

Name: \_\_\_\_\_

**CHEM 322. Midterm 3**  
**Spring 2014**  
**Watson, Hietbrink**

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Data tables are provided on pages 12 and 13 of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are 15 pages in this exam. Please check that your test has 15 pages before you begin. The last 2 pages are blank and may be used as scratch paper.

**Please circle your lecture:**

Hietbrink 8:00 am class

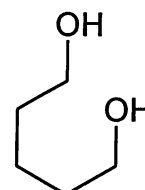
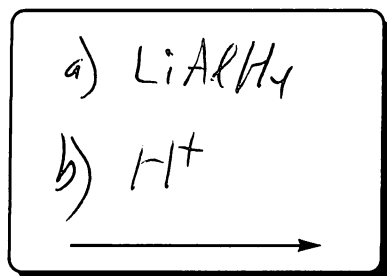
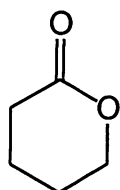
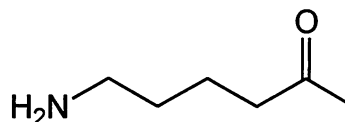
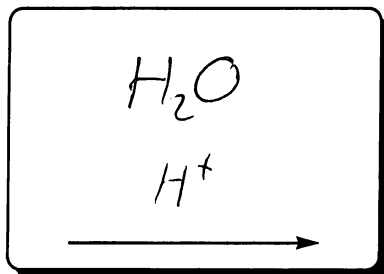
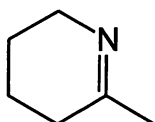
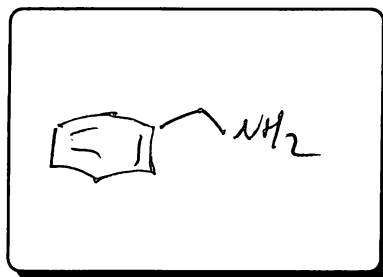
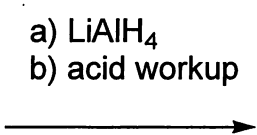
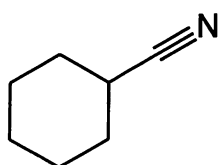
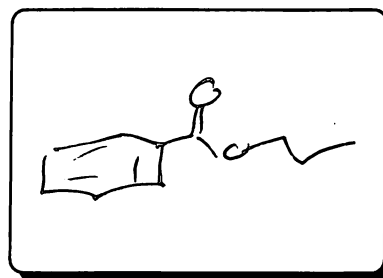
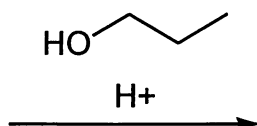
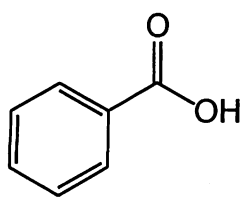
Hietbrink 11:15 am class

Watson class

<b>Question</b>	<b>Points</b>
1	_____ /32
2	_____ /56
3	_____ /24
4	_____ /24
5	_____ /50
6	_____ /24
7	_____ /40
<b>Total</b>	_____ /250

Name: \_\_\_\_\_

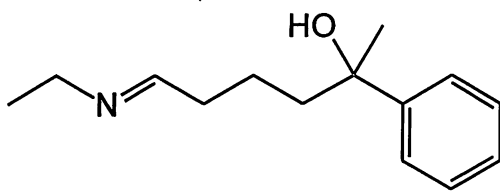
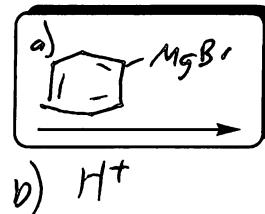
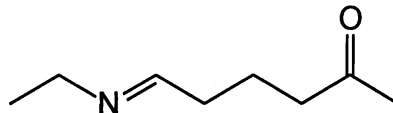
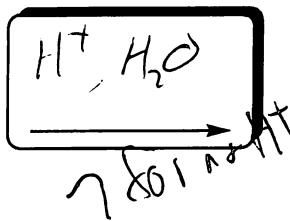
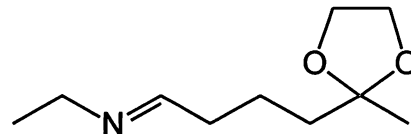
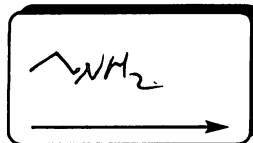
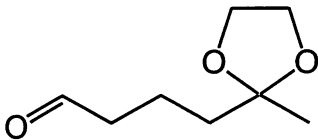
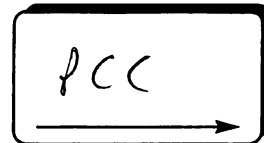
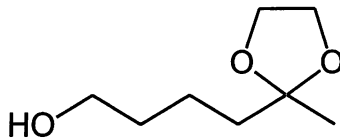
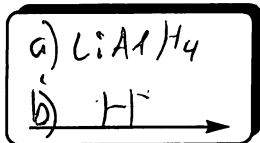
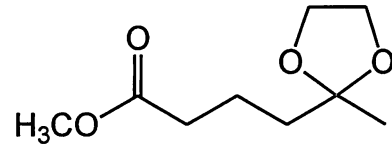
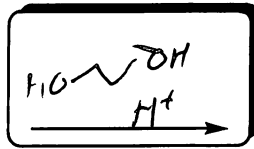
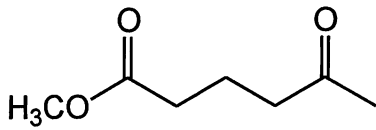
1. (32 points) Please fill in the missing starting materials or products of the following reactions.



