CHEM 4341/6371 Fall 2017

Homework 5 Questions

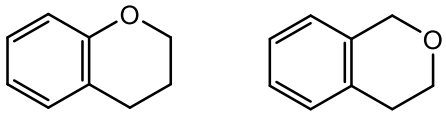
Answers must be submitted on the answer form. You may collaborate on the development of strategies to answer these problems, but completion of your final answers should be done independently of others.

Staple pages together

Maintaining a focus on mass spectrometry

1. Provide the structures of the compounds corresponding to mass spectra **a-c**, which are $C_{11}H_{14}O_2$ esters. *Consult the textbook regarding the fragmentation of aromatic esters.*

2. Spectra **d** and **e** correspond to the following two compounds. Which spectrum matches each compound? Provide detailed mechanisms, for the appropriate compound, to account for the formation of the fragments that give rise to the peaks at m/z = 106 and 104 in these spectra, respectively.



3. Provide a structure that is consistent with mass spectrum **f** (there is more than one possible isomer, draw any one of these)
   Hints:
   - What halogens does this compound contain, and how many? (consult the textbook regarding the appearance of the M, M+2 and M+4 peaks for halogen containing compounds).
   - What other element is suggested by the odd value of m/z for the molecular ion
   - The ratios of peak heights within the clusters of peaks around m/z = 161, 145 and 133 are similar to that of the molecular ion cluster. This suggests that these fragments contain all of the halogens in the molecule. This being the case, which other elements account for the loss of 30,46 and 58 amu, respectively? (Consult the appendices in the textbook).
   - With knowledge of the type and number of halogens (from the molecular ion cluster), and the presence of other elements (from the appearance of halogen containing fragments), what combination of C and H do you need to account for the molecular mass?
   - Draw a reasonable structure for this combination of atoms (your structure should only contain common functional groups and other structural features)

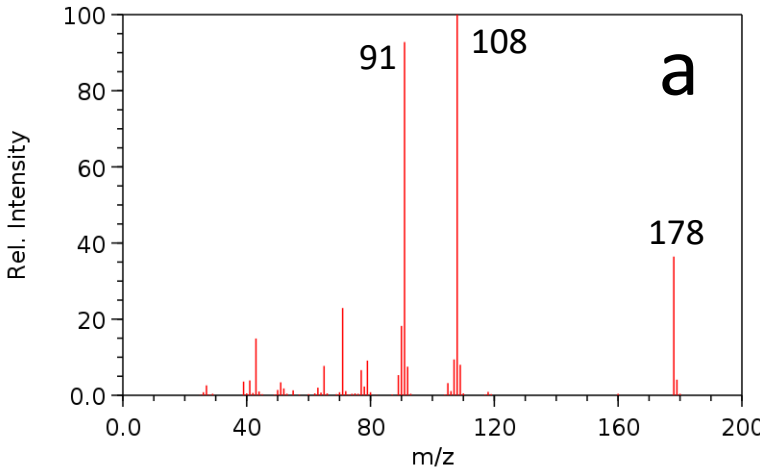
4. Provide a structure that is consistent with mass spectrum **g** (there is more than one possible isomer, draw any one of these)
   You might want to proceed in the same manner as in question 3.
   The cluster of peaks around 156 and 139 have similar ratios of peak heights, suggesting that they contain the same atoms that contribute to the pattern of peak heights in the molecular ion cluster. What fragmentation processes lead to these clusters? This should give you a good clue about the functional group that is present.

