First letter of last name →

Organic Chemistry I
Pham - Chem 14C
University of California, Los Angeles
Winter 2019 - Exam 2 – 02/28/19

I hereby state that I have neither given nor received aid to or from other students during this exam. I vouch for the honesty and integrity of each and every answer given.

*Signature*_____***KEY***_____ *ID#*_____

*Name (printed)*_____

***Circle** your TA*: Stephanie Shuaijing Sanghyun Danlei

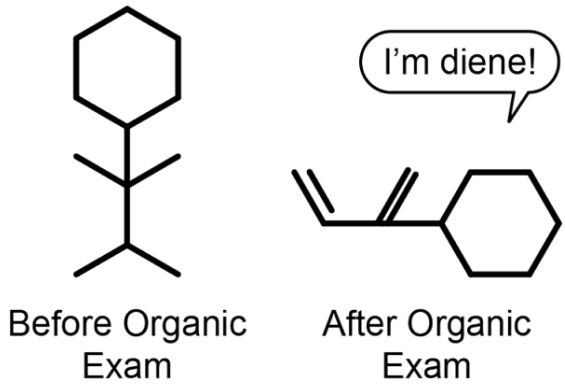
***Circle** your Lecture*: Lecture 1 Lecture 2

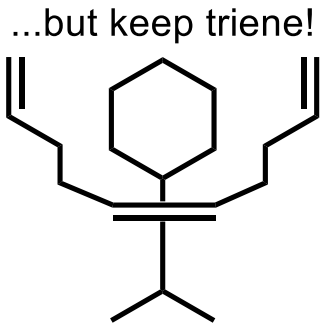
Use the back side of each sheet as scratch paper.

See back pages for periodic table and correlation tables (aka more scratch paper).

	Possible	Your score
I. Mass Spec.	16	
II. IR Spec.	14	
III. NMR Spec.	19	
IV. Mixed Spec.	25	
V. Multiple Choice	27	
Bonus	0 (6)	
Total	100*	

*Yes the total is 101. Think of it as an extra extra credit point. Good luck!

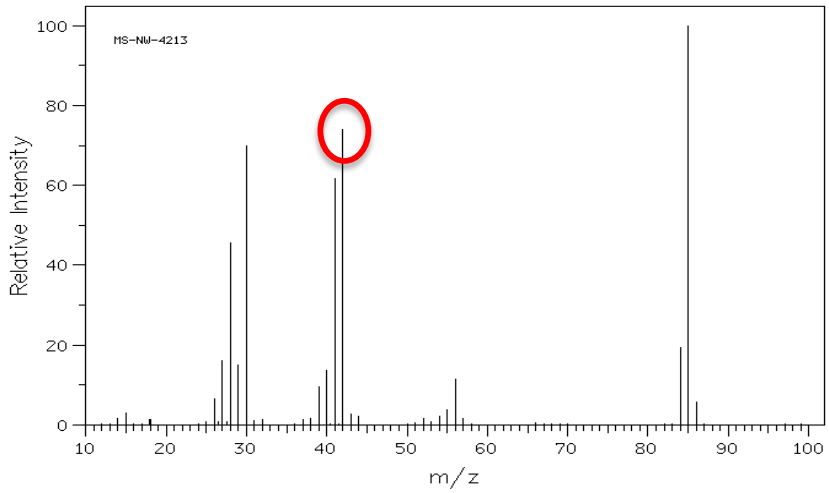




Last Name _____

I. Mass Spectrometry (16 pts) Answer the following questions about mass spectrometry.

a) (2 pts) **Molecule A** generates the mass spectrum below; the **molecular ion peak** is located at *m/z* = 85. **Circle the peak** corresponding to the **most abundant fragment** (i.e. not the parent peak).



Peak Data

m/z = 85 Rel. Intensity: 100%
m/z = 86 Rel. Intensity: 4.1%

b) (10 pts) Which of the following formulae are **possible** for Molecule A? If a structure/formula is not possible, **provide a quick explanation** why (*fewer than 8 words*).

Formula	Possible?	Brief Explanation (if "Not Possible")
$C_3H_{19}NO$	Yes / No	Breaks 2n+2 rule
C_3H_3NCl	Yes / No	M+2 shows no Br, Cl, S
$C_4H_9N_2$	Yes / No	Must have odd # of N
C_4H_7NO	Yes / No	
C_4HN_3	Yes / No	Molecular weight =/= 85

c) (4 pts) If you were told that Molecule A **contains a fluorine atom but no oxygens**, what could be the molecular formula for Molecule A?

