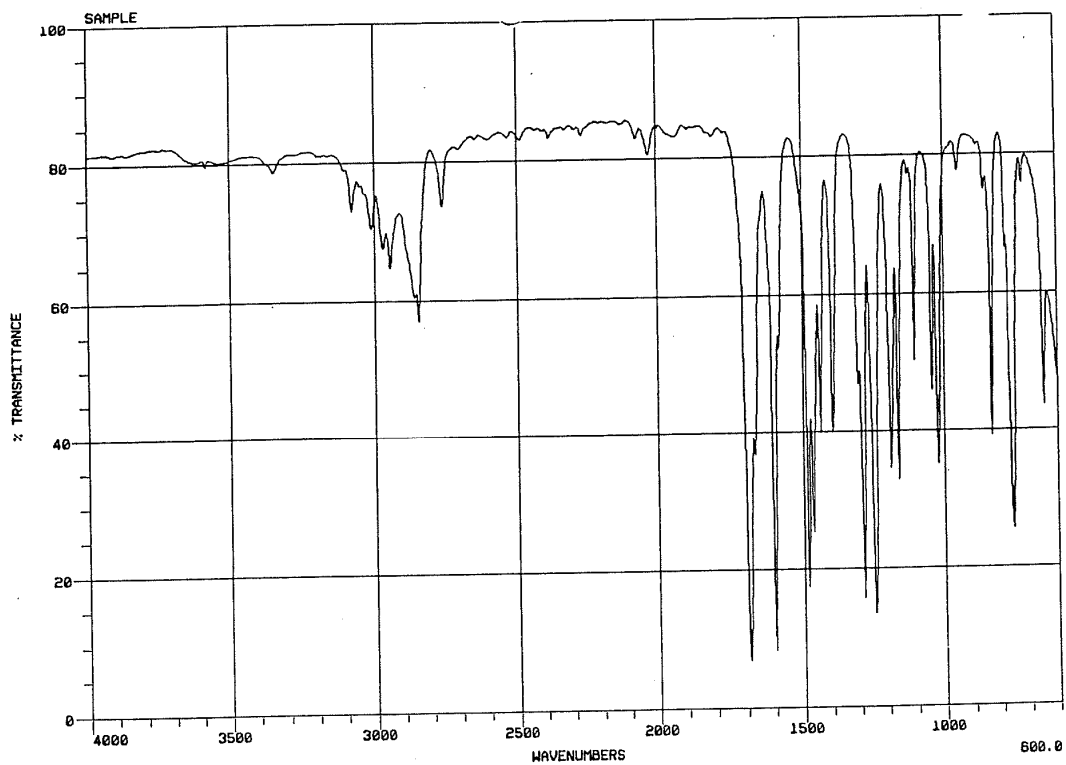
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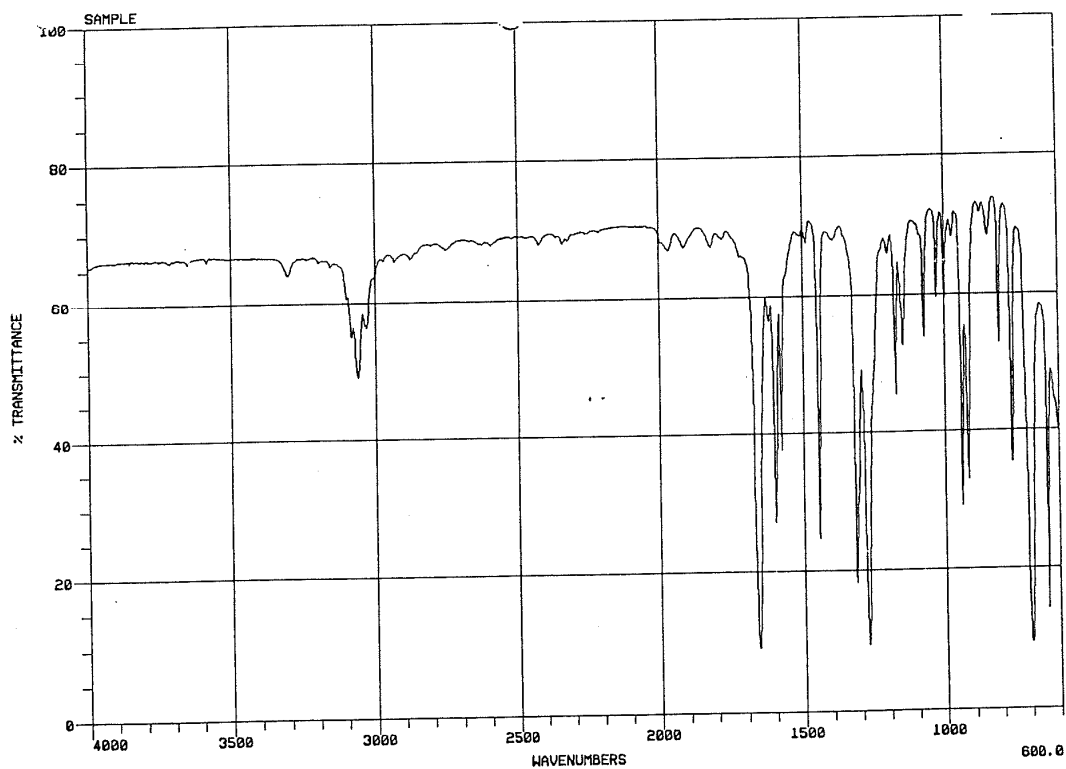
2.



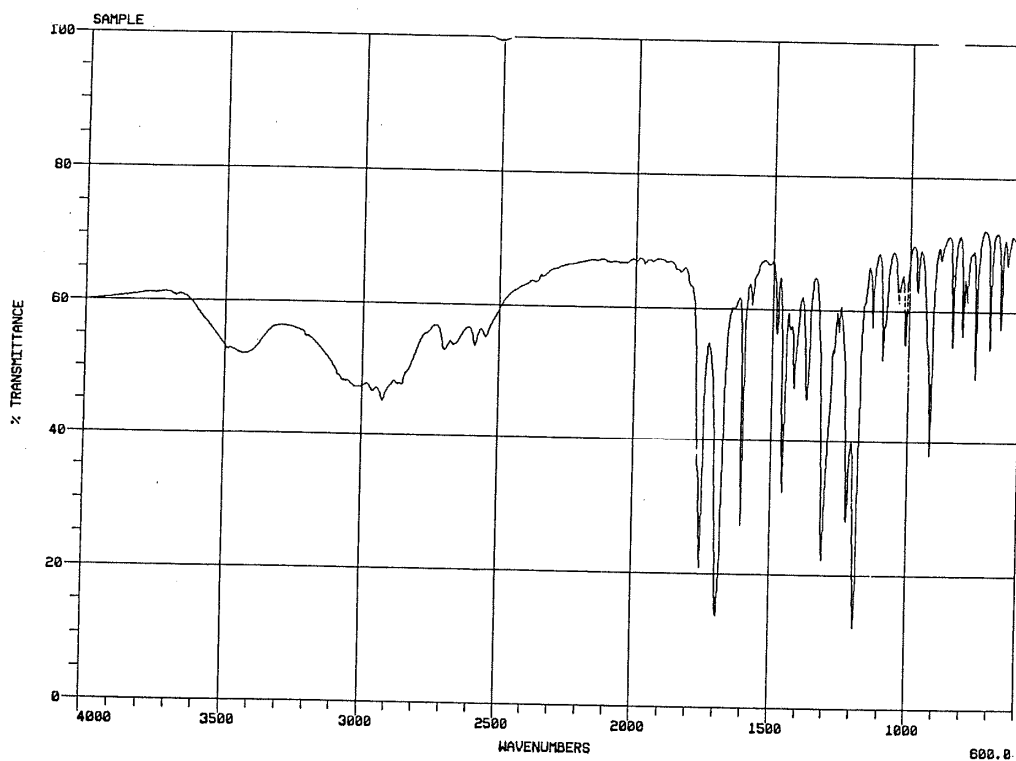
3.



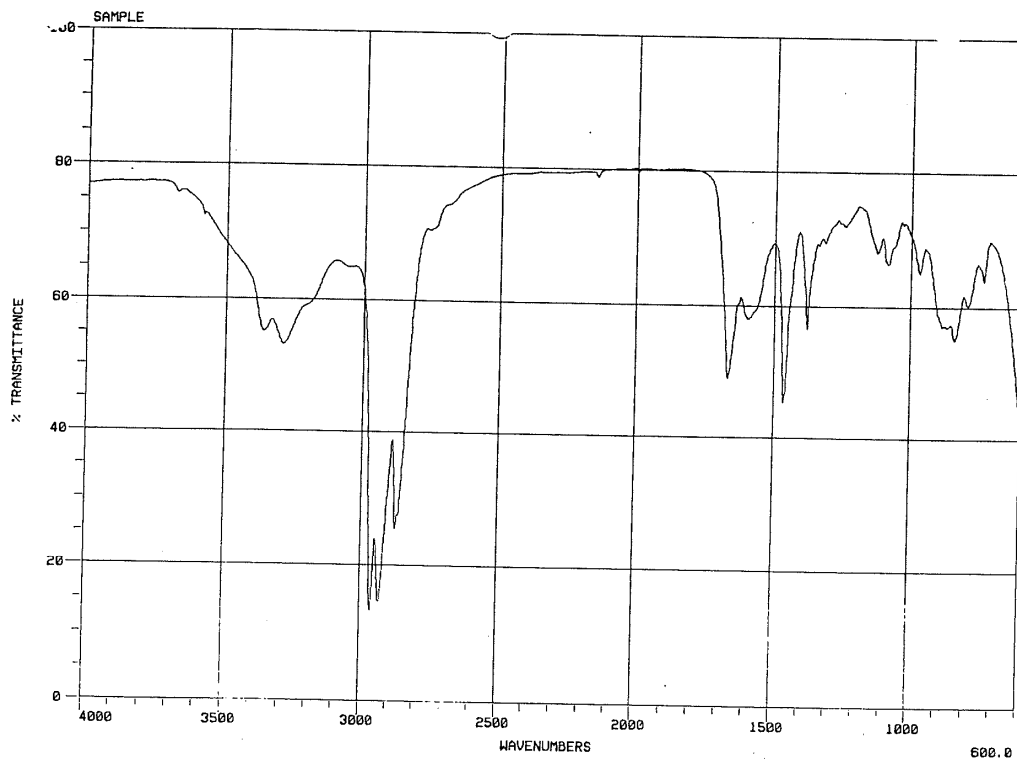
4.



