CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Quiz #5

Due: Monday, December 1st, 2014

5:00 p.m. (in Monsanto Hall 103)

Student Name (Printed)	
Student Signature	

Instructions & Scoring

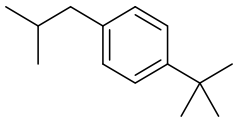
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. You must submit a hard copy of your answer sheet. Answer sheets submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should 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		18
III		21
IV		11
V		20
TOTAL		100

This quiz focuses on Chapters 13 and 14 in Janice Smith's *Organic Chemistry*, 4th ed.

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.

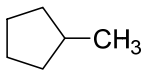
(1) _____ How many signals appear in the proton-decoupled ^{13}C NMR spectrum for compound **A**? (Do not count signals that arise from solvent, reference standards, or impurities).



A

(a) eight
(b) nine
(c) eleven
(d) thirteen
(e) fourteen

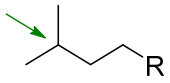
(2) _____ How many sets of protons with equivalent chemical shifts are found in compound **B**?



B

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

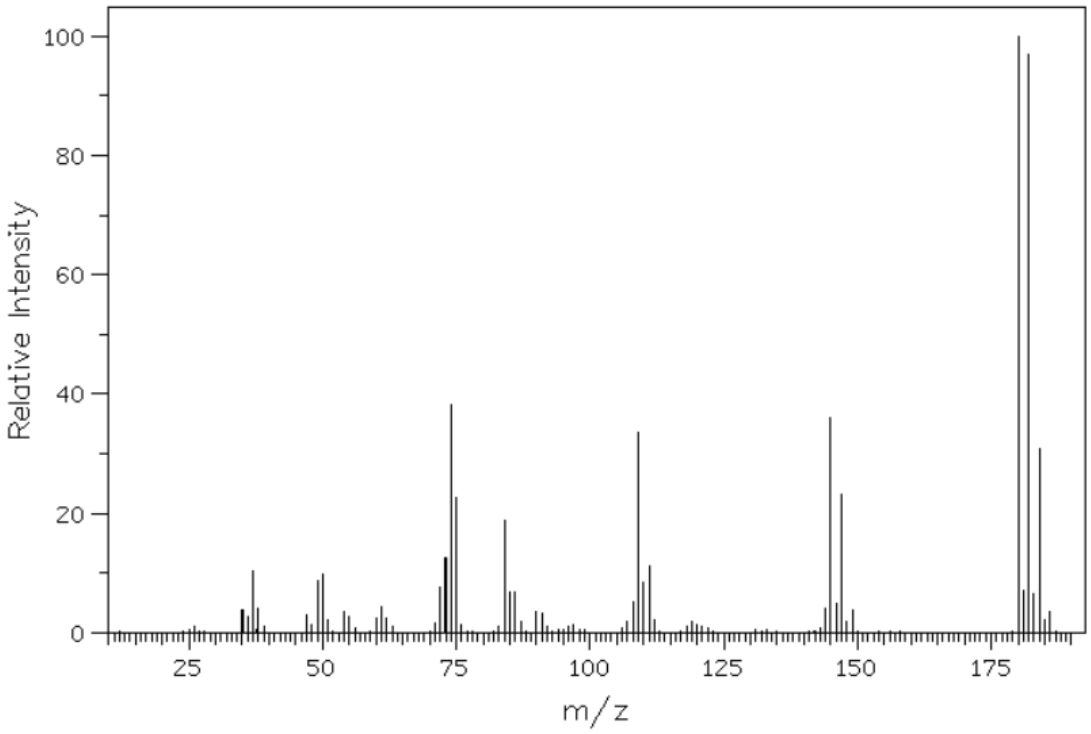
(3) _____ If all of the protons on adjacent carbon atoms in compound **C** were to couple with identical coupling constants (*J*), into how many smaller peaks would the signal for the indicated proton be split (e.g., a doublet is split into 2 peaks, a triplet is split into 3 peaks, etc.)?



