CHEM 266 – Exam-1 **Name**_____

(February 22th, 2016)

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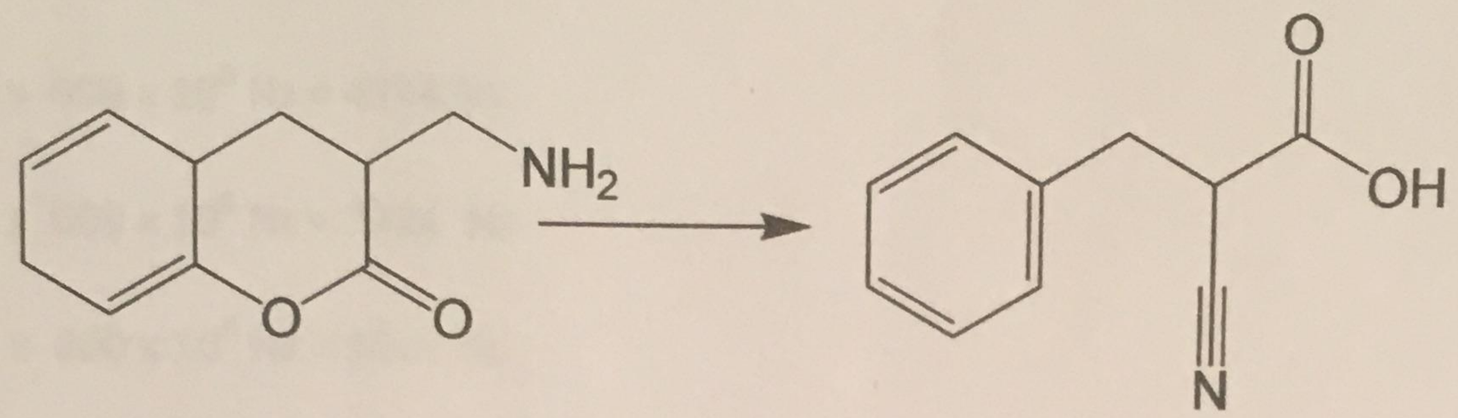

Reactant

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$\tilde{\upsilon}_{CHsp2}$ = 3050 cm^{-1}

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$\tilde{\upsilon}_{C=O}$ = 1750 cm^{-1}

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Explain (3 pts)

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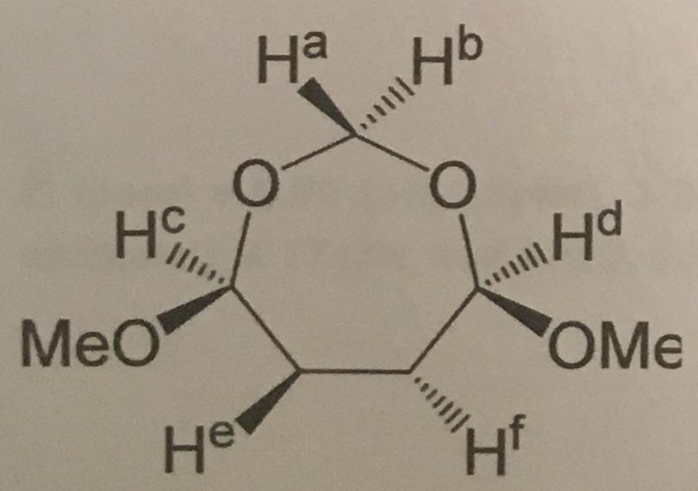

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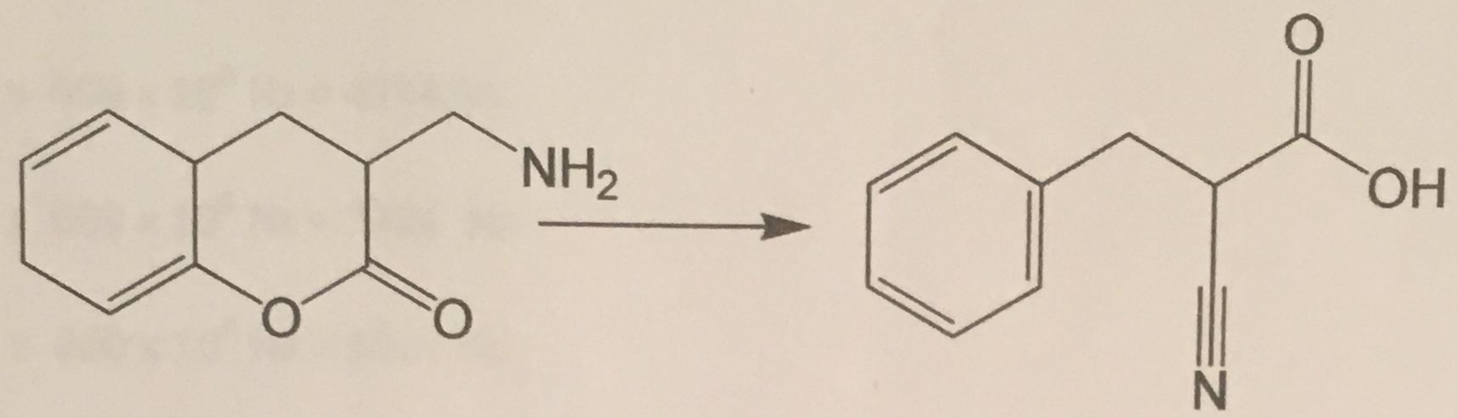

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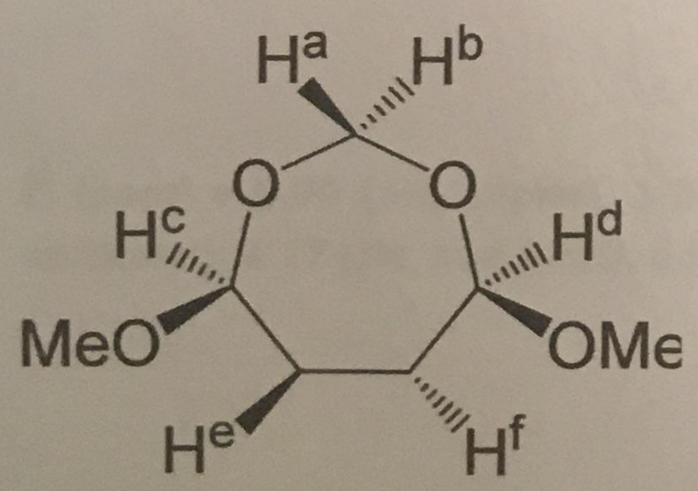

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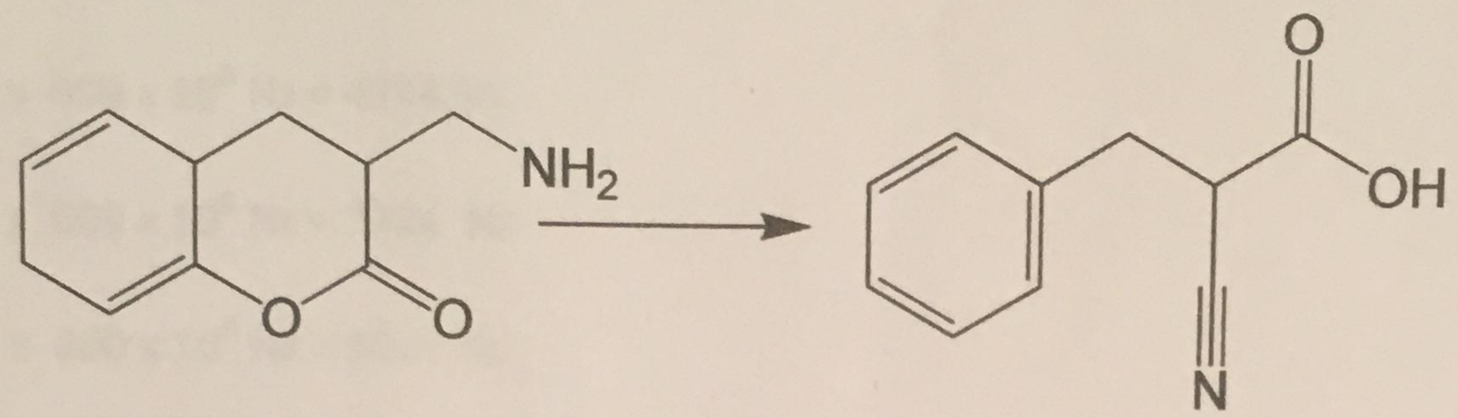

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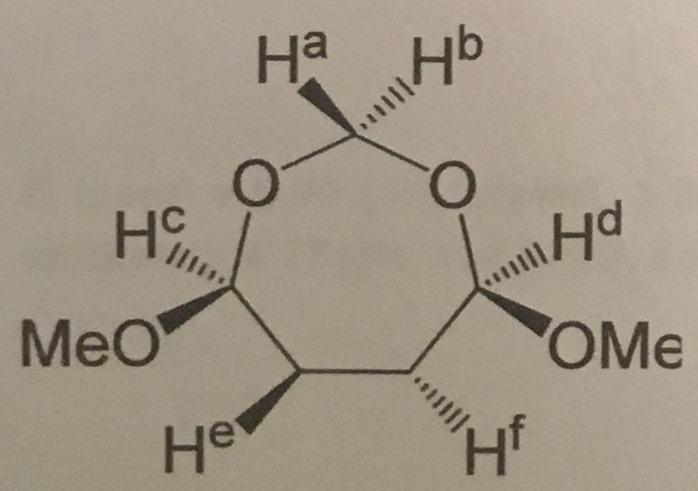

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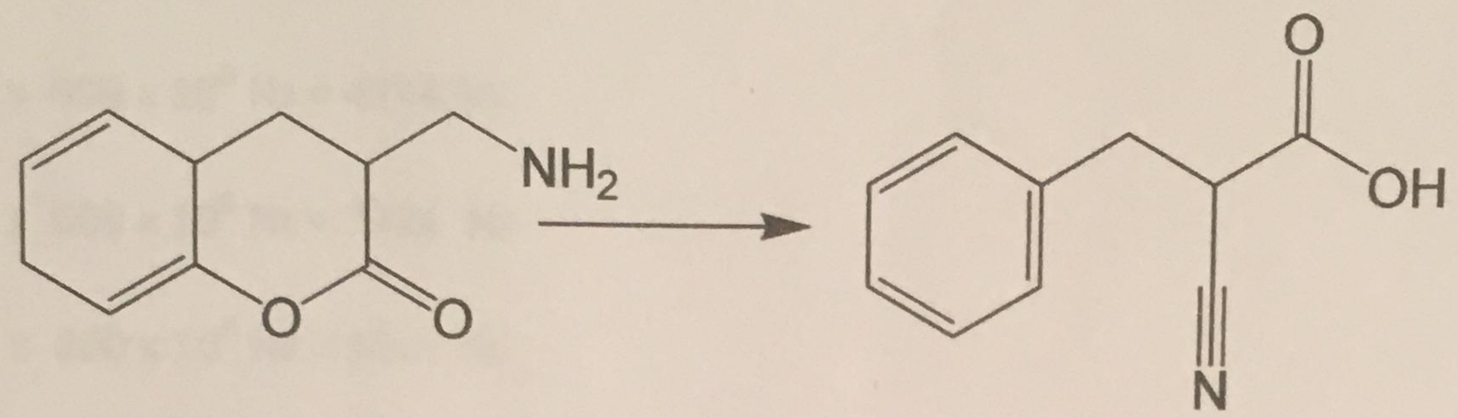

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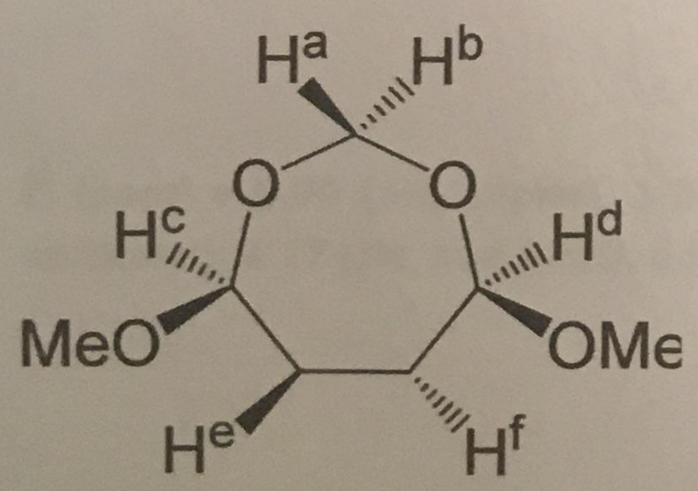

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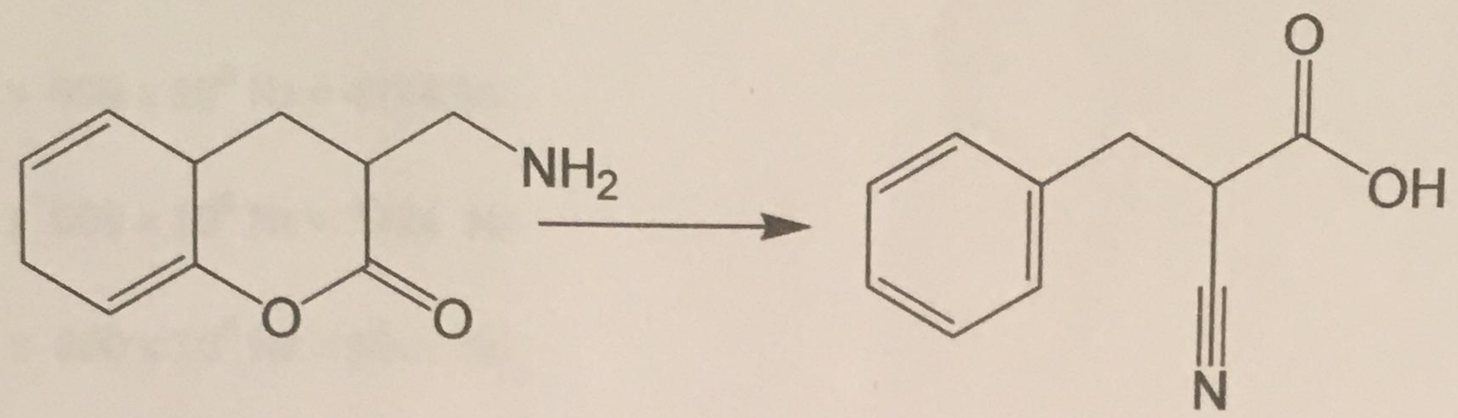

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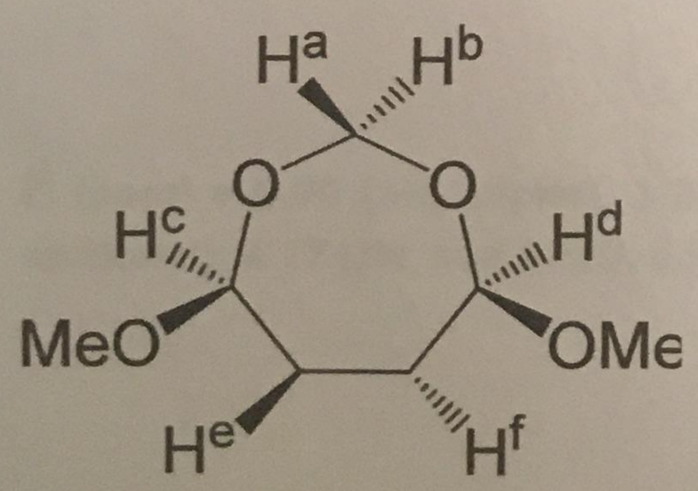

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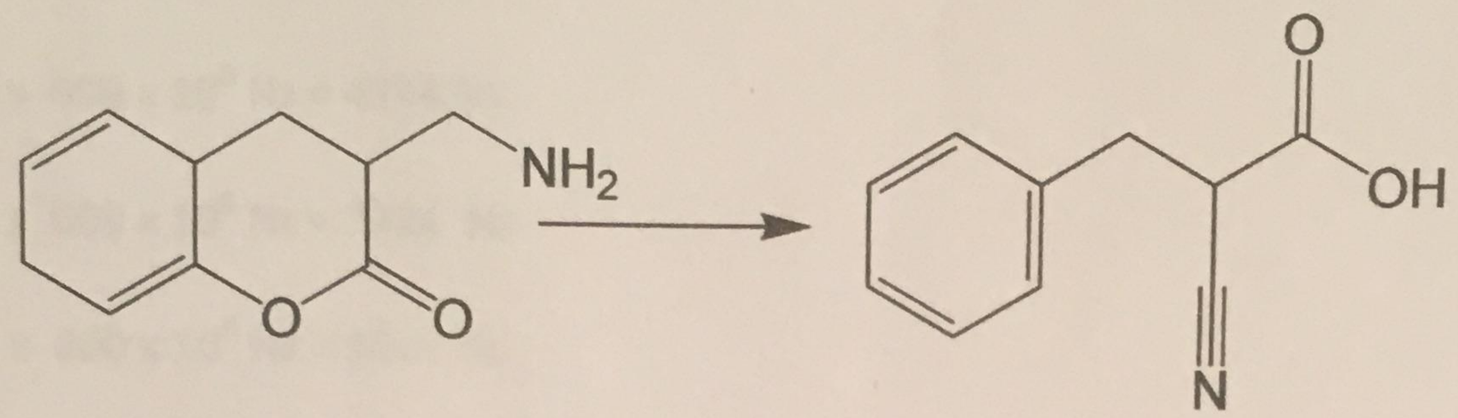

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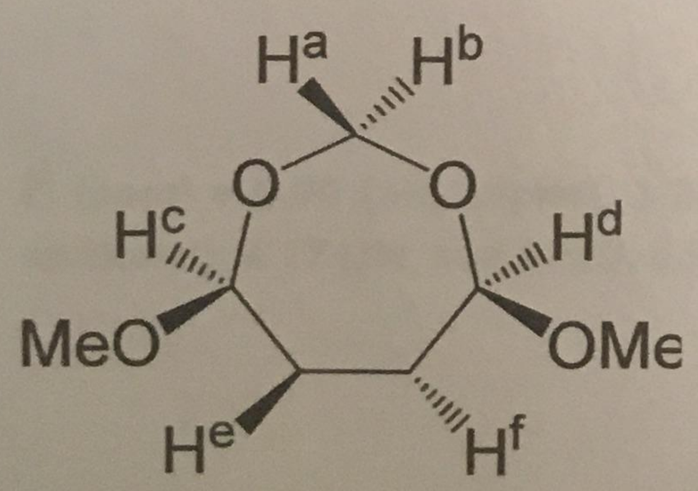

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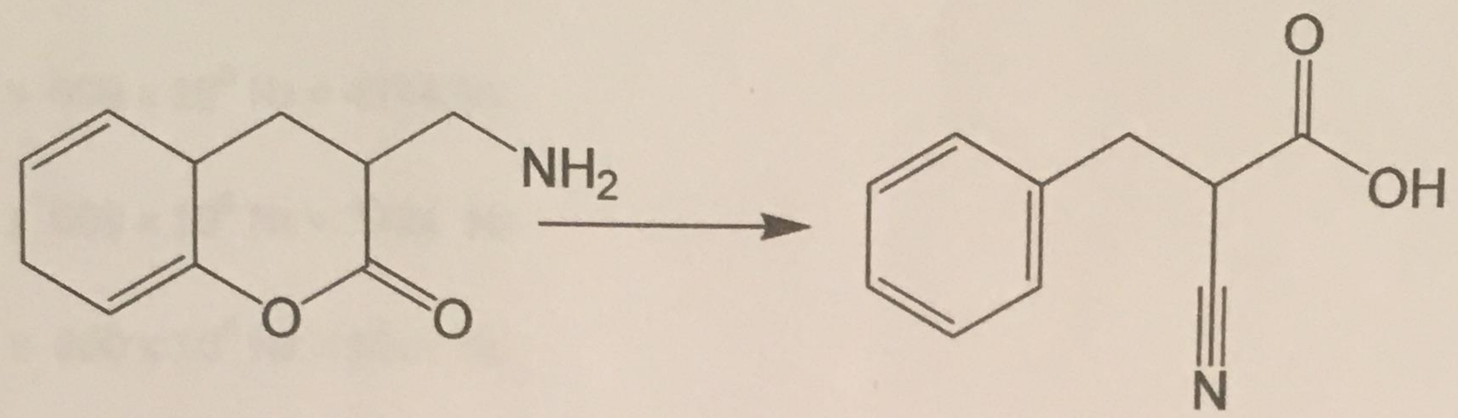

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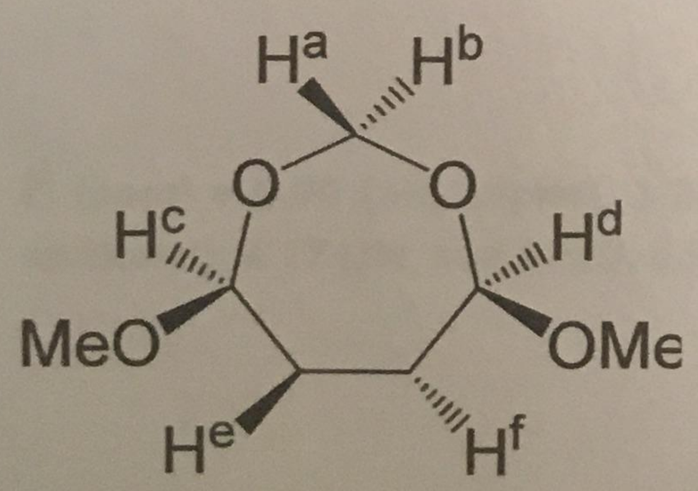

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3. A 600 MHz spectrometer records protons that absorb at 7.34 ppm, 6.86 ppm, 4.54 ppm, 1.78 ppm and 1.15 ppm. (10 pts)

(a) How far downfield (in hertz) from TMS would these protons absorb? (7.5 pts)

$\nu_1 = 7.34 \times 10^{-6} \times 600 \times 10^6$ Hz = 4404 Hz

$\nu_2 = 6.86 \times 10^{-6} \times 600 \times 10^6$ Hz = 4116 Hz

$\nu_3 = 4.54 \times 10^{-6} \times 600 \times 10^6$ Hz = 2724 Hz

$\nu_4 = 1.78 \times 10^{-6} \times 600 \times 10^6$ Hz = 1068 Hz

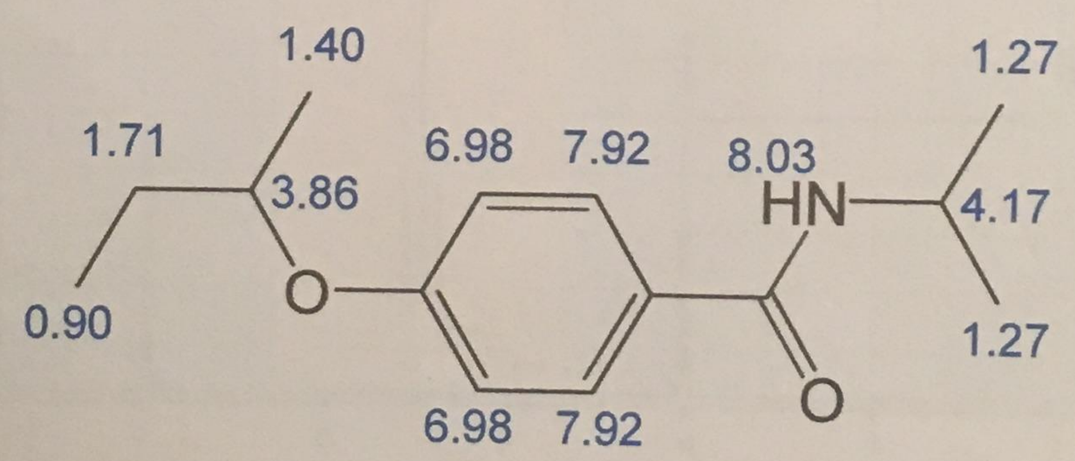
$\nu_5 = 1.15 \times 10^{-6} \times 600 \times 10^6$ Hz = 690 Hz

(b) If the spectrum was recorded on a 200 MHz spectrometer, what would be the chemical shifts for these protons in ppm? (2.5 pts)

The chemical shift will be the same:

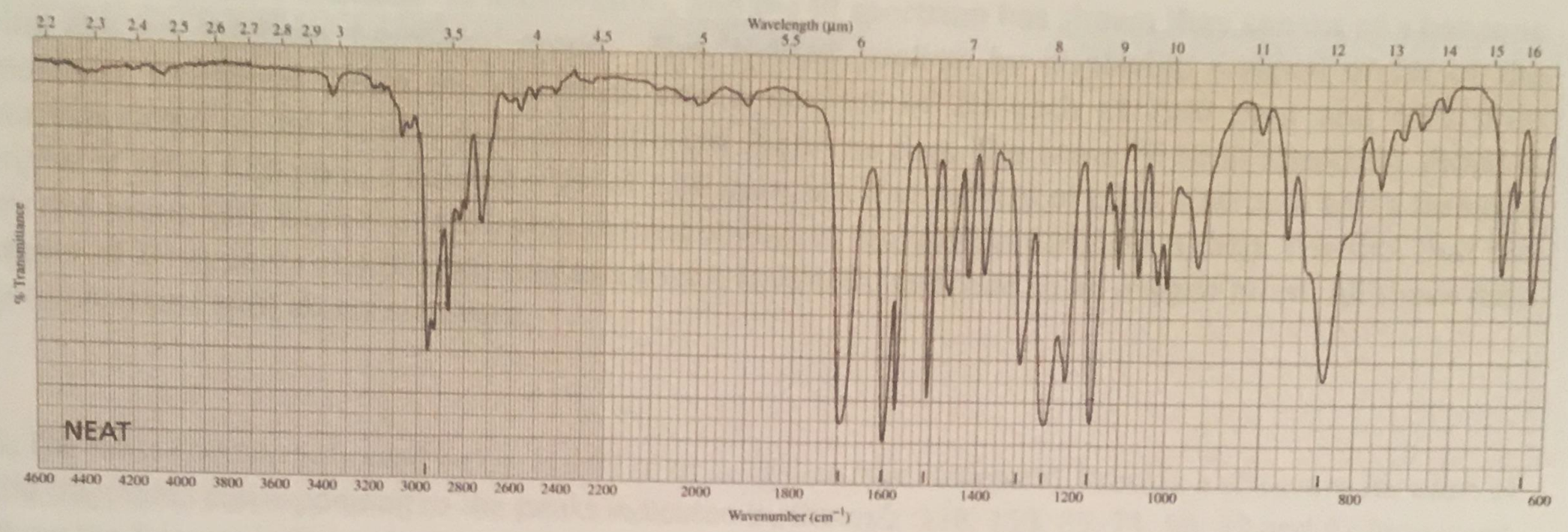
δ_1 = 7.34 ppm **δ_2 = 6.86 ppm** **δ_3 = 4.54 ppm** **δ_4 = 1.78 ppm** **δ_5 = 1.15 ppm**

4. Predict the number of signals expected, their splitting, their relative area and their relative intensity in the ^{1}H-NMR spectrum of the following compound. (9 pts)



δ (ppm) = 0.90 (3H, triplet), 1.27 (6H, multiplet), 1.40 (3H, doublet), 1.71 (2H, quintet), 3.86 (1H, multiplet), 4.17 (1H, multiplet), 6.98 (2H, doublet), 7.92 (2H, doublet), 8.03 (1H, broad singlet)

5. (a) Identify the major signals and the corresponding bonds vibration present in the compound having the following IR spectrum; Molecular formula $C_{11}H_{14}O_2$ (7.5 pts)



nl = 11 + 1 – ½ 14 = 5

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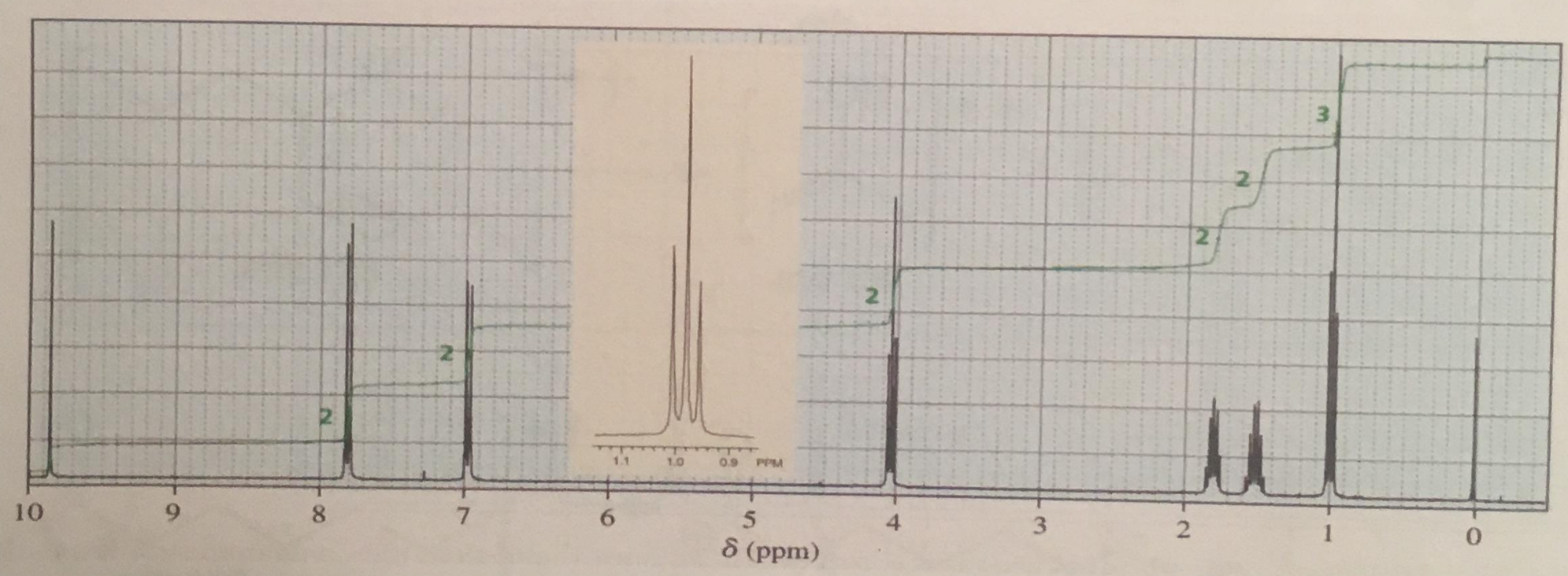
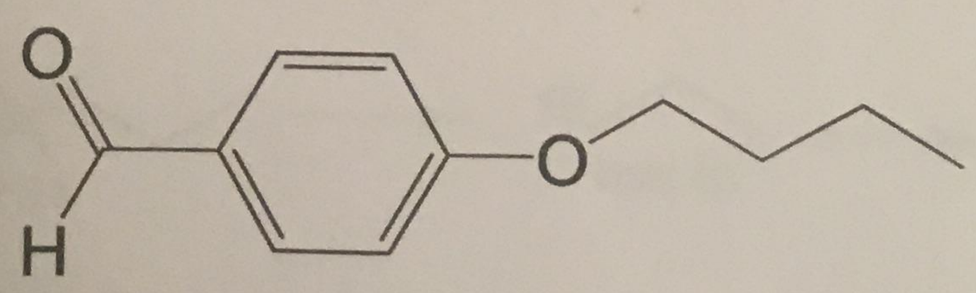
(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer.



Structure (4.5 pts)



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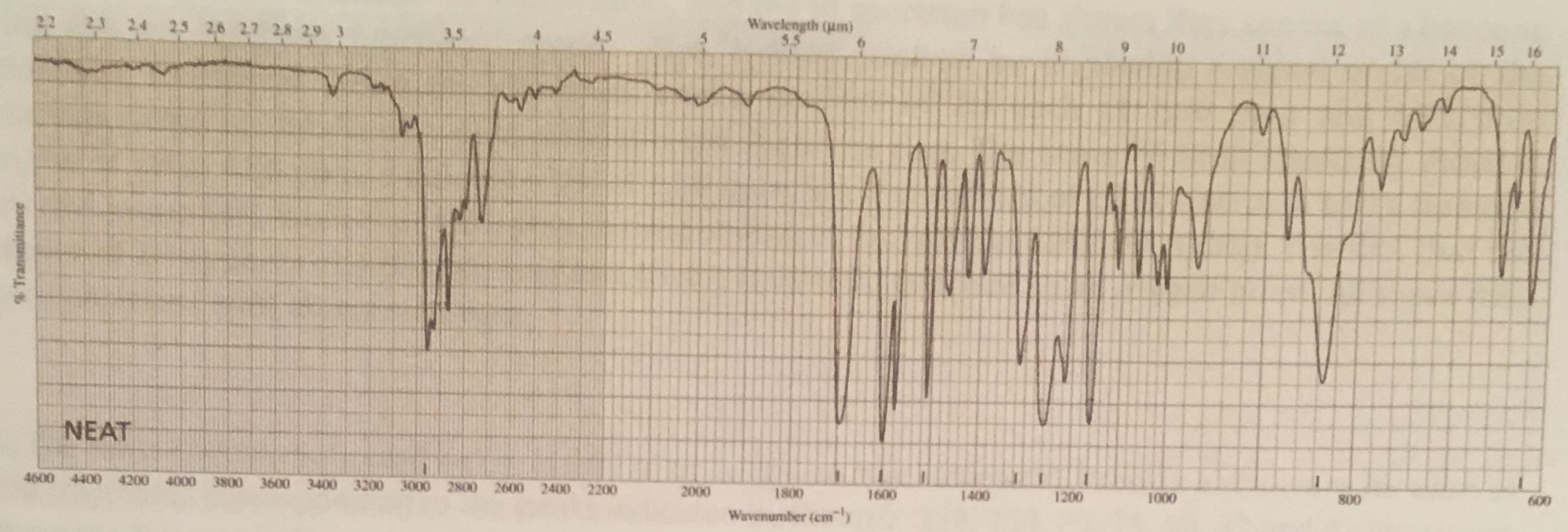

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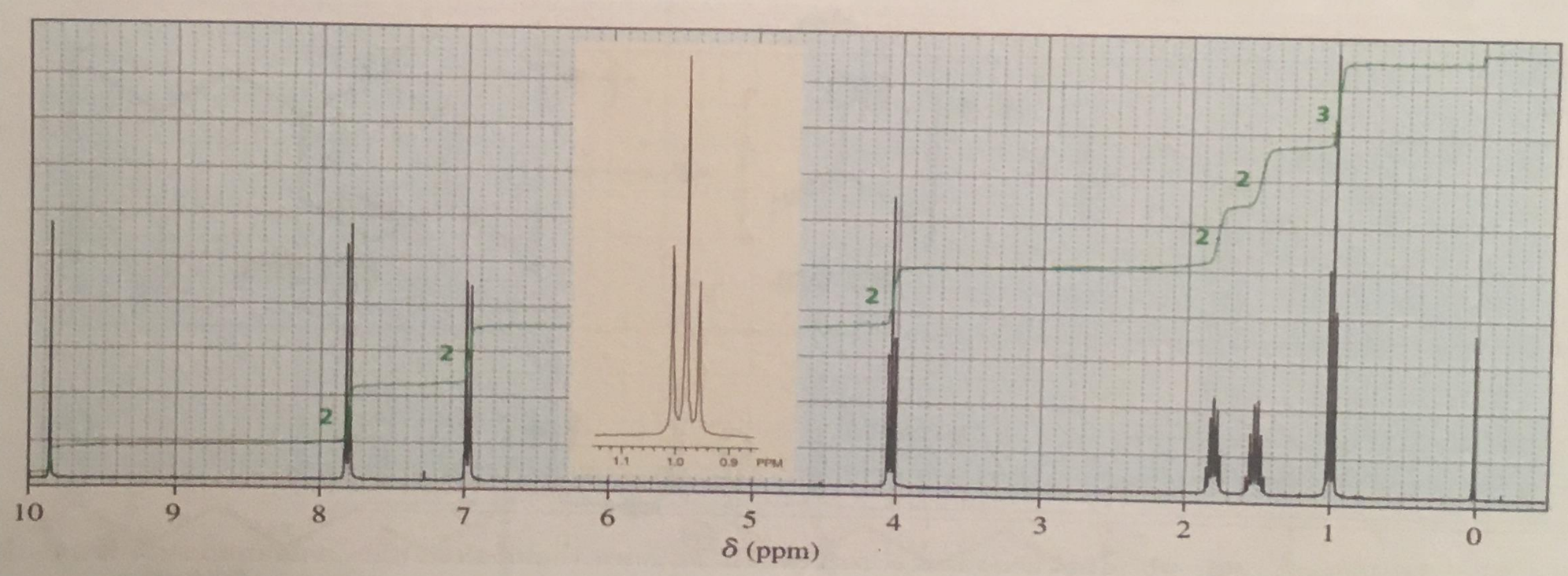
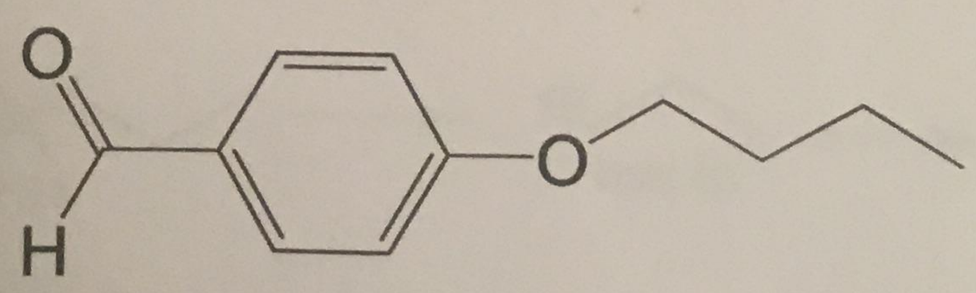
(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer.



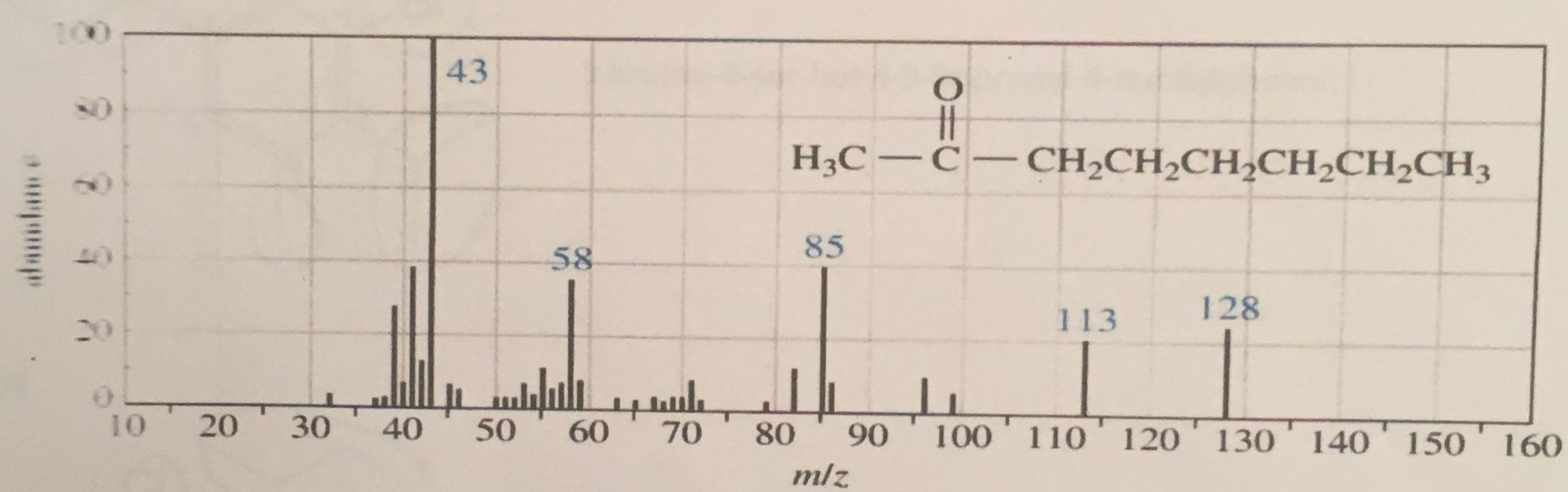
Structure (4.5 pts)

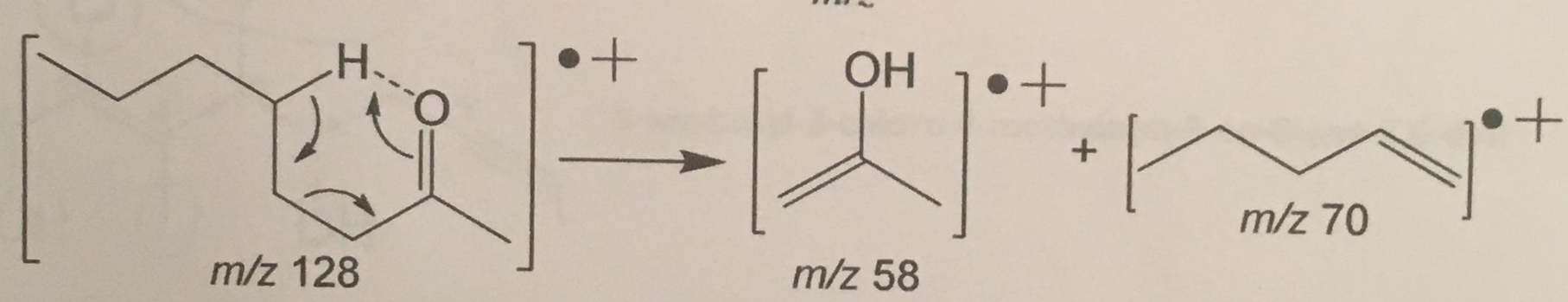


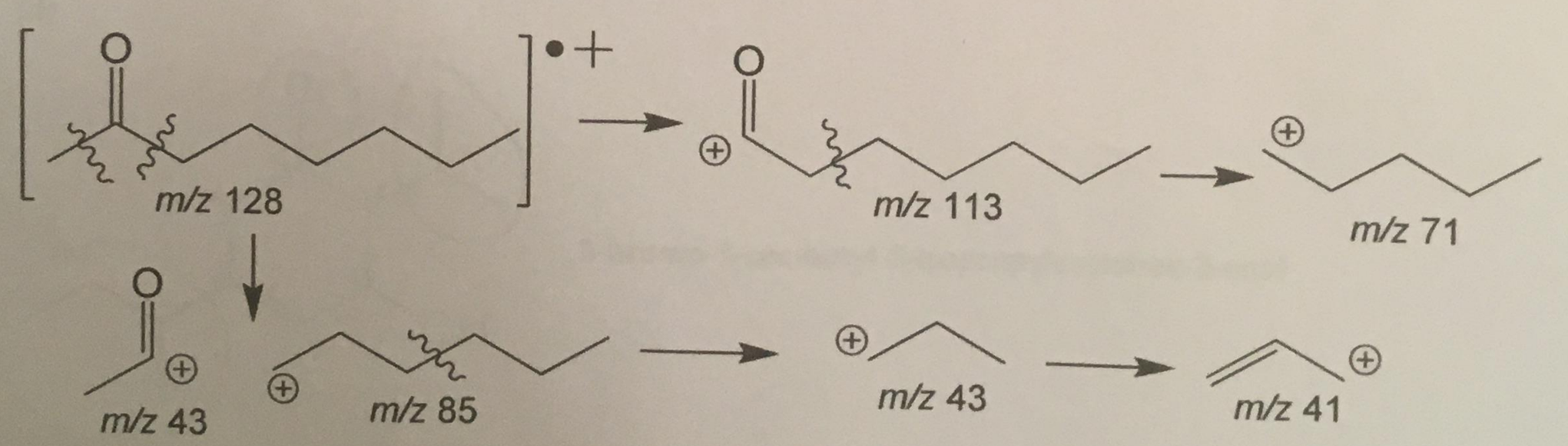
Explain (4 pts)

This molecule has 5 elements of insaturation, and the IR spectrum has shown they consist of a benzene ring and an aldehyde functional group. The ^{1}H-NMR confirm by displaying a signal of 1H of the aldehyde functional group at 9.85 ppm, and a doublet of 2H each at 7.80 ppm and 6.98 ppm corresponding to the 4H of a para-disubstituted benzene ring. The same ^{1}H-NMR spectrum shows a triplet of 2H at 4.05 ppm, a quintet of 2H at 1.80 ppm, another quintet of 2H at 1.50 ppm and a terminal methyl group (3H, triplet) at 1.01 ppm corresponding to an n-butyl ($CH_2CH_2CH_2CH_3$). The fact that the triplet of 2H appears at 4.05 ppm suggests that it is directly attached to an oxygen atom. All these data are consistent with above structure.

6. The mass spectrum showed below is that of octan-2-one (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 128, 113, 85, 71, 58, 43 and 41 (you must show the fragmentation pattern to receive full credit) (7 pts).



