NAME _____

ID # _____

HONORS ELEMENTARY ORGANIC CHEMISTRY I (2331H)

10:30 am – 12:30 pm, December 16, 2013

Final Exam

There will be two ways that you can pick up your graded final exam:

- You can pick up your graded exam from Andy at office hours that he will hold on Thursday, December 19th (9:30-11 am) in Coffman Union Starbucks.
- Alternately, you will be able to pick up your exam in private from Chemistry department staff in 115 Smith beginning Friday, December 20th.

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

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.

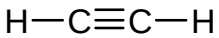
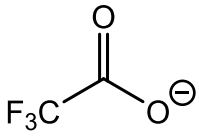
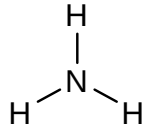
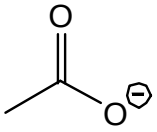
NAME _____

Scoring:

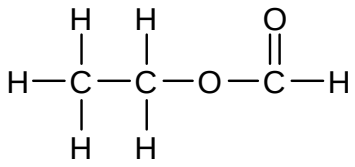
1. _____ / 14	6. _____ / 16
2. _____ / 18	7. _____ / 15
3. _____ / 4	8. _____ / 34
4. _____ / 22	9. _____ / 24
5. _____ / 12	10. _____ / 41

Total Score: _____ / 200

1. (14 pts) For each of the pairs of acids (or bases) below,
   - Draw the conjugate base (or acid).
   - Circle whether you think the first acid (or base) is more or less acidic (or basic) than the second.

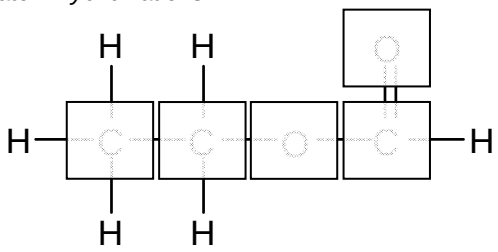
Acid	Conjugate Base	Base	Conjugate Acid
			
is		is	
MORE ACIDIC **LESS ACIDIC**		**MORE BASIC** **LESS BASIC**	
than		than	
			

2. (18 pts) For ethyl formate (drawn at right), in the boxes provided:



- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges. Then, circle which resonance structure you think is the most significant, and which is the least. **Circle only one MOST and one LEAST.**
- Draw a Lewis wedge/dashed-bond structure that illustrates the most stable three-dimensional conformation of the molecule. Draw all atoms, bonds, and charges, but omit lone pairs.
- In the boxes provided, write the hybridization state on any atom heavier than hydrogen.

atom hybridizations:



MOST *or* **LEAST** *significant?*

3-dimensional representation

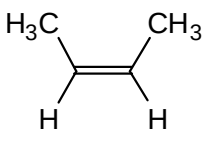
resonance structure

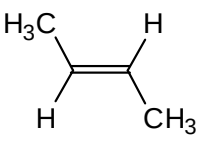
resonance structure

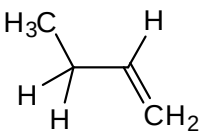
MOST *or* **LEAST** *significant?*

MOST *or* **LEAST** *significant?*

3. (4 pts) Each of the alkenes on the right hydrogenates—adds H_2—exothermically (with $\Delta H_{hyd} < 0$) to form butane. **Which one hydrogenates the most exothermically?** (Circle one molecule.)

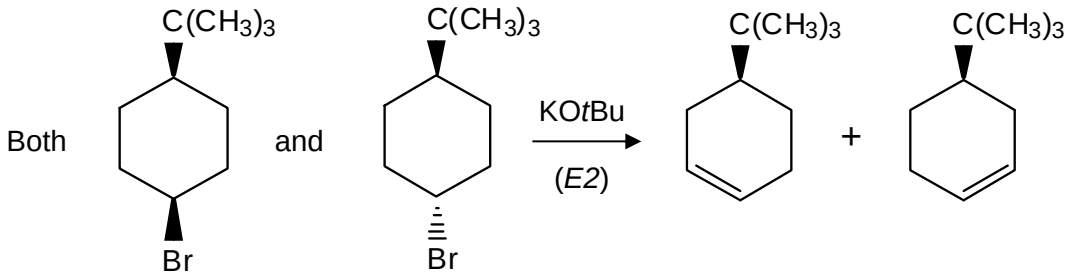






4. (22 pts) In the presence of a strong base, each of the bromo-*tert*-butylcyclohexanes below undergoes E2 elimination to produce an alkene. However, one of the two reacts much faster than the other. In this problem, you will explain why.

.



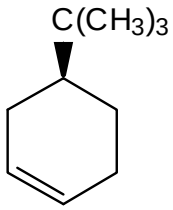
(a) Each of the starting cyclohexanes has two equilibrating chair conformers; for each starting material, one chair is much more stable than the other. In the boxes below, draw the more stable conformers for each starting material. Feel free to omit the ring hydrogens, but draw all non-hydrogen substituents.

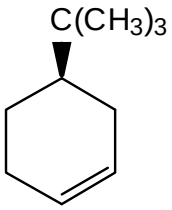
More stable *chair conformer for* ***cis*** *isomer*	***More stable*** *chair conformer for* ***trans*** *isomer*

(b) Of the conformers you drew above, only one will react with KO*t*Bu via E2. In the box on the right, re-draw the one stable conformer that will undergo E2. Then, "push electrons" (using curved arrows) to show how one of the two products would be generated from starting material and the tBuO$^-$ base. (You don't need to draw the product, just push electrons.)

