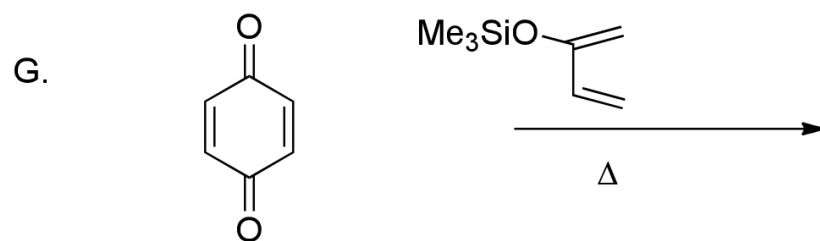
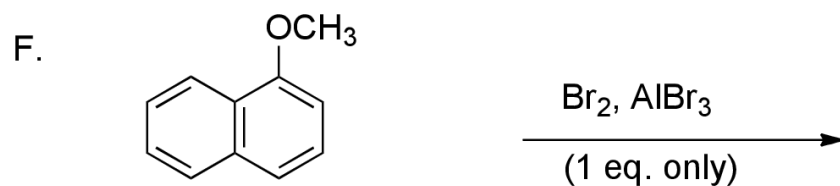
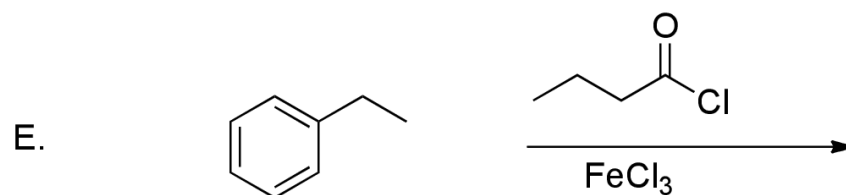
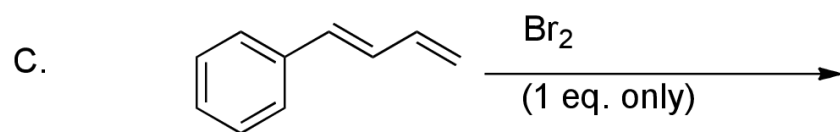
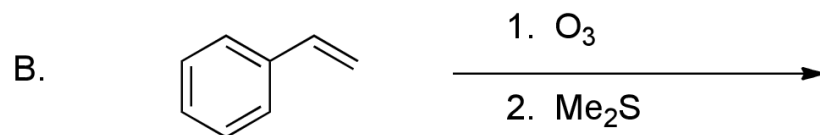
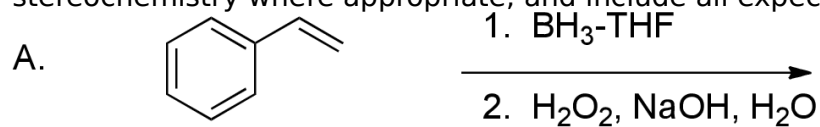
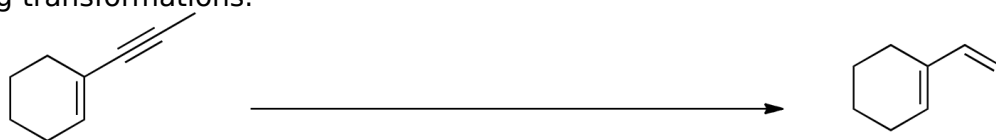


1. (35 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.



2. (35 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.

A.



B.



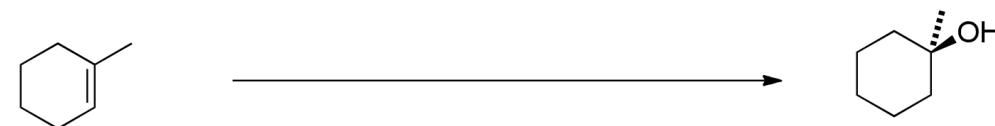
C.



D.



E.



F.

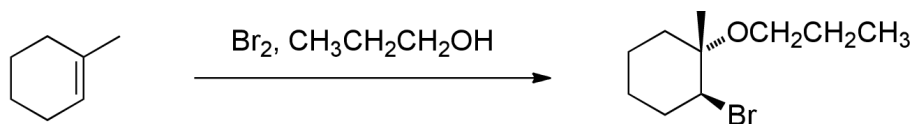


G.

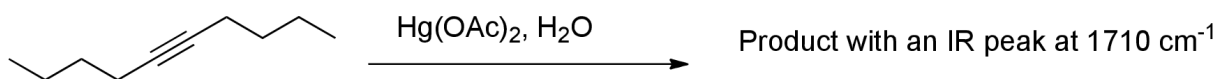


3. (28 points) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

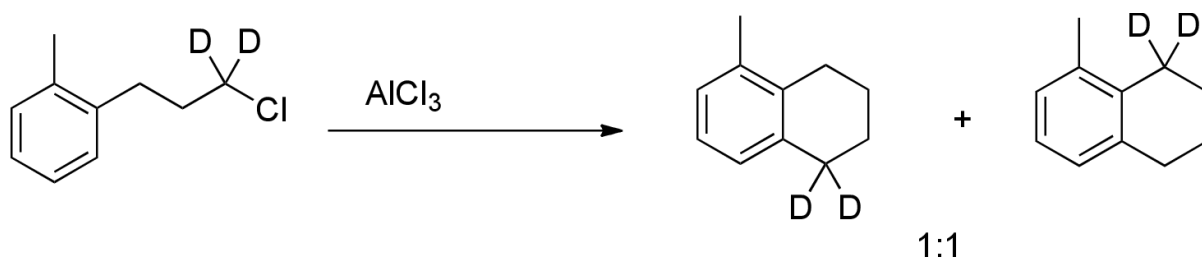
A.



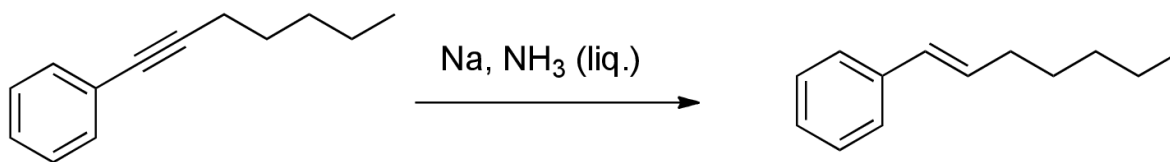
B.



C.



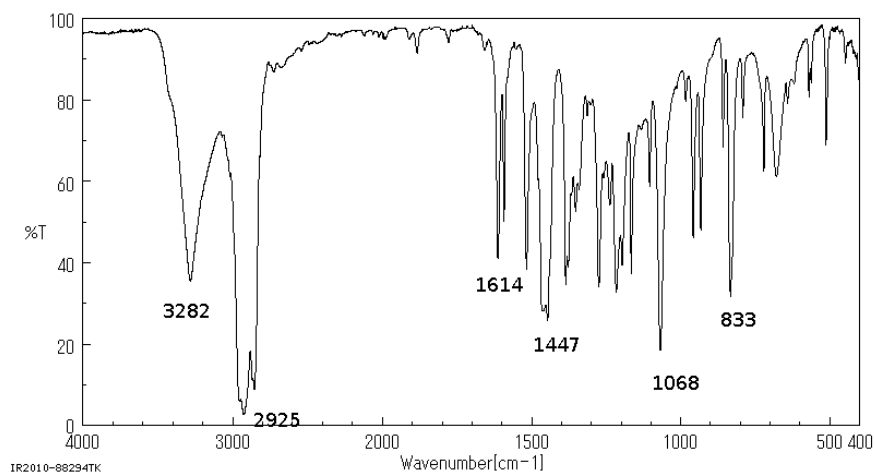
D.



