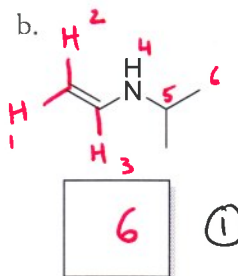
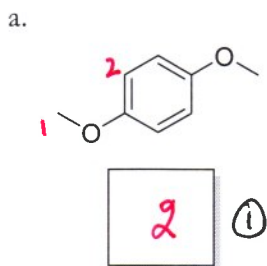
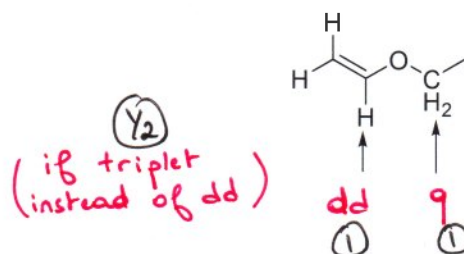


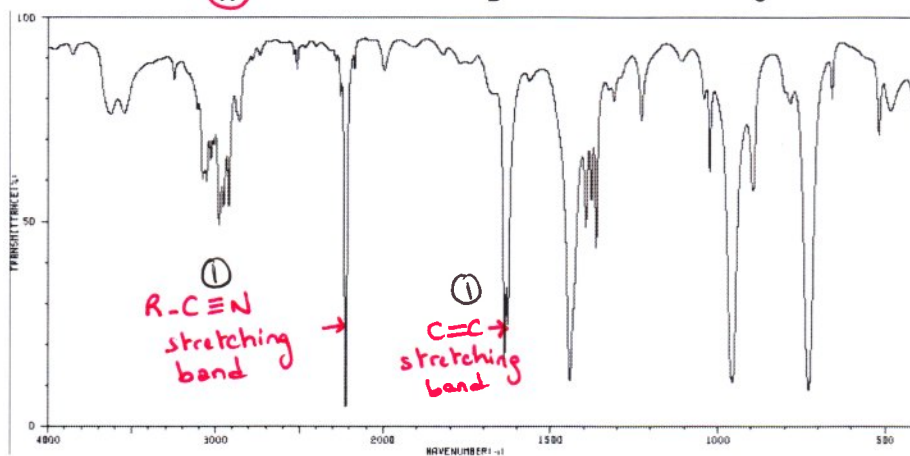
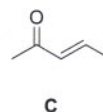
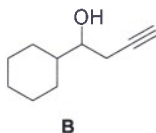
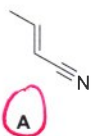
1. What is the number of signals that should be observed in the ^1H NMR spectra of each of these molecules? (2 points)



