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

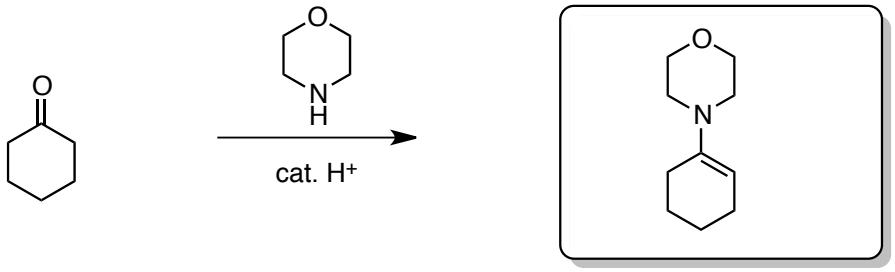
Hietbrink 11:15 am class

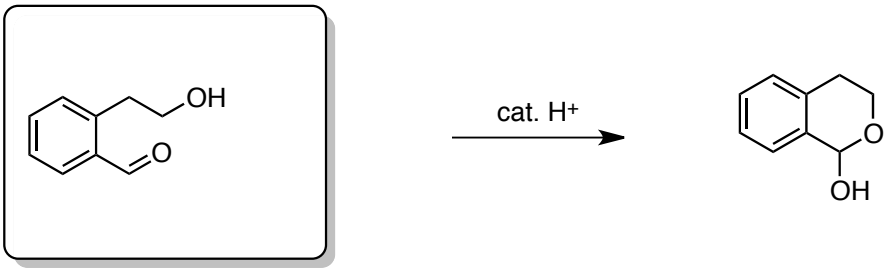
Watson class

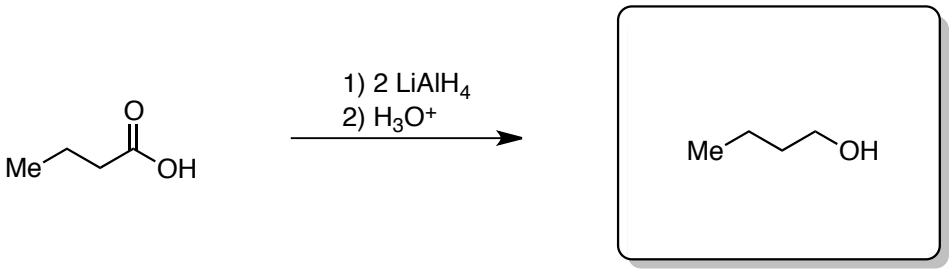
Question	Points
1	_____ /32
2	_____ /56
3	_____ /24
4	_____ /24
5	_____ /50
6	_____ /24
7	_____ /40
Total	_____ /250

