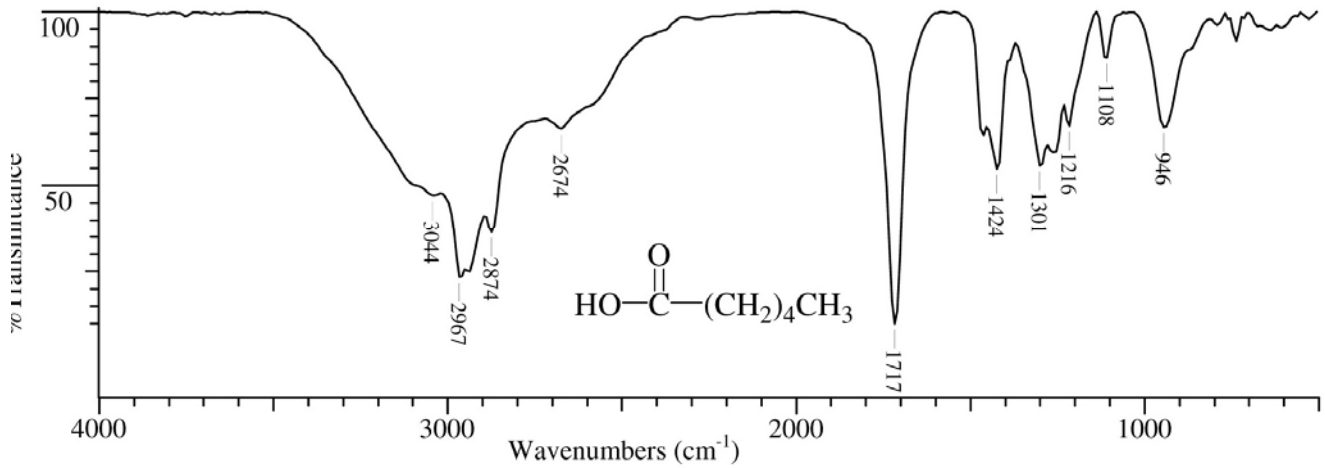
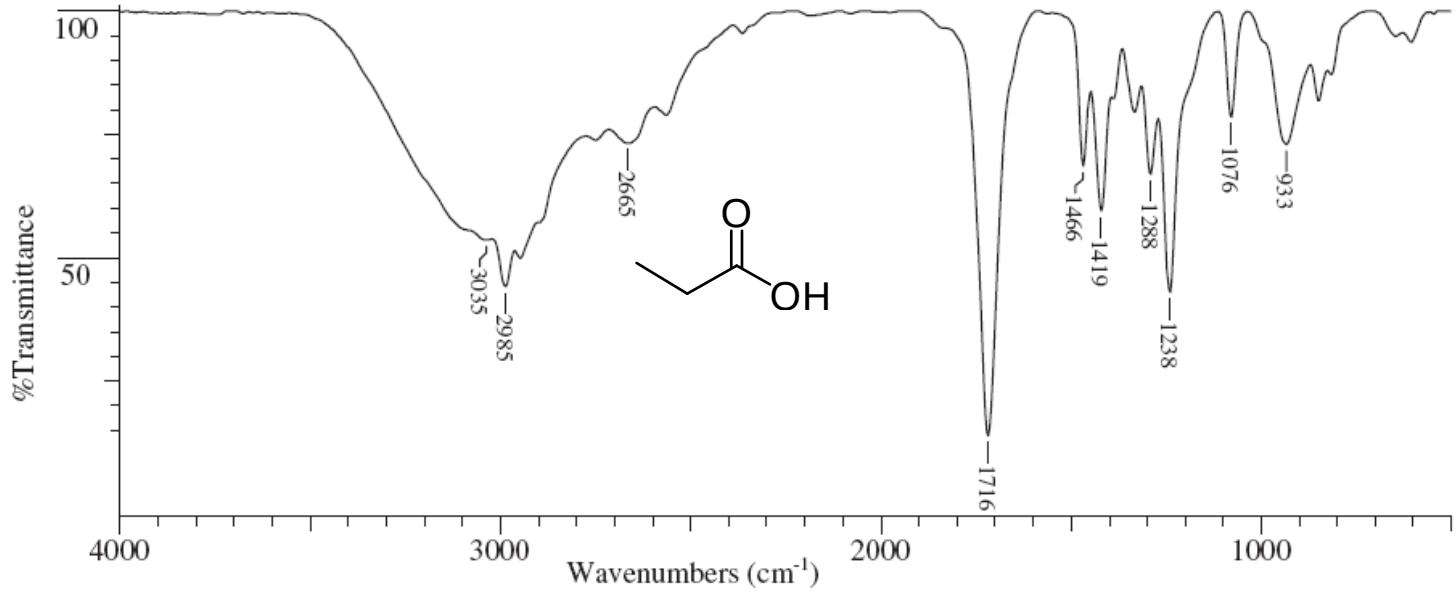
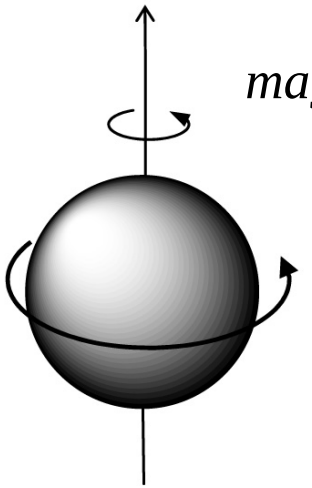
第9章 核磁共振(Nuclear Magnetic Resonance: ^{1}H NMR and ^{13}C NMR）

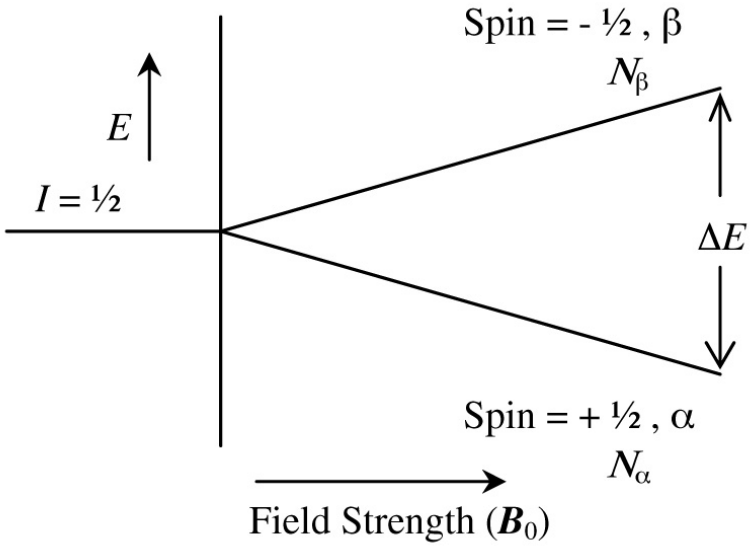




1）核磁共振的原理

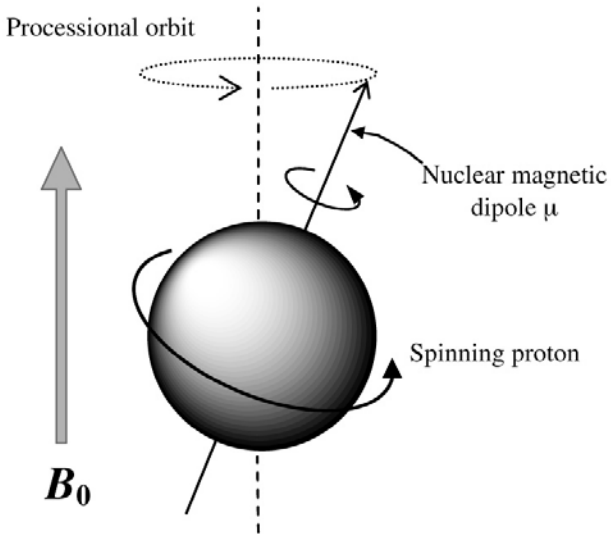


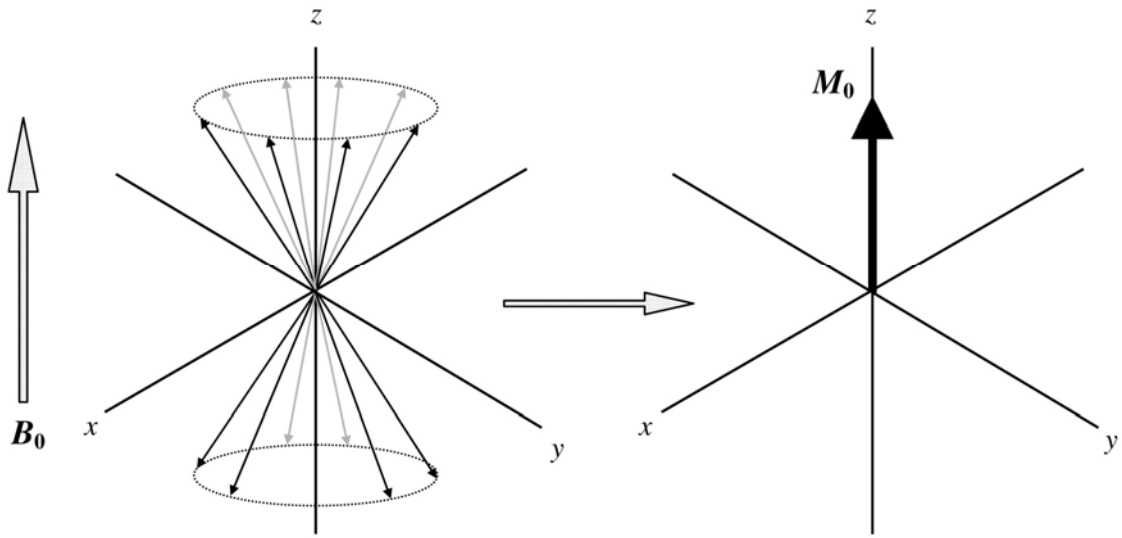
Atomic mass is odd，atomic number is odd or even, $^{1}H_{1}$, $^{13}C_{6}$, $^{15}N_{7}$, $^{19}F_{9}$, $^{31}P_{15}$: I = 1/2.



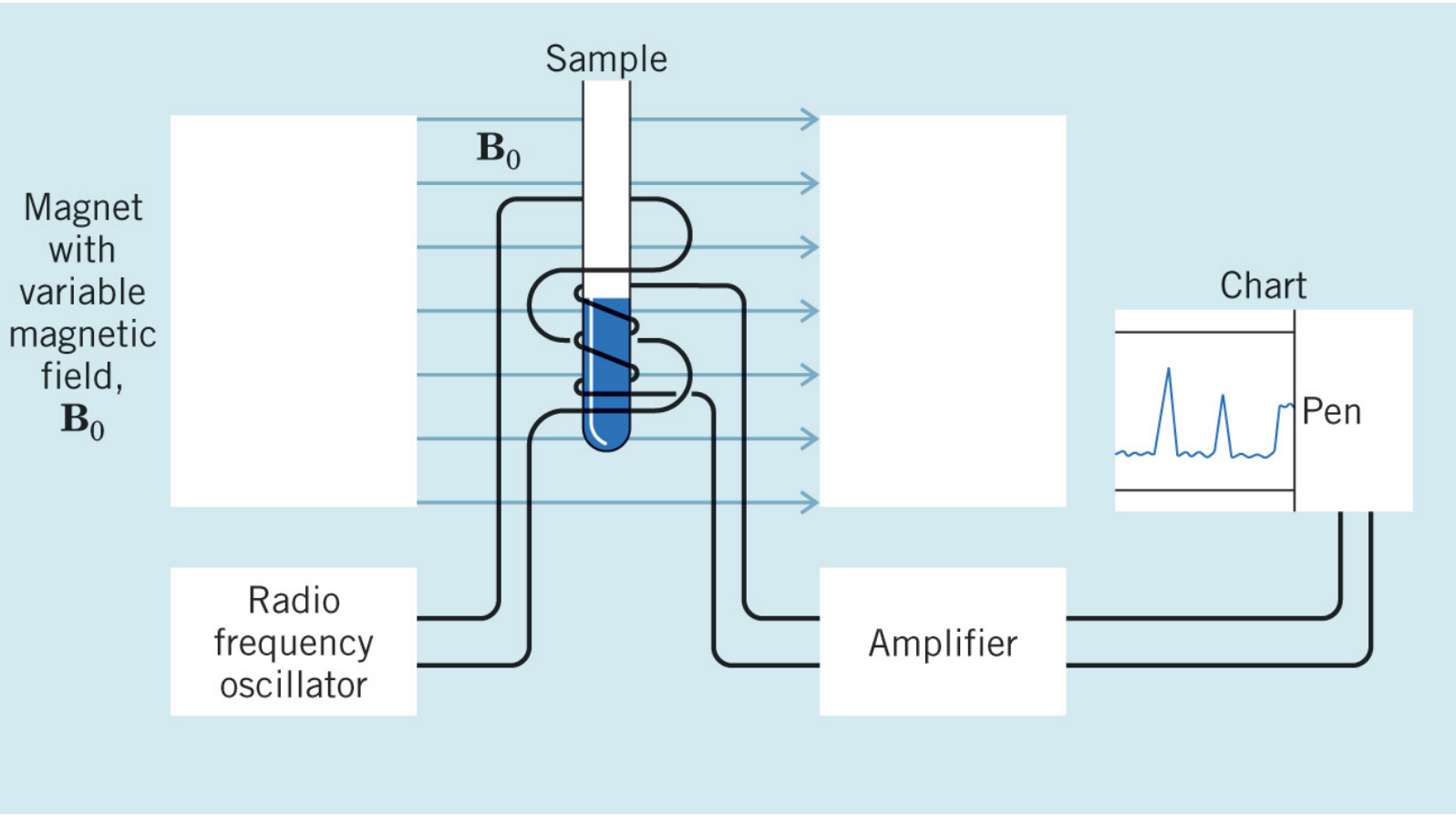
當在一個特定的外磁場中(B0)，磁性核的自旋取向為量子化的(2I + 1)

