NAME _____

ID # _____

HONORS ELEMENTARY ORGANIC CHEMISTRY I (2331H)

9:05 – 9:55 am, December 9, 2013

Exam 4

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 Friday, and you will need to pick up your exam in private from Chemistry department staff in 115 Smith beginning Thursday, December 12th. 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 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.

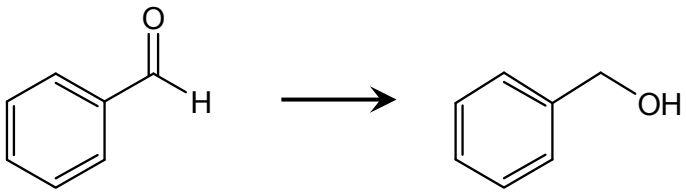
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME _____

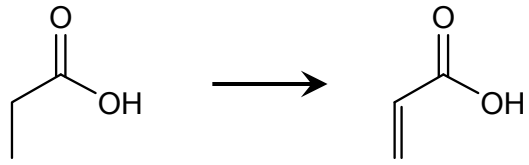
Scoring:	1. _____ / 9	4. _____ / 16
	2. _____ / 10	5. _____ / 16
	3. _____ / 16	6. _____ / 33

Total Score: _____ / 100

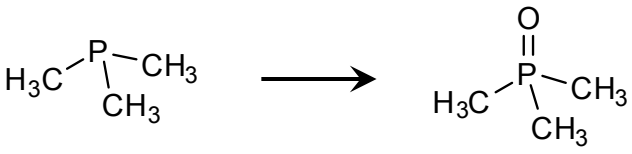
1. (9 pts) Identify each of the transformations below as a reduction, an oxidation, or neither. **Circle only one answer for each transformation**.



