

CHEM 203

Final Exam

December 15, 2010

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This test contains 15 pages

Time: 2h 30 min

1. _____ / 16

2. _____ / 15

3. _____ / 24

4. _____ / 35

5. _____ / 36

6. _____ / 36

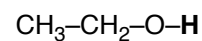
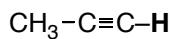
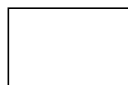
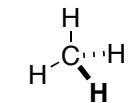
7. _____ / 40

8. _____ / 48

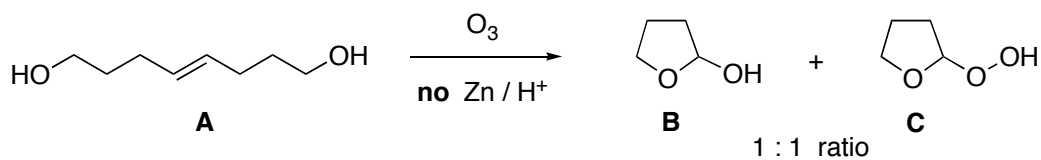
TOTAL _____ / 250 = _____ / 100

This exam counts for 45% of your CHEM 203 final grade

1. (16 pts.) Indicate the approximate pKa's for the Bronsted dissociation of the proton in boldface in the following molecules (write your answers in the appropriate boxes)



2. (15 pts.) Write a detailed mechanism to account for the observation that treatment of compound **A** with ozone, but **without** the usual Zn/H⁺ step, furnishes a 1 : 1 mixture of products **B** and **C**:



3. (24 pts.) Draw:

a. Accurate mechanisms for an example of S_N2 reaction and an example of S_N1 reaction:

S_N2 :

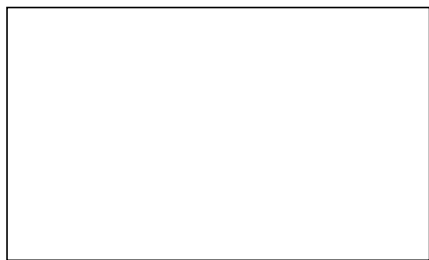
S_N1 :

b. A chemical equation showing an example of Williamson reaction (without mechanism):

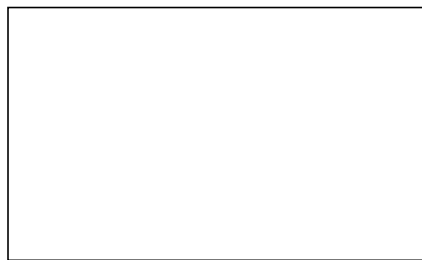
c. A chemical equation showing an example of Wittig reaction (without mechanism):

- d. A chiral Schiff base:
- e. An achiral epoxide that will react with aq. H_2SO_4 to form a chiral diol:
- f. An olefin containing at least than 3 C atoms that will produce the same diol when treated either with OsO_4 followed by aq. NaHSO_3 , or with MCPBA followed by aq. H_2SO_4 .
- g. An alcohol containing at least 4 C atoms that is likely to undergo dehydration without rearrangement and one also containing at least 4 C atoms that is likely to undergo rearrangement during dehydration (write your answers in the appropriate boxes):

not likely to rearrange

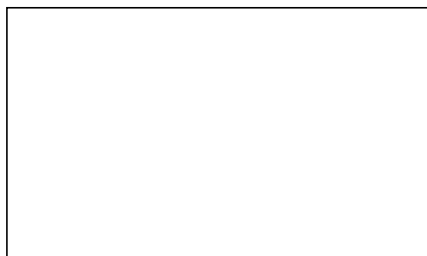


likely to rearrange

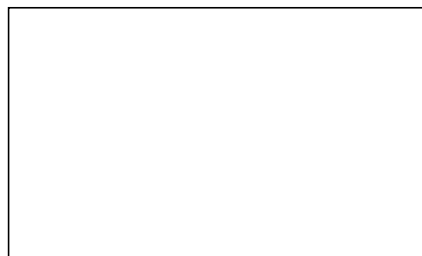


- h. An alcohol that forms the same product when treated either with PCC or with the Jones reagent, and one that forms one product when treated with PCC, but a different product when treated with the Jones reagent (write your answers in the appropriate boxes):