$$\nu = \frac{\gamma B_0}{2\pi}$$

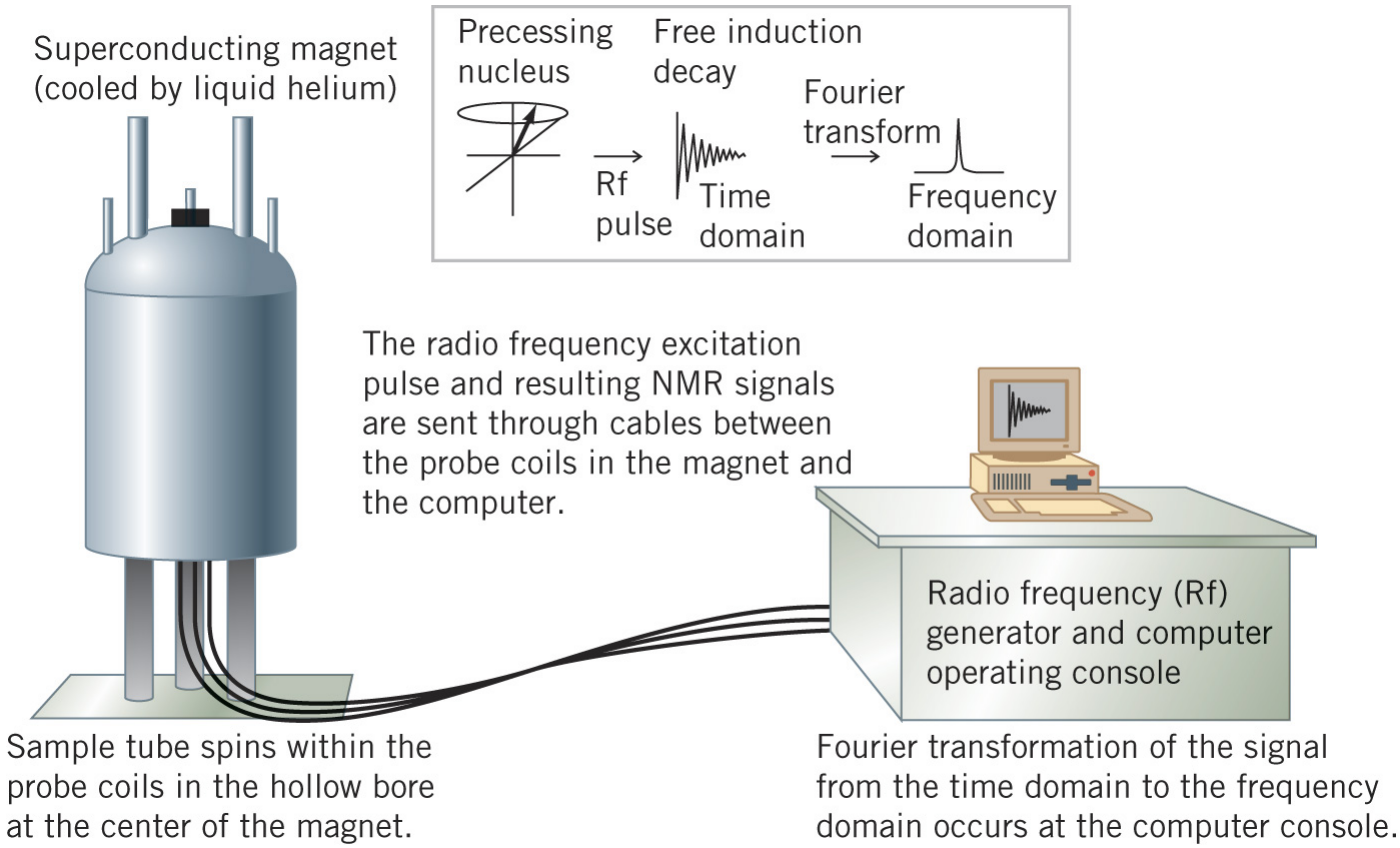




2）核磁共振的儀器



Continuous-wave

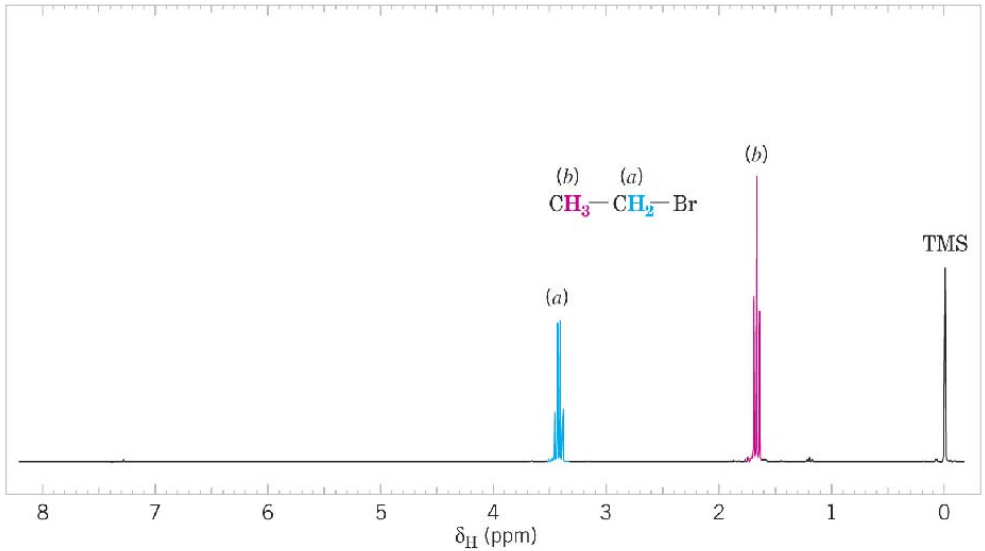


Fourier Transform

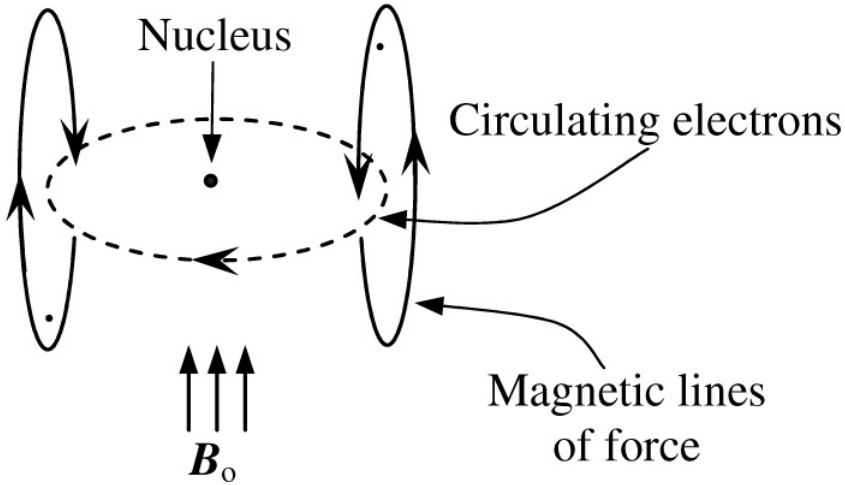
3）^{1}H NMR所能提供的訊息

A）化學位移（chemical shift）

高頻，少屏蔽（less shielding）

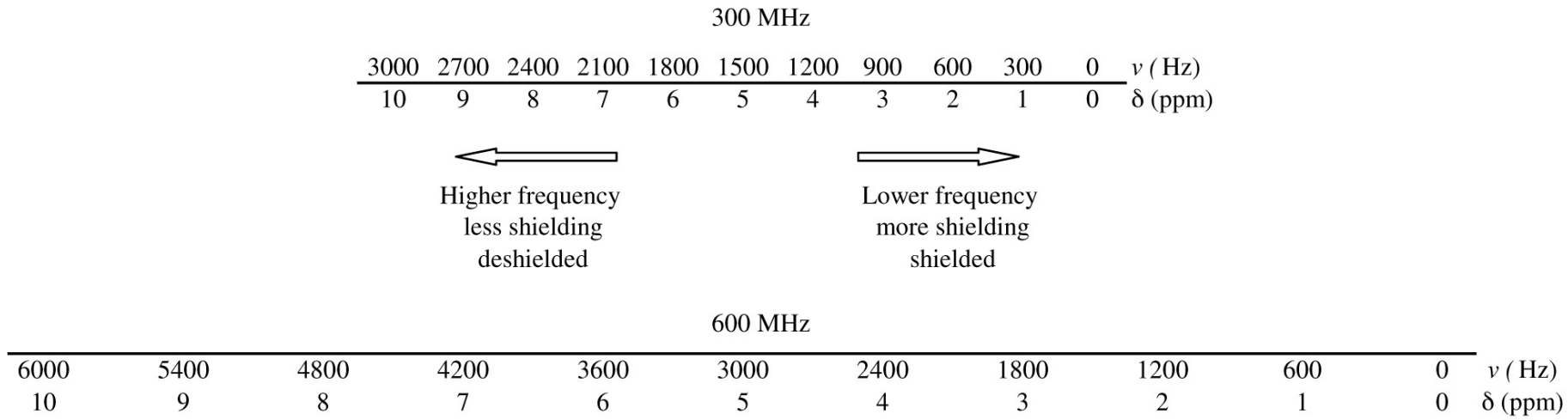


低頻，多屏蔽（more shielding）



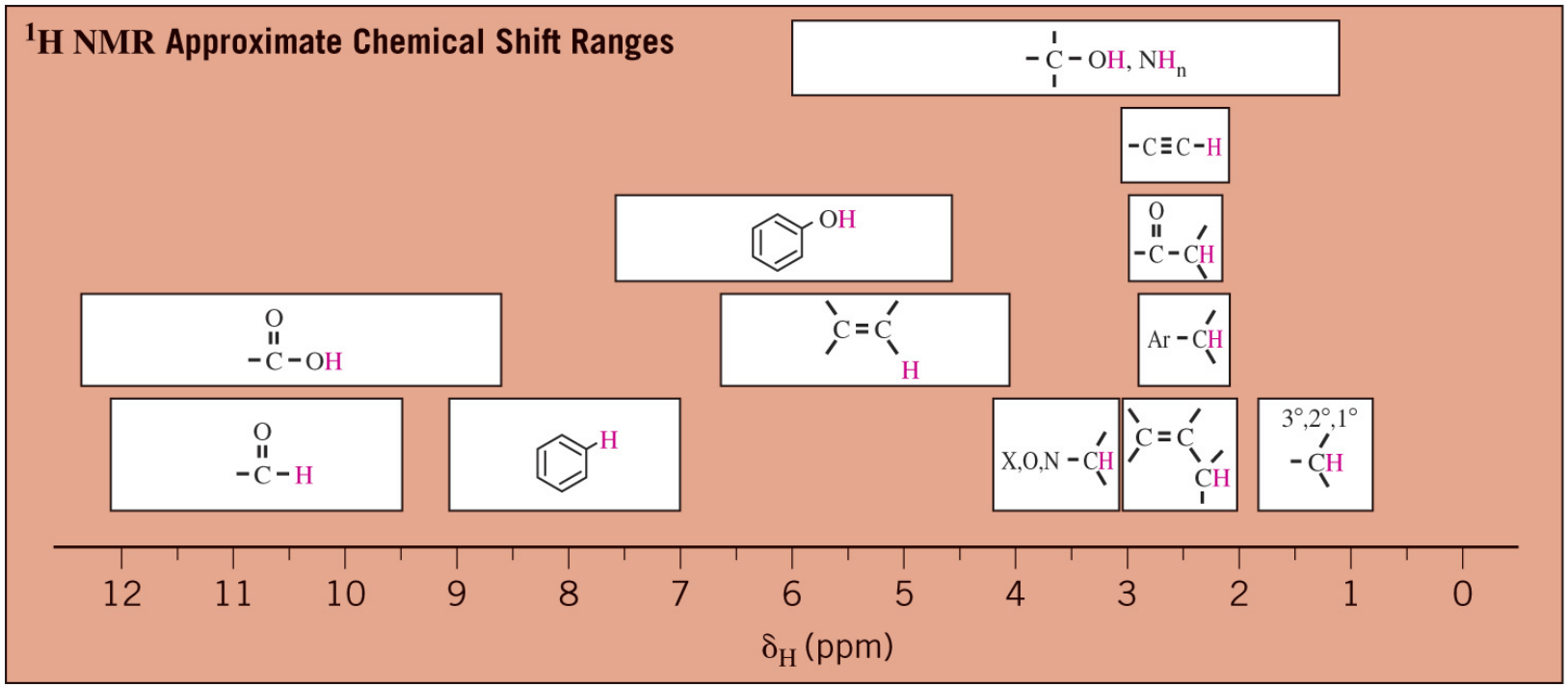
$$\nu_{effect} = \frac{\gamma}{2\pi} B_0(1 - \sigma)$$

化學位移：以TMS為標準(δ = 0 ppm）質子在光譜中的相對位置。



$$\frac{300\ \text{Hz}}{300 \times 10^6\ \text{Hz}} \times 10^6 = 1\ \text{ppm}$$

$$\frac{600\ \text{Hz}}{600 \times 10^6\ \text{Hz}} \times 10^6 = 1\ \text{ppm}$$

