


HOMEWORK PROBLEMS: IR SPECTROSCOPY

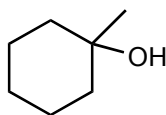
1. You find a bottle on the shelf only labeled C_3H_6O . You take an IR spectrum of the compound and find major peaks at 2950, 1720, and 1400 cm^{-1} . Draw a molecule that might be the compound in the bottle.

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

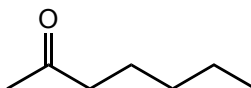
2. For each of the following compounds, draw an isomer that changes the functional groups in the molecule. Name all the functional groups. Indicate the major absorbances you would expect to find in the IR spectrum for each isomer, and highlight how you could use IR to tell them apart.

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.

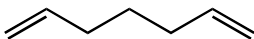


alcohol O-H at 3500

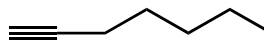


ketone C=O at 1720

b.

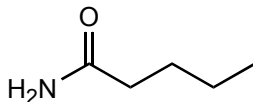


alkene C=C bands near 1600

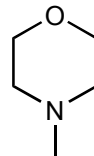


terminal alkyne C≡C band near 2200
alkyne C-H near 3300

c.

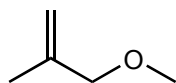


amide N-H bands near 3300
C=O band near 1680

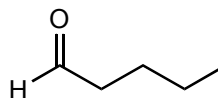


amine and ether
C-N and C-O bands in the fingerprint region

d.

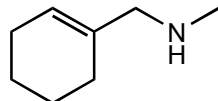


alkene and ether
C=C bands near 1650
C-O bands in the fingerprint region

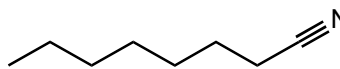


aldehyde C-H at 2700, 2900
C=O at 1730

e.

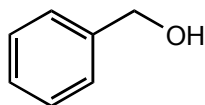


amine and alkene
C-N bands in the fingerprint region
C=C bands near 1650

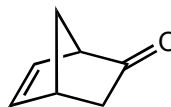


nitrile C≡N at 2250

f.



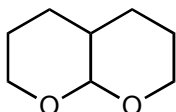
alcohol (and aromatic ring)
O-H at 3500



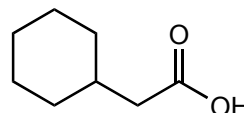
ketone (and alkene)
C=O at 1720

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.

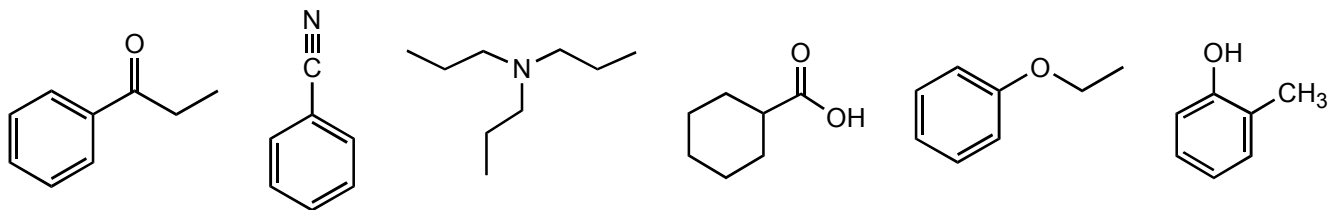


ether C-O bands in the fingerprint region
(actually a special kind of ether-like
functionalgroup called an acetal)

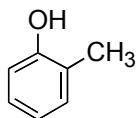


carboxylic acid
O-H at 2500-3200
C=O at 1720

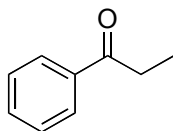
3. Given the following compounds and the data in the ensuing problems identify which compound corresponds with each scenario of given IR data.



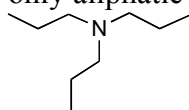
a. With O-H stretch at 3414 cm^{-1} , aliphatic C-H, and aromatic/vinyl C-H (below and above 3000 cm^{-1}), must be:



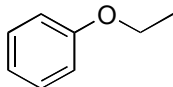
b. With C=O peak at 1687 cm^{-1} (C=O in conjugation), aliphatic C-H, and aromatic/vinyl C-H (below and above 3000 cm^{-1}), must be:



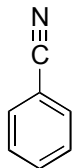
c. With only aliphatic C-H, must be:



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

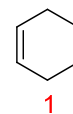
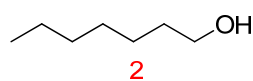
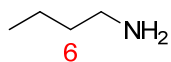
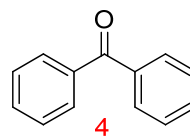
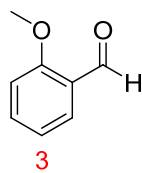
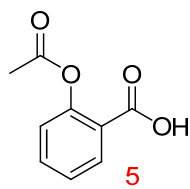


because no $\text{C}\equiv\text{N}$ at about 2200 cm^{-1} , can't be:

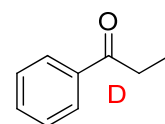
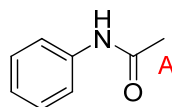
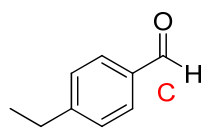
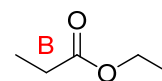
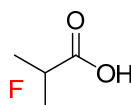
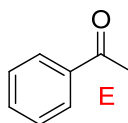
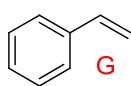


4. For the infrared spectra below (numbers 1-6; and letters A-G), pick out the molecule from the list that would correspond to the spectrum for that compound.

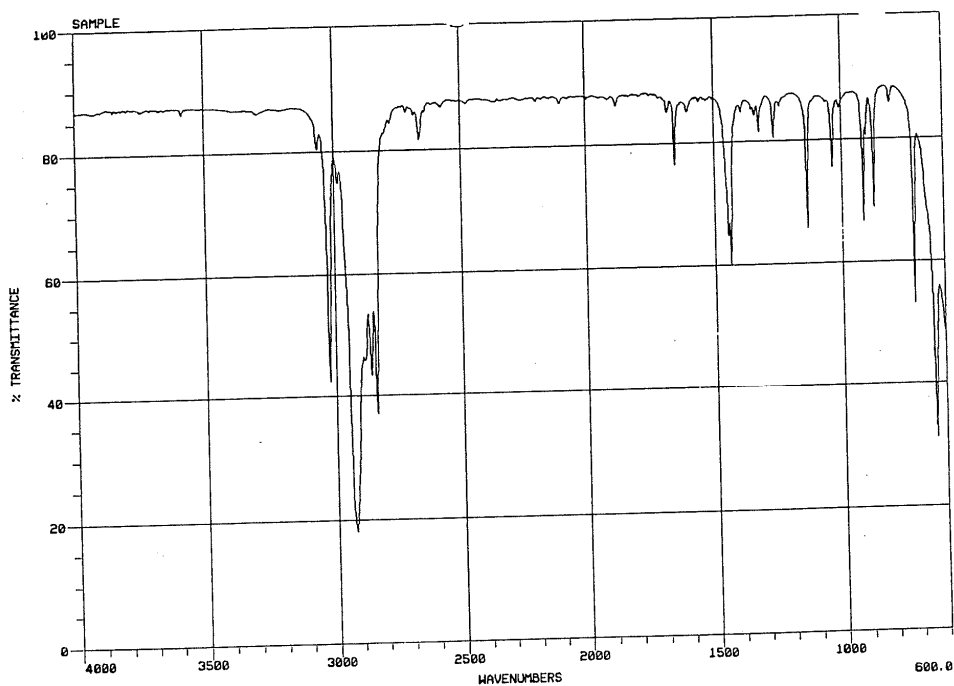
Spetra 1-6



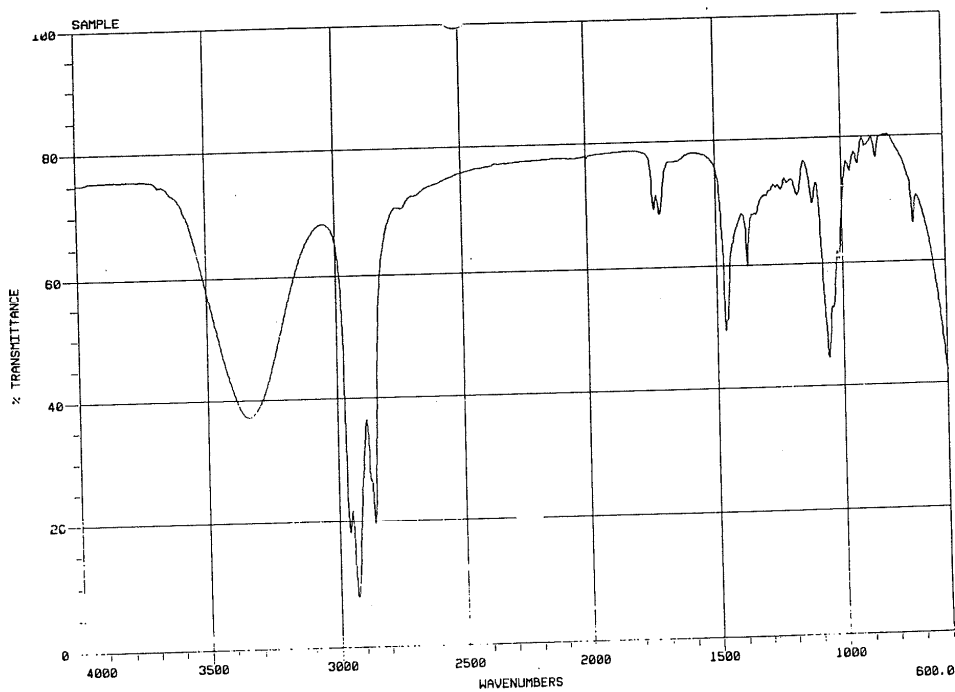
Spetra A-G



1.



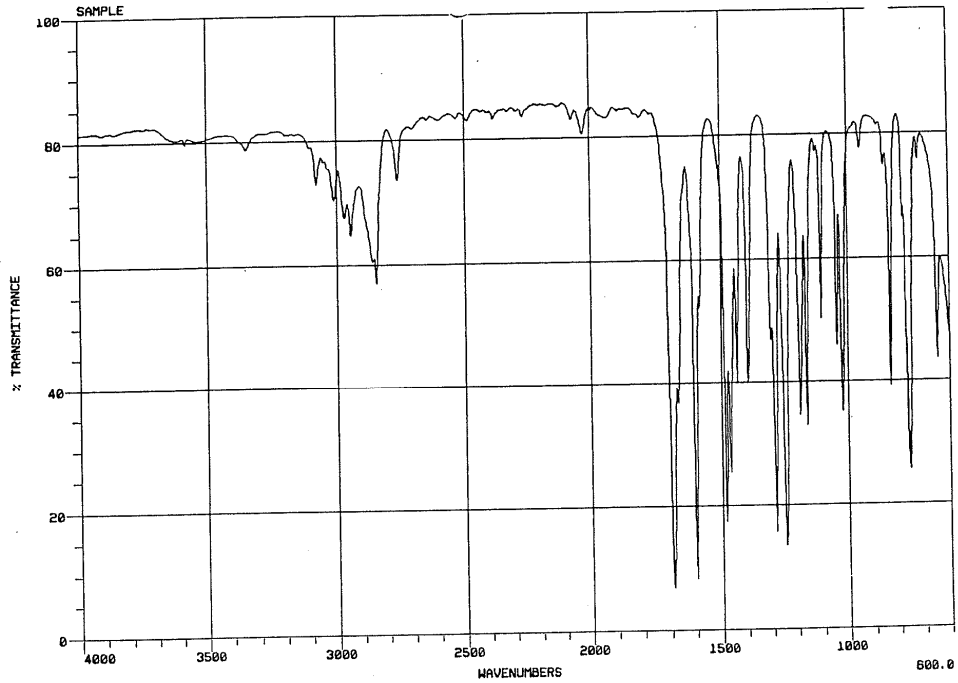
2.



