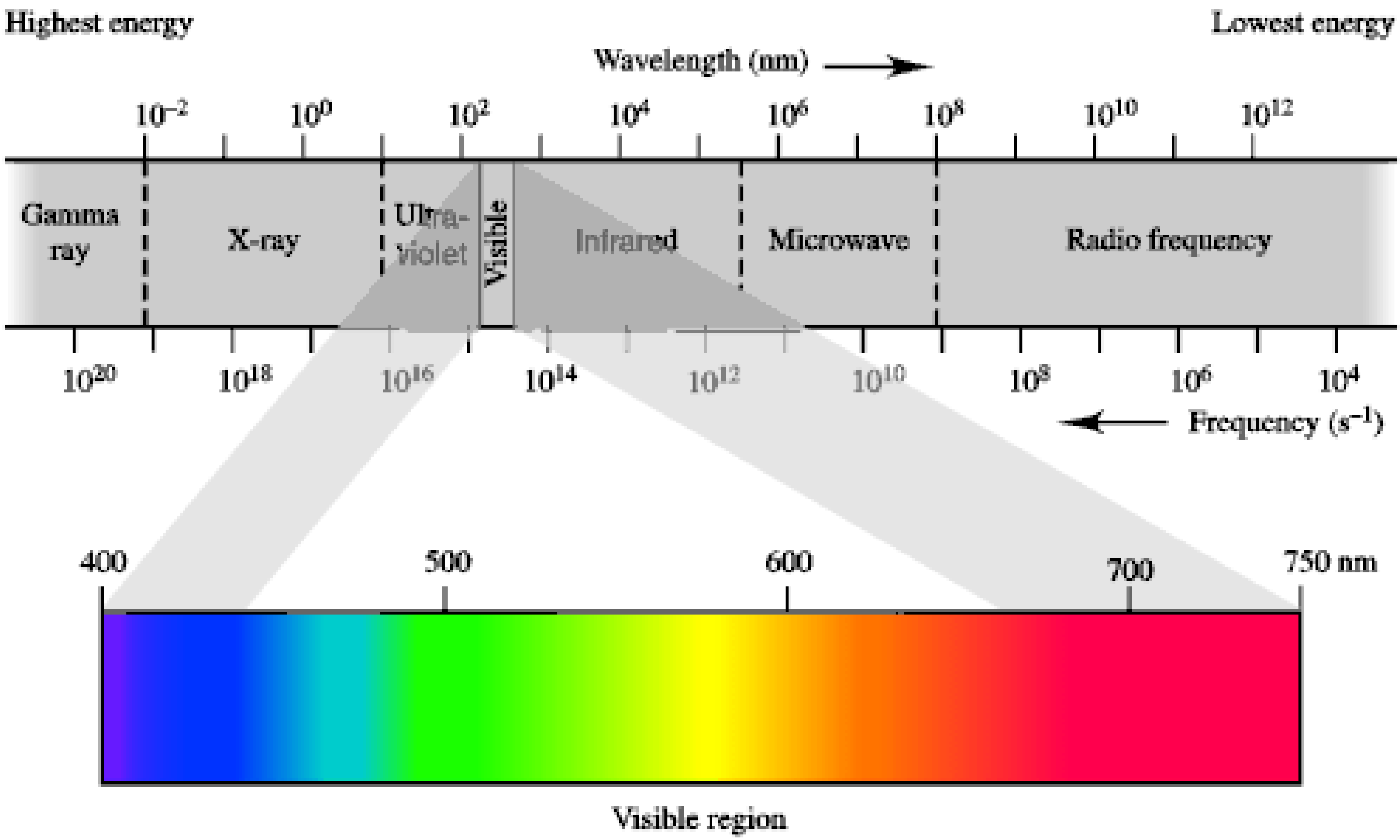
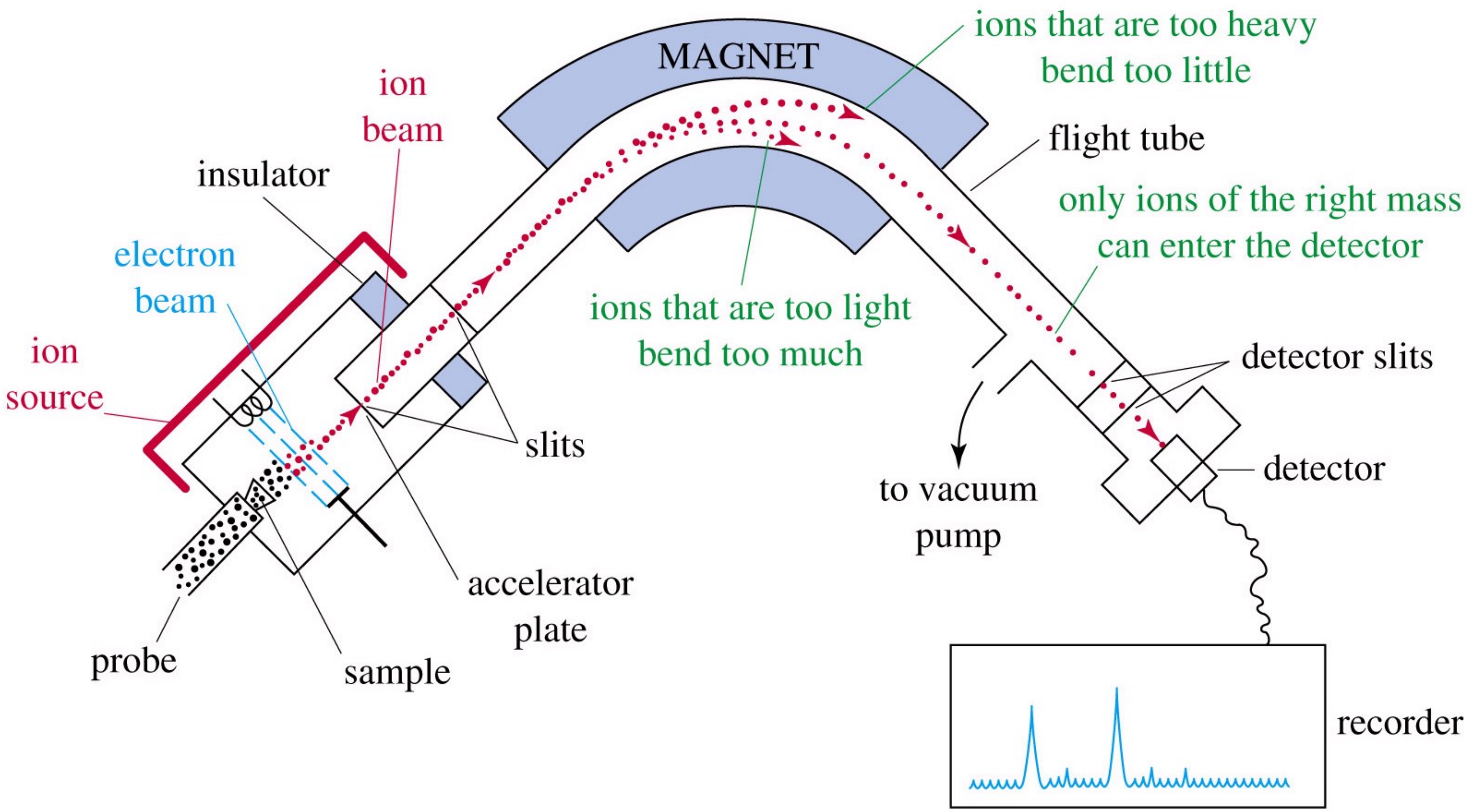
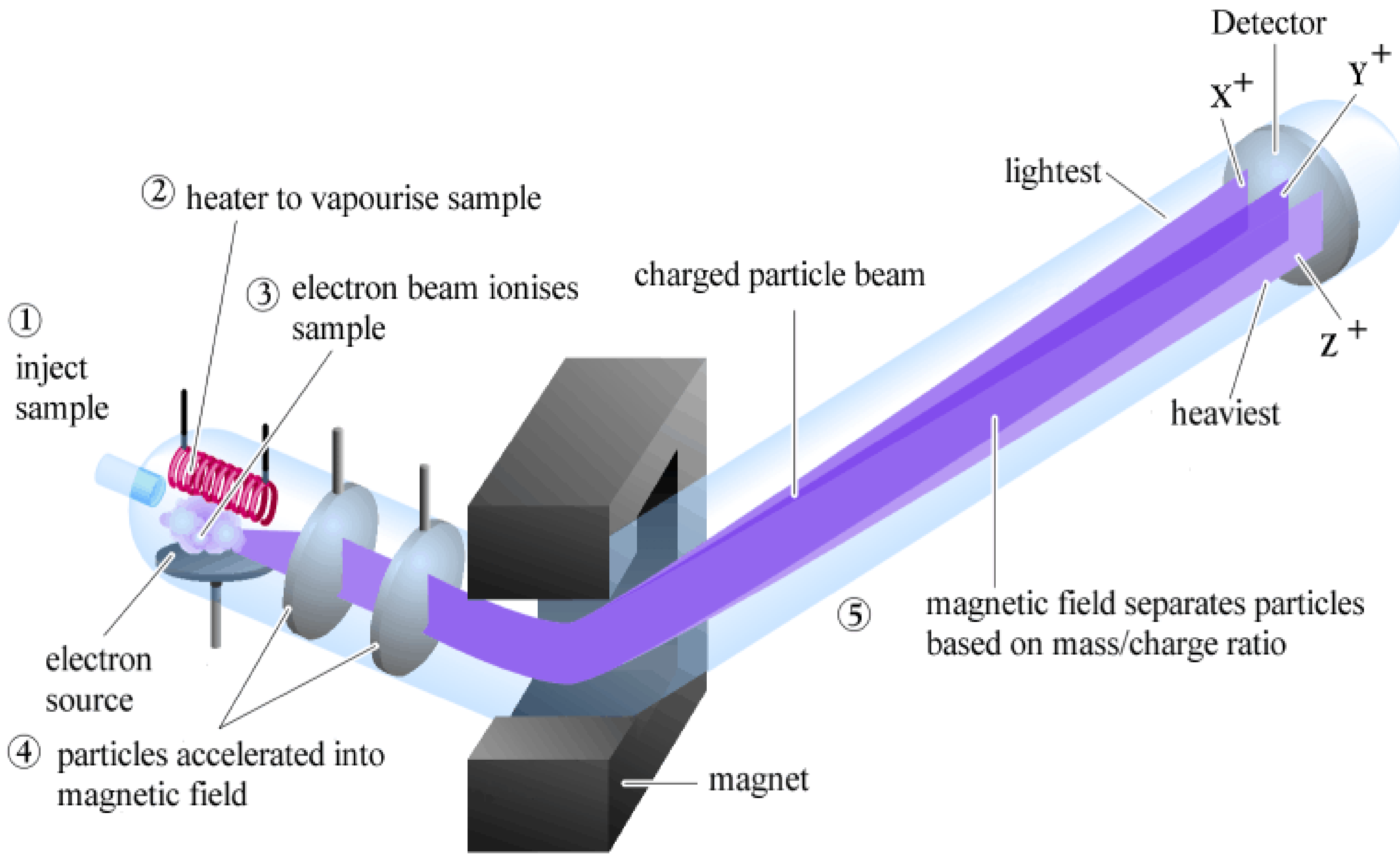


Highest energy
Lowest energy
Wavelength (nm)
10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12}
Gamma ray
X-ray
Ultra-violet
Visible
Infrared
Microwave
Radio frequency
10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4}
Frequency (s^{-1})
400
500
600
700
750 nm
Visible region

Mass Spectrometry

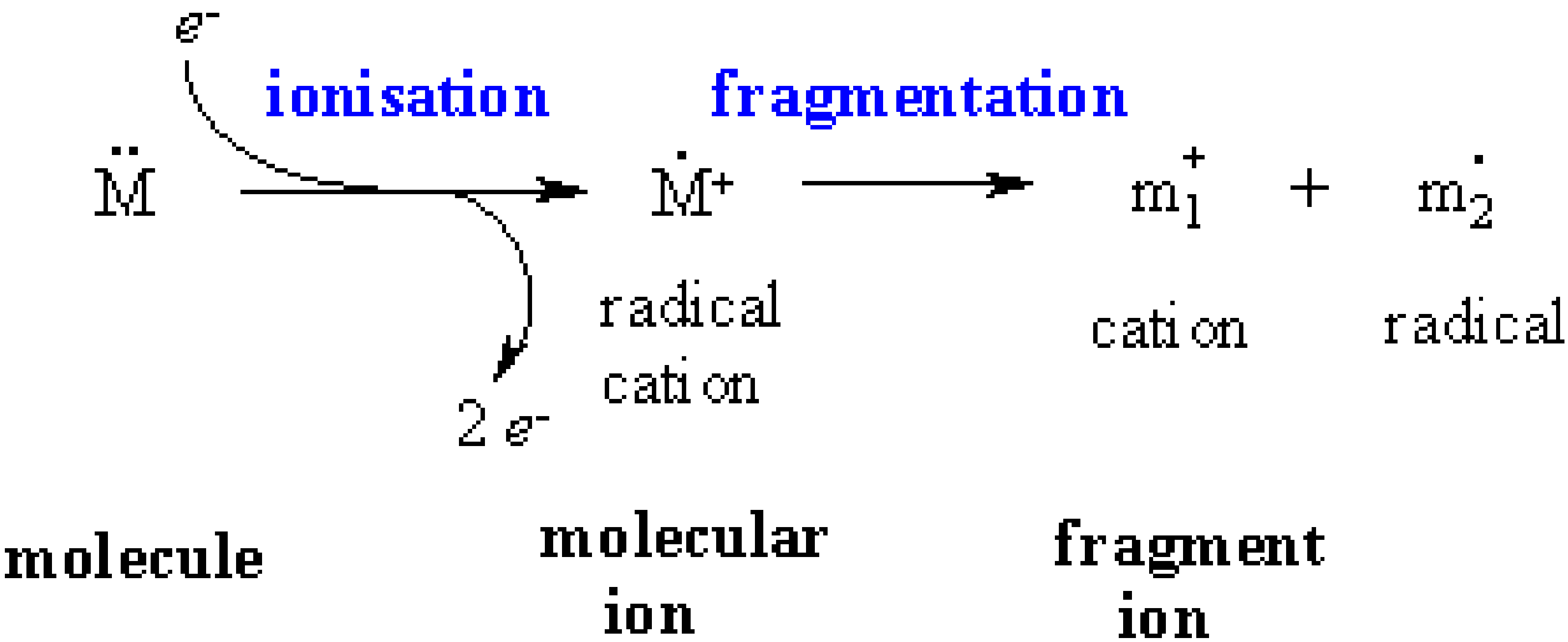




① inject sample
② heater to vapourise sample
③ electron beam ionises sample
electron source
④ particles accelerated into magnetic field
charged particle beam
magnet
⑤
magnetic field separates particles based on mass/charge ratio
lightest
heaviest
Detector
X+
Y+
Z+

Ionization to Radical Cation

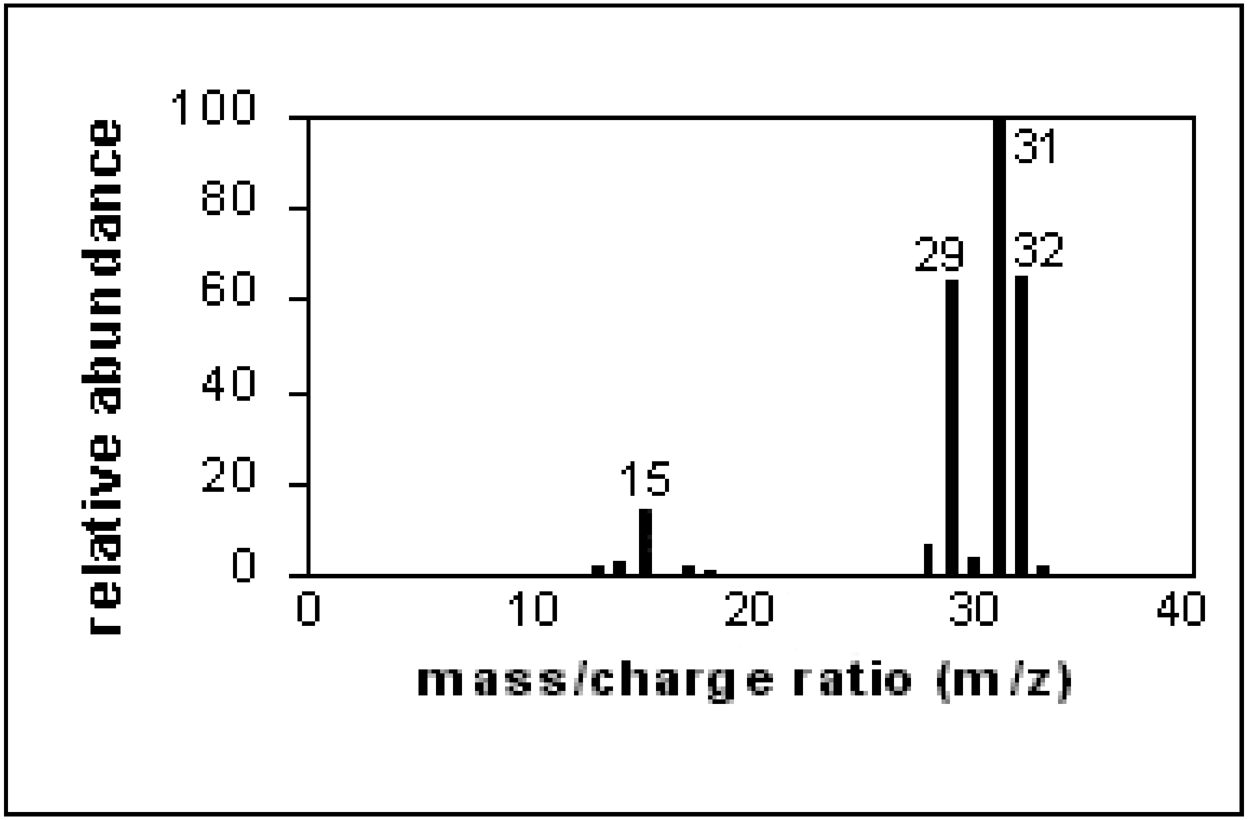
Molecular Ion (m^+)



