CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Quiz #5

Due: Monday, November 30th, 2015

1:10 p.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

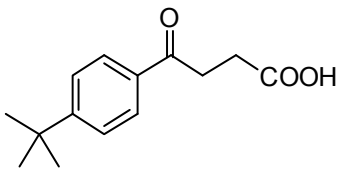
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		30
II		16
III		18
IV		18
V		18
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

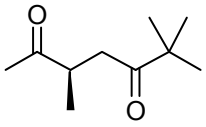
(1) C Not counting those corresponding to solvents or reference standards, how many signals appear in the ^{13}C NMR spectrum for compound **A**?



A

(a) six
(b) eight
(c) ten
(d) twelve
(e) fourteen

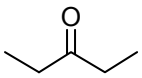
(2) C How many sets of inequivalent protons contribute to the ^{1}H NMR spectrum of compound **B**? Note that a set can contain as few as one proton, so long as it is magnetically inequivalent from the others.



B

(a) four
(b) five
(c) six
(d) seven
(e) eight

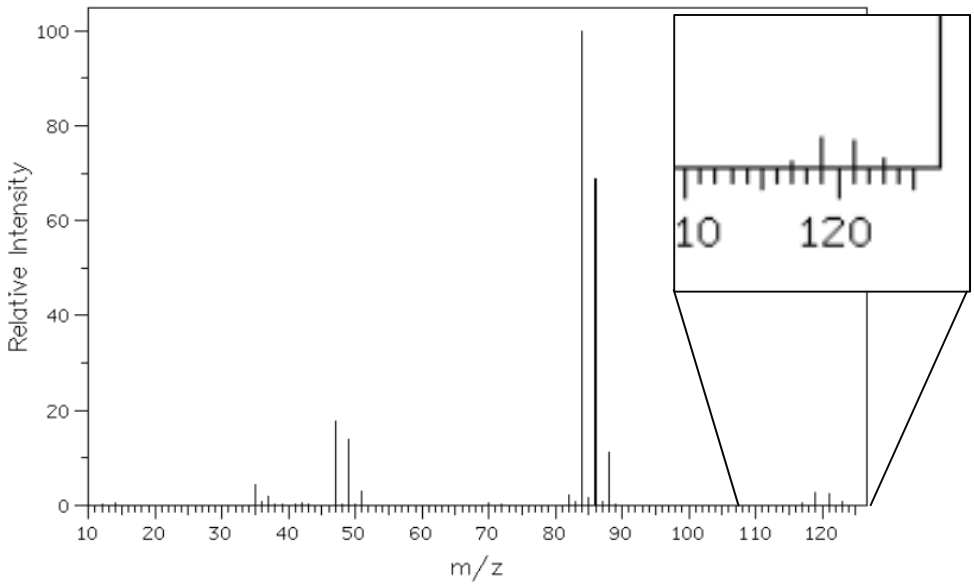
(3) D Assuming it will be different from the molecular ion, what do you expect to be the base peak for compound **C**?



C

(a) m/z 12
(b) m/z 15
(c) m/z 16
(d) m/z 57
(e) m/z 86

(4) D Which of the following molecular formulas is consistent with the following mass spectrum?

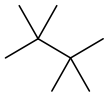


Source: Spectral Database for Organic Compounds, #10716
http://sdbs.db.aist.go.jp/

(a) C_3H_5Br
(b) CHClBr
(c) $CHCl_3$
(d) $CDCl_3$
(e) C_8H_9N

(5) A Which of the following compounds does <u>not</u> have an ^{1}H NMR spectrum composed of a single peak?

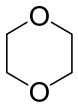
(a)



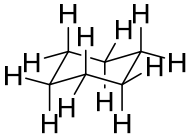
(b)

CH_2ClBr

(c)