C

(a) four
(b) seven
(c) nine
(d) twelve
(e) twenty-one

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

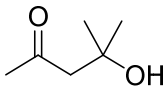


(a) zero
(b) one
(c) two
(d) three
(e) four

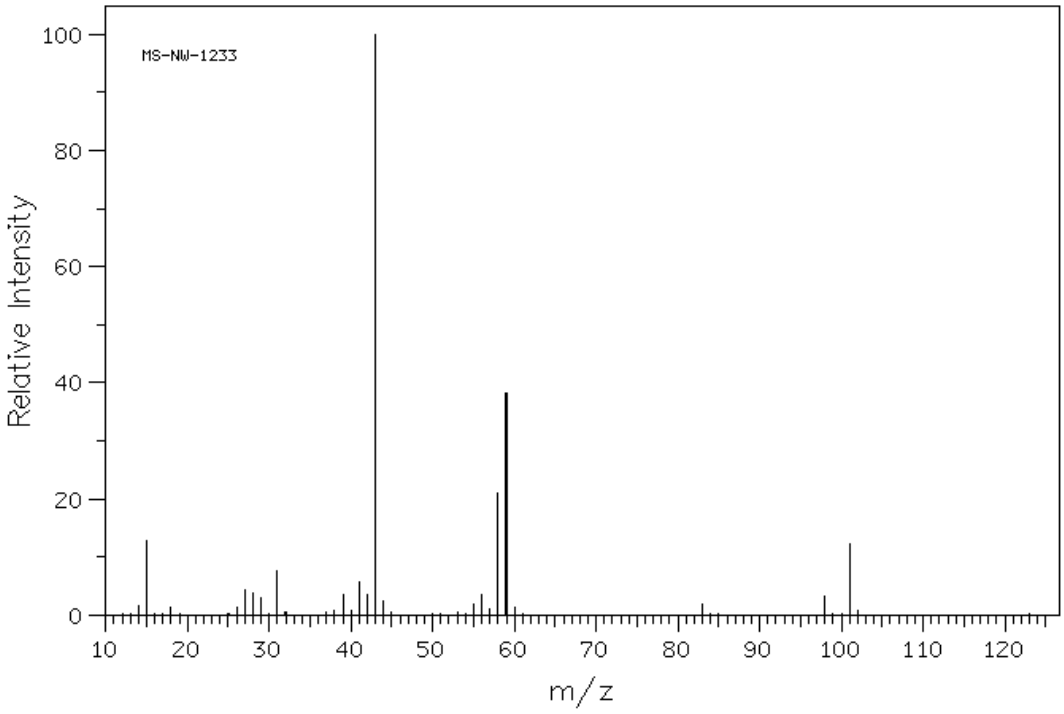
(5) _____ Which of the following statements is most correct?

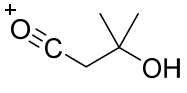
(a) a sample of methane that is 100% 16 Da (atomic mass units) will have one peak in its ^{12}C NMR spectrum
(b) a sample of methane that is 100% 16 Da (atomic mass units) will have zero peaks in its ^{13}C NMR spectrum
(c) a sample of methane that is 100% 16 Da (atomic mass units) will have zero peaks corresponding to stretches in its IR spectrum
(d) statements (a) and (b) are both correct
(e) statements (a), (b), and (c) are all correct

(6) _____ Which of the following species does <u>not</u> correspond to the peak of a fragment in the mass spectrum of 4-hydroxy-4-methyl-2-pentanone (**E**)?



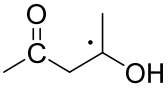
E





(a)

(b)



(c)

(d)

all of the above fragments appear in the spectrum

(e)

Problem II. Assignment of an NMR Spectrum (18 points). High-resolution mass spectral analysis of a pure sample of compound **G** reveals it to have a molecular formula of $C_6H_8Cl_2O$. The ^1H NMR spectrum of **G** in CCl_4 has the following signals:

Signal	Chemical Shift (ppm)	Multiplicity	Integration
a	2.27	singlet	1000
b	2.18	doublet	334
c	1.57	singlet	1000
d	1.23	doublet	334

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

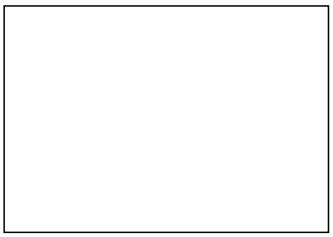
Problem III. (21 points) Roadmap Problem. Provide structures for compounds **H**, **K**, and **M** given the information listed below.

