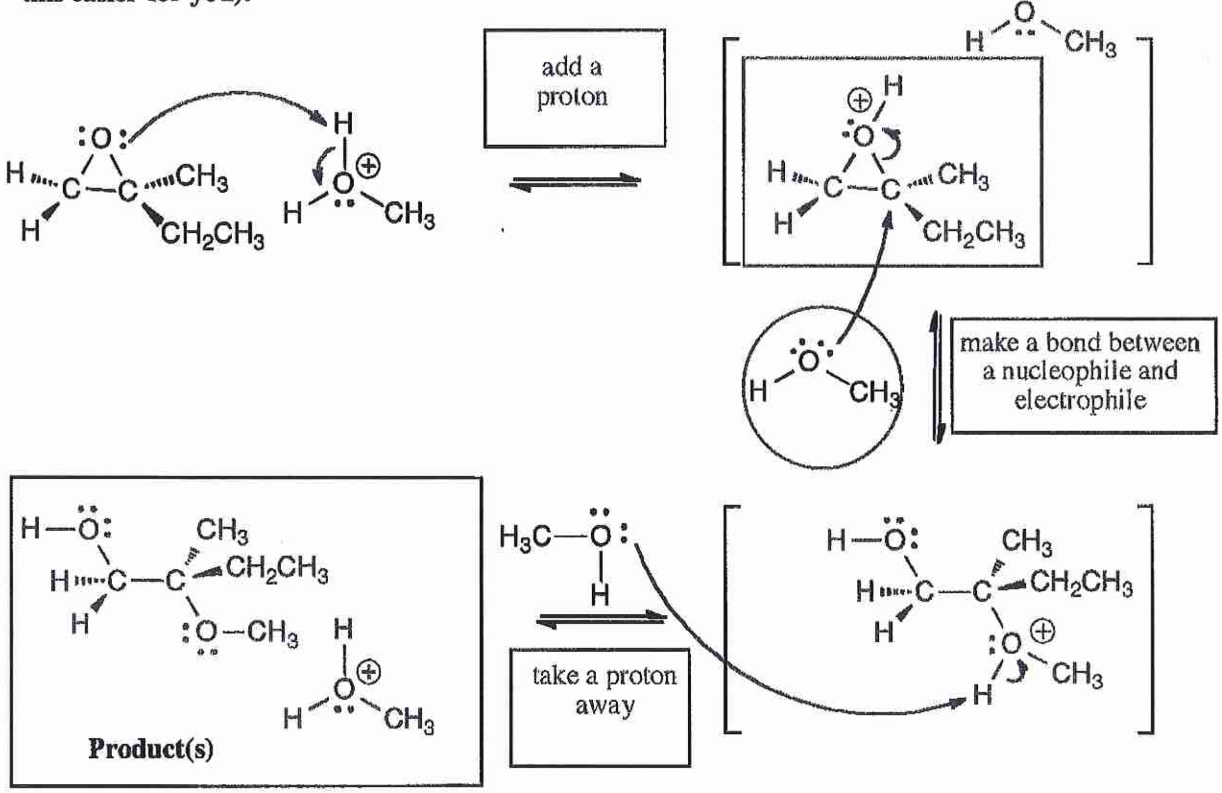
20. (25 pts.) **For the reaction of this epoxide with methanol in acid, fill in the details of the mechanism. Draw the appropriate chemical structures and use arrows to show how pairs of electrons are moved to** make and break bonds during the reaction. **For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". MAKE SURE TO NOTICE THE QUESTIONS AT THE BOTTOM. Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer for this problem (we are making this easier for you).**



A) (2 pts) During the reaction, would the pH rise, fall, or stay the same. In one sentence, explain your answer.

The pH would stay the same because acid is a catalyst here.

