CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Hour Examination #4

Wednesday, December 2nd, 2015

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

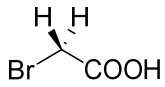
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources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

Problem	Points Earned	Points Available
I		30
II		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.

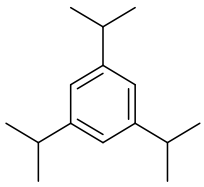
(1) A Which of the following statements regarding compound **A** is <u>not</u> true?



A

(a) the ^{1}H NMR spectrum of **A** has three signals
(b) the ^{13}C NMR spectrum of **A** has two signals
(c) the IR spectrum of **A** will have a strong absorption near 1725 cm^{-1}
(d) the IR spectrum of **A** will have a broad absorption ~2500–3500 cm^{-1}
(e) the molecular ion of **A** is split 1:1 between m/z 138 and 140

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



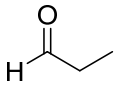
B

$C_{15}H_{24}$

(a) three
(b) four
(c) five
(d) six
(e) more than six

(3) D

The ^{1}H NMR spectrum of compound **C** contains three signals, two of which are split into triplets. What is the multiplicity of the third signal?



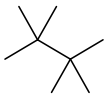
C

(a) singlet
(b) triplet
(c) quartet
(d) quartet of doublets
(e) triplet of triplets

(4) B

Which of the following compounds has one signal in its ^{1}H NMR spectrum or one signal in its ^{13}C NMR spectrum, but not just one signal in both spectra? In other words, which of the following compounds has an NMR spectrum with just one peak and the NMR spectrum of the other nucleus with more than one peak?

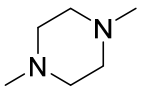
(a)



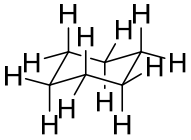
(b)

$H_2C{=}CHBr$

(c)

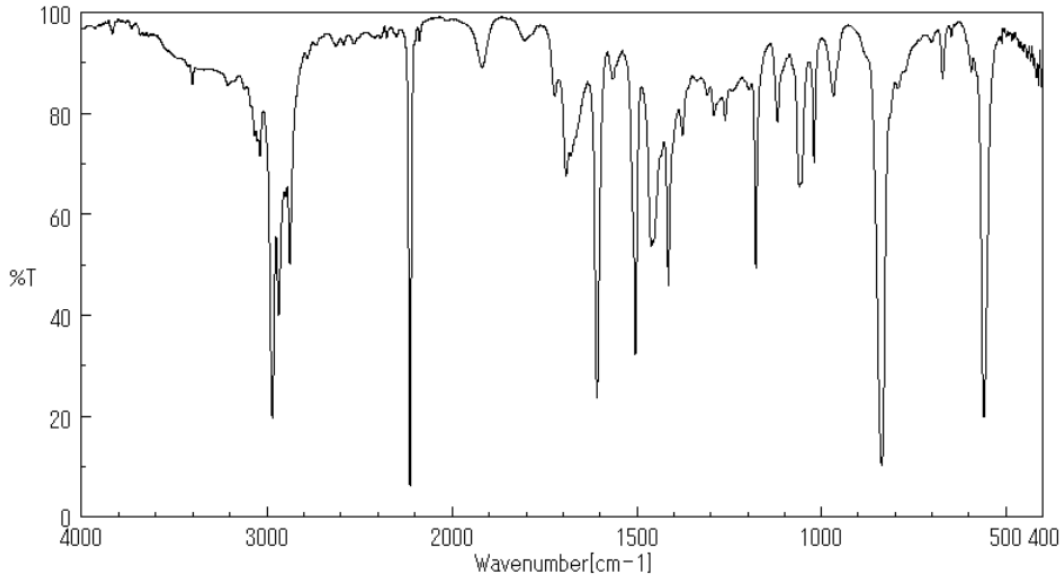


(d)

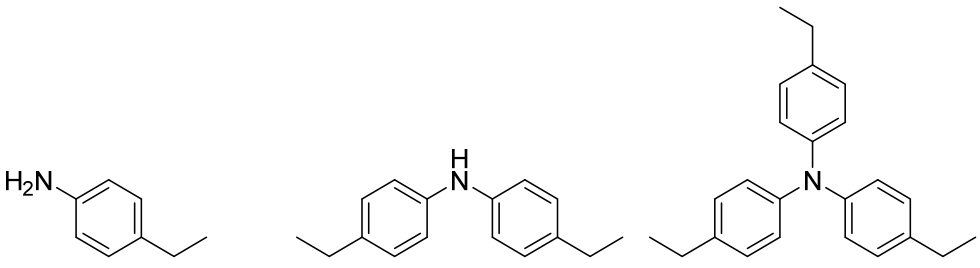


(e)

(5) D Which of the following compounds is consistent with the IR spectrum shown below?



