NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 10:20 am, July 31, 2012

Exam 4

There will be two ways that you can pick up your graded Exam 4:

- You can pick up your graded exam from Andy at office hours that he will hold on Monday, August 6th (9:30-10:30 am) at Coffman Union Starbucks.
- Alternately, you will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 6th at noon. Exams that are not picked up within two weeks will be disposed of.

A periodic table, a chart of reaction conditions, and a table of typical NMR chemical shifts 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.

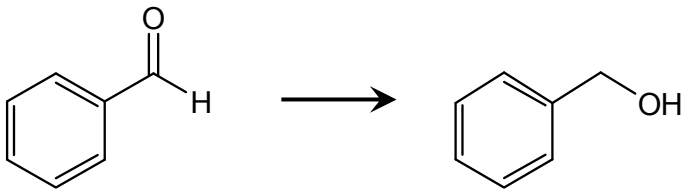
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME _____

Scoring:	1. _____ / 9	4. _____ / 16
	2. _____ / 15	5. _____ / 12
	3. _____ / 20	6. _____ / 28

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**.



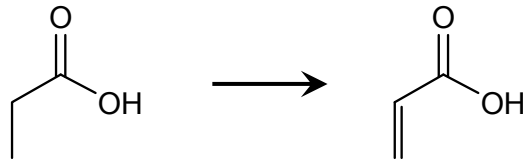
REDUCTION

or

OXIDATION

or

NEITHER



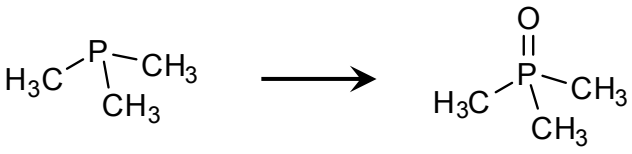
REDUCTION

or

OXIDATION

or

NEITHER



REDUCTION

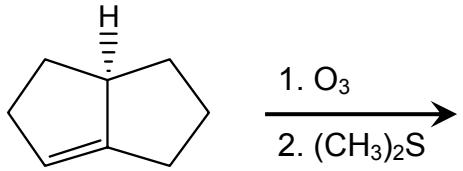
or

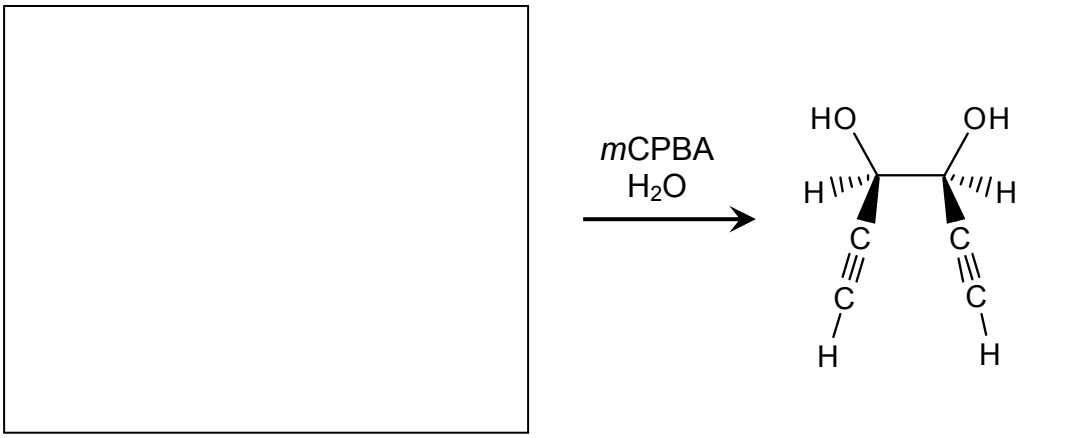
OXIDATION

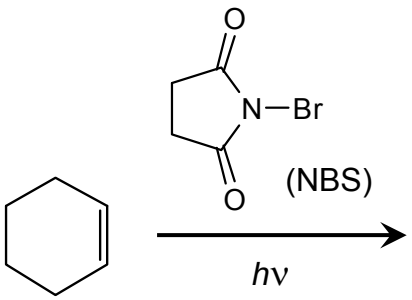
or

NEITHER

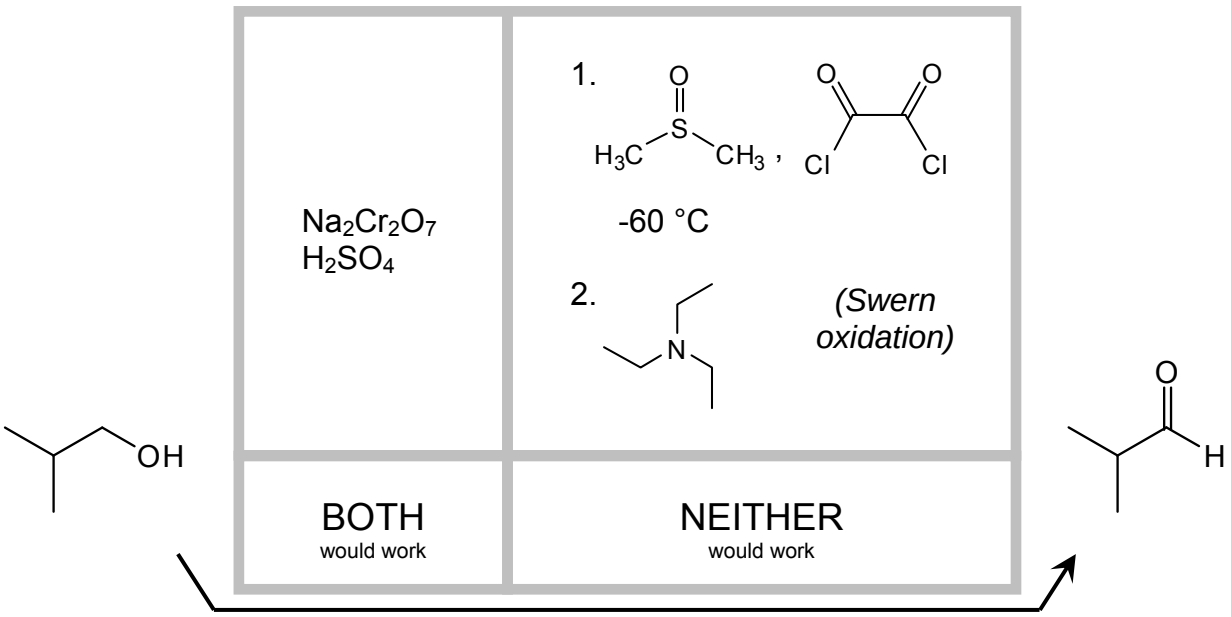
2. (15 pts) For each of the reactions below, **fill in the empty box corresponding to reactants or products**. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".