Glossary

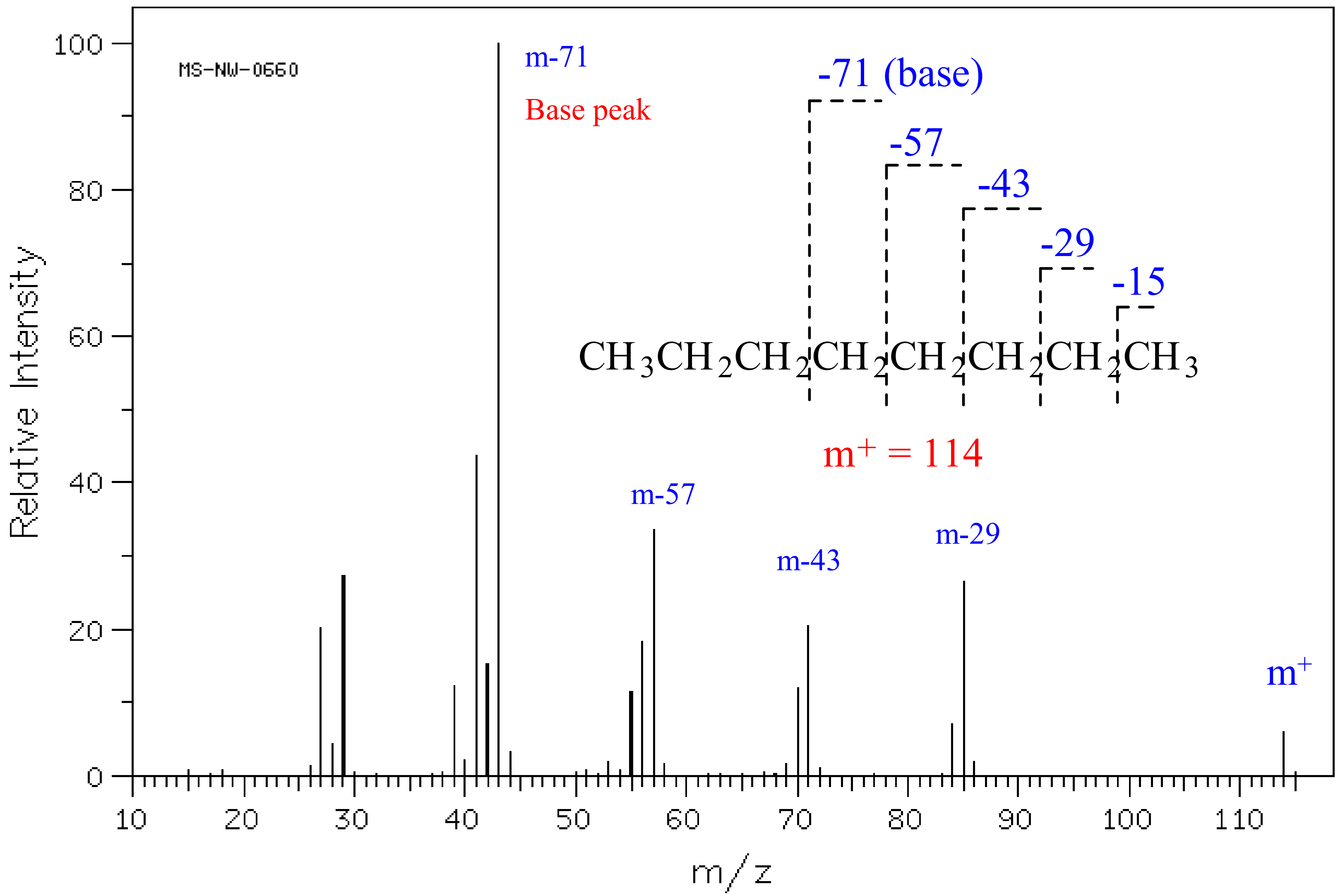
- **Molecular ion** - The ion obtained by the loss of one electron from the molecule (m^+)
- **Base peak** - The most intense peak in the MS, assigned 100% intensity
- **Radical cation** - positively charged species with an odd number of electrons
- **Fragment ions** - Lighter cations (and radical cations) formed by the decomposition of the molecular ion. These often correspond to ***stable*** carbcations.
- **m/z** - mass to charge ratio

Methanol



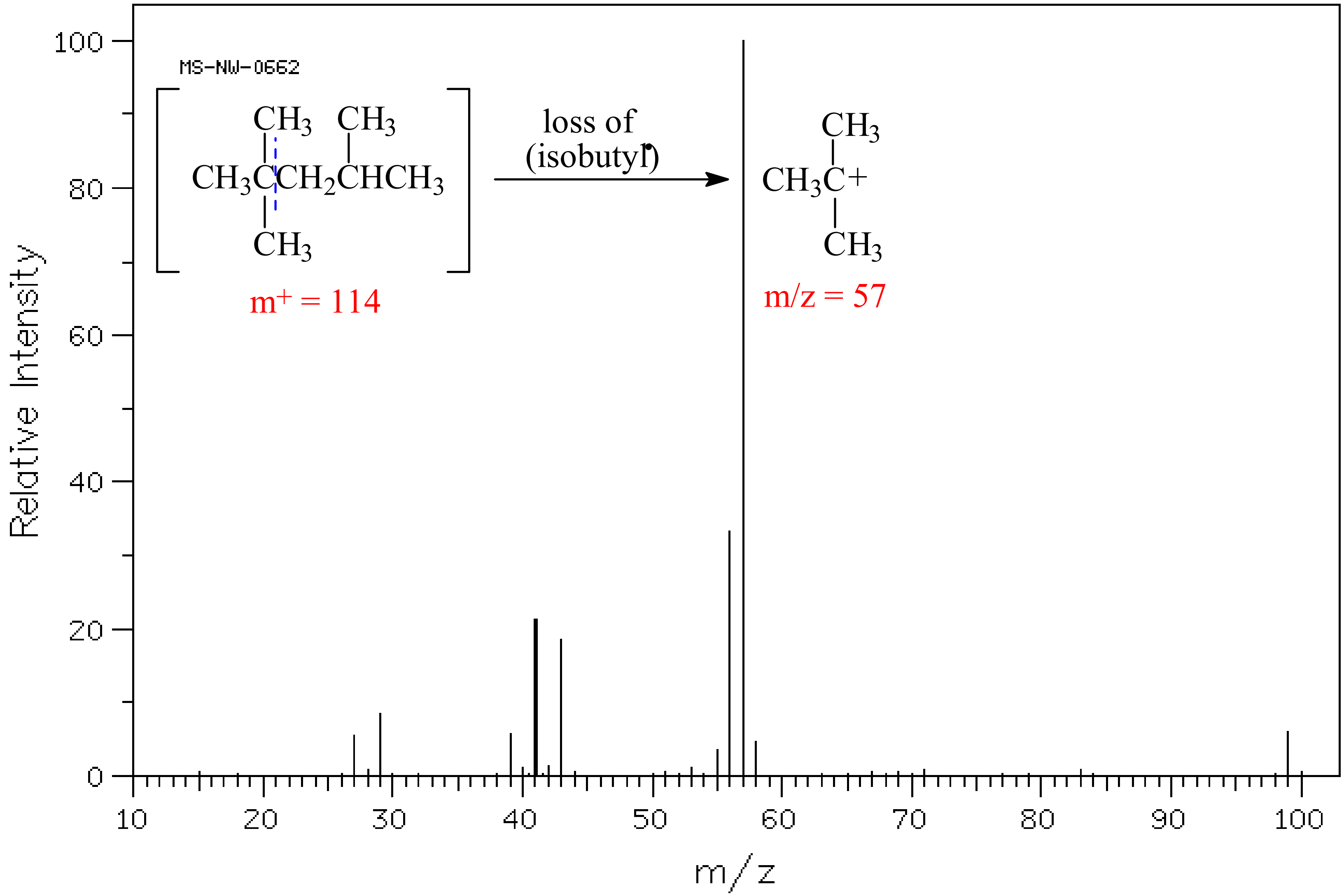
ions	m/z
$CH_3OH^{+\cdot}$	32
$H_2C=OH^+$	31
$HC\equiv O^+$	29
H_3C^+	15

Octane, $m^+ = 114$

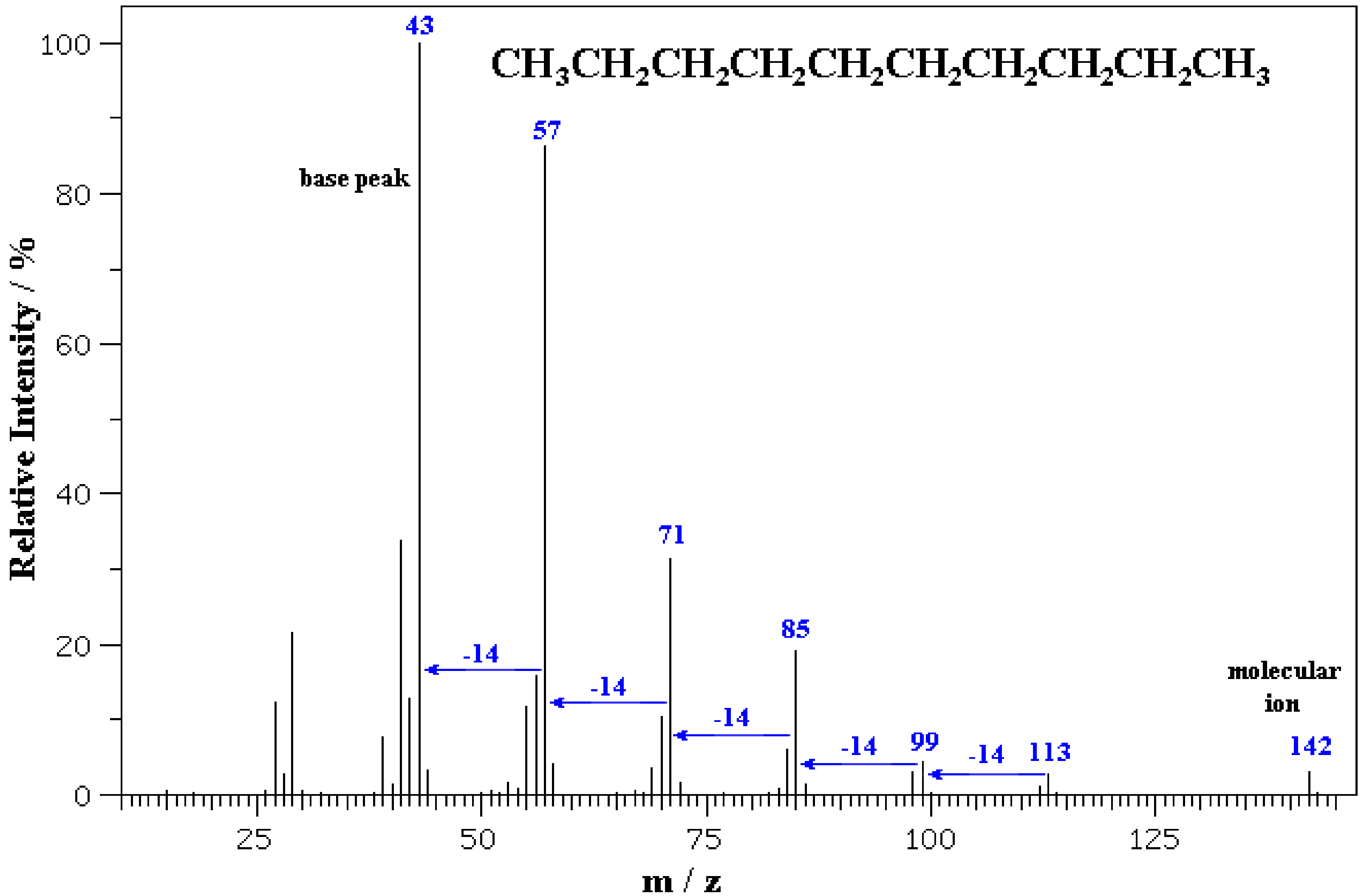


MS-NW-0660
m-71
Base peak
-71 (base)
-57
-43
-29
-15
CH3CH2CH2CH2CH2CH2CH2CH3
m+ = 114
m-57
m-43
m-29
m+
Relative Intensity
m/z

Isooctane, no molecular ion

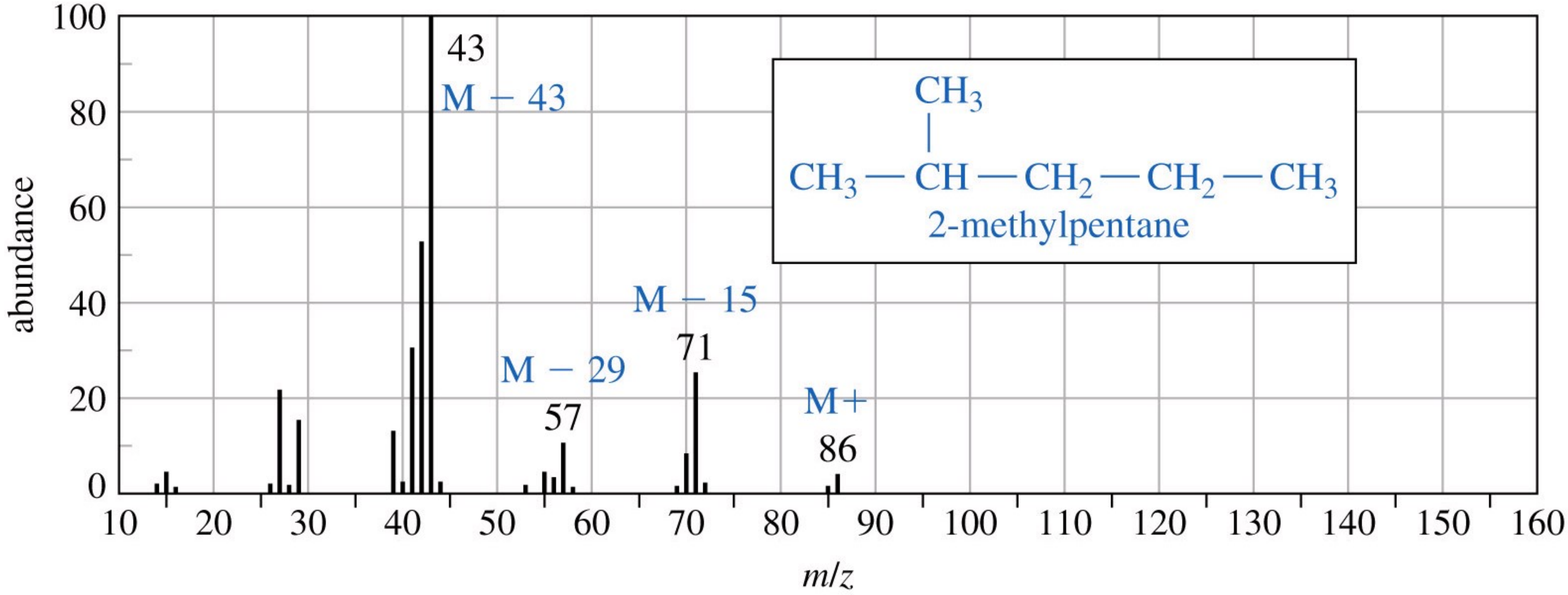


Decane

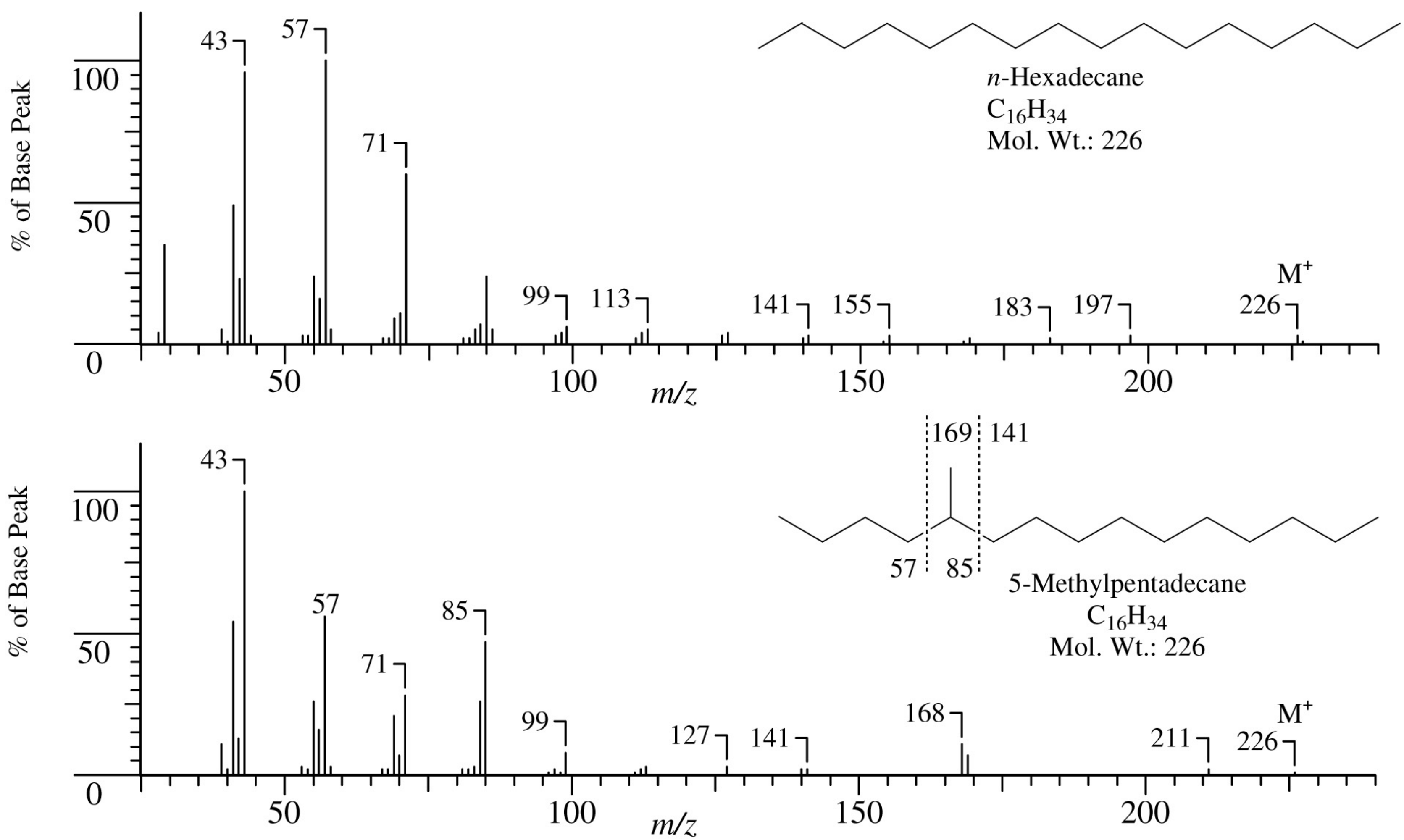


CH3CH2CH2CH2CH2CH2CH2CH2CH2CH3
43
base peak
57
71
85
99
113
142
molecular ion
-14
-14
-14
-14
-14
Relative Intensity / %
100
80
60
40
20
0
25
50
75
100
125
m / z

