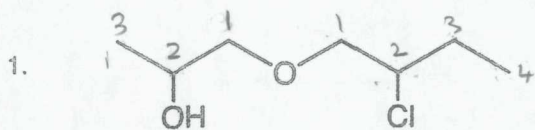


Spring 2010 - Exam 1

A. Nomenclature: (16 points)

Give an acceptable name for each of the following compounds. Be sure to indicate the stereochemistry where appropriate.



1-(2-chlorobutoxy)-2-Propanol

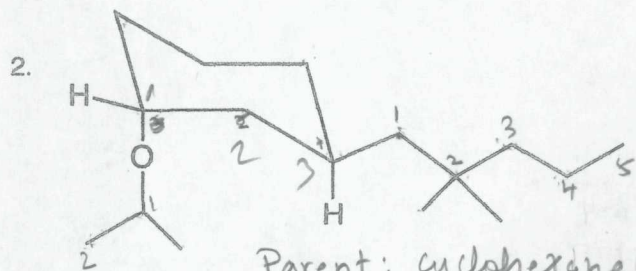
Parent:

2-Propanol

Subs

1-(2-chlorobutoxy)

4



(trans)-1-isopropoxy-3-(2,2-dimethylpentyl)cyclohexane

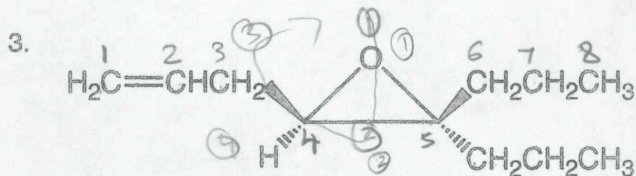
Parent: cyclohexane

Stereo: (trans)

Subs: 1-isopropoxy

3-(2,2-dimethylpentyl)

4



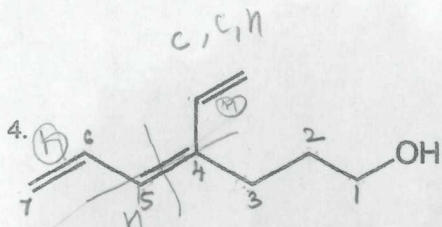
(4R)-4,5-epoxy-5-Propyloctene

Parent: octene

Subs: 4,5-epoxy  
5-propyl

Stereo (4R)

4



(4Z)-4-ethenylhepta-4,6-diene-1-ol

Parent: hepta-4,6-diene-1-ol

Subs: 4-ethenyl

Stereo: (4Z)

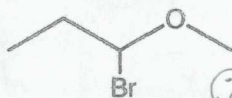
4

B. Facts: Total points = 18

1. Place the following halides in order of increasing reactivity in an SN1 process. (1=least reactive, 3=most reactive) (3 pts.)



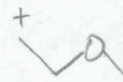
2



3



1

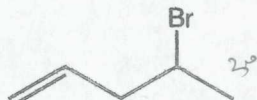


3

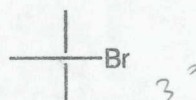
2. Place the following halides in order of increasing reactivity in an SN2 process. (1=least reactive, 3=most reactive) (3 pts.)



3



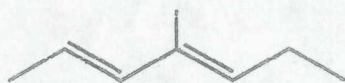
2



1

3

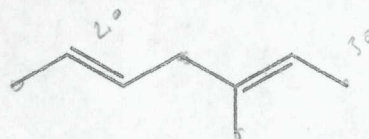
3. Place the following alkenes in order of increasing stability. (1=least stable, 3=most stable) (3 pts.)



3



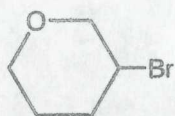
1



2

3

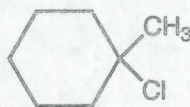
4. Place a Y in the box below any halide that will form a useful Grignard reagent and an N below any that will not. (4 pts.)



Y



N



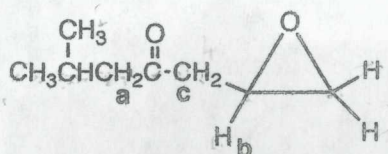
Y



N

4

5. Answer the following questions for the molecule below and place the answers in the appropriate boxes. (i) How many distinct types of protons are present in the molecule? (ii) How many distinct carbons are present? (iii) and (iv) What are the theoretically predicted multiplicities (splitting patterns) of the signals for protons a and b? (v) What is the multiplicity of the signal for carbon c in the proton-coupled  $^{13}\text{C}$  NMR? (5 pts.)



(i) # of proton types

(ii) # of carbon types

(iii) multiplicity of Ha

(iv) multiplicity of Hb

(v) multiplicity of Cc

5

(2+1)(2)(2)

(3)(2)(2)

6x2 = 12

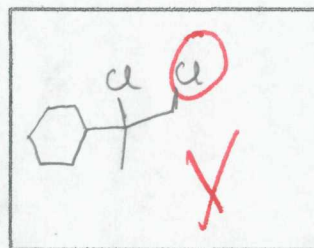
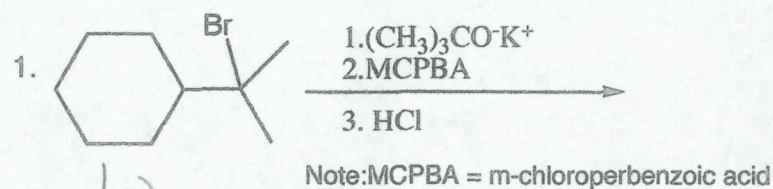
2

18

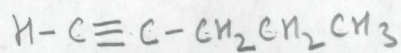
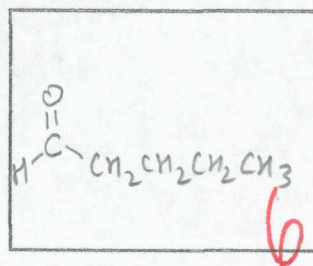
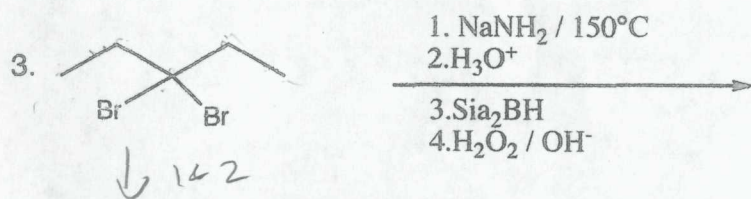
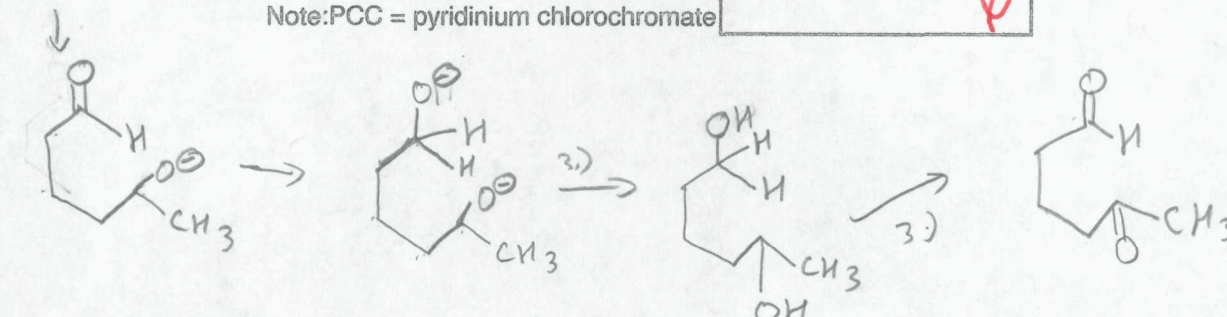
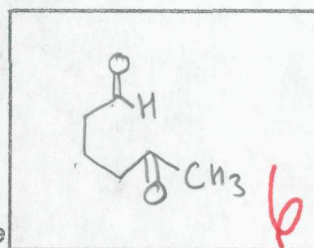
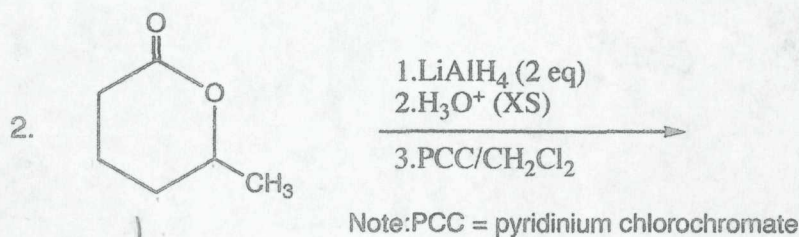
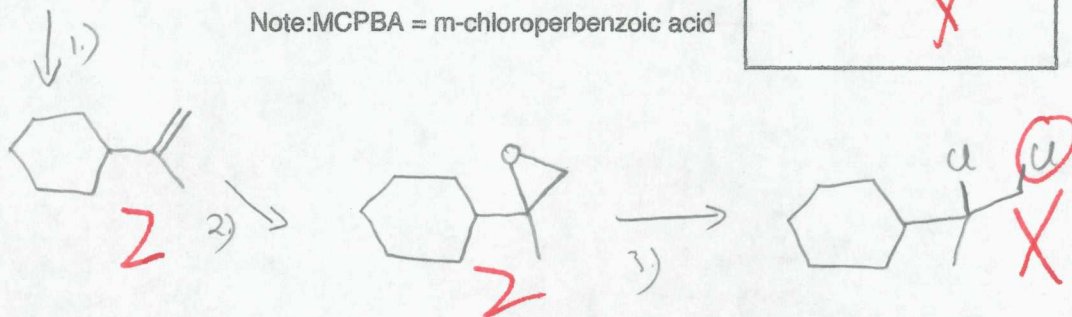
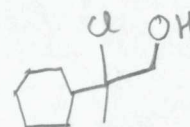


C. Reactions: Total = 30 points, 6 points each

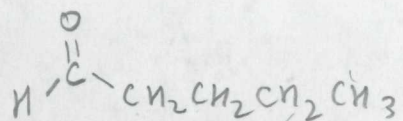
Please provide the major product in the answer box unless indicated otherwise. Indicate stereochemistry with wedges and dashes if applicable. Partial credit is awarded only when intermediate products in a multi-step reaction are shown below the reaction.



Correct Ans:-

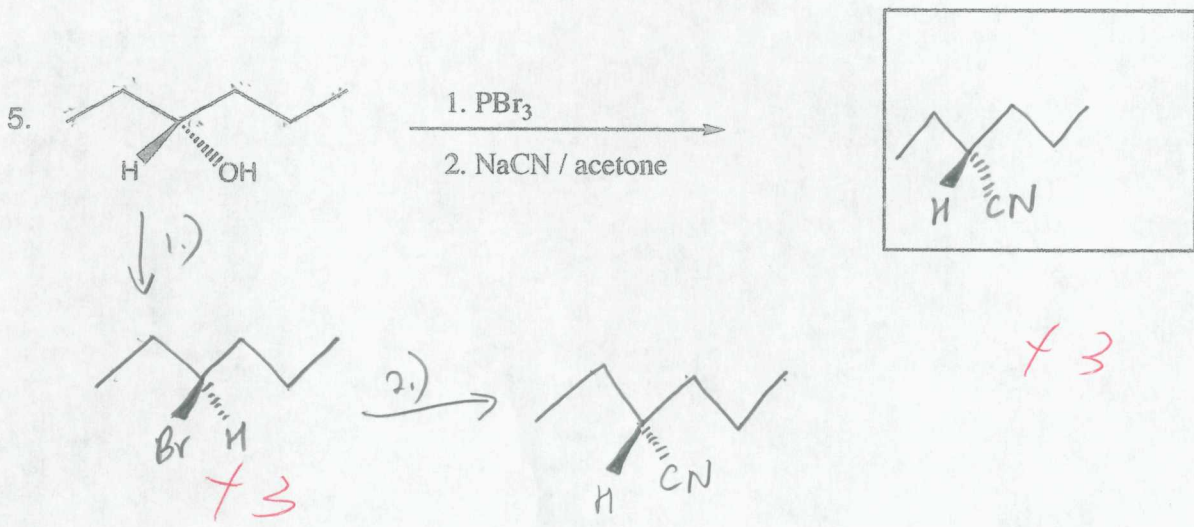
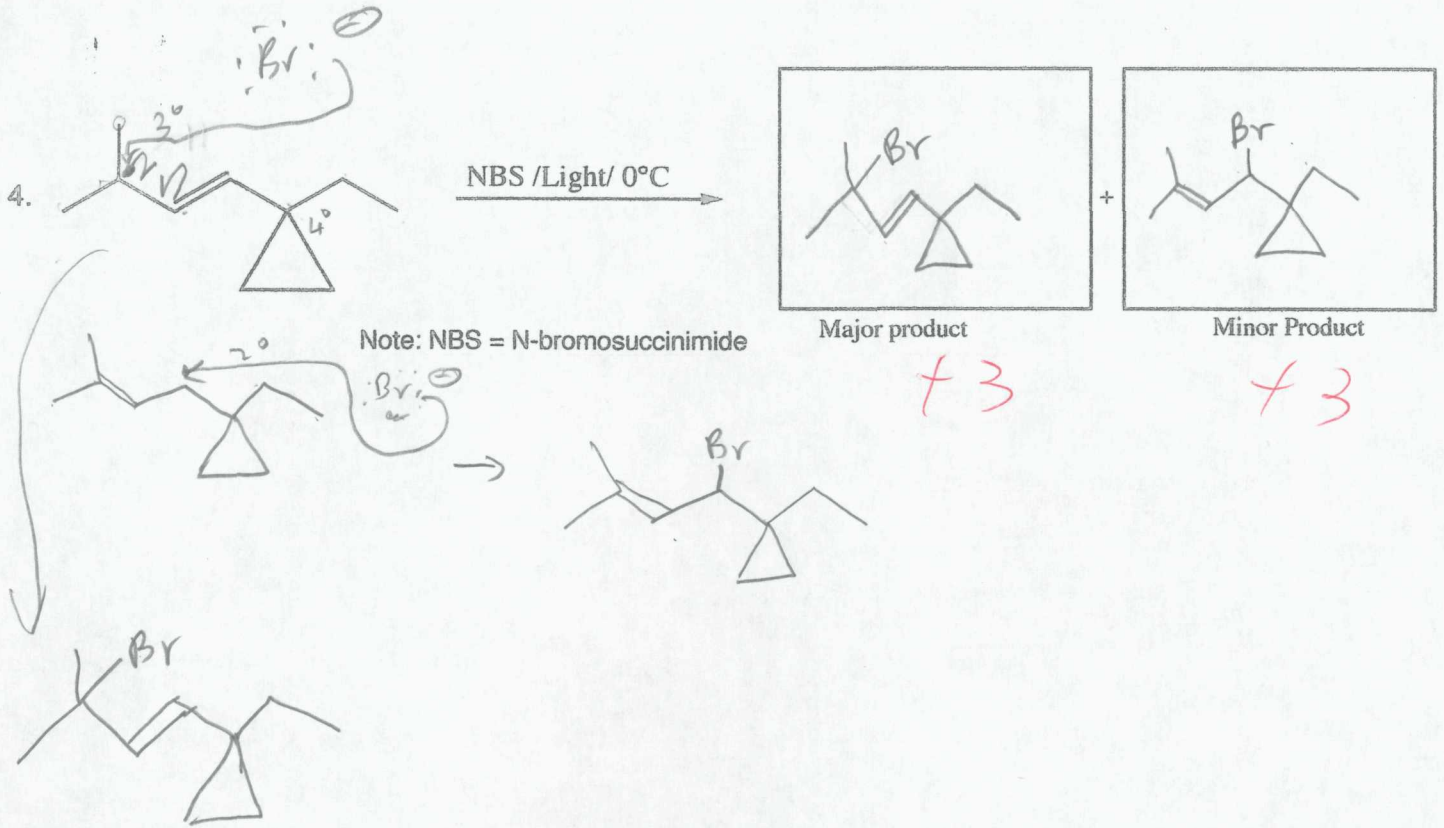


↓ 3)



3

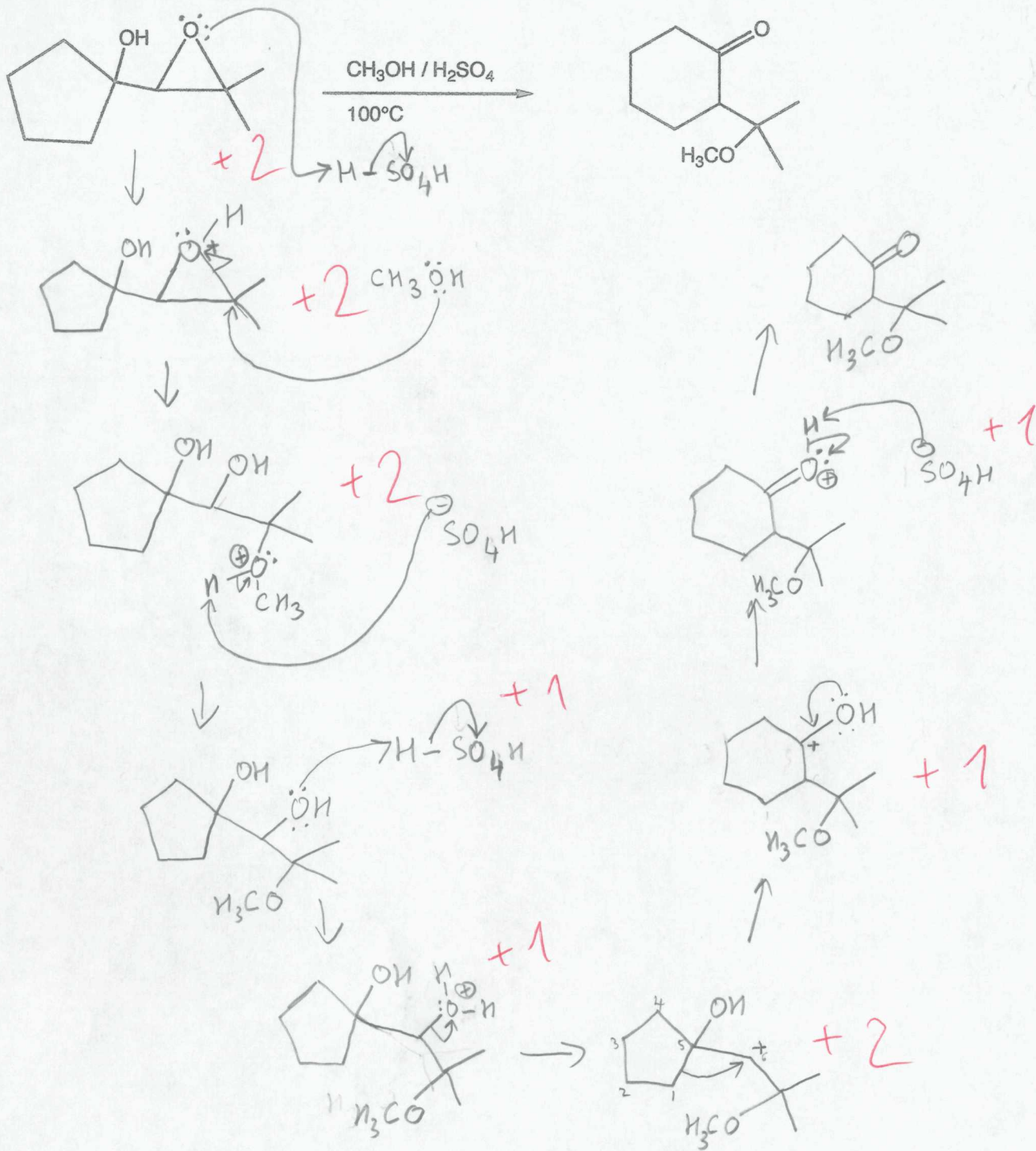
16





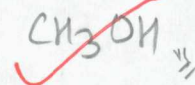
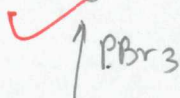
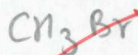
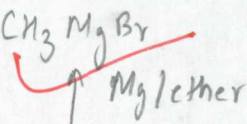
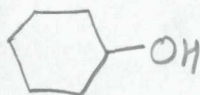
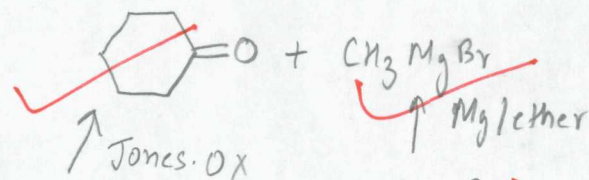
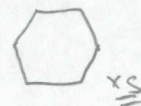
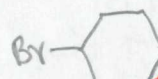
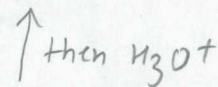
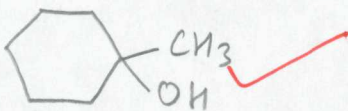
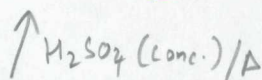
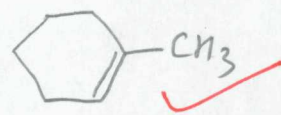
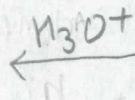
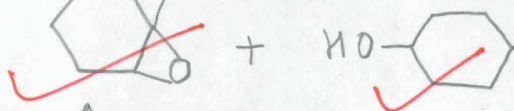
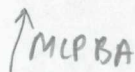
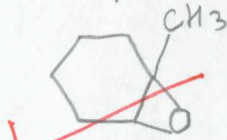
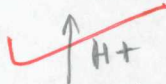
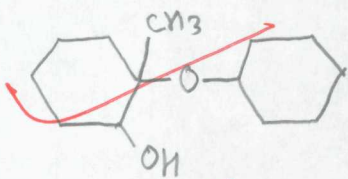
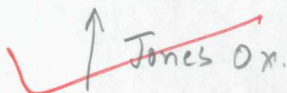
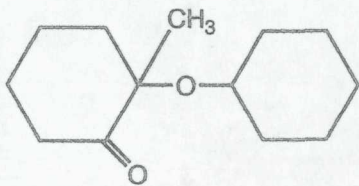
D. Mechanism: (11 points)

Provide a clear mechanism to explain the formation of the product. Use curved arrows to indicate "electron flow". Remember to show only one step at a time. Show all intermediates and all formal charges. Do not show transition states!



E. Synthesis: 12 Points

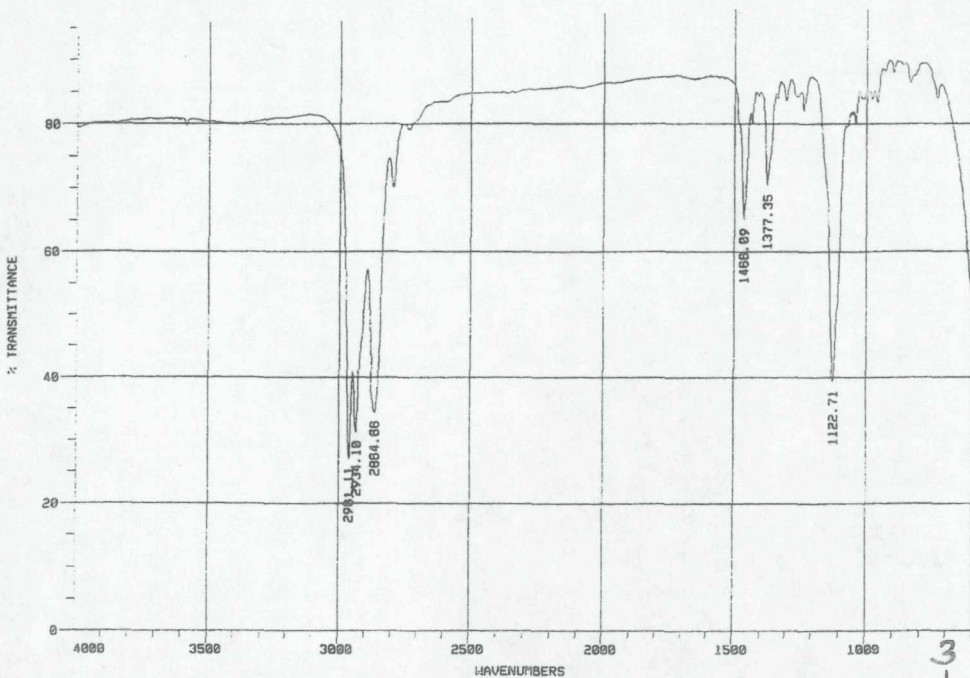
Synthesize the molecule below using any of the following reagents: cyclohexane and alcohols, alkanes, alkenes, and/or alkynes of two carbons or less, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.





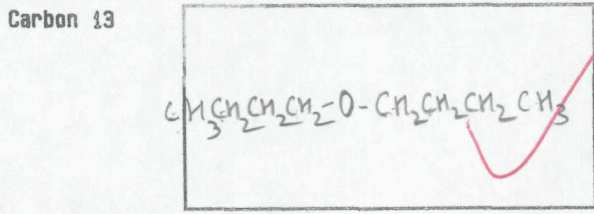
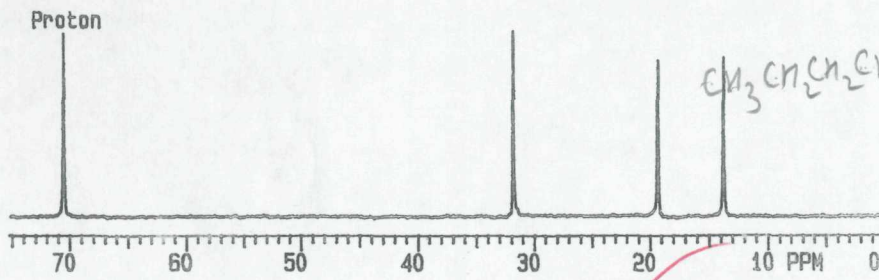
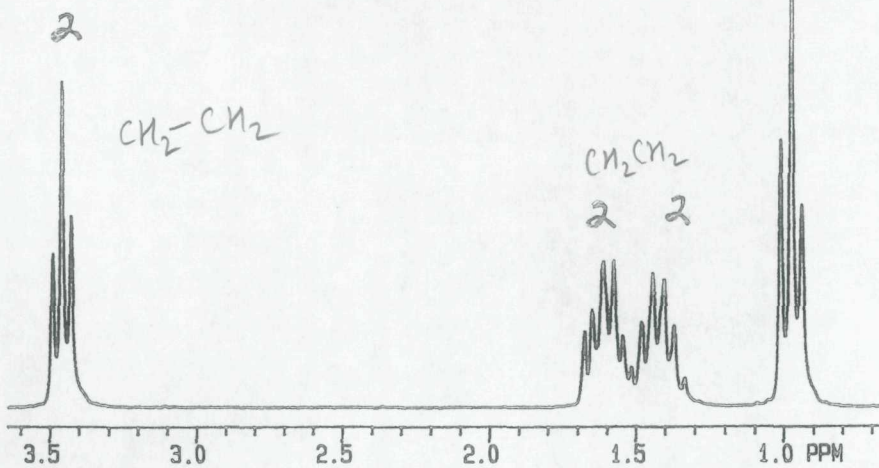
F. Spectroscopy: 12 Points

A compound with the formula  $C_8H_{18}O$  exhibits the IR,  $^1H$  NMR and proton decoupled  $^{13}C$  NMR spectra shown below. Please identify this compound and draw the structure in the box provided below.



