NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
1st Midterm
Feb. 13, 2014

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.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points	
1		(14)
2		(19)
3		(15)
4		(5)
5		(5)
6		(5)
7		(24)
8		(17)
9		(18)
10		(20)
11		(14)
12		(23)
13		(10)
14		(19)
15		(13)
16		(16)
17		(12)
Total		(249)

Student Honor Code

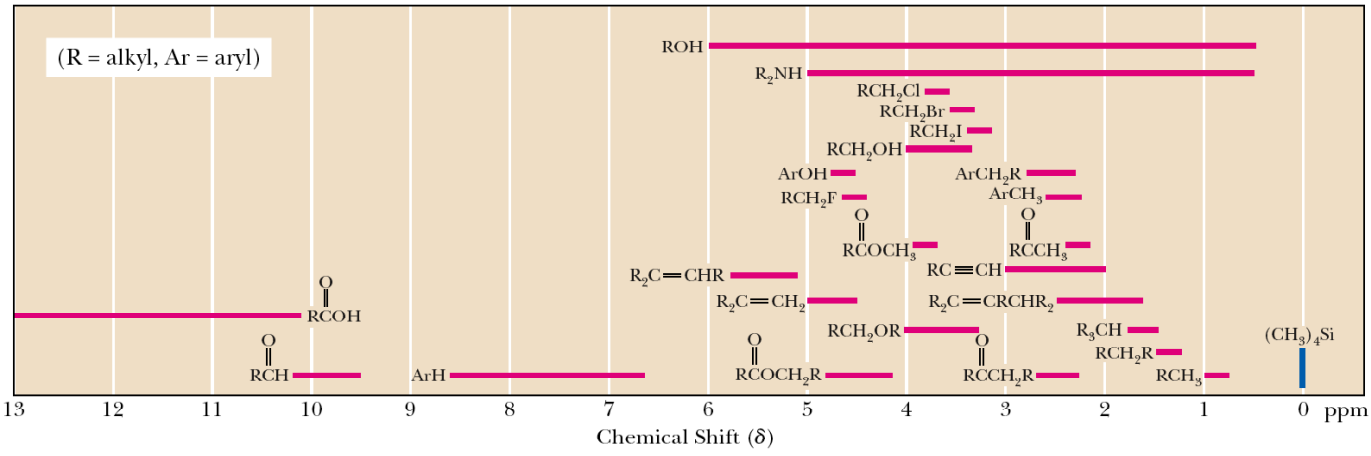
"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

_____

(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
		RCH_2OH	3.4-4.0
R_2NH	0.5-5.0	RCH_2Br	3.4-3.6
ROH	0.5-6.0	RCH_2Cl	3.6-3.8
RCH_3	0.8-1.0	$RCOCH_3$	3.7-3.9
RCH_2R	1.2-1.4	$RCOCH_2R$	4.1-4.7
R_3CH	1.4-1.7	RCH_2F	4.4-4.5
$R_2C{=}CRCHR_2$	1.6-2.6	$ArOH$	4.5-4.7
$RC{\equiv}CH$	2.0-3.0	$R_2C{=}CH_2$	4.6-5.0
$RCCH_3$	2.1-2.3	$R_2C{=}CHR$	5.0-5.7
$RCCH_2R$	2.2-2.6	$H_2C{-}CH_2$	3.3-4.0
$ArCH_3$	2.2-2.5	RCH	9.5-10.1
RCH_2NR_2	2.3-2.8	$RCOH$	10-13
RCH_2I	3.1-3.3		
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. (1 pt each) Circle all the statements that are true. In other words, do not circle the statements that are false.

A. Moving charge generates a magnetic field, and a moving magnetic field causes charges to move.

B. Atomic nuclei have a quantum mechanical property of "spin" that can be thought of as a small magnetic field around the nucleus created as if the positive charge of the nucleus were circulating.

C. We care about the nuclei ^{1}H and ^{13}C since these are commonly found in organic molecules and they have spin quantum numbers of 3/2.

D. Electromagnetic radiation of enough or more than enough energy can be absorbed by a nucleus and excite it from the lower energy +1/2 spin state to the higher energy -1/2 spin state, a process referred to as resonance.

E. Electromagnetic radiation of only the exactly right amount of energy can be absorbed by a nucleus and excite it from the lower energy +1/2 spin state to the higher energy -1/2 spin state, a process referred to as resonance.

F. The distance between peaks in a split signal is called chemical shift.

G. Different hydrogen atoms in a molecule take different amounts of energy to flip their spins, and the different energies can be correlated to structure of the molecule.

H. The distance between a signal and the standard TMS is called coupling constant.

I. For alkyl groups with freely rotating C-C bonds, splitting by n adjacent H atoms will give n+1 peaks.

J. For H atoms on the C atoms of three-membered rings or on the sp^2 hybridized C atoms of alkenes, splitting by n adjacent H atoms will always give (n x n)+1 peaks.

K. The signal for a CH_2 group next to a chiral center will never be split, it will be a singlet.

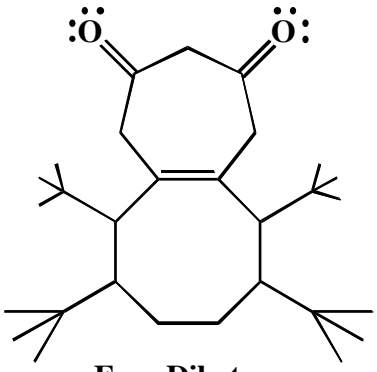
L. All geminal H atoms split each other, giving rise to double peaks with large chemical shifts.

M. The H atoms of relatively acidic functional groups (alcohols, carboxylic acids, amines) exchange rapidly, so they often do not split the signals of adjacent hydrogens.

N. NMR stands for No More Regrets, time to develop a plan for lifelong physical fitness.

2. (cont.) (1 pt each)

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 is 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.



Frog Diketone

This is not part of a question. This little molecule creature is simply supposed to make you smile!

3. (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 wil be looking for a minumum of 7 key points here.

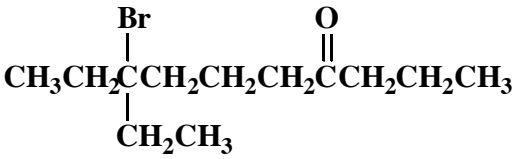
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field 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**.

4. (3 pts) The most important question in organic chemistry is:

Where are the electrons?

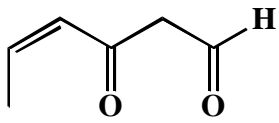
5. (3 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



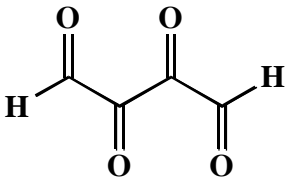
8-Bromo-8-ethyl-4-decanone

B.



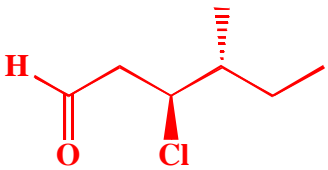
(*Z*)-3-oxo-4-hexenal

C.