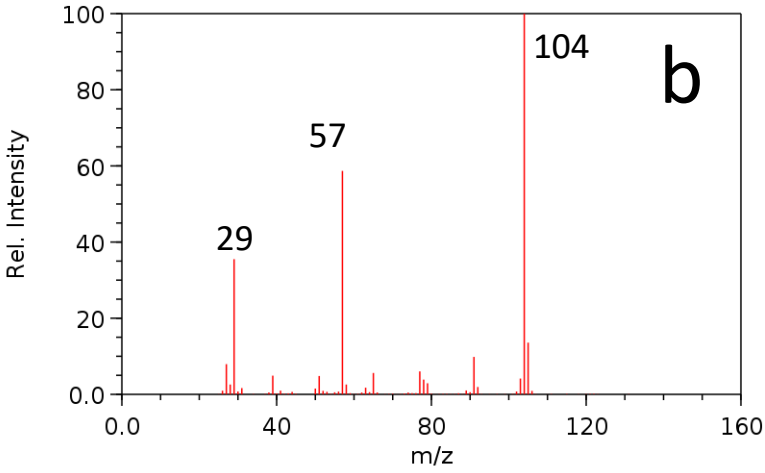
5. Provide a structure that is consistent with mass spectrum **h**.
   Some things to note:
   - There this a major peak corresponding to exactly half of the molecular weight, and nothing of note between m/z = 92 and 184.
   - There is a significant peak at m/z = 77.

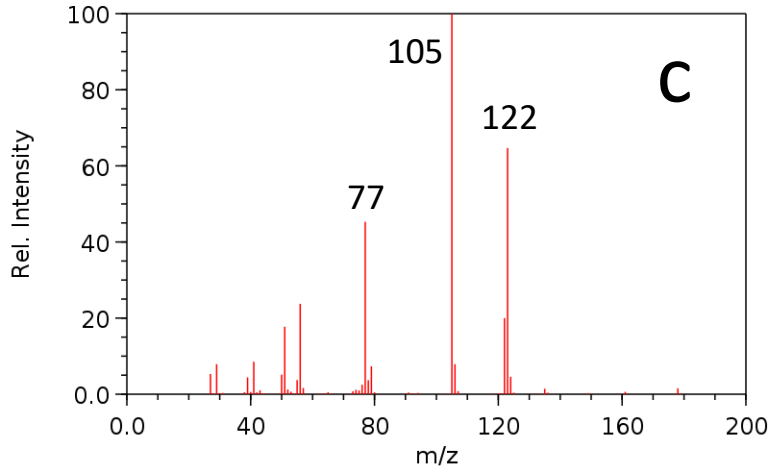
6. In the course notes there is an analysis of the fragmentation of hexyl butanoate. Perform a similar predication of the peaks you expect for each of the types of fragmentation for pentyl 2-methylbutanoate, $CH_3CH_2CH(CH_3)COOCH_2CH_2CH_2CH_2CH_3$. Compare your expectation to the actual spectrum (spectrum **i**), which peaks are present, which are absent? Provide the analysis by completing the table on the answer sheet.
   Loss of alkyl (15, 29, 43, etc), loss of RO (31, 45, 59, …), McLafferty rearrangement (loss of alkene, 28, 42, 56, …), and McLafferty+1 (loss of C_nH_{2n-1}: 27,41, 55, …) lead to loss of familiar series of masses from the molecular ion.

7. And now try the reverse process… can we analyze the mass spectrum of a $C_{10}H_{20}O_2$ ester (spectrum **j**) in terms of the common modes of fragmentation of esters? What structural features can be assigned to each of the fragment peaks? Provide the analysis by completing, to the extent possible, the table on the answer sheet.
   Which peaks correspond to the different types of fragmentation. What structural features can be derived from each of these fragmentations in the mass spectrum?

