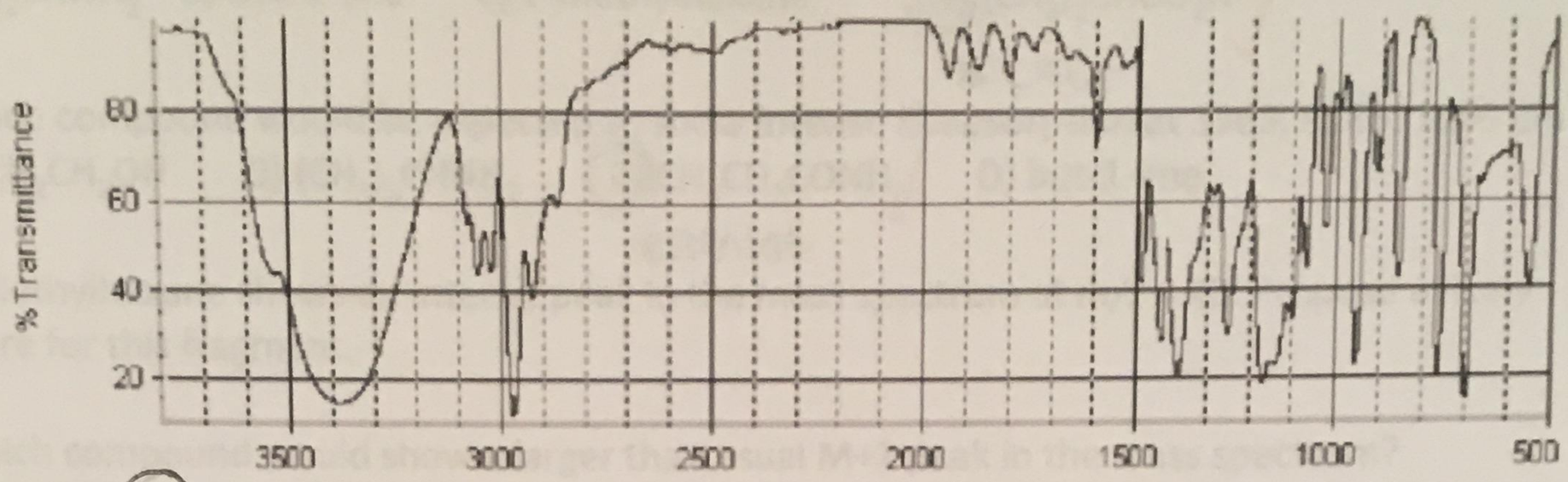
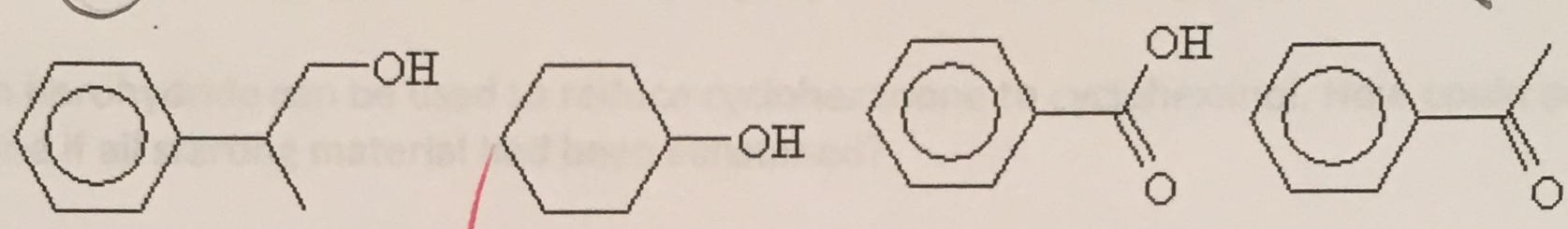
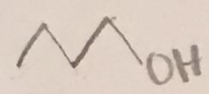
Which of the following structures is consistent with the IR spectra shown below?

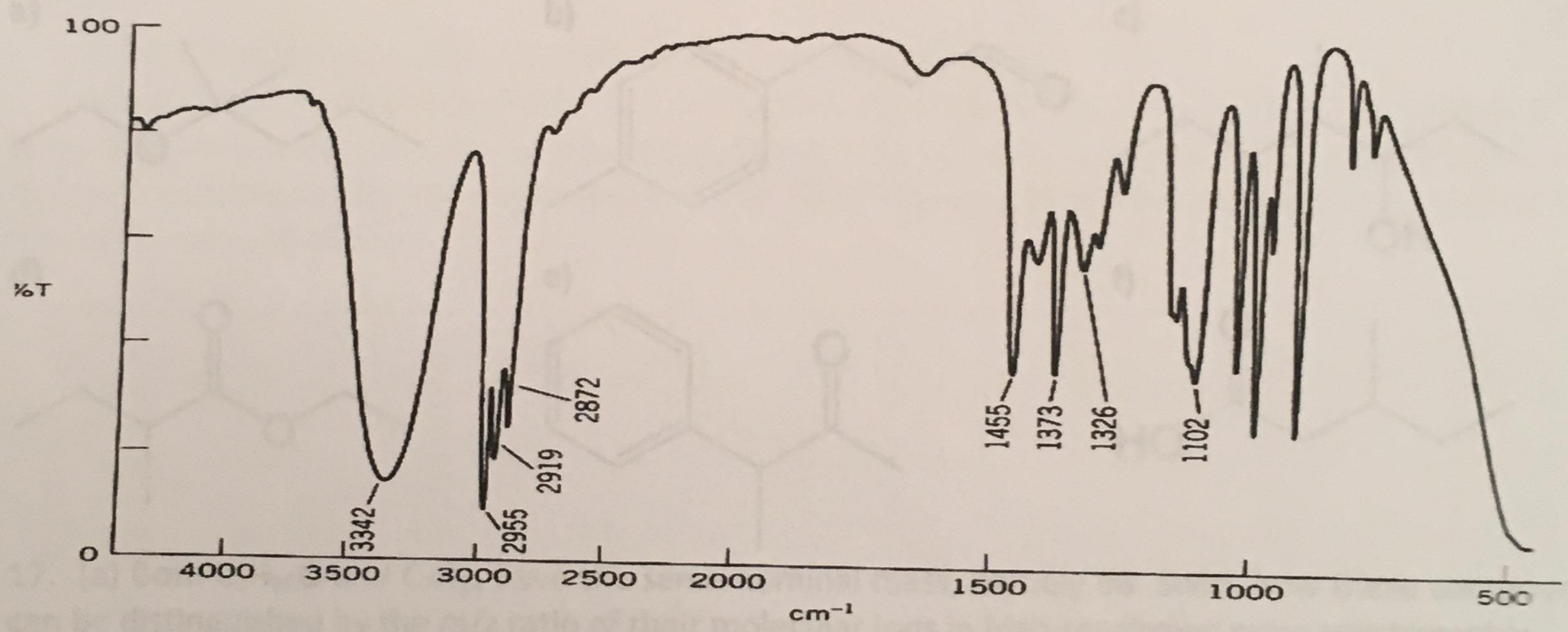


A) B) C) D)

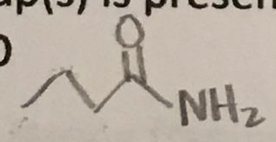


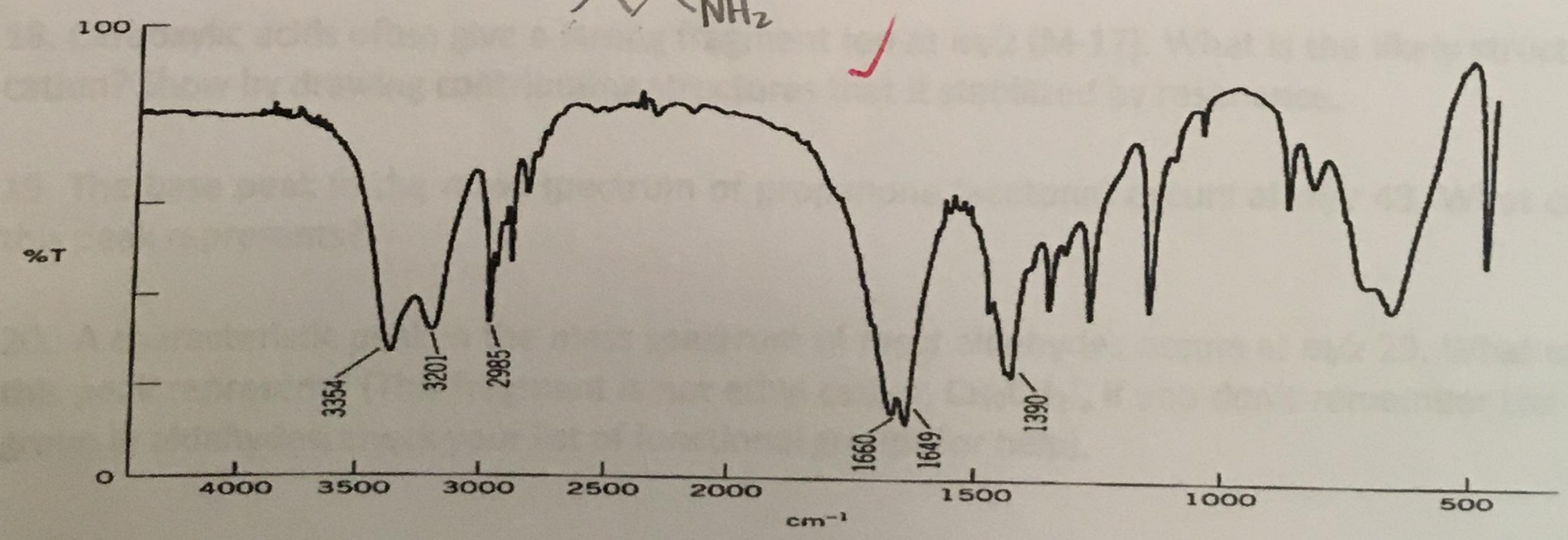
9. Explain which functional group(s) is present in the compound that has the following IR spectra
The molecular formula is $C_4H_{10}O$





10. Explain which functional group(s) is present in the compound that has the following IR spectra
The molecular formula is C_4H_9NO





11. Which compound would be expected to show intense IR absorption at 1715 cm^{-1}?

A) $(CH_3)_2CHNH_2$ B) hex-1-yne C) 2-methylhexane D) $(CH_3)_2CHCO_2H$

*C=O

12. Which compound would be expected to show intense IR absorption at 3363, 3185, 1660 cm^{-1}?

A) $CH_3CH_2CH_2OH$ B) $(CH_3)_2CHNH_2$ C) $CH_3CH_2CONH_2$ D) but-1-ene

*amide

13. 2-Methylhexane shows an intense peak in the mass spectrum at *m/z* = 43. Propose a likely structure for this fragment.

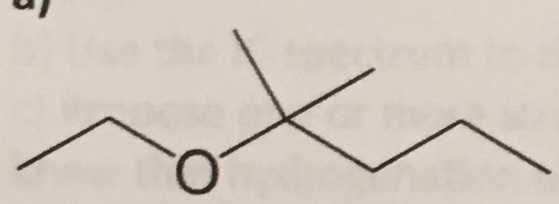
14. Which compound would show a larger than usual M+2 peak in the mass spectrum?

A) $CH_3CH_2SCH_3$ B) $(CH_3)_2CHNH_2$ C) $CH_3CH_2CO_2H$ D) $CH_3(CH_2)_2CH_3$

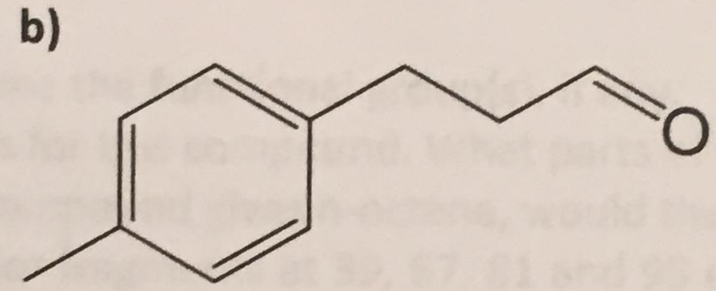
15. Sodium borohydride can be used to reduce cyclohexanone to cyclohexanol. How could one use IR to determine if all starting material had been consumed?

16. Predict the major fragments and their *m/z* that would appear in the mass spectra of these compounds:

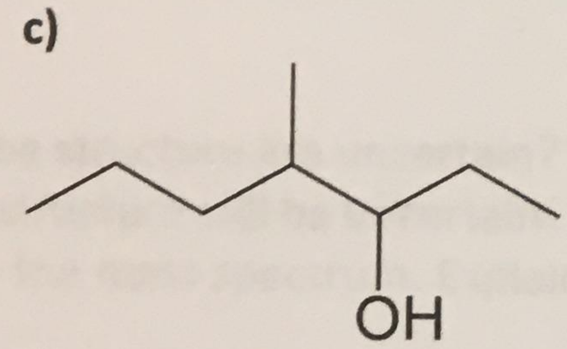
a)



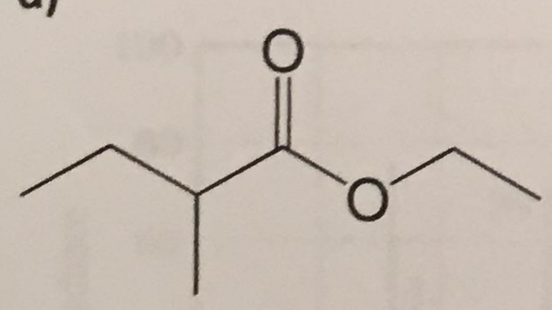
b)



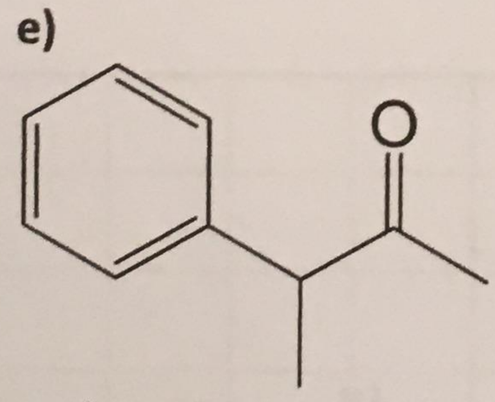
c)



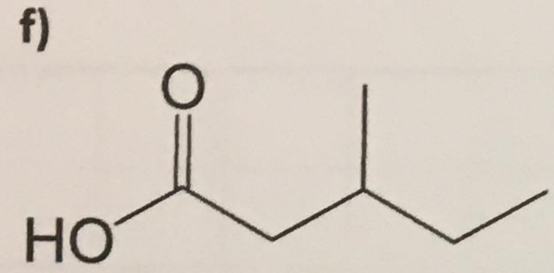
d)



e)



f)



17. (a) Both $C_6H_{10}O$ and C_7H_{14} have the same nominal mass, namely 98. Show how these compounds can be distinguished by the *m/z* ratio of their molecular ions in high-resolution mass spectrometry.

b) same question for C_6H_9N and C_5H_5NO.

18. Carboxylic acids often give a strong fragment ion at *m/z* (M-17). What is the likely structure of this cation? Show by drawing contributing structures that it stabilized by resonance.

19. The base peak in the mass spectrum of propanone (acetone) occurs at *m/z* 43. What cation does this peak represents?

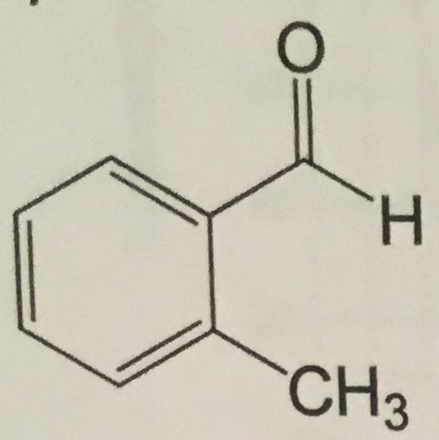
20. A characteristic peak in the mass spectrum of most aldehydes occurs at *m/z* 29. What cation does this peak represent? (This fragment is not ethyl cation, $CH_3CH_2^+$, if you don't remember the functional group in aldehydes, check your list of functional groups for help).

WORKSHEET I

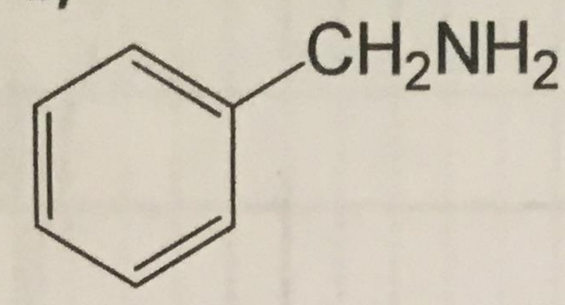
Part I

1. Predict the positions of the major absorption bands in the IR spectra of the following compounds

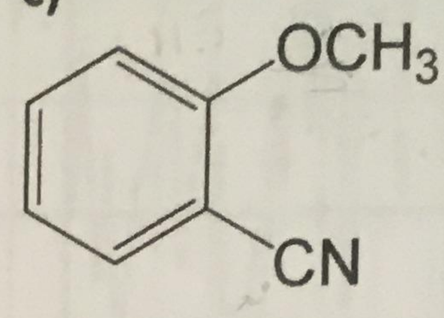
a)



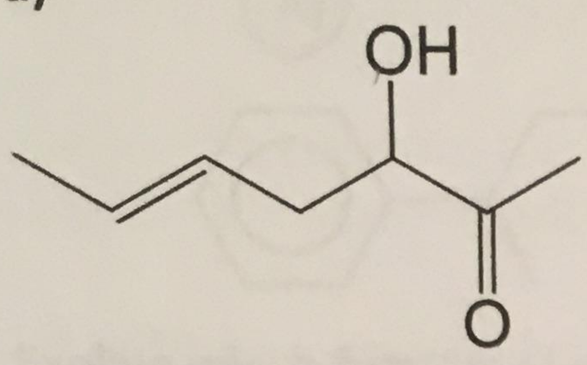
b)



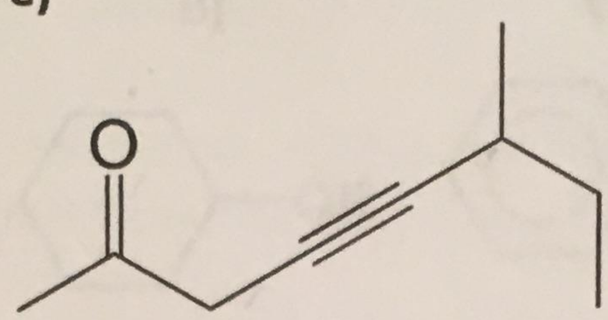
c)



d)



e)



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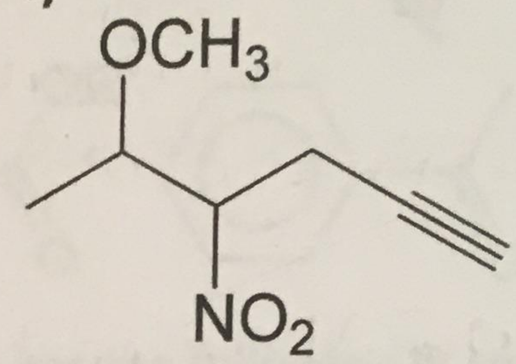


2. Which compound would be expected to show intense IR absorption at 3300 cm^{-1}?

A) $CH_3C{\equiv}CCH_3$ B) butane C) but-1-ene D) $CH_3CH_2C{\equiv}CH$ ✓

*CHsp

3. Which compound would be expected to show intense IR absorption at 2820, 2710 and 1705 cm^{-1}?

A) $CH_3COCH_2CH_3$ B) $PhCOCH_3$ C) PhCHO ✓ D) $CH_2{=}CHCOCH_3$

*aldehyde ✓

4. Which compound would be expected to show intense IR absorption at 2250 cm^{-1}?

A) $CH_3CH_2CH_2CO_2H$ B) $(CH_3)_2CHCH_2OH$ C) $(CH_3)_2CHCN$ ✓ D) $CH_3CH_2CH_2CONH_2$

*nitrite

5. Deduce a possible structure for the following compounds from their IR absorptions below.

(a) C_3H_3Br: 3300, 2900, 2100 cm^{-1}

(b) C_3H_5N: 2950, 2250 cm^{-1}

(c) C_5H_8O: 2950, 1750 cm^{-1}

(d) C_4H_8O: 2950, 2820, 2715, 1715 cm^{-1}

(e) C_6H_{10}: 3040, 2980, 1660 cm^{-1}

6. How could IR spectroscopy be used to distinguish between the following pair of compounds? You should also list all the major absorption bands in the IR spectra of each of compound.

(a) $CH_3OCH_2CH_3$ and $CH_3CH_2CH_2OH$

(b) $HOCH_2CH_2CHO$ and $CH_3CH_2CO_2H$

(c) $CH_3COCH{=}CHCH_2CH_3$ and $CH_3COCH_2CH_2CH{=}CH_2$

(d) $CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$

(e) $CH_2{=}CHCH_2CH(CH_3)_2$ and $CH_3CH_2CH_2CH(CH_3)_2$

7. Ethyne ($HC{\equiv}CH$) does not show IR absorption in the region 2000-2500 cm^{-1} because:

A) C–H stretches occur at lower energies.

B) $C{\equiv}C$ stretches occur at about 1640 cm^{-1}.

C) there is no change in the dipole moment when the $C{\equiv}C$ bond in ethyne stretches. ✓

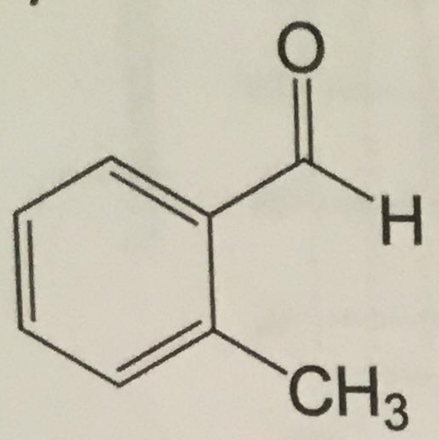
D) there is a change in the dipole moment when the $C{\equiv}C$ bond in ethyne stretches.

WORKSHEET I

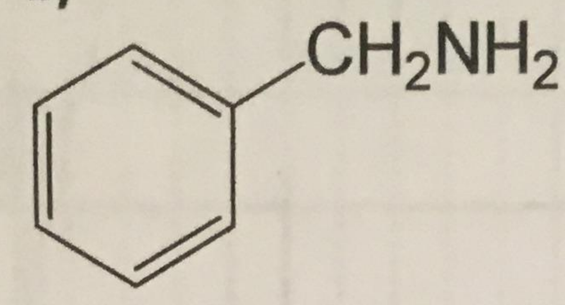
Part I

1. Predict the positions of the major absorption bands in the IR spectra of the following compounds

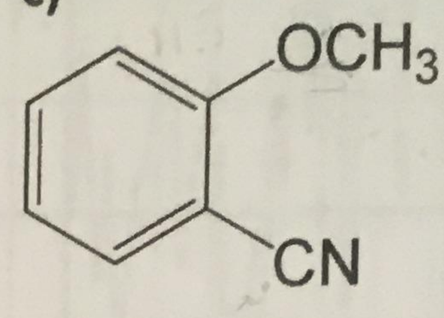
a)



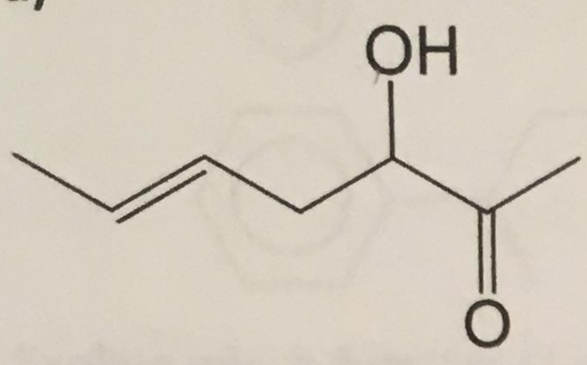
b)



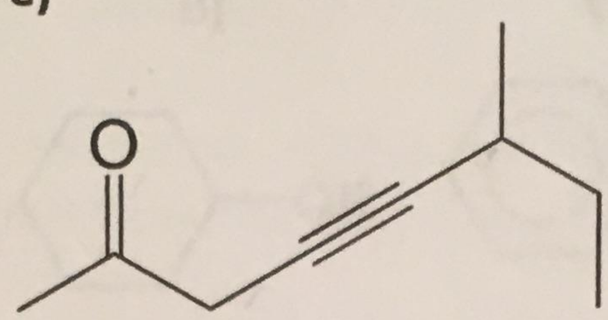
c)



d)



e)



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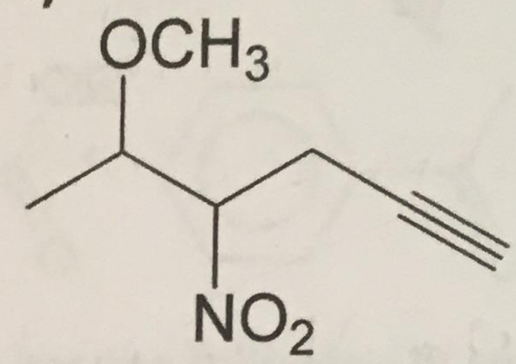

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*nitrite

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(d) $CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$

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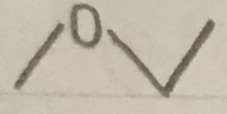
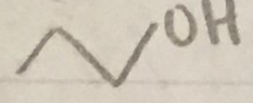
Part 6:

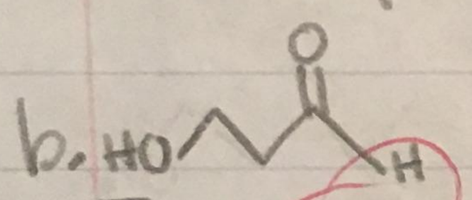
a. 

$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓

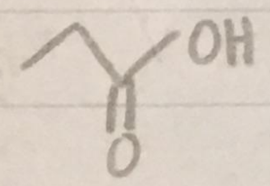


$\bar{\nu}$ OH = 3300-3500 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓

Compound 2 will have a broad band stretching around 3300-3500 cm^{-1} for the O-H bond that is not present in compound 1.

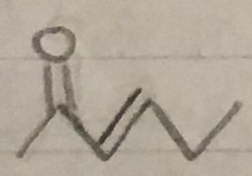
b. 

$\bar{\nu}$ OH = 2500-3300 cm^{-1} ✓ NO
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C-H = 2820 and 2720 cm^{-1} ✓ ✓
$\bar{\nu}$ C=O = 1725 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓

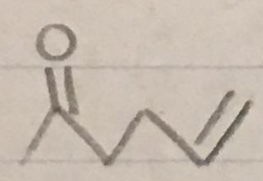


$\bar{\nu}$ OH = 2500-3300 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=O = 1710 cm^{-1} ✓

Compound 1 contains an aldehyde that has C-H stretches at 2820 + 2720 cm^{-1} which compound 2 lacks. Also the C-O bond is not visible in compound 2.

c. 

$\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=O = 1680 cm^{-1} ✓
$\bar{\nu}$ C=C = 1590 cm^{-1} ✓



$\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=O = 1700 cm^{-1} ✓
$\bar{\nu}$ C=C = 1605 cm^{-1} ✓

The wavenumber of the C=O and C=C bonds in compound 1 are lower because they are conjugated. ✓

Worksheet Section 1

Part 1:

a. $\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C(=O)-H = 2820 and 2720 cm^{-1} ✓
$\bar{\nu}$ C=C = 1450 - 1500 cm^{-1} ✓ (conj. in ring)
$\bar{\nu}$ C=O = 1725 cm^{-1} conjugated → 1700 - 1680 cm^{-1}

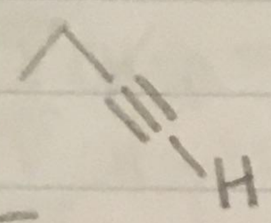
bending of Aromatic 600 - 800 cm^{-1}

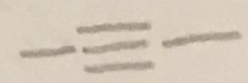
b. $\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=C = 1450 - 1500 cm^{-1} (conj. in ring) ✓
$\bar{\nu}$ C-N = 1200 cm^{-1} ✓
$\bar{\nu}$ N-H = 3300 cm^{-1} (2 peaks).

c. $\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=C = 1450 - 1500 cm^{-1} ✓
$\bar{\nu}$ C≡N = 2250 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓

d. $\bar{\nu}$ OH = 2500 - 3300 cm^{-1} ✓
$\bar{\nu}$ CHsp^2 = 3100 cm^{-1} ✓
$\bar{\nu}$ CH sp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C=O = 1700 cm^{-1} ✓
$\bar{\nu}$ C=C = 1605 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓

e. $\bar{\nu}$ C≡C = 2100 cm^{-1} ✓
$\bar{\nu}$ C=O = 1700 cm^{-1} ✓
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1} ✓

d. 

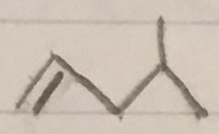


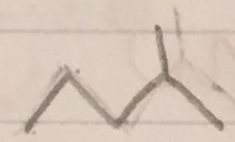
$\bar{\nu}$ CHsp = 3300 cm^{-1}
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1}
$\bar{\nu}$ C≡C = 2100 cm^{-1}

$\bar{\nu}$ CHsp^3 = 2950 cm^{-1}

There is no signal at 3300 cm^{-1} for CHsp^3 in compound 2 because the triple bond is internal. The C≡C bond is also not visible in compound 2 because there is no change in dipole moment.

not always

e 



$\bar{\nu}$ CHsp^2 = 3100 cm^{-1}
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1}
$\bar{\nu}$ C=C = 1600 cm^{-1}

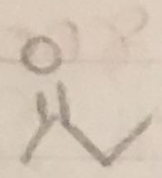
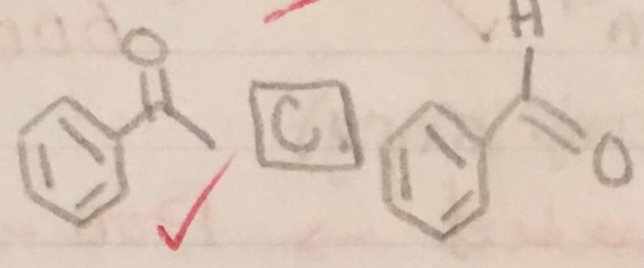
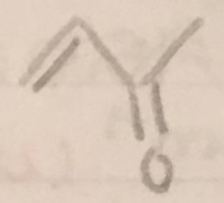
$\bar{\nu}$ CHsp^3 = 2950 cm^{-1}

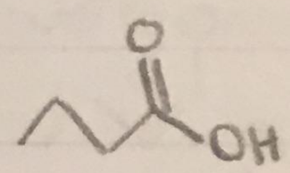
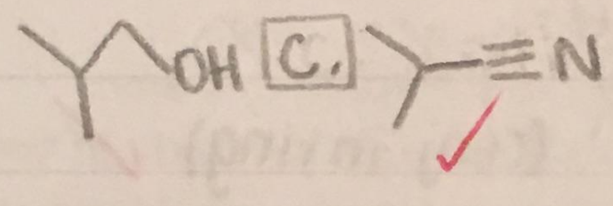
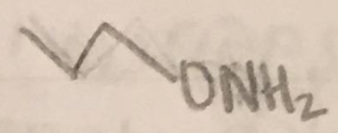
Compound 2 wouldn't have a peak at 3100 cm^{-1} or 1600 cm^{-1} because there are no double bonds.

Part 9:
The broad band around 3300 cm^{-1} suggests the presence of an alcohol. The peaks around 2900 cm^{-1} suggest the presence of the C-Hsp^3 bond of an alkane.

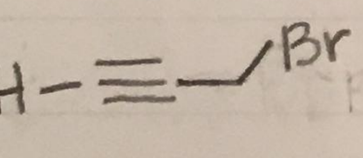
Part 10:
This compound contains an amide and an alkane. The N-H bonds of the amide are shown by the peaks at 3354 cm^{-1} and 3201 cm^{-1}. The C=O bond is represented by the peaks around 1650 cm^{-1}. The C-H bond of the alkane is shown at 2985 cm^{-1}.

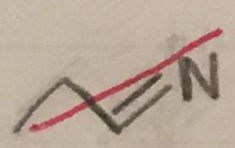
f. $\bar{\nu}$ CH sp = 3300 cm^{-1} ✓
$\bar{\nu}$ CH sp^3 = 2950 cm^{-1} ✓
$\bar{\nu}$ C≡C = 2100 cm^{-1} ✓
$\bar{\nu}$ NO_2 = 1500 cm^{-1} ✓ and 1300 cm^{-1} ✓
$\bar{\nu}$ C-O = 1200 cm^{-1} ✓
~~$\bar{\nu}$ C-N = 1200 cm^{-1}~~ no

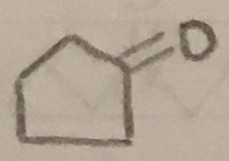
3. a.  b.  c. 

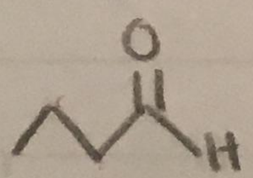
4. a.  b.  d. 

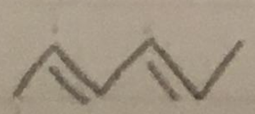
Part 5:

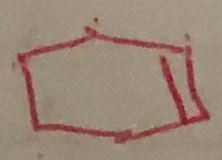
a.  ✓ CHsp = 3300 CHsp³ = 2900 C≡C = 2100

b.  C≡N CHsp³ = 2900 C=N = 2250 C≡N

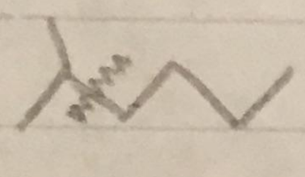
c.  ✓ CHsp³ = 2900 C=O = 1705

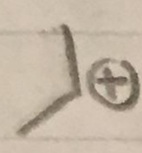
d.  ✓ CHsp³ = 2950 aldehyde = 2820+2715 C=O = 1715

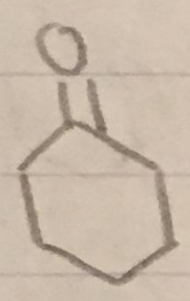
e.  ✓ CHsp² = 3040 CHsp³ = 2980 C=C = 1640



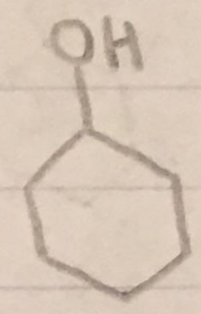
Worksheet Section 1

13.  2-methylhexane

 $m/z = 43$

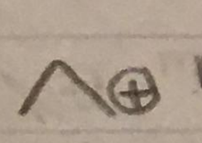
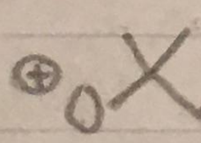
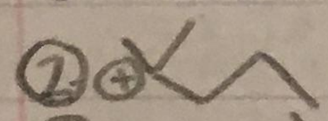
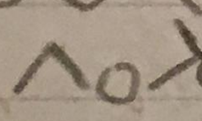
15. 

cyclohexanone
$\bar{\nu}$ C-H sp³ = 2950 cm⁻¹
$\bar{\nu}$ C=O = 1710 cm⁻¹

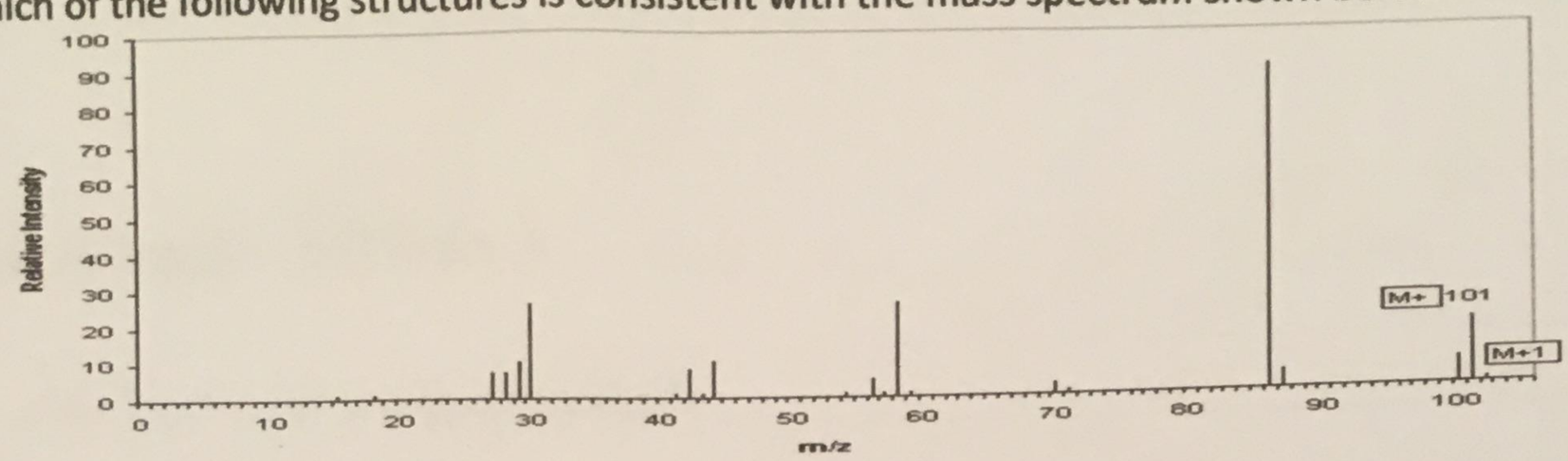


cyclohexanol
$\bar{\nu}$ O-H = 3200-3600 cm⁻¹
$\bar{\nu}$ C-H sp³ = 2950 cm⁻¹

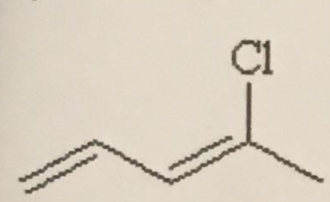
You would check for a signal around 1710 cm⁻¹ if there is no signal there then all of the starting ketone has been consumed.

16.
a. ①  $m/z = 18$  $m/z = 101$
②  $m/z = 85$ $m/z = 45$
③  $m/z = 87$

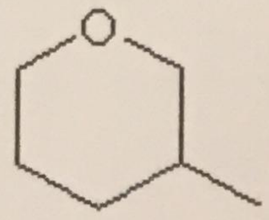
21. Which of the following structures is consistent with the mass spectrum shown below?



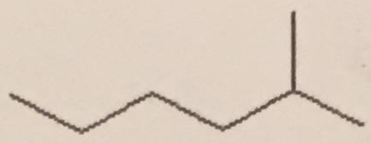
A)



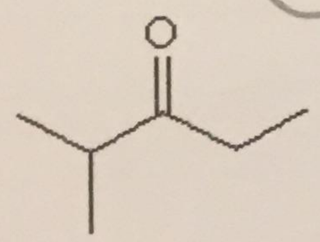
B)



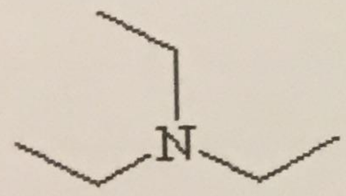
C)



D)

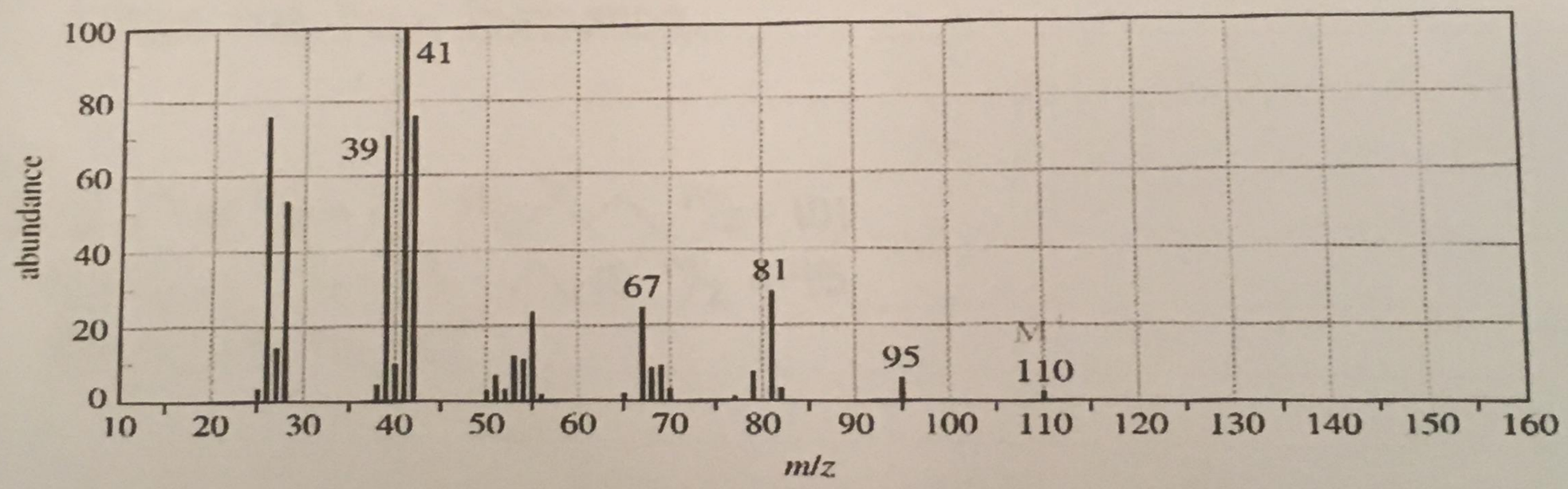


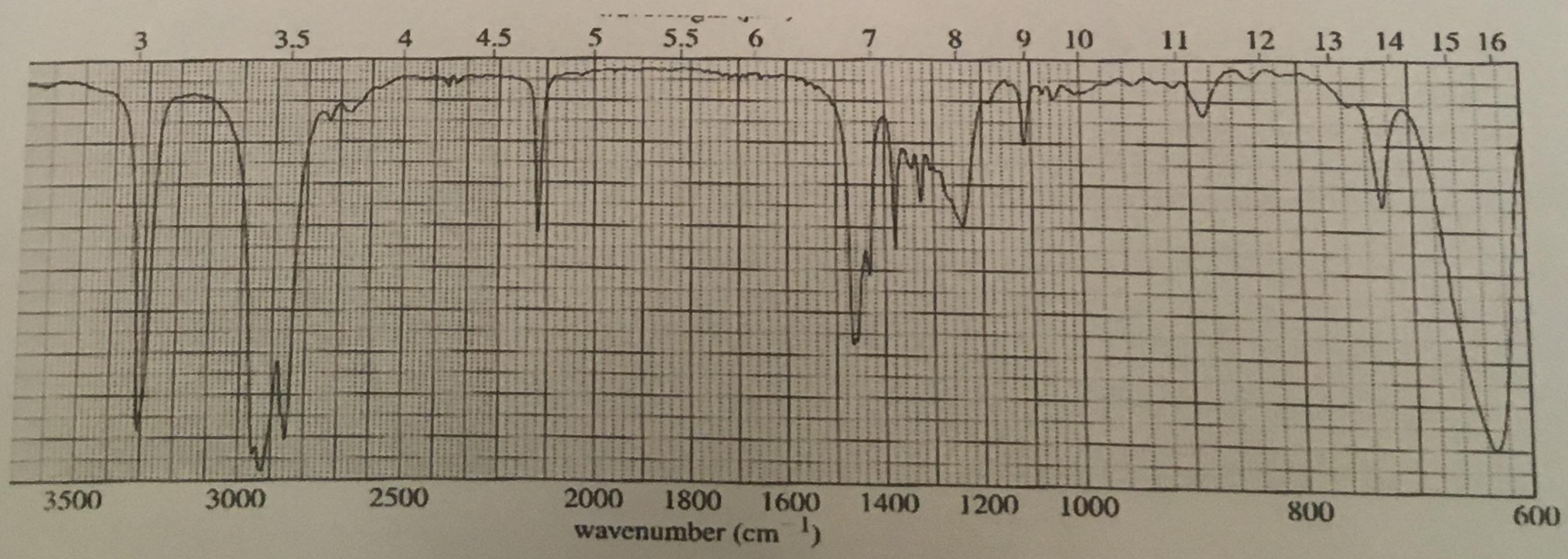
E



*odd number

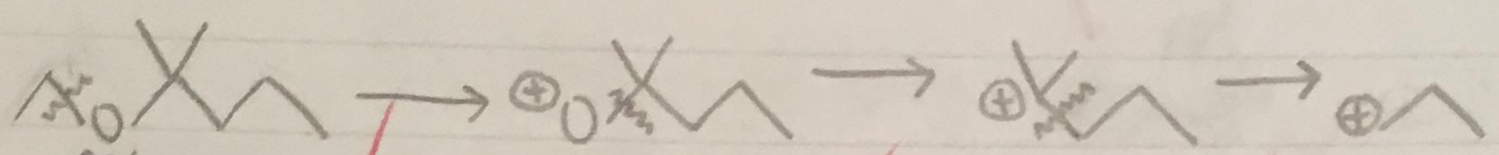
23. An unknown, foul-smelling hydrocarbon gives the mass spectrum and infrared spectrum shown.
a) Use the mass spectrum to propose a molecular formula. How many elements of unsaturation are there?
b) Use the IR spectrum to determine the functional group(s), if any.
c) Propose one or more structures for this compound. What parts of the structure are uncertain? If you knew that hydrogenation of the compound gives n-octane, would the structure still be uncertain?
d) Propose structures for the major fragments at 39, 67, 81 and 95 in the mass spectrum. Explain why the base peak is so strong.



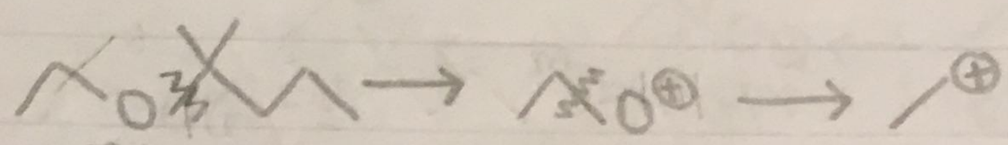


Section 16

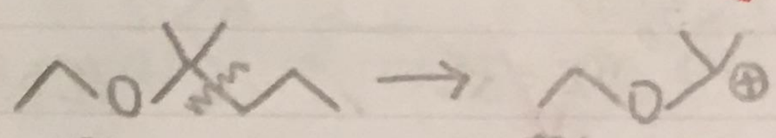
a.



m/z = 130 ✓ m/z = 101 ✓ m/z = 85 ✓ m/z = 43 ✓

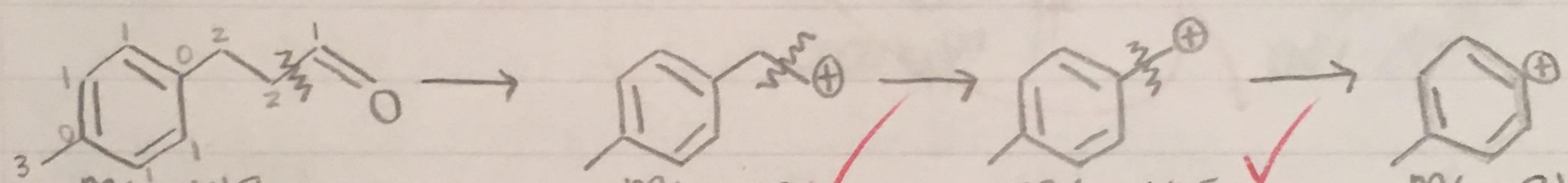


m/z = 130 m/z = 45 ✓ m/z = 29 ✓

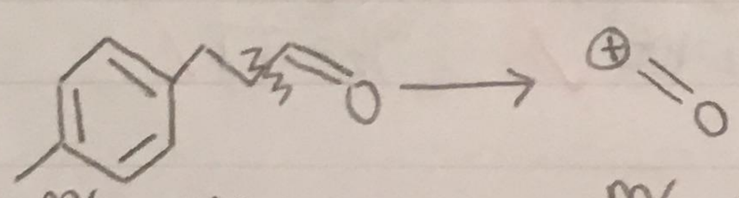


m/z = 130 m/z = 87 ✓

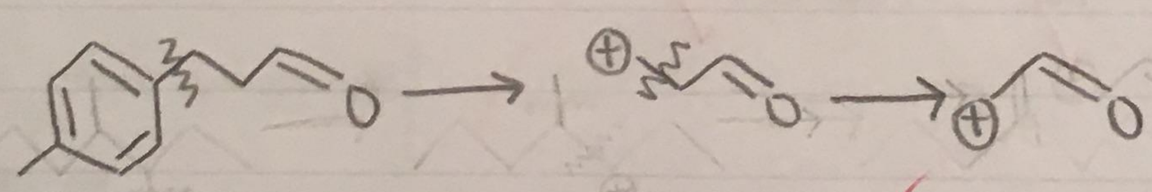
b.



m/z = 148 m/z = 119 ✓ m/z = 105 ✓ m/z = 91 ✓



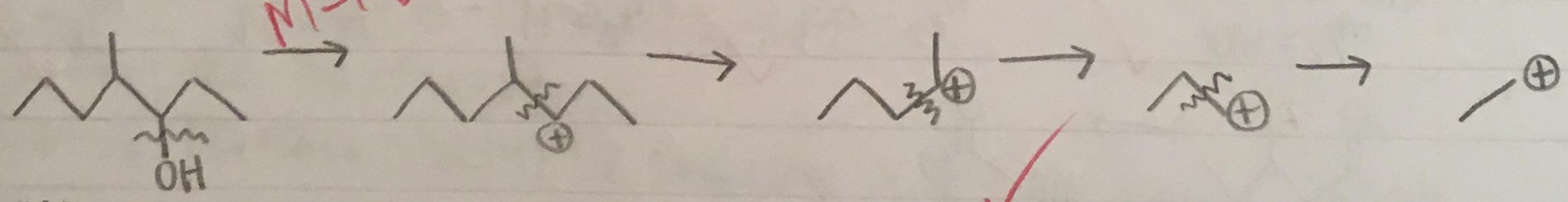
m/z = 148 m/z = 29 ✓



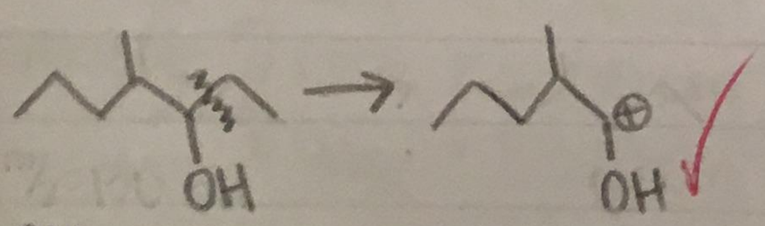
m/z = 148 m/z = 57 ✓ m/z = 43 ✓

d.

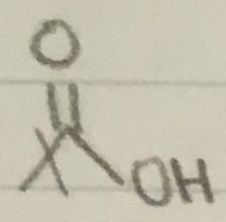
M-18



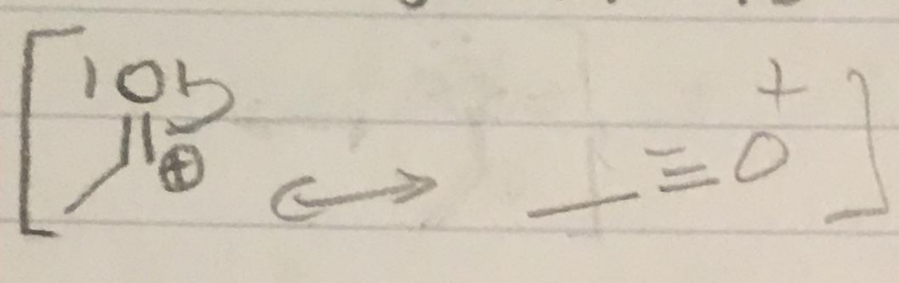
m/z = 130 m/z = 113 m/z = 71 ✓ m/z = 43 ✓ m/z = 29 ✓

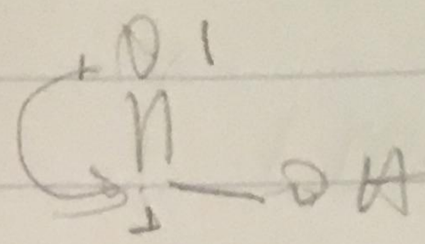


m/z = 130 m/z = 101 ✓

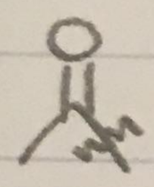
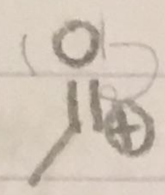
18.  m/z = 60

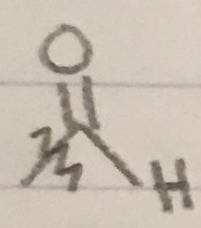
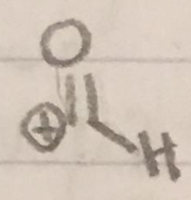
60 − 17 = 43





m/z 45

19.  m/z = 58  m/z = 43

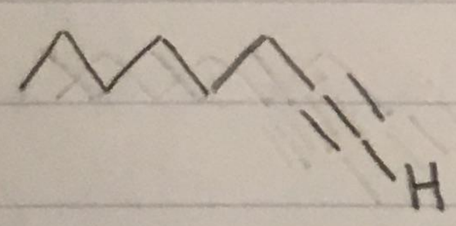
20.  m/z = 44  m/z = 29

23.

b. alkane CH sp³ = 2950 cm⁻¹

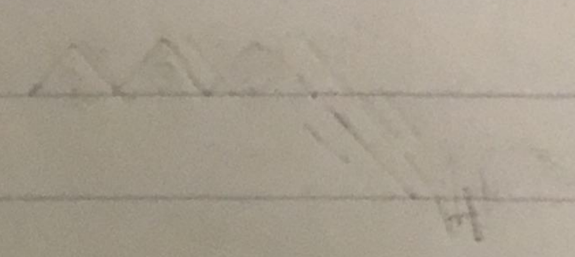
alkyne C≡C = 2100 cm⁻¹

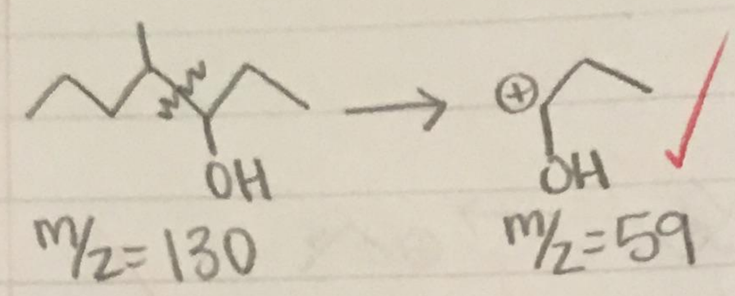
≡C–H sp = 3300 cm⁻¹

c. 

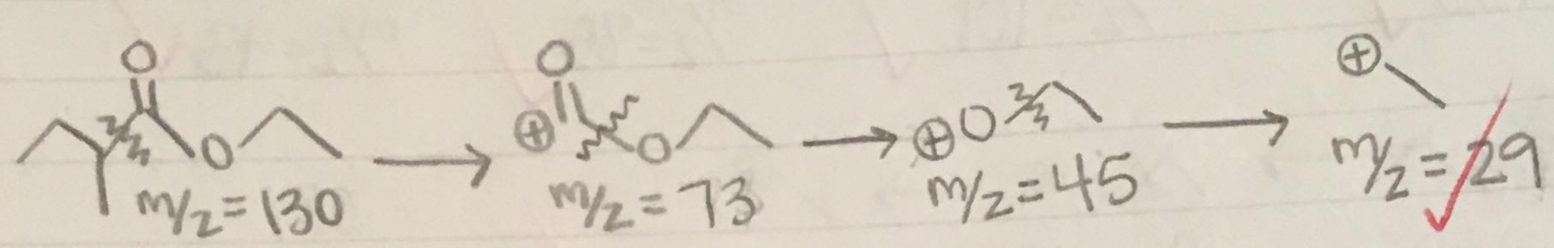
a. C_8H_{14} = 8+1 − ½(14) = 2 elements of unsaturation

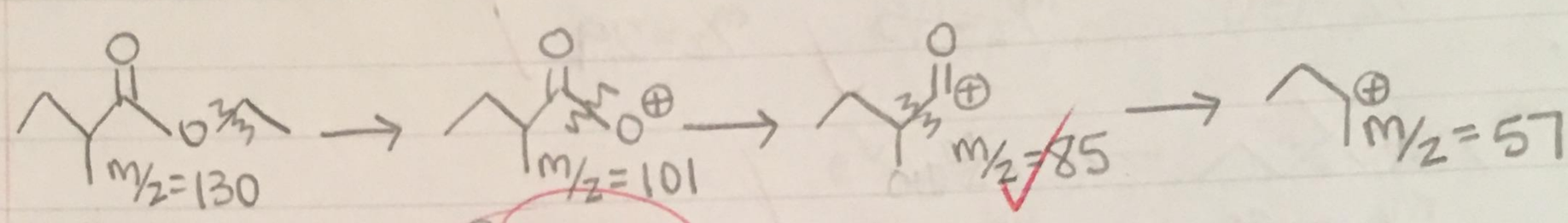
NI

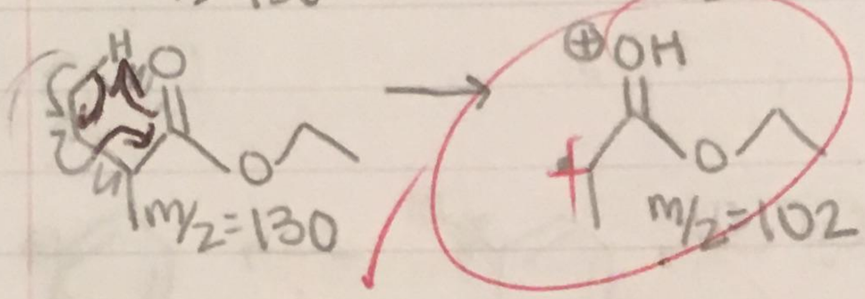
d. 


