NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 10:20 am, August 5, 2015

Exam 4

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 11th at 1 PM. Exams that are not picked up within two weeks will be disposed of.

A periodic table and tables of typical NMR chemical shifts 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.

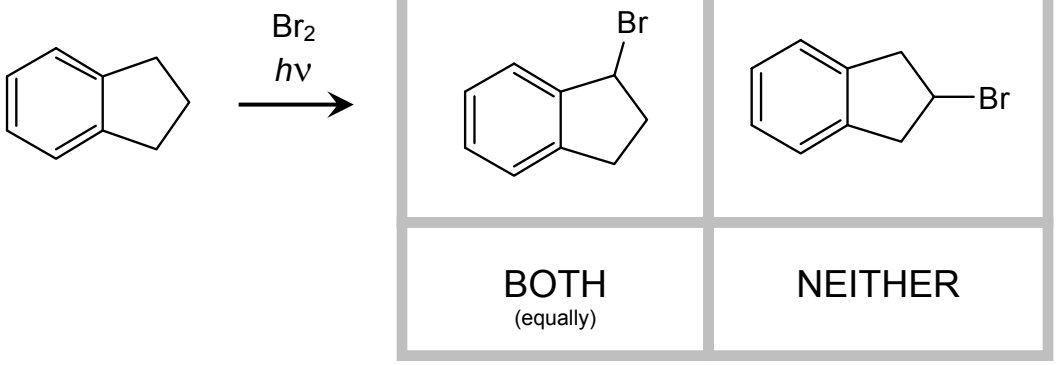
NAME _____

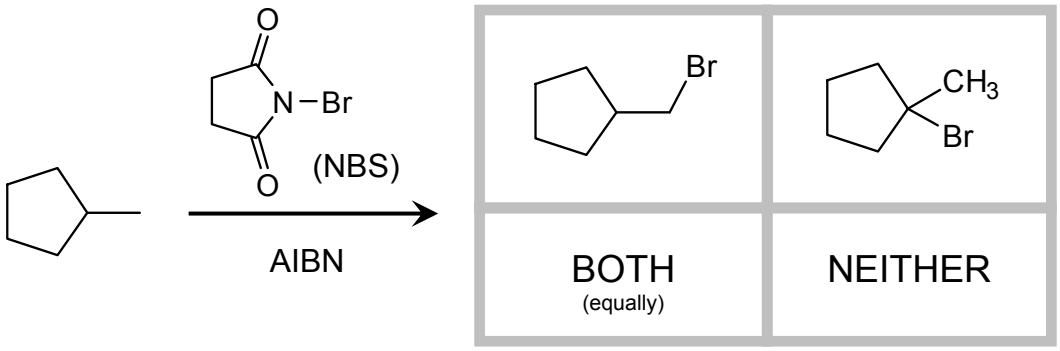