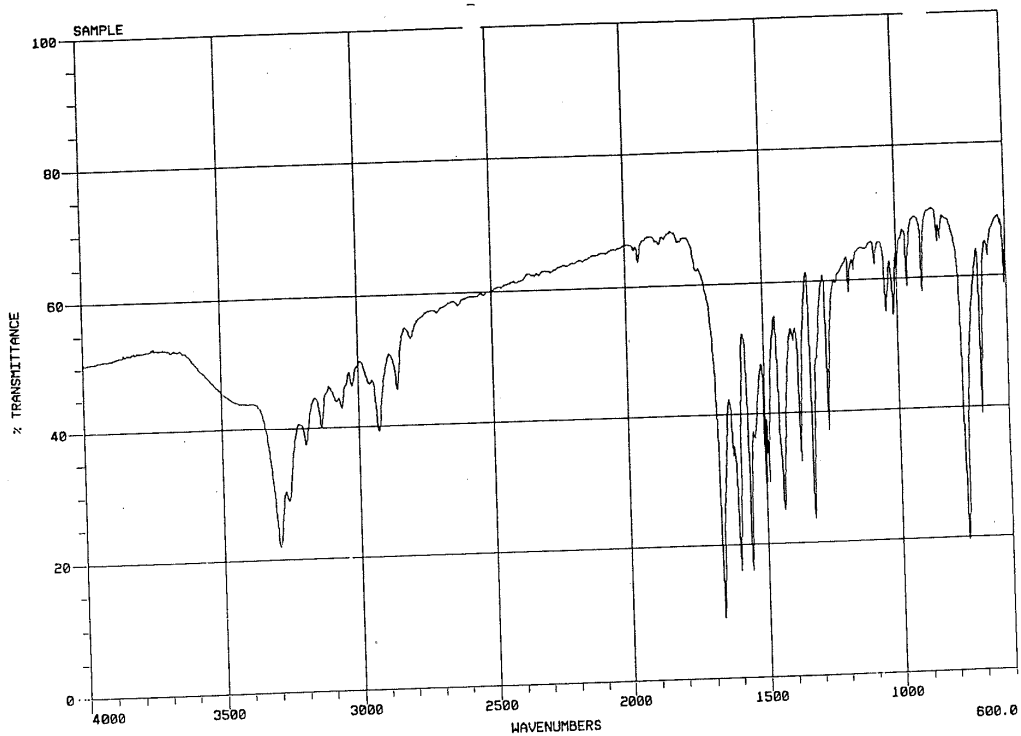
5.



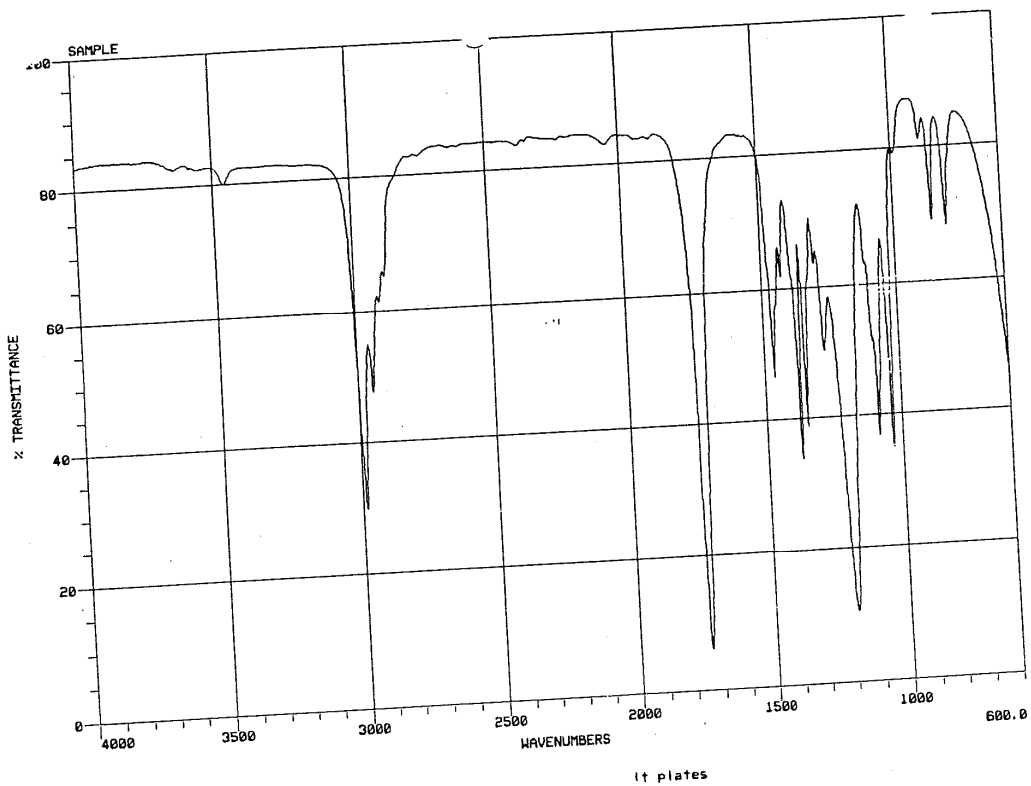
6.



A.

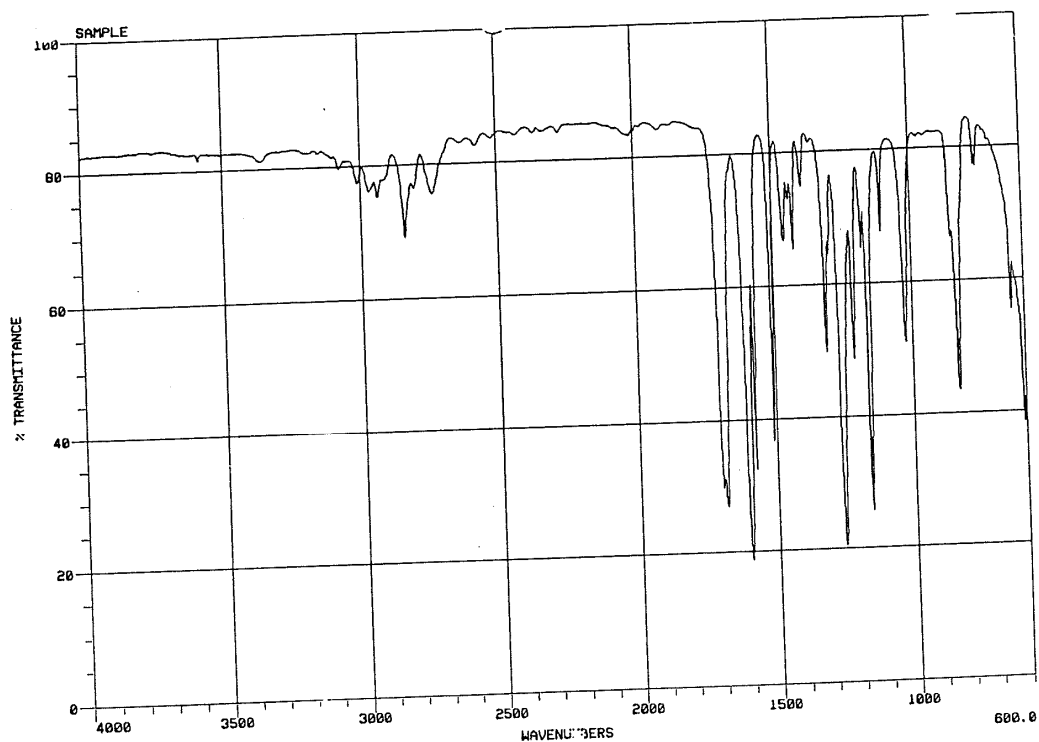


B.

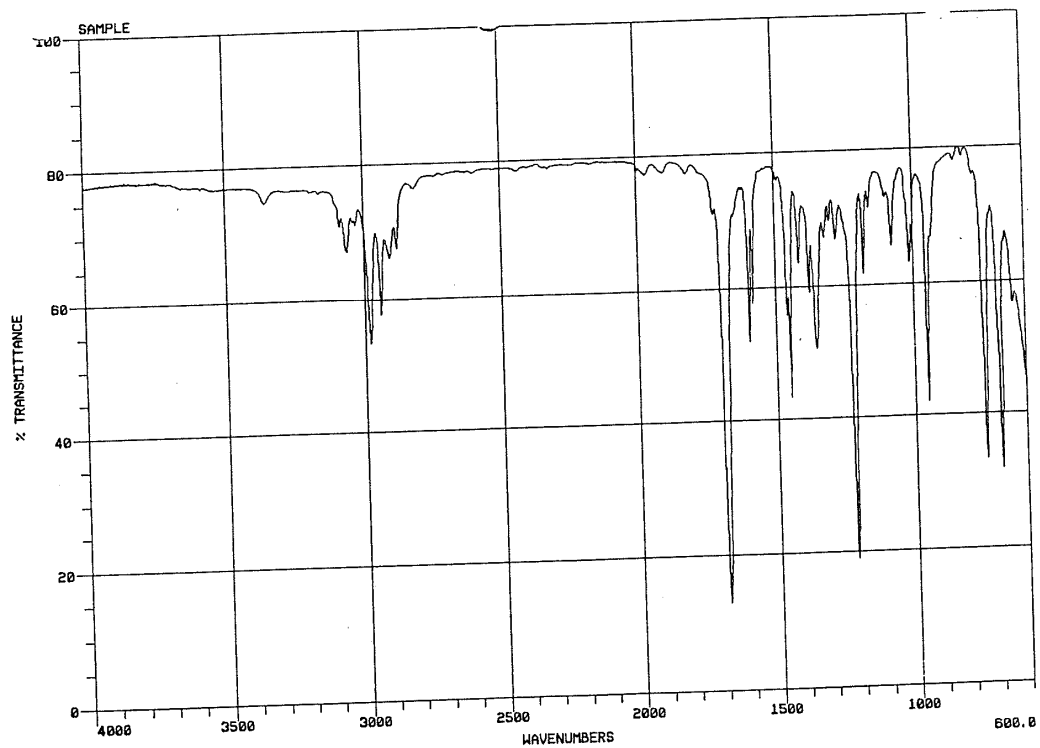


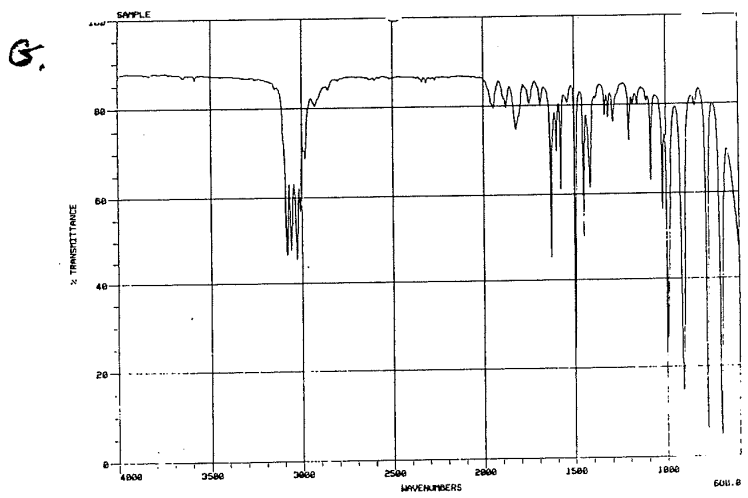
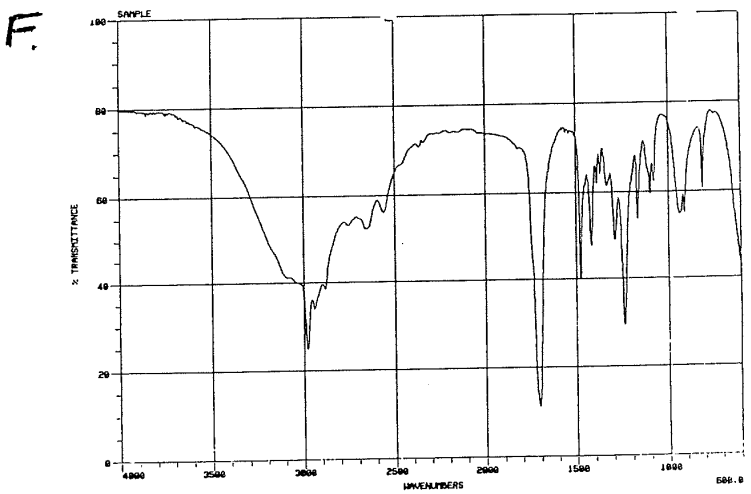
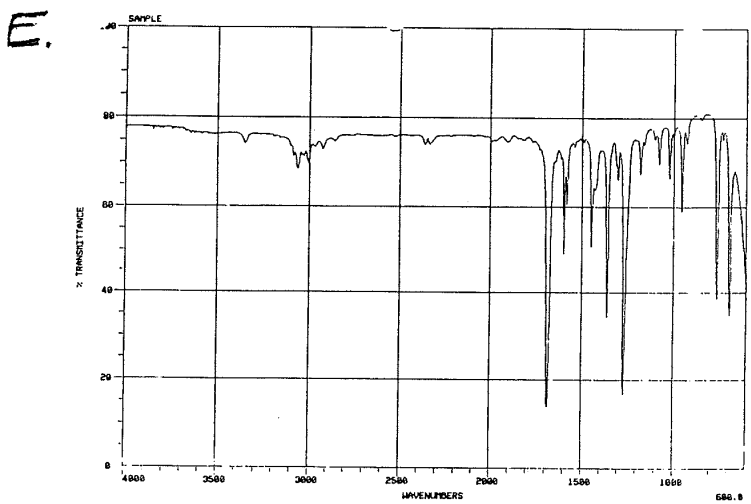
11 plates

C.