REDUCTION
or
OXIDATION
or
NEITHER

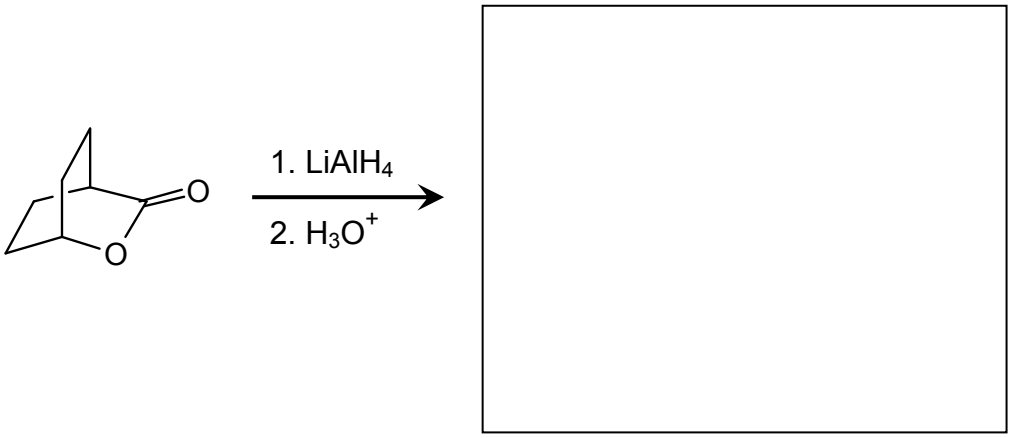


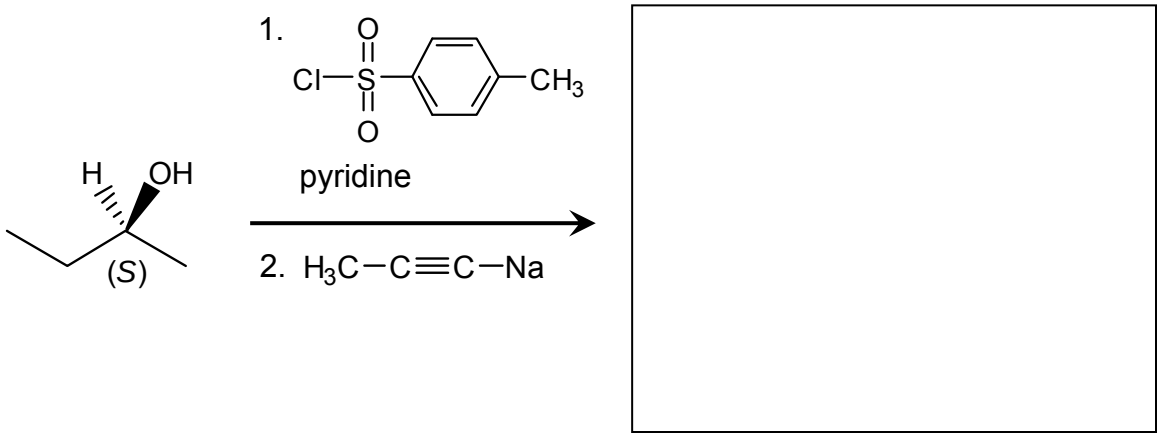
REDUCTION
or
OXIDATION
or
NEITHER



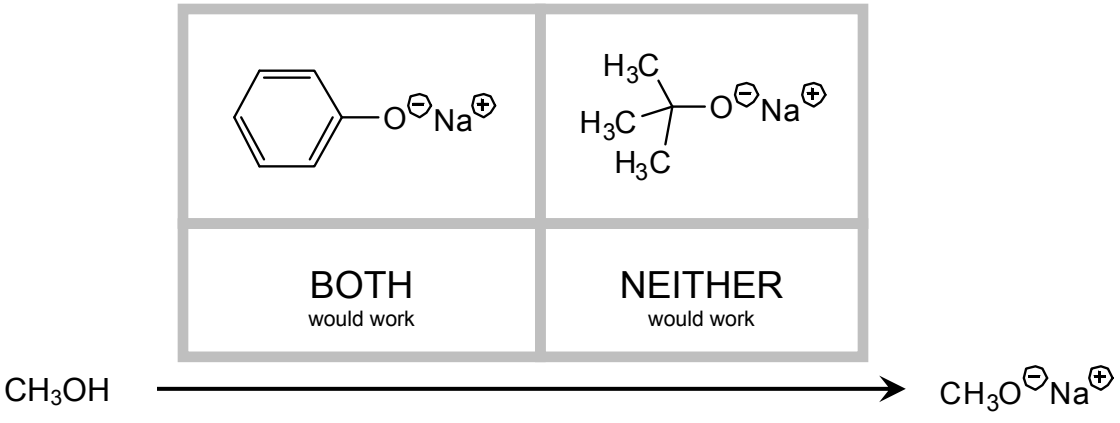
REDUCTION
or
OXIDATION
or
NEITHER

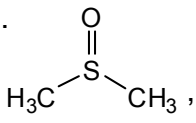
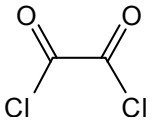
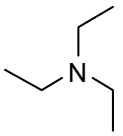
