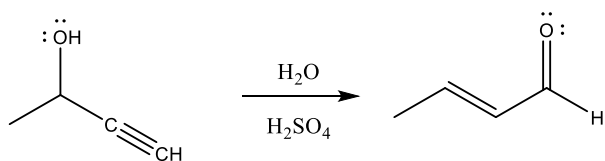


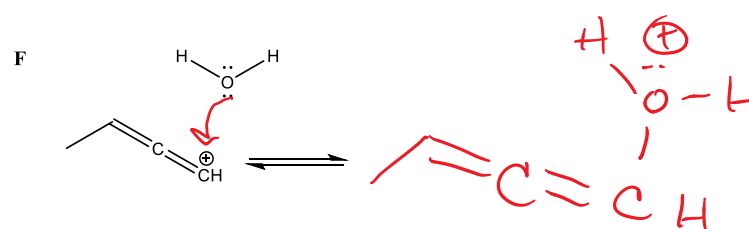
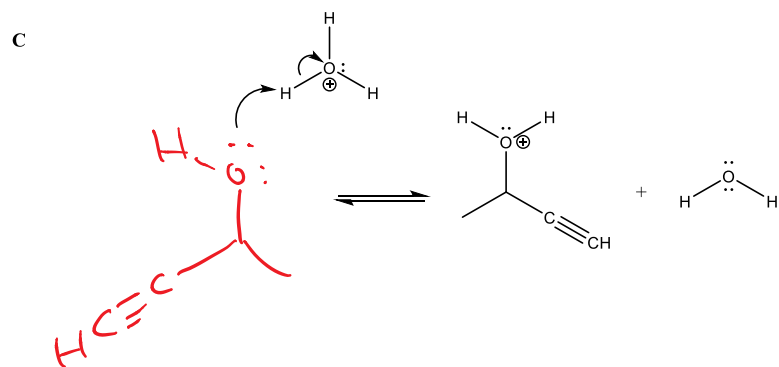
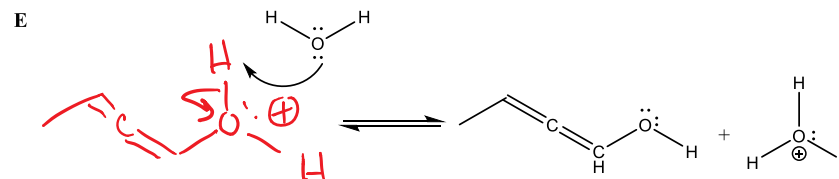
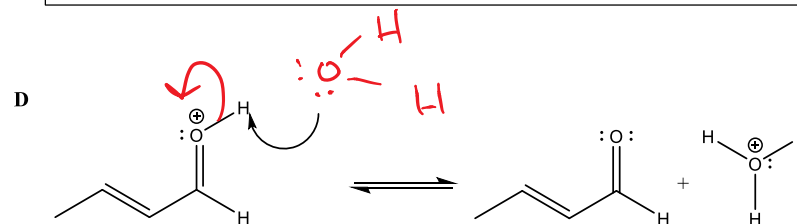
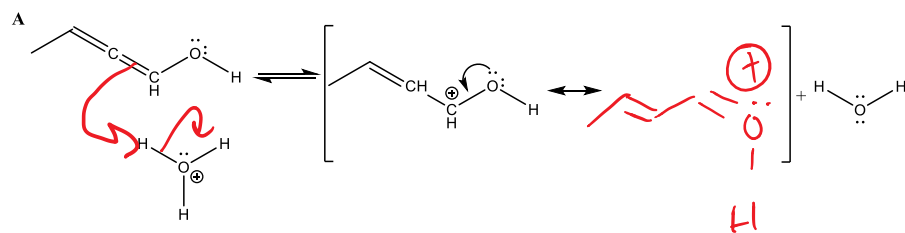
2. The reaction below proceeds through a six-step mechanism (after proton transfer from sulfuric acid to water). The steps of the reaction are labeled below as **A-F**. These steps are not in the correct order and are missing some mechanistic arrows, reactants, and/or products. Your tasks are to **i. complete each step by filling in all missing items** and **ii. place the steps in the correct sequential order** (in the box provided at the top right of the page). You may use the last page as scratch paper. (19)

Overall Reaction:



Order of Steps:

C **B** **F** **E** **A** **D**
 1st 2nd 3rd 4th 5th 6th



3. Indicate whether each statement **a-e** is **true (T)** or **false (F)**. (15)

F a. A secondary alcohol can be oxidized to a carboxylic acid with $\text{CrO}_3/\text{H}_2\text{SO}_4(\text{aq})$.

F b. The hydration of a triple bond always results in an aldehyde product.

