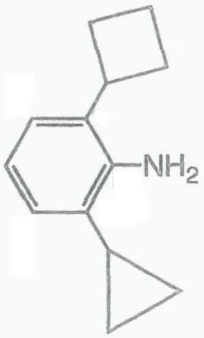
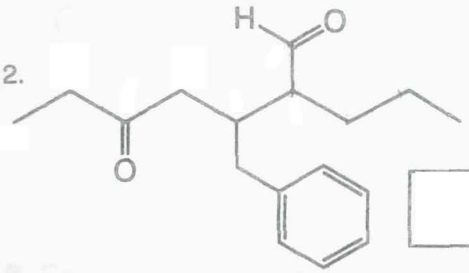
**A. Nomenclature:** (12 points)
Give an acceptable IUPAC name for each of the following compounds. Be sure to indicate the **stereochemistry** where appropriate.

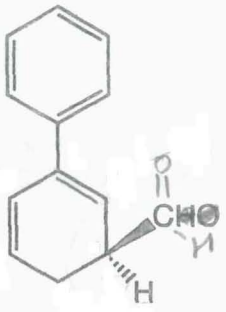
1.




2.

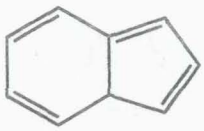



3.



**B. Facts:** 17 points

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



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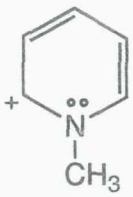


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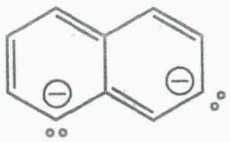

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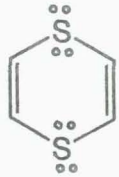


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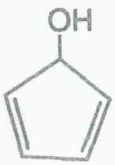
2. Rank the following alcohols in order of increasing rate of dehydration. (1=slowest rate, 3=fastest rate) (3 pts.)

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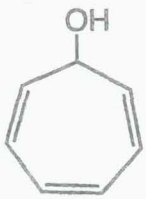


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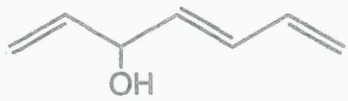


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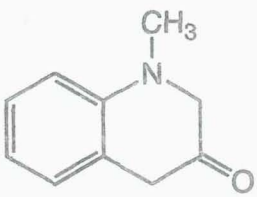
3. Rank the following substituted benzene compounds in order of increasing reactivity in an electrophilic aromatic substitution reaction with $Br_2$ / $FeBr_3$. (1=least reactive, 3=most reactive) (3 pts.)

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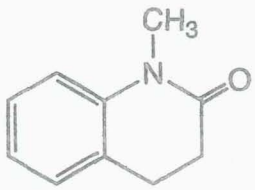


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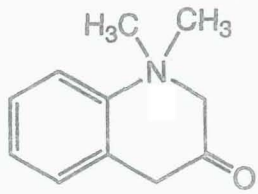


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4. Rank the following compounds in order of increasing reactivity in a Diels-Alder reaction. (1=least reactive, 3=most reactive) (3 pts.)

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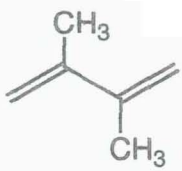


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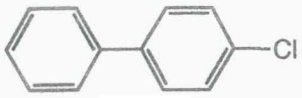
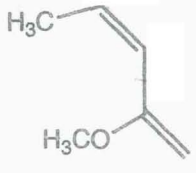
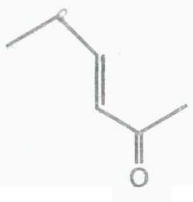
**C. Reactions**: Total = 35 points, 7 points each
Please provide the major product in the answer box. Indicate **stereochemistry** if applicable. Partial credit is awarded only when intermediate products in a multi-step reaction are shown below the reaction.

1. 