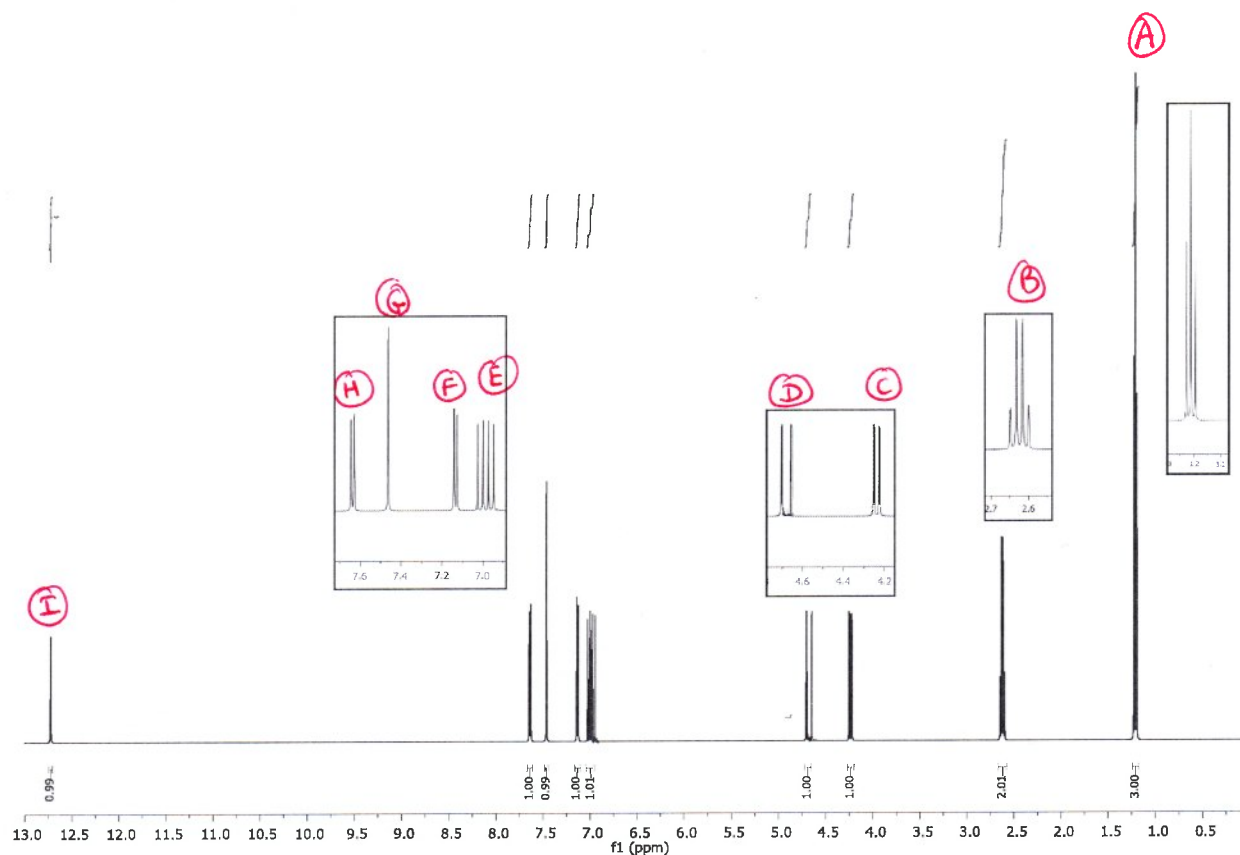
2. Indicate the multiplicity that will be observed in a ^1H NMR spectra for each of the indicated proton in the following molecule? (2 points)



3. Assign the correct molecule to the infrared spectra provided below. Explain your choice. (3 points)



4. The ^1H NMR spectra of an unknown with a molecular formula of $\text{C}_{11}\text{H}_{12}\text{O}_3$ is shown below with the expansion of the different regions. The IR spectra has shown significant stretch broad band around 3100 cm^{-1} and two strong sharp bands at 1711 cm^{-1} and 1620 cm^{-1} . The questions that follow will guide you in the determination of its structure. (18 points in total)



- a- Determine the degree of unsaturation. Show your calculation. (2 points)

$$\text{DU} = \frac{2C + 2 - H + N - X}{2} = \frac{2(11) + 2 - 12 + 0 - 0}{2} = 6 \text{ (1)}$$

- b- What type of functional groups do the significant bands in the IR spectra represent? (3 points)

- Broad band around 3100 cm^{-1} : stretching band of O-H (1)
- Strong sharp band at 1711 cm^{-1} : stretching band of C=O (1)
- Sharp band at 1620 cm^{-1} : C=C stretching band (1)

- c- Fill in the table with all ^1H NMR characteristics for each signal and write down pertinent comments/ideas. (9 points)


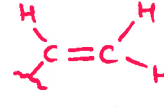
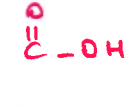
1/4 per row

