

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
1st Midterm
Feb. 23, 2006

SIGNATURE: _____

**Please print the
first three letters
of your last name
in the three boxes**

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

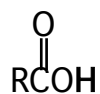
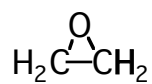
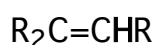
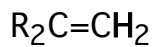
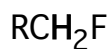
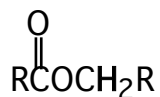
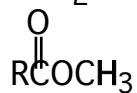
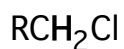
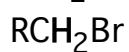
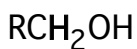
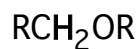
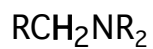
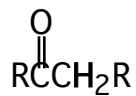
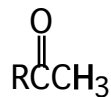
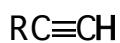
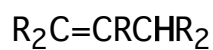
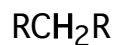
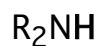
For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IS IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT

Note: You must have your answers written in pen if you want a regrade!!!!

| Page | Points | |
|------------|--------|-------|
| 1 | | (22) |
| 2 | | (22) |
| 3 | | (32) |
| 4 | | (5) |
| 5 | | (5) |
| 6 | | (5) |
| 7 | | (5) |
| 8 | | (5) |
| 9 | | (12) |
| 10 | | (21) |
| 11 | | (19) |
| 12 | | (18) |
| 13 | | (20) |
| 14 | | (13) |
| 15 | | (13) |
| 16 | | (16) |
| Total | | (233) |
| HW | | |
| T Score | | |

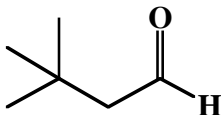
Type of Hydrogen
(R = alkyl, Ar = aryl)

Type of Hydrogen
(R = alkyl, Ar = aryl)

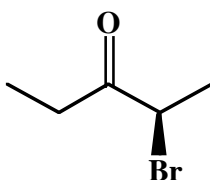


* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.

1. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



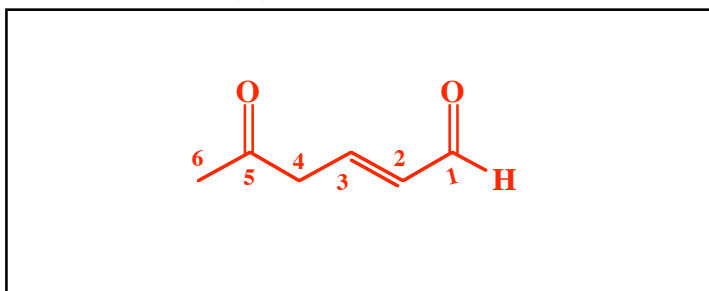
3,3-Dimethylbutanal



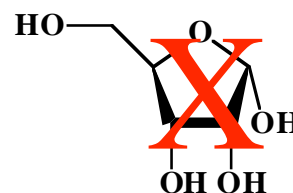
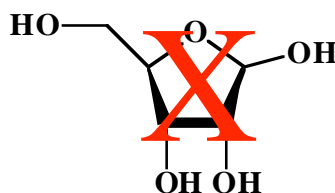
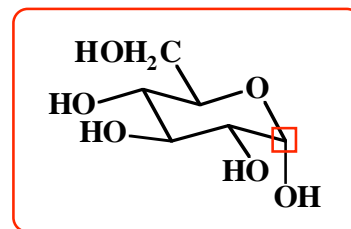
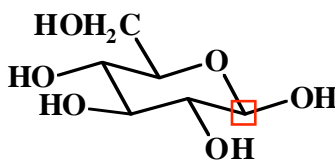
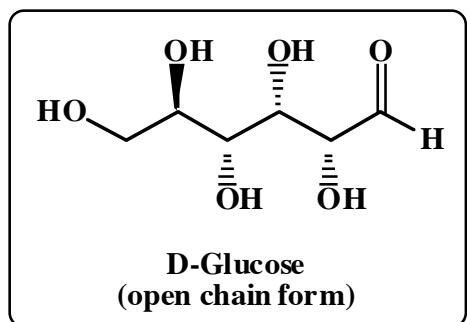
(R)-2-Bromo-3-pentanone

2. (4 pts) In the space provided, draw the following molecule:

(E)-5-Oxo-2-hexenal



3. (10 pts total) On the lefthand side, D-glucose is drawn in the open chain form. For the four cyclic structures shown, draw a large "X" through the two structures that DO NOT represent the cyclic form of the D-Glucose molecule. Next, for the structures that ARE the cyclic forms of D-Glucose 1) draw small boxes around the anomeric carbon atoms then 2) draw a circle around the structure that is in the alpha (α) form



4. (2 pts each) In each sentence, fill in the blank with the word that fits the best. You may notice a striking resemblance between these sentences and rules of the day!!!

Atomic nuclei, like electrons, have a quantum mechanical property of spin, which can be thought of as a small magnetic field around the nucleus created as if the positive charge of the nucleus were circulating.

The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.

Electron density is induced to circulate in a strong external magnetic field, which in turn produces a magnetic field that opposes the external magnetic field. The greater the electron density around a nucleus, the more shielded it is, and the lower the energy (frequency) of electromagnetic radiation required to flip its nuclear spin.

Equivalent hydrogen atoms in a molecule give the same NMR signal, because they have an identical relationship to all the other atoms in the molecule.

THEORY: When there are two sets of adjacent H atoms, the number of peaks multiply.

For example, a CH₂ group with a CH₂ group and a CH₃ group on either side shows a theoretical maximum of 3 x 4 = 12 peaks in its signal!

PRACTICE: For alkyl groups that can rotate freely, complex splittings simplify because the coupling constants ("J") are all about the same. In practice, if there are n adjacent H atoms, equivalent or not, you will see $n + 1$ peaks in a signal. This is an approximation, but almost always true on spectra taken with all but the most sophisticated NMR spectrometers

4. (2 pts each) Fill in each blank with the word that best completes the following descriptions of FT-NMR and MRI.

In the FT NMR method, the FT stands for Fourier transform.

The basic idea is that a short pulse using a range of radio frequencies are used to flip the spins of all of the hydrogen nuclei at once. Then, the nuclear spins relax back to the +1/2 spin state and when they do, they emit electromagnetic radiation at the precise frequency at which they absorb. The Fourier transform (FT) analysis of the signals is used to derive the original frequencies characteristic of the resonance of each type of H atom in the molecule. The important advantage of the FT NMR method is that many spectra can be acquired in a short period of time. The data is averaged, greatly increasing the signal to noise ratio of the spectra.

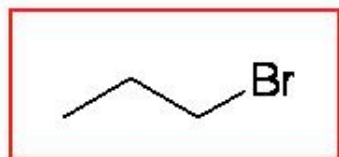
5. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (**i.e. slice inside patient**). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of protons, especially the protons from water and fat, in the different tissues**.