2. (10 pts) For each of the reactions below, **fill in the empty box corresponding to products**. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".

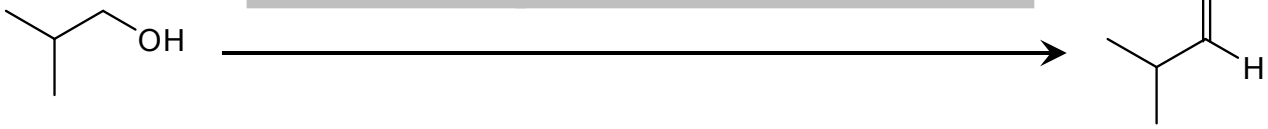




3. (16 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

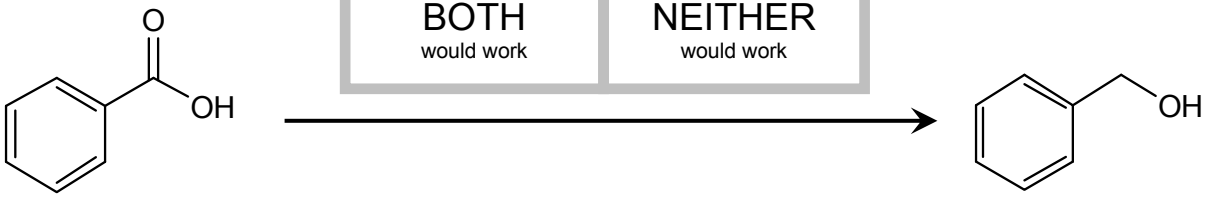


$Na_2Cr_2O_7$ H_2SO_4	1.  ,  -60 °C 2.  *(Swern oxidation)*
BOTH would work	NEITHER would work

