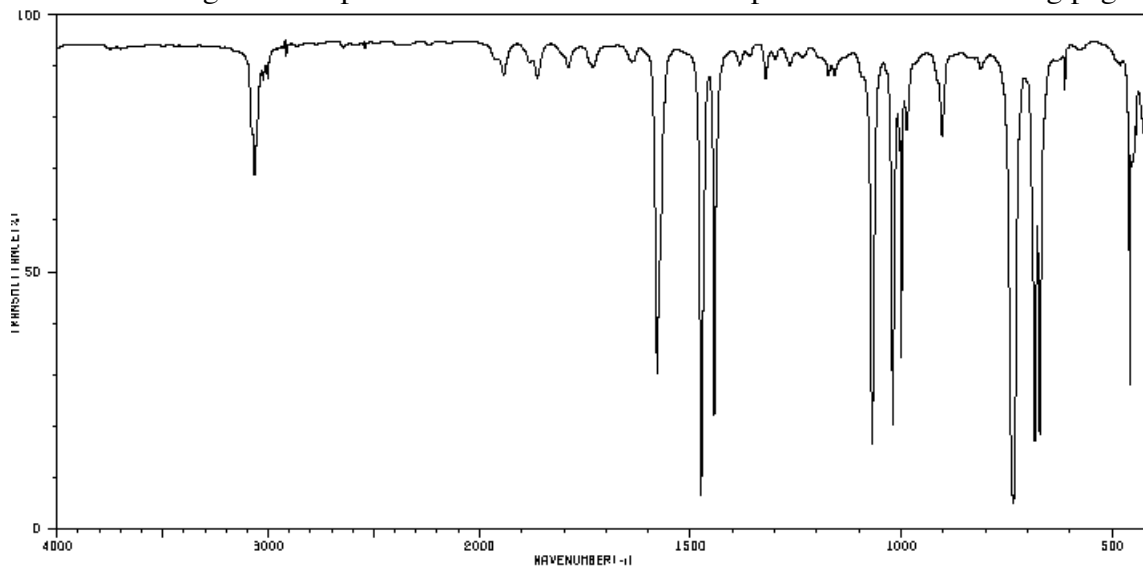


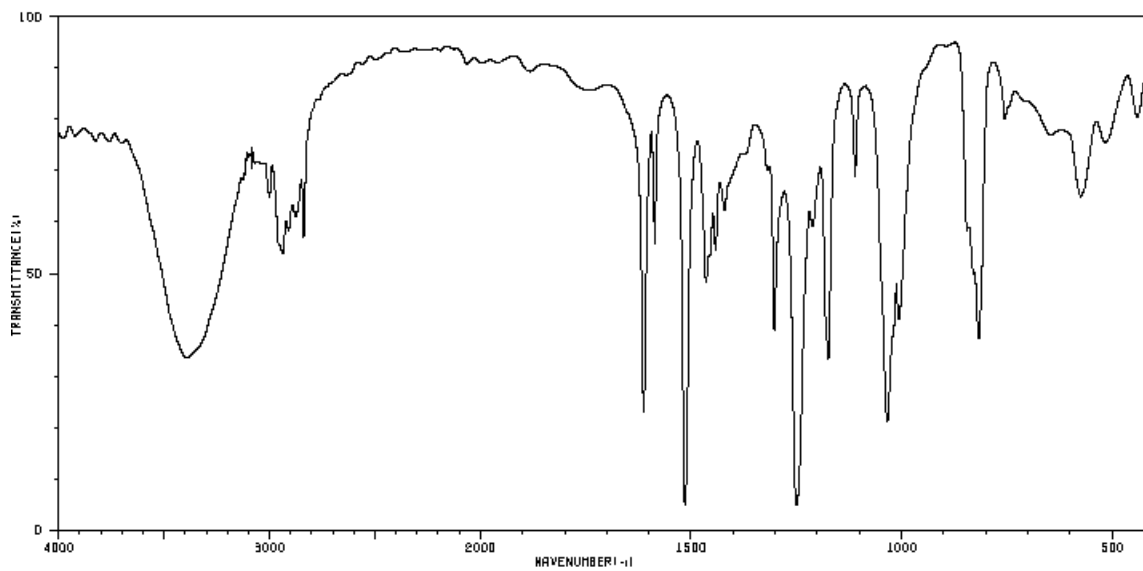
E. B. Skibo

Problem Set #4
CHM 333
November 28, 2008

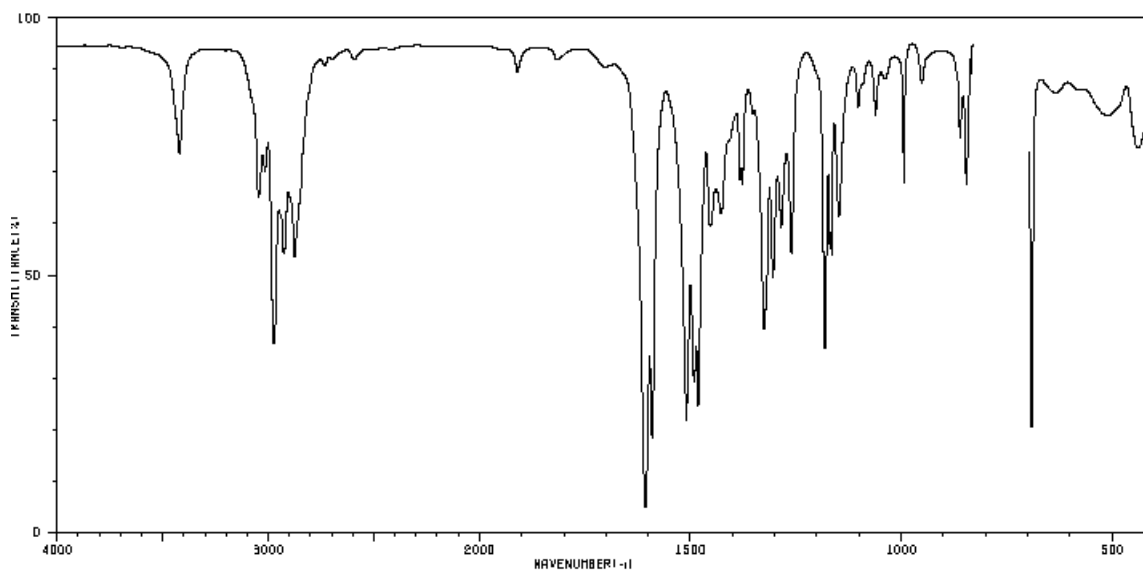
1. Match the following four IR spectra with the selection of compounds on the following page.