Mechanism for E2-reactive conformer

(c) Are the two products chiral? For each structure, **circle** whether you think the molecule is chiral or achiral. Then, **label each chiral center** with its appropriate Cahn-Ingold-Prelog designation [(*R*) or (*S*)]. Make it clear which atom in the drawing you are labeling.





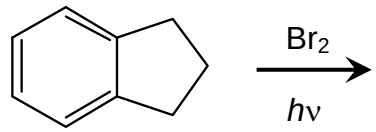
CHIRAL *or* **ACHIRAL** ?

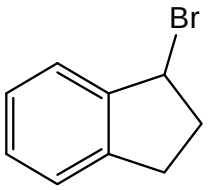
CHIRAL *or* **ACHIRAL** ?

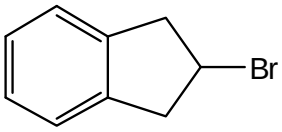
(d) What is the stereochemical relationship between the two products? (Circle one answer.) Are they

ENANTIOMERS *or* **DIASTEREOMERS** *or* **NEITHER** ?

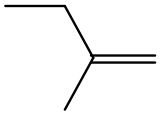
5. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

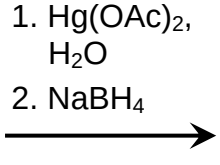


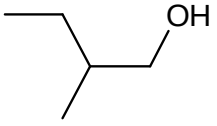


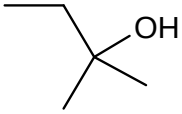


BOTH (equally) NEITHER

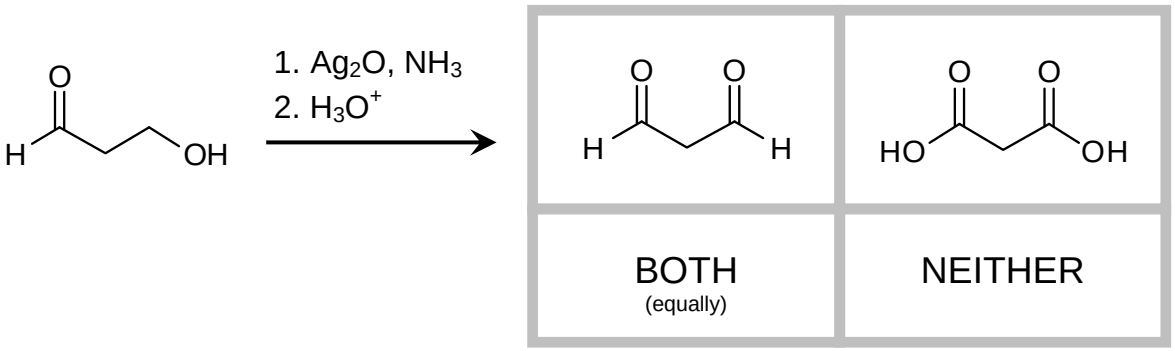




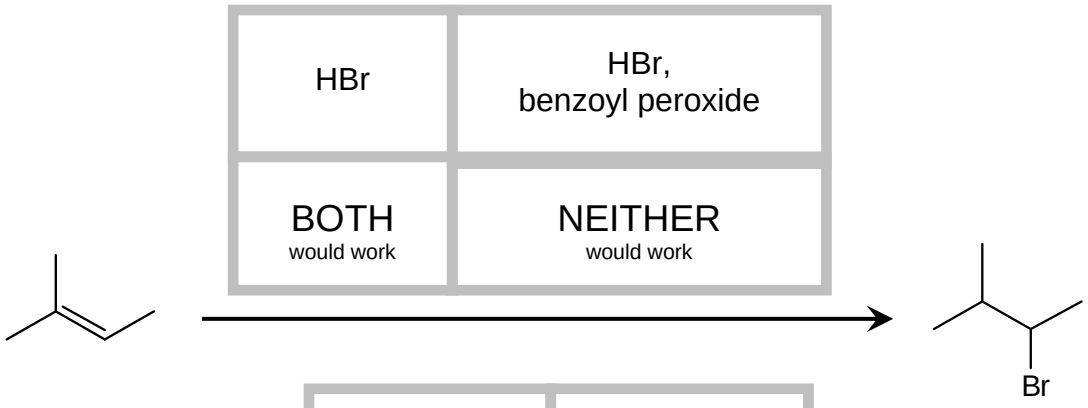


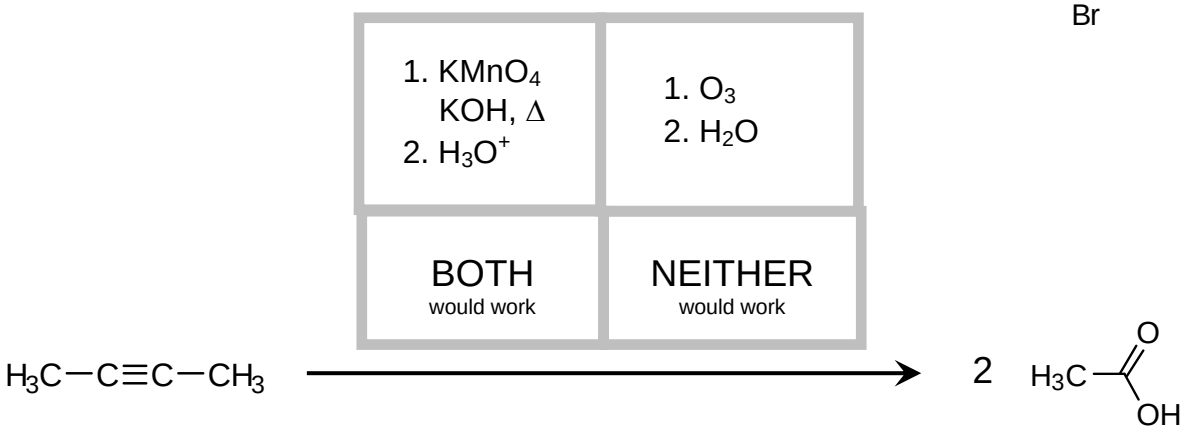


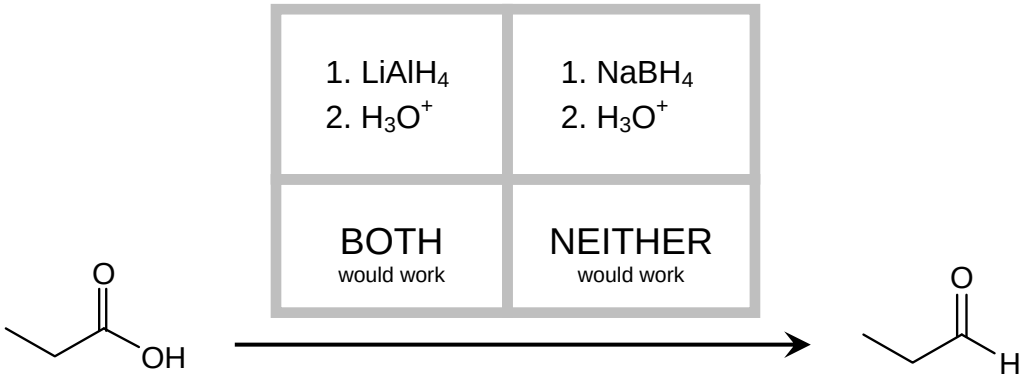
BOTH (equally) NEITHER

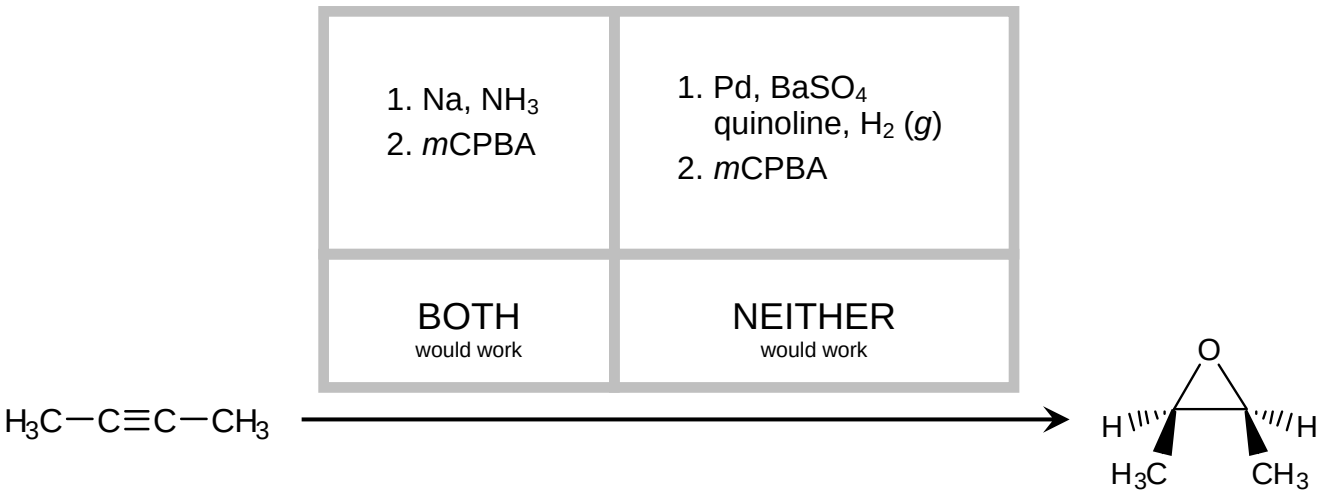


6. (16 pts) Each of the reactions *on the next page* is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

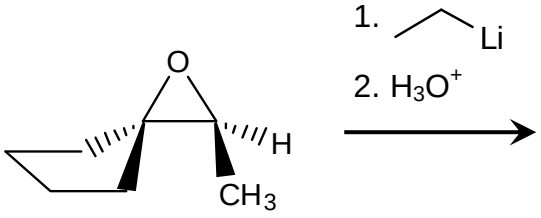


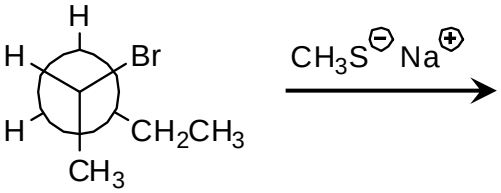


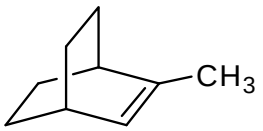




7. (15 pts) For each of the reactions on the following pages, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)