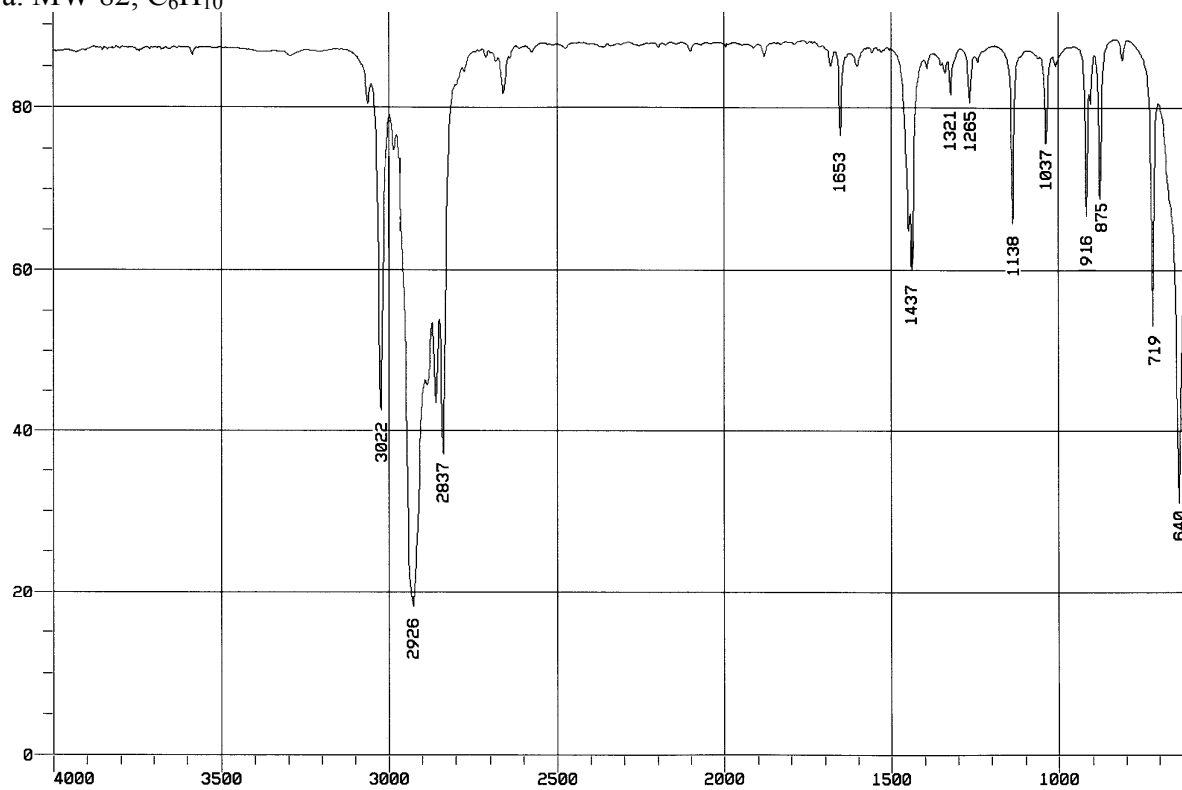
D.



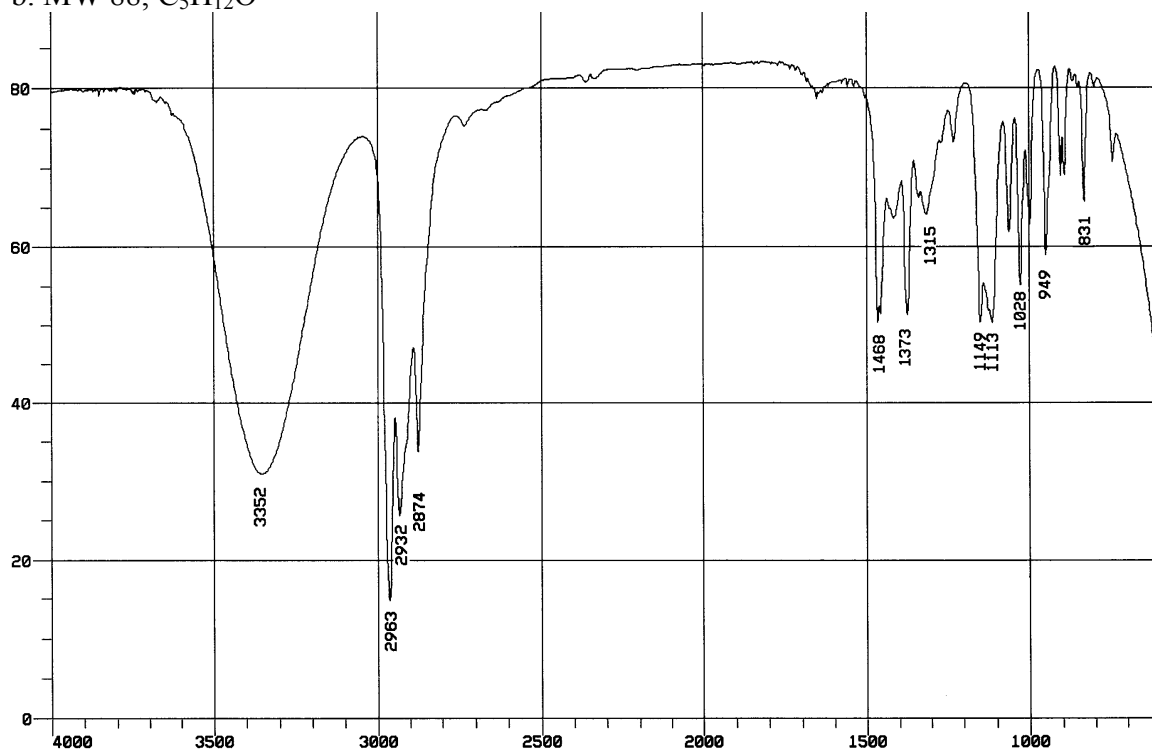


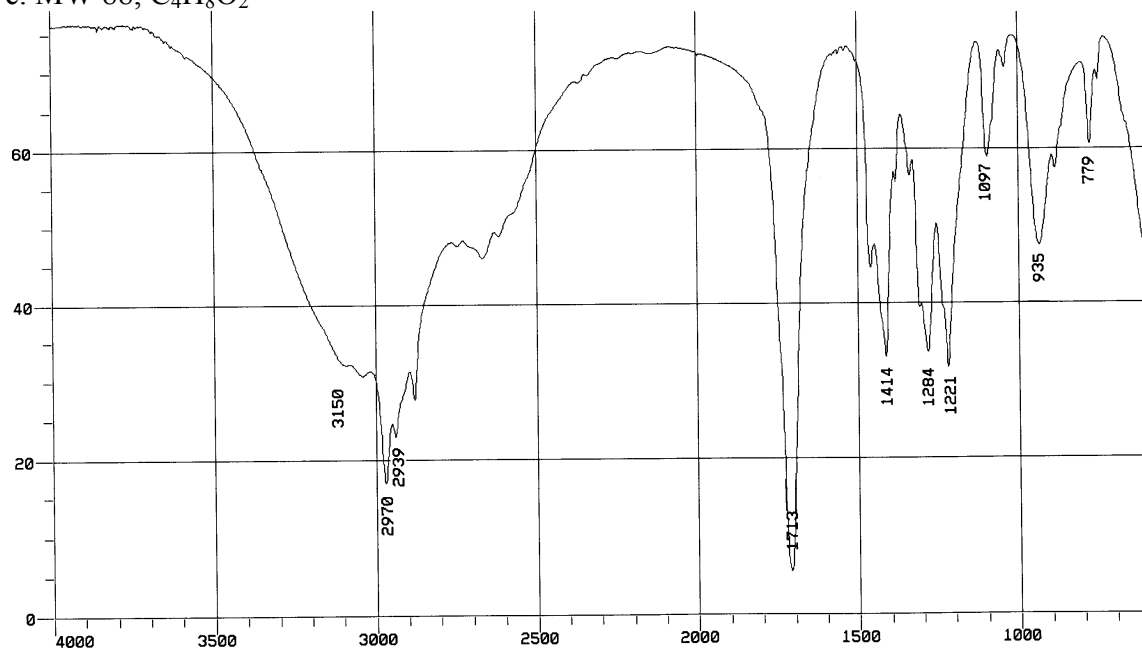
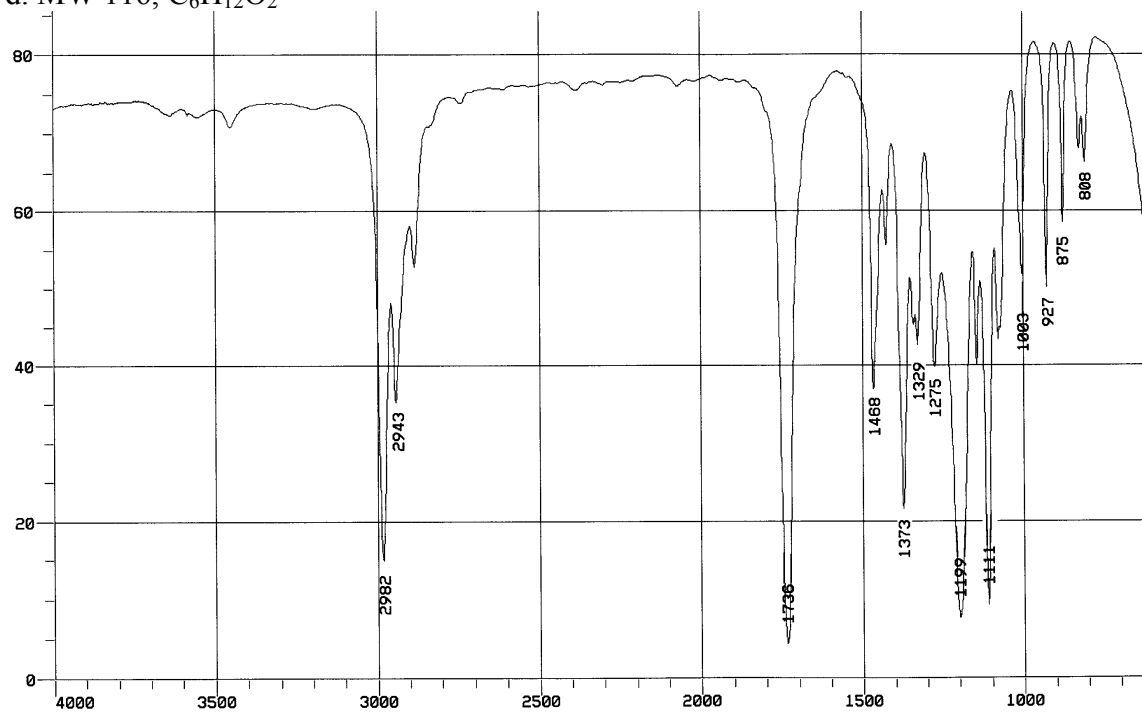
5. For each case, draw at least one possible isomer that is consistent with the molecular formula and the IR spectrum.