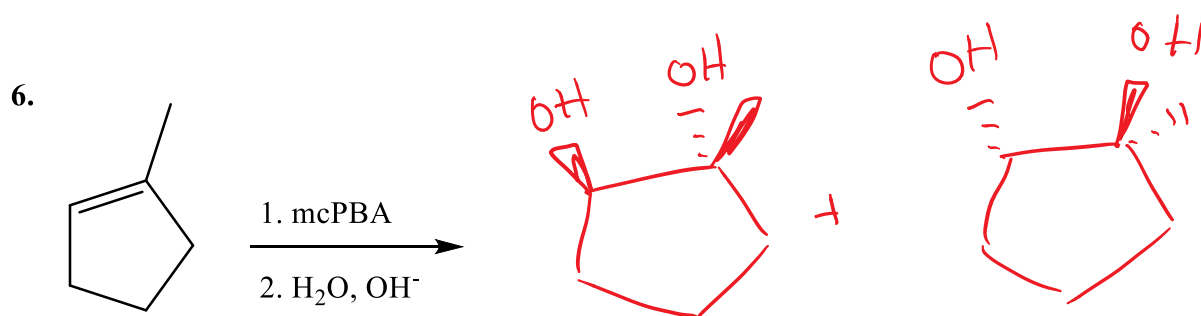
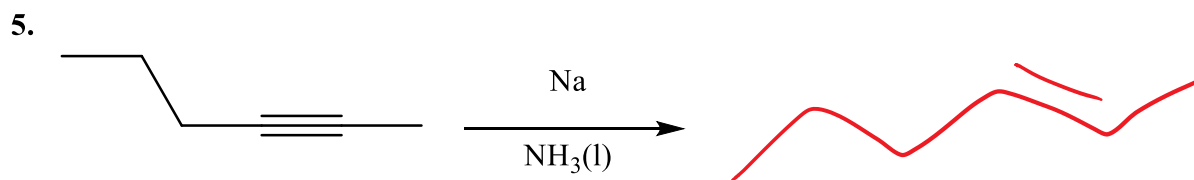
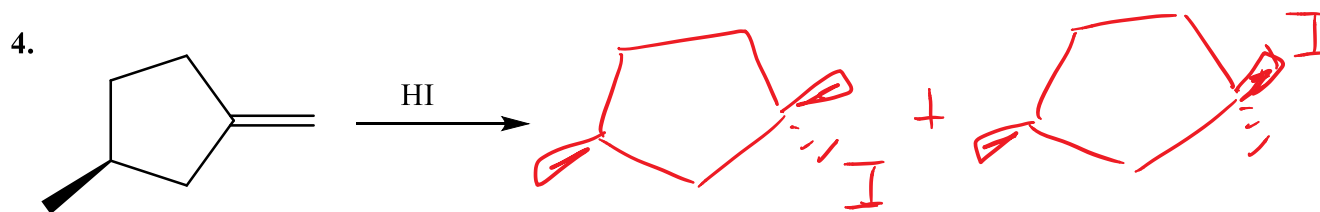
T c. Oxidative cleavage of 1 mol of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$ would yield 1 mol of an aldehyde and 1 mol of a ketone.

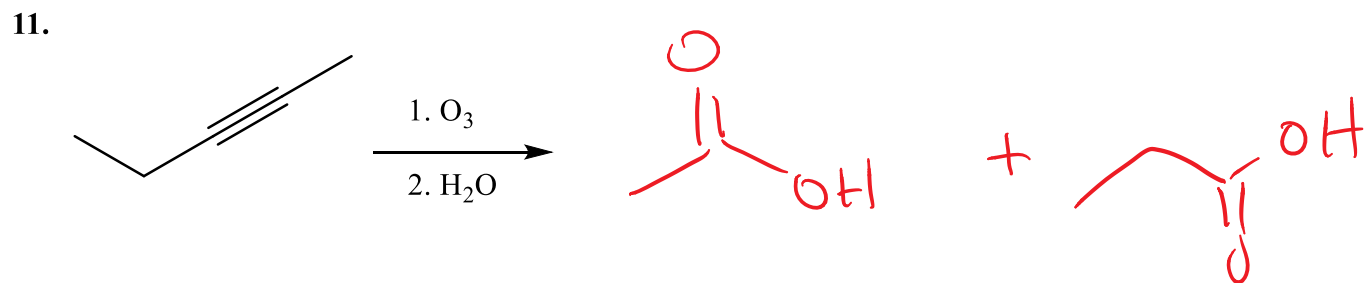
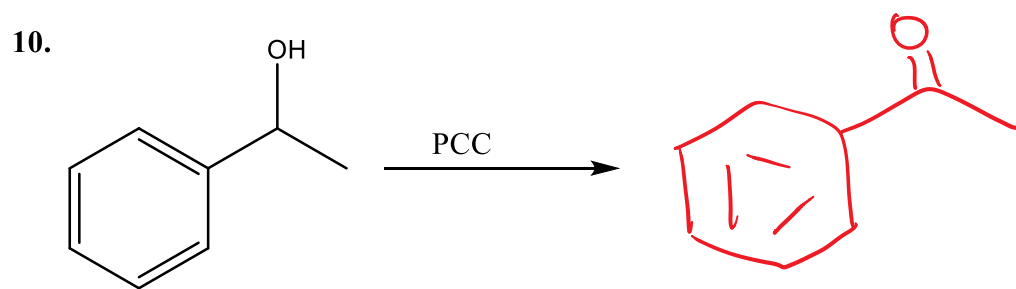
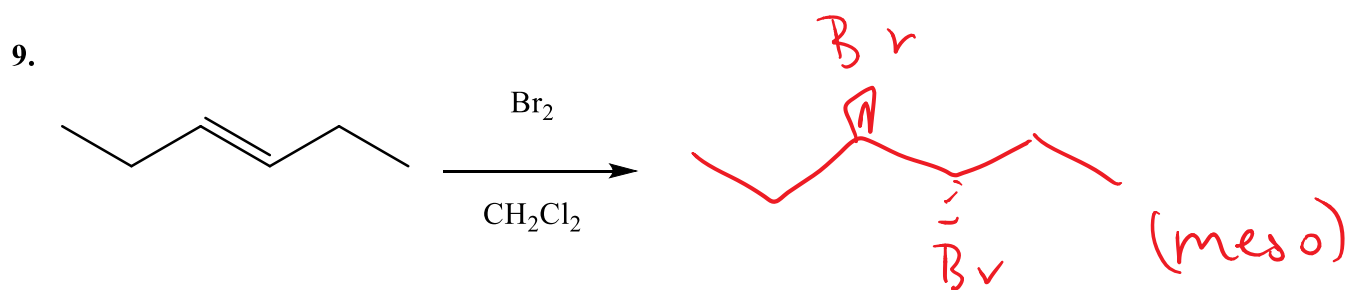
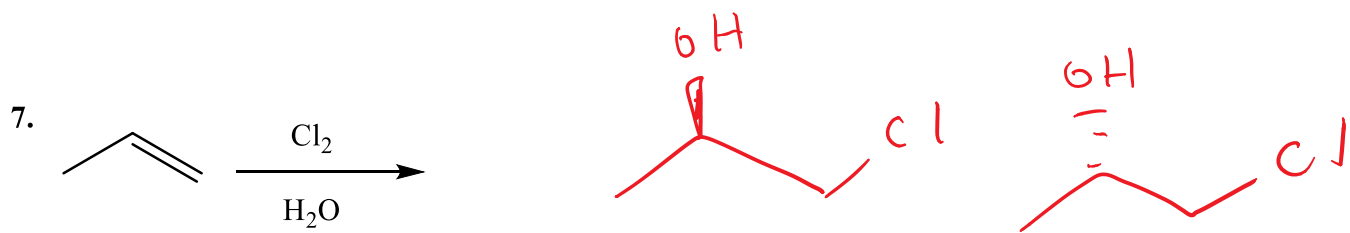
T d. The addition of HCl to an asymmetric alkene is an example of a process that follows Markovnikov's rule.