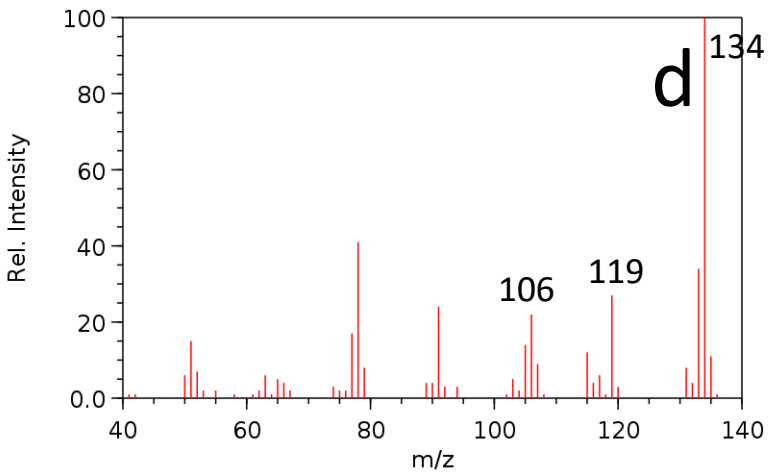
$C_{11}H_{14}O_2$
esters

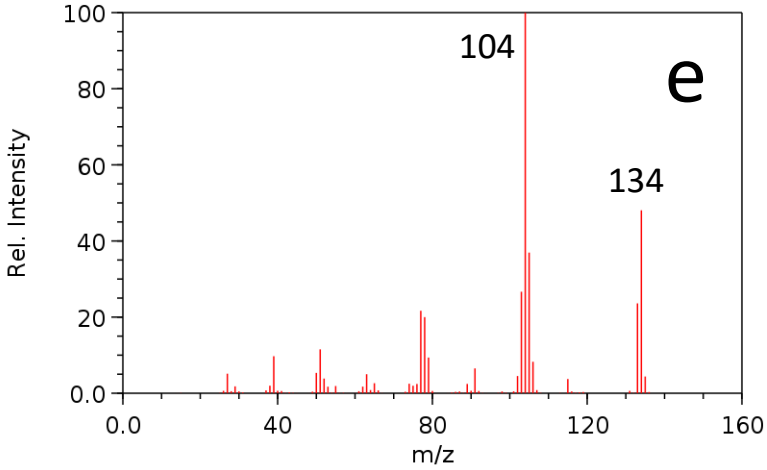




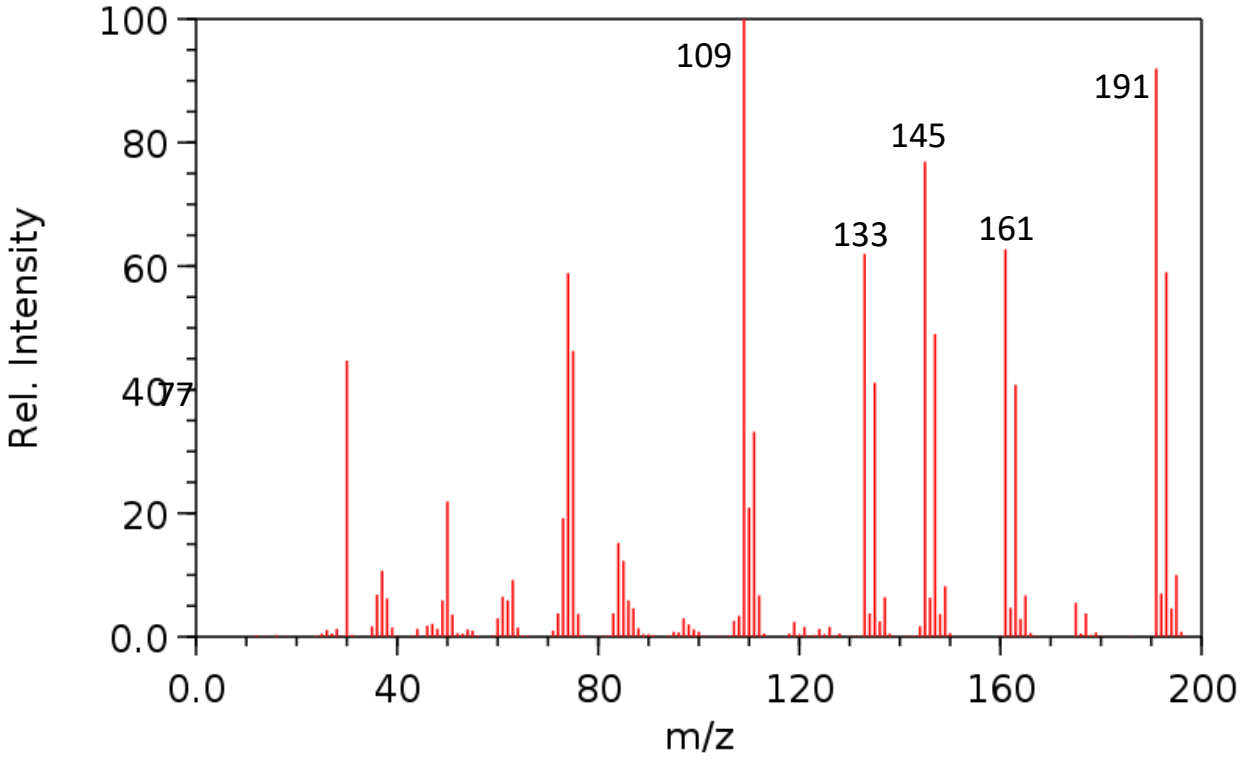


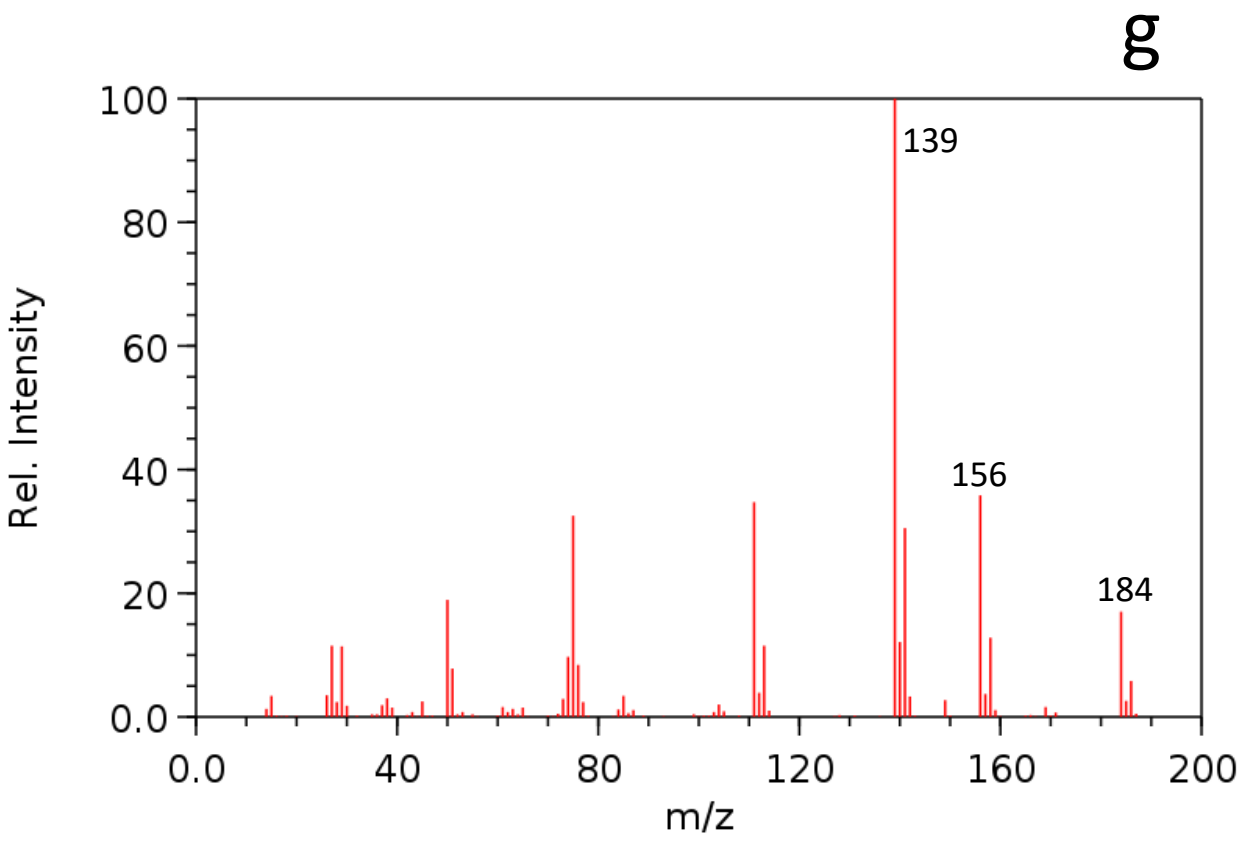
