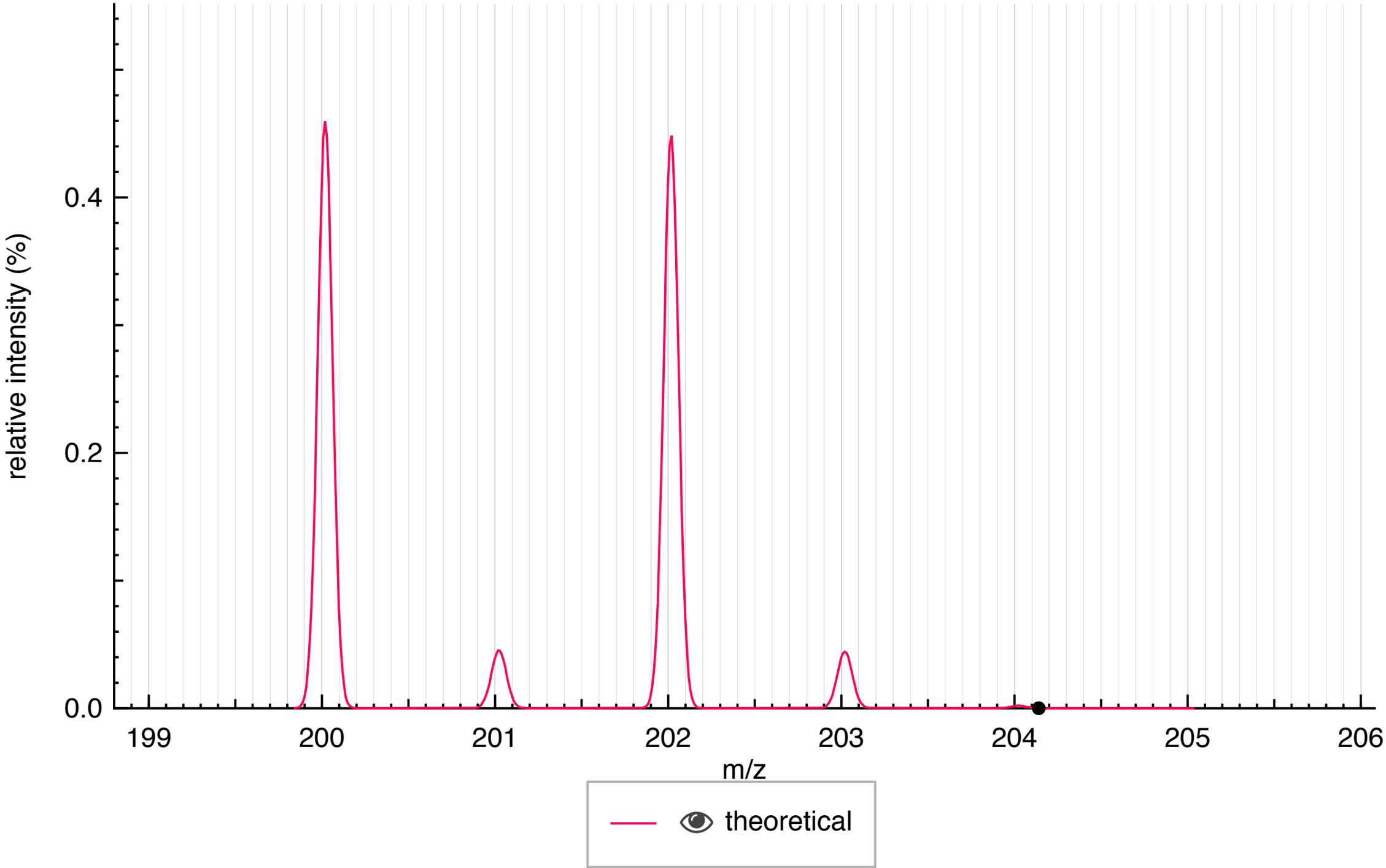
Tables de référence

	Masse nominale	Abondance relative (%)	Abondance (%)	Masse isotopique [u]	Masse atomique
H	1 2	100 0.01	99.99 0.01	1.007825 2.014101	1.008
C	12 13	100 1.08	98.93 1.07	12.000000 13.003354	12.011
N	14 15	100 0.37	99.64 0.36	14.003074 15.000108	14.007
O	16 17 18	100 0.04 0.20	99.76 0.04 0.20	15.994914 16.999131 17.999161	15.999
P	31	100	100	30.973761	30.974
S	32 33 34 36	100 0.79 4.47 0.01	94.99 0.75 4.25 0.01	31.972071 32.971458 33.967866 35.967080	32.065
F	19	100	100	18.998403	18.998
Cl	35 37	100 32.00	75.76 24.24	34.968852 36.965902	35.453
Br	79 81	100 97.28	50.69 49.31	78.918337 80.916290	79.903
I	127	100	100	126.904473	126.904
				Electron: 0.00054858	Proton: 1.00728

	Masse nominale	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.008
	2	0.01	2.014
C	12	98.93	12.000
	13	1.07	13.003
N	14	99.64	14.003
	15	0.36	15.000
O	16	99.76	15.995
	17	0.04	16.999
	18	0.20	17.999
P	31	100	30.974
S	32	94.99	31.972
	33	0.75	32.971
	34	4.25	33.968
	36	0.01	35.967
F	19	100	18.998
Cl	35	75.76	34.969
	37	24.24	36.966
Br	79	50.69	78.918
	81	49.31	80.916
		Electron: 0.00055	Proton: 1.00728

ms=200 Da, prec.: 200ppm



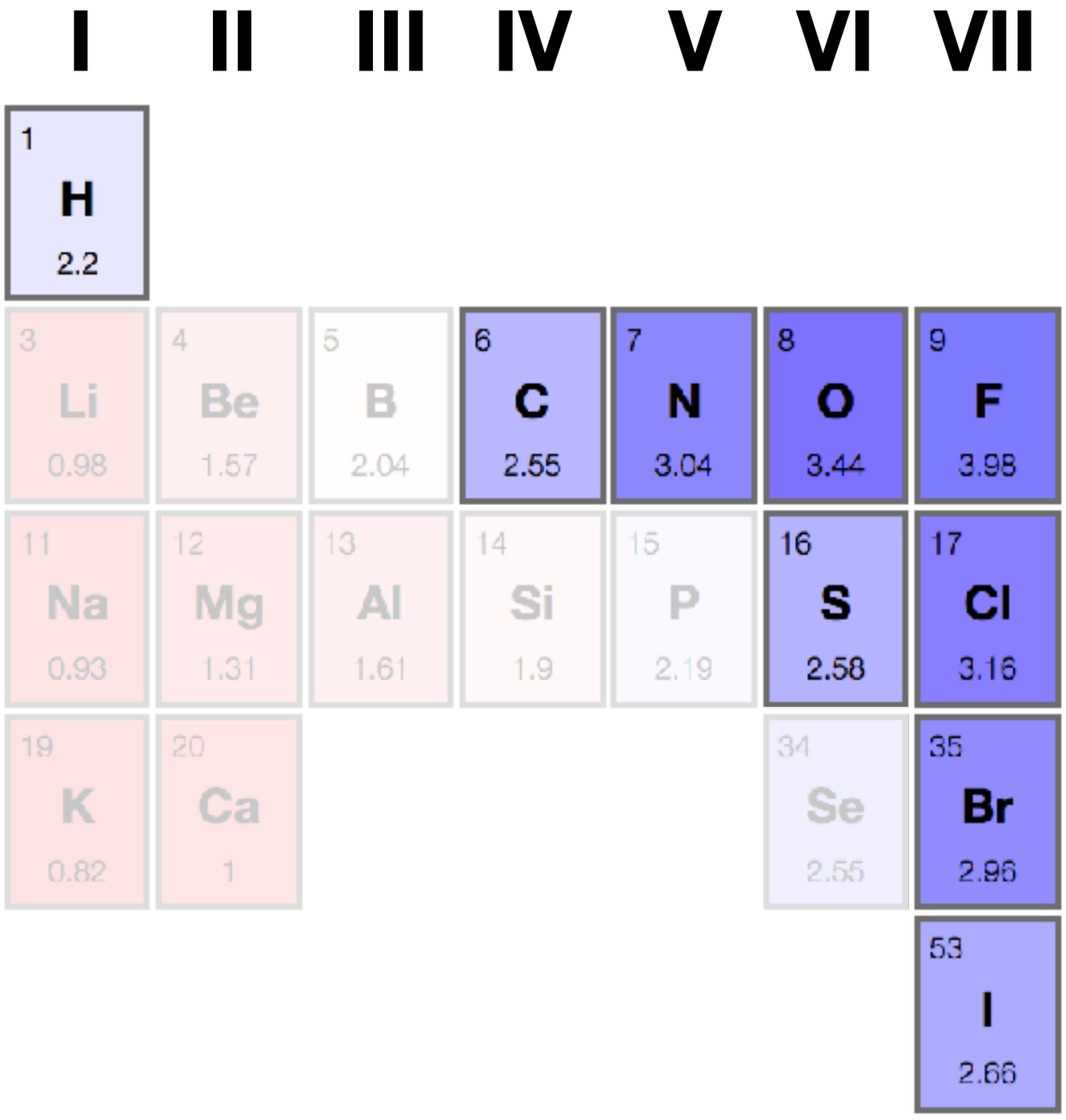
	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.0078
	2	0.01	2.0141
C	12	98.93	12.0000
	13	1.07	13.0033
N	14	99.64	14.0030
	15	0.36	15.0001
O	16	99.76	15.9949
	17	0.04	16.9991
	18	0.20	17.9991

Electron: 0.0005

Element	A (masse)	A (%)	A+1 (masse)	A+1 (%)	A+2 (masse)	A+2 (%)	A+x (masse)	A+x (%)
H	1	100	2	0.01				
C	12	100	13	1.08				
N	14	100	15	0.37				
O	16	100	17	0.04	18	0.20		
P	31	100						
S	32	100	33	0.79	34	4.47	36	0.01
F	19	100						
Cl	35	100			37	32.00		
Br	79	100			81	97.28		
I	127	100						

Element	A (masse)	A (%)	Δ_{A+1} (masse)	A+1 (%)	$\Delta_{A+1\,/\,C}$ * 1000
H	1	100	1.006276	0.01	2.92
C	12	100	1.003354	1.08	0
N	14	100	0.997034	0.37	-6.32
O	16	100	1.004217	0.04	0.86
P	31	100	-		
S	32	100	0.999387	0.79	-3.97
F	19	100	-		
Cl	35	100	-		
Br	79	100	-		
I	127	100	-		

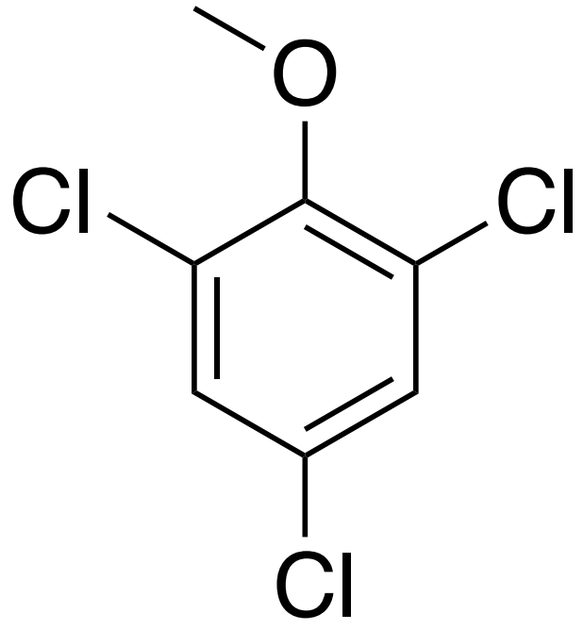
Electronegativity



Cours d'analyse structurale

Luc Patiny
luc.patiny@epfl.ch

Introduction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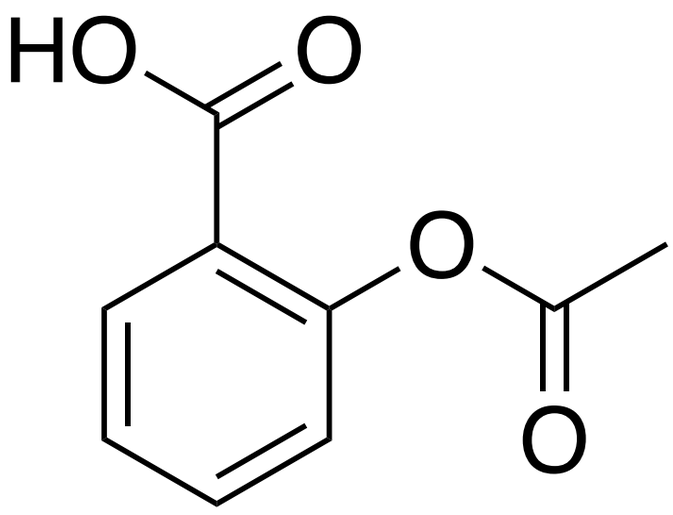
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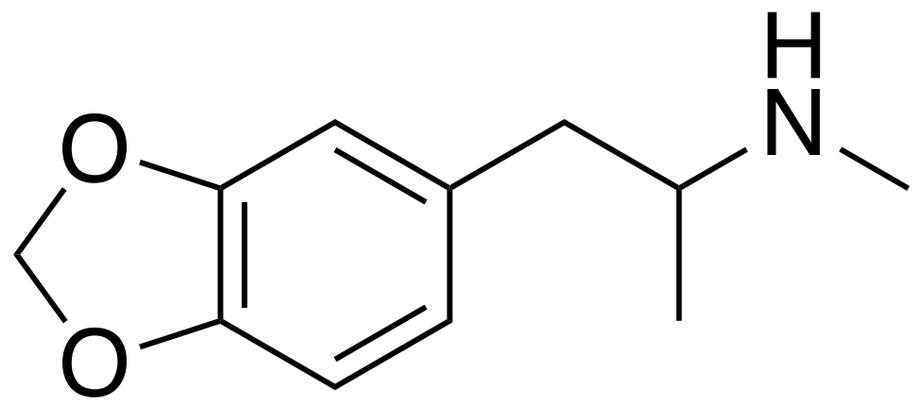
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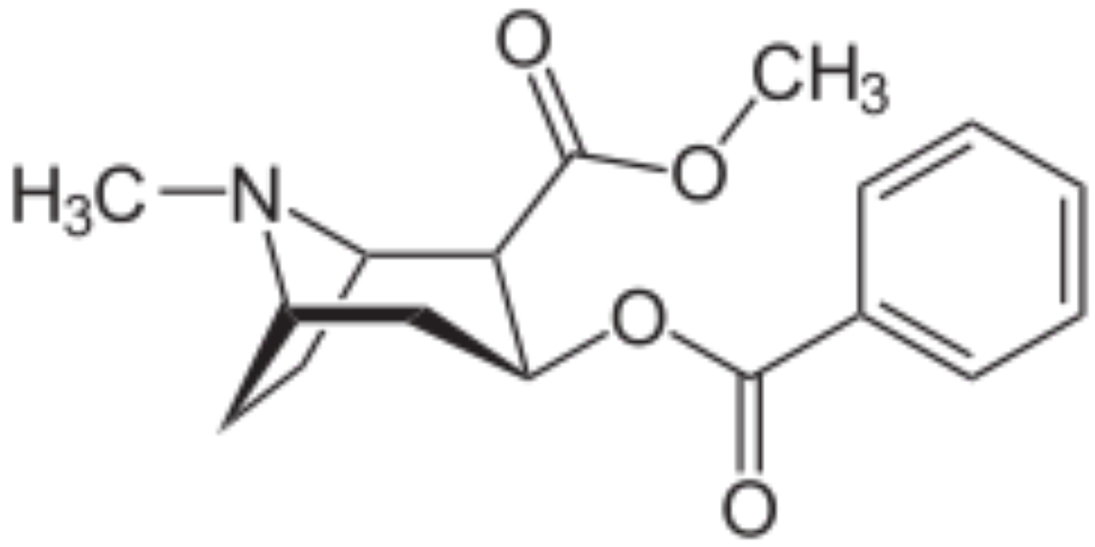
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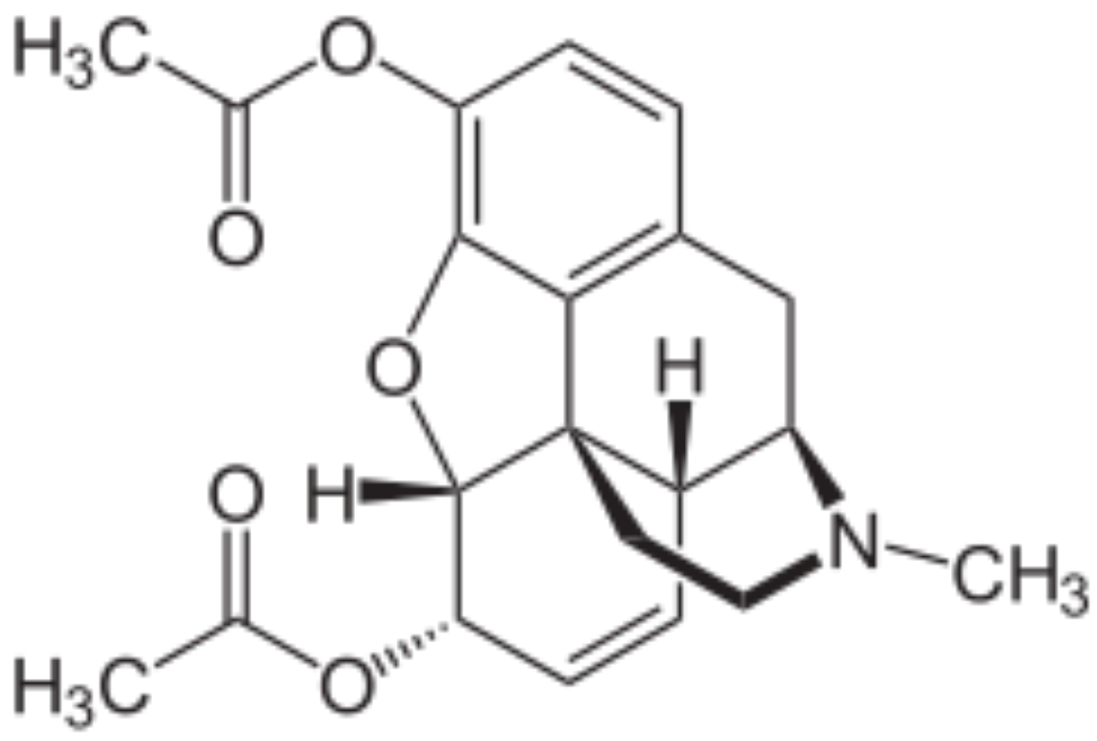
CH3
H3C
N
O
O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CH3
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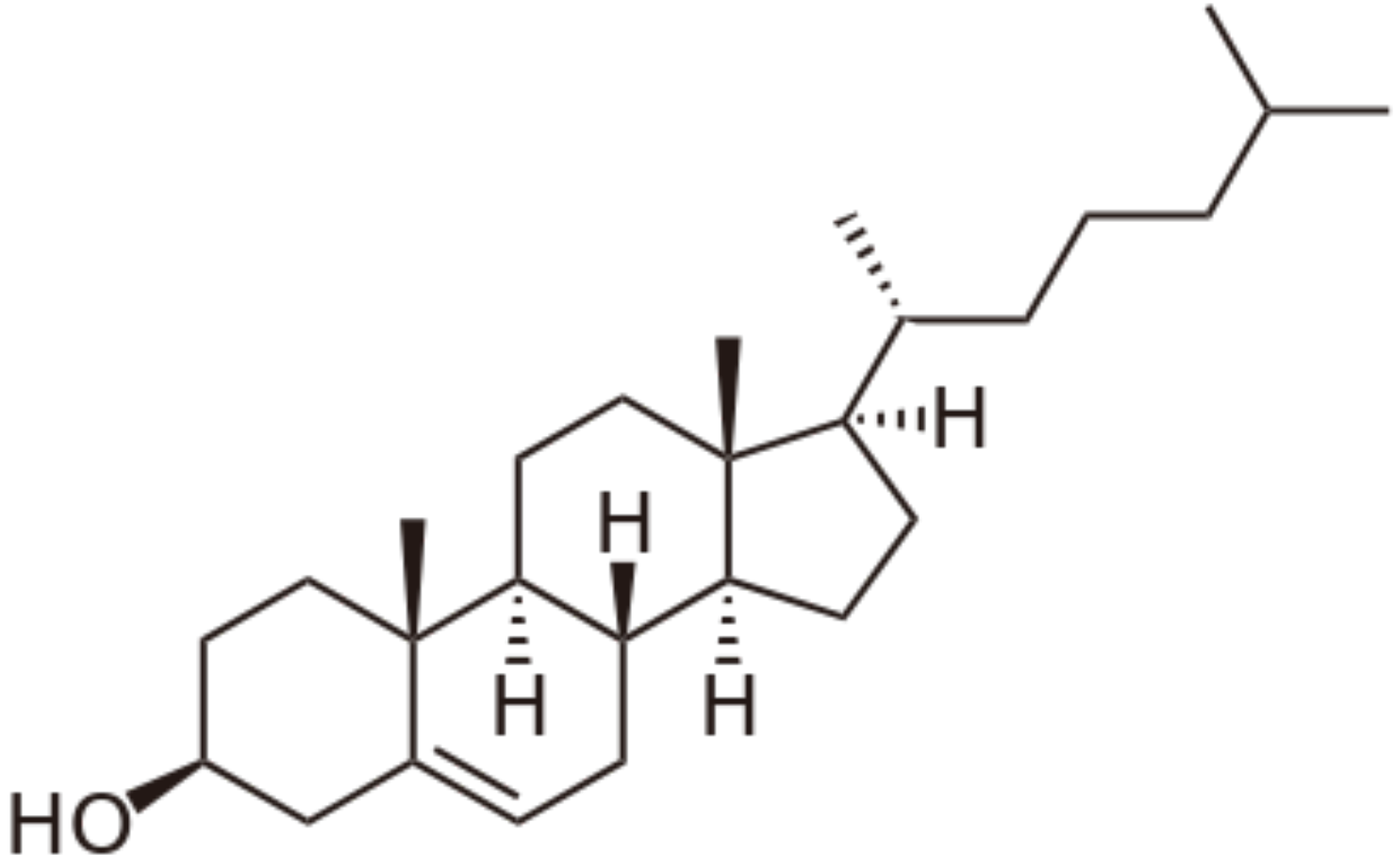
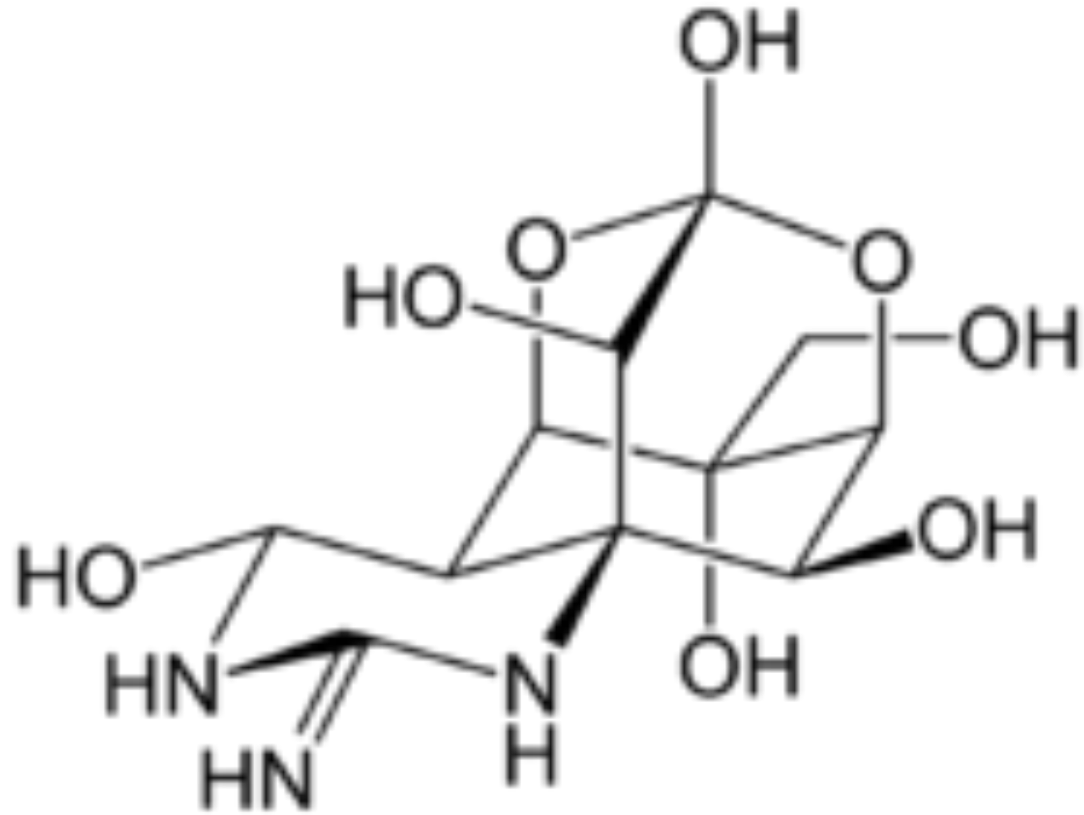
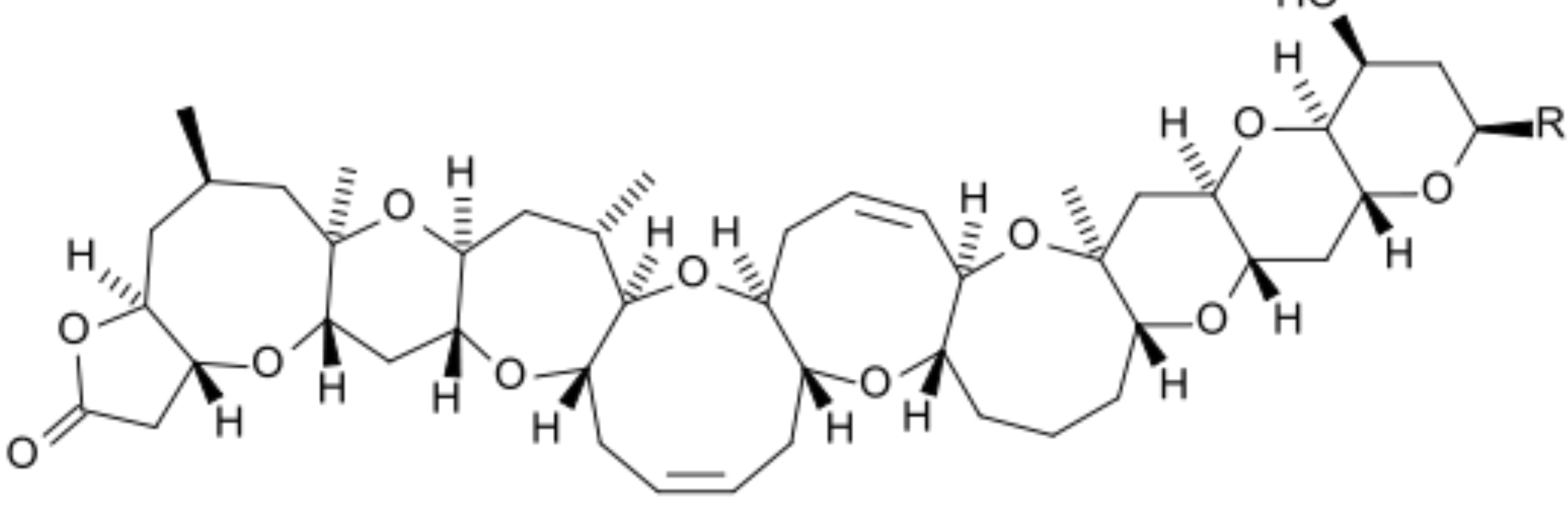
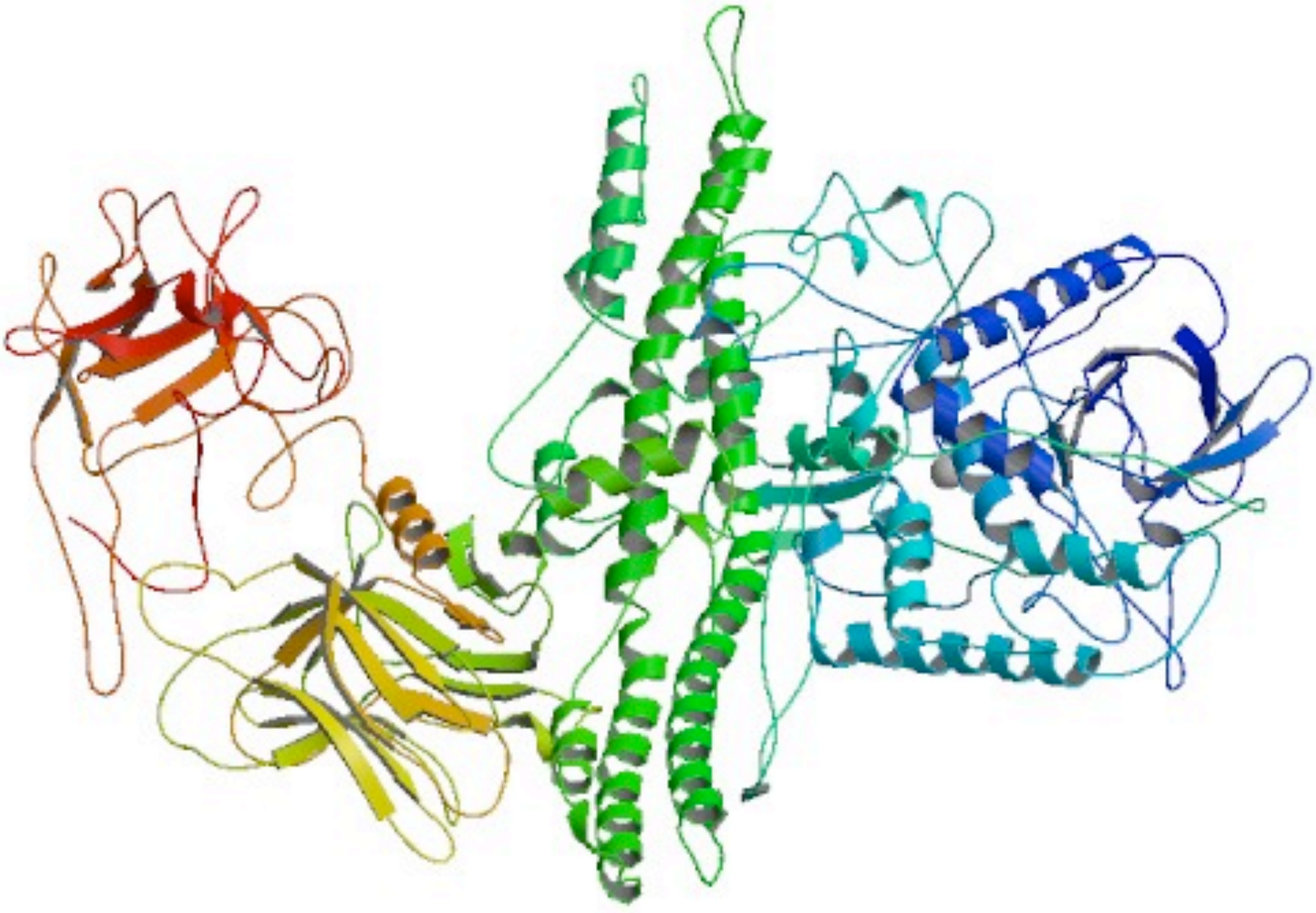

H
H
H
H
HO







DOUZE CAS, UN MORT... CE QUE L'ON SAIT SUR LES CAS DE BOTULISME DÉTECTÉS EN FRANCE

Sophie Cazaux Le 13/09/2023 à 11:47

12 cas de botulisme ont été identifiés en France ces derniers jours, liés à des sardines servies dans un restaurant de Bordeaux. Un décès a été recensé en Île-de-France. En raison du délai d'incubation de la maladie, les autorités s'attendent à détecter des cas jusqu'à ce week-end.

Link

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.0082		Alkali metals		Lanthanoids	Nonmetals												2 **He** 4.002…
			Alkalin earth metals		Actinoids	Halogens												
			Transition metals		Post-transition metals	Noble gases												
					Metalloids													
2	3 **Li** 6.942	4 **Be** 9.012…											5 **B** 10.812	6 **C** 12.0112	7 **N** 14.0072	8 **O** 15.9992	9 **F** 18.99…	10 **Ne** 20.1797
3	11 **Na** 22.98…	12 **Mg** 24.3059											13 **Al** 26.98…	14 **Si** 28.0854	15 **P** 30.97…	16 **S** 32.062	17 **Cl** 35.452	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.95…	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.93…	26 **Fe** 55.845	27 **Co** 58.93…	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.9049	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90…	40 **Zr** 91.224	41 **Nb** 92.90…	42 **Mo** 95.96	43 **Tc** 98	44 **Ru** 101.07	45 **Rh** 102.9…	46 **Pd** 106.42	47 **Ag** 107.8…	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.6	53 **I** 126.9…	54 **Xe** 131.293
6	55 **Cs** 132.9…	56 **Ba** 137.327	57-71	72 **Hf** 178.49	73 **Ta** 180.9…	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.9…	80 **Hg** 200.592	81 **Tl** 204.389	82 **Pb** 207.2	83 **Bi** 208.9…	84 **Po** 209	85 **At** 210	86 **Rn** 222
7	87 **Fr** 223	88 **Ra** 226	89-103	104 **Rf** 267	105 **Db** 268	106 **Sg** 269	107 **Bh** 270	108 **Hs** 269	109 **Mt** 278	110 **Ds** 281	111 **Rg** 281	112 **Cn** 285	113 **Nh** 286	114 **Fl** 289	115 **Mc** 289	116 **Lv** 293	117 **Ts** 294	118 **Og** 294

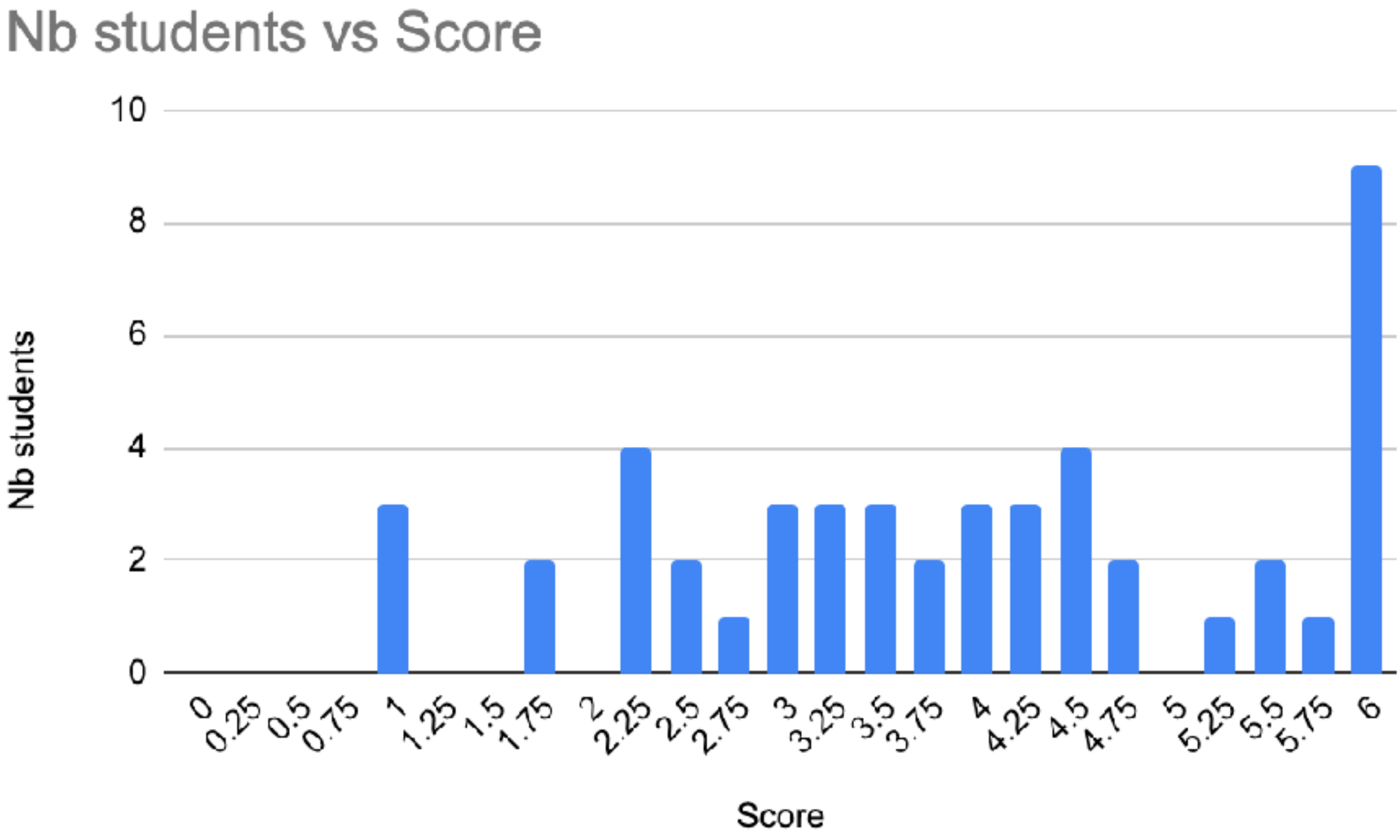
				57 **La** 138.9…	58 **Ce** 140.116	59 **Pr** 140.9…	60 **Nd** 144.242	61 **Pm** 145	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.9…	66 **Dy** 162.5	67 **Ho** 164.9…	68 **Er** 167.259	69 **Tm** 168.9…	70 **Yb** 173.054	71 **Lu** 174.9…
				89 **Ac** 227	90 **Th** 232.0…	91 **Pa** 231.0…	92 **U** 238.0…	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 266

I	II	III	IV	V	VI	VII
1 **H** 1.0082						
3 Li 6.942	4 Be 9.012…	5 B 10.812	6 **C** 12.0112	7 **N** 14.0072	8 **O** 15.9992	9 **F** 18.99…
11 Na 22.98…	12 Mg 24.3059	13 Al 26.98…	14 Si 28.0854	15 P 30.97…	16 **S** 32.062	17 **Cl** 35.452
19 K 39.0983	20 Ca 40.078	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 **Br** 79.9049
37 Rb 85.4678	38 Sr 87.62	49 In 114.818	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 **I** 126.9…

Stratégie

Examen

ESC


Nb students vs Score
Nb students
10
8
6
4
2
0
0
0.25
0.5
0.75
1
1.25
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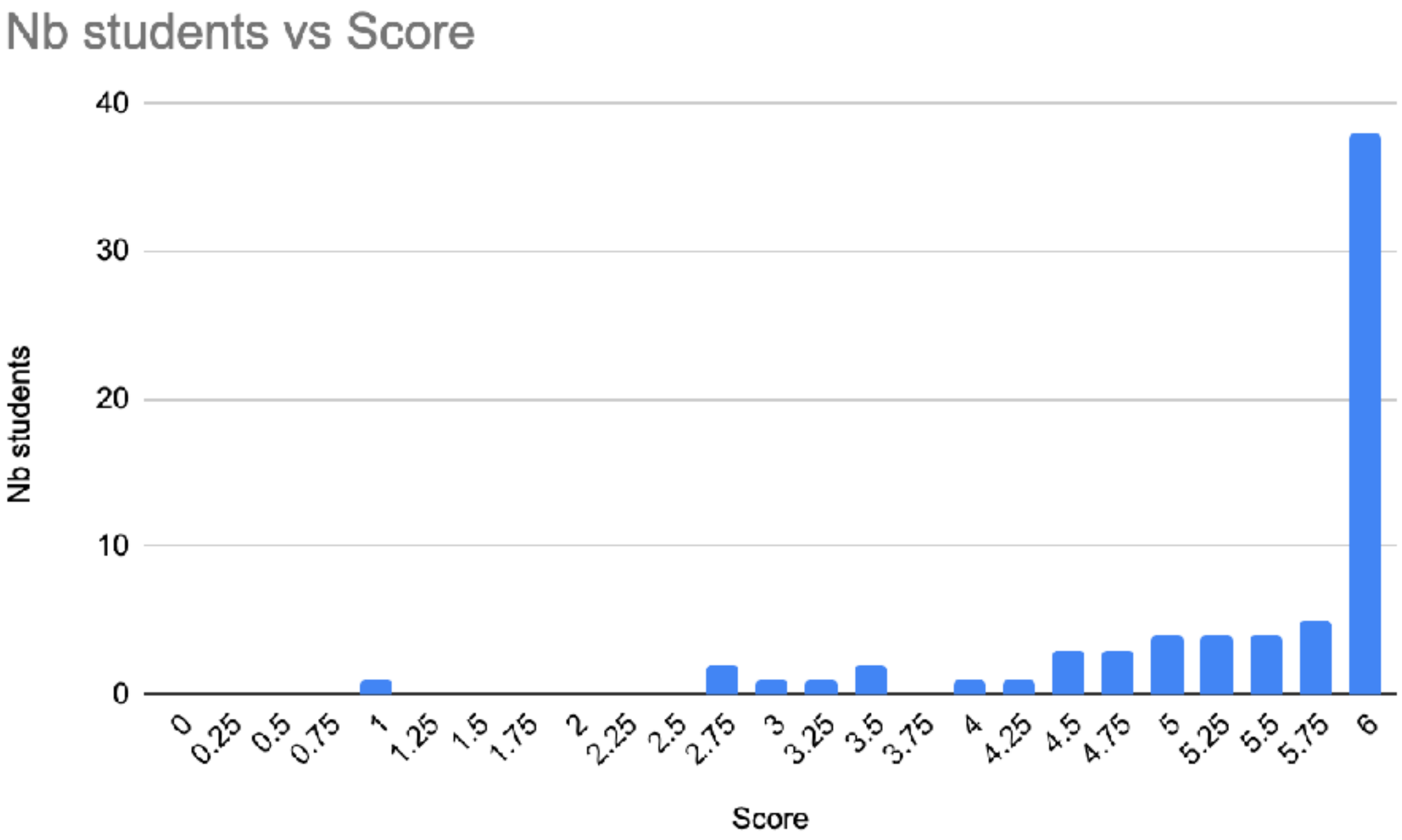
1.75
2
2.25
2.5
2.75
3
3.25
3.5
3.75
4
4.25
4.5
4.75
5
5.25
5.5
5.75
6
Score

SCGC


Nb students vs Score
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30
20
10
0
Nb students
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1
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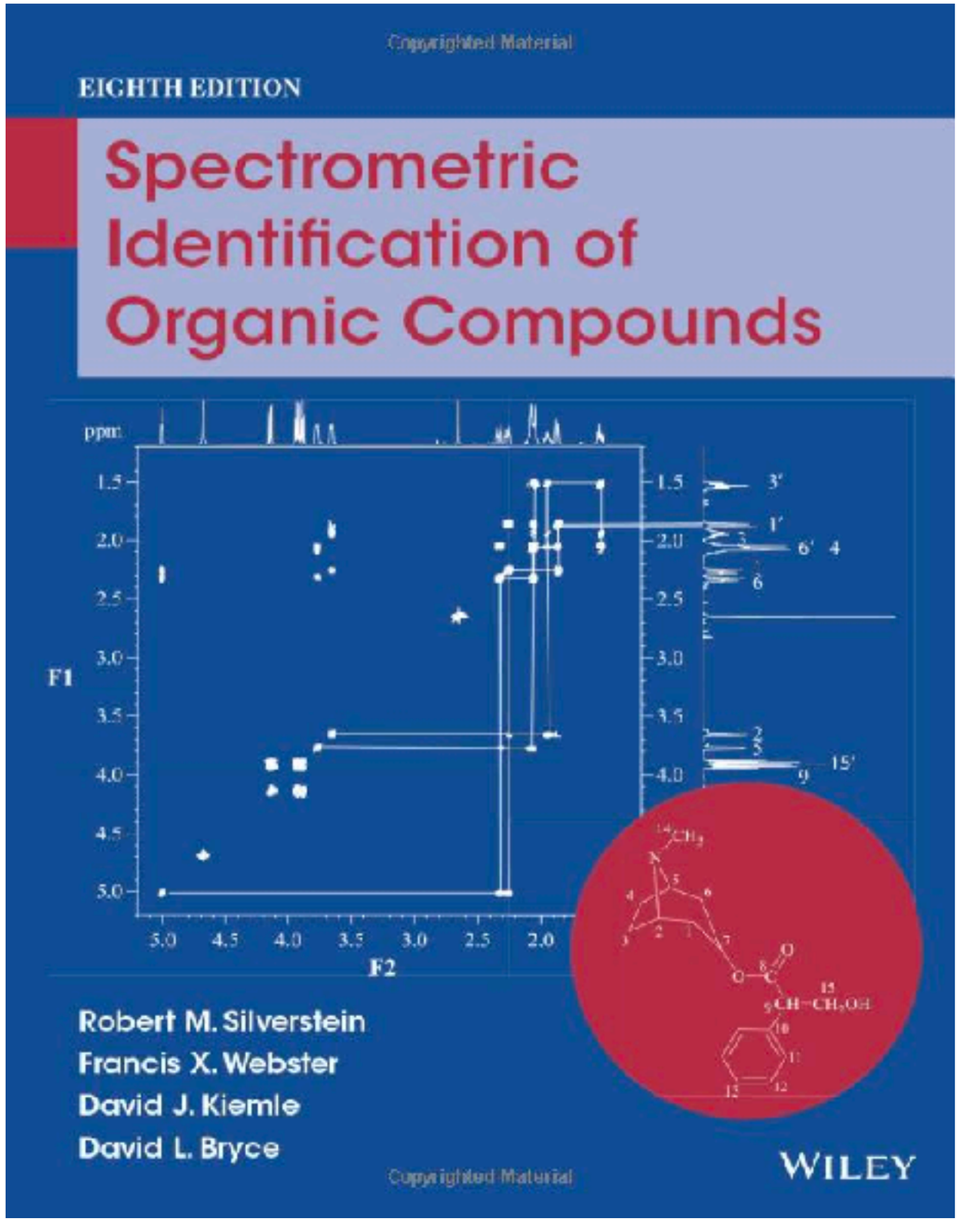
2
2.25
2.5
2.75
3
3.25
3.5
3.75
4
4.25
4.5
4.75
5
5.25
5.5
5.75
6
Score

Ressources

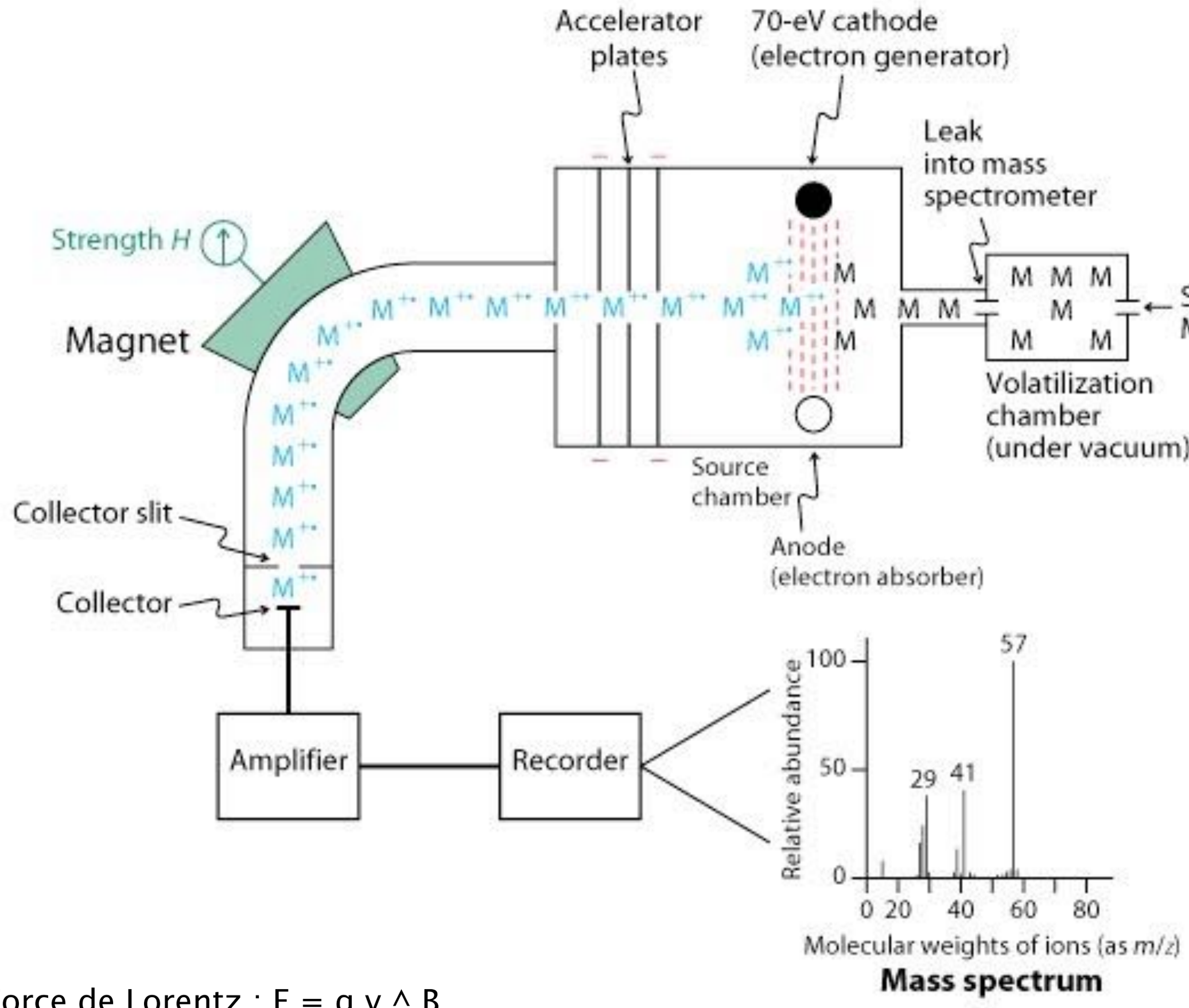
https://moodle.epfl.ch/course/view.php?id=16119

https://spectra.cheminfo.org

Livre de référence



Spectrométrie de masse



Force de Lorentz : F = q v ^ B

Signal correspondant à un carbone chargé positivement en spectrométrie de masse

1 carbone

- < 12u
- = 12u
- > 12u
- Impossible d'être certain

Answer

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.0078
	2	0.01	2.0141
C	12	98.93	12.0000
	13	1.07	13.0033
N	14	99.64	14.0030
	15	0.36	15.0001

Electron: 0.0005

	Isotope	Abondance (%)	Masse isotopique [u]
C	12	98.93	12.0000
	13	1.07	13.0033

Electron: 0.0005

Exercice

- **Dessiner le spectre de masse théorique de C_2^{++}**

	Isotope	Abondance (%)	Masse isotopique [u]
C	12	98.93	12.0000
	13	1.07	13.0033

Electron: 0.0005

	Isotope	Abondance (%)	Masse isotopique [u]
C	12	98.93	12.0000
	13	1.07	13.0033

Electron: 0.0005

https://spectra.cheminfo.org

Exercice pour déterminer le nombre de charge (z) de la molécule observée en masse

Définitions

Unité de masse atomique unifiée

Unité égale à (quasi *) 1/12 de la masse
d’un isotope 12 du carbone
= 1.660539 10^{-27} kg

Unité: Da (dalton) ou u

* exactement jusqu'au 20 mai 2019

Masse atomique

Moyenne pondérée des masses des isotopes naturels stables d’un élément donné

	Isotope	Abondance (%)	Masse isotopique [u]
C	12	98.93	12.0000
	13	1.07	13.0033

Masse moléculaire

Masse calculée en utilisant la masse atomique de chaque élément.