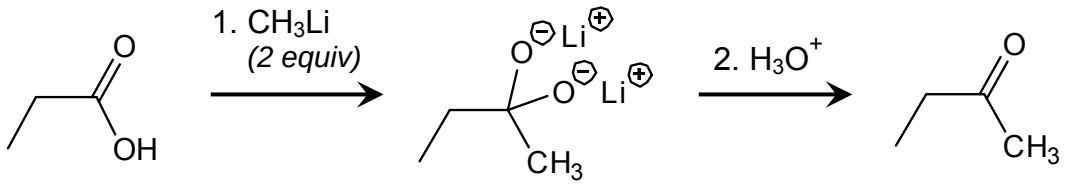


1. CH_3MgBr *(excess)* 2. H_3O^+	1. CH_3Li *(excess)* 2. H_3O^+
BOTH would work	NEITHER would work

1. $LiAlH_4$ 2. H_3O^+	1. $NaBH_4$ 2. H_3O^+
BOTH would work	NEITHER would work

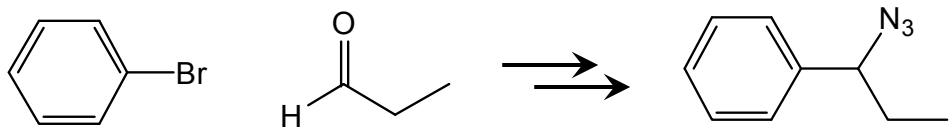


4. (16 pts) Draw a mechanism (using "electron pushing") for both of the reaction steps shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)

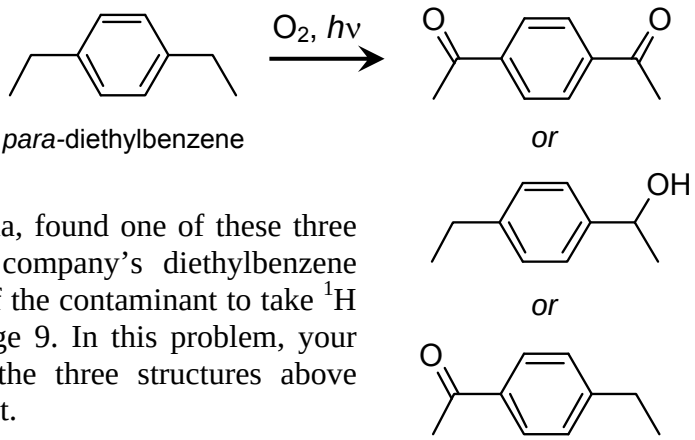


Mechanism:

5. (16 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.

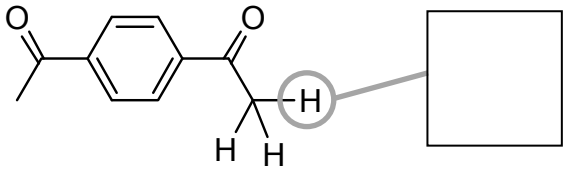
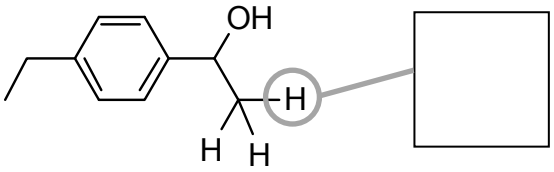
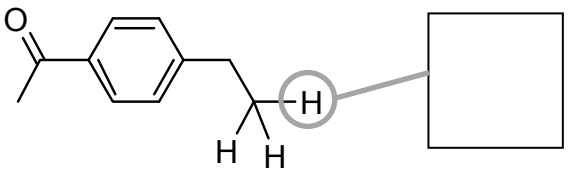


6. (33 pts) *para*-Diethylbenzene, an industrial solvent, can be oxidized by oxygen and light to any of the three products shown on the right. Cameron, a chemical engineer at Chevron Phillips' chemical plant in St. James, Louisiana, found one of these three products as a contaminant in the company's diethylbenzene product stream. He isolated enough of the contaminant to take ^{1}H and ^{13}C NMR spectra, shown on page 9. In this problem, your task will be to identify which of the three structures above corresponds to Cameron's contaminant.



(a) How many resonances would you expect to see in the ^{1}H NMR of each of the potential oxidation products? In other words, how many inequivalent sets of protons are there in each structure? Write your answers in the boxes in the *left-hand* column below.

(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, and write your answers in the boxes in the *right-hand* column below.

# ^{1}H NMR resonances expected		*type of multiplet for this proton*
		
		
		

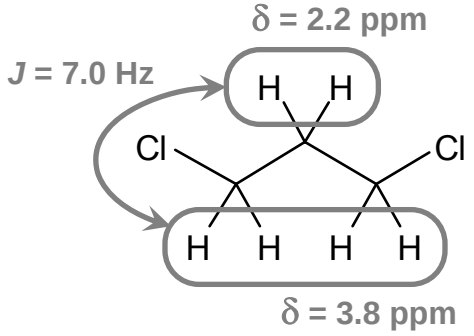
abbreviations for multiplets

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

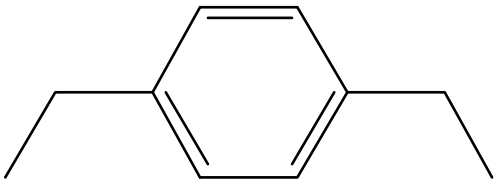
(c) ^{1}H and ^{13}C spectra for the isolated molecule are shown on the next page. Which of the three products is the contaminant? On the unfinished skeleton in the box below, indicate your choice by drawing in any appropriate functional groups, as well as all hydrogens. Then,

- 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*).

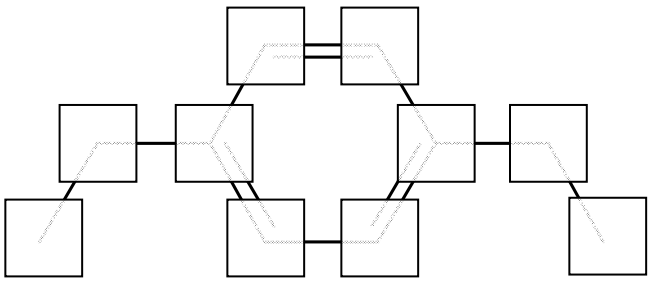
Format for answer to (c):

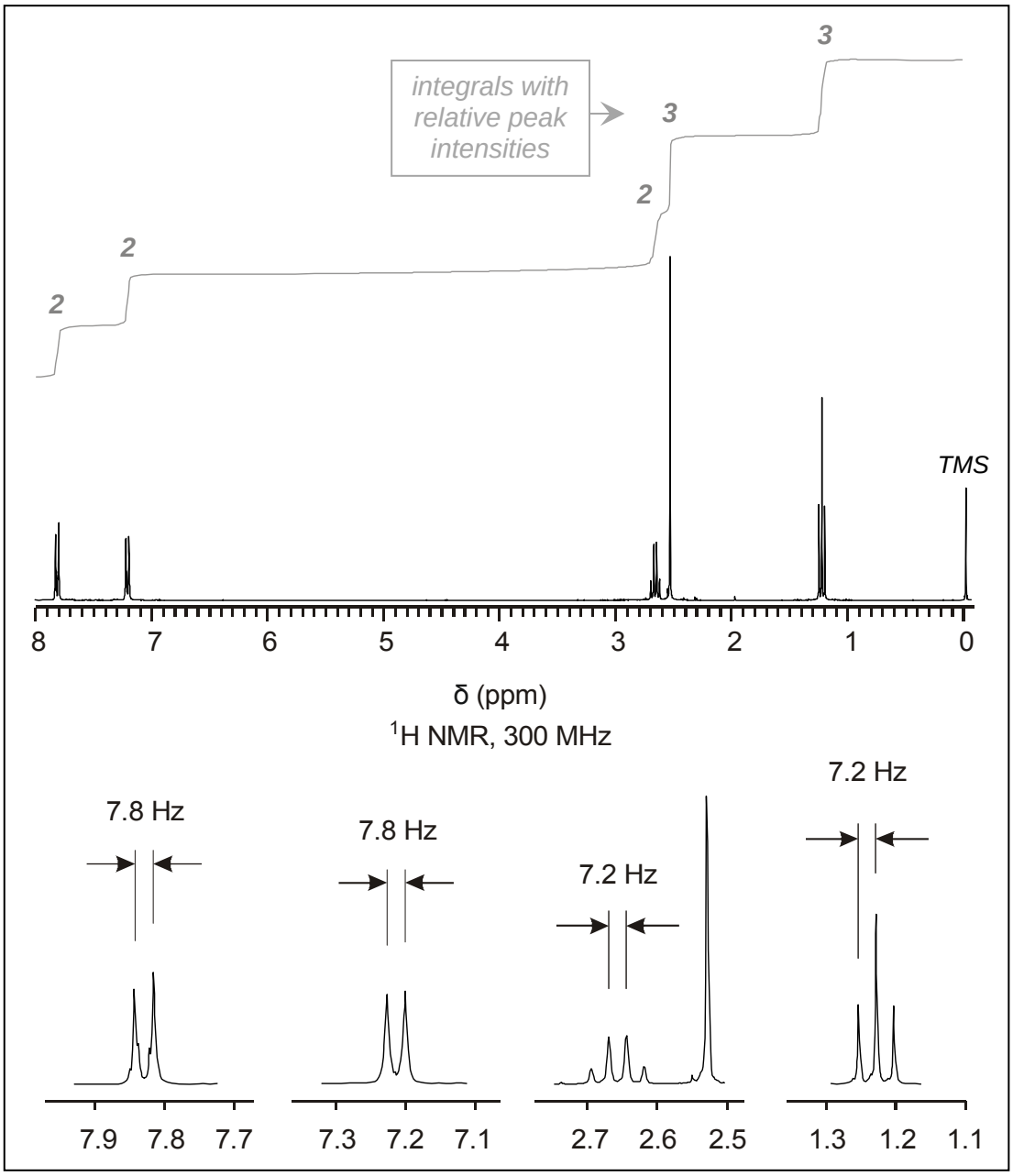


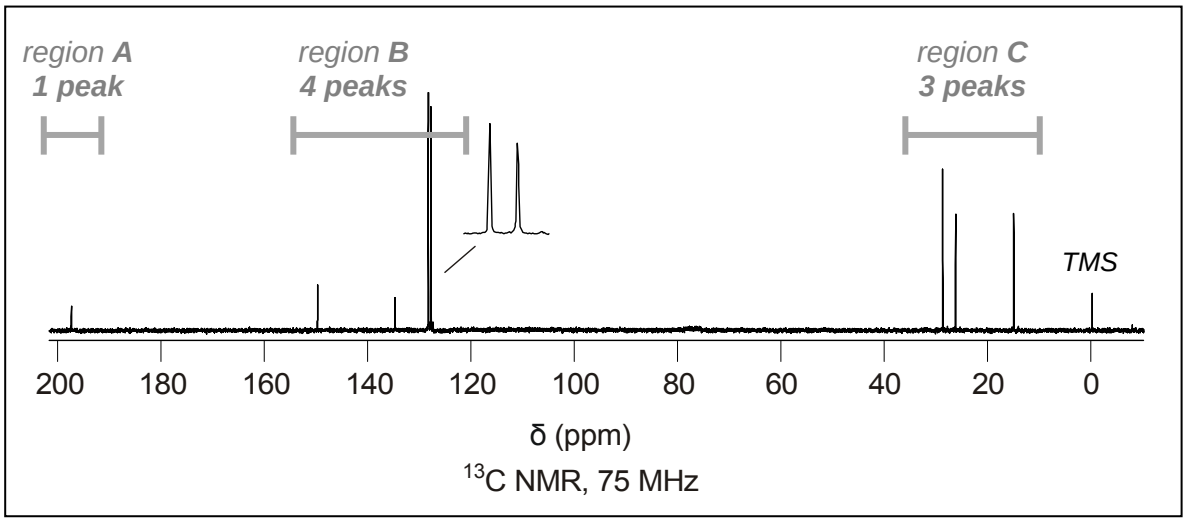
Your answer to (c):



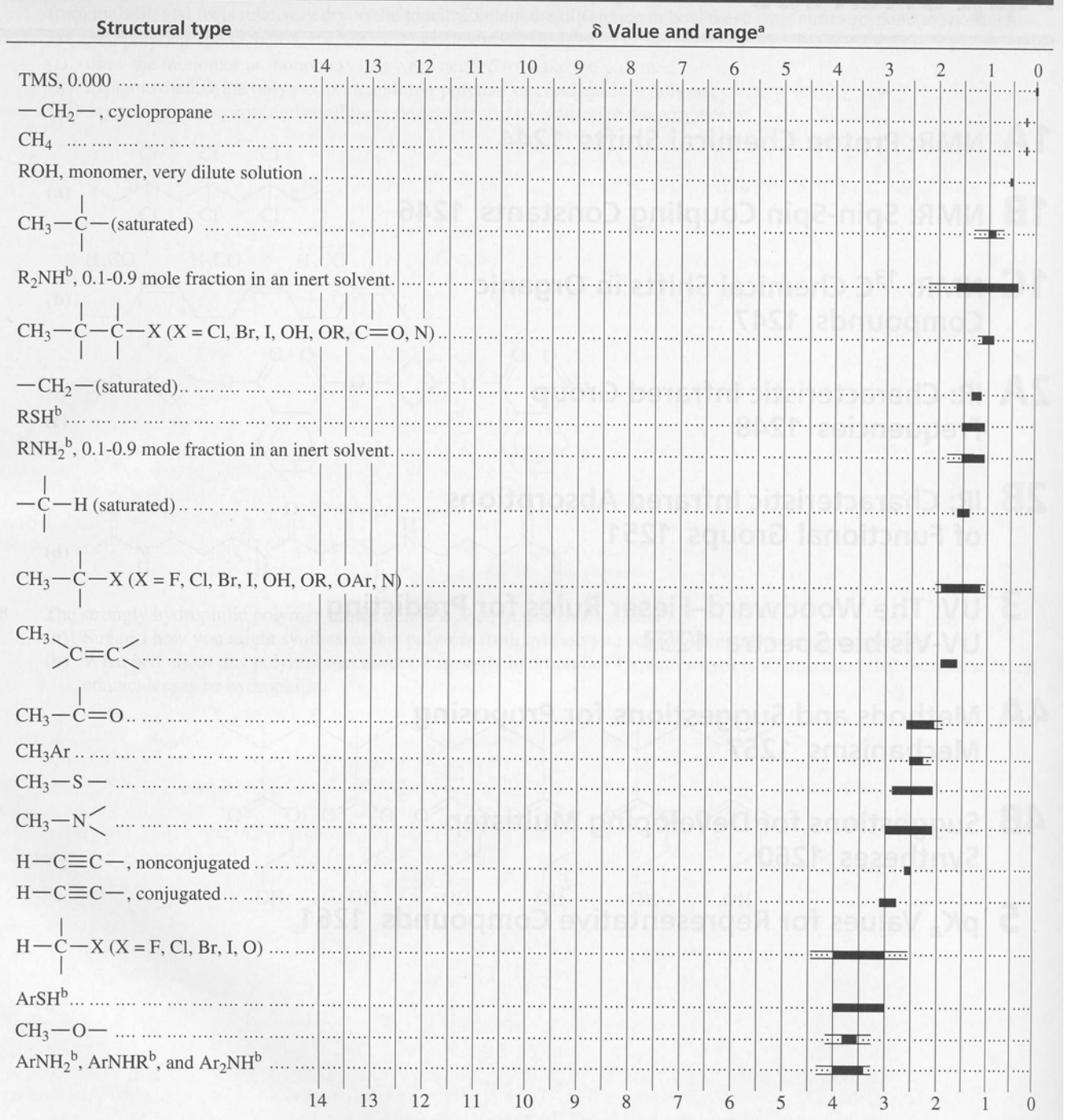
(d) The ^{13}C NMR spectrum of the contaminant showed 8 peaks, which appear in three distinct regions of the spectrum. I've labeled these regions **A**, **B** and **C** on the ^{13}C spectrum on the next page. As you did above, re-draw your proposed contaminant structure below (though this time you can 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.**




integrals with relative peak intensities
3
3
2
2
2
TMS
8
7
6
5
4
3
2
1
0
δ (ppm)
^{1}H NMR, 300 MHz
7.8 Hz
7.8 Hz
7.2 Hz
7.2 Hz
7.9
7.8
7.7
7.3
7.2
7.1
2.7
2.6
2.5
1.3
1.2
1.1


