NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 10:20 am, August 2, 2011

Exam 4

Form A

If you want to pick this exam up on Wednesday in class (in public), please check the box on the right: ☐

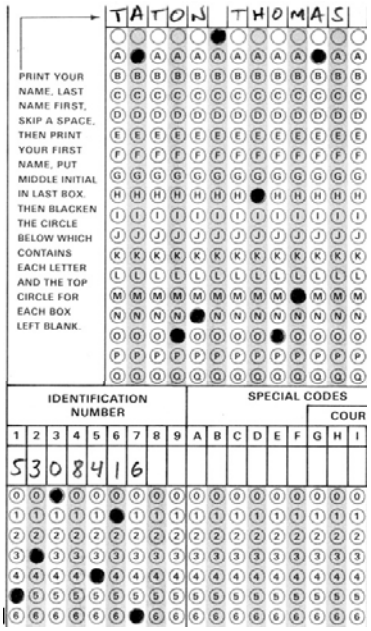
If you do not check the box, I will not bring your exam to class on Wednesday, and you will need to pick up your exam in private from Chemistry department staff in 115 Smith beginning Thursday, August 4th. Exams that are not picked up within two weeks will be disposed of.

A periodic table, a chart of reaction conditions, and tables of typical NMR chemical shifts and coupling constants 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 at the top of this page, and fill in the bubbles on the multiple-choice answer sheet for your name and your 7-digit student ID number. When the exam begins, also write your name at the top of page 5.

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

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

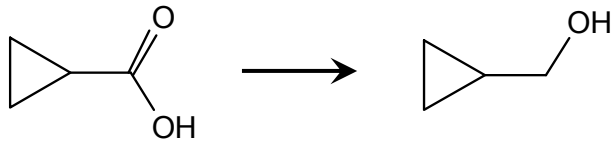


Multiple-Choice Problems

Please answer these problems on the bubble sheet.

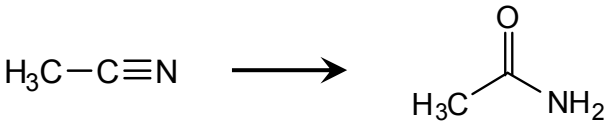
(3 pts each) Identify each of the transformations below as a reduction, an oxidation, or neither.

1.



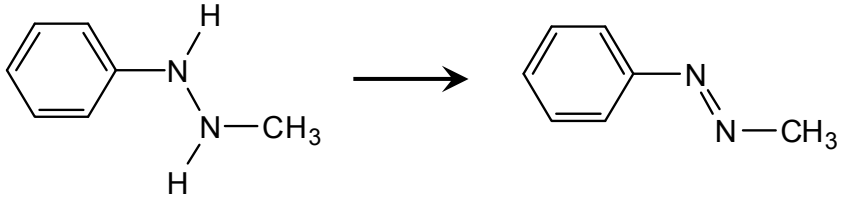
a. reduction
b. oxidation
c. neither

2.



a. reduction
b. oxidation
c. neither

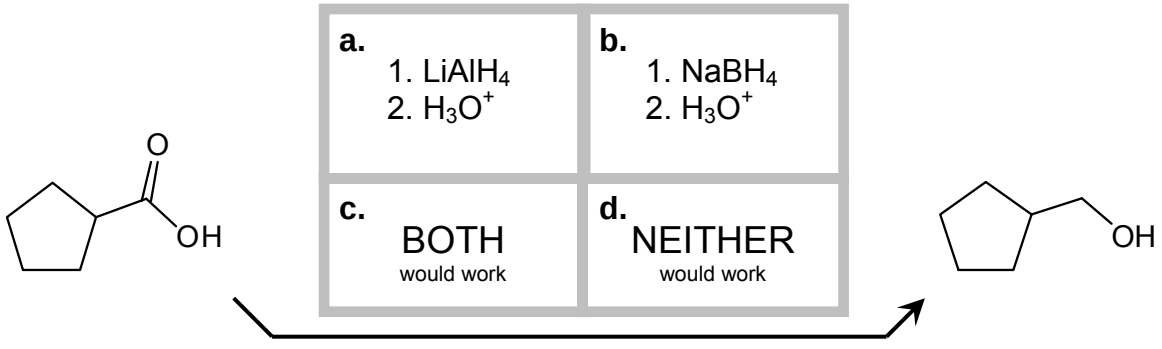
3.



