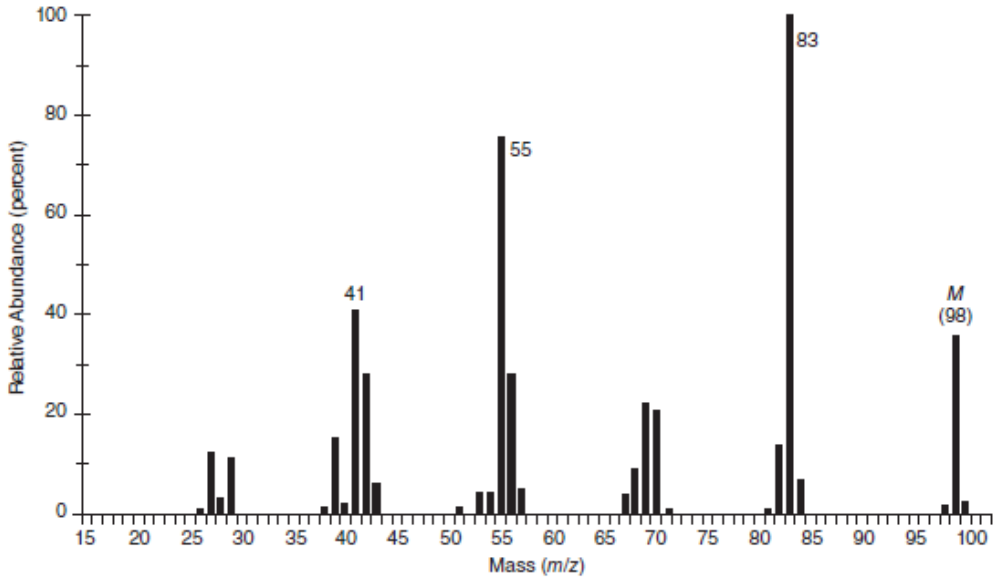
Homework # 3

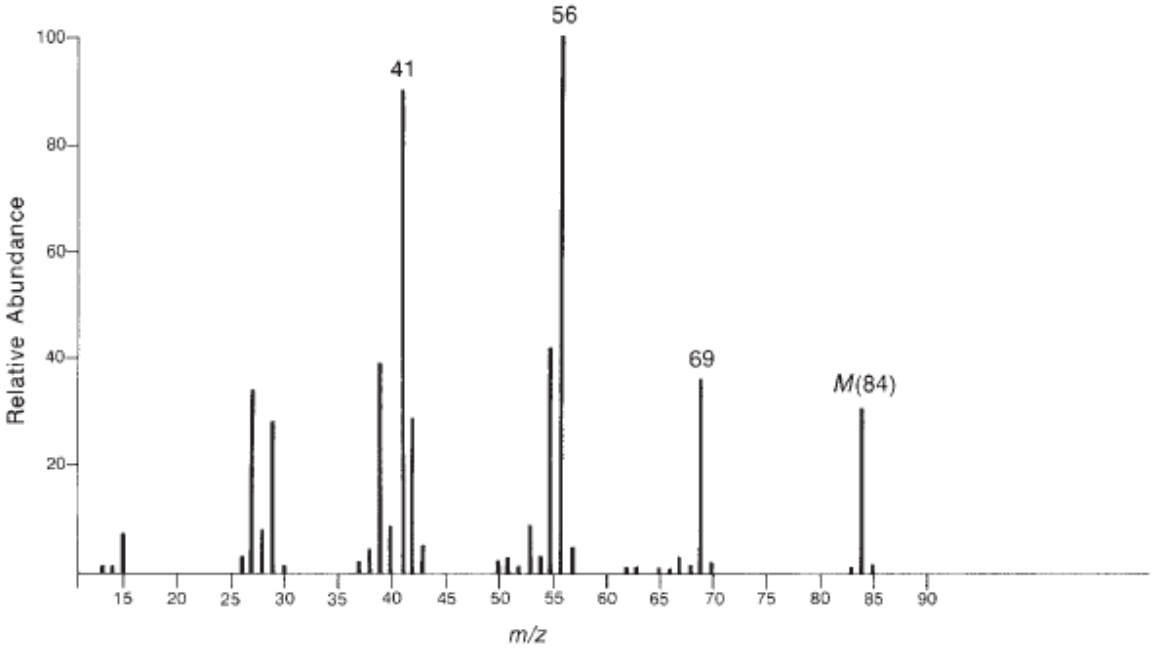
Mass Spectroscopy

1. Assign a structure that would be expected to give rise to each of the following mass spectra. *Note*: Some of these problems may have more than one reasonable answer. In some cases, infrared spectral data have been included in order to make the solution to the problems more reasonable. We recommend that you review the index of hydrogen deficiency (Section 1.4) and the Rule of Thirteen (Section 1.5) and apply those methods to each of the following problems.

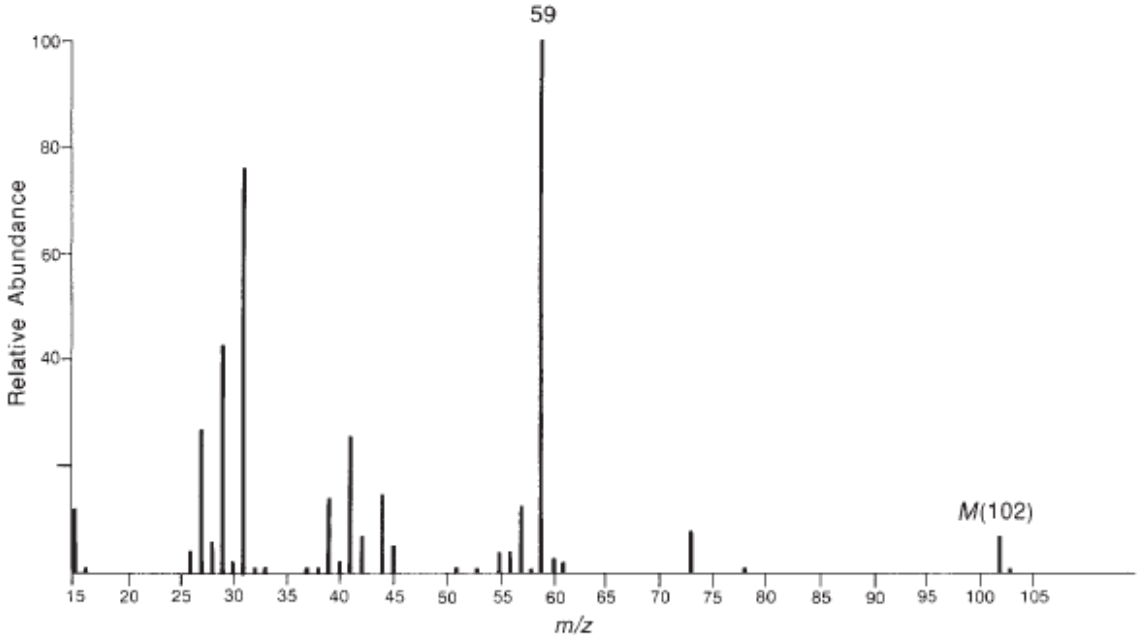
*(a) The infrared spectrum has no interesting features except aliphatic C—H stretching and bending.



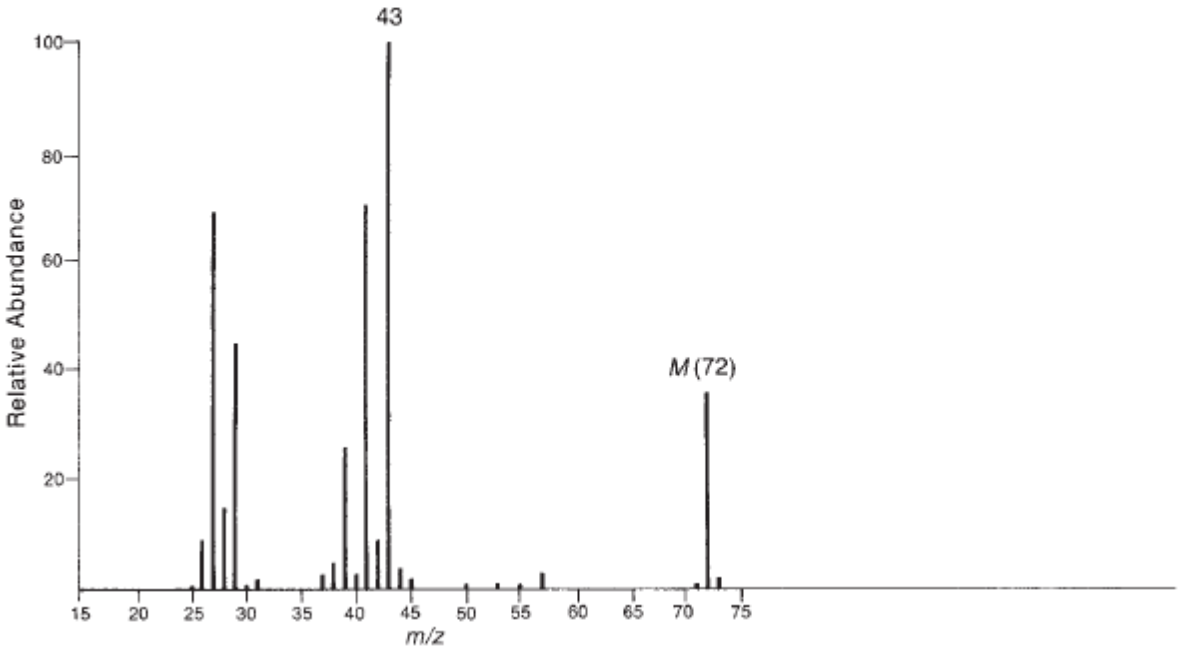
*(b) The infrared spectrum has a medium-intensity peak at about 1650 cm^{-1}. There is also a C—H out-of-plane bending peak near 880 cm^{-1}.