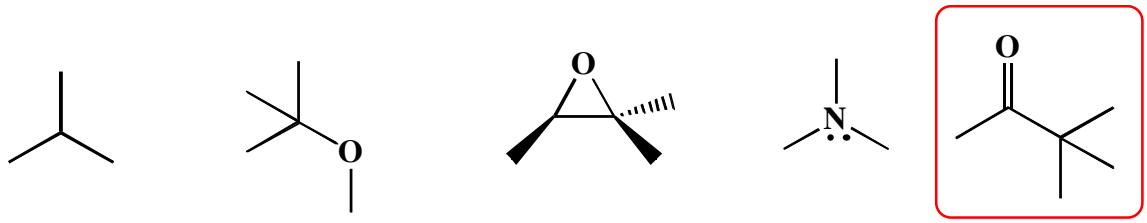


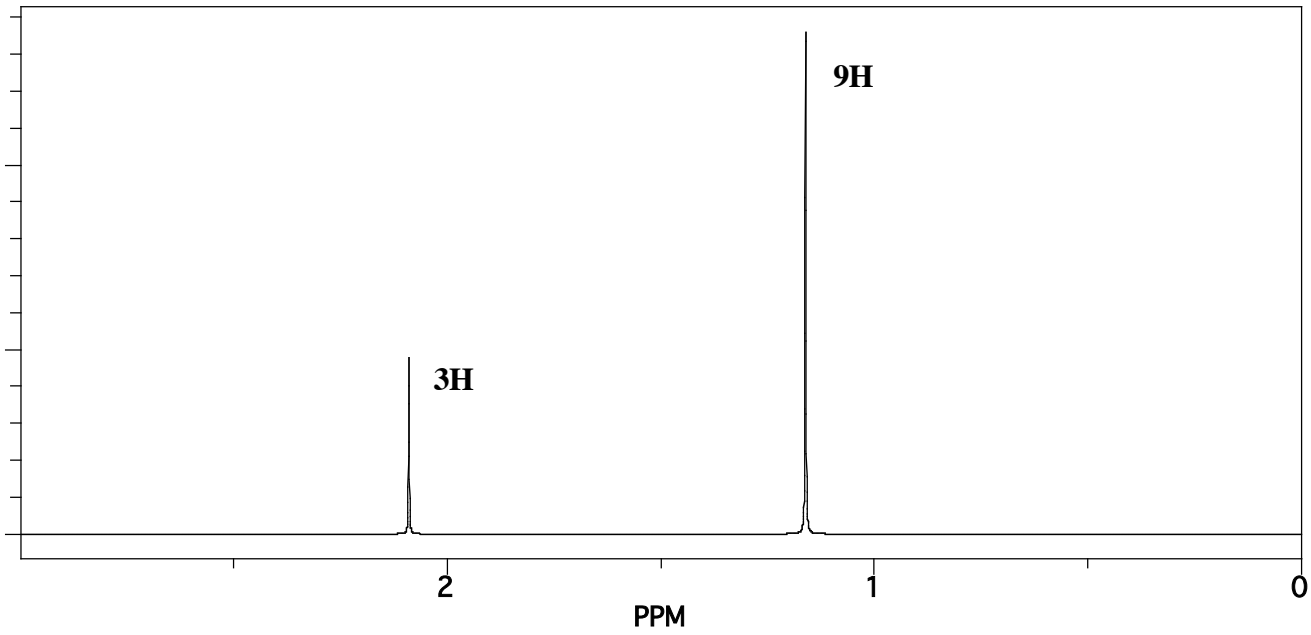
2,3-Dioxobutanedial (2,3-Dioxosuccinaldehyde)

D. (3*S*,4*R*)-3-chloro-4-methylhexanal

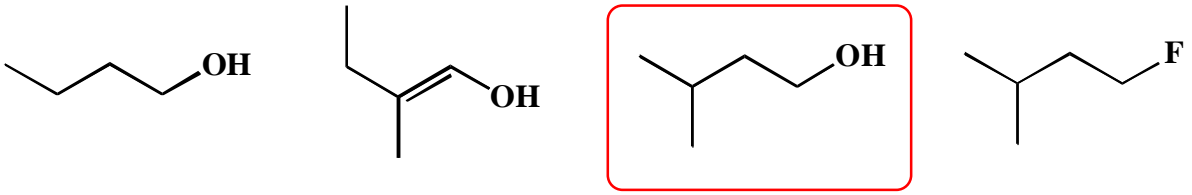


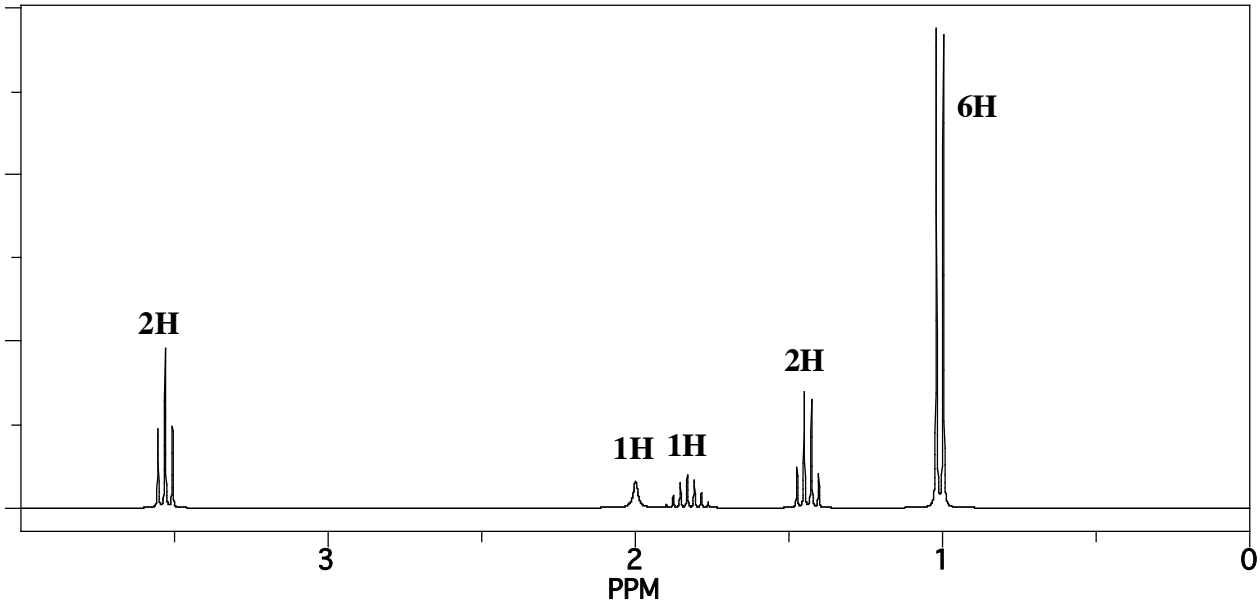
6. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



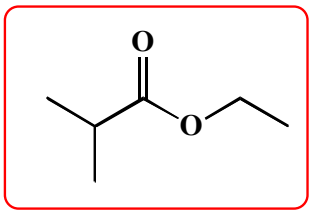


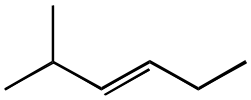
7. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.

