

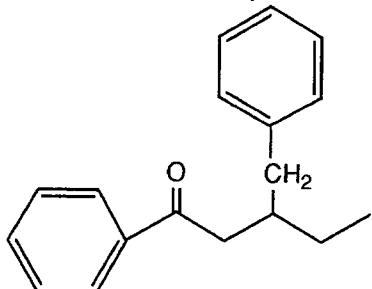
# CHEM 3332 - EXAM 2

## A. Nomenclature (3 points each, 9 total points)

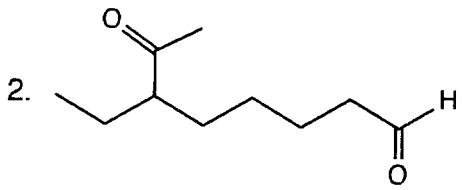
Please provide an acceptable name for each of the following compounds.

Bean-Cai-2  
Chem 3332

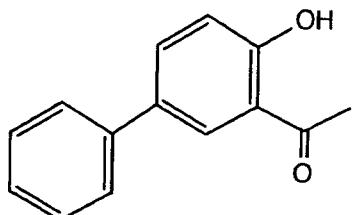
1.



2.

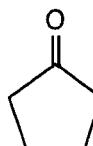
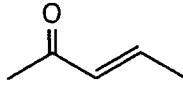
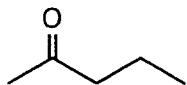


3.

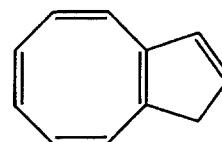
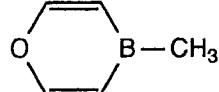
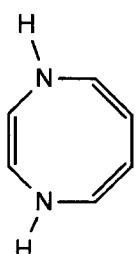


**B. Facts** (3 points each, 18 total points)

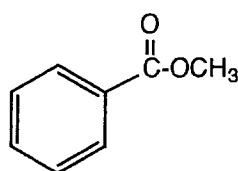
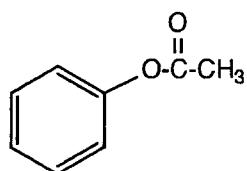
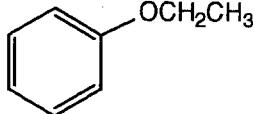
1. Place the following compounds in order of increasing frequency ( $\text{cm}^{-1}$ ) of the C=O stretch. (1=lowest frequency, 3=highest frequency)



2. Label the compounds below as aromatic, nonaromatic, or antiaromatic. (Assume all are planar.)

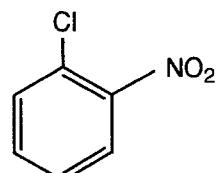
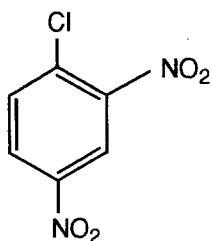
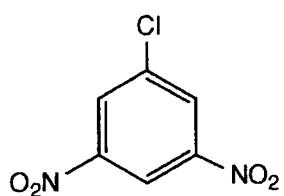


3. Place the following compounds in order of increasing reactivity in an electrophilic aromatic substitution reaction. (1=least reactive, 3=most reactive)

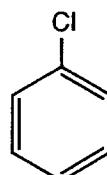
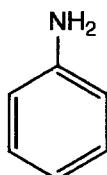
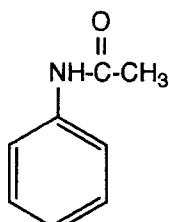


2

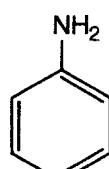
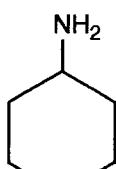
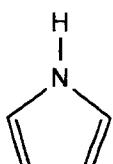
4. Place the following compounds in order of increasing reactivity in an nucleophilic aromatic substitution reaction with hydroxide. (1=least reactive, 3=most reactive)



5. Place the following compounds in order of increasing rate of product formation by Friedel-Crafts acylation. (1=slowest, 3=fastest)



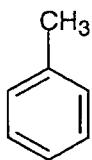
6. Place the following compounds in order of increasing basicity. (1=least basic, 3=most basic)



**C. Reactions (6 points each; 30 points total)**

Please provide the **major product**, or **necessary reagents**, or **starting material** in the **box** provided below. Be sure your drawing indicates stereochemistry if applicable.