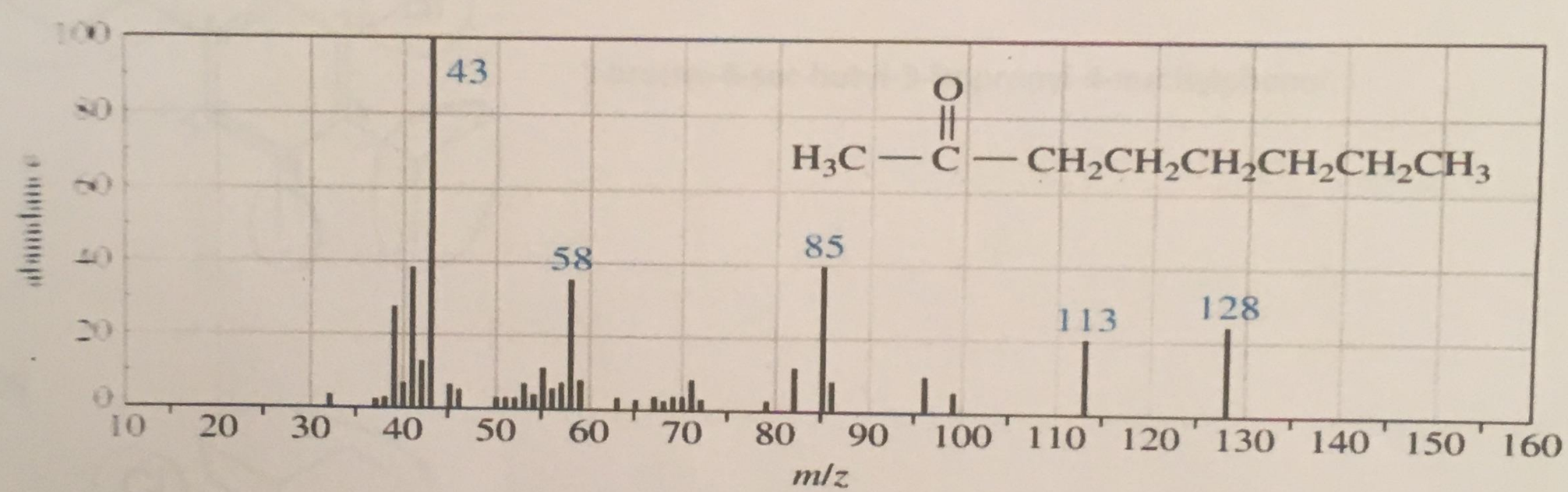


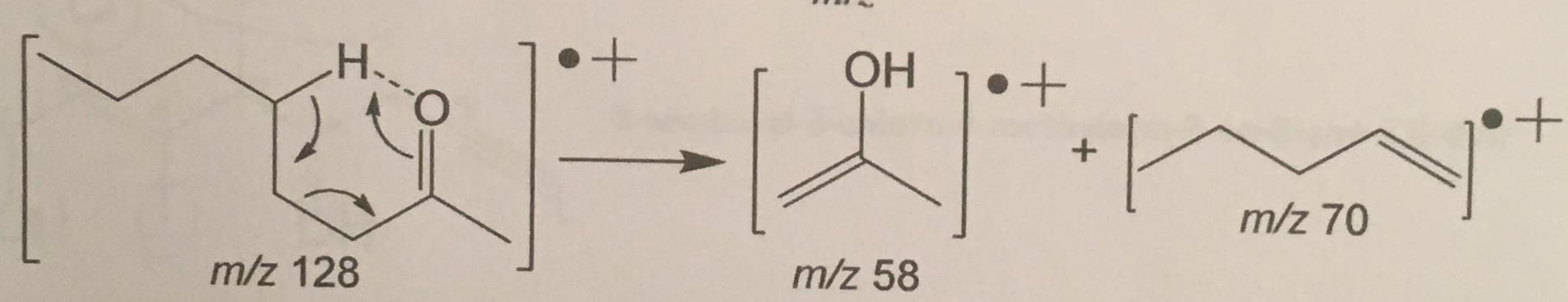


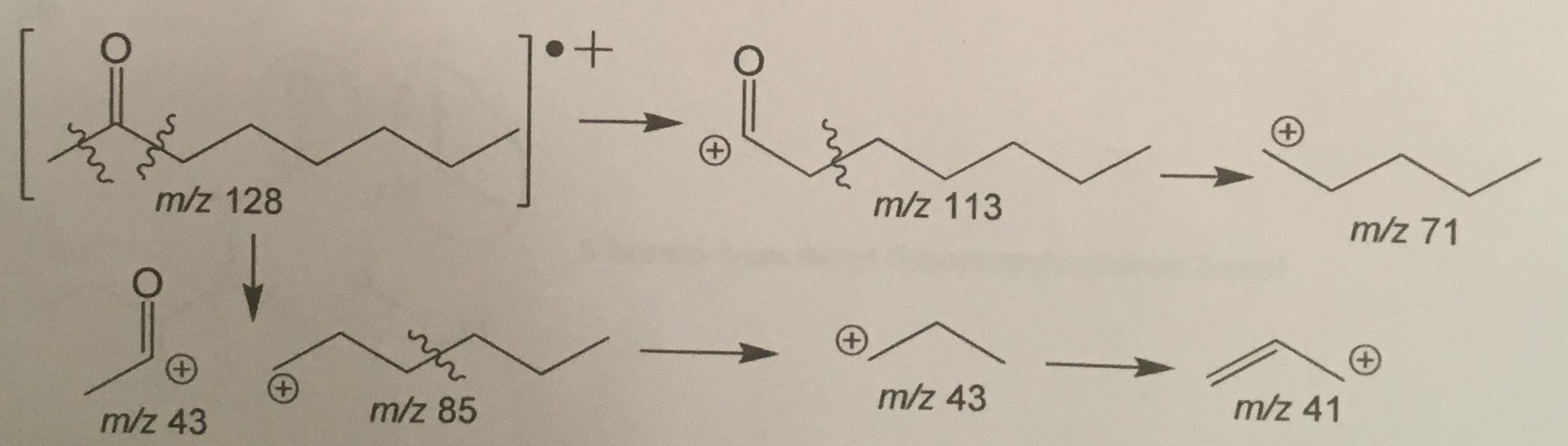
Explain (4 pts)

This molecule has 5 elements of insaturation, and the IR spectrum has shown they consist of a benzene ring and an aldehyde functional group. The ^{1}H-NMR confirm by displaying a signal of 1H of the aldehyde functional group at 9.85 ppm, and a doublet of 2H each at 7.80 ppm and 6.98 ppm corresponding to the 4H of a para-disubstituted benzene ring. The same ^{1}H-NMR spectrum shows a triplet of 2H at 4.05 ppm, a quintet of 2H at 1.80 ppm, another quintet of 2H at 1.50 ppm and a terminal methyl group (3H, triplet) at 1.01 ppm corresponding to an n-butyl ($CH_2CH_2CH_2CH_3$). The fact that the triplet of 2H appears at 4.05 ppm suggests that it is directly attached to an oxygen atom. All these data are consistent with above structure.

6. The mass spectrum showed below is that of octan-2-one (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 128, 113, 85, 71, 58, 43 and 41 (you must show the fragmentation pattern to receive full credit) (7 pts).

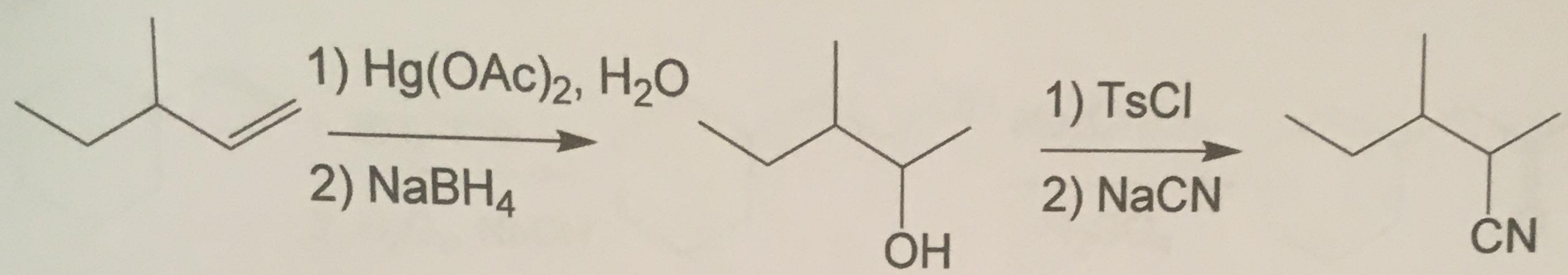




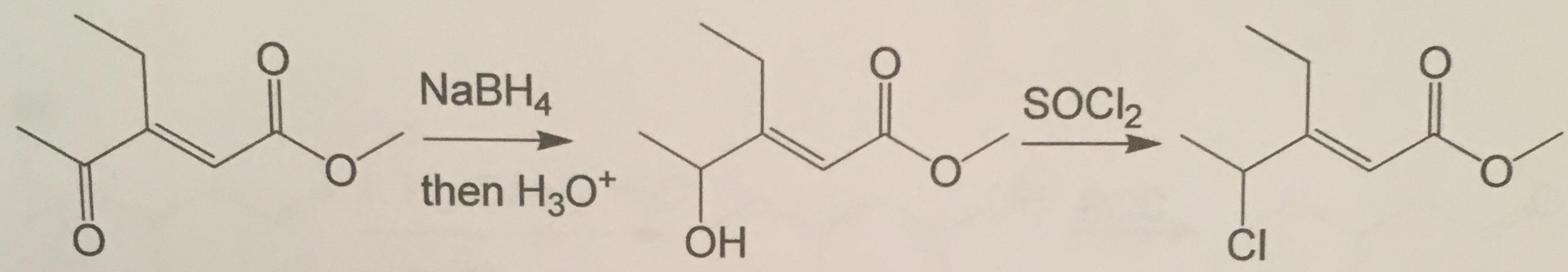


8. Predict the major product(s) expected from the following reaction sequences (3.5 x 6 = 21 pts)

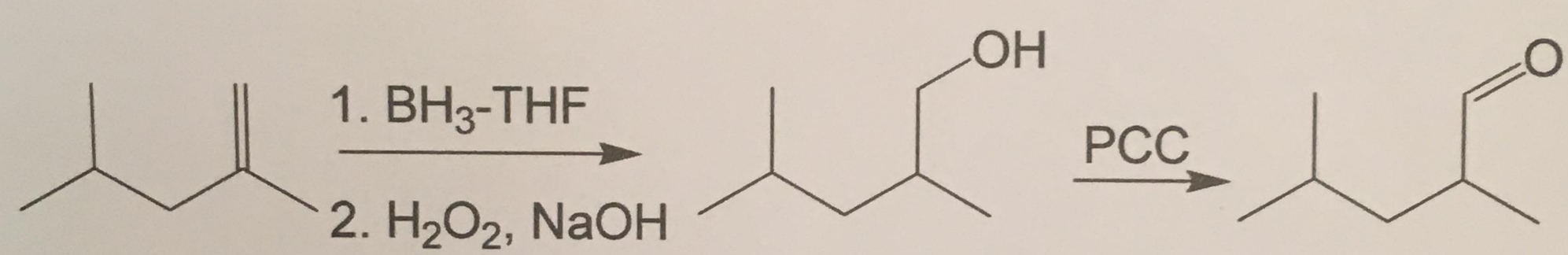
(a)



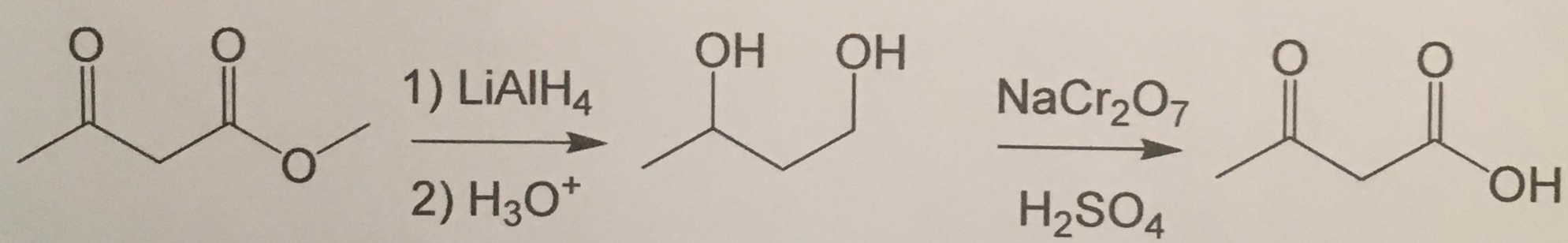
(b)



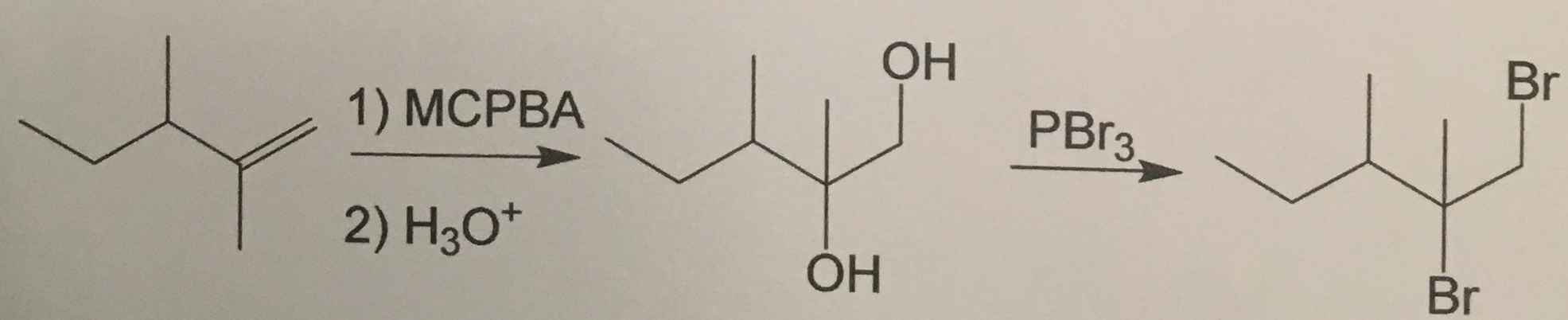
(c)



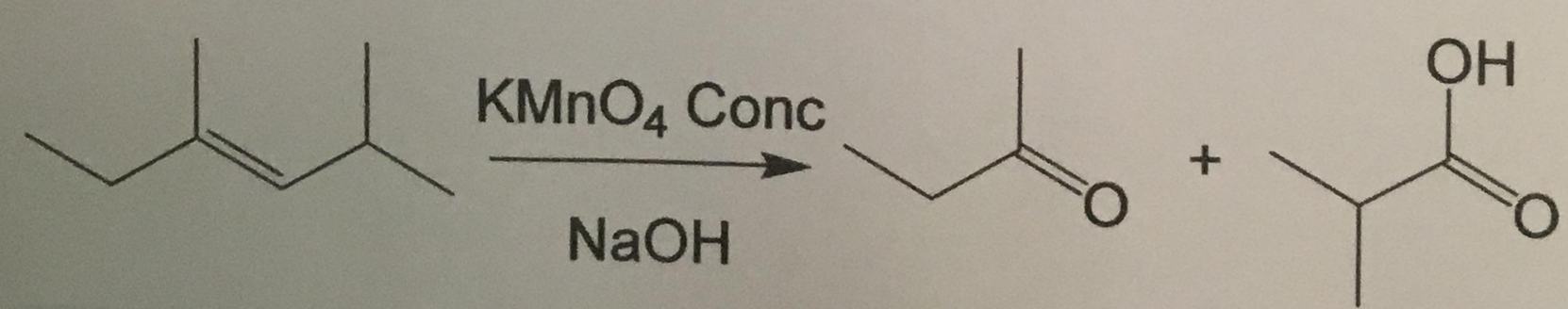
(d)



(e)

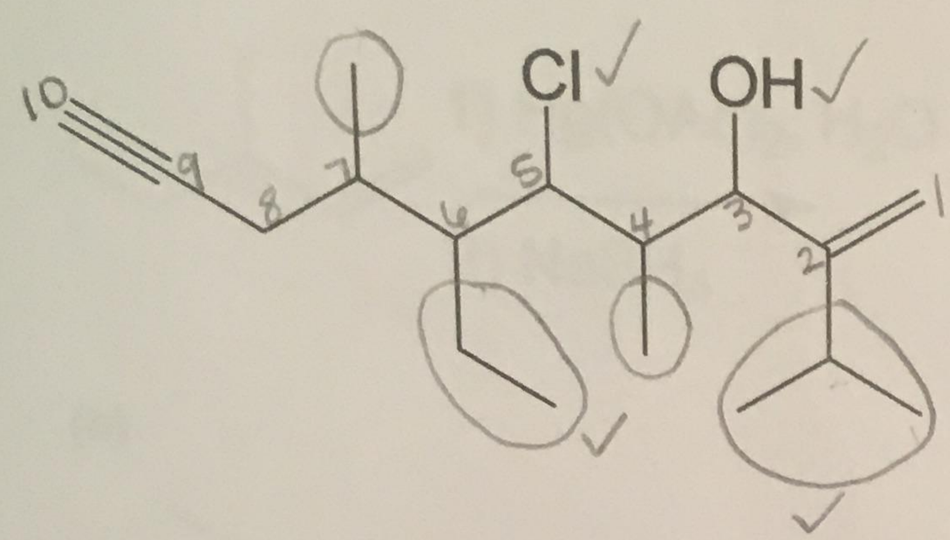


(f)



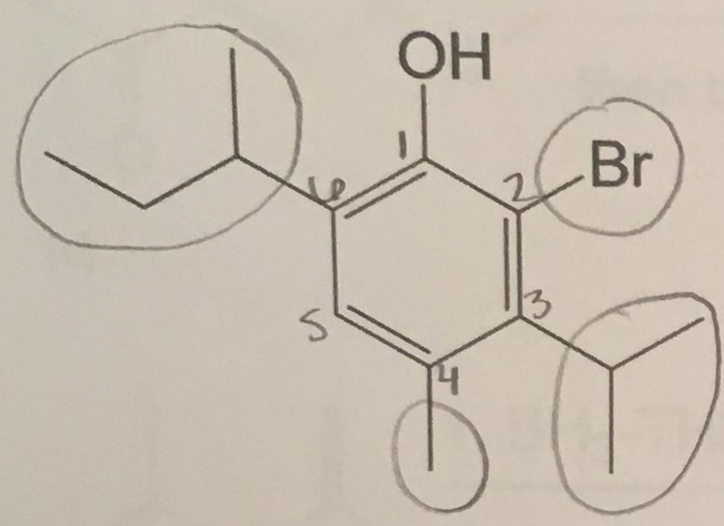
7. Name the following compounds (3 x 4 = 12 pts)

(a)



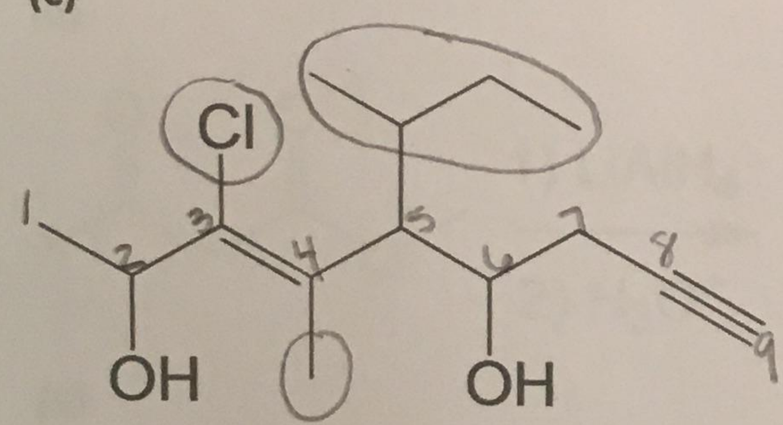
5-chloro-6-ethyl-2-isopropyl-4,7-dimethyldec-1-en-9-yn-3-ol

(b)



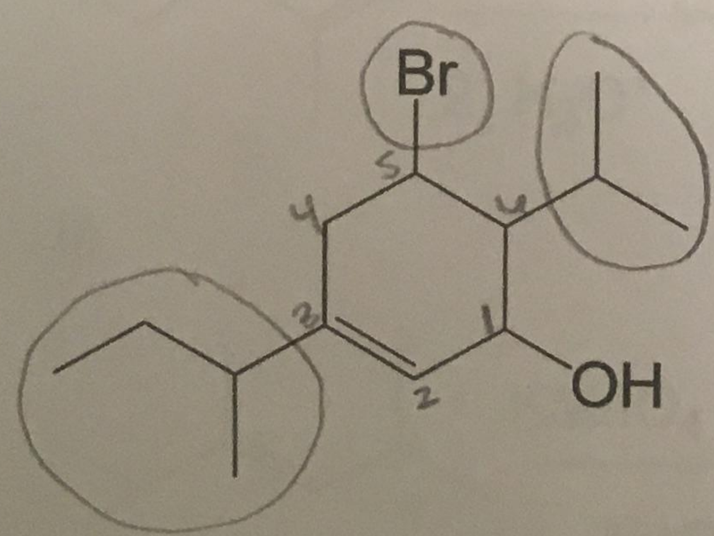
2-bromo-6-sec-butyl-3-isopropyl-4-methylphenol

(c)



5-sec-butyl-3-chloro-4-methylnon-3-en-8-yne-2,6-diol

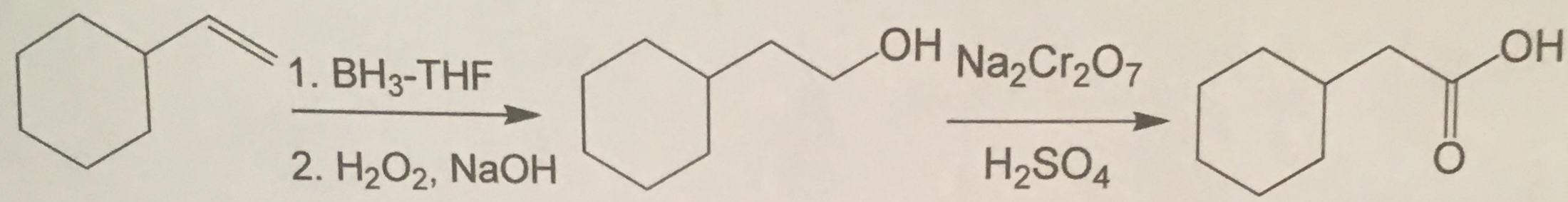
(d)



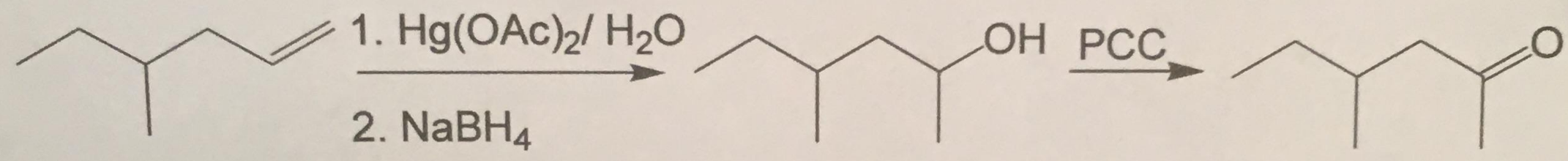
5-bromo-3-sec-butyl-6-isopropylcyclohex-2-enol

9. Show how you would synthesize each of the following compounds from the given starting material(s). You must draw keys intermediates to receive full credit (3 x 2 = 6 pts).

(a)



(b)



3- Circle the compound that you would be expected to show intense IR absorption at 3328, 3312, 2950, 1660 cm^{-1}? (4 pts)

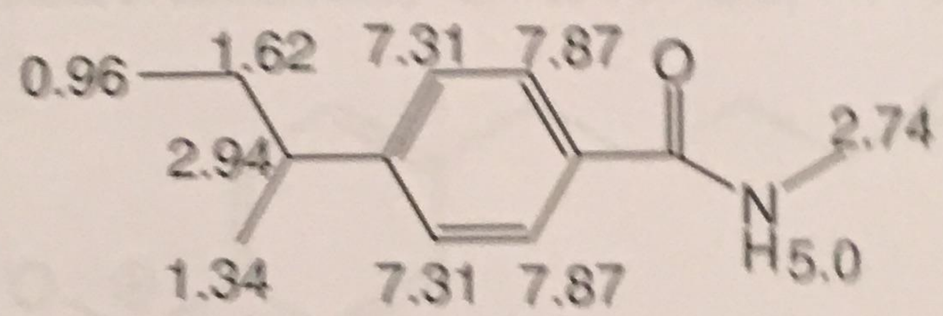
A) $CH_3CH_2COCH_2NH_2$ B) $(CH_3)_2CHNH_2$ C) $CH_3CH_2CONH_2$ D) $CH_3CH_2COCH_2OH$

4- Both $C_6H_9N_2$ and C_6H_7NO have the same nominal mass (109 $gmol^{-1}$). Show how these compounds can be distinguished by the *m/z* ratio of their molecular ions in a high-resolution mass spectrometry experiment (C 12.0107 $gmol^{-1}$, H 1.00794 $gmol^{-1}$, N 14, 0067 $gmol^{-1}$, O 15.9994 $gmol^{-1}$) (5 pts)

$C_6H_9N_2$ = 109.14906
C_6H_7NO = 109.12588

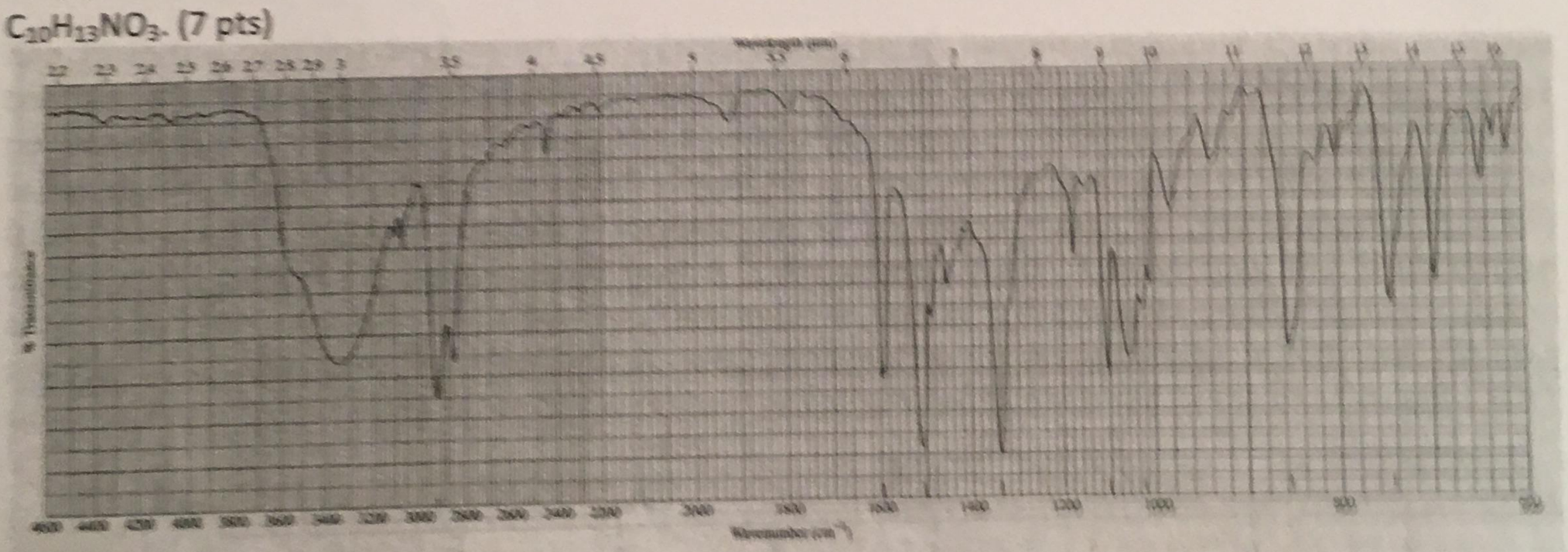
With the normal mass spectrum, there is no decimal to the mass value obtained, in which case the tow molecules show the exact same mass at 109 g. However, at high resolution, the values obtained could have up to 5 decimals; in that case, the two compounds are different in mass, and thus distinguishable.

5- Predict the number of signals expected, their chemical shifts, their splitting, and their relative area in the ^1H NMR spectrum of the following compound (8 pts)



δ(ppm): 0.96 (3H, triplet), 1.34 (3H, doublet), 1.62 (2H, quintet), 2.74 (3H, s), 2.94 (1H, quintet), 5.0 (1H, brs, NH), 7.31 (2H, doublet), 7.87 (2H, doublet).

6- (a) Identify the major signals present in the following IR spectrum; the Molecular formula is $C_{10}H_{13}NO_3$. (7 pts)

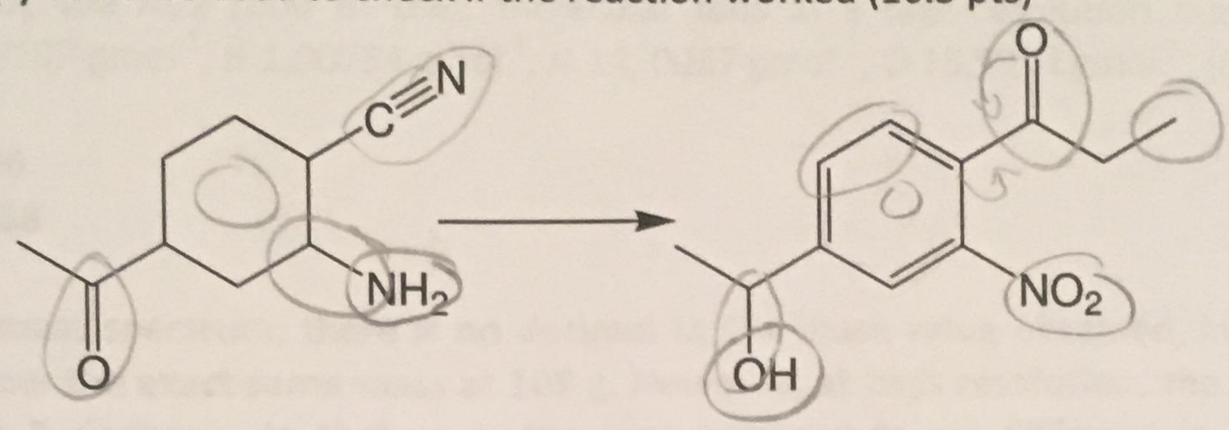


$\bar{\upsilon}_{OH}$ = 3500 cm^{-1}; $\bar{\upsilon}_{CHsp2}$ = 3100 cm^{-1}; $\bar{\upsilon}_{CHsp3}$ = 2950 cm^{-1}; $\bar{\upsilon}_{C=C}$ = 1600 cm^{-1};
$\bar{\upsilon}_{NO2}$ = 1500 and 1300 cm^{-1}; $\bar{\upsilon}_{CO}$ = 1100 cm^{-1} $\bar{\upsilon}_{CH_bending_aromatic}$ = 600 - 800 cm^{-1}

CHEM 266 – EXAM 1 **NAME**_____**Keys**_____

February 19 (Spring 2014)

1- You have just performed the following transformation in the lab; predict the type of bonds corresponding to the major signals found in the IR spectra of both the product and the reactant. Explain how IR spectroscopy could be used to check if the reaction worked (10.5 pts)



Reactant

$\ddot{U}_{NH}$ = 3500 and 3300 cm^{-1}

$\ddot{U}_{CHsp3}$ = 2950 cm^{-1}

$\ddot{U}_{CN}$ = 2200 cm^{-1}

$\ddot{U}_{C=O}$ = 1760 cm^{-1}

$\ddot{U}_{C-N}$ = 1200 cm^{-1}

Product

$\ddot{U}_{OH}$ = 3500 cm^{-1}

$\ddot{U}_{CHsp2}$ = 3010 cm^{-1}

$\ddot{U}_{CHsp3}$ = 2950 cm^{-1}

$\ddot{U}_{C=O}$ = 1680 cm^{-1}

$\ddot{U}_{C=C}$ = 1600 cm^{-1}

$\ddot{U}_{No2}$ = 1500 and 1300 cm^{-1}

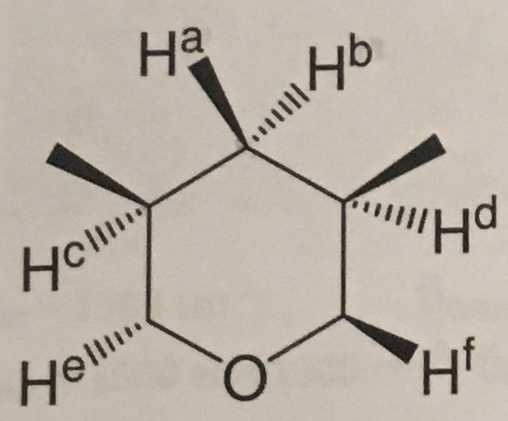
$\ddot{U}_{C-O}$ = 1050 cm^{-1}

$\ddot{U}_{CH_bend}$ = 600 and 800 cm^{-1}

Explain (2.5 pts)

The reactant will show two sharp bands for NH around 3500 – 3300 cm^{-1}, the signal CN at 2200 cm^{-1} and a signal of C-N at 1200 cm^{-1} that will not be present in the product. On the other hand, the product will show a broad band around 3500 cm^{-1} for the OH bond, signals around 3010 cm^{-1} (C-H aromatic), 1600 cm^{-1} (C=C) and around 600 cm^{-1} (C-H bending) all characteristic of the aromatic ring. It will also show bands around 1500 and 1300 cm^{-1} for the NO_2 and around 1050 cm^{-1} for the C-O. All these later signals will be absent in the reactant.

2- State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated). (2 x 5 = 10 pts)



H^a and H^b are____**Homotopic**_____

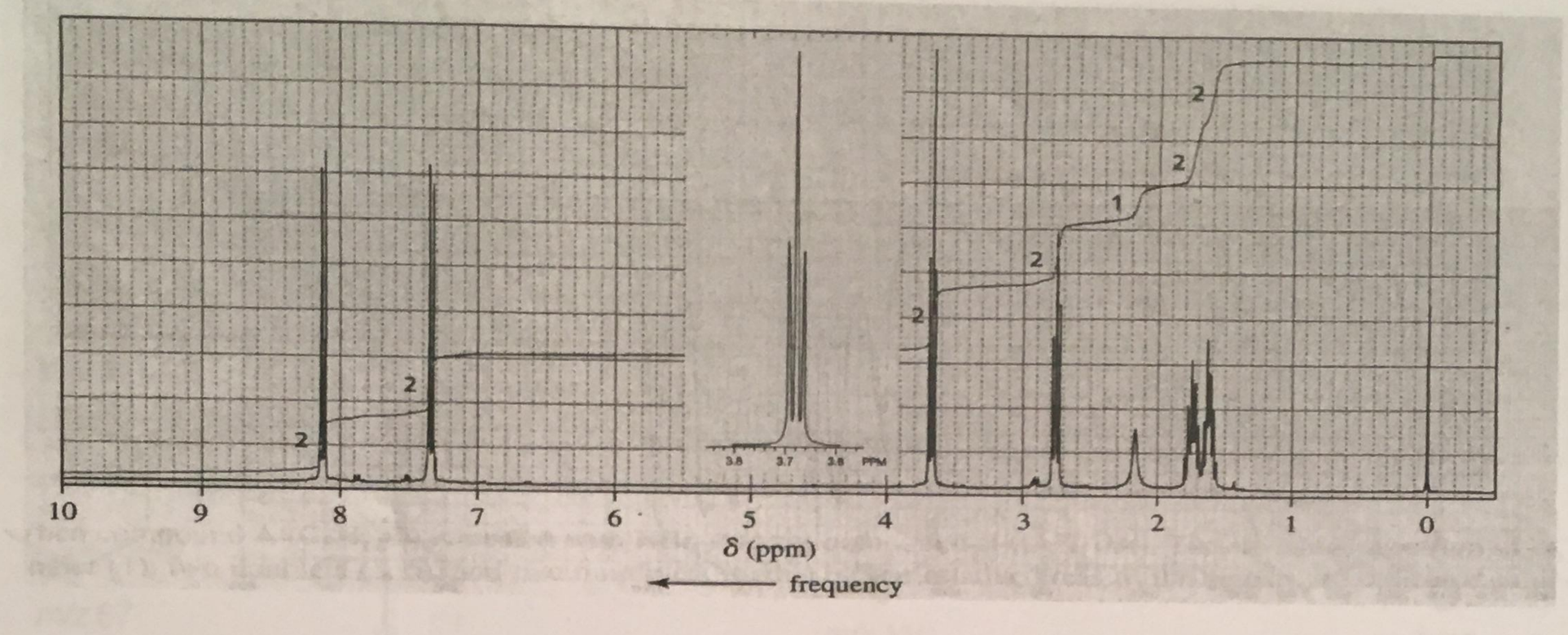
H^b and H^c are____**Unrelated**_____

H^b and H^f are ____**Unrelated**_____

H^c and H^d are____**Enantiotopic**_____

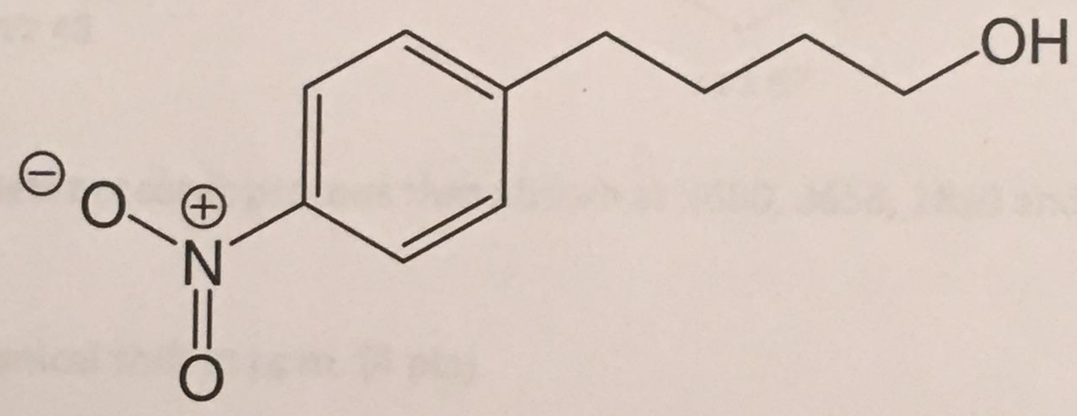
H^e and H^f are ____**Diastereotopic**_____

(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer. (10 pts)



Structure (5 pts)

$C_{10}H_{13}NO_3$: number of element of insaturation; nI = 10 + 1 - ½(13) + ½ = 5 elements of insaturations



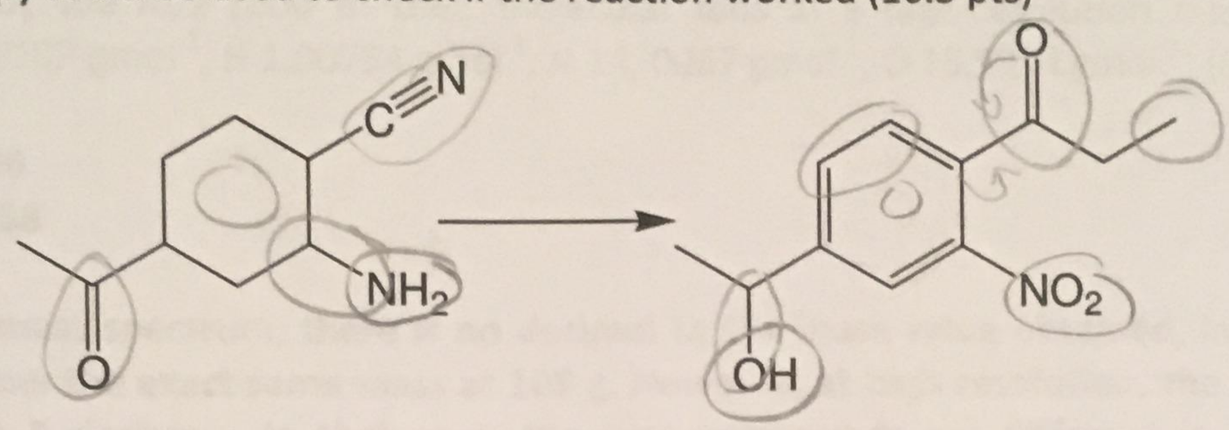
Explain (5 pts)

The molecule contains 5 elements of insaturation. The IR has also indicated that the molecule contains an OH group, and aromatic ring and a nitro group. The doublets of 2H around 8.2 and 7.3 ppm suggest that molecule contains a para-disubstituted aromatic ring. The same spectrum displays a series of two triplets of 2H and two multiplet of 2H corresponding to a series of $CH_2CH_2CH_2CH_2$. The triplet at 3.6 ppm suggests that the corresponding CH_2 is connected to an oxygen atom, while the triplet of 2H around 2.8 ppm suggests that it is connected to the benzene ring. The broad singlet around 2.2 ppm corresponds to the OH. The fact that one of the doublets on the aromatic ring is around 8.2 ppm suggests that the nitro group is connected on the aromatic ring. In this case, the long chain carrying the OH at the other end is connect at the *para* position to the to the nitro group.

CHEM 266 – EXAM 1 **NAME**_____**Keys**_____

February 19 (Spring 2014)

1- You have just performed the following transformation in the lab; predict the type of bonds corresponding to the major signals found in the IR spectra of both the product and the reactant. Explain how IR spectroscopy could be used to check if the reaction worked (10.5 pts)



Reactant

$\ddot{U}_{NH}$ = 3500 and 3300 cm^{-1}

$\ddot{U}_{CHsp3}$ = 2950 cm^{-1}

$\ddot{U}_{CN}$ = 2200 cm^{-1}

$\ddot{U}_{C=O}$ = 1760 cm^{-1}

$\ddot{U}_{C-N}$ = 1200 cm^{-1}

Product

$\ddot{U}_{OH}$ = 3500 cm^{-1}

$\ddot{U}_{CHsp2}$ = 3010 cm^{-1}

$\ddot{U}_{CHsp3}$ = 2950 cm^{-1}

$\ddot{U}_{C=O}$ = 1680 cm^{-1}

$\ddot{U}_{C=C}$ = 1600 cm^{-1}

$\ddot{U}_{No2}$ = 1500 and 1300 cm^{-1}

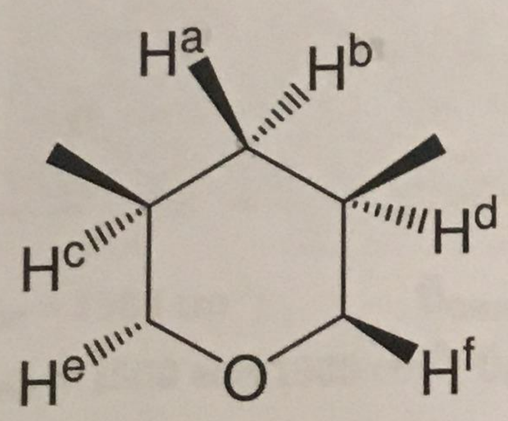
$\ddot{U}_{C-O}$ = 1050 cm^{-1}

$\ddot{U}_{CH_bend}$ = 600 and 800 cm^{-1}

Explain (2.5 pts)

The reactant will show two sharp bands for NH around 3500 – 3300 cm^{-1}, the signal CN at 2200 cm^{-1} and a signal of C-N at 1200 cm^{-1} that will not be present in the product. On the other hand, the product will show a broad band around 3500 cm^{-1} for the OH bond, signals around 3010 cm^{-1} (C-H aromatic), 1600 cm^{-1} (C=C) and around 600 cm^{-1} (C-H bending) all characteristic of the aromatic ring. It will also show bands around 1500 and 1300 cm^{-1} for the NO_2 and around 1050 cm^{-1} for the C-O. All these later signals will be absent in the reactant.