Name: \_\_\_\_\_

*for wrong RGH  
for no HT*

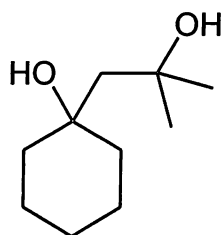
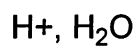
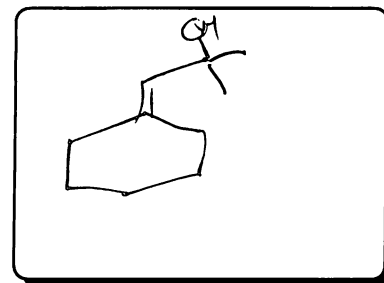
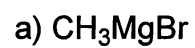
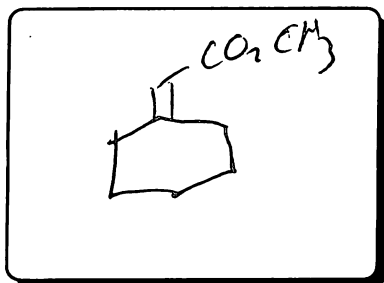
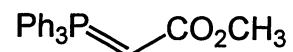
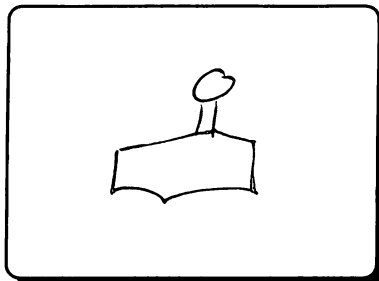
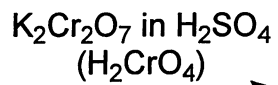
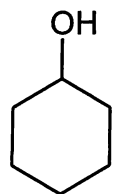
2. (56 points) Please provide the necessary reagents to complete the following transformations.