2-Methylpentane



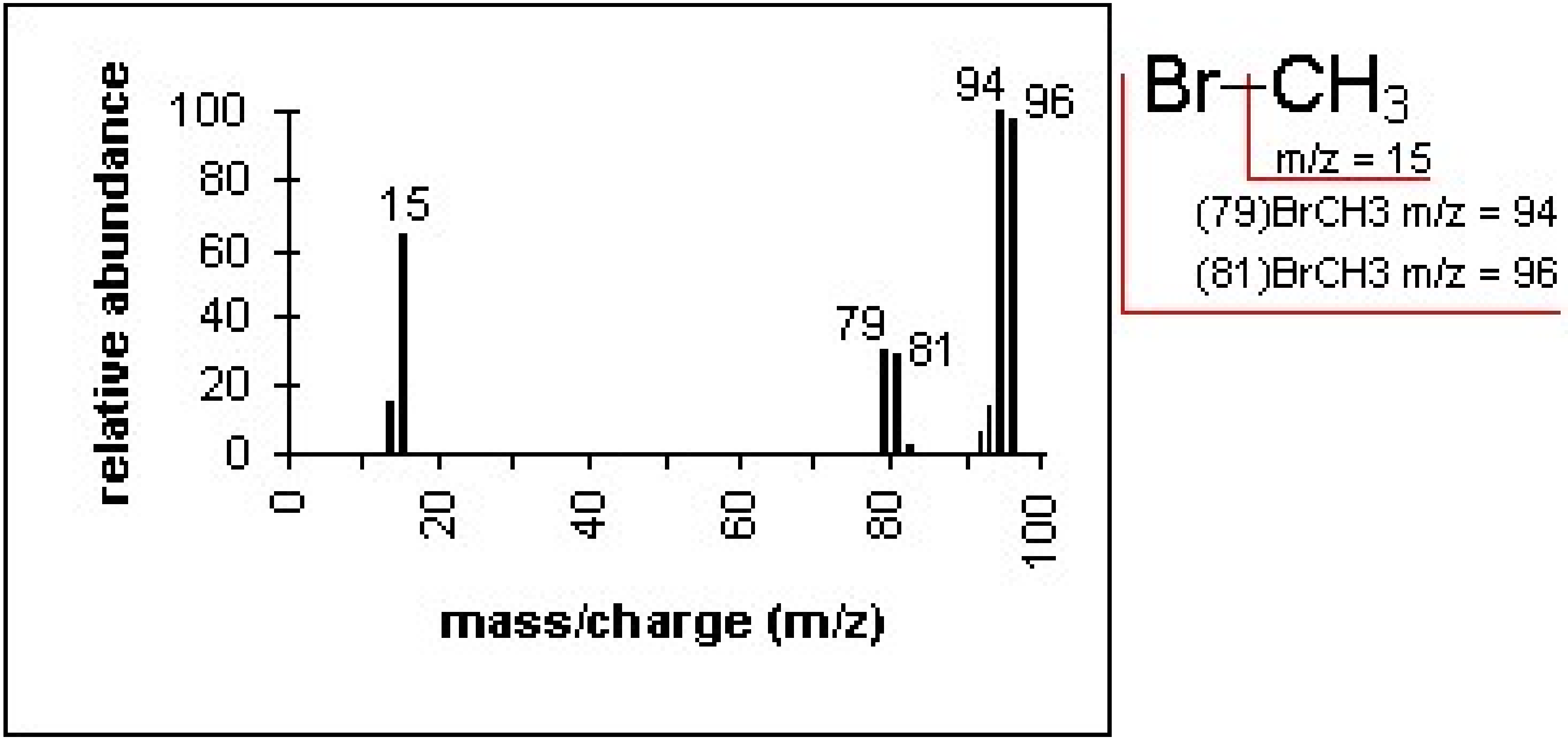
Effect of Branching in Hydrocarbons



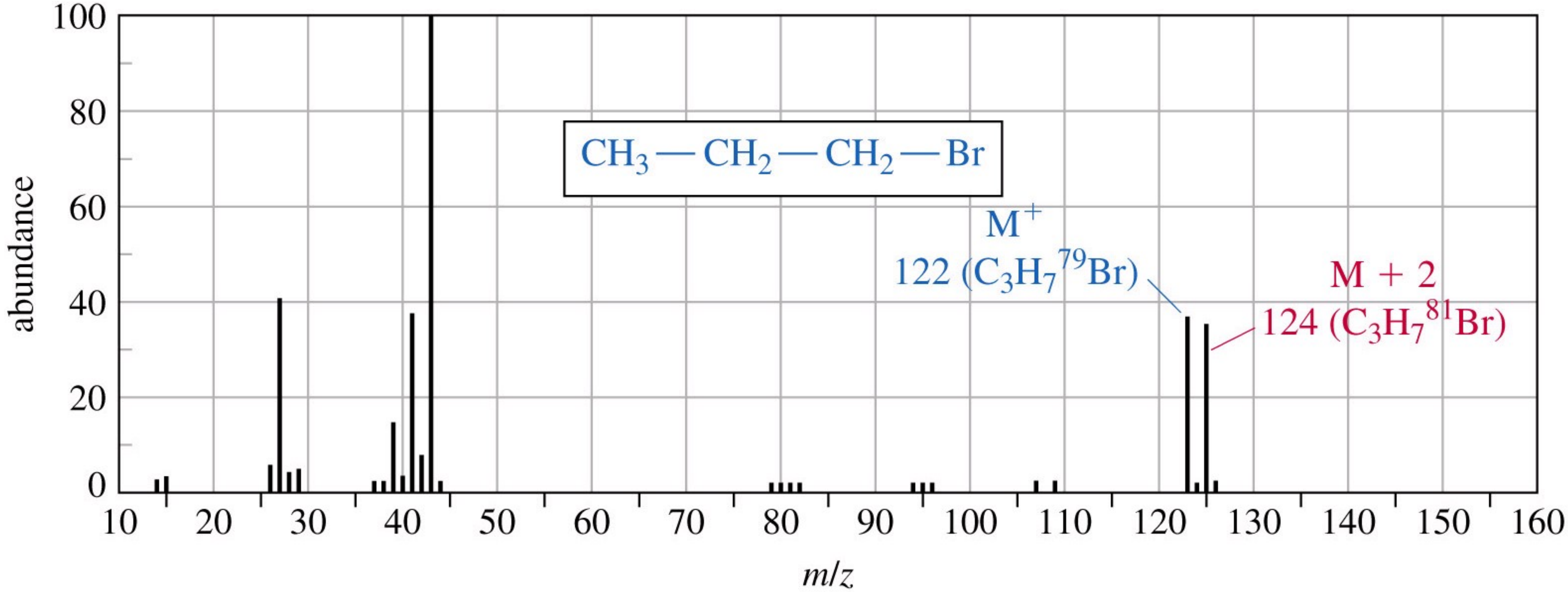
Isotopes

- **Mass spectrometers are capable of separating and detecting individual ions even those that only differ by a single atomic mass unit.**
- **As a result molecules containing different isotopes can be distinguished.**
- **This is most apparent when atoms such as bromine or chlorine are present (^{79}Br : ^{81}Br, intensity 1:1 and ^{35}Cl : ^{37}Cl, intensity 3:1) where peaks at "M" and "M+2" are obtained.**
- **The intensity ratios in the isotope patterns are due to the natural abundance of the isotopes.**
- **"M+1" peaks are seen due the the presence of ^{13}C in the sample.**