F e. The treatment of $\text{CH}_3\text{C}\equiv\text{CCH}_3$ with excess H_2 in the presence of Pd-C will yield a mixture of diastereomers.

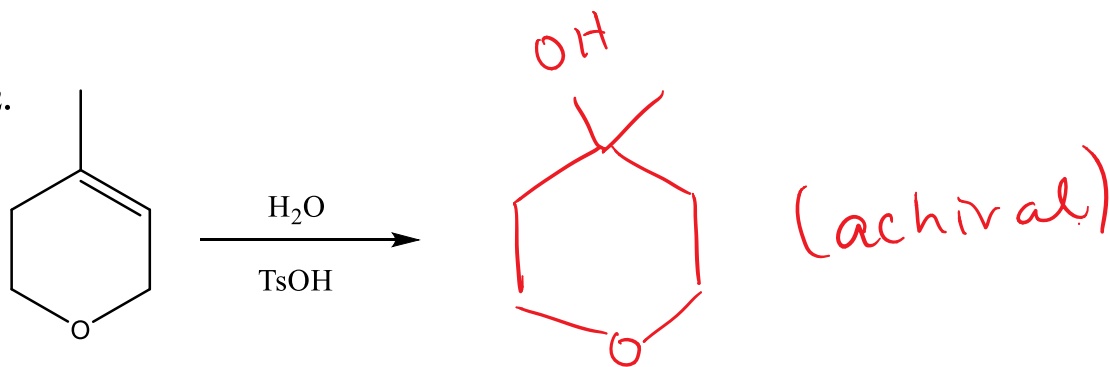
B. Predict the Products. (54 pts total)

For **each** of the questions below (4-12) draw the major organic product(s), showing stereochemistry when appropriate. (6 pts each)





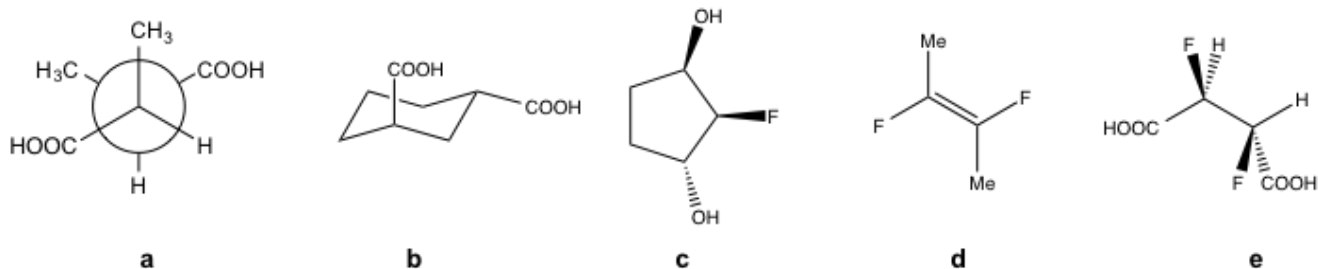
12.



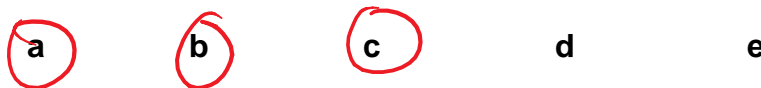
Part II: Old Material (70 points total)

A. Structure/Mechanism/Reactivity. (34 pts total)

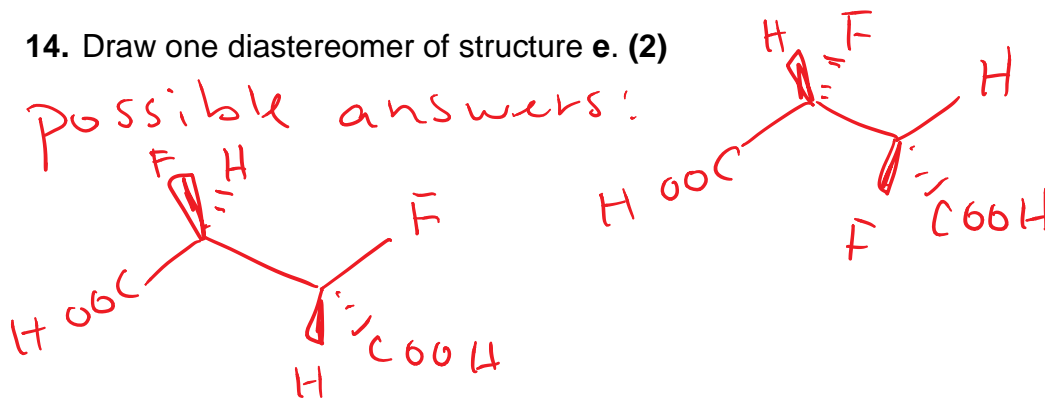
Consider structures **a-e** below then answer questions 13-15.