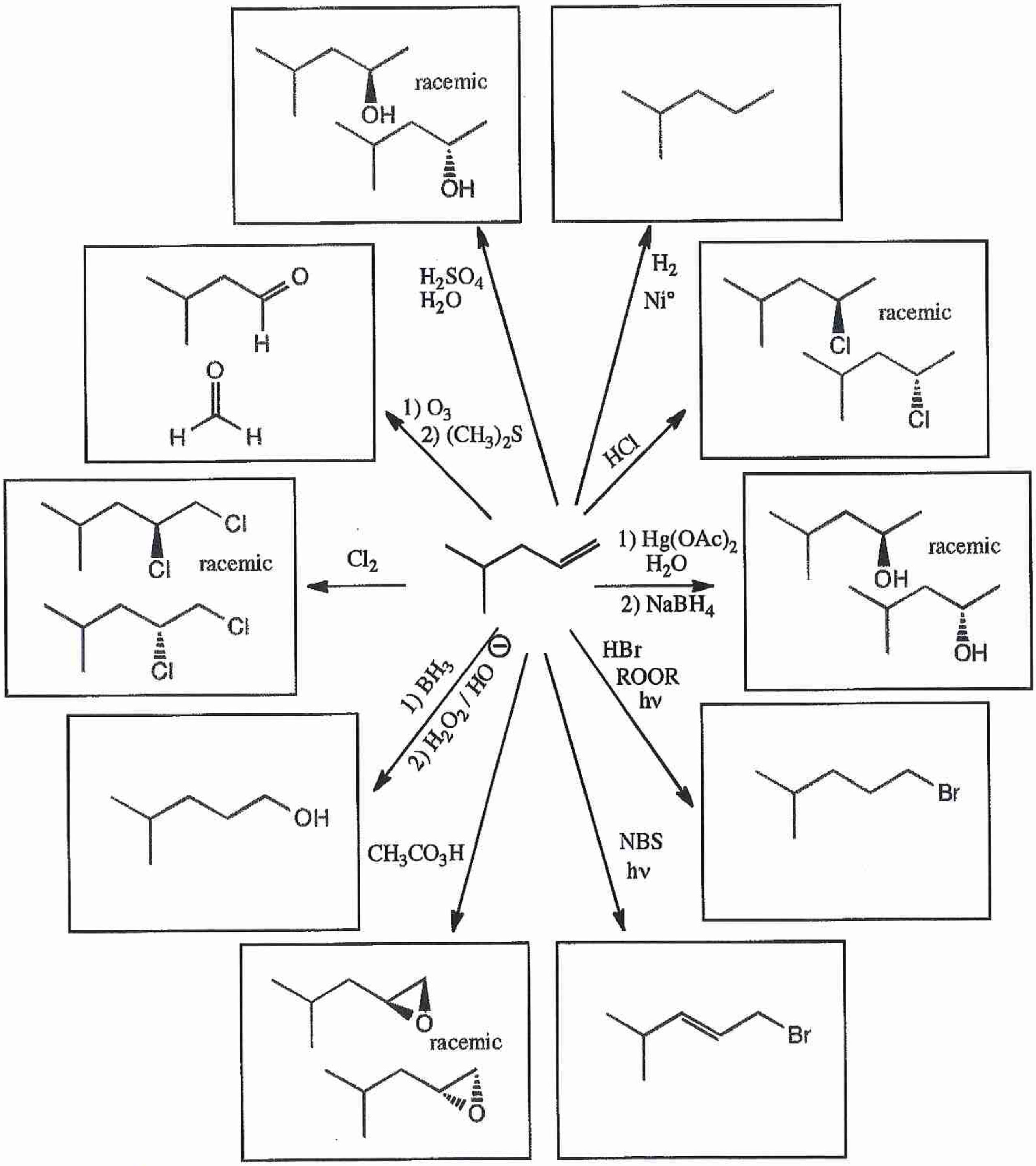
B) (2 pts) Of the four energy diagrams listed on page 11, which one best describes the reaction mechanism you drew: **C**

C) (4 pts) **For this part of the question, ignore all proton transfer steps.** For each step that involves a nucleophile reacting with an electrophile, **draw a circle around the nucleophile and a box around the electrophile.**

NOTICE ALL THREE PARTS OF THIS (A-C)

