Name: _____

CHEM 322. Midterm 2: Make-Up Exam

Spring 2014
Watson, Hietbrink

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Tables of spectral data and a periodic table are provided at the end of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are 14 pages in this exam. Please check that your test has 14 pages before you begin. The last 2 pages are blank and may be used as scratch paper.

Please circle your lecture:

Hietbrink 8:00 AM class

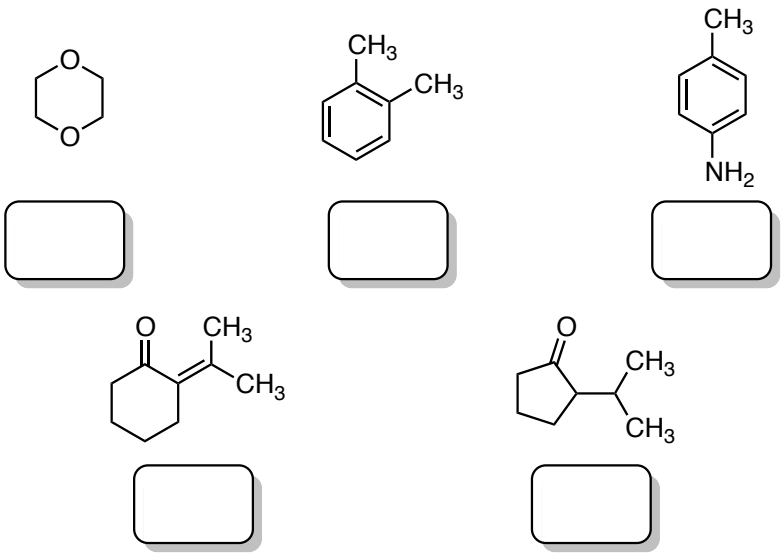
Hietbrink 11:15 AM class

Watson class

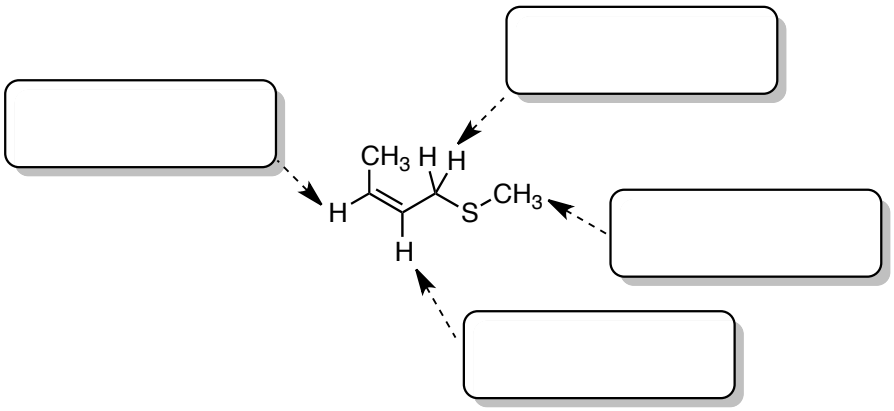
Question	Points
1	_____ /25
2	_____ /20
3	_____ /20
4	_____ /10
5	_____ /40
6	_____ /30
7	_____ /15
8	_____ /50
9	_____ /40
Total	_____ /250

Name: _____

1. (25 points) Predict how many signals you would see in the 13C spectrum of each of these molecules. Put your answer in the box below the molecule.



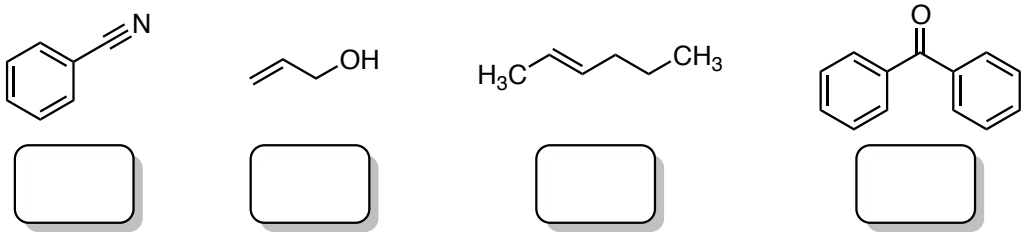
2. (20 points) The 1H NMR of this compound should have four signals. Predict the splitting pattern (singlet, doublet, doublet of doublets, etc) you would see for each signal.

