NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:05 – 9:55 am, December 10, 2014

Exam 4

You will be able to pick up your graded Exam 4 from Chemistry department staff in 115 Smith beginning Thursday, December 11th at 3 PM. Exams that are not picked up within two weeks will be disposed of.

A periodic table, and tables of typical NMR chemical shifts, coupling constants, and IR frequencies are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

Right now, write your name and student ID number at the top of this page. When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

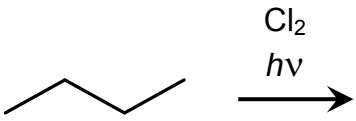
NAME _____

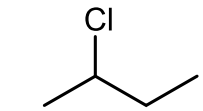
Scoring: 1. _____ / 12 3. _____ / 38

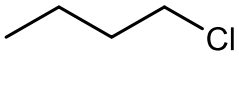
2. _____ / 22 4. _____ / 28

Total Score: _____ / 100

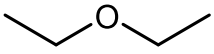
1. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

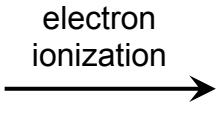


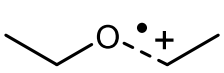


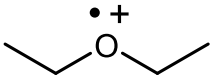


BOTH (equally) NEITHER

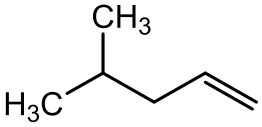


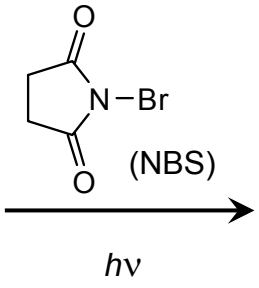


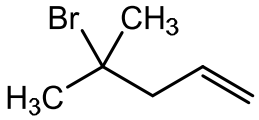


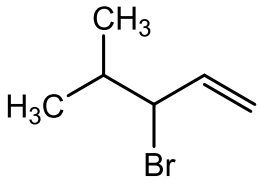


BOTH (equally) NEITHER



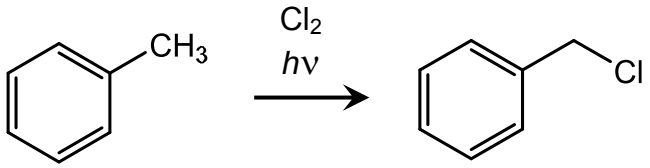






BOTH (equally) NEITHER

2. (22 pts)
   a. Draw a mechanism (using "electron pushing") for the radical reaction shown below. Draw each mechanistic step explicitly, in its own box, and label each step as an initiation or propagation step. (Do not draw any termination steps in this part.) Use only the molecules shown in the problem; don't invoke generic species.



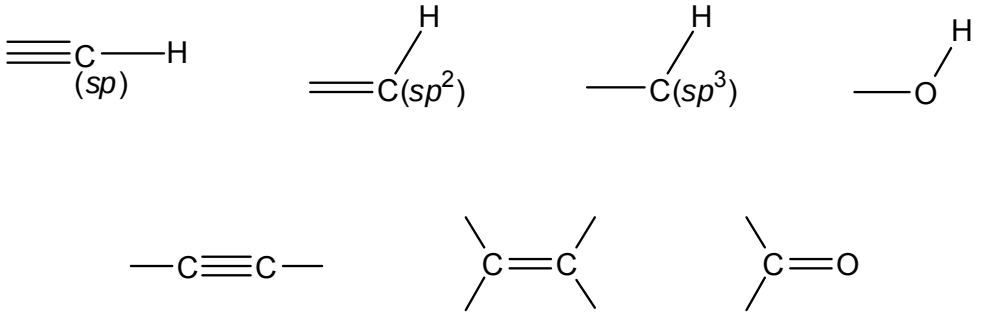
Mechanism, step 1:	*Is this an* **initiation** *or* **propagation** *step? (Circle one.)*
Mechanism, step 2:	**initiation** *or* **propagation** *? (Circle one.)*
Mechanism, step 3:	**initiation** *or* **propagation** *? (Circle one.)*

b. In the box on the right, draw the mechanism of a termination step that you would expect for the reaction on the previous page.