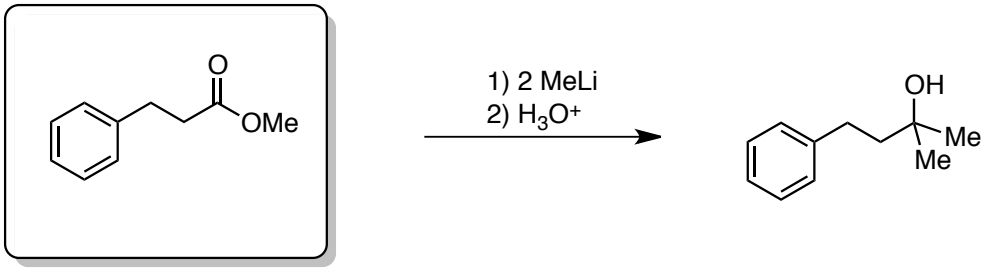
Name: _____

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



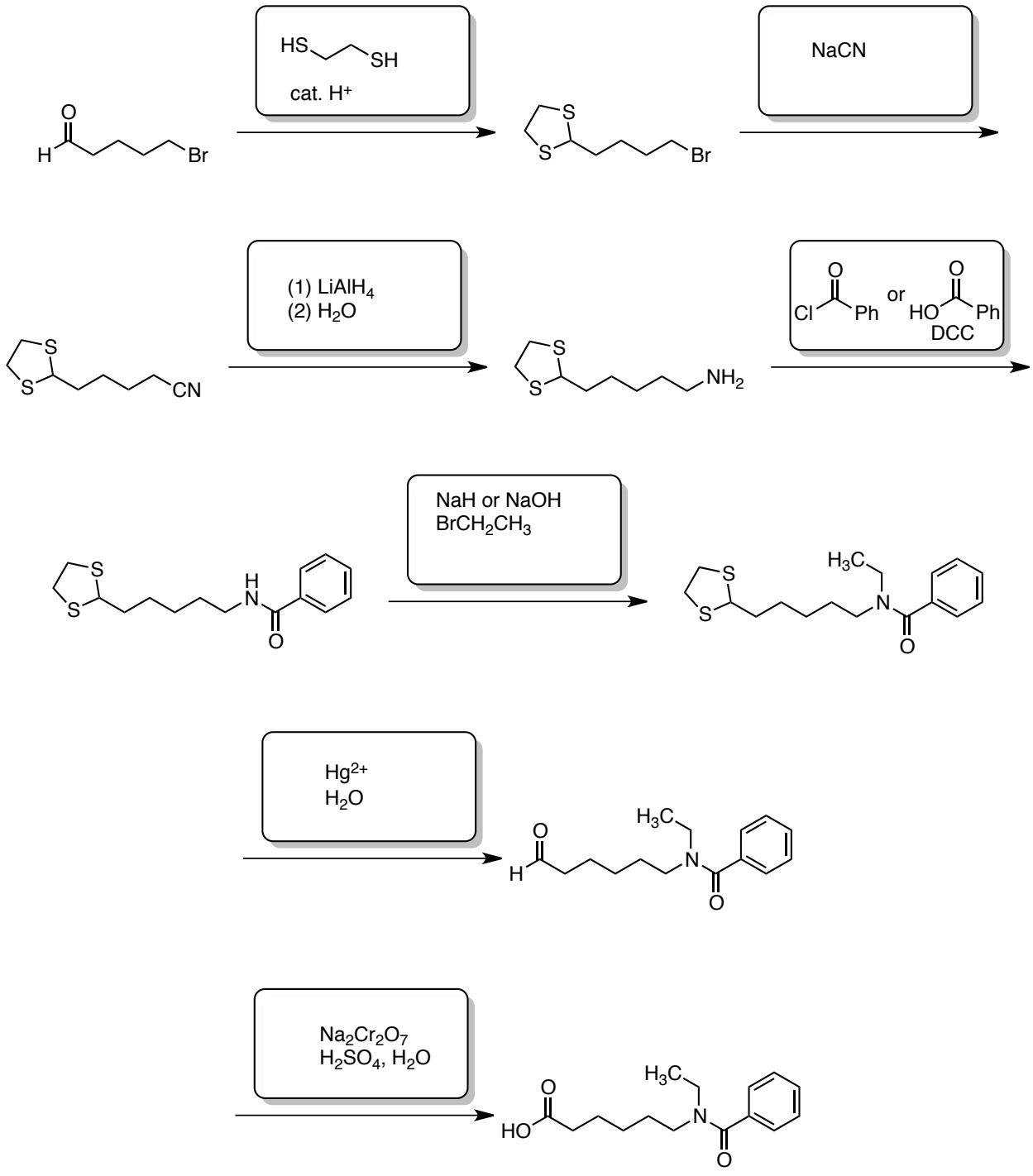






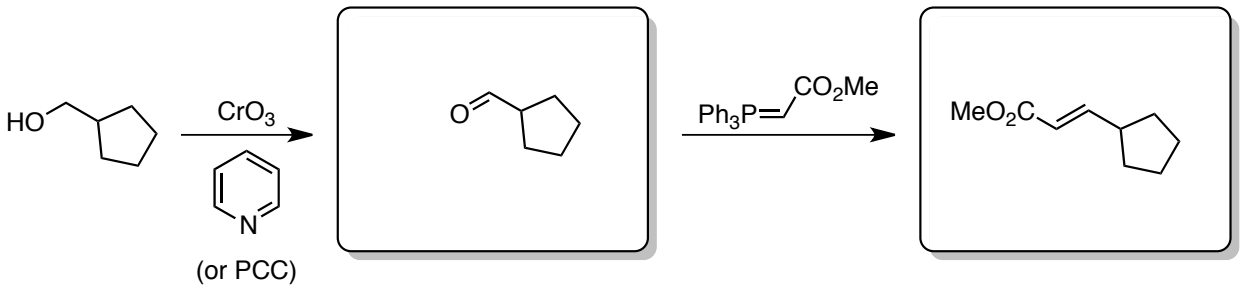
Name: _____

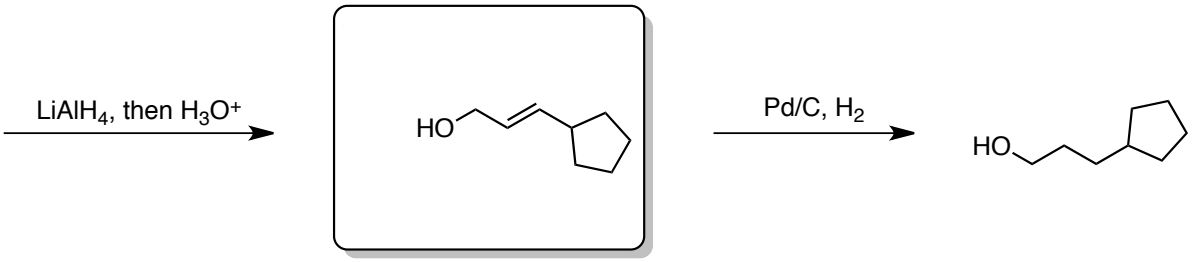
2. (56 points) Please provide the necessary reagents to complete the following transformations.