3/4 per row

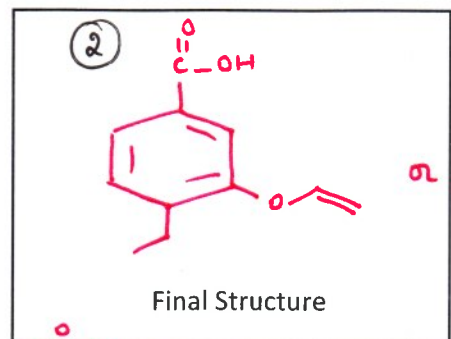
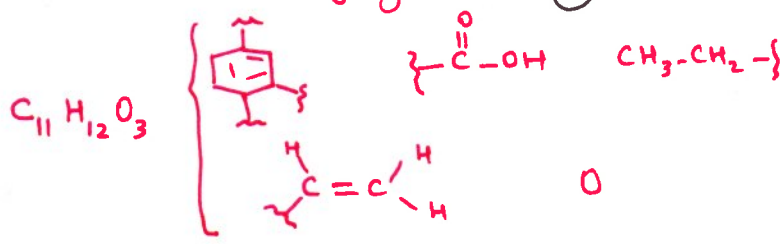
1/4 : for identifying neighboring protons
 1/2 : for chemical shift analysis

Signal	δ (ppm)	Integration	Multiplicity	Comments/ideas
A	1.22	3	t	CH_3 next to 2H \Rightarrow $\text{CH}_3\text{-CH}_2$
B	2.63	2	q	CH_2 next to 3H \Rightarrow $\text{CH}_2\text{-CH}_3$ $\delta_{\text{CH}_2} \Rightarrow$ possibilities: $\text{CH}_2\text{-C(=O)}$; $\text{CH}_2\text{-Ph}$; $\text{CH}_2\text{-C=C}$ } $\text{HC-CH}_2\text{-EWG}$
C	4.22	1	d	CH next to 1H \Rightarrow CH-CH δ_{CH} shows that CH could be: $\text{C}=\text{CH}$ or CH-O
D	4.68	1	d	CH next to 1H \Rightarrow CH-CH δ_{CH} shows it's a CH of alkene \Rightarrow $\text{HC}=\text{CH}$
E	6.98	1	dd	CH next to 2 chemically non-equivalent protons $\delta_{\text{CH}} \Rightarrow$ alkene CH \Rightarrow $\text{CH}=\text{CH}_2$
F	7.14	1	d	Aromatic protons. Total number of protons = 3 \Rightarrow Trisubstituted benzene with no symmetry (3 signals)
G	7.48	1	s	
H	7.64	1	d	
I	12.55	1	s	Carboxylic acid proton \Rightarrow C(=O)-OH

d- Identify the possible fragments then draw the final structure of the unknown in this box below. (4 points)
 PS: all fragments should add up to give the same number of atoms in the molecular formula.

Total degree of unsaturation = 6 {   

Possible fragments: (2)



Acceptable incorrect structures:



for full mark

Partial credits on:

if 2 fragments were connected as one substituent resulting in disubstituted benzene

half ^{4/8} of the mark

5. Circle the correct answer : (4 points)

a- Which molecule reacts faster in an E2 reaction with hydroxide?



b- Which molecule reacts faster in an S_N2 reaction?



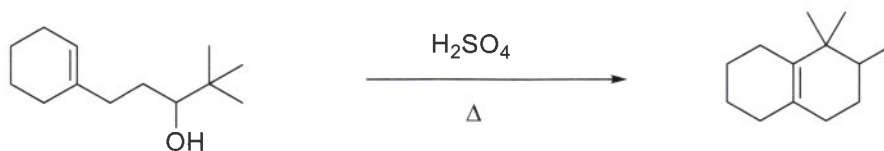
c- Which molecule reacts faster in an E1 reaction?



d- Which molecule reacts faster in an S_N1 reaction?



