

NAME (Print): \_\_\_\_\_

Chemistry 320N  
Dr. Brent Iverson  
1st Midterm  
Feb. 19, 2015

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.

**You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK or red 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 INCIDENTS 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
<b>1</b>	<b>(20)</b>
<b>2</b>	<b>(11)</b>
<b>3</b>	<b>(5)</b>
<b>4</b>	<b>(5)</b>
<b>5</b>	<b>(5)</b>
<b>6</b>	<b>(12)</b>
<b>7</b>	<b>(12)</b>
<b>8</b>	<b>(16)</b>
<b>9</b>	<b>(19)</b>
<b>10</b>	<b>(26)</b>
<b>11</b>	<b>(15)</b>
<b>12</b>	<b>(16)</b>
<b>13</b>	<b>(15)</b>
<b>14</b>	<b>(10)</b>
<b>15</b>	<b>(13)</b>
<b>16</b>	<b>(16)</b>
<b>17</b>	<b>(13)</b>
<b>18</b>	<b>(17)</b>
<b>Total</b>	<b>(246)</b>

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## **Student Honor Code**

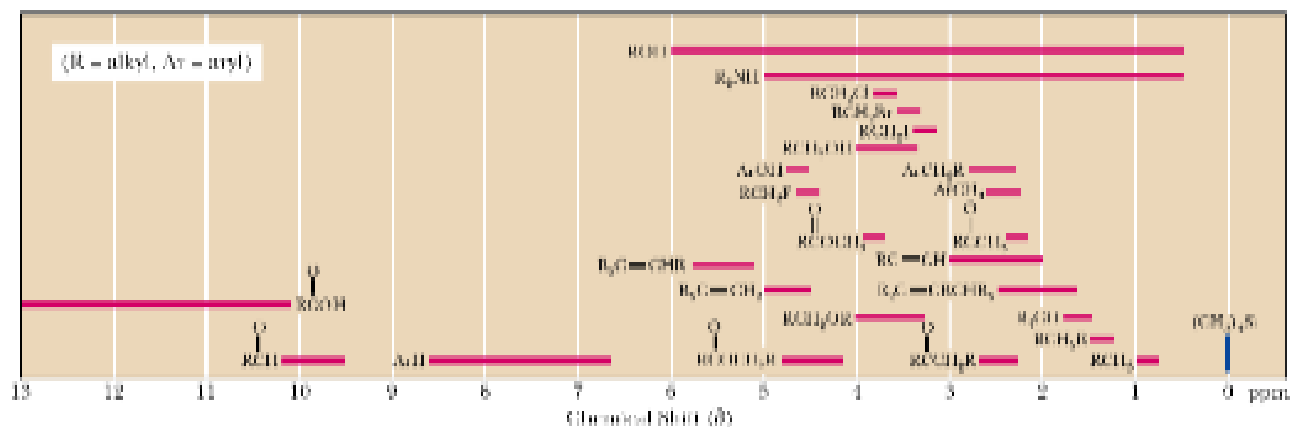
**“As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity.”**

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(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ ) <sup>a</sup>	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ ) <sup>a</sup>
$R_2NH$	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
$\begin{array}{c} O \\    \\ RCOCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\    \\ RCOCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ / \backslash \\ H_2C \quad CH_2 \end{array}$	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		

<sup>a</sup> Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



1. (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.

2. (1 pt. each) Suppose you place a sample of a molecule in a very strong laboratory magnetic field. Circle the following statements that are true:

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

A  $^1\text{H}$  nucleus surrounded by greater electron density feels a stronger net magnetic field (external magnetic field plus the induced magnetic field from the circulating electron density) compared to a  $^1\text{H}$  nucleus surrounded by less electron density.

A  $^1\text{H}$  nucleus surrounded by greater electron density is considered to be more shielded.

A  $^1\text{H}$  nucleus surrounded by greater electron density comes into resonance (absorbs electromagnetic radiation) at a higher frequency (larger ppm).

At room temperature, for a given H atom, slightly more than half of the nuclei are in the  $+1/2$  spin state, while slightly less than half are in the  $-1/2$  spin state.

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

3. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

The two most important isotopes for organic chemistry structure determination by NMR are \_\_\_\_\_ and \_\_\_\_\_.

Nuclei with spin quantum number  $1/2$  are quantized in one of two orientations: \_\_\_\_\_ (lower energy) or \_\_\_\_\_ (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 \_\_\_\_\_ to the strength of the magnetic field experienced by the nucleus.

Electron density is induced to move in a strong external magnetic field, and this movement induces a magnetic field that is opposed to the external magnetic field. This has the effect of \_\_\_\_\_ the underlying nuclei from the external magnetic field.

All other factors being the same, the signal for an  $^1\text{H}$  atom with greater electron density around it will come at \_\_\_\_\_ ppm in an NMR spectrum compared to a similar  $^1\text{H}$  atom with less electron density.