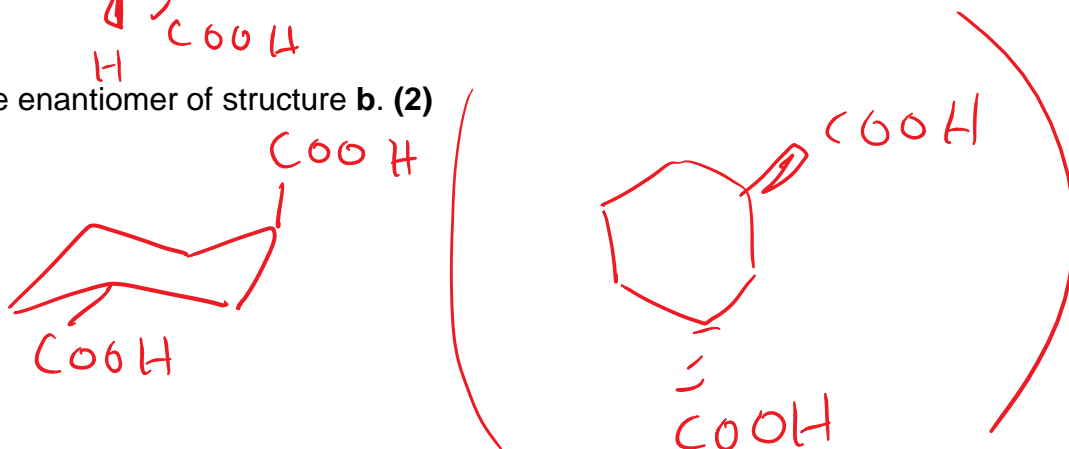
13. Which structure(s) **a-e** would be optically **active**? Circle all correct answers. (6)



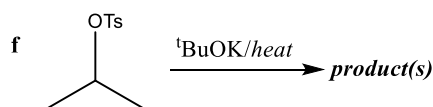
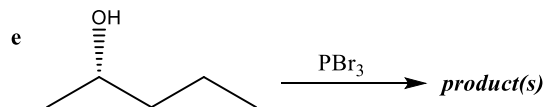
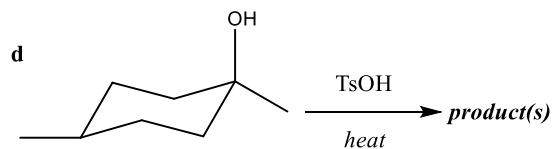
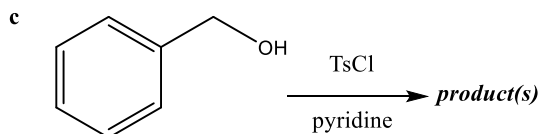
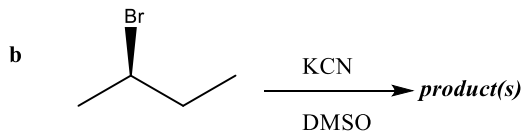
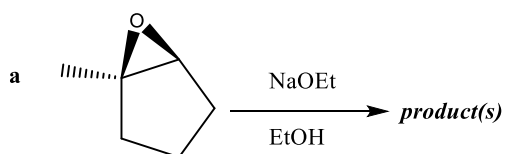
14. Draw one diastereomer of structure **e**. (2)



15. Draw the enantiomer of structure **b**. (2)



Consider reactions **a-f** below then answer questions **16-21**. (18 pts)