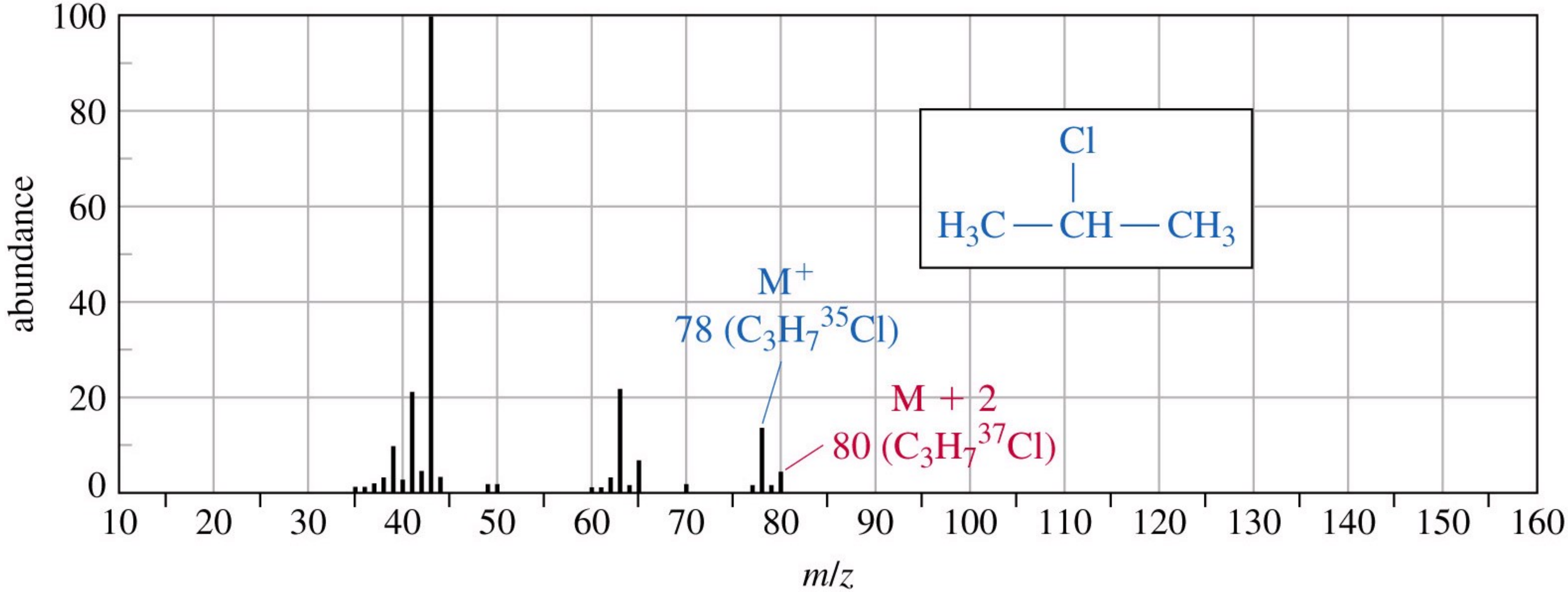
Bromomethane



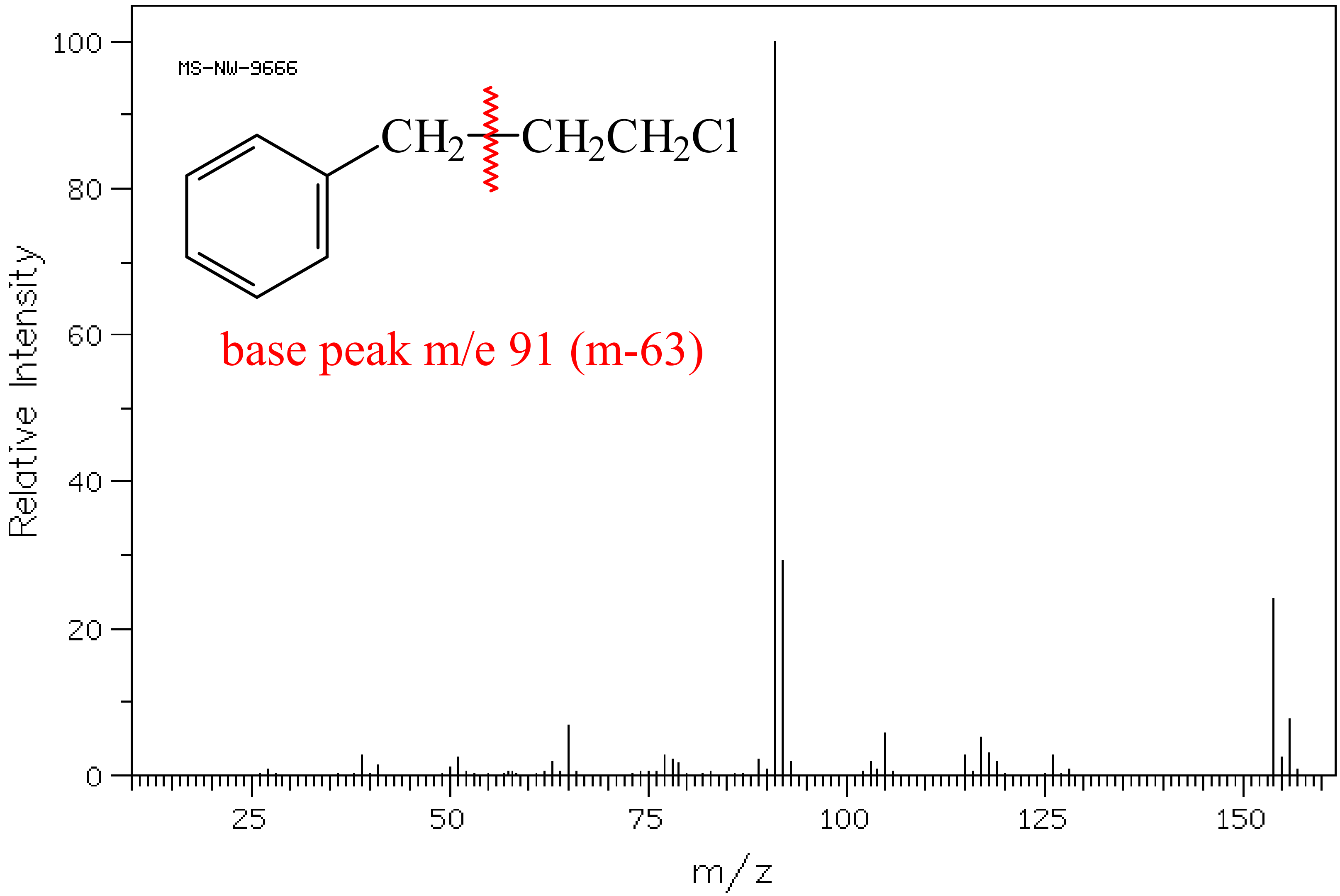
1-Bromopropane



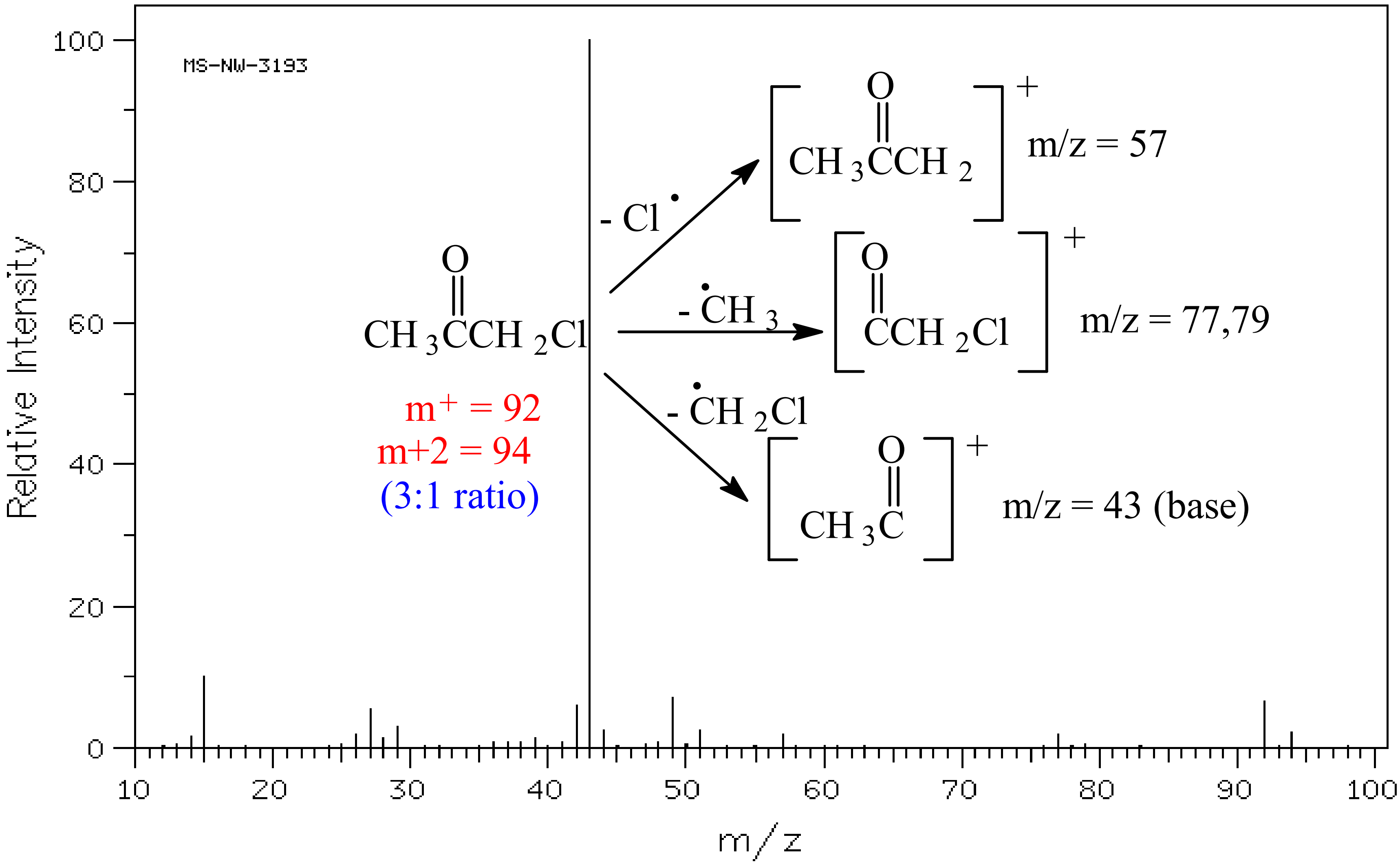
2-Chloropropane



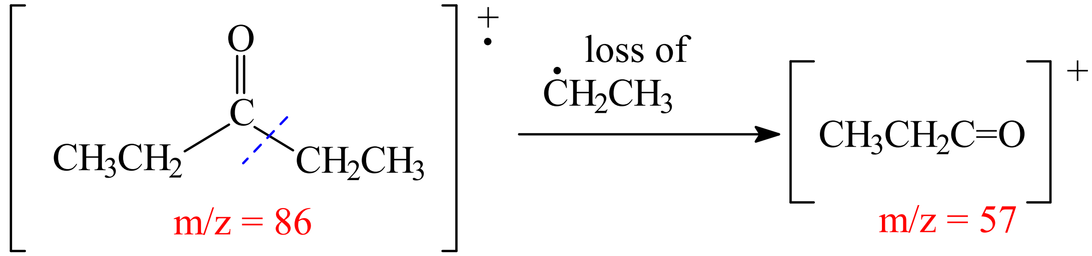
(3-Chloropropyl)benzene

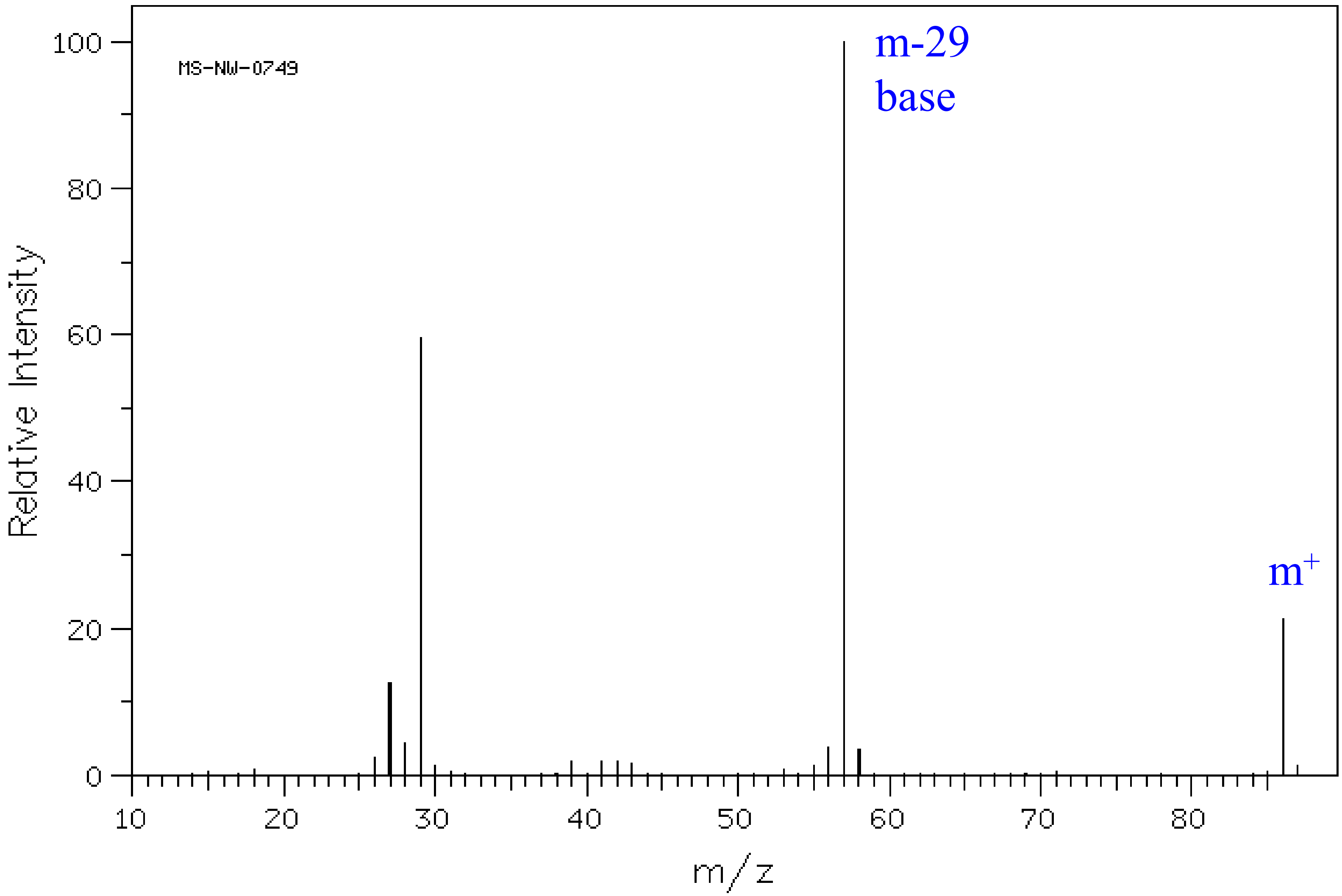


Chloroacetone

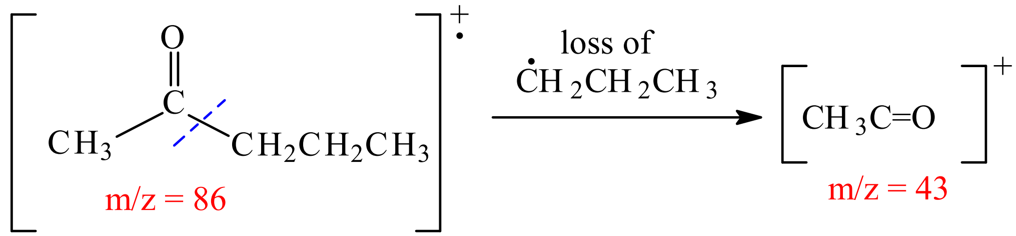


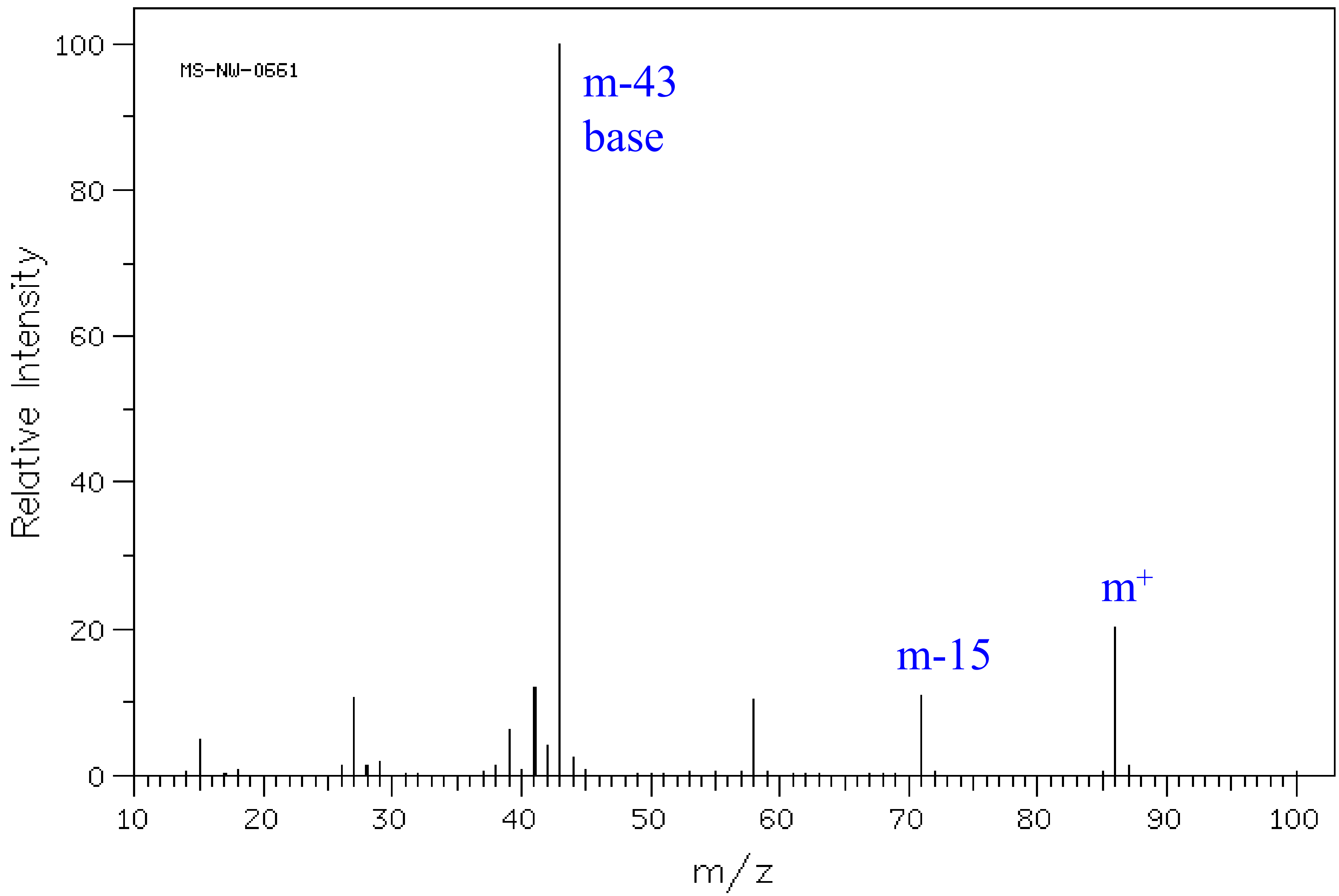
3-Pentanone


O
C
CH_3CH_2
CH_2CH_3
+
m/z = 86
loss of
$\dot{C}H_2CH_3$
$CH_3CH_2C{=}O$
+
m/z = 57

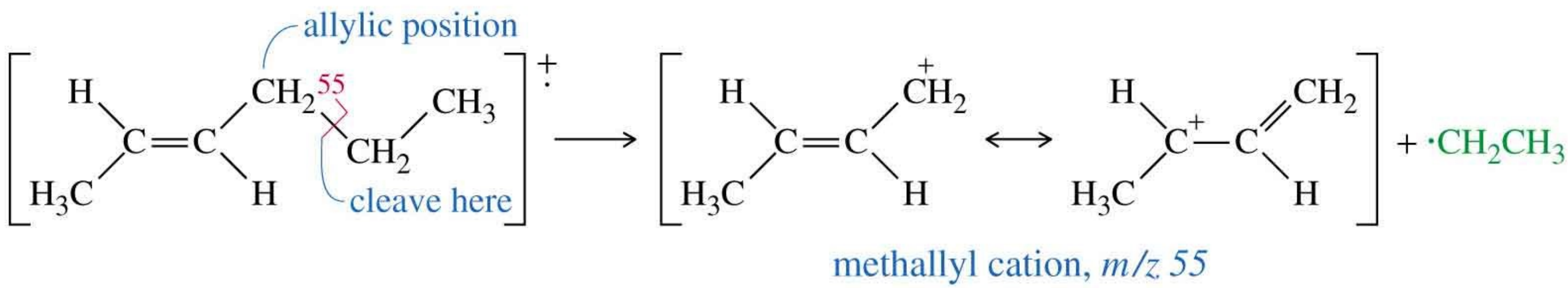

MS-NW-0749
m-29
base
m+
Relative Intensity
m/z
0
20
40
60
80
100
10
20
30
40
50
60
70
80

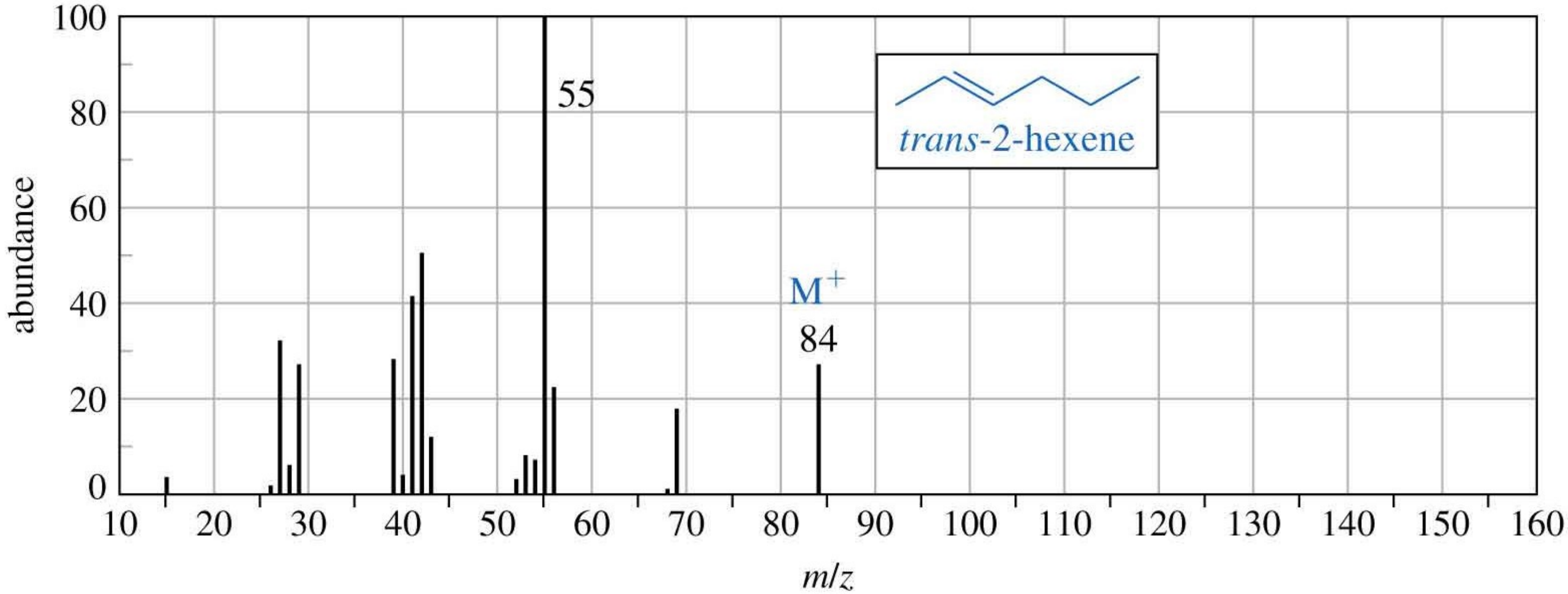
2-Pentanone


O
C
CH3
CH2CH2CH3
m/z = 86
loss of
ĊH2CH2CH3
CH3C=O
m/z = 43

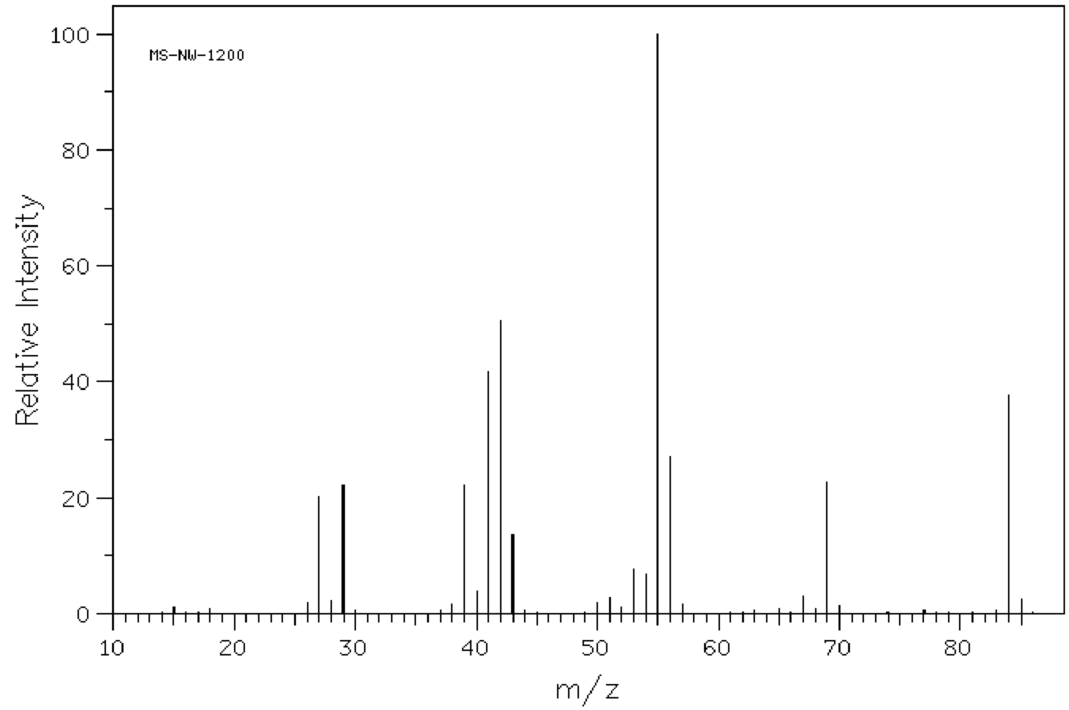

MS-NW-0661
m-43
base
m-15
m+
Relative Intensity
m/z
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100

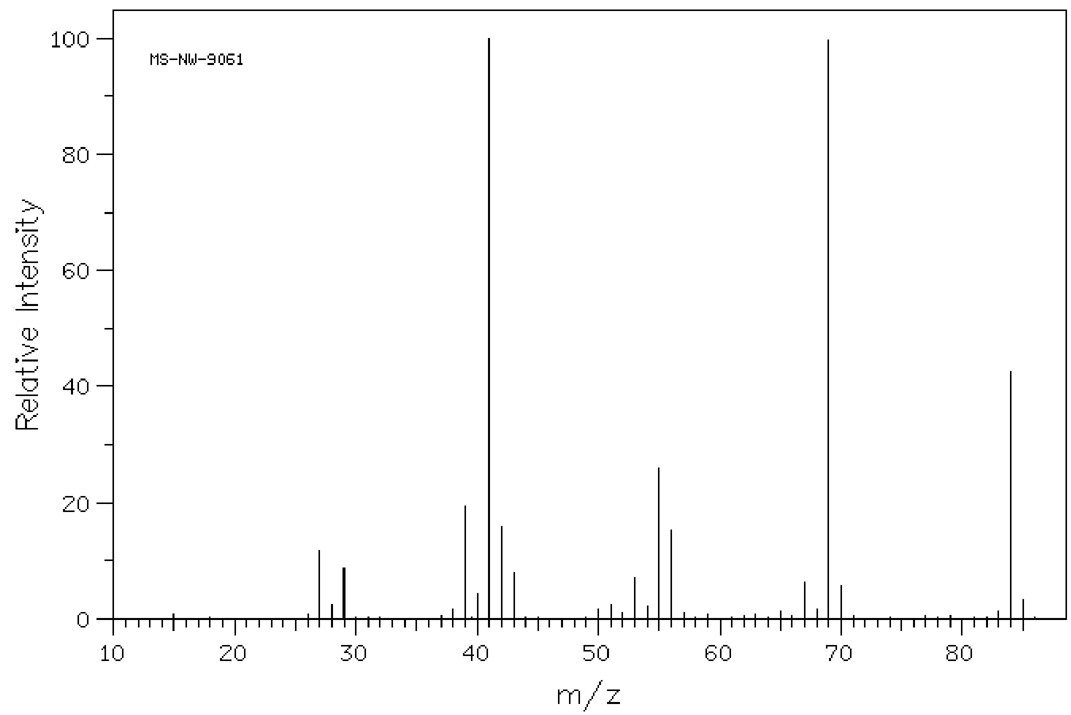
(E) 2-Hexene


allylic position
55
cleave here
methallyl cation, m/z 55
+ ·CH2CH3

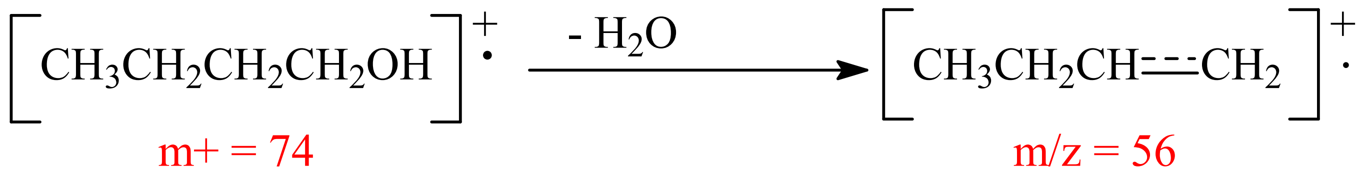

abundance
m/z
55
M+
84
trans-2-hexene
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