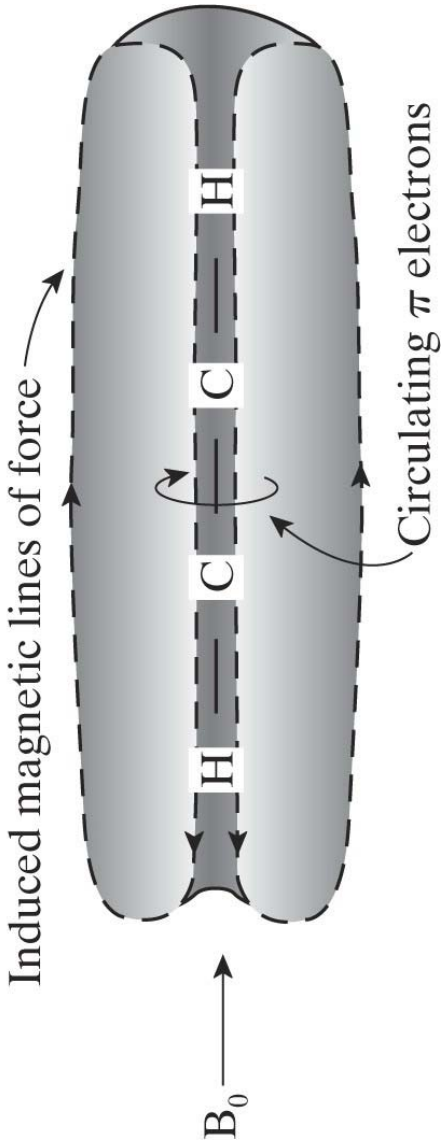


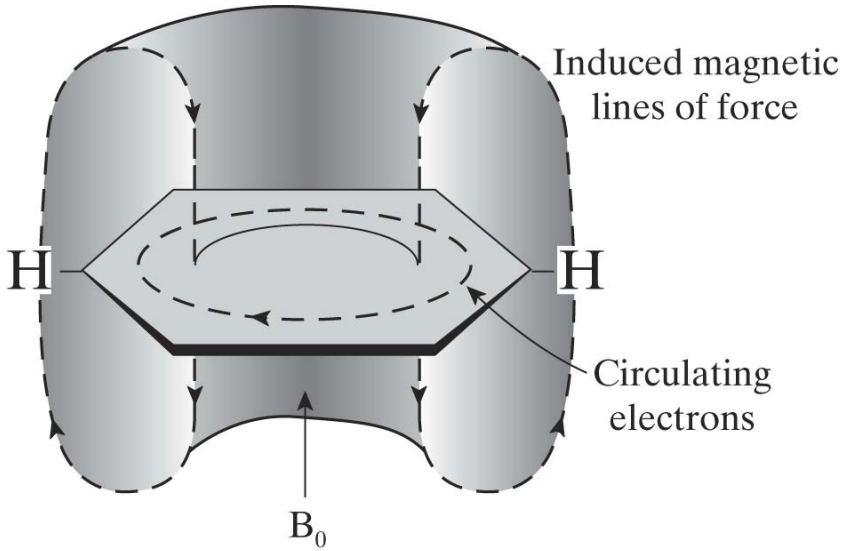
影響化學位移的因素：

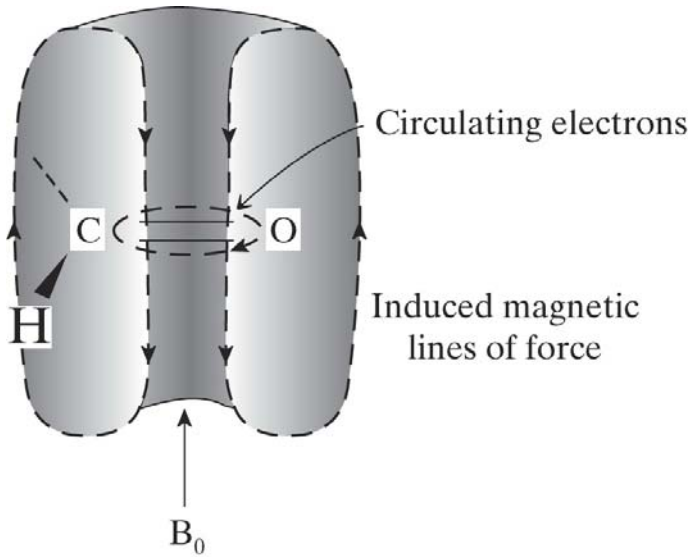
a) inductive effect (誘導效應):

	CH3F	CH3OH	CH3Cl	CH3Br	CH3I	CH3H	TMS
(ppm)	4.06	3.40	3.05	2.68	2.16	0.23	0
X	4.0	3.5	3.0	2.8	2.5	2.1	1.8

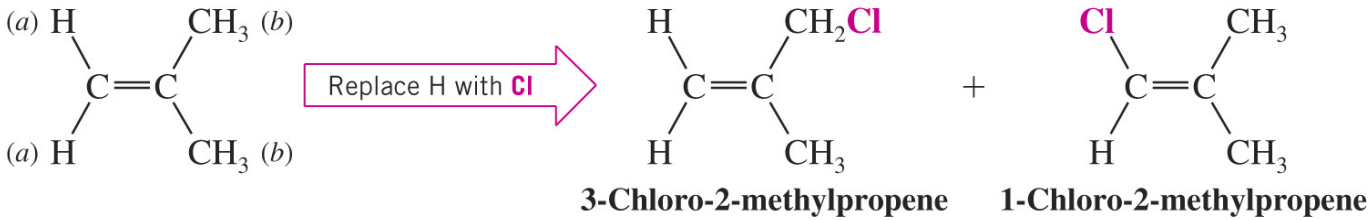
b）分子在外加磁場中的取向： 化學位移：Ar-H＞R_2C=CR-H＞RC≡C-H＞R_3CH





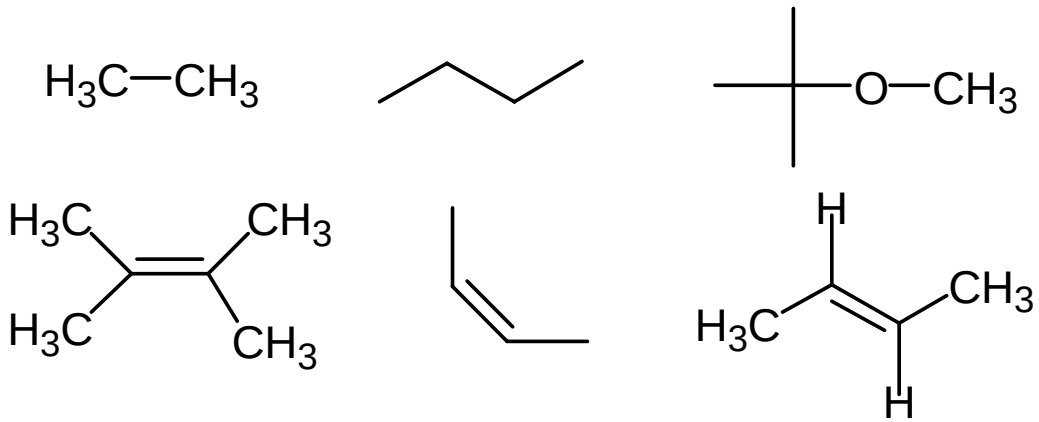


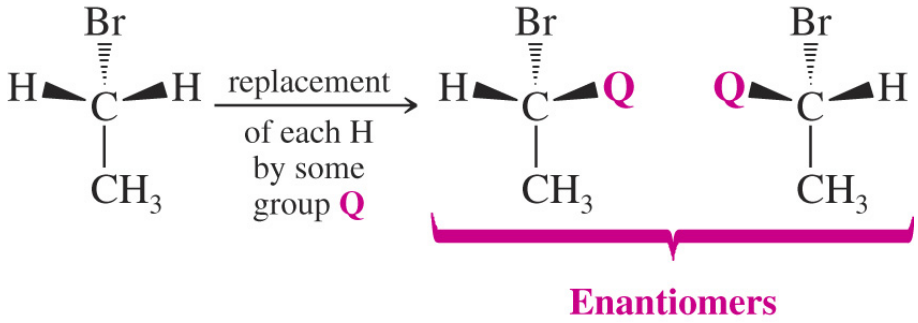
b)等價氫原子(homolytic hydrogen atoms)有相同的化學位移 （chemical shift equivalent）。



Chemically equivalent protons are in the same environment and will produce only one signal

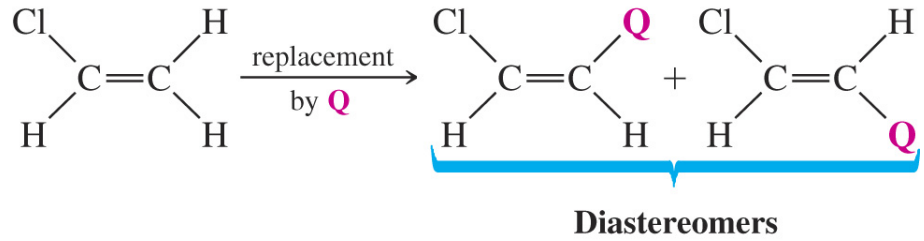
Hydrogens are chemically equivalent or homotopic if replacing each one in turn by the same group would lead to an identical compound





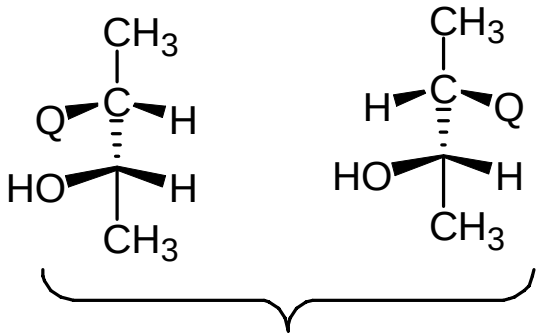
If replacement of each of two hydrogens by some group leads to enantiomers, those hydrogens are enantiotopic

In the absence of a chiral influence, enantiotopic hydrogens have the same chemical shift and appear in the same signal

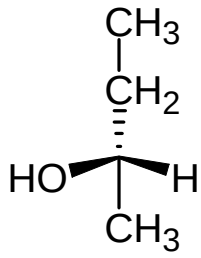


If replacement of each of two hydrogens by some group leads to diastereomers, the hydrogens are diastereotopic

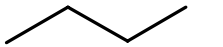
Diastereotopic hydrogens have different chemical shifts and will give different signals