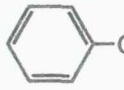
$$\xrightarrow[\text{2. Zn(Hg) / HCl}]{\text{1. } CH_3C(=O)Cl \text{ / } AlCl_3}$$
$$\xrightarrow{\text{3. Na / } NH_3 \text{ / } CH_3OH \text{ (XS)}}$$

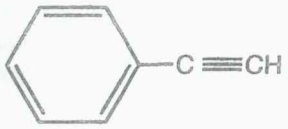
2.  + 

$$\xrightarrow{\text{Heat}}$$

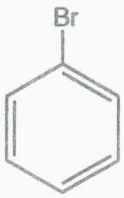
3. $CH_3CH{=}CHCH_3$

$$\xrightarrow[\text{2. } (CH_3)_2S]{\text{1. } O_3}$$
$$\xrightarrow{\text{3. } Na_2Cr_2O_7 \text{ / } H_2SO_4 \text{ / } H_2O}$$

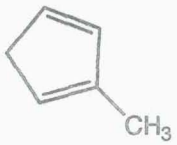
4.  / $H^+$

4. 

$\xrightarrow[\text{2. } Br_2 / FeBr_3 \\ \text{3. } HNO_3 / H_2SO_4]{\text{1. } H_2SO_4 / H_2O / HgSO_4}$

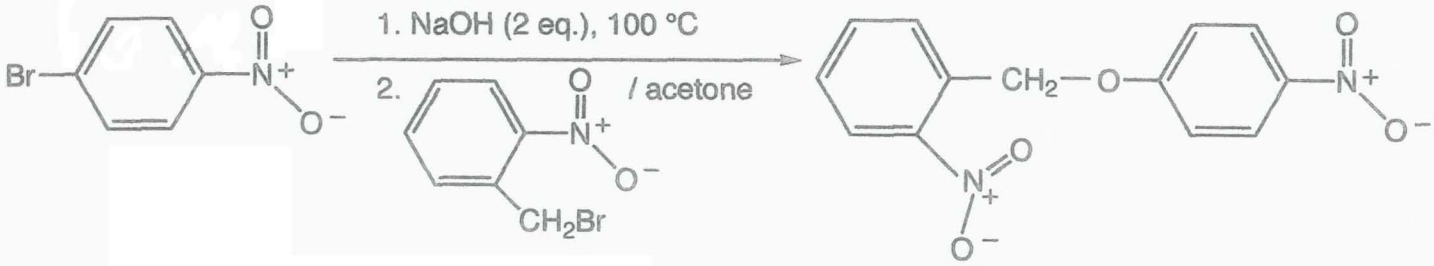
5. 

$\xrightarrow[\text{2.} Na_2Cr_2O_7 / H_2SO_4 / H_2O \\ \text{3.}]{\text{1. NaOH (2 eq.), 350 °C, 2500 psi}}$



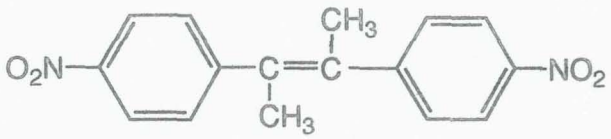
**D. Mechanism**: (12 points )