2-methyl-2-pentene
and
2-hexene

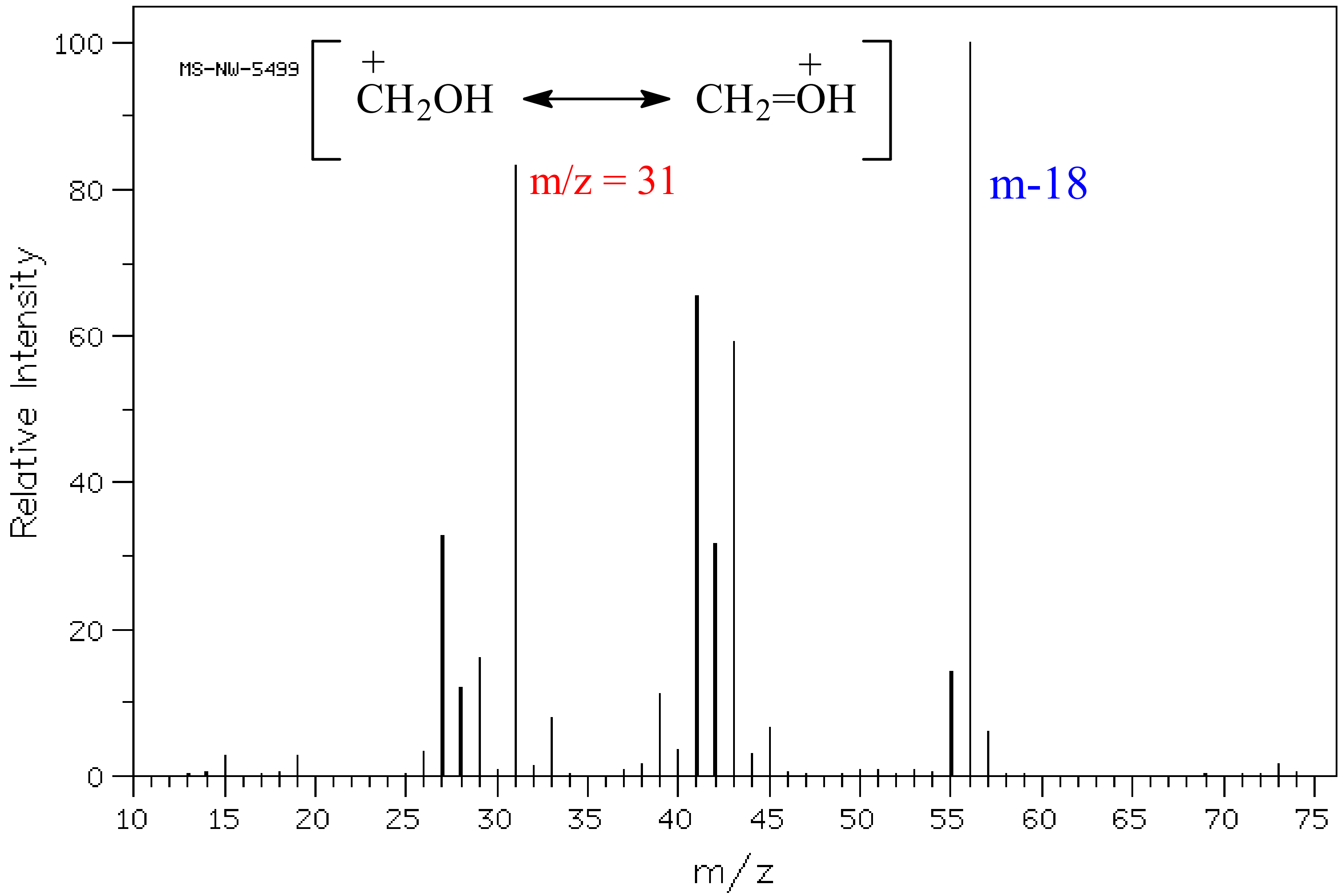




1-Butanol

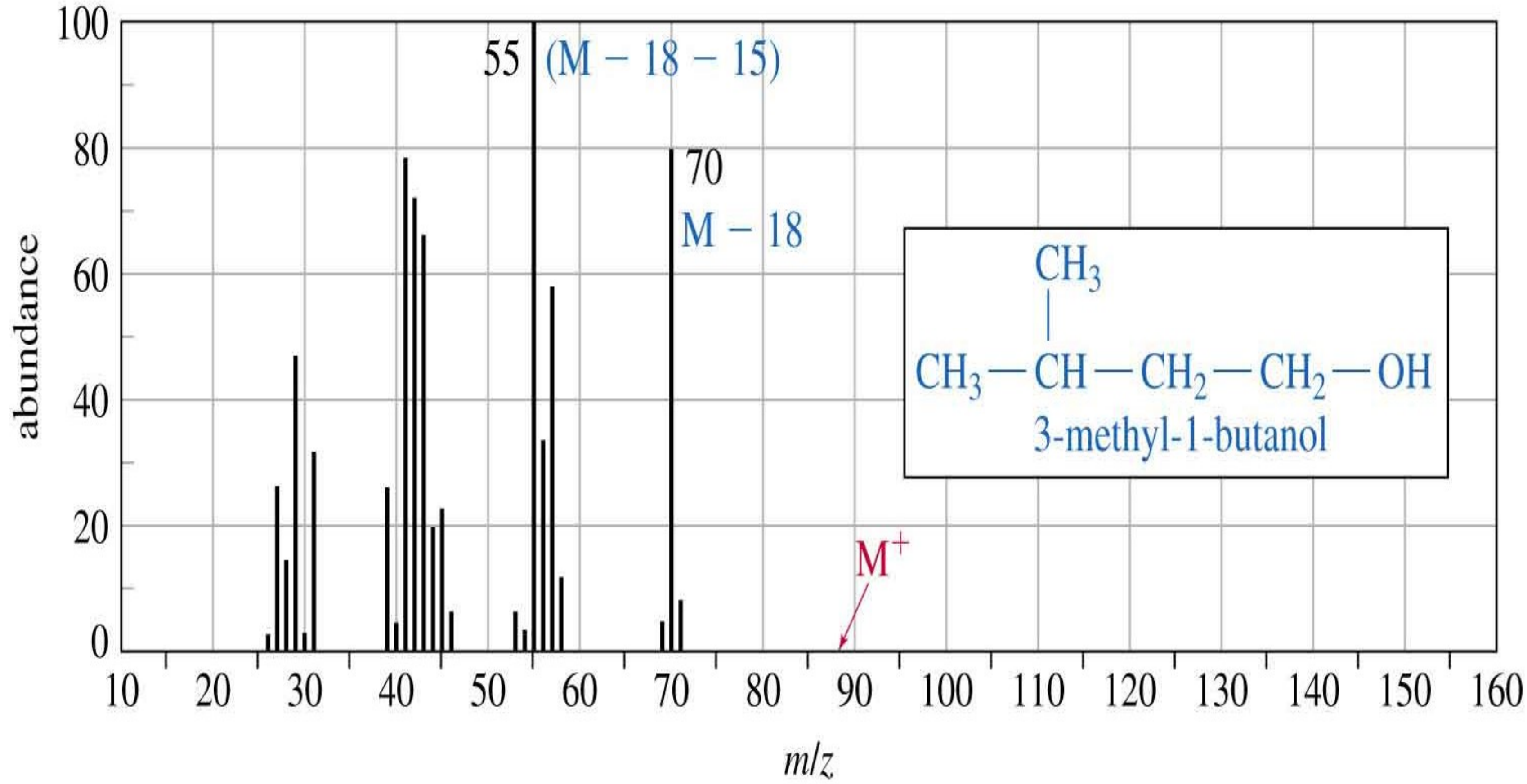


CH3CH2CH2CH2OH
- H2O
CH3CH2CH--CH2
m+ = 74
m/z = 56

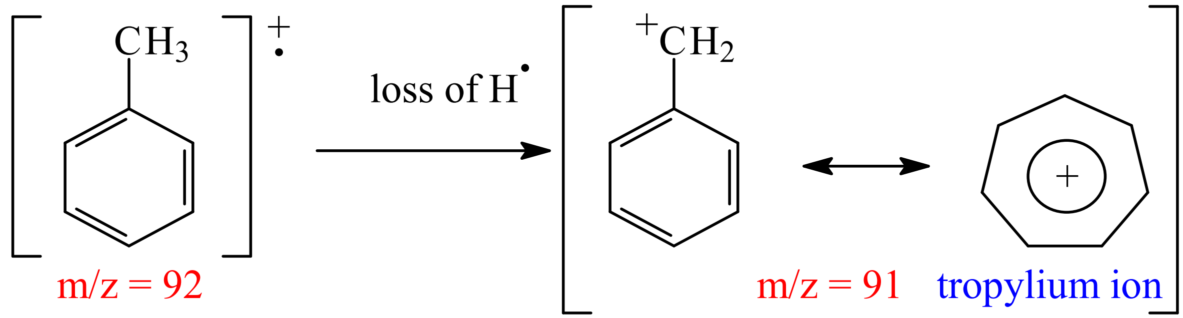


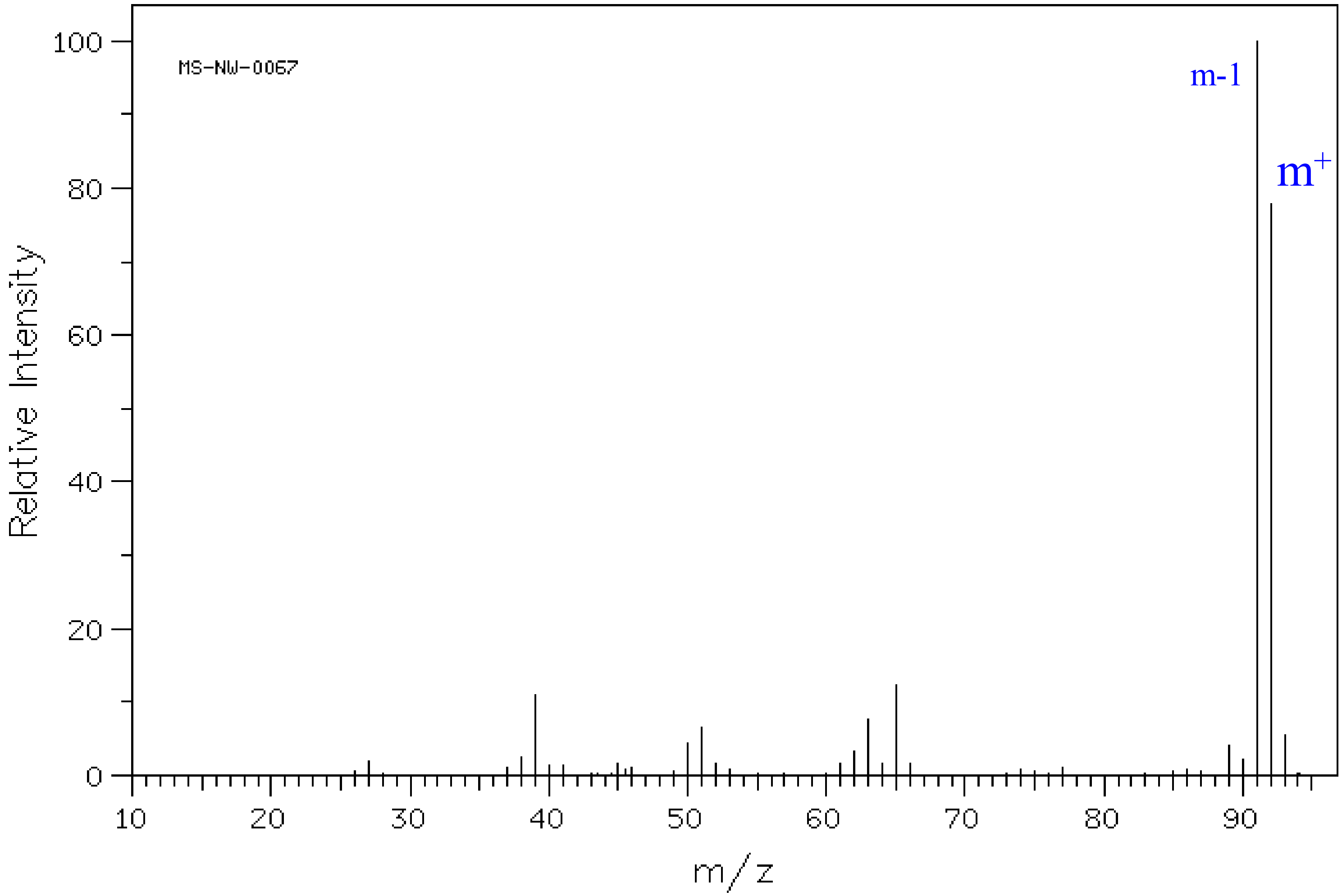
MS-NW-5499
CH2OH
CH2=OH
m/z = 31
m-18
Relative Intensity
m/z

1° Alcohols: Loss of H_2O

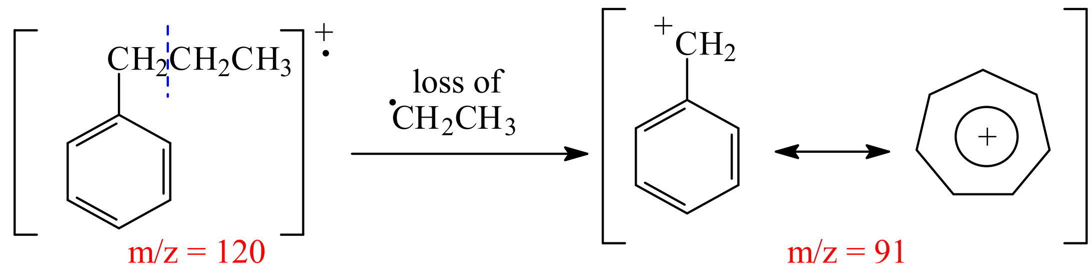


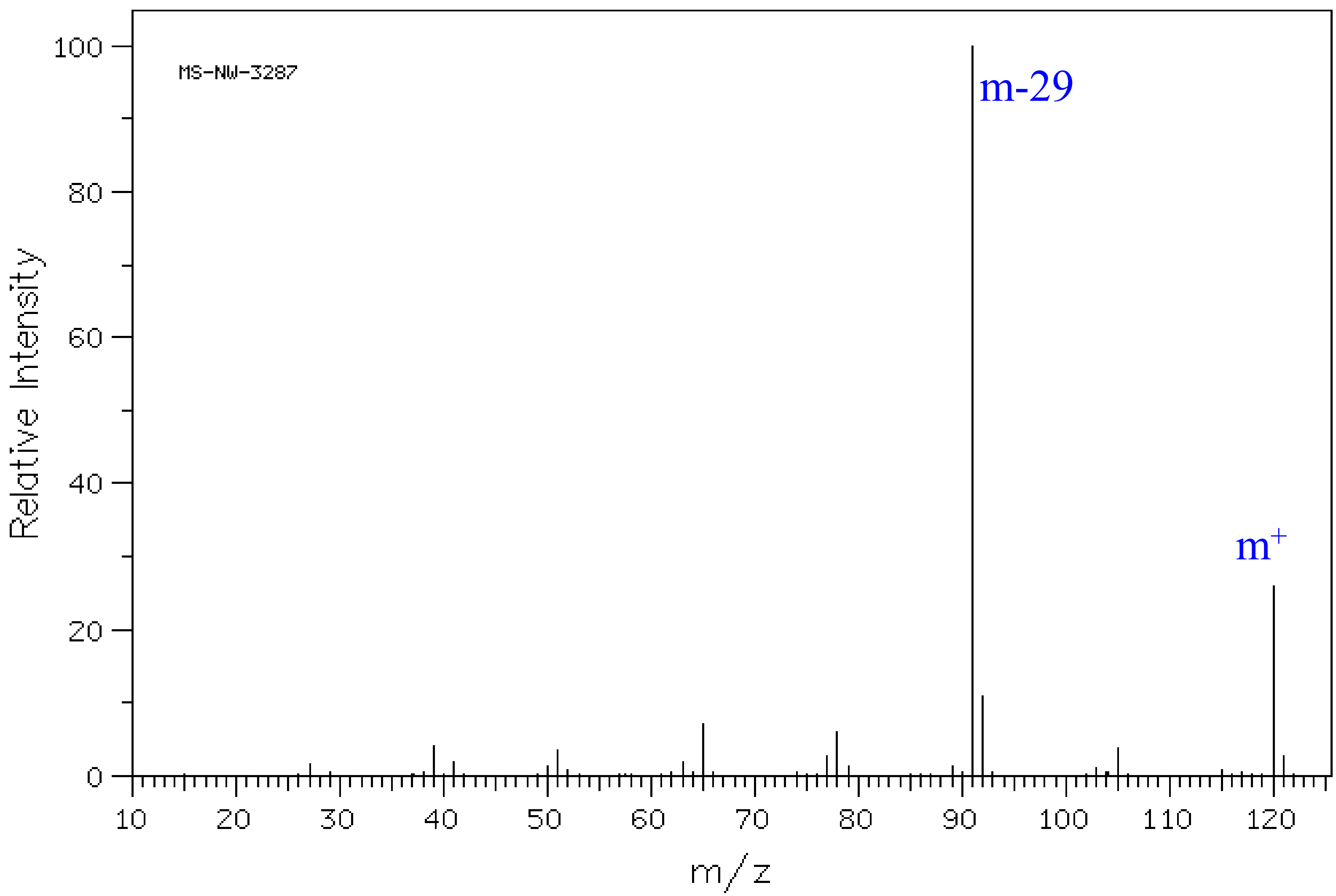
Toluene


CH3
m/z = 92
loss of H•
+CH2
m/z = 91
tropylium ion

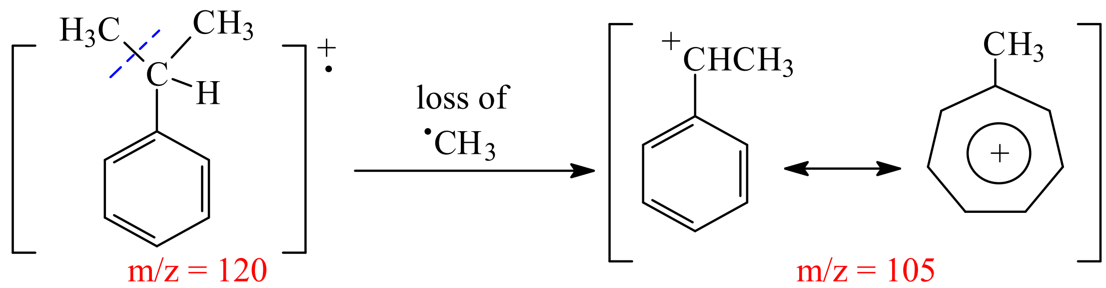

MS-NW-0067
m-1
m+
Relative Intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
m/z