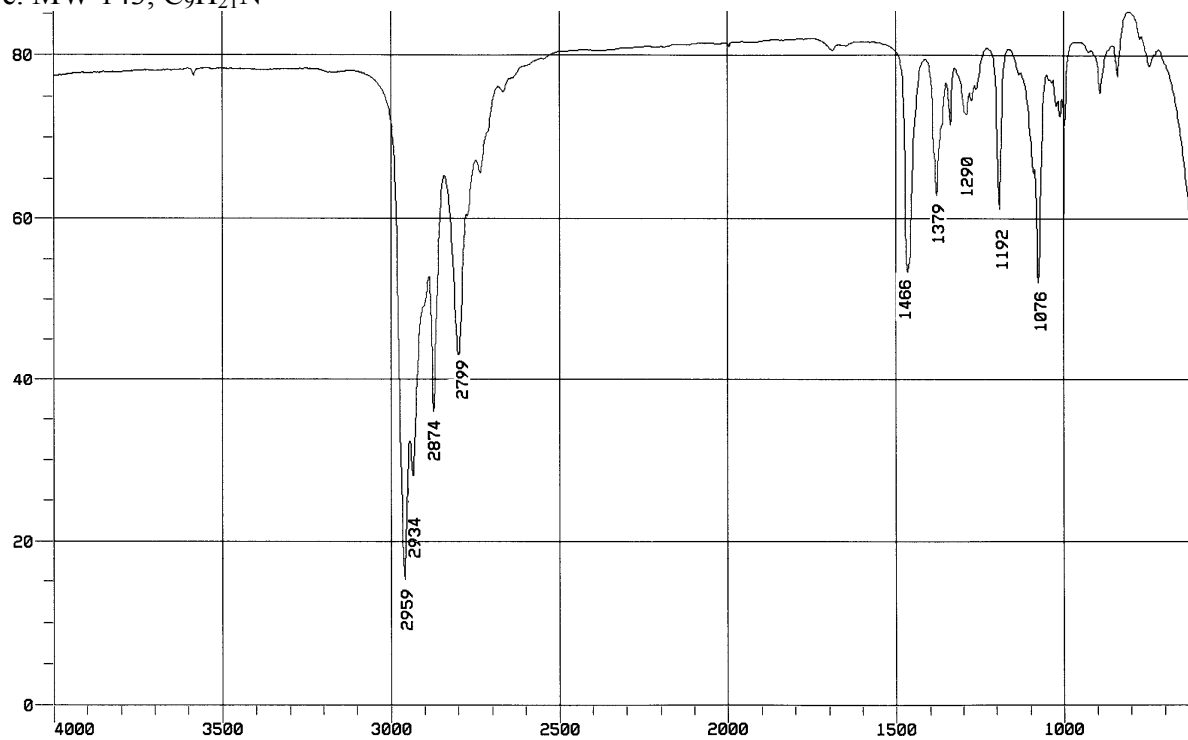
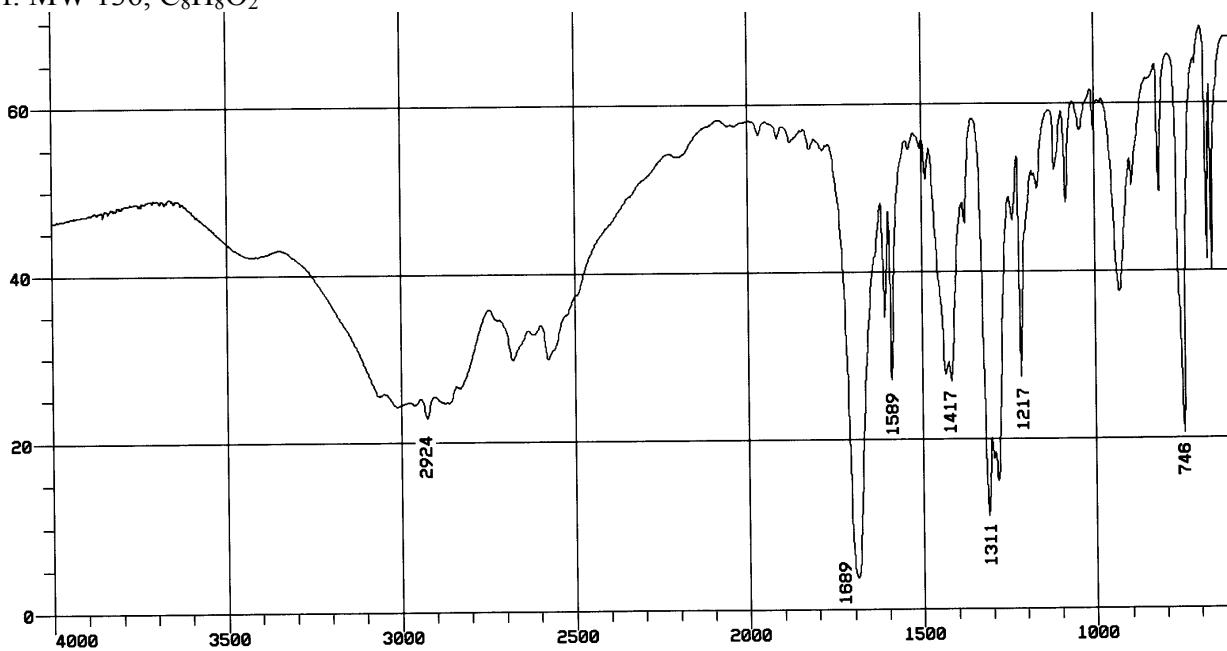
a. MW 82, C_6H_{10}



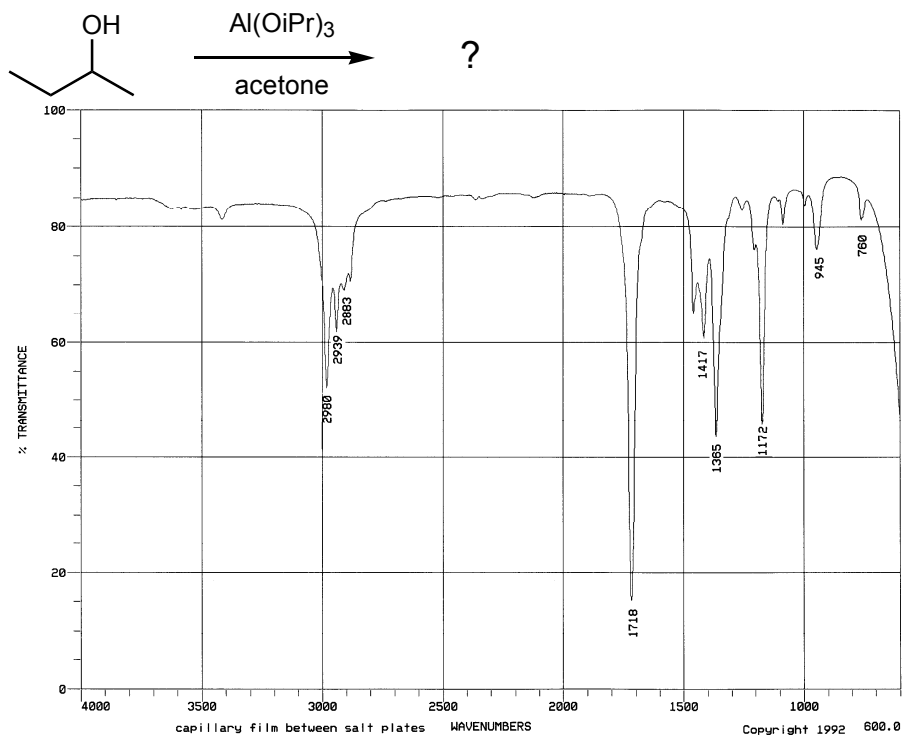
b. MW 88, $C_5H_{12}O$



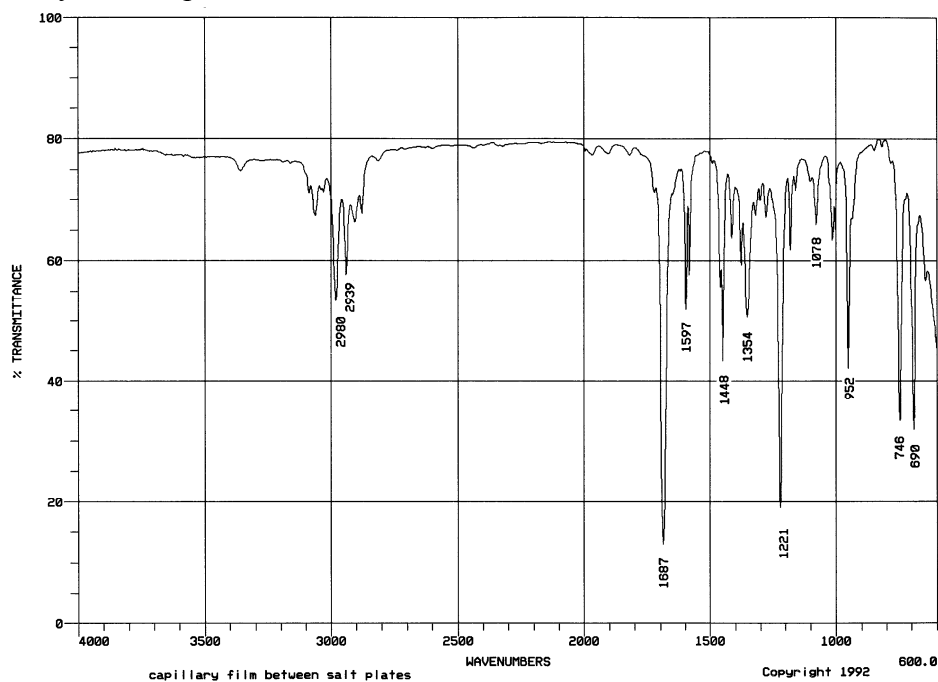
c. MW 88, $C_4H_8O_2$ d. MW 116, $C_6H_{12}O_2$ 

e. MW 143, $C_9H_{21}N$ f. MW 136, $C_8H_8O_2$ 

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.)

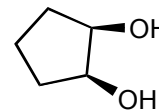
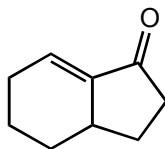
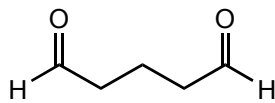
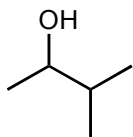


7. Is the following compound an aldehyde, ketone, ester, or carboxylic acid? Explain the location of the carbonyl in the spectrum.



8. When a ketone is in conjugation with a π -bond, the $\text{C}=\text{O}$ 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 $\text{C}=\text{O}$ peak of an ester with conjugation to come in the IR spectrum?