*9 ea + 2*

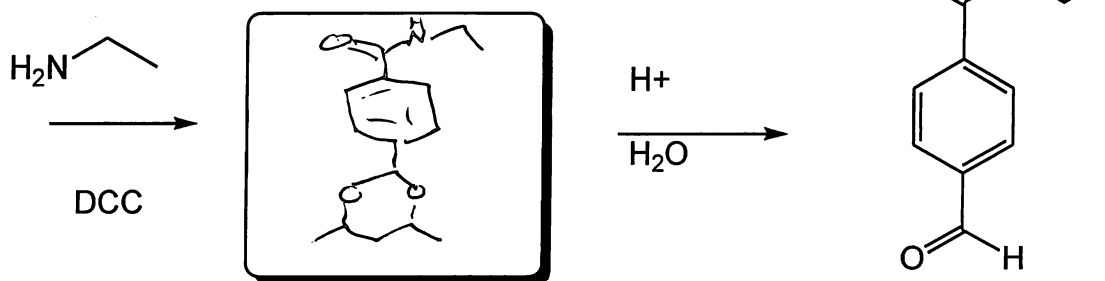
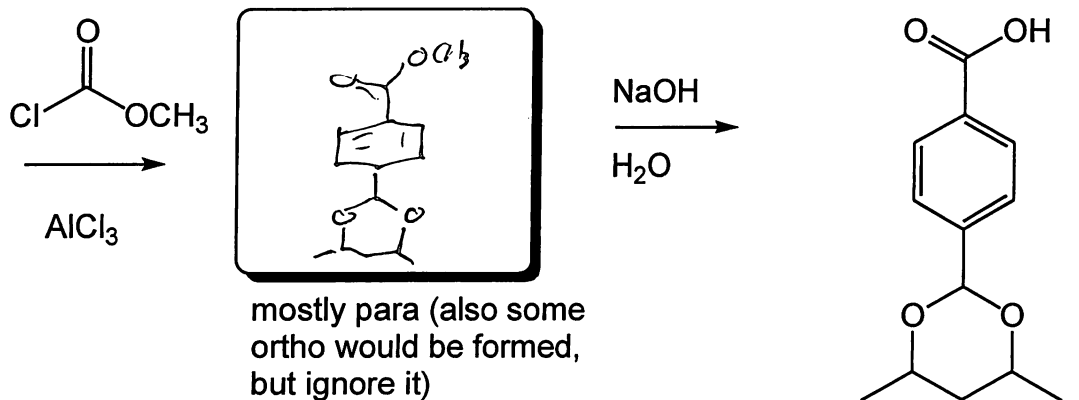
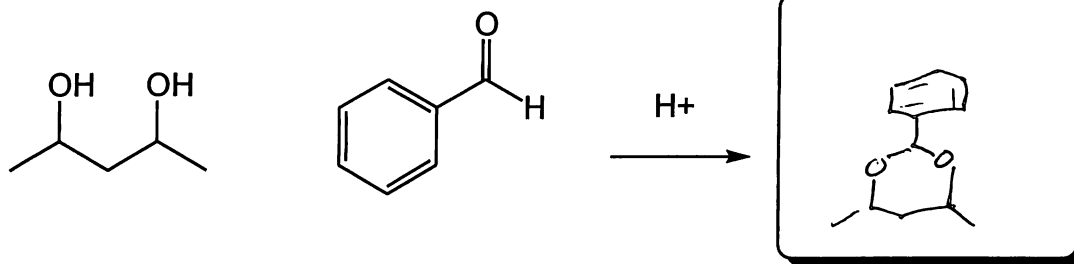
Name: \_\_\_\_\_

3. (24 points) Please fill in the products of the following reactions. If no reaction is expected, state "No Reaction".



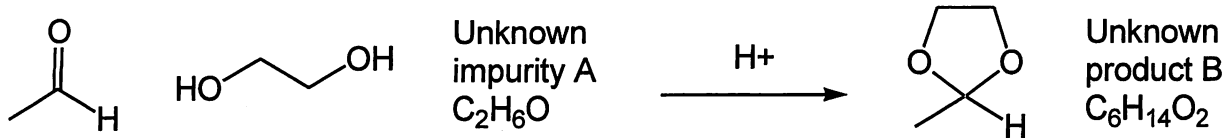
Name: \_\_\_\_\_

4. (24 points) Please fill in the products of the following reactions. If no reaction is expected, state "No Reaction".