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

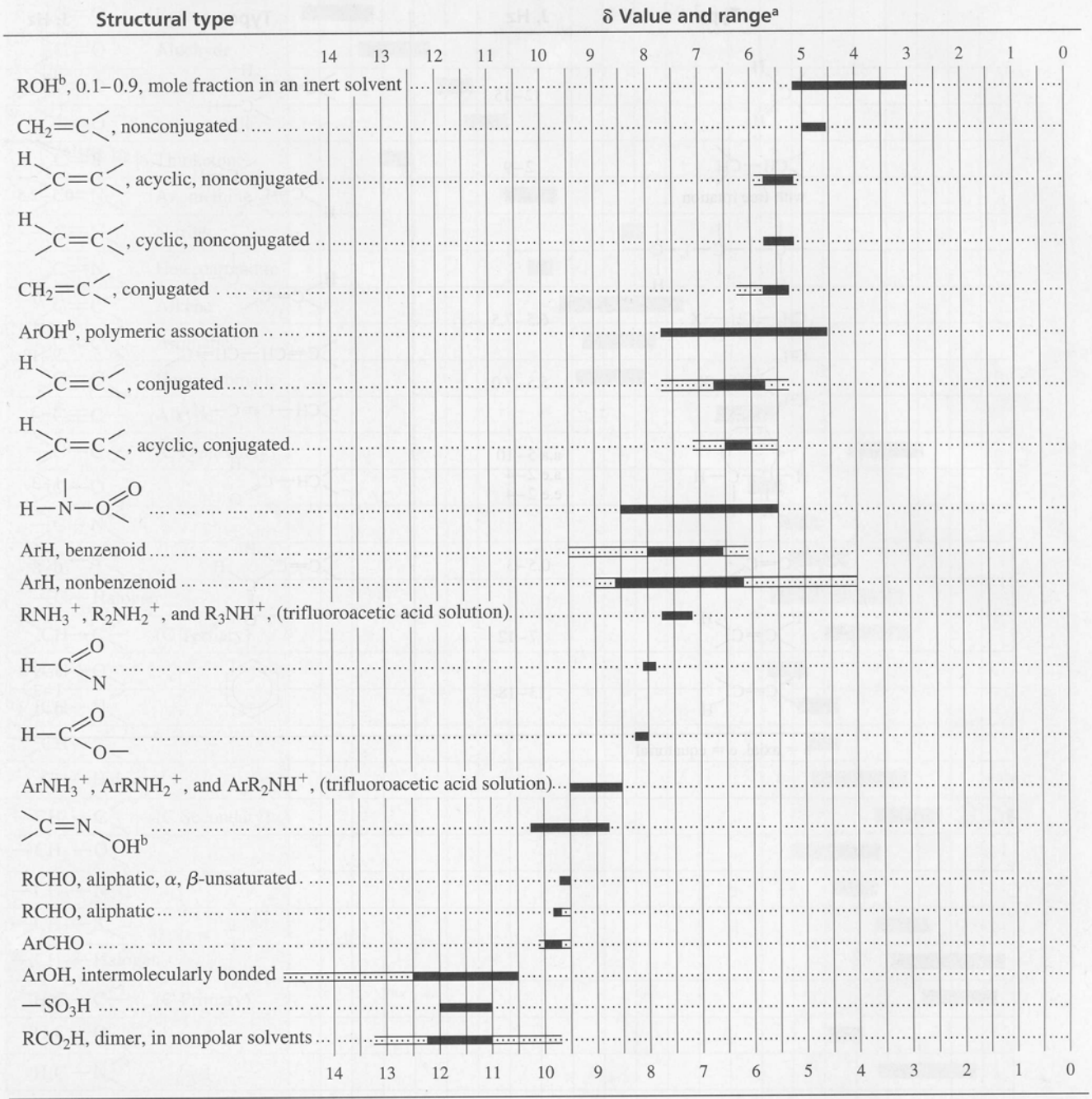
APPENDIX 1A NMR: Proton Chemical Shifts



[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.

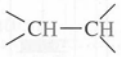
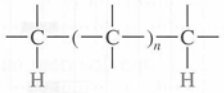
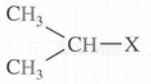
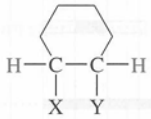
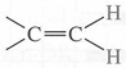
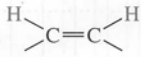
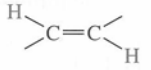
APPENDIX 1A NMR: Proton Chemical Shifts

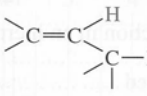
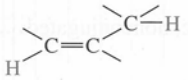
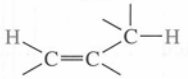
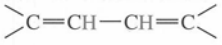
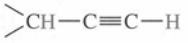
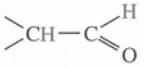
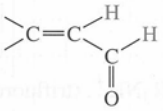
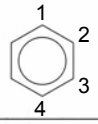


[a] Normally, absorptions for the functional groups indicated will be found within the range shown in black. Occasionally, a functional group will absorb outside this range. Approximate limits are indicated by extended outlines.

