

Purpose

To identify the structure of an organic unknown predominantly by acquiring and analyzing various spectra (MS, ^1H NMR, ^{13}C NMR, and IR spectra).

Unknown Number

U314

Experimental Details

Given a liquid sample of unknown U314, a neat sample in salt plates was used to obtain an IR spectrum using a Jasco FT/IR-4000. After completing a background scan, the U314 IR spectrum was acquired by pipetting a drop of liquid sample between two salt plates, previously cleaned with ethanol, and scanning them.

The mass spectrum (along with a GC spectrum) was obtained in a Hewlett Packard 5973 Mass Selective Detector using a sample prepared by filling a tared, capped vial with ethanol and one drop of the liquid unknown sample.

The ^1H NMR spectrum was obtained with a Varian EM360A NMR Spectrometer using a few drops of unknown sample along with deuterated chloroform solvent in an NMR tube.

The ^{13}C NMR spectrum was given, as was a high resolution ^1H NMR spectrum.

Data (annotated spectra attached following report)

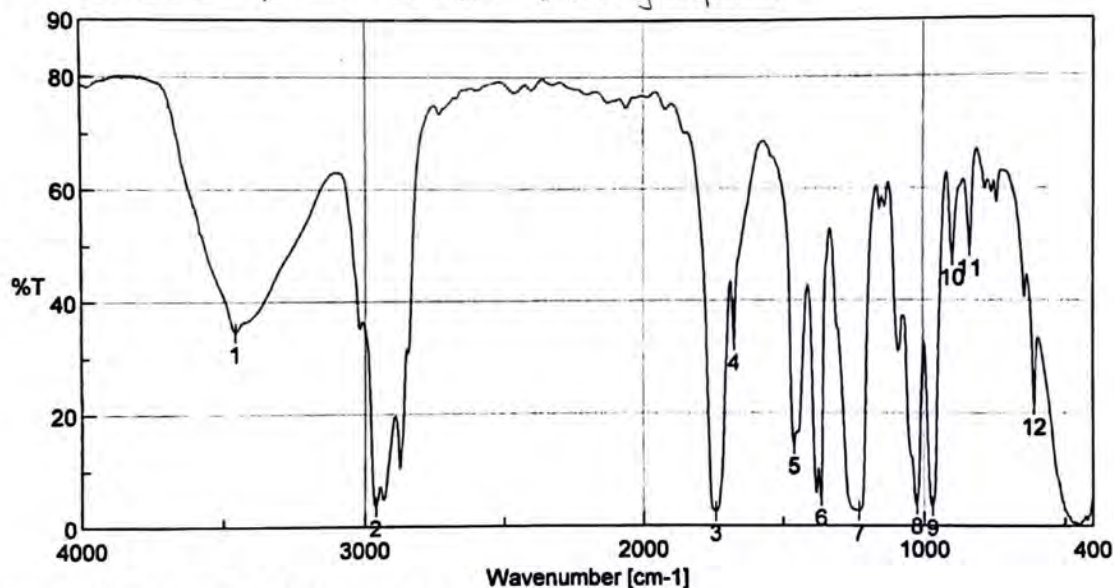


Figure 1 IR spectrum of Unknown U314

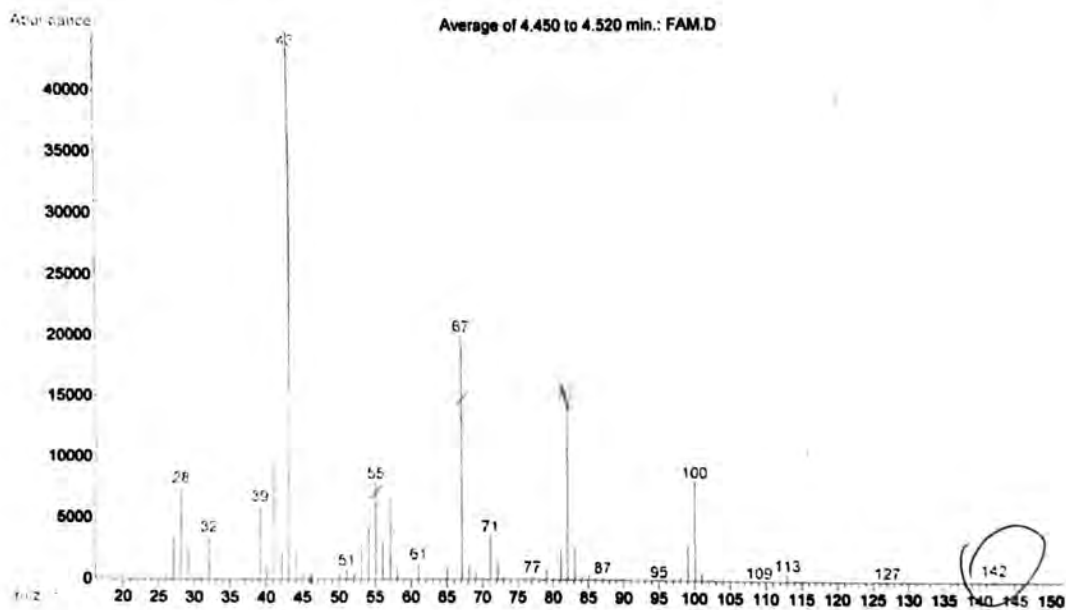


Figure 2 Mass spectrum of Unknown U314

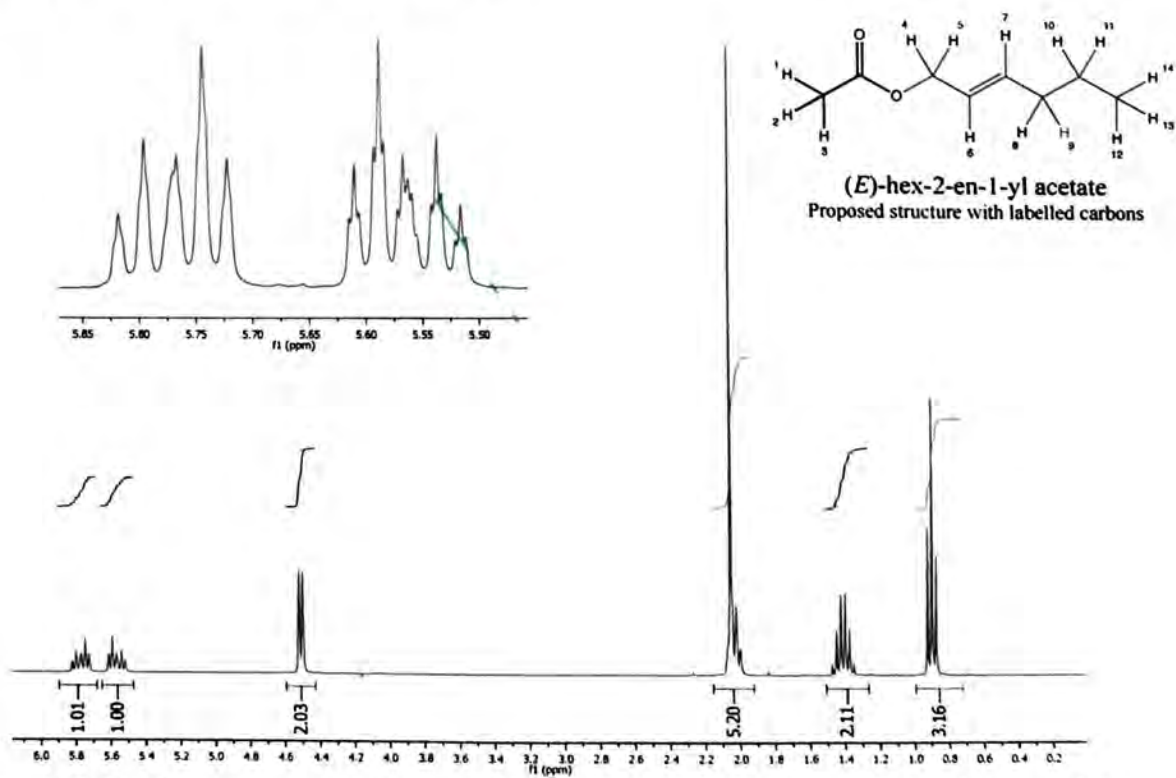


Figure 3 ¹H NMR spectrum of Unknown U314 (low resolution spectrum attached separately)