1.

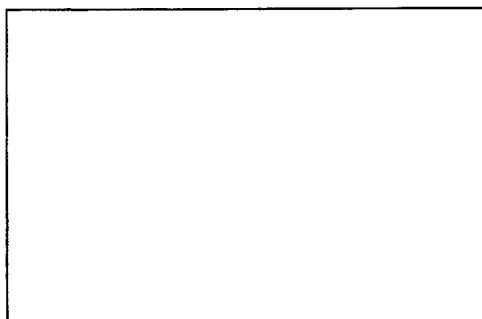


1.  $\text{KMnO}_4$ ,  $\text{HO}^-$ ,  $\text{H}_2\text{O}$ ,  $\Delta$

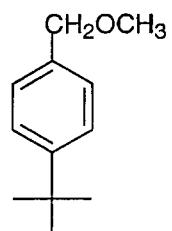
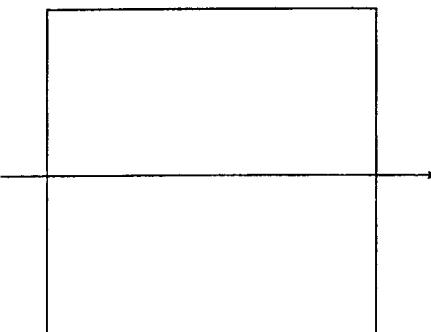
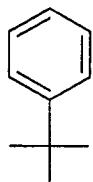
2.  $\text{H}_3\text{O}^+$

3.  $\text{SOCl}_2$

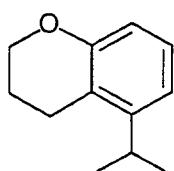
4. C=C1CCCCC1,  $\text{AlCl}_3$



2.



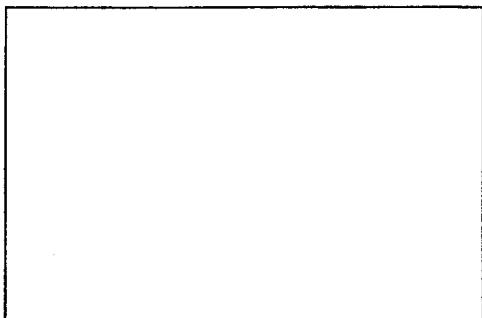
3.



1.  $\text{Br}_2$ ,  $\text{FeBr}_3$

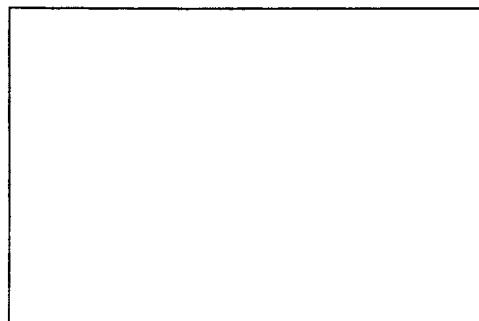
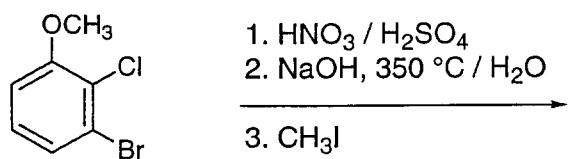
2.  $\text{HI}$  (excess)