termination mechanism:

3. (38 pts) The spectra on page 6 correspond to a pure molecule; high-resolution mass spectrometry determined an exact mass of 110.0732 amu for the highest-mass (parent, $\mathbf{M}^+$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_7H_{10}O}$.

a. Considering only the features in the IR spectrum, what functional groups might the unknown molecule possibly have? **Circle all answers that apply.**



b. **What is the structure of the molecule**? In the box at right, draw your molecule's structure, including all hydrogens. Then, considering the ^{1}H NMR spectrum, circle each set of equivalent H's, and label each circle with its unique ^{1}H NMR chemical shift. (You do not need to label coupling constants *J*.)

your molecule
($C_7H_{10}O$)

c. Is the ^{1}H resonance at $\delta = 1.4$ ppm the farthest **upfield** or **downfield** ?

d. Are the protons at $\delta = 1.4$ ppm the most **shielded** or **deshielded** ?

e. Do the spins at $\delta = 1.4$ ppm precess ("wobble") the **fastest** or **slowest** ?

f. The parent mass peak at $m/z = 110$ corresponds to a radical cation ($\mathbf{M}^{\bullet+}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw $\mathbf{M}^{\bullet+}$; re-draw the structure you drew in part (b), but specifically indicate which electron is removed by drawing the molecule with one less electron. *Feel free to omit the hydrogens you drew in part (b).*

***M*$^{\bullet+}$**
($C_7H_{10}O^+$)

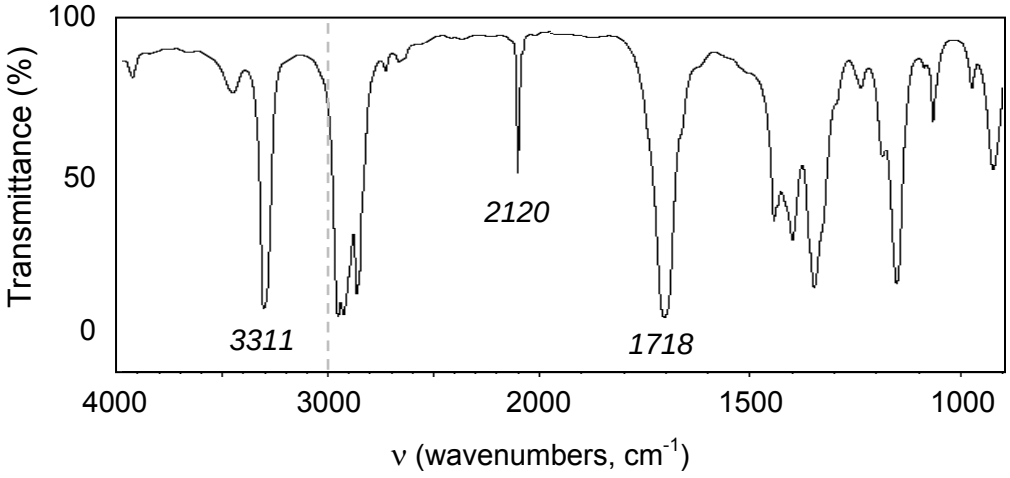
g. The parent ion fragments to form a daughter ion with $m/z = 95$. In the box on the next page, draw a mechanism (using "arrow pushing") that shows how fragmentation of the parent you drew in part (f) generates this ion, and that identifies the structure of this ion.