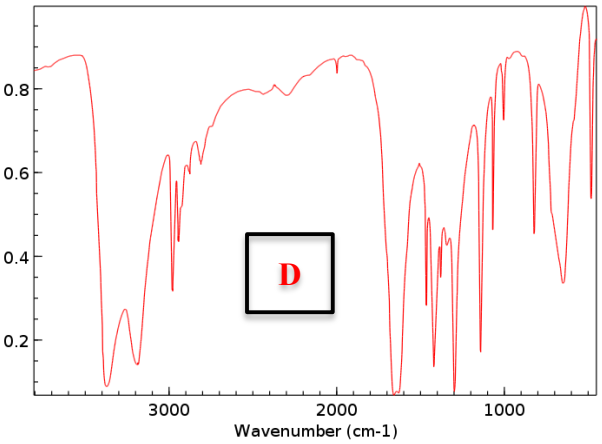
C_4H_4NF

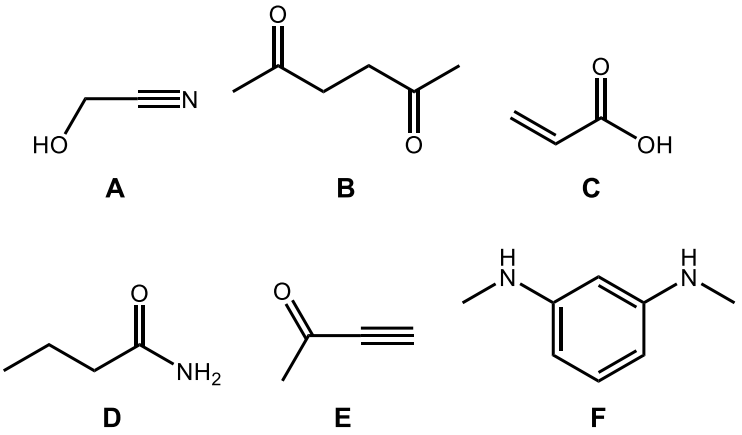
Molecular formula of A

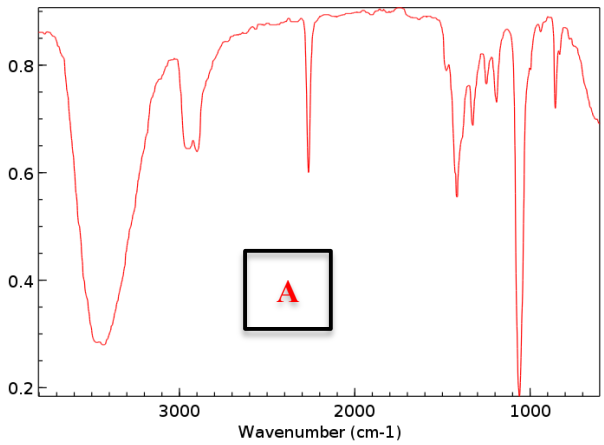
Last Name _____

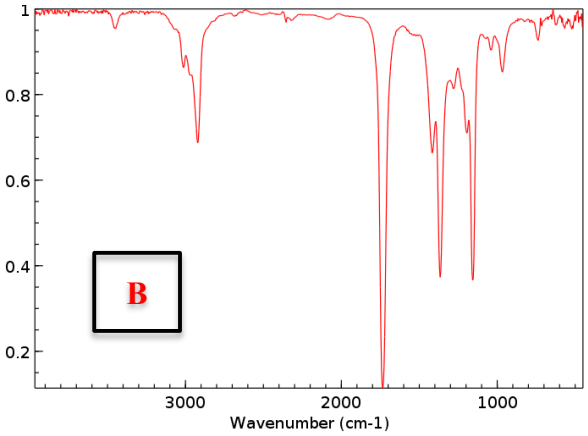
II. Infrared Spectroscopy (14 pts) Answer the following questions about IR spectroscopy.

a) (6 pts) Of the following molecules, identify the **most likely structure** corresponding to these IR spectra by **inserting the letter** of the correct structure into the **boxes provided**.

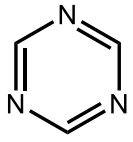








b) (8 pts) As seen in your IR table, the C=C bond stretches for an alkene (like cyclohexene) show up around 1680-1620 cm^{-1}. However, C=C bond stretches in benzene occur at lower wavenumbers; **briefly explain why**. Also, do you expect the **C=N stretch** of 1,3,5-triazine to have a **weaker or stronger** intensity than the **C=C of benzene? Briefly explain**.



C=N stretch intensity:

weaker or stronger than benzene?

Wavenumber: *~1680 - 1620 cm^{-1}* *~1600 cm^{-1}*

1,3,5-triazine

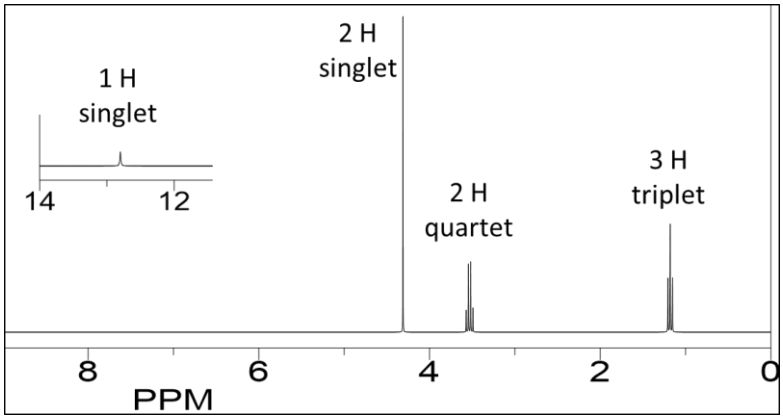
Explanations:

The benzene ring has conjugation, resulting in more partial-single-bond character (and thus a weaker bond), leading to a decrease in wavenumber

The C=N stretch will have a stronger (more intense) peak due to C=N being more polar than C=C

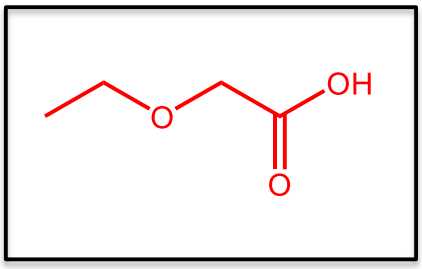
Last Name _____

III. Nuclear Magnetic Resonance Spectroscopy (19 pts) Molly Q. and Adam are debating over the structure of their product. They know that its **molecular formula is $C_4H_8O_3$** and were able to determine the **presence of a carboxylic acid**, along with this ^{1}H-NMR spectrum:



a) (2 pts) What is the ***Degrees of Unsaturation (DoU)*** for the unknown compound? **1**

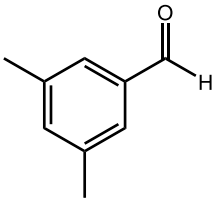
b) (10 pts) Using the information in the NMR spectrum, **draw the structure** of Molly and Adam's unknown product **in the box below**. (You may use the white space for scratch work; only the molecule in the box will be graded.)

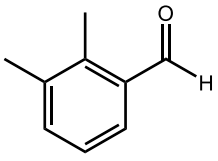


c) (2 pts) Besides the carboxylic acid, what **other functional group** is present in the molecule? (Don't put "alkane")

ether

d) (5 pts) Explain how you could distinguish between these two aromatic aldehydes using **either ^{1}H-NMR or ^{13}C-NMR** (not both).





Explanation:

The first molecule would have 6 total C-NMR signals (4 aromatic) due to symmetry, while the second molecule will have 9.

or

The first molecule would have one signal for all 6 H's on the methyls due to symmetry, while the second would have two different signals

Last Name _____

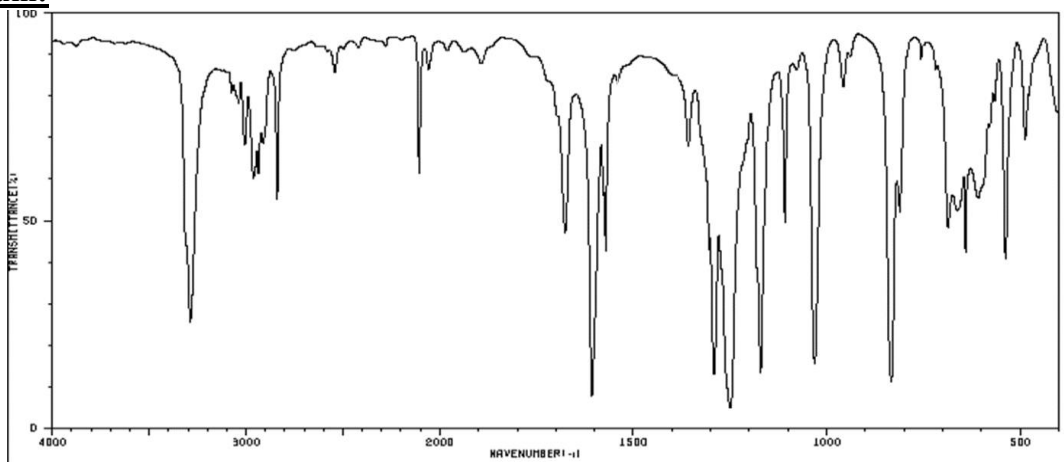
IV. Mixed Spectra Problem (25 pts) Using the following data and spectra, **deduce the molecular structure** and **IHD** of the unknown compound B. **Draw your compound** in the box provided **at the end of the question**. For the possibility of partial credit (in case your structure is incorrect), provide ***legible and relevant information*** you deduced in **the box provided on the following page**.

Mass spectrum: [M]: *m/z* = 124 Relative abundance: 100%
[M+1]: Relative abundance: 9.1%
[M+2]: Relative abundance: 0.9%

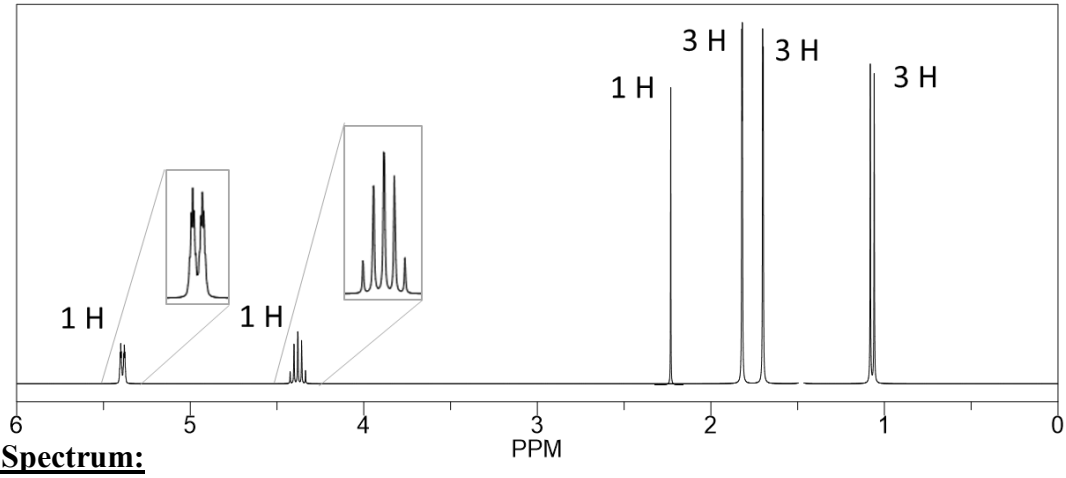
$C_8H_{12}O$
Molecular formula of B

Index of Hydrogen Deficiency (IHD): **3**

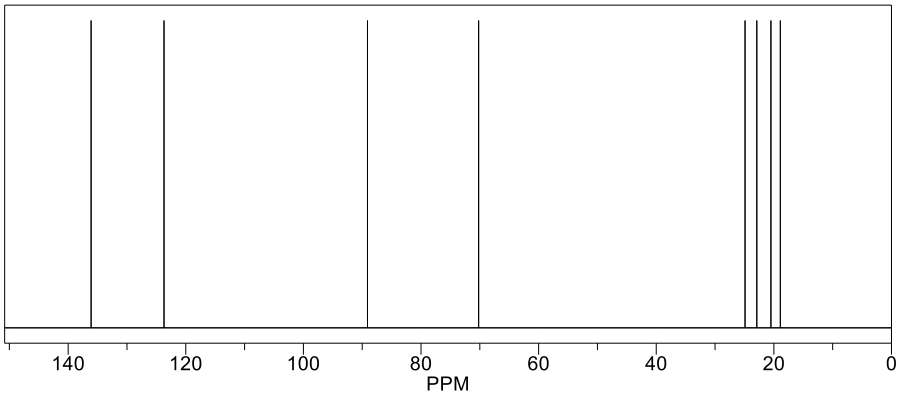
IR Spectrum:



^{1}H-NMR Spectrum:



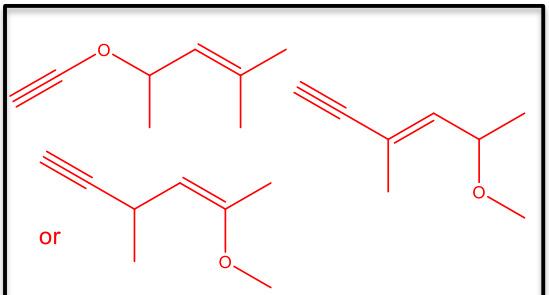
^{13}C-NMR Spectrum:



Last Name _____

Relevant Analysis for Mixed Spectra Problem (e.g. Formula, NMR Pieces, etc.)

(25 pts) **Clearly draw** the structure of your molecule here:



(and some other isomers accepted)

Molecular structure of B

Last Name _____

V. Multiple Choice, For the Most Part (27 pts, 3 pts each) – For each question, choose the *best* answer and **write the letter of your answer in the box(es) provided**. For True or False questions, write **T** for True and **F** for False.

C 1. Which of the following functional groups would exhibit the **highest frequency** in an IR spectrum?

a) ester b) alkyne c) alcohol d) ketone e) aldehyde

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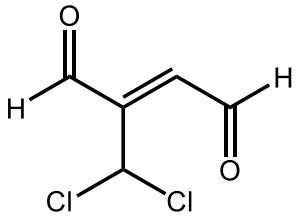
2. For the following molecule, how many **different signals*** are predicted in the…

… ^{1}H-NMR: **4**

… ^{13}C-NMR: **5**

Write **a number in the corresponding boxes*



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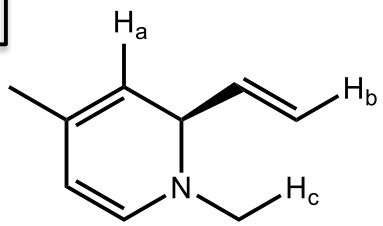
3. What is the **expected splitting pattern** for the signal of the indicated hydrogens? Assume equal coupling constants.

H_a: **B** H_b: **C** H_c: **A**

a) singlet d) quartet

b) doublet e) more than quartet

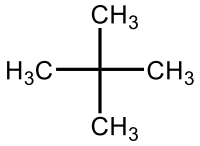
c) triplet f) Impossible to tell



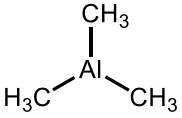
B 4. Relative to tetramethylsilane (TMS), which of these molecules contains hydrogens that will show up on an **NMR spectrum** with a **negative chemical shift**?

a) A b) B c) C

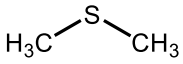
d) More than one of them



A



B



C

B 5. Which of the following statements is **false**?

a) $[CH_3CH_2CH_2]^+$ is a fragment that **can be detected** by a **mass spectrometer**
b) Chlorine (Cl_2) is an **IR-active** molecule
c) Boron-10 (^{10}B) contains an **NMR-active** nucleus

T 6. **T**rue or **F**alse: Two **enantiomers** will generate the **same** (or indistinguishably similar) **mass and IR spectra**.

Last Name _____

BONUS (6 pts)**: Answer** the next few questions for some extra credit points. These are *strictly extra points*, meaning that missing these will not be detrimental to your grade.

B1) (3 pts) C_{60}, shown below, is a molecule we briefly came across in an earlier Fun Friday.

How many **^{1}H-NMR** signals do you expect for C_{60}? __0__
How many **^{13}C-NMR** signals? __1__
Explain your reasoning for both answers above:

There are no hydrogens in C_{60}, and all the carbons are equivalent

---

B2) (3 pts) The LAs have been an integral part of your development this quarter, so let's see if you remember who they are. For **0.5 pt each**, **name any 6 of the 12 Discussion LAs/UAs** as you can (first names allowed).

LA 1: ___Ariana____ LA 2: ___Michelle___ LA 3: ___Natalie____
LA 4: ___Jennifer___ LA 5: ___Jason_____ LA 6: __Amanda___

Also accepted: Christopher, Wesley, Adira, Arian, Matt, Tiffany, Yidan

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

M contributors		M + 1 contributors		M + 2 contributors	
Isotope	Natural abundance	Isotope	Natural abundance	Isotope	Natural abundance
^{1}H	99.985 %	^{2}H	0.015 %	^{3}H	ppm
^{12}C	98.893 %	^{13}C	1.107 %	^{14}C	ppm
^{14}N	99.634 %	^{15}N	0.366 %		
^{16}O	99.759 %	^{17}O	0.037 %	^{18}O	0.204 %
^{19}F	100.0 %				
^{32}S	95.0 %	^{33}S	0.76 %	^{34}S	4.22 %
^{35}Cl	75.77 %			^{37}Cl	24.23 %
^{79}Br	50.69 %			^{81}Br	49.31 %
^{127}I	100.0 %				

Bond	Stretching Frequency	Intensity and Shape
Zone 1: 3700-3200 cm^{-1}		
Alcohol O-H	3650-3200 cm^{-1}	usually strong and broad
Alkyne ≡C-H	3340-3250 cm^{-1}	usually strong and sharp
Amine or amide N-H	3500-3200 cm^{-1}	medium; often broad
Zone 2: 3200-2700 cm^{-1}		
Aryl* or vinyl** sp^2 C-H	3100-3000 cm^{-1}	variable
Alkyl sp^3 C-H	2960-2850 cm^{-1}	variable
Aldehyde C-H	~2900, ~2700 cm^{-1}	medium; two peaks
Carboxylic acid O-H	3000-2500 cm^{-1}	usually strong; very broad

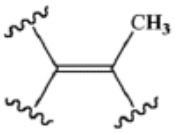
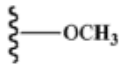
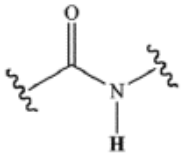
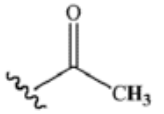
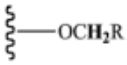
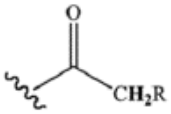
* attached to benzene ring **attached to alkene

Bond	Stretching Frequency	Intensity and Shape
Zone 3: 2300-2000 cm^{-1}		
Alkyne C≡C	2260-2000 cm^{-1}	variable and sharp
Nitrile C≡N	2260-2220 cm^{-1}	variable and sharp
Zone 4: 1850-1650 cm^{-1}		
Ketone C=O	1750-1705 cm^{-1}*	strong
Ester C=O	1750-1735 cm^{-1}*	strong
Aldehyde C=O	1740-1720 cm^{-1}*	strong
Carboxylic acid C=O	1725-1700 cm^{-1}*	strong
Amide C=O	1690-1650 cm^{-1}*	strong

Bond	Stretching Frequency	Intensity and Shape
Zone 5: 1680-1450 cm^{-1}		
Alkene C=C	1680-1620 cm^{-1}	variable
Benzene C=C	~1600 cm^{-1} and ~1500-1450 cm^{-1}	variable; 1600 cm^{-1} often two peaks

Last Name _____

Tables of Average ^{1}H-NMR and ^{13}C-NMR Chemical shifts (δ, ppm)

RCH_3	0.9	RC≡CH	2.5	benzene–H	6.5 – 8
RCH_2R acyclic	1.3	$RNHCH_3$	2 – 3	aldehyde RCHO	9.5 – 11
RCH_2R cyclic	1.5	RCH_2X (X = Cl, Br, I)	3.5	RNH_2	1 – 3
R_3CH	1.5 – 2.0	RCH_2NR_2	2.3 – 2.7	benzene–NH_2	3 – 5
	1.8		3.3 – 4.0		5 – 9
	2.0 – 2.6		3.6 – 4.6	ROH	1 – 5
	2.2 – 3.0	$R_2C=CH_2$	5.0	benzene–OH	4 – 7
benzene–CH_3	2.3	$RCH=CR_2$	5.3	RCOOH	10 – 13
benzene–CH_2R	2.6				

RCH_3	0 – 40	RCH_2Cl	35 – 80	benzene ring sp^2 C	110 – 160
RCH_2R	15 – 55	R_3COH	40 – 80	C=O ester	160 – 180
R_3CH	20 – 60	R_3COR	40 – 80	C=O amide	165 – 180
RCH_2I	0 – 40	RC≡CR	65 – 85	C=O carboxylic acid	175 – 185
RCH_2Br	25 – 65	$R_2C=CR_2$	100 – 150	C=O aldehyde, ketone	180 – 220