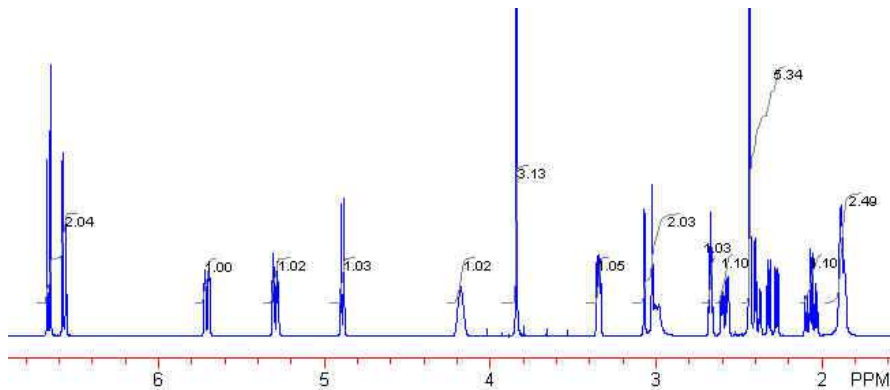




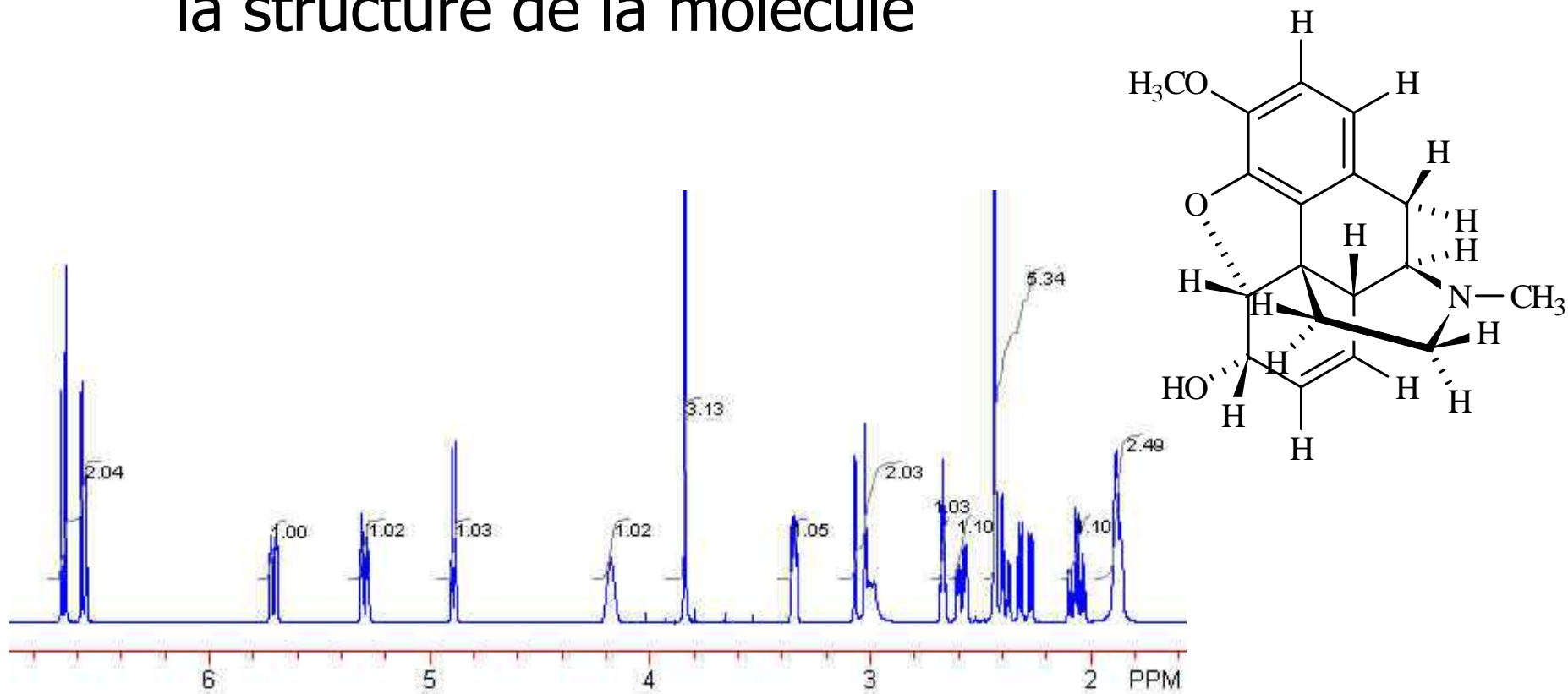
Chapitre B3b

Spectroscopie de RMN Une aide à la détermination des structures



Objectif

Extraire des informations spectrales
la structure de la molécule



La RMN, une aide à la détermination des structures

- Bases physiques de la RMN
- Enregistrement d'un spectre de RMN
- Déplacement chimique
- Couplage spin-spin
- Analyse d'un spectre de RMN
- Equivalences chimique et magnétique



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Noyaux magnétiques

- Existence d'un moment cinétique de spin nucléaire $I \rightarrow$ moment magnétique de spin μ
- Exemples : ${}^1_1\text{H}$ ${}^{13}_6\text{C}$



Principe de la méthode

- Noyau de H = minuscule aimant \Rightarrow moment magnétique quantifié :

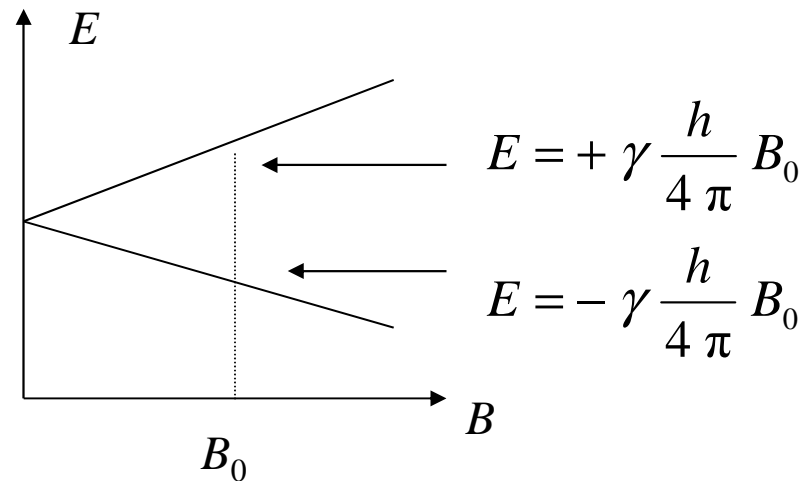
$$\mu_z = \gamma \frac{h}{2\pi} m_I \qquad m_I = \pm 1/2$$

- qui s'oriente dans un champ magnétique uniforme \vec{B}_0



Principe de la méthode

- 2 niveaux d'énergie accessibles au noyau



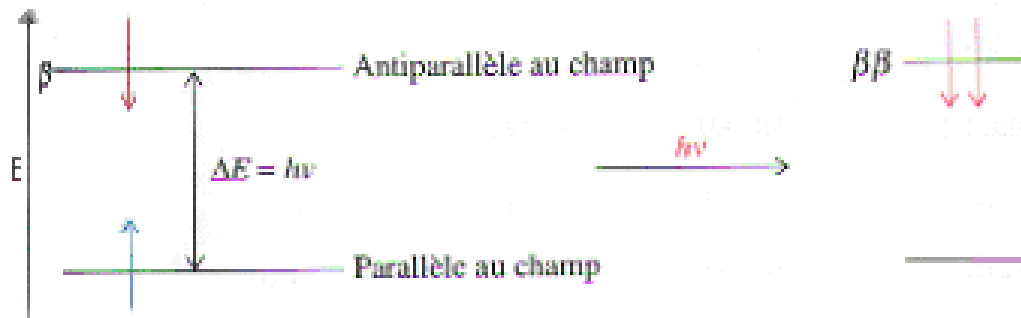
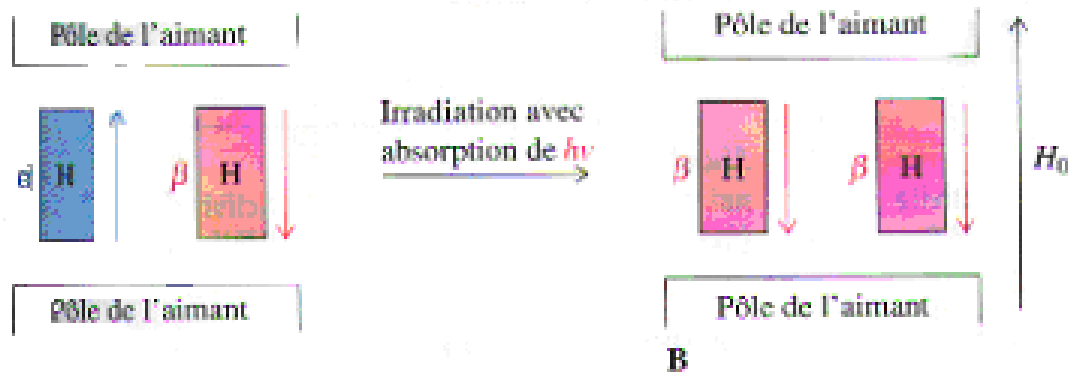
Les niveaux sont également peuplés à 300K

Comment déséquilibrer le peuplement ?

Excitation par un rayonnement électromagnétique



Principe de la méthode



$\nu_0 = 90\text{MHz}$
pour
 $B_0 = 2\text{T}$

un rayonnement électromagnétique ayant exactement la fréquence $\nu_0 = \frac{\gamma}{2\pi} B_0$
sera absorbé par les noyaux

Fréquence de Larmor



La RMN, une aide à la détermination des structures

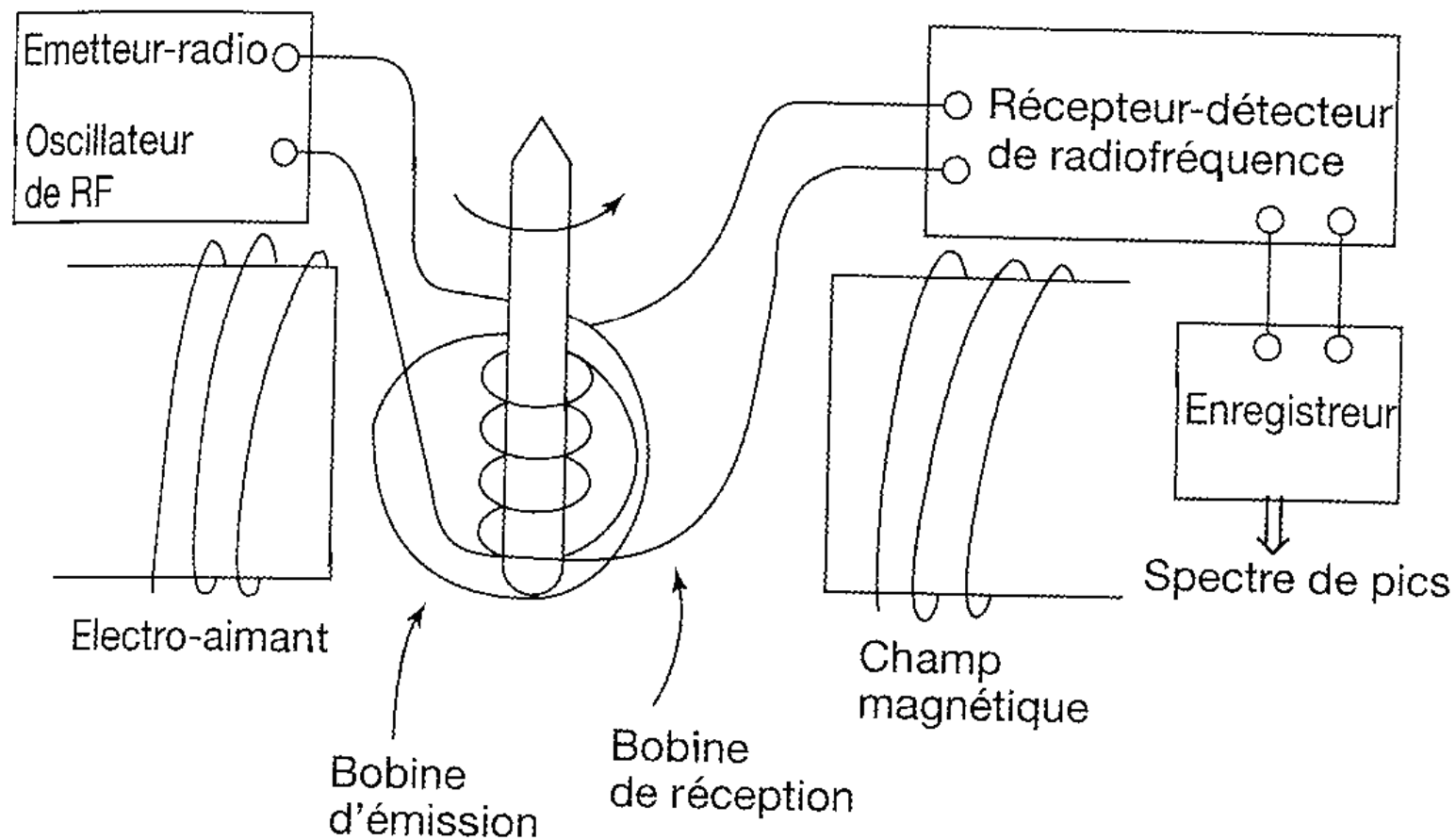
- Bases physiques de la RMN
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Un appareillage typique : 500 MHz



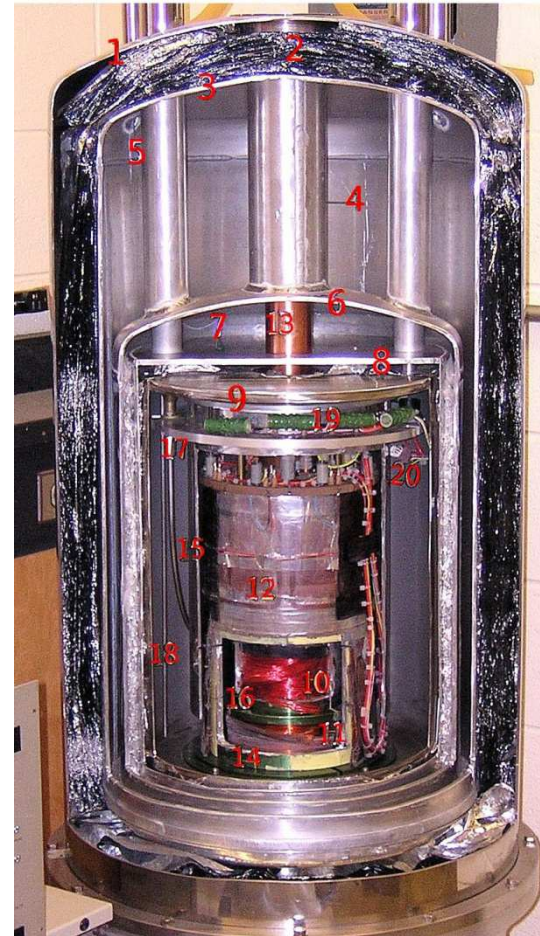
Appareil



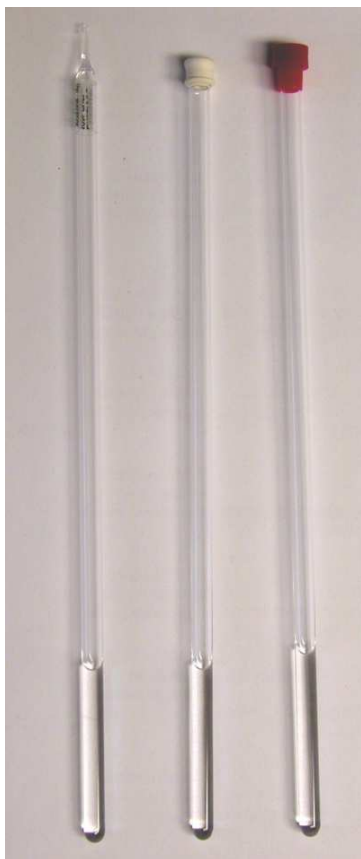
Vue en coupe (!) d'un aimant supraconducteur de 6,34 T



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Porte échantillon

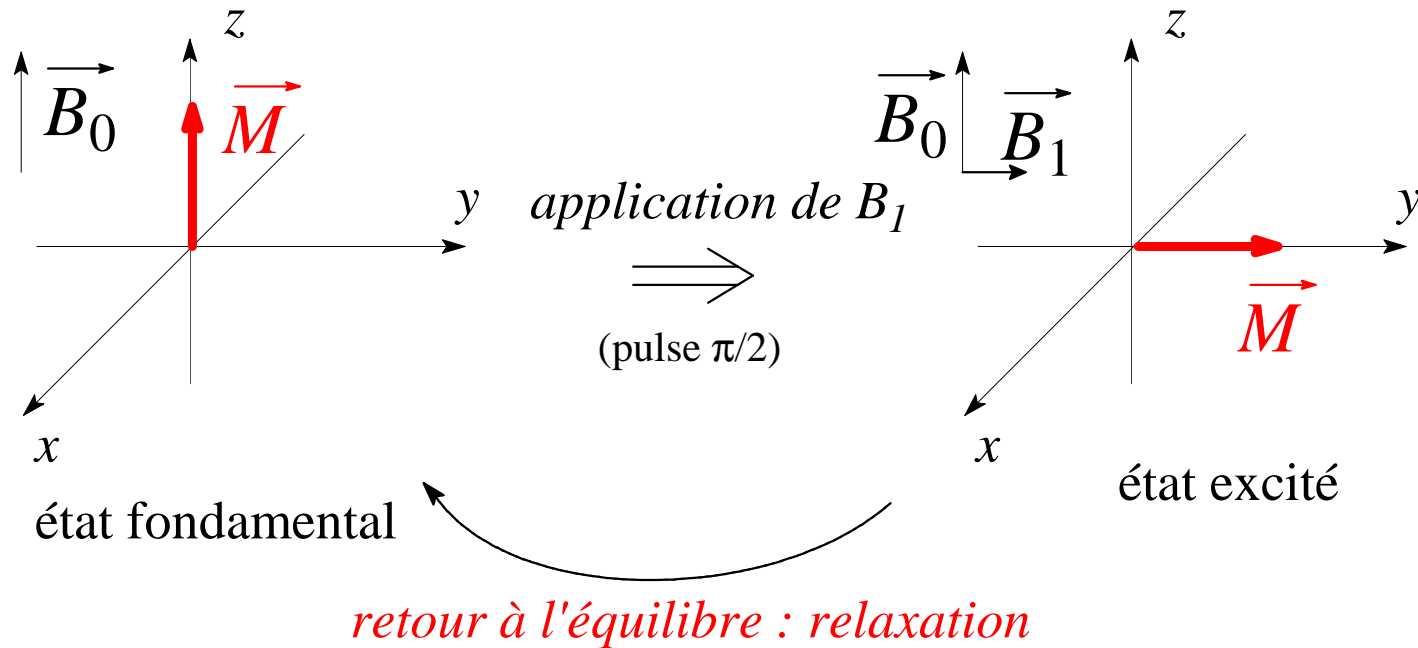


Le solvant classique est le (^2H)trichlorométhane (ou chloroforme deutéré) :

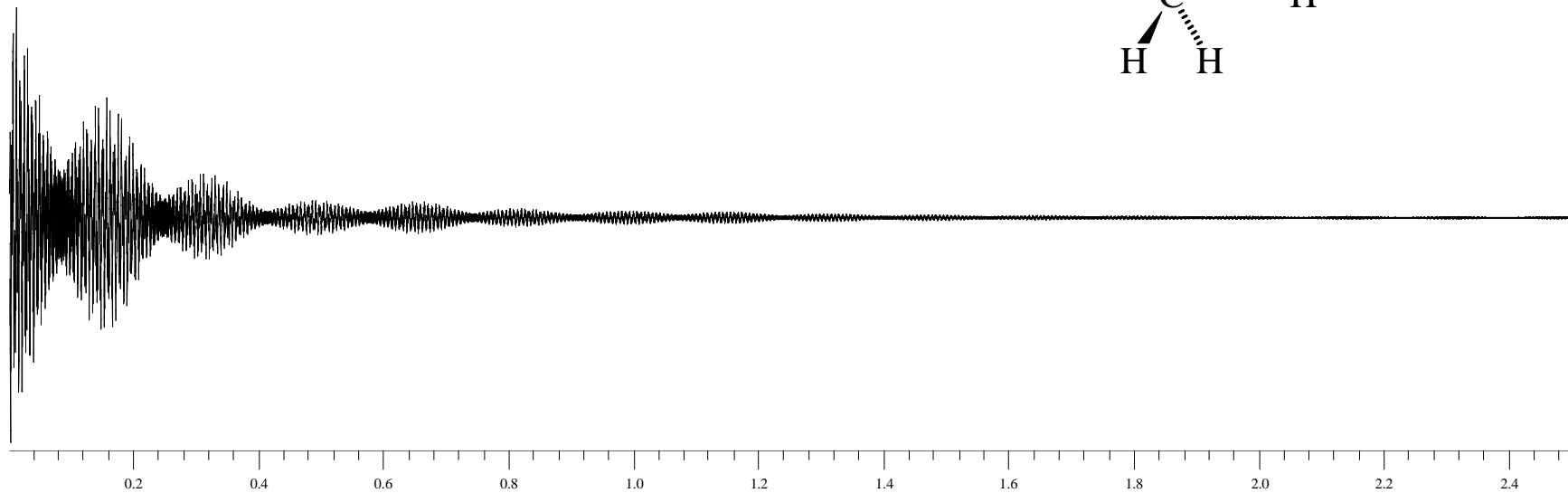
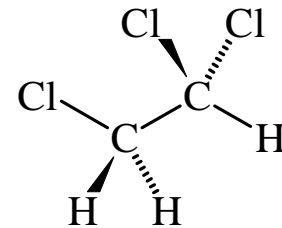
- il solubilise nombreux composés organiques
- il ne donne pas de signal parasite (pas de noyau d'hydrogène) ;
- Il est inerte, volatil et peu coûteux.



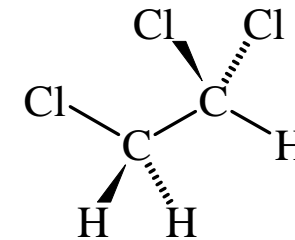
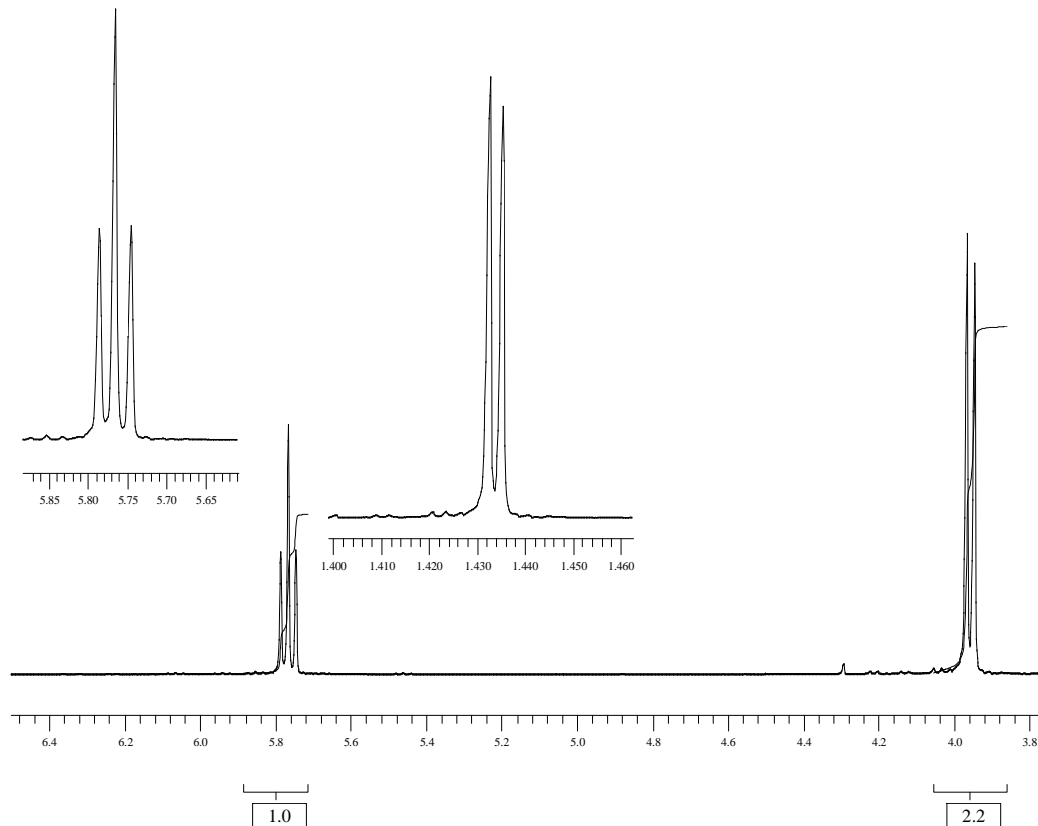
Principe d'une expérience de RMN par impulsion



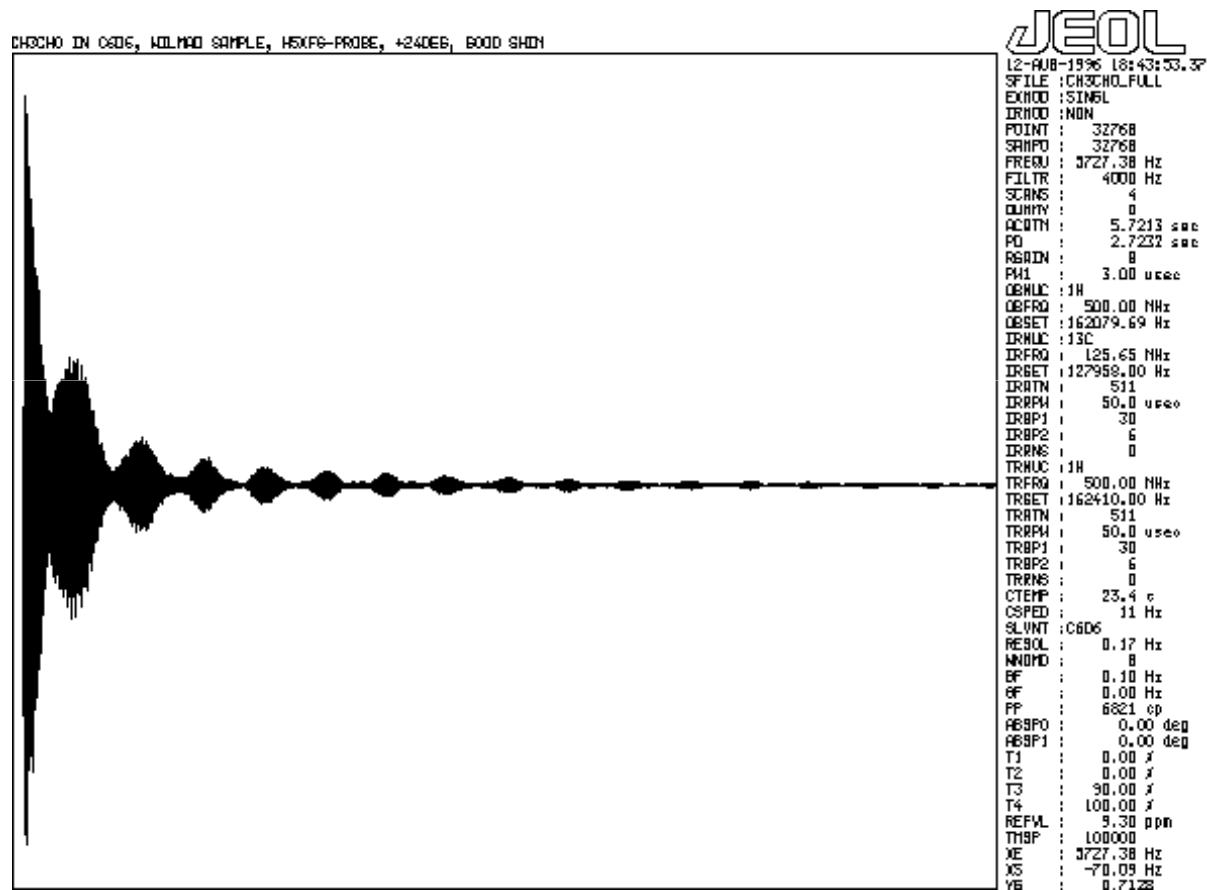
Le F.I.D. pour un système de deux noyaux couplés



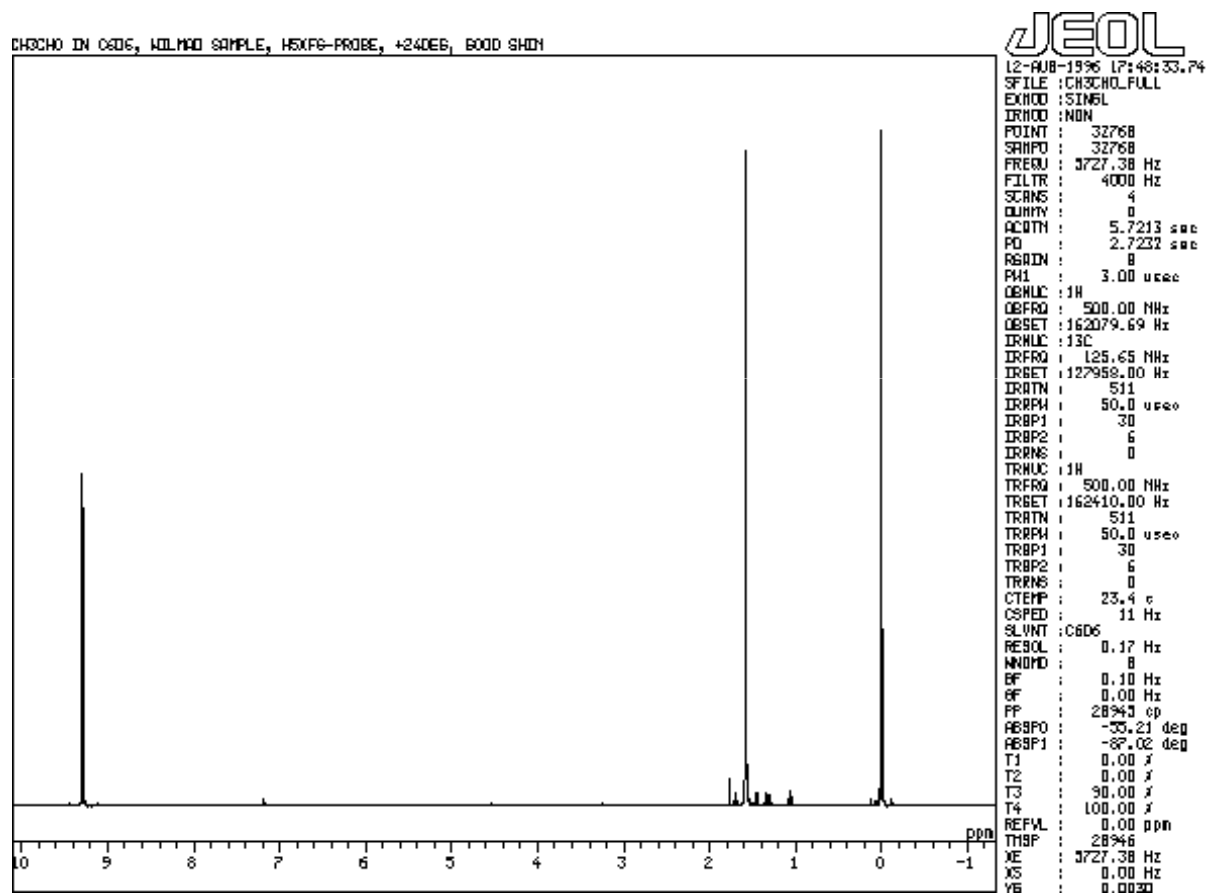
Le signal après TF



Un peu de musique...



Le spectre...



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Mais pourquoi y a-t-il plusieurs signaux ?
On a parlé d'une fréquence unique !

*Les noyaux d'hydrogène ne sont pas isolés !
L'environnement d'un noyau modifie son comportement.*

Abscisse : déplacement chimique δ lié à l'environnement du proton

Ordonnée : intensité du signal

Courbe d'intégration : aire des signaux



Blindage / déblindage

- Plus la densité électronique autour des noyaux est élevée, plus le coefficient de blindage est grand, plus les noyaux sont blindés vis-à-vis de B_0
- Plus la densité électronique est faible, plus les noyaux sont déblindés.
- Le blindage déplace la résonance vers de plus faibles fréquences, $\Delta\nu$ ne dépassant pas 1kHz pour une fréquence de résonance de 100 MHz (rapport 10×10^6)

$$\nu_i = \frac{\gamma}{2\pi} B_i = \frac{\gamma}{2\pi} B_0 (1 - \sigma_i)$$

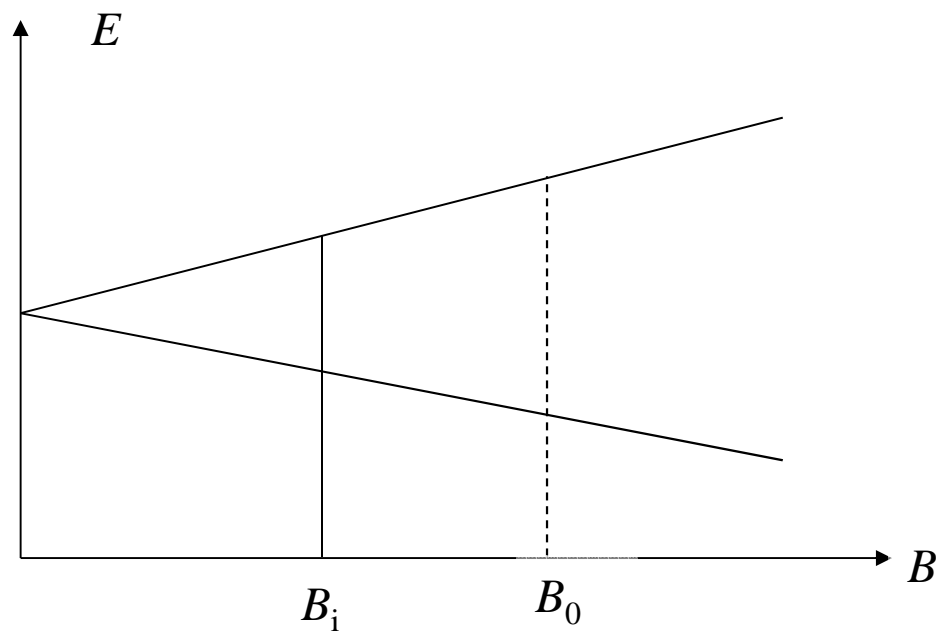
faible densité e^-
déblindage

forte densité e^-
blindage

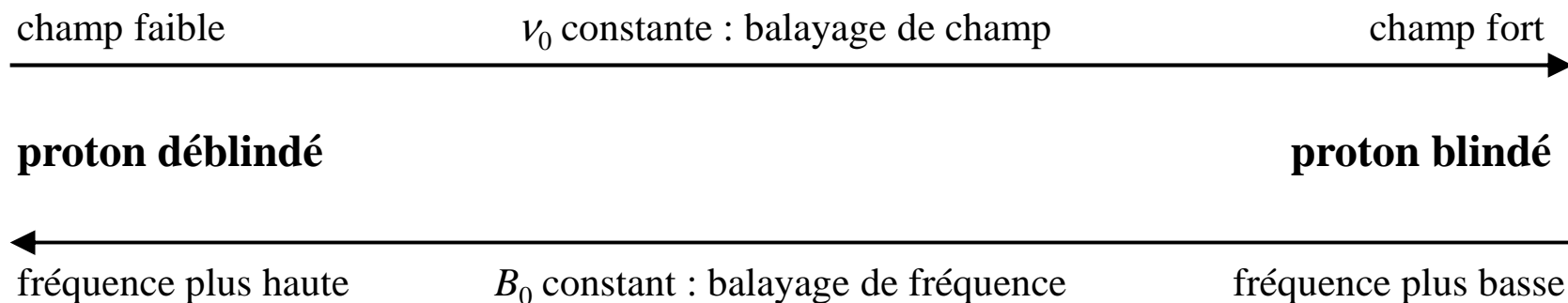
ν ←



Blindage / déblindage



Blindage / déblindage



Comment repérer le signal puisque ν_i est très proche de ν_0 ?

Comment normaliser le signal mesuré (fréquence), pour le rendre indépendant de l'appareil ?



Déplacement chimique

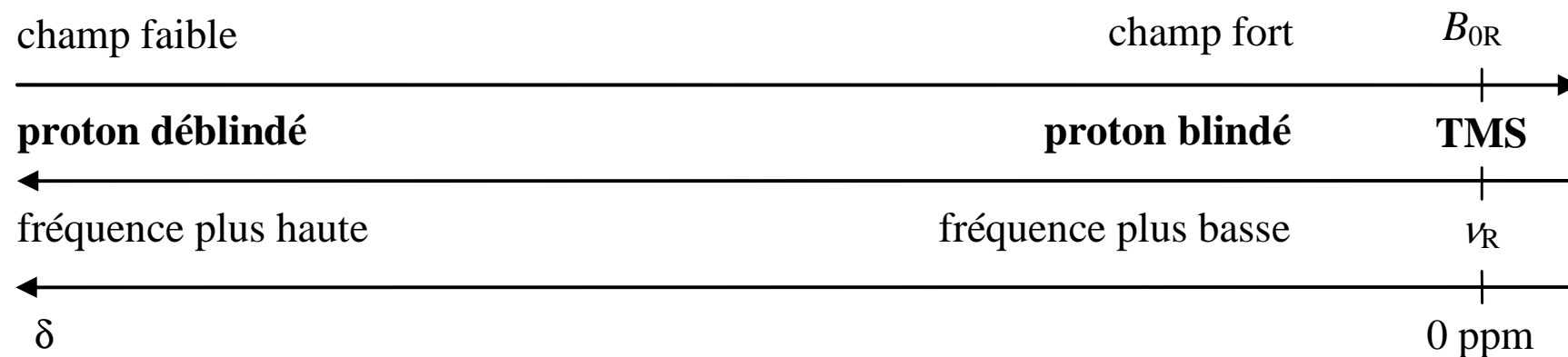
- on standardise la fréquence mesurée
on obtient le **déplacement chimique, δ** , nombre sans dimension, exprimé en ppm (parties par millions : le facteur 10^6 vient de l'ordre de grandeur des $\Delta\nu$)

$$\delta_i \text{ (ppm)} = 10^6 \frac{\nu_i - \nu_R}{\nu_0}$$

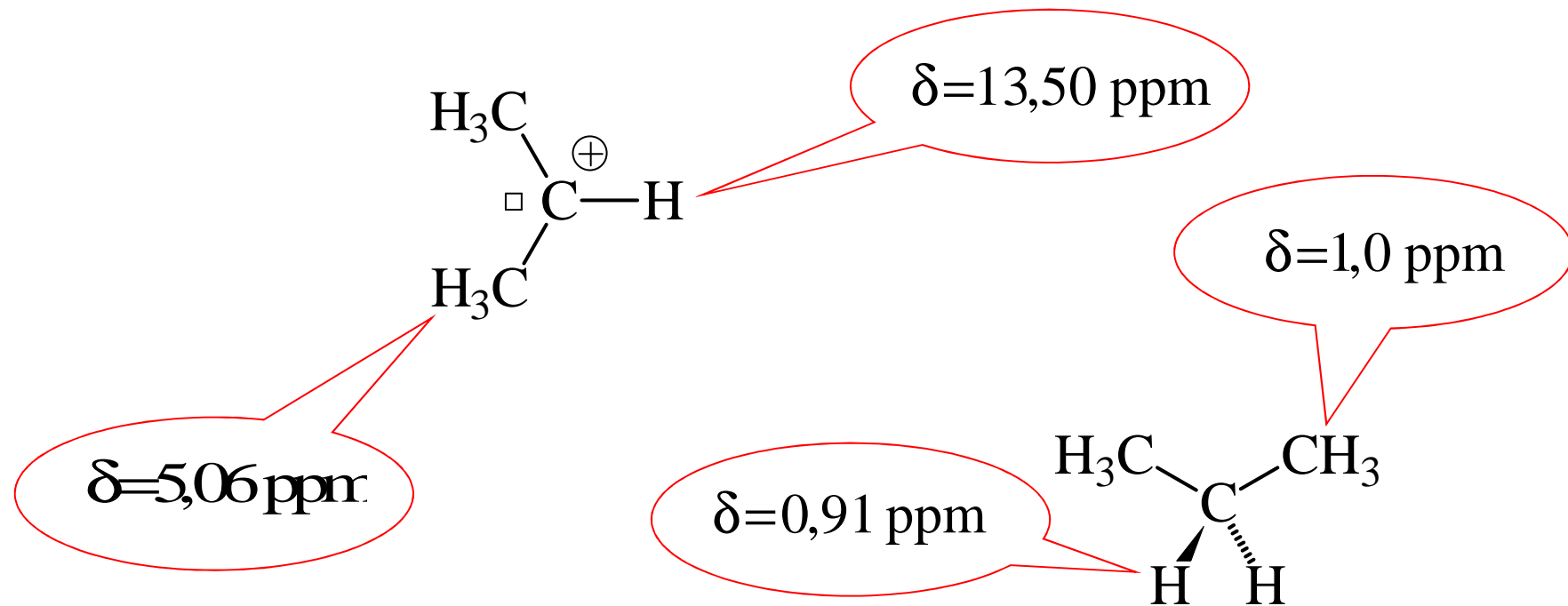
- On utilise un standard interne, le tétraméthylsilane (**TMS**) $\text{Si}(\text{CH}_3)_4$ de blindage supérieur à la très grande majorité de tous les autres composés



Déplacement chimique



Déplacement chimique

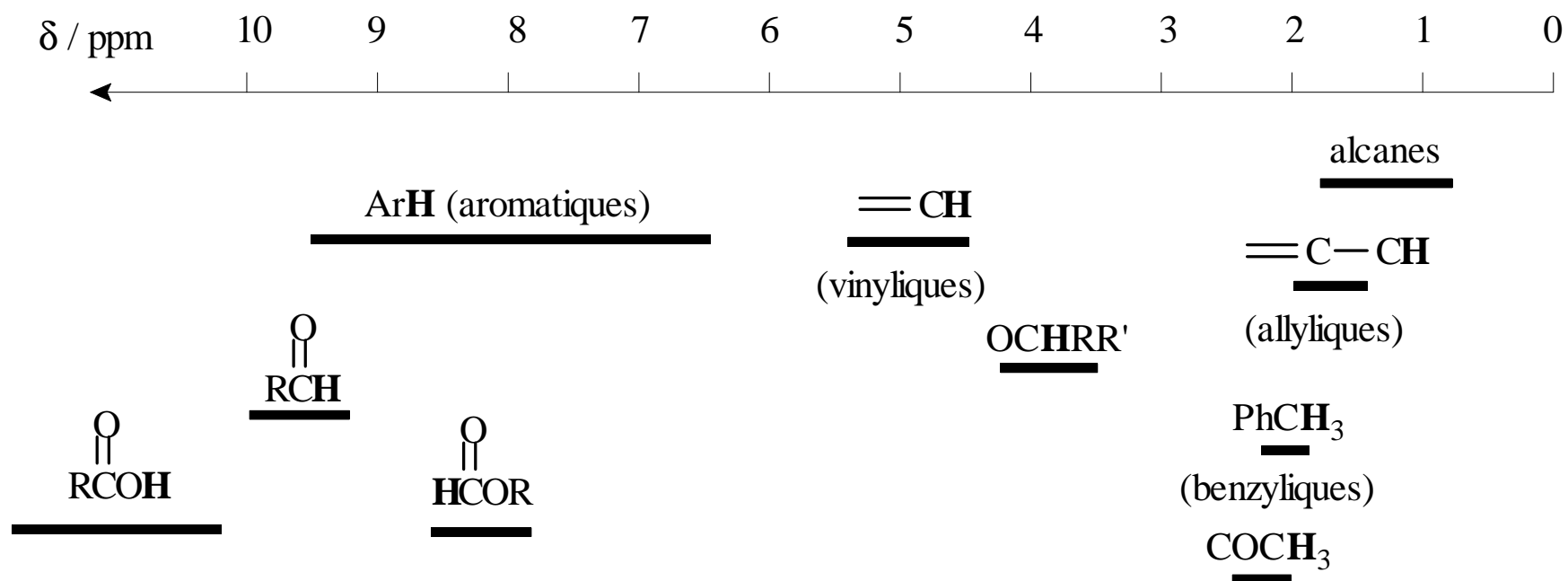


Influence de l'électronégativité sur le déplacement chimique

	F-CH ₃	Cl-CH ₃	Br-CH ₃	I-CH ₃	H-CH ₃	Li-CH ₃
$\delta(\text{H}) / \text{ppm}$	4,13	2,84	2,45	1,98	0,13	- 1,3
électronégativité	4,0	3,0	2,8	2,5	2,1	1,9

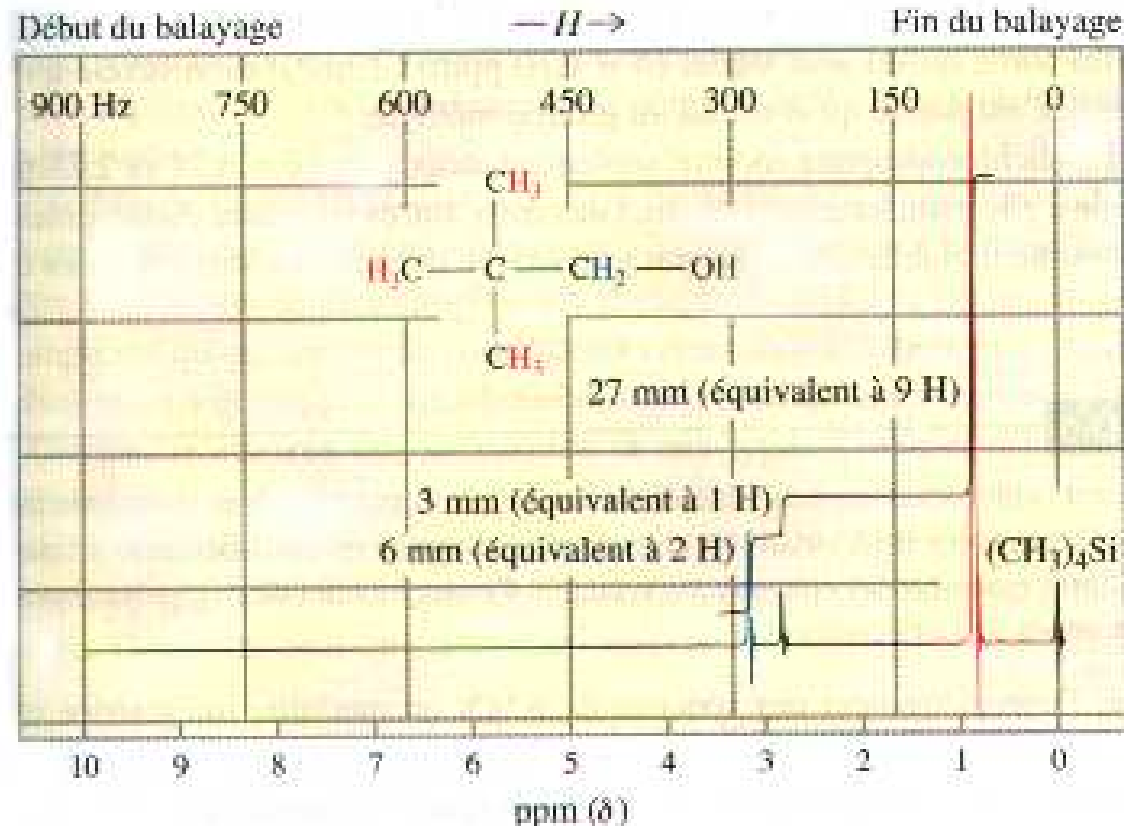


Table schématique de valeurs de déplacement chimique

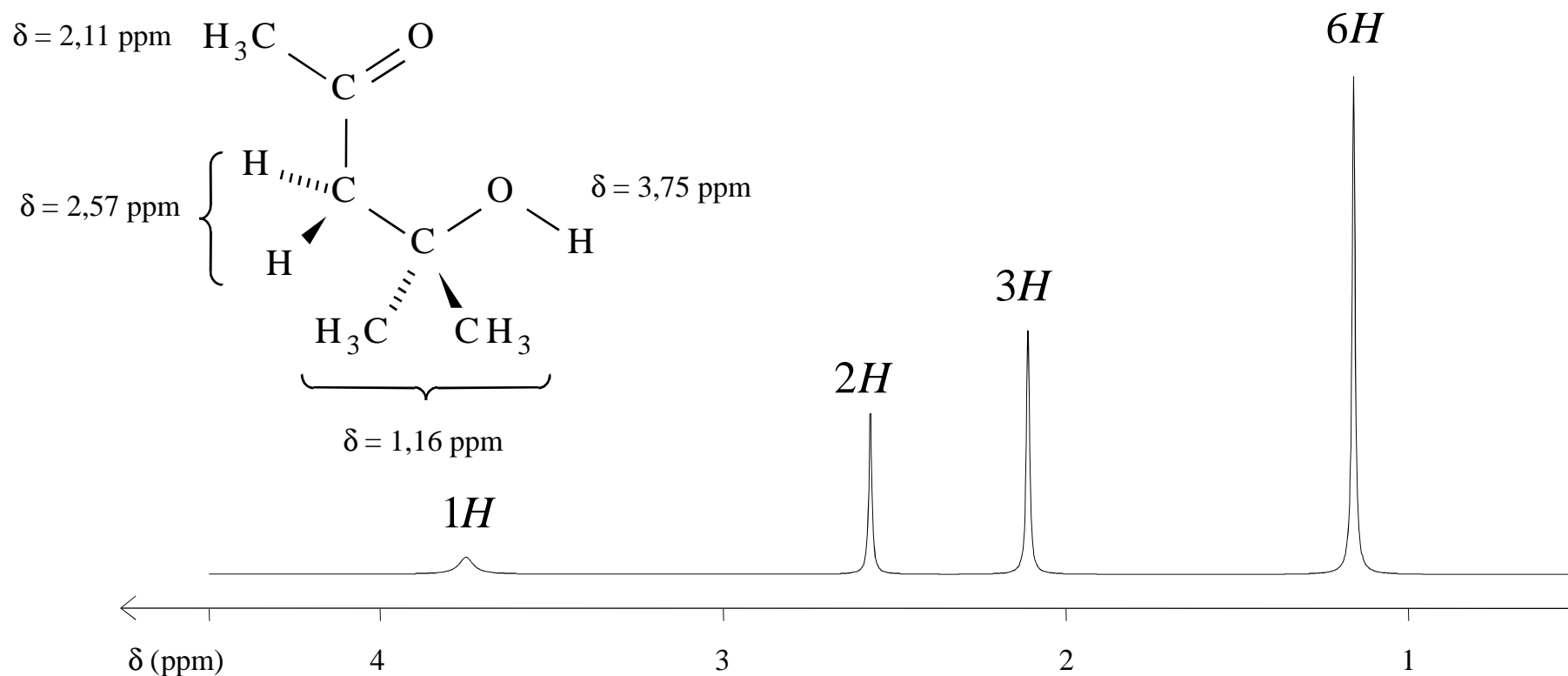


Intégration

L'aire sous les pics est proportionnelle au nombre relatif de noyaux responsables de ce signal : les appareils enregistrent automatiquement ces aires, c'est l'intégration.