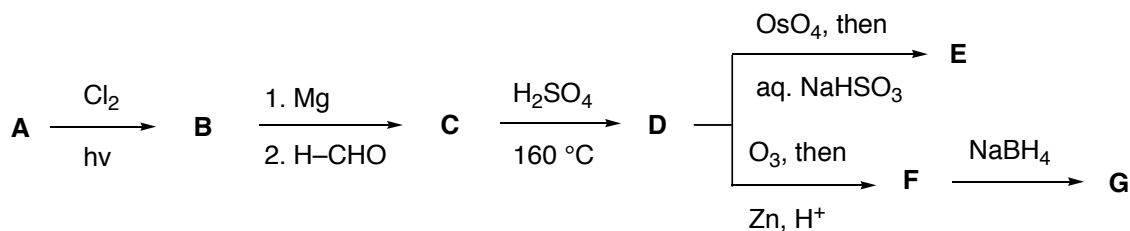
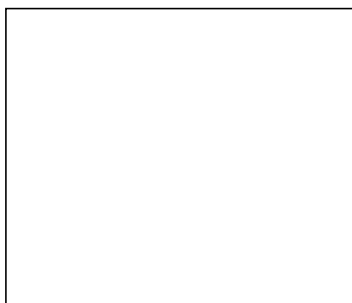
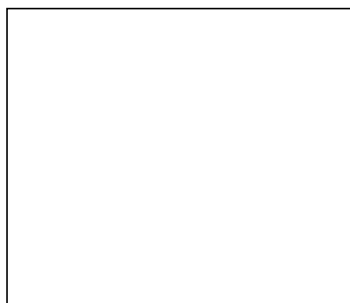
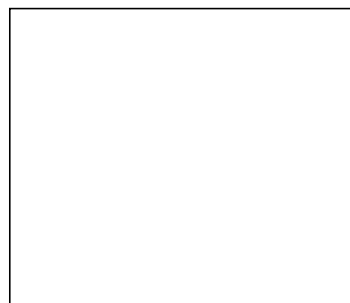
gives the same product

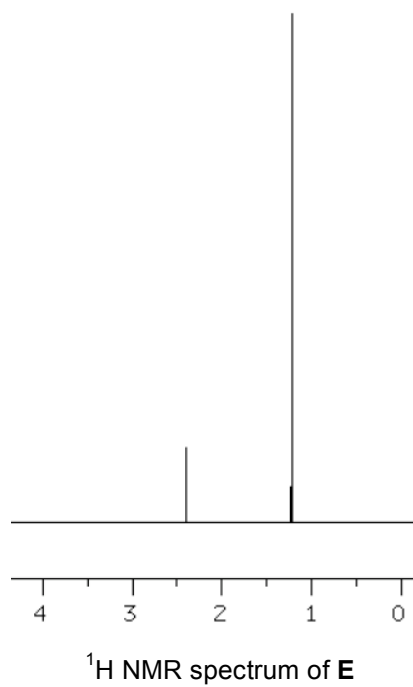
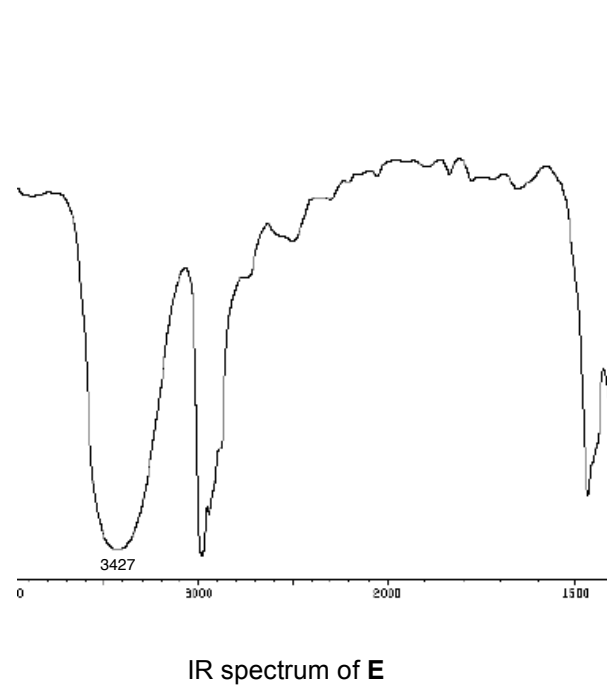
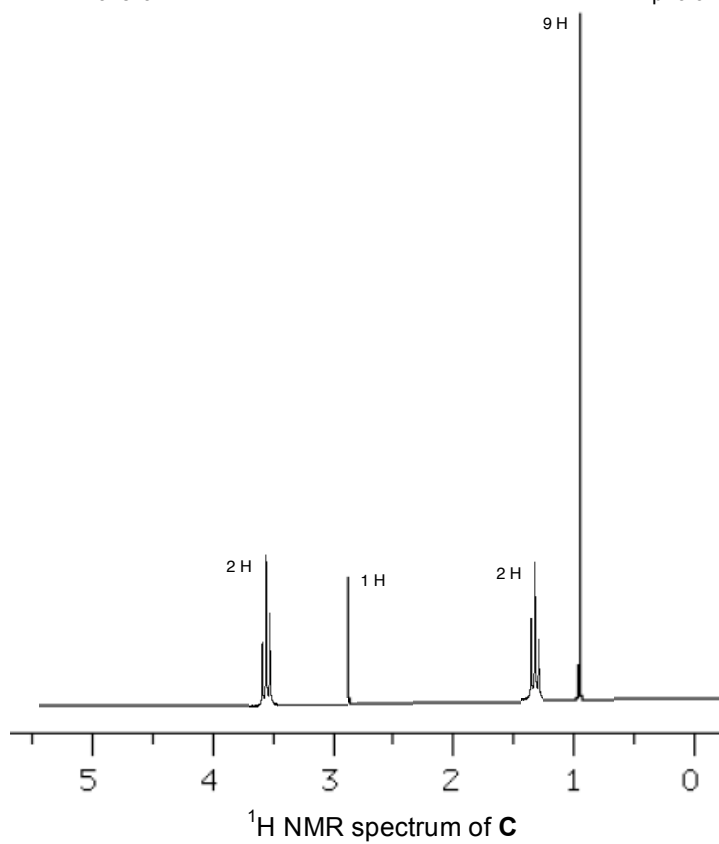
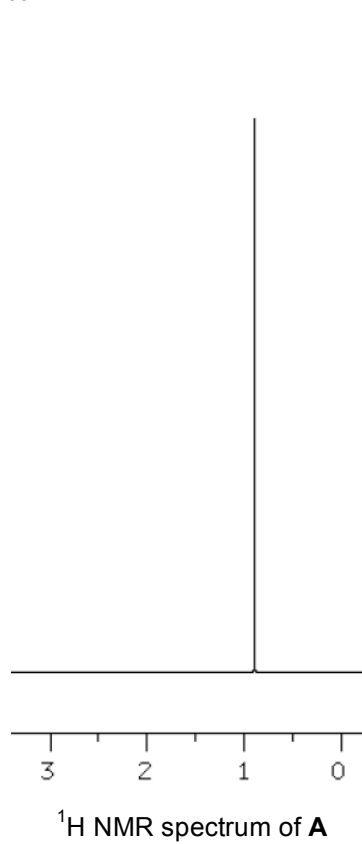