Signature _____

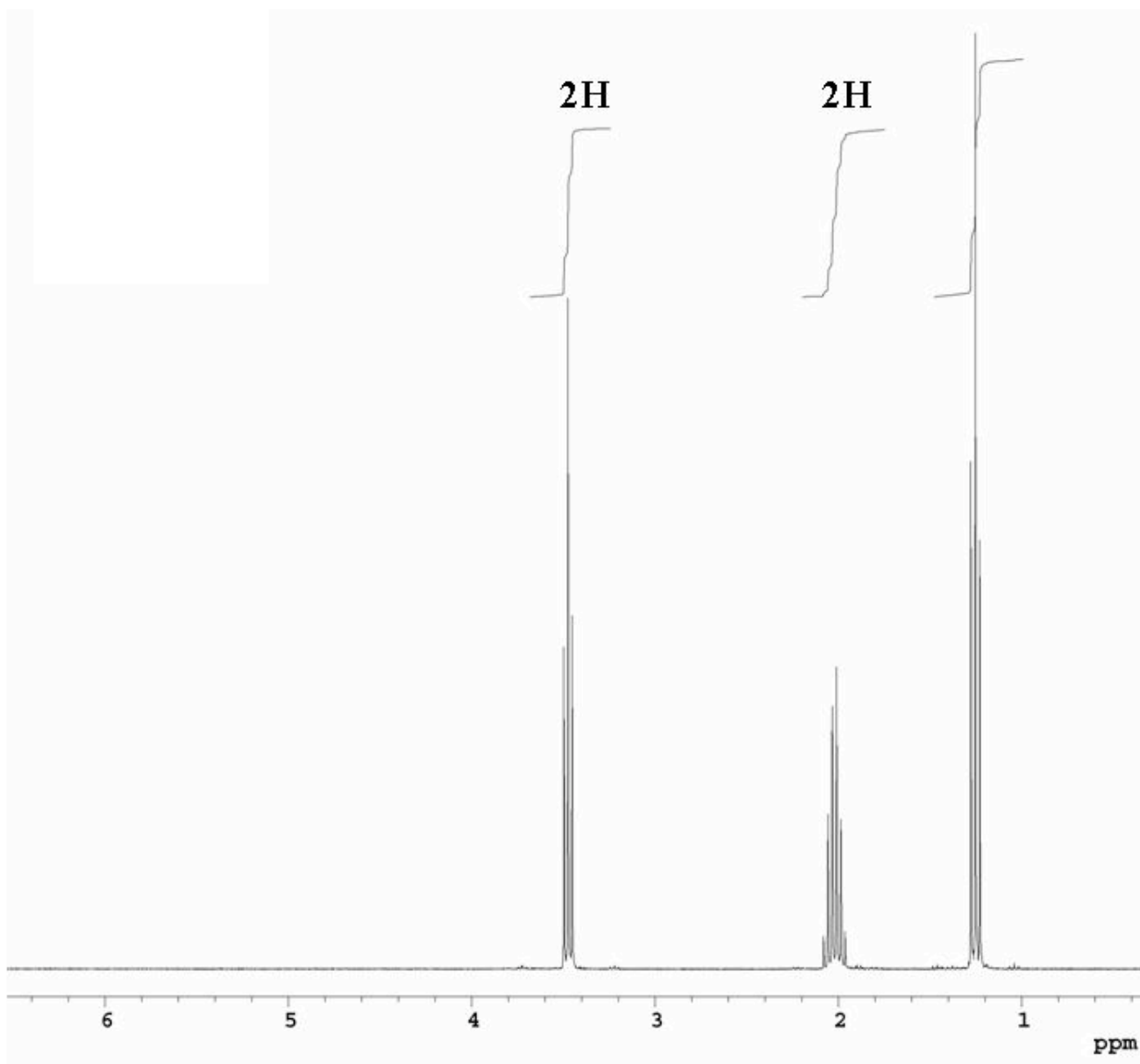
Pg 4 _____(5)

6. (5 pts each) Circle the molecule that corresponds to the spectrum shown.

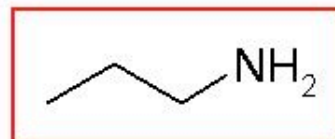


(Note: No D₂O has been added)

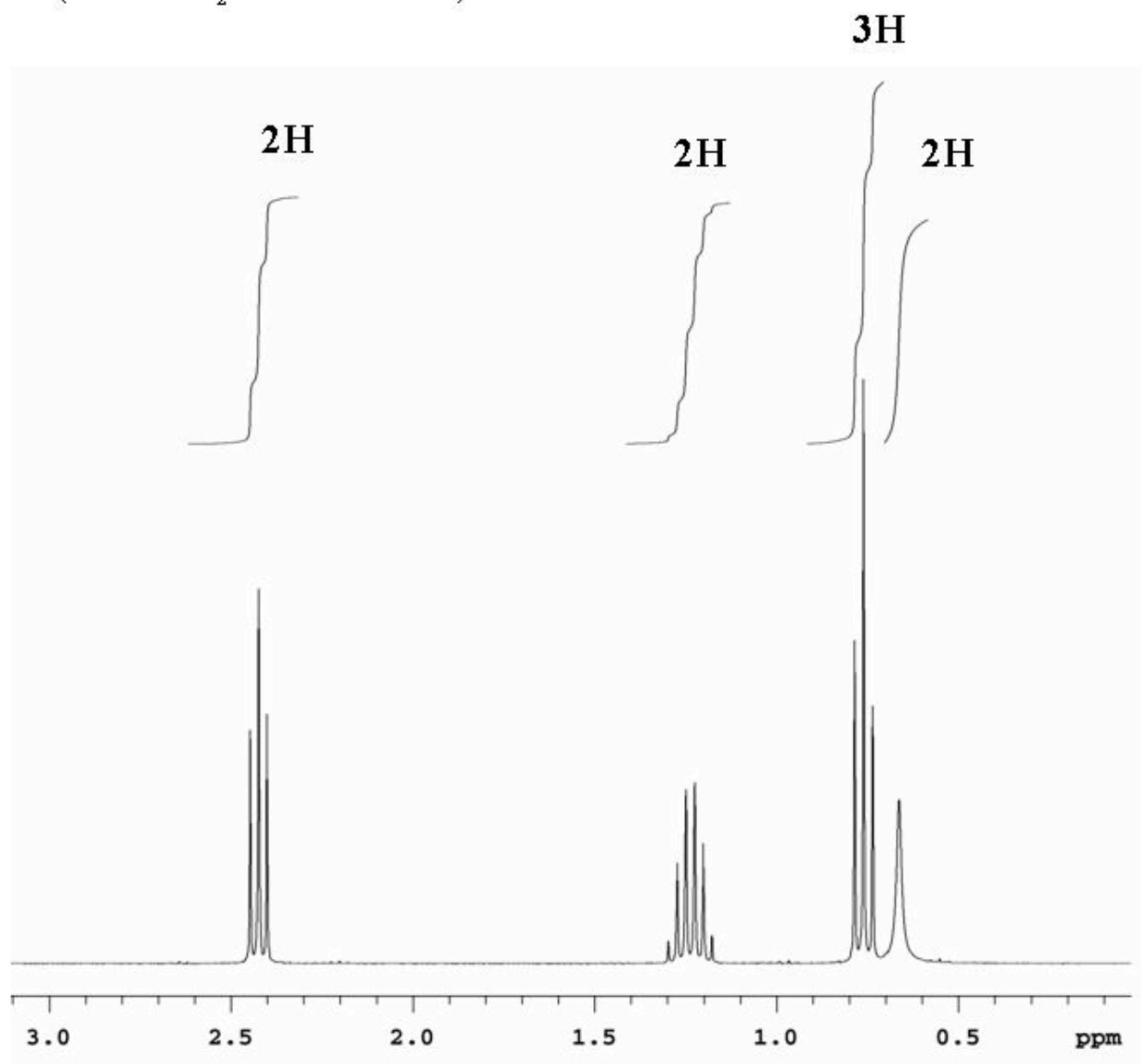
3H



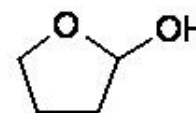
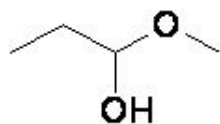
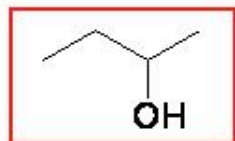
7. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