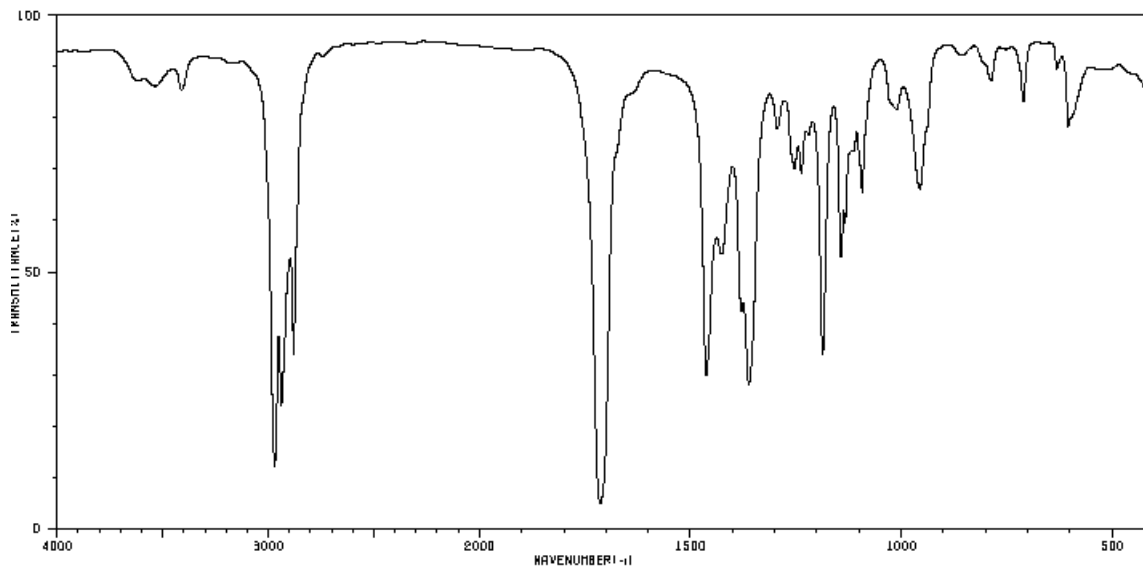
a. A



b. F

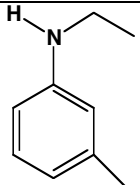
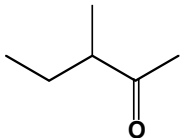
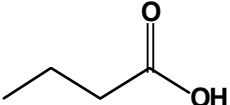
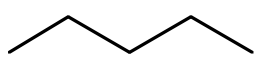
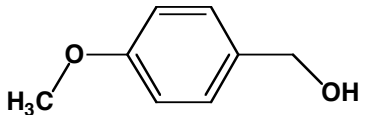


c. C

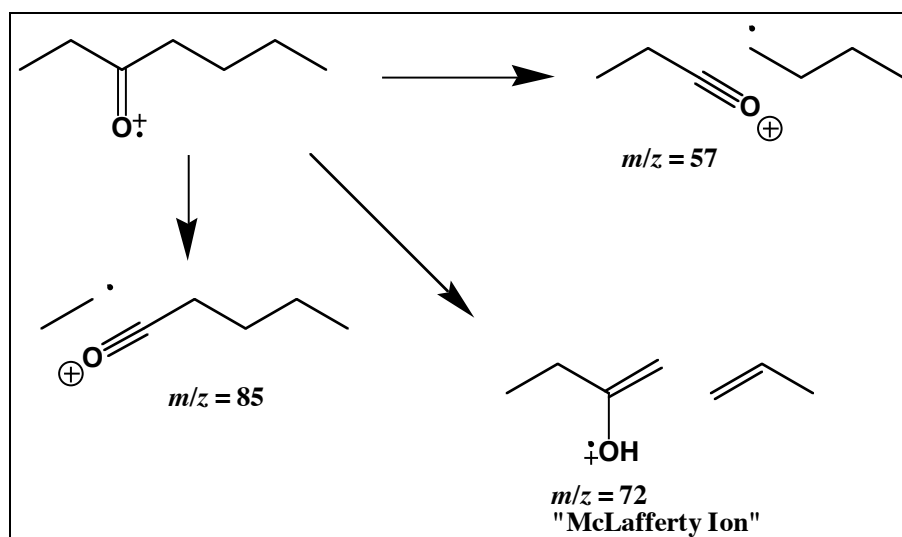
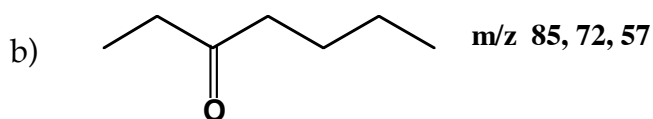
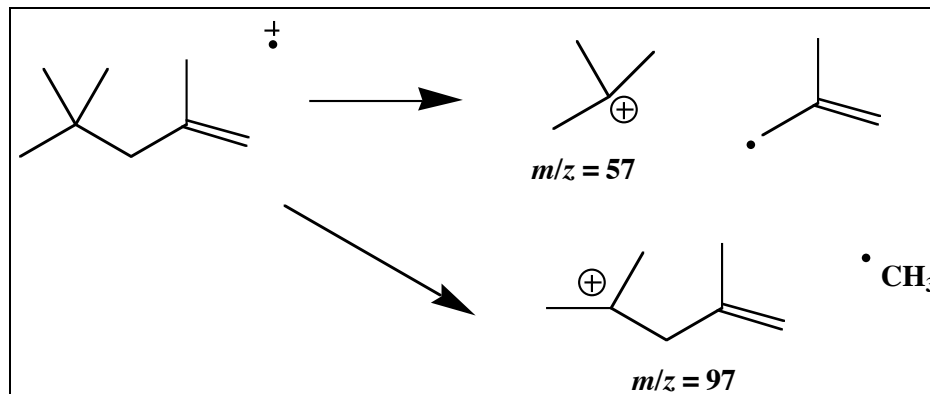
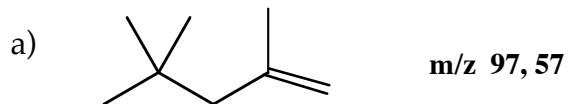


d. E

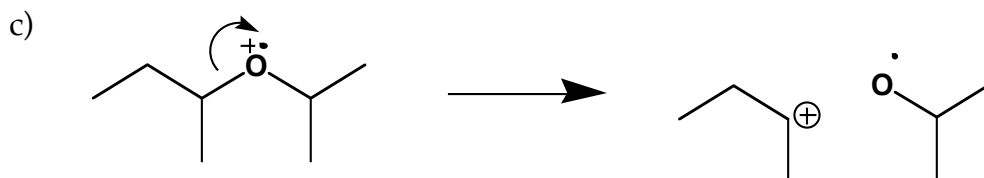
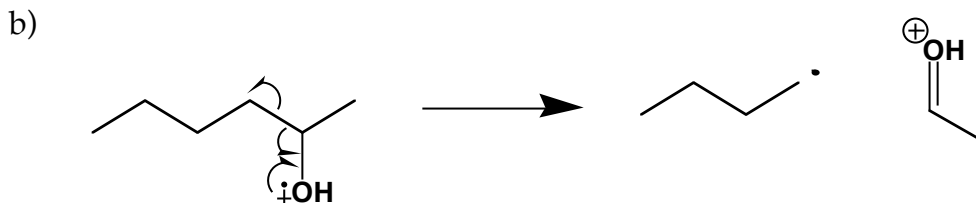
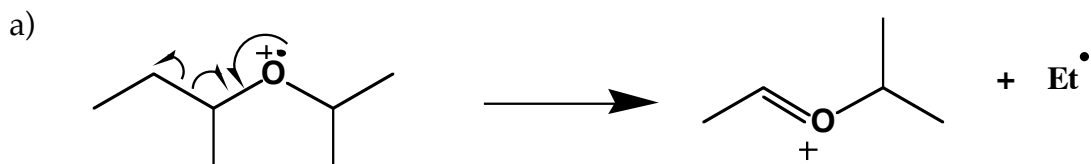
Your choices:

<p>A. None of the above</p>	<p>C.</p> 	<p>E.</p> 
<p>B.</p> 	<p>D.</p> 	<p>F.</p> 

