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)	Solutions
Student Signature	N/A

Instructions & Scoring

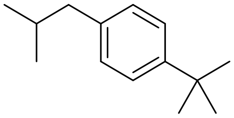
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. You must submit a hard copy of your answer sheet. Answer sheets submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should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

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.

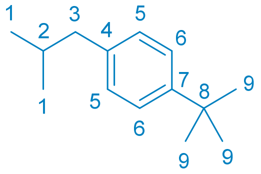
(1) ____B____ How many signals appear in the proton-decoupled ^{13}C NMR spectrum for compound **A**? (Do not count signals that arise from solvent, reference standards, or impurities).



A

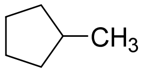
(a) eight
(b) nine
(c) eleven
(d) thirteen
(e) fourteen

The nine sets of equivalent carbon atoms in compound **A** are:

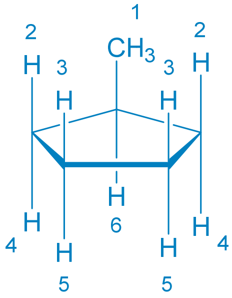


A

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



B

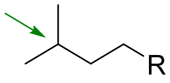


B

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

The six sets of equivalent hydrogen atoms in compound **B** are labeled above.

(3) C 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.)?

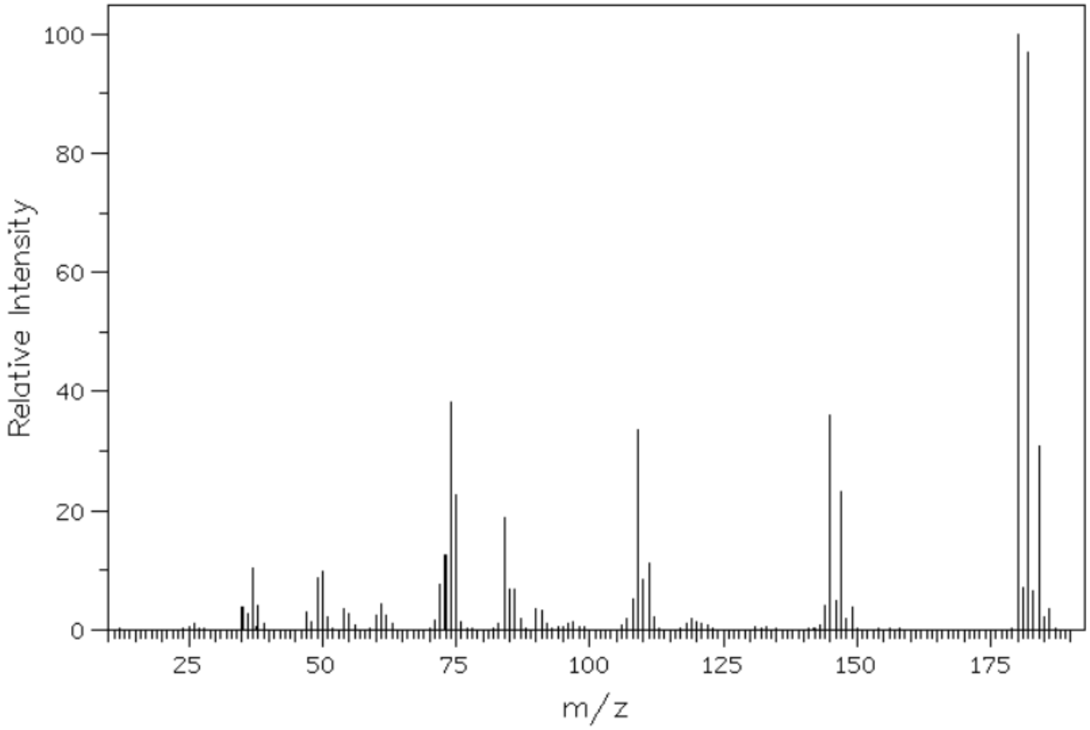


C

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

When all the *J* values are equal, you apply the m+n+1 rule. Here, that is 6+2+1 = 9.