$$\frac{(16+2)-18}{2} = 0$$

$$\frac{18-18}{2} = 0$$



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TABLE 13.3 Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT ( $\delta$ , ppm)
1° Alkyl, RCH <sub>3</sub>	0.8–1.0
2° Alkyl, RCH <sub>2</sub> R	1.2–1.4
3° Alkyl, R <sub>3</sub> CH	1.4–1.7
Allylic, R <sub>2</sub> C=C—CH <sub>3</sub>   R	1.6–1.9
Ketone, RCCH <sub>3</sub>    O	2.1–2.6
Benzylic, ArCH <sub>3</sub>	2.2–2.5
Acetylenic, RC≡CH	2.5–3.1
Alkyl iodide, RCH <sub>2</sub> I	3.1–3.3
Ether, ROCH <sub>2</sub> R	3.3–3.9
Alcohol, HOCH <sub>2</sub> R	3.3–4.0
Alkyl bromide, RCH <sub>2</sub> Br	3.4–3.6
Alkyl chloride, RCH <sub>2</sub> Cl	3.6–3.8
Vinylic, R <sub>2</sub> C=CH <sub>2</sub>	4.6–5.0
Vinylic, R <sub>2</sub> C=CH   R	5.2–5.7
Aromatic, ArH	6.0–9.5
Aldehyde, RCHO    O	9.5–9.6
Alcohol hydroxyl, ROH	0.5–6.0 <sup>a</sup>
Amino, R—NH <sub>2</sub>	1.0–5.0 <sup>a</sup>
Phenolic, ArOH	4.5–7.7 <sup>a</sup>
Carboxylic, RCOH    O	10–13 <sup>a</sup>

<sup>a</sup> The chemical shifts of these protons vary in different solvents and with temperature and concentration.

TABLE 13.4 Approximate carbon-13 chemical shifts


TYPE OF CARBON ATOM	CHEMICAL SHIFT ( $\delta$ , ppm)
1° Alkyl, RCH <sub>3</sub>	0–40
2° Alkyl, RCH <sub>2</sub> R	10–50
3° Alkyl, RCHR <sub>2</sub>	15–50
Alkyl halide or amine, —C—X (X = Cl, Br, or N—)	10–65
Alcohol or ether, —C—O	50–90
Alkyne, —C≡	60–90
Alkene, >C=	100–170
Aryl, 	100–170
Nitriles, —C≡N	120–130
Amides, —C(=O)—N—	150–180
Carboxylic acids, esters, —C(=O)—O	160–185
Aldehydes, ketones, —C(=O)—	182–215

TABLE 13.2 Characteristic infrared absorptions of groups

GROUP	FREQUENCY RANGE (cm <sup>-1</sup> )	INTENSITY <sup>a</sup>
<b>A. Alkyl</b>		
C—H (stretching)	2853–2962	(m–s)
Isopropyl, —CH(CH <sub>3</sub> ) <sub>2</sub>	1380–1385 and 1365–1370	(s) (s)
<i>tert</i> -Butyl, —C(CH <sub>3</sub> ) <sub>3</sub>	1385–1395 and ~1365	(m) (s)
<b>B. Alkenyl</b>		
C—H (stretching)	3010–3095	(m)
C=C (stretching)	1620–1680	(v)
R—CH=CH <sub>2</sub>	} (out-of-plane C—H bendings)	985–1000 (s) and 905–920 (s)
R <sub>2</sub> C=CH <sub>2</sub>		880–900 (s)
<i>cis</i> -RCH=CHR		675–730 (s)
<i>trans</i> -RCH=CHR		960–975 (s)
<b>C. Alkynyl</b>		
≡C—H (stretching)	~3300	(s)
C≡C (stretching)	2100–2260	(v)
<b>D. Aromatic</b>		
Ar—H (stretching)	~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)		
Monosubstituted	and	690–710 (very s) 730–770 (very s)
<i>o</i> Disubstituted		735–770 (s)
<i>m</i> Disubstituted	and	680–725 (s) 750–810 (very s)
<i>p</i> Disubstituted		800–840 (very s)
<b>E. Alcohols, Phenols, and Carboxylic Acids</b>		
O—H (stretching)		
Alcohols, phenols (dilute solutions)	3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)	3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)	2500–3000	(broad, v)
<b>F. Aldehydes, Ketones, Esters, and Carboxylic Acids</b>		
C=O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic acids	1710–1780	(s)
Amides	1630–1690	(s)
<b>G. Amines</b>		
N—H	3300–3500	(m)
<b>H. Nitriles</b>		
C≡N	2220–2260	(m)

<sup>a</sup> Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.