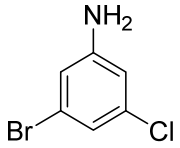
Source: Spectral Database for Organic Compounds, #51555
http://sdbs.db.aist.go.jp/



(a) (b) (c)

(d) (e)

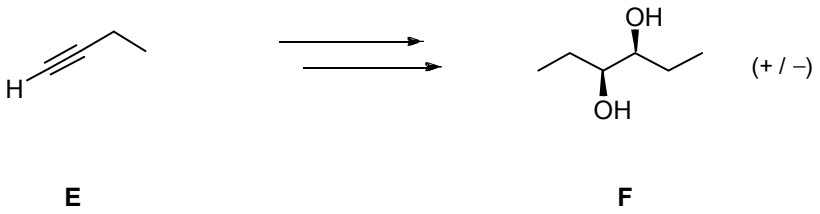
(6) C Which of the following statements regarding compound **D** is not true?



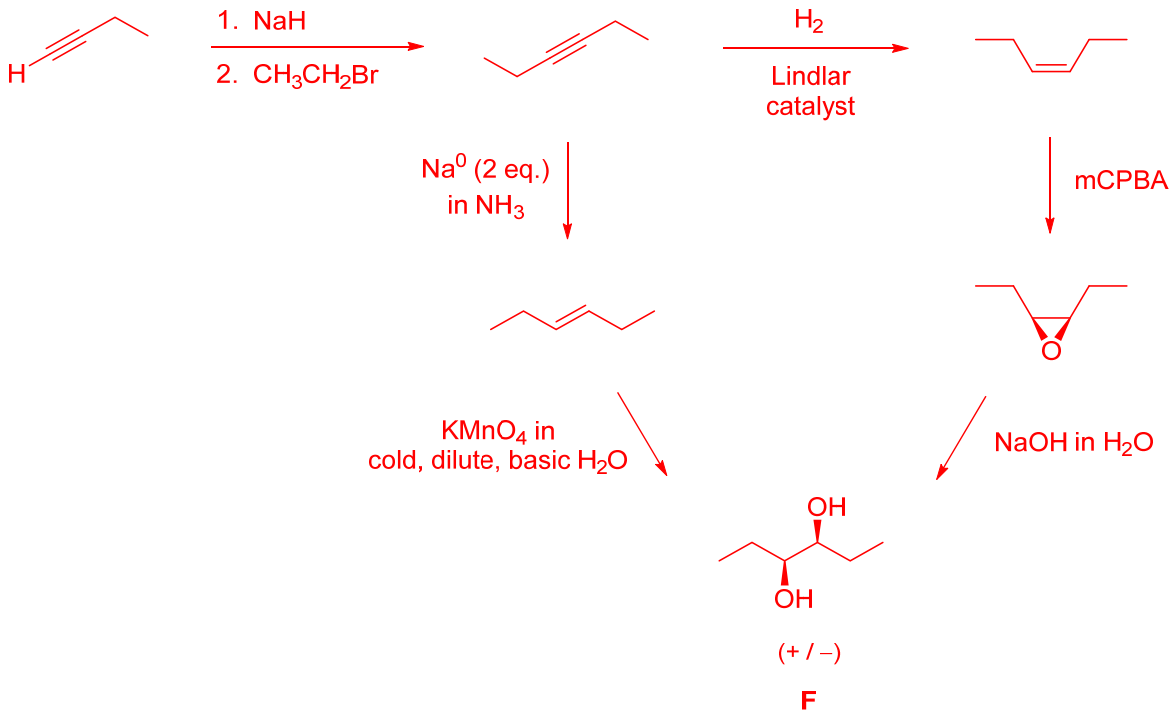
D

(a) one signal in the ^{1}H NMR spectrum of **D** in $CDCl_3$ will disappear when the solvent is changed to D_2O
(b) the molecular ion of **D** will have an m/z value that is odd (not even)
(c) the molecular ion of **D** will be split into two peaks in approximately 3:1 intensity
(d) the IR spectrum of **D** will have two absorptions >3000 cm^{-1} corresponding to N–H stretching
(e) none of the above (i.e., all of the above statements are correct)