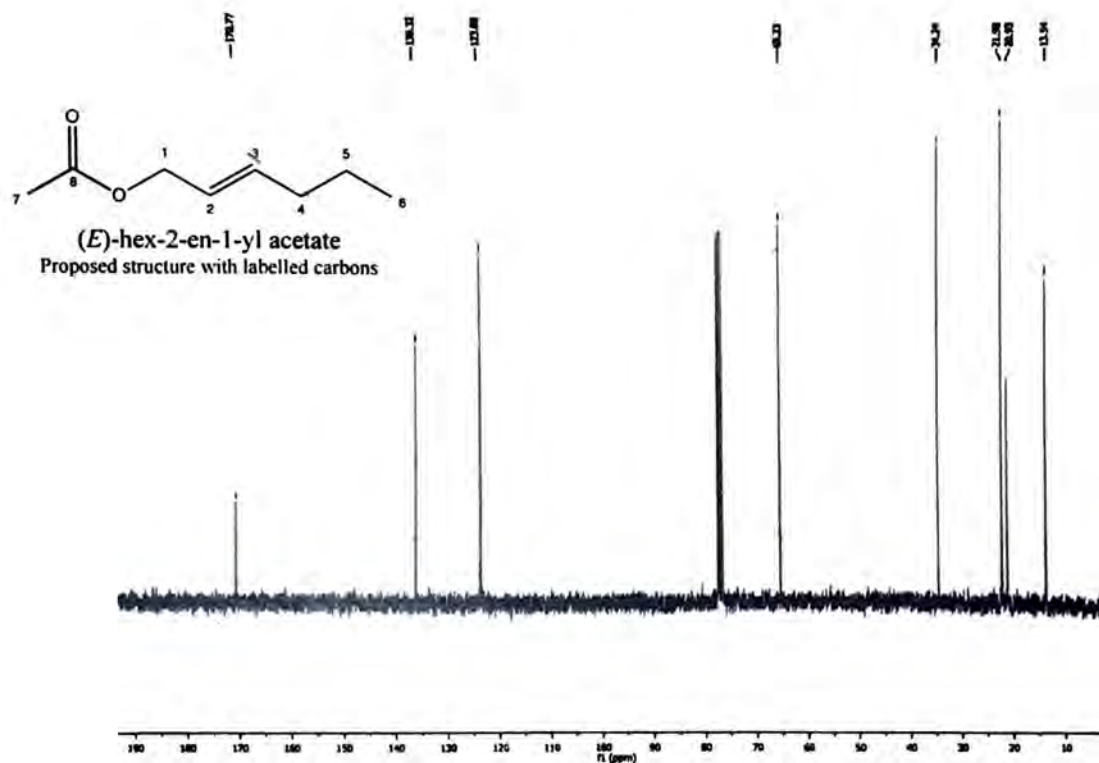


Figure 4 ^{13}C NMR spectrum of Unknown U314

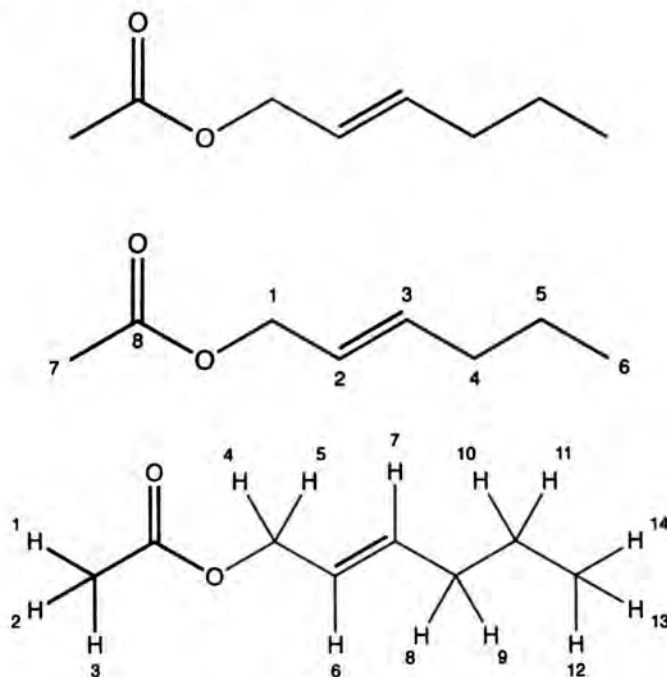


Figure 5 Proposed (*E*)-hex-2-en-1-yl acetate structure of Unknown U314 (top) with labelled carbons (middle) and labeled protons (bottom)

Spectral Analyses

Table 1 IR spectrum absorption maxima (cm^{-1}), intensity, and prominent peak assignments (refer to peak number in Figure 1)

Peak	Absorption Maximum (cm^{-1})	Intensity	Peak Assignment
1	3459.67	34.532	alcohol hydroxyl group (-OH) [†]
2	2960.2	3.54709	alkyl C-H bond
3	17941.41	2.56147	carbonyl, carboxylic acid [‡] (C=O) [‡]

[†]appears despite the structure not being an alcohol, likely due to a rearrangement in which the singly bonded oxygen within the ester, gains a hydrogen, possibly due to a hydroscopic tendency

[‡]appears slightly higher than ester carbonyl, more like a carboxylic acid carbonyl, suggesting a rearrangement which naturally occurs or a hydroscopic tendency

Table 2 MS spectrum major fragments and molecular ion identification

m/z	$m/z - m/z_{\text{molecular ion}}$	Fragment lost	Predicted Identity
142	0	—	molecular ion ($\text{C}_8\text{H}_{14}\text{O}_2$)
127	15	- CH_3	$\text{C}_7\text{H}_{11}\text{O}_2$
113	29	- C_2H_5	$\text{C}_6\text{H}_9\text{O}_2$
100	42	- C_3H_6	$\text{C}_5\text{H}_8\text{O}_2$
87	55	- C_4H_7	$\text{C}_4\text{H}_7\text{O}_2$
82	60	$\text{CH}_3\text{-COOH}$	C_6H_{10} (rearrangement involved)
67	75	$\text{C}_2\text{H}_5\text{O-CH=OH}$	C_5H_7 (double rearrangement involved)
55	87	- $\text{C}_4\text{H}_7\text{O}_2$	C_4H_7
43	99	- OC_6H_{11}	$\text{CH}_3\text{C=O}$

Table 3 ^1H NMR spectrum (Figure 3) analysis (refer to labelled protons on Figure 5 or below)