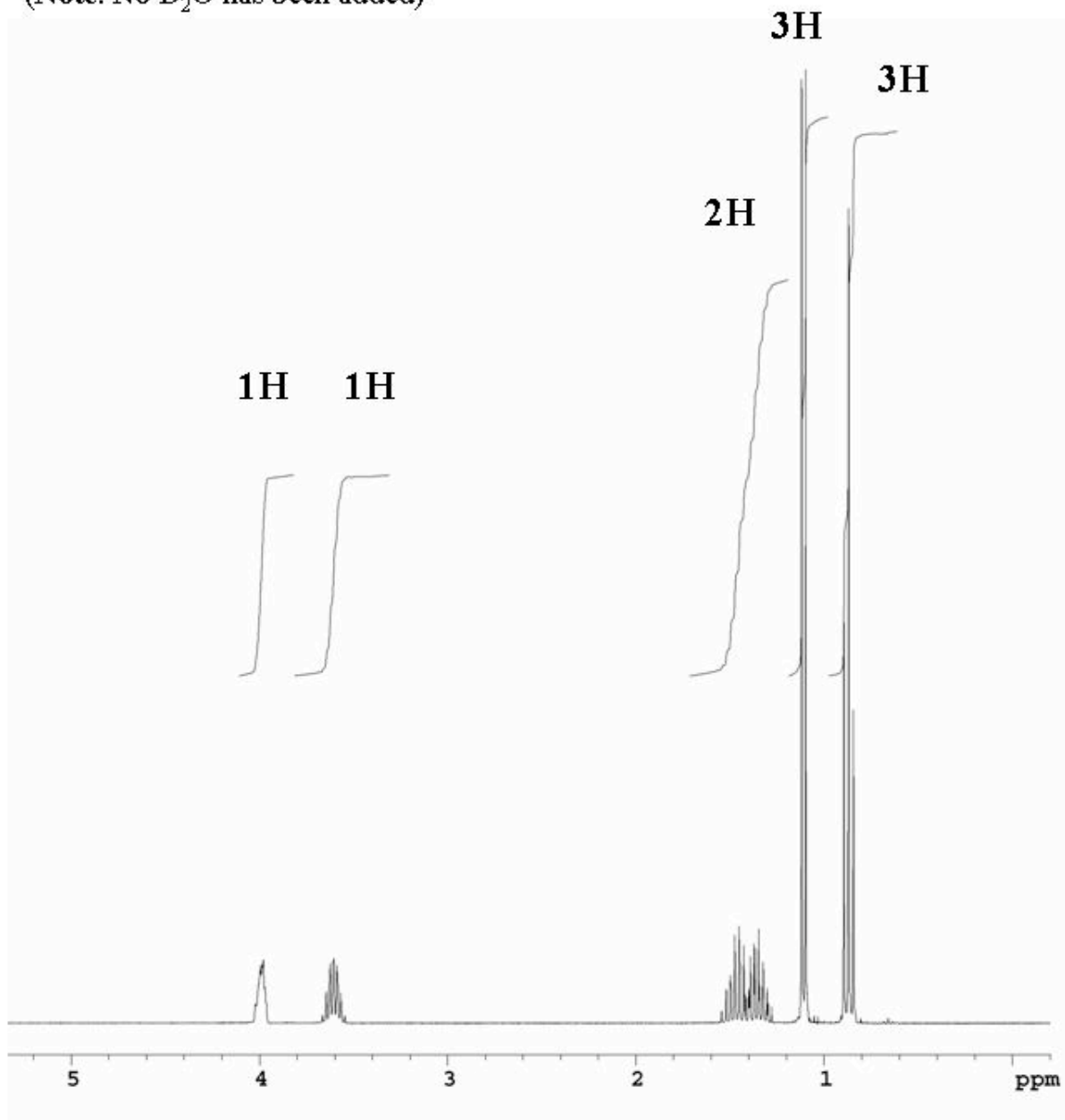
(Note: No D₂O has been added)



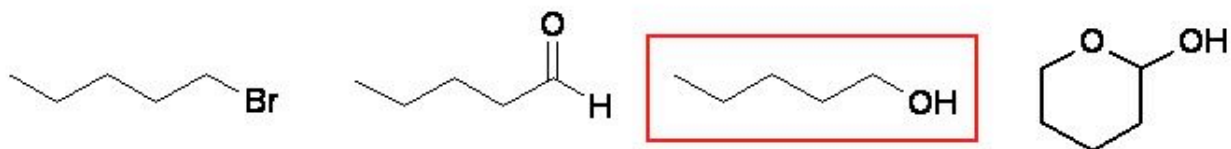
8. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



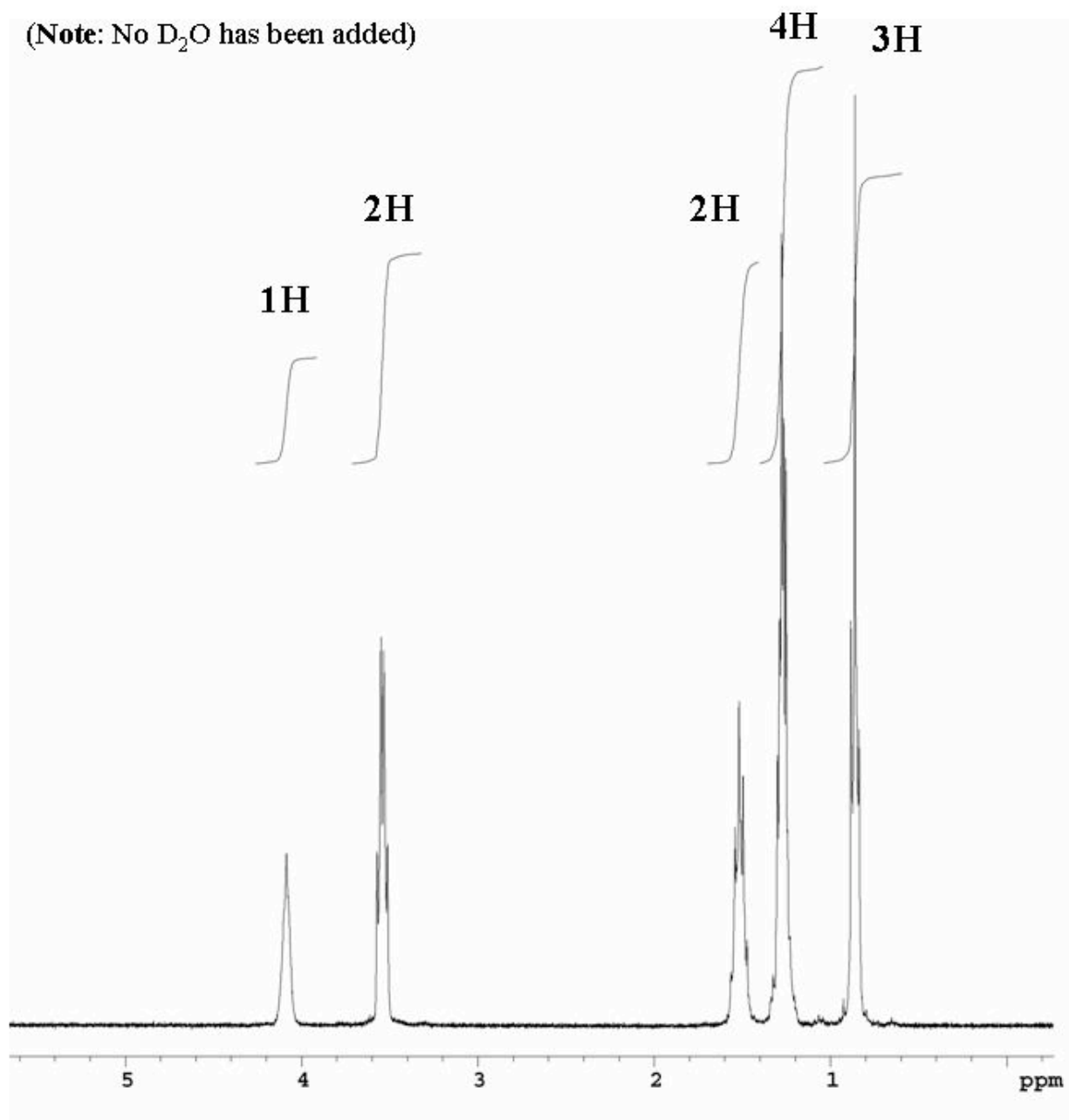
(Note: No D₂O has been added)



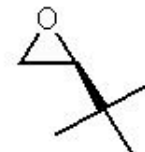
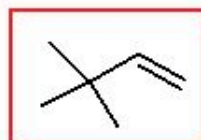
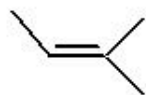
9. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



