

QFL-1345

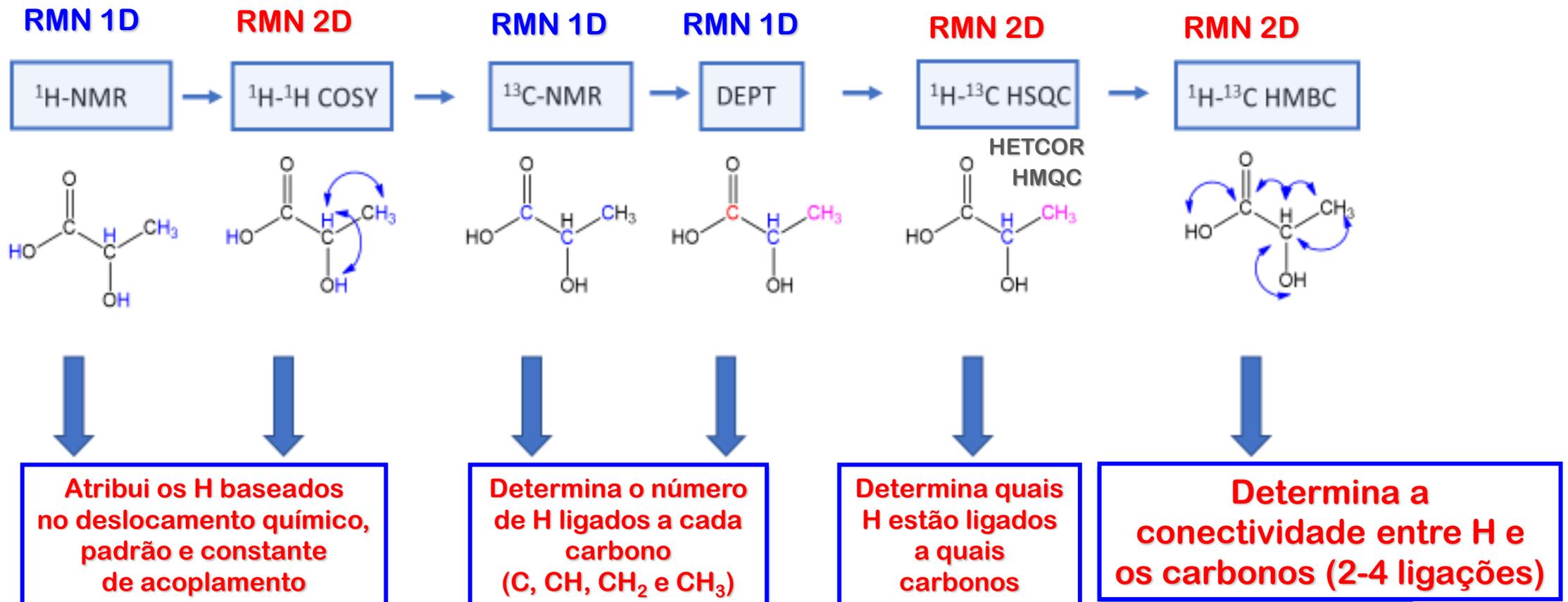
RMN 2D

26 de junho de 2023

Principais informações obtidas de um espectro de RMN de ^{13}C NMR

- 1) Posição de absorção (deslocamento químico em δ - ppm);
- 2) Tipos de carbonos (CH_3 , CH_2 , CH , C):
(APT, DEPT, Ed-HSQC);
- 3) Proporção de carbonos (quase não se usa);
- 4) Podem ser a partir de espectros de correlação 2D:
COSY (H acoplados);
HSQC (C-H diretamente ligados);
HMBC (C-H a 2-4 ligações);
NOESY (interações espaciais)

Sequencia de experimentos em RMN



RMN bidimensionais (RMN 2D)

- Princípio: Interação de spins nucleares (^1H com ^1H , ^1H com ^{13}C , etc.) em mapas de contorno de duas dimensões

- Aplicações:

Simplifica análises em casos complexos ou ambíguos;

Fornece informações não obtidas pelos espectros de RMN 1D.