OH
m/z=130
OH
m/z=59

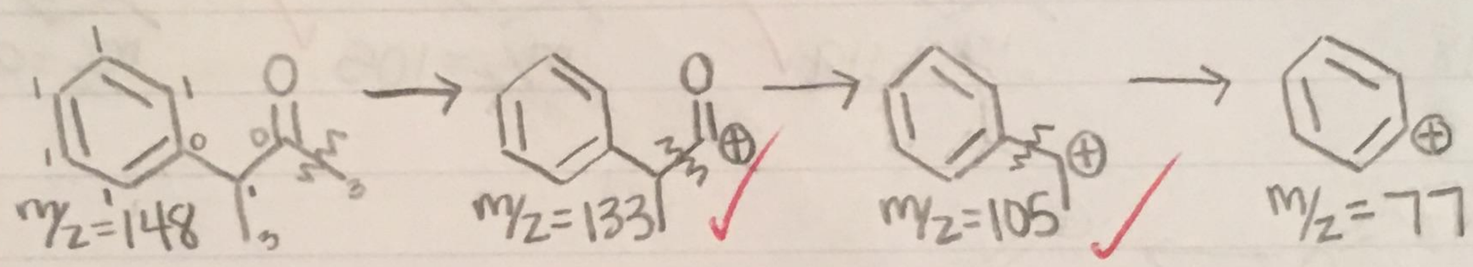
d.


m/z=130
m/z=73
m/z=45
m/z=29


m/z=130
m/z=101
m/z=85
m/z=57


m/z=130
OH
m/z=102

e.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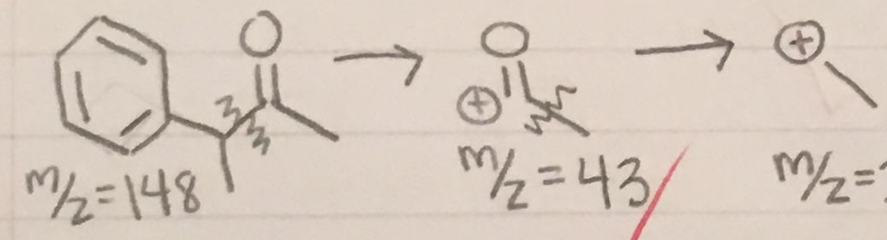
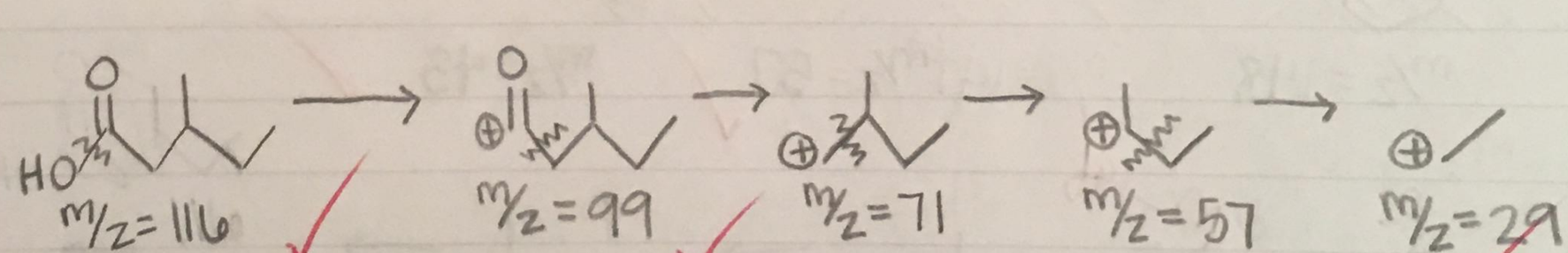
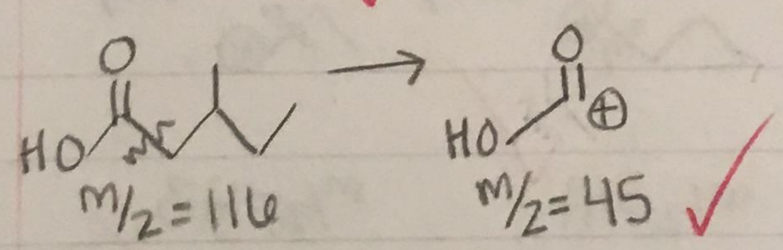
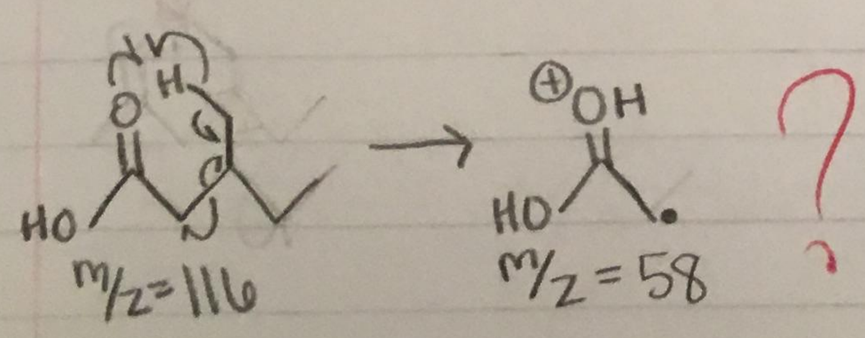
m/z=77


m/z=148
m/z=43
m/z=29

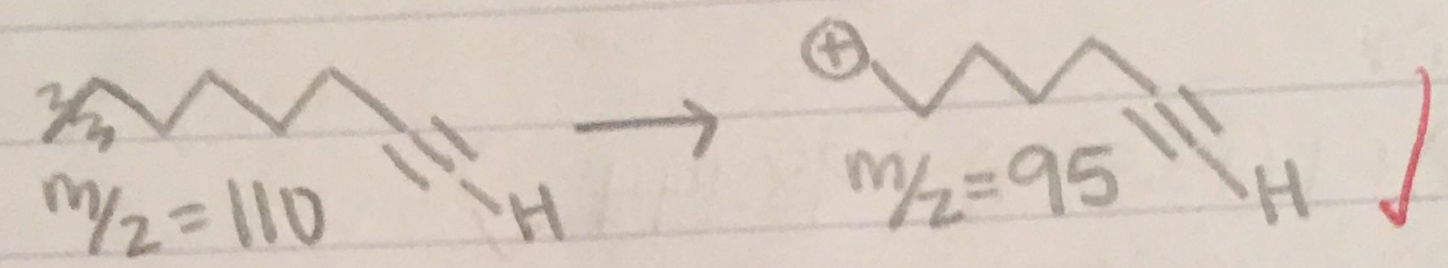
f.

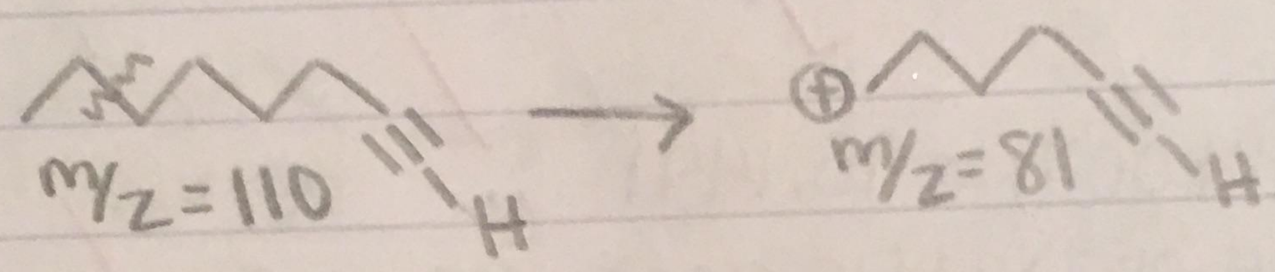

HO
m/z=116
m/z=99
m/z=71
m/z=57
m/z=29

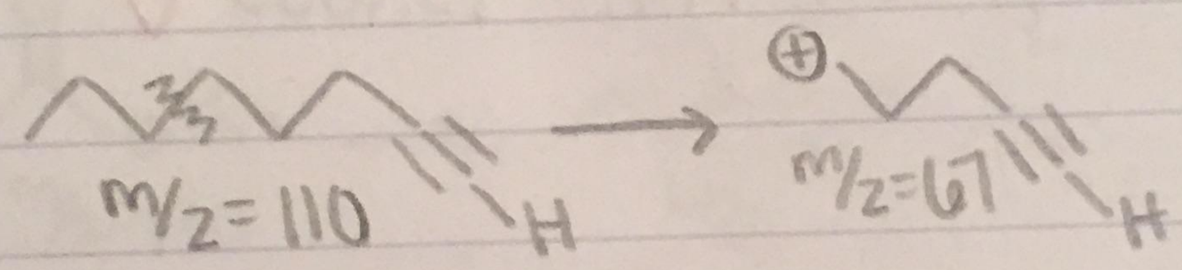

HO
m/z=116
HO
m/z=45

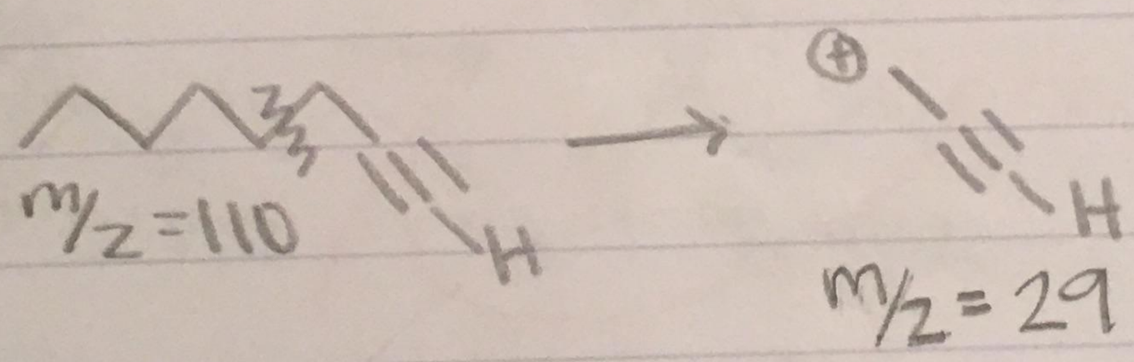

H
HO
m/z=116
OH
HO
m/z=58

d.









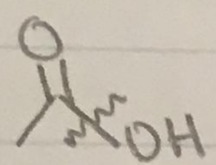
17.

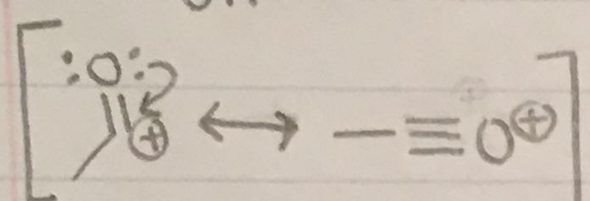
a. $6(12.011)+10(1.0079)+1(15.999)=98.144$

$7(12.011)+14(1.0079)=98.1876$

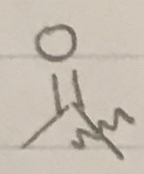
b. $6(12.011)+9(1.0079)+1(14.007)=95.1441$

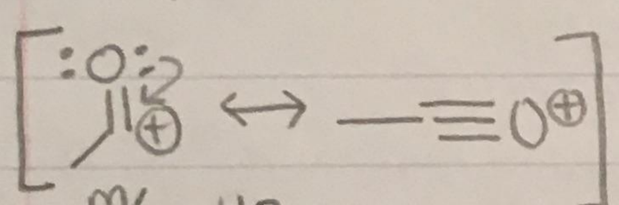
$5(12.011)+5(1.0079)+1(14.007)+1(15.999)=95.1005$

18.  $m/z=60$

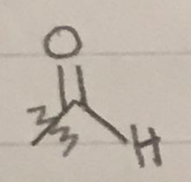


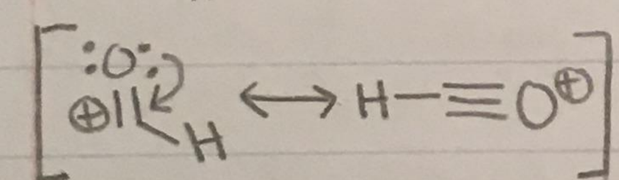
$m/z=43$

19.  $m/z=58$

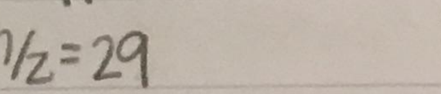


$m/z=43$

20.  $m/z=44$



$m/z=29$

23. a.  $110-15-13=82/12=6$

$8(12)=96$ $110-96=14$

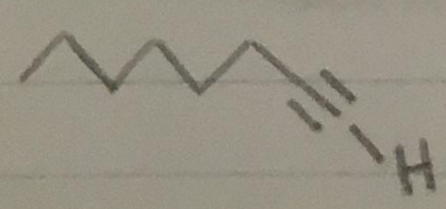
C_8H_{14} $NI=8+1-\frac{1}{2}(14)=2$ elements of unsaturation

b. alkane $\bar{\nu}_{CH\,sp^3}=2950\,cm^{-1}$

alkyne $\bar{\nu}_{C\equiv C}=2100\,cm^{-1}$

$\bar{\nu}_{CH\,sp}=3300\,cm^{-1}$

?

c. 

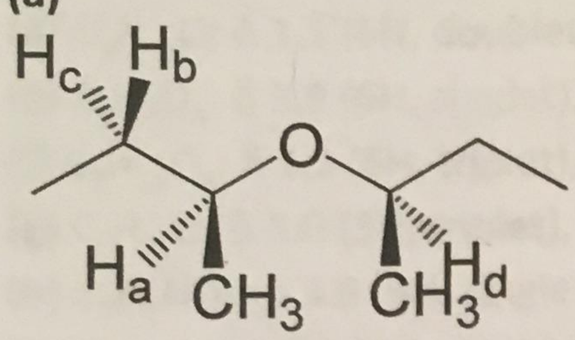
WORKSHEET II

1. On a 90 MHz spectrometer, calculate the frequency at which a proton absorbs if it appears at 4.20 ppm.

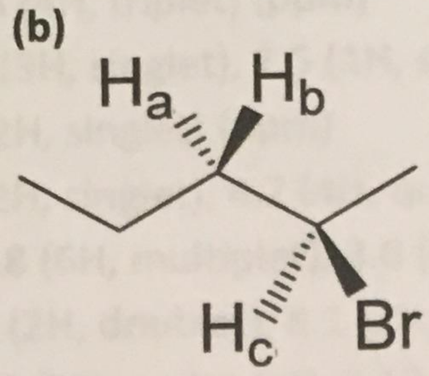
2. Using a 60 MHz spectrometer, the protons in dichloromethane appear at 5.30 ppm. When the same sample is placed in a 100 MHz instrument, where does the signal appear?
A) 8.33 B) 5.30 C) 3.18 D) cannot be determined from information given

3. State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated)

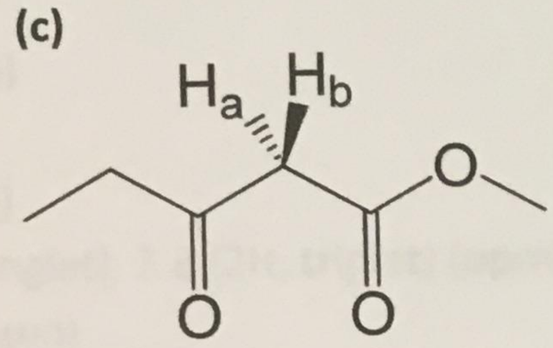
(a)



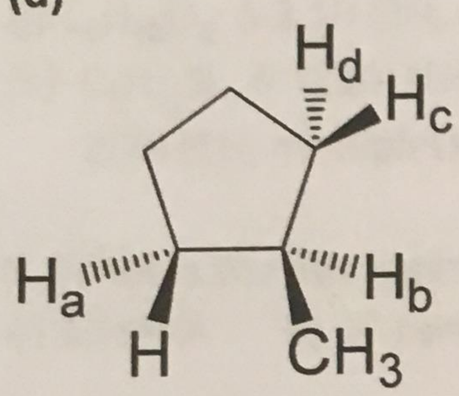
(b)



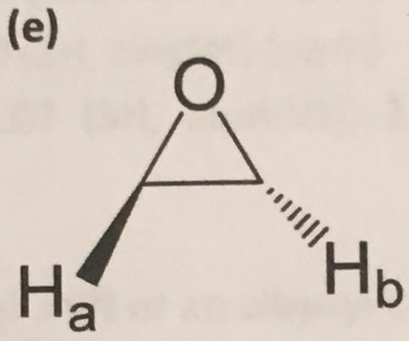
(c)



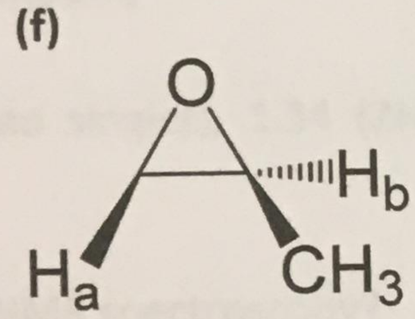
(d)



(e)



(f)



4. The chair form of cyclohexane has protons in two distinct environments, axial and equatorial. When the proton NMR of cyclohexane is run on a 100-MHz instrument at 23°C, only one signal for the compound is observed. Explain this apparent contradiction.

5. How might the proton spectrum of ultrapure dimethylamine, $(CH_3)_2NH$, differ from the spectrum of this compound to which D_2O has been added?

6. Predict the number of signals expected (disregarding splitting) in the ^1H spectrum of the following compounds:
(a) *m*-xylene (1,3-dimethylbenzene).
(b) *o*-chlorophenol (2-chlorophenol).
(c) dibutyl ether.
(d) 1,1-dimethylcyclobutane.
(e) *m*-dichlorobenzene (1,3-dichlorobenzene).

7. Predict the number of signals expected, their splitting, and their relative area in the ^{1}H-NMR spectrum of the following compounds

(a) $CH_3CH_2OCH_3$.
(b) $(CH_3)_3CCHO$.
(c) 2-methylpropane (isobutane).
(d) 1,2-dichloroethane ($ClCH_2CH_2Cl$).

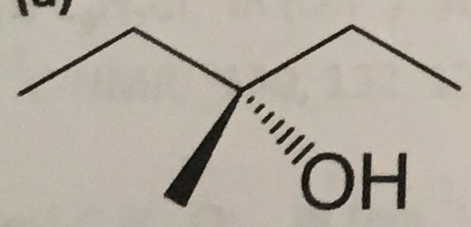
8. Deduce the identity of the following compound from the ^{1}H-NMR data given.

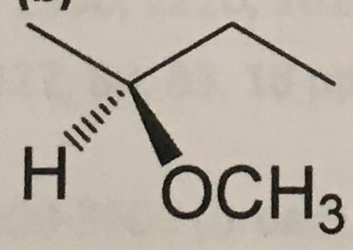
(a) $C_3H_3Cl_5$: δ 4.5 (1H, triplet), 6.1 (2H, doublet) (ppm)
(b) C_4H_7BrO: δ 2.2 (3H, singlet), 3.5 (2H, triplet), 4.5 (2H, triplet) (ppm)
(c) $C_3H_6Br_2$: δ 2.4 (2H, quintet), 3.5 (4H, triplet) (ppm)
(d) $C_5H_{10}O$: δ 1.1 (6H, doublet), 2.2 (3H, singlet), 2.5 (1H, septet) (ppm)
(e) $C_6H_8O_4$: δ 3.9 (6H, singlet), 6.1 (2H, singlet) (ppm)
(f) $C_7H_{12}O_4$: δ 1.3 (6H, triplet), 3.4 (2H, singlet), 4.2 (4H, quartet) (ppm)
(g) $C_5H_{12}O$: δ 1.0 (3H, triplet), 1.2-1.8 (6H, multiplet), 3.0 (1H, broad singlet), 3.8 (2H, triplet) (ppm)
(h) $C_7H_7NO_3$: δ 3.9 (3H, singlet), 6.9 (2H, doublet), 8.1 (2H, doublet) (ppm)
(i) $C_8H_{18}O$: δ 0.89 (6H, doublet), 1.87 (1H, multiplet), 3.17 (2H, doublet)(ppm)
(j) $C_6H_{10}O_2$: δ 2.19 (3H, singlet), 2.70 (2H, singlet) (ppm)
(k) $C_4H_{11}N$: δ 0.90 (3H, triplet), 1.07 (3H, doublet), 1.14 (2H, broad singlet), 1.34 (2H, multiplet), 2.79 (1H, multiplet) (ppm)

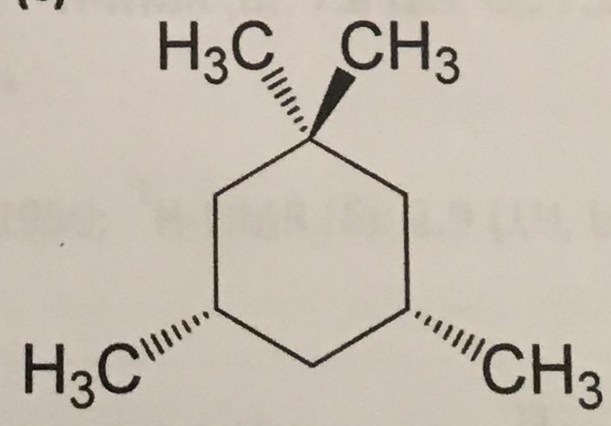
9. What is the approximate chemical shift of an alkynyl carbon in ^{13}C-NMR spectroscopy?
A) 10 ppm B) 30 ppm C) 70 ppm D) 120 ppm E) 200 ppm

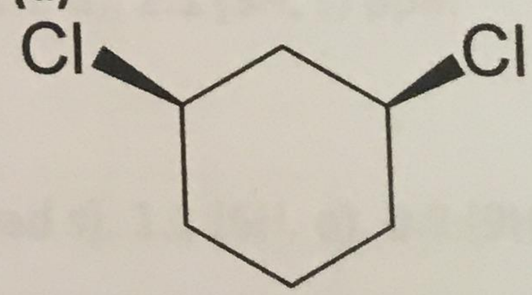
10. Predict the number of signals expected in the proton spin decoupled ^{13}C-NMR spectrum of the following compounds:
(a) *o*-diethylbenzene (1,2-diethylbenzene).
(b) *p*-diethylbenzene (1,4-diethylbenzene).

11. Predict the number of signals expected (disregarding splitting) in the ^{1}H-NMR and in the proton spin decoupled ^{13}C NMR spectra of the compound shown below.

(a)


(b)


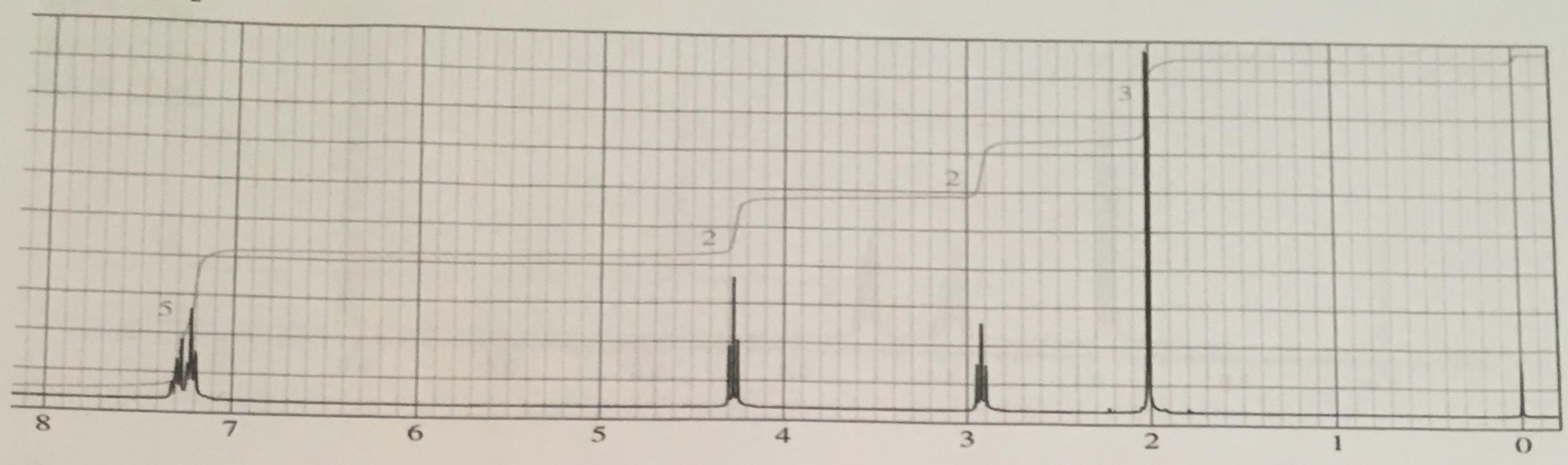
(c)


(d)


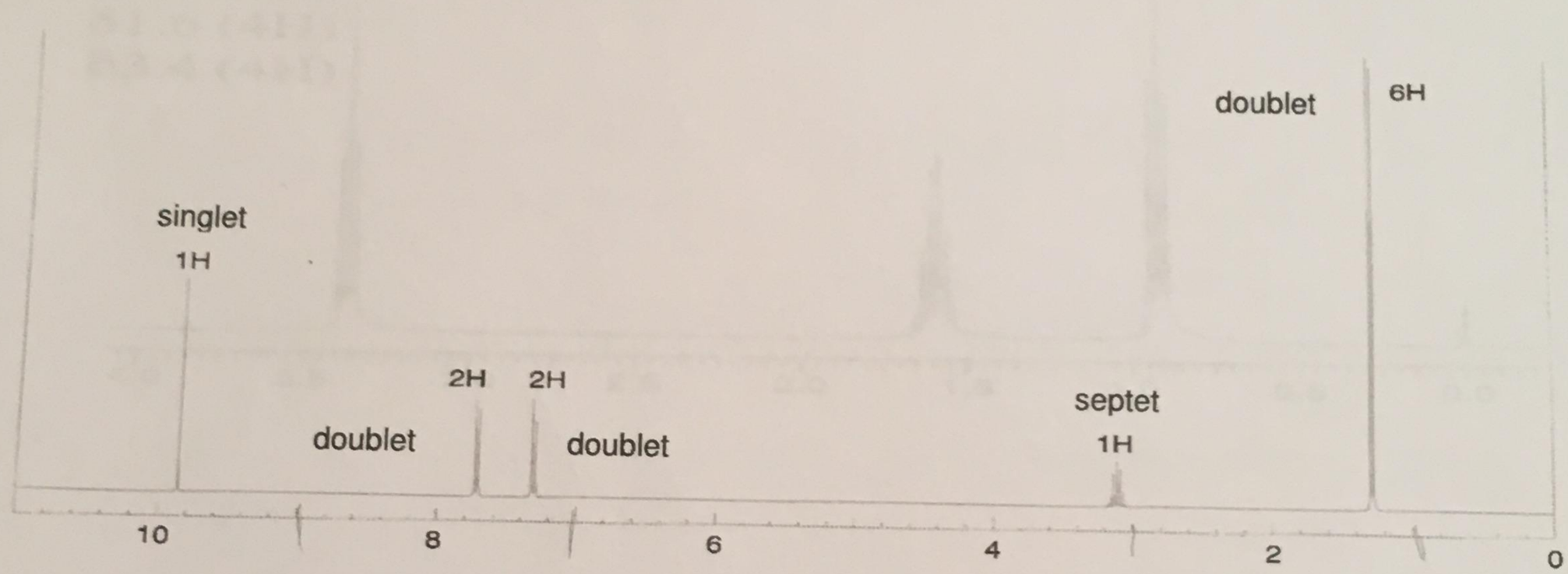
12. Deduce the identity of the following compound from the ^{13}C NMR data given.
C_9H_{12}: δ 21.3 (quartet), 127.2 (doublet), 138.0 (singlet) (ppm)

14. Deduce the identity of the following compound from the ^1H- NMR spectrum and the data given.

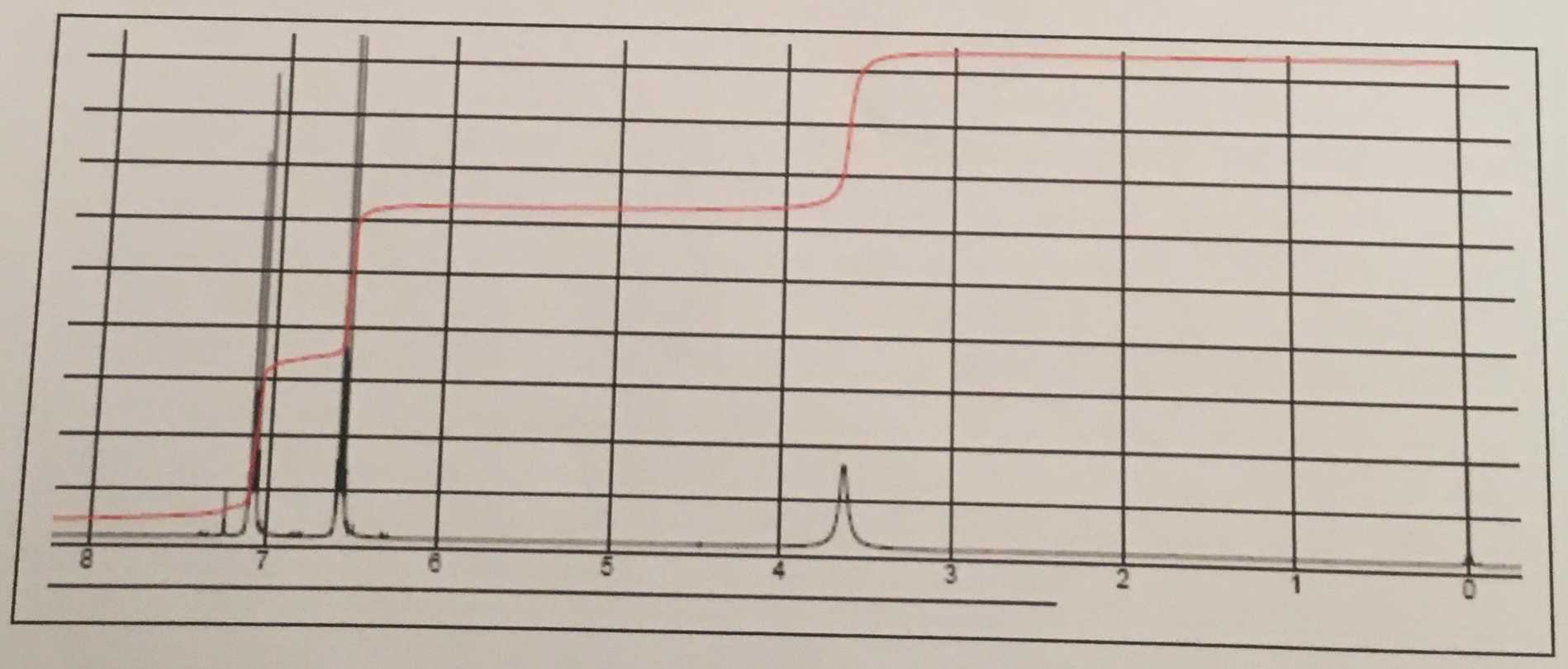
(a) $C_{10}H_{12}O_2$



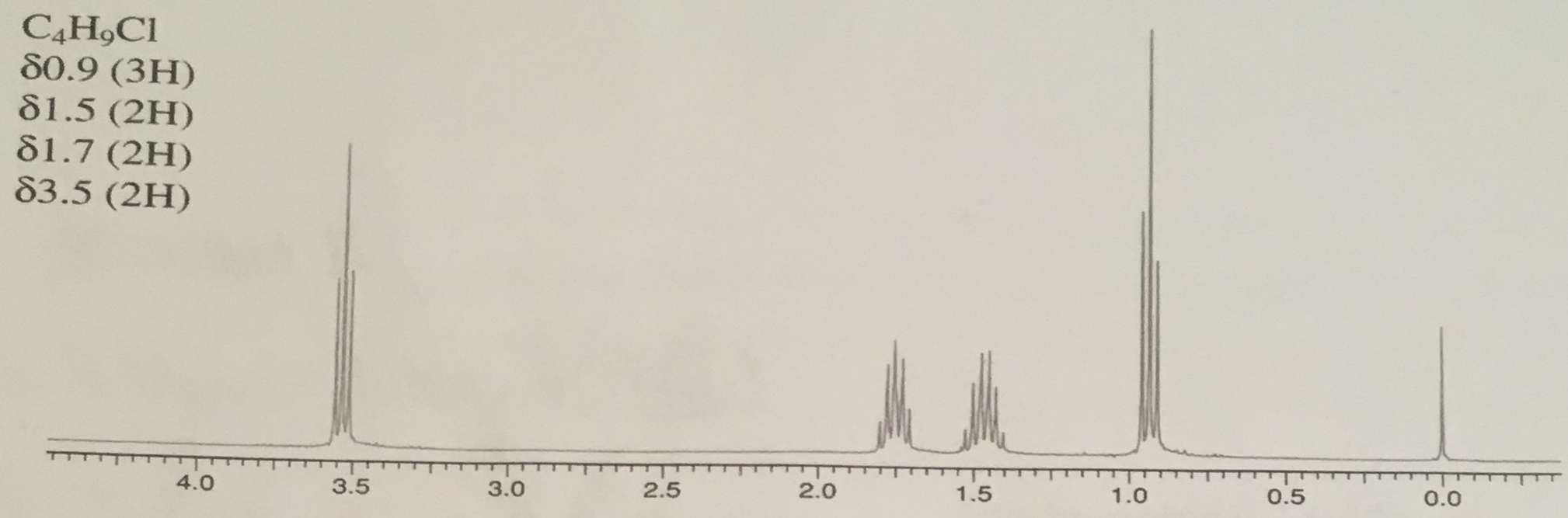
(b) $C_{10}H_{12}O$



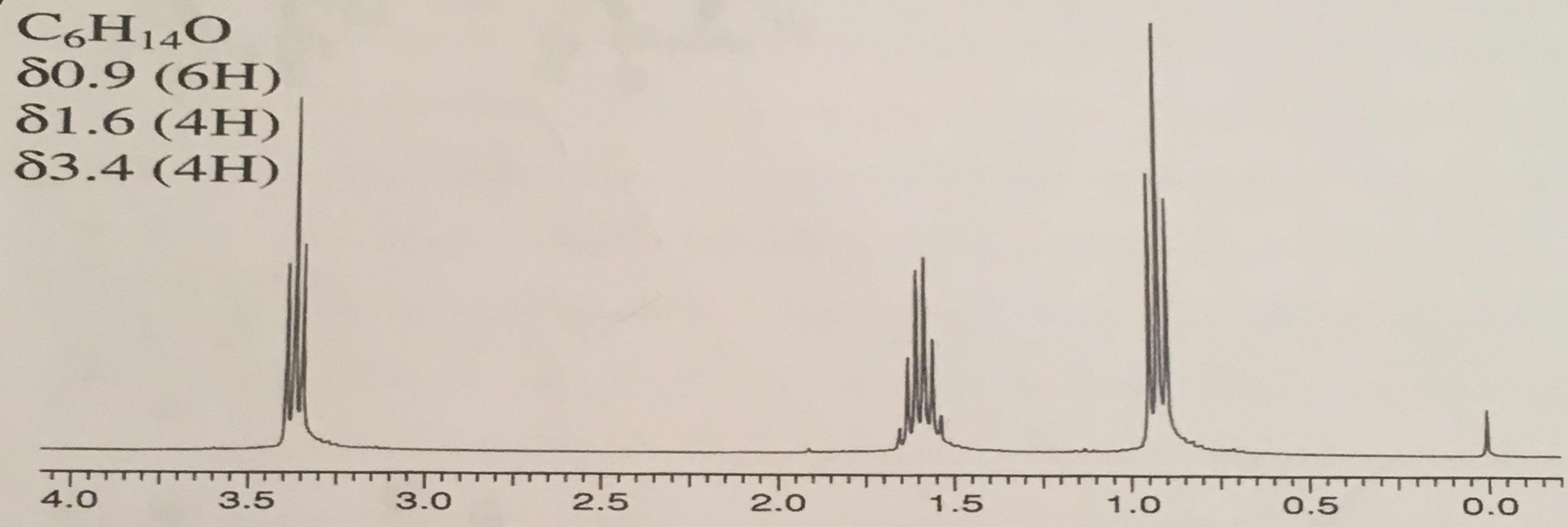
(c) C_6H_6NCl



(d)


C_4H_9Cl
δ0.9 (3H)
δ1.5 (2H)
δ1.7 (2H)
δ3.5 (2H)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

(e)


$C_6H_{14}O$
δ0.9 (6H)
δ1.6 (4H)
δ3.4 (4H)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

13. Deduce the identity of the following compound from the given spectral data.

(a) $C_7H_{10}O_2$: ^{1}H-NMR, δ 1.16 (3H, singlet), 2.21 (2H, singlet)
^{13}C-NMR: δ 216.25 (singlet), 52.57 (singlet), 34.51 (triplet), 20.22 (quartet) (ppm)

(b) C_3H_4BrN: ^{1}H-NMR, δ 2.98 (2H, triplet), 3.53 (2H, triplet)
^{13}C-NMR: δ 21.05 (triplet), 23.87 (triplet), 118.08 (singlet) (ppm); IR, 2963, 2254 cm^{-1}

(c) $C_5H_{10}O$: ^{1}H-NMR, δ 1.2 (6H, doublet), 2.1 (3H, singlet), 2.8 (1H, septet) (ppm)
IR: 2980, 1710 cm^{-1}; MS, *m/z* 71, 43

(d) C_8H_{10}: ^{1}H-NMR, δ 1.20 (3H, triplet), 2.60 (2H, quartet), 7.12 (5H, multiplet) (ppm)
IR: 3050, 2970, 1600 cm^{-1}; MS, *m/z* 91

(e) $C_4H_8O_2$: ^{1}H-NMR (δ) 1.23 (3H, triplet), 2.00 (3H, singlet), 4.02 (2H, quartet) (ppm)
IR: 2980, 1740 cm^{-1}

(f) C_8H_{14} : IR (cm^{-1}): 2950, 2180; ^{1}H-NMR (δ): 0.9 (3H, t), 1.0 (9H, s), 2.3 (2H, q) (ppm).

(g) $C_4H_8O_3$: IR (cm^{-1}): 2800-3300 (broad), 2950, 1750; ^{13}C-NMR (δ): 17.7 (q), 65.4 (q), 72.3 (d), 210.8 (s) (ppm)

(h) C_6H_{10}: IR (cm^{-1}): 2950, 2230; ^{1}H-NMR (δ): 2.0 (1H, septet), 1.8 (3H, s), 0.9 (6H, d) ppm
^{13}C-NMR (δ): 78, 72, 45, 18, 15 ppm

(i) $C_5H_8Cl_2$: IR (cm^{-1}): 2950; ^{1}H-NMR (δ): 1.4 (4H, t), 1.2 (4H, t) ppm; ^{13}C-NMR (δ):62, 26, 23 ppm

(j) $C_7H_{14}O_2$: IR (cm^{-1}): 2950, 1740; ^{1}H-NMR (δ):2.3 (2H, q), 1.0 (3H, t), 0.9 (9H, s) ppm
^{13}C-NMR (δ): 185, 78, 29, 14, 12 ppm

(k) $C_5H_{10}O$: IR (cm^{-1}):2950, 1720; ^{1}H-NMR (δ): 2.6 (1H, septet), 2.1 (3H, s), 1.0 (6H, d) ppm
^{13}C-NMR (δ): 195, 42, 18, 11 ppm

(l) C_9H_7Cl: IR (cm^{-1}): 3050, 2950, 2220, 1620; ^{1}H-NMR (d): 7.8 (2H, d), 7.2 (2H, d), 2.1 (3H, s) ppm
^{13}C-NMR: 140, 132, 125, 122, 88, 83, 18 ppm

(m) $C_7H_{16}O$: IR (cm^{-1}): 3200-3600 (broad), 2950; ^{1}H-NMR (δ): 2.9 (1H, broad s), 1.2 (6H, q), 0.9 (9H, t) ppm; ^{13}C-NMR (δ): 70, 25, 12 ppm

(n) $C_5H_{10}O$: IR (cm^{-1}): 2950; ^{1}H-NMR (δ):3.5 (4H, s), 0.9 (6H, s) ppm; ^{13}C-NMR (δ): 64, 41, 12 ppm

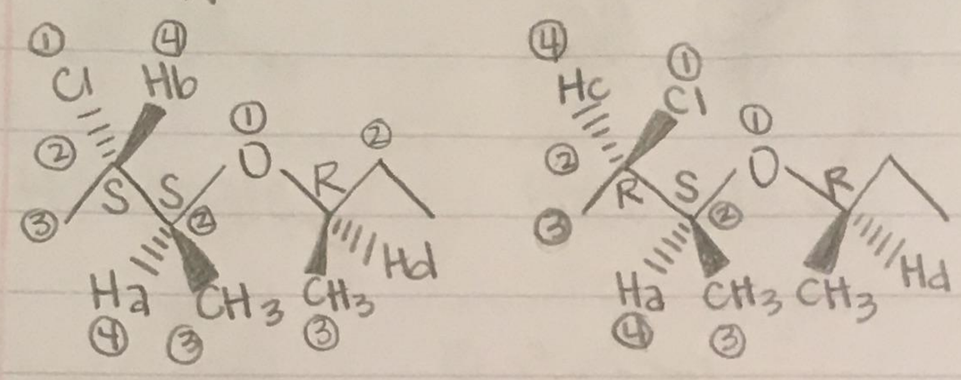
(o) $C_7H_{16}O$: IR (cm^{-1}): 3200-3600 (broad), 2950; ^{1}H-NMR (δ): 2.8 (1H, broad s), 1.0 (6H, s), 0.9 (9H, s) ppm; ^{13}C-NMR (δ): 68, 39, 16, 13 ppm

Worksheet II

1. 4.20 ppm × 90 MHz = $\boxed{378\ Hz}$

3.

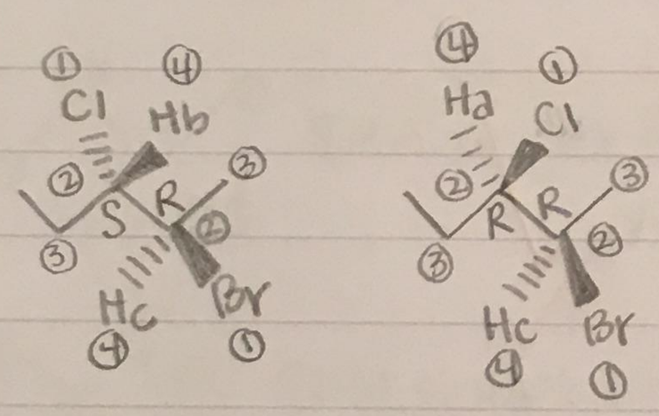
a.



diastereotopic: c+b ✓

equivalent: ~~a+d~~ enan.

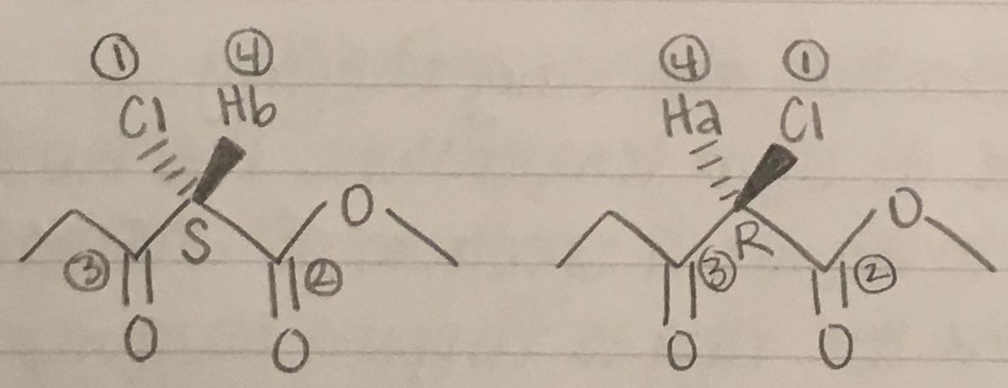
b.



diastereotopic: a+b ✓

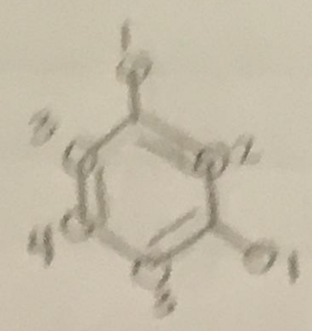
Ha & Hc ?

c.

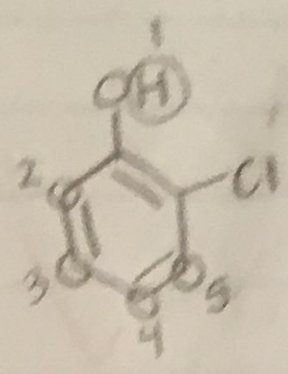


enantiotopic: a+b ✓

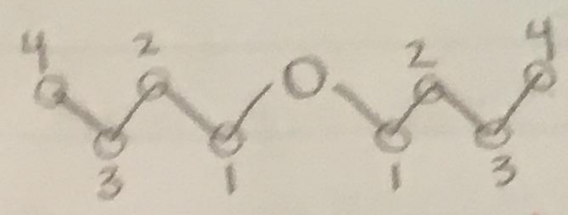
6.

a. 

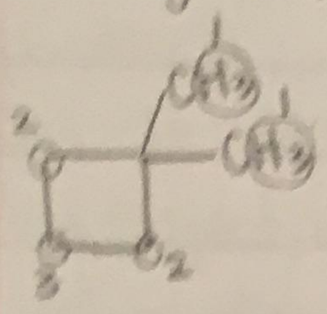
4 signals

b. 

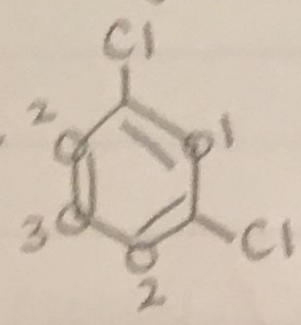
5 signals

c. 

4 signals

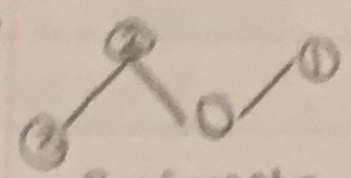
d. 

3 signals

e. 

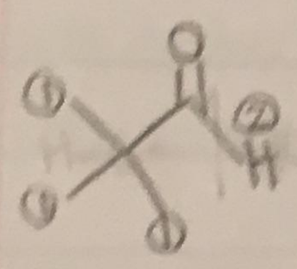
3 signals

7.

a. 

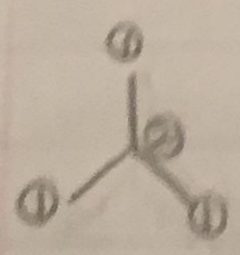
① 3H, singlet, 3.4ppm ② 2H, quartet, 3.7ppm ③ 3H, triplet, 1.4ppm

3 signals

b. 

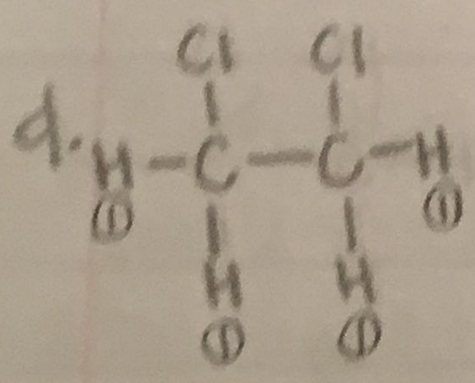
① 9H, singlet, 1.1ppm ② 1H, singlet, 10ppm

2 signals

c. 

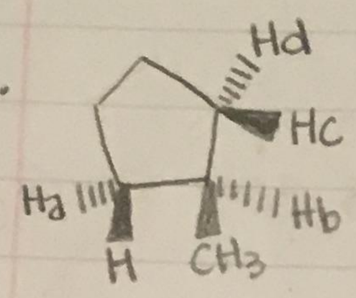
① 9H, doublet, 0.9ppm ② 1H, multiplet, 1.7ppm

2 signals

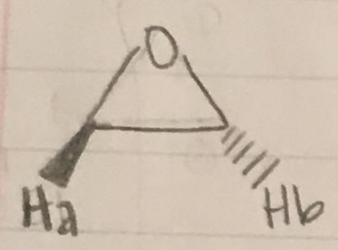
d. 

① 4H, singlet, 4ppm

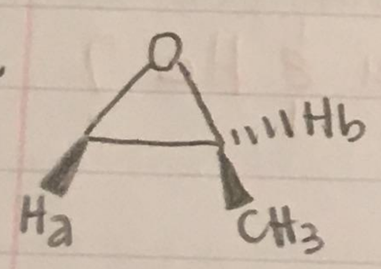
1 signal

d. 

diastereotopic: d + c
unrelated: a + b

e. 

equivalent: a + b

f. 

unrelated: a + b

4. Only one signal is observed because the ring flipping occurs at a very rapid rate at room temperature. The NMR spectrometer is too slow to aquire a spectrum of a single chair conformation. Because the ring is flipping so quickly, the spectrometer only "sees" an average electronic environment of the protons, and only one signal is produced.

5. If D_2O is added, deuterium will exchange with the N-H protons and the N-H peak will become absent or much less intense in the second spectrum.

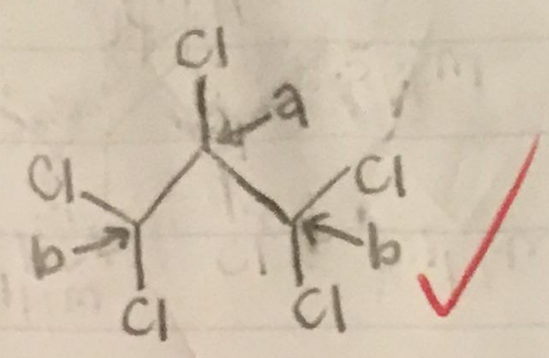
8.

a. $C_3H_3Cl_5$

NI = 4 − 4 = 0

a. 1H, triplet, 4.5 ppm

b. 2H, doublet, 6.1 ppm



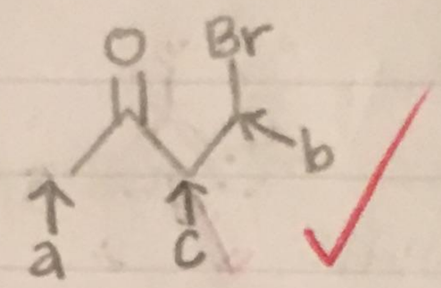
b. C_4H_7BrO

NI = 5 − 4 = 1

a. 3H, singlet, 2.2 ppm

b. 2H, triplet, 3.5 ppm

c. 2H, triplet, 4.5 ppm

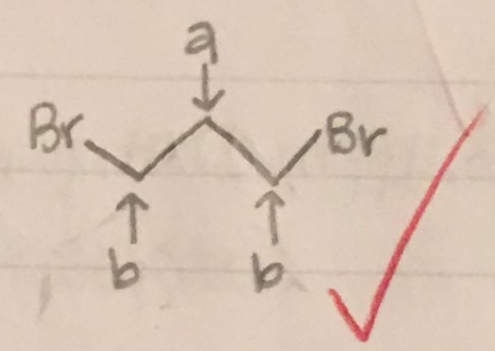


c. $C_3H_6Br_2$

NI = 4 − 4 = 0

a. 2H, quintet, 2.4 ppm

b. 4H, triplet, 3.5 ppm



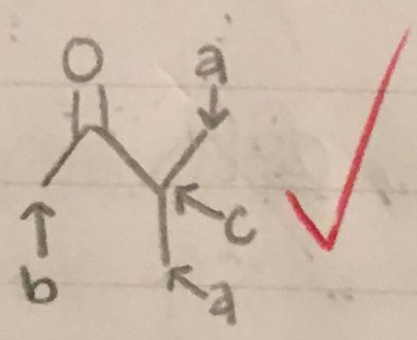
d. $C_5H_{10}O$

NI = 6 − 5 = 1

a. 6H, doublet, 1.1 ppm

b. 3H, singlet, 2.2 ppm

c. 1H, septet, 2.5 ppm

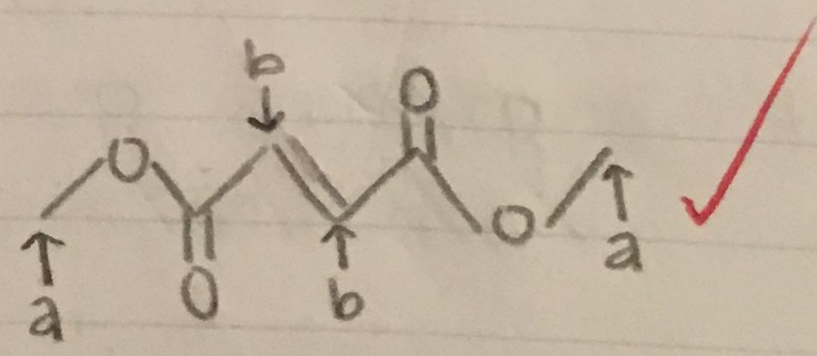


e. $C_6H_8O_4$

NI = 7 − 4 = 3

a. 6H, singlet, 3.9 ppm

b. 2H, singlet, 6.1 ppm



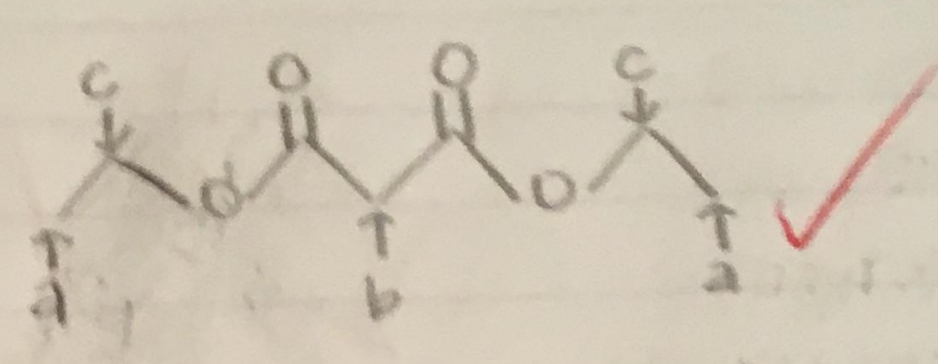
f. $C_7H_{12}O_4$

NI = 8 − 6 = 2

a. 6H, triplet, 1.3 ppm

b. 2H, singlet, 3.4 ppm

c. 4H, quartet, 4.2 ppm



g. $C_5H_{12}O$

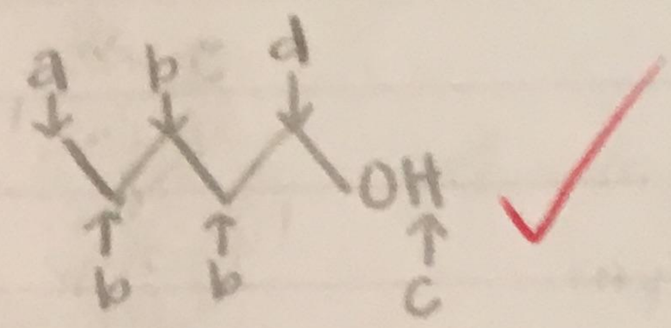
NI = 6 − 6 = 0

a. 3H, triplet, 1.0 ppm

b. 6H, multiplet, 1.2–1.8 ppm

c. 1H, broad singlet, 3.0 ppm

d. 2H, triplet, 3.8 ppm



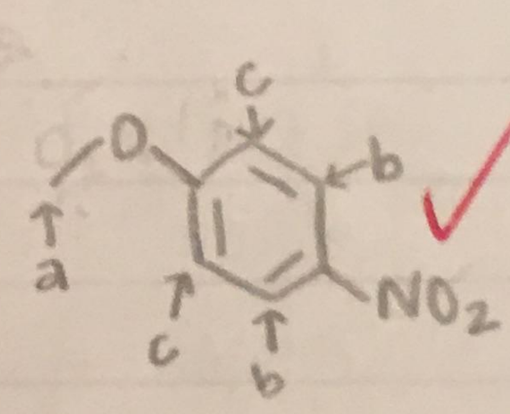
h. $C_7H_7NO_3$

NI = 8 − ½(7) + ½ = 5

a. 3H, singlet, 3.9 ppm

b. 2H, doublet, 6.9 ppm

c. 2H, doublet, 8.1 ppm



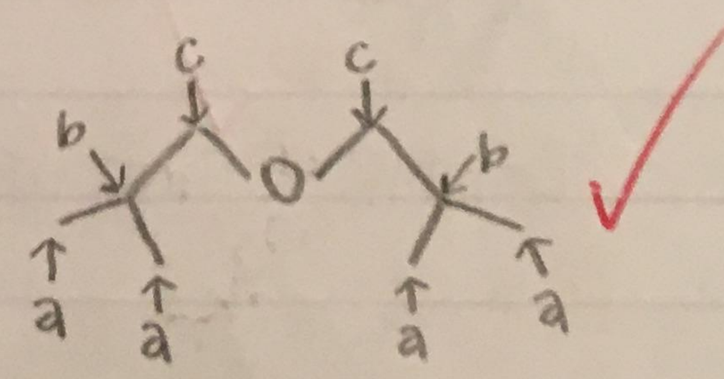
i. $C_8H_{18}O$

NI = 9 − 9 = 0

a. 6H, doublet, .89 ppm

b. 1H, multiplet, 1.87 ppm

c. 2H, doublet, 3.17 ppm

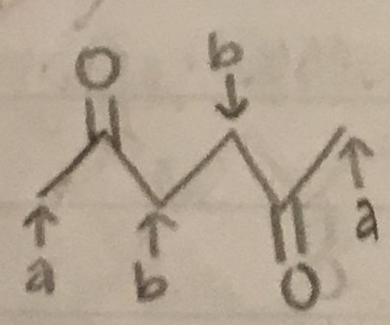


j. $C_6H_{10}O_2$

NI = 7 − 5 = 2

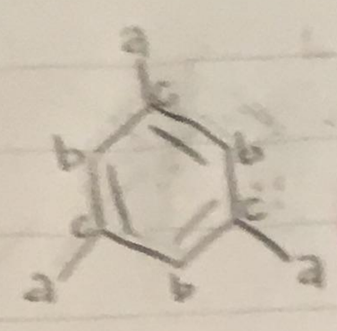
a. 3H, singlet, 2.19 ppm

b. 2H, singlet, 2.70 ppm



12. C_9H_{12}

NI = 10 − 6 = 4



a. 21.3 quartet

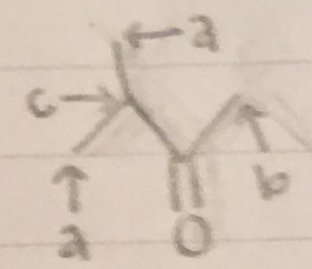
b. 127.2 doublet

c. 138.0 singlet

13.