16. List all reactions **a-f** that would proceed through a carbocation.

d

17. List all reactions **a-f** that would yield a chiral product.

a b e

18. List all reactions **a-f** that would yield an alkene as the major product.

d f

19. The rate of reaction **b** would increase if [KCN] was increased.

True

False

20. The rate of reaction **e** would increase if the alcohol were tertiary instead of secondary.

True

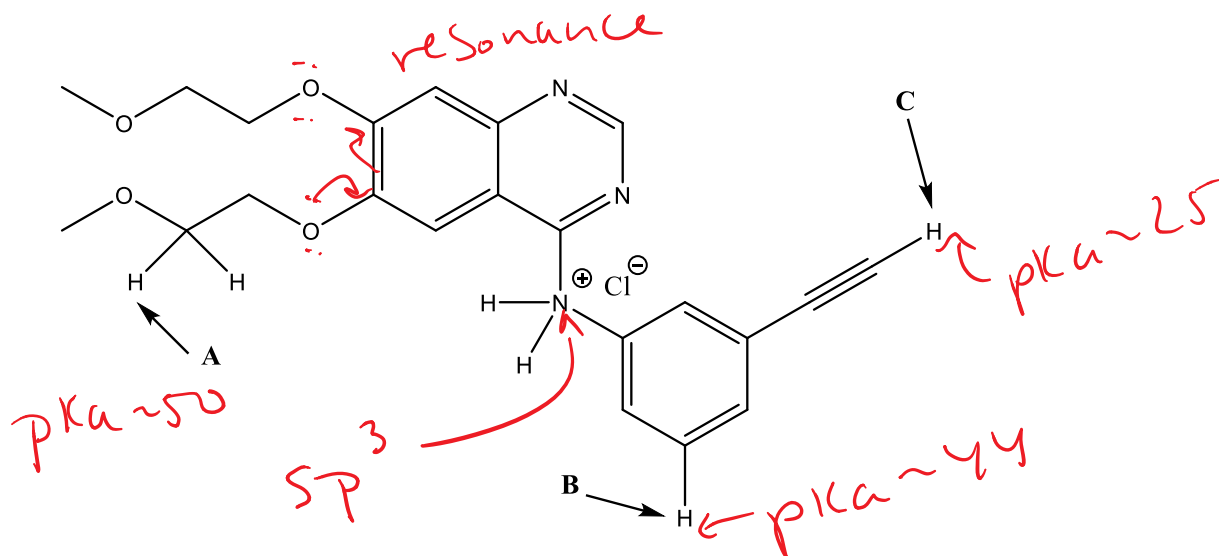
False

21. The rate of reaction **f** would increase if the tosylate were tertiary instead of secondary.

True

False

Consider the structure below (erlotinib hydrochloride, a lung cancer drug marketed as Tarceva) and answer question 22.



22. For a-c circle your answers. (6)

a. One nitrogen atom in this compound is sp^3 -hybridized.

True False

b. At least one oxygen atom in this compound will have some sp^2 -character.

True False

c. If protons A, B, and C are listed in order of *increasing* pKa, the correct order is:

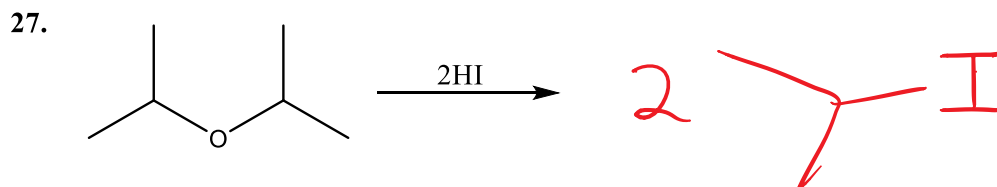
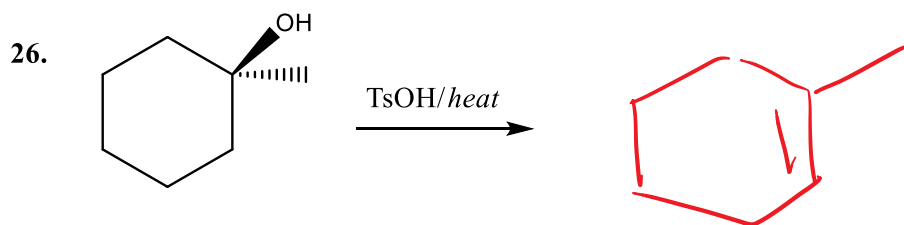
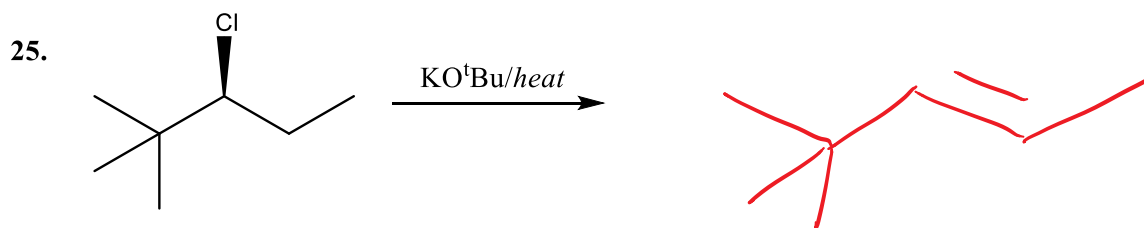
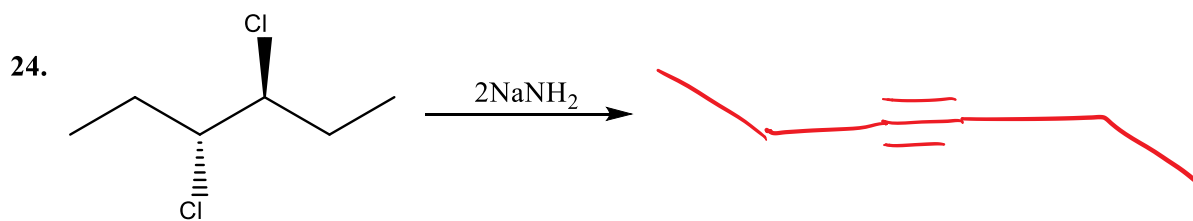
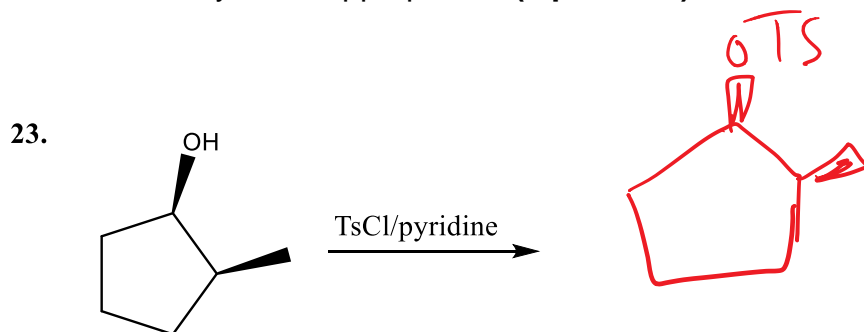
B < C < A C < B < A B < A < C A < C < B A < B < C

Bonus Question: Why is the drug given in the form of a salt? (2 pts)