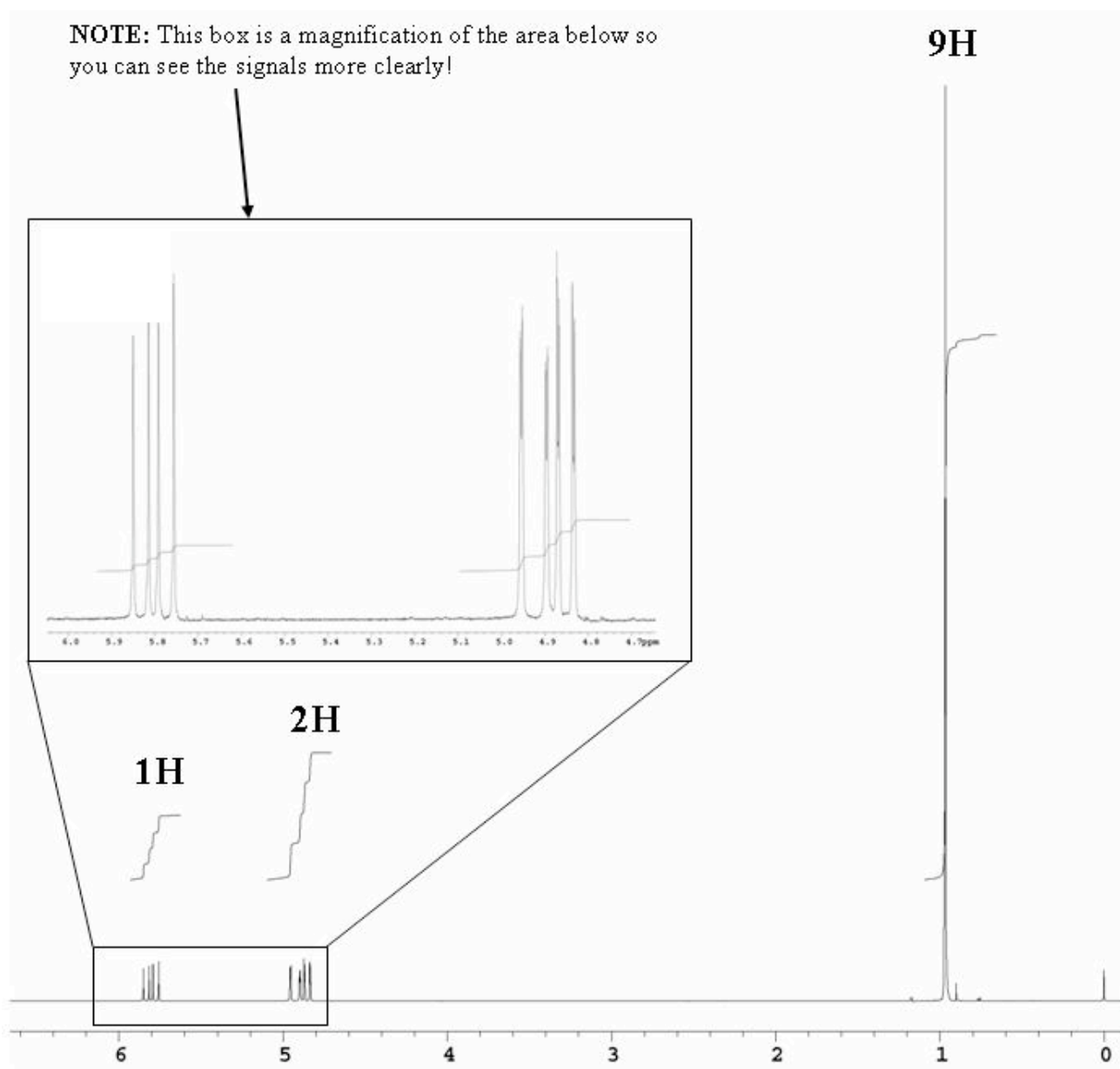
(Note: No D₂O has been added)



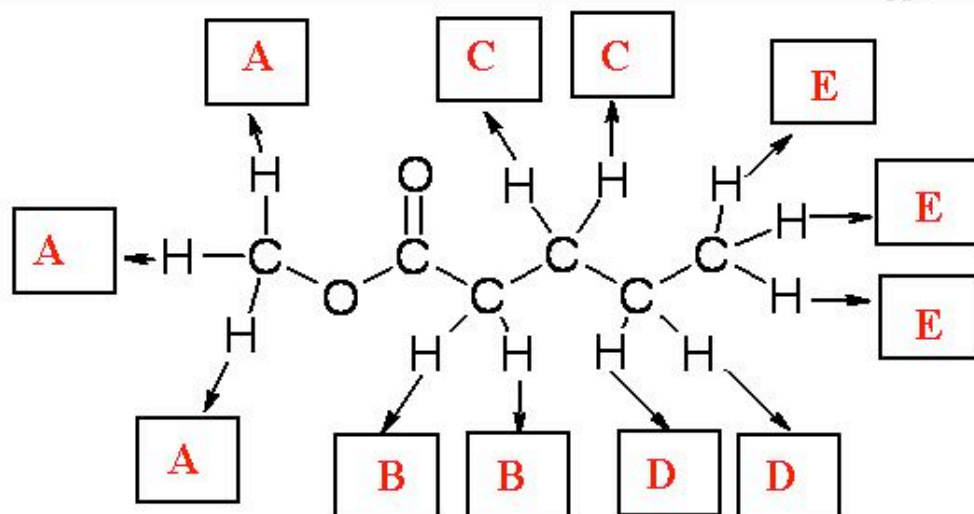
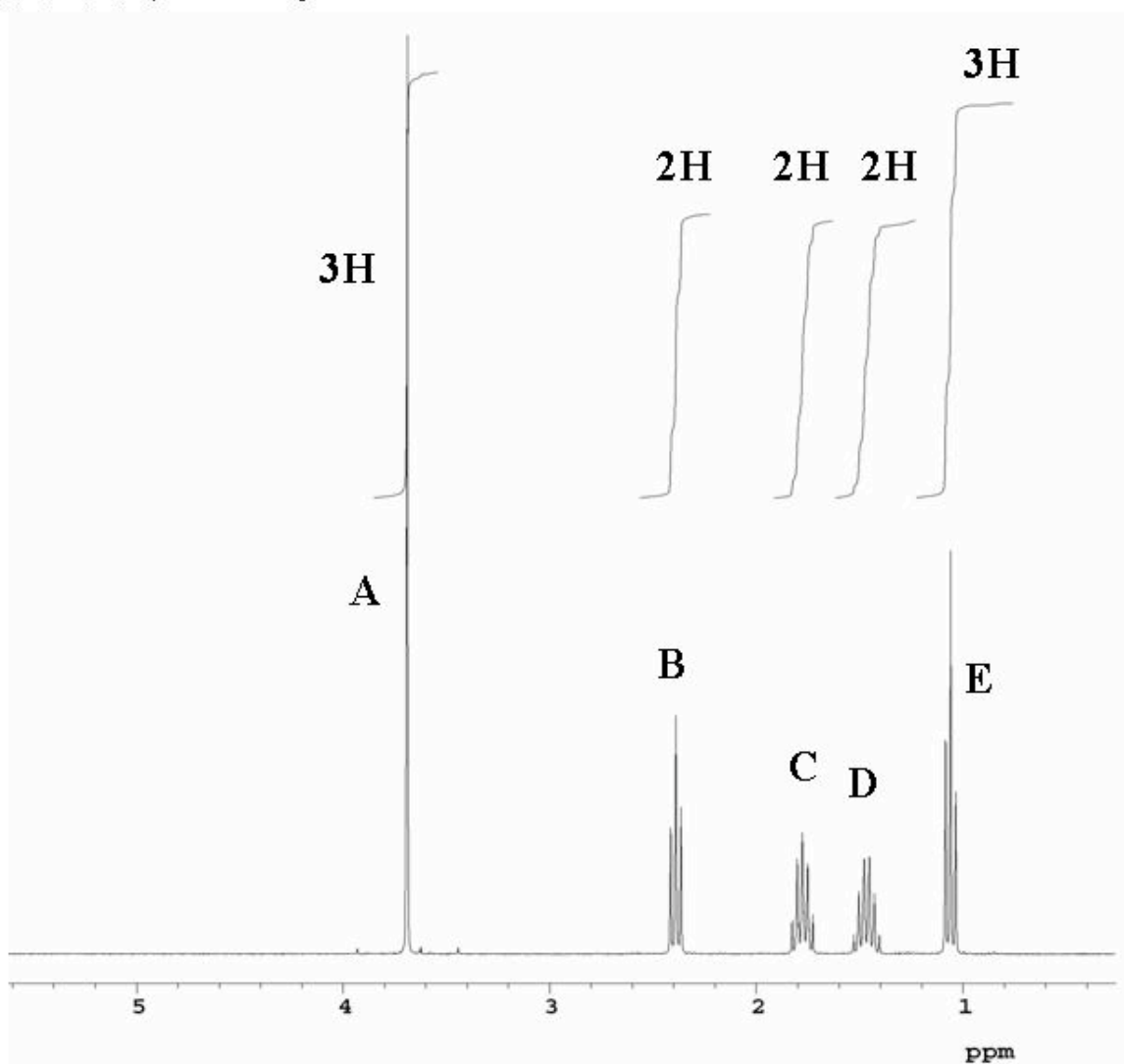
10. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