C. $C_5H_{10}O$

NI = 6 − 5 = 1



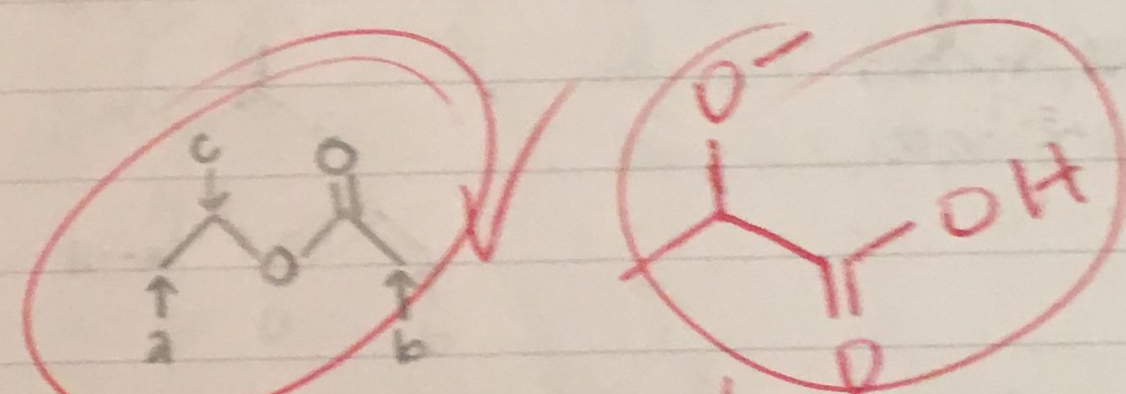
a. 6H, doublet, 1.2 ppm

b. 3H, singlet, 2.1 ppm

c. 1H, septet, 2.8 ppm

e. $C_4H_8O_2$

NI = 5 − 4 = 1



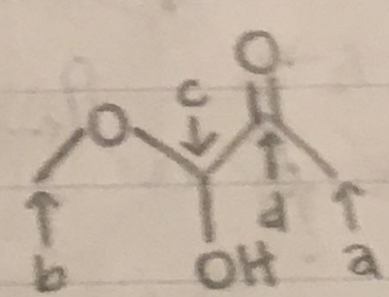
a. 3H, triplet, 1.23 ppm

b. 3H, singlet, 2.00 ppm

c. 2H, quartet, 4.02 ppm

g. $C_4H_8O_3$

NI = 5 − 4 = 1



a. 17.7 ppm, quartet

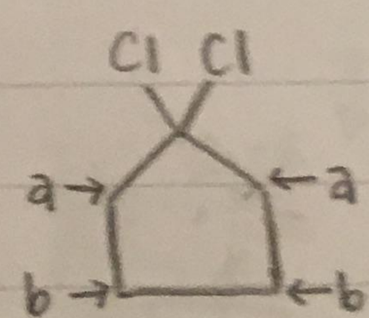
b. 65.4 ppm, quartet

c. 72.3 ppm, doublet

d. 210.8 ppm, singlet

i. $C_5H_8Cl_2$

NI = 6 − 5 = 1



a. 4H, triplet, 1.4 ppm

b. 4H, triplet, 1.2 ppm

K. $C_4H_{11}N$

$NI = 5 - \frac{1}{2}(11) + \frac{1}{2} = 0$

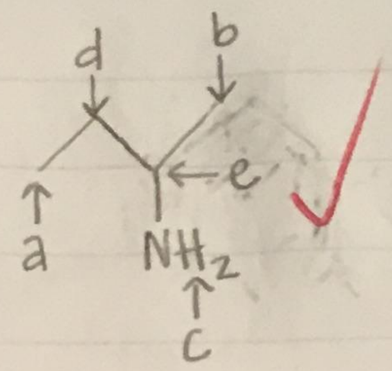
a. 3H, triplet, .90 ppm ✓

b. 3H, doublet, 1.07 ppm ✓

c. 2H, broad singlet, 1.14 ppm

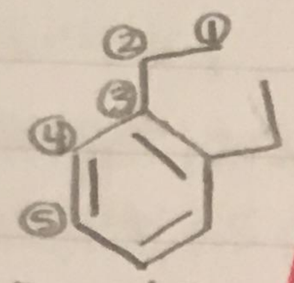
d. 2H, multiplet, 1.34 ppm ✓

e. 1H, multiplet, 2.79 ppm



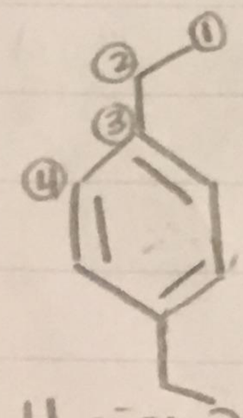
10.

a.



5 signals ✓

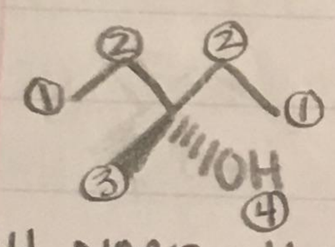
b.



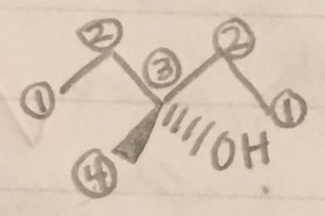
4 signals ✓

11.

a.

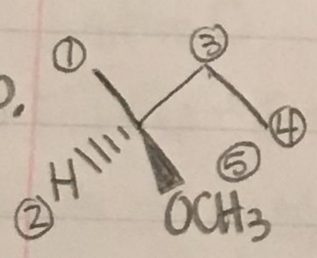


^{1}H-NMR = 4 signals ✓

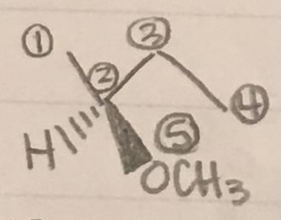


^{13}C-NMR = 4 signals ✓

b.

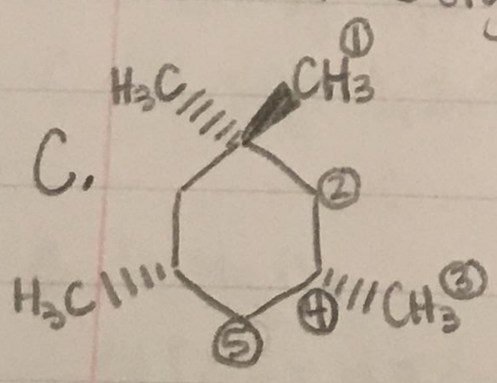


^{1}H-NMR = 5 signals ✓

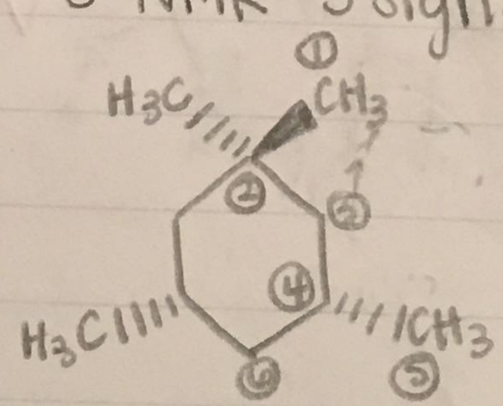


^{13}C-NMR = 5 signals ✓

c.

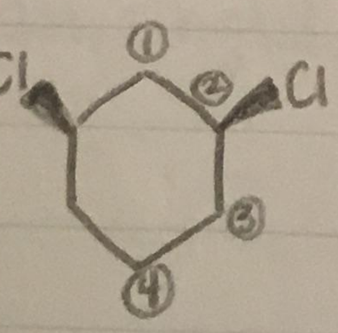


^{1}H-NMR = 5 signals ✓

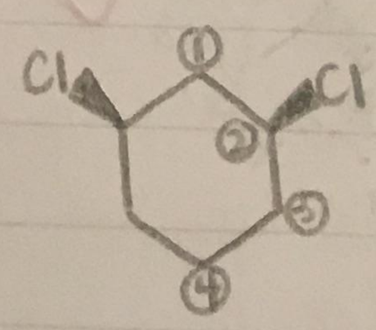


^{13}C-NMR = 6 signals ✓

d.



^{1}H-NMR = 4 signals ✓



^{13}C-NMR = 4 signals ✓

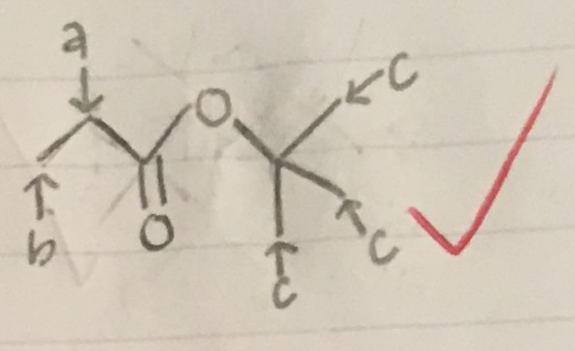
j. $C_7H_{14}O_2$

NI = 8 − 7 = 1

a. 2H, quartet, 2.3 ppm

b. 3H, triplet, 1.0 ppm

c. 9H, singlet, 0.9 ppm



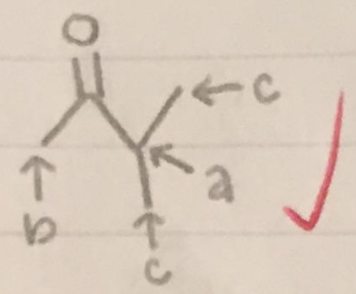
K. $C_5H_{10}O$

NI = 6 − 5 = 1

a. 1H, septet, 2.6 ppm

b. 3H, singlet, 2.1 ppm

c. 6H, doublet, 1.0 ppm



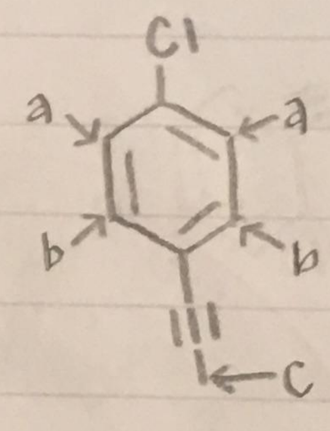
l. C_9H_7Cl

NI = 10 − 4 = 6

a. 2H, doublet, 7.8 ppm

b. 2H, doublet, 7.2 ppm

c. 3H, singlet, 2.1 ppm



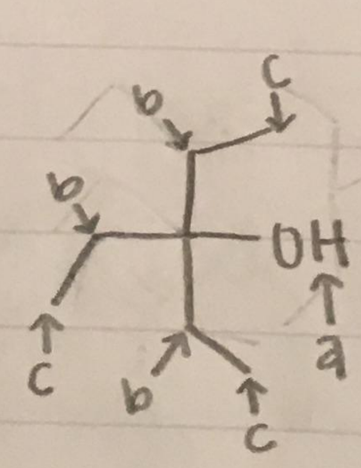
m. $C_7H_{16}O$

NI = 8 − 8 = 0

a. 1H, broad singlet, 2.9 ppm

b. 6H, quartet, 1.2 ppm

c. 9H, triplet, 0.9 ppm

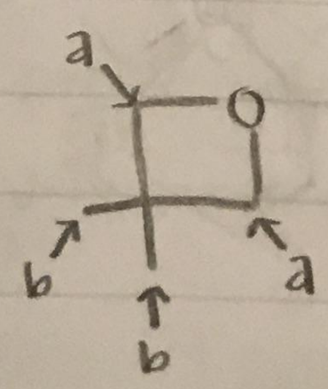


n. $C_5H_{10}O$

NI = 6 − 5 = 1

a. 4H, singlet, 3.5 ppm

b. 6H, singlet, 0.9 ppm



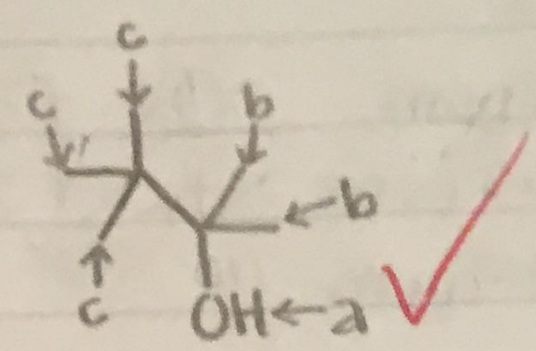
0. $C_7H_{16}O$

NI = 8 − 8 = 0

a. 1H, broad singlet, 2.8ppm

b. 6H, singlet, 1.0 ppm

c. 9H, singlet, 0.9ppm



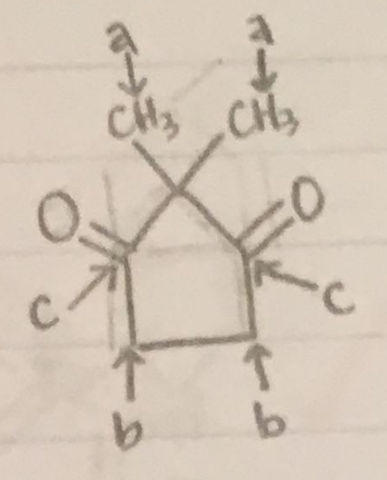
a. $C_7H_{10}O_2$

NI = 8 − 5 = 3

a. 3H, singlet, 1.16 ppm

b. 2H, singlet, 2.21 ppm

c. 216.25 singlet



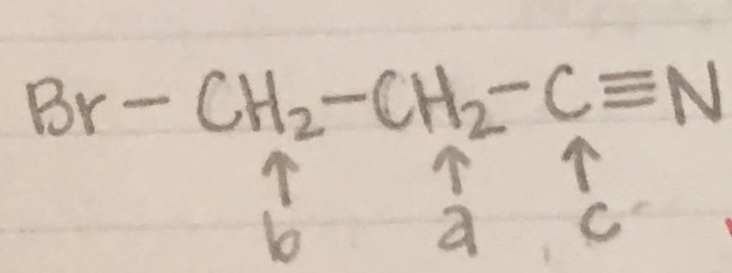
b. C_3H_4BrN

NI = 4 − ½(5) + ½ = 2

a. 2H, triplet, 2.98 ppm

b. 2H, triplet, 3.53 ppm

c. 118.08, singlet



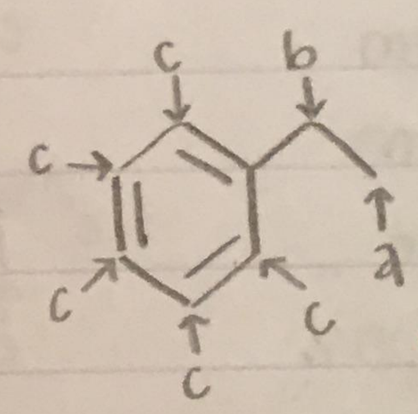
d. C_8H_{10}

NI = 9 − 5 = 4

a. 3H, triplet, 1.20ppm

b. 2H, quartet, 2.60ppm

c. 5H, multiplet, 7.12 ppm



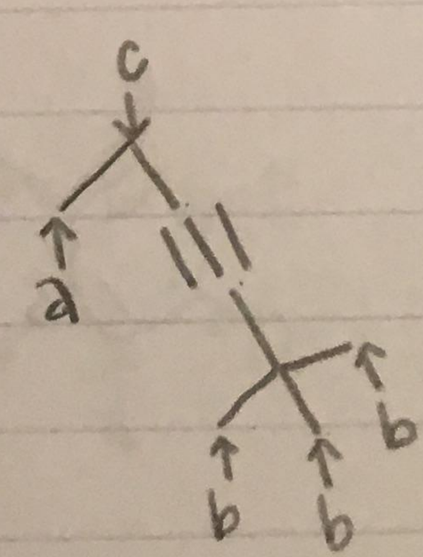
f. C_8H_{14}

NI = 9 − 7 = 2

a. 3H, triplet, 0.9 ppm

b. 9H, singlet, 1.0 ppm

c. 2H, quartet, 2.3ppm



d. C_4H_9Cl

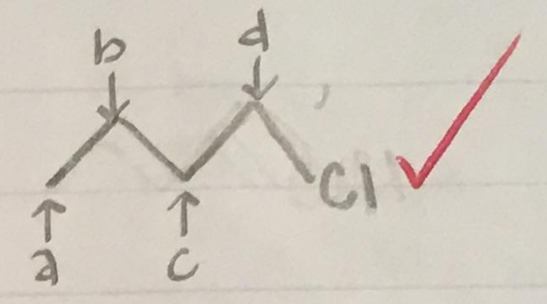
a. NI = 5 − 5 = 0

a. 3H, triplet, 0.9 ppm

b. 2H, multiplet, 1.5 ppm

c. 2H, quintet, 1.7 ppm

d. 2H, triplet, 3.5 ppm



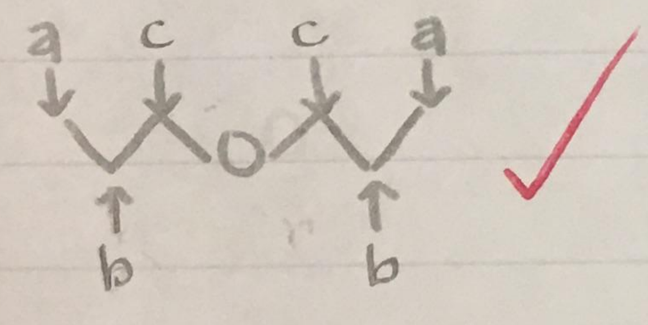
e. $C_6H_{14}O$

NI = 7 − 7 = 0

a. 6H, triplet, 0.9 ppm

b. 4H, multiplet, 1.6 ppm

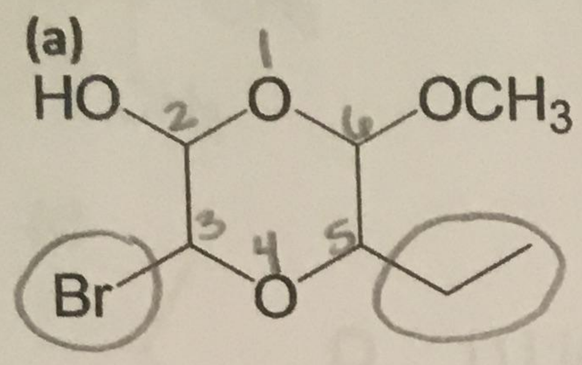
c. 4H, triplet, 3.4 ppm



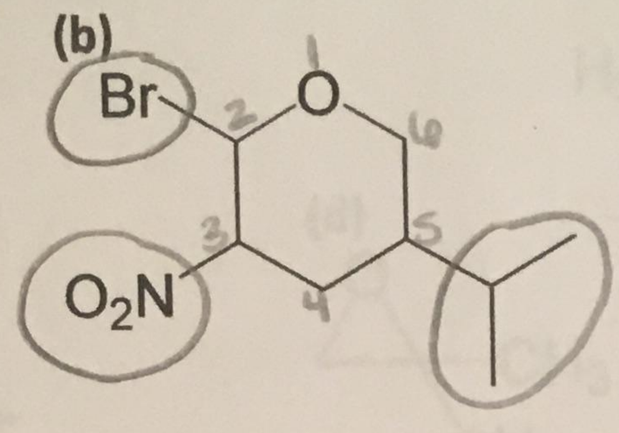
WORKSHEET IV

1. Name the following compounds. Indicate the steochemistry (if any) and label the hydroxyl groups (if any) as primary, secondary or tertiary.

(a)



(b)



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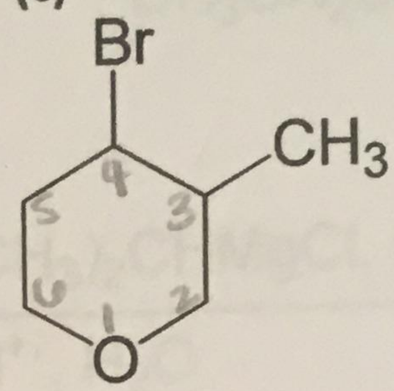

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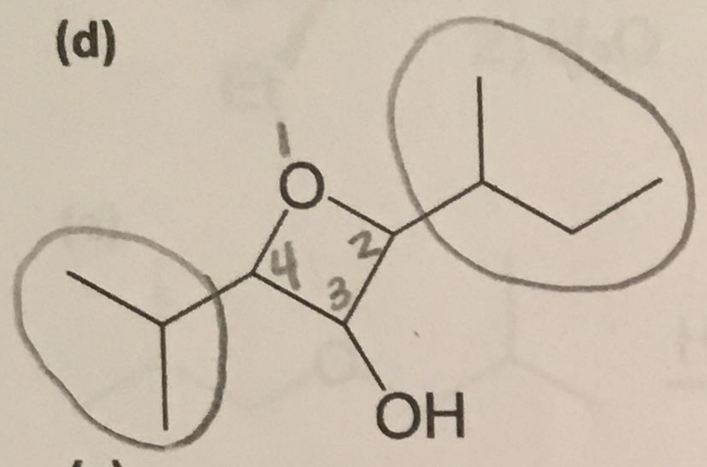

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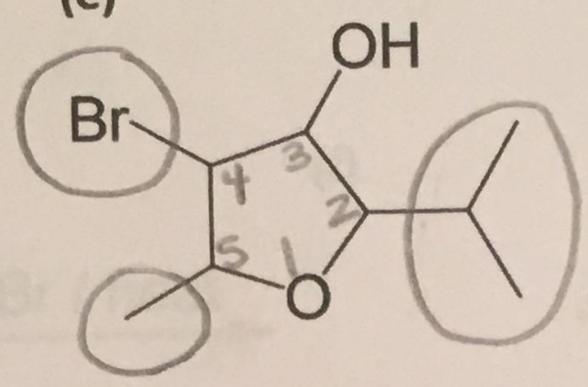

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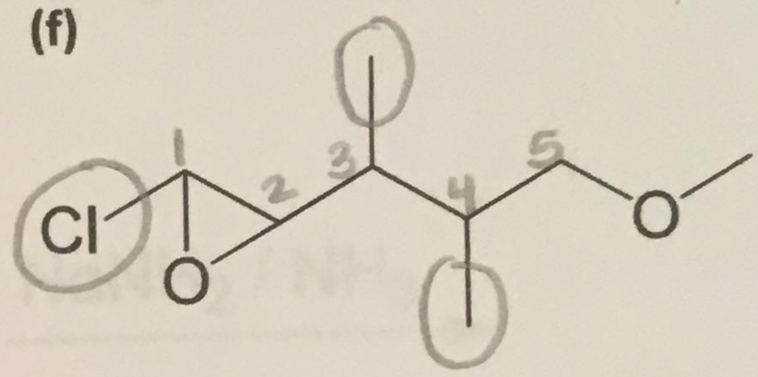

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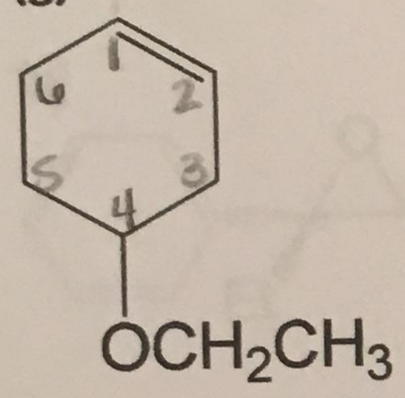
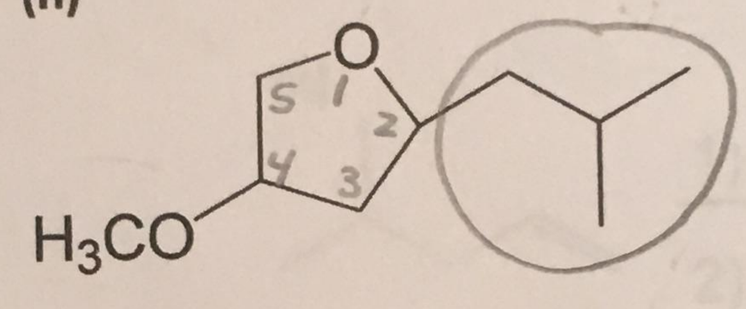


(h)



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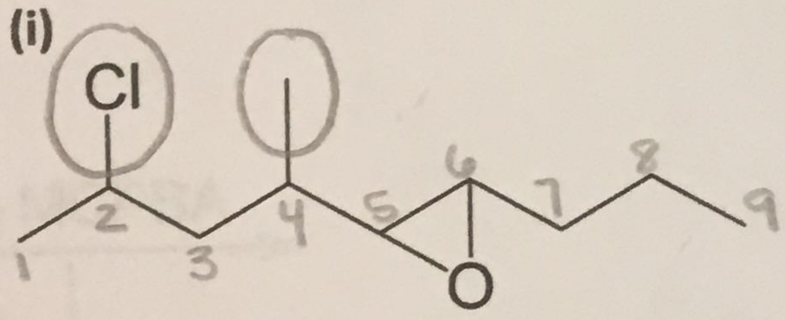

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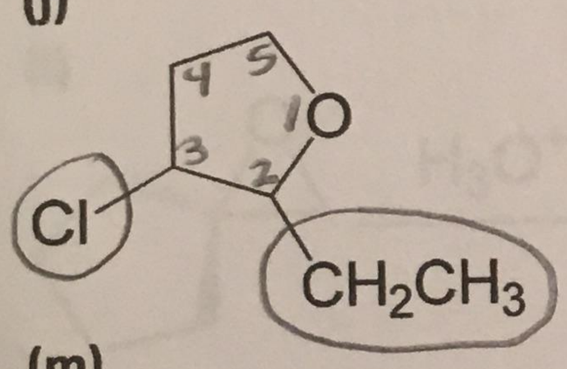

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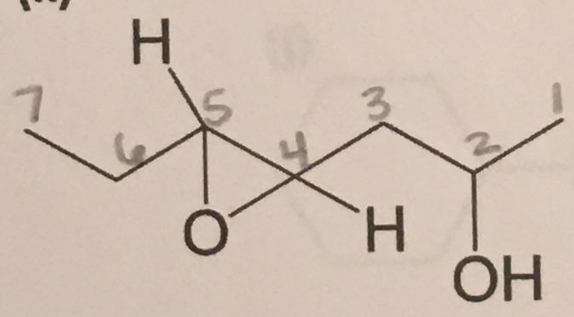

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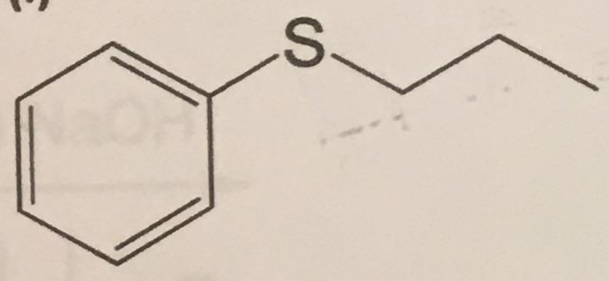

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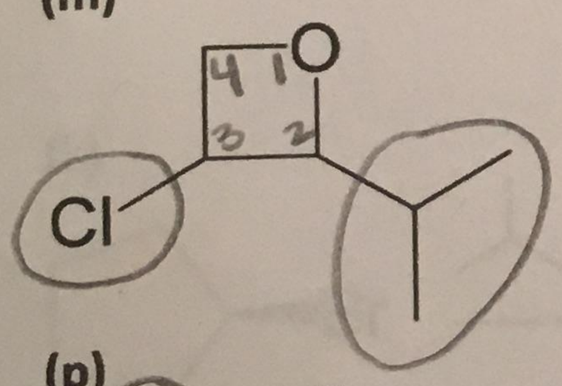

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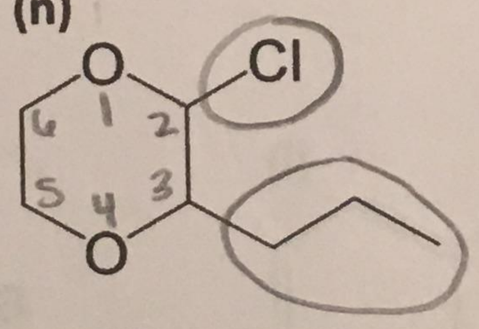

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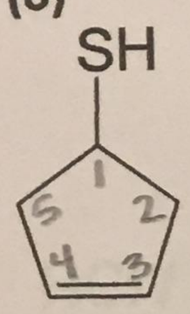

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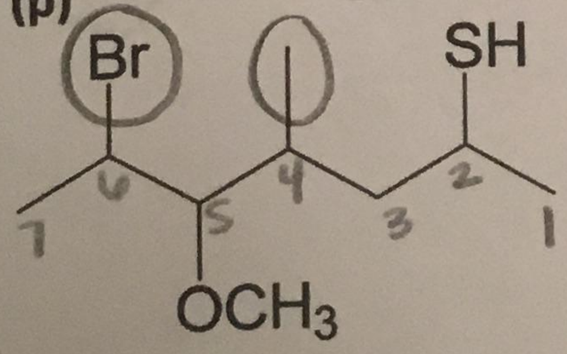

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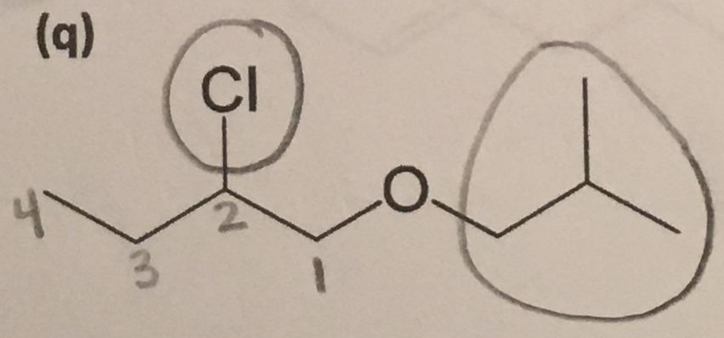

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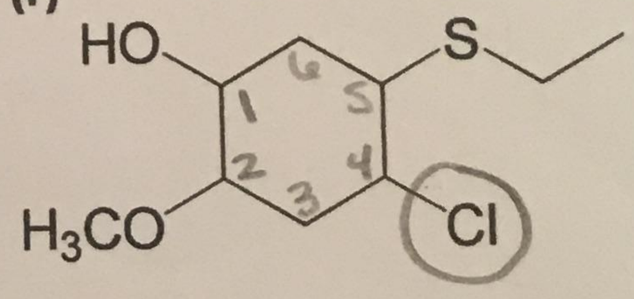

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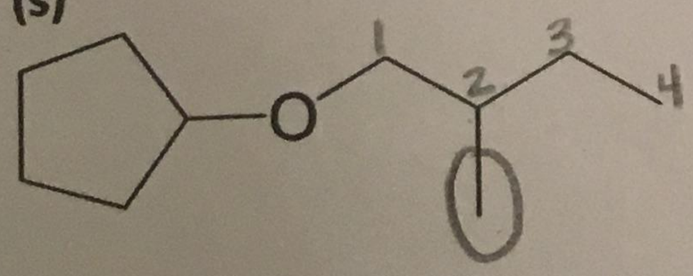

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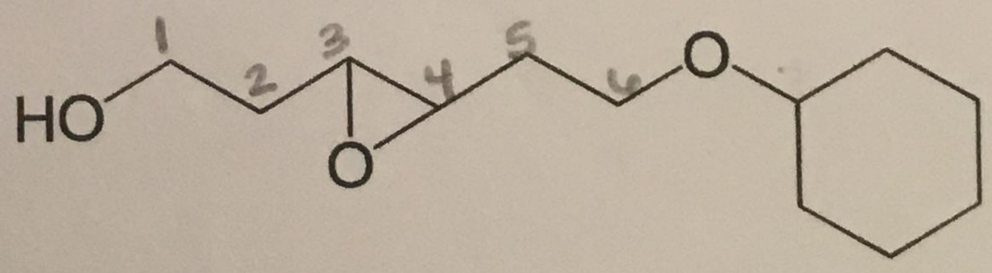


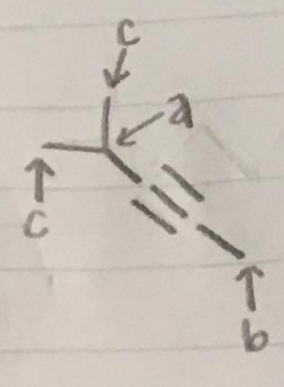
h. C_6H_{10}

NI = 7 − 5 = 2

a. 1H, septet, 2.0 ppm

b. 3H, singlet, 1.8 ppm

c. 6H, doublet, 0.9 ppm



14.

a. $C_{10}H_{12}O_2$

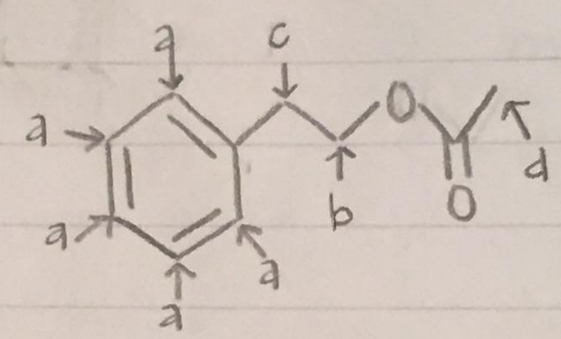
NI = 11 − 6 = 5

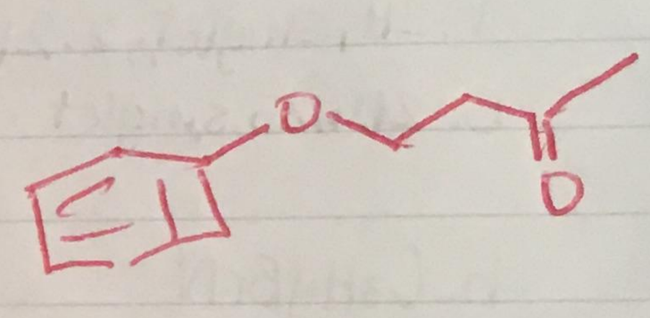
a. 5H, multiplet, 7.2 ppm

b. 2H, triplet, 4.3 ppm

c. 2H, triplet, 2.9 ppm

d. 3H, singlet, 2 ppm





b. $C_{10}H_{12}O$

NI = 11 − 6 = 5

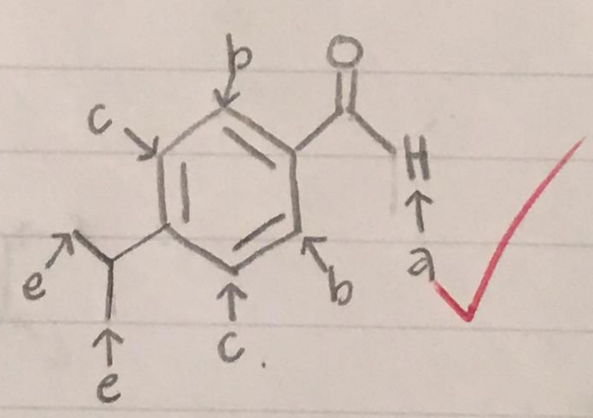
a. 1H, singlet, 9.9 ppm

b. 2H, doublet, 7.8 ppm

c. 2H, doublet, 7.3 ppm

d. 1H, septet, 3.1 ppm

e. 6H, doublet, 1.3 ppm



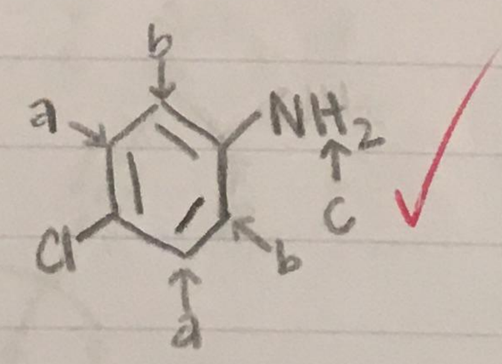
c. C_6H_6NCl

NI = 7 − ½(7) + ½ = 4

a. 2H, doublet, 7.1 ppm

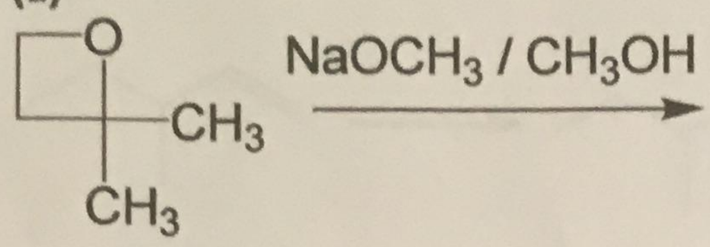
b. 2H, doublet, 6.6 ppm

c. 2H, singlet, 3.7 ppm

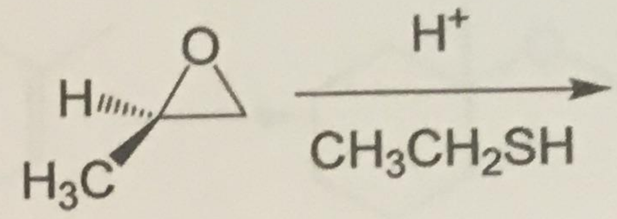


. Give the major product(s) of each of the following reaction (after workup with aqueous acid)

(a)



(b)



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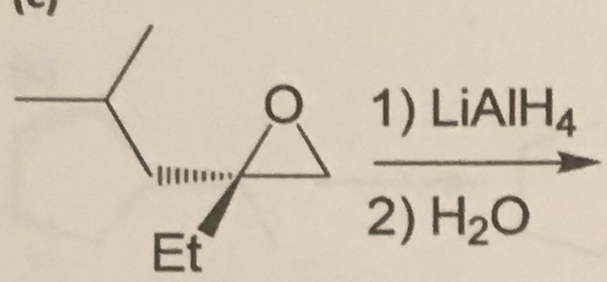
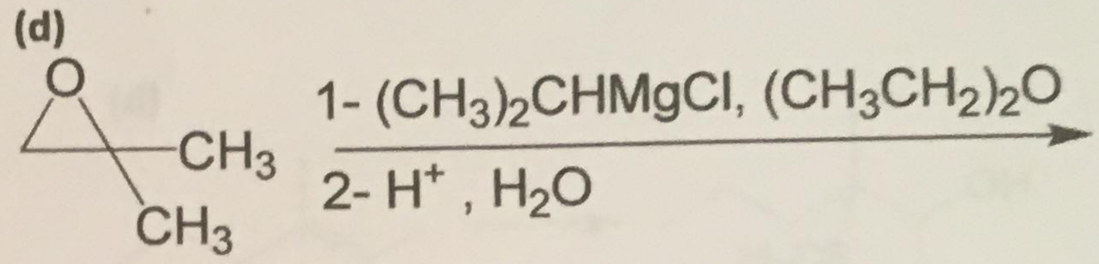


(d)



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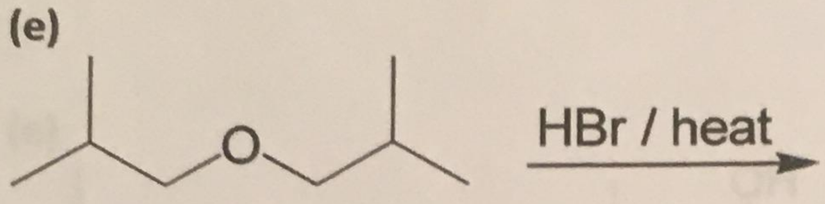

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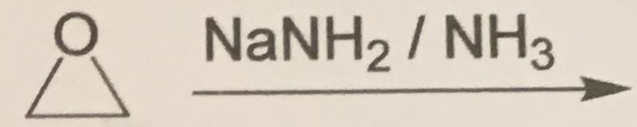

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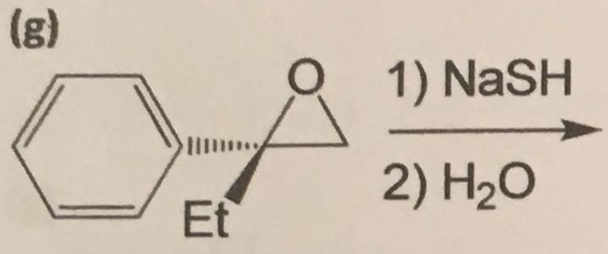

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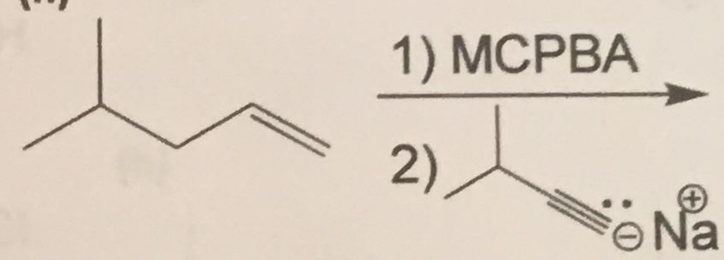

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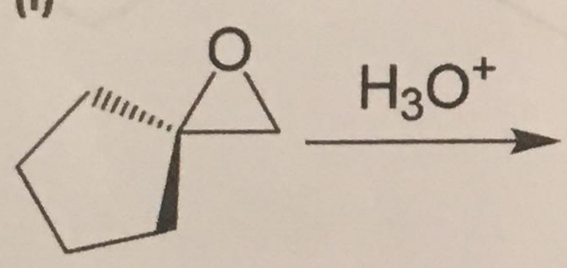

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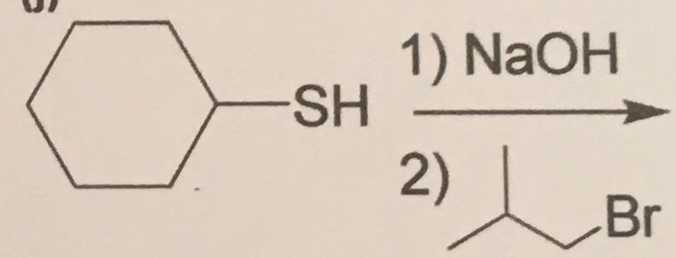

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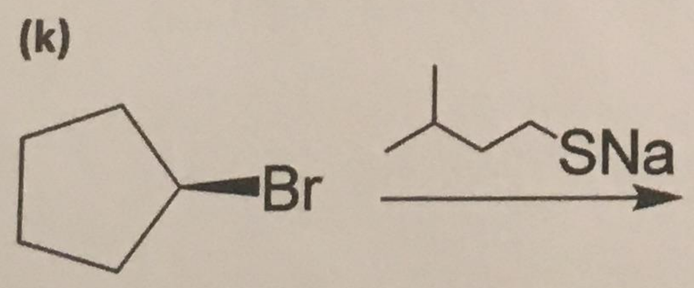

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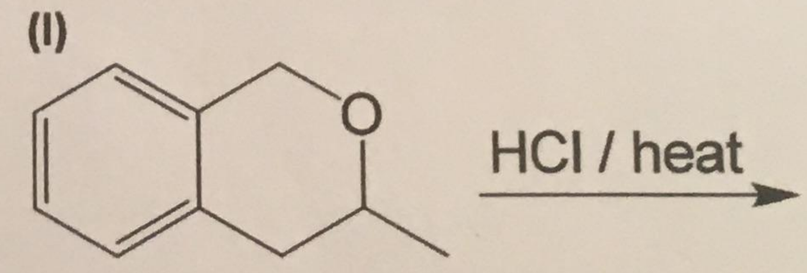


Worksheet IV

Part 1:

a. 3-bromo-5-ethyl-6methoxy-1,4-dioxan-2-ol

b. 2-bromo-5-isopropyl-3-nitrooxane

c. 4-bromo-3-methyloxane

d. 2-sec-butyl-4-isopropyloxetan-3-ol

e. 4-bromo-2-isopropyl-5-methyloxolan-3-ol

f. 1-chloro-1,2-epoxy-5-methoxy-3,4-dimethylpentane

g. (1Z)4-ethoxycyclohex-1-ene

h. 2-isobutyl-4-methoxyoxolane

i. 2-chloro-5,6-epoxy-4-methylnonane

j. 3-chloro-2-ethyloxolane

k. 4,5-epoxyheptan-2-ol

l. 1-propylthiobenzene

m. 3-chloro-2-isopropyloxetane

n. 2-chloro-3-propyl-1,4-dioxane

o. (3Z)cyclopent-3-ene-1-thiol

p. 6-bromo-5-methoxy-4-methylheptane-2-thiol

q. 2-chloro-1-isobutoxybutane

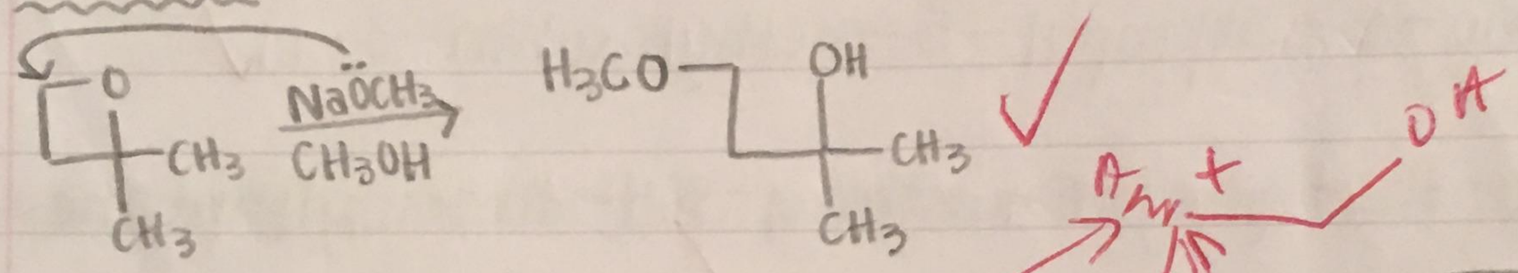
r. 4-chloro-5-ethylthio-2-methoxycyclohexan-1-ol

s. 1-cyclopentoxy-2-methylbutane

t. 6-cyclohexoxy-3,4-epoxyhexan-1-ol

Part 2:

a.



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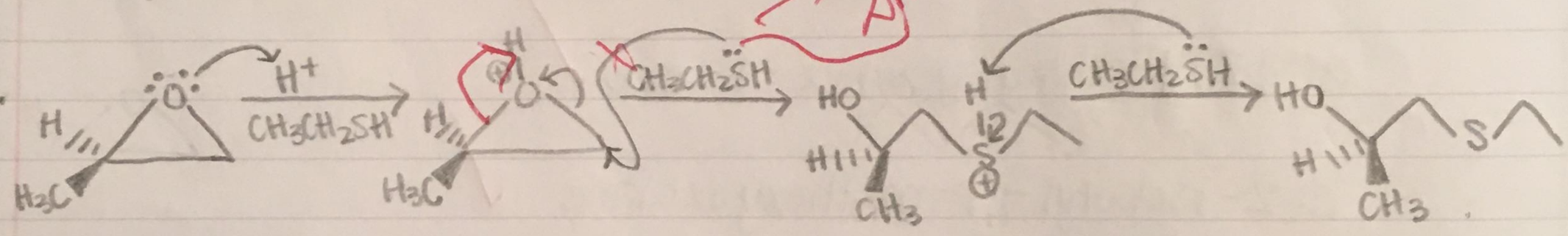

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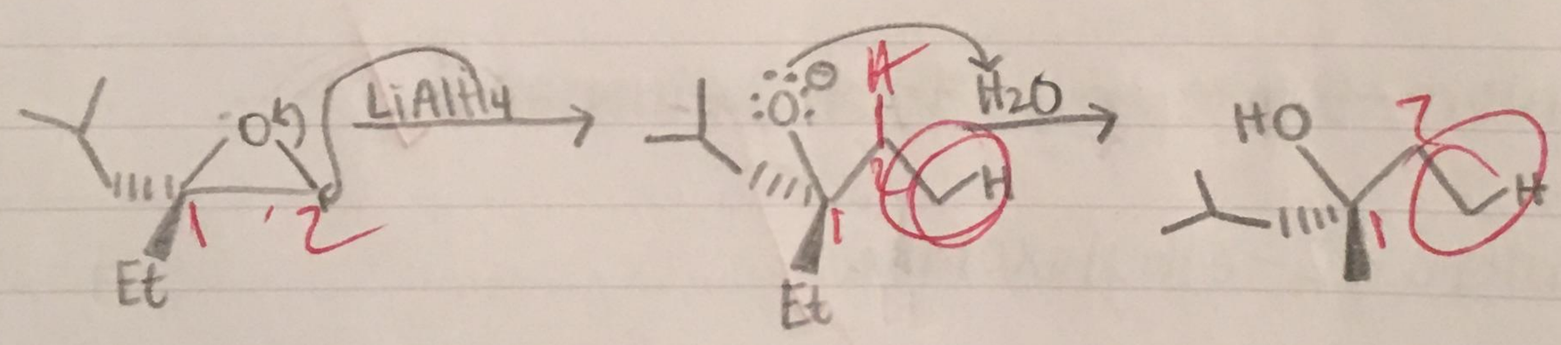
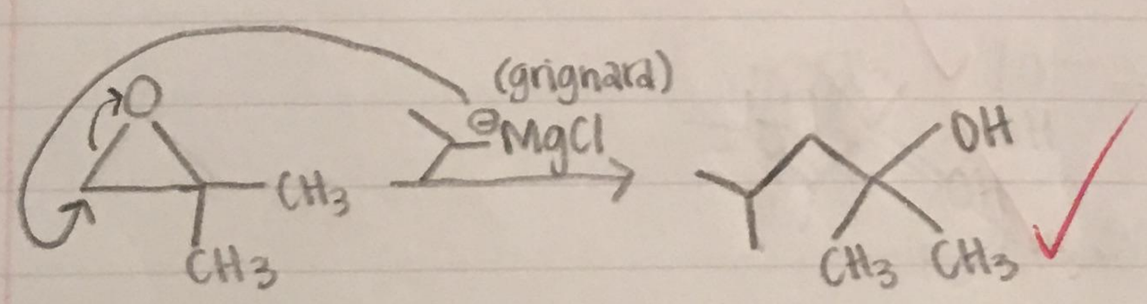


d.



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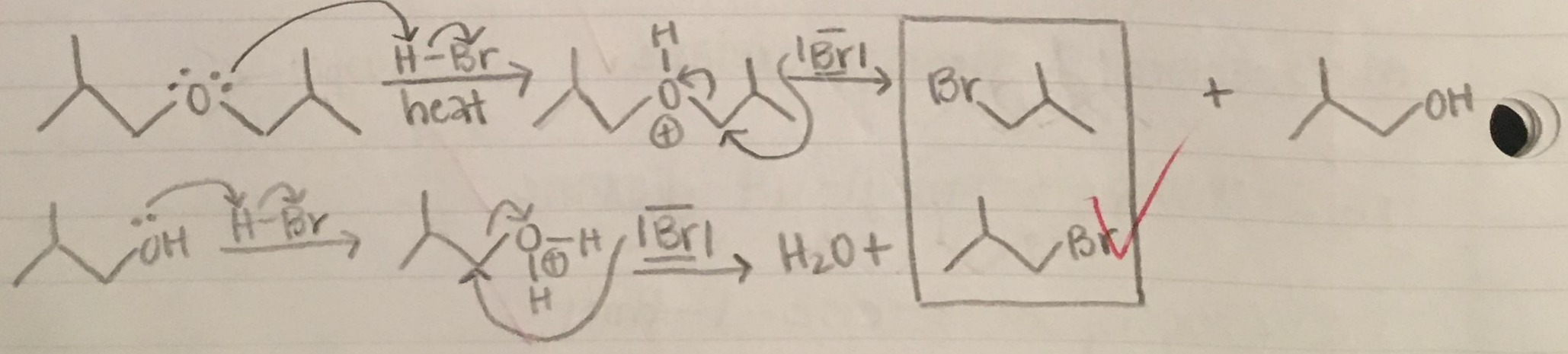
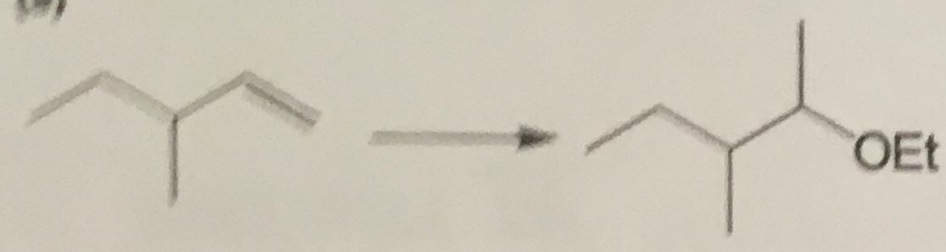
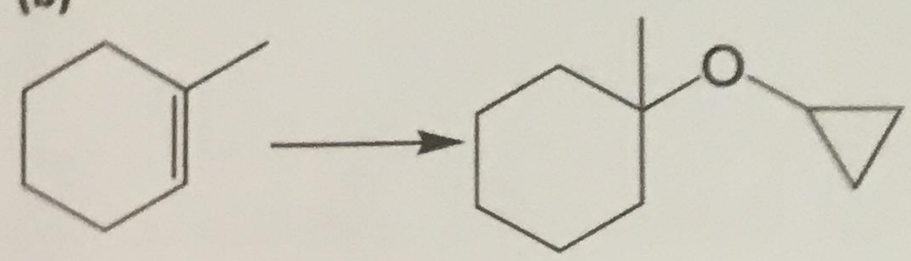


How would you prepare the following compounds from the given starting materials?

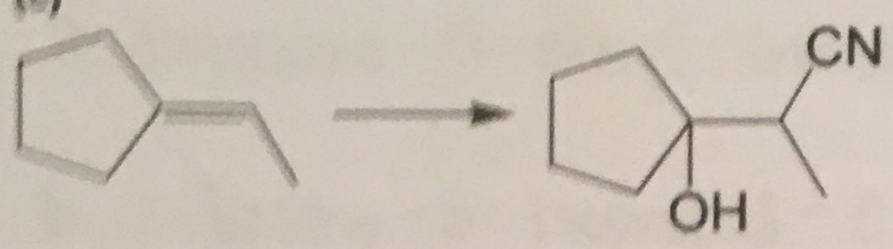
(a)



(b)



(c)



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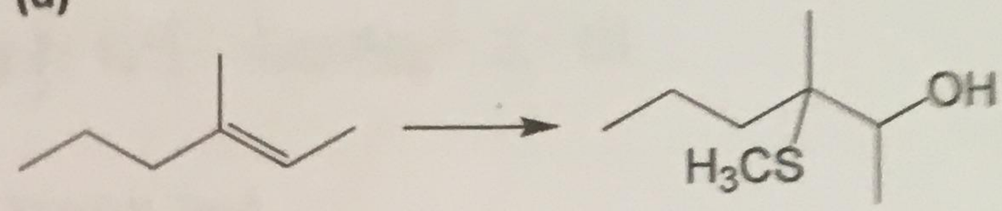

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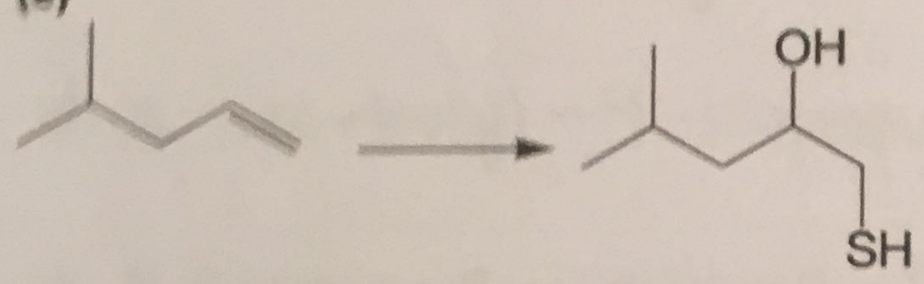

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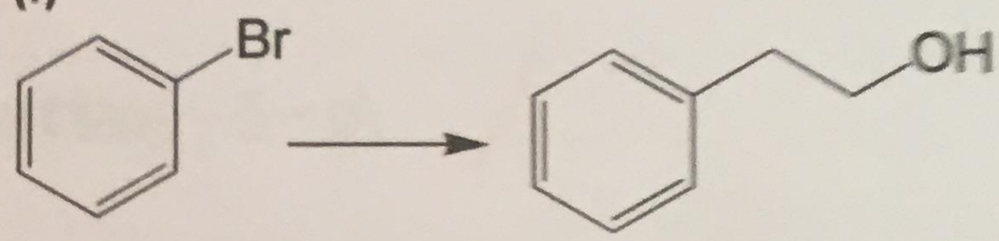
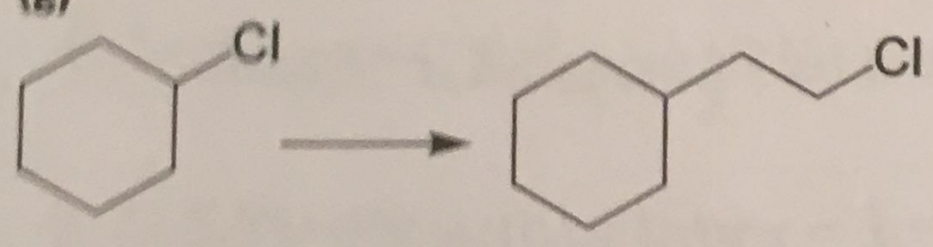


(g)



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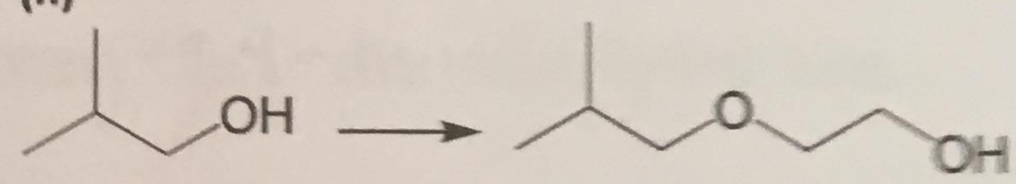
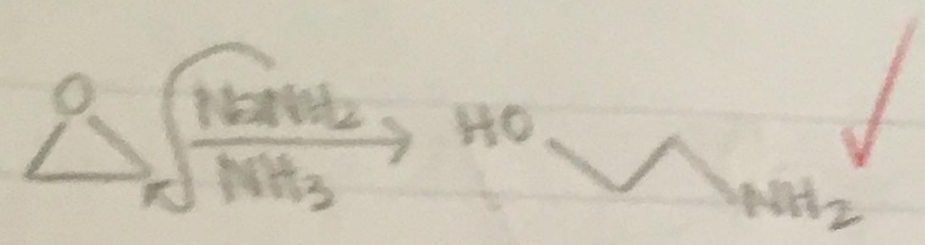
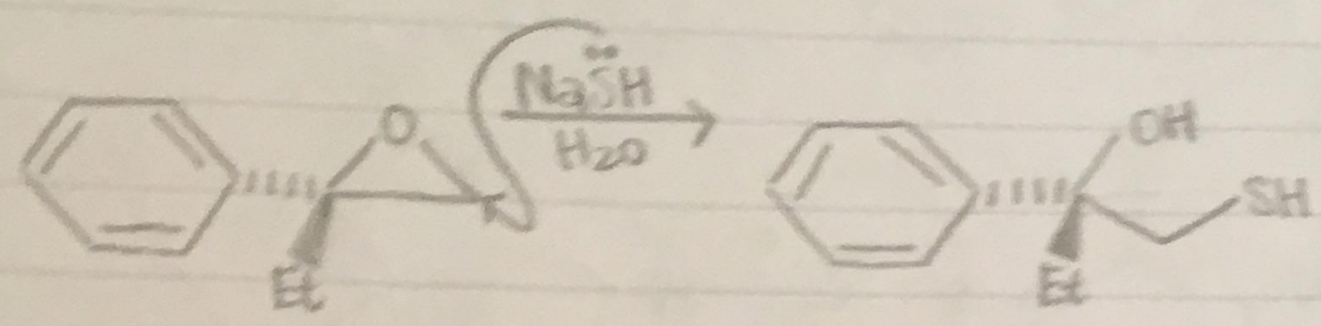
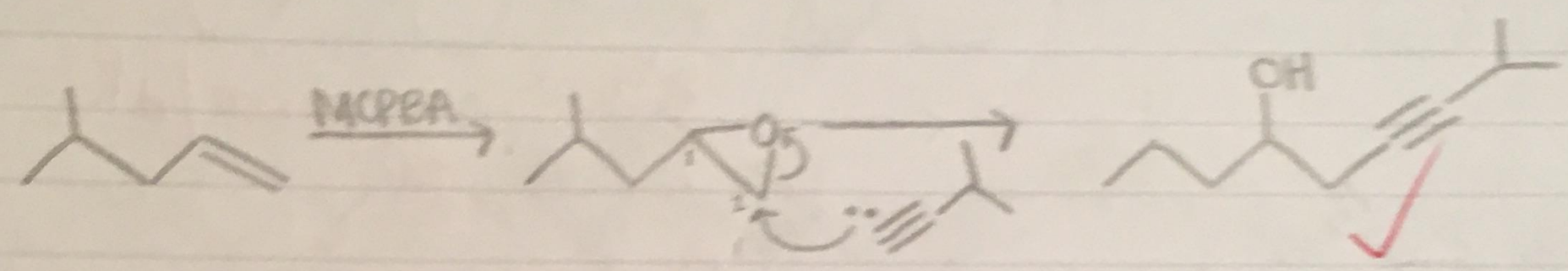
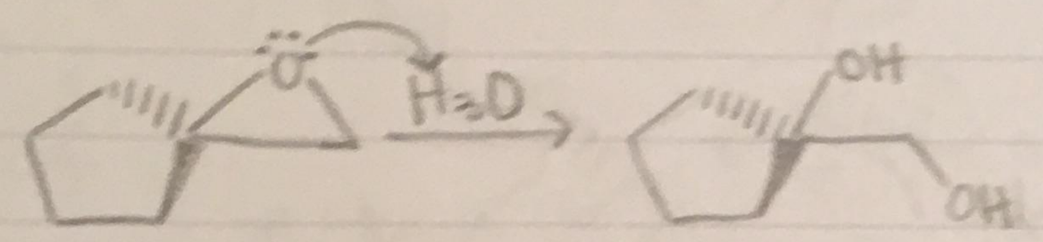
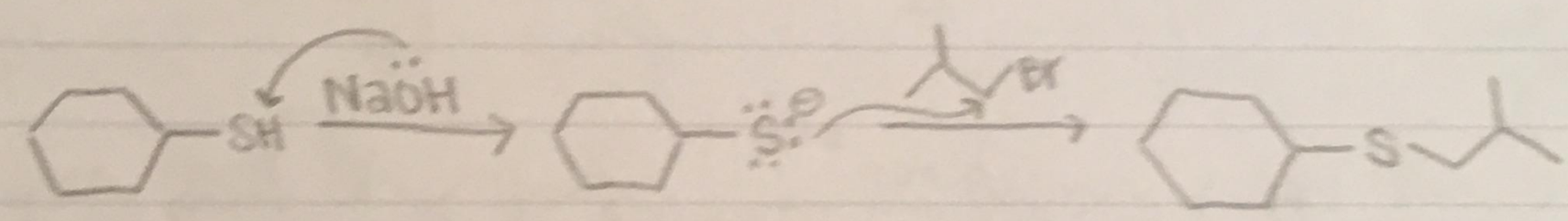


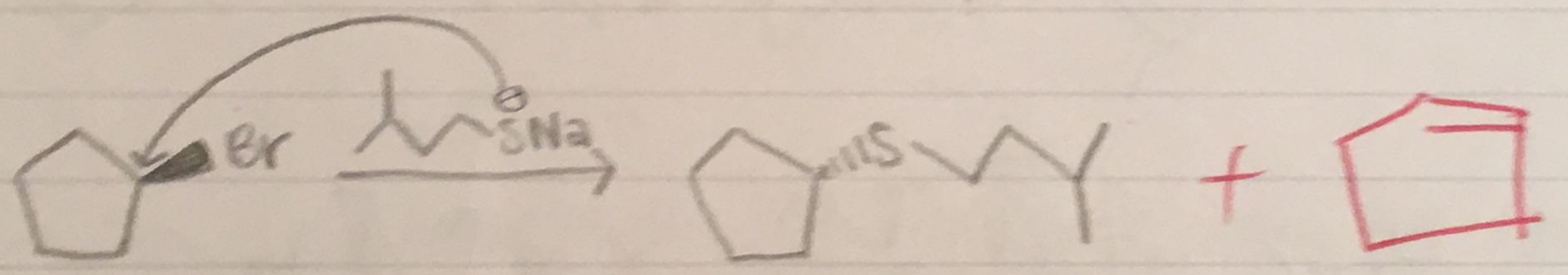
f. 