Salts are more water-soluble

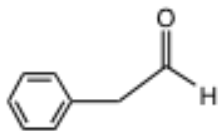
B. Predict the Product(s) (20 pts total)

For **each** of the questions below (23-27), draw the major organic product(s), showing stereochemistry when appropriate. (4 pts each)

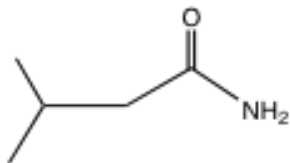


C. Spectroscopy (16 pts total)

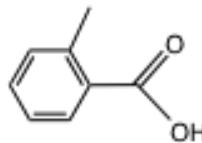
28. Match each structure **A-D** with an IR spectrum (1-4). Write your answers on the lines underneath the structures. (8)



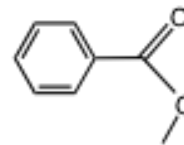
A



B



C



D

Answers:

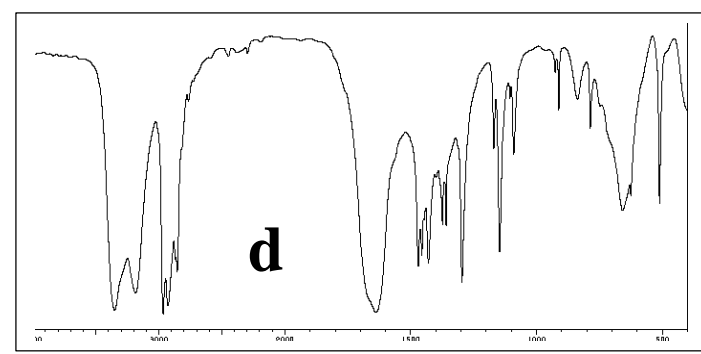
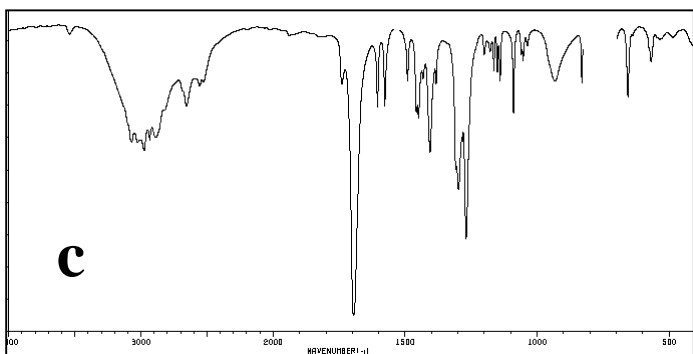
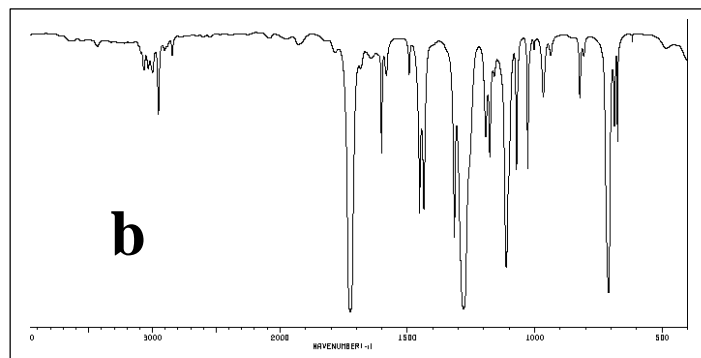
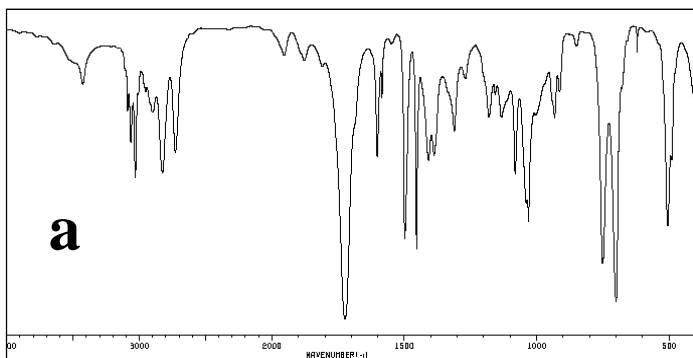
a

d

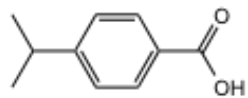
c

b

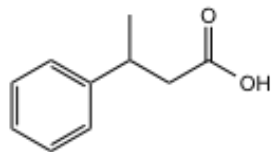
IR Spectra:



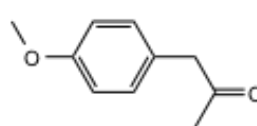
29. Match each of the four structures (1-4) below with an proton NMR spectrum (a-d). Write your answers on the lines underneath the structures. (8)