$C_9H_{10}O_2$

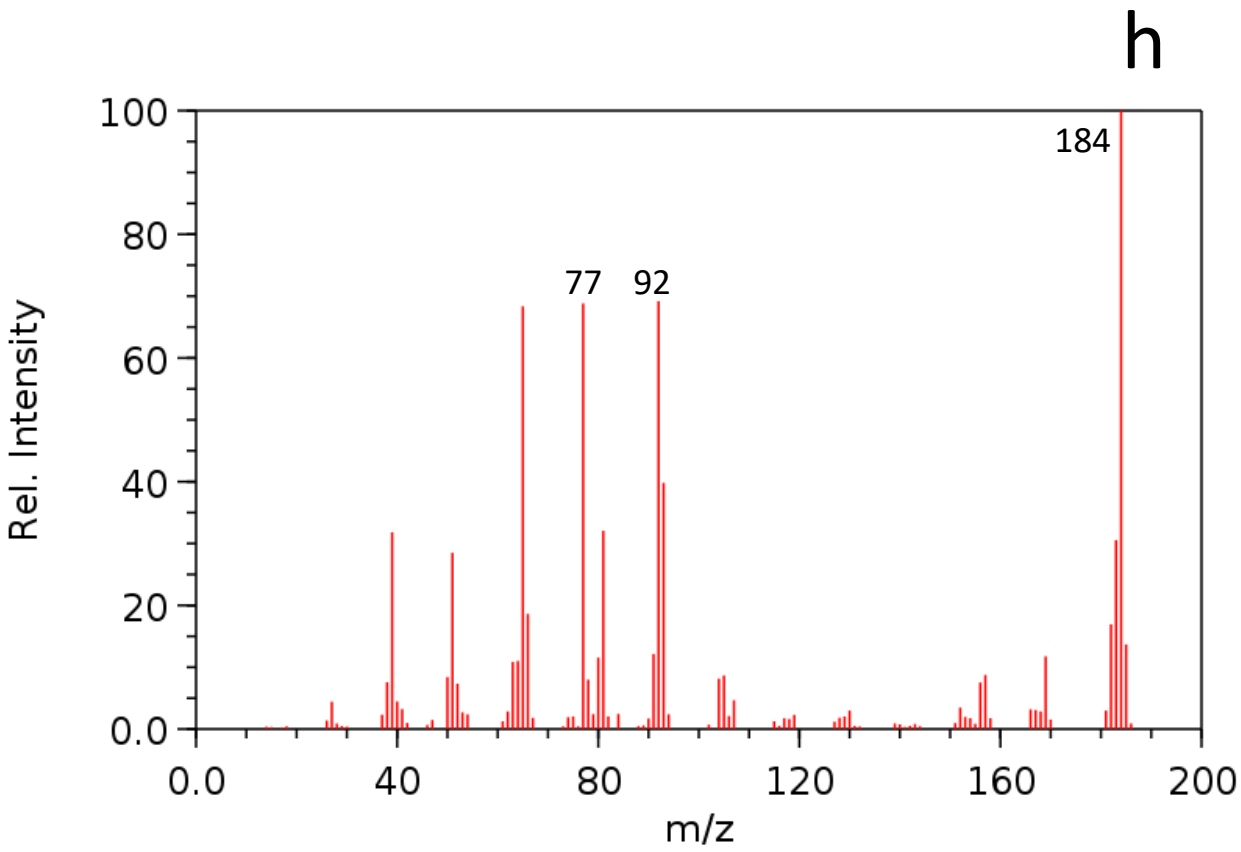

d
134
106
119
Rel. Intensity
m/z
100
80
60
40
20
0.0
40
60
80
100
120
140

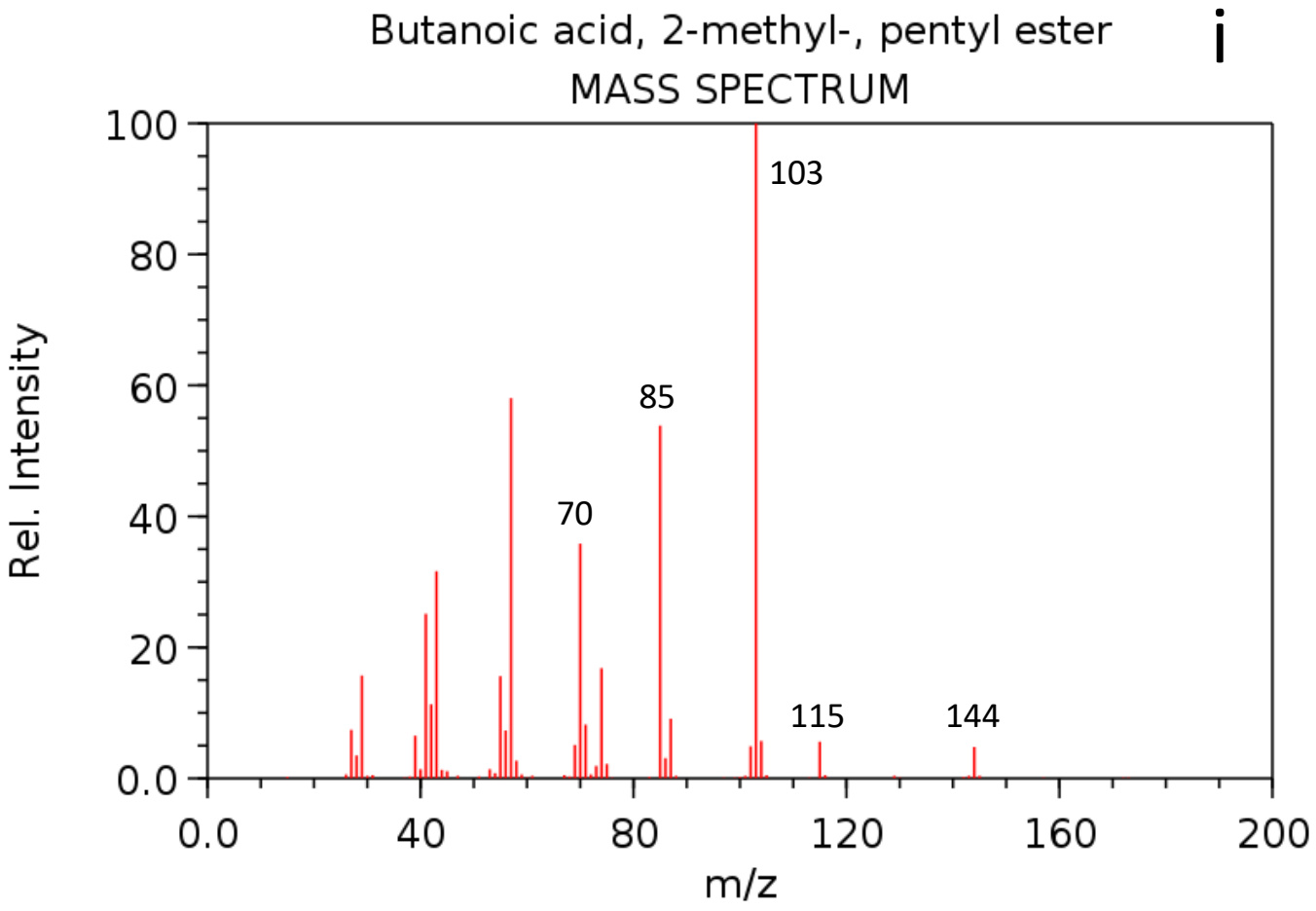

e
104