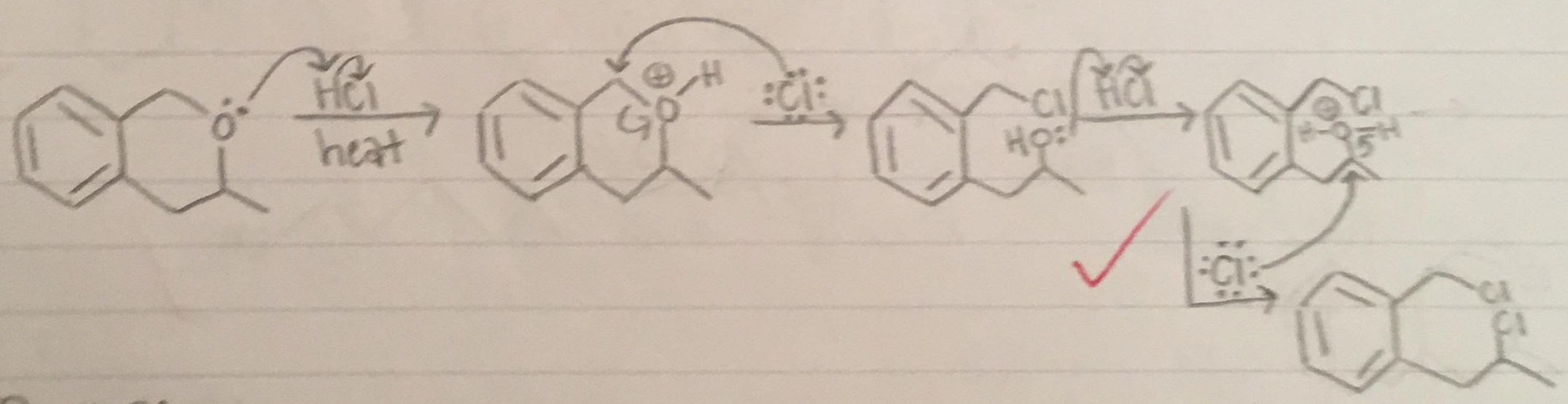
g. 

h. 

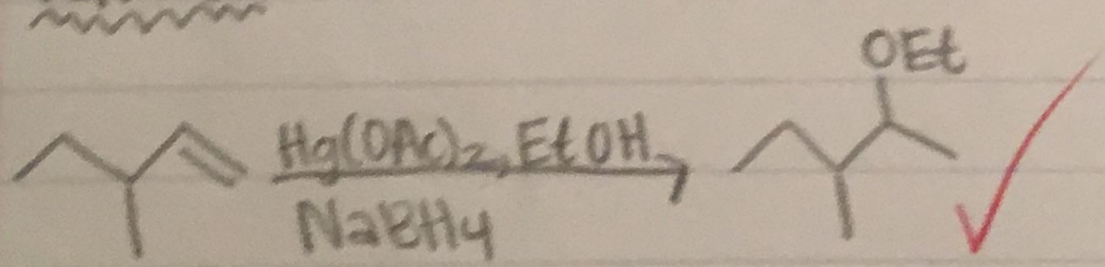
i. 

j. 

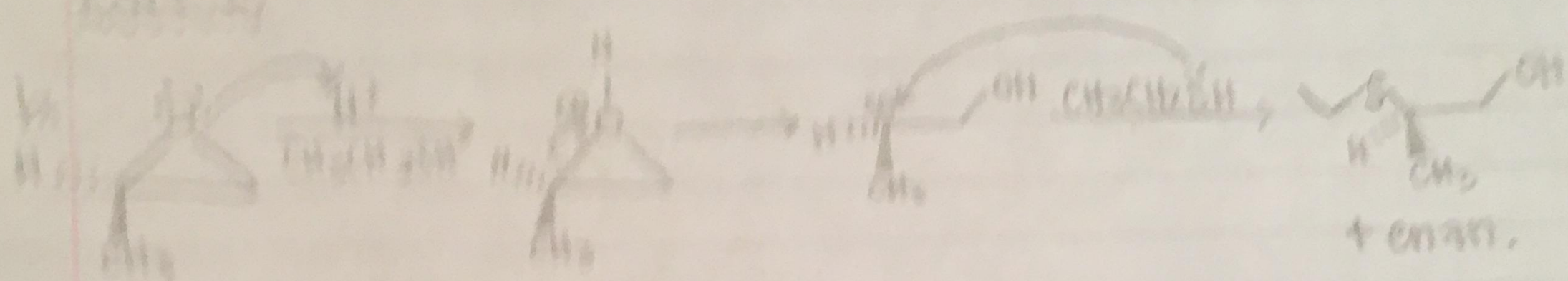
k. 

l. 

Part 3:

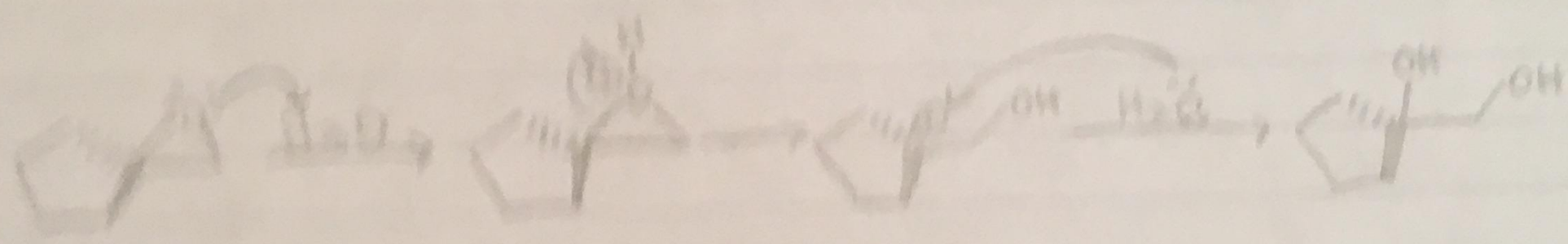
a. 

EXAM 2)



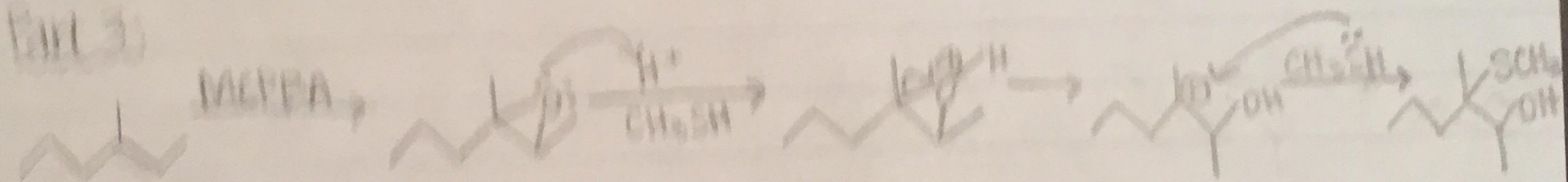
+ enan.

1.)



EXAM 3)

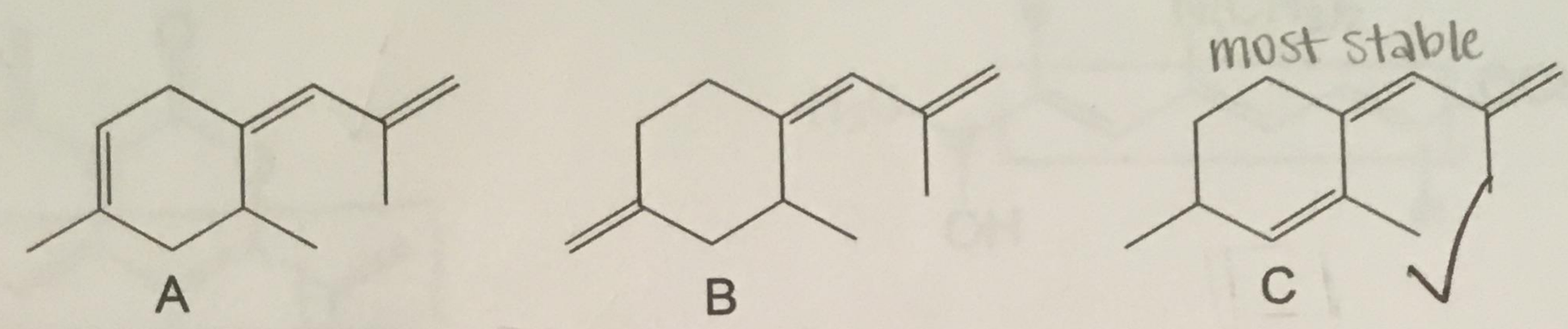
1.)



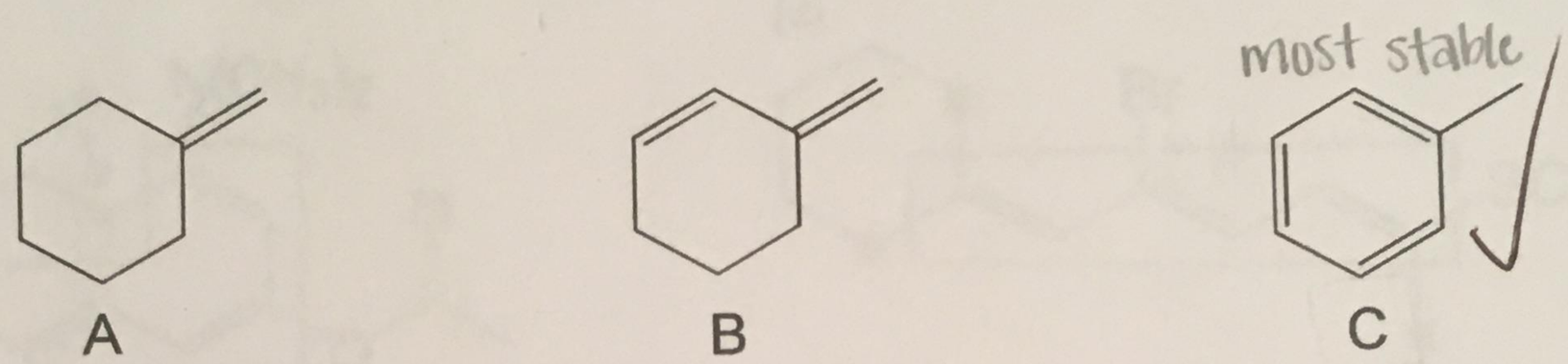
WORKSHEET V

1. In each set of compounds, identify the most stable

(a)

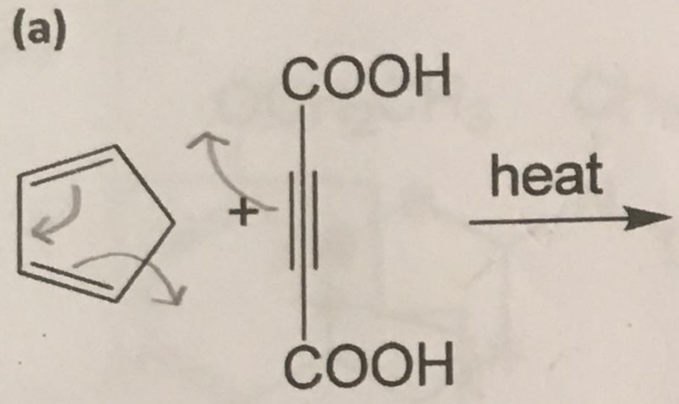


(b)

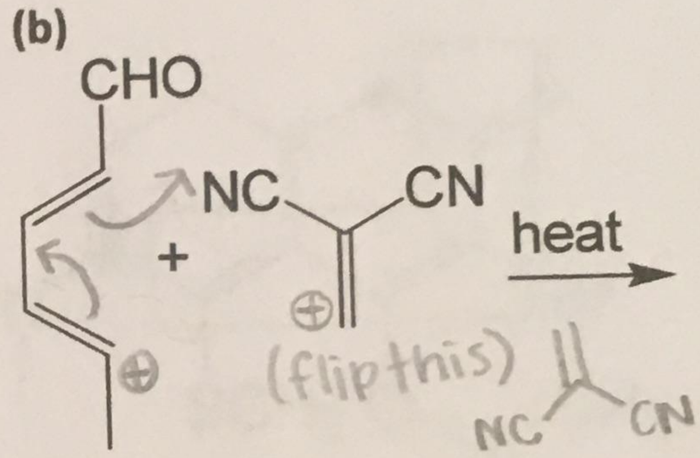


2. What is the product(s) of the following reactions?

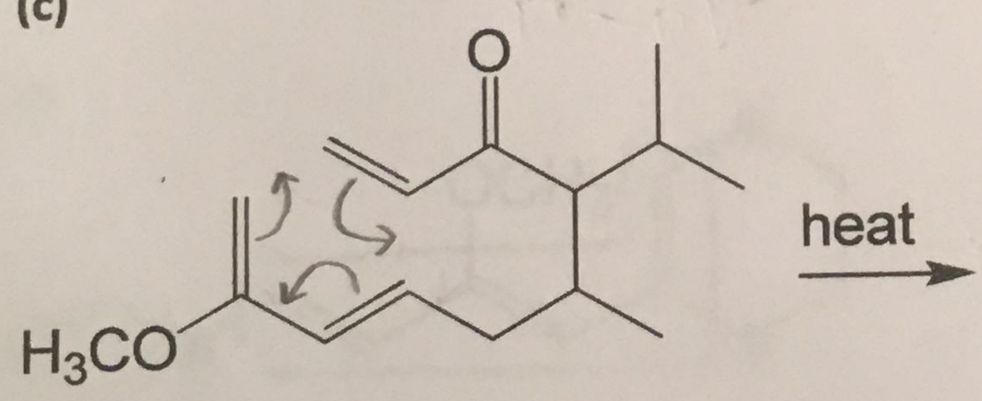
(a)



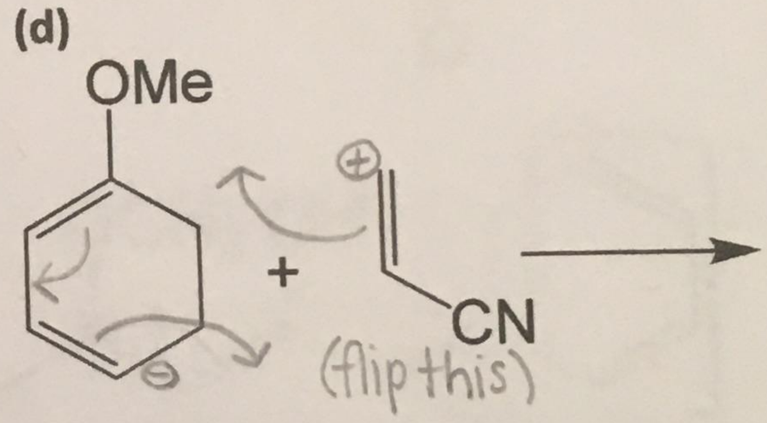
(b)



(c)



(d)



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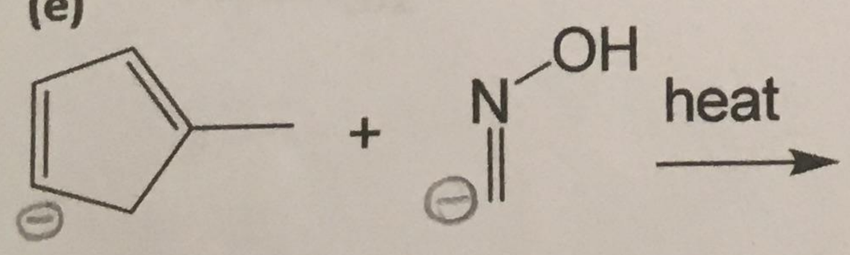

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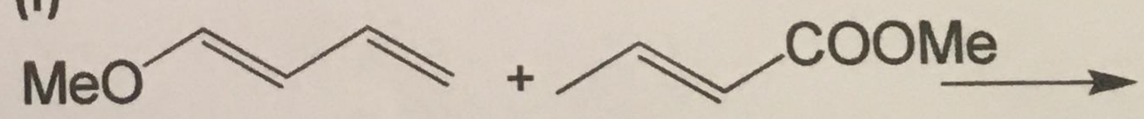

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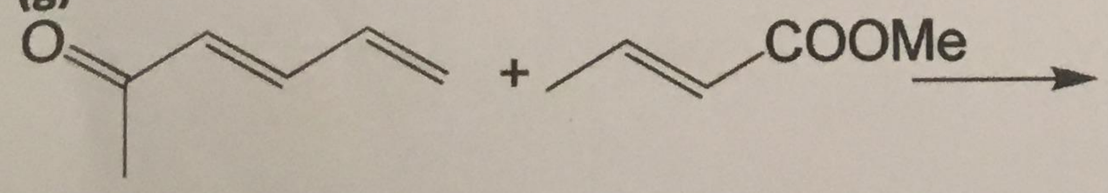

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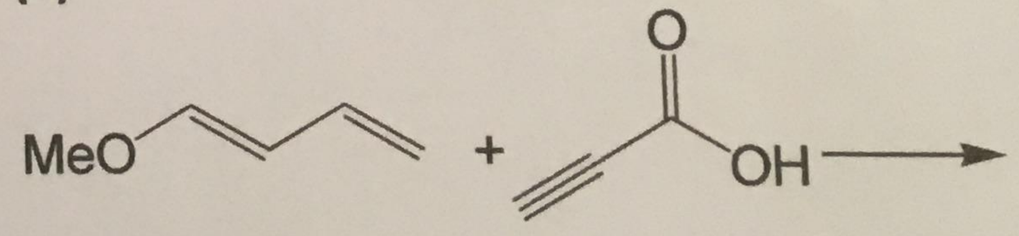
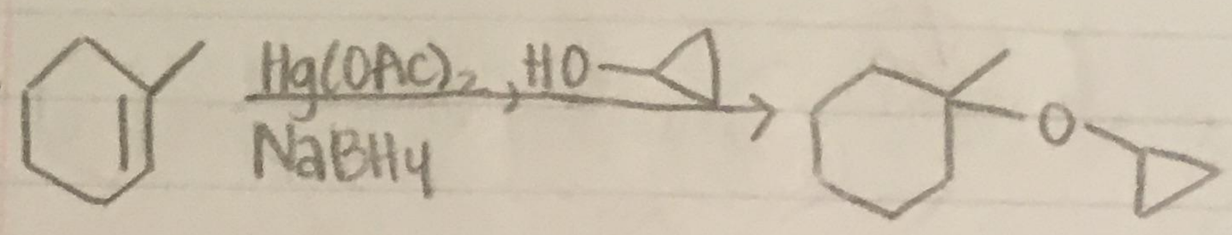
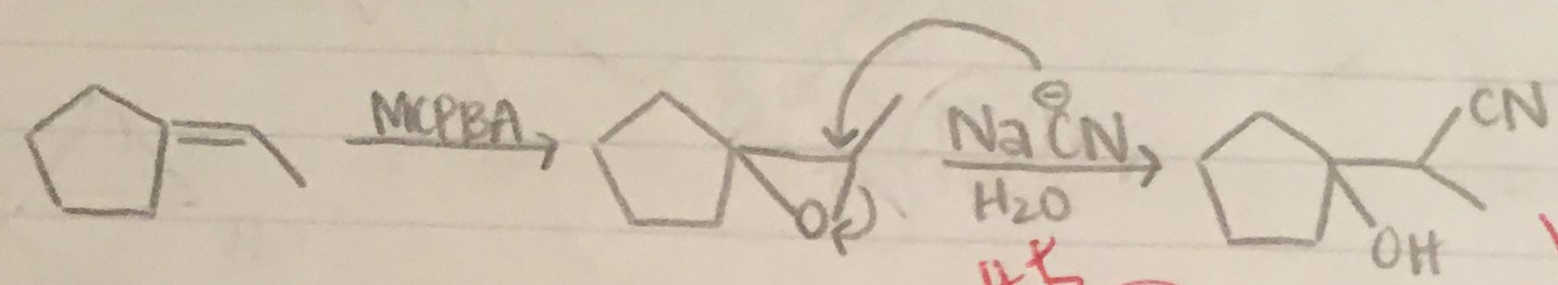
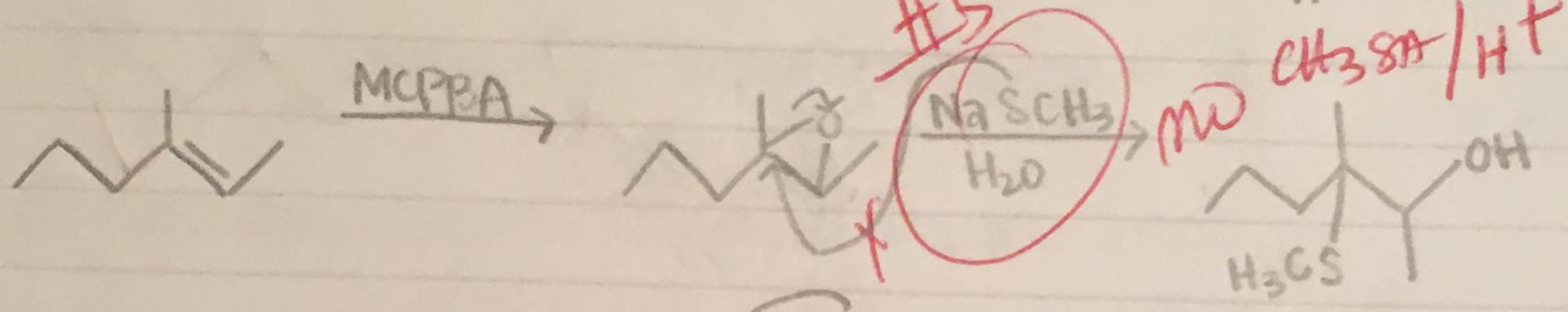
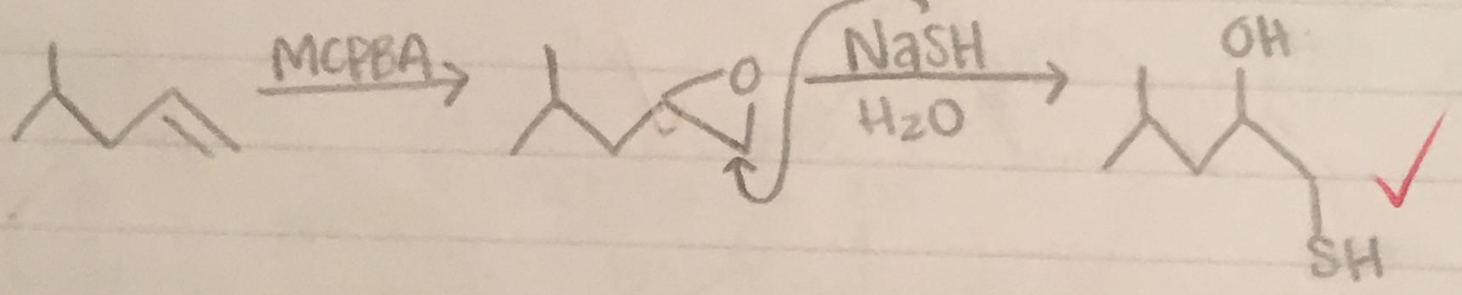
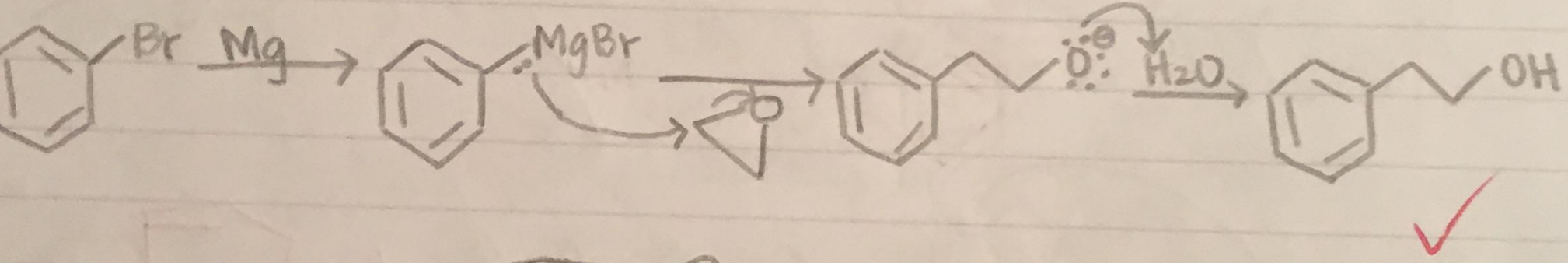


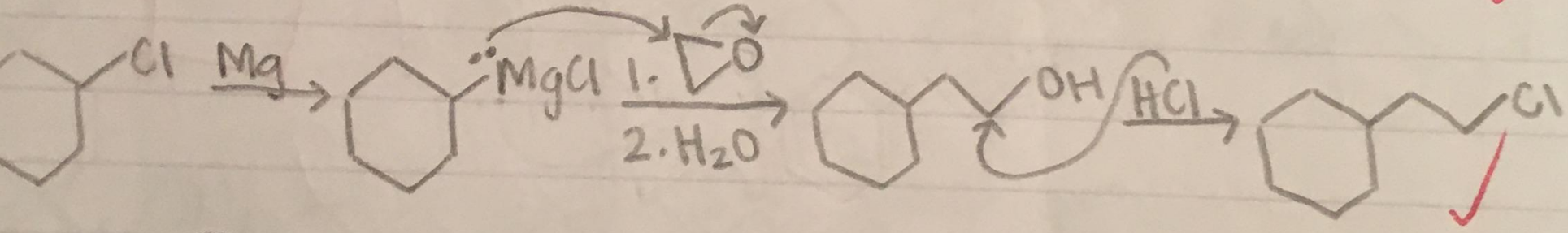
b. 
Hg(OAc)2, HO
NaBH4
O

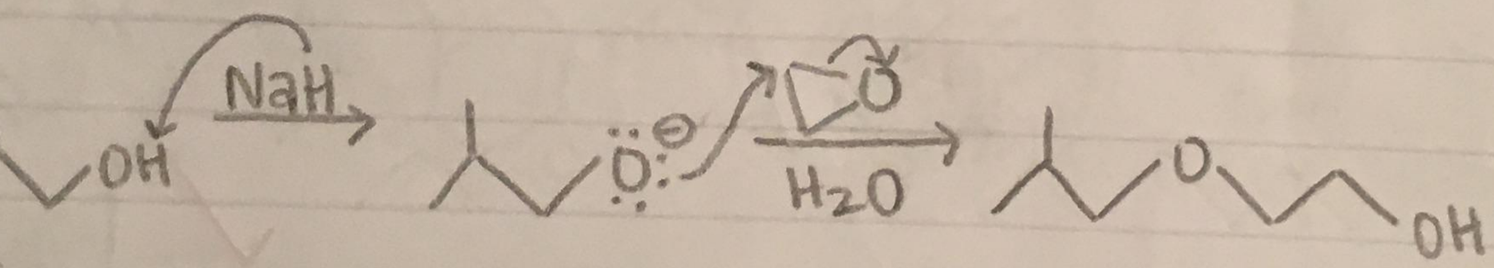
c. 
MCPBA
NaCN
H2O
CN
OH

d. 
MCPBA
NaSCH3
H2O
CH3SH/H+
OH
H3CS

e. 
MCPBA
NaSH
H2O
OH
SH

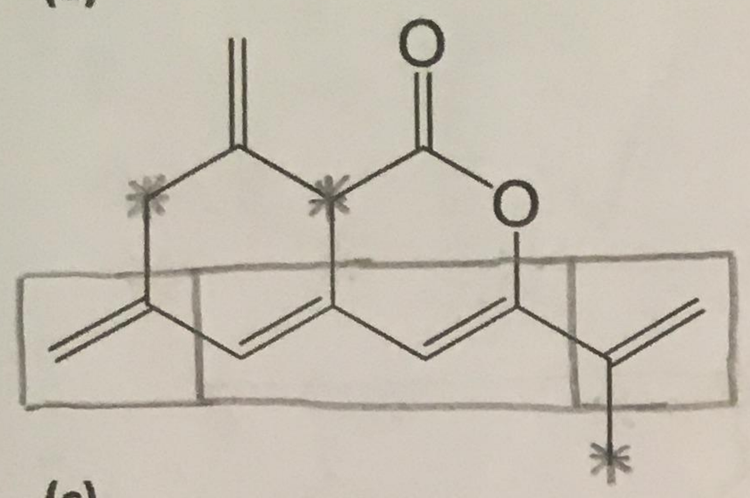
f. 
Br
Mg
MgBr
H2O
OH

g. 
Cl
Mg
MgCl
1.
2. H2O
OH
HCl
Cl

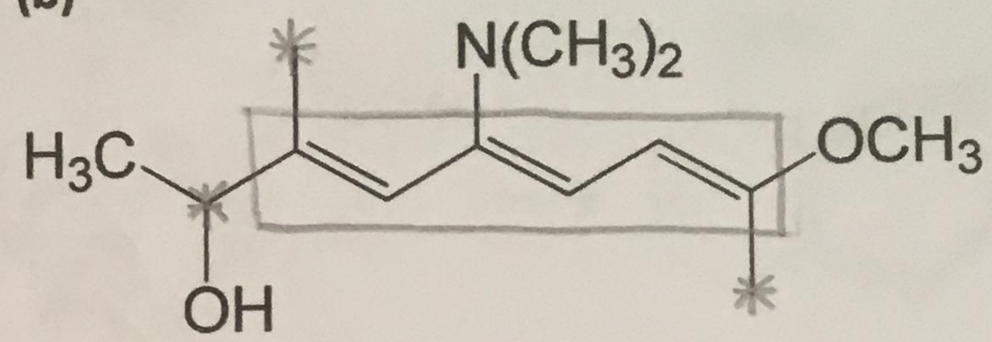
h. 
OH
NaH
H2O
O
OH

3. Use the Woodward-Fieser rule and the table from your course material to estimate the λ_{max} for the following cross-conjugated systems

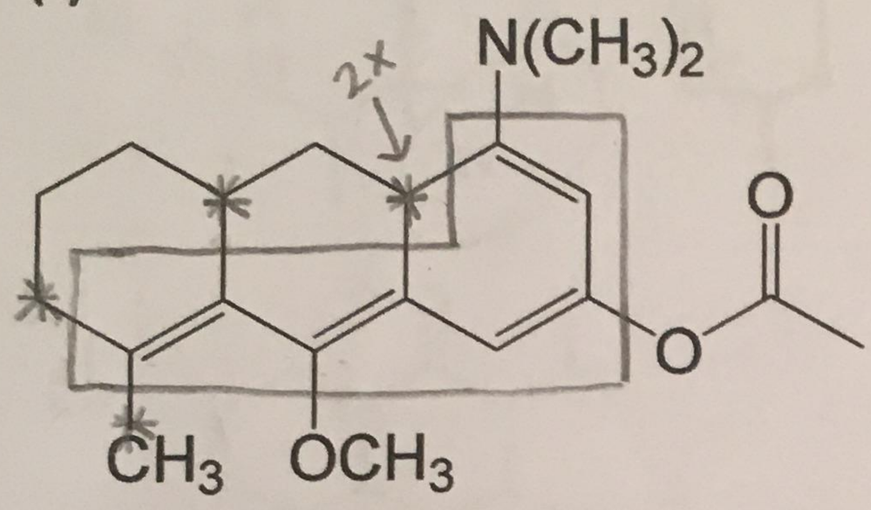
(a)



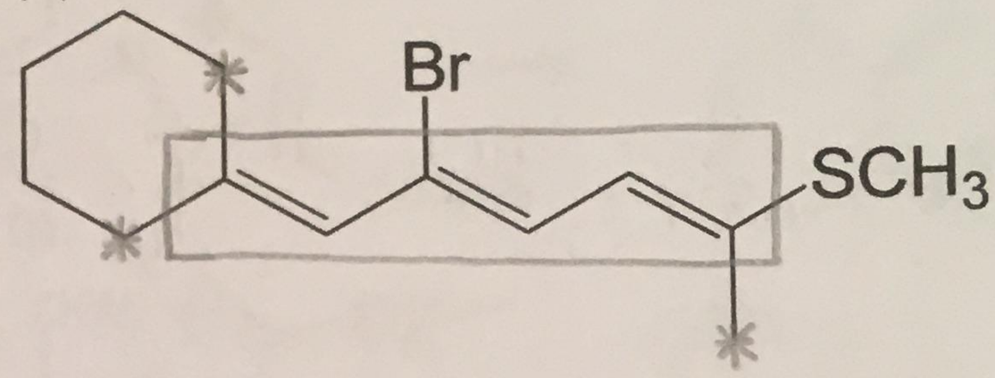
(b)



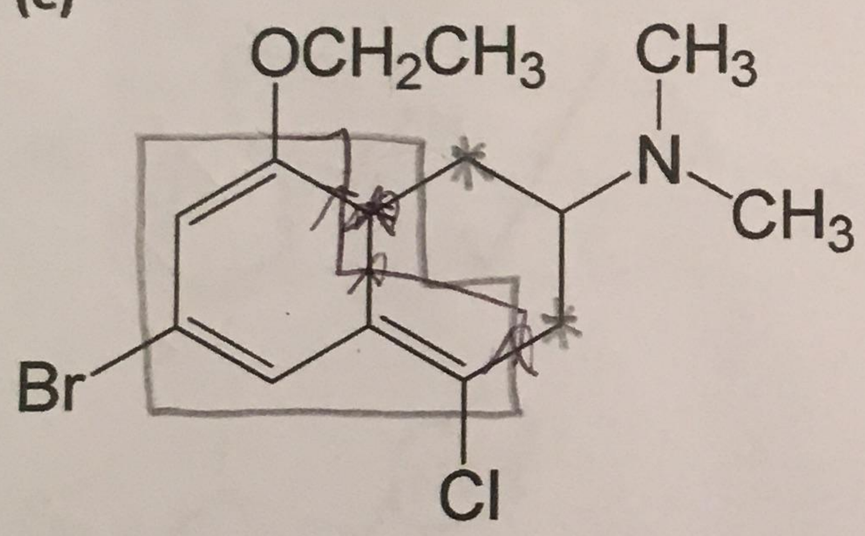
(c)



(d)



(e)



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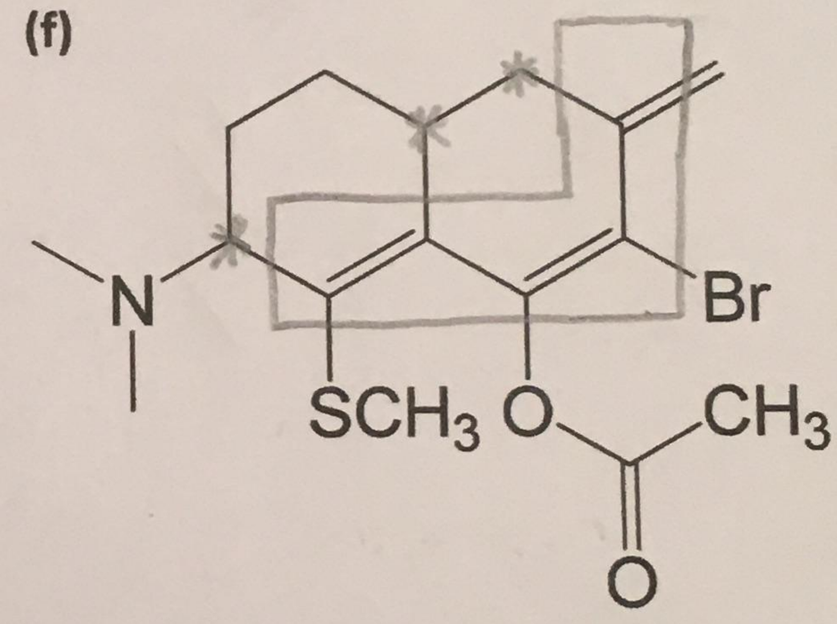
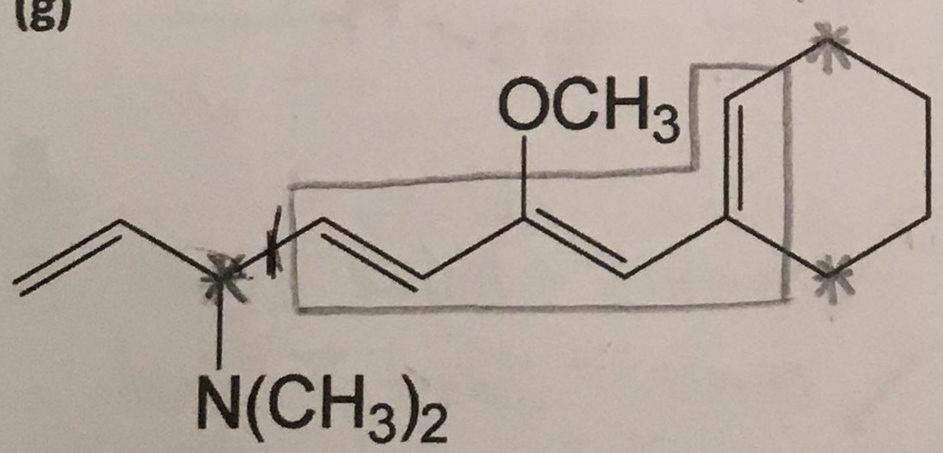


(g)



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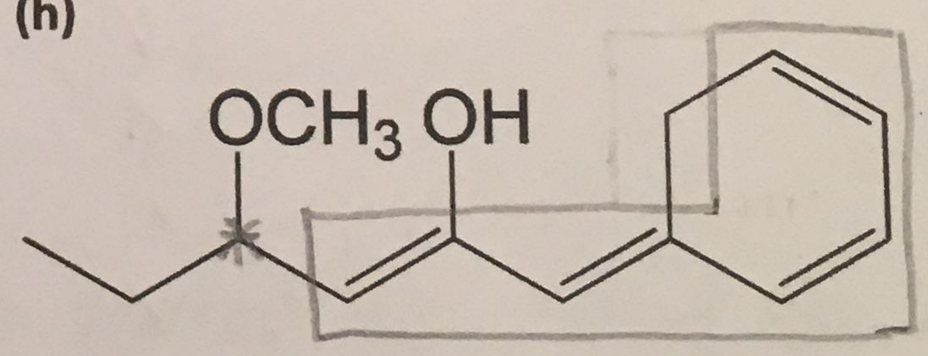


c. parent value = 253 nm
add. C=C bonds = 60 nm ✓
C-alkyl sub. = 25 nm ✓
ester = 0 nm ✓
O-alkyl = 6 nm ✓
N(alkyl)$_2$ = 60 nm ✓
exocyclic C=C = +10 nm ✓
414 nm

d. parent value = 217 nm ✓
add. C=C bond = 30 nm ✓
C-alkyl = 15 nm ✓
Br = 5 nm ✓
S-alkyl = 30 nm ✓
exocyclic C=C = +5 nm ✓
302 nm

e. parent value = 253 nm ✓
add. C=C bonds = 30 nm ✓
C-alkyl sub. = 15 nm
Cl = 5 nm ✓
Br = 5 nm ✓
O-alkyl = 6 nm ✓
exocyclic C=C = +5 nm
314 nm

f. parent value = 214 nm ✓
add. C=C bonds = 30 nm ✓
C-alkyl sub. = 15 nm ✓
ester = 0 nm
Br = 5 nm ✓
S-alkyl = 30 nm ✓
exocyclic C=C = +10 nm ✓
304 nm

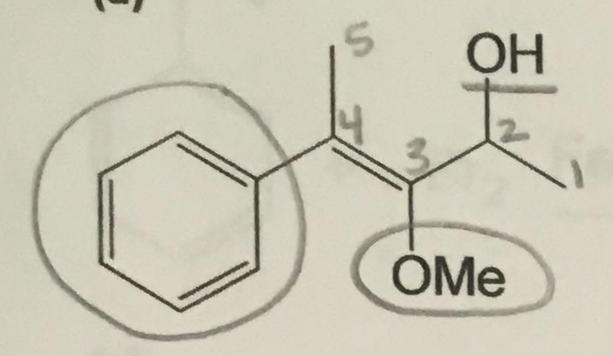
g. parent value = 217 nm ✓
add. C=C bonds = 30 nm ✓
C-alkyl sub. = 15 nm ✓
O-alkyl = +6 nm ✓
268 nm

g. parent value = 253 nm ✓
add. C=C bonds = 60 nm ✓
C-alkyl sub. = 15 nm
exocyclic C=C = +5 nm ✓
~~323 nm~~
333 nm

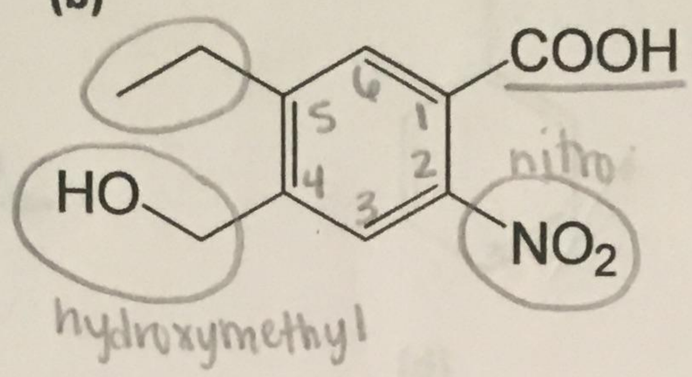
WORKSHEET VI

1. Name the following compounds

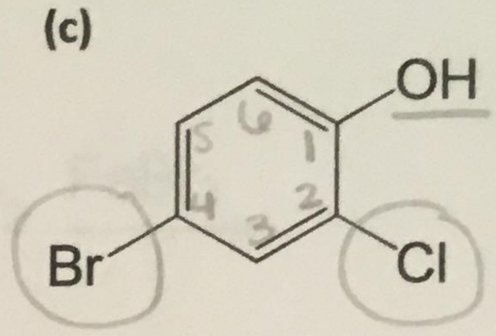
(a)



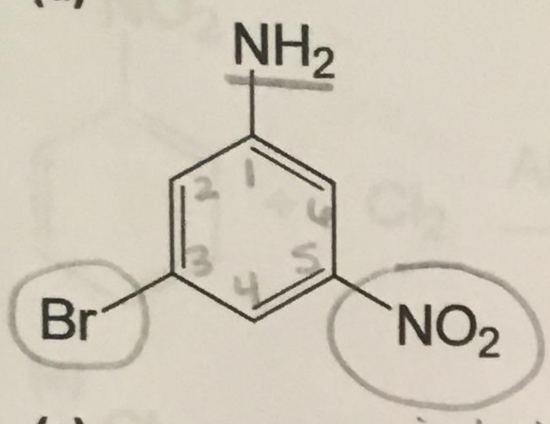
(b)



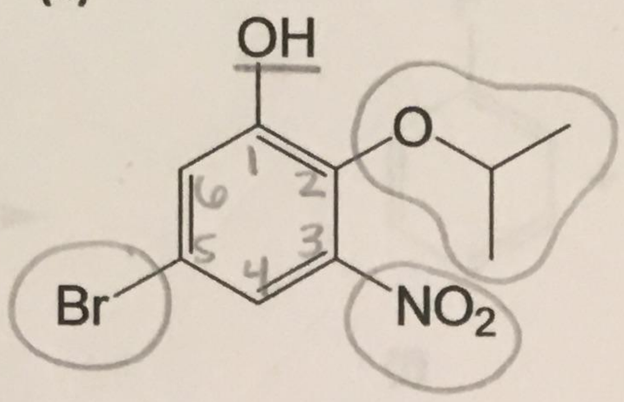
(c)



(d)



(e)



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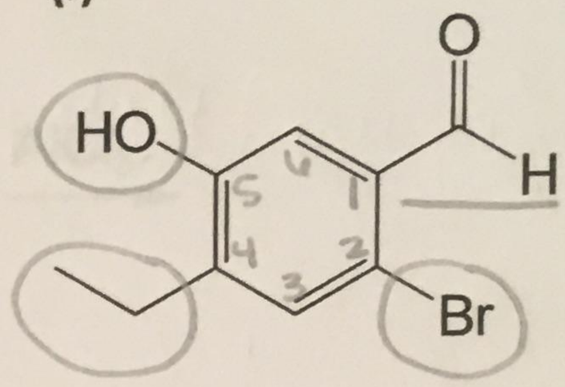

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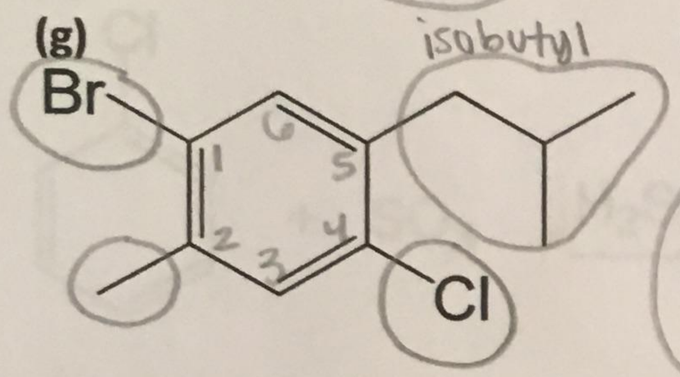

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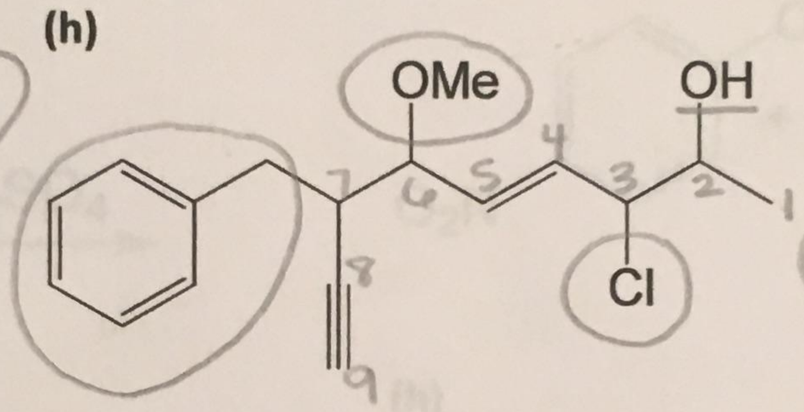

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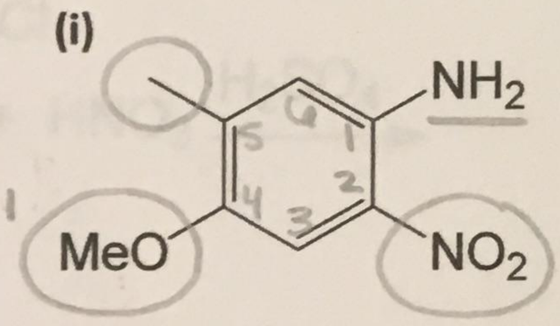
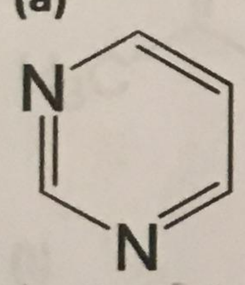


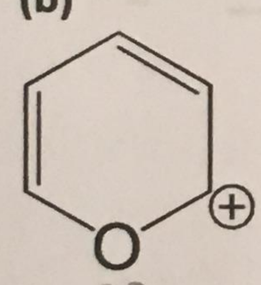
2. Classify the following compounds as aromatic, antiaromatic or nonaromatic

(a)



lone pairs don't count

(b)



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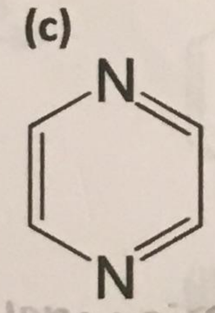
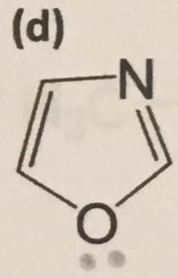


lone pairs don't count

(d)



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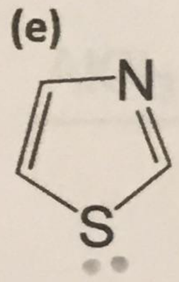

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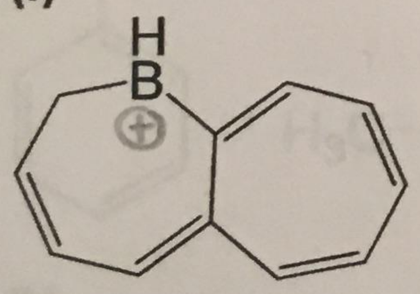

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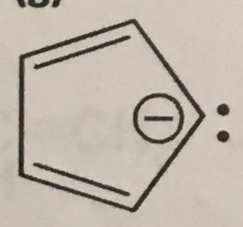

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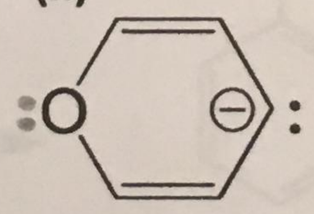

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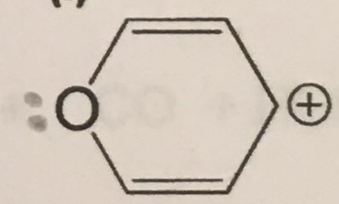

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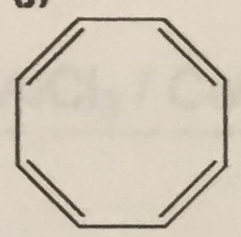

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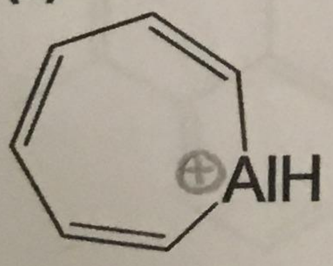

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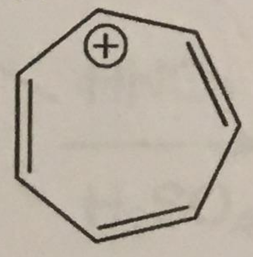

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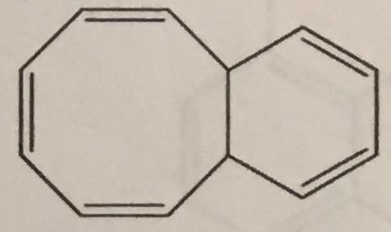

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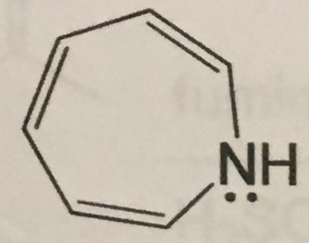

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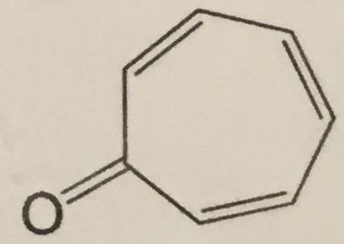

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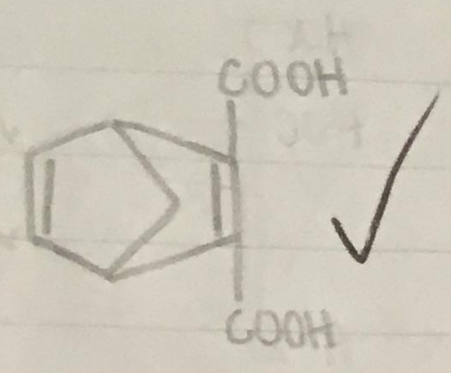
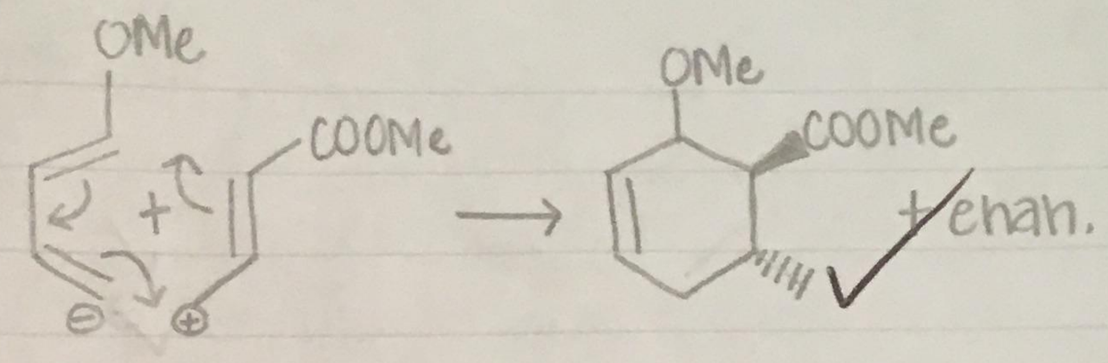
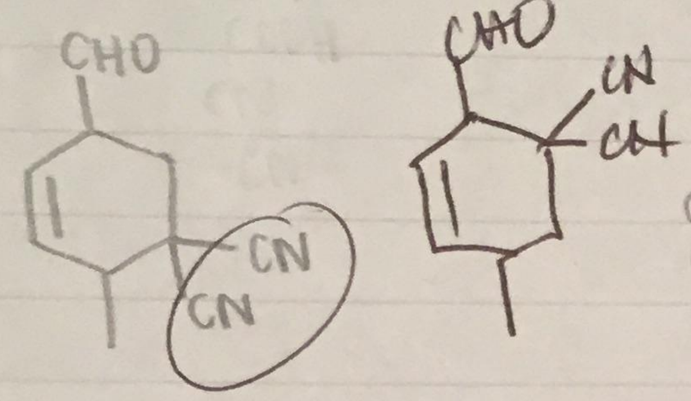
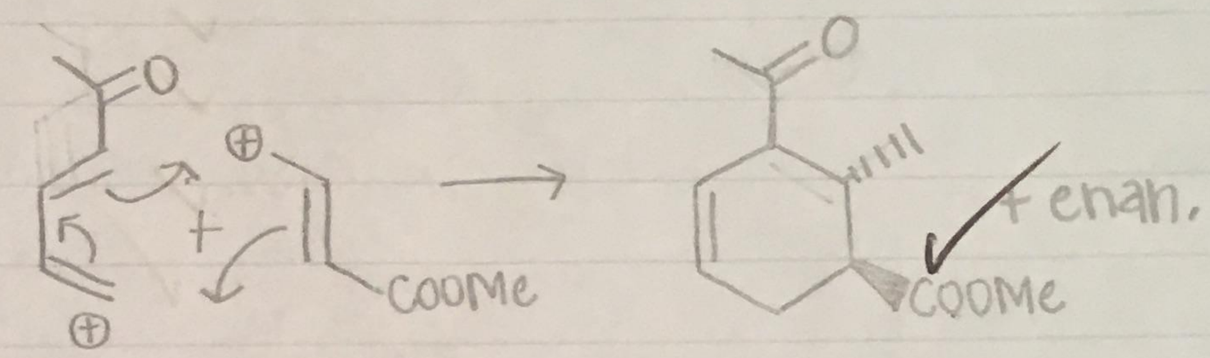
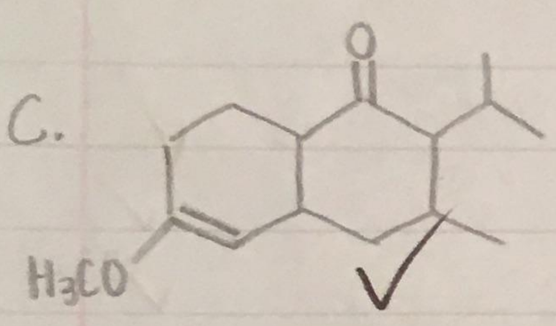
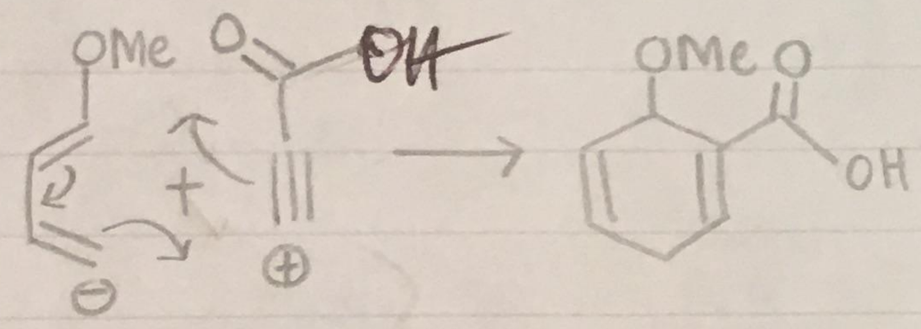
a. 

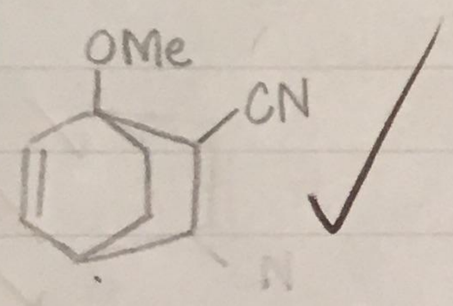
f. 