Chemical shift (in ppm)	Relative integration	Multiplicity	Proton identification label
≈ 0.9	3.16	triplet	3 saturated C-Hs (12, 13, 14)
≈ 1.41	2.11	multiplet	2 saturated C-Hs (10, 11)
≈ 2.02	$\approx 2^*$	multiplet*	2 allylic C-Hs (8,9)
≈ 2.05	$\approx 3^*$	singlet	3 allylic [†] C-Hs (1, 2, 3)
≈ 4.5	2.03	doublet	2 X-C-Hs (4, 5)
≈ 5.55	1.00	multiplet	1 vinylic C-H (6 or 7 [‡])
≈ 5.75	1.01	multiplet	1 vinylic C-H (6 [‡] or 7)

*overlapping integration made it difficult/impossible to discern exactly

[†]appears in allylic region due to vicinity to carbonyl double bond

[‡]likelier possibility due to relative shielding

Proposed structure with labelled protons for reference:

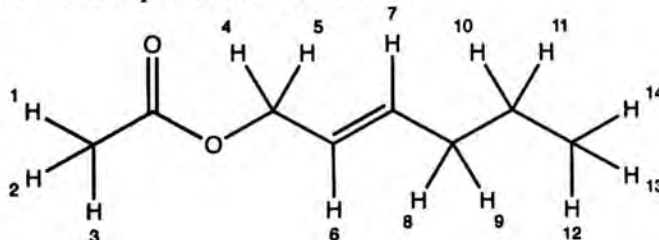
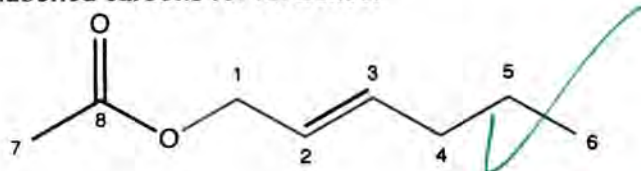


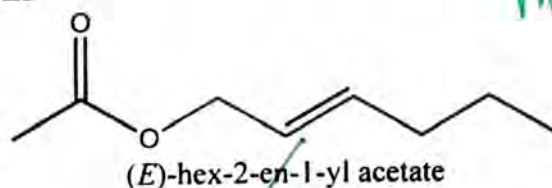
Table 4 ^{13}C NMR spectrum absorption maxima (cm^{-1}) and peak assignments (refer to labelled carbons on Figure 5 or below)

Chemical shift (in ppm)	Carbon identification label
13.54	sp^3 carbon (6)
20.93	sp^3 carbon (7)
21.98	sp^3 carbon (5)
34.24	sp^3 carbon (4)
65.23	sp^3 carbon (1)
123.88	sp^2 carbon (3)
136.32	sp^2 carbon (2)
170.77	carbonyl (ester) carbon (8)

Proposed structure with labelled carbons for reference:



Discussion/Conclusions



According to the MS, the molecular ion is 142 g. Given a maximum of 1 nitrogen, this even mass rules out the presence of a nitrogen. The lack of isotopes visible in the MS also rules out the presence of bromine or chlorine. However, at least two oxygens are present according to the hydroxyl and carbonyl stretches present in the IR spectrum, several fragments visible in the MS, and an ^1H NMR peak corresponding to a proton on a carbon bonded to a halogen. Taking into account the presence of 8 carbon environments, according to the ^{13}C NMR, and some factor of 14 hydrogens, according to the relative integrations of the ^1H NMR, the molecular formula can be deduced to be $\text{C}_8\text{H}_{14}\text{O}_2$.

The molecular formula suggests two degrees of unsaturation, in the form of a carbonyl, as the IR and ^{13}C NMR reveal, as well as a carbon-carbon double bond, apparent through the vinylic peaks of the ^1H NMR and sp^2 peaks in the ^{13}C NMR. The fragment at 43 m/z in the IR is characteristic of an ester. The unusually high carbonyl absorption and presence of a hydroxyl stretch on the IR seem to contradict the presence of an ester, but are in agreement, providing more information on the unknown and its characteristics. These discrepancies are likely due to a rearrangement centered around the ester structure within the unknown. The analysis of m/z 82, 67, and 43 of the MS in Table 3 sheds light on this. The ester carbonyl ^{13}C NMR peak as well as the ^1H NMR peak of a proton on a carbon attached to the non-carbonyl oxygen confirm the ester.

Observing the first two fragments lost in the MS, it seems that the structure includes a saturated terminal carbon bonded to a saturated, allylic carbon. The lowest chemical shift on the ^1H NMR suggests the three protons of the terminal carbon with its integration along with the two protons on the adjacent carbon with its triplet splitting pattern. Meanwhile, that second carbon's sextet splitting pattern suggests the following carbon in the chain also possesses two hydrogens, for a total of five adjacent hydrogens. The only other carbons with two hydrogens apparent in the ^1H NMR are the allylic carbon and that bonded to oxygen. However, the latter has a doublet splitting pattern, so only the allylic carbon is feasible in this location (this suggests that the splitting pattern for this carbon is a quartet rather than a triplet, which was previously unclear due to overlapping on the ^1H NMR).

By definition, the vinylic carbons must follow. Examining the vinylic ^1H NMR peaks, it is clear that the two sp^2 carbons, also visible in ^{13}C NMR, each possess one hydrogen and are bonded each other. Their multiplet coupling requires them both be attached carbons with two or more hydrogens. By deduction, the other allylic carbon must then be the same one that is bonded to an oxygen and two hydrogens in the ^1H NMR. Its doublet splitting pattern confirms only one adjacent hydrogen.