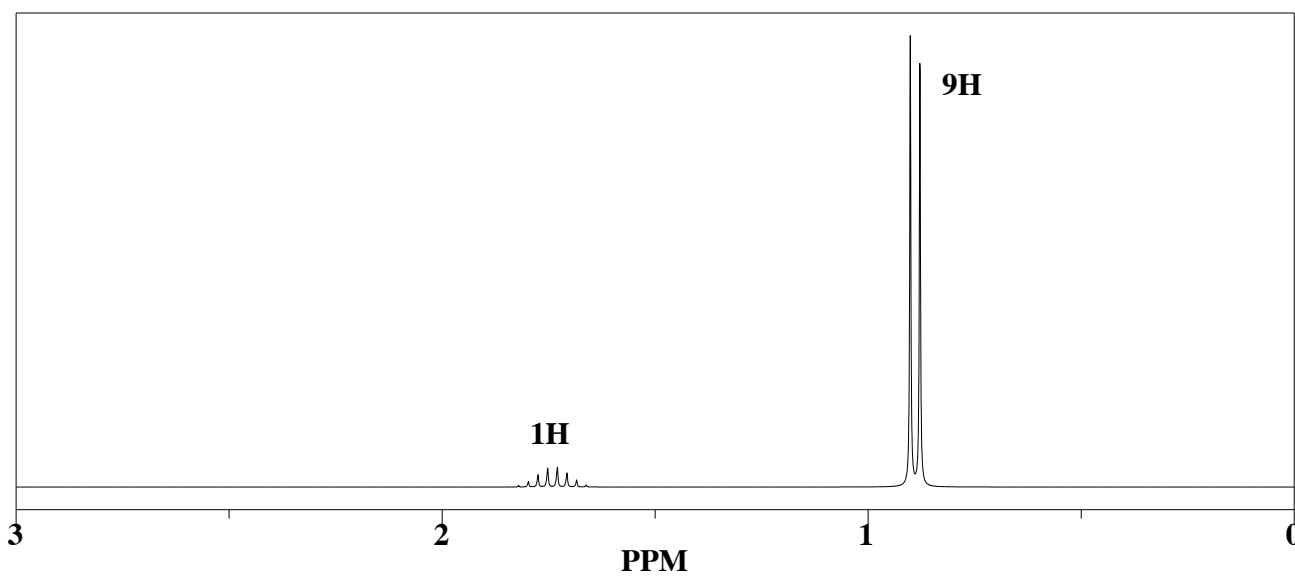
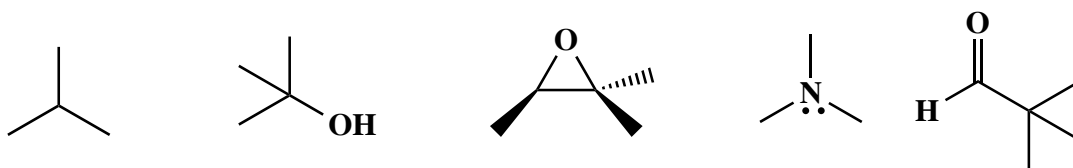
The \_\_\_\_\_ of adjacent nuclei influence each other (couple) if the  $^1\text{H}$  atoms are no more than \_\_\_\_\_ bonds apart, the spin states couple.

The \_\_\_\_\_ is the distance between peaks in a  $^1\text{H}$  NMR signal that has been split due to spin-spin coupling.

Signature \_\_\_\_\_

Pg 3 \_\_\_\_\_(5)

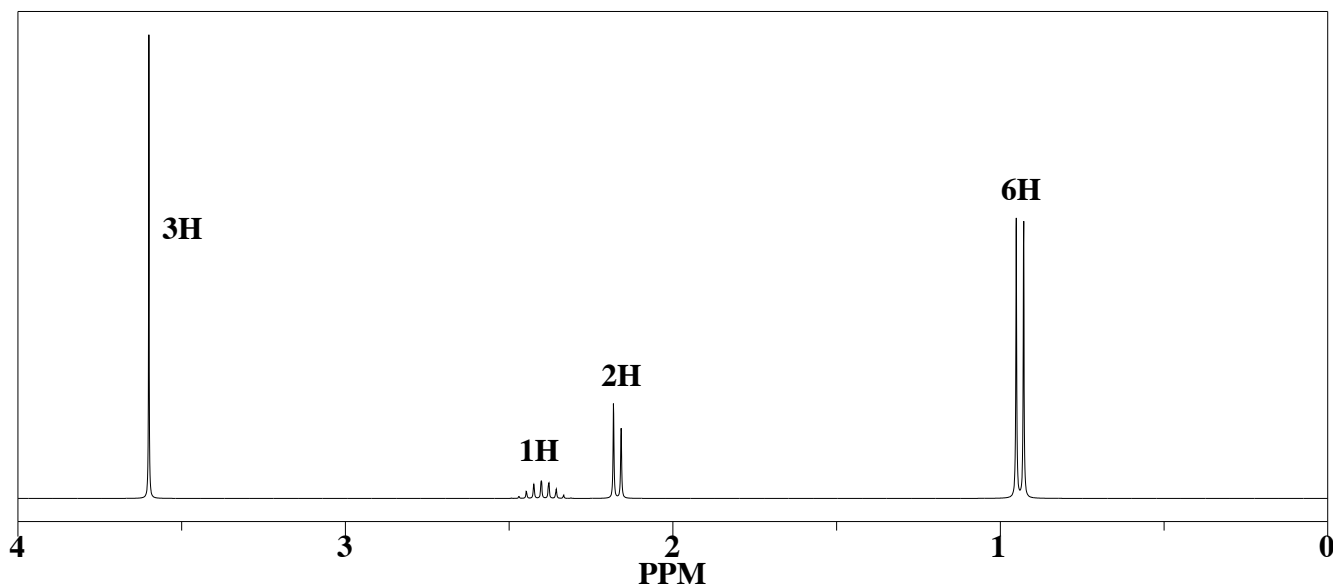
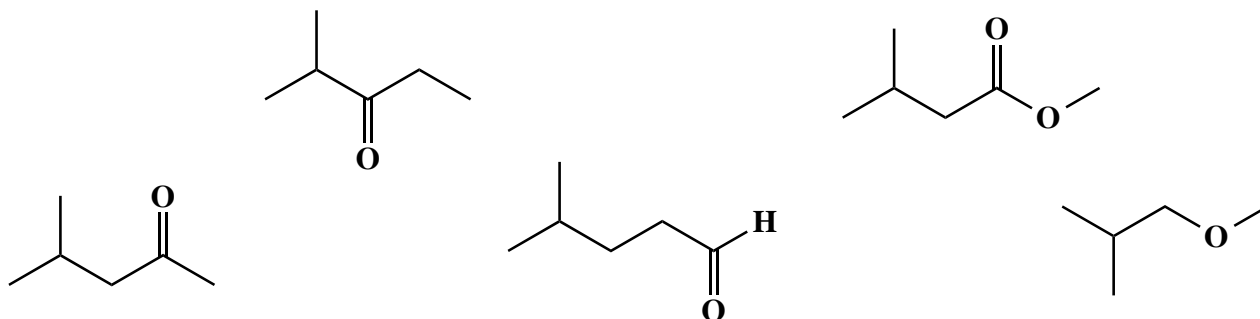
4. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



