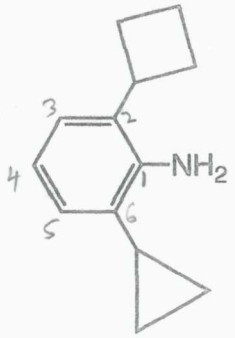
A. Nomenclature: (12 points)
Give an acceptable IUPAC name for each of the following compounds. Be sure to indicate the **stereochemistry** where appropriate.

1.

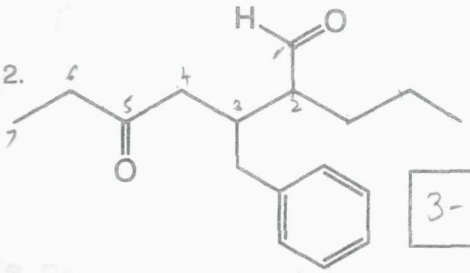


2-cyclobutyl-6-cyclopropyl aniline

4

cyclobutyl
cyclopropyl

2.

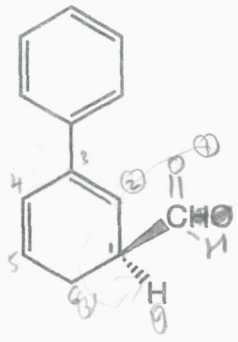


2-propyl 5-oxo
3-benzyl

3-benzyl-5-oxo-2-propylheptanal

4

3.



(S)-3-phenyl-2,4-cyclohexadiene carbaldehyde

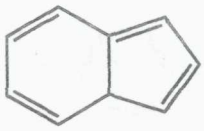
4

3-phenyl

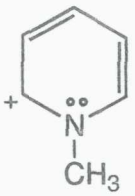
12

B. Facts: 17 points

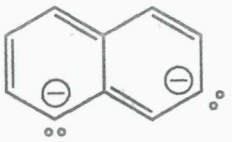
1. Label the molecules below as aromatic (**AR**), antiaromatic (**AA**), or nonaromatic (**NA**). Assume all are planar. (8 pts.)



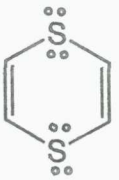
NA ✓



AR ✓



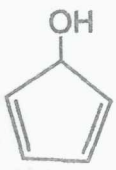
~~NA~~ AA ← correct Ans



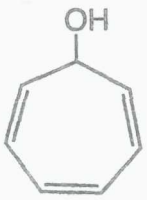
NA ✓

6

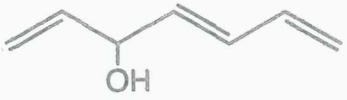
2. Rank the following alcohols in order of increasing rate of dehydration. (1=slowest rate, 3=fastest rate) (3 pts.)



1



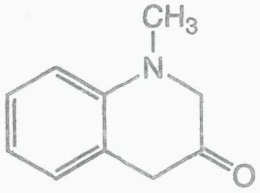
3



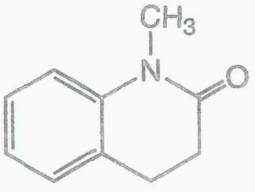
2

3 ✓

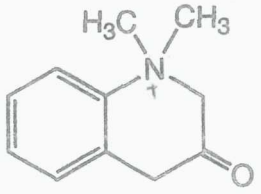
3. Rank the following substituted benzene compounds in order of increasing reactivity in an electrophilic aromatic substitution reaction with Br_2 / $FeBr_3$. (1=least reactive, 3=most reactive) (3 pts.)



3



2



1

3 ✓

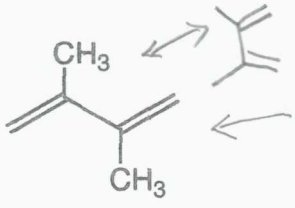
4. Rank the following compounds in order of increasing reactivity in a Diels-Alder reaction. (1=least reactive, 3=most reactive) (3 pts.)

locked in s-cis

~~2~~ 3

No alkyl groups

~~1~~ 1



2 methyl groups donate e- density making the diene better nucleophile.