Scoring: 1. _____ / 12 3. _____ / 37

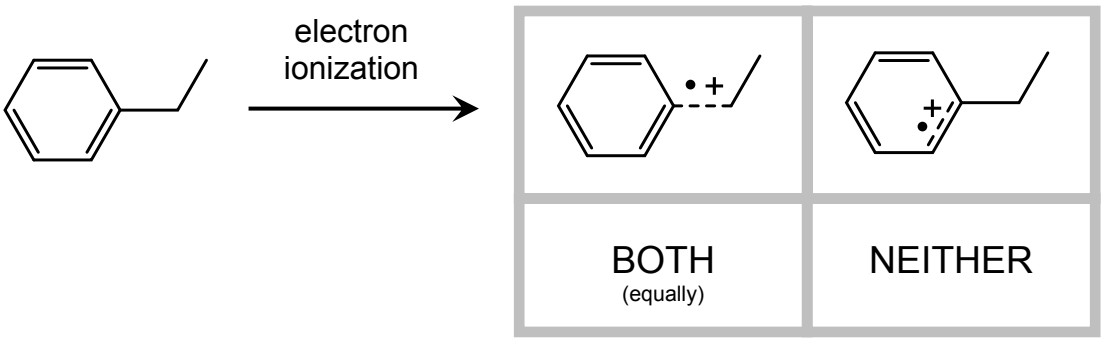
2. _____ / 15 4. _____ / 36

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.**





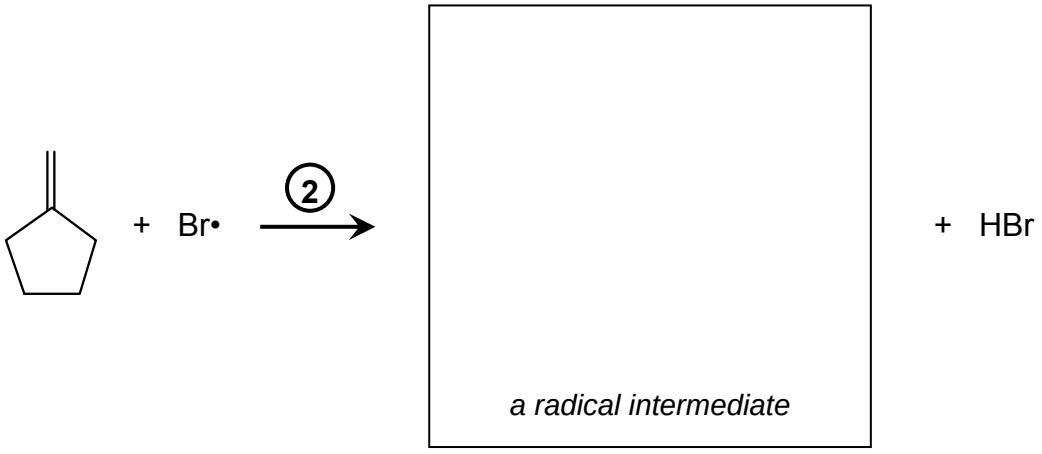


2. (15 pts) The free-radical chain mechanism of radical bromination has two propagation steps, which we have in lecture numbered ② and ③ :

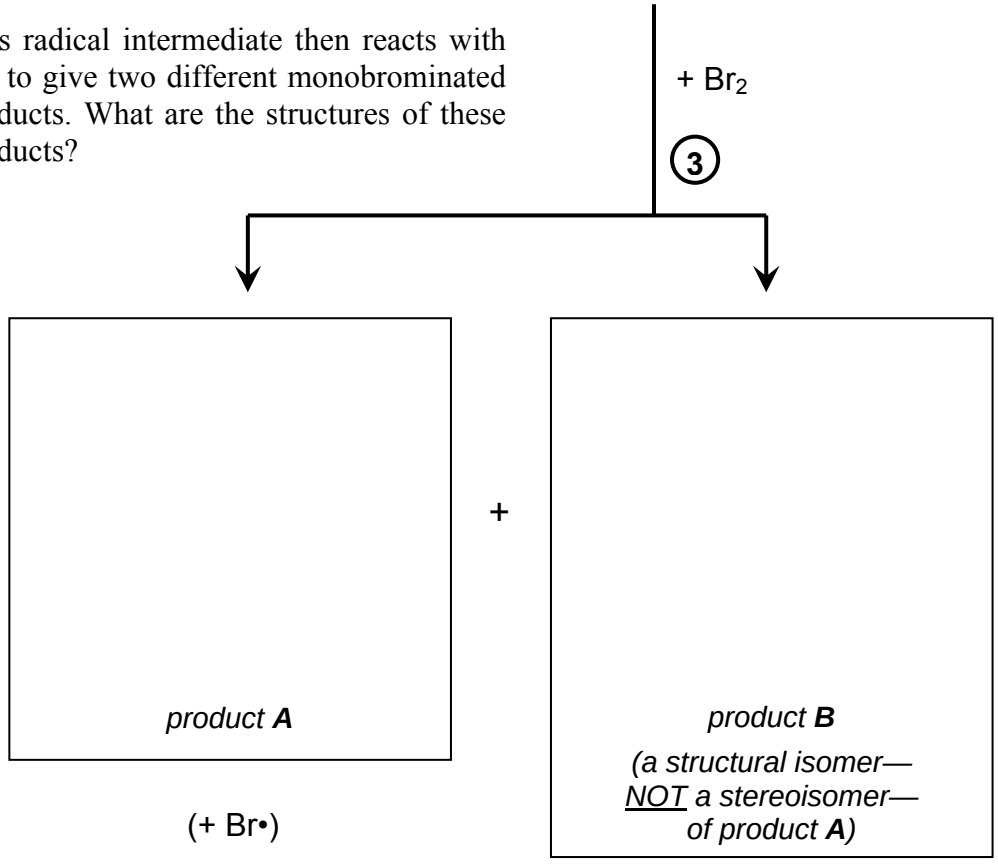
   ② abstraction of an H from R-H by Br•; and