Signature \_\_\_\_\_

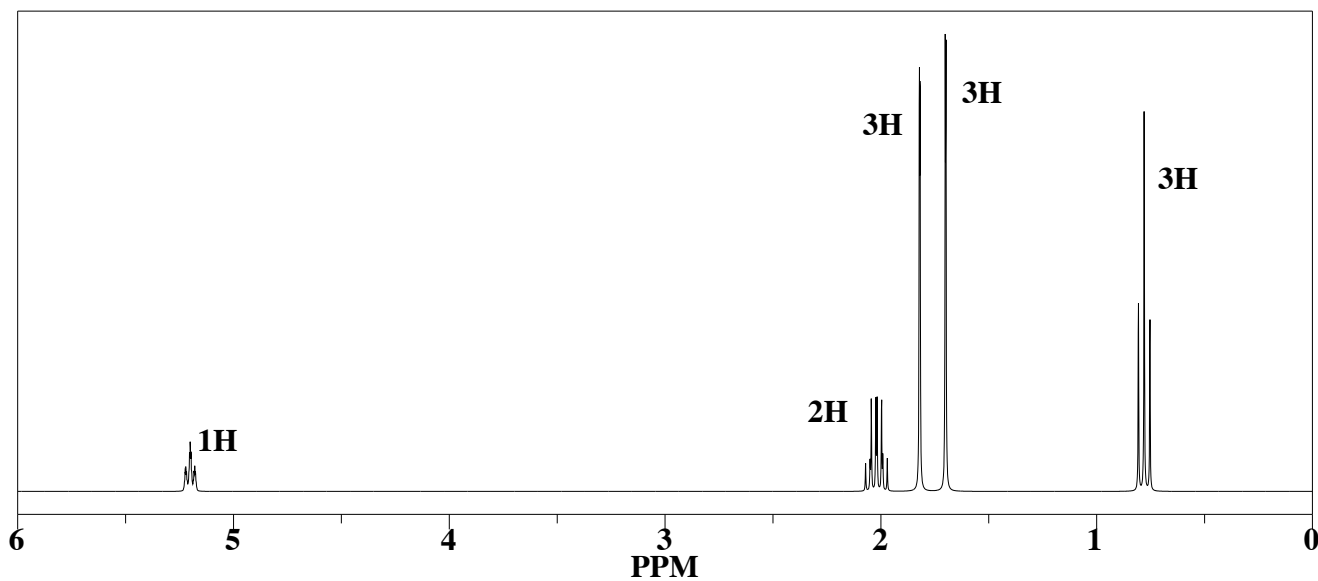
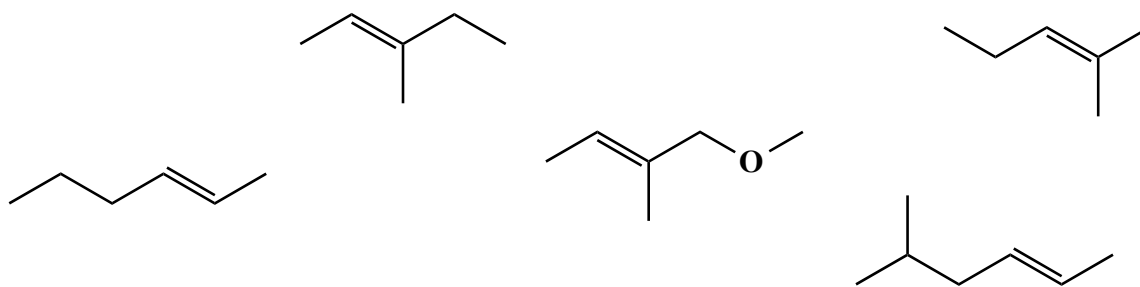
Pg 4 \_\_\_\_\_(5)