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.**



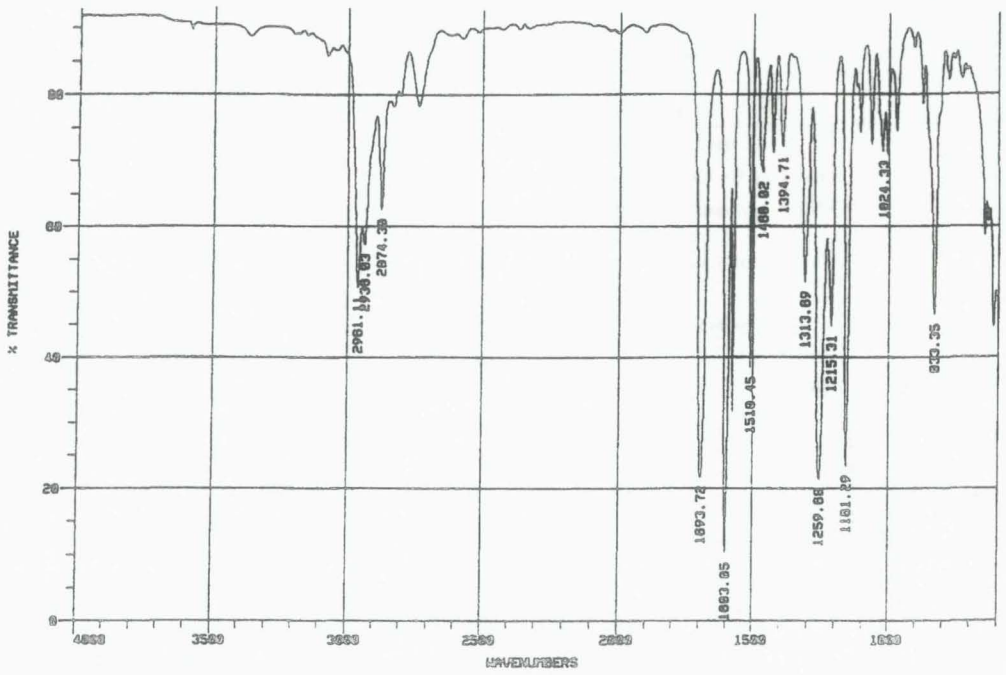
**E. Synthesis**: 12 Points

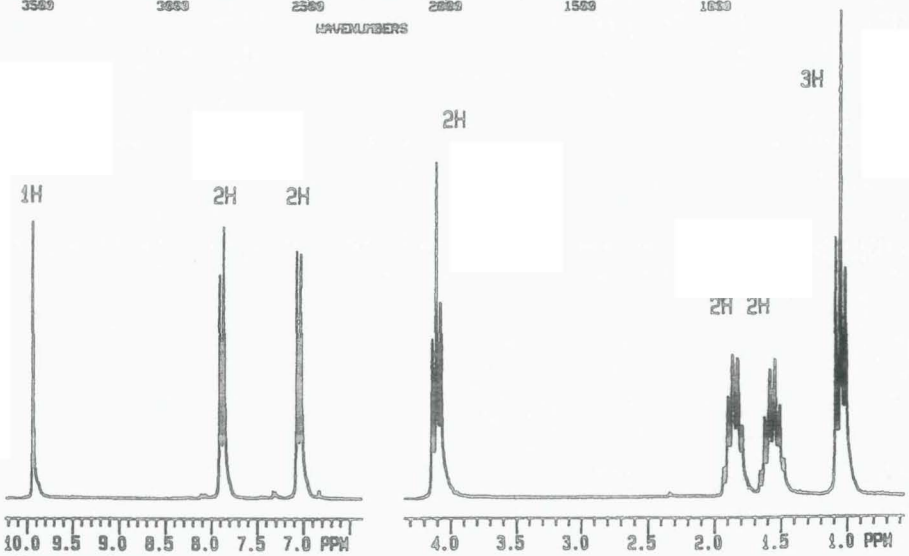
Synthesize the molecule below using any of the following reagents: benzene, alcohols of two carbons or less, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids. You may ignore stereochemistry.



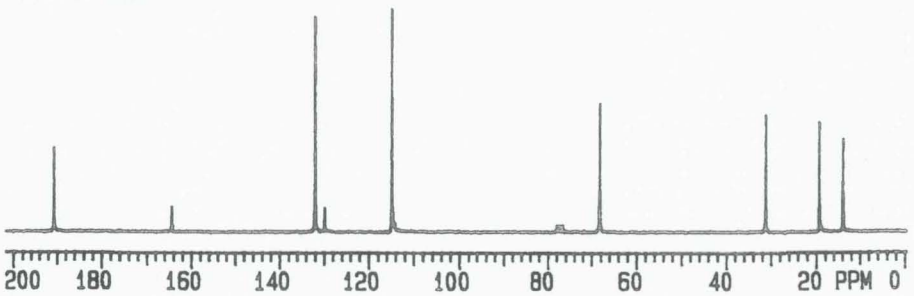
## F. Spectroscopy: 12 Points

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.




Proton NMR




Carbon 13 NMR

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.