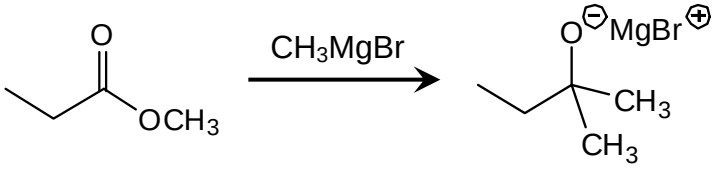




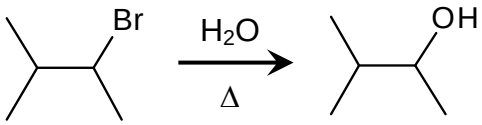


1. BH_3•THF
2. H_2O_2, ^-OH

8. (34 pts) Draw a mechanism (using "electron pushing") for each of the reactions shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)



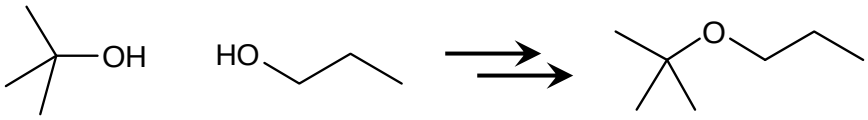
Mechanism:



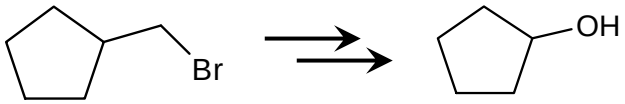
Mechanism:

One of the intermediates you drew in this mechanism could be stabilized by a 1,2-hydride shift. What alcohol product would be generated if this shift occurred?

9. (24 pts) For each set of starting materials and products shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.

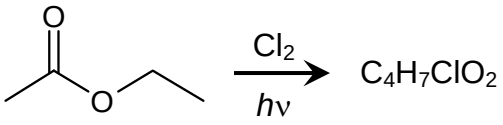


Multistep synthesis:

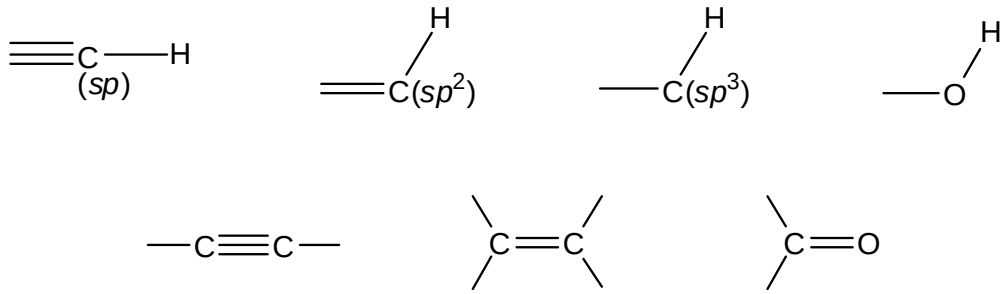


Multistep synthesis:

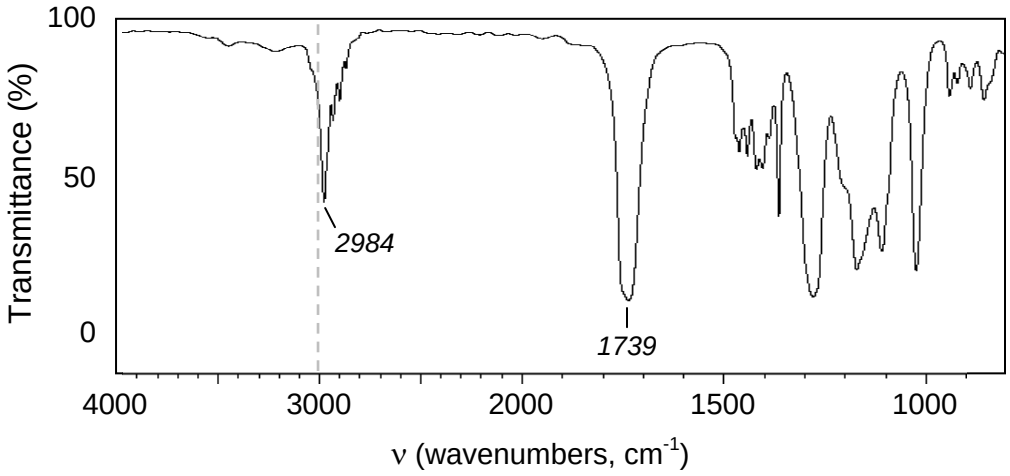
10. (41 pts) Radical chlorination of ethyl acetate (the starting material on the right) gives predominantly one product. This product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 122.0135 amu for one of the highest-mass (parent, $\mathbf{M}^+$) peaks in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_4H_7ClO_2}$.