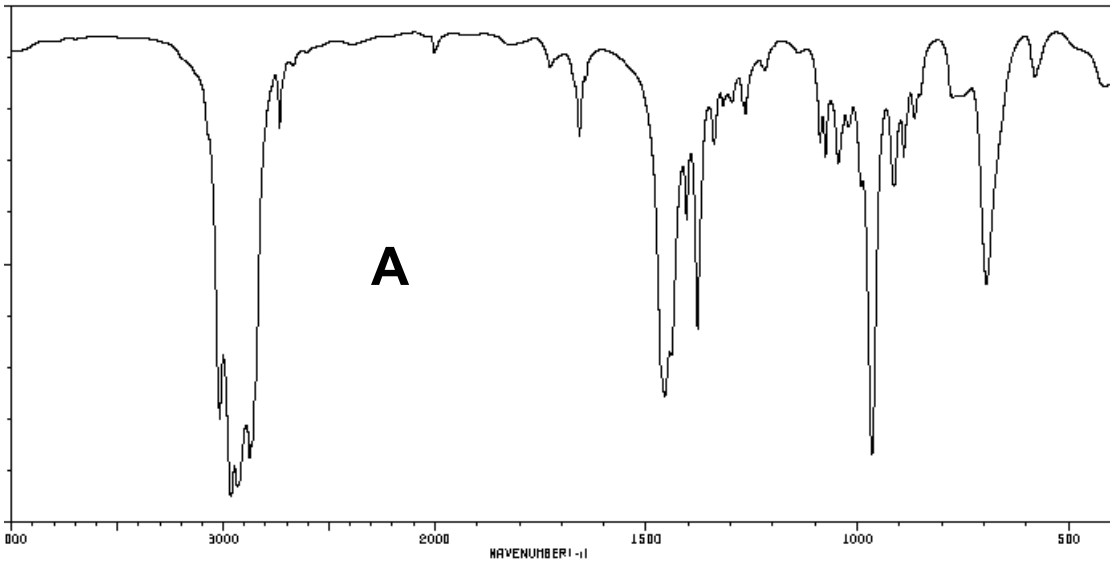


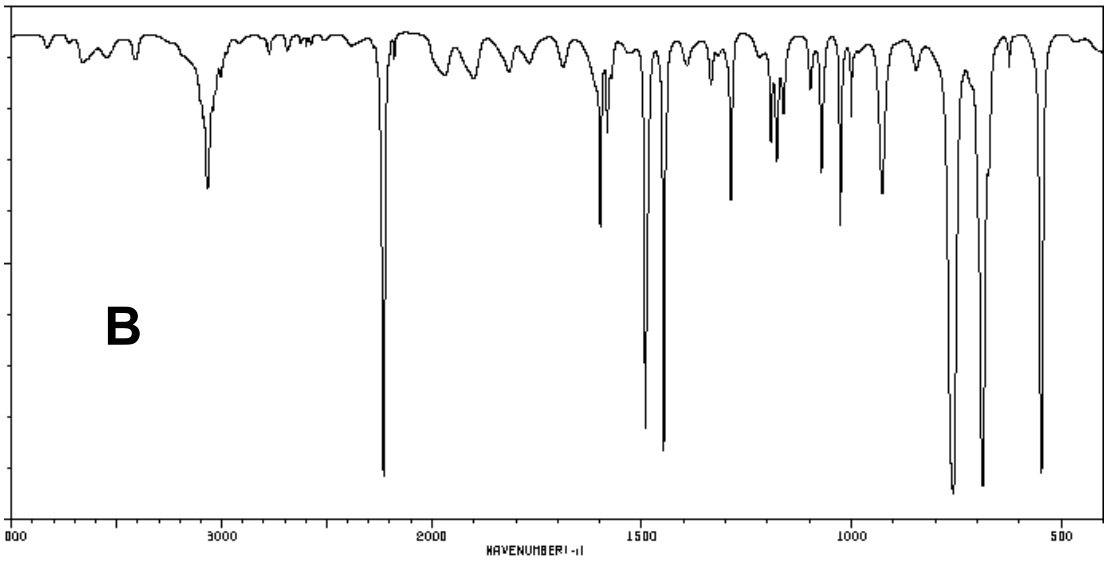
Name: _____

3. (20 points) Below are the IR spectra for four of these eight compounds. Put the letter of the spectrum in the box below the appropriate compound.

a) Spectra A and B refer to two of these four compounds.