2- State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated). (2 x 5 = 10 pts)



H^a and H^b are____**Homotopic**_____

H^b and H^c are____**Unrelated**_____

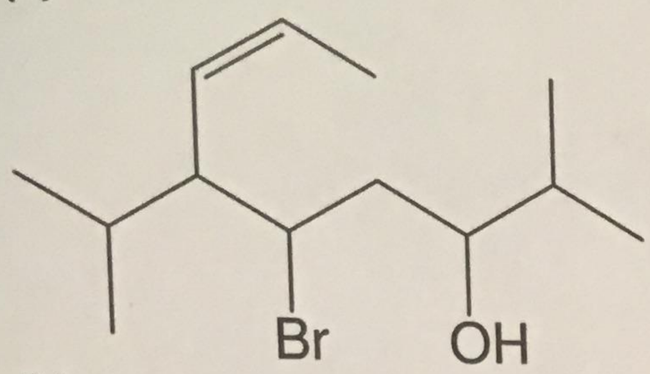
H^b and H^f are ____**Unrelated**_____

H^c and H^d are____**Enantiotopic**_____

H^e and H^f are ____**Diastereotopic**_____

9- Name the following compounds (4 x 6 = 24 pts)

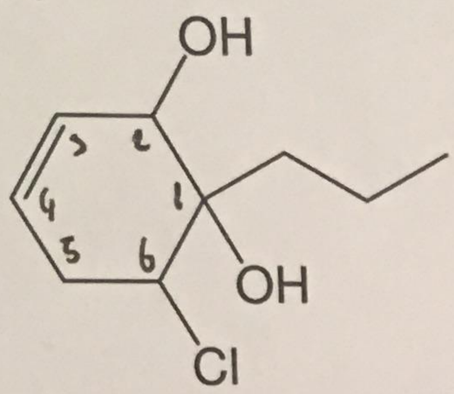
(a)



5-bromo-6-isopropyl-2-methylnon-7-en-3-ol

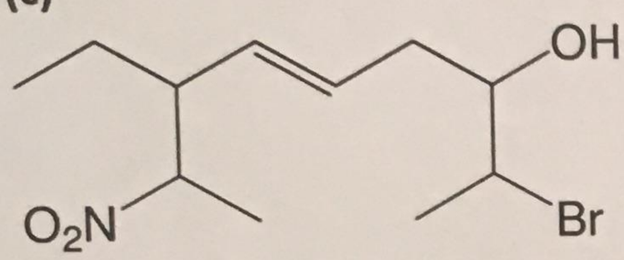
5-bromo-2-methyl-6-(1-methylethyl)non-7-en-3-ol

(b)



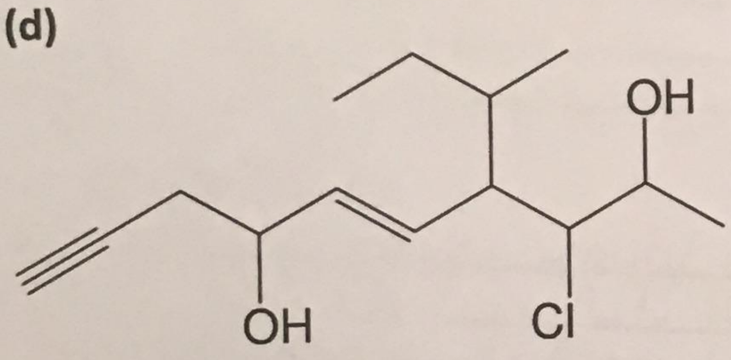
6-chloro-1-propylcyclohex-3-ene-1,2-diol

(c)



2-bromo-7-ethyl-8-nitronon-5-en-3-ol

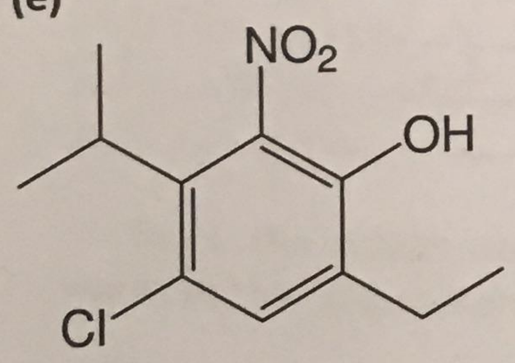
(d)



4-sec-butyl-3-chlorodec-5-en-9-yne-2,7-diol

3-chloro-4-(1-methylpropyl)dec-5-en-9-yne-2,7-diol

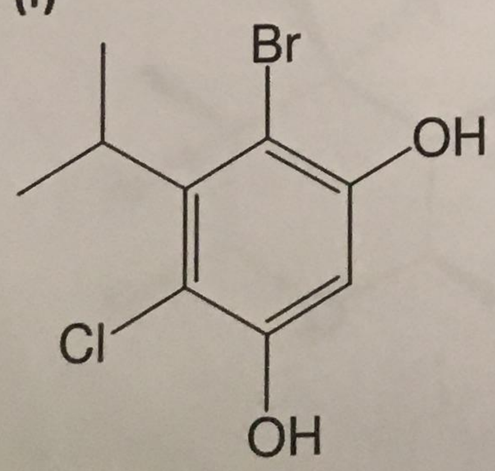
(e)



4-chloro-6-ethyl-3-isopropyl-2-nitrophenol

4-chloro-6-ethyl-3-(1-methylethyl)-2-nitrophenol

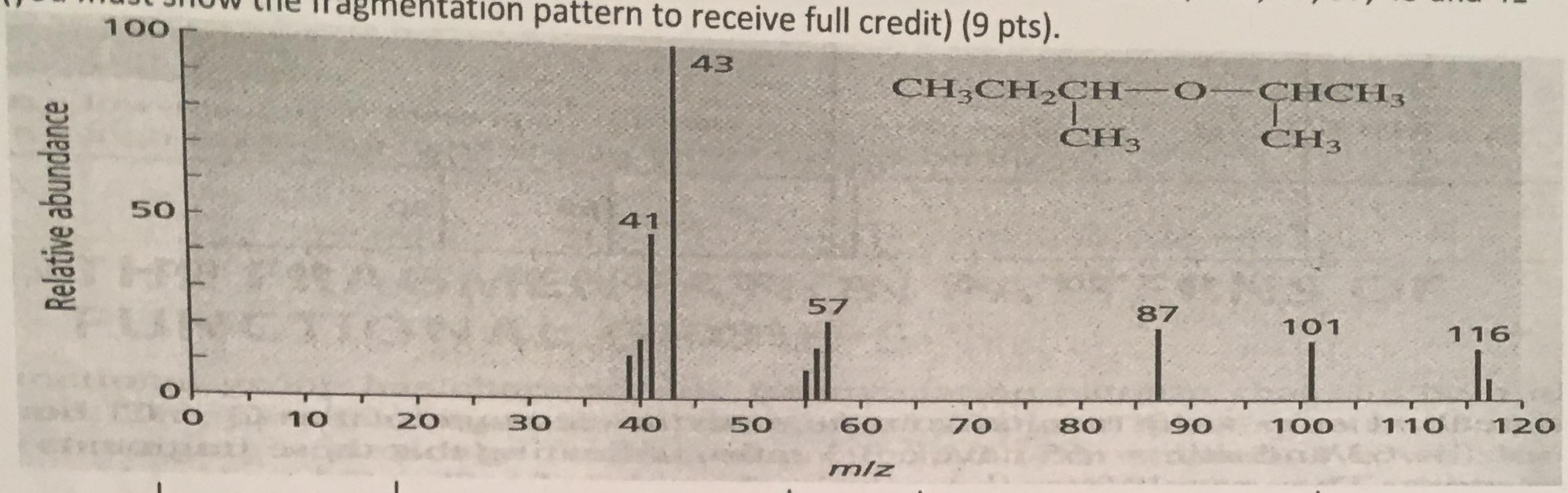
(f)

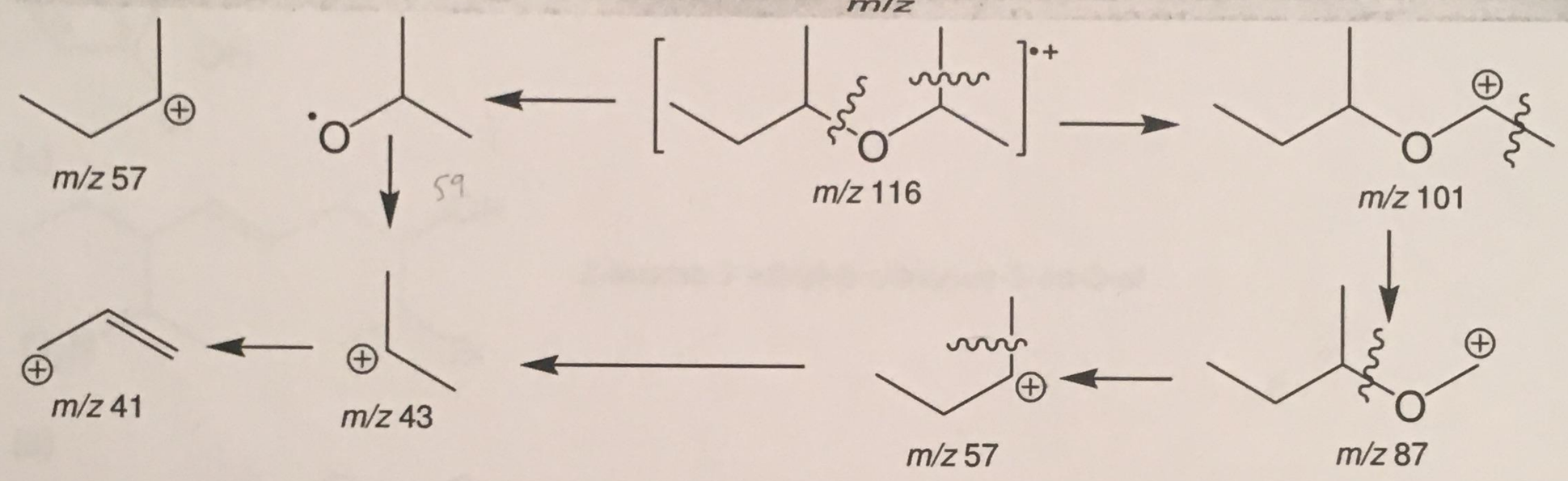


4-bromo-6-chloro-5-isopropylbenzene-1,3-diol

4-bromo-6-chloro-5-(1-methylethyl)benzene-1,3-diol

7- The mass spectrum showed below is that of 2-isopropoxybutane (see structure). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 116, 101, 87, 57, 43 and 41 (you must show the fragmentation pattern to receive full credit) (9 pts).





8- A 800 MHz spectrometer records protons that absorb at 5680, 3658, 2830 and 1569 Hz downfield from TMS. (10 pts)

(a) Determine their chemical shift in ppm. (4 pts)

δ_1 = 5680 / 800 = 7.10 ppm **δ_2 = 3658 / 800 = 4.57 ppm**

δ_3 = 2830 / 800 = 3.54 ppm **δ_4 = 1569 / 800 = 1.96 ppm**

(b) Predict these protons' chemical shift in ppm if a 300 MHz spectrometer was used instead. (2 pts)

The chemical shift remains the same regardless of the equipment used so:

δ_1 = 5680 / 800 = 7.10 ppm **δ_2 = 3658 / 800 = 4.57 ppm**

δ_3 = 2830 / 800 = 3.54 ppm **δ_4 = 1569 / 800 = 1.96 ppm**

(c) In a 300 MHz spectrometer, how far downfield (in hertz) from TMS would this proton absorb? (4 pts)

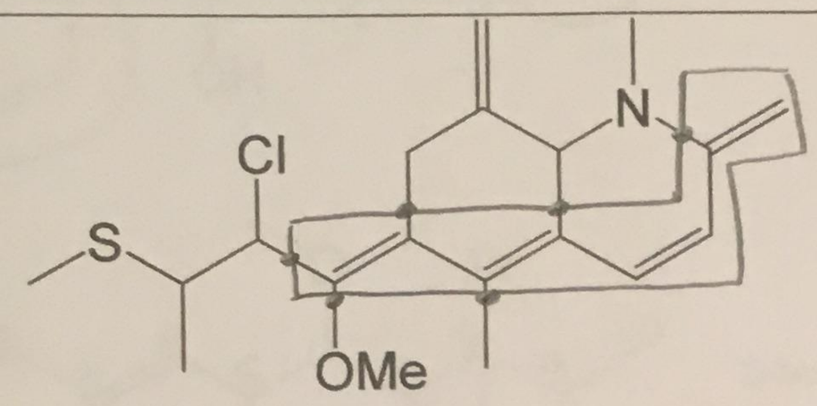
υ_1 = 7.10 x 300 = 2130 Hz **υ_2 = 4.57 x 300 = 1371 Hz**

υ_3 = 3.54 x 300 = 1062 Hz **υ_4 = 1.96 x 300 = 588 Hz**

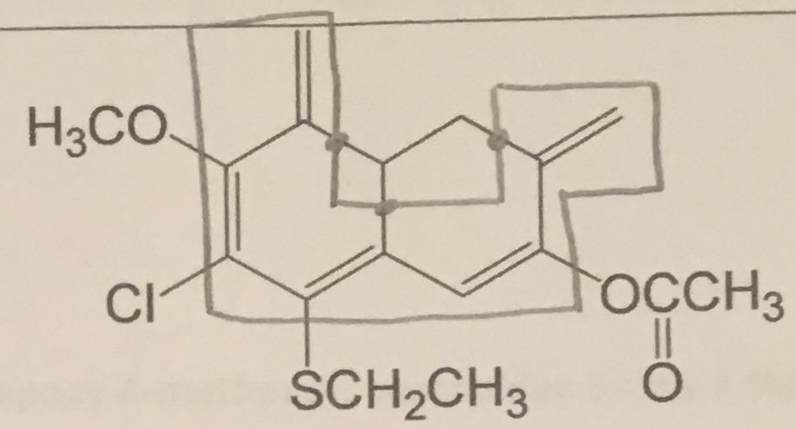
EXAM – 2 – Spring
March 21, 2016

NAME: Keys

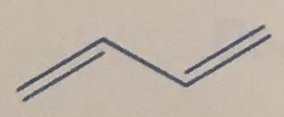
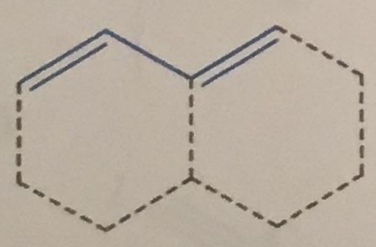
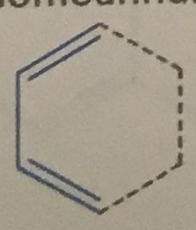
1. Use the Woodward-Fieser table to estimate the λ_{max} observed in a UV spectra of the following cross-conjugated systems (5 pts)



Parent	214
Additional C=C	60
C-alkyl	20
Exocyclic C=C	15
N(alkyl)2	60
Oalkyl	6
	375 nm



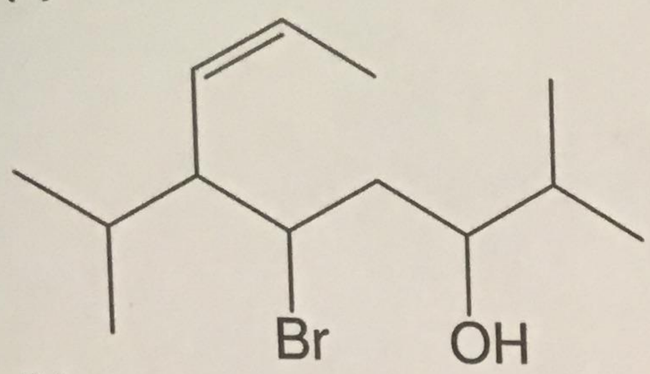
Parent	253
Additional C=C	90
C-alkyl	15
Exocyclic C=C	15
S-alkyl	30
O-alkyl	6
Cl	5
$OCOCH_3$	0
	414 nm

Acyclic 	217 nm
Heteroannular 	214 nm
Homoannular 	253 nm

For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each substituent	
C-substituent	+ 5 nm
Cl	+ 5 nm
Br	+ 5 nm
O-Alkyl	+ 6 nm
$OCOCH_3$	+ 0 nm
$N(alkyl)_2$	+ 60 nm
S-alkyl	+ 30 nm
Solvent correction	+ 0 nm

9- Name the following compounds (4 x 6 = 24 pts)

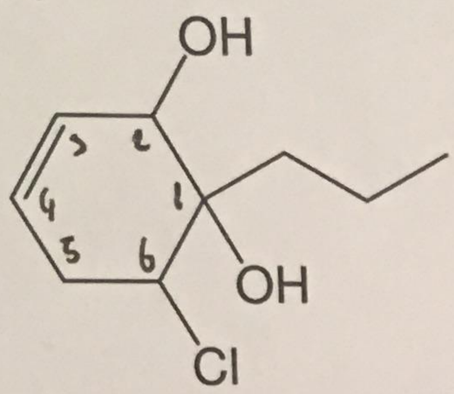
(a)



5-bromo-6-isopropyl-2-methylnon-7-en-3-ol

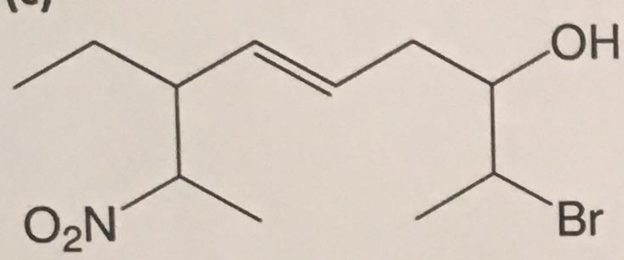
5-bromo-2-methyl-6-(1-methylethyl)non-7-en-3-ol

(b)



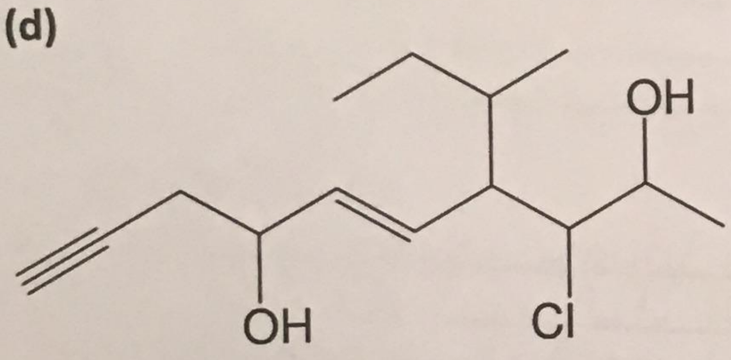
6-chloro-1-propylcyclohex-3-ene-1,2-diol

(c)



2-bromo-7-ethyl-8-nitronon-5-en-3-ol

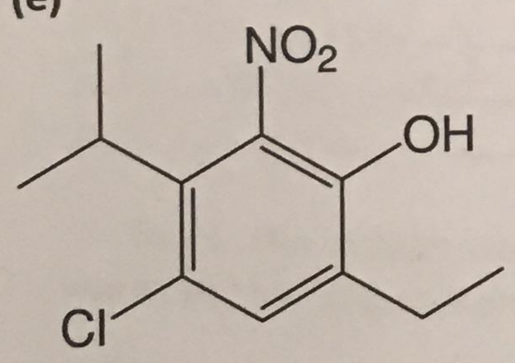
(d)



4-sec-butyl-3-chlorodec-5-en-9-yne-2,7-diol

3-chloro-4-(1-methylpropyl)dec-5-en-9-yne-2,7-diol

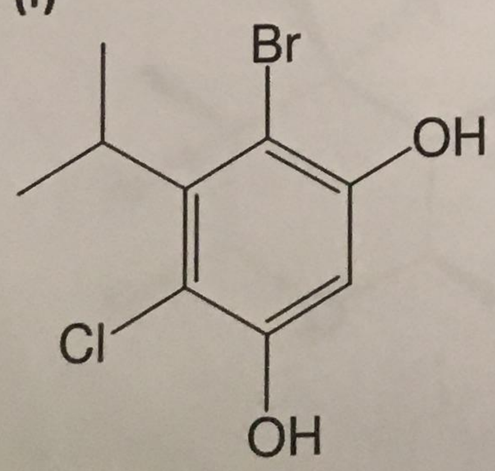
(e)



4-chloro-6-ethyl-3-isopropyl-2-nitrophenol

4-chloro-6-ethyl-3-(1-methylethyl)-2-nitrophenol

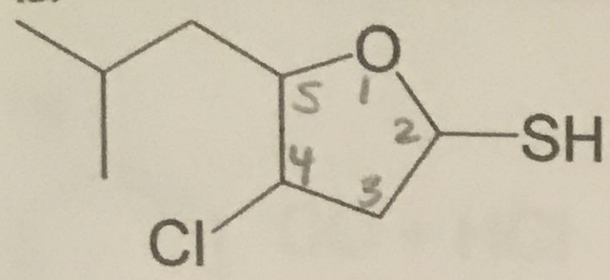
(f)



4-bromo-6-chloro-5-isopropylbenzene-1,3-diol

4-bromo-6-chloro-5-(1-methylethyl)benzene-1,3-diol

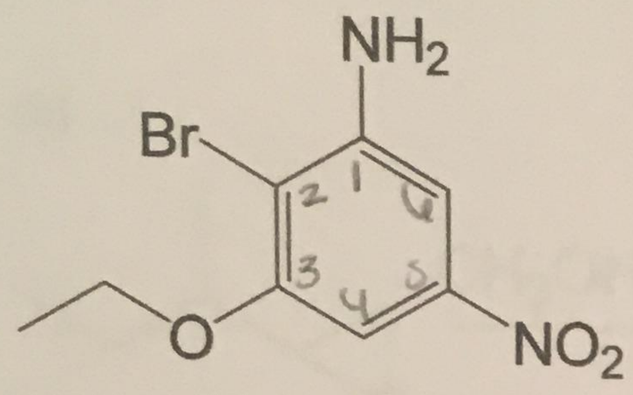
(g)



4-chloro-5-isobutyltetrahydrofuran-2-thiol

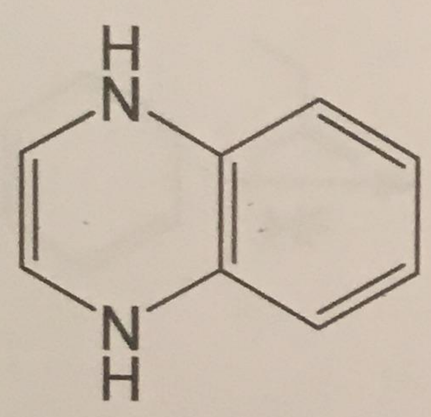
Or 4-chloro-5-isobutyloxolane-2-thiol

(h)

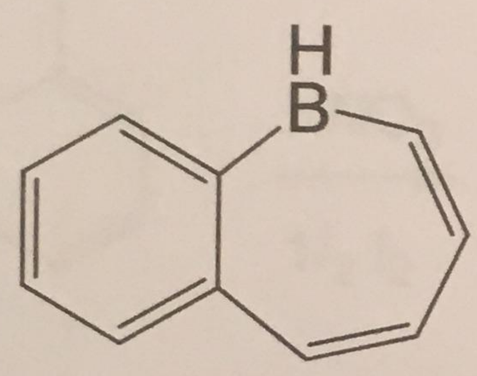


2-bromo-3-ethoxy-5-nitroaniline

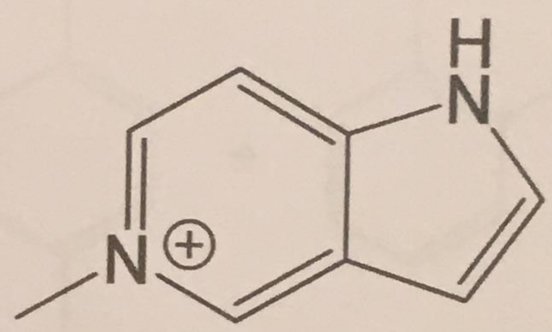
3. Classify the following molecules as aromatic, anti-aromatic or non-aromatic (8 pts)



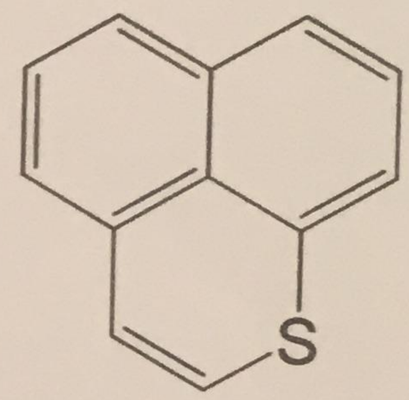
Antiaromatic



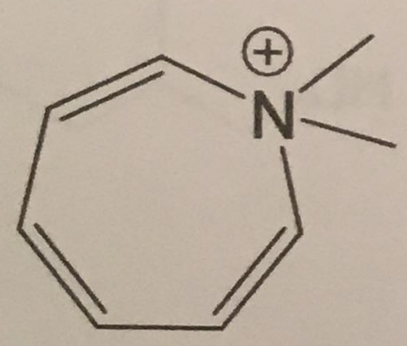
Aromatic



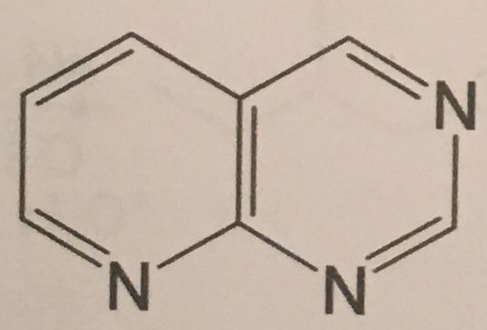
Aromatic



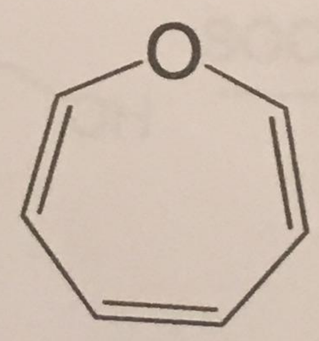
Aromatic



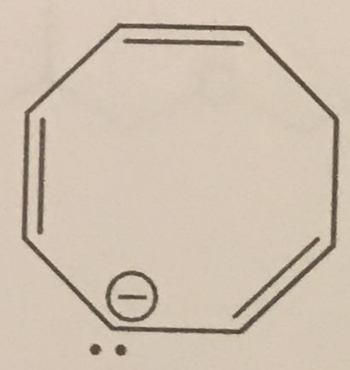
Non-aromatic



Aromatic

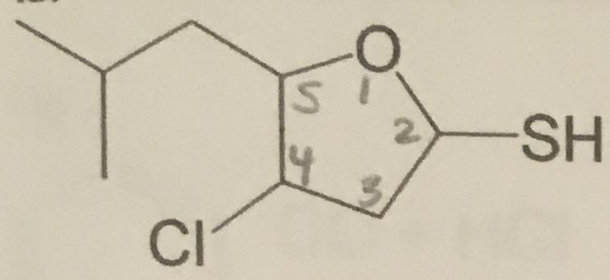


Antiaromatic



Non-aromatic

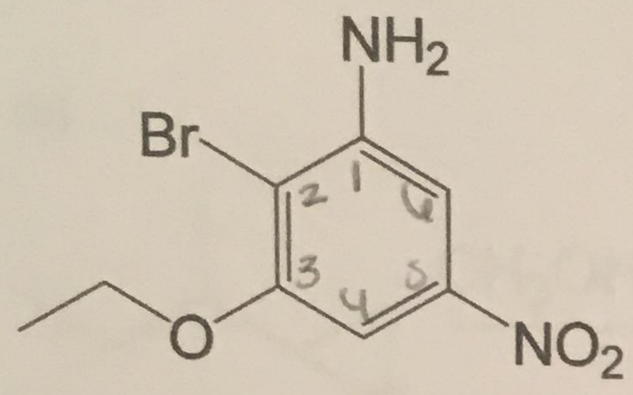
(g)



4-chloro-5-isobutyltetrahydrofuran-2-thiol

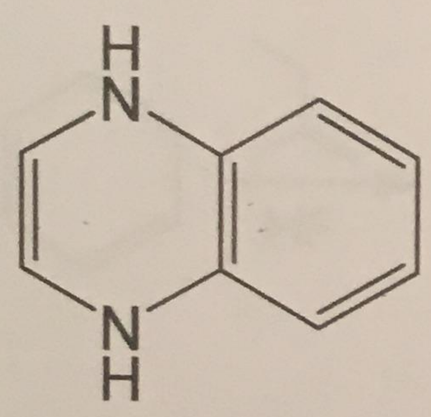
Or 4-chloro-5-isobutyloxolane-2-thiol

(h)

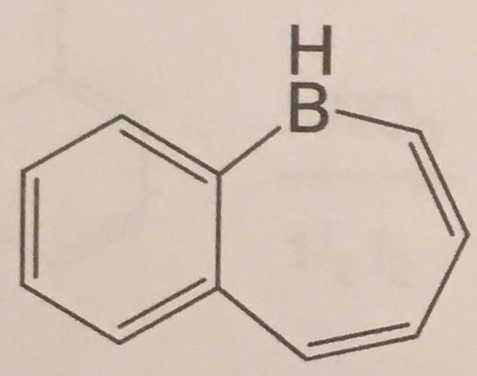


2-bromo-3-ethoxy-5-nitroaniline

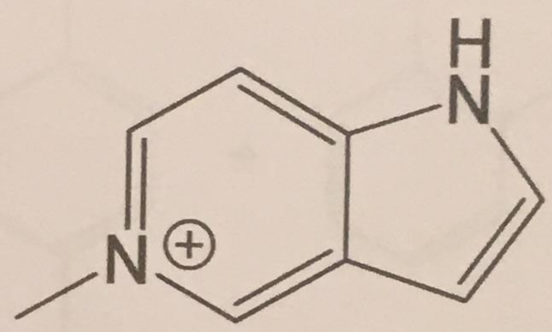
3. Classify the following molecules as aromatic, anti-aromatic or non-aromatic (8 pts)



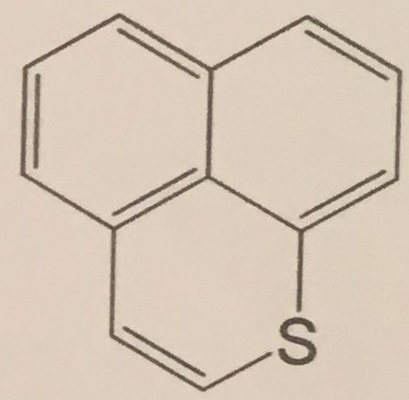
Antiaromatic



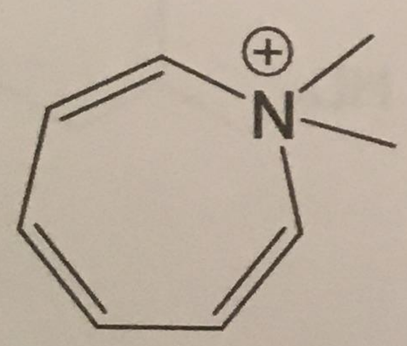
Aromatic



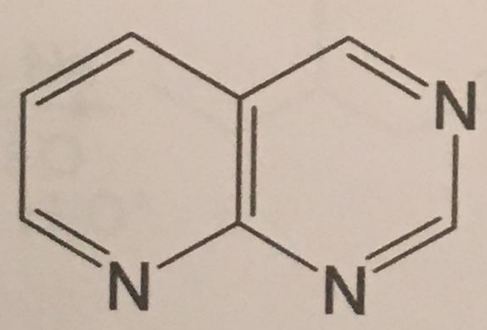
Aromatic



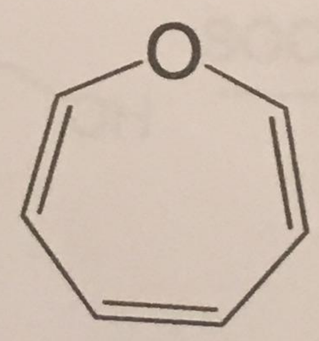
Aromatic



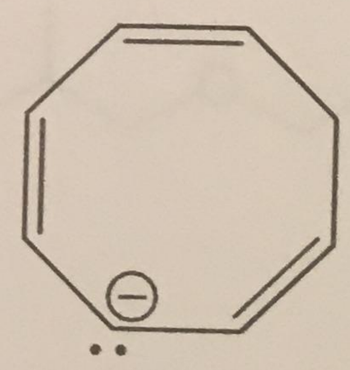
Non-aromatic



Aromatic



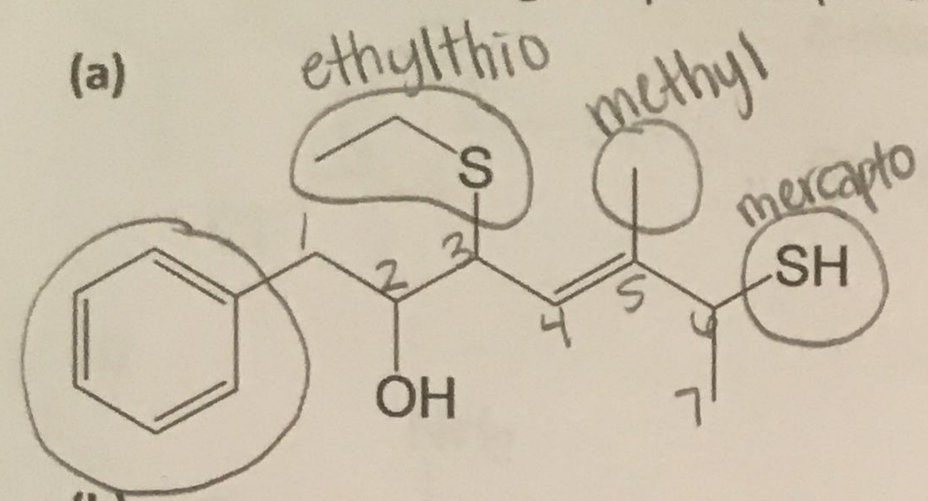
Antiaromatic



Non-aromatic

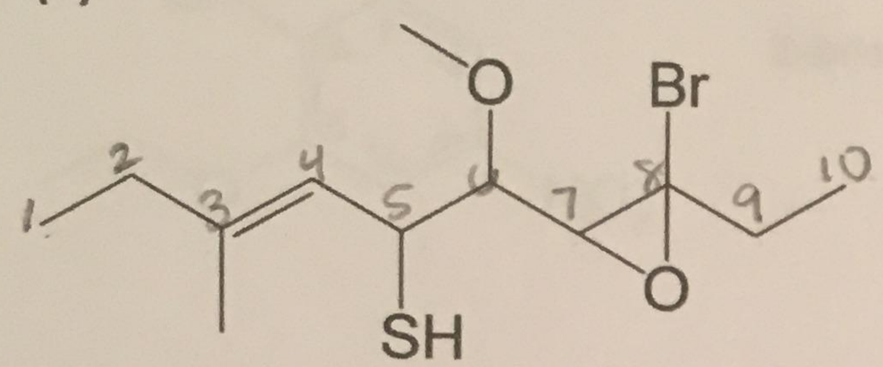
2. Name the following compounds (3 x 8 = 24 pts)

(a)



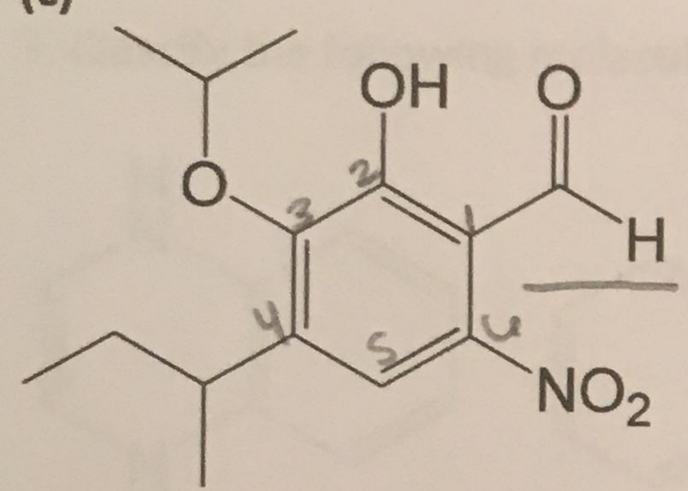
3-(ethylthio)-6-mercapto-5-methyl-1-phenylhept-4-en-2-ol

(b)



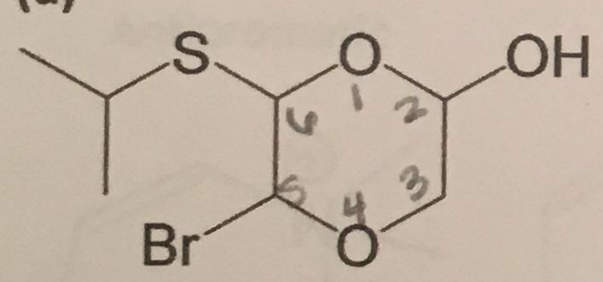
8-bromo-7,8-epoxy-6-methoxy-3-methyldec-3-ene-5-thiol

(c)



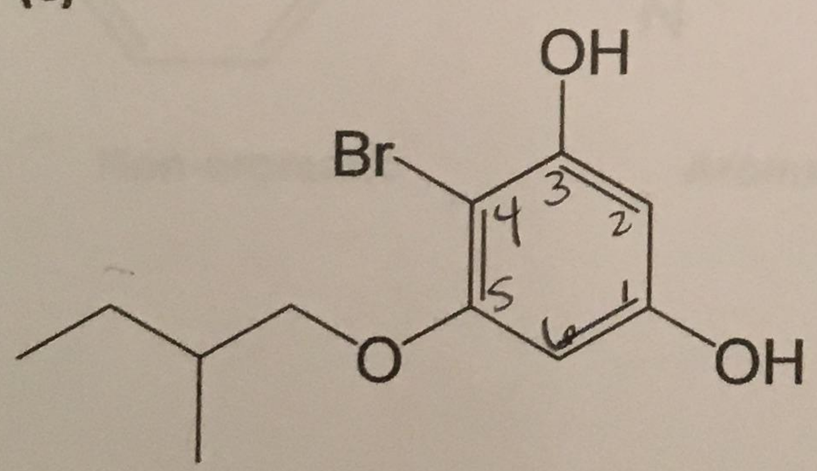
4-sec-butyl-2-hydroxy-3-isopropoxy-6-nitrobenzaldehyde

(d)



5-bromo-6-(isopropylthio)-1,4-dioxan-2-ol

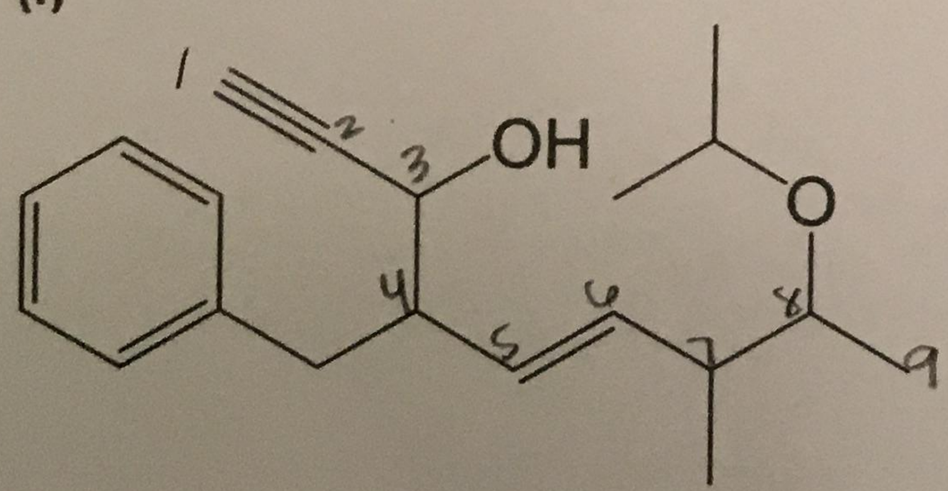
(e)



4-bromo-5-(2-methylbutoxy)benzene-1,3-diol

Or 4-bromo-5-sec-pentoxybenzene-1,3-diol

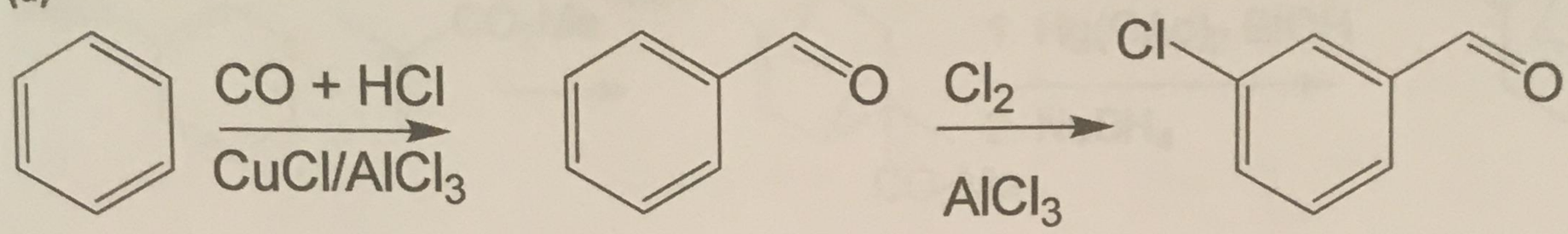
(f)



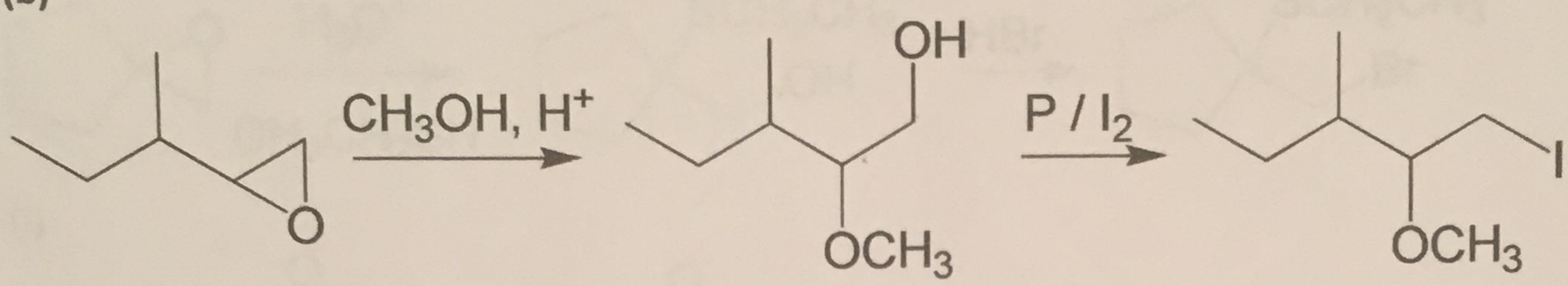
4-benzyl-8-isopropoxy-7-methylnon-5-en-1-yn-3-ol

4. Predict the major product(s) expected from the following reaction sequences (3 x 13 = 39 pts)

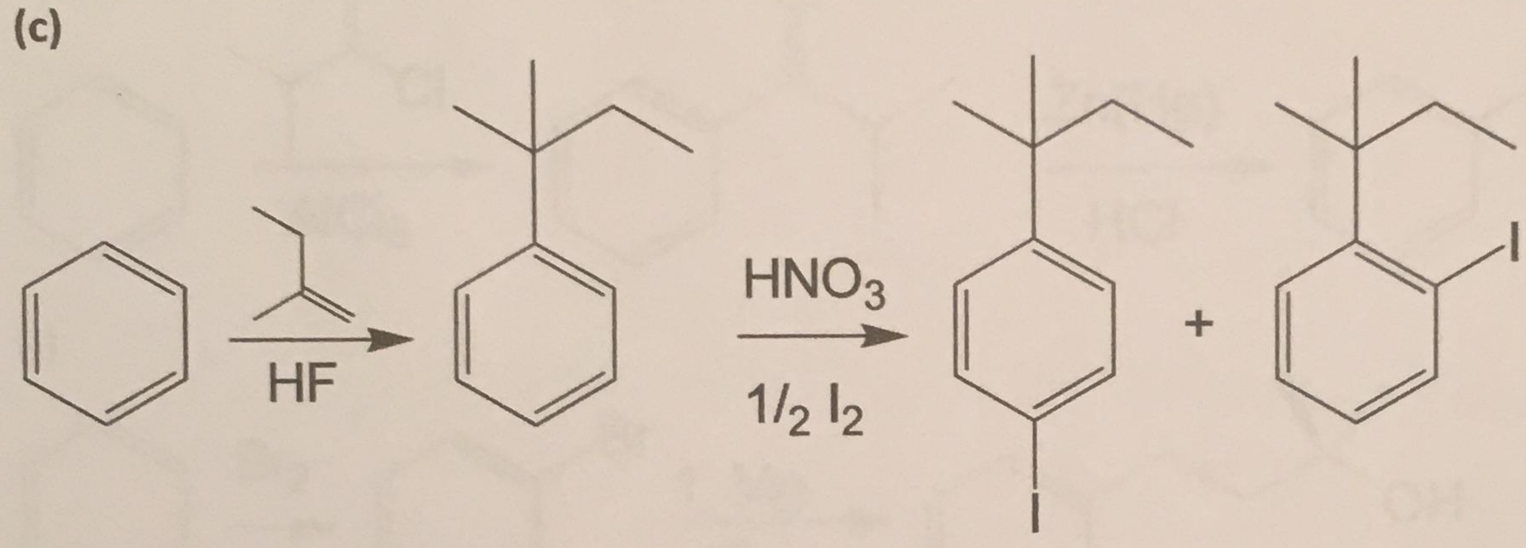
(a)



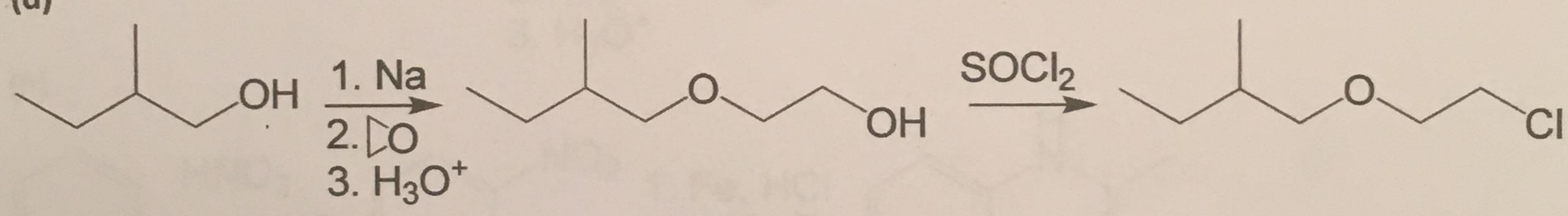
(b)



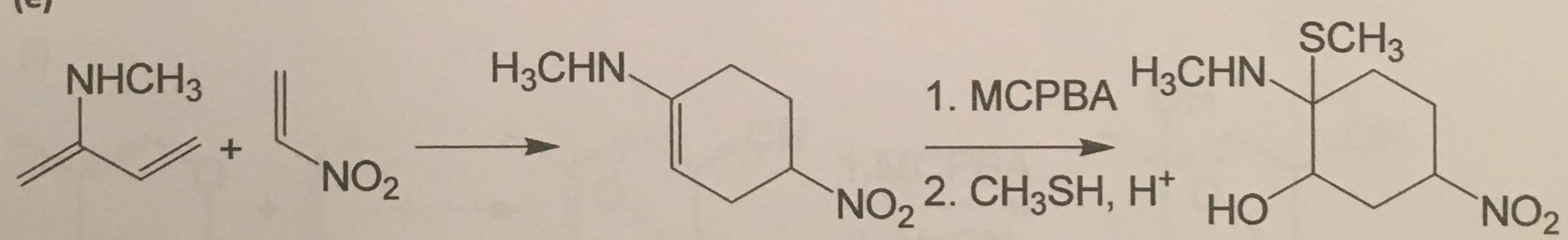
(c)