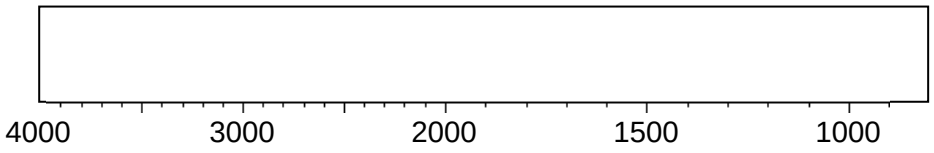
(a) Based on the features in the IR spectrum below, what functional groups would you expect the unknown molecule to have? **Circle all answers that apply.**



IR Spectrum:



(b) What part of this IR spectrum is the "fingerprint region"? In the box below, color/shade in the range of frequencies that correspond to the "fingerprint region".



(c) Compared to NMR, does IR require **MORE** *or* **LESS** material?

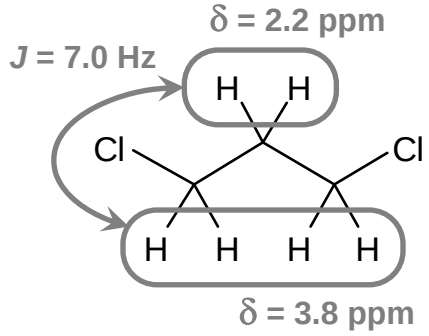
(d) Compared to mass spec, does IR require **MORE** *or* **LESS** material?

(e) **What is the structure of the product**? In the box below, draw the molecule's structure, including all hydrogens. Then, considering the ^{1}H NMR spectrum below,

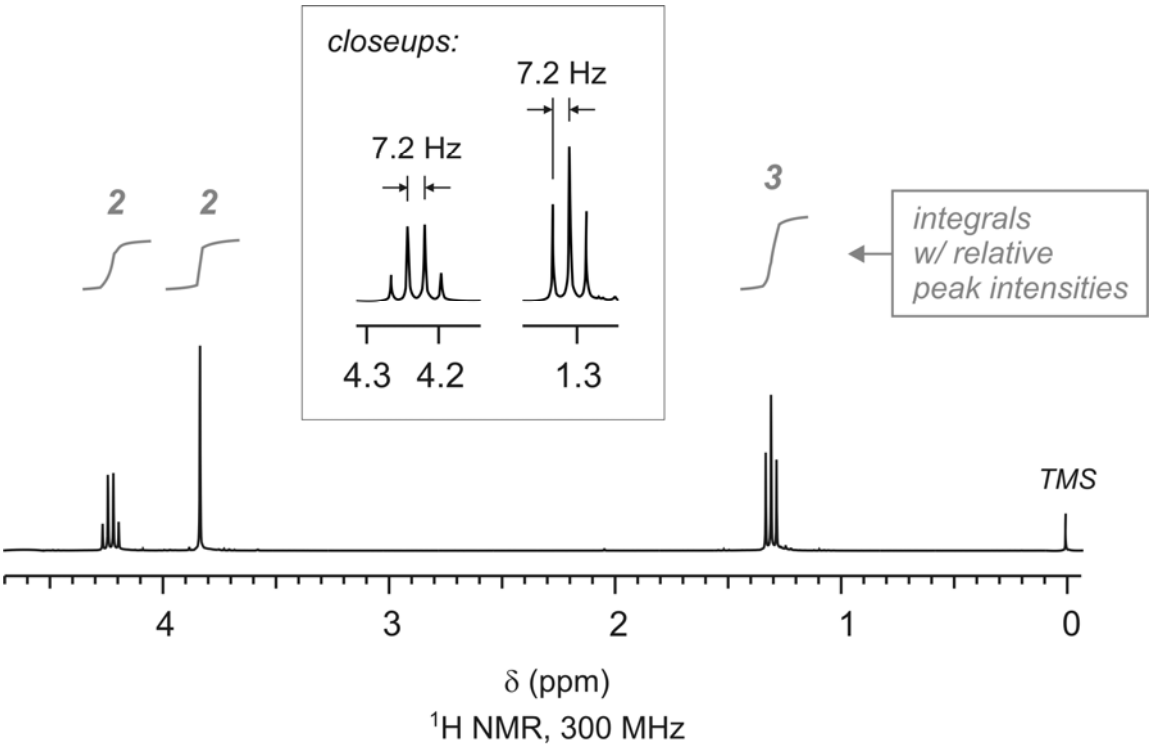
- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

the product
($C_4H_7ClO_2$)

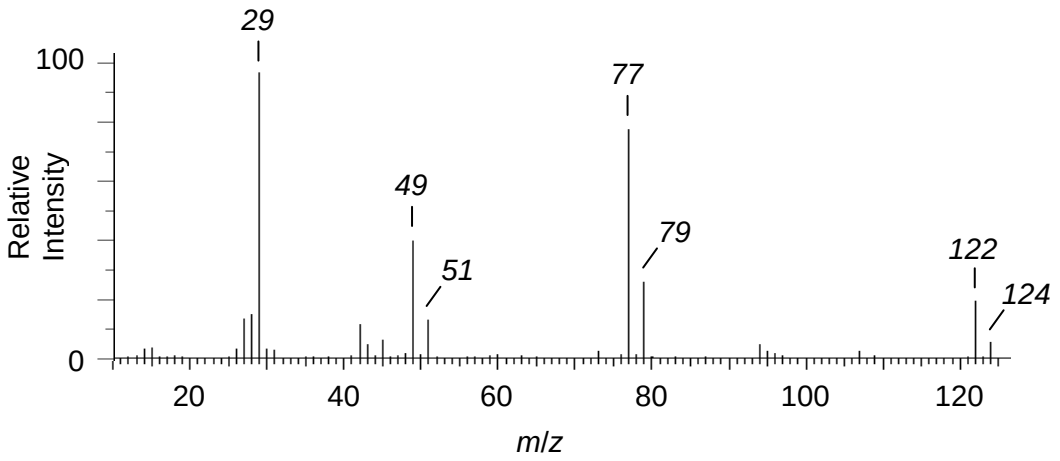
Format for answer to (c):