2. Show equations to account for the major fragments ions with the m/z values provided.

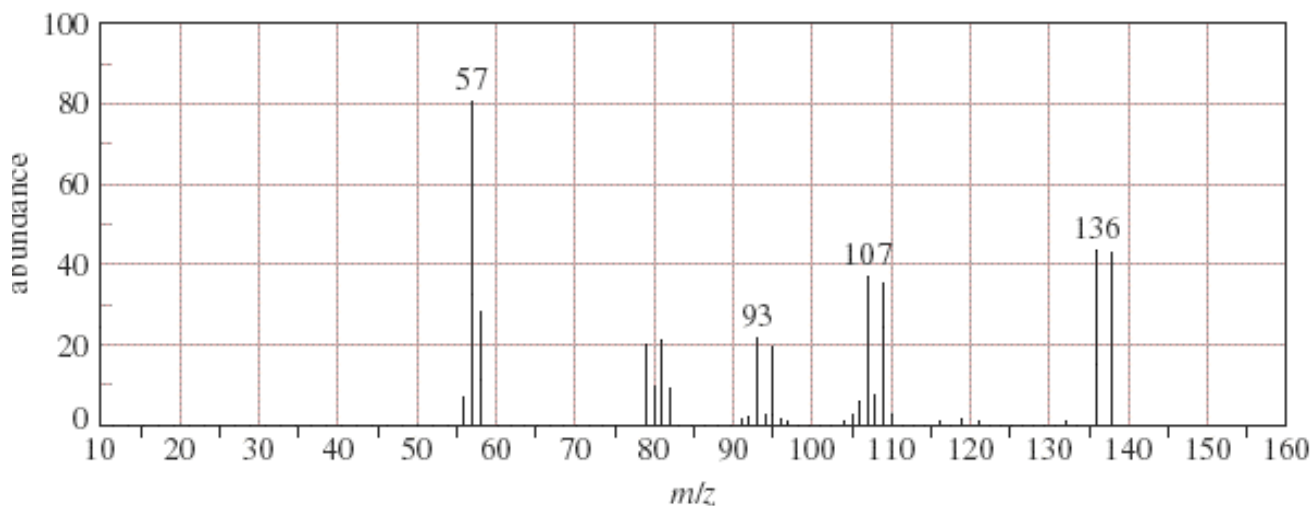


3. Provide mechanisms for the following fragmentations by adding curved arrows



4. Provide the structures of the following compounds using the mass spectra provided.

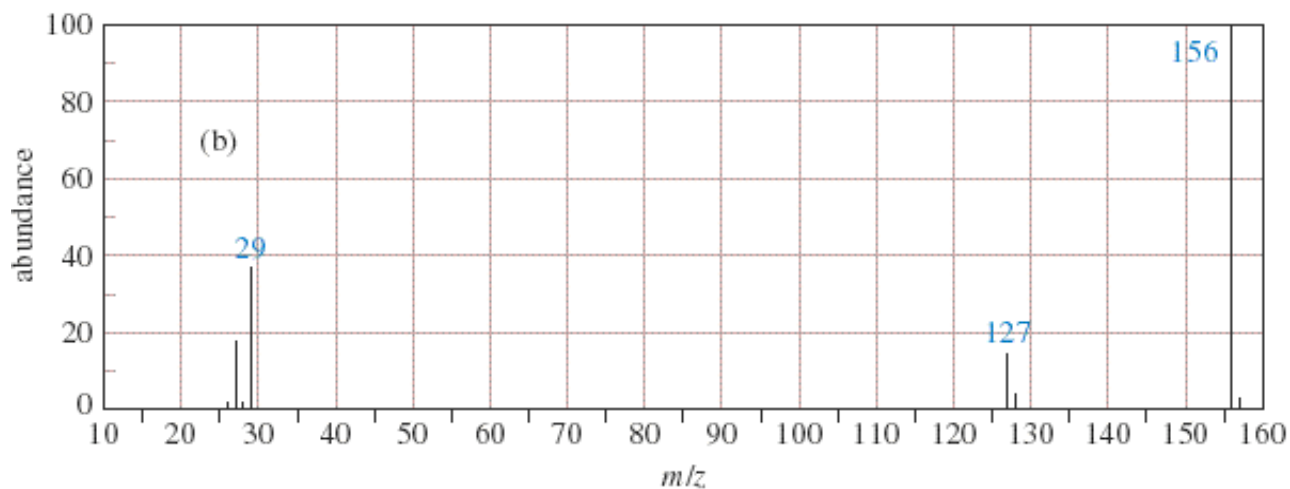
a) This compound was left over from a first semester undergraduate laboratory experiment.



- Has one bromine
- Base peak = 57, must be a secondary butyl carbocation because the peak is intense.

2-bromobutane prepared by the addition of HBr to 2-butene in an undergraduate lab experiment.

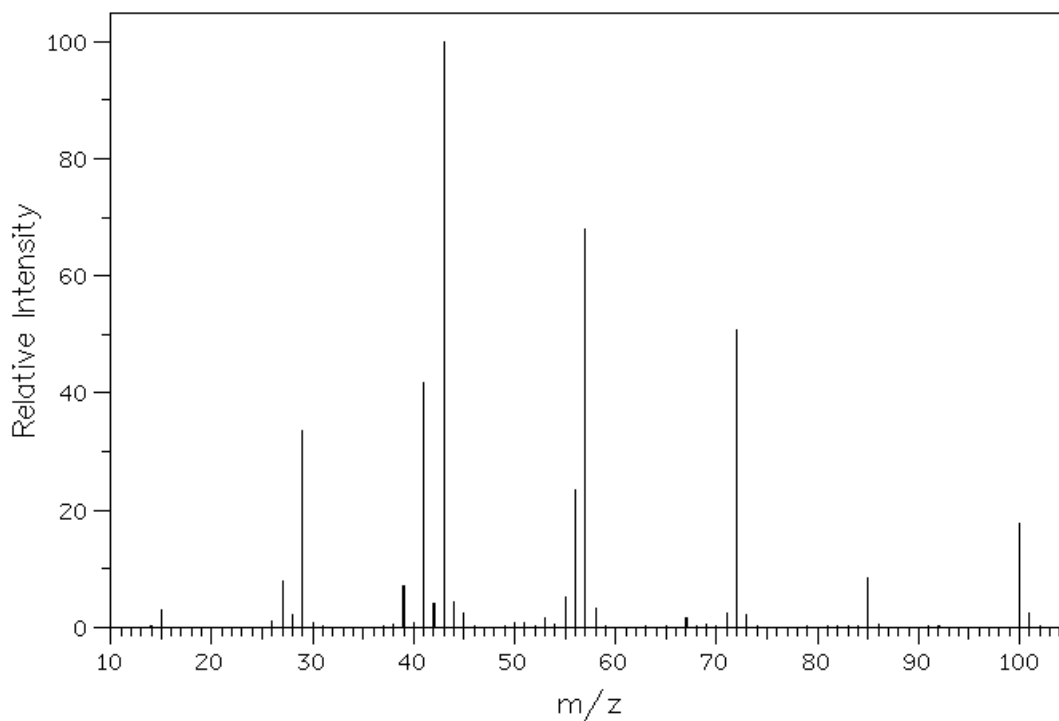
b) The following compound is found in most organic laboratories.



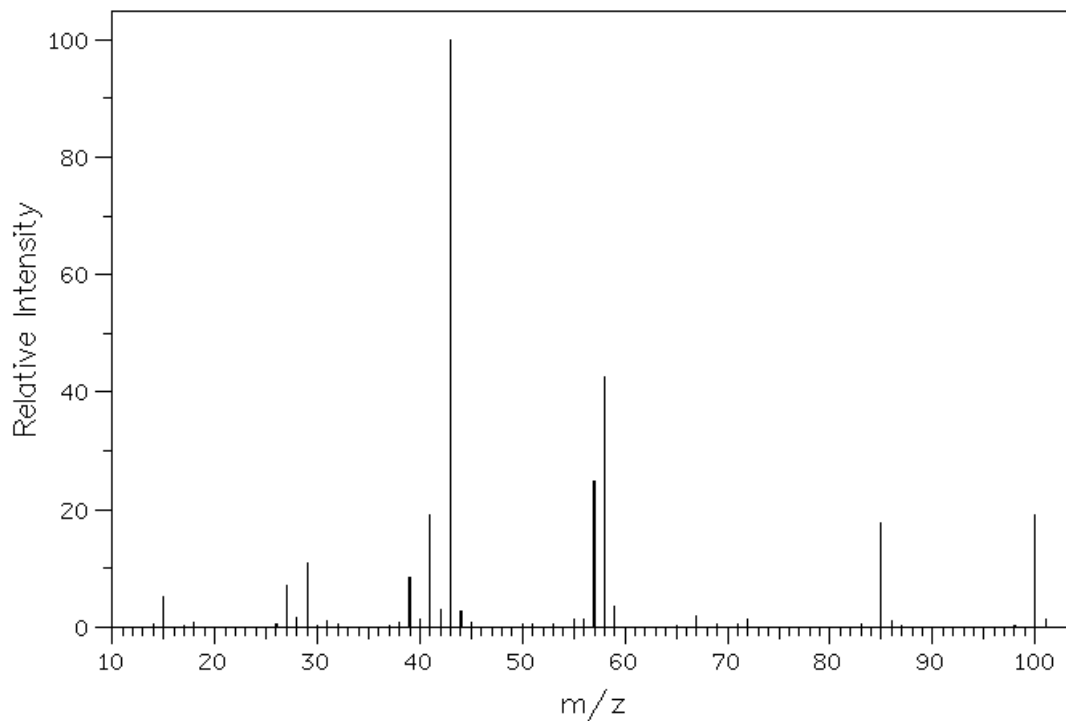
- $m/z = 29$, ethyl
- a big element, $m/z = 127$, must be iodine
- Ethyl iodide

5. The mass spectra of 3-methyl-2-pentanone and 4-methyl-2-pentanone as follows. Explain which spectrum goes with each compound. What is the structure of the ion responsible for the peak at m/z 43 in each spectrum?