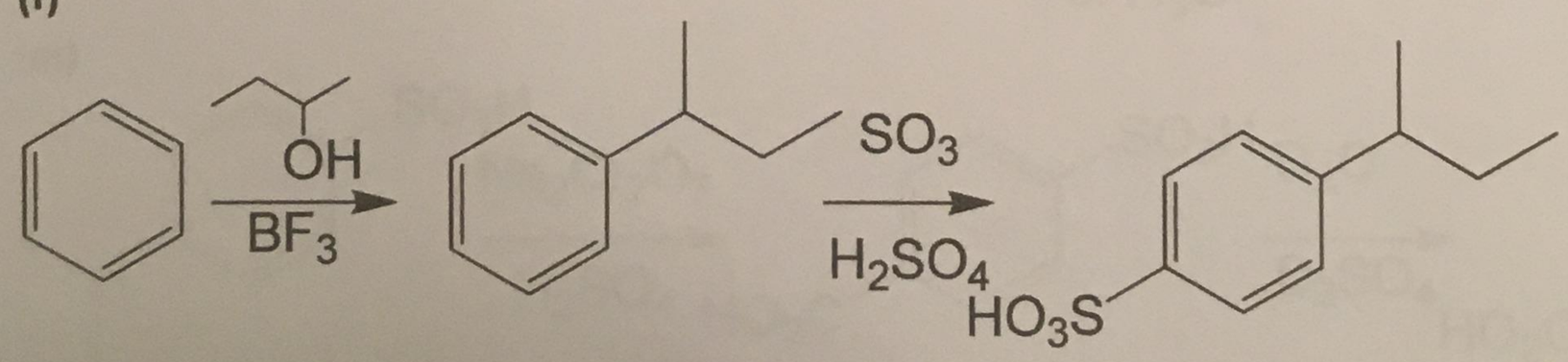
(d)



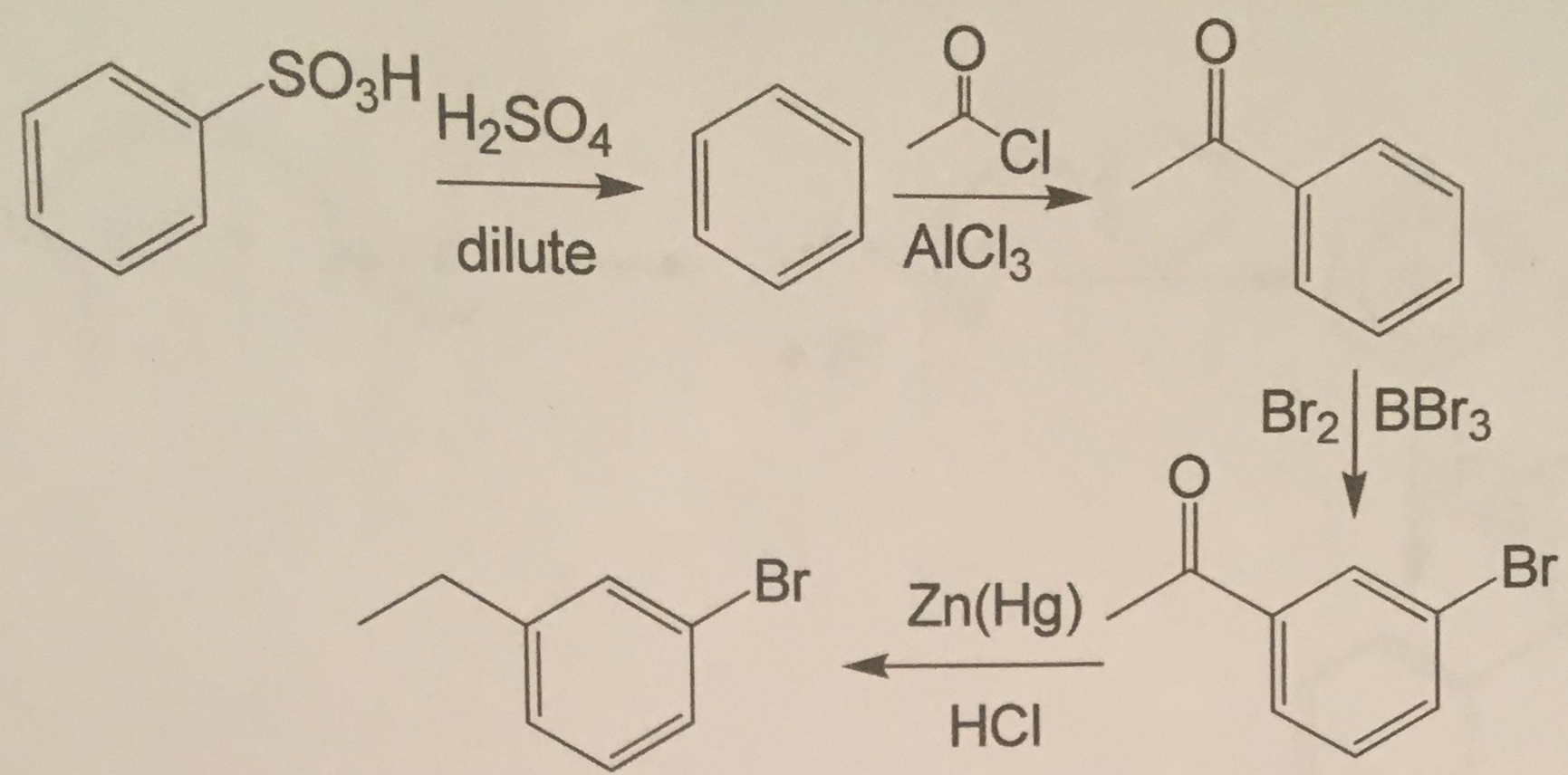
(e)



(f)

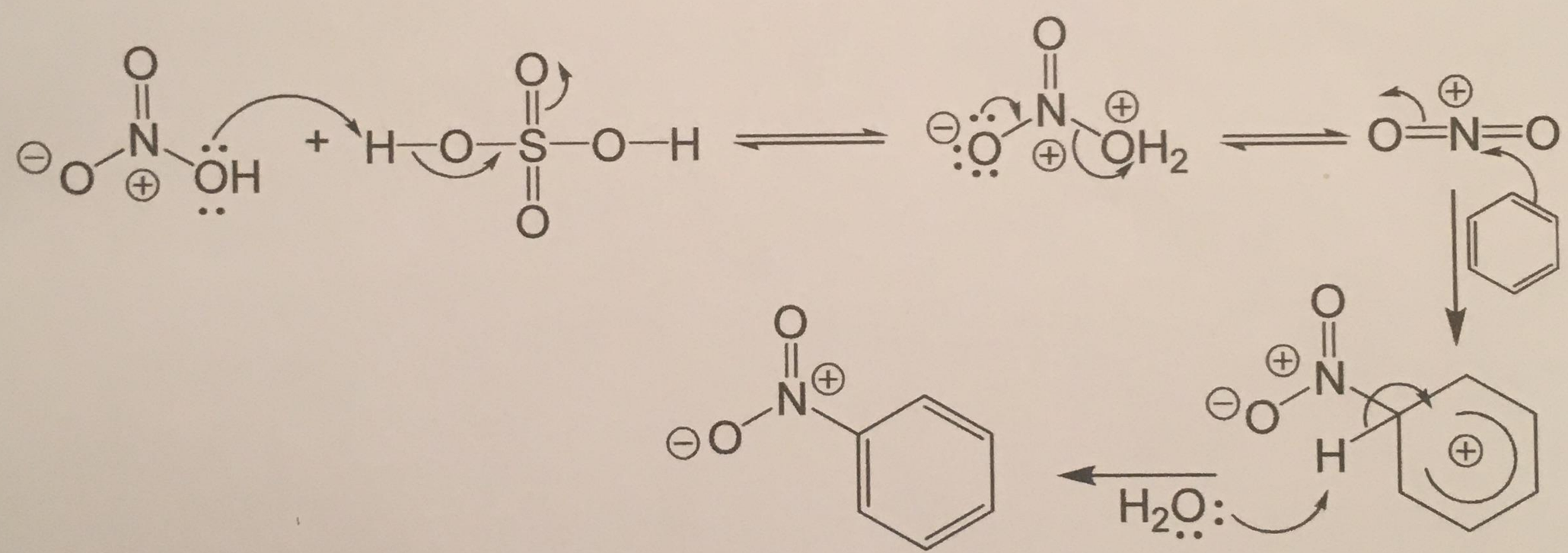


(e)

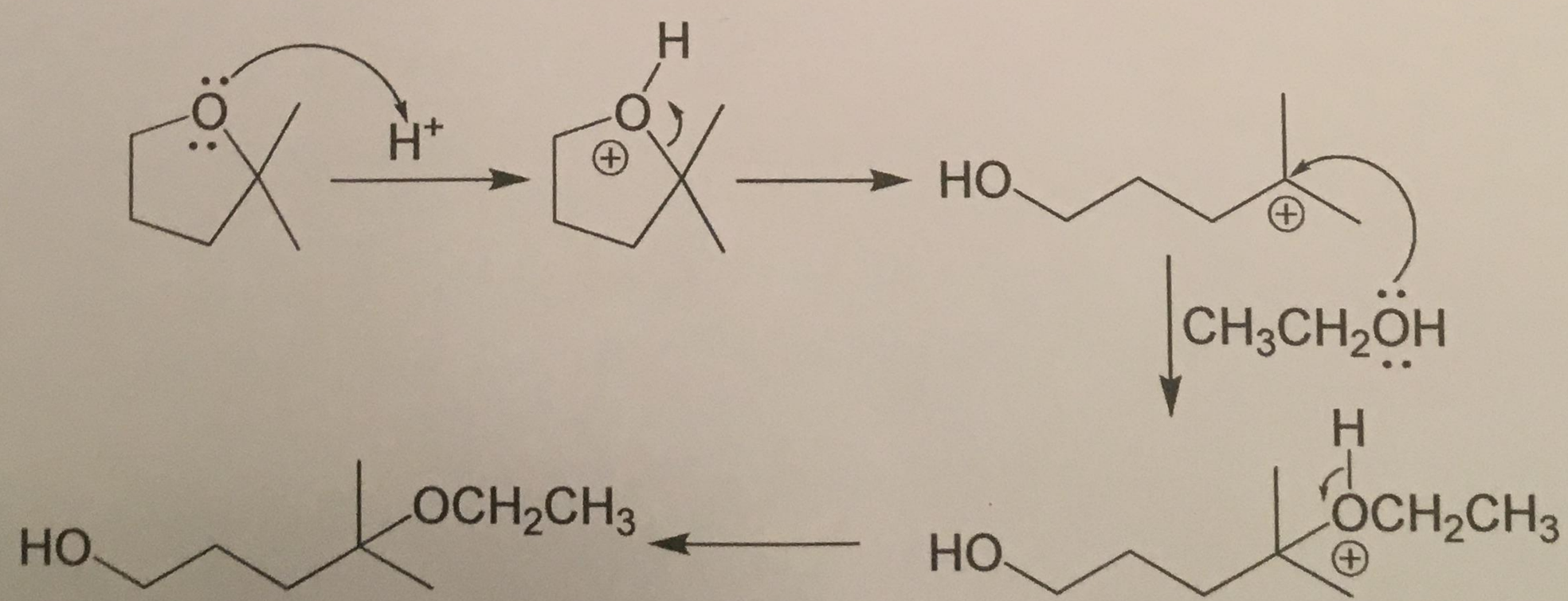


6. Propose a mechanism consistent with the following reactions (you must show all the intermediates to receive full credit) (3 x 3 = 9 pts)

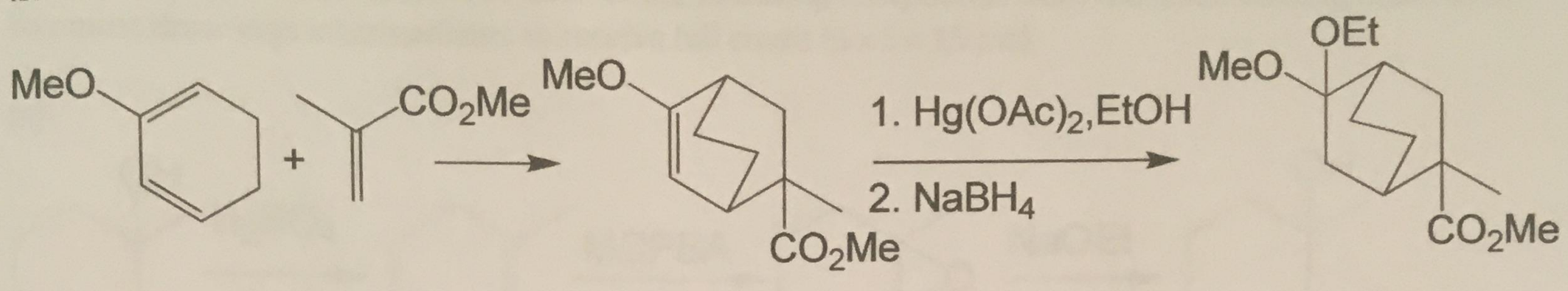
(a)



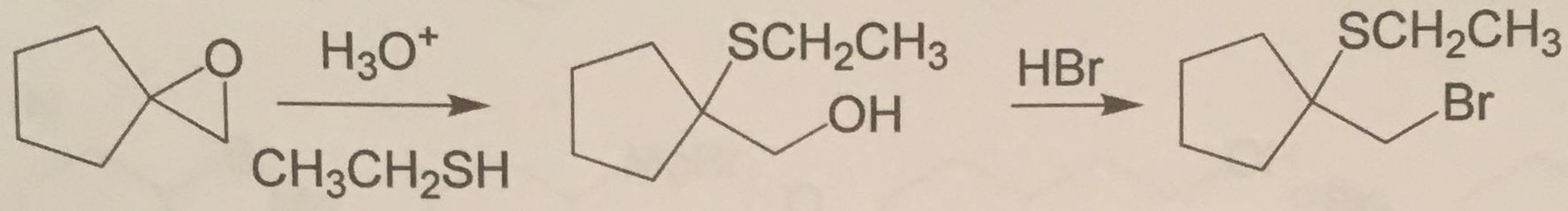
(b)



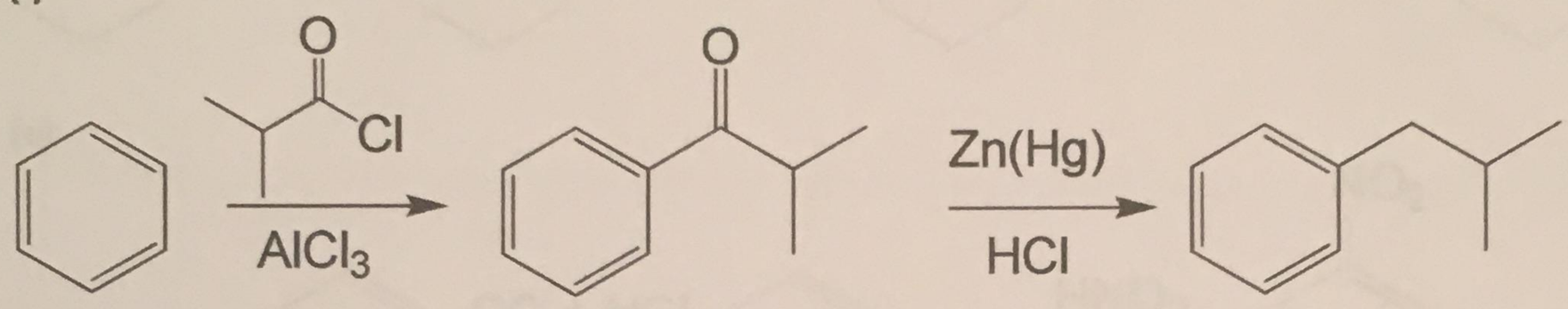
(g)


MeO
CO2Me
MeO
CO2Me
1. Hg(OAc)2,EtOH
2. NaBH4
OEt
MeO
CO2Me

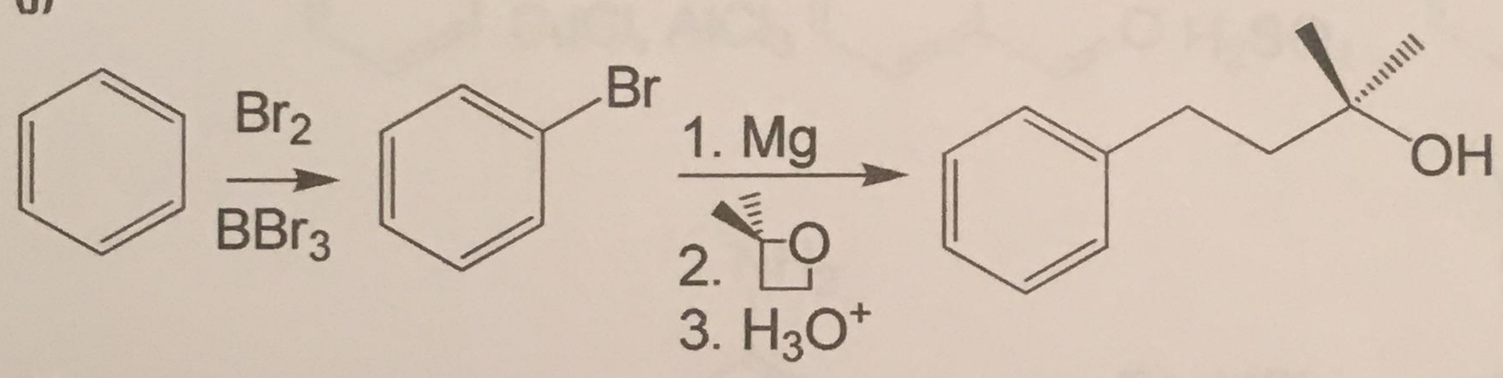
(h)


O
H3O+
CH3CH2SH
SCH2CH3
OH
HBr
SCH2CH3
Br

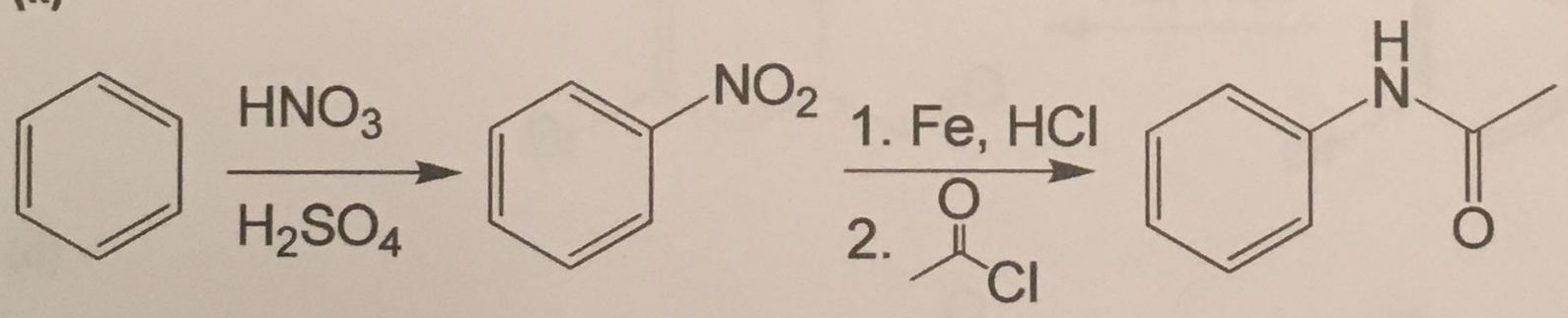
(i)


O
Cl
AlCl3
O
Zn(Hg)
HCl

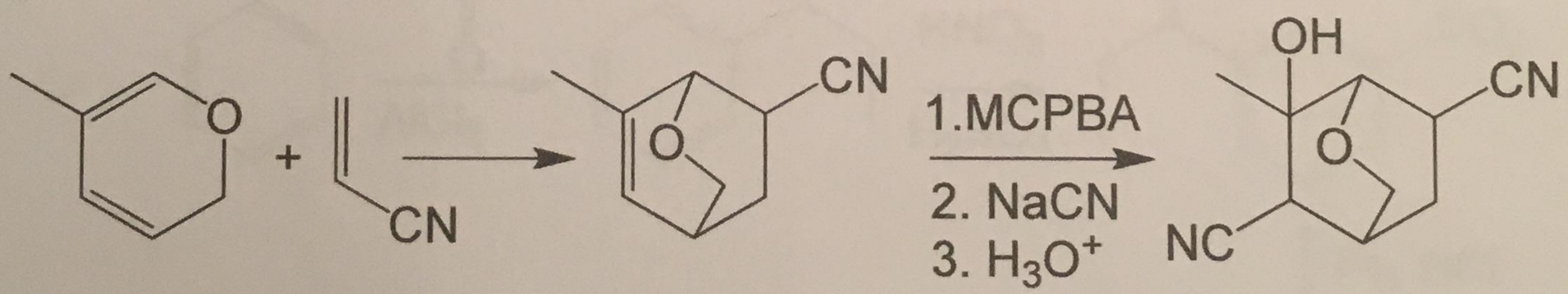
(j)


Br2
BBr3
Br
1. Mg
2.
O
3. H3O+
OH

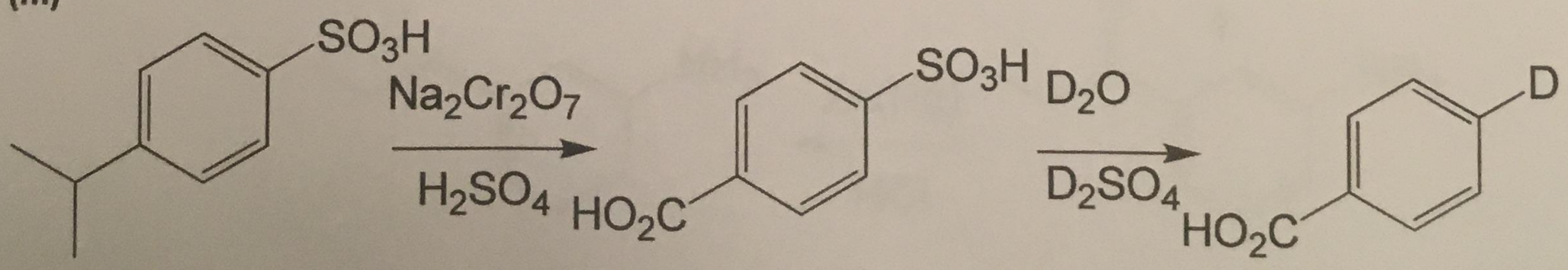
(k)


HNO3
H2SO4
NO2
1. Fe, HCl
2.
O
Cl
H
N
O

(l)

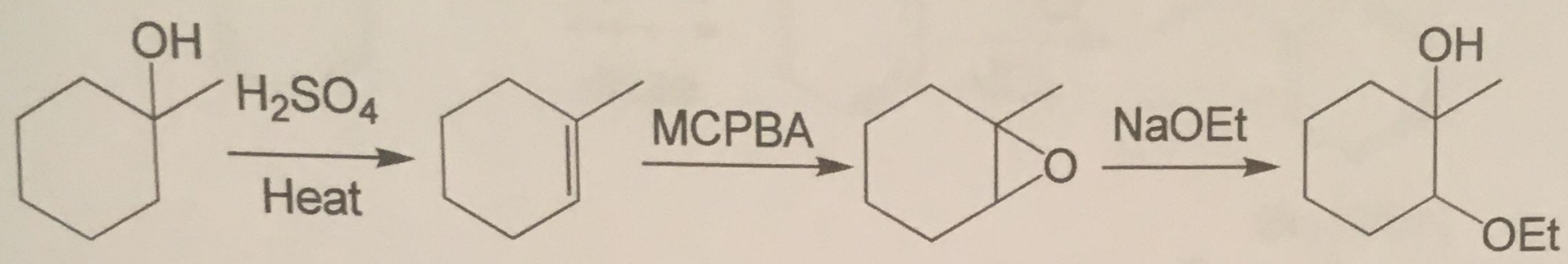

O
+
CN
CN
O
1.MCPBA
2. NaCN
3. H3O+
OH
CN
O
NC

(m)

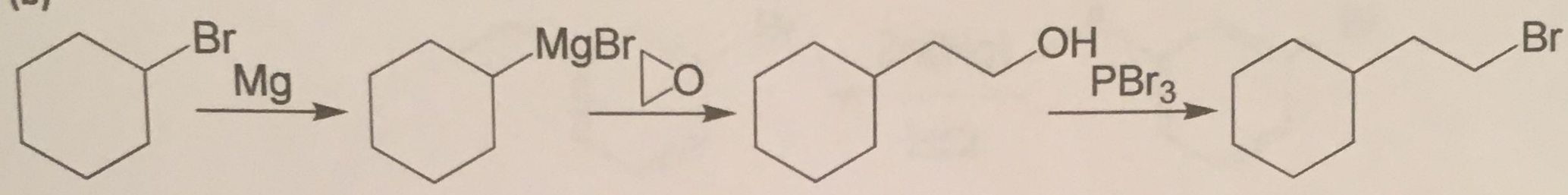

SO3H
Na2Cr2O7
H2SO4
SO3H
HO2C
D2O
D2SO4
D
HO2C

5. Show how you would synthesize each of the following compounds from the given starting material(s). You must draw keys intermediates to receive full credit (3 x 5 = 15 pts)

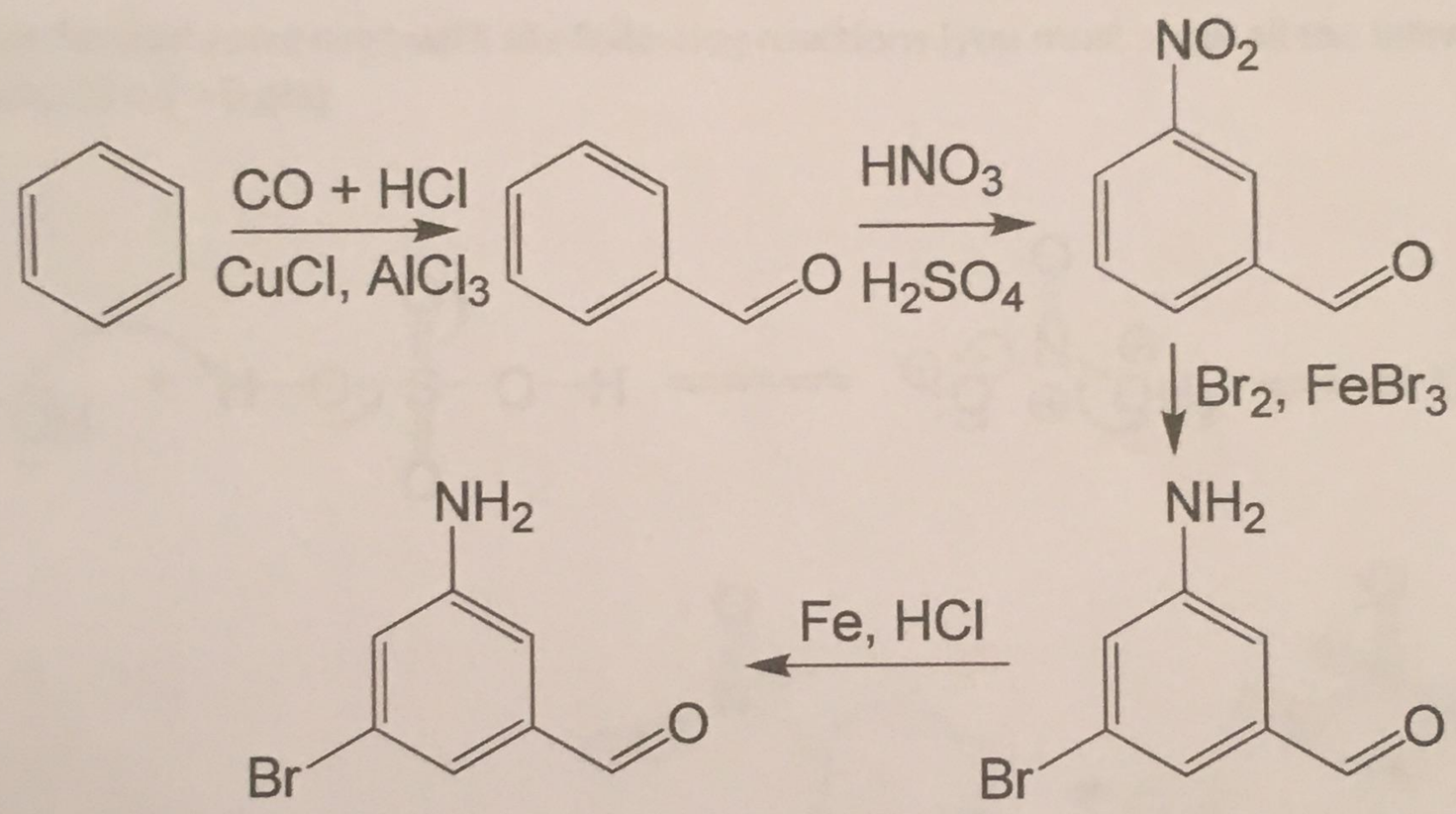
(a)



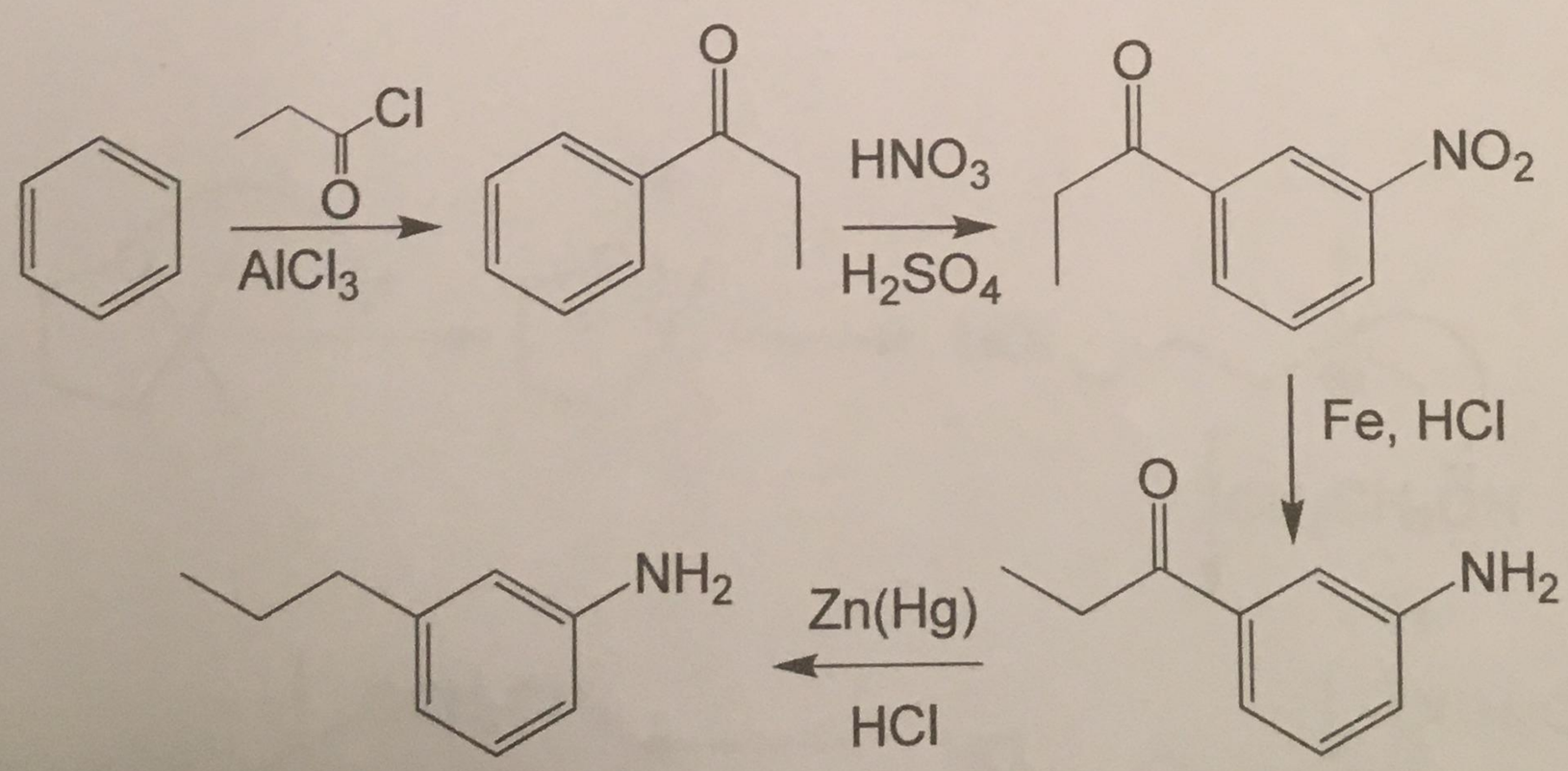
(b)



(c)



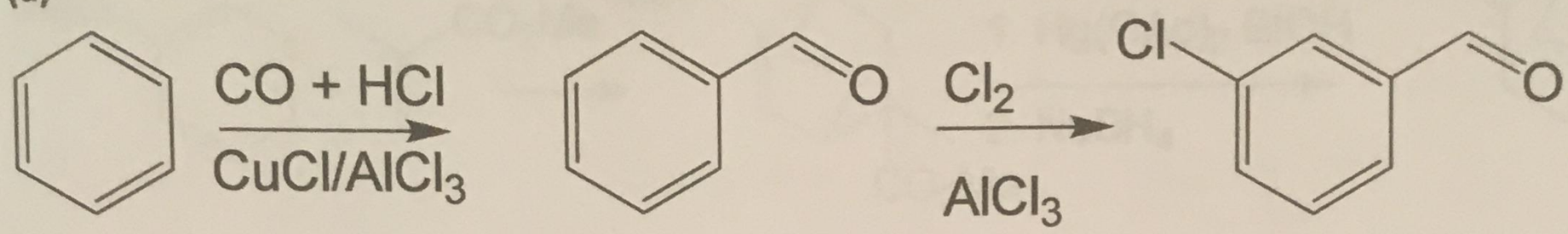
(d)



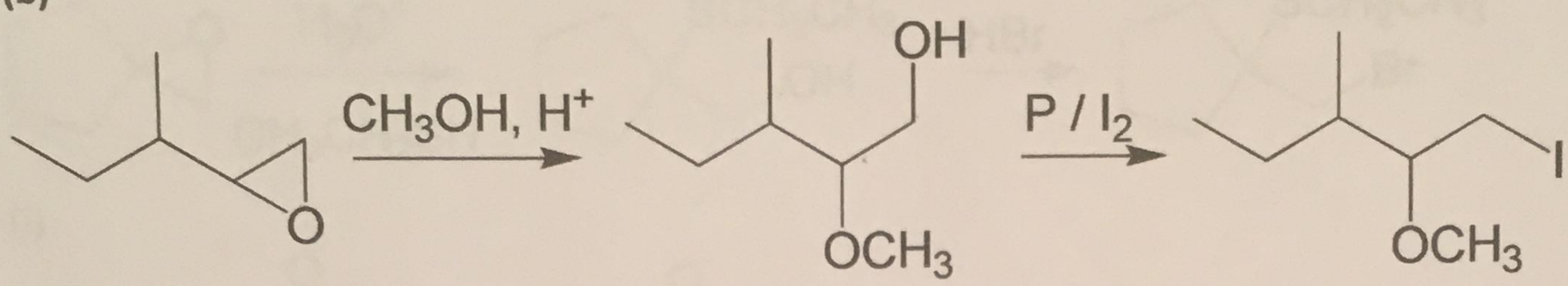
– to remove use: dilute H_2SO_4

4. Predict the major product(s) expected from the following reaction sequences (3 x 13 = 39 pts)

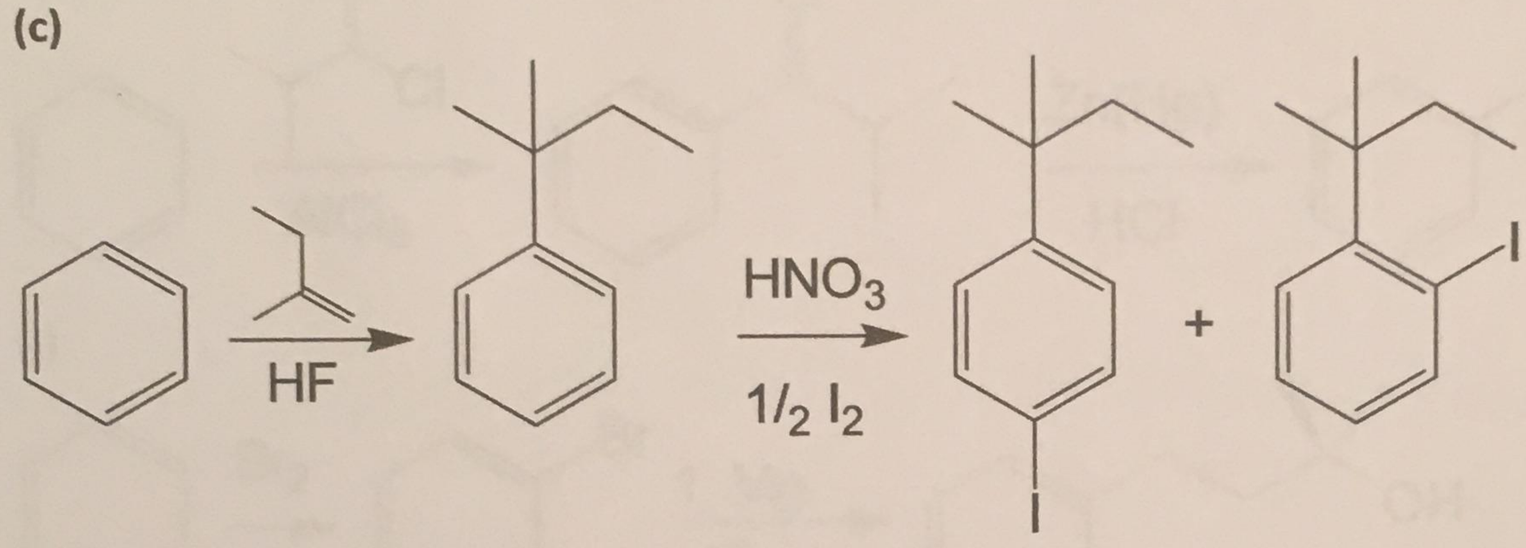
(a)



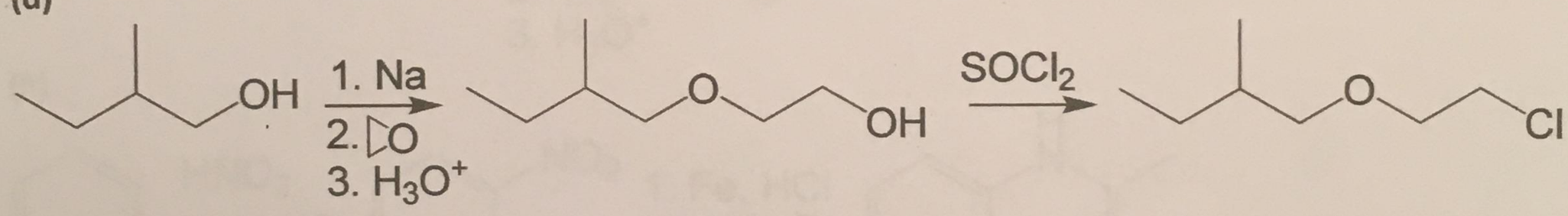
(b)



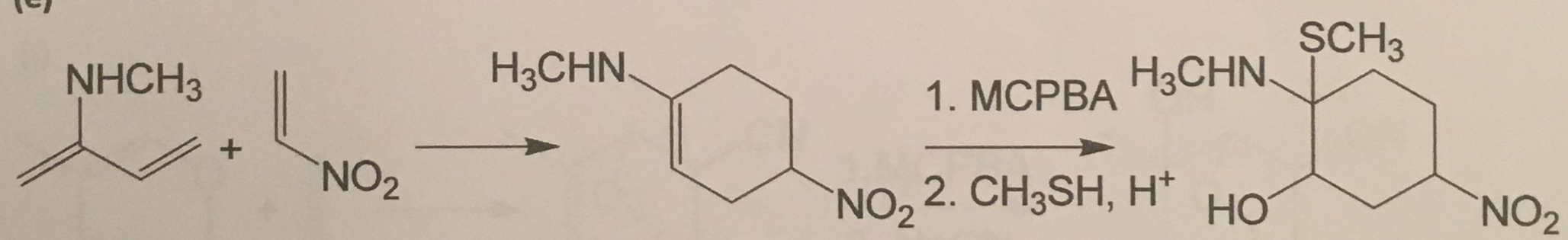
(c)



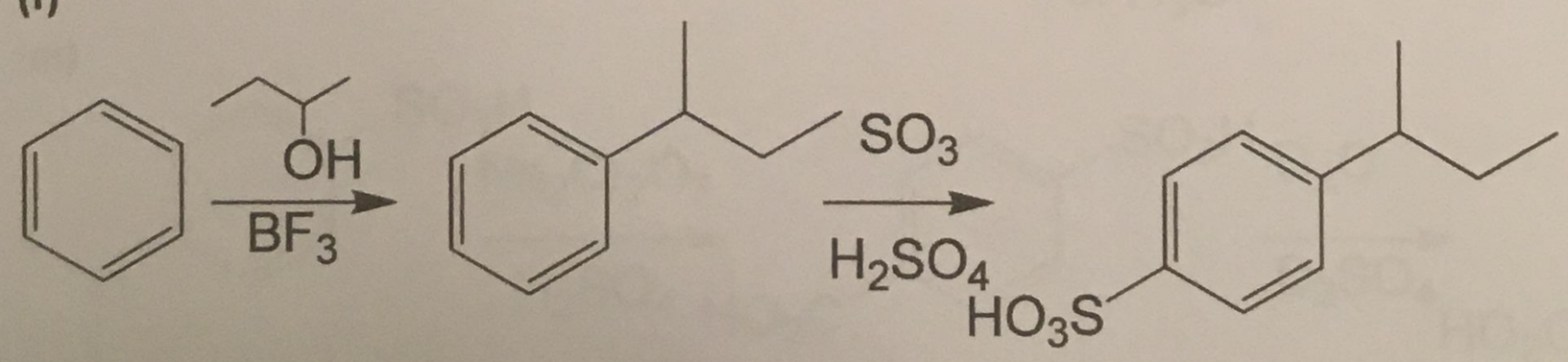
(d)



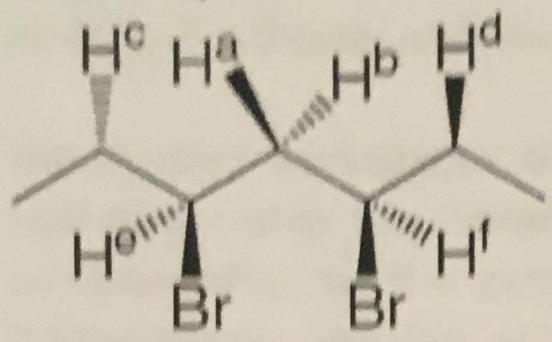
(e)



(f)



2. State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated). (2 x 4 = 8 pts)



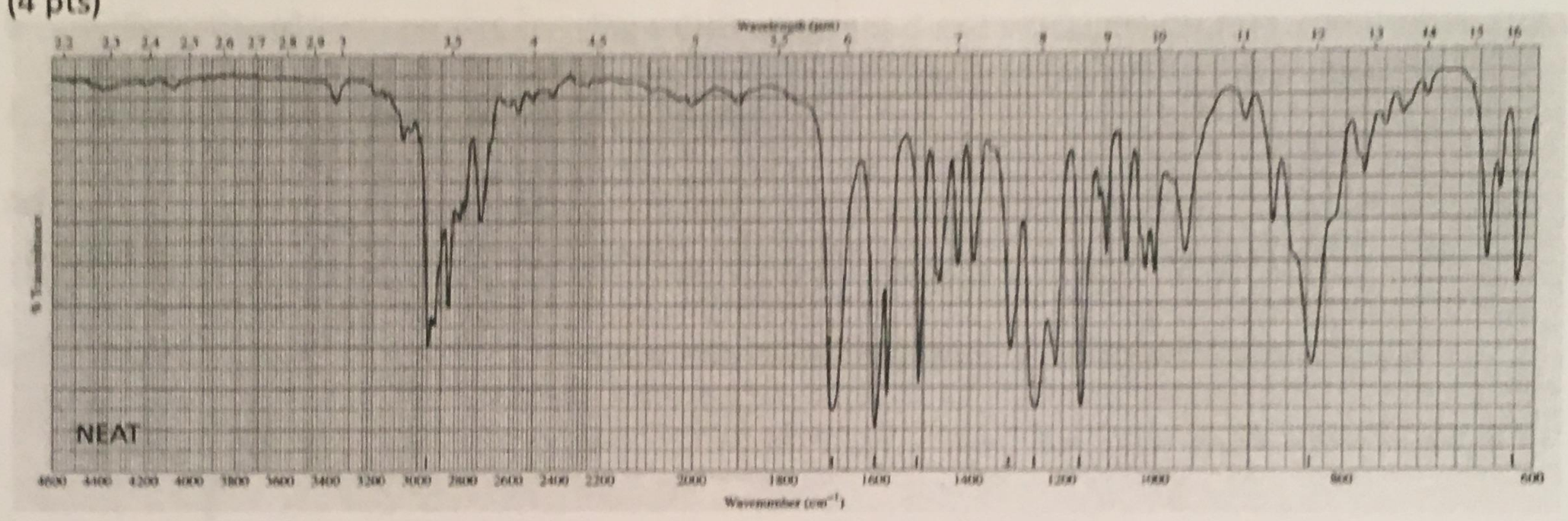
H^a and H^b are _____ **equivalent** _____