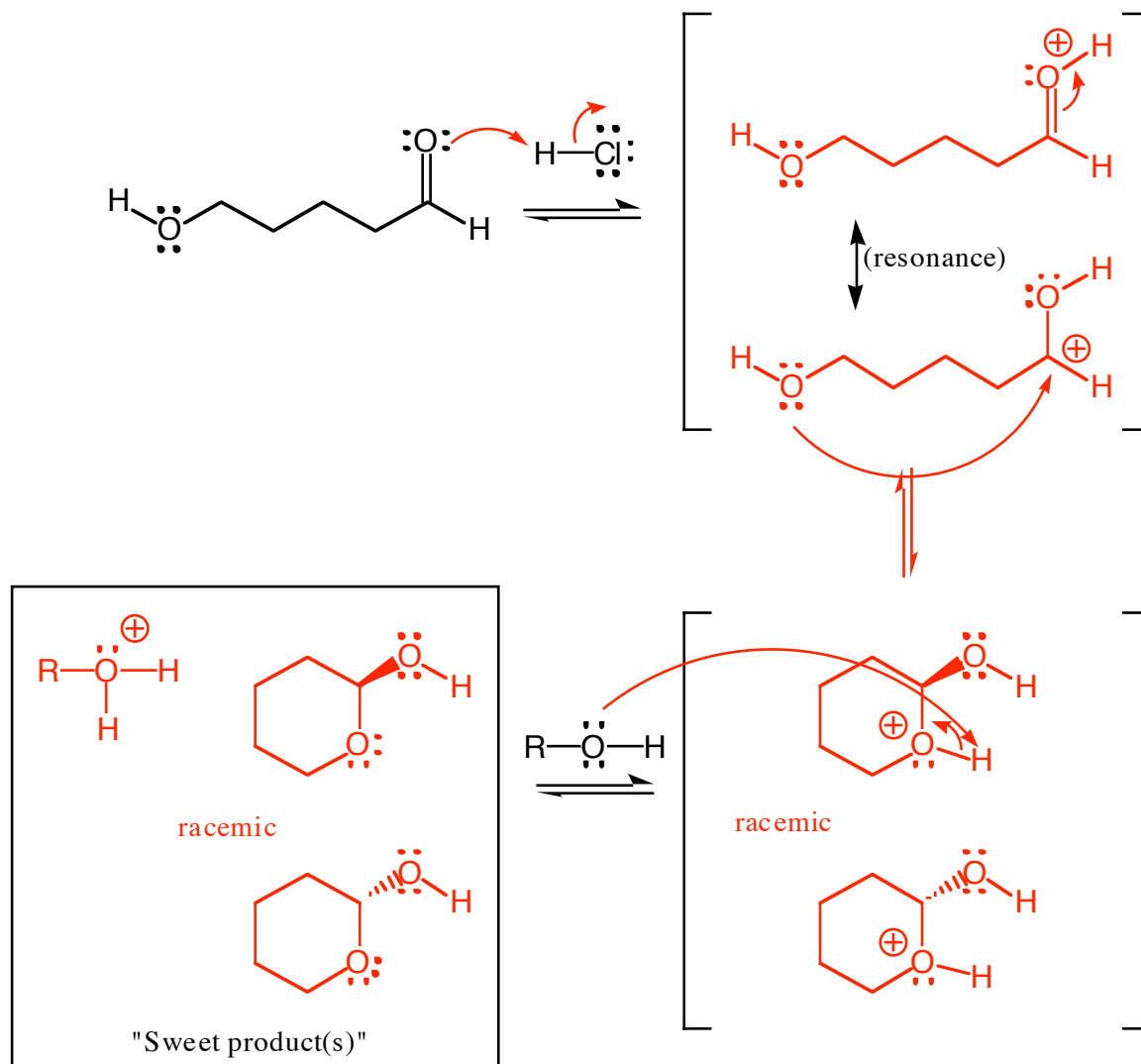
NOTE: This box is a magnification of the area below so you can see the signals more clearly!



11. (1 pt each) This one is different. In the boxes indicated by the arrows, list the letter of the signal (A, B, C, D, E) that corresponds to the indicated H atoms for the molecule shown below.

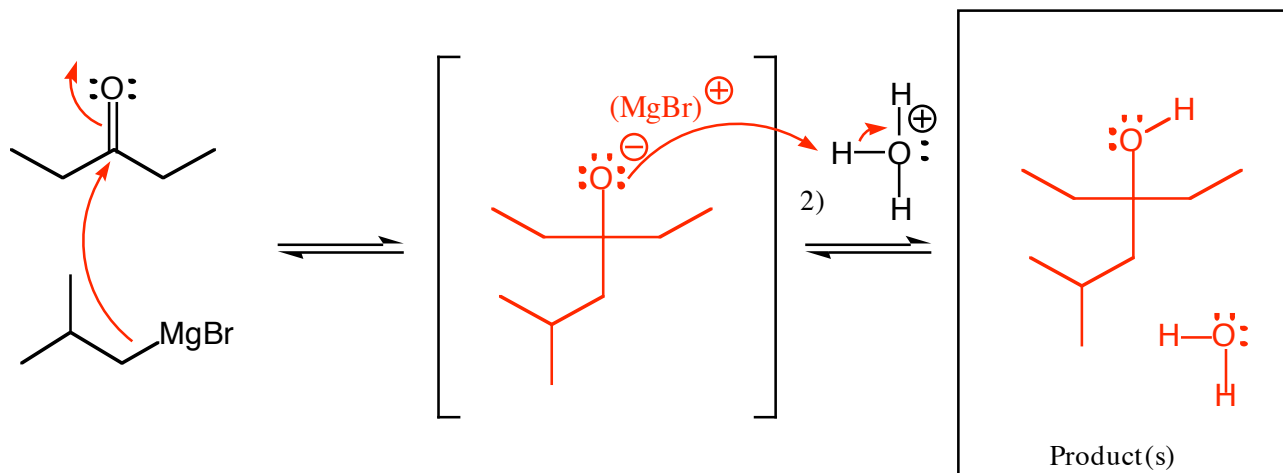


12. (19 pts.) Complete the mechanism for the following cyclic hemiacetal formation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **In the box with the resonance arrow, you need to draw both resonance contributing structures. IF A RACEMIC MIXTURE IS FORMED IN ANY STEP, YOU MUST DRAW BOTH ENANTIOMERS AND LABEL THE MIXTURE AS "RACEMIC".** I realize these directions are complex, so please read them again to make sure you know what we want. You only need to indicate the flow of electrons on one structure (i.e. contributing structure or enantiomer) per intermediate.