Exemple de spectre sans couplage visible



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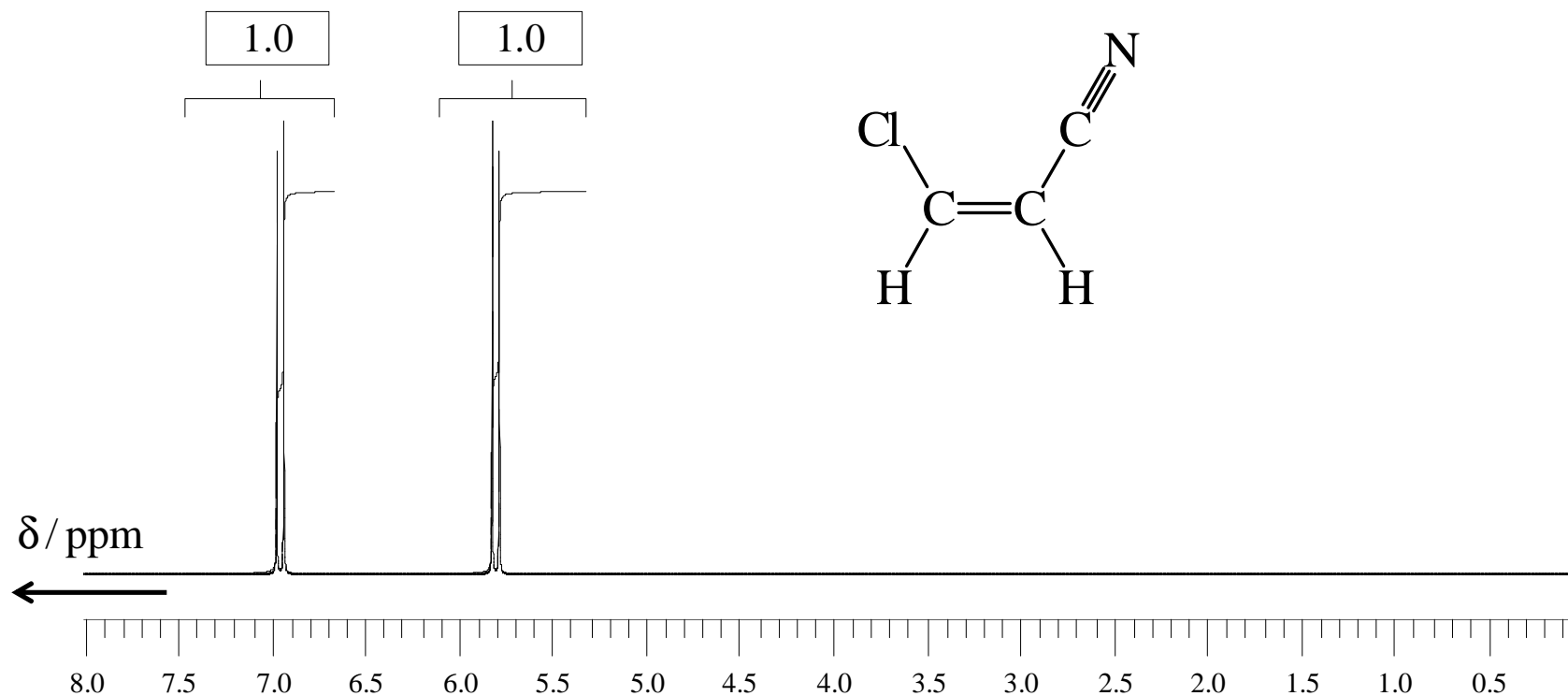


Couplage spin-spin

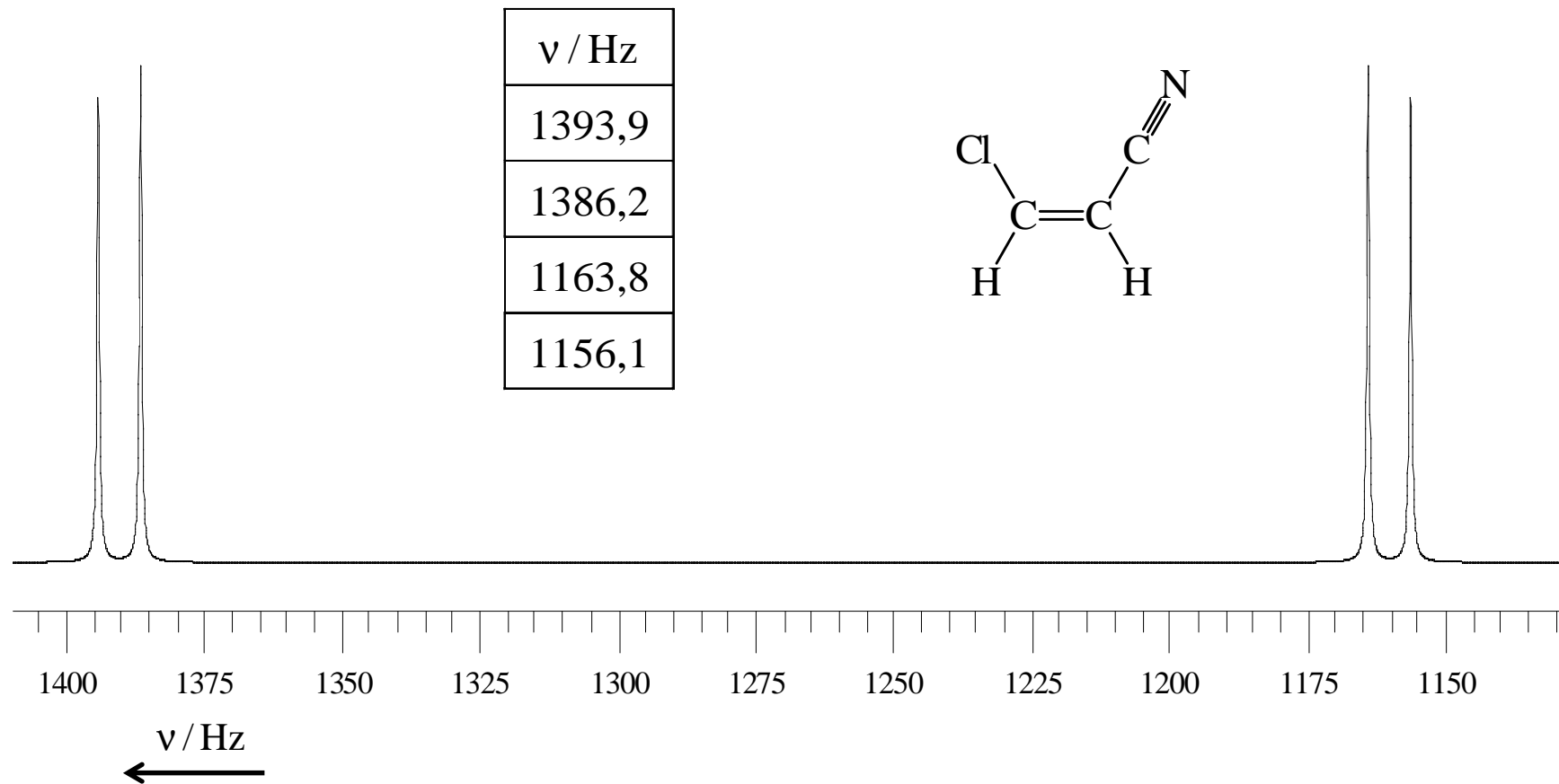
- Mise en évidence
- Constantes de couplage
- Nomenclature des systèmes de spin
- Étude du système le plus simple (AX)
- Système AMX
- Système AX₂
- Système AX_m



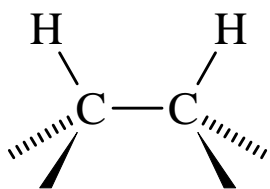
Spectre de RMN du 3-chloropropène nitrile le système AX



Agrandissement (spectre AX)

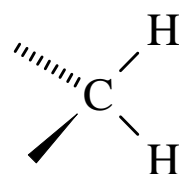


Valeurs typiques de constantes J



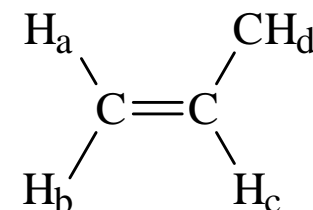
$${}^3J = 6 - 8 \text{ Hz}$$

La valeur dépend de l'angle dièdre



$${}^2J = (-18) \rightarrow (-10) \text{ Hz}$$

Le signe de la constante de couplage n'influe pas sur la forme du massif.



$${}^2J_{ab} = 0 - 3 \text{ Hz}$$

$${}^3J_{ac} = 12 - 18 \text{ Hz}$$

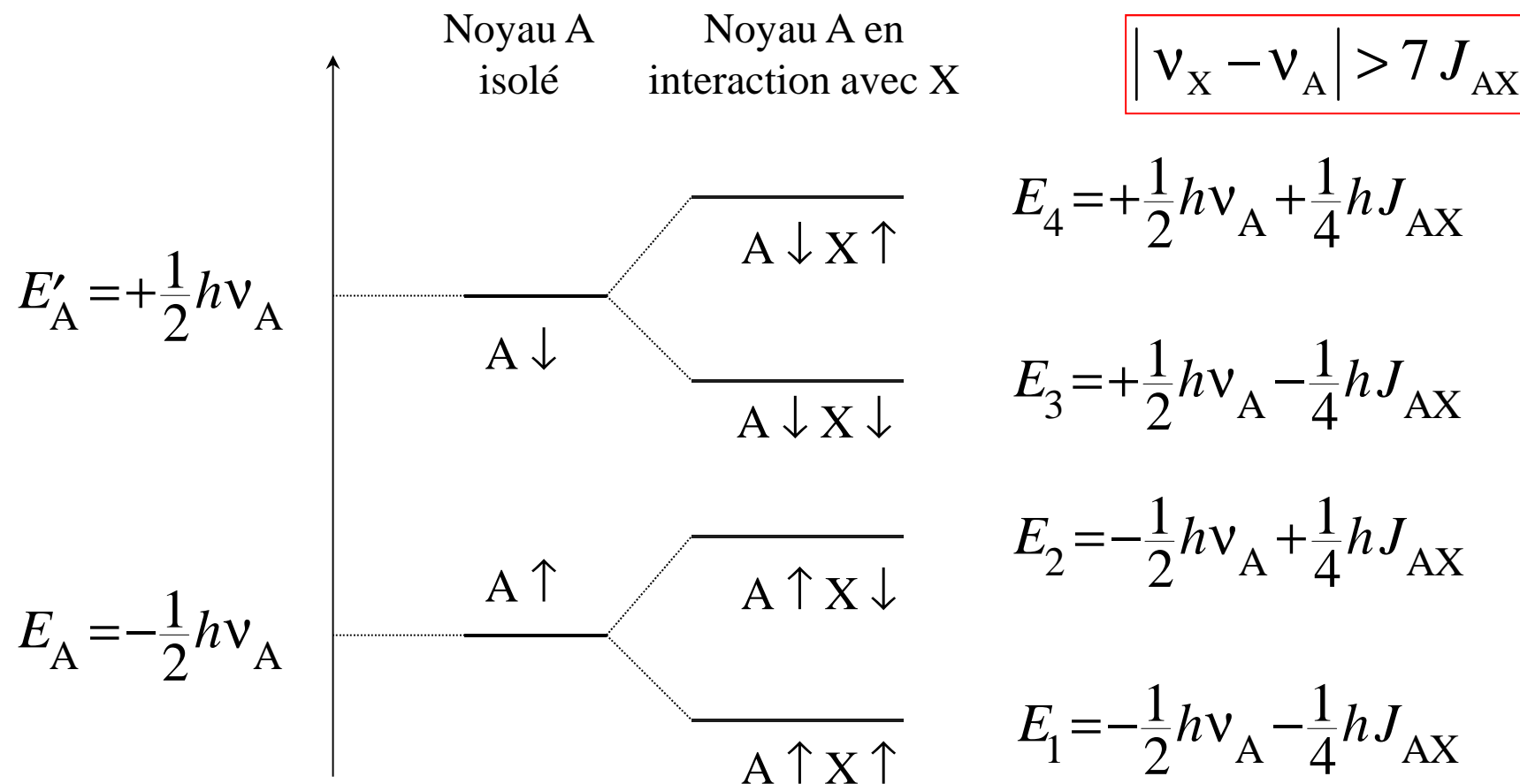
$${}^3J_{bc} = 6 - 12 \text{ Hz}$$

$${}^3J_{cd} = 5 - 10 \text{ Hz}$$

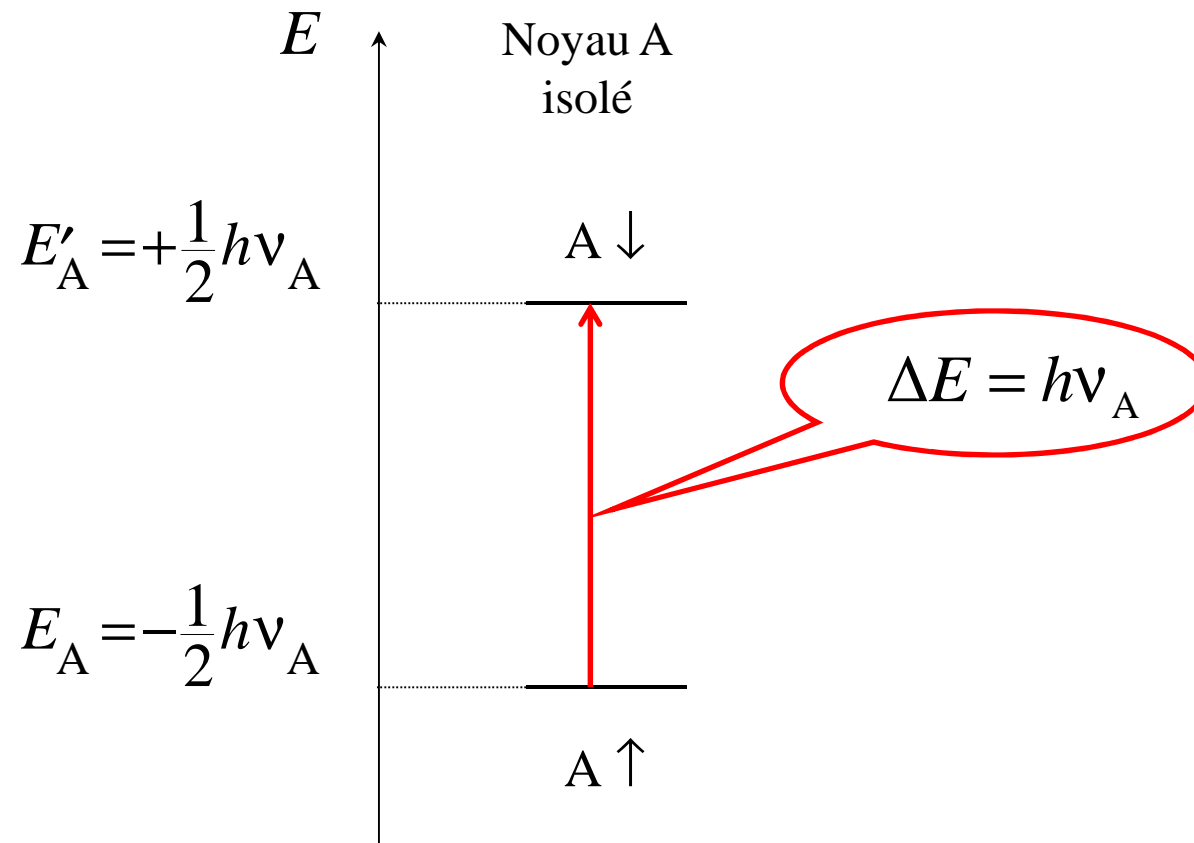
$${}^4J_{ad}, {}^4J_{bd} = 0 - 2 \text{ Hz}$$



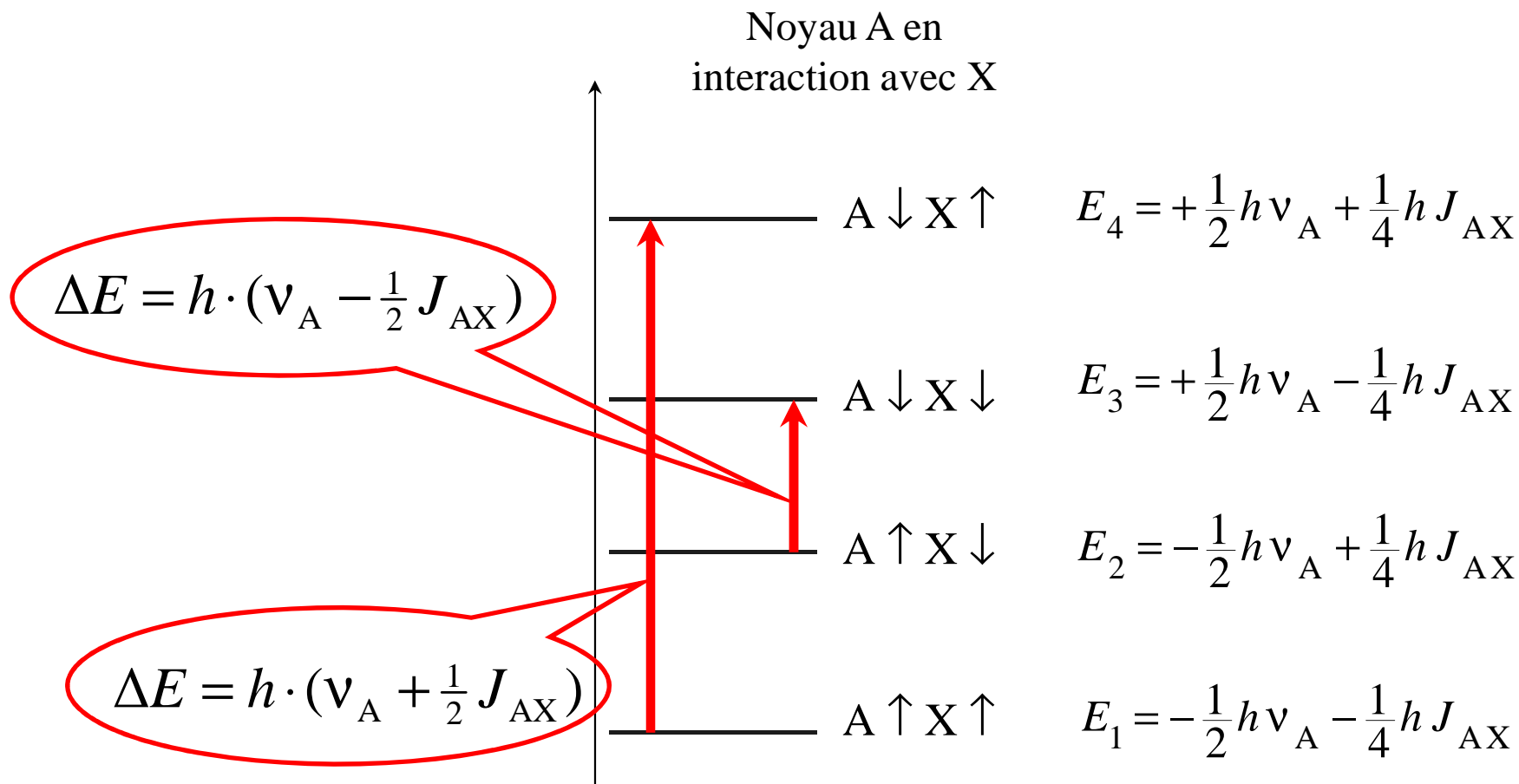
Niveaux d'énergie pour un système AX



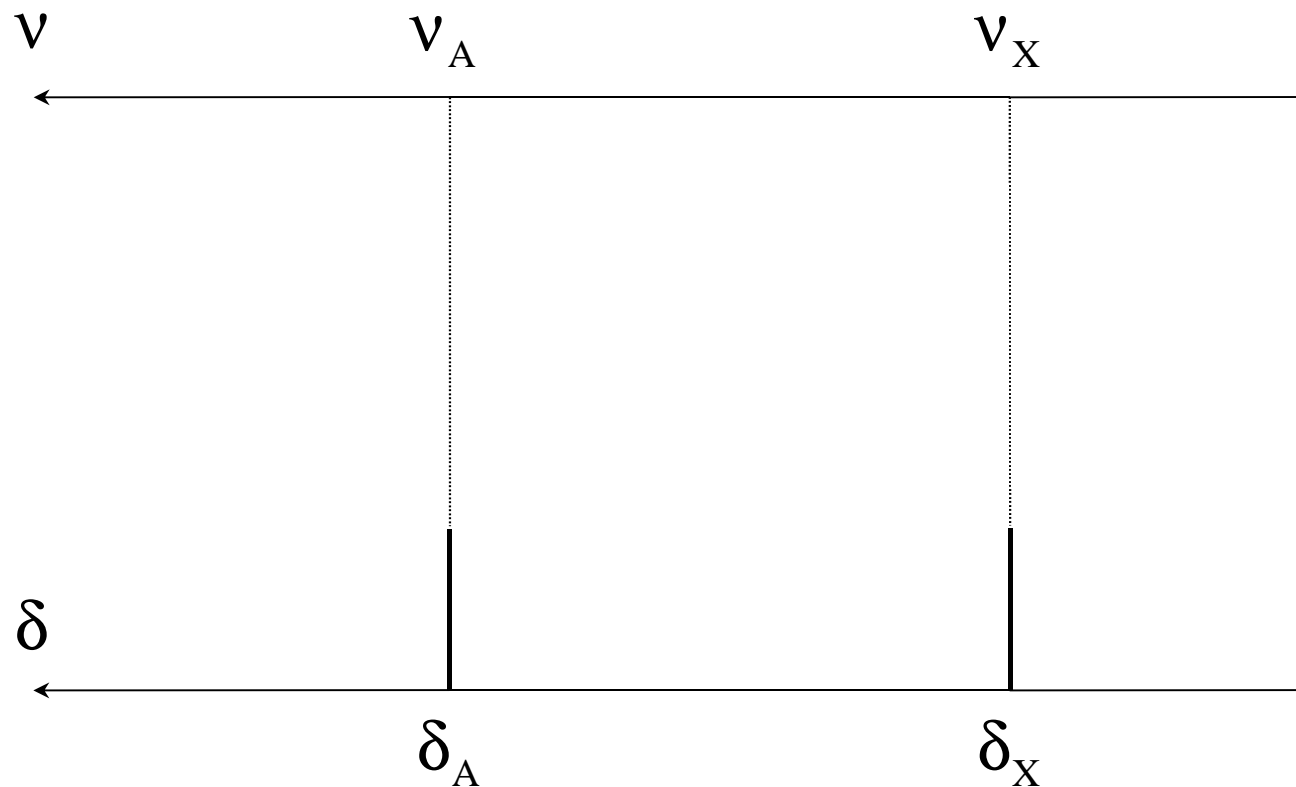
Transition pour un noyau A isolé



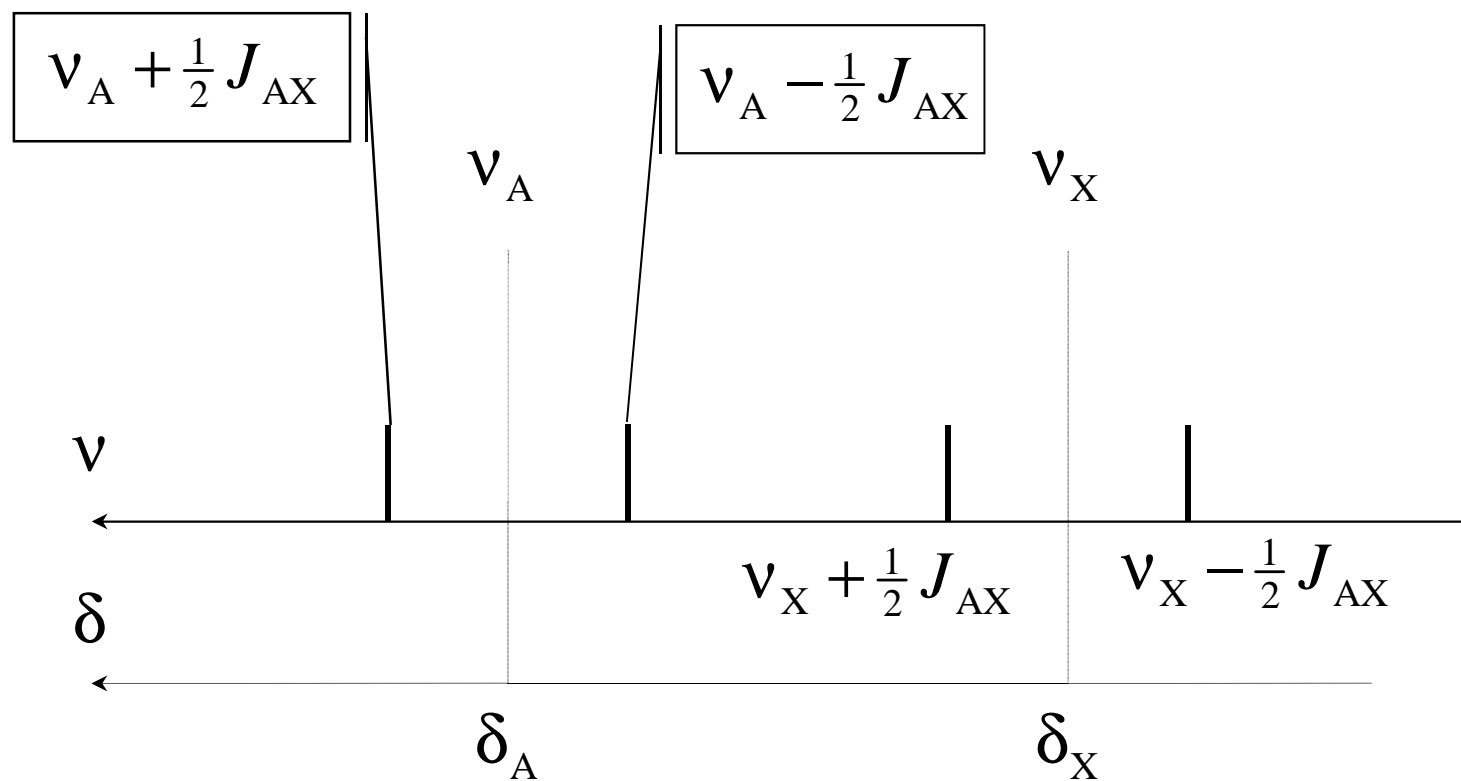
Transitions pour un système AX



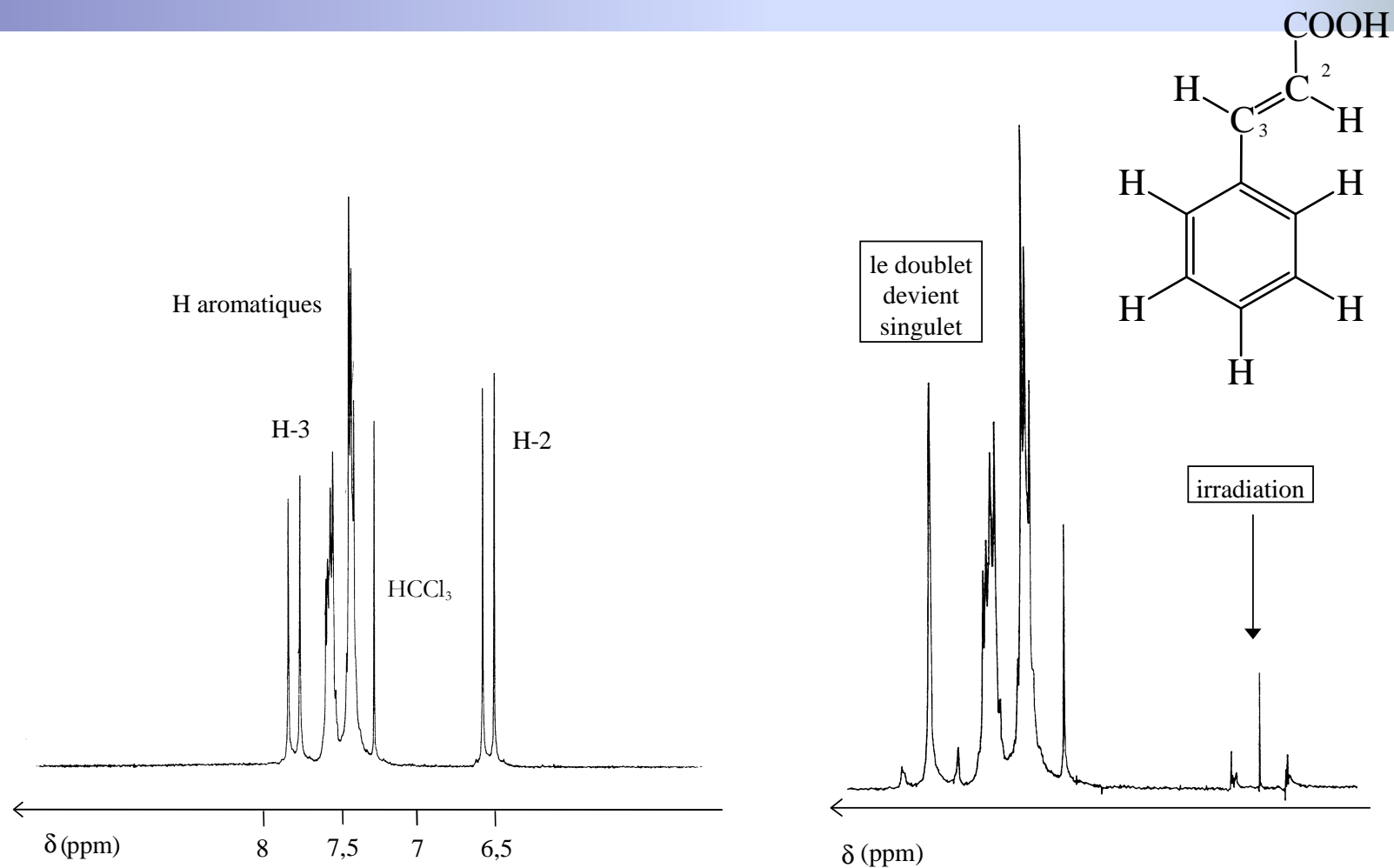
Allure du signal pour deux noyaux A et X sans interaction



Allure du signal pour un système AX



Effets du découplage



Influence de l'intensité du champ sur la forme du signal : AX \rightarrow AB

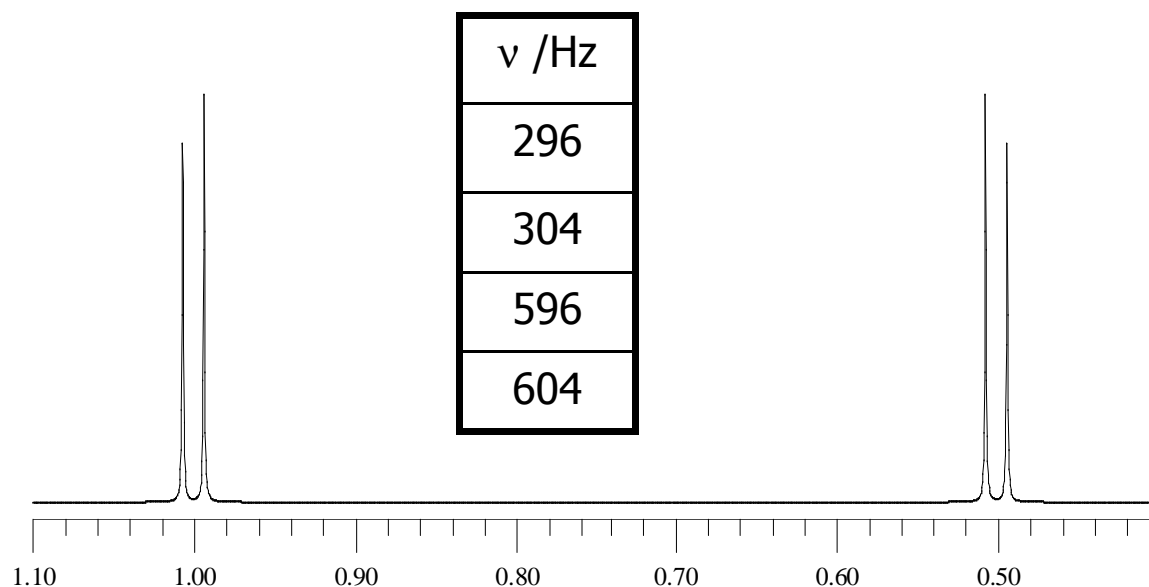
Spectre enregistré à 600 MHz,
avec $\Delta\delta = 0,5$ ppm et $J = 8$ Hz

