CHEM 4341/6371 Fall 2017

Homework 2 Questions

Answers must be submitted on the answer form. You may collaborate on the development of strategies to answer these problems, but completion of your final answers should be done independently of others.

PART A

Provide neatly drawn line-bond structures for compounds **1**-**10** consistent with the following sets of data. While some data sets might lead you to more than one possible solution, *provide the structure of your single best answer*.

Some challenges of dealing with real experimental data:

- Note that the values of %mass from combustion analyses are all ±0.4%.
- Some of the signals in the ^{1}H NMR spectra have been expanded. The multiplicity of some signals is noted. It is up to you to determine the multiplicity of others. For some peaks, it is impossible to determine multiplicity and you will need to solve the problem without multiplicity information for that peak.
- Computers (including those attached to NMR spectrometers) do not know which peaks (individual lines) belong to a particular signal (multiplet). Integrals may be for a single multiplet, or for more than one multiplet (the latter is especially true for closely-spaced multiplets). It is up to you to make this determination.
- Each peak in the ^{13}C NMR spectra is labeled with an arrow. In some cases it is difficult to discern the presence of closely-spaced peaks without significantly expanding the spectrum – so these arrows help
- Some C=O compounds (strong peak at ~1700 cm^{-1}) give an "overtone" in the IR spectrum as a peak at ~3400 cm^{-1}. This might lead to some initial uncertainly about whether a peak in this region is due to the presence of an O-H or N-H bond.

PART B

These two pages (together with associated spectra for compounds **A**-**X** and data tables) are similar in style to an exam that might be completed in 50 min.

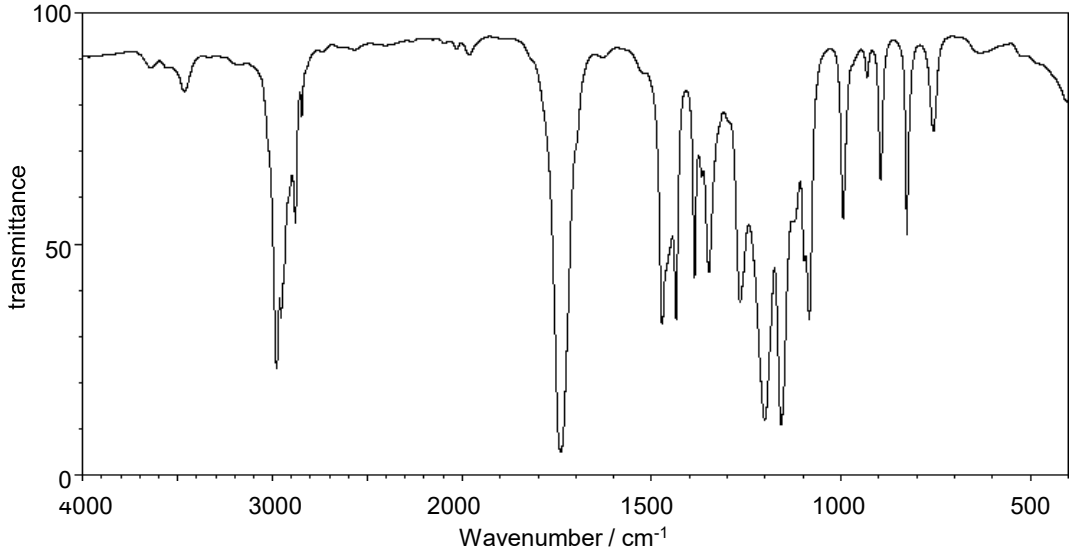
Compound #:

1

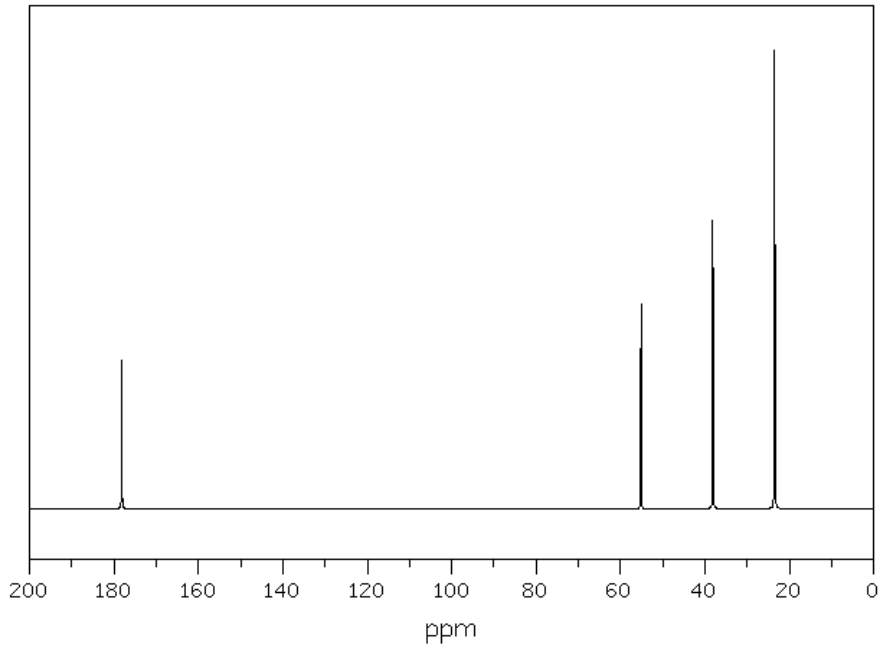
Elemental Analysis: C, 59.01; H, 9.76

Mass Spec: M^+ *m/e*= 102

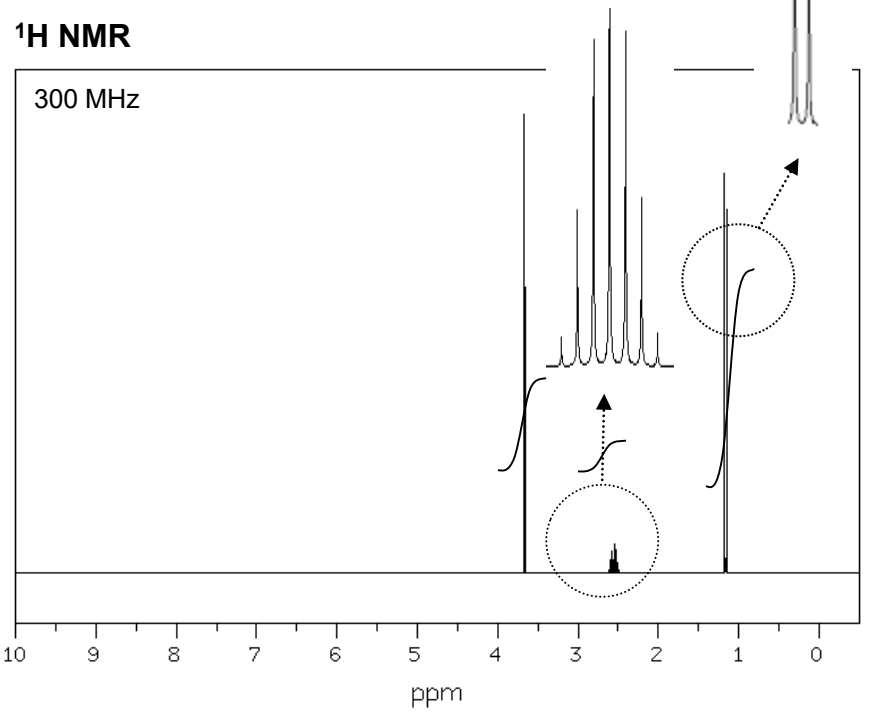
IR



^{13}C NMR



^{1}H NMR



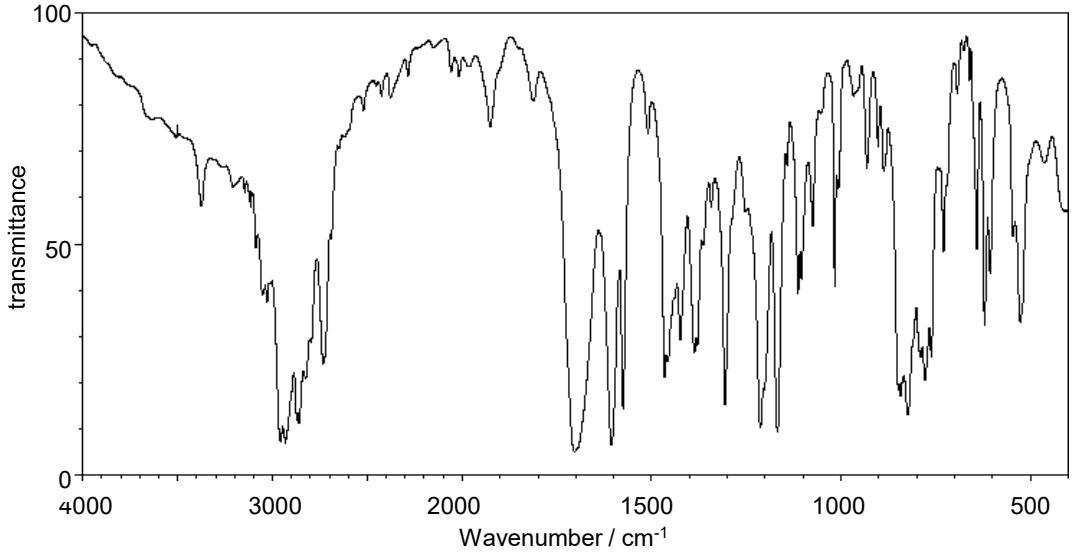
Compound #:

2

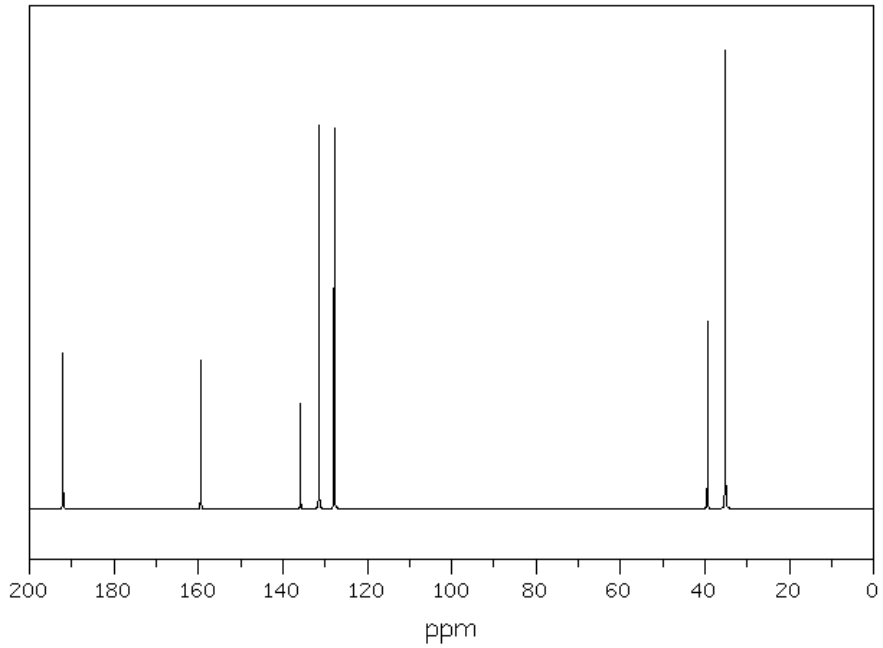
Elemental Analysis: C, 81.38; H, 8.71

Mass Spec: M^+ *m/e*= 162

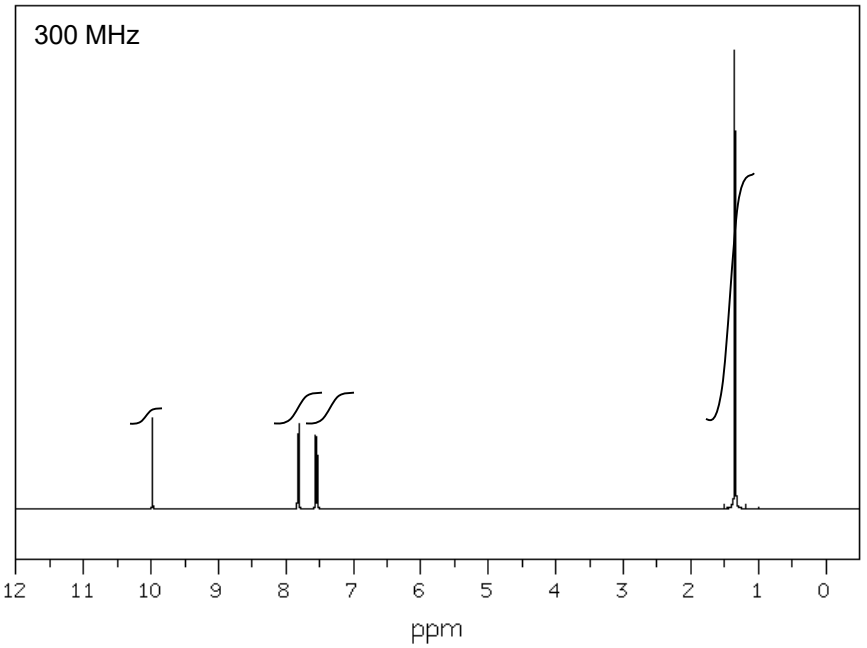
IR



^{13}C NMR



^{1}H NMR

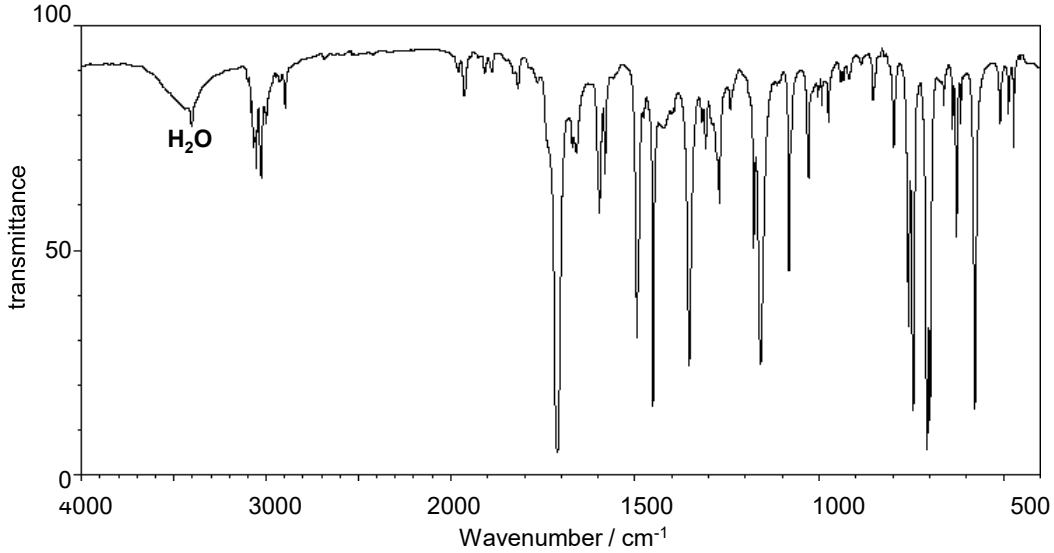


Empirical Formula: $C_{15}H_{14}O$

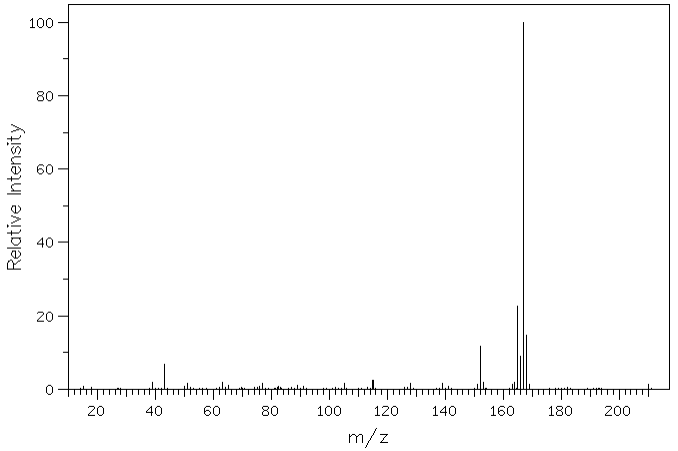
Compound #:

3

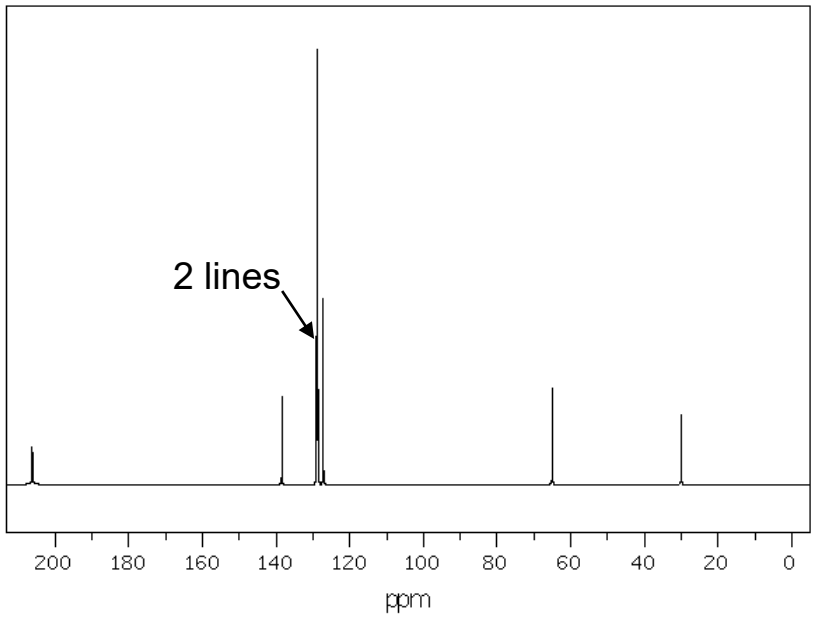
IR



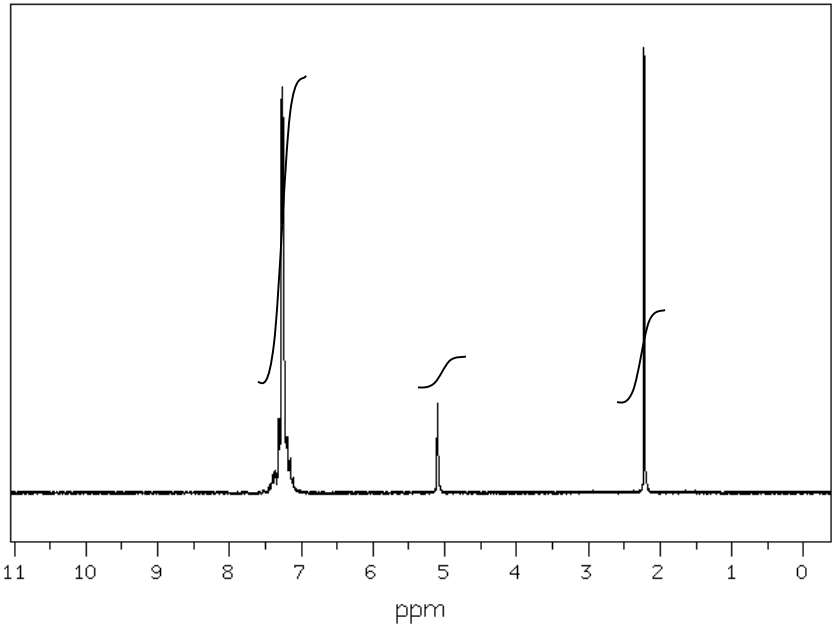
Mass Spec



^{13}C NMR



^{1}H NMR



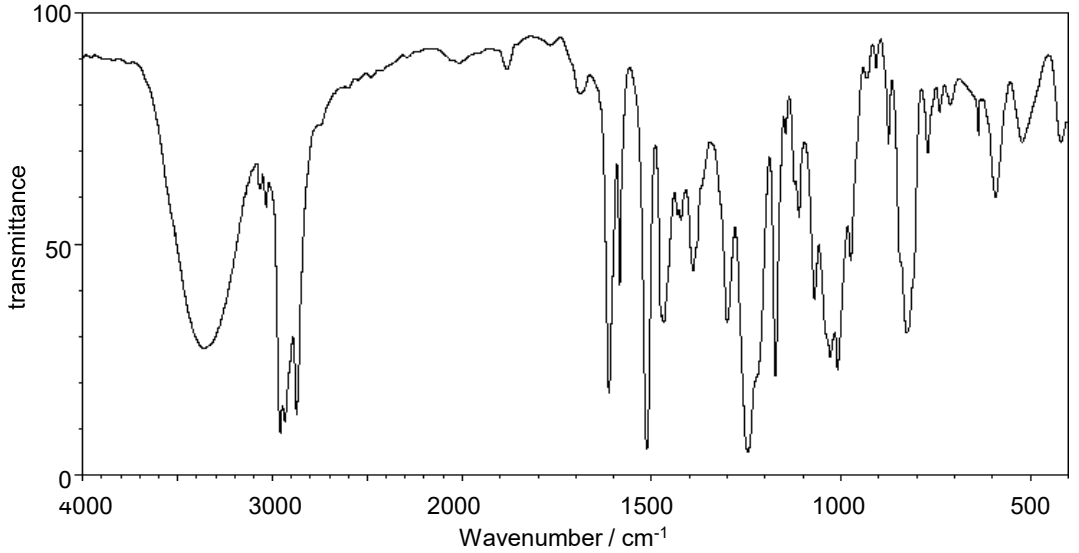
Compound #:

4

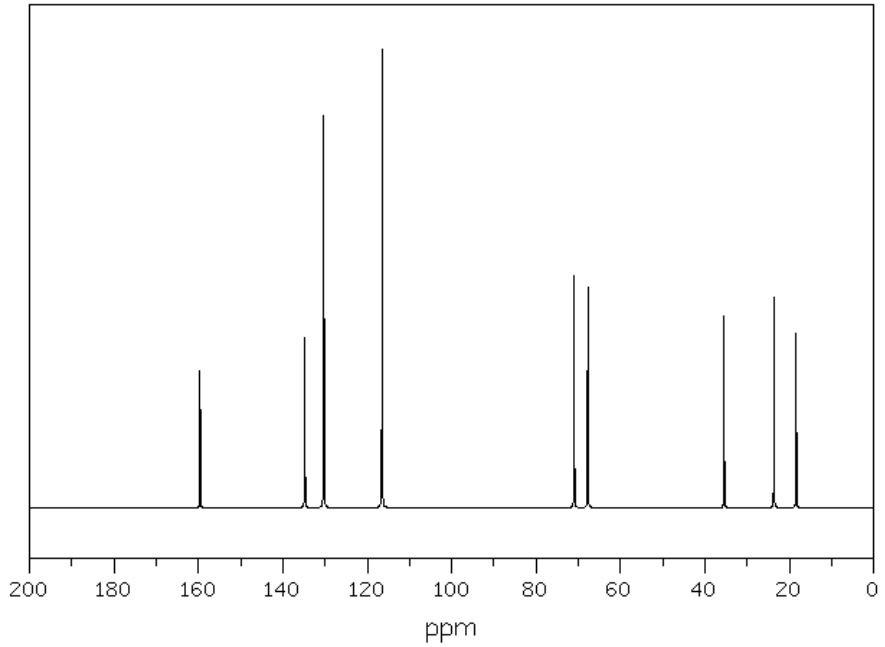
Elemental Analysis: C, 73.23; H, 9.01

Mass Spec: M^+ *m/e*= 180

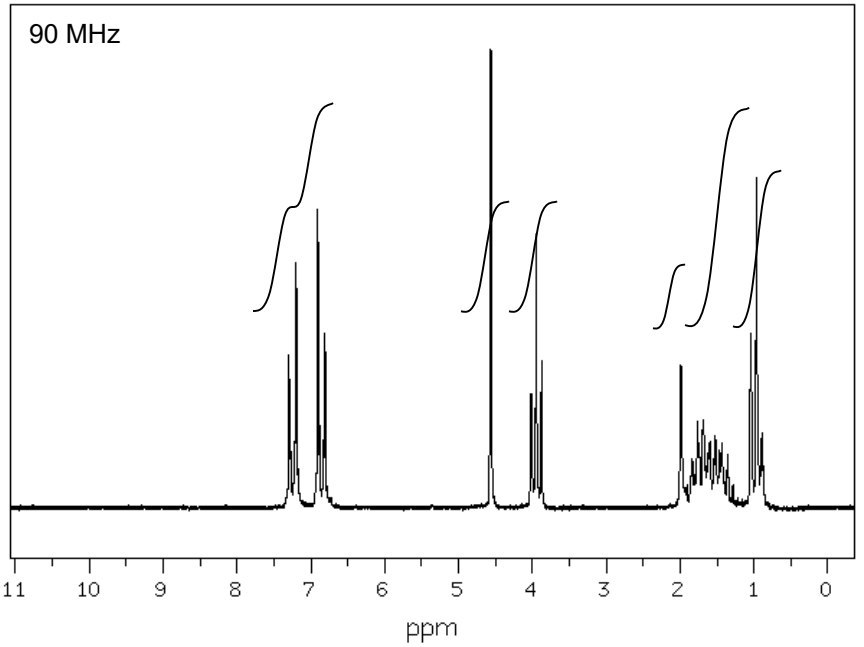
IR



^{13}C NMR



^{1}H NMR



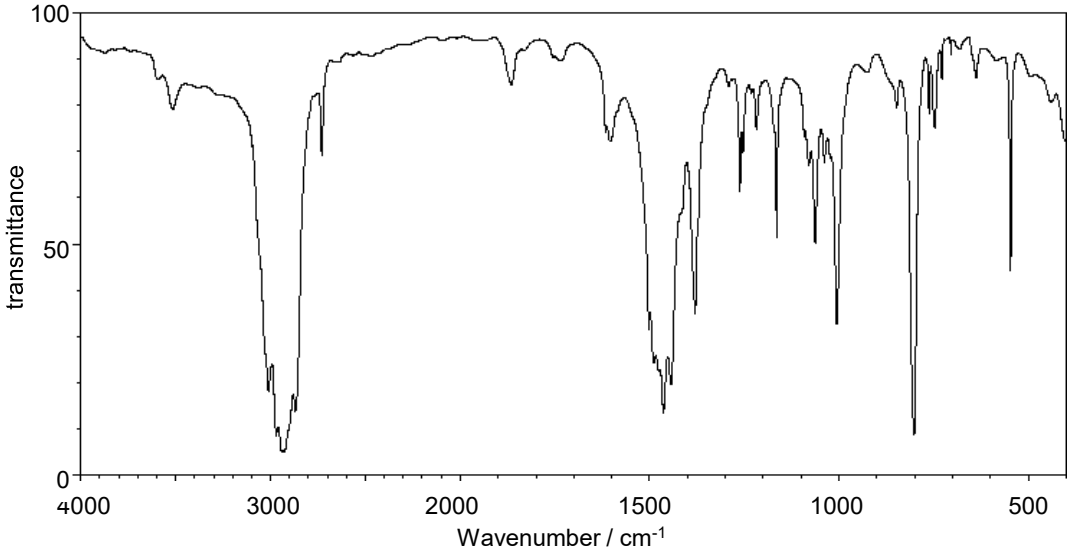
Empirical Formula: C_6H_9

Mass Spec: M^+ *m/e*= 162

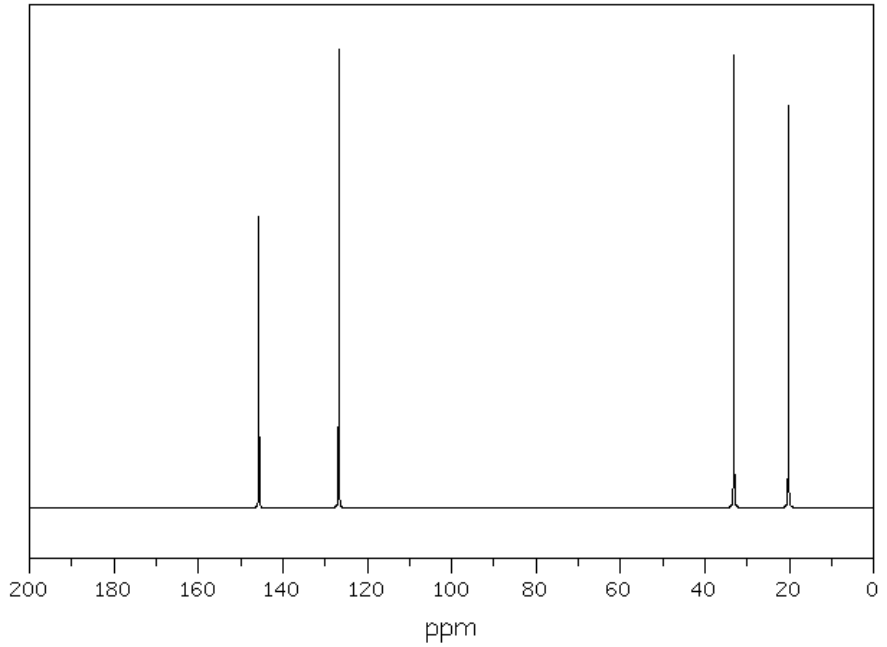
Compound #:

5

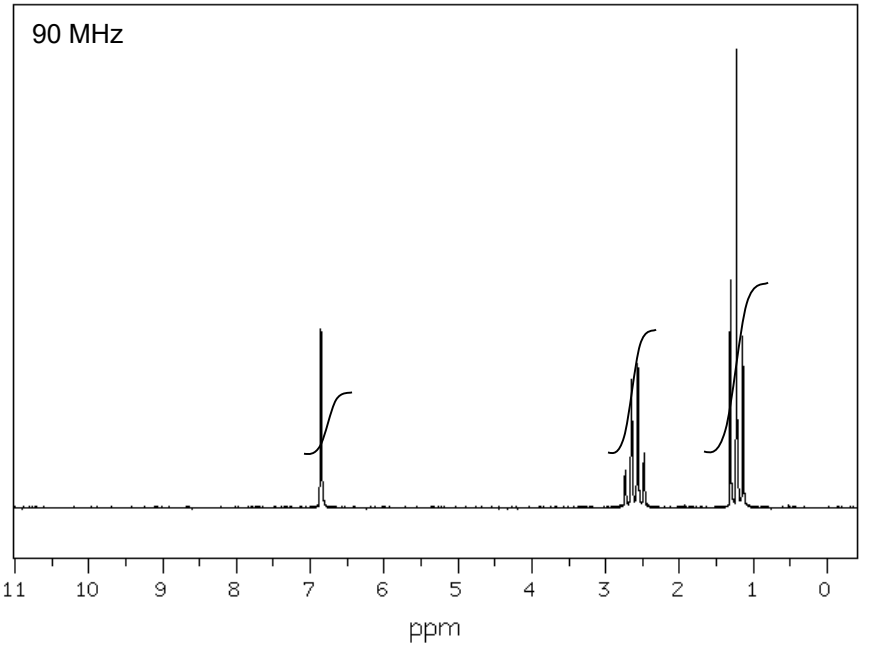
IR



^{13}C NMR



^{1}H NMR



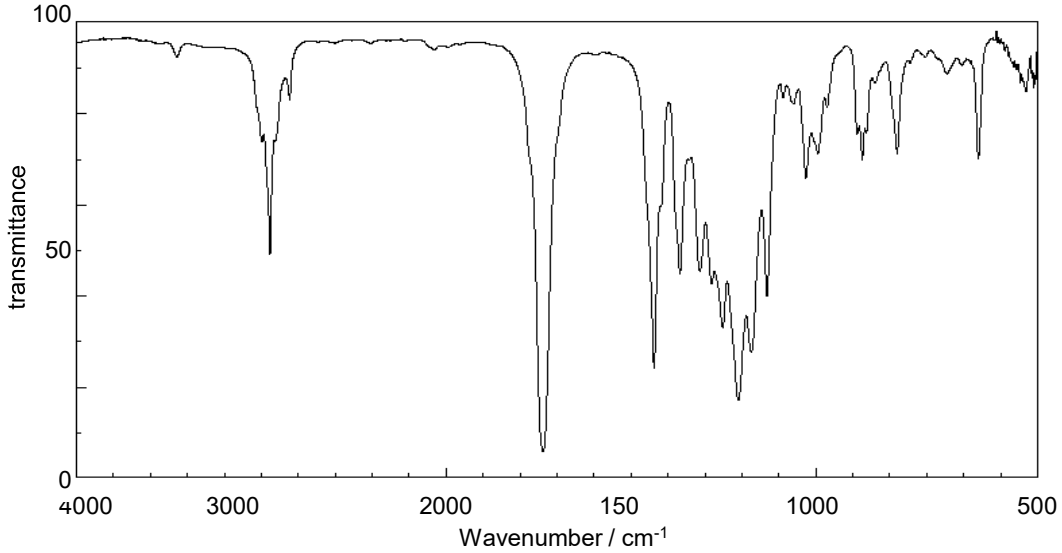
Compound #:

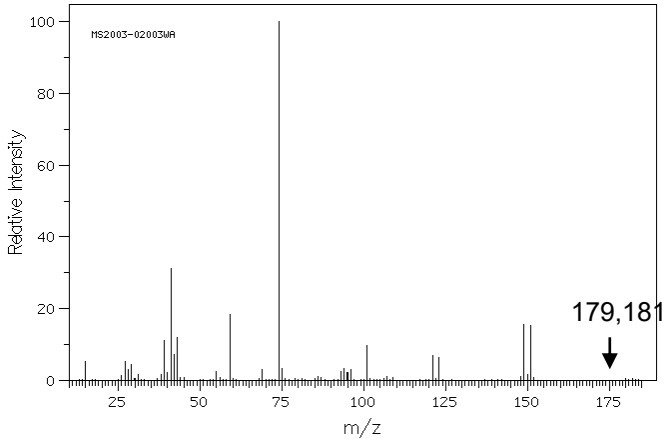
6

Empirical Formula: $C_5H_9BrO_2$

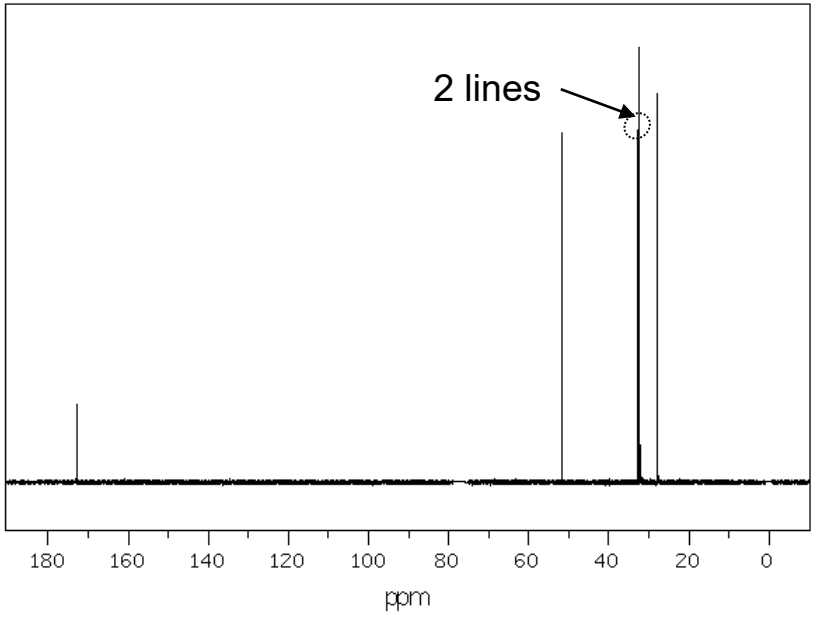
Mass Spec: M^+ *m/e*= 179 and 181

IR

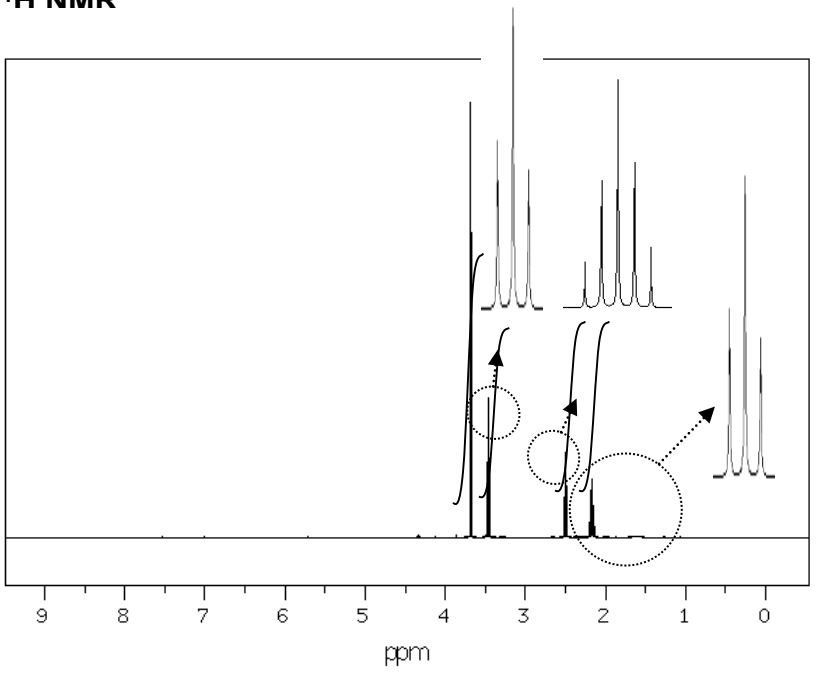




^{13}C NMR



^{1}H NMR



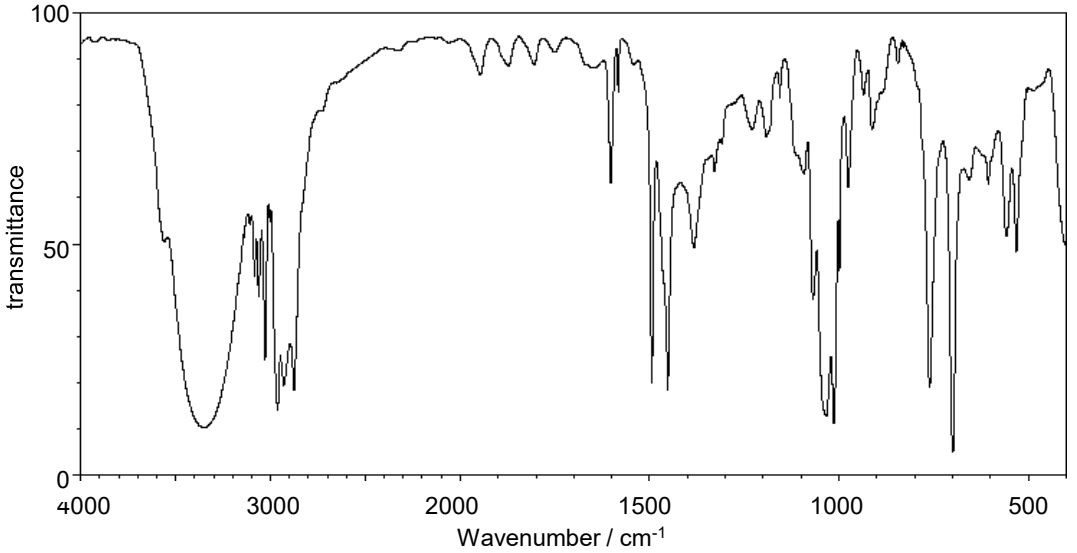
Empirical Formula:$C_9H_{12}0$

Mass Spec: M^+ *m/e*= 136

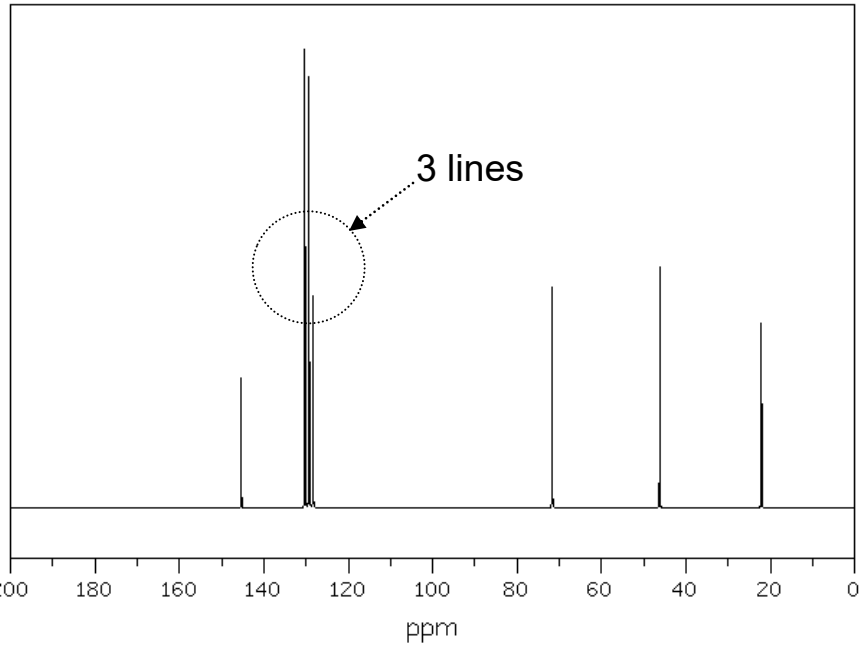
Compound #:

7

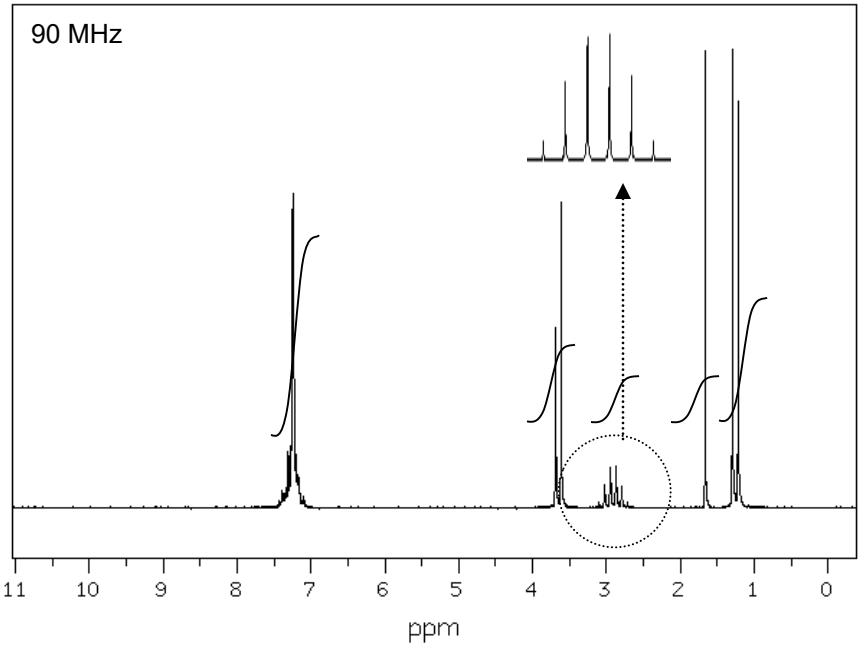
IR



^{13}C NMR



^{1}H NMR



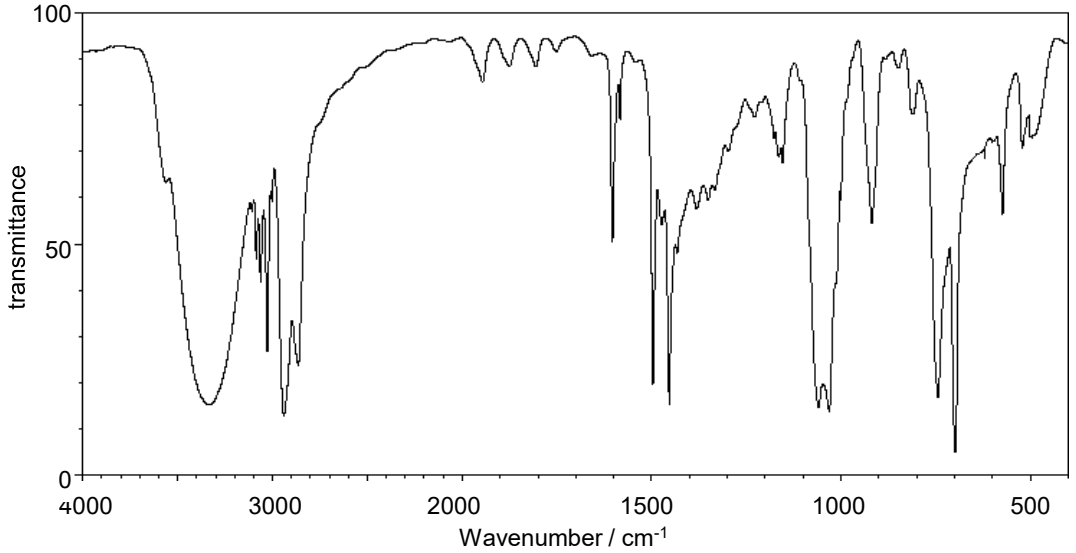
Compound #:

8

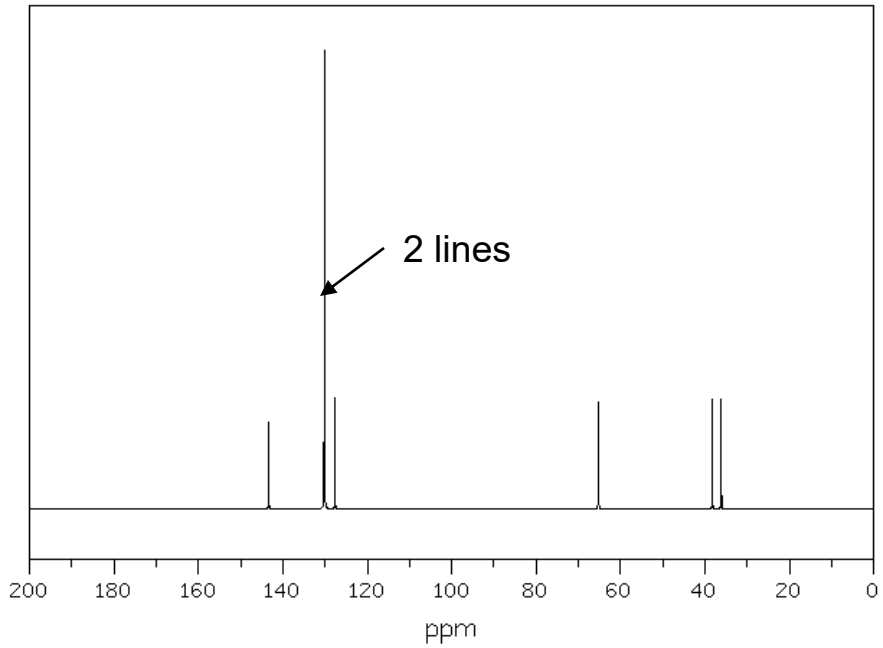
Empirical Formula: $C_9H_{12}O$

Mass Spec: M^+ *m/e*= 136

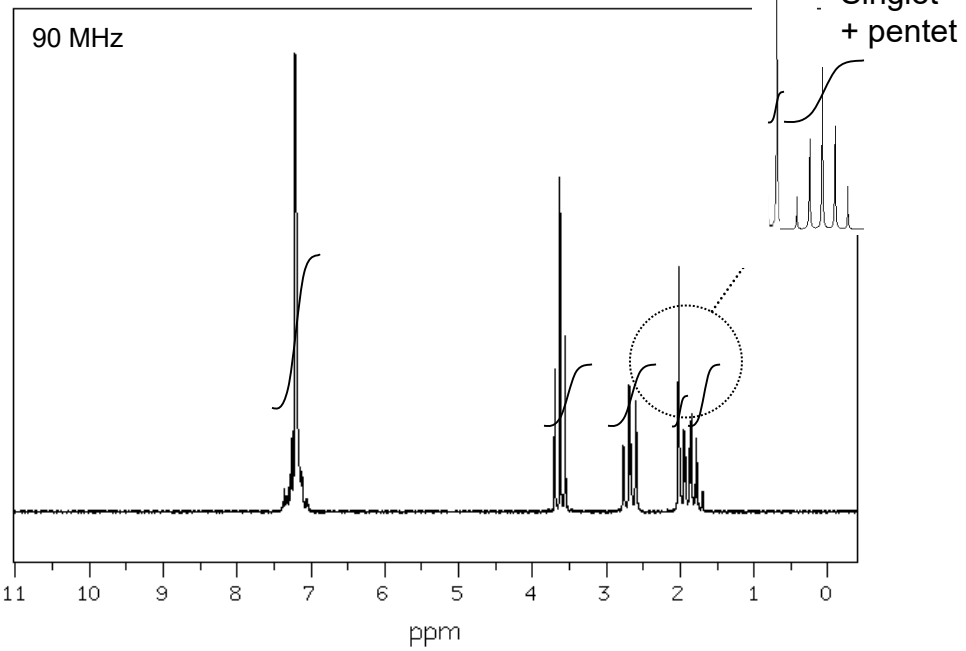
IR



^{13}C NMR



^{1}H NMR

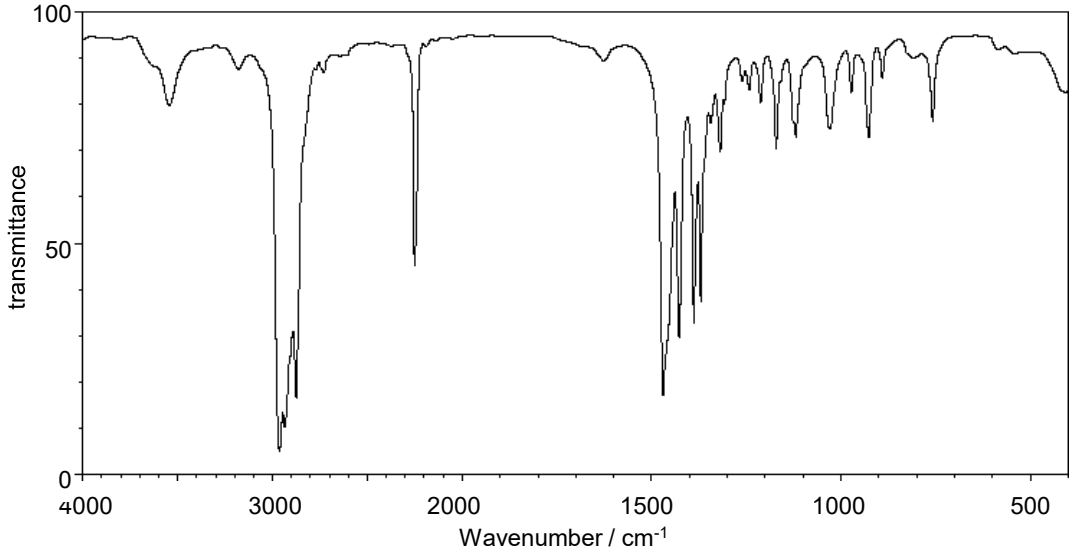


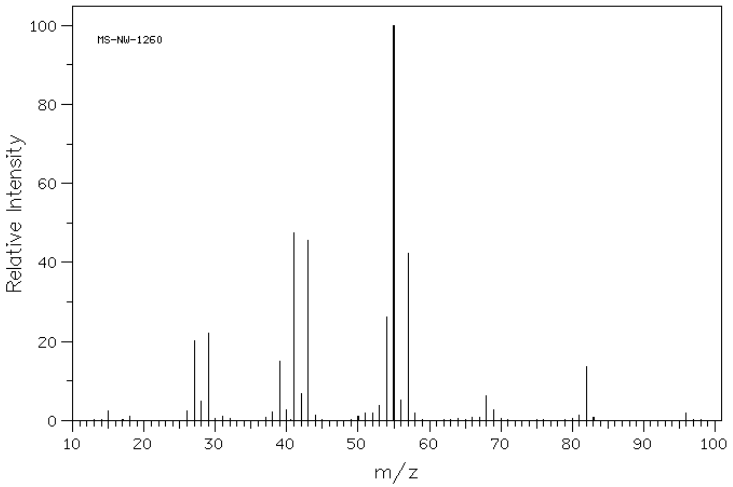
Empirical Formula: $C_6H_{11}N$

Compound #:

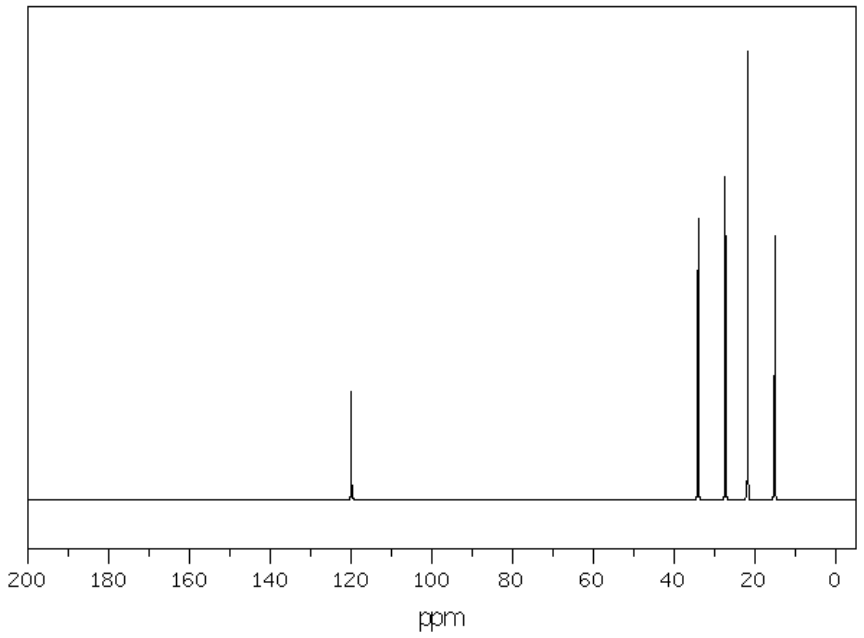
9

IR

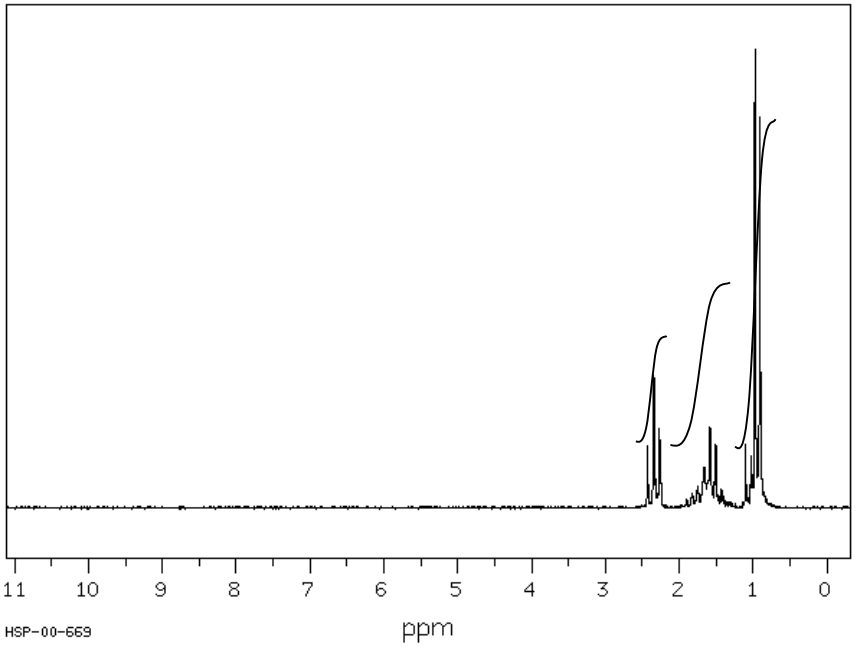




^{13}C NMR



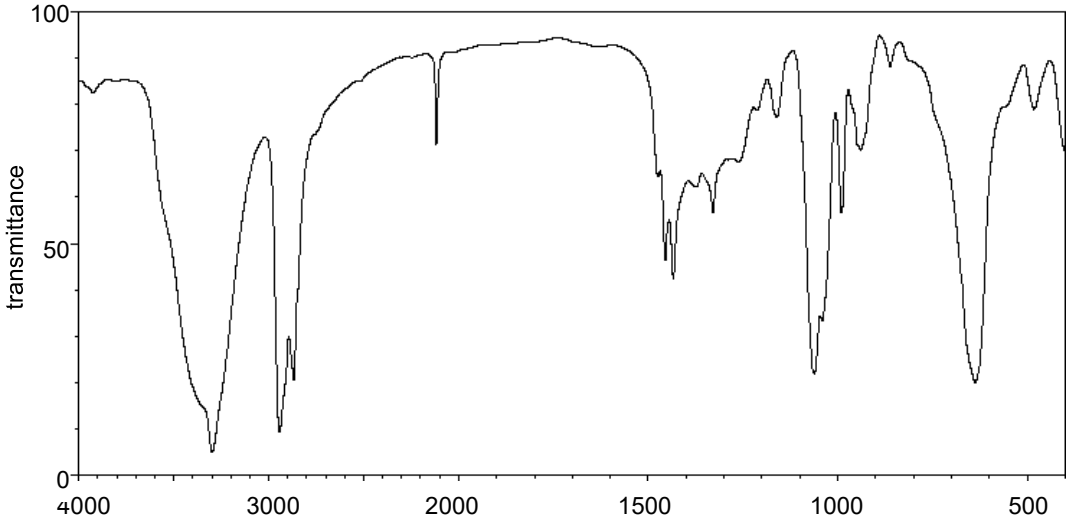
^{1}H NMR

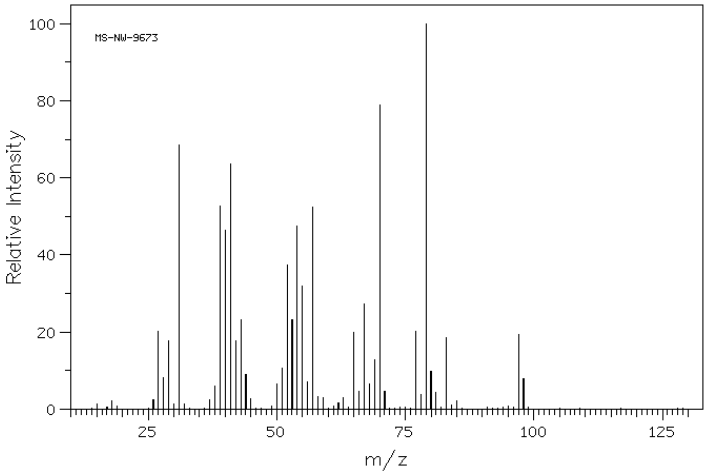


Empirical Formula: $C_6H_{10}O$

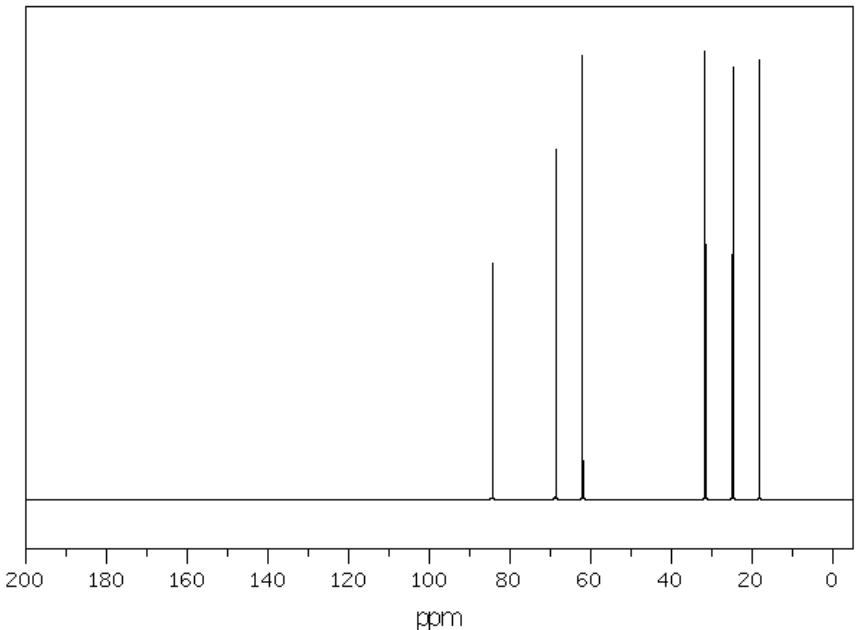
Compound #:
10

IR

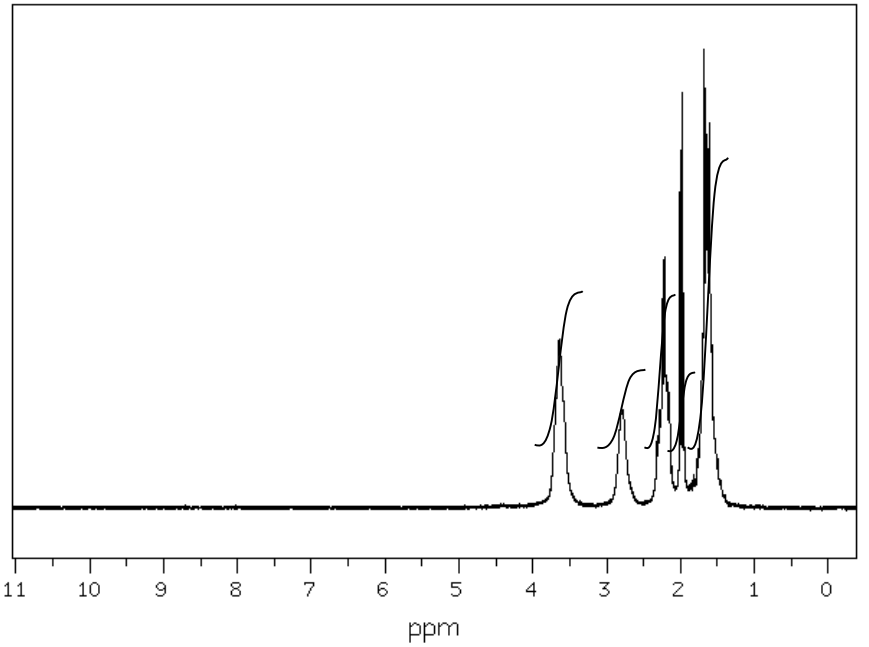




^{13}C NMR



^{1}H NMR



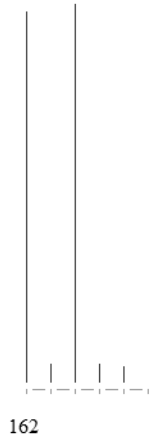
HW2 - Part B of this homework assignment resembles the first exam. Provide your answers on the homework answer form.

1. [10 points on exam]
What is the molecular formula of a compound containing C, H, Cl and O, and with MW below 200, that gives the following combustion analysis?
C, 39.35.%; H, 4.39%; Cl, 38.73%?

Molecular Formula: _____

2. [10 points on exam]
What is the molecular formula of a compound that best fits the following molecular ion isotope cluster in the mass spectrum?

m/z	height
162.	98.0
163.	5.2
164.	100.0
165.	5.3
166.	4.5



Molecular Formula: _____

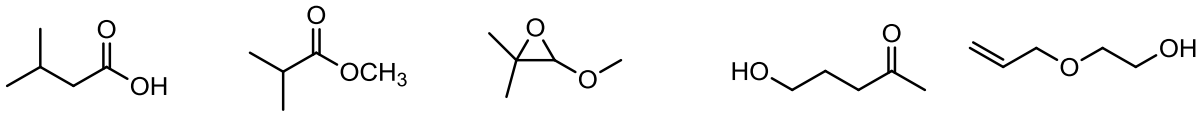
3. [40 points on exam] Provide *neatly drawn* line-bond structures for compounds **A-D** (spectra on attached pages). Provide a single structure that best fits the data provided.
If you cannot solve a problem, provide as much information as you can about the structure. For example: functional groups that are present (e.g., alcohol, amine. alkene, alkyne – probably from IR); and other structural fragments (e.g., monosubstituted benzene, isopropyl, ethyoxy , CH_2CH_2 – probably from ^{1}H NMR). *If possible, you should account for all of the atoms that are present in the molecule.*

Compound A	Compound B
Compound C	Compound D

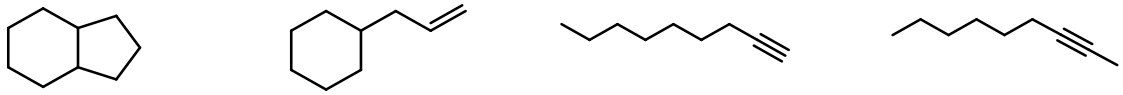
4. [40 points on exam]

Match spectra **E-X** to the following compounds (spectra on attached pages):

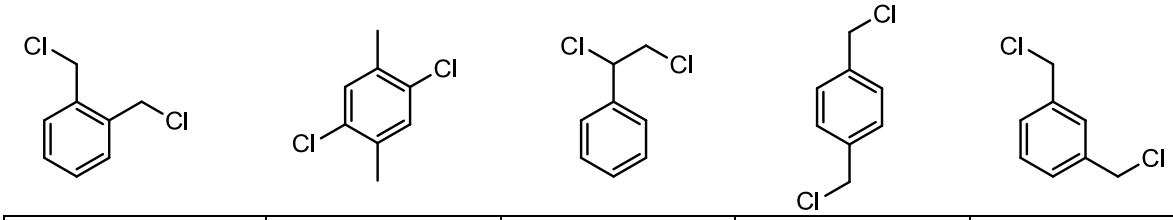
(a) **E-I**, all $C_5H_{10}O_2$



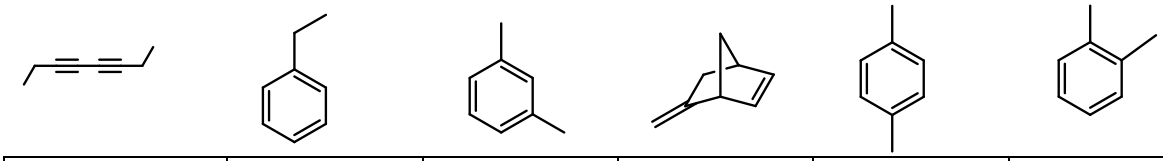
(b) **J-M**, all C_9H_{16}



(c) **N-R**, all $C_8H_8Cl_2$



(d) **S-X**, all C_8H_{10}

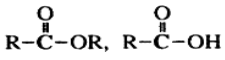
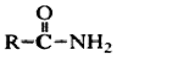
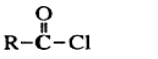
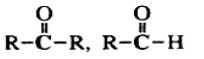


Typical ranges for IR stretching vibrations

Functional Group	*Range, cm^{-1}*	*Intensity and shape*
sp^3 C—H	2850-2960	medium to strong; sharp
sp^2 C—H	3010-3190	medium to strong; sharp
sp C—H	about 3300	medium to strong; sharp
C═C	1620-1660	weak to medium; sharp
C≡C	2100-2260	weak to medium; sharp
N—H	3300-3500	medium; broad
O—H (H-bonded)	3200-3550	strong; broad
O—H (carboxylic acid)	2500-3000	medium; very broad
C—O	1050-1150	medium to strong; sharp
C=O	1630-1780	medium to strong; sharp
C≡N	2200-2260	medium; sharp

APPENDIX 7

Approximate ^{13}C Chemical-Shift Values (ppm) for Selected Types of Carbon

Types of Carbon	Range (ppm)	Types of Carbon	Range (ppm)
$R-CH_3$	8–30	C≡C	65–90
R_2CH_2	15–55	C=C	100–150
R_3CH	20–60	C≡N	110–140
C—I	0–40		110–175
C—Br	25–65		155–185
C—N	30–65		155–185
C—Cl	35–80		160–170
C—O	40–80		185–220

Typical ^1H NMR chemical shifts

Type of proton	chemical shift (δ)
$(CH_3)_4Si$	0.00
CH_3-C-R (sp^3)	0.9 - 1.8
-CH_2-C-R (sp^3)	1.1 - 2.0
-CH-C-R (sp^3)	1.3 - 2.1
H-C-N	2.2 - 2.9
H-C-O	3.3 - 3.7
H-C-Cl	3.1 - 4.1
H-C-Br	2.7 - 4.1
H-C-C=O	2.1 - 2.5
H-C-C=C	1.6 - 2.6
H-C-Ar	2.3 - 2.8
H-C=O (sp^2)	9 - 10
H-C=C (sp^2)	4.5 - 6.5
H-Ar (sp^2)	6.5 - 8.5
H-C C (sp)	2.5
H-N (amine)	1 - 3
H-OR (alcohol)	0.5 - 5
H-OAr (phenol)	6 - 8
H-O_2CR (acid)	10 - 13

Hydrogen 1 H 1.01							Helium 2 He 4.00
Lithium 3 Li 6.94	Beryllium 4 Be 9.01	Boron 5 B 10.81	Carbon 6 C 12.01	Nitrogen 7 N 14.01	Oxygen 8 O 16.00	Fluorine 9 F 19.00	Neon 10 Ne 20.18
Sodium 11 Na 22.99	Magnesium 12 Mg 24.31	Aluminum 13 Al 26.98	Silicon 14 Si 28.09	Phosphorus 15 P 30.97	Sulfur 16 S 32.07	Chlorine 17 Cl 35.45	Argon 18 Ar 39.95
Potassium 19 K 39.10	Calcium 20 Ca 40.08	Gallium 31 Ga 69.72	Germanium 32 Ge 72.61	Arsenic 33 As 74.92	Selenium 34 Se 78.96	Bromine 35 Br 79.90	Krypton 36 Kr 83.80
Rubidium 37 Rb 85.47	Strontium 38 Sr 87.62	Indium 49 In 114.82	Tin 50 Sn 118.71	Antimony 51 Sb 121.76	Tellurium 52 Te 127.60	Iodine 53 I 126.90	Xenon 54 Xe 131.29

TABLE 2-2 *Isotopic Contributions for Carbon and Hydrogen*

If the abundance of the ion A^+ is 100 (after correction for ^{13}C isotopic contributions to it), then its isotopic contributions will be:

	$(A+1)^+$	$(A+2)^+$		$(A+1)^+$	$(A+2)^+$
C_1	1.1	0.000	C_{21}	23	2.5
C_2	2.2	0.012	C_{22}	24	2.8
C_3	3.3	0.036	C_{23}	25	3.0
C_4	4.4	0.073	C_{24}	26	3.3
C_5	5.5	0.12	C_{25}	28	3.6
C_6	6.6	0.18	C_{26}	29	3.9
C_7	7.7	0.25	C_{27}	30	4.2
C_8	8.8	0.34	C_{28}	31	4.5
C_9	9.9	0.44	C_{29}	32	4.9
C_{10}	11.0	0.54	C_{30}	33	5.2
C_{11}	12.1	0.67	C_{31}	34	5.6
C_{12}	13.2	0.80	C_{32}	35	6.0
C_{13}	14.3	0.94	C_{33}	36	6.4
C_{14}	15.4	1.10	C_{34}	37	6.8
C_{15}	16.5	1.27	C_{35}	39	7.2
C_{16}	17.6	1.46	C_{36}	40	7.6
C_{17}	18.7	1.65	C_{37}	41	8.0
C_{18}	19.8	1.86	C_{38}	42	8.5
C_{19}	20.9	2.07	C_{39}	43	8.9
C_{20}	22.0	2.30	C_{40}	44	9.4

For each additional element present, add *per atom:*

$(A+1)^+$: N, 0.37; O, 0.04; Si, 5.1; S, 0.80.
$(A+2)^+$: O, 0.20; Si, 3.4; S, 4.4; Cl, 32.5; Br, 98.0.

Typical values for $(A+3)^+$: C_{10}, 0.016; C_{15}, 0.06; C_{20}, 0.15; C_{25}, 0.31; C_{30}, 0.54; C_{35}, 0.87; C_{40}, 1.3. $(A+4)^+$: C_{25}, 0.018; C_{40}, 0.13.

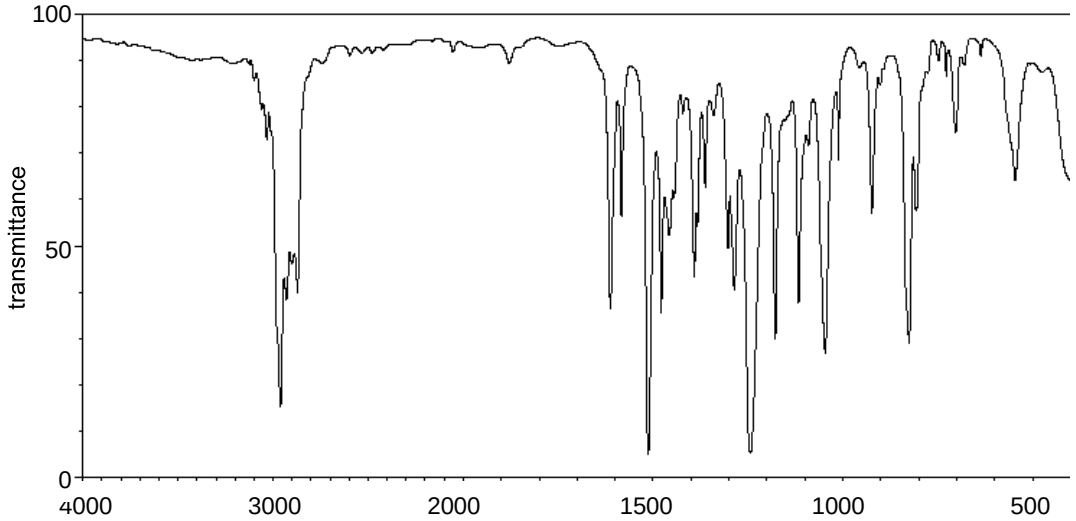
Calculated assuming $^{13}C/^{12}C = 1.08\%$ with 1.5 H atoms per C atom; ±0.5 H/C changes the intensity of $(A+1)^+$ by only ±0.7% of its value, $(A+2)^+$ by ± 1.5% of its value.