Compound **H** has no stereoisomers and an ^{1}H NMR spectrum that (among other signals) includes a singlet. The molecular ion peak for **H** is split into major peaks at m/z 162 and 164, and these peaks have relative intensities of 100:97. When **H** is treated with potassium *tert*-butoxide, compound **J** is the major product. Compound **J** has a ^{13}C NMR spectrum with four signals. Hydroboration–oxidation of **J** yields **K** as the major product. High-resolution mass spectrometry of **K** reveals it to have a molecular formula of $C_6H_{12}O$. The infrared spectrum of **K** has a broad absorption near 3400 cm^{-1} and no significant peak between 1700 and 1800 cm^{-1}. When **K** is treated with an aqueous solution of potassium permanganate, compound **M** is produced as the major product. The mass spectrum of **M** has a molecular ion at m/z 114, and its ^{1}H NMR spectrum has a broad peak at δ 11.89 that disappears upon addition of D_2O. The IR spectrum of **M** has a very broad and intense absorption from ~2200–3600 cm^{-1}

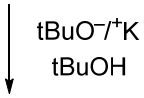
<u>Compounds & Reactions</u>

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

H

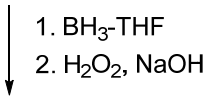


- ^{1}H NMR spectrum includes a signal that is a singlet
- Has no stereoisomers
- Electron-impact MS has M^+ peak of 162 and $[M+2]^+$ peak of 164 in an intensity ratio of 100:97

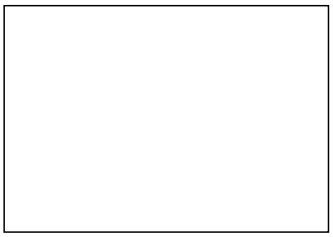


- ^{13}C NMR spectrum has 4 signals

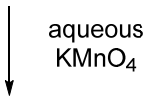
compound **J**



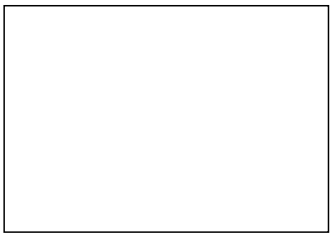
K



- High-resolution MS gives a molecular formula of $C_6H_{12}O$
- IR spectrum has a broad peak ~3400 cm^{-1}
- IR spectrum has no significant absorption between 1700 and 1800 cm^{-1}

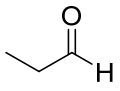


M



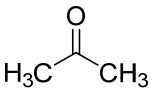
- ^{1}H NMR spectrum has a broad peak at δ 11.89 that disappears upon addition of D_2O
- MS has M^+ peak at m/z 114
- IR spectrum has a very broad and intense absorption from ~2200–3600 cm^{-1}

Problem IV. Explanation (11 points). Explain the following trend in the absorption corresponding to C=O stretching in the IR spectra of the following molecules. Hint: consider the two predominant resonance forms for carbonyl groups.