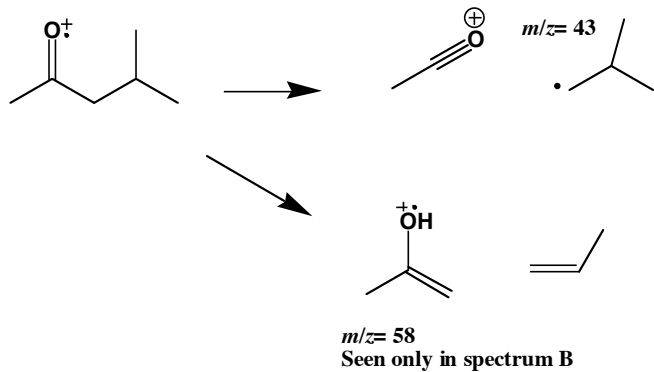
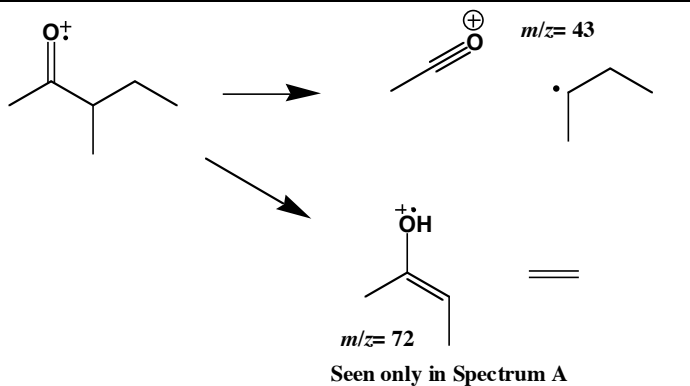
A.



B.



Expected fragmentation pattern

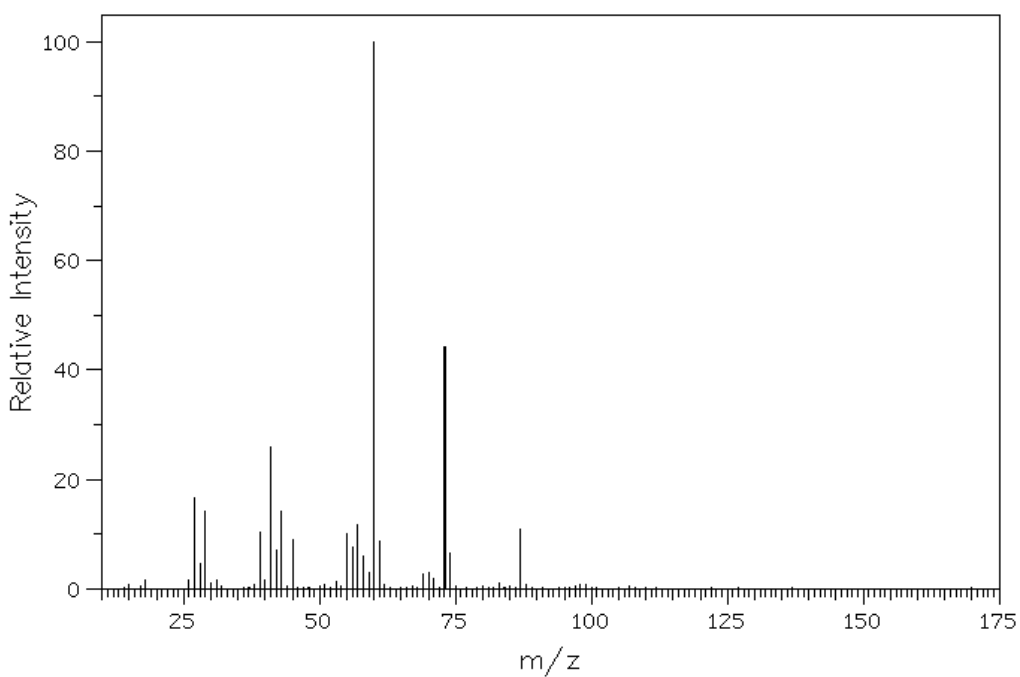
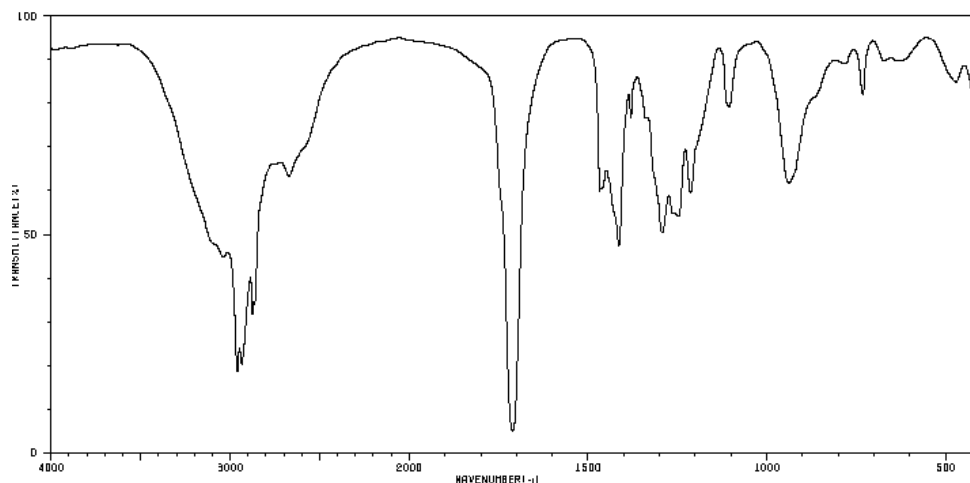


Spectrum A is 3-methyl-2-pentanone
And Spectrum B is 4-methyl-2-pentanone.

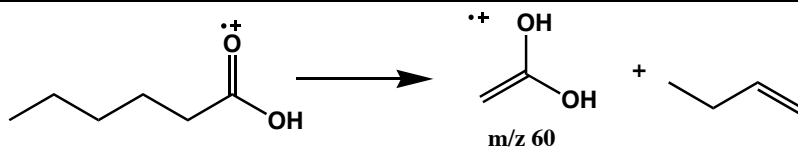
The m/z 43 is methyl acylium ion.