Correlation Spectroscopy (COSY) ^1H - ^1H (^2J - ^5J ; geminal, vicinal, W, zig-zag, etc)

Heteronuclear Correlation Spectroscopy (HETCOR)

Heteronuclear Multiple-Quantum Coherence (HMQC)

Heteronuclear Single Quantum Coherence (HSQC)

Heteronuclear Multiple Bond Correlation (HMBC)

Nuclear Overhauser Effect Spectroscopy (NOESY)

Incredible Natural Abundance Double Quantum Transfer Experiment (INADEQUATE)

^1H - ^{13}C

^1H - ^{13}C (^2J - ^4J)

Pelo espaço e não via ligações

^{13}C - ^{13}C

Constantes de acoplamento $^1\text{H} - ^{13}\text{C}$

HETCOR
HMQC
HSQC
DEPT

$^{13}\text{C}-\text{H}$ couplings

$^1\text{J}_{\text{CH}}$ -one bond $^{13}\text{C} - ^1\text{H}$ coupling

range from 120-320 H_z and increases linearly with increasing carbon 's'-character.

	CH_3-CH_3	$\text{CH}_2=\text{CH}_2$	C_6H_6	$\text{HC}\equiv\text{CH}$
% s-character:	25%	33%	33%	50%
$^1\text{J}_{\text{CH}}$ (H_z):	125	156	159	249

$$^1\text{J}_{\text{CH}} = 5 \times (\% \text{ s}) \text{ H}_z.$$

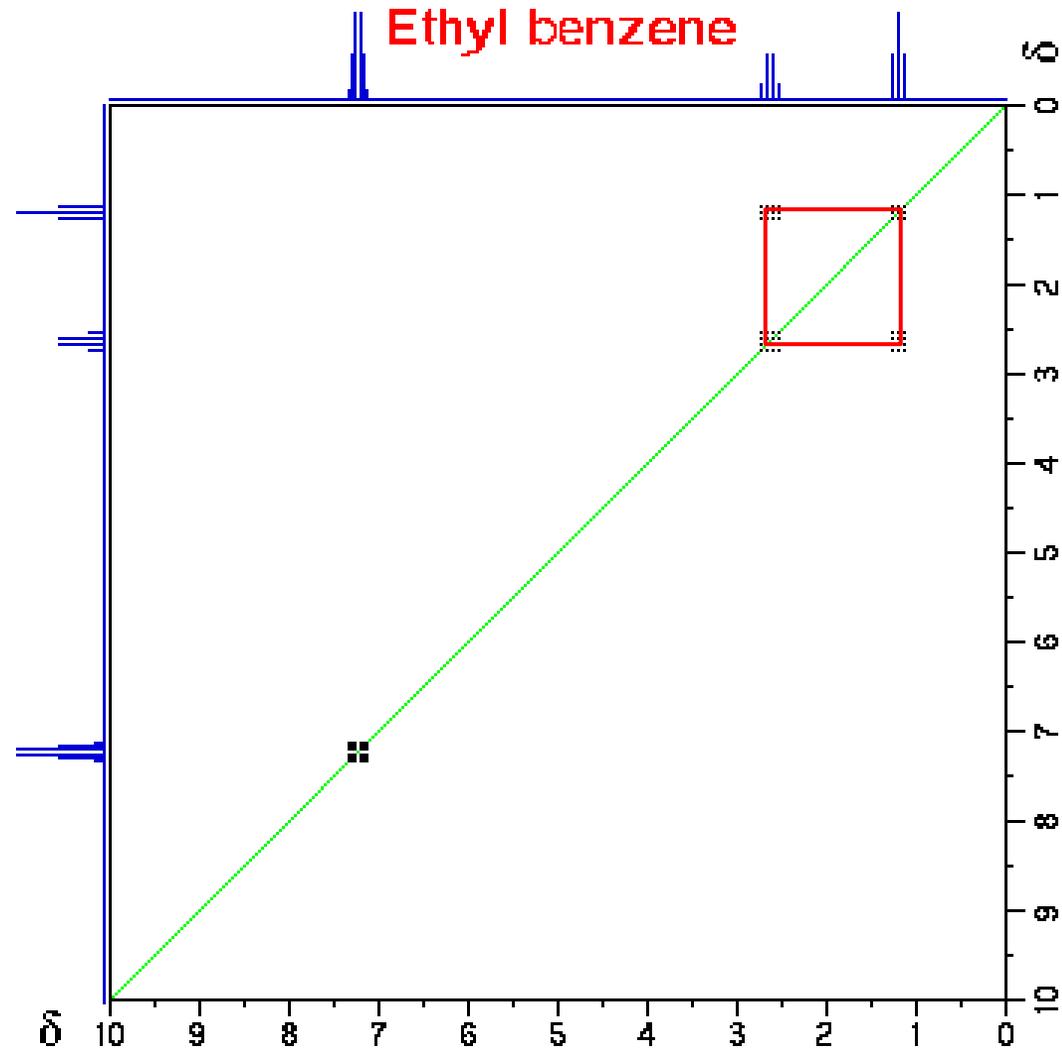
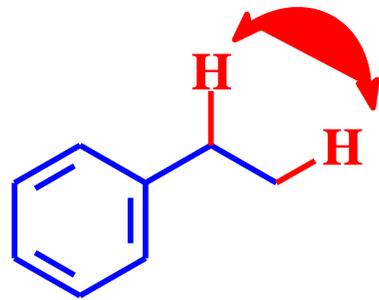
HMBC