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

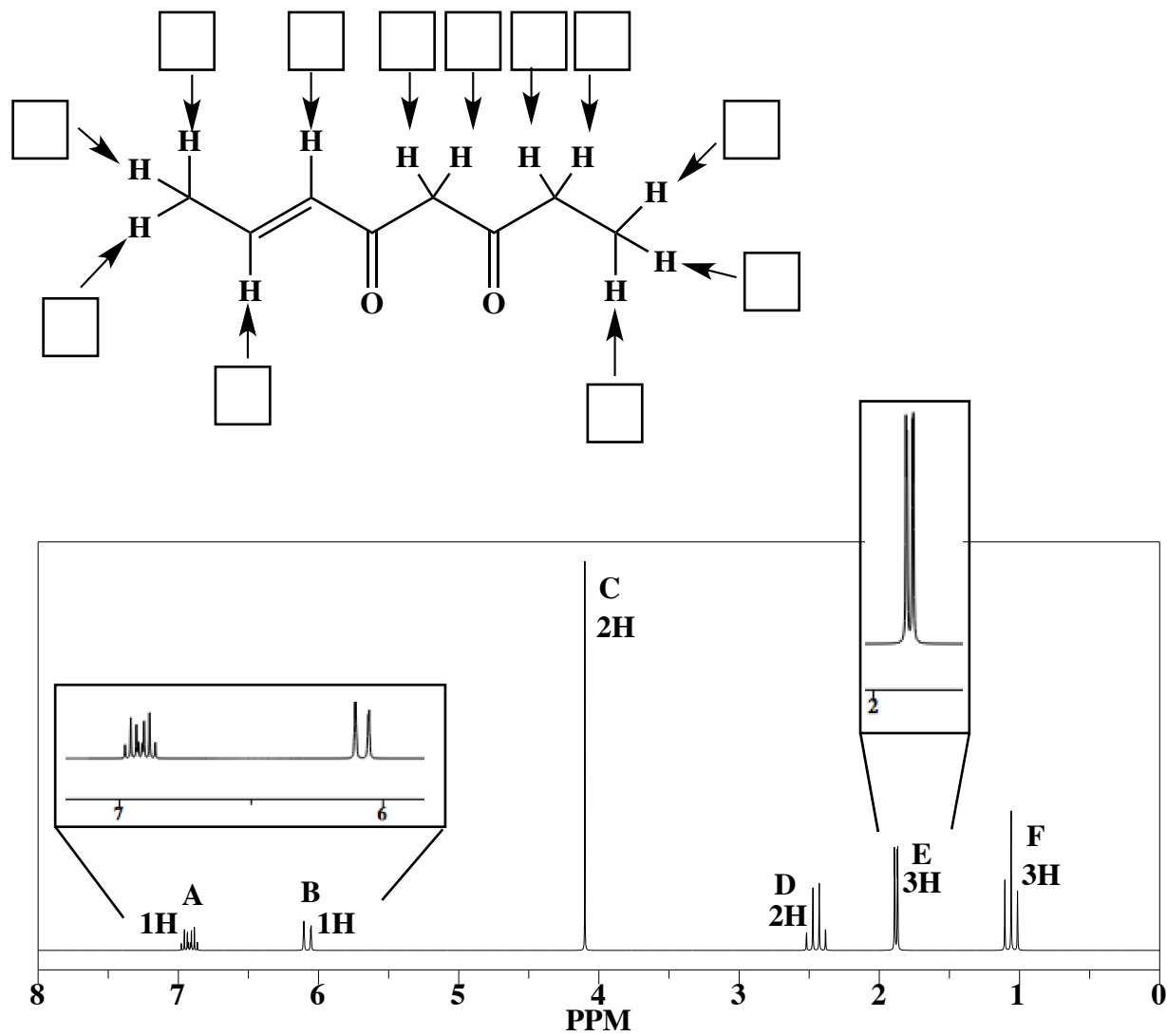




6. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



7. (12 pts) In the boxes provided, place that letter (A, B, C, etc.) that corresponds to the signals in the spectrum provided below.



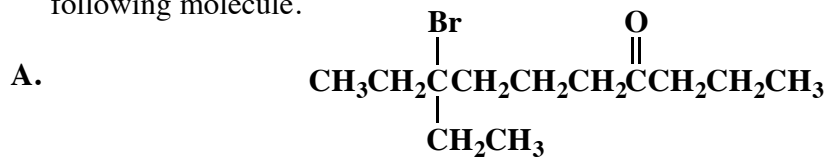
Signature \_\_\_\_\_

Pg 7 \_\_\_\_\_(12)

8. (3 pts) The most important question in organic chemistry is:

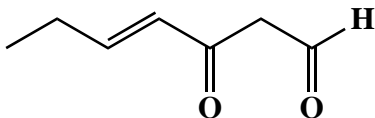
\_\_\_\_\_

9. (3 pts each) For parts A and B write an acceptable IUPAC name or draw a structural formula for the following molecule.



\_\_\_\_\_

B.

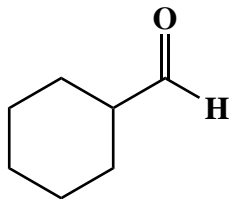


C. In the box provided, please draw a structure that corresponds to the following IUPAC name.

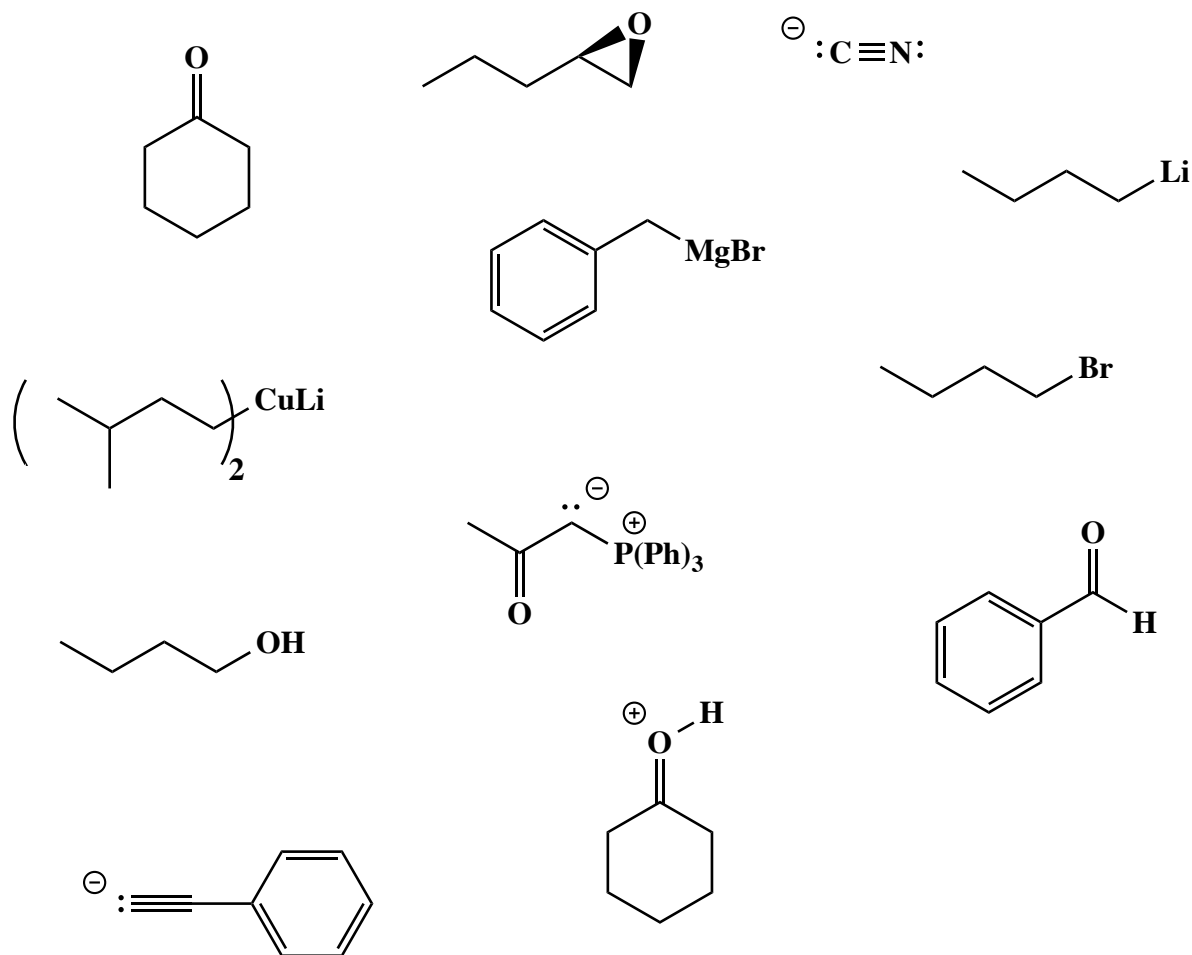
**(4*R*,5*R*)-5-hydroxy-2,4-dimethyl-3-heptanone**



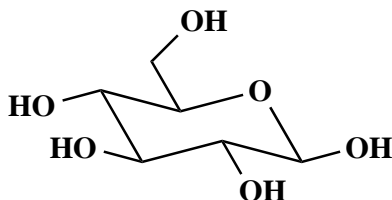
10. (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.



11. (12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. For the following DRAW A BOX AROUND ANY SPECIES THAT CAN BE CONSIDERED AN ELECTROPHILE, and DRAW A CIRCLE AROUND ANY SPECIES THAT CAN BE CONSIDERED A NUCLEOPHILE. Notice that some of the nucleophiles can also be considered bases, but we are not worrying about that for this questions.



13. (7 pts) Shown below is one form of glucose. **Draw a circle around the hemiacetal group (Yep this sweet molecule has a "hemi" in it!)** Then answer the question below the structure.



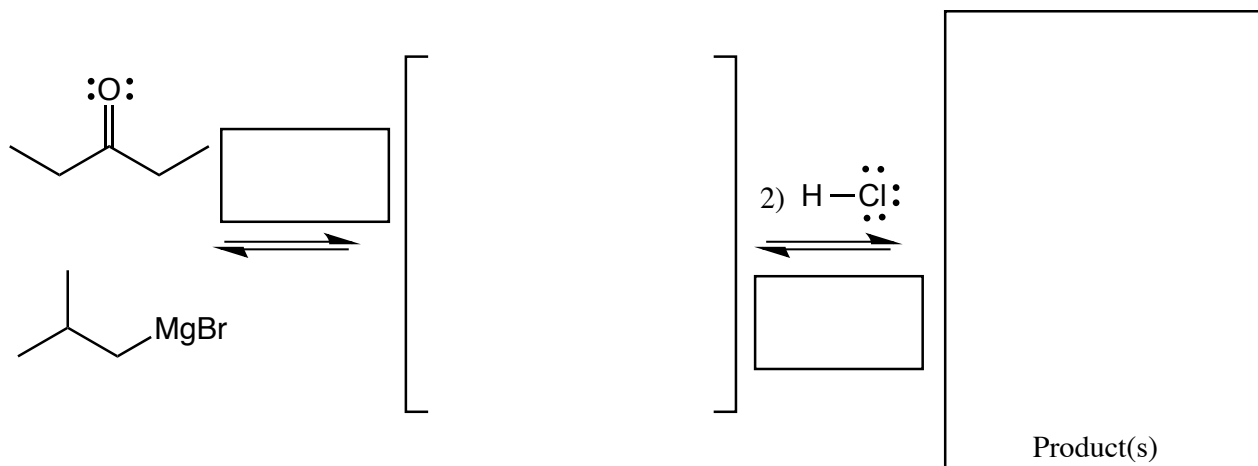
**Circle the correct statement:**

The structure represents the  $\alpha$  form of glucose

The structure represents the  $\beta$  form of glucose

The structure represents the  $\Delta\Gamma$  form of glucose

14. (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 MARK IT WITH AN ASTERISK AND WRITE "RACEMIC" IF APPROPRIATE.** I realize these directions are complex, so please read them again to make sure you know what we want.