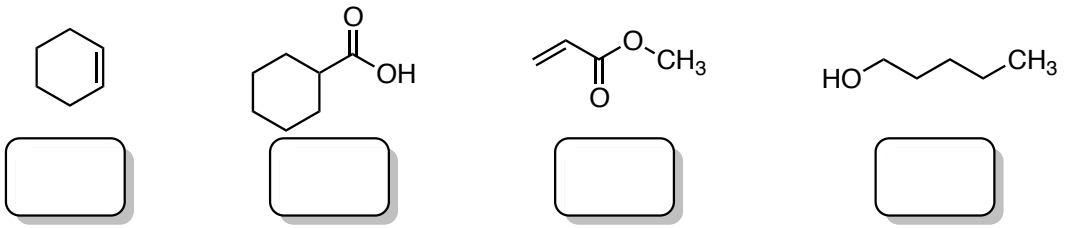


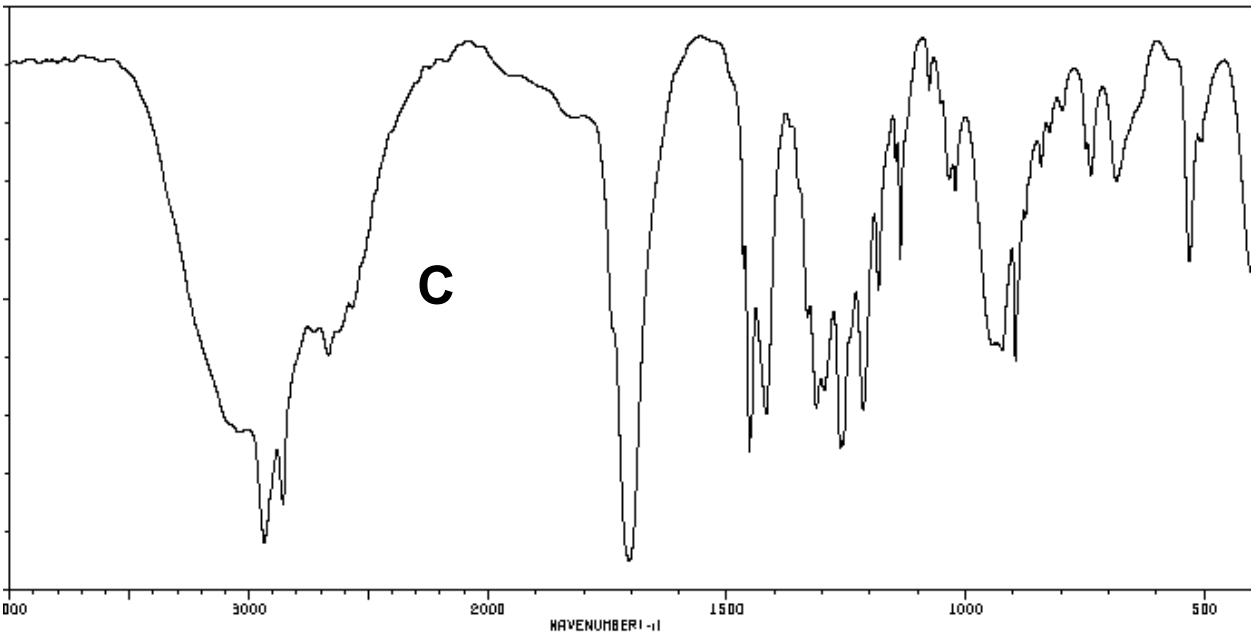


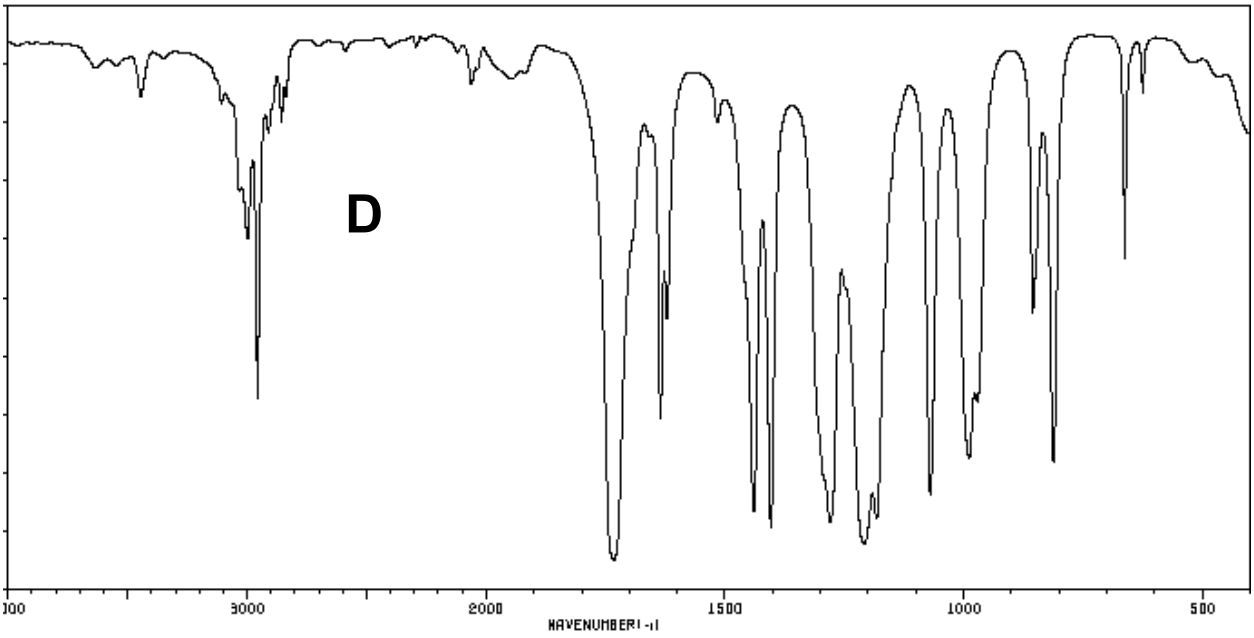


Name: _____

b) Spectra C and D refer to two of these four compounds.