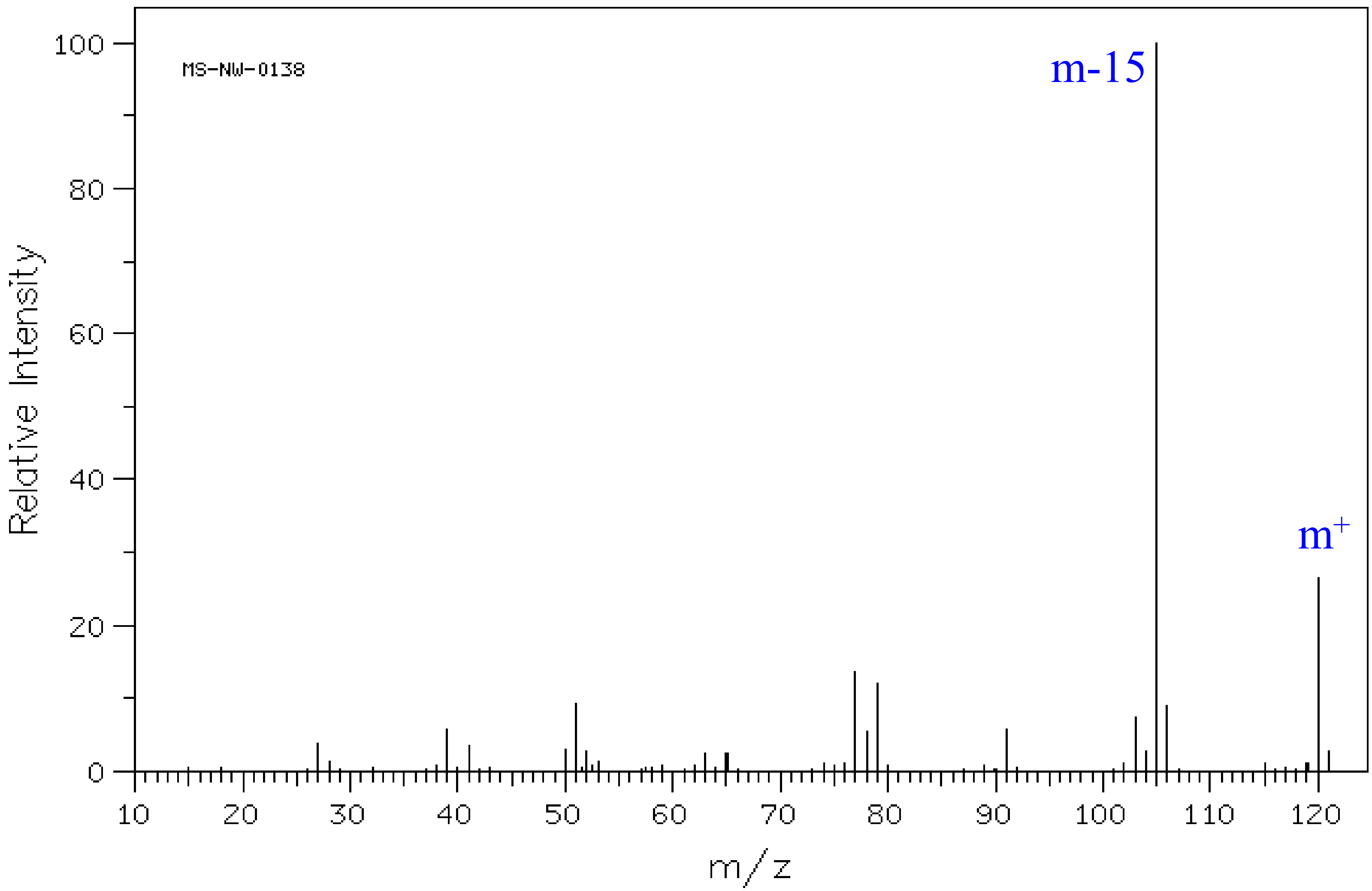
Propylbenzene



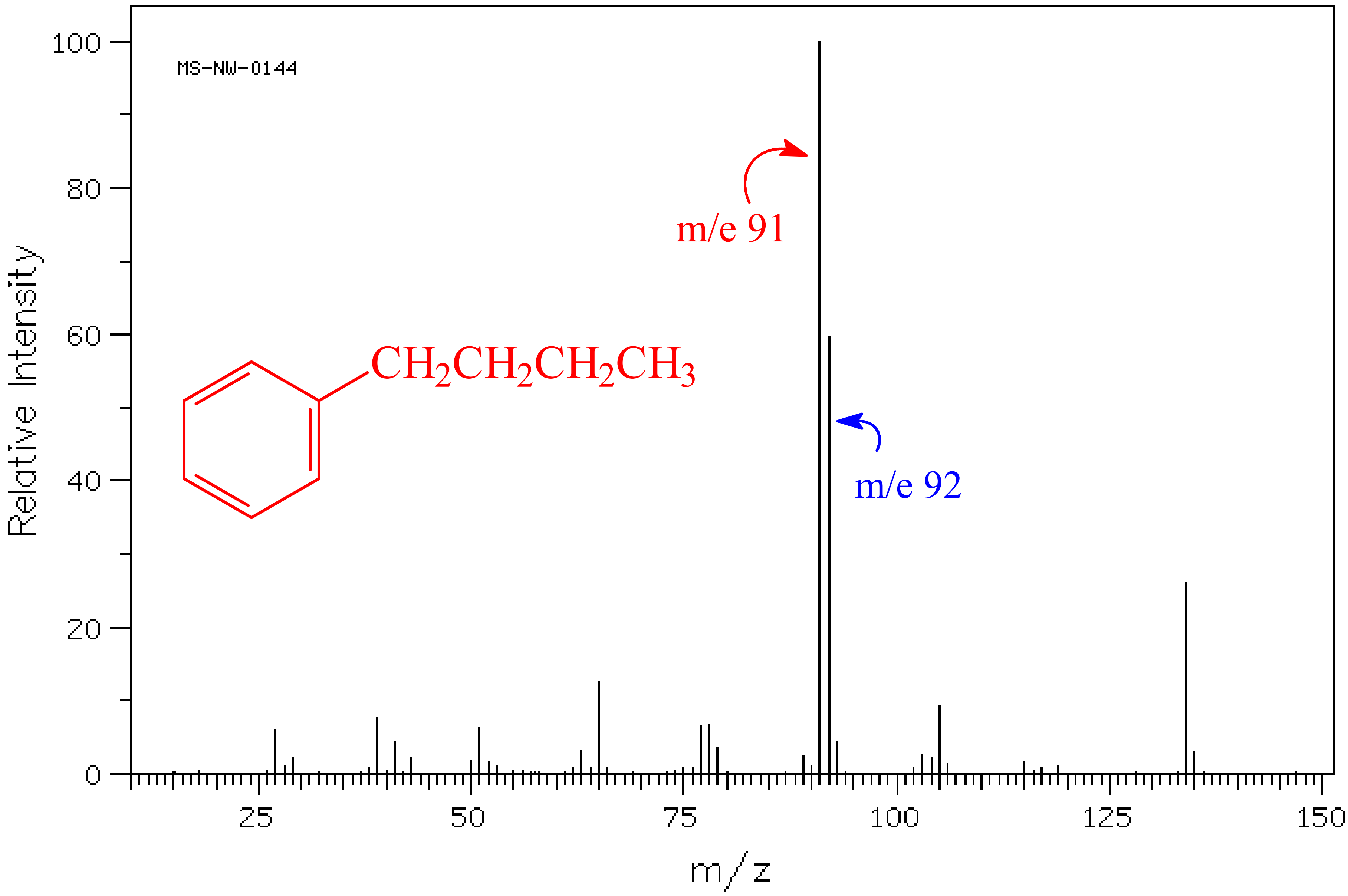


Isopropylbenzene

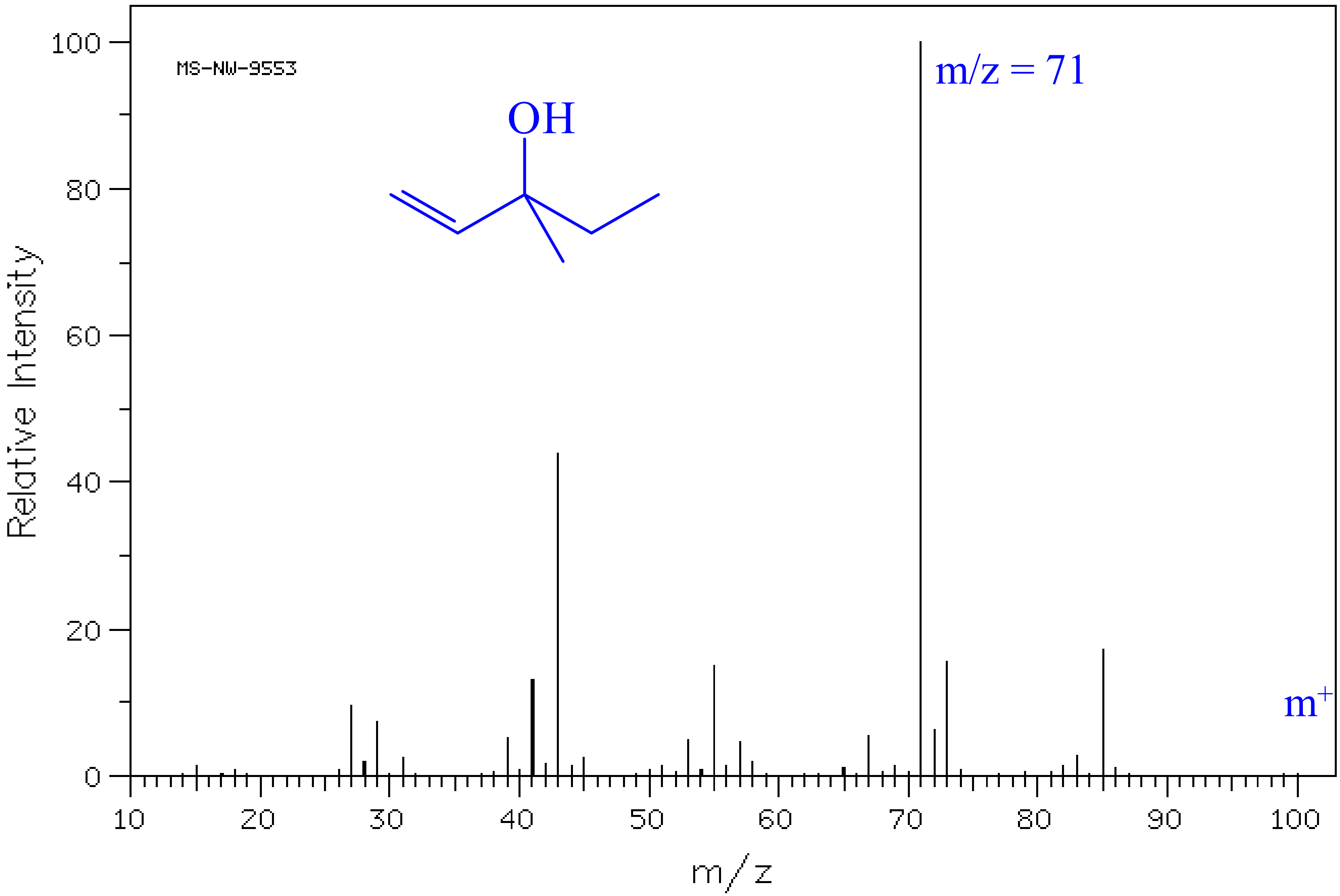




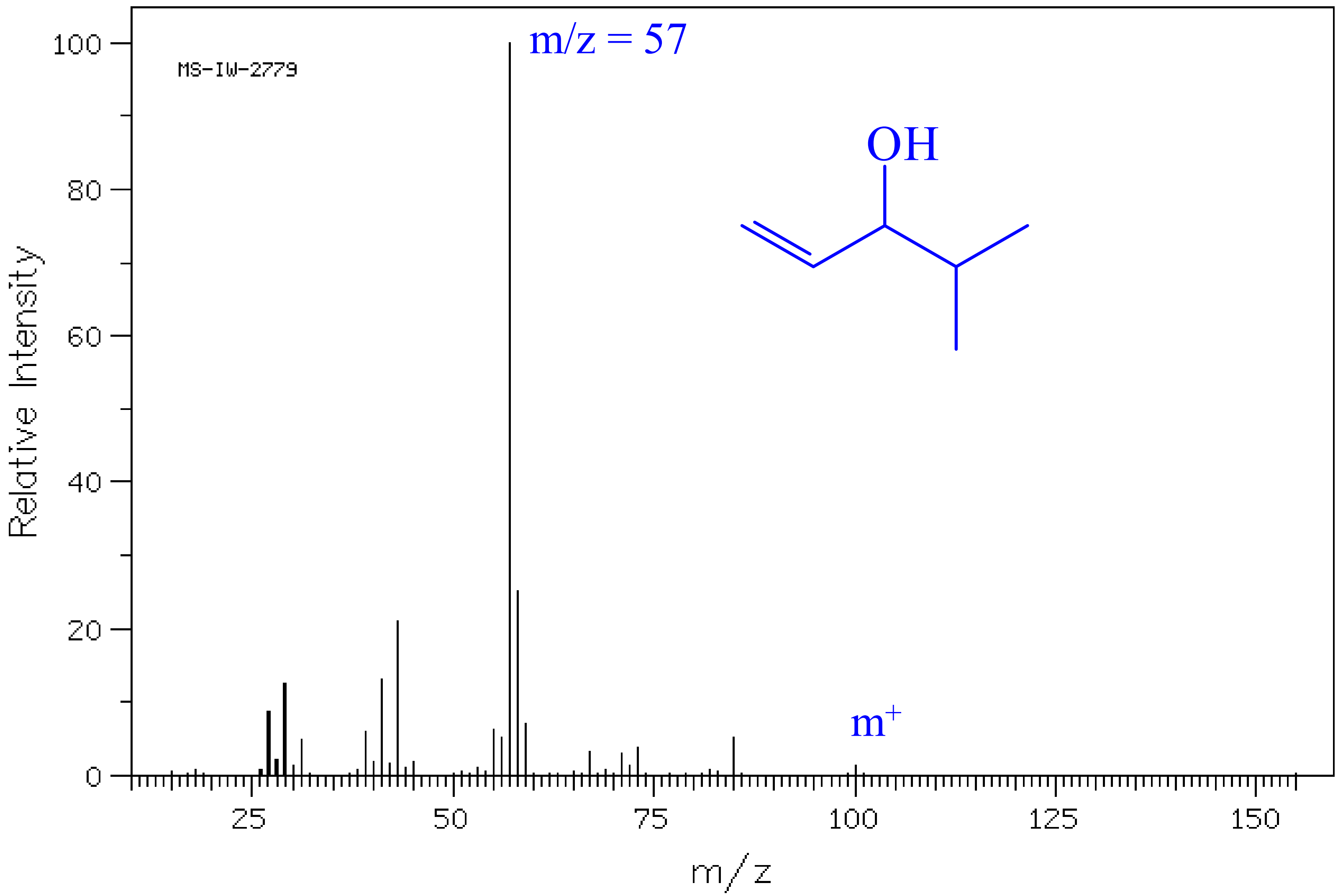
n-Butylbenzene



3-Methyl-1-penten-3-ol

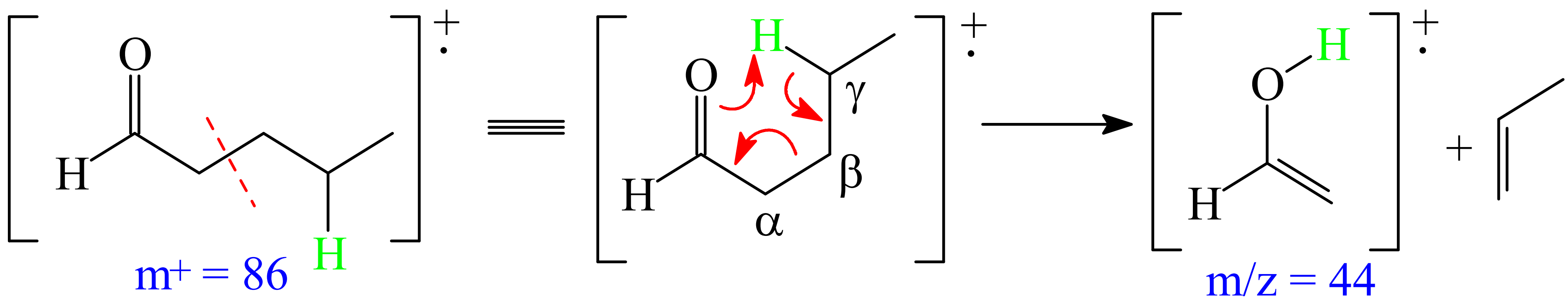


4-Methyl-1-penten-3-ol



McLafferty Rearrangement

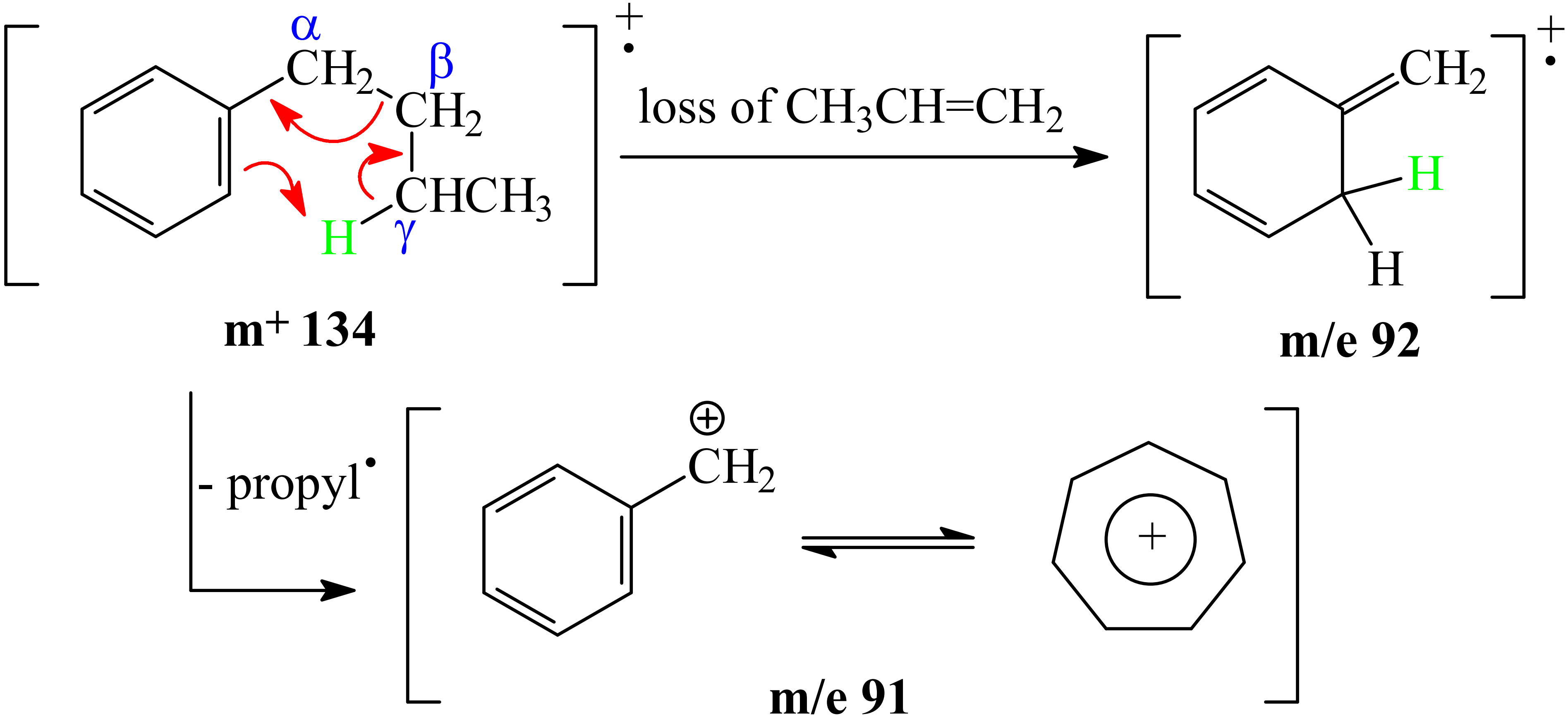
link to SDBS



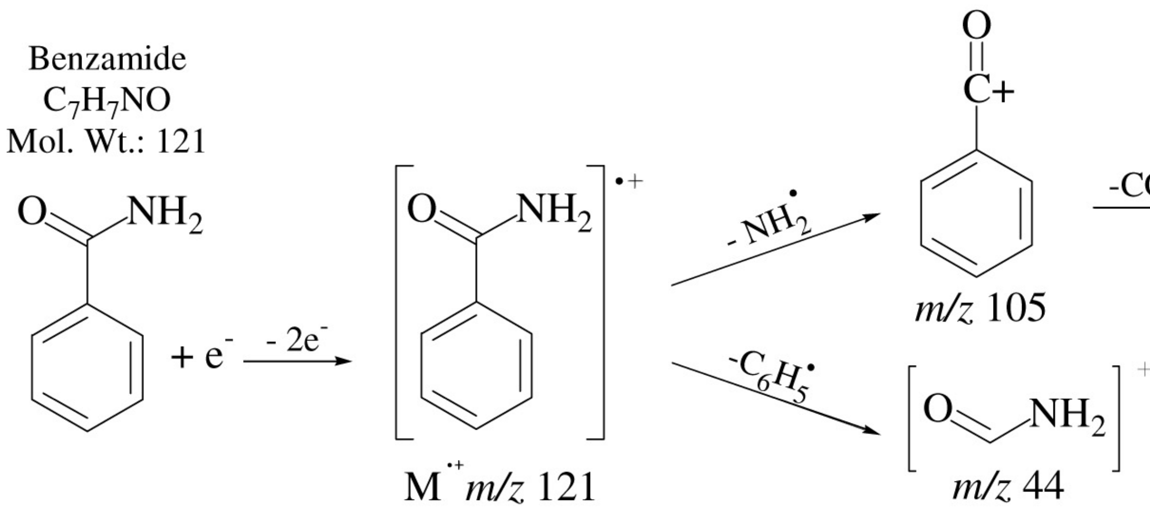
H transfer from γ carbon

results in loss of a neutral alkene