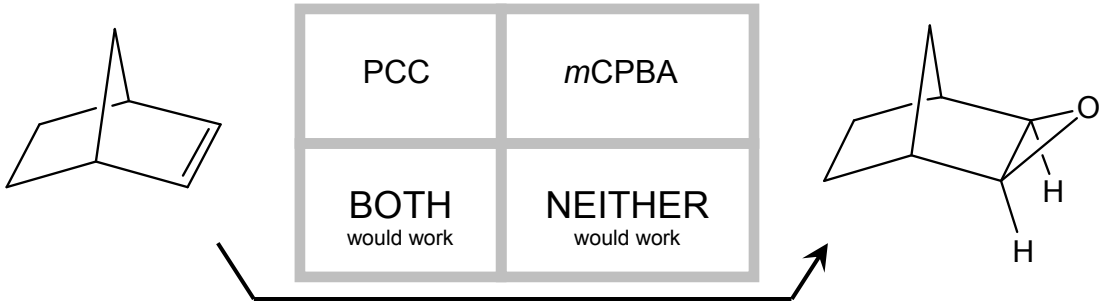


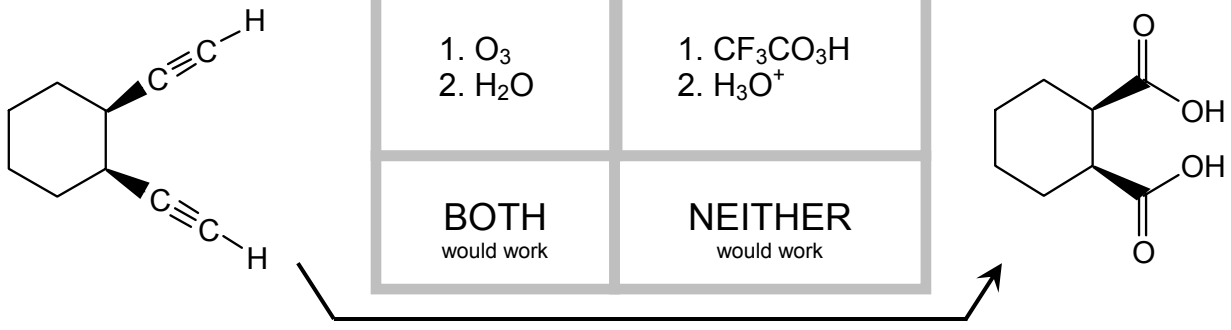


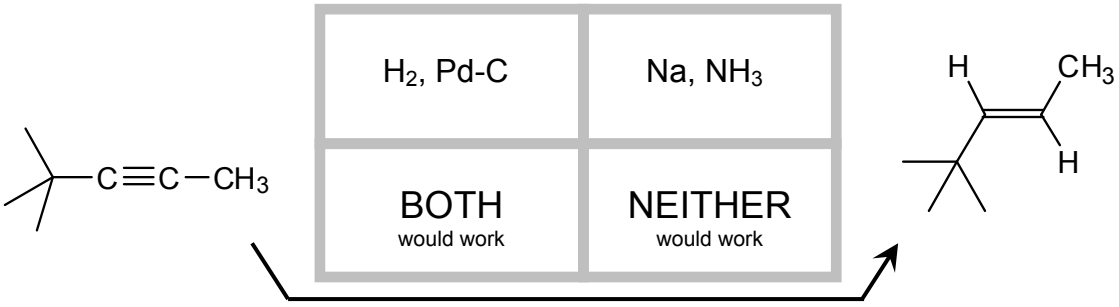


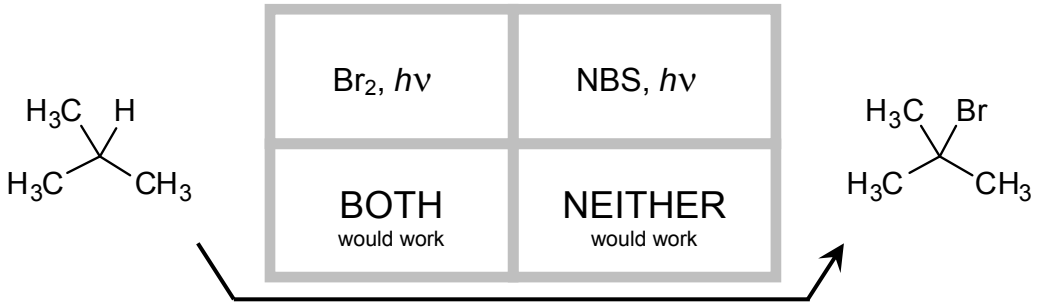
3. (20 pts) Each of the reactions on the next two pages is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**


1.
2.
$Na_2Cr_2O_7$
H_2SO_4
-60 °C
(Swern oxidation)
OH
O
H
BOTH
would work
NEITHER
would work