   ③ reaction of R• with Br_2 to form R-Br.

   a) Radical bromination of ethylenecyclopentane goes predominantly through a single radical intermediate R•. **What is the structure of the radical intermediate?**

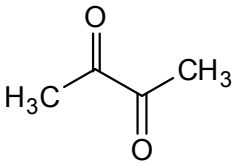


   b) This radical intermediate then reacts with Br_2 to give two different monobrominated products. What are the structures of these products?

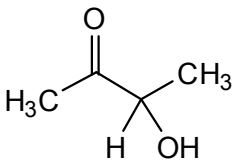


3. (37 pts) In the early 2000's, the National Institute for Occupational Safety and Health (NIOSH) began documenting lung disease in employees of companies that packaged microwave popcorn. NIOSH investigators narrowed the possible causative agent down to three substances: diacetyl, acetoin, and 2,3-butanediol, all of which are used in artificial butter flavoring and were inhaled in large amounts at that time by the employees. In this problem, you will identify one of the three compounds isolated from a popcorn packaging plant—in this case, not the inhaled toxin—based on its ^{1}H and ^{13}C NMR spectra.

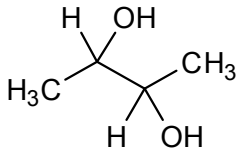
a. How many resonances would you expect to see in the ^{1}H NMR of each of these additives? In other words, how many inequivalent sets of protons are there in each structure? Write your answers in the boxes on the right.



diacetyl



acetoin

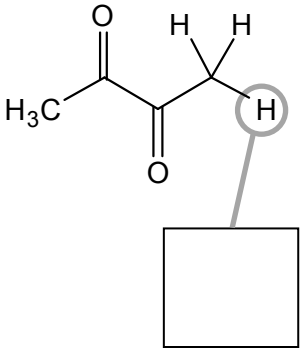


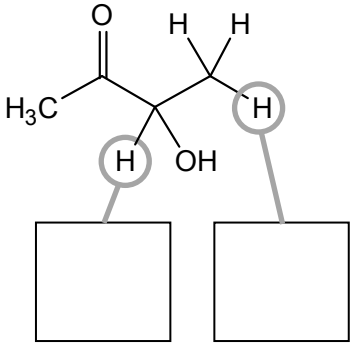
2,3-butanediol

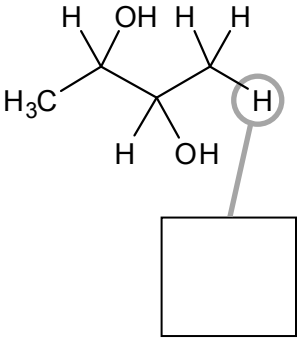
 # ^{1}H NMR resonances expected

b. Each proton highlighted in the structures below 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 in these molecules.) Use the abbreviations on the chart on the right.

abbreviations for multiplets			
s:	singlet	*q*:	quartet
d:	doublet	*qn*:	quintet
t:	triplet	*sx*:	sextet





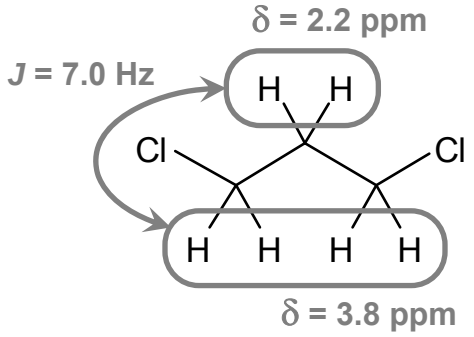


(Problem 3 continued on next page)