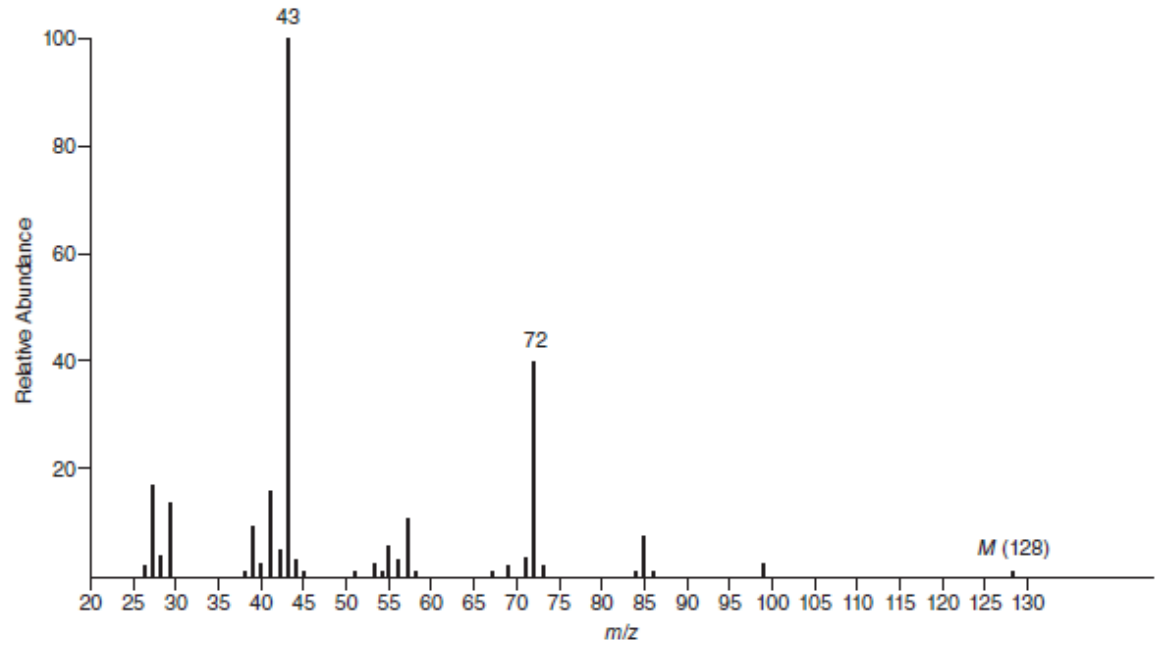
*(d) This unknown contains oxygen, but it does not show any significant infrared absorption peaks above 3000 cm^{-1}.



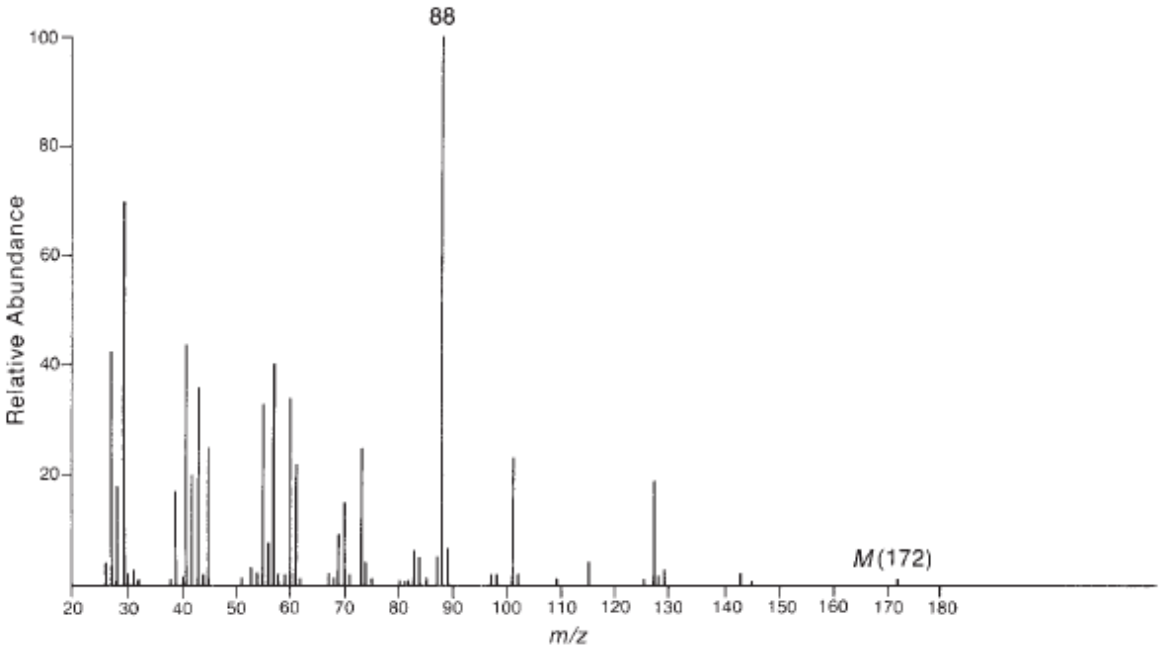
*(e) The infrared spectrum of this unknown shows a strong peak near 1725 cm^{-1}.



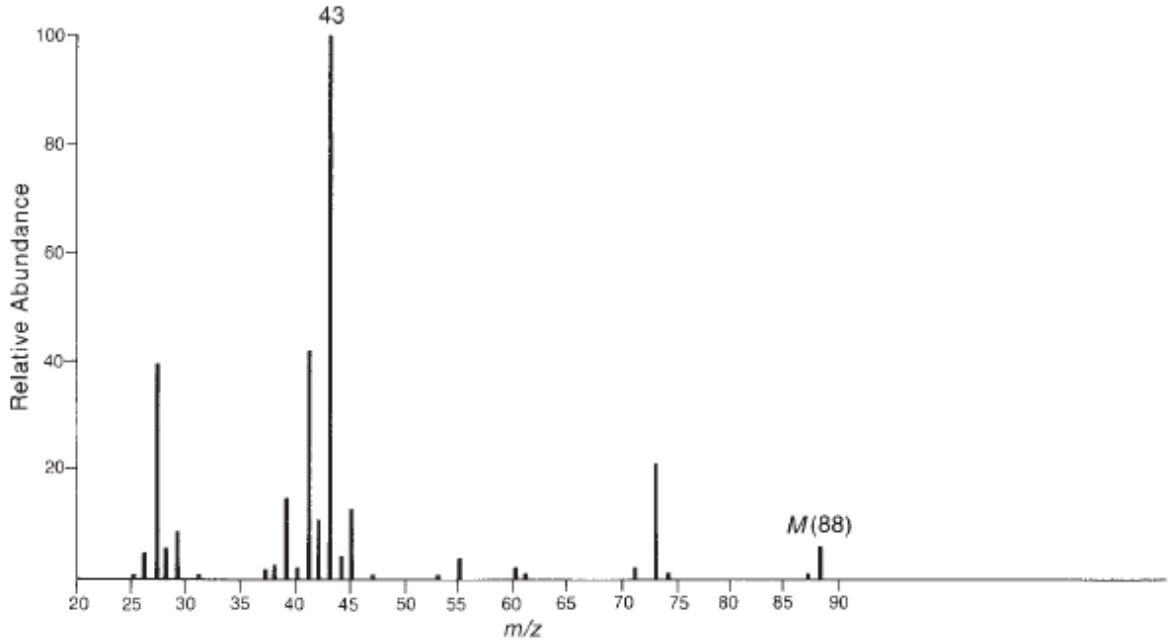
*(f) The infrared spectrum of this unknown shows a strong peak near 1715 cm^{-1}.