Signature____________________

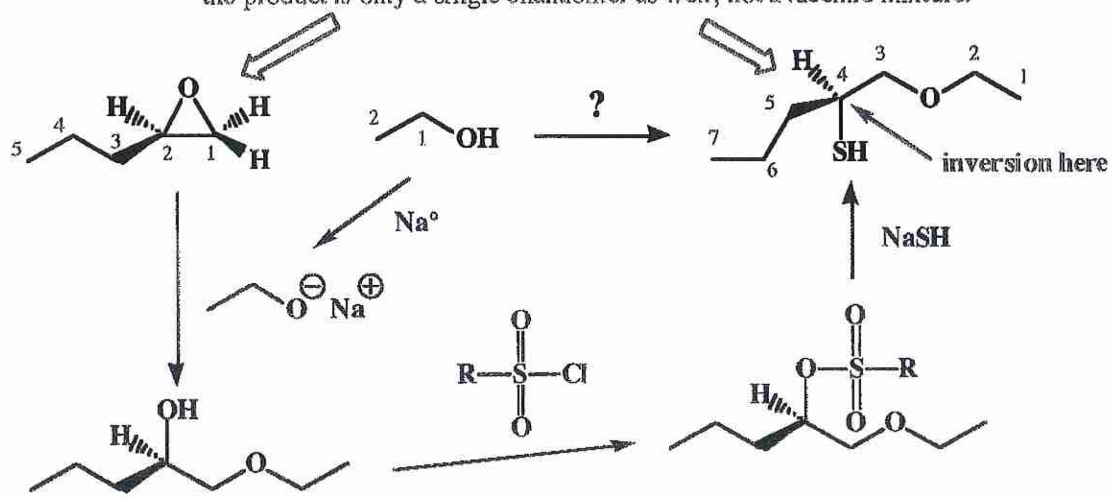
21. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangments take place.



22. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.

For this one, all of the carbon atoms in the product must come from the starting materials shown.

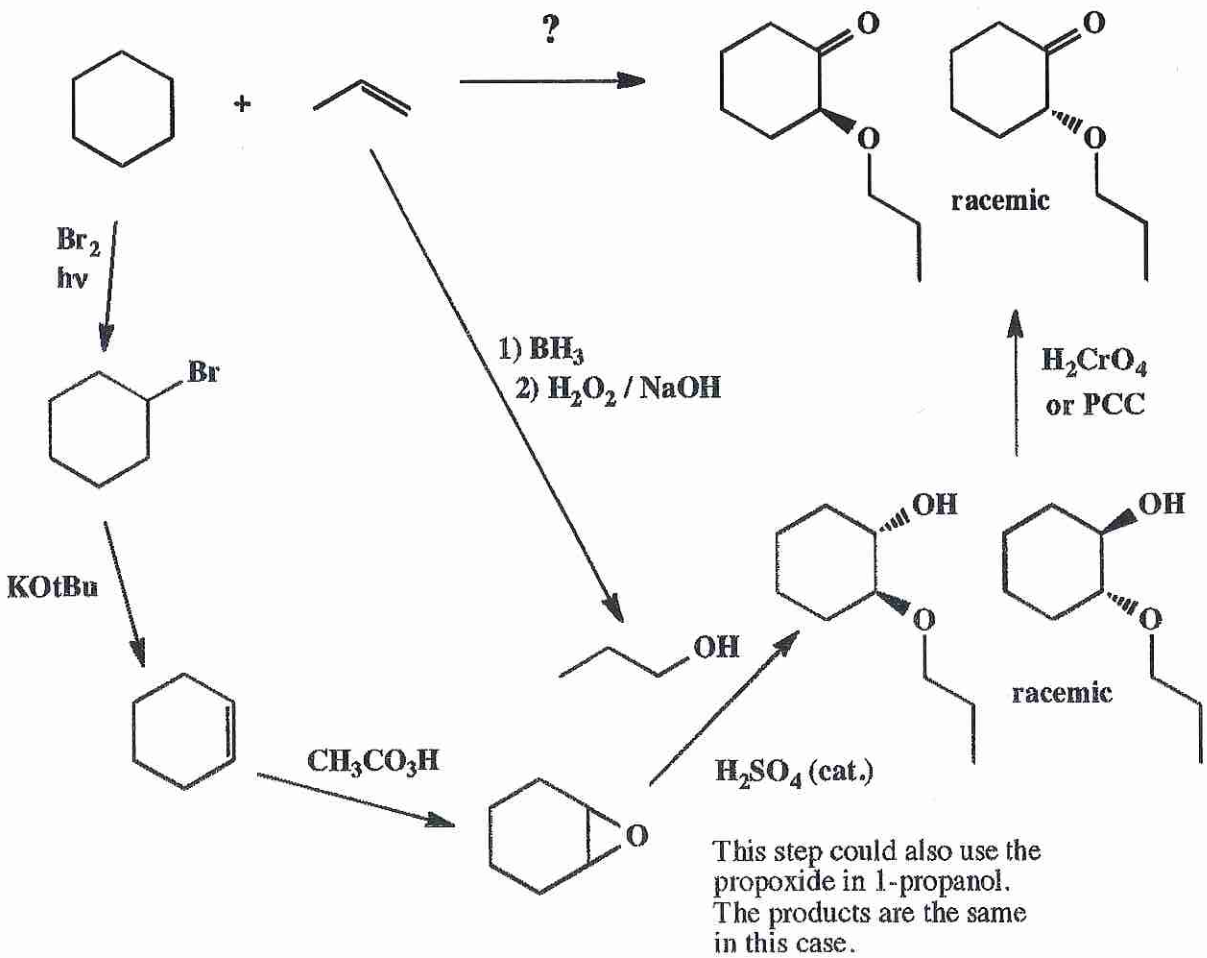
G) 10 pts **Recognize** that this is a single enantiomer starting material, so it is reasonable that the product is only a single enantiomer as well, not a racemic mixture.