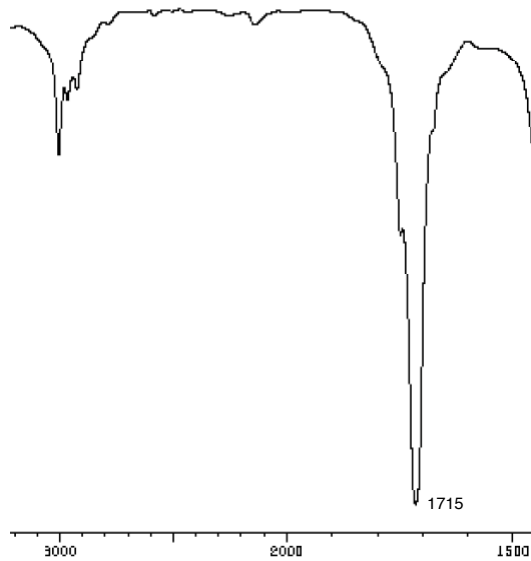
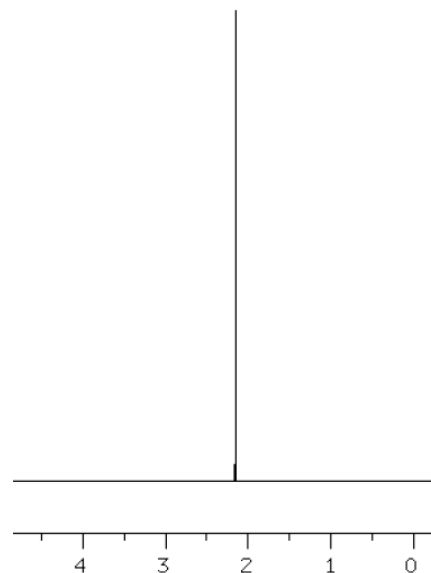
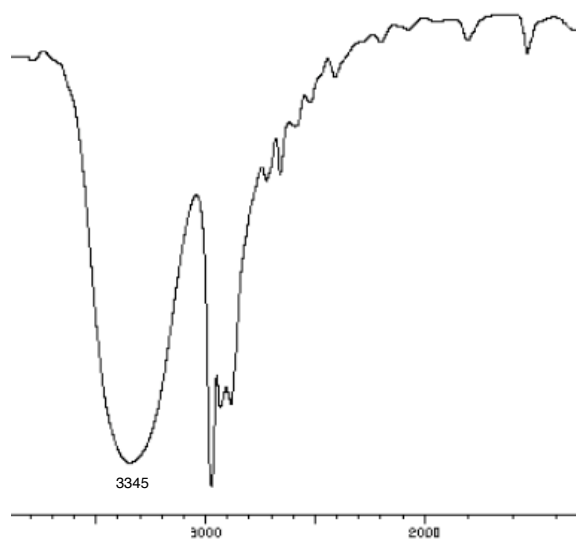
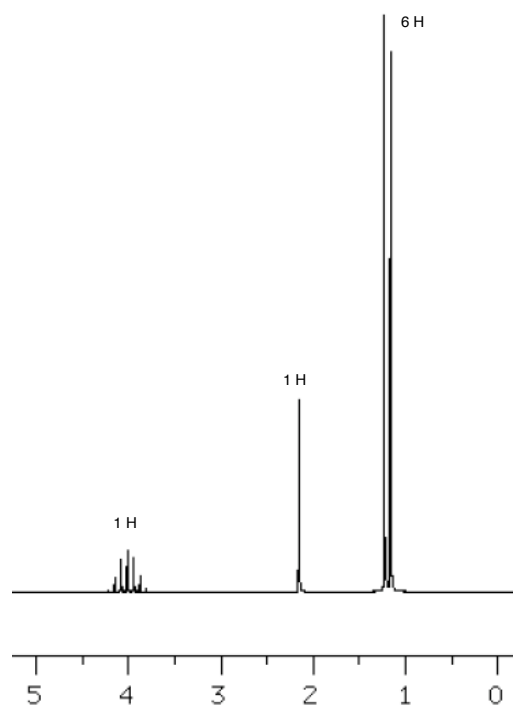
gives two different products