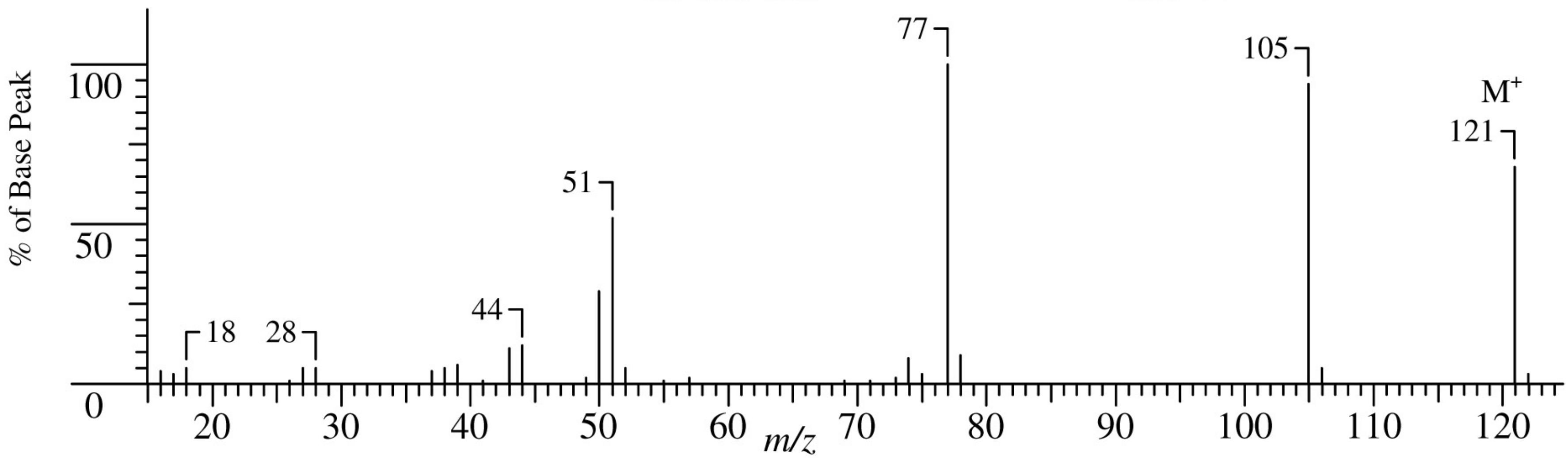
McLafferty Rearrangements in Alkyl Benzenes



Benzamide

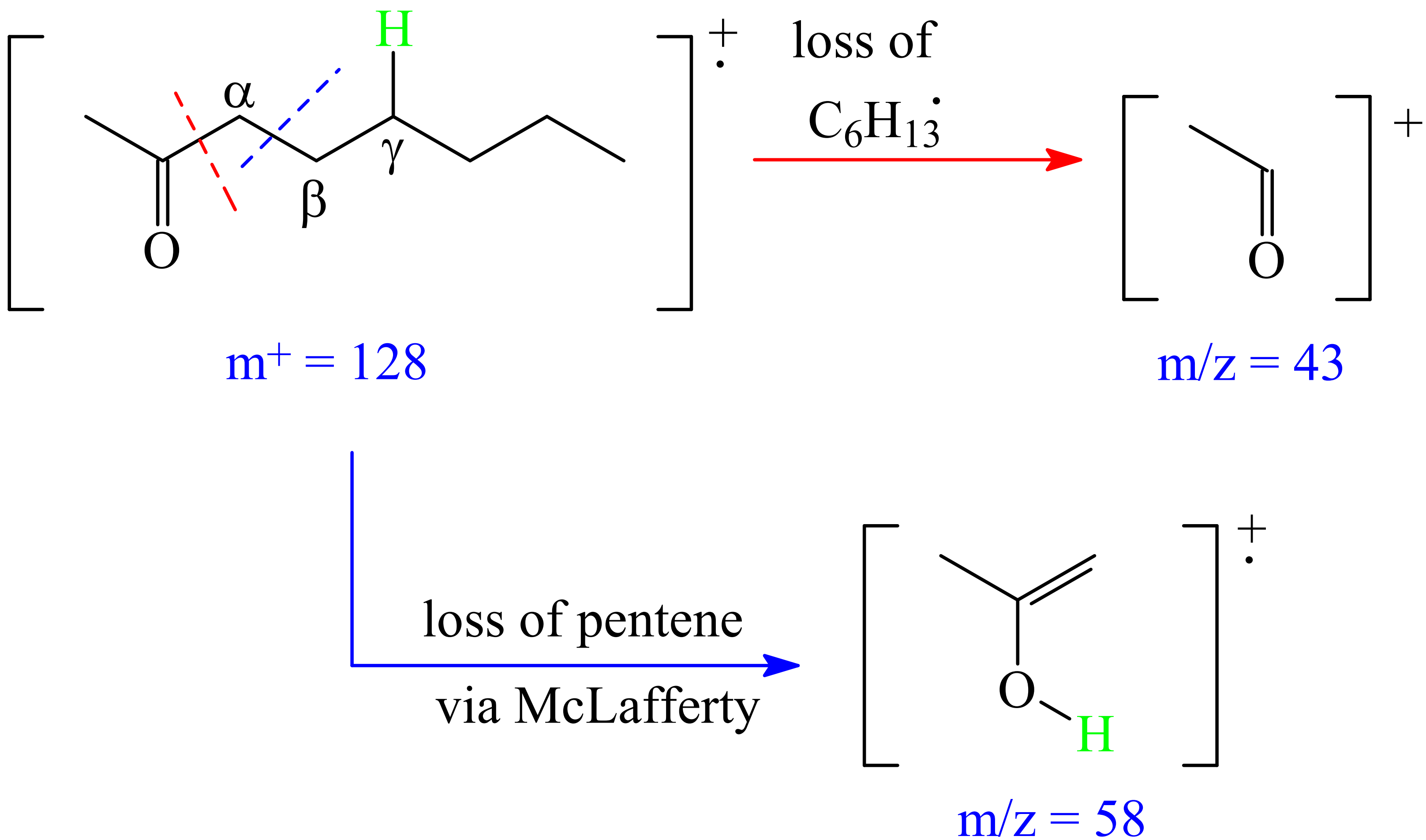


Benzamide
C7H7NO
Mol. Wt.: 121
O
NH2
+ e-
- 2e-
•+
- NH2•
C+
-CO
m/z 105
m/z 77
-C6H5•
O
NH2
m/z 44
M•+ m/z 121



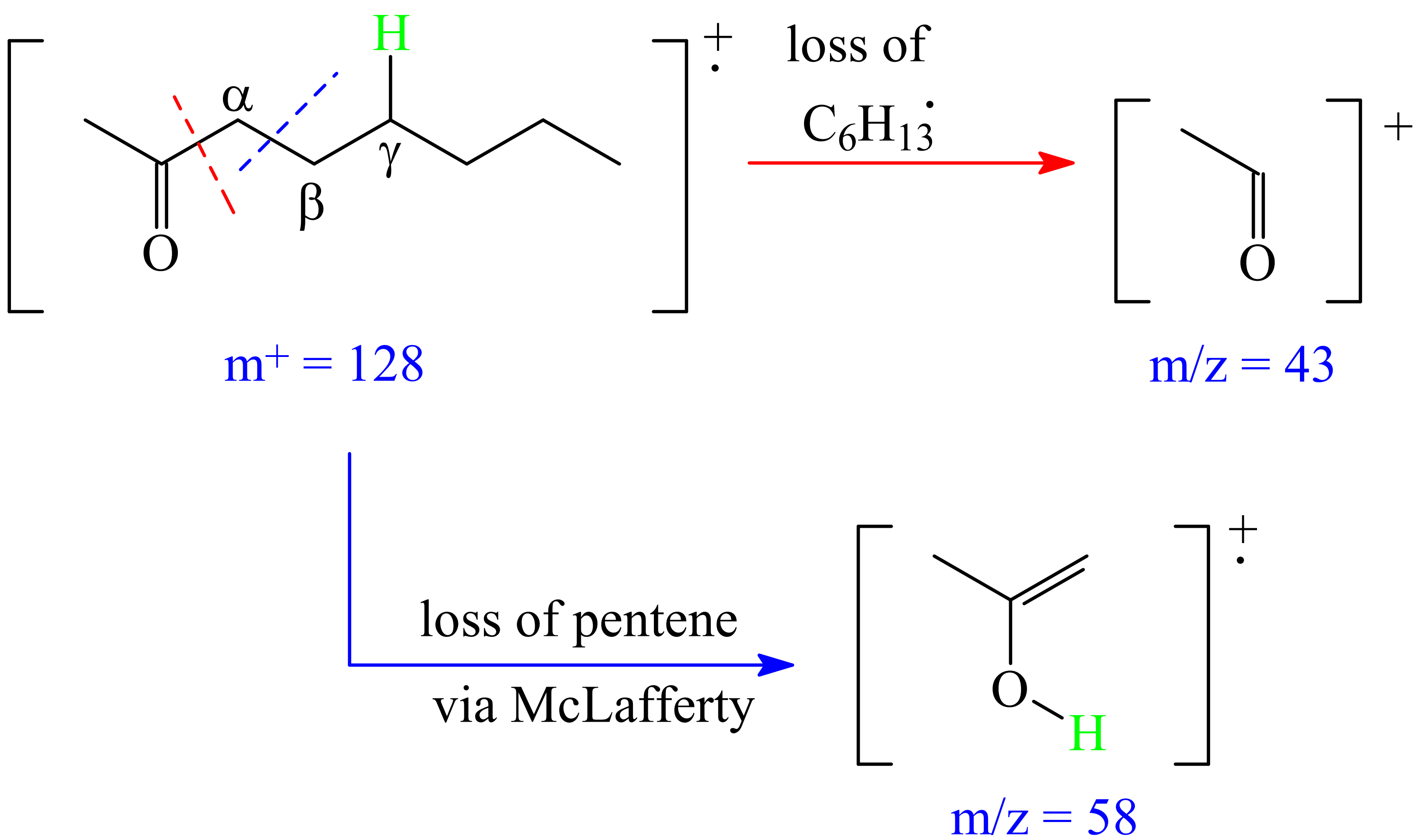
% of Base Peak
100
50
0
18
28
44
51
77
105
M+
121
20
30
40
50
60
70
80
90
100
110
120
m/z

2-Octanone

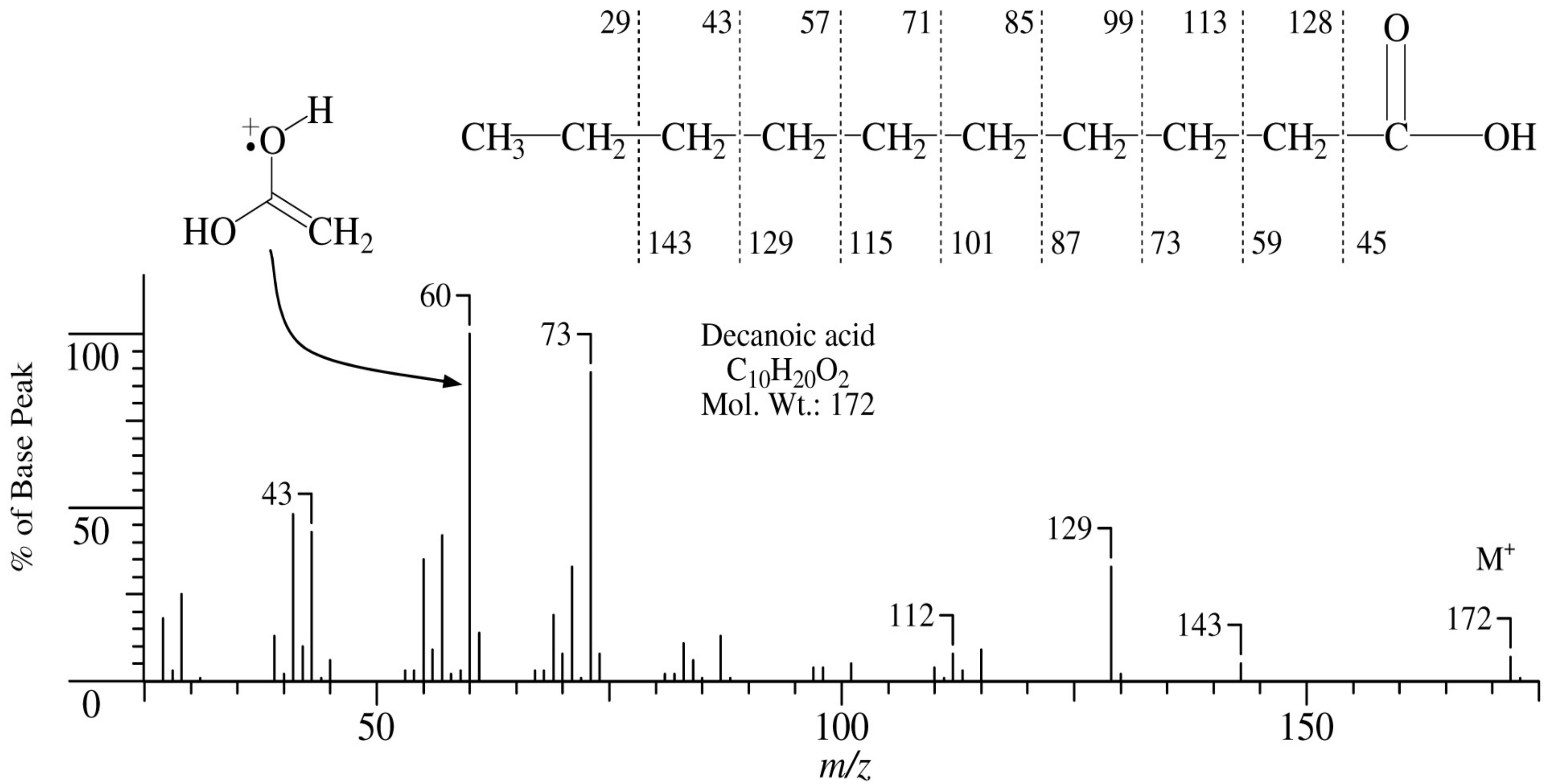


H
α
β
γ
O
+
loss of
C6H13
O
+
m+ = 128
m/z = 43
loss of pentene
via McLafferty
+
O
H
m/z = 58