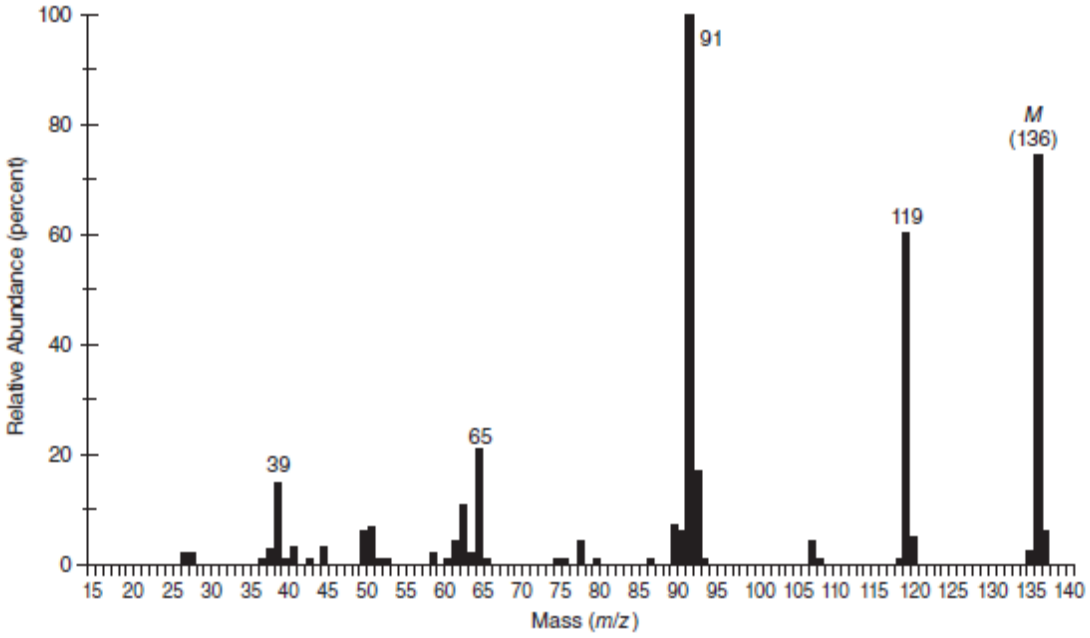
*(g) The infrared spectrum of this compound lacks any significant absorption above 3000 cm^{-1}. There is a prominent peak near 1740 cm^{-1} and another strong peak near 1200 cm^{-1}.



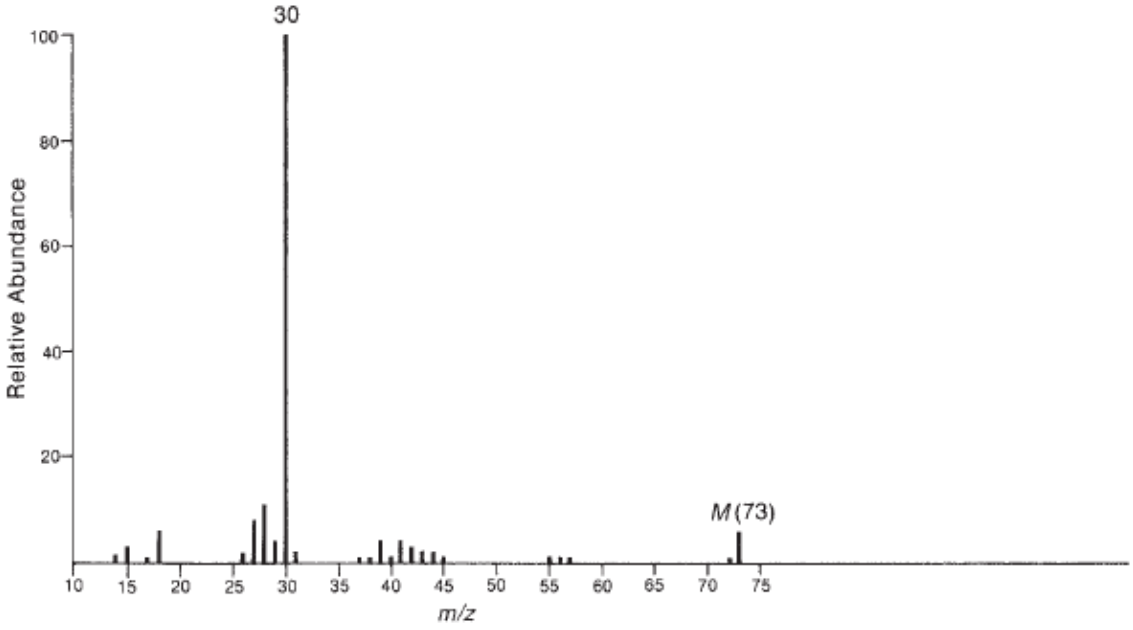
*(h) The infrared spectrum of this substance shows a very strong, broad peak in the range of 2500–3000 cm^{-1}, as well as a strong, somewhat broadened peak at about 1710 cm^{-1}.



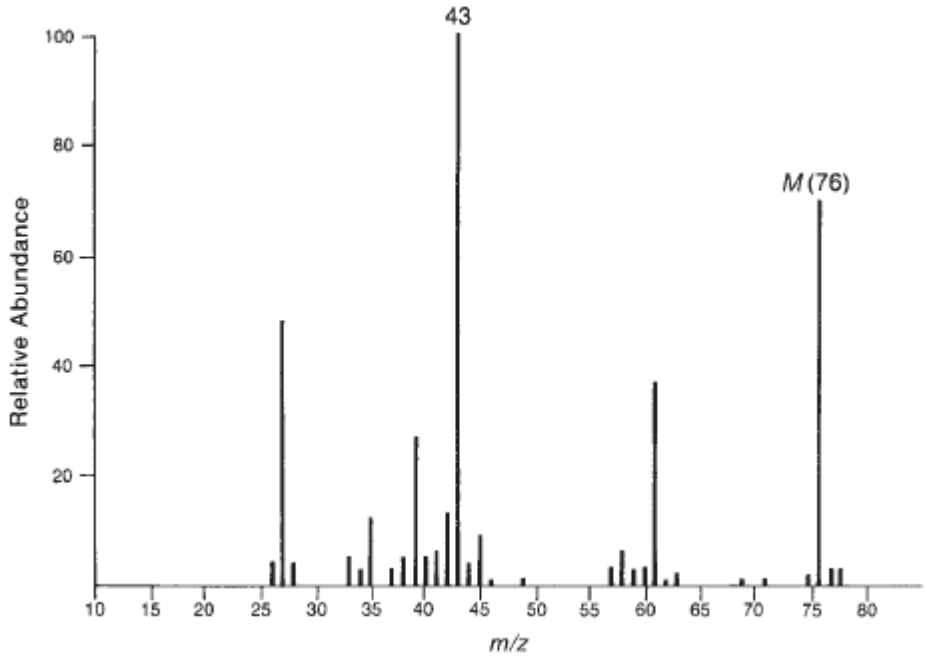
*(i) The ^{13}C NMR spectrum of this unknown shows only four peaks in the region 125–145 ppm. The infrared spectrum shows a very strong, broad peak extending from 2500 to 3500 cm^{-1}, as well a strong and somewhat broadened peak at 1680 cm^{-1}.



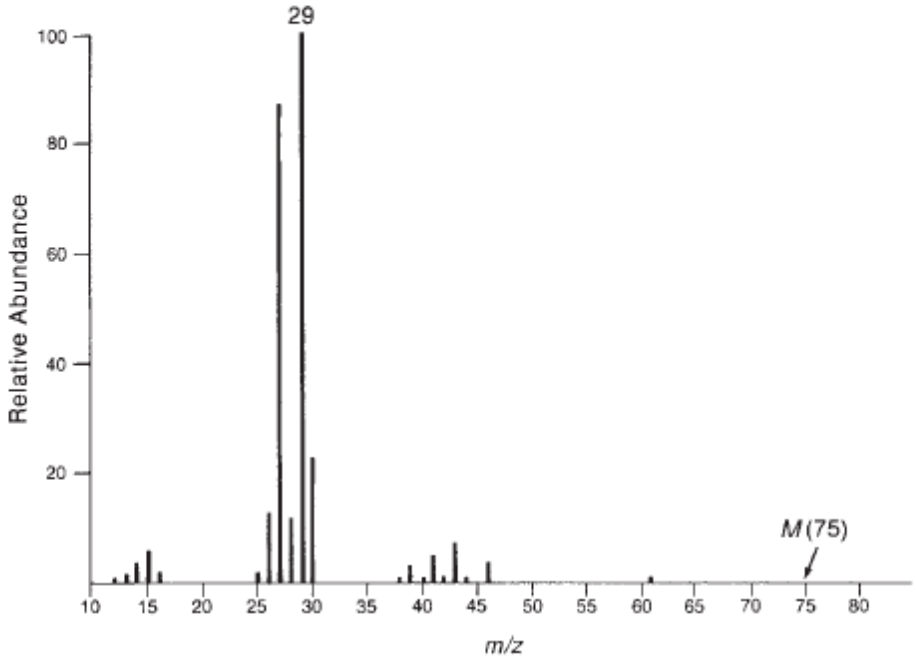
*(j) Note the molecular ion on this substance has odd mass.