Recognize that the key to this problem is the stereochemstry and regiochemistry of the product. Regiochemistry first. The CH_3CH_2O group is attached to the less hindered carbon of the starting epoxide. That means an S_N2 reaction using the alkoxide was used, not CH_3CH_2OH and acid that would have put the CH_3CH_2O group on the more substituted carbon of the epoxide. Next notice that the stereochemistry of the product requires inversion of the chiral center of the original epoxide (carbon labelled as "4"). To get inversion of the chiral center, you need to use the sulfonyl chloride route. Converting the -OH group to a halogen before the S_N2 reaction would have given double inversion or retention, namely the wrong stereoisomer as product.

24 (cont).) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

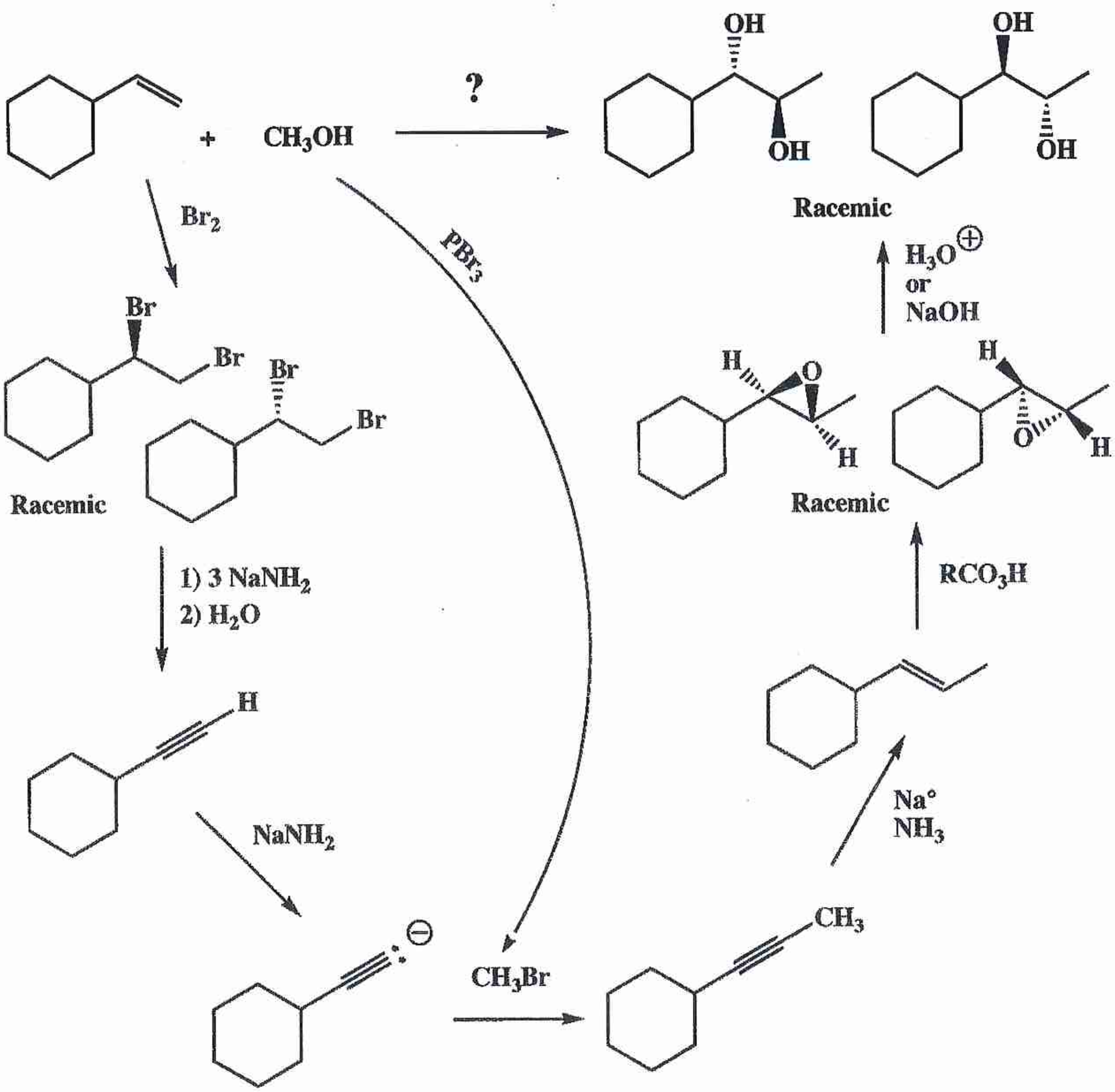
D) (16 pts)



Recognize the product as having a ketone, which in this class can only be made through ozonolysis of an alkene or oxidation of an alcohol. We can rule out ozonolysis because counting carbons makes it clear there are no C-C bonds broken, thus propose the last step as an oxidation of the alcohol. The hard part of this synthesis is to **recognize** that to make the vicinal ether-alcohol in high yield you must use 1-propanol to open an epoxide in either acid (shown) or basic conditions. Alkylating a vicinal diol would not work for this because the yield would be seriously compromised by creating a statistical mixture of products. The rest of the required chemistry is fairly straitforward.

17. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. **If a racemic mixture is produced at any point in the synthesis,you must indicate it by drawing both enantiomers and writing "racemic".**

D. (22 pts) All of the carbons in the products must come from the starting materials.



Recognize two key elements of the product. First, it has one carbon more thant the cyclohexyl starting material, indicating that alkylation of a terminal alkyne is involved. Second, **recognize** the product racemic mixture as coming from either the *anti* addition of OH to a *trans* epoxide (pathway shown) or the equally correct syn addition to a Z alkene (not shown).

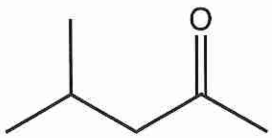
	# of equiv H	ratio (large → small)
I	4	6 : 3 : 2 : 1
II	4	6 : 3 : 2 : 1
III	7	6 : 3 : 3 : 1 : 1 : 1 : 1
IV	3	9 : 3 : 2
V	5	6 : 3 : 3 : 1 : 1
VI	3	9 : 3 : 2
VII	5	6 : 3 : 3 : 1 : 1
VIII	5	6 : 3 : 3 : 1 : 1
IX	4	6 : 3 : 2 : 1

(Tue: # of equivalent Hydrogens + integration ratios)
(Friday: match to spectra)

Signature_______________________ Pg 4 ___________(15)

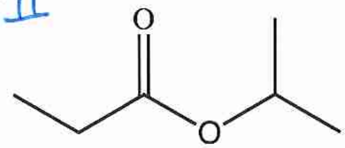
7. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but nine molecules.