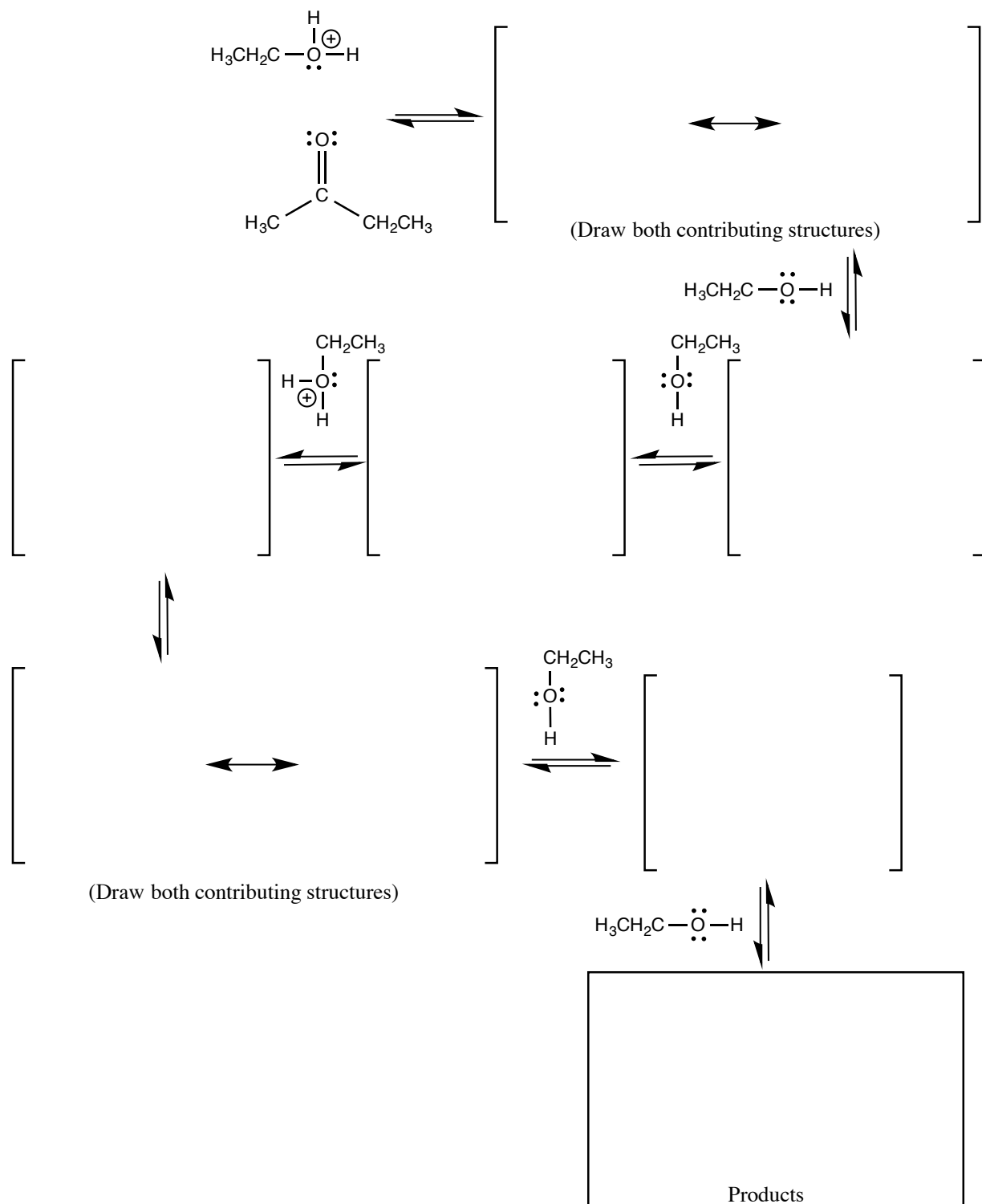


**In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.**

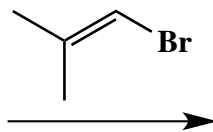
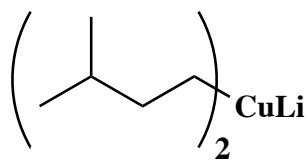
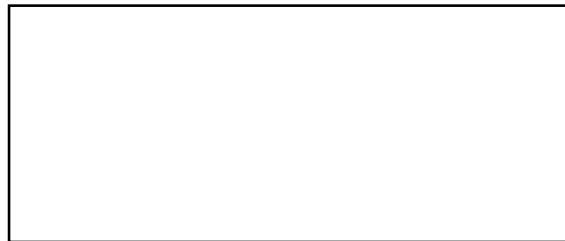
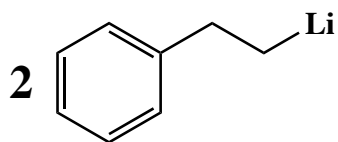
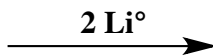
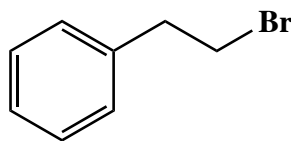
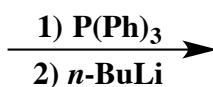
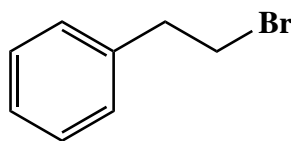
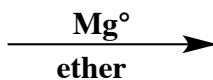
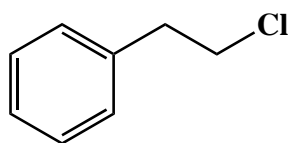
↑↑  
**NOTICE THIS**

15. (26 pts. total) 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 MARK IT WITH AN ASTERISK AND WRITE RACEMIC IF APPROPRIATE.** Do not draw arrows to indicate how one contributing structure relates to the other.

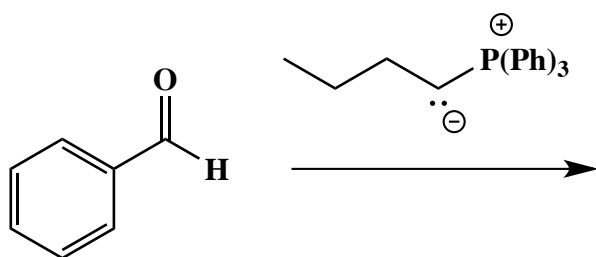
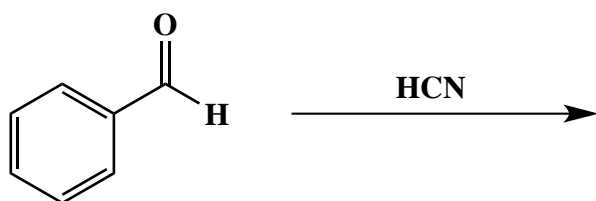
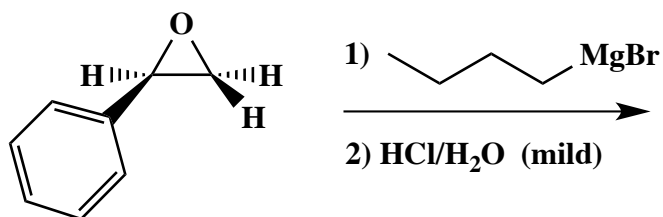
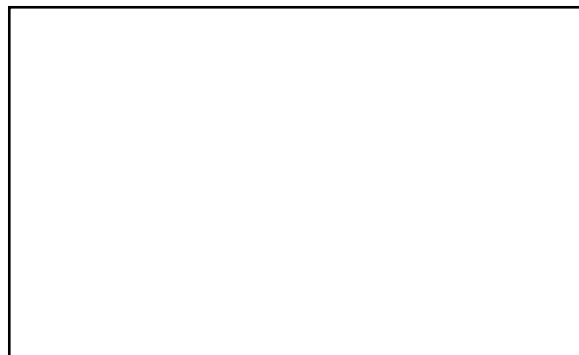
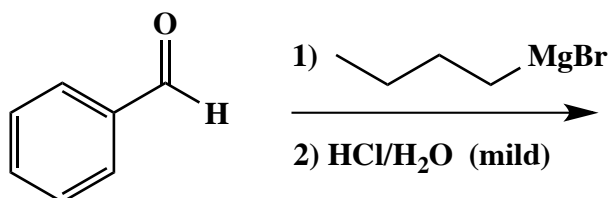
*Acid Catalyzed Acetal Formation from a Ketone*