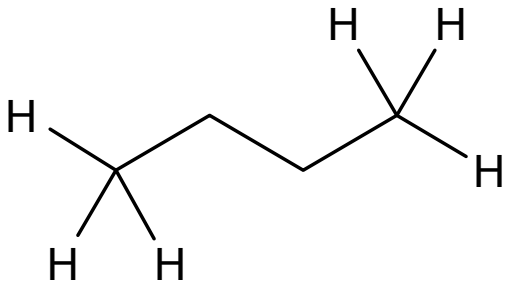
c. ^{1}H and ^{13}C spectra for the isolated molecule are shown on the next page. Is the molecule diacetyl, acetoin, or 2,3-butanediol? On the unfinished skeleton in the box below, indicate your choice by drawing in the functional groups on the two center carbons, as well as all hydrogens. Then,

- 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*).

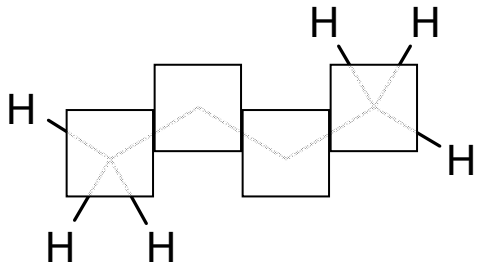
Format for answer to (c):



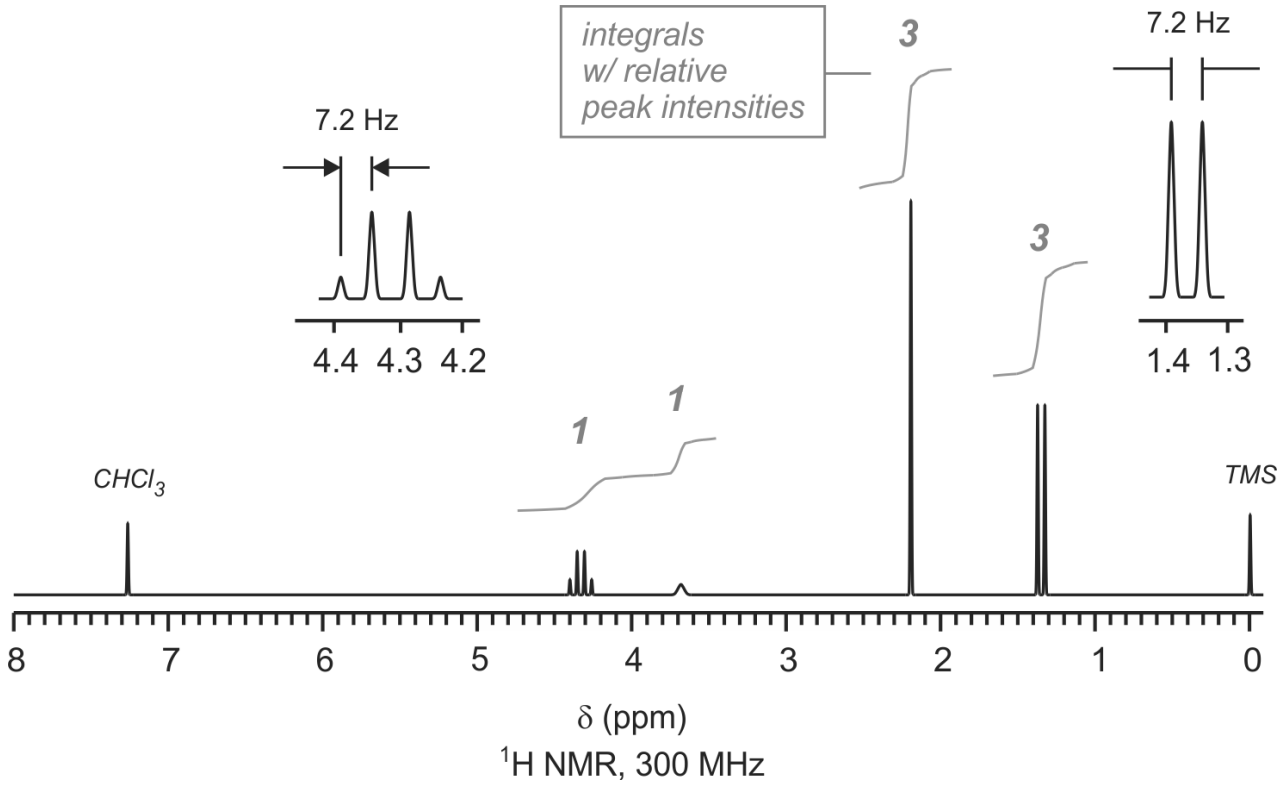
Your answer to (c):