Molecular Formula: $C_{11}H_{16}O$

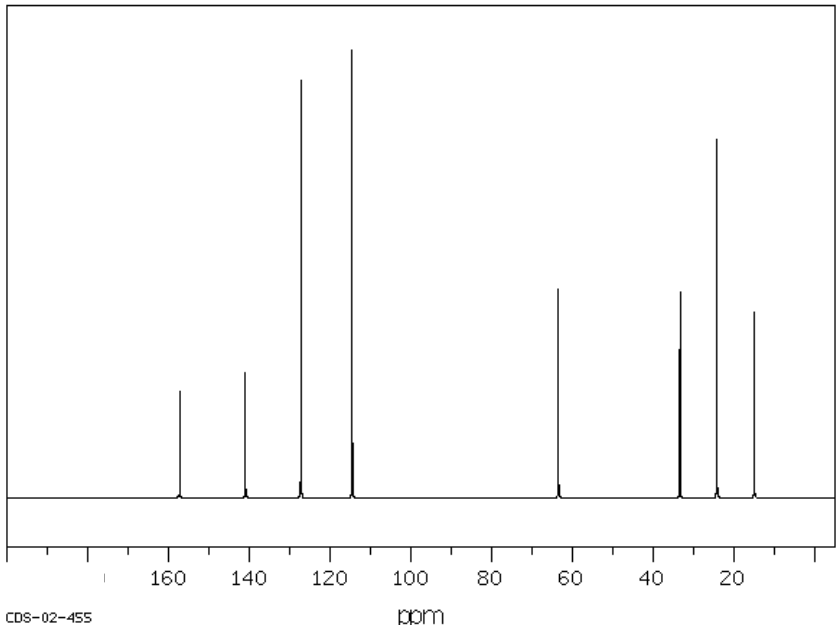
Compound :

A

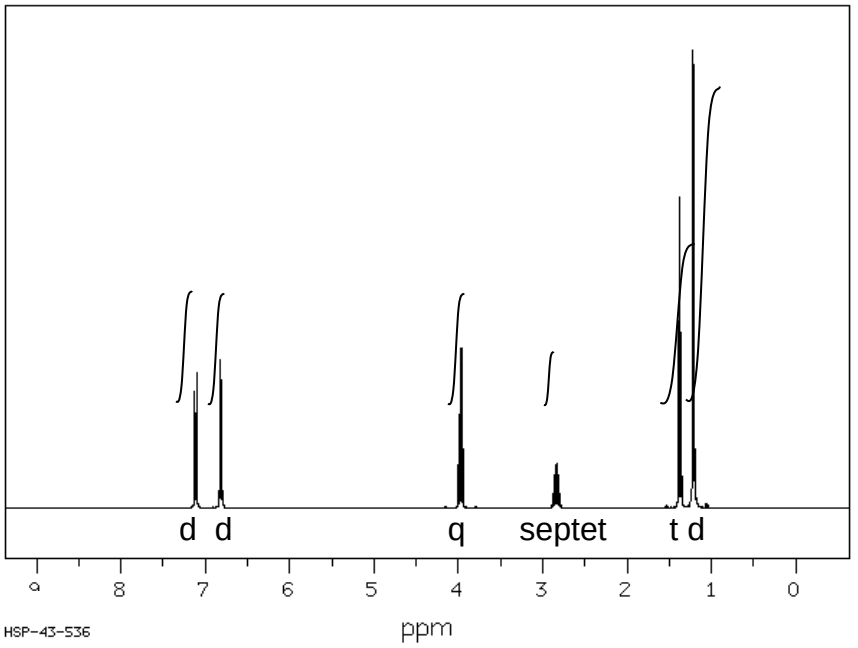
IR



^{13}C NMR



^{1}H NMR

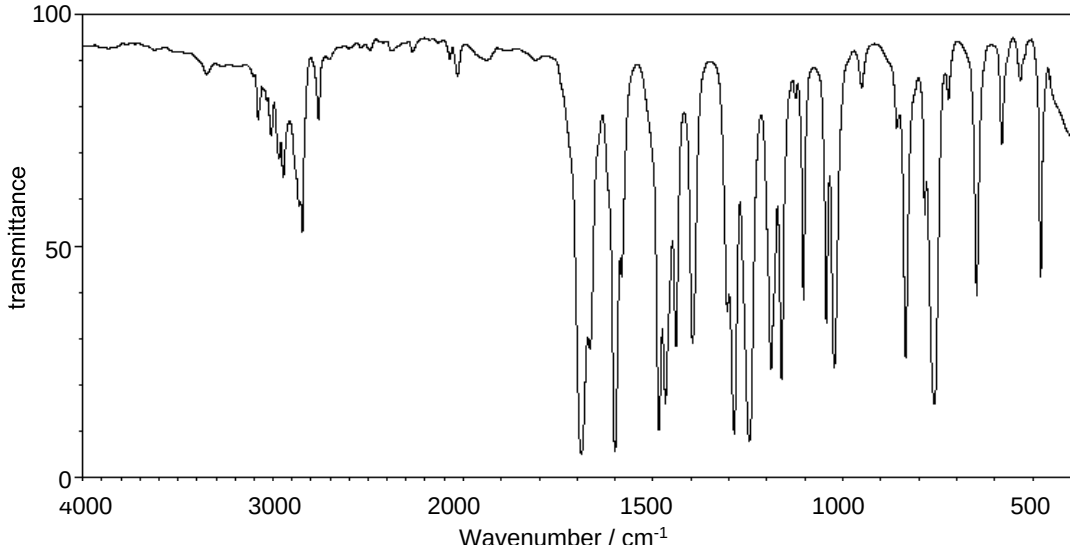


Compound :

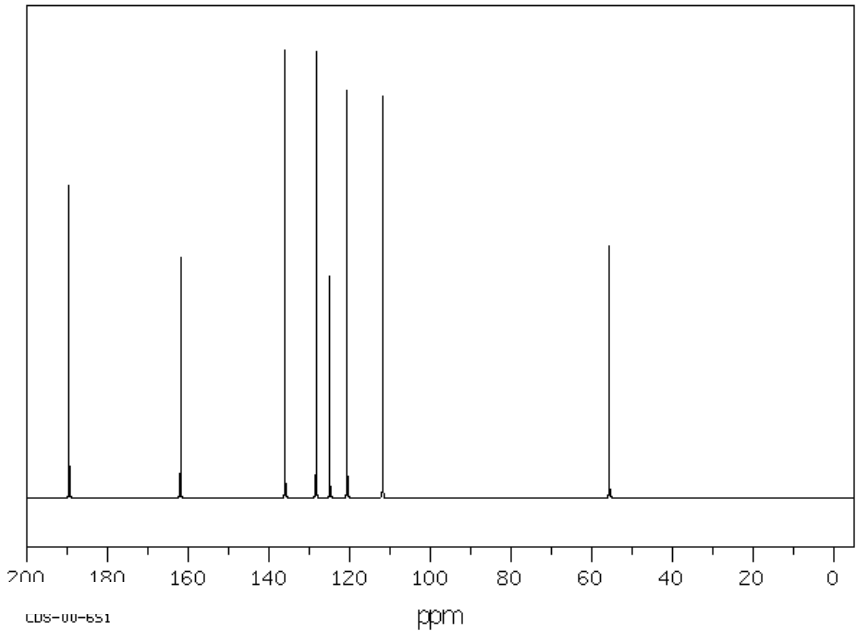
B

Molecular Formula: $C_8H_8O_2$

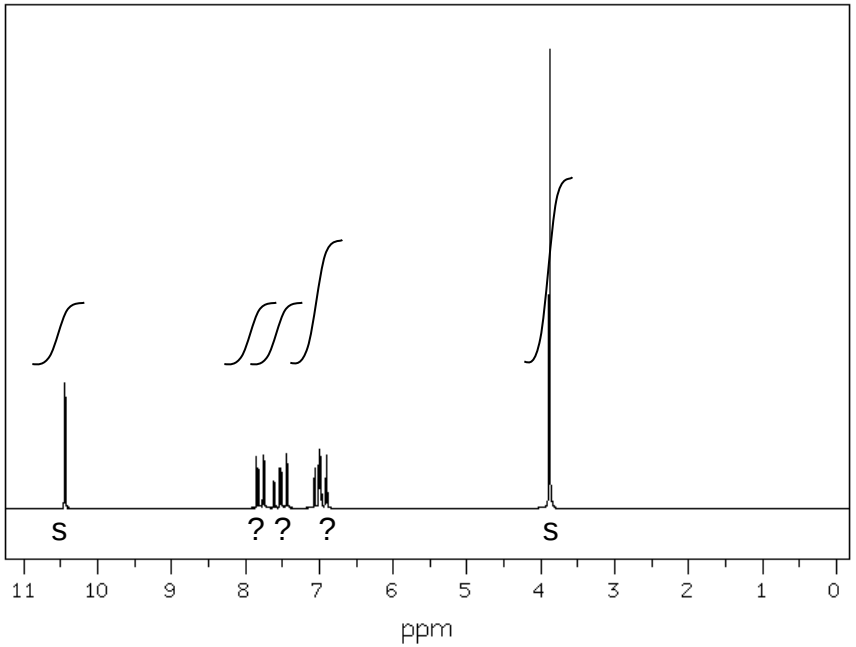
IR



^{13}C NMR



^{1}H NMR

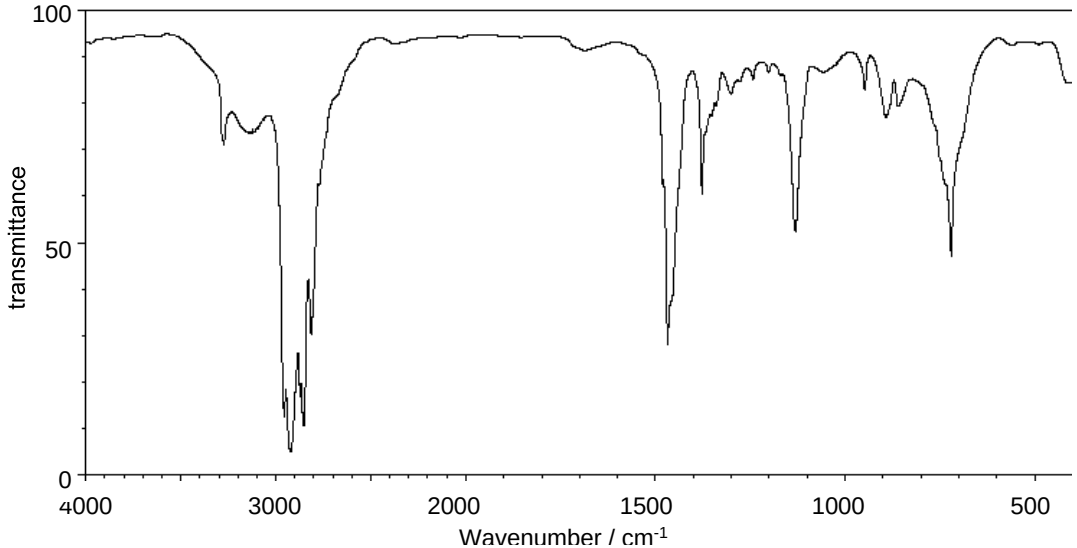


Molecular Formula: $C_{16}H_{35}N$

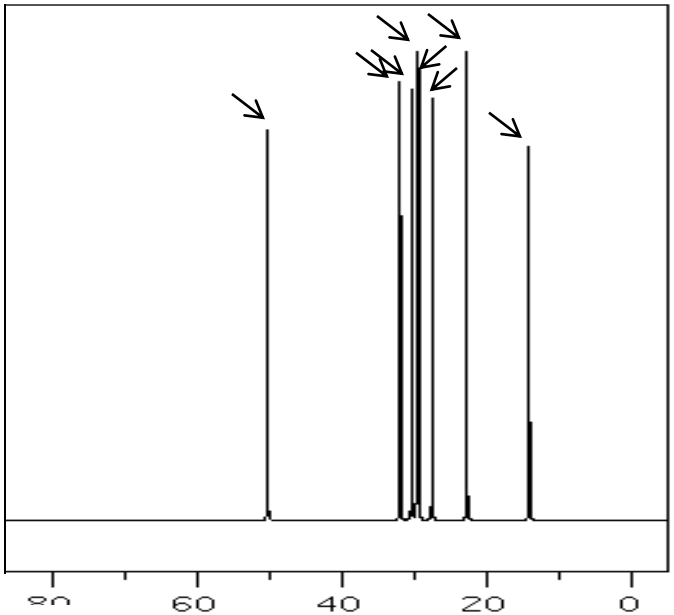
Compound :

C

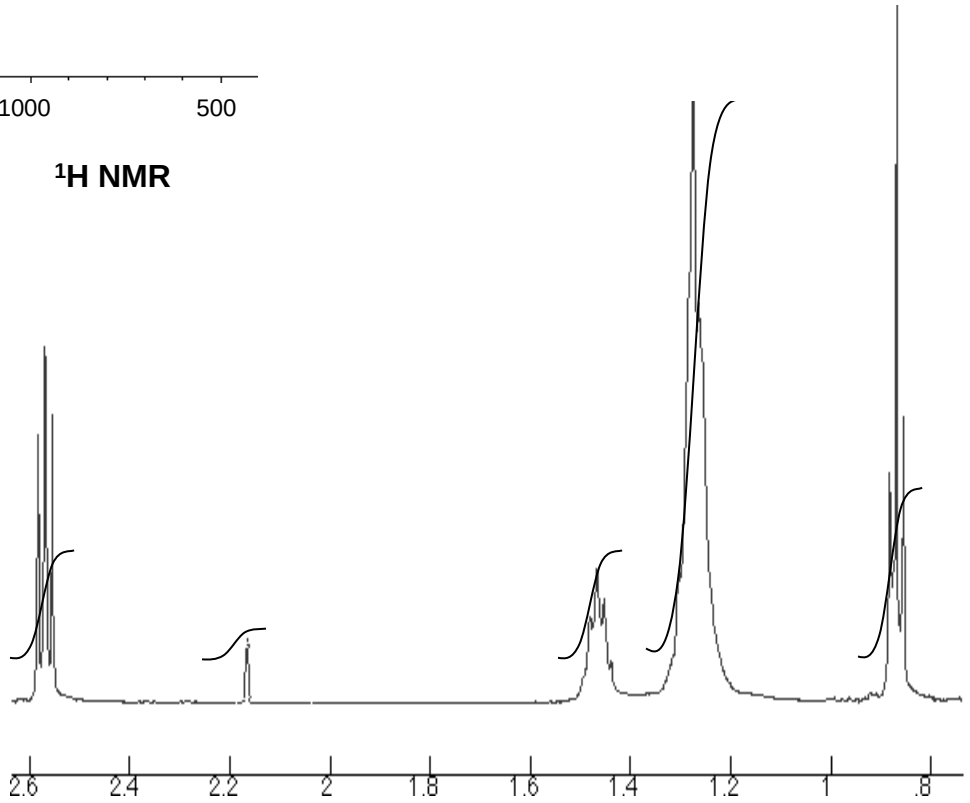
IR



^{13}C NMR (there are 8 signals)