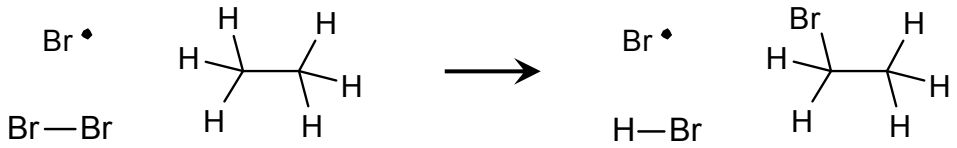

PCC
mCPBA
O
H
H
BOTH
would work
NEITHER
would work


H
C≡C
C≡C
H
1. O_3
2. H_2O
1. CF_3CO_3H
2. H_3O^+
O
OH
OH
O
BOTH
would work
NEITHER
would work

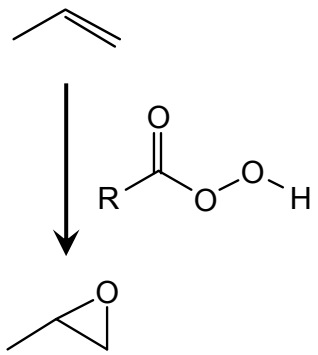

C≡C−CH3
H_2, Pd-C
Na, NH_3
H
CH3
H
BOTH
would work
NEITHER
would work



4. (16 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 "R•" as a generic radical.)

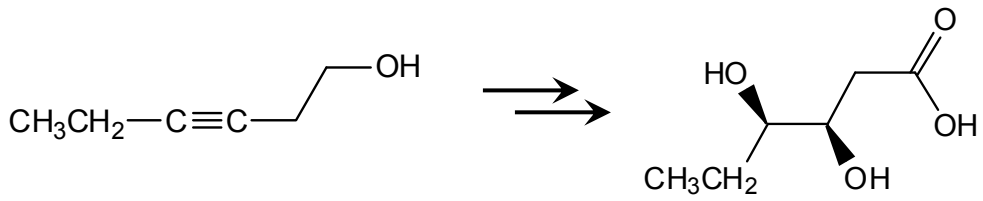


Mechanism (two steps!):

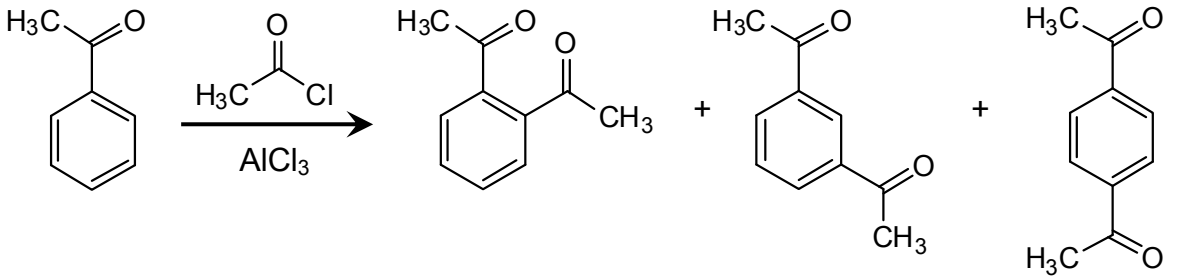


Mechanism (one step!):

5. (12 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.