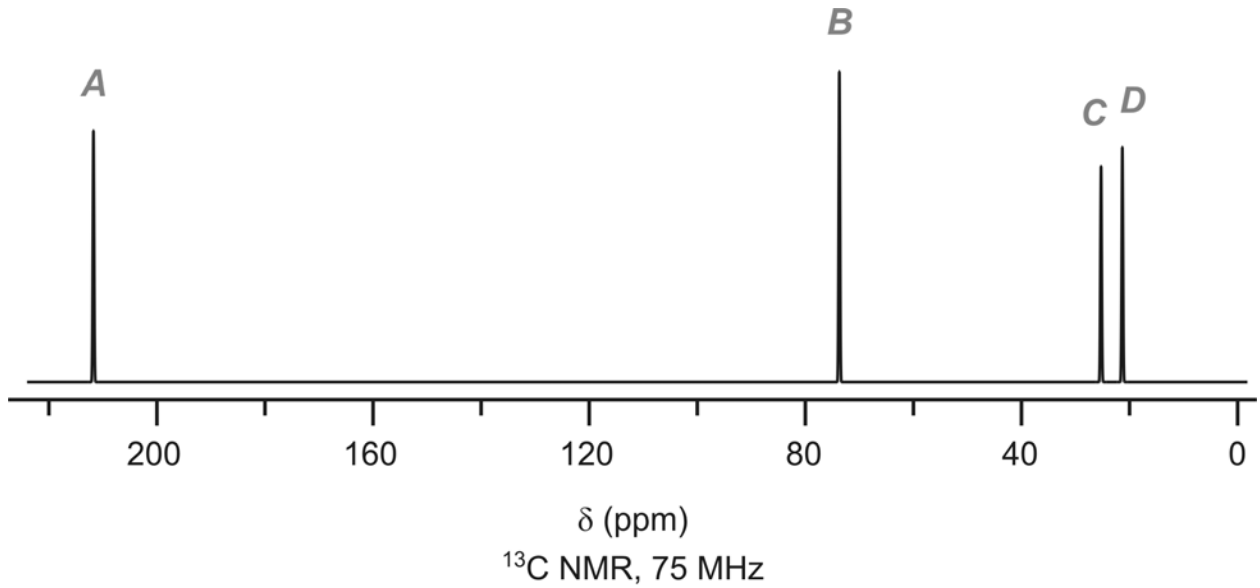


d. There are four peaks in the ^{13}C NMR spectrum of our unknown molecule, labeled **A**, **B**, **C**, and **D**. Which carbons in your molecule do these peaks correspond to? As you did above in part (c), add functional groups to the two center carbons in the skeleton below to indicate whether you think the molecule is diacetyl, acetoin or 2,3-butanediol. Then, write a letter in each box to assign the ^{13}C NMR to the corresponding carbon atoms in the structure. **Fill all 4 boxes.**