6. Provide the structures of the following compounds using the IR and mass spectra provided. Assign peaks that were important in making your structural assignment.

a)

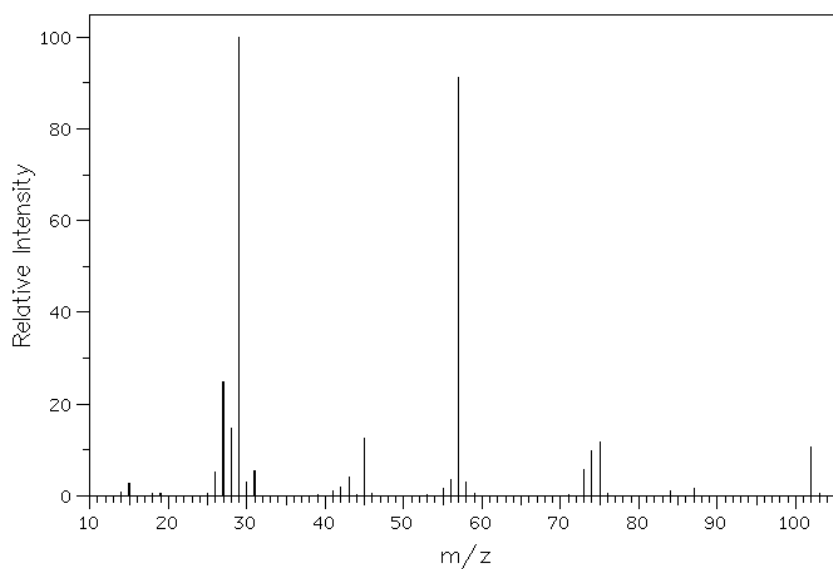
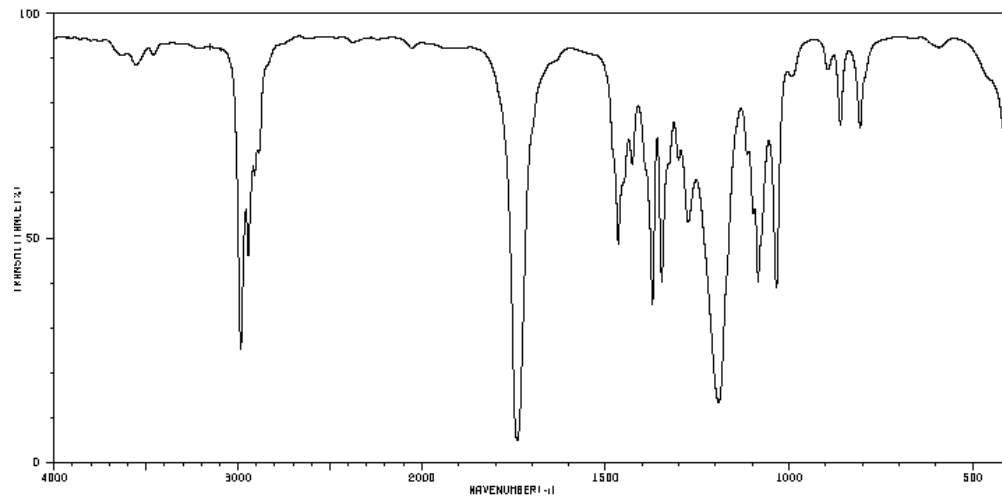


- A Carboxylic acid, m/z 45
- Has 4 sets of fragments differing by 14 m/z starting at m/z 29 (ethyl), therefore five carbon chain: m/z 71
- Expected parent mass at m/z 116, not observed. Consider McLafferty rearrangement
- Base peak at m/z 60 corresponds to McLafferty ion

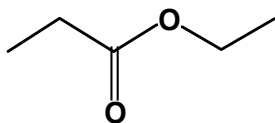


Answer hexanoic Acid

b)

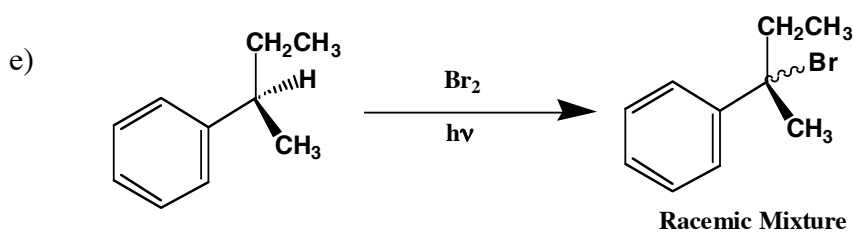
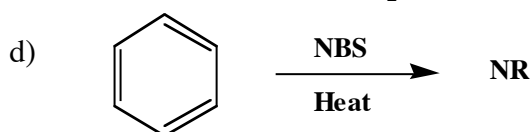
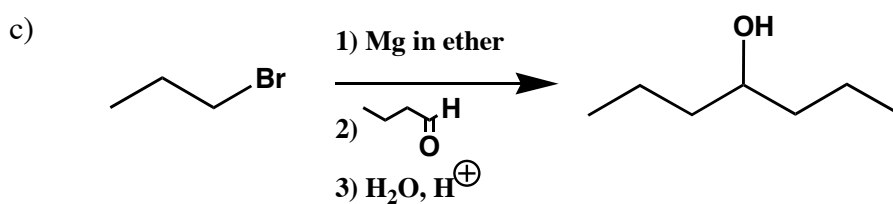
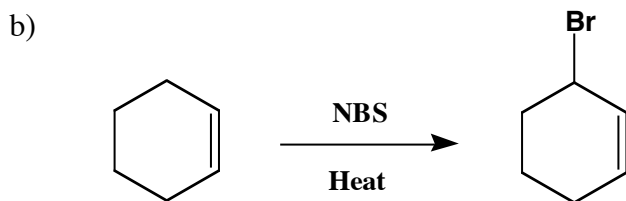
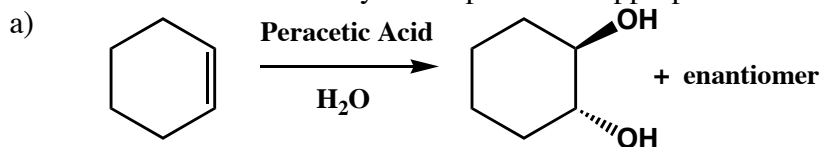


Answer:

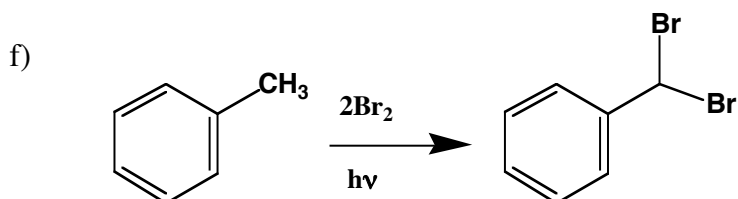


- IR shows a carbonyl and the MS clearly shows an ethyl at m/z 29. These groups account for m/z 57, leaving m/z 45 to be accounted for.
- The IR also shows a strong band at 1200 cm^{-1} for a CO stretch. Together with the carbonyl indicate the presence of an ester.
- Subtracting the mass of oxygen from m/z 45 leaves m/z 29, an ethyl group.
- The MS also shows m/z 57, the ethyl acylium ion

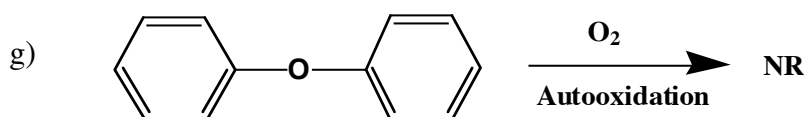
7. Predict the major organic product of the following reactions. If there is no reaction, write "NR" as your answer. Show stereochemistry of the product if appropriate.