$^2\text{J}_{\text{CH}}$ -two bond ($^{13}\text{C}-\text{C}-^1\text{H}$) coupling constants

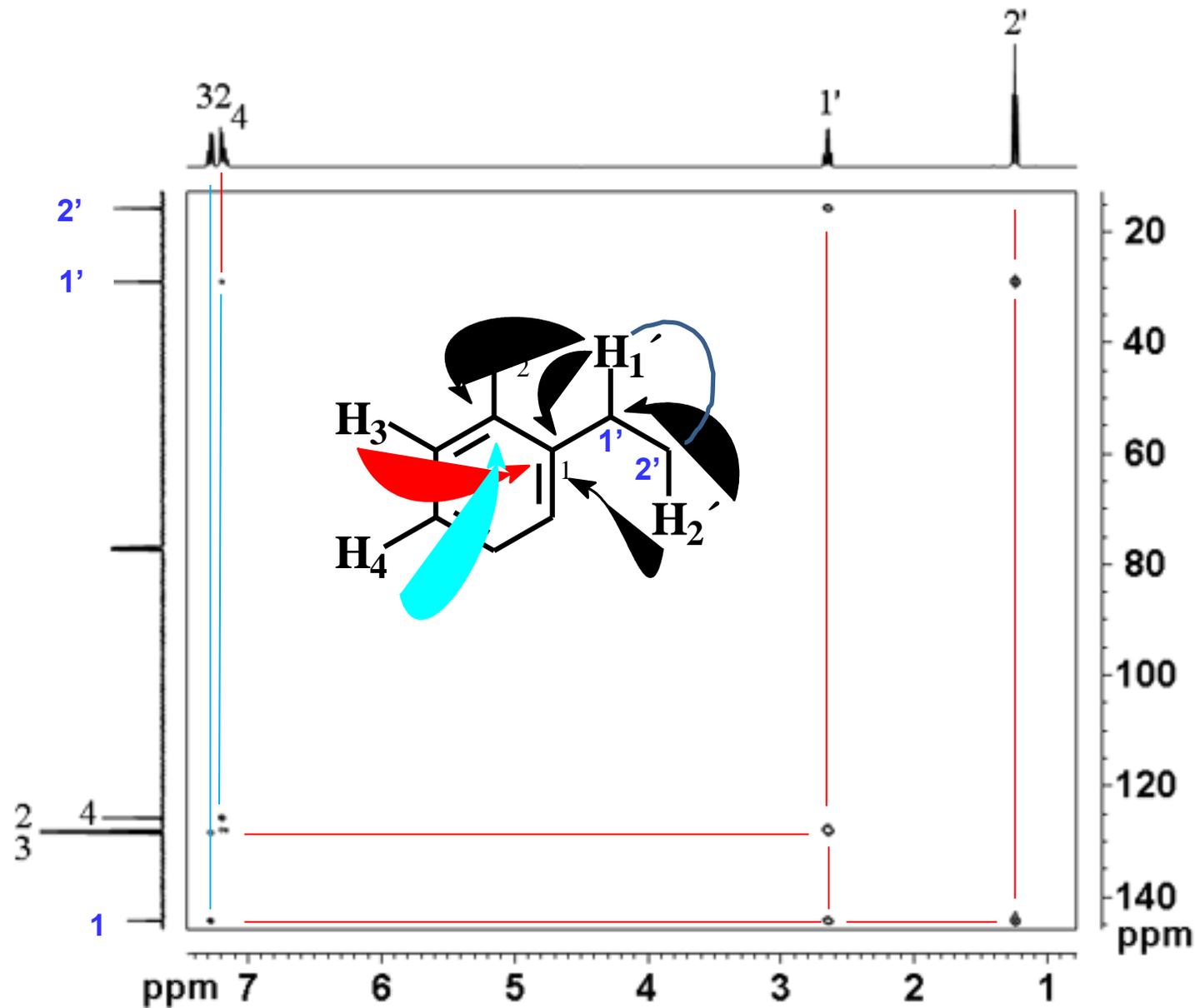
$^2\text{J}_{\text{CH}}$ are between 5 and 60 H_z but usually *ca.* 12 H_z .