H^a and H^d are _____ **Unrelated** _____

H^c and H^d are _____ **Diastereotopic** _____

H^e and H^f are _____ **Enantiotopic** _____

3. (a) Identify the major signals present in the following IR spectrum; the Molecular formula is $C_{11}H_{14}O_2$ (4 pts)



$\ddot{\upsilon}_{C\text{-}H_Ar}$ = 3100 cm^{-1}

$\ddot{\upsilon}_{C\text{-}H_Alkane}$ = 2950 cm^{-1}

$\ddot{\upsilon}_{C\text{-}H_Aldehyde}$= 2880 and 2700 cm^{-1}

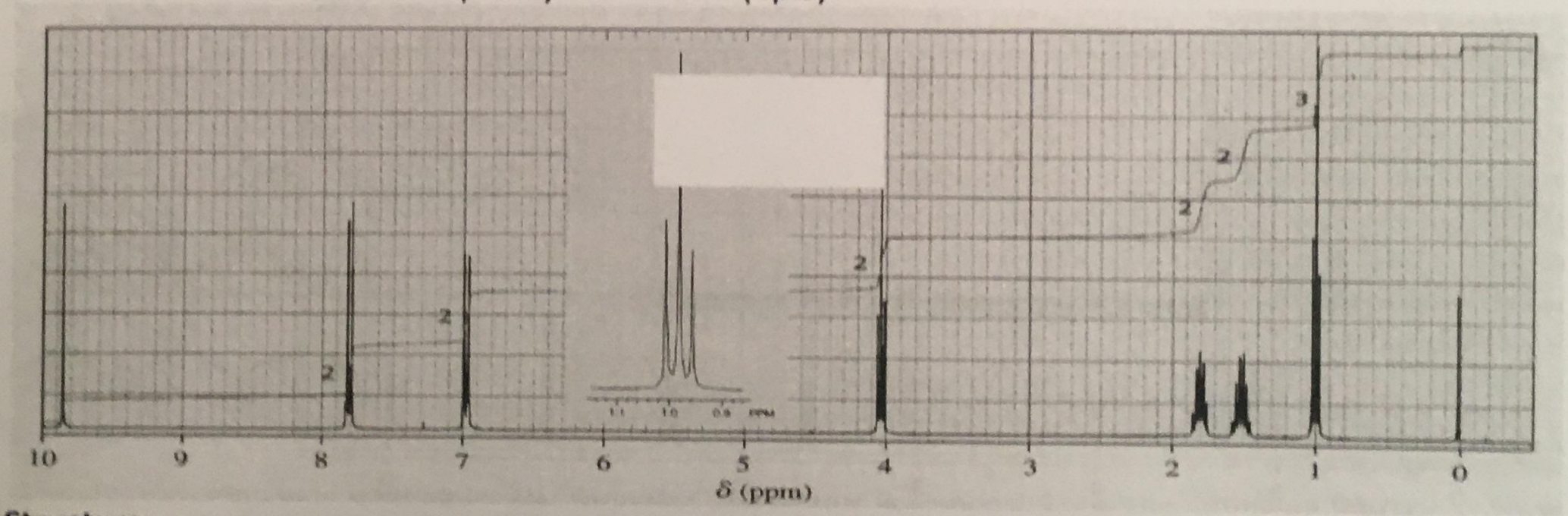
$\ddot{\upsilon}_{C=O}$ = 1700 cm^{-1}

$\ddot{\upsilon}_{C=C}$ = 1600 cm^{-1}

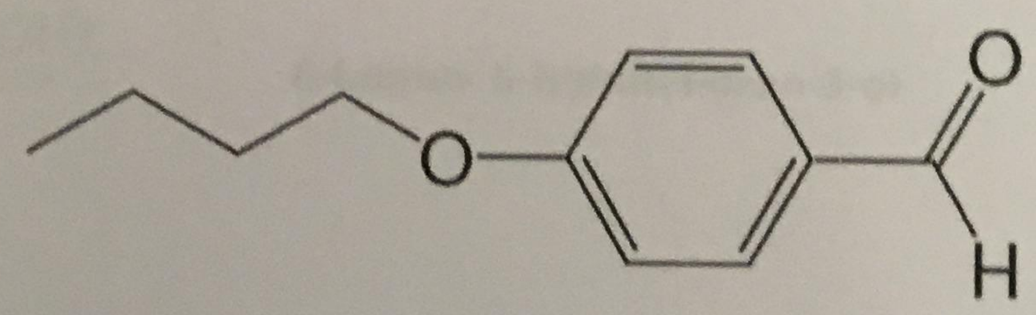
$\ddot{\upsilon}_{C\text{-}O_r}$ = 1100 cm^{-1}

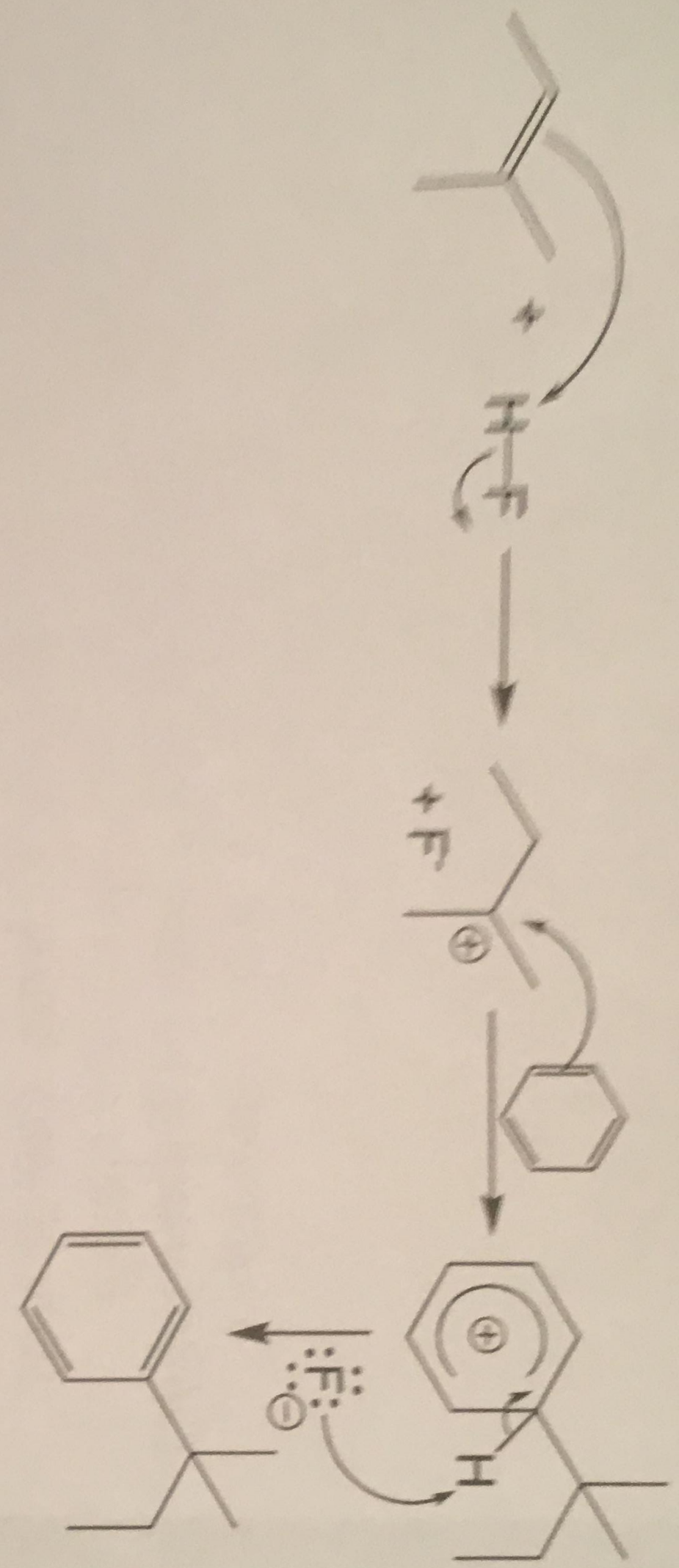
$\ddot{\upsilon}_{C\text{-}H_Ar_ben}$ = 600 – 800 cm^{-1}

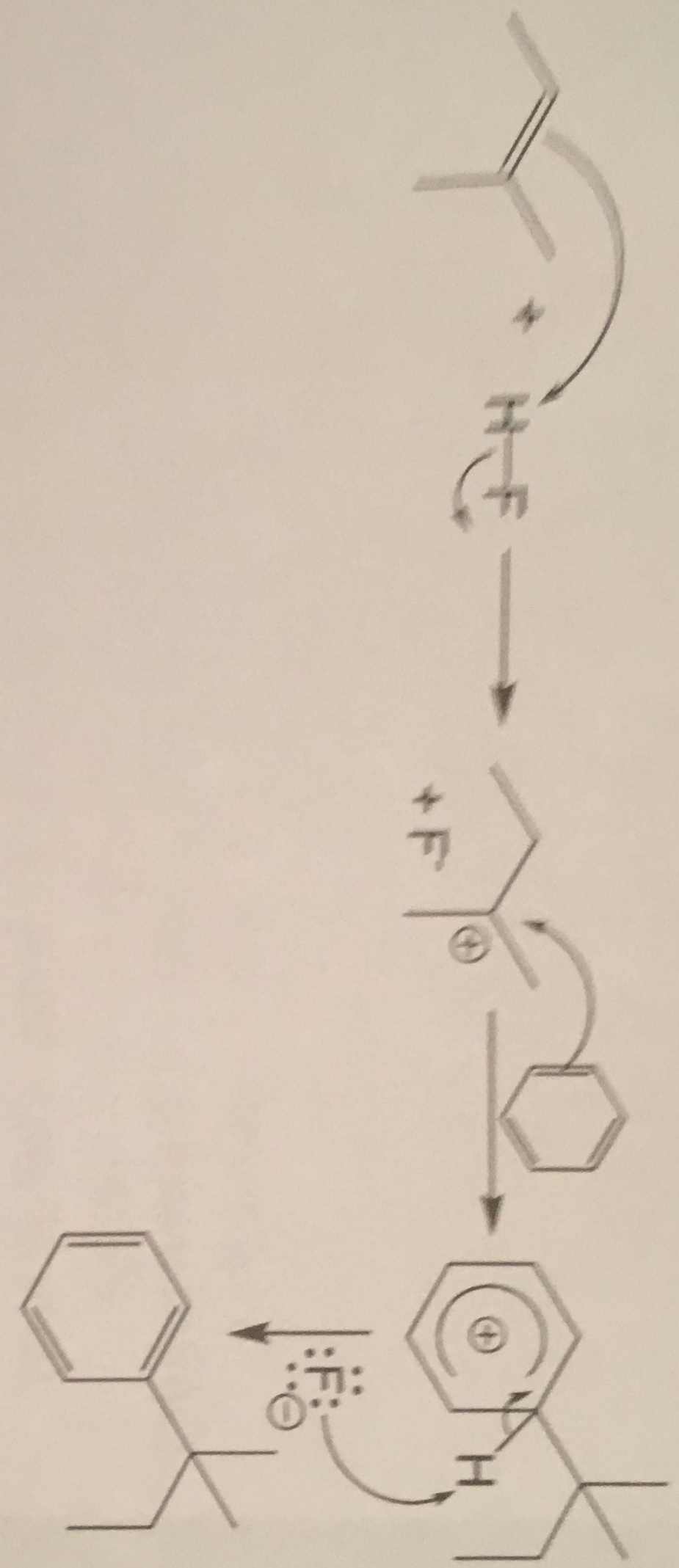
(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer. (4pts)



Structure



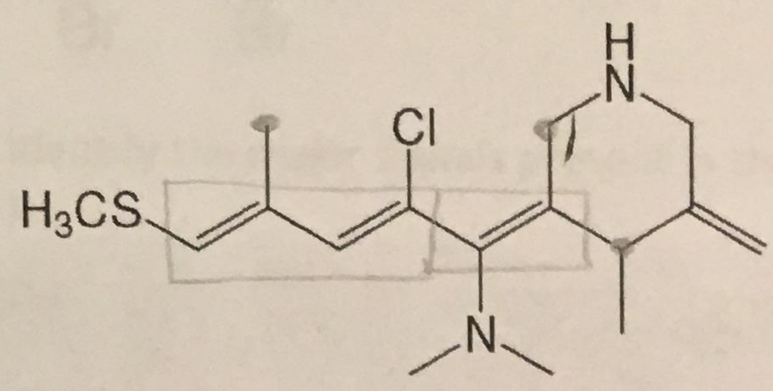




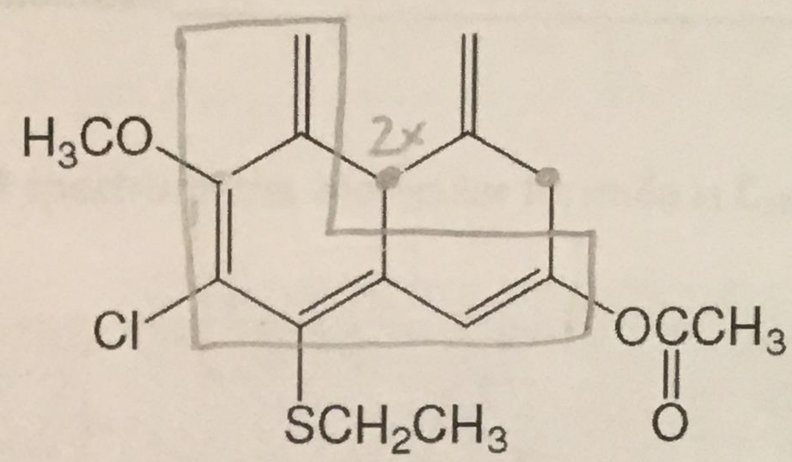
CHEM 266 – EXAM 1 **NAME**_____**Keys**_____

Spring 2014 (March 19)

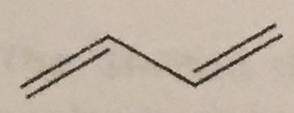
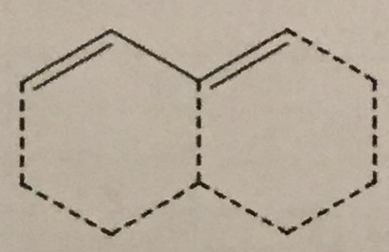
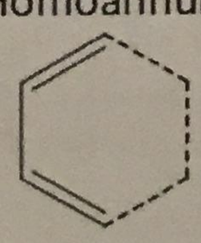
1. Use the Woodward-Fieser table to estimate the λ_{max} observed in a UV spectra of the following cross-conjugated systems (6 pts)



Parent value	=	**217**
1. Extra conjugated C=C	=	**30**
1. Exocyclic C=C	=	**5**
1. $N(CH_3)_3$	=	**60**
3 Alkyl groups	=	**15**
1. Cl	=	**5**
1. SCH_3	=	**30**
		362



Parent value	=	**253**
2. Extra conjugated C=C	=	**60**
2. Exocyclic C=C	=	**10**
SCH_2CH_3	=	**30**
3 Alkyl groups	=	**15**
Cl	=	**5**
OCH_3	=	**6**
		379

Acyclic 	**217 nm**
Heteroannular 	**214 nm**
Homoannular 	**253 nm**

For each additional conjugated double bond	**+ 30 nm**
For each exocyclic double bond	**+ 5 nm**
For each substituent	
C-substituent	**+ 5 nm**
Cl	**+ 5 nm**
Br	**+ 5 nm**
O-Alkyl	**+ 6 nm**
$OCOCH_3$	**+ 0 nm**
$N(alkyl)_2$	**+ 60 nm**
S-alkyl	**+ 30 nm**
Solvent correction	**+ 0 nm**

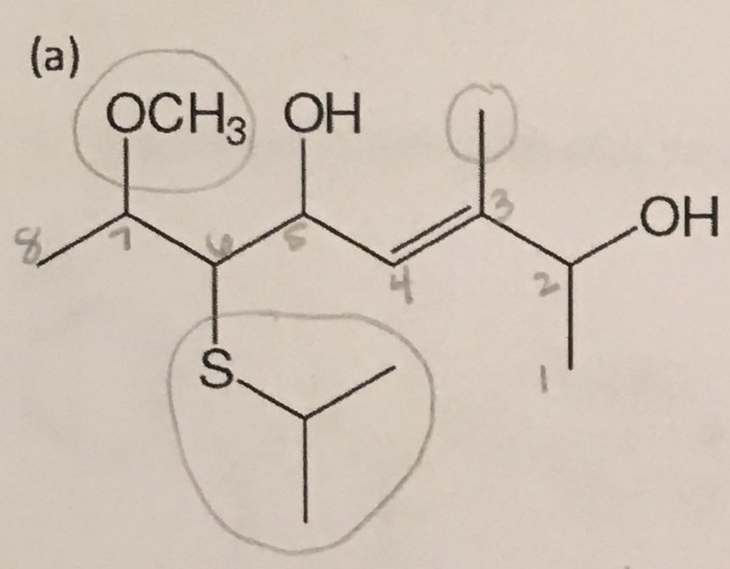
Explain (4 pts)

nI = 12 – 7 = 5 insaturations

The IR spectrum suggests that the molecule contains an aldehyde, an aromatic ring, and akyl chain as well as an ether functional group. The ^{1}H-NMR shows 2 doublets of 2H at 7.0ppm and at 7.8 ppm corresponding to the protons on a 1,4-disubstituted aromatic ring. This ring accounts for 4 insaturations, and the aldehyde corresponds to the last insaturation. The same NMR spectrum shows a series of 2H triplet at 4.00 ppm suggesting a CH_2 linked to an oxygen and to another CH_2. Two multiplets of 2H and a triplet of 3H corresponding to a $CH_2CH_2CH_3$. So, the compound consists in a 1,4-disubstitued benzene ring carrying a CHO on one end and a $OCH_2CH_2CH_2CH3$ at the other end.

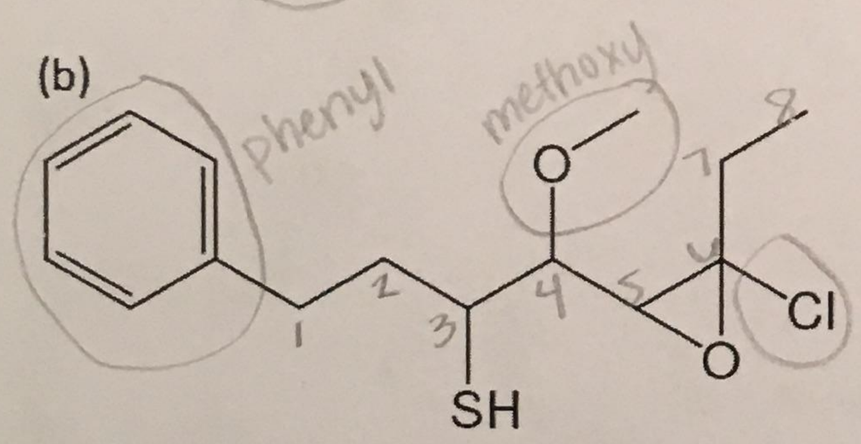
4. Name the following compounds (3 x 6 = 18 pts)

(a)



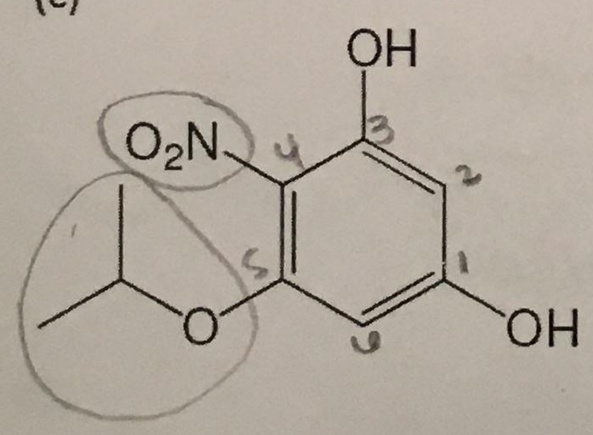
6-isopropylthio-7-methoxy-3-methyloct-3-ene-2,5-diol

(b)



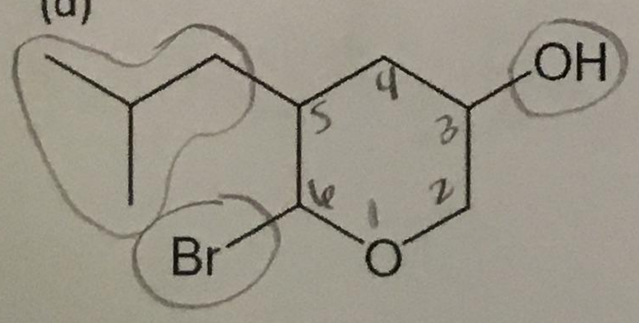
6-chloro-5,6-epoxy-4-methoxy-1-phenyloctane-3-thiol

(c)



5-isopropoxy-4-nitrobenzene-1,3-diol

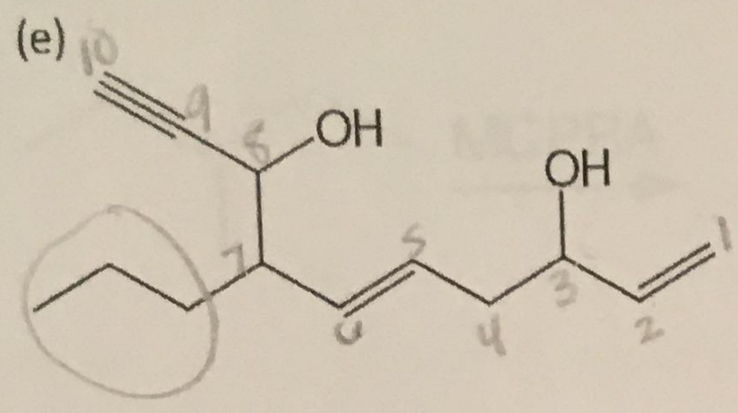
(d)



6-bromo- 5-isobutyl-oxan-3-ol

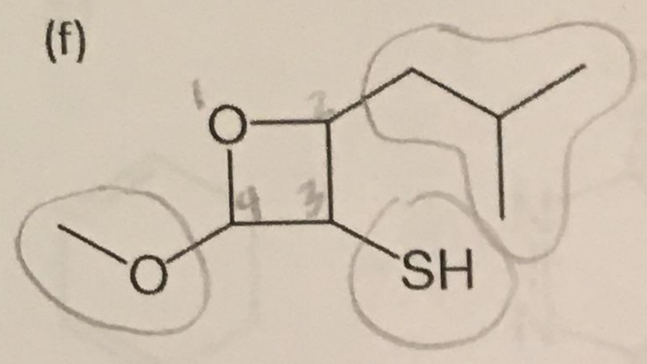
oxane

(e)



7-propyldeca-1,5-dien-9-yne-3,8-diol

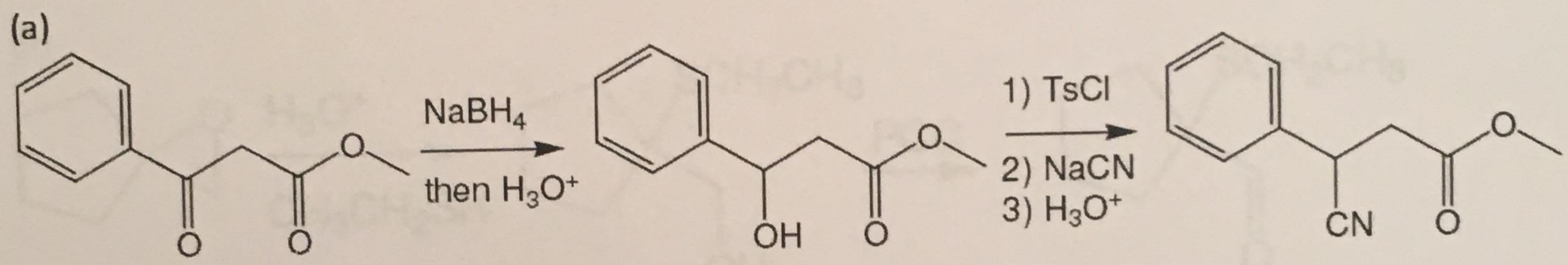
(f)



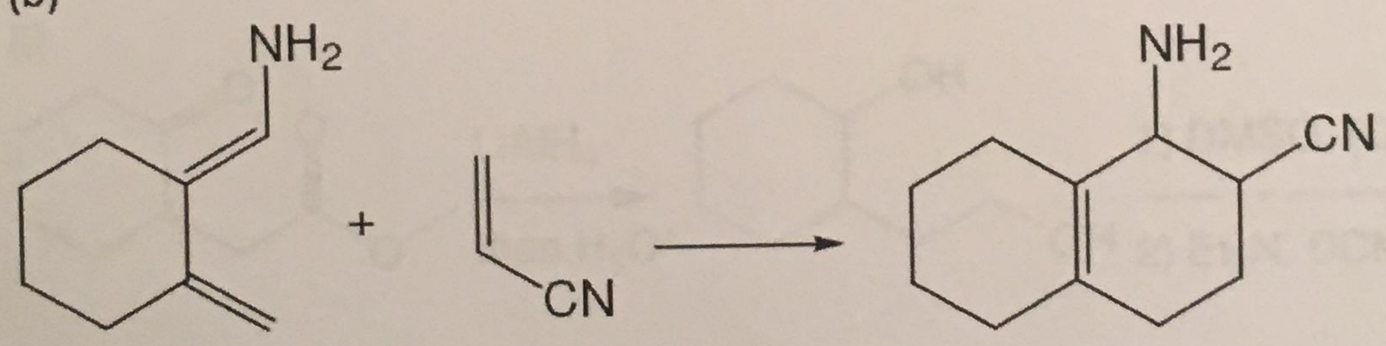
2-isobutyl-4-methoxyoxetane-3-thiol

5. Predict the major product(s) expected from the following reactions (3 x 11 = 33 pts)

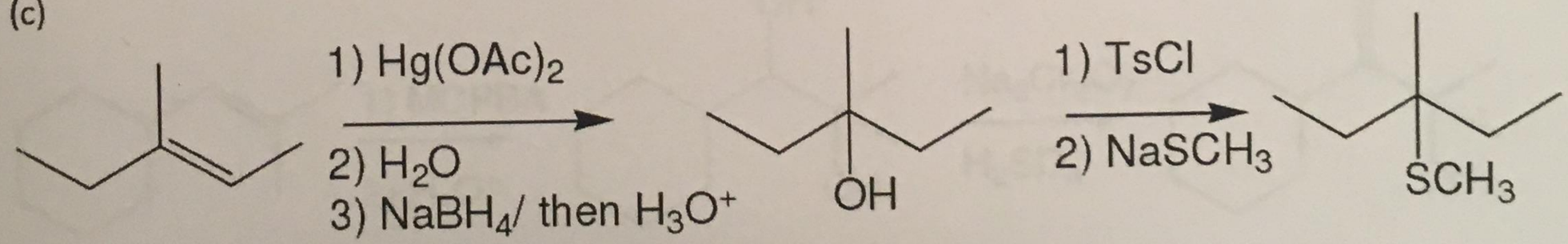
(a)



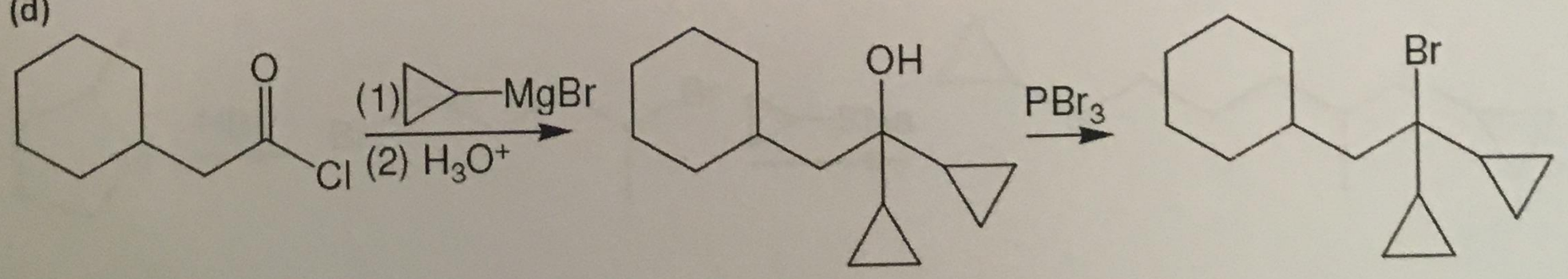
(b)



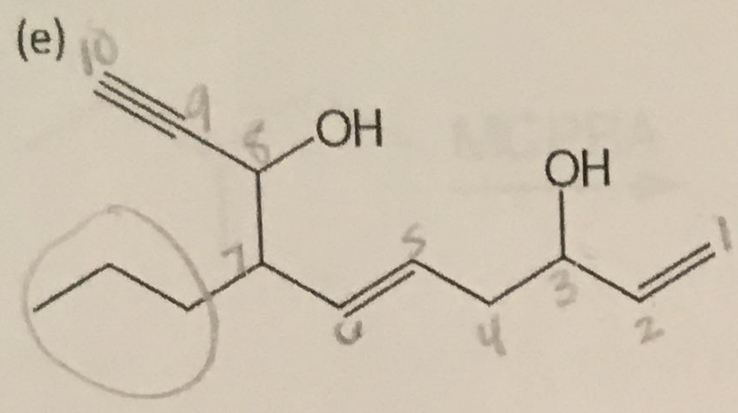
(c)



(d)

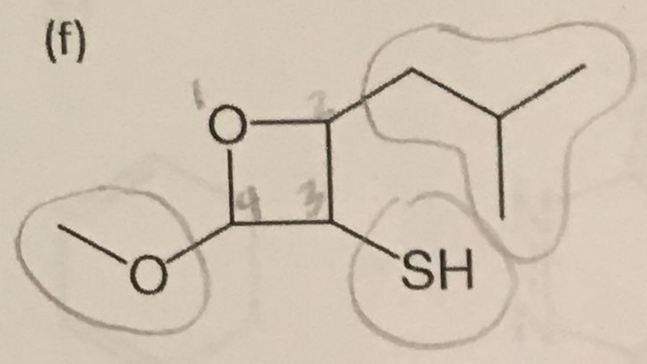


(e)



7-propyldeca-1,5-dien-9-yne-3,8-diol

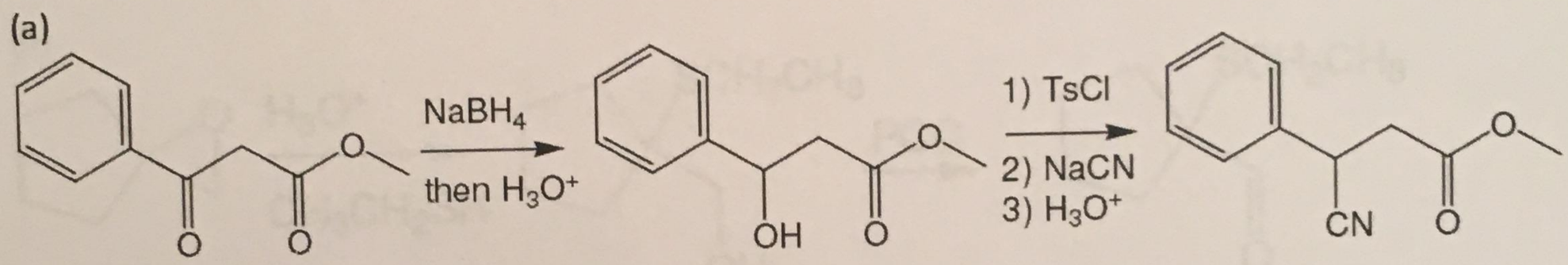
(f)



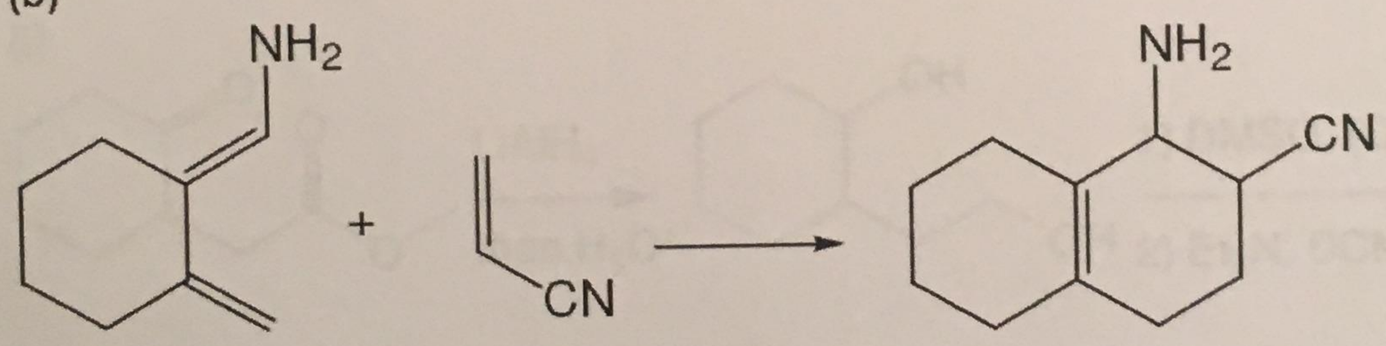
2-isobutyl-4-methoxyoxetane-3-thiol

5. Predict the major product(s) expected from the following reactions (3 x 11 = 33 pts)

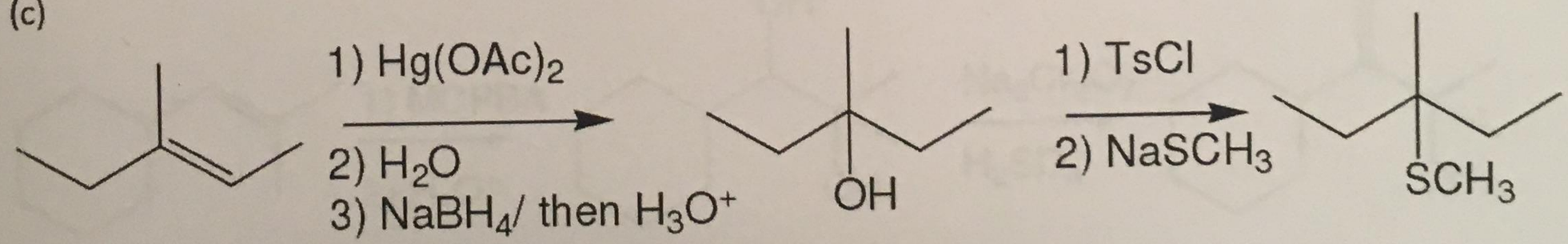
(a)



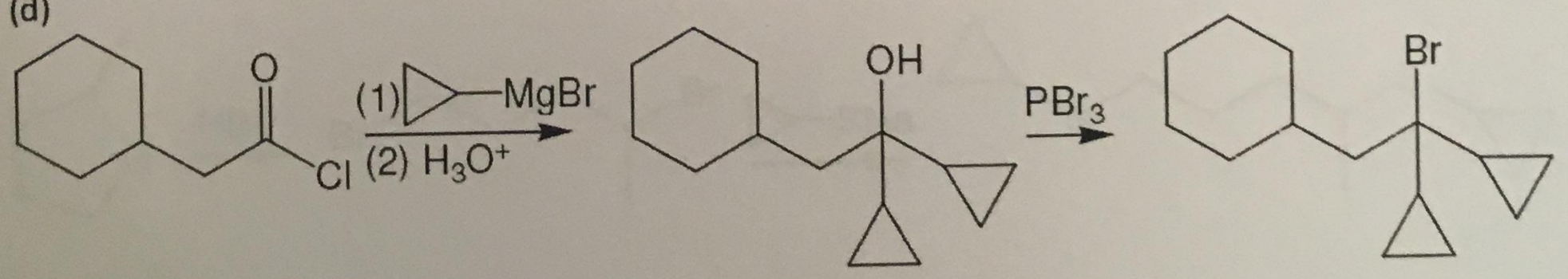
(b)



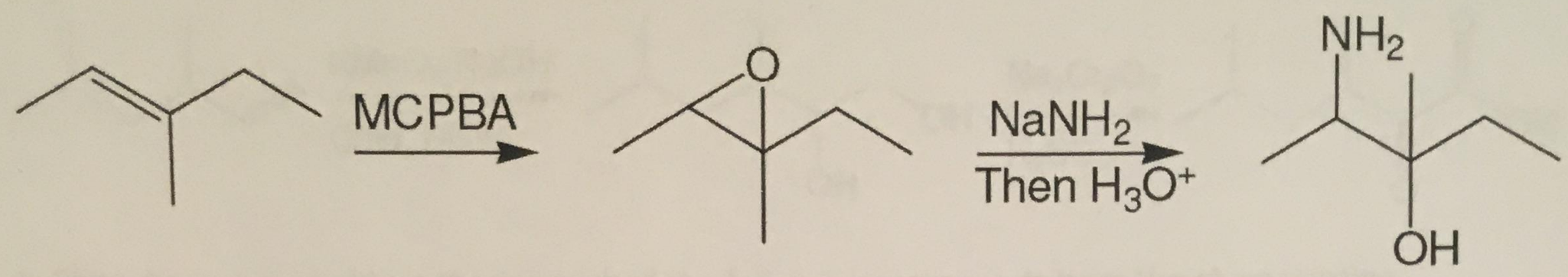
(c)



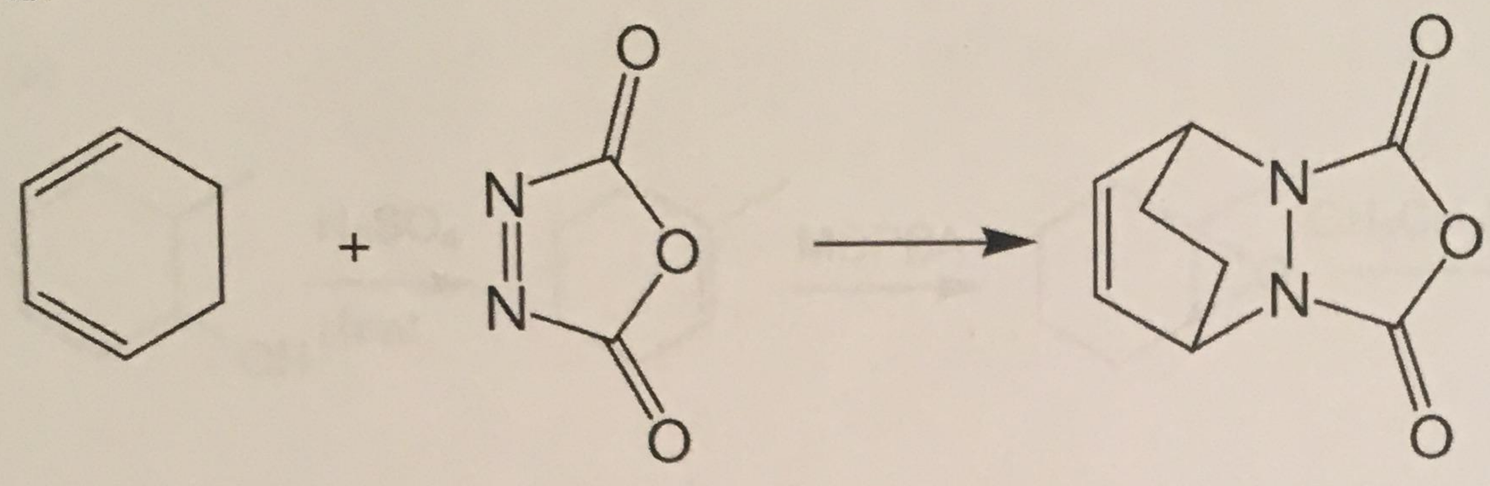
(d)



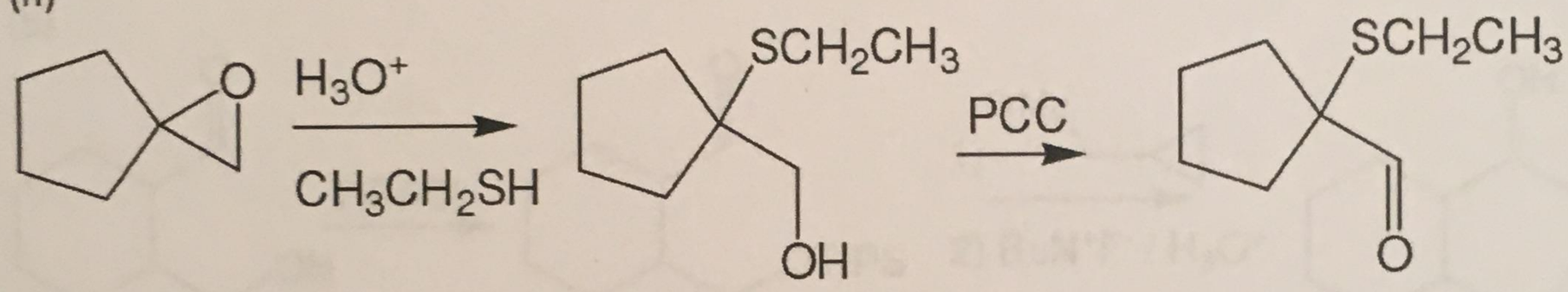
(f)


MCPBA
O
NaNH2
Then H3O+
NH2
OH

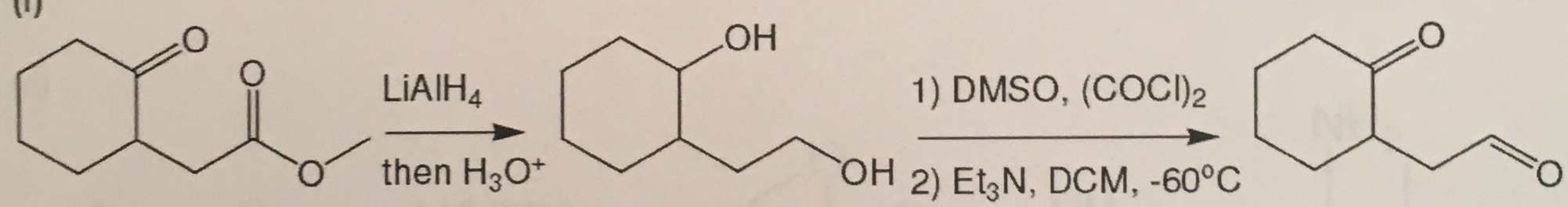
(g)


+
O
N
N
O
O
N
N
O
O
O

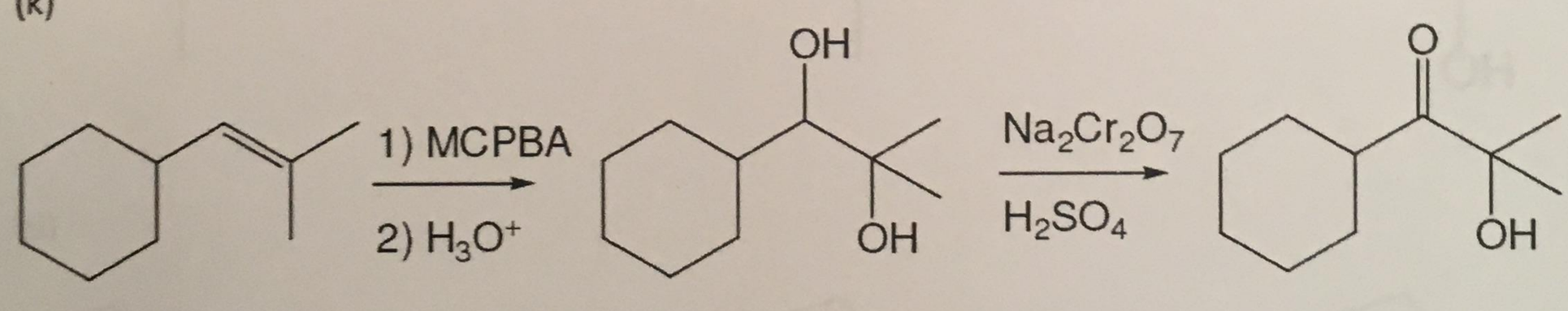
(h)