Name: _____

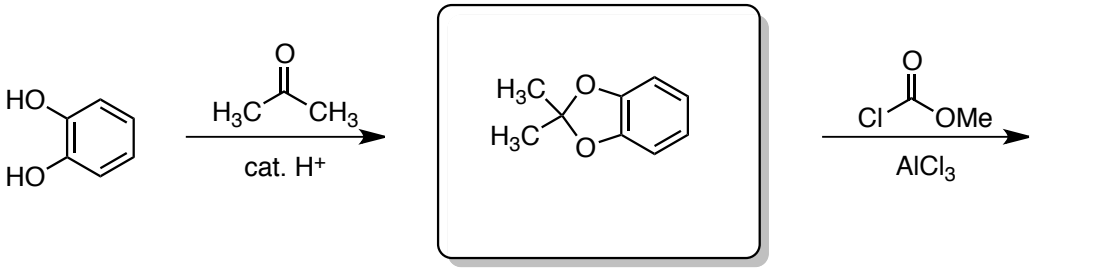
3. (24 points) Please fill in the products of the following reactions. If no reaction is expected, state “No Reaction”.

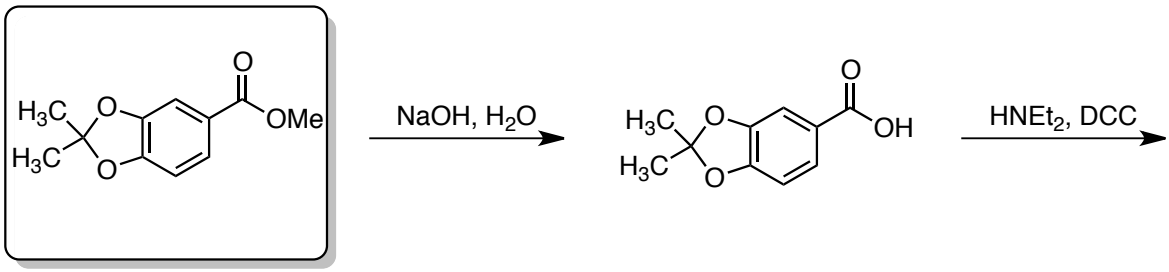


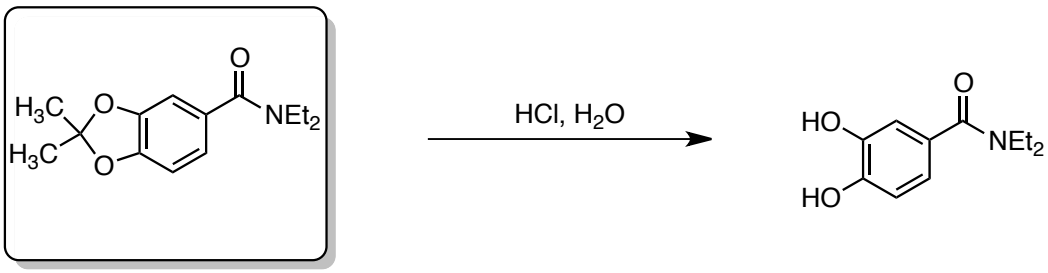


Name: _____

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

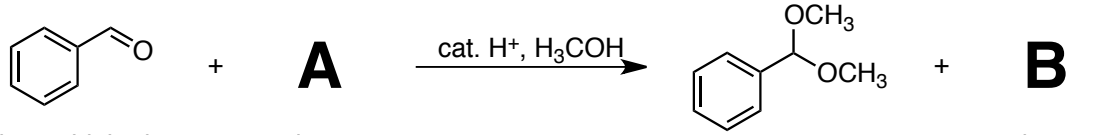






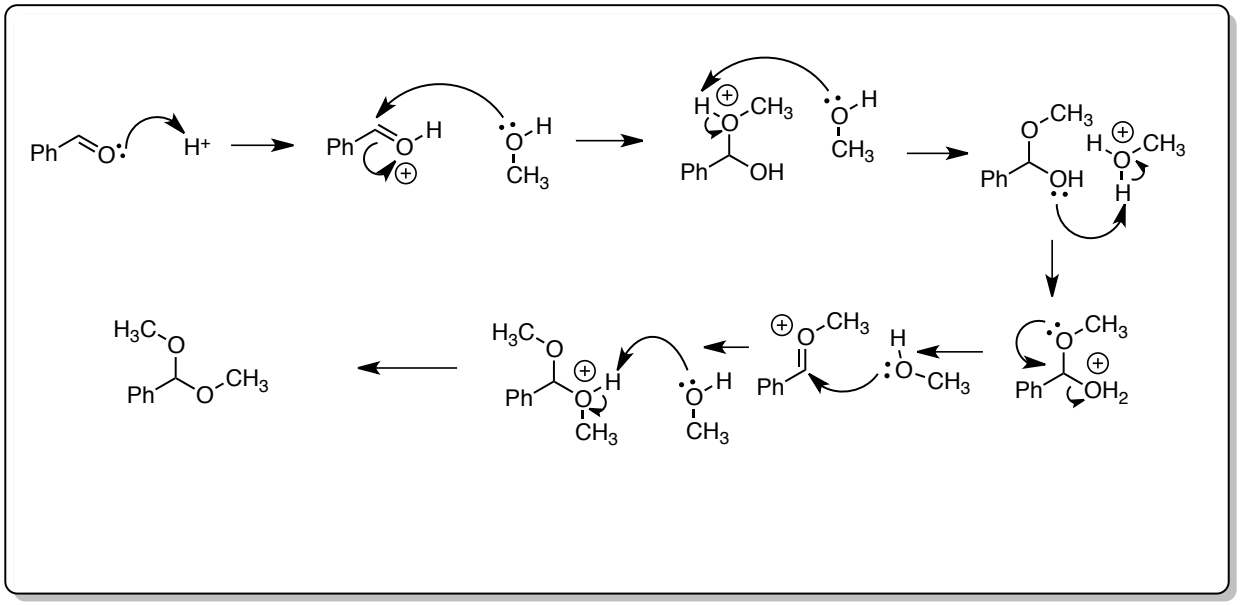
Name: _____

5. (50 points) Dr. Oops wanted to prepare the dimethyl acetal of benzaldehyde. She found an old bottle of benzaldehyde on her lab shelf and ran the following reaction. She observed 2 products from this reaction. Confused, she checked her starting material (benzaldehyde) 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.



benzaldehyde | unknown impurity ($C_7H_6O_2$) | benzaldehyde dimethyl acetal (desired product) | unknown product ($C_8H_8O_2$)

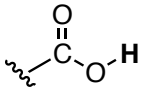