(4) ___D___ 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 chlorine atoms does the molecule contain?



Source: Spectral Database for Organic Compounds, #546
http://sdbs.db.aist.go.jp/

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

The key feature of spectra with chlorine atoms is the divided molecular ion peak that corresponds to the fact that the relative abundance of ^{35}Cl:^{37}Cl is approximately 75:25. Thus, hydrocarbons with one chlorine atom will have an M:M+2 peak intensity ratio of 75:25 (or 3:1). With two chlorine atoms, the M:M+2:M+4 ratio is 56:38:6. With three chlorine atoms, the M:M+2:M+4:M+6 ratio is 42:42:14:2. This is the approximate pattern observed above (in the mass spectrum for 1,2,3-trichlorobenzene). You can work out the math by calculating the probability of each combination. Use Pascal's triangle and an approach similar to binomial expansion:

M peak	M+2 peak	M+4 peak	M+6 peak	Relative Ratio of Peak Intensity
$(1)(.75)^1(.25)^0$	$(1)(.75)^0(.25)^1$			= .75 : .25
$(1)(.75)^2(.25)^0$	$(2)(.75)^1(.25)^1$	$(1)(.75)^0(.25)^2$		= .56 : .38 : .06
$(1)(.75)^3(.25)^0$	$(3)(.75)^2(.25)^1$	$(3)(.75)^1(.25)^2$	$(1)(.75)^0(.25)^3$	= .42 : .42 : .14 : .02

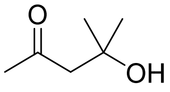
(5) ____B____ Which of the following statements is most correct?

(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

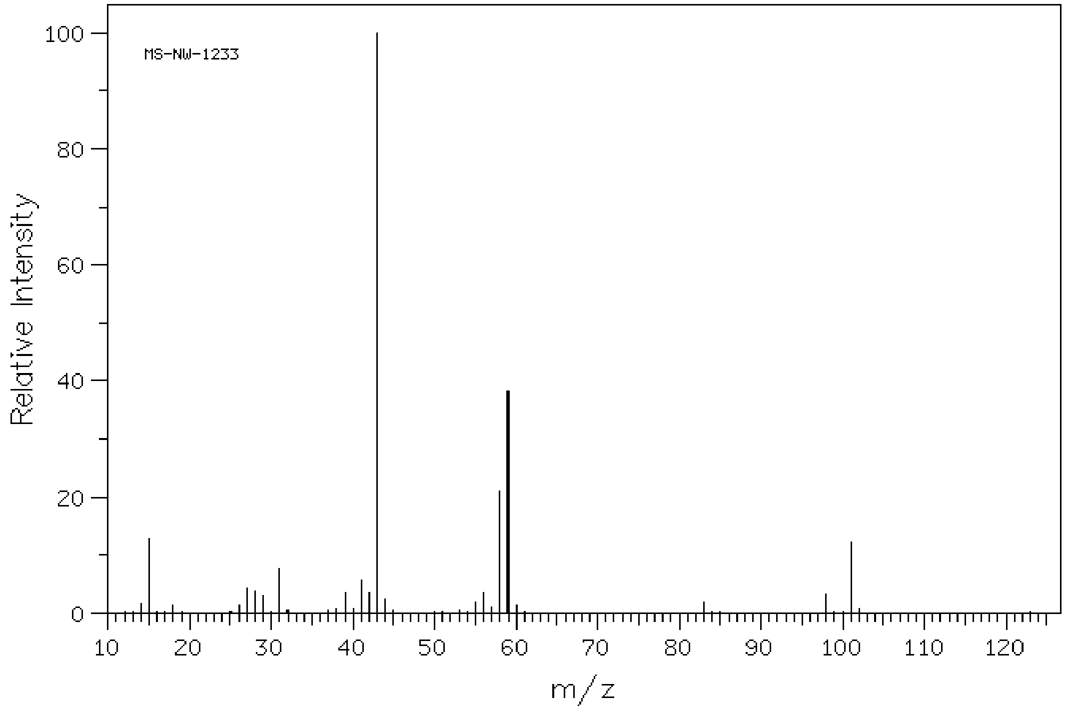
It's best to approach these problems by evaluating all of the statements, one by one. Statement (a) is false. There is no such thing as a ^{12}C NMR spectrum, and if there were such a thing, the spectrum would have no peaks because ^{12}C does not have an NMR-active nucleus. Statement (b) is true. If all of the methane present has a mass of 16 a.m.u., all of the carbon present must be ^{12}C (not ^{13}C) since the smallest mass hydrogen can have is 1 a.m.u. (for ^{1}H). The ^{12}C carbon will not show up in a ^{13}C NMR spectrum, so no peaks will show up in the ^{13}C NMR spectrum. Statement (c) is false, because the compound will have C–H stretches among several bending modes. Statements (d) and (e) are false because (a) and (c) are false.