$$\delta_X = 0,50 \text{ ppm}$$

$$\delta_A = 1,00 \text{ ppm}$$

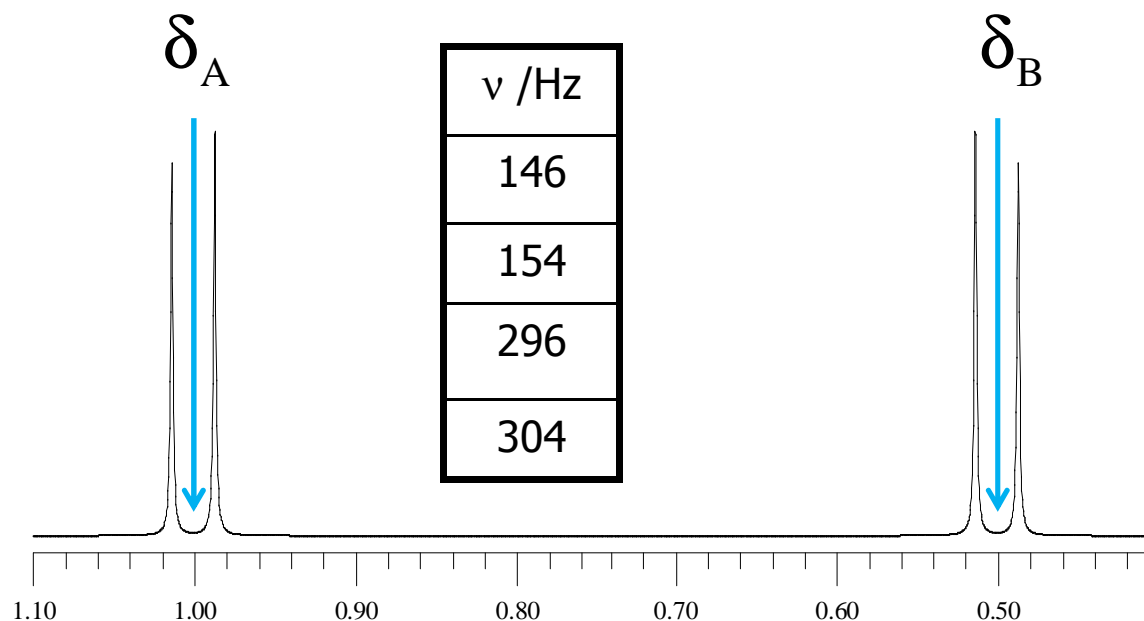
$$\Delta\nu = 300 \text{ Hz}$$

$$\frac{\Delta\nu}{J} = 37,5$$



Influence de l'intensité du champ sur la forme du signal : AX \rightarrow AB

Spectre enregistré à 300 MHz,
avec $\Delta\delta = 0,5$ ppm et $J = 8$ Hz



$$\delta_X = 0,50 \text{ ppm}$$

$$\delta_A = 1,00 \text{ ppm}$$

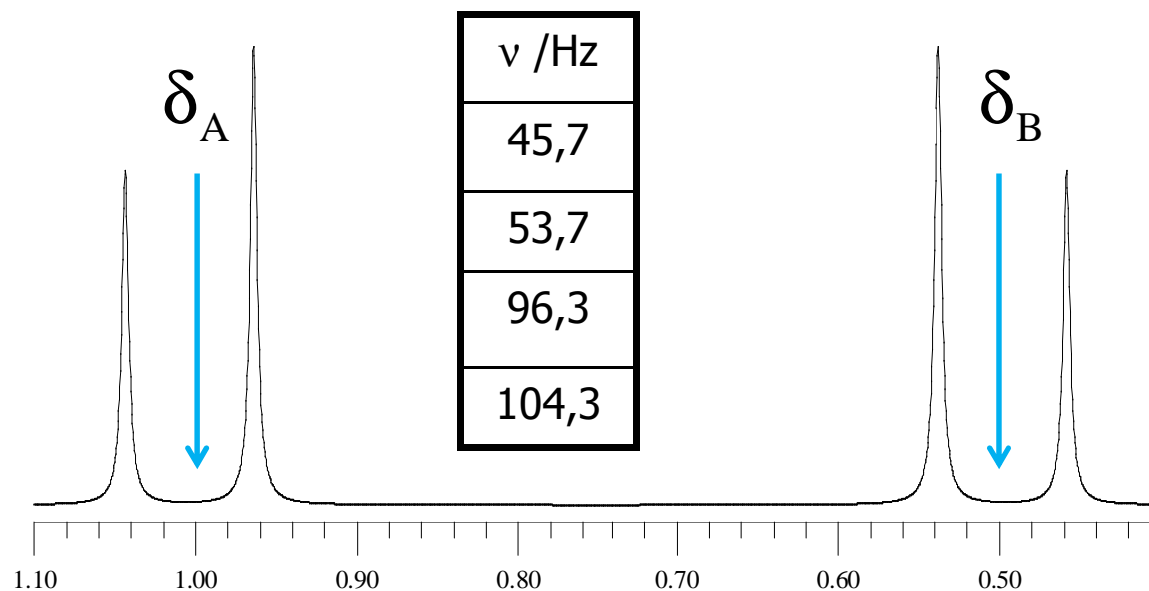
$$\Delta\nu = 150 \text{ Hz}$$

$$\frac{\Delta\nu}{J} = 18,75$$



Influence de l'intensité du champ sur la forme du signal : AX \rightarrow AB

Spectre enregistré à 100 MHz,
avec $\Delta\delta = 0,5$ ppm et $J = 8$ Hz



$$\delta_B = 0,50 \text{ ppm}$$

$$\delta_A = 1,00 \text{ ppm}$$

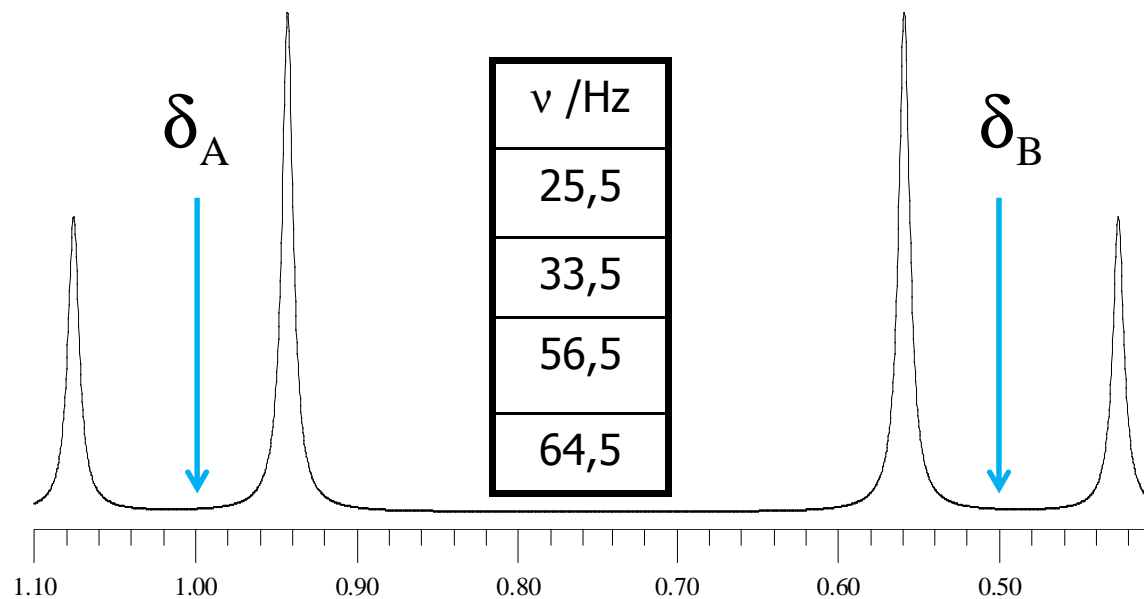
$$\Delta\nu = 50 \text{ Hz}$$

$$\frac{\Delta\nu}{J} = 6,25$$



Influence de l'intensité du champ sur la forme du signal : AX \rightarrow AB

Spectre enregistré à 60 MHz,
avec $\Delta\delta = 0,5$ ppm et $J = 8$ Hz



$$\delta_B = 0,50 \text{ ppm}$$

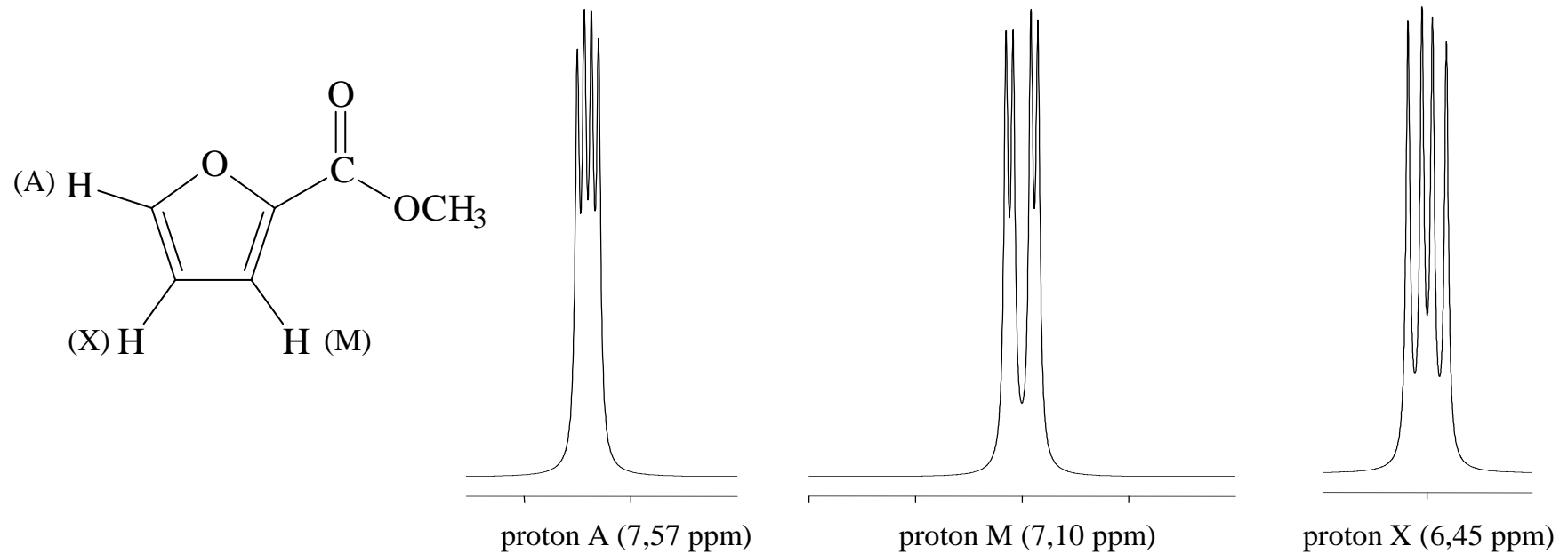
$$\delta_A = 1,00 \text{ ppm}$$

$$\Delta\nu = 30 \text{ Hz}$$

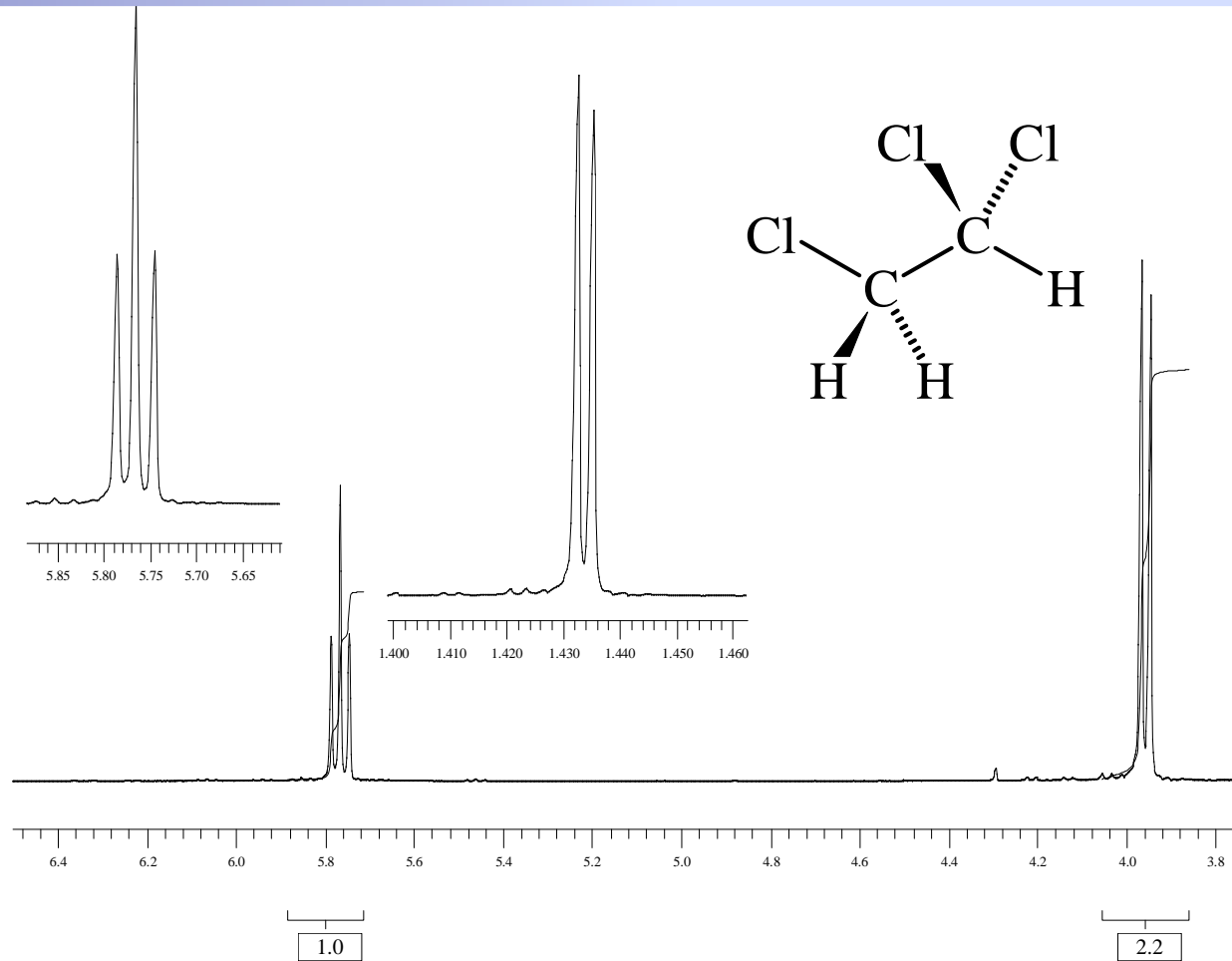
$$\frac{\Delta\nu}{J} = 3,75$$



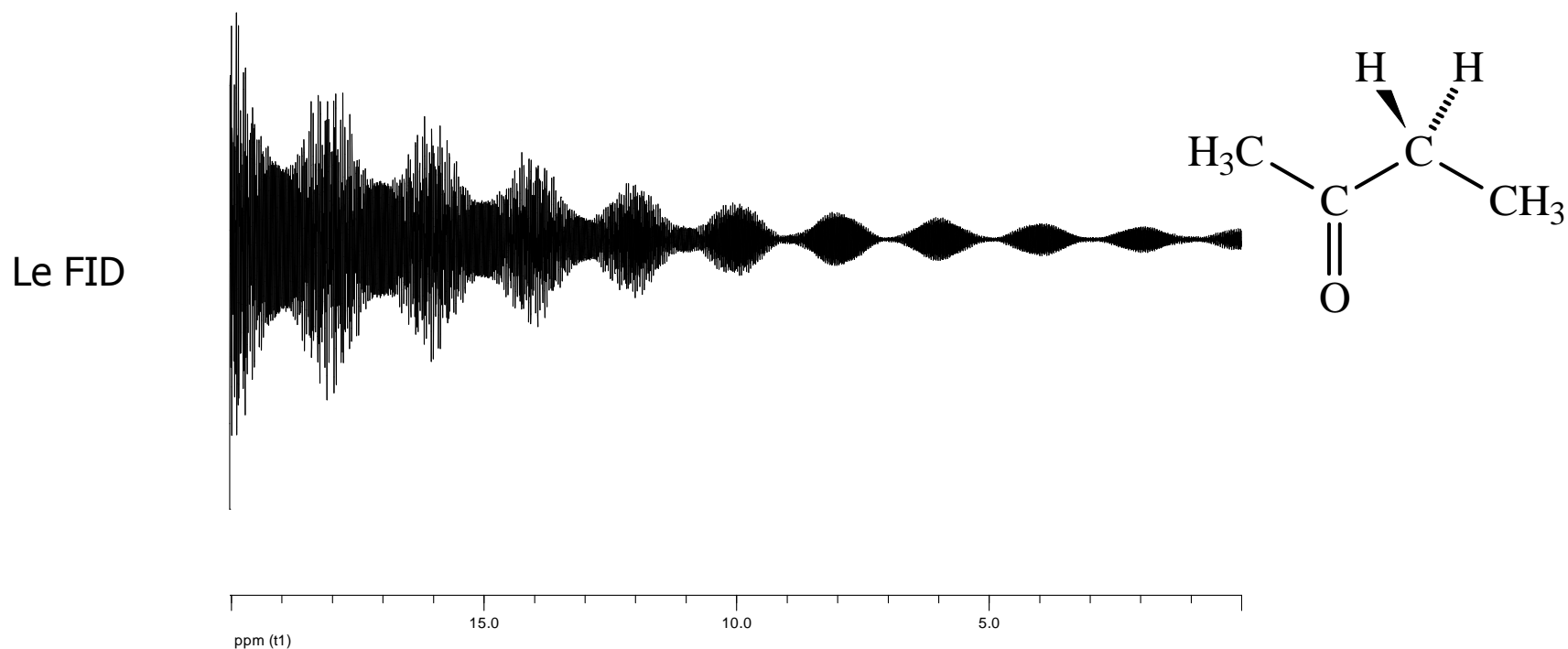
Spectre de type AMX



Systeme AX₂



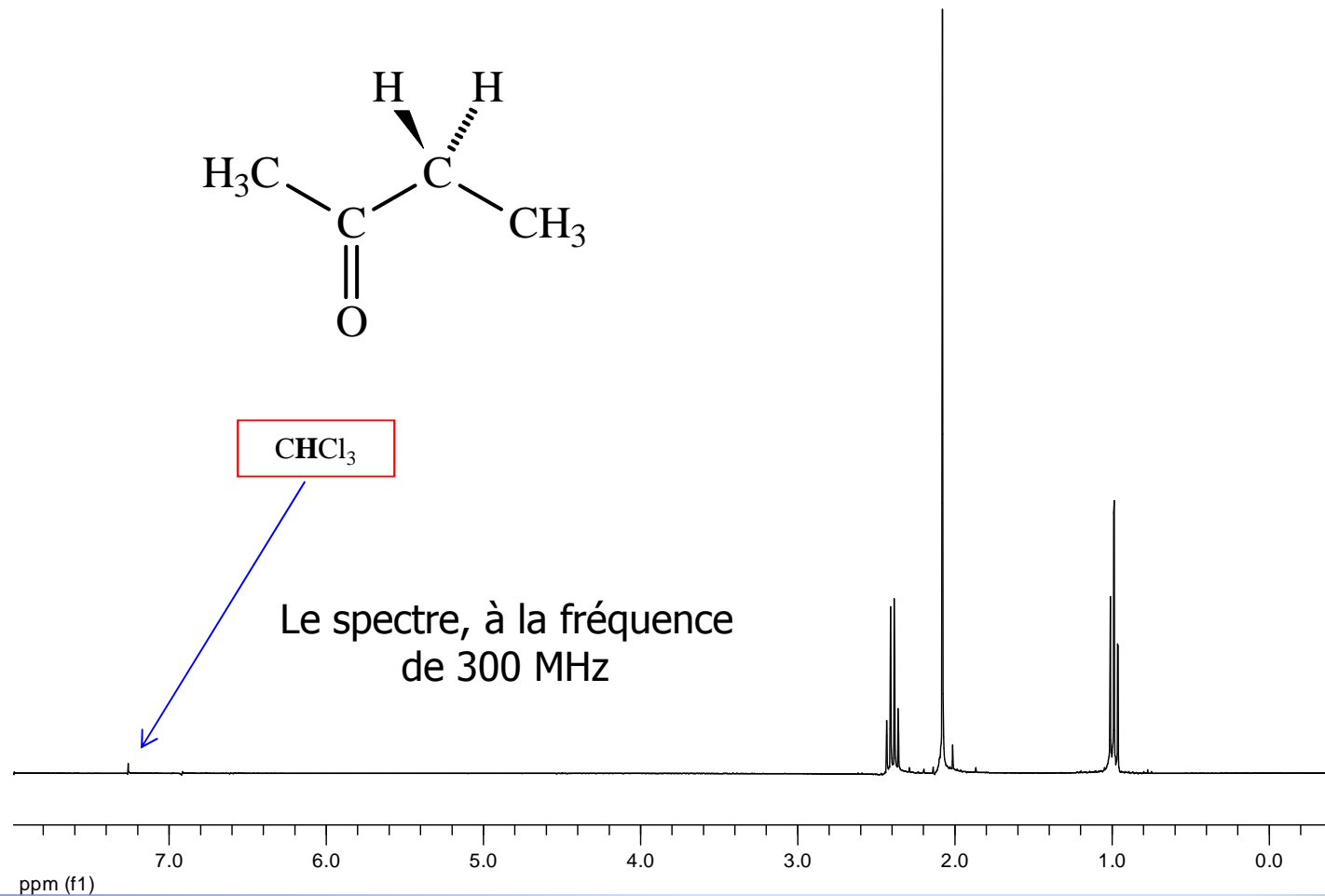
Spectre RMN ^1H de la butanone



Enregistrement en solution dans CDCl_3 , à la fréquence de 300 MHz
(archive de la *Pacific Lutheran University, USA*)

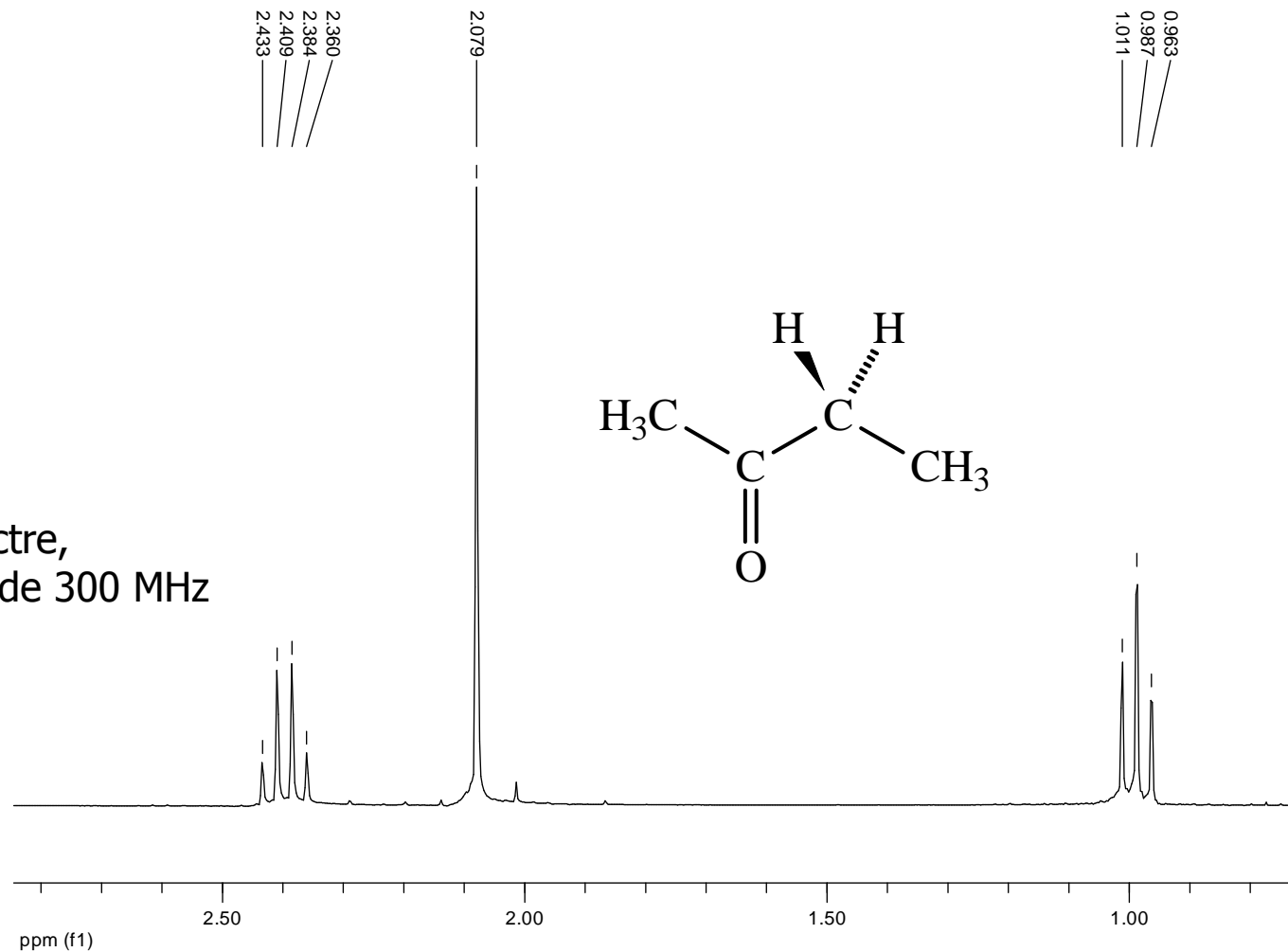


Spectre RMN ^1H de la butanone



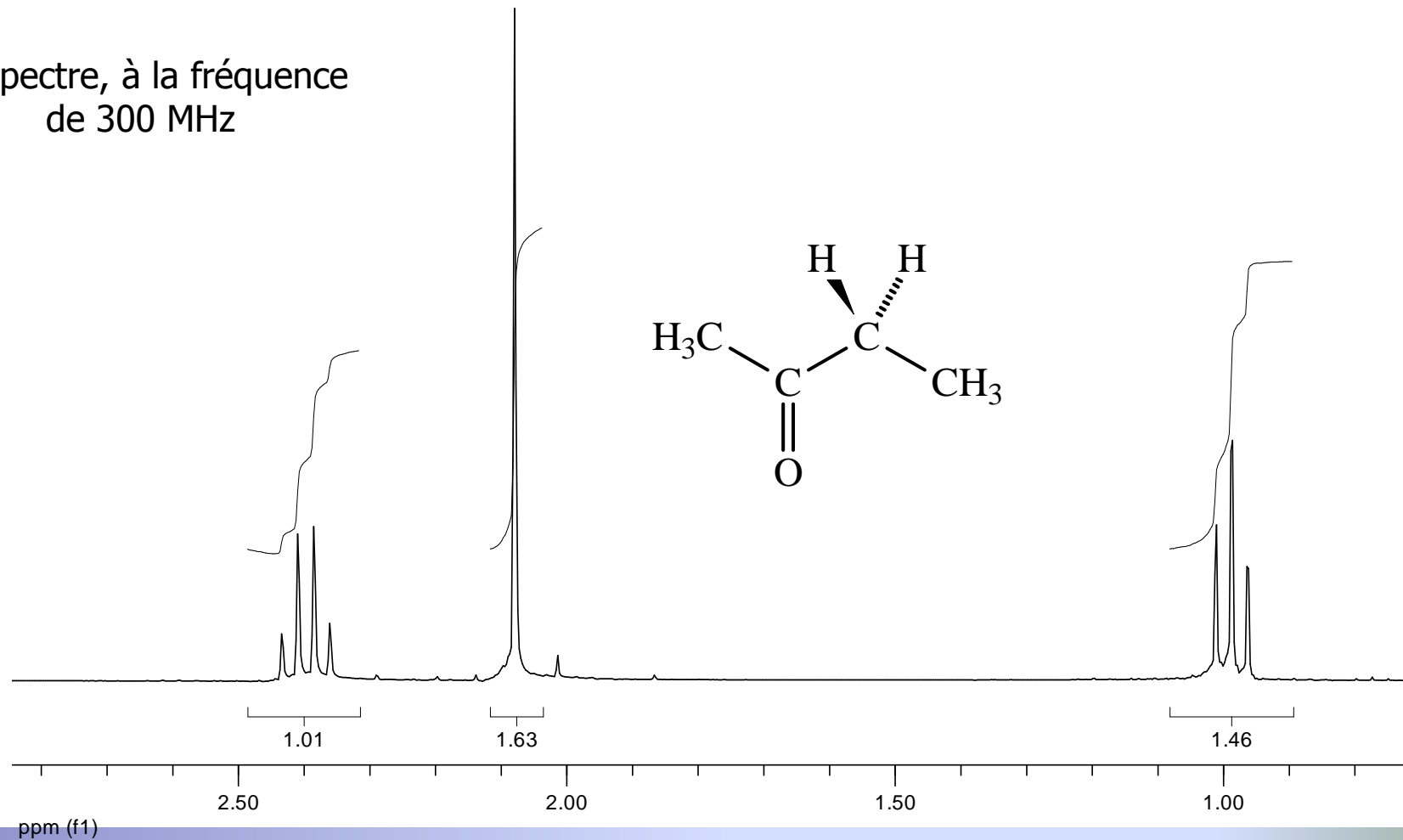
Spectre RMN ^1H de la butanone

Le spectre,
à la fréquence de 300 MHz

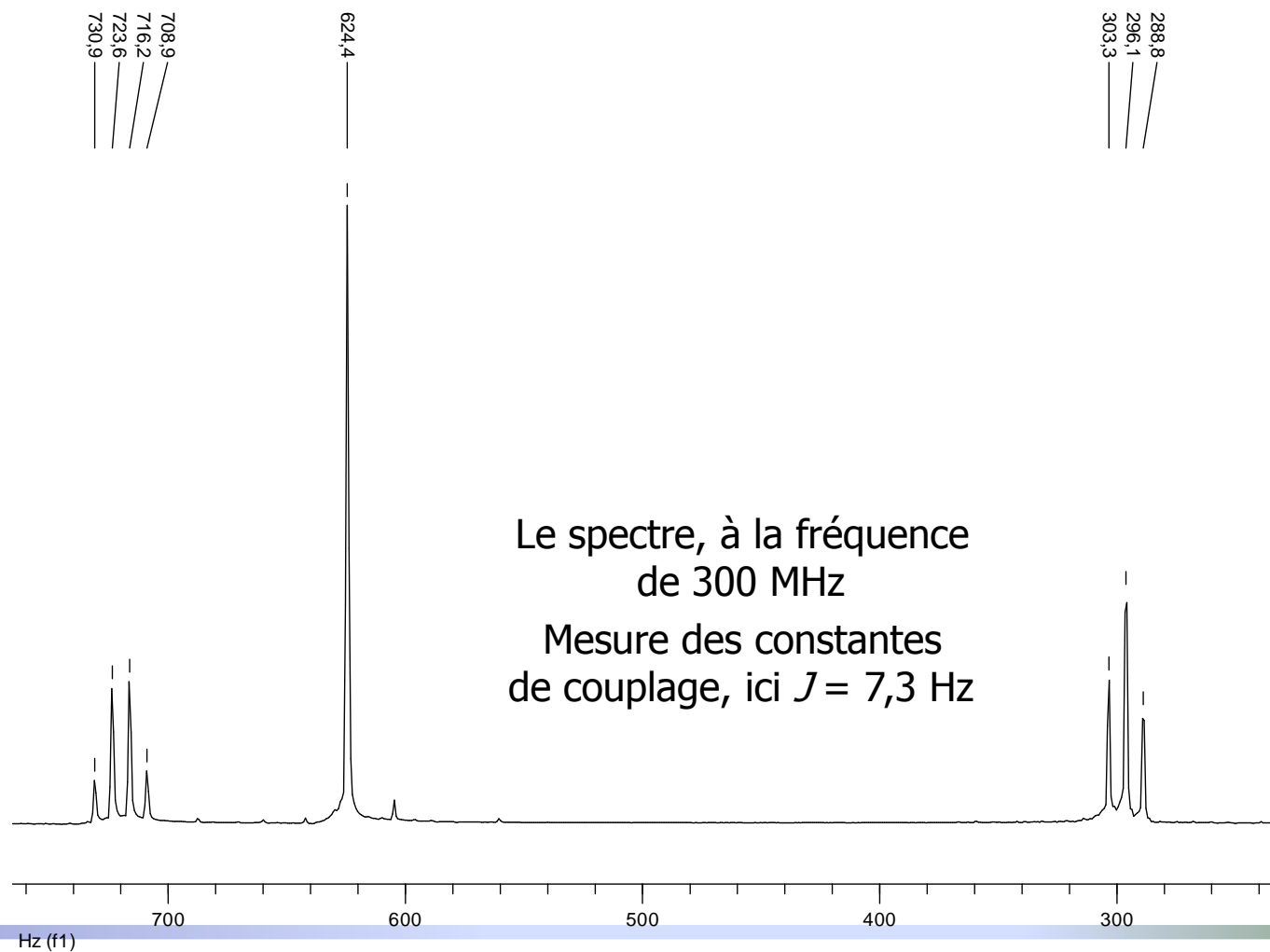
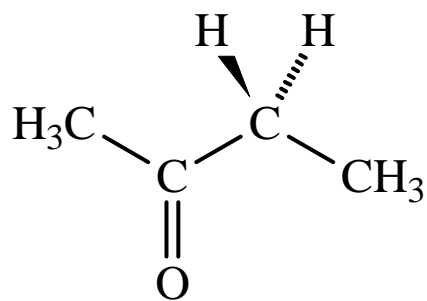


Spectre RMN ^1H de la butanone

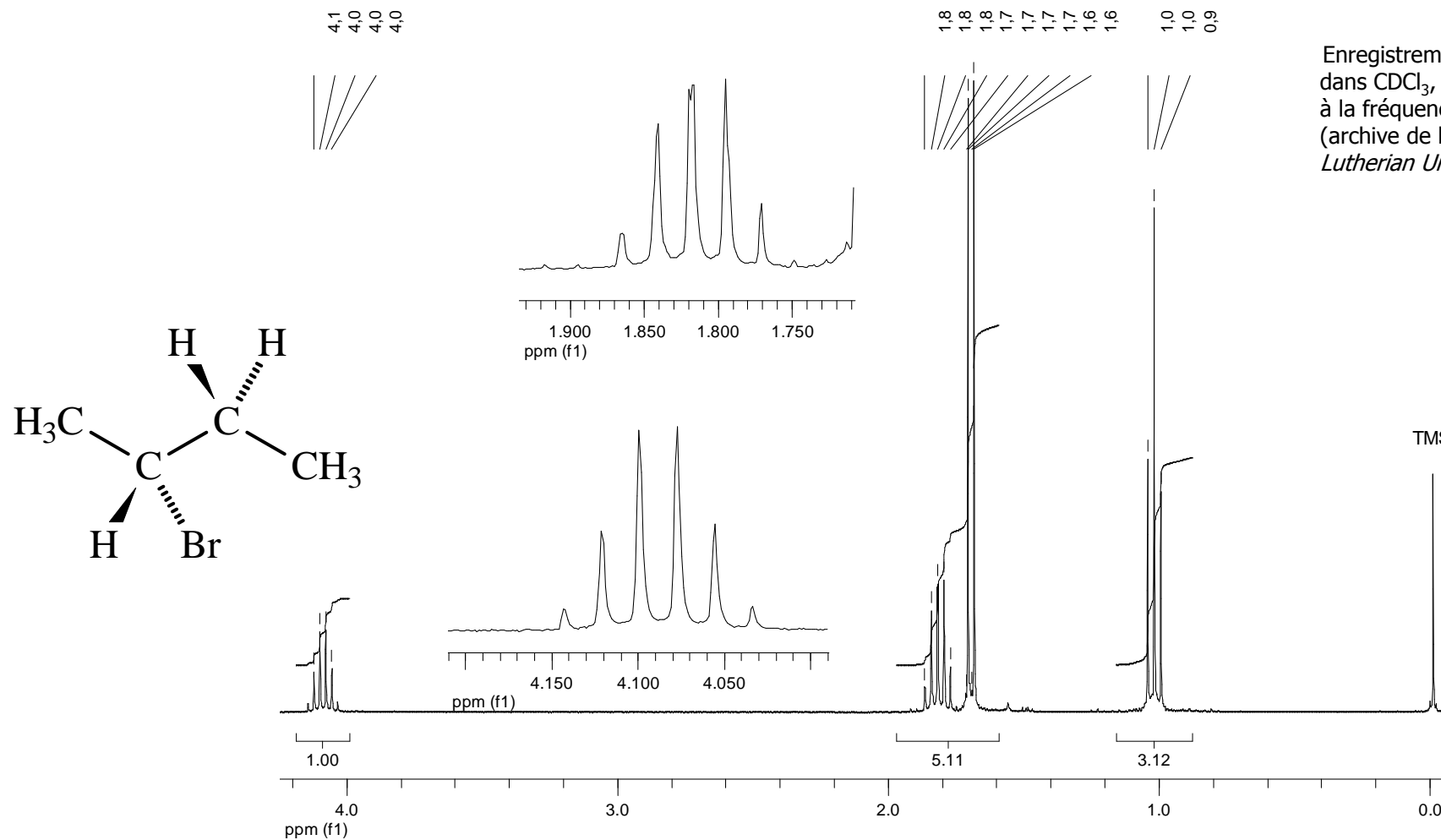
Le spectre, à la fréquence
de 300 MHz



Spectre RMN ^1H de la butanone



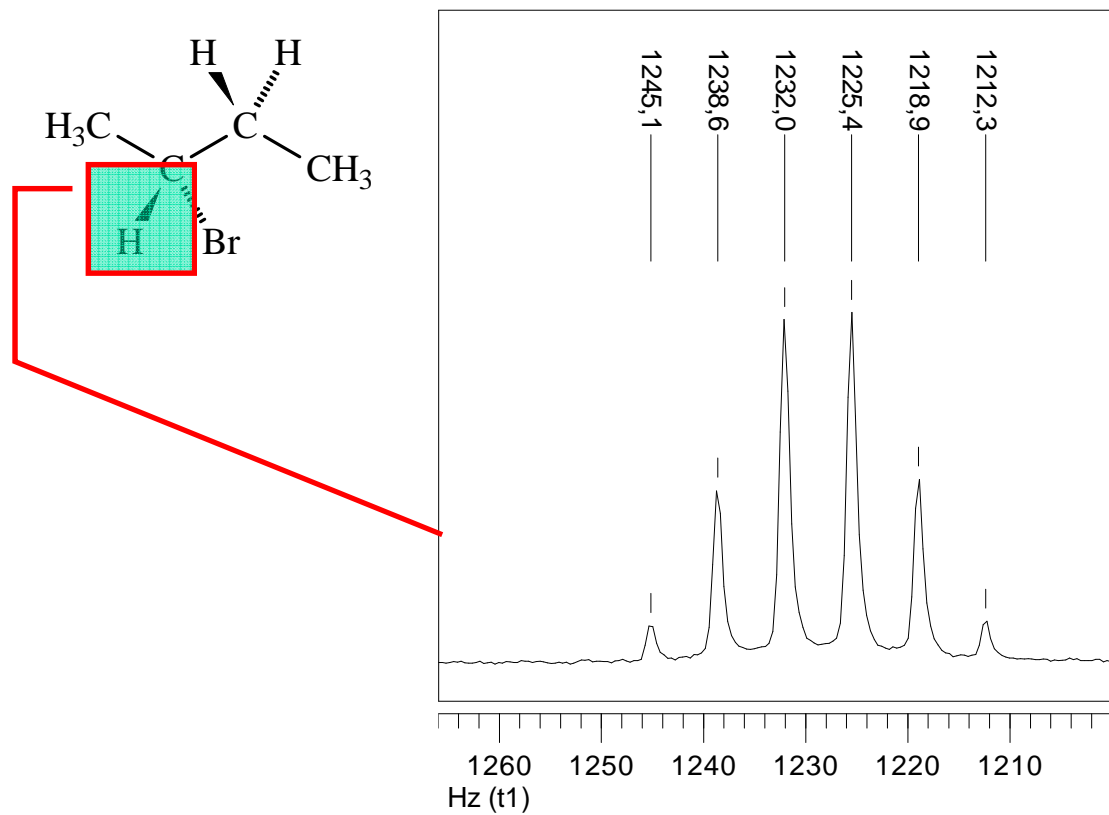
Spectre RMN ^1H du 2-bromobutane



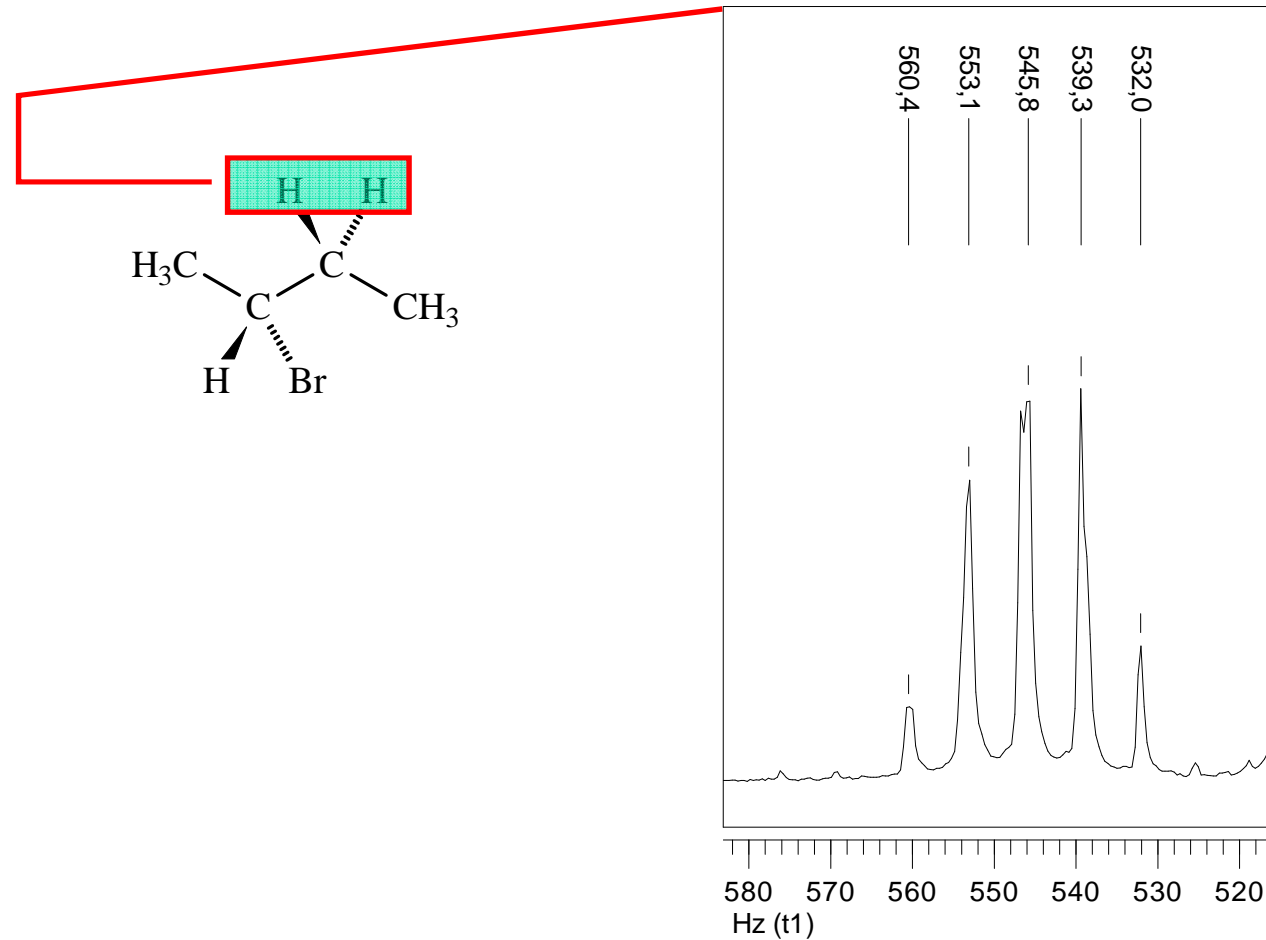
Enregistrement en solution dans CDCl_3 , à la fréquence de 300 MHz (archive de la *Pacific Lutheran University, USA*)



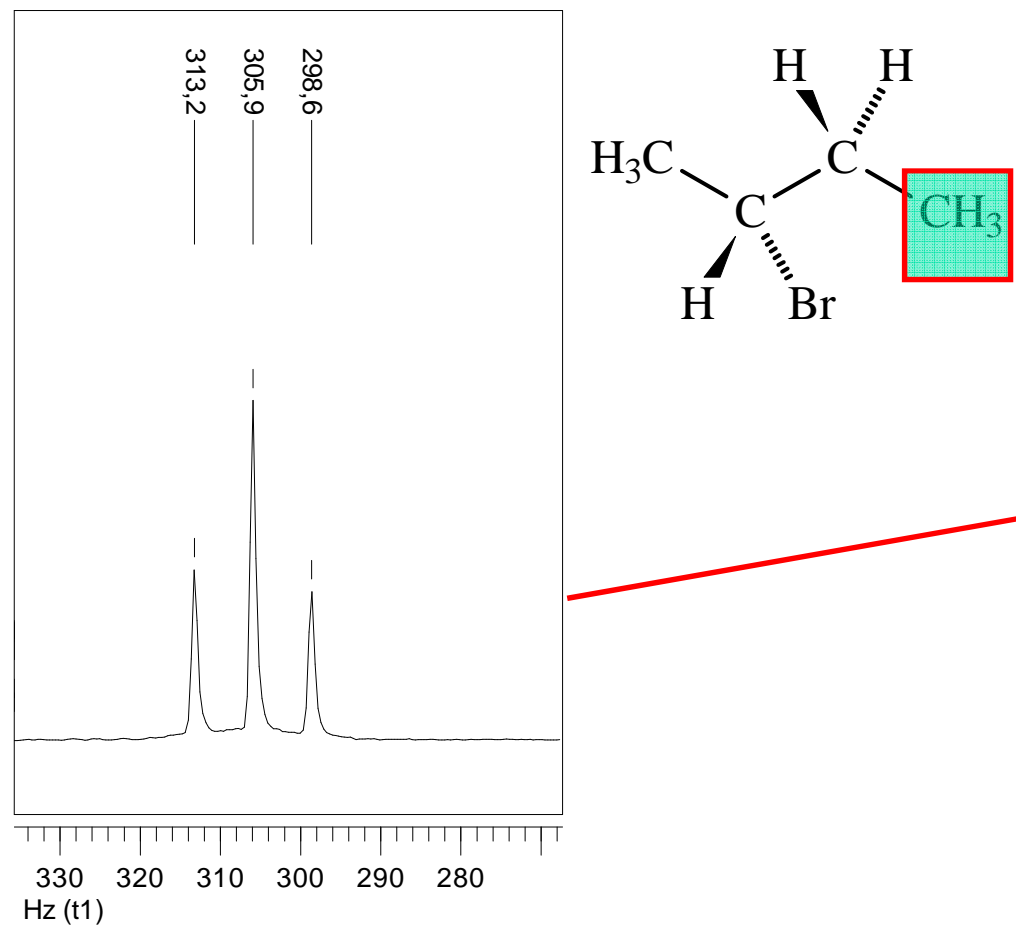
Spectre RMN ^1H du 2-bromobutane



Spectre RMN ^1H du 2-bromobutane

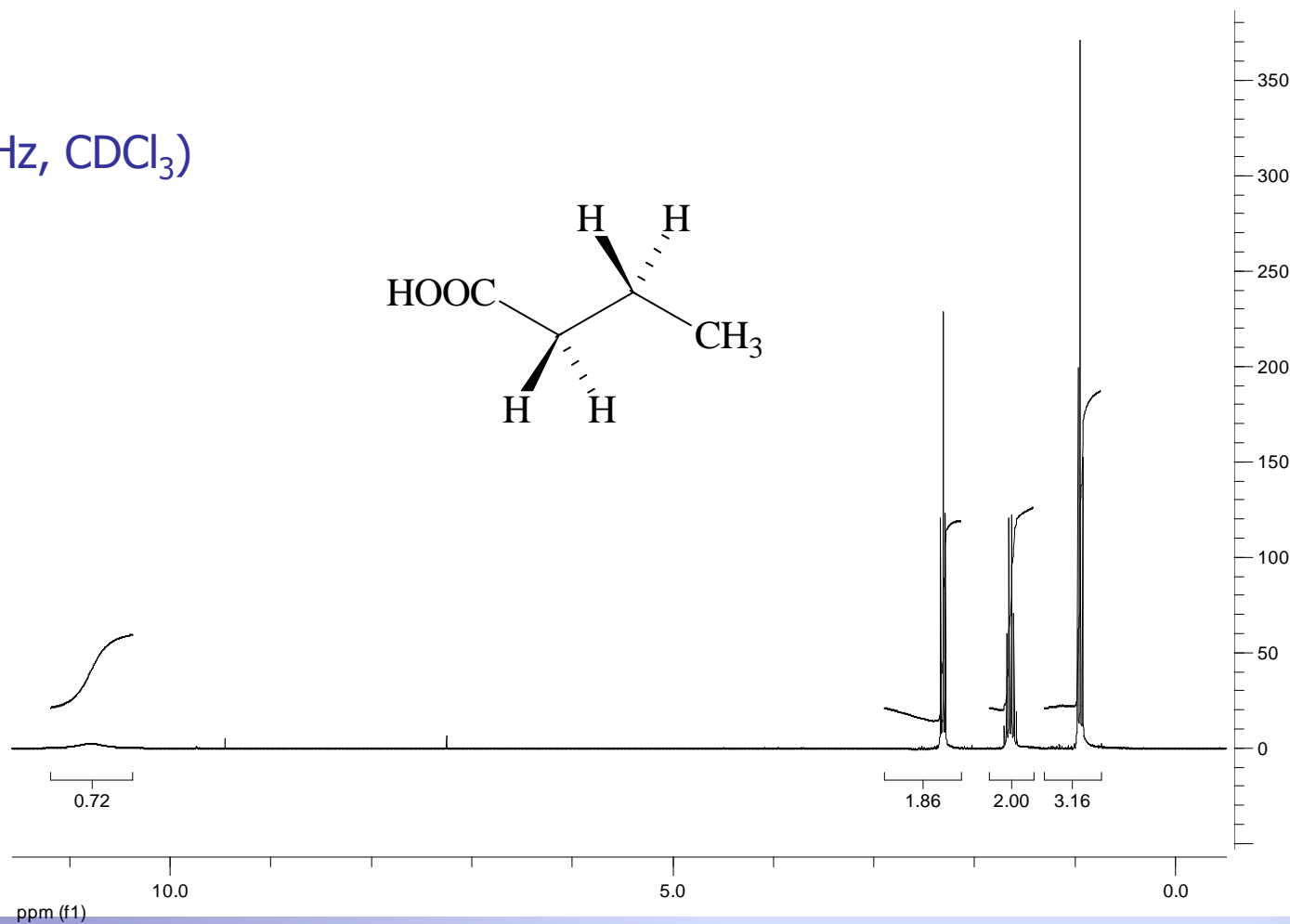


Spectre RMN ^1H du 2-bromobutane

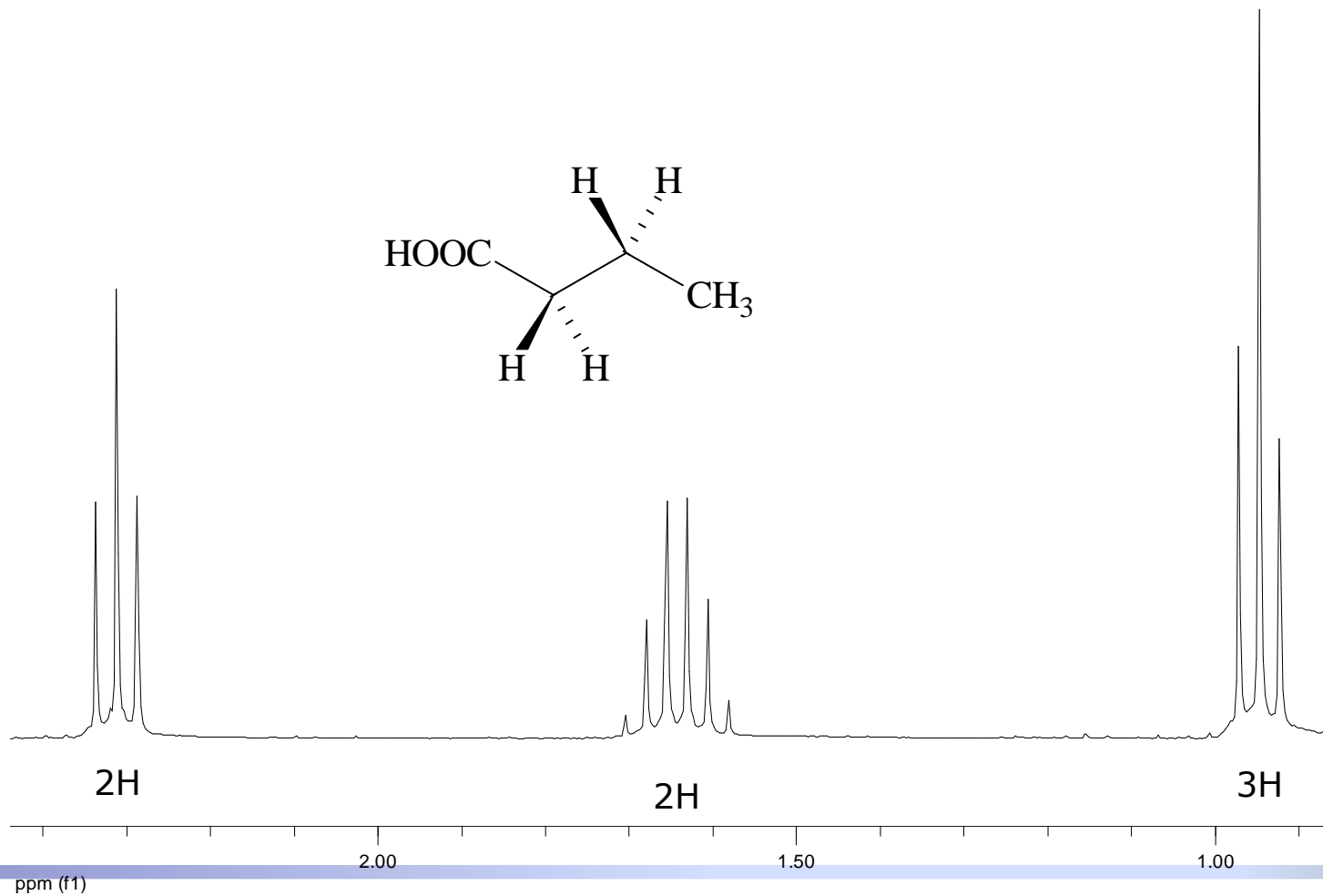


Spectre RMN ^1H de l'acide butanoïque

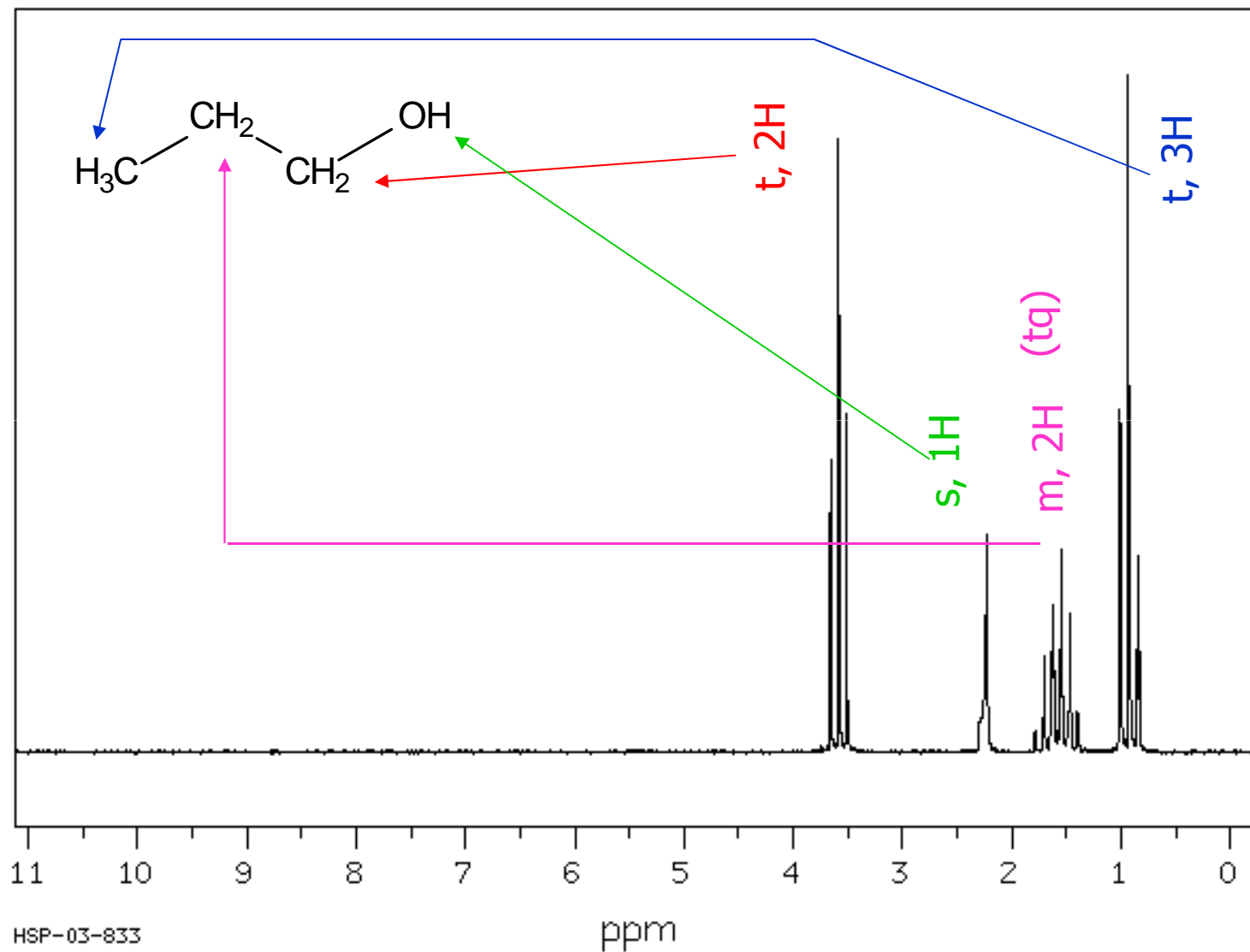
(300 MHz, CDCl_3)