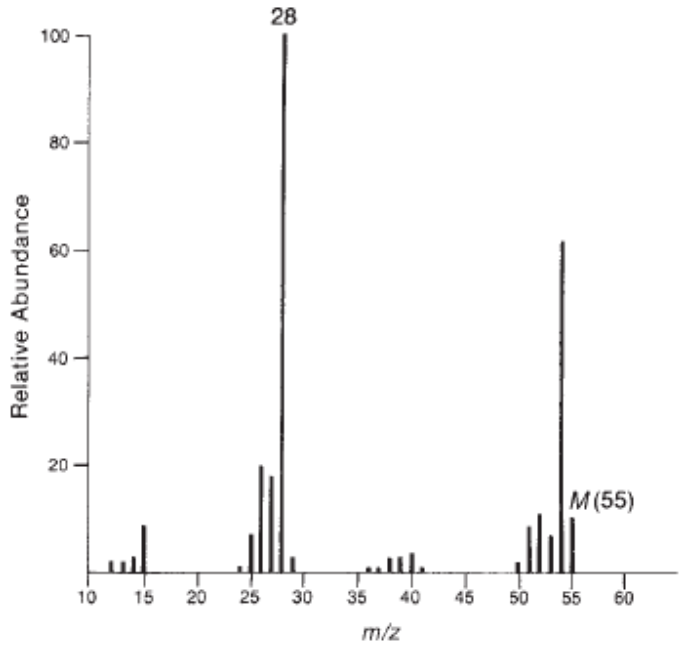
*(k) Notice the $M + 2$ peak in the mass spectrum.



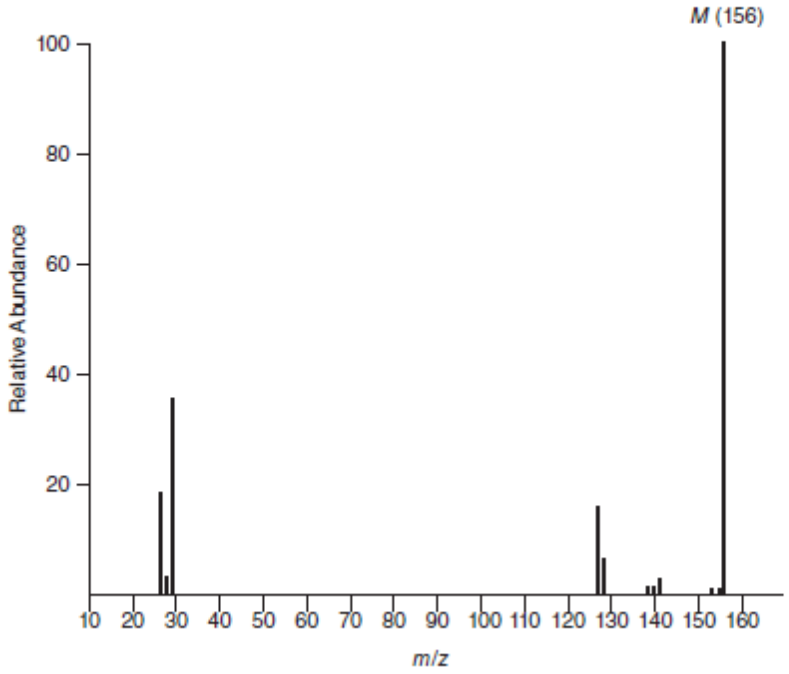
*(l) The infrared spectrum of this unknown shows two strong peaks, one near 1350 cm^{-1} and the other near 1550 cm^{-1}. Notice that the mass of the molecular ion is *odd*.



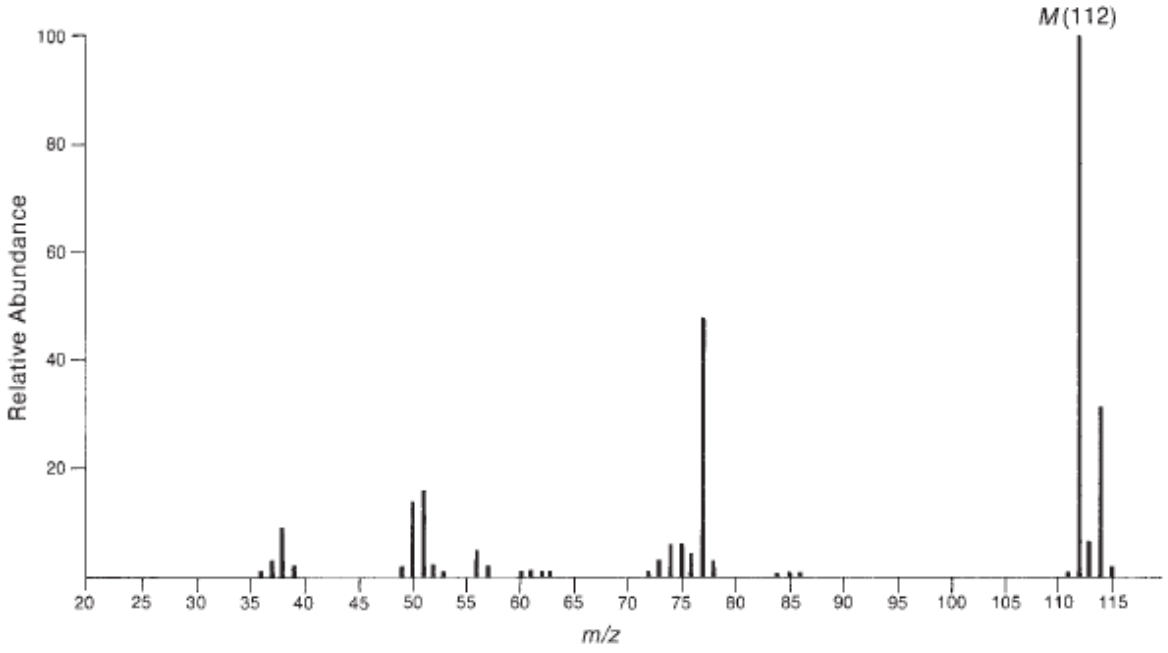
*(m) There is a sharp peak of medium intensity near 2250 cm^{-1} in the infrared spectrum of this compound.



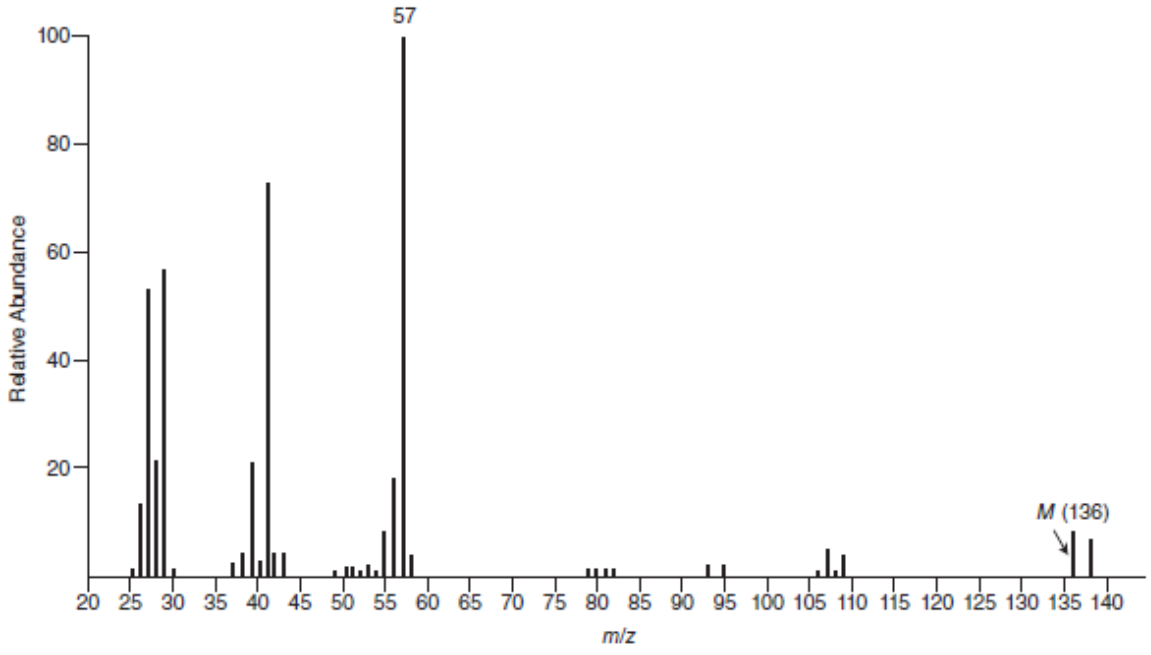
*(n) Consider the fragment ions at $m/z = 127$ and 128. From what ions might these peaks arise?