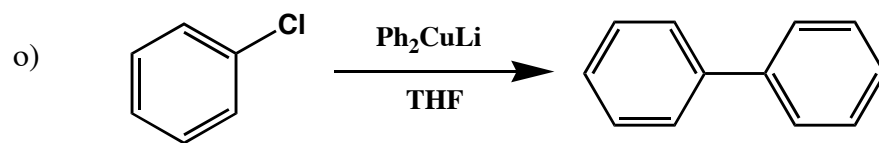
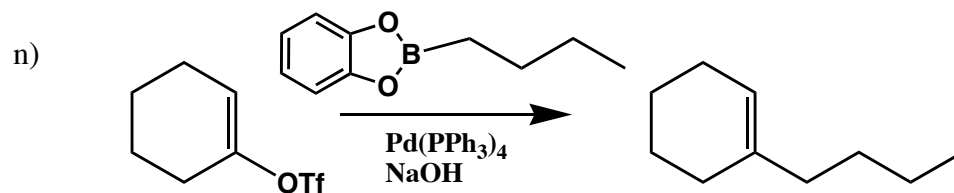
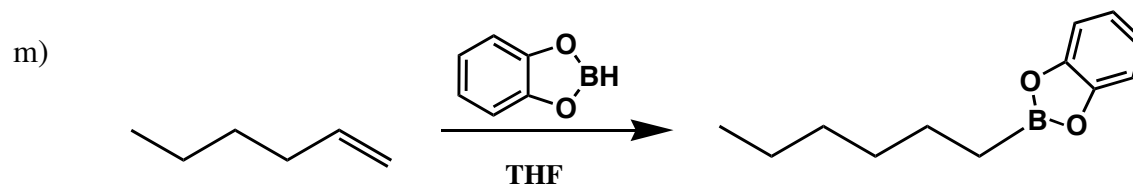
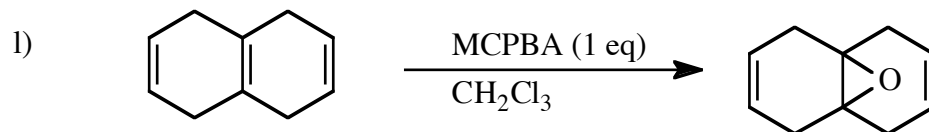
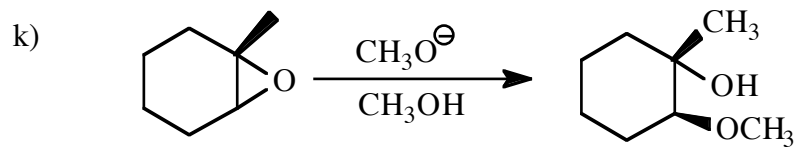
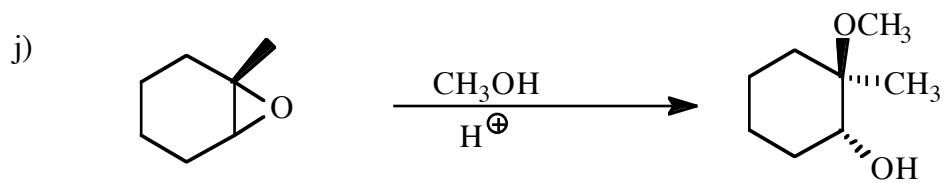
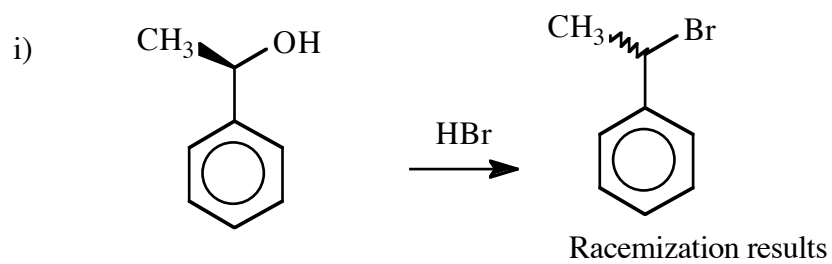
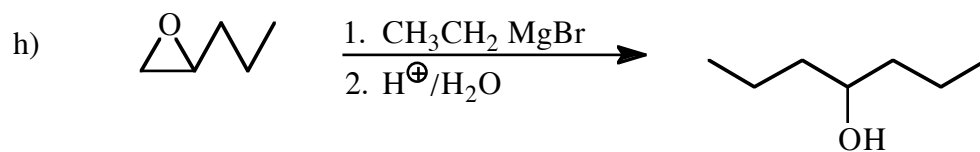


Show the stereochemical result

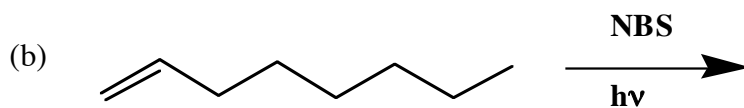
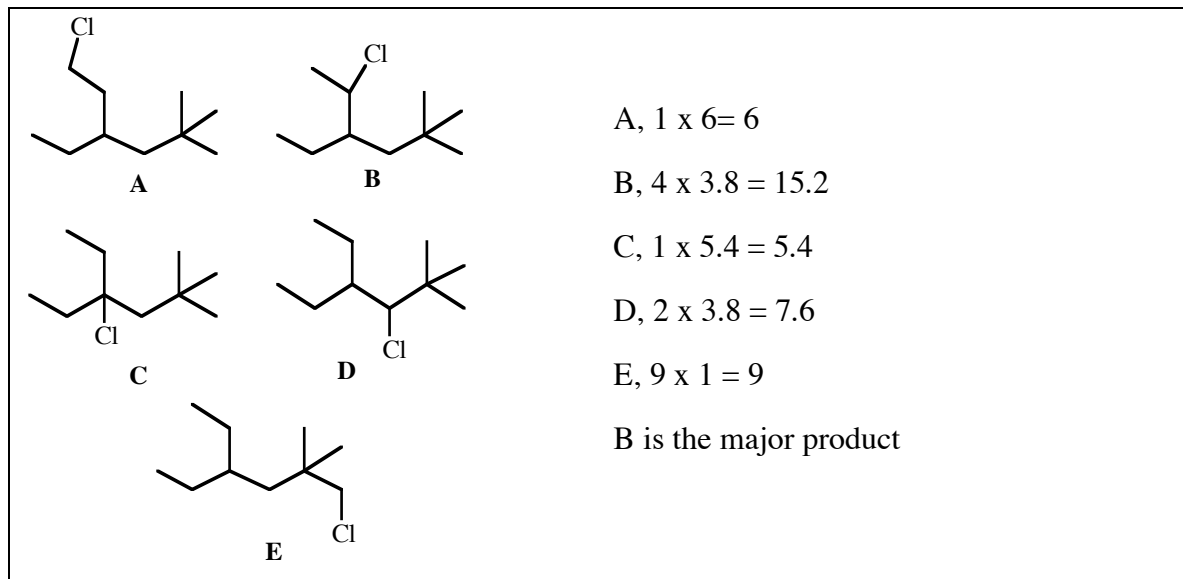
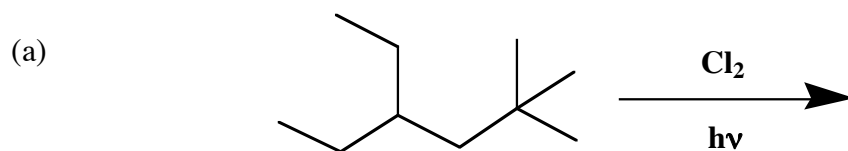


Note that there are two equivalents of bromine

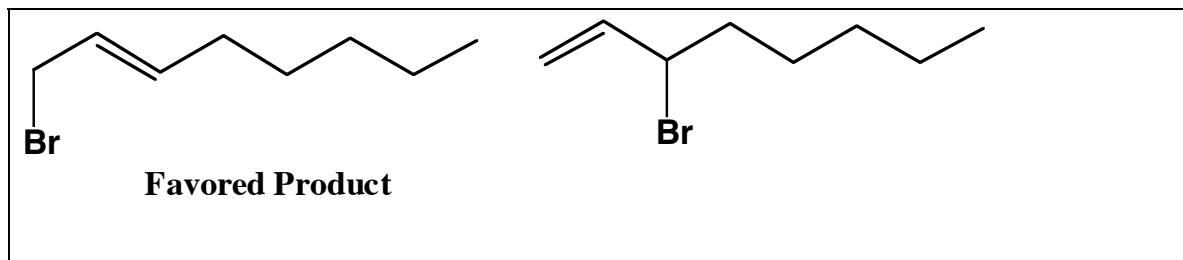




8. Predict all the possible monochlorination products of the alkane shown below. Which product is formed in the highest yield?