$^3\text{J}_{\text{CH}}$ -three bond ($^{13}\text{C}-\text{C}-\text{C}-^1\text{H}$) $\sim 4-8 \text{ Hz}$

Espectro de RMN 2D (^1H - ^1H COSY) do etilbenzeno



Espectro de RMN 2D (HMBC) do etilbenzeno

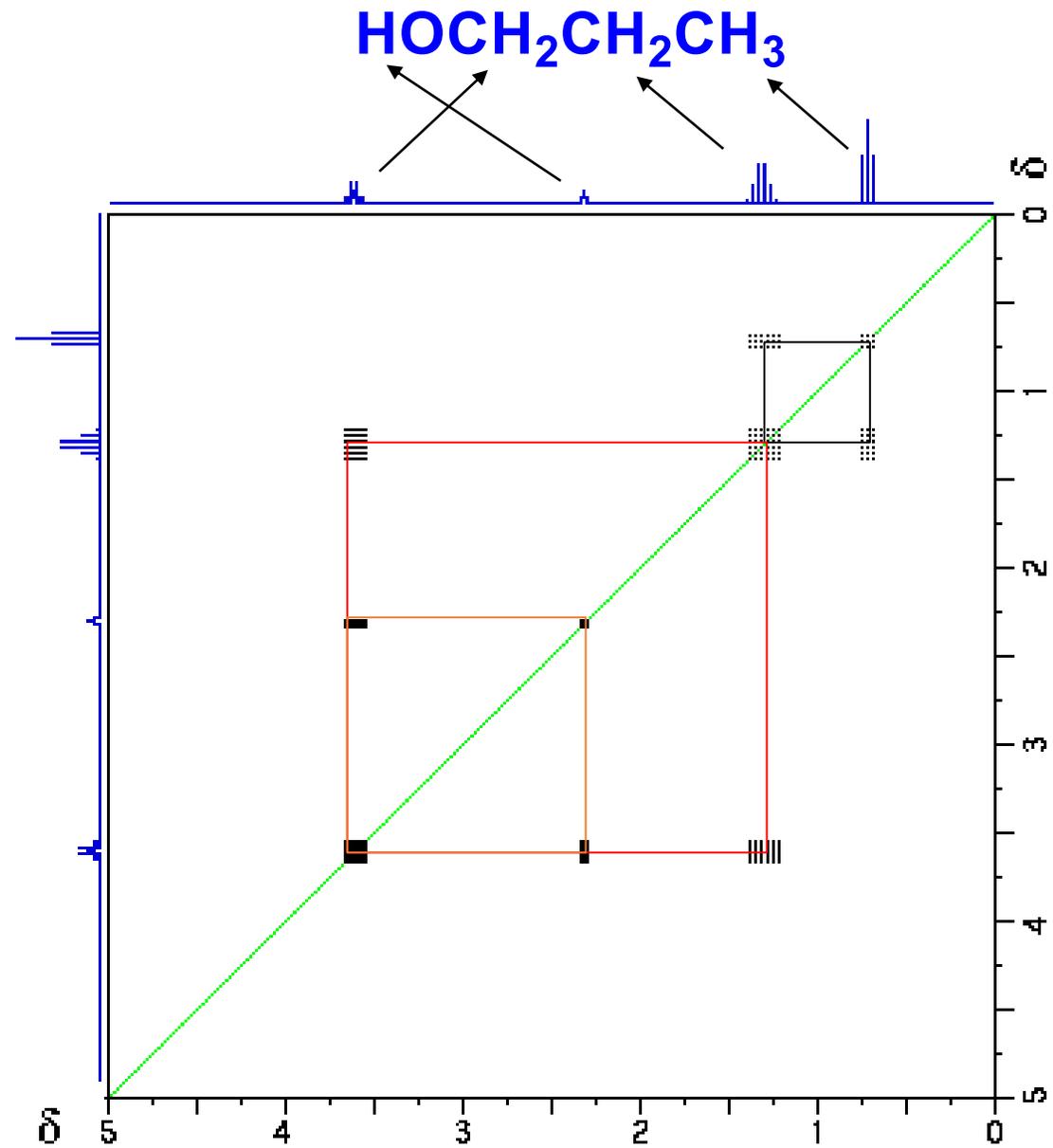


HMBC:
Heteronuclear
Multiple-bond
Correlation

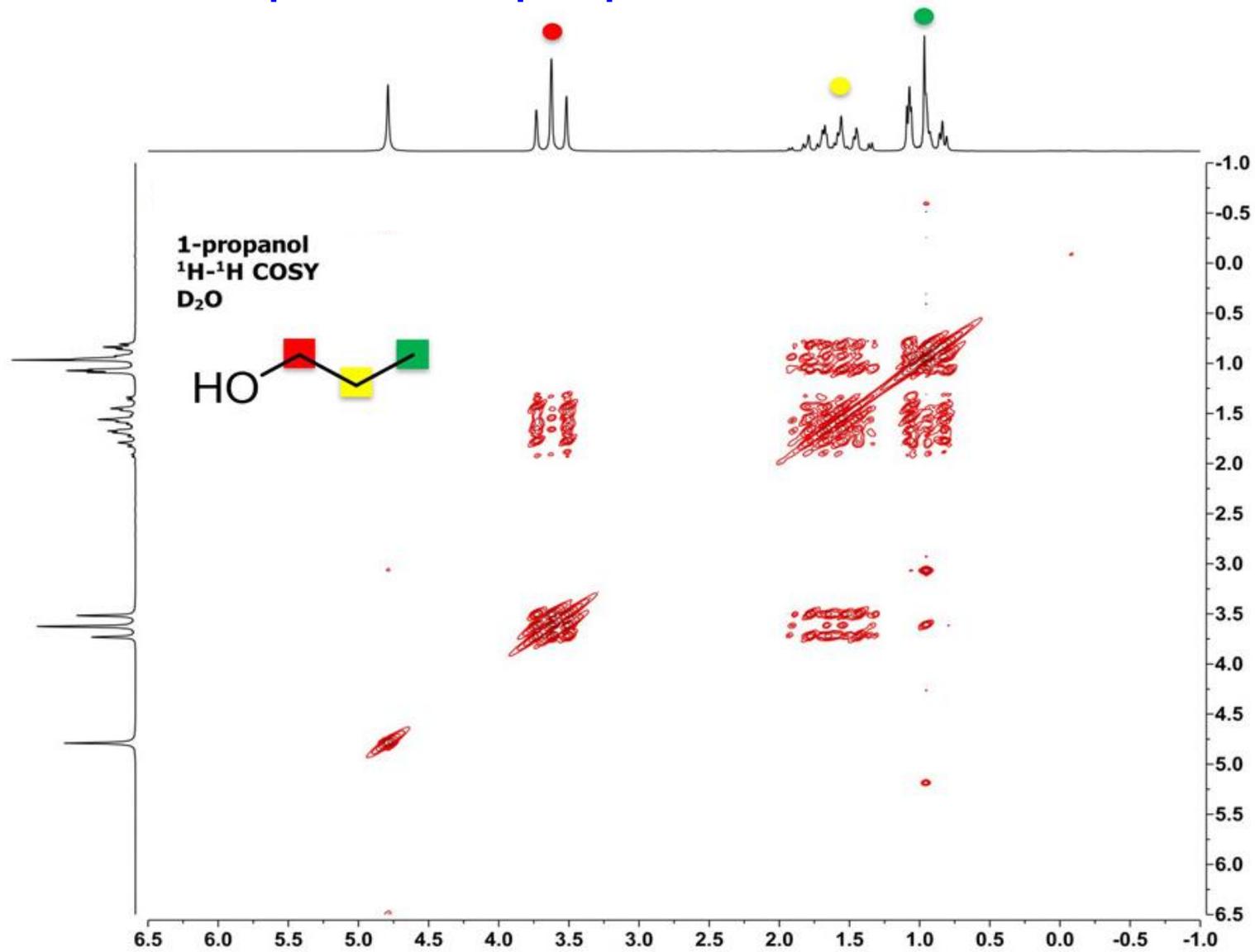
Fornece informações de correlações de 2 e 3 ligações;

Se o parâmetro de J for alterado para 2-4 Hz pode detectar correlações de 4-5 ligações.