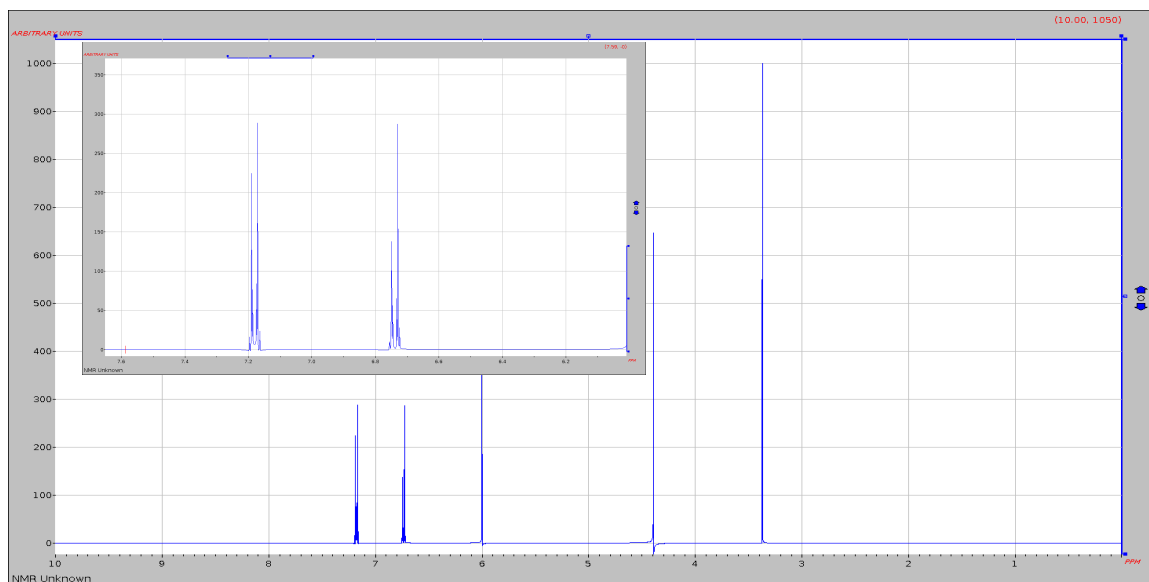
4. (25 points) A molecule has the molecular formula $C_8H_{10}O_2$.

A. How many degrees of unsaturation does it have?

B. The infrared spectrum is shown below. Circle any peaks that tell you what functional groups are present, and list those functional groups. Several peaks are identified to help you estimate the scale.



C. The ^1H NMR with expansion (6-7.5 ppm) is shown below; integrations are listed below the spectrum. Propose a structure that is consistent with all this data. (Failing a complete structure, suggest what fragments are present for partial credit.)



Integrals:

7.18 ppm: 2H

6.74 ppm: 2H

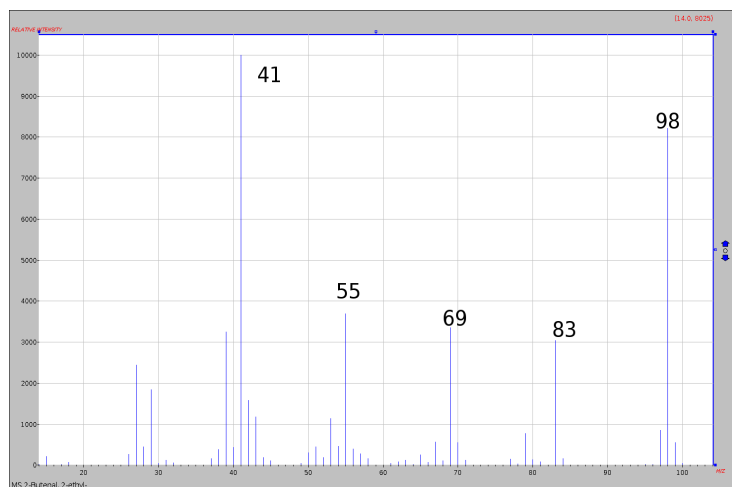
6.00 ppm: 1H

4.39 ppm: 2H

3.37 ppm: 3H

5. (25 points) The mass, IR, ^1H and ^{13}C NMR spectra for a compound are shown below.

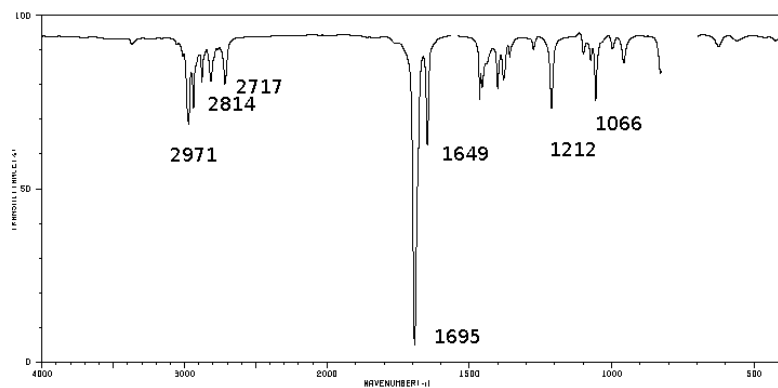
MS:



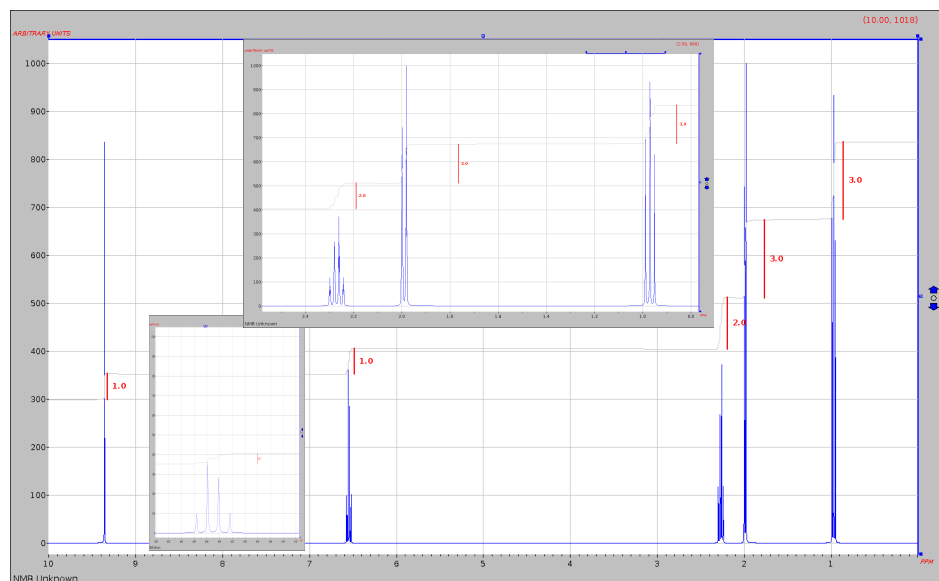
Partial peak listing:

Mass	Intensity, % of base
41.0	100.0
42.0	15.9
43.0	11.8
44.0	1.9
55.0	36.9
56.0	4.0
69.0	33.6
70.0	5.5
71.0	1.2
83.0	30.4
84.0	1.7
97.0	8.6
98.0	82.2
99.0	5.6

IR:



^1H NMR (insets are 0.5-2.5 ppm above; 6.2-6.8 ppm below):



Integrals:

9.36 ppm	1H
6.55 ppm	1H
2.27 ppm	2H
1.99 ppm	3H
0.97 ppm	3H

^{13}C NMR:

194.84
149.42
146.38
16.96
14.51
12.99

(continued next page)

A. From the mass spectrum (and clues in other spectra), deduce the molecular formula.

B. Propose a structure that fits the data. (If you cannot come up with a complete structure, provide as much analysis of the data as you can.) Be sure to:

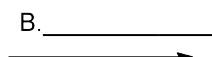
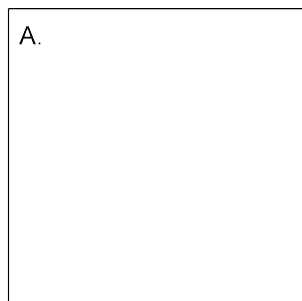
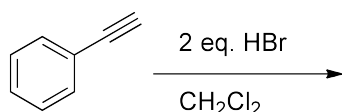
-Calculate the degrees of unsaturation

-Specify functional groups, the evidence you use to identify them, and the impact on the DoU count

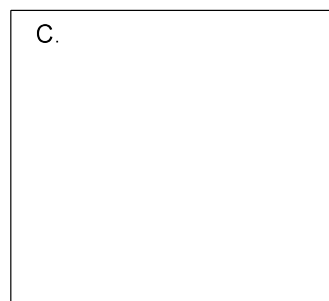
-Identify coupling relationships that allow you to identify structural pieces

-Any corroborating evidence you can see that confirms the structure.

6. (32 points) Fill in the missing intermediates or reagents in the following multistep synthesis.

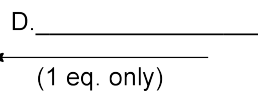
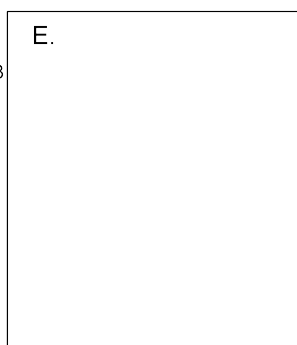
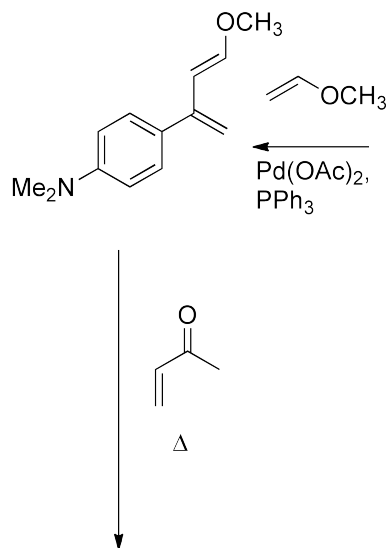


$^1\text{H NMR}$:
8.1 d
7.3 d
2.8 s

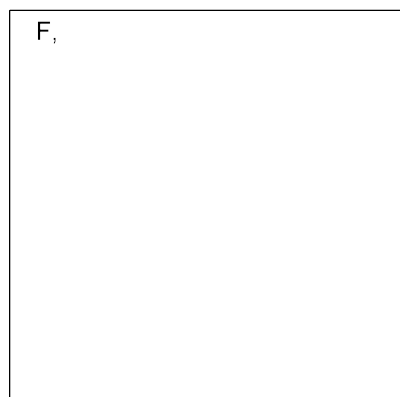
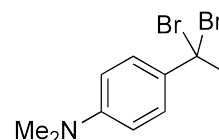


MS Parent ion peaks:
262 (50%)
264 (100%)
266 (50%)

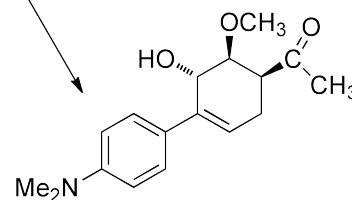
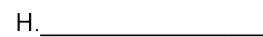
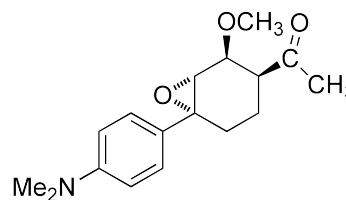
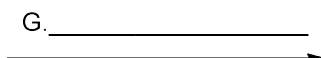
1. Fe/HCl
2. 2 eq. CH_3I ,
 K_2CO_3



$^1\text{H NMR}$:
7.02 d, 2H
6.67 d, 2H
5.02 s, 1H
5.01 s, 1H
2.86 s, 6H

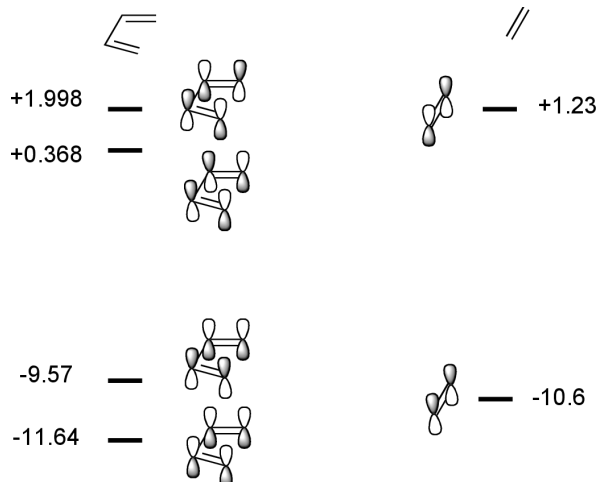


IR: 1725 cm^{-1}

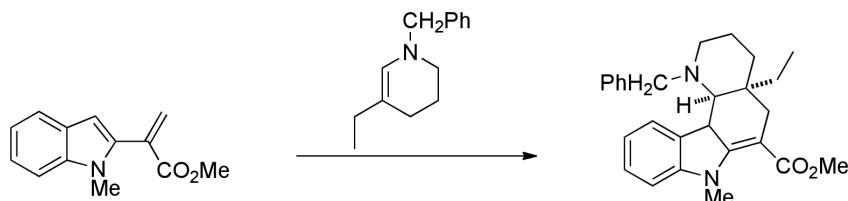


7. (20 points) Normally, the Diels-Alder reaction involves a diene with an electron-donating group reacting with a dienophile that has an electron-withdrawing substituent.

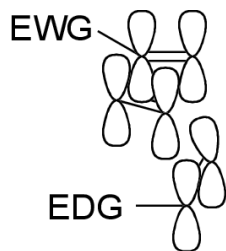
A. Based on the MO diagram below depicting the orbitals in the unsubstituted case (and their energies, in eV), describe why this particular pair of substituents enhances the Diels-Alder reaction. Use the molecular orbital description of the bonding in the reactants and the transition state.



B. There are examples of what are called “inverse demand” Diels-Alder reactions, where the electron donor is on the dienophile, and the electron-withdrawing group is on the diene. An example is shown:



In the diagram below, shade in the phases of the orbitals to represent the major HOMO-LUMO interaction in the transition state for this inverse-demand Diels-Alder reaction. (Hint: think about how you would adapt your answer to Part A to explain what happens here.)



EWG = Electron-Withdrawing Group
EDG = Electron-Donating Group

Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules

Type of hydrogen ^a	Chemical shift δ in ppm	
Primary alkyl, RCH_3	0.8–1.0	
Secondary alkyl, RCH_2R'	1.2–1.4	
Tertiary alkyl, R_3CH	1.4–1.7	
Allylic (next to a double bond), $R_2C=C\begin{matrix} CH_3 \\ R' \end{matrix}$	1.6–1.9	
Benzylic (next to a benzene ring), $ArCH_2R$	2.2–2.5	
Ketone, $RC(=O)CH_3$	2.1–2.6	
Alkyne, $RC\equiv CH$	1.7–3.1	
Chloroalkane, RCH_2Cl	3.6–3.8	
Bromoalkane, RCH_2Br	3.4–3.6	
Iodoalkane, RCH_2I	3.1–3.3	
Ether, RCH_2OR'	3.3–3.9	
Alcohol, RCH_2OH	3.3–4.0	
Terminal alkene, $R_2C=CH_2$	4.6–5.0	
Internal alkene, $R_2C=CH\begin{matrix} R' \end{matrix}$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, $RC(=O)H$	9.5–9.9	
Alcoholic hydroxy, ROH	0.5–5.0	(variable)
Thiol, RSH	0.5–5.0	(variable)
Amine, RNH_2	0.5–5.0	(variable)

^aR, R', alkyl groups; Ar, aromatic group (not argon).

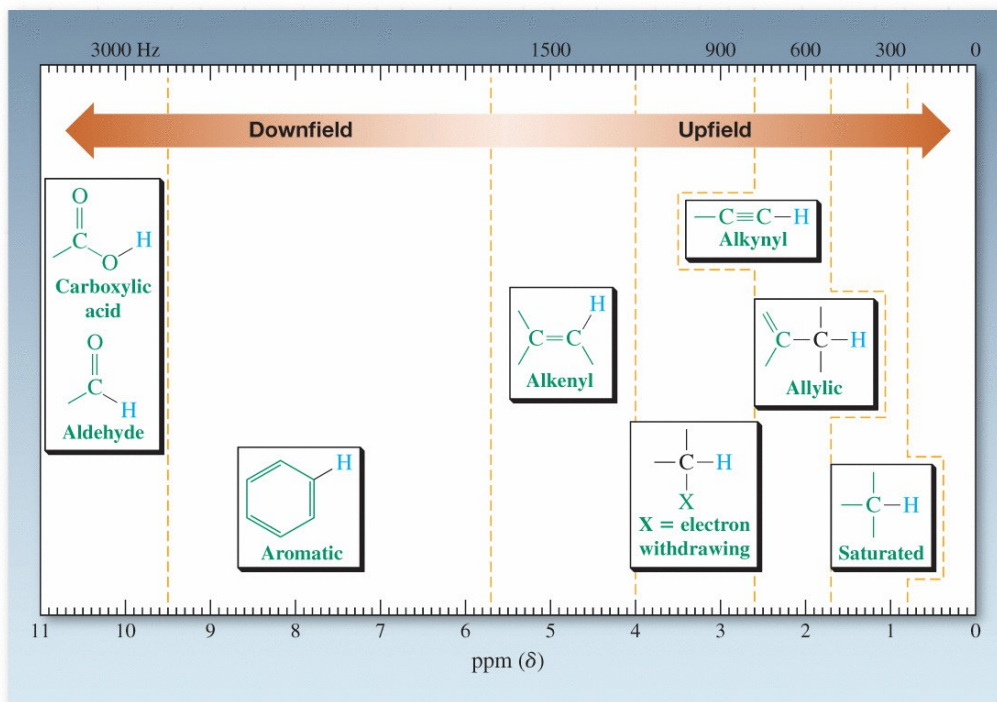


Table 10-6 Typical ^{13}C NMR Chemical Shifts

Type of carbon	Chemical shift δ (ppm)
Primary alkyl, RCH_3	5–20
Secondary alkyl, $\text{RCH}_2\text{R}'$	20–30
Tertiary alkyl, R_3CH	30–50
Quaternary alkyl, R_4C	30–45
Allylic, $\text{R}_2\text{C}=\underset{\text{R}''}{\text{C}}\text{CH}_2\text{R}'$	20–40
Chloroalkane, RCH_2Cl	25–50
Bromoalkane, RCH_2Br	20–40
Ether or alcohol, $\text{RCH}_2\text{OR}'$ or RCH_2OH	50–90
Carboxylic acids, RCOOH	170–180
Aldehyde or ketone, $\text{RCH}=\overset{\text{O}}{\parallel}$ or $\text{RCR}'=\overset{\text{O}}{\parallel}$	190–210
Alkene, aromatic, $\text{R}_2\text{C}=\text{CR}_2$	100–160
Alkyne, $\text{RC}\equiv\text{CR}$	65–95

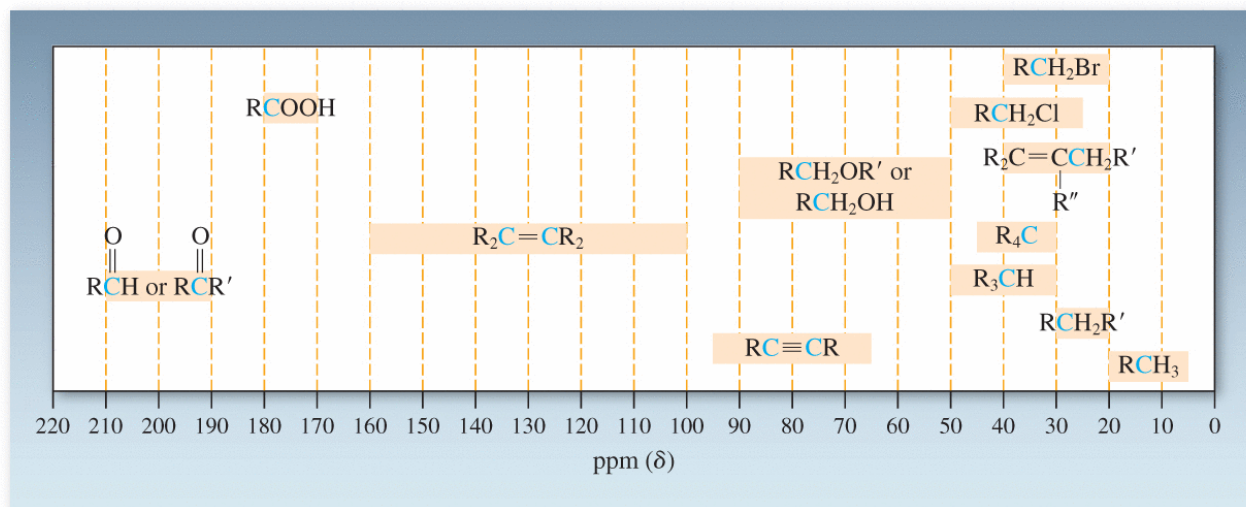
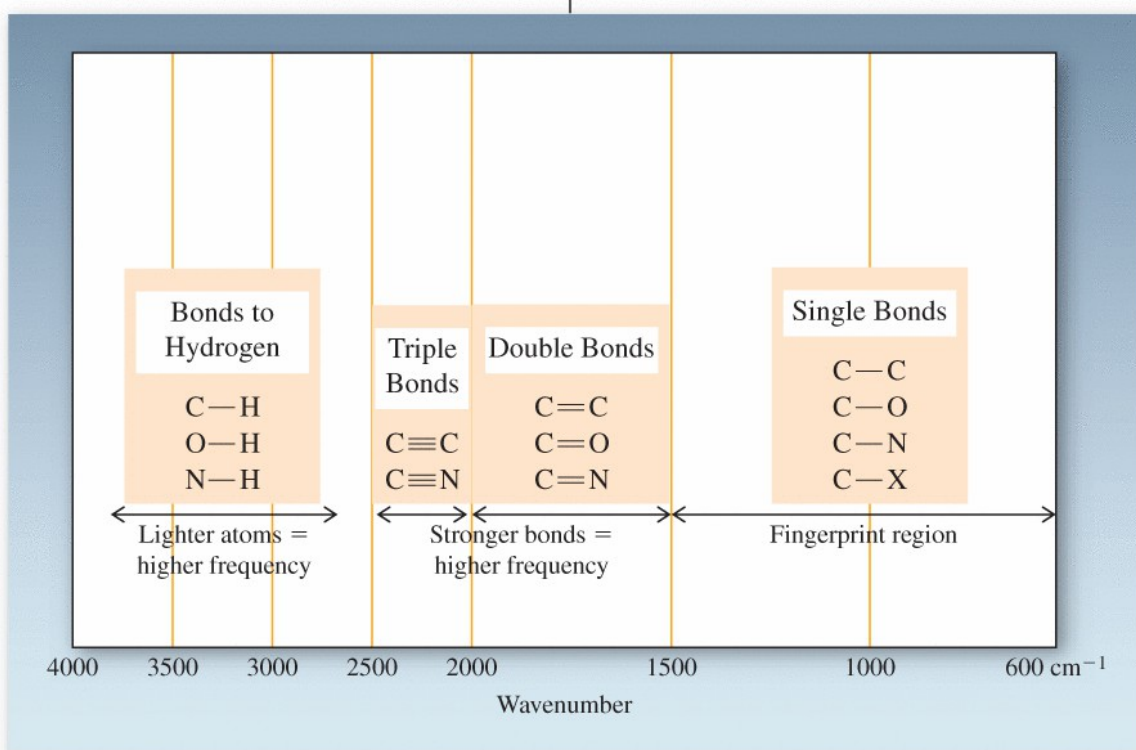


Table 11-4

Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ (cm ⁻¹)	Bond or Functional Group	$\tilde{\nu}$ (cm ⁻¹)
RO—H (alcohols)	3200–3650	RC≡N (nitriles)	2220–2260
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCO—H} \end{array}$ (carboxylic acids)	2500–3300	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RCH, RCR}' \end{array}$ (aldehydes, ketones)	1690–1750
R ₂ N—H (amines)	3250–3500	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$ (esters)	1735–1750
RC≡C—H (alkynes)	3260–3330	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$ (carboxylic acids)	1710–1760
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$ (alkenes)	3050–3150	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ (alkenes)	1620–1680
$\begin{array}{c} \\ \text{—C—H} \\ \end{array}$ (alkanes)	2840–3000	$\begin{array}{c} \\ \text{RC—OR}' \\ \end{array}$ (alcohols, ethers)	1000–1260
RC≡CH (alkynes)	2100–2260		

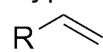

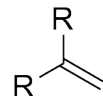
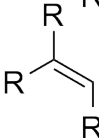
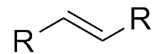
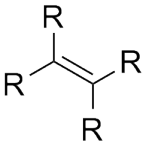


← Increasing wavenumber (energy)

Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH ₃ -H	105
CH ₃ CH ₂ -H	101
(CH ₃) ₂ CH-H	98.5
(CH ₃) ₃ C-H	96.5
CH ₃ -F	110
CH ₃ -Cl	85
CH ₃ -Br	70
CH ₃ -I	57
CH ₃ CH ₂ -F	111
CH ₃ CH ₂ -Cl	84
CH ₃ CH ₂ -Br	70
CH ₃ CH ₂ -I	56
(CH ₃) ₂ CH-F	111
(CH ₃) ₂ CH-Cl	84
(CH ₃) ₂ CH-Br	71
(CH ₃) ₂ CH-I	56
(CH ₃) ₃ C-F	110
(CH ₃) ₃ C-Cl	85
(CH ₃) ₃ C-Br	71
(CH ₃) ₃ C-I	55

Typical Heats of Hydrogenation

	-30 kcal/mol		-28.2 kcal/mol
	-27.9 kcal/mol		-26.5 kcal/mol
	-27.4 kcal/mol		-26.3 kcal/mol