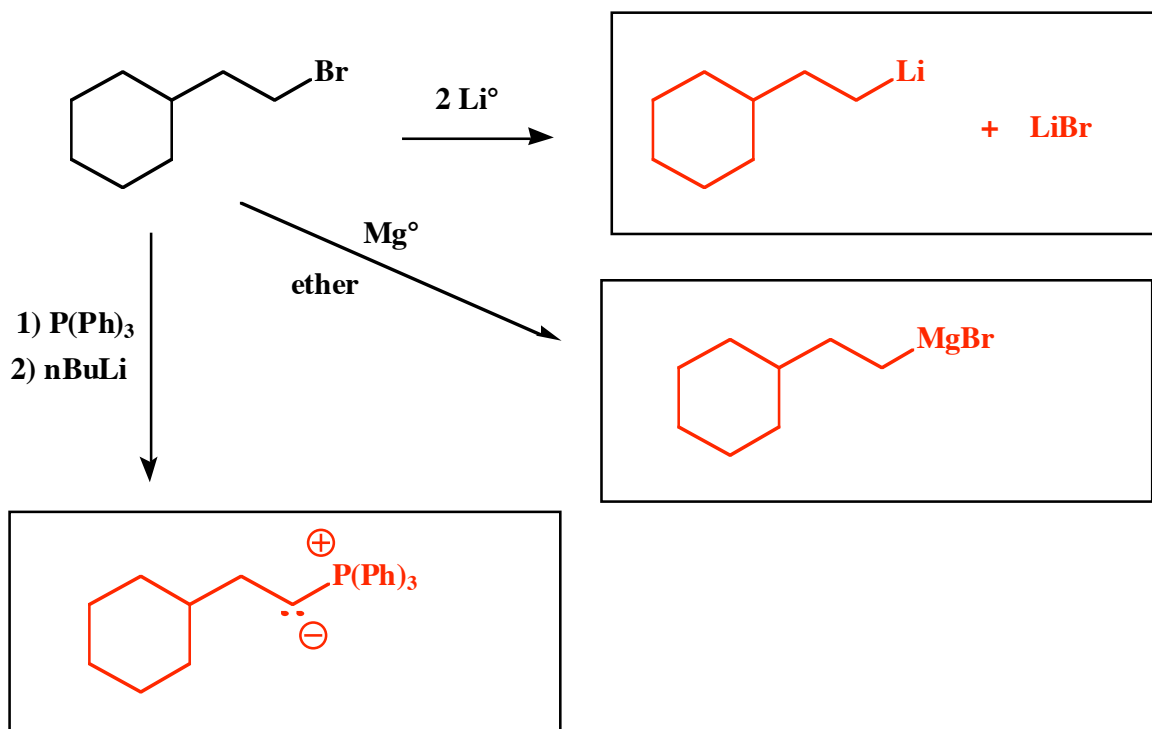


Did you remember to draw both resonance contributing structures and both enantiomers as appropriate?

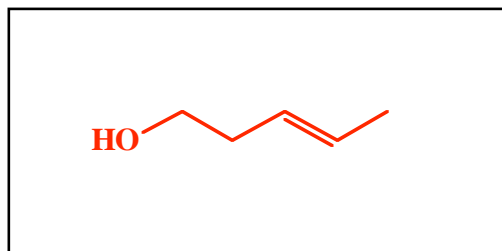
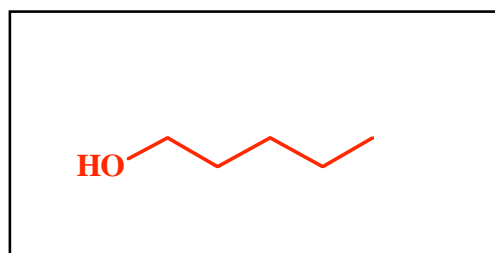
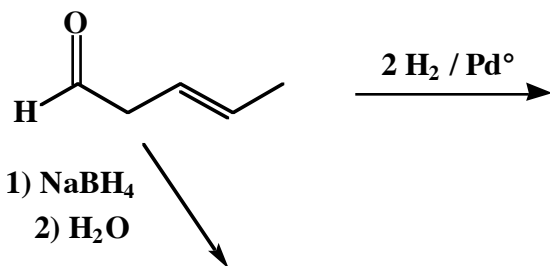
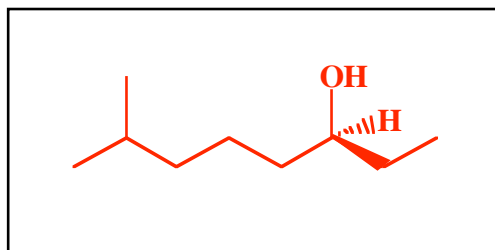
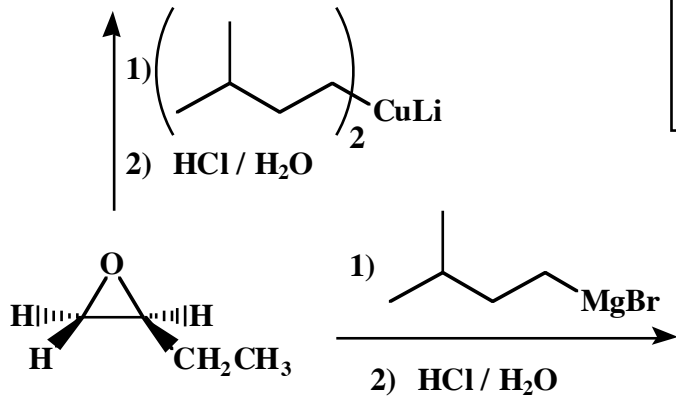
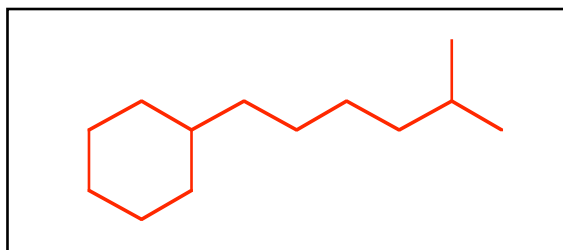
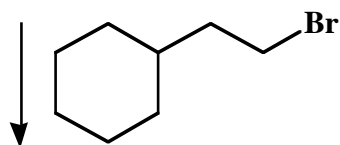
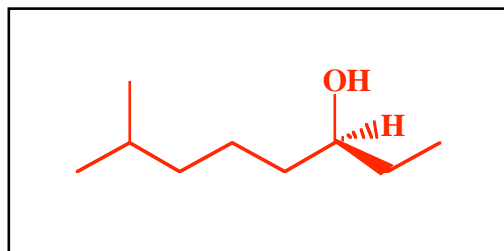
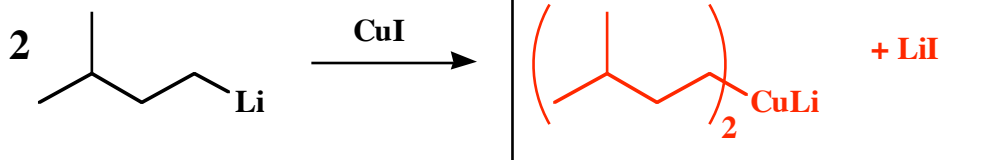
13. (10 pts.) Complete the mechanism for the following Grignard reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A RACEMIC MIXTURE IS FORMED IN ANY STEP, YOU MUST DRAW BOTH ENANTIOMERS AND LABEL THE MIXTURE AS "RACEMIC".** I realize these directions are complex, so please read them again to make sure you know what we want.