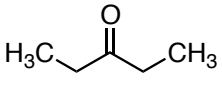






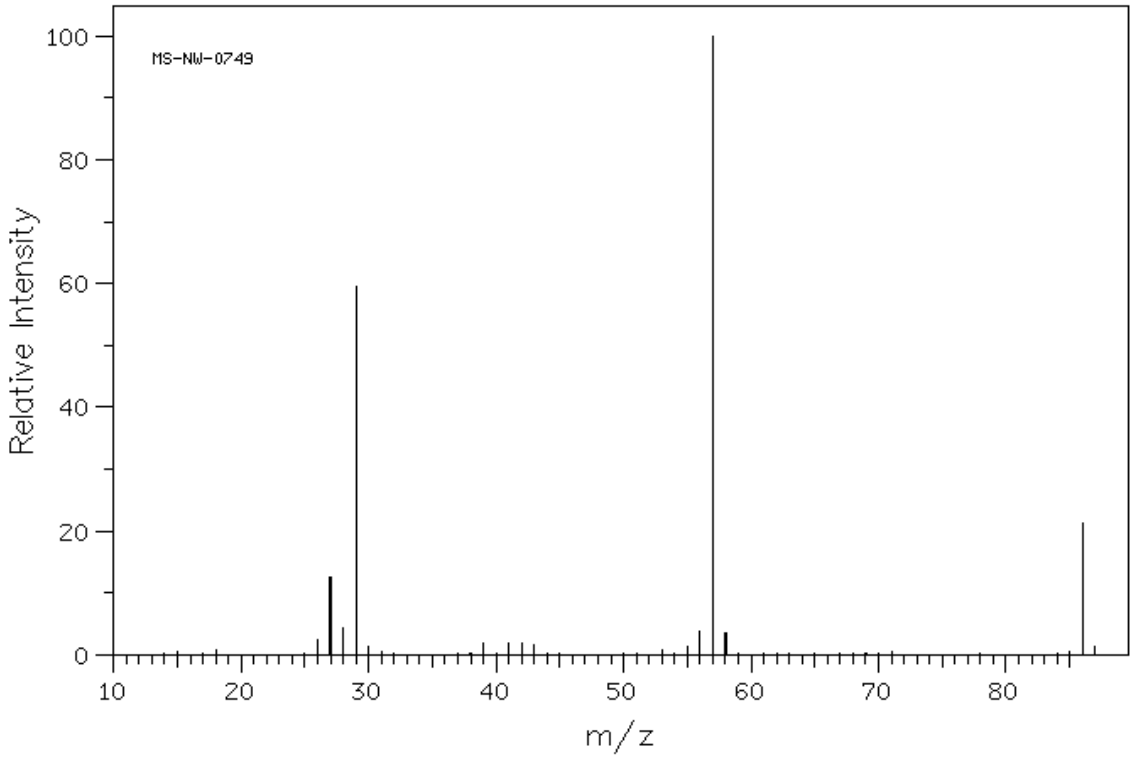
Name: _____

4. (10 points) Below is the mass spectrum of 3-pentanone. In the boxes, explain the large peak at 57 and the small peak at 87.