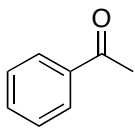
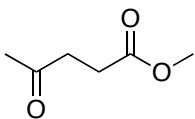
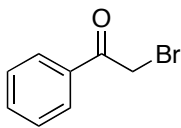
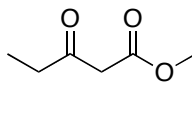
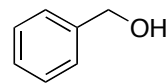
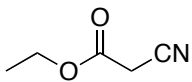
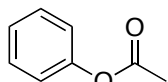
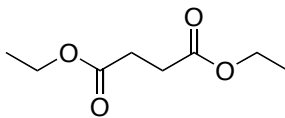
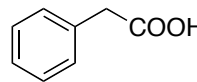
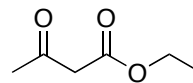
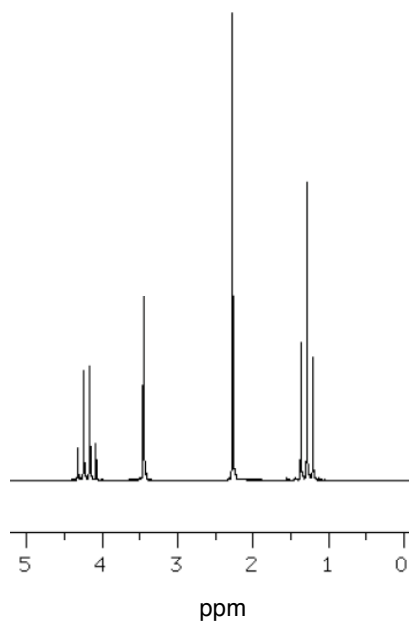
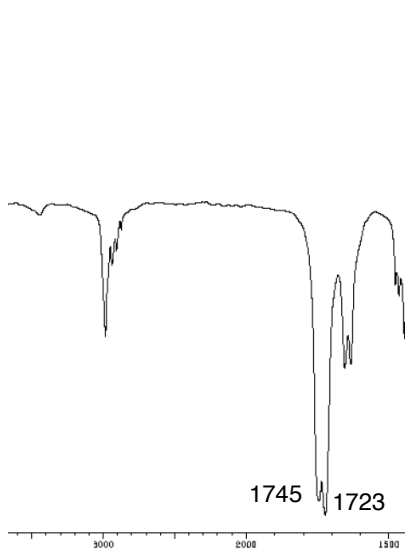
4. (35 pts.) The ^1H NMR spectrum of an alkane, **A**, exhibited only a singlet at 0.9 ppm. Treatment of **A** with $\text{Cl}_2 / h\nu$ afforded a monochloro derivative, **B**, which upon reaction with metallic Mg followed by formaldehyde, $\text{H}-\text{CHO}$, produced compound **C**. The IR spectrum of **C** displayed a strong, broad absorption at 3340 cm^{-1} . The ^1H NMR spectrum of **C** is shown below. Reaction of **C** with H_2SO_4 at $160\text{ }^\circ\text{C}$ yielded compound **D**. When substance **D** was treated with OsO_4 followed by aqueous NaHSO_3 , compound **E** emerged. Furthermore, ozonolysis of **D** followed by Zn/H^+ produced only **F**, which upon treatment with NaBH_4 furnished **G**. The ^1H NMR spectra of **E** and **G** are also provided below. Deduce the structures of compounds **A** – **G** and write your answers in the appropriate boxes.