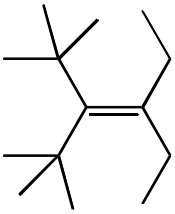


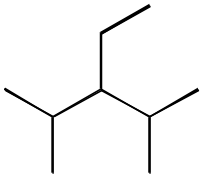


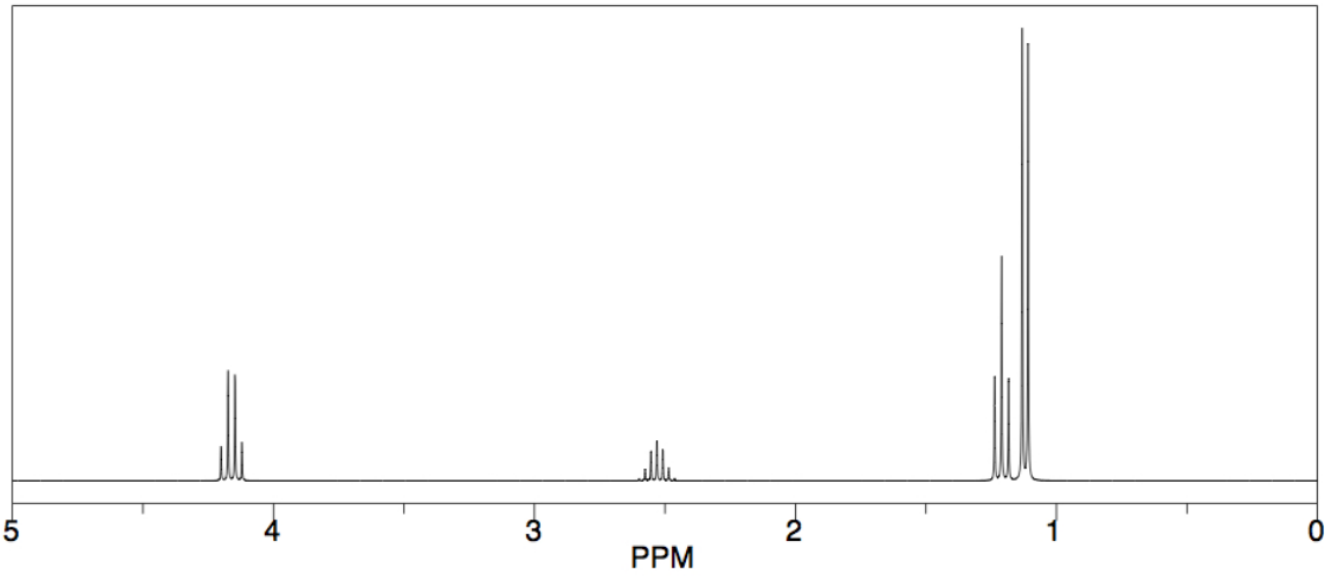
8. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



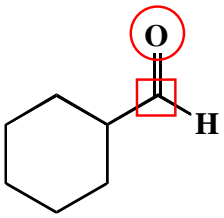




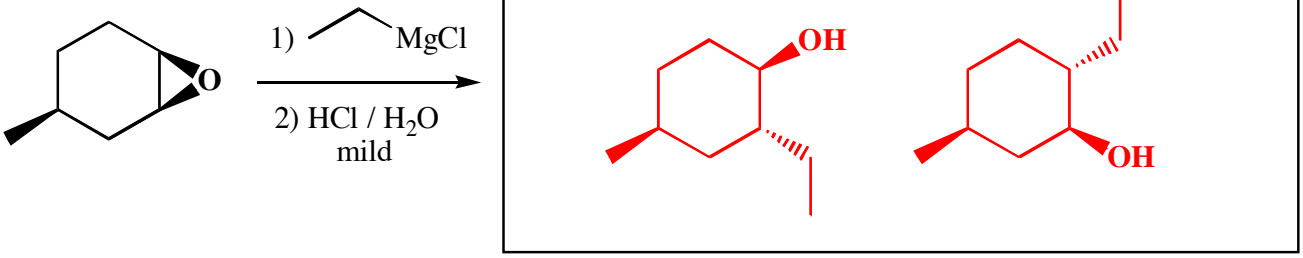




9. (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.

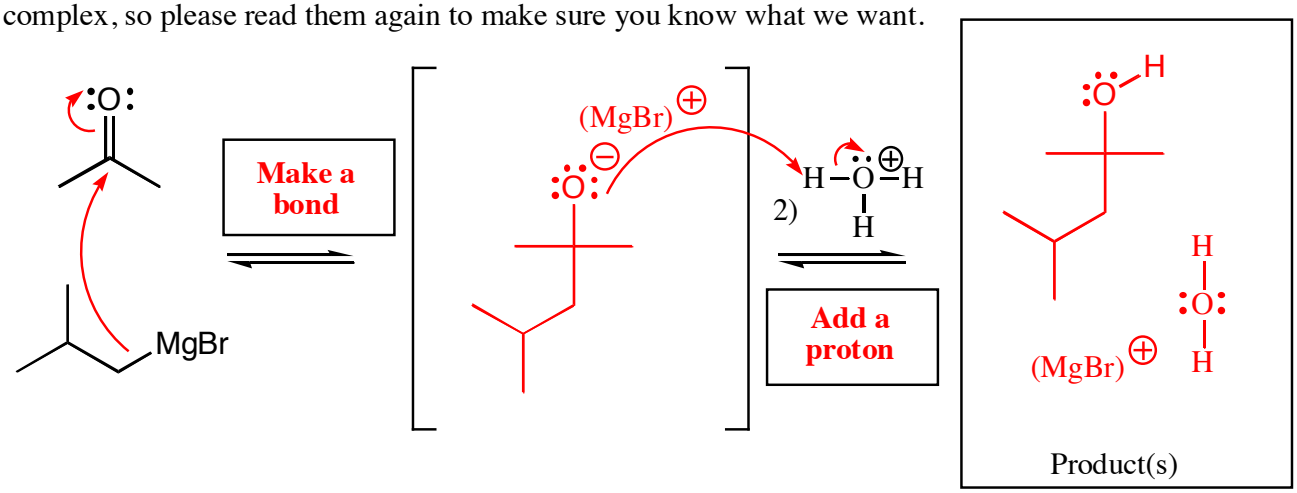


10. (8 pts) Stereochemistry is one of the most important concepts of organic chemistry. Using your knowledge of the reaction mechanism, draw the stereoisomers produced in the following Grignard reaction.



NOTICE THIS ⟹ **Are the products you drew a racemic mixture of enantiomers?** No

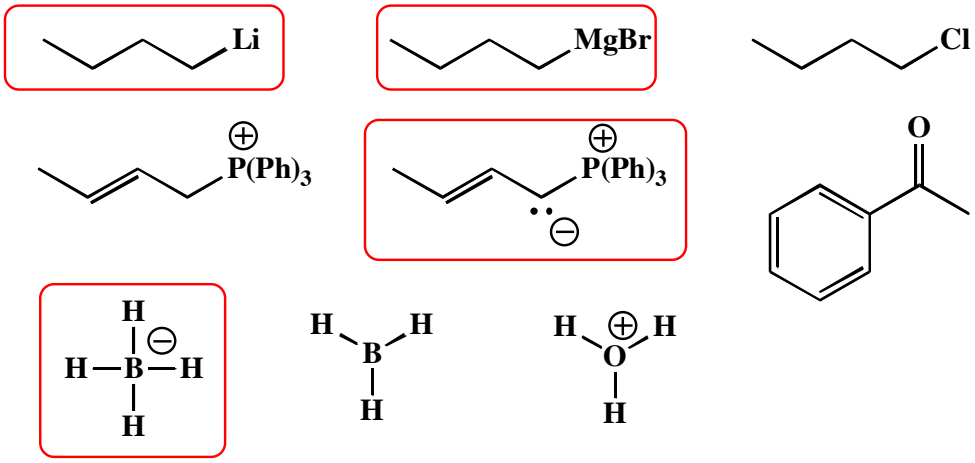
11. (12 pts. total) Complete the mechanism for the following Grignard reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, 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.



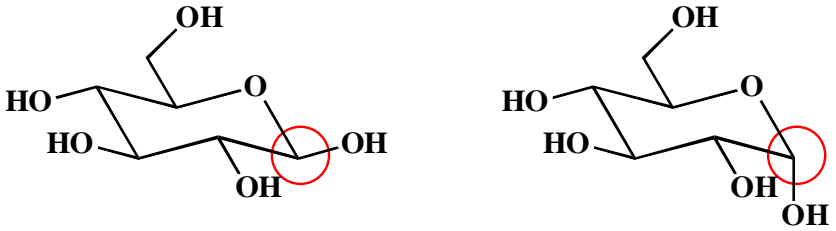
2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

⇑
NOTICE THIS

12. (9 pts) From the list below, circle all the molecules that would be considered nucleophiles in reactions we have seen. Some of them might also be bases, but do not worry about that for this question.