I



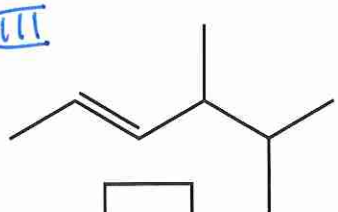
[ ]

II



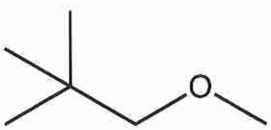
[ ]

III



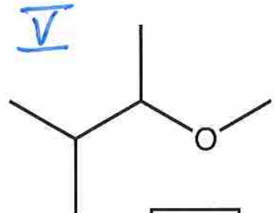
[ ]

IV



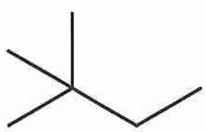
[A]

V



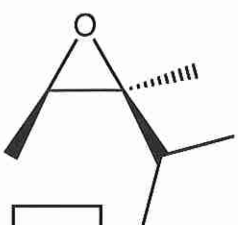
[ ]

VI



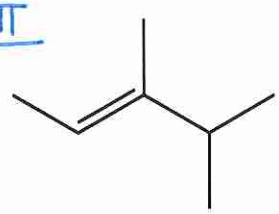
[ ]

VII



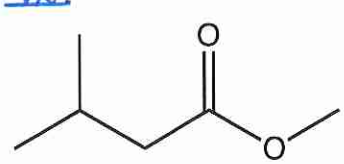
[ ]

VIII



[C]

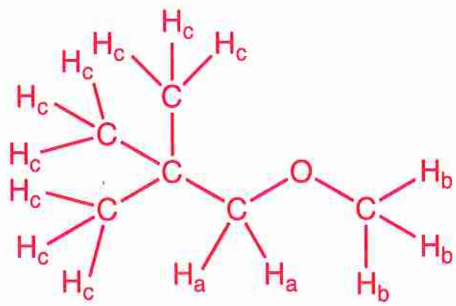
IX

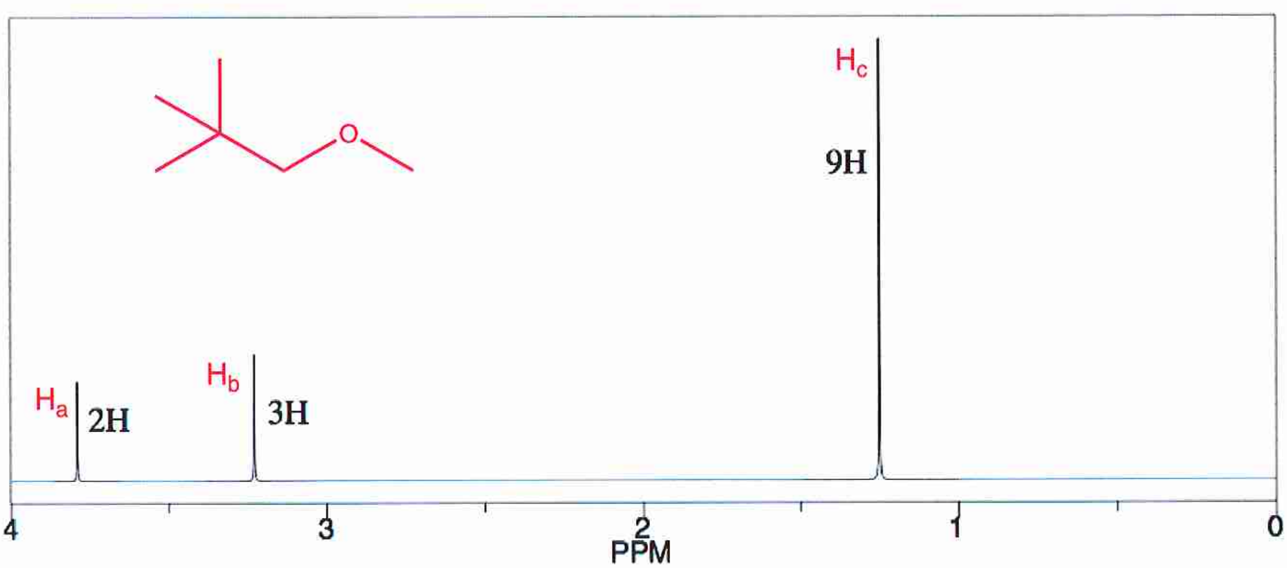


[B]

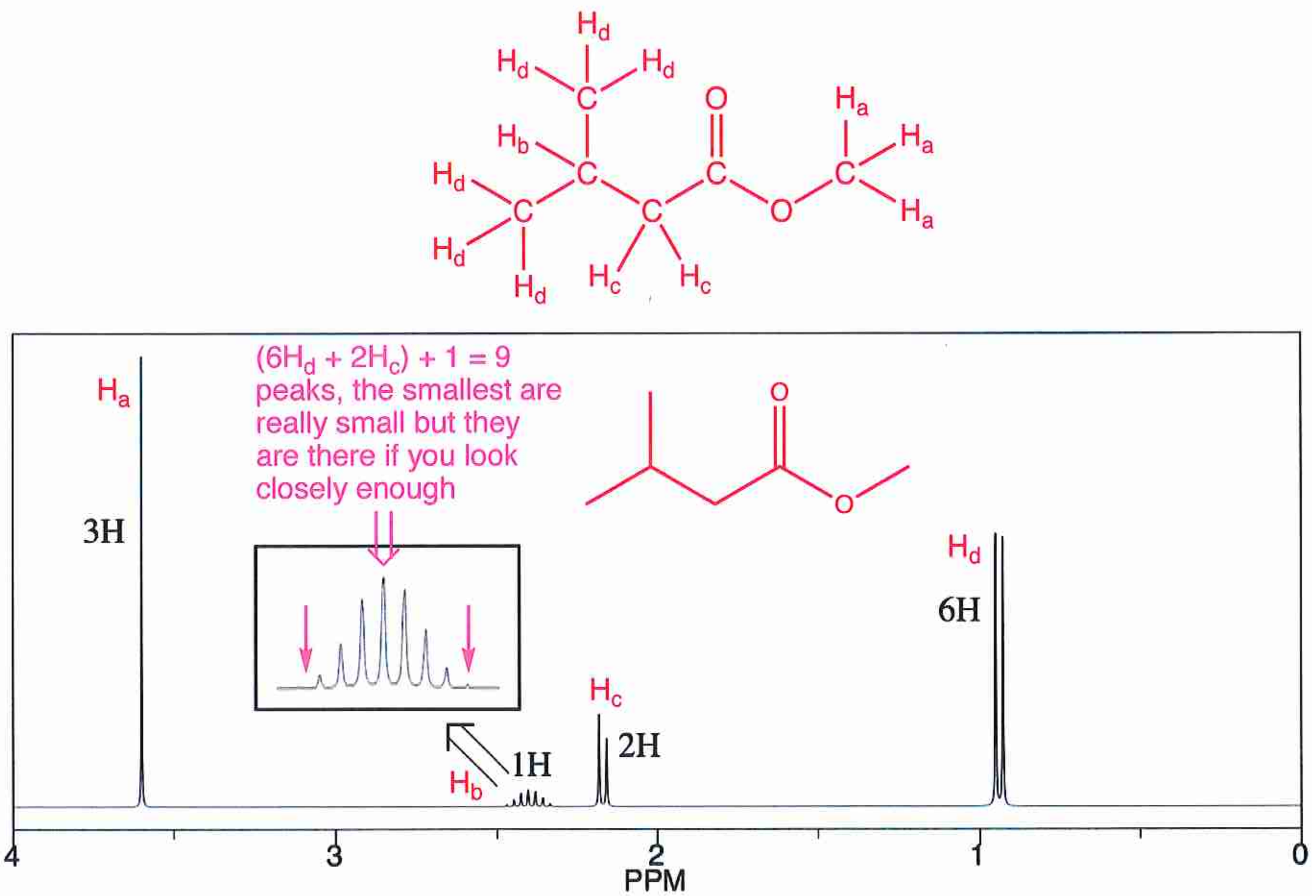
Signature____________________

Spectrum A

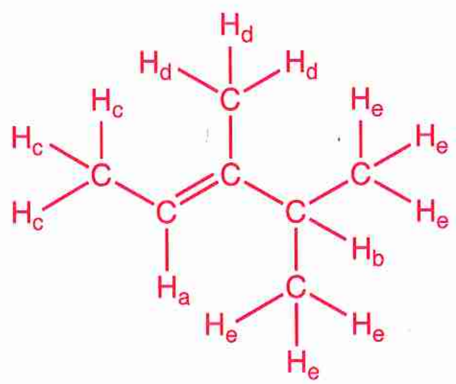


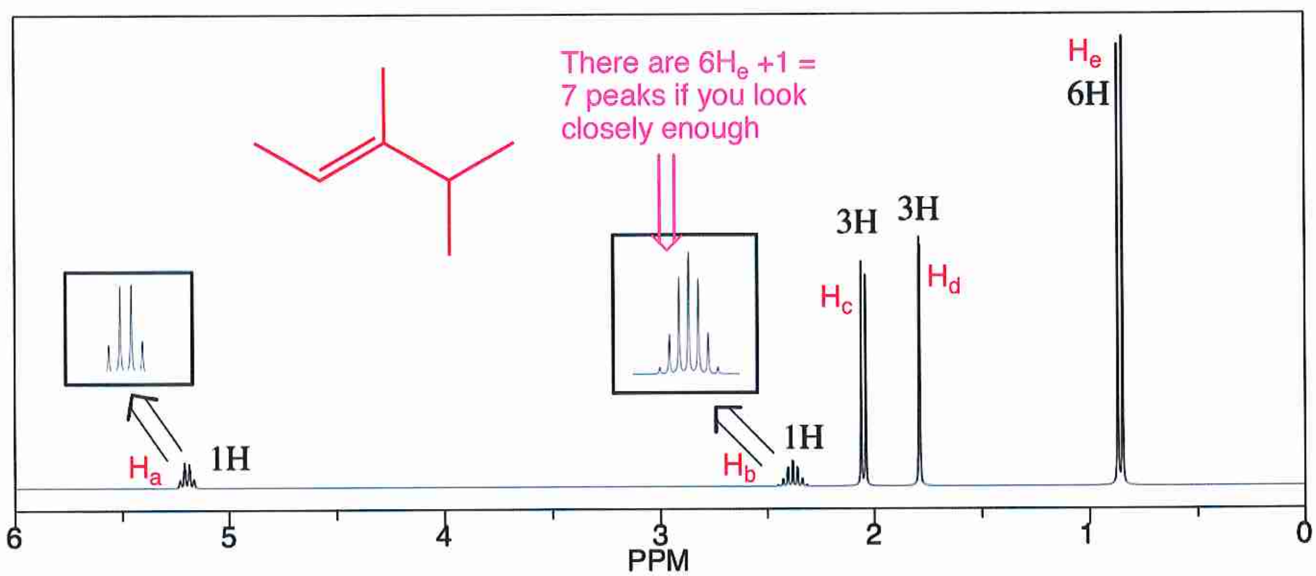


Spectrum B


Hd
Hd
Hd
Hb
Hd
Hd
Hd
Hc
Hc
O
O
Ha
Ha
Ha
(6Hd + 2Hc) + 1 = 9 peaks, the smallest are really small but they are there if you look closely enough
O
O
Ha
3H
Hd
6H
Hc
2H
1H
Hb
4
3
2
1
0
PPM

Spectrum C


Hd
Hd
Hd
C
Hc
He
Hc
C
C
C
C
He
Hc
C
He
Hb
Ha
C
He
He
He


There are 6He +1 =
7 peaks if you look
closely enough
He
6H
3H
3H
Hc
Hd
Ha
1H
Hb
1H
6
5
4
3
PPM
2
1
0