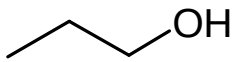


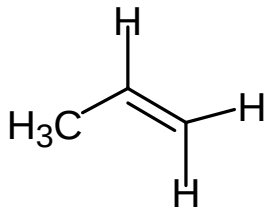
diastereomer

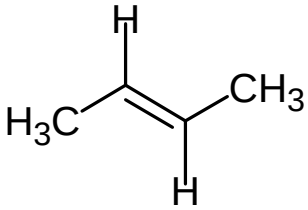


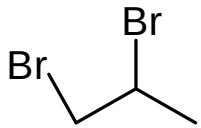
6 signals



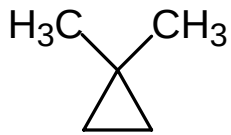




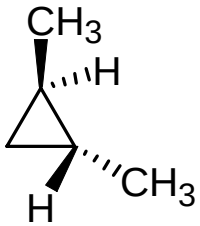




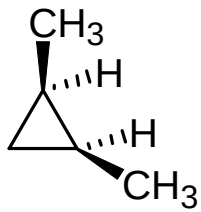
4 signals



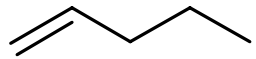
2 signals

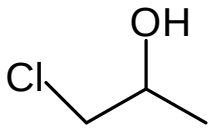


3 signals



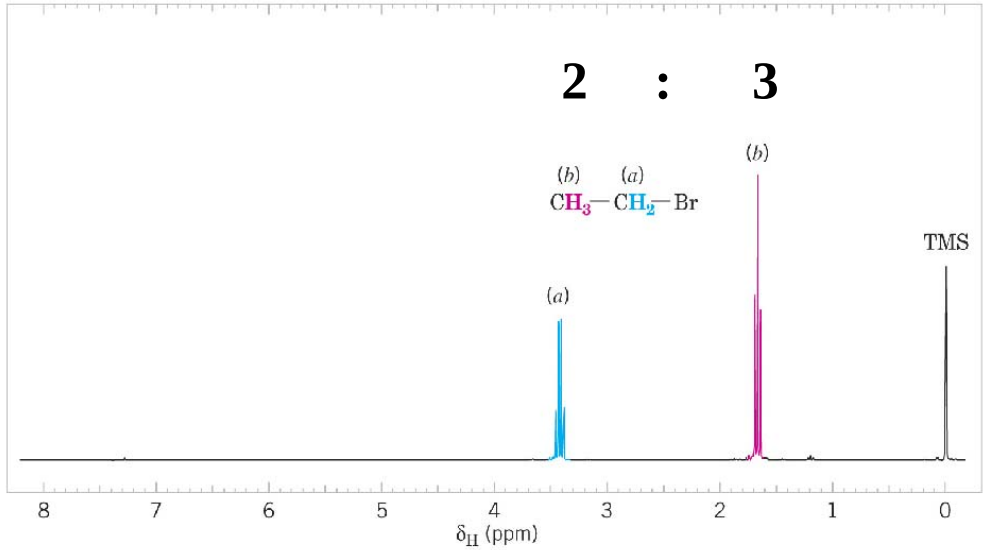
3 signals

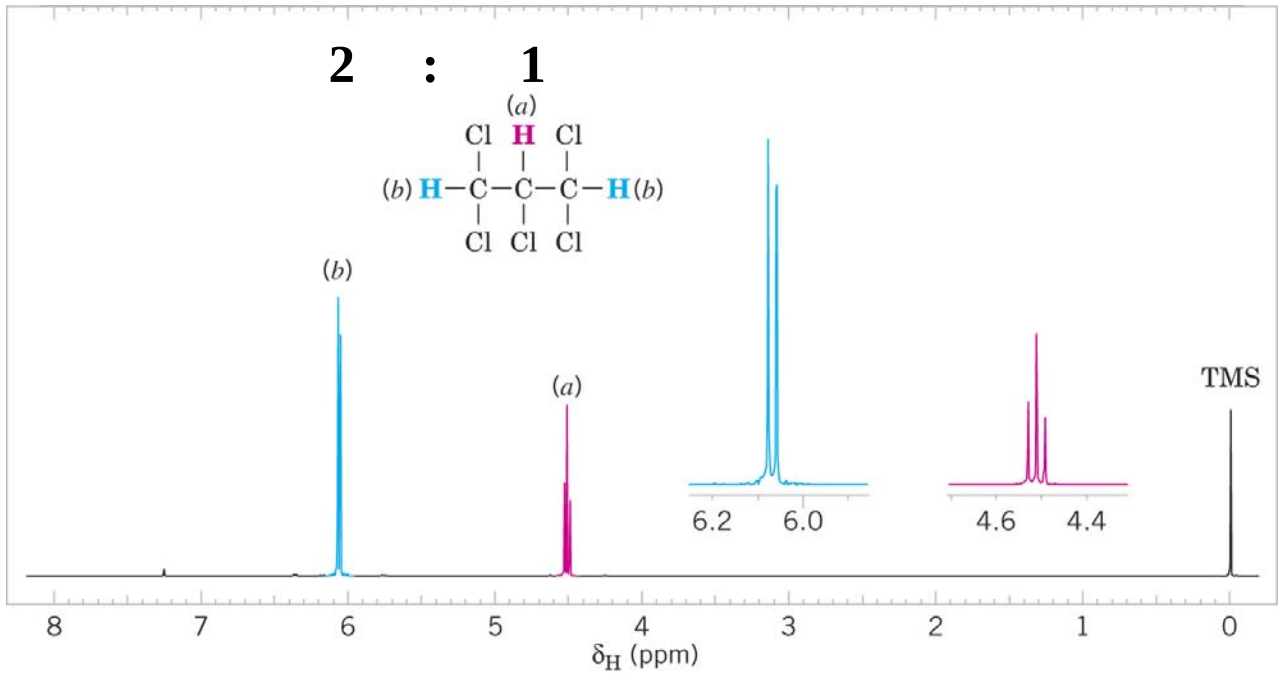




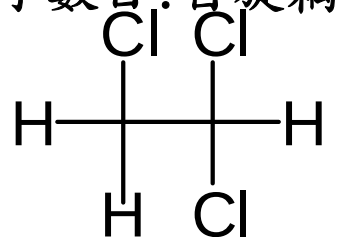
5 signals

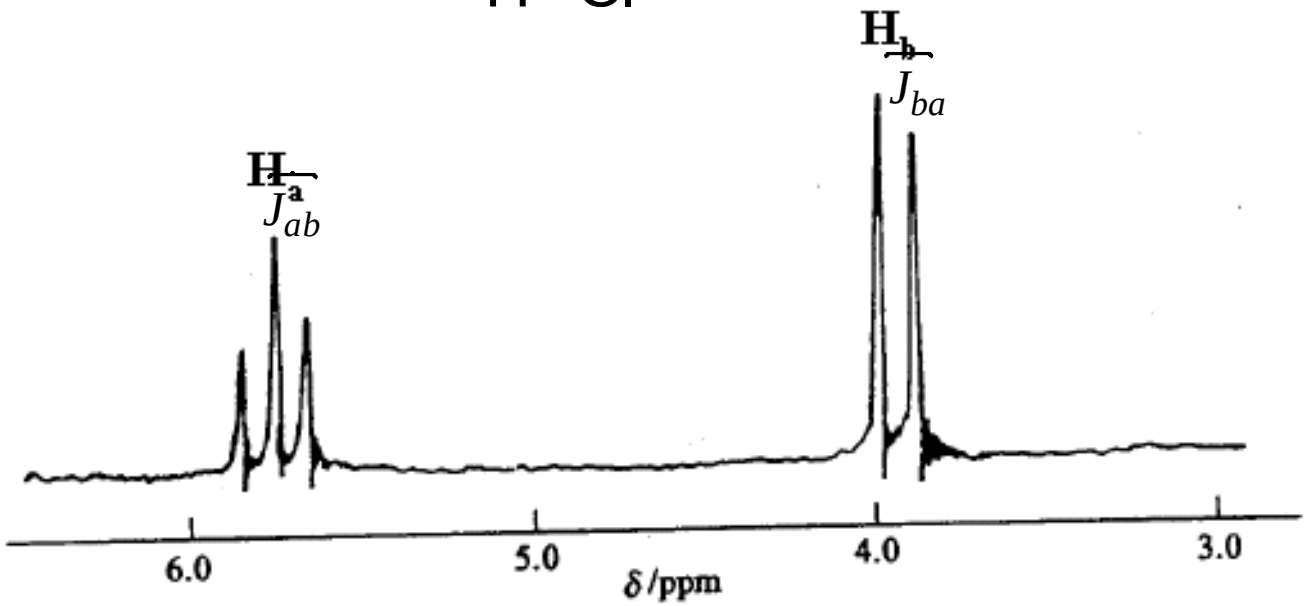
A）氫原子的相對數目


2 : 3
(b) (a)
CH3—CH2—Br
(b)
TMS
(a)
8 7 6 5 4 3 2 1 0
δH (ppm)


2 : 1
(a)
Cl H Cl
(b) H—C—C—C—H (b)
Cl Cl Cl
(b)
(a)
TMS
6.2 6.0
4.6 4.4
8 7 6 5 4 3 2 1 0
δH (ppm)

B）相鄰碳原子上的氫原子數目:自旋耦合 （ **spin-spin coupling** ）





n Multiplicity	Relative Intensity	Spins	Coupling Pattern

0 *Singlet* (s)

1 *Doublet* (d)

2 *Triplet* (t)

3 *Quartet* (q)