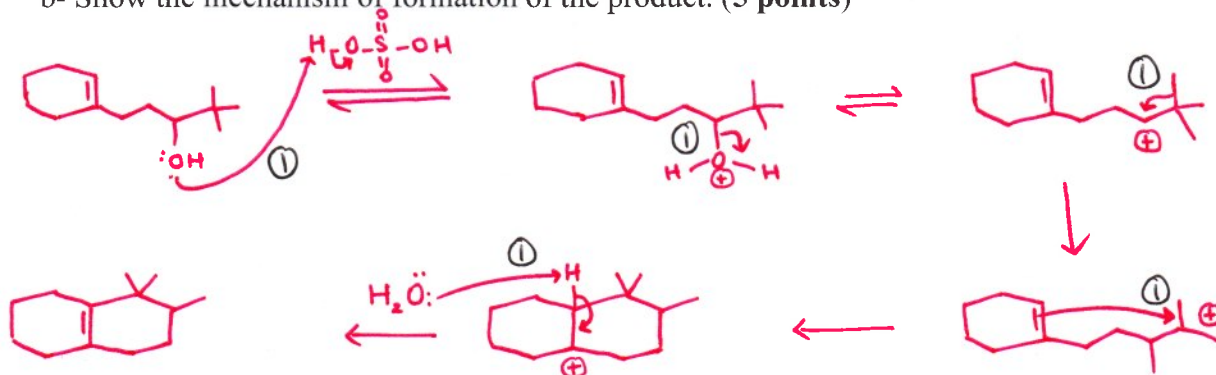
6. For this reaction below: (6 points)



a- Determine the type of reaction that took place. (1 point)