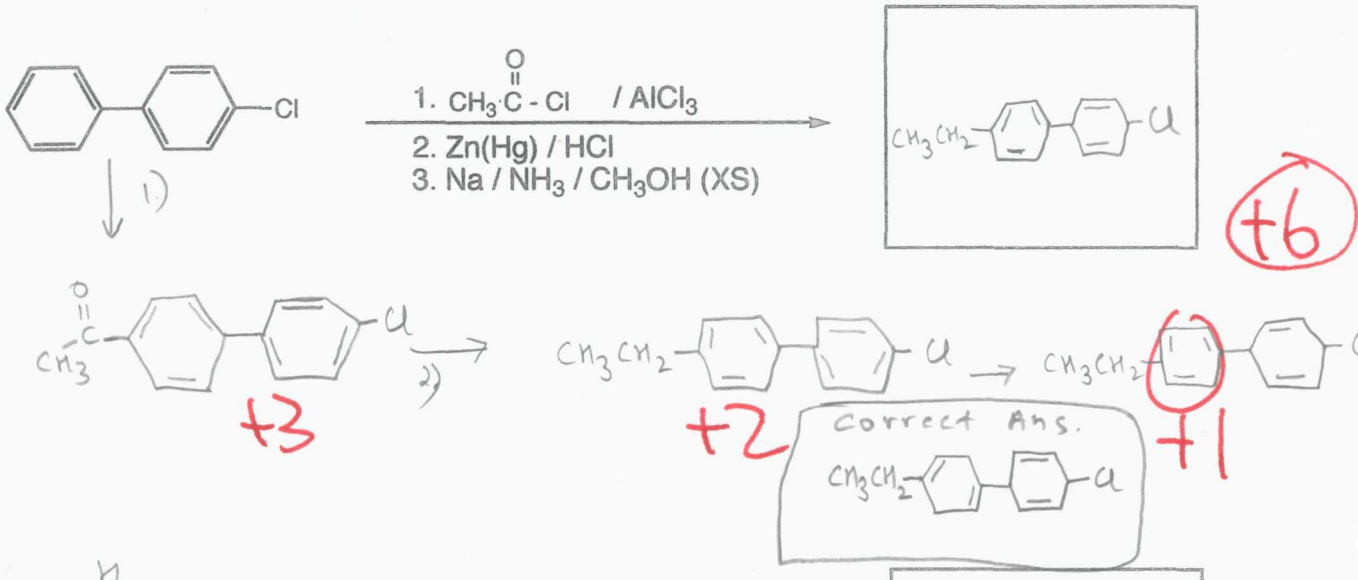
~~3~~ 2

2

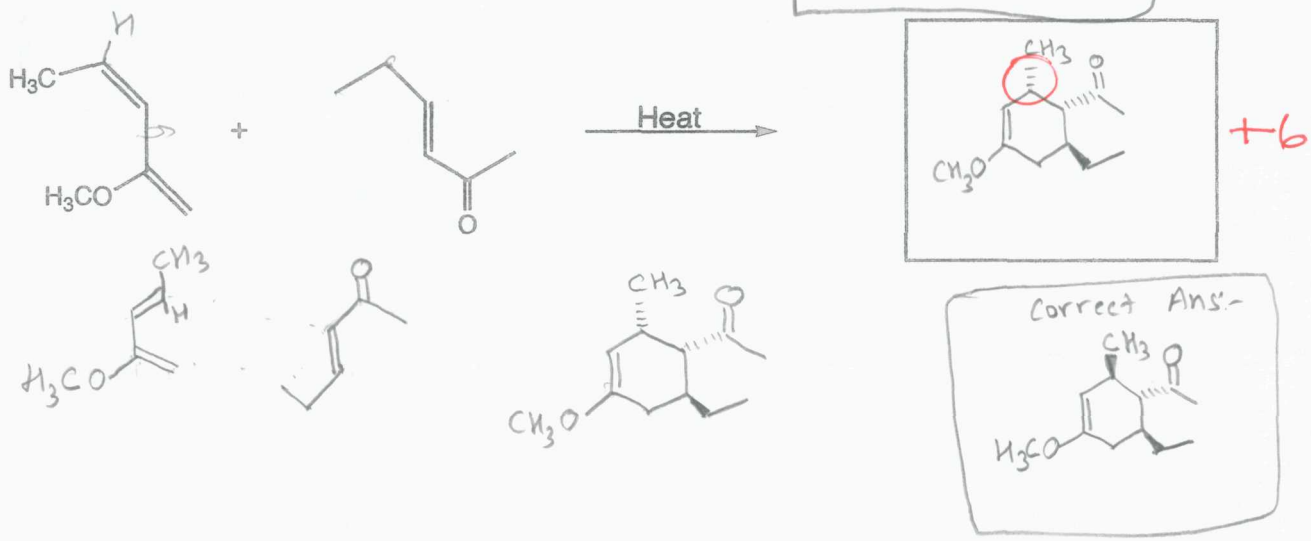
12

C. Reactions: Total = 35 points, 7 points each
Please provide the major product in the answer box. Indicate **stereochemistry** if applicable. Partial credit is awarded only when intermediate products in a multi-step reaction are shown below the reaction.

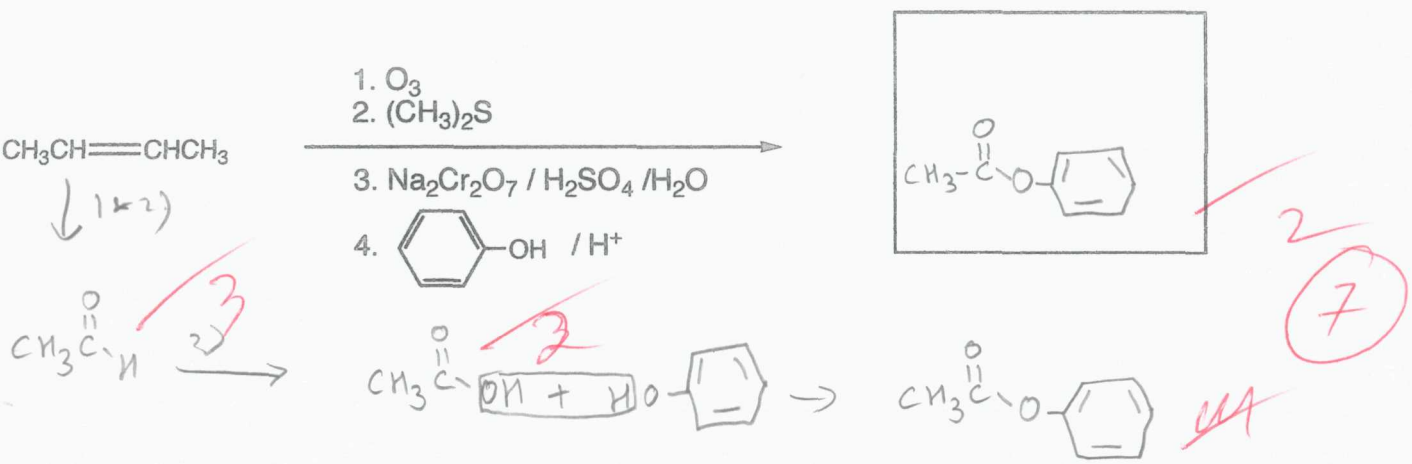
1.



2.