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

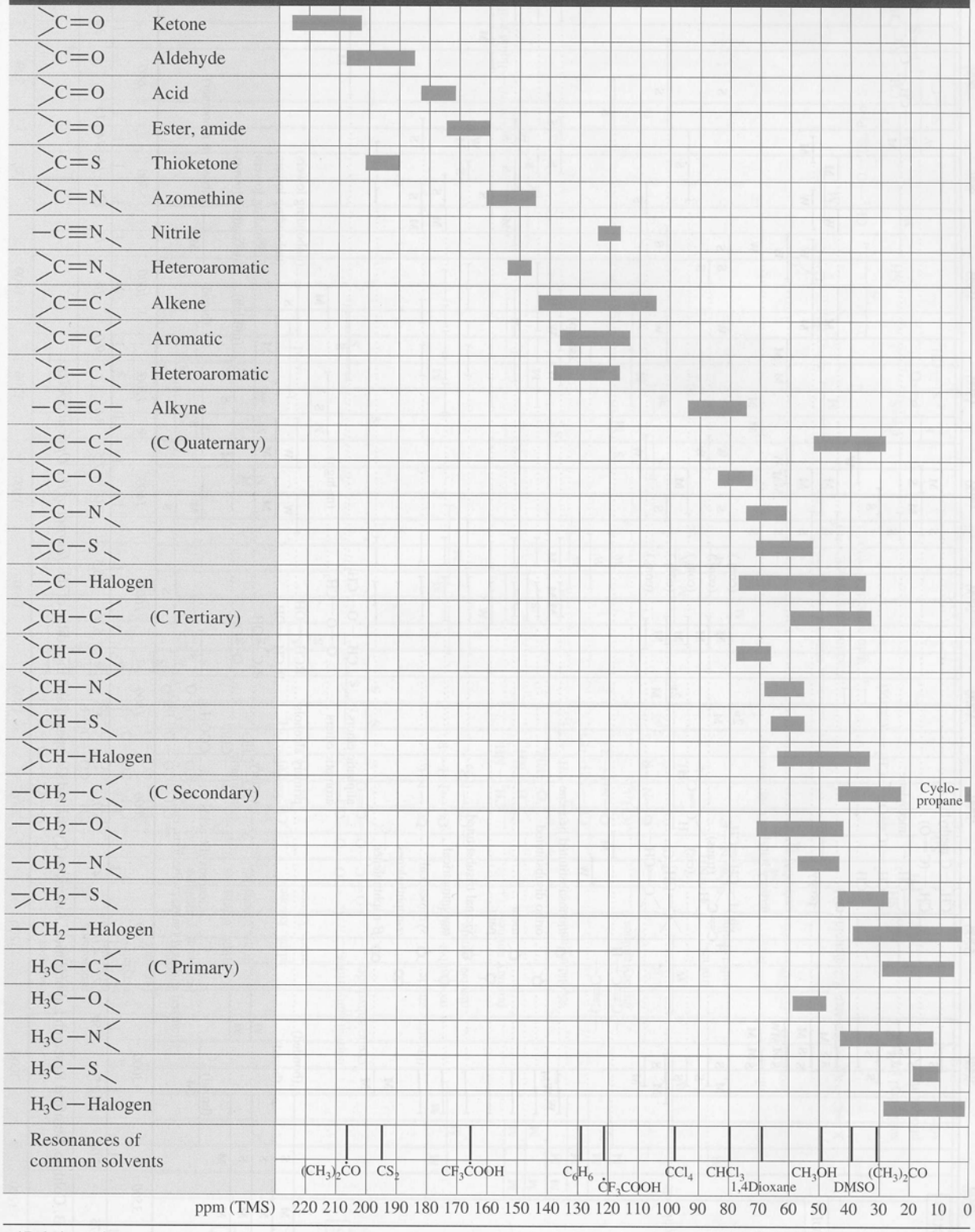
APPENDIX 1B NMR: Spin-Spin Coupling Constants

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.

Exam 4 Chart of Reaction Conditions

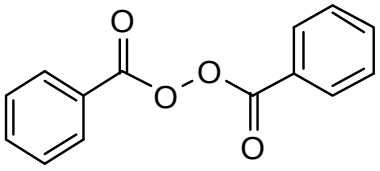
Reactions to consider from Ch. 6-7 (Exam 2): Acid-Base, S_N2, S_N1, E2, E1

Cl_2 *or* Br_2, $h\nu$

HBr

Br_2

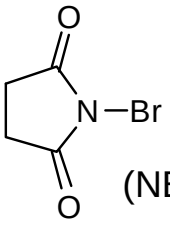
HBr



(benzoyl peroxide)

H_2SO_4
H_2O

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

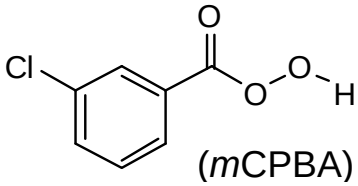


(NBS)

$h\nu$ *or* AIBN

Br_2
H_2O *or* ROH

1. BH_3•THF
2. H_2O_2, OH^-



(*m*CPBA)

*m*CPBA
H_2O

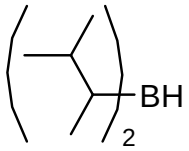
$Pt/H_2(g)$

$NaNH_2$

1. O_3
2. $(CH_3)_2S$

Na
NH_3

1.



(“Sia_2BH”)

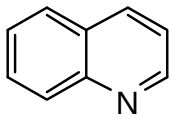
2. H_2O_2, NaOH

KMnO$_4$
(cold, dilute)
H_2O, OH^-

KMnO$_4$
H_2O, pH 7

O_3
H_2O

Pd, $BaSO_4$
$H_2(g)$



(quinoline)

$HgSO_4$
H_2SO_4

1. $LiAlH_4$
2. H_2O

KMnO$_4$
KOH, Δ

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

$SOCl_2$
pyridine

(*t*BuLi)

1. Ag_2O
   NH_3
2. H_3O^+

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.