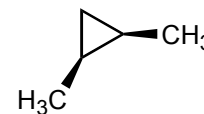
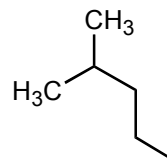
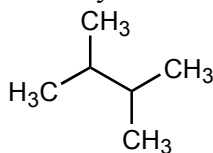
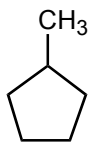
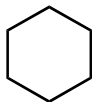
9. For each of the following compounds, indicate how many peaks you would expect in its ^{13}C NMR spectrum and the approximate location of each peak.



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.

formula	^{13}C NMR peaks
C_3H_6	1
C_6H_{10}	3
$\text{C}_4\text{H}_{10}\text{O}$	3
$\text{C}_5\text{H}_9\text{Br}$	3
C_6H_8	6
C_6H_8	4

11. You have been given a sample of one of the C_6 compounds shown below. You take the ^{13}C NMR and find 2 peaks in the spectrum. Which compound do you have?

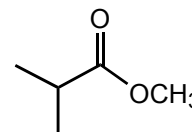
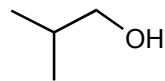
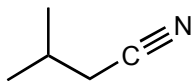
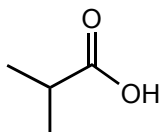


12. You have an unknown that you are told is one of the four compounds below, and it exhibits the following spectral data. Which compound do you have?

^{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).



How to Approach IR

In trying to analyze the spectrum of an unknown, you should concentrate your first efforts toward determining the presence (or absence) of a few major functional groups. The C=O, O-H, N-H, C-O, C=C, C≡C, C≡N, and NO₂ peaks are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the CH absorptions near 3000 cm⁻¹ (3.33 μ); almost all compounds have these absorptions. Do not worry about subtleties of the exact type of environment in which the functional group is found. Below is a major check list of the important gross features.

- Is a carbonyl group present?
The C=O group gives rise to a strong absorption in the region 1820–1660 cm⁻¹ (5.5–6.1 μ). The peak is often the strongest in the spectrum and of medium width. You can't miss it.
- If C=O is present, check the following types (if absent, go to 3).

ACIDS	is OH also present? – <i>broad</i> absorption near 3400–2400 cm ⁻¹ (usually overlaps C-H)
AMIDES	is NH also present? – medium absorption near 3500 cm ⁻¹ (2.85 μ) sometimes a double peak, with equivalent halves
ESTERS	is C-O also present? – strong intensity absorptions near 1300–1000 cm ⁻¹ (7.7–10 μ)
ANHYDRIDES	have <i>two</i> C=O absorptions near 1810 and 1760 cm ⁻¹ (5.5 and 5.7 μ)
ALDEHYDES	is aldehyde CH present? – two weak absorptions near 2850 and 2750 cm ⁻¹ (3.50 and 3.65 μ) on the right-hand side of CH absorptions
KETONES	The above 5 choices have been eliminated
- If C=O is absent

ALCOHOLS } PHENOLS }	Check for OH – <i>broad</i> absorption near 3600–3300 cm ⁻¹ (2.8–3.0 μ) – confirm this by finding C-O near 1300–1000 cm ⁻¹ (7.7–10 μ)
AMINES	Check for NH – medium absorptions(s) near 3500 cm ⁻¹ (2.85 μ)
ETHERS	Check for C-O (and absence of OH) near 1300–1000 cm ⁻¹ (7.7–10 μ)
- Double Bonds and/or Aromatic Rings
 - C=C is a *weak* absorption near 1650 cm⁻¹ (6.1 μ)
 - medium to strong absorptions in the region 1650–1450 cm⁻¹ (6–7 μ) often imply an aromatic ring
 - confirm the above by consulting the CH region; aromatic and vinyl CH occurs to the left of 3000 cm⁻¹ (3.33 μ) (aliphatic CH occurs to the right of this value)
- Triple Bonds
 - C≡N is a medium, sharp absorption near 2250 cm⁻¹ (4.5 μ)
 - C≡C is a weak but sharp absorption near 2150 cm⁻¹ (4.65 μ)
 - Check also for acetylenic CH near 3300 cm⁻¹ (3.0 μ)
- Nitro Groups
 - *two* strong absorptions at 1600–1500 cm⁻¹ (6.25–6.67 μ) and 1390–1300 cm⁻¹ (7.2–7.7 μ)

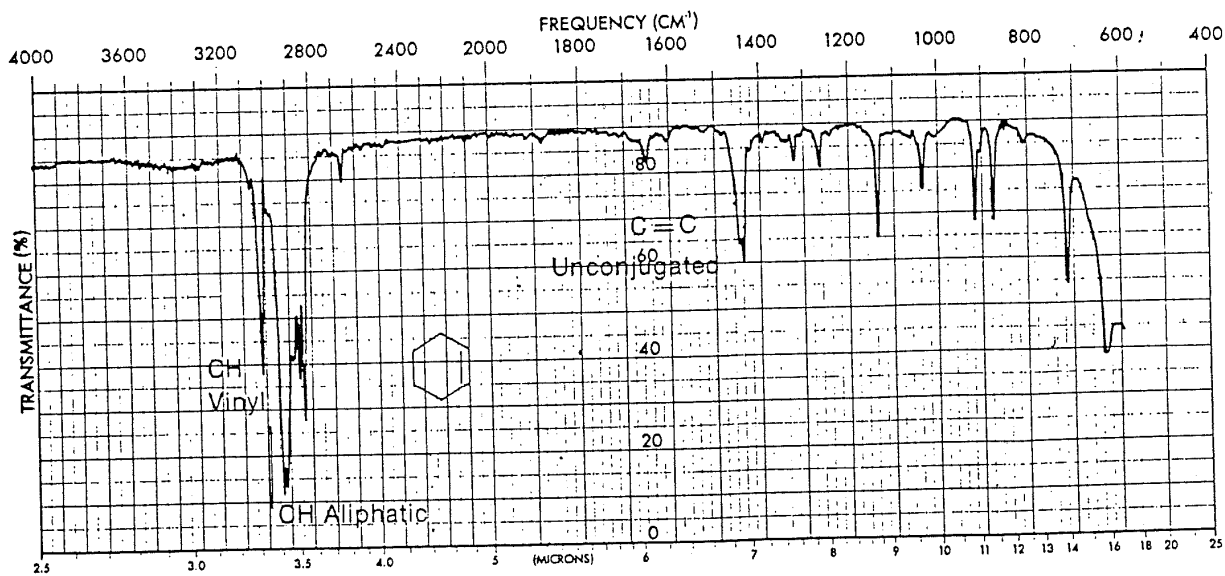
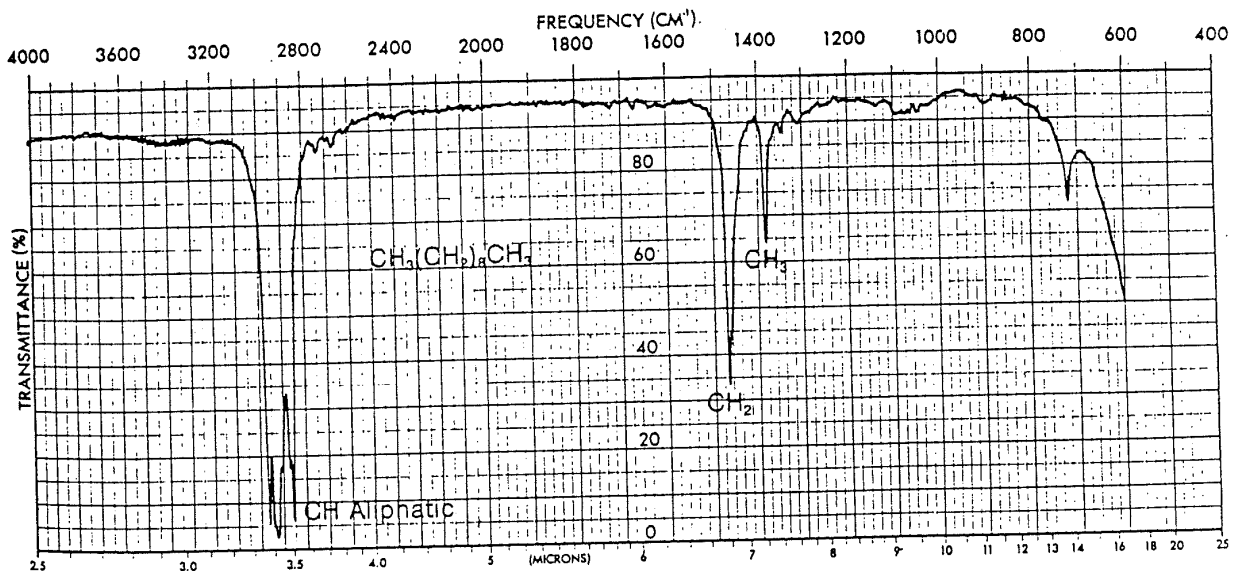
Table 12.1 Characteristic IR Absorptions of Some Functional Groups

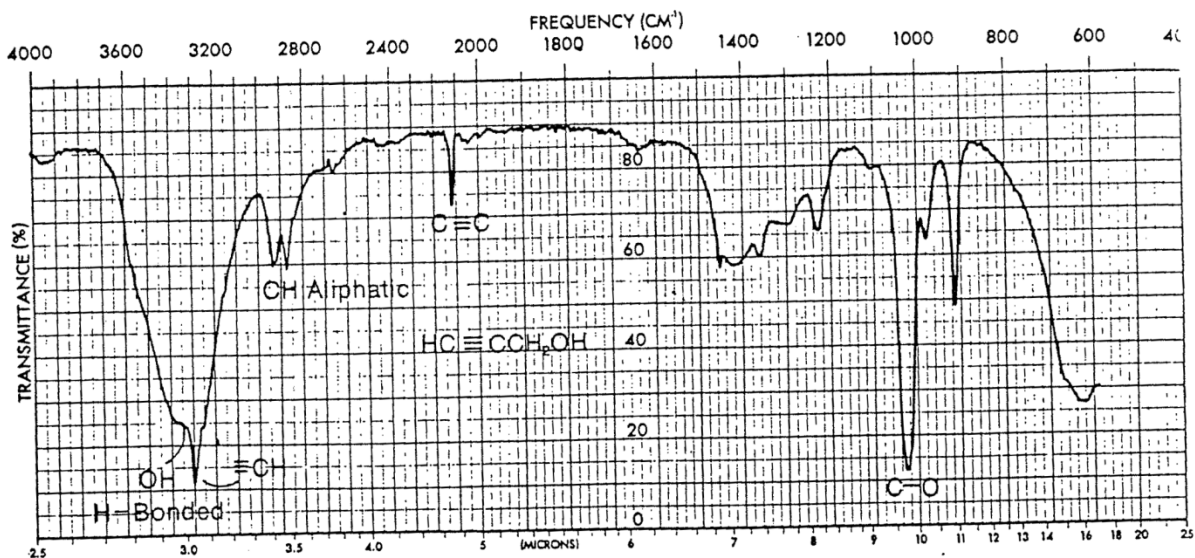
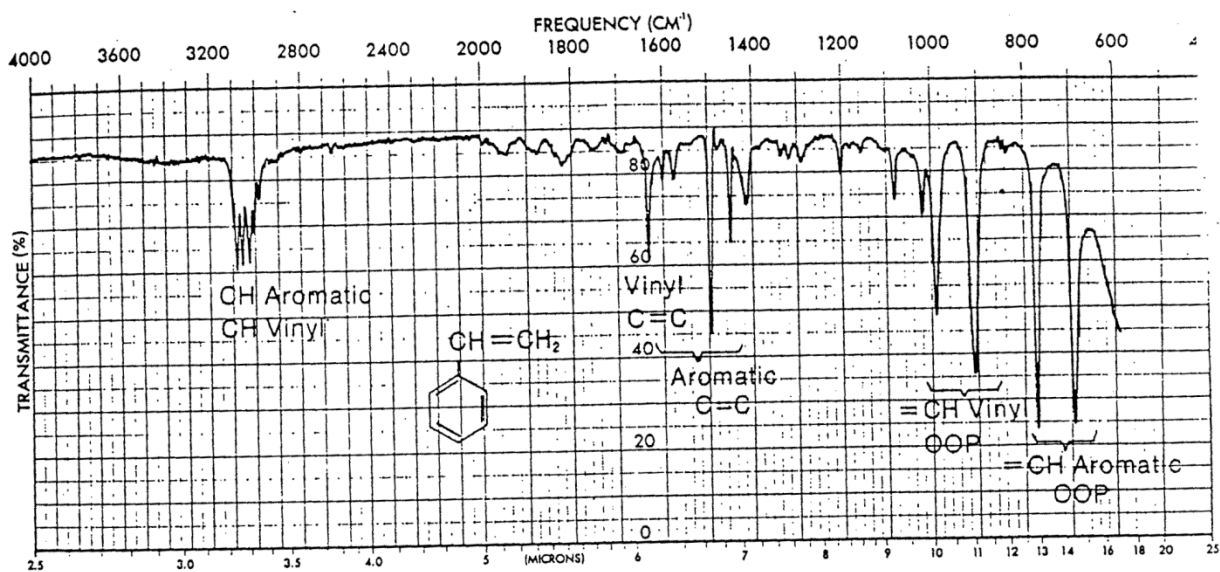
Functional Group	Absorption (cm ⁻¹)	Intensity	Functional Group	Absorption (cm ⁻¹)	Intensity
Alkane			Amine		
** C-H	2850-2960	Medium	** N-H	3300-3500	Medium
Alkene			** C-N	1030-1230	Medium
** =C-H	3020-3100	Medium	Carbonyl compound		
** C=C	1640-1680	Medium	** C=O	1670-1780	Strong
Alkyne			Carboxylic acid		
** ≡C-H	3300	Strong	** O-H	2500-3100	Strong, broad
** C≡C	2100-2260	Medium	Nitrile		
Alkyl halide			** C=N	2210-2260	Medium
C-Cl	600-800	Strong	Nitro		
C-Br	500-600	Strong	NO ₂	1540	Strong
Alcohol			(two bands 1600 and 1500)		
** O-H	3400-3650	Strong, broad	Aldehyde		
** C-O	1050-1150	Strong	C-H	2800 - 2700	Medium
Arene					
** C-H	3030	Weak			
** Aromatic ring	1660-2000	Weak			
	1450-1600	Medium			

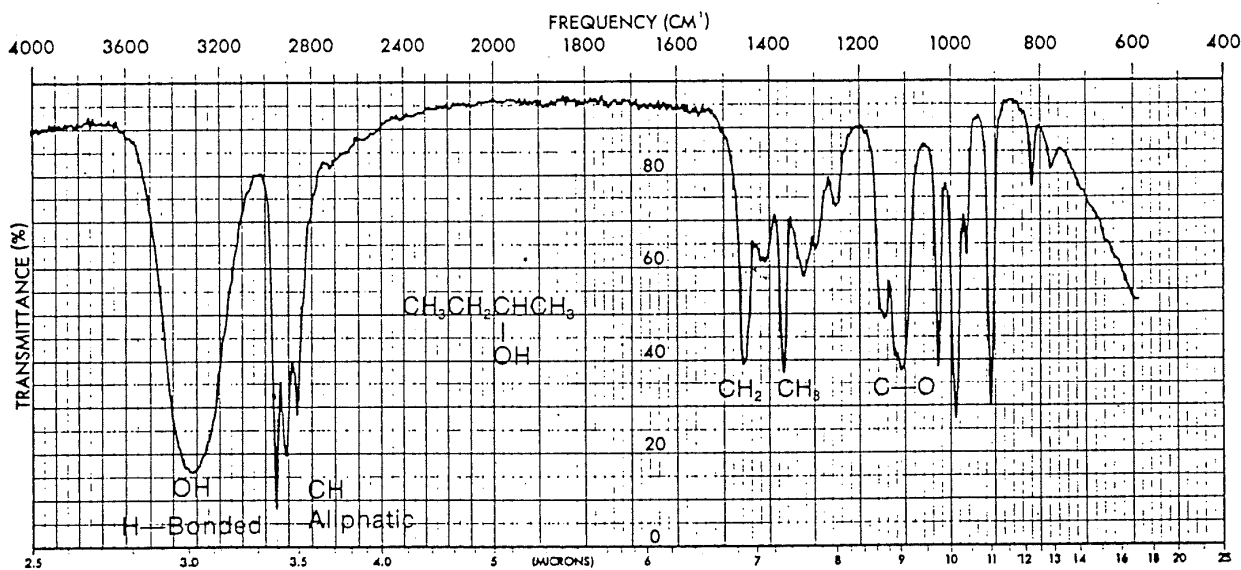
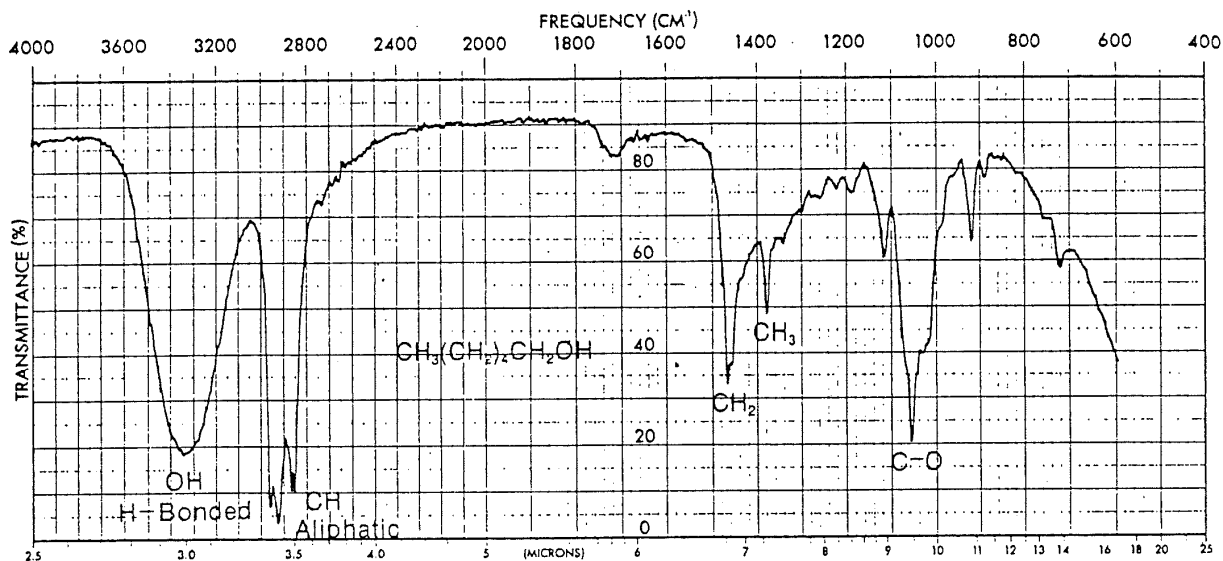
all values listed are for bond stretching

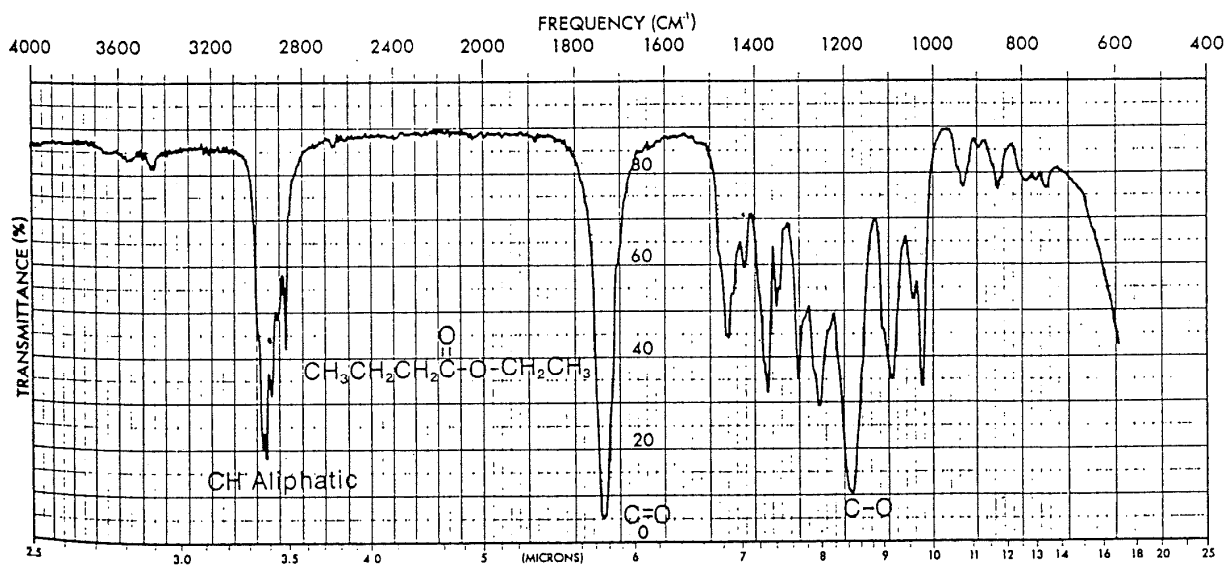
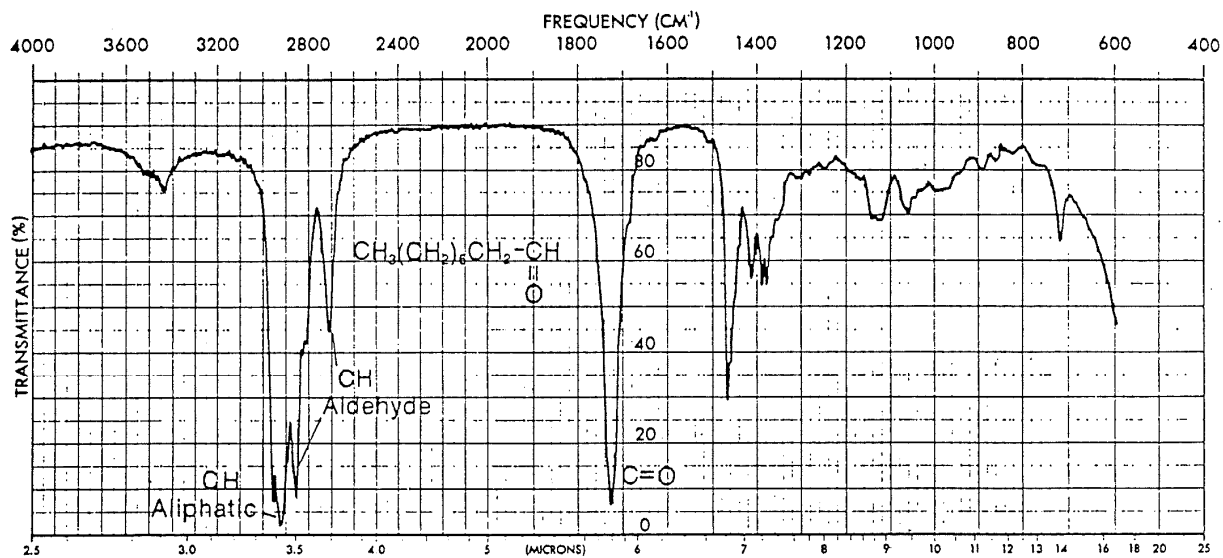
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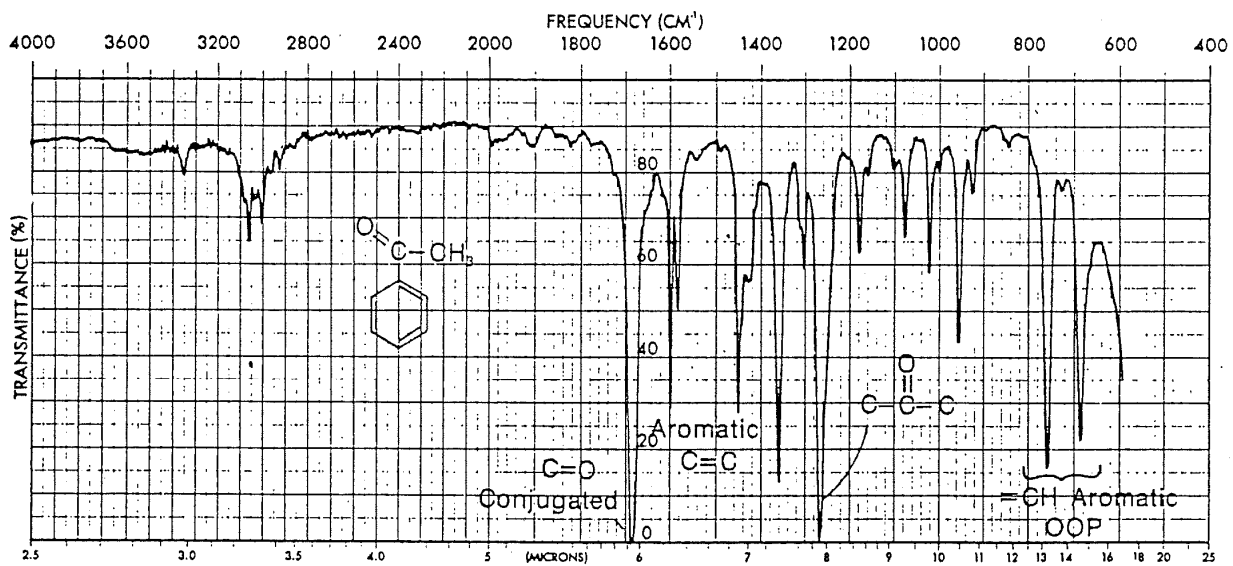
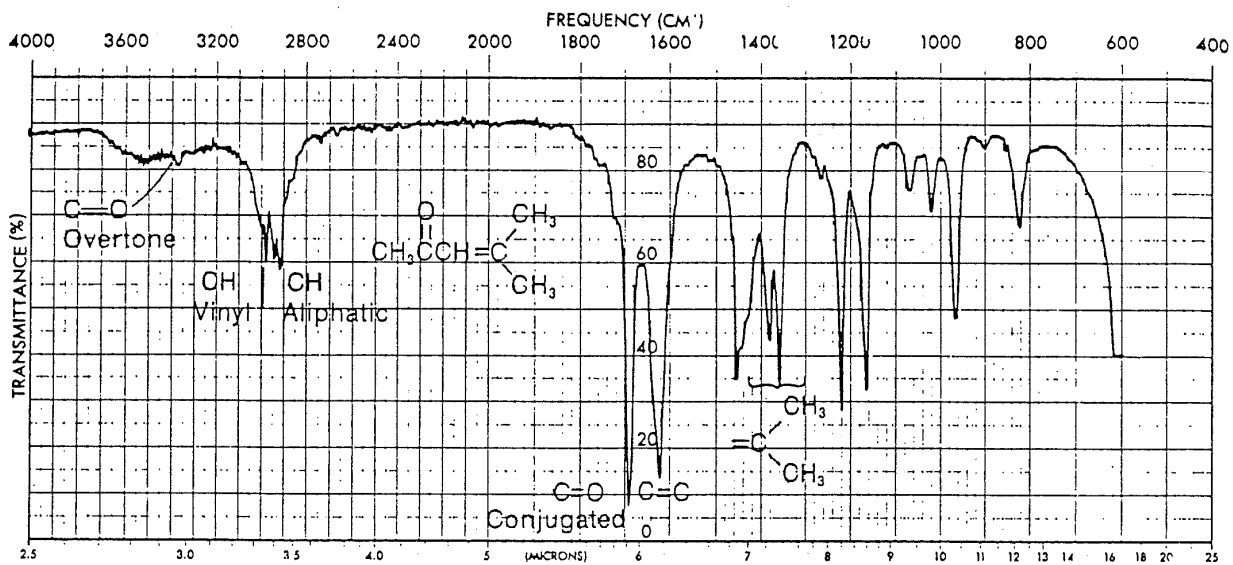
SAMPLE IR SPECTRA

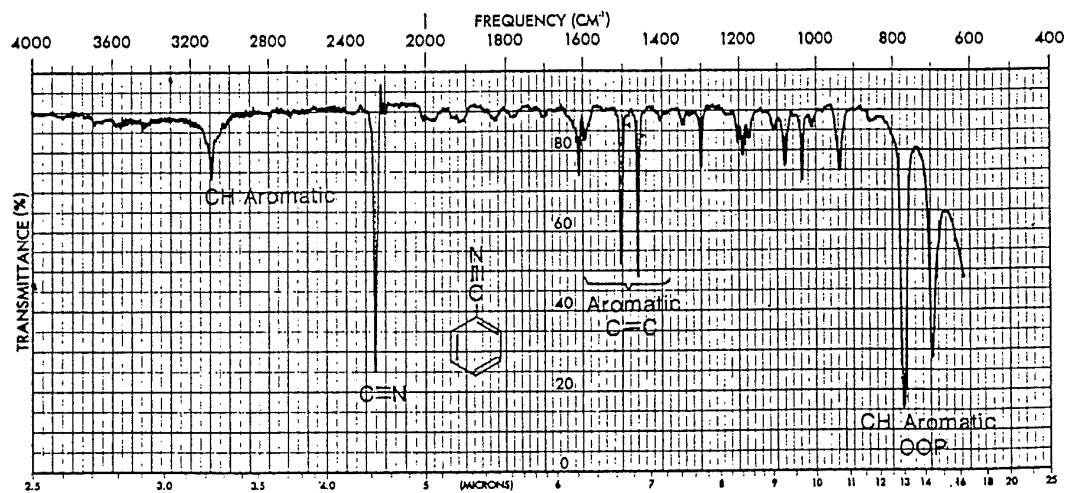
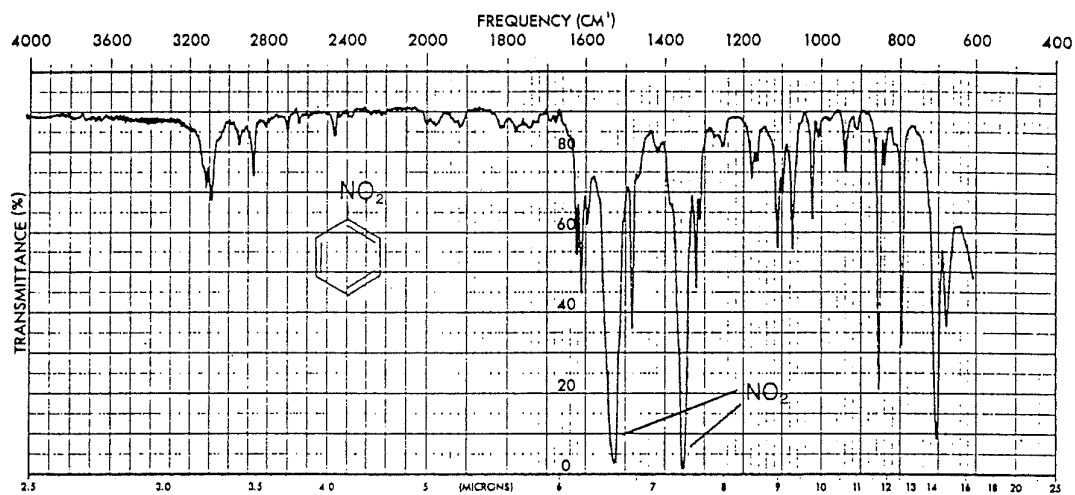
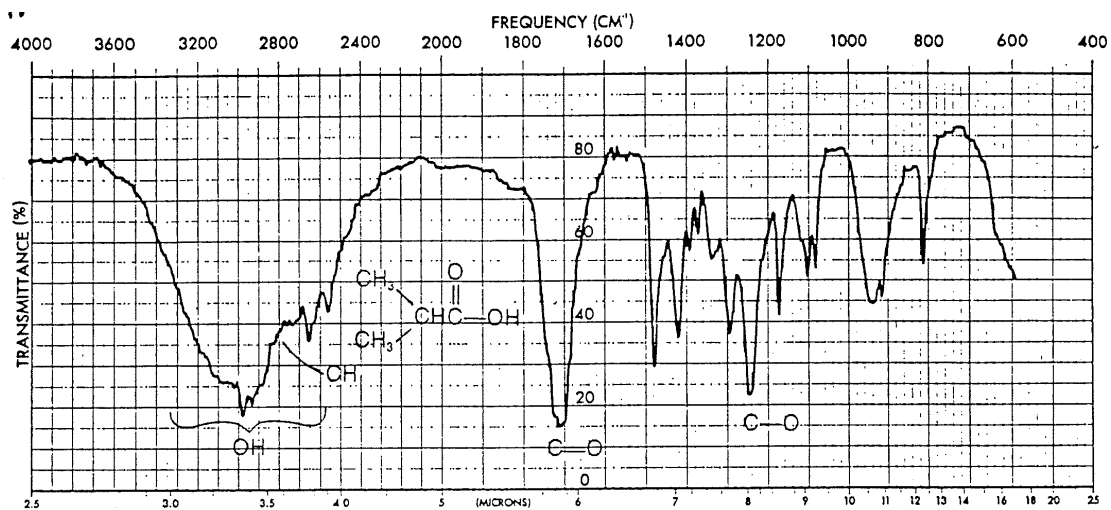




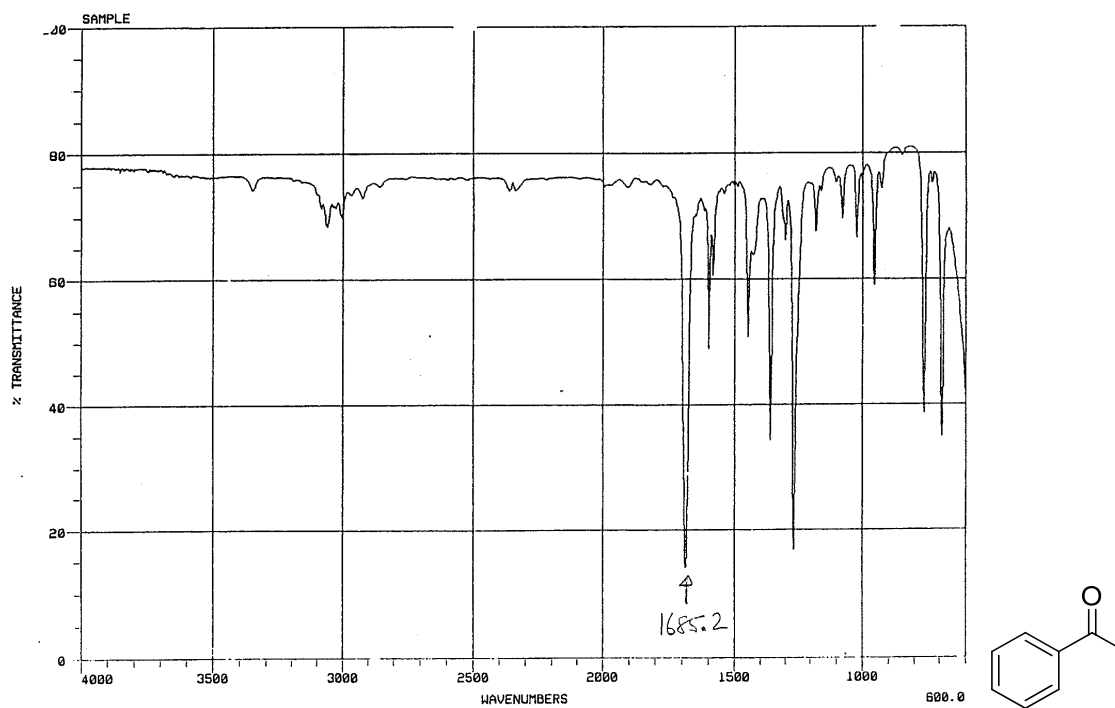
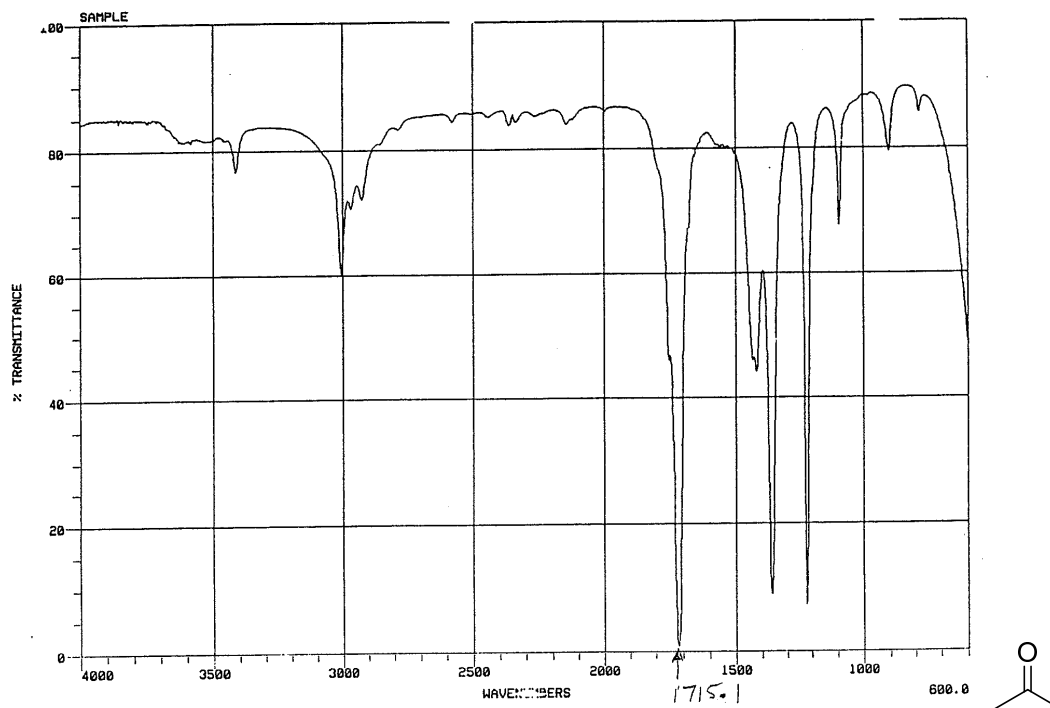




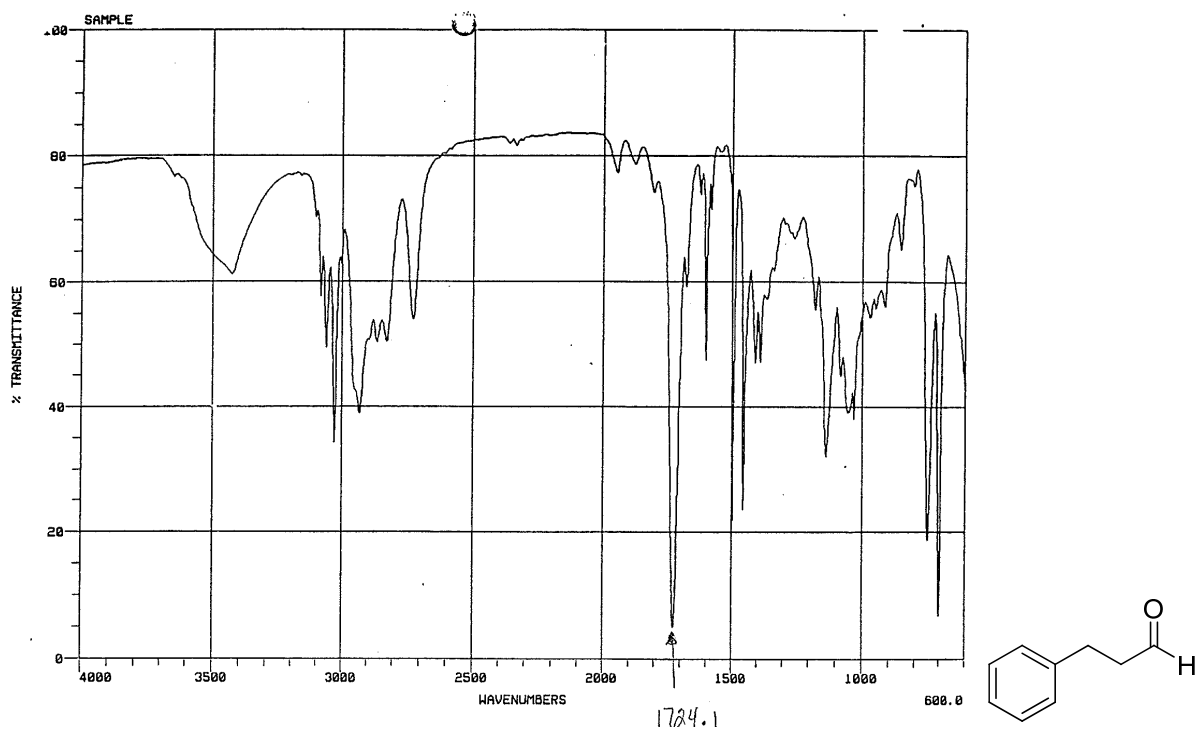




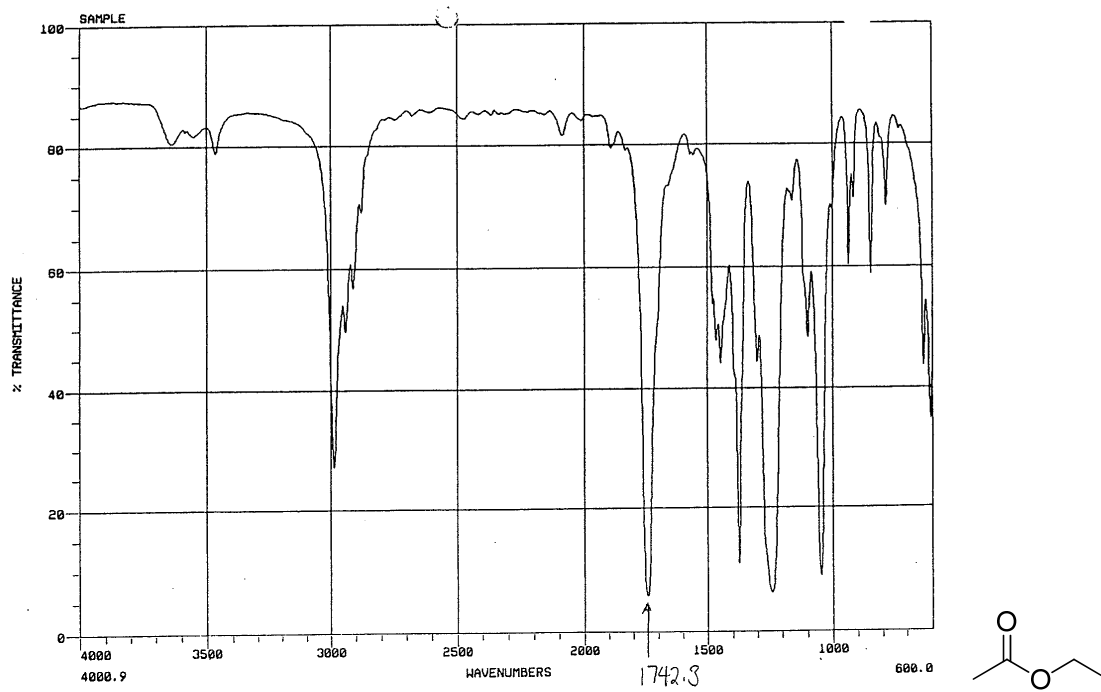
Sample IR Spectra: Carbonyl Compounds

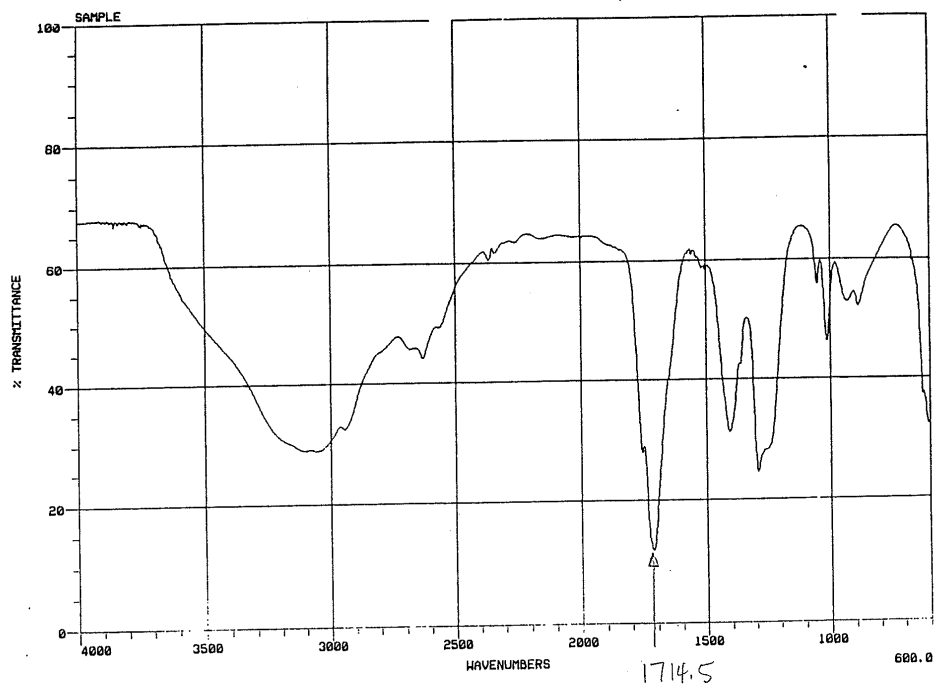


Note how conjugation reduces wavenumber for C=O stretch



Note how aldehydes and esters differ from ketones (both higher wavenumber for C=O stretch; aldehyde also has additional C-H stretch at 2700 cm⁻¹ and ester has C-O near 1200 cm⁻¹)





Note how acids and amides differ from ketones (acid has very broad O-H stretch, amide has N-H stretch along with lower wavenumber for C=O stretch)