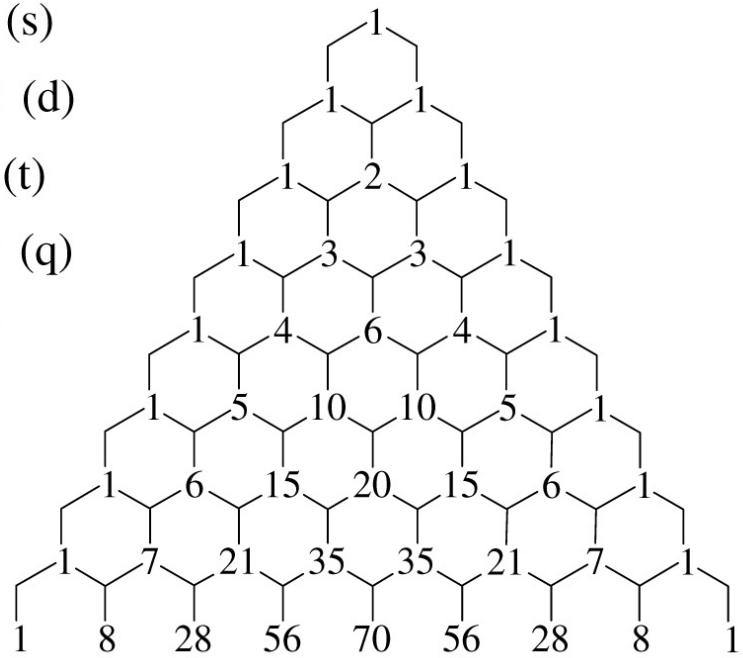
4 *Quintet*

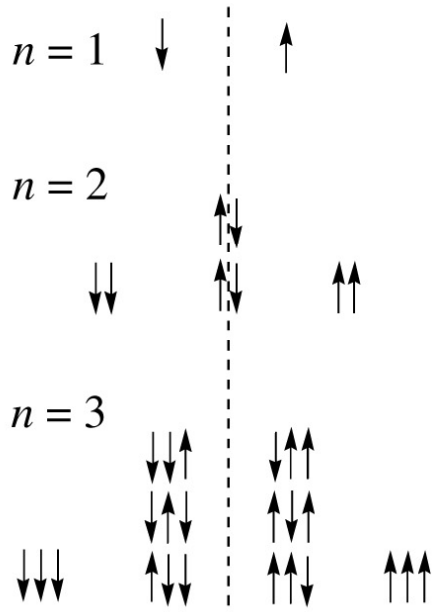
5 *Sextet*

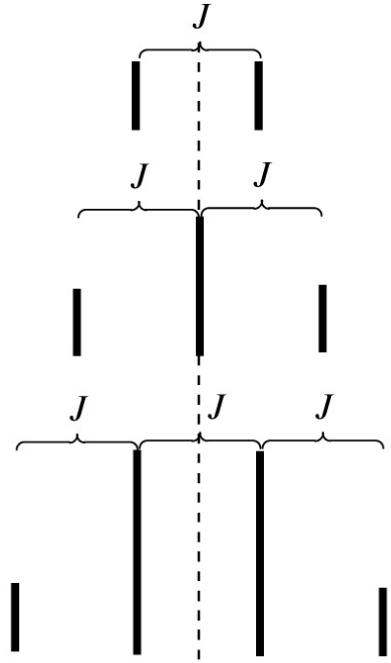
6 *Septet*

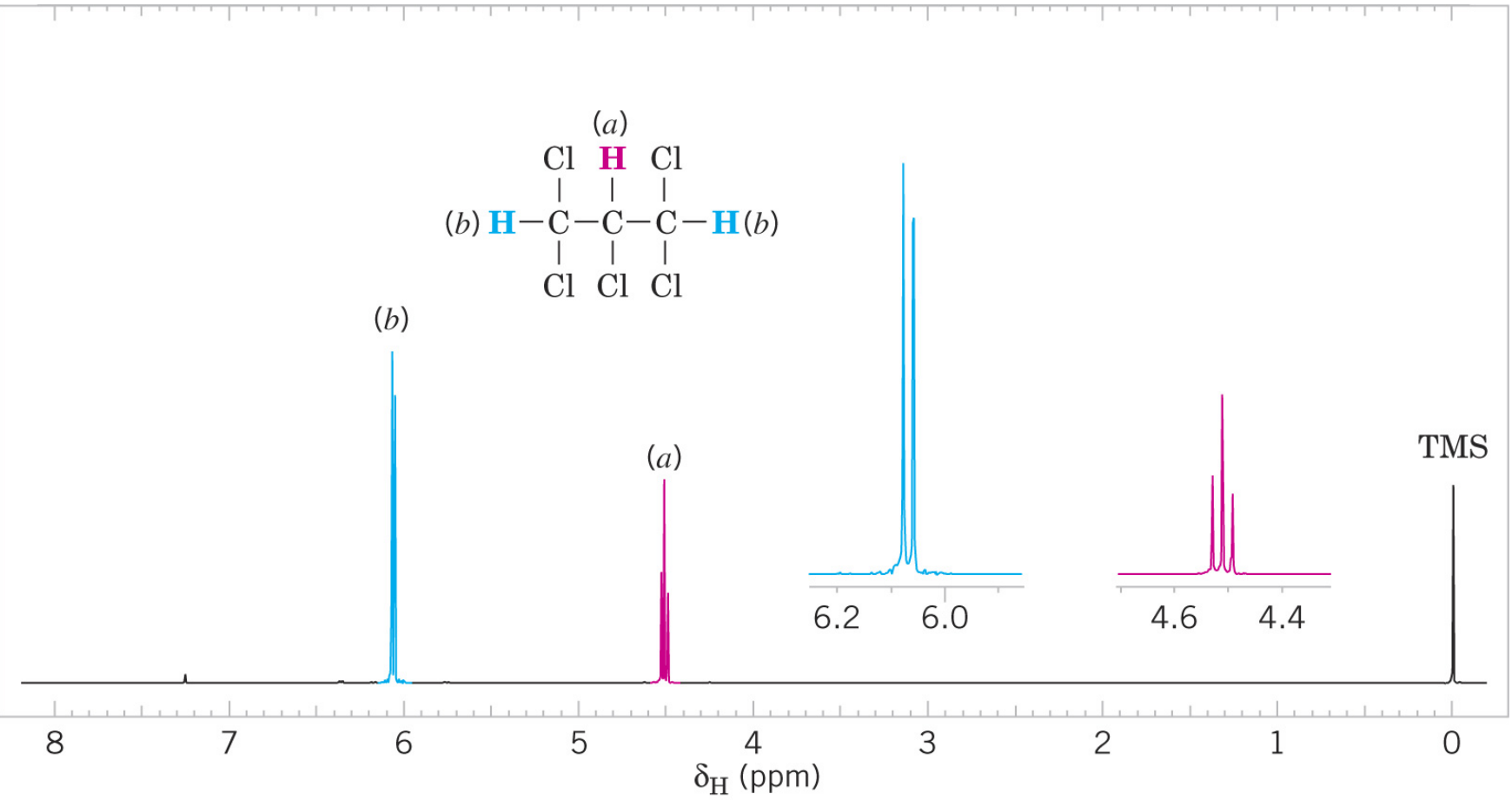
7 Octet

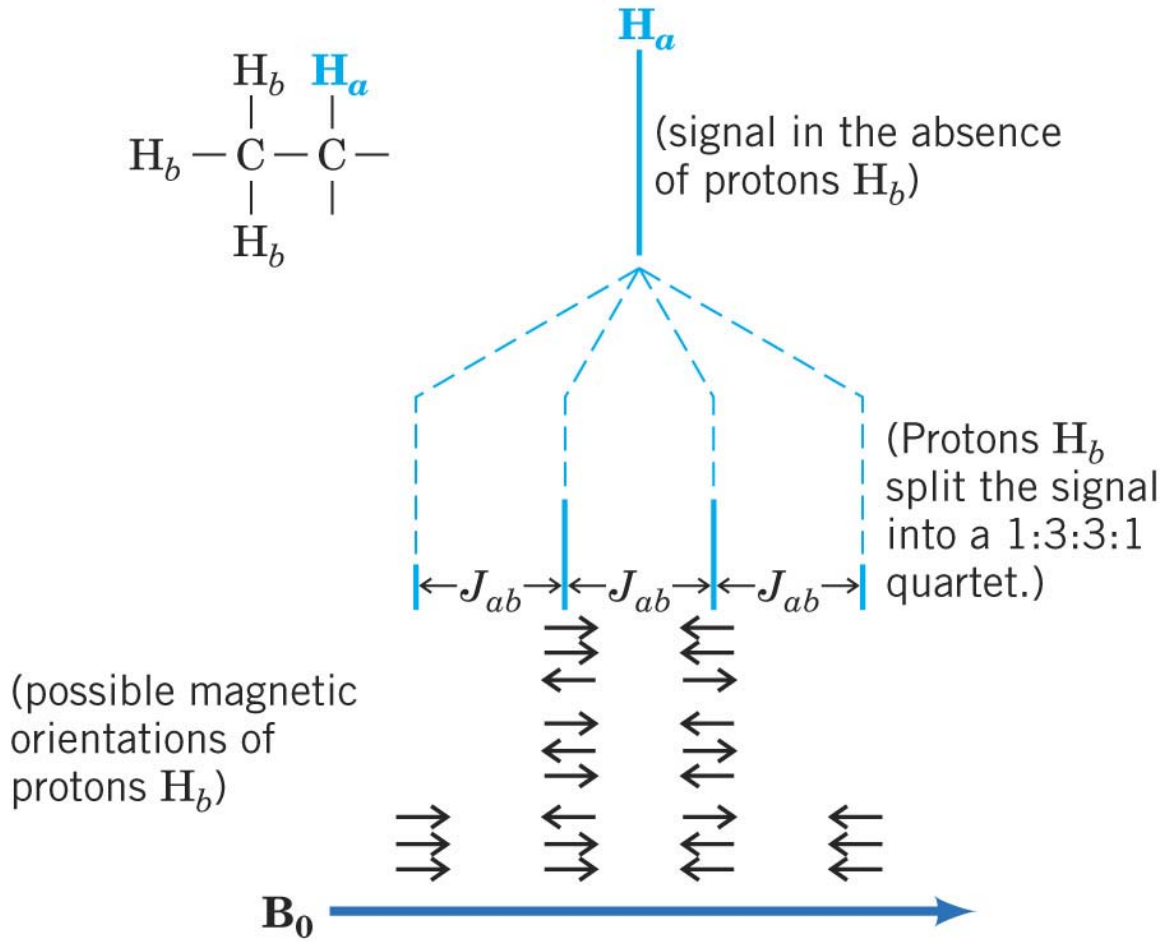
8 *Nonet*

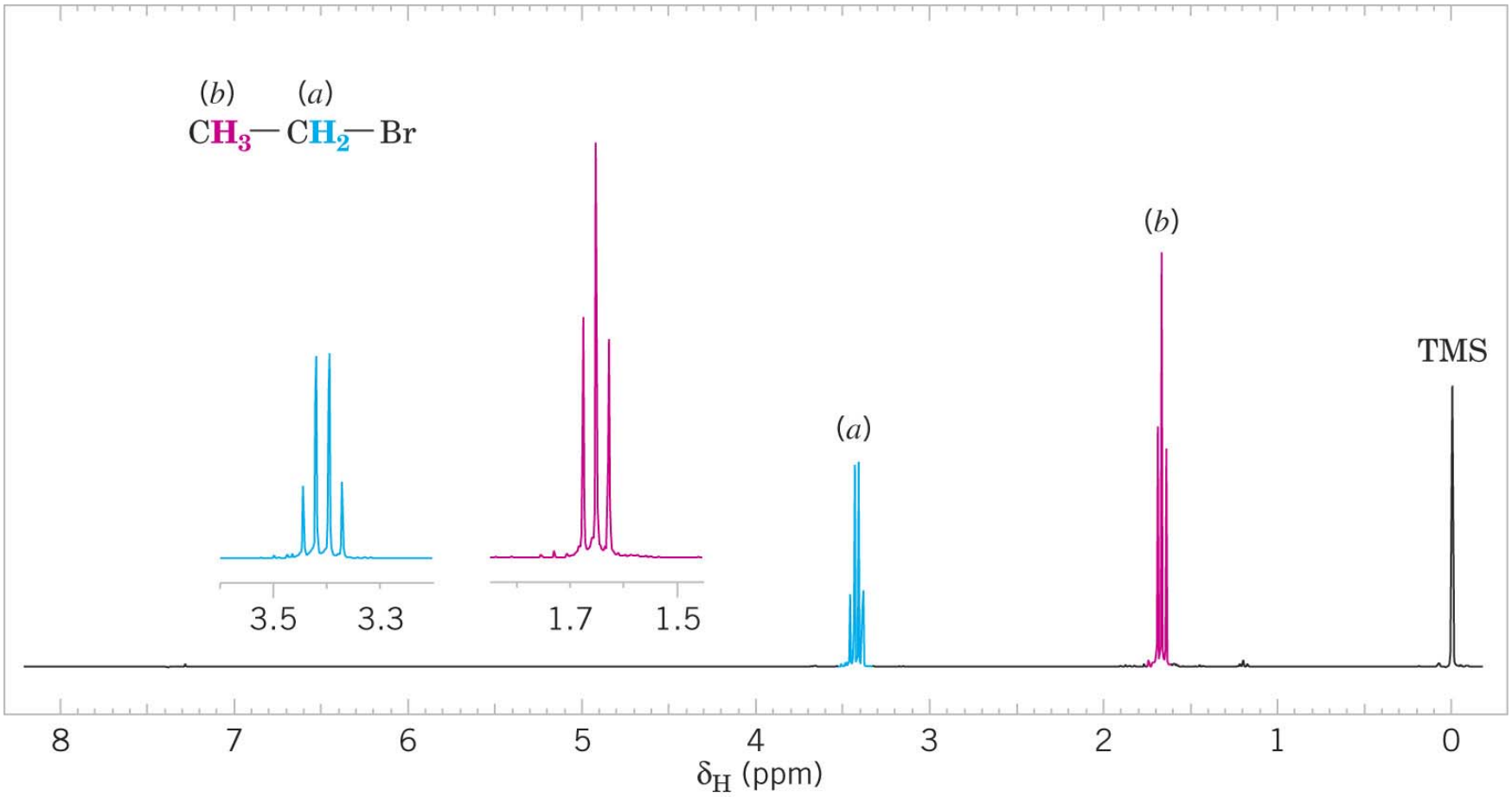


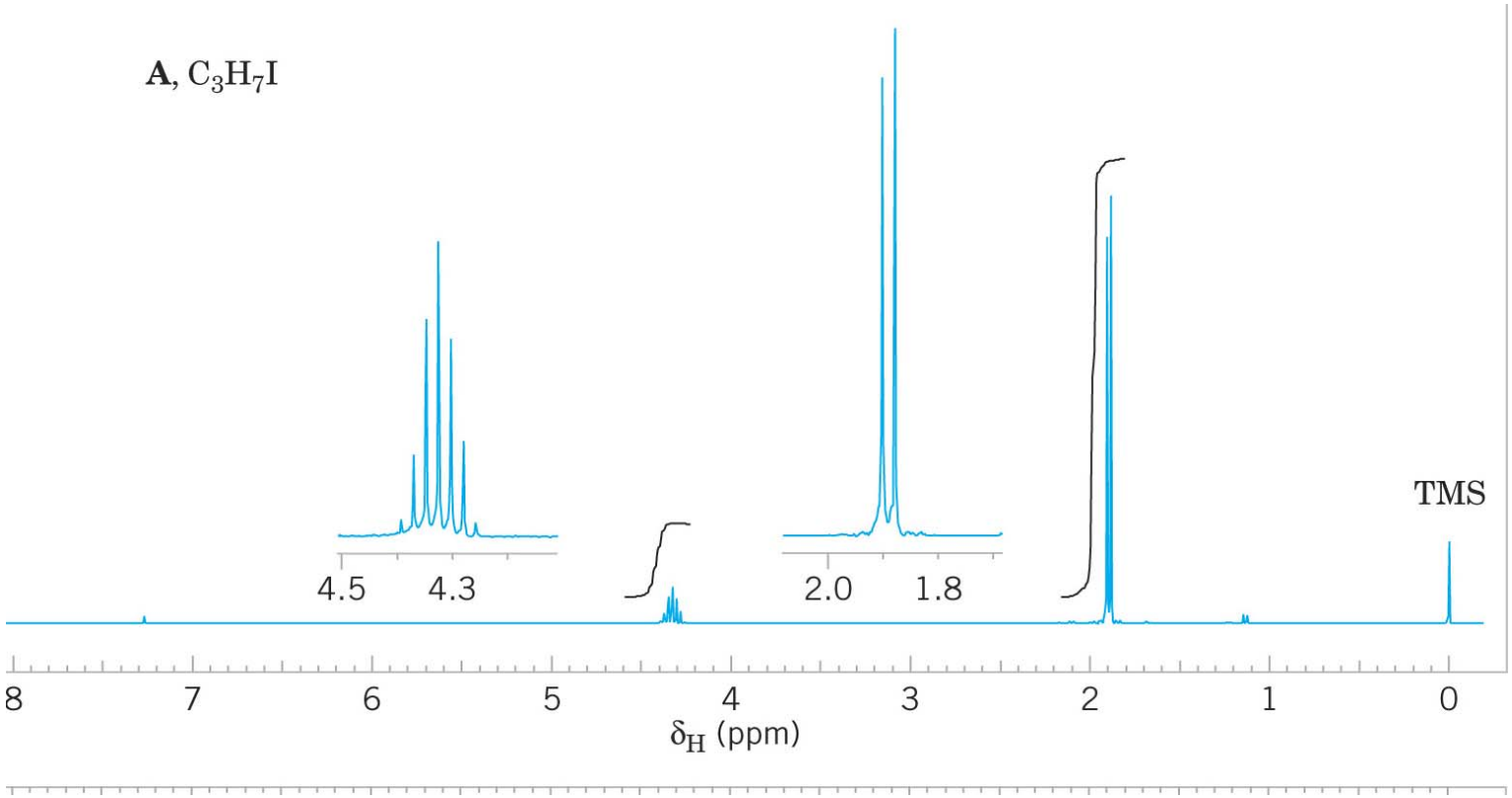




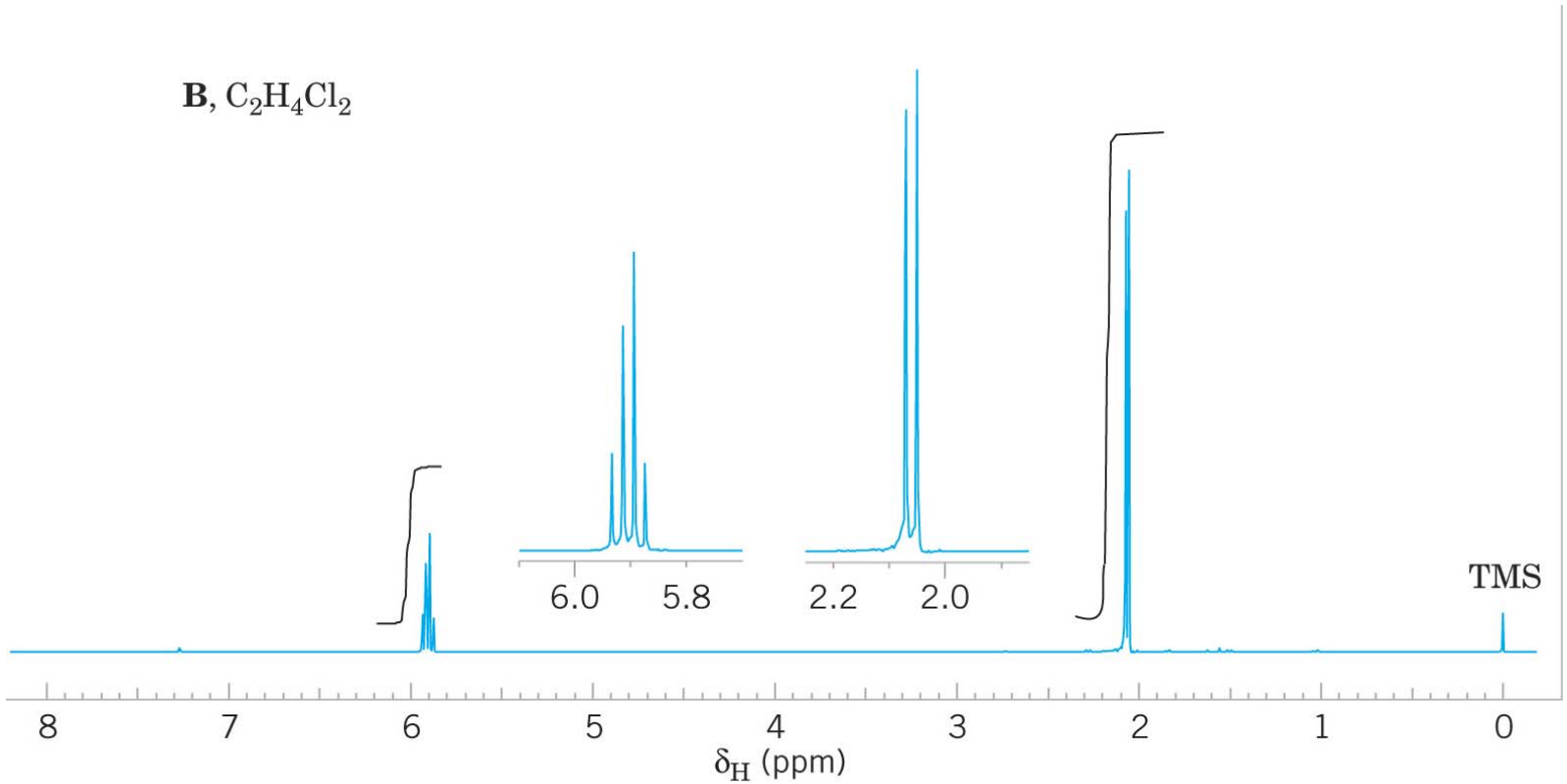

(a)
Cl H Cl
(b) H—C—C—C—H (b)
Cl Cl Cl
(b)
(a)
TMS
6.2
6.0
4.6
4.4
8
7
6
5
4
3
2
1
0
δH (ppm)