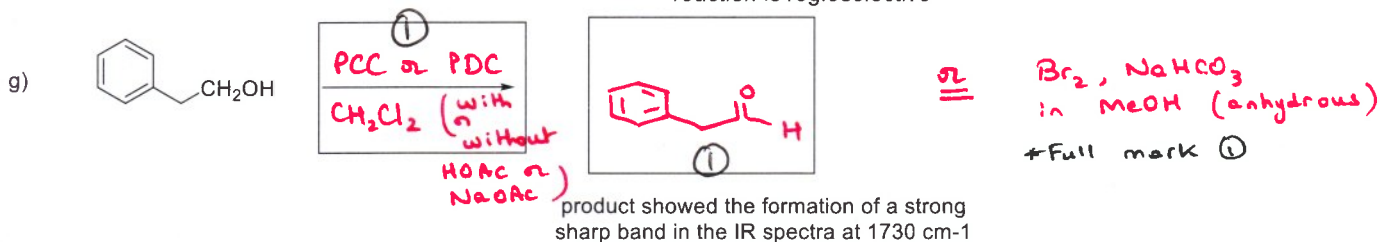
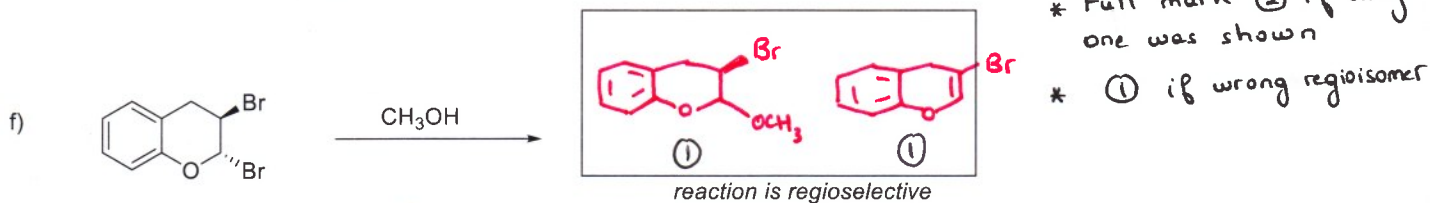
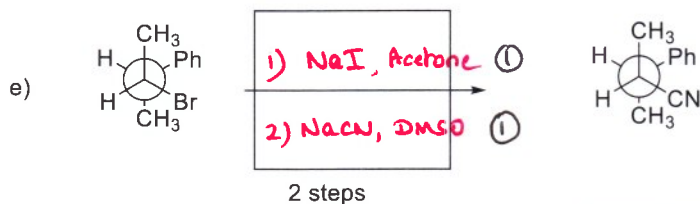
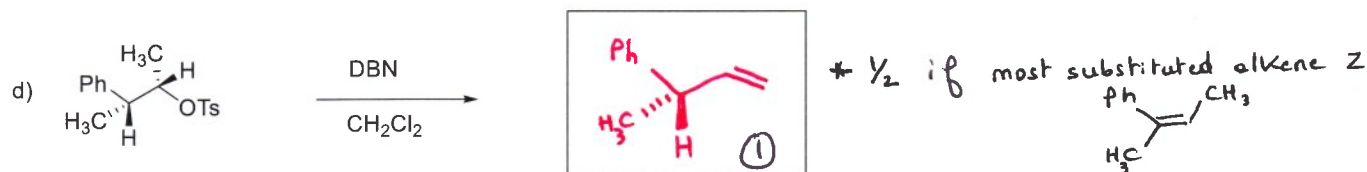
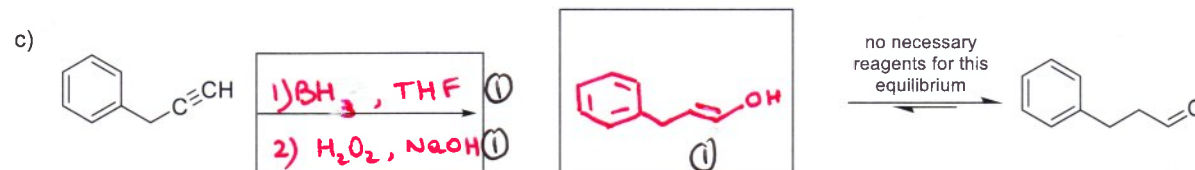
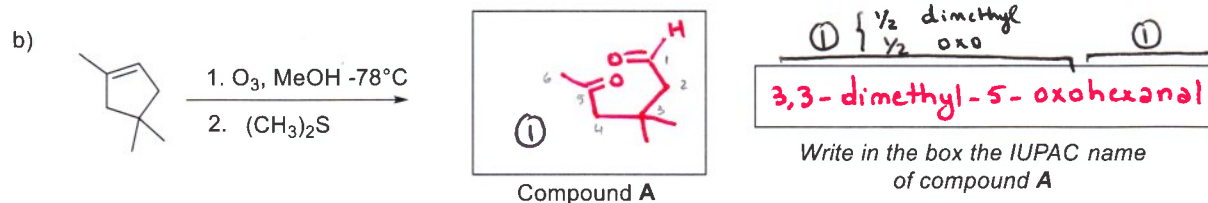
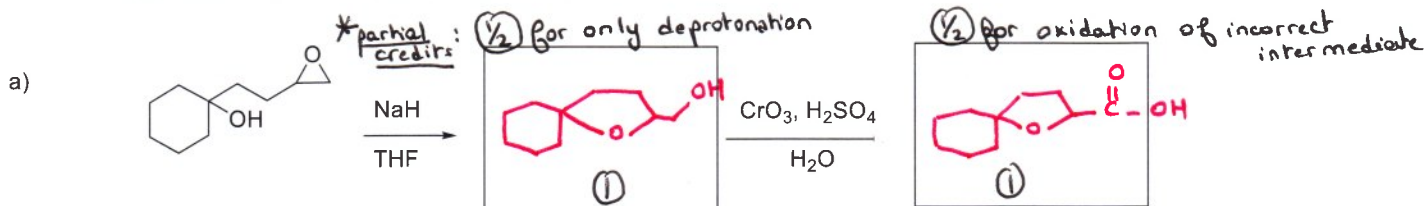
E1 (S_N1 is also acceptable)

b- Show the mechanism of formation of the product. (5 points)



if arrow correct but missing carbocation (1/2)

7. Complete each of these following reactions (i.e. fill in the boxes with the missing reagent(s) or product(s)). (15 points)