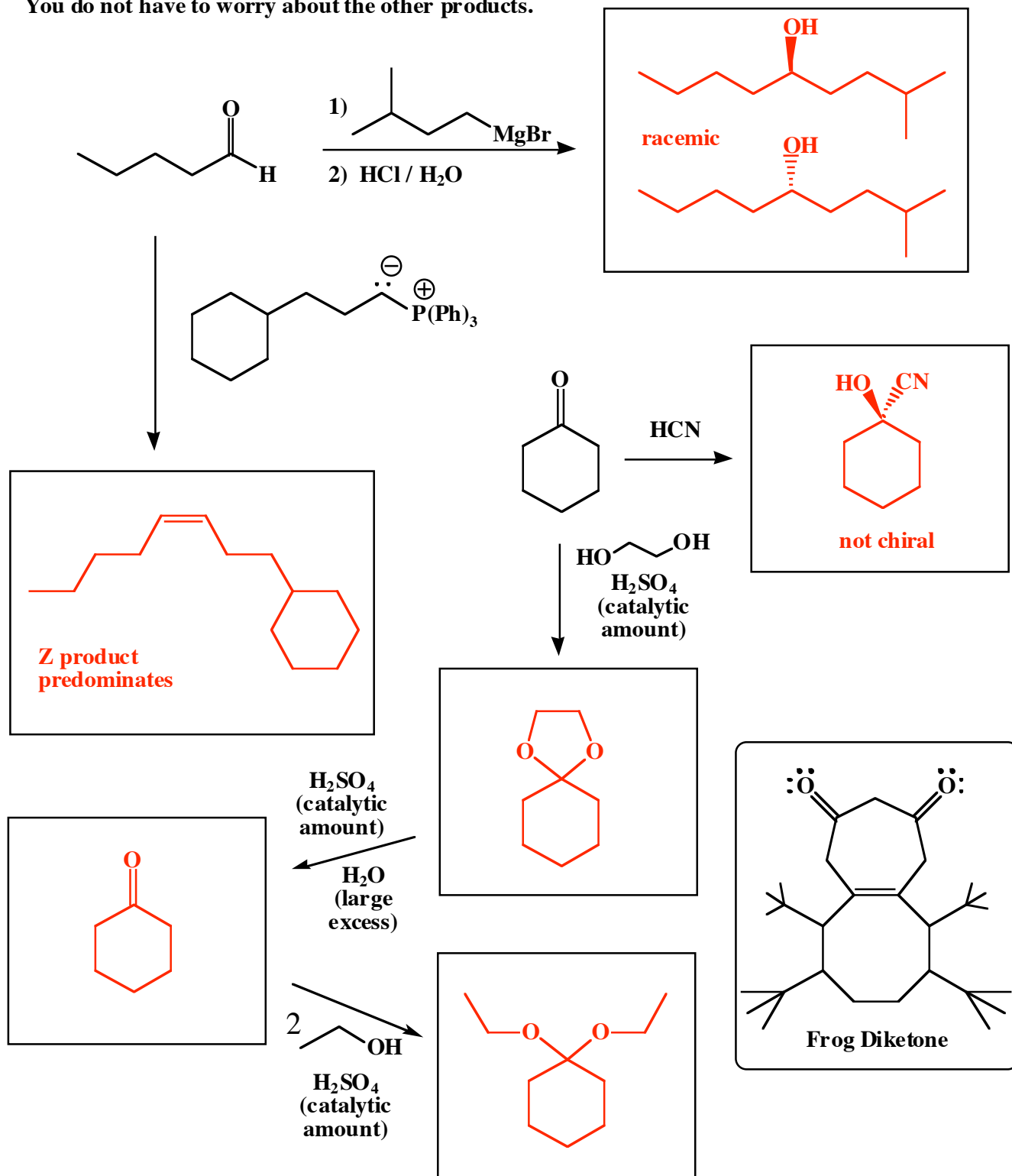
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure.** Use wedges (\blacktriangleleft) and dashes ($\cdots|||$) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.



15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes ($\cdots|||$) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.

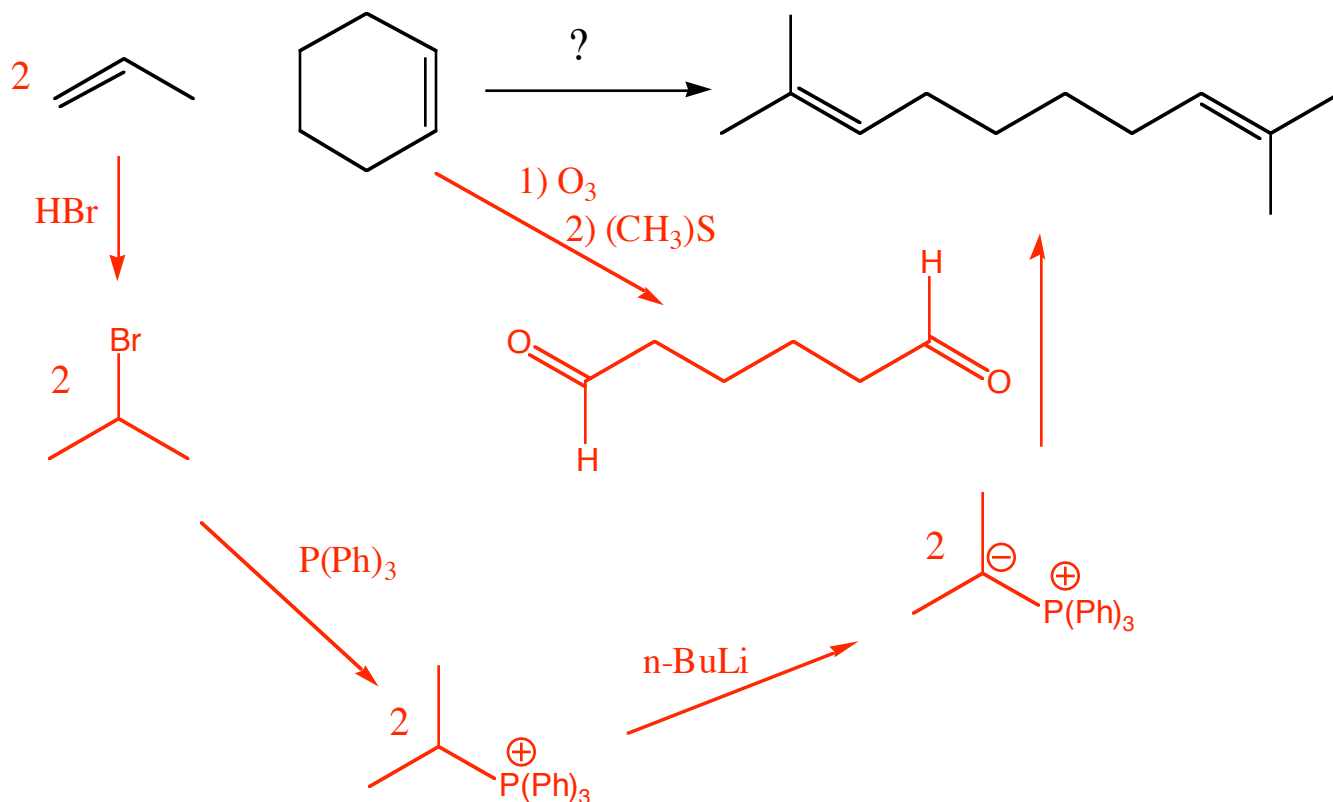


16. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes (\dashv) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.



17. 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.

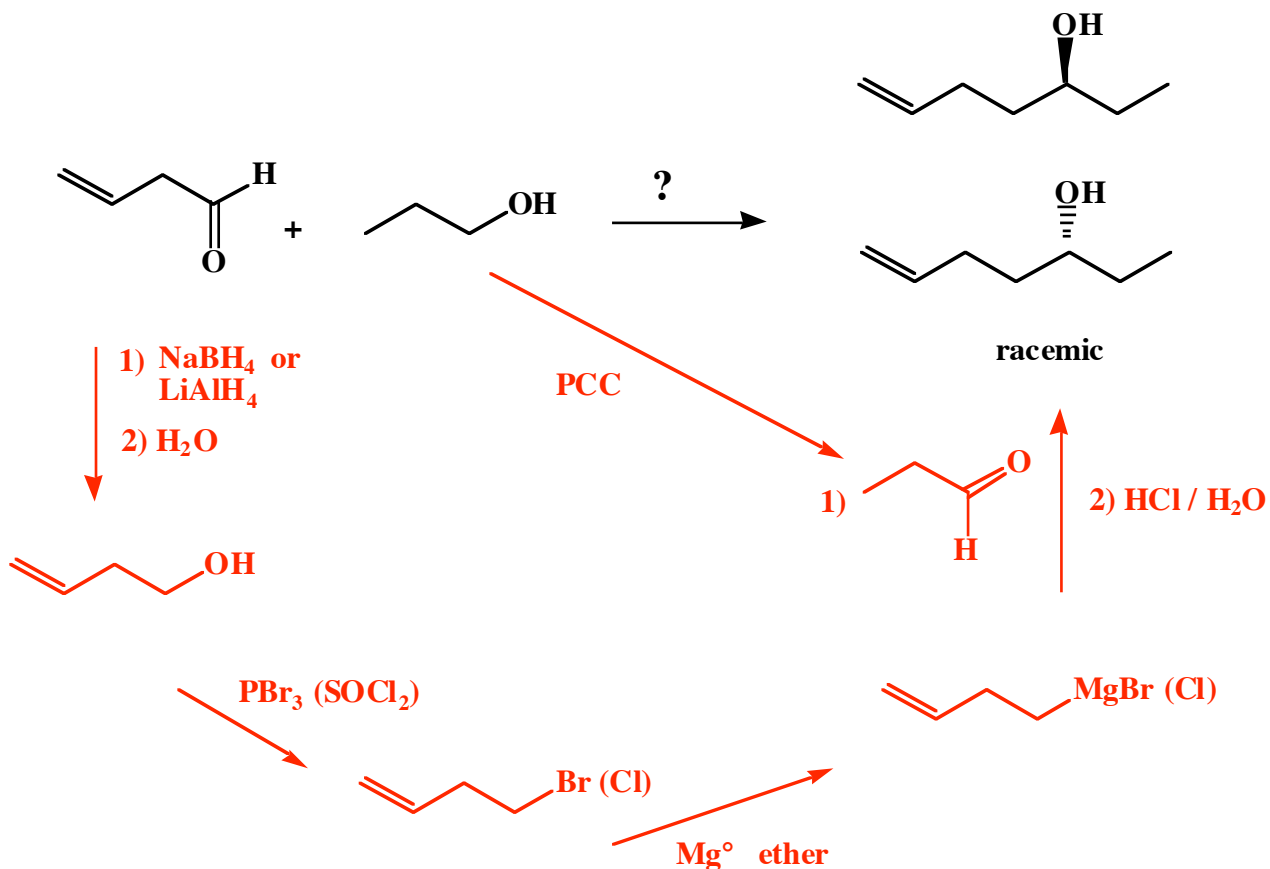
(13 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Count carbons in the product (12) and realize that two molecules of the 3-carbon unit need to be added to one of the 6-carbon unit. **Recognize** that the last step makes alkenes in the locations required for carbon-carbon bond formation, indicating a Wittig reaction as the last step. **Recognize** that the ring can be opened to give the required dialdehyde by an ozonolysis. **Recognize** that the required Wittig ylide can be derived from the starting alkene via reaction with HBr (Markovnikov addition) followed by the unusual steps of adding P(Ph)_3 followed by strong base ($n\text{-BuLi}$).

18. 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.

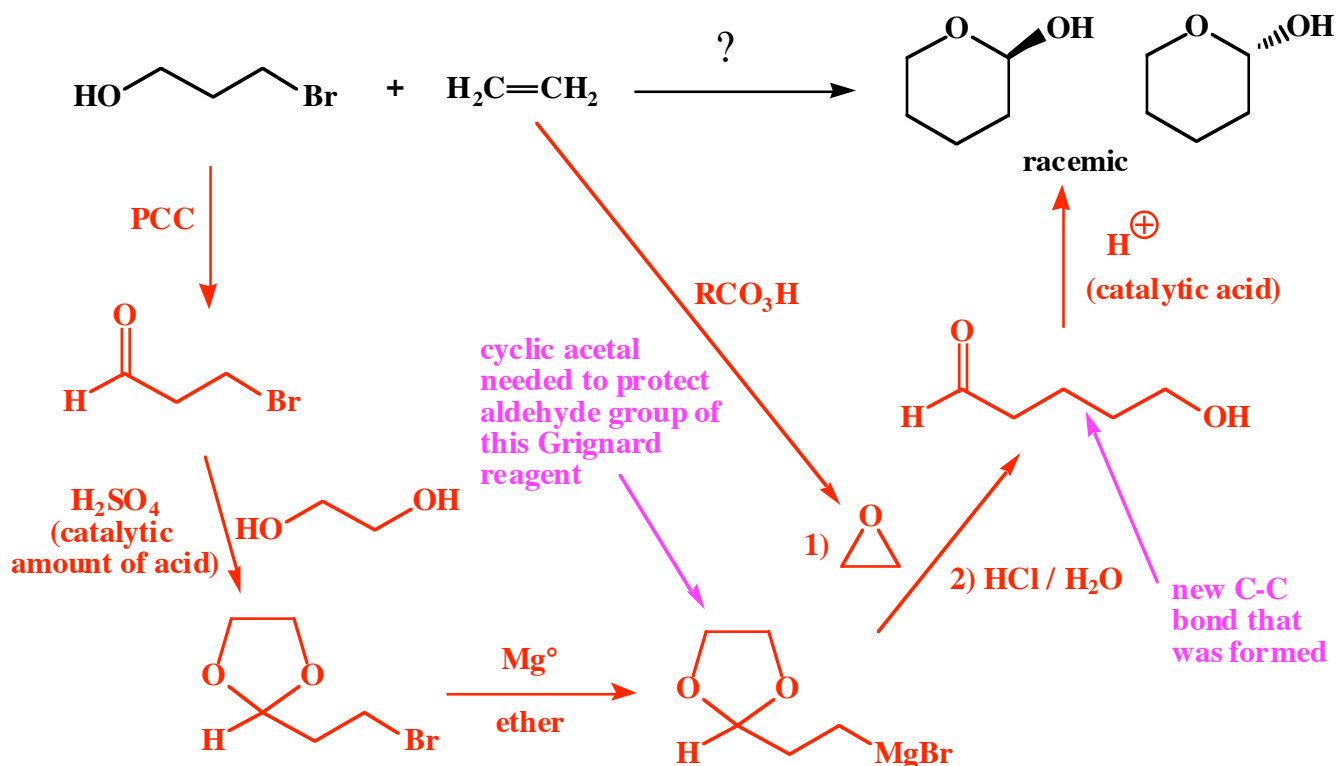
(13 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Recognize that the product is an alcohol, the Key Recognition Element of a Grignard reaction. In this case, the reaction must be between propionaldehyde and the Grignard made from the cyclohexene piece. These in turn, are made from a PCC reaction of the starting alcohol and cyclohexene bromide derivative, respectively. This latter reagent can be prepared from a selective reduction of the starting cyclohexene aldehyde using a hydride reagent. H_2 / Pd would have reduced the $\text{C}=\text{C}$ as well.

17. 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.

(16 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Recognize that the final product is a cyclic hemiacetal of 5-hydroxypentanal. Counting carbons tells you that one molecule from each starting material (3 + 2) is used. The first hard part of this synthesis is realizing that an epoxide (ethylene oxide) was used since the alcohol group is on the end even though the new carbon-carbon bond is formed between carbons 3 and 4 of the 5-hydroxypentanal. Given that insight, you need to recognize that a cyclic acetal protecting group was needed to protect the aldehyde group on the required Grignard reagent as discussed in class. This approach required that the starting 3-bromopropanol is oxidized with PCC to give the corresponding 3-bromopropanal in the first step.