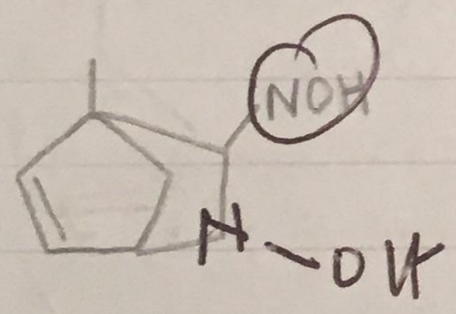
b. 

g. 

c. 

h. 

d. 

e. 

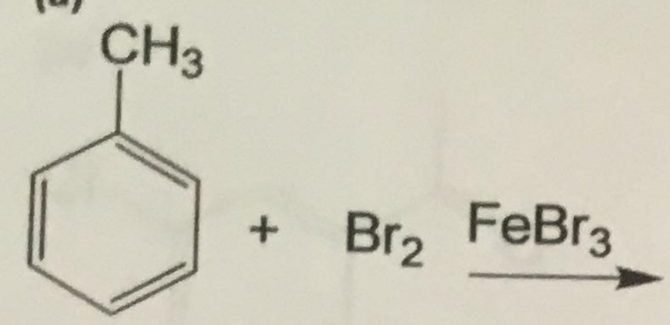
3.

a. parent value = 214 nm
add. C=C bonds = 60 nm
C-alkyl sub. = 15 nm x 3.
ester = 0 nm
exocyclic C=C = +10 nm
299 nm

b. parent value = 217 nm
add. C=C bonds = 30 nm
C-alkyl sub = 15 nm
O-alkyl = 6 nm
N(alkyl)2 = +60 nm
328 nm

3. Give the major product(s) of each of the following reaction

(a)



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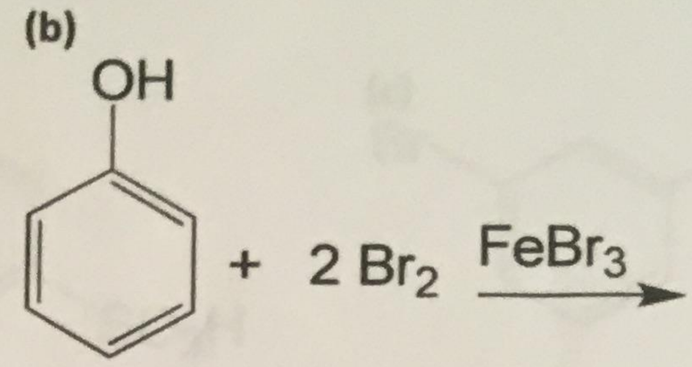

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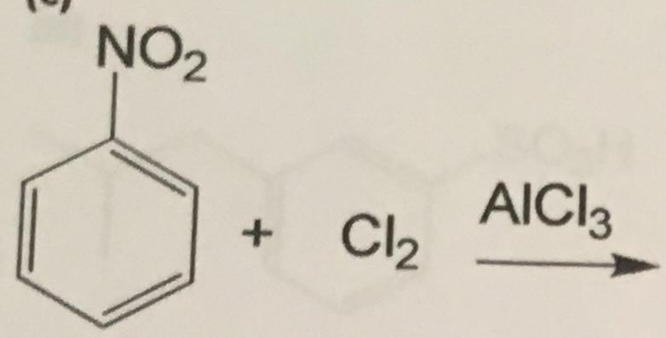
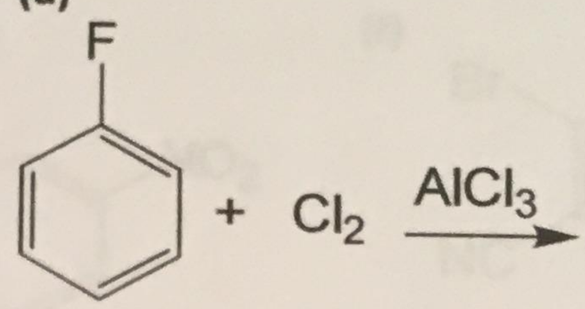


(d)



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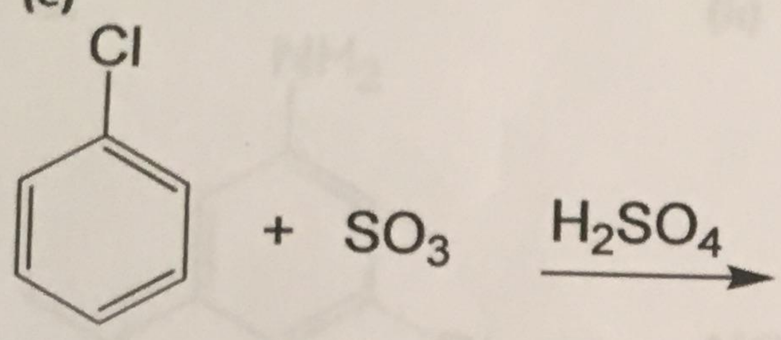

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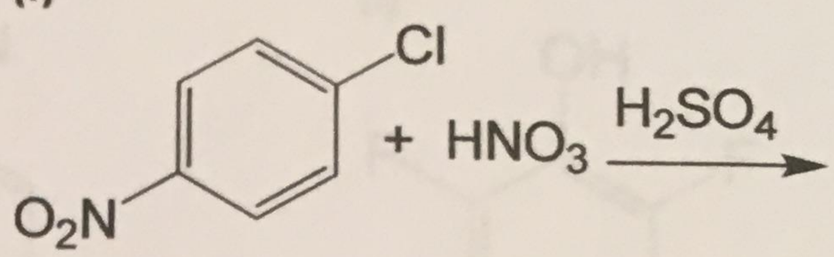
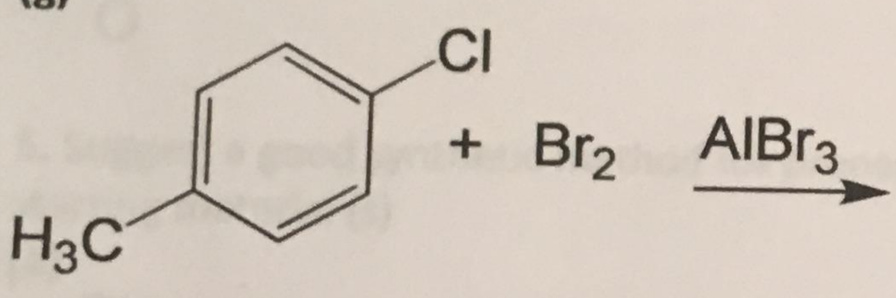


(g)



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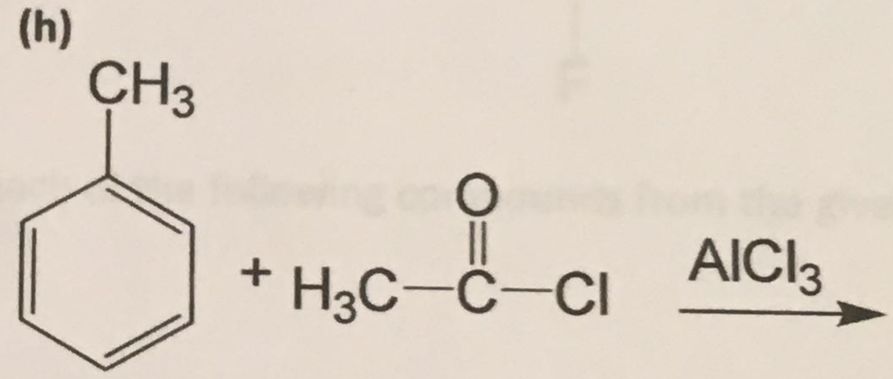
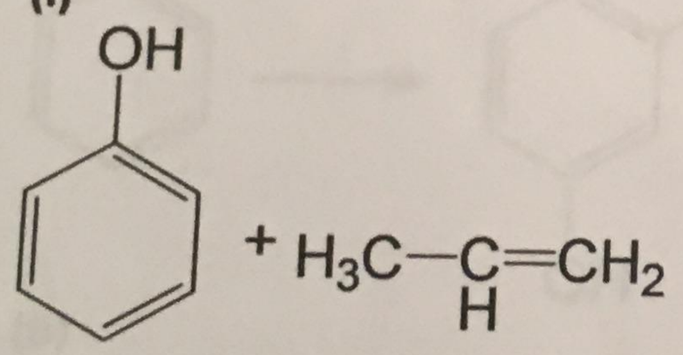


(i)



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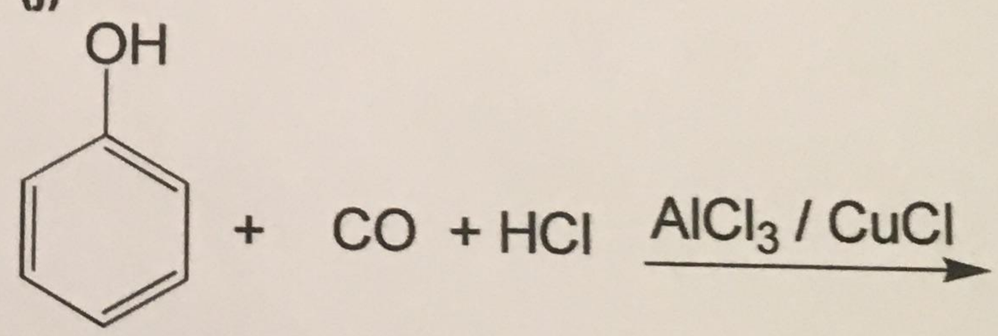

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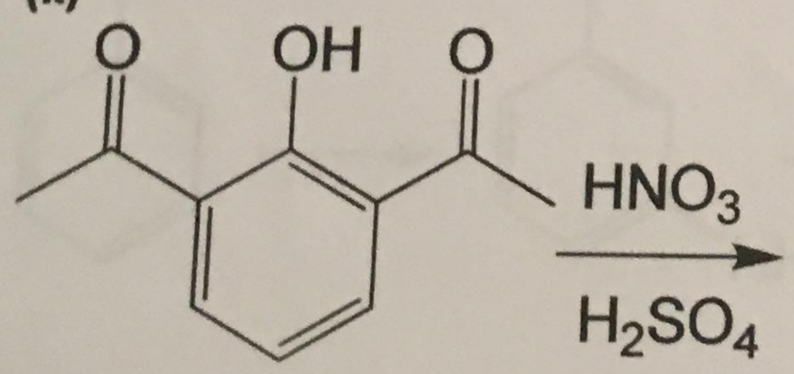

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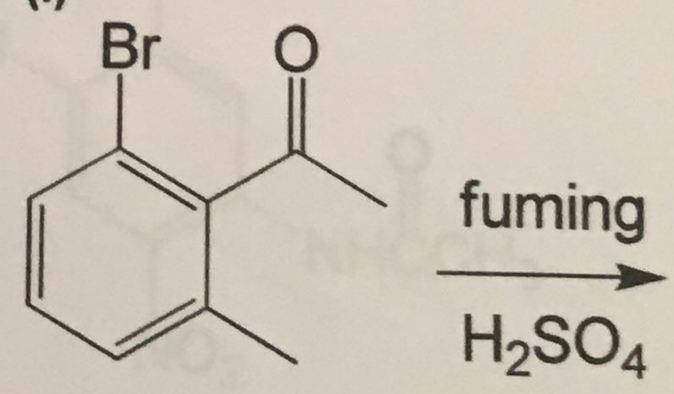


Part 1:

a. 3-methoxy-4-phenylpent-3-en-2-ol (3Z)

b. 5-ethyl-4-hydroxymethyl-2-nitrobenzoic acid

c. 4-bromo-2-chlorophenol

d. 3-bromo-5-nitroaniline

e. 5-bromo-2-isopropoxy-3-nitrophenol

f. 2-bromo-4-ethyl-5-hydroxybenzaldehyde

g. 1-bromo-4-chloro-5-isobutyl-2-methylbenzene

h. 7-benzyl-3-chloro-6-methoxynon-8-yn-4-en-2-ol

i. 4-methoxy-5-methyl-2-nitroaniline

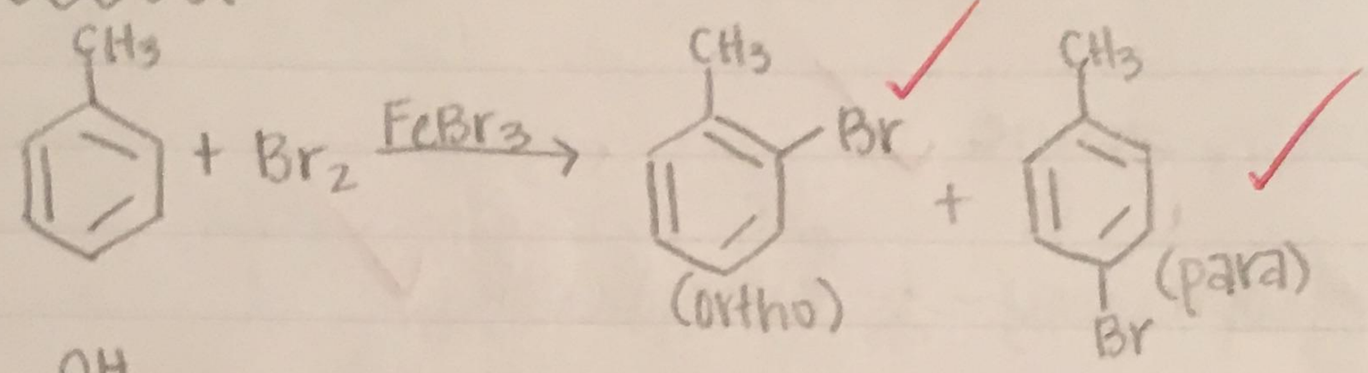
Part 2:

	Classification	# of electrons
a.	aromatic	6
b.	aromatic	6
c.	aromatic	6
d.	aromatic	6
e.	aromatic	6
f.	nonaromatic	10 (not conjugated)
g.	aromatic	6
h.	antiaromatic	8
i.	aromatic	6
j.	antiaromatic	8 (if planar)

	classification	# of electrons
k.	aromatic	6
l.	aromatic	6
m.	nonaromatic	10 (not conjugated)
n.	antiaromatic	8
o.	antiaromatic	8

Part 3:

a.



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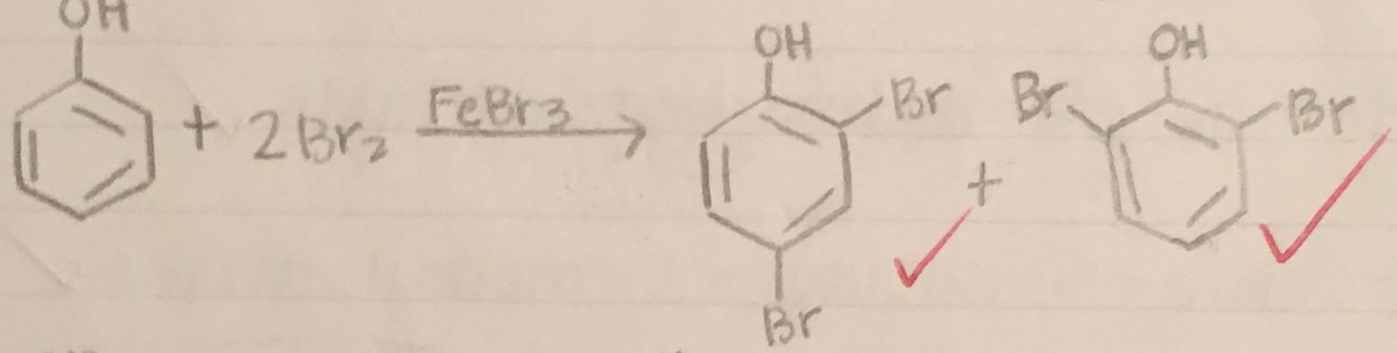

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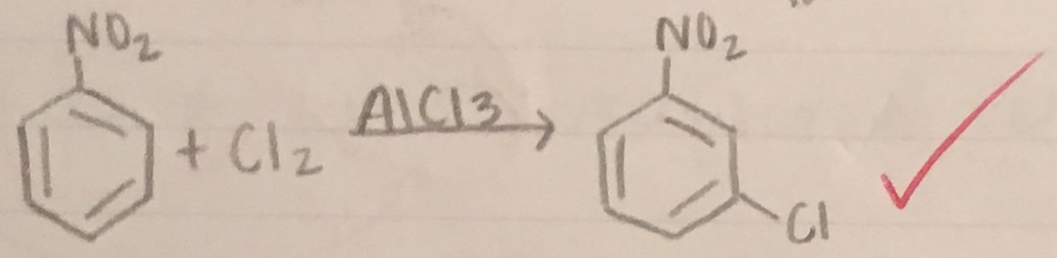

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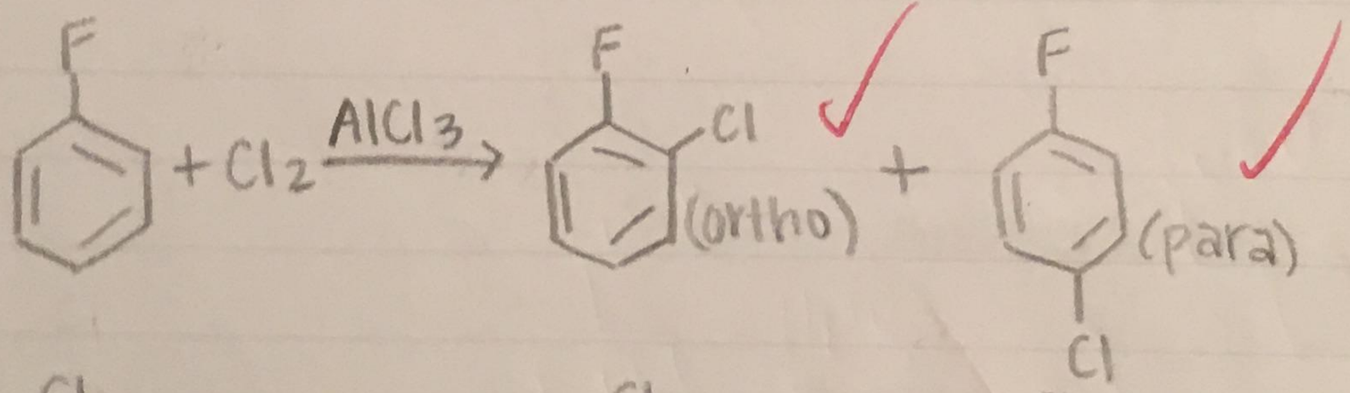

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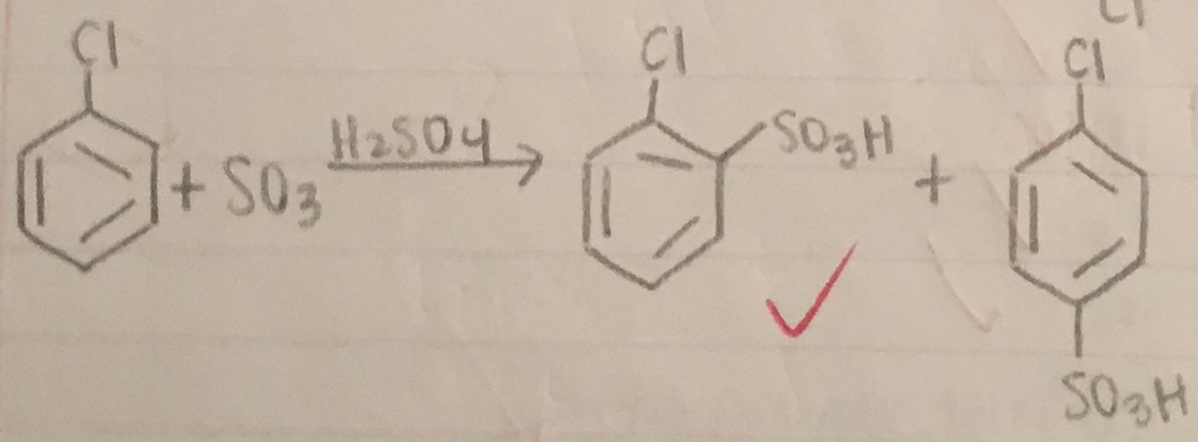

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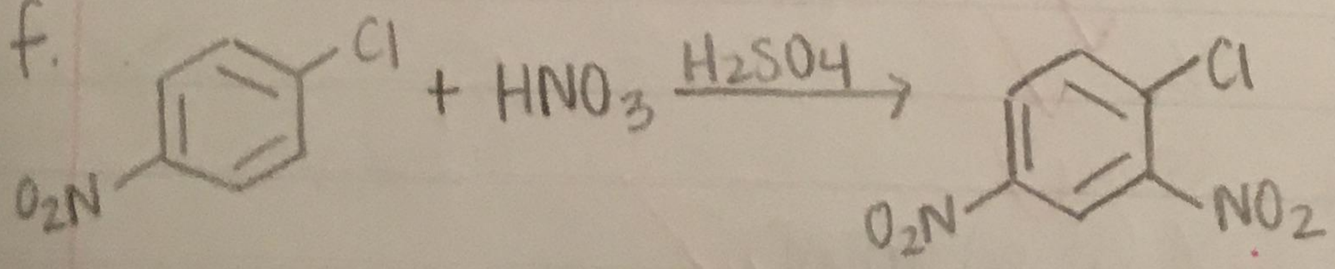
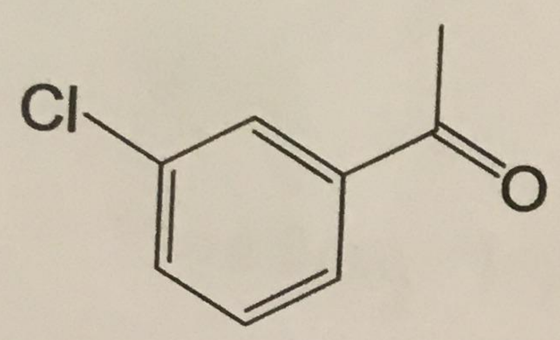


4. Show how you would synthesize these compounds from benzene (you should list all the reactants and the proper reaction conditions)

(a)



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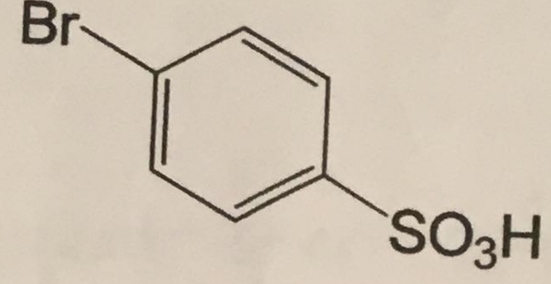

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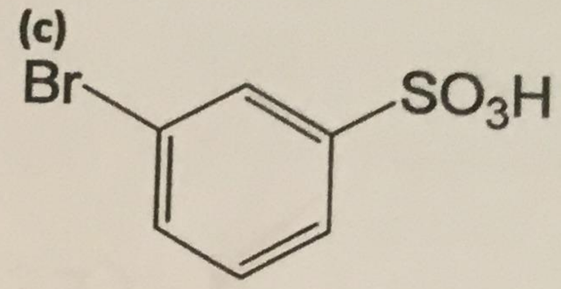

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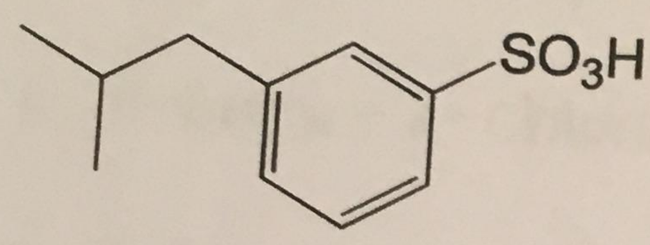

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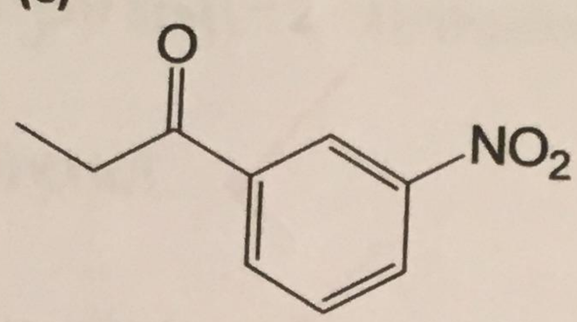
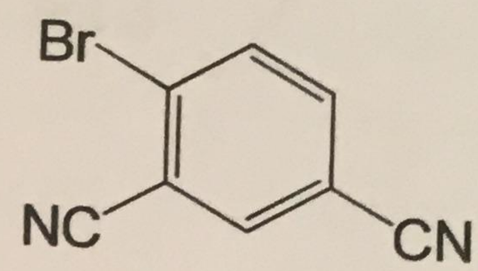


(f)



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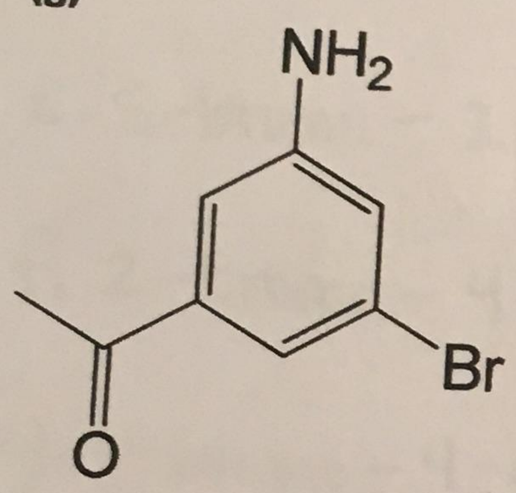

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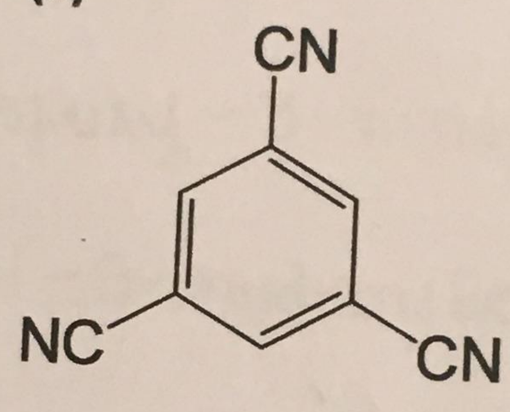
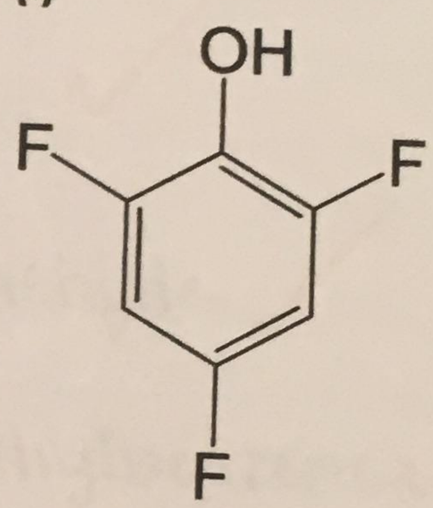
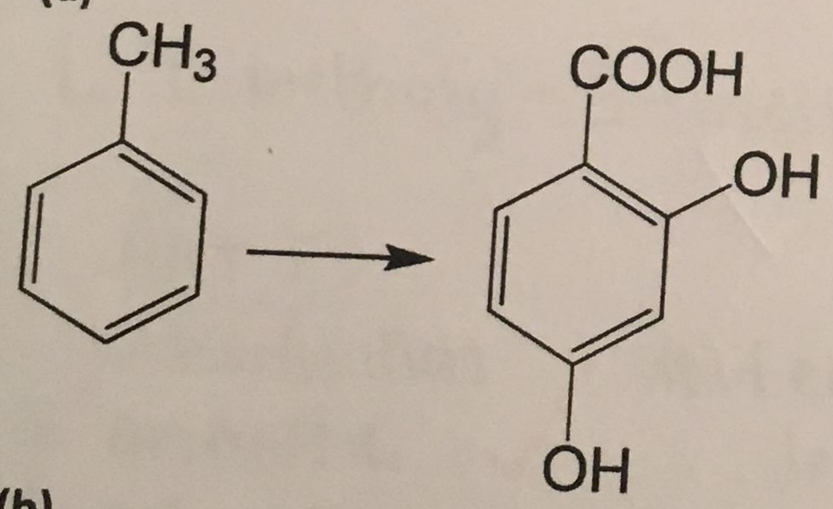


(i)



5. Suggest a good synthetic method for preparing each of the following compounds from the given starting material (s)

(a)



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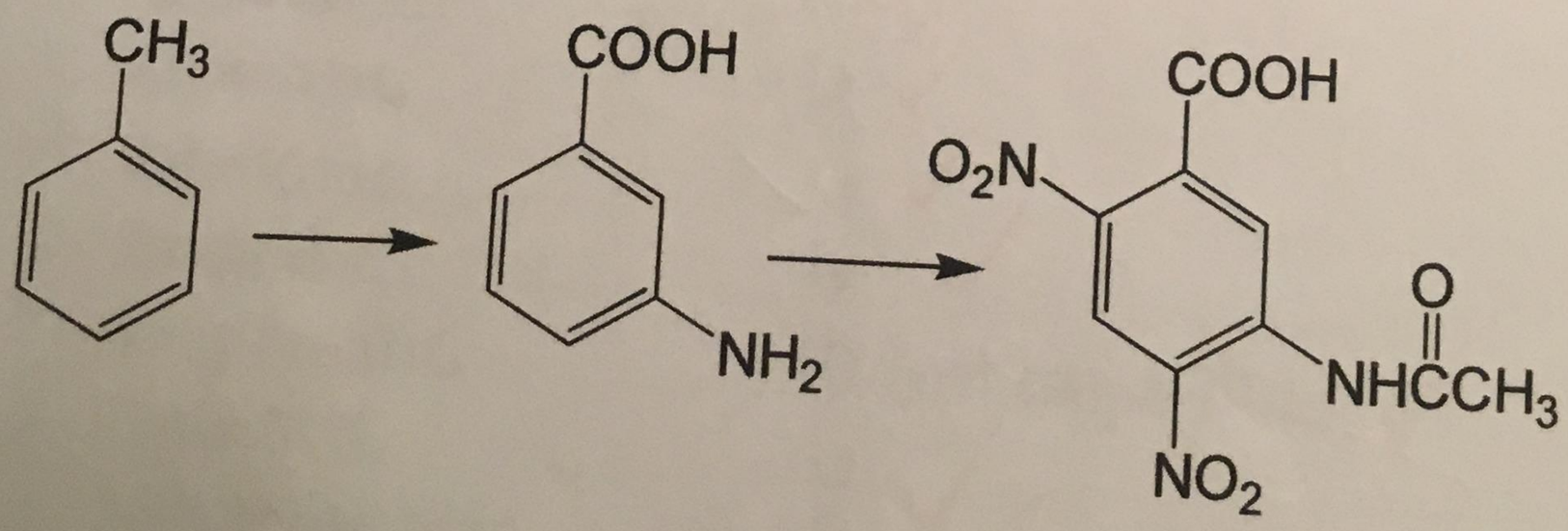
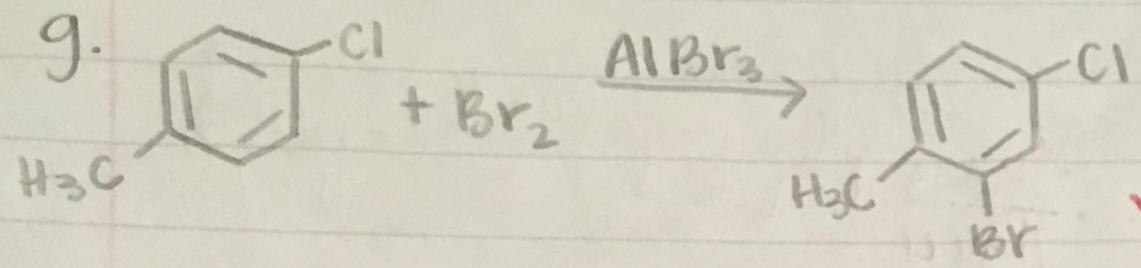
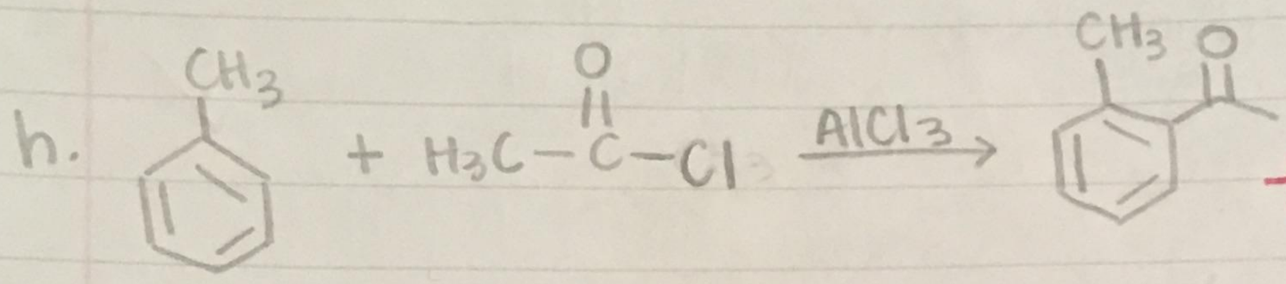
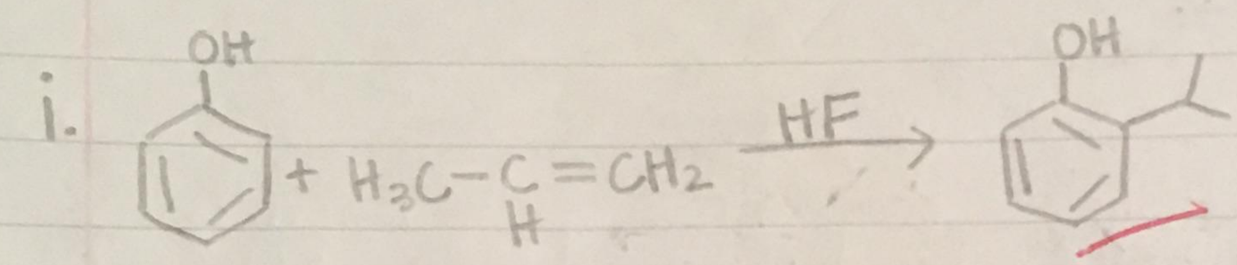


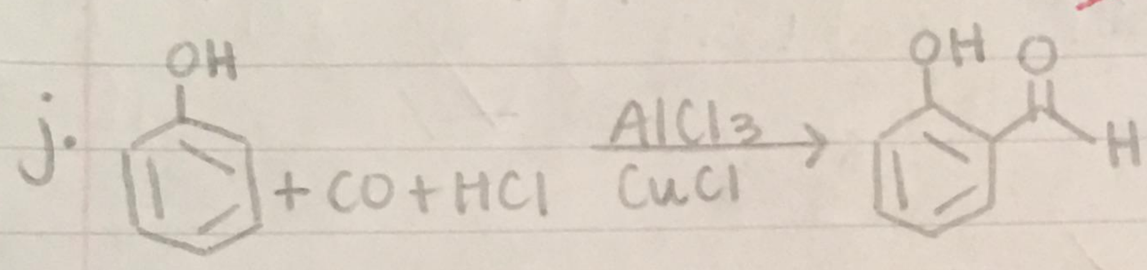
g. 

h. 

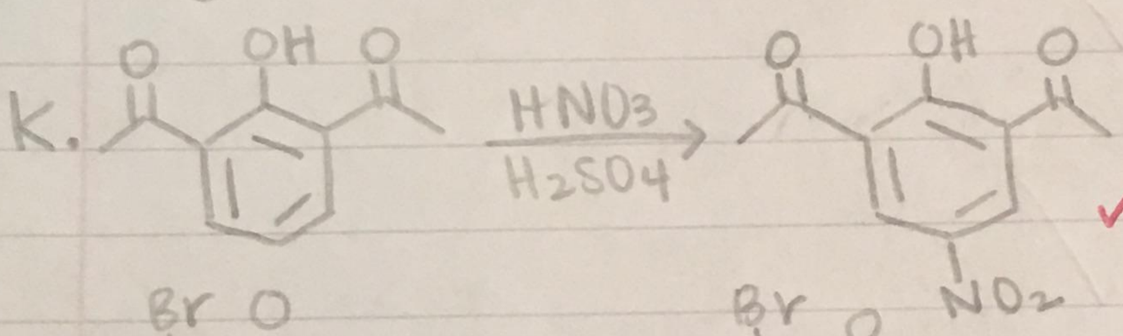
+ para (major).

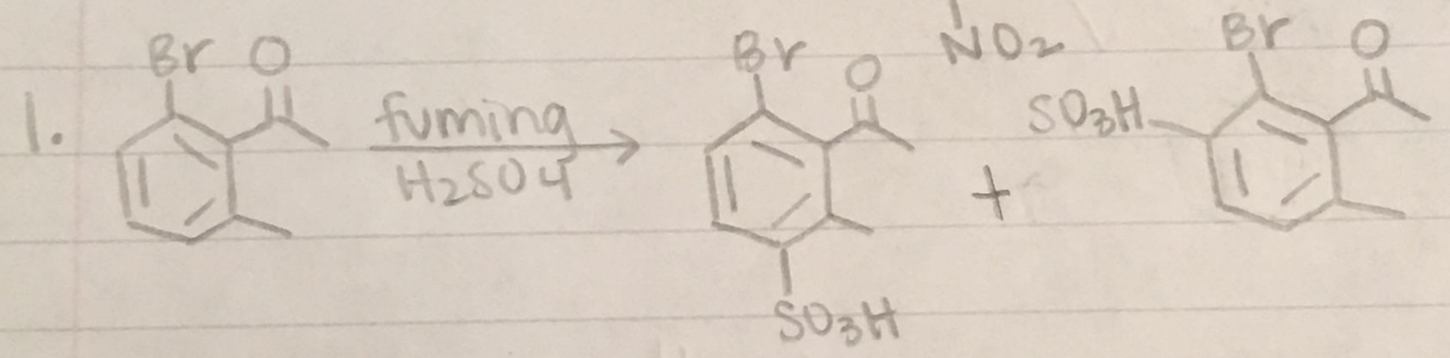
i. 

+ para (major).

j. 

+ para (major).

k. 

l. 

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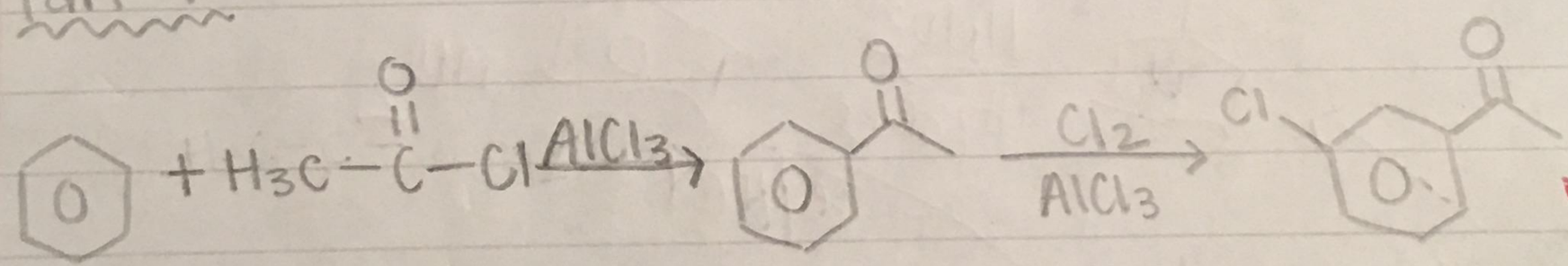
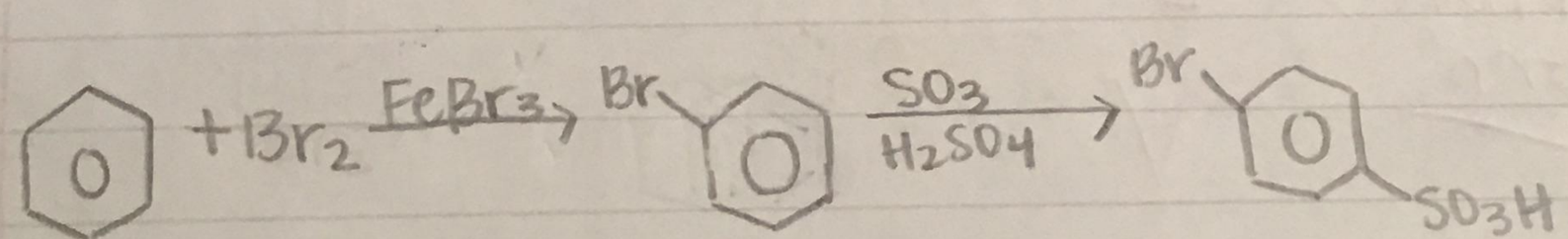
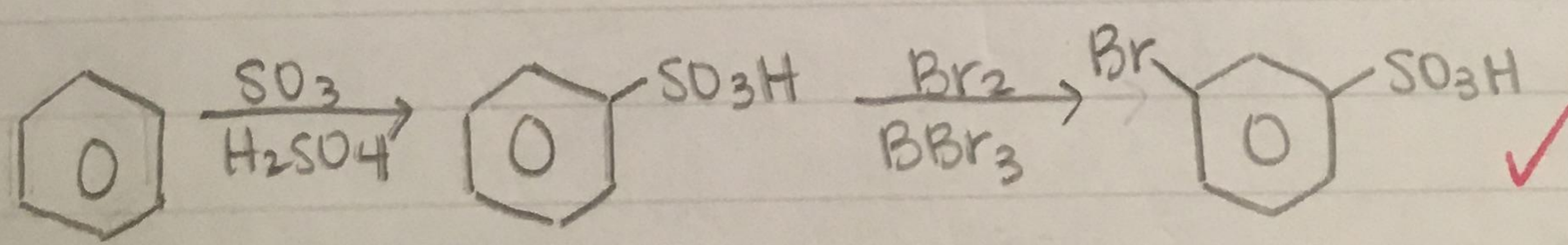
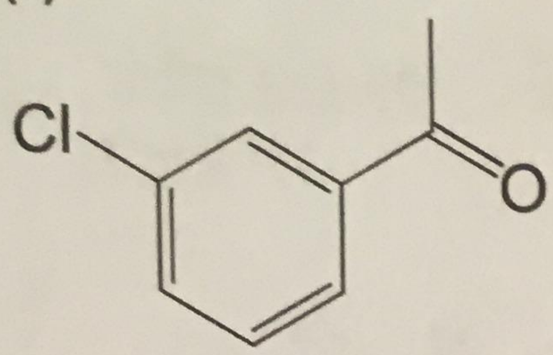
a. 

b. 

c. 

4. Show how you would synthesize these compounds from benzene (you should list all the reactants and the proper reaction conditions)

(a)



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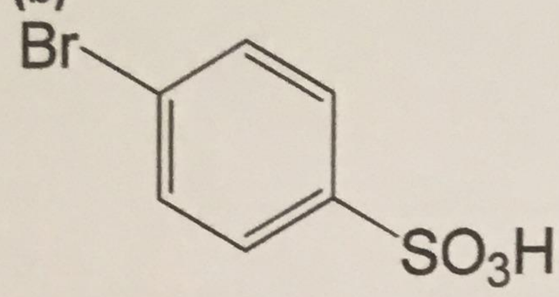

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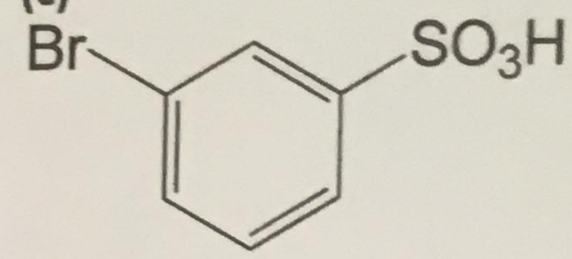

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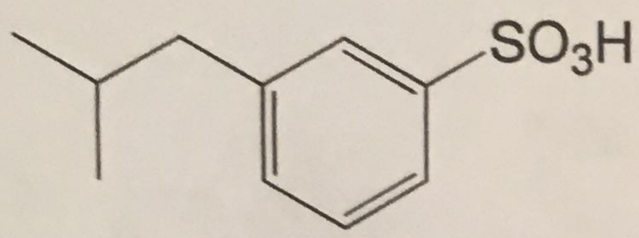

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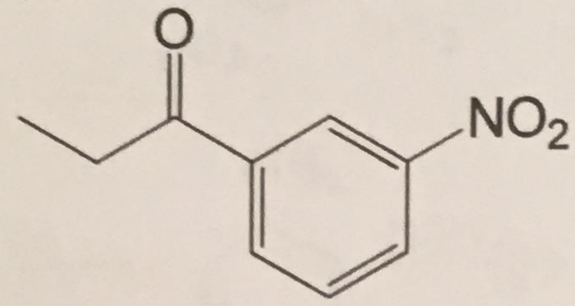

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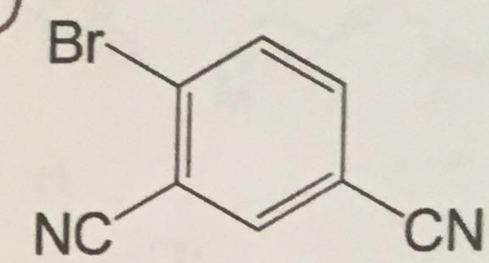
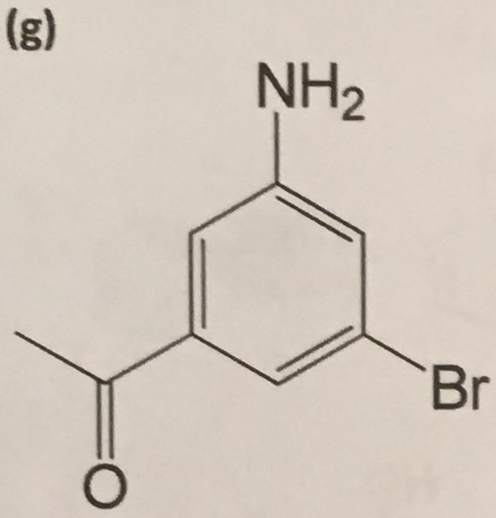
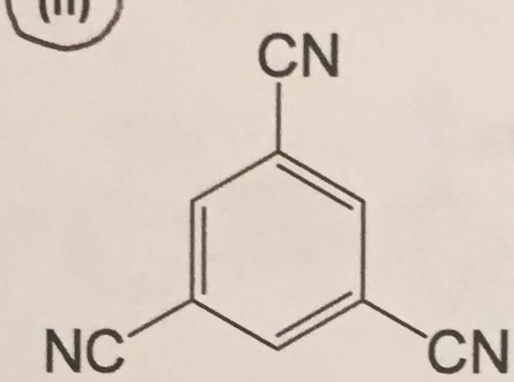


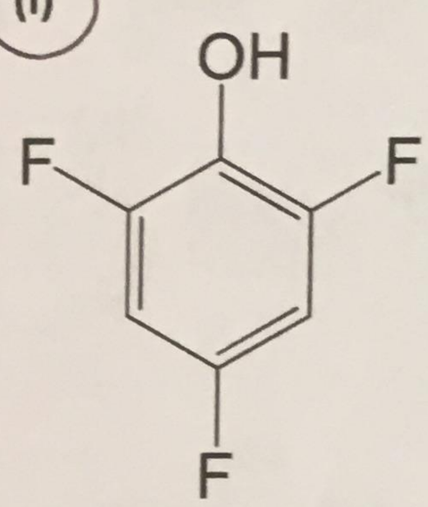
(g)



(h)

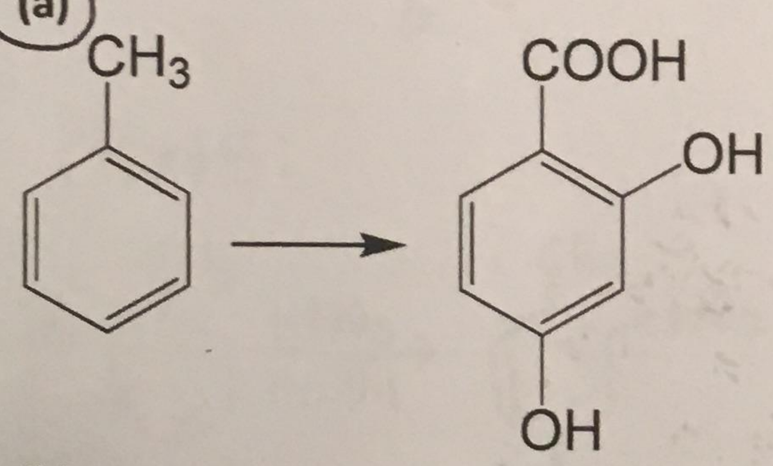


(i)

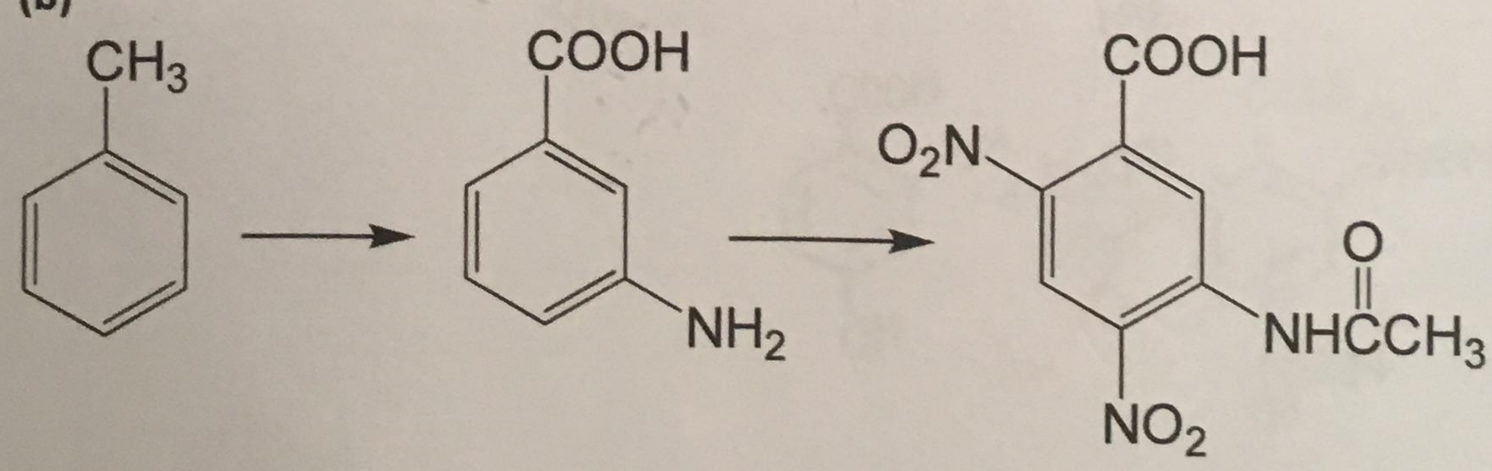


5. Suggest a good synthetic method for preparing each of the following compounds from the given starting material (s)

(a)



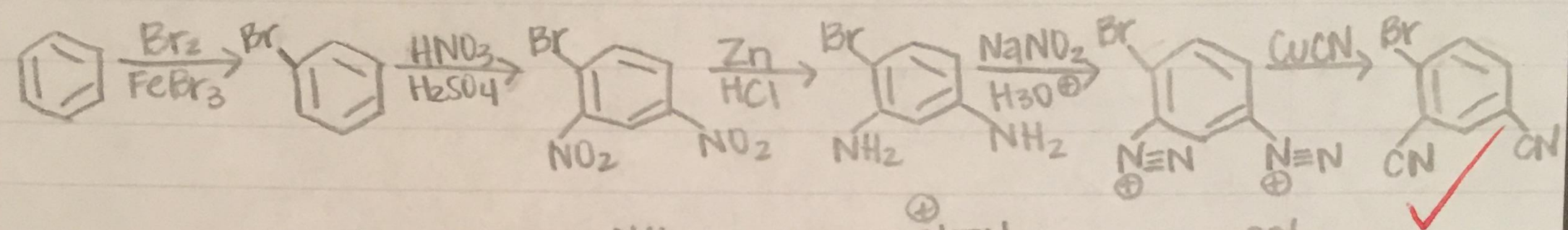
(b)



Worksheet VI

Part 4:

f.



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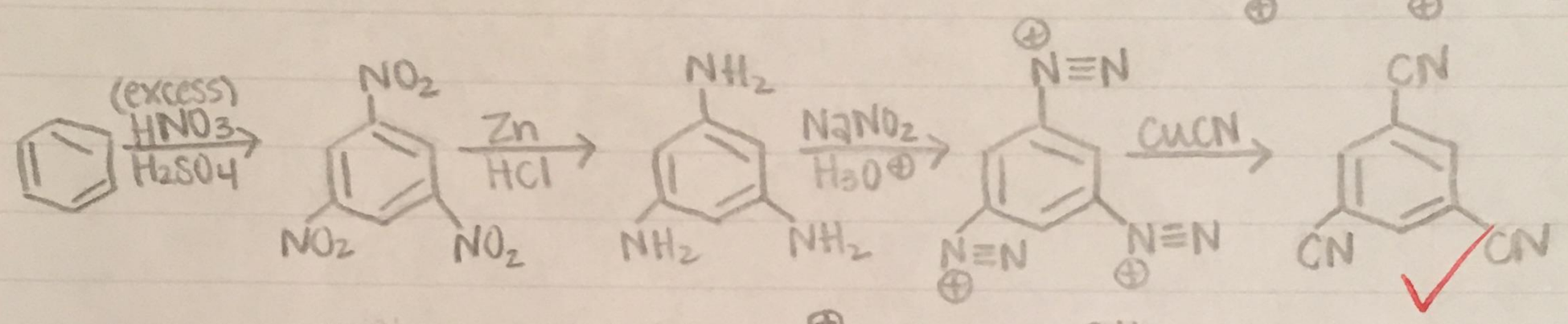

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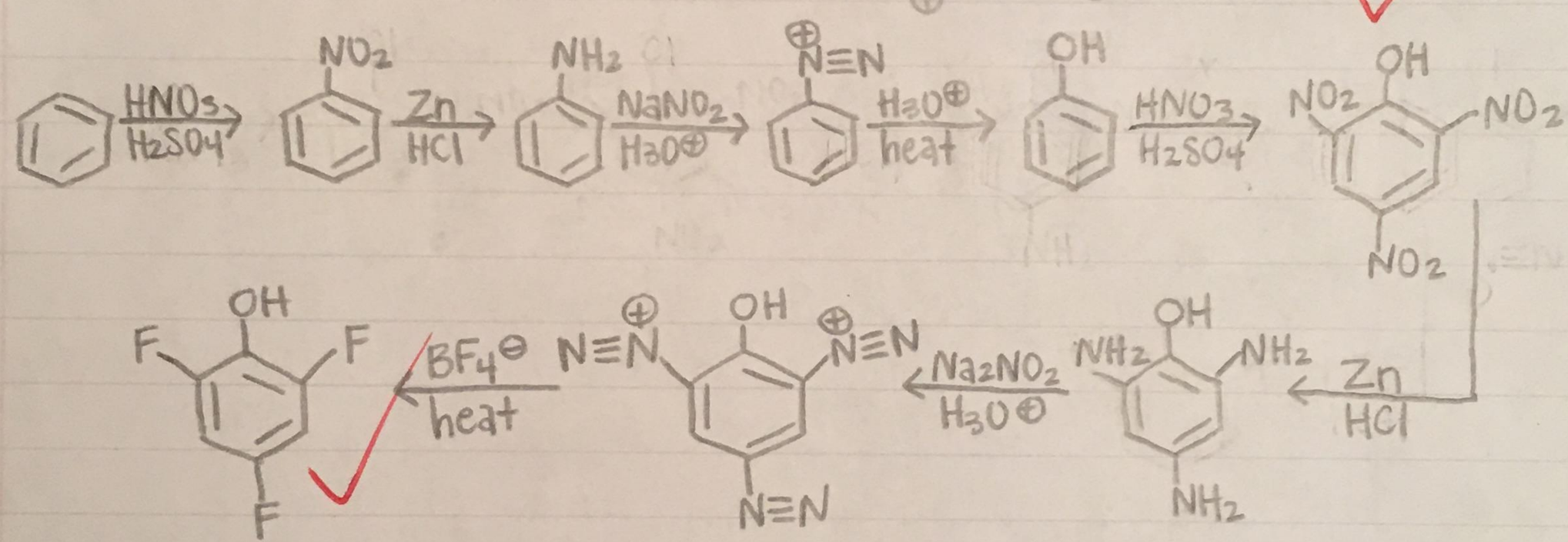
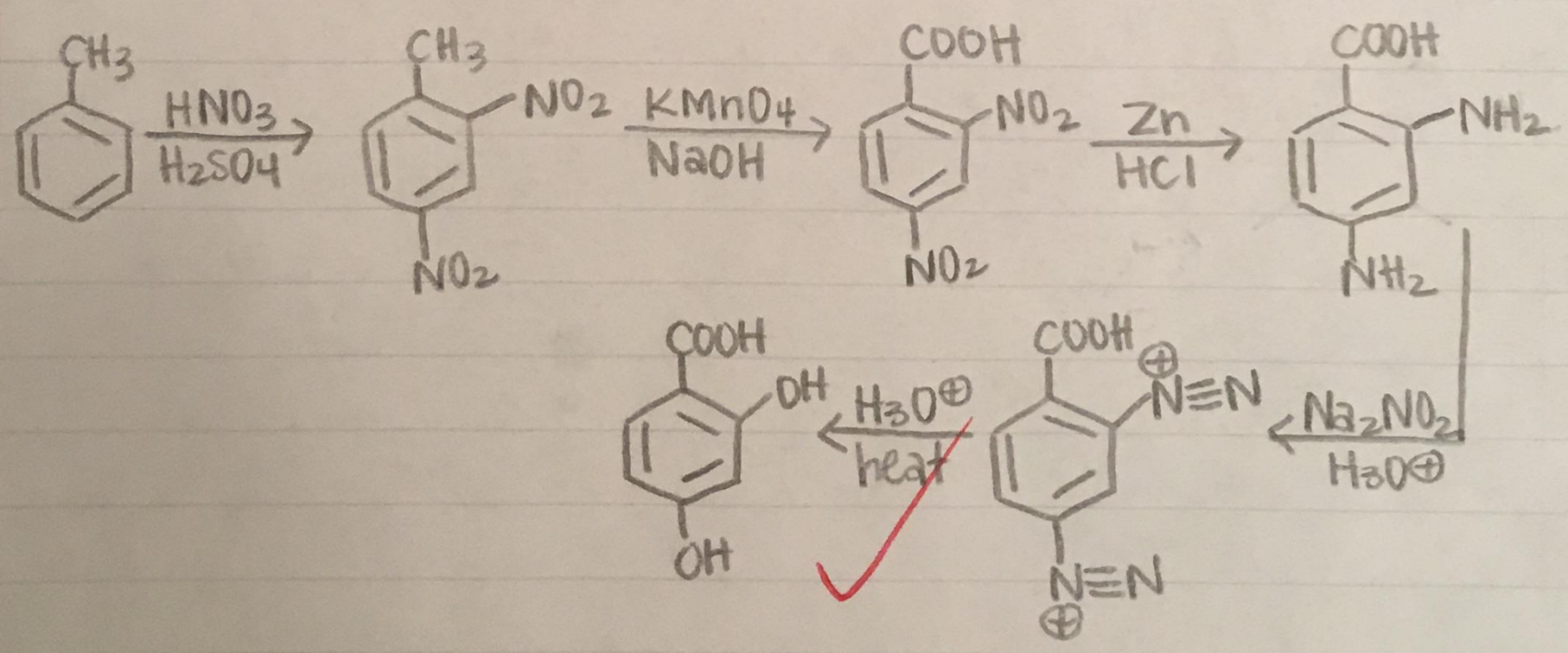


Part 5:

a.