57

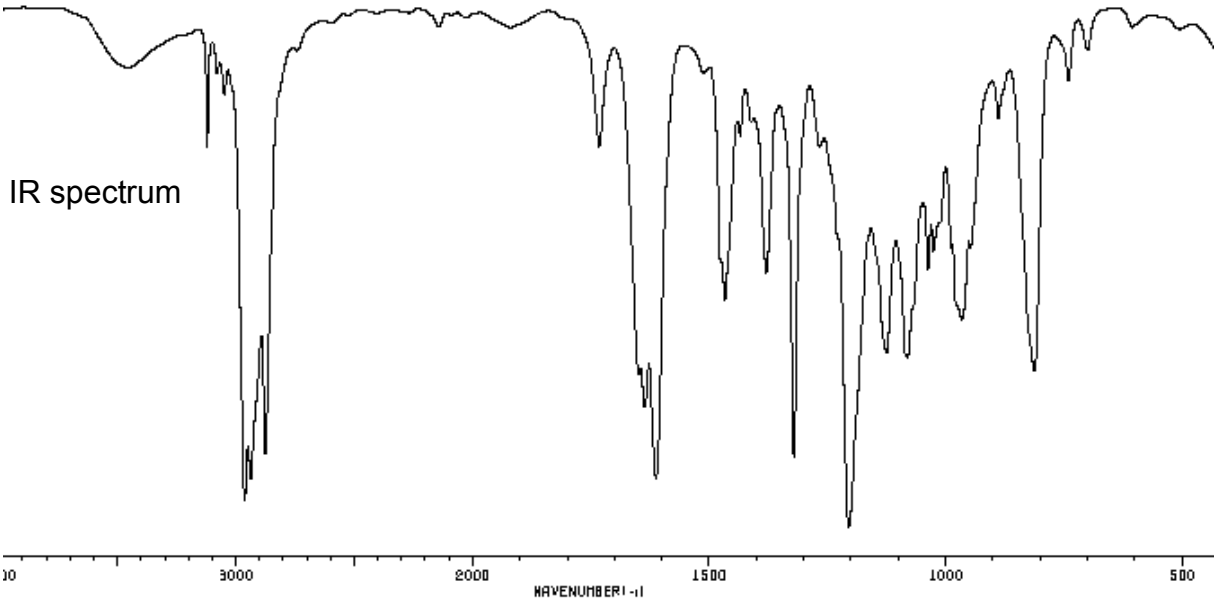
87



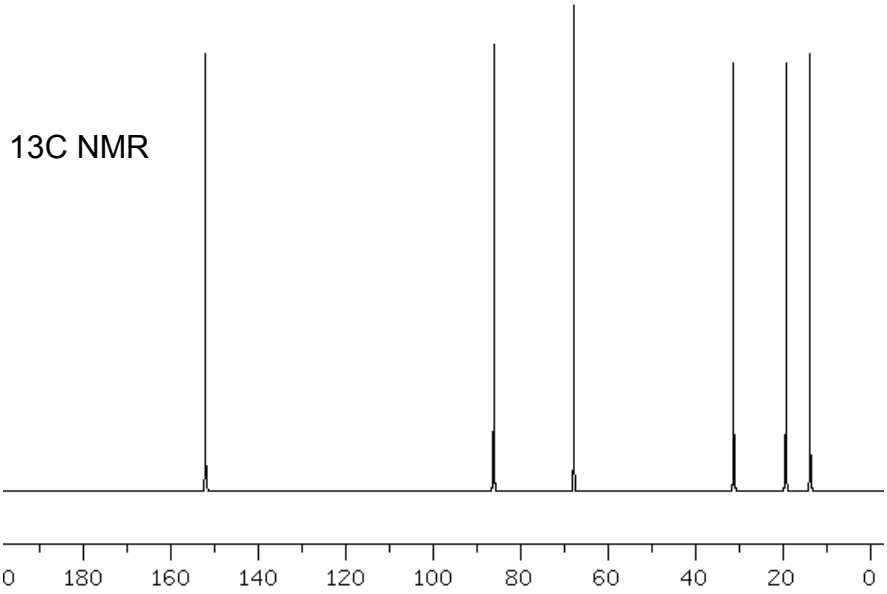
Name: _____

5. (40 points) Here are the IR, ^{13}C NMR, and ^{1}H NMR spectra for an unknown with the formula $C_6H_{12}O$. Answer the following questions.