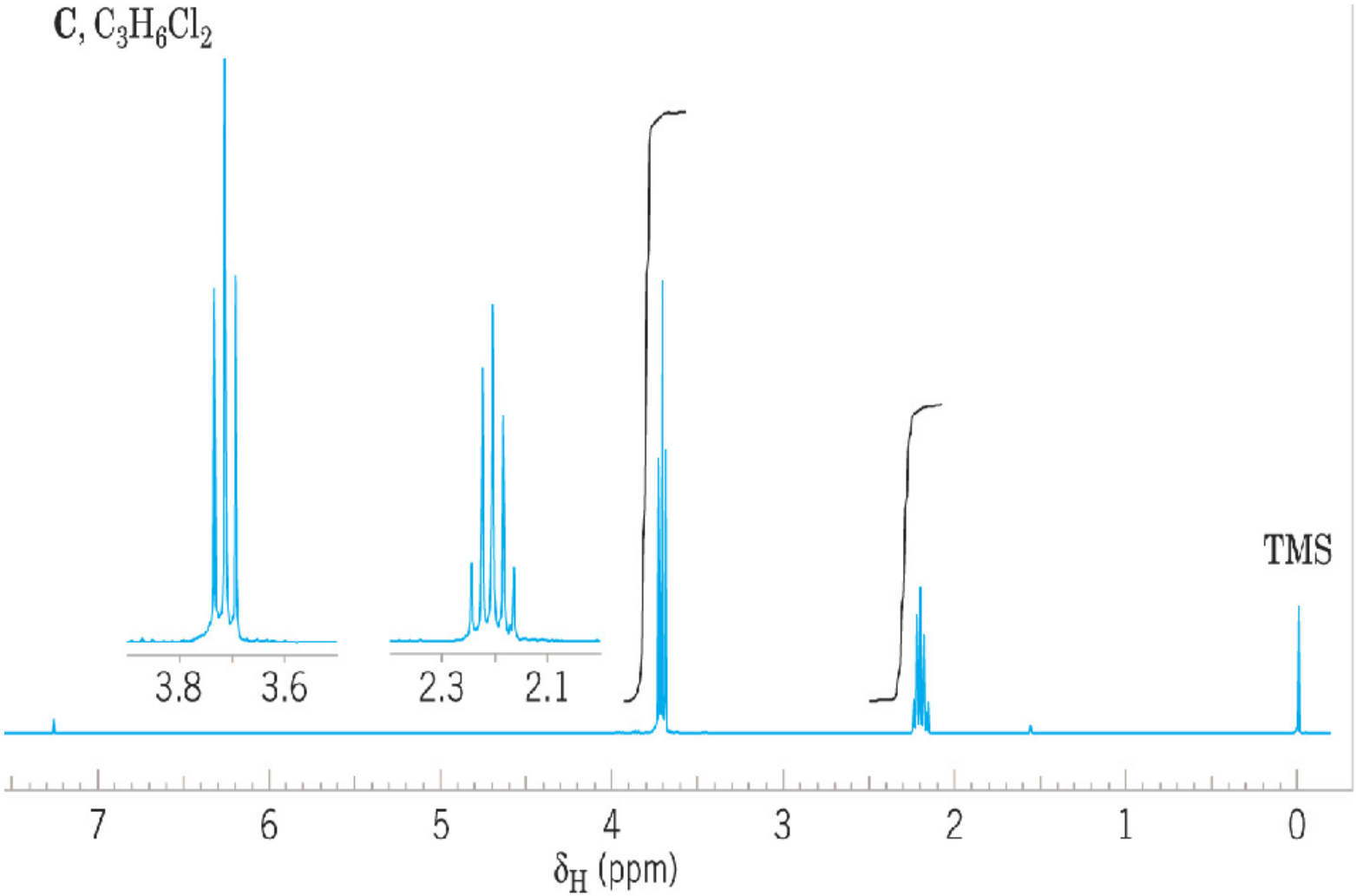

H_b H_a
$H_b - C - C -$
H_b
H_a
(signal in the absence of protons H_b)
(Protons H_b split the signal into a 1:3:3:1 quartet.)
J_{ab}
J_{ab}
J_{ab}
(possible magnetic orientations of protons H_b)
B_0

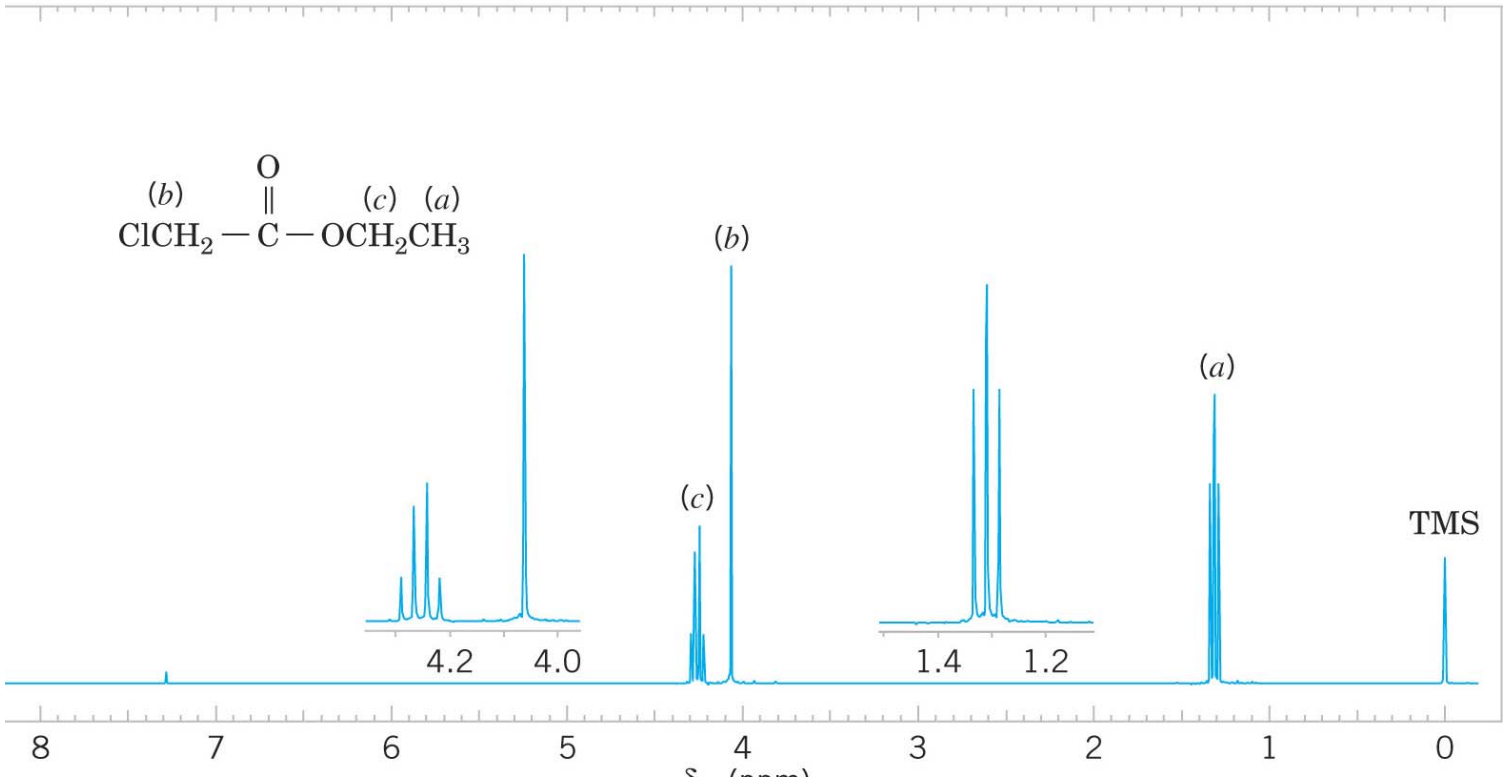

(b) (a)
CH3—CH2—Br
(b)
TMS
(a)
3.5
3.3
1.7
1.5
8
7
6
5
4
3
2
1
0
δH (ppm)