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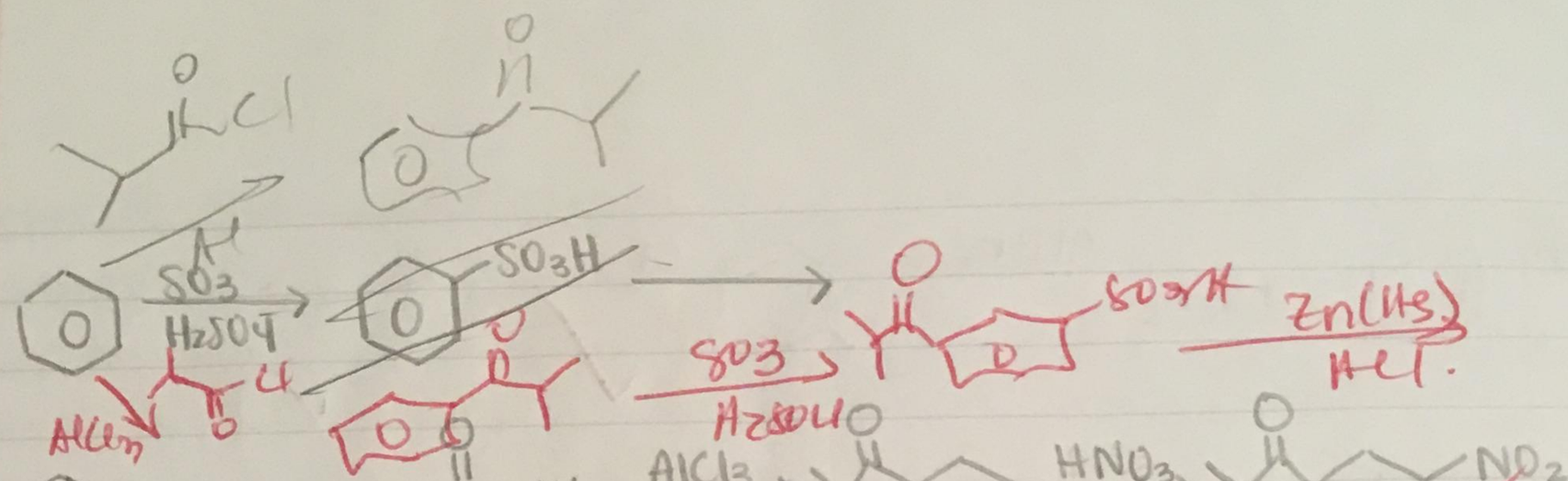

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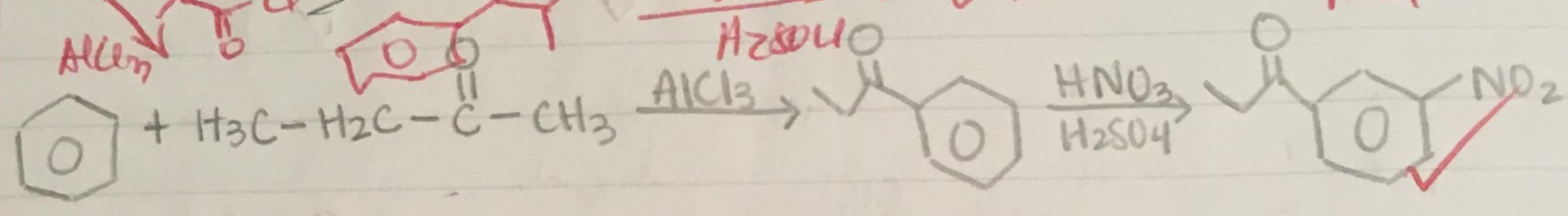
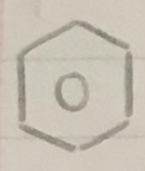
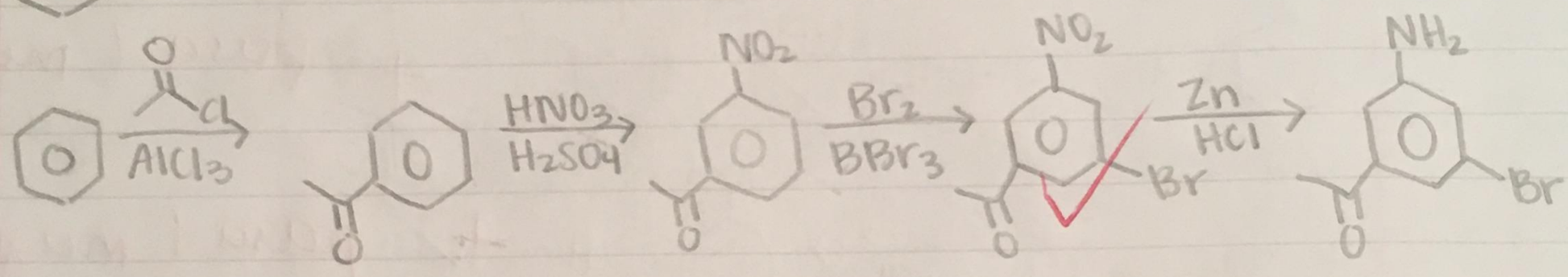
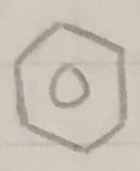


f.  haven't covered?

g.

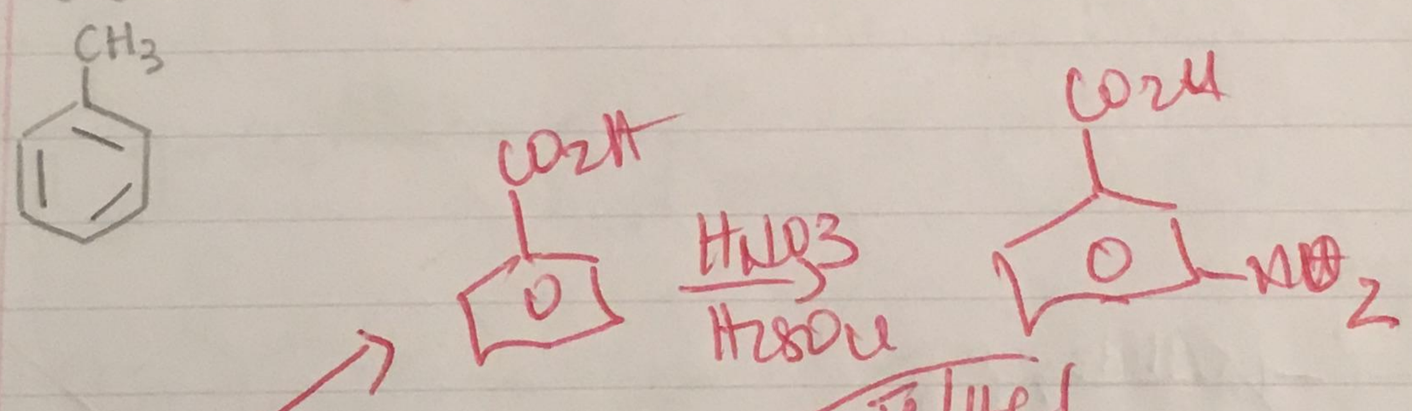


h.  haven't covered? ✓

i. haven't covered? ✓

Part 5:

a.



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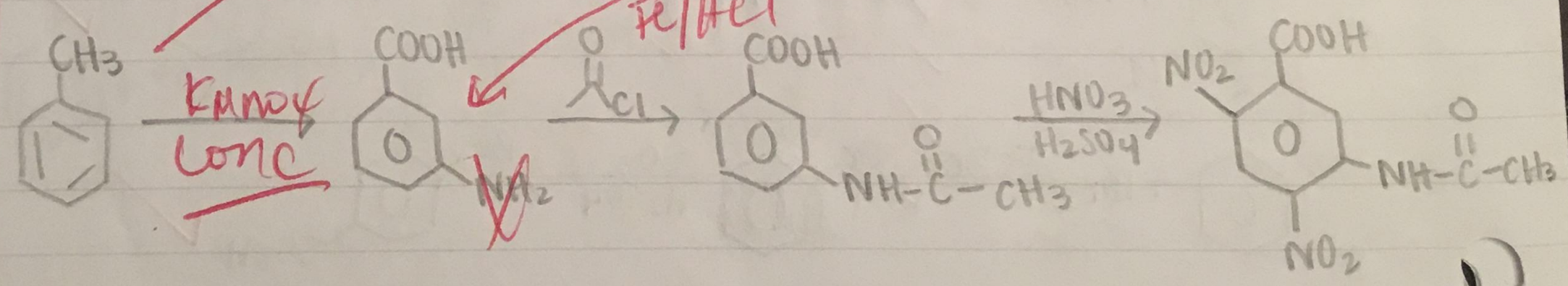

WORKSHEET VII

1. Name the following compounds

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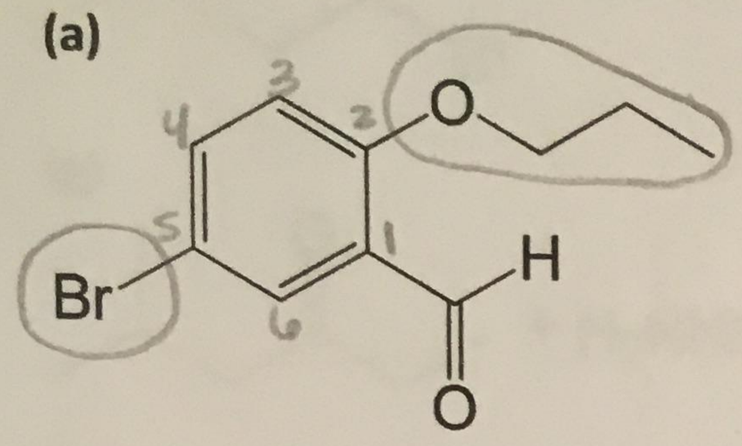
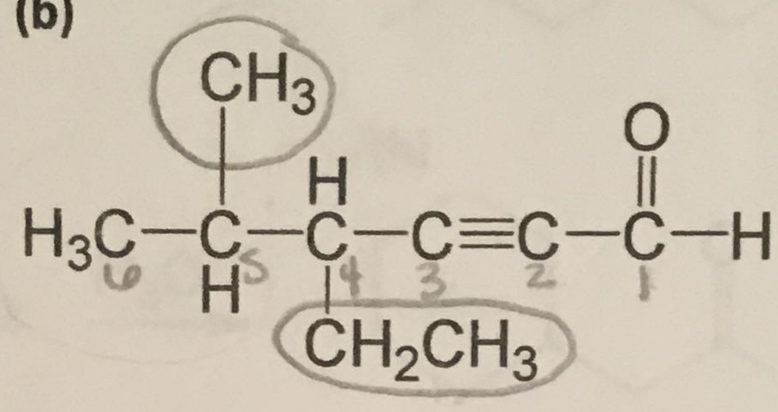
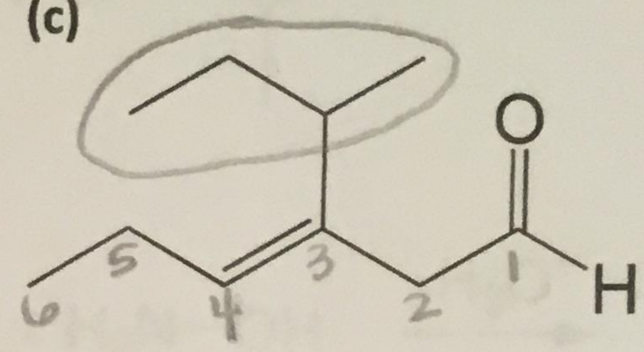


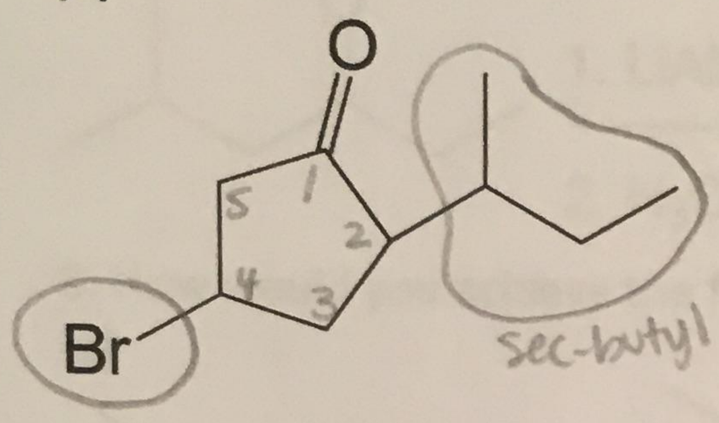
(b)



(c)



(d)



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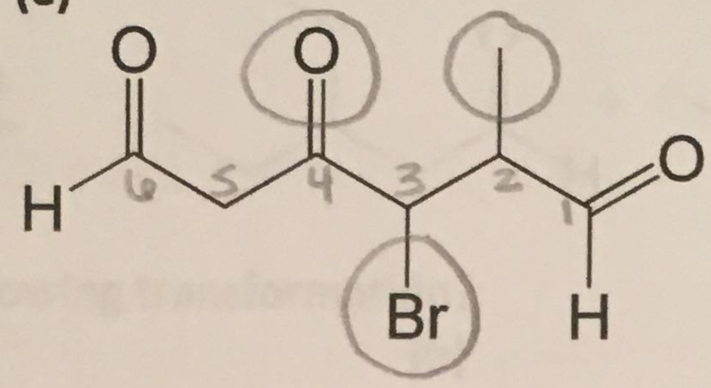

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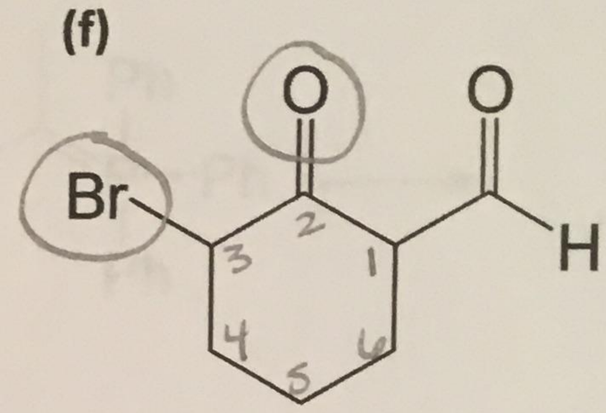
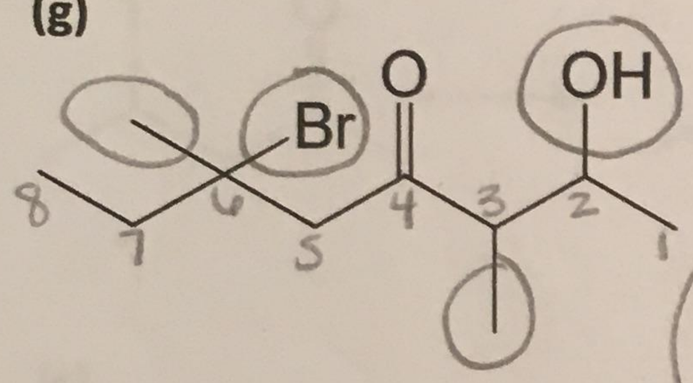
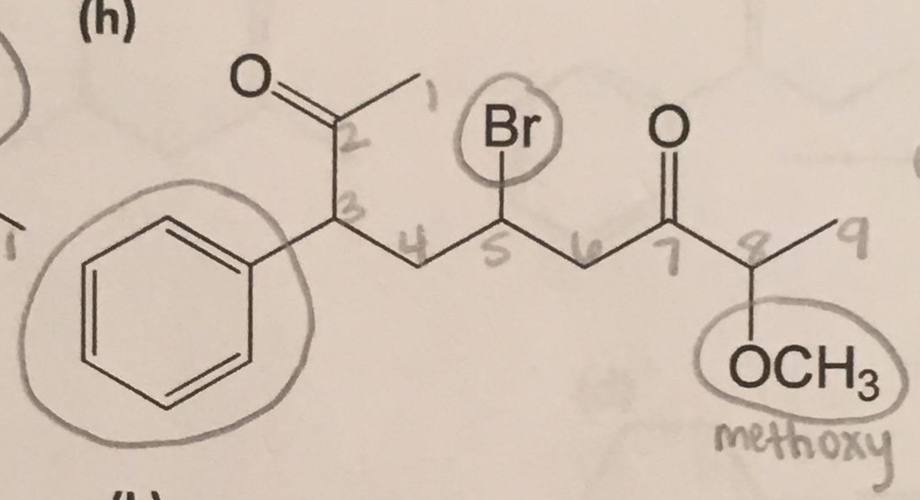


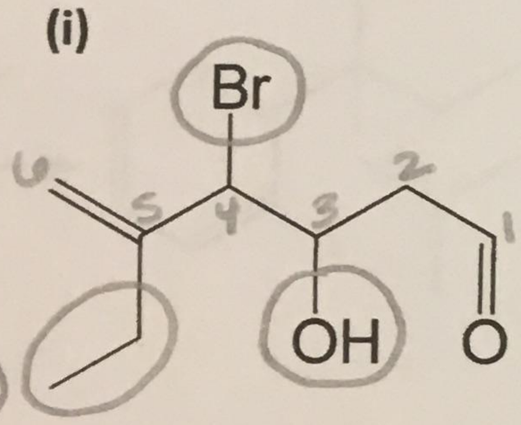
(g)



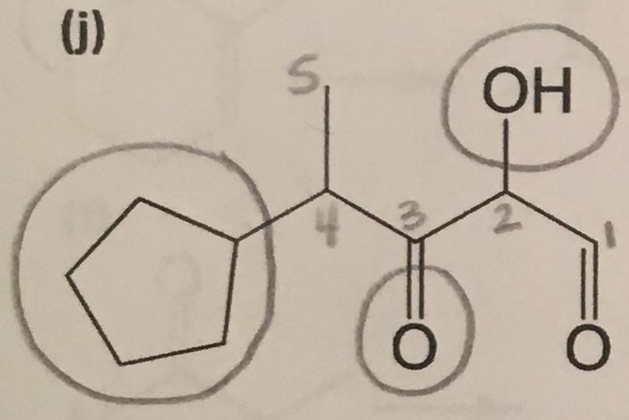
(h)



(i)



(j)



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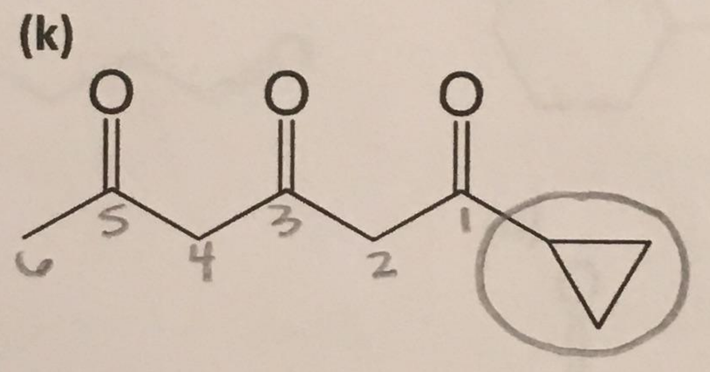
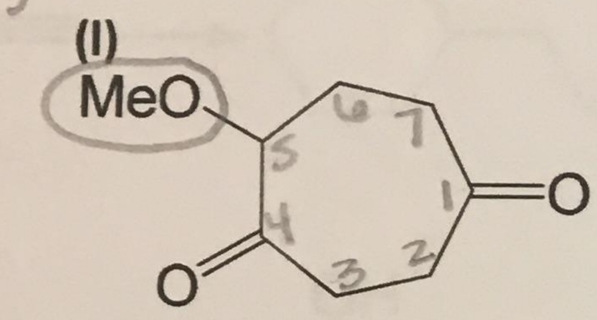
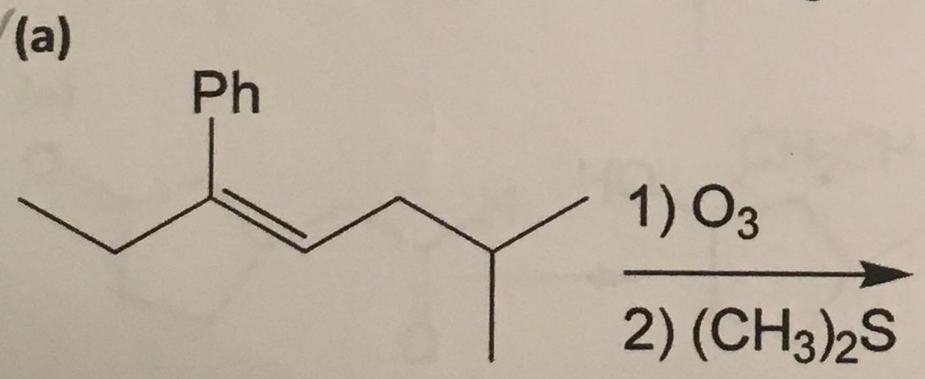


(l)

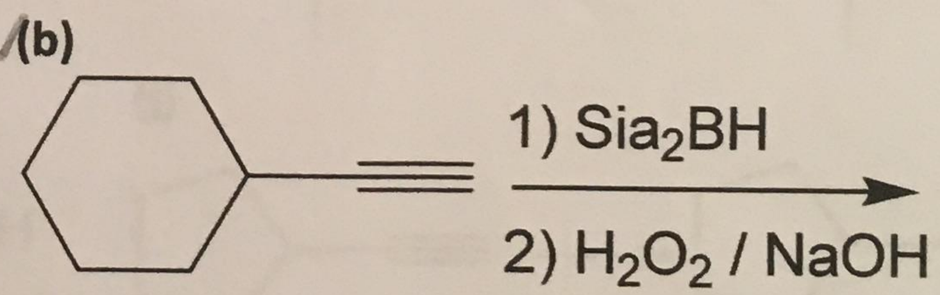


2. Draw the product(s) of the following reactions

✓(a)



✓(b)



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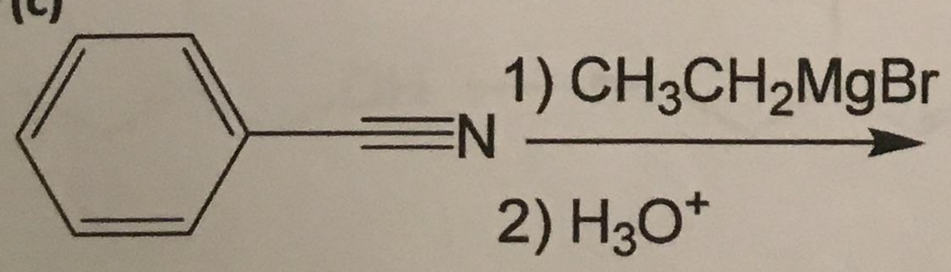

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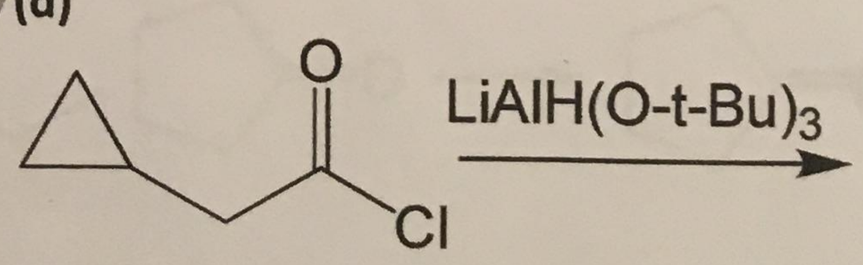


Worksheet VIII

Part 1:

a. 5-bromo-2-propoxybenzaldehyde

b. 4-ethyl-5-methylhex-2-yn-1-al

c. 3-sec-butylhex-3-en-1-al

d. 4-bromo-2-sec-butylcyclopentan-1-one

e. 3-bromo-2-methyl-4-oxohexane-1,6-dial

f. 3-bromo-2-oxocyclohexanecarbaldehyde

g. 6-bromo-2-hydroxy-3,6-dimethyloctan-4-one

h. 5-bromo-8-methoxy-3-phenylnonane-2,7-dione

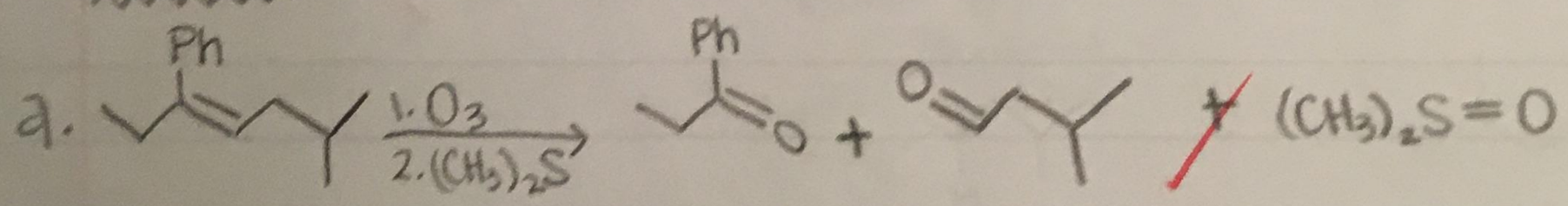
i. 4-bromo-5-ethyl-3-hydroxyhex-5-en-1-al

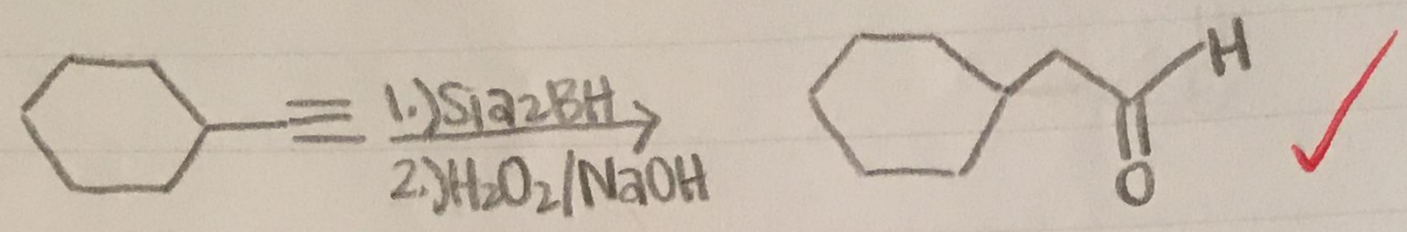
j. 4-cyclopentyl-2-hydroxy-3-oxopentan-1-al

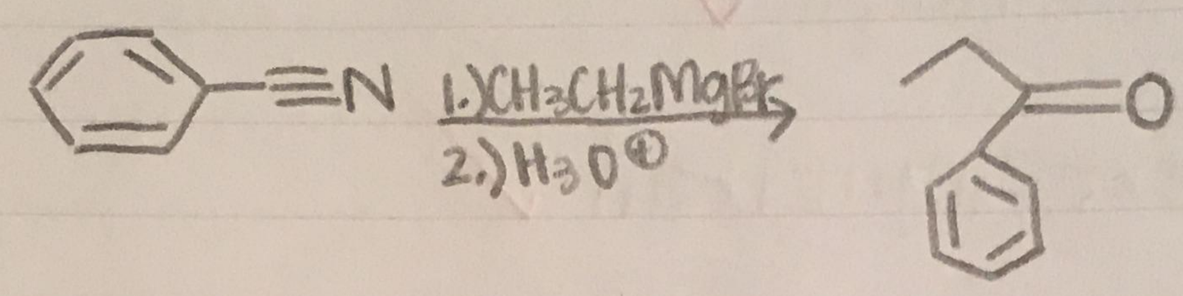
k. 1-cyclopropylhexane-1,3,5-trione

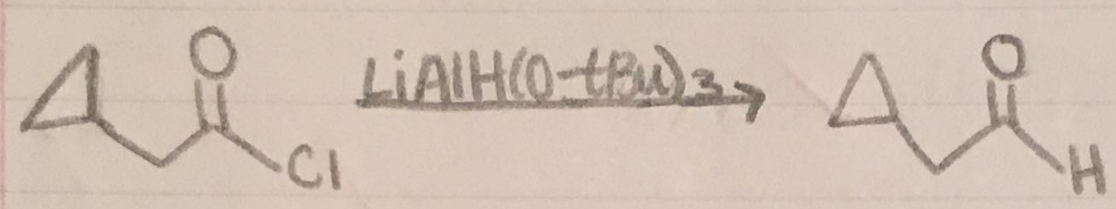
l. 5-methoxycycloheptane-1,4-dione

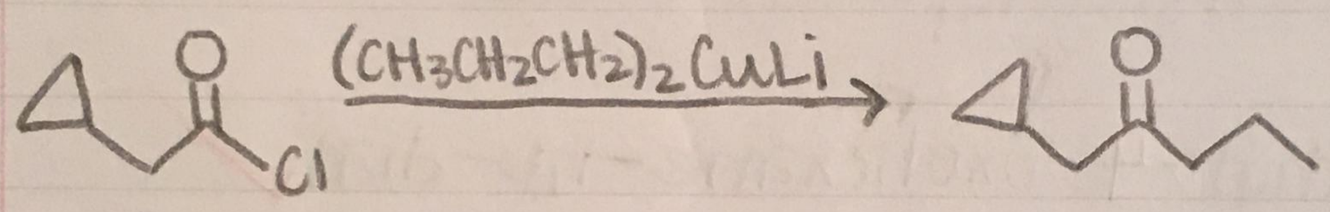
Part 2:

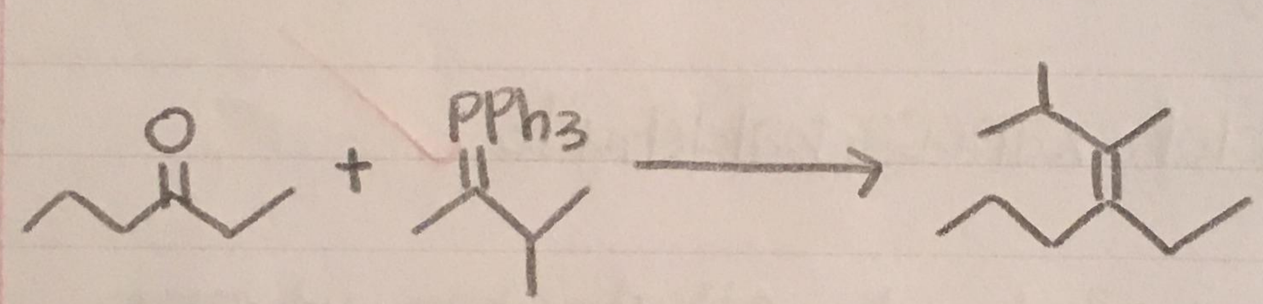
a. 

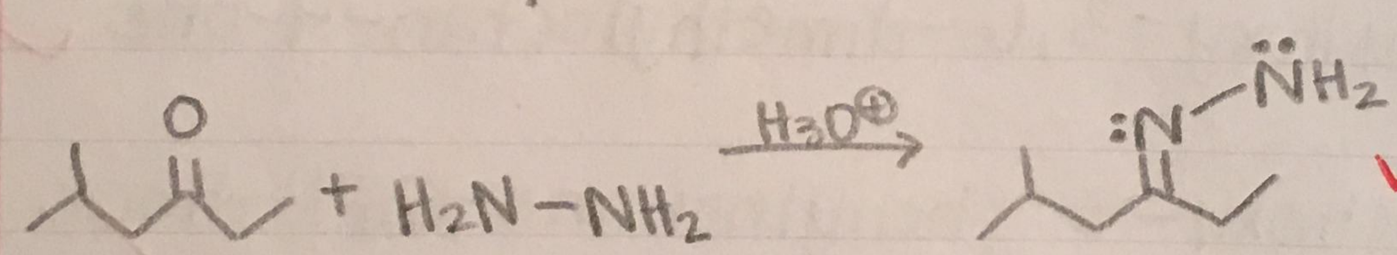
b. 
1.) Sia2BH
2.) H2O2/NaOH
H
O

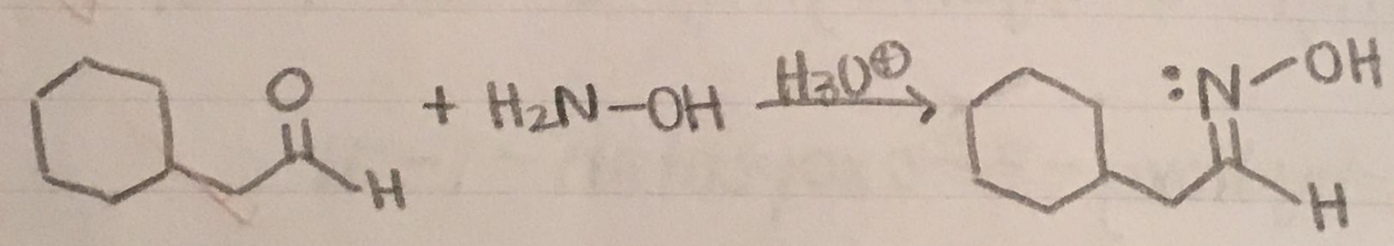
c. 
N
1.) CH3CH2MgBr
2.) H3O⊕
O

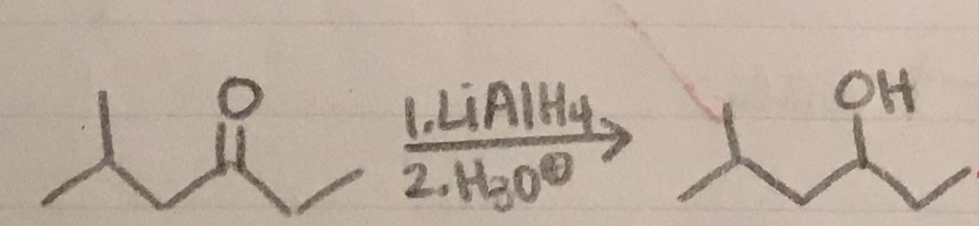
d. 
Cl
LiAlH(O-tBu)3
H

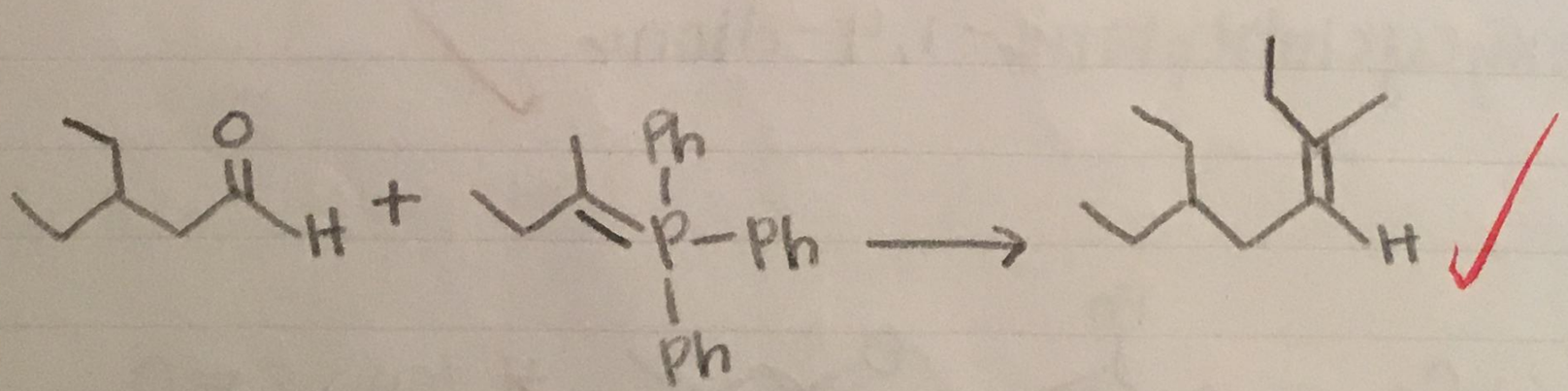
e. 
Cl
(CH3CH2CH2)2CuLi

f. 
PPh3

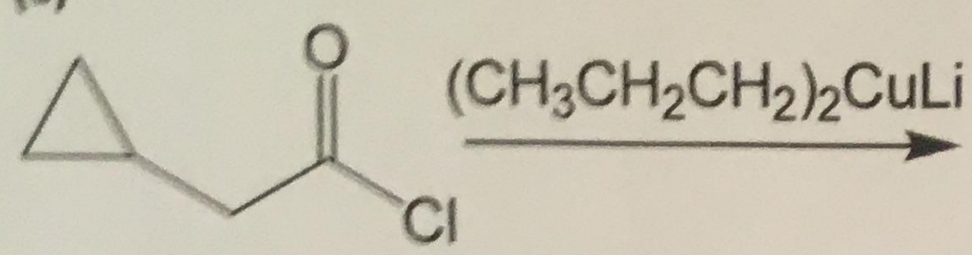
g. 
H2N–NH2
H3O⊕
NH2

h. 
H2N–OH
H3O⊕
OH
H

i. 
1.LiAlH4
2.H3O⊕
OH

j. 
H
Ph
P–Ph
Ph
H

(e)



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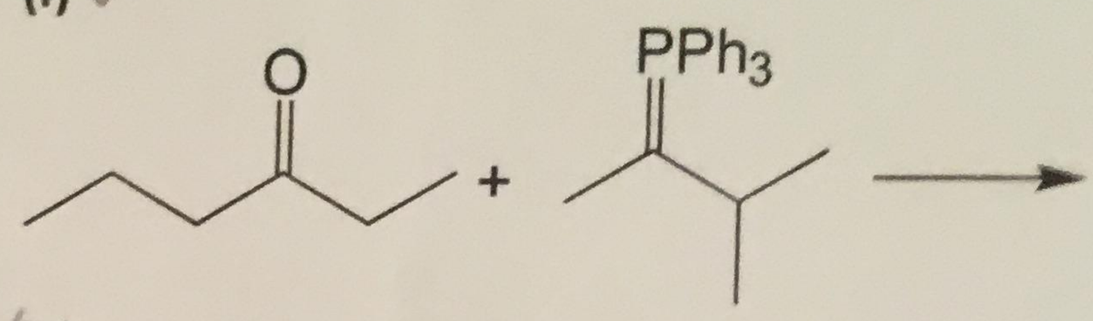

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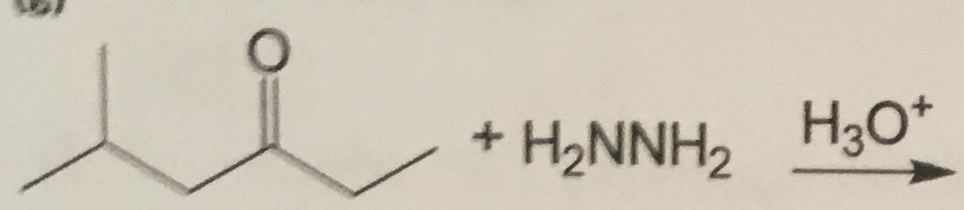

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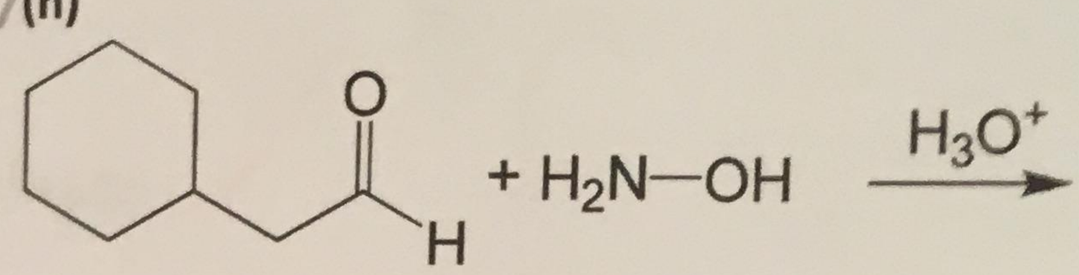

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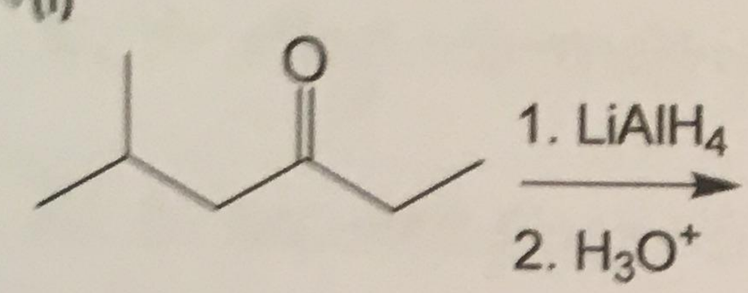
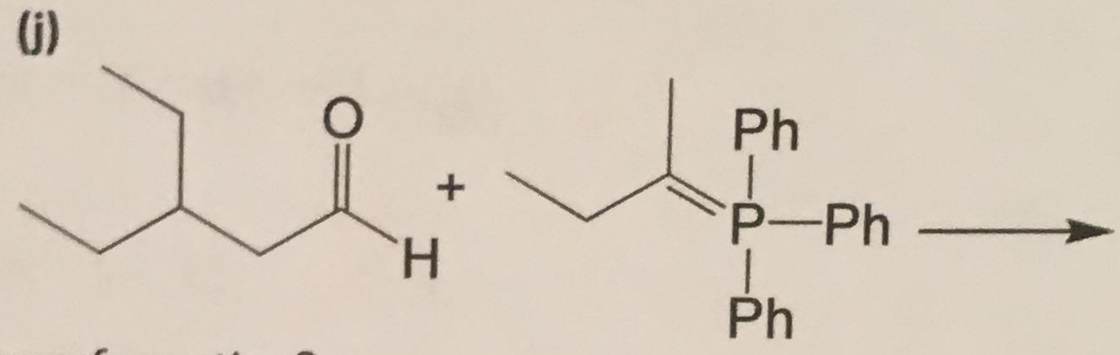
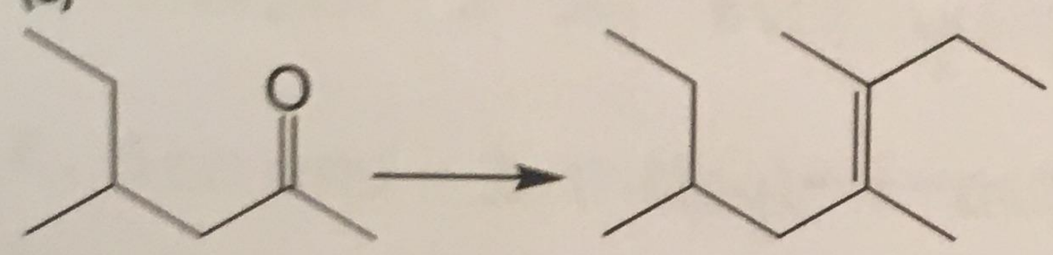


(j)

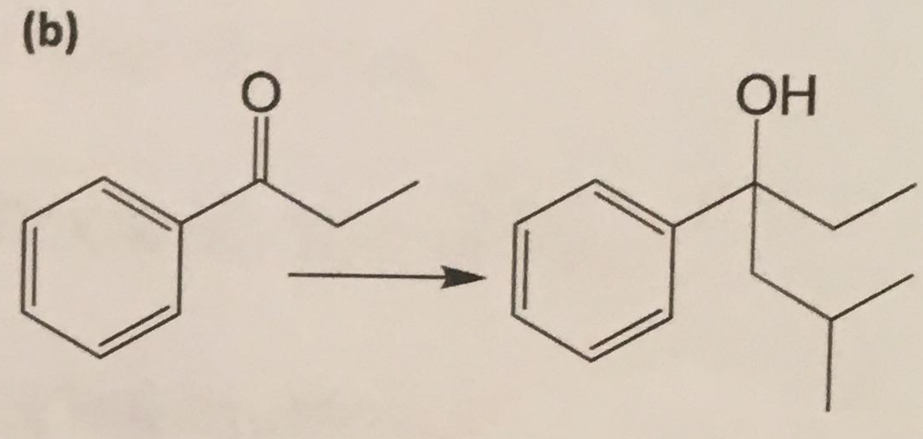


3. How would you achieve the following transformation?

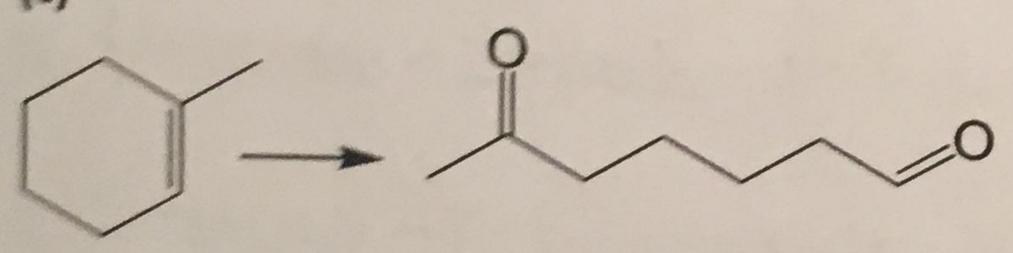
(a)



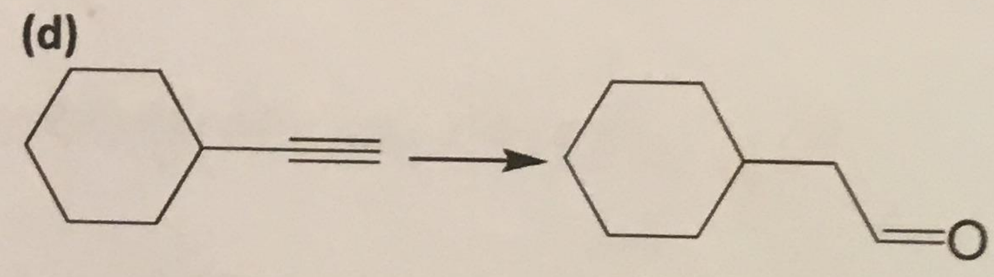
(b)



(c)



(d)



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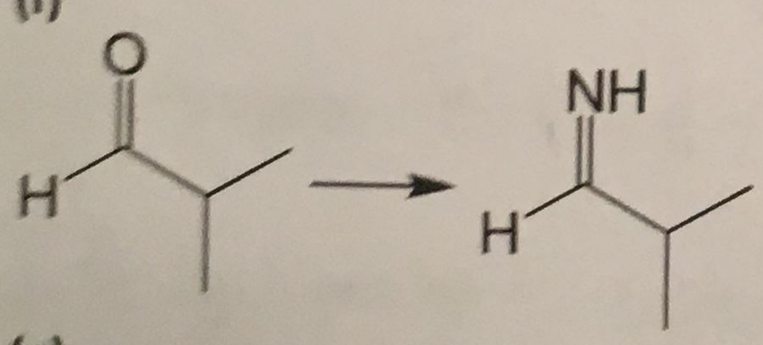

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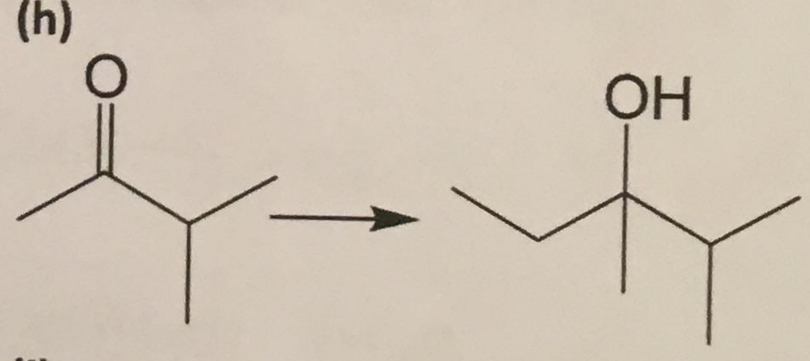
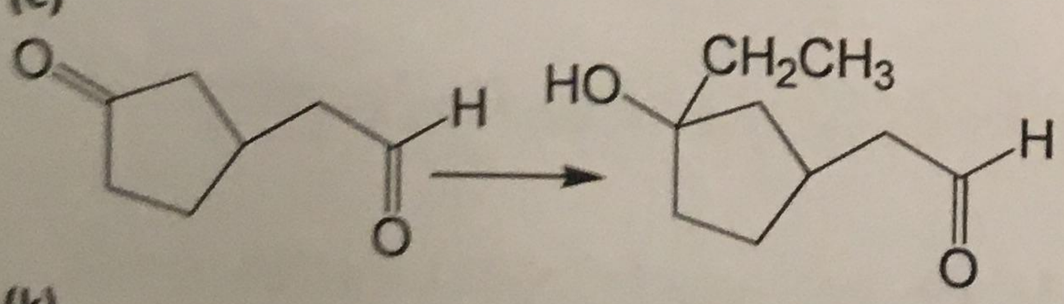


(e)



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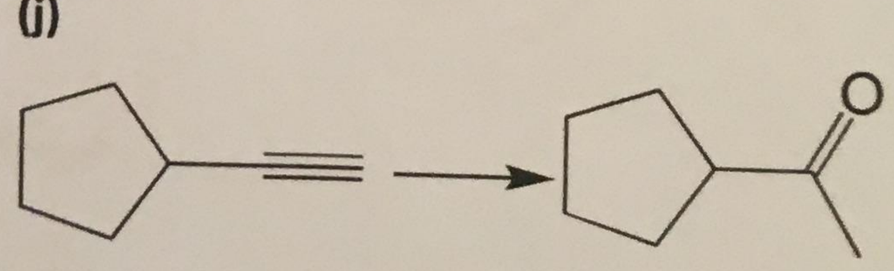
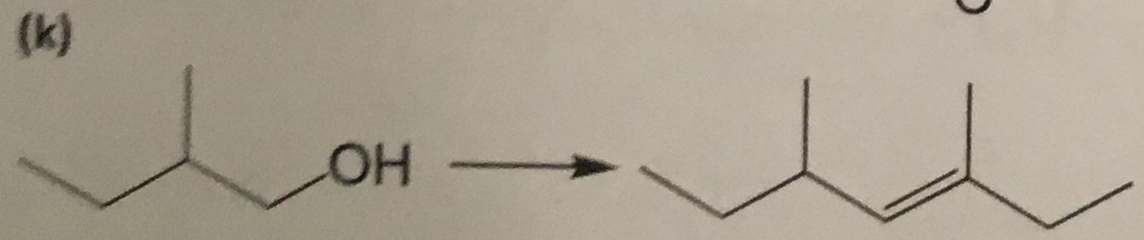
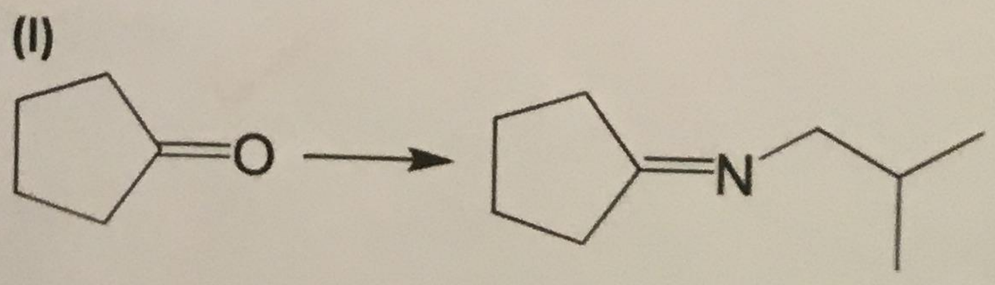


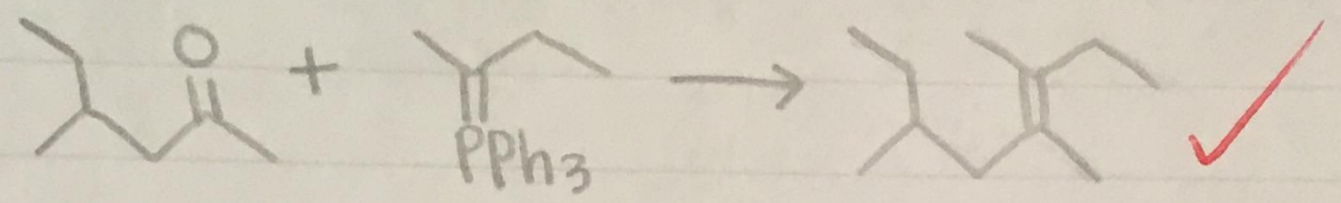
(k)

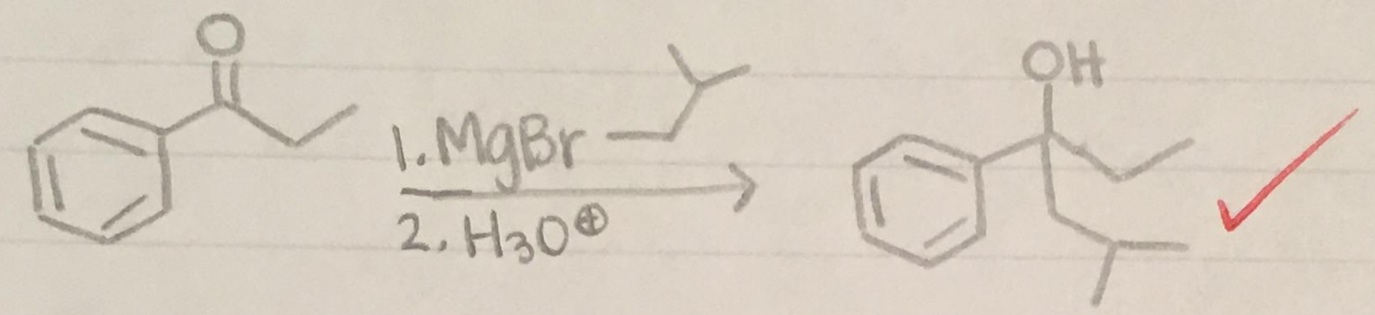


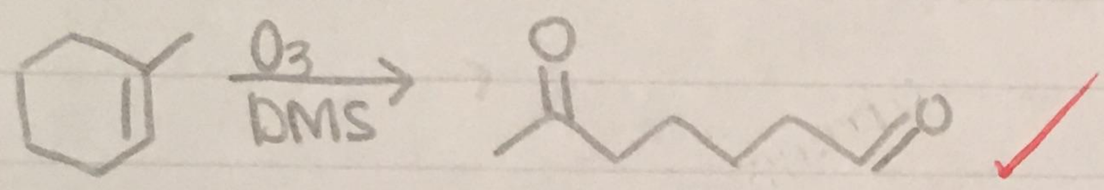
(l)

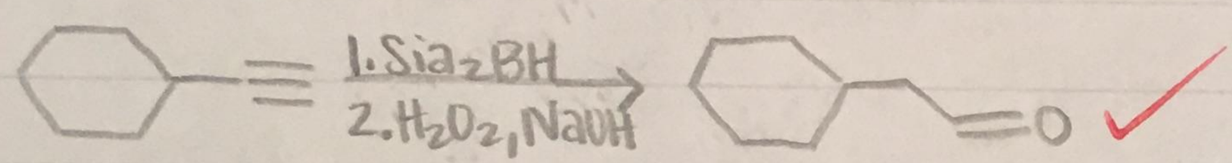


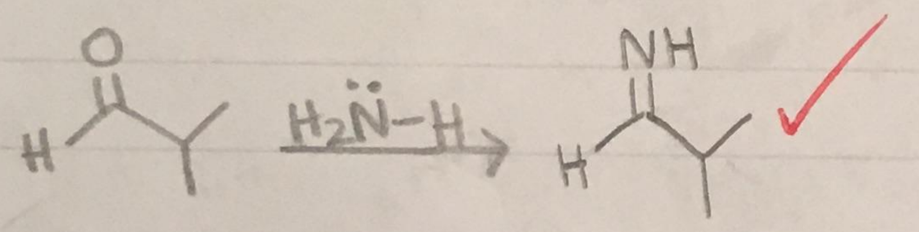
Part 3:

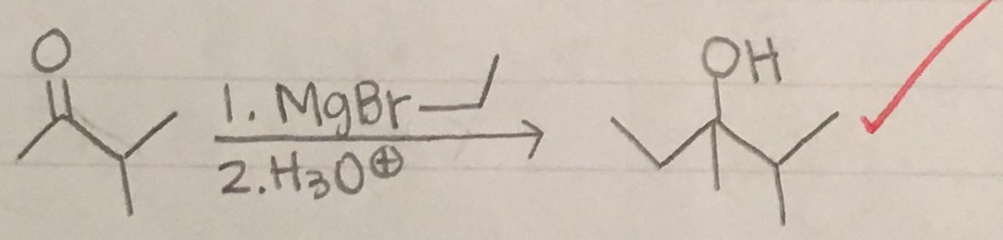
a. 

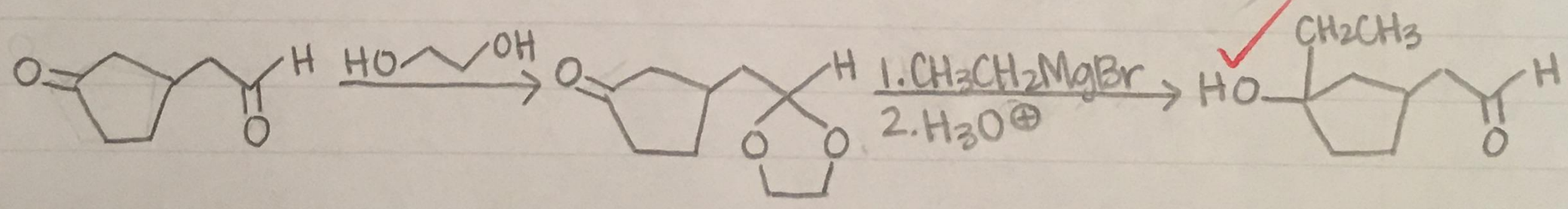
b. 

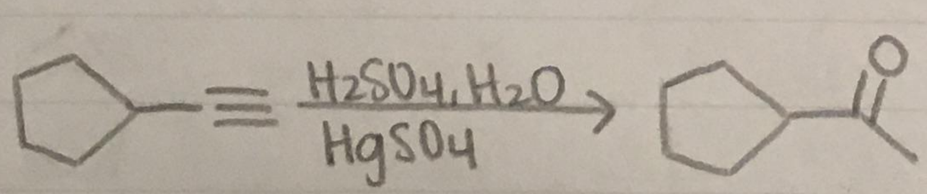
c. 

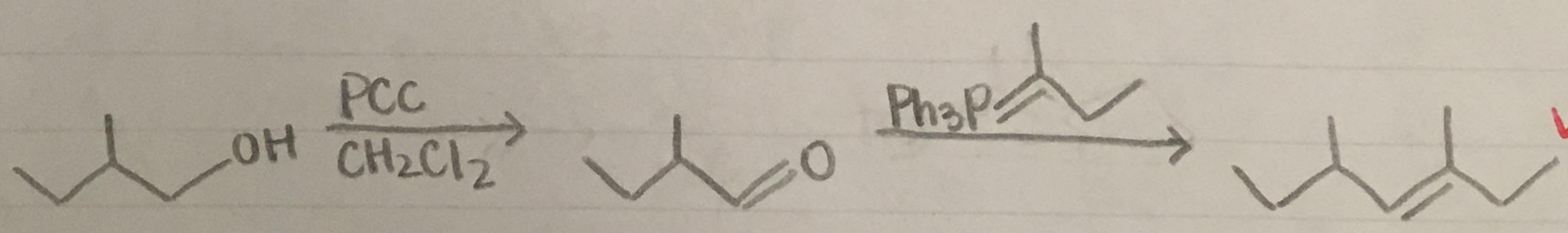
d. 