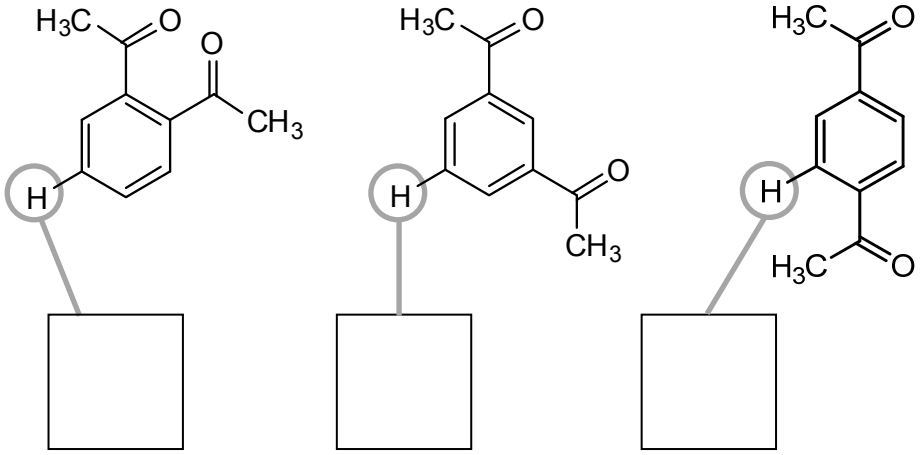


6. (28 pts) When acetylbenzene is combined with acetyl chloride and a Lewis acid catalyst—in a reaction that you will learn about in CHEM 2302—three different diacetylbenzenes are generated as products. In this problem, you will imagine that you are a chemist that has performed this reaction, and that you have isolated one of the three products. You have performed ^{1}H and ^{13}C NMR spectra on this product, shown on page 9. In the questions that follow, you will decide which of the three products you have isolated.



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

 # ^{1}H NMR resonances expected

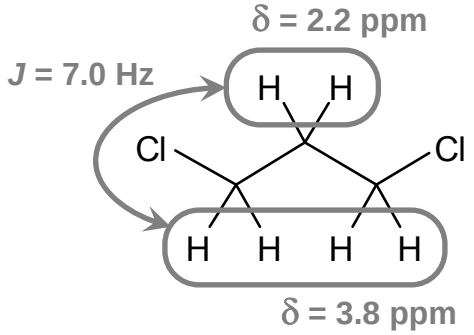


type of multiplet for this proton

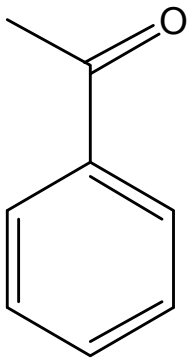
(b) Each proton highlighted in the structures above could be split by neighboring protons. What kind of multiplet should each proton produce in a ^{1}H NMR spectrum? (Assume that there is no long-range coupling for the circled proton. But there might be for the others!) Use the abbreviations on the chart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

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

Format for answer to (c):



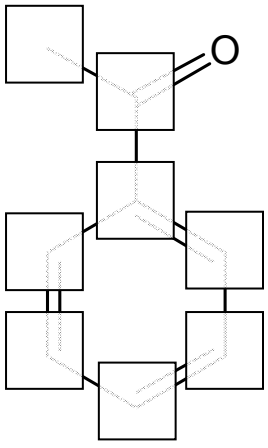
Your answer to (c):