^{1}H NMR Spectrum:



Mass Spectrum:



(f) Some of the peaks in the electron-ionization (EI) mass spectrum, including the parent peak, are accompanied by a smaller peak 2 amu higher. (In other words, some peaks with mass *m* are accompanied by another peak, about 1/3 as tall, with mass *m*+2.) Why? *Please be brief; you can probably answer this question in less than 10 words.*

Explain why:

(g) The parent mass peak at *m*/*z* = 122 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 (e), 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 (e).*

$M^{\bullet+}$
($C_4H_7ClO_2^+$)

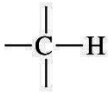
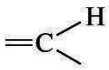
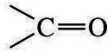
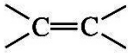
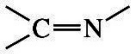
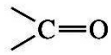
(h) The parent ion fragments to form a daughter ion with m/z = 77. What is the structure of this daughter ion? *You do not need to do electron pushing to answer this part—just draw the cation.*

fragment cation with m/z = 77

(i) The parent ion also fragments to form a daughter ion with mass 73 amu (not observed), which then fragments further to give an ion with m/z = 29. In the box below, draw a mechanism (using "arrow pushing") that shows these two sequential fragmentation steps, starting with your answer to part (g).

Mechanism that explains m/z = 29 peak

Summary of IR Stretching Frequencies

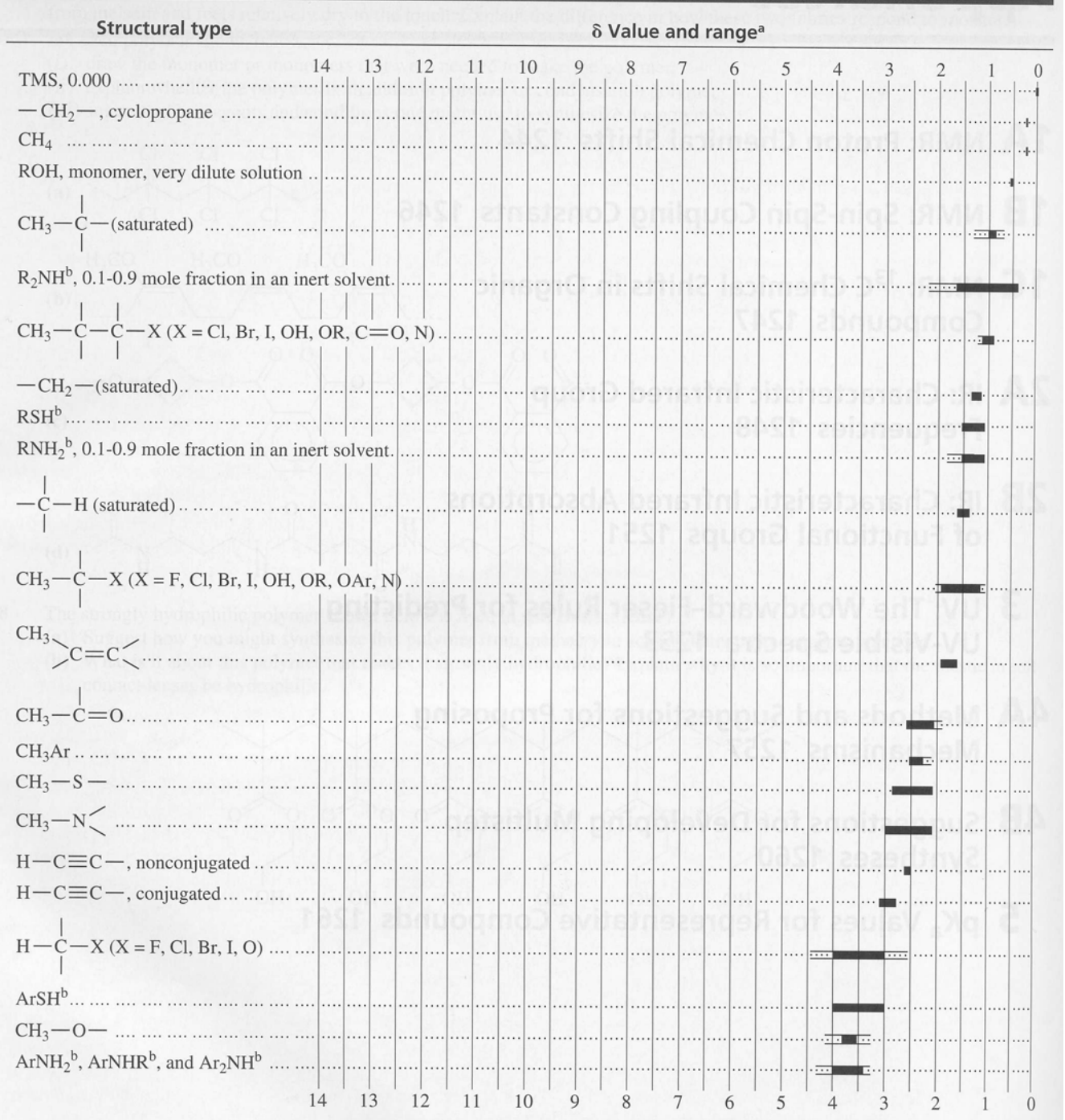
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane		just below 3000 cm^{-1}
	alkene		just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl		ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene		conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine		stronger than C=C
	amide		stronger than C=C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