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 (  $\cdots\parallel$  ) 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.

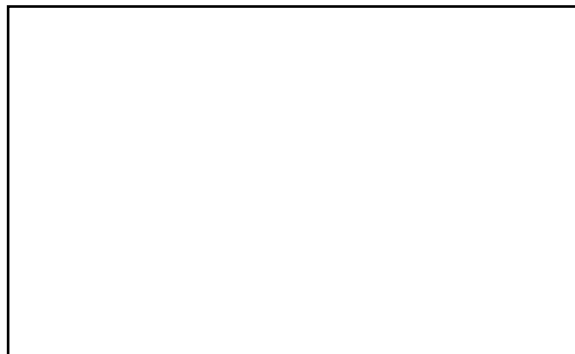
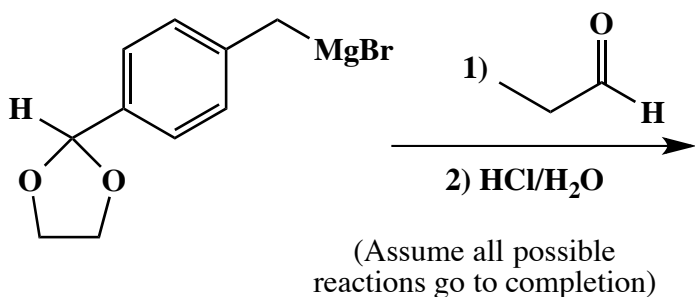
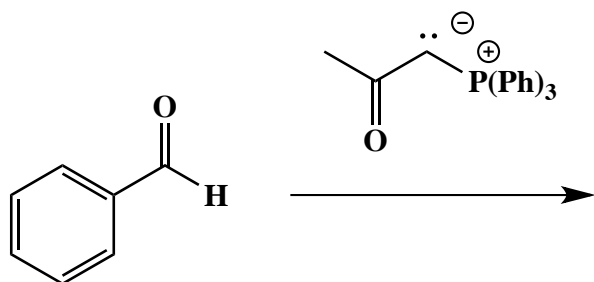
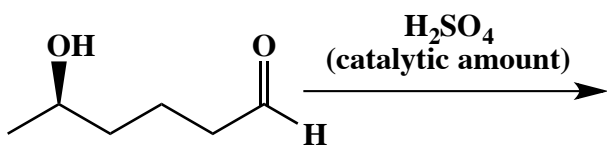
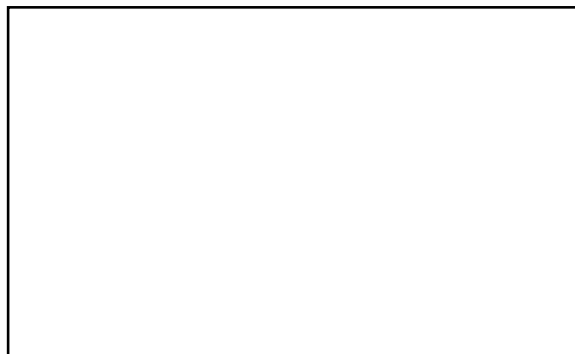
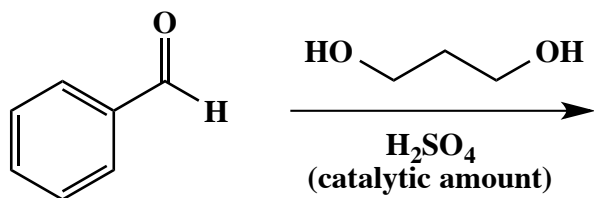


16. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (  $\blacktriangleleft$  ) and dashes (  $\cdots$  ) 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.



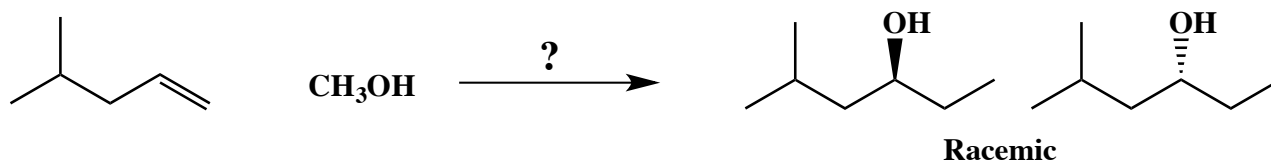


16. (3,4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (  $\blacktriangleleft$  ) and dashes (  $\dashv$  ) 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.



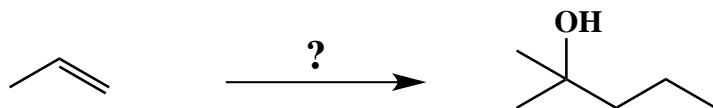
17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, you can either draw both enantiomers or simply draw one structure and label all chiral centers with an asterisk (\*). Either way, you must write racemic if appropriate.

(10 pts) **All of the carbon atoms of the products must come from the starting materials.**



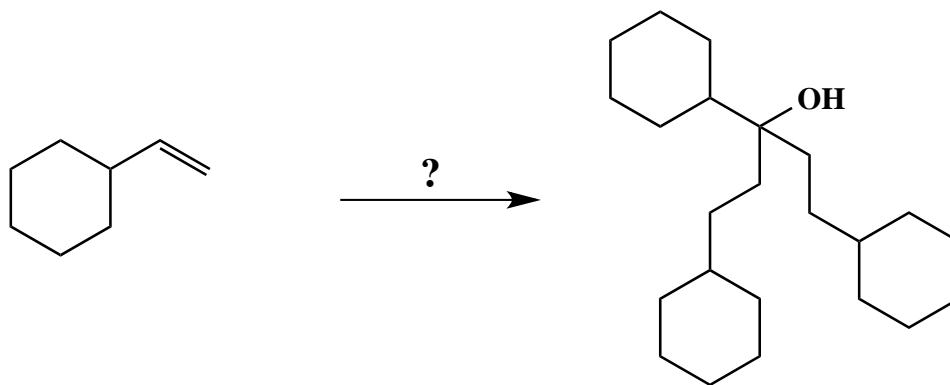
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(13 pts) **All of the carbon atoms of the products must come from the starting materials.**



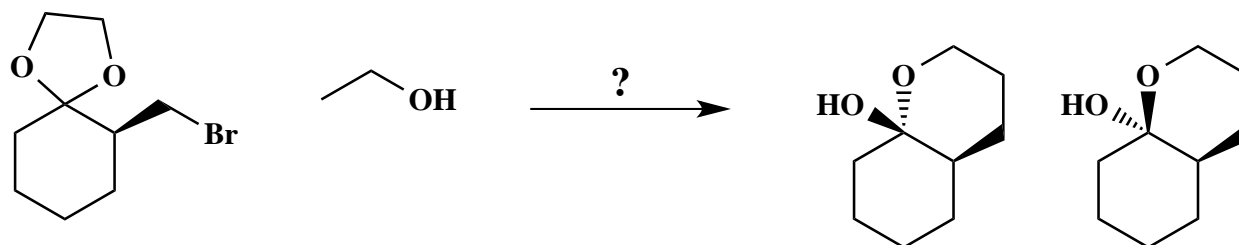
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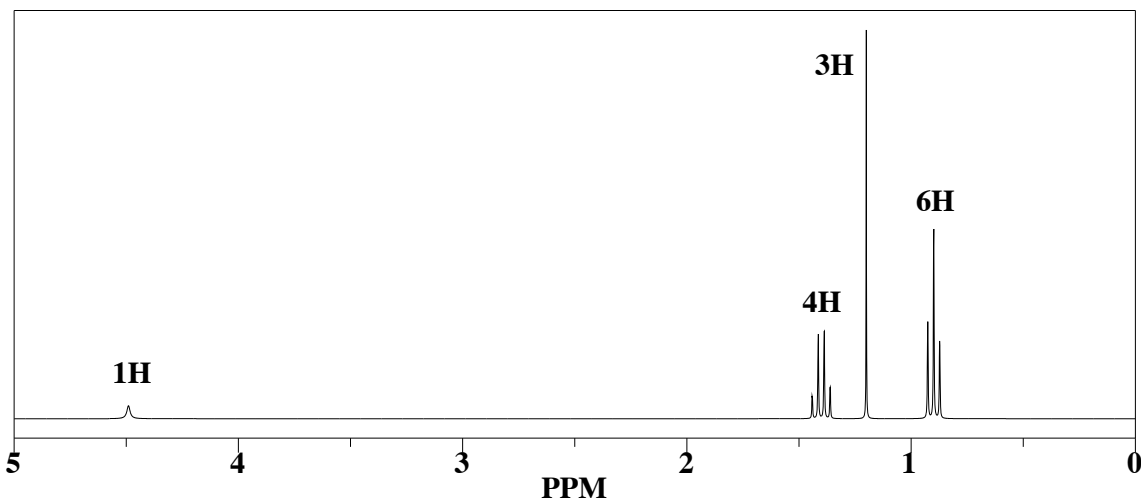
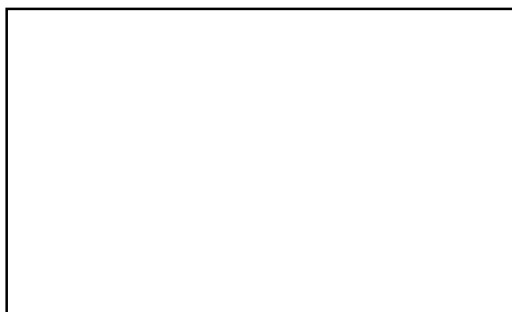
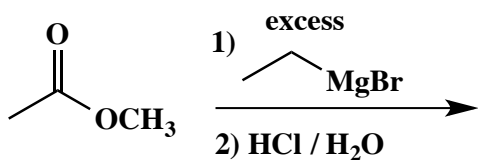


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(13 pts) **All of the carbon atoms of the products must come from the starting materials.**



18. (10 pts) You have not seen the following reaction before, it comes from chapter 18. You might find it useful to know that  $\text{RO}^\ominus$  groups can serve as a leaving group. The NMR spectrum is of the predominant product. Using your growing intuition about chemical reactivity as well as the NMR, draw the structure of the product of this reaction.



19. (7 pts) Reactions in context: Following is a Wittig reaction used in the published synthesis of a pharmaceutical called Ifetroban used to treat hypertension. Draw the product of the reaction.