13. (4 pts) Shown below are the two forms of D-glucose that are most commonly found in biological systems. **Draw a circle around the anomeric carbon atom on each structure.** Then answer the questions below the structures.



Circle the correct statement:

The structure on the left represents the α form of D-glucose, the structure on the right represents the β form of D-glucose.

The structure on the left represents the δ form of D-glucose, the structure on the right represents the γ form of D-glucose.

The structure on the left represents the β form of D-glucose, the structure on the right represents the α form of D-glucose.

Circle the correct statement:

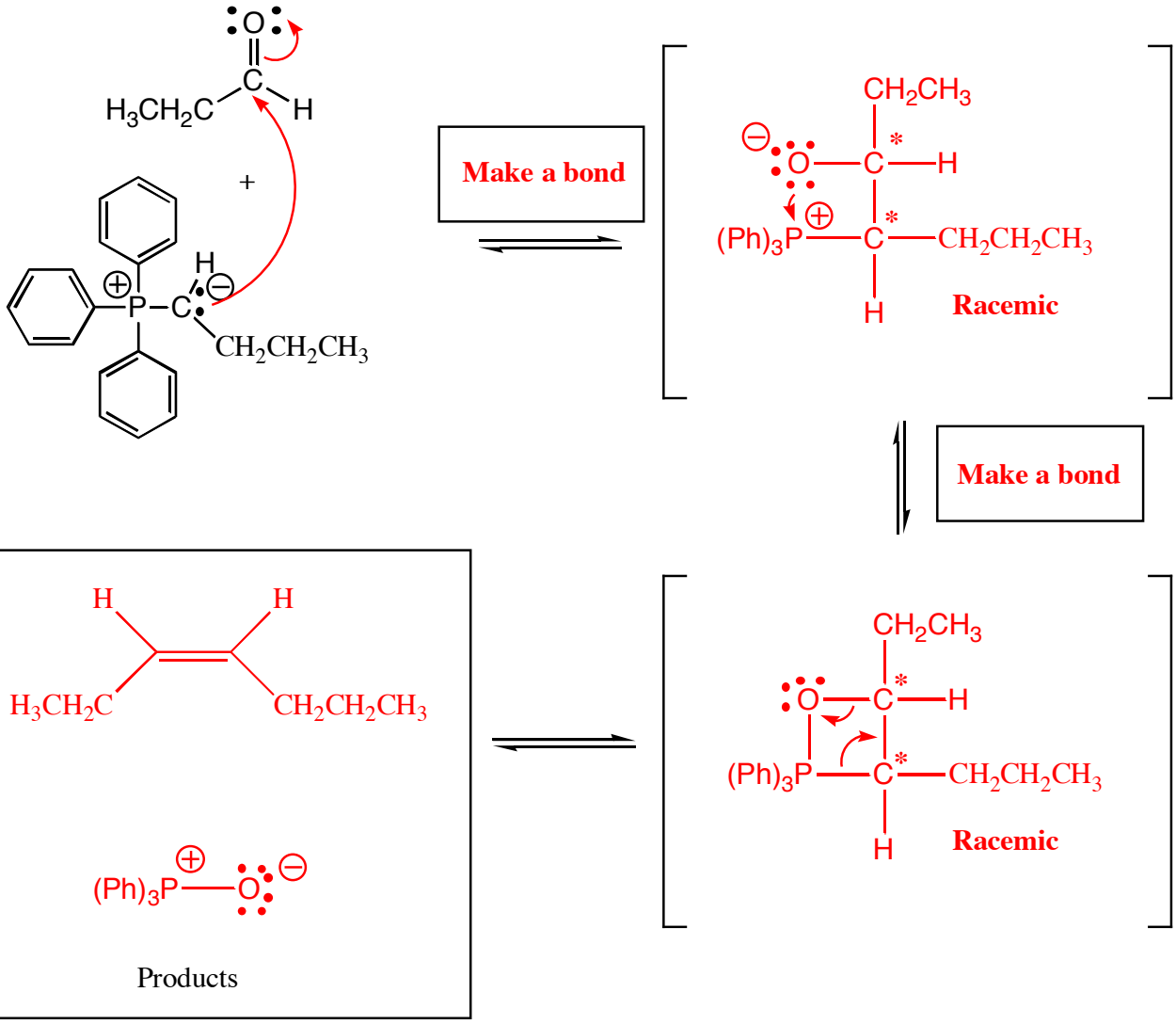
The above structures are examples of cyclic acetals.

The above structures are examples of cyclic hemiacetals.

The above structures are examples of cyclic hemispheres.

The above structures are examples of psychic acetals.

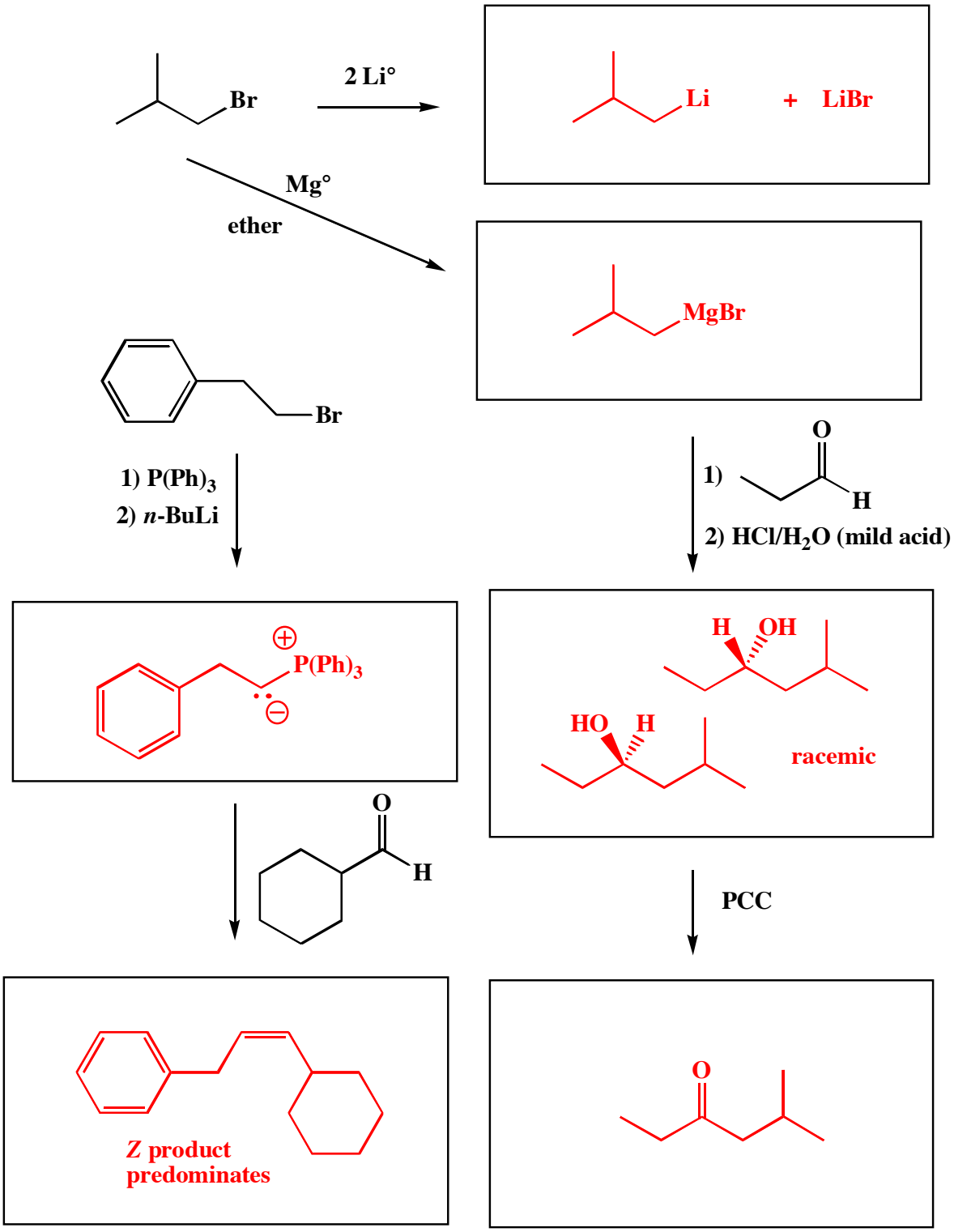
14. (18 pts. total) Complete the mechanism for the following Wittig reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A RACEMIC MIXTURE IS CREATED IN AN INTERMEDIATE, MARK ALL CHIRAL CENTERS WITH AN ASTERISK AND WRITE RACEMIC. IF A RACEMIC MIXTURE IS CREATED IN THE FINAL PRODUCTS, YOU NEED TO DRAW BOTH ENANTIONMERS, AND WRITE RACEMIC.** I realize these directions are complex, so please read them again to make sure you know what we want.