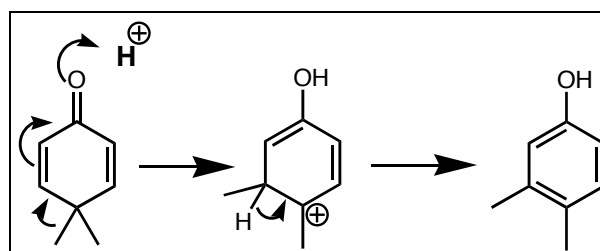
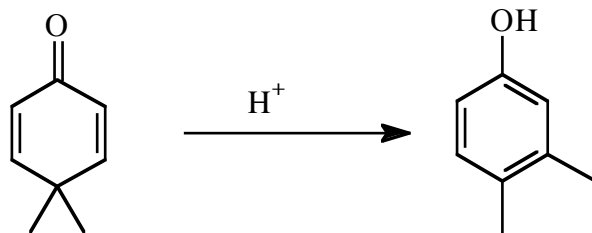


Thermodynamic product favored

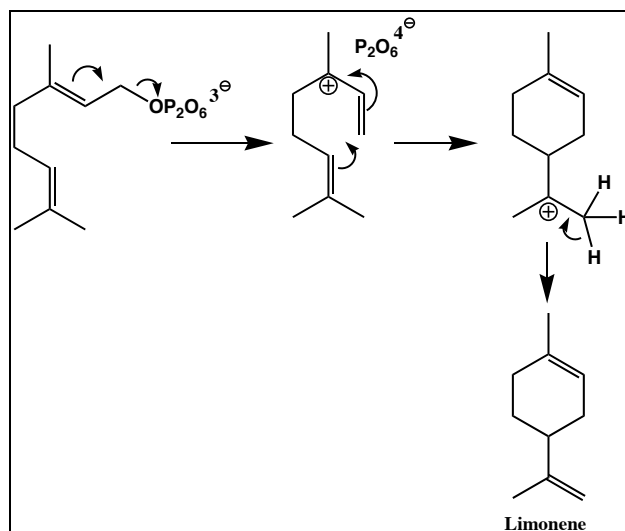
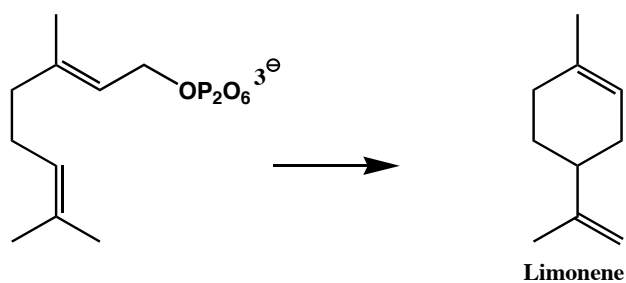


9. For each of the following rearrangements provide a mechanism. Show intermediates present in the reaction along with curved arrows and proton transfers.

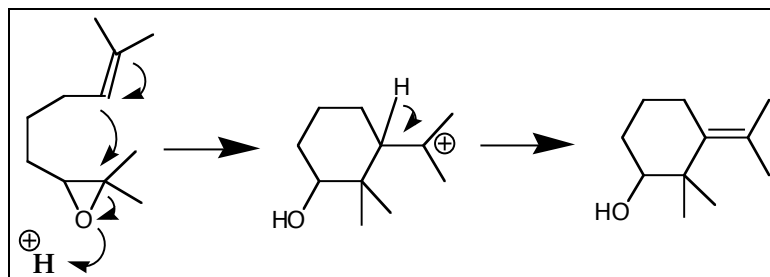
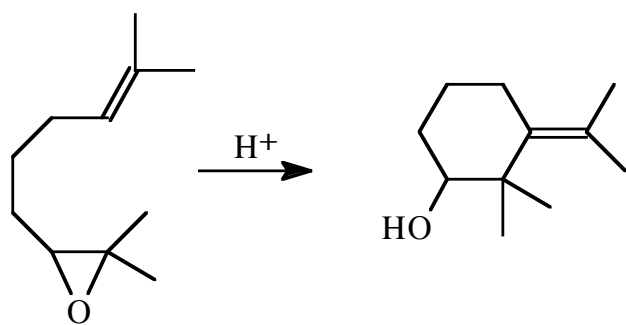
a)



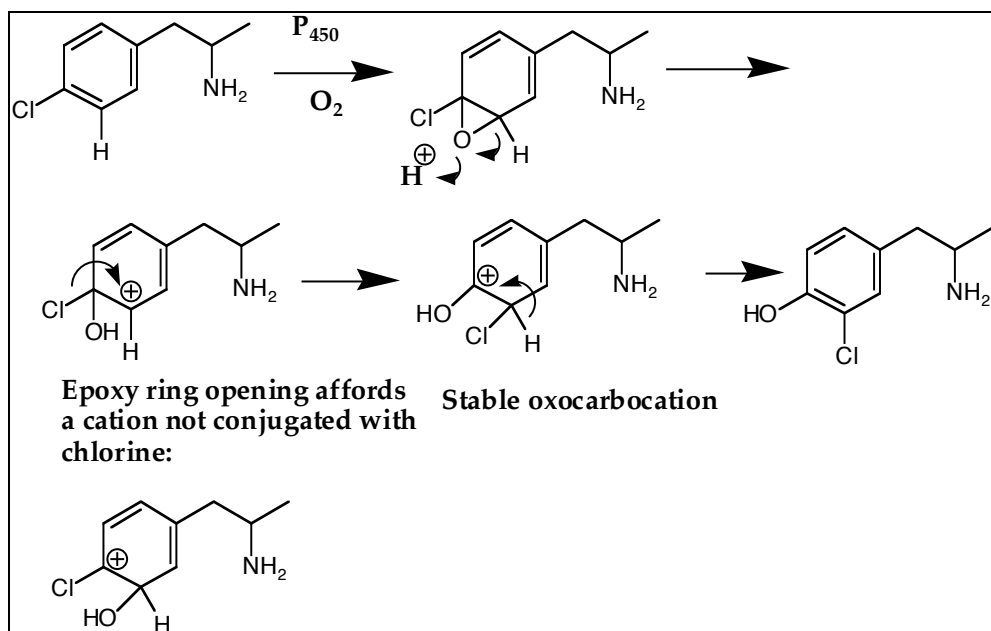
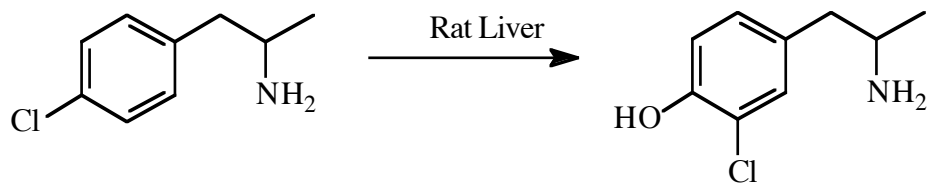
(b) Hydroxyl groups are activated as leaving groups in nature when functionalized as pyrophosphates. Geranyl pyrophosphate is converted to limonene via elimination of pyrophosphate to afford a carbocation that is eventually converted to limonene. Show a mechanism.