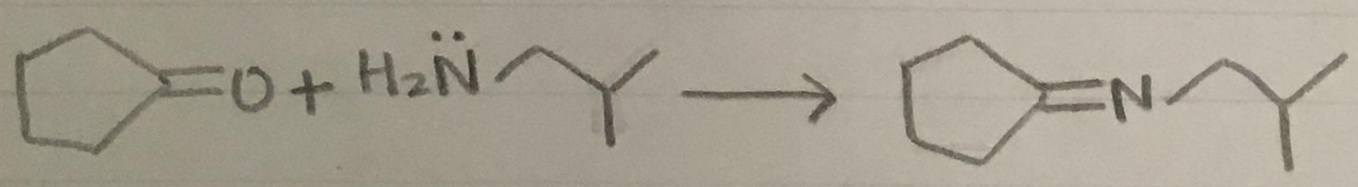
f. 

h. 

e. 

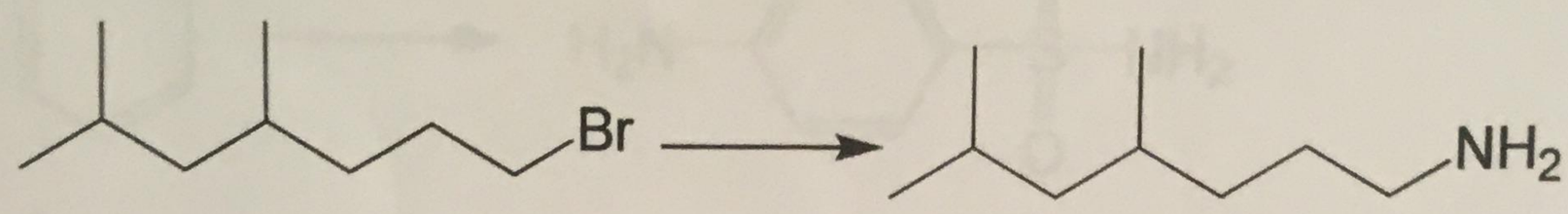
j. 

k. 

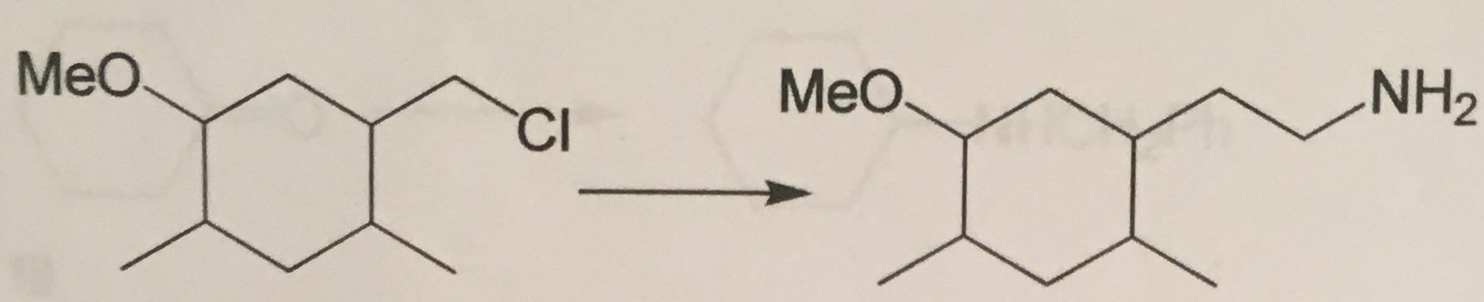
l. 

3. How would you achieve the following transformation?

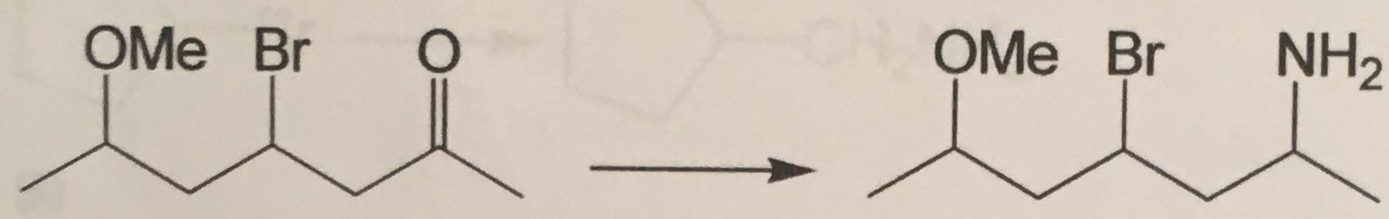
(a)



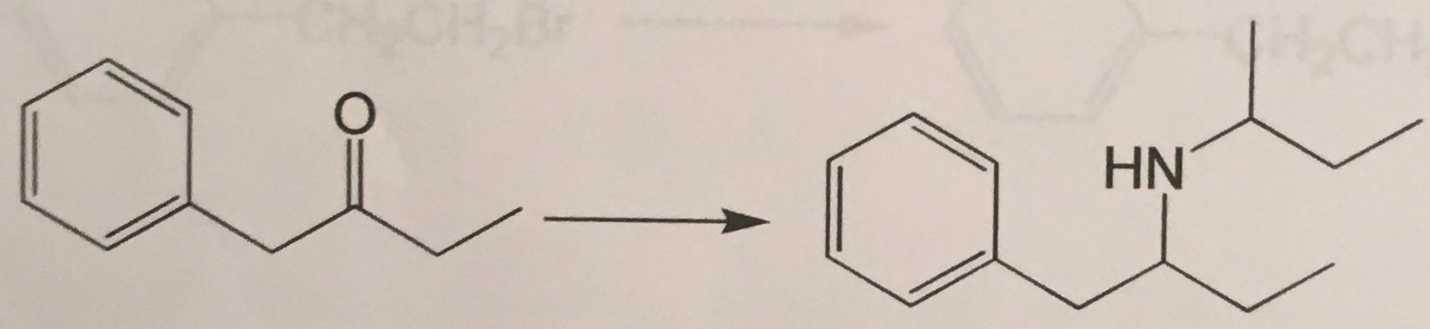
(b)



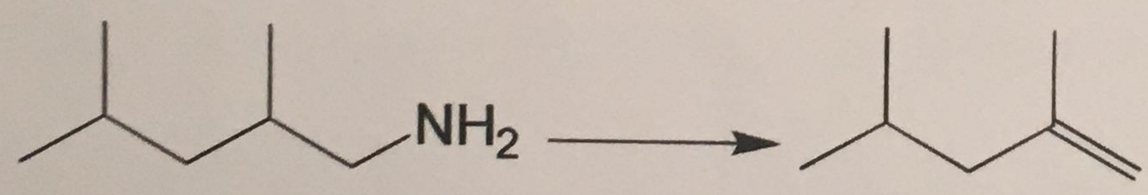
(c)



(d)



(e)



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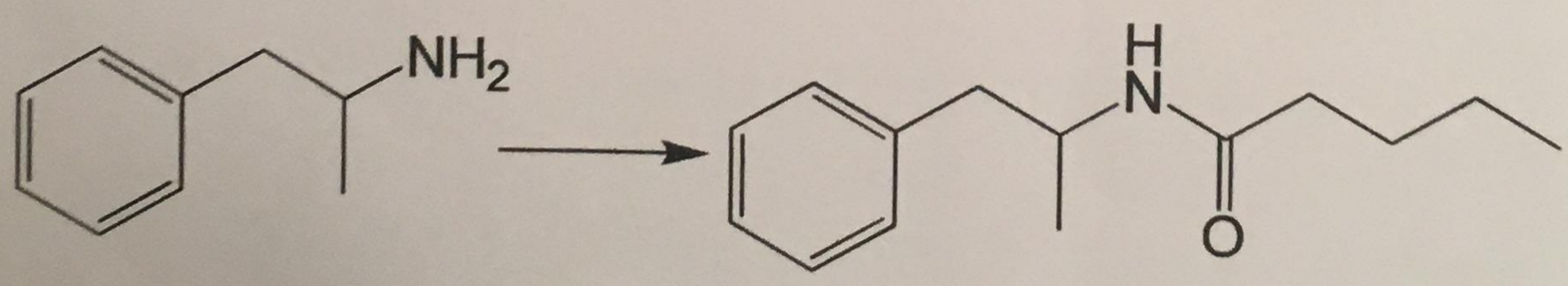
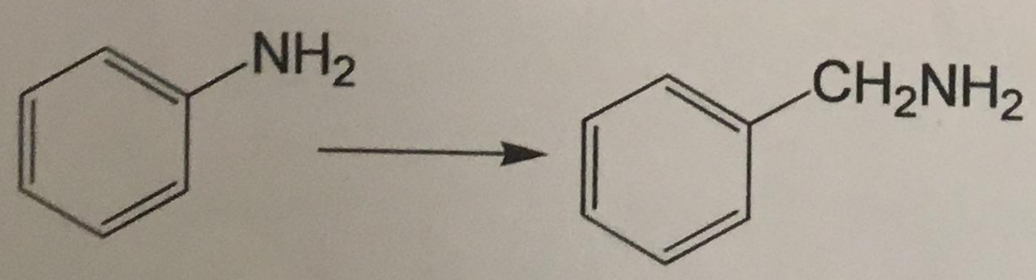
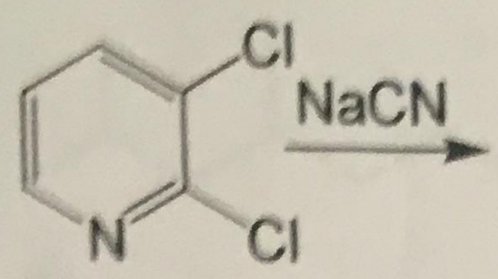


(g)

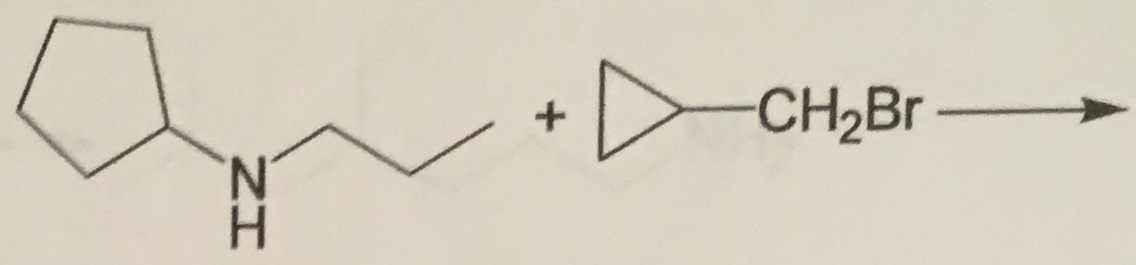


2. Give the major product(s) of each of the following reaction

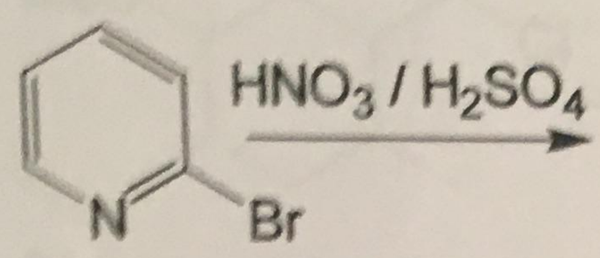
(a)



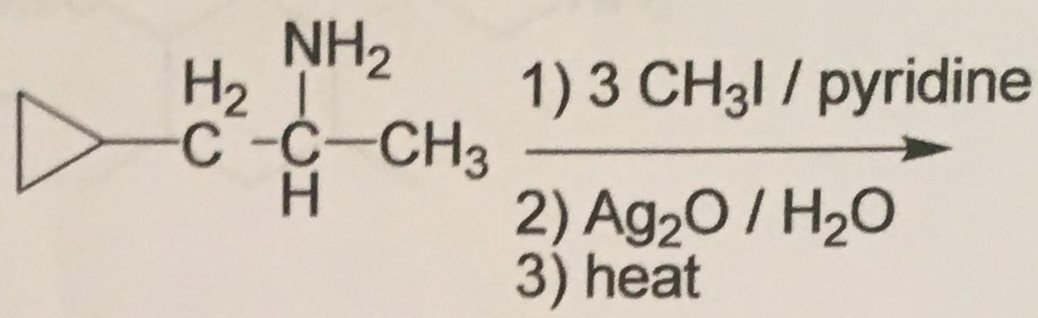
(b)



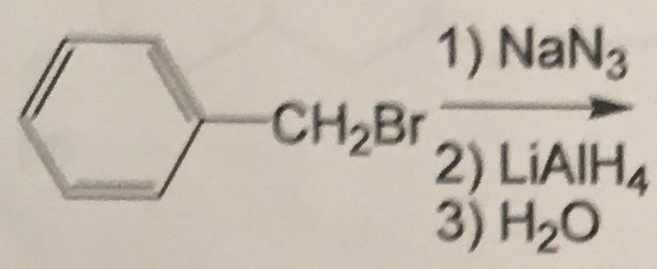
(c)



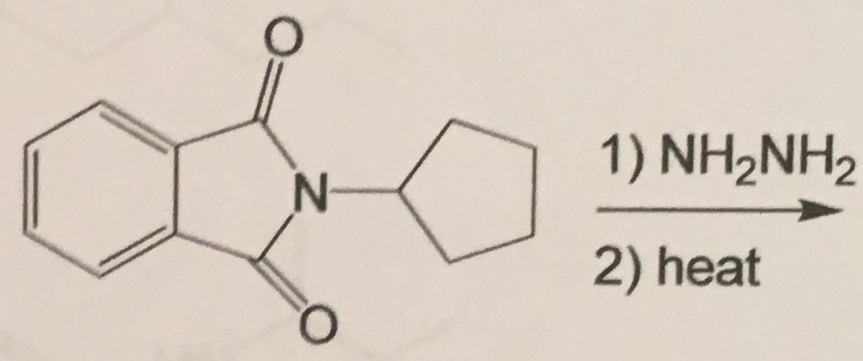
(d)



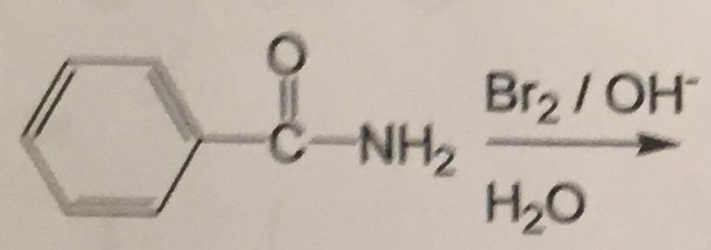
(e)



(f)



(g)



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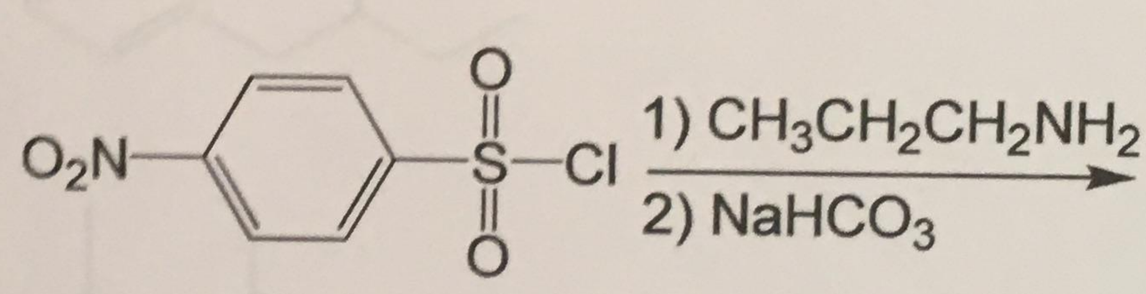
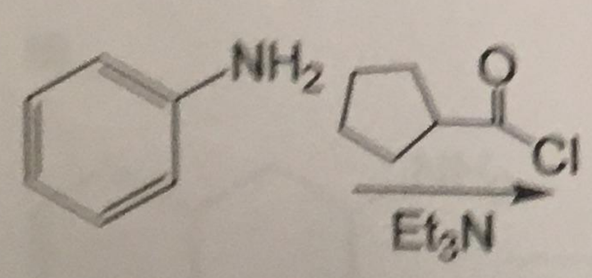


(i)



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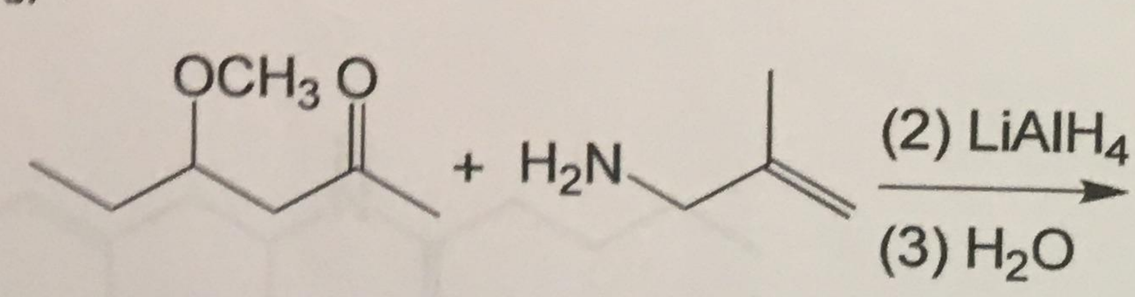
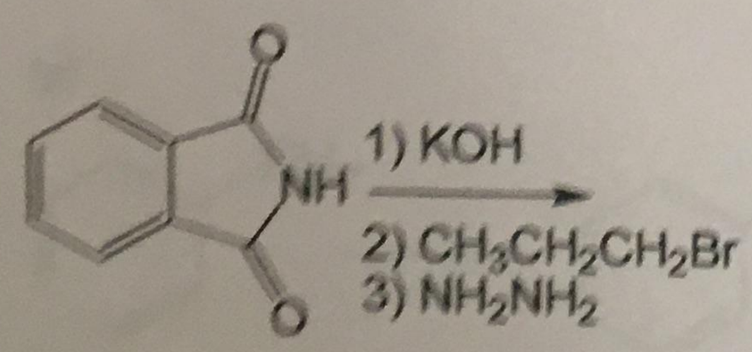


(k)



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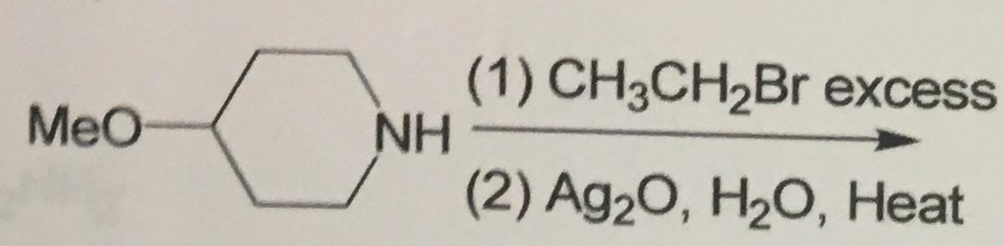

WORKSHEET VIII

1. Name the following compounds

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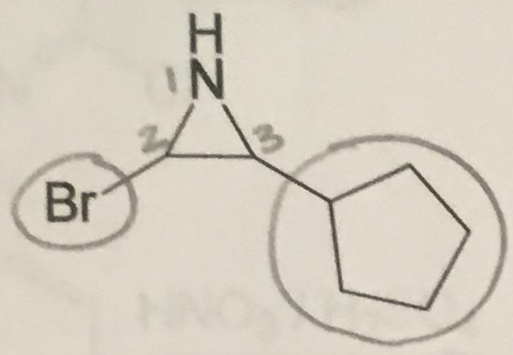

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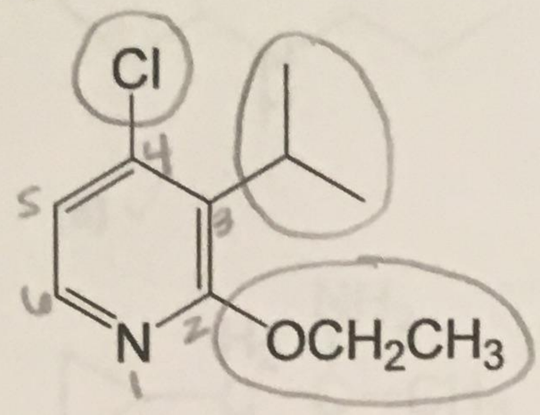

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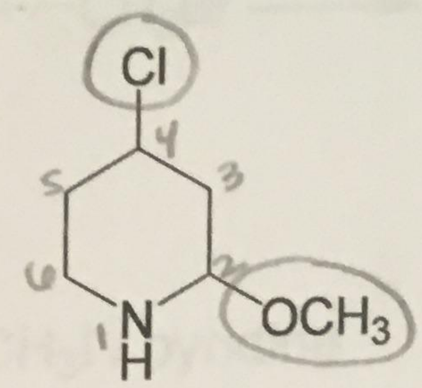

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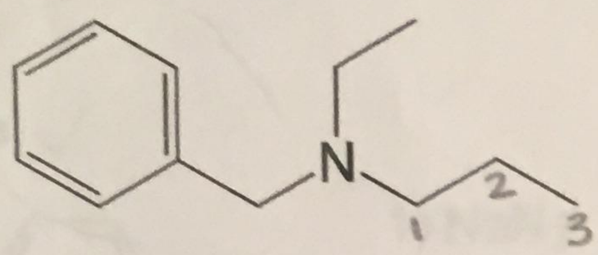

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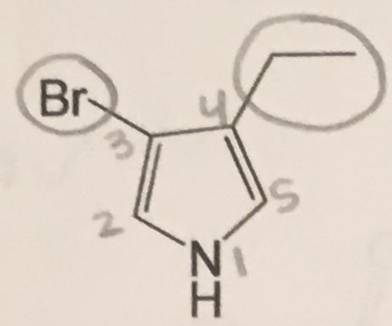

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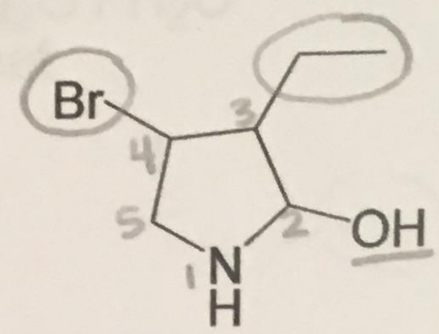

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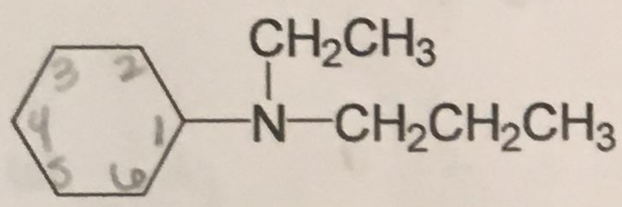

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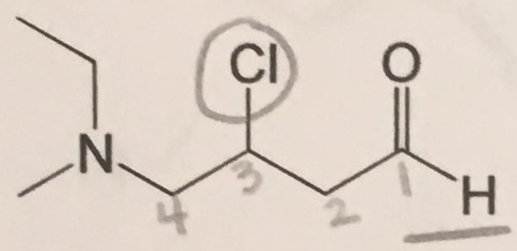

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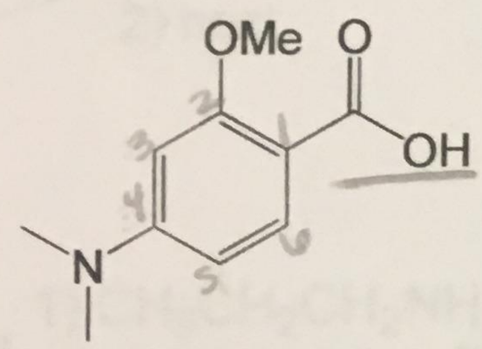

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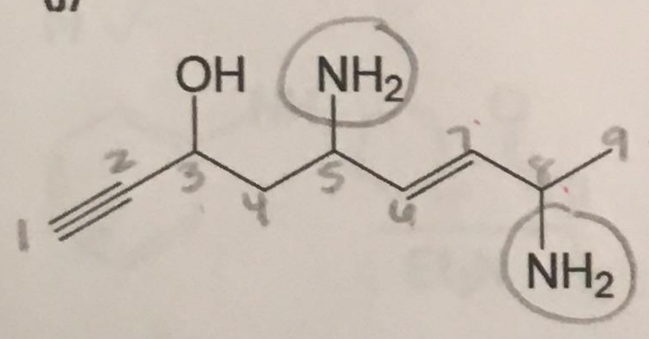

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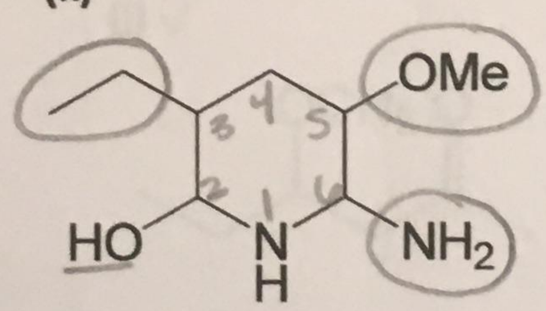

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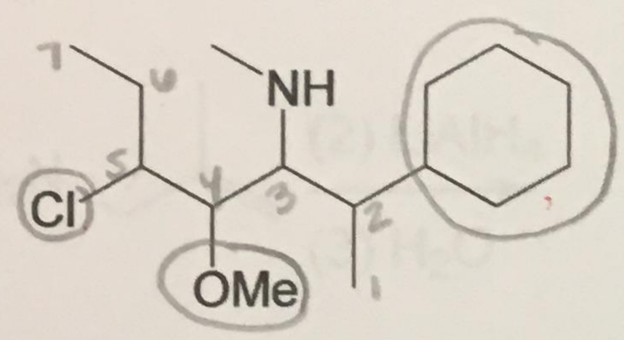

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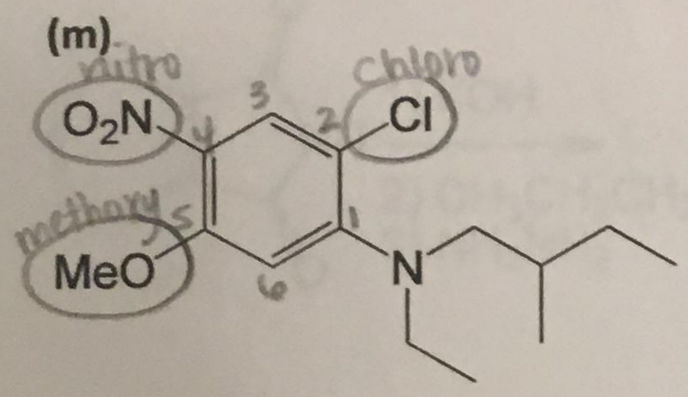

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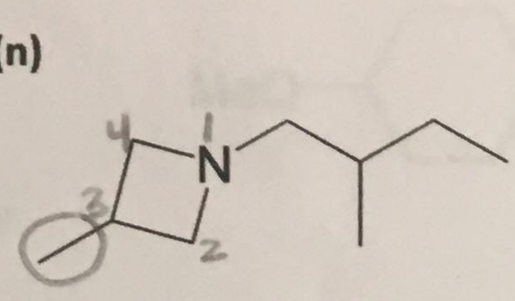

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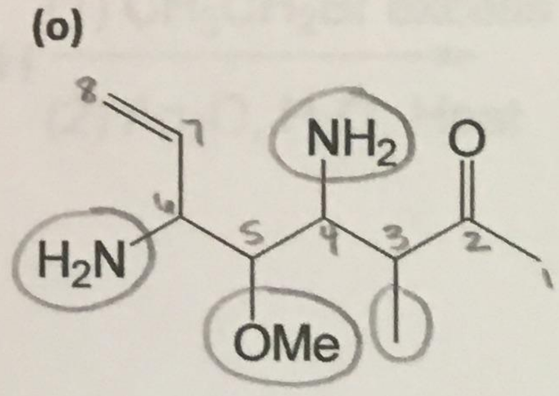

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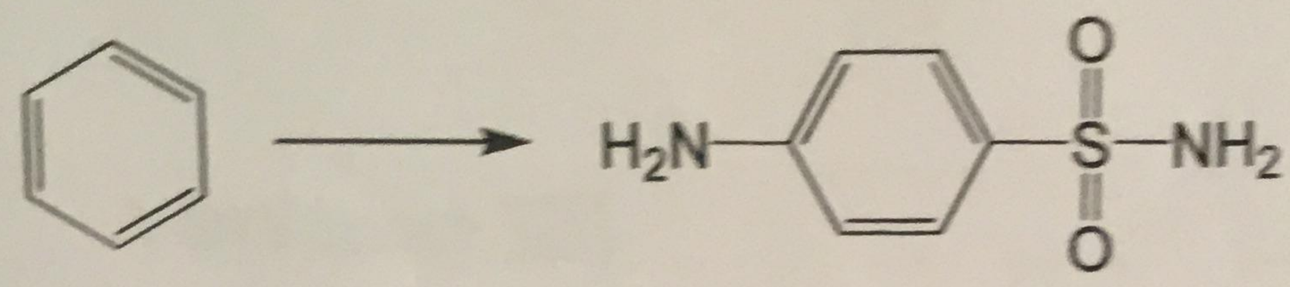

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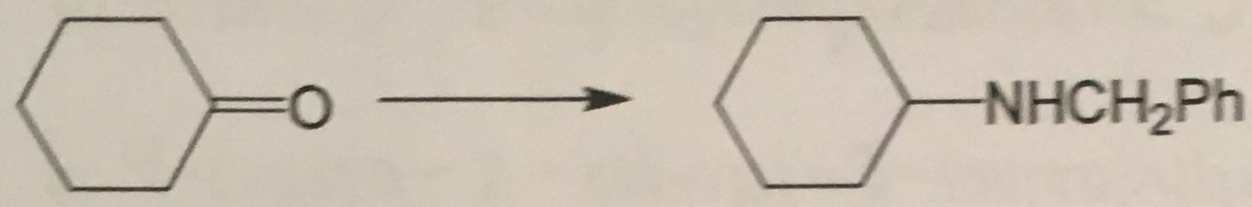

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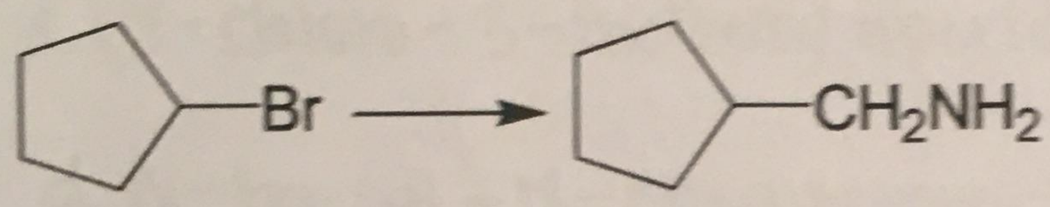

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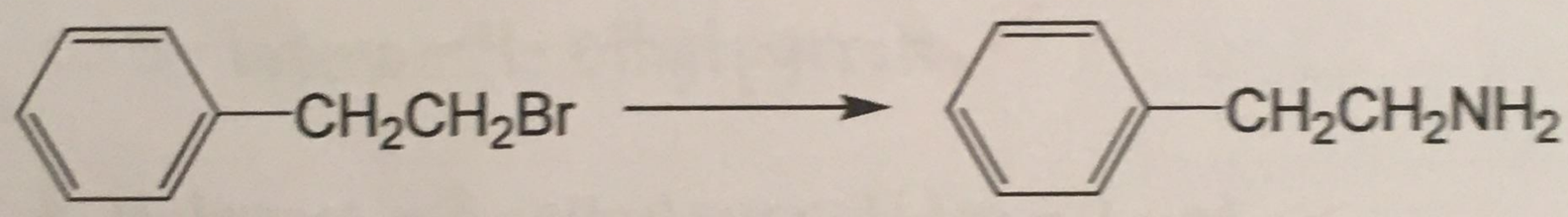
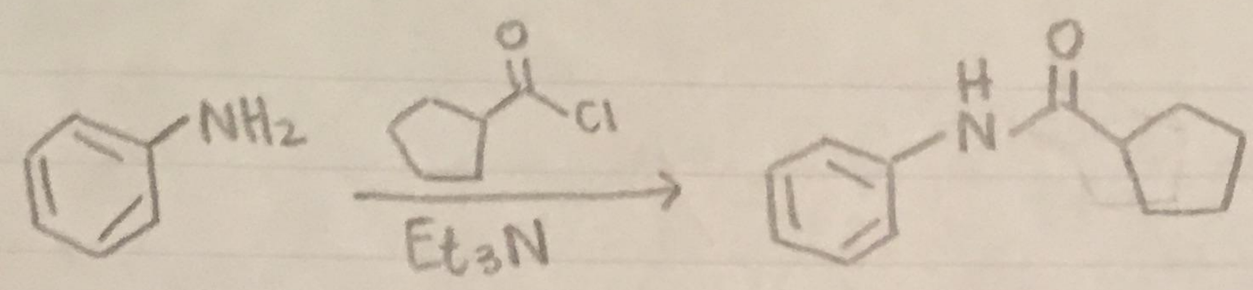
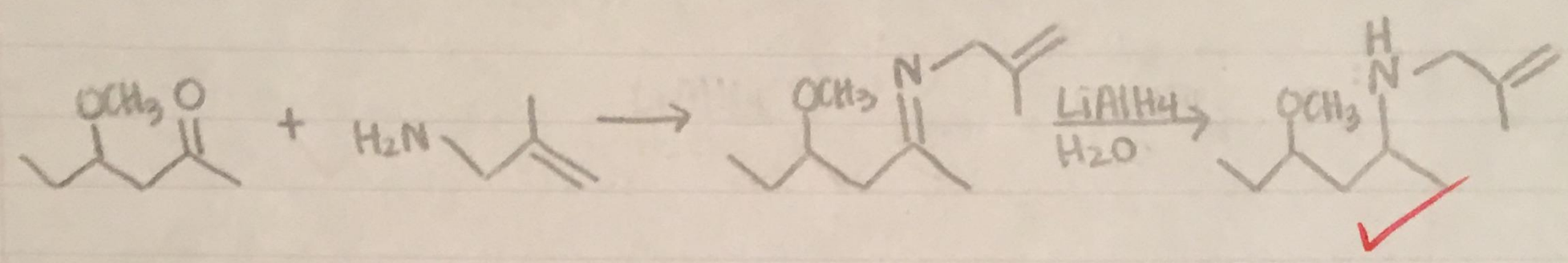
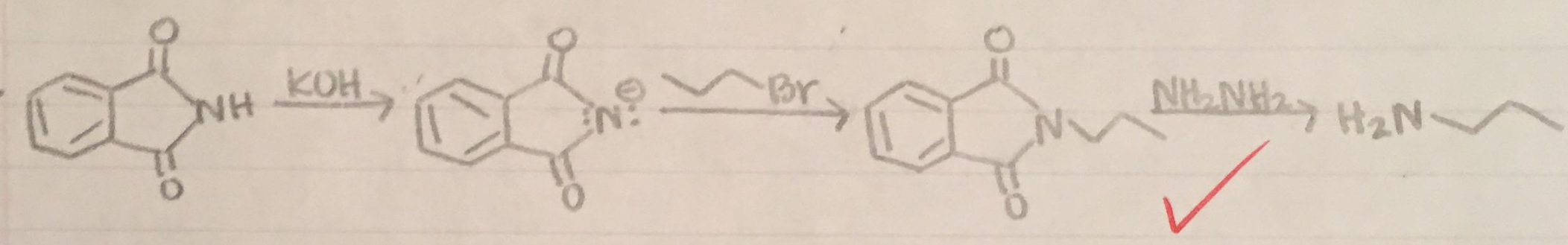
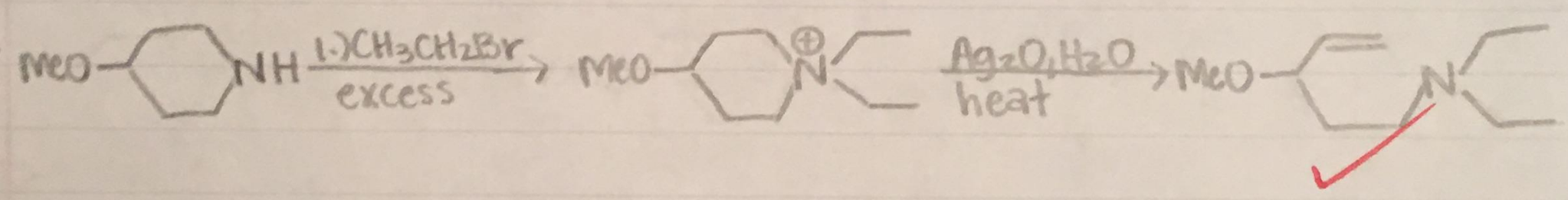


i. 

j. 

K. 

L. 

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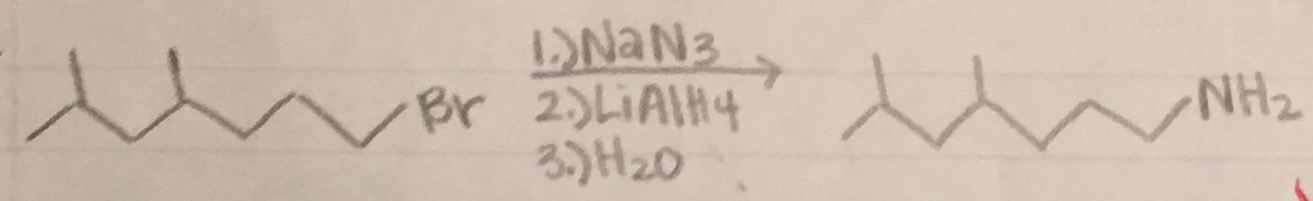
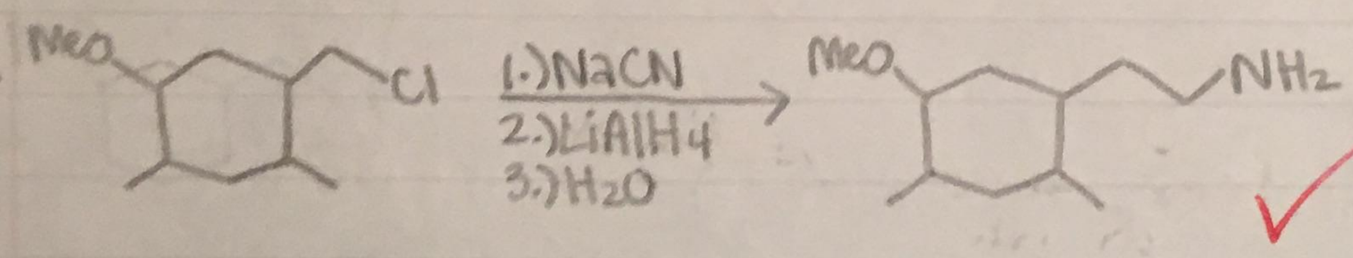
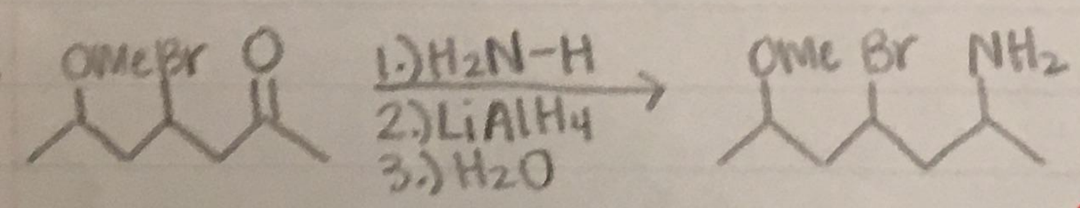
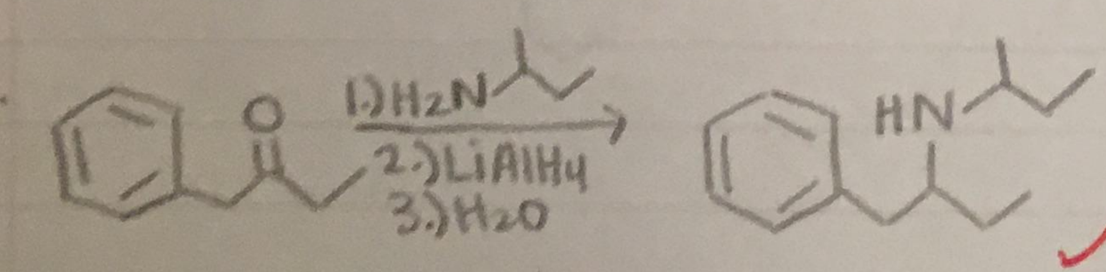
a. 

b. 

c. 

d. 

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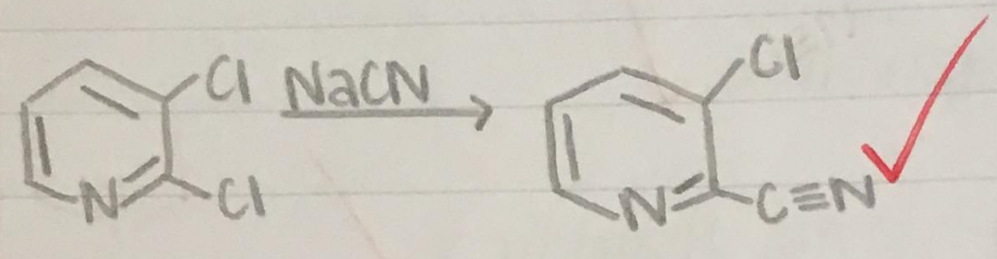
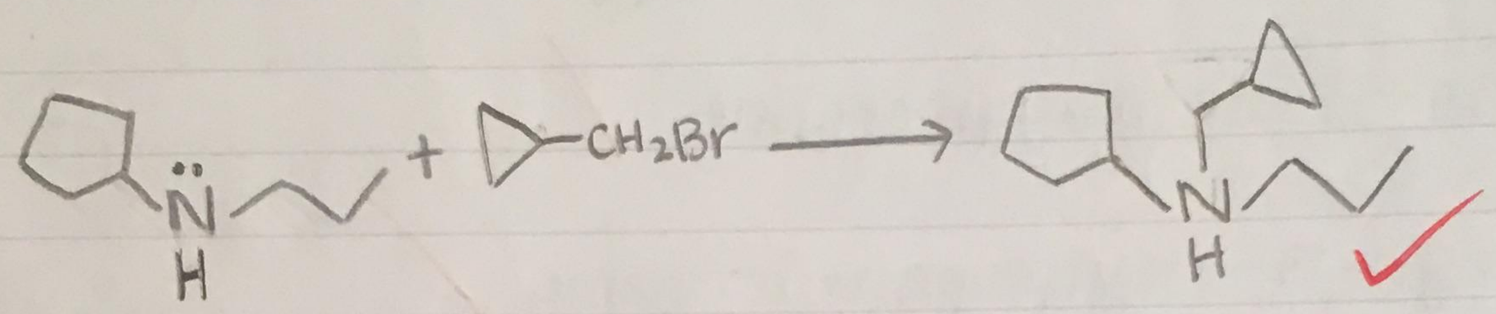
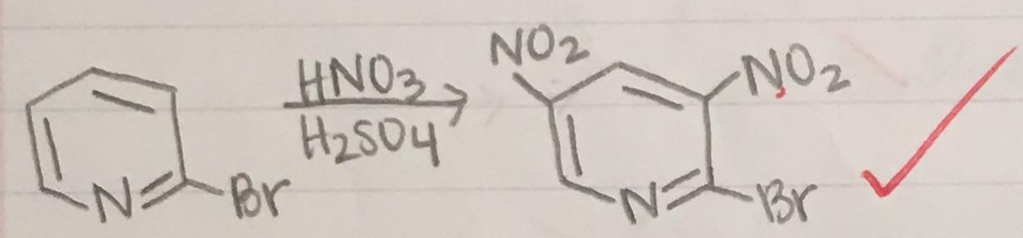
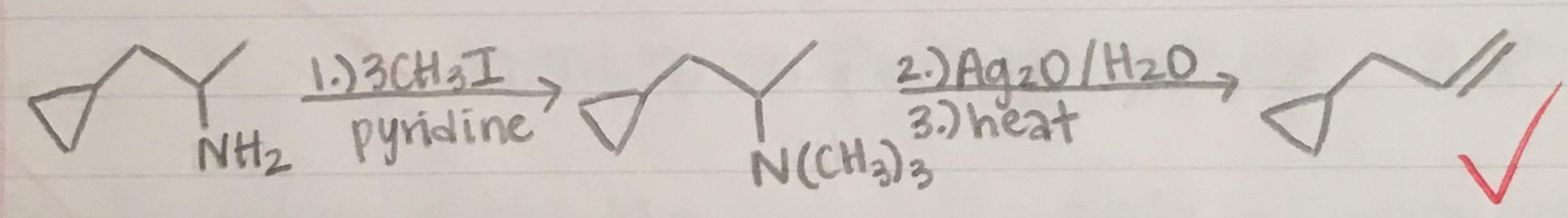
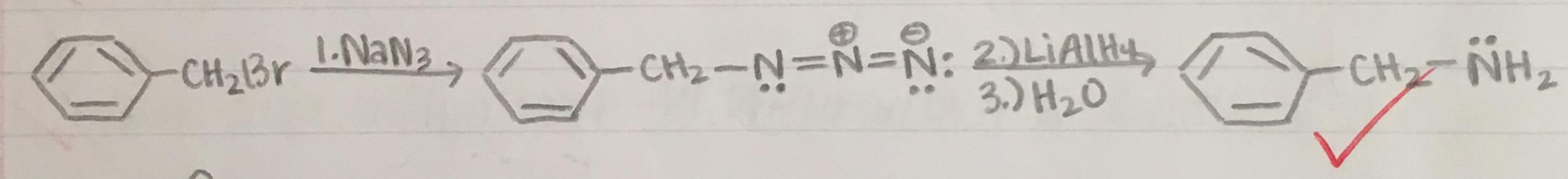
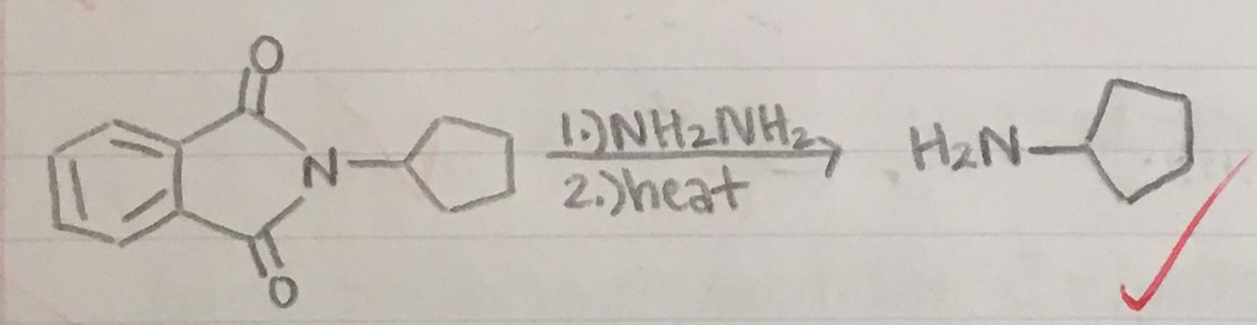
a. 

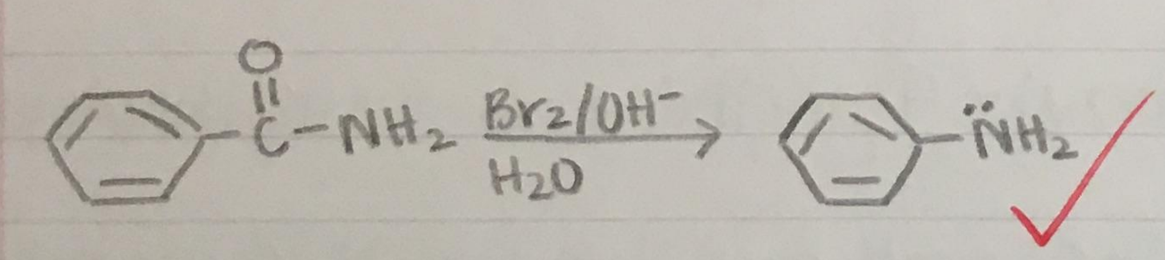
b. 

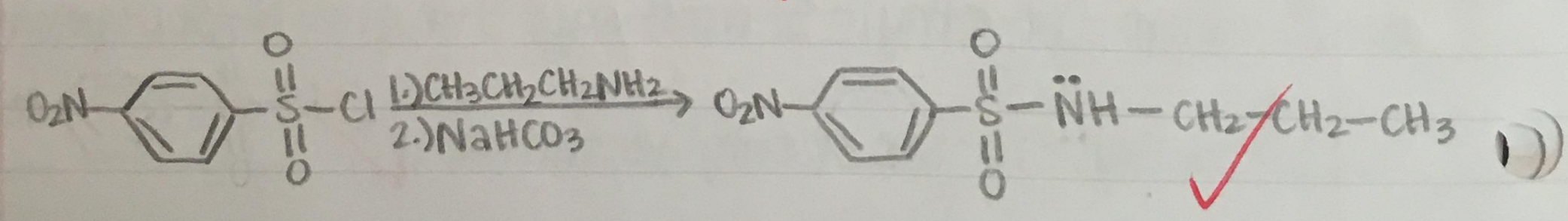
c. 

d. 

e. 

f. 

g. 

h. 

Worksheet VIII

Part 1:

a. 2-bromo-3-cyclopentylaziridine

b. 4-chloro-2-ethoxy-3-isopropylpyridine

c. 4-chloro-3-methoxypiperidine

d. N-benzyl-N-ethylpropan-1-amine

e. 3-bromo-4-ethylpyrrole

f. 4-bromo-3-ethylpyrrolidin-2-ol

g. N-ethyl-N-propylcyclohexan-1-amine

h. 4-amino-3-chloro-N-ethyl-N-methylbutan-1-al

i. 4-amino-2-methoxy-N,N-dimethylbenzoic acid

j. 5,8-diaminonon-6-en-1-yn-3-ol

k. 6-amino-3-ethyl-5-methoxypiperidin-2-ol

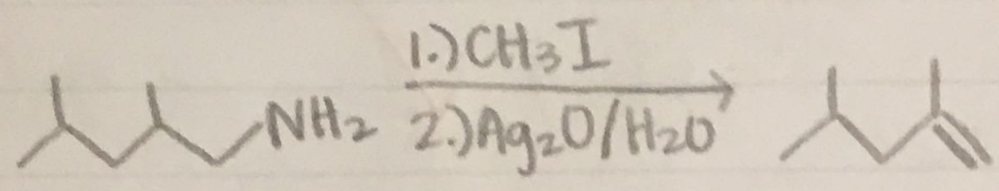
l. 5-chloro-2-cyclohexyl-4-methoxy-N-methylheptan-3-amine

m. 2-chloro-N-ethyl-5-methoxy-4-nitro-N-sec-pentylaniline

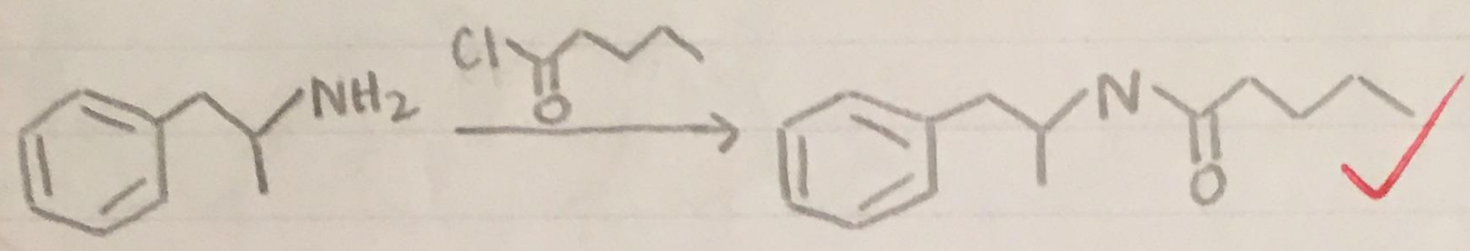
n. 3-methyl-N-sec-pentylazetidine

o. 4,6-diamino-5-methoxy-3-methyloct-7-en-2-one

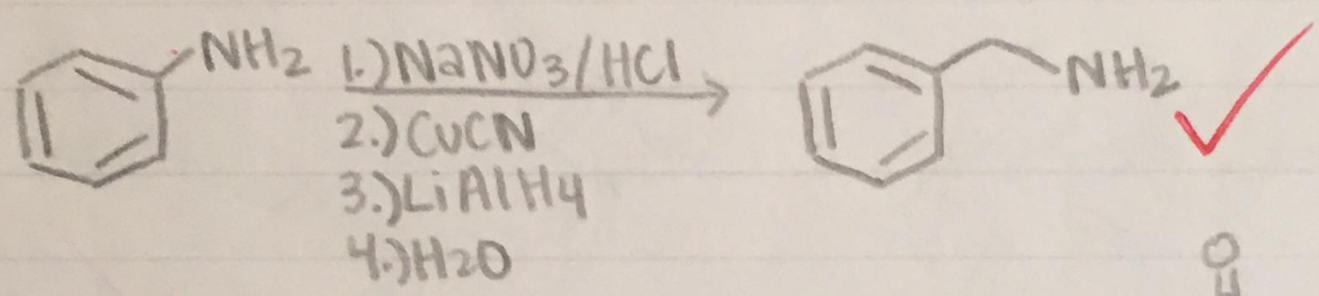
e.


NH2
1.) CH3I
2.) Ag2O/H2O

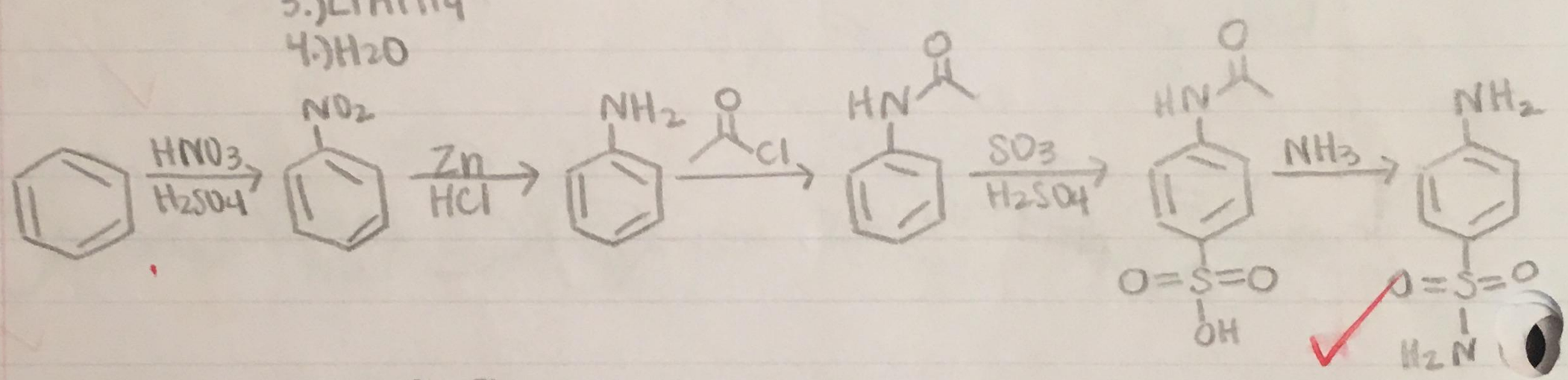
f.


NH2
Cl
N

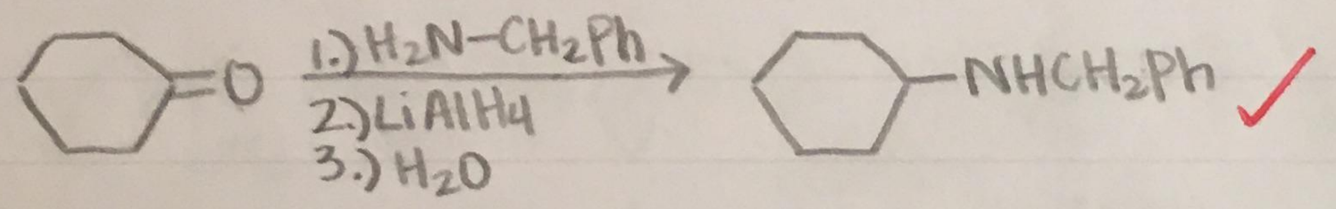
g.


NH2
1.) NaNO3/HCl
2.) CuCN
3.) LiAlH4
4.) H2O
NH2

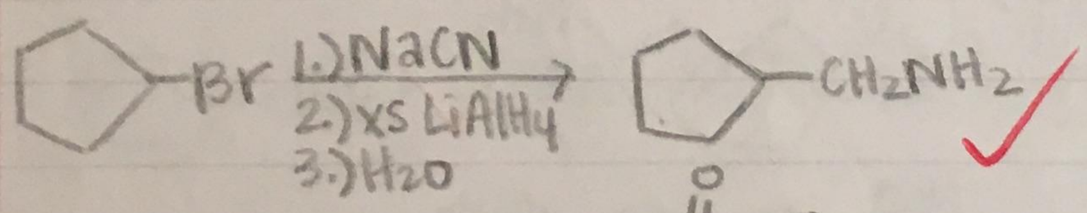
h.


HNO3
H2SO4
NO2
Zn
HCl
NH2
Cl
HN
SO3
H2SO4
O=S=O
OH
NH3
NH2
O=S=O
H2N

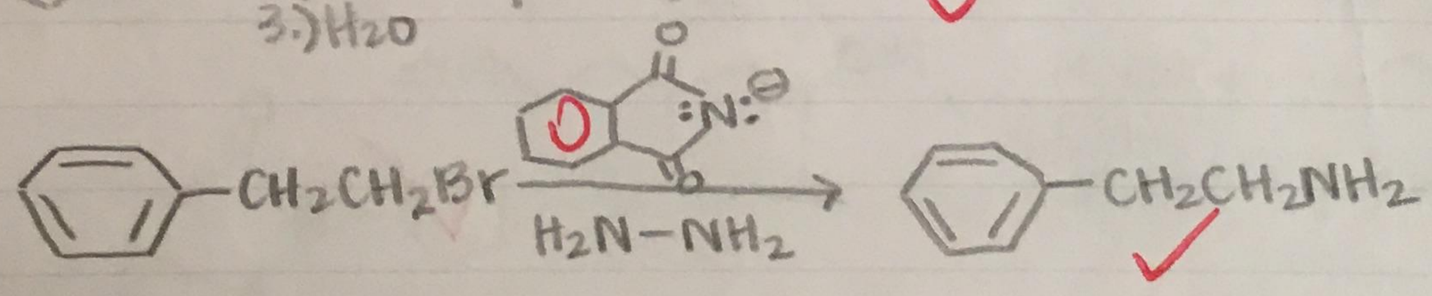
i.


O
1.) H2N-CH2Ph
2.) LiAlH4
3.) H2O
NHCH2Ph

j.