The only hydrogen environment remaining, made of 3 allylic hydrogens, must come from an sp^3 carbon. Its singlet splitting pattern suggests it is attached to a carbon without hydrogens. The only unaccounted carbon environment apparent in the ^{13}C NMR, the carbonyl carbon, fits this description. It is then most likely that this carbonyl carbon is bonded to the aforementioned oxygen, forming the elusive ester mentioned earlier.

This reasoning defines unknown U314 as hex-2-en-1-yl acetate. However, further analysis (boiling point, melting point, etc.) is required to confirm the stereochemistry. With the information at hand, the *E* isomer seems more plausible since protons associated with the vinylic carbons have different chemical shifts, suggesting different environments. These protons would be expected to have the same environment, and thus chemical shift, given the *cis/Z* isomer. At the same time, the chemical shift associated with hydrogens 8 and 9 would have been expected to be greater, given increased shielding due to larger neighboring structures. However, the presence of nearby oxygens, while unlikely to have an effect, adds a slight ambiguity that necessitates further analysis beyond the provided spectra.

References

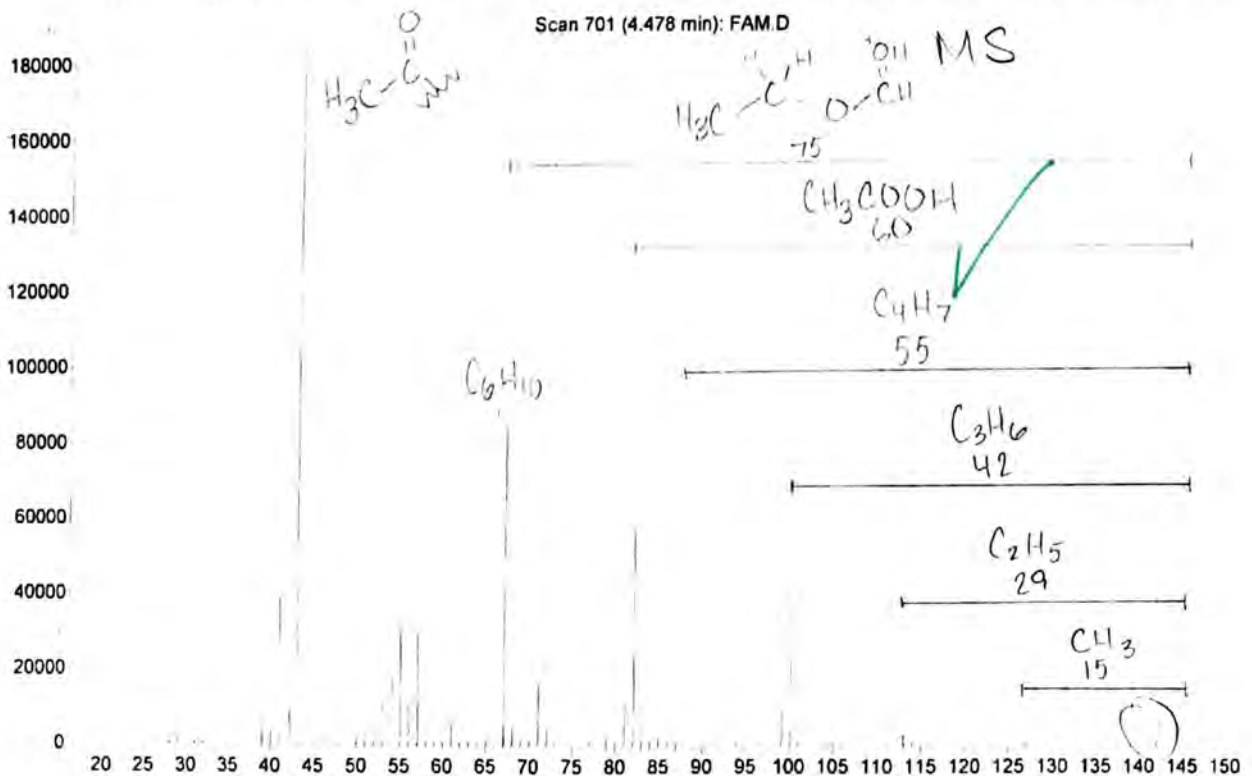
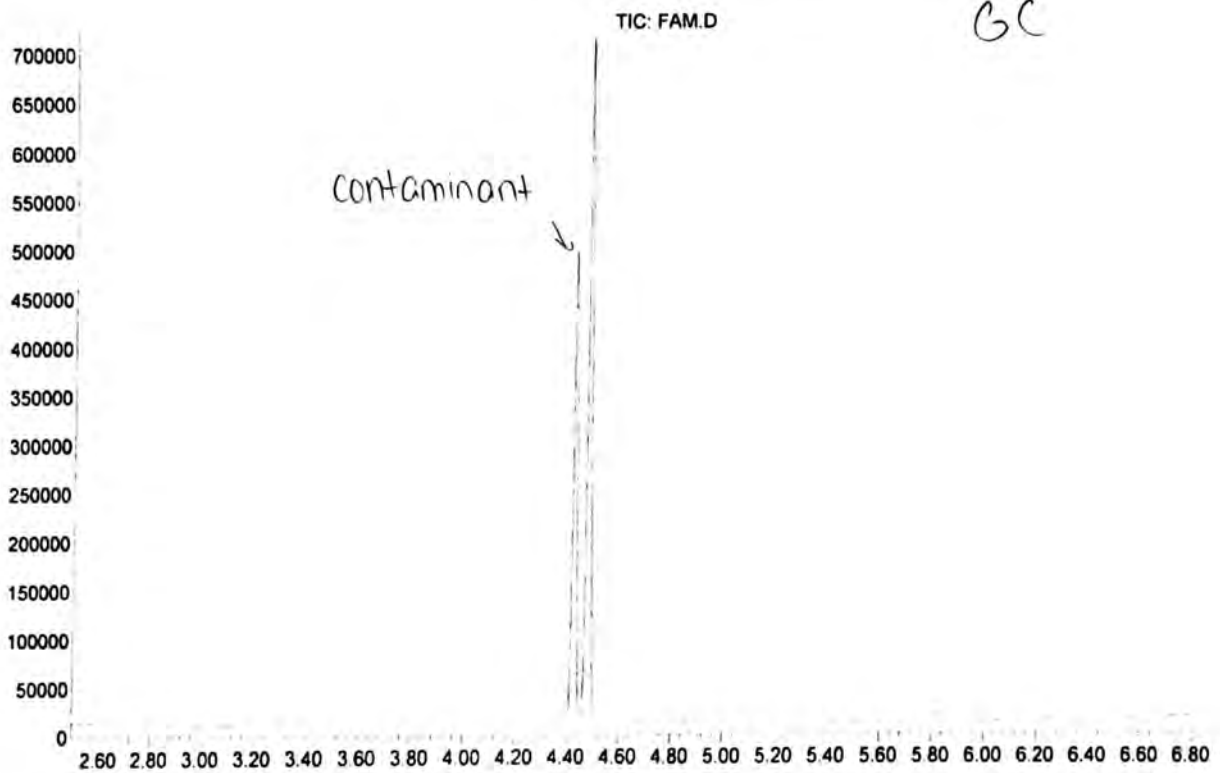
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Table of Common Fragments, *wfu.edu*. (2019). Wake Forest University.