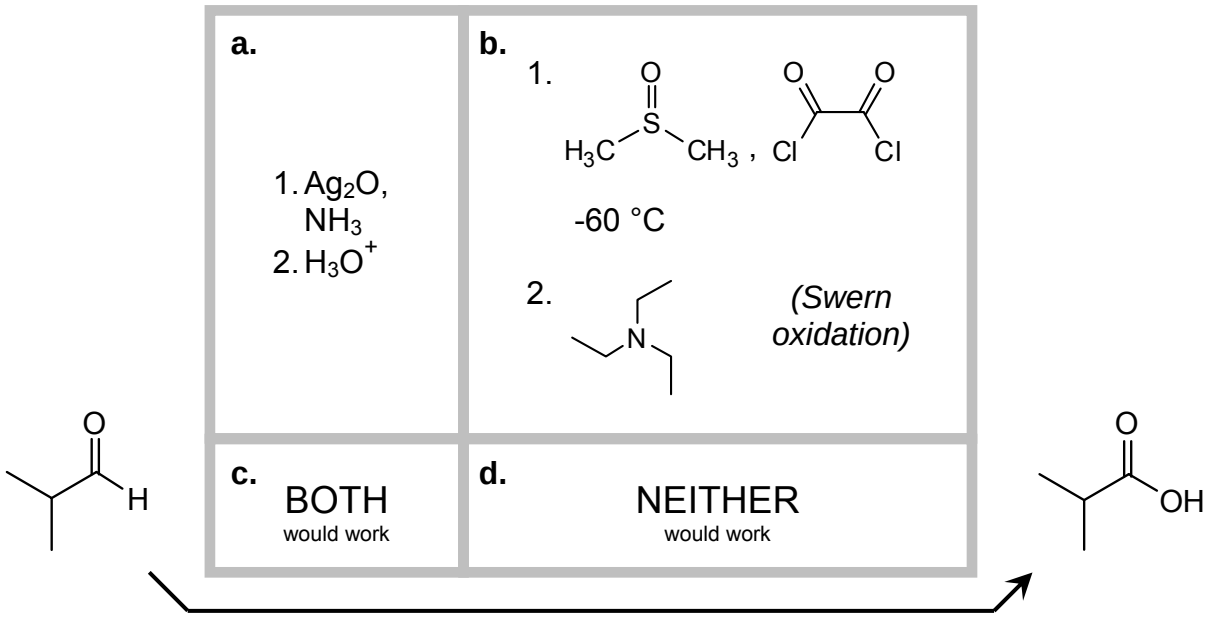
a. reduction
b. oxidation
c. neither

(4 pts each) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, answer with the corresponding letter. If both sets of conditions would accomplish the reaction, answer (c) "BOTH". If neither set of reaction conditions would succeed, answer (d) "NEITHER".

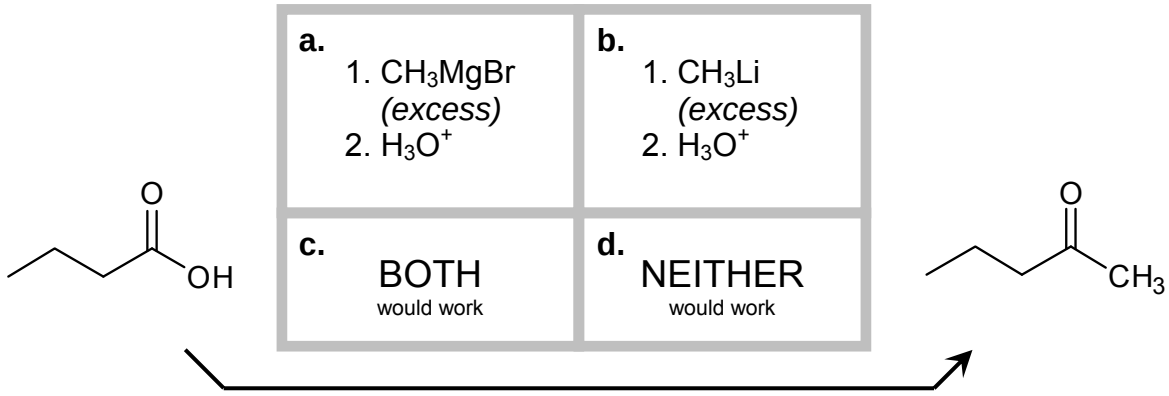
4.



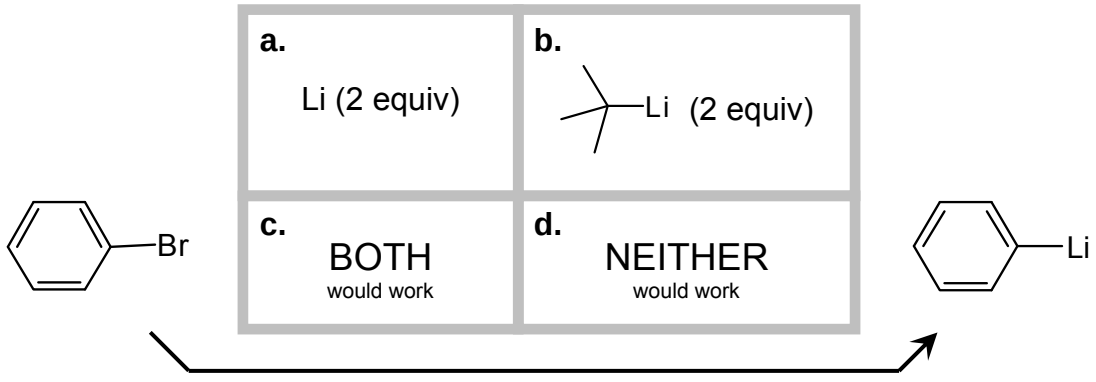
5.



6.



7.



Multiple-choice problems 8-19 are found later in the exam, on pages 6-7.