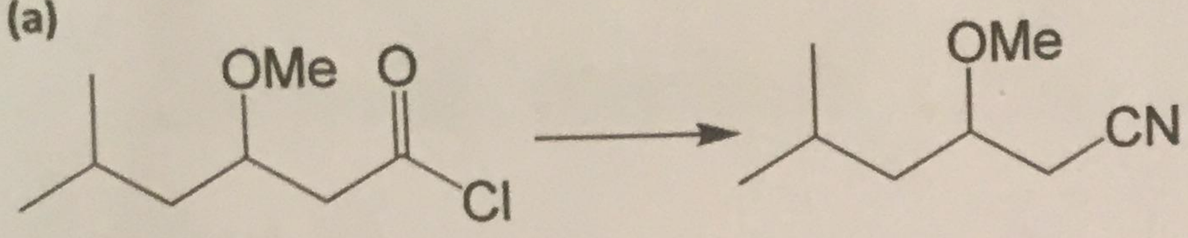

Br
1.) NaCN
2.) xs LiAlH4
3.) H2O
CH2NH2

k.


CH2CH2Br
O
N
H2N-NH2
CH2CH2NH2

. Suggest a good synthetic method for preparing each of the following compounds from the given starting material(s)

(a)



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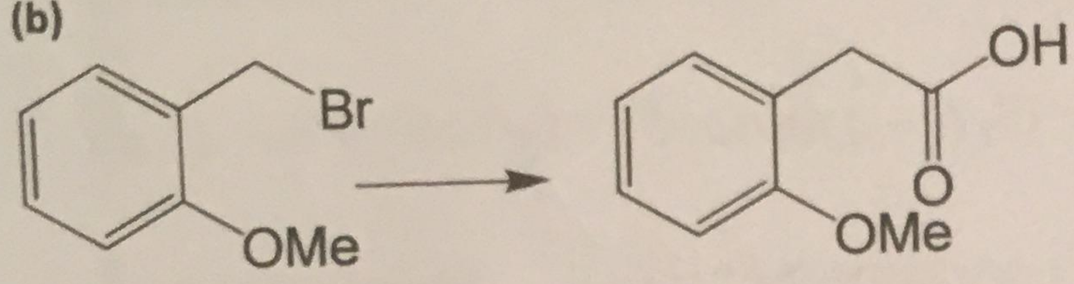

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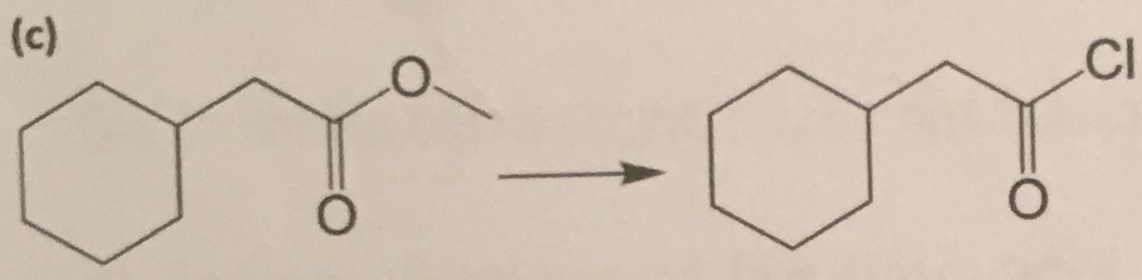

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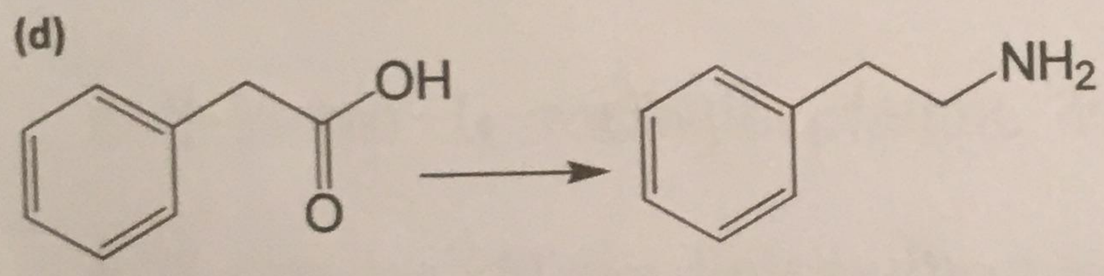

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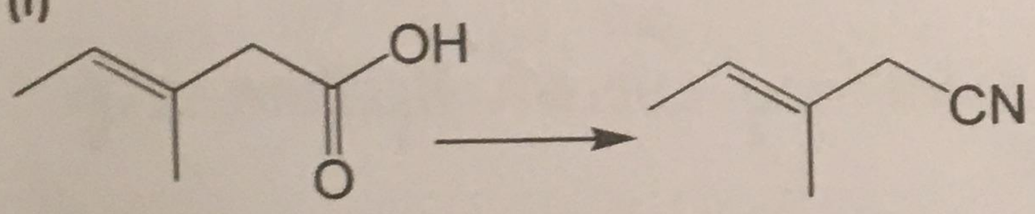

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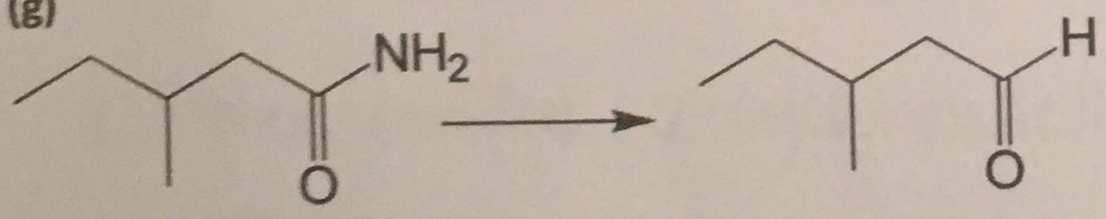

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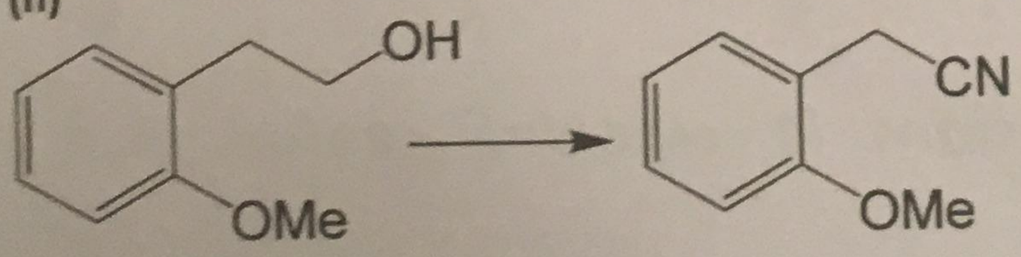
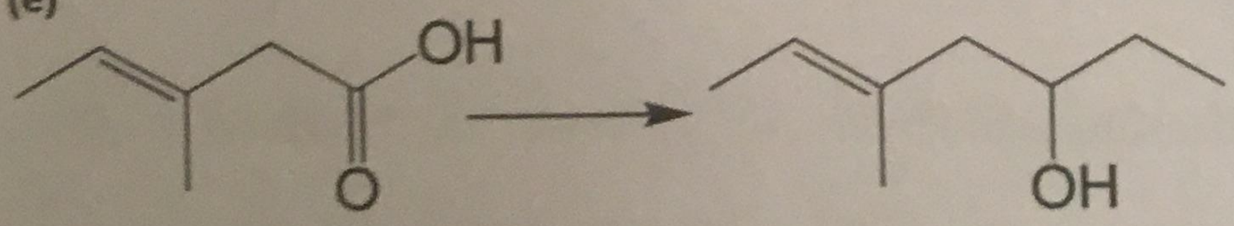


(e)



Give the major product(s) of each of the following reaction

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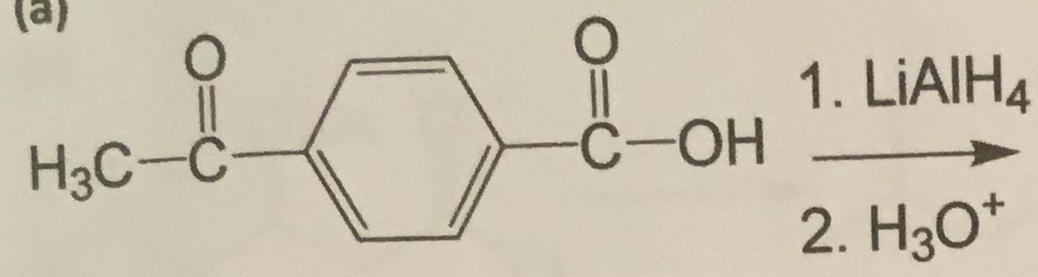
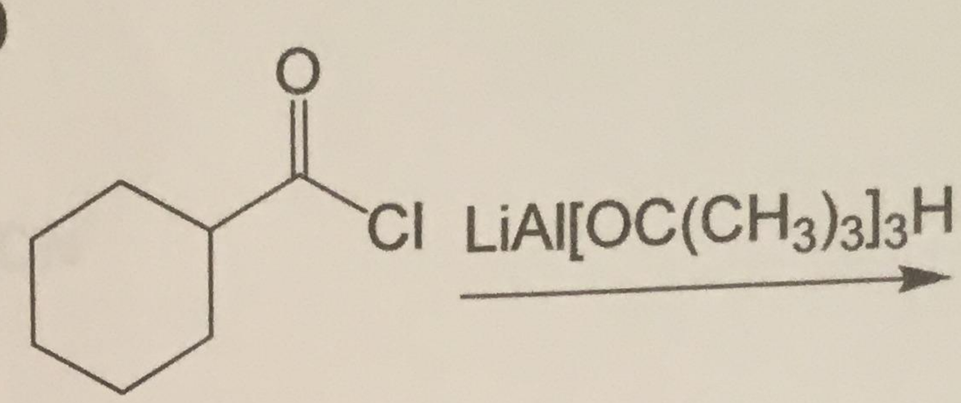


(b)



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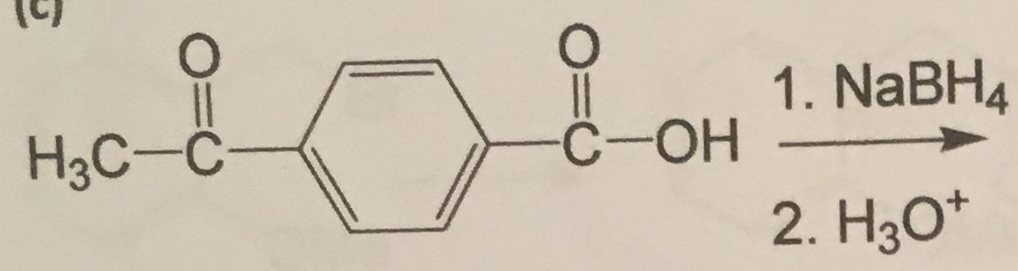

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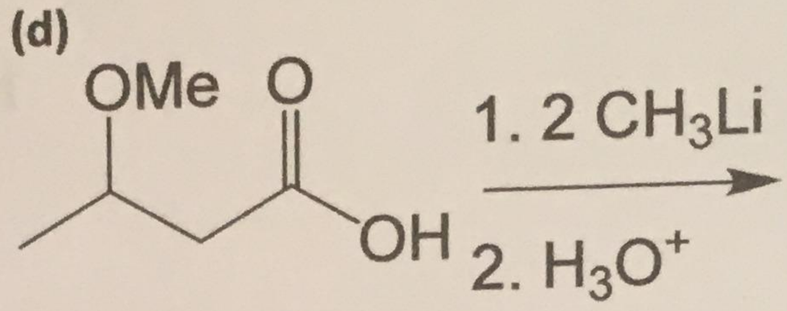

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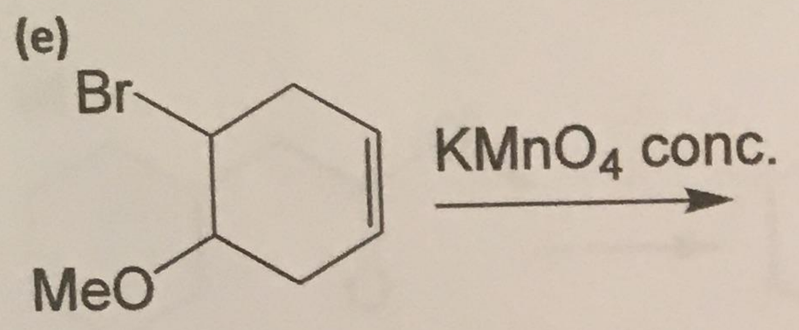

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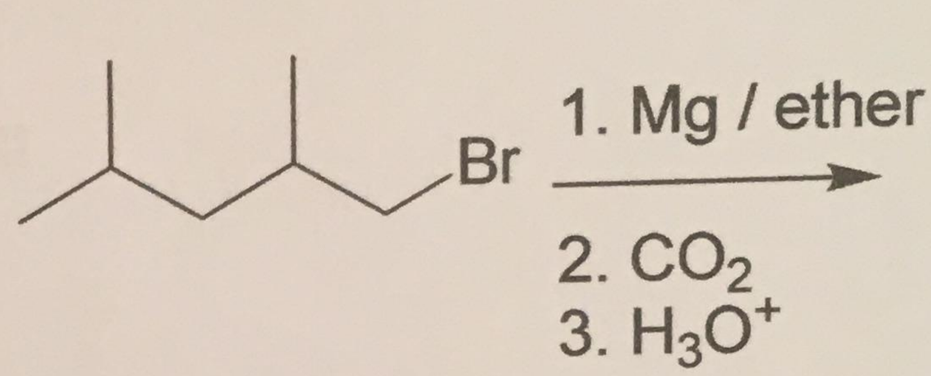

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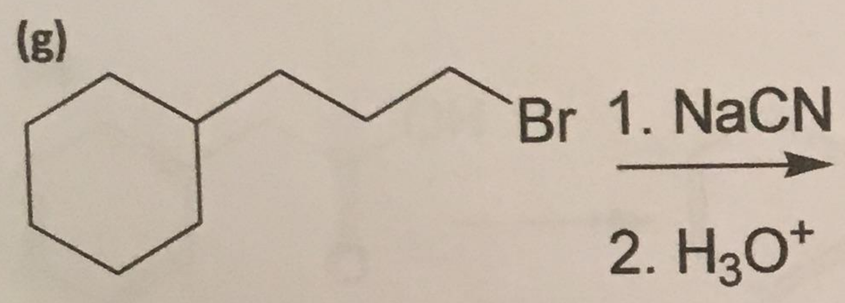

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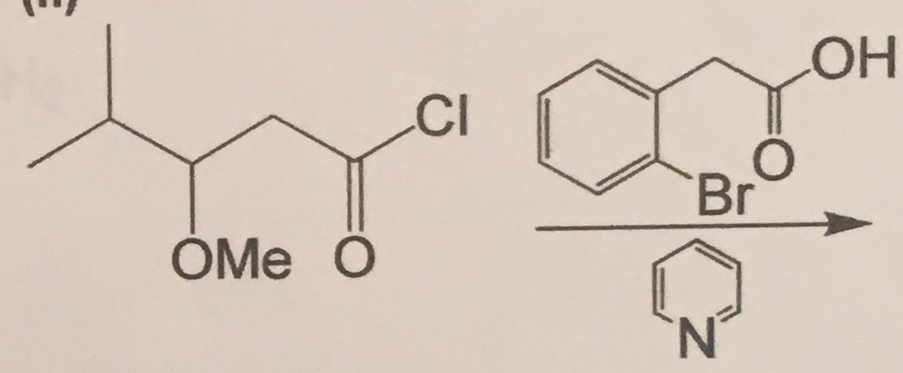

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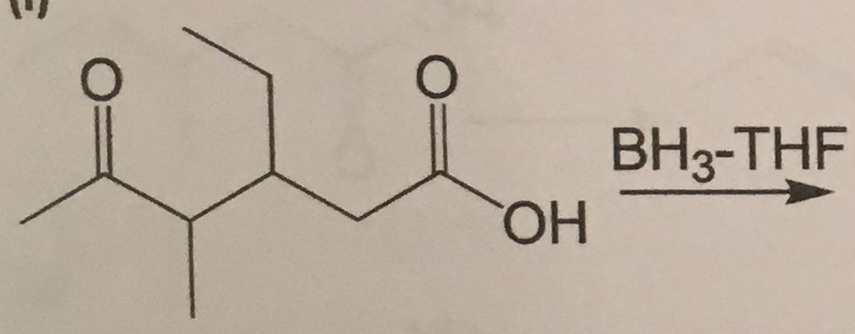

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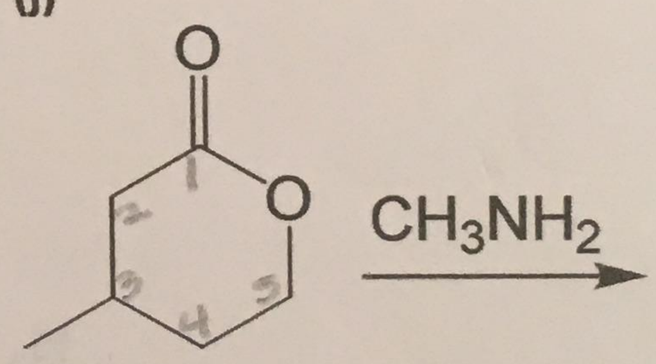

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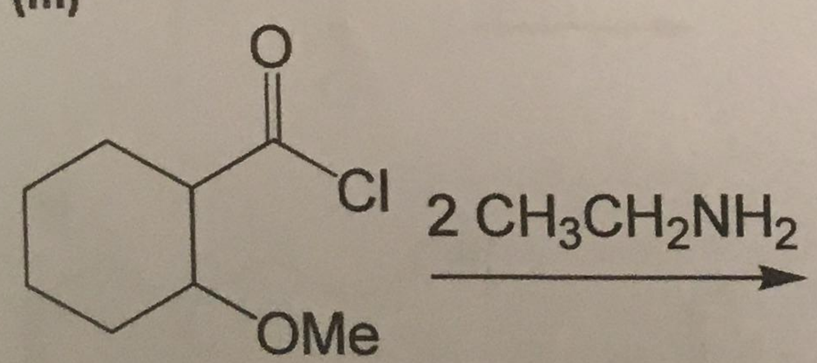

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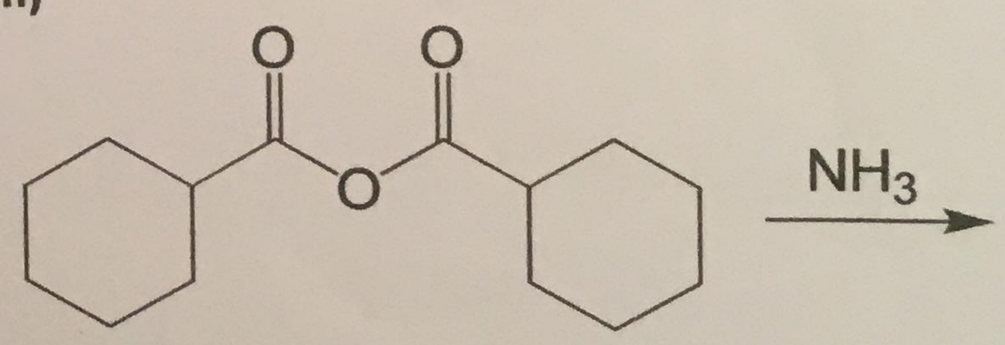

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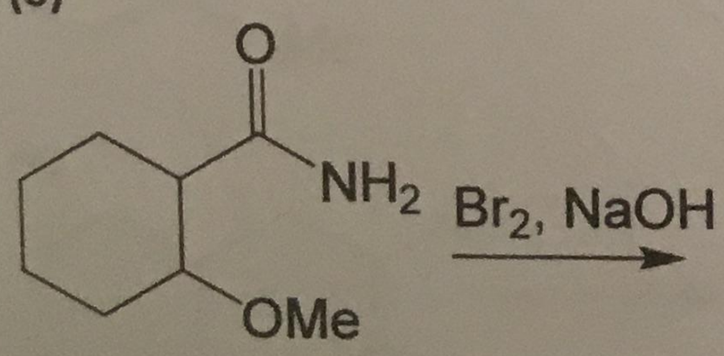

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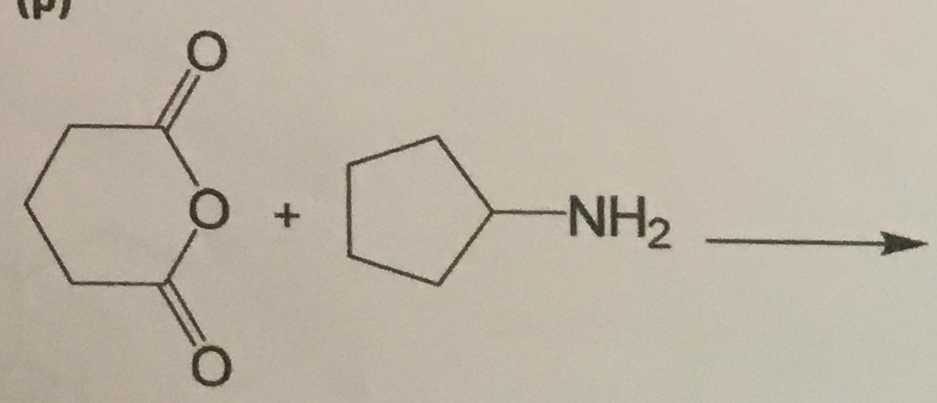

5/3/16

WORKSHEET IX

1. Name the following compounds

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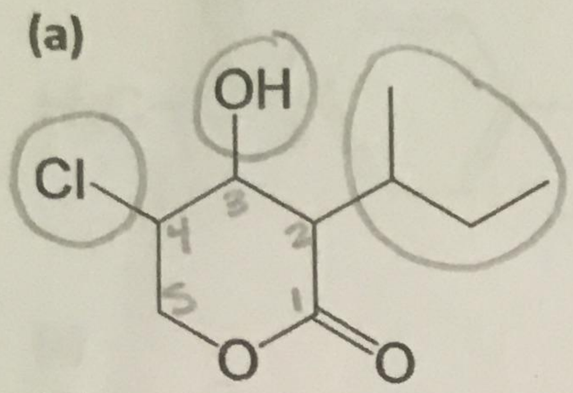

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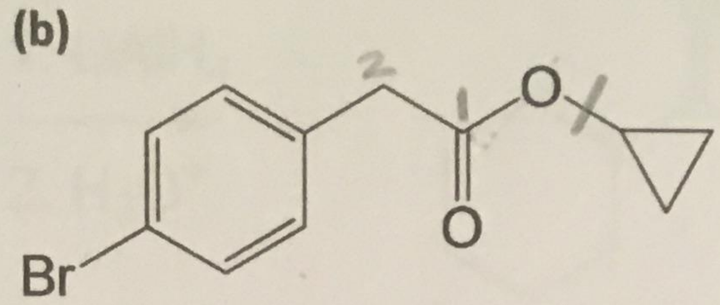

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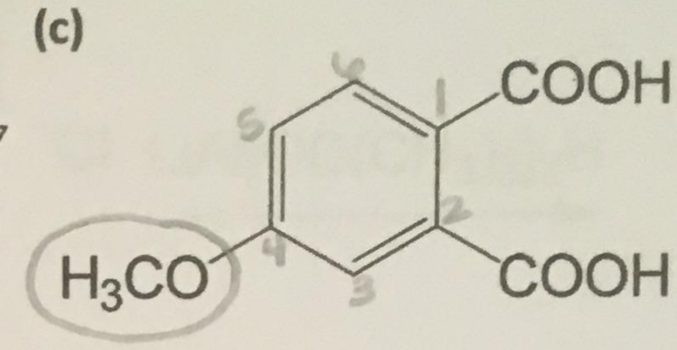

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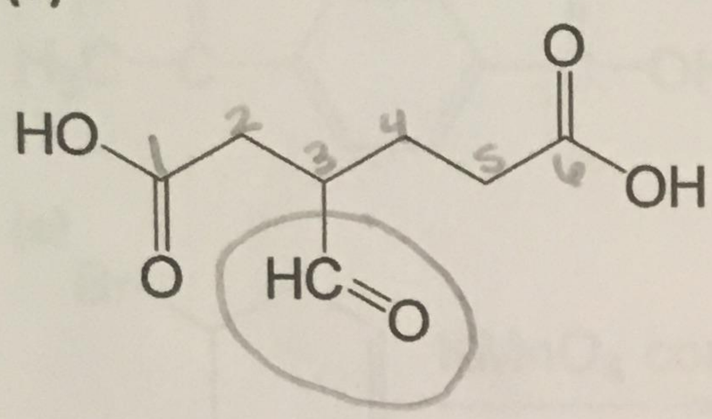

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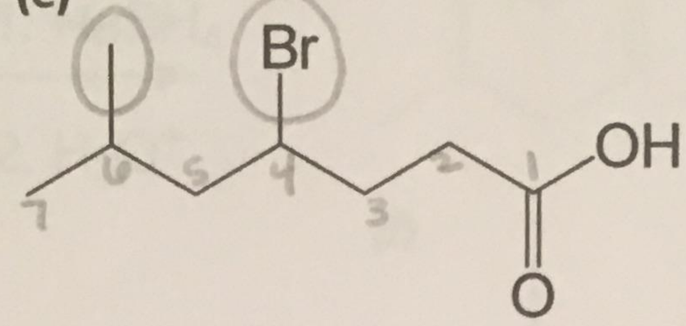

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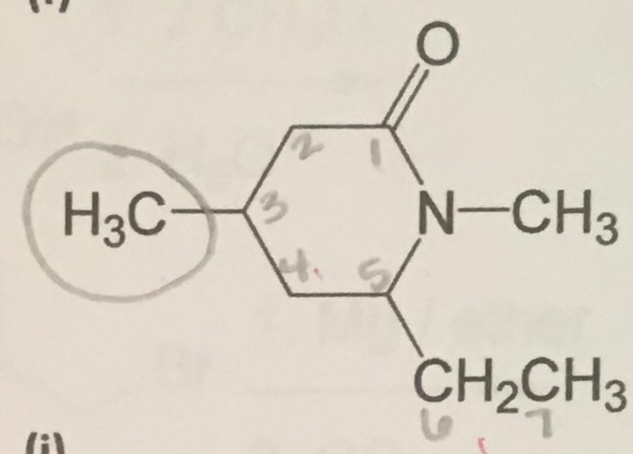

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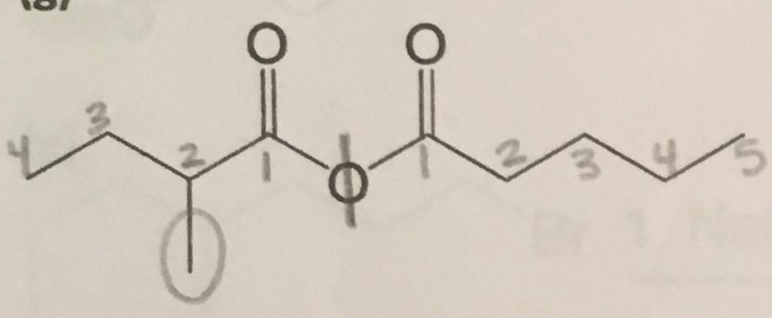

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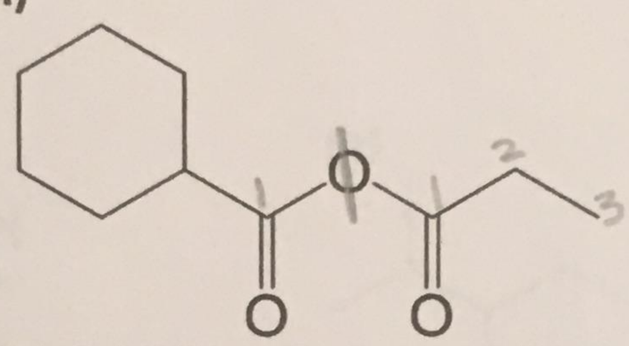

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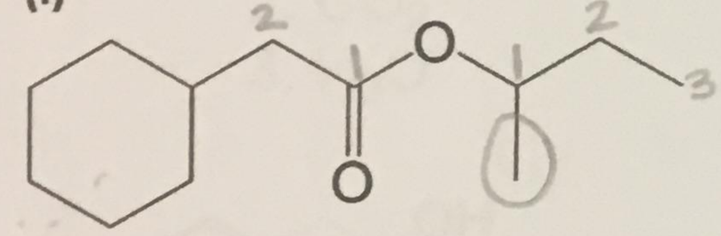

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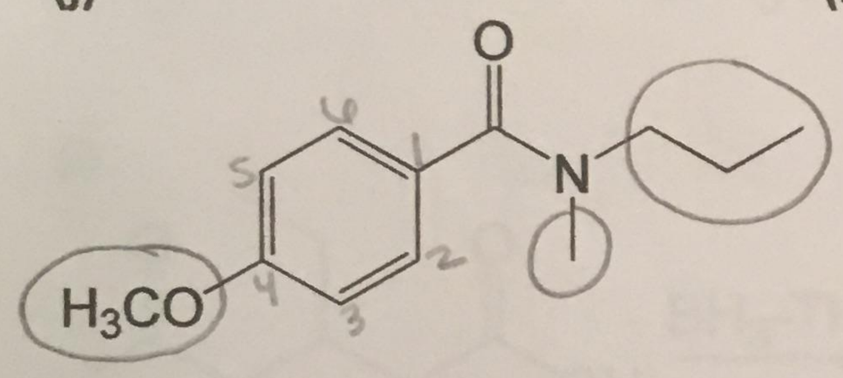

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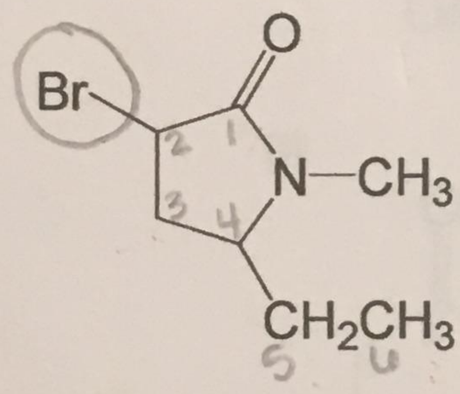

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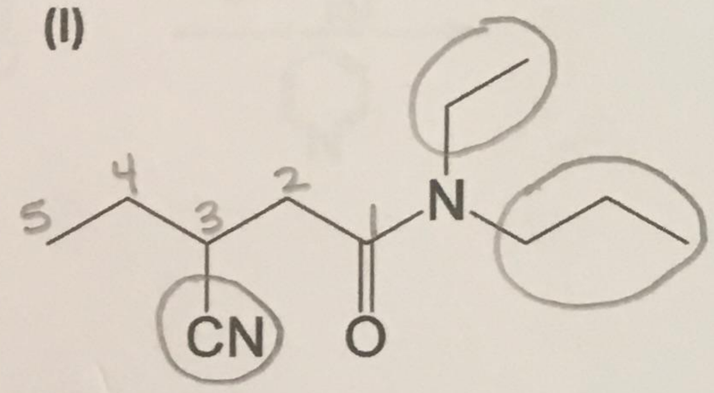

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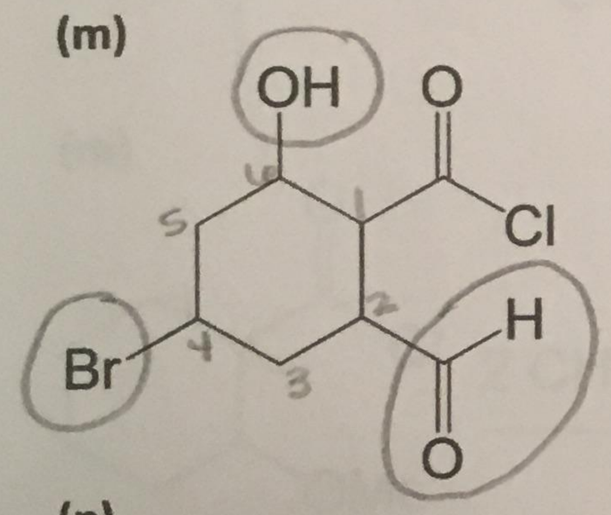

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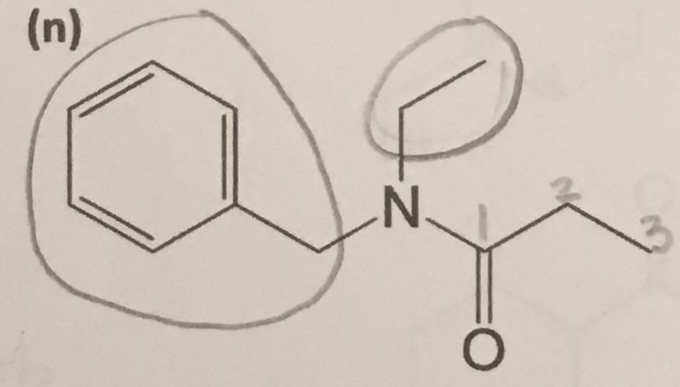

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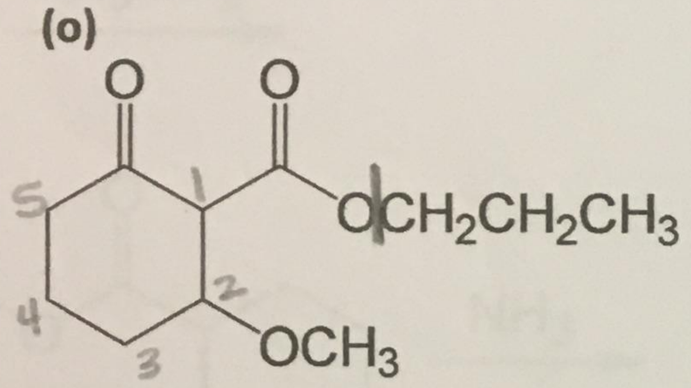

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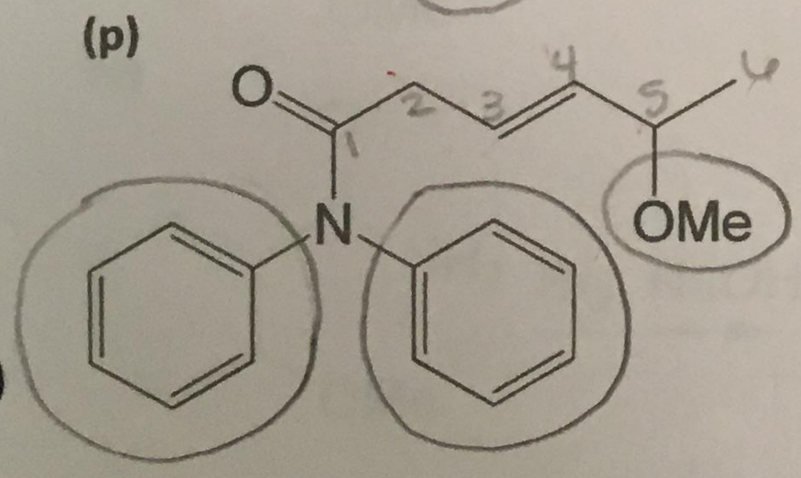

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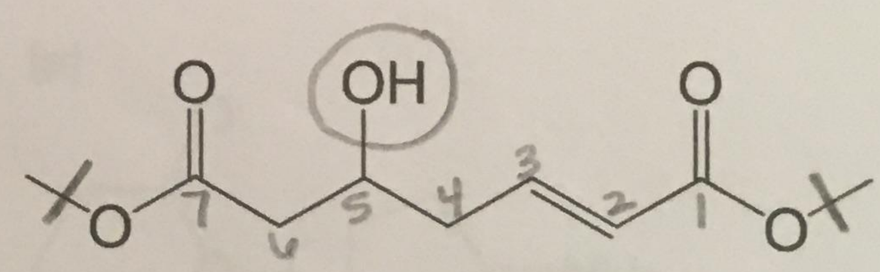


Section IX Worksheet

Part 1:

a. 2-sec-butyl-4-chloro-3,5-dihydroxypentanoic acid lactone

b. cyclopropyl 2-(4-bromophenyl)ethanoate

c. 4-methoxybenzene-1,2-dicarboxylic acid

d. 3-formylhexane-1,6-dioic acid

e. 4-bromo-6-methylheptanoic acid

f. 5-amino-N,3-dimethylheptanoic acid lactam

g. 2-methylbutanoic pentanoic anhydride

h. cyclohexanecarboxylic propanoic anhydride

i. 1-methylpropyl 2-cyclohexylethanoate

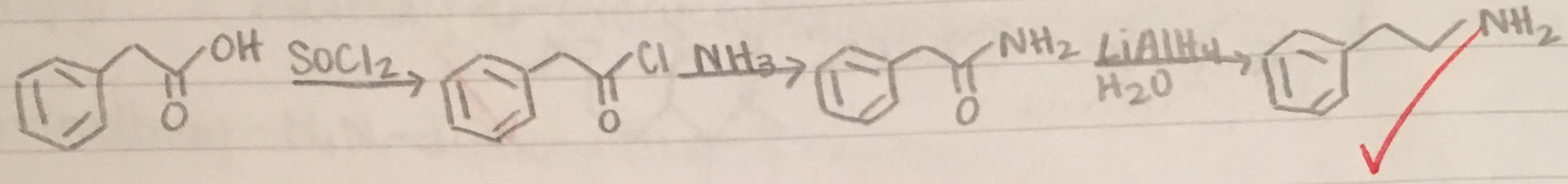
j. 4-methoxy-N-methyl-N-propylbenzamide

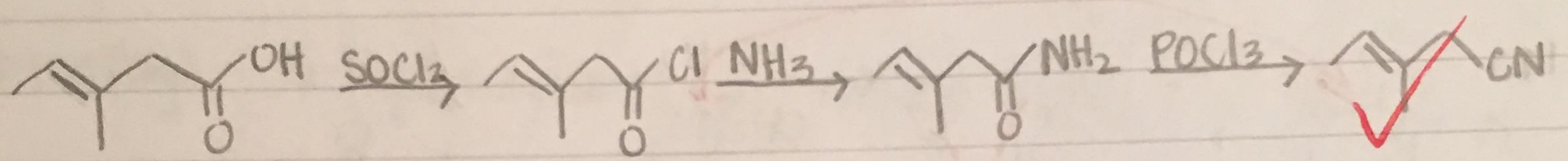
k. 4-amino-2-bromo-N-methylhexanoic acid lactam

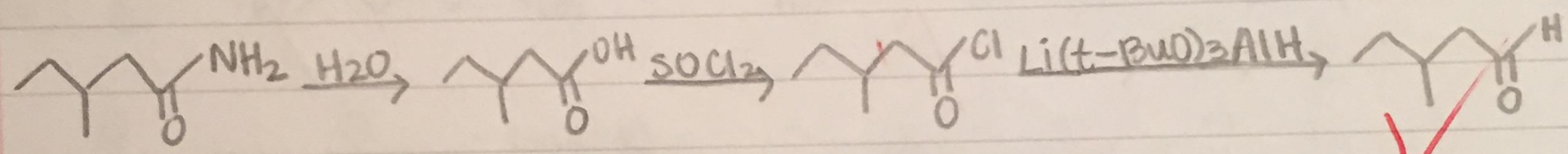
l. 3-cyano-N-ethyl-N-propylpentanamide

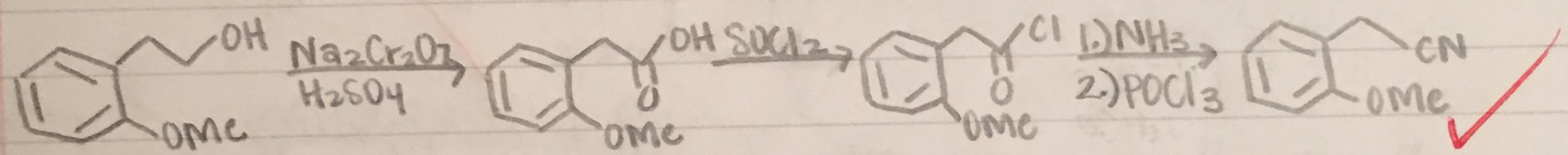
m. 4-bromo-2-formyl-6-hydroxycyclohexanecarbonyl chloride

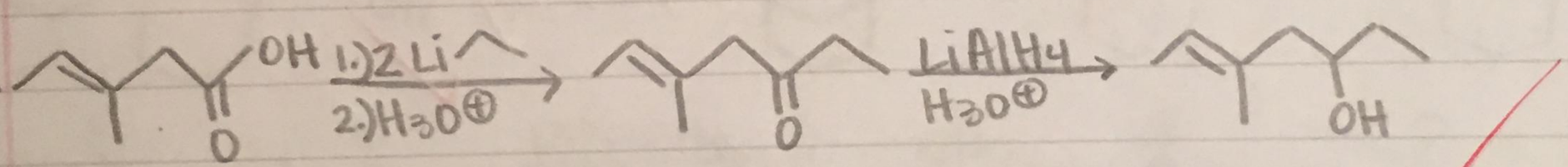
n. N-benzyl-N-ethylpropanamide

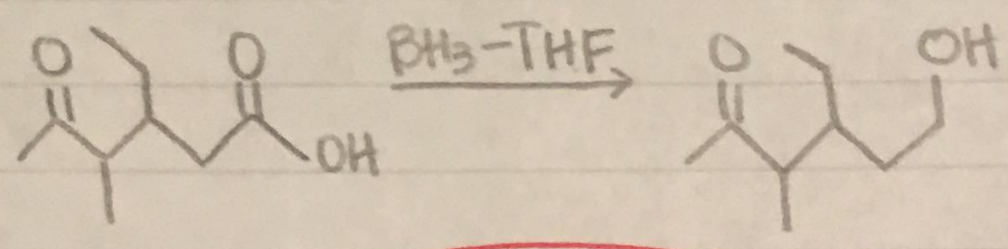
d. 
OH
SOCl2
Cl
NH3
NH2
LiAlH4
H2O
NH2

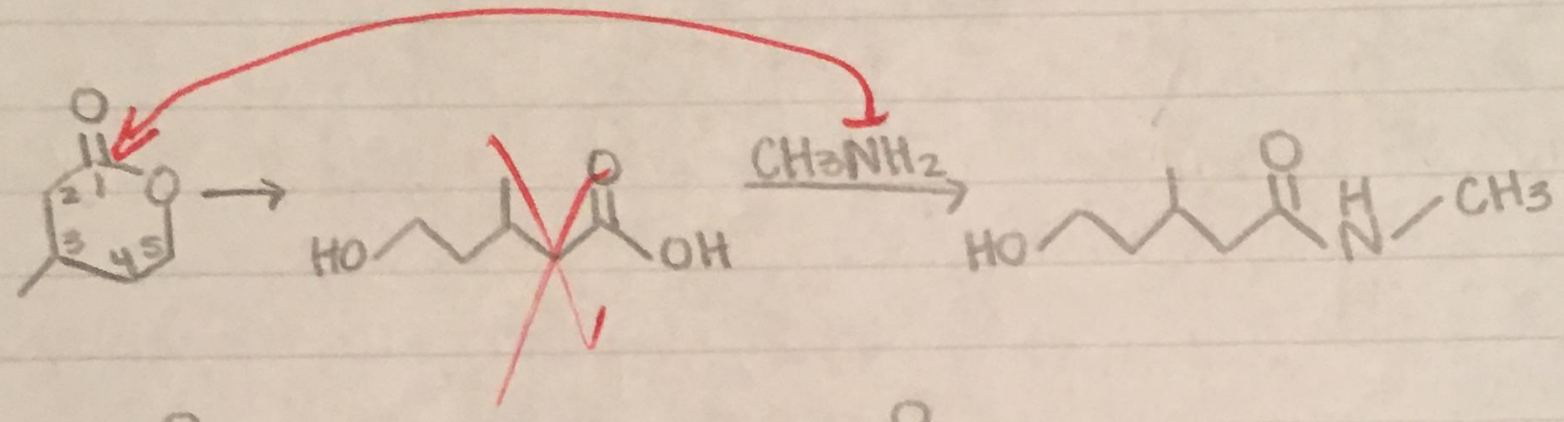
f. 
OH
SOCl2
Cl
NH3
NH2
POCl3
CN

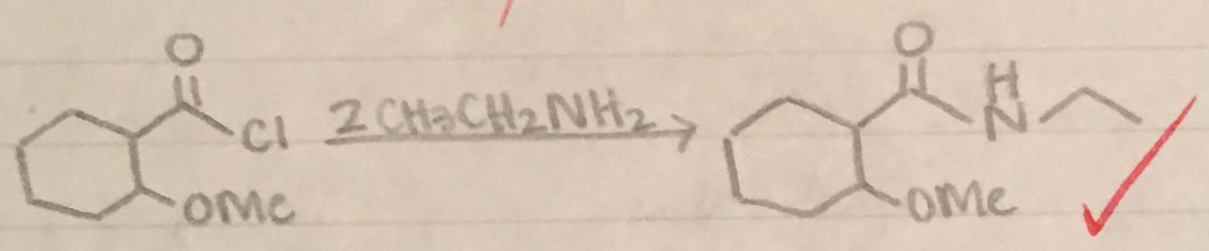
g. 
NH2
H2O
OH
SOCl2
Cl
Li(t-BuO)3AlH
H

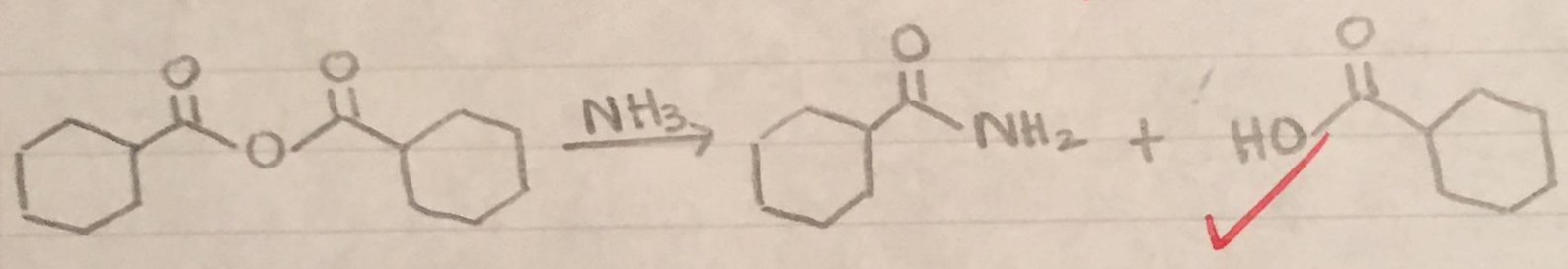
h. 
OH
OMe
Na2Cr2O7
H2SO4
OH
OMe
SOCl2
Cl
OMe
1.) NH3
2.) POCl3
CN
OMe

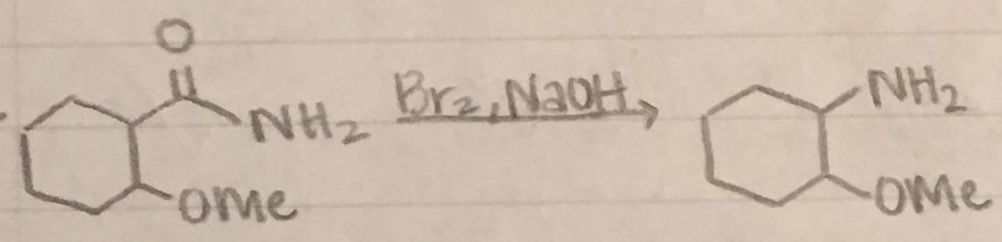
e. 
OH
1.) 2 Li
2.) H3O⊕
LiAlH4
H3O⊕
OH

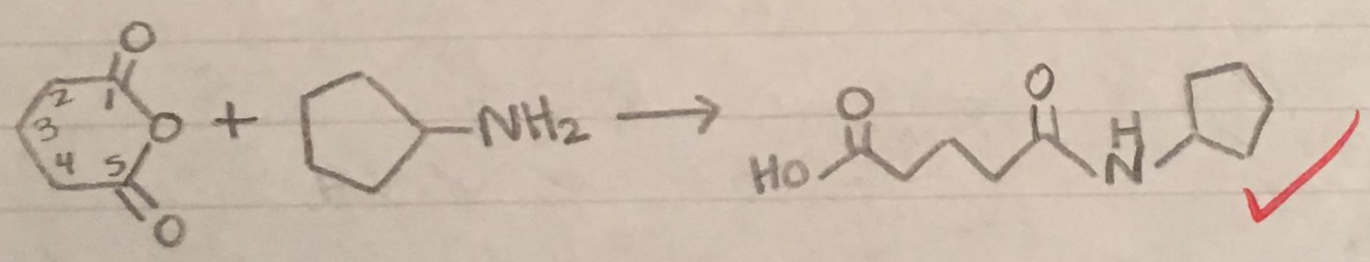
i. 

j. 

m. 

n. 

o. 

p. 

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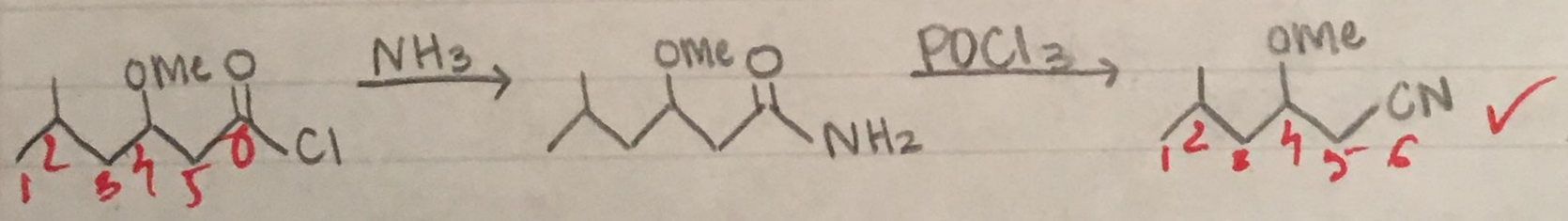
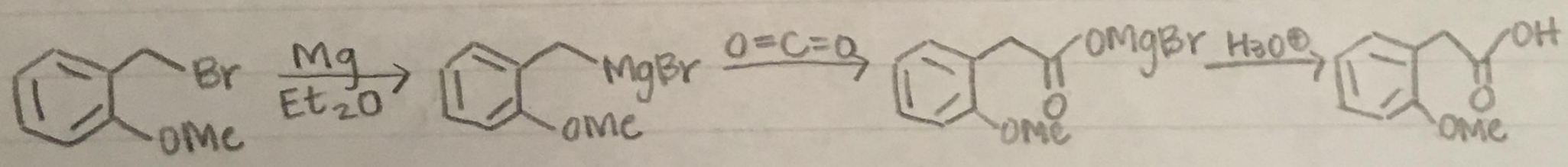
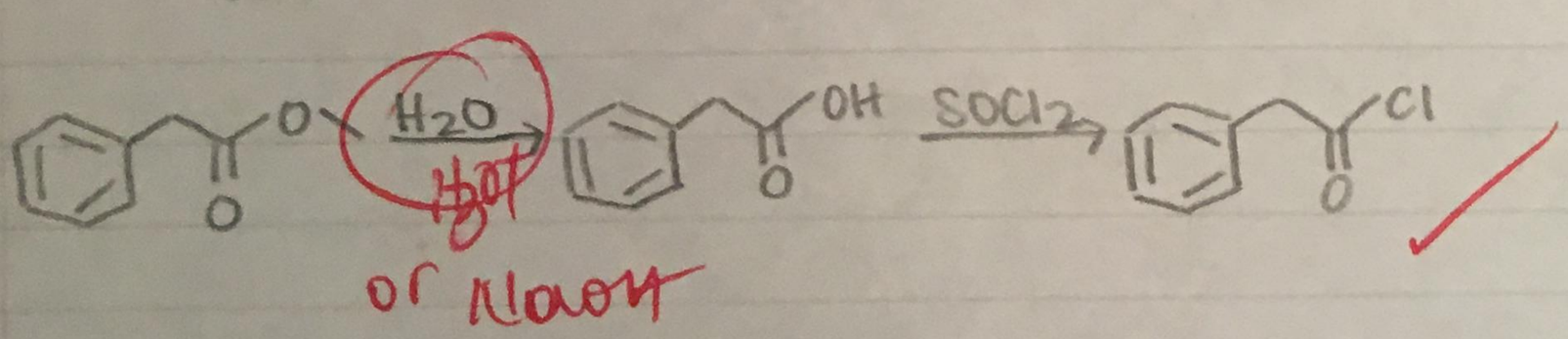
a. 

b. 

c. 

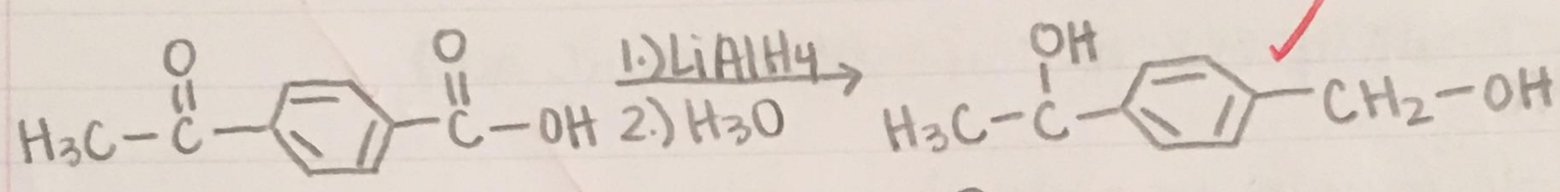
o. propyl 2-methoxy-6-oxocyclohexanecarboxylate

p. 5-methoxy-N,N-diphenylhex-3-enamide

q. dimethyl 5-hydroxyhept-2-enedioate

Part 2:

a.



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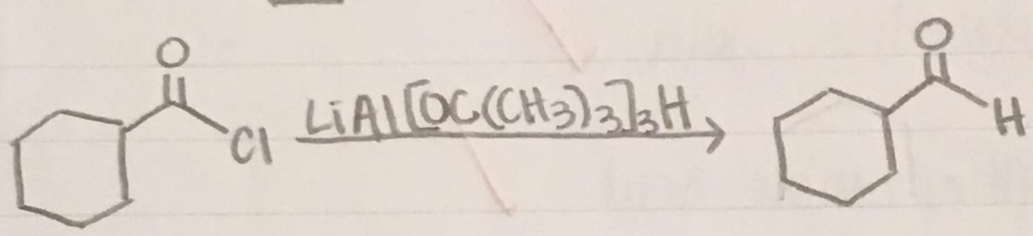

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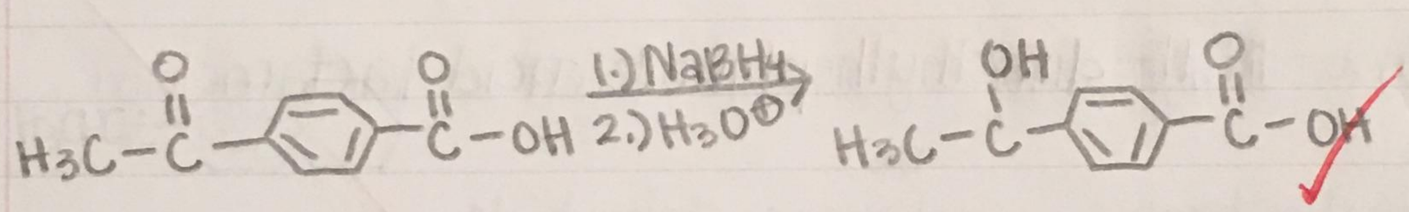
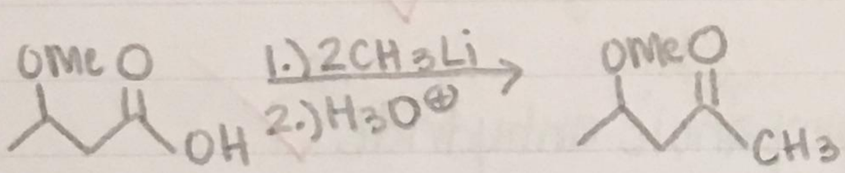
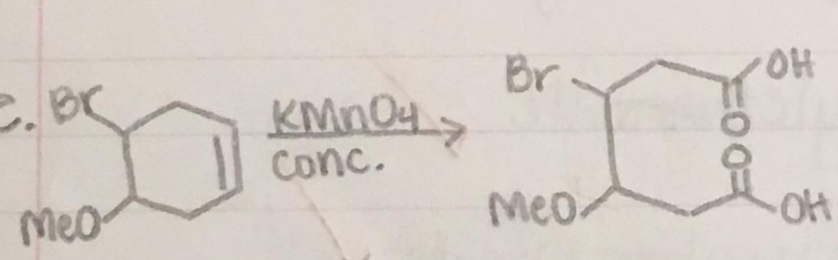


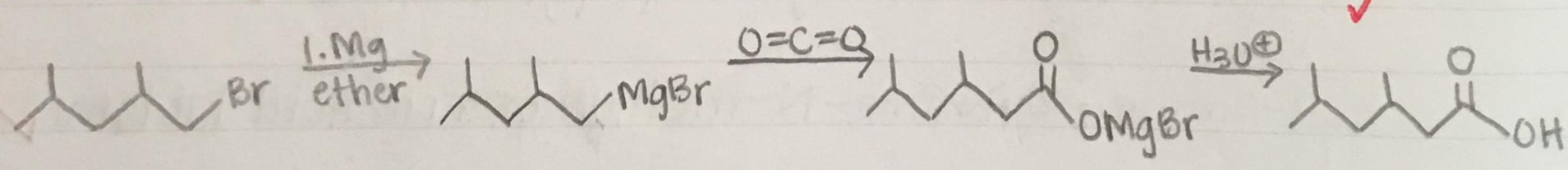
d.



e.



f.



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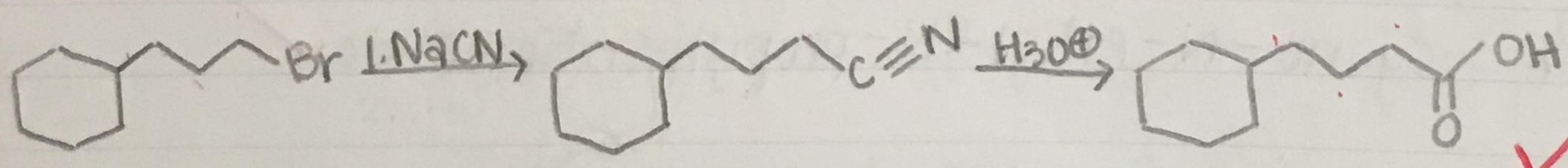
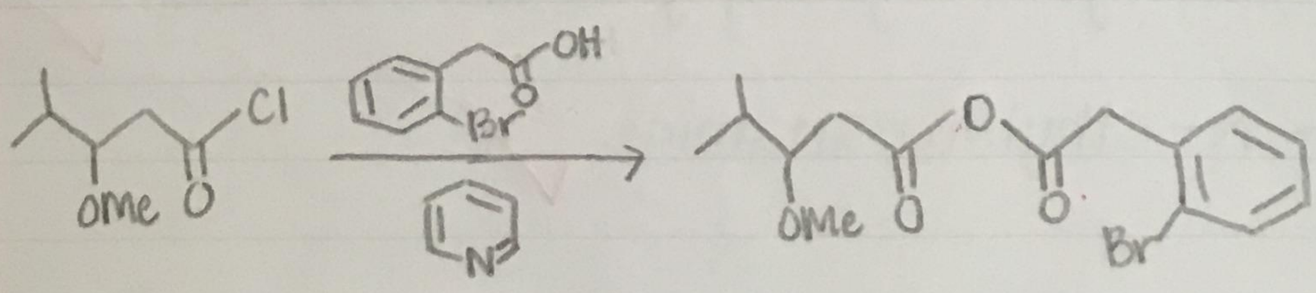
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