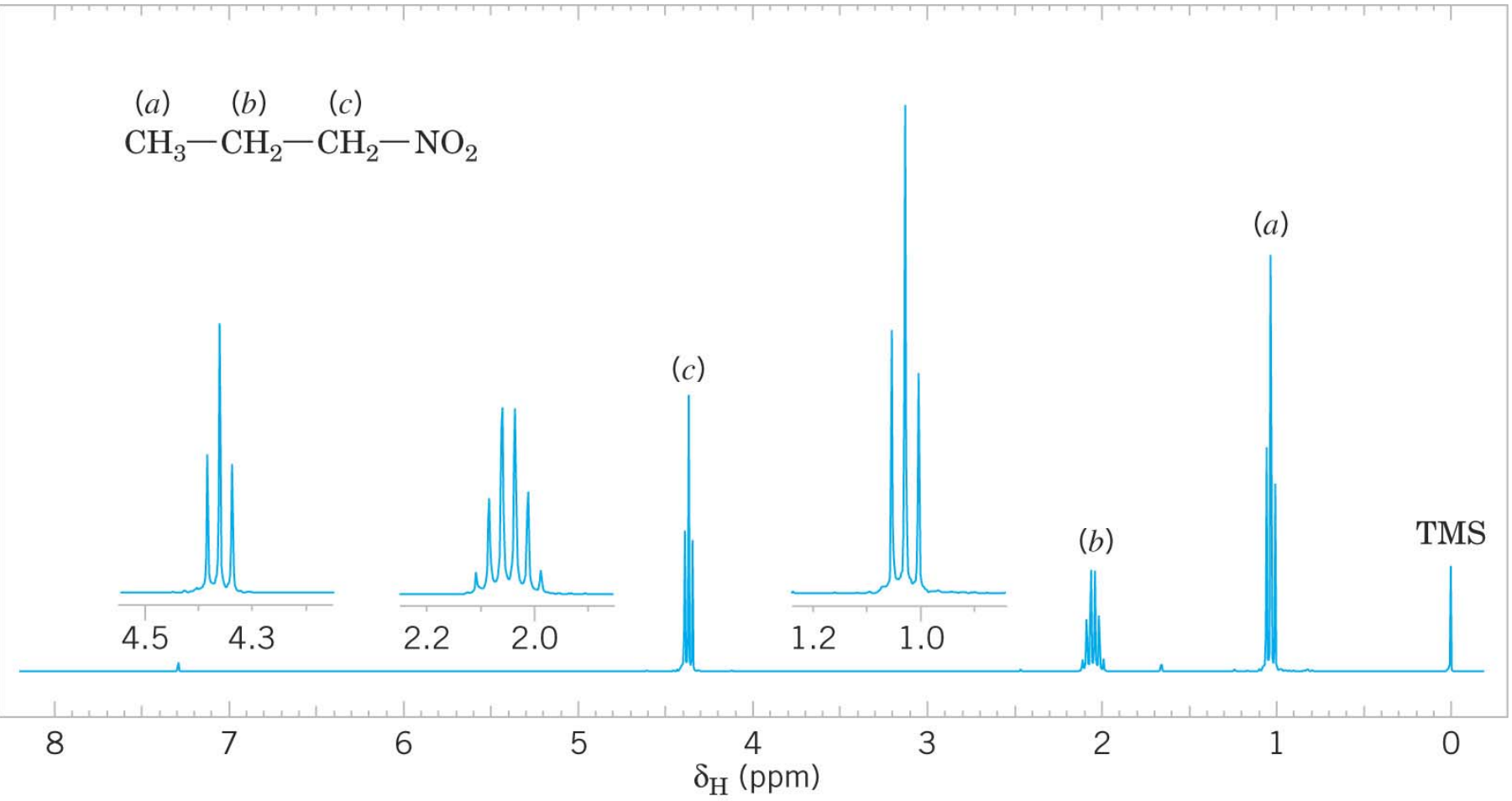


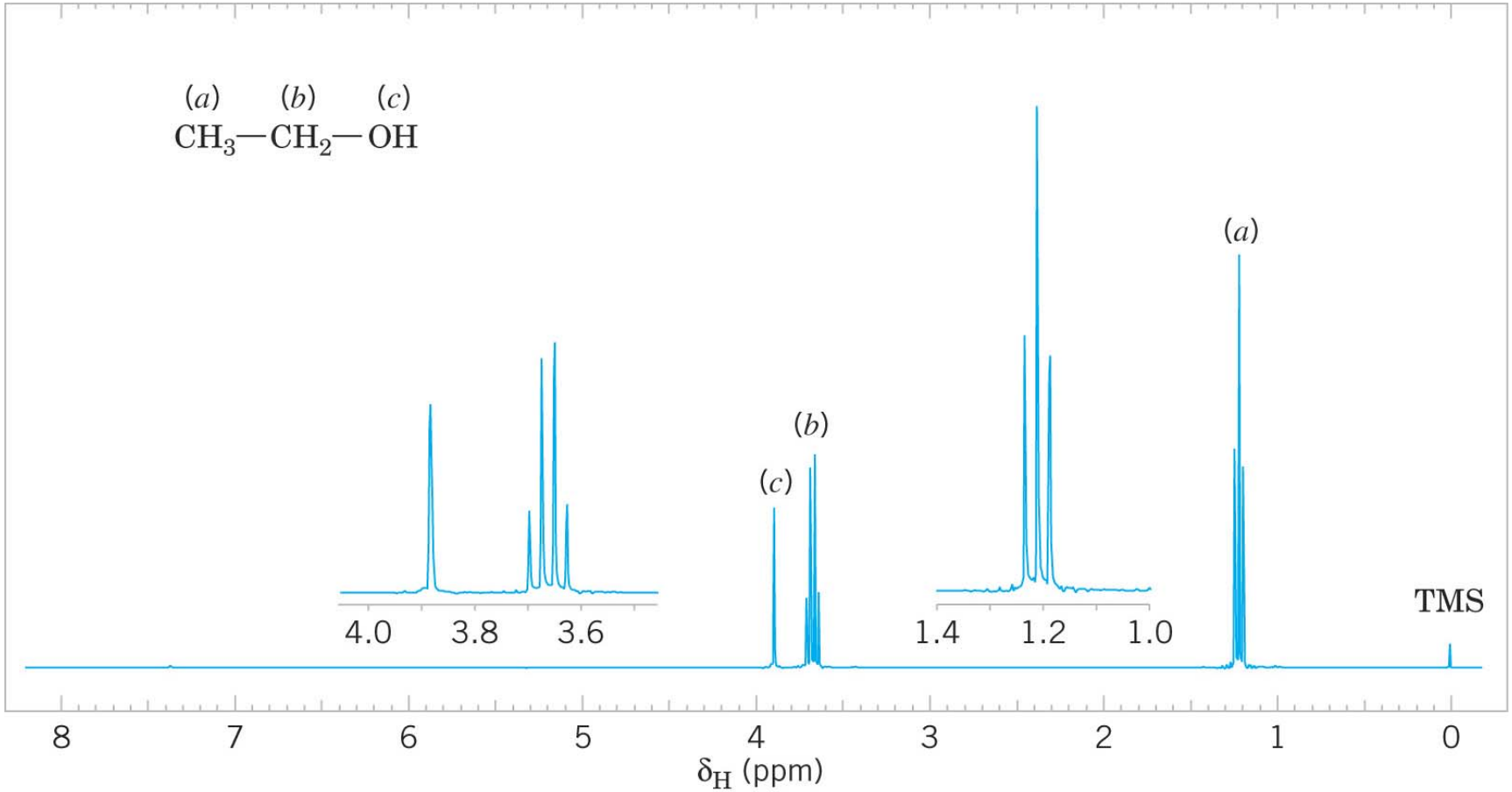
Unsaturated Index = carbons - 〔 (hydrogens) / 2 〕 - 〔(halogens) / 2 〕 + 〔 (nitrogens) / 2 〕 + 1


B, $C_2H_4Cl_2$
6.0
5.8
2.2
2.0
TMS
8
7
6
5
4
3
2
1
0
δ_H (ppm)

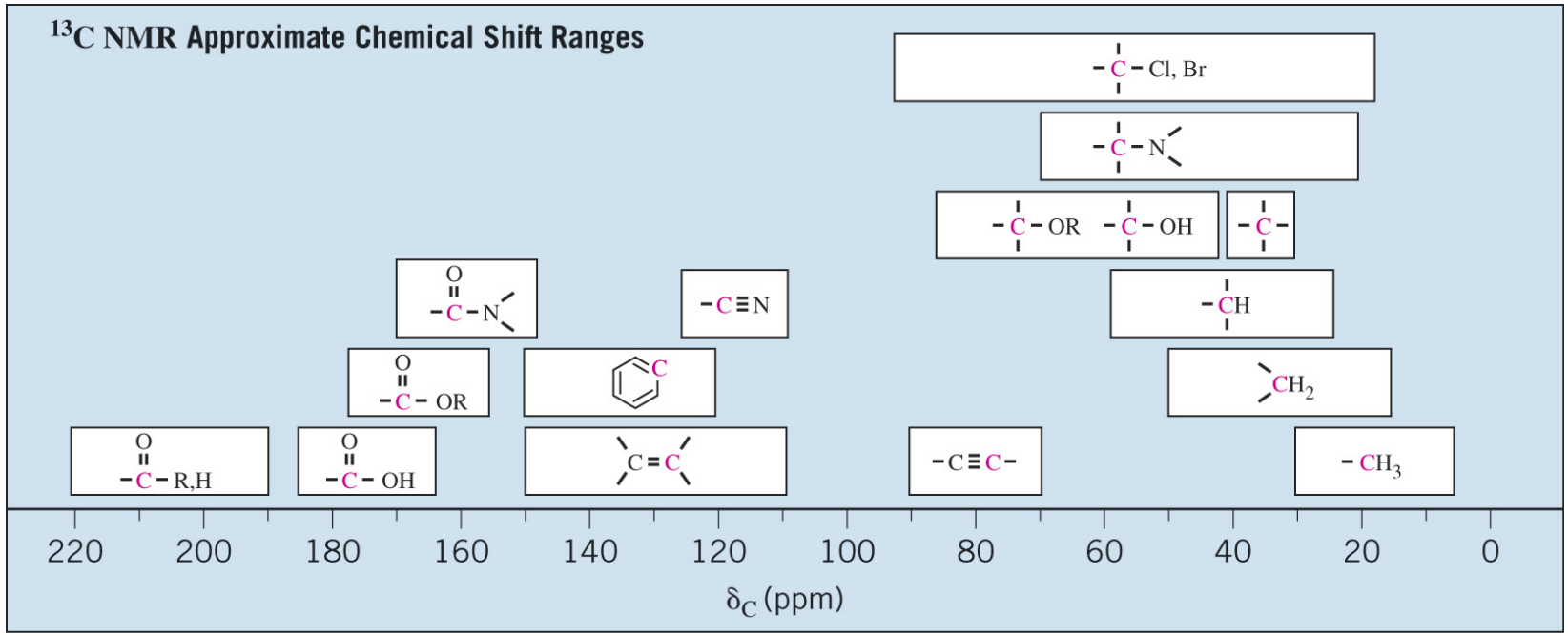

C, $C_3H_6Cl_2$
3.8
3.6
2.3
2.1
TMS
7
6
5
4
3
2
1
0
δ_H (ppm)

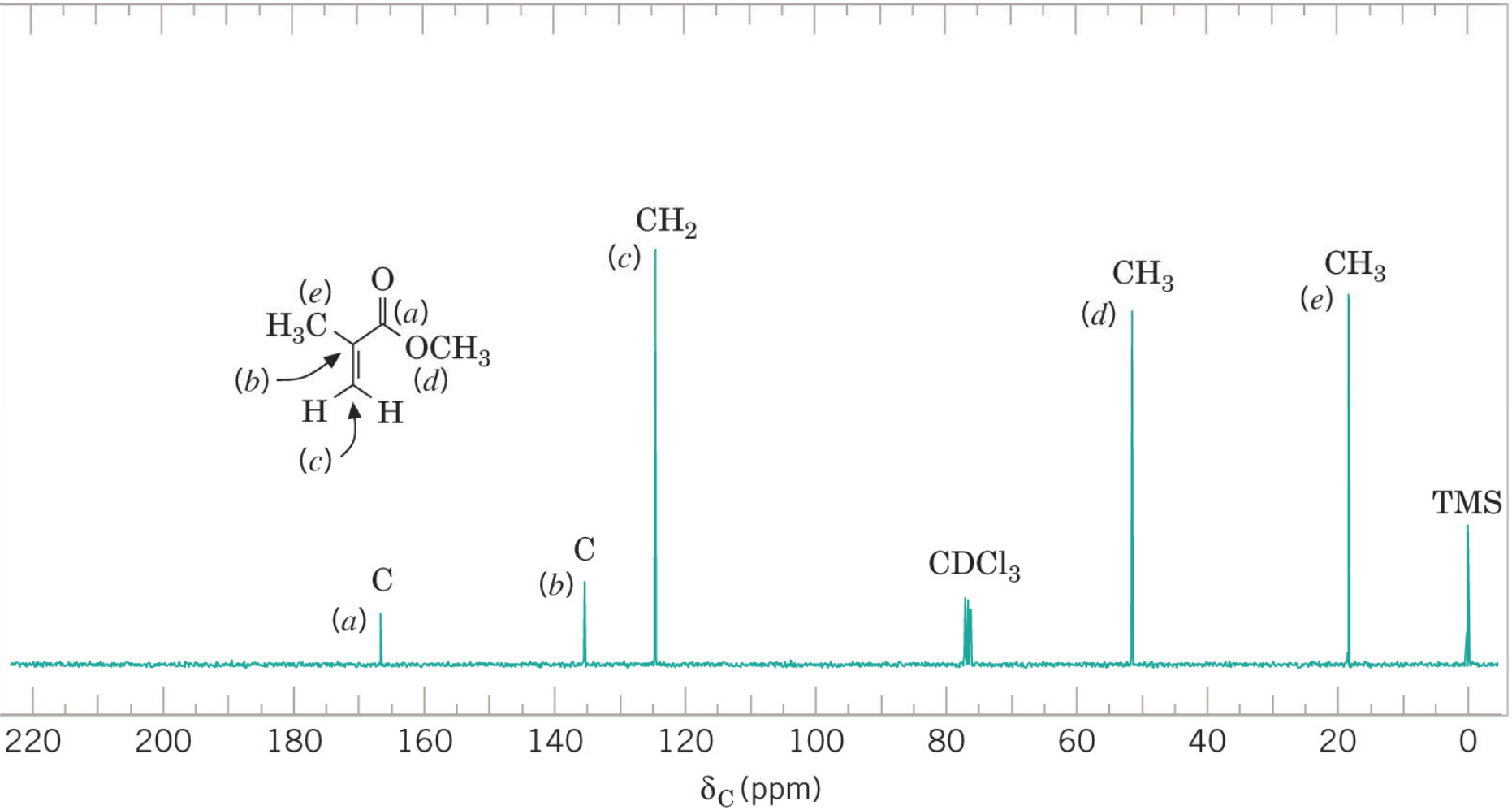

(b)
O
(c) (a)
ClCH2 — C — OCH2CH3
(b)
(c)
(a)
TMS
4.2
4.0
1.4
1.2
8
7
6
5
4
3
2
1
0


(a) (b) (c)
CH3—CH2—CH2—NO2
(a)
(c)
(b)
TMS
4.5
4.3
2.2
2.0
1.2
1.0
8
7
6
5
4
3
2
1
0
δH (ppm)

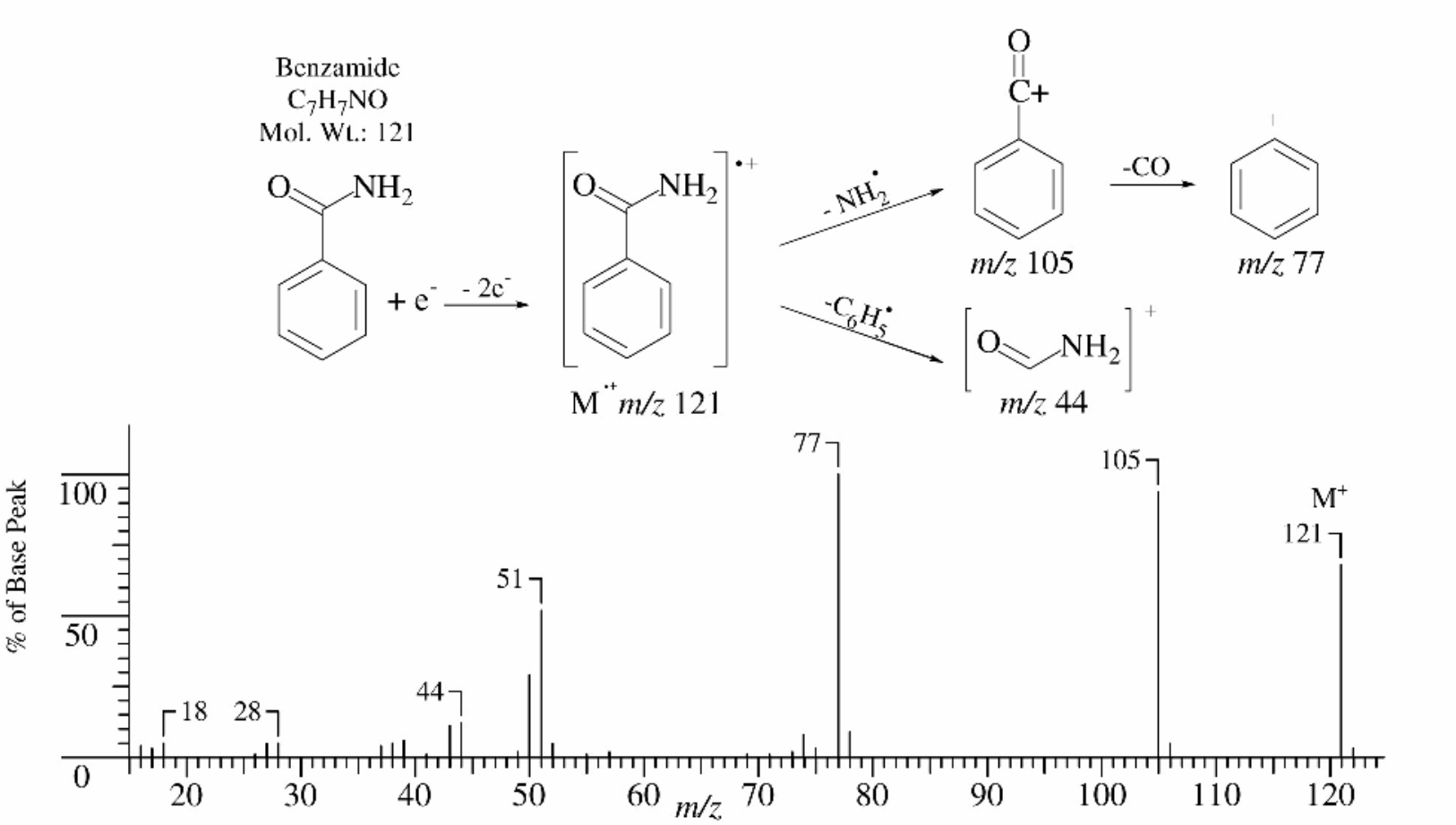

(a) (b) (c)
CH3—CH2—OH
(a)
(b)
(c)
TMS
4.0
3.8
3.6
1.4
1.2
1.0
8
7
6
5
4
3
2
1
0
δH (ppm)