(6) C

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**)?

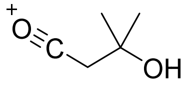


E



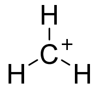
Source: Spectral Database for Organic Compounds, #10287
http://sdbs.db.aist.go.jp/

m/z 101

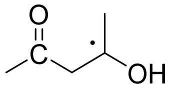


(a)

m/z 15

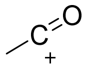


(b)



(c)

m/z 43



(d)

all of the above fragments appear in the spectrum

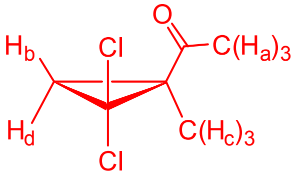
(e)

Only charged fragments appear in mass spectra. Remember, m/z is the mass-to-<u>charge</u> ratio. Fragment (c) probably forms, but it is an uncharged radical, so it won't show up as a peak.

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

Source: Spectral Database for Organic Compounds, #8925
http://sdbs.db.aist.go.jp/



G

2,2-dichloro-1-methylcyclopropyl methyl ketone

(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.

In hindsight, this was not the best molecule for an NMR-assignment problem. I ended up accepting a number of alternative structures and assignments that one could reasonably expect to give a similar spectrum. Still, these are real data and some aspects of the assignment are unquestionable.

You should begin by calculating the number of rings and/or π bonds from the molecular formula ($C_6H_8Cl_2O$): [6(2)+1(0)+2–8–2]/2 = 2. One of these two we might guess to be a carbonyl group, because the molecule has an oxygen atom and there are no signals around δ 3.5–4 that would suggest protons alpha to an sp^3-hybridized oxygen. Furthermore, methyl groups alpha to a carbonyl group have ~δ 2.1, which looks like a good candidate for signal (a).

The fact that there are no signals with δ >2.3 suggests you should try using the last degree of unsaturation to form a ring instead of a C=C π bond (since you only have carbon atoms leftover after "using" the lone oxygen in the carbonyl group). The integration and splitting (singlet) of signal (c) suggest a methyl group with no neighboring hydrogens.

Acceptable answers given the limited data presented include: (i) swapping H_b and H_d, (ii) swapping H_b or H_d with a Cl atom, and much less convincingly (iii) swapping the methyl substituent with a neighboring Cl atom. The exact assignments presented above require more data than you are provided, since these types of data are largely beyond the scope of this course.

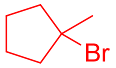
Problem III. (21 points) Roadmap Problem. Provide structures for compounds **H**, **K**, and **M** given the information listed below.

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}

Compounds & Reactions

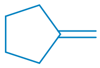
Pertinent Spectral Data for Associated Compound

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

$\downarrow$ $tBuO^{-}/^{+}K$, tBuOH

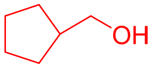


compound **J**

- ^{13}C NMR spectrum has 4 signals

$\downarrow$ 1. BH_3-THF, 2. H_2O_2, NaOH

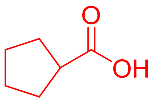
K



- 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}

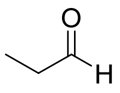
$\downarrow$ aqueous $KMnO_4$

M

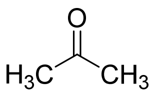


- ^{1}H NMR spectrum has a broad peak at δ 11.89 that disappears upon addition of D_2O
- MS has M^{+} peak at m/z 114
- IR spectrum has a very broad and intense absorption from ~2200–3600 cm^{-1}

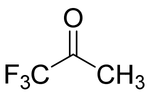
Problem IV. Explanation (11 points). Explain the following trend in the absorption corresponding to C=O stretching in the IR spectra of the following molecules. Hint: consider the two predominant resonance forms for carbonyl groups.


propanal

1739 cm^{-1}

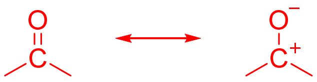

acetone

1715 cm^{-1}


1,1,1-trifluoroacetone

1771 cm^{-1}

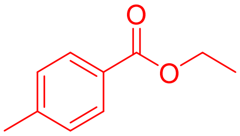
Carbonyl groups have two important resonance forms:


I **II**

Notice that one resonance form (**II**) has a single bond between the carbon and oxygen atoms, while the other (**I**) has a double bond. The double bond is a stronger, “stiffer” bond that will require more energy to stretch. The trend above can be explained by how the substituents of the carbonyl group favor resonance form **I** versus **II**. The methyl groups in acetone are electron donating and help favor resonance form **II**, making the C–O bond less stiff and easier to stretch. The fluorine atoms in 1,1,1-trifluoroacetate are electron withdrawing and help disfavor the positive charge on carbon in resonance form **II**. Thus, **II** will contribute less character to the resonance hybrid and the C–O bond will be stiffer, requiring a photon of higher energy to stretch.

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: ethyl *p*-toluate

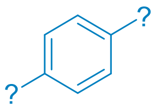
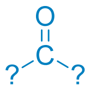


N

In most spectroscopy problems in sophomore organic chemistry, you are given some clues in addition to one or more spectra to help narrow your focus. In this problem, you are given nothing aside from spectra to determine the identity of an organic compound. Now you know what it feels like to be a real organic chemist—except for the fact that these spectra of a pure compound were just dropped in your lap. More than half of the problem is making and isolating the pure compound.

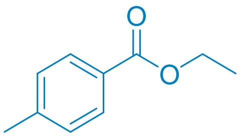
The first thing to do is to scan quickly through the spectra and see if anything "jumps out" at you. You are looking for tell-tale data that strongly signal the presence of certain functional groups or arrangements. From the IR spectrum, the absorption around 1700 cm^{-1} strongly suggests the presence of a carbonyl group. The mass spectrum suggests the molecule weighs at least 164 (and the lack of a significant M+2 peak suggests no Cl or Br is present). The ^{1}H NMR spectrum contains some of the most useful information toward pointing us in the right direction. The two doublets between δ 7–8 are usually indicative of a benzene ring where the groups are substituted at the 1- and 4-positions. This 1,4-substituted benzene ring motif is supported by the four peaks in the ^{13}C NMR spectrum between δ 120–150. The δ 167 peak in the ^{13}C NMR jives with the presence of the carbonyl group first suggested by the IR spectrum.