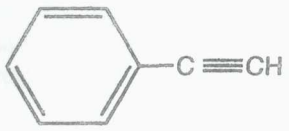


3. $CH_3CH{=}CHCH_3$

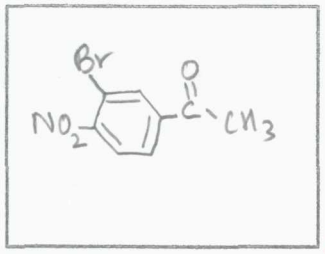


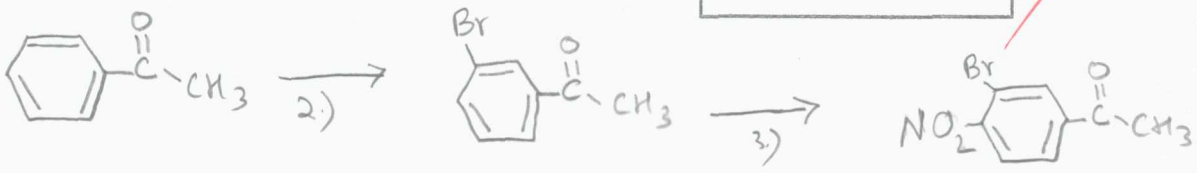
19

4.

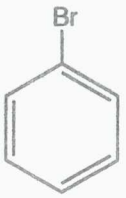


1. H_2SO_4 / H_2O / $HgSO_4$
2. Br_2 / $FeBr_3$
3. HNO_3 / H_2SO_4

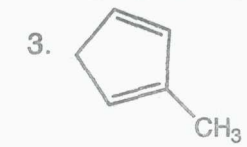


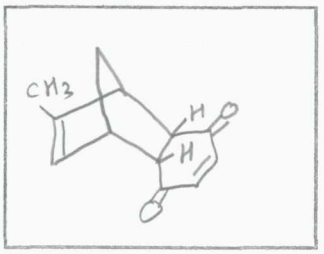


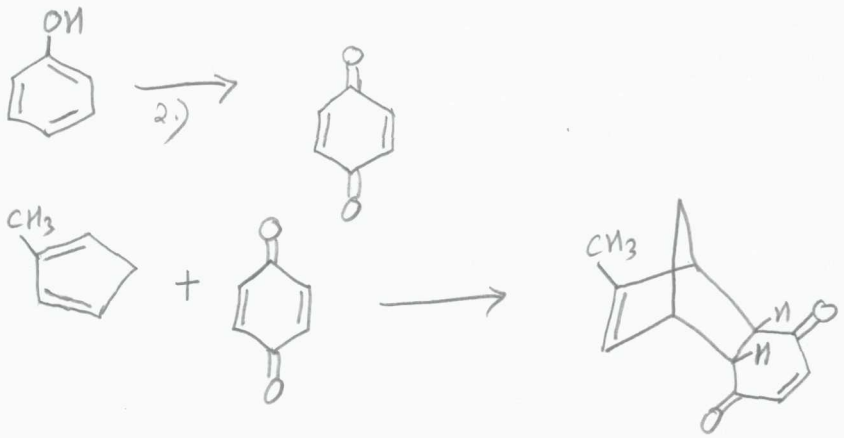
5.