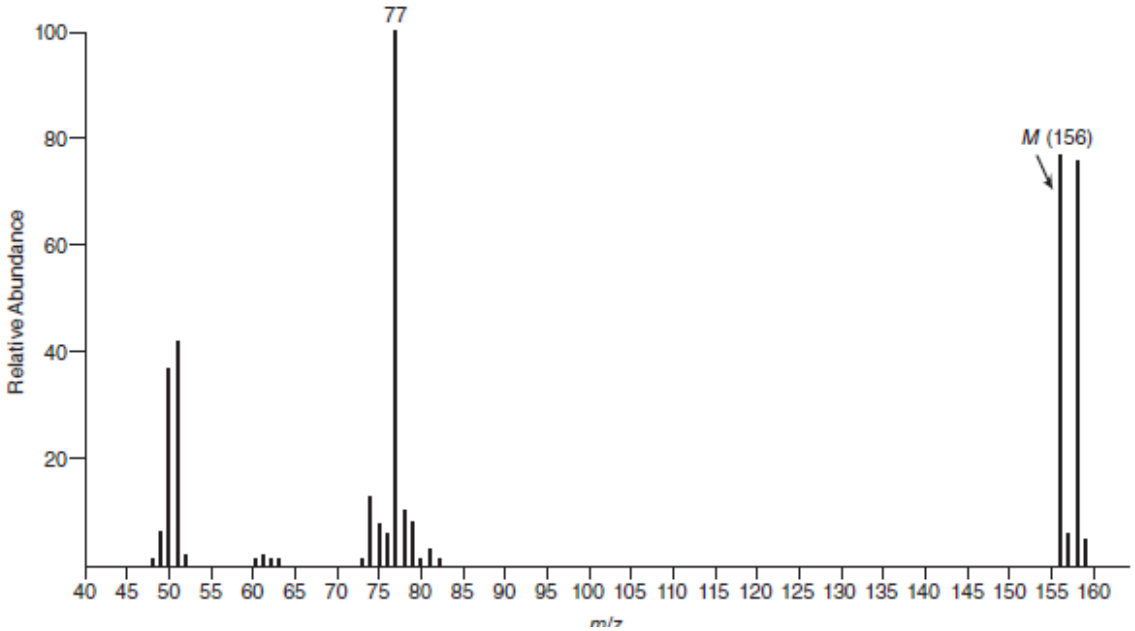
*(o)


M (112)
Relative Abundance
100
80
60
40
20
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115
m/z

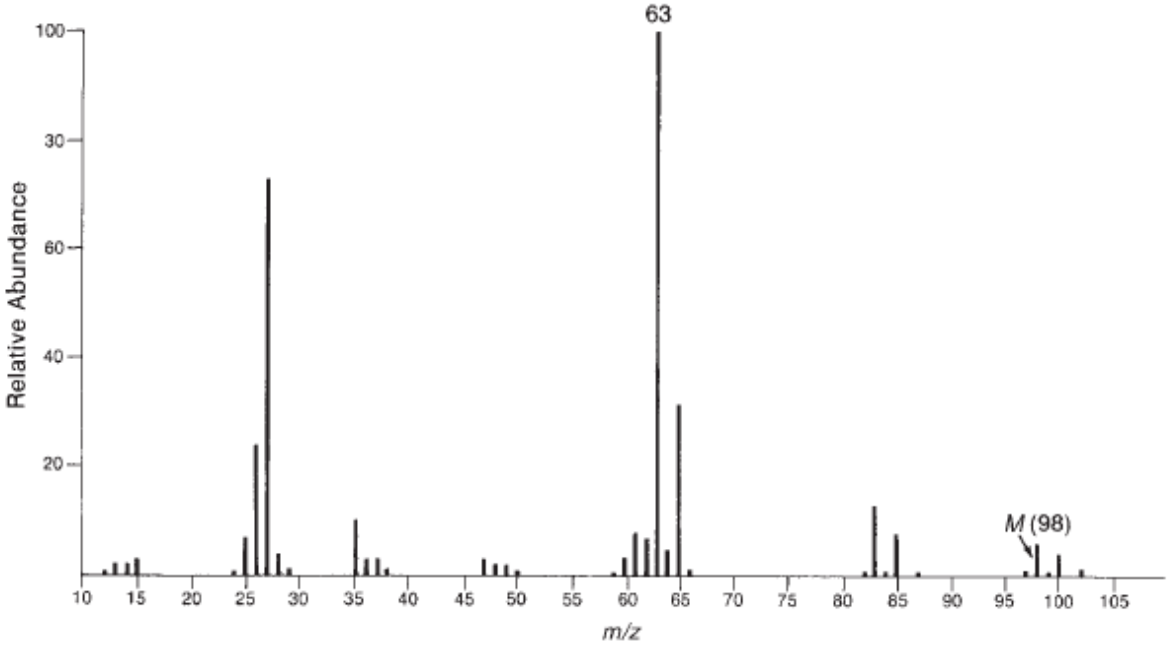
*(p)


57
M (136)
Relative Abundance
100
80
60
40
20
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140
m/z

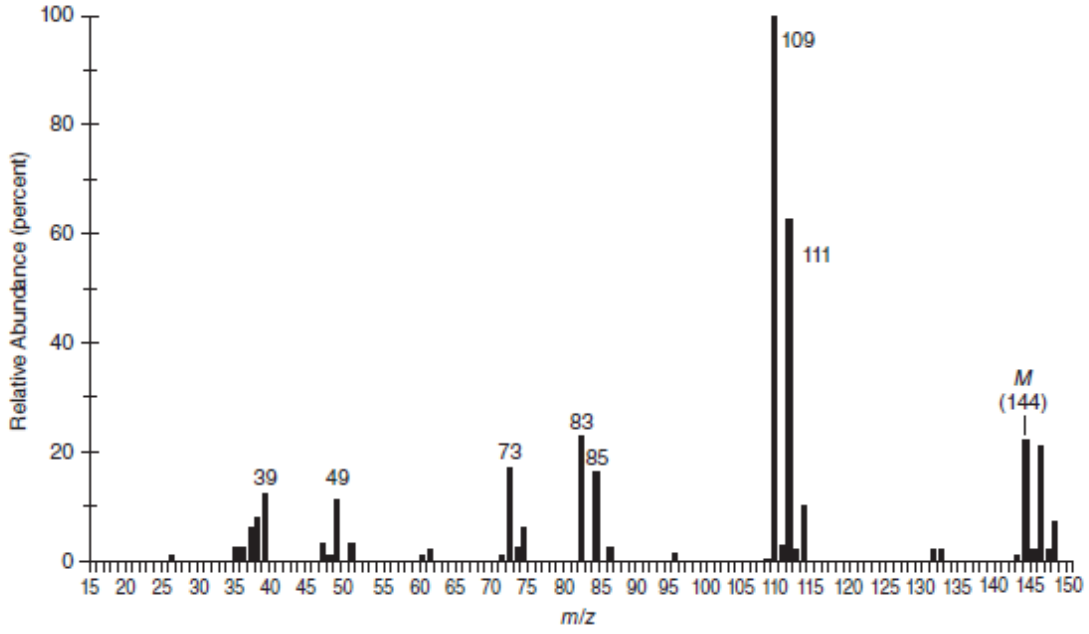
*(q)


77
M (156)
Relative Abundance
100
80
60
40
20
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160
m/z

*(r)

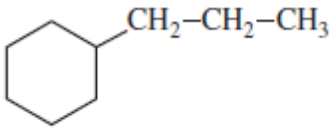
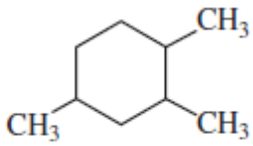

63
M (98)
Relative Abundance
100
30
60
40
20
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105
m/z

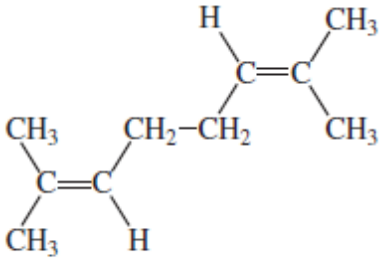
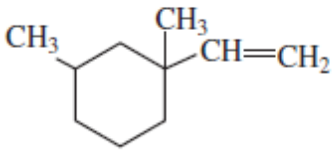
*(s) The infrared spectrum of this unknown shows a sharp peak at 3087 cm^{-1} and a sharp peak at 1612 cm^{-1} in addition to other absorptions. The unknown contains chlorine atoms, but some of the isotopic peaks ($M + n$) are too weak to be seen.