NAME _____

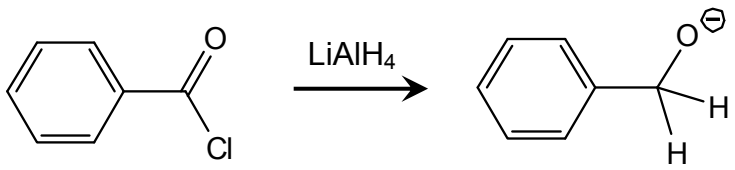
Scoring: 20. _____ / 12 22. _____ / 10

21. _____ / 15 23. _____ / 12

Total Score: _____ / 49

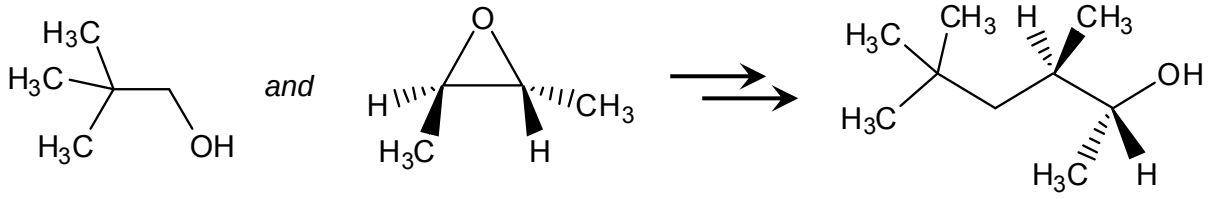
20. (12 pts) For the reaction shown below, draw a mechanism that explains how the product is generated from the starting material. In your answer, make sure that you:

- Draw each step of the mechanism separately;
- Use "electron pushing" to show where the electrons in each step go;
- Use only the molecules that you are given; do not invoke reactants or solvents that aren't in the problem.

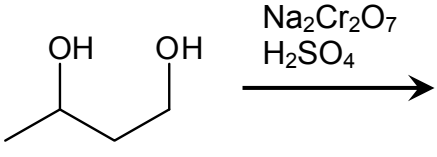


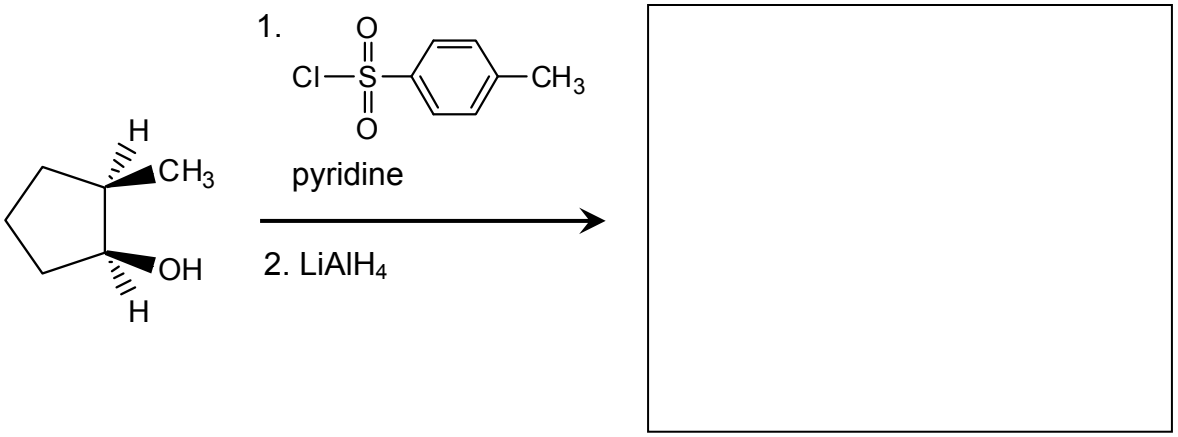
Mechanism:

21. (15 pts) **Propose a multistep synthesis** of the product shown below from the given starting materials, along with any reagents we have covered 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.



22. (10 pts) Draw the missing reactant or product in the empty boxes. For products, give the predominant, most favored product. Illustrate stereochemistry in your answer where appropriate. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



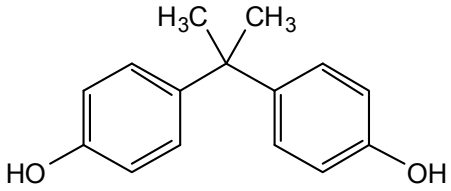


Bisphenol A (BPA), a component of polycarbonate plastics, has received a great deal of press over the last few weeks because of the possibility that the molecule might mimic estrogen and thus interfere with normal hormone function, especially in infants. In 2009, Minnesota became the first U.S. state to ban the sale of products intended for infants—including plastic cups and bottles—that contain BPA.

As a state inspector, you extract an additive from a polycarbonate sippy cup and subject it to ^{1}H and ^{13}C NMR analysis. The resulting NMR spectra are shown on page 9. In this problem, you will determine whether the additive is BPA, or the BPA substitute *meta*-bisphenol (MBP).

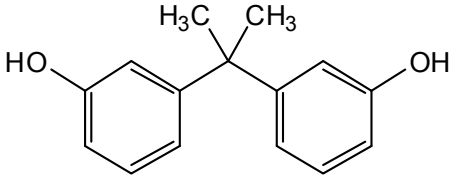
Answer the following questions on your multiple-choice bubble form.