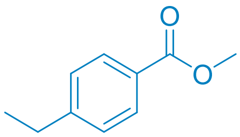
So far, we've identified two tell-tale signatures also corroborated by at least one of the other spectra. Let's draw out these pieces and see where we stand in terms of mass:

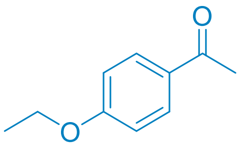
N			C_5H_0? C_4H_{12}? C_3H_8O? $C_2H_4O_2$?
	C_6H_4	C_1O_1	
m/z 164	m/z 76	m/z 28	leftover = 60

Accounting for the carbonyl group and benzene ring, we have m/z 60 leftover from the suspected molecular ion. A number of possibilities that add up to 60 are listed above. Let's turn to the ^{13}C NMR spectrum to help guide us. We've already accounted for all of the signals above δ 100 with the carbonyl and benzene groups. There are three peaks below δ 100 that are unaccounted for, so far. These suggest three alkyl carbon atoms, so let's focus on C_3H_8O as the best possibility for the leftover atoms.

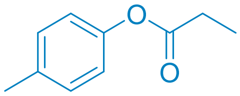
Now, if we look at the ^{1}H NMR spectrum, the splitting pattern suggests these remaining three carbon atoms could be present as a methyl group (singlet, 3H) and ethyl group (downfield quartet + upfield triplet, 5H total). With the need to account for a remaining oxygen atom, we have six candidates (**N1**–**N6**) that come immediately to mind:

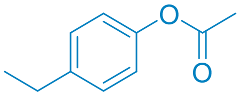

N1

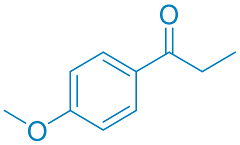

N2


N3

1

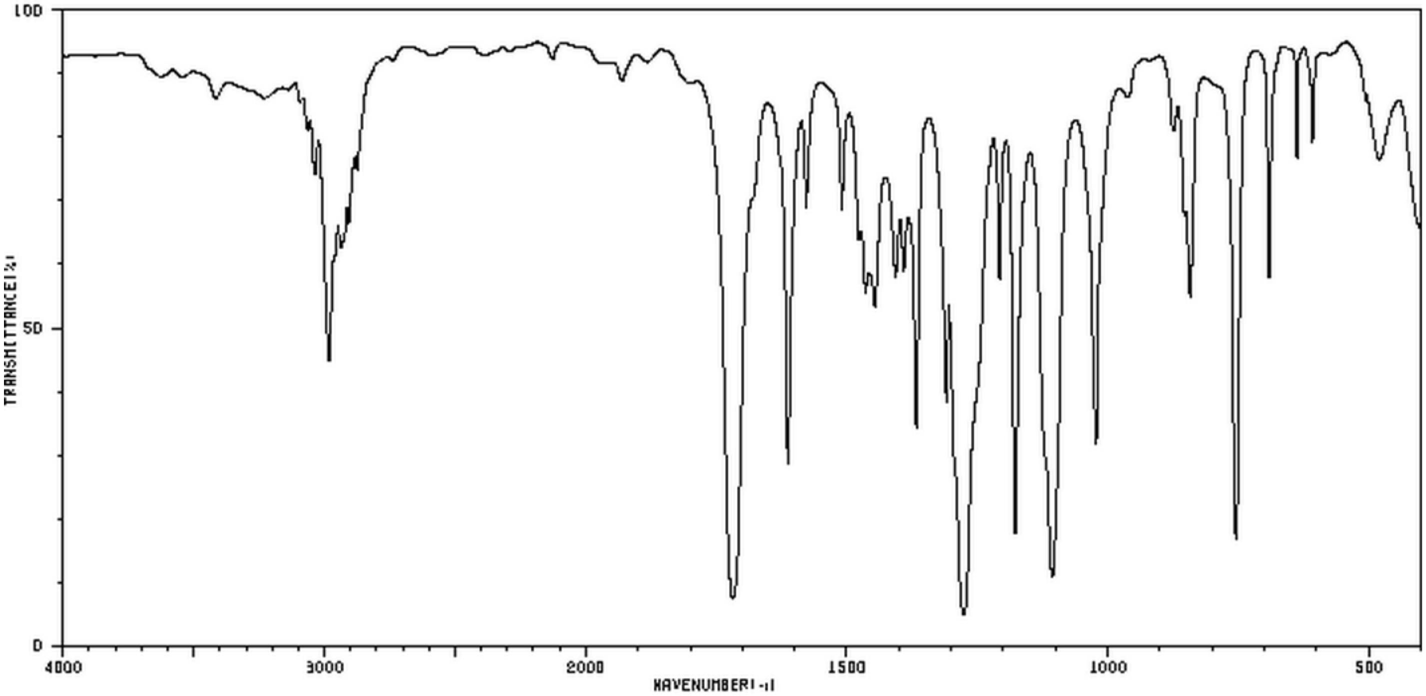

N4


N5


N6

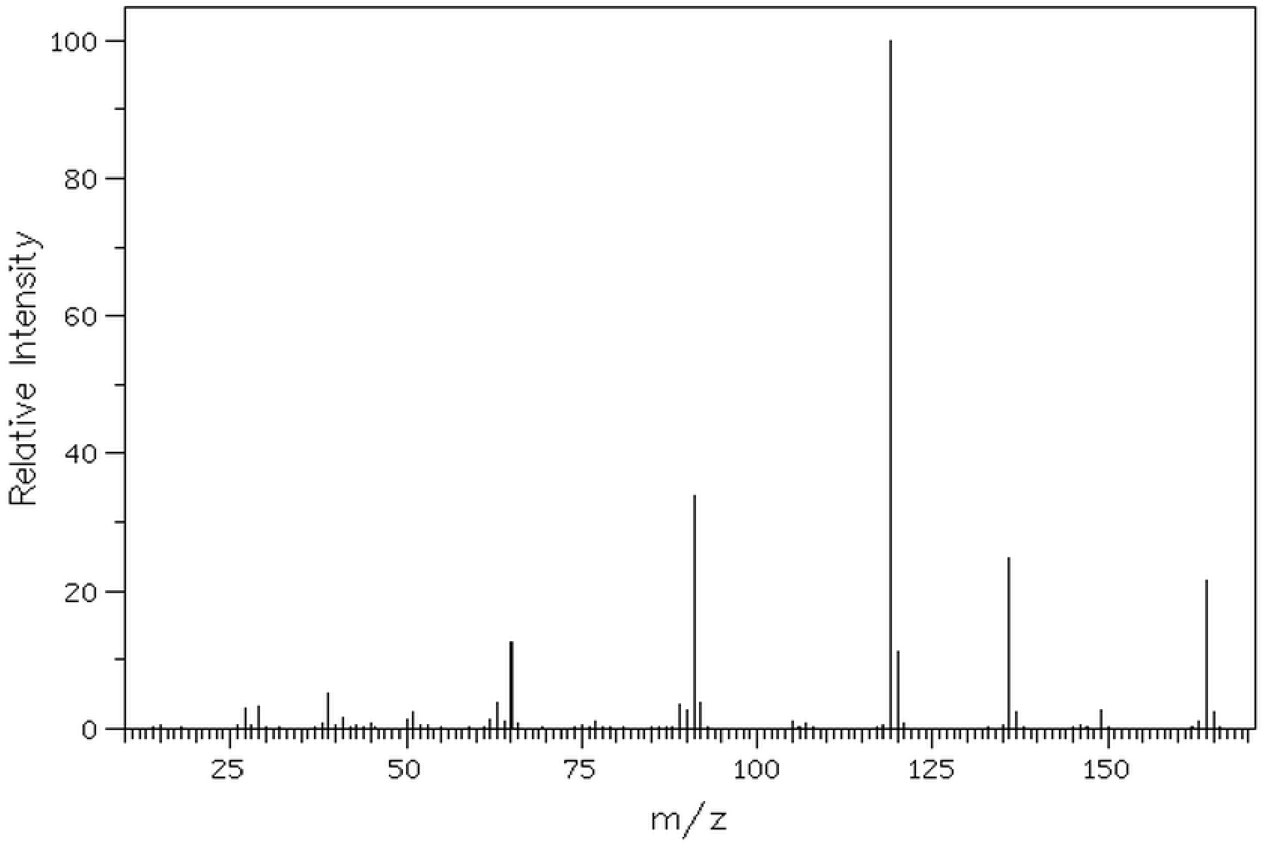
We can use the ^{1}H NMR spectrum to narrow down the candidates. The downfield quartet at δ 4.4 suggests the CH_2 group of the ethyl group must be bonded to the (deshielding) oxygen atom. This eliminates all of the candidates except for **N1** and **N3**. The IR absorption for the carbonyl group being significantly above 1700 cm^{-1} rather than below suggests an ester (**N1**) rather than a conjugated carbonyl group (**N3**). The base peak at m/z 119 is also strongly suggestive of **N1** over **N3**. This peak arises as M − $CH_3CH_2O^{\bullet}$ radical to form the acylium cation from the ester.