O
H3O+
CH3CH2SH
SCH2CH3
OH
PCC
SCH2CH3
O

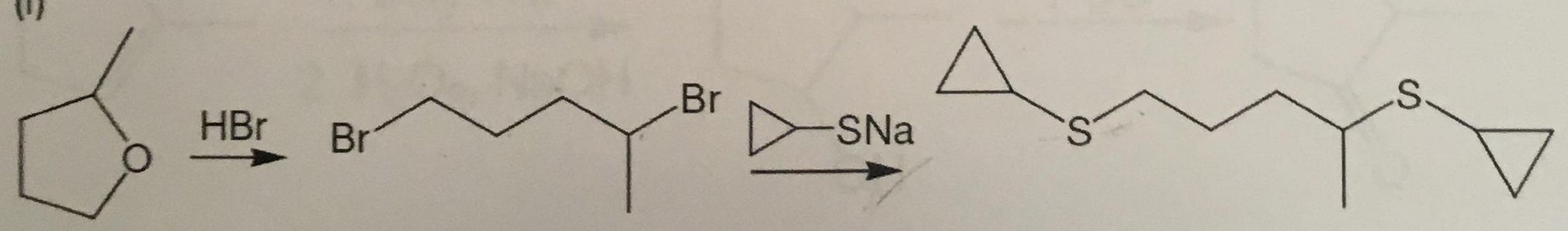
(i)


O
O
O
LiAlH4
then H3O+
OH
OH
1) DMSO, (COCl)2
2) Et3N, DCM, -60°C
O
O

(k)


1) MCPBA
2) H3O+
OH
OH
Na2Cr2O7
H2SO4
O
OH

(l)

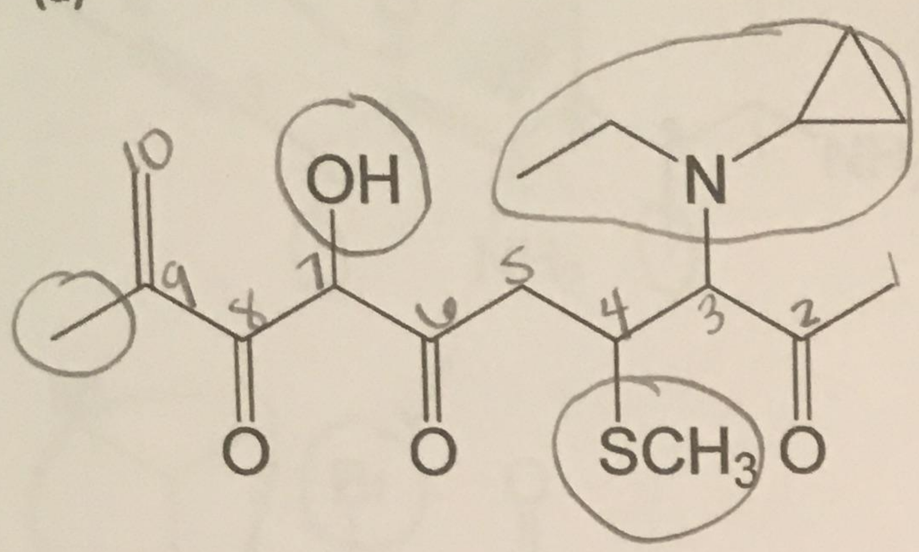

O
HBr
Br
Br
SNa
S
S

CHEM 266 – EXAM 3 (SPRING 2016) **NAME**_____

Wednesday April 20, 2016

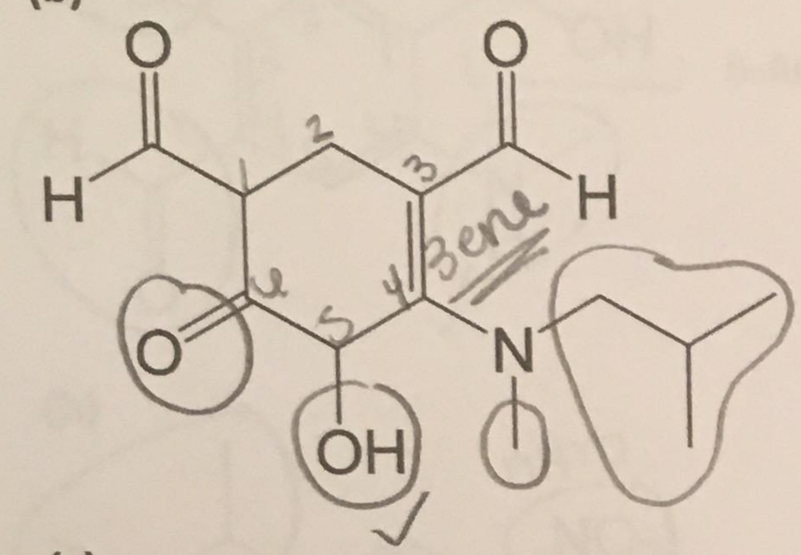
1. Name the following compounds (3 x 8 = 24 pts)

(a)



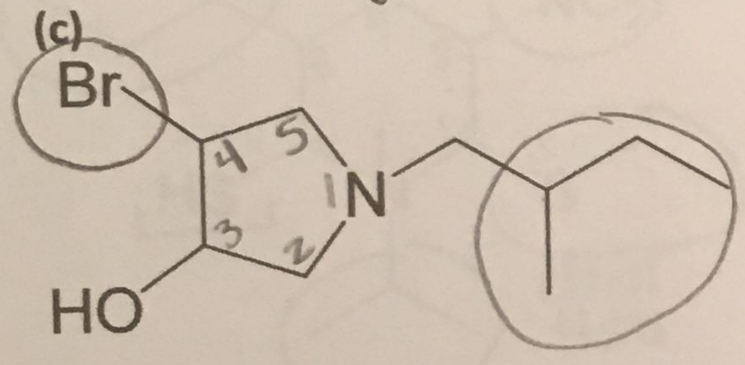
3 Amino-N-cyclopropyl-N-ethyl-7-hydroxy-9-methyl-4-methylthiodec-9-ene-2,6,8-trione

(b)



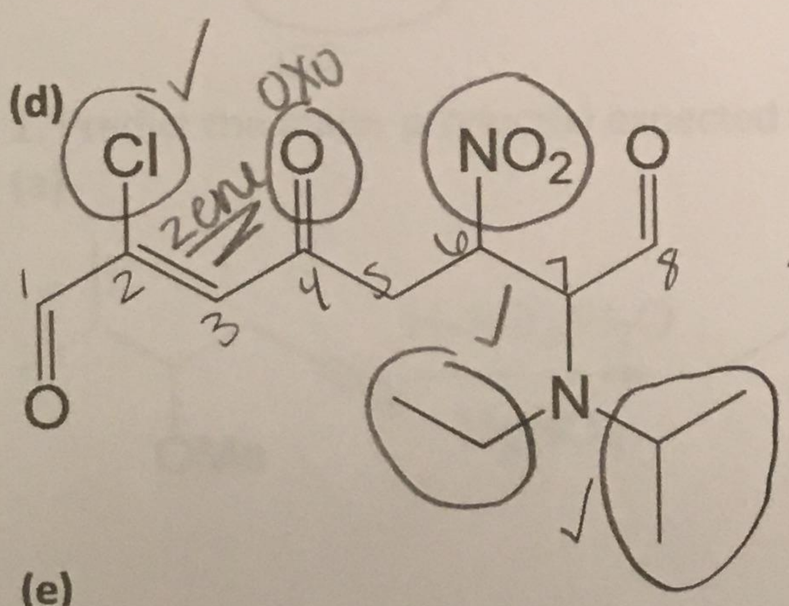
4-Amino-5-hydroxy-N-isobutyl-N-methyl-6-oxocyclohex-3-ene-1,3-dicarbaldehyde

(c)



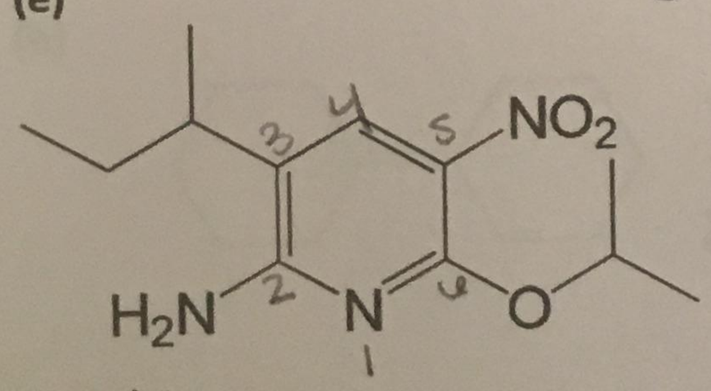
4-bromo-1-(2-methylbutyl)pyrrolidin-3-ol
Or 4-brom-N-sec-pentylpyrrolidin-3-ol

(d)



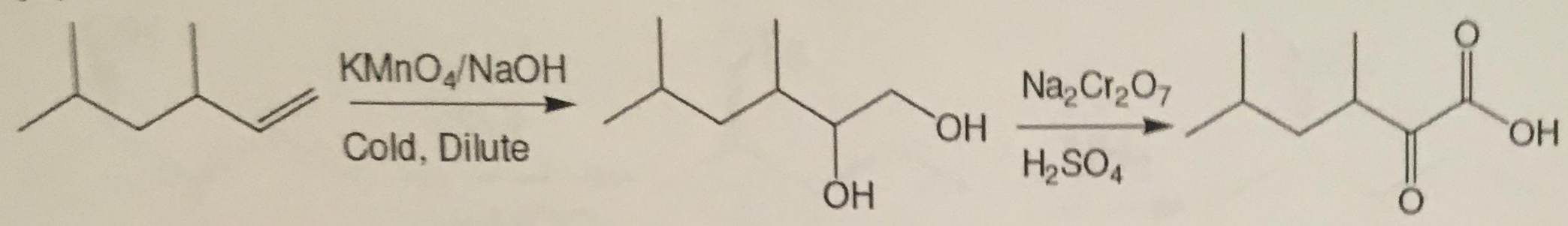
7-amino-2-chloro-N-ethyl-N-isopropyl-6-nitro-4-oxooct-2-enedial

(e)



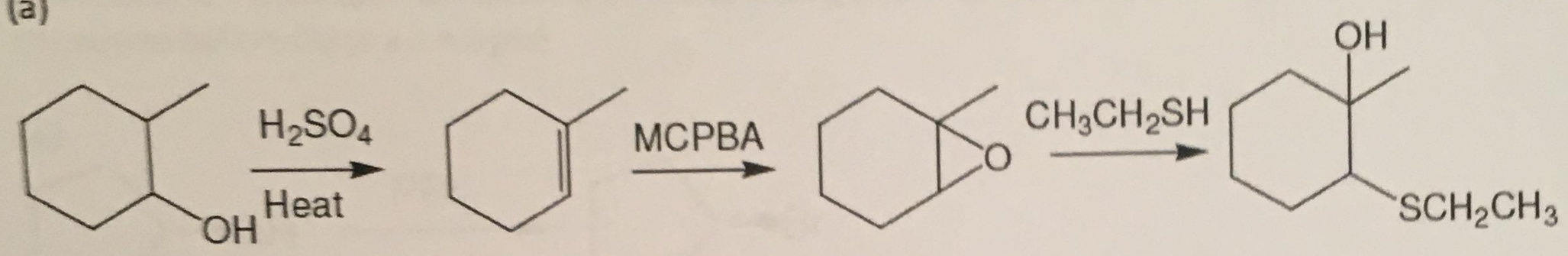
3-*sec*-butyl-6-isopropoxy-5-nitropyridin-2-amine

(m)

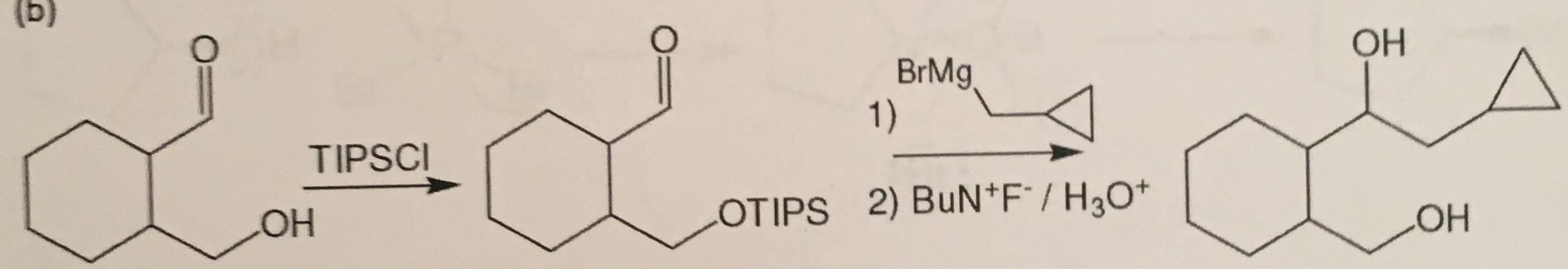


6. Show how you would synthesize each of the following compounds from the given starting material(s) (3 x 5 = 15 pts)

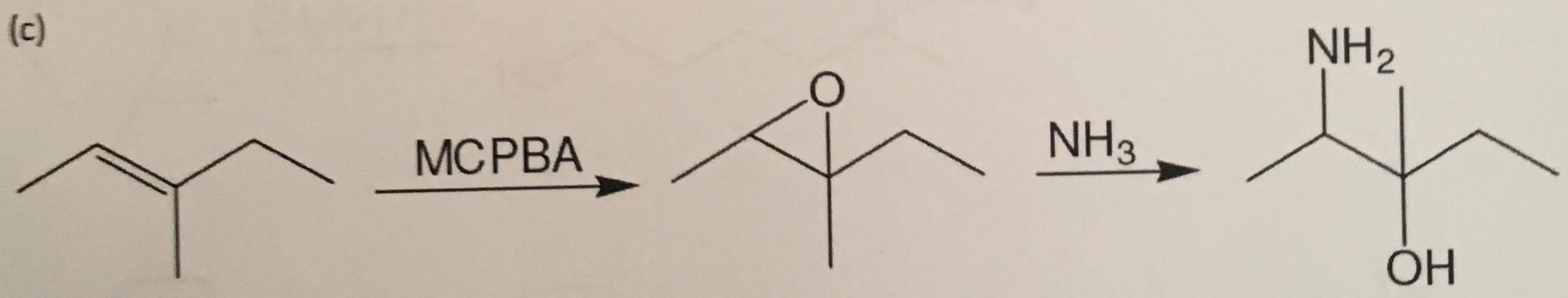
(a)



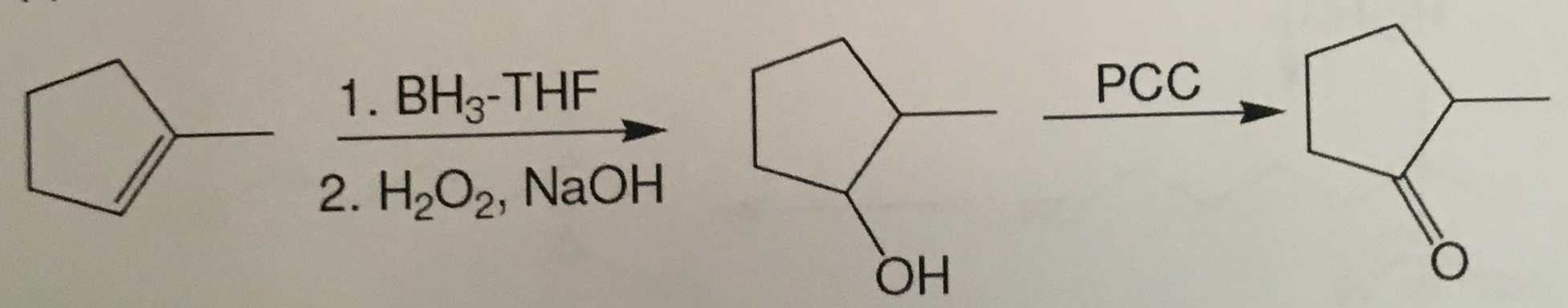
(b)



(c)



(d)

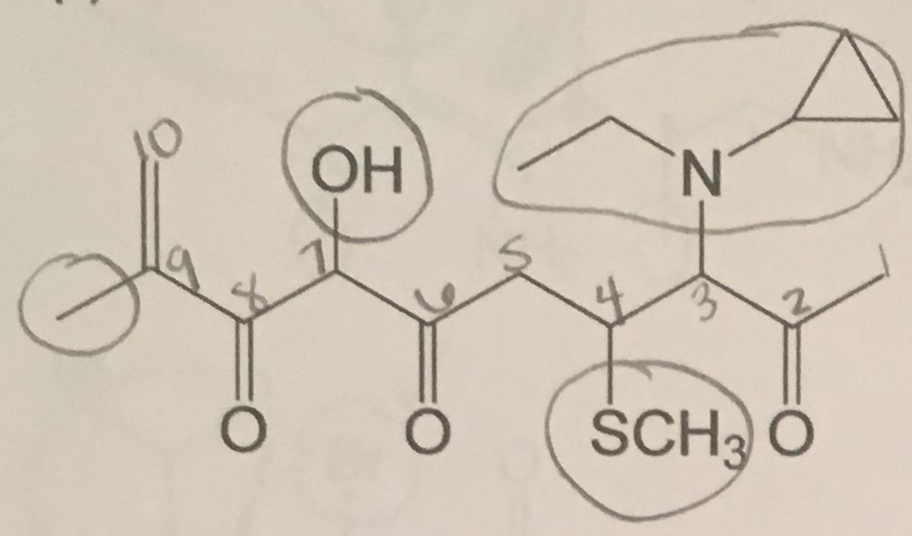


CHEM 266 – EXAM 3 (SPRING 2016) **NAME**_____

Wednesday April 20, 2016

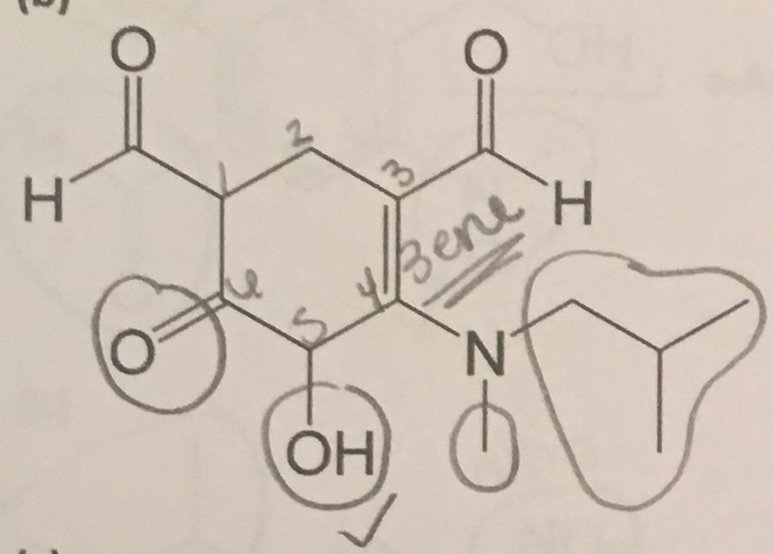
1. Name the following compounds (3 x 8 = 24 pts)

(a)



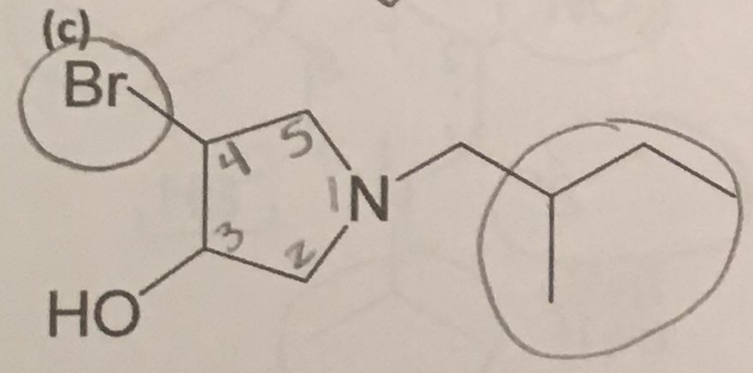
3 Amino-N-cyclopropyl-N-ethyl-7-hydroxy-9-methyl-4-methylthiodec-9-ene-2,6,8-trione

(b)



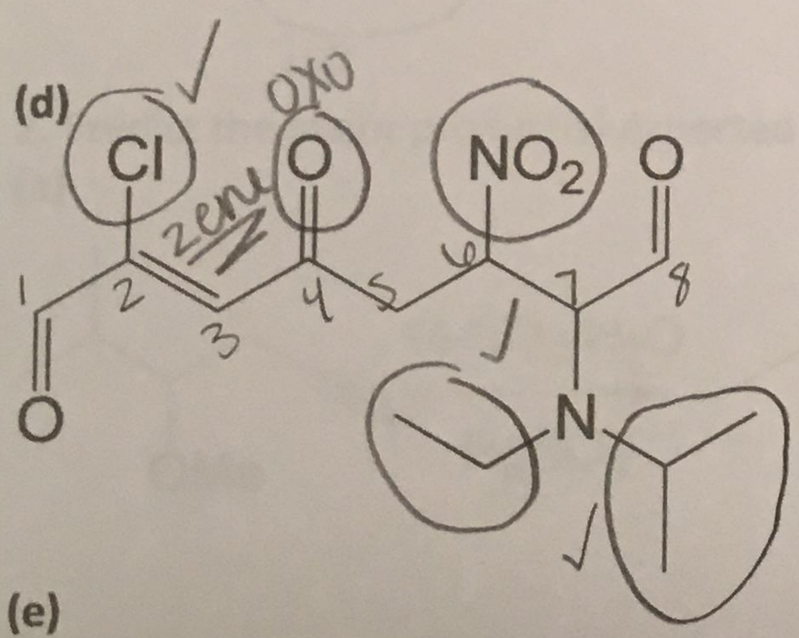
4-Amino-5-hydroxy-N-isobutyl-N-methyl-6-oxocyclohex-3-ene-1,3-dicarbaldehyde

(c)



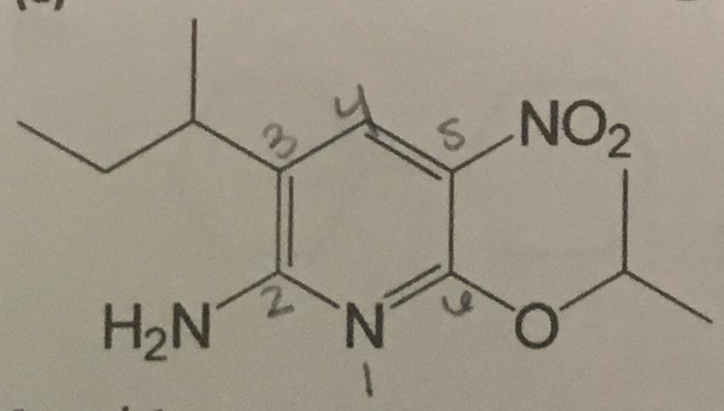
4-bromo-1-(2-methylbutyl)pyrrolidin-3-ol
Or 4-brom-N-sec-pentylpyrrolidin-3-ol

(d)



7-amino-2-chloro-N-ethyl-N-isopropyl-6-nitro-4-oxooct-2-enedial

(e)



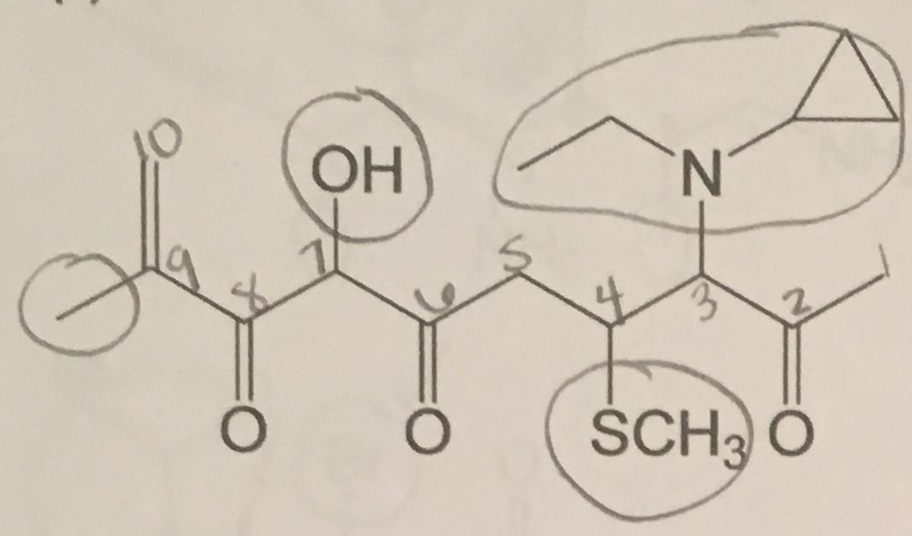
3-*sec*-butyl-6-isopropoxy-5-nitropyridin-2-amine

CHEM 266 – EXAM 3 (SPRING 2016) **NAME**_____

Wednesday April 20, 2016

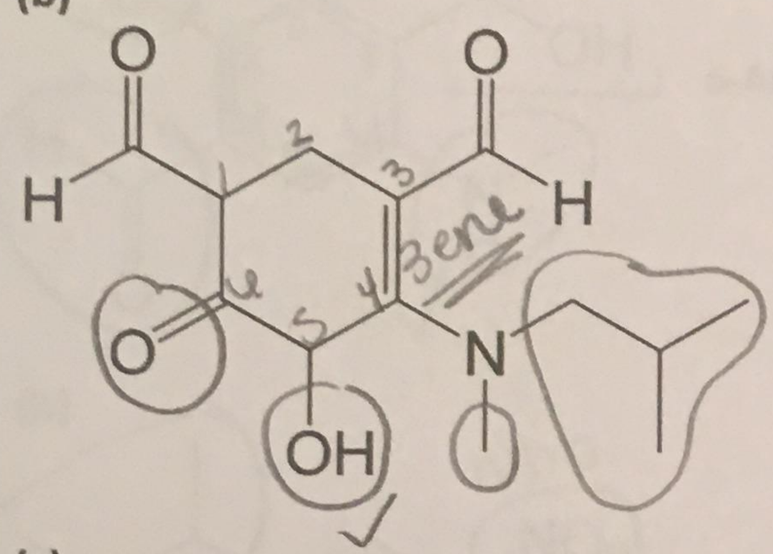
1. Name the following compounds (3 x 8 = 24 pts)

(a)



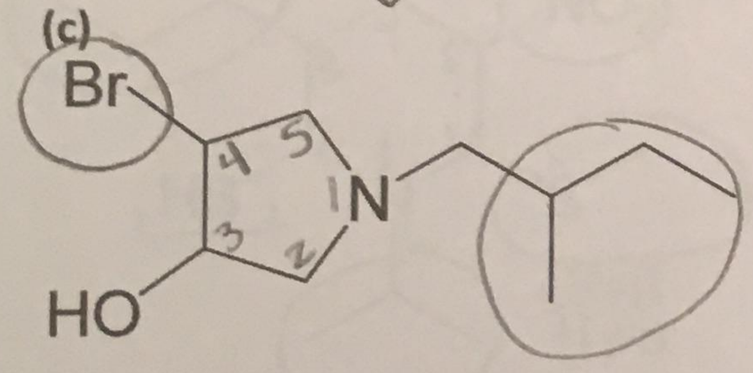
3 Amino-N-cyclopropyl-N-ethyl-7-hydroxy-9-methyl-4-methylthiodec-9-ene-2,6,8-trione

(b)



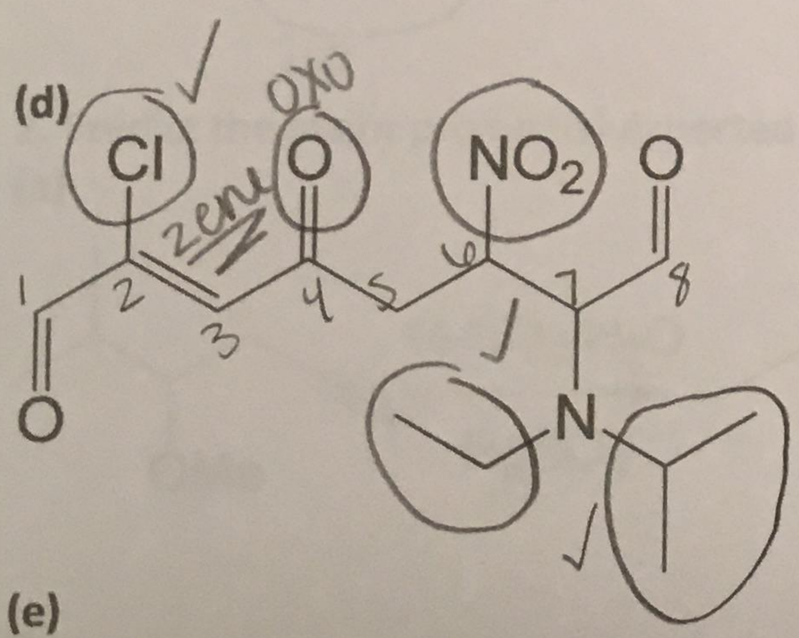
4-Amino-5-hydroxy-N-isobutyl-N-methyl-6-oxocyclohex-3-ene-1,3-dicarbaldehyde

(c)



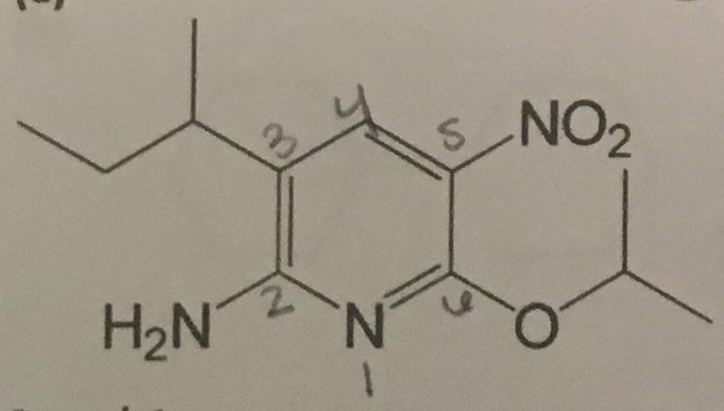
4-bromo-1-(2-methylbutyl)pyrrolidin-3-ol
Or 4-brom-N-sec-pentylpyrrolidin-3-ol

(d)



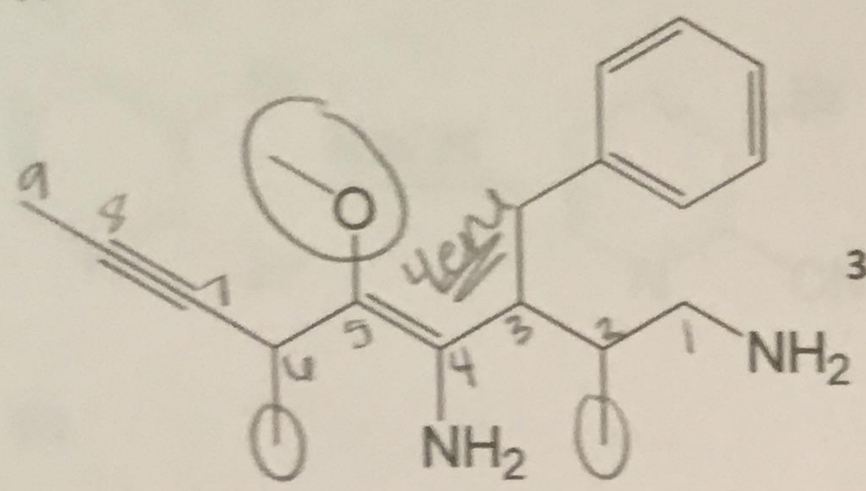
7-amino-2-chloro-N-ethyl-N-isopropyl-6-nitro-4-oxooct-2-enedial

(e)



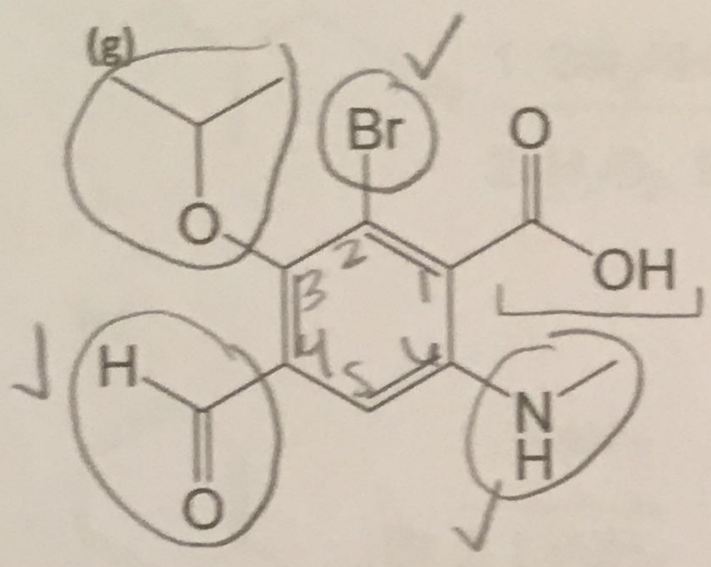
3-*sec*-butyl-6-isopropoxy-5-nitropyridin-2-amine

(f)



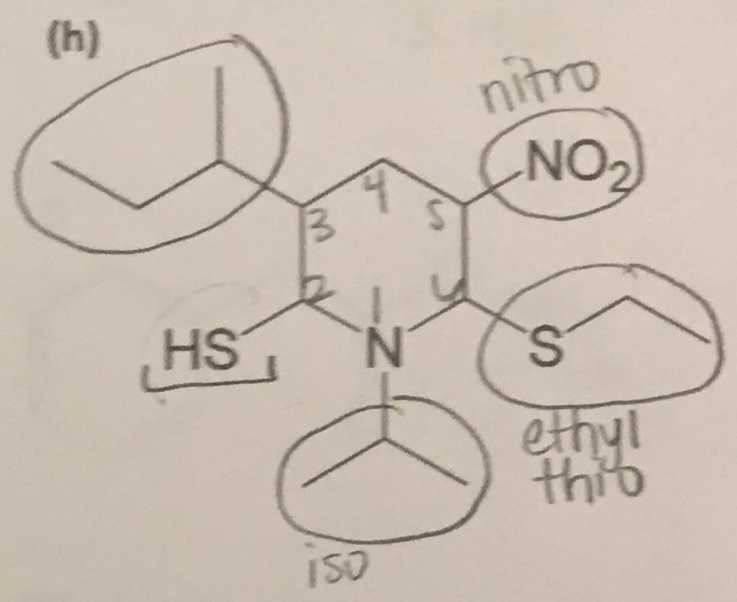
3-benzyl-5-methoxy-2,6-dimethylnon-4-en-7-yne-1,4-diamine

(g)



6-Amino-2-bromo-4-formyl-3-isopropoxy-N-methylbenzoic acid

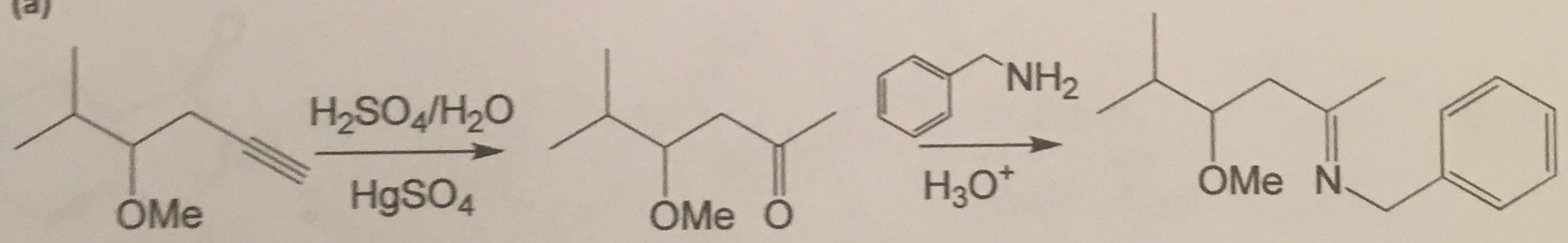
(h)



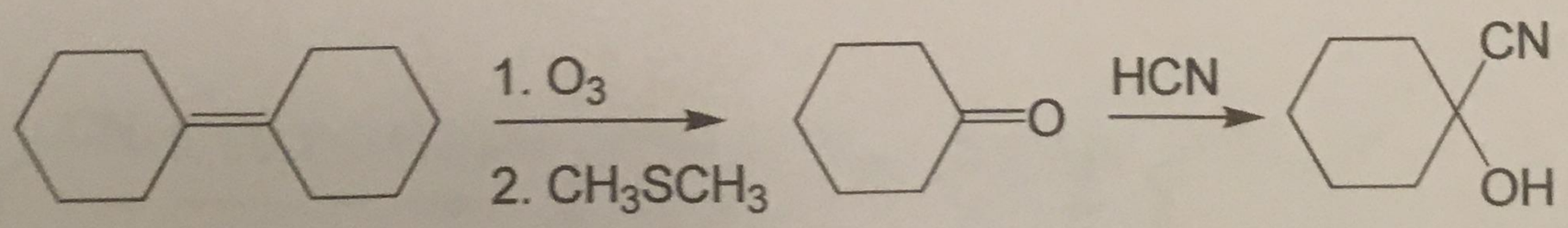
3-sec-butyl-6-ethylthio-1-isopropyl-5-nitropiperidine-2-thiol

2. Predict the major product(s) expected from the following reactions (3 x 16 = 48 pts)

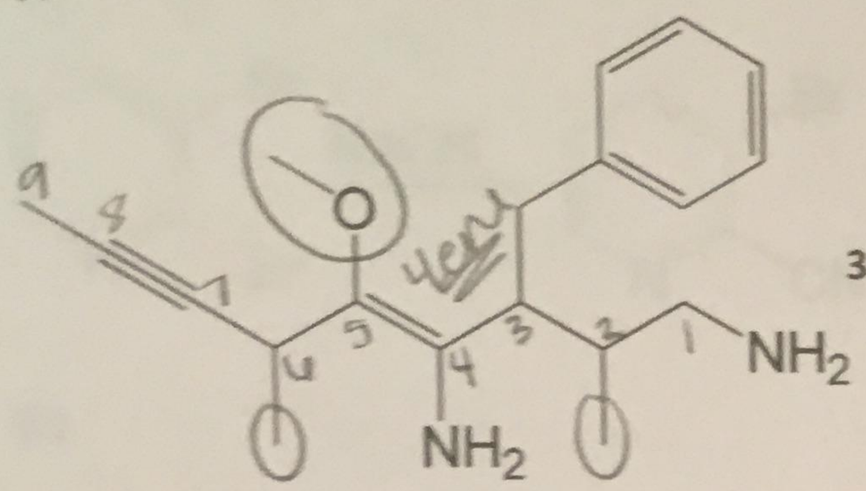
(a)



(b)

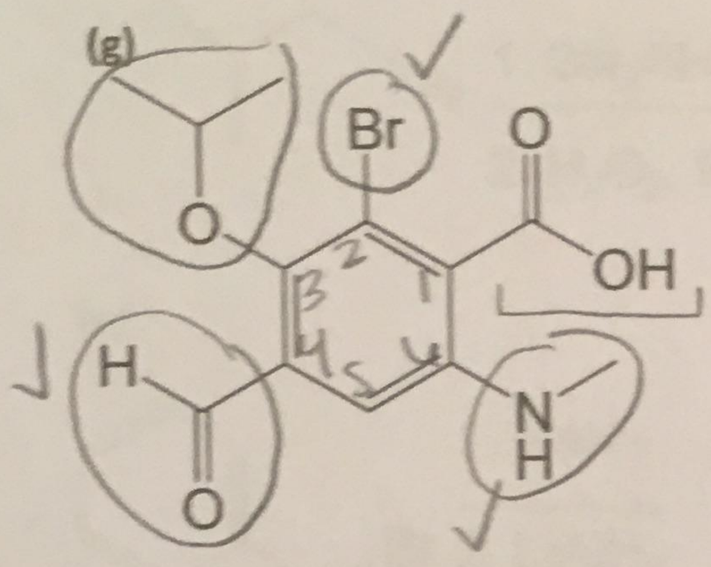


(f)



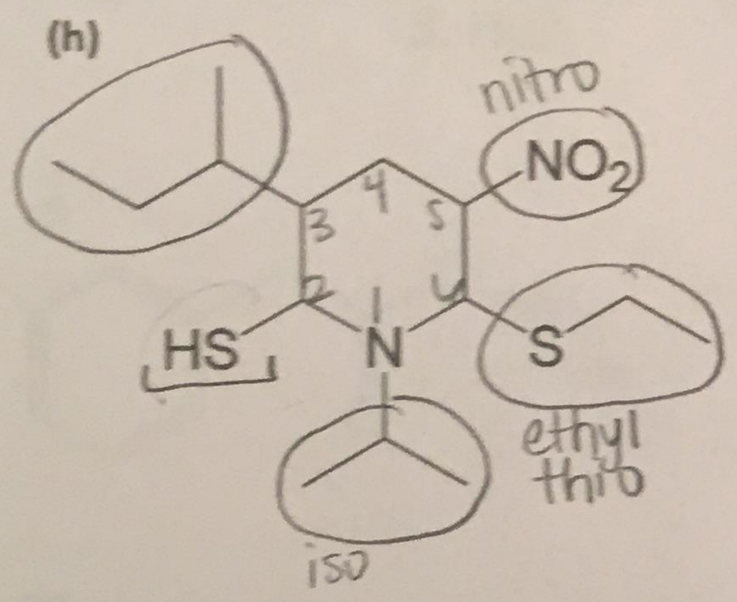
3-benzyl-5-methoxy-2,6-dimethylnon-4-en-7-yne-1,4-diamine

(g)



6-Amino-2-bromo-4-formyl-3-isopropoxy-N-methylbenzoic acid

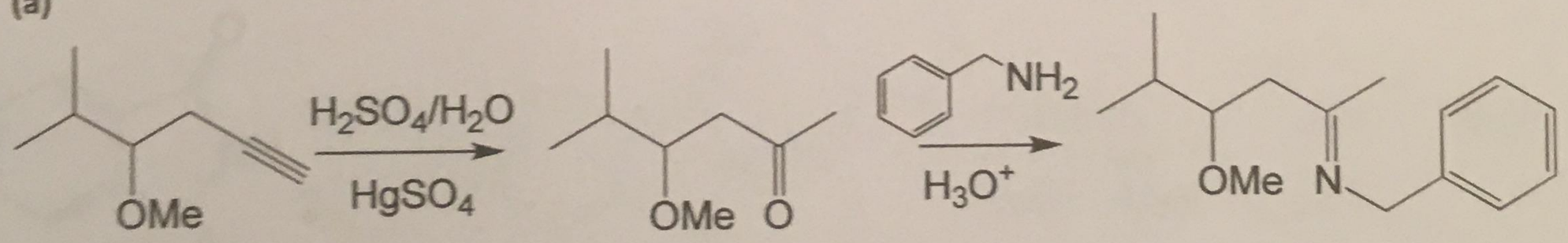
(h)



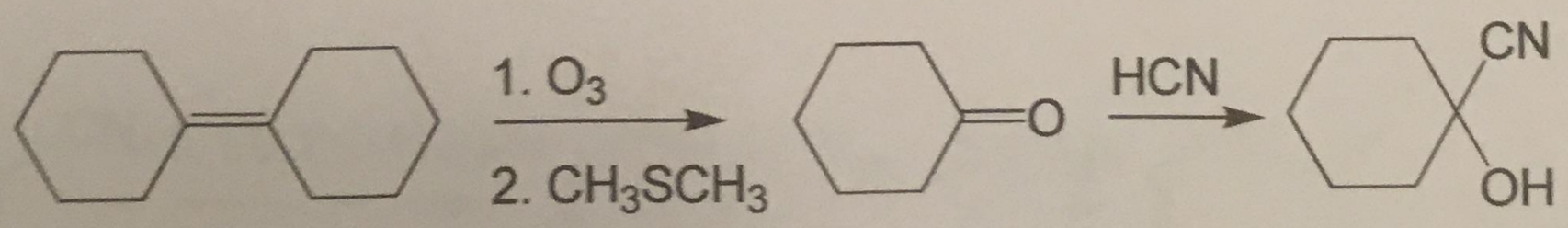
3-sec-butyl-6-ethylthio-1-isopropyl-5-nitropiperidine-2-thiol

2. Predict the major product(s) expected from the following reactions (3 x 16 = 48 pts)

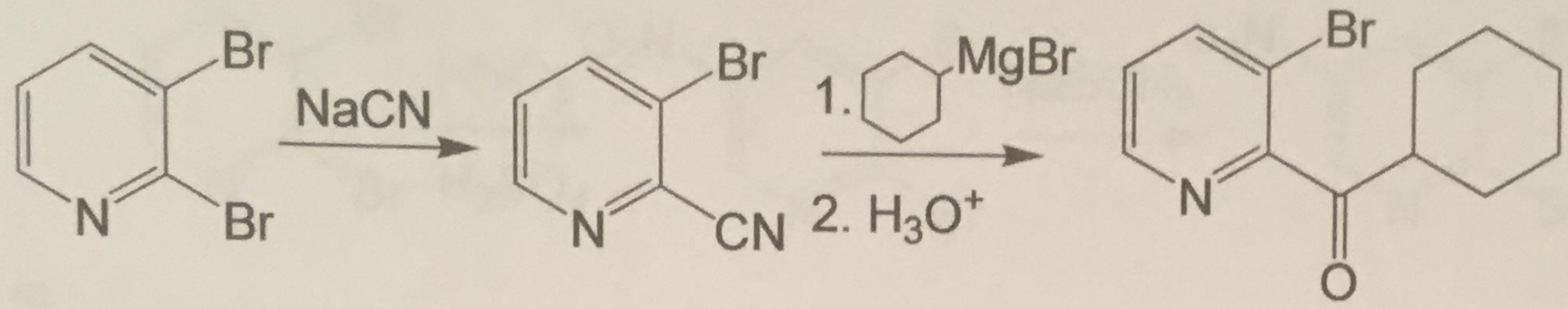
(a)