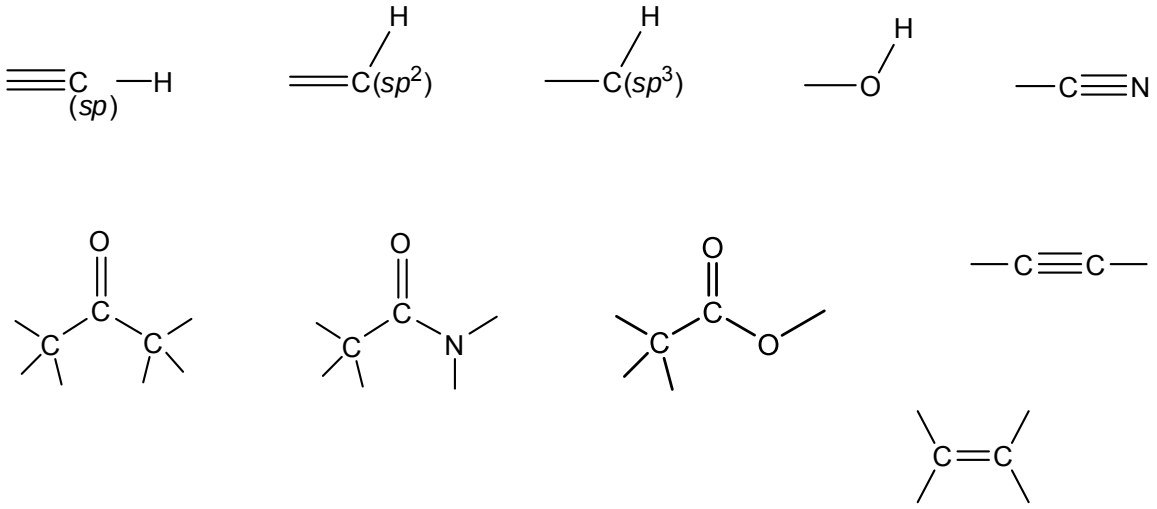
e. Is the ^1H resonance of $CHCl_3$ at $\delta = 7.26$ ppm the farthest **upfield** or **downfield** ?





4. (36 pts) The spectra on pages 8-9 correspond to a pure solvent molecule, collected from the waste stream of a chemical plant. High-resolution mass spectrometry determined an exact mass of 101.0841 amu for the highest-mass (parent, $\mathbf{M}^+$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_5H_{11}NO}$.

   a. Based on the features above 1600 cm^{-1} in the IR spectrum, what functional groups could 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
($C_5H_{11}NO$)

   c. How many resonances would you expect to see in the ^{13}C NMR of your molecule?

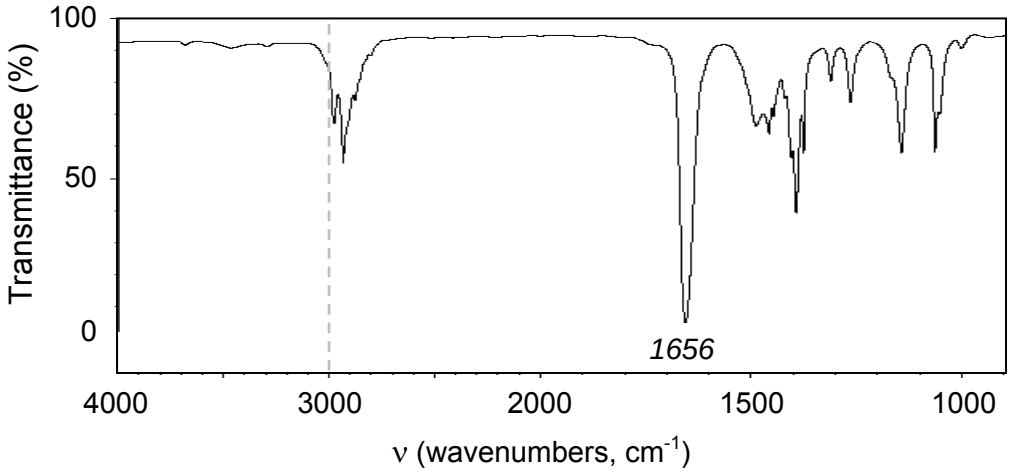
d. The mass spectrum shows two high-mass fragment peaks at m/z = 72 and m/z = 57. In each of the two boxes below, draw a mechanism (via "electron pushing") that shows how the radical cation of the parent molecule you drew in part (c) could yield these fragments.