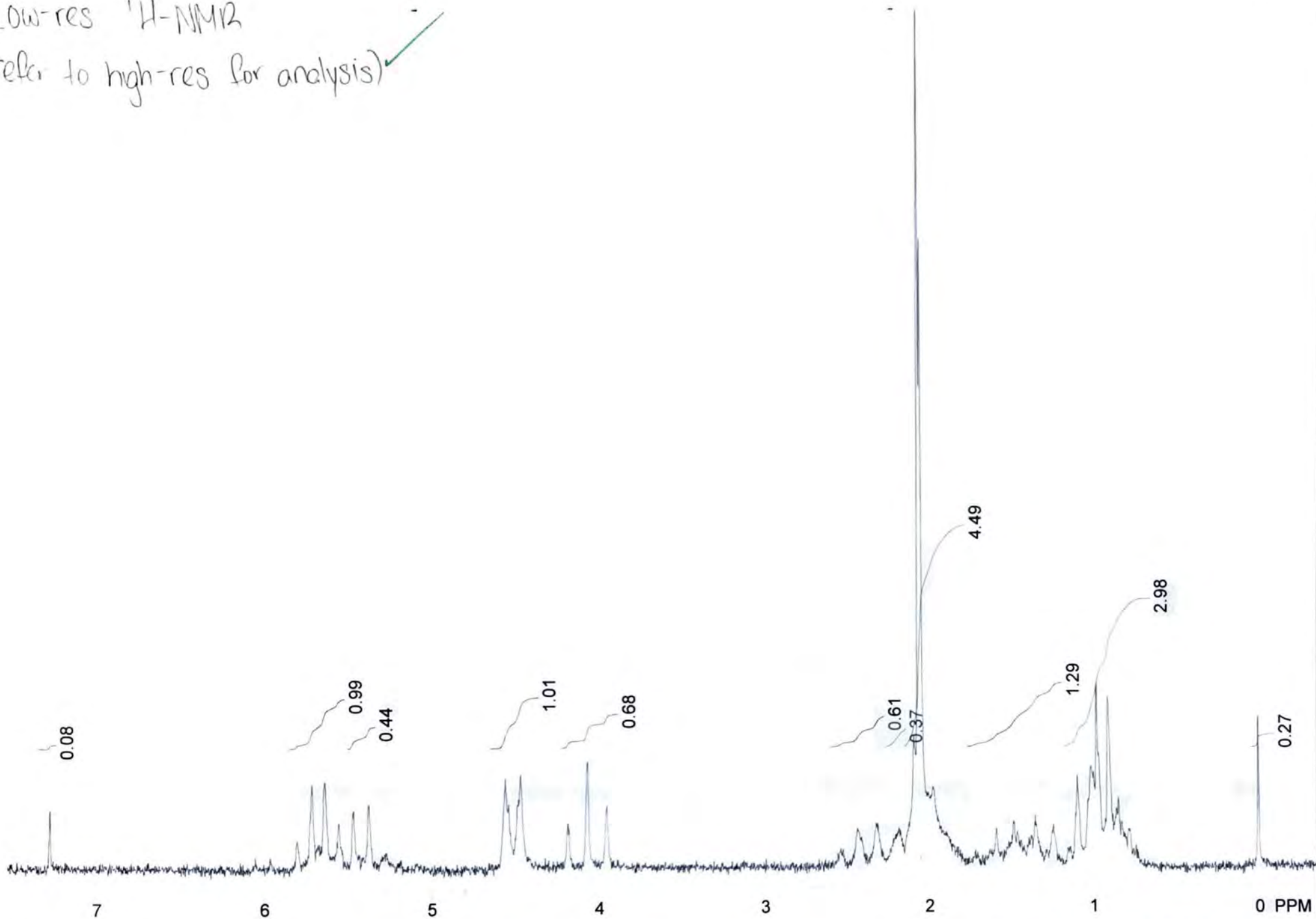
Table of IR Absorptions, *WebSpectra.chem.ucla.edu*. (2019). University of California, 2000.

