CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Hour Examination #4

Wednesday, December 3rd, 2014

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	
Student Signature	

Instructions & Scoring

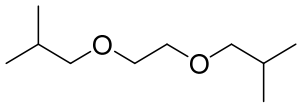
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of hand-written notes and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		30
II		18
III		21
IV		11
V		20
TOTAL		100

This exam focuses on Chapters 13 and 14 in Janice Smith's *Organic Chemistry*, 4th edition

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.

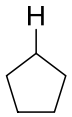
(1) _____ How many signals appear in the proton-decoupled ^{13}C NMR spectrum for compound **A**? (Do not count signals that arise from solvent, reference standards, or impurities).



A

(a) three
(b) four
(c) six
(d) eight
(e) ten

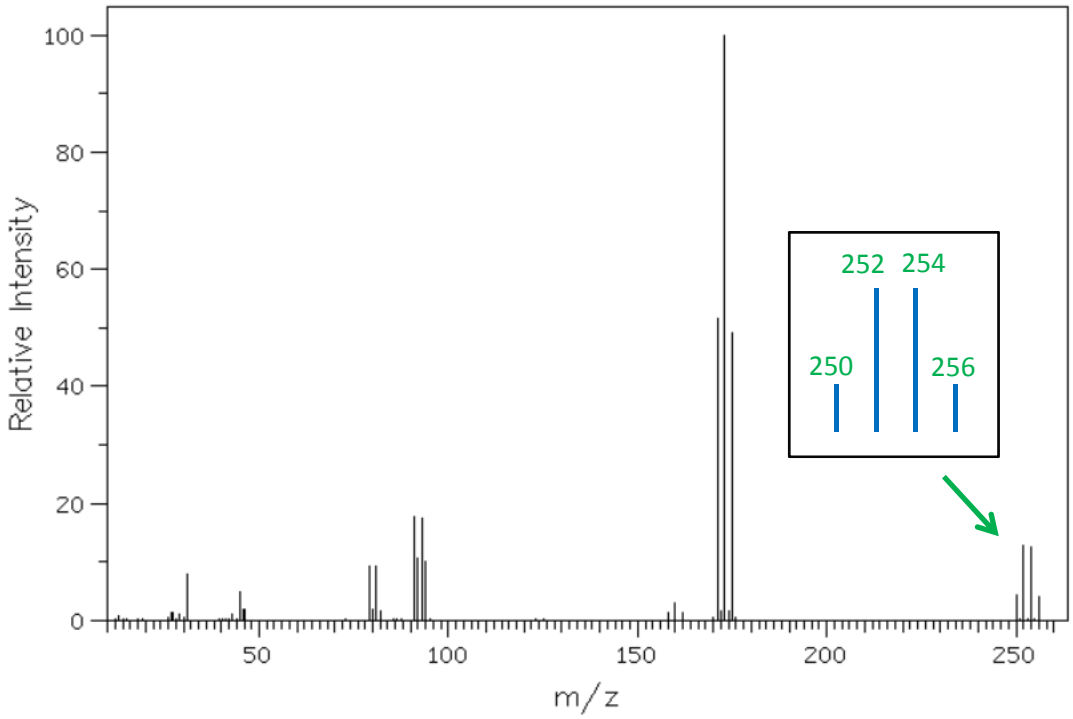
(2) _____ One of the ten hydrogen atoms in compound **B**, cyclopentane, is drawn explicitly below. What is the multiplicity of the signal corresponding to the labeled hydrogen atom?



B

(a) singlet
(b) doublet
(c) triplet
(d) triplet of triplets
(e) doublet of triplet of triplets

(3) _____ Compound **C** is composed solely of carbon, hydrogen, and bromine atoms. Given the mass spectrum below, which includes the molecular ion, how many <u>bromine atoms</u> does the molecule contain?

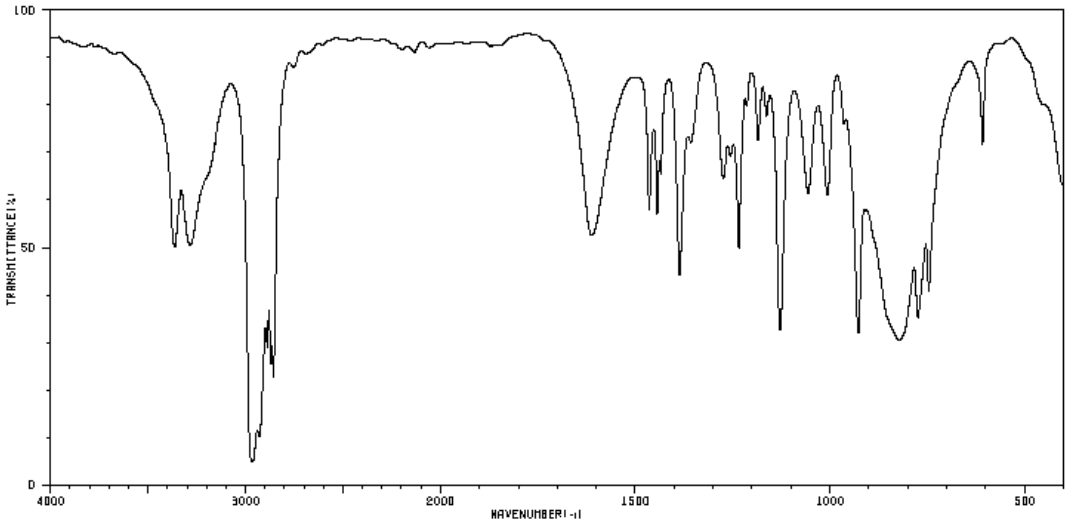


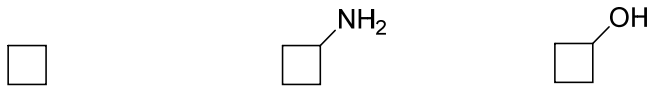
(a) zero
(b) one
(c) two
(d) three
(e) four

(4) _____ Which of the following statements is the most correct and complete of the choices given?

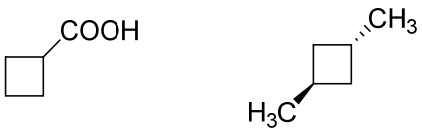
(a) uncharged fragments do not show up as peaks in mass spectra
(b) carbon atoms with 6 protons and 6 neutrons do not give rise to signals in NMR spectra
(c) bond stretches that are not associated with a change in dipole moment do not show up as peaks in IR spectra
(d) statements (a) and (b) are both correct, while (c) is incorrect
(e) statements (a), (b), and (c) are all correct

(5) _____ The IR spectrum shown below is consistent with which of the following structures?



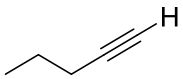


(a) (b) (c)

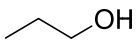


(d) (e)

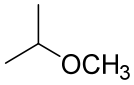
(6) _____ Which of the following compounds will lose one or more signals from its ^{1}H NMR spectrum when D_2O is selected as the solvent versus $CDCl_3$?



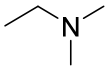
(a)



(b)



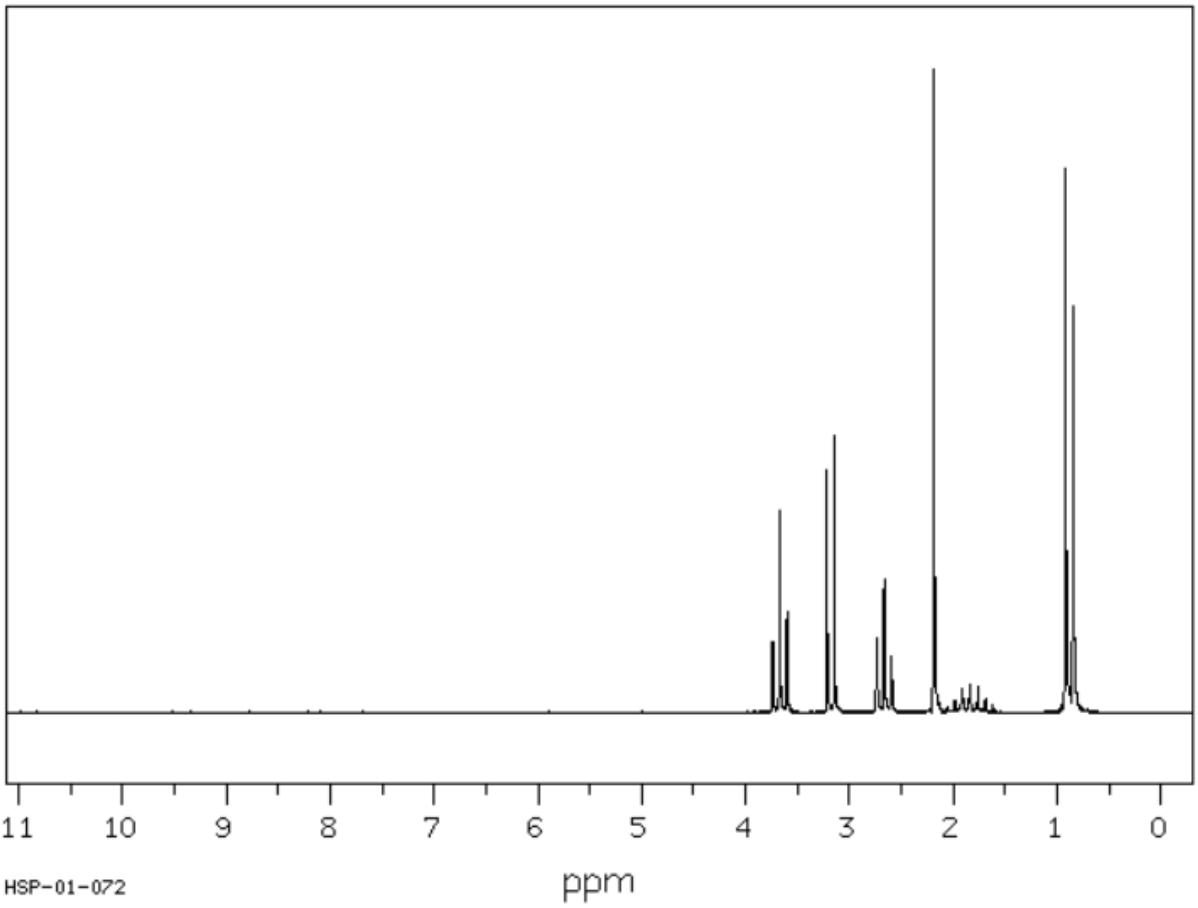
(c)



(d)

(e)

Problem II. Assignment of an NMR Spectrum (18 points). High-resolution mass spectral analysis of a pure sample of compound **D** reveals it to have a molecular formula of $C_8H_{16}O_2$. The ^1H NMR spectrum of **D** in $CDCl_3$ has the following signals:



Signal	Chemical Shift (ppm)	Multiplicity	Integration
a	3.66	triplet	16
b	3.18	doublet	16
c	2.66	triplet	15
d	2.19	singlet	24
e	1.84	multiplet	8
f	0.88	doublet	49

(i) Draw a Lewis structure for compound **D** 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.

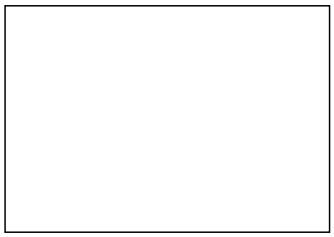
Problem III. (21 points) Roadmap Problem. Provide structures for compounds **E**, **F**, and **H** given the information listed below.

Compound **E** is a single, pure compound and has no optical activity. None of the signals in the ^{1}H NMR spectrum of **E** is a doublet. The molecular ion peak for **E** is split into major peaks at m/z 136 and 138, and these peaks have relative intensities of ~1:1. When **E** is treated with potassium hydroxide, compound **F** is a minor product. High-resolution mass spectrometry of **F** reveals it to have a molecular formula of $C_4H_{10}O$. Compound **F** has a ^{13}C NMR spectrum with four signals and a broad absorption peak at ~3300 cm^{-1} in the infrared. Treatment of **F** with phosphorus oxychloride and pyridine gives **G**, whose ^{13}C NMR spectrum also has four signals, but whose IR spectrum lacks a broad absorption peak at ~3300 cm^{-1}. Treatment of **G** with bromine, followed by excess sodamide, heat, then a mild acid quench produces compound **H**. The infrared spectrum of **H** has a sharp absorption near 3300 cm^{-1}. When **H** is treated with sodium hydride, bubbles are produced. The mass spectrum of **H** has a molecular ion at m/z 54.

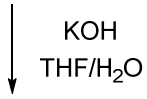
<u>Compounds & Reactions</u>

<u>Pertinent Spectral Data for Associated Compound</u>

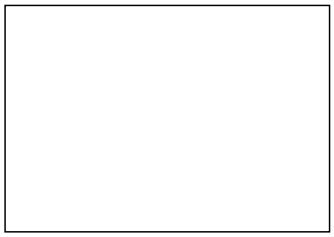
E



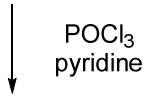
- Compound **H** is pure and has no optical activity
- None of the signals in ^{1}H NMR is a doublet
- Electron-impact MS has M^+ peak of 136 and $[M+2]^+$ peak of 138 in an intensity ratio of ~1:1



F

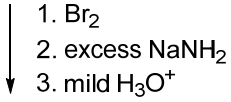


- High-resolution MS gives a molecular formula of $C_4H_{10}O$
- ^{13}C NMR spectrum has 4 signals
- IR spectrum has a broad peak ~3300 cm^{-1}

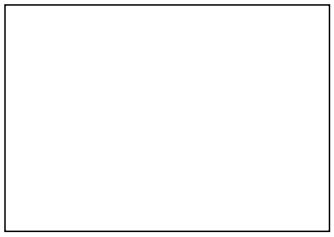


compound **G**

- ^{13}C NMR spectrum has 4 signals
- IR spectrum has no broad peak at ~3300 cm^{-1} and no strong absorption between 1700 and 1800 cm^{-1}

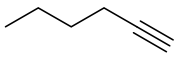


H



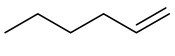
- IR spectrum has a sharp peak ~3300 cm^{-1}
- MS has a molecular ion peak at m/z 54
- Bubbles form upon addition of NaH

Problem IV. Explanation (11 points). Explain the following trend in the absorptions corresponding to the most energetic C–H stretching mode observed in the IR spectra of the following molecules.



J

1-hexyne
3311 cm^{-1}



K

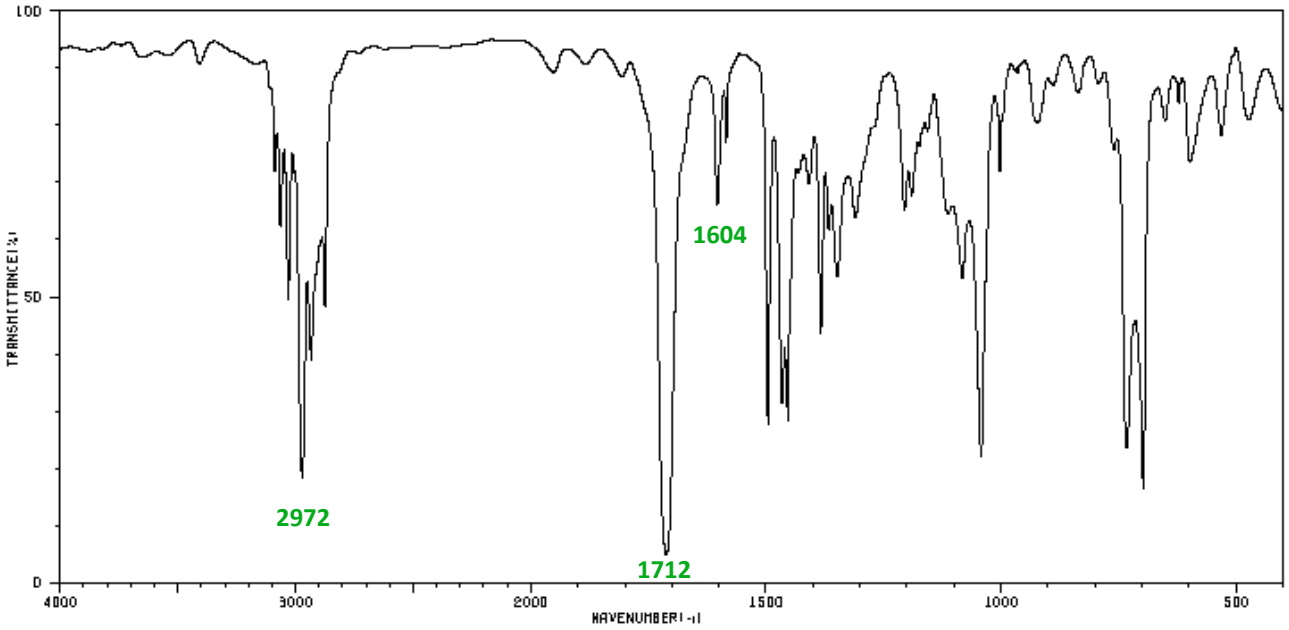
1-hexyne
3079 cm^{-1}

L

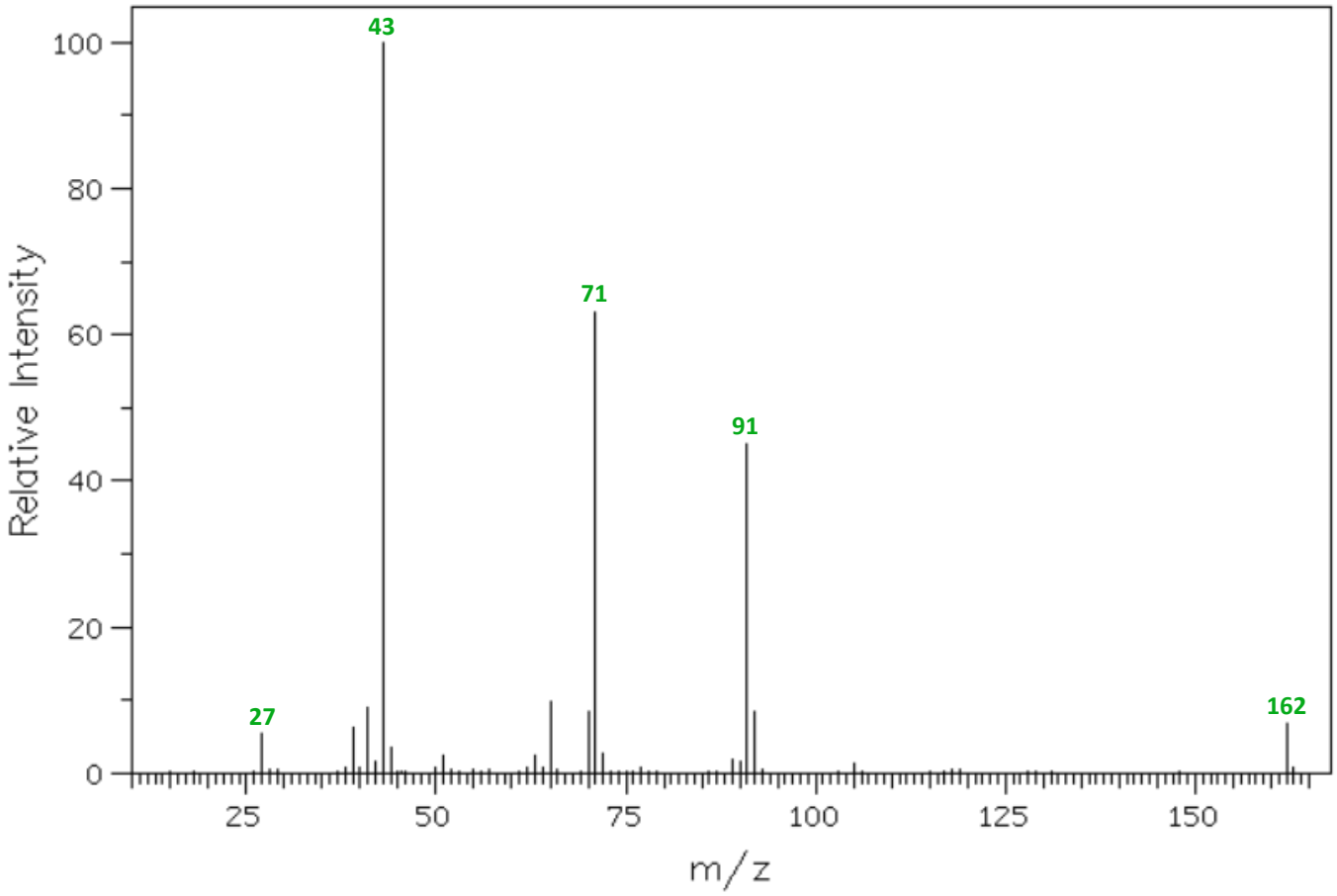
1-hexyne
2959 cm^{-1}

Problem V. Structure Determination (20 points). Given the spectra shown below for compound **N**, 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.

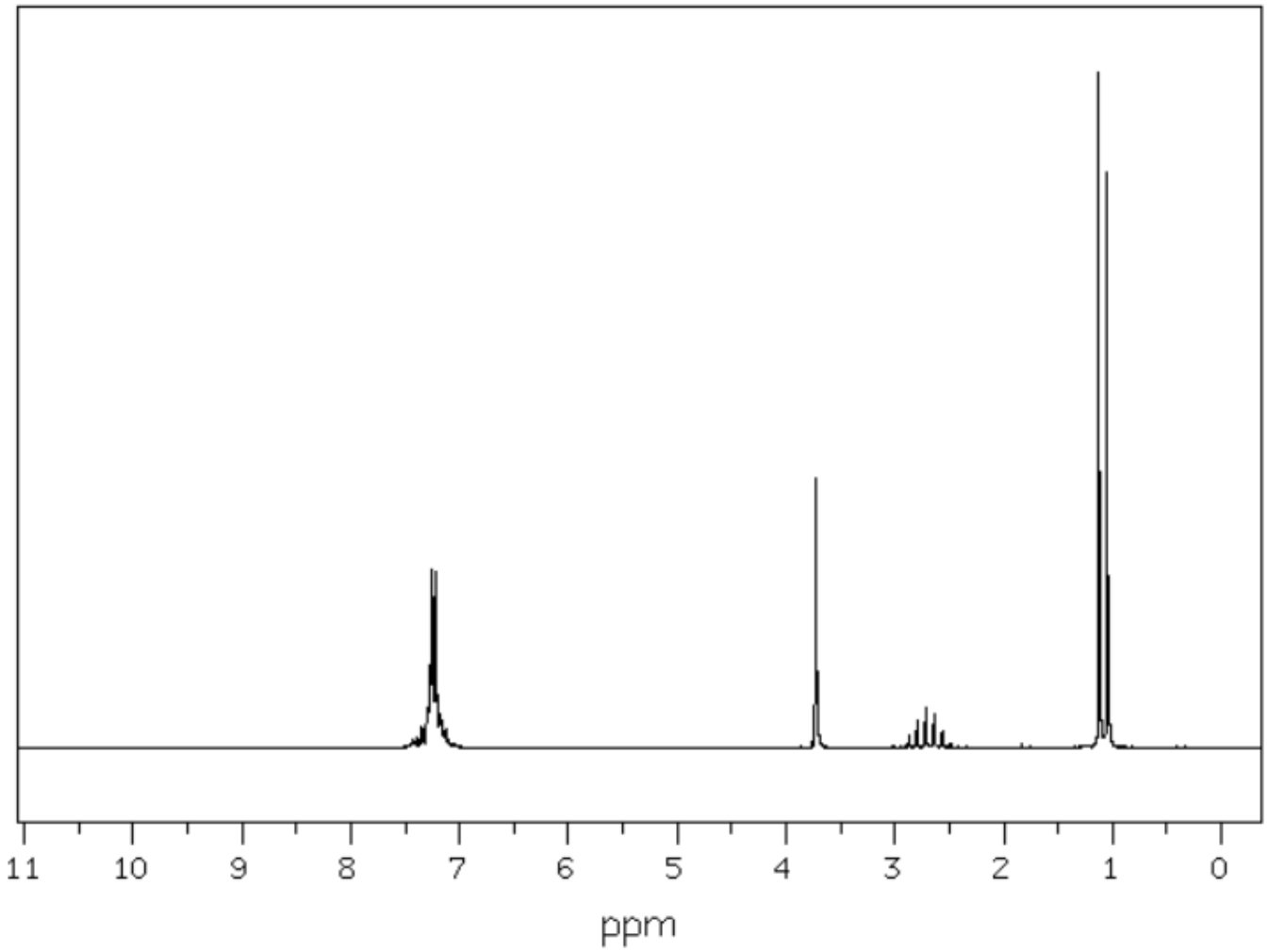
IR Spectrum:



Mass Spectrum:

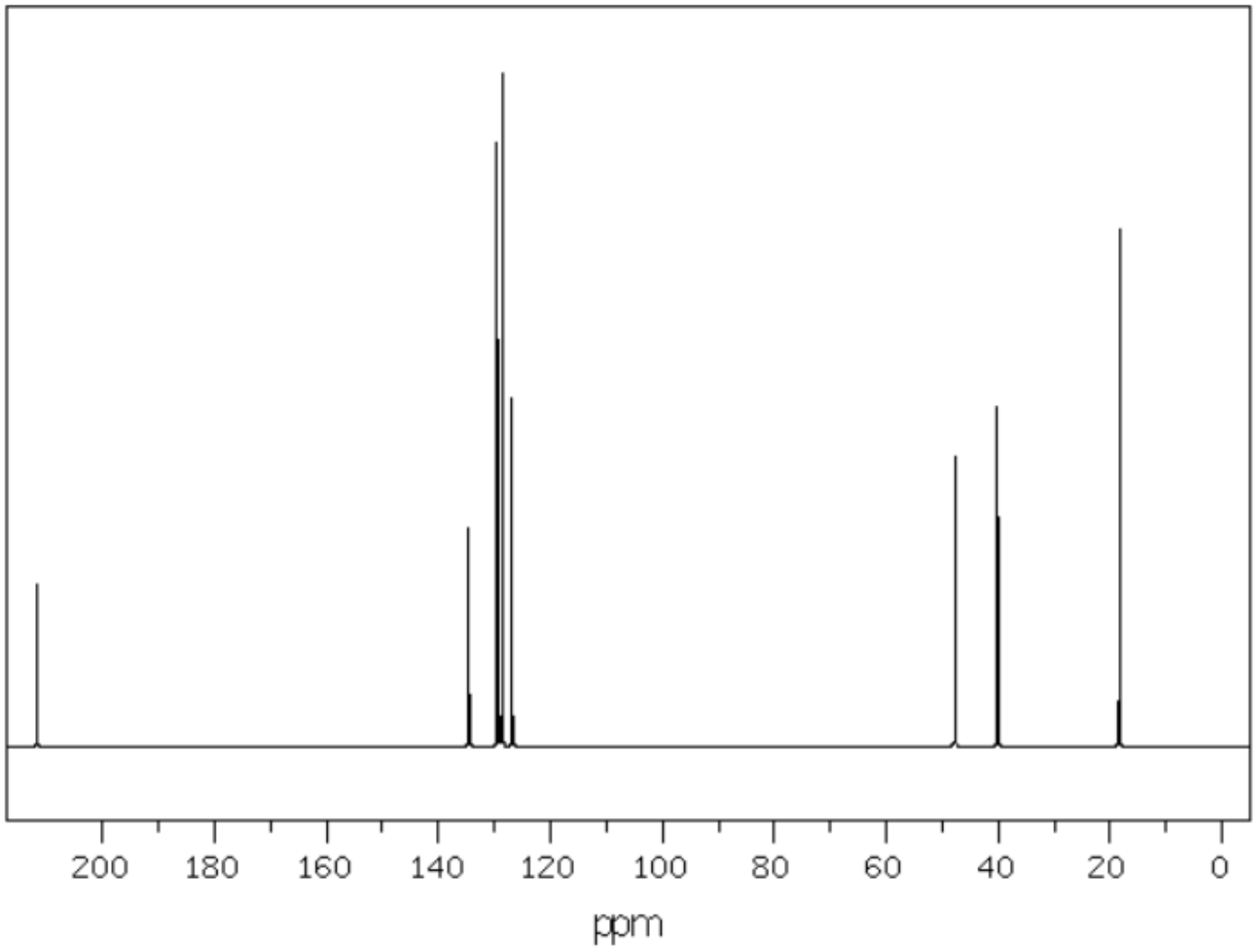


^{1}H NMR Spectrum:



Chemical Shift (ppm)	Multiplicity	Integration
7.47–7.02	multiplet	49
3.72	singlet	20
2.70	septet	10
1.09	doublet	59

Proton-decoupled ^{13}C NMR Spectrum:



Chemical Shift (ppm)	Multiplicity	Intensity
211.69	singlet	239
134.52	singlet	325
129.46	singlet	895
128.58	singlet	1000
126.82	singlet	517
47.66	singlet	431
40.06	singlet	502
18.31	singlet	766