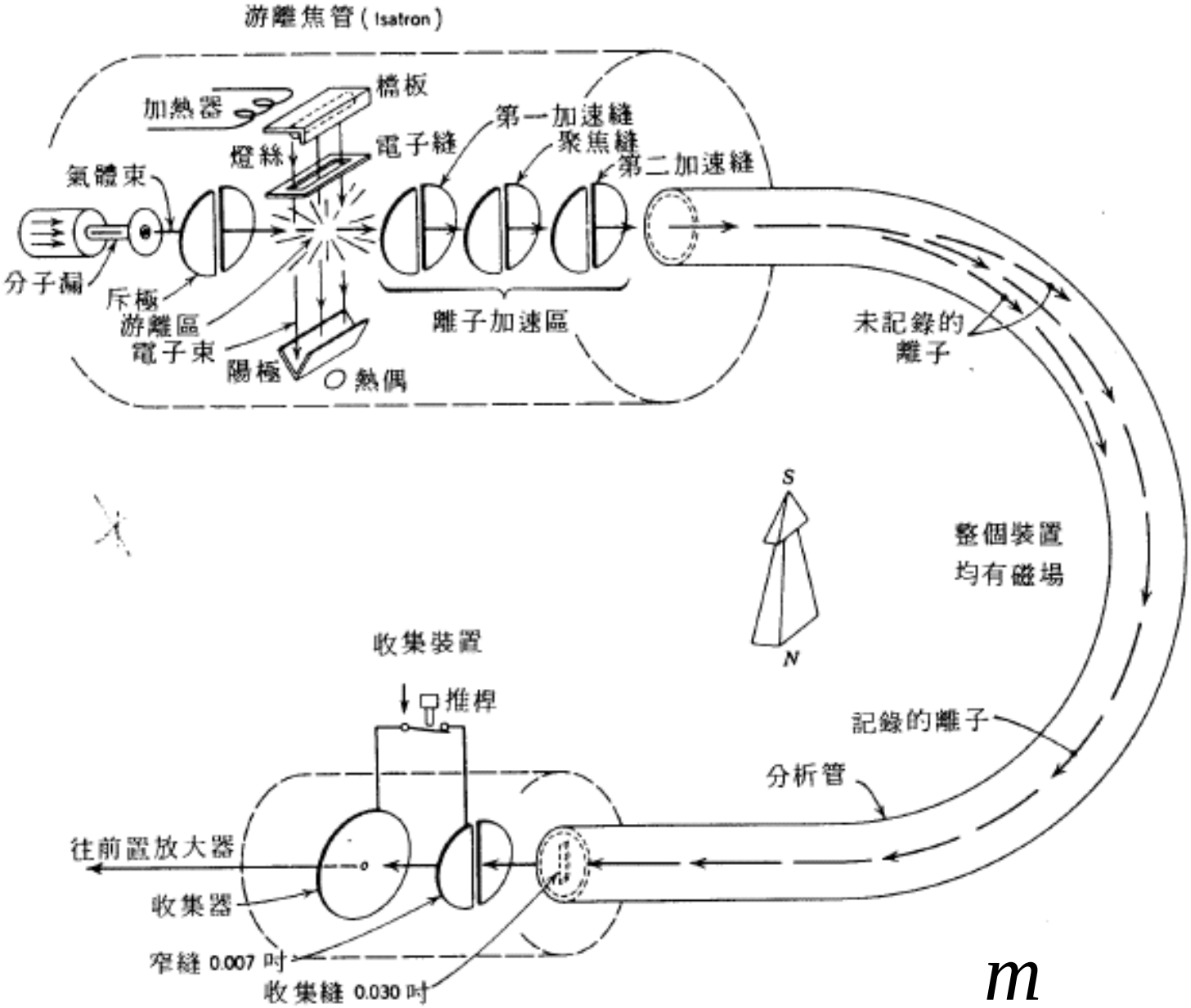
4) ^{13}C NMR


13C NMR Approximate Chemical Shift Ranges
C Cl, Br
C N
C OR
C OH
C
CH
CH2
CH3
C≡C
C=C
C≡N
C
O C N
O C OR
O C R,H
O C OH
220
200
180
160
140
120
100
80
60
40
20
0
δC (ppm)


(e)
O
H3C
(a)
OCH3
(b)
(d)
H
H
(c)
CH2
(c)
CH3
(d)
CH3
(e)
TMS
C
(a)
C
(b)
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
δC (ppm)

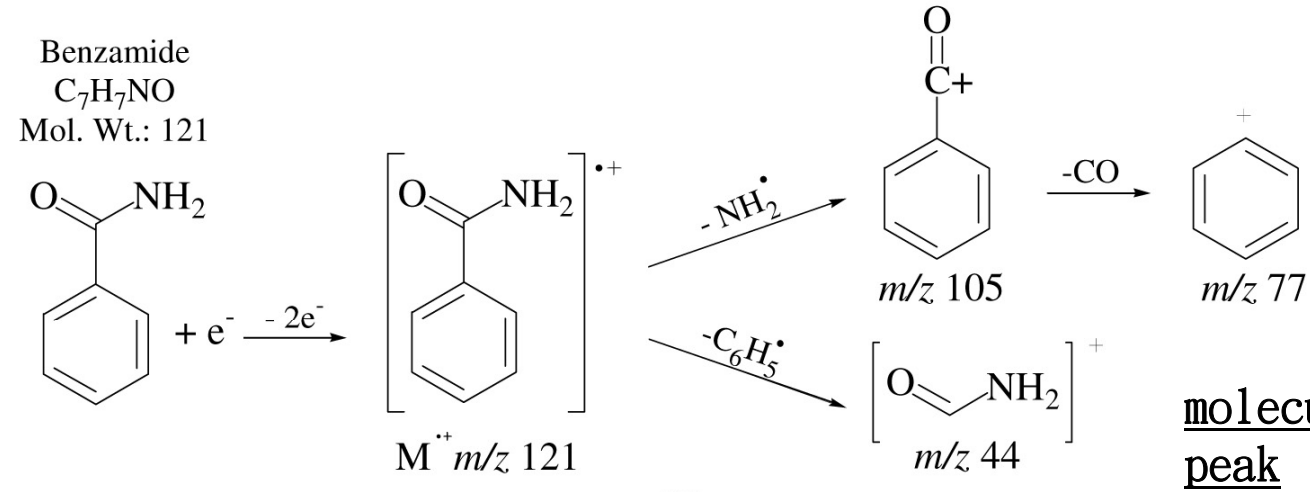
5) Mass


Benzamide
C7H7NO
Mol. Wt.: 121
+ e⁻
- 2e⁻
M⁺· m/z 121
- NH2·
-C6H5·
m/z 105
-CO
m/z 77
m/z 44
% of Base Peak
100
50
0
18
28
44
51
77
105
M+
121
20
30
40
50
60
m/z
70
80
90
100
110
120



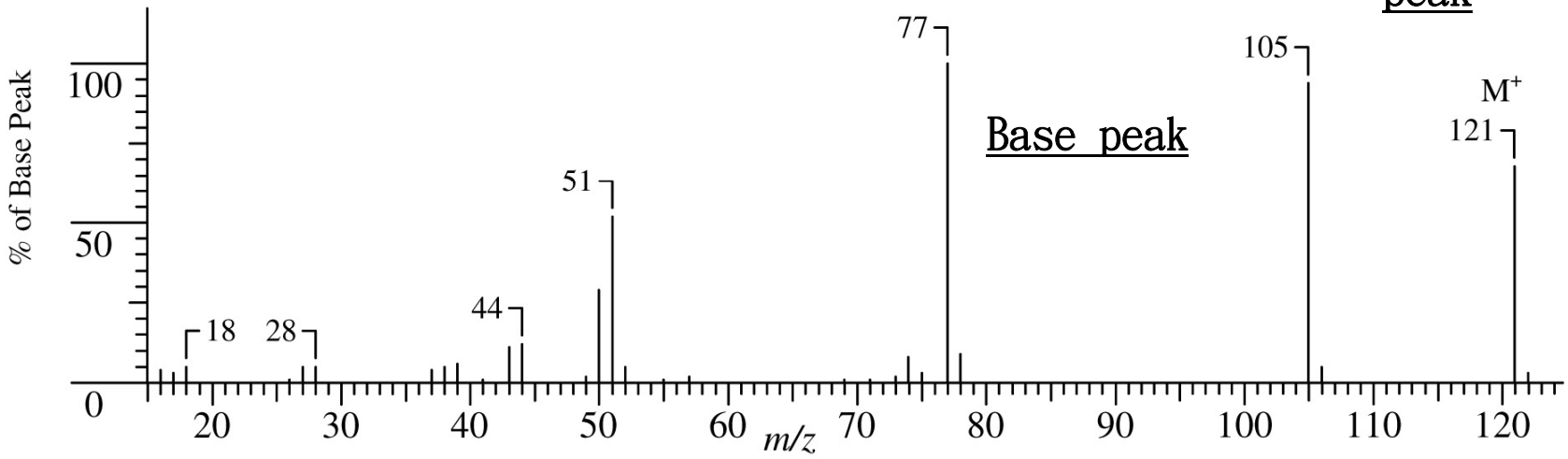
$$\frac{m}{z} = \frac{B^2 r^2}{2V}$$

Fragment ions



Abundance

molecular ion peak

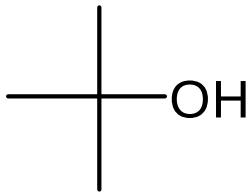


* *Peaks' heights are proportional to the number of ions of each mass*

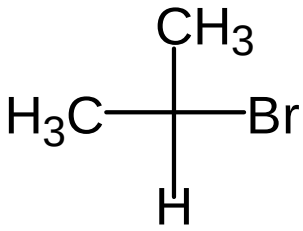
Exercise page 441

9.29:

a) C4H10O:

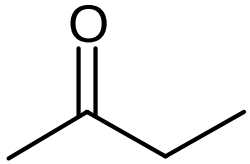


b) C3H7Br:



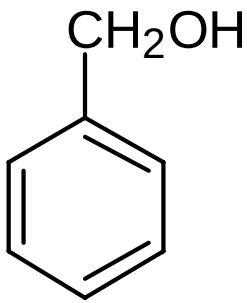
c) C4H8O:

(UN = 1)

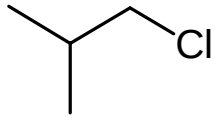


d) C7H8O:

(UN = 4)

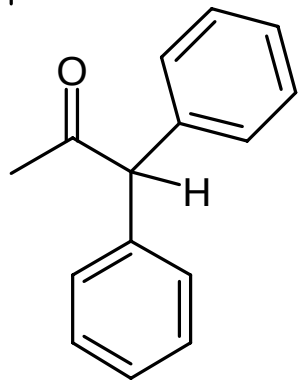


e) C_4H_9Cl:



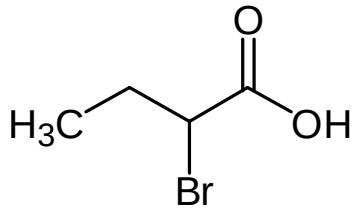
f) $C_{15}H_{14}O$:

(UN = 9)



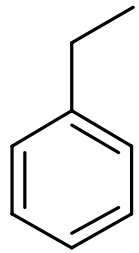
g) $C_4H_7BrO_2$:

(UN =1)



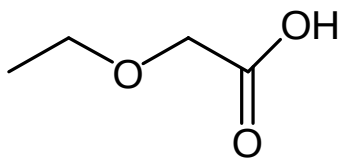
h) C_8H_{10}:

(UN =4)



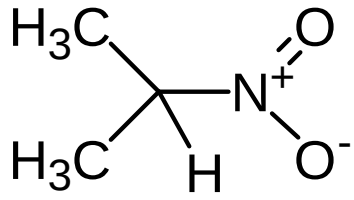
i) $C_4H_8O_3$:

(UN =1)



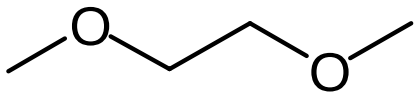
j) C_3H_7NO:

(UN = 1)



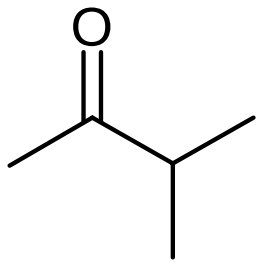
k) $C_4H_{10}O_2$:

(UN = 0)



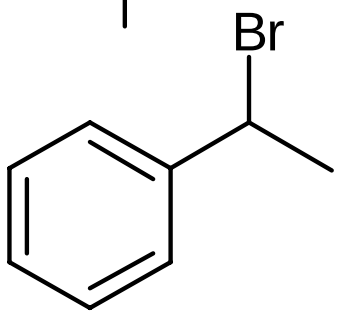
l) $C_5H_{10}O$:

(UN = 1)



m) C_8H_9Br:

(UN = 4)



9.31: