

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
1st Midterm
Feb. 19, 2009

SIGNATURE: _____

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

--	--	--

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 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		(23)
2		(11)
3		(26)
4		(6)
5		(5)
6		(5)
7		(5)
8		(5)
9		(-)
10		(5)
11		(12)
12		(14)
13		(35)
14		(23)
15		(18)
16		(10)
17		(13)
18		(13)
19		(19)
Total		(248)
%		
T Score		
HW		
(HW score + Exam Grade) \implies	Total Grade	

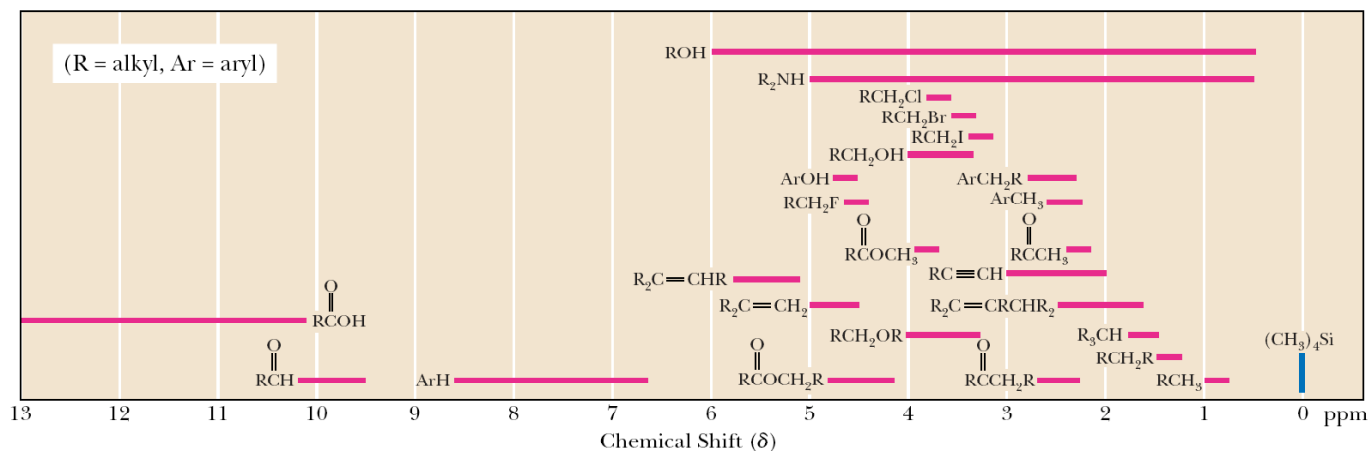
Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\ \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\ \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ / \quad \backslash \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{array}{c} O \\ \\ RCH \end{array}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{array}{c} O \\ \\ RCOH \end{array}$	10-13
RCH_2OR	3.3-4.0		

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



1. (3 pts) For this class, the most important question in organic chemistry is:

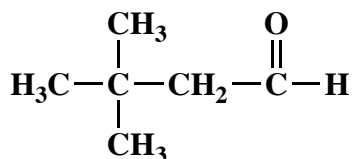
Where are the electrons?

2. (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.**

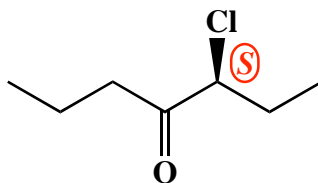
3. (3 pts each) Write an acceptable IUPAC name for the following molecules:

A.



3,3-Dimethylbutanal

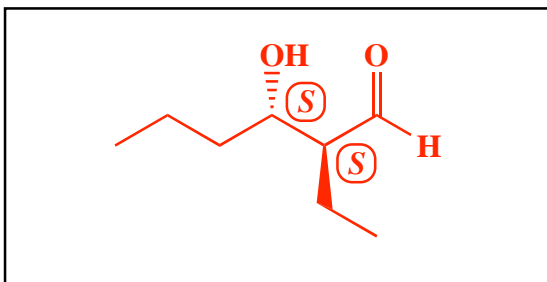
B.



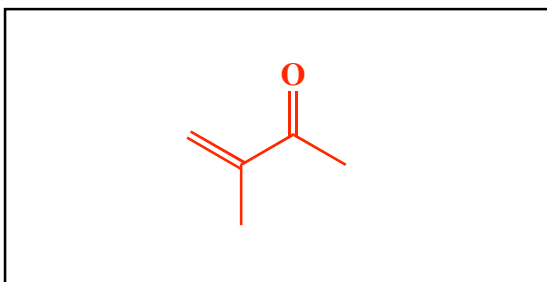
(S)-3-Chloro-4-heptanone

4. (3 pts each) Write a structure that corresponds to the following IUPAC names:

A. (2*S*, 3*S*)-3-Hydroxy-2-ethylhexanal



B. 3-Methyl-3-butene-2-one



5. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

In the NMR experiments most useful to organic chemists, the nuclei ^1H and ^{13}C are the most important since these are commonly found in organic molecules and they have spin quantum numbers of $1/2$. Nuclei with spin quantum number $1/2$ are quantized in one of two orientations, " $+1/2$ " (lower energy) or " $-1/2$ " (higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively. The difference in energy between nuclear spin states is proportional to the strength of the magnetic field experienced by the nucleus.

6. (2 pts each) **Circle** all of the following statements about NMR that are **true** (do nothing if the statements are false).

If electromagnetic energy of the precise energy difference between the +1/2 and -1/2 spins states is used to irradiate the sample, the energy is absorbed as the spin "flips" from the +1/2 state to the -1/2 state.

If electromagnetic energy of the precise energy difference between the +1/2 and -1/2 spins states is used to irradiate the sample, the energy is absorbed as the spin "flips" from the -1/2 state to the +1/2 state.

"Resonance" in NMR refers to the phenomenon of absorption of energy when a nuclear spin "flips."

Equivalent hydrogen atoms in a molecule give the same NMR signal.

Equivalent hydrogen atoms in a molecule have identical relationships to all the other atoms in the molecule.

Hydrogen atoms in a molecule are equivalent if they are attached to the same freely rotating sp^3 hybridized carbon atom.

Hydrogen atoms in a molecule are equivalent if they are in groups that are related by a symmetry element, such as being reflections of each other when the molecule is bisected by a plane of symmetry.

Two hydrogen atoms in a molecule are equivalent if they are attached to a carbon atom that is part of a non-symmetrical three-membered ring.

The physical basis of spin-spin splitting is that nuclei no more than three bonds away from the hydrogen of interest have a small magnetic field associated with their +1/2 or -1/2 spin state.

The physical basis of shielding is that electron density is induced to circulate in a strong magnetic field, and this circulation produces its own magnetic field that opposes the external magnetic field.

The physical basis of spin-spin splitting is that electron density is induced to circulate in a strong magnetic field, and this circulation produces its own magnetic field that opposes the external magnetic field.

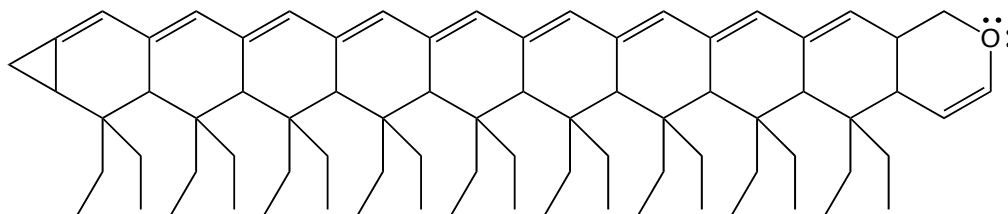
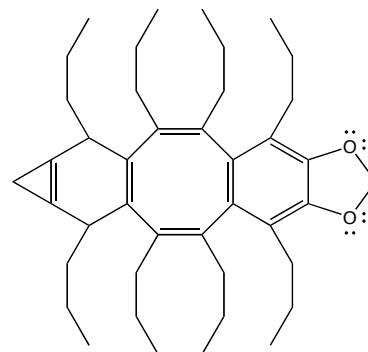
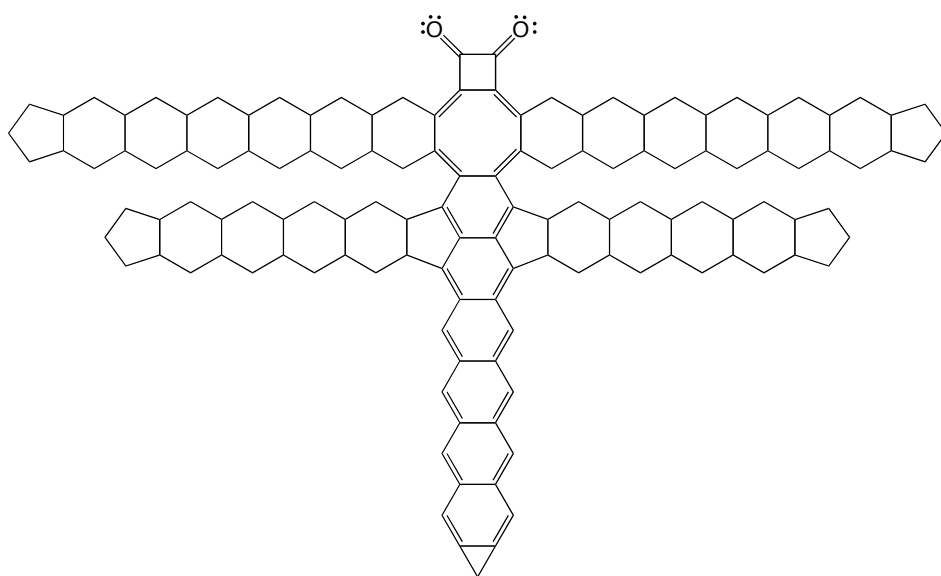
THEORY: The signal for a $-CH_2-$ group with a $-CH_2-$ group and a $-CH_3$ group on either side could show up to $3 \times 4 = 12$ peaks.

PRACTICE: For alkyl groups with freely rotating sp^3 hybridized carbon atoms, complex splittings simplify because 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. This is an approximation, but almost always true on spectra taken with all but the most sophisticated NMR spectrometers.

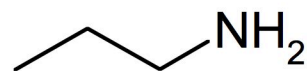
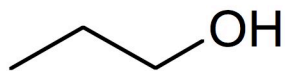
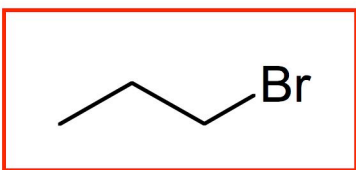
7. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

In the so-called "FT" approach to NMR, all the nuclear spins are flipped instantaneously with a multi-frequency pulse, then the rate at which the spins "relax" back to the +1/2 (or lower energy) state is monitored. This latter approach uses a mathematical algorithm called Fourier transform (FT) to reconstruct individual resonance frequencies for the different equivalent sets of hydrogen atoms so the spectra can be plotted.

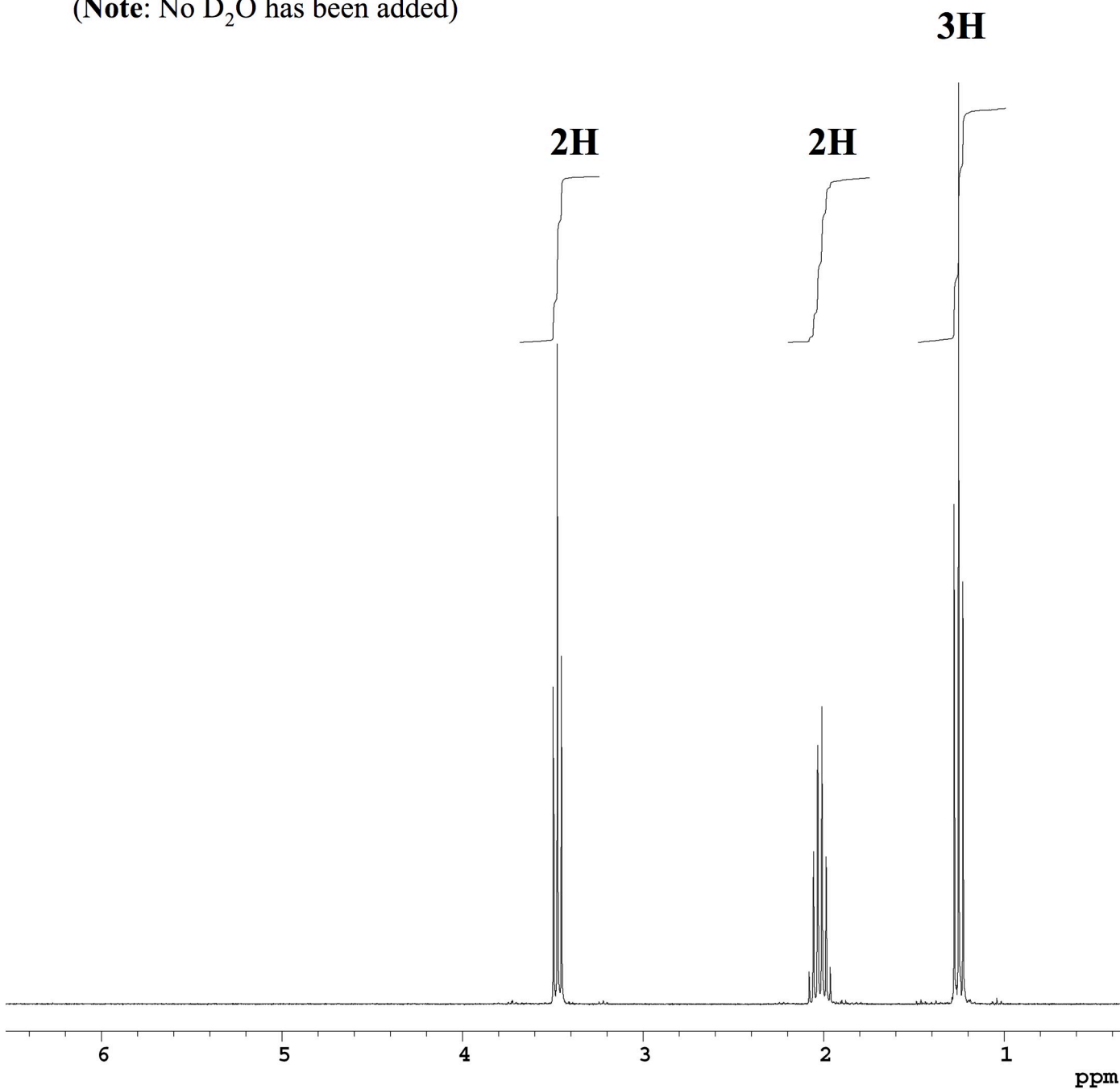
Here are some recently discovered molecular insects.



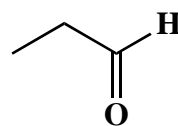
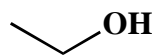
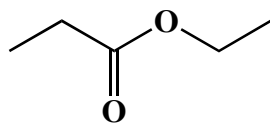
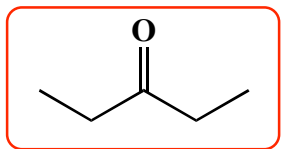
8. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



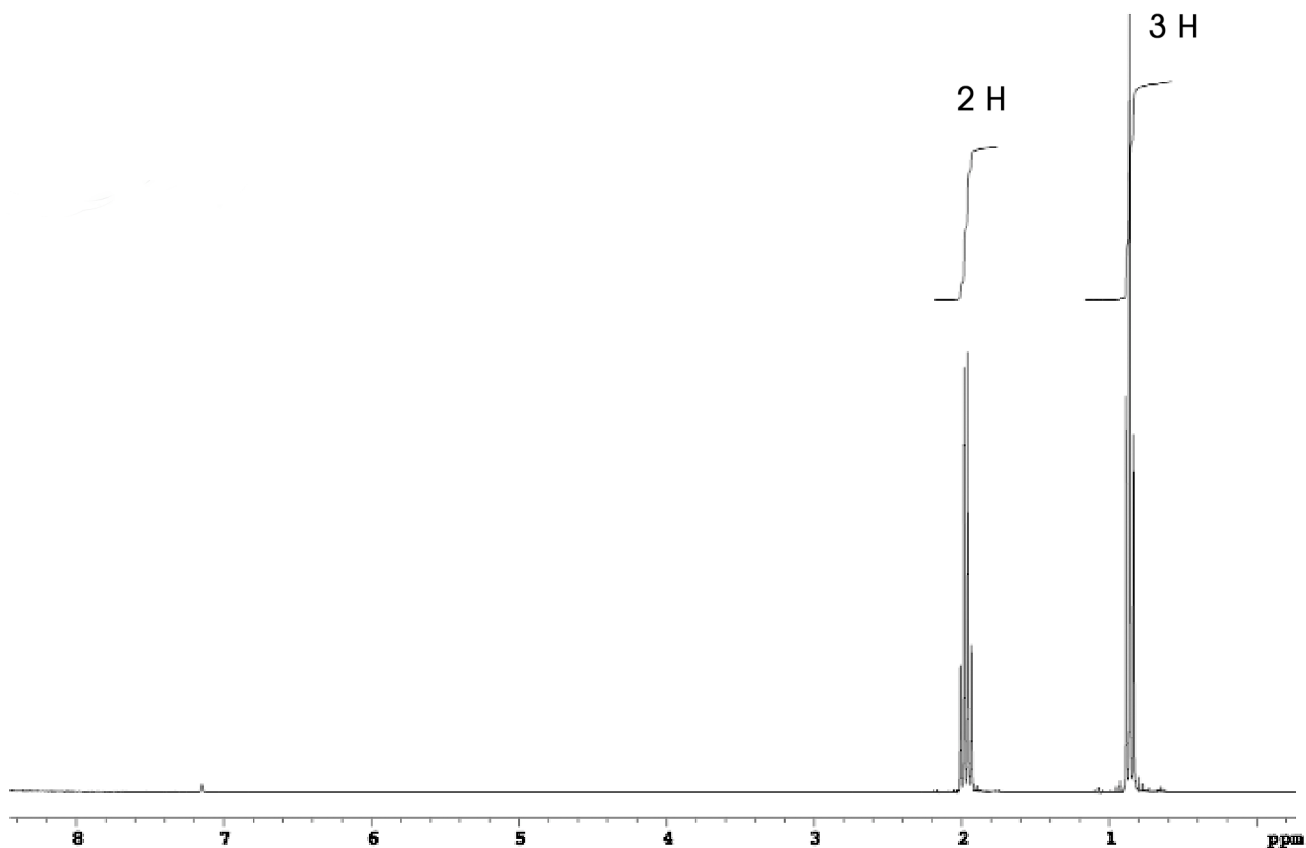
(Note: No D₂O has been added)



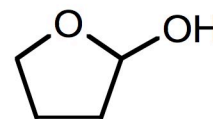
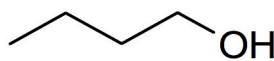
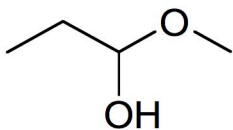
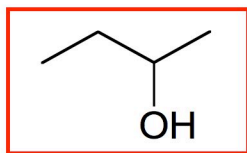
9. (5 pts) Circle the structure that corresponds to the following spectrum.



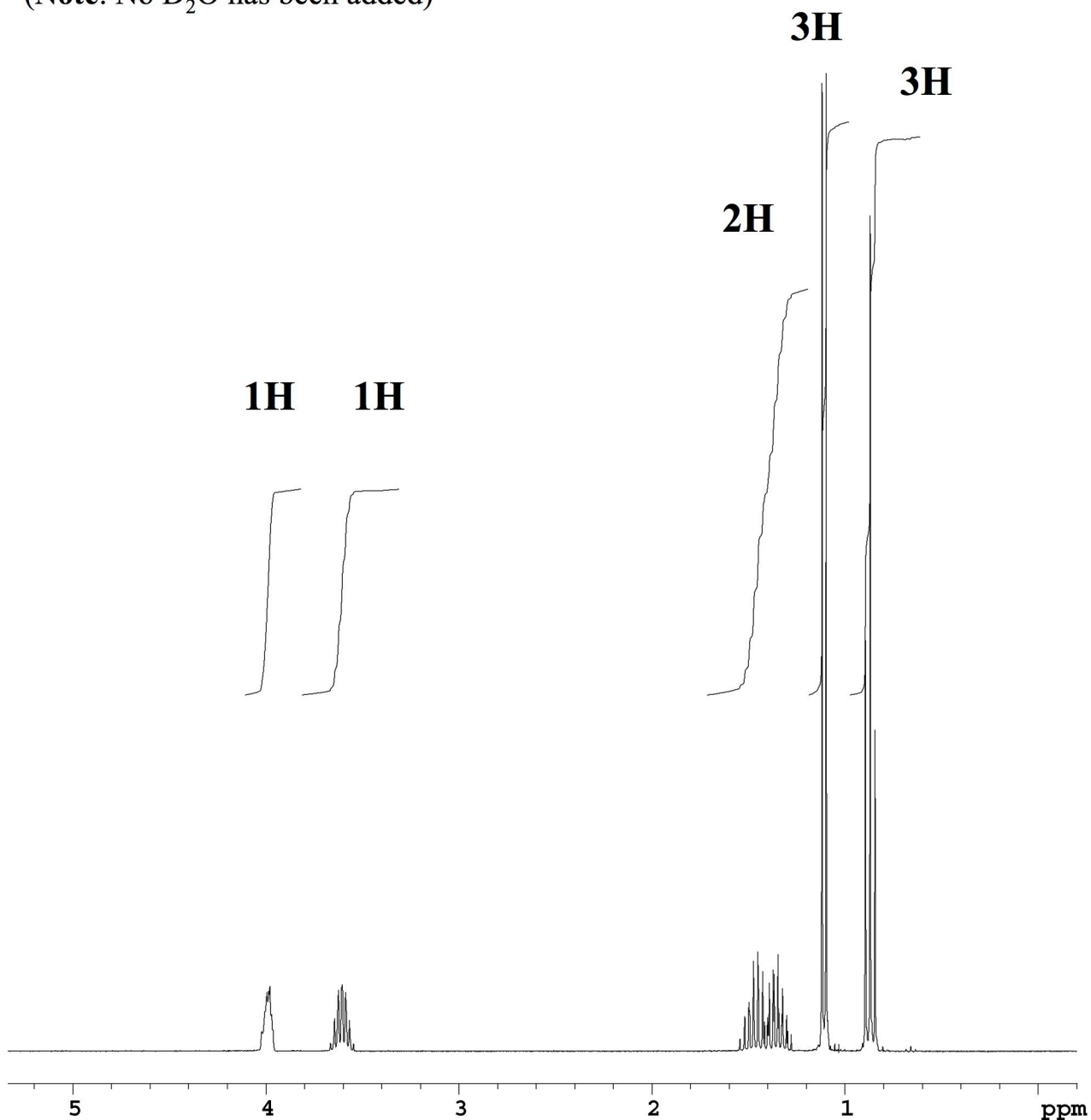
(No D₂O was added to the sample)



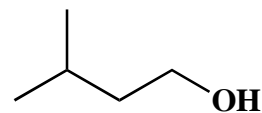
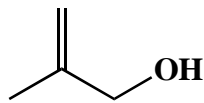
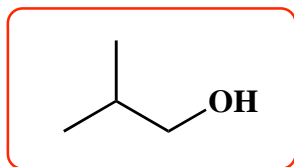
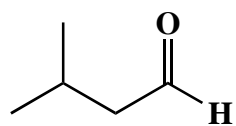
10. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



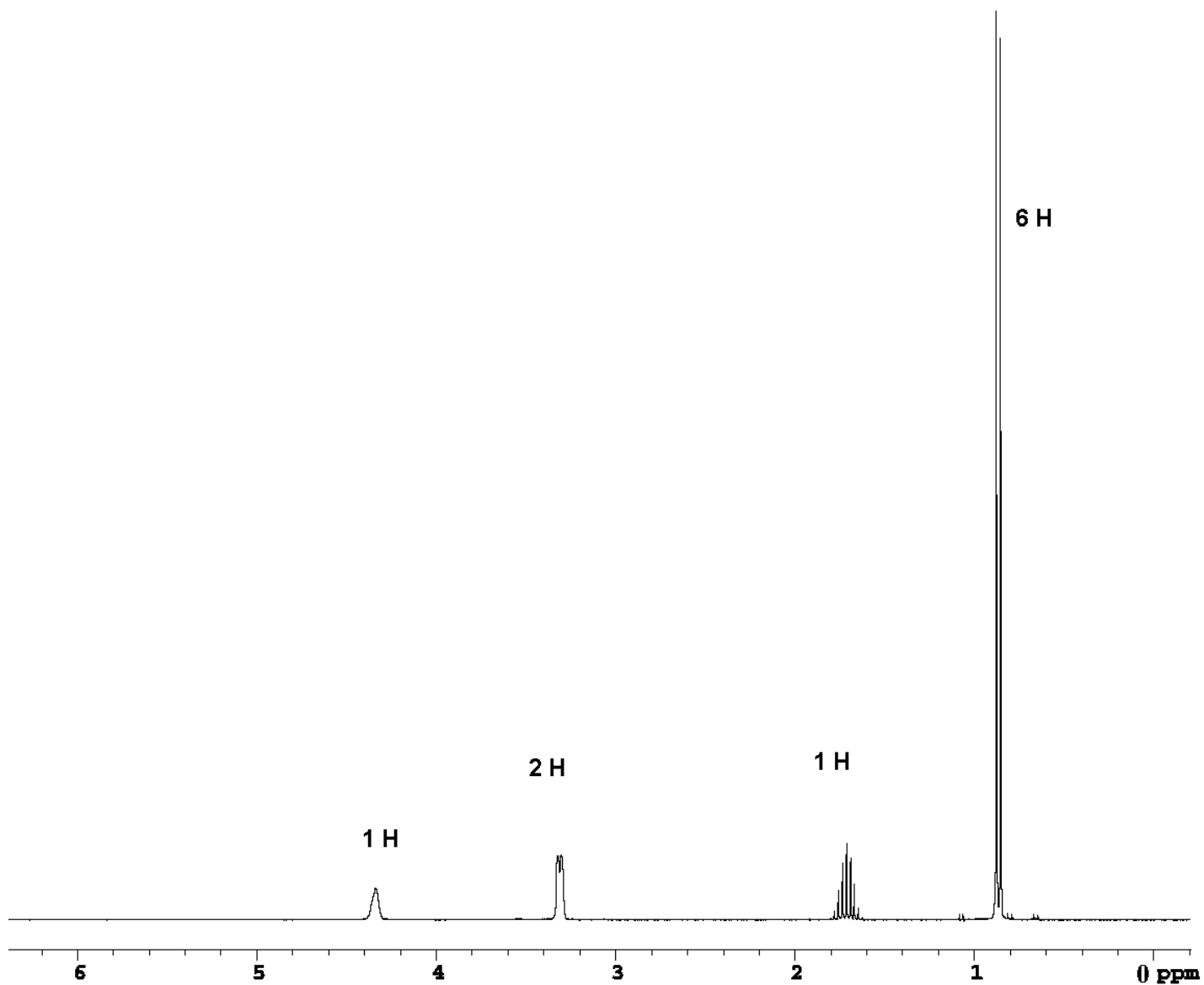
(Note: No D₂O has been added)



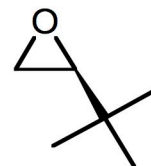
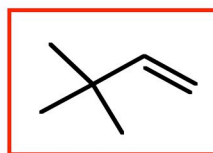
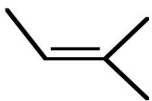
11. (5 pts) Circle the structure that corresponds to the following spectrum.



(No D₂O was added to the sample)

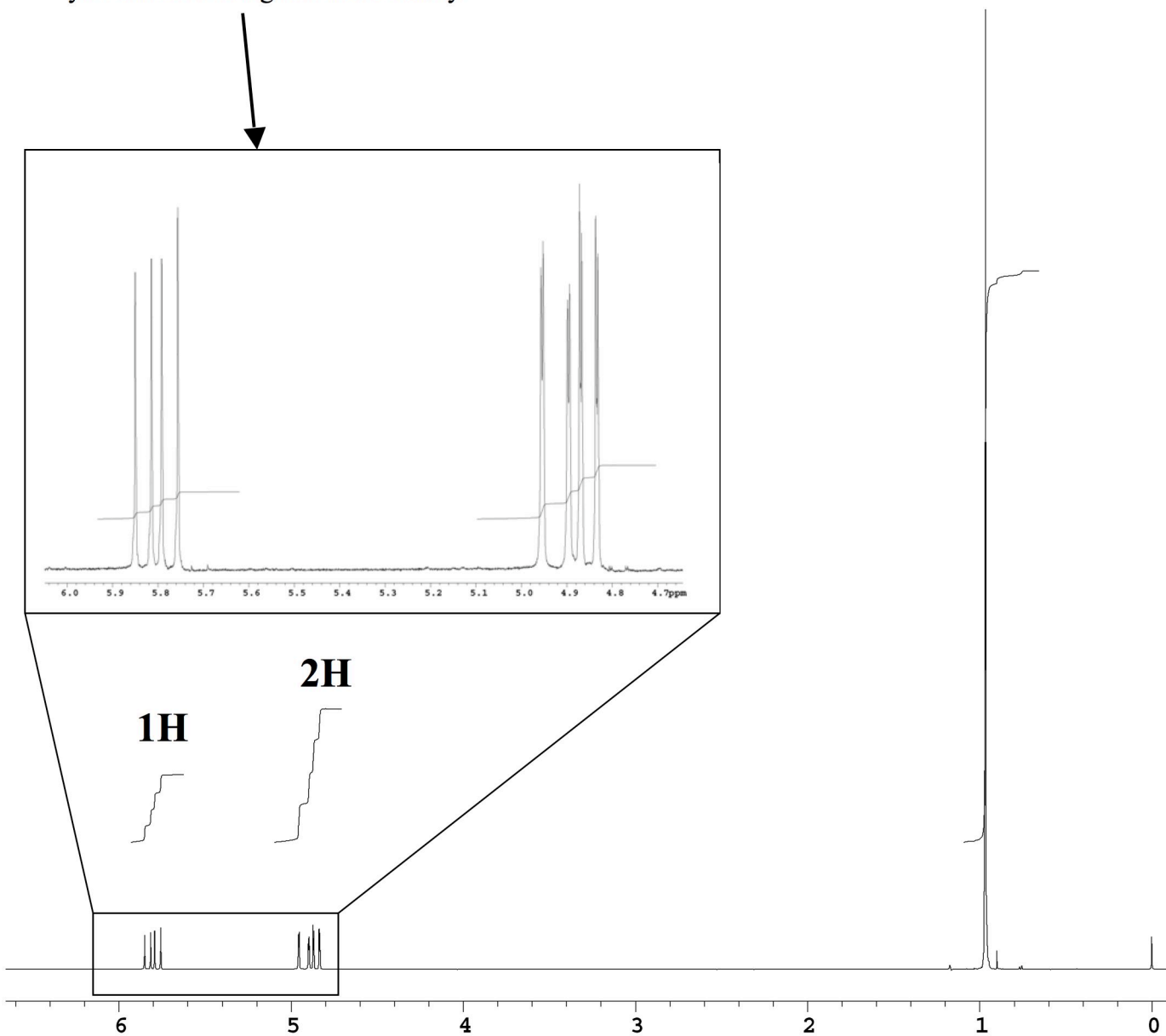


13. (5 pts each) Circle the molecule that corresponds to the spectrum shown.



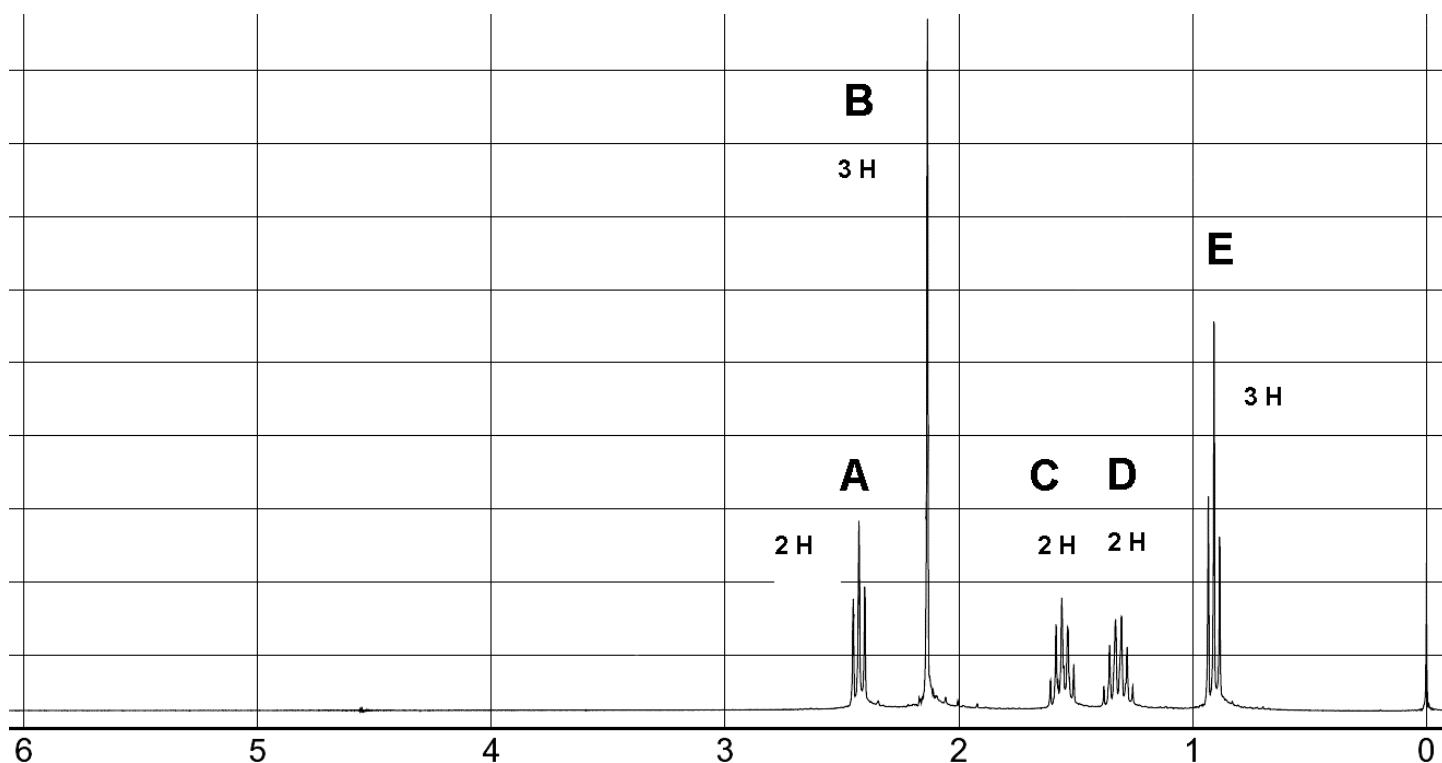
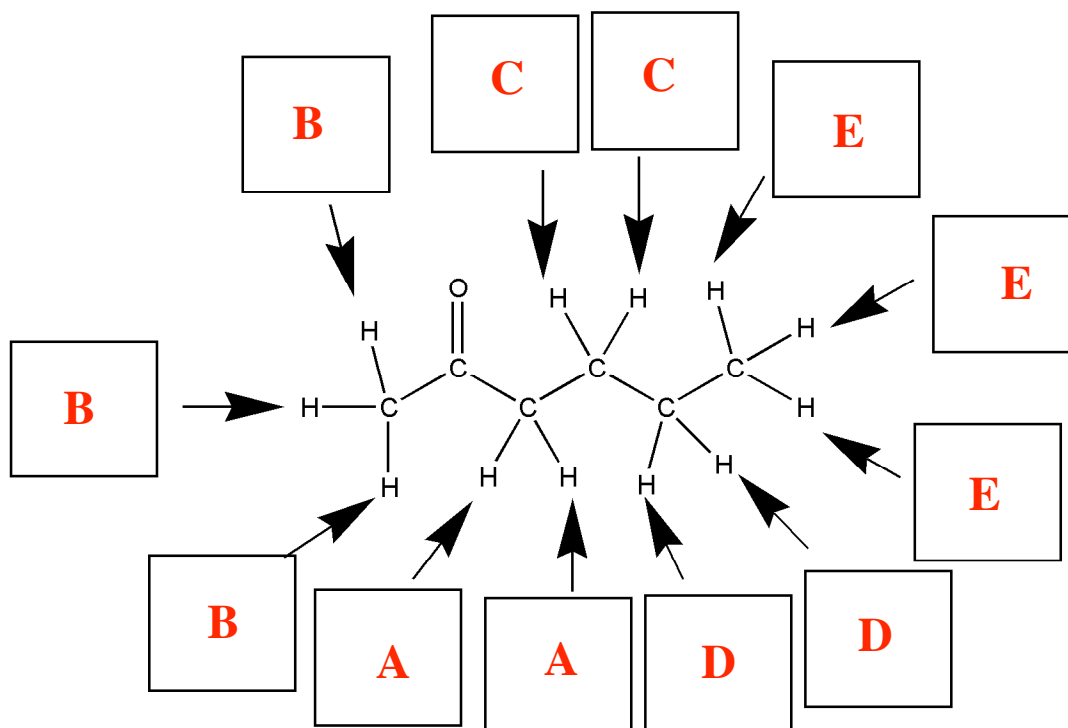
NOTE: This box is a magnification of the area below so you can see the signals more clearly!

9H



14. (12 pts) The following $^1\text{H-NMR}$ spectrum of 2-hexanone has signals labeled with letters. In the boxes provided on the structure, place the letter of the signal that corresponds to the H atoms indicated by the arrows. Because of equivalence, more than one box can get the same letter!

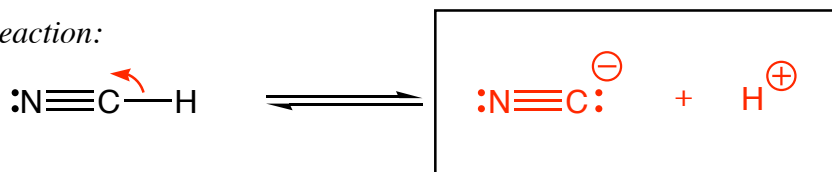
(No D_2O was added to the sample)



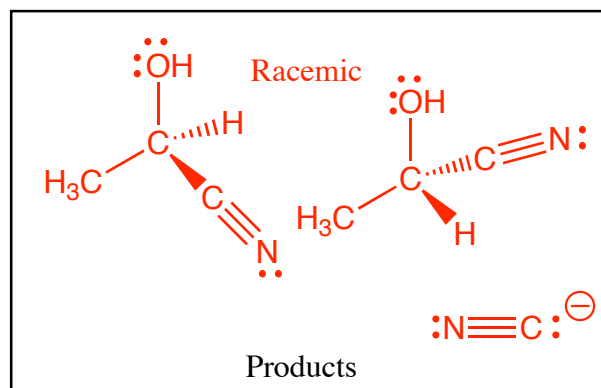
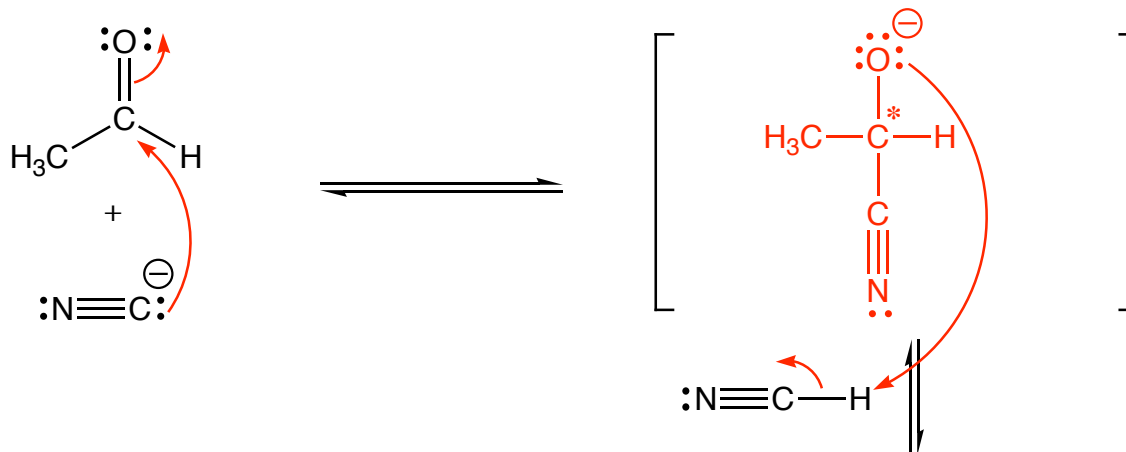
15. (14 pts.) Complete the mechanism for the following reaction of an aldehyde with HCN. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.

HCN Reacting with an Aldehyde

Equilibrium present in reaction:

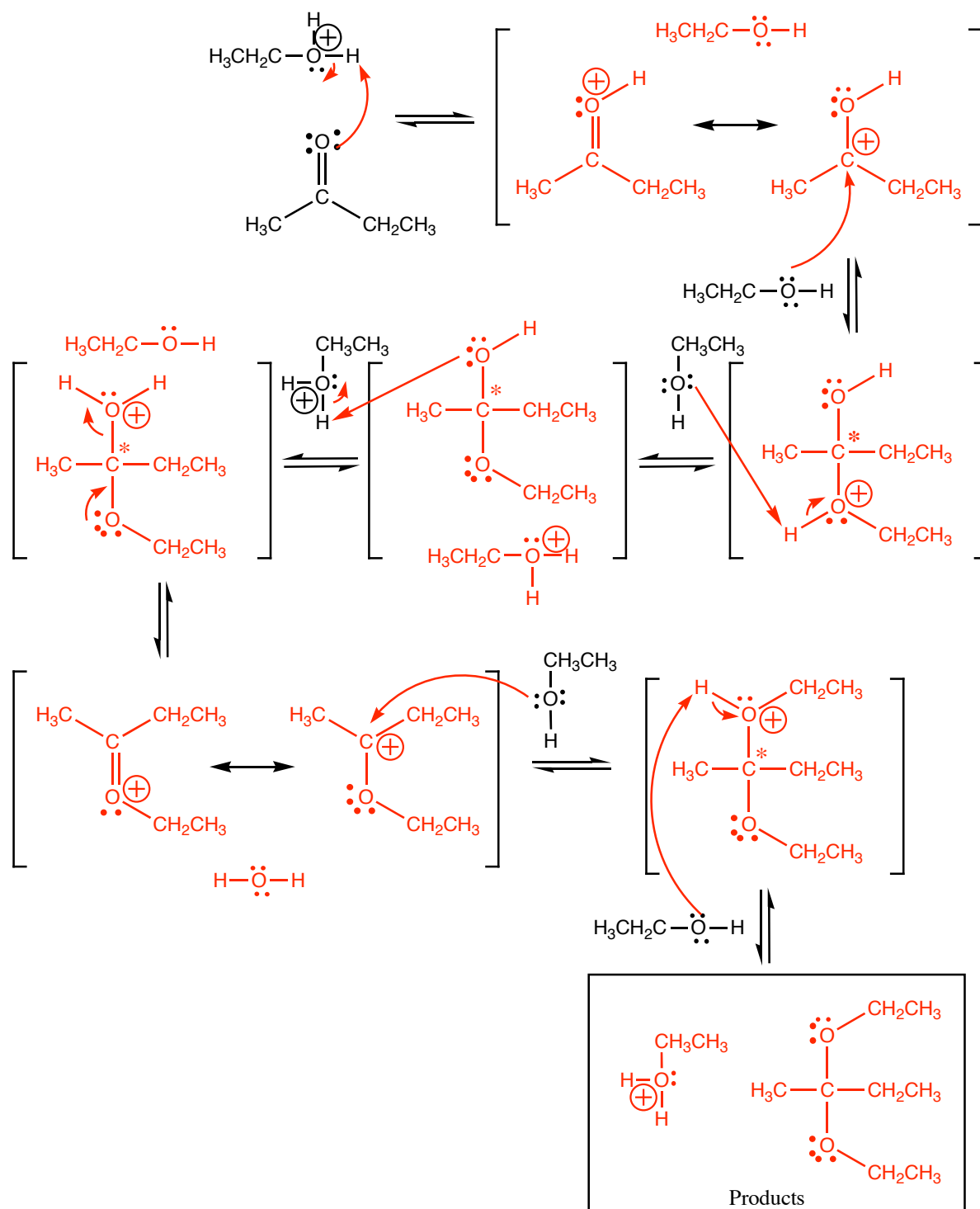


Actual reaction:

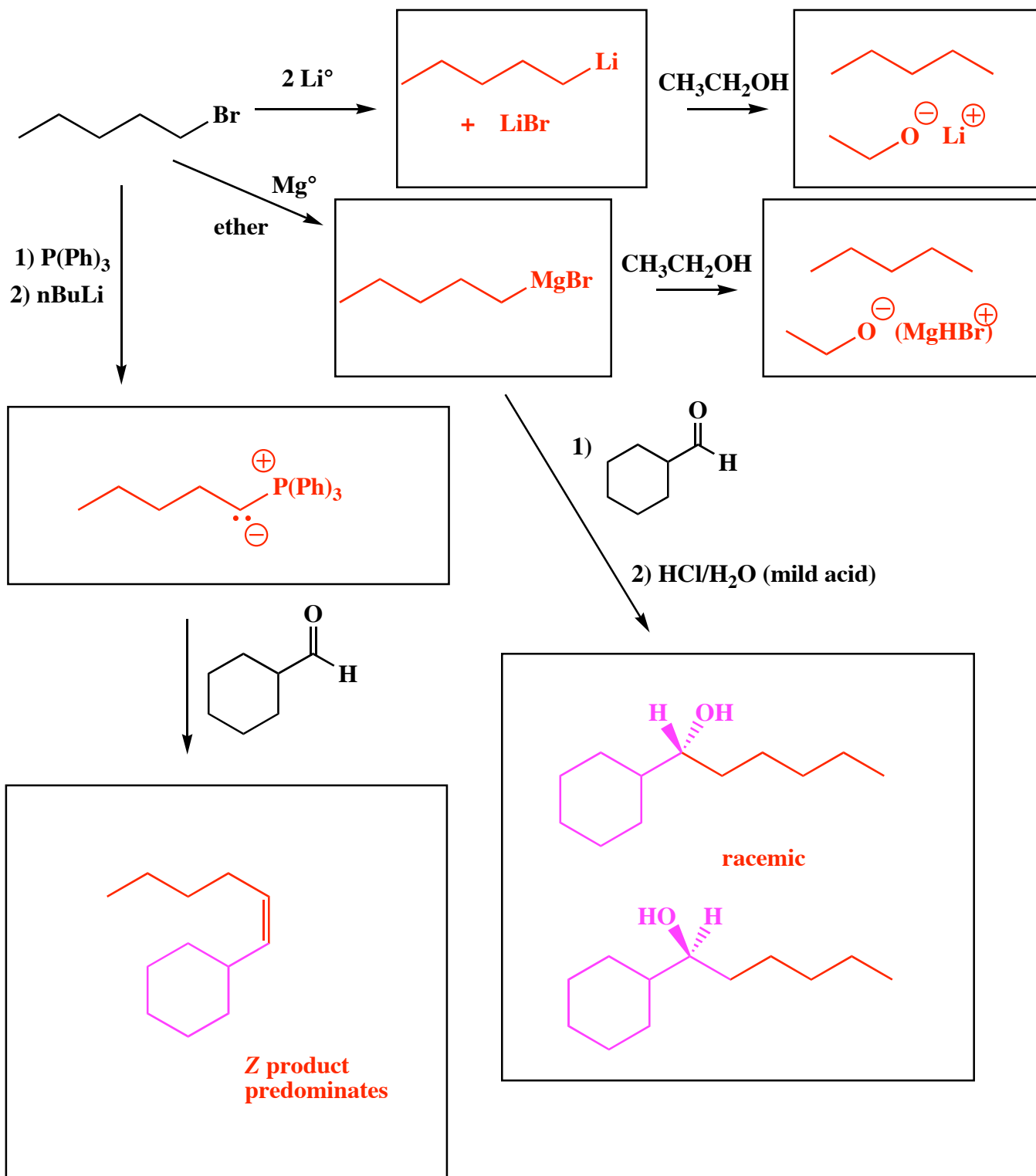


16. (35 pts.) Complete the mechanism for the following acetal formation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.

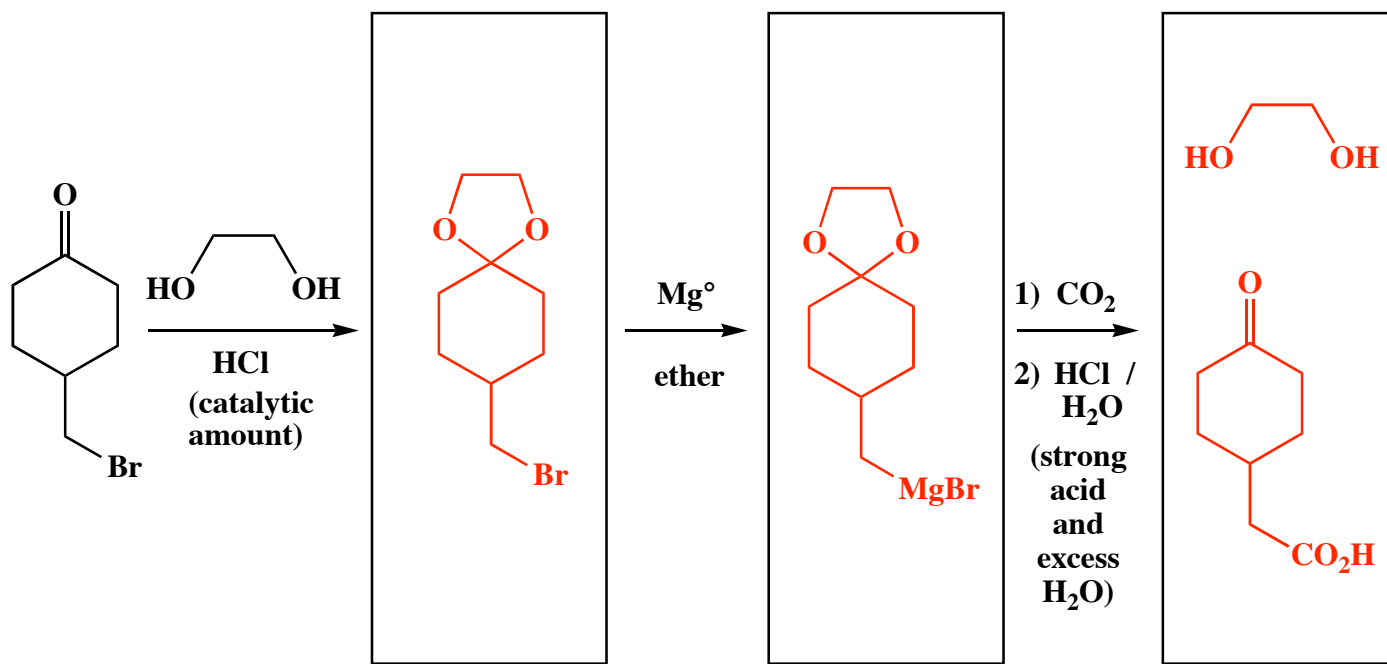
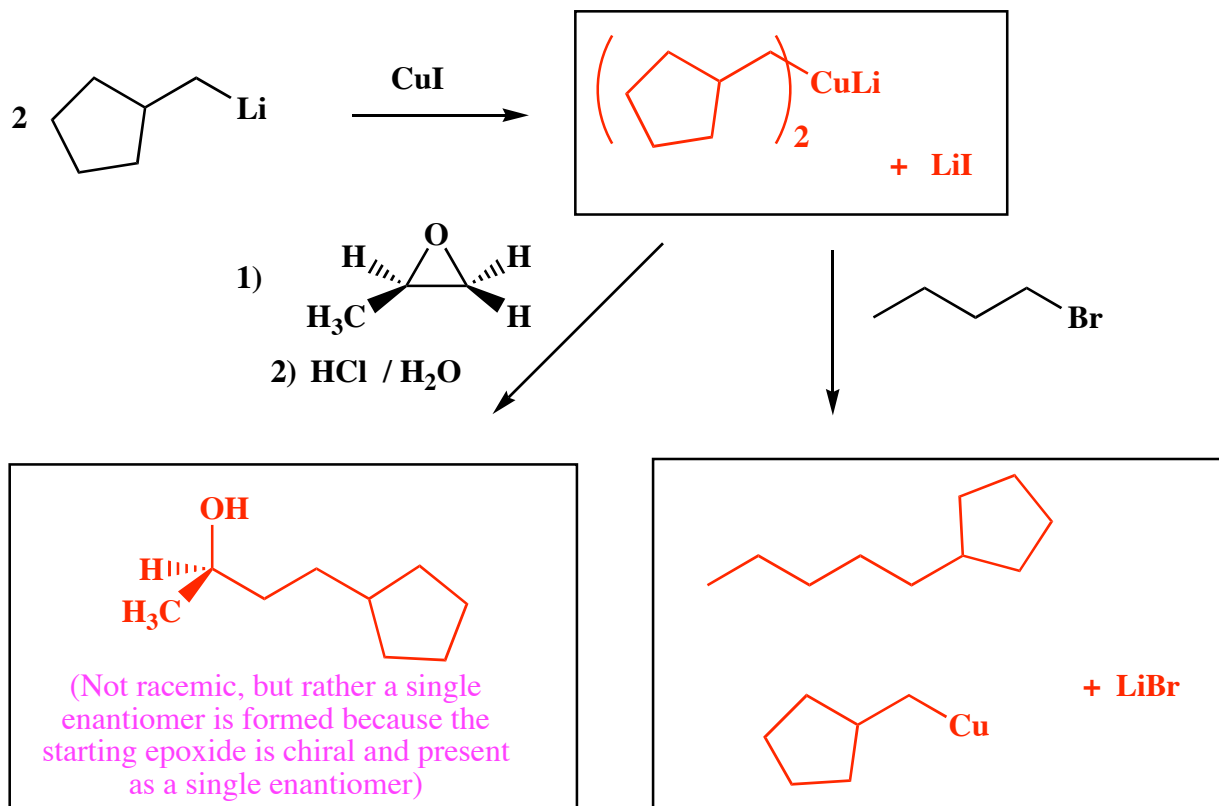
Acid Catalyzed Acetal Formation from a Ketone



17. (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.

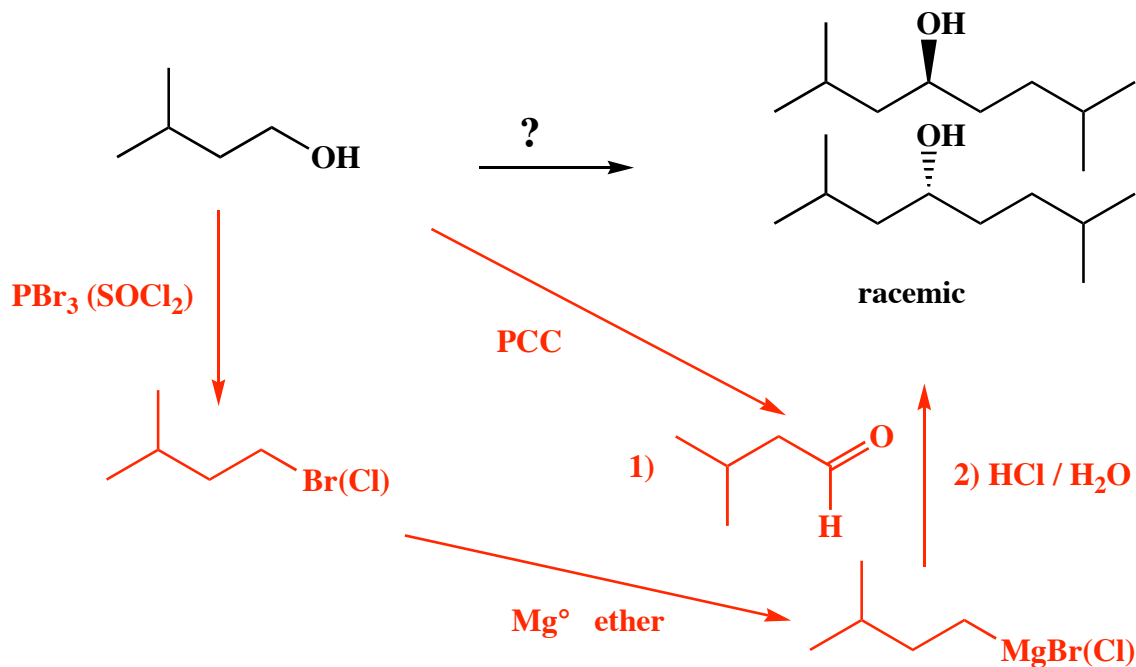


18. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes (\cdots) to indicate 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.



19. (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 put an asterisk (*) next to any new chiral center created along the way. You do NOT need to use wedges and dashes and you do NOT need to draw both enantiomers, just mark any new chiral center with an asterisk (*) AND write "racemic" if appropriate.

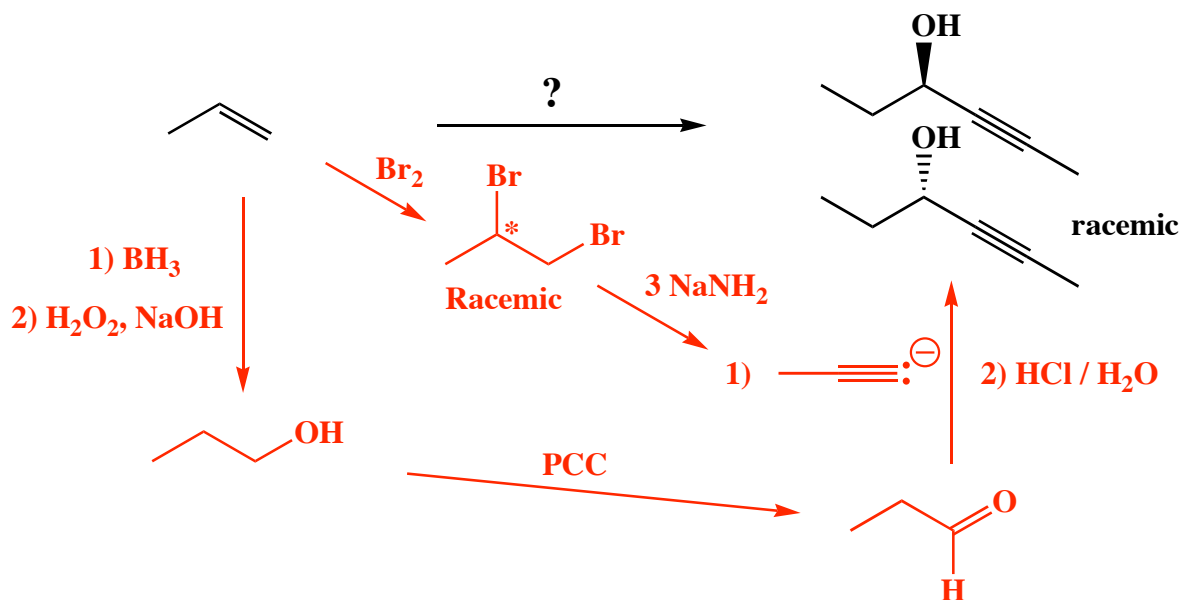
(10 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Recognize that the product has eight carbons, exactly twice that of the starting alcohol, so assume two molecules of starting material must be connected. **Recognize** also that the product is an alcohol with an OH group adjacent to the new C-C bond, the Key Recognition Element of a Grignard reaction. In this case, the reaction must be between butyraldehyde and the Grignard made from the 1-bromobutane. These, in turn, are made from a PCC reaction of the starting alcohol (to give the aldehyde) and the sequence of PBr_3 then Mg in ether, respectively. Note that it is perfectly acceptable to use SOCl_2 in place of PBr_3 , since chloro-Grignard reagents are suitable replacements for bromo-Grignards.

19. (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 put an asterisk (*) next to any new chiral center created along the way. You do NOT need to use wedges and dashes and you do NOT need to draw both enantiomers, just mark any new chiral center with an asterisk (*) AND write "racemic" if appropriate.

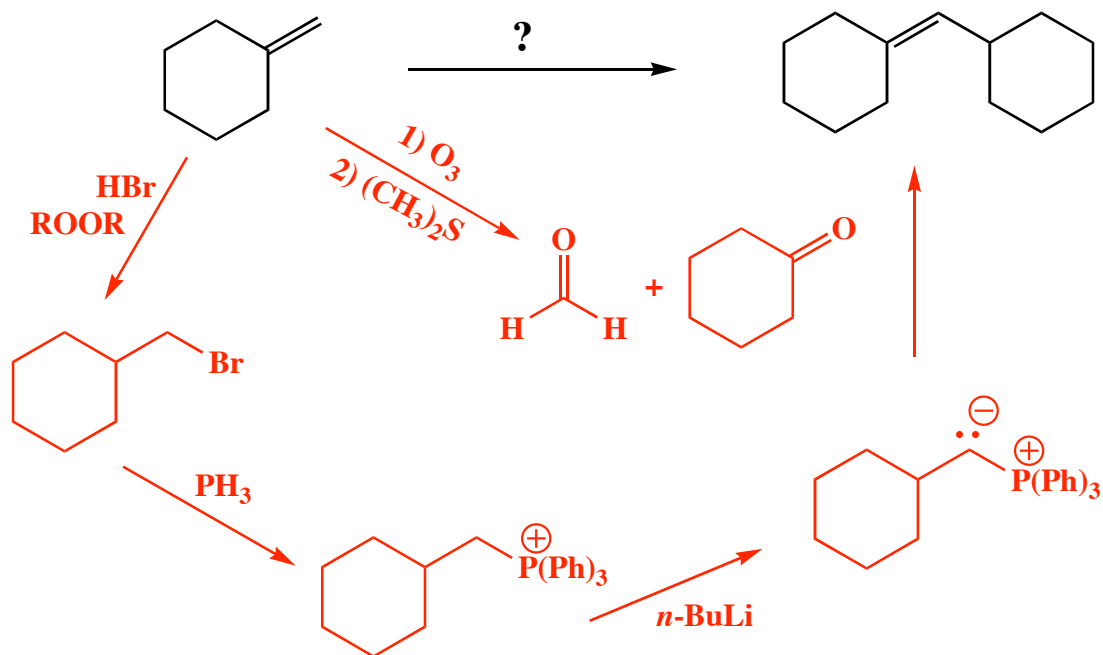
(13 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Recognize that the product has six carbons, exactly twice that of the starting alkene, so assume two molecules of starting material must be connected. **Recognize** also that the product is an alcohol with an OH group adjacent to the new C-C bond with an alkyne next to that, the Key Recognition Element of an alkyne anion reacting with an aldehyde. In this case, the reaction must be between propanal and the anion from the 1-propyne. These, in turn, are made from a PCC reaction of 1-propanol (to give the aldehyde). 1-Propanol comes from the non-Markovnikov hydroboration/oxidation reaction that places an -OH group on the less substituted side of the starting alkene. The sequence of Br₂ then three equivalents of NaNH₂, respectively, gives the 1-propyne.

19. (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 put an asterisk (*) next to any new chiral center created along the way. You do NOT need to use wedges and dashes and you do NOT need to draw both enantiomers, just mark any new chiral center with an asterisk (*) AND write "racemic" if appropriate.

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

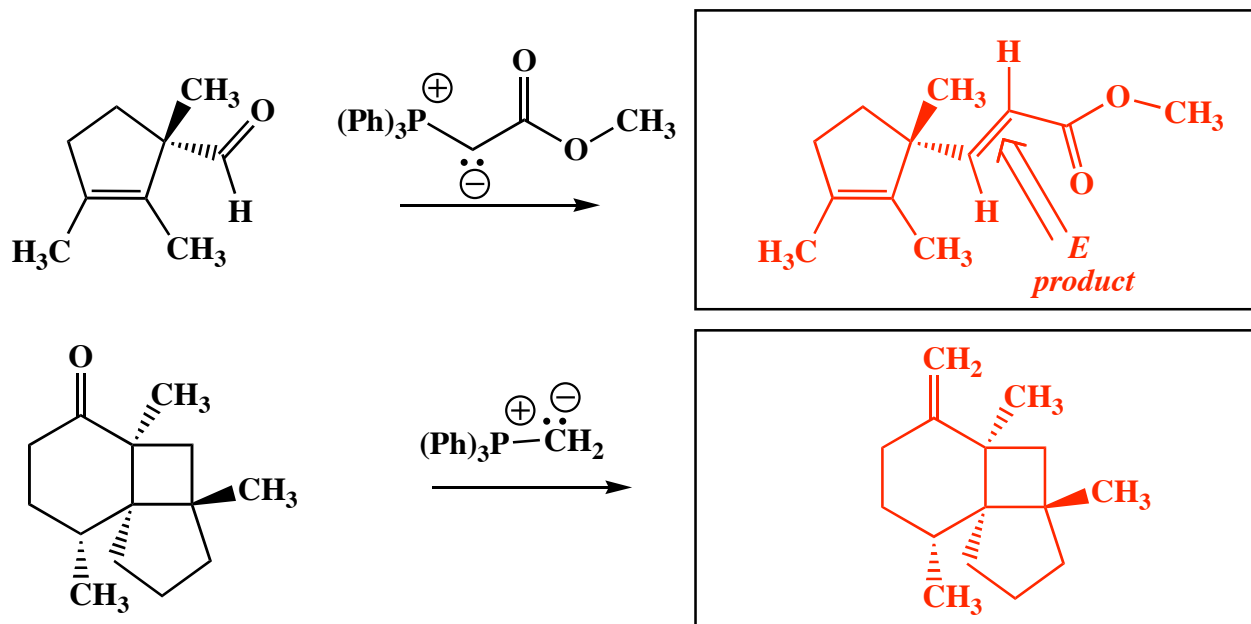


Recognize that the product has thirteen carbons, exactly twice that of the starting alkene **MINUS 1**, so assume two molecules of starting material must be connected, although **ONE** carbon must be removed (i.e. a seven carbon piece must react with a six carbon piece). **Recognize** also that the product has an alkene for a new C-C bond, the Key Recognition Element of a Wittig reaction. In this case, the reaction must be between cyclohexanone and the Wittig (phosphonium ylide) made from 1-bromomethylcyclohexane. Cyclohexanone, in turn, is made from ozonolysis of the starting alkene, and this nicely removes the single carbon atom as required. The bromomethylcyclohexane comes from reaction of the starting alkene with HBr in the presence of peroxides to give the non-Markovnikov addition regiochemistry resulting in the desired placement of -Br at the less substituted side of the alkene.

Note that it would also be possible to carry out the reverse Wittig reaction between the cyclohexyl aldehyde and a Wittig reagent made from bromocyclohexane.

SAVE THESE UNTIL THE END

20. (5 pts. each) A fundamental principle of organic chemistry is that functional groups react the same in complex molecules as they do in simple ones. The following two Wittig reactions use more complicated molecules than you are accustomed to seeing, but they react the same. Draw the product of each reaction, making sure to indicate stereochemistry with wedges and dashes.



21. (9 pts.) Here is an APPLY WHAT YOU KNOW QUESTION. You have not seen this before, but with a little information and your background in organic chemistry, we think you can figure it out. Here is what you do not know. Sulfonium ylides can be formed that are analogous to phosphonium ylides (Wittig reagents). However, the sulfonium ylides react with carbonyl compounds to give epoxides. For the following reaction (which you have never seen) predict the intermediate and flow of electrons that leads to the epoxide product. **Draw arrows that indicate the flow of all electrons, and be sure to show all lone pairs and formal charges in your intermediate and put an asterisk "*" next to any new chiral center created.**