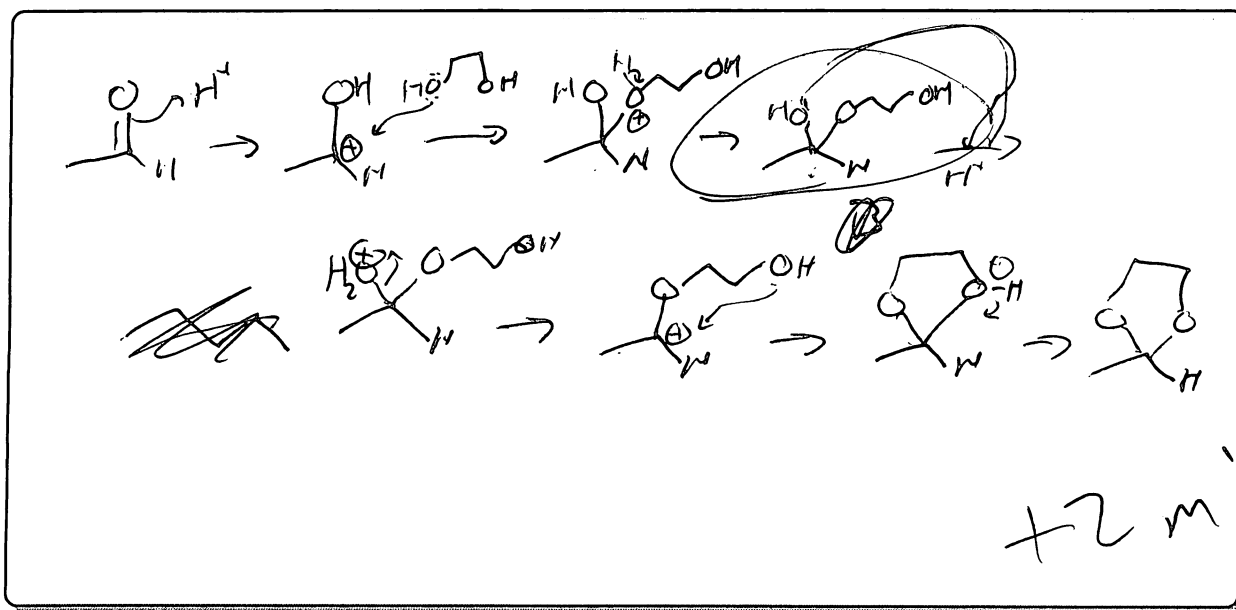


Name: \_\_\_\_\_

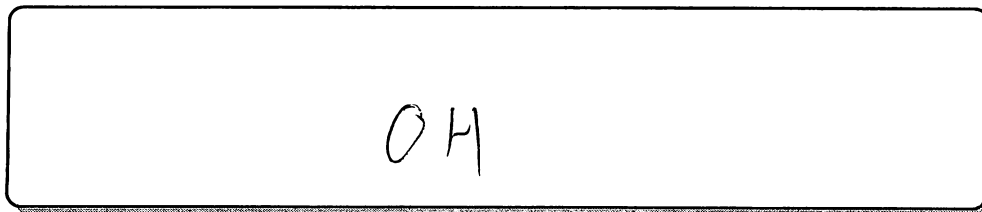
5. (50 points) Dr. Oops wanted to prepare the cyclic acetal below from acetaldehyde. She found an old bottle of acetaldehyde on her lab shelf and ran the following reaction. She observed 2 products from this reaction. Confused, she checked her starting material (acetaldehyde) and found that it contained an impurity. Spectra for A and B are shown on the following pages. Based on these spectra and your chemical knowledge, please answer the following questions.



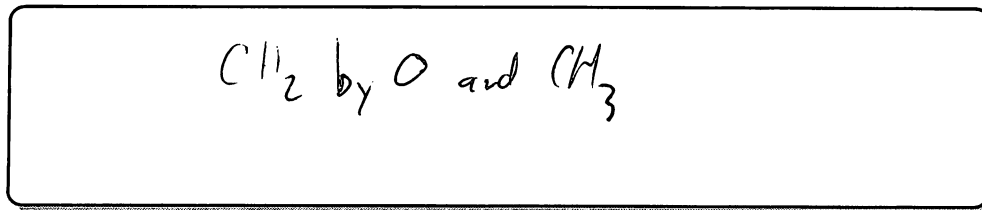
(a) Please draw a reasonable arrow-pushing mechanism for the formation the cyclic acetal from acetaldehyde (i.e., Dr. Oops' desired reaction).



(b) For impurity A, what does the IR peak at  $3200\text{ cm}^{-1}$  indicate?



(c) For impurity A, what does the  $^1\text{H}$  NMR peak at  $\sim 3.9\text{ ppm}$  indicate?



Name: \_\_\_\_\_

(d) For impurity A, what does the  $^{13}\text{C}$  NMR peak at 19 ppm indicate?

3

$\text{sp}^3\text{C}$  (not by O)

(e) What is the structure of impurity A?

10



(f) For product B, what does the  $^1\text{H}$  NMR peak at 4.7 ppm indicate?

3

CH by  $\text{CH}_3$  also by O

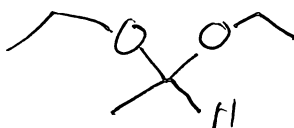
(g) For product B, what does the  $^{13}\text{C}$  NMR peak at 60 ppm indicate?