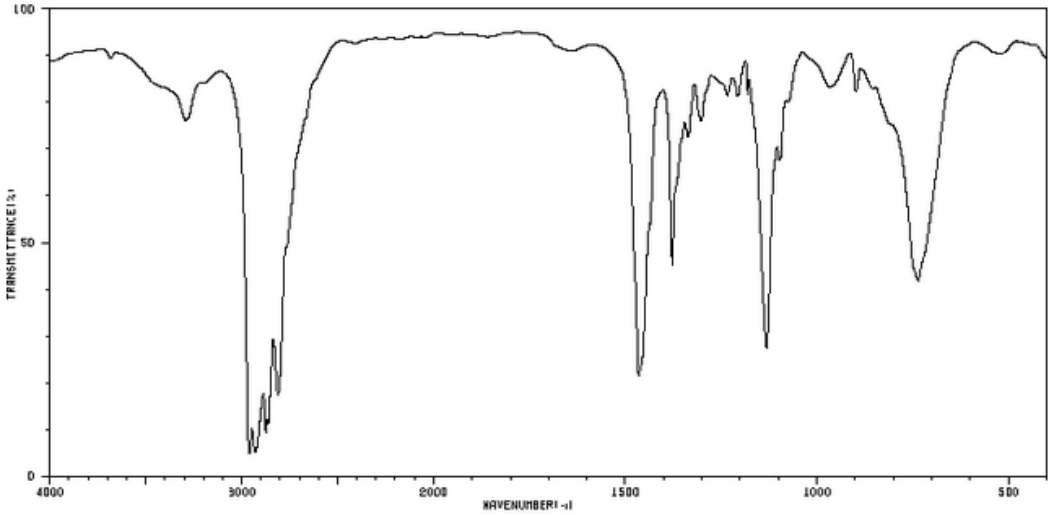


(d)

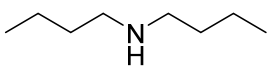


(e)

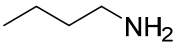
(6) A Which of the following compounds is consistent with the IR spectrum shown below?



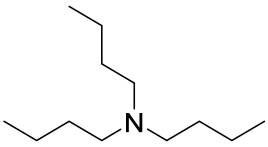
Source: Spectral Database for Organic Compounds, #1672
http://sdbs.db.aist.go.jp/



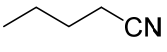
(a)



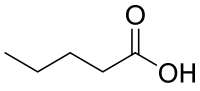
(b)



(c)

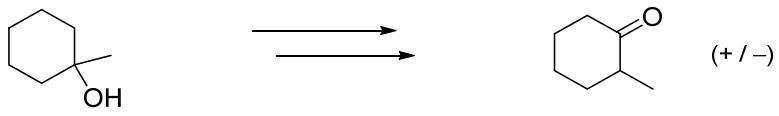


(d)

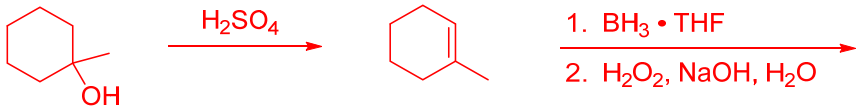


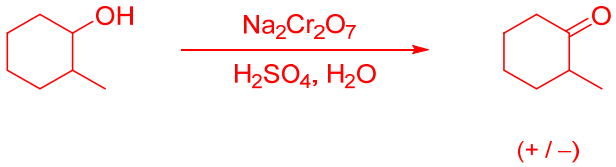
(e)

Problem II. Synthesis (16 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **H** from compound **G**. You may use any other reagents you wish. Your final product can be produced as the racemate.



G **H**

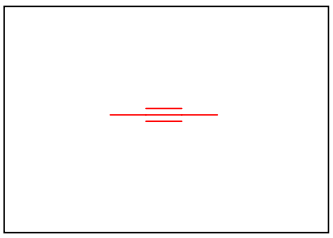
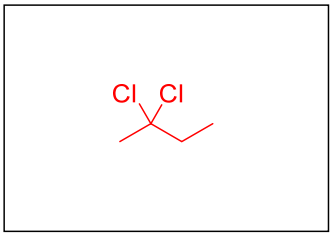
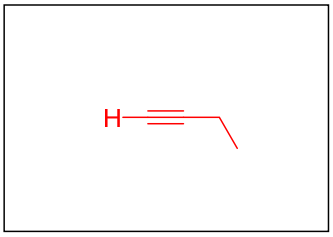




Problem III. (18 points) Roadmap Problem. Provide structures for compounds **J**, **K**, and **M** given the information listed below.

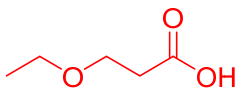
Compound **J** is a hydrocarbon with an ^{1}H NMR spectrum composed of a single peak. Its electron-impact mass spectrum has a molecular ion peak at m/z 54. When **J** is treated with excess HCl gas, compound **K** is the major product. Compound **K** has a ^{13}C NMR spectrum with four signals and an ^{1}H NMR spectrum with three signals: δ 2.4 (quartet), 2.2 (singlet), 1.3 (triplet). Heating **K** with sodamide produces compound **M** as the product, following acidic workup. Its electron-impact mass spectrum also has a molecular ion peak at m/z 54, but its ^{1}H NMR spectrum has three signals.

Source: Spectral Database for Organic Compounds, #263
http://sdbs.db.aist.go.jp/

Compounds & Reactions	Pertinent Spectral Data for Associated Compound
J 	• Hydrocarbon • Electron-impact MS has M^+ peak of m/z 54 • ^{1}H NMR spectrum has a single peak
excess HCl	
K 	• ^{13}C NMR spectrum has 4 signals • ^{1}H NMR spectrum has three signals: roughly δ 2.4 (quartet), 2.2 (singlet), 1.3 (triplet)
1. $NaNH_2$, heat 2. H_2O	
M 	• Hydrocarbon • Electron-impact MS has M^+ peak of m/z 54 • ^{1}H NMR spectrum has three signals

Problem IV. Assignment of an NMR Spectrum (18 points). High-resolution mass spectral analysis of a pure sample of compound **P** reveals it to have a molecular formula of $C_5H_{10}O_3$. The ^1H NMR spectrum of **P** in $CDCl_3$ has the following signals:

Chemical Shift (ppm)	Multiplicity	Integration
11.20	singlet, broad	32
3.71	triplet	67
3.53	quartet	64
2.64	triplet	65
1.21	triplet	98



P

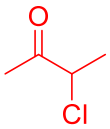
3-ethoxypropionic acid

Source: Spectral Database for Organic Compounds, #4639
http://sdbs.db.aist.go.jp/

(i) Draw a Lewis structure for compound **P** consistent with the data provided above.

(ii) For each chemical shift, draw an arrow pointing to one of the hydrogens that gives rise to that signal.

Problem V. Structure Determination (20 points). Given the spectra shown below for compound **Q**, provide its structure. If you desire partial credit in the event you provide an incorrect answer, show your reasoning by noting important features of the spectra and the portions of the molecule that give rise to these features.

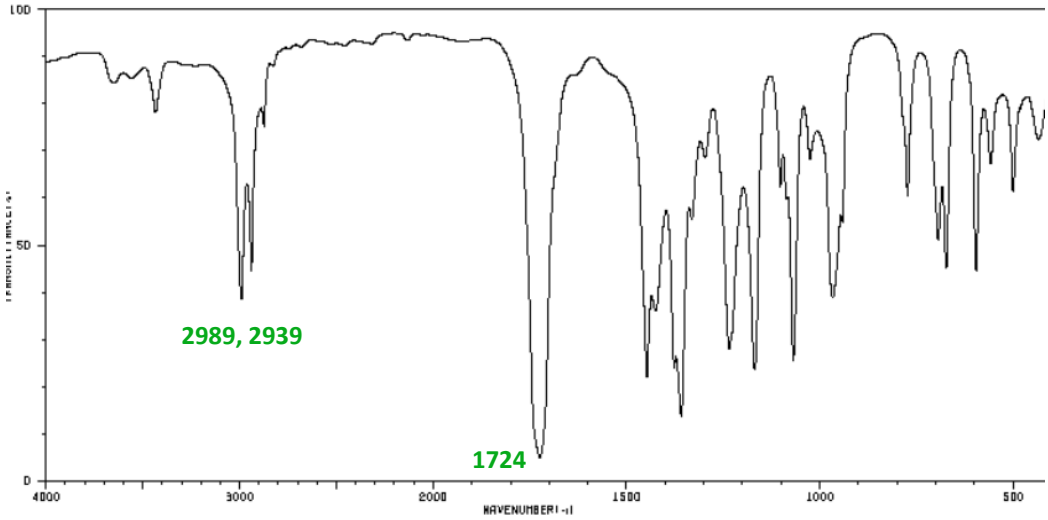


N

3-chloro-2-butanone

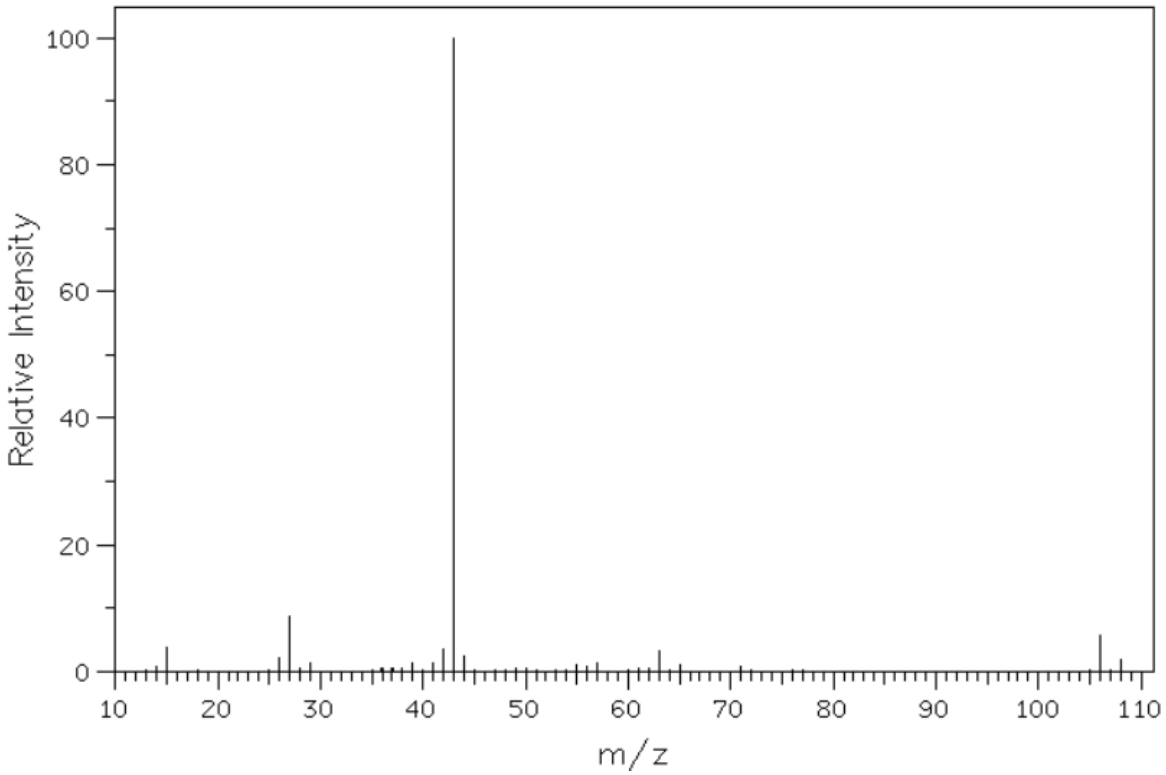
Source: Spectral Database for Organic Compounds, #4006
http://sdbs.db.aist.go.jp/

IR Spectrum:



Source: Spectral Database for Organic Compounds, #4006
http://sdbs.db.aist.go.jp/

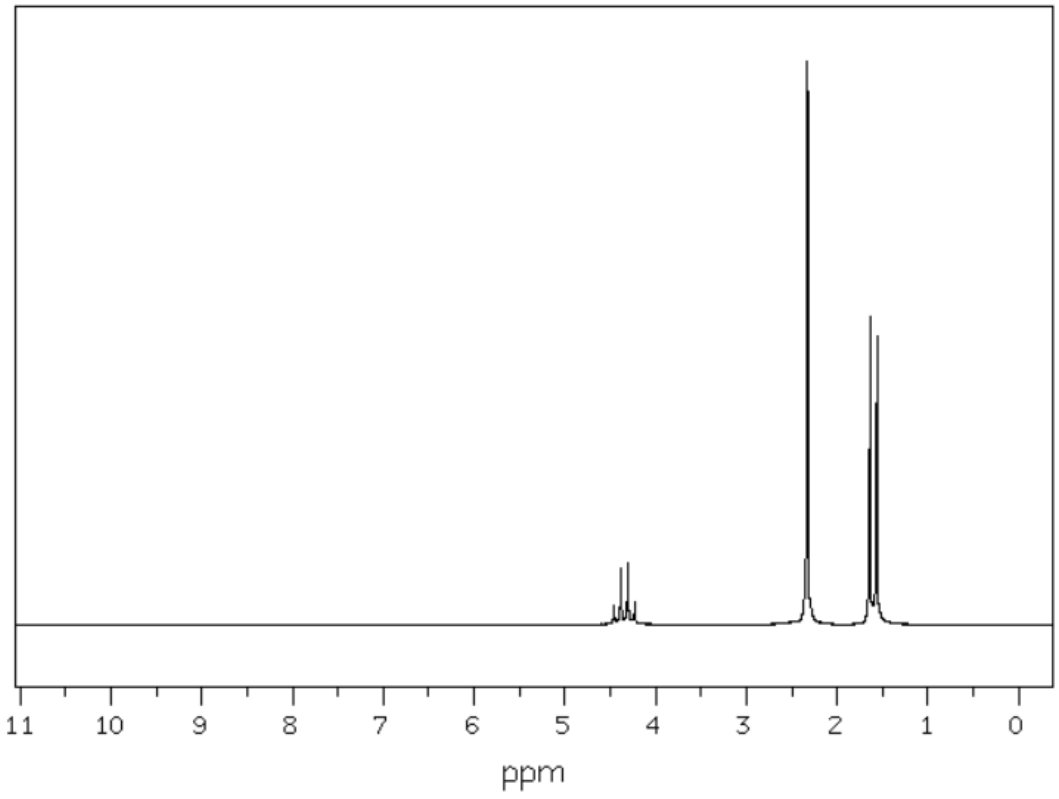
Mass Spectrum:



Source: Spectral Database for Organic Compounds, #4006
http://sdbs.db.aist.go.jp/

m/z	Intensity
15.0	3.8
26.0	2.2
27.0	8.8
29.0	1.2
39.0	1.2
41.0	1.3
42.0	3.4
43.0	100.0
44.0	2.3
55.0	1.1
57.0	1.3
63.0	3.3
65.0	1.0
106.0	5.8
108.0	1.9

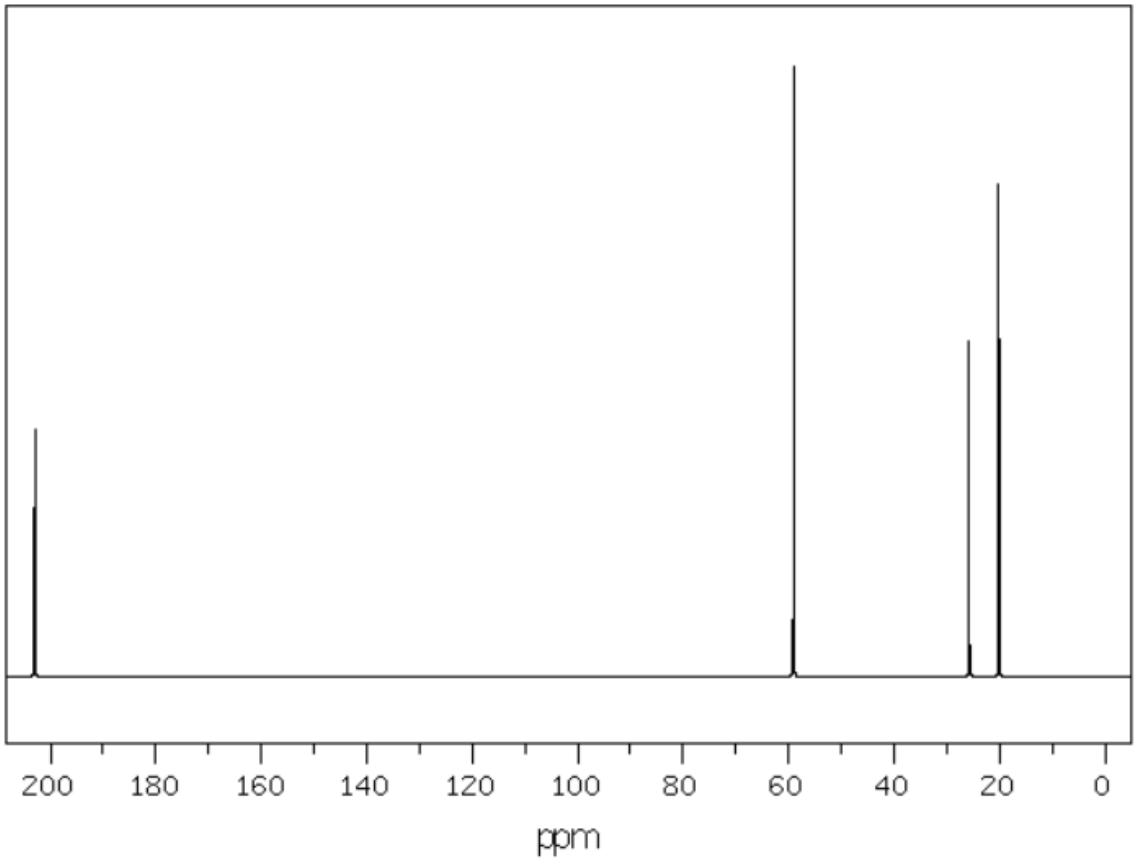
^{1}H NMR Spectrum:



Source: Spectral Database for Organic Compounds, #4006
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Integration
4.32	quartet	274
2.33	singlet	819
1.61	doublet	824

Proton-decoupled ^{13}C NMR Spectrum:



Source: Spectral Database for Organic Compounds, #4006
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Intensity
202.95	singlet	405
59.06	singlet	1000
25.72	singlet	550
20.08	singlet	805