Spectre RMN 1H de l'acide butanoïque



propan-1-ol



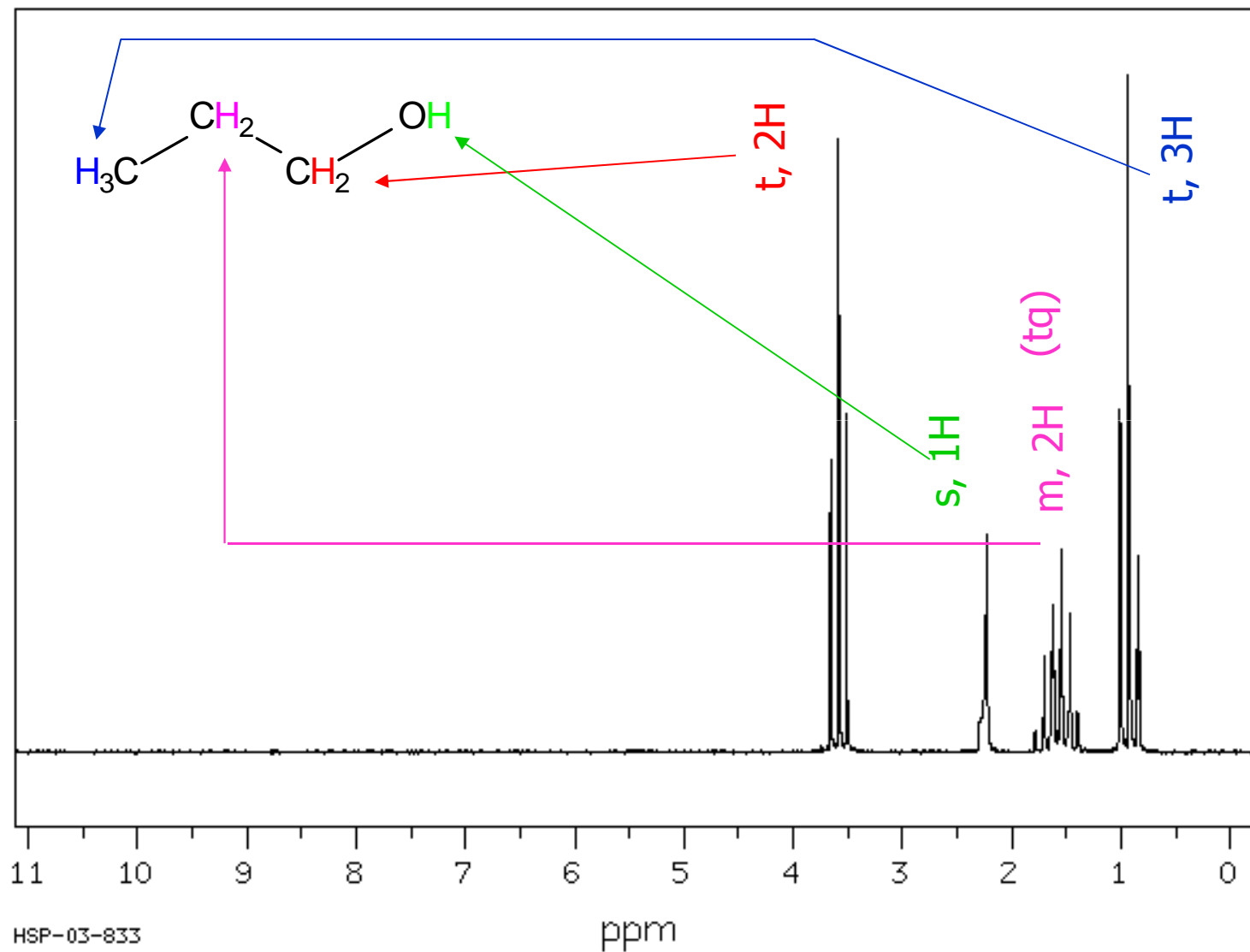
HSP-03-833

11-12 OICh

spectroscopie RMN

59

propan-1-ol



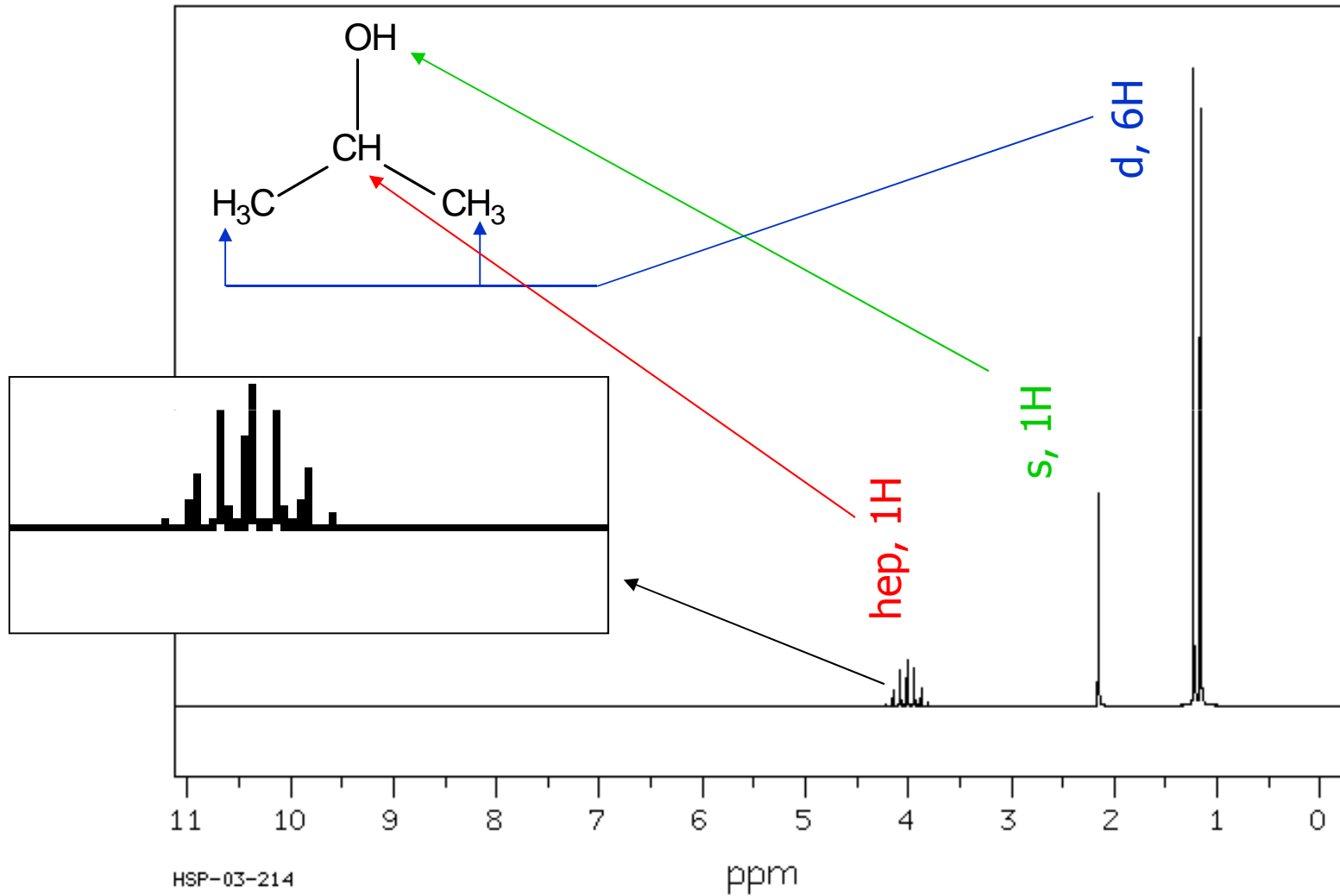
HSP-03-833

11-12 OICh

spectroscopie RMN

60

propan-2-ol

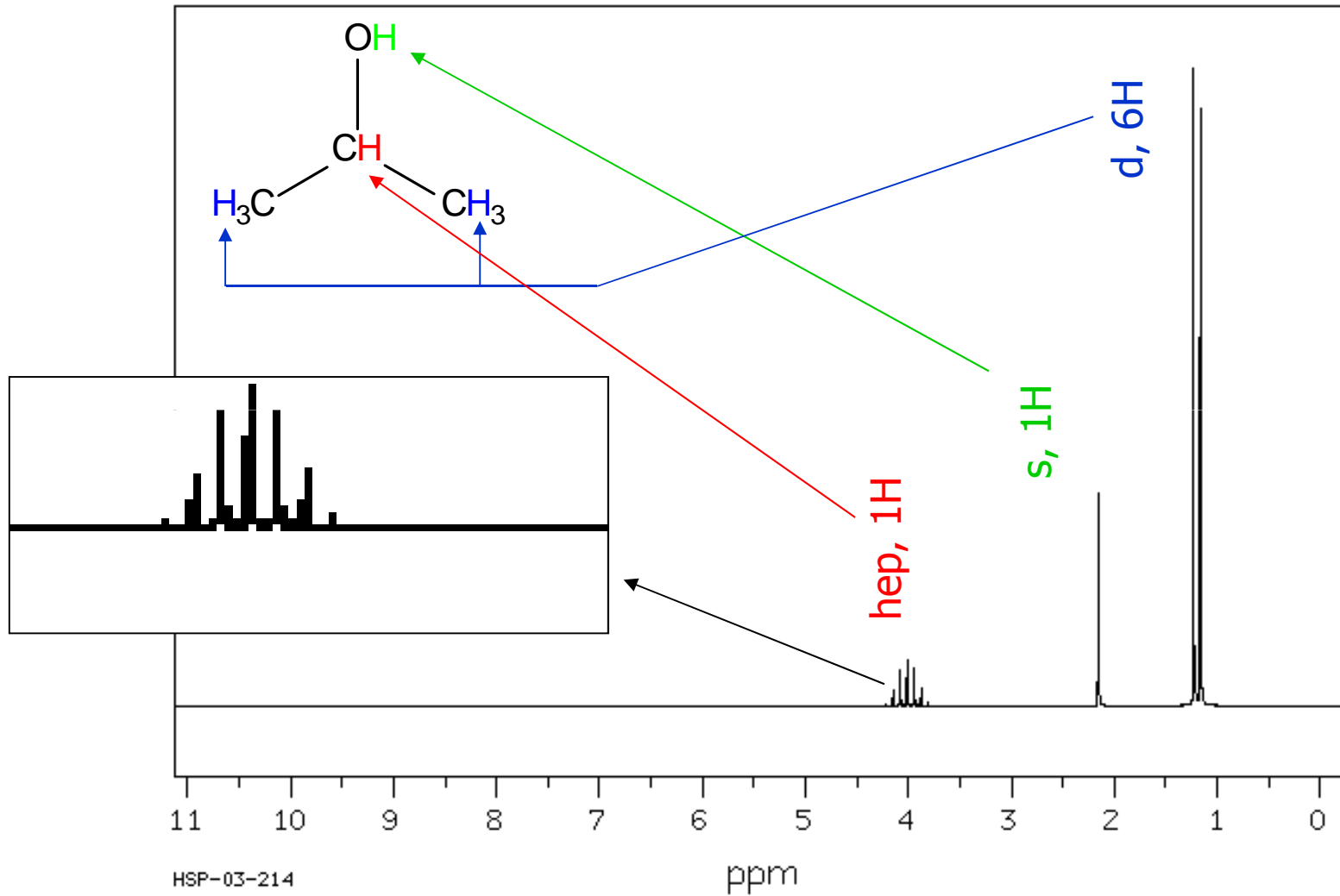


HSP-03-214

ppm



propan-2-ol



HSP-03-214

ppm

grande symétrie de la molécule \Leftrightarrow grande simplicité du spectre

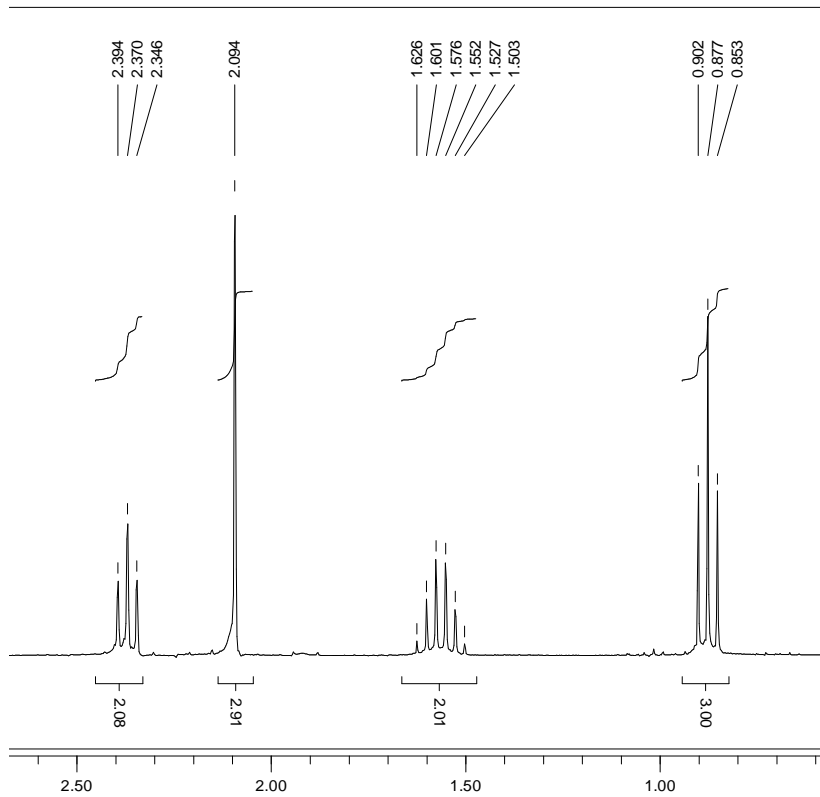
11-12 OICh

spectroscopie RMN

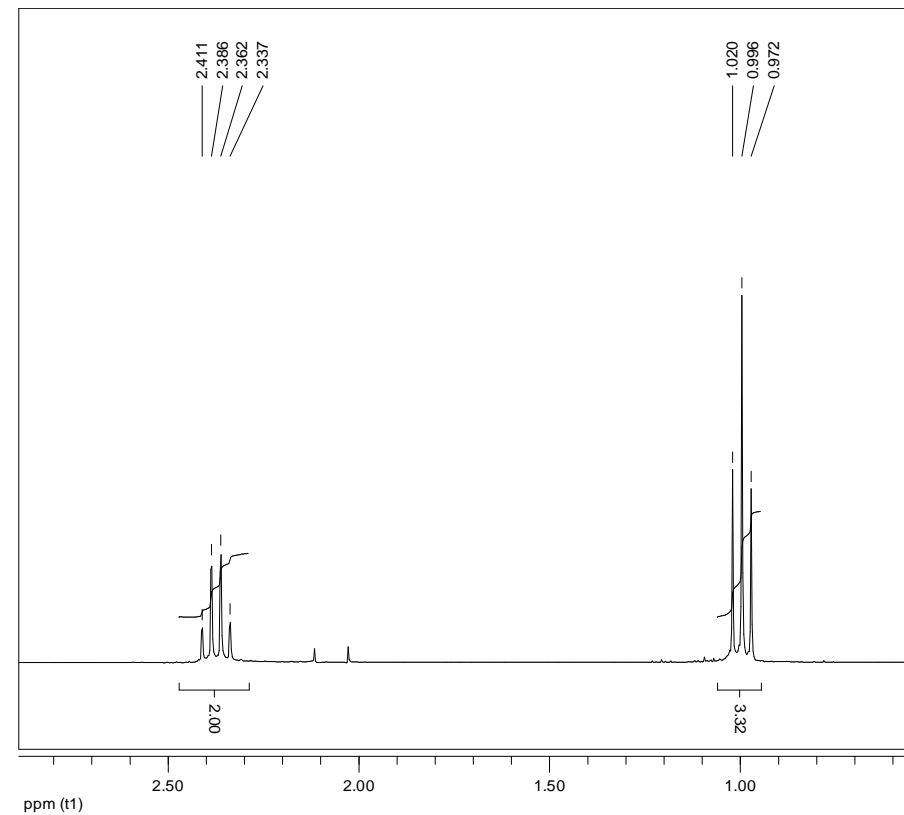
62



Influence des symétries : C₅H₁₀O



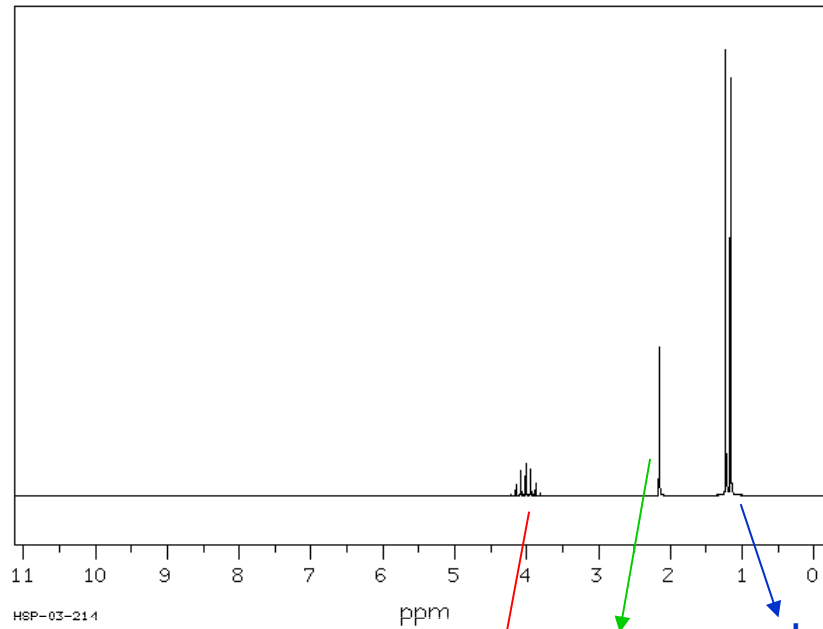
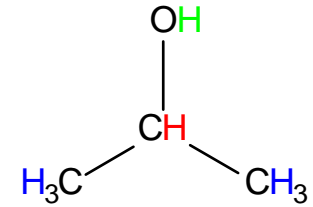
IR : $\sigma = 1716 \text{ cm}^{-1}$



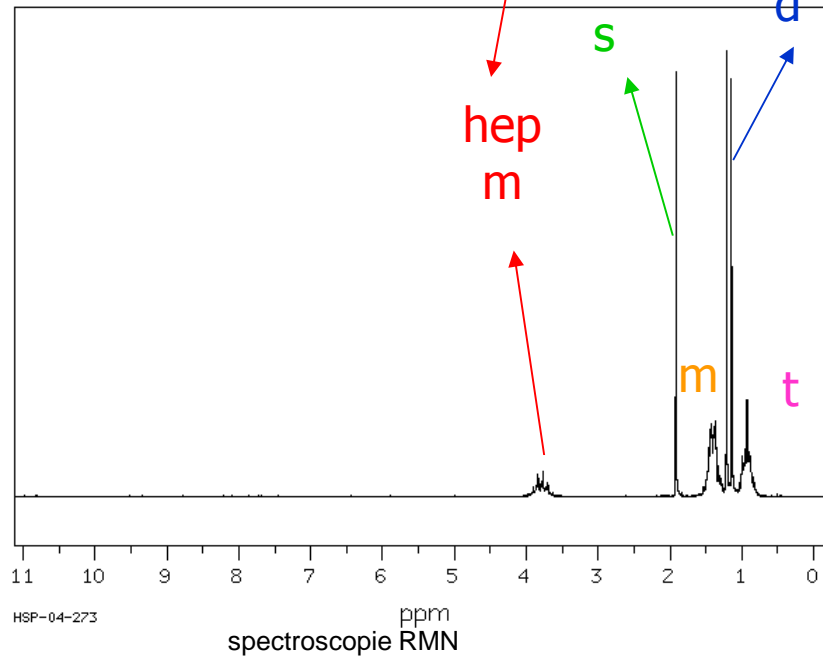
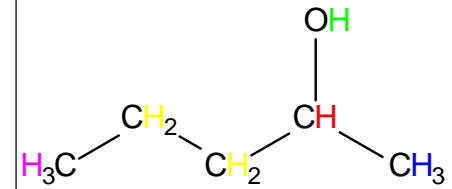
IR : $\sigma = 1717 \text{ cm}^{-1}$



propan-2-ol

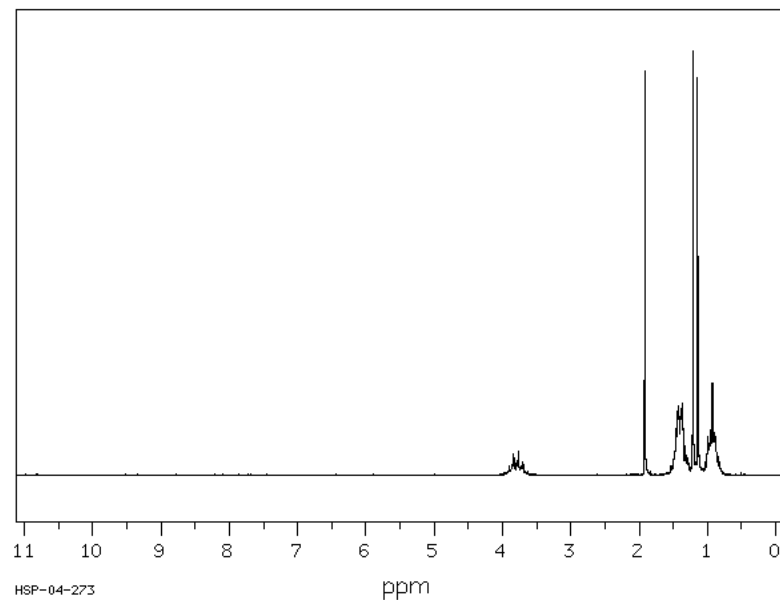
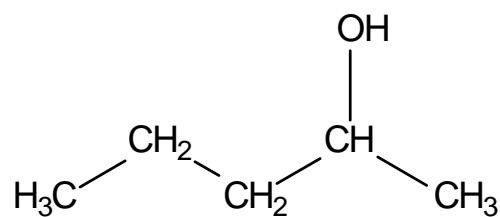


pentan-2-ol

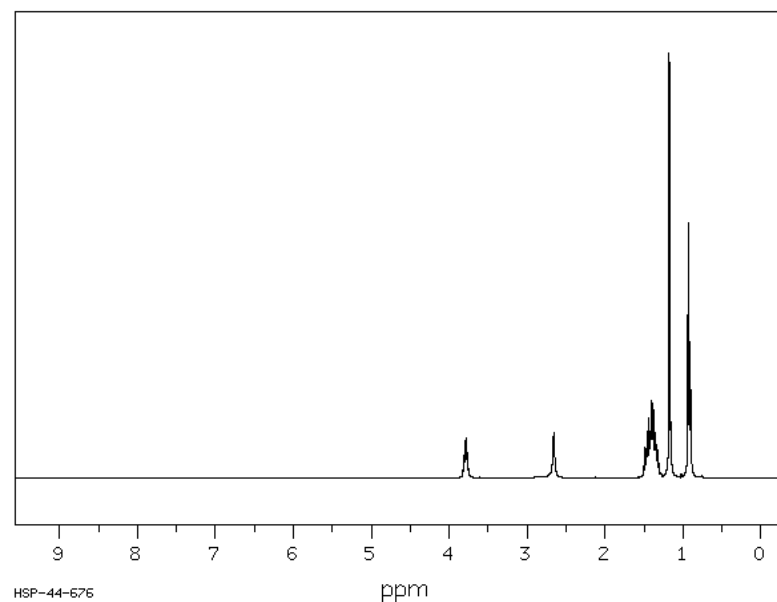


pentan-2-ol

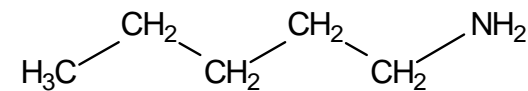
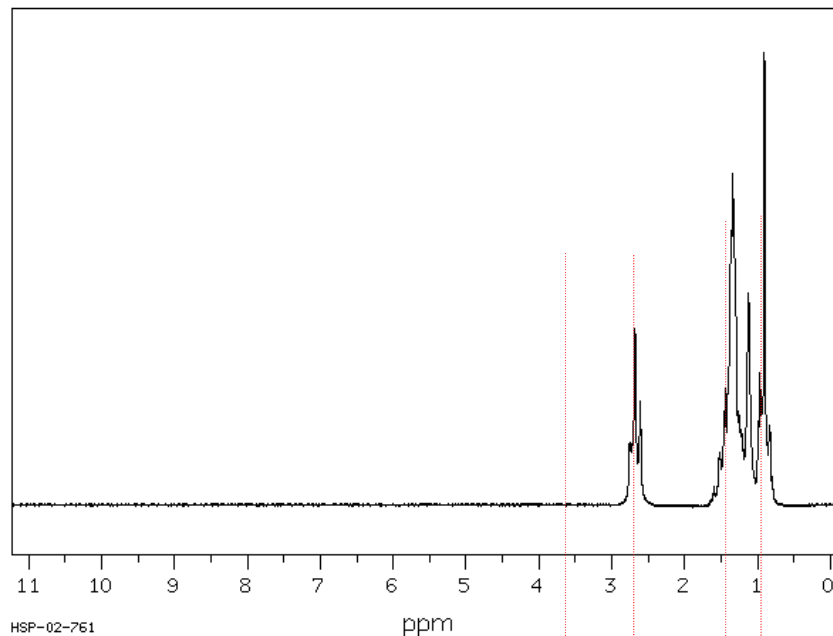
90 MHz



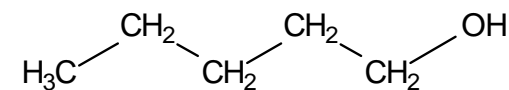
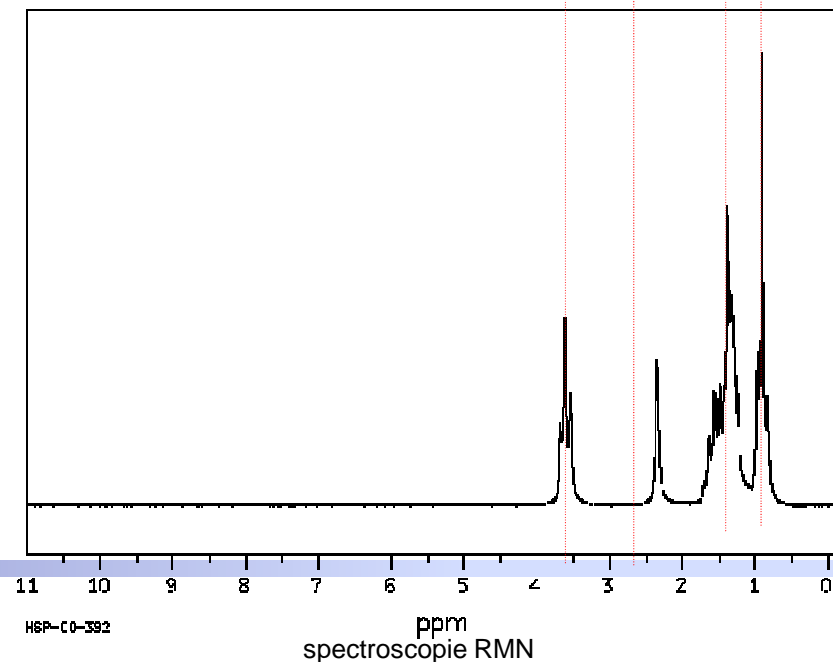
400 MHz



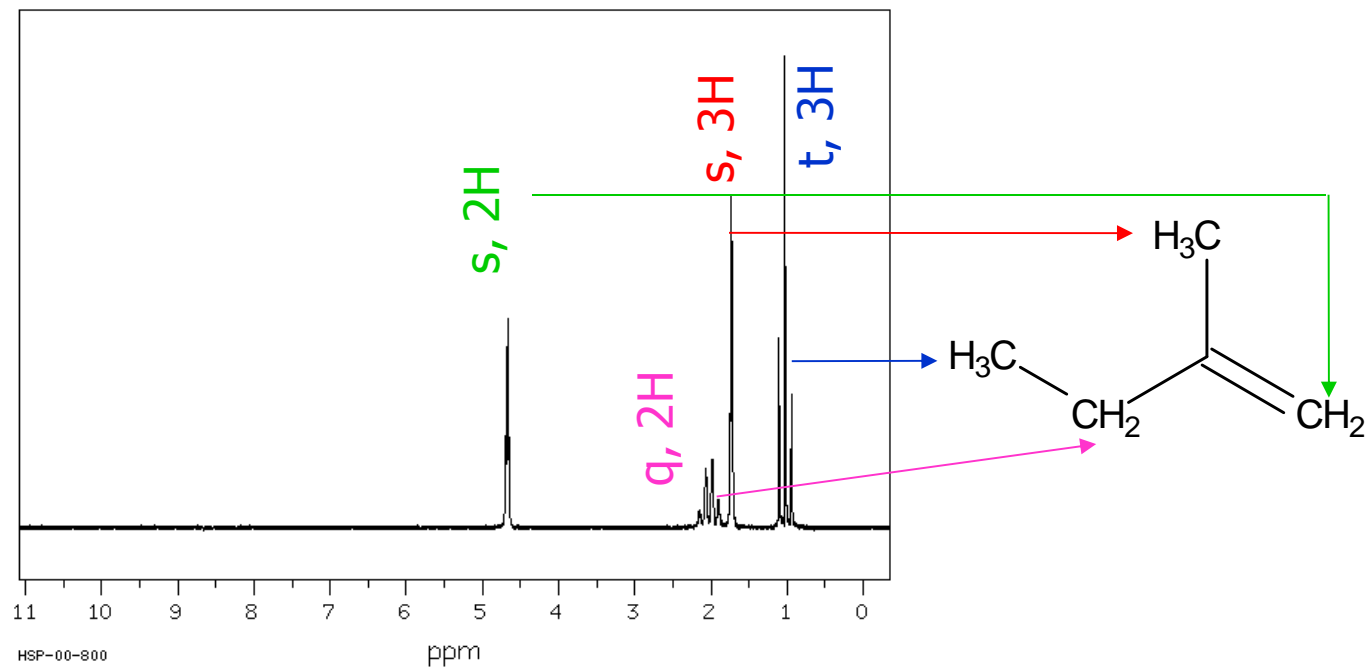
pentylamine



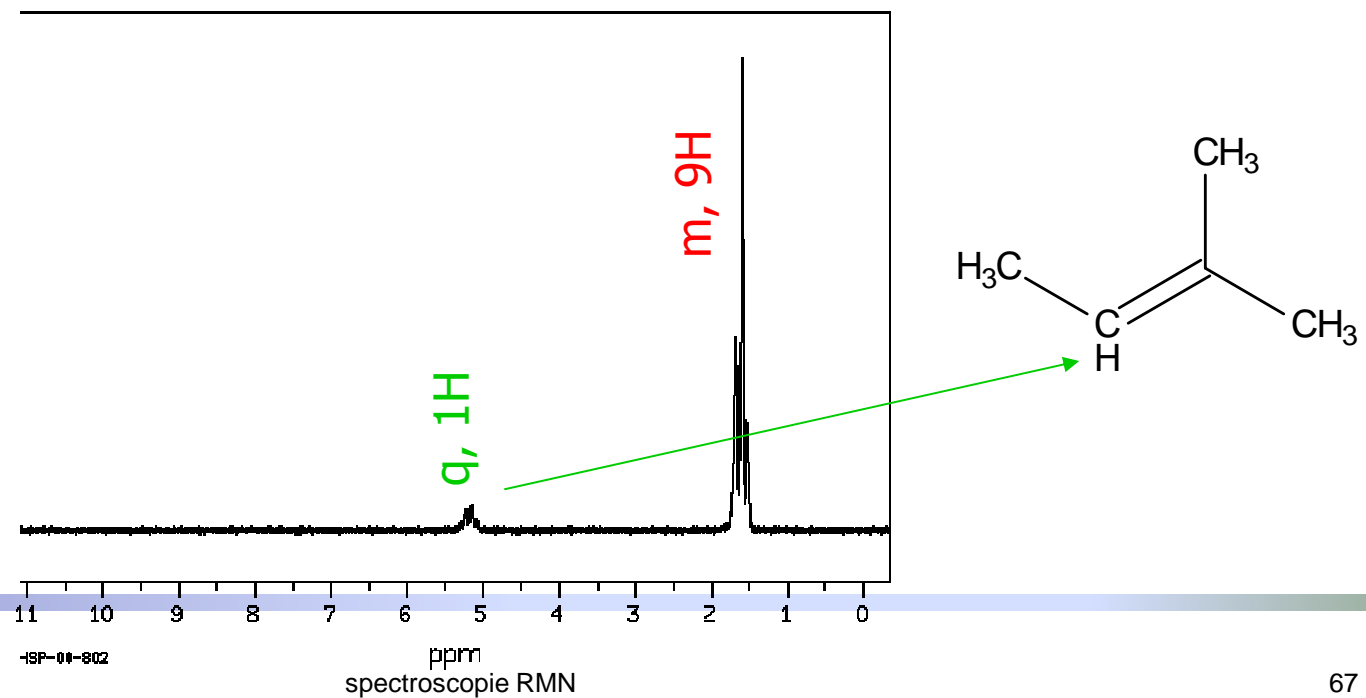
pentan-1-ol



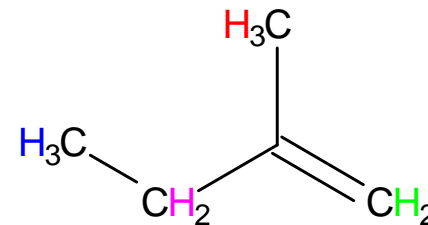
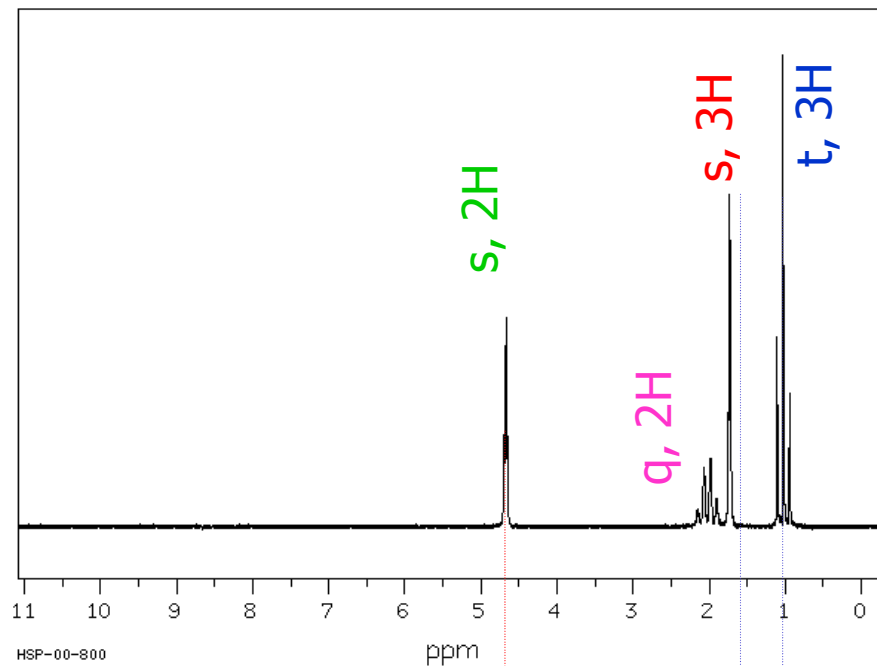
2-méthyl but-1-ène



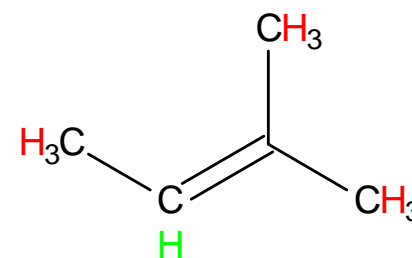
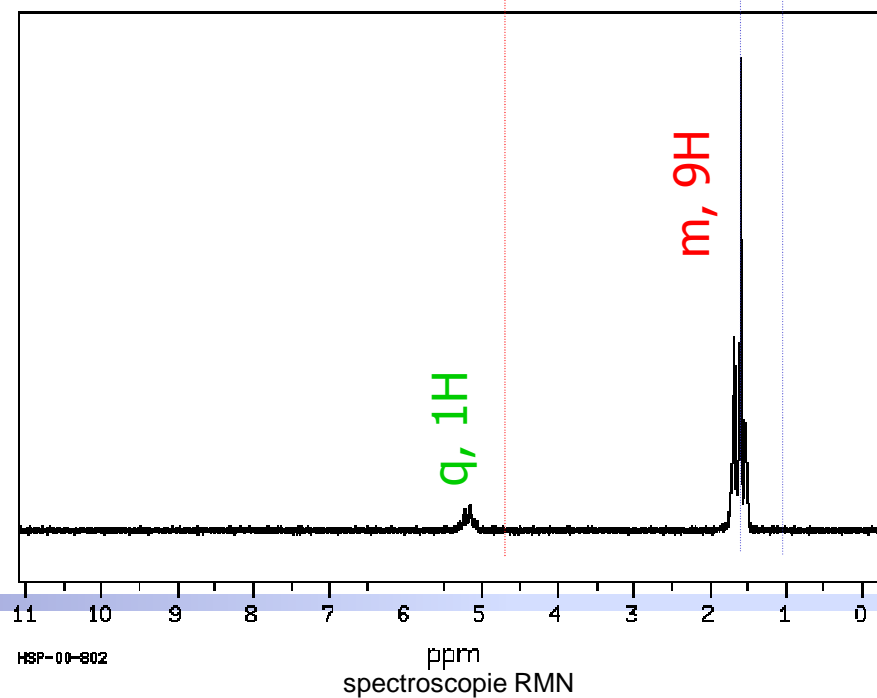
2-méthyl but-2-ène