	Isotope	Abondance (%)	Masse isotopique [u]	Masse atomique
H	1 2	99.99 0.01	1.008 2.014	1.008
C	12 13	98.93 1.07	12.000 13.003	12.011

Masse nominale

Masse calculée en utilisant la masse entière de l’isotope majoritaire de chaque élément.

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.008
	2	0.01	2.014
C	12	98.93	12.000
	13	1.07	13.003

Masse isotopique

Masse calculée en utilisant les masses des isotopes considérés

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.008
	2	0.01	2.014
C	12	98.93	12.000
	13	1.07	13.003

Masse monoisotopique (masse exacte)

Masse calculée en utilisant les masses des isotopes majoritaires de chaque élément

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.008
	2	0.01	2.014
C	12	98.93	12.000
	13	1.07	13.003

	Masse nominale	Abondance relative (%)	Abondance (%)	Masse isotopique [u]	Masse atomique
H	1 2	100 0.01	99.99 0.01	1.007825 2.014101	1.008
C	12 13	100 1.08	98.93 1.07	12.000000 13.003354	12.011
N	14 15	100 0.37	99.64 0.36	14.003074 15.000108	14.007
O	16 17 18	100 0.04 0.20	99.76 0.04 0.20	15.994914 16.999131 17.999161	15.999
P	31	100	100	30.973761	30.974
S	32 33 34 36	100 0.79 4.47 0.01	94.99 0.75 4.25 0.01	31.972071 32.971458 33.967866 35.967080	32.065
F	19	100	100	18.998403	18.998
Cl	35 37	100 32.00	75.76 24.24	34.968852 36.965902	35.453
Br	79 81	100 97.28	50.69 49.31	78.918337 80.916290	79.903
I	127	100	100	126.904473	126.904
					Electron: 0.00054858

https://spectra.cheminfo.org

Exercice pour déterminer la masse monoisotopique

https://forms.gle/ps6voMgXnJkzmvNT6

Quelle formule brute correspond le mieux à une molécule mono chargée positivement dont la masse observée est 30.0450

30.0450

- CH2O
- C2H6
- NO

Answer

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.0078
	2	0.01	2.0141
C	12	98.93	12.0000
	13	1.07	13.0033
N	14	99.64	14.0030
	15	0.36	15.0001
O	16	99.76	15.9949
	17	0.04	16.9991
	18	0.20	17.9991

30.0450: CH_2O, C_2H_6 ou NO ?

Electron: 0.0005

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.0078
	2	0.01	2.0141
C	12	98.93	12.0000
	13	1.07	13.0033
N	14	99.64	14.0030
	15	0.36	15.0001
O	16	99.76	15.9949
	17	0.04	16.9991
	18	0.20	17.9991

30.0450: CH_2O, C_2H_6 ou NO ?

Distribution isotopique
1 seul atome

Exercice

- **Dessinez le spectre de masse (masse nominale) de :**
  - $C^{+\bullet}$
  - $Cl^{+\bullet}$
  - $Br^{+\bullet}$
  - $S^{+\bullet}$

$C^{+\bullet}$ - $Cl^{+\bullet}$ - $Br^{+\bullet}$ - $S^{+\bullet}$

	Masse nominale	Abondance relative (%)	Abondance (%)	Masse isotopique [u]	Masse atomique
H	1	100	99.99	1.007825	1.008
	2	0.01	0.01	2.014101	
C	12	100	98.93	12.000000	12.011
	13	1.08	1.07	13.003354	
N	14	100	99.64	14.003074	14.007
	15	0.37	0.36	15.000108	
O	16	100	99.76	15.994914	15.999
	17	0.04	0.04	16.999131	
	18	0.20	0.20	17.999161	
P	31	100	100	30.973761	30.974
S	32	100	94.99	31.972071	32.065
	33	0.79	0.75	32.971458	
	34	4.47	4.25	33.967866	
	36	0.01	0.01	35.967080	
F	19	100	100	18.998403	18.998
Cl	35	100	75.76	34.968852	35.453
	37	32.00	24.24	36.965902	
Br	79	100	50.69	78.918337	79.903
	81	97.28	49.31	80.916290	

Electron: 0.00054858

Elem	A	A	A+1	A+1	A+2	A+2	A+4	A+4
H	1	100	2	0.01				
C	12	100	13	1.08				
N	14	100	15	0.37				
O	16	100	17	0.04	18	0.20		
P	31	100						
S	32	100	33	0.79	34	4.47	36	0.01
F	19	100						
Cl	35	100			37	32.00		
Br	79	100			81	97.28		
I	127	100						

$C^{+\bullet}$

$Cl^{+\bullet}$

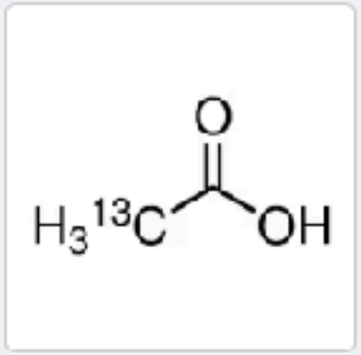
$Br^{+\bullet}$

$S^{+\bullet}$

Distribution isotopique - plusieurs atomes

Isotopomères

2 molécules ayant le même nombre de chacun des isotopes à des positions différentes.



All Photos (1)

Documents

SDS

COO/COA

More Documents »

279307 Sigma-Aldrich

Acetic acid-2-^{13}C

(0) Write a review

99 atom % ^{13}C

Synonym(s):
^{13}C Labeled acetic acid, Glacial acetic acid 2 ^{13}C

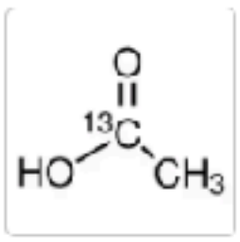
Linear Formula:
$^{13}CH_3CO_2H$

CAS Number:	1563-80-0	Molecular Weight:	61.04	MDL number:	MFCD00074856
PubChem Substance ID:	24856876	NACRES:	NA.12		

SKU	Pack Size	Availability	Price	Quantity
279307-1G	1 G	Only 4 left in stock (more on the way) Details...	CHF 317.00	− +

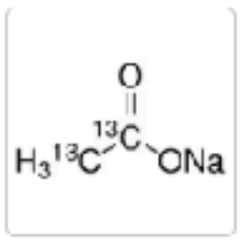
Add to Cart

RECOMMENDED PRODUCTS



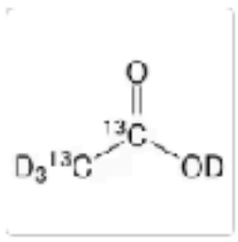
Sigma Aldrich
279285
Acetic acid-1-^{13}C
99 atom % ^{13}C

View Price and Availability



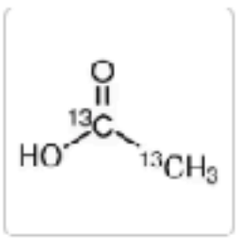
Sigma Aldrich
282014
Sodium acetate-$^{13}C_2$
99 atom % ^{13}C

View Price and Availability



Sigma Aldrich
607401
Acetic acid-$^{13}C_2$,d4
99 atom % ^{13}C, 98 atom % D

View Price and Availability



Sigma Aldrich
282022
Acetic acid-$^{13}C_2$
99 atom % ^{13}C

View Price and Availability

Isotopologues

2 molécules différents uniquement par leur composition isotopique

Isotopologue majoritaire

Composition isotopique la plus abondante.

Link

Distribution isotopique

Ensemble des isotopologues avec leur masse et intensité relative respective

Exercice

- **Dessiner la distribution isotopique de:**
  - $C_2^{+\bullet}$
  - $Cl_2^{+\bullet}$
  - $Br_2^{+\bullet}$

	Masse nominale	Abondance (%)	Masse isotopique [u]	Masse atomique
C	12 13	98.93 1.07	12.000 13.003	12.011
Cl	35 37	75.76 24.24	34.969 36.966	35.453
Br	79 81	50.69 49.31	78.918 80.916	79.903

Electron: 0.00054858

	Masse nominale	Abondance (%)	Masse isotopique [u]	Masse atomique
C	12 13	98.93 1.07	12.000 13.003	12.011
Cl	35 37	75.76 24.24	34.969 36.966	35.453
Br	79 81	50.69 49.31	78.918 80.916	79.903

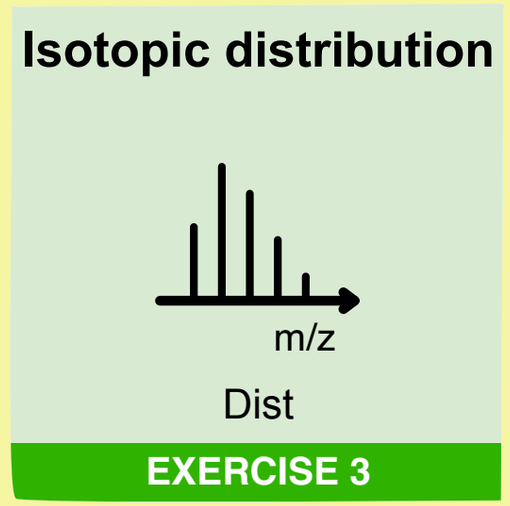
Elem	A	A	A+1	A+1	A+2	A+2	A+4	A+4
H	1	100	2	0.01				
C	12	100	13	1.08				
N	14	100	15	0.37				
O	16	100	17	0.04	18	0.20		
P	31	100						
S	32	100	33	0.79	34	4.47	36	0.01
F	19	100						
Cl	35	100			37	32.00		
Br	79	100			81	97.28		
I	127	100						

- $C_2^{+\bullet}$
- $Cl_2^{+\bullet}$
- $Br_2^{+\bullet}$

https://spectra.cheminfo.org

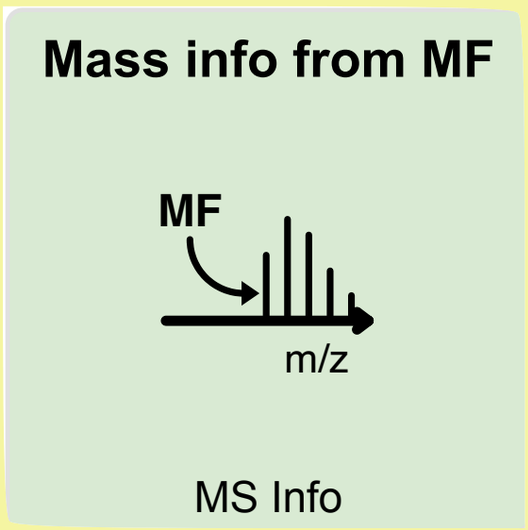
Trouver la MF au départ de la distribution isotopique

Autres exercices sur https://www.chemcalc.org

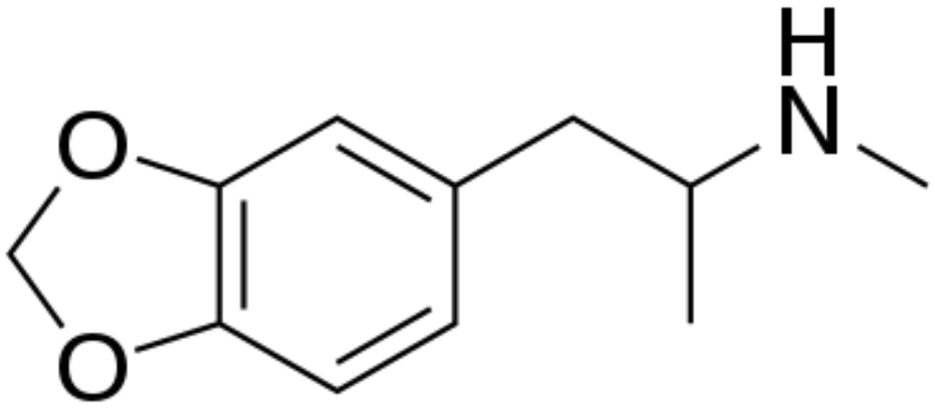


https://spectra.cheminfo.org

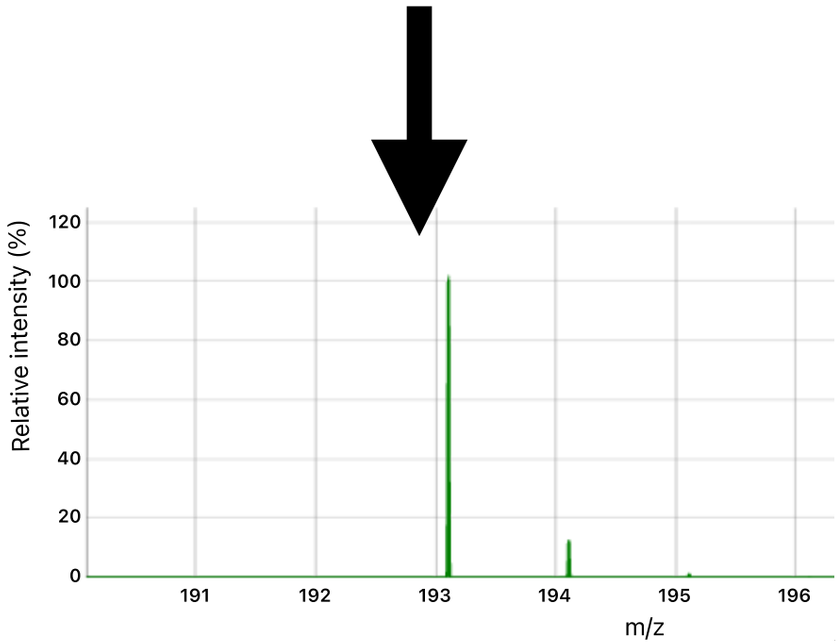
Impact des Cl, Br, S sur la distribution isotopique



Distribution isotopique - Calcul théorique



$C_{11}H_{15}NO_2$



1. Au départ de la formule brute

- **Calculer les combinaisons possibles des isotopes: pour atteindre**
  - **M**
  - **M+1**
  - **M+2….**
- **Remarque: pour simplifier on ne va pas considérer ^{2}H et ^{17}O qui sont très peu abondants**

	Masse nominale	Abondance relative (%)	Abondance (%)	Masse isotopique [u]	Masse atomique
H	1 2	100 0.01	99.99 0.01	1.007825 2.014101	1.008
C	12 13	100 1.08	98.93 1.07	12.000000 13.003354	12.011
N	14 15	100 0.37	99.64 0.36	14.003074 15.000108	14.007
O	16 17 18	100 0.04 0.20	99.76 0.04 0.20	15.994914 16.999131 17.999161	15.999
P	31	100	100	30.973761	30.974
S	32 33 34 36	100 0.79 4.47 0.01	94.99 0.75 4.25 0.01	31.972071 32.971458 33.967866 35.967080	32.065
F	19	100	100	18.998403	18.998
Cl	35 37	100 32.00	75.76 24.24	34.968852 36.965902	35.453
Br	79 81	100 97.28	50.69 49.31	78.918337 80.916290	79.903
I	127	100	100	126.904473	126.904
					Electron: 0.00054858

$C_{11}H_{15}NO_2$

2. Pour chaque élément

- **Calculer l'abondance A pour chaque élément séparément. en utilisant la formule suivante:**

$$A = \frac{n!}{a! \cdot b! \cdot c! \cdot \ldots} \cdot r_1^a \cdot r_2^b \cdot r_3^c \cdot \ldots$$

Où:

- n est le nombre total d'atomes de l'élément
- a, b, c sont les nombres de chaque type d'isotope (a + b + c + ... = n)
- r_1. r_2. r_3 sont les abondances de chaque isotope

$C_{11}H_{15}NO_2$

$$A = \frac{n!}{a! \cdot b! \cdot c! \cdot \ldots} \cdot r_1^a \cdot r_2^b \cdot r_3^c \cdot \ldots$$

3. Pour chaque pic isotopique

- **Calculer l'abondance totale au moyen de la formule suivante:**

$$Abondance = A_{element1} \cdot A_{element2} \cdot A_{element3} \cdot \ldots$$

$C_{11}H_{15}NO_2$

Abondance

M	$^{12}C_{11}H_{15}{}^{14}NO_2$
M+1	$^{12}C_{10}{}^{13}CH_{15}{}^{14}NO_2$
	$^{12}C_{11}H_{15}{}^{15}NO_2$

4. En fonction de la résolution

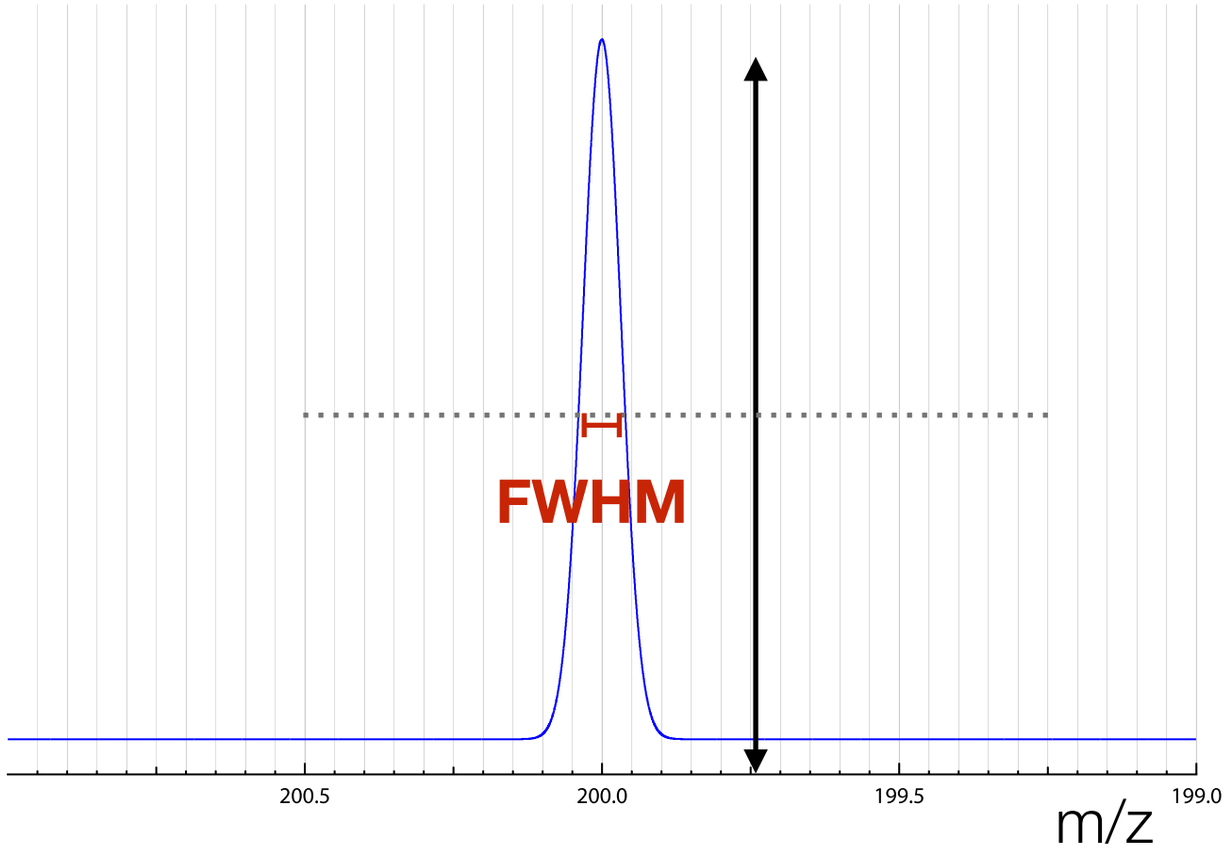
- **regrouper les masses qui sont proches**

$^{12}C_{11}H_{15}{}^{14}NO_2$	**193.11028**
$^{12}C_{10}{}^{13}CH_{15}{}^{14}NO_2$	**194.11363**
$^{12}C_{11}H_{15}{}^{15}NO_2$	**194.10731**

Résolution / Précision (Exactitude)

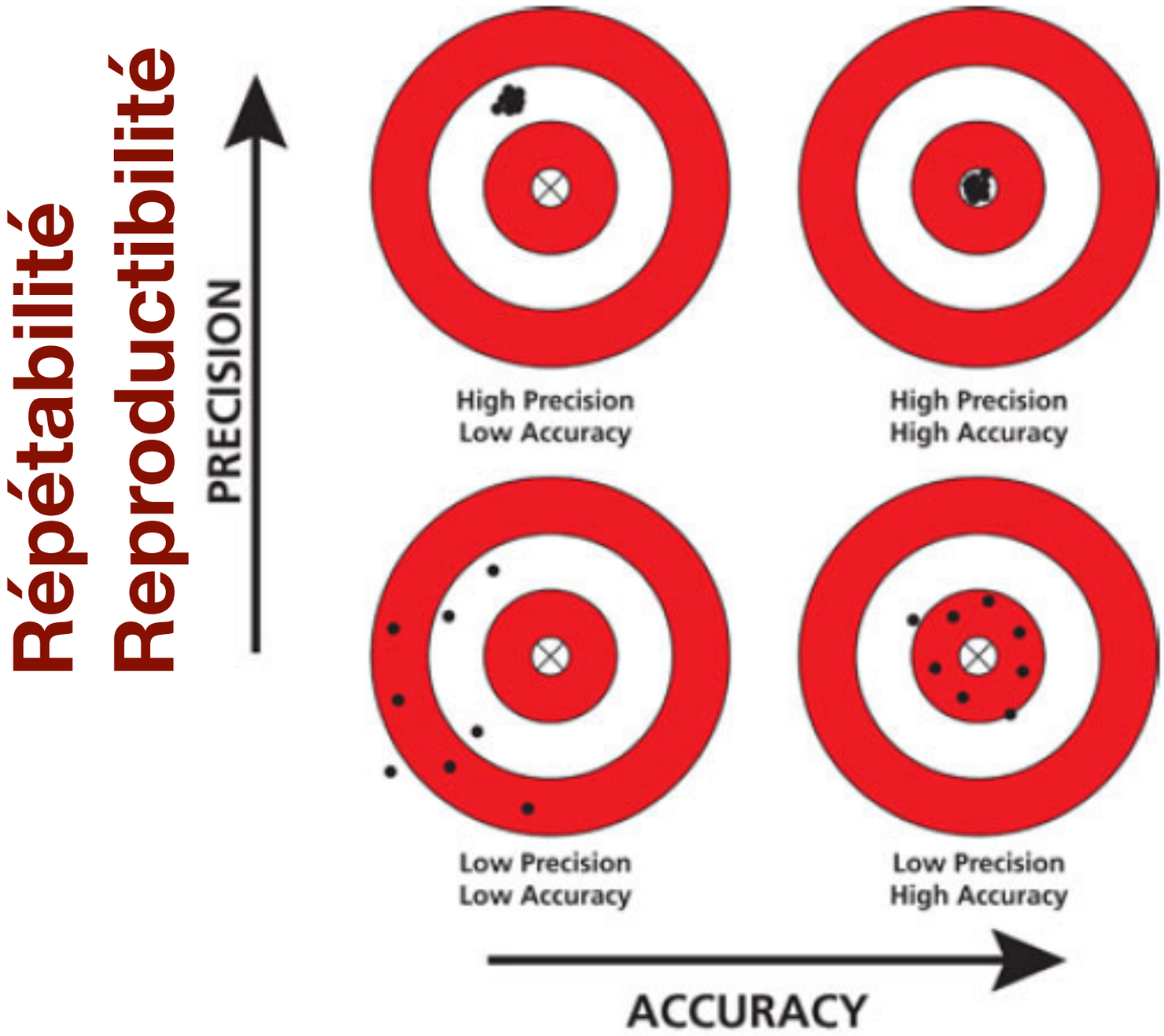
Résolution

$$R = \frac{m/z}{FWHM}$$



FWHM: Full Width Half Maximum

Répétabilité / Précision



Répétabilité

=

precision

Exactitude

=

accuracy

Exactitude / Précision

Exactitude / Précision

$$Précision = Mass\ accuracy = \frac{m_{experimental} - m_{theory}}{m_{theory}} * 10^6 ppm$$

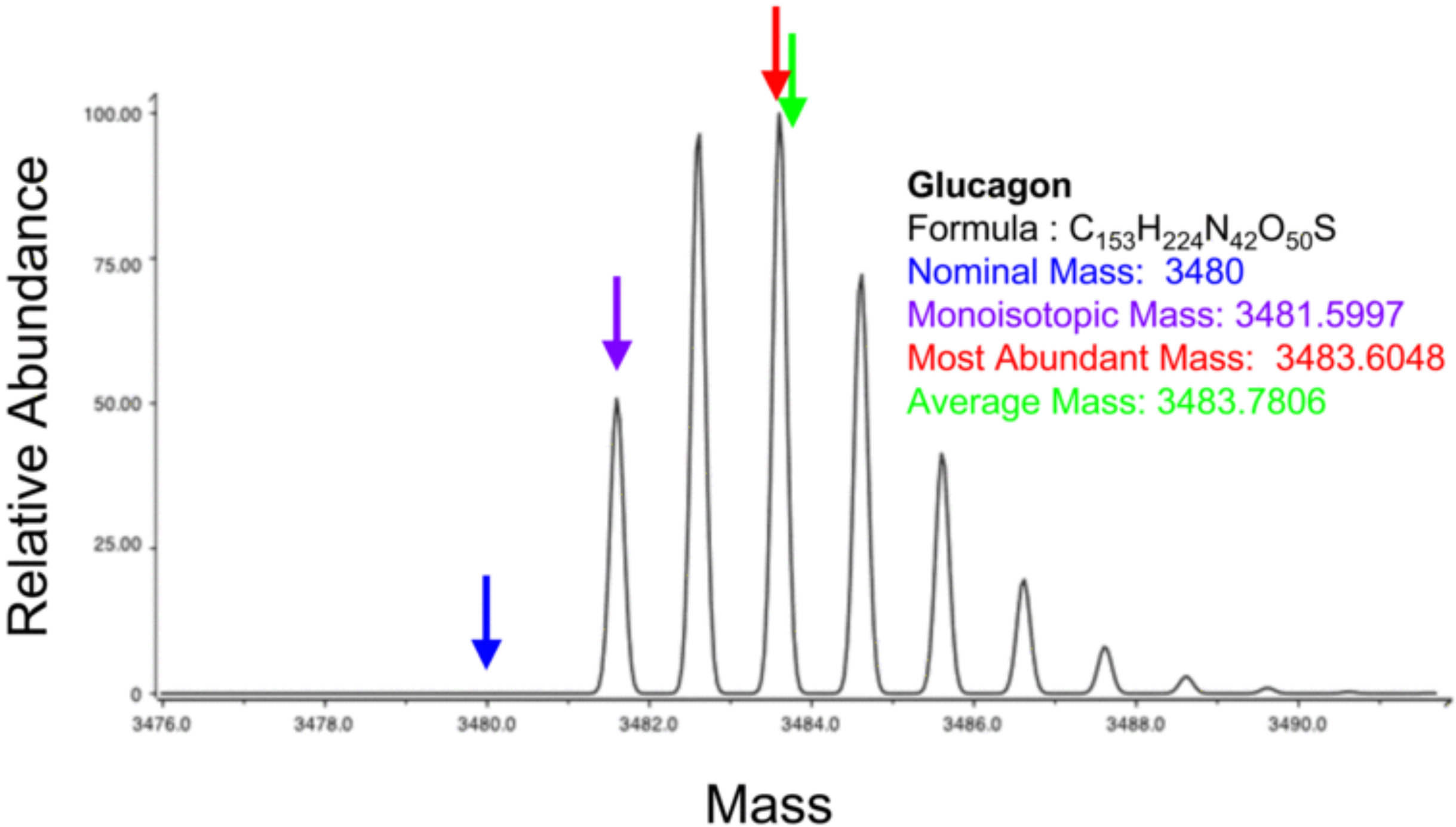
Structure fine (M+1)

	Isotope	Abondance (%)	Masse isotopique [u]
H	1	99.99	1.0078
	2	0.01	2.0141
C	12	98.93	12.0000
	13	1.07	13.0033
N	14	99.64	14.0030
	15	0.36	15.0001
O	16	99.76	15.9949
	17	0.04	16.9991
	18	0.20	17.9991
S	32	94.99	31.972071
	33	0.75	32.971458
	34	4.25	33.967866
	36	0.01	35.967080

Element	A (masse)	A (%)	Δ_{A+1} (masse)	A+1 (%)	$\Delta_{A+1\,/\,C}$ * 1000
H	1	100	1.006276	0.01	2.92
C	12	100	1.003354	1.08	0
N	14	100	0.997034	0.37	-6.32
O	16	100	1.004217	0.04	0.86
P	31	100	-		
S	32	100	0.999387	0.79	-3.97
Si	28	100	0.999568	5.08	-3.79
F	19	100	-		
Cl	35	100	-		
Br	79	100	-		
I	127	100	-		

Masse majoritaire

Masse correspondante au pic majoritaire observé dans le spectre de masse


Relative Abundance
100.00
75.00
50.00
25.00
0
3476.0
3478.0
3480.0
3482.0
3484.0
3486.0
3488.0
3490.0
Mass
Glucagon
Formula : C153H224N42O50S
Nominal Mass: 3480
Monoisotopic Mass: 3481.5997
Most Abundant Mass: 3483.6048
Average Mass: 3483.7806

Link

Exercices intégrés

Trouver la formule brute au départ d’un spectre de masse.

Link

HR mass spectrum → MF

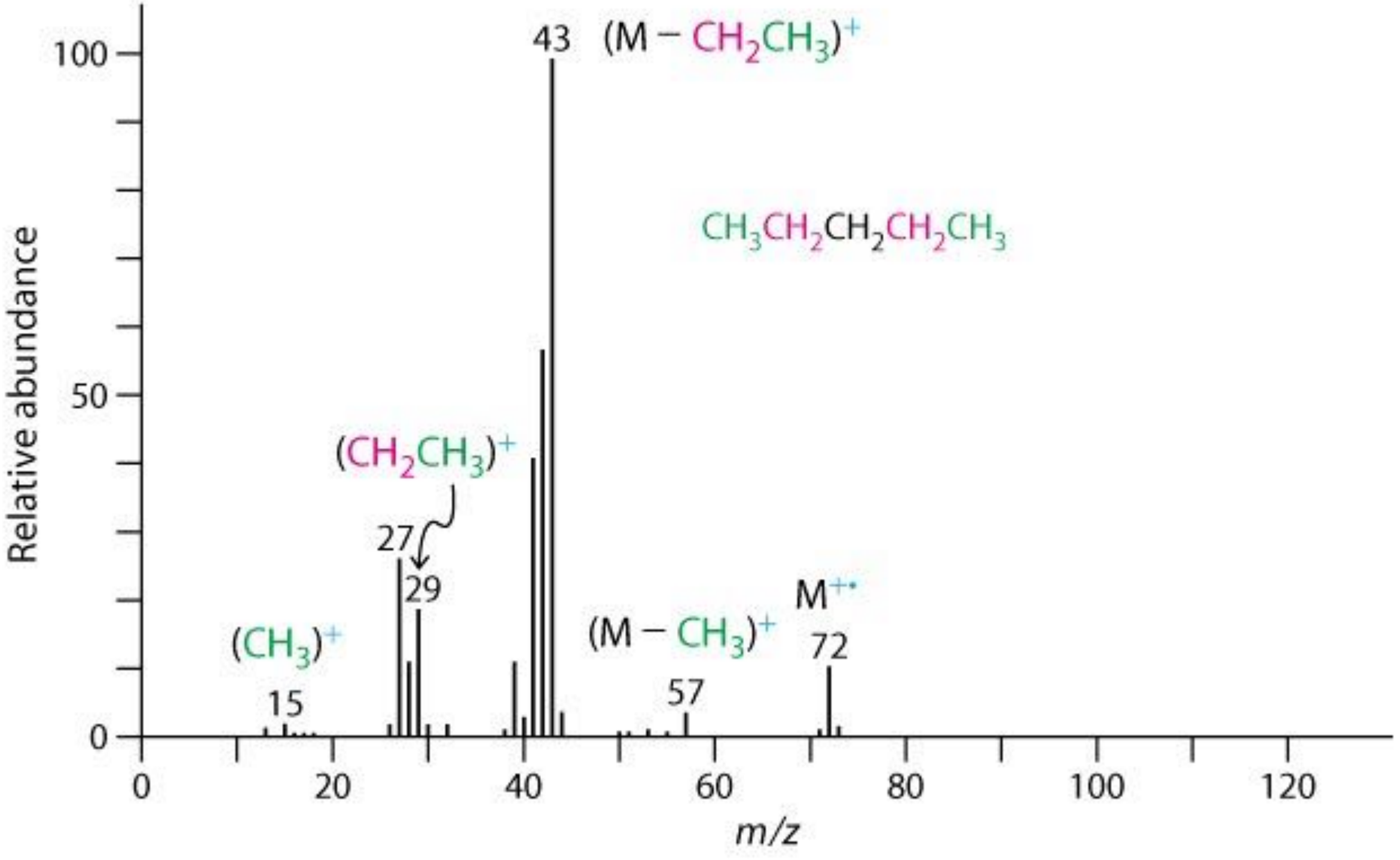
- **Identifier le pic expérimental correspondant à la masse monoisotopique (M*)**
  - **Il s'agit du pic le plus à gauche de la distribution isotopique de la molécule non fragmentée**
- **Calculer la masse monoisotopique de la molécule neutre**
  - **Multiplier la masse par le nombre de charge (z) (on observe m/z en masse)**
  - **Enlever (ou ajouter) la masse de l'ionisation**
- **Observer la distribution isotopique**
  - **Présence / absence de Br, Cl, S ?**
  - **Attention à la charge !**
- **Analyser M* + 1 (ou M* + 1/z si plusieurs fois chargé)**
  - **Présence de N (-6/z mDa) ou de S (-4/z mDa)**
- **Idée du nombre de carbone en fonction de la hauteur relative de l'intensité de M* et du pic en (M* + 1/z)**
- **Calcul de l'erreur sur la masse**
  - **On multiplie la masse observée (M*) par l'erreur en 'ppm' / 10^6**
  - **La valeur obtenue est l'erreur autorisée sur la masse observée**
- **Avec toutes ces informations on obtient un nombre limité de formules brutes possibles**

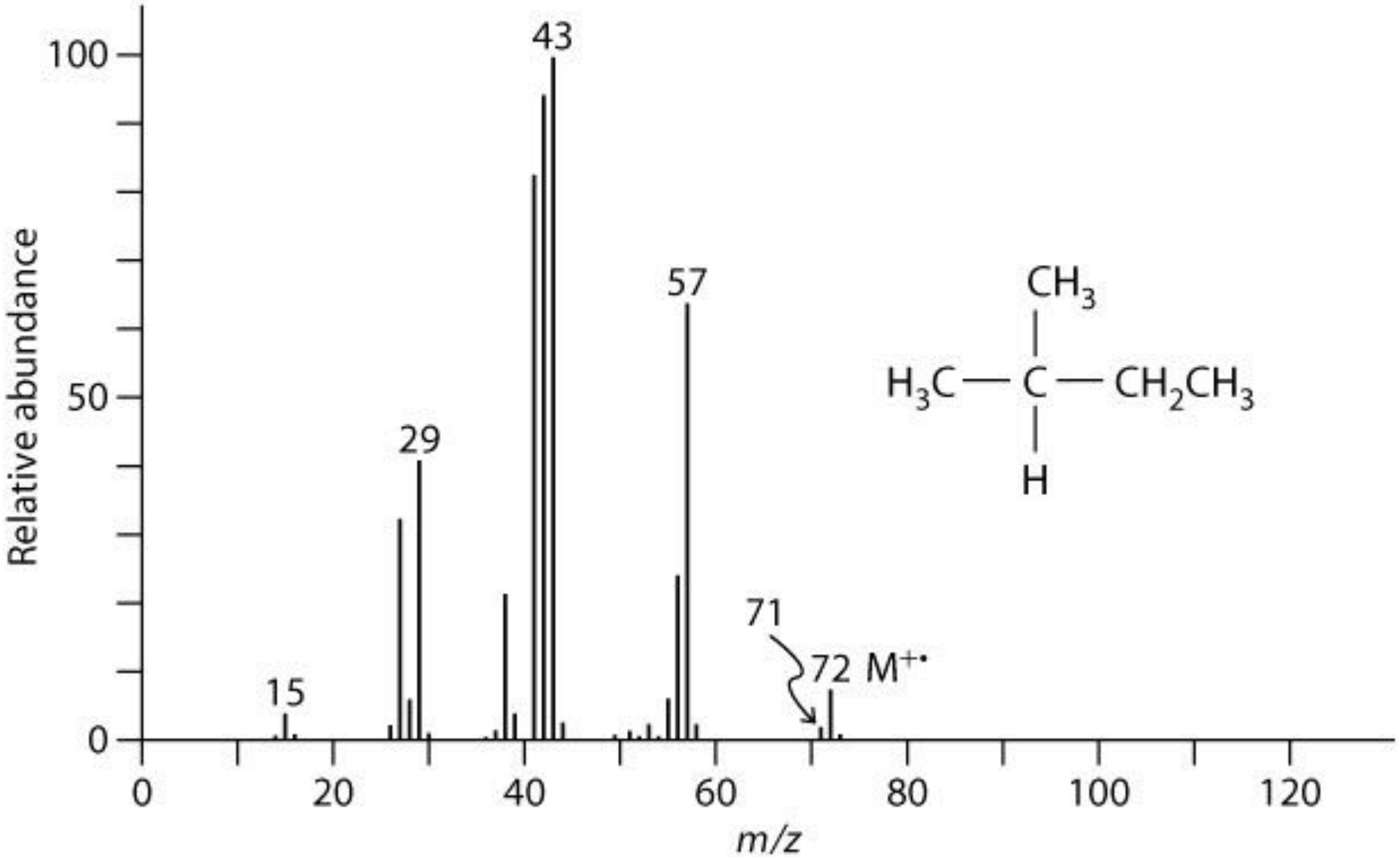
M*: masse expérimentale correspondant à la masse monoisotopique
M: masse monoisotopique correspondant à la molécule neutre