*fragmentation to m/z = **95**:*

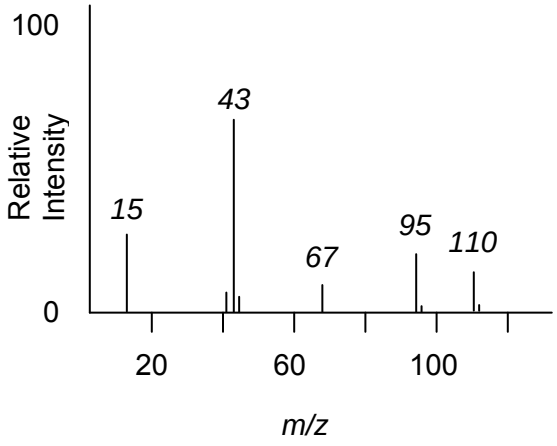
h. Draw structures for the *m/z* = 67 and *m/z* = 15 ions. You do not need to draw any mechanisms in this part.

m/z = ***67***:	*m/z* = ***15***:

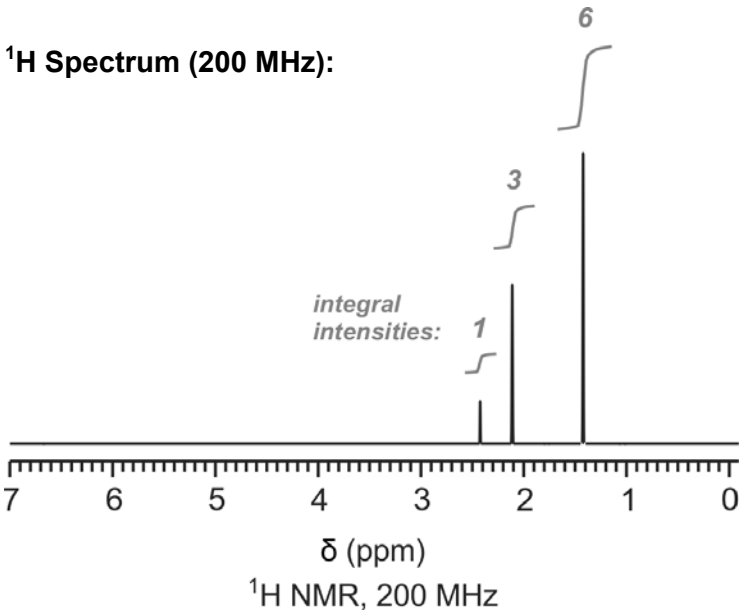
IR Spectrum:



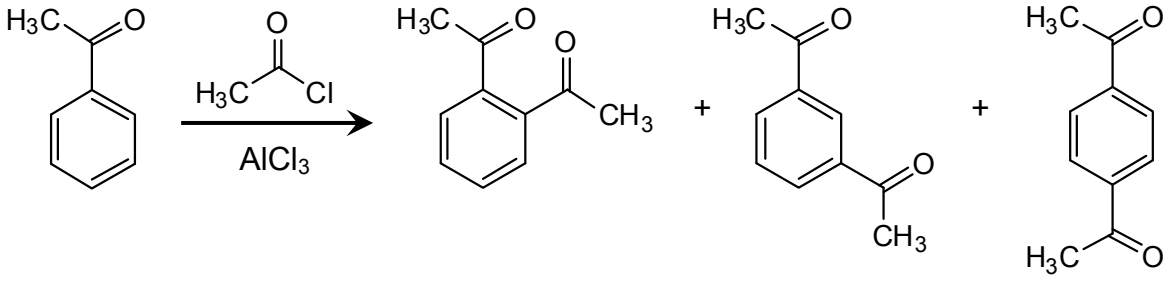
EI-Mass Spectrum



^{1}H Spectrum (200 MHz):