3

$\text{sp}^3\text{C}$  by O

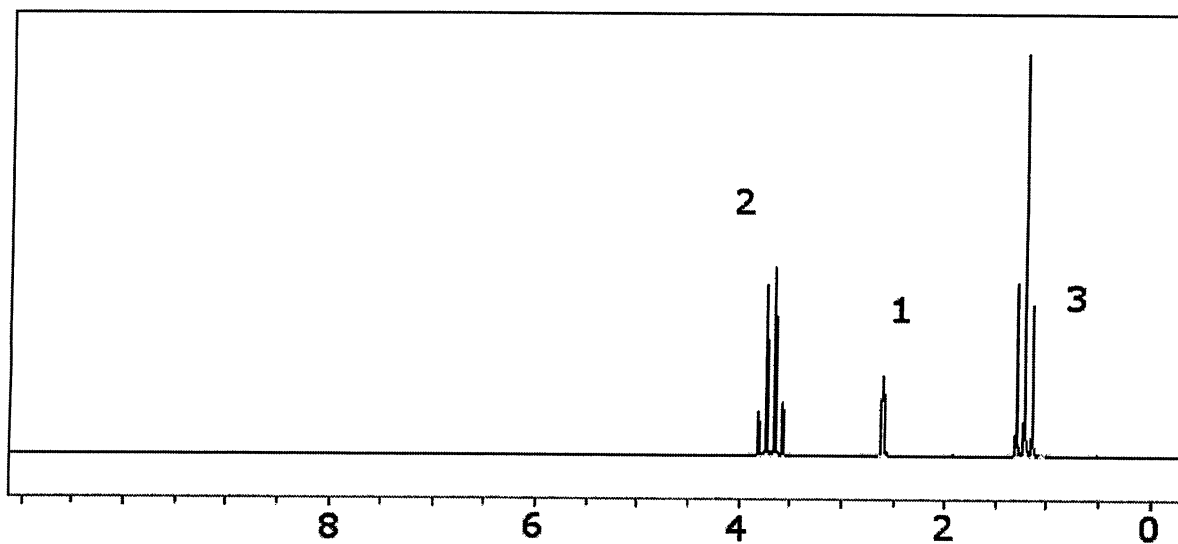
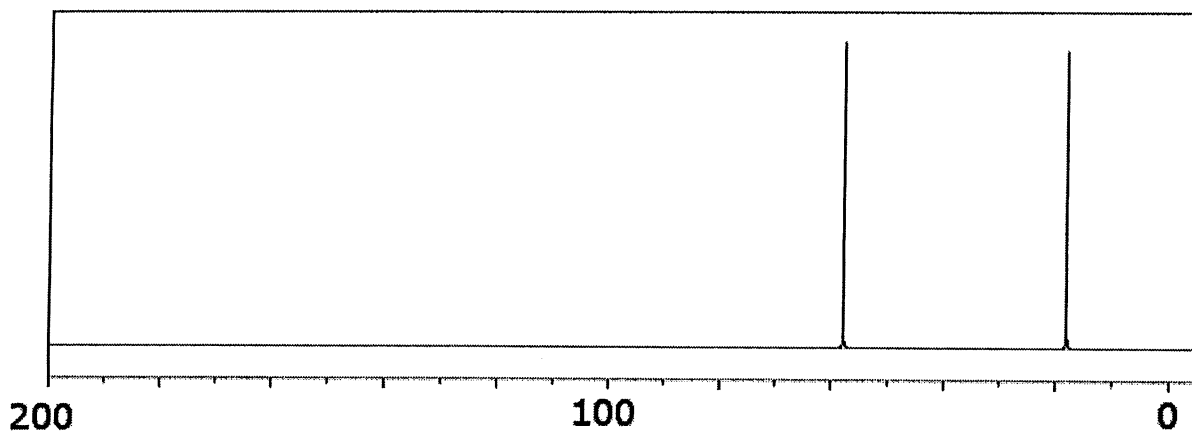
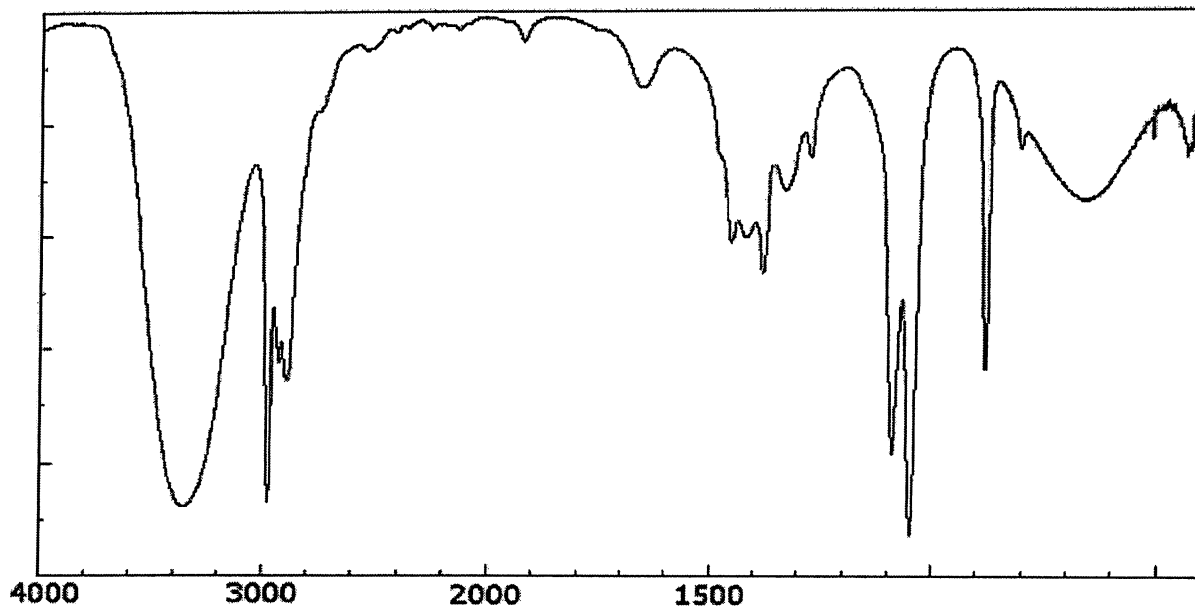
(h) What is the structure of product B?