1. NaOH (2 eq.), 350 °C, 2500 psi
2. $Na_2Cr_2O_7$ / H_2SO_4 / H_2O
3.

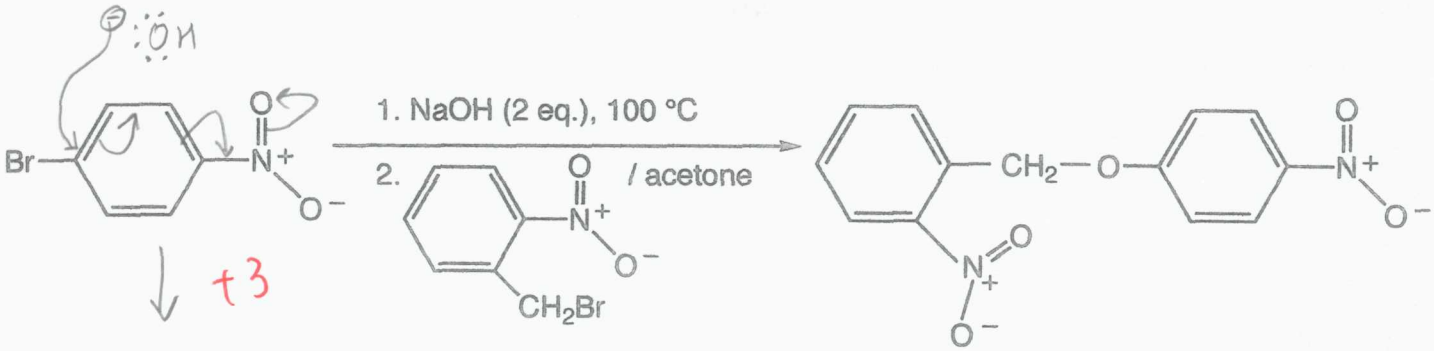


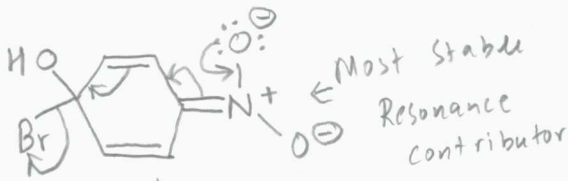


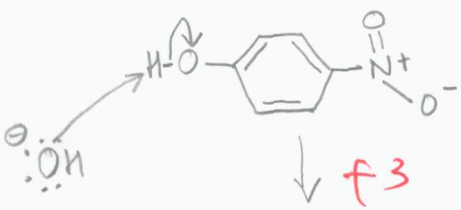


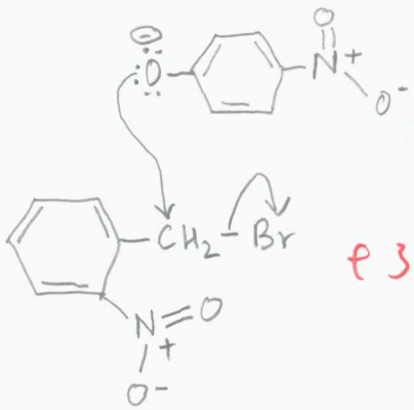
D. Mechanism: (12 points)

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. When more than one resonance contributor may be drawn, be sure to draw the most stable contributor.**





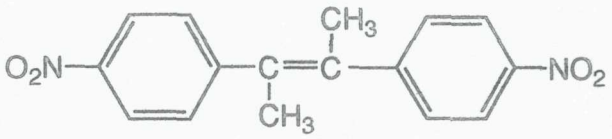




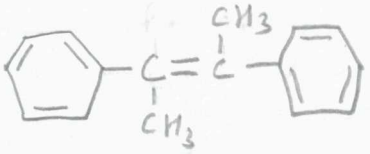
12

E. Synthesis: 12 Points

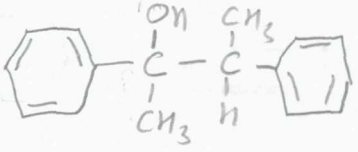
Synthesize the molecule below using any of the following reagents: benzene, alcohols of two carbons or less, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids. You may ignore stereochemistry.



↑ HNO_3/H_2SO_4 (2eq)

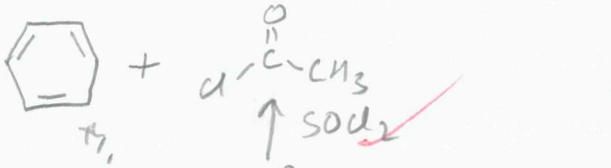


↑ conc. H_2SO_4 / Δ

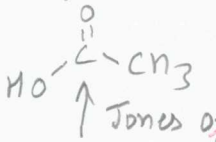


↑ then H_3O^+

↑ $AlCl_3$ ↑ Mg / ether

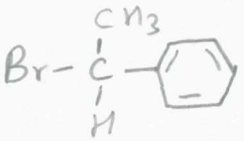


↑ $SOCl_2$

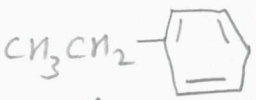


↑ Jones ox.