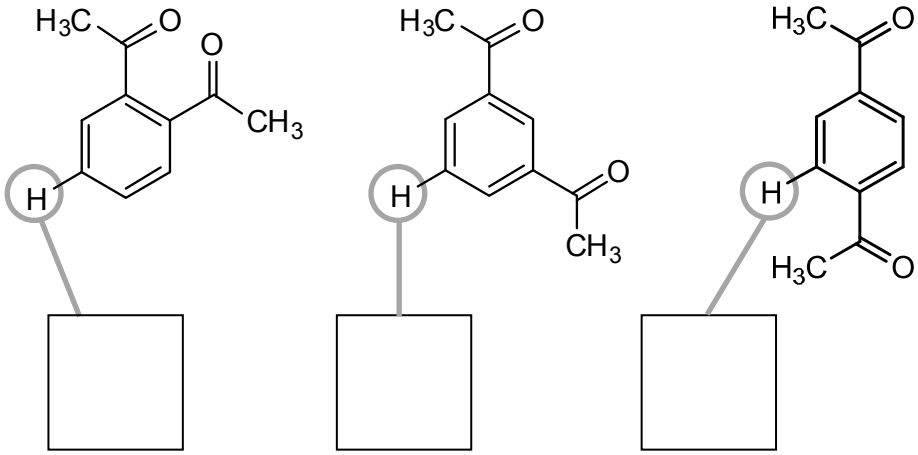


4. (28 pts) When acetophenone is combined with acetyl chloride and a Lewis acid catalyst—in a reaction that you will learn about in CHEM 2302—three different diacetylbenzenes could be generated as products. Normally this reaction doesn't work, but in this problem, we will imagine that you are a chemist that has performed this reaction, and that you have isolated one of these three products. You have performed ^{1}H and ^{13}C NMR spectra on this product, shown on page 9. In the questions that follow, you will decide which of the three products you have isolated.



a. How many resonances would you expect to see in the ^{1}H NMR of each of these products? In other words, how many inequivalent sets of protons are there in each structure? Write your answers in the boxes below.

 # ^{1}H NMR resonances expected

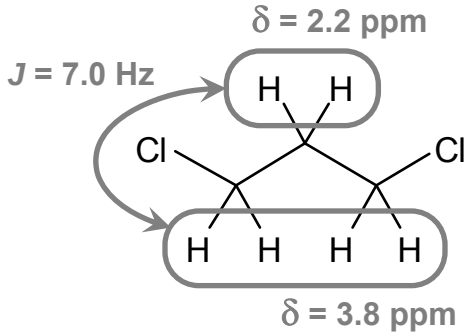


type of multiplet for this proton

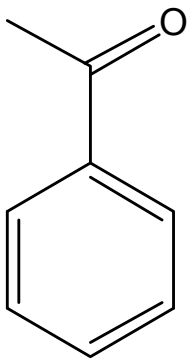
b. Each proton highlighted in the structures above could be split by neighboring protons. What kind of multiplet should each proton produce in a ^{1}H NMR spectrum? (Assume that there is no long-range coupling for the circled proton. But there might be for the others!) Use the abbreviations on the chart on the right, and write your answers in the boxes above.

abbreviations for multiplets	
s:	singlet
d:	doublet
t:	triplet
q:	quartet
dd:	doublet of doublets

Format for answer to (c):



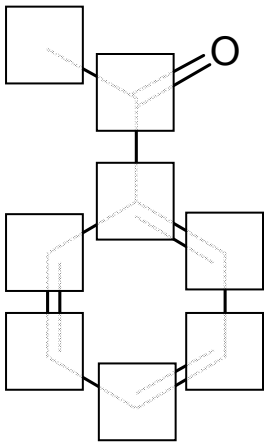
Your answer to (c):

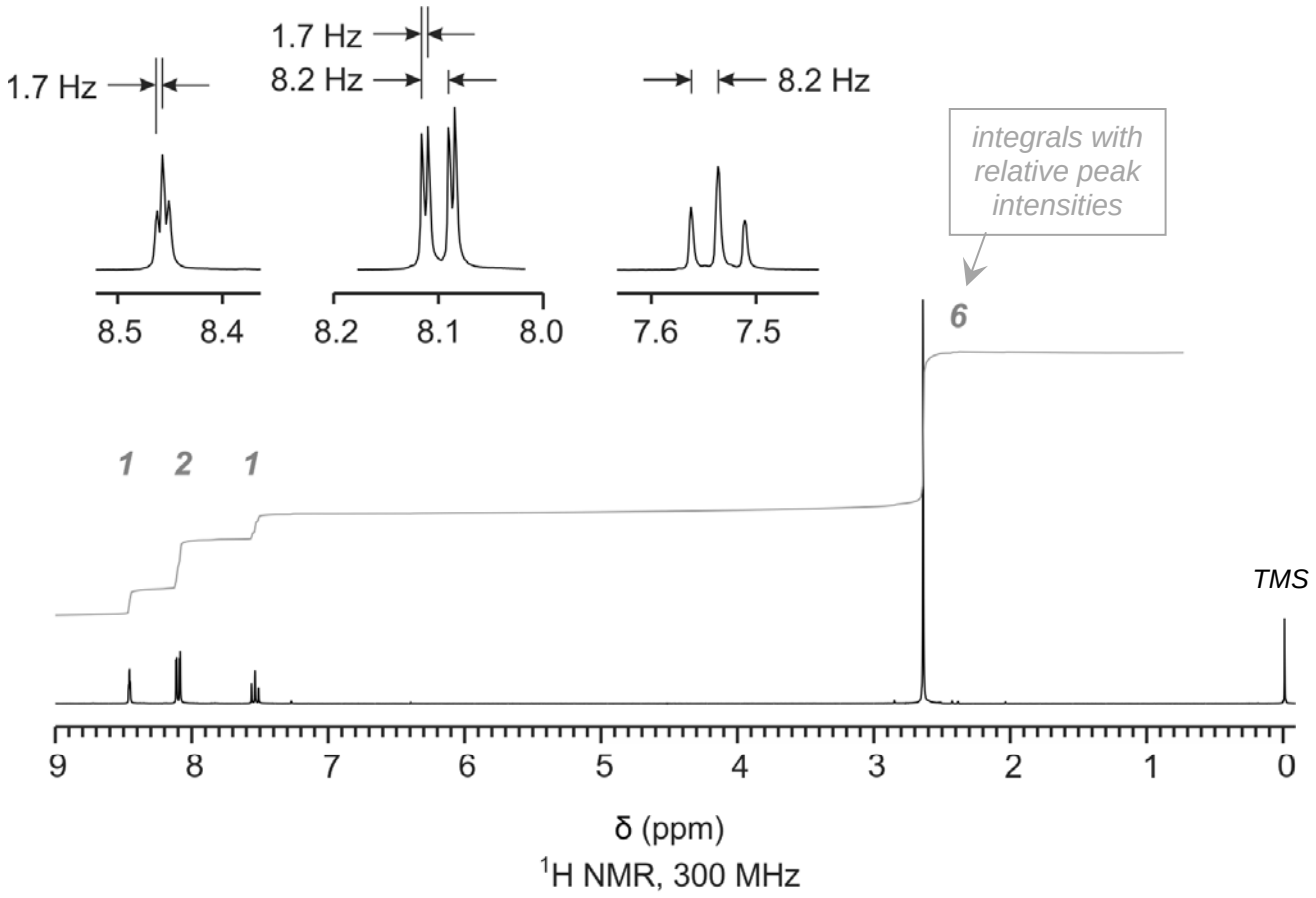


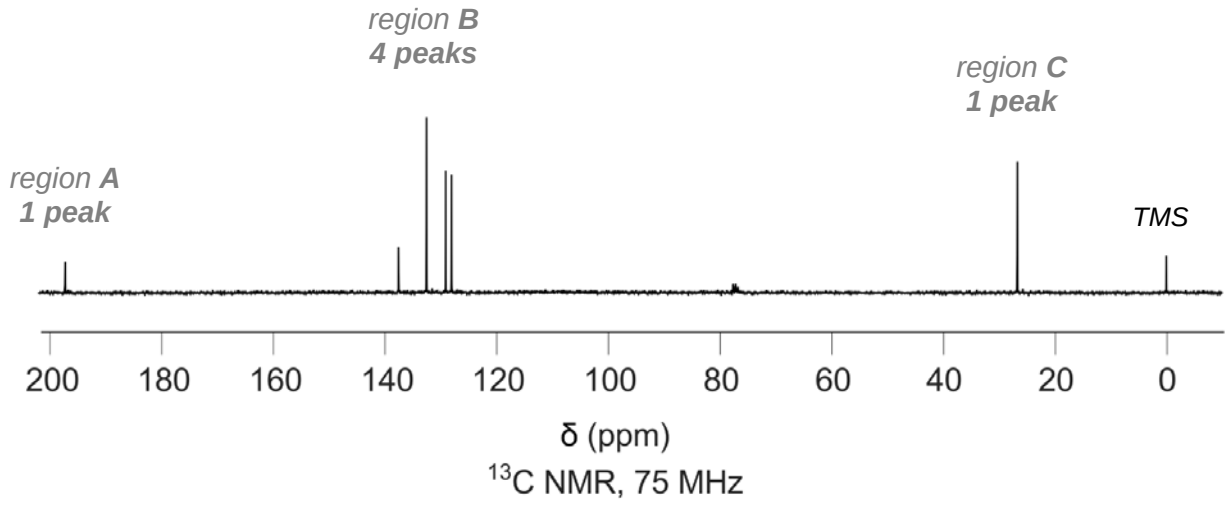
c. ^{1}H and ^{13}C spectra for the isolated molecule are shown on the next page. Which of the three products did you isolate? On the unfinished skeleton in the box at right, indicate your choice by drawing in any appropriate functional groups, as well as all hydrogens. Then,

- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

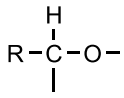
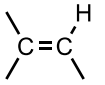
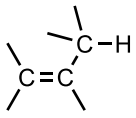
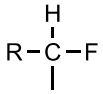
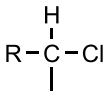
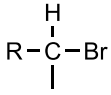
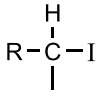
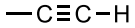
d. The ^{13}C NMR spectrum of the isolated product showed 6 peaks, which appear in three distinct regions of the spectrum. I've labeled these regions **A**, **B** and **C** on the ^{13}C spectrum on the next page. As you did above, re-draw your proposed product