*fragment to yield mas **72**:*	*fragment to yield mass **57**:*

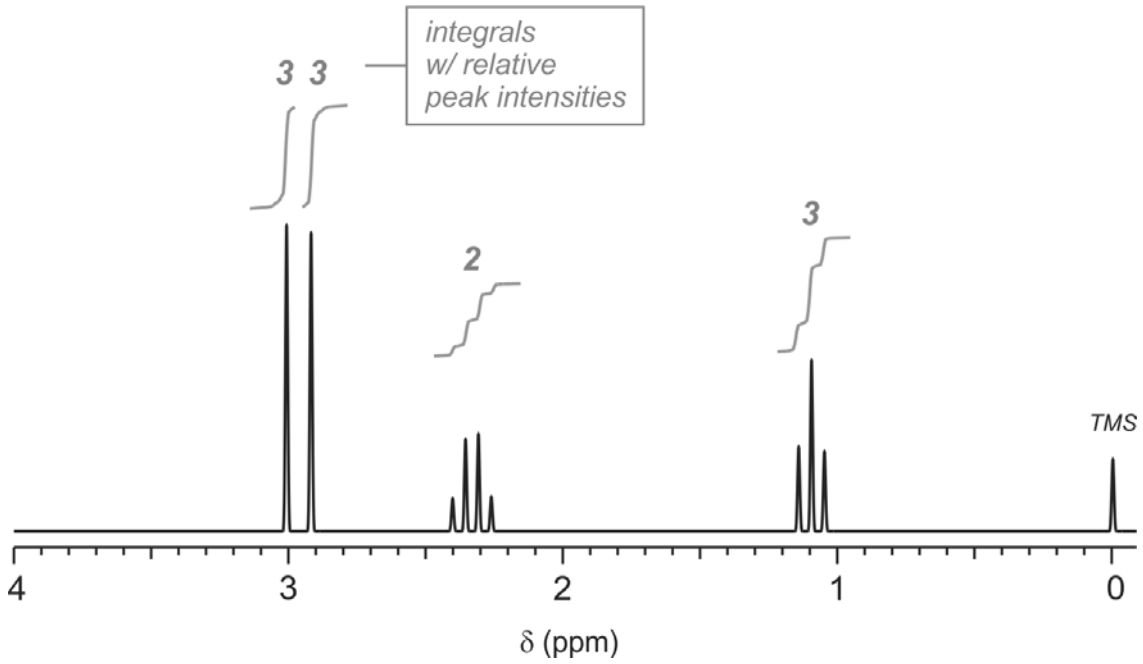
e. In the mass spectrum, adjacent to the m/z = 44 and 101 peaks, there are smaller peaks that are one mass unit higher (at m/z = 45 and 102). In class, we said that $[\mathbf{M+1}]^+$ peaks could correspond to ions that had one ^{13}C atom in place of a ^{12}C. Looking at the mass spectrum, is this a plausible explanation for the m/z = 45 and 102 peaks? (Circle one each line.)

The peak at m/z = **45**	**could**	or	**could not**	be due to m/z = 44 ions bearing one ^{13}C.
The peak at m/z = **102**	**could**	or	**could not**	be due to m/z = 101 ions bearing one ^{13}C.

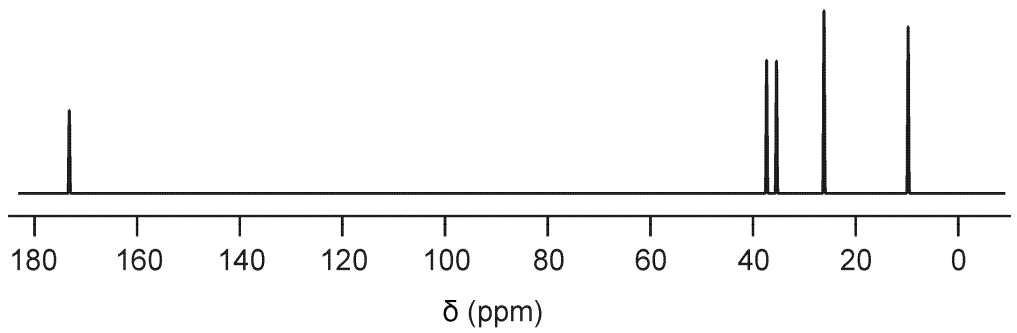
IR Spectrum:



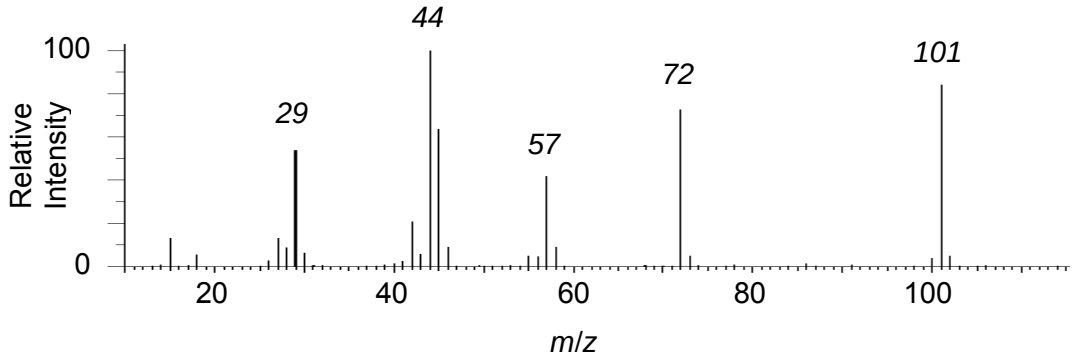
^{1}H Spectrum (200 MHz):



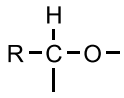
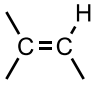
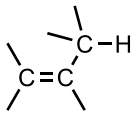
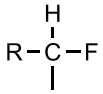
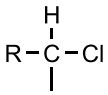
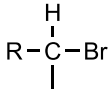
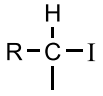
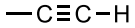
^{13}C Spectrum (50 MHz):

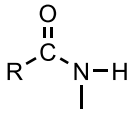
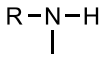
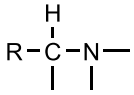
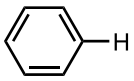
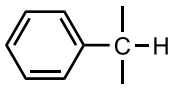
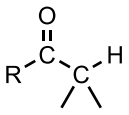
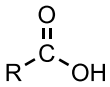
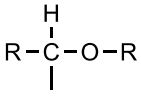


Mass Spectrum:

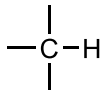
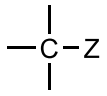
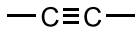
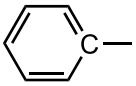


^{1}H NMR Chemical Shifts

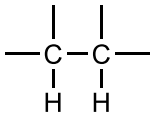
Compound Type	Chemical Shift (ppm)
Alcohol	
	1-5
	3.4-4.0
Aldehyde	
	9-10
Alkane	0.9-2.0
RCH_3	~0.9
R_2CH_2	~1.3
R_3CH	~1.7
Alkene	
 sp^2 C-H	4.5-6.0
 allylic sp^3 C-H	1.5-2.5
Alkyl Halide	
	4.0-4.5
	3.0-4.0
	2.7-4.0
	2.2-4.0
Alkyne	
	~2.5

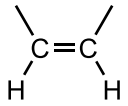
Compound Type	Chemical Shift (ppm)
Amide	
	7.5-8.5
Amine	
	0.5-5.0
	2.3-3.0
Aromatic compound	
 sp^2 C-H	6.5-8
 benzylic sp^3 C-H	1.5-2.5
Carbonyl compound	
 sp^3 C-H on the α carbon	2.0-2.5
Carboxylic acid	
	10-12
Ether	
	3.4-4.0

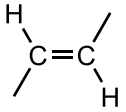
^{13}C NMR Chemical Shifts

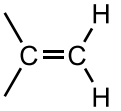
Carbon Type	Structure	Chemical Shift (ppm)
Alkyl, sp^3 hybridized C		5-45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30-80
Alkynyl, *sp* hybridized C		65-100
Alkenyl, sp^2 hybridized C		100-140
Aryl, sp^2 hybridized C		120-150
Carbonyl C		160-210

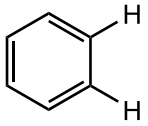
Typical ^{1}H-^{1}H Coupling Constants (*J*)

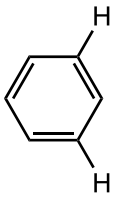
 (free rotation) ~7 Hz

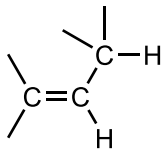
 (cis) 5-10 Hz

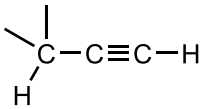
 (trans) 11-18 Hz

 (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.