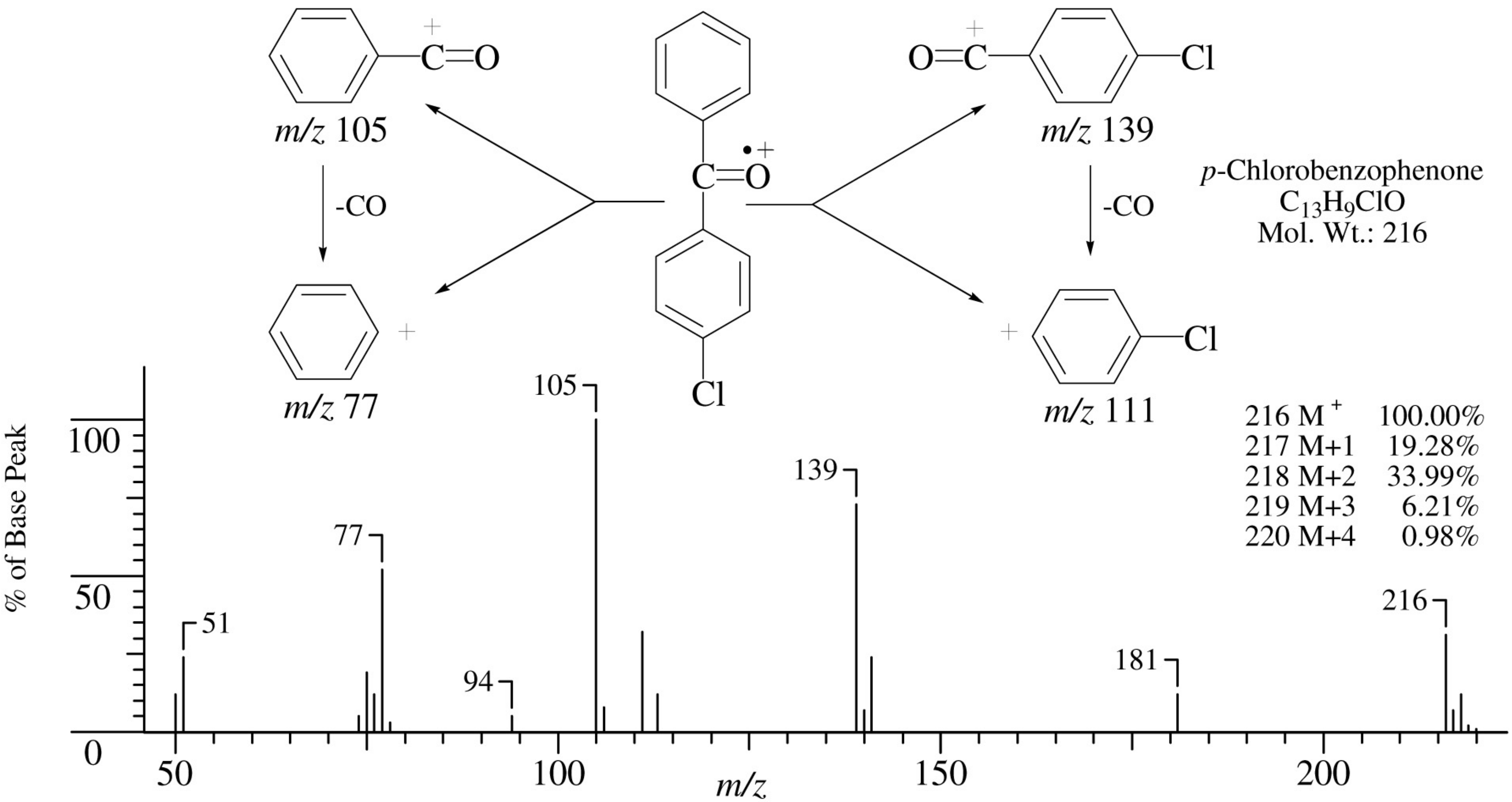
2-Octanone


H
α
β
γ
O
+
loss of
C6H13
O
+
m+ = 128
m/z = 43
loss of pentene
via McLafferty
+
O
H
m/z = 58

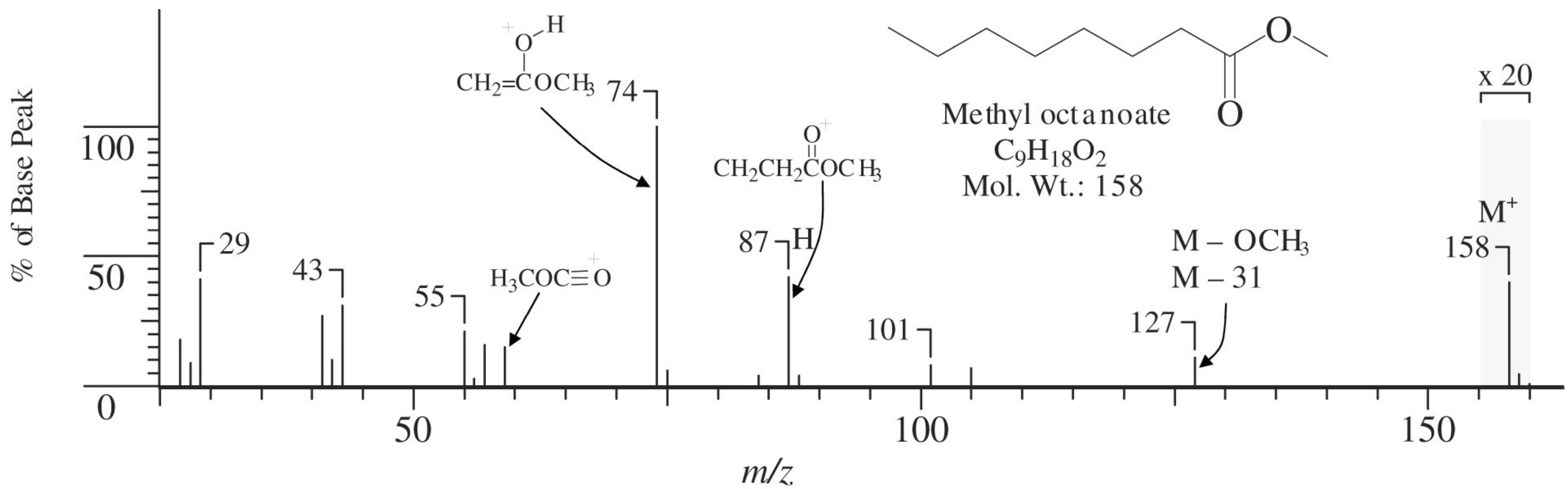
Decanoic Acid



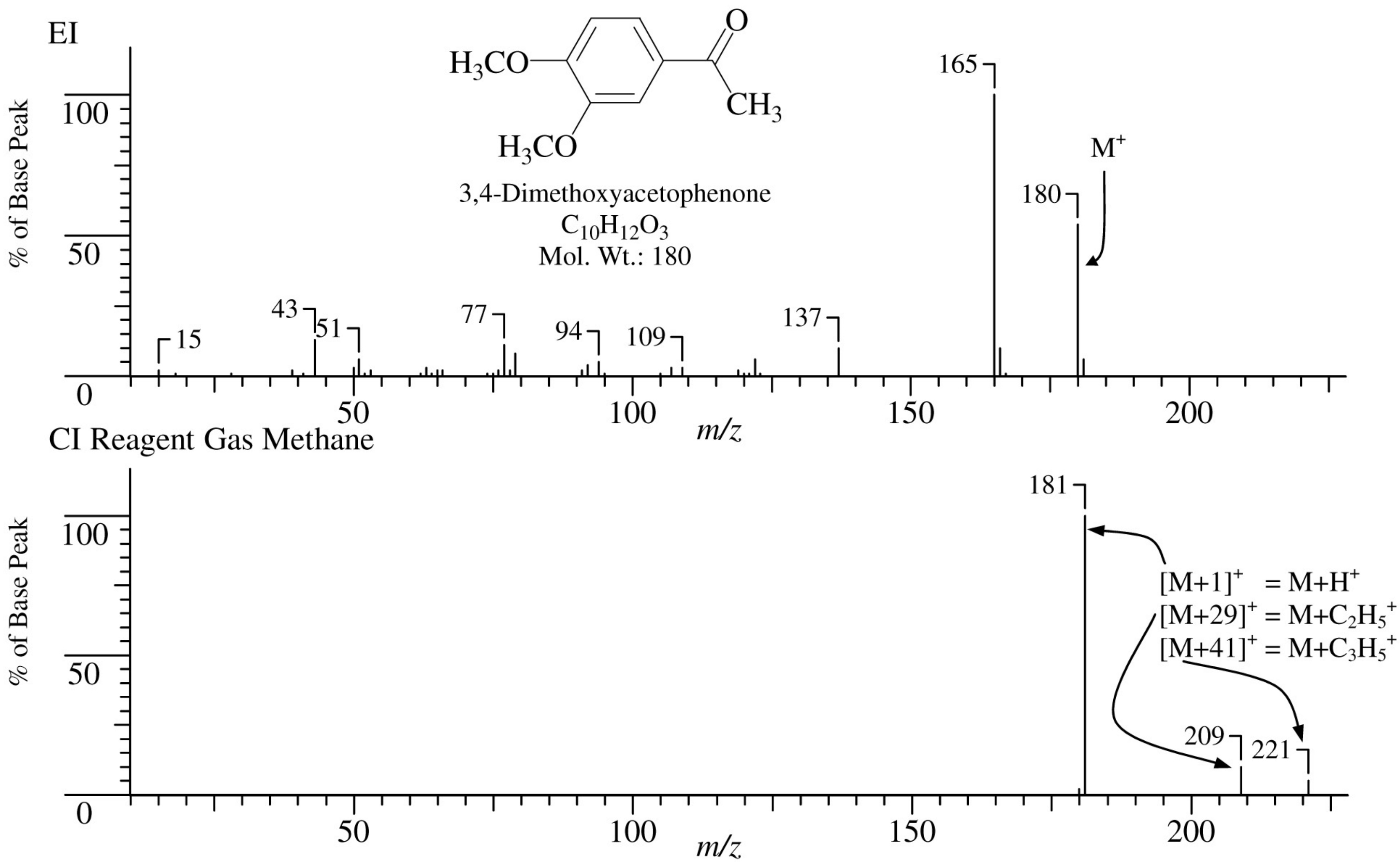
p-Chloroacetophenone



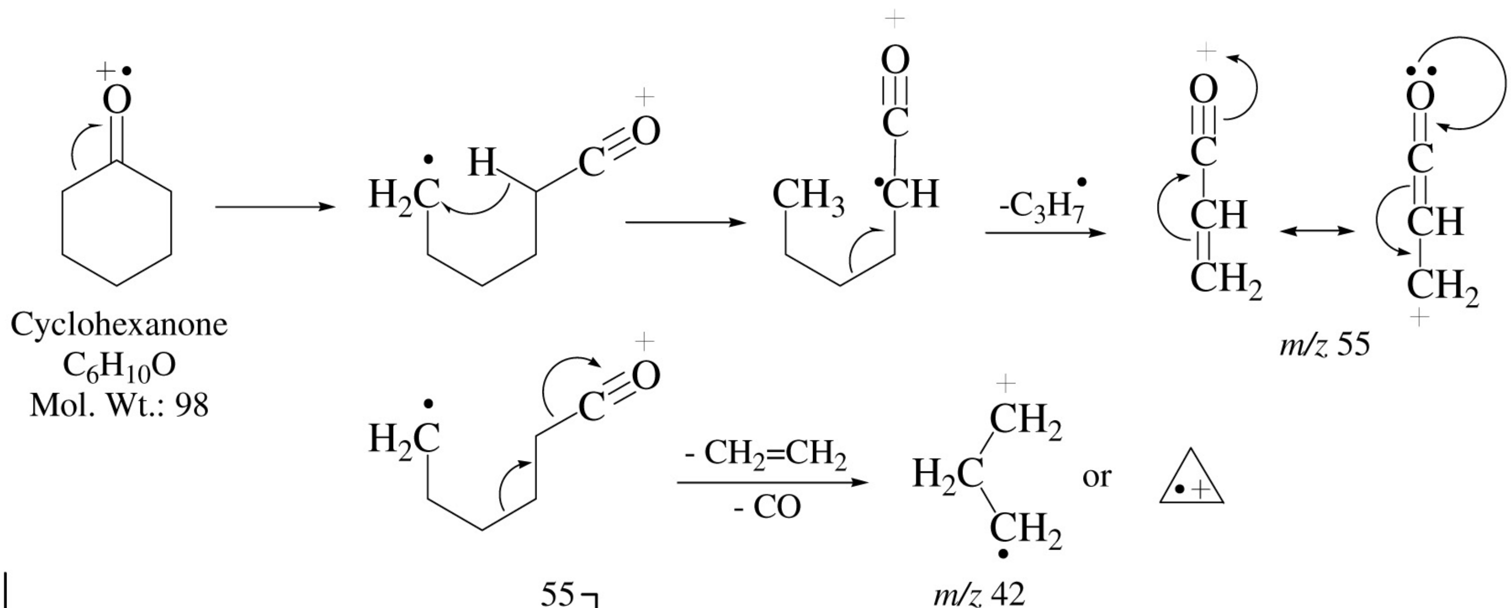
Methyl Octanoate

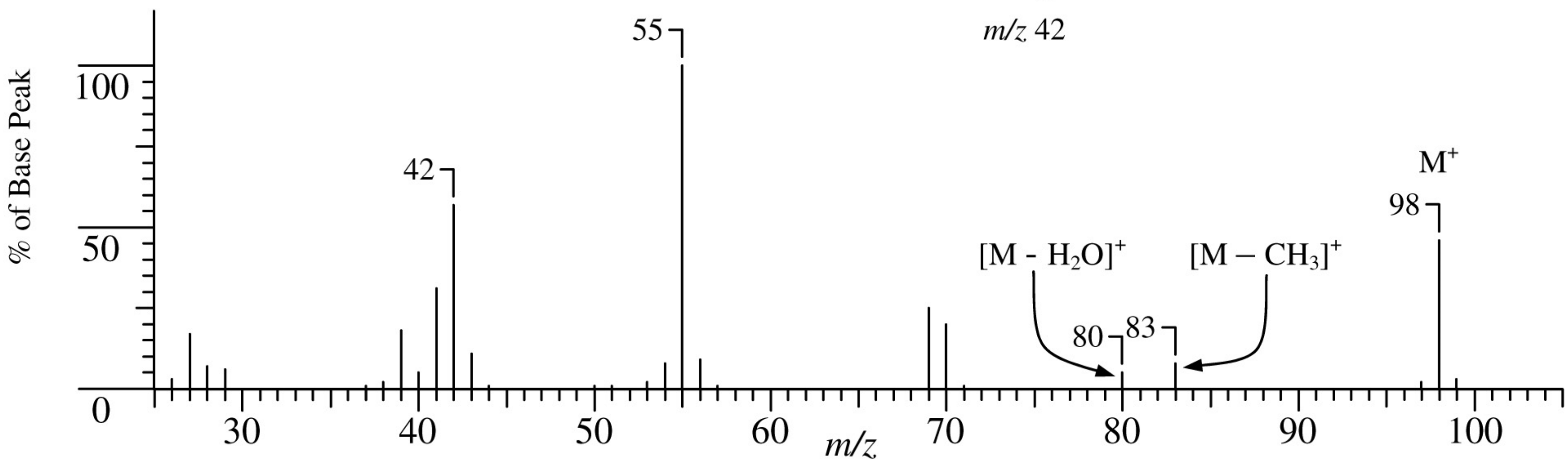


2,4-Dimethoxyacetophenone



Cyclohexanone





High Resolution Mass Spectrometry

Determination of Molecular Formula

CO
N_2
C_2H_4
CH_2N

all show m^+ at 28

exact mass

CO	27.9949
N_2	28.0062
C_2H_4	28.0312
CH_2N	28.0187

TABLE 1.4 Exact Masses of Isotopes.

Element	Atomic Weight	Nuclide	Mass
Hydrogen	1.00794	^{1}H	1.00783
		$D(^{2}H)$	2.01410
Carbon	12.01115	^{12}C	12.00000 (std)
		^{13}C	13.00336
Nitrogen	14.0067	^{14}N	14.0031
		^{15}N	15.0001
Oxygen	15.9994	^{16}O	15.9949
		^{17}O	16.9991
		^{18}O	17.9992
Fluorine	18.9984	^{19}F	18.9984
Silicon	28.0855	^{28}Si	27.9769
		^{29}Si	28.9765
		^{30}Si	29.9738
Phosphorus	30.9738	^{31}P	30.9738
Sulfur	32.0660	^{32}S	31.9721
		^{33}S	32.9715
		^{34}S	33.9679
Chlorine	35.4527	^{35}Cl	34.9689
		^{37}Cl	36.9659
Bromine	79.9094	^{79}Br	78.9183
		^{81}Br	80.9163
Iodine	126.9045	^{127}I	126.9045

Isotope Ratios Can Help to Determine Molecular Formula

		Relative intensities (%)		
MF	MW	M	M+1	M+2
CO	28.0	100	1.12	0.2
N_2	28.0	100	0.76	----
C_2H_4	28.0	100	2.23	0.01

Comparisons of Molecular Weights and Precise Masses

MF	MW	exact mass
C_3H_8O	60.1	60.05754
$C_2H_8N_2$	60.1	60.06884
$C_2H_4O_2$	60.1	60.02112
CH_4N_2O	60.1	60.03242

TABLE 1.3 Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				

Determine the Formula

fragment finder

	Molecular mass	m+1	m+2
	110	111	112
rel. intensity (%)	100	6.96	0.60

exact mass = 110.0376

Determine the Formula

	Molecular mass	m+1	m+2
	118	119	120
rel. intensity (%)	100	7.45	4.55

TABLE 1.3 Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				

Subtract Sulfur's contribution

fragment finder

	Molecular mass	m+1	m+2
	118	119	120
rel. intensity (%)	100	7.45	4.55
subtract sulfur (32)	86	87	88
	100	**6.67**	**0.15**

Determine the Molecular Formula

	Molecular mass	m+1	m+2
	154	155	156
rel. intensity (%)	100	15.41	3.77

Compound gives four signals in the C-13 NMR spectrum

	Molecular mass	m+1	m+2	m+4
	190	191	192	194
rel. intensity (%)	100	6.48	130.77	31.81