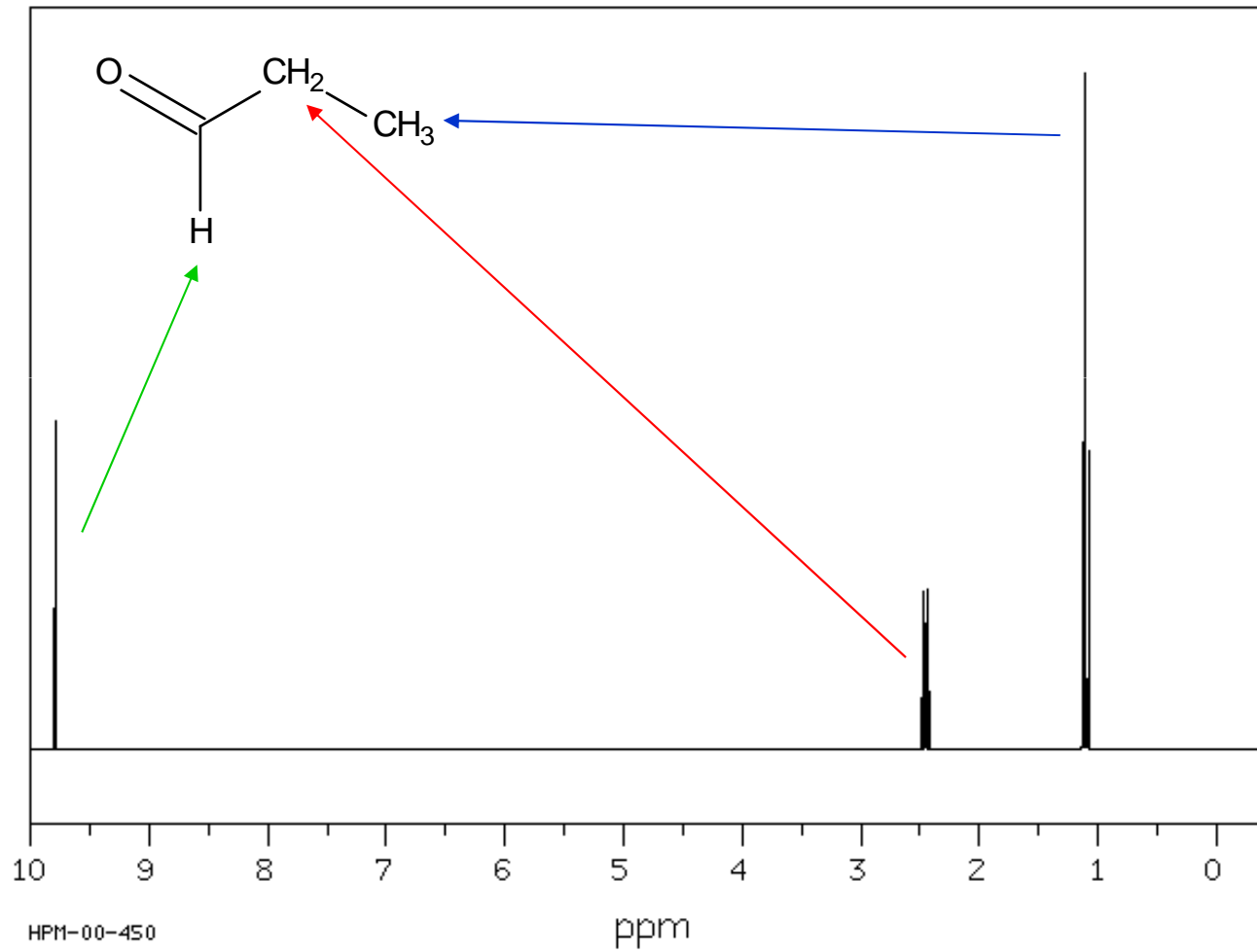
2-méthyl
but-1-ène



2-méthyl
but-2-ène



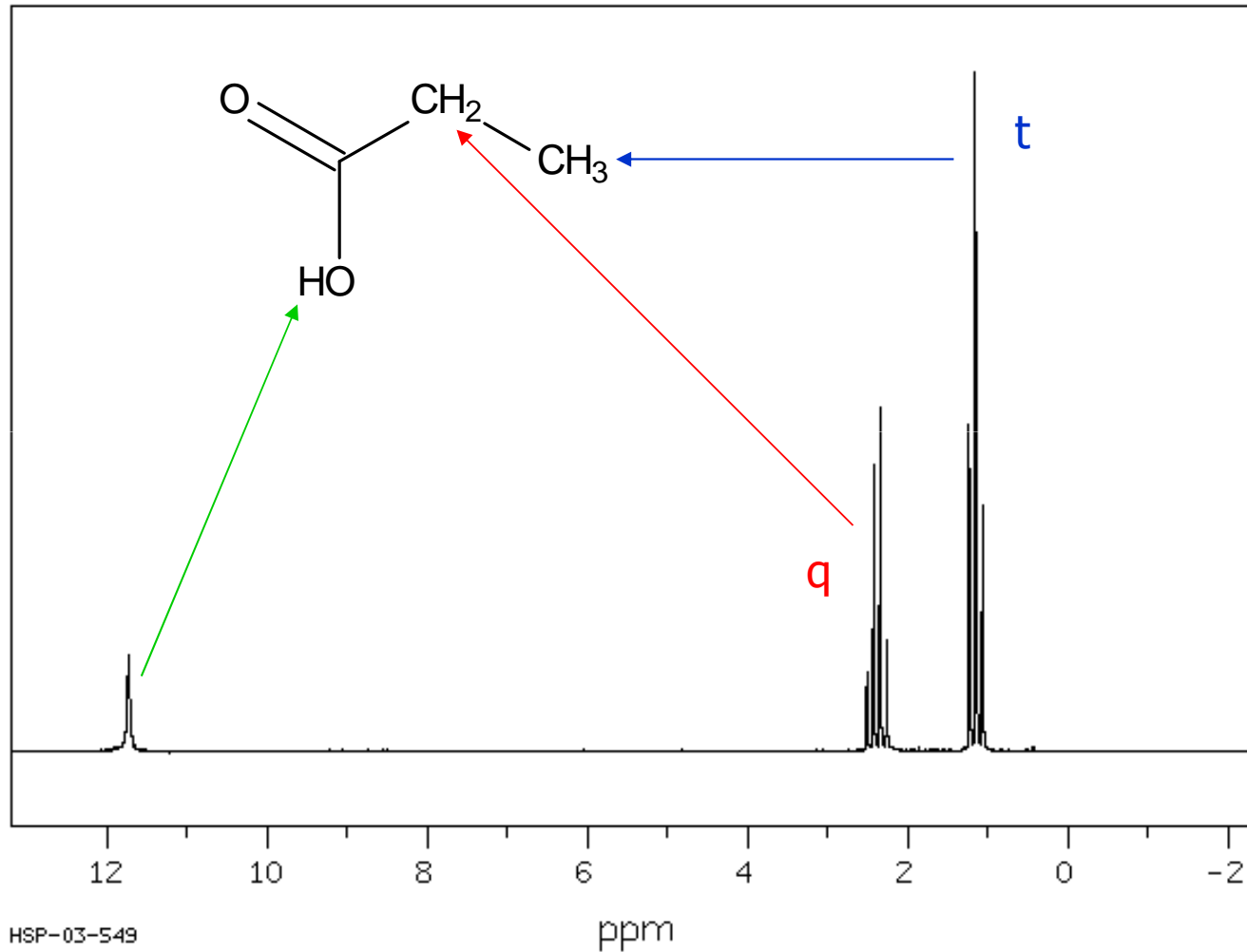
propanal



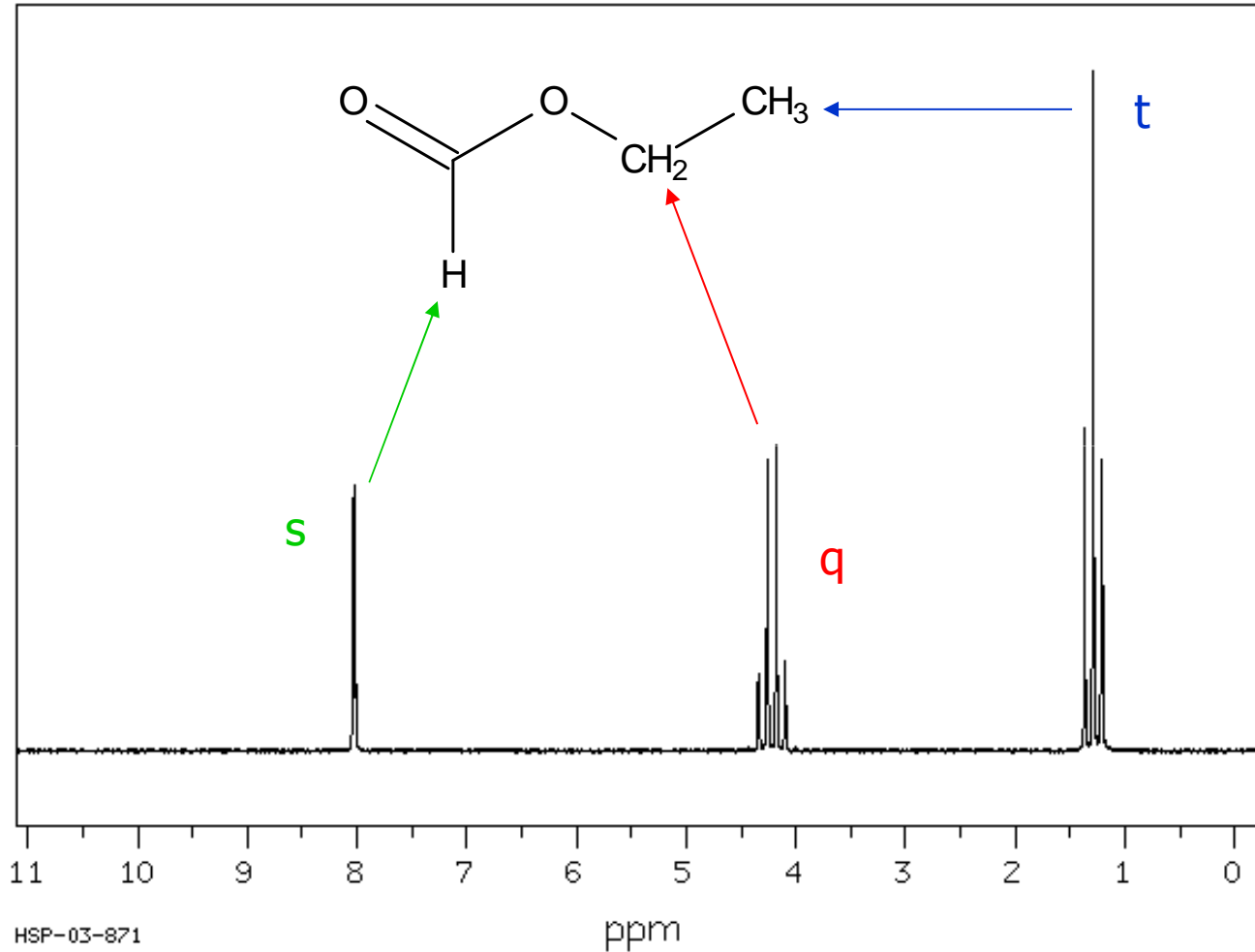
HPM-00-450



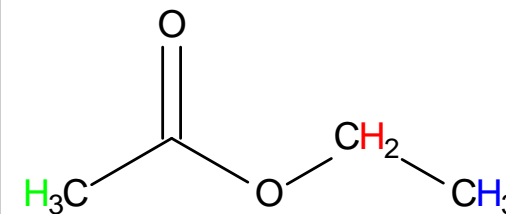
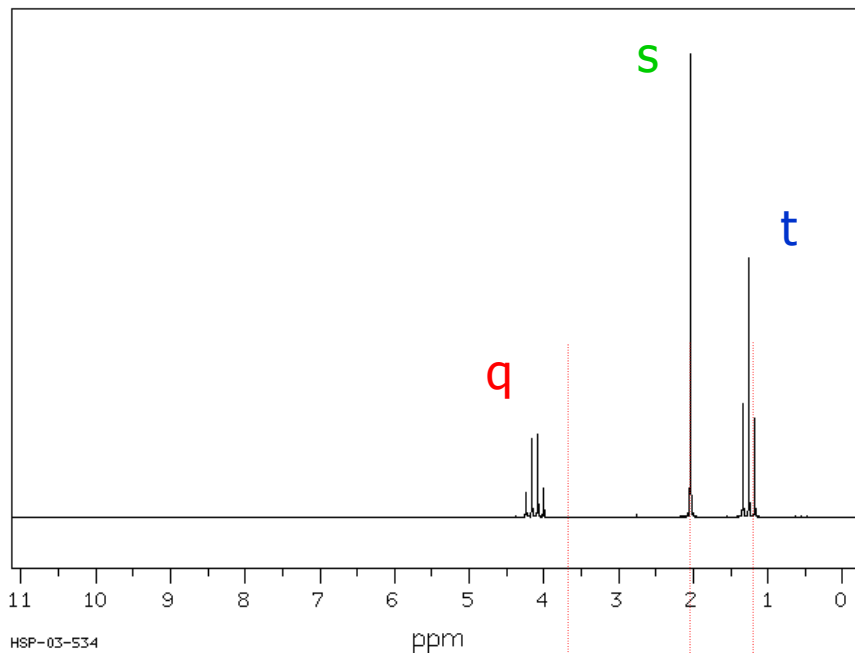
acide propanoïque



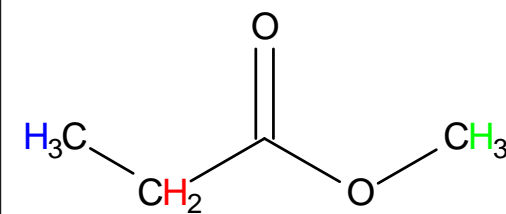
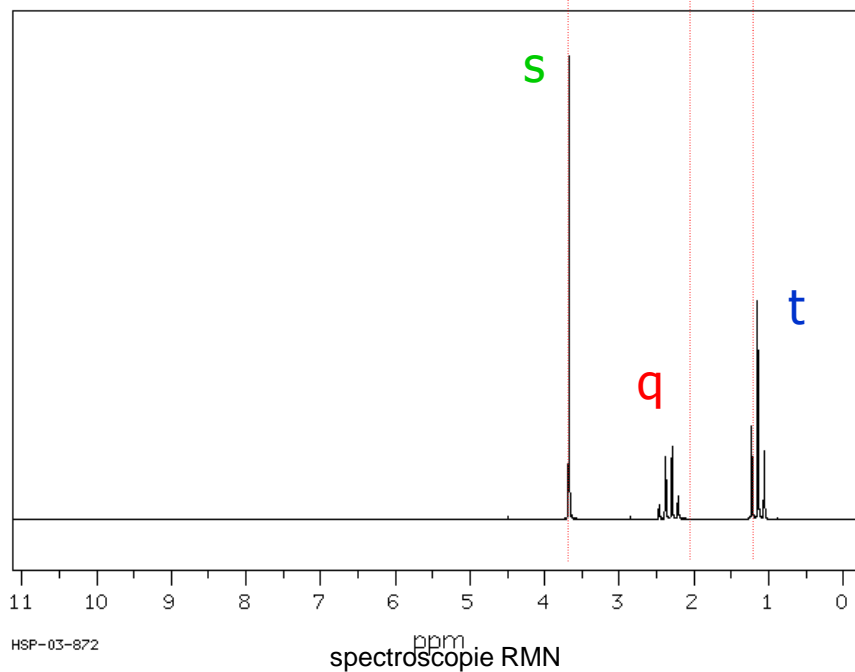
méthanoate d'éthyle



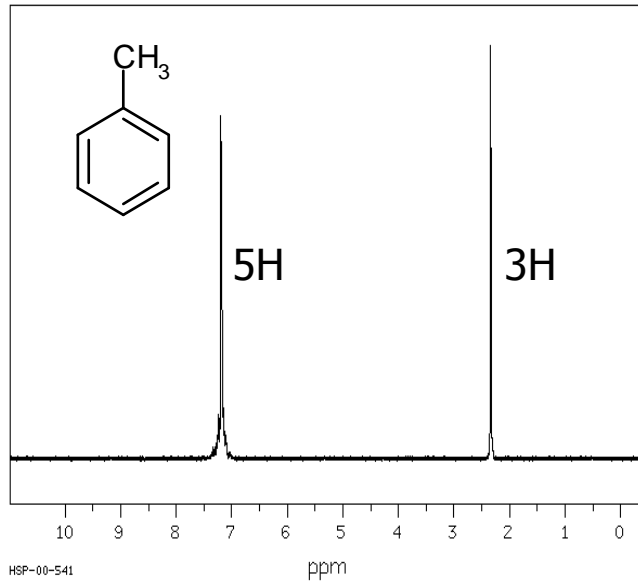
éthanoate d'éthyle



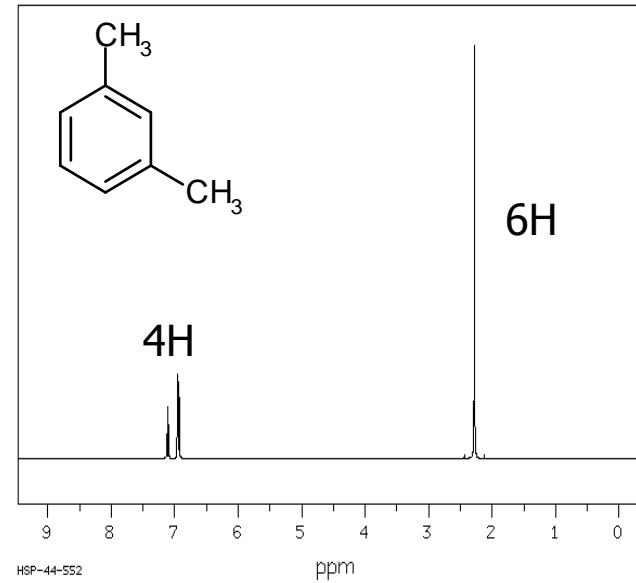
propanoate de méthyle



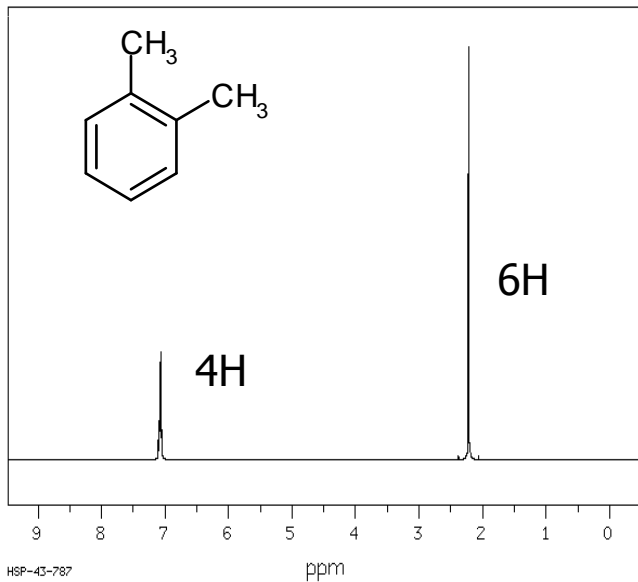
toluène



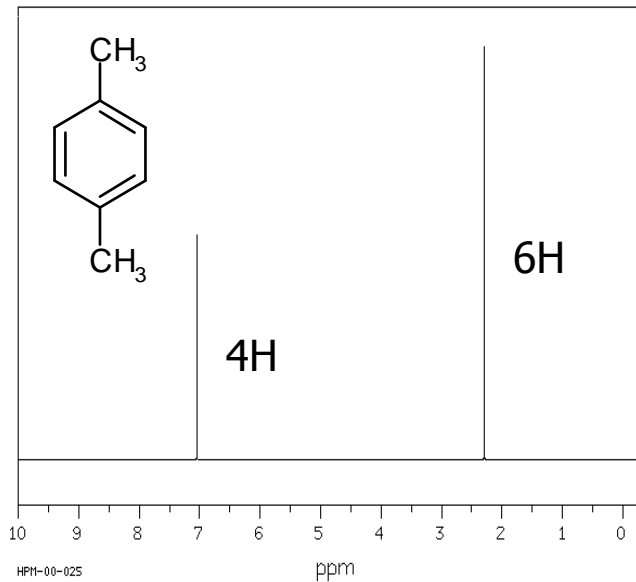
méta-
xylène



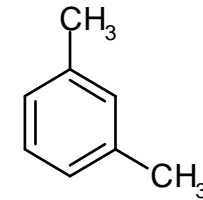
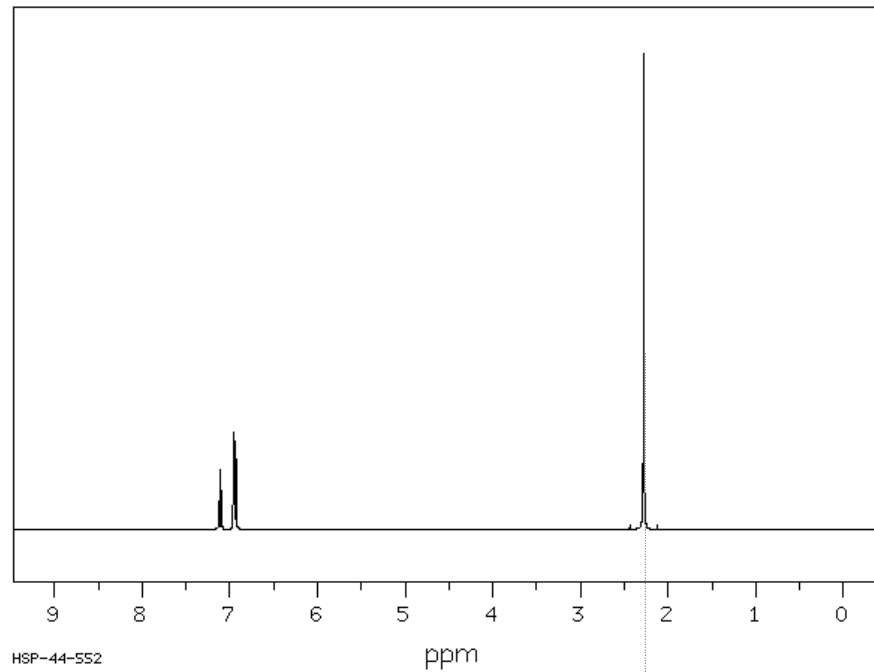
ortho-
xylène



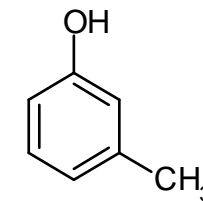
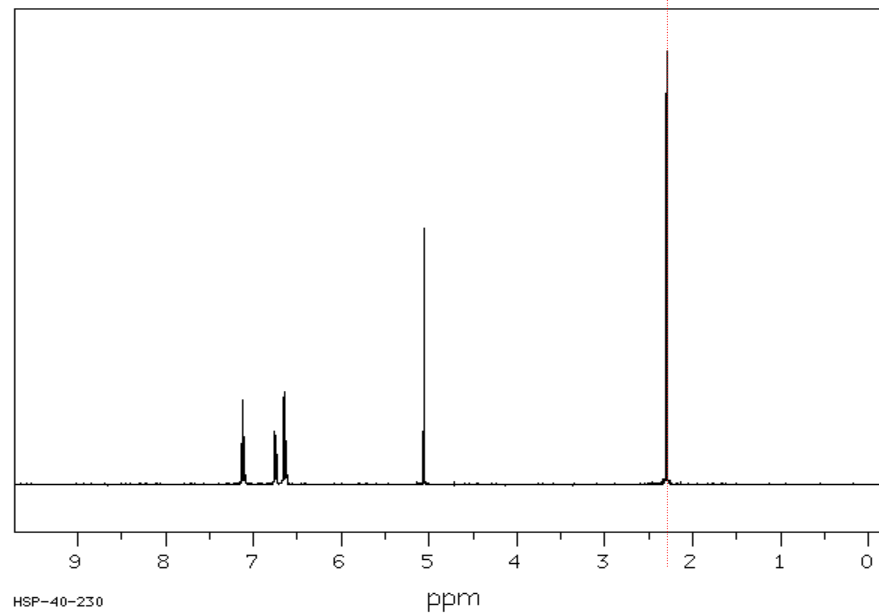
para-
xylène



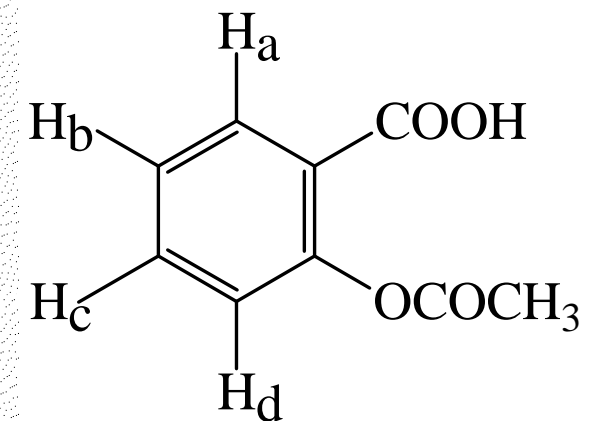
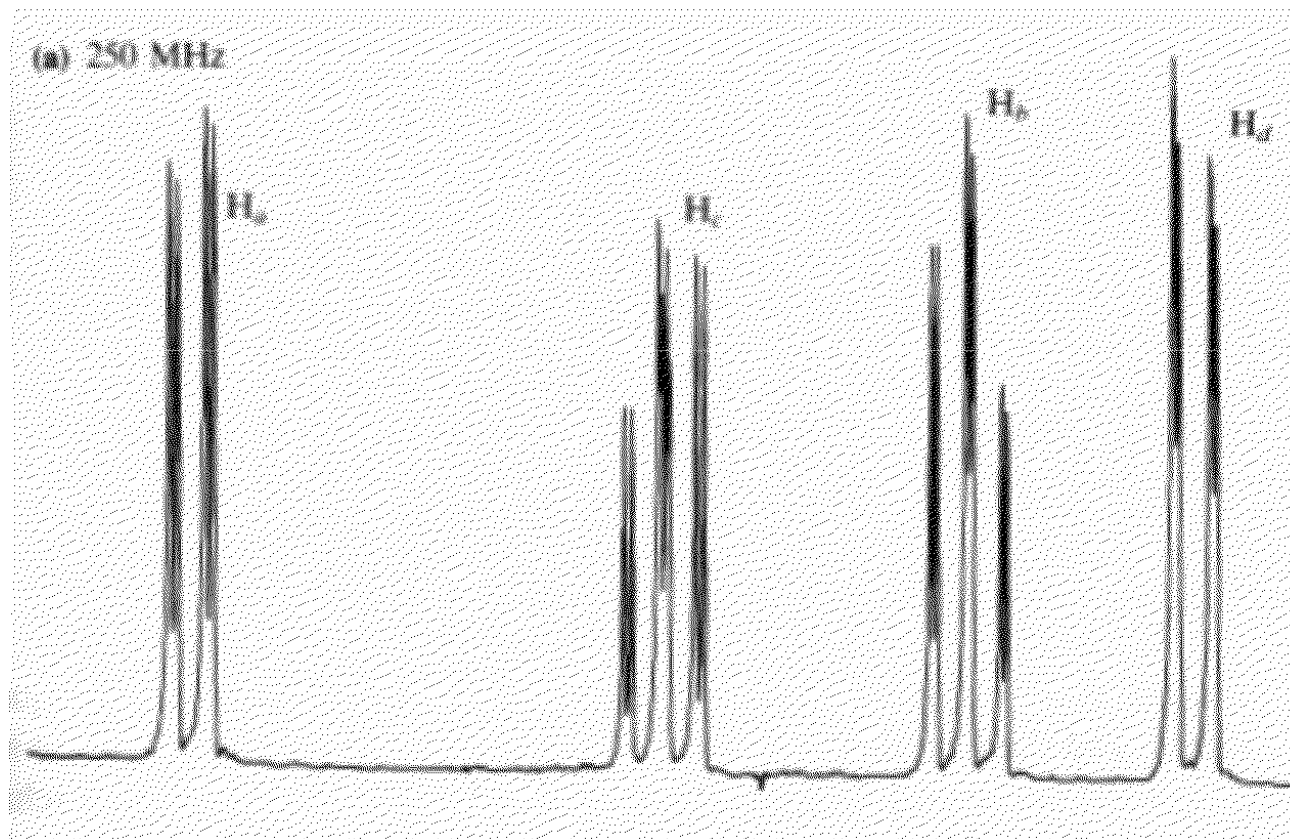
méta-xylène



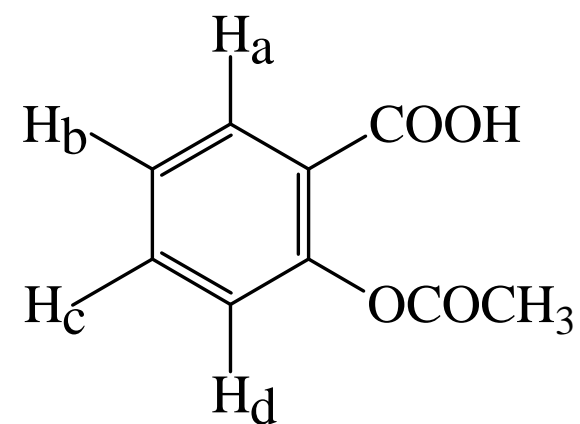
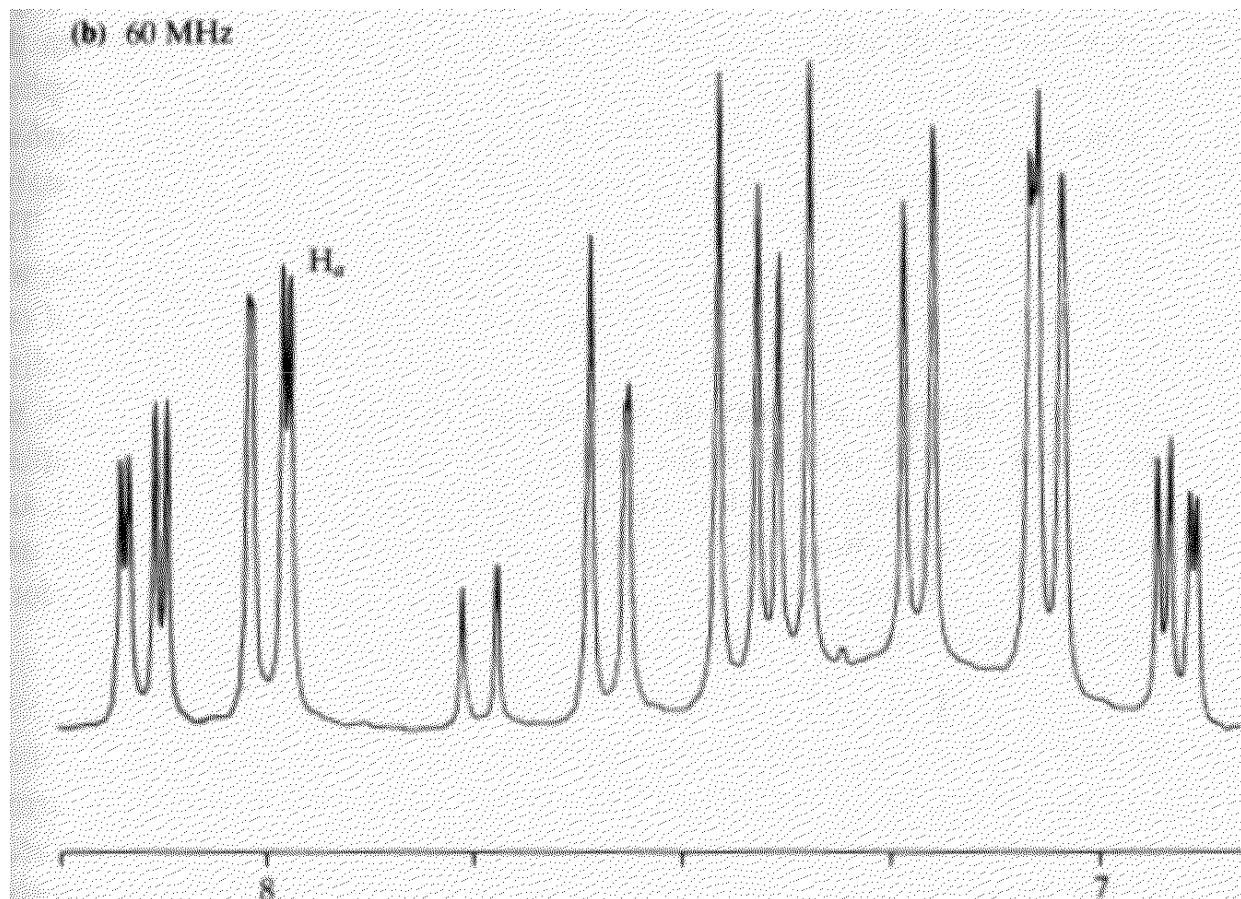
méta-crésol



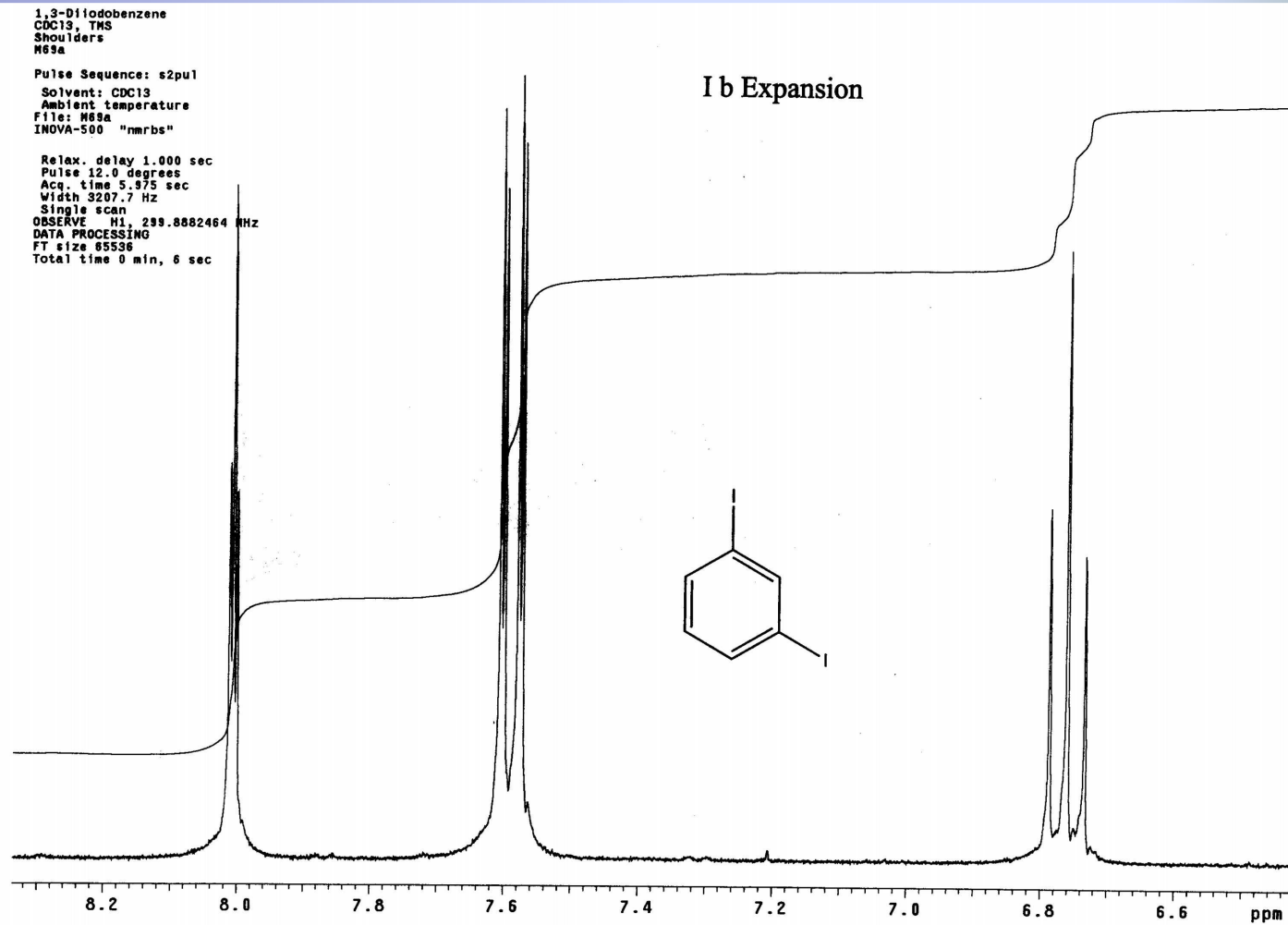
Influence de l'intensité du champ



Influence de l'intensité du champ

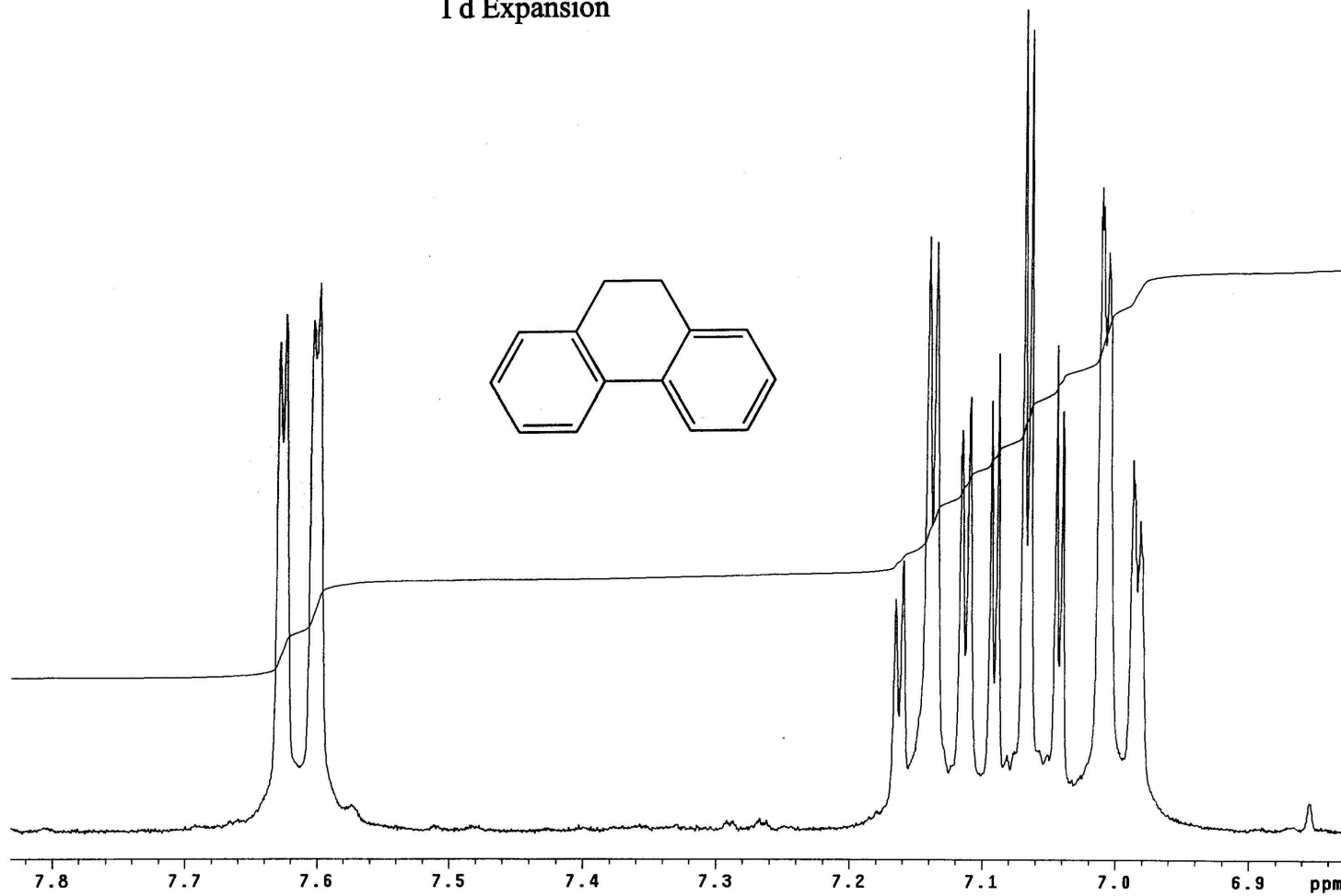


Systemes aromatiques

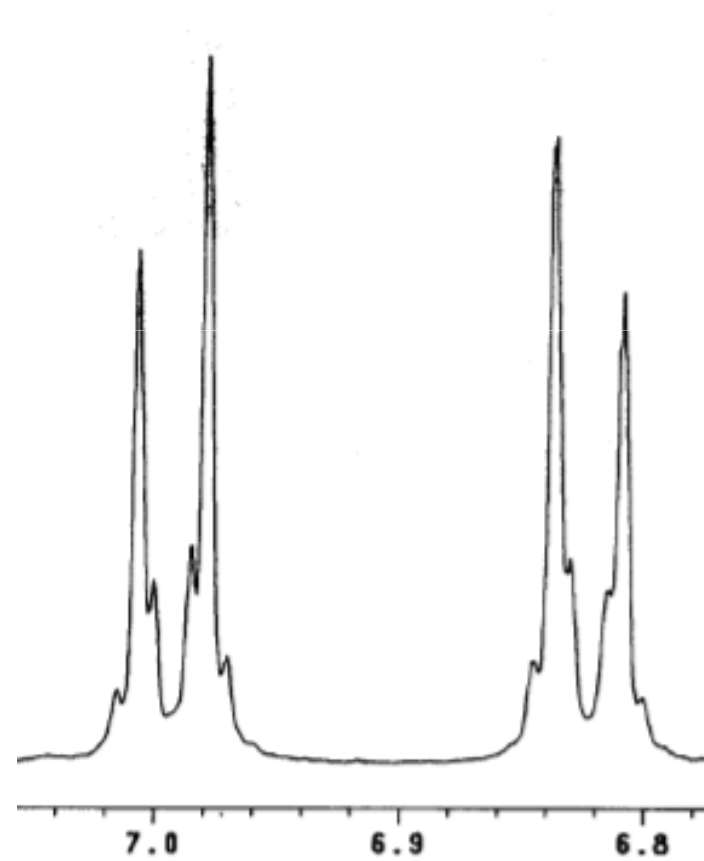
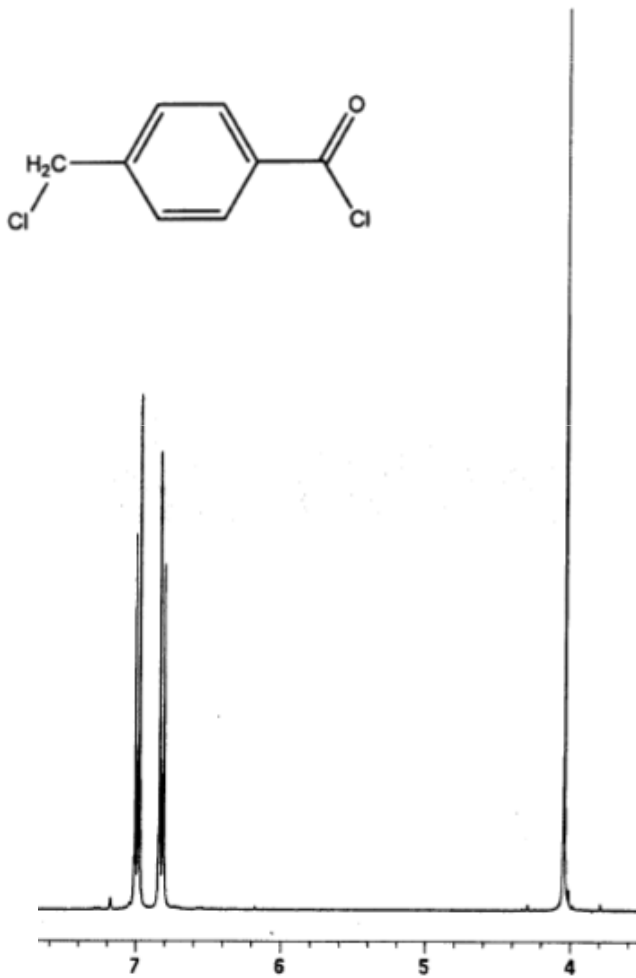


Motif complexe

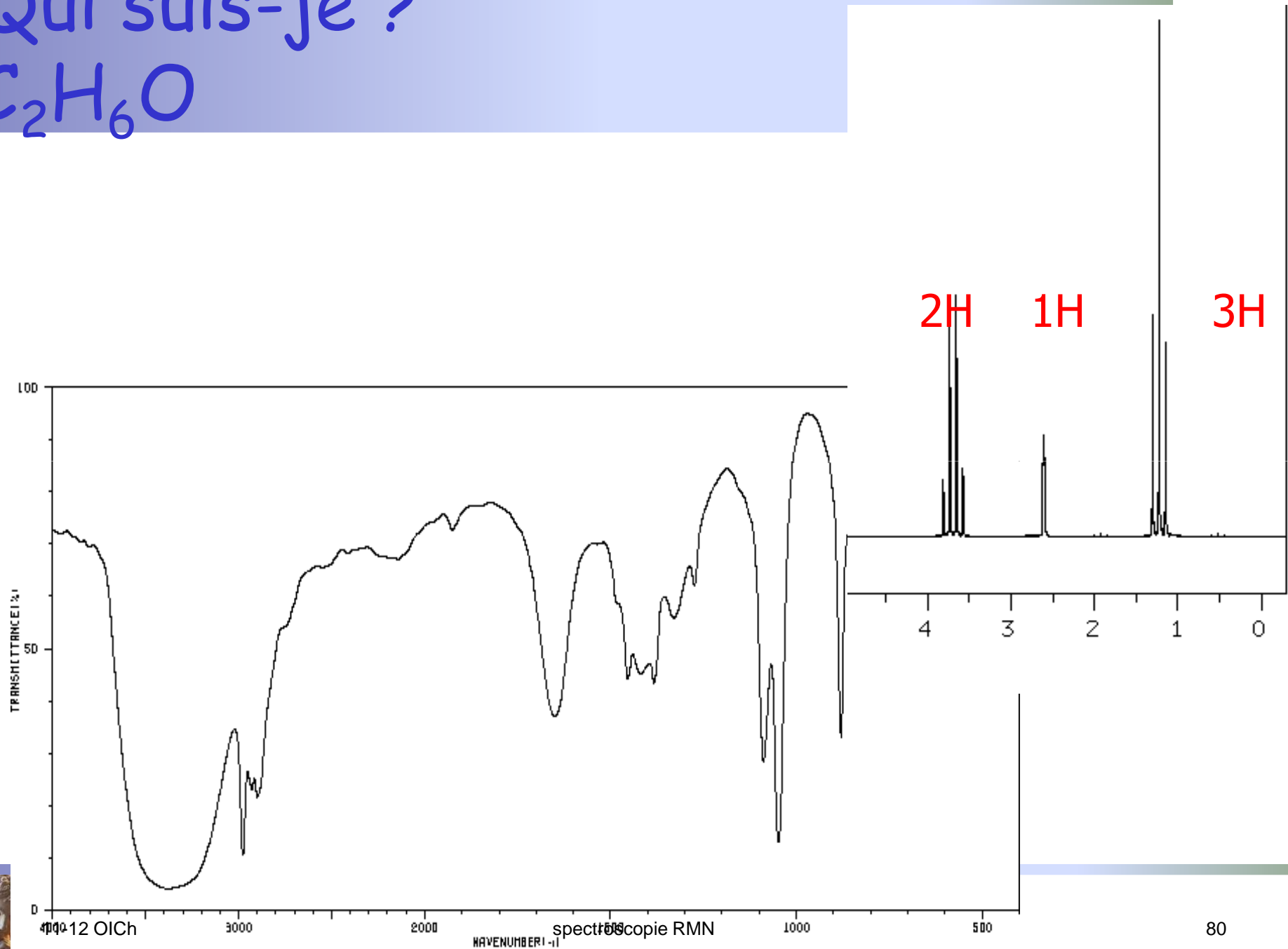
I d Expansion

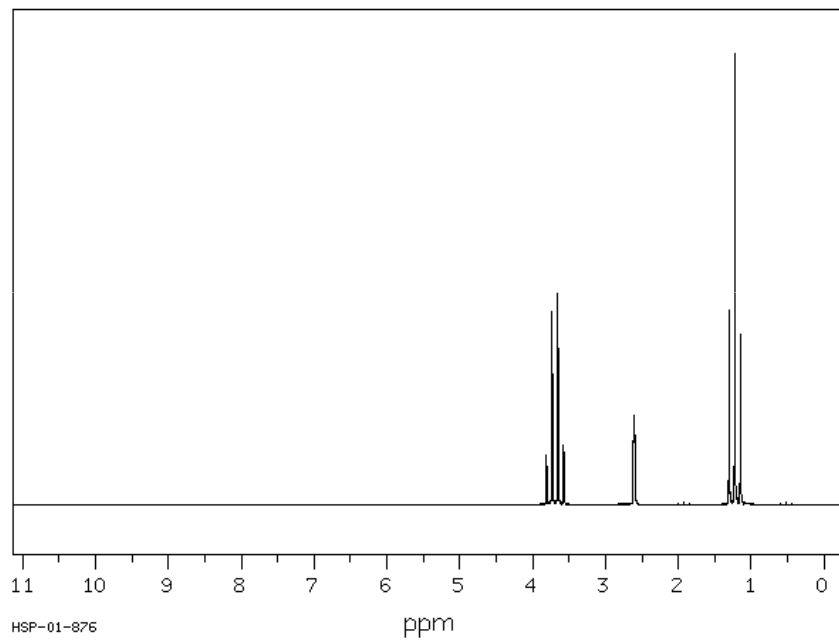


Systemes non analysables



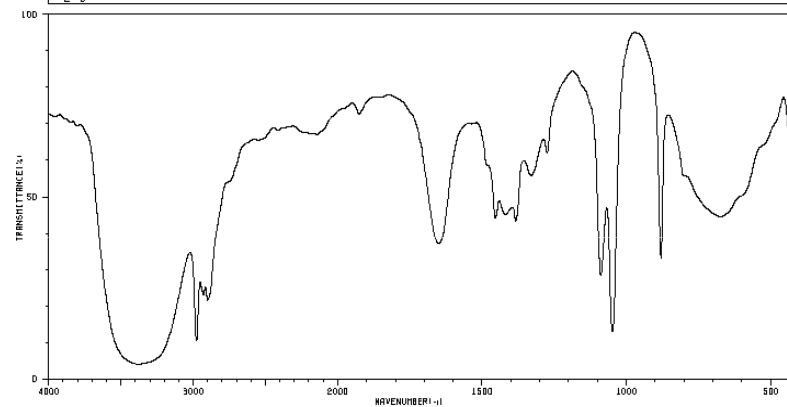
Qui suis-je ?
 C_2H_6O





HSP-01-876

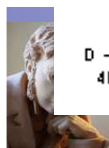
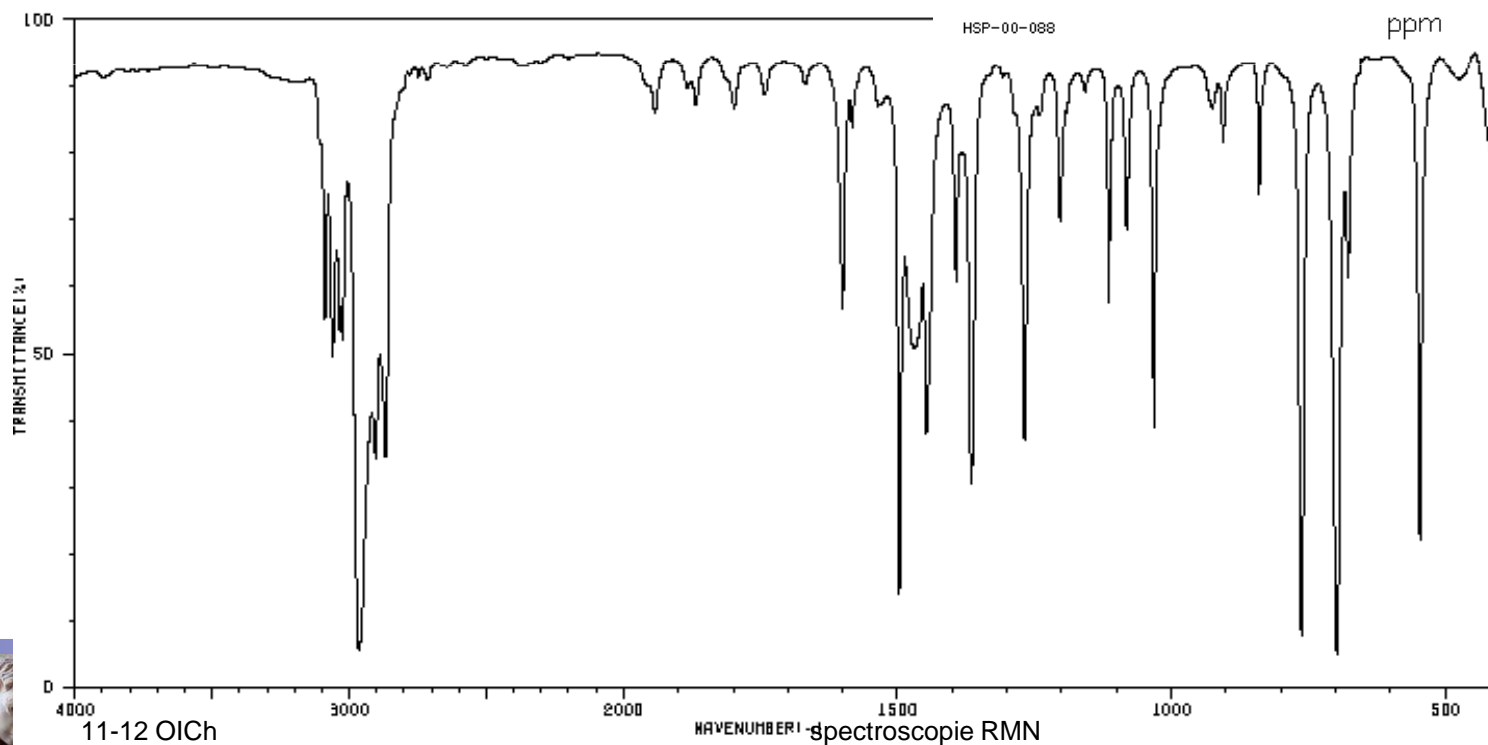
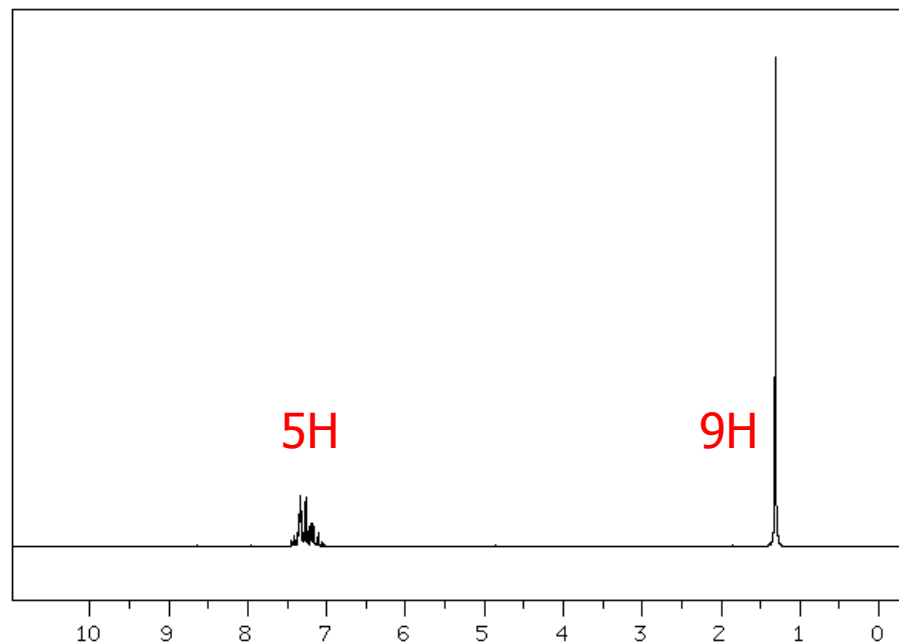
HIT-NO=1374	SCORE= ()	SDBS-NO=1300	IR-NIDA-21941 : LIQUID FILM
ETHYL ALCOHOL			
C ₂ H ₅ O			

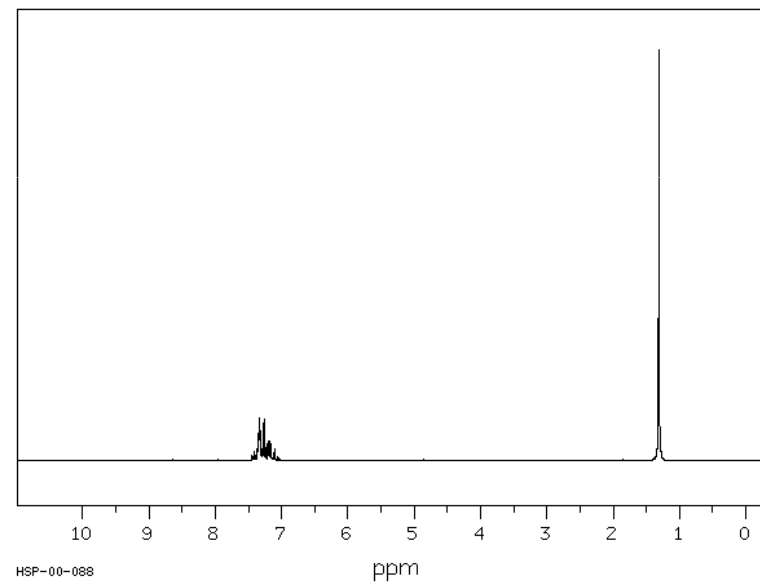
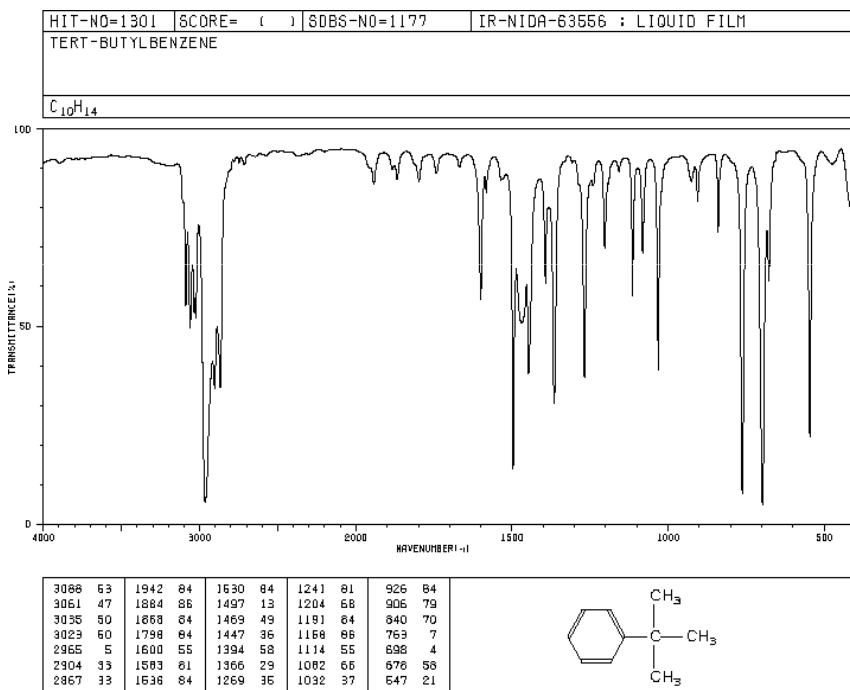


2977	4	1384	32
2930	13	1329	44
2899	12	1276	62
1926	62	1089	18
1650	26	1048	6
1464	33	880	22
1418	33		

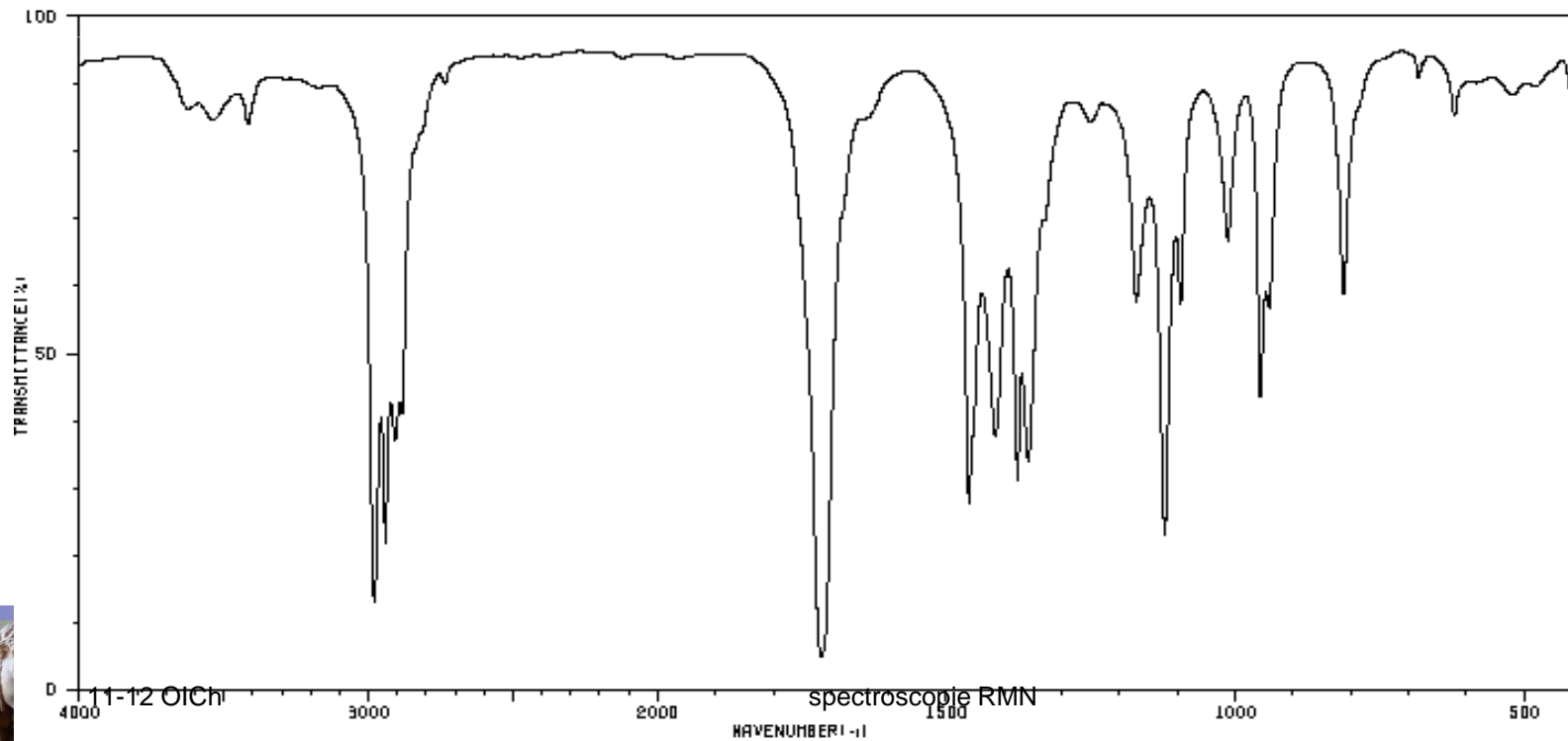
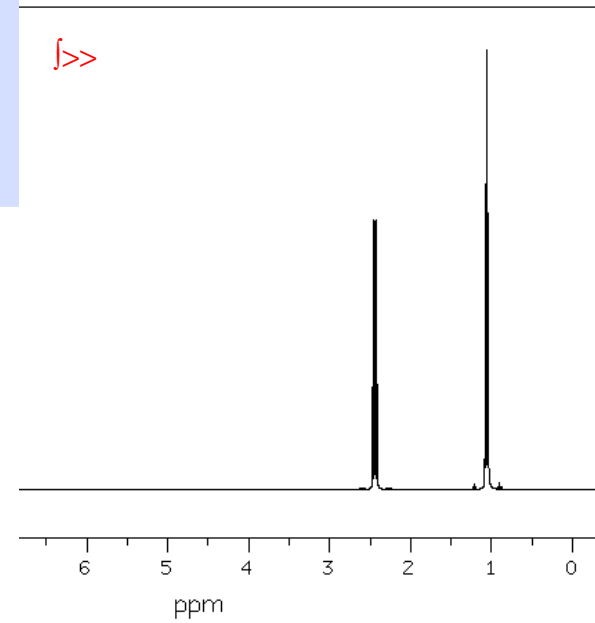
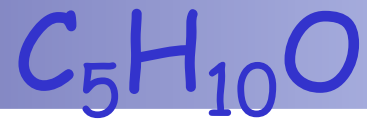


Qui suis-je ?

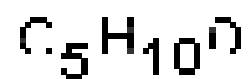




Qui suis-je ?



Courbe intégrale:



a = 4,2mm

b = 8,4mm

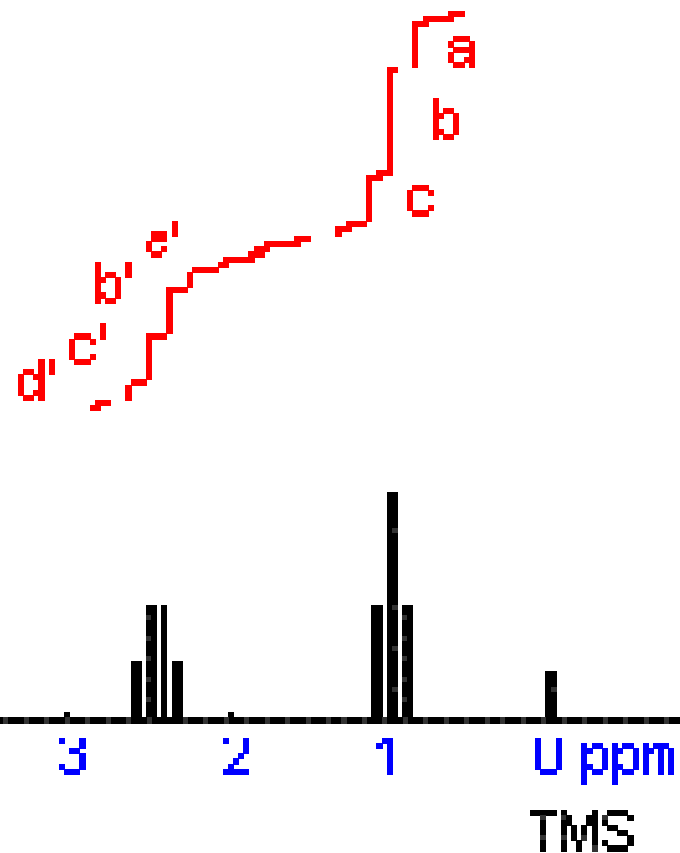
c = 4,2mm

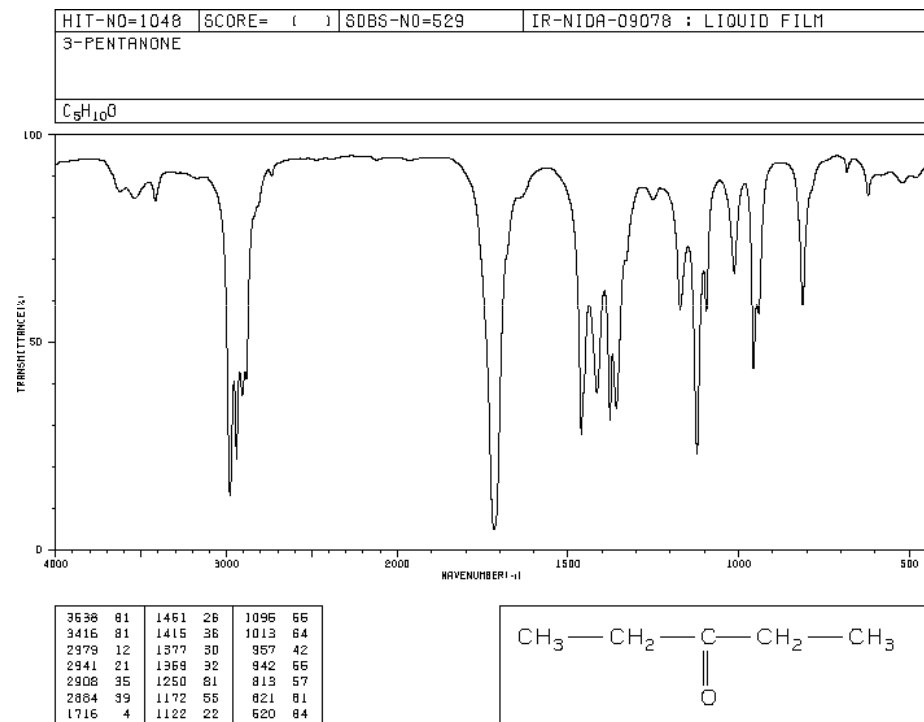
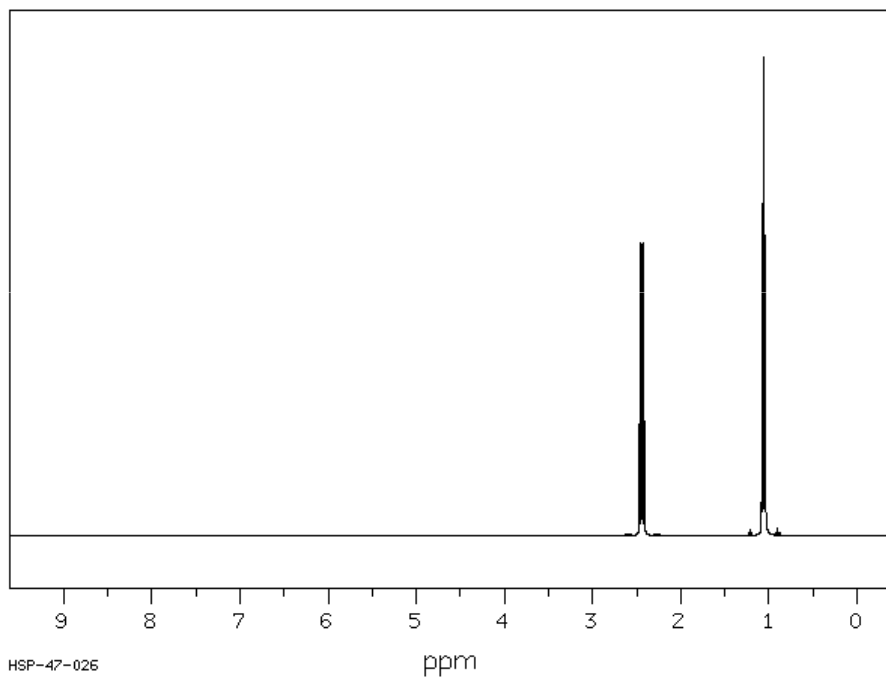
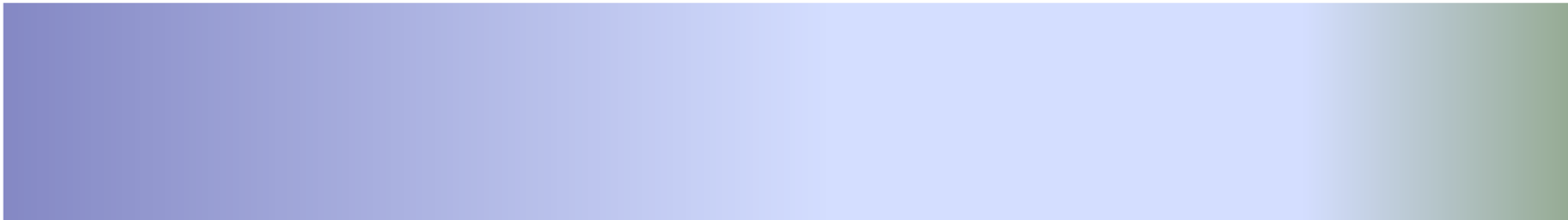
a' = 1,4mm

b' = 4,2mm

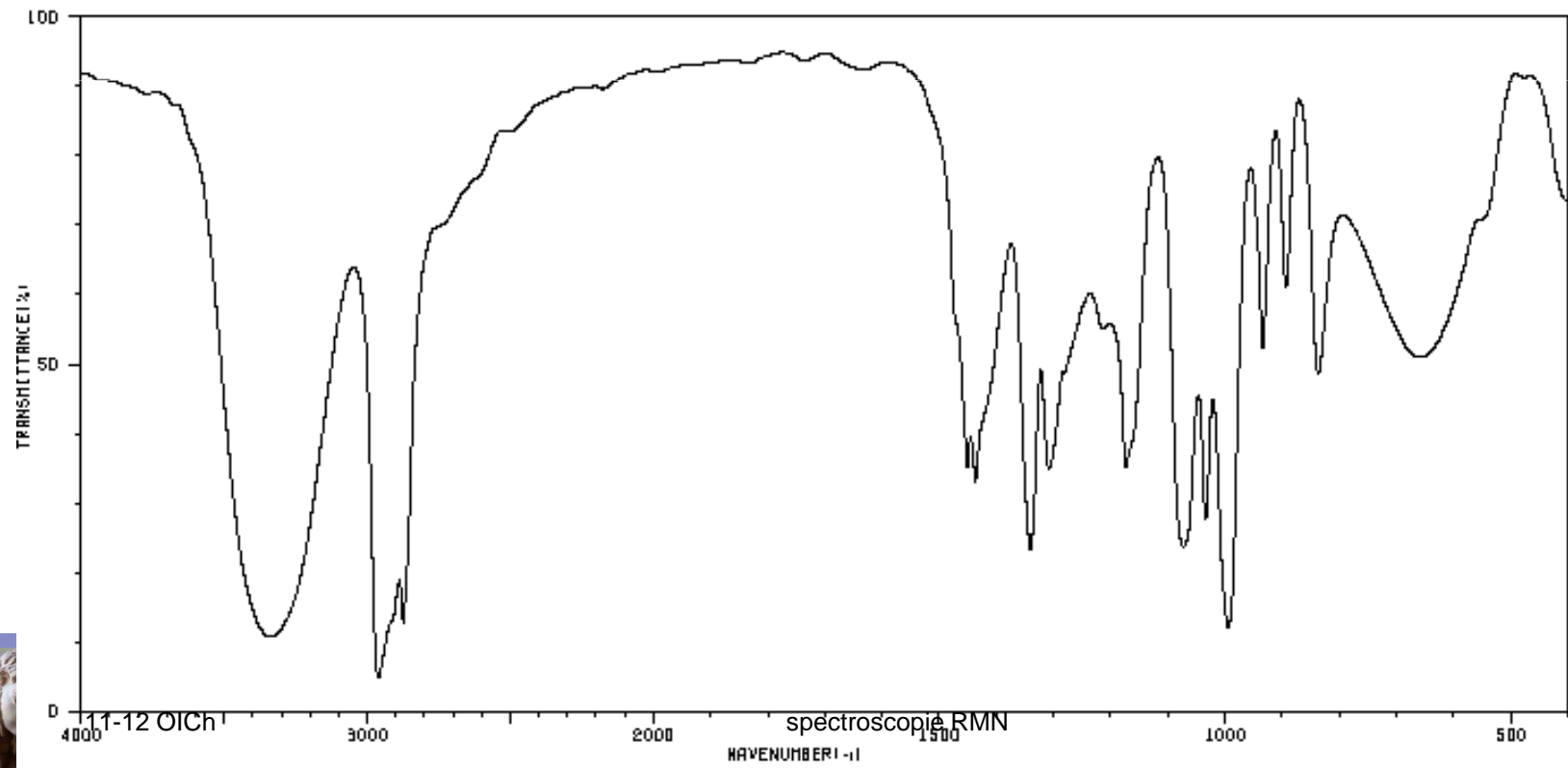
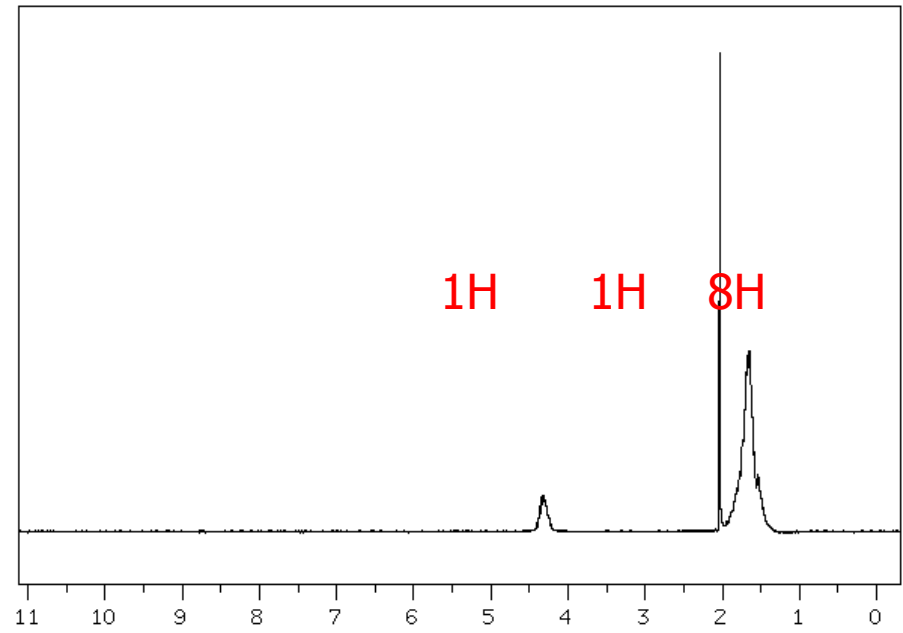
c' = 4,2mm

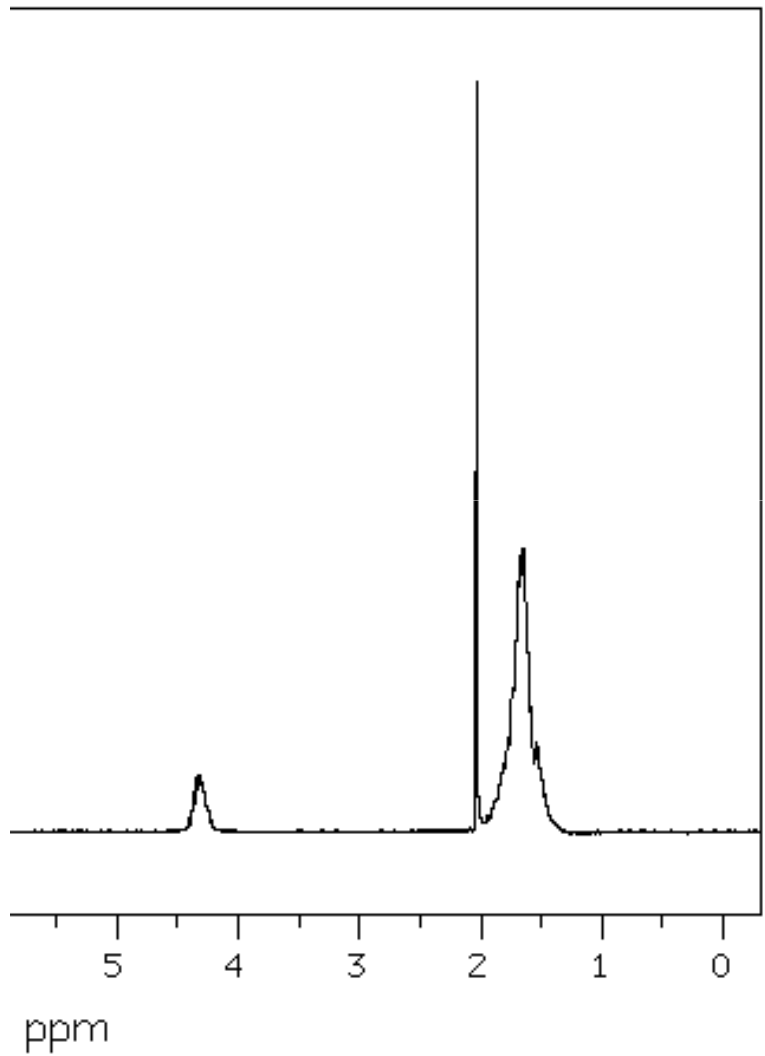
d' = 1,4mm



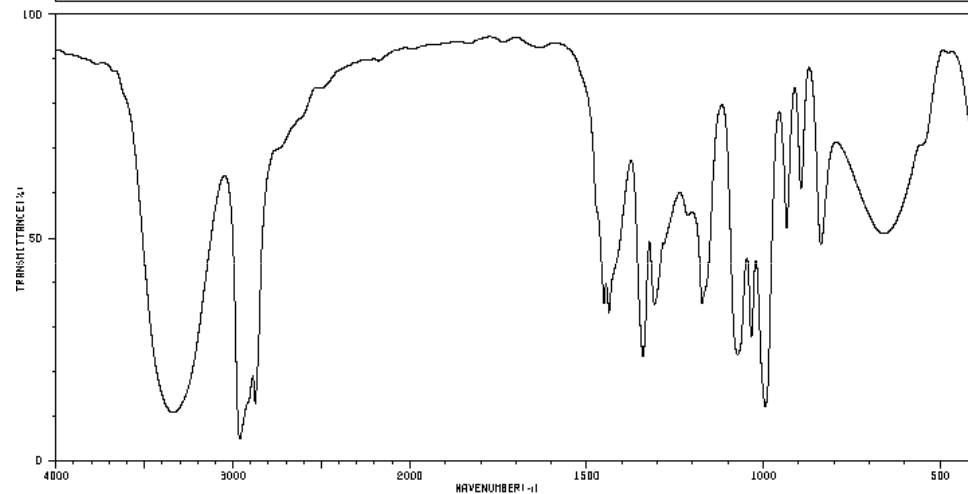


Qui suis-je ?

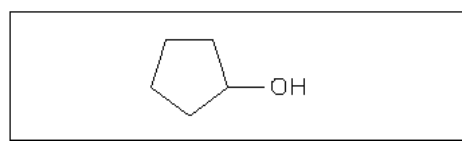




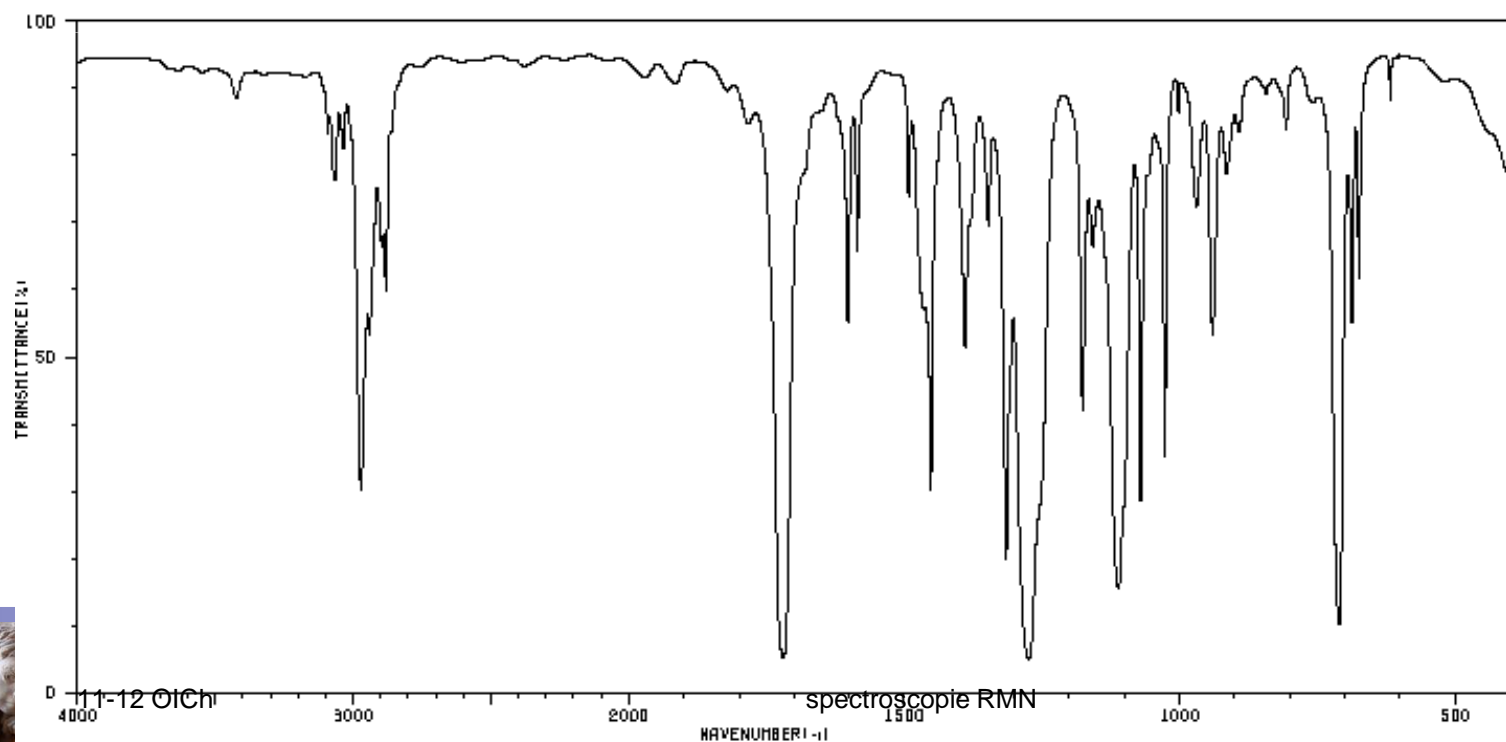
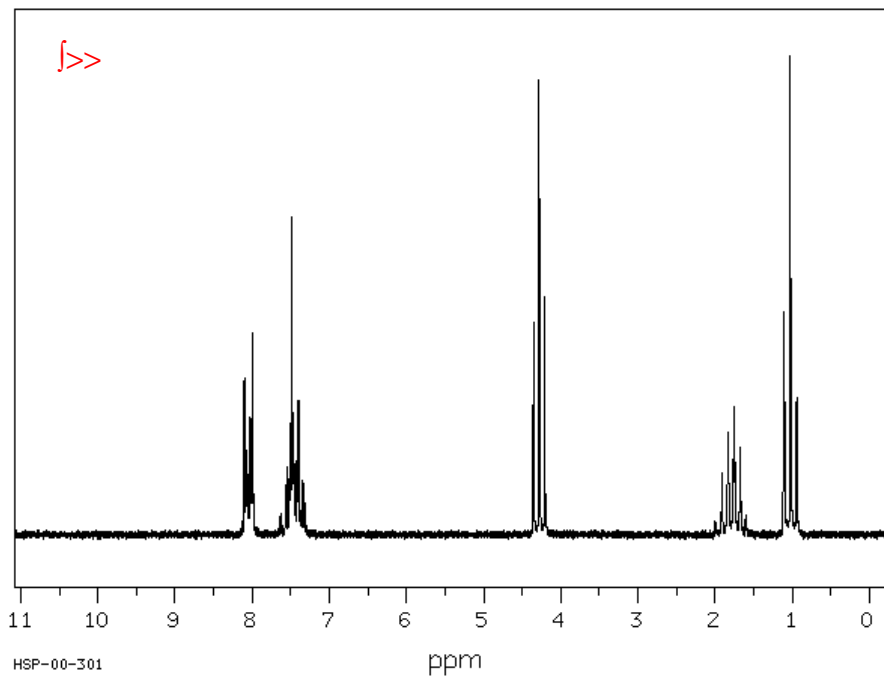
HIT-NO=4177	SCORE= ()	SOBS-NO=10527	IR-NIDA-03148 : LIQUID FILM
CYCLOPENTANOL			
C ₅ H ₁₀ O			

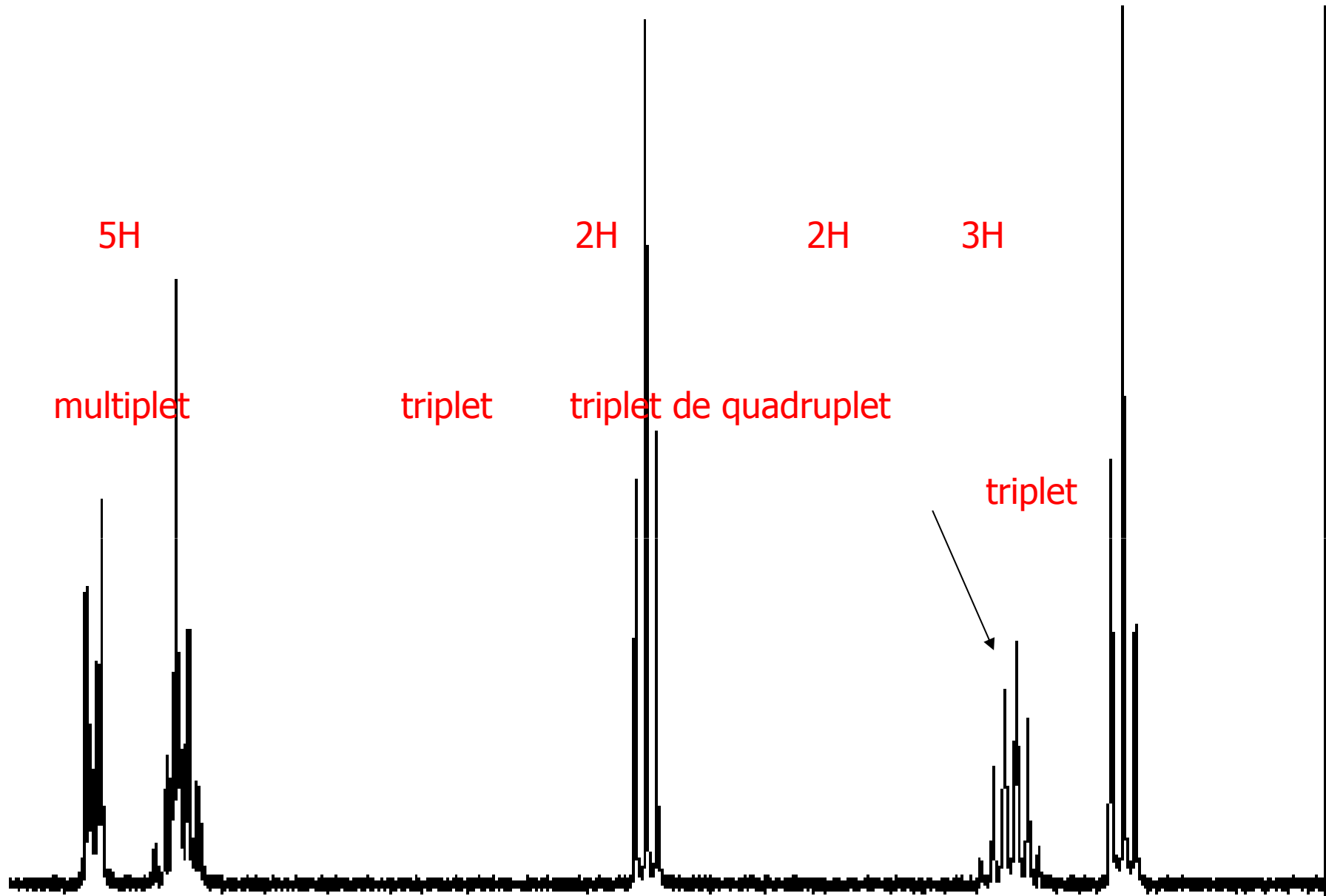


3346	10	1308	34	837	47
3335	10	1174	34	664	49
2961	4	1073	23	656	49
2879	12	1034	26		
1451	34	994	12		
1438	32	934	50		
1341	23	894	58		



Qui suis-je ?





8

11-12 OICh

7

6

5

spectroscopie RMN

4

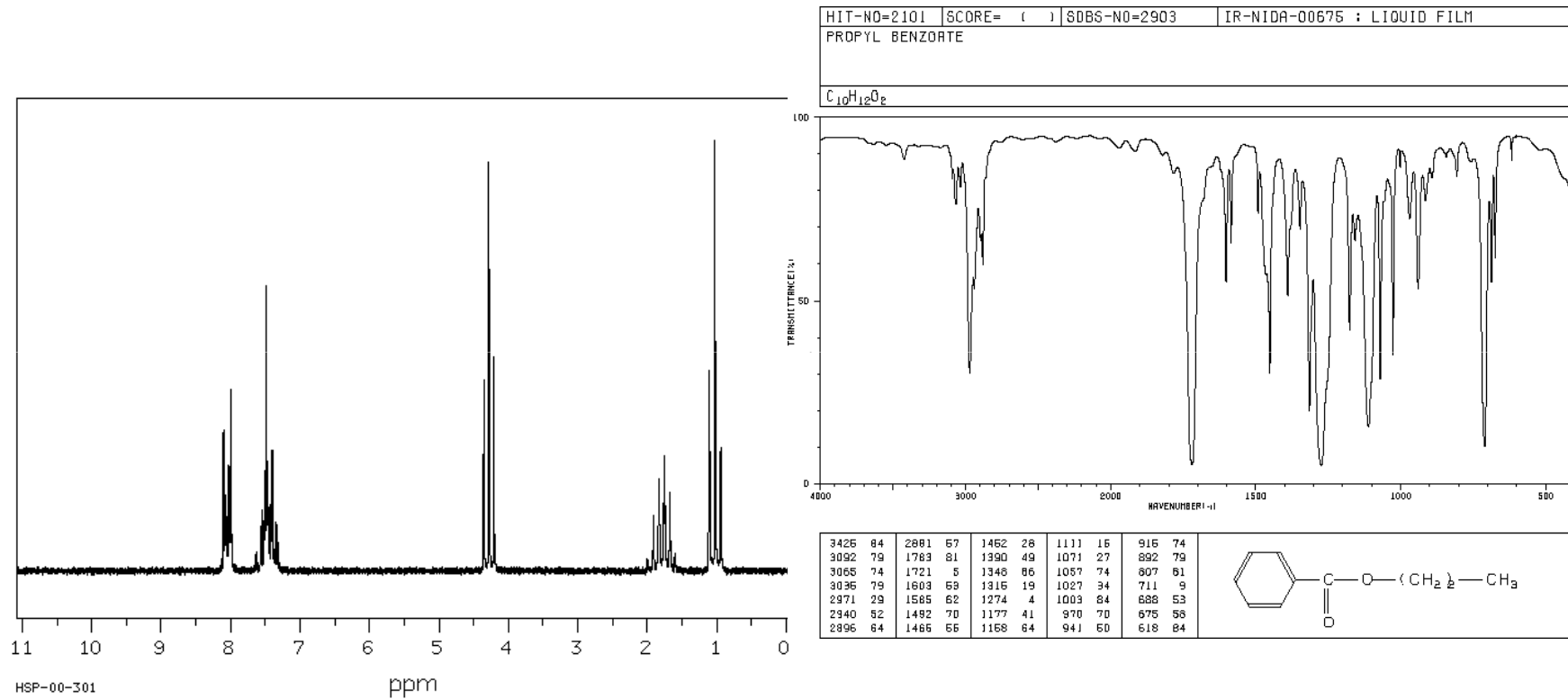
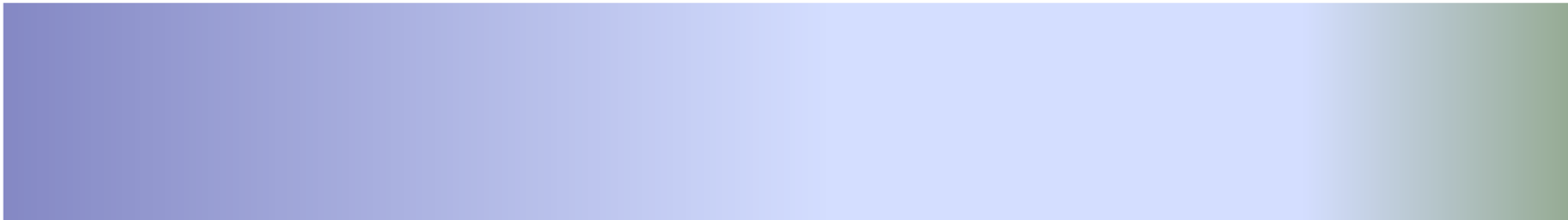
3

2

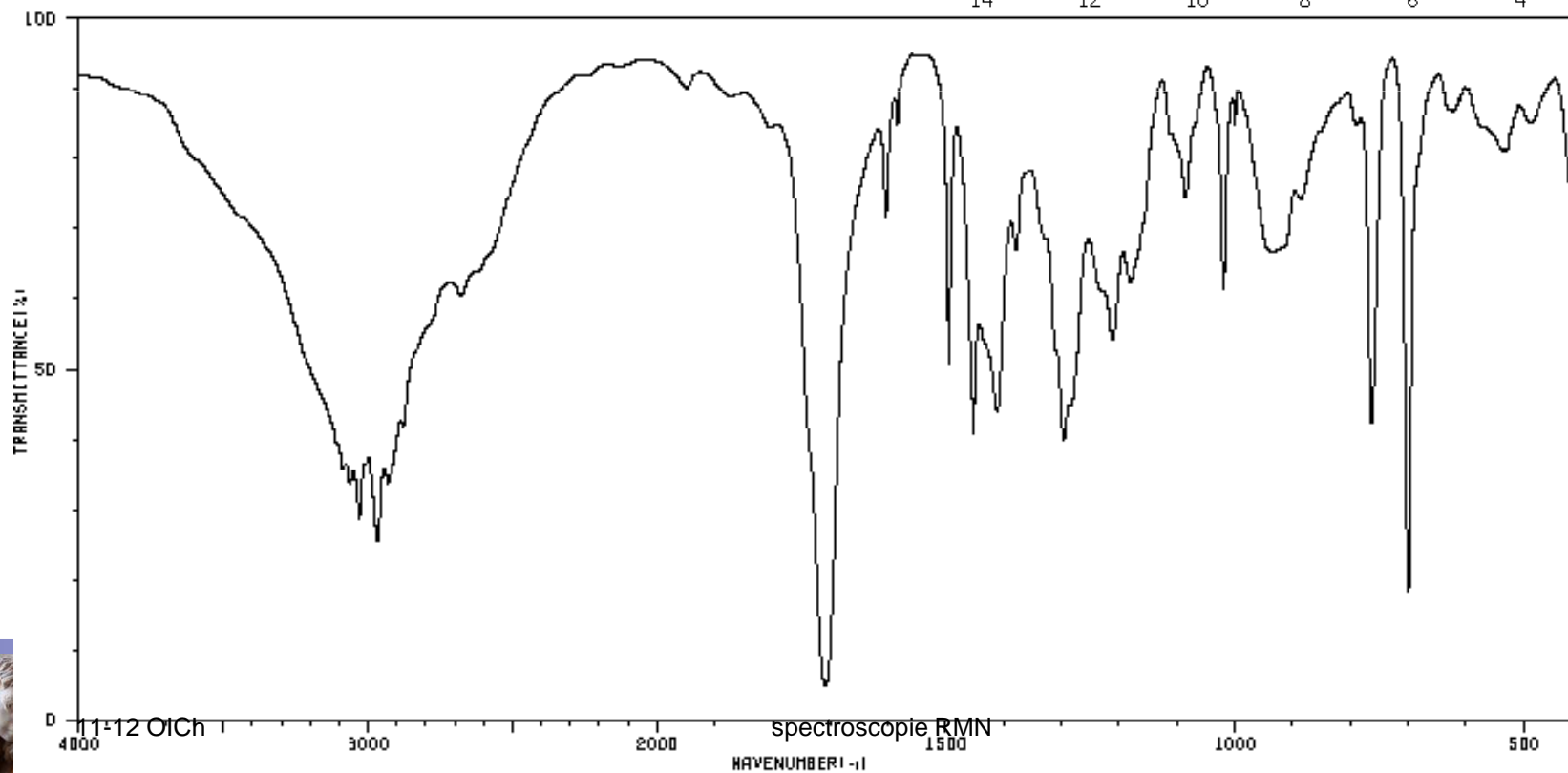
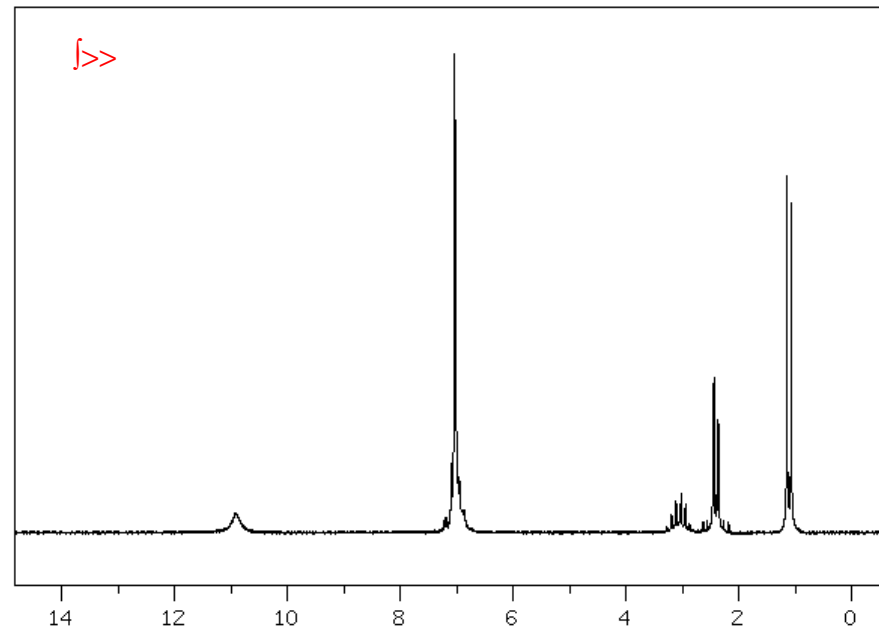
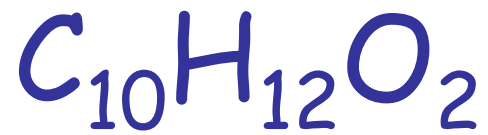
1

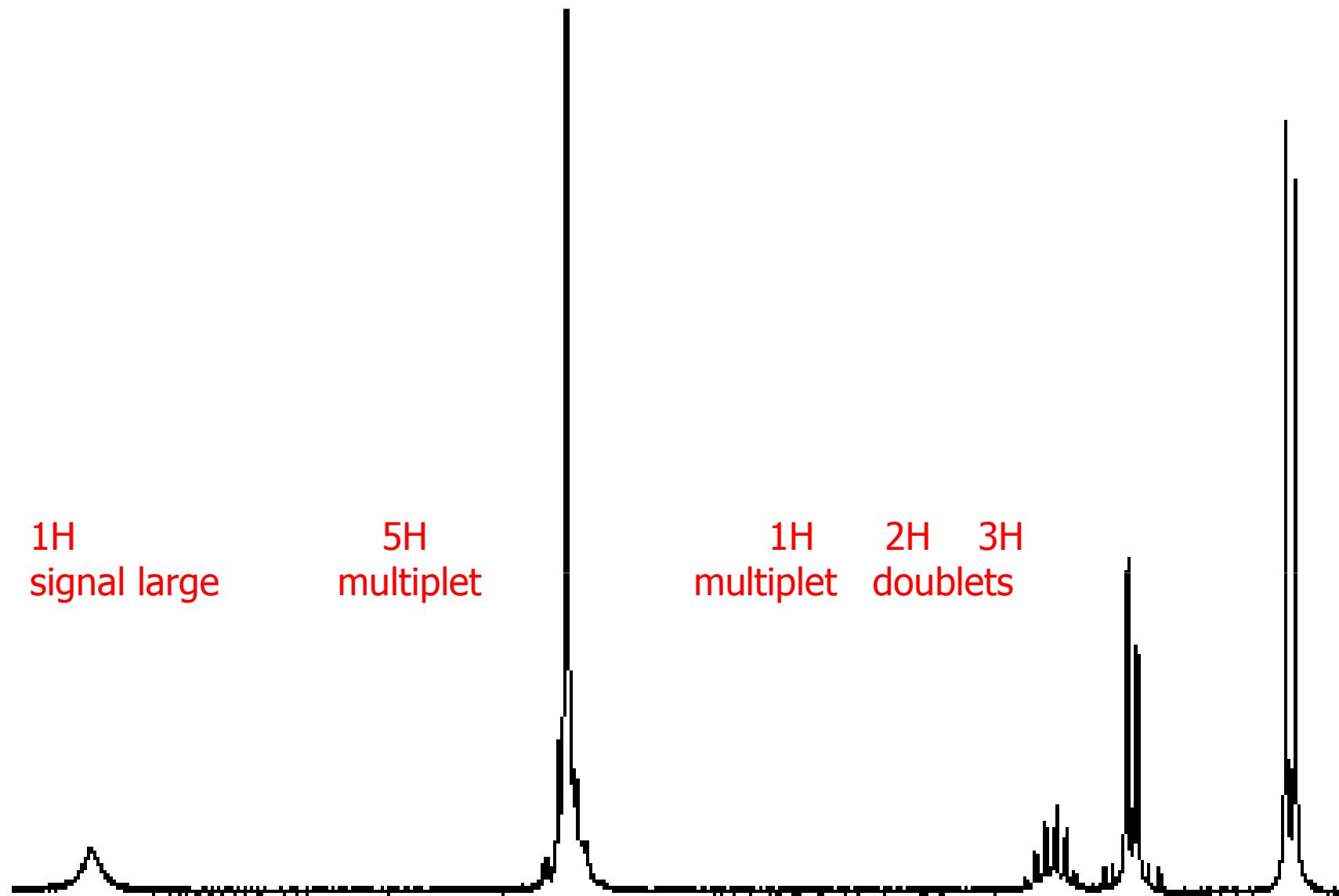
0

90



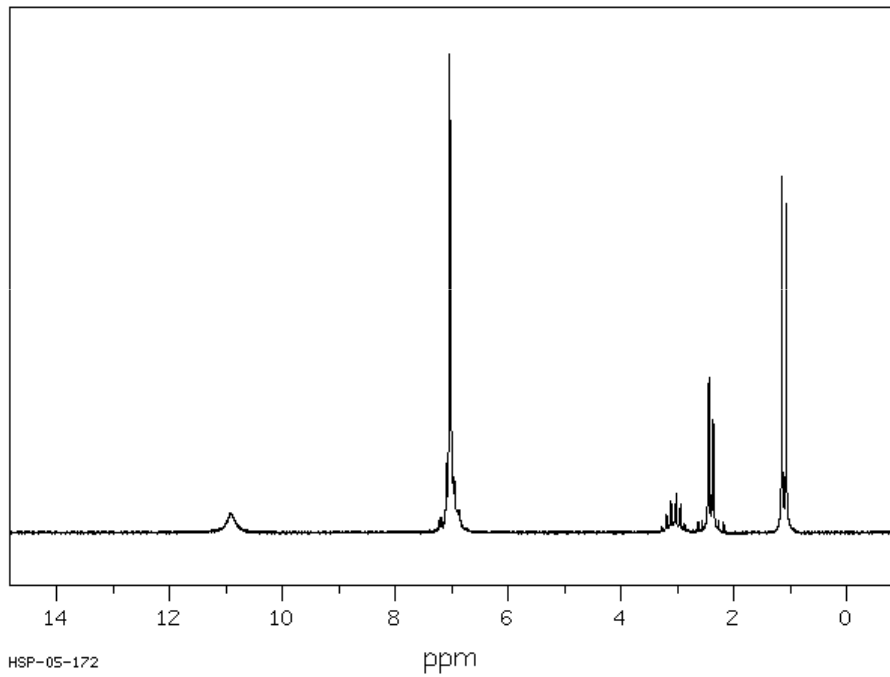
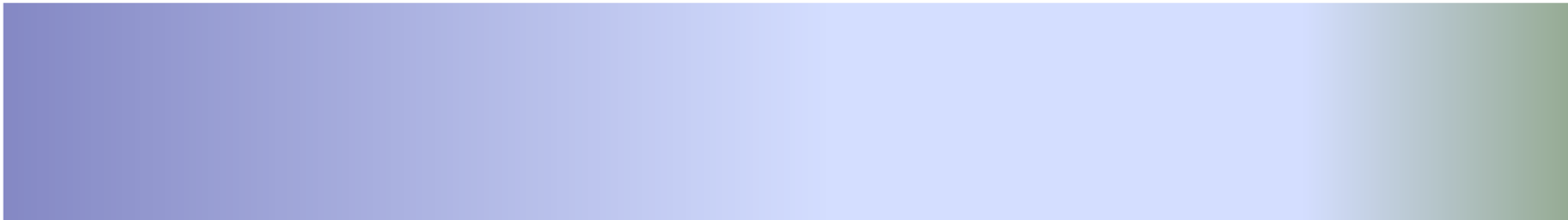
Qui suis-je ?



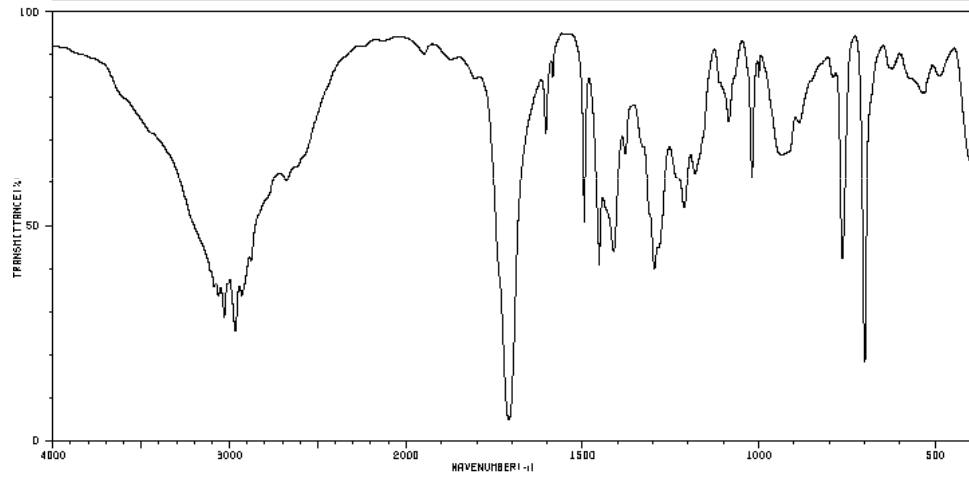


11-12 ppm spectroscopie RMN 8 6 4 2 93

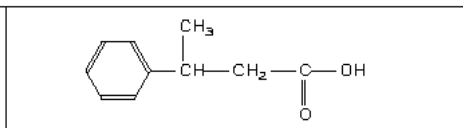




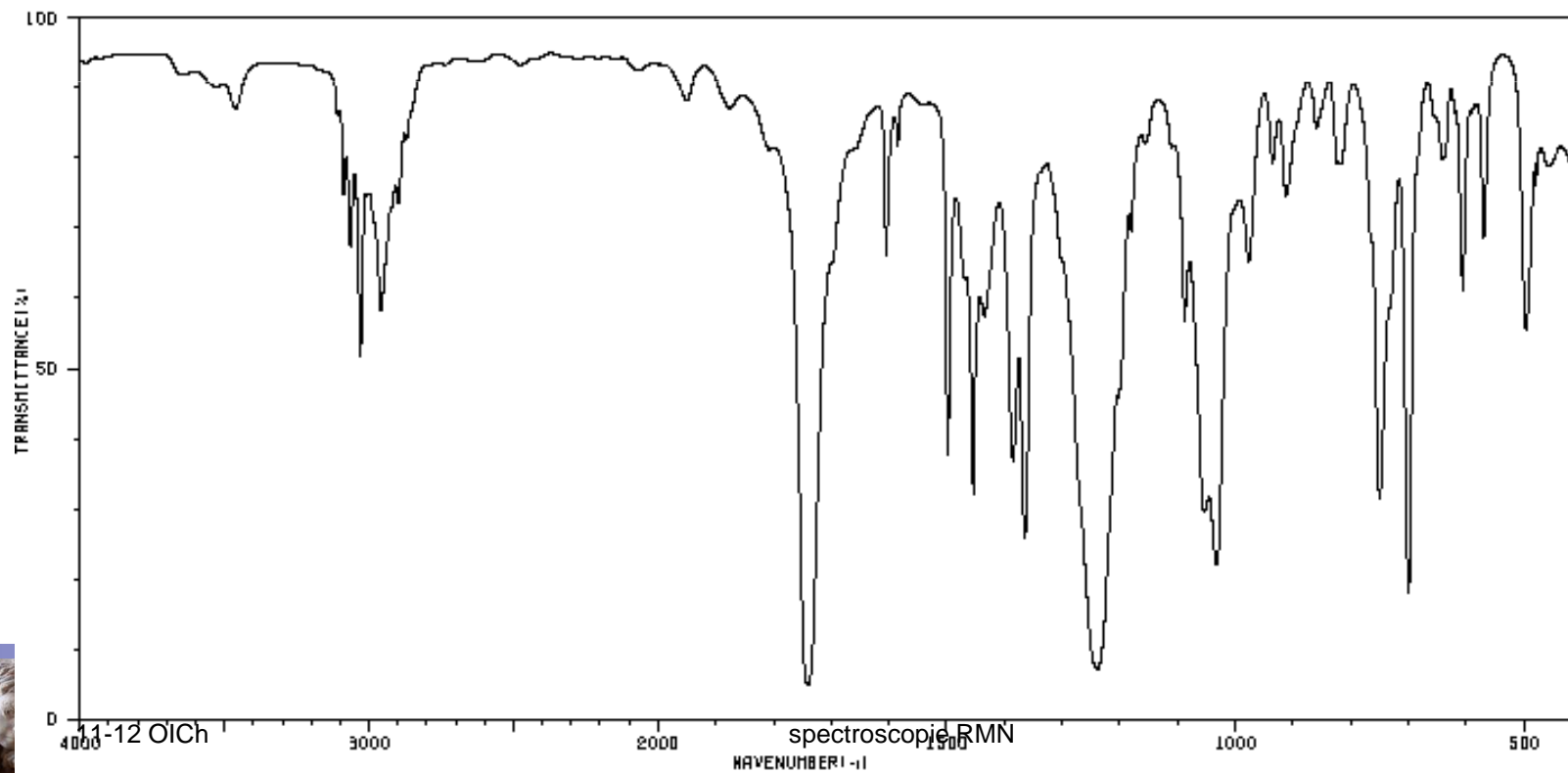
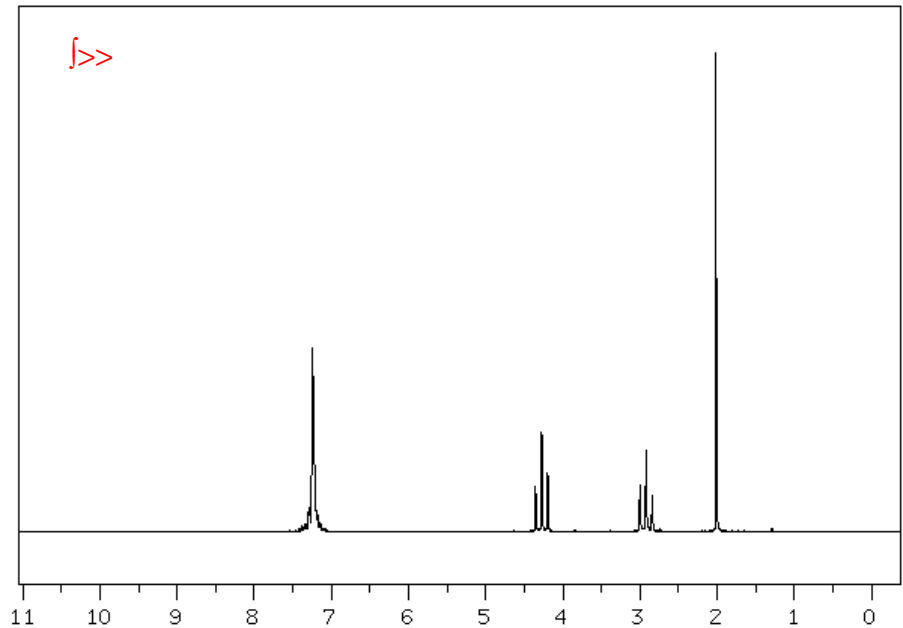
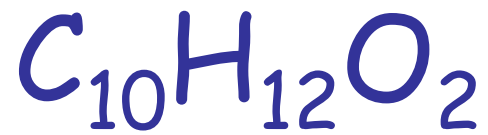
HIT-NO=861 SCORE= () SDBS-NO=137 IR-NIDA-65264 : LIQUID FILM
3-PHENYLBUTYRIC ACID
 $C_{10}H_{12}O_2$

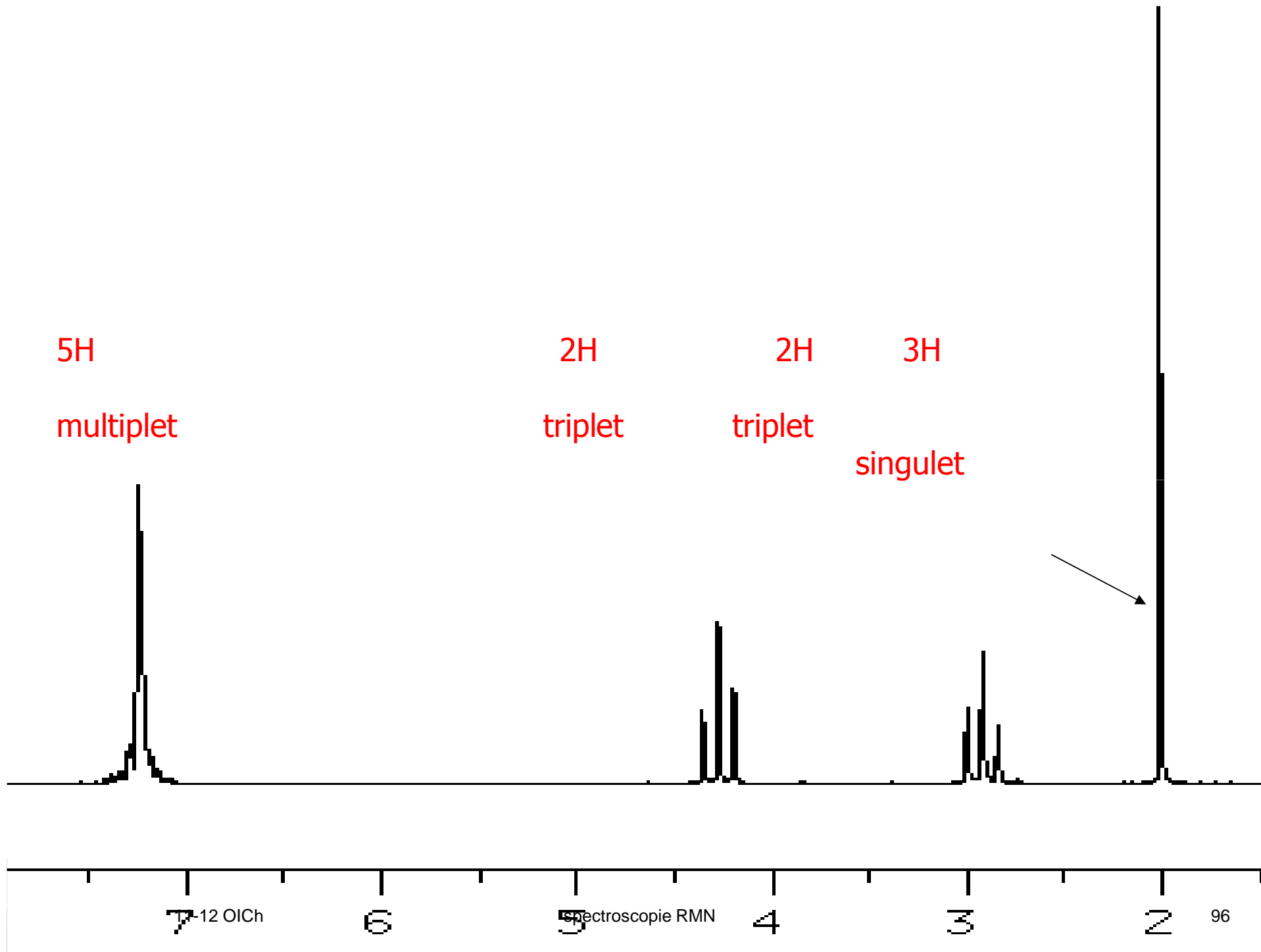


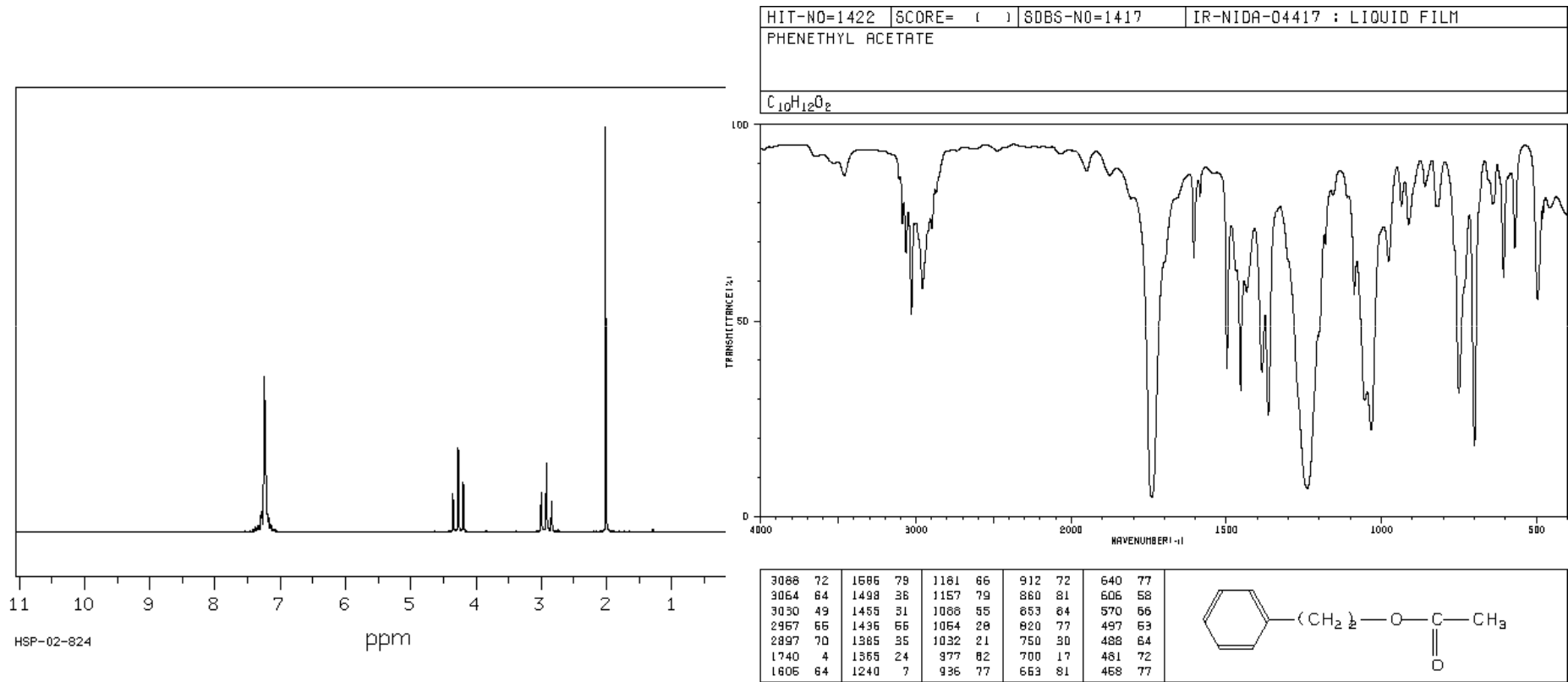
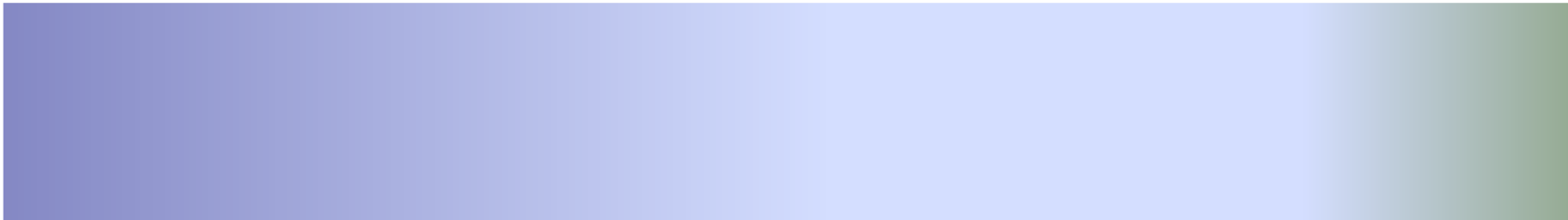
3063	32	1584	81	1212	52	924	64	533	79
3030	27	1495	49	1181	60	885	70	527	79
2367	24	1453	39	1085	72	780	61	466	51
2431	32	1411	42	1020	69	764	41		
2676	58	1379	64	1000	81	700	17		
1706	4	1297	38	936	84	629	64		
1604	68	1284	43	929	64	623	84		



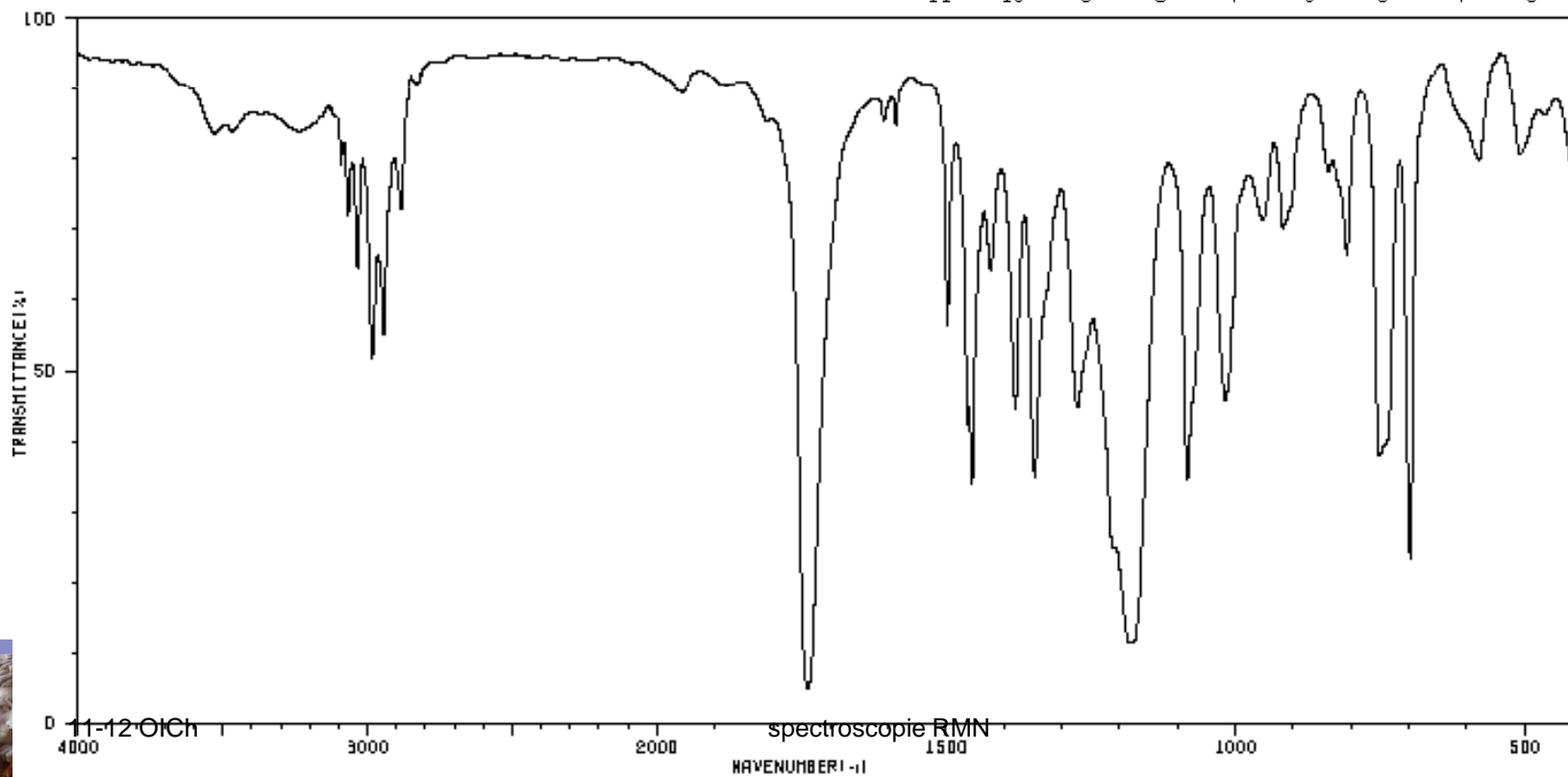
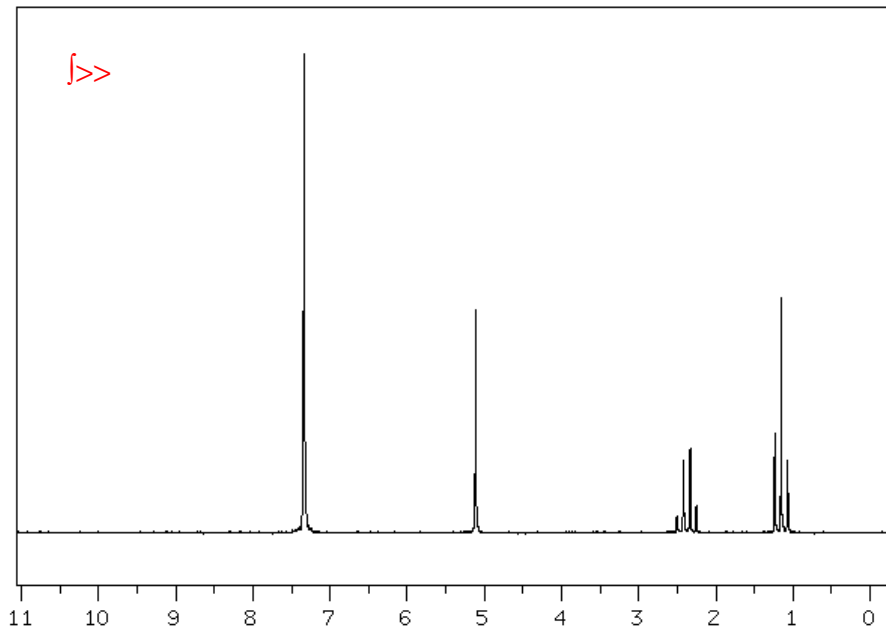
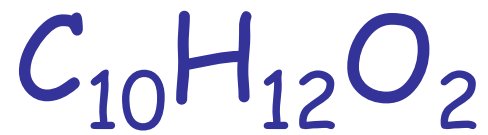
Qui suis-je ?

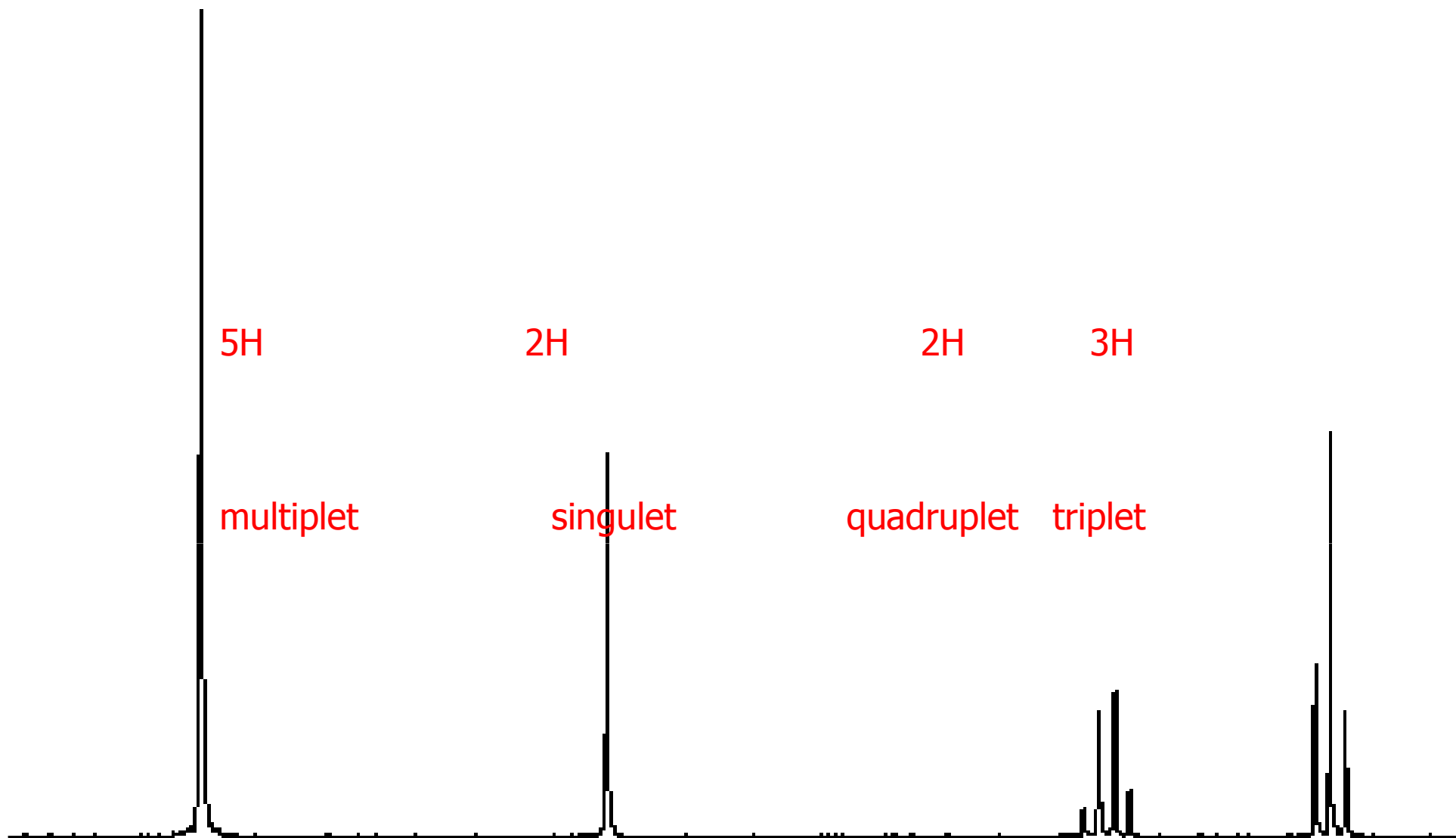






Qui suis-je ?





8

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3

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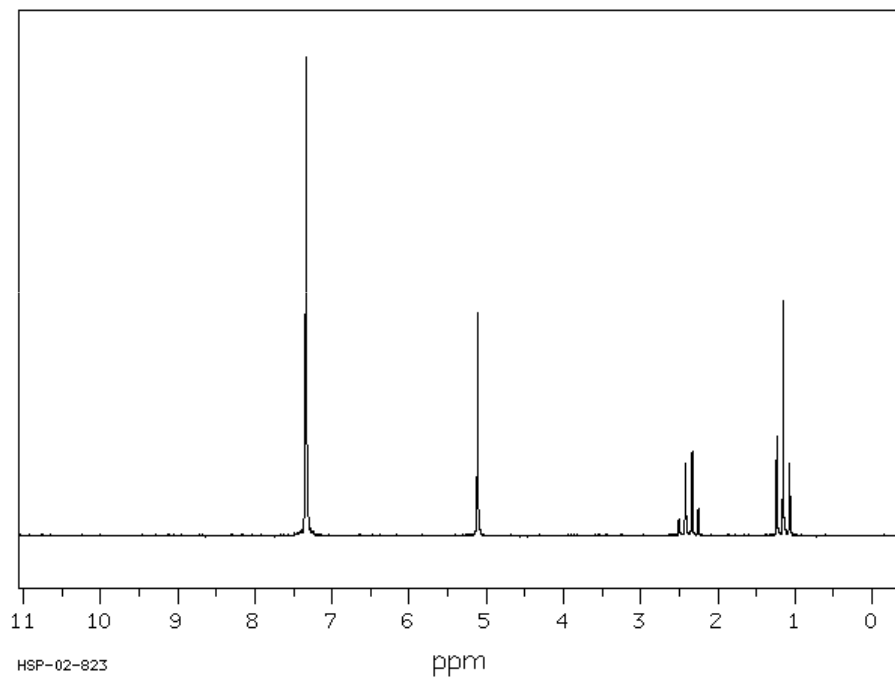
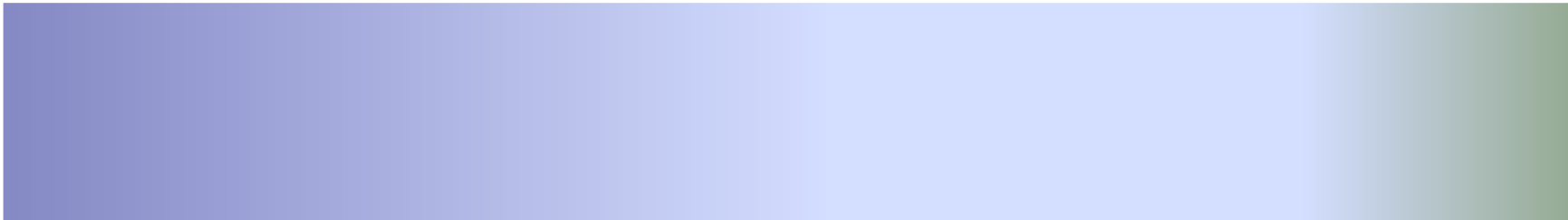
1

11-12 OICh

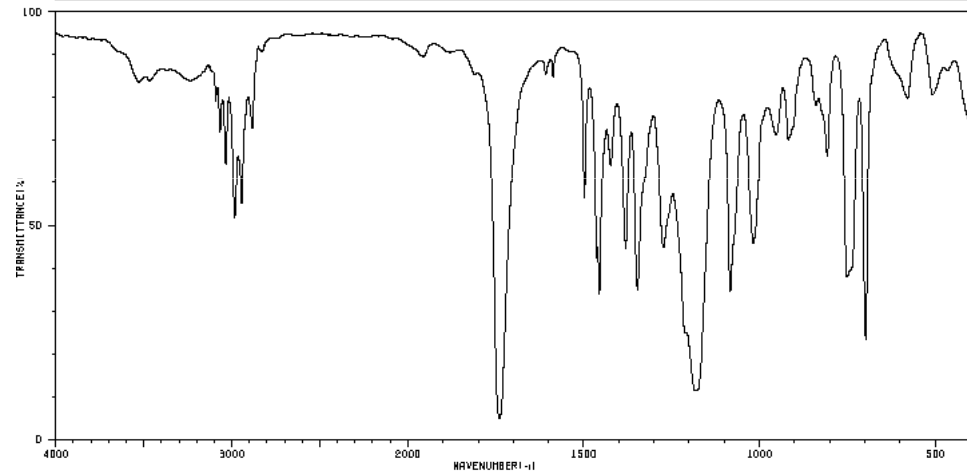
ppm

spectroscopie RMN

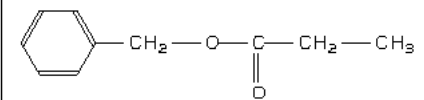
99



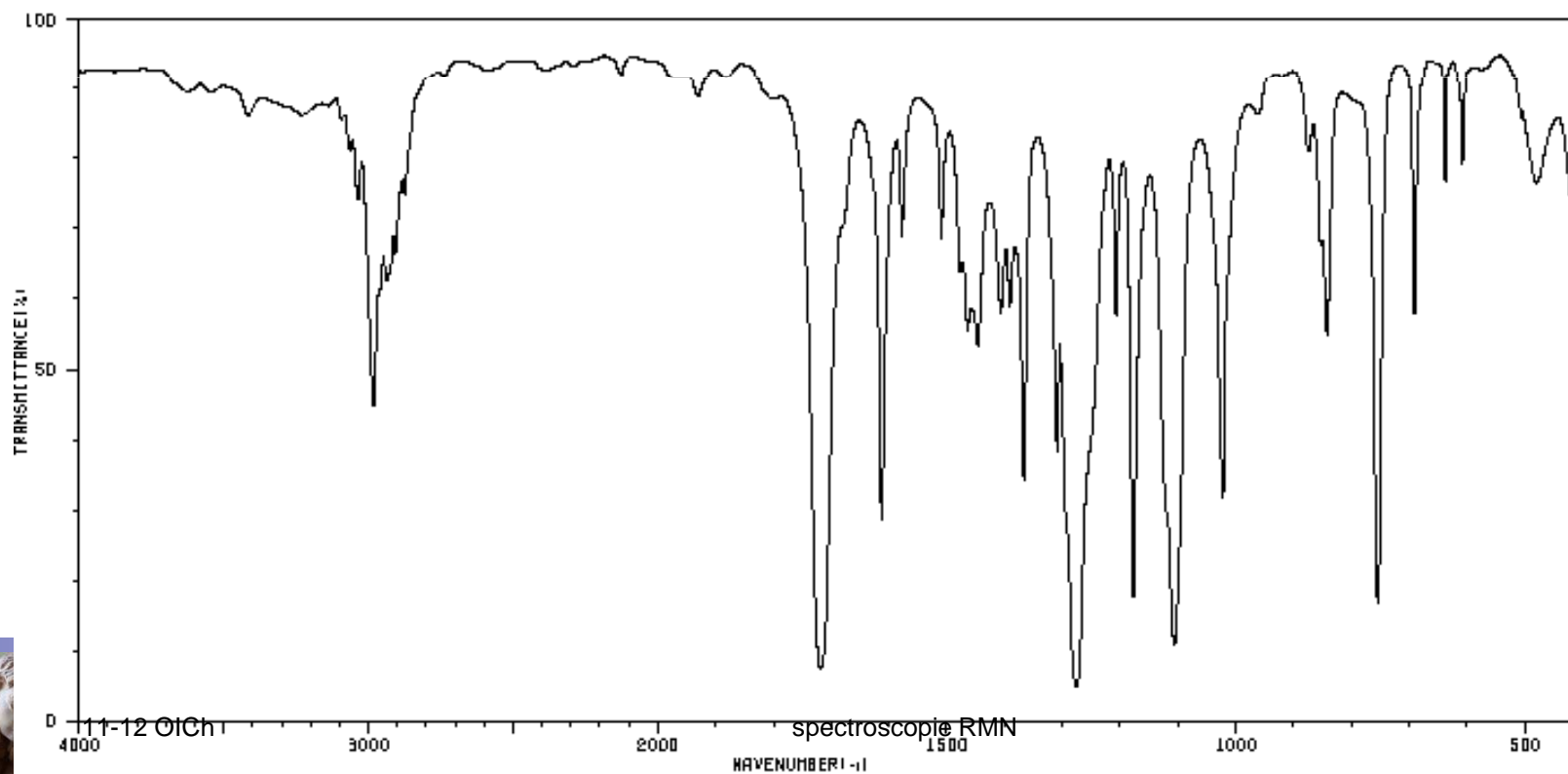
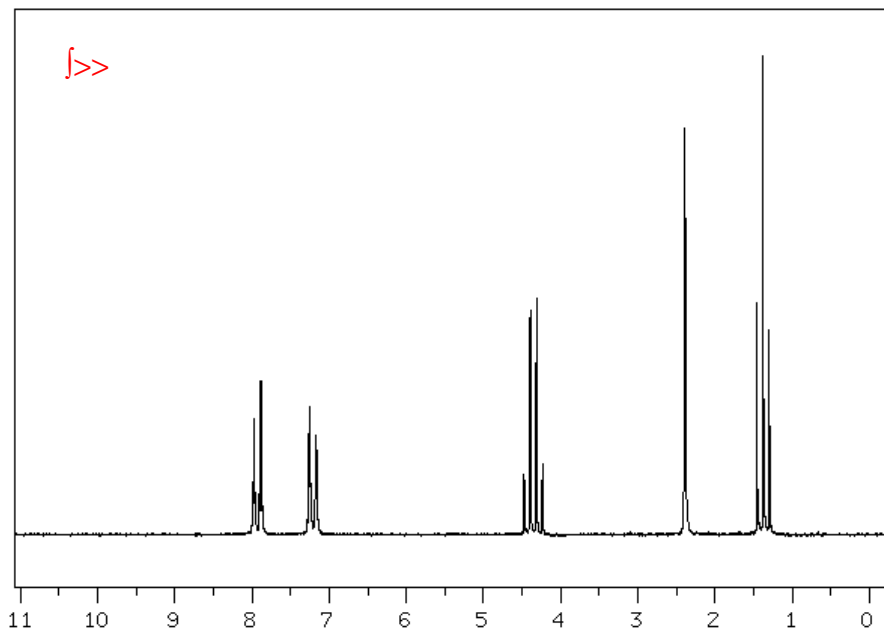
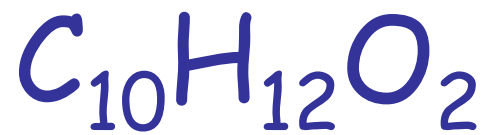
HIT-NO=1523 SCORE= () SDBS-NO=1712 IR-NIDA-67240 : LIQUID FILM
BENZYL PROPIONATE
 $C_{10}H_{12}O_2$

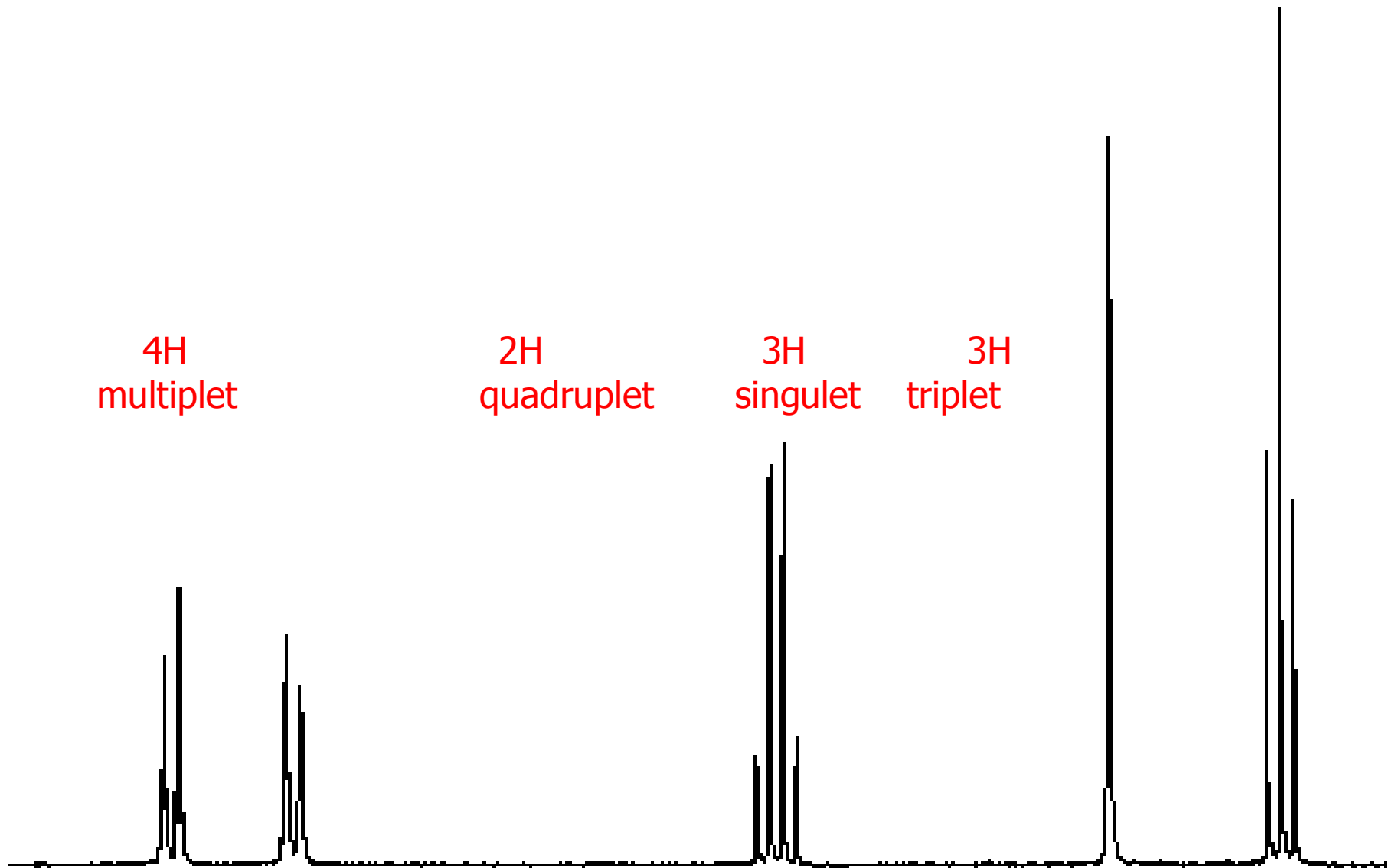


3626	81	2884	70	1456	32	1176	10	808	64
3236	81	1957	88	1423	62	1083	33	751	36
3090	77	1740	4	1381	45	1017	45	745	37
3067	70	1608	81	1348	33	953	68	739	38
3034	62	1588	81	1274	43	918	68	698	22
2983	49	1498	59	1267	47	912	68	580	77
2944	53	1463	41	1184	10	840	74	608	77



Qui suis-je ?



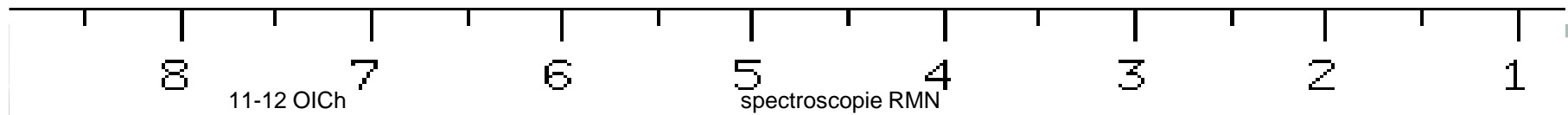


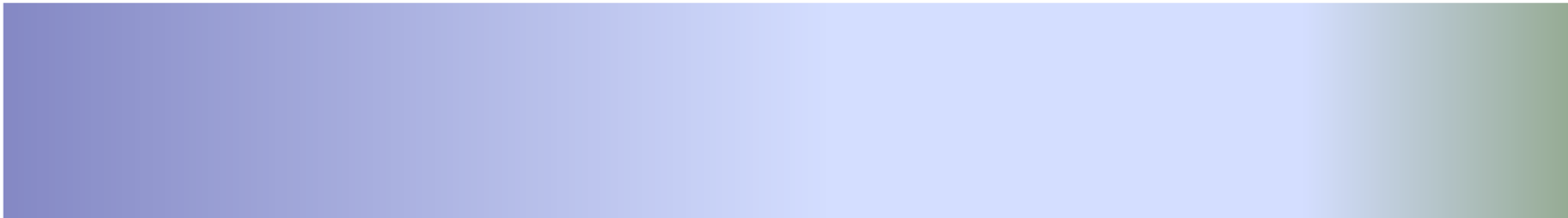
4H
multiplet

2H
quadruplet

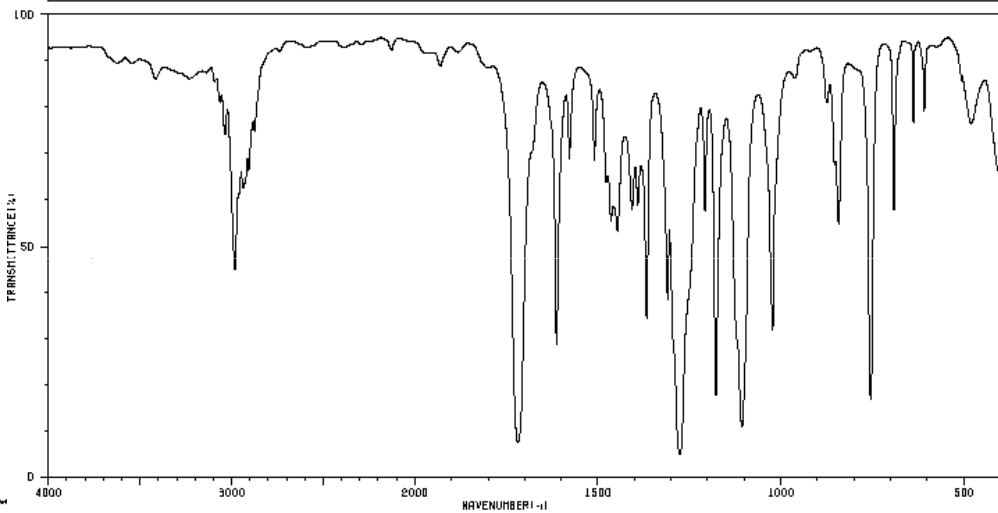
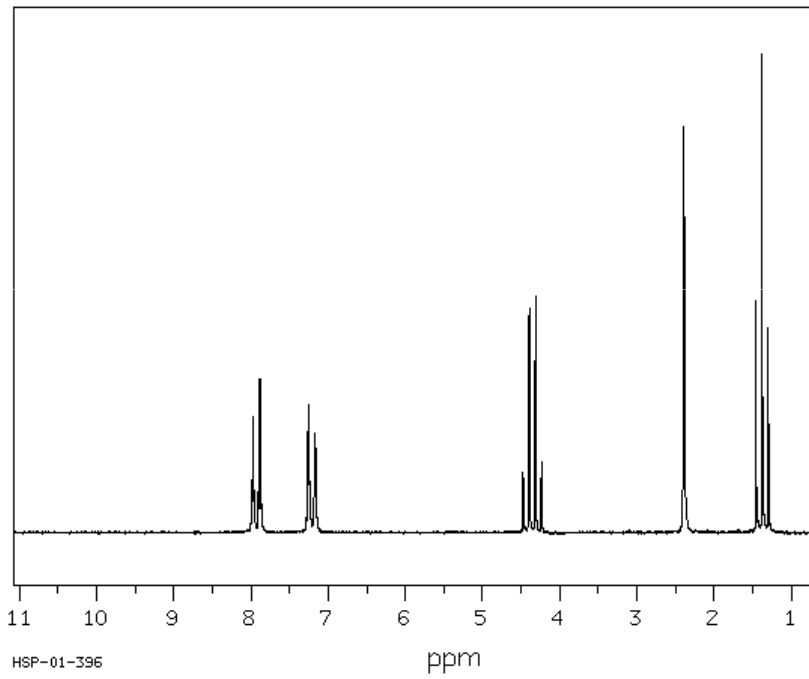
3H
singlet

3H
triplet

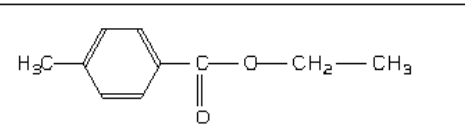




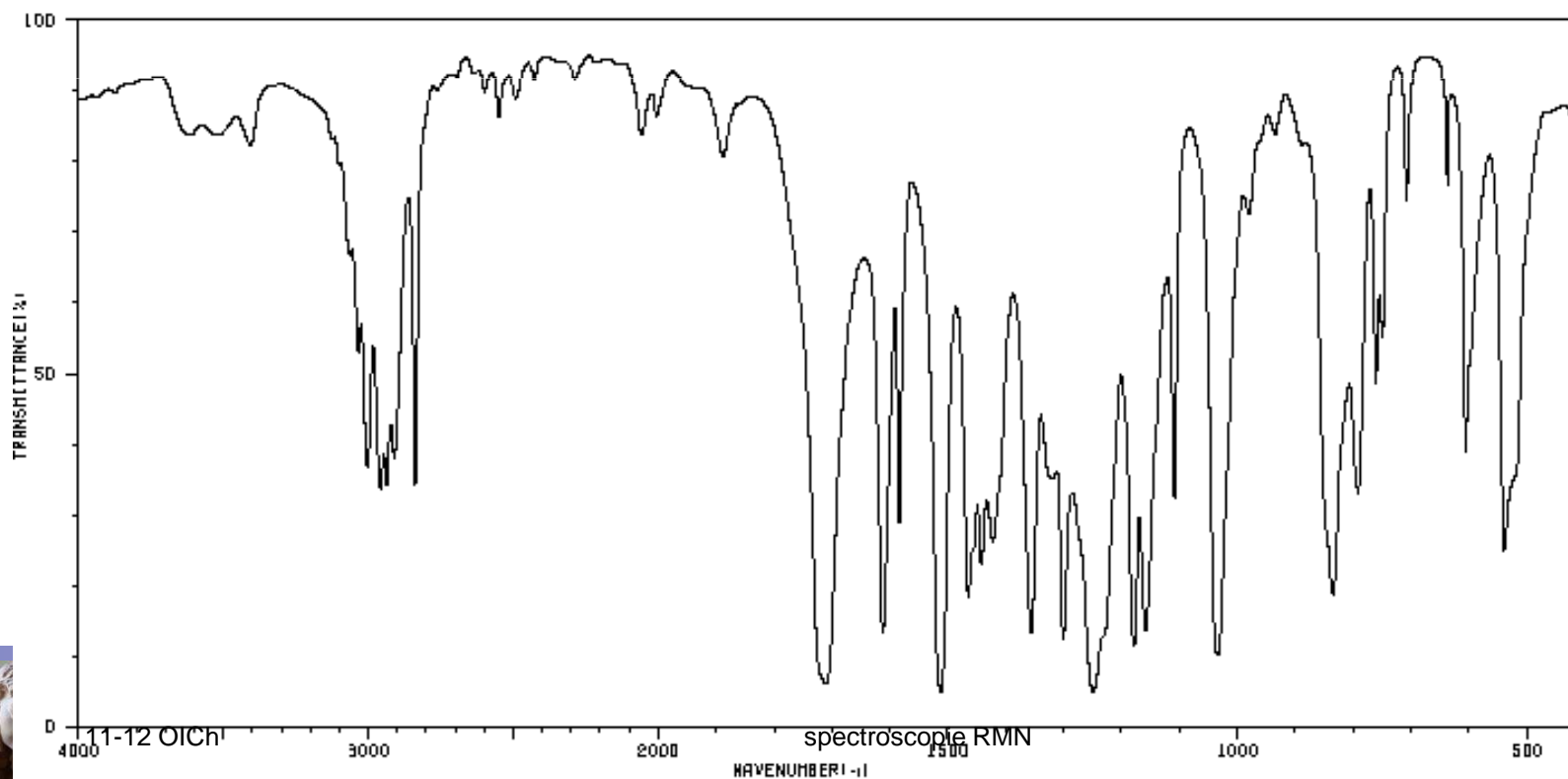
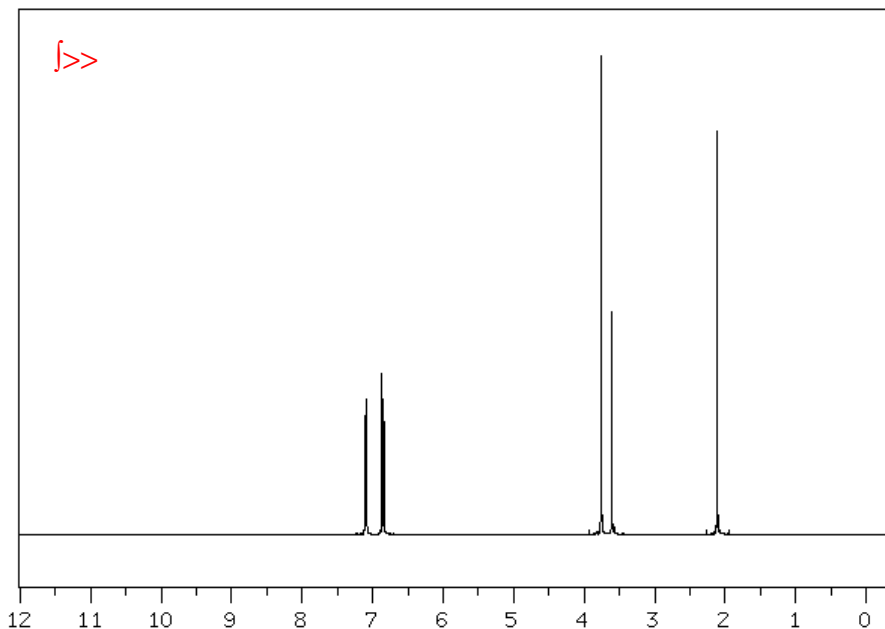
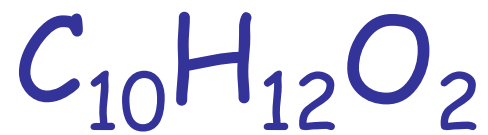
HIT-NO=1855 | SCORE= () | SDBS-NO=2369 | IR-NIDA-63549 : LIQUID FILM
ETHYL P-TOLUATE
C₁₀H₁₂O₂

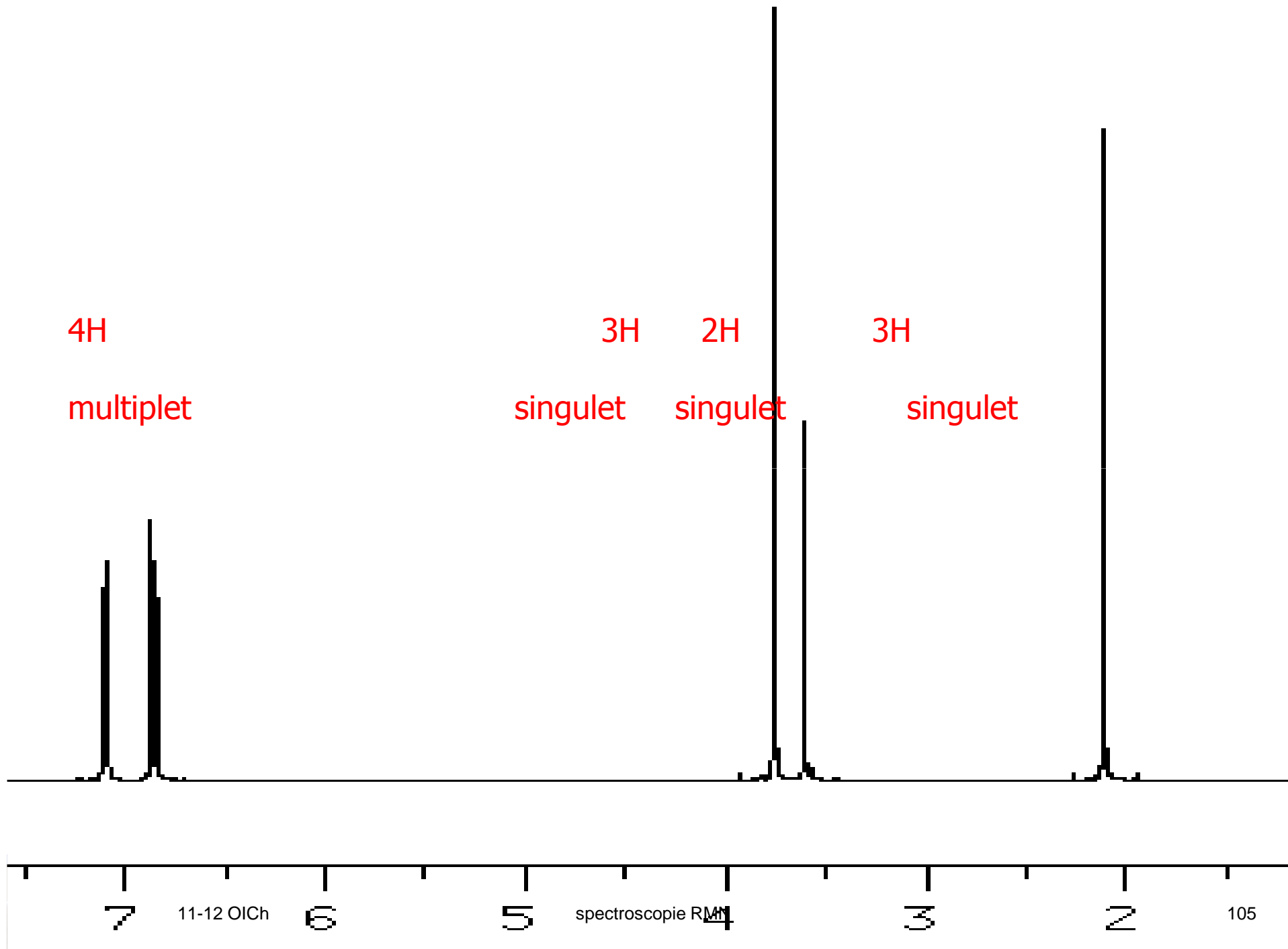


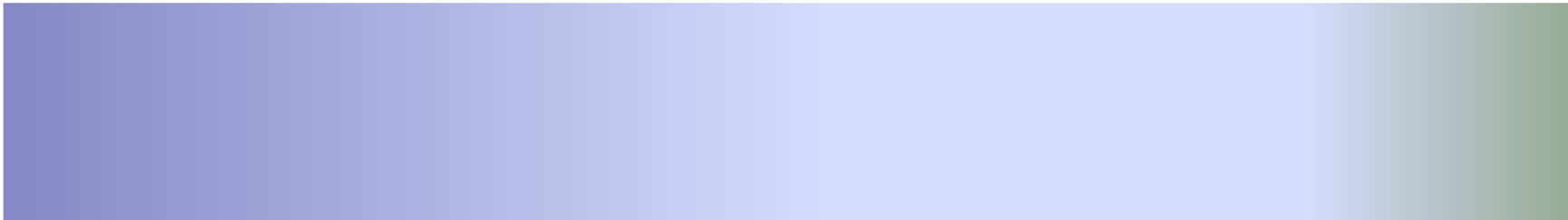
3417	81	2907	64	1464	63	1276	4	863	66
3228	84	2874	72	1458	57	1208	55	842	52
3064	77	1718	7	1447	50	1178	17	755	16
3036	72	1613	27	1407	65	1107	10	692	65
2982	43	1578	66	1391	57	1022	30	638	74
2961	56	1510	65	1357	33	962	84	606	77
2936	60	1478	62	1310	36	874	77	480	74



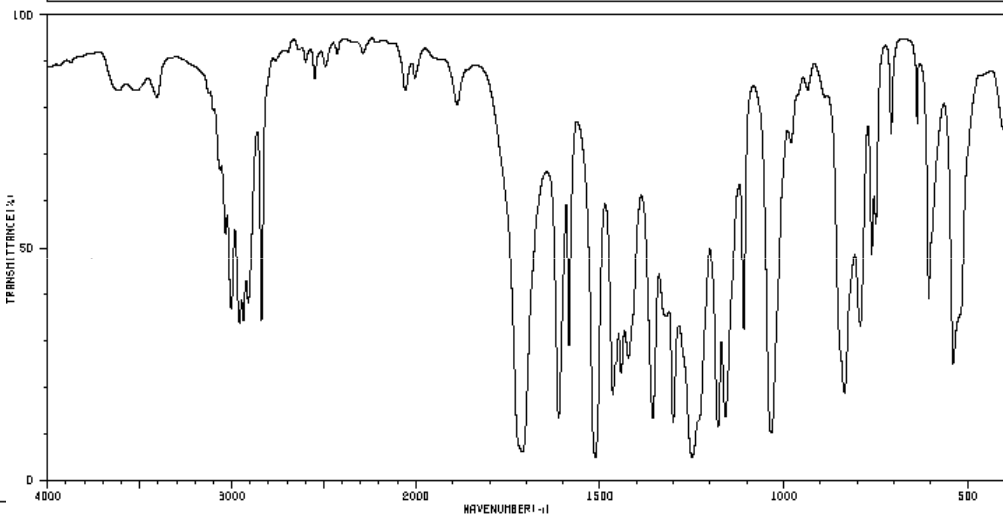
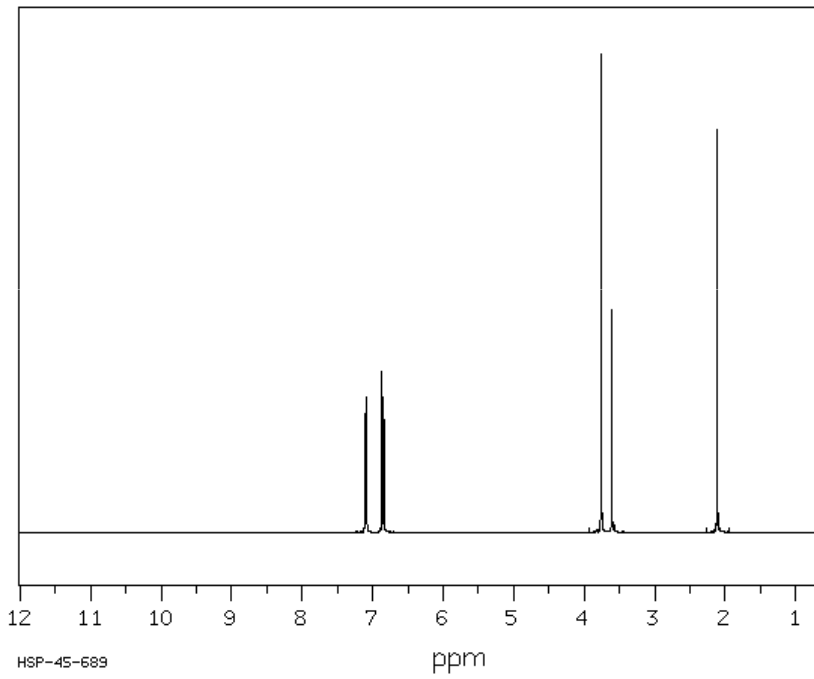
Qui suis-je ?



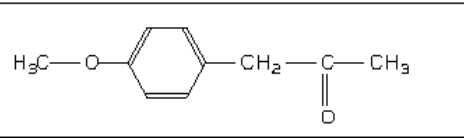




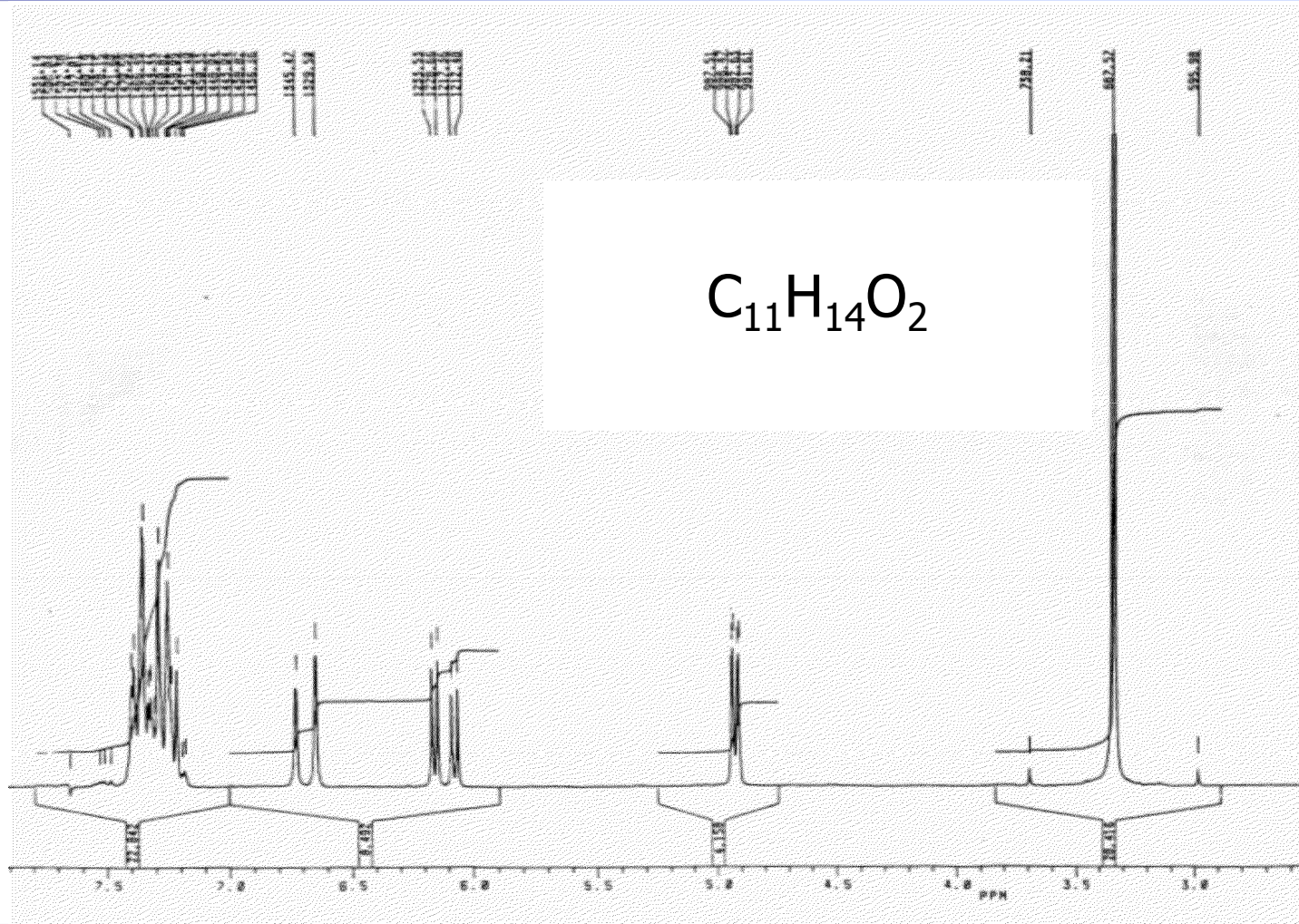
HIT-NO=3127 SCORE= () SDBS-NO=5806 IR-NIDA-09227 : LIQUID FILM
(P-METHOXYPHENYL) ACETONE
 $C_{10}H_{12}O_2$



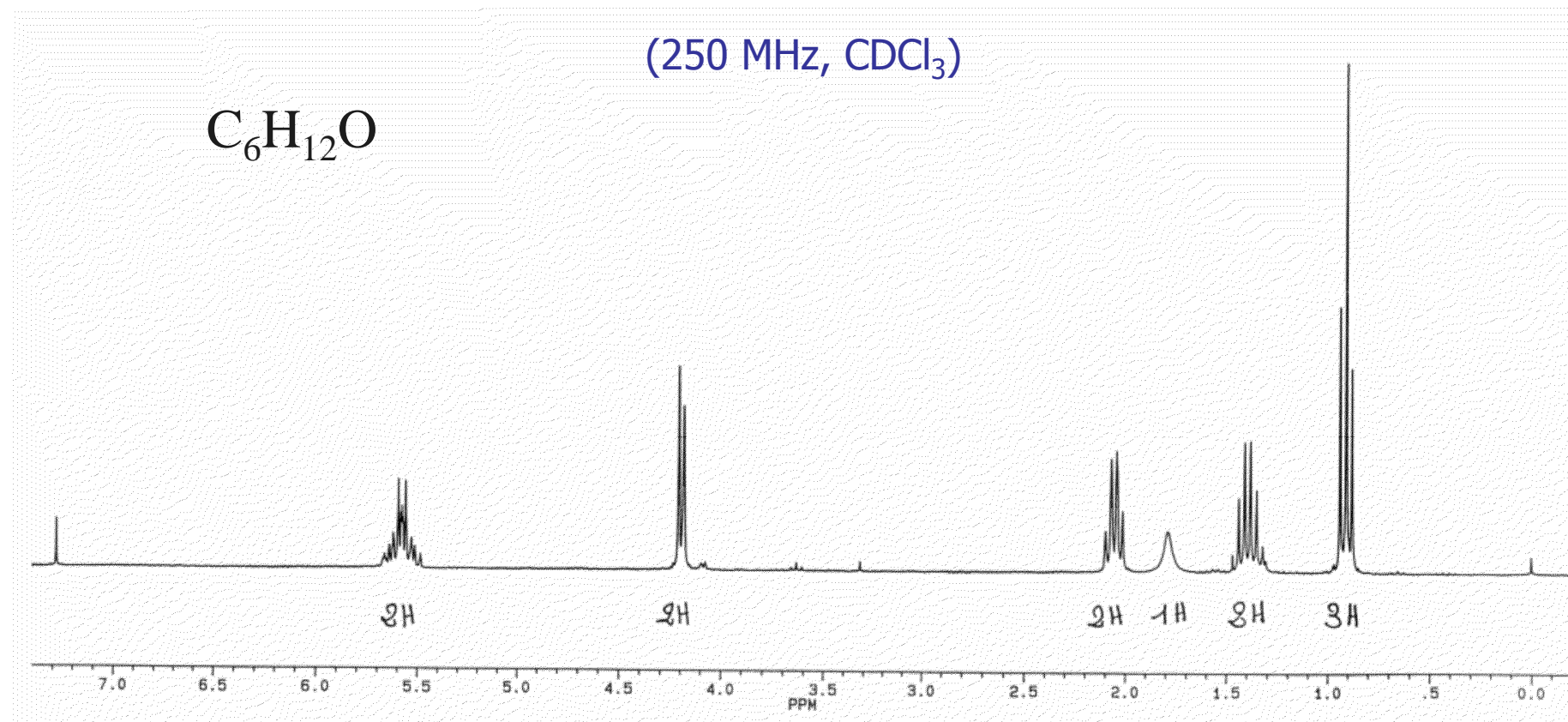
3623	81	2911	36	1612	4	1249	4	792	32
3516	81	2837	33	1465	17	1179	10	761	45
3406	79	2058	81	1442	21	1159	19	750	53
3034	60	1888	77	1423	25	1109	31	708	72
3003	35	1711	5	1357	12	1034	9	638	74
2957	32	1612	12	1320	34	980	70	606	37
2936	33	1584	27	1301	12	836	18	539	23



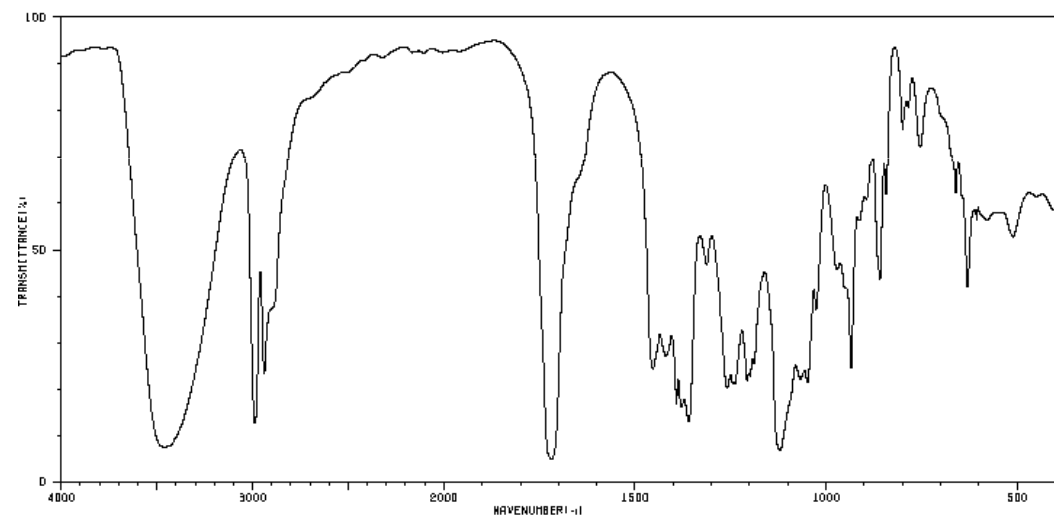
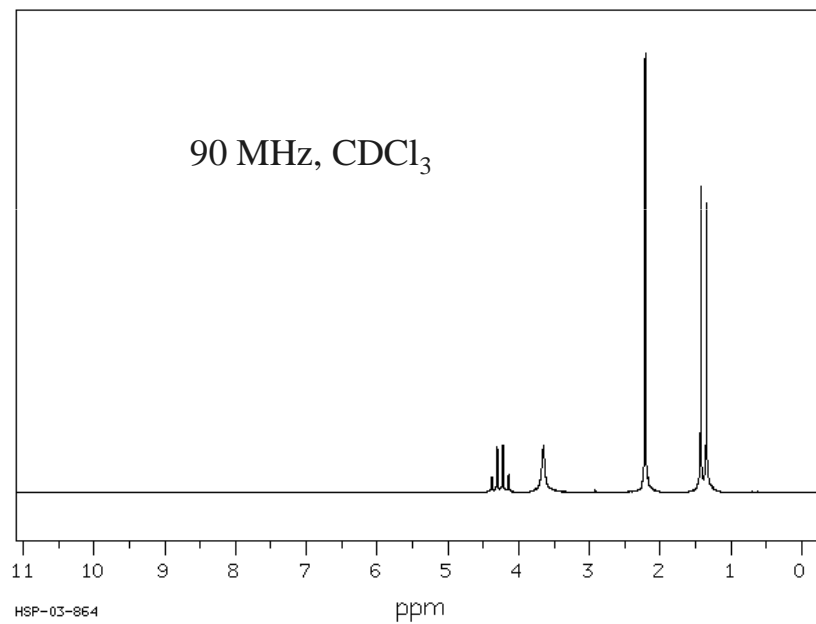
Spectre RMN ^1H d'un composé inconnu



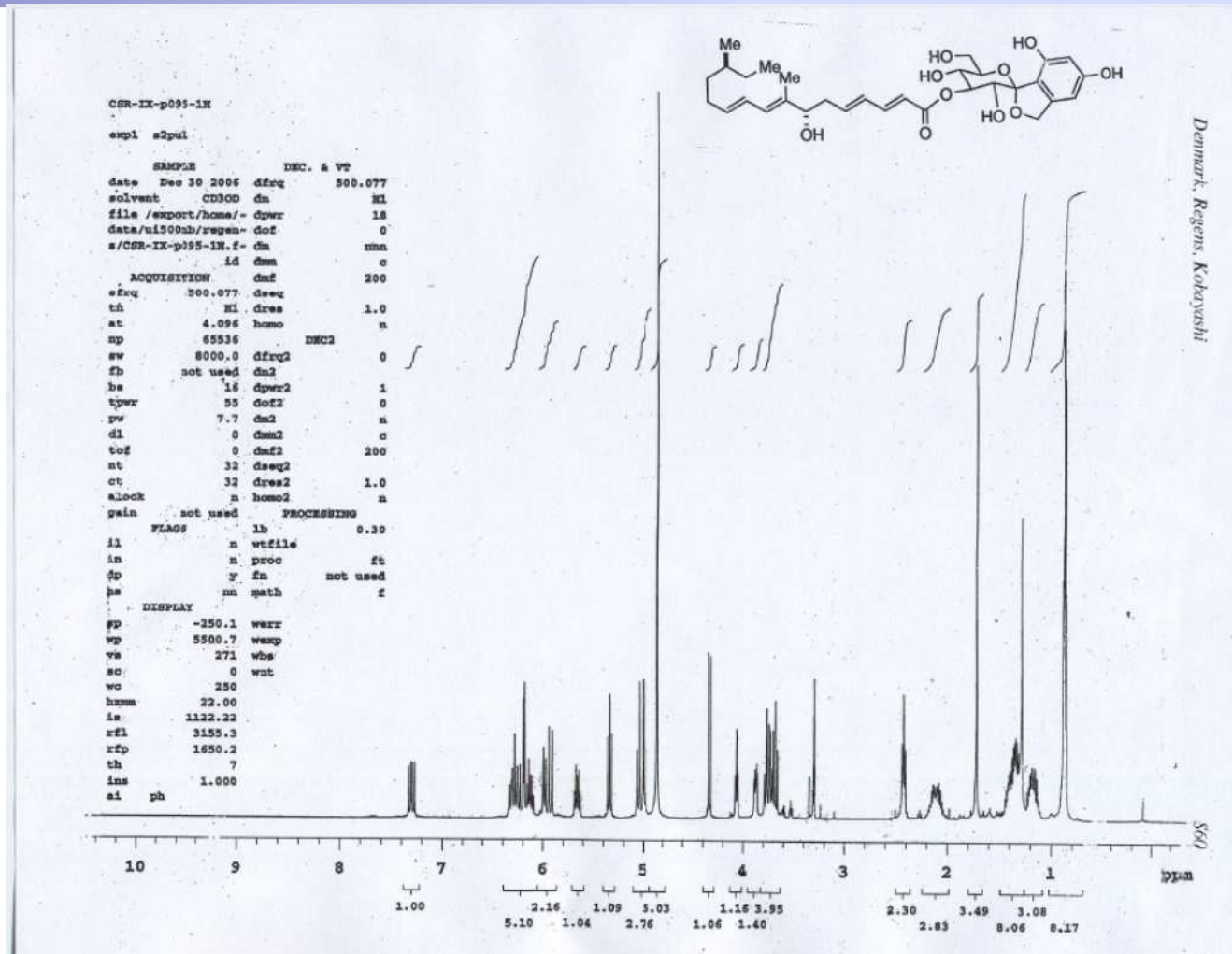
Spectre de RMN ^1H d'un composé inconnu (*bis repetita*)



Spectres d'un composé inconnu



Spectre de RMN de la papulacandine



Denmark, Regens, Kobayashi