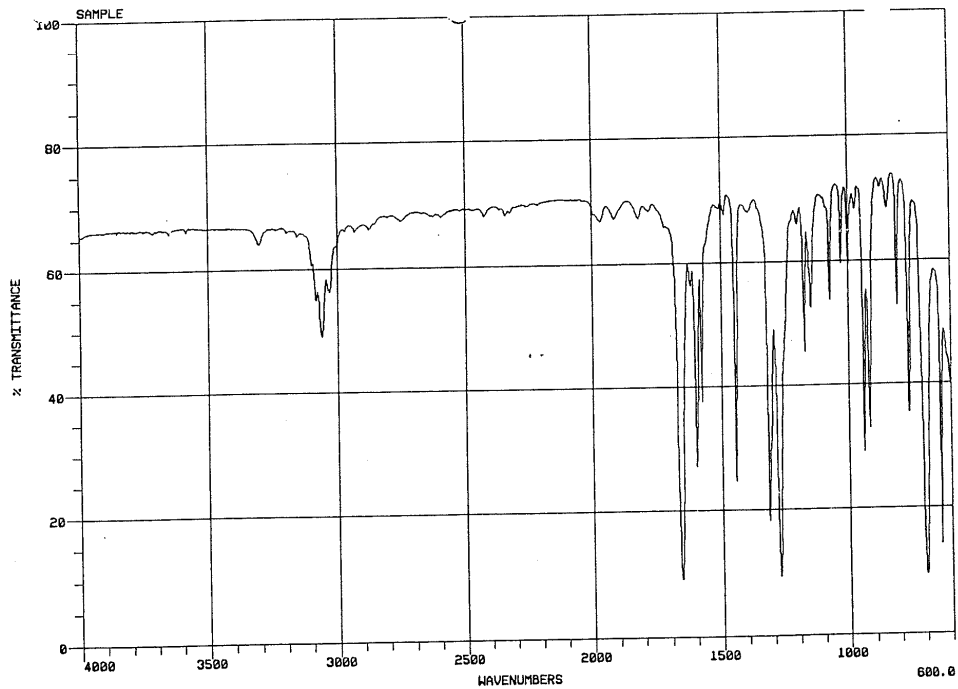
Spectra 1: alkene C-H stretch above 3000cm^{-1} , alkane C-H stretch below 3000cm^{-1} , weak C=C near 1650cm^{-1}

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

3.



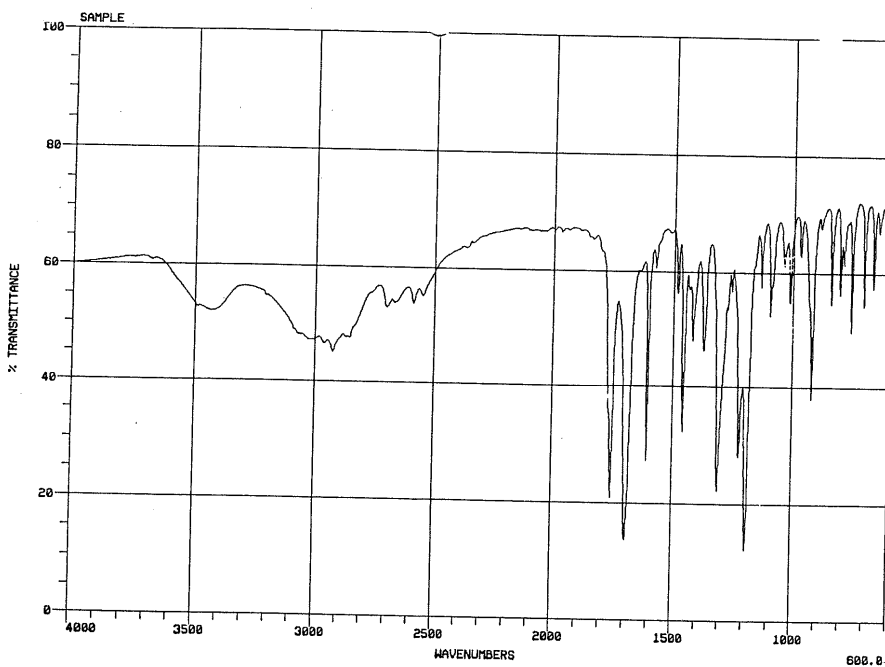
4.



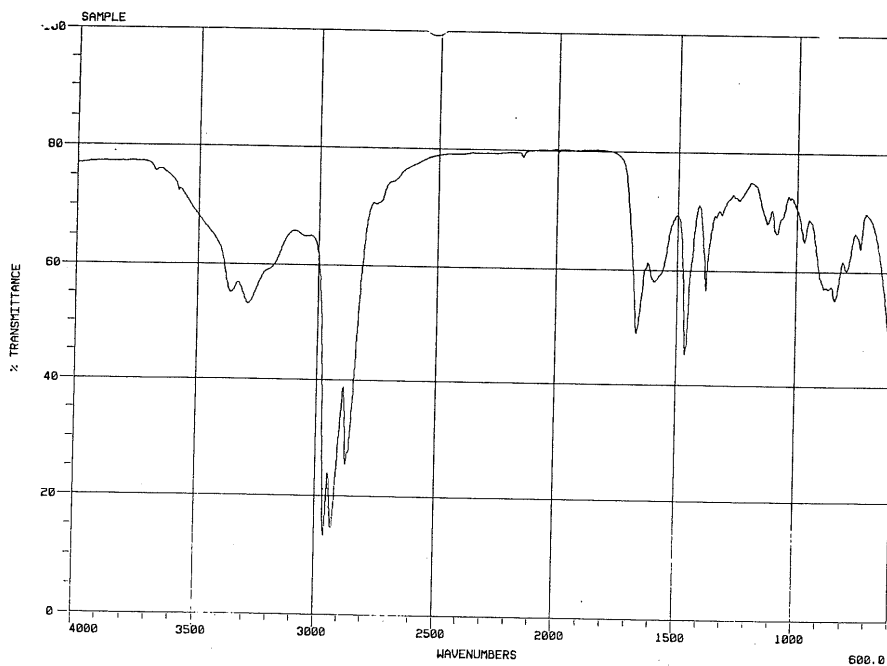
Spectra 3: alkene C-H stretch above 3000cm^{-1} , alkane C-H stretch below 3000cm^{-1} , aldehyde C-H stretch near 2700cm^{-1} , C=O 1700cm^{-1} , weak C=C near 1600 and 1500cm^{-1}

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

5.



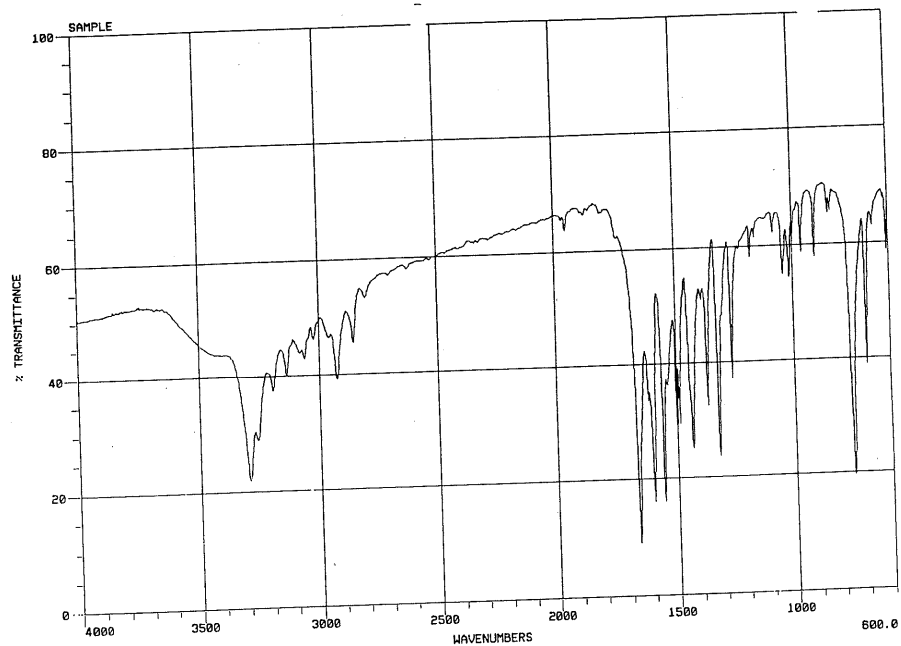
6.



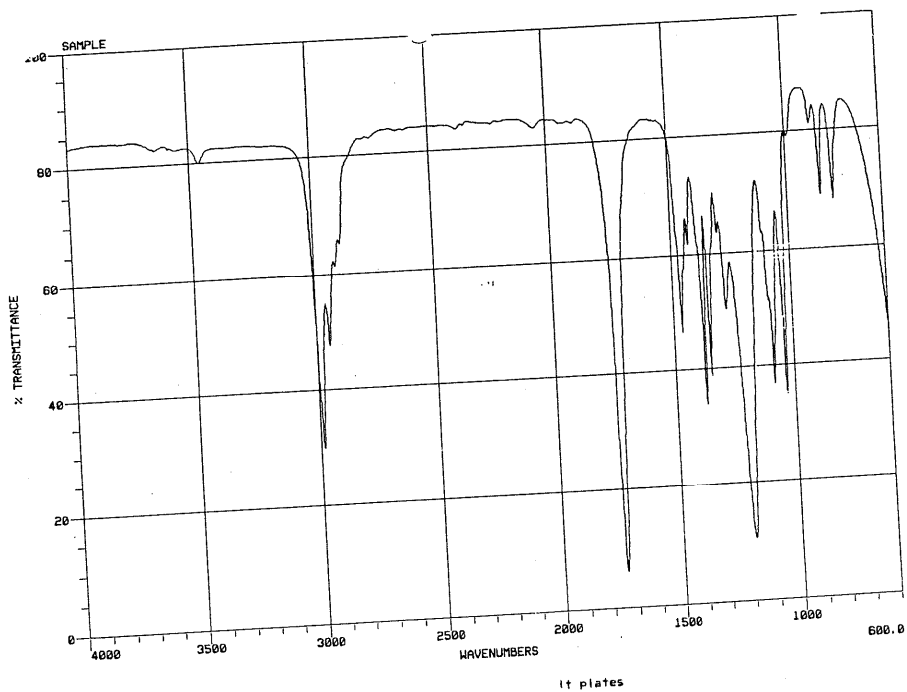
Spectra 5: very broad O-H of acid $3500\text{-}2500\text{cm}^{-1}$, alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1} harder to see with broad acid O-H, two C=O stretches 1750cm^{-1} and 1700cm^{-1} , weak C=C near 1600 and 1450cm^{-1}

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

A.



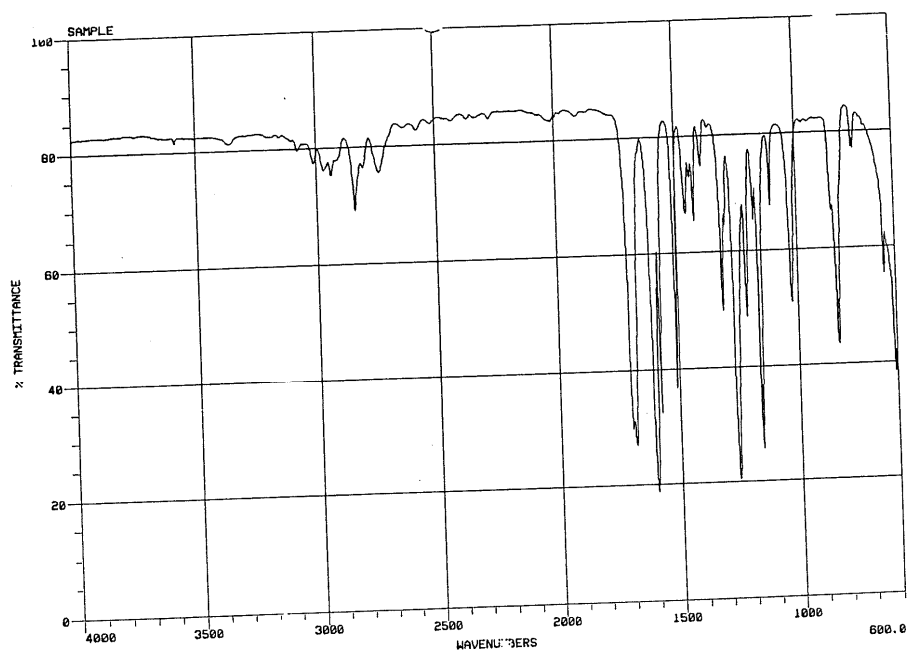
B.