Compound **A**Compound **B**Compound **C**Compound **D**Compound **E**Compound **F**Compound **G**

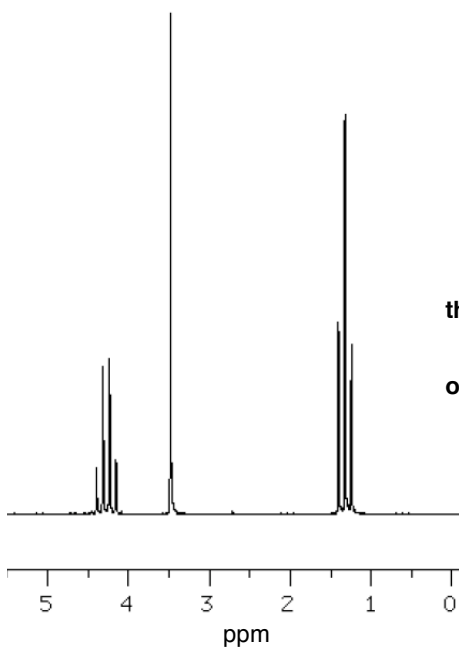
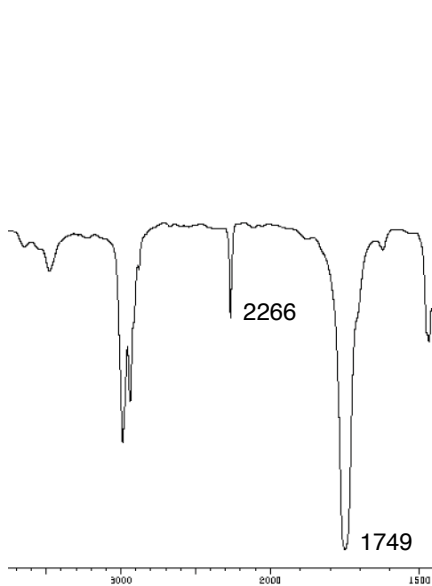


IR spectrum of **F**¹H NMR spectrum of **F**IR spectrum of **G**¹H NMR spectrum of **G**

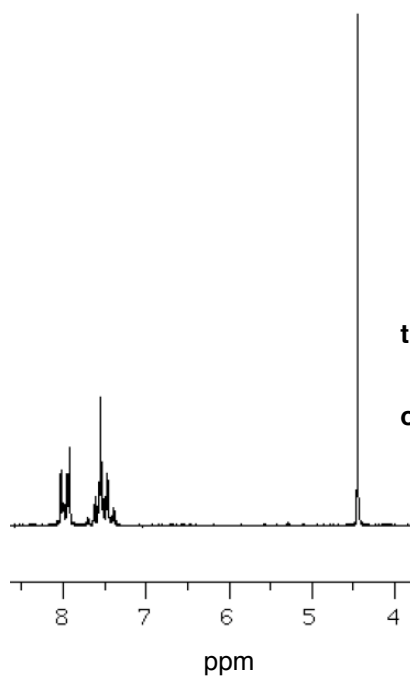
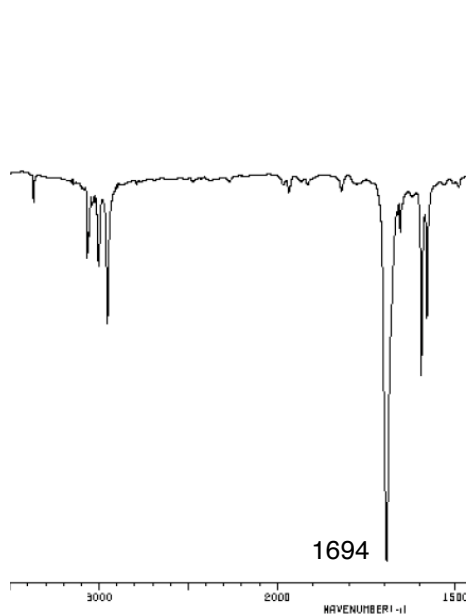
5. (36 pts.) Indicate which among compounds **a-j** produce the spectra shown below:

**a****b****c****d****e****f****g****h****i****j**

these are the spectra
of compound:

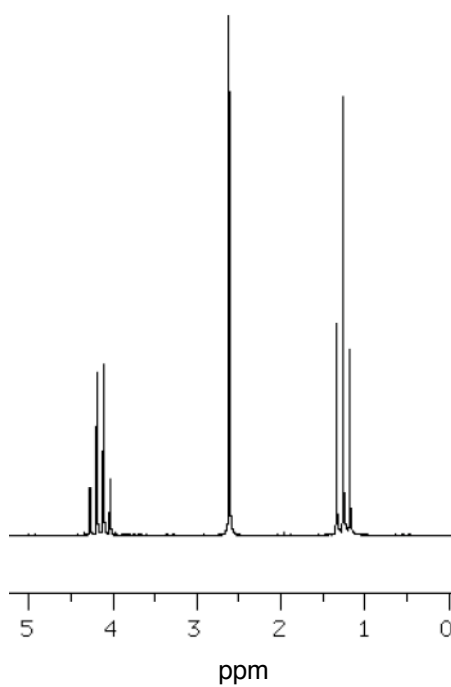
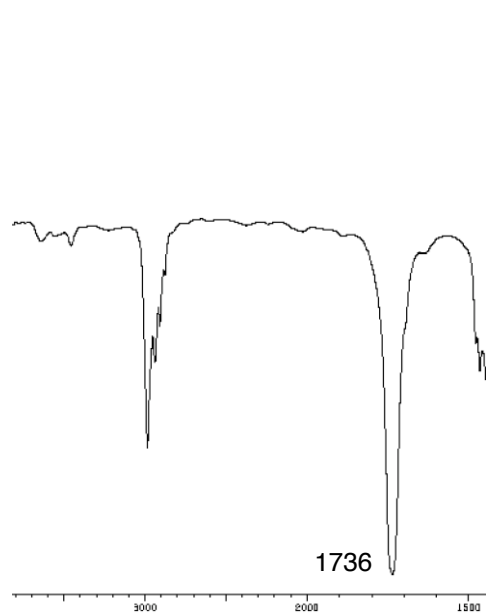


these are the spectra
of compound:



these are the spectra

of compound:

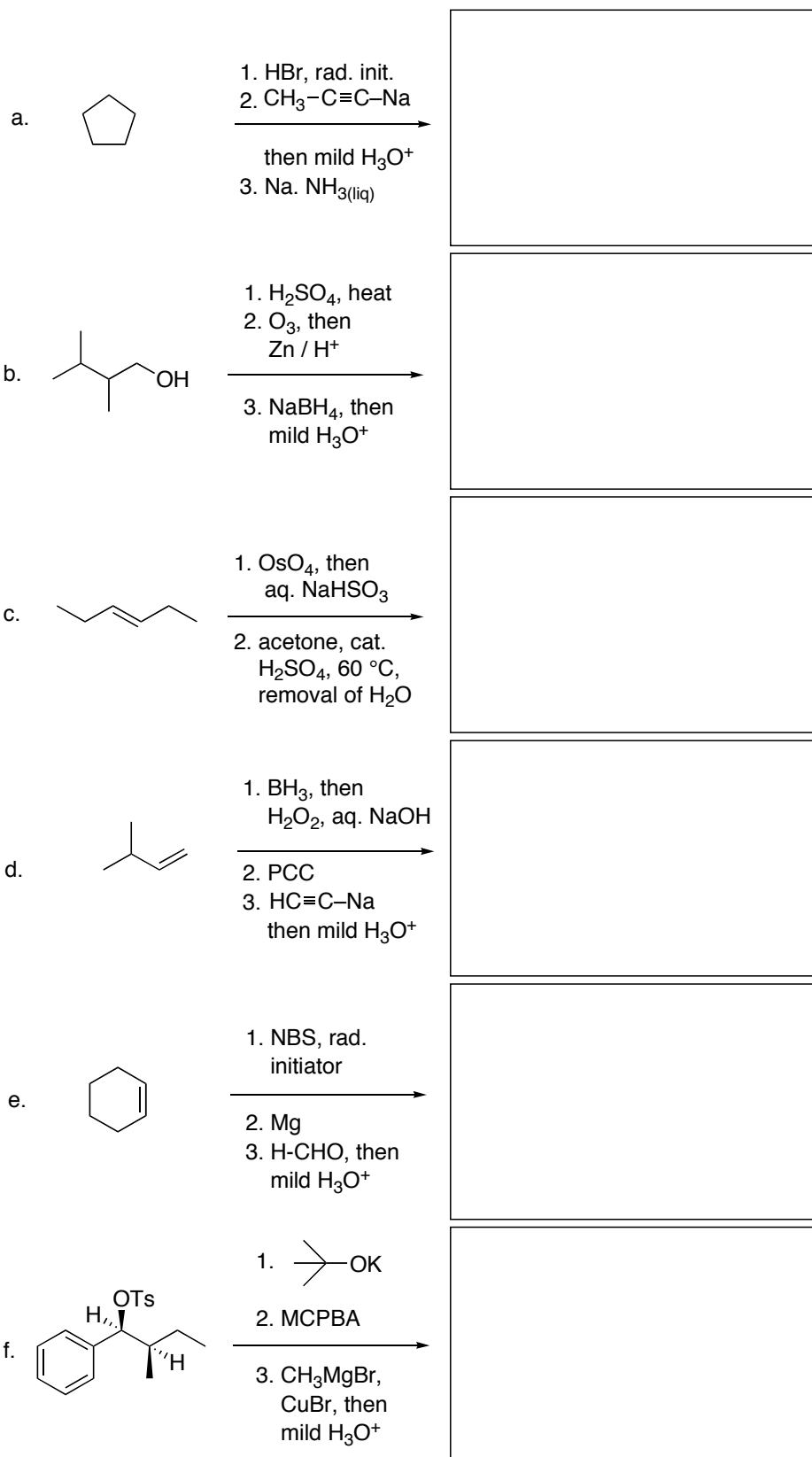


these are the spectra

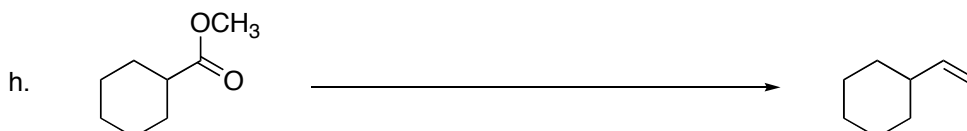
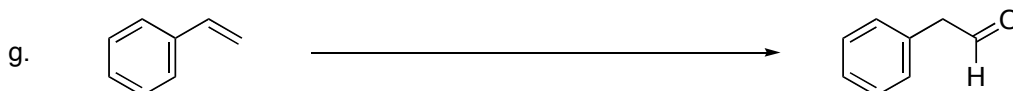
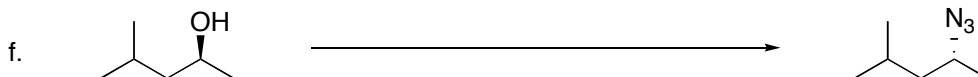
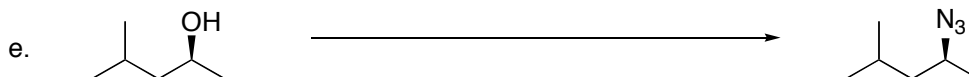
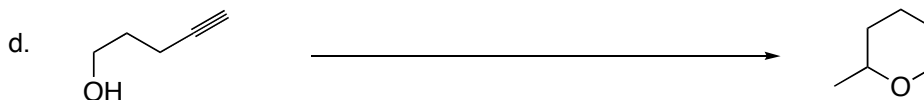
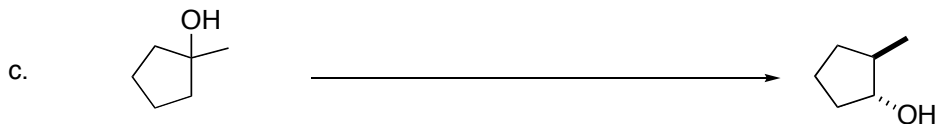
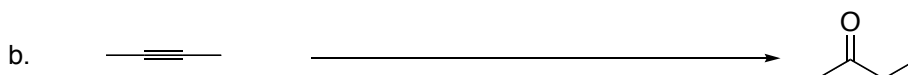
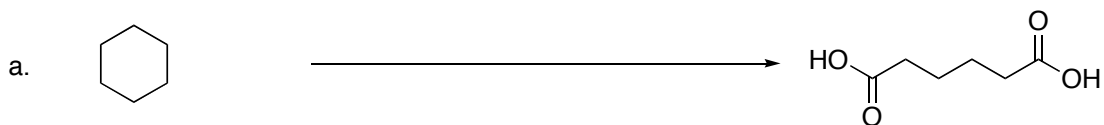
of compound:



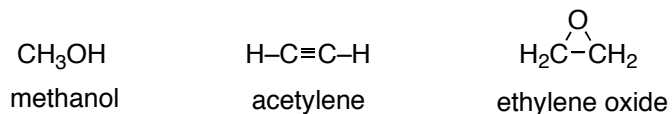
6. (36 pts.) Draw the structure of the major product expected from each of the following reactions. If no overall change is predicted, answer **"NO REACTION."** **Important:** where appropriate, molecules must be drawn with the correct configuration



7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations shown below. List such reagents above / below the reaction arrows. If a product does not appear to be available from the substrate shown by any method known to you, write "**INACCESSIBLE**" on the reaction arrow.

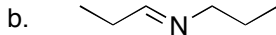
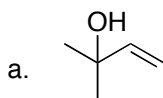


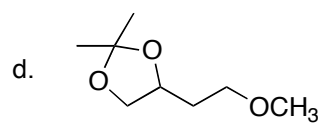
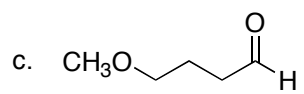
8. (48 pts.) Propose a good synthesis of the molecules shown below using **only methanol**, **NaCN**, **acetylene** and **ethylene oxide** (see below) as the sources of carbon atoms. Intermediates / products obtained during an earlier sequence may be employed in a subsequent procedure, without showing their preparation again. Assume the availability of all necessary reagents (such as bases, acids, BH_3 , Mg, TsCl, PCC, PBr_3 , MCPBA, etc.).



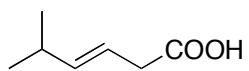
Important:

- aqueous workups at the end of each reaction are understood and need not to be shown.
- It is not necessary to write mechanisms

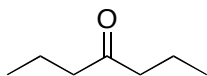




e.



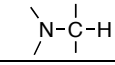
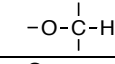
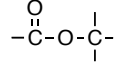


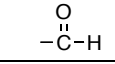

f.



Characteristic Infrared Absorptions of Common Functional Groups

Functional Group	Bond	Frequency Range (cm ⁻¹)	Functional Group	Bond	Frequency Range (cm ⁻¹)
Alcohol	O-H	3400 – 3650 (s, broad)	Nitrile	C≡N	2210 – 2260 (w – m)
	C-O	1050 – 1150 (s)	Carboxylic acid	O-H	2500-3100 (s, broad)
Ether	C-O	1000 – 1260		C=O	1700 – 1720 (s)
Amine	N-H	3300 – 3350 (m)	Ester	C=O	1710 – 1750 (s)
Alkane	C-H	2850 – 2950 (m – s)	Acyl halide	C=O	1770 – 1820 (s)
Alkene	=C-H	3020 – 3100 (m)	Acid anhydride	C=O	1740 – 1790 (s)
	C=C	1640 – 1680 (m)			1800 – 1850 (s)
Alkyne	≡C-H	3270 – 3330 (s)	Amide	C=O	1630 – 1700 (s)
	C≡C	2100 – 2260 (w – m)	Aldehyde, ketone	C=O	1680 – 1730 (s)

Characteristic Proton (¹H) NMR Chemical Shifts

Type of Hydrogen	Structure	Chemical Shift δ (ppm)	Type of Hydrogen	Structure	Chemical Shift δ (ppm)
Reference	(CH ₃) ₄ Si	0.00	Amines		2.3 – 3.0
Alkane, primary	-CH ₃	0.7 – 1.3	Alcohol, ether		3.3 – 4.0
Alkane, secondary	-CH ₂ -	1.2 – 1.4	Ester		3.7 – 4.8
Alkane, tertiary		1.4 – 1.7	Olefinic	C=C-H	5.0 – 6.5
Allylic, primary	C=C-CH ₃	1.6 – 1.9	Aromatic	Ar-H	6.5 – 8.0
Methyl carbonyl		2.1 – 2.5	Aldehyde		9.7 – 10.0
Aromatic methyl	Ar-CH ₃	2.5 – 2.7	Amine	-NH ₂	1 – 5, variable
Alkyne	≡C-H	2.5 – 2.7	Alcohol	-OH	1 – 5, variable
Alkyl halide (X = Cl, Br, I)		2.5 – 4.5	Carboxylic acid	-COOH	11.0 – 12.0