(3 pts each) 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?



bisphenol A
(BPA)

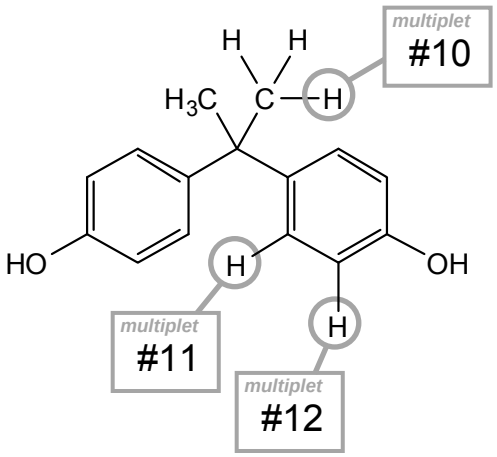
8. The ^{1}H NMR of bisphenol A should show
   a. 3 resonances;
   b. 4 resonances;
   c. 5 resonances;
   d. 6 resonances;
   e. none of the above.



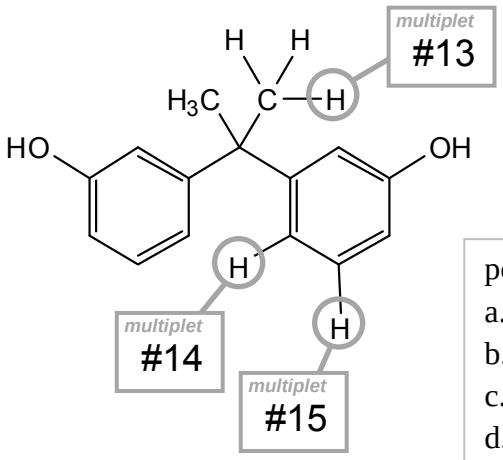
meta-bisphenol
(MBP)

9. The ^{1}H NMR of *meta*-bisphenol should show
   a. 3 resonances;
   b. 4 resonances;
   c. 5 resonances;
   d. 6 resonances;
   e. none of the above.

(2 pts each) Each proton circled in the structures below could have its resonance 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.)



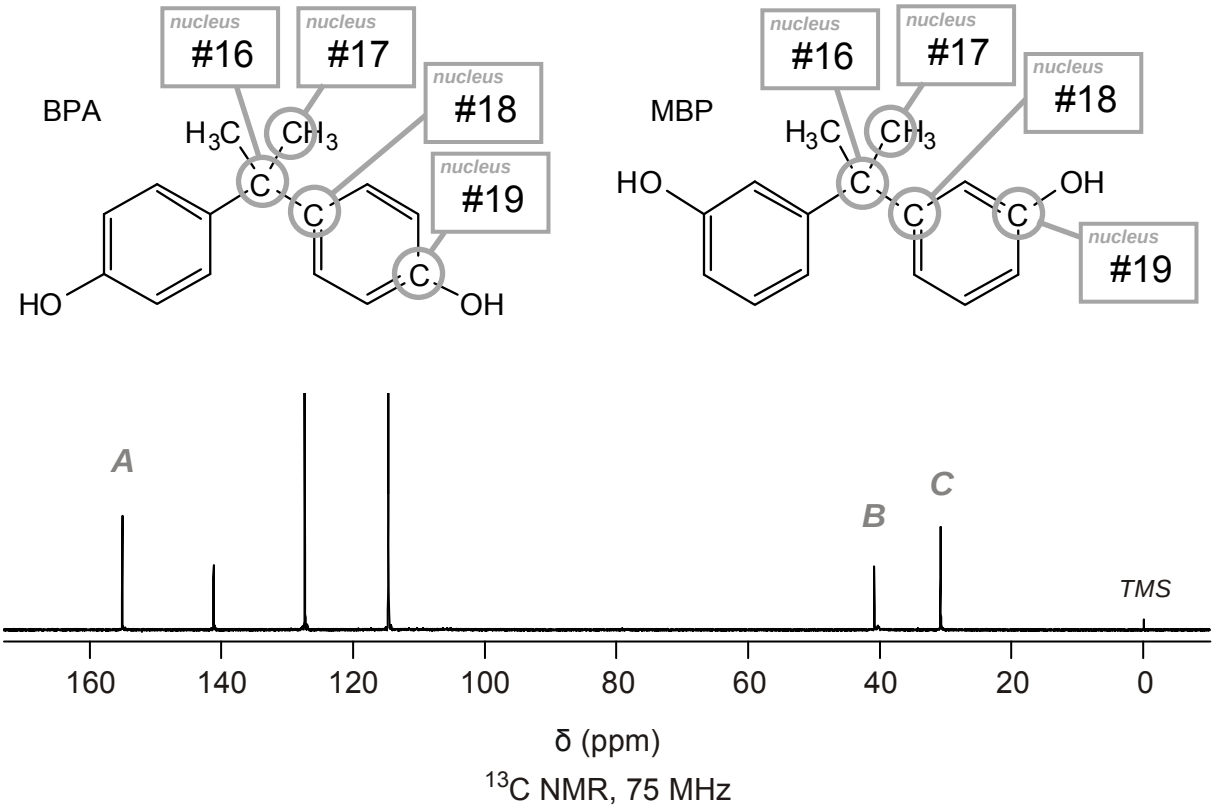
bisphenol A
(BPA)



meta-bisphenol
(MBP)

possible answers:
a. singlet
b. doublet
c. triplet
d. quartet
e. none of the above