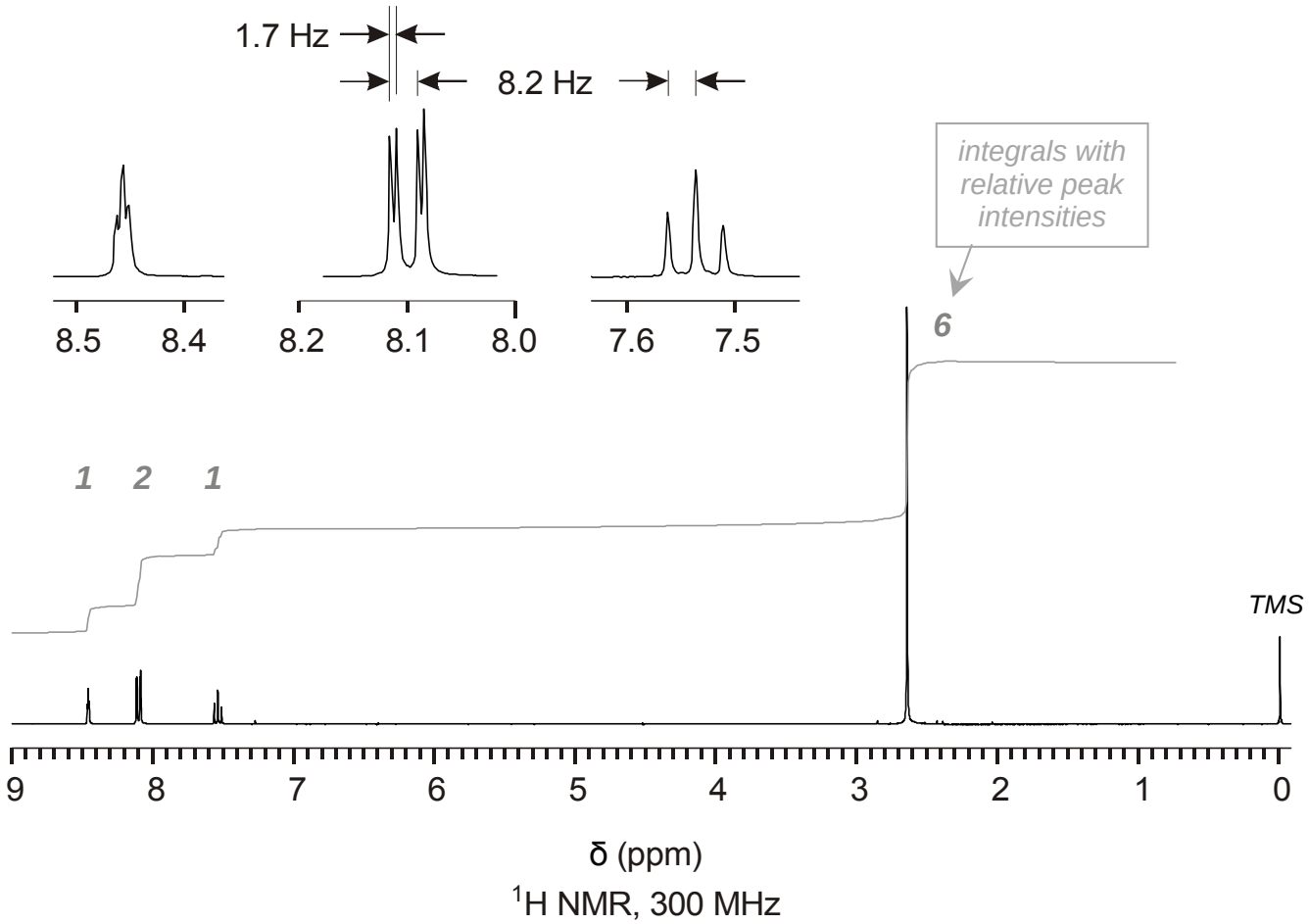


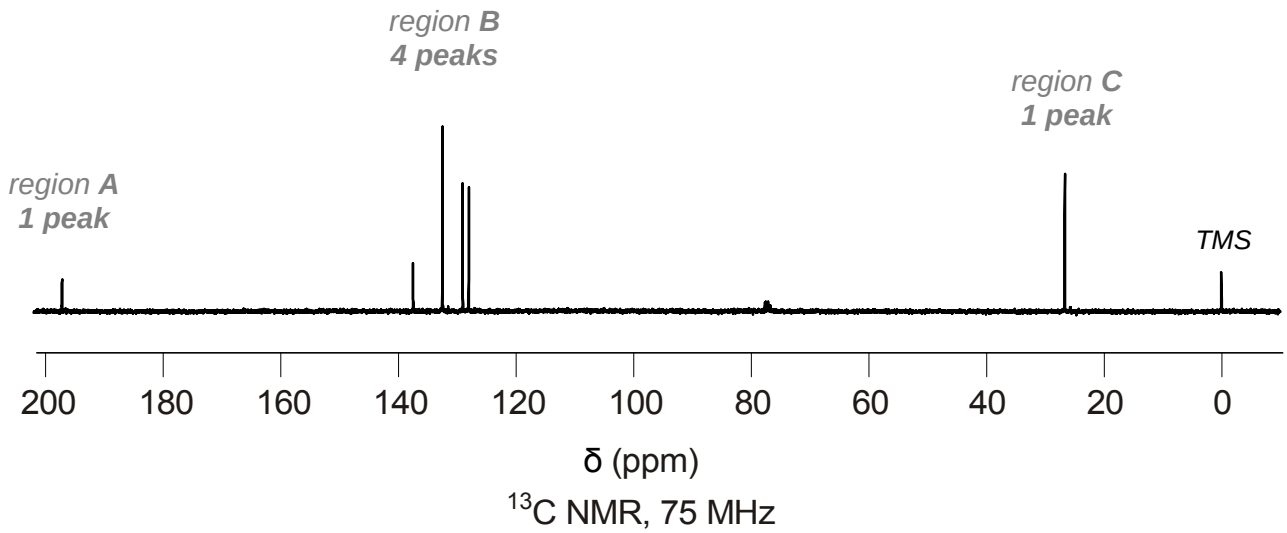
(c) ^{1}H and ^{13}C spectra for the isolated molecule are shown on the next page. Which of the three products did you isolate? On the unfinished skeleton in the box at right, indicate your choice by drawing in any appropriate functional groups, as well as all hydrogens. Then,

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

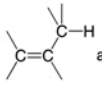
(d) The ^{13}C NMR spectrum of the isolated product showed 6 peaks, which appear in three distinct regions of the spectrum. I've labeled these regions **A**, **B** and **C** on the ^{13}C spectrum on the next page. As you did above, re-draw your proposed contaminant structure below (though this time 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.**

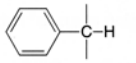



1.7 Hz
8.2 Hz
integrals with relative peak intensities
6
1 2 1
TMS
8.5 8.4 8.2 8.1 8.0 7.6 7.5
9 8 7 6 5 4 3 2 1 0
δ (ppm)
^{1}H NMR, 300 MHz


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

^{1}H NMR Absorptions

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	
—C≡C–H	~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 Absorptions

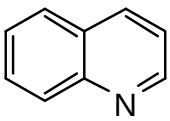
Carbon type	Structure	Chemical shift (ppm)
Alkyl, sp^3 hybridized C		5–45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30–80
Alkynyl, *sp* hybridized C	—C≡C—	65–100
Alkenyl, sp^2 hybridized C		100–140
Aryl, sp^2 hybridized C		120–150
Carbonyl C		160–210

Exam 4 Chart of Reaction Conditions

$Pt/H_2(g)$

$NaNH_2$

$Pd, BaSO_4$
$H_2(g)$



(quinoline)

$Na_2Cr_2O_7$
H_2SO_4

1. BH_3•THF
2. H_2O_2, OH^-

1. O_3
2. $(CH_3)_2S$

Na
NH_3

$HgSO_4$
H_2SO_4

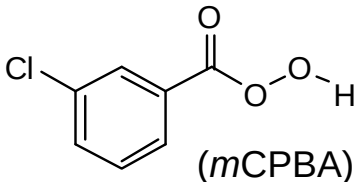
1. $(COCl)_2$
   DMSO
   -60 °C
2. Et_3N

(Swern oxidation)

H_2SO_4
H_2O

$SOCl_2$
pyridine

*m*CPBA
H_2O



(*m*CPBA)

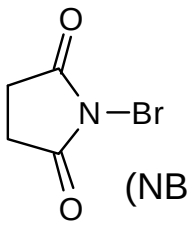
$KMnO_4$
(cold, dilute)
H_2O, OH^-

1. O_3
2. H_2O

$KMnO_4$
H_2O, pH 7

TsCl
pyridine

Cl_2 *or* Br_2,
$h\nu$



(NBS)

$h\nu$ *or* AIBN

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

PBr_3

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.