134
Rel. Intensity
m/z
100
80
60
40
20
0.0
0.0
40
80
120
160

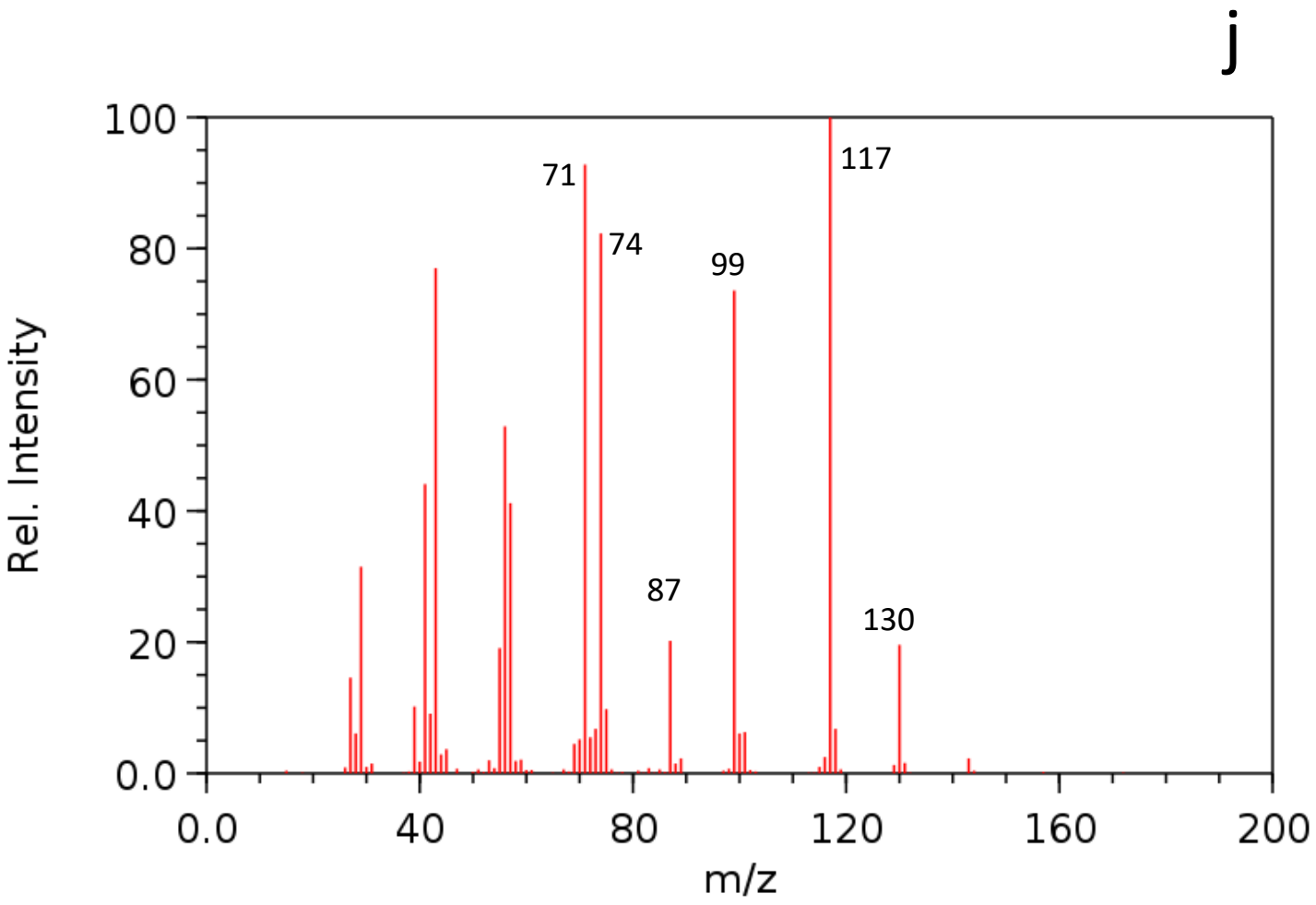
f


100
80
60
40
20
0.0
Rel. Intensity
109
191
145
133
161
77
0.0
40
80
120
160
200
m/z


g
100
80
60
40
20
0.0
Rel. Intensity
139
156
184
0.0
40
80
120
160
200
m/z


h
100
80
60
40
20
0.0
Rel. Intensity
184
77
92
0.0
40
80
120
160
200
m/z


Butanoic acid, 2-methyl-, pentyl ester
MASS SPECTRUM
i
Rel. Intensity
100
80
60
40
20
0.0
0.0
40
80
120
160
200
m/z
103
85
70
115
144


j
100
80
60
40
20
0.0
Rel. Intensity
71
74
99
117
87
130
0.0
40
80
120
160
200
m/z