2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

NOTICE THIS

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 (◄) and dashes (····ıı) 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.**



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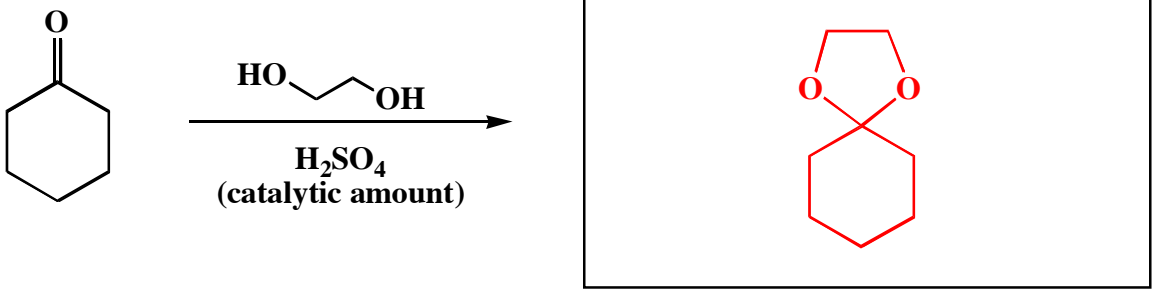

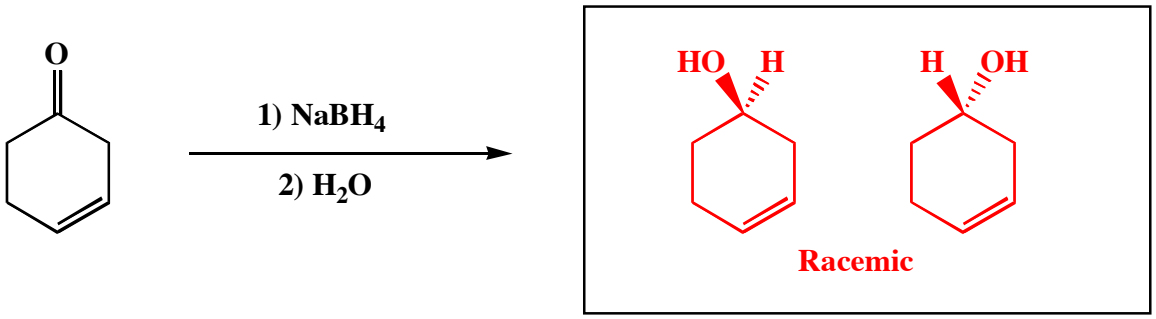