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 Instrument : GC/MS Ins
 Sample Name: Unknown #314
 Misc Info : MATTHEW FAM
 Vial Number: 17



Best guess Interpretation
 (we seen

Low-res ¹H-NMR
(refer to high-res for analysis)



FamU314NMR

F1: 60.010

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SW1: 1000

PW: 13.6 us

PD: 3.0 sec

OF1: 361.1

NA: 1

LB: 0.0

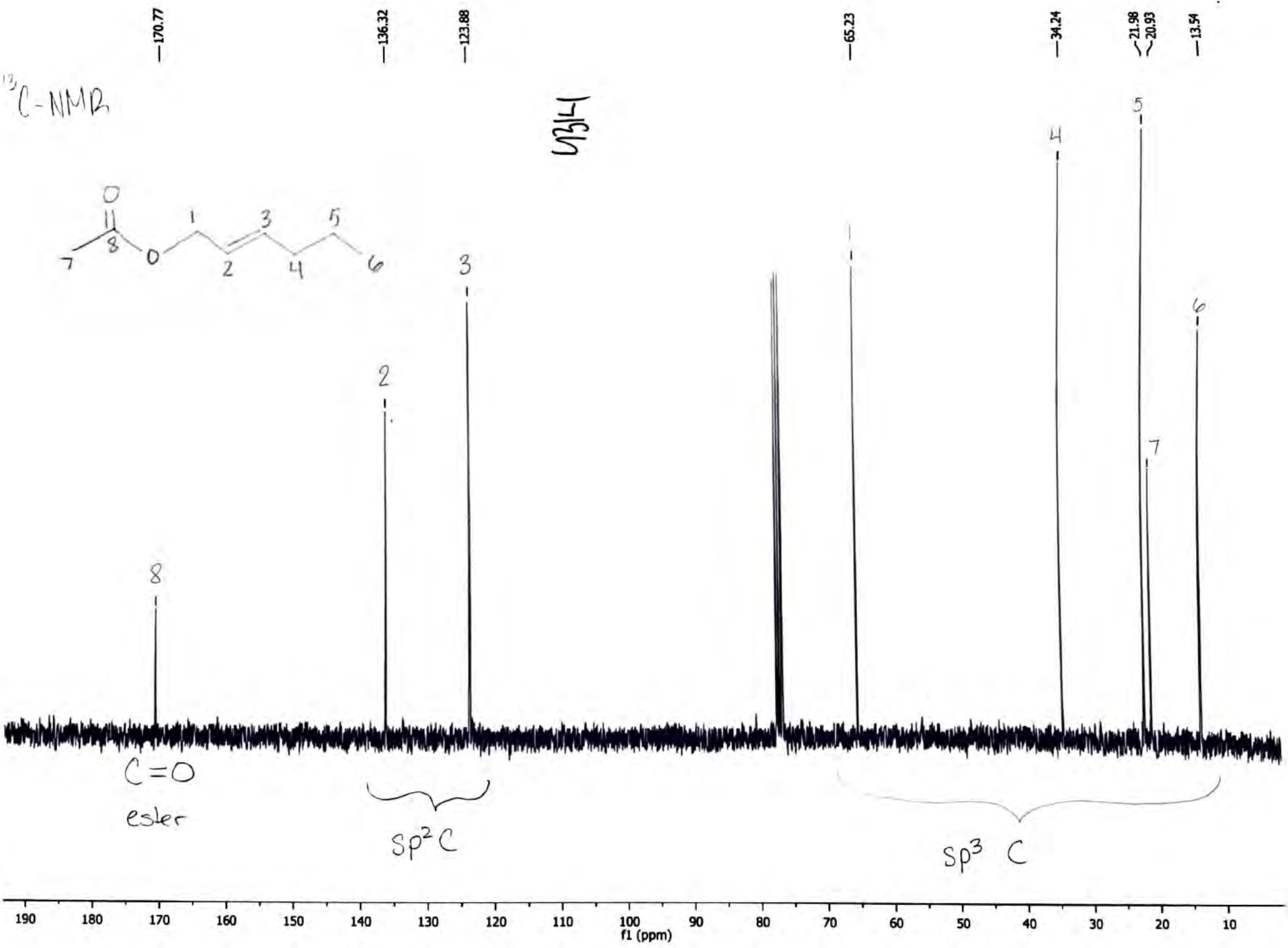
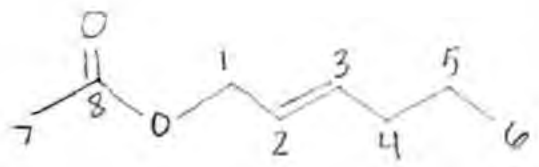
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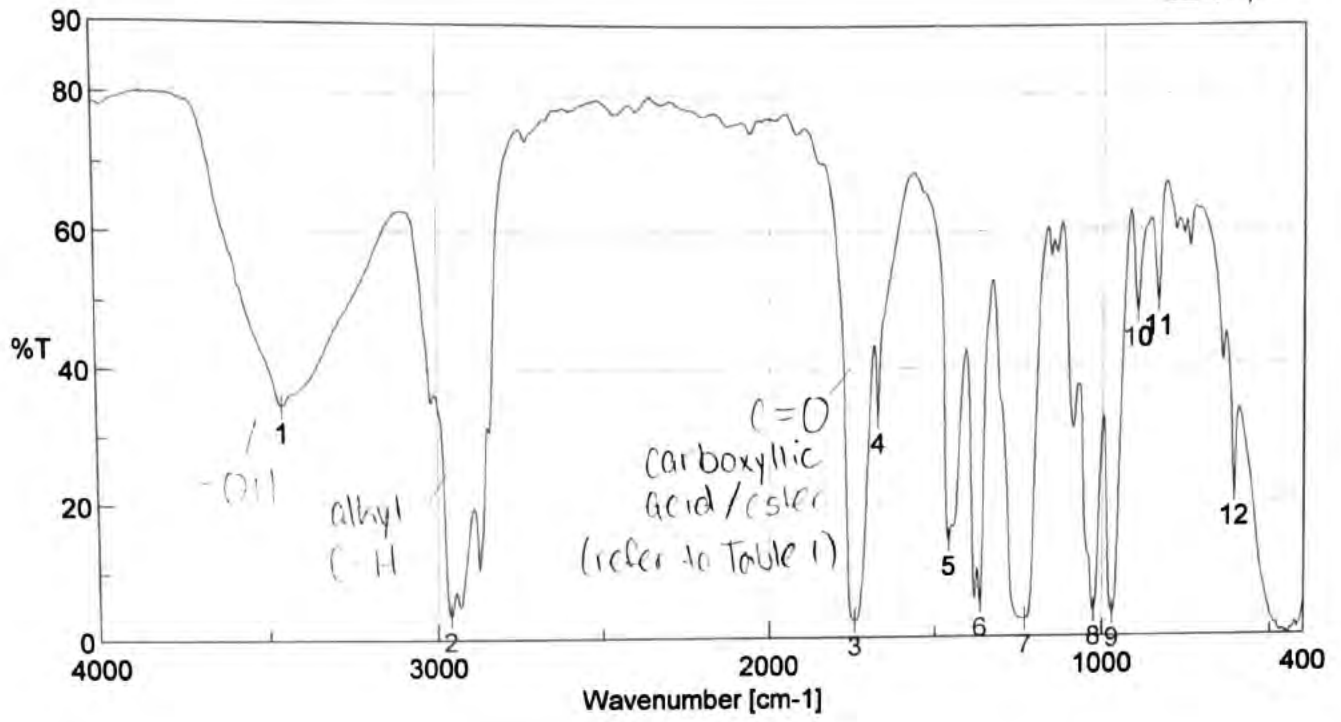
Nuts - temp

¹³C-NMR

MPH



IR



Results of Peak Find

No.	Position	Intensity
1	3459.67	34.532
2	2960.2	3.54709
3	1741.41	2.56147
4	1672.95	32.6432
5	1458.89	14.4269
6	1363.43	5.21473
7	1230.36	2.64628
8	1024.98	3.79271
9	969.055	3.44055
10	894.809	47.8514
11	834.062	49.4737
12	607.467	21.3702

[Comments]

Sample name
 Comment
 User
 Division
 Company Darmouth College

[Measurement Information]

Model Name FT/IR-4100typeA
 Serial Number B187561016

Measurement Date 6/24/2019 4:08 PM

Light Source Standard
 Detector TGS
 Accumulation 8
 Resolution 4 cm-1
 Zero Filling On
 Apodization Cosine
 Gain Auto (2)
 Aperture Auto (7.1 mm)
 Scanning Speed Auto (2 mm/sec)
 Filter Auto (30000 Hz)