IR Spectrum:



Source: Spectral Database for Organic Compounds, #2369
http://sdbs.db.aist.go.jp/

Mass Spectrum:

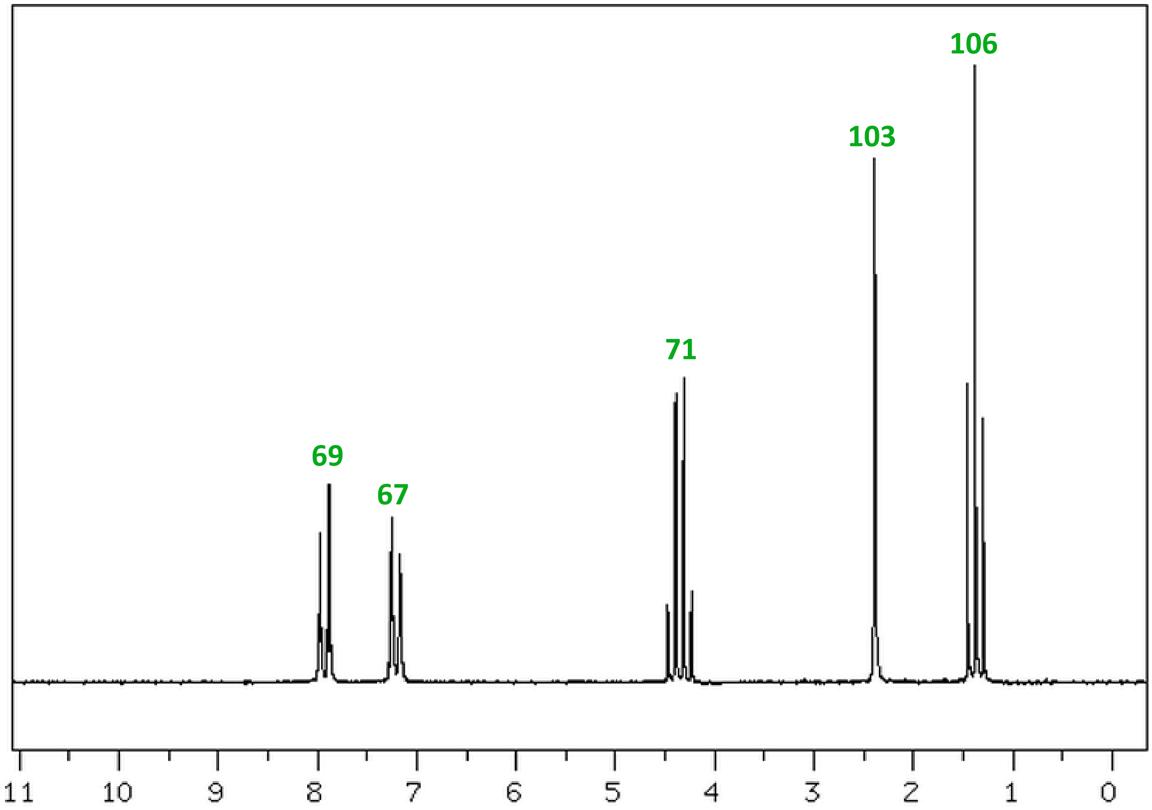


Source: Spectral Database for Organic Compounds, #2369
http://sdbs.db.aist.go.jp/