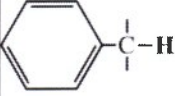
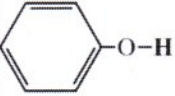
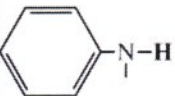
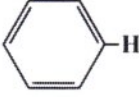


Acid	pK _a value (H ₂ O solvent)	Acid	pK _a value (H ₂ O solvent)
HI	-10		9
HBr	-9		9.9
HCl	-8		10.6
	-6.2	H ₂ O	15.7
	-3.8		17
H ₂ SO ₄	-3		20
	-2.6		24
CH ₃ OH ₂ ⁺	-2.2	H ₂	36
H ₃ O ⁺	-1.7	NH ₃	38
HNO ₃	-1.3		50
HF	3.17		51
	4.76	BuSH	10-11
H ₂ S	7.00	PhSH	≈7

IR important absorption bands (cm⁻¹): stretching

C-H Alkyl	C-H	2850-2960	m, sharp
Alkene	C-H	≥3000	m, sharp
	C=C	1650	w, sharp
Alcohol	RO-H	3200-3650	s, broad (<i>hydrogen bonded</i>)
Carboxylic acid	RC(=O)O-H	2500-3300	s, broad
Amine	R ₂ N-H	3300-3500	m, a little broad
*Carbonyl	R ₂ C=O	1650-1780	s, sharp
Nitrile	RC≡N	2220-2260	w, sharp
Alkyne	C≡C-H	~3300	w, sharp
	C≡C	2100-2260	w, sharp
Ether	C-O-C	~1200	s, sharp
Phenyl	C=C	1450-1600	m
	C-H	3030	w to m
Nitro	NO ₂	1350-1560	s

Table of approximate chemical shifts of most protons.

$R-CH_3$		0.7 - 1.3	$R-\overset{ }{N}-\overset{ }{C}-H$	2.2 - 2.9
$R-CH_2-R$		1.2 - 1.4	$R-S-\overset{ }{C}-H$	2.0 - 3.0
R_3CH		1.4 - 1.7		
$R-\overset{ }{C}=\overset{ }{C}-\overset{ }{C}-H$		1.6 - 2.6	$I-\overset{ }{C}-H$	2.0 - 4.0
$R-\overset{O}{\parallel}{C}-\overset{ }{C}-H, H-\overset{O}{\parallel}{C}-\overset{ }{C}-H$		2.1 - 2.4	$Br-\overset{ }{C}-H$	2.7 - 4.1
$RO-\overset{O}{\parallel}{C}-\overset{ }{C}-H, HO-\overset{O}{\parallel}{C}-\overset{ }{C}-H$		2.1 - 2.5	$Cl-\overset{ }{C}-H$	3.1 - 4.1
$N\equiv C-\overset{ }{C}-H$		2.1 - 3.0	$R-\overset{O}{\parallel}{S}-O-\overset{ }{C}-H$	ca. 3.0
		2.3 - 2.7	$RO-\overset{ }{C}-H, HO-\overset{ }{C}-H$	3.2 - 3.8
$R-C\equiv C-H$		1.7 - 2.7	$R-\overset{O}{\parallel}{C}-O-\overset{ }{C}-H$	3.5 - 4.8
$R-S-H$	var	1.0 - 4.0 ^b	$O_2N-\overset{ }{C}-H$	4.1 - 4.3
$R-\overset{ }{N}-H$	var	0.5 - 4.0 ^b	$F-\overset{ }{C}-H$	4.2 - 4.8
$R-O-H$	var	0.5 - 5.0 ^b		
	var	4.0 - 7.0 ^b	$R-\overset{ }{C}=\overset{ }{C}-H$	4.5 - 6.5
	var	3.0 - 5.0 ^b		6.5 - 8.0
$R-\overset{O}{\parallel}{C}-\overset{ }{N}-H$	var	5.0 - 9.0 ^b	$R-\overset{O}{\parallel}{C}-H$	9.0 - 10.0
			$R-\overset{O}{\parallel}{C}-OH$	11.0 - 12.0