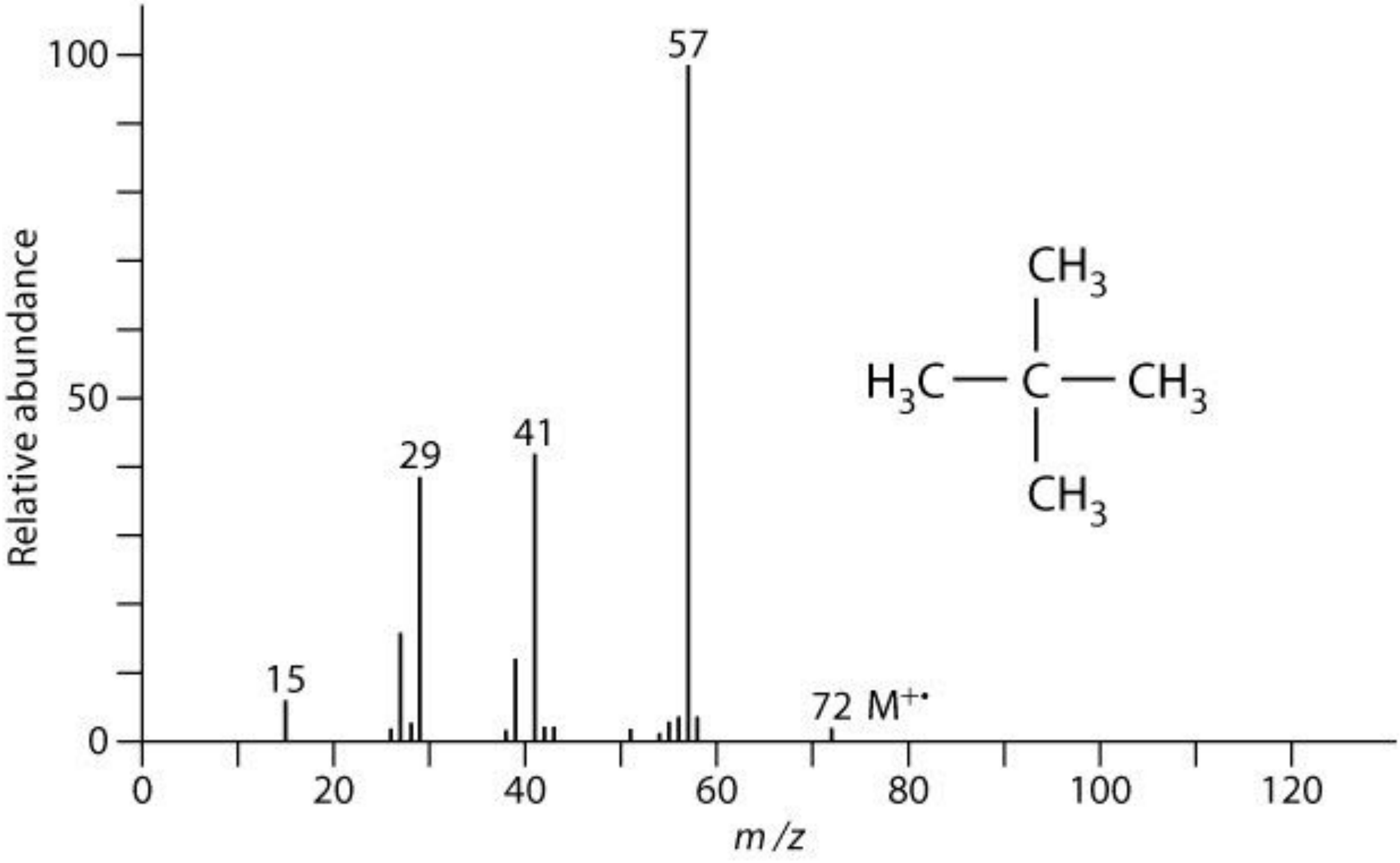
https://spectra.cheminfo.org

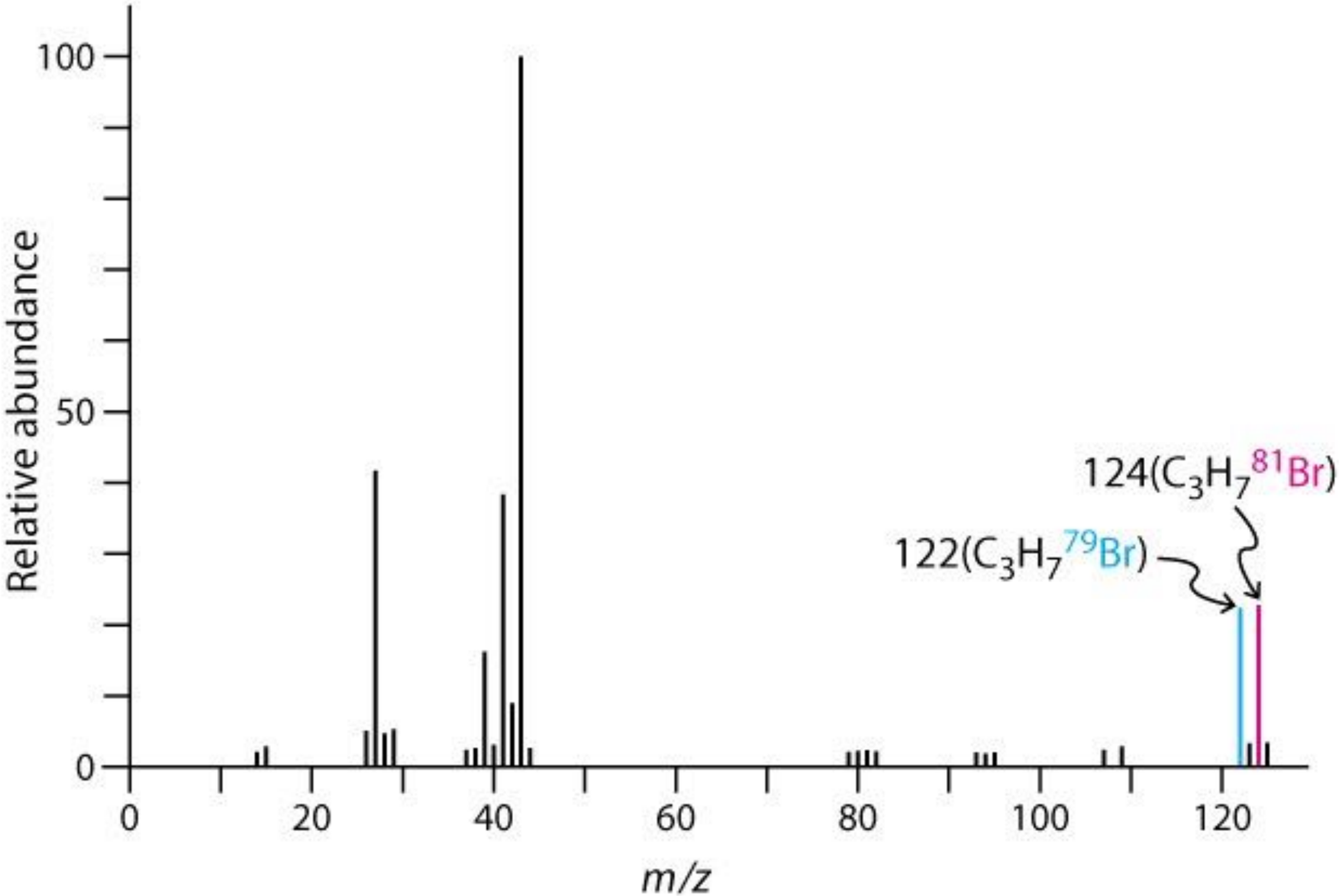
Impact électronique et fragmentation

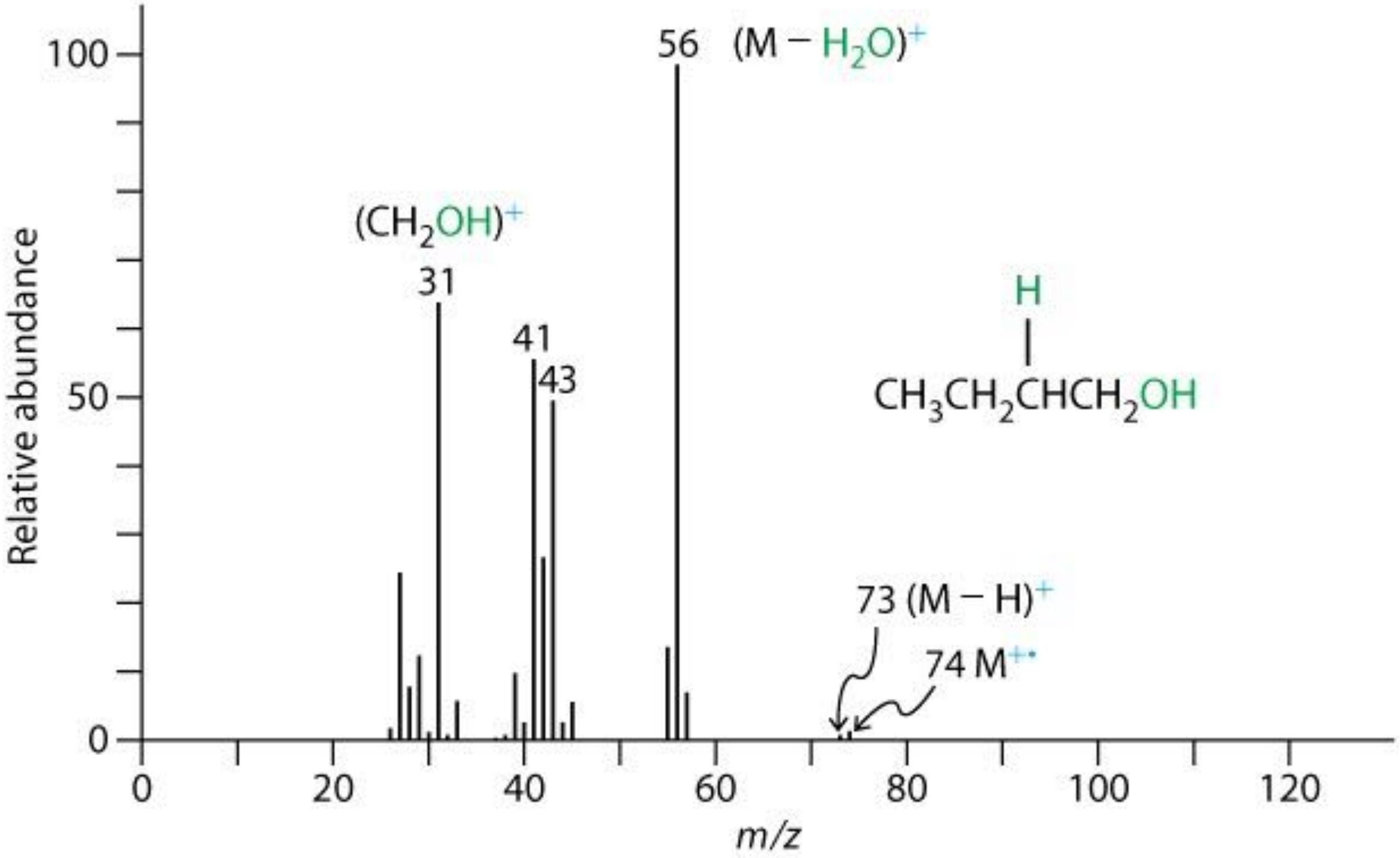
Electron ionization / Electron impact ionization

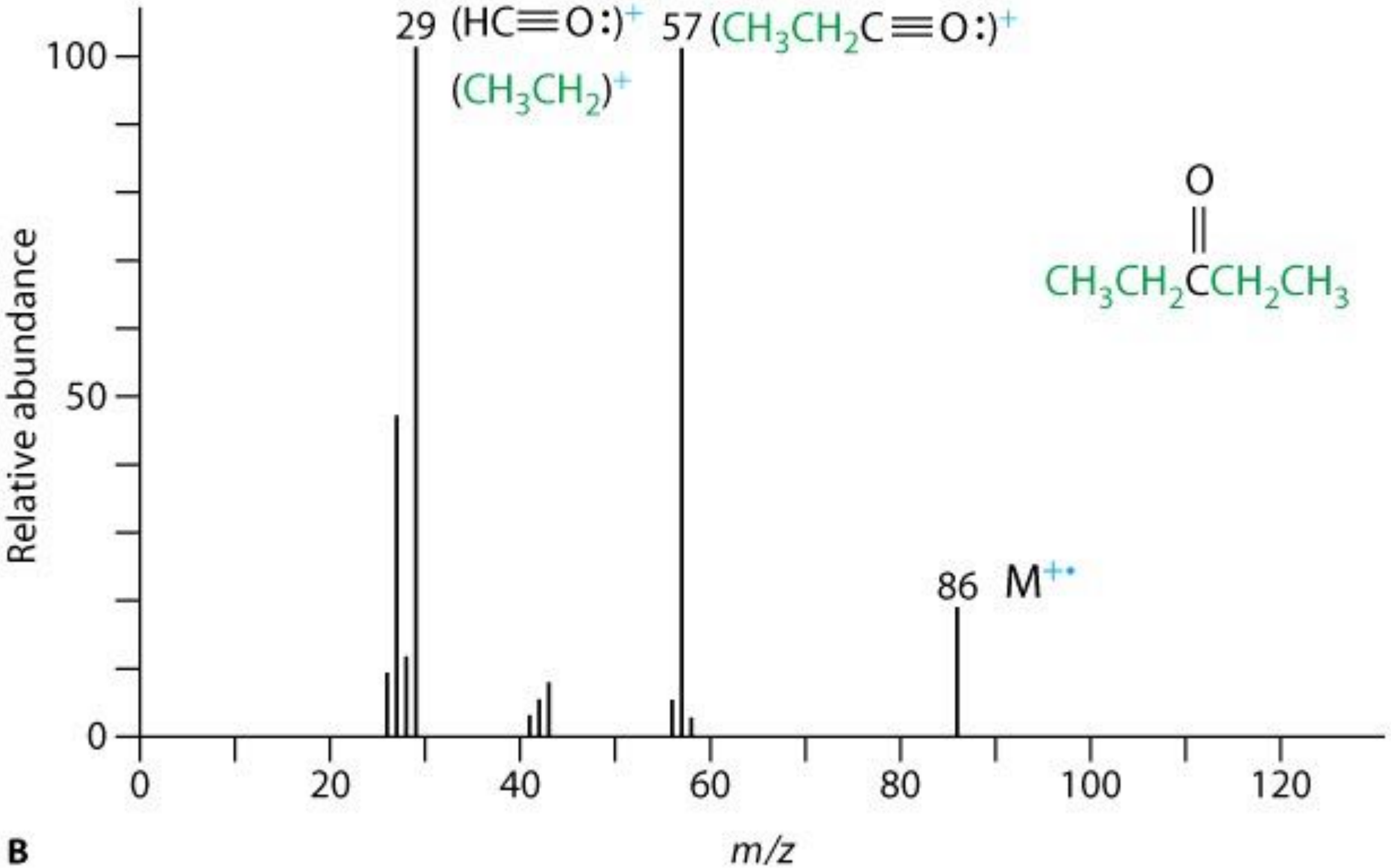

43 (M − CH2CH3)+
CH3CH2CH2CH2CH3
(CH2CH3)+
27
29
(CH3)+
15
(M − CH3)+
57
M+•
72
Relative abundance
100
50
0
0
20
40
60
80
100
120
m/z


Relative abundance
100
50
0
43
57
29
15
71
72 M+•
0
20
40
60
80
100
120
m/z
CH3
H3C — C — CH2CH3
H

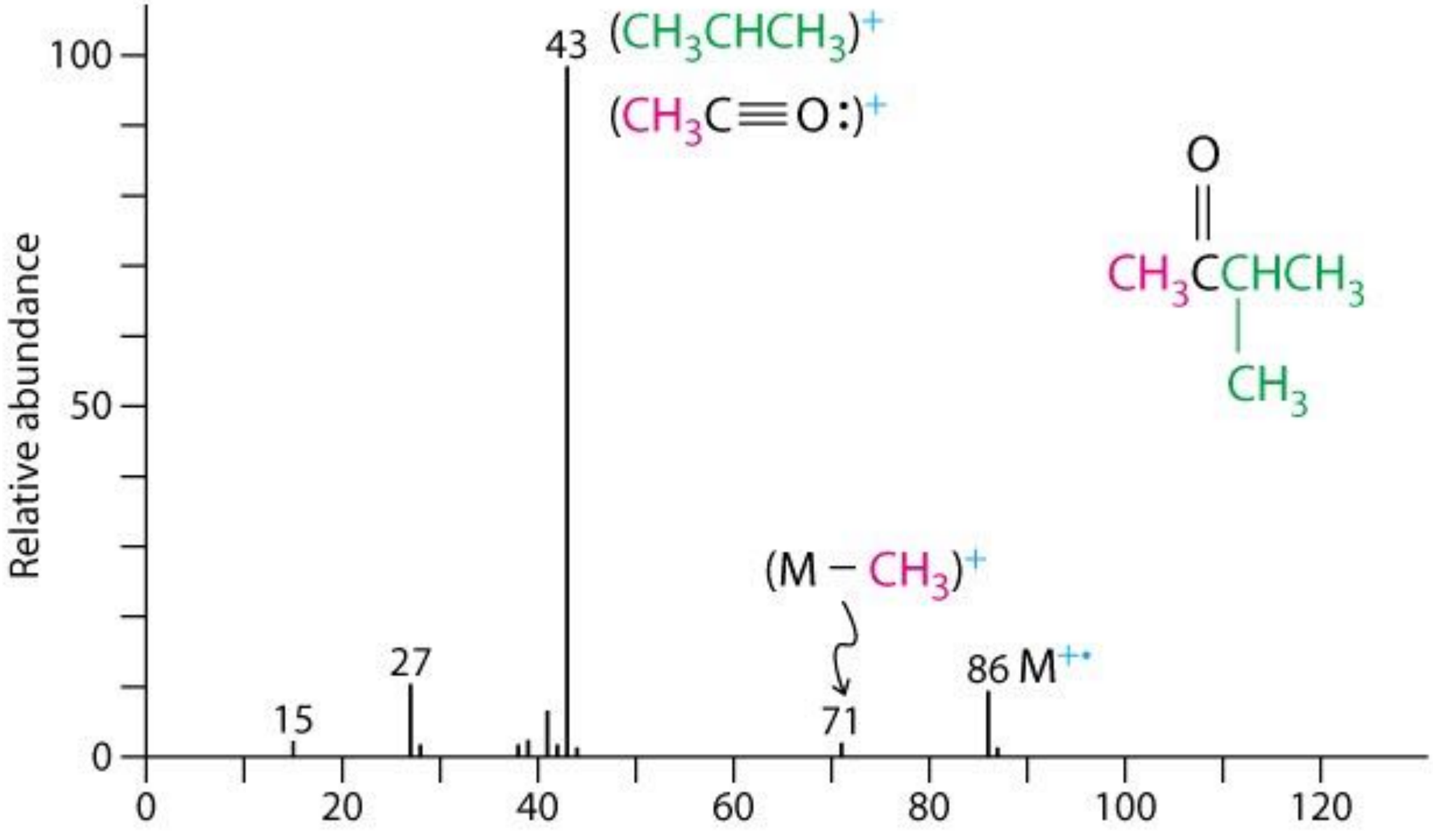

100
50
0
Relative abundance
57
41
29
15
72 M+•
0
20
40
60
80
100
120
m/z
CH3
H3C — C — CH3
CH3


Relative abundance
100
50
0
0
20
40
60
80
100
120
m/z
124(C3H7 81Br)
122(C3H7 79Br)

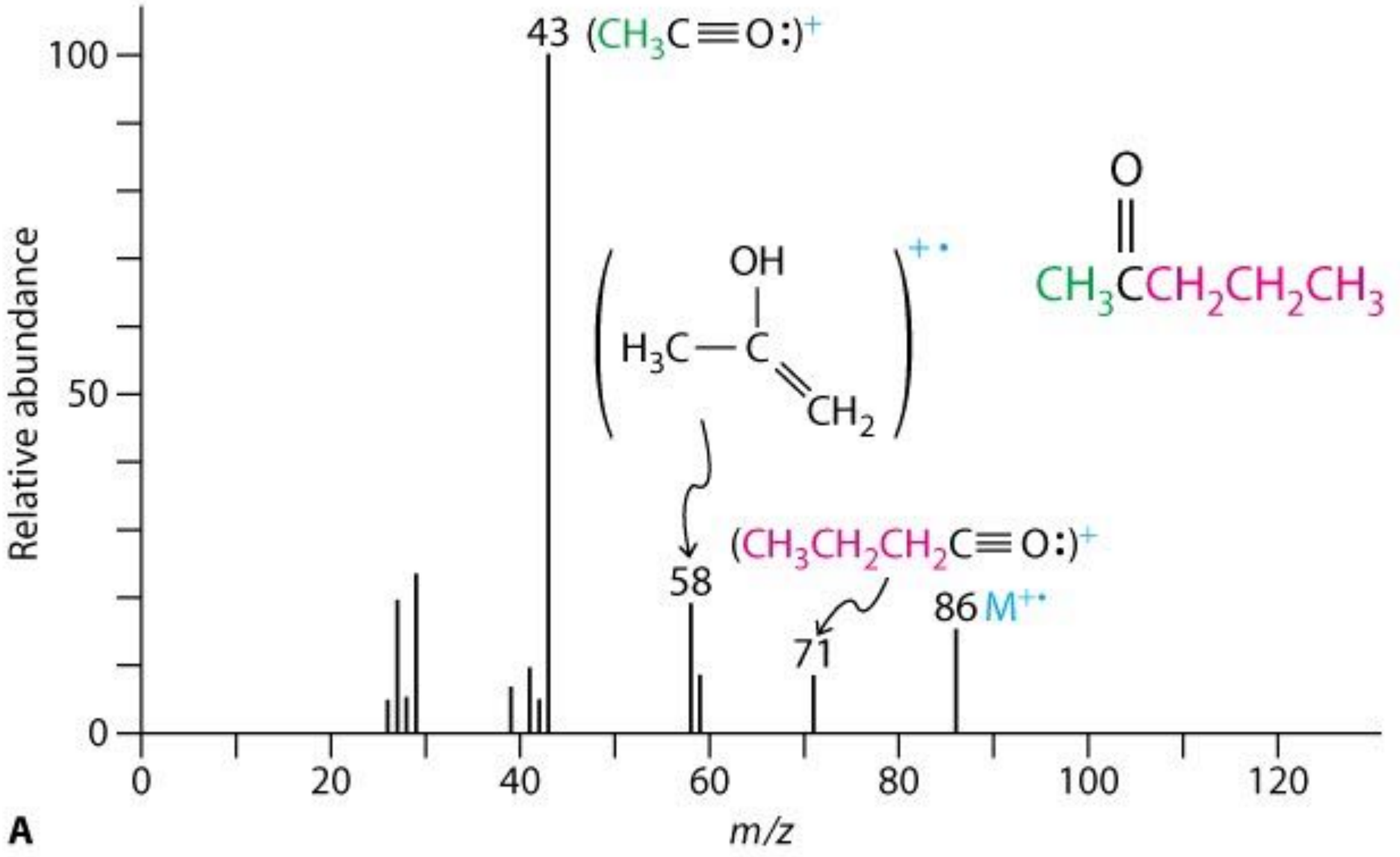

100
50
0
Relative abundance
0
20
40
60
80
100
120
m/z
56 (M − H2O)+
(CH2OH)+
31
41
43
73 (M − H)+
74 M+•
H
CH3CH2CHCH2OH


29 (HC≡O:)+
(CH3CH2)+
57 (CH3CH2C≡O:)+
O
CH3CH2CCH2CH3
86 M+•
100
50
0
Relative abundance
0
20
40
60
80
100
120
m/z

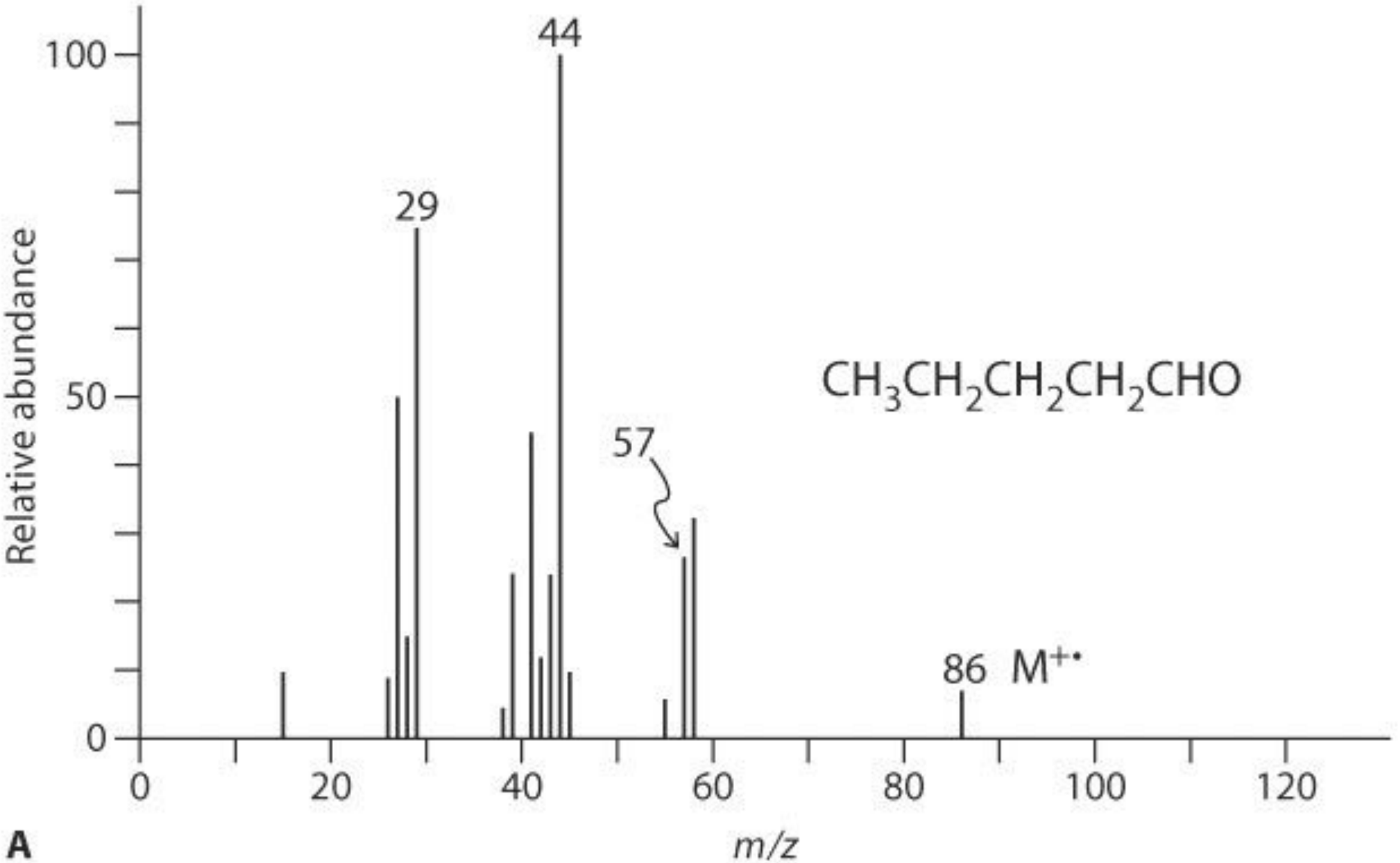
B


100
50
0
Relative abundance
43
$(CH_3CHCH_3)^+$
$(CH_3C{\equiv}O:)^+$
O
CH_3CCHCH_3
CH_3
$(M - CH_3)^+$
27
15
71
86 $M^{+\bullet}$
0
20
40
60
80
100
120
m/z

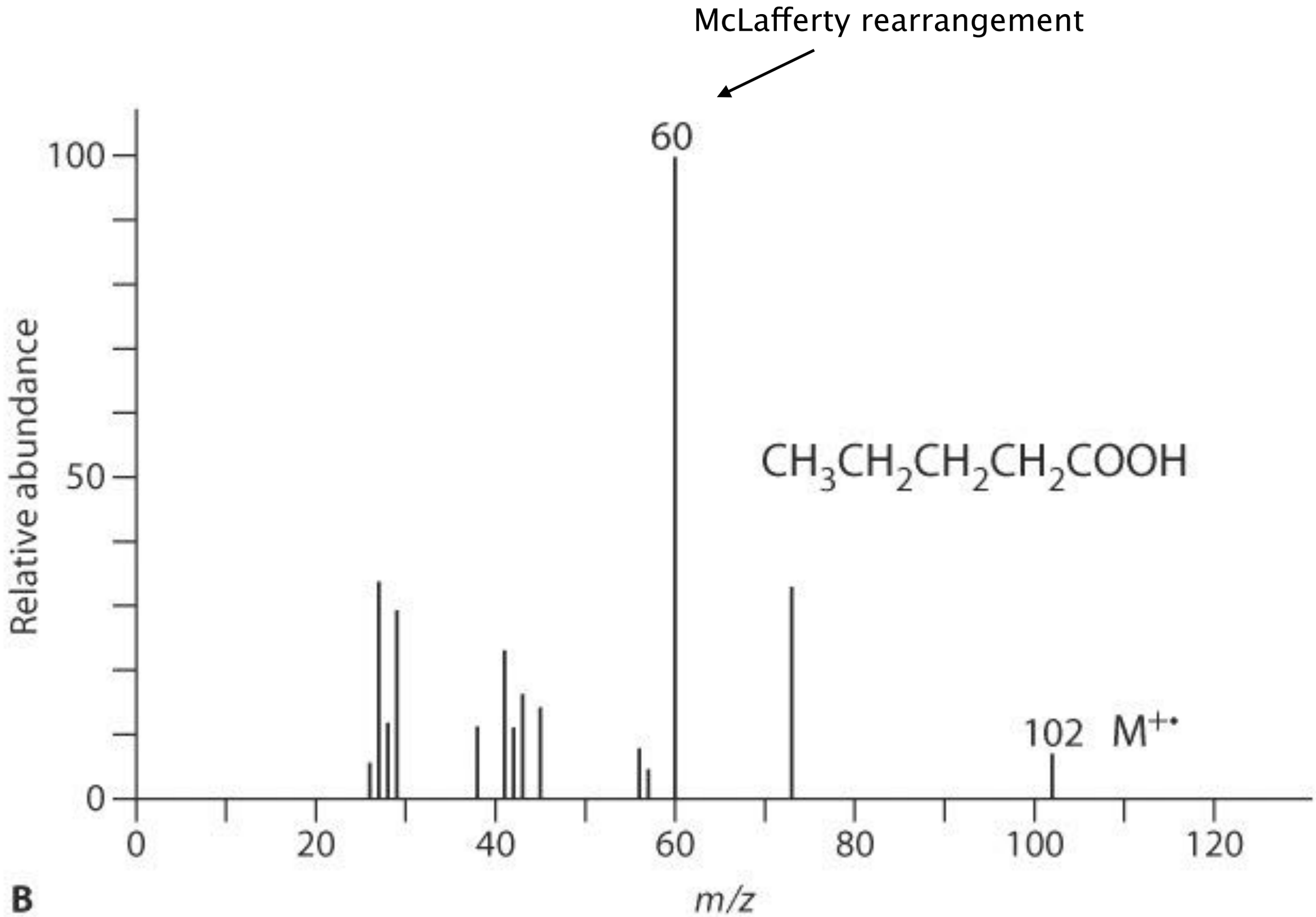
c


43 $(CH_3C{\equiv}O:)^+$
OH
H_3C-C
CH_2
$^{+\bullet}$
O
$CH_3CCH_2CH_2CH_3$
$(CH_3CH_2CH_2C{\equiv}O:)^+$
58
71
86 $M^{+\bullet}$
Relative abundance
100
50
0
0
20
40
60
80
100
120
m/z

A


Relative abundance
100
50
0
0
20
40
60
80
100
120
m/z
44
29
57
86 M+•
CH3CH2CH2CH2CHO

A


McLafferty rearrangement
60
100
50
0
Relative abundance
$CH_3CH_2CH_2CH_2COOH$
102 $M^{+\bullet}$
0
20
40
60
80
100
120
m/z

B

Quelques masses importantes

Δ m	Assignation
15	Methyl
29	Ethyl / CHO
43	Propyl / CH3CO
57	Butyl / CH3CH2CO
77	Phenyl
91	Benzyl
18	Perte H_2O: alcool
60	$CH_2C(OH)_2$: acide carboxylique
35 / 37	Cl
79 / 81	Br

https://webbook.nist.gov/chemistry/

https://spectra.cheminfo.org

The Encyclopedia of Mass Spectrometry
Volume 9: Historical Perspectives, Part A: The Development of Mass Spectrometry
2016, Pages 271-284

A History of the Forensic Applications of Mass Spectrometry

Glen P. Jackson, Mark A. Barkett

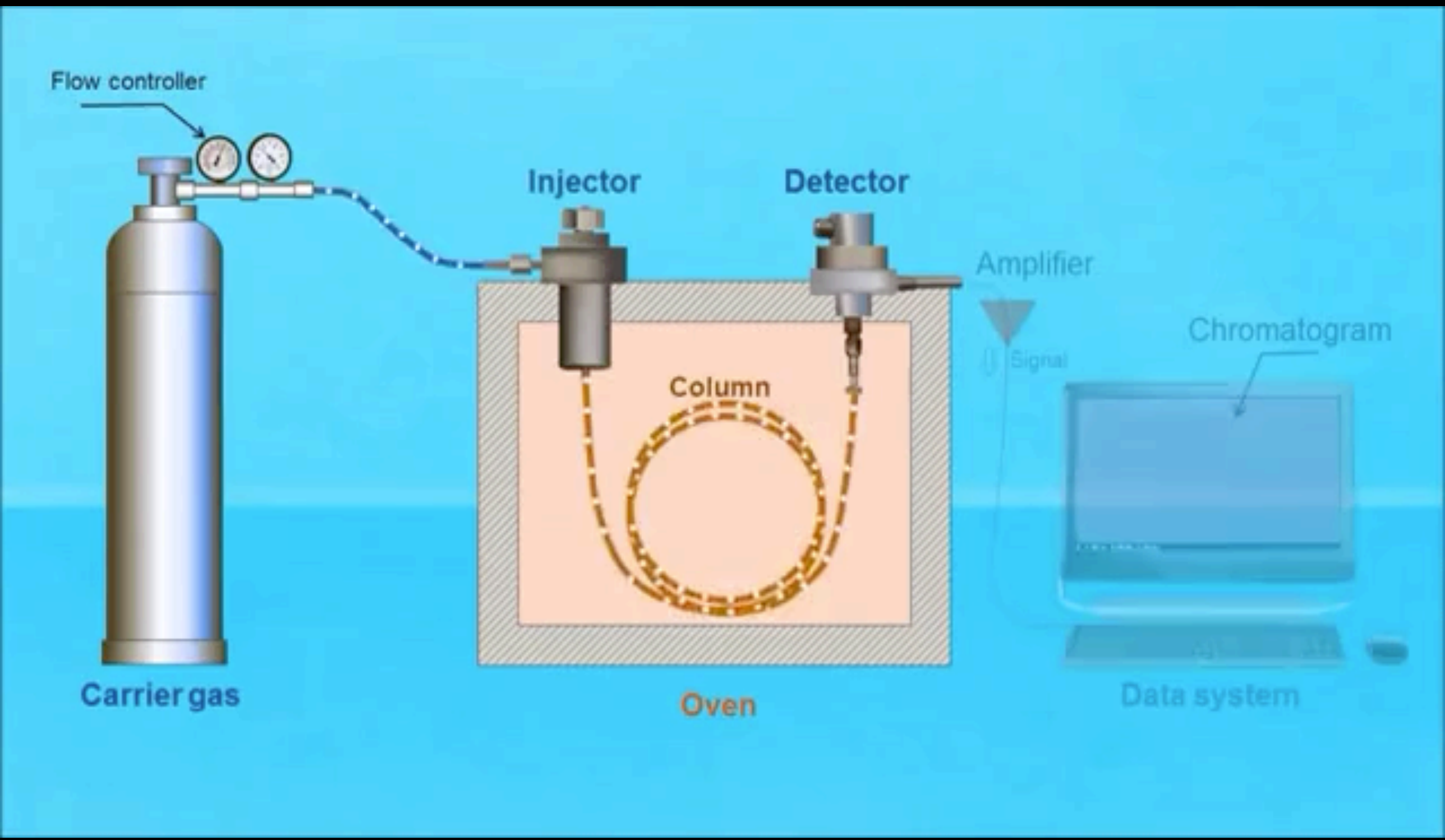
Mass spectrometry occupies a prominent role in the historical evolution of the instrumental analysis of forensic evidence. Most forensic evidence submissions are scheduled drugs, and mass spectrometry, combined with gas chromatography, has provided the gold standard in drug identification for decades. In the earliest ‘forensic’ applications in the 1950s and 1960s, mass spectrometry was used to help identify the elemental compositions and structures of natural products/drugs such as the cannabinoids and tropane alkaloids.

DOI:10.1016/B978-0-08-043848-1.00040-7

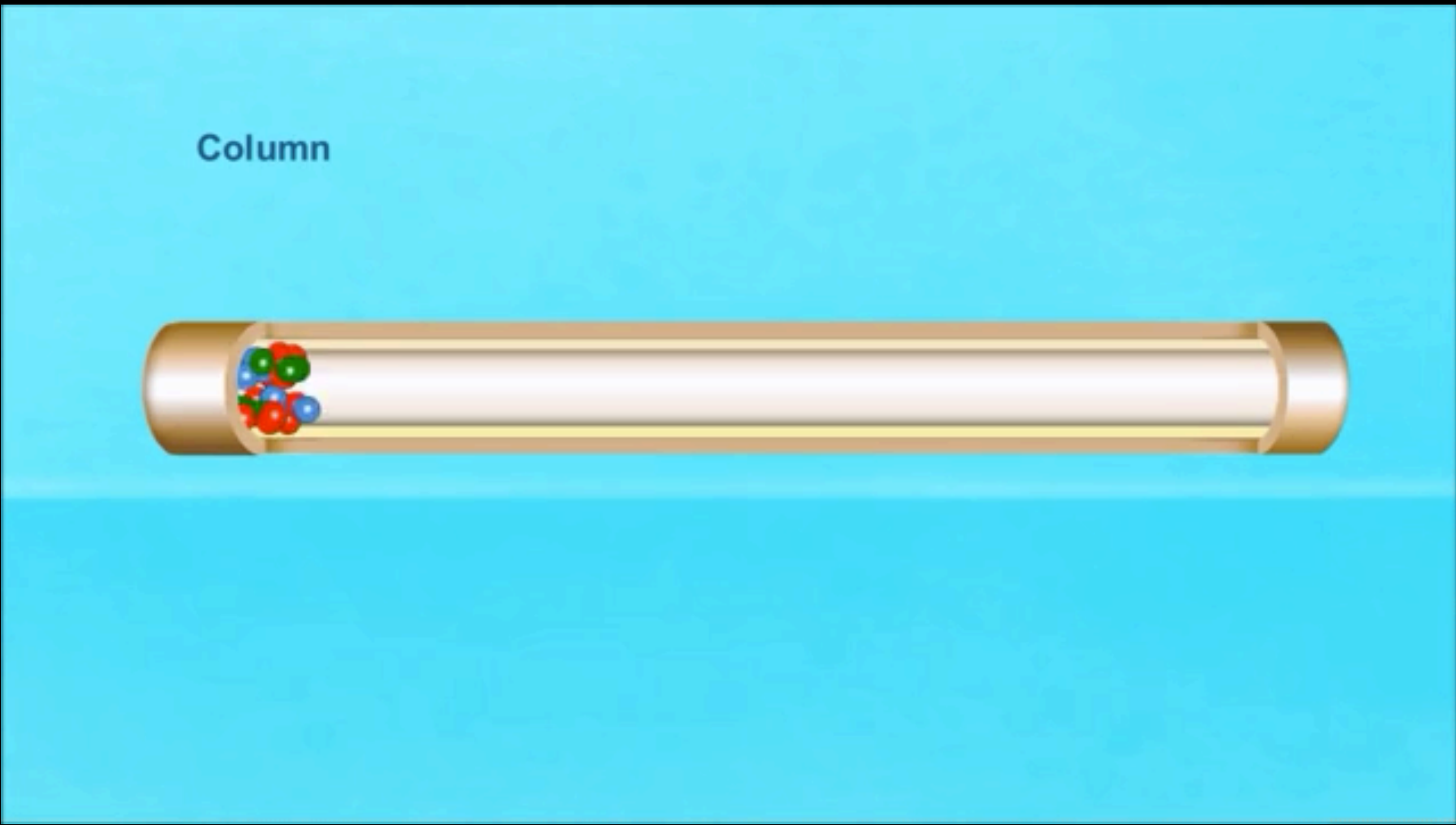
GC-MS

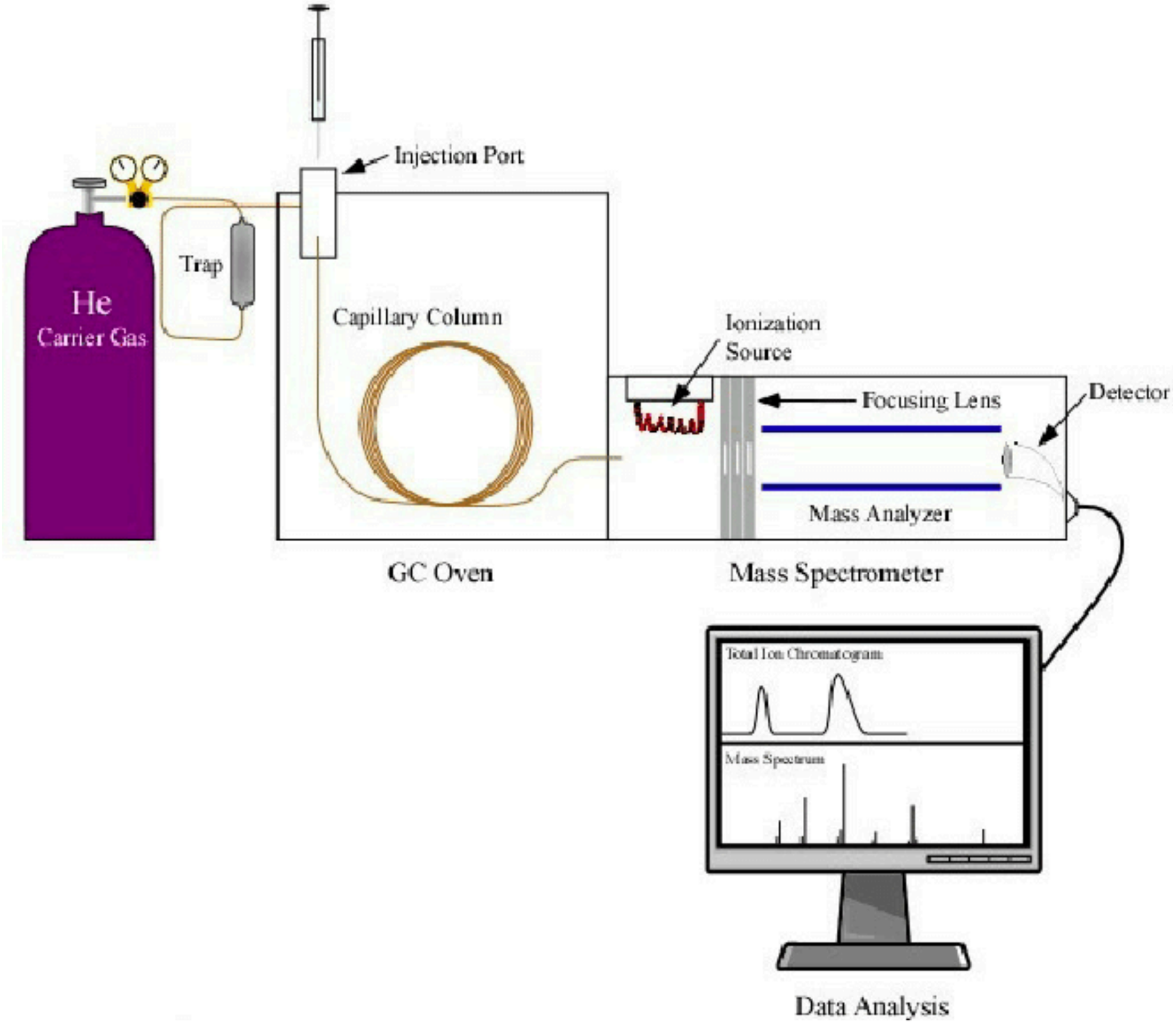
Gas chromatography / Mass spectrometry

Chromatography

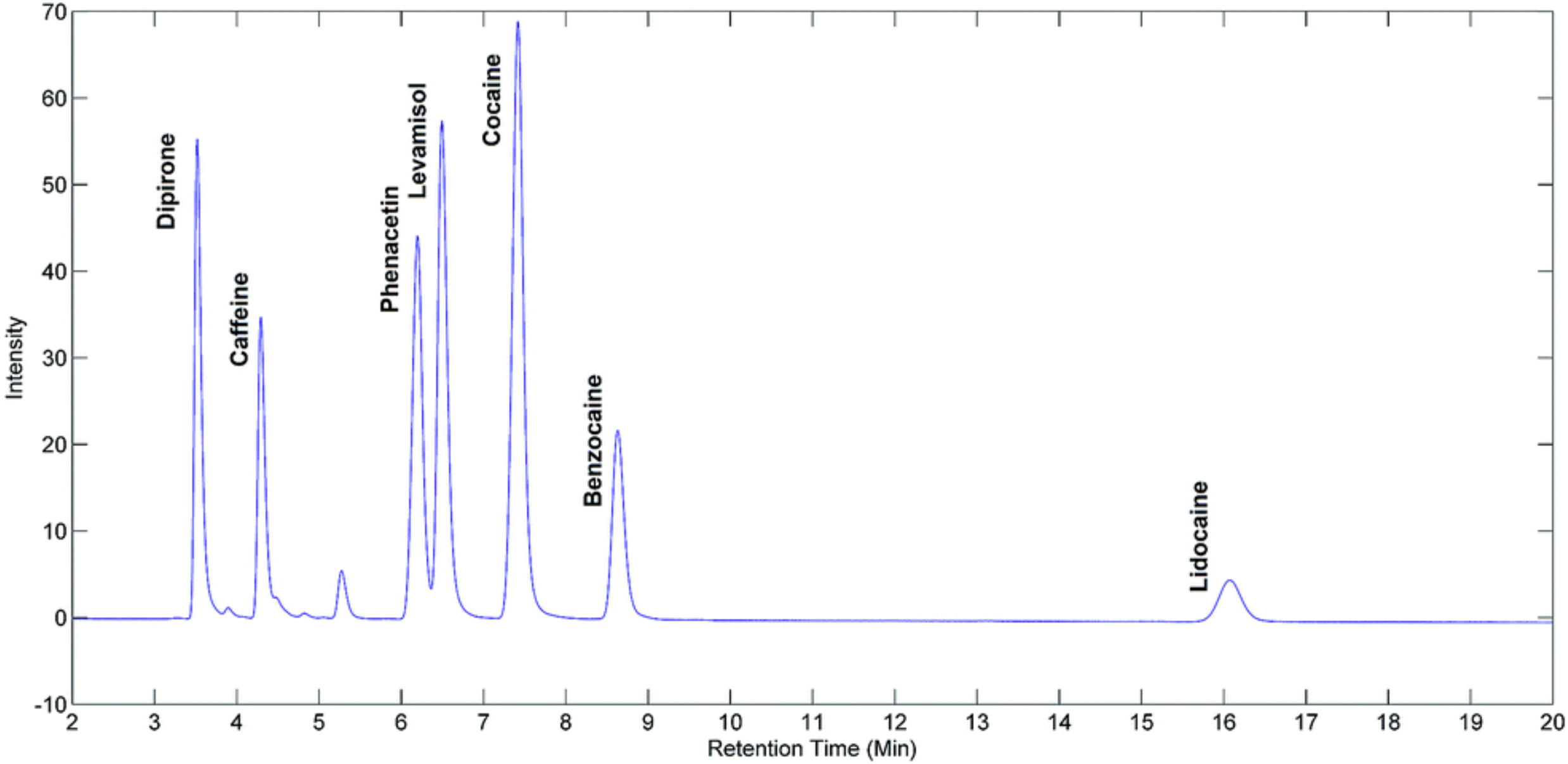


Chromatography column




Injection Port
Trap
He
Carrier Gas
Capillary Column
Ionization
Source
Focusing Lens
Detector
Mass Analyzer
GC Oven
Mass Spectrometer
Total Ion Chromatogram
Mass Spectrum
Data Analysis

EI/CI-1200L (Varian)


Dipirone
Caffeine
Phenacetin
Levamisol
Cocaine
Benzocaine
Lidocaine
Intensity
Retention Time (Min)
70
60
50
40
30
20
10
0
-10
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Demo

Degré d'insaturation (DBE)

"Double bond equivalent"

Nombre de liaisons "pi" + nombre de cycles

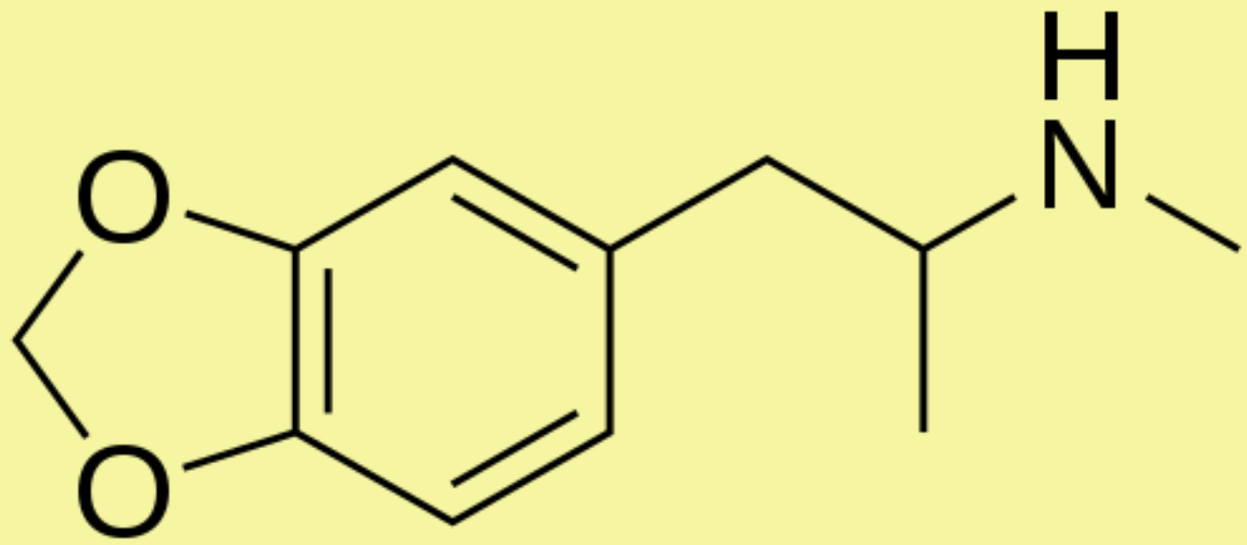
Nombre de H_2 à ajouter pour avoir une molécule acyclique saturée

https://spectra.cheminfo.org

Isomères de structure

GDB-11 GDB-13 GDB-17

https://gdb.unibe.ch/downloads/



https://spectra.cheminfo.org

Data workflow

STORE

DB

EXTRACT KNOWLEDGE

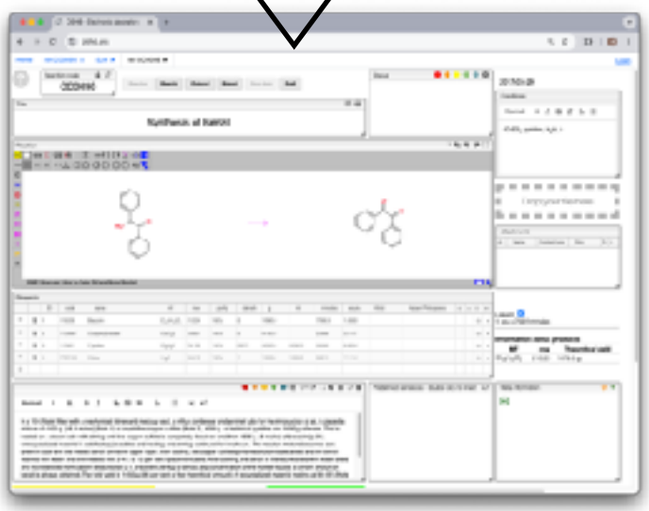
Comparison
Similarity
Machine learning

RETRIEVE

SHARE

Reporting
Patent
Export data
Zenodo (FAIR)
API / Python
...

ELN



PROCESS

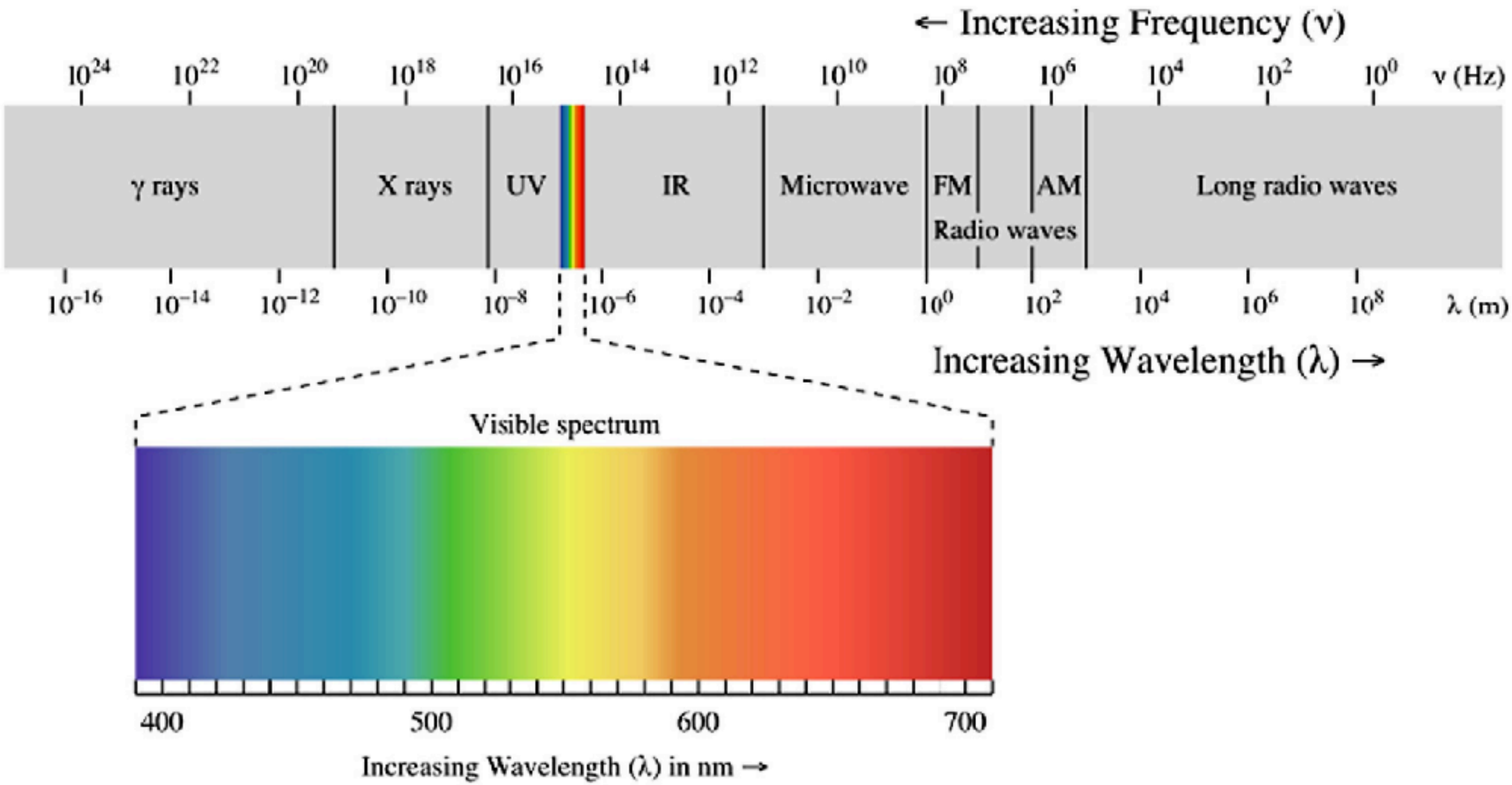
NMR spectra
Mass analysis
Image analysis

https://eln.epfl.ch

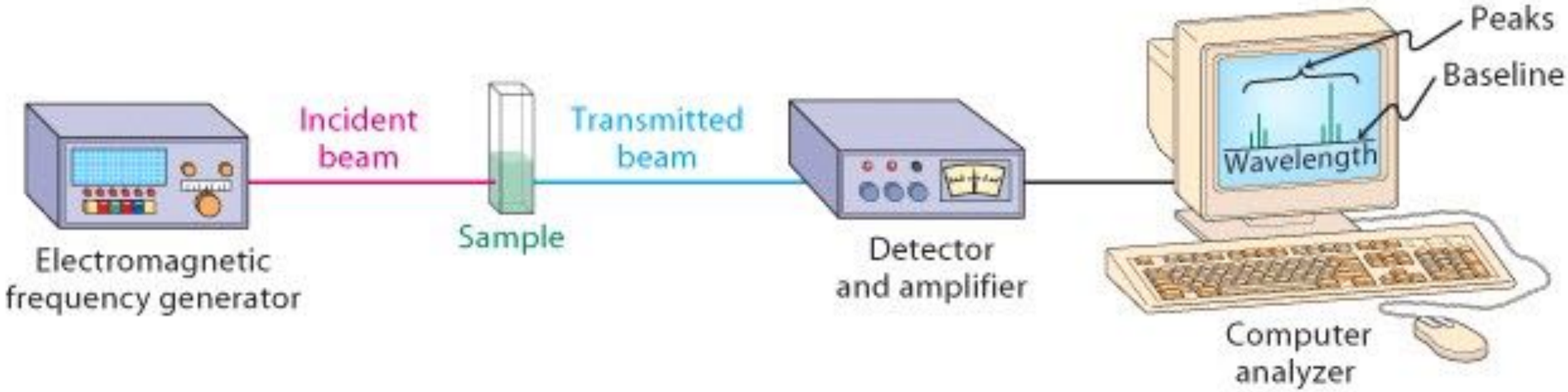
https://demo.scipeaks.com

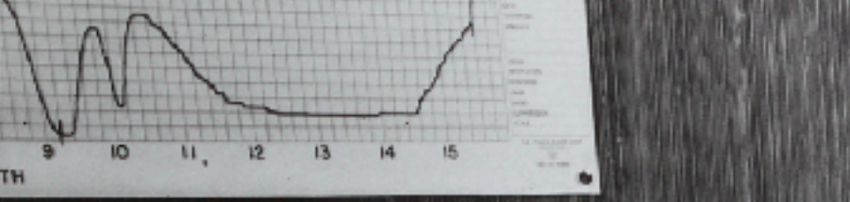
Spectroscopie infrarouge

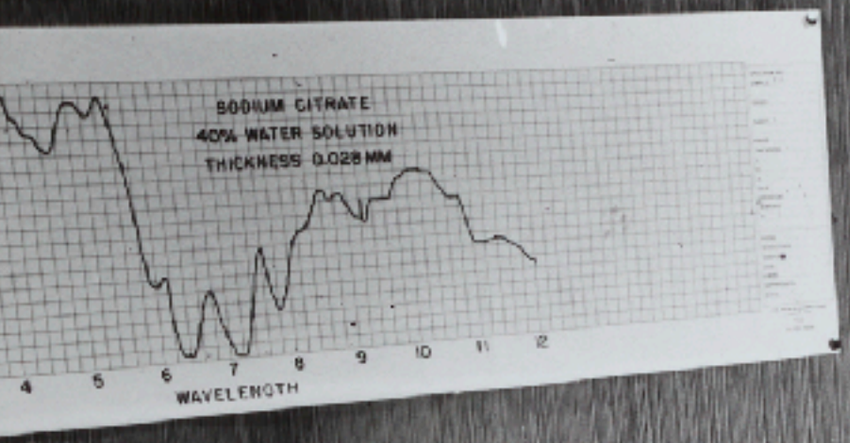
Electromagnetic spectrum



IR spectrophotometer

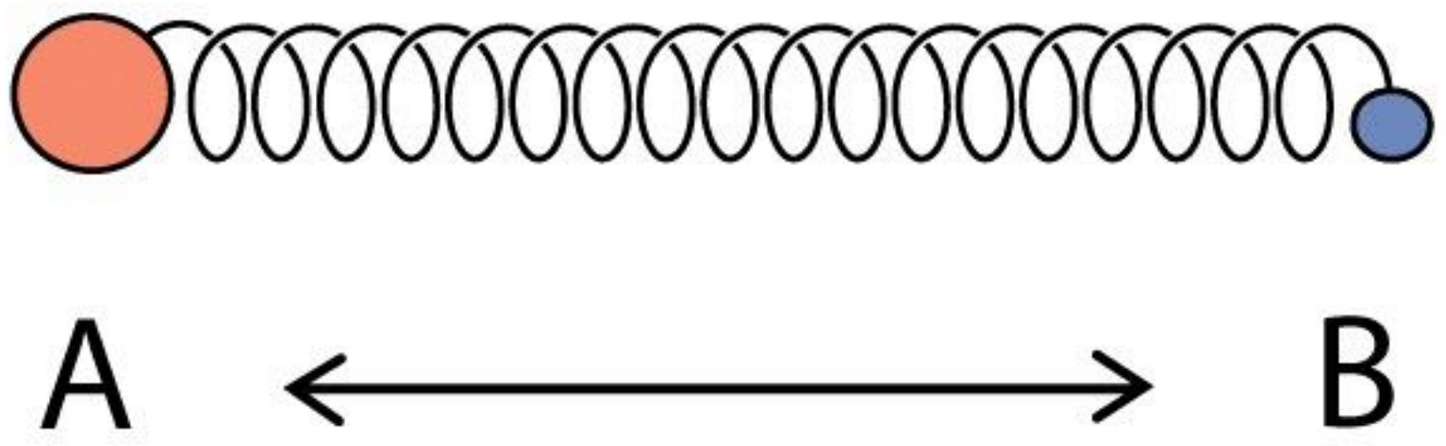



9 10 11 12 13 14 15
TH


SODIUM CITRATE
40% WATER SOLUTION
THICKNESS 0.028 MM
4 5 6 7 8 9 10 11 12
WAVELENGTH

IR of ethylbenzene

Loi de Hooke



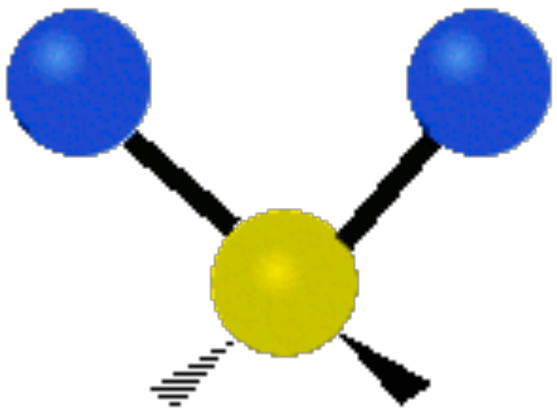
Frequency (v)

$$\overline{v} = \frac{1}{2\pi}\sqrt{f\frac{m_1 + m_2}{m_1 m_2}}$$

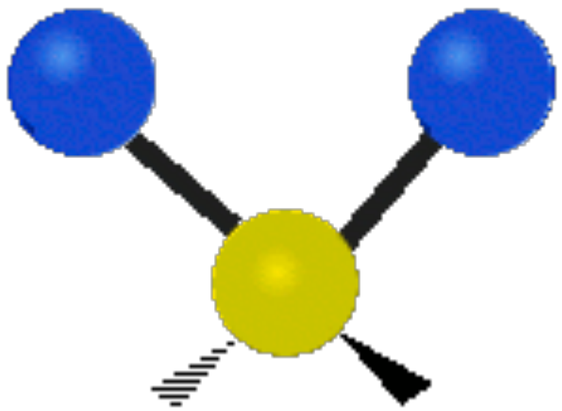
$$\overline{\nu} = \frac{1}{\lambda} = k\sqrt{f\frac{m_1 + m_2}{m_1 m_2}}$$

Vibrations moléculaires

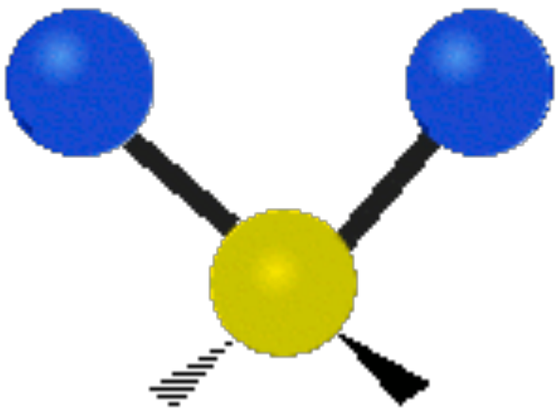
Vibrations moléculaires



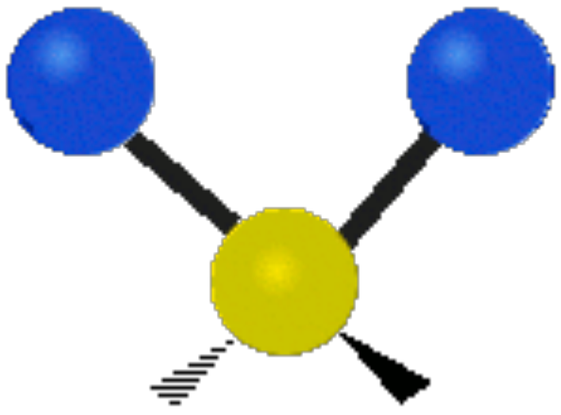
Symmetrical stretching



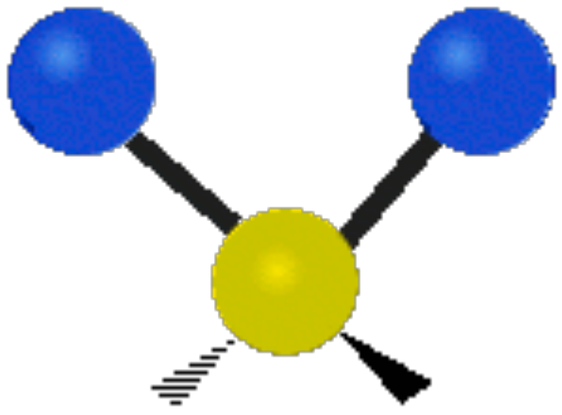
Scissoring



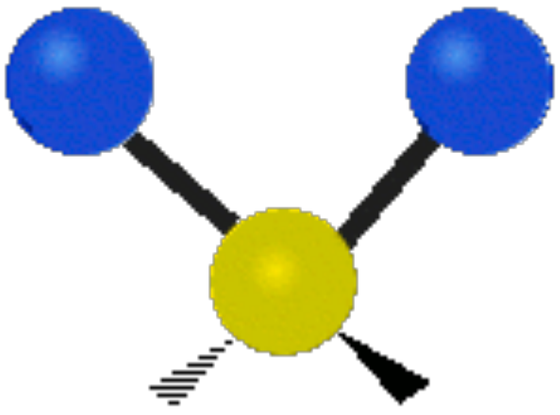
Wagging



Asymmetrical stretching



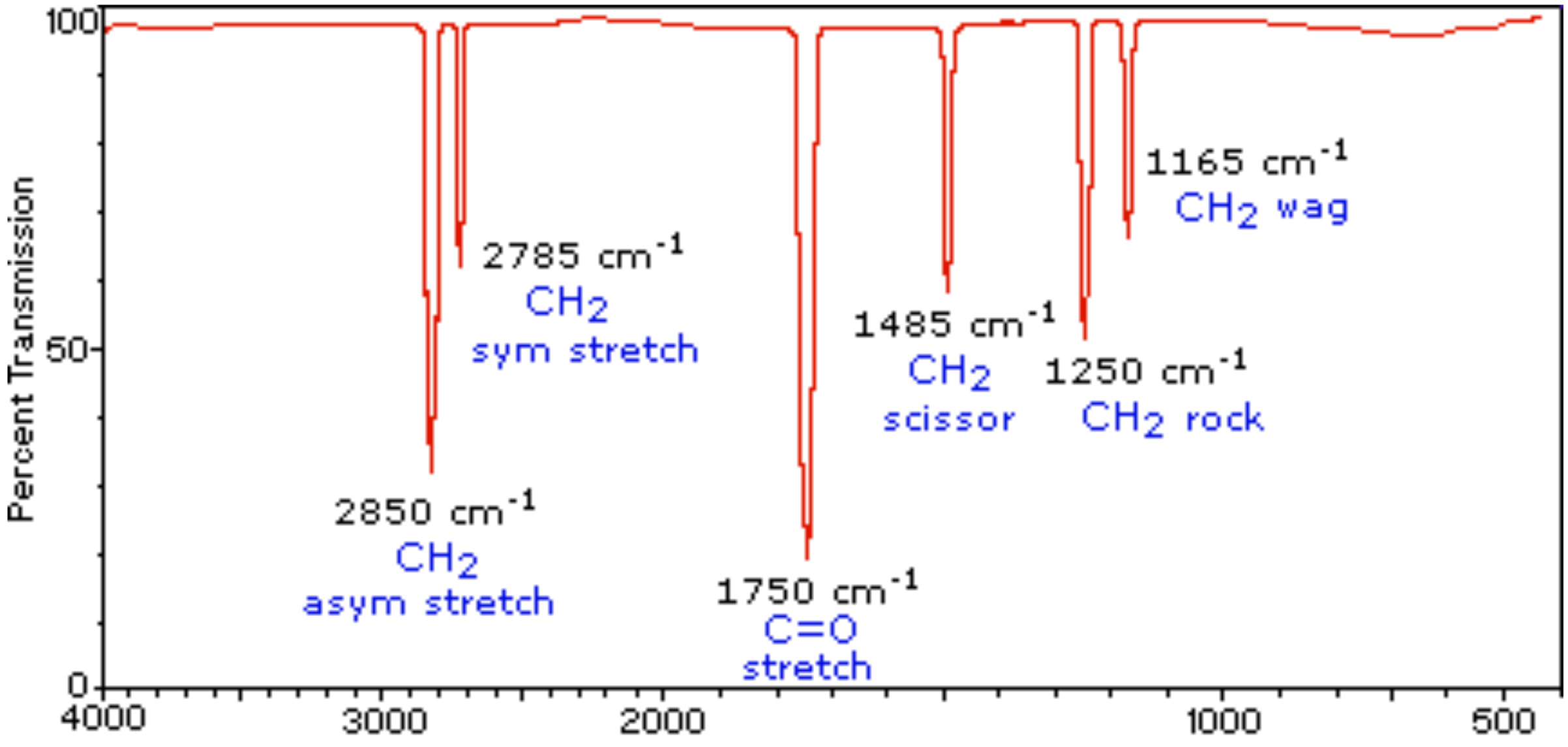
Rocking



Twisting

Images from wikipedia

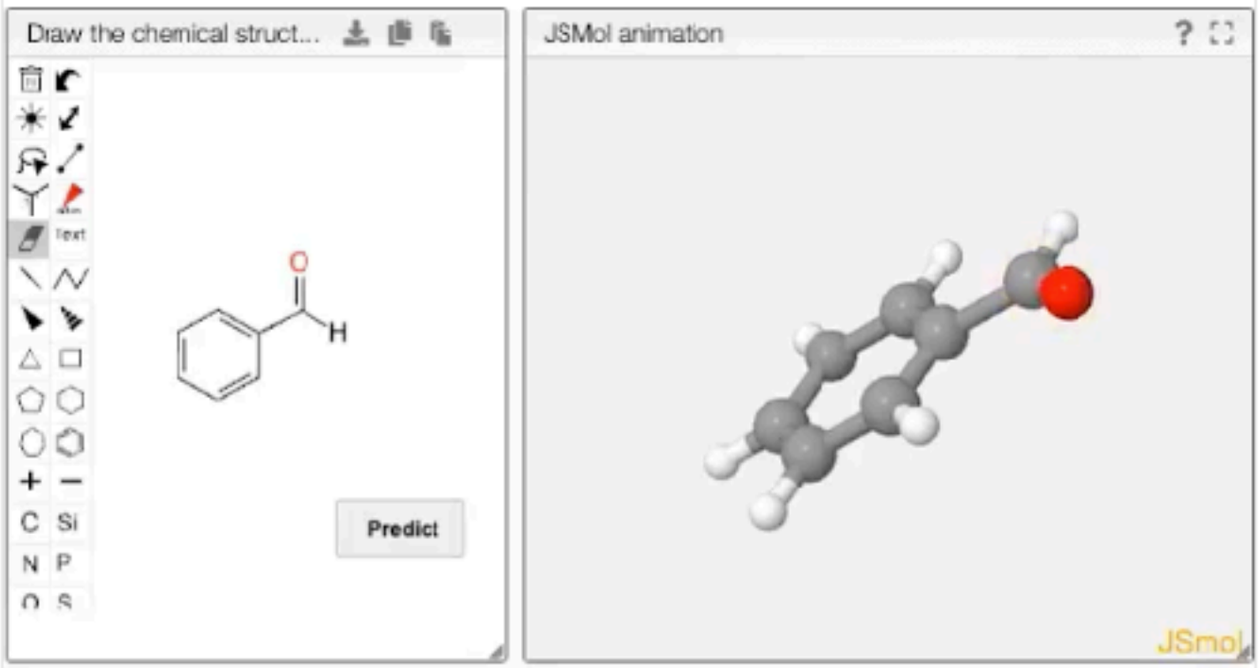
Formaldehyde

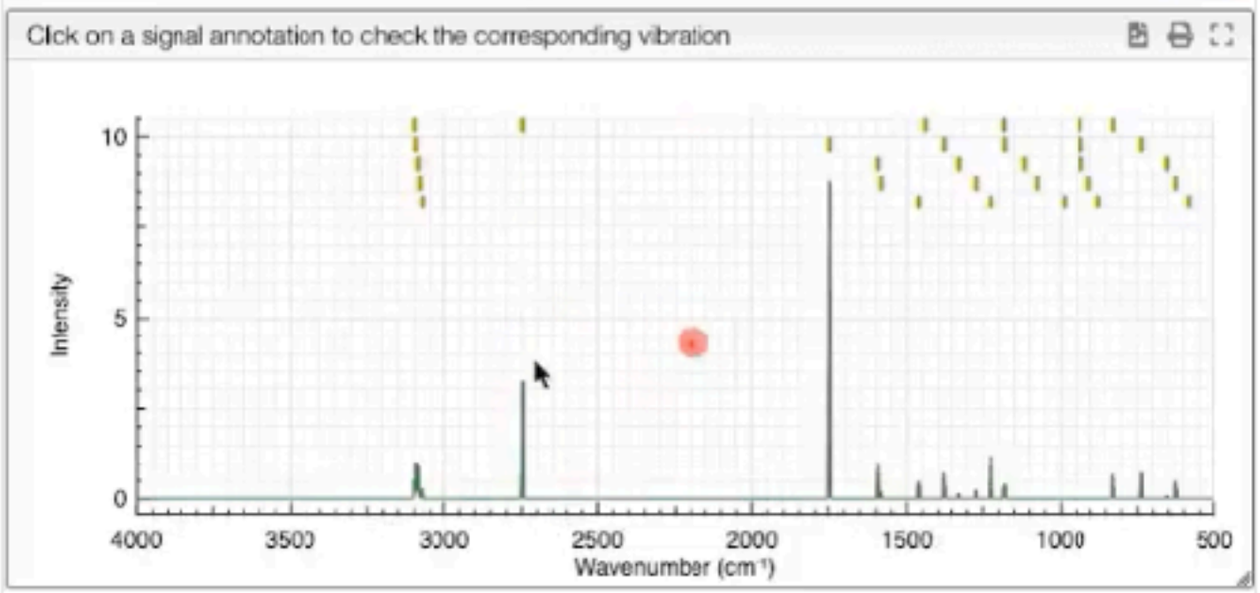


Luc Patiny · You
Chief Scientific Officer at Zakodium
2yr ·

Would you like to finally understand infrared spectroscopy ?
Are you teaching IR spectroscopy or organic chemistry ?

...see more





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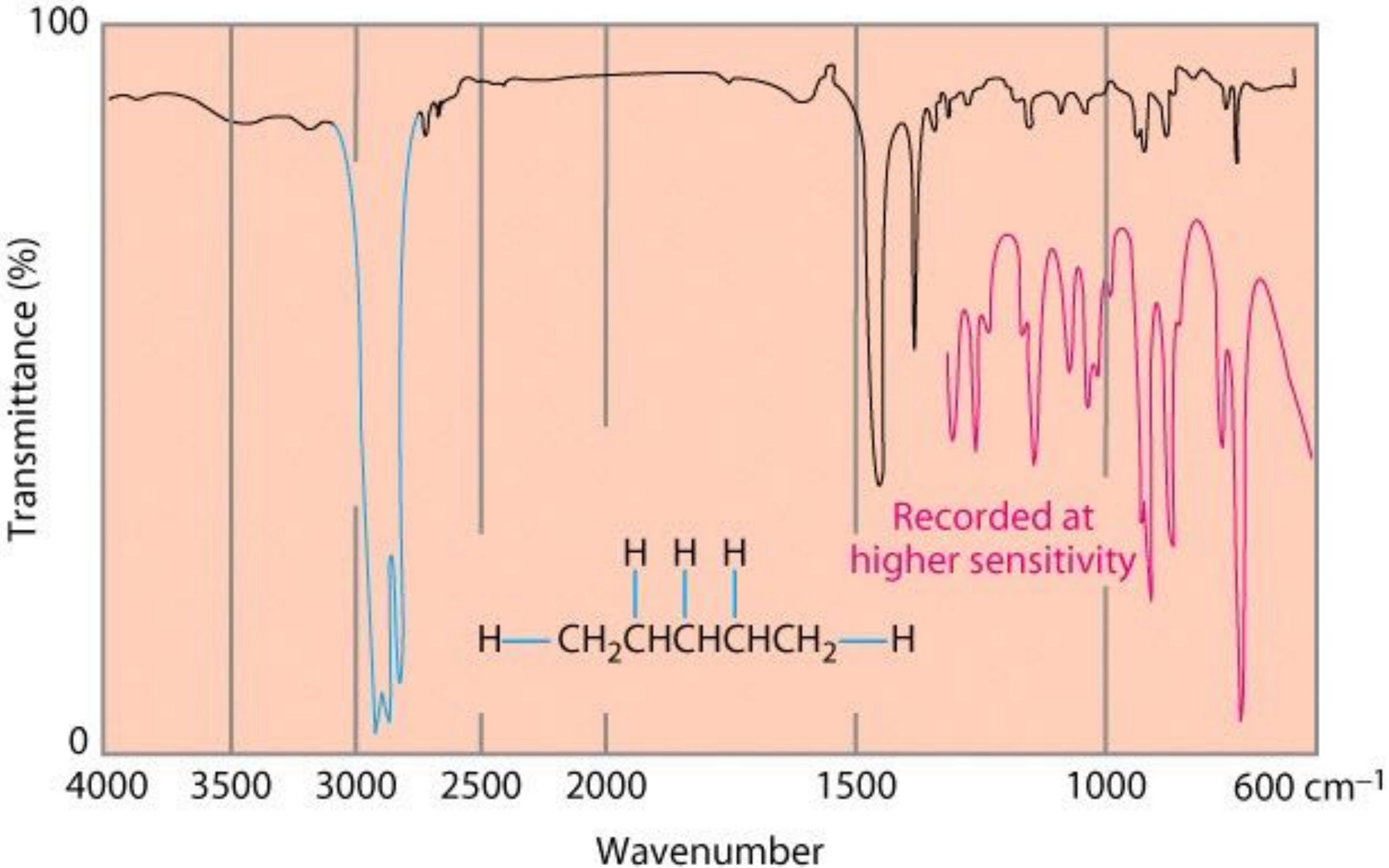
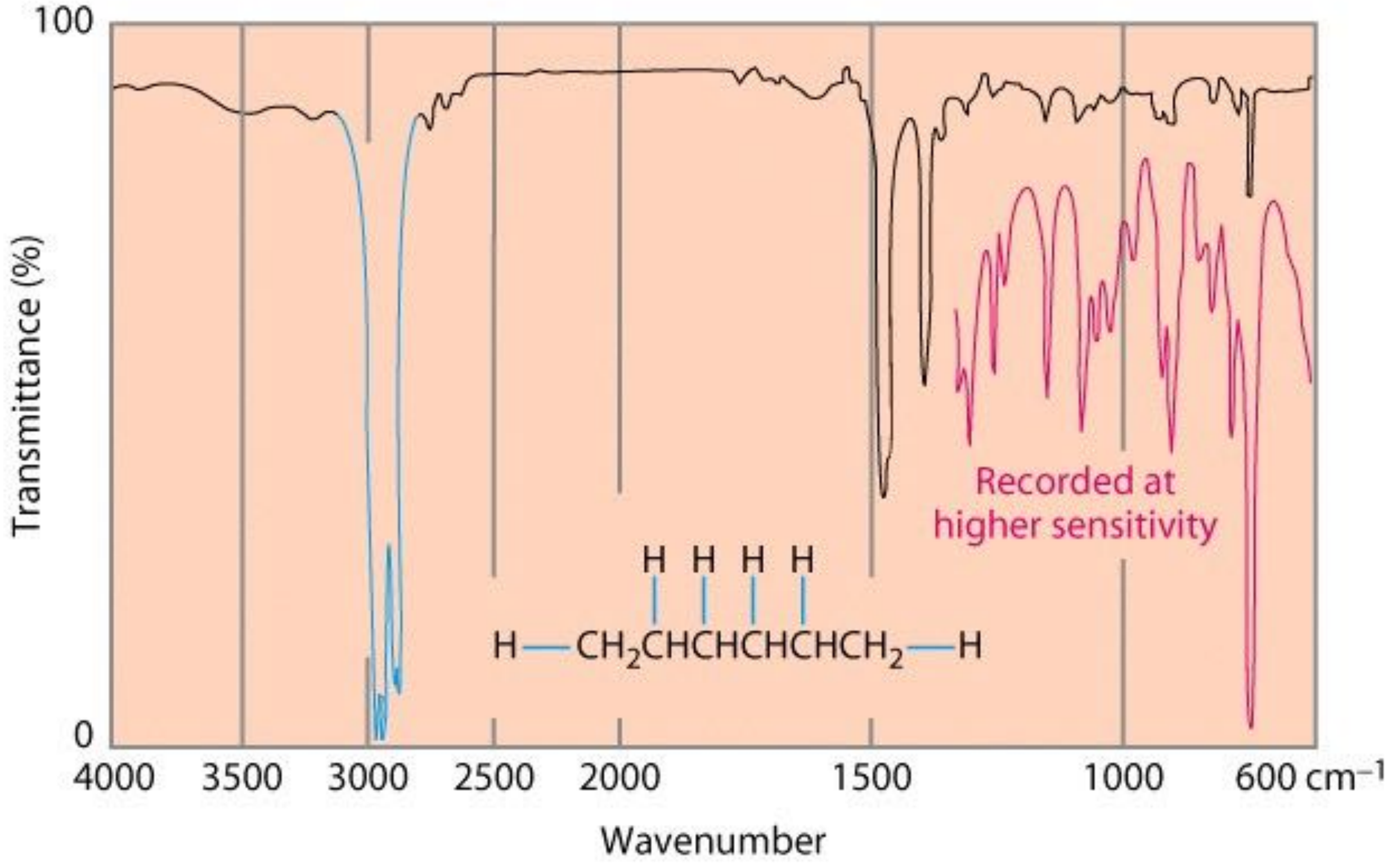
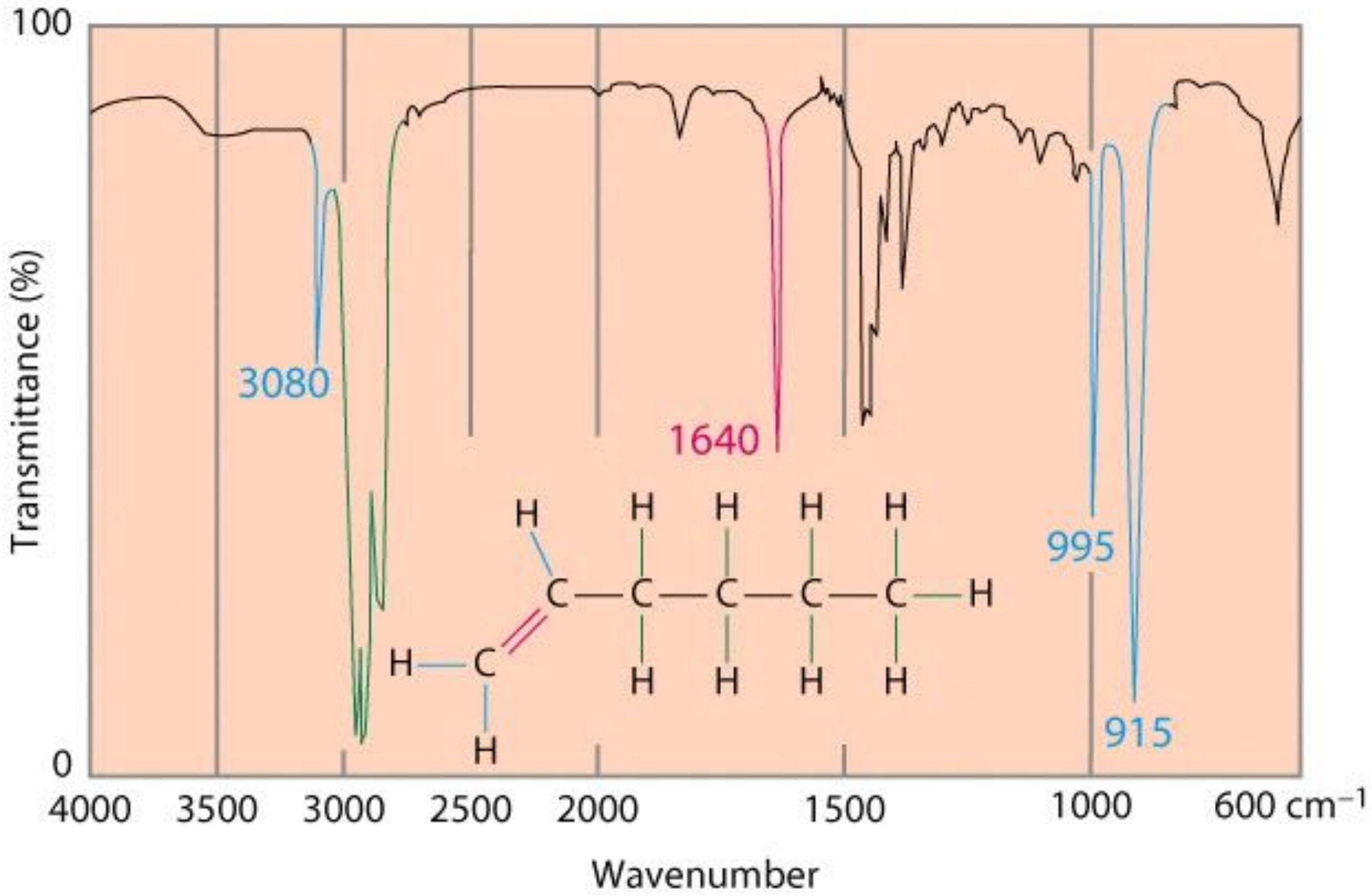
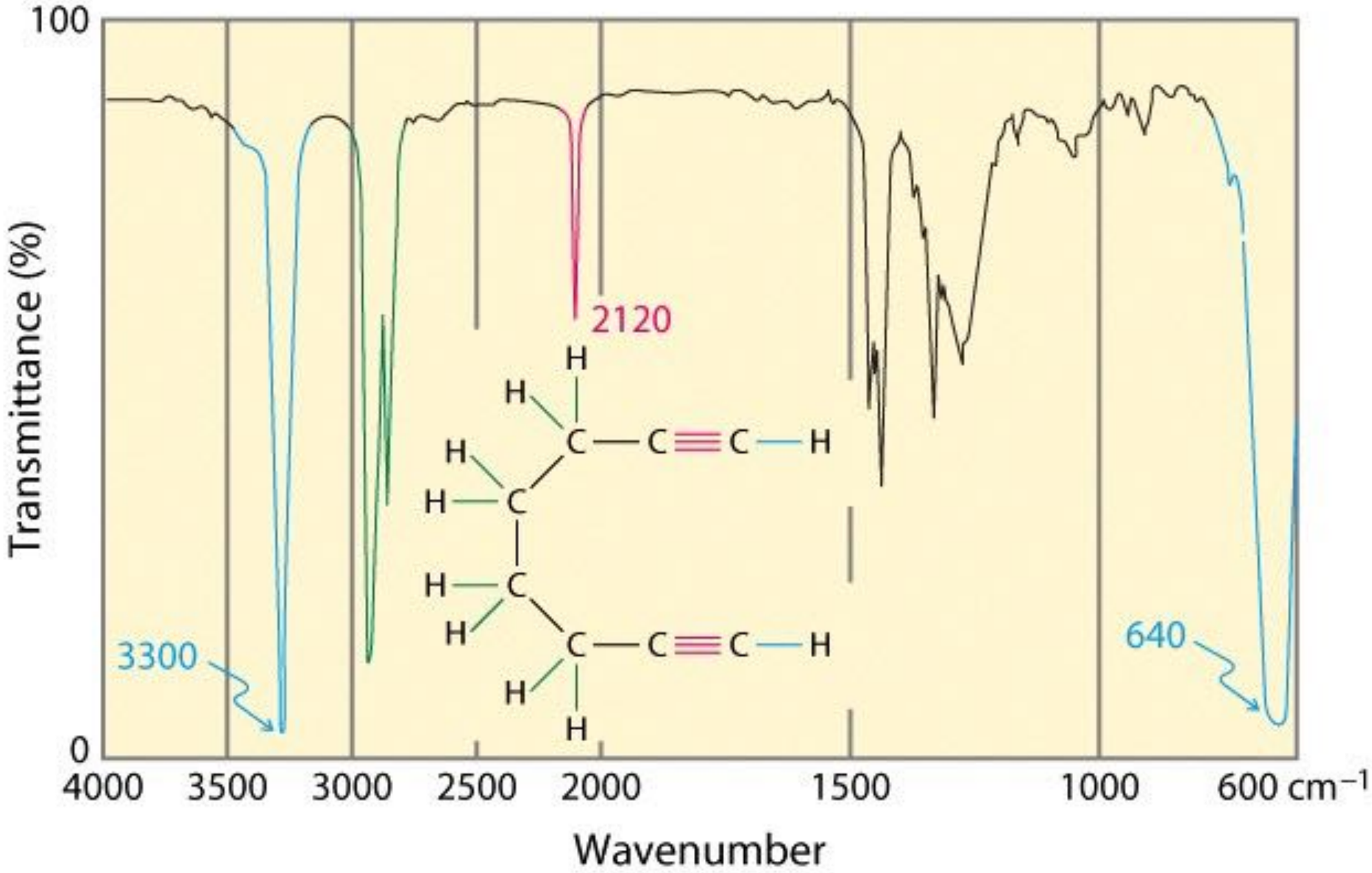
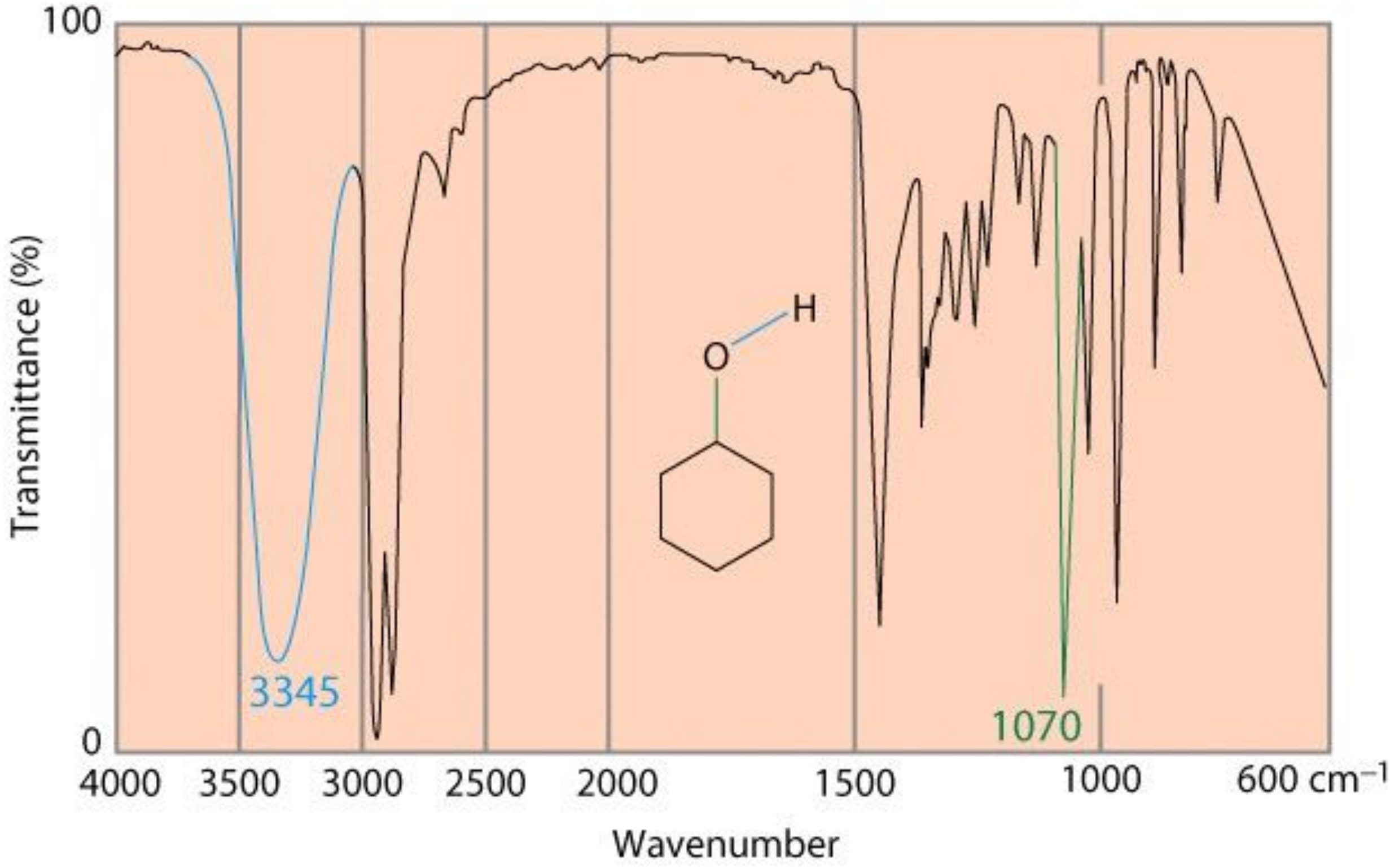
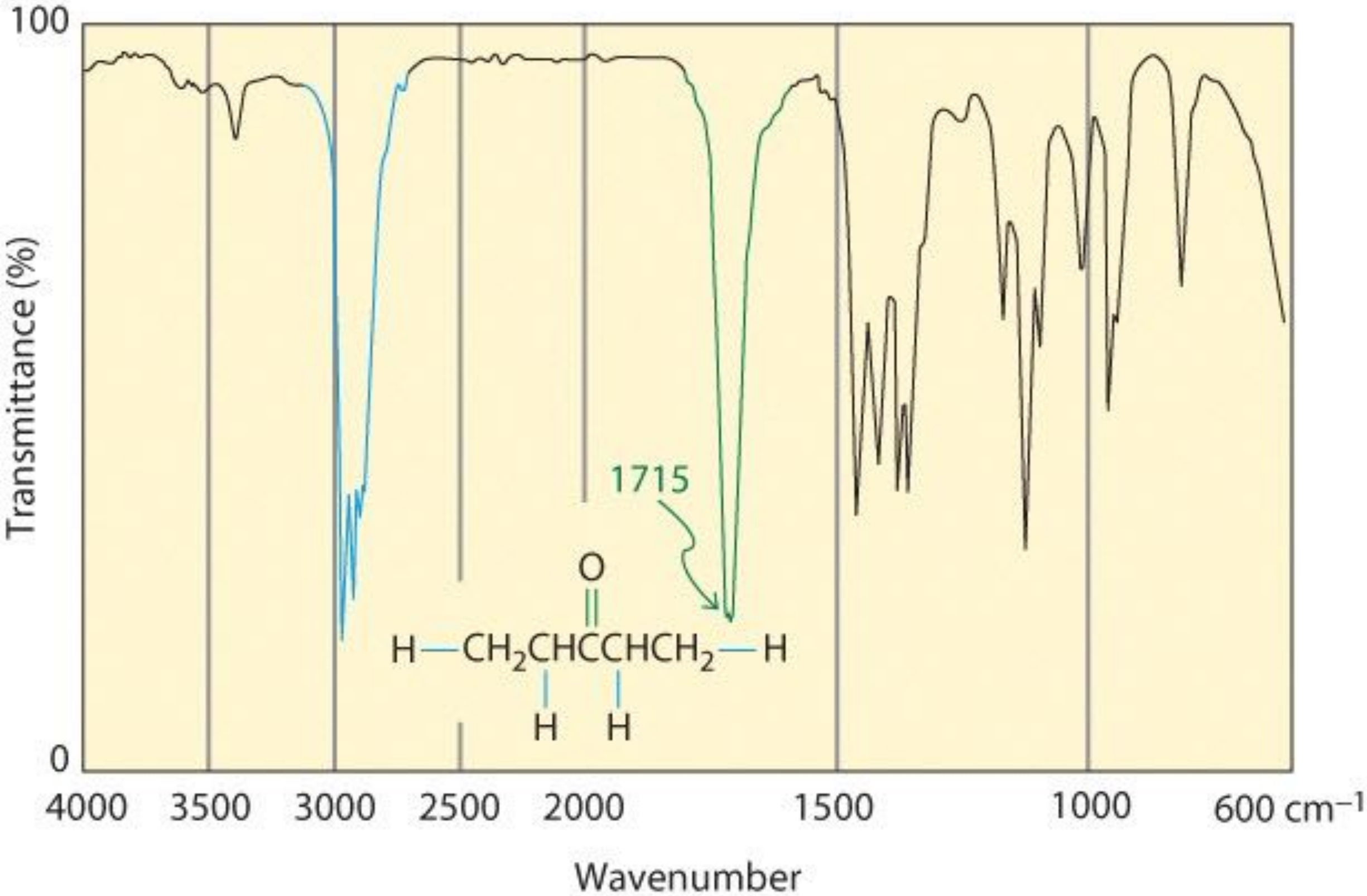

100
Transmittance (%)
0
H H H
H—CH2CHCHCHCH2—H
Recorded at
higher sensitivity
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber

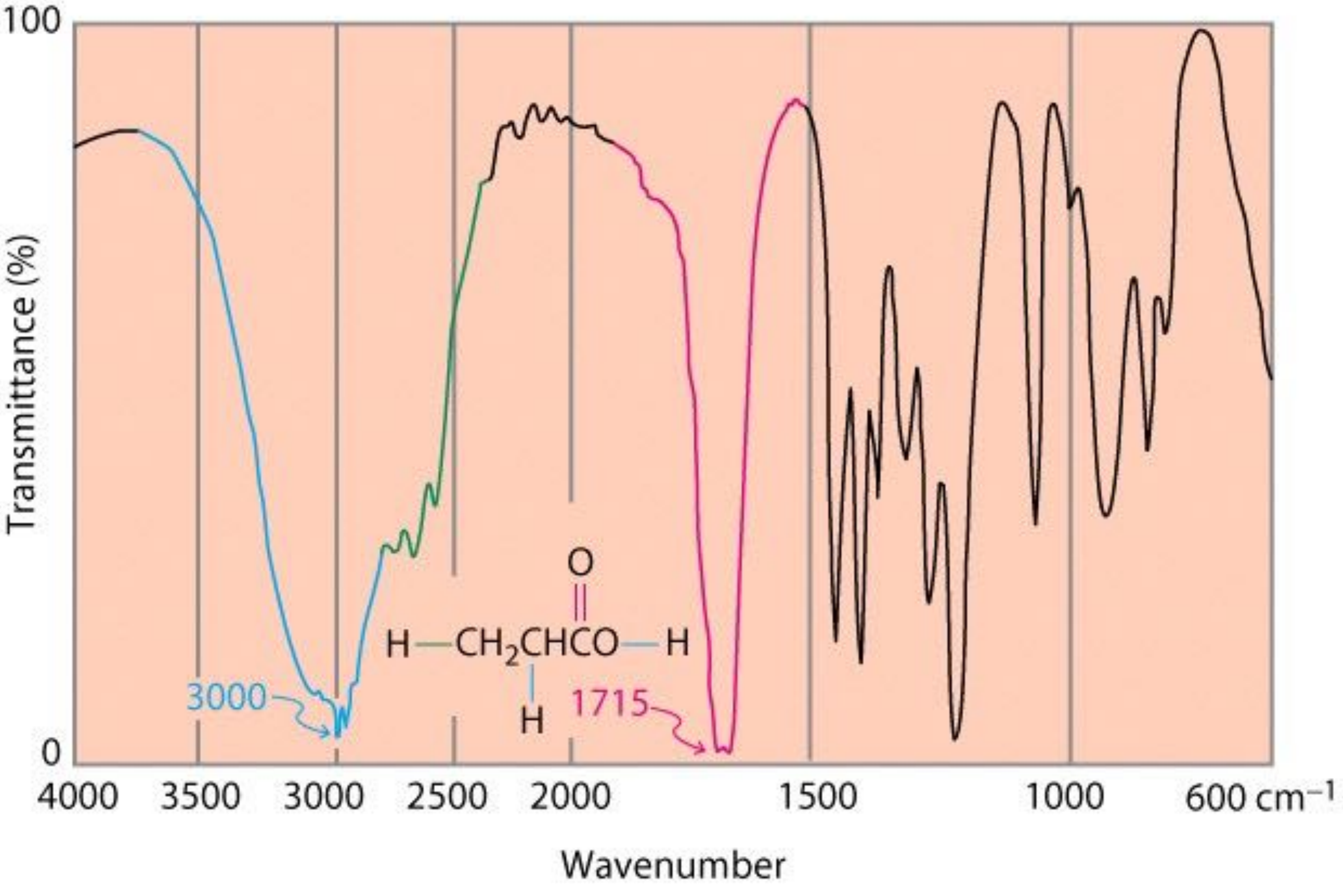

100
Transmittance (%)
0
Recorded at
higher sensitivity
H H H H
H—CH2CHCHCHCHCH2—H
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber


100
Transmittance (%)
0
3080
1640
995
915
H
C
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber


100
Transmittance (%)
0
2120
3300
640
H
H
H
H
H
H
H
H
H
H
C
C
C
C
C
C
H
H
H
H
H
H
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber


100
Transmittance (%)
0
O
H
3345
1070
4000
3500
3000
2500
2000
1500
1000
600 cm⁻¹
Wavenumber


100
Transmittance (%)
0
1715
O
H—CH2CHCCHCH2—H
H H
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber


100
Transmittance (%)
0
4000
3500
3000
2500
2000
1500
1000
600 cm⁻¹
Wavenumber
3000
1715
O
H—CH2CHCO—H
H

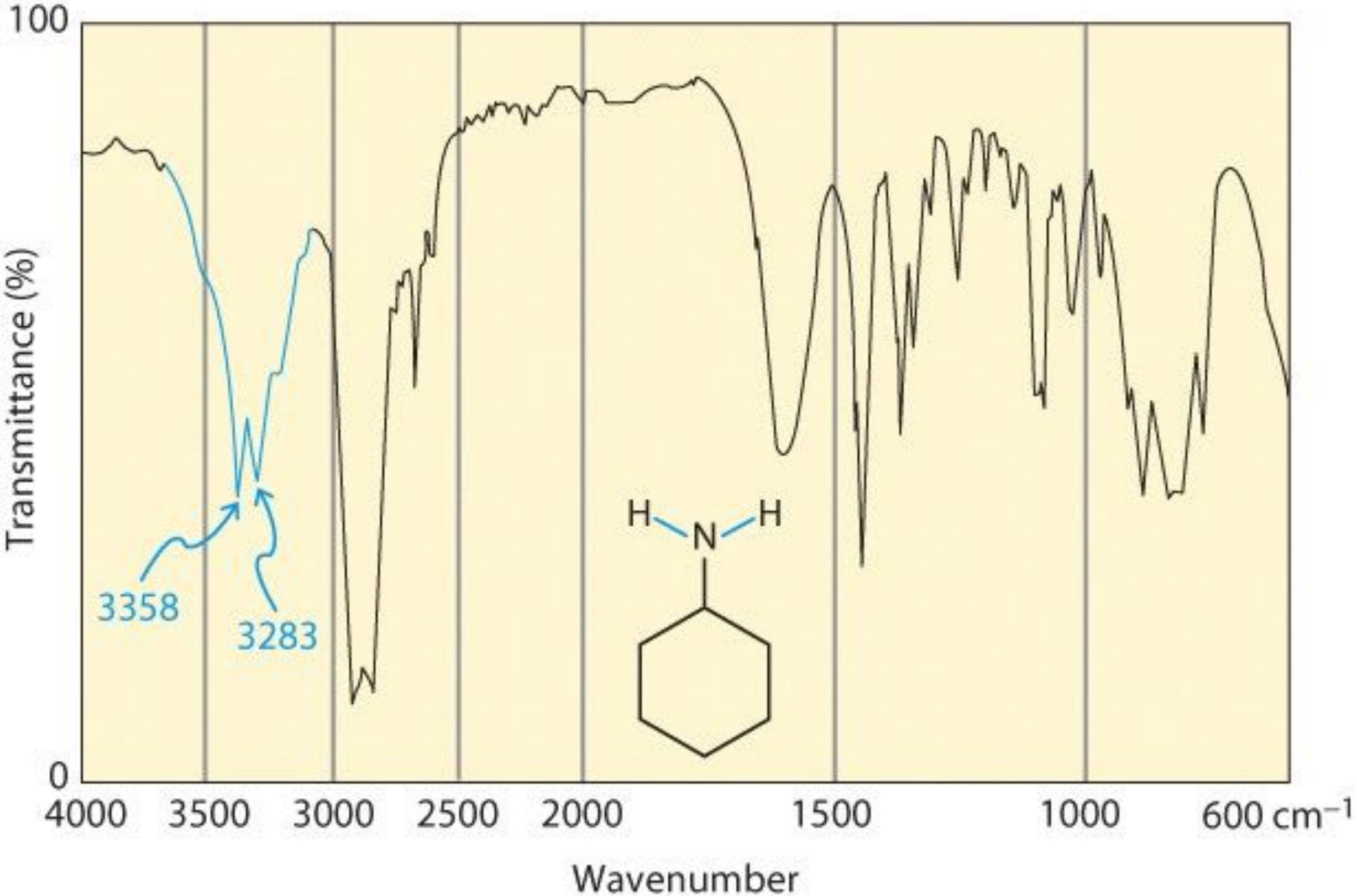
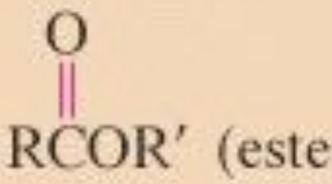
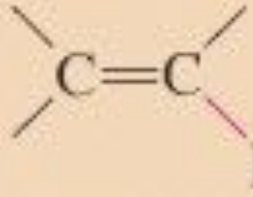
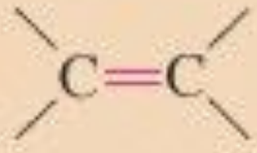
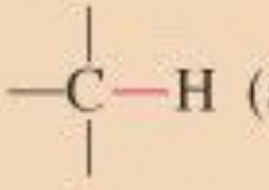
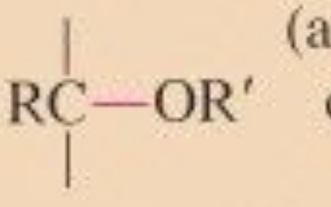
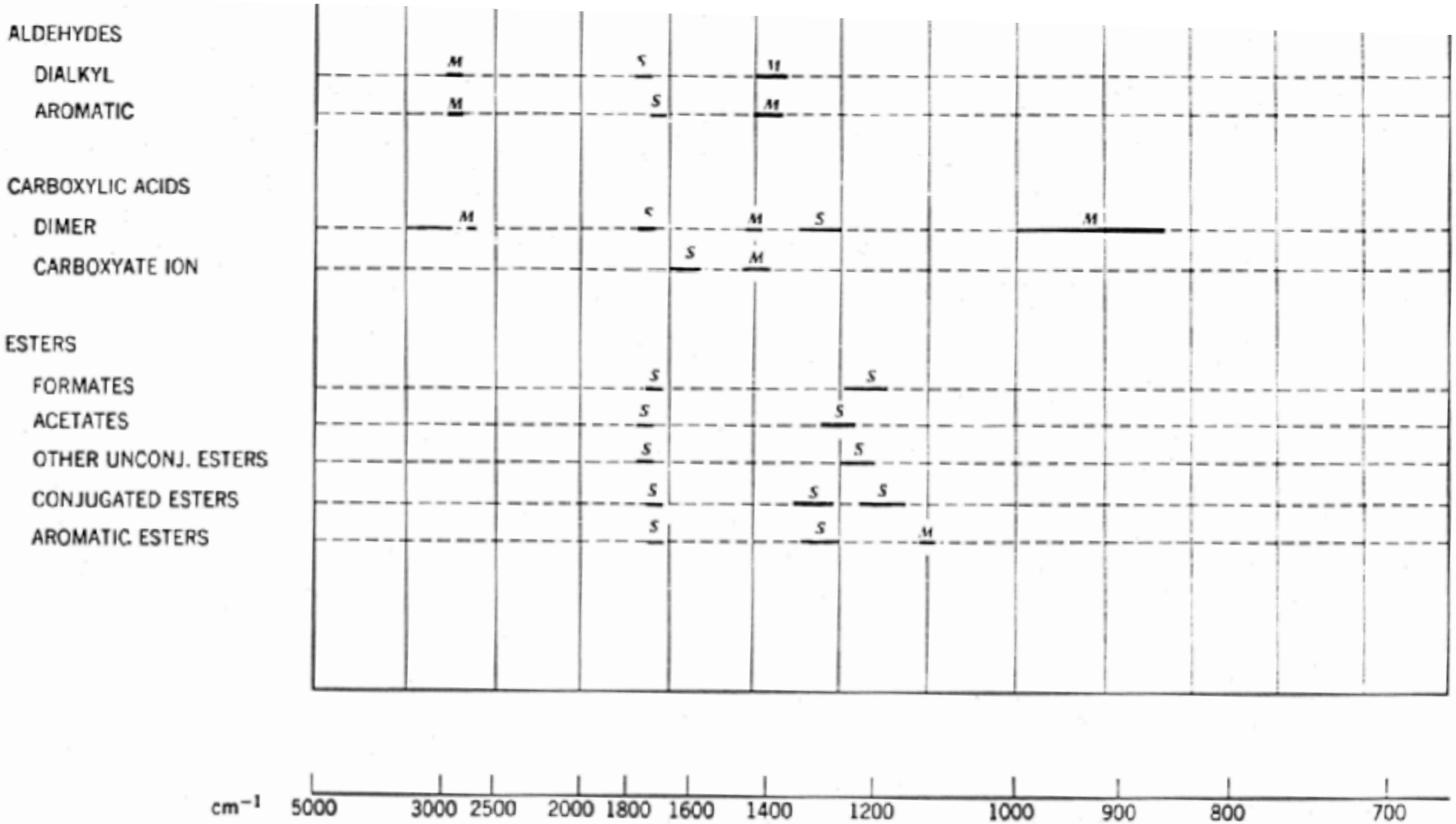

100
Transmittance (%)
0
3358
3283
H
N
H
4000
3500
3000
2500
2000
1500
1000
600 cm⁻¹
Wavenumber

TABLE 11-4 Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or functional group	$\tilde{\nu}$ (cm^{-1})	Bond or functional group	$\tilde{\nu}$ (cm^{-1})
RO—H (alcohols)	3200–3650	RC≡N (nitriles)	2220–2260
 (carboxylic acids)	2500–3300	 (aldehydes, ketones)	1690–1750
R_2N—H (amines)	3250–3500	 (esters)	1735–1750
RC≡C—H (alkynes)	3260–3330	 (carboxylic acids)	1710–1760
 (alkenes)	3050–3150	 (alkenes)	1620–1680
 (alkanes)	2840–3000	 (alcohols, ethers)	1000–1260
RC≡CH (alkynes)	2100–2260		



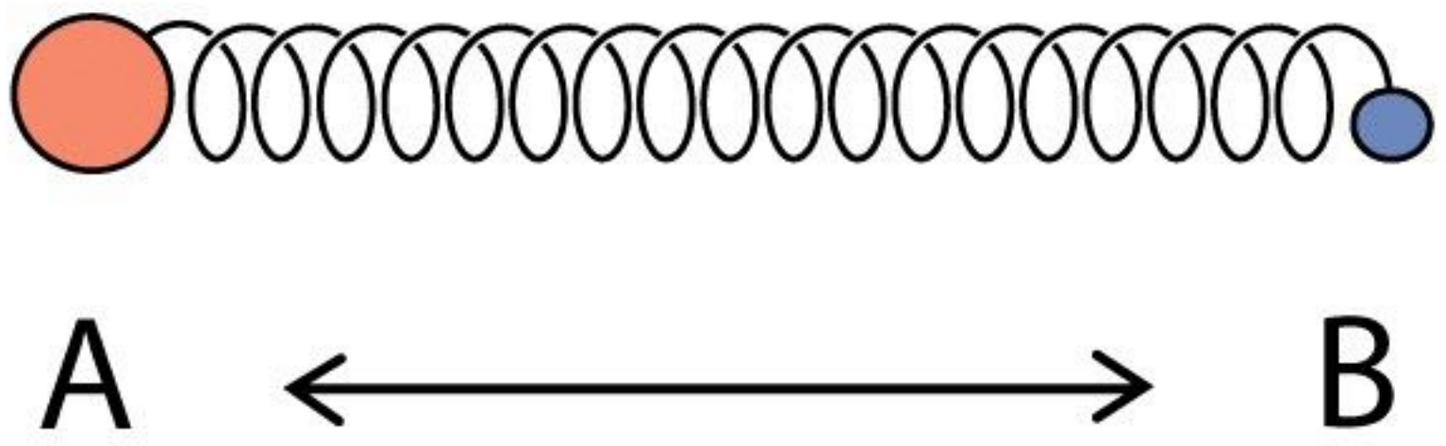
*Three bands, sometimes a fourth band for ketals and a fifth band for acetals.

Link

Principal Component Analysis (PCA)

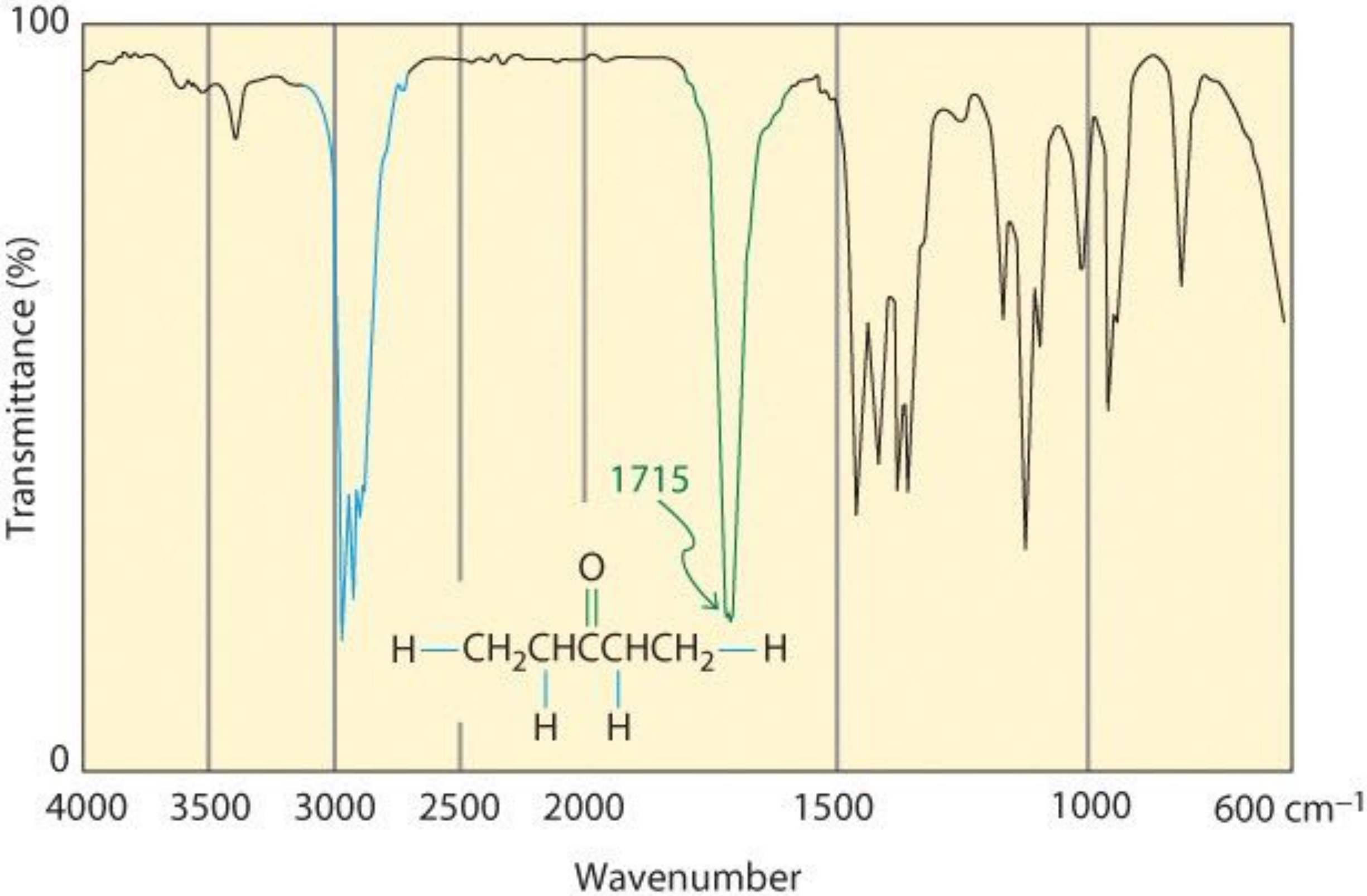
https://demo.scipeaks.com

Loi de Hooke



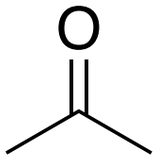
Frequency (v)

$$\overline{v} = \frac{1}{2\pi}\sqrt{f\frac{m_1 + m_2}{m_1 m_2}}$$

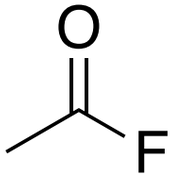

100
Transmittance (%)
0
1715
O
H—CH2CHCCHCH2—H
H H
4000
3500
3000
2500
2000
1500
1000
600 cm−1
Wavenumber

Carbonyl as a probe

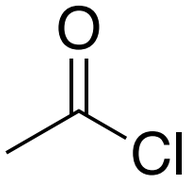
Carbonyl as a probe



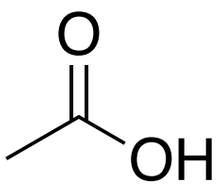
1715 cm^{-1}



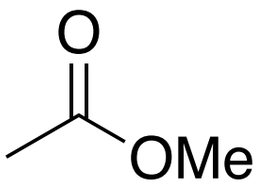
1870 cm^{-1}



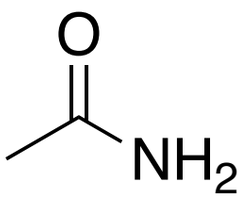
1800 cm^{-1}



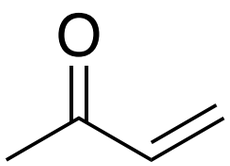
1720 cm^{-1}



1750 cm^{-1}



1680 cm^{-1}



1700 cm^{-1}

Diastereotopicity

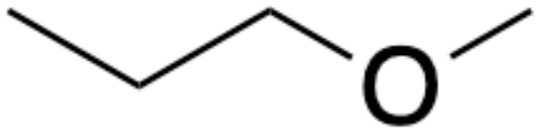
diethyl ether

Combien d'hydrogènes différents ?

- 1
- 2
- 3
- 4
- 5
- 10

Answer

methyl propyl ether

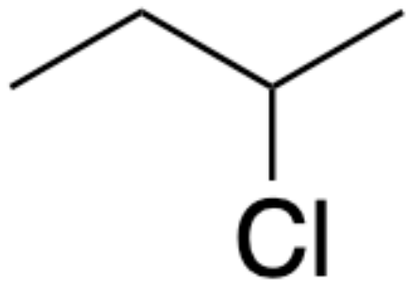


Combien d'hydrogènes différents ?

- 1
- 2
- 3
- 4
- 5
- 10

Answer

2-chlorobutane

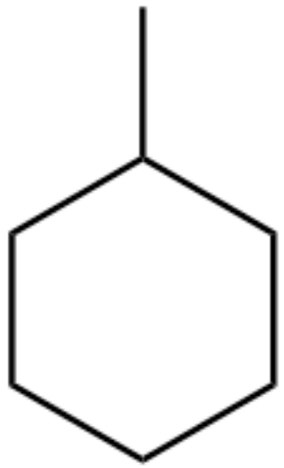


Combien d'hydrogènes différents ?

- 1
- 2
- 3
- 4
- 5
- 9

Answer

methylcyclohexane

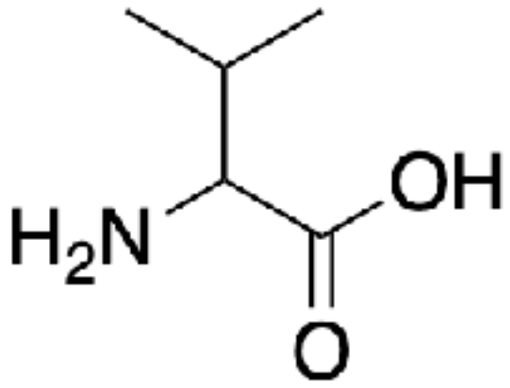


How many kind of protons

- 5
- 6
- 7
- 8
- 9
- 10

Answer

valine



Combien d'hydrogènes différents ?

- 1
- 2
- 3
- 4
- 5
- 6
- 7

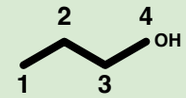
Answer

https://spectra.cheminfo.org

Diastereotopic

Dia

Nb different Hs



= 4

NbH

EXERCISE 10

analytical chemistry

pubs.acs.org/ac

Article

OctoChemDB: An Aggregated Database for Small Molecule Identification Using High-Resolution MS Data

Ricardo Silvestre,[⊥] Rémi Martinent, Laure Menin, Natalia Gasilova, Vincent Mutel, Cyril Portmann, and Luc Patiny*,[⊥]

Cite This: *Anal. Chem.* 2026, 98, 6102–6108

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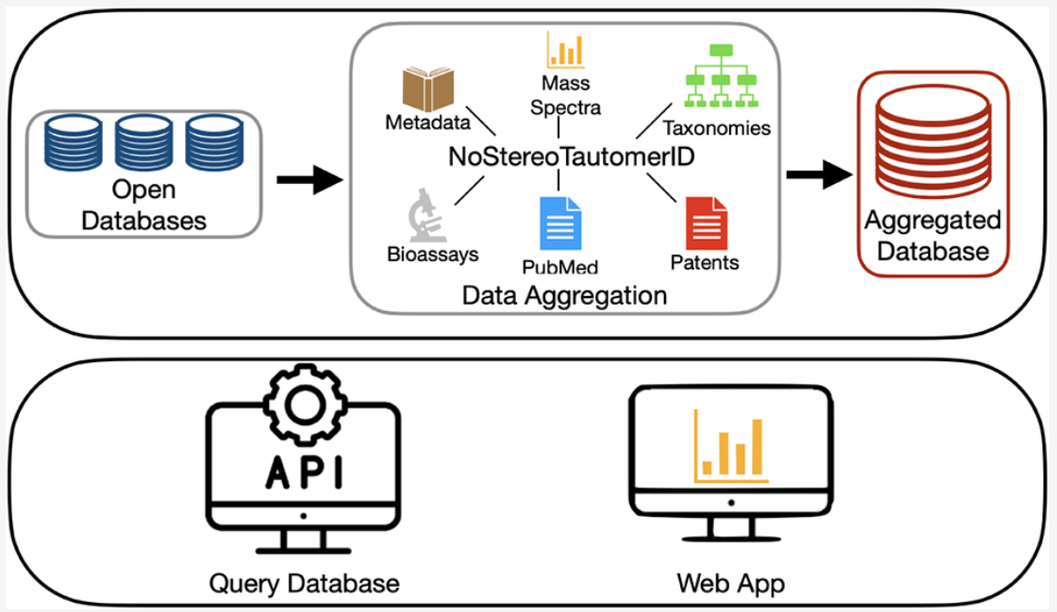
ABSTRACT: High-resolution mass spectrometry (HRMS) is a cornerstone technology to dereplicate small molecules by comparing their MS spectral data to references in extensive chemical databases. However, most existing chemical databases lack robust support for processing spectral data or enabling direct *m*/*z*-based searches, limiting their usefulness for rapid compound identification. To address this, we developed OctoChemDB, a centralized database that aggregates and harmonizes chemical, biological, and spectral data from multiple open-access resources such as PubChem, MassBank, and GNPS. To make this data programmatically accessible, we implemented a REpresentational State Transfer Application Program Interface (REST API) that allows external tools and software to query the database using customizable parameters. This API serves as the core access point for developers and researchers to integrate OctoChemDB data into their own workflows and applications. As a practical demonstration of how the API can be used, we built a web application, available at https://octochemdb.cheminfo.org/, that enables users to perform *m*/*z*-based searches, predict molecular formulas, assess isotopic similarity, analyze fragmentation patterns,

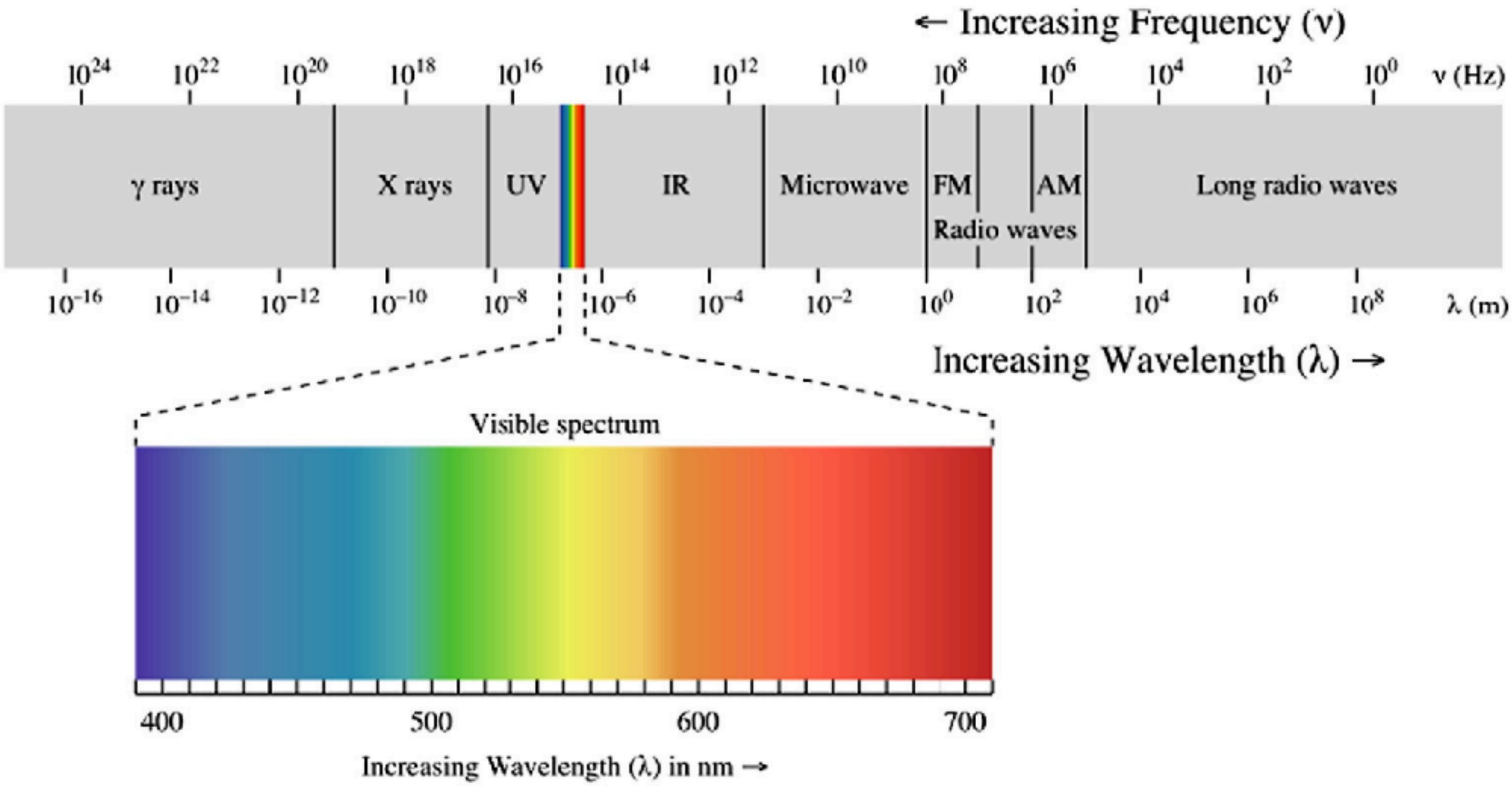


RMN

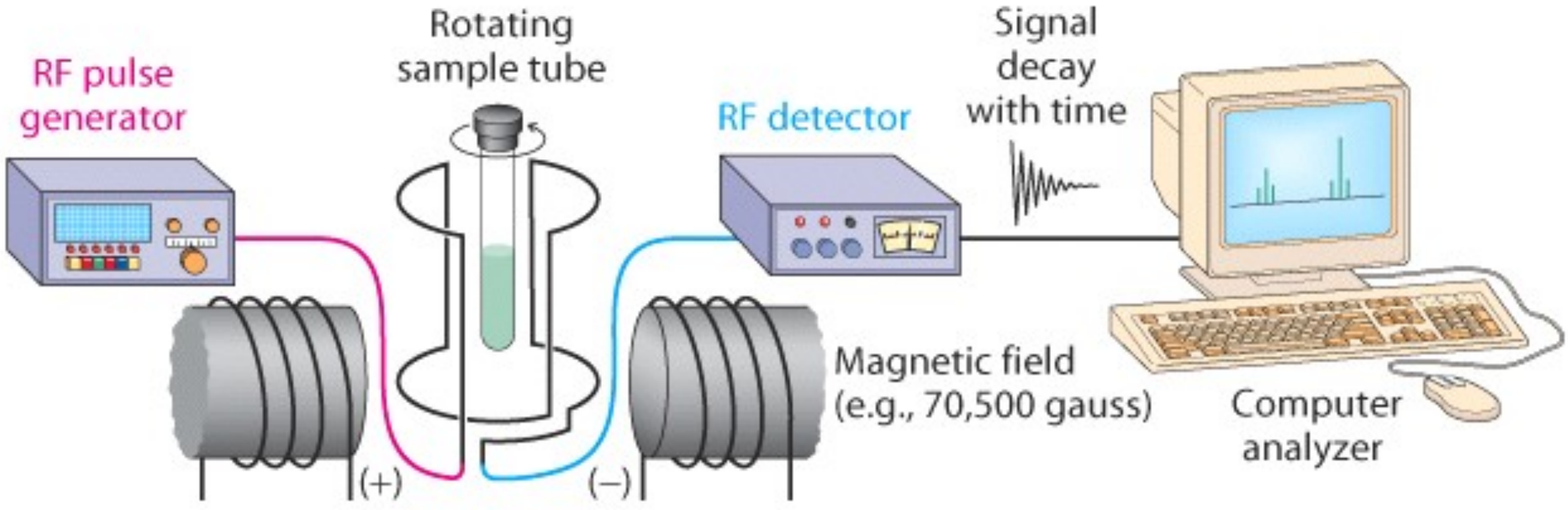
Résonance Magnétique Nucléaire

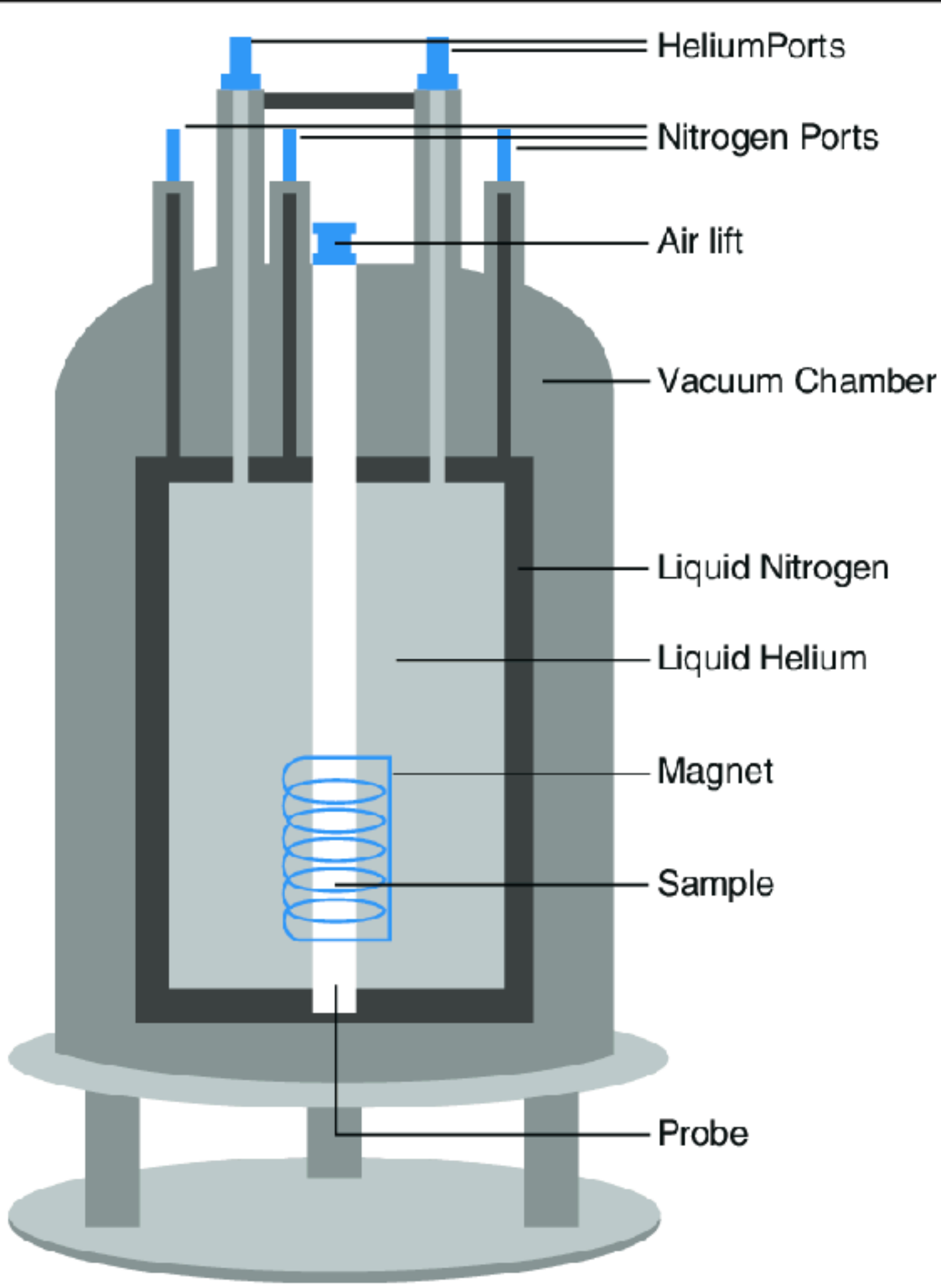
Prix Nobel:
- 1991 Richard Ernst
- 2002 Kurt Wüthrich

Electromagnetic spectrum

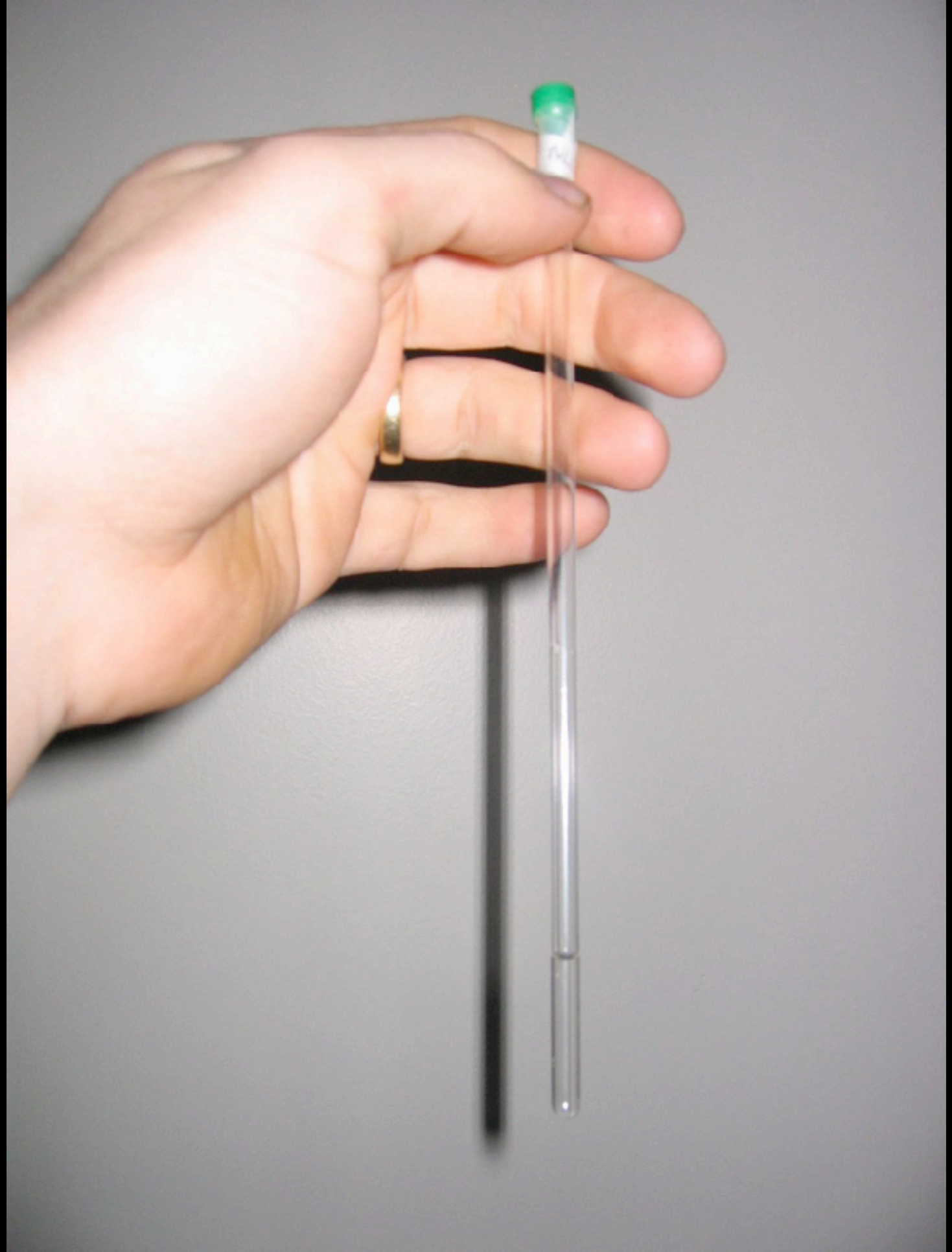


NMR spectroscopy

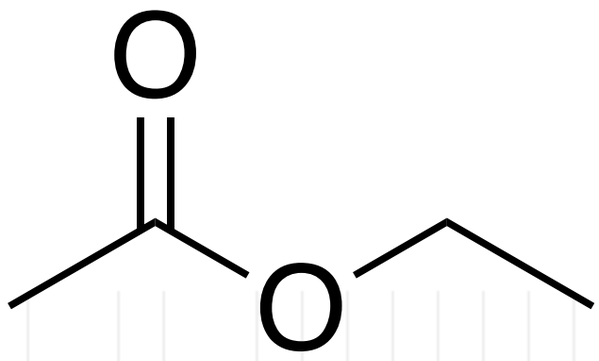


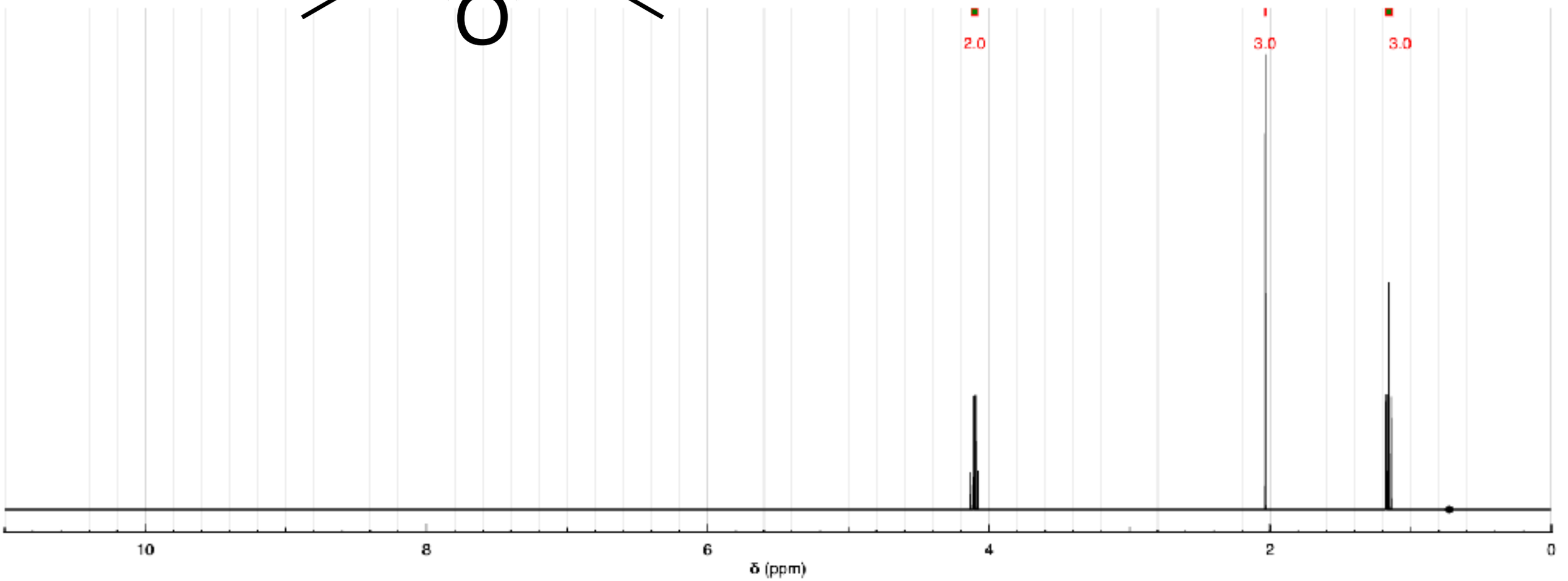

HeliumPorts
Nitrogen Ports
Air lift
Vacuum Chamber
Liquid Nitrogen
Liquid Helium
Magnet
Sample
Probe


BRUKER
Ascend™ 600
BRUKER
AVANCE III 600



ethyl acetate





Caractéristiques des principaux noyaux

Noyau	Spin I	Abondance naturelle (%)	υ obs. (MHz) (B_0=2.3488 T)	Rapport gyromagnétique γ [10^7 rad T^{-1} s^{-1}]	Relative sensibility
^{1}H	1/2	99.98	100	26.7519	100
^{2}H	1	0.016	15.3	4.1066	0.96
^{10}B	3	19.58	10.7	2.8746	1.99
^{11}B	3/2	80.42	32.0	8.5843	16.5
^{12}C	0	98.9	–	–	–
^{13}C	1/2	1.108	25.1	6.7283	1.59
^{14}N	1	99.63	7.2	1.9338	0.10
^{15}N	1/2	0.37	10.1	–2.712	0.10
^{16}O	0	99.96	–	–	–
^{17}O	5/2	0.037	13.6	-3.6279	2.91
^{19}F	1/2	100	97.1	25.181	83.3
^{29}Si	1/2	4.70	19.9	–5.3188	0.78
^{31}P	1/2	100	40.4	10.841	6.63

Pauling electronegativity values

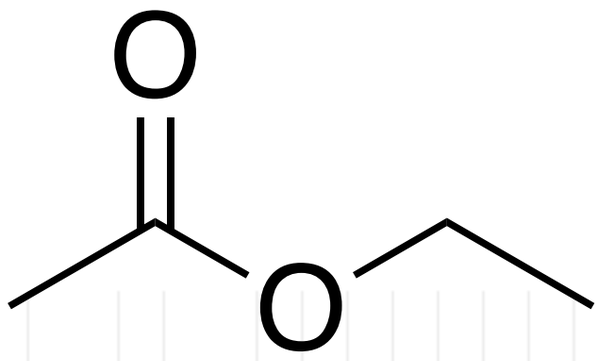
Dr. Scott
Easy Hard Science

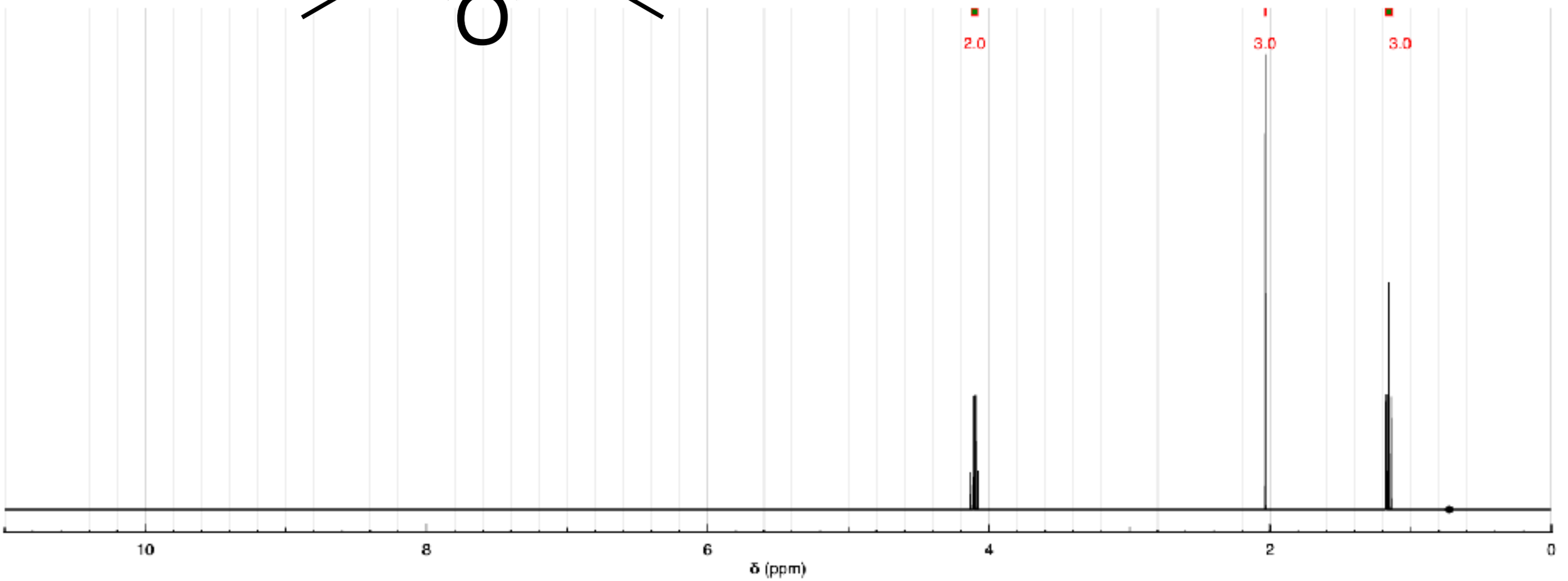
H 2.1																	He N/A
Li 1.0	Be 1.5											B 1.5	C 2.5	N 3.0	O 3.5	F 4.0	Ne N/A
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar N/A
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr N/A*
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe N/A*
Cs 0.7	Ba 0.9		Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn N/A
Fr 0.7	Ra 0.9																

Anisotropie magnétique

Déplacements chimiques

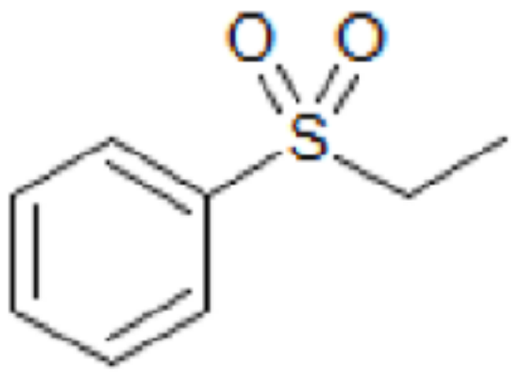
ethyl acetate



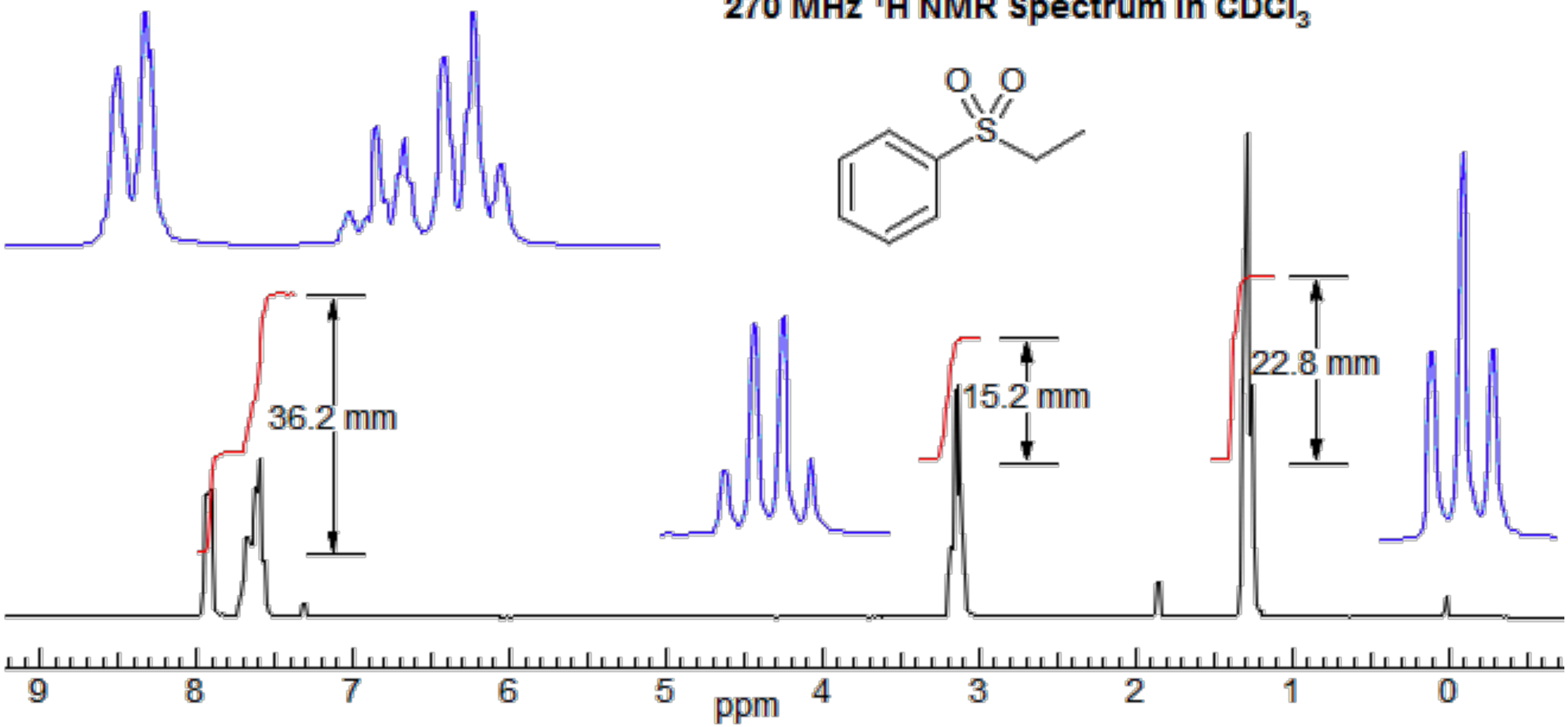


Exercices simples : Solvants

RMN ^{1}H



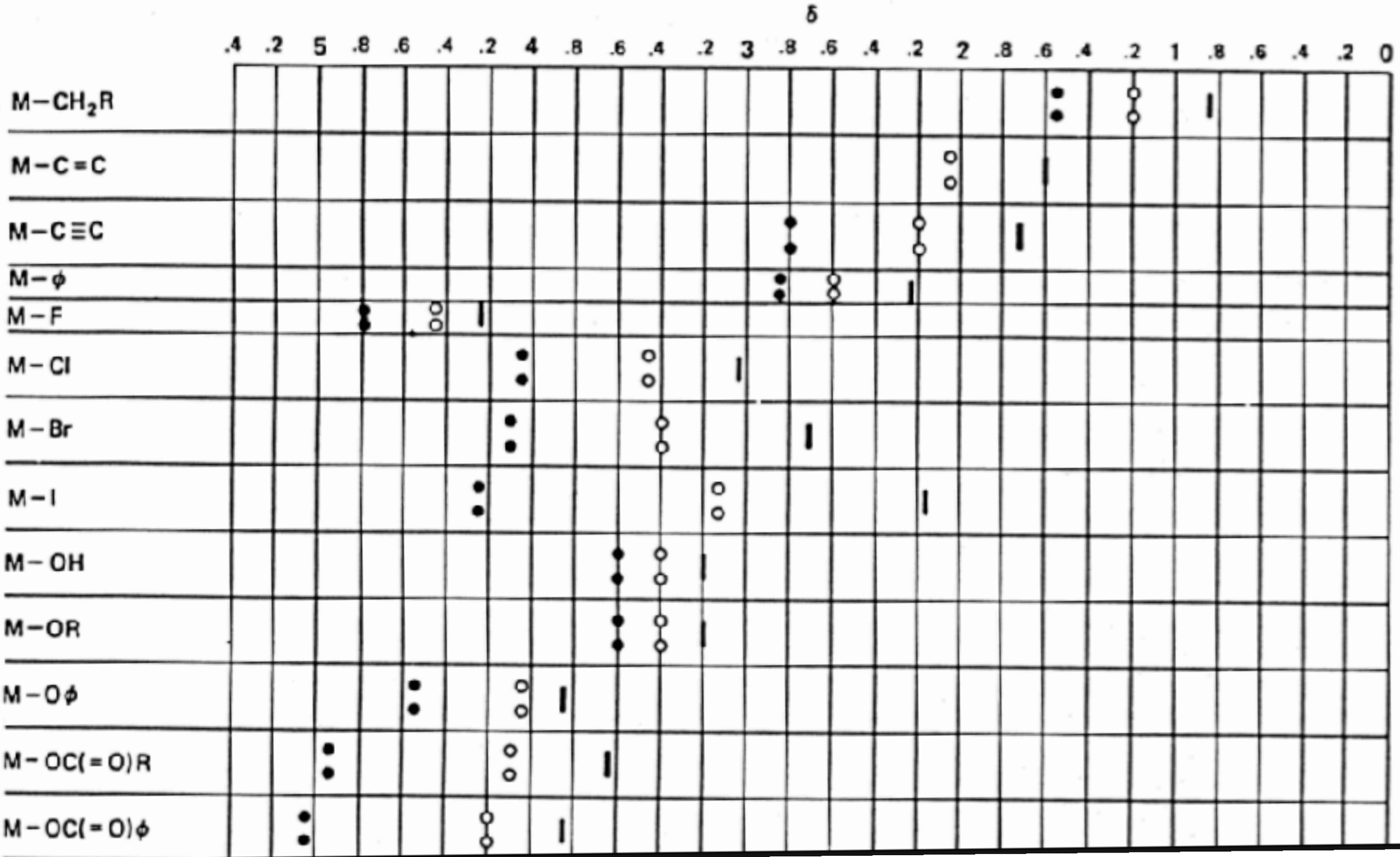
270 MHz ^{1}H NMR Spectrum in $CDCl_3$



Tables de références

CHART 1. CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α - POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—Y).

| M = methyl
| M = methylene
| M = methine

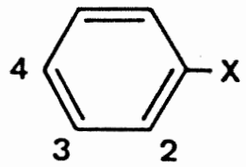


$$\delta_{CH_2R_1R_2} = 1.25 + \sum_{1}^{2} z_i \qquad \delta_{CHR_1R_2R_3} = 1.50 + \sum_{1}^{3} z_i$$

	Substituent	z_i
C	-alkyl	0.0
	-C=C-	0.8
	-C≡C-	0.9
	-phenyl	1.3
H	-Cl	2.0
A	-Br	1.9
L	-I	1.4
	-OH	1.7
	-O-alkyl	1.5
O	-O-phenyl	2.3
	-OCO-alkyl	2.7
	-OCO-phenyl	2.9
	$-NH_2$	1.0
N	$-N\text{-alkyl}_2$	1.0
	$-NO_2$	3.0
S	-S-alkyl	1.0
	-CHO	1.2
O	-CO-alkyl	1.2
‖	-COOH	0.8
C	-COO-alkyl	0.7
/\	-CN	1.2

$$\delta_{CH_2R_1R_2} = 0.23 + Z_{R_1} + Z_{R_2}$$

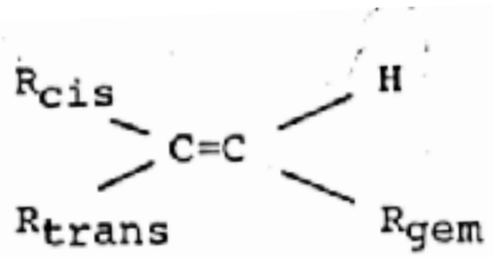
	Substituent R	Z_R	
C	-alkyl	see p. H17	
	-C=C-	1.33	
	-C≡CH	1.52	
	-C≡Calkyl	1.52	
	-C≡Cphenyl	1.77	
	-phenyl	1.85	
HAL	-F	3.15	
	-Cl	2.48	
	-Br	2.29	
O	-OH	2.46	
	-Oalkyl	2.27	
	-Ophenyl	2.89	
	-OCOalkyl	2.98	
	-OCOphenyl	3.23	
N	$-NH_2$	1.69	
	-NHalkyl	1.60	
	$-N(alkyl)_2$	1.41	
	$-NHphenyl^2$	2.15	
	-N(alkyl)phenyl	2.39	
	$-NH_3^+$	2.31	for D_2O a)
	$-NH_2^+$alkyl	2.31	for D_2O a)
	$-NH^+(alkyl)_2$	2.46	for D_2O a)
	$-N^+(alkyl)_3$	2.56	for D_2O b)
	-NHCOalkyl	2.23	
	-N(alkyl)COalkyl	2.23	
	-NHCOphenyl	2.33	
S	-SH	1.63	
	-Salkyl	1.63	
	-Sphenyl	1.92	
O ‖ C /\	-COalkyl	1.58	
	-COphenyl	2.08	
	-COOH	1.49	
	-COOalkyl	1.49	
	-COOphenyl	1.74	
	$-CONH_2$	1.39	
	$-CON(alkyl)_2$	1.39	
	-CONHphenyl	1.59	
	-C≡N	1.73	



$$\delta_{H_i} = 7.26 + Z_i$$

	Substituent X	Z_2	Z_3	Z_4
	-H	0	0	0
	$-CH_3$	-0.20	-0.12	-0.22
	$-CH_2CH_3$	-0.14	-0.06	-0.17
	$-CH(CH_3)_2$	-0.13	-0.08	-0.18
	$-C(CH_3)_3$	0.02	-0.08	-0.21
	$-CH_2Cl$	0.00	0.00	0.00
	$-CF_3$	0.32	0.14	0.20
C	$-CCl_3$	0.64	0.13	0.10
	$-CH_2OH$	-0.07	-0.07	-0.07
	$-CH=CH_2$	0.06	-0.03	-0.10
	-CH=CH-phenyl	0.15	-0.01	-0.16
	-C≡CH	0.15	-0.02	-0.01
	-C≡C-phenyl	0.19	0.02	0.00
	-phenyl	0.37	0.20	0.10
	-F	-0.26	0.00	-0.20
H	-Cl	0.03	-0.02	-0.09
A	-Br	0.18	-0.08	-0.04
L	-I	0.39	-0.21	0.00
	-OH	-0.56	-0.12	-0.45
	$-OCH_3$	-0.48	-0.09	-0.44
	$-OCH_2CH_3$	-0.46	-0.10	-0.43
O	-O-phenyl	-0.29	-0.05	-0.23
	$-OCOCH_3$	-0.25	0.03	-0.13
	-OCO-phenyl	-0.09	0.09	-0.08
	$-OSO_2CH_3$	-0.05	0.07	-0.01

$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$



	Substituent R	Z_{gem}	Z_{cis}	Z_{trans}
	-H	0	0	0
	-alkyl	0.45	-0.22	-0.28
	-alkyl ring[1]	0.69	-0.25	-0.28
	$-CH_2$-aromatic	1.05	-0.29	-0.32
	$-CH_2X$, X: F, Cl, Br	0.70	0.11	-0.04
	$-CHF_2$	0.66	0.32	0.21
	$-CF_3$	0.66	0.61	0.32
C	$-CH_2O$	0.64	-0.01	-0.02
	$-CH_2N$	0.58	-0.10	-0.08
	$-CH_2S$	0.71	-0.13	-0.22
	$-CH_2CO$, CH_2CN	0.69	-0.08	-0.06
	-C=C isolated	1.00	-0.09	-0.23
	-C=C conjugated[2]	1.24	0.02	-0.05
	-C≡C	0.47	0.38	0.12
	-aromatic free rotation	1.38	0.36	-0.07
	-aromatic fixed[3]	1.60	-	-0.05
	-aromatic o-substituted	1.65	0.19	0.09
H	-F	1.54	-0.40	-1.02
A	-Cl	1.08	0.18	0.13
L	-Br	1.07	0.45	0.55
	-I	1.14	0.81	0.88

Couplage spin-spin

$Cl_2CH–CHBr_2$

Couplage spin-spin

$Cl_2CH–CH_2Br$

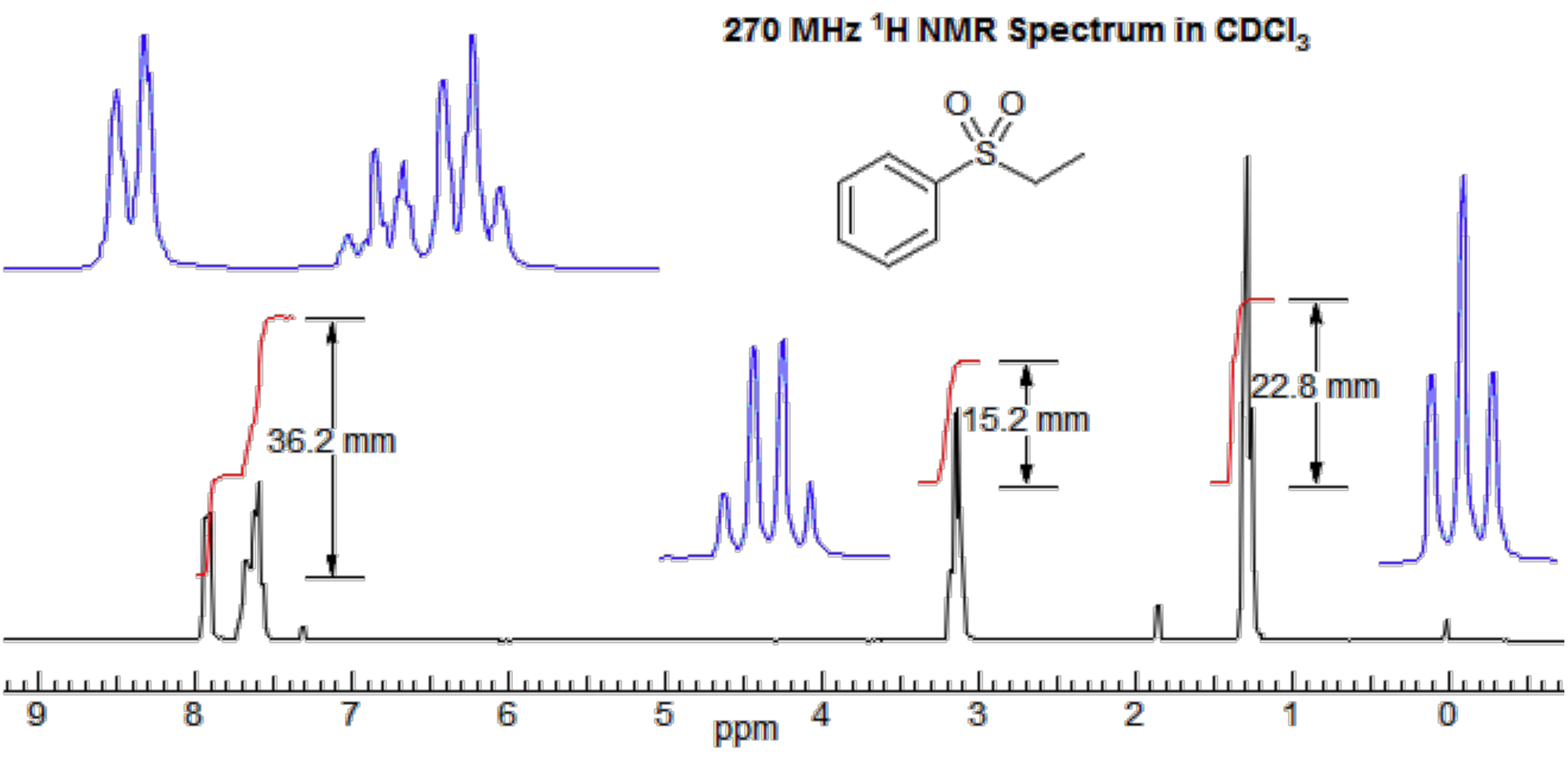
Triangle de Pascal

^{2}J, ^{3}J, ^{4}J - Via spin électronique

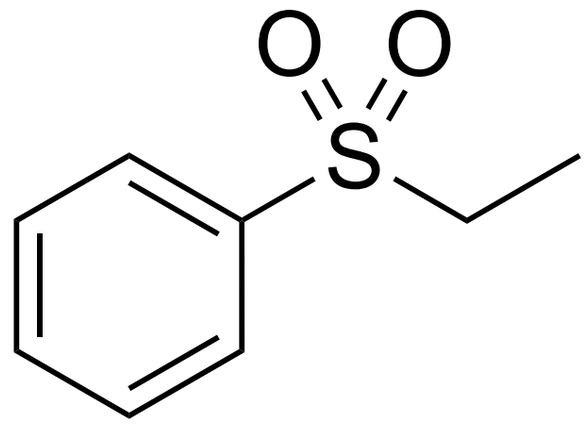
spectra.cheminfo.org

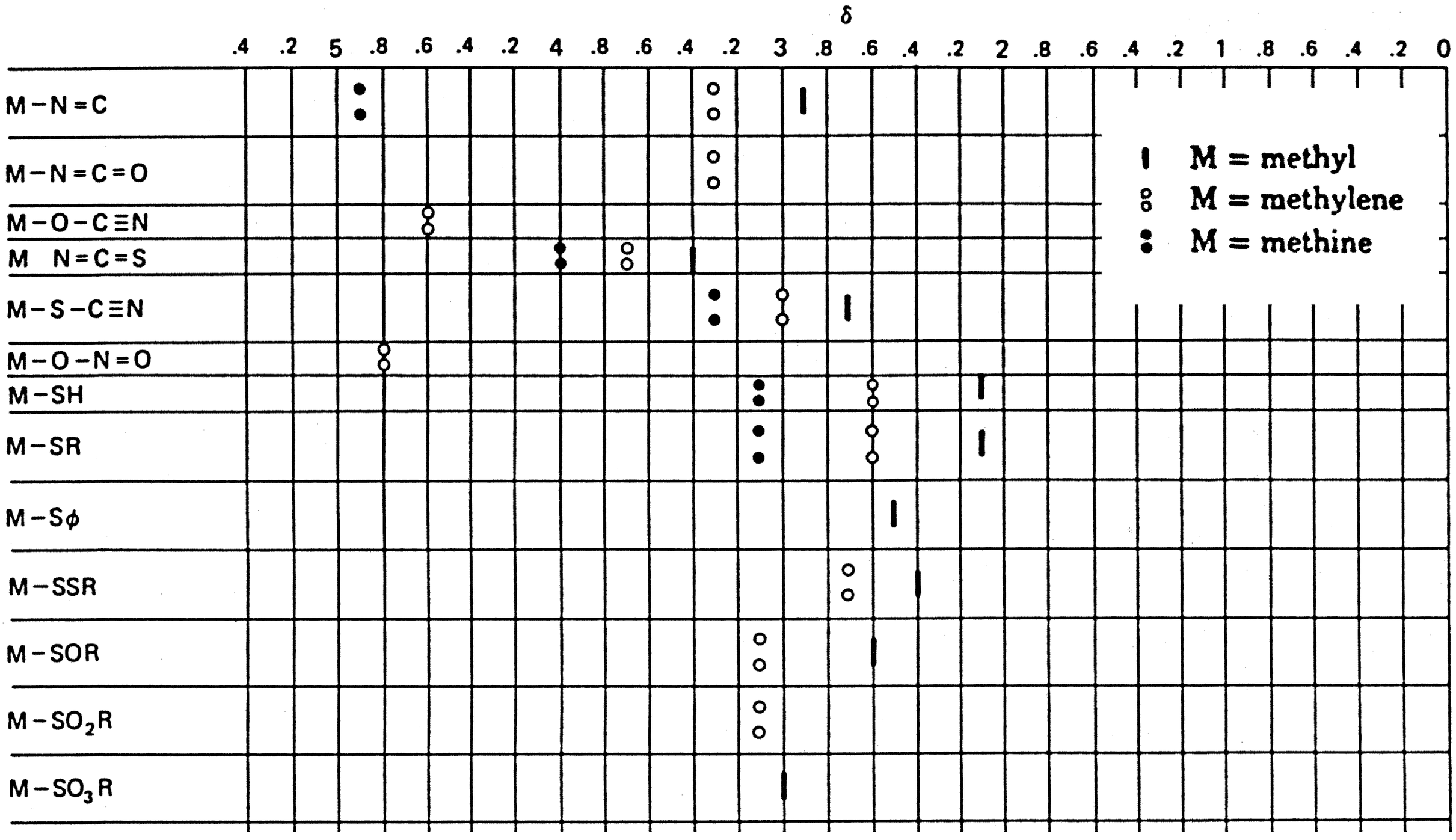
Exercices semaine 9

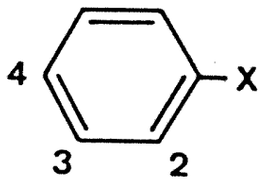
Résumé: attribution d'un spectre



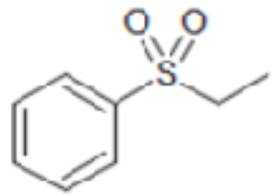
Prédire un spectre

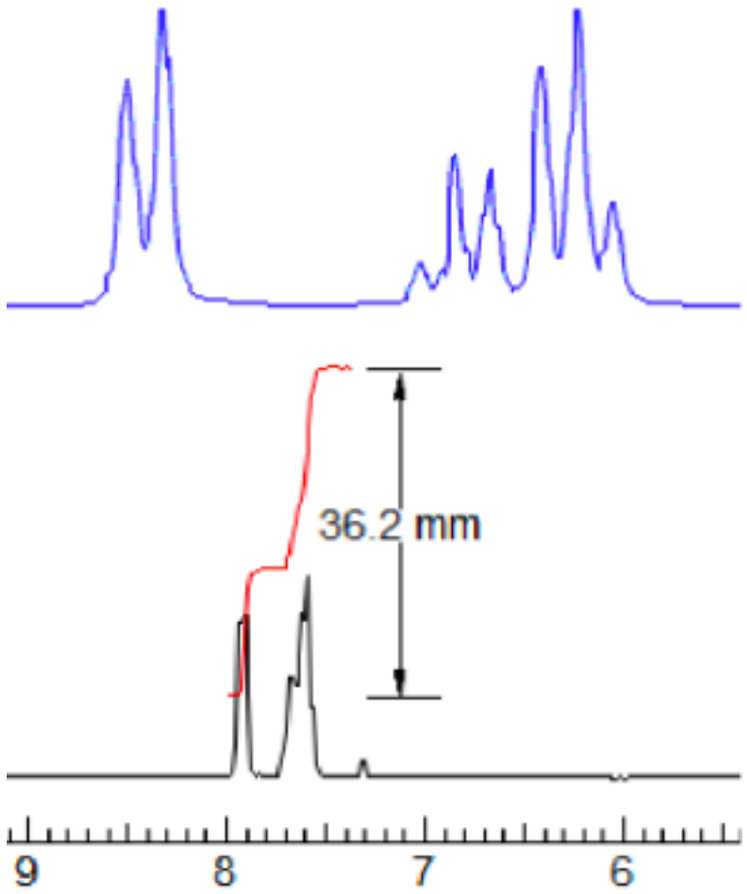



δ
.4 .2 5 .8 .6 .4 .2 4 .8 .6 .4 .2 3 .8 .6 .4 .2 2 .8 .6 .4 .2 1 .8 .6 .4 .2 0
M−N=C
M−N=C=O
M−O−C≡N
M N=C=S
M−S−C≡N
M−O−N=O
M−SH
M−SR
M−Sϕ
M−SSR
M−SOR
M−SO2R
M−SO3R
M = methyl
M = methylene
M = methine



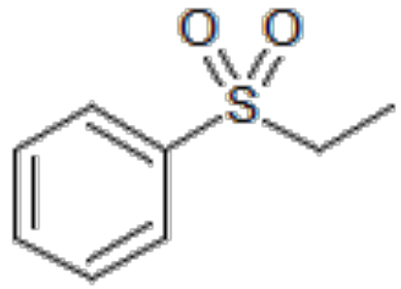
$$\delta_{H_i} = 7.26 + Z_i$$



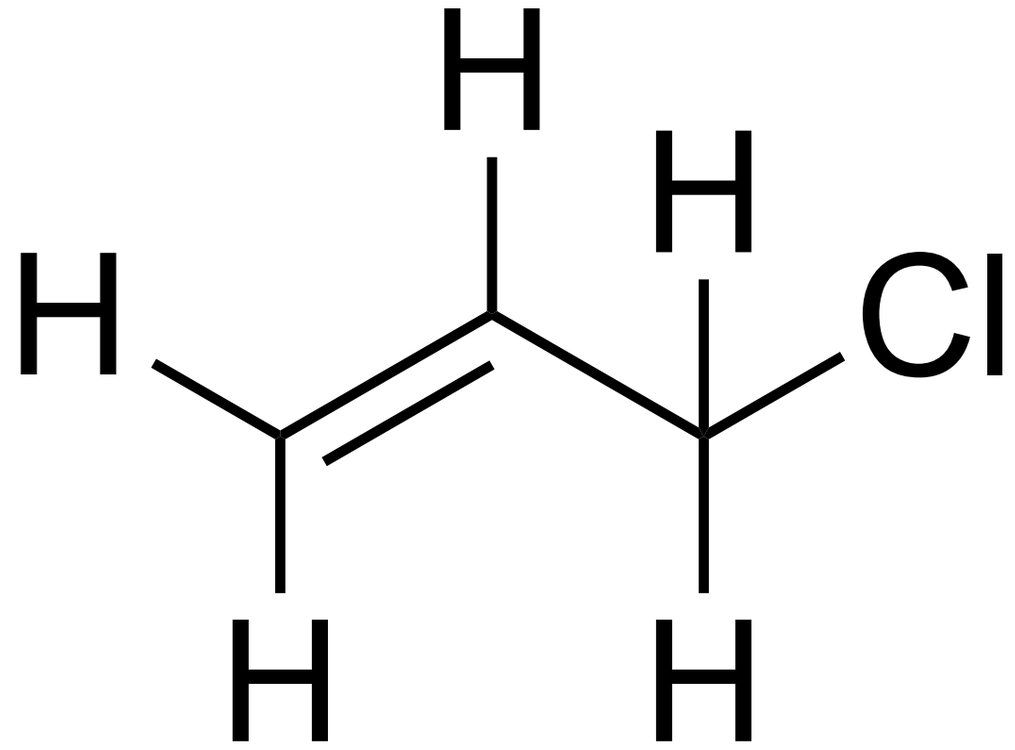


	Substituent X	Z_2	Z_3	Z_4
N	$-NH_2$	-0.75	-0.25	-0.65
	$-NHCH_3$	-0.80	-0.22	-0.68
	$-N(CH_3)_2$	-0.66	-0.18	-0.67
	$-N^+(CH_3)_3\ I^-$	0.69	0.36	0.31
	$-NHCOCH_3$	0.12	-0.07	-0.28
	$-N(CH_3)COCH_3$	-0.16	0.05	-0.02
	$-NHNH_2$	-0.60	-0.08	-0.55
	-N=N-phenyl	0.67	0.20	0.20
	-NO	0.58	0.31	0.37
	$-NO_2$	0.95	0.26	0.38
S	-SH	-0.08	-0.16	-0.22
	$-SCH_3$	-0.08	-0.10	-0.24
	-S-phenyl	0.06	-0.09	-0.15
	$-SO_3CH_3$	0.60	0.26	0.33
	$-SO_2Cl$	0.76	0.35	0.45
O=C<	-CHO	0.56	0.22	0.29
	$-COCH_3$	0.62	0.14	0.21
	$-COCH_2CH_3$	0.63	0.13	0.20
	$-COC(CH_3)_3$	0.44	0.05	0.05
	-CO-phenyl	0.47	0.13	0.22
	-COOH	0.85	0.18	0.27
	$-COOCH_3$	0.71	0.11	0.21
	$-COOCH(CH_3)_2$	0.70	0.09	0.19
	-COO-phenyl	0.90	0.17	0.27
	$-CONH_2$	0.61	0.10	0.17
	-COCl	0.84	0.22	0.36
	-COBr	0.80	0.21	0.37
	-CH=N-phenyl	∿0.6	∿0.2	∿0.2

270 MHz ^{1}H NMR Spectrum in $CDCl_3$



^{2}J, ^{3}J, ^{4}J - Via spin électronique



Simulation

2.35T = 100MHz

Unité : J en Hz - ! B_0

Measure Simulation

Karplus

Couplage fort (AB)

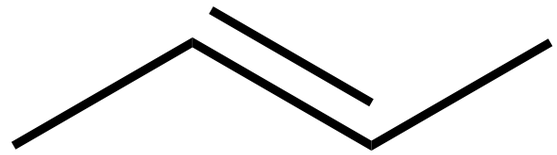
$$\frac{\Delta\delta}{J} < 10$$

Effet de second ordre, effet de 'toit'

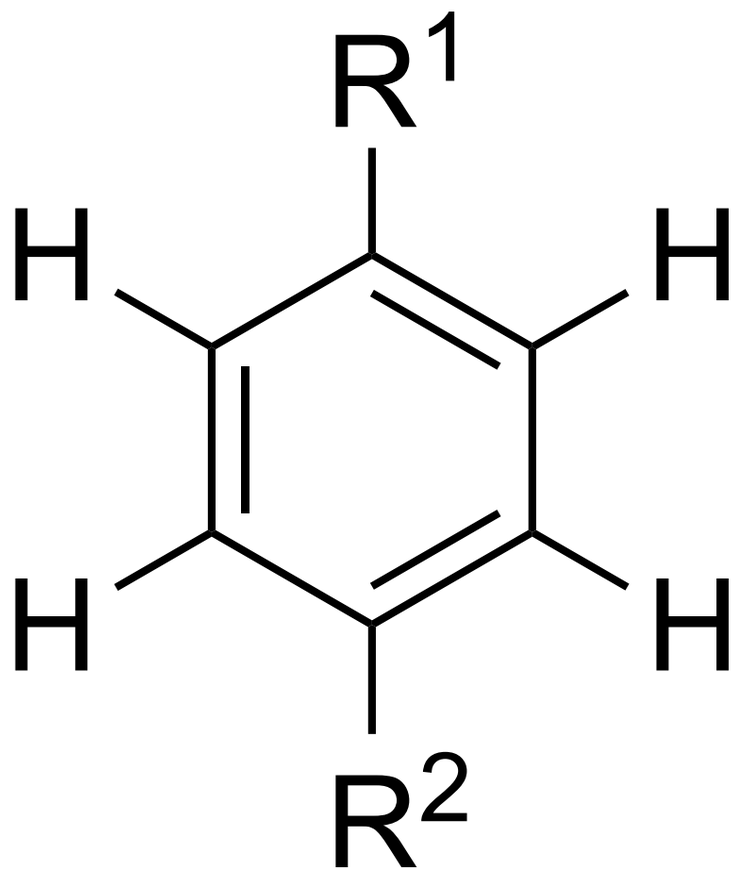
Simulation

Magnetically equivalent

- Homotopique ou énantiotopique
- Couplé avec les mêmes atomes



Aromatiques p-disubstitués

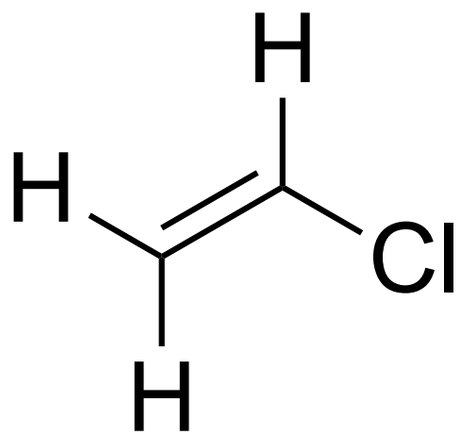


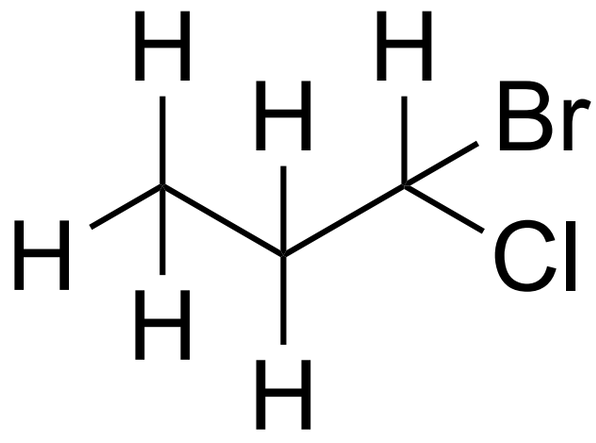
Simulation

AB A_2B ABX AMX AA'XX' ...

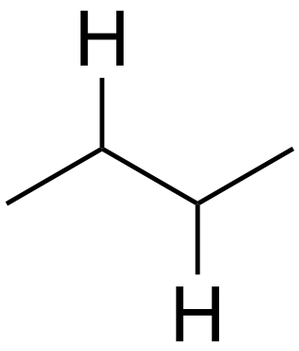
- Une lettre par type d'atome
- Lettres A, X, M
  - Consécutive si couplage fort
- Si même type d'atome mais pas magnétiquement équivalent: '

AB A_2B ABX AMX AA'XX' …

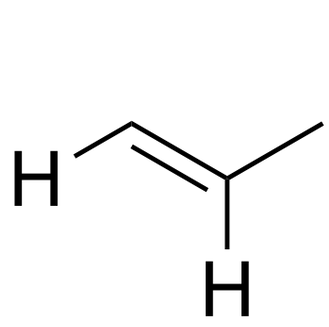




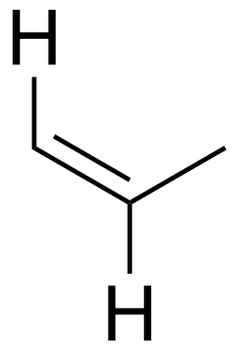
Les couplages



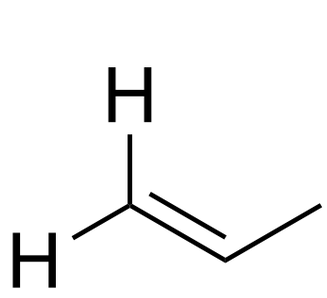
$^{3}J \approx 7$ Hz



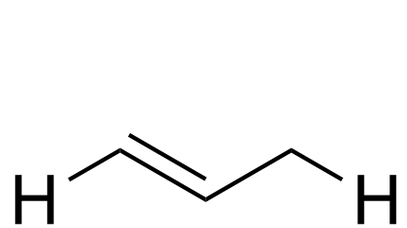
$^{3}J_{cis} \approx 10$ Hz



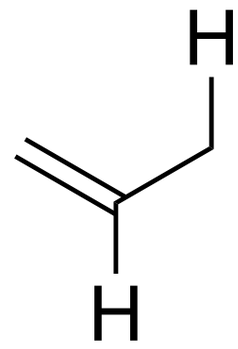
$^{3}J_{trans} \approx 16$ Hz



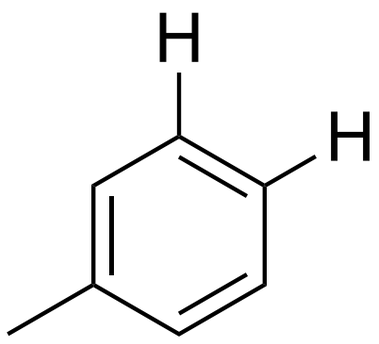
$^{2}J_{gem} \approx 2$ Hz



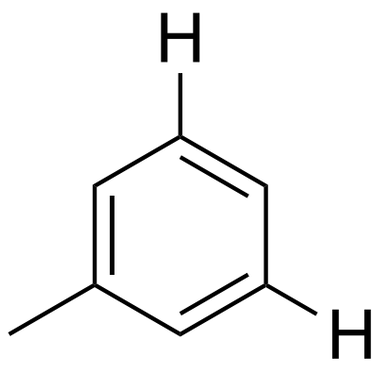
$^{4}J \approx 7$ Hz



$^{3}J \approx 7$ Hz

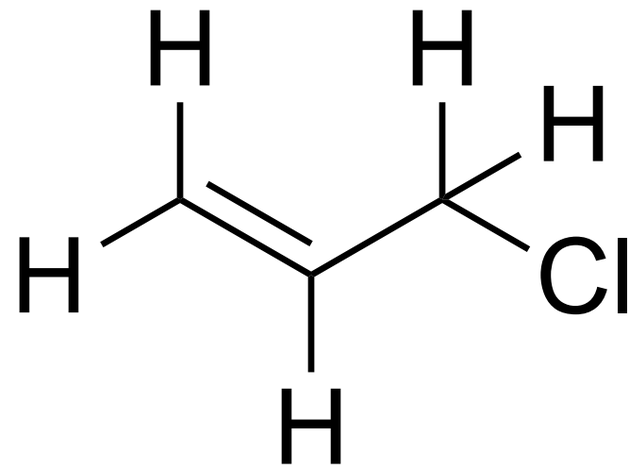


$^{3}J \approx 8$ Hz



$^{4}J \approx 2$ Hz

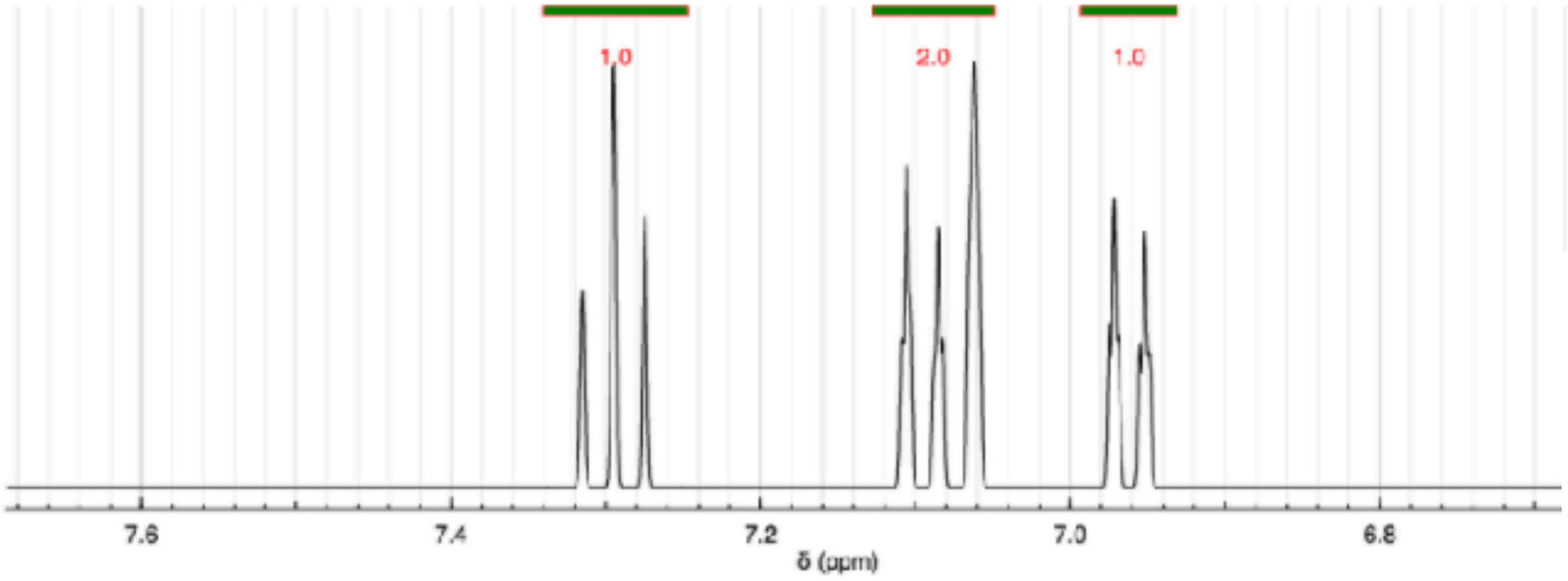
Allyl chloride



https://app.nmrium.com/predict?smiles=C%3DCCCl

Aromatiques disubstitués

https://forms.gle/vuAt9dNJ9Dvs2CTa9



Quelle est la substitution ?

- ortho
- meta
- para
- impossible d'être certain

Answer

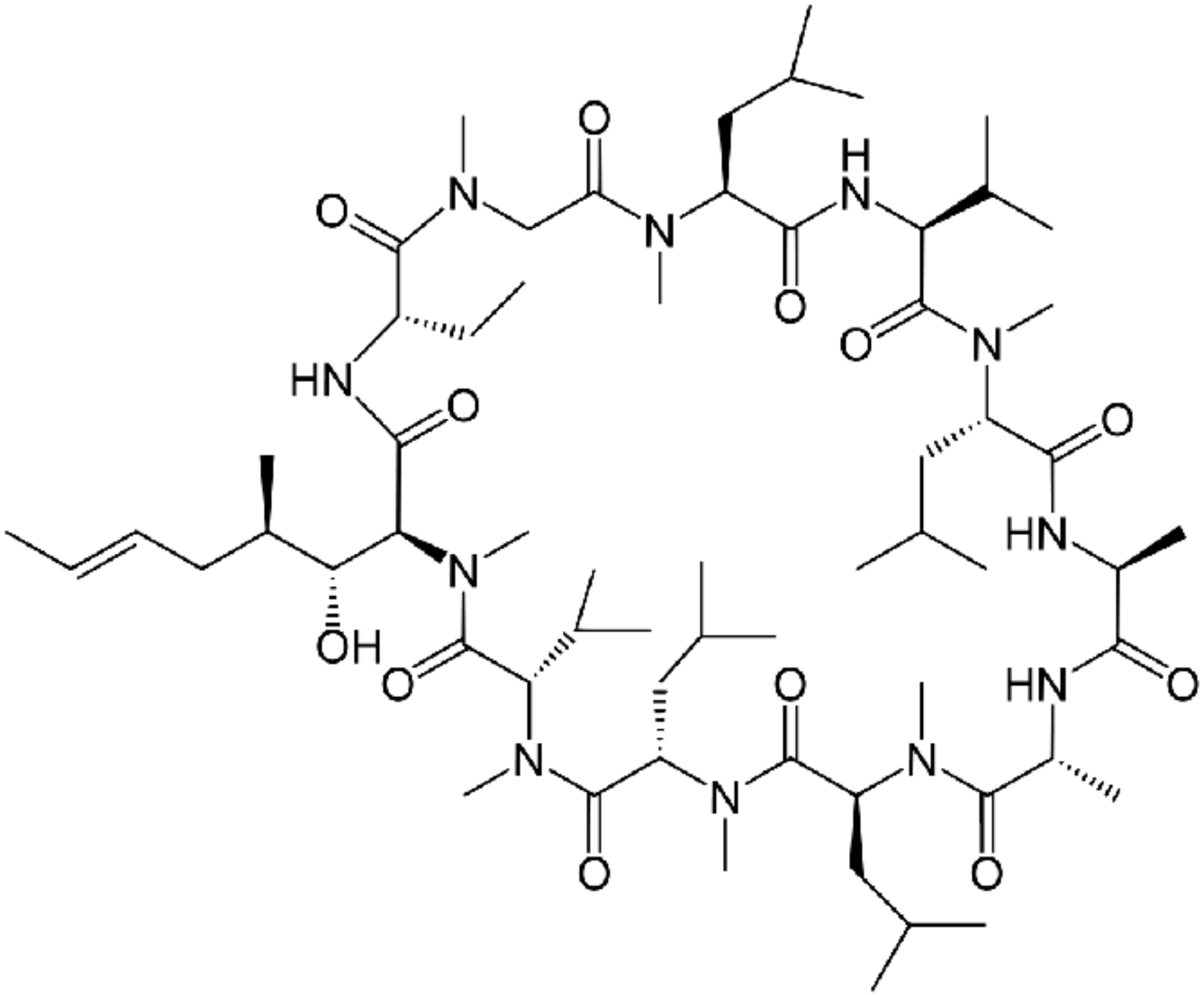
https://spectra.cheminfo.org

NMR

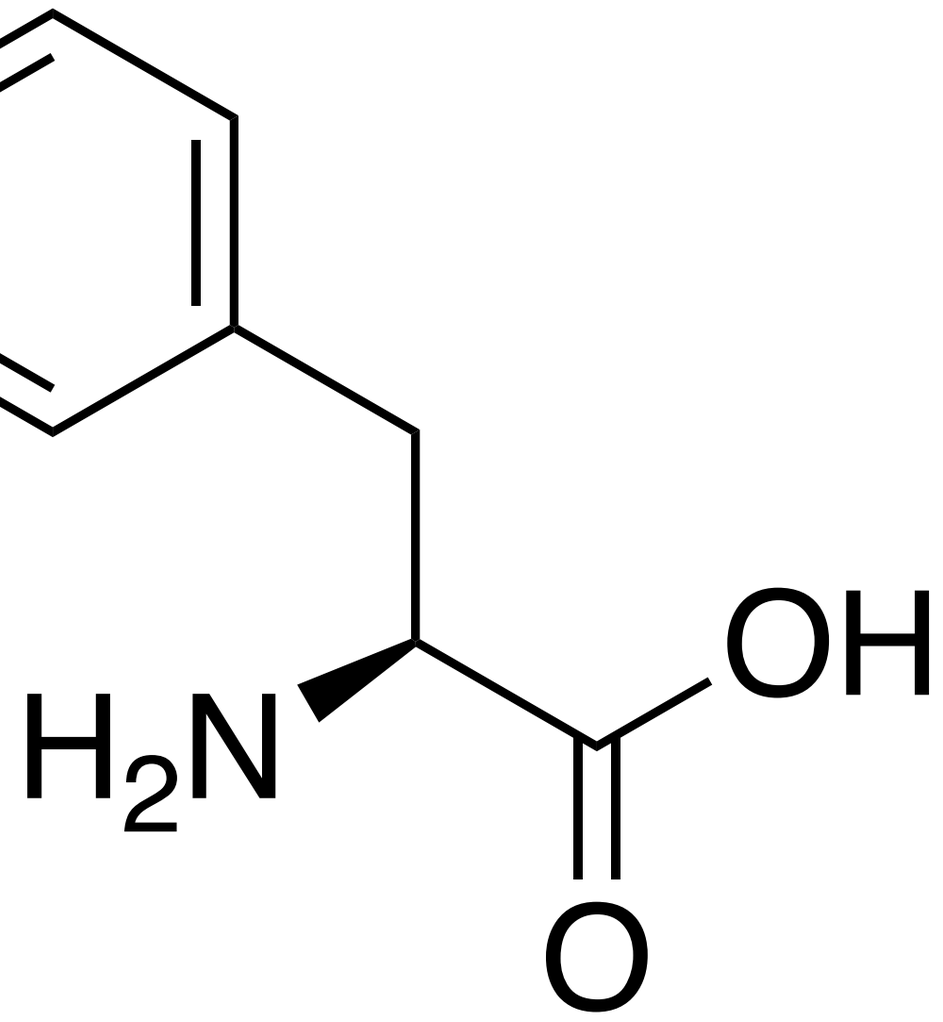
Boc protected amino-acids

Acides aminés

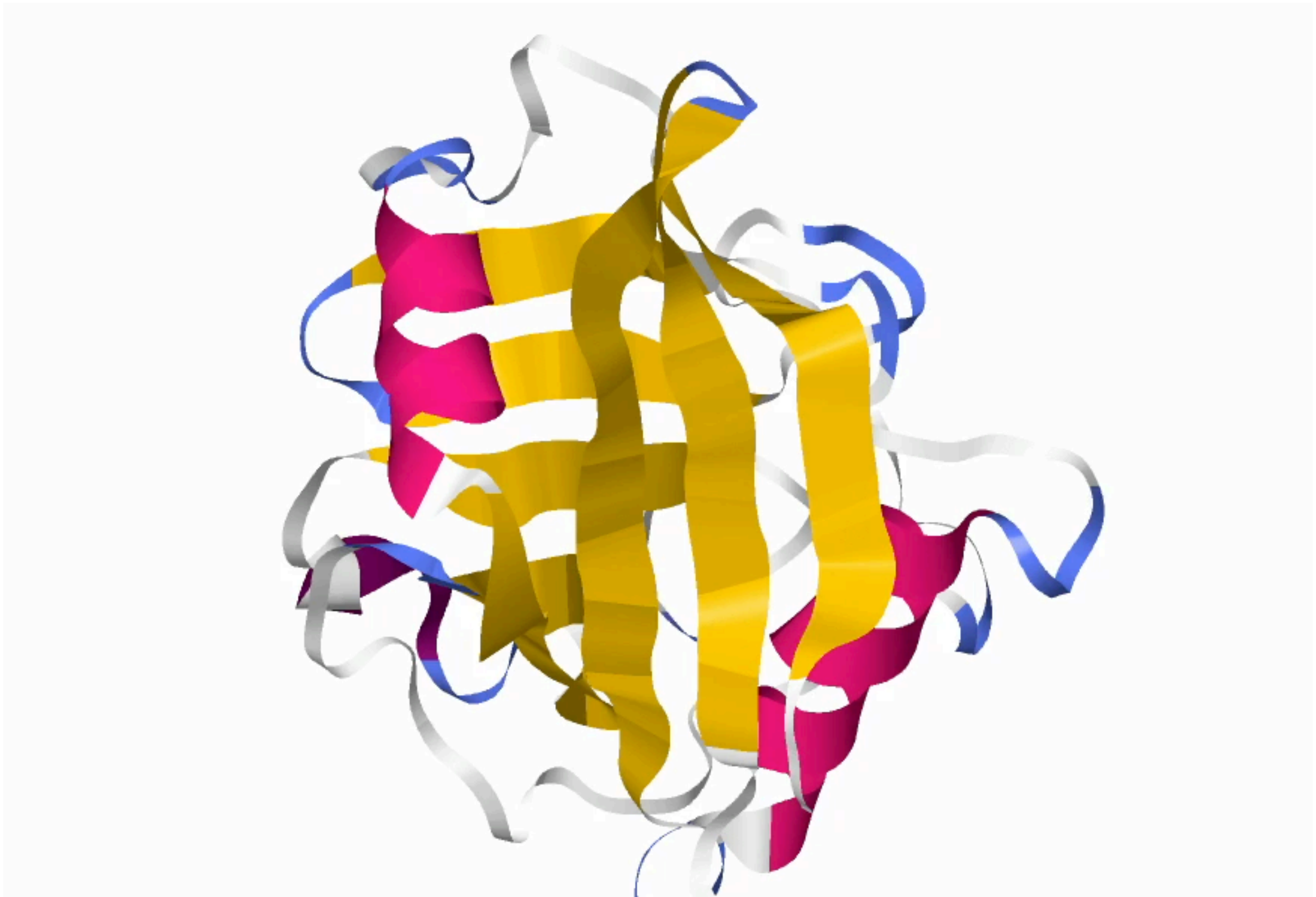
Cyclosporine



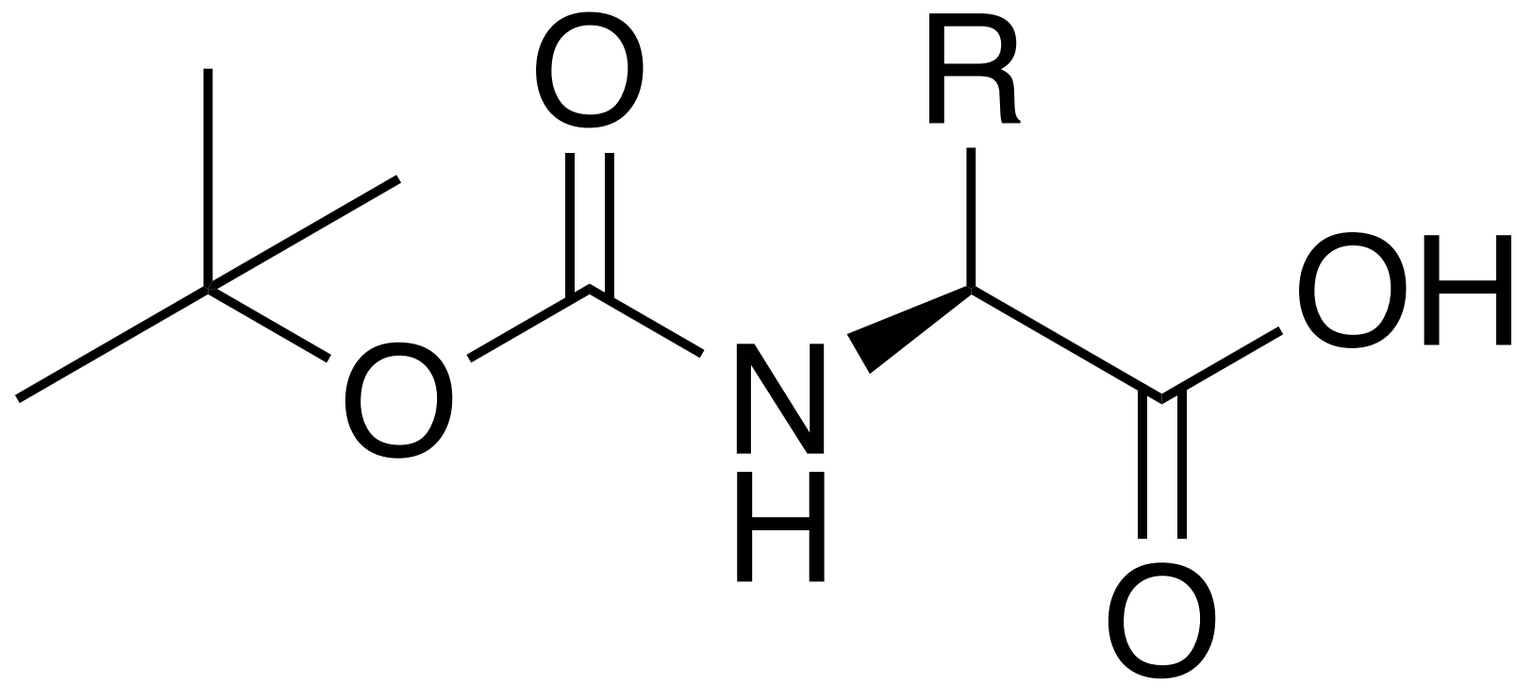
Phénylalanine



Acides aminés protéinogènes



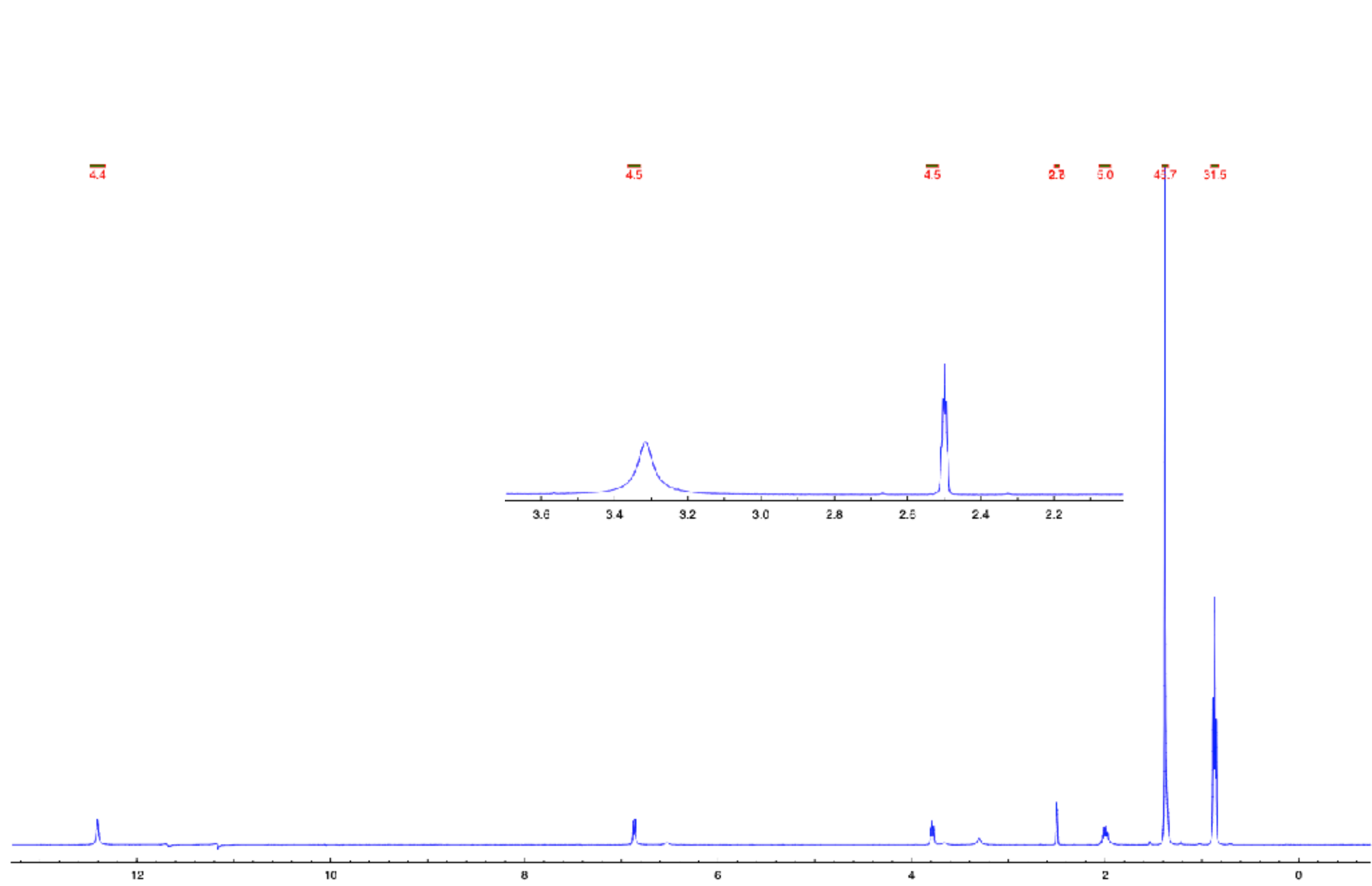
Acides aminés 'Boc'



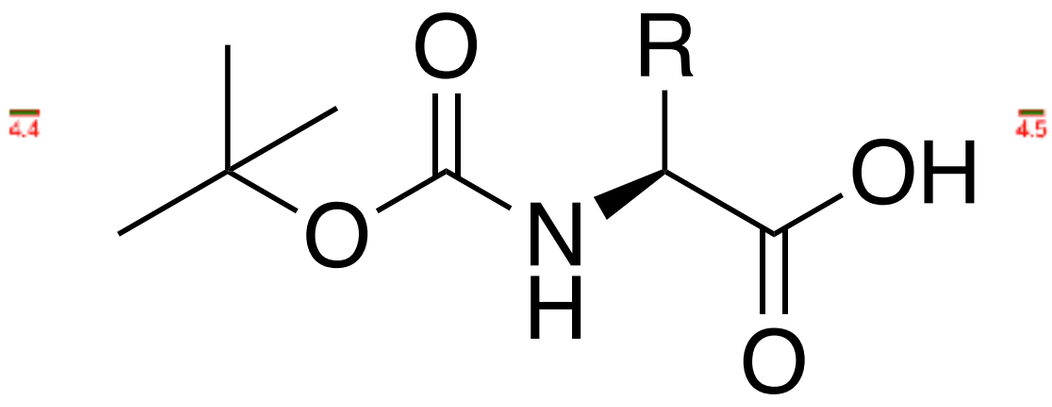
DMSO-d6

DMSO-d6

Noyau	Spin I	Abondance naturelle (%)	υ obs. (MHz) (B_0=2.3488 T)	Rapport gyromagnétique γ [10^7 rad T^{-1} s^{-1}]	Relative sensibility
^{1}H	1/2	99.98	100	26.7519	100
^{2}H	1	0.016	15.3	4.1066	0.96
^{10}B	3	19.58	10.7	2.8746	1.99

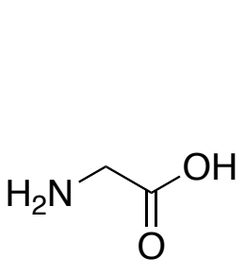


DMSO-d6

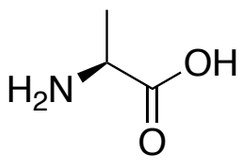

O
R
O
N
H
OH
O

H2O
DMSO-d5
12
10
8
6
4
2
0

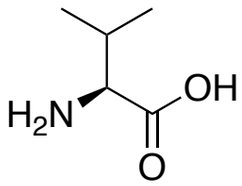
20 acides aminés protéinogènes



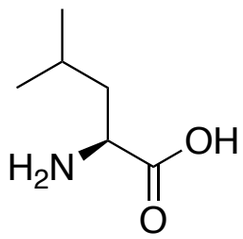
GLY



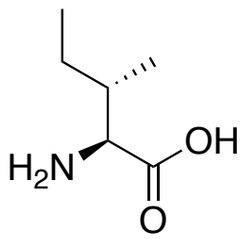
ALA



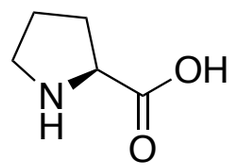
VAL



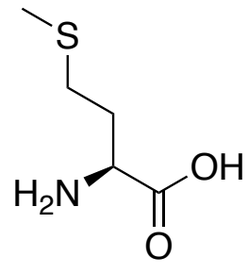
LEU



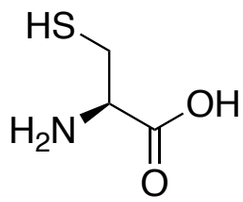
ILE



PRO



MET



CYS

ASP

ASN

GLU

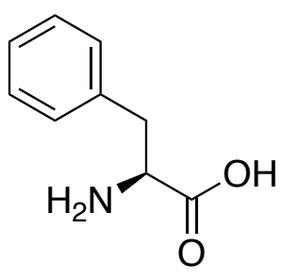
GLN

LYS

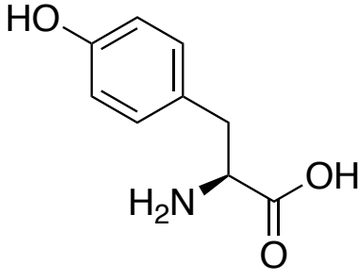
ARG

SER

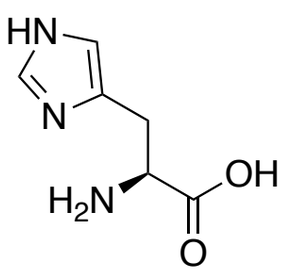
THR



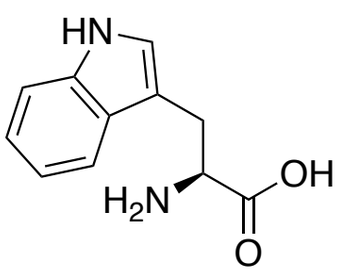
PHE



TYR



HIS



TRP

Exercises 6 - BocAA

Exercices intégrés

^{13}C NMR

Caractéristiques des principaux noyaux

Noyau	Spin I	Abondance naturelle (%)	υ obs. (MHz) (B_0=2.3488 T)	Rapport gyromagnétique γ [10^7 rad T^{-1} s^{-1}]	Relative sensibility
^{1}H	1/2	99.98	100	26.7519	100
^{2}H	1	0.016	15.3	4.1066	0.96
^{10}B	3	19.58	10.7	2.8746	1.99
^{11}B	3/2	80.42	32.0	8.5843	16.5
^{12}C	0	98.9	–	–	–
^{13}C	1/2	1.108	25.1	6.7283	1.59
^{14}N	1	99.63	7.2	1.9338	0.10
^{15}N	1/2	0.37	10.1	–2.712	0.10
^{16}O	0	99.96	–	–	–
^{17}O	5/2	0.037	13.6	-3.6279	2.91
^{19}F	1/2	100	97.1	25.181	83.3
^{29}Si	1/2	4.70	19.9	–5.3188	0.78
^{31}P	1/2	100	40.4	10.841	6.63

Noyau	Spin I	Abondance naturelle (%)	υ obs. (MHz) (B_0=2.3488 T)	Rapport gyromagnétique γ [10^7 rad T^{-1} s^{-1}]	Relative sensibility
^{1}H	1/2	99.98	100	26.7519	100
^{2}H	1	0.016	15.3	4.1066	0.96
^{12}C	0	98.9	–	–	–
^{13}C	1/2	1.108	25.1	6.7283	1.59

Problème de sensibilité

Pas intégrable !

Single Scan

1 Scan - 5 seconds

4 Scans - 20 seconds

16 Scans - 80 seconds

3

2

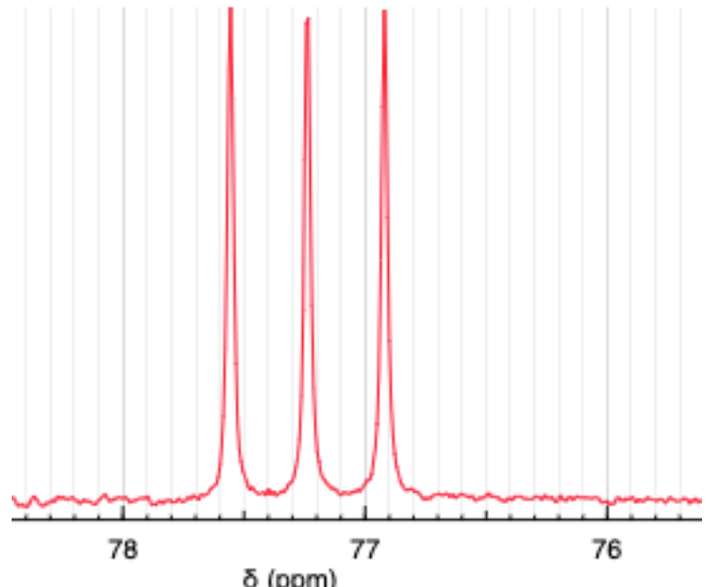
1

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

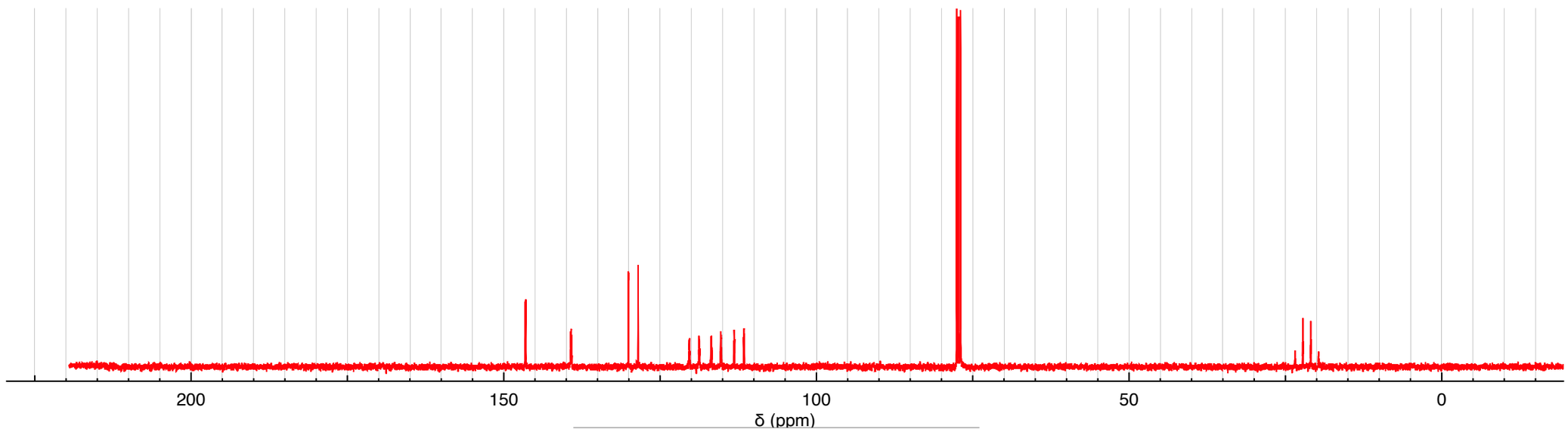
Le $CDCl_3$: ^1J = ~ 120Hz

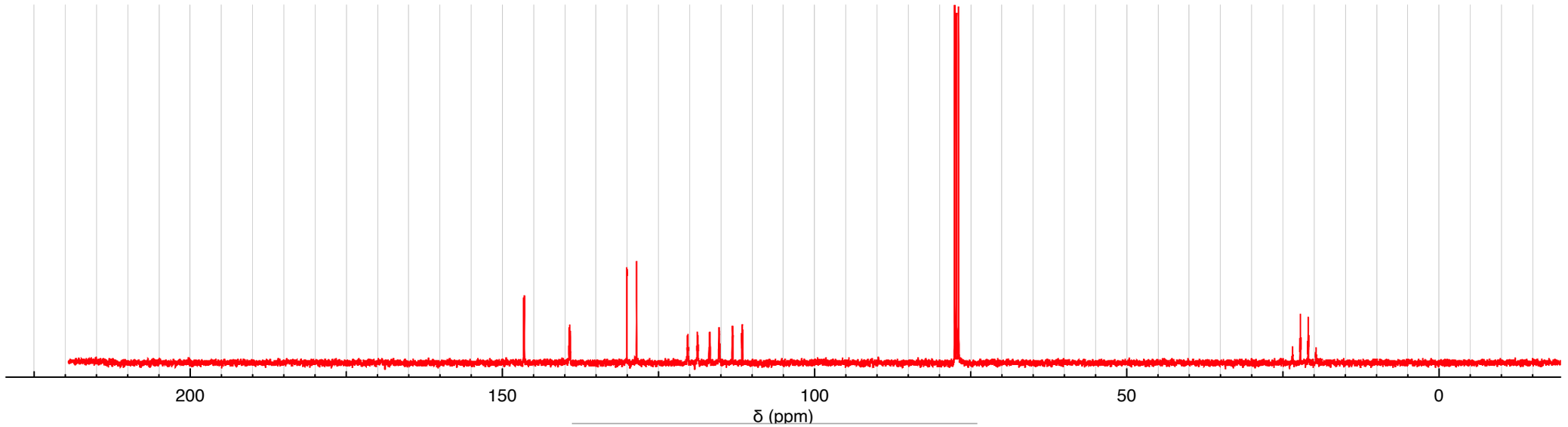
Noyau	Spin I	Abondance naturelle (%)	υ obs. (MHz) (B_0=2.3488 T)	Rapport gyromagnétique γ [10^7 rad T^{-1} s^{-1}]	Relative sensibility
^1H	1/2	99.98	100	26.7519	100
^2H	1	0.016	15.3	4.1066	0.96
^{12}C	0	98.9	–	–	–
^{13}C	1/2	1.108	25.1	6.7283	1.59

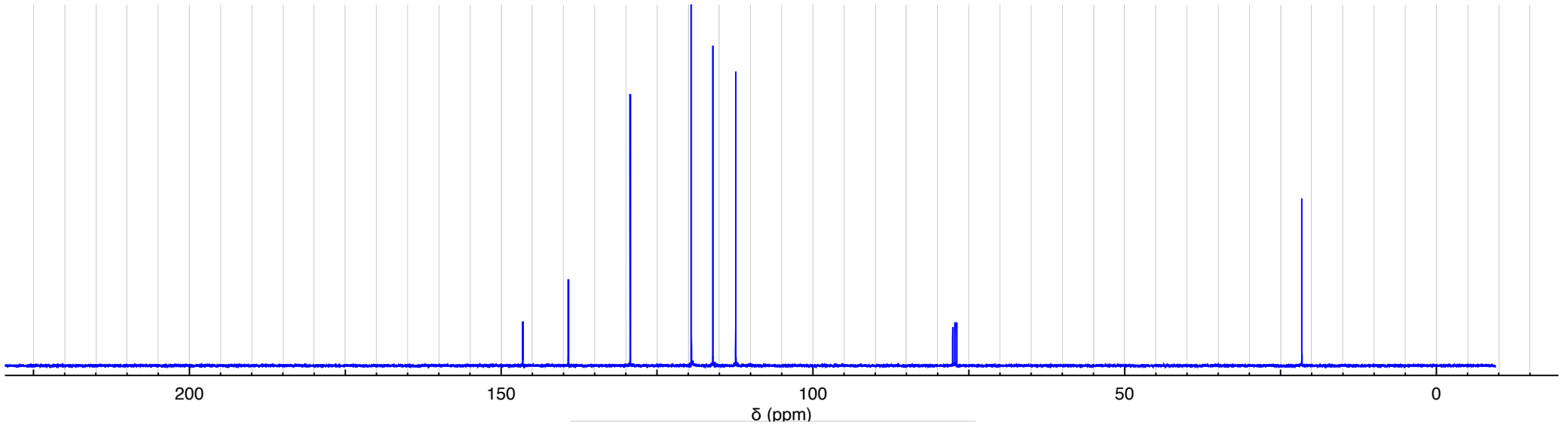


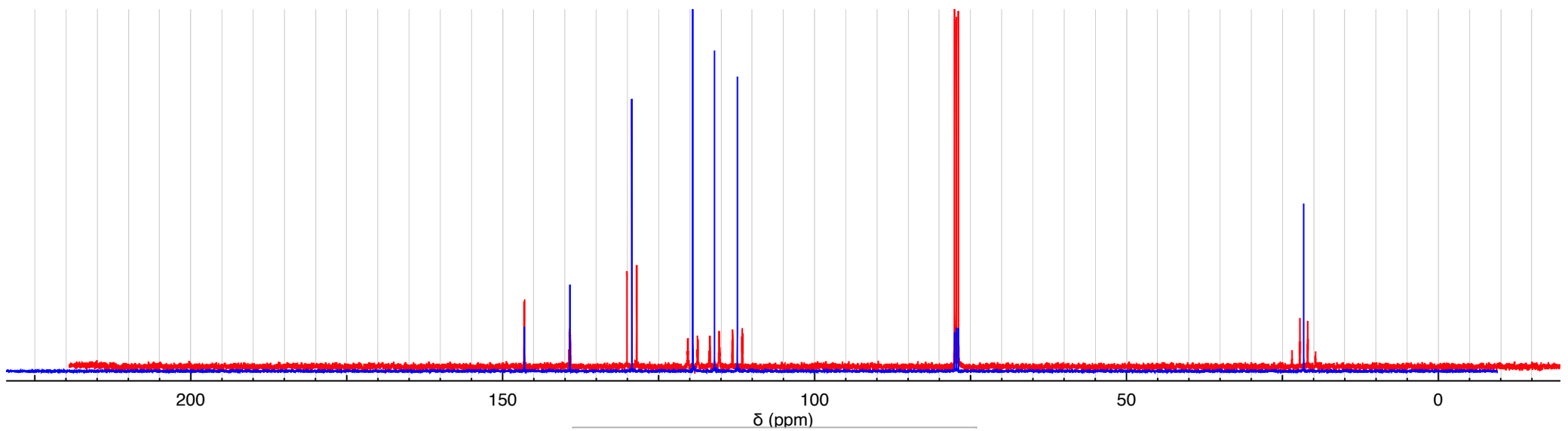
Couplage: 1 -> 3(4) liaisons

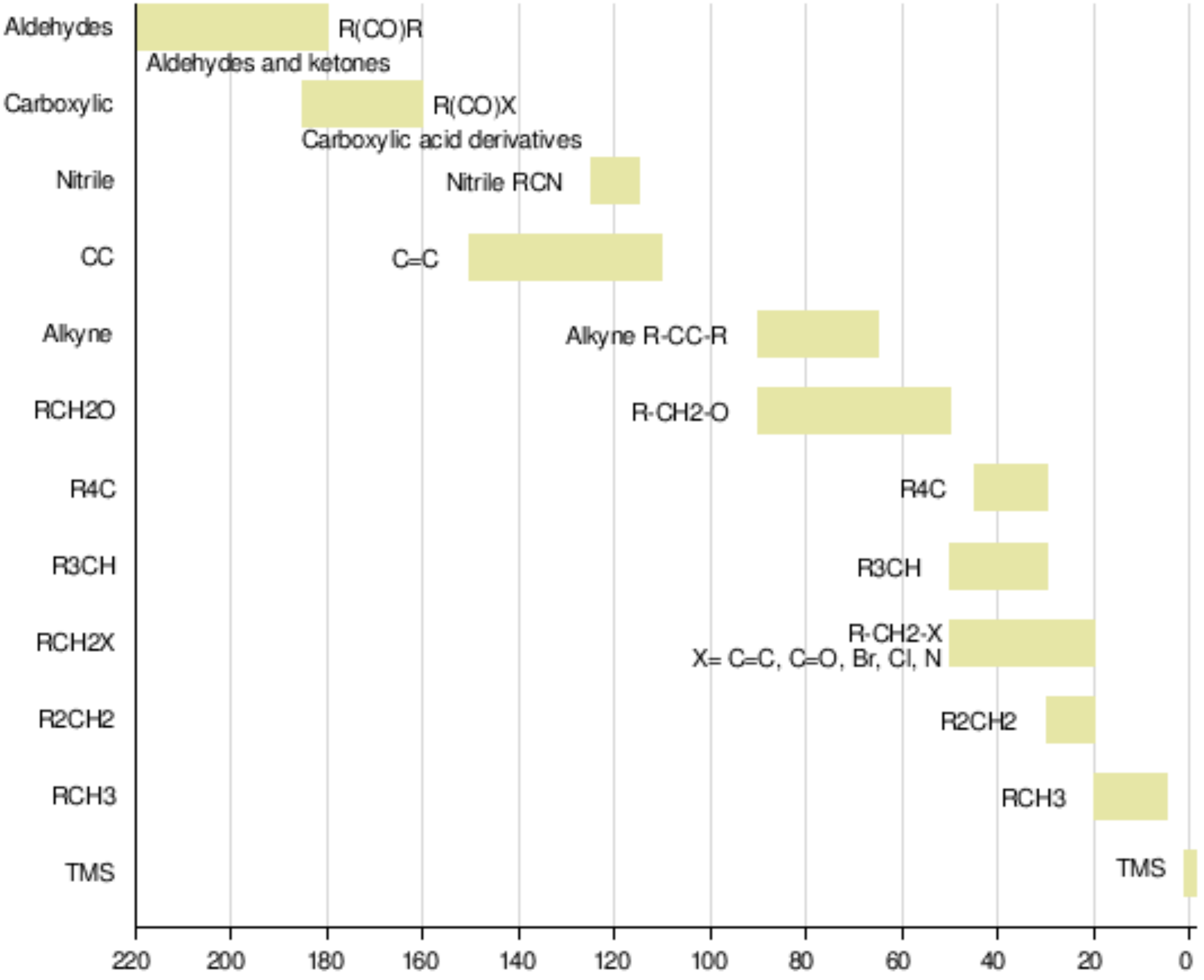
Découplage




200
150
100
50
0
δ (ppm)


200
150
100
50
0
δ (ppm)


200
150
100
50
0
δ (ppm)


Aldehydes
R(CO)R
Aldehydes and ketones
Carboxylic
R(CO)X
Carboxylic acid derivatives
Nitrile
Nitrile RCN
CC
C=C
Alkyne
Alkyne R-CC-R
RCH2O
R-CH2-O
R4C
R4C
R3CH
R3CH
RCH2X
R-CH2-X
X= C=C, C=O, Br, Cl, N
R2CH2
R2CH2
RCH3
RCH3
TMS
TMS
220
200
180
160
140
120
100
80
60
40
20
0

13C exercises

Evaluation cours pour ESC

https://cape-quest.epfl.ch/evasys/online.php?p=3EDUJ

Exemple d'examen

Question 1

Tables de références

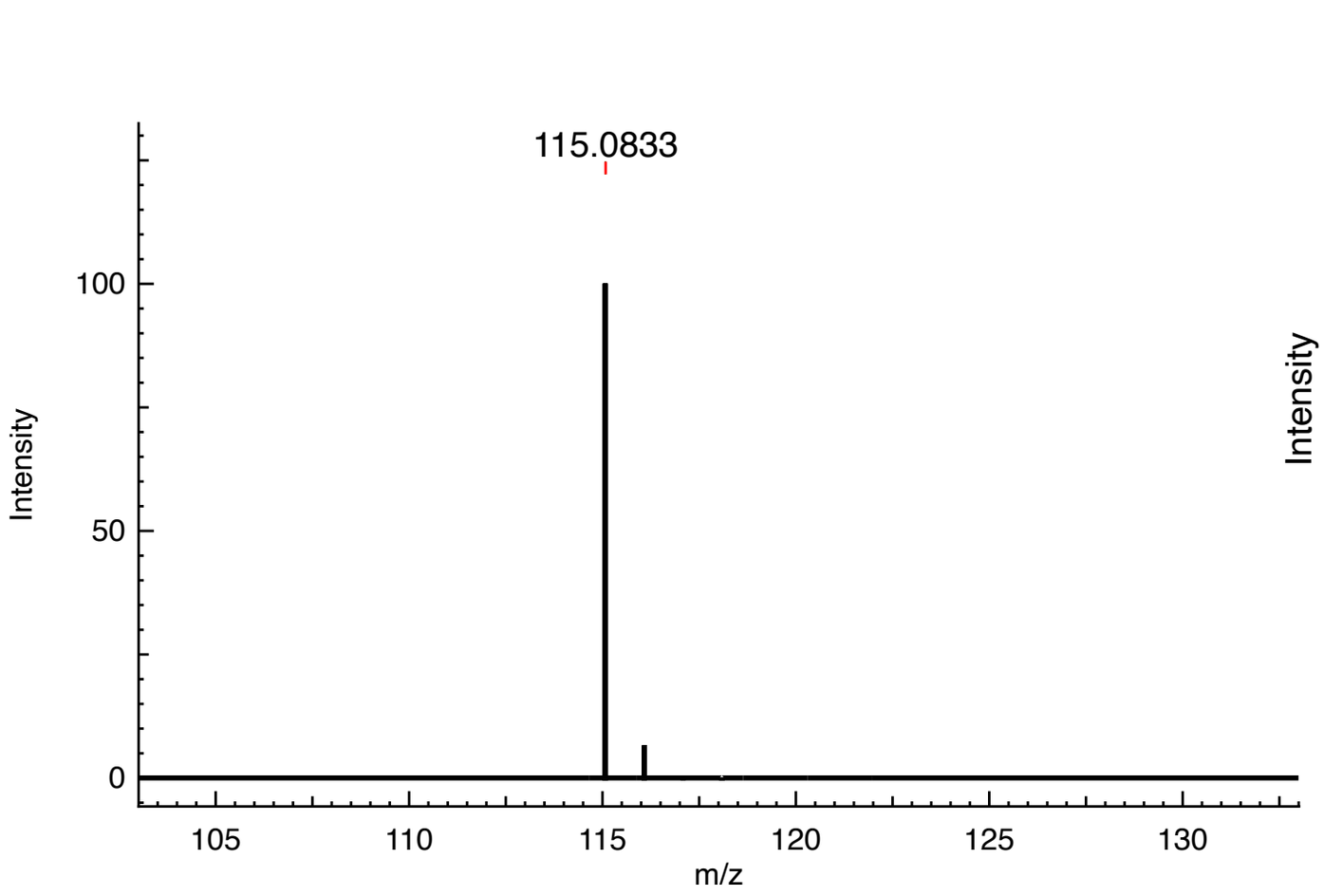
Veuillez déterminer pour le produit inconnu :

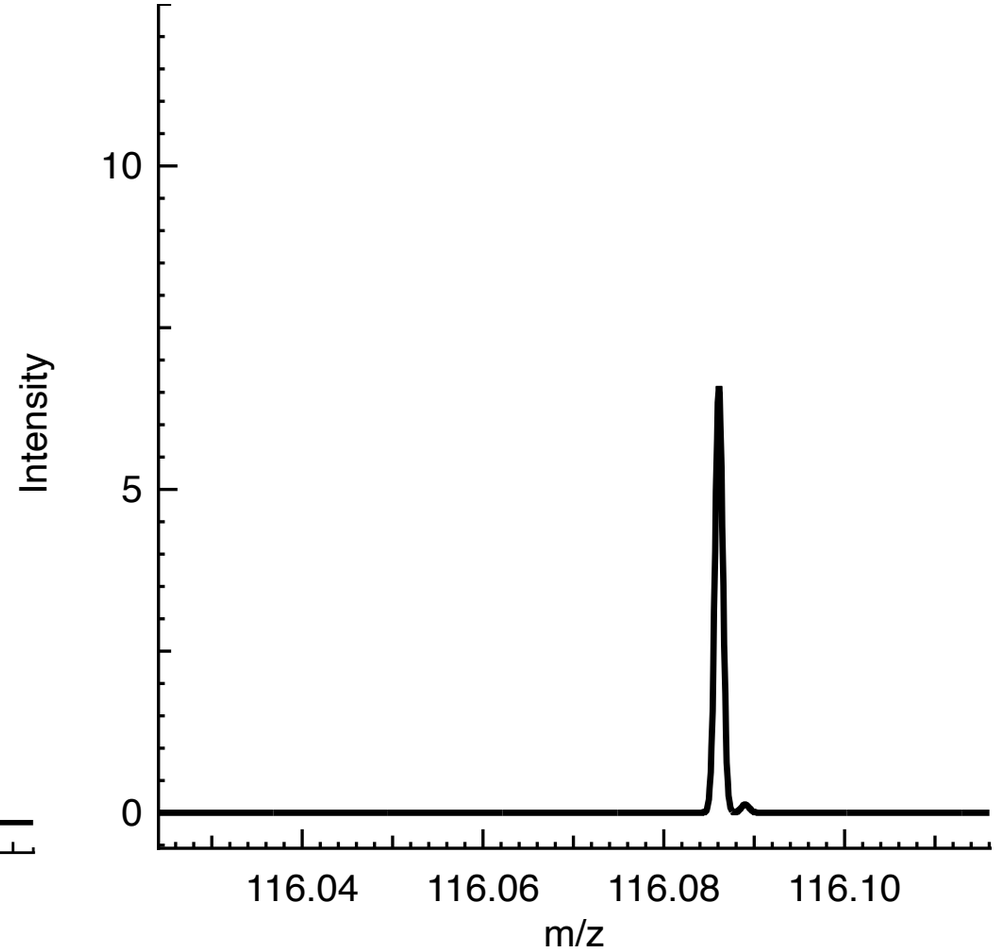
1. La formule brute
2. Le degré d'insaturation
3. La structure chimique

La formule brute se trouve dans le formulaire annexé. Le produit inconnu possède les spectres caractéristiques suivants :

Spectre de masse

Le spectre de masse (ionisation par électrospray (ESI)) du produit inconnu donne un signal correspondant à la masse monoisotopique de la molécule simplement protonée ($M + H^+$) à 115.0833 Da avec une précision de 100 ppm.





Spectre infrarouge

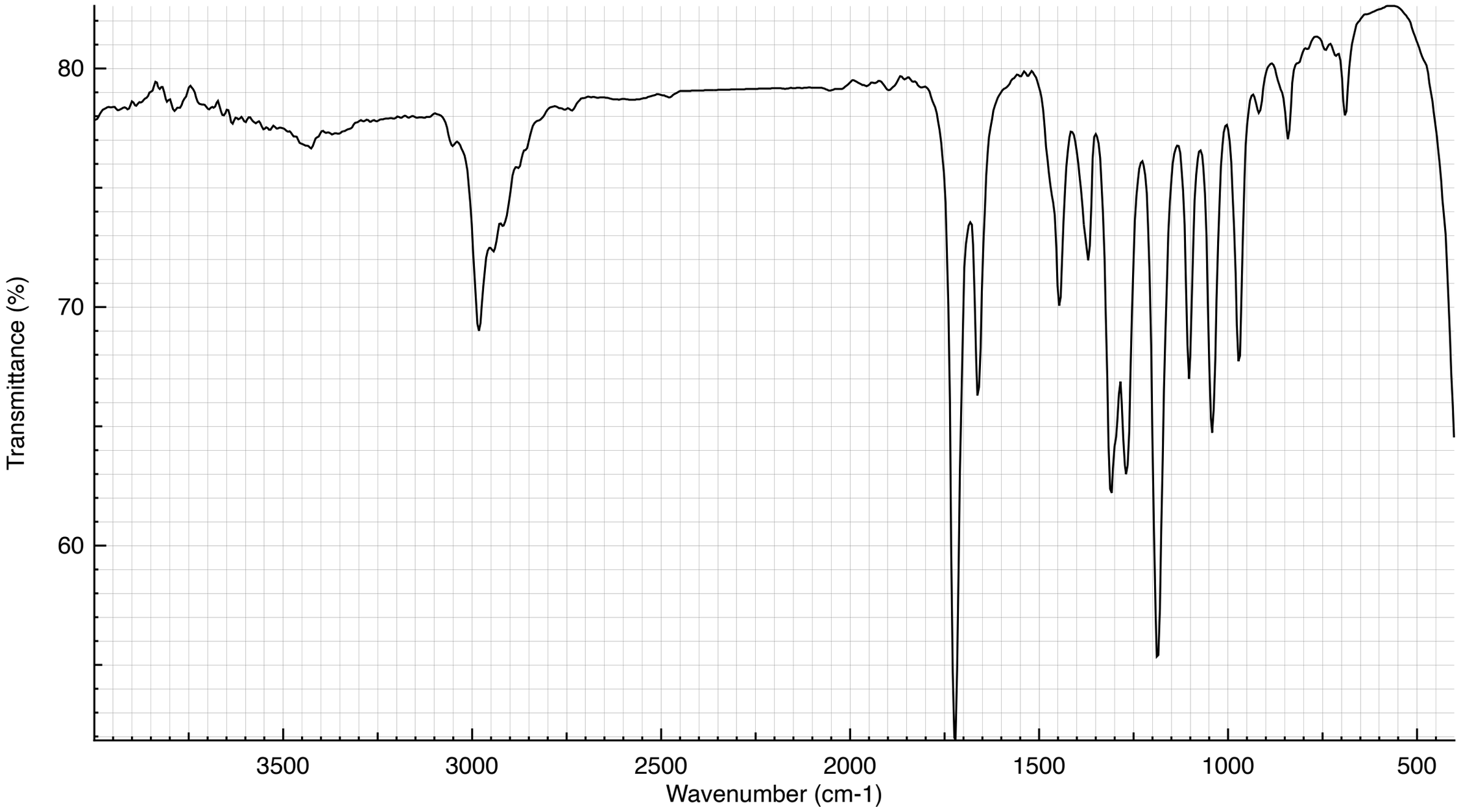
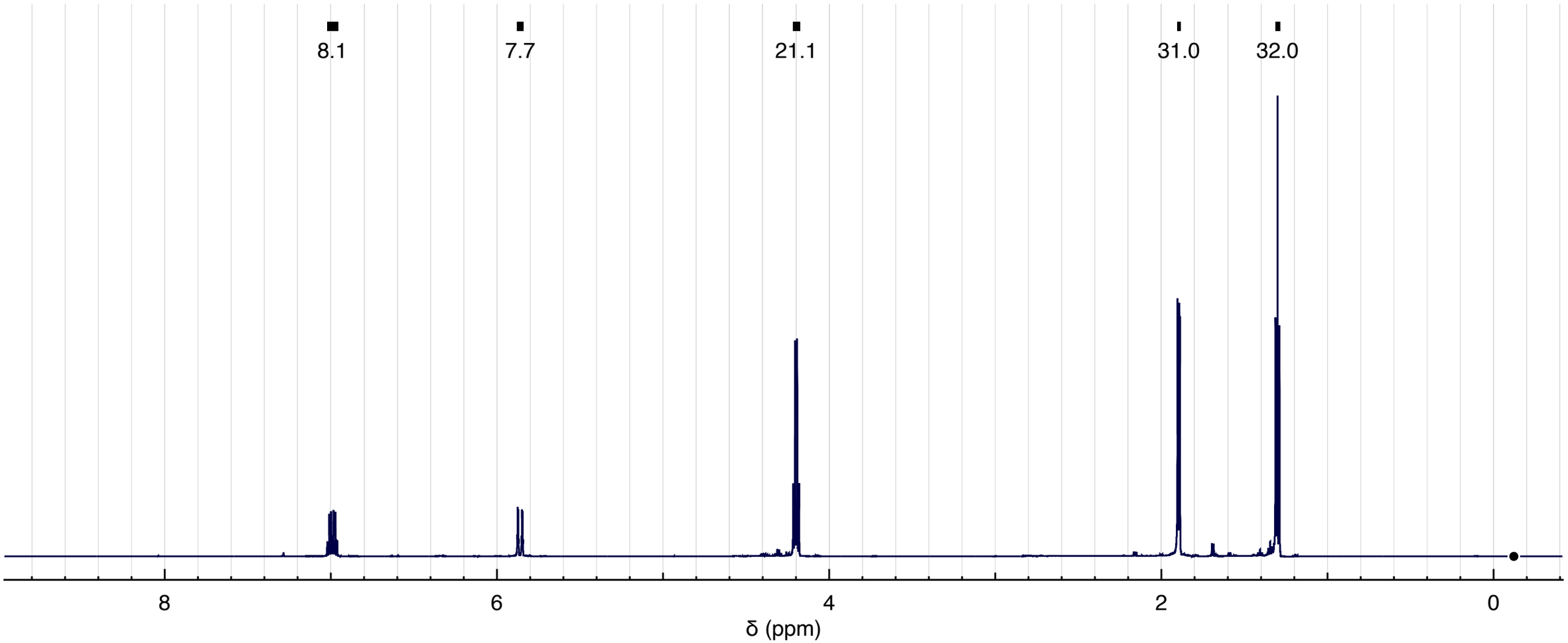
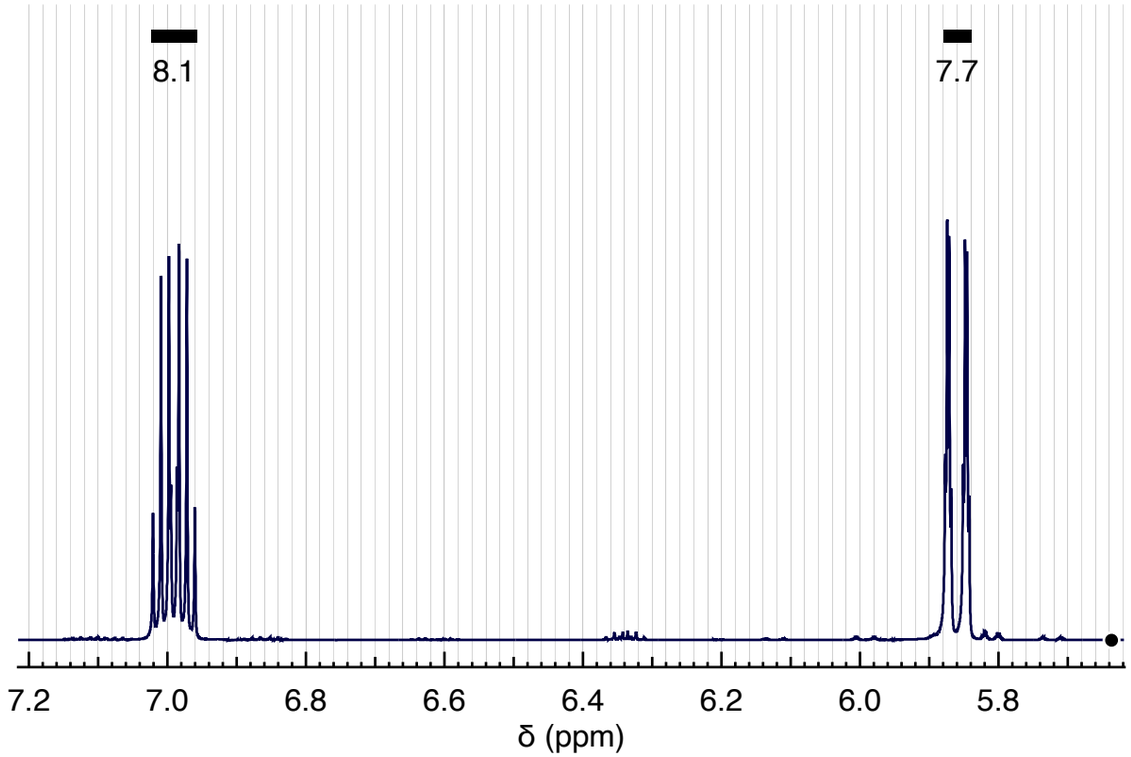
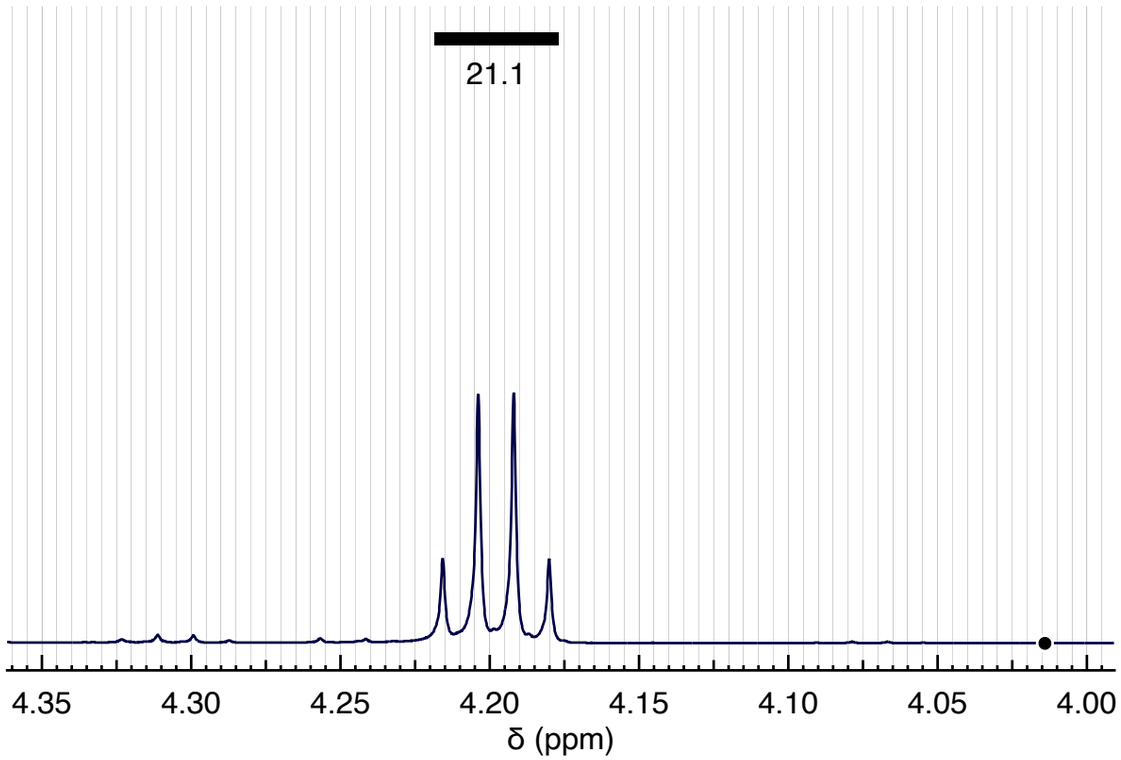


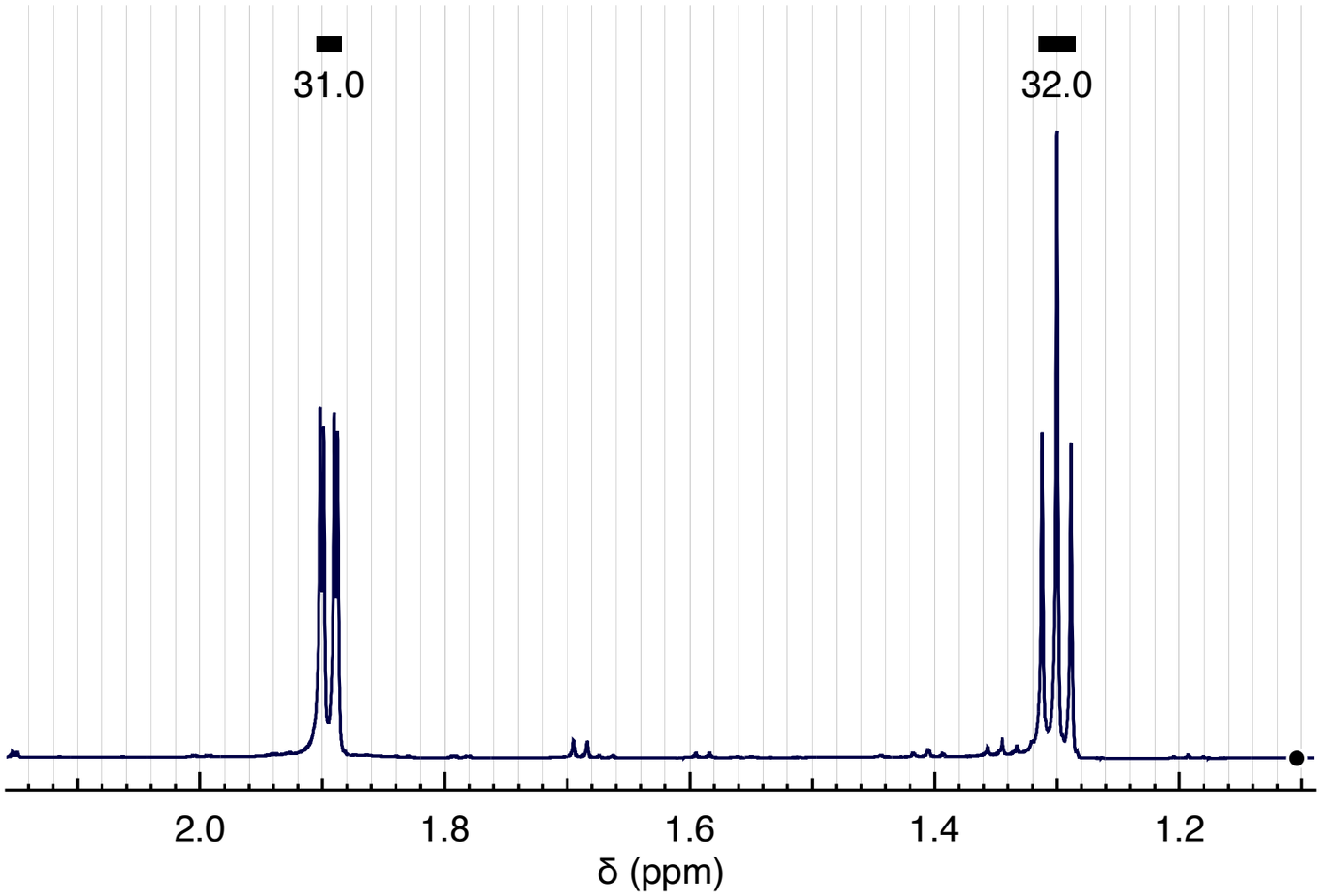
Figure: spectre IR, transmittance (%) en fonction du nombre d'onde (cm^{-1})

Spectre RMN ^{1}H 400 MHz (ppm, $CDCl_3$)




8.1
7.7
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
δ (ppm)


21.1
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
δ (ppm)


31.0
32.0
2.0
1.8
1.6
1.4
1.2
δ (ppm)

Question 5

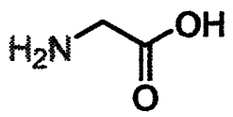
Veuillez donner la structure correspondant à l'acide aminé protéinogène protégé sur l'azote par un 'Boc' (*tert*-butyloxycarbonyl).

Vous avez comme information le spectre RMN ci-après.

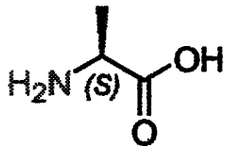
Veuillez indiquer les signaux caractéristiques qui ont permis d'identifier l'acide aminé !

Le solvant est le méthanol deutéré (4 deutériums). Il a 2 caractéristiques importantes :

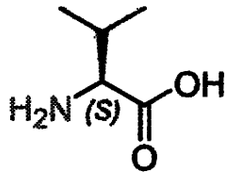
- Le solvant résiduel est un quintuplet en 3.3ppm
- Les protons échangeables (OH, NH) vont être remplacés par du deuterium et ne seront pas visible dans le spectre RMN du proton. A la place ils apparaîtrons tous ensemble dans un même signal aux alentours de 4.9ppm.



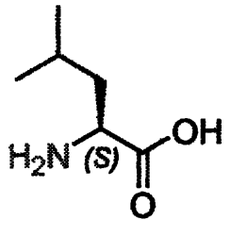
Glycine
Gly
G



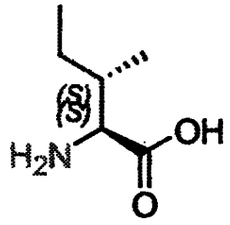
Alanine
Ala
A



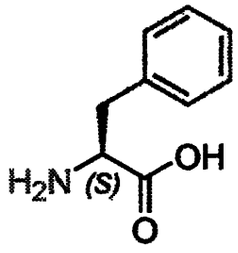
Valine
Val
V



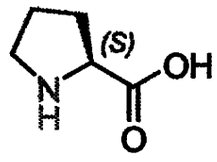
Leucine
Leu
L



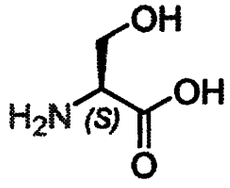
Isoleucine
Ile
I



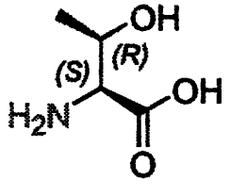
Phenylalanine
Phe
F



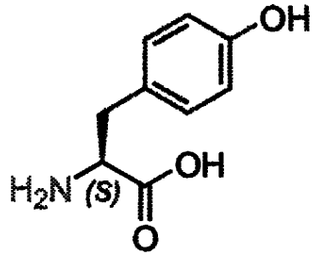
Proline
Pro
P



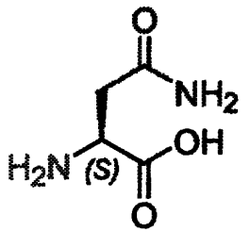
Serine
Ser
S



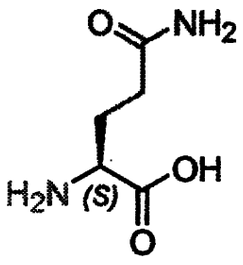
Threonine
Thr
T



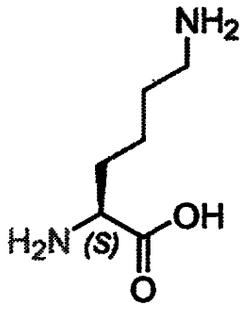
Tyrosine
Tyr
Y



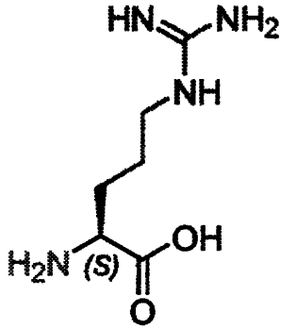
Asparagine
Asn
N



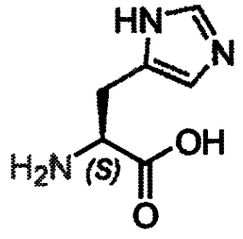
Glutamine
Gln
Q



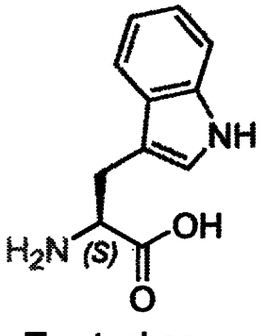
Lysine
Lys
K



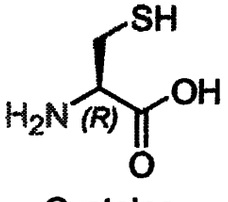
Arginine
Arg
R



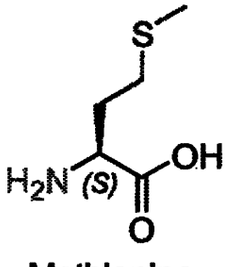
Histidine
His
H



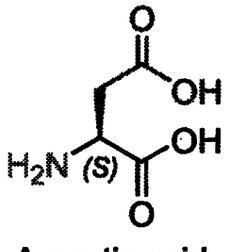
Tryptophan
Trp
W



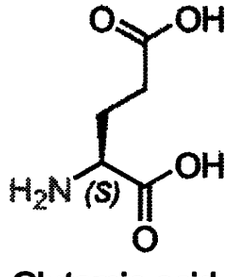
Cysteine
Cys
C



Methionine
Met
M

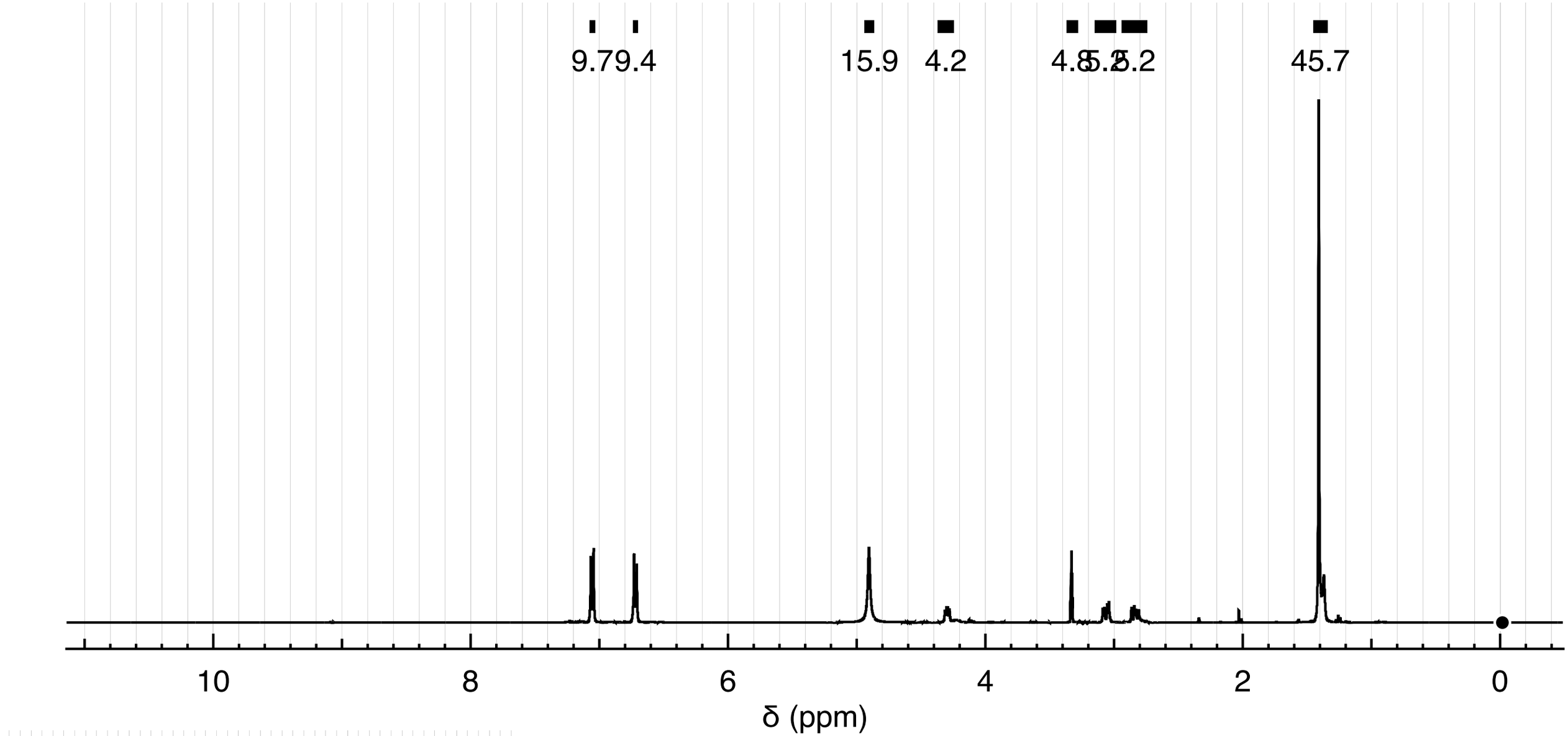


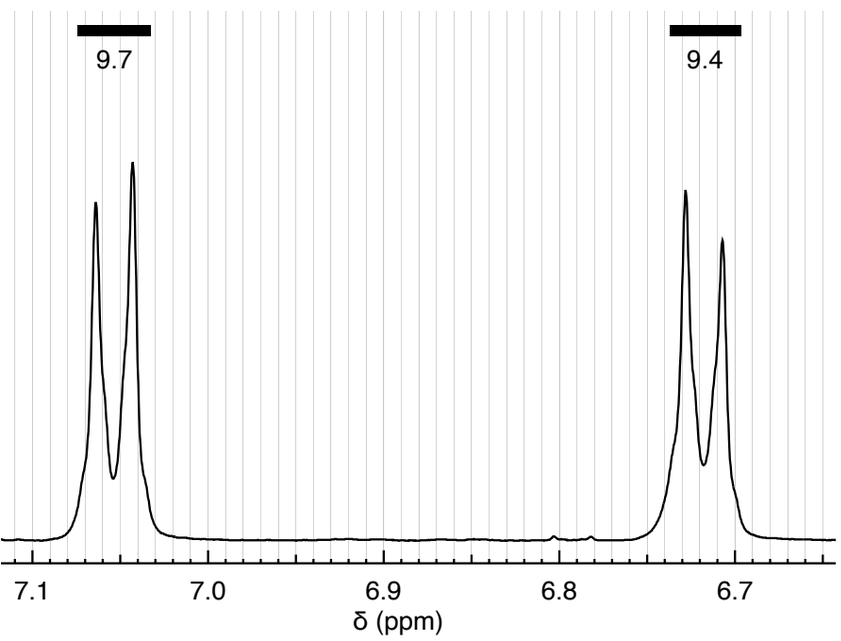
Aspartic acid
Asp
D

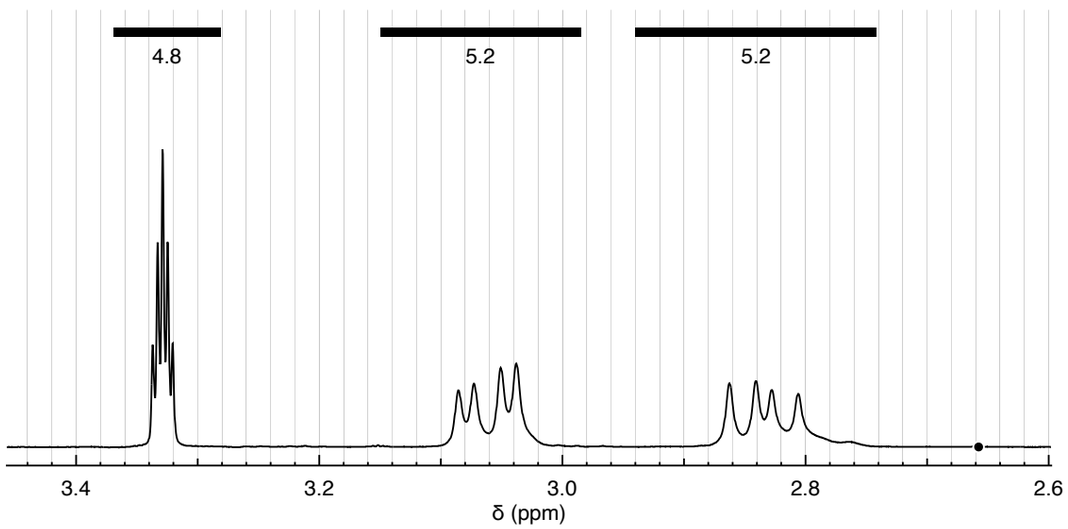


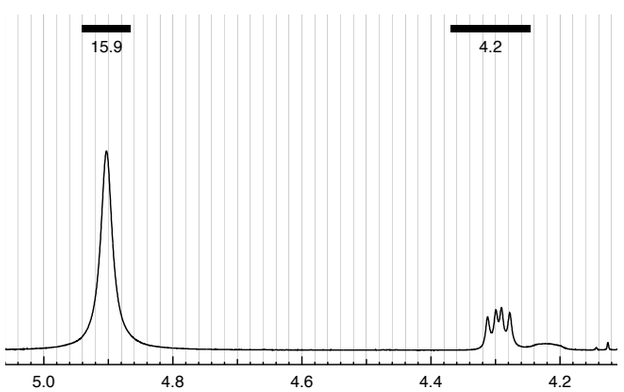
Glutamic acid
Glu
E

Spectre RMN ^{1}H 400 MHz





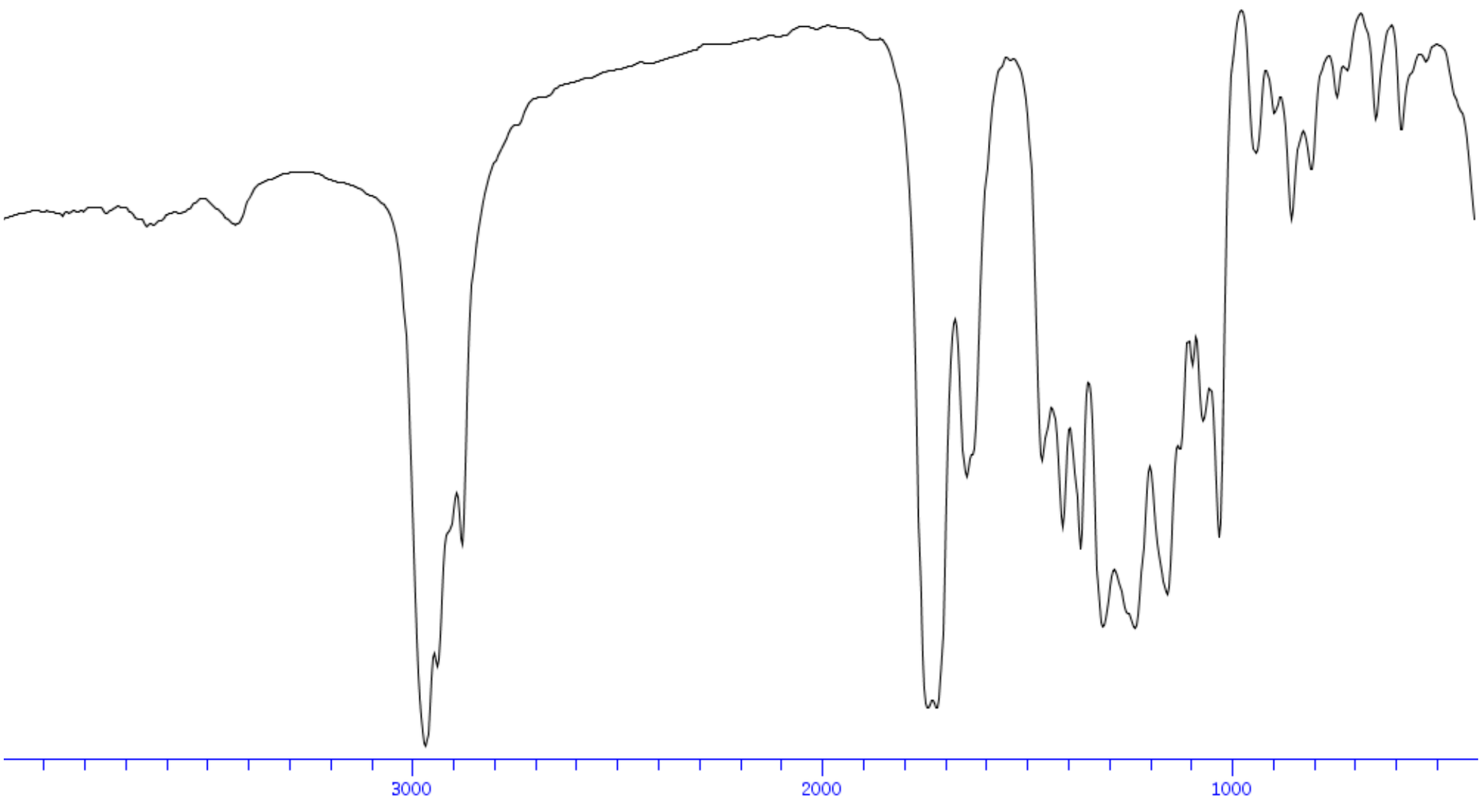




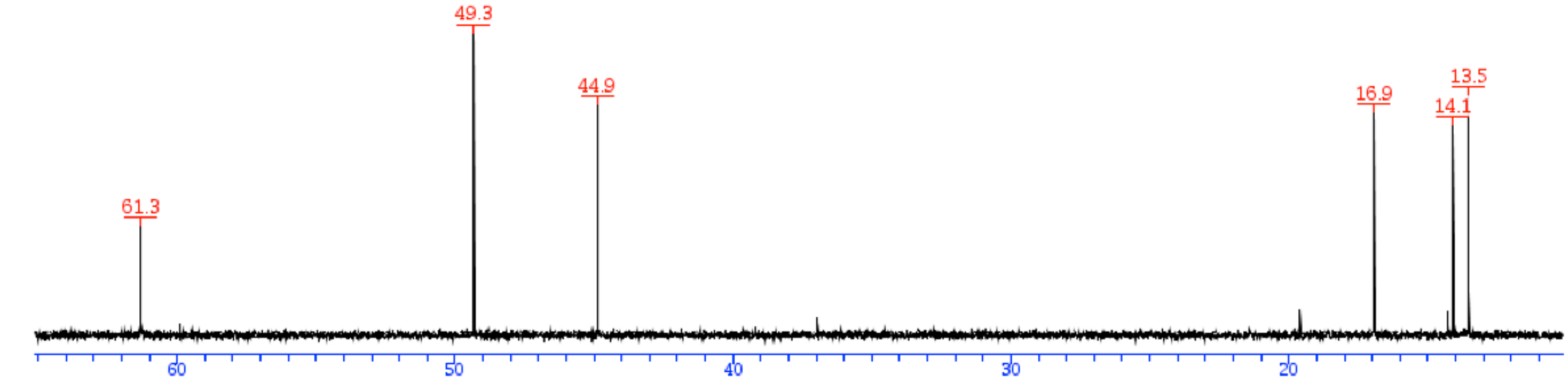
Question 4

Donnez le nombre d'insaturation et dessinez la structure du produit chimique inconnu qui a comme formule brute $C_8H_{14}O_3$ et possédant les spectres caractéristiques suivants :

Spectre infra-rouge:



RMN ^{13}C découplé à 100 MHz ($CDCl_3$).



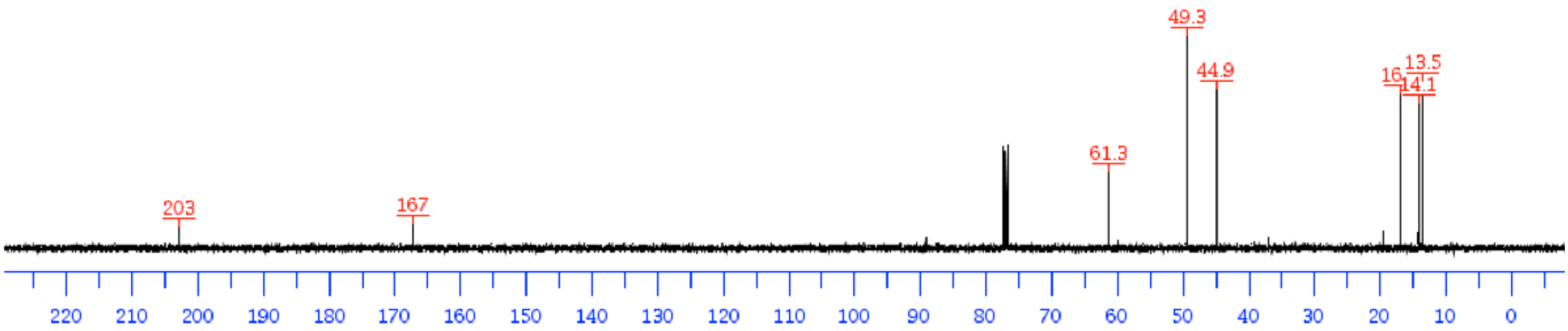
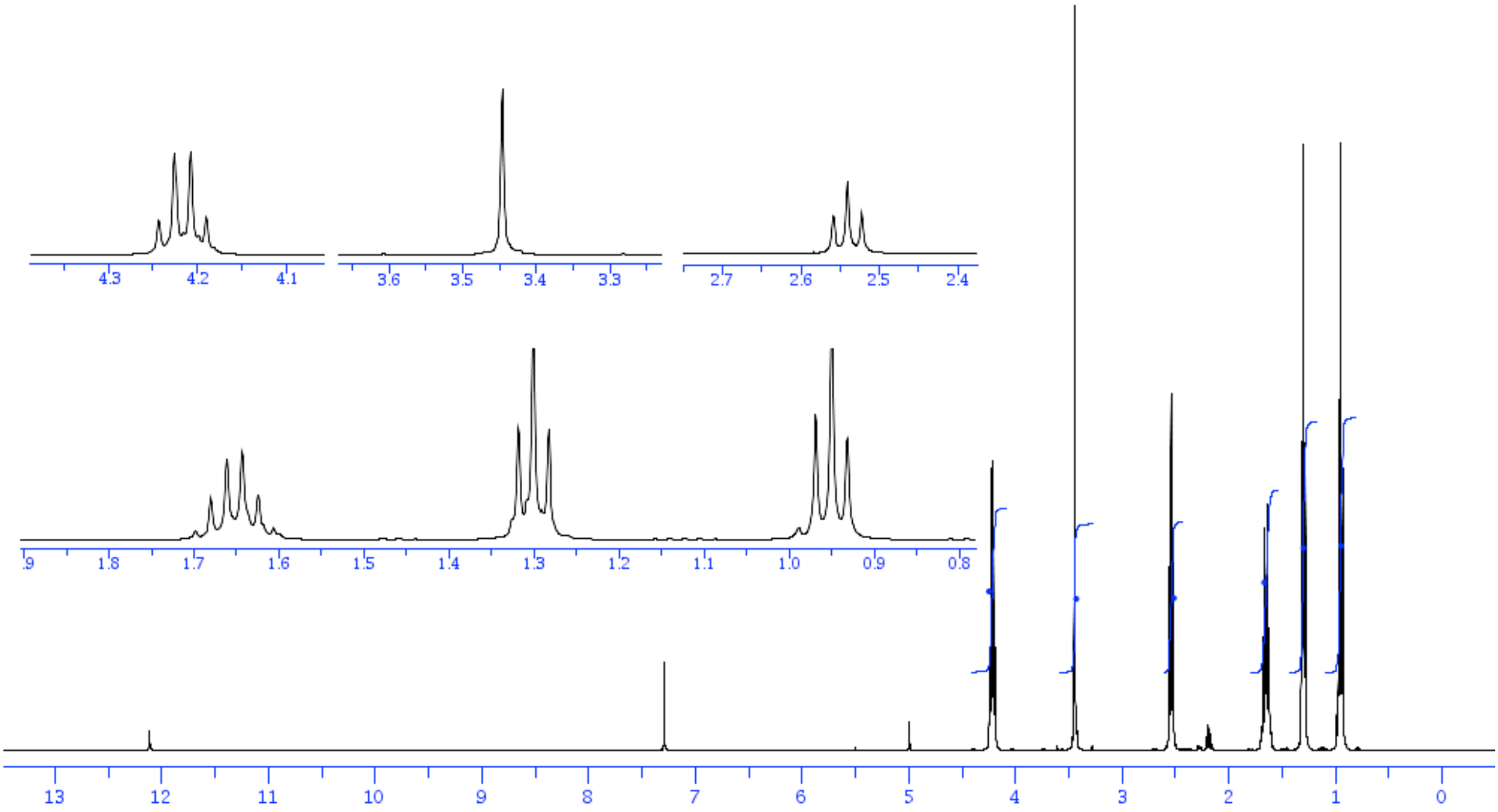


Figure: Spectre RMN ^{13}C découplé. Les signaux relatifs au produit inconnu possèdent une étiquette avec le déplacement chimique. Au-dessus, agrandissement de la zone 0 à 65 ppm.


4.3
4.2
4.1
3.6
3.5
3.4
3.3
2.7
2.6
2.5
2.4
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
13
12
11
10
9
8
7
6
5
4
3
2
1
0

Question 4

Tables de références

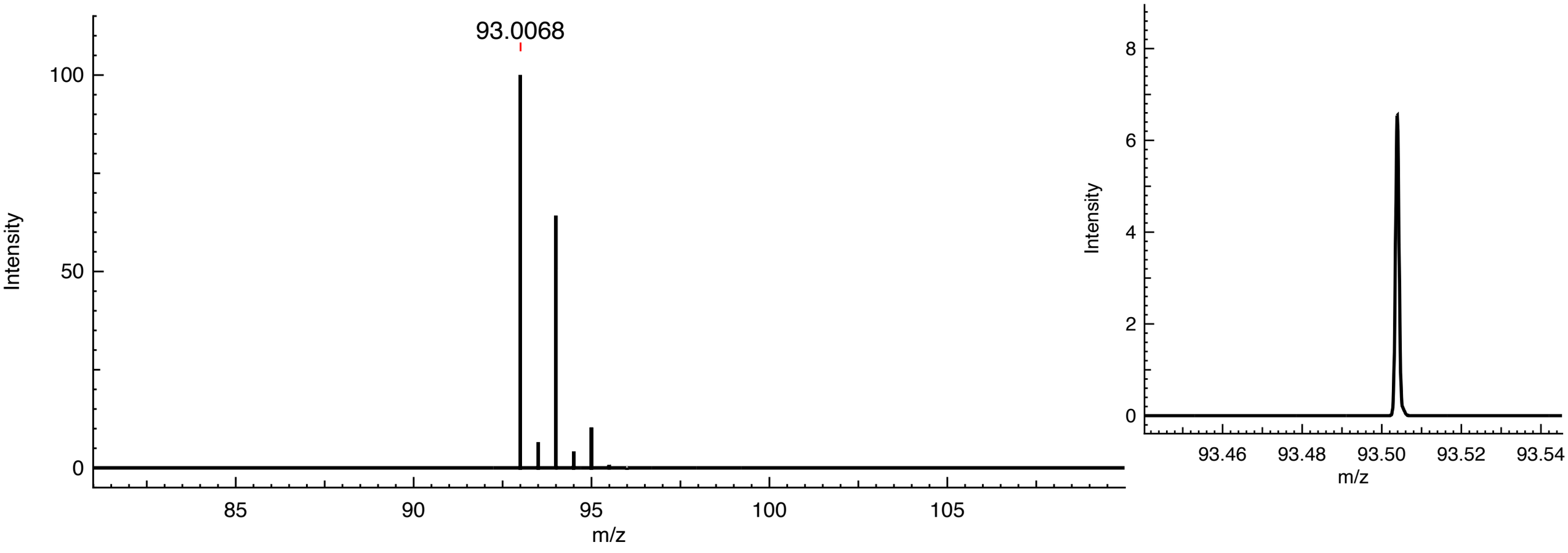
Veuillez déterminer pour le produit inconnu :

1. La formule brute
2. Le degré d'insaturation
3. La structure chimique

La formule brute se trouve dans le formulaire annexé. Le produit inconnu possède les spectres caractéristiques suivants :

Spectre de masse

Le spectre de masse du produit inconnu donne un signal correspondant à la masse monoisotopique de la molécule doublement protonée ($M+2H^+$) en 93.0068 Da avec une précision de 100 ppm.



Spectre RMN ^{1}H 400 MHz