3.  $\text{NBS}$  (excess),  $\text{h}\nu$

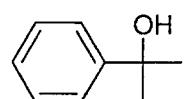
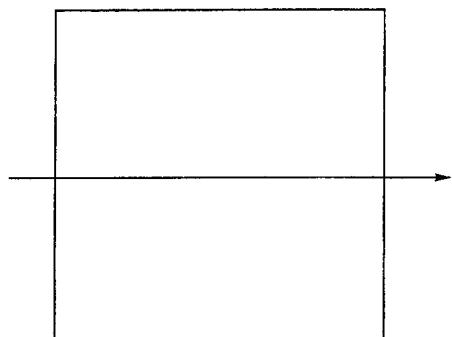
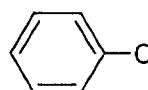


**Rxns (continued)**

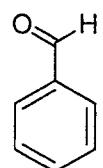
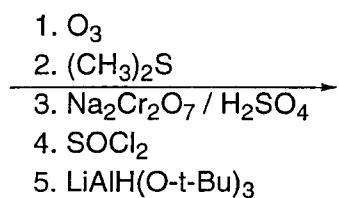
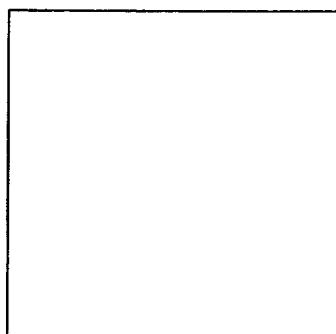
4.



5.



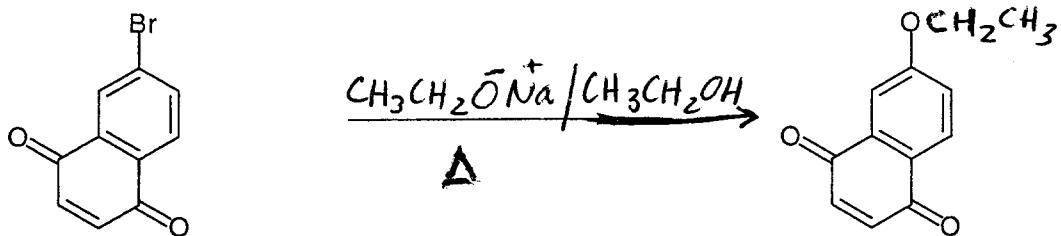
6.



**D. Mechanisms:** (9 points each)

Provide reasonable mechanisms for reactions 1 and 2. Use curved arrows to indicate "electron flow". **Show all intermediates and all formal charges.** If there is more than one resonance structure, you must show the "best" (i.e., lowest energy) structure.

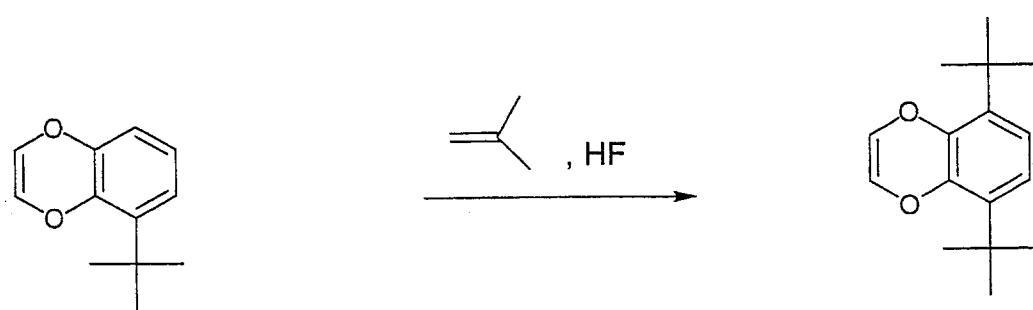
1.



6

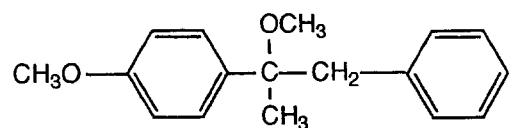


2.