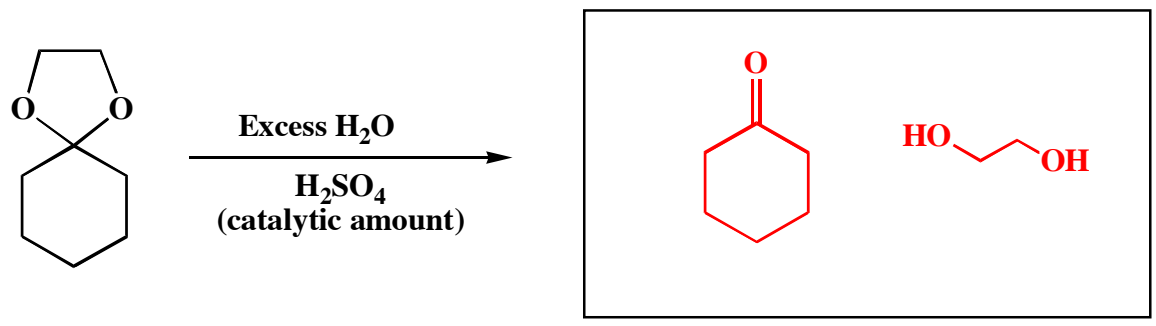

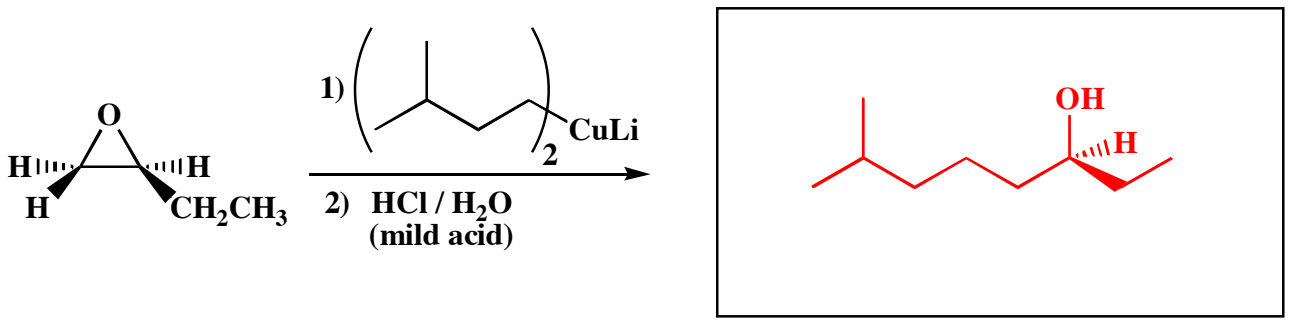

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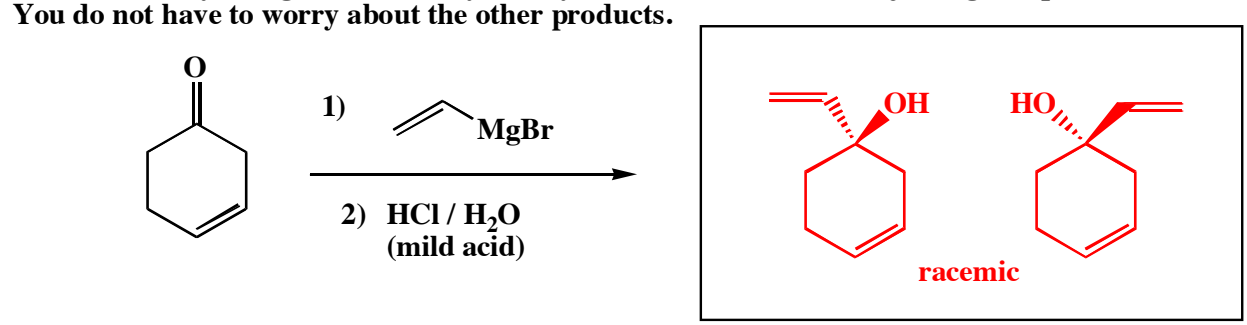
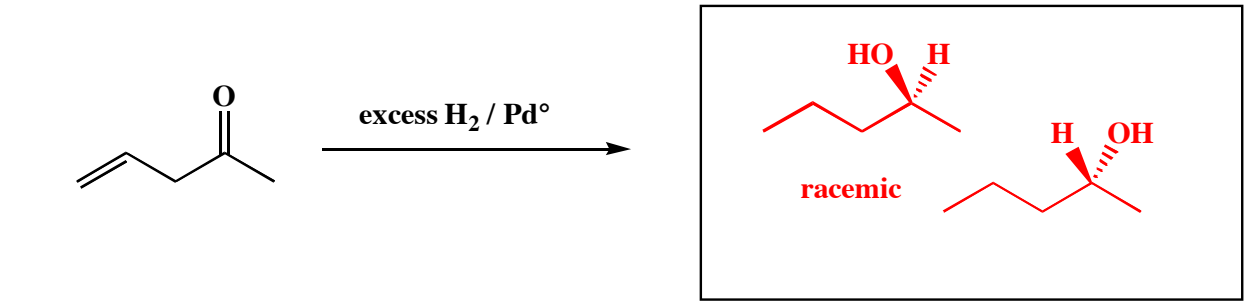
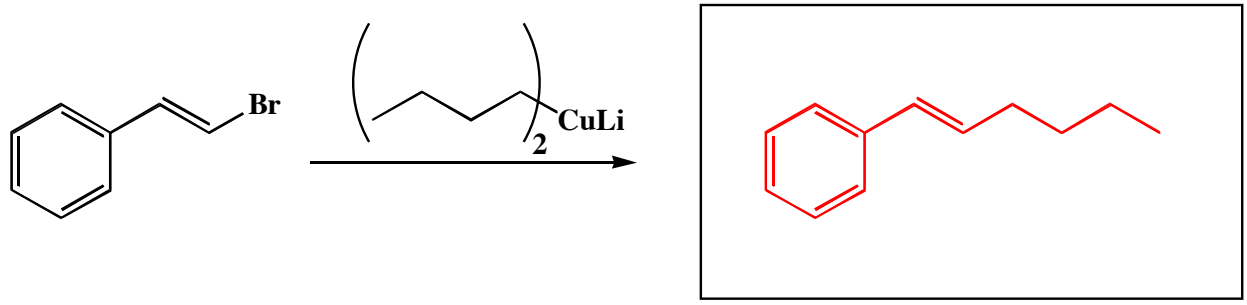
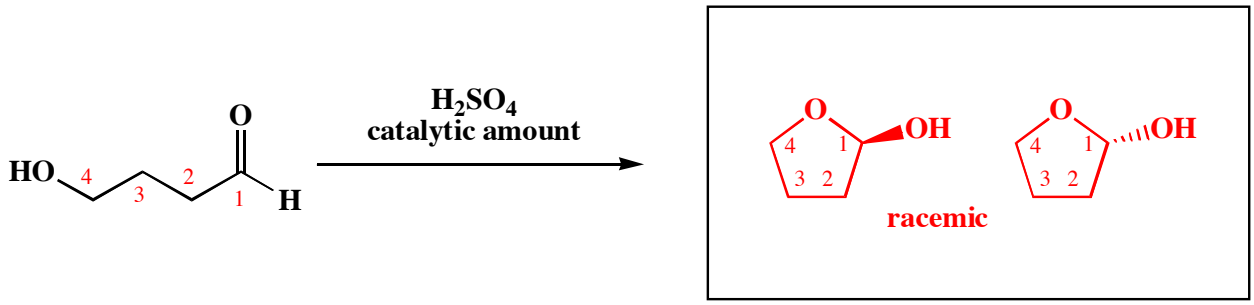
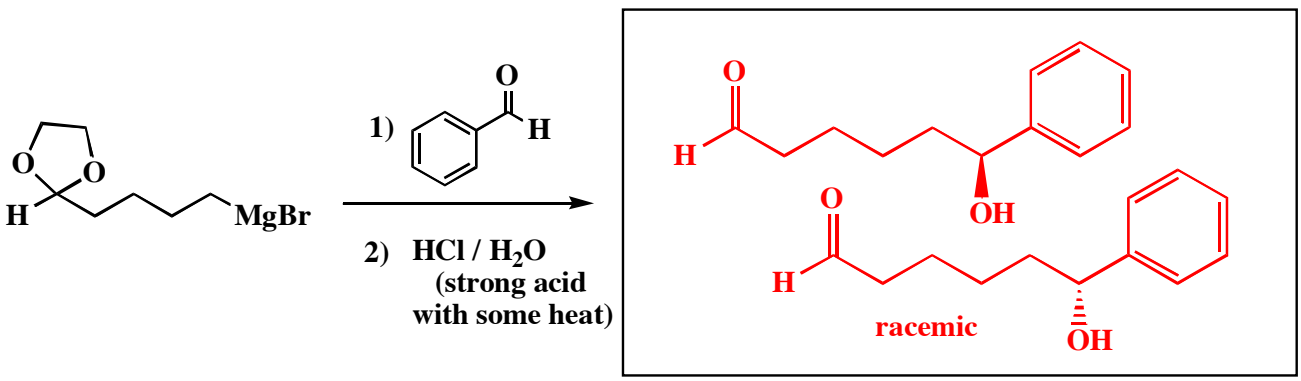