(2 pts each) The ^{13}C NMR spectrum of the additive is shown below, and could be consistent with either BPA or MBP. Three peaks on the spectrum are labeled **A**, **B**, and **C**. Which carbons of BPA or MBP could these peaks correspond to? Four chemically similar carbons in the structures of BPA and MBP are circled below. If you would assign one of the ^{13}C NMR peaks to that carbon, fill in the appropriate bubble. If you feel that none of the labeled peaks correspond to the circled carbon, fill in bubble **D** for "none of the above".

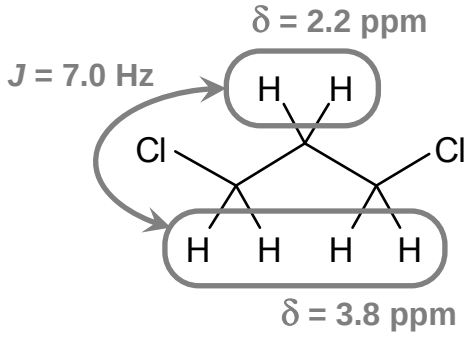


^{13}C NMR, 75 MHz

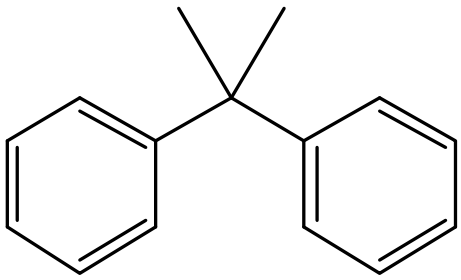
23. (12 pts) Given the ^{1}H spectrum below, is the additive BPA or MBP? On the unfinished skeleton in the box below, indicate your choice by drawing in the two –OH groups, <u>as well as all hydrogens</u>. Then,

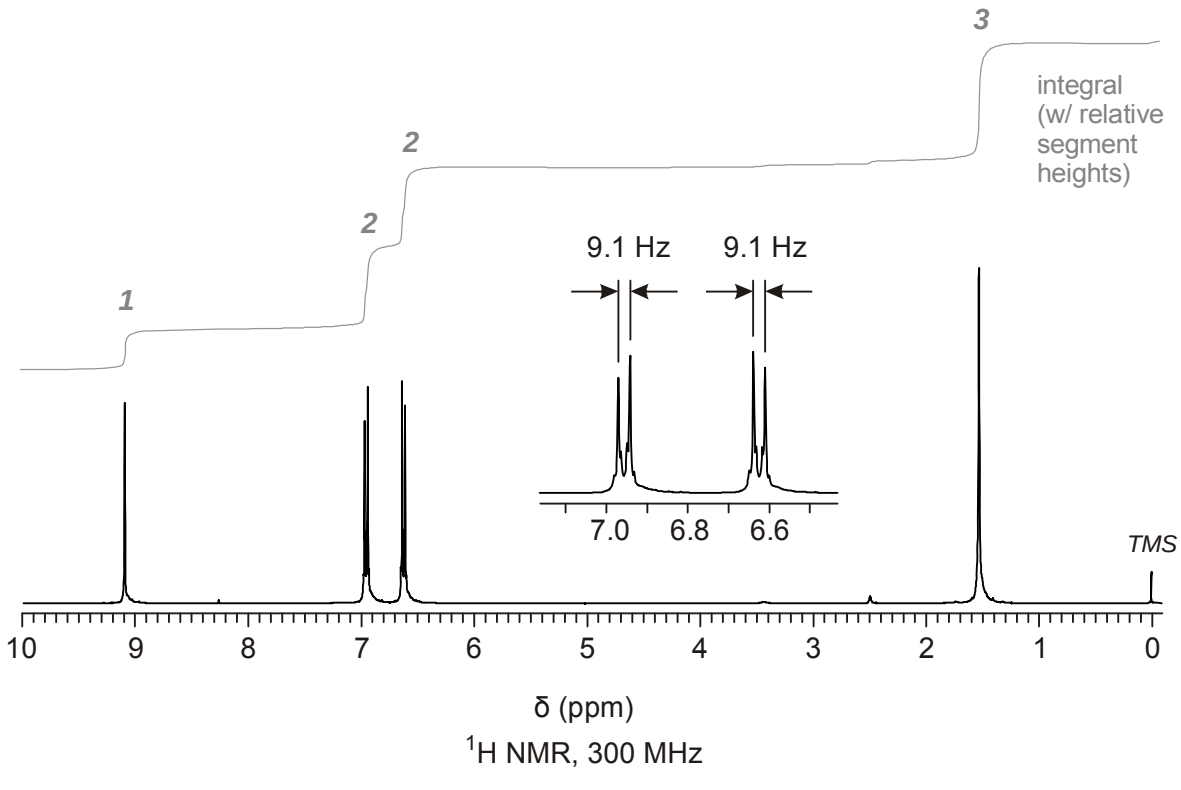
- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