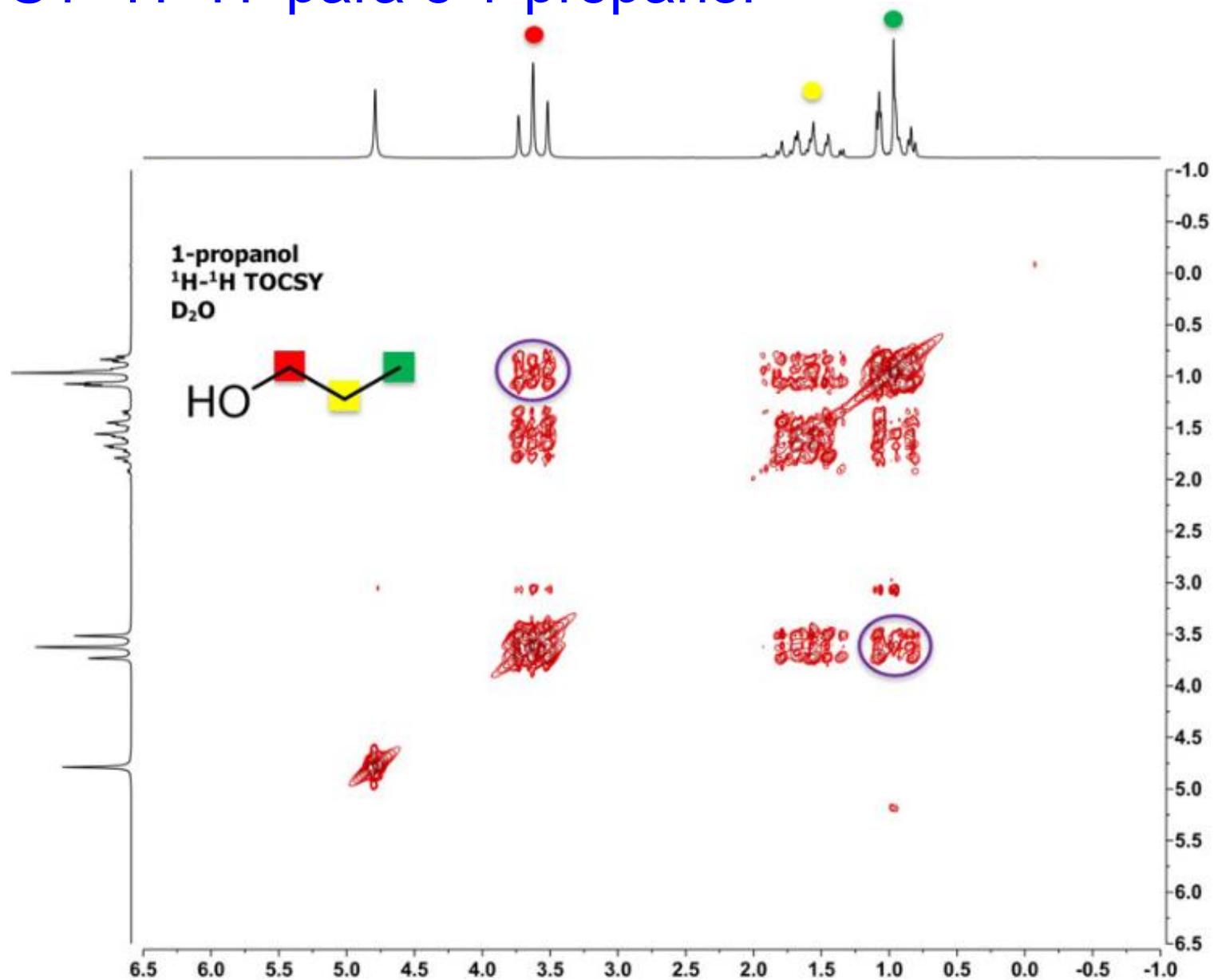
Espectro de COSY ^1H - ^1H para o 1-propanol