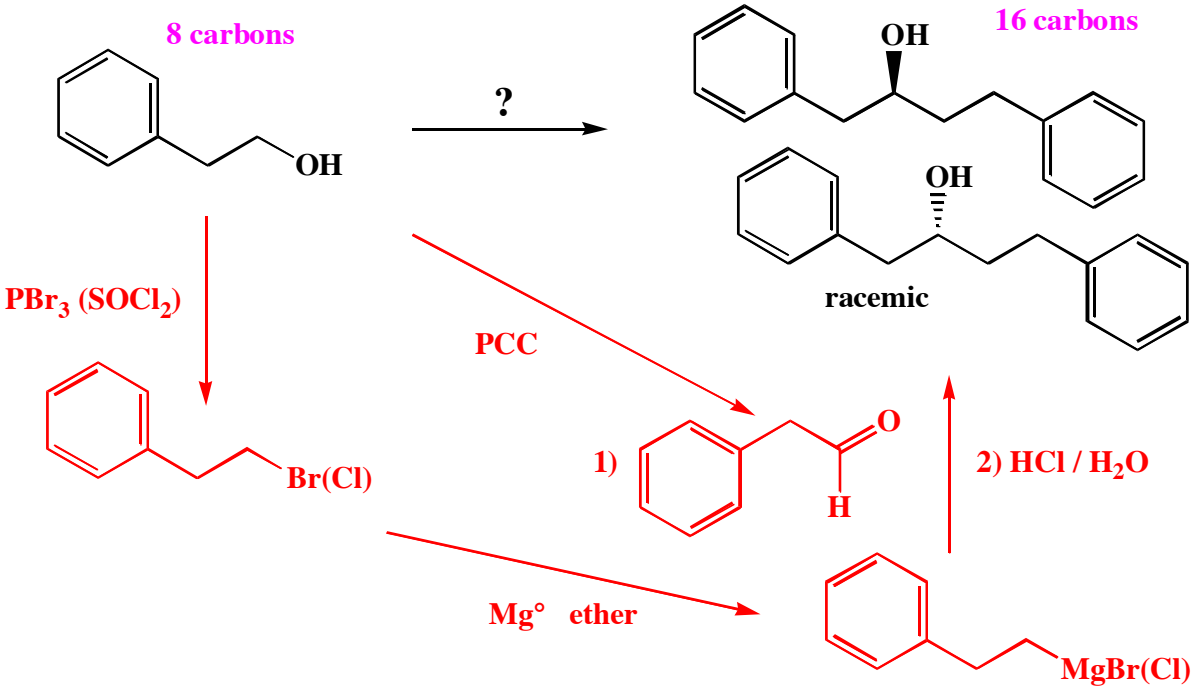






16. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

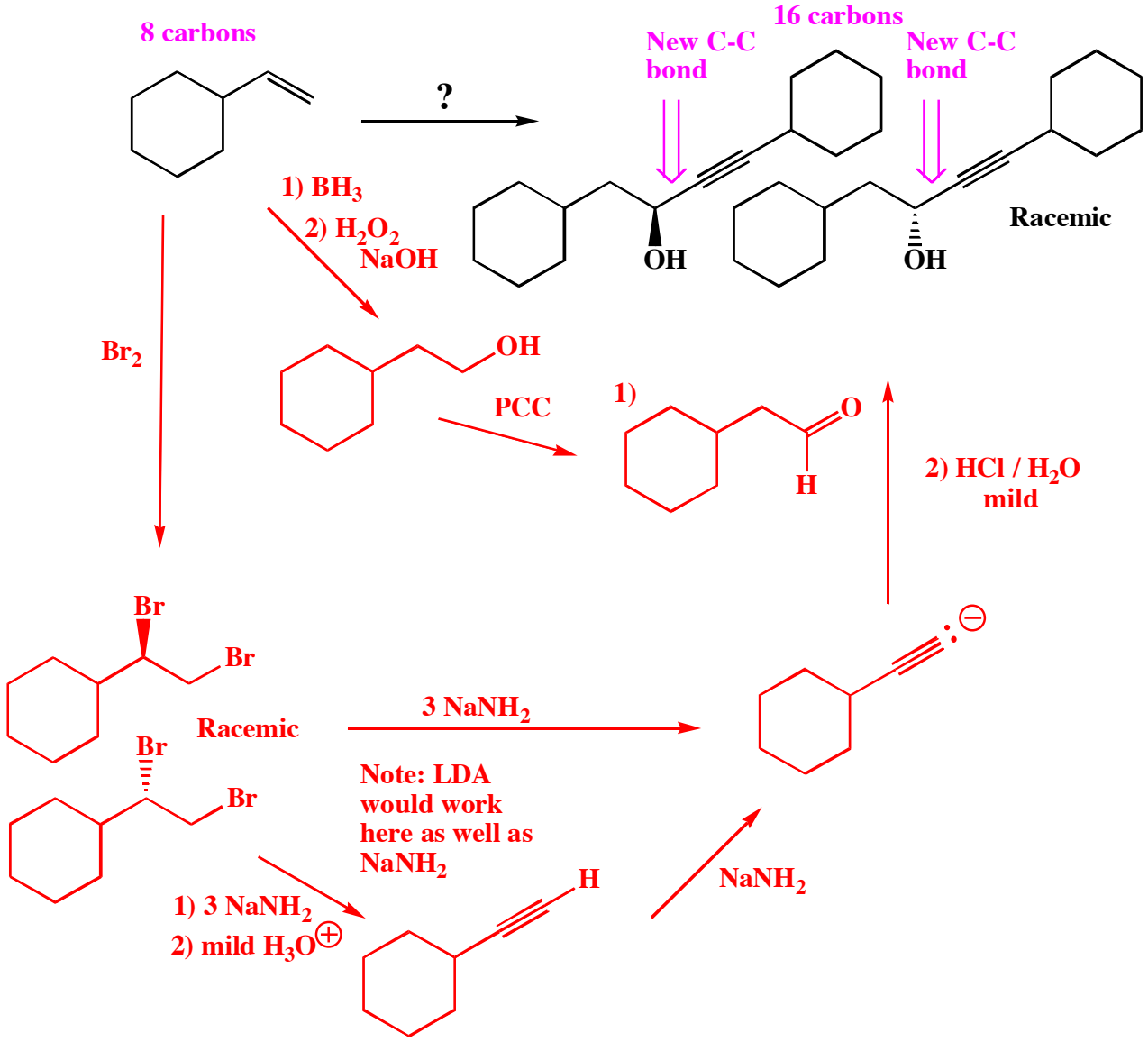
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize that the product has eight carbons, exactly twice that of the starting alcohol, so assume to 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 betweeen 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.

16. 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 you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

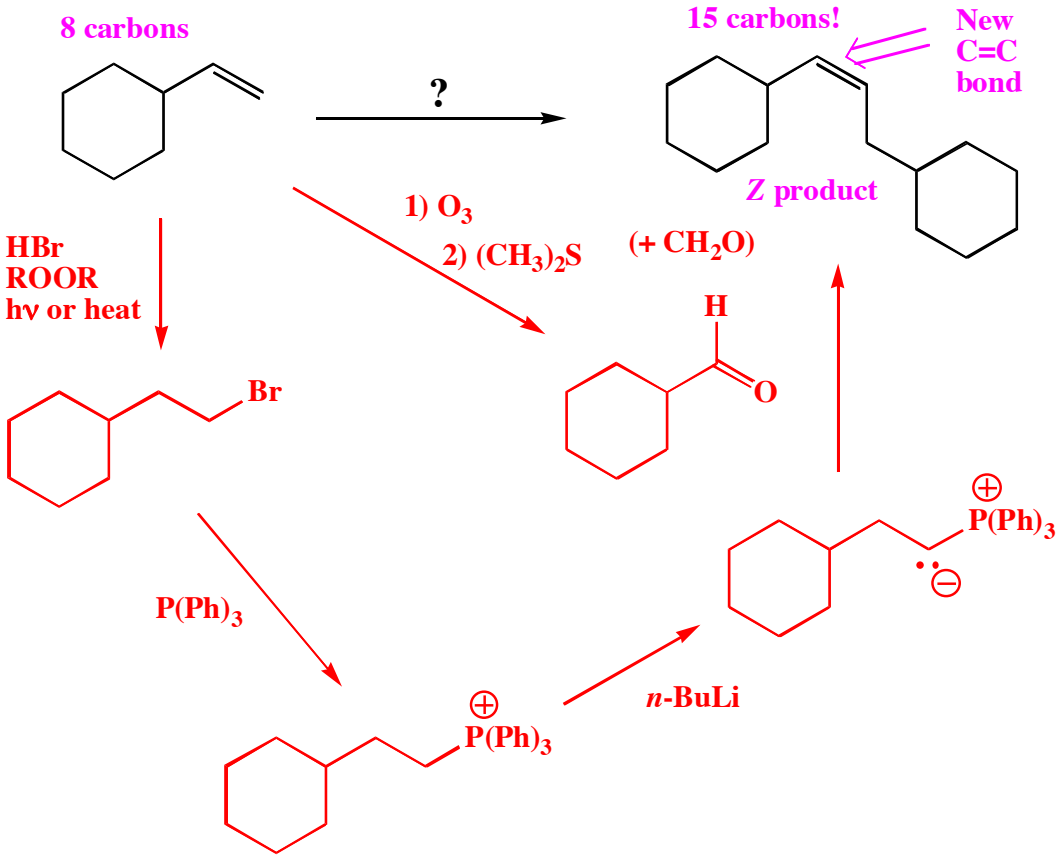
(19 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize the product as the KRE of the reaction of an aldehyde with an alkyne, with the new C-C bonnd as shown by the arrow. **Recognize further** that the required aldehyde can be made from the starting alkene in two steps: non-Markovnikov addition of an OH group via hyroboration-oxidation followed by PCC. **Recognize** that the required alkyne cam be made from the starting alkene by cruising right up "I-35" of the semester 1 roadmap, namely addition of halogen followed by reaction with strong base. Note that three equivalents of strong base are required because a terminal alkyne is the product. You can choose to protonate or not after the double elimination, both are OK.