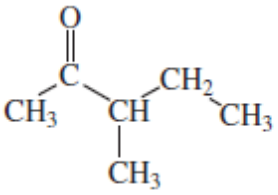
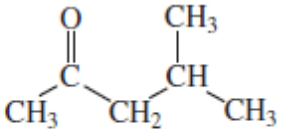


2. The mass spectrum of 3-butyn-2-ol shows a large peak at $m/z = 55$. Draw the structure of the fragment and explain why it is particularly stable.

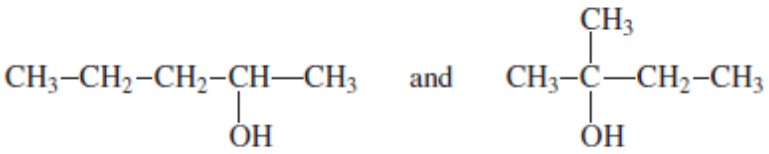
3. How could the following pairs of isomeric compounds be differentiated by mass spectrometry?

(a)  and 

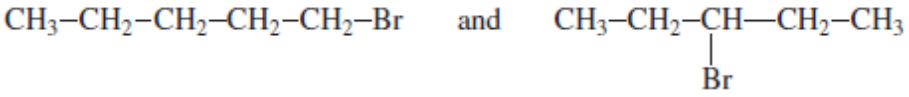
(b)  and 

(c)  and 

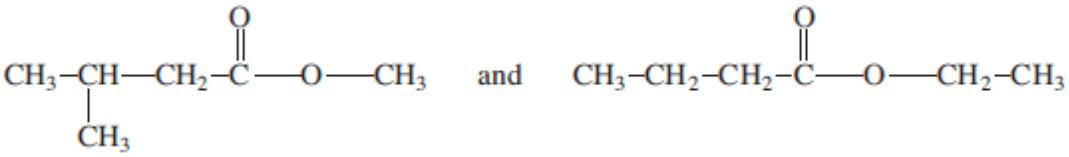
(d)


CH3–CH2–CH2–CH—CH3
OH
and
CH3
CH3–C—CH2–CH3
OH

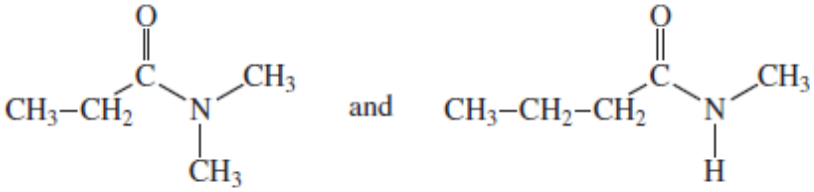
(e)


CH3–CH2–CH2–CH2–CH2–Br
and
CH3–CH2–CH—CH2–CH3
Br

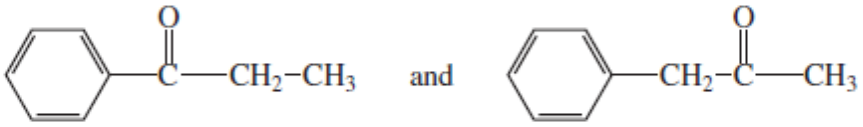
(f)

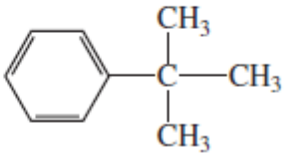
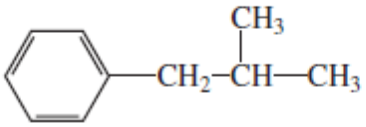

O
CH3–CH—CH2–C—O—CH3
CH3
and
O
CH3–CH2–CH2–C—O—CH2–CH3

(g)


O
C
CH3
CH3–CH2
N
CH3
and
O
C
CH3
CH3–CH2–CH2
N
H

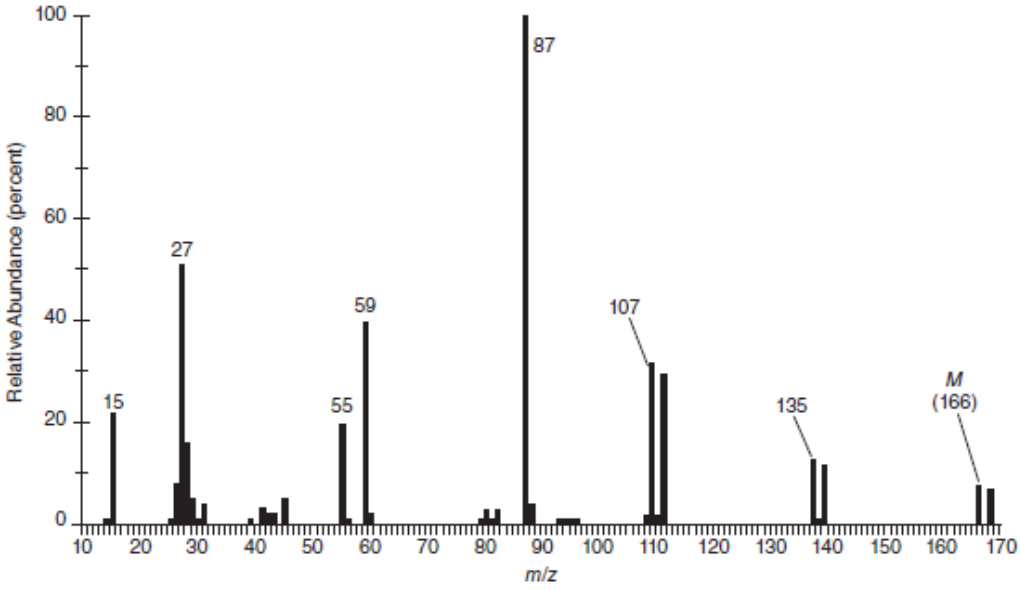
(h) $CH_3-CH_2-CH_2-CH_2-NH_2$ and $CH_3-CH_2-CH_2-NH-CH_3$

(i)  and

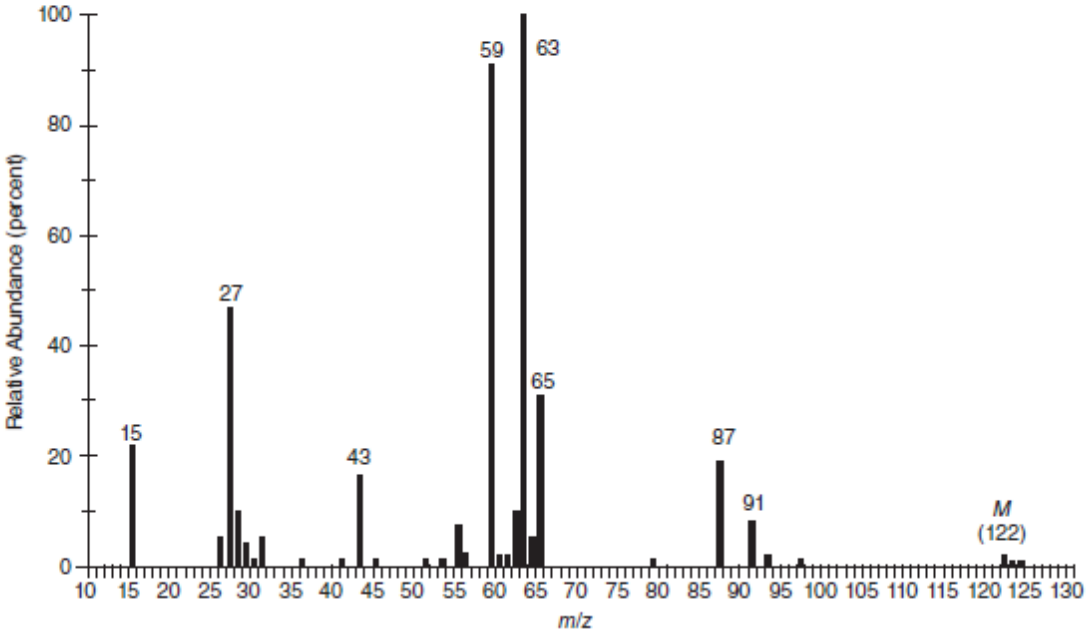
(j)  and 

4. Use the mass spectrum and either the NMR spectrum (Chapter 5) or the infrared spectrum (Chapter 2) to deduce the structure of each of the following compounds.