Isotopic Composition of Some Common Elements

Element	M^+		M+1		M+2	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{15}N	0.4%		
oxygen	^{16}O	99.8%			^{18}O	0.2%
sulfur	^{32}S	95.0%	^{33}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{127}I	100.0%				

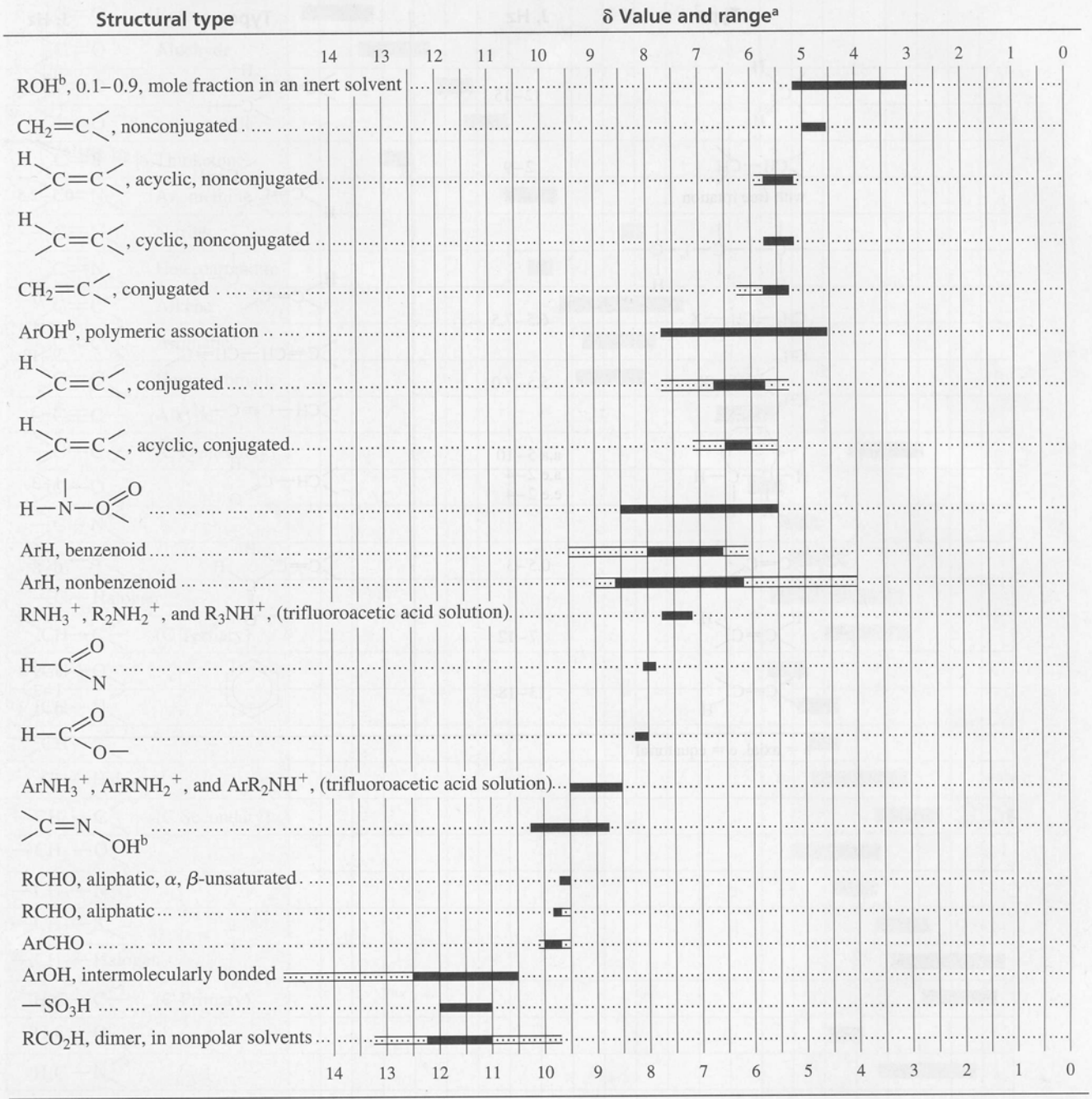
APPENDIX 1A NMR: Proton Chemical Shifts



[a] Normally, absorptions for the functional groups indicated will be found within the range shown in black. Occasionally, a functional group will absorb outside this range. Approximate limits are indicated by extended outlines.

[b] Absorption positions of these groups are concentration-dependent and are shifted to lower δ values in more dilute solutions.