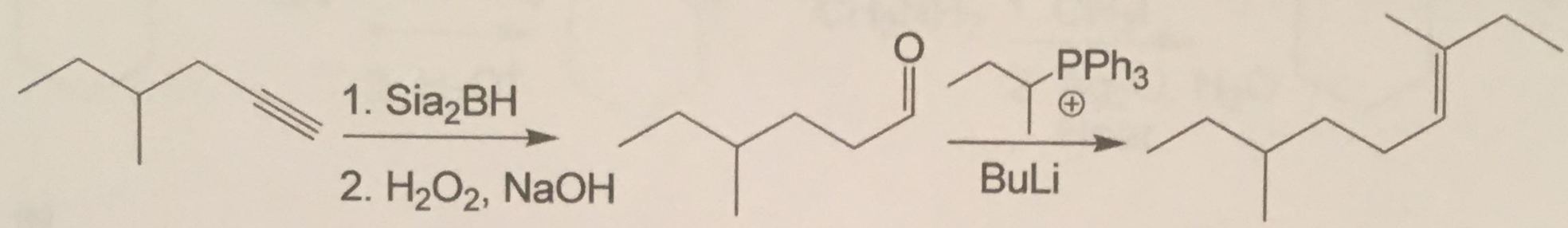
(b)



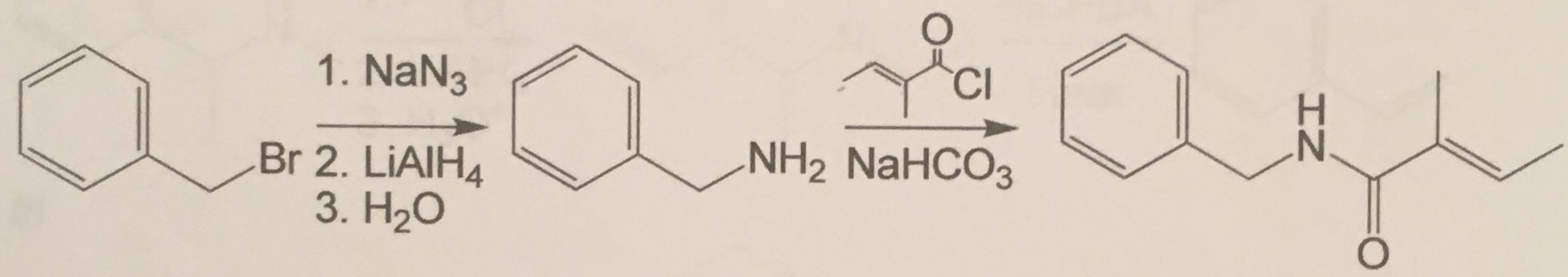
(c)


Br
Br
N
NaCN
Br
N
CN
1.
MgBr
2. H_3O^+
Br
N
O

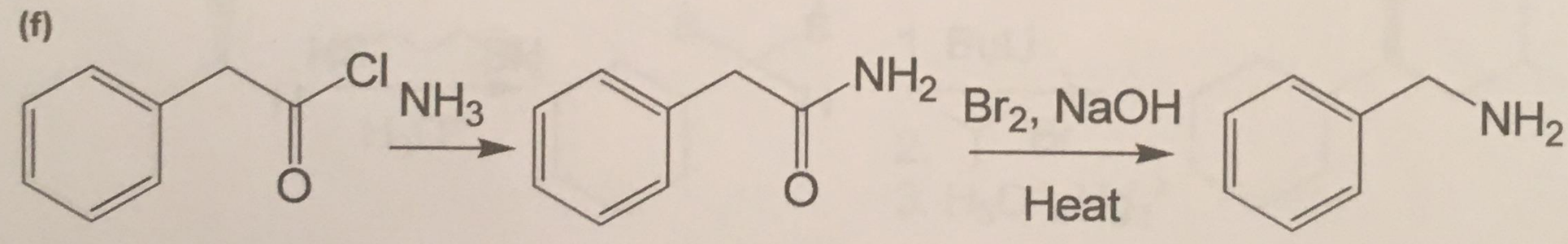
(d)


1. Sia_2BH
2. H_2O_2, NaOH
O
PPh_3
⊕
BuLi

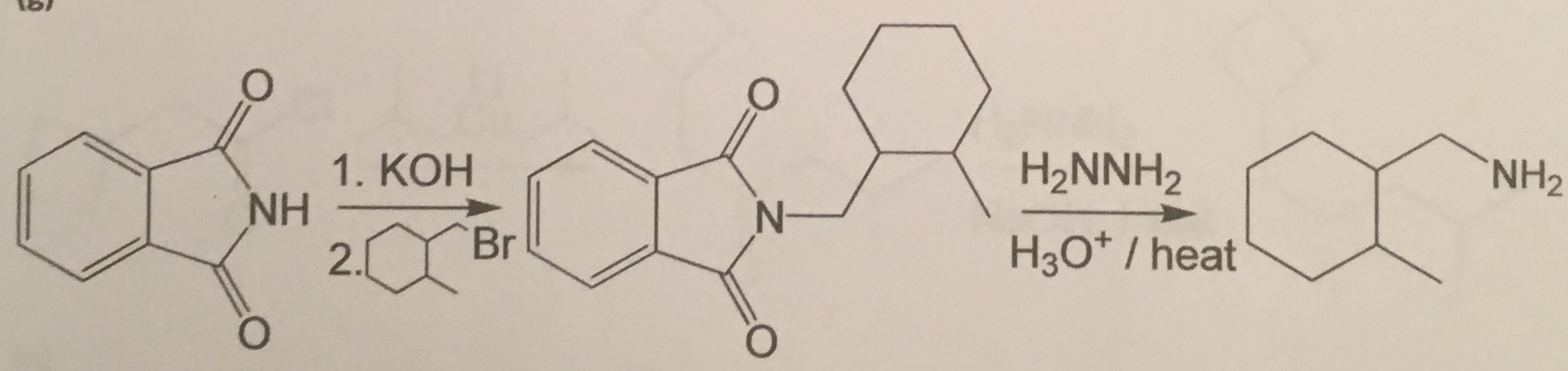
(e)


1. NaN_3
2. $LiAlH_4$
3. H_2O
Br
NH_2
O
Cl
$NaHCO_3$
H
N
O

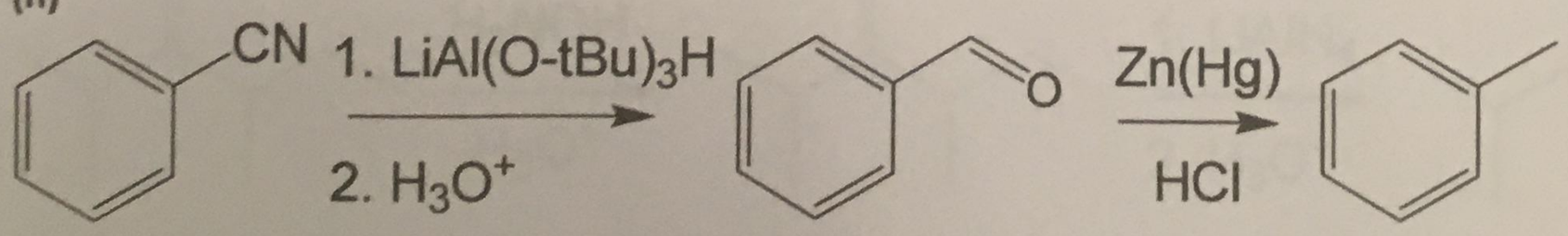
(f)


Cl
O
NH_3
NH_2
O
Br_2, NaOH
Heat
NH_2

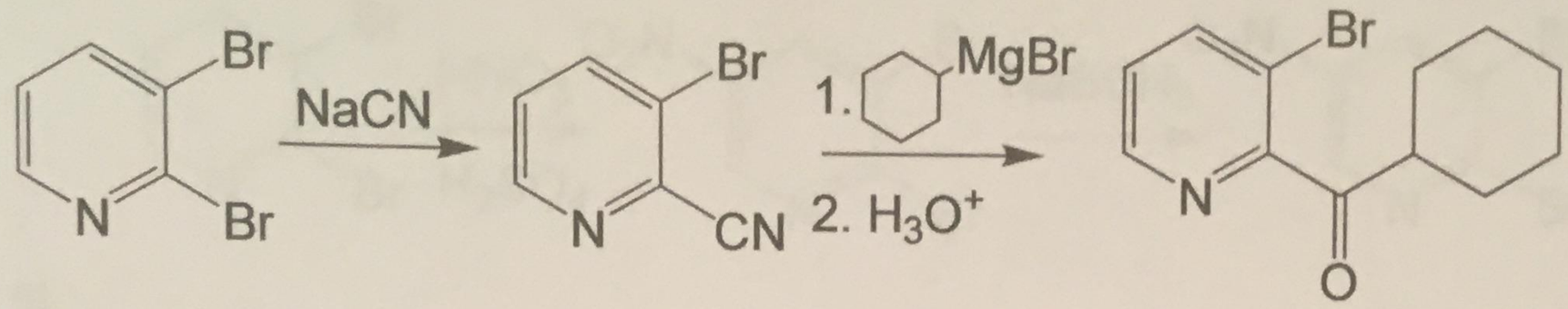
(g)


O
NH
O
1. KOH
2.
Br
O
N
O
H_2NNH_2
H_3O^+ / heat
NH_2

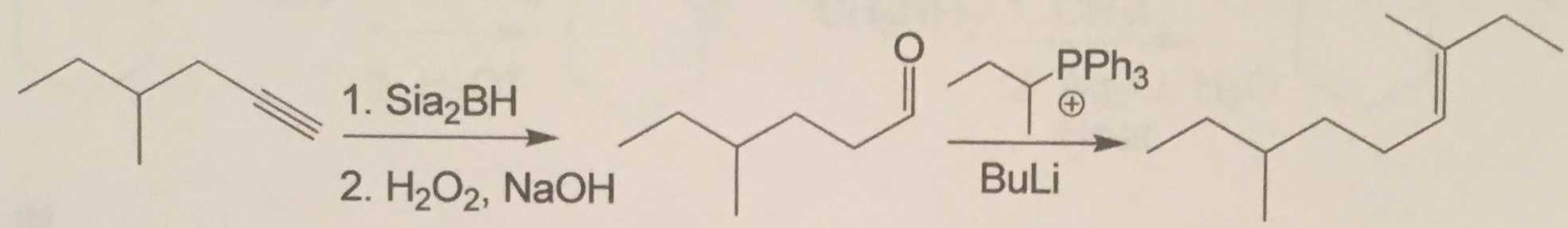
(h)


CN
1. $LiAl(O\text{-}tBu)_3H$
2. H_3O^+
O
Zn(Hg)
HCl

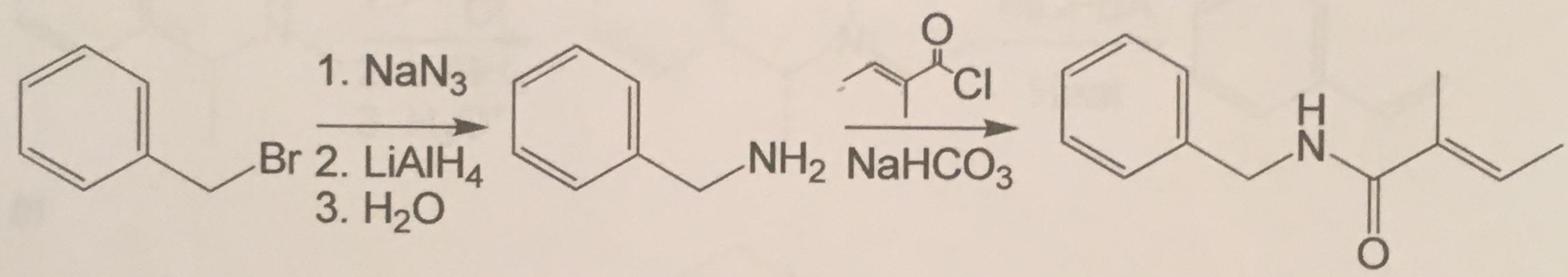
(c)


Br
Br
N
NaCN
Br
N
CN
1.
MgBr
2. H_3O^+
Br
N
O

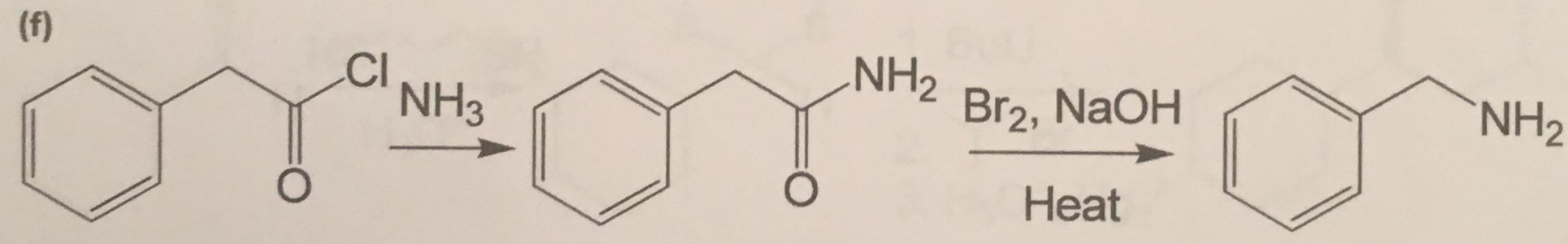
(d)


1. Sia_2BH
2. H_2O_2, NaOH
O
PPh_3
⊕
BuLi

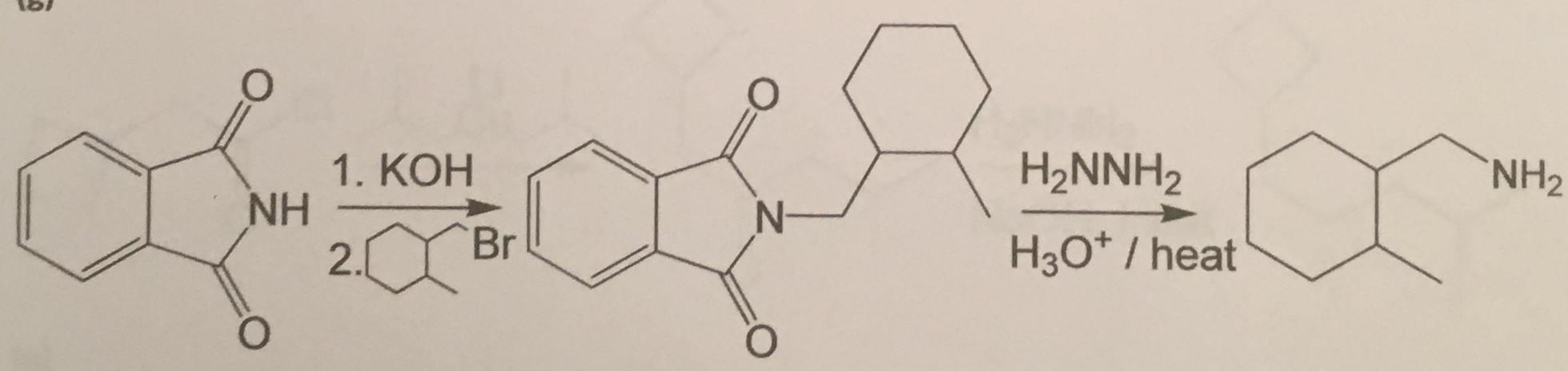
(e)


1. NaN_3
2. $LiAlH_4$
3. H_2O
Br
NH_2
O
Cl
$NaHCO_3$
H
N
O

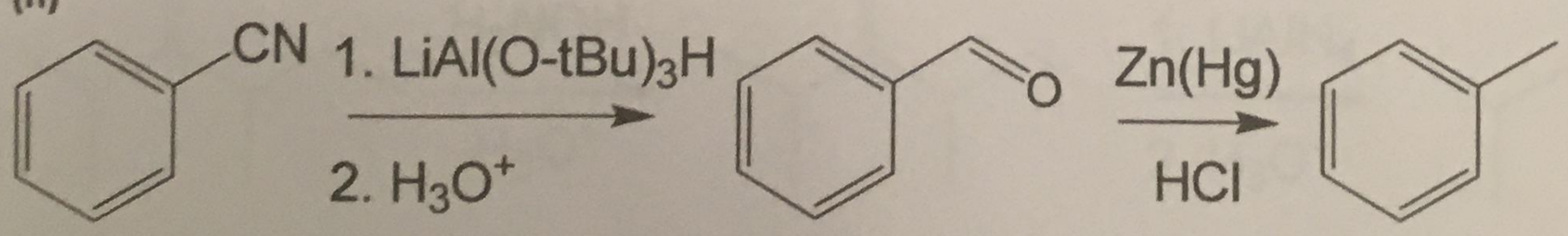
(f)


Cl
O
NH_3
NH_2
O
Br_2, NaOH
Heat
NH_2

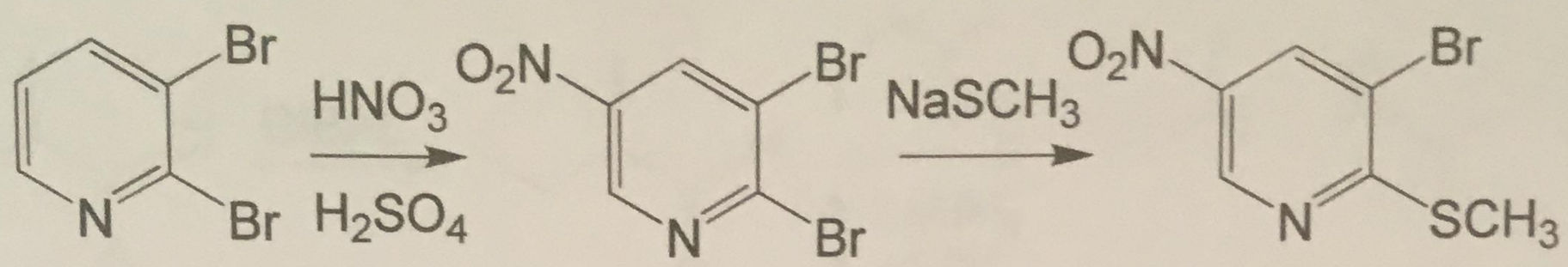
(g)


O
NH
O
1. KOH
2.
Br
O
N
O
H_2NNH_2
H_3O^+ / heat
NH_2

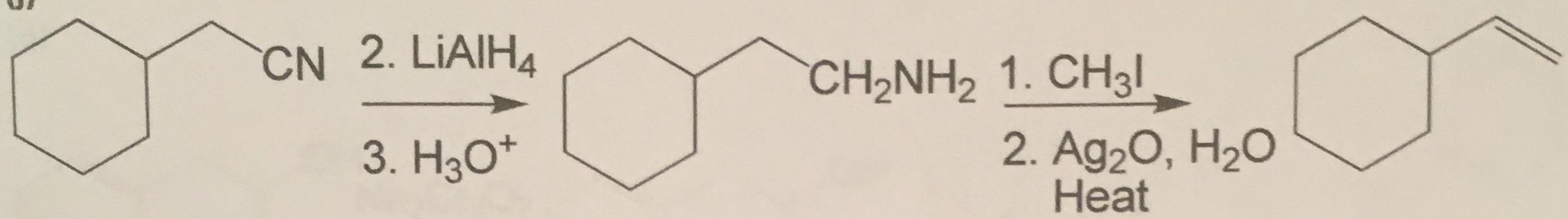
(h)


CN
1. $LiAl(O\text{-}tBu)_3H$
2. H_3O^+
O
Zn(Hg)
HCl

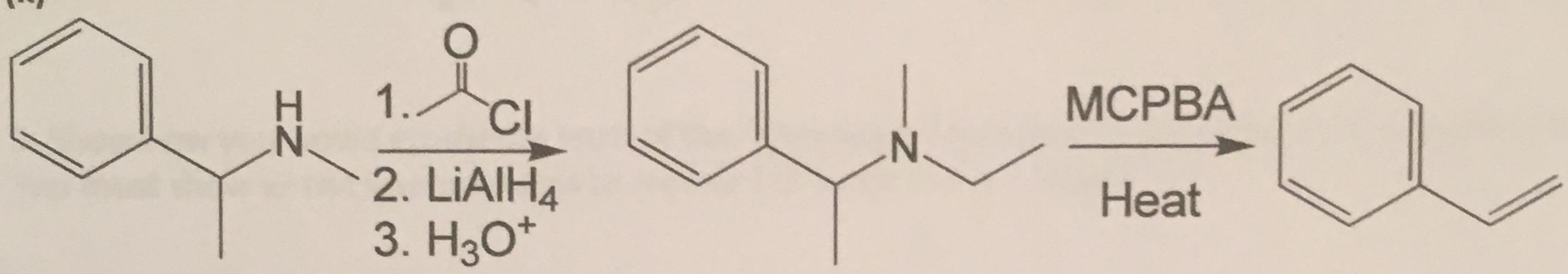
(i)


Br
N
Br
HNO3
H2SO4
O2N
Br
N
Br
NaSCH3
O2N
Br
N
SCH3

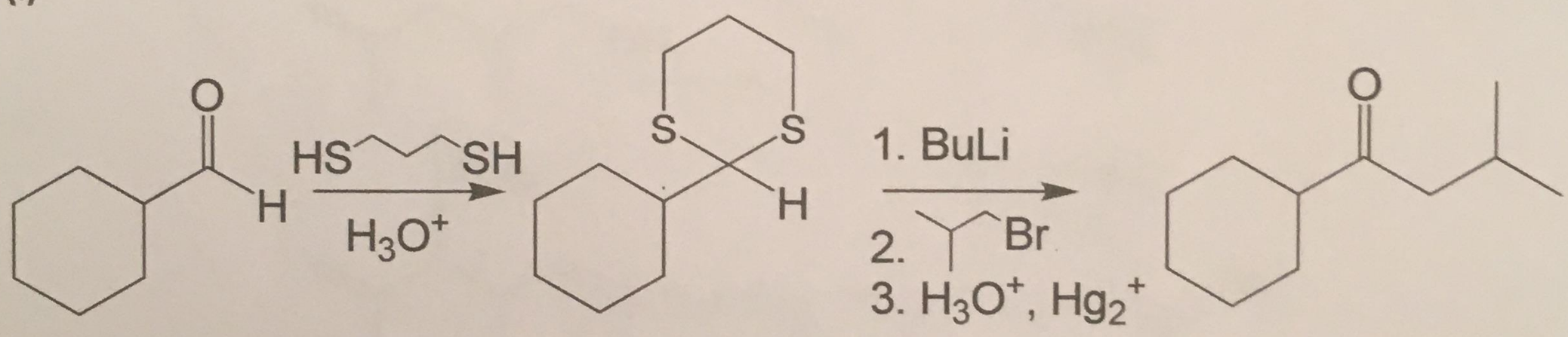
(j)


CN
2. LiAlH4
3. H3O+
CH2NH2
1. CH3I
2. Ag2O, H2O
Heat

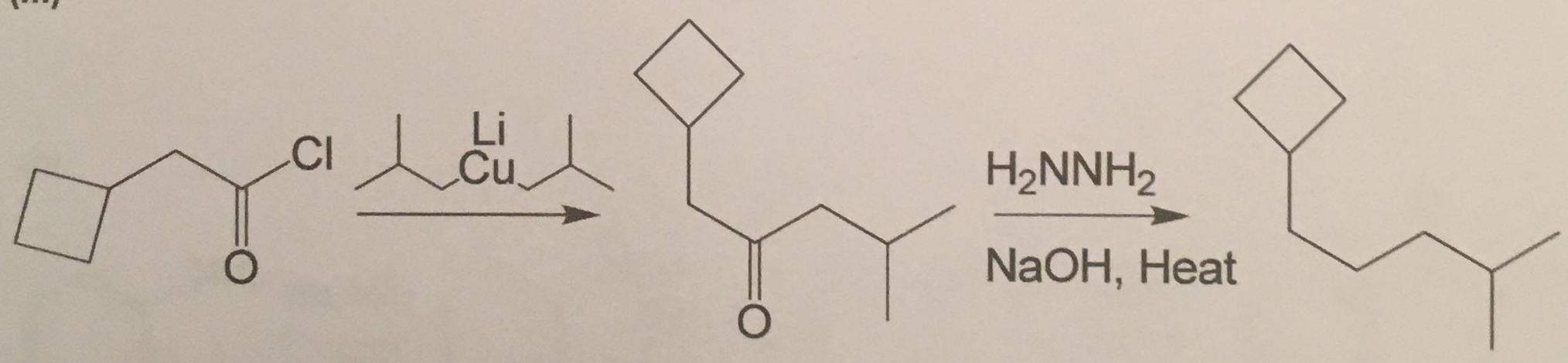
(k)


H
N
O
1.
Cl
2. LiAlH4
3. H3O+
N
MCPBA
Heat

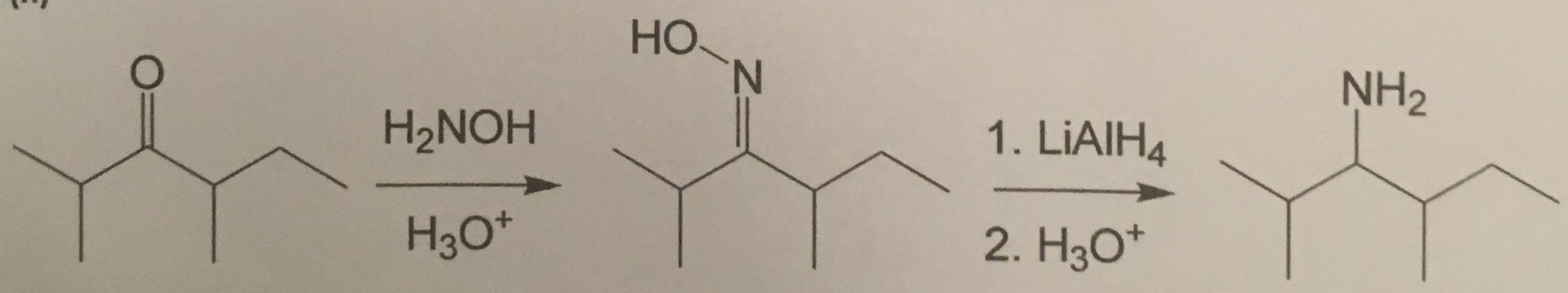
(l)


O
H
HS
SH
H3O+
S
S
H
1. BuLi
2.
Br
3. H3O+, Hg2+
O

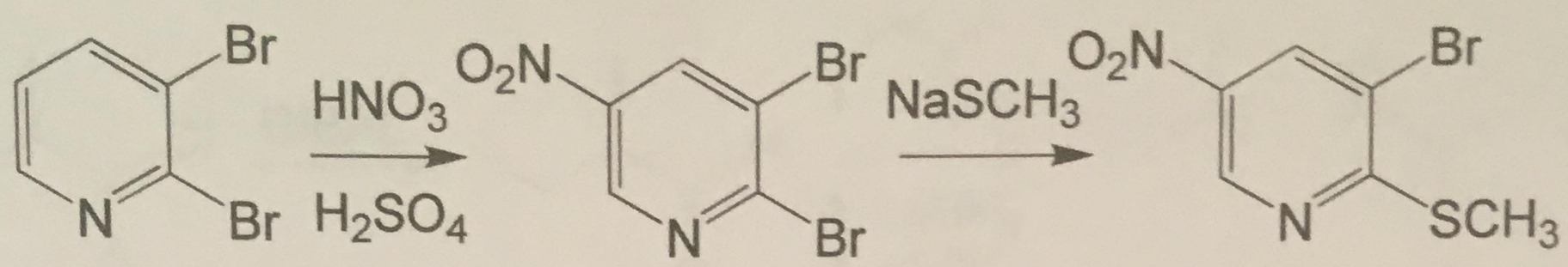
(m)


Cl
O
Li
Cu
O
H2NNH2
NaOH, Heat

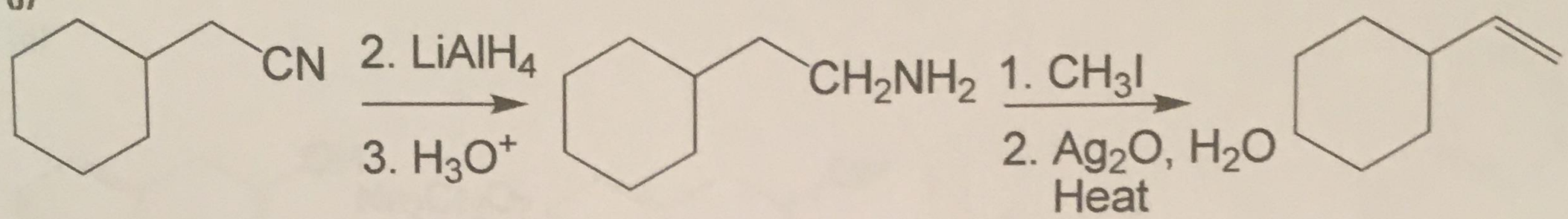
(n)


O
H2NOH
H3O+
HO
N
1. LiAlH4
2. H3O+
NH2

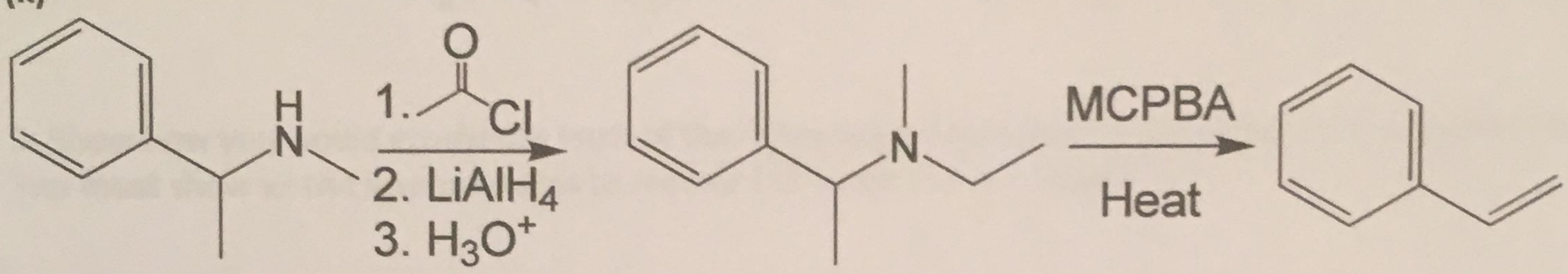
(i)


Br
N
Br
HNO3
H2SO4
O2N
Br
N
Br
NaSCH3
O2N
Br
N
SCH3

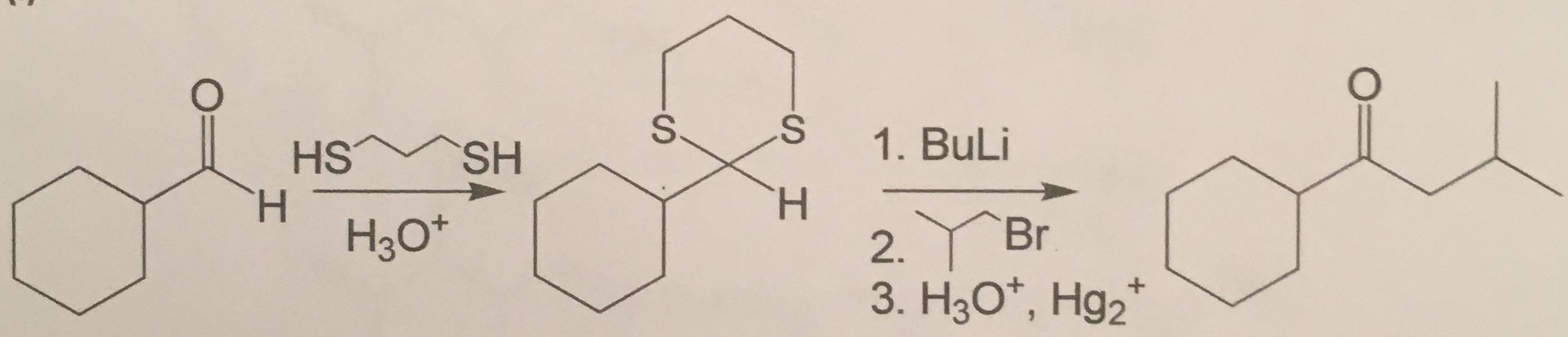
(j)


CN
2. LiAlH4
3. H3O+
CH2NH2
1. CH3I
2. Ag2O, H2O
Heat

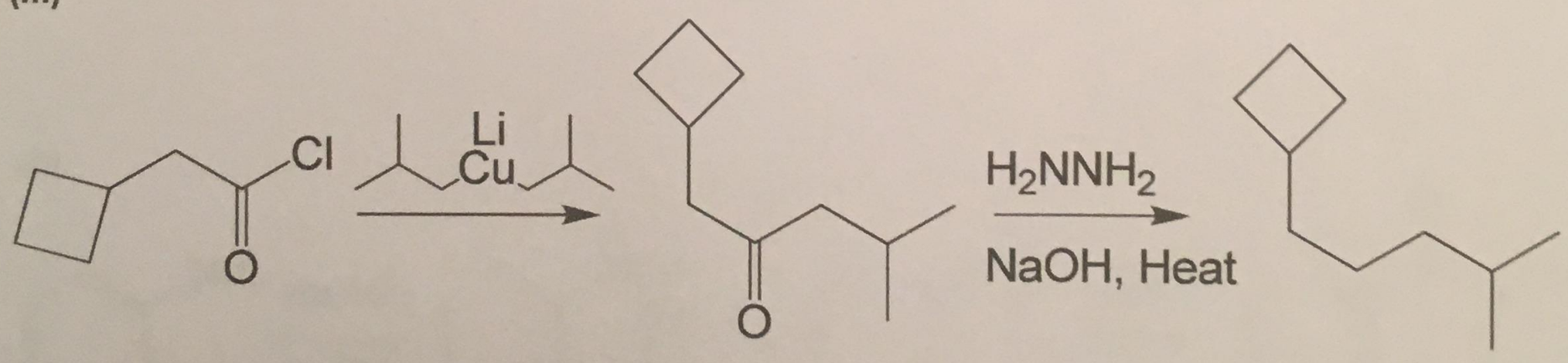
(k)


H
N
O
1.
Cl
2. LiAlH4
3. H3O+
N
MCPBA
Heat

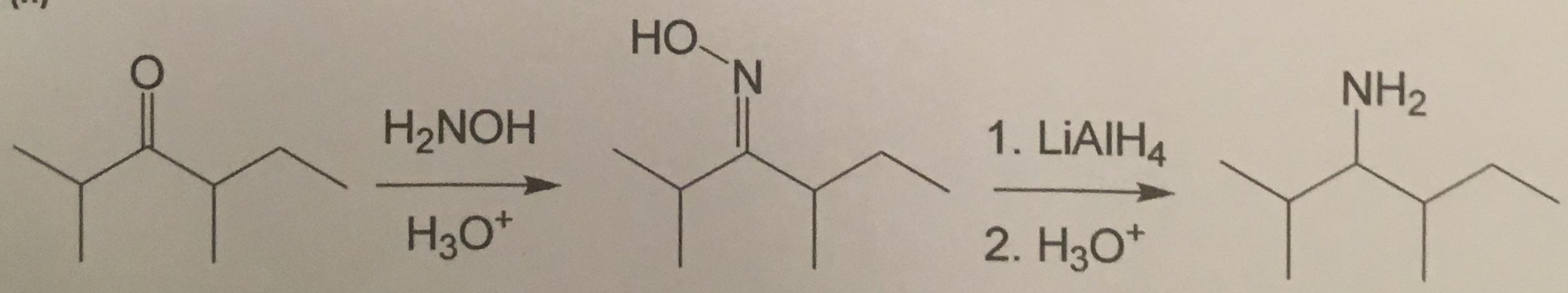
(l)


O
H
HS
SH
H3O+
S
S
H
1. BuLi
2.
Br
3. H3O+, Hg2+
O

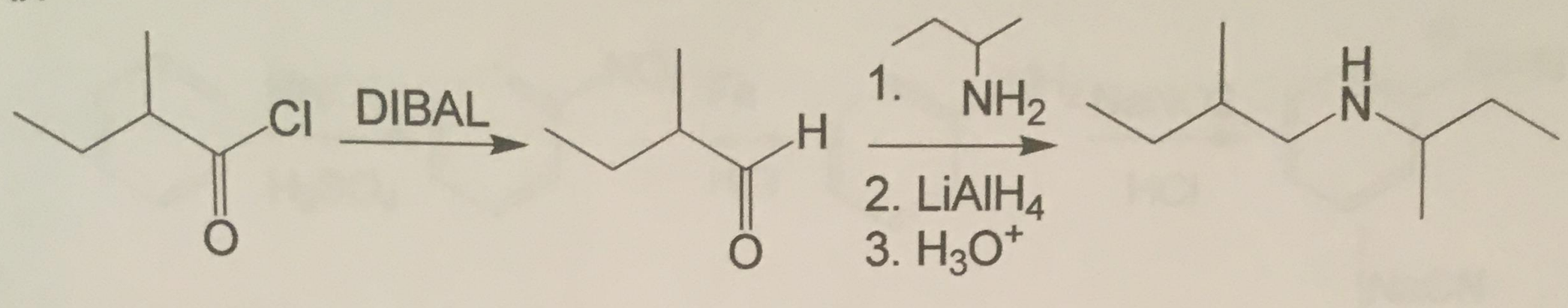
(m)


Cl
O
Li
Cu
O
H2NNH2
NaOH, Heat

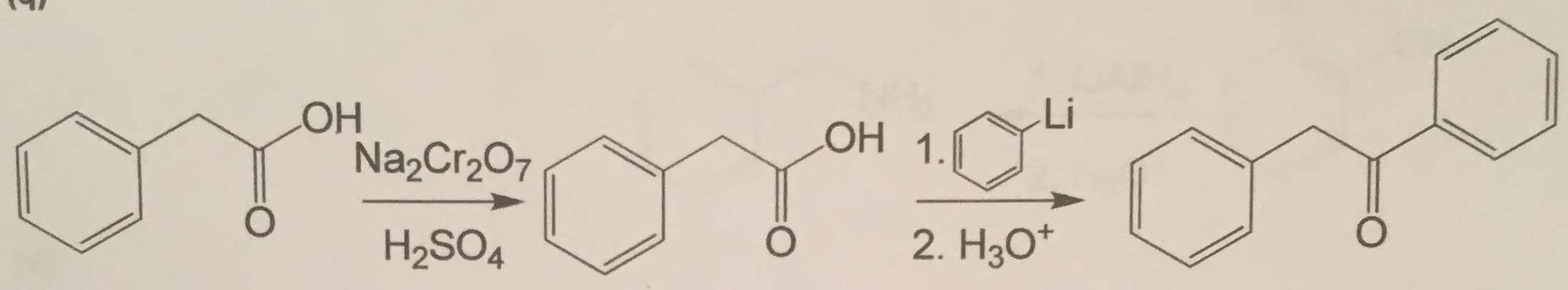
(n)


O
H2NOH
H3O+
HO
N
1. LiAlH4
2. H3O+
NH2

(p)

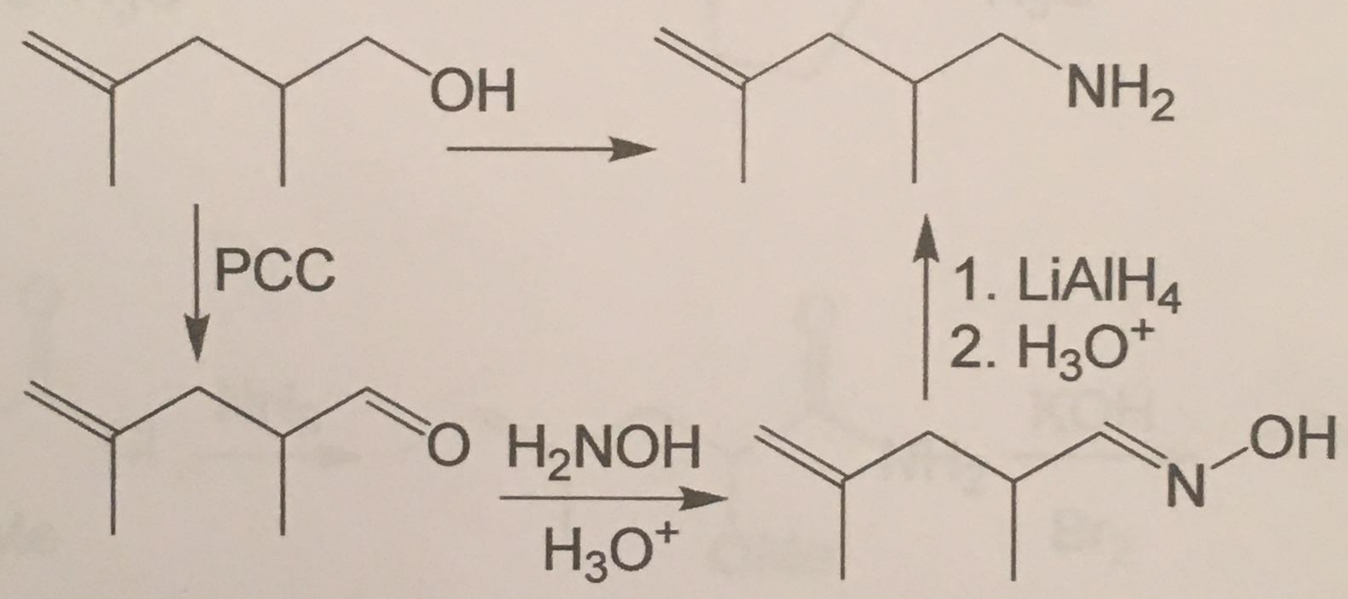


(q)

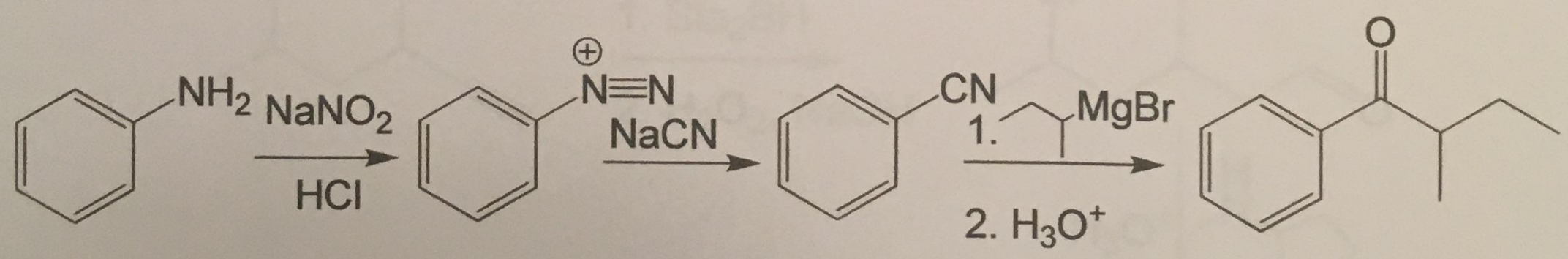


3. Show how you would synthesize each of the following compounds from the given starting material(s). You **must** show all the intermediates to receive full credit (3 x 6 = 18 pts)

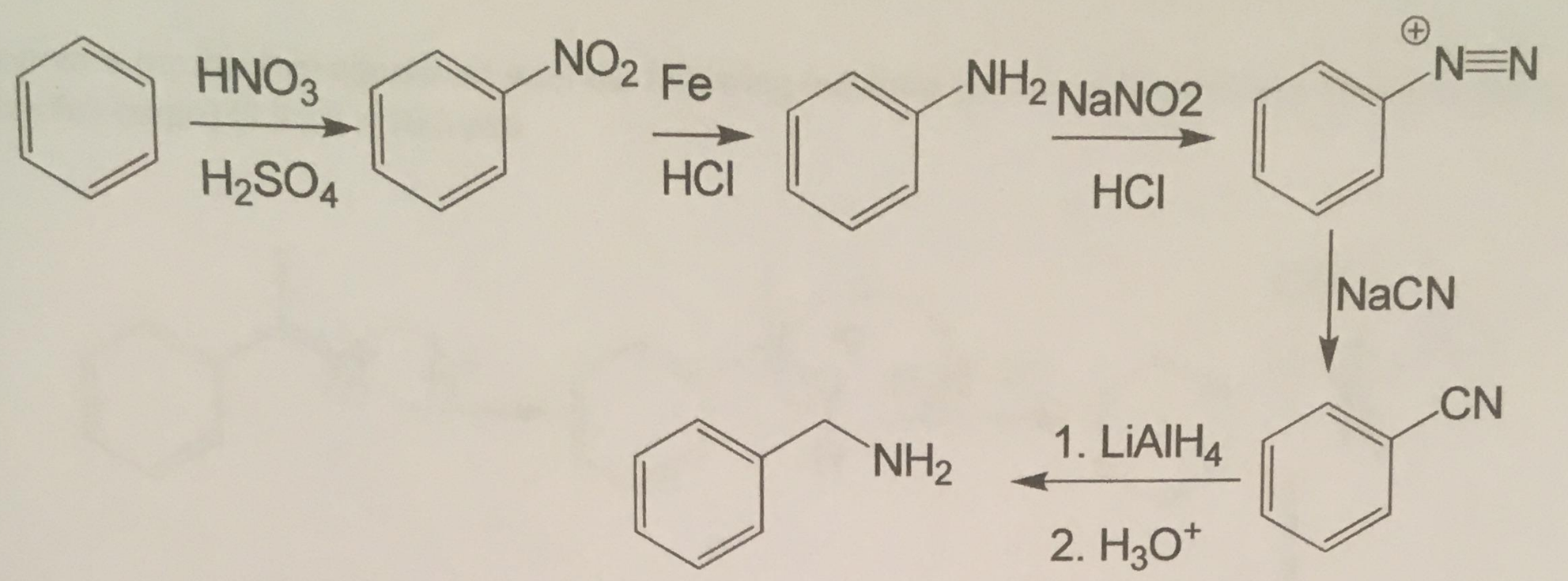
(a)