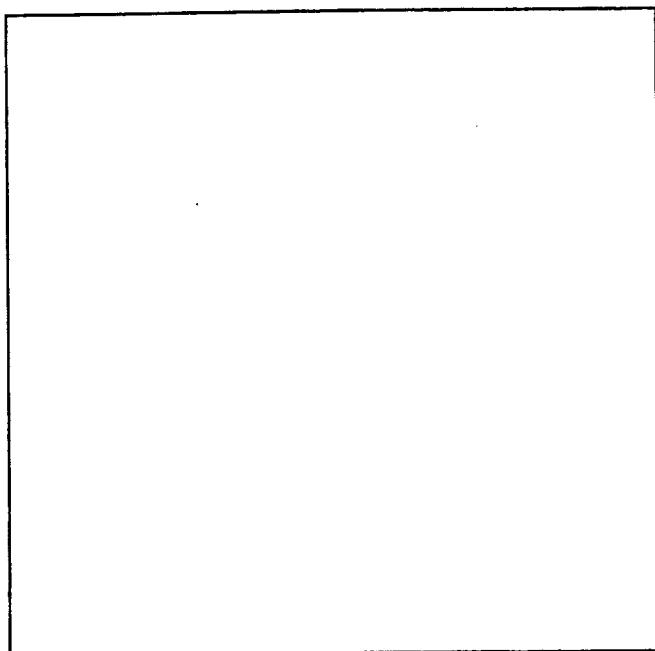
**E. Synthesis:** (15 points)

Synthesize the compound below using any of the following reagents: alkanes, alkenes, alkynes or alcohols of **two carbons or less**; benzene; any oxidizing or reducing agents; and any peroxyacids.

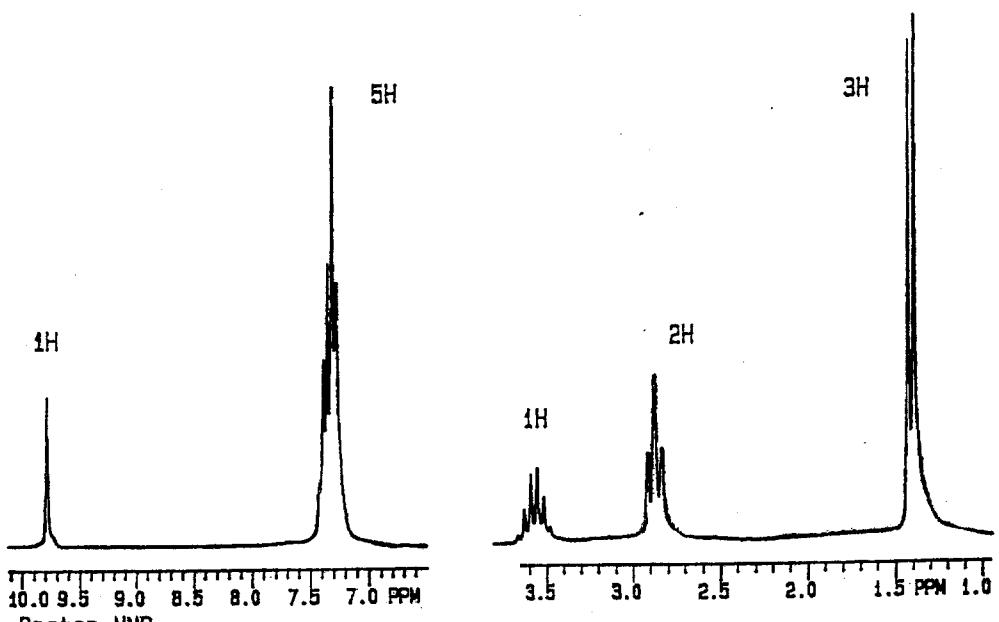
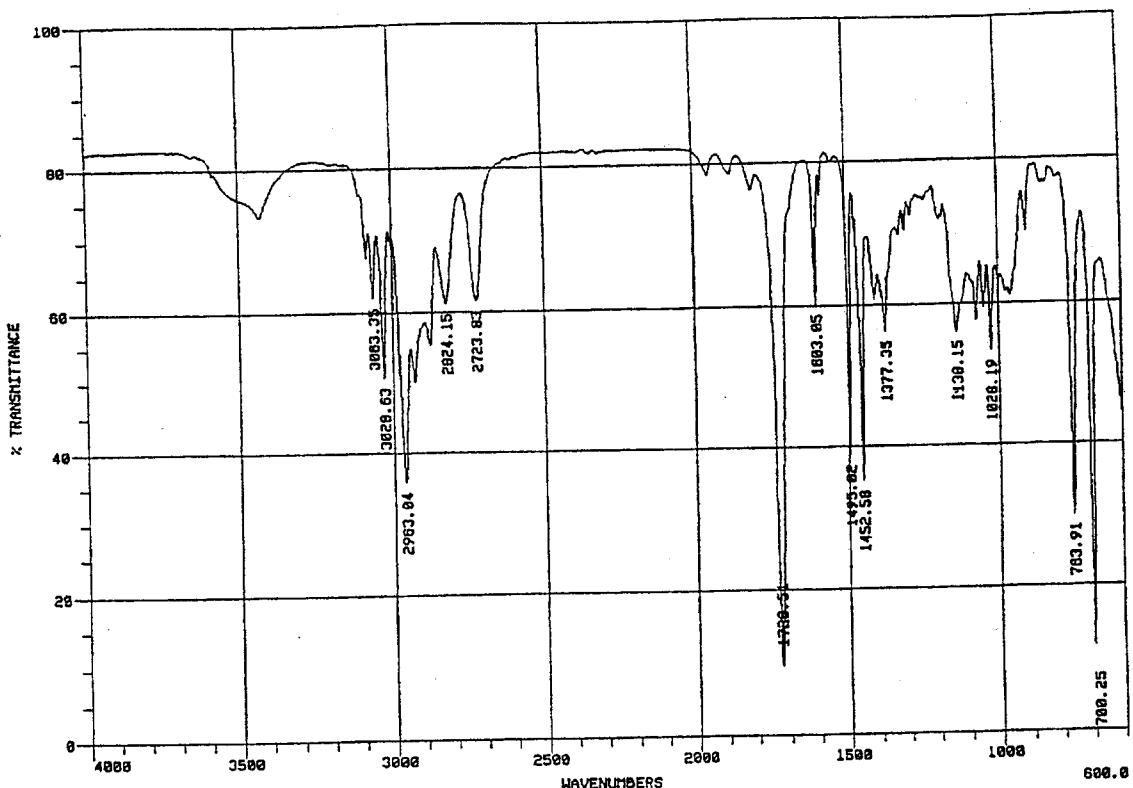


**F. Spectroscopy: 10 Points**

A compound with the formula **C<sub>10</sub>H<sub>12</sub>O** exhibits the IR, <sup>1</sup>H NMR, and proton-decoupled <sup>13</sup>C NMR spectra shown on the following page. Please identify this compound and draw the structure in the box provided below.



$C_{10}H_{12}O$



There are two  
unresolved lines,  
126.4 and 126.7 ppm.

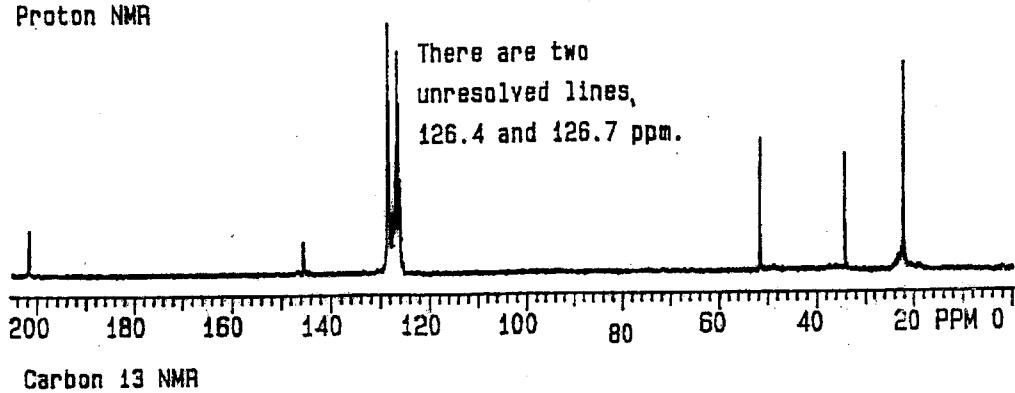


TABLE 13.2 Characteristic infrared absorptions of groups

GROUP	FREQUENCY RANGE ( $\text{cm}^{-1}$ )	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>	985–1000 and 905–920	(s) (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>		
$\equiv\text{C}$ —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	690–710 and 730–770	(very s) (very s)
<i>o</i> Disubstituted	735–770	(s)
<i>m</i> Disubstituted	680–725	(s)
<i>p</i> Disubstituted	750–810 800–840	(very s) (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)

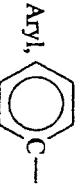
<sup>a</sup> Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

**TABLE 13.3** Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT ( $\delta$ , ppm)
$1^\circ$ Alkyl, $\text{RCH}_3$	0.8–1.0
$2^\circ$ Alkyl, $\text{RCH}_2\text{R}$	1.2–1.4
$3^\circ$ Alkyl, $\text{R}_3\text{CH}$	1.4–1.7
Allylic, $\text{R}_2\text{C}=\text{C}(\text{R})-\text{CH}_3$	1.6–1.9
Ketone, $\text{RC}\overset{\parallel}{\underset{\text{O}}{ }}\text{CH}_3$	2.1–2.6
Benzyllic, $\text{ArCH}_3$	2.2–2.5
Acetylenic, $\text{RC}\equiv\text{CH}$	2.5–3.1
Alkyl iodide, $\text{RCH}_2\text{I}$	3.1–3.3
Ether, $\text{ROCH}_2\text{R}$	3.3–3.9
Alcohol, $\text{HOCH}_2\text{R}$	3.3–4.0
Alkyl bromide, $\text{RCH}_2\text{Br}$	3.4–3.6
Alkyl chloride, $\text{RCH}_2\text{Cl}$	3.6–3.8
Vinyllic, $\text{R}_2\text{C}=\text{CH}-\text{CH}_2$	4.6–5.0
Vinylic, $\text{R}_2\text{C}=\text{CH}-\text{R}$	5.2–5.7
Aromatic, $\text{ArH}$	6.0–9.5
Aldehyde, $\text{RCH}\overset{\parallel}{\underset{\text{O}}{ }}$	9.5–9.6
Alcohol hydroxyl, $\text{ROH}$	0.5–6.0 <sup>a</sup>
Amino, $\text{R}-\text{NH}_2$	1.0–5.0 <sup>a</sup>
Phenolic, $\text{ArOH}$	4.5–7.7 <sup>a</sup>
Carboxylic, $\text{RC}\overset{\parallel}{\underset{\text{O}}{ }}\text{OH}$	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)
$1^\circ$ Alkyl, $\text{RCH}_3$	0–40
$2^\circ$ Alkyl, $\text{RCH}_2\text{R}$	10–50
$3^\circ$ Alkyl, $\text{RCHR}_2$	15–50
Alkyl halide or amine, $-\overset{\mid}{\text{C}}-\text{X}$ ( $\text{X} = \text{Cl}, \text{Br}$ , or $\overset{\mid}{\text{N}}-$ )	10–65
Alcohol or ether, $-\overset{\mid}{\text{C}}-\text{O}$	50–90
Alkyne, $-\overset{\mid}{\text{C}}\equiv$	60–90
Alkene, $\text{C}\overset{\backslash}{\underset{/}{\text{C}}}=\text{}$	100–170
Aryl, 	100–170
Nitriles, $-\text{C}\equiv\text{N}$	120–130
Amides, $-\overset{\mid}{\text{C}}-\text{N}-$	150–180
Carboxylic acids, esters, $-\overset{\parallel}{\underset{\text{O}}{ }}\text{C}-\text{O}$	160–185
Aldehydes, ketones, $-\overset{\parallel}{\underset{\text{O}}{ }}\text{C}-$	182–215