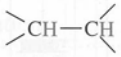
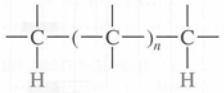
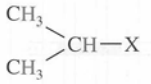
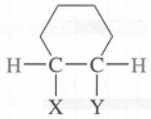
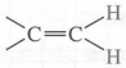
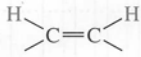
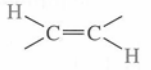
APPENDIX 1A NMR: Proton Chemical Shifts

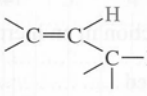
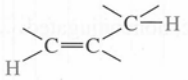
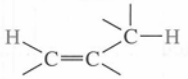
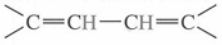
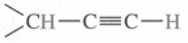
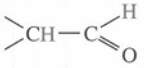
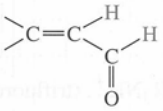
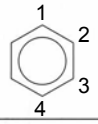


[a] Normally, absorptions for the functional groups indicated will be found within the range shown in black. Occasionally, a functional group will absorb outside this range. Approximate limits are indicated by extended outlines.

[b] Absorption positions of these groups are concentration-dependent and are shifted to lower δ values in more dilute solutions.

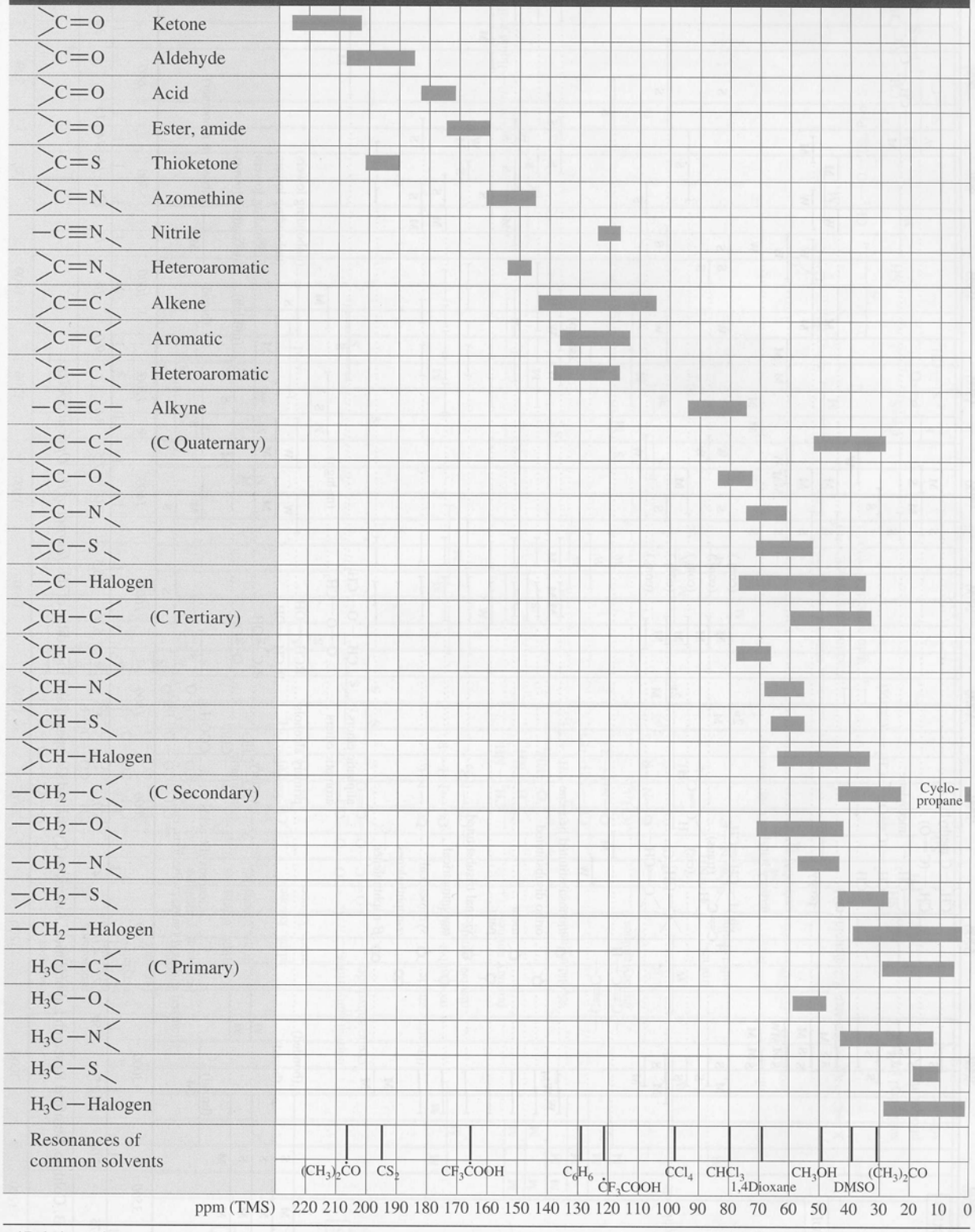
APPENDIX 1B NMR: Spin-Spin Coupling Constants

Type	J, Hz
	12–15
	2–9
with free rotation	~7
	~0
$CH_3—CH_2—X$	6.5–7.5
	5.5–7.0
	a,a 5–10 a,e 2–4 e,e 2–4
	0.5–3
	7–12
	13–18

Type	J, Hz
	4–10
	0.5–2.5
	~0
	9–13
	2–3
	1–3
	6–8
	H1-H2 6–9 H1-H3 1–3 H1-H4 0–1

a = axial, e = equatorial

APPENDIX 1C NMR: ^{13}C Chemical Shifts in Organic Compounds*:



*Relative to internal tetramethylsilane.

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.