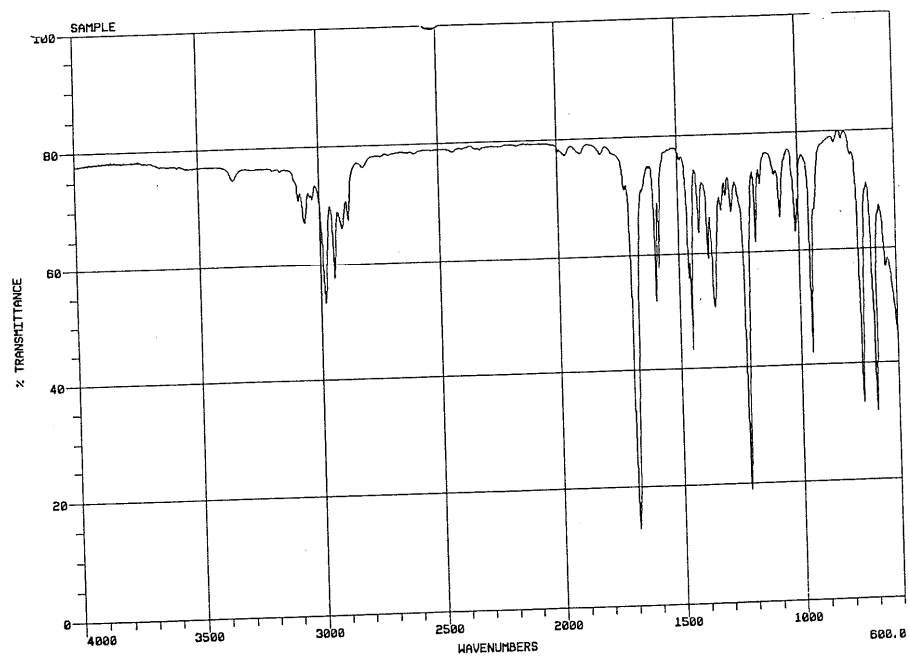
Spectra A: N-H of amide 3300cm^{-1} , alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1} , C=O stretch below 1700cm^{-1} , C=C near 1600 and 1550cm^{-1}

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

C.

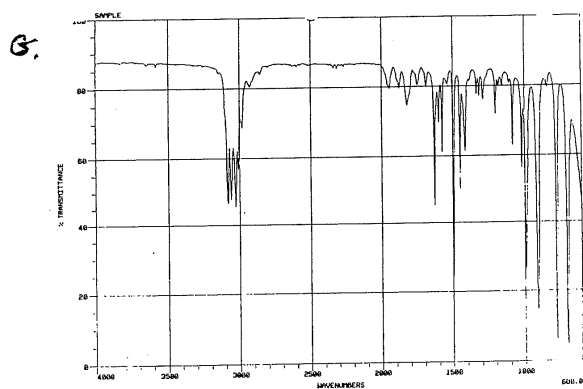
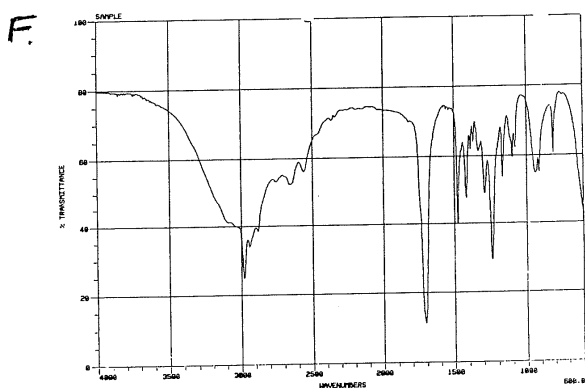
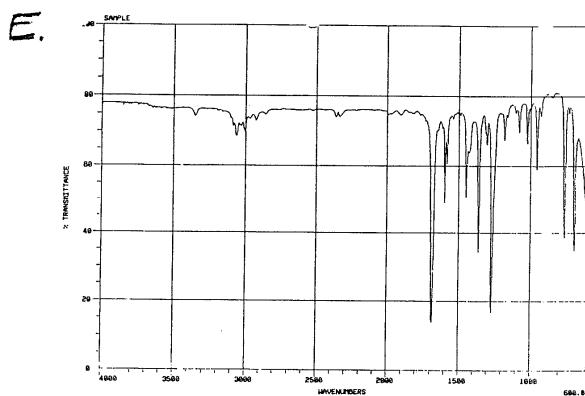


D.



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}



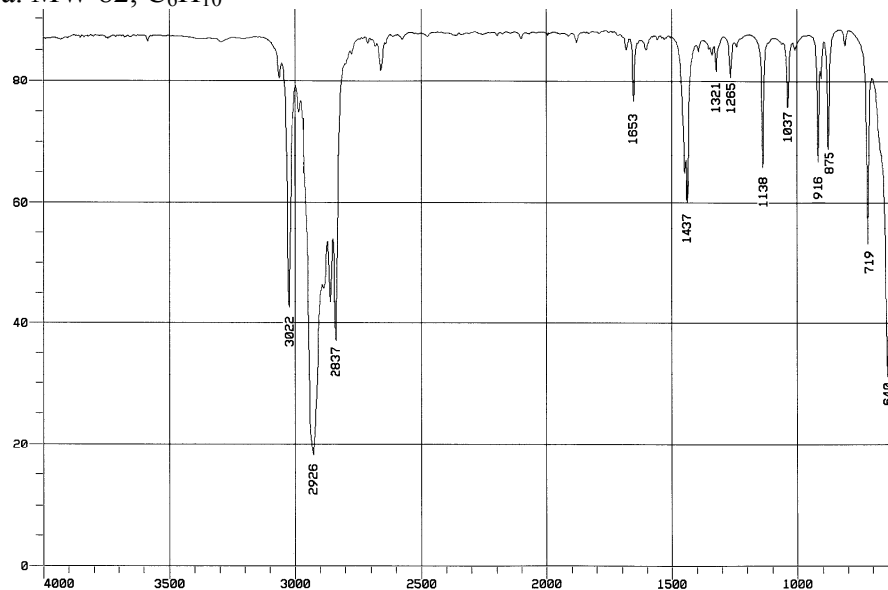
Spectra E: alkene C-H stretch above 3000cm^{-1} and alkane C-H stretch below 3000cm^{-1} , C=O stretch just below 1700cm^{-1} , C=C near 1600 and 1450cm^{-1}

Spectra F: very broad O-H of acid $3500\text{-}2000\text{cm}^{-1}$, 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.

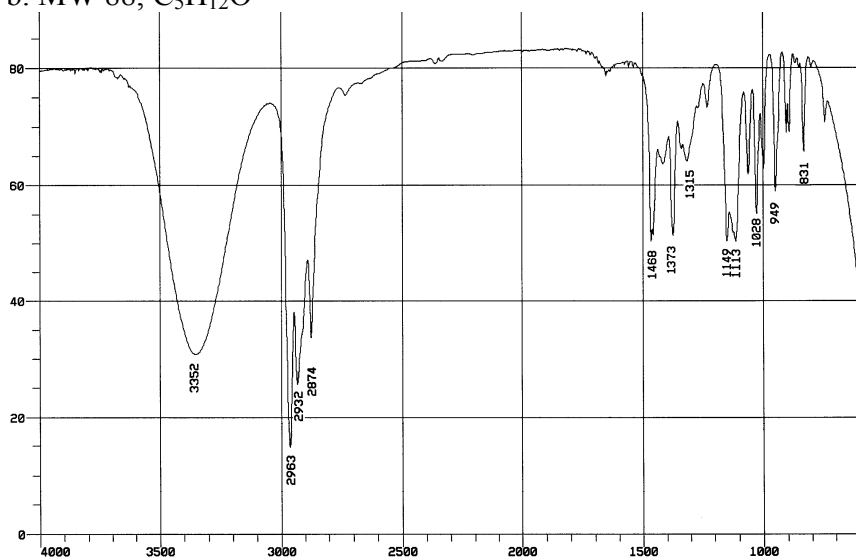
a. MW 82, C₆H₁₀



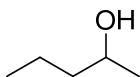
Peak at 3022 indicates C-H of alkene. no other major functional groups. Actual compound is cyclohexene.



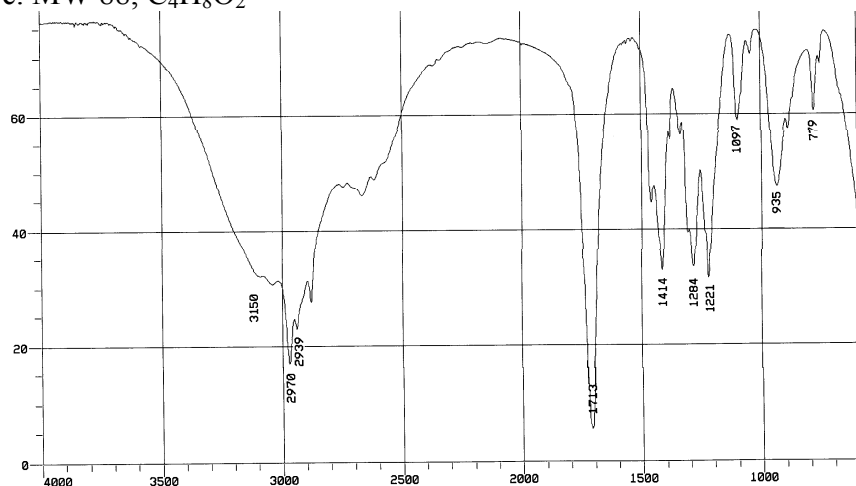
b. MW 88, C₅H₁₂O



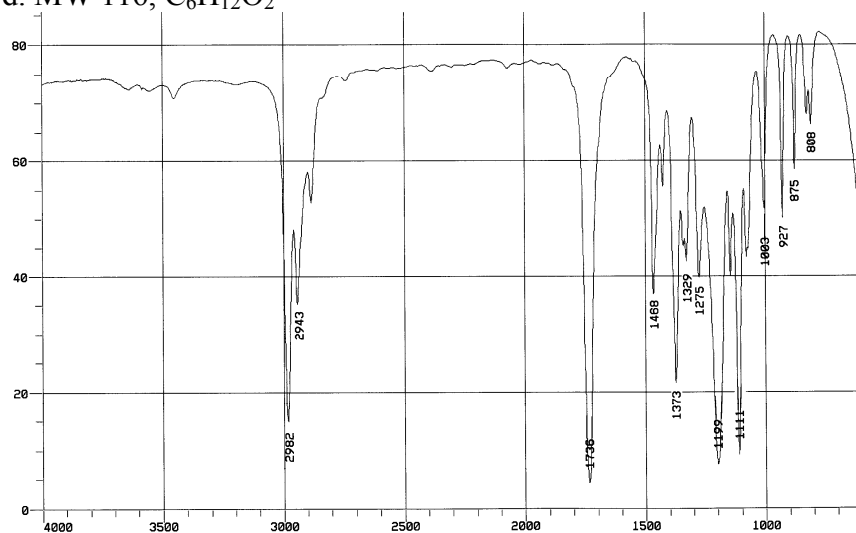
IR shows an alcohol (and not much else). Actual compound is 2-pentanol.