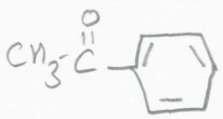
CH_3CH_2OH



↑ NBS / hν



↑ Zn(Hg) / HCl(aq)



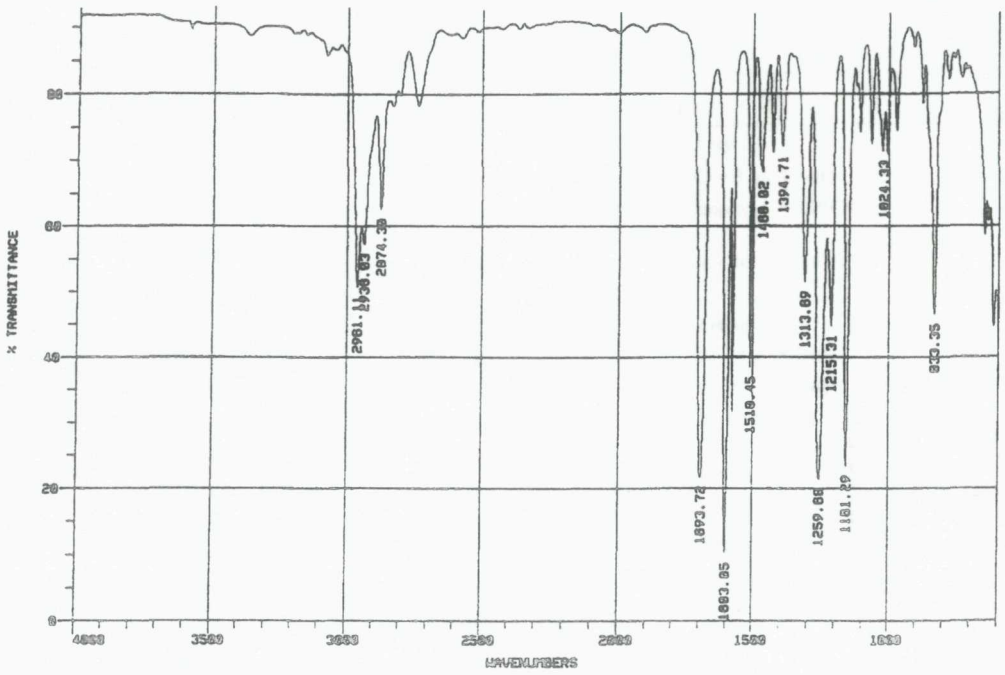
+12

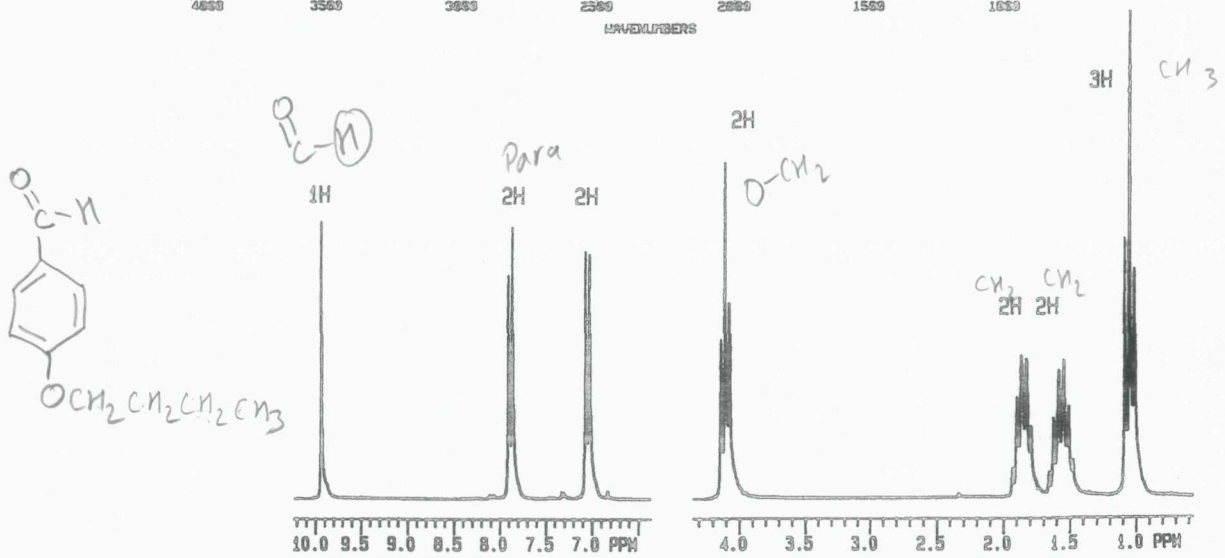
F. Spectroscopy: 12 Points

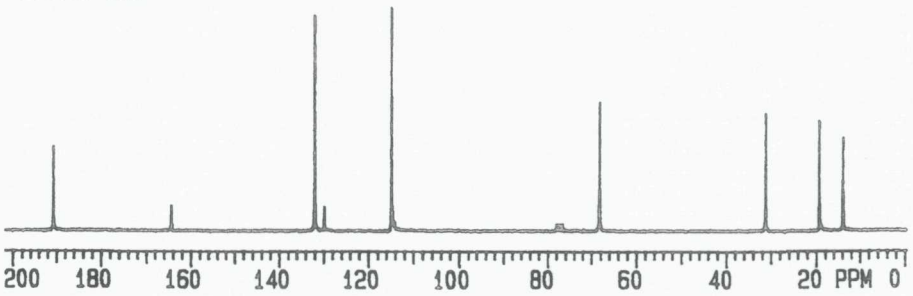
A compound with the formula $C_{11}H_{14}O_2$ exhibits the IR, ^1H NMR and proton decoupled ^{13}C NMR spectra shown below. Please identify this compound and draw the structure in the box provided below.

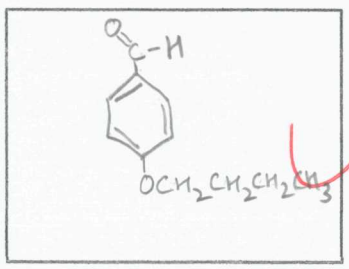
$22+2 = \frac{24-14}{2}$

U.N = 5









12

Sp 2010
Exam 1

TABLE 13.3 Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Ketone, $RC(=O)CH_3$	2.1–2.6
Benzylic, $ArCH_3$	2.2–2.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl chloride, RCH_2Cl	3.6–3.8
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Aldehyde, $RC(=O)H$	9.5–9.6
Alcohol hydroxyl, ROH	0.5–6.0[a]
Amino, $R{-}NH_2$	1.0–5.0[a]
Phenolic, ArOH	4.5–7.7[a]
Carboxylic, $RC(=O)OH$	10–13[a]

[a] 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 (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-\overset{|}{C}-X$ (X = Cl, Br, or $-\overset{|}{N}-$)	10–65
Alcohol or ether, $-\overset{|}{C}-O$	50–90
Alkyne, $-C{\equiv}$	60–90
Alkene, $>C{=}$	100–170
Aryl, 	100–170
Nitriles, $-C{\equiv}N$	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^{-1})	INTENSITY[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $-CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $-C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
$R-CH{=}CH_2$ (out-of-plane C—H bendings)		985–1000	(s)
	and	905–920	(s)
$R_2C{=}CH_2$ (out-of-plane C—H bendings)		880–900	(s)
cis-RCH=CHR (out-of-plane C—H bendings)		675–730	(s)
trans-RCH=CHR (out-of-plane C—H bendings)		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o Disubstituted		735–770	(s)
m Disubstituted		680–725	(s)
	and	750–810	(very s)
p Disubstituted		800–840	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
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)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
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)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

[a] Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.