IR spectrum

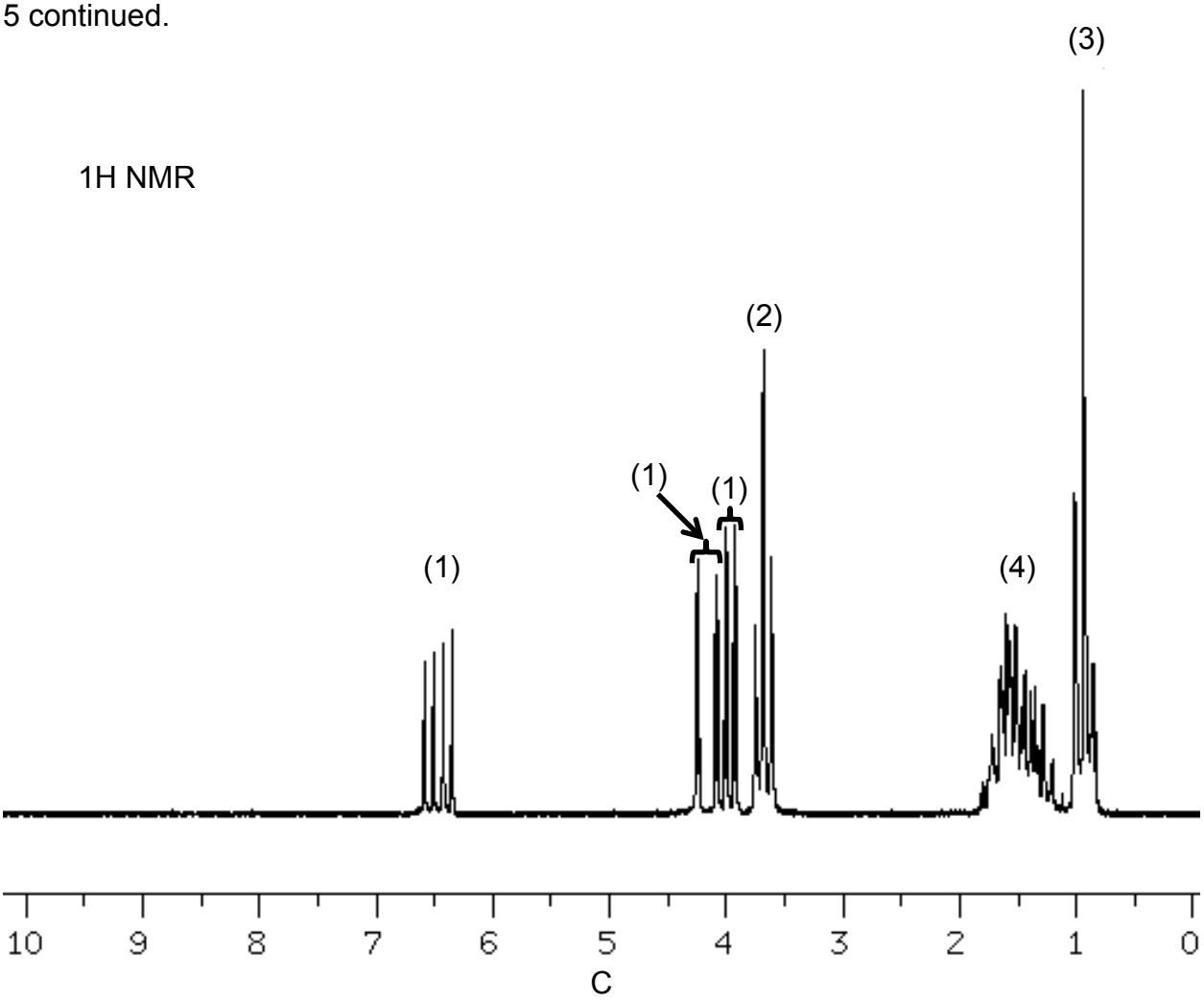


13C NMR



Name: _____

5 continued.



Name: _____

5 continued. (40 points) These questions all refer to the spectra on the previous 2 pages.

a) How many degrees of unsaturation are in this compound?

b) Is there symmetry in this compound?

c) In the IR, what does the signal at about 1600 suggest?

d) In the 13C NMR, what does the chemical shift of the signal at about 152 suggest?

e) In the 1H NMR, what does the chemical shift of the signal at about 6.5 suggest?

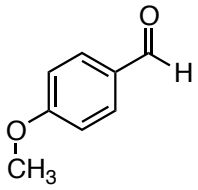
f) In the 1H NMR, what does the integration of the signal at about 0.9 suggest?