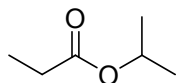
c. MW 88, C₄H₈O₂



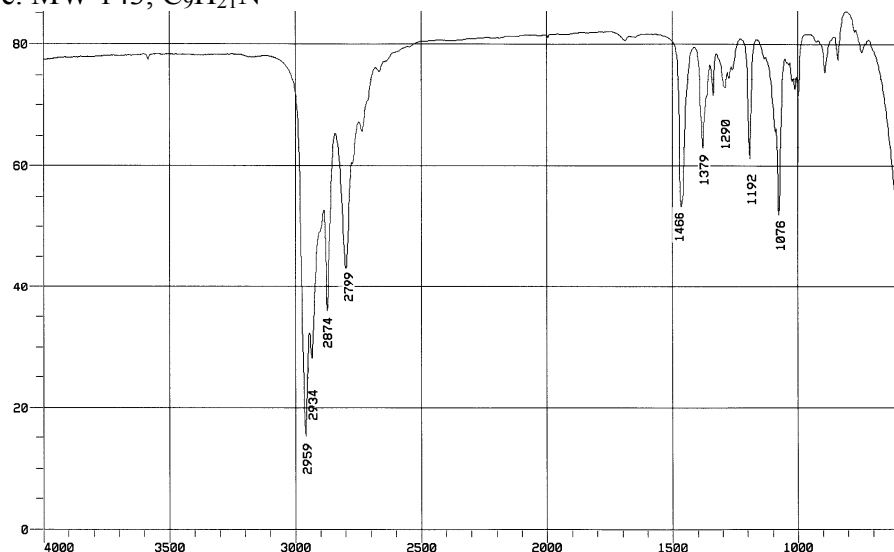
d. MW 116, C₆H₁₂O₂



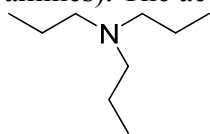
IR shows the characteristic signature of an ester (carbonyl at 1736, C-O at 1199). Many isomers possible. The actual one is isopropyl propanoate.



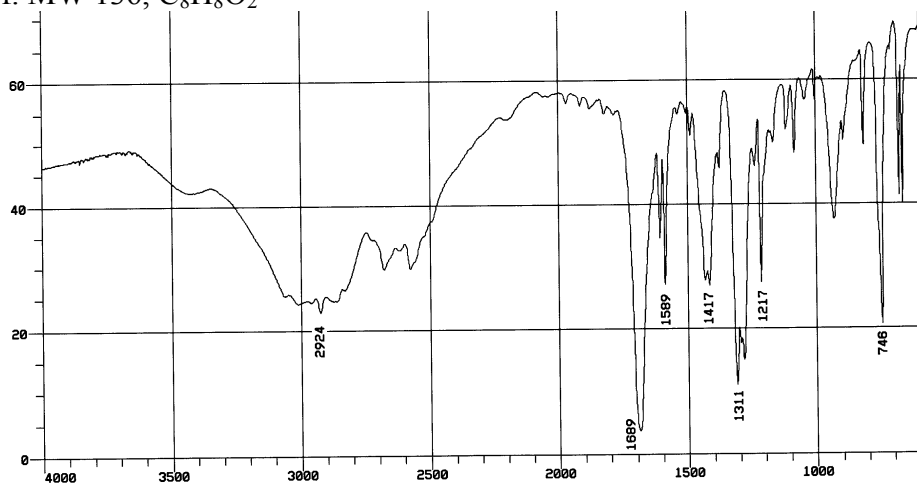
e. MW 143, C₉H₂₁N



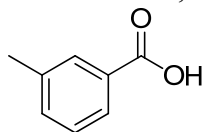
IR shows not much of anything. What do we do? This structure must be completely saturated (no multiple bonds in IR), and contain any amine isomers that have no N-H bonds (only tertiary amines). The actual compound is tripropylamine.



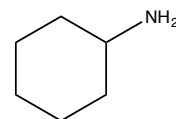
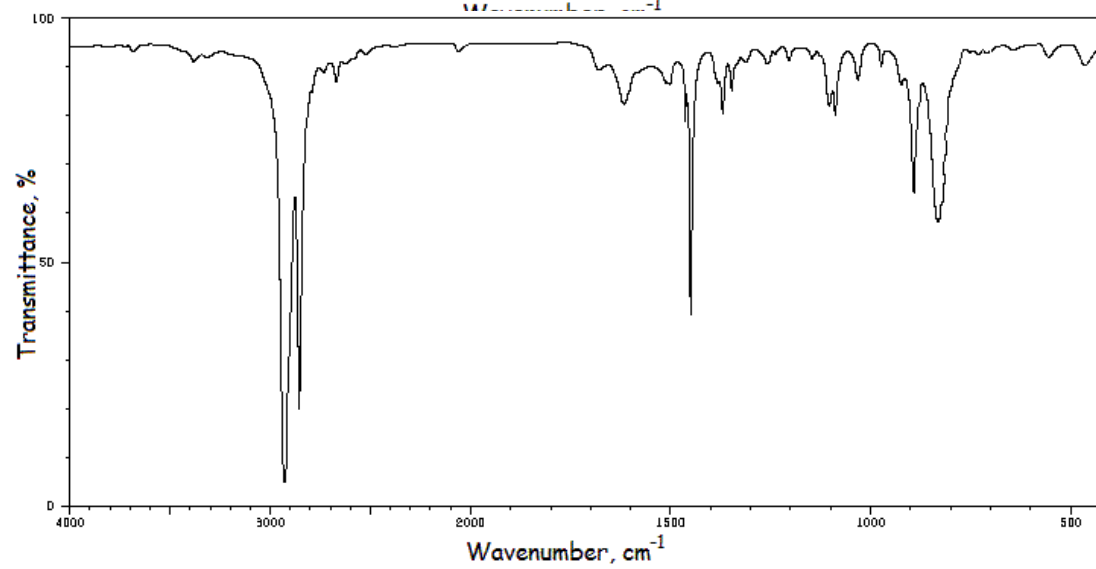
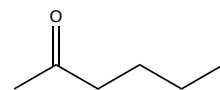
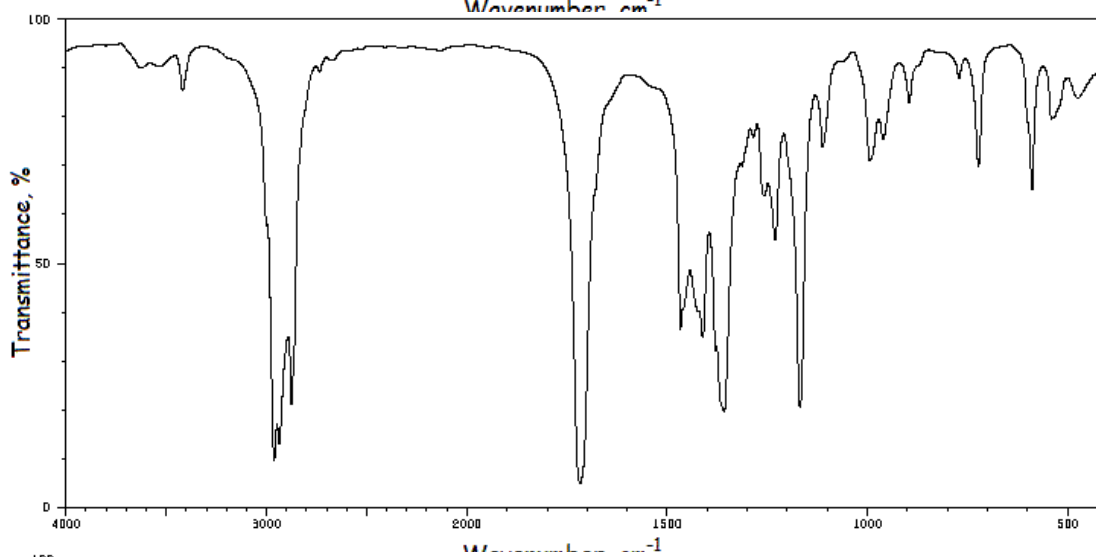
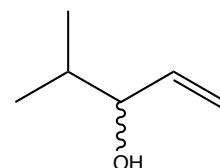
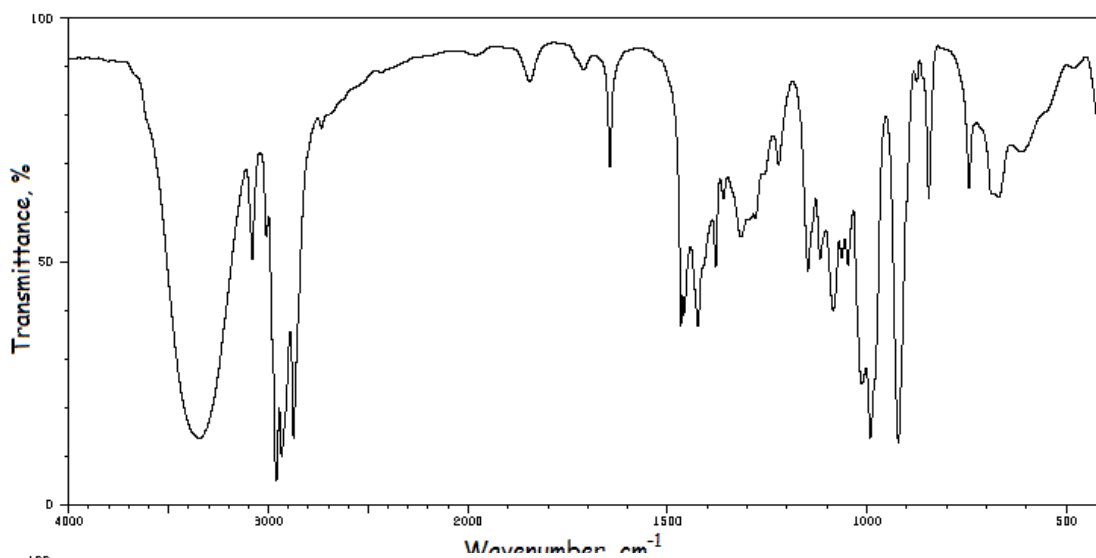
f. MW 136, C₈H₈O₂