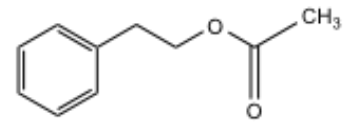
1



2



3



4

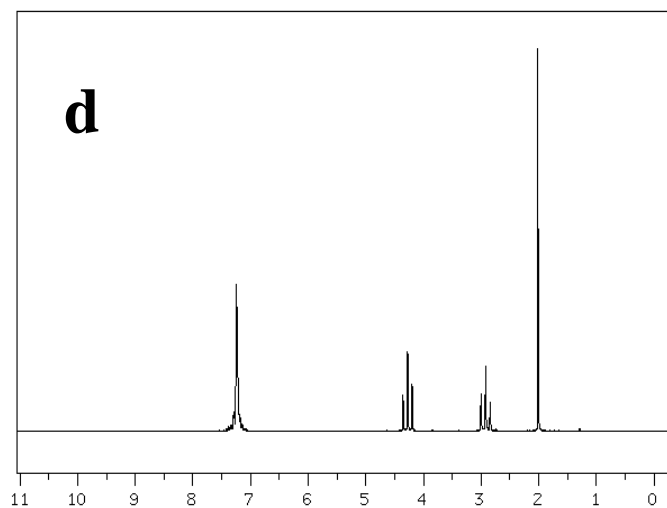
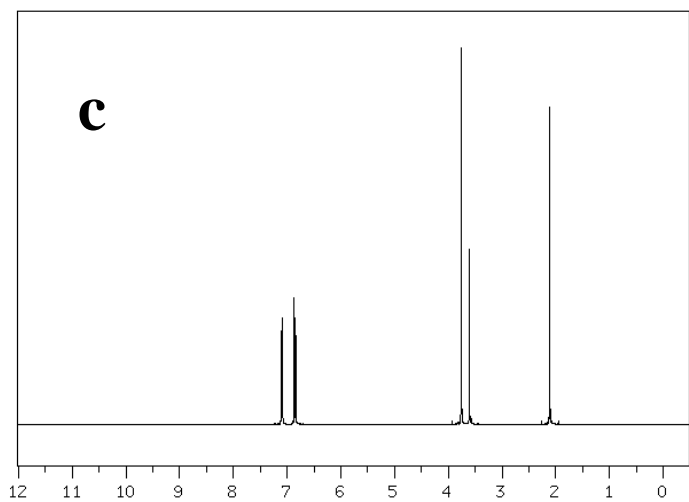
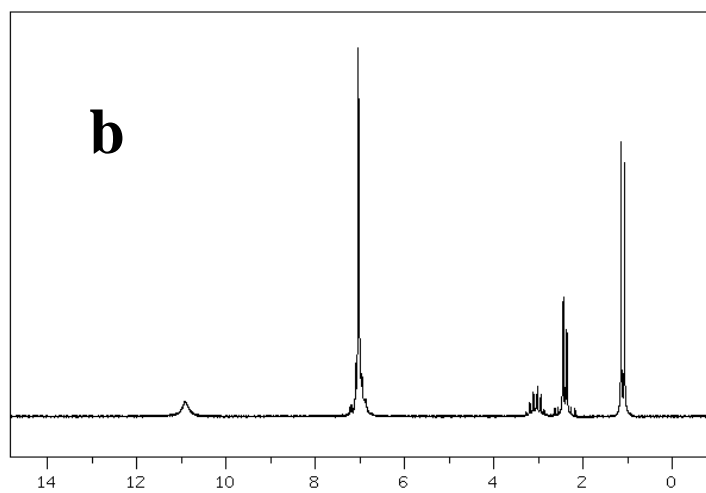
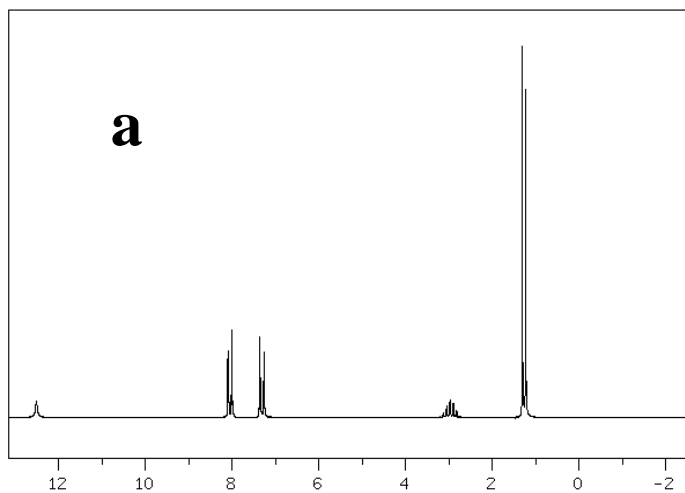
Answers:

a

b

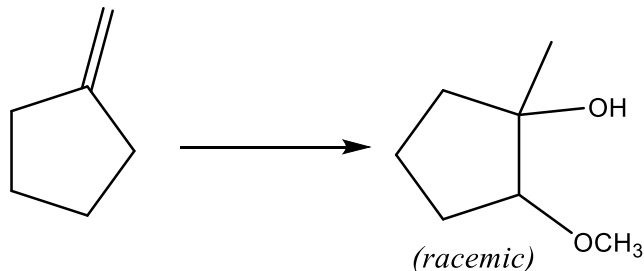
c

d

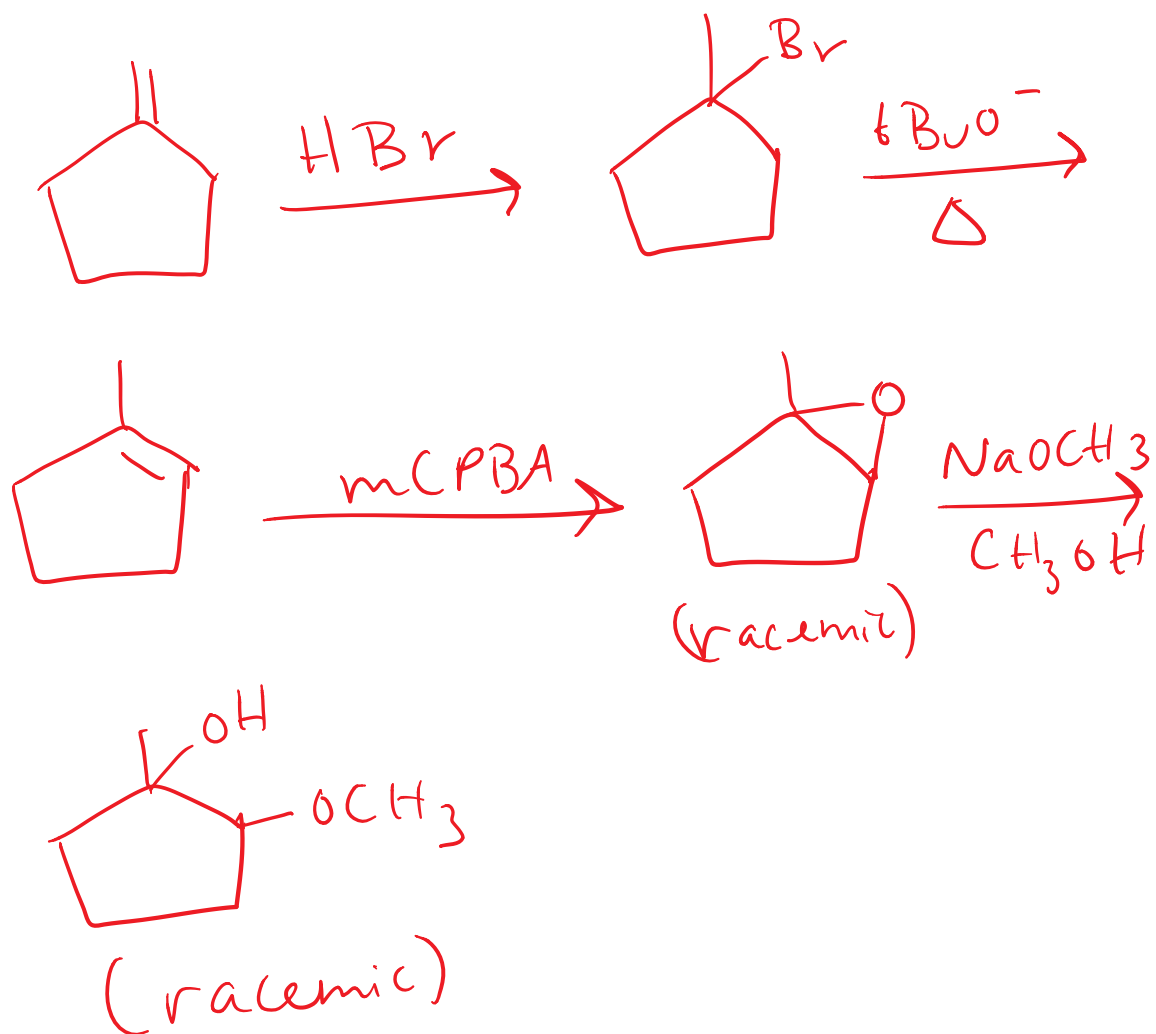


Part III: Synthesis. May use "Old" and "New" Material (40 pts total)

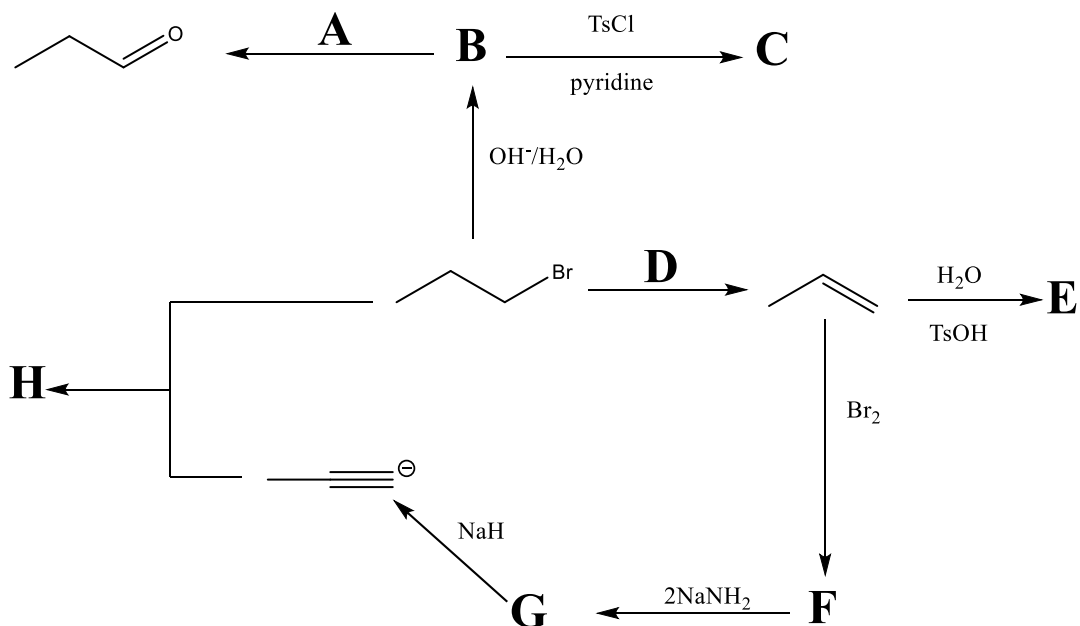
30. Propose a reasonable synthesis, starting from the indicated substrate in each case. You may use any inorganic reagents you deem necessary. You may also use any organic acids, bases, oxidizing, or reducing agents. (16 pts)



One possible answer:



31. Complete the reaction scheme below by filling in the appropriate missing products and reactants. Place your answers in the provided table on the next page. (24)



ANSWERS:

A	PCC	E	
B		F	
C		G	
D	<p>$t\text{BuO}^- / \Delta$ or DBU / Δ or DBN / Δ</p>	H	