^{1}H NMR

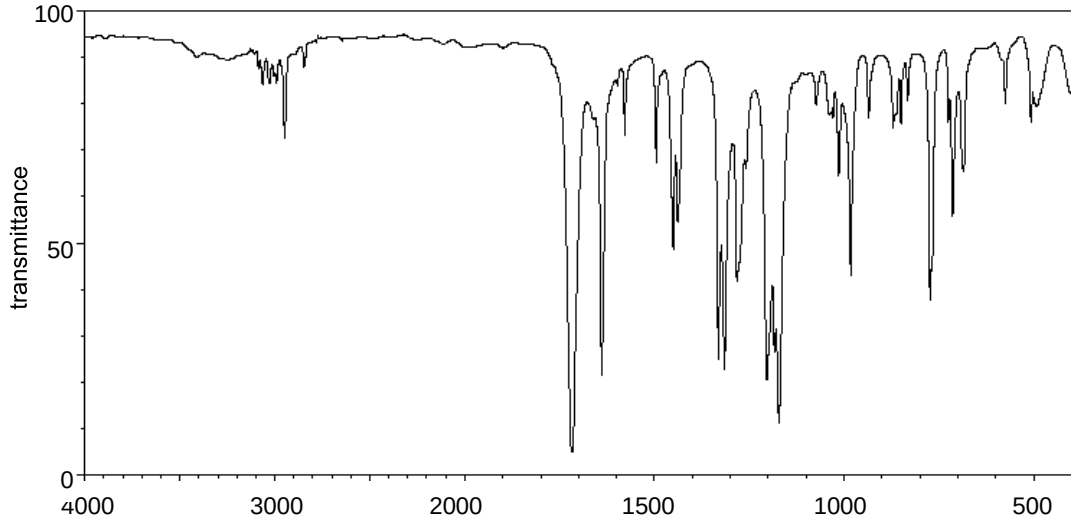


Compound :

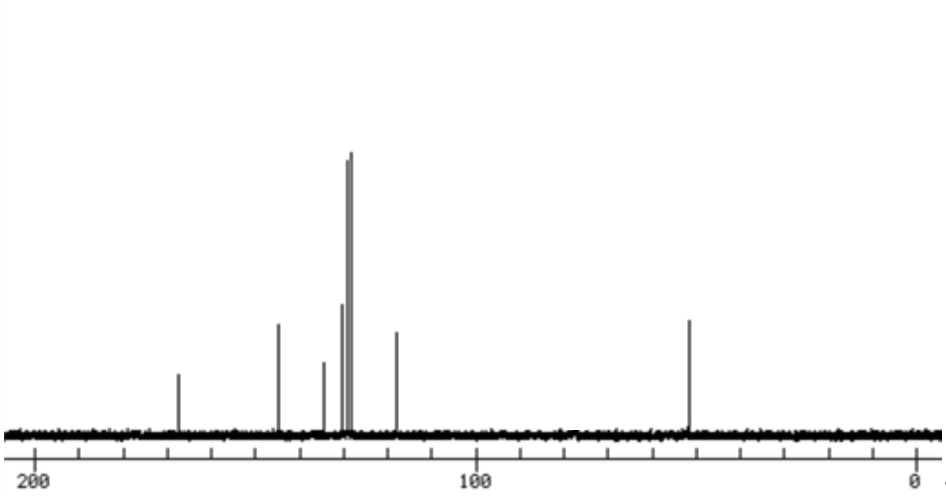
D

Molecular Formula: $C_{10}H_{10}O_2$

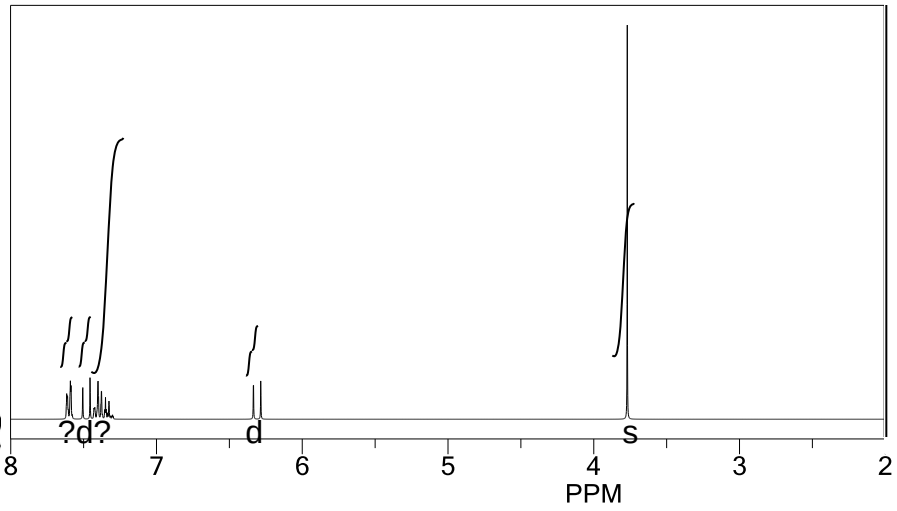
IR

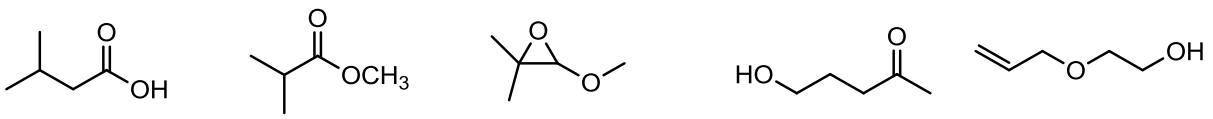


^{13}C NMR

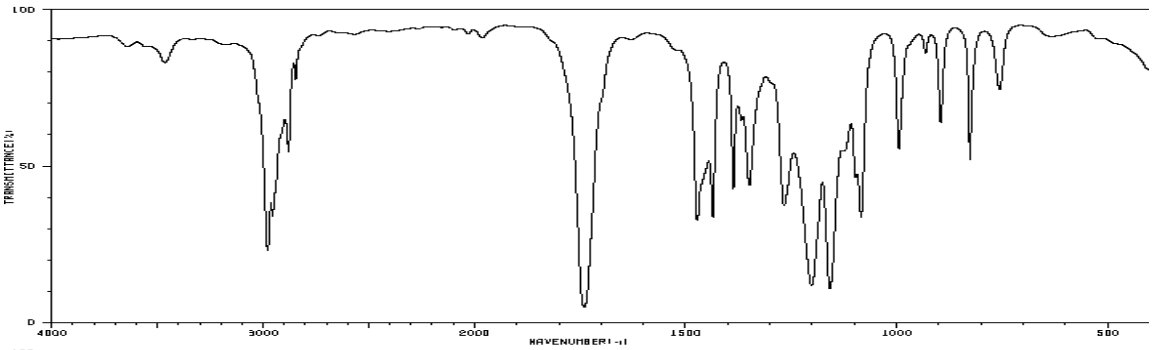


^{1}H NMR




O
OH
O
OCH3
O
O
HO
O
O
OH

E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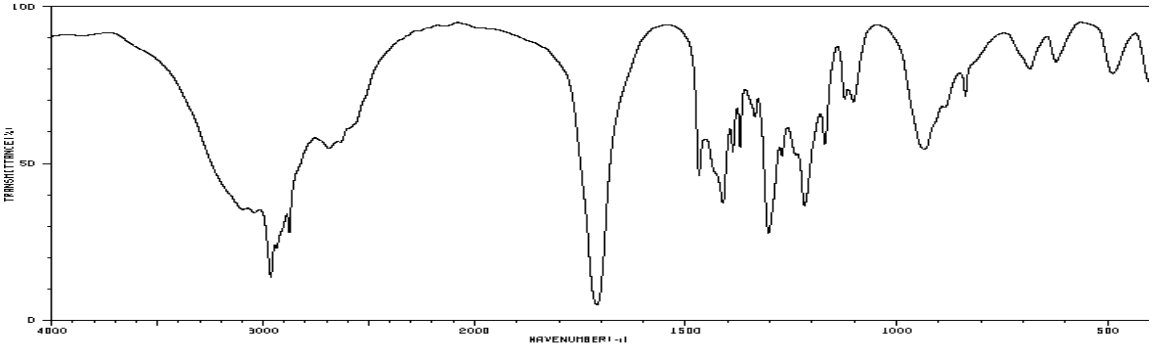
0
4000
3000
2000
1500
1000
500

F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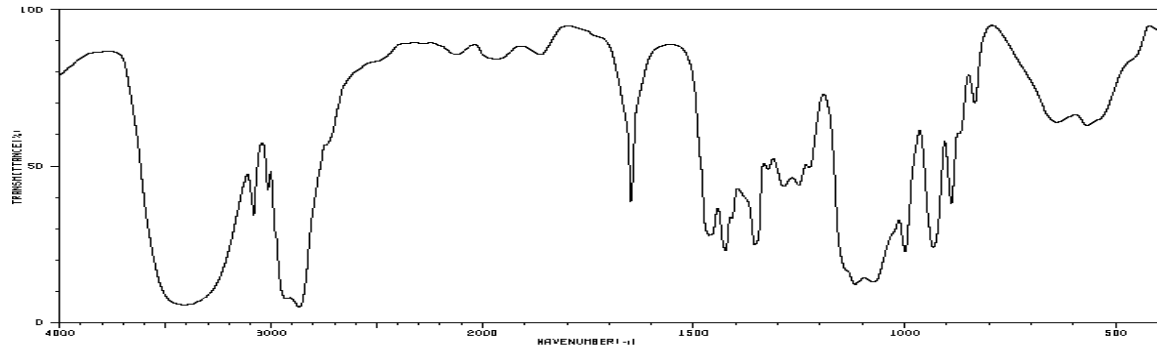
50
0
4000
3000
2000
1500
1000
500

G


100
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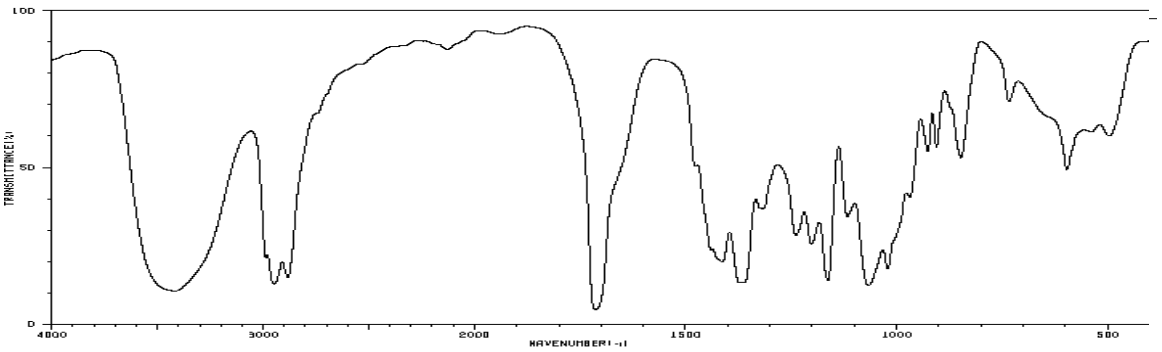
3000
2000
1500
1000
500

H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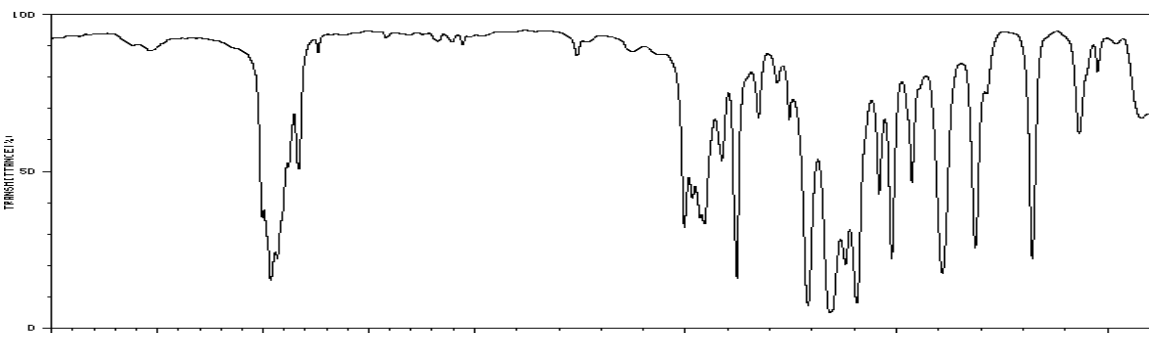
I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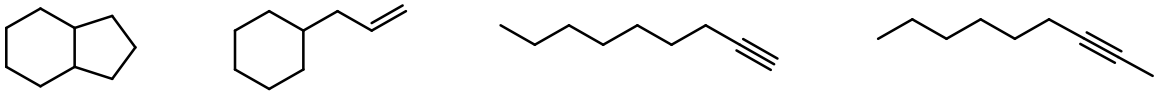
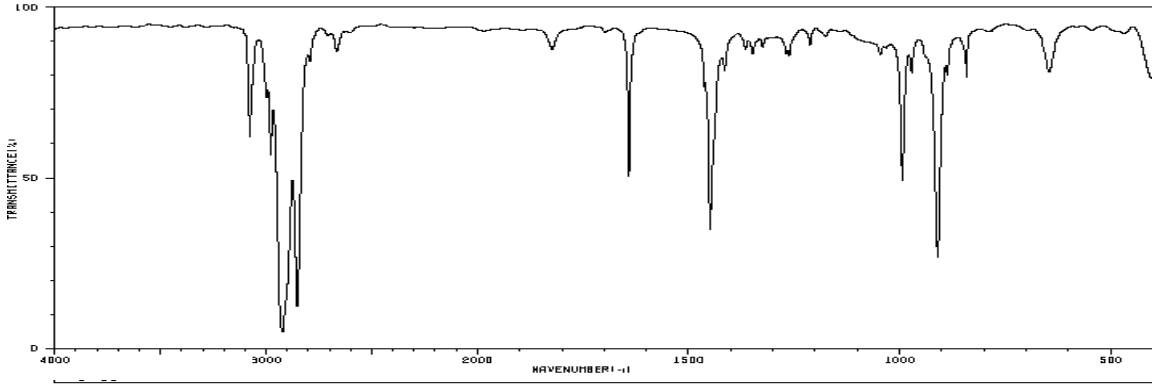