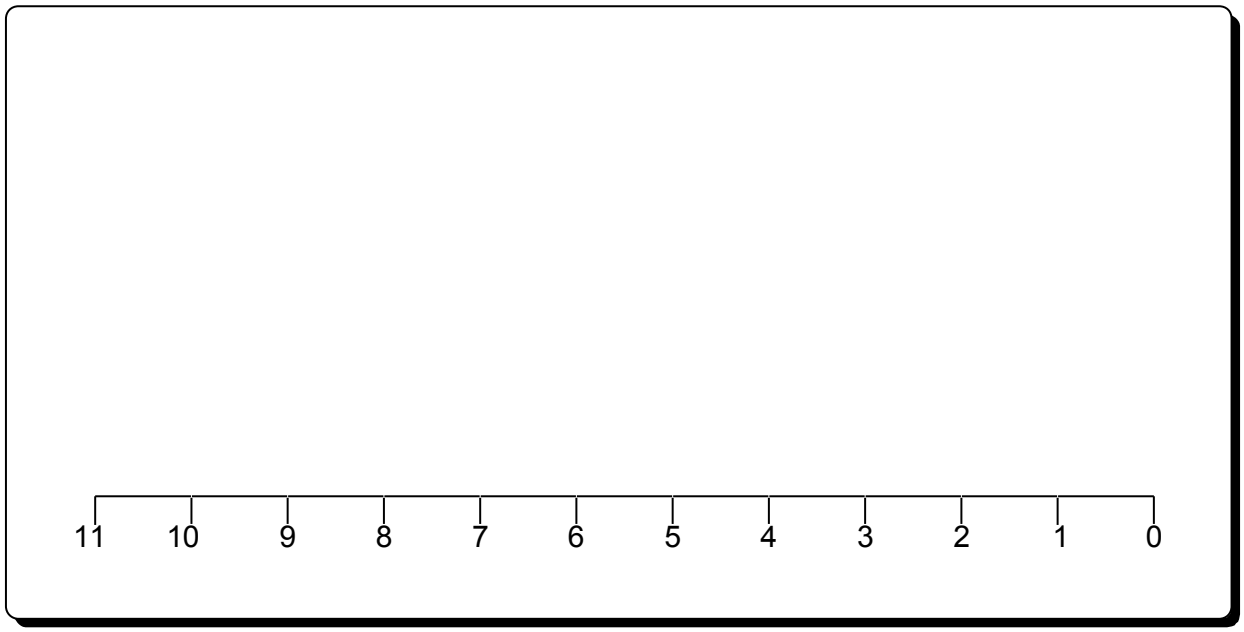
g) In the 1H NMR, what does the splitting pattern of the signal at about 3.6 suggest?

h) What is the structure of this unknown?

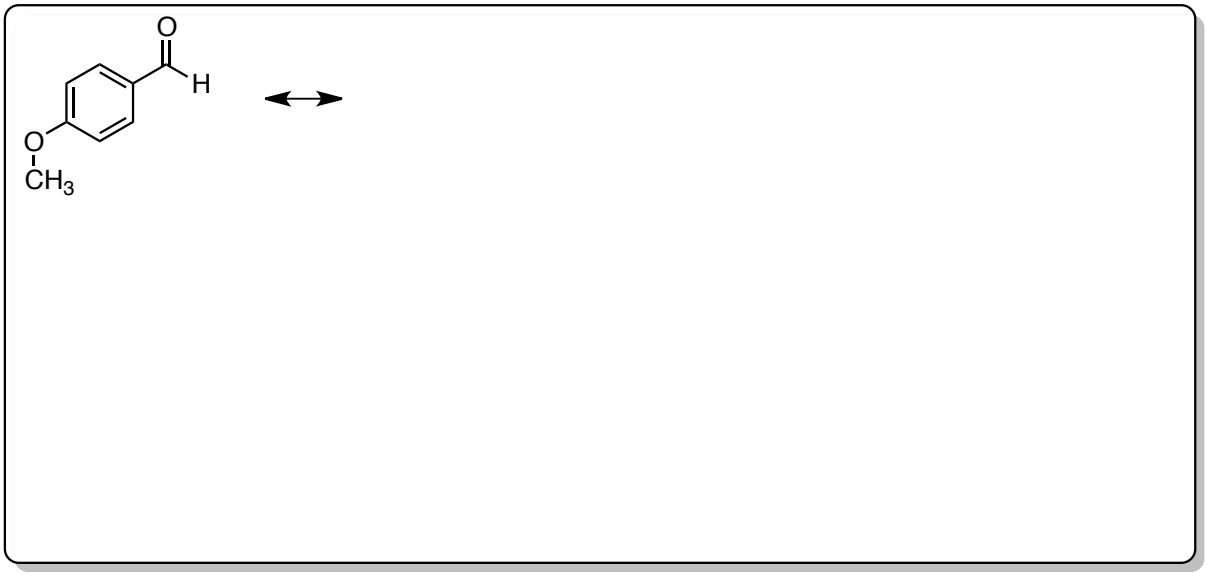
Name: _____

6. (30 points) Draw what you would expect to see in the 1H NMR of this compound. Your drawing should clearly show the number of signals, their approximate chemical shift (within 1 PPM) and the expected splitting pattern.



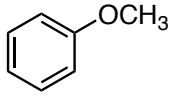


7. (15 points) Draw the important resonance structures for this compound.

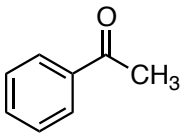


Name: _____

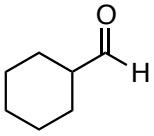
8. (50 points) Predict the major organic product or products for the following reactions.



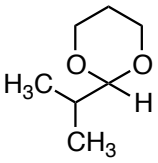
$\xrightarrow{\text{Li, } NH_3}$



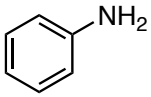
$\xrightarrow[\text{HCl/MeOH}]{\text{Zn/Hg}}$
Δ



$\xrightarrow[H^+]{\text{excess } CH_3OH}$



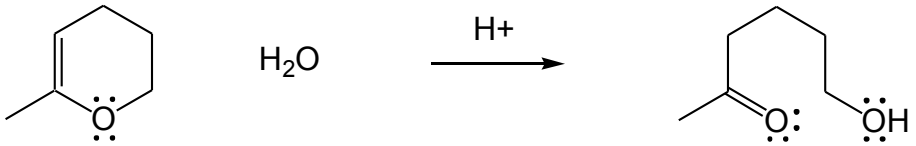
$\xrightarrow[H^+]{\text{excess } H_2O}$



$\xrightarrow[\text{2) } HBF_4]{\text{1) HONO, HCl}}$

Name: _____

9. (40 points) Please draw a reasonable arrow-pushing mechanism for the following reaction.



Name: _____

Approximate IR Absorption Frequencies

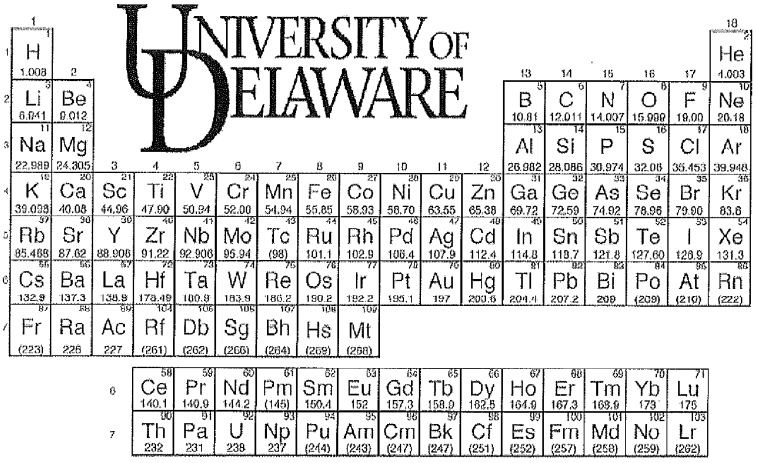
Bond	Frequency (cm^{-1})	Intensity
O–H (alcohol)	3650–3200	Strong, broad
O–H (carboxylic acid)	3300–2500	Strong, very broad
N–H	3500–3300	Medium, broad
C–H	3300–2700	Medium
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong

Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH_x	1.7–2.3
O=C–CH_x	2.0–2.7
Ph–CH_x	2.3–3.0
≡C–H	2.5
R_2N–CH_x	2.0–2.7
I–CH_x	3.2
Br–CH_x	3.4
Cl–CH_x	3.5
F–CH_x	4.4
O–CH_x	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH_x	0.5–5.0
$CONH_x$	10–13
RCOOH	10–13

Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	–20–10
Carbonyls, C=O	
R_2C=O	190–220
RXC=O (X = O or N)	150–180



Name: _____

This page was intentionally left blank and may be used for scratch paper.

Name: _____

This page was intentionally left blank and may be used for scratch paper.