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



E **F**

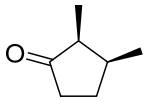
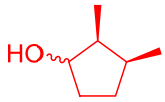
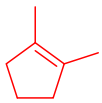
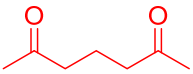


F

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

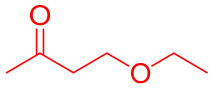
Compound **G** is the ketone shown below. Treatment of **G** with sodium borohydride in water affords compound **H** in a reaction you will learn next semester. **H** has a strong, broad absorption in the IR around 3300 cm^{-1} and no significant absorption near 1715 cm^{-1}. Its electron-impact mass spectrum has a molecular ion peak at m/z 114. Treatment of **H** with a catalytic amount of anhydrous sulfuric acid and heat yields **J** as the major product. The electron-impact mass spectrum of **J** has a molecular ion peak at m/z 96. Its ^{1}H NMR spectrum has three signals: δ 2.26, 1.75, 1.61, in a relative integration ratio of 2:1:3. When **J** is subjected to ozonolysis with reductive workup, a single organic product, **K**, is produced. **K** has a molecular ion of m/z 128. Its ^{13}C NMR spectrum has four signals and its IR spectrum has a strong absorption near 1718 cm^{-1}.

Source: Spectral Database for Organic Compounds, #16141
http://sdbs.db.aist.go.jp/

Compounds & Reactions	Pertinent Spectral Data for Associated Compound
 compound **G**	
$NaBH_4$ / H_2O	
H  (draw either of two diastereomers)	• Broad IR absorption ~3300 cm^{-1}; no strong absorption near 1715 cm^{-1} • Electron-impact MS has M^+ peak of m/z 114
H_2SO_4	
J 	• Electron-impact MS has M^+ peak of m/z 96 • ^{1}H NMR spectrum has three signals: δ 2.26, 1.75, 1.61 with an integration ratio of 2:1:3
1. O_3 2. DMS	
K 	• Electron-impact MS has M^+ peak of m/z 128 • ^{13}C NMR spectrum has four signals • Broad IR absportion ~1718 cm^{-1}

Problem IV. Assignment of an NMR Spectrum (18 points). High-resolution mass spectral analysis of a pure sample of compound **M** reveals it to have a molecular formula of $C_6H_{12}O_2$. The ^1H NMR spectrum of **M** in $CDCl_3$ has the following signals:

Chemical Shift (ppm)	Multiplicity	Integration
3.67	triplet	8
3.50	quartet	8
2.68	triplet	8
2.18	singlet	13
1.18	triplet	12



M

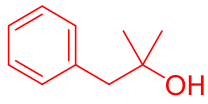
4-ethoxy-2-butanone

Source: Spectral Database for Organic Compounds, #5540
http://sdbs.db.aist.go.jp/

(i) Draw a Lewis structure for compound **M** 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 (18 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.