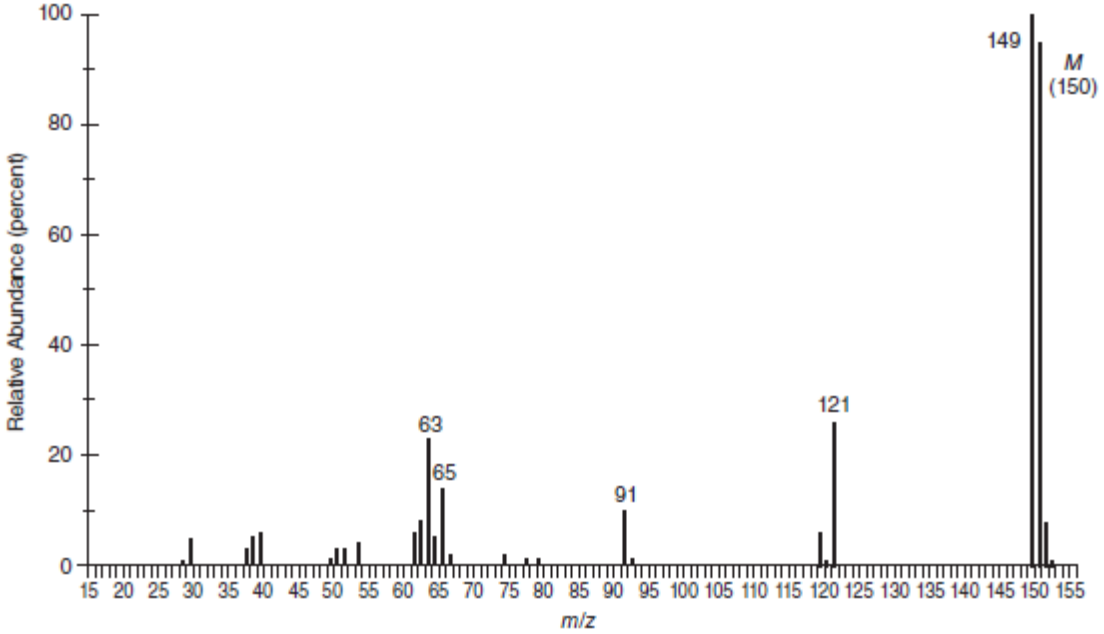
(a) $C_4H_7BrO_2$ ^1H NMR, 300 MHz, 2.9 ppm (triplet, 2H), and 3.8 ppm (singlet, 3H)



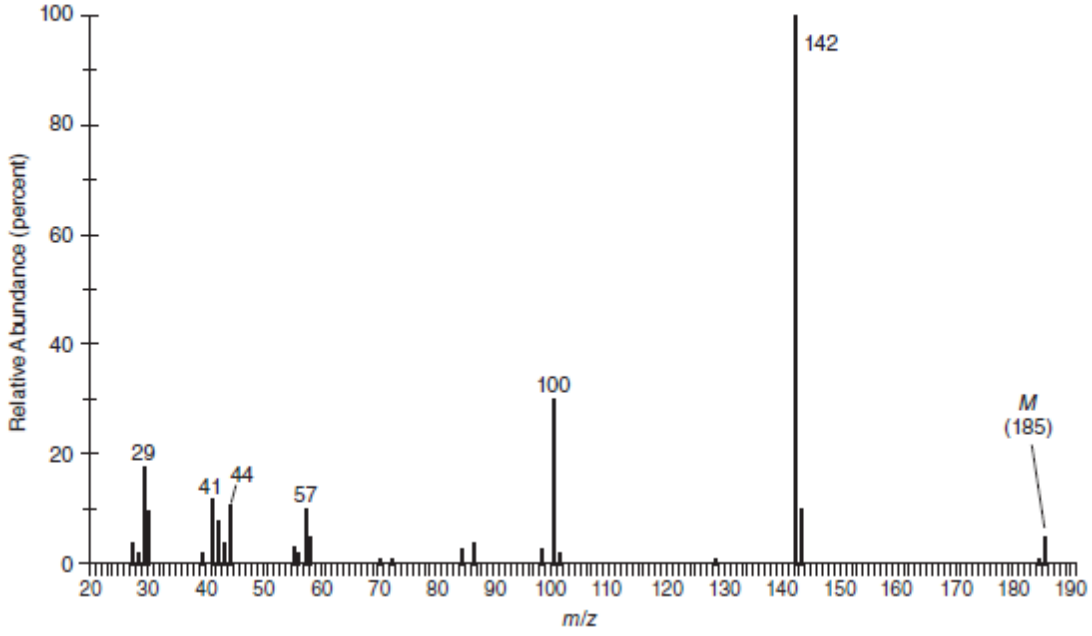
(b) $C_4H_7ClO_2$ ^1H NMR, 300 MHz, 1.7 ppm (doublet, 3H), 3.8 ppm (singlet, 3H), and 4.4 ppm (quartet, ^1H)



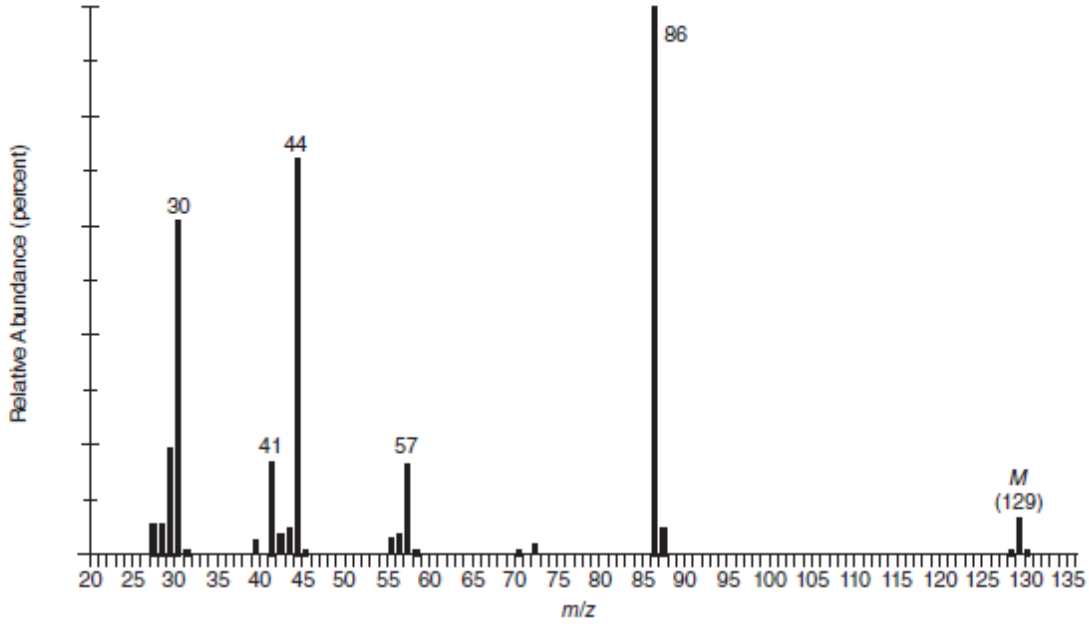
(c) $C_8H_6O_3$ ^1H NMR, 300 MHz, 6.1 ppm (singlet, 2H), 6.9 ppm (doublet, 1H), and 7.3 ppm (singlet, 1H), 7.4 ppm (doublet, 1H), 9.8 ppm (singlet, 1H); significant IR absorbances at 1687, 1602, 1449, 1264, 1038, 929, and 815 cm^{-1}.