10



Name: \_\_\_\_\_

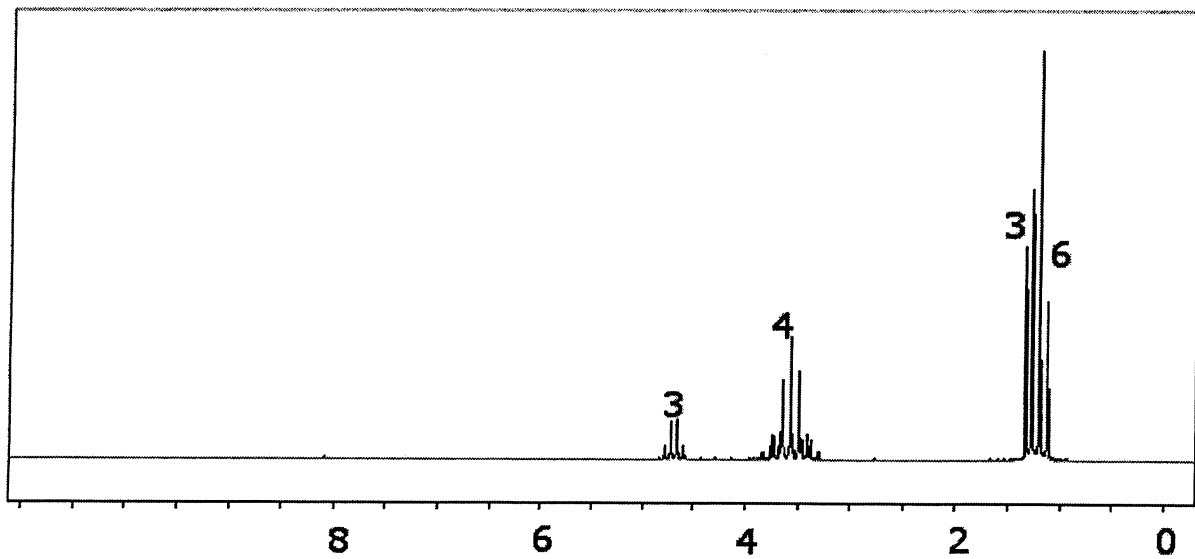
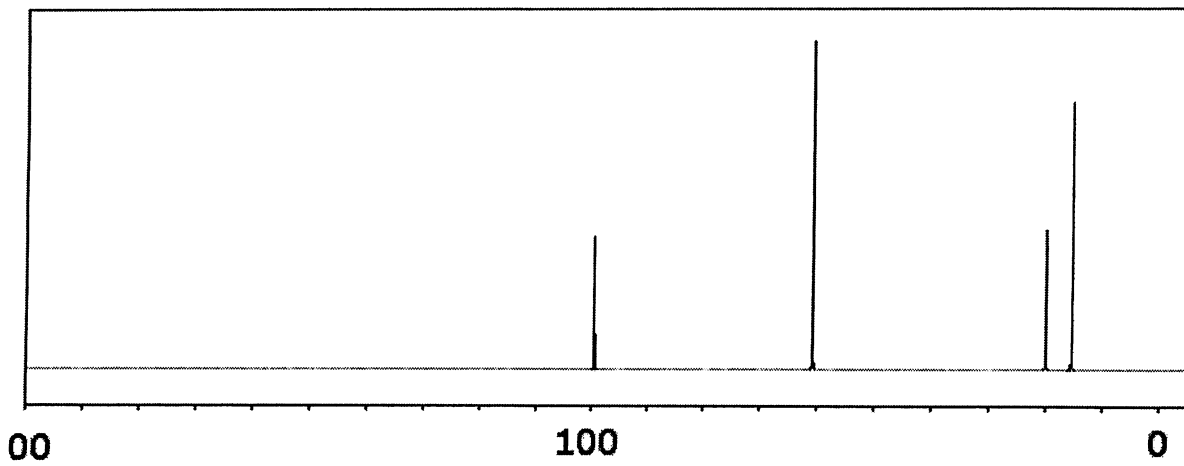
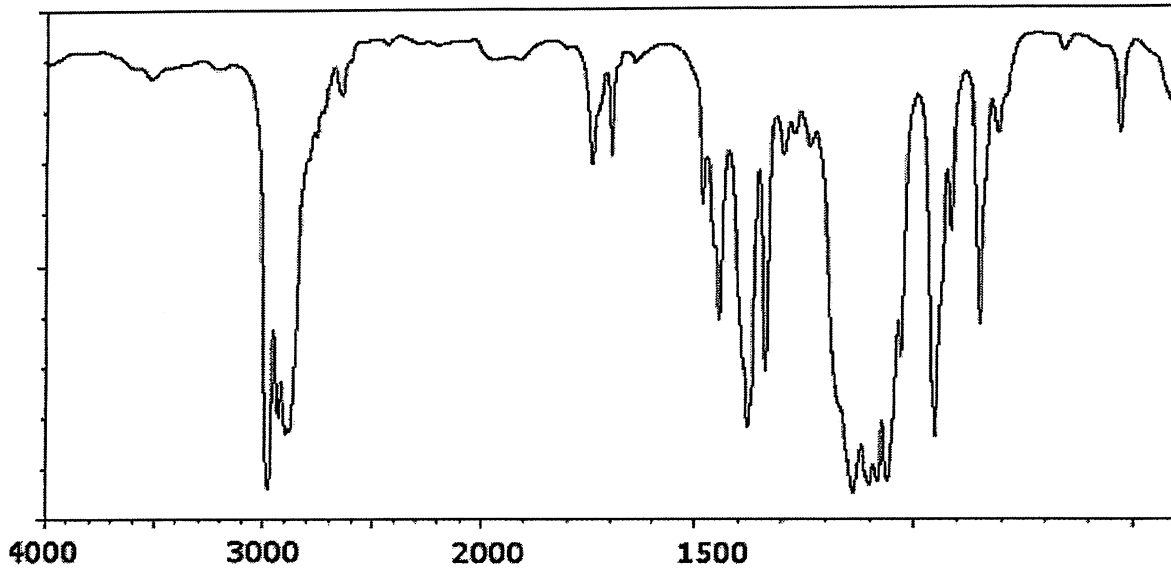
Unknown Impurity A:





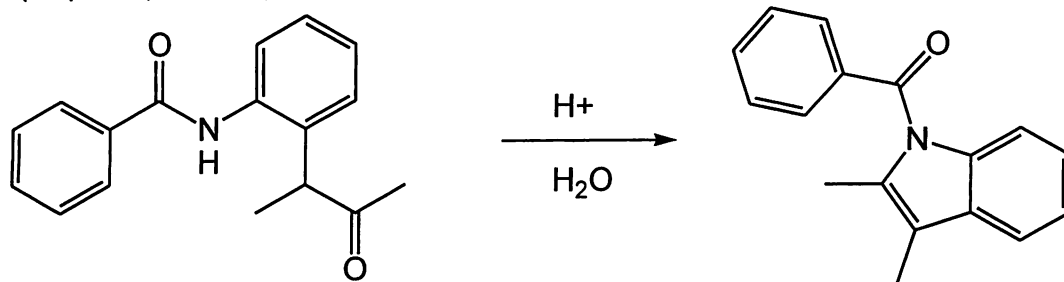
Name: \_\_\_\_\_

Unknown Product B:



Name: \_\_\_\_\_

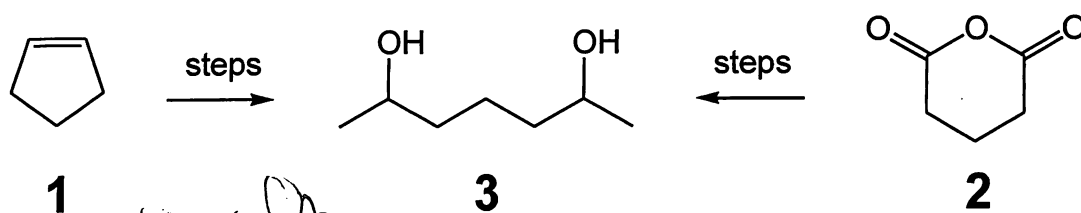
6. (24 points) Please provide a reasonable arrow-pushing mechanism for the following reaction.



Blank area for providing the arrow-pushing mechanism.

Name: \_\_\_\_\_

7. (40 points) Please suggest a synthesis of diol **3** starting from *either* cyclopentene (**1**) or cyclic anhydride **2**. Clearly indicate which starting material (**1** or **2**) you have chosen in your answer.



*10 King King*  
 $\text{Cyclopentene} \xrightarrow[\text{b) DMS}]{\text{a) O}_3} \text{Hexanedial} \xrightarrow[\text{b) H}^+]{\text{a) CH}_3\text{MgBr}} \text{1,5-Hexanediol}$   
 (13)      (13)      (13)      +1  
*or -2 no a, b*

$\text{Cyclic Anhydride} \xrightarrow[\text{b) H}^+]{\text{a) LiAlH}_4} \text{1,5-Hexanediol} \xrightarrow{\text{PCC}} \text{Hexanedial} \xrightarrow[\text{b) H}^+]{\text{a) CH}_3\text{MgBr}} \text{1,5-Hexanediol}$   
 (8)      (8)      (8)      (8)

4 min

Name: \_\_\_\_\_

**Approximate IR Absorption Frequencies**

Bond	Frequency (cm <sup>-1</sup> )	Intensity
O-H (alcohol)	3650–3200	Strong, broad
O-H (carboxylic acid)	3300–2500	Strong, very broad
N-H	3500–3300	Medium, broad
C-H	3300–2700	Medium
C≡N	2260–2220	Medium
C=C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C-O	1250–1050	Strong

**Approximate <sup>1</sup>H NMR Chemical Shifts**

Hydrogen	δ (ppm)
CH <sub>3</sub>	0.8–1.0
CH <sub>2</sub>	1.2–1.5
CH	1.4–1.7
C=C-CH <sub>x</sub>	1.7–2.3
O=C-CH <sub>x</sub>	2.0–2.7
Ph-CH <sub>x</sub>	2.3–3.0
≡C-H	2.5
R <sub>2</sub> N-CH <sub>x</sub>	2.0–2.7
I-CH <sub>x</sub>	3.2
Br-CH <sub>x</sub>	3.4
Cl-CH <sub>x</sub>	3.5
F-CH <sub>x</sub>	4.4
O-CH <sub>x</sub>	3.2–3.8
C=CH	4.5–7.5
Ar-H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH <sub>x</sub>	0.5–5.0
CONH <sub>x</sub>	5.0–10.0
RCOOH	10–13

**Approximate <sup>13</sup>C NMR Chemical Shifts**

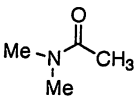
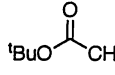
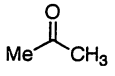
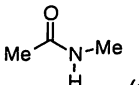

Carbon	δ (ppm)
<i>Alkanes</i>	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
<i>Alkenes</i>	
C=C	80–145
<i>Alkynes</i>	
C≡C	70–90
<i>Aromatics</i>	
Benzene	110–170
Benzene	128.7
<i>Alcohols, Ethers</i>	
C-O	50–90
<i>Amines</i>	
C-N	40–60
<i>Halogens</i>	
C-F	70–80
C-Cl	25–50
C-Br	10–40
C-I	-20–10
<i>Carbonyls, C=O</i>	
R <sub>2</sub> C=O	190–220
RXC=O (X = O or N)	150–180

Name: \_\_\_\_\_

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1																	18															
1	H																	He														
2	Li	Be															B	C	N	O	F	Ne										
3	Na	Mg															Al	Si	P	S	Cl	Ar										
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn														
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										(223)	(228)	(227)	(261)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)
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**pKa TABLE**

compound	pKa
Bu-H	48
Ph-H	43
H <sub>2</sub>	~36
iPr <sub>2</sub> N-H	~35
 (amide α-H)	25
 (ester)	24
 (ketone)	17-20
 (amide N-H)	~18
iPrOH	16-18
H <sub>2</sub> O	16
Et <sub>3</sub> N-H <sup>+</sup>	10
 (carboxylic acid)	-1-6
H <sub>3</sub> O <sup>+</sup>	-2
HCl	-8

Name: \_\_\_\_\_

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