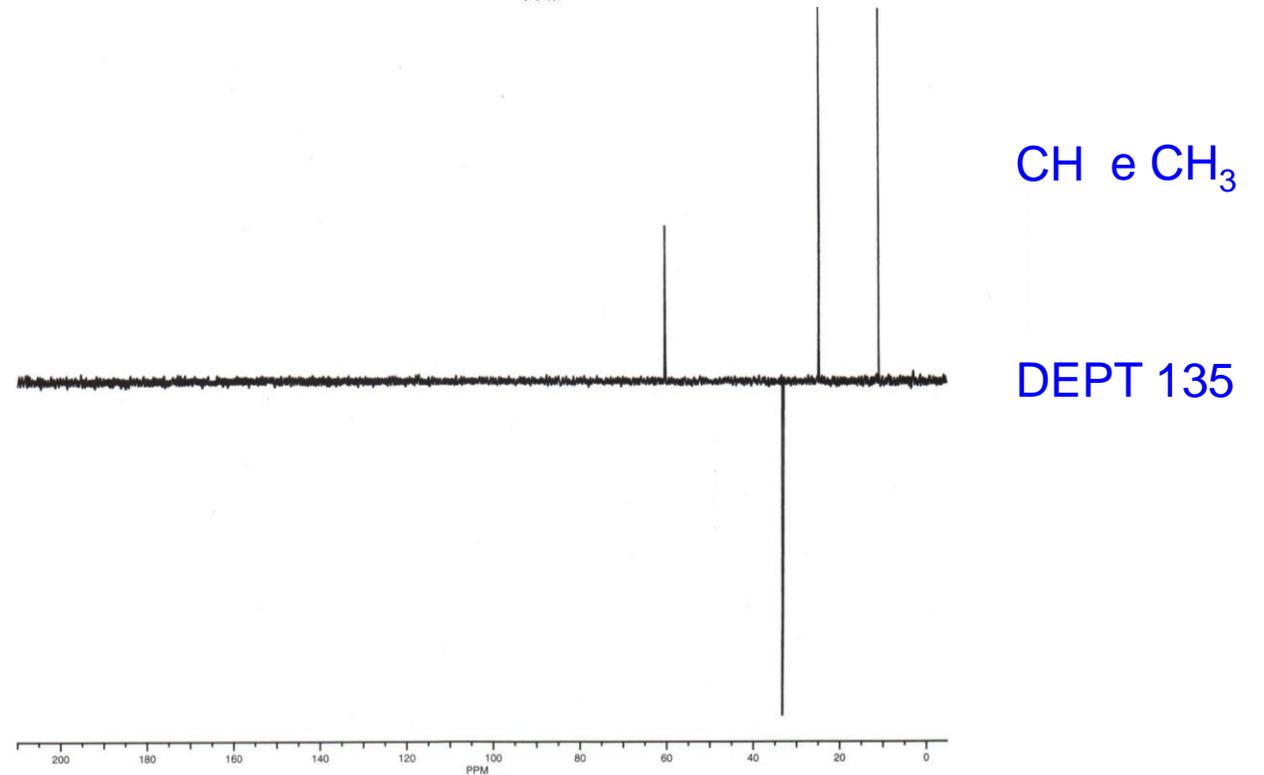
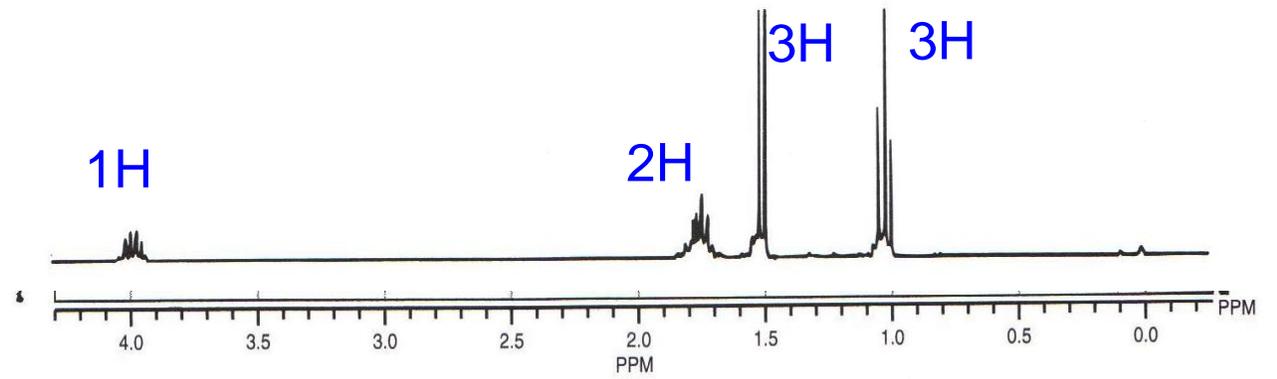
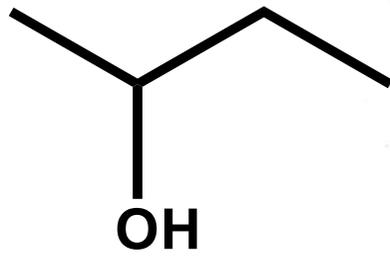
Espectro de COSY ^1H - ^1H para o 1-propanol



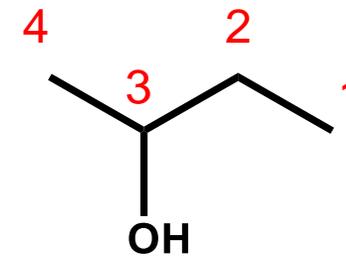