J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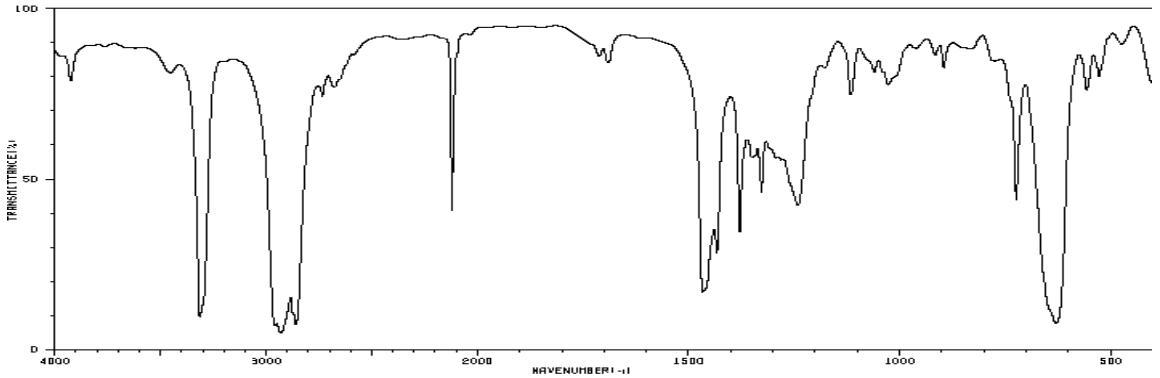
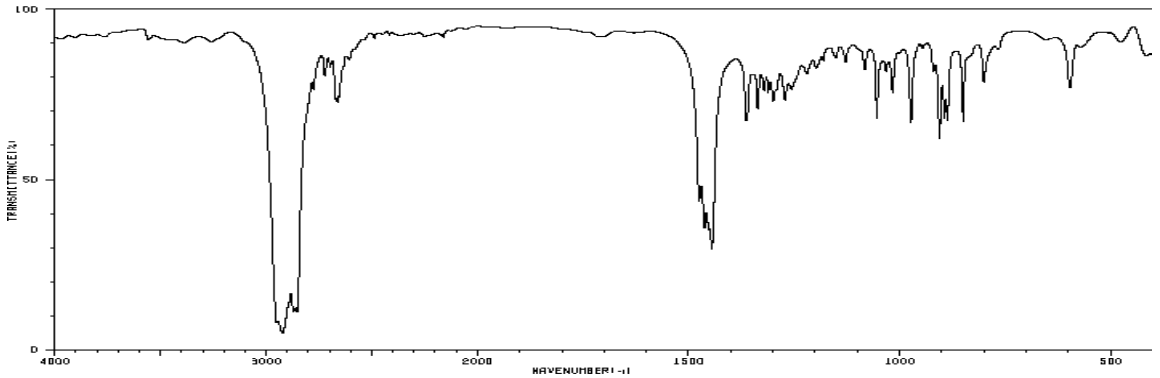
500

K


100
50
0
4000
3000
2000
1500
1000
500

L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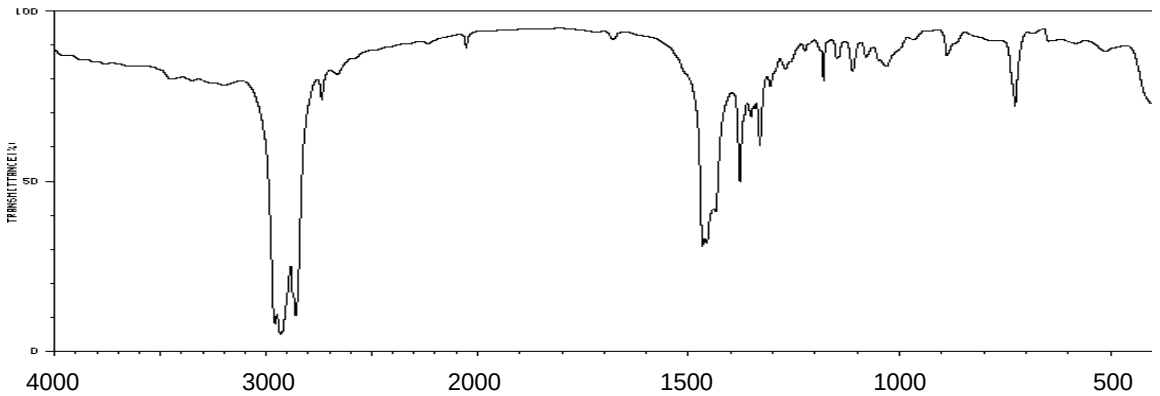
500

M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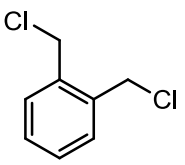
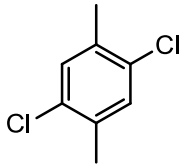

Cl
Cl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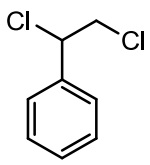
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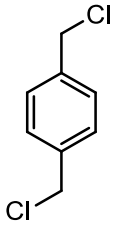
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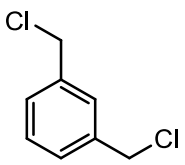
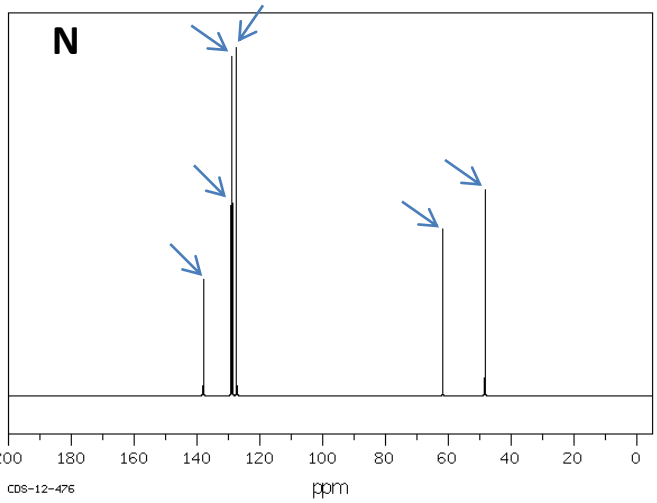

Cl
Cl


N
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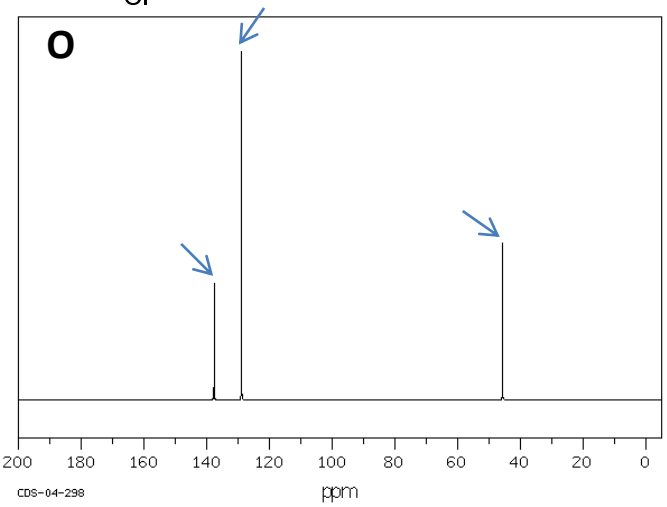
CDS-12-476
ppm


O
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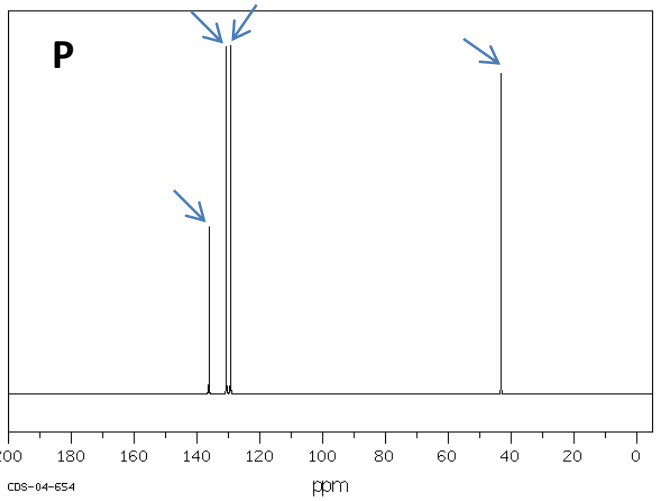
CDS-04-298
ppm


P
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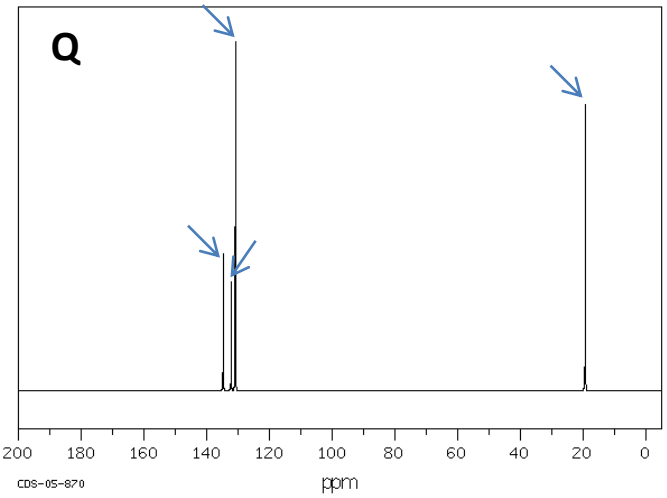
CDS-04-654
ppm


Q
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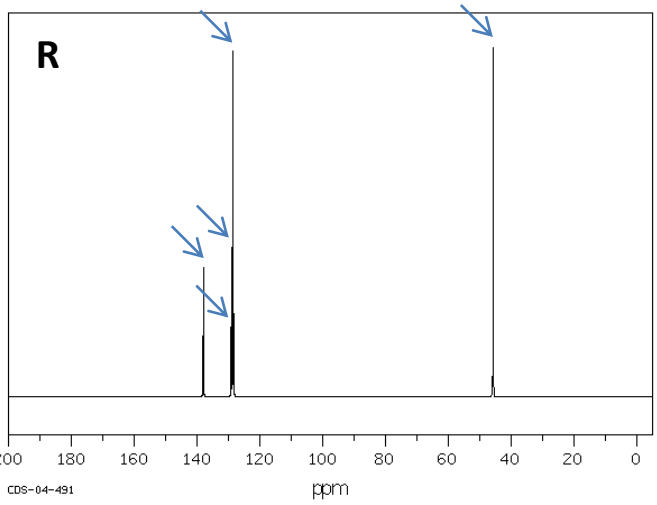
CDS-05-870
ppm


R
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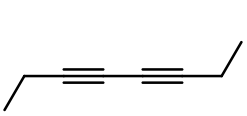
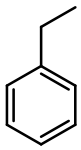
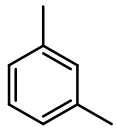
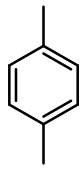
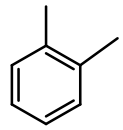
CDS-04-491
ppm



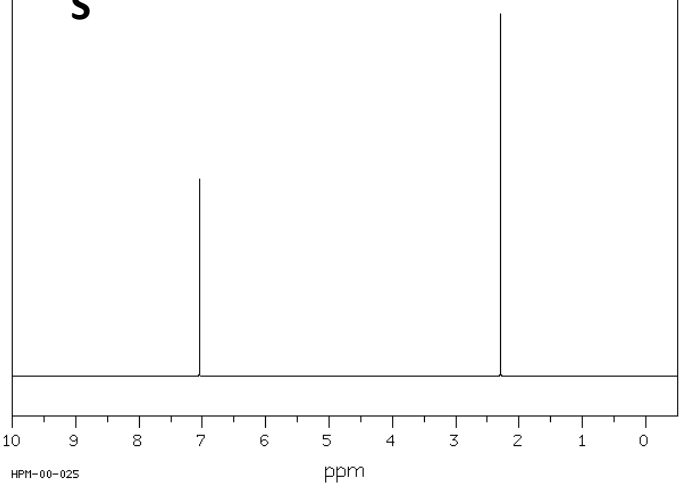




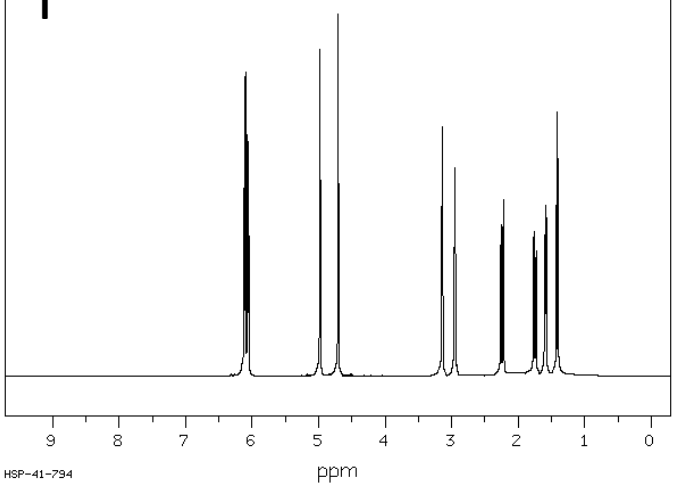




S


10 9 8 7 6 5 4 3 2 1 0
HPM-00-025
ppm

T


9 8 7 6 5 4 3 2 1 0
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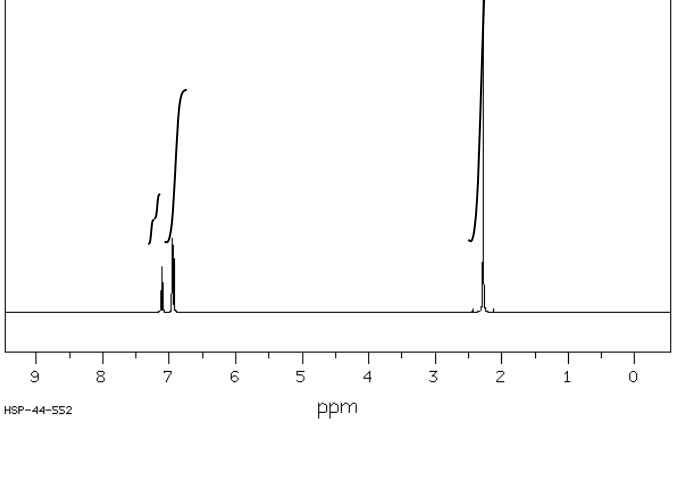
U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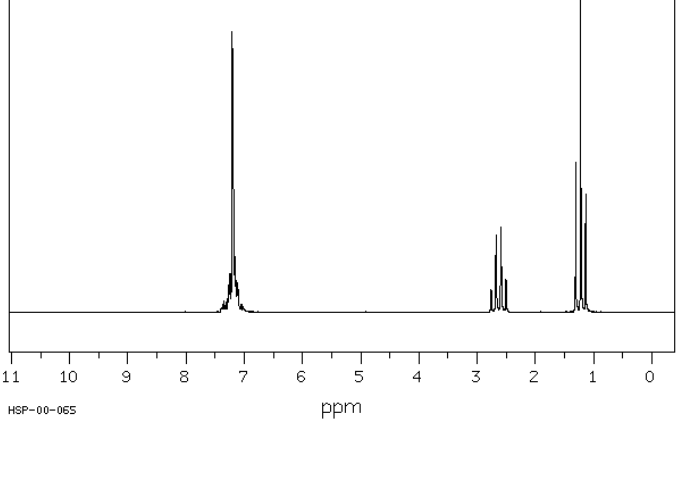
ppm

V


11 10 9 8 7 6 5 4 3 2 1 0
HSP-00-065
ppm

W

9 8 7 6 5 4 3 2 1 0
HSP-43-787
ppm

X

11 10 9 8 7 6 5 4 3 2 1 0
HSP-01-106
ppm