structure on the right (though this time you can omit H's). Then, in each empty box, write the letter **A**, **B**, or **C** to indicate the region of the ^{13}C NMR you would expect to find that carbon resonance. **Fill all boxes.**

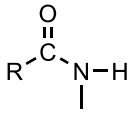
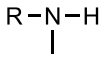
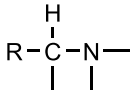
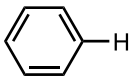
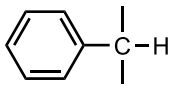
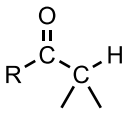
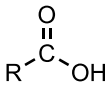
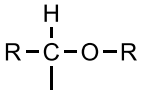



1.7 Hz
1.7 Hz
8.2 Hz
8.2 Hz
integrals with relative peak intensities
6
1 2 1
TMS
8.5 8.4 8.2 8.1 8.0 7.6 7.5
9 8 7 6 5 4 3 2 1 0
δ (ppm)
1H NMR, 300 MHz

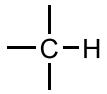
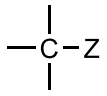
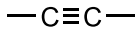
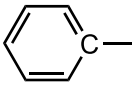

region B
4 peaks
region C
1 peak
region A
1 peak
TMS
200 180 160 140 120 100 80 60 40 20 0
δ (ppm)
13C NMR, 75 MHz

^{1}H NMR Chemical Shifts

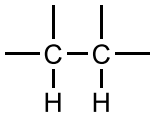
Compound Type	Chemical Shift (ppm)
Alcohol	
	1-5
	3.4-4.0
Aldehyde	
	9-10
Alkane	0.9-2.0
RCH_3	~0.9
R_2CH_2	~1.3
R_3CH	~1.7
Alkene	
 sp^2 C-H	4.5-6.0
 allylic sp^3 C-H	1.5-2.5
Alkyl Halide	
	4.0-4.5
	3.0-4.0
	2.7-4.0
	2.2-4.0
Alkyne	
	~2.5

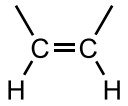
Compound Type	Chemical Shift (ppm)
Amide	
	7.5-8.5
Amine	
	0.5-5.0
	2.3-3.0
Aromatic compound	
 sp^2 C-H	6.5-8
 benzylic sp^3 C-H	1.5-2.5
Carbonyl compound	
 sp^3 C-H on the α carbon	2.0-2.5
Carboxylic acid	
	10-12
Ether	
	3.4-4.0

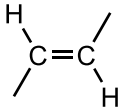
^{13}C NMR Chemical Shifts

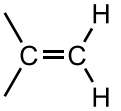
Carbon Type	Structure	Chemical Shift (ppm)
Alkyl, sp^3 hybridized C		5-45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30-80
Alkynyl, *sp* hybridized C		65-100
Alkenyl, sp^2 hybridized C		100-140
Aryl, sp^2 hybridized C		120-150
Carbonyl C		160-210

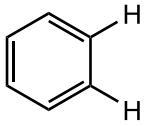
Typical ^{1}H-^{1}H Coupling Constants (*J*)

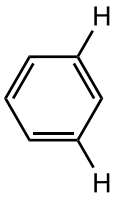
 (free rotation) ~7 Hz

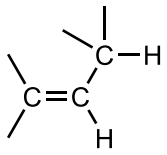
 (cis) 5-10 Hz

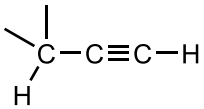
 (trans) 11-18 Hz

 (geminal) 0-3 Hz

 (ortho) ~8 Hz

 (meta) ~2 Hz

 (allylic) ~6 Hz

 (propargyl) ~2 Hz

IR Absorption Frequencies

Bond	Functional group	Wavenumber (cm^{-1})	Comment
O – H			
	• ROH	3600–3200	broad, strong
	• RCOOH	3500–2500	very broad, strong
N – H			
	• RNH_2	3500–3300	two peaks
	• R_2NH	3500–3300	one peak
	• $RCONH_2$, RCONHR	3400–3200	one or two peaks; N – H bending also observed at 1640 cm^{-1}
C – H			
	• C_{sp} – H	3300	sharp, often strong
	• C_{sp^2} – H	3150–3000	medium
	• C_{sp^3} – H	3000–2850	strong
	• C_{sp^2} – H of RCHO	2830–2700	one or two peaks
C ≡ C		2250	medium
C ≡ N		2250	medium
C = O			strong
	• RCOCl	1800	
	• $(RCO)_2O$	1800, 1760	two peaks
	• RCOOR	1745–1735	increasing $\tilde{\nu}$ with decreasing ring size
	• RCHO	1730	
	• R_2CO	1715	increasing $\tilde{\nu}$ with decreasing ring size
	• R_2CO, conjugated	1680	
	• RCOOH	1710	
	• $RCONH_2$, RCONHR, $RCONR_2$	1680–1630	increasing $\tilde{\nu}$ with decreasing ring size
C = C			
	• Alkene	1650	medium
	• Arene	1600, 1500	medium
C = N		1650	medium

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01	2 2A																2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.