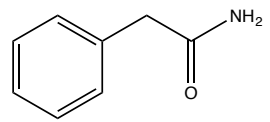
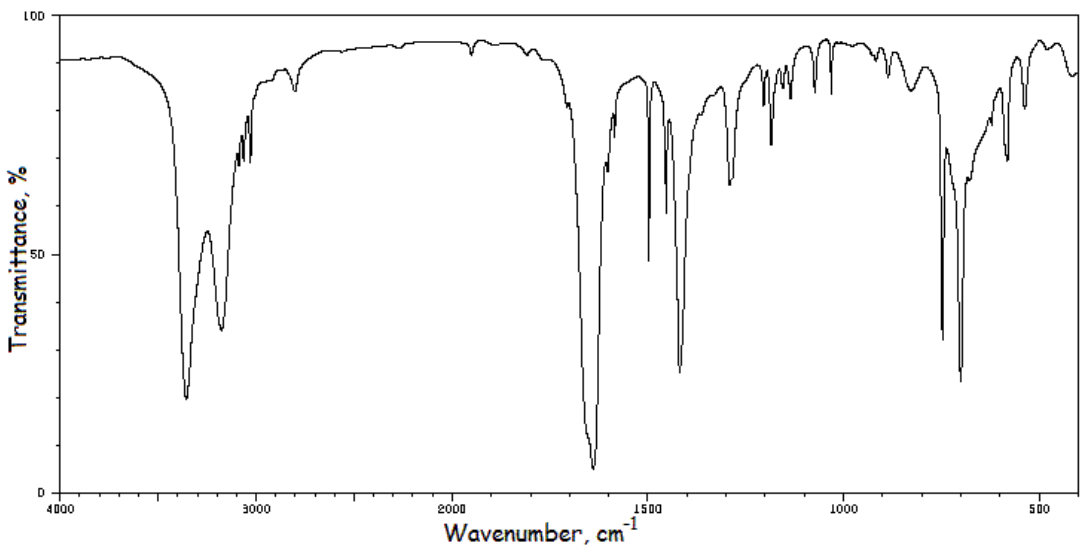
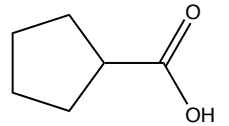
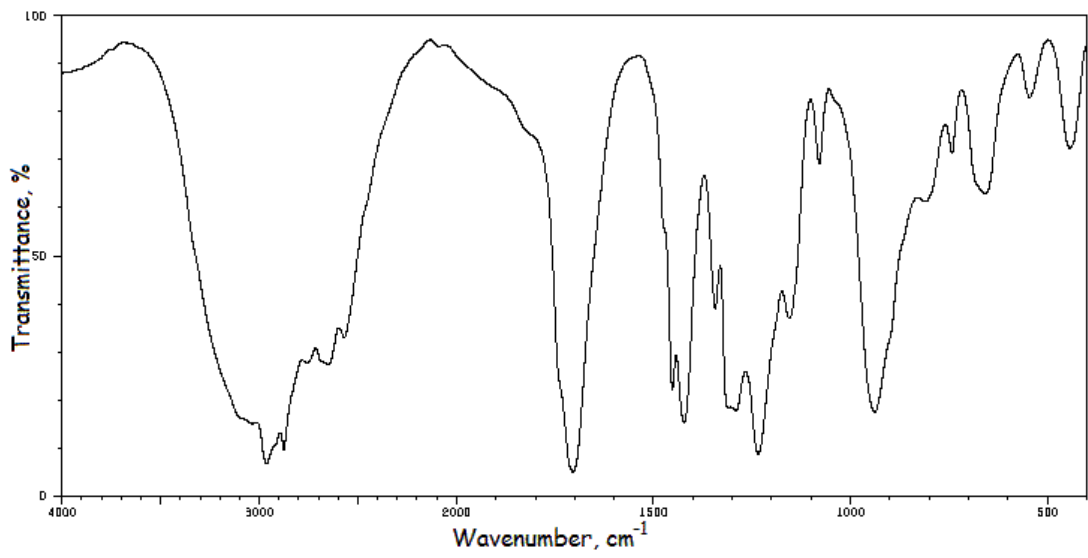
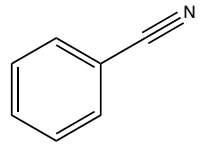
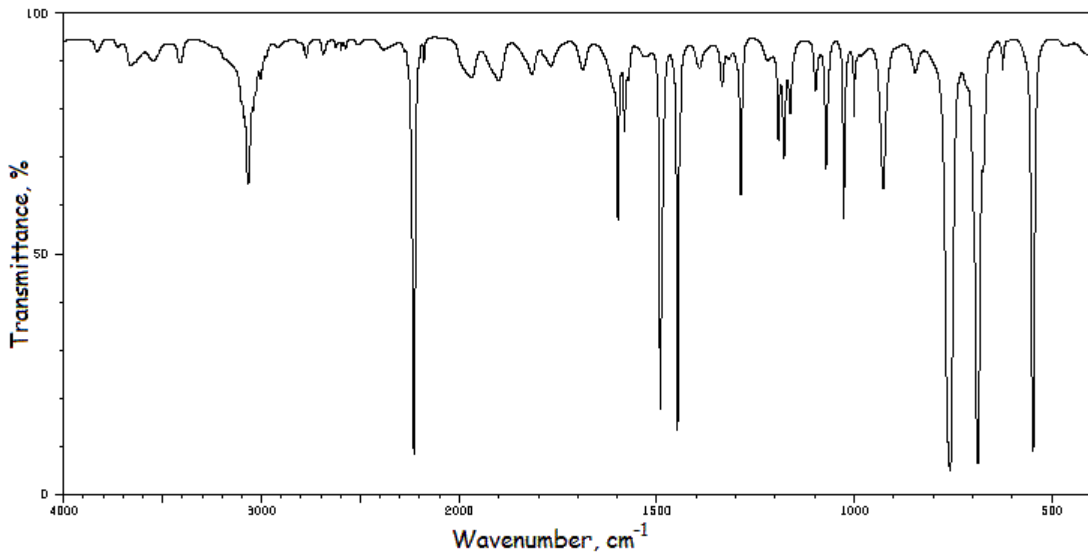


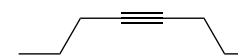
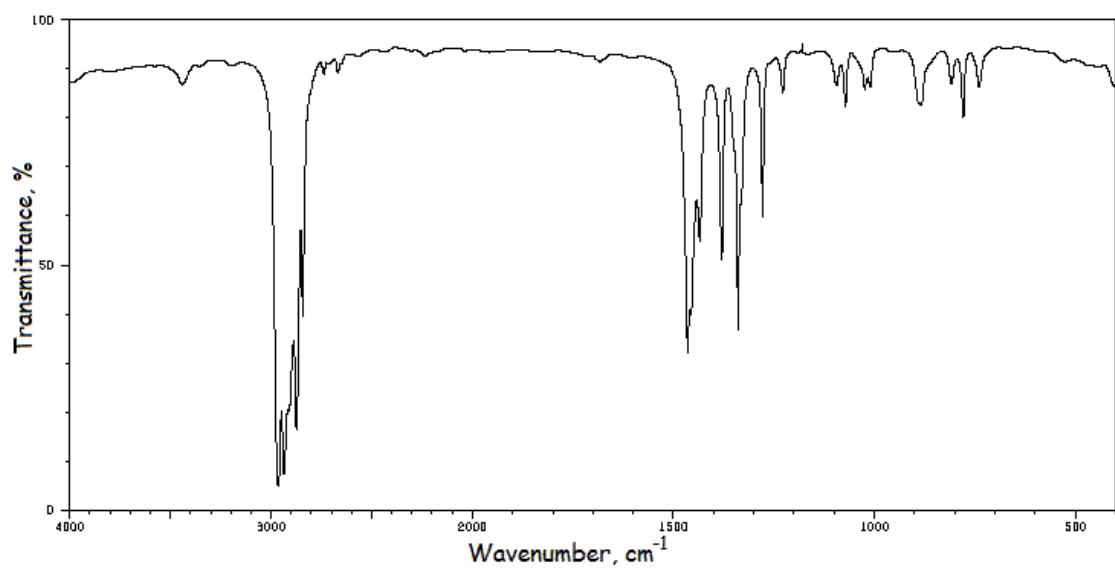
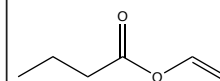
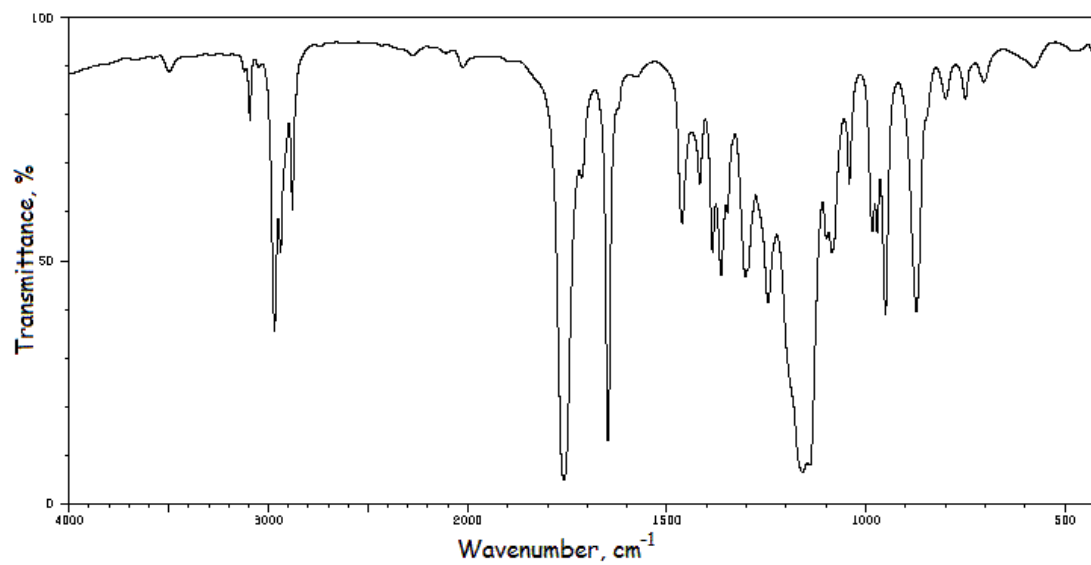
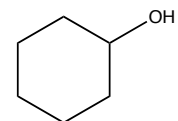
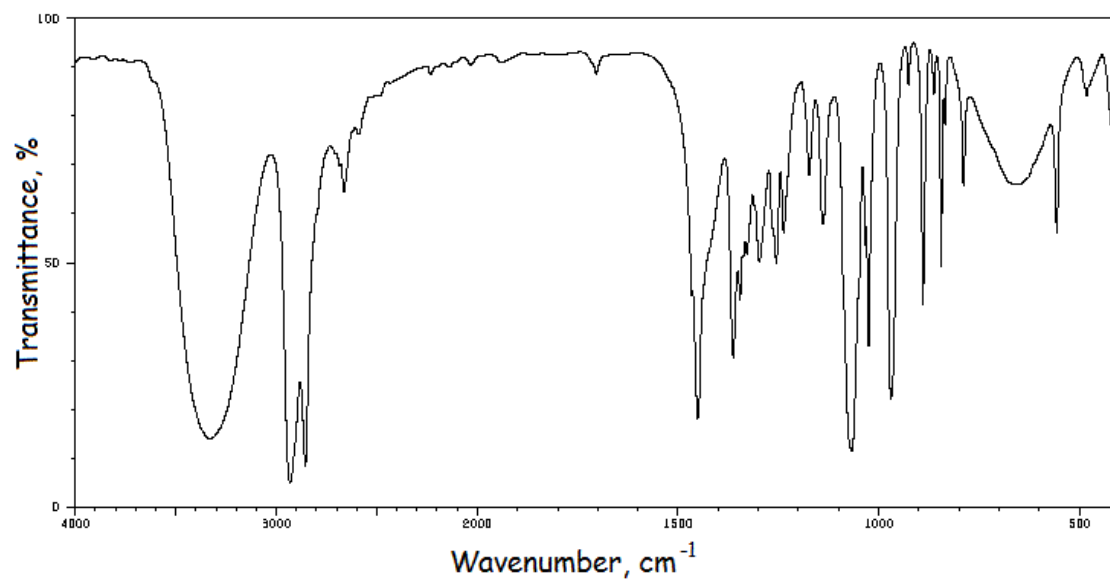
IR looks like a carboxylic acid (carbonyl plus broad, low energy O-H). However, the value for the carbonyl (1689) is lower than expected, which leads one to suspect conjugation. Thinking conjugation and five degrees of unsaturation, I jump to a benzene ring. The best isomers are all benzoic acids, and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

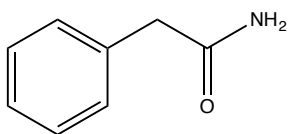
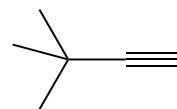
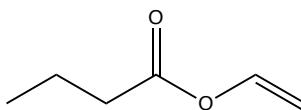
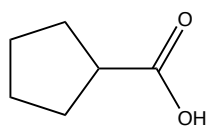
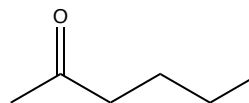
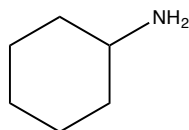
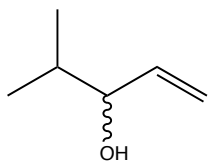
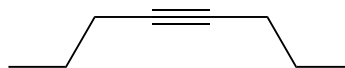
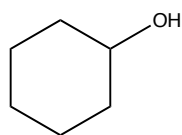
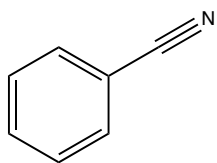
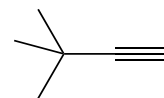
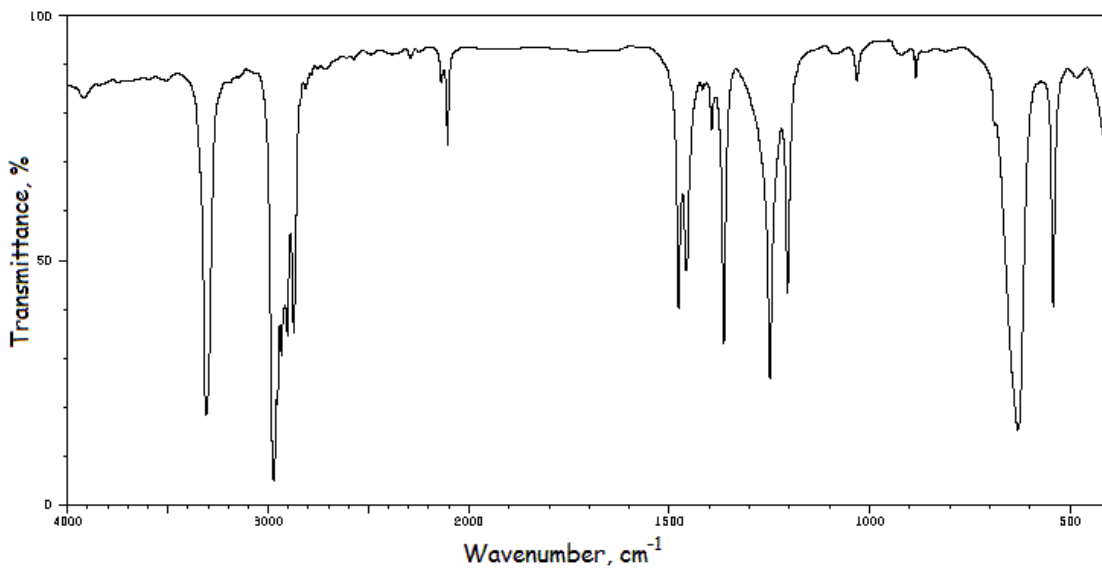


Each one of the following IR spectra (shown below) corresponds to one of the ten compounds at the bottom of the list. Match each spectrum to the correct structure. Look for important functional groups.







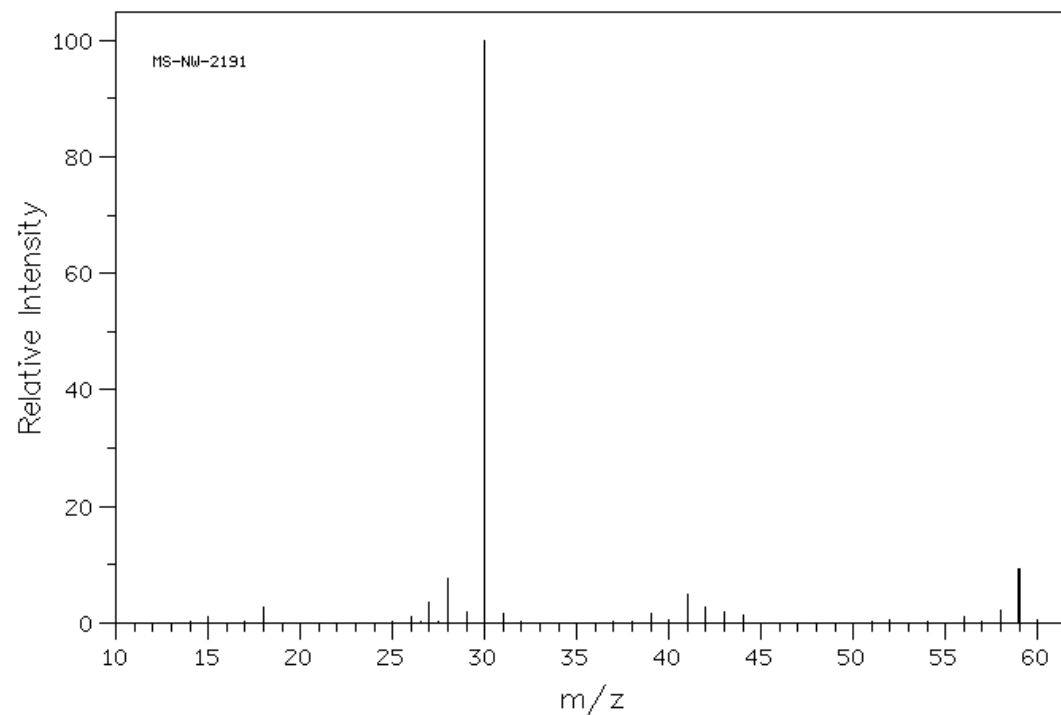
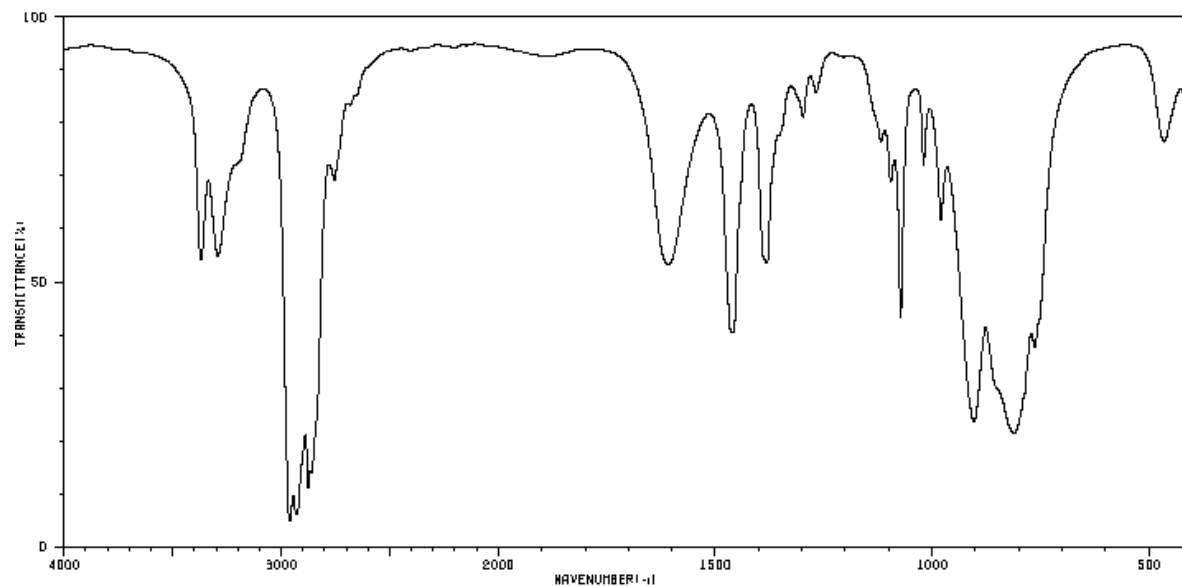


Combined IR Spectroscopy and Mass Spectrometry Problems

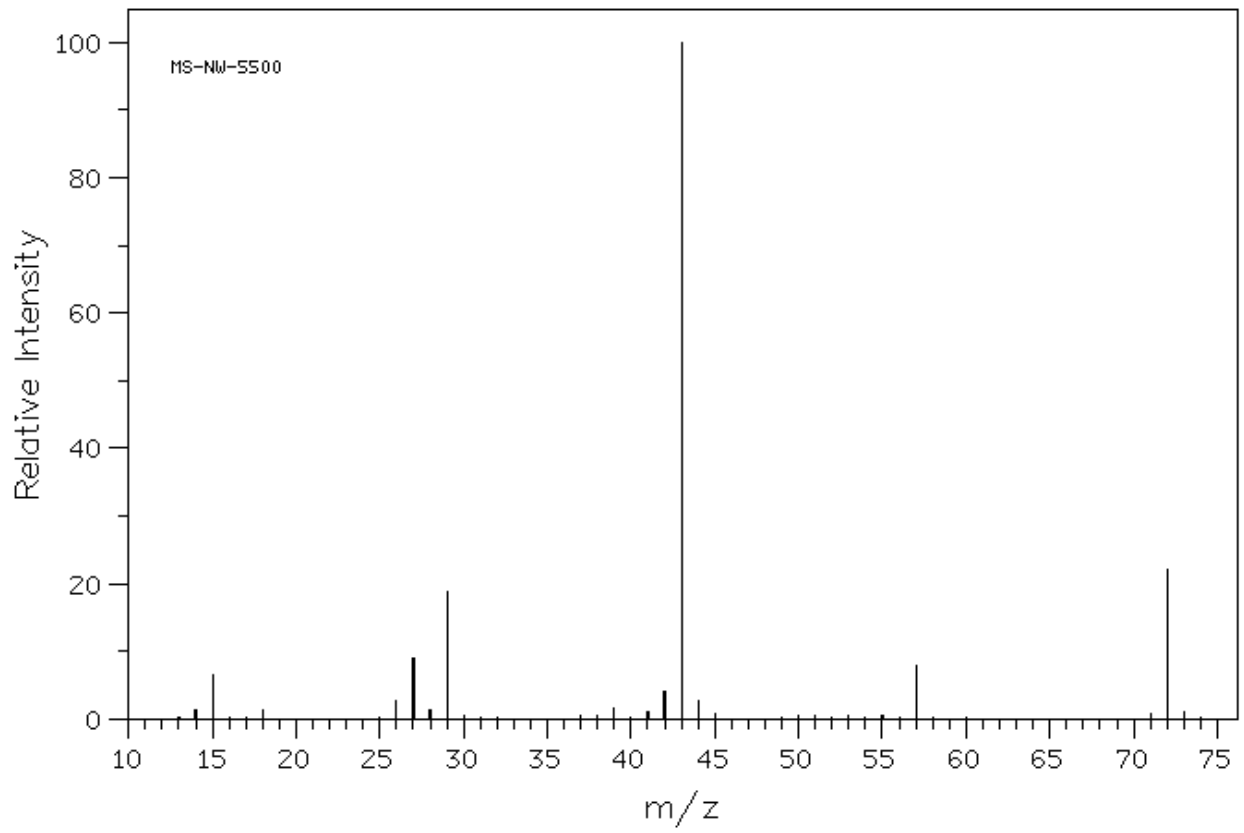
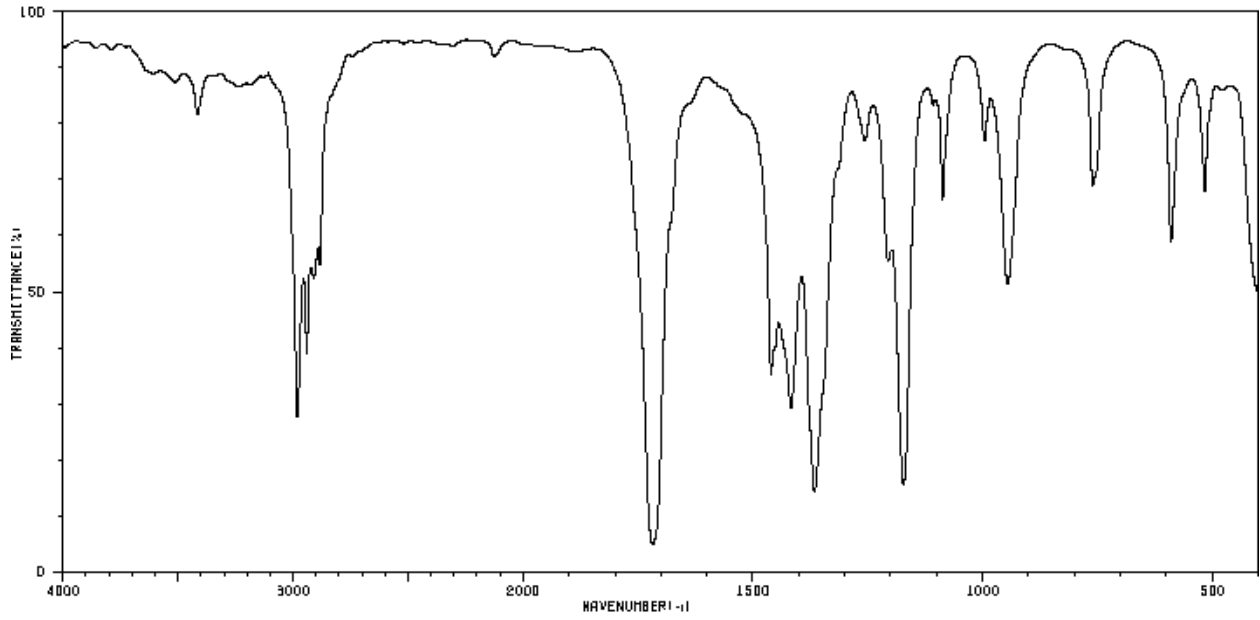
Determine the molecular formula and possible structures for each unknown based on the given spectra. Use the IR Correlation Table. Note: $\text{DOU} = \#C_s + 1 - 0.5(\#H_s - \#N_s + \#\text{halogens})$.

SHOW YOUR WORK!

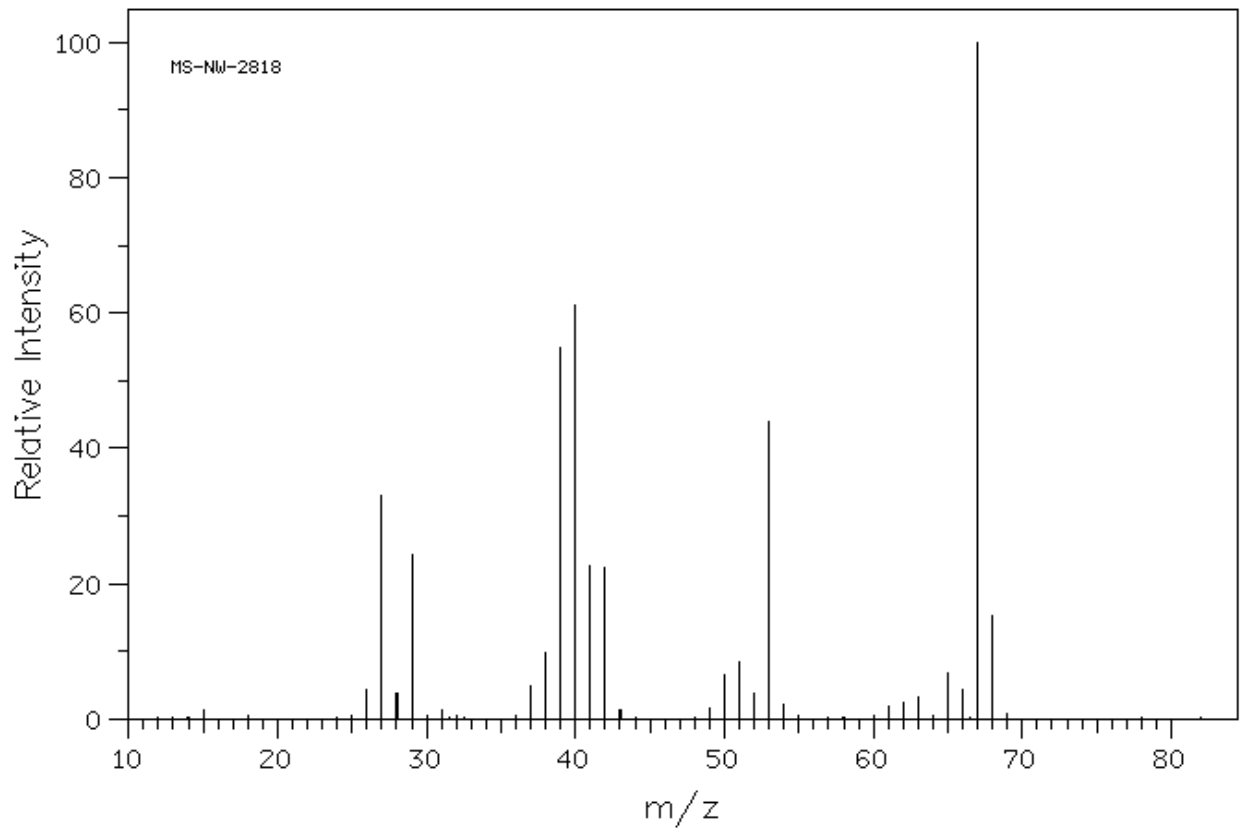
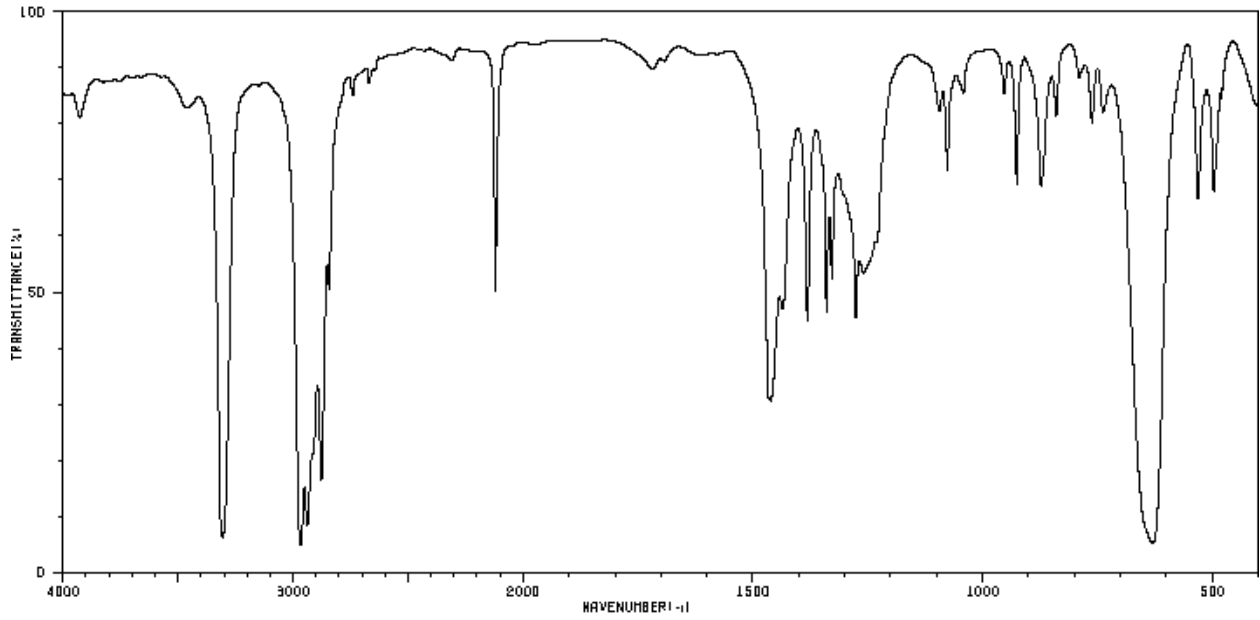
1.



2.

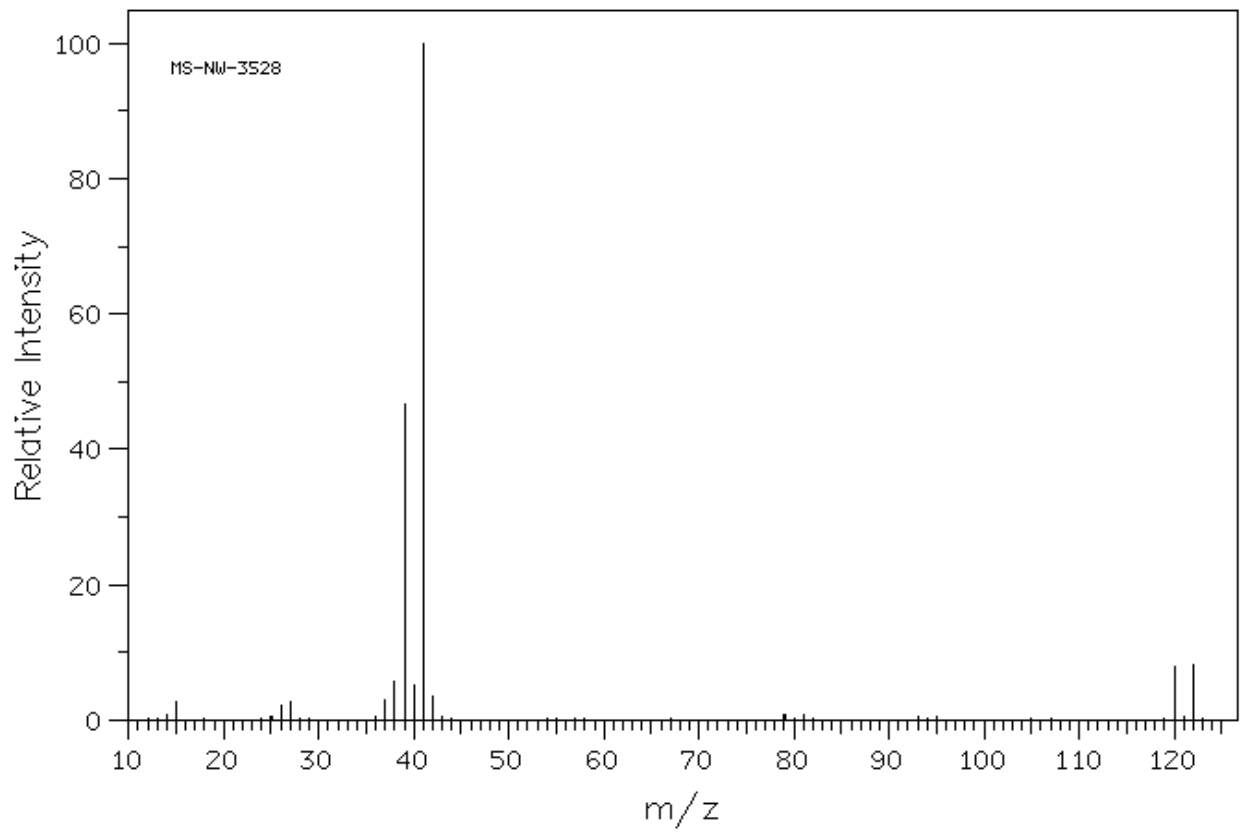
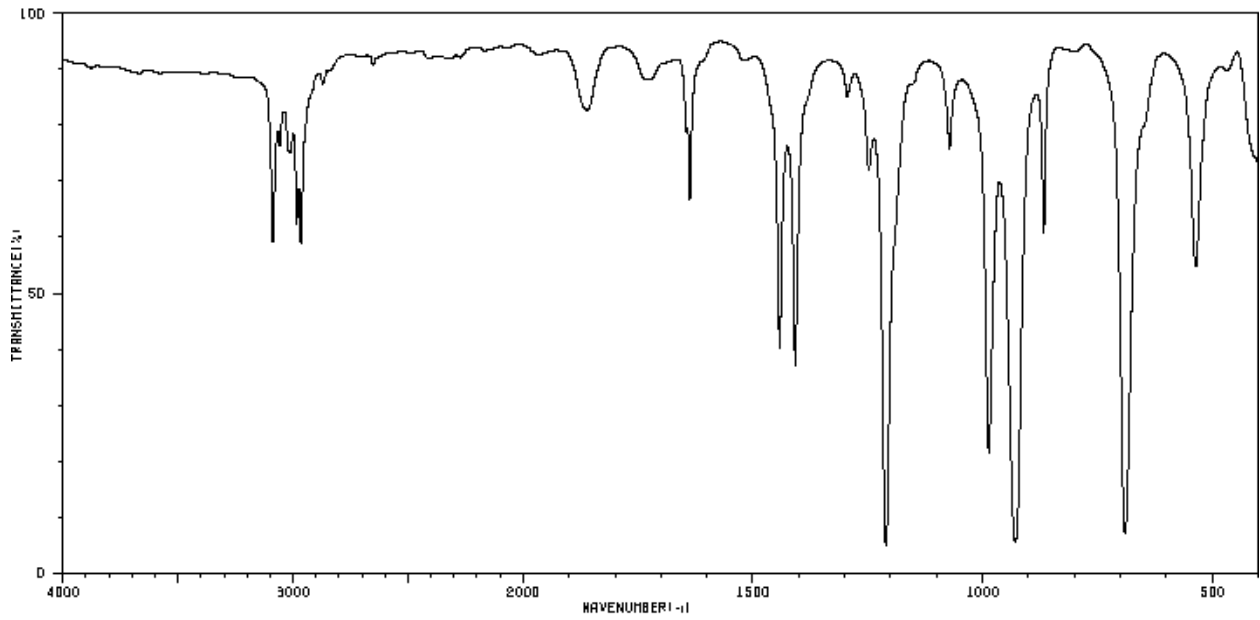


3.