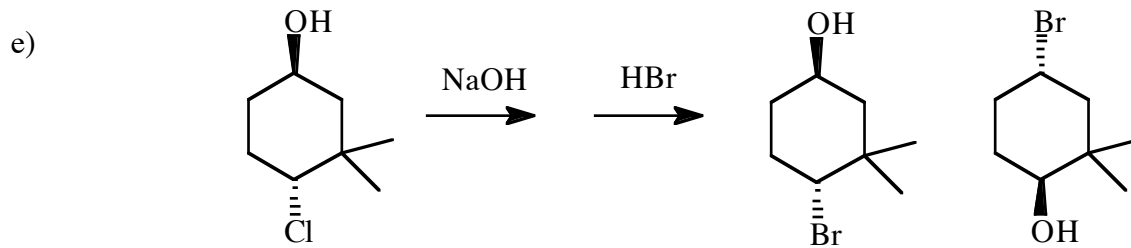


c)

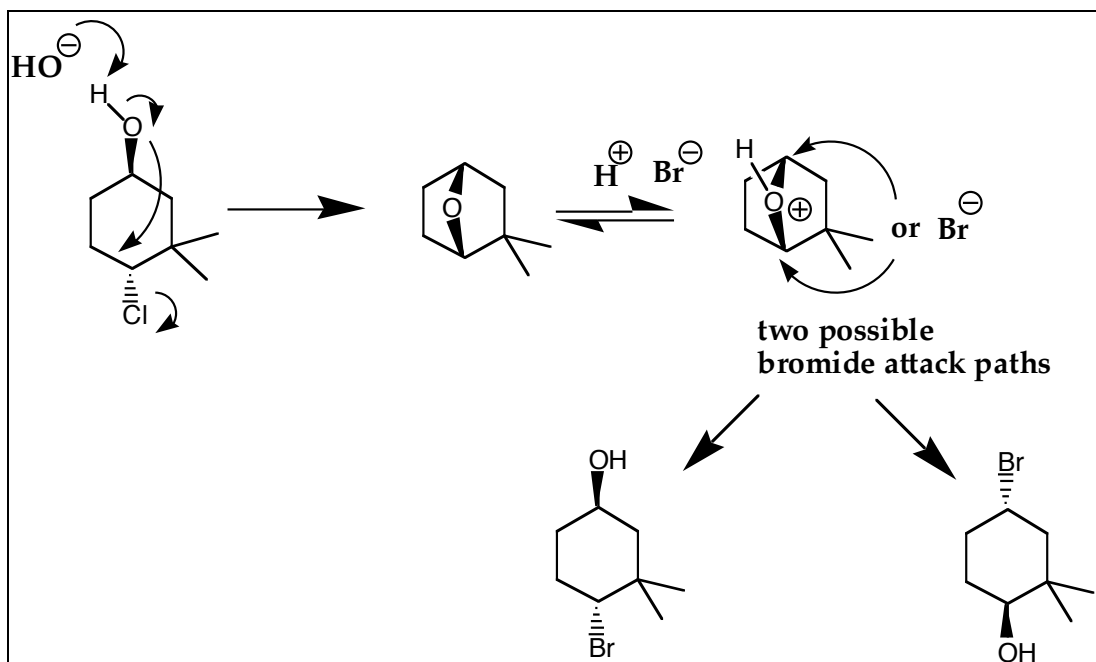


d)

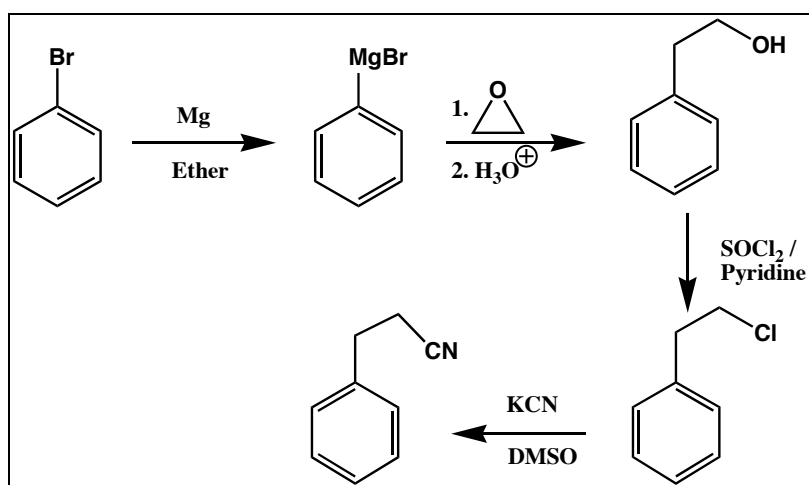
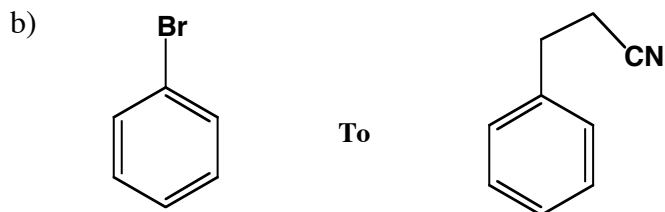
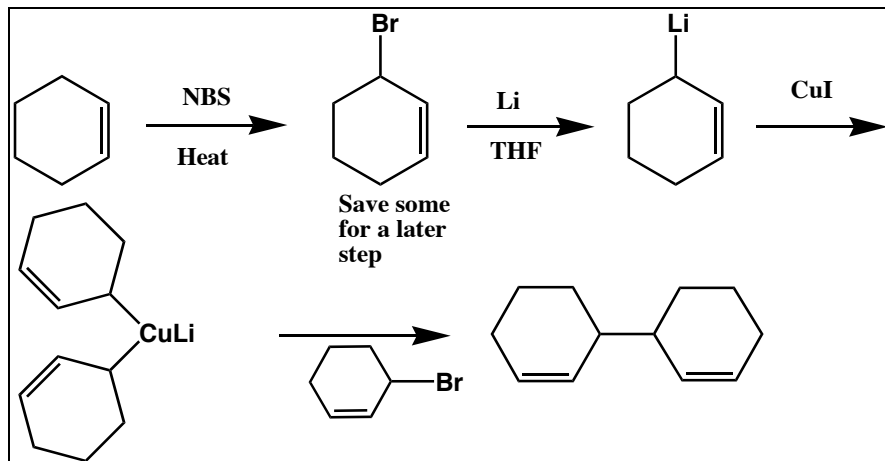
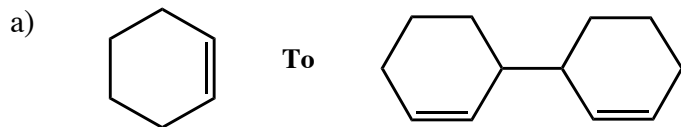




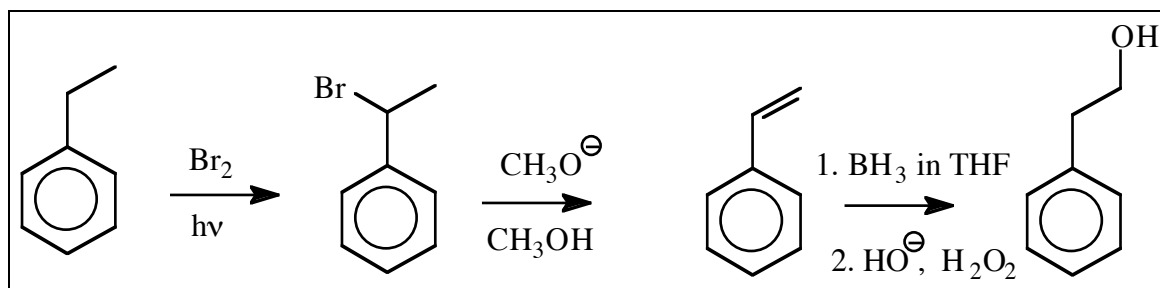
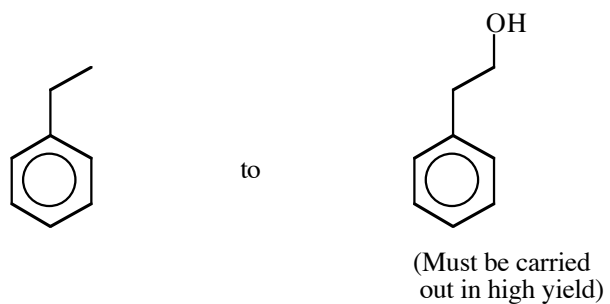
Also show the structure of the intermediate



10. Show the synthetic steps along with the reagents necessary to carry out the following transformations. Be sure to show structures of discrete intermediates.



c)



d)