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:

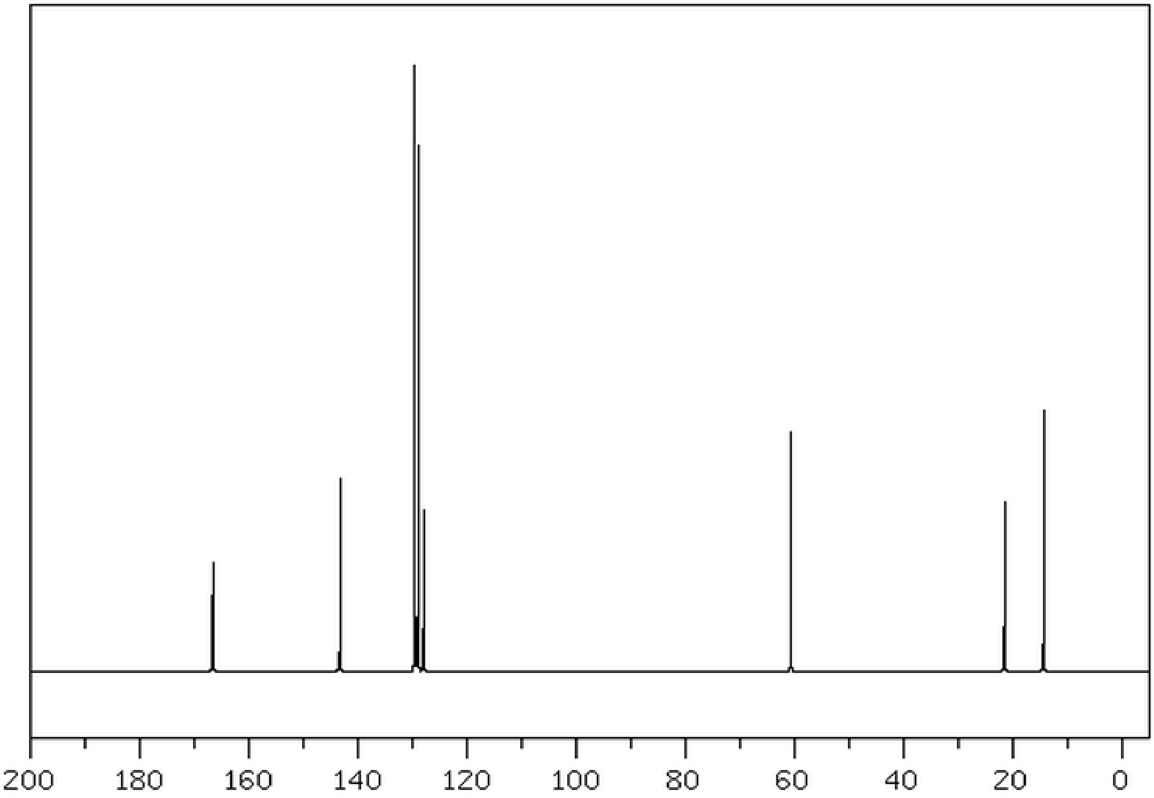
Integrations listed in green over signals



Source: Spectral Database for Organic Compounds, #2369
http://sdbs.db.aist.go.jp/

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:



Source: Spectral Database for Organic Compounds, #2369
http://sdbs.db.aist.go.jp/

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