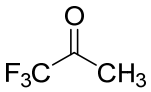
propanal

1739 cm^{-1}



acetone

1715 cm^{-1}

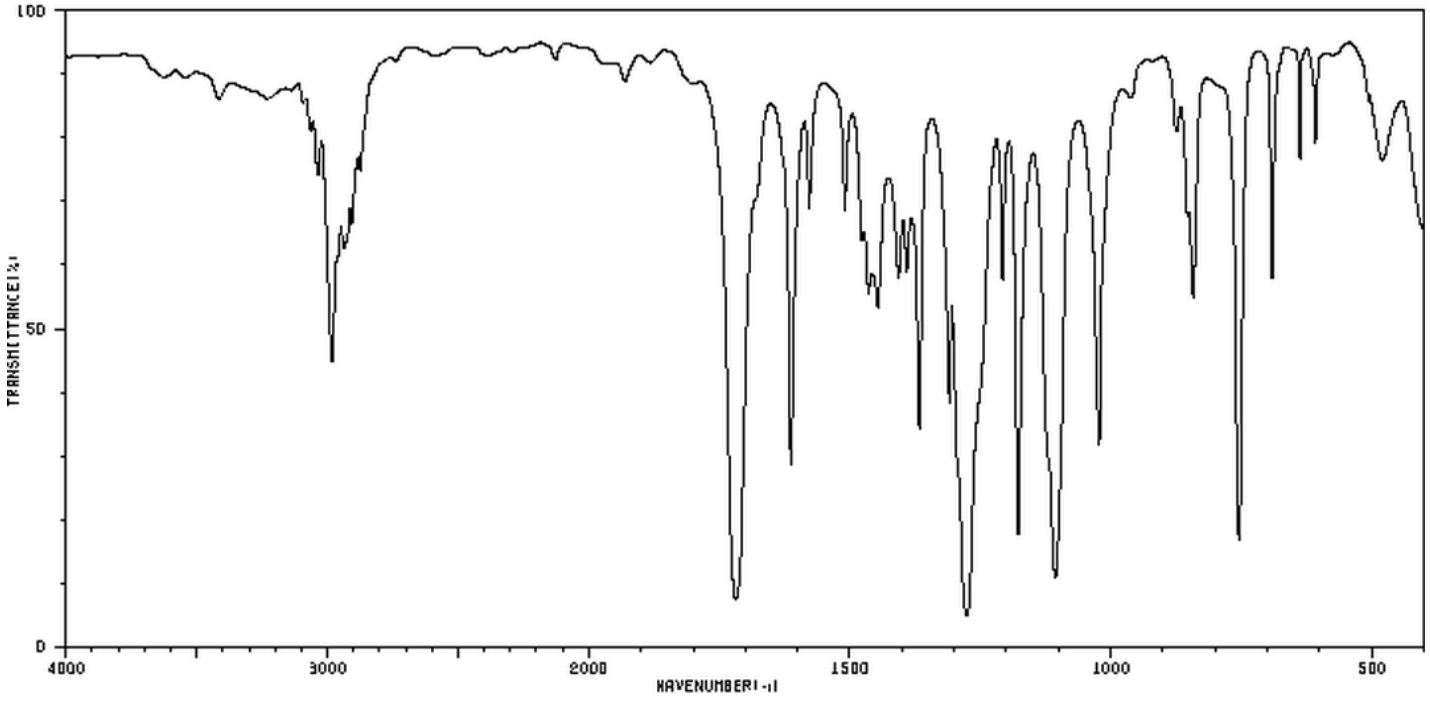


1,1,1-trifluoroacetone

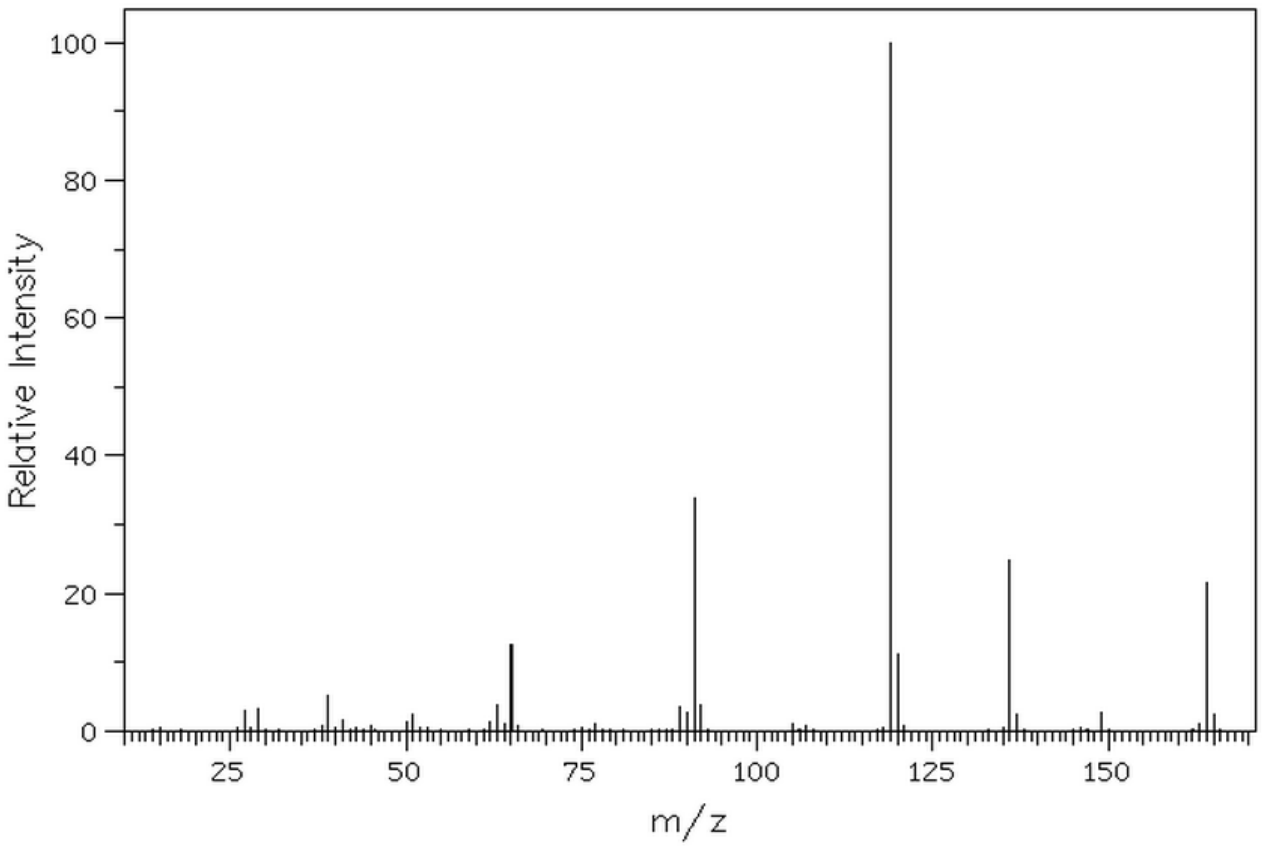
1771 cm^{-1}

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:



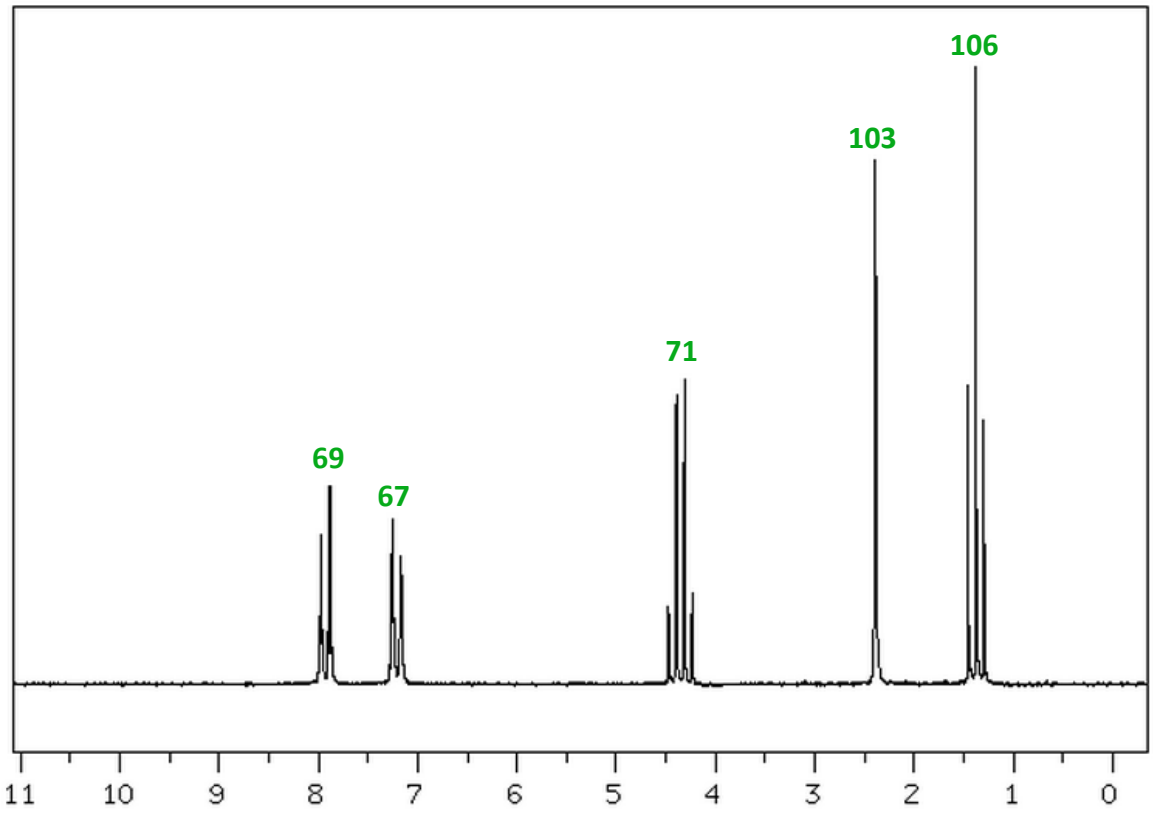
Mass Spectrum:



m/z	Intensity
27.0	3.1
29.0	3.2
39.0	5.1
41.0	1.6
50.0	1.4
51.0	2.4
62.0	1.2
63.0	3.8
64.0	1.1
65.0	12.4
77.0	1.1
89.0	3.6
90.0	2.6
91.0	33.9
92.0	3.9
105.0	1.1
119.0	100.0
120.0	11.1
136.0	24.9
137.0	2.4
149.0	2.8
163.0	1.0
164.0	21.5
165.0	2.4

