

Name \_\_\_\_\_

You may use model kits but no other material with chemical information without instructor approval.

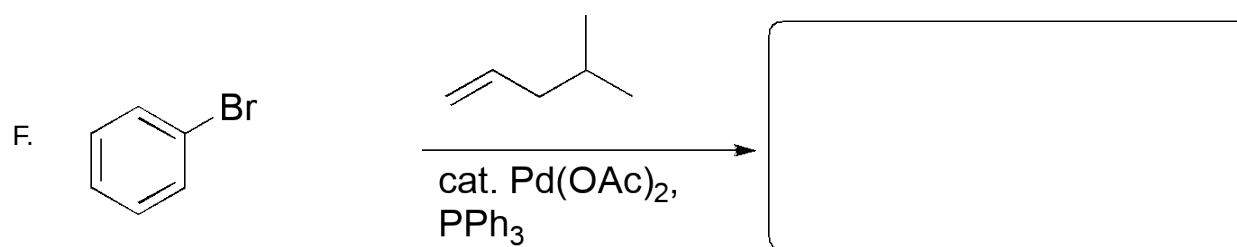
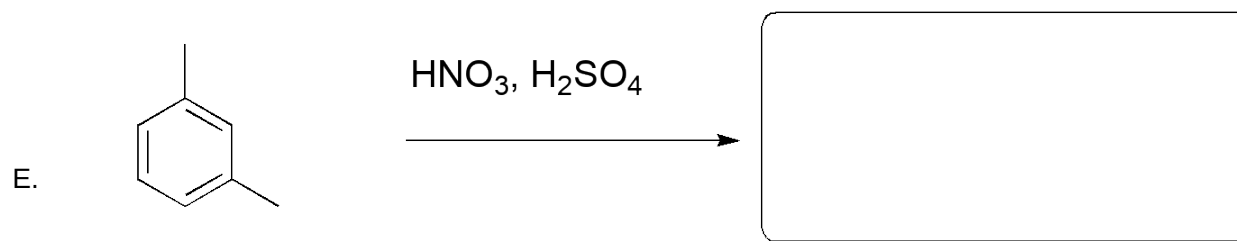
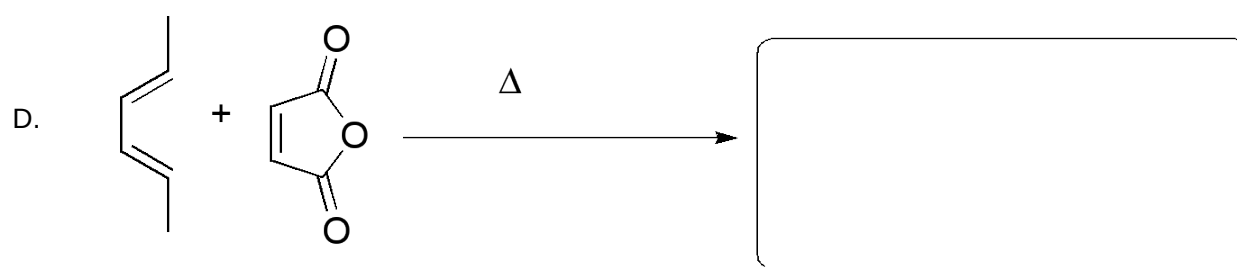
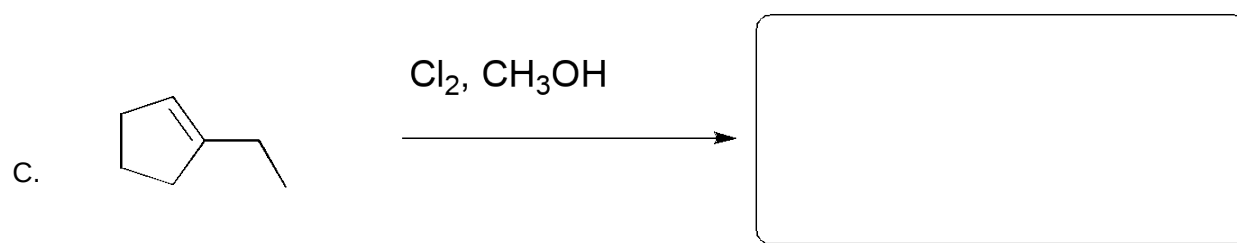
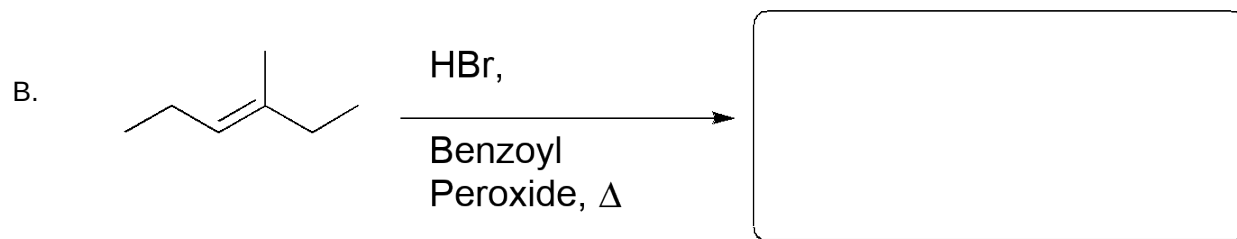
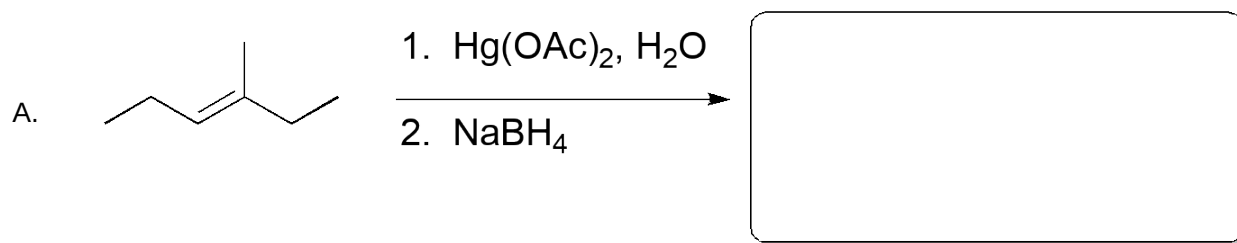
Please do not use any electronic devices other than calculators.

hydrogen 1 <b>H</b> 1.0079																	helium 2 <b>He</b> 4.0026	
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122											boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180	
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305											aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948	
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	seelenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80	
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29	
caesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 * *	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	unnilium 110 <b>Uun</b> [271]	ununium 111 <b>Uuu</b> [272]	unbinium 112 <b>Uub</b> [277]	unseesium 114 <b>Uuq</b> [289]					

\* Lanthanide series

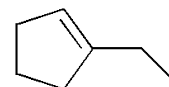
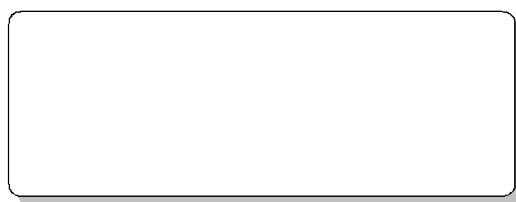
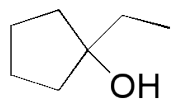
lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]

1. (5 points each; 30 total) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.

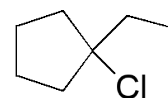
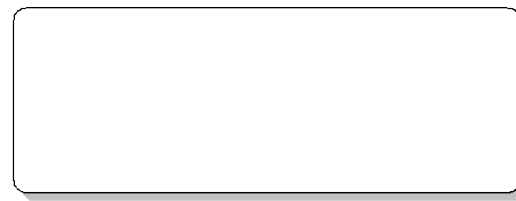
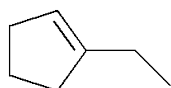


2. (5 points each; 25 total) Write (in the box provided) the reagents and/or conditions needed to accomplish the following transformations.

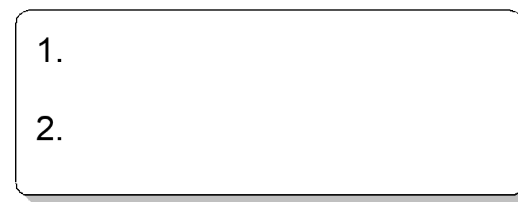
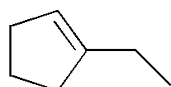
A.



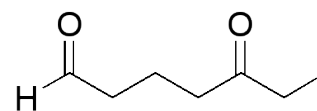
B.



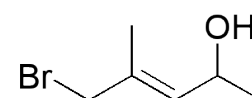
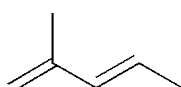
C.



(2 steps--list both reagents needed)

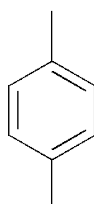


D.

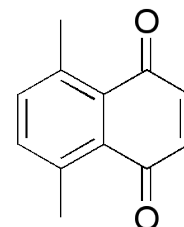


Specify condition to get this as major product

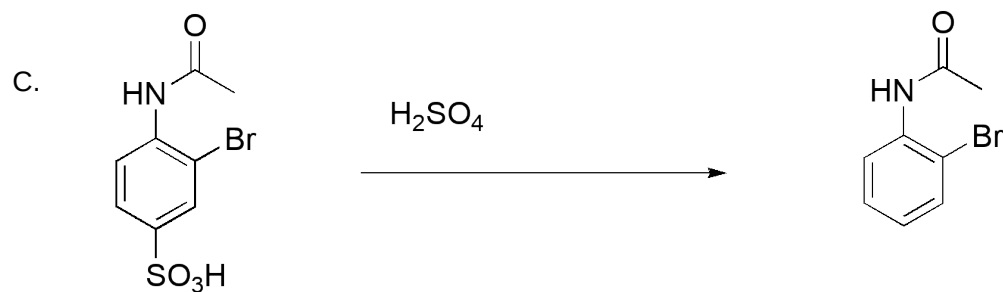
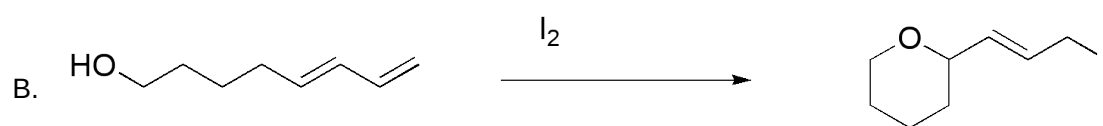
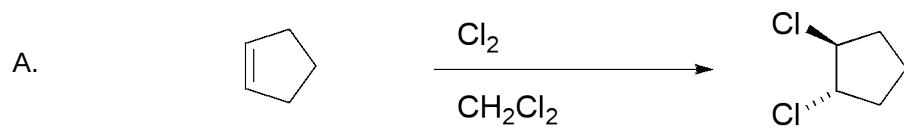
E.



(2 compounds needed.)

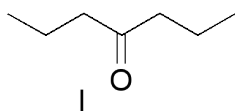


3. (10 points each; 30 total) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

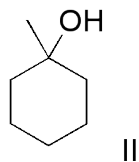


4. (6 points each box; 36 total) Indicate in the box a characteristic spectral peak for one compound whose presence will distinguish each pair of isomers.

A.



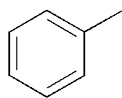
IR



$^1\text{H}$  NMR

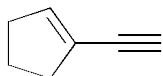
$^{13}\text{C}$  NMR

B.



III

IR



IV

$^1\text{H}$  NMR

$^{13}\text{C}$  NMR

5 (10 points each; 30 total) Draw each structure with hydrogens, and predict the  $^1\text{H}$  NMR spectrum (sketch clearly, or list peaks) of each of the following compounds. Include the spin-spin coupling patterns, but you need not specify J values. Estimate chemical shift to within 1 ppm.

A. 2-Bromobutane

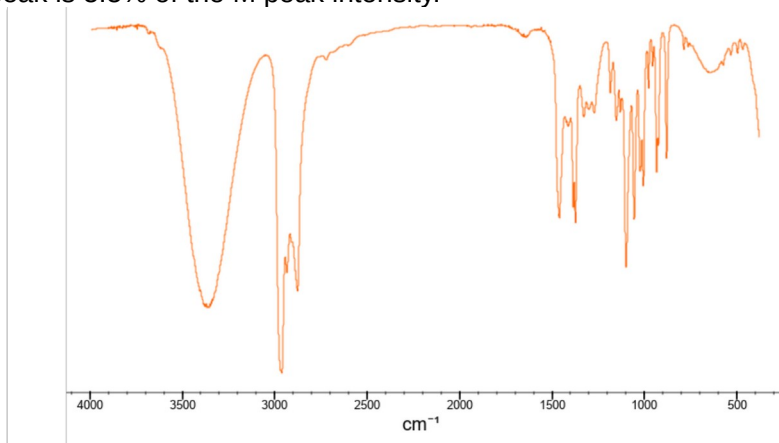
B. (4-chlorophenyl)-ethene

C. 3-ethylbenzoic acid

6. (11 points each, 22 points total) Identify each compound based on the spectroscopic information provided. For partial credit, include as much of your analysis (DoU, fragments or functional groups) that you can provide.

A. MS parent ion  $m/z = 88$ ;  $M+1$  peak is 5.5% of the  $M$  peak intensity.

IR:  $3300-3600\text{ cm}^{-1}$ .



$^1\text{H}$  NMR:

0.902 d 3H

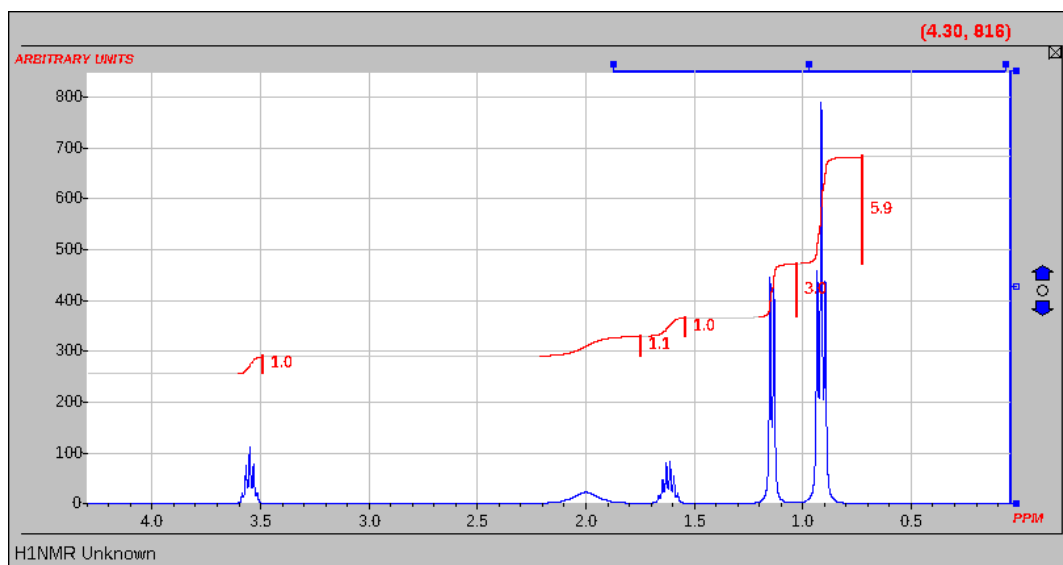
0.925 d 3H

1.142 d 3H

1.62 sept 1H

2.0 br 1H

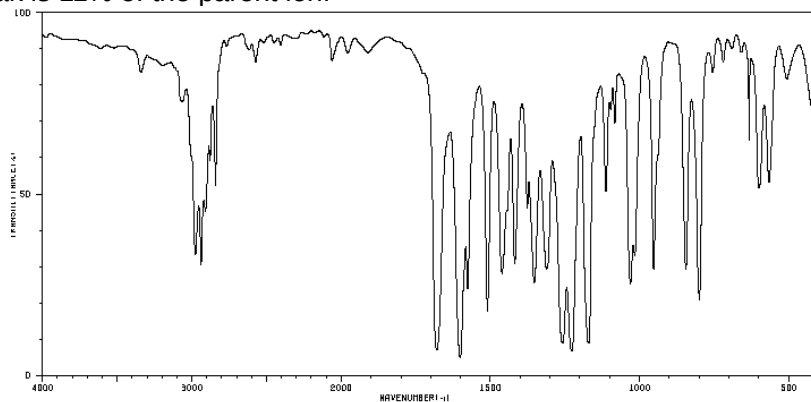
3.55 quin 1H



(Note: the "triplet" upfield is actually two different doublets that overlap.)

B. MS: Parent ion  $m/z = 164$ ; M+1 peak is 11% of the parent ion.

IR: 1680, 1602  $\text{cm}^{-1}$



$^1\text{H}$  NMR:

1.20 t 3H

2.92 q 2H

3.83 s 3H

6.91 d 2H

7.92 d 2H

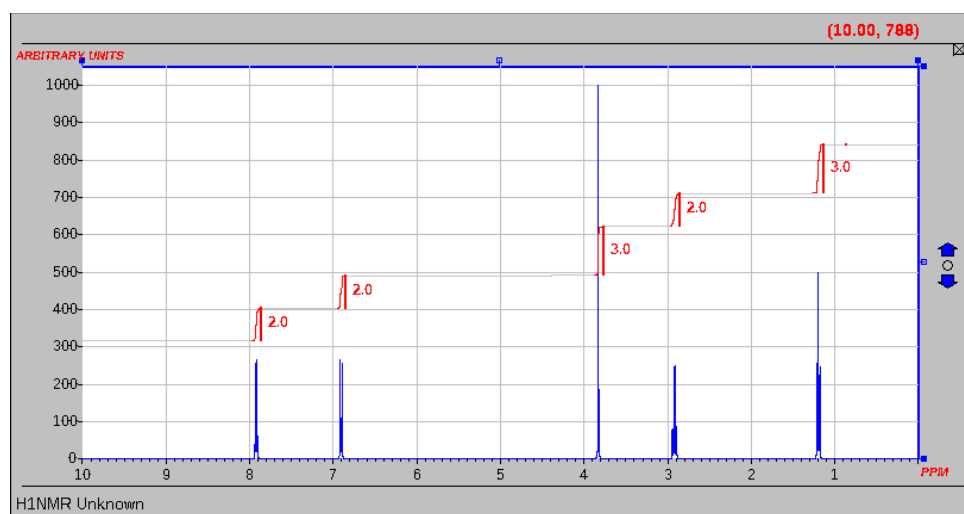
$^{13}\text{C}$  NMR:

8.45, 31.39, 55.39

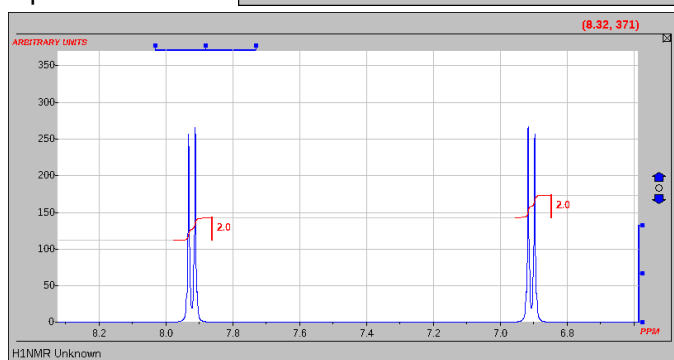
113.74, 129.90,

130.21, 163.39,

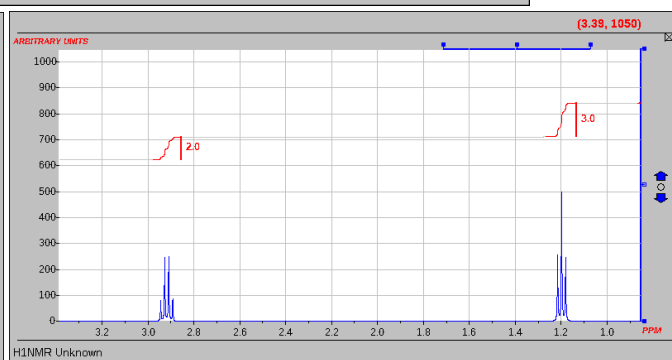
199.30



Expansions:



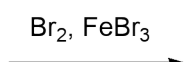
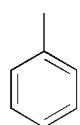
6.6-8.3 ppm



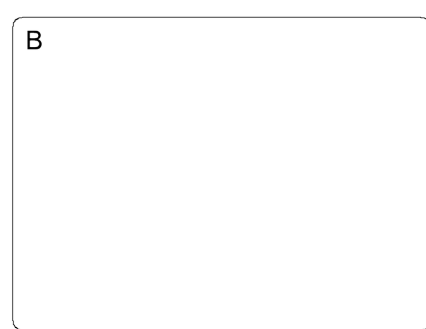
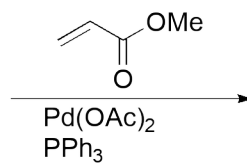
1.0-3.2 ppm



7. (9 points per box, 27 points total) Provide structures for each empty box. Use your understanding of both reaction chemistry and spectroscopic behavior to arrive at the answers. Include stereochemistry.

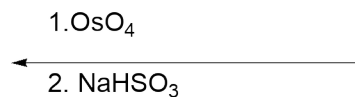


$^{13}\text{C}$  NMR:  
 136.7  
 131.2  
 130.8  
 119.1  
 20.9



IR:  $1712 \text{ cm}^{-1}$ . UV:  $\lambda_{\text{max}} = 310 \text{ nm}$

$^1\text{H}$  NMR:  
 7.67 (1 H, d,  $J = 16.0 \text{ Hz}$ )  
 7.42 (2 H, d,  $J = 8.0 \text{ Hz}$ )  
 7.19 (2 H, d,  $J = 8.0 \text{ Hz}$ )  
 6.40 (1 H, d,  $J = 16.0 \text{ Hz}$ )  
 3.80 (3 H, s)  
 2.37 (3 H, s)



IR: 3400 (broad),  $1736 \text{ cm}^{-1}$ ;  
 UV:  $\lambda_{\text{max}} = 260 \text{ nm}$   
 MS parent ion region:  
 210 100%  
 211 11.96%  
 212 1.36%

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 <sub>3</sub> -H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH <sub>3</sub> -F	110
CH <sub>3</sub> -Cl	85
CH <sub>3</sub> -Br	70
CH <sub>3</sub> -I	57
CH <sub>3</sub> CH <sub>2</sub> -F	111
CH <sub>3</sub> CH <sub>2</sub> -Cl	84
CH <sub>3</sub> CH <sub>2</sub> -Br	70
CH <sub>3</sub> CH <sub>2</sub> -I	56
(CH <sub>3</sub> ) <sub>2</sub> CH-F	111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	84
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	71
(CH <sub>3</sub> ) <sub>2</sub> CH-I	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	85
(CH <sub>3</sub> ) <sub>3</sub> C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-I	55

Typical Heats of Hydrogenation

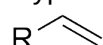

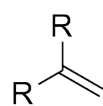
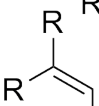
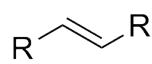
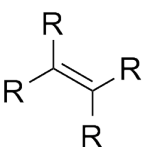
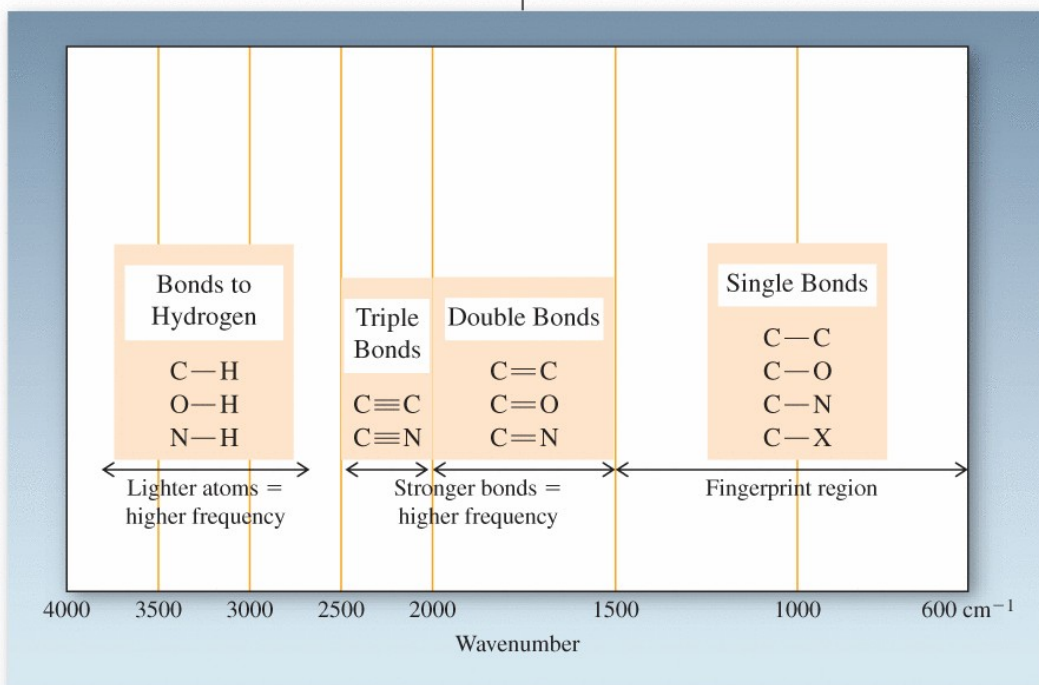
	-30 kcal/mol		-28.2 kcal/mol
	-27.9 kcal/mol		-26.5 kcal/mol
	-27.4 kcal/mol		-26.3 kcal/mol

Table 11-4

### Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	Bond or Functional Group	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )
RO—H (alcohols)	3200–3650	RC $\equiv$ 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 <sub>2</sub> N—H (amines)	3250–3500	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$ (esters)	1735–1750
RC $\equiv$ 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 $\equiv$ CH (alkynes)	2100–2260		

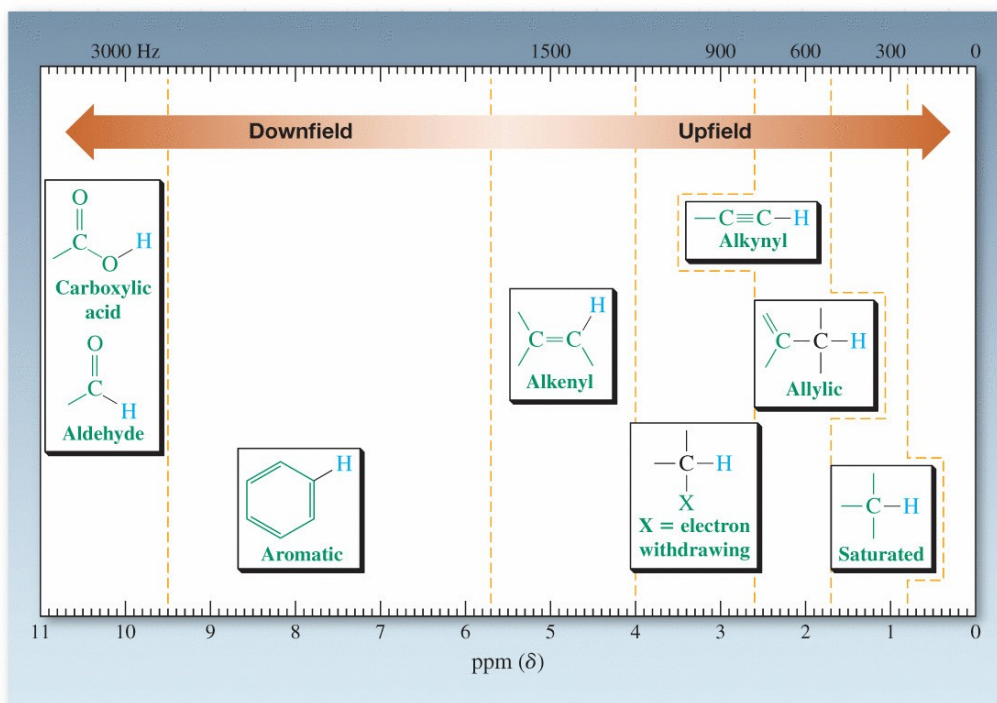


← Increasing wavenumber (energy)

**Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules**

Type of hydrogen <sup>a</sup>	Chemical shift $\delta$ in ppm	
Primary alkyl, $\text{RCH}_3$	0.8–1.0	Alkane and alkane-like hydrogens
Secondary alkyl, $\text{RCH}_2\text{R}'$	1.2–1.4	
Tertiary alkyl, $\text{R}_3\text{CH}$	1.4–1.7	
Allylic (next to a double bond), $\text{R}_2\text{C}=\text{C}-\text{CH}_3$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $\text{ArCH}_2\text{R}$	2.2–2.5	
Ketone, $\text{RCCH}_3$	2.1–2.6	
Alkyne, $\text{RC}\equiv\text{CH}$	1.7–3.1	Hydrogens adjacent to electronegative atoms
Chloroalkane, $\text{RCH}_2\text{Cl}$	3.6–3.8	
Bromoalkane, $\text{RCH}_2\text{Br}$	3.4–3.6	
Iodoalkane, $\text{RCH}_2\text{I}$	3.1–3.3	
Ether, $\text{RCH}_2\text{OR}'$	3.3–3.9	
Alcohol, $\text{RCH}_2\text{OH}$	3.3–4.0	
Terminal alkene, $\text{R}_2\text{C}=\text{CH}_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $\text{R}_2\text{C}=\text{CHR}'$	5.2–5.7	
Aromatic, $\text{ArH}$	6.0–9.5	
Aldehyde, $\text{RCH}=\text{O}$	9.5–9.9	
Alcoholic hydroxy, $\text{ROH}$	0.5–5.0	(variable)
Thiol, $\text{RSH}$	0.5–5.0	(variable)
Amine, $\text{RNH}_2$	0.5–5.0	(variable)

<sup>a</sup>R, R', alkyl groups; Ar, aromatic group (not argon).



**Table 10-6** Typical  $^{13}\text{C}$  NMR Chemical Shifts

Type of carbon	Chemical shift $\delta$ (ppm)
Primary alkyl, $\text{RCH}_3$	5–20
Secondary alkyl, $\text{RCH}_2\text{R}'$	20–30
Tertiary alkyl, $\text{R}_3\text{CH}$	30–50
Quaternary alkyl, $\text{R}_4\text{C}$	30–45
Allylic, $\text{R}_2\text{C}=\text{CCH}_2\text{R}'$   $\text{R}''$	20–40
Chloroalkane, $\text{RCH}_2\text{Cl}$	25–50
Bromoalkane, $\text{RCH}_2\text{Br}$	20–40
Ether or alcohol, $\text{RCH}_2\text{OR}'$ or $\text{RCH}_2\text{OH}$	50–90
Carboxylic acids, $\text{RCOOH}$	170–180
Aldehyde or ketone, $\text{RCH}=\text{O}$ or $\text{RCR}'=\text{O}$	190–210
Alkene, aromatic, $\text{R}_2\text{C}=\text{CR}_2$	100–160
Alkyne, $\text{RC}\equiv\text{CR}$	65–95