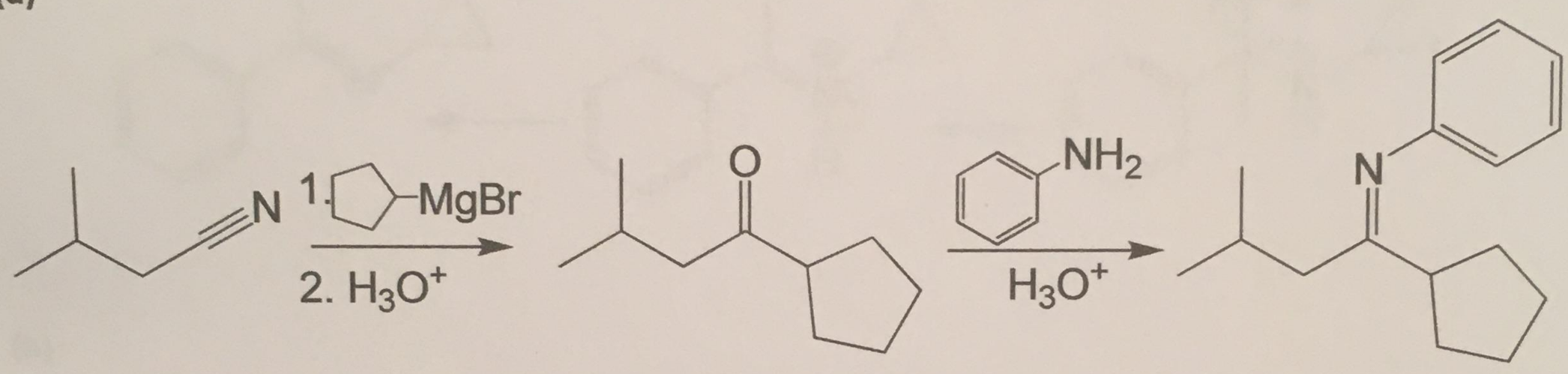
(b)



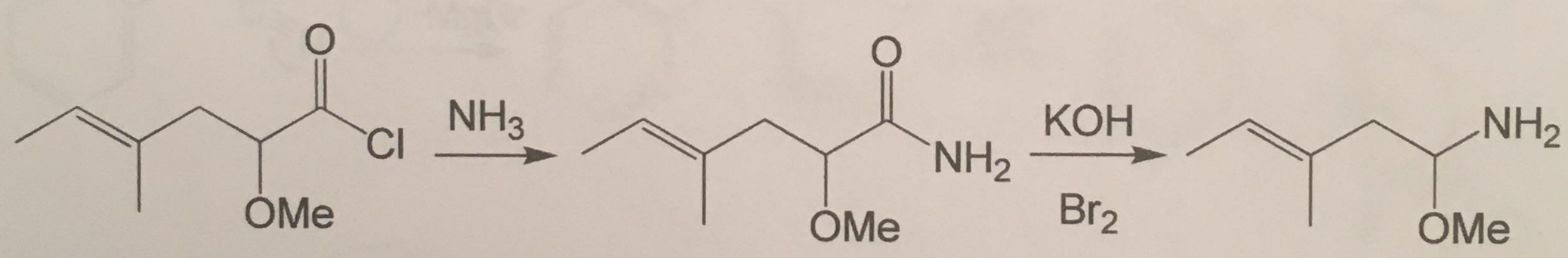
(c)


HNO3
H2SO4
NO2
Fe
HCl
NH2
NaNO2
HCl
N≡N
NaCN
CN
1. LiAlH4
2. H3O+
NH2

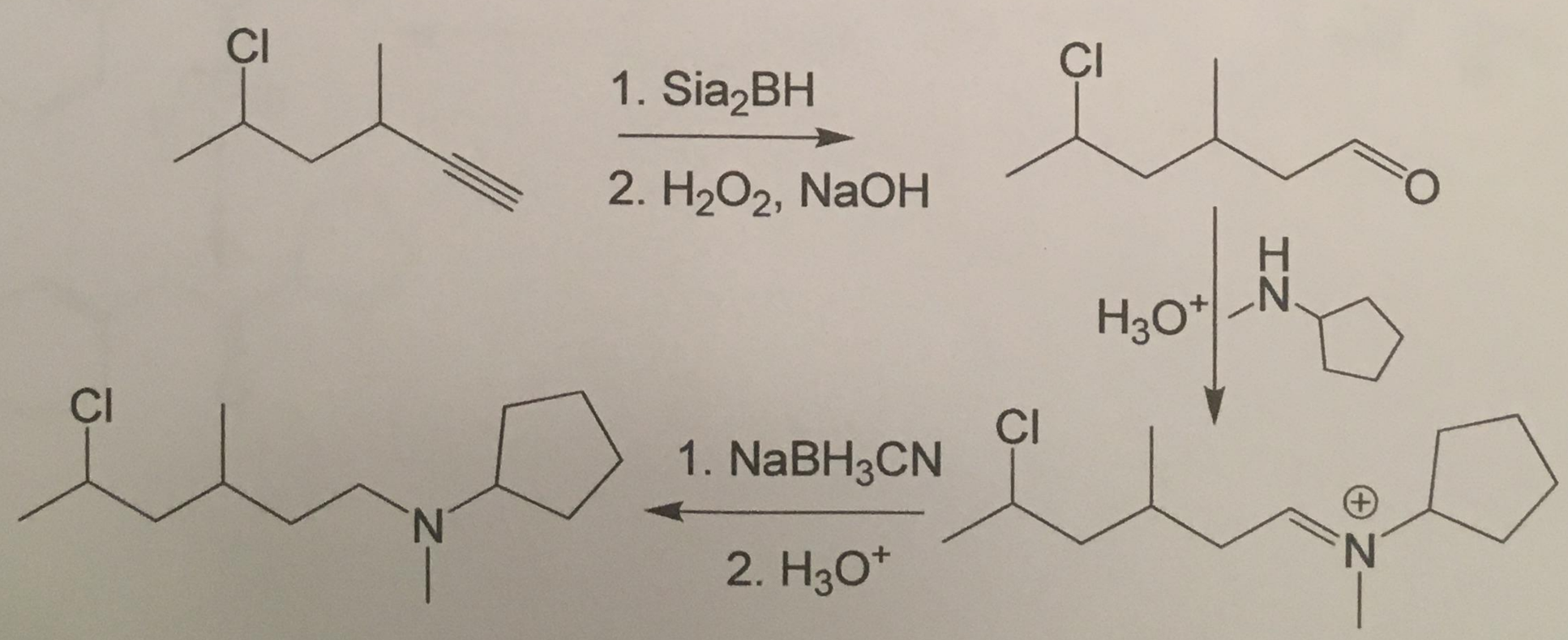
(d)


N
1.
MgBr
2. H3O+
O
NH2
H3O+
N

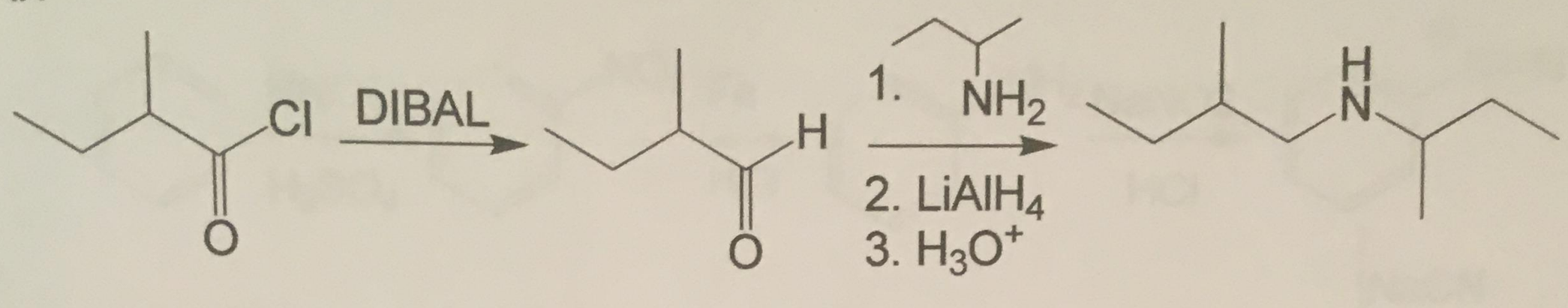
(e)


O
Cl
OMe
NH3
O
NH2
OMe
KOH
Br2
NH2
OMe

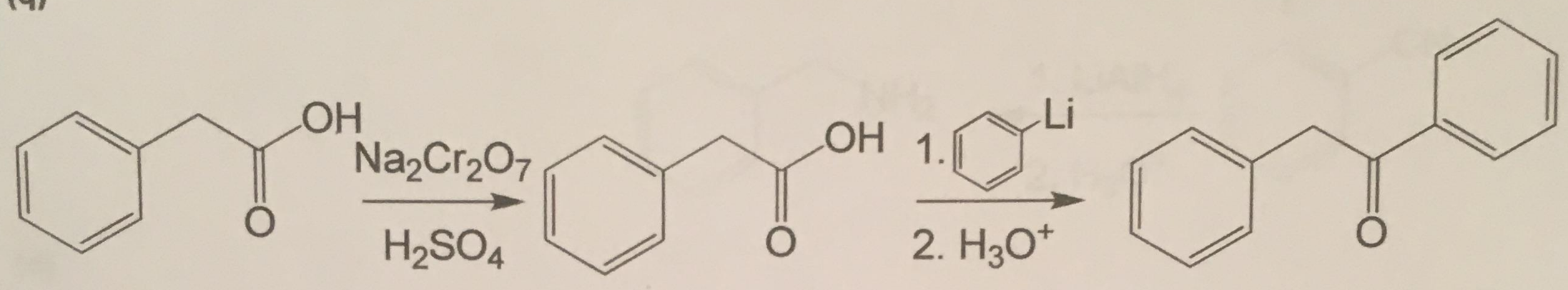
(f)


Cl
1. Sia2BH
2. H2O2, NaOH
Cl
O
H3O+
H
N
Cl
N
1. NaBH3CN
2. H3O+
Cl
N

(p)

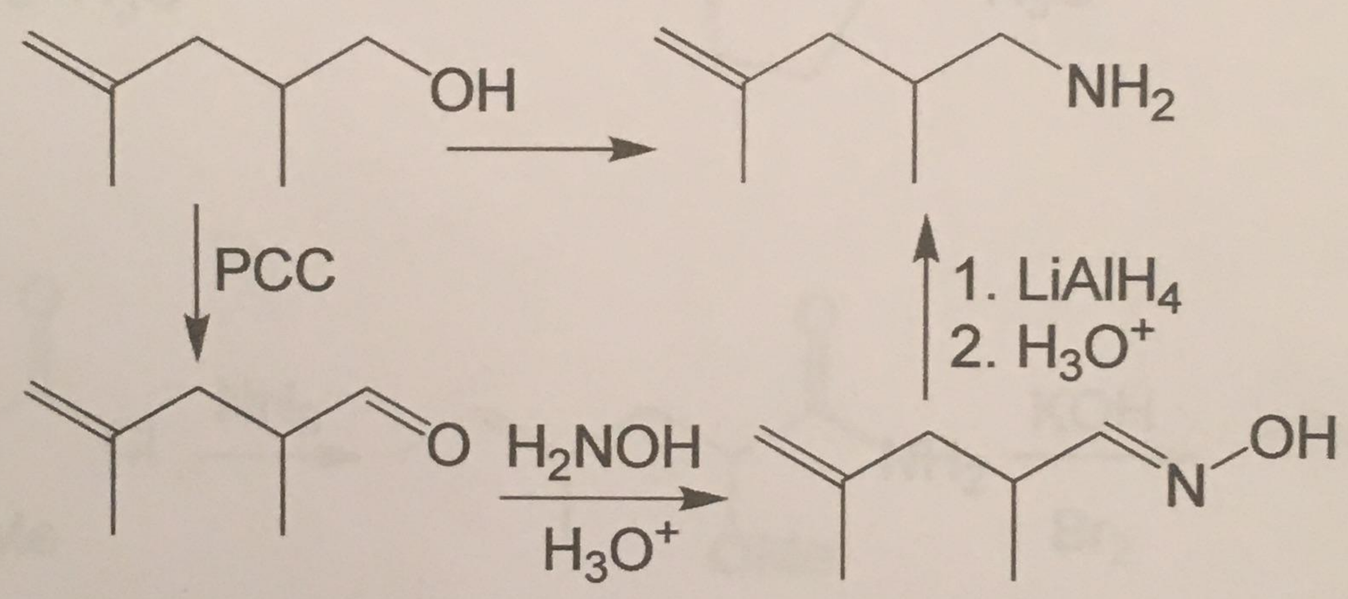


(q)

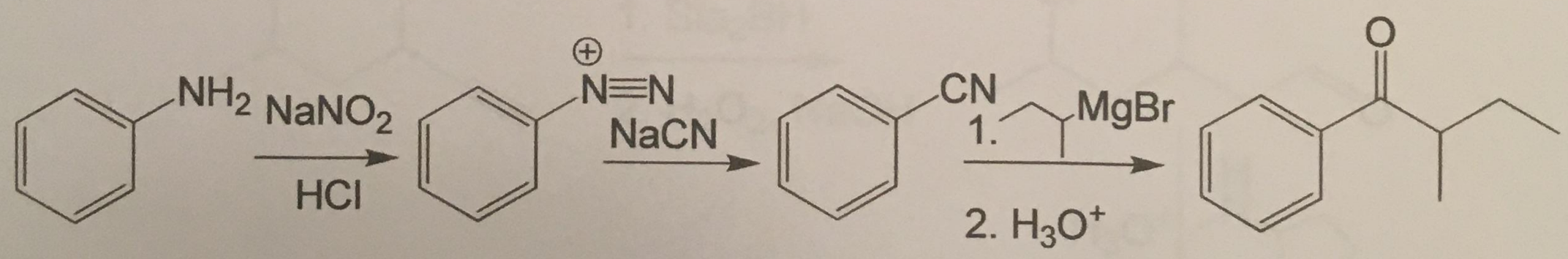


3. Show how you would synthesize each of the following compounds from the given starting material(s). You **must** show all the intermediates to receive full credit (3 x 6 = 18 pts)

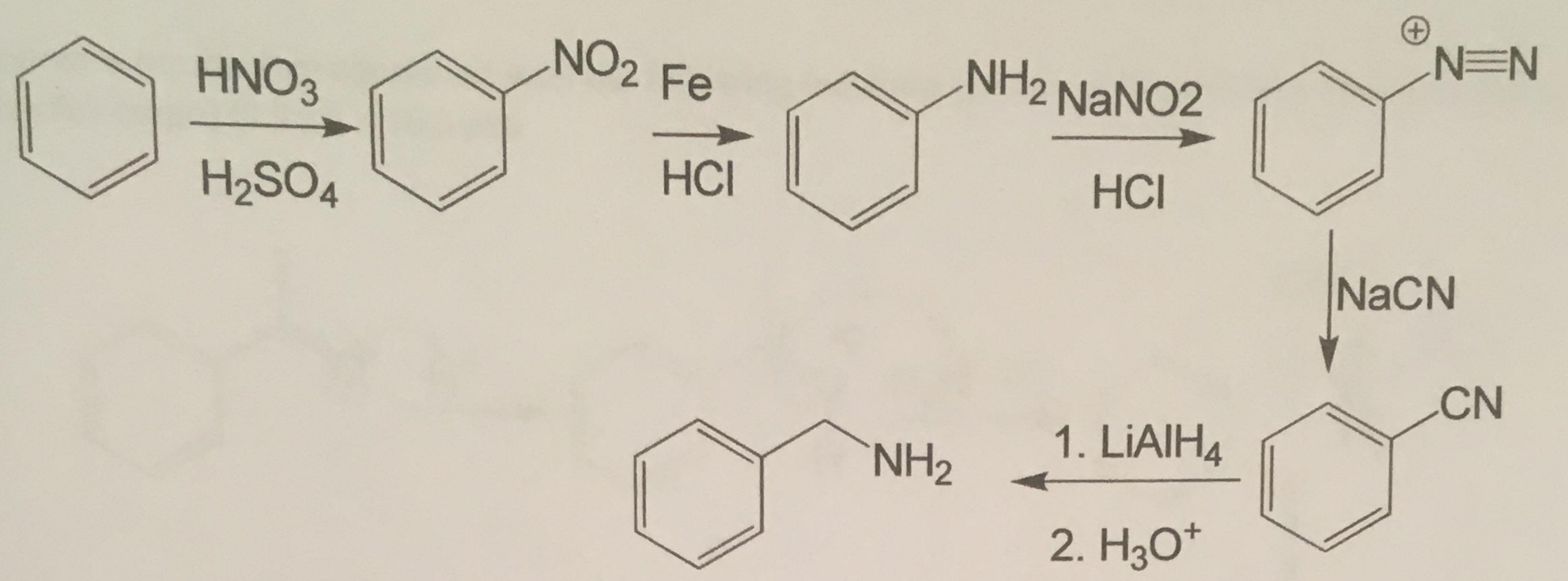
(a)



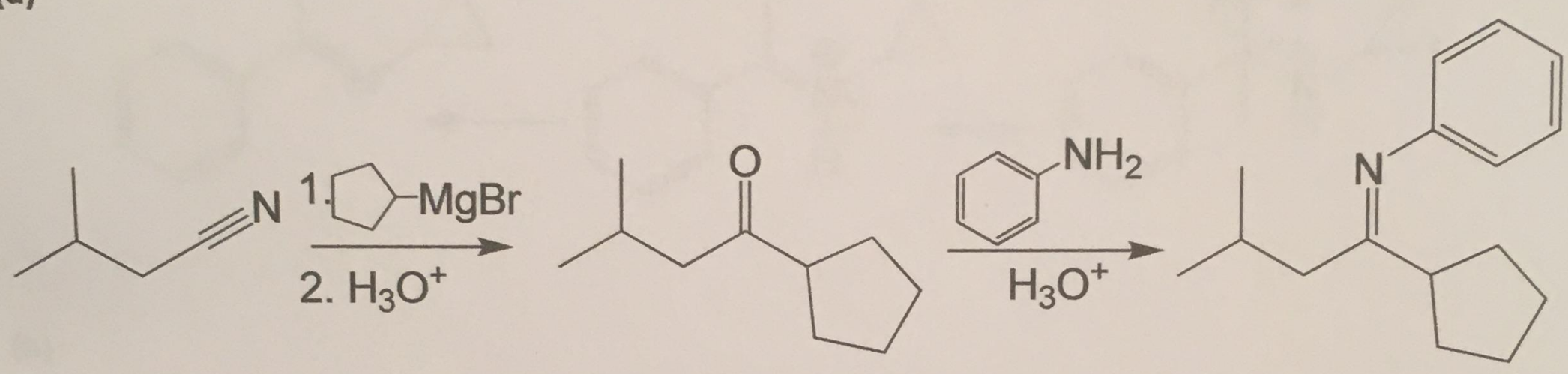
(b)



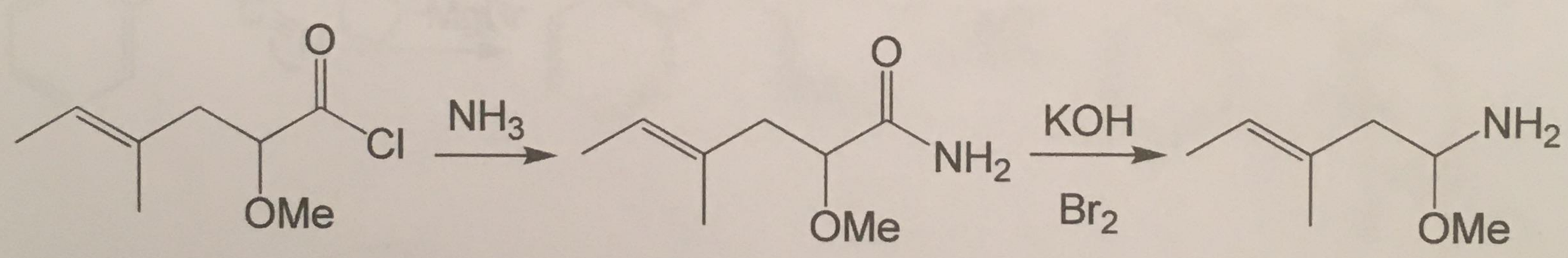
(c)


HNO3
H2SO4
NO2
Fe
HCl
NH2
NaNO2
HCl
N≡N
NaCN
CN
1. LiAlH4
2. H3O+
NH2

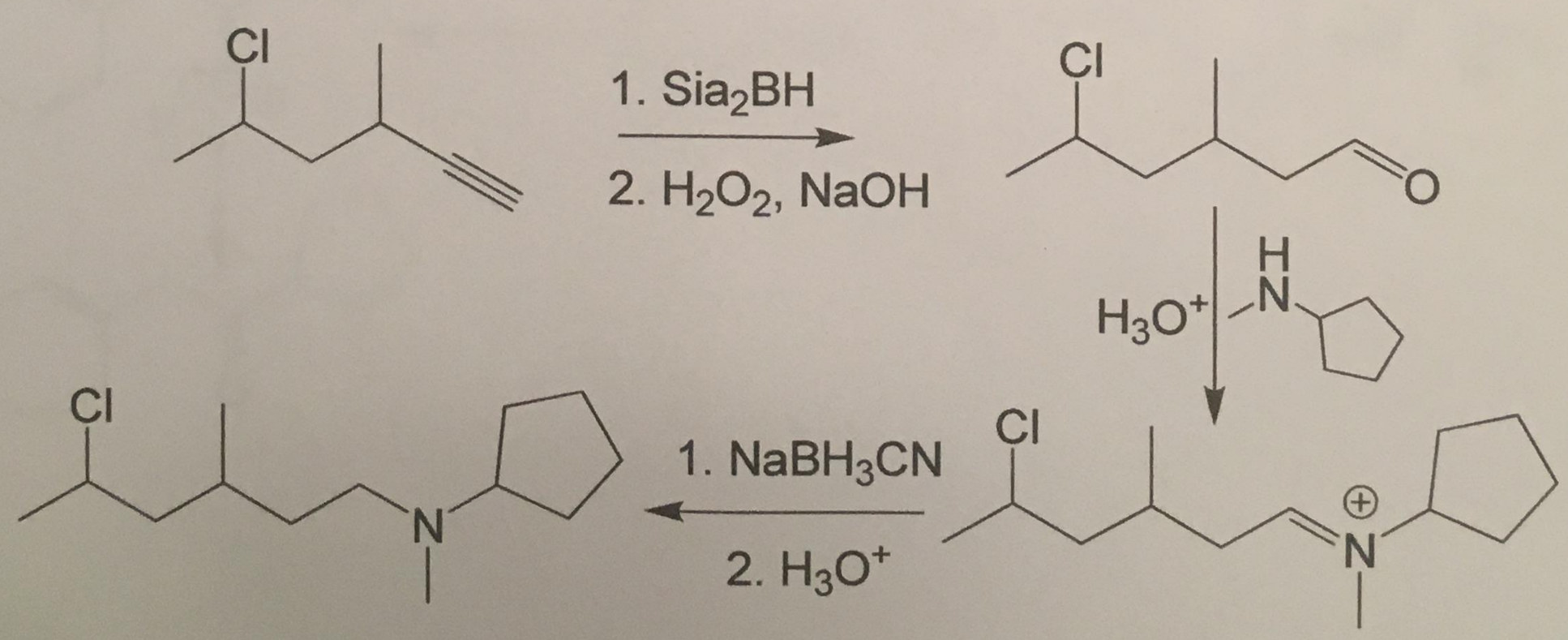
(d)


N
1.
MgBr
2. H3O+
O
NH2
H3O+
N

(e)

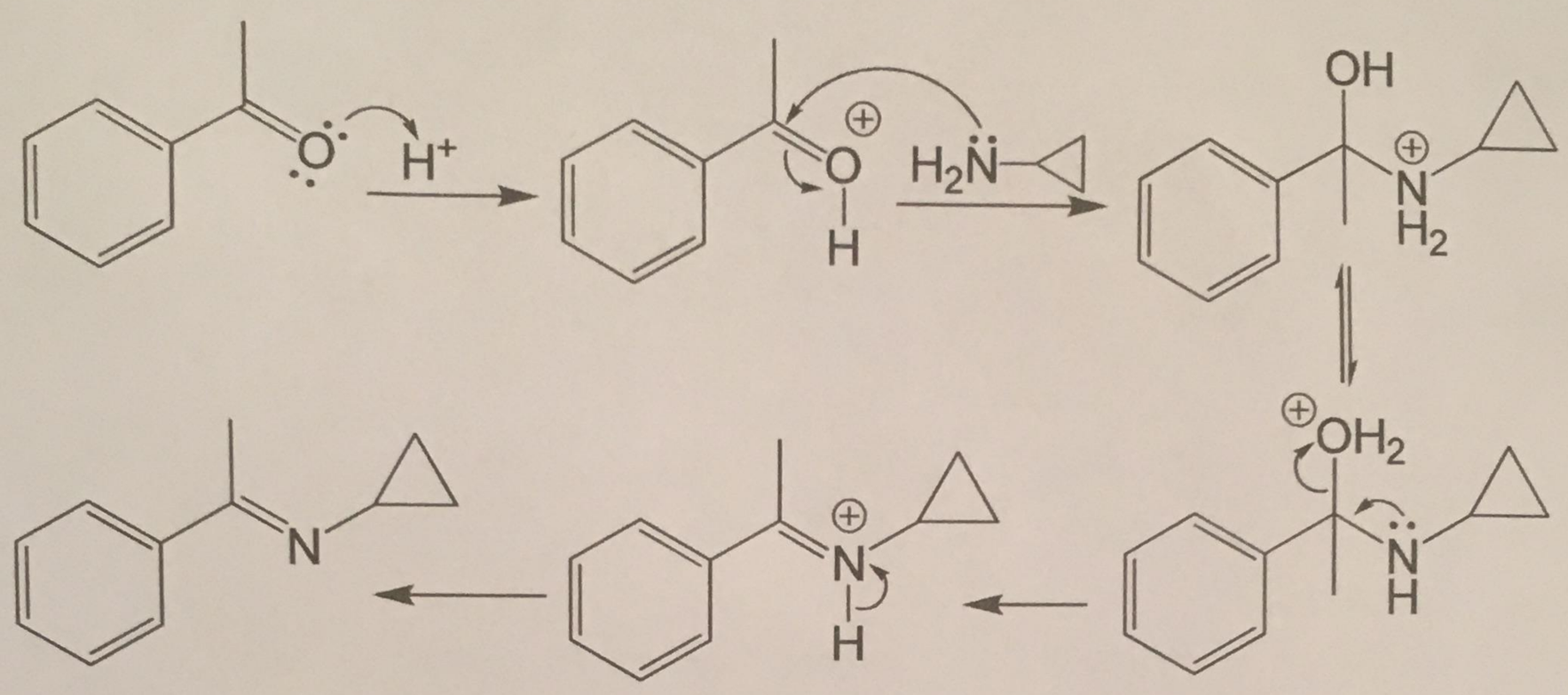

O
Cl
OMe
NH3
O
NH2
OMe
KOH
Br2
NH2
OMe

(f)

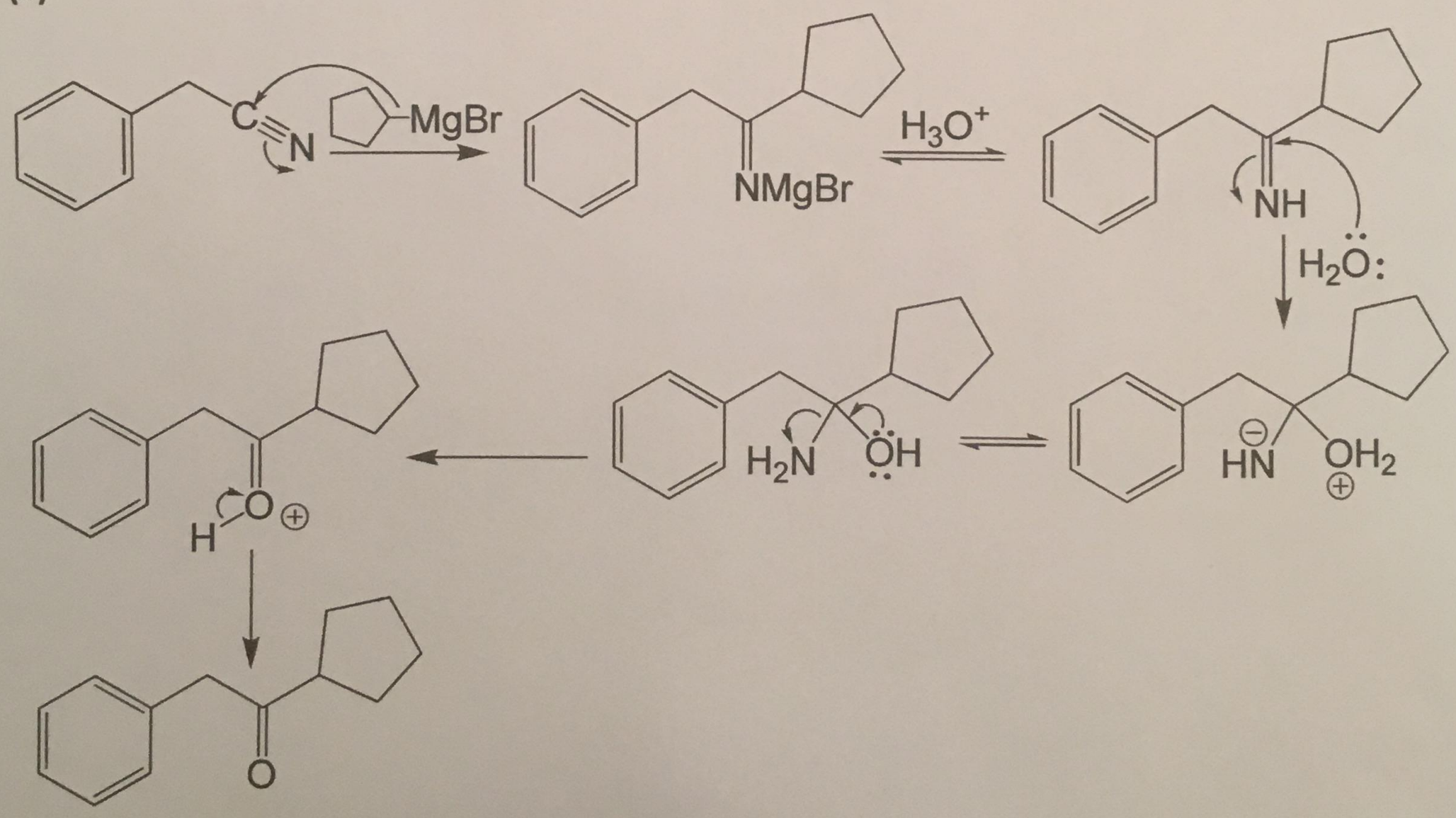

Cl
1. Sia2BH
2. H2O2, NaOH
Cl
O
H3O+
H
N
Cl
N
1. NaBH3CN
2. H3O+
Cl
N

4. Propose a mechanism consistent with the following reactions (you must show all the intermediates to receive full credit) (3.5 x 3 = 10.5 pts)

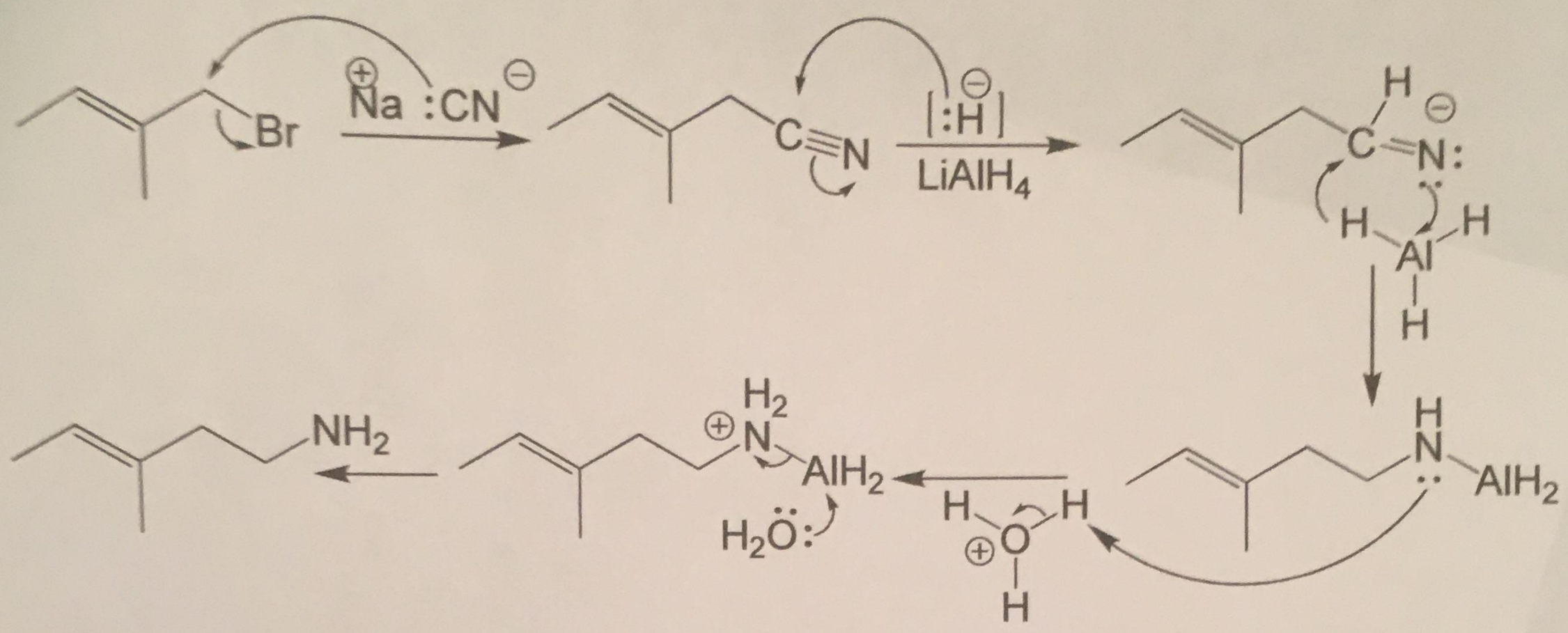
(a)



(b)

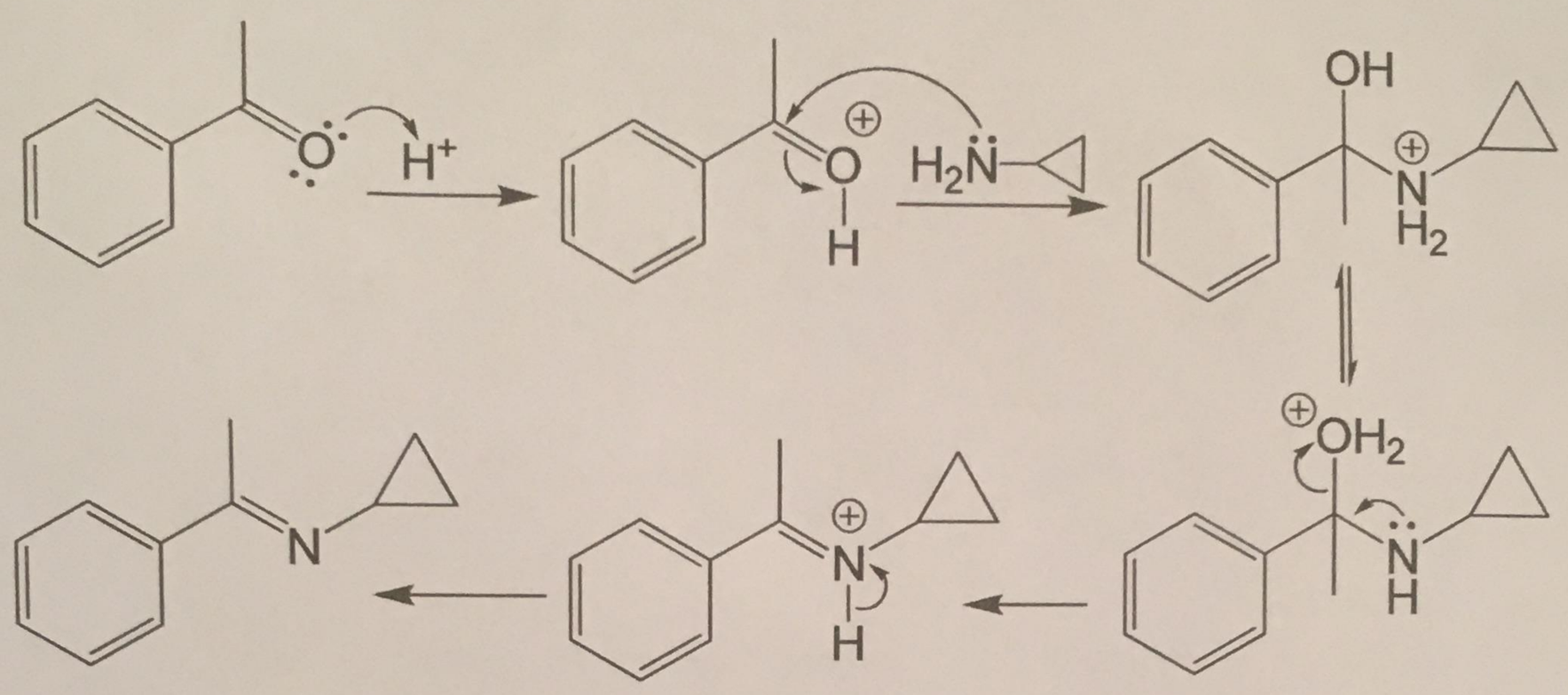


(c)

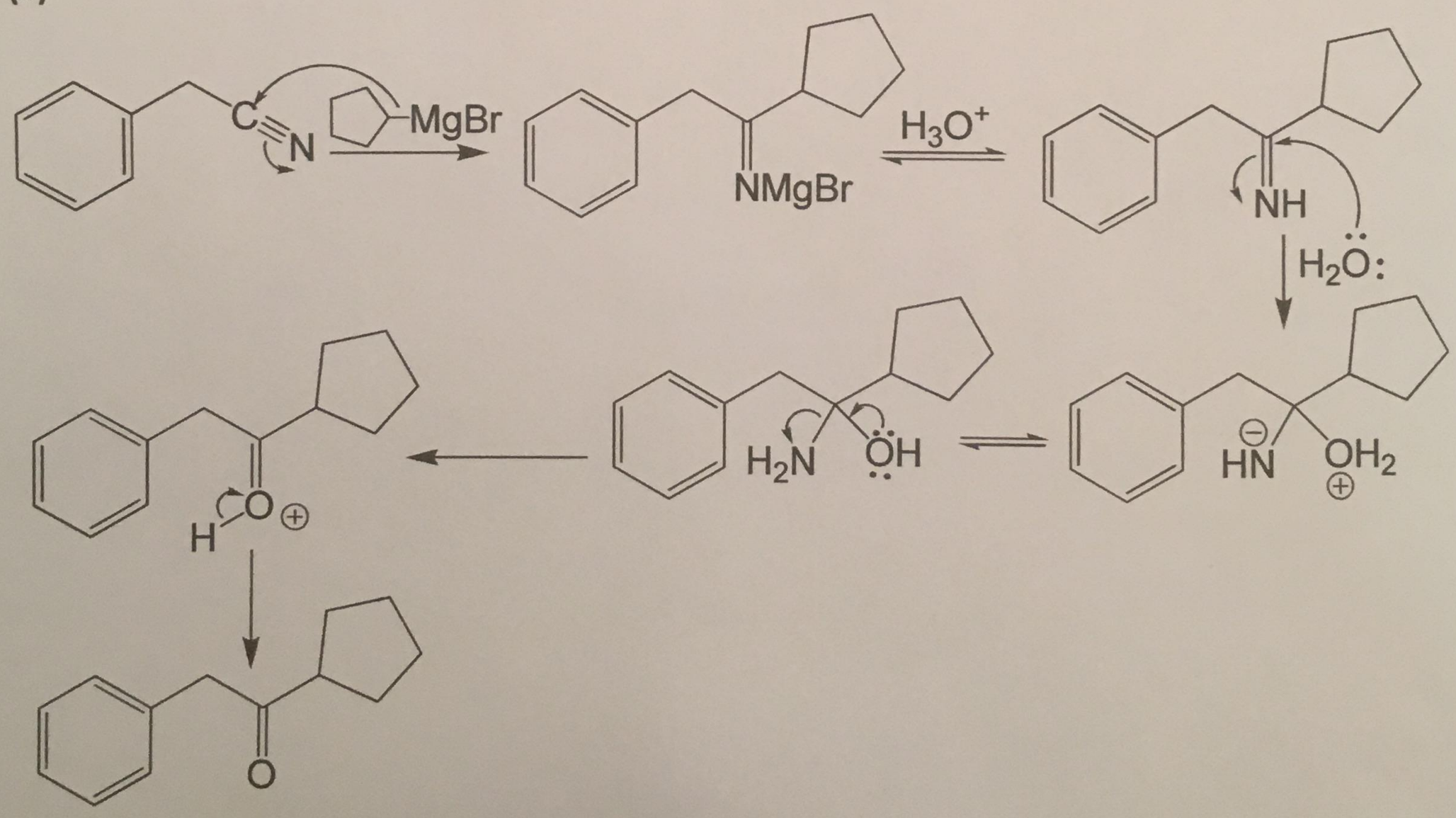
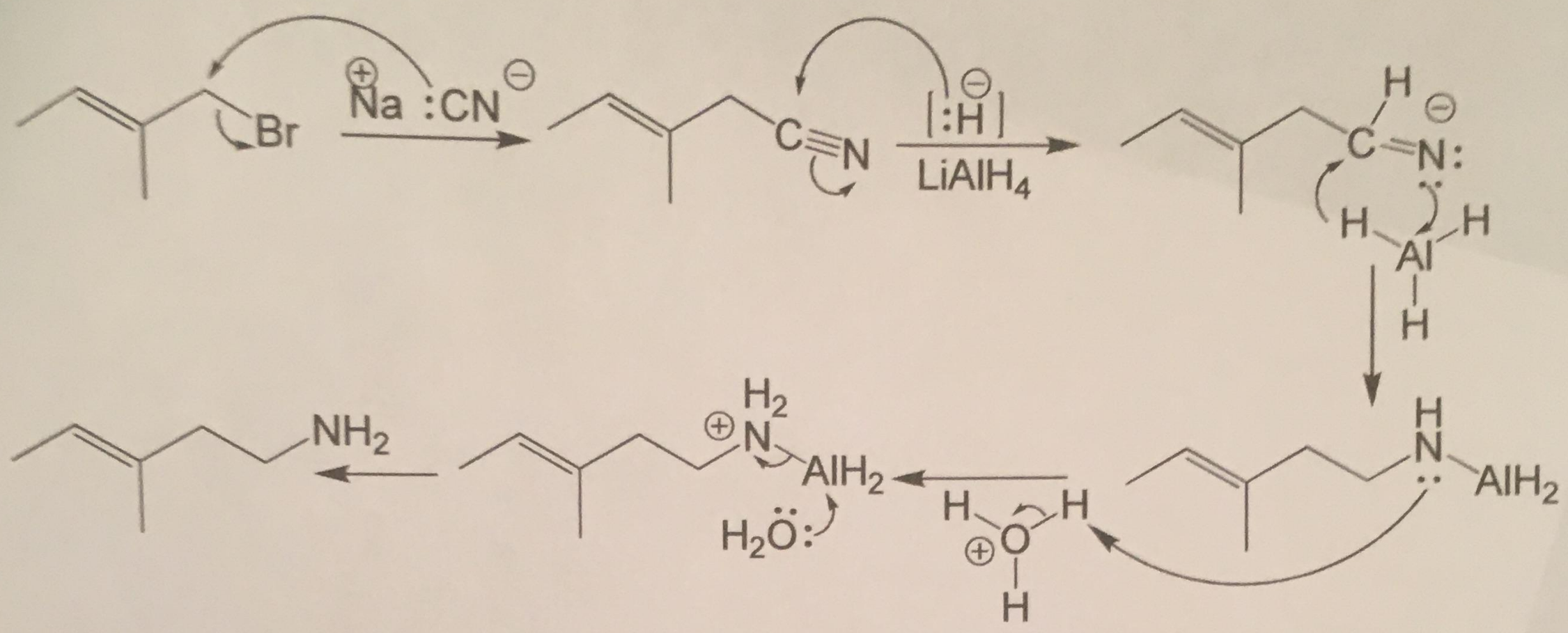


4. Propose a mechanism consistent with the following reactions (you must show all the intermediates to receive full credit) (3.5 x 3 = 10.5 pts)

(a)



(b)



(c)