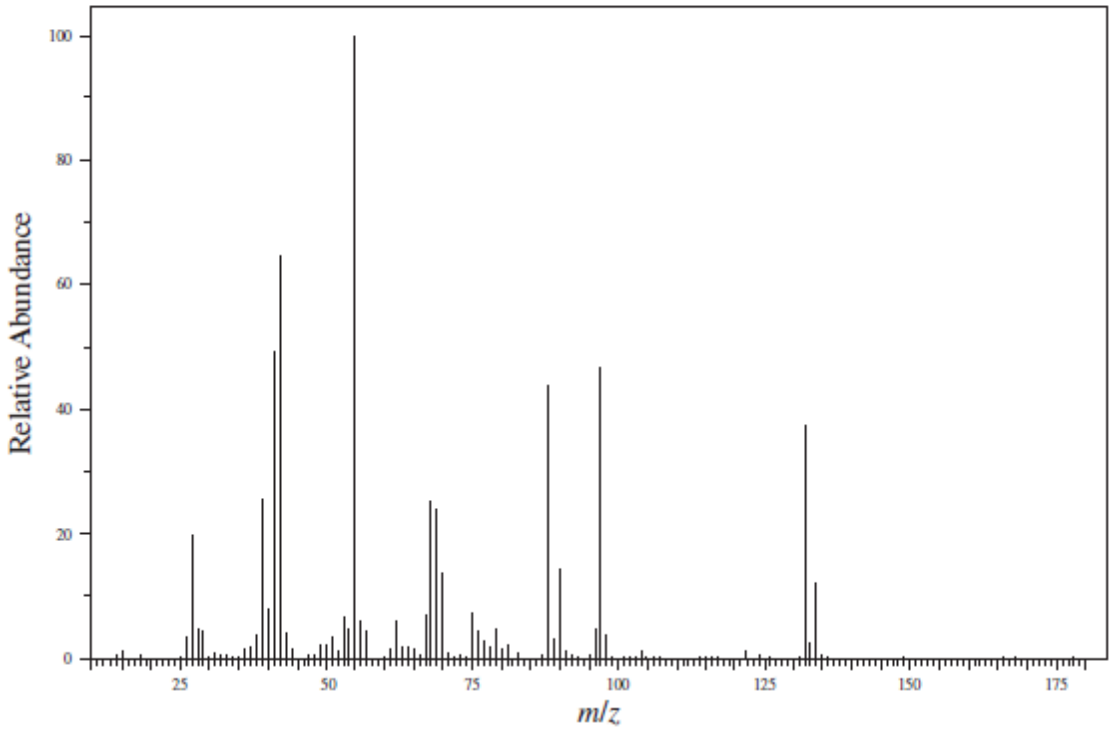
(d) The infrared spectrum lacks any significant peaks above 3000 cm^{-1}.



(e) The infrared spectrum contains a single, strong peak at 3280 cm^{-1}.



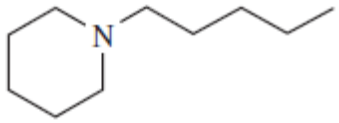
(f) The infrared spectrum contains a single, strong peak at 1723 cm^{-1}.



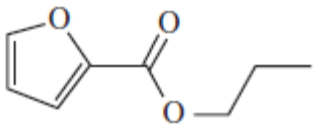
5. For each structure shown below

- Identify the site of initial ionization under EI conditions.
- Determine the structure of the ion indicated by the *m/z* value(s).
- Draw a fragmentation mechanism that accounts for the formation of the fragment ions.

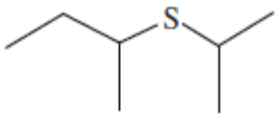
(a) Fragment ion at $m/z = 98$ (base peak in spectrum)



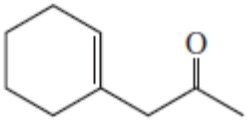
(b) Fragment ion at $m/z = 95$ (base peak in spectrum)



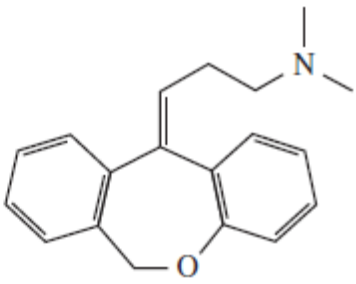
(c) Fragment ions at $m/z = 103$ and 61 (base peak)



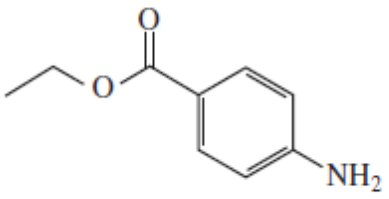
(d) Fragment ions at $m/z = 95$ (base peak) and 43



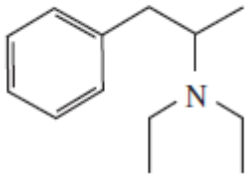
(e) Fragment ion at $m/z = 58$ (base peak)



(f) Fragment ion at $m/z = 120$ (base peak)

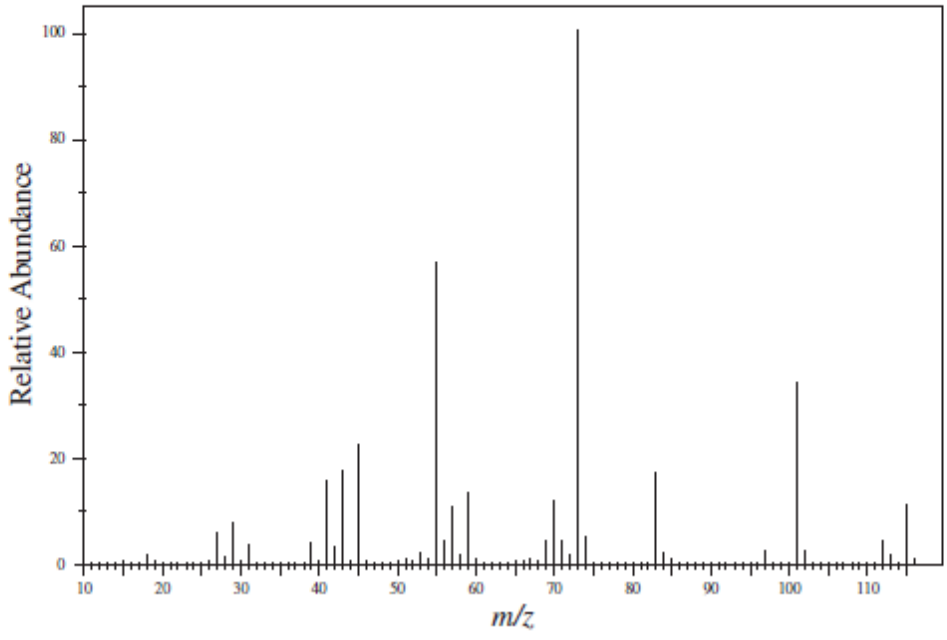


(g) Fragment ions at $m/z = 100$ (base peak), 91, 72, and 44

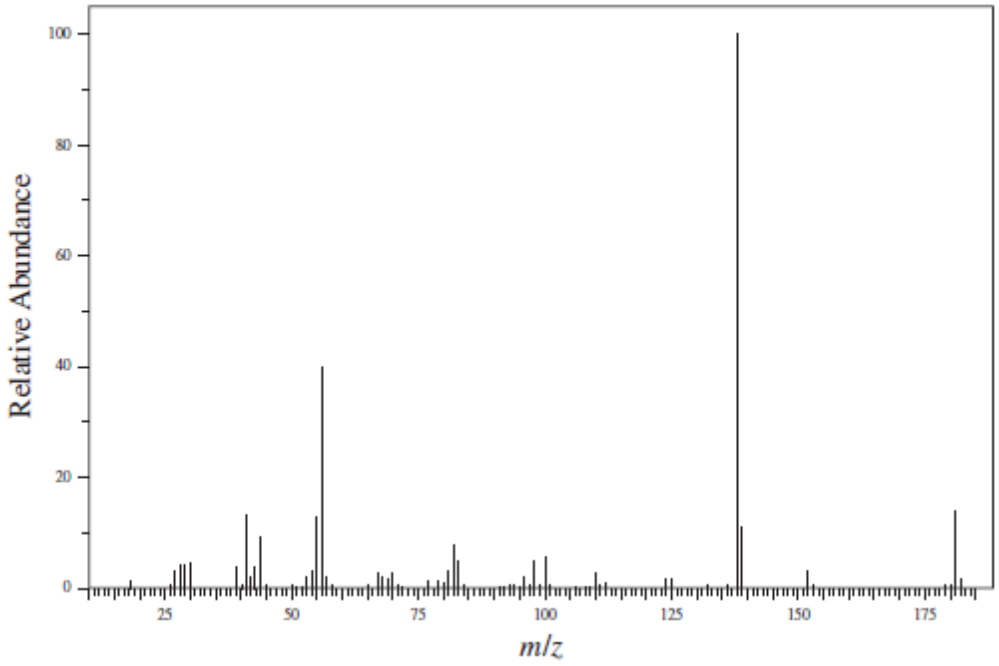


6. For each mass spectrum below, determine the structure of the prominent fragment ions and draw a fragmentation mechanism to explain their formation.

(a) 3-Methyl-3-heptanol



(b) Dicyclohexylamine



(c) 3,3,5-Trimethylcyclohexanone