(a) Please draw a reasonable arrow-pushing mechanism for the formation of benzaldehyde dimethyl acetal from benzaldehyde (i.e., Dr. Oops' desired reaction).



(b) For impurity **A**, what does the IR peak at 1690 cm^{-1} indicate?

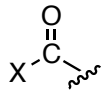
C=O

(c) For impurity **A**, what does the ^1H NMR peak at ~ 12 ppm indicate?



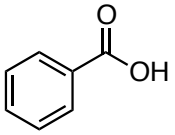
Name: _____

(d) For impurity **A**, what does the ^{13}C NMR peak at 172 ppm indicate?

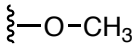


X = heteroatom (in this problem, an oxygen)

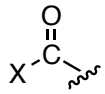
(e) What is the structure of impurity **A**?



(f) For product **B**, what does the ^{1}H NMR peak at 3.9 ppm indicate?

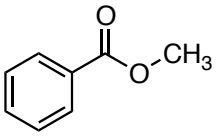


(g) For product **B**, what does the ^{13}C NMR peak at 168 ppm indicate?



X = heteroatom (in this problem, an oxygen)

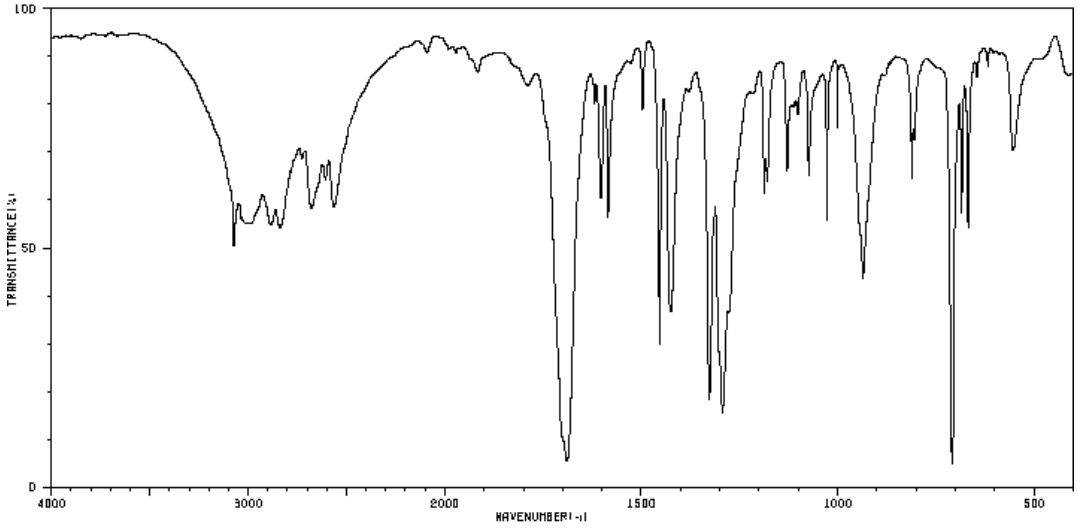
(h) What is the structure of product **B**?



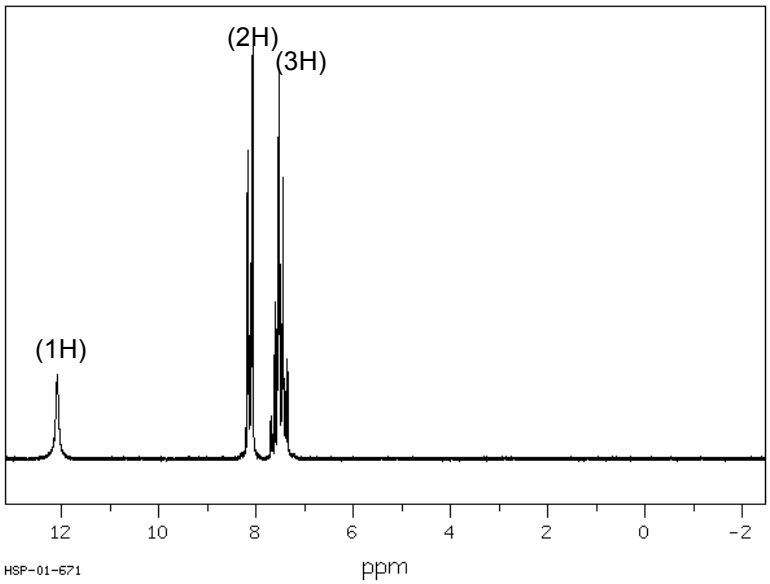
Name: _____

Unknown Impurity A:

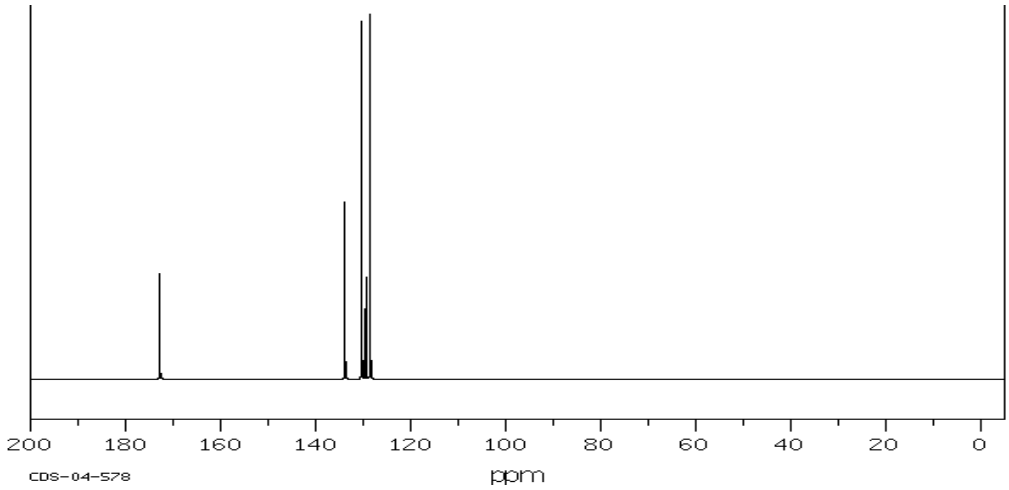
IR



^{1}H NMR



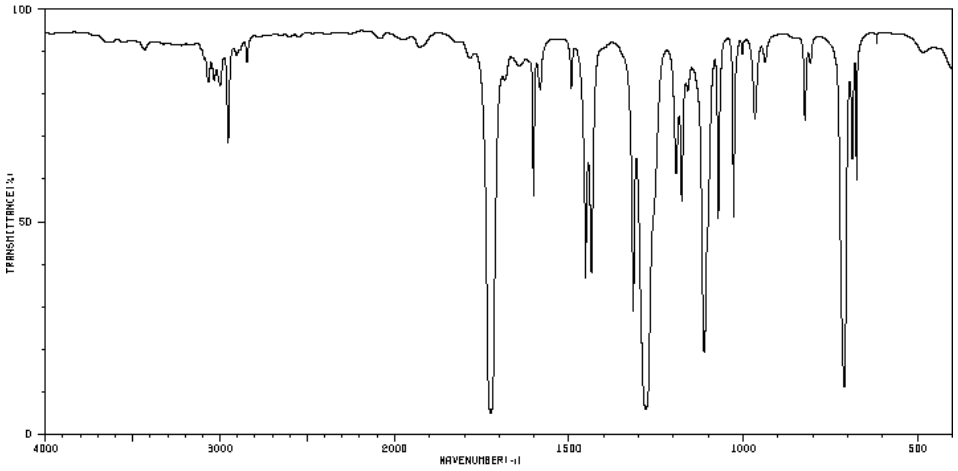
^{13}C NMR



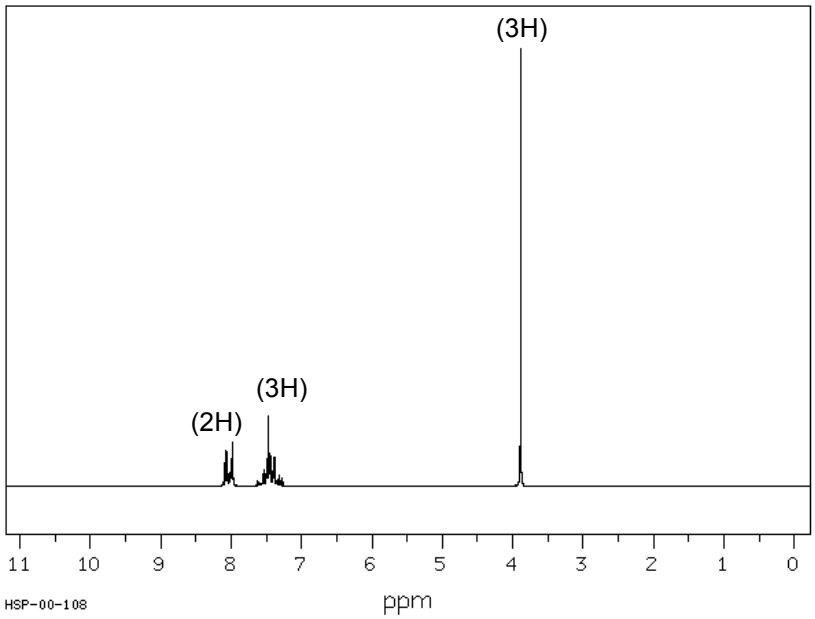
Name: _____

Unknown Product B: _____

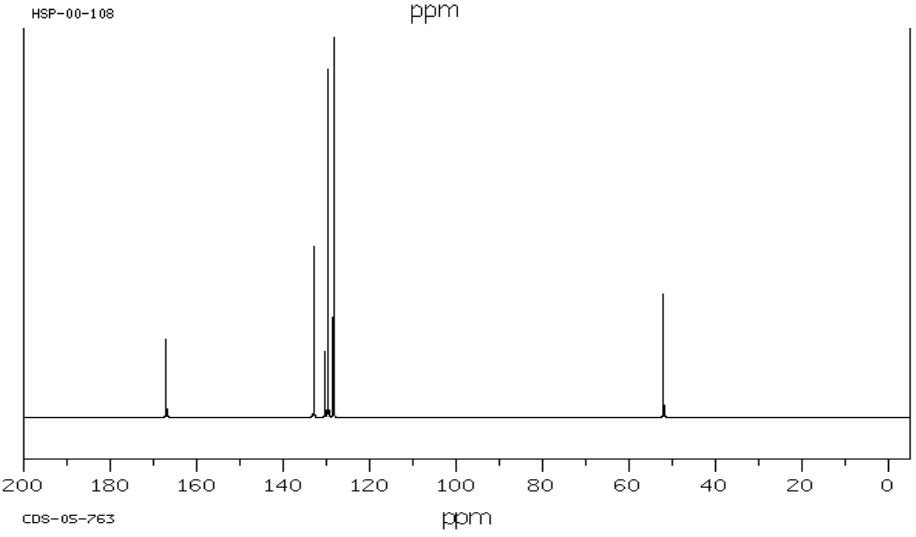
IR



^{1}H NMR

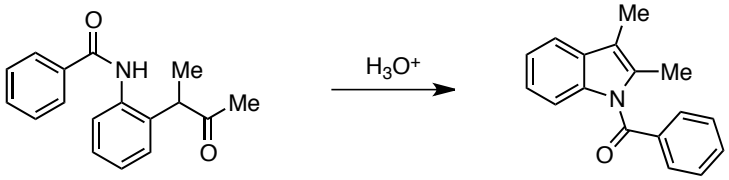


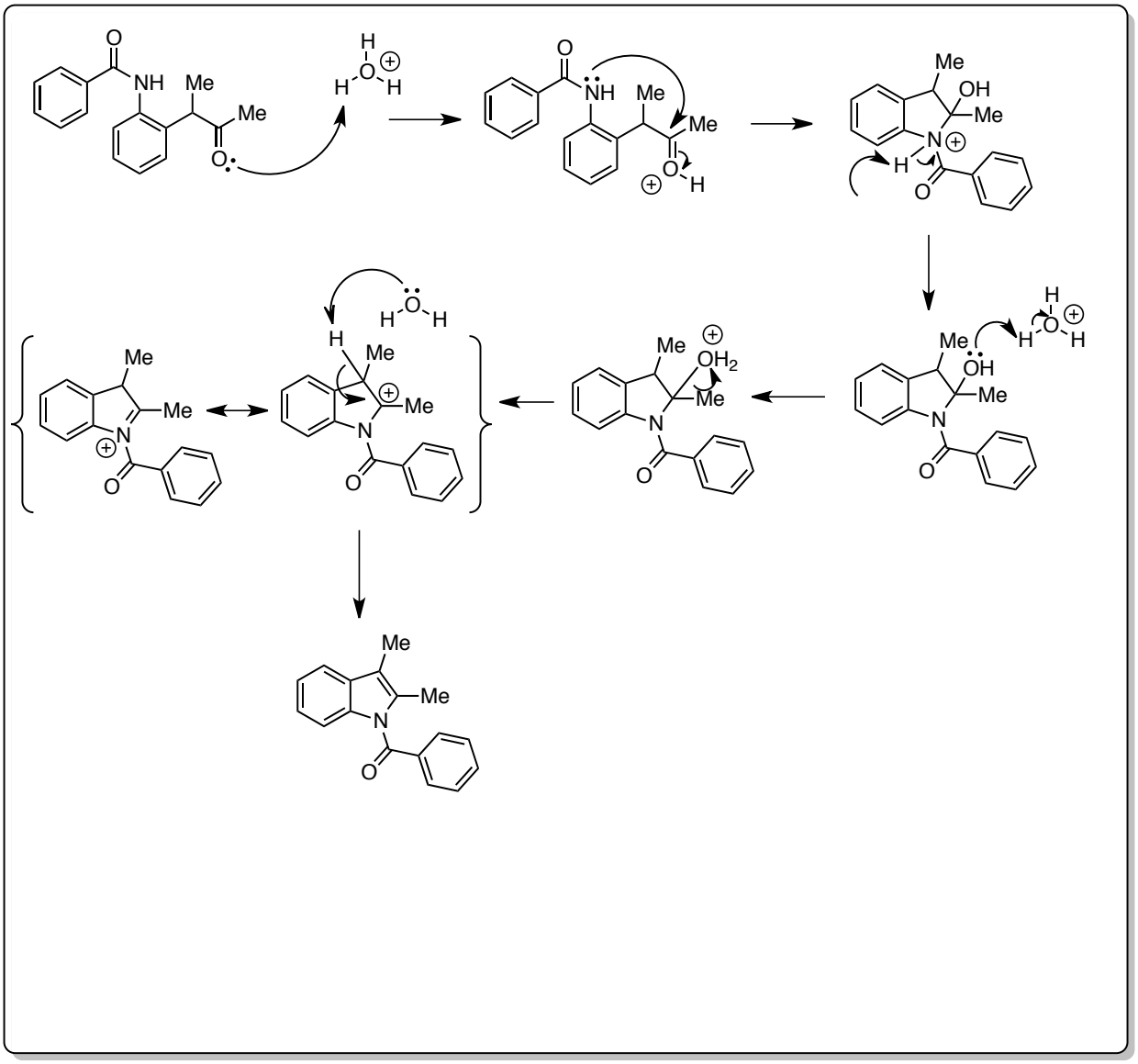
^{13}C NMR



Name: _____

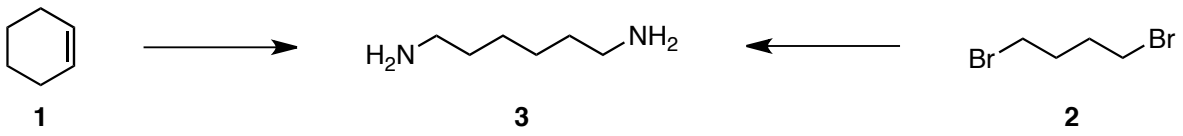
6. (24 points) Please provide a reasonable arrow-pushing mechanism for the following reaction.





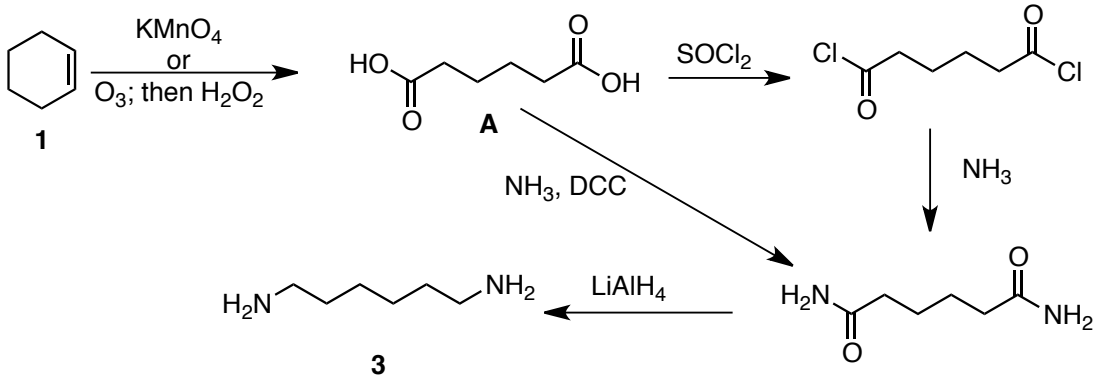
Name: _____

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



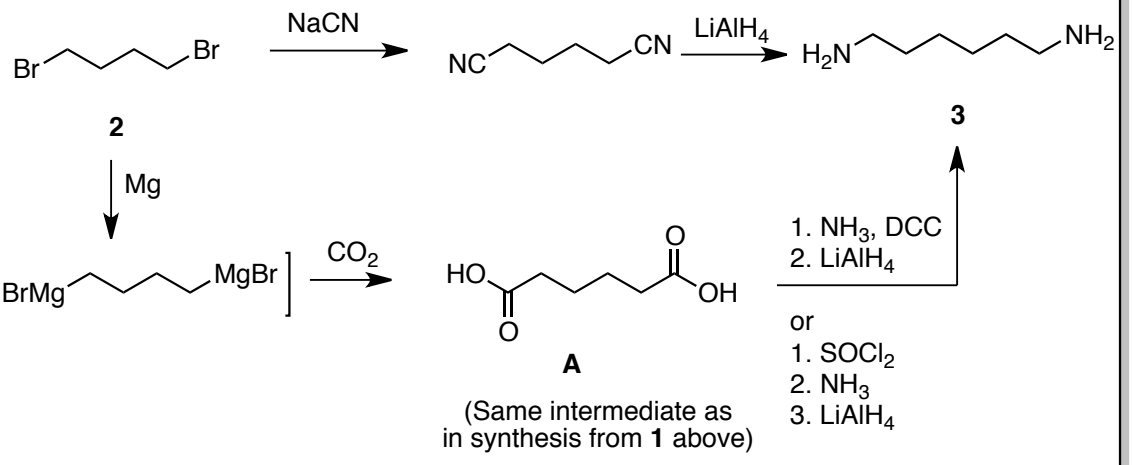
1 **3** **2**

From **1**:



1 **A** **3**

From **2**:



2 **3**

(Same intermediate as in synthesis from **1** above)

Please note: No arrow-pushing mechanism was required for this question.

Name: _____

Approximate IR Absorption Frequencies

Bond	Frequency (cm^{-1})	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

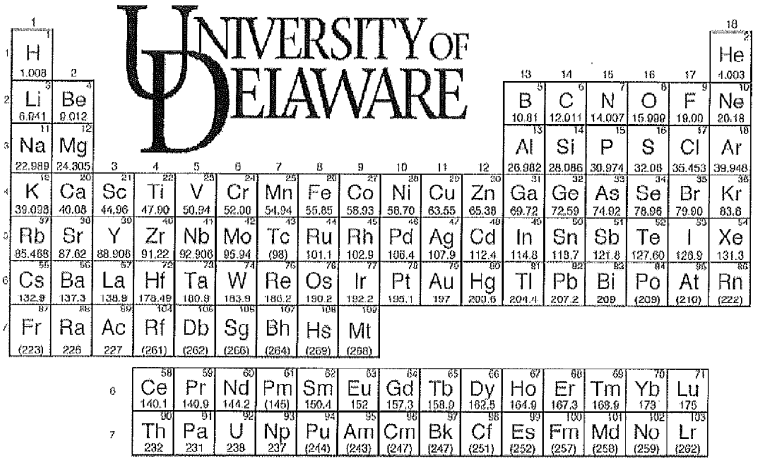
Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
$C=C–CH_x$	1.7–2.3
$O=C–CH_x$	2.0–2.7
$Ph–CH_x$	2.3–3.0
≡C–H	2.5
$R_2N–CH_x$	2.0–2.7
$I–CH_x$	3.2
$Br–CH_x$	3.4
$Cl–CH_x$	3.5
$F–CH_x$	4.4
$O–CH_x$	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_x	0.5–5.0
$CONH_x$	5.0–10.0
RCOOH	10–13

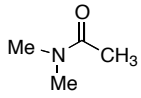
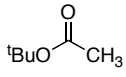
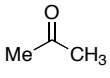
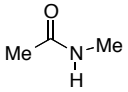
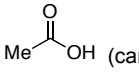
Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	–20–10
Carbonyls, C=O	
$R_2C=O$	190–220
RXC=O (X = O or N)	150–180

Name: _____



pKa TABLE

compound	pKa
Bu-H	48
Ph-H	43
H_2	~36
iPr_2N-H	~35
 (amide α-H)	25
 (ester)	24
 (ketone)	17-20
 (amide N-H)	~18
iPrOH	16-18
H_2O	16
Et_3N-H$^+$	10
 (carboxylic acid)	-1-6
H_3O^+	–2
HCl	–8

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