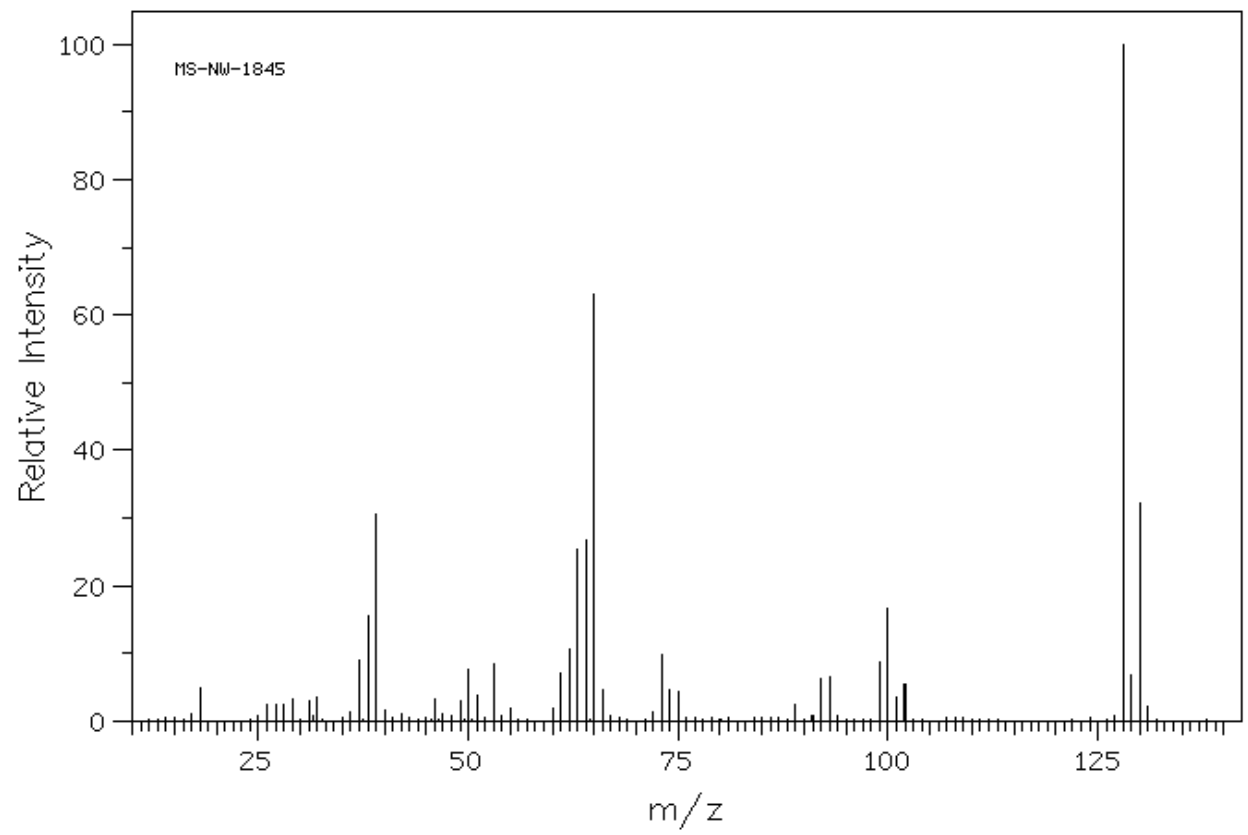
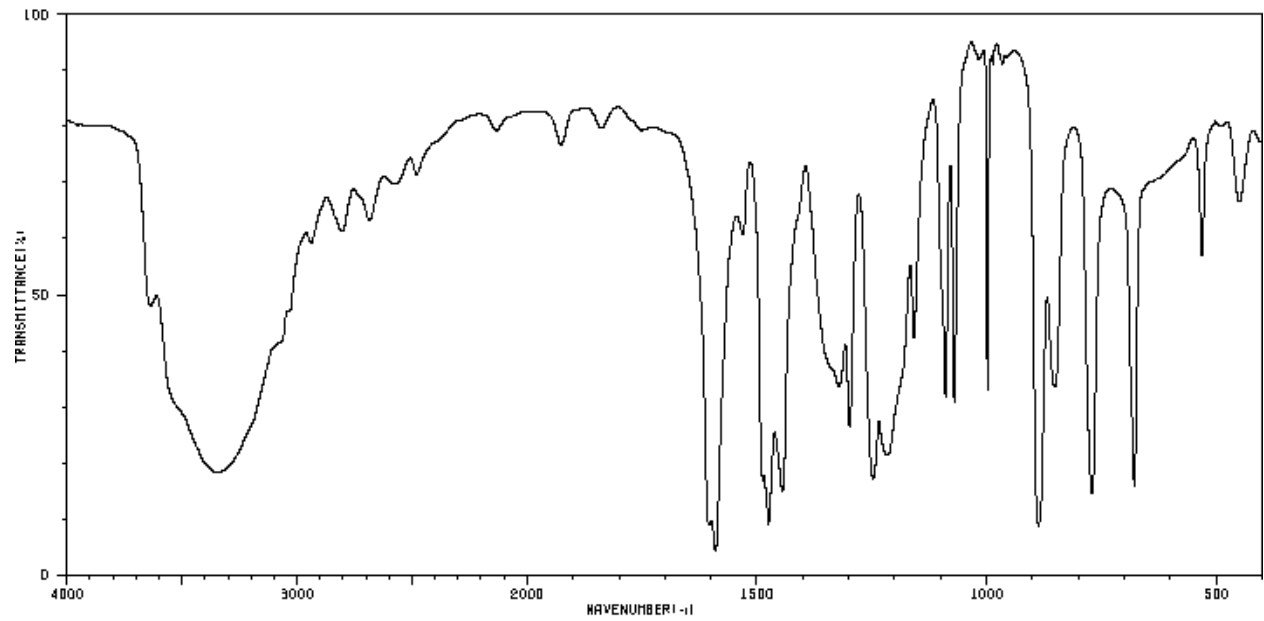


$M^+ = 68$

4.



5.

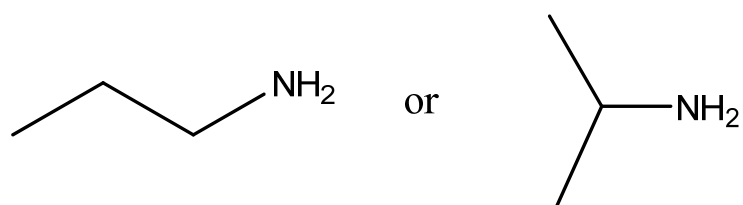


Answers

1. $m/z = 59$, odd mass means odd # of Ns. IR (2 peaks at $3300\text{-}3500\text{ cm}^{-1}$ and 1 peak at 1600 cm^{-1}): NH_2 . $59 - 16 (\text{NH}_2) = 43$. $43/12 = 3\text{Cs} + 7\text{Hs}$. Total of 9Hs (two from NH_2): $\text{C}_3\text{H}_9\text{N}$.

DOU = 0.

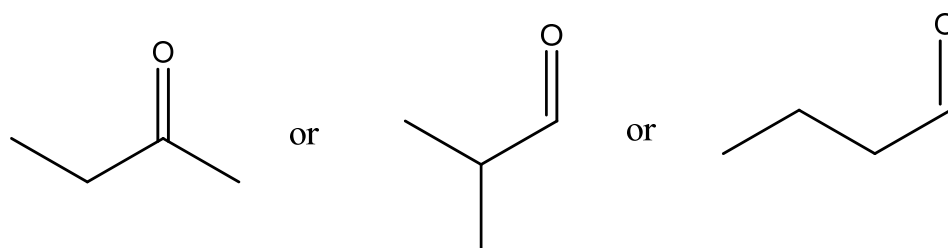
Structures:



2. $m/z = 72$. IR ($\sim 1700\text{ cm}^{-1}$): $\text{C}=\text{O}$. $72 - 28 (\text{C}=\text{O}) = 44$. $44/12 = 3\text{Cs} + 8\text{Hs}$. Total of 4Cs:

$\text{C}_4\text{H}_8\text{O}$. DOU = 1.

Structures:

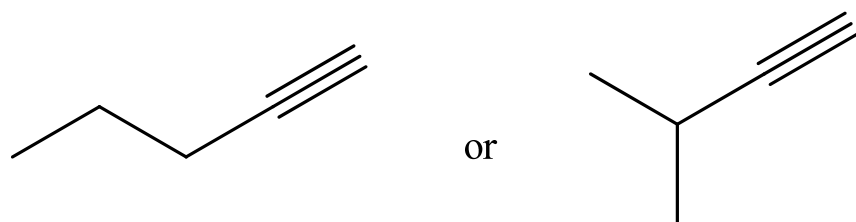


3. $m/z = 68$. IR ($2100\text{-}2200\text{ cm}^{-1}$): $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$. IR (3300 cm^{-1} , sharp): $\text{C}\equiv\text{C-H}$.

Thus, it's $\text{C}\equiv\text{C}$ NOT $\text{C}\equiv\text{N}$. $68 - 25 (\text{C}\equiv\text{C-H}) = 43$. $43/12 = 3\text{Cs} + 7\text{Hs}$.

Total of 5Cs and 8Hs: C_5H_8 . DOU = 2.

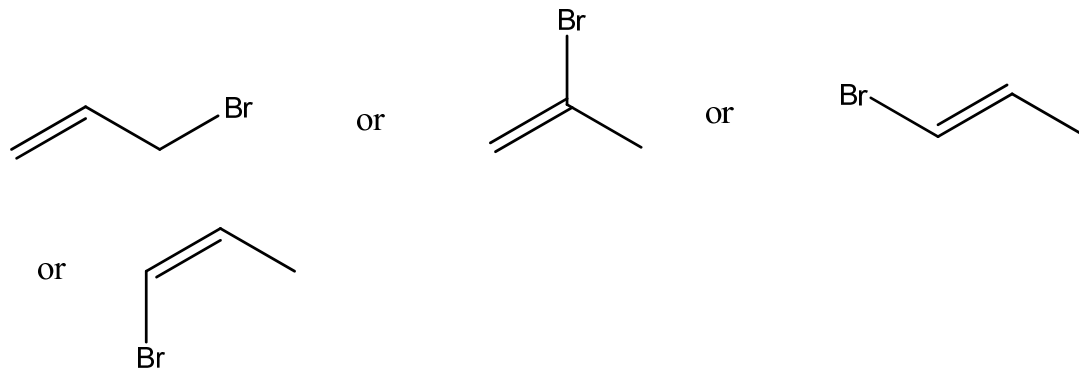
Structures:



4. $M = 120$, $M+2 = 122$ (1:1, 1 Br present). $120 - 79$ (Br) = 41. $41/12 = 3\text{Cs} + 5\text{Hs}$.

$\text{C}_3\text{H}_5\text{Br}$. $\text{DOU} = 1$.

Structures:



5. $M = 128$, $M+2 = 130$ (3:1, 1 Cl present). IR ($3200\text{-}2600\text{ cm}^{-1}$, broad): OH.

IR ($1450\text{-}1600\text{ cm}^{-1}$): benzene $\text{C}=\text{C}$. $128 - 35$ (Cl) $- 17$ (OH) = 76. $76/12 = 6\text{Cs} + 4\text{Hs}$ (from benzene). Total of 5Hs: $\text{C}_6\text{H}_5\text{ClO}$. $\text{DOU} = 4$.

Structures:

