

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)	Solutions
Student Signature	N/A

Instructions & Scoring

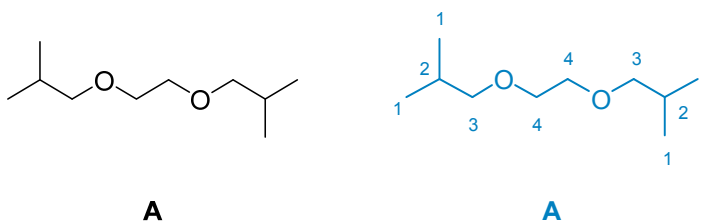
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes and your plastic model kit. No electronic resources are permitted 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

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.

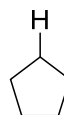
- (1) B How many signals appear in the proton-decoupled ^{13}C NMR spectrum for compound **A**? (Do not count signals that arise from solvent, reference standards, or impurities).



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

The sets of equivalent carbon atoms are labeled in the structure above.

- (2) A 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?



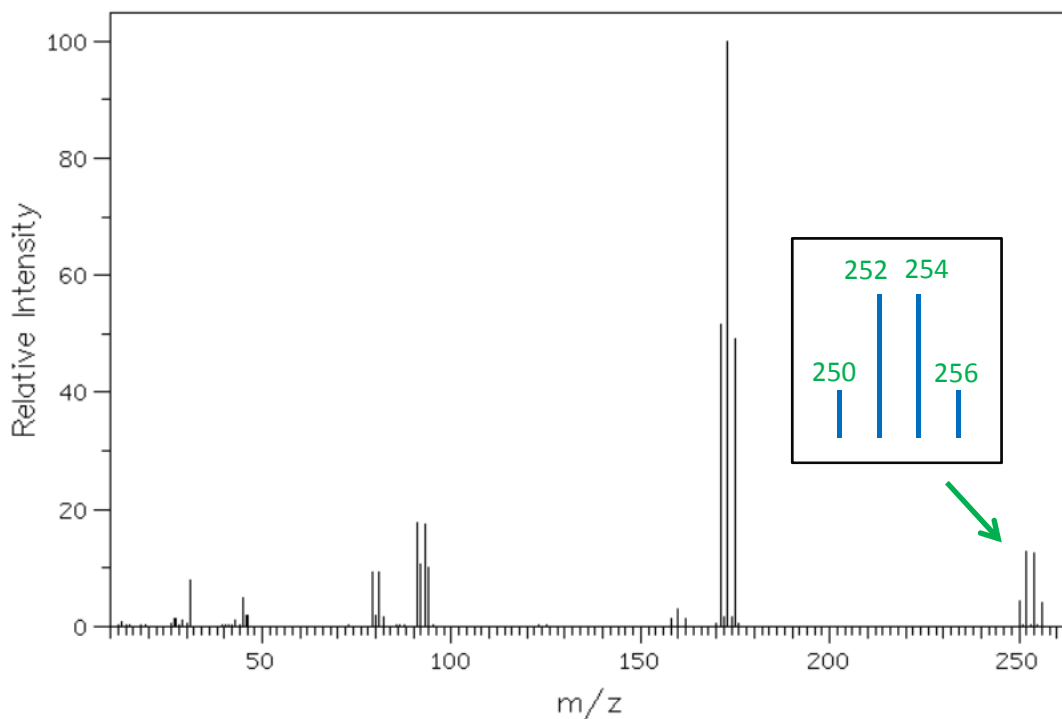
B

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

All of the hydrogen atoms in cyclopentane are equivalent, so there is no spin-spin splitting in the ^1H NMR spectrum. The spectrum contains a single singlet at δ 1.51.

(3) D

Compound **C** is composed solely of carbon, hydrogen, and bromine atoms. Given the mass spectrum below, which includes the molecular ion, how many bromine atoms does the molecule contain?



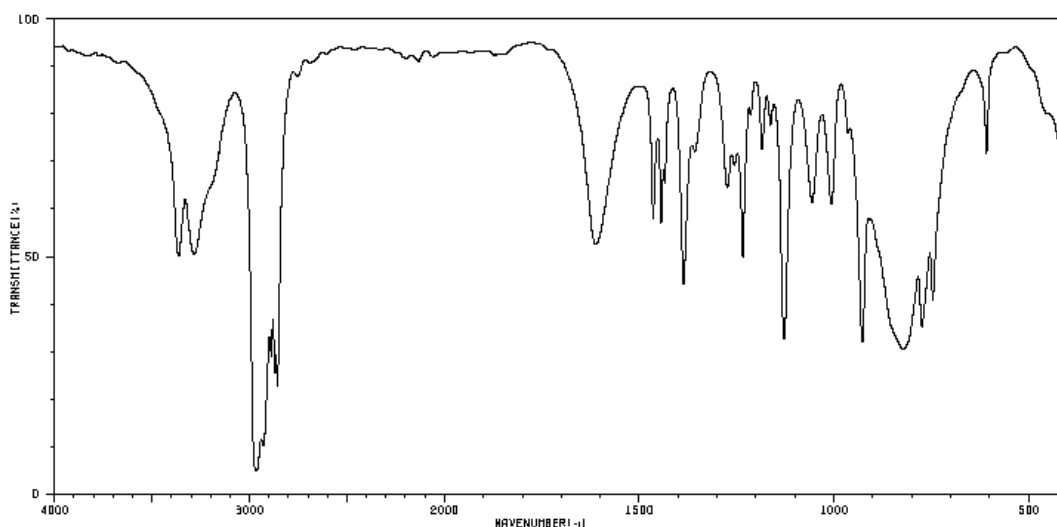
- (a) zero
- (b) one
- (c) two
- (d) three
- (e) four

This is a mass spectrum of tribromomethane.

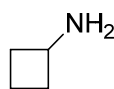
(4) E Which of the following statements is the most correct and complete of the choices given?

- (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

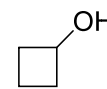
(5) B The IR spectrum shown below is consistent with which of the following structures?



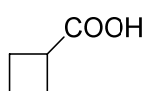
(a)



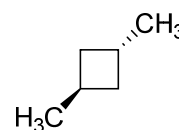
(b)



(c)



(d)

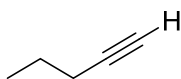


(e)

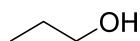
The key feature of the spectrum are the twin peaks above 3000 cm⁻¹. They are characteristic of primary amines and correspond to the symmetric and anti-symmetric N-H stretching modes.

(6) ^B

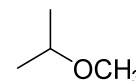
Which of the following compounds will lose one or more signals from its ^1H NMR spectrum when D_2O is selected as the solvent versus CDCl_3 ?



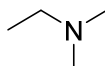
(a)



(b)



(c)



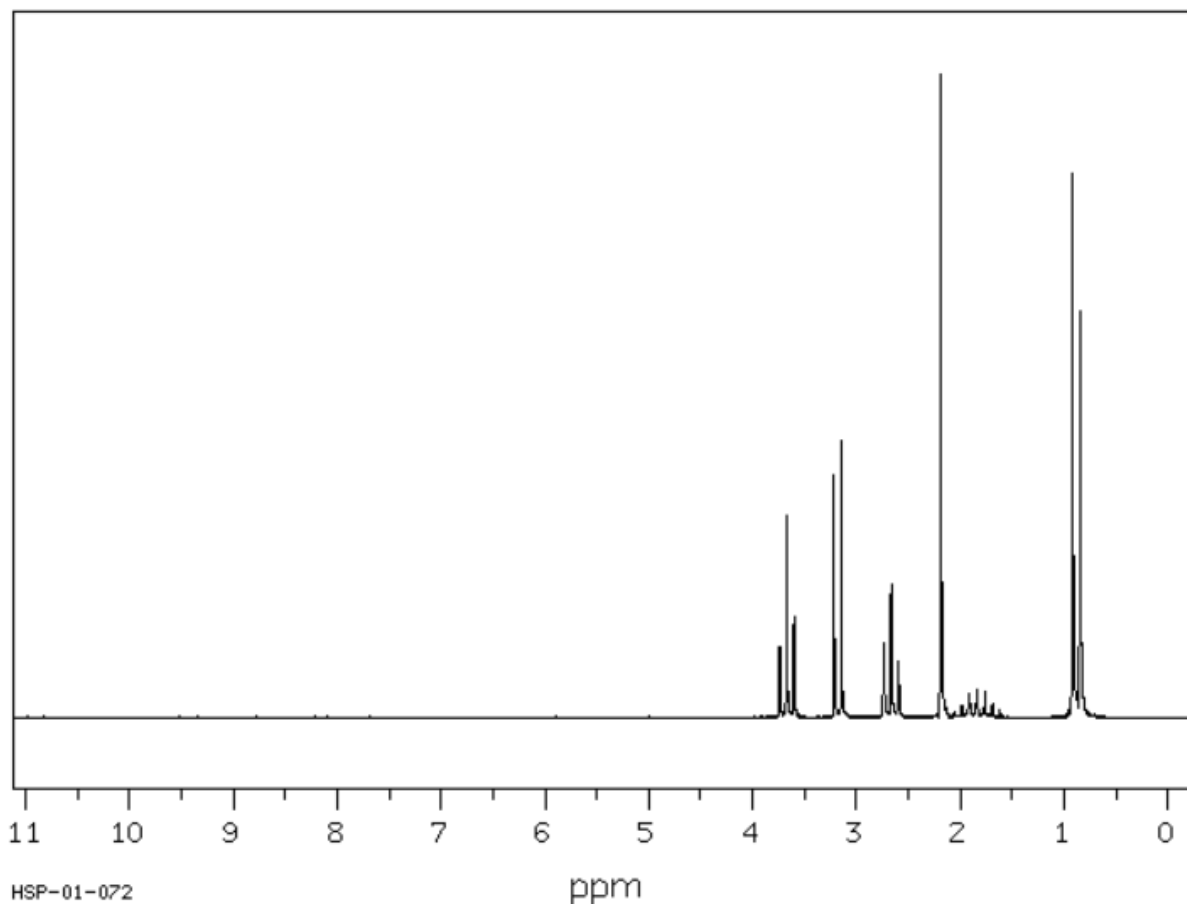
(d)



(e)

In protic deuterated solvent (e.g., D_2O or CH_3OD), protic ^1H hydrogens (those bonded to electronegative elements) on the sample compound will exchange for deuterium and their signal will disappear from the ^1H NMR spectrum.

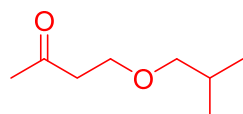
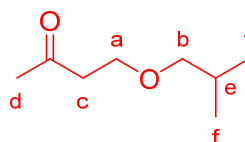
Problem II. Assignment of an NMR Spectrum (18 points). High-resolution mass spectral analysis of a pure sample of compound **D** reveals it to have a molecular formula of $C_8H_{16}O_2$. The 1H NMR spectrum of **D** in $CDCl_3$ has the following signals:



Source: Spectral Database for Organic Compounds, #6249
<http://sdb.sdb.aist.go.jp/>

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

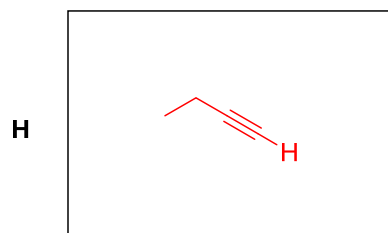
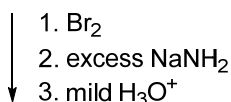
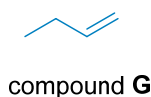
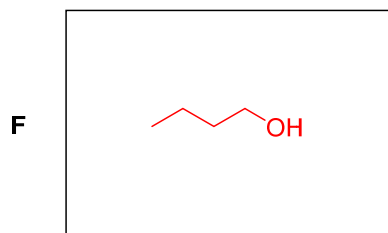
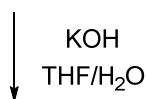
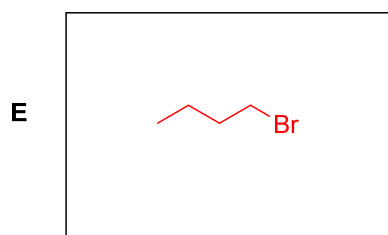
- (i) Draw a Lewis structure for compound **D** consistent with the data provided above.
 (ii) For each chemical shift, draw an arrow pointing to one of the hydrogens that gives rise to that signal.

**D****D**

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 ^1H 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 $\sim 1:1$. 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 $\text{C}_4\text{H}_{10}\text{O}$. Compound **F** has a ^{13}C NMR spectrum with four signals and a broad absorption peak at $\sim 3300\text{ cm}^{-1}$ 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 $\sim 3300\text{ cm}^{-1}$. 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.

Compounds & Reactions



Pertinent Spectral Data for Associated Compound

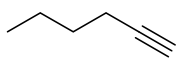
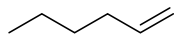
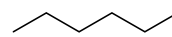
- Compound **H** is pure and has no optical activity
- None of the signals in ^1H NMR is a doublet
- Electron-impact MS has M^+ peak of 136 and $[M+2]^+$ peak of 138 in an intensity ratio of $\sim 1:1$

- High-resolution MS gives a molecular formula of $\text{C}_4\text{H}_{10}\text{O}$
- ^{13}C NMR spectrum has 4 signals
- IR spectrum has a broad peak $\sim 3300\text{ cm}^{-1}$

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

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

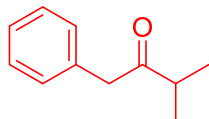
Problem IV. Explanation (11 points). Explain the following trend in the absorptions corresponding to the most energetic C–H stretching mode observed in the IR spectra of the following molecules.

**J**1-hexyne
3311 cm^{-1} **K**1-hexene
3079 cm^{-1} **L**1-hexyne
2959 cm^{-1}

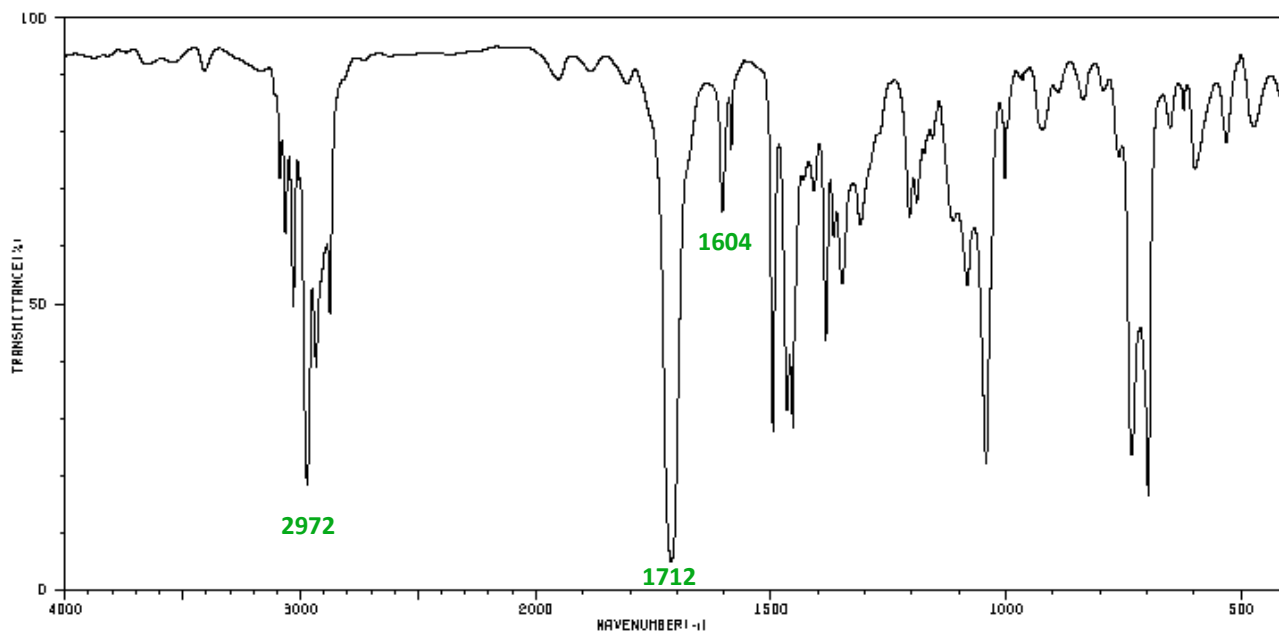
First, it is important to note we are comparing the C–H stretches, not stretches of C–C vs. C=C vs. C≡C. In compound **J**, the ≡C–H bond is formed by the overlap of an sp -hybridized orbital and a $1s$ orbital (on H). For **K**, the =C–H bond is formed by an sp^2 -hybridized orbital and a $1s$ orbital. For **L**, the C–H bonds are formed by sp^3 -hybridized orbitals and a $1s$ orbitals. Bonds that form from orbitals with more s character are typically stronger, stiffer bonds. Stronger bonds have stretching modes of higher energy, and thus, higher wavenumber absorptions in the IR.

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.

Correct answer: 3-methyl-1-phenyl-2-butanone

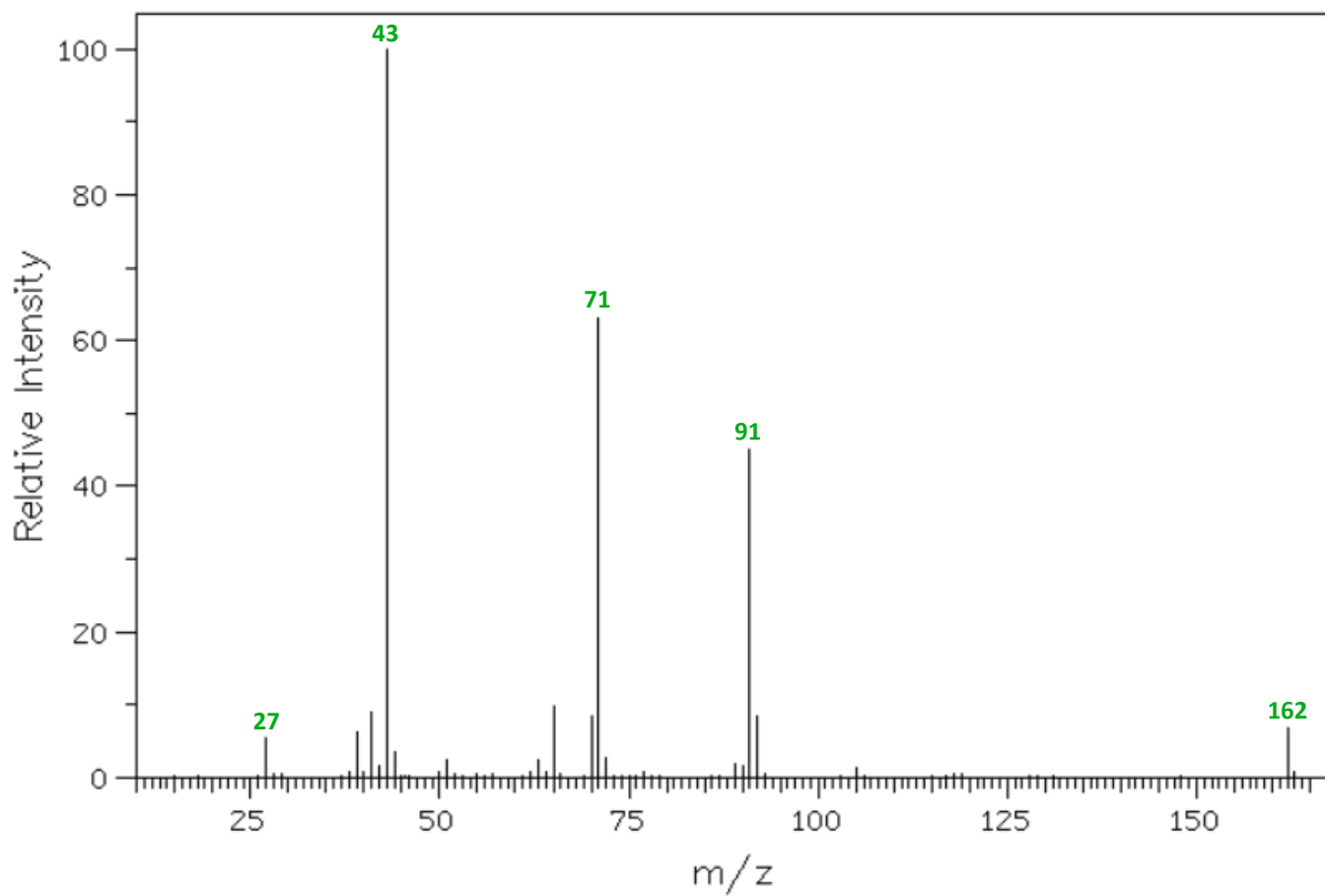
**N**

IR Spectrum:

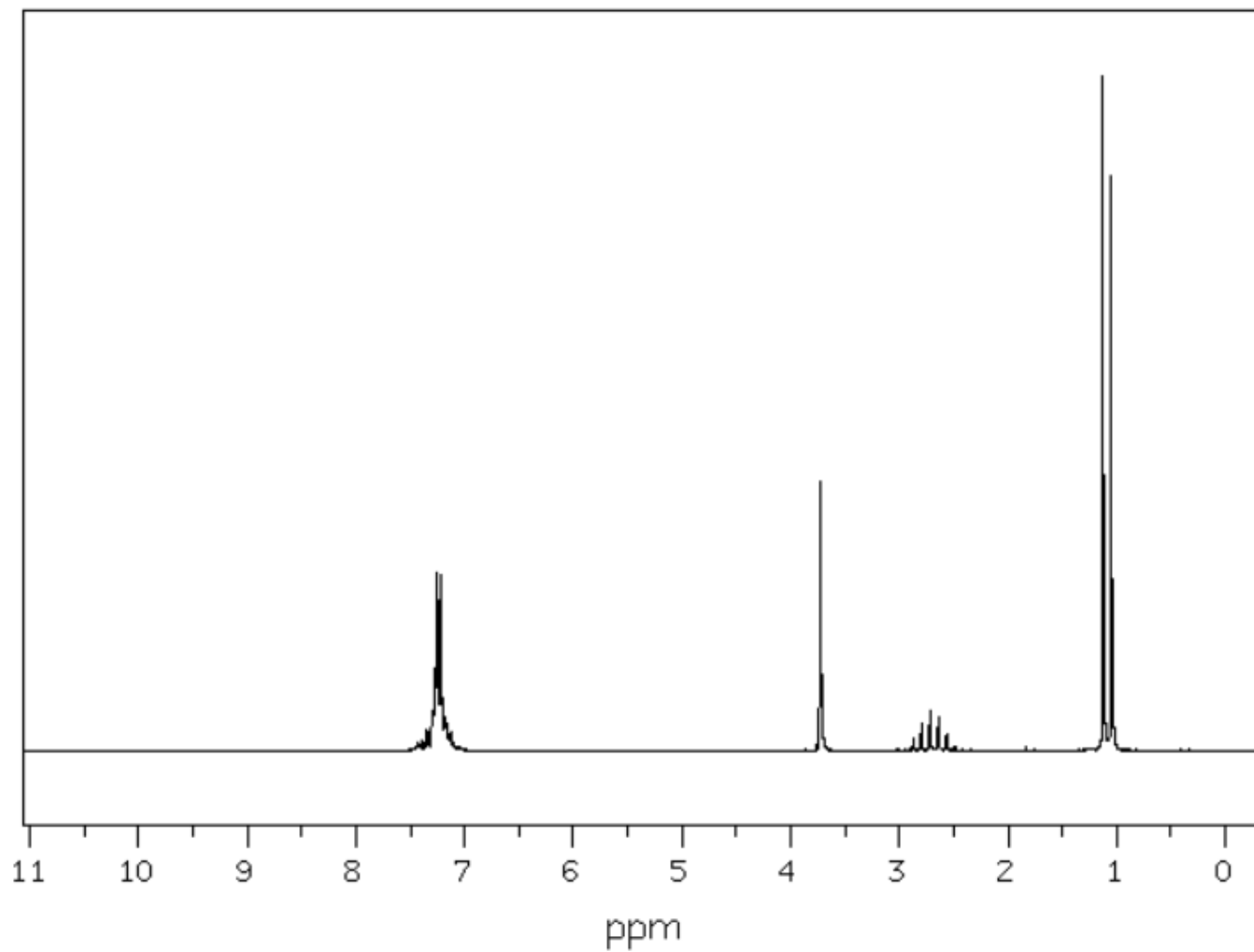


Source: Spectral Database for Organic Compounds, #6919
<http://sdfs.db.aist.go.jp/>

Mass Spectrum:

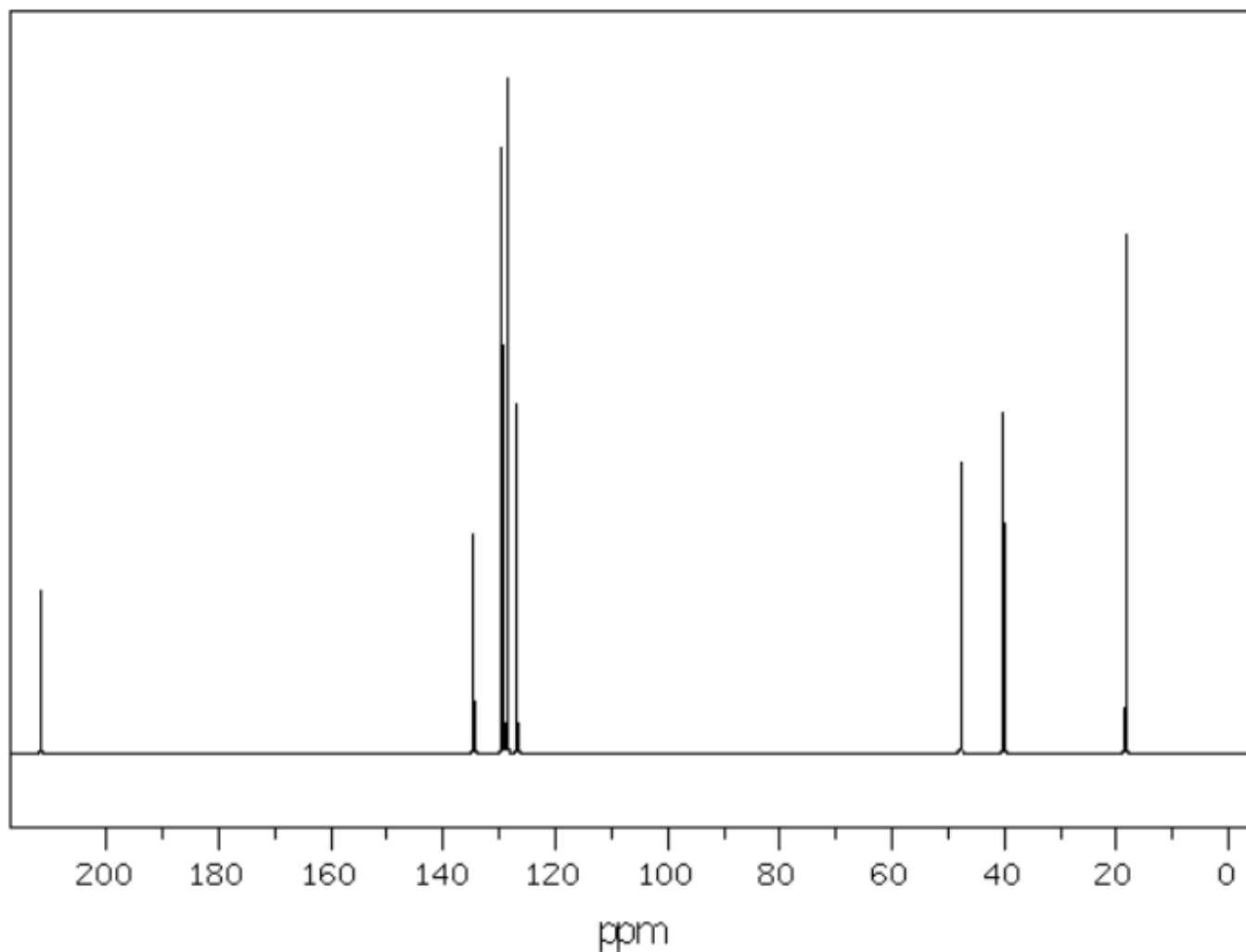


Source: Spectral Database for Organic Compounds, #6919
<http://sdfs.db.aist.go.jp/>

^1H NMR Spectrum:

Source: Spectral Database for Organic Compounds, #6919
<http://sdfs.db.aist.go.jp/>

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:

Source: Spectral Database for Organic Compounds, #6919
<http://sdfs.db.aist.go.jp/>

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