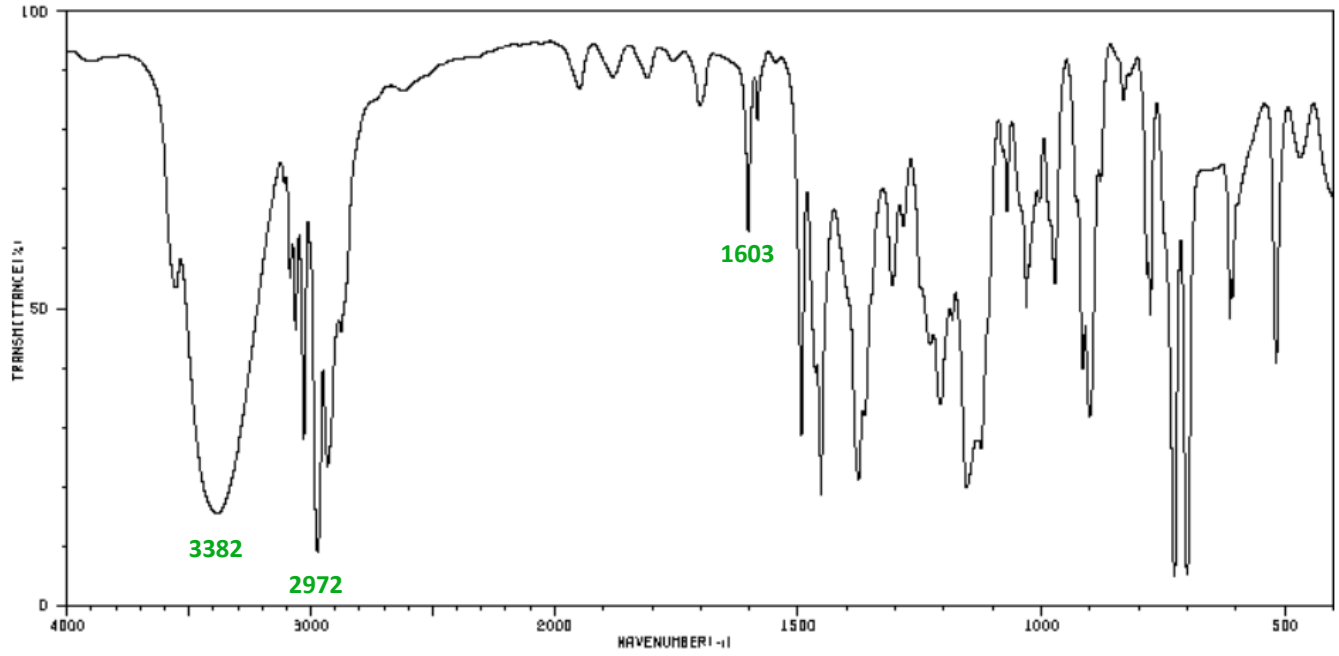


N

2-methyl-1-phenyl-2-propanol

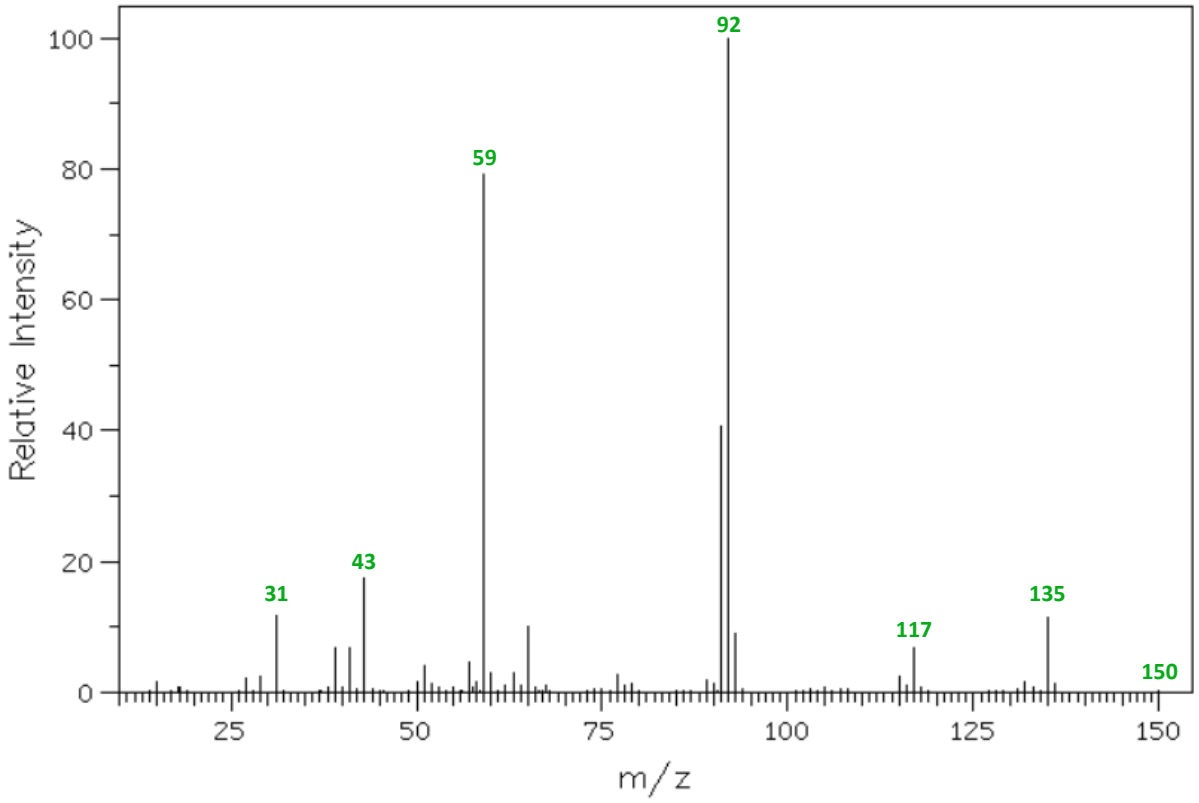
Source: Spectral Database for Organic Compounds, #6739
http://sdbs.db.aist.go.jp/

IR Spectrum:



Source: Spectral Database for Organic Compounds, #6739
http://sdbs.db.aist.go.jp/

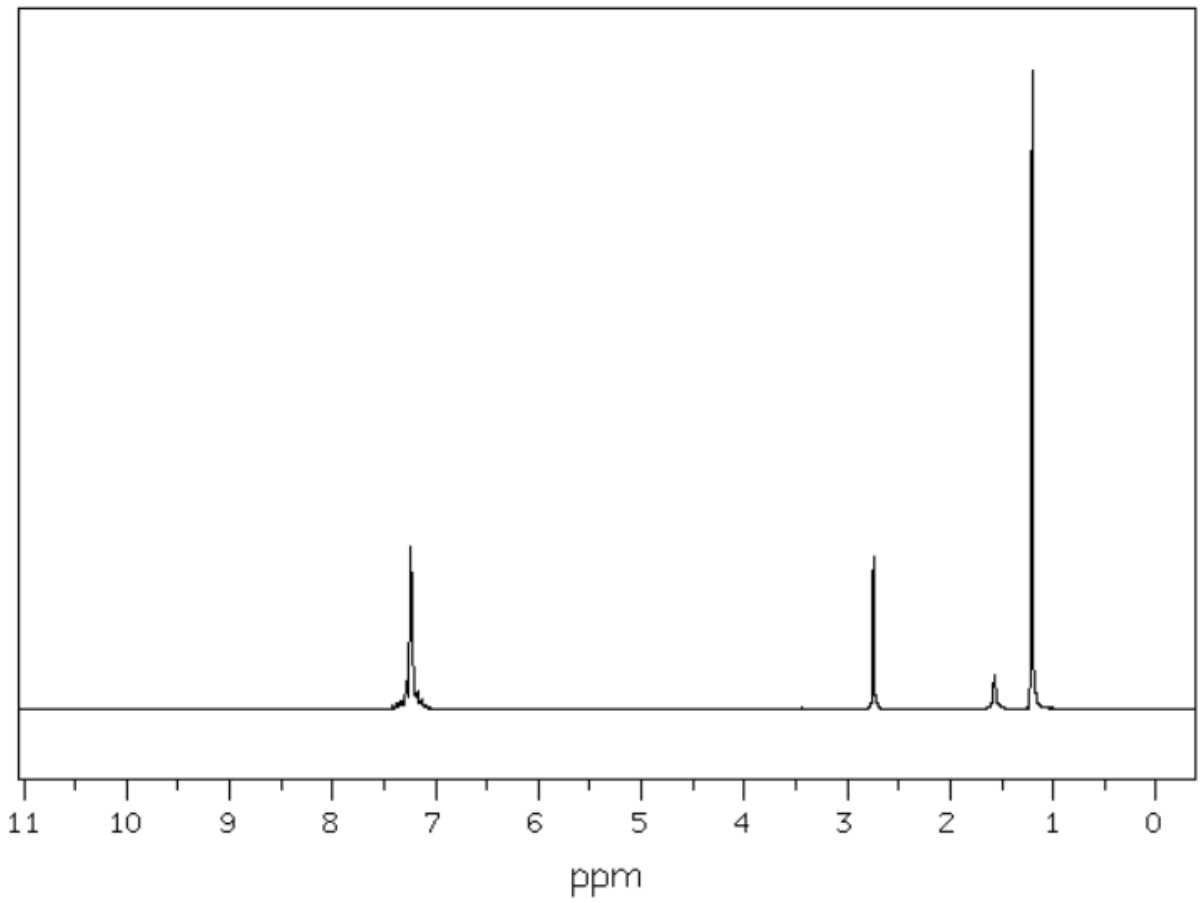
Mass Spectrum:



Source: Spectral Database for Organic Compounds, #6739
http://sdbs.db.aist.go.jp/

Note: Yes, there is indeed a small peak at m/z 150

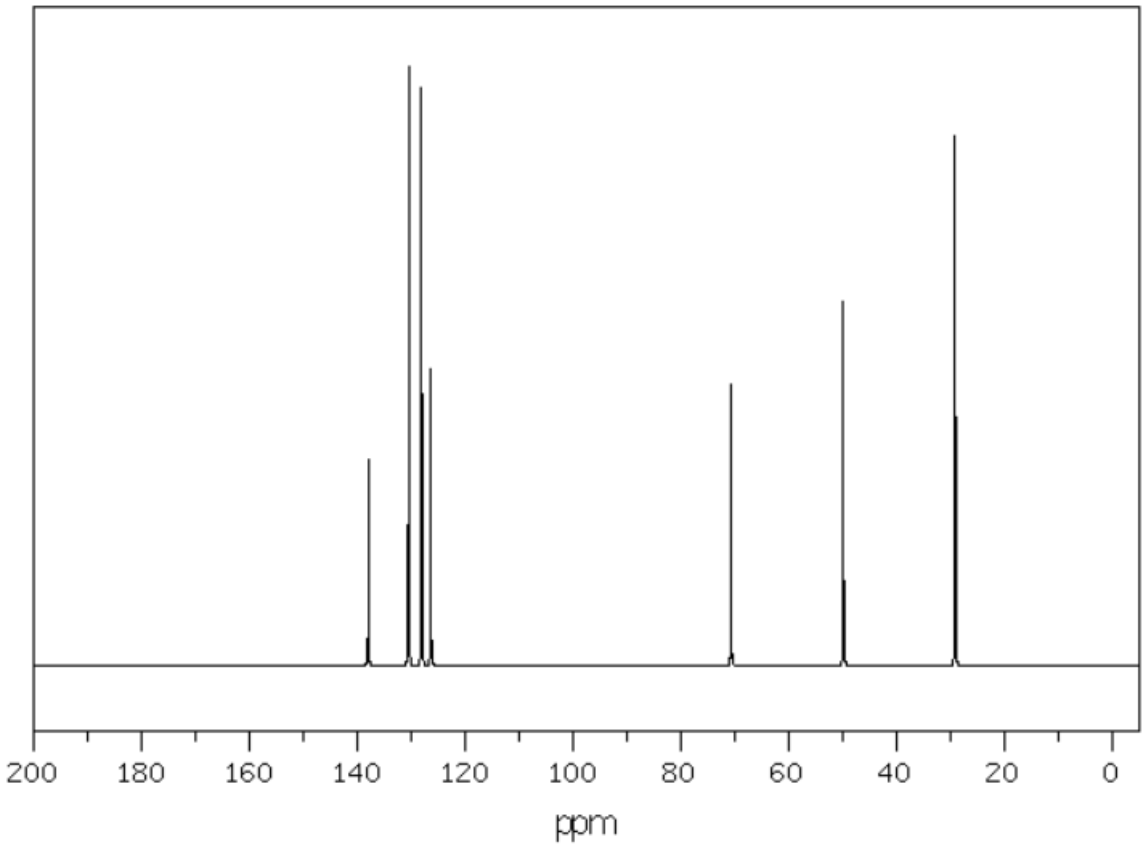
^{1}H NMR Spectrum:



Source: Spectral Database for Organic Compounds, #6739
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Integration
7.45–7.03	multiplet	34
2.75	singlet	14
1.57	singlet	7
1.21	singlet	43

Proton-decoupled ^{13}C NMR Spectrum:



Source: Spectral Database for Organic Compounds, #6739
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Intensity
137.96	singlet	344
130.48	singlet	1000
128.07	singlet	962
126.36	singlet	495
70.69	singlet	468
49.87	singlet	608
29.14	singlet	882