16. 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 you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

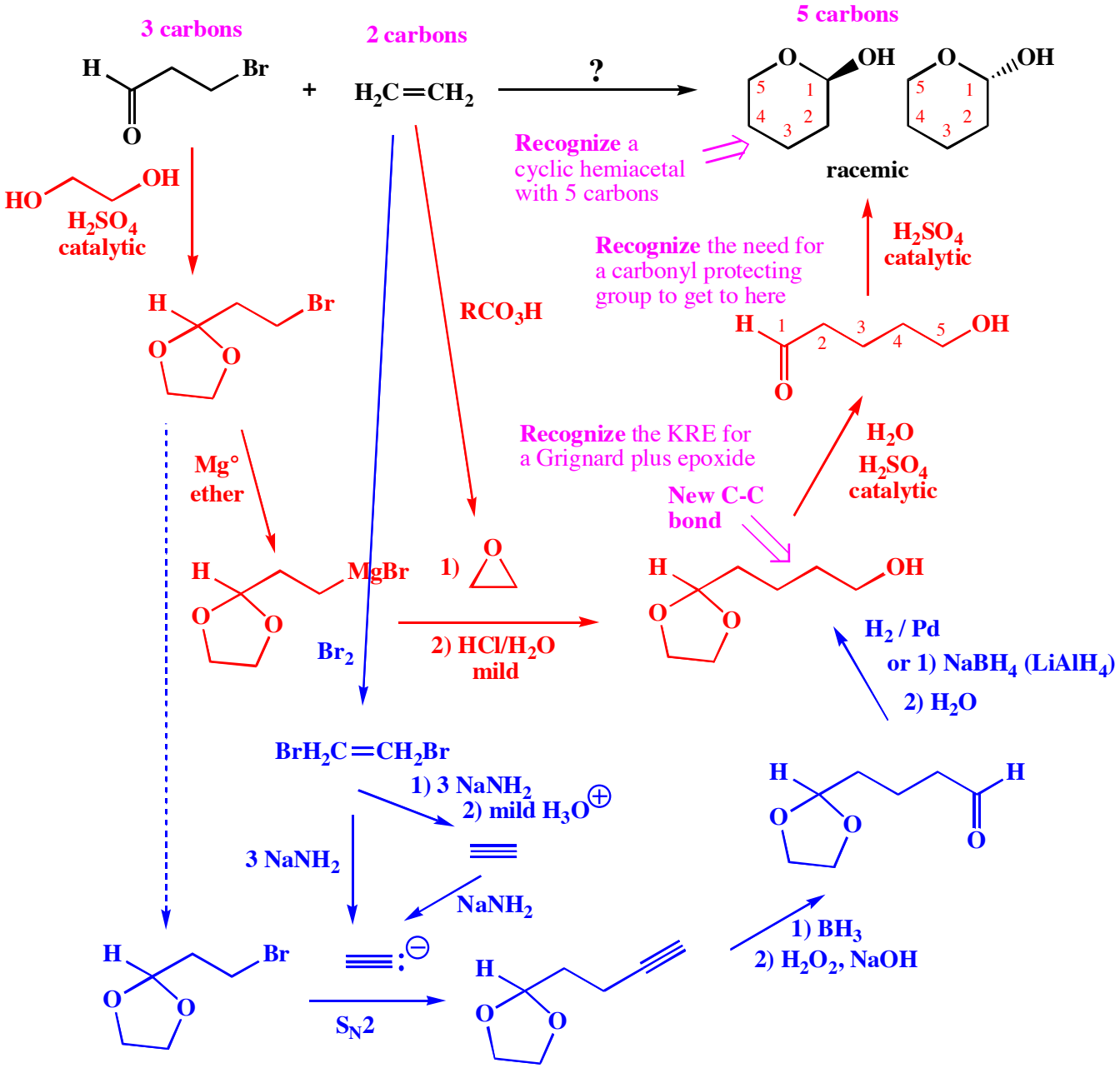
(13 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



The key to this problem is recognizing that there are 8 carbons in the starting alkene, but only 15 in the product. That means one needs to be taken away before the final step. **Recognize further** that the product is a *Z* alkene with a new C=C bond, the KRE of a Wittig reaction. Make the required Wittig reagent from a combination of non-Markovikov addition of HBr to the starting alkene by using peroxide in the presence of light or heat followed by the usual two step sequence of $P(Ph)_3$ and *n*-BuLi. **Recognize further** that you can make the one-carbon shorter aldehyde from the starting alkene though ozonlysis. Note that formaldehyde is also made in this step, but we do not need it.

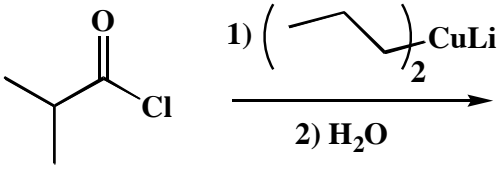
16. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

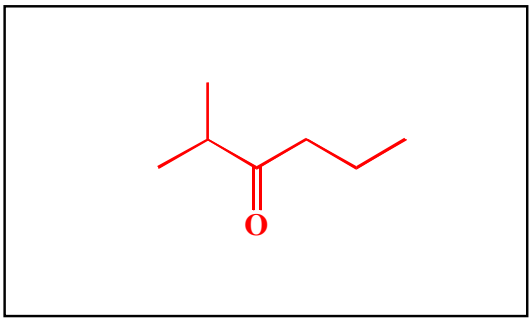
(16 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**

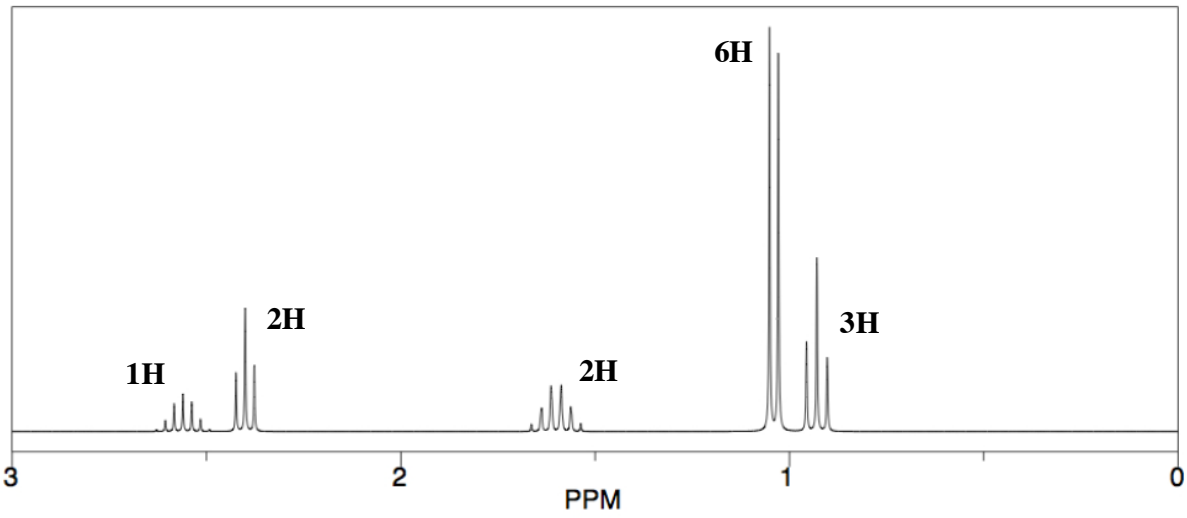


You can get to the product using alkyne chemistry from last semester, but it will take you several more steps.

17. (5 pts) You have not seen the following reaction before, it comes from chapter 18. The NMR spectrum is of the predominant product. Using your grwoing intuition about chemical reactivity as well as the NMR, draw the structure of the product of this reaction.







18. (7 pts) Reactions in context: Following is a Wittig reaction used in the published synthesis of a pharmaceutical candidate. Draw the product of the reaction