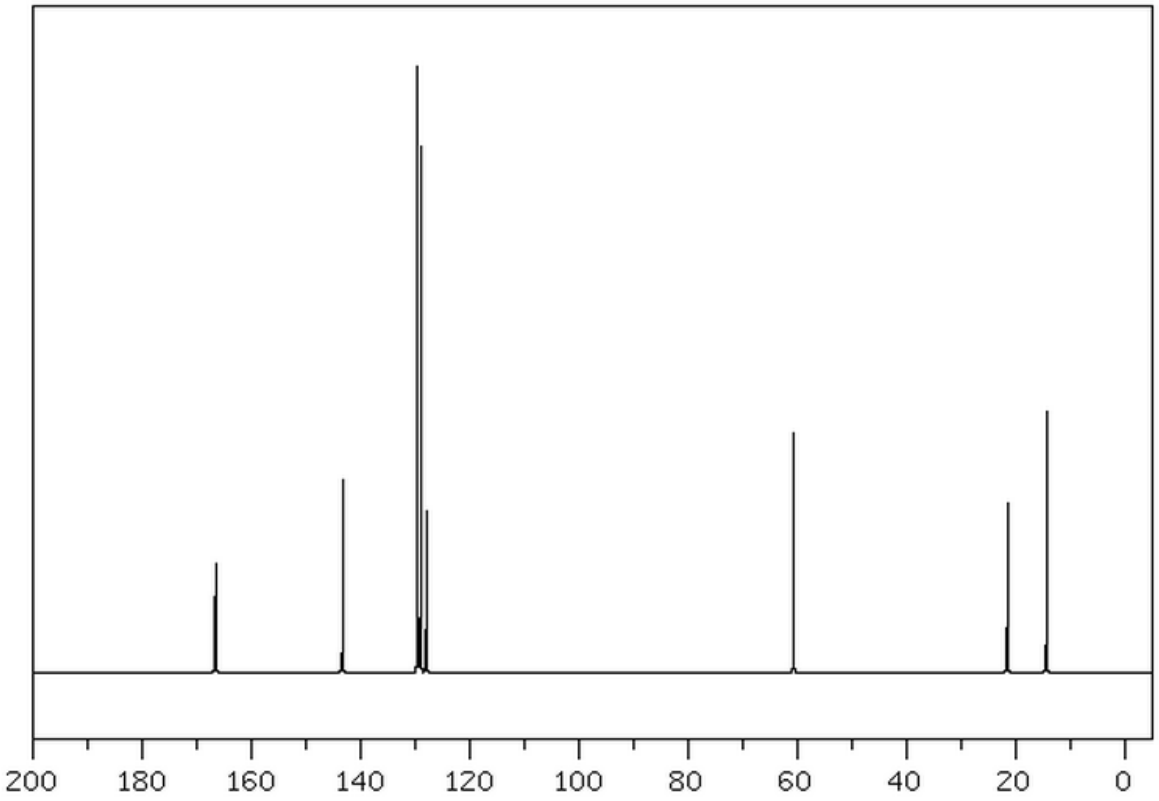
^{1}H NMR Spectrum:

Integrations listed in green over signals



Hz	ppm	Inten.
716.13	7.997	30
714.38	7.977	243
712.69	7.958	89
707.88	7.904	88
706.13	7.885	321
704.38	7.865	59
652.25	7.283	33
650.50	7.264	211
649.81	7.256	267
648.50	7.241	105
647.81	7.234	76
643.88	7.190	54
643.19	7.182	79
642.56	7.175	136
641.94	7.168	206
641.25	7.161	176
639.50	7.141	32
400.56	4.473	127
393.44	4.394	468
386.31	4.314	494
379.19	4.234	148
214.00	2.390	848
130.25	1.455	485
123.25	1.377	1000
116.06	1.296	427

Proton-decoupled ^{13}C NMR Spectrum:



Chemical Shift (ppm)	Multiplicity	Intensity
166.61	singlet	179
143.35	singlet	318
129.63	singlet	1000
129.04	singlet	866
127.99	singlet	264
60.69	singlet	393
21.55	singlet	279
14.36	singlet	428