Format for answer to problem 23:

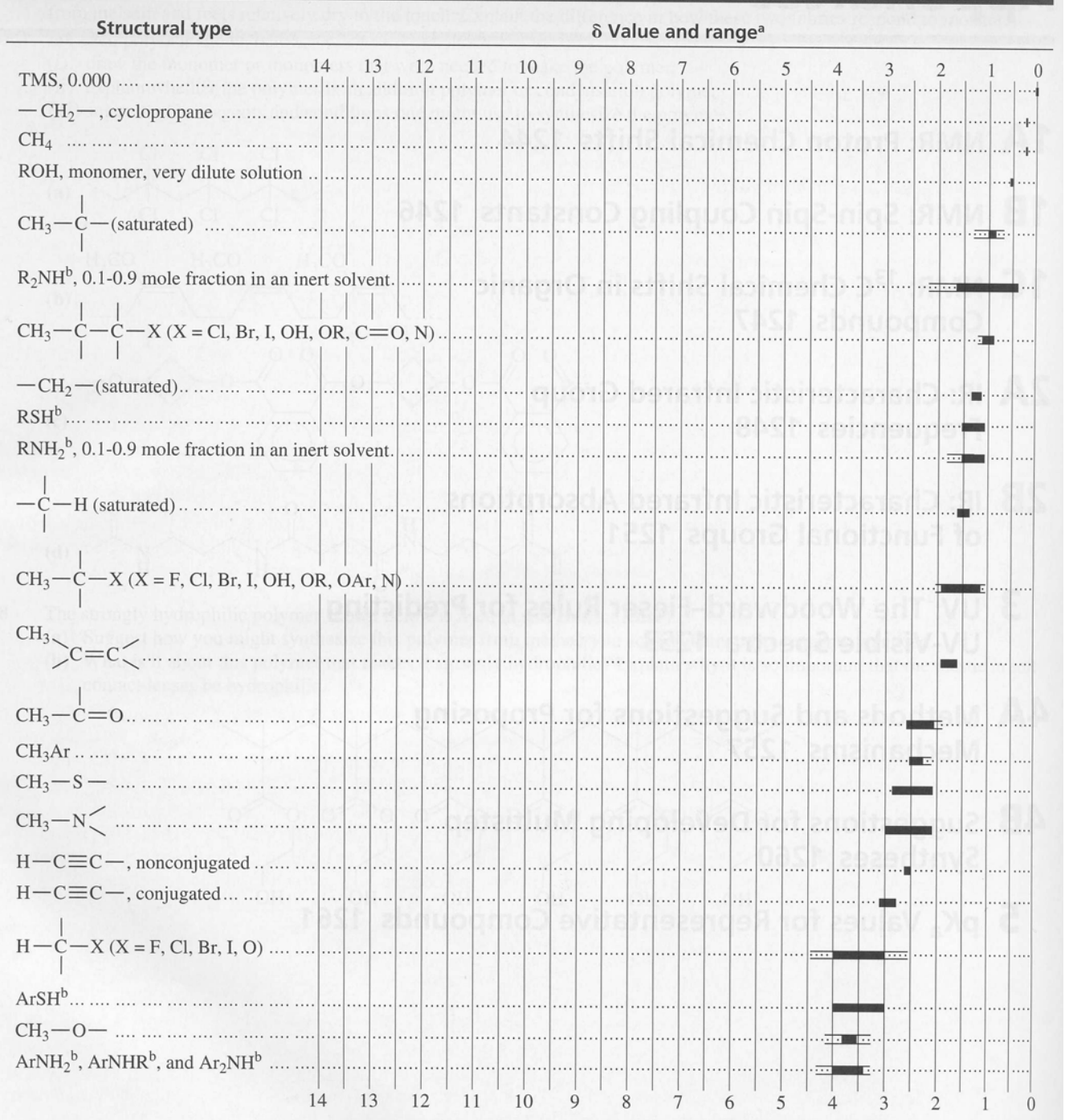


Your answer to problem 23:





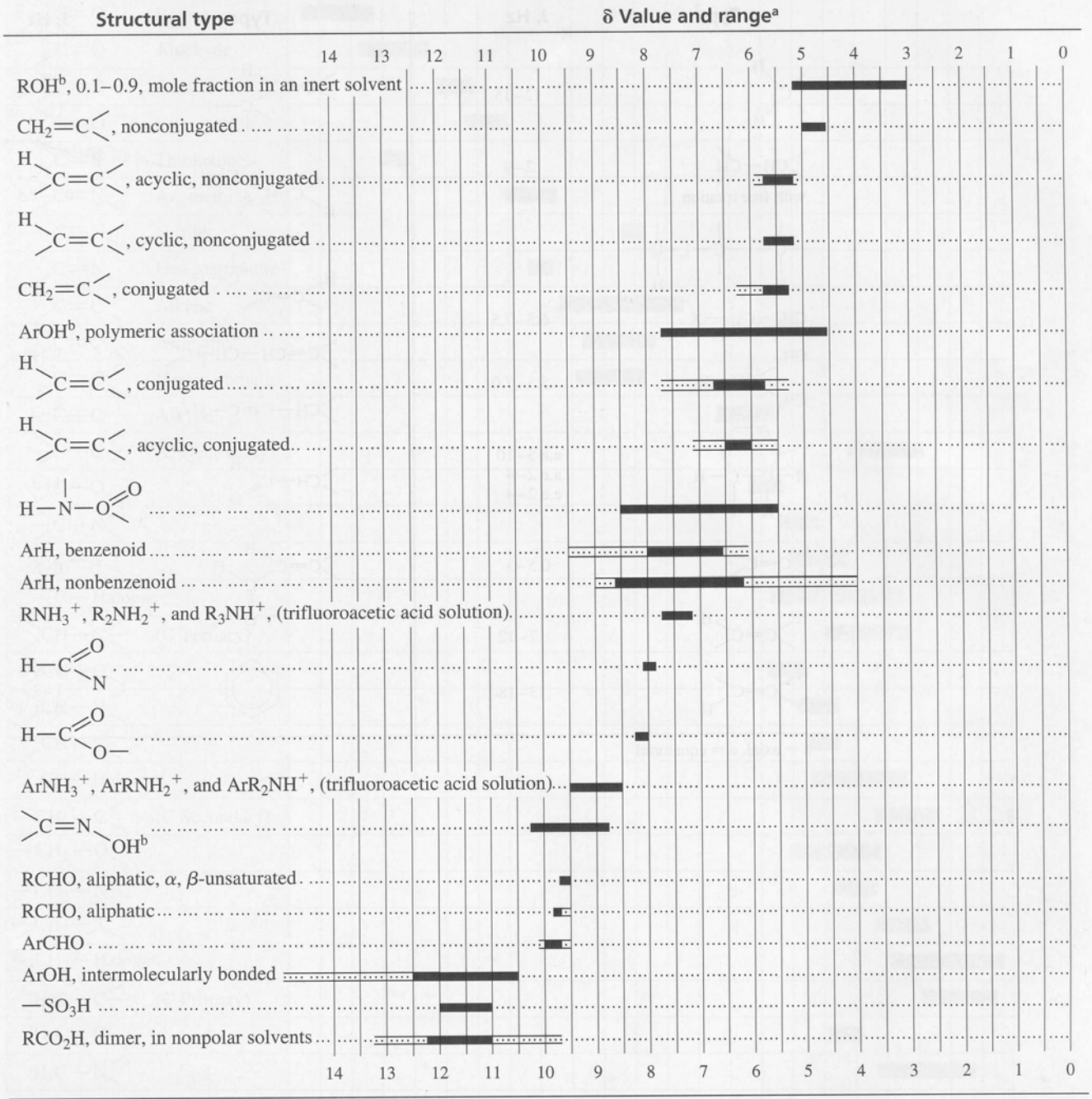
APPENDIX 1A NMR: Proton Chemical Shifts



[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



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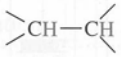
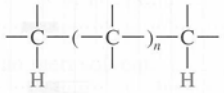
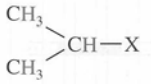
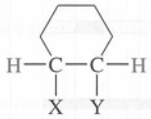
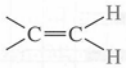
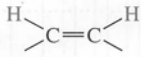
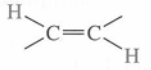
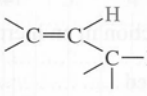
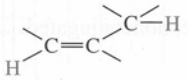
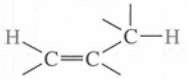
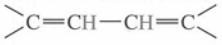
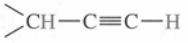
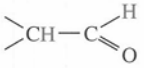
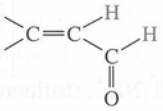
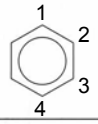
[b] Absorption positions of these groups are concentration-dependent and are shifted to lower δ values in more dilute solutions.

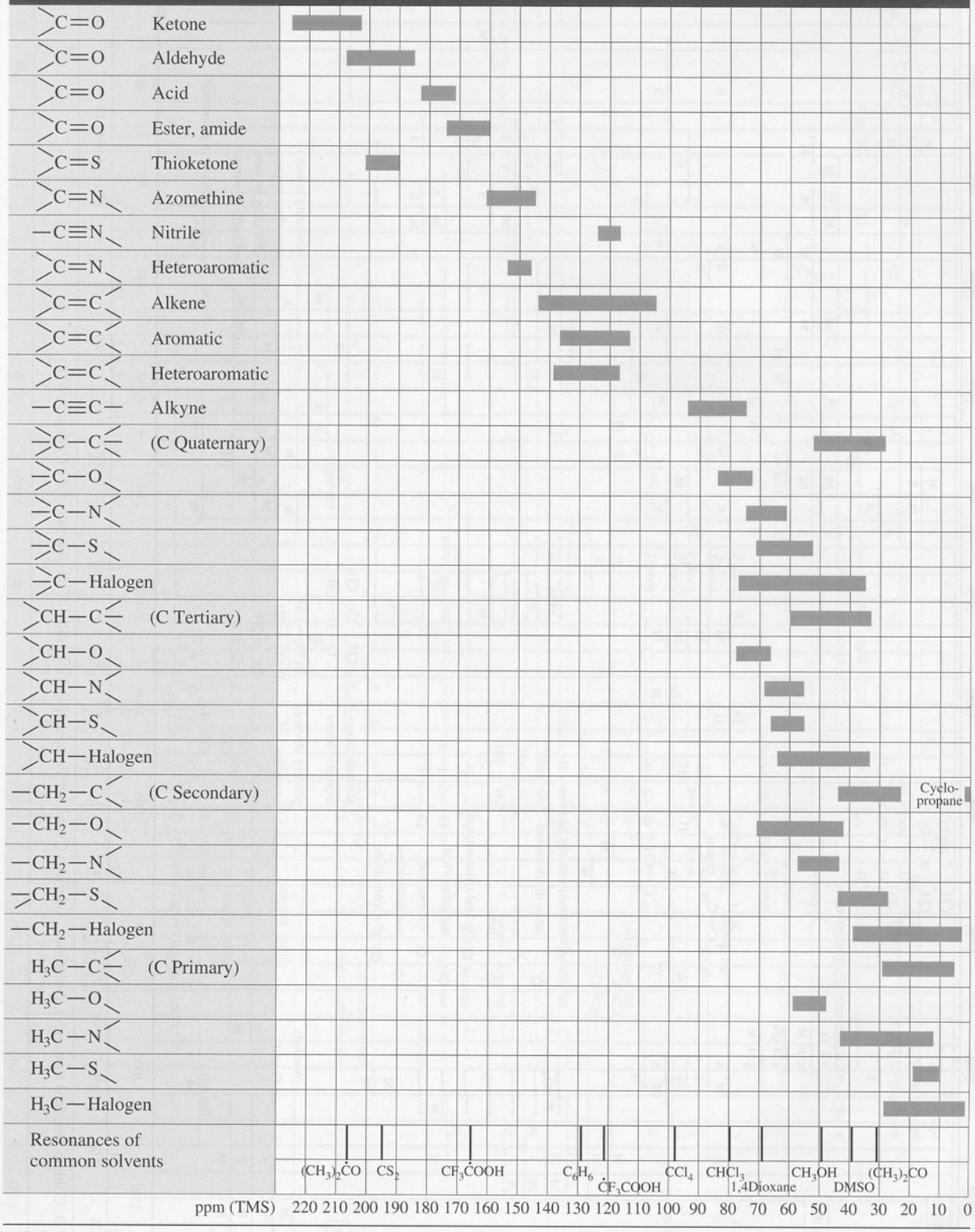
APPENDIX 1B NMR: Spin-Spin Coupling Constants

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.

Exam 4 Chart of Reaction Conditions

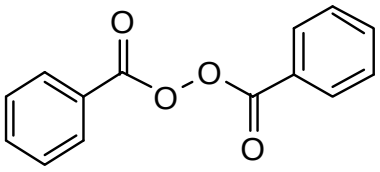
Reactions to consider from Ch. 6-7 (Exam 2): Acid-Base, S_N2, S_N1, E2, E1

Cl_2 *or* Br_2, *h*ν

HBr

Br_2

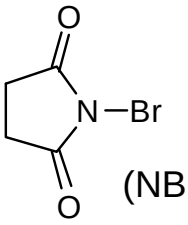
HBr



(benzoyl peroxide)

H_2SO_4
H_2O

1. $Hg(OAc)_2$
   H_2O *or* ROH
2. $NaBH_4$

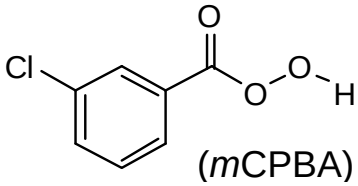


(NBS)

*h*ν *or* AIBN

Br_2
H_2O *or* ROH

1. BH_3•THF
2. H_2O_2, OH^-



(*m*CPBA)

*m*CPBA
H_2O

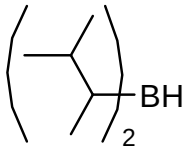
$Pt/H_2(g)$

$NaNH_2$

1. O_3
2. $(CH_3)_2S$

Na
NH_3

1.



("Sia_2BH")

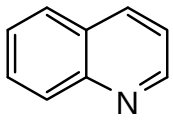
2. H_2O_2, NaOH

$KMnO_4$
(cold, dilute)
H_2O, OH^-

$KMnO_4$
H_2O, pH 7

1. O_3
2. H_2O

Pd, $BaSO_4$
$H_2(g)$



(quinoline)

$HgSO_4$
H_2SO_4

1. $LiAlH_4$
2. H_2O

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

Mg
Et_2O

Li
hexane

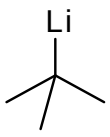
PBr_3

1. $NaBH_4$
2. H_2O

1. $(COCl)_2$
   DMSO
   -60 °C
2. Et_3N
   (Swern oxidation)

$Na_2Cr_2O_7$
H_2SO_4

TsCl
pyridine



(*t*BuLi)

1. Ag_2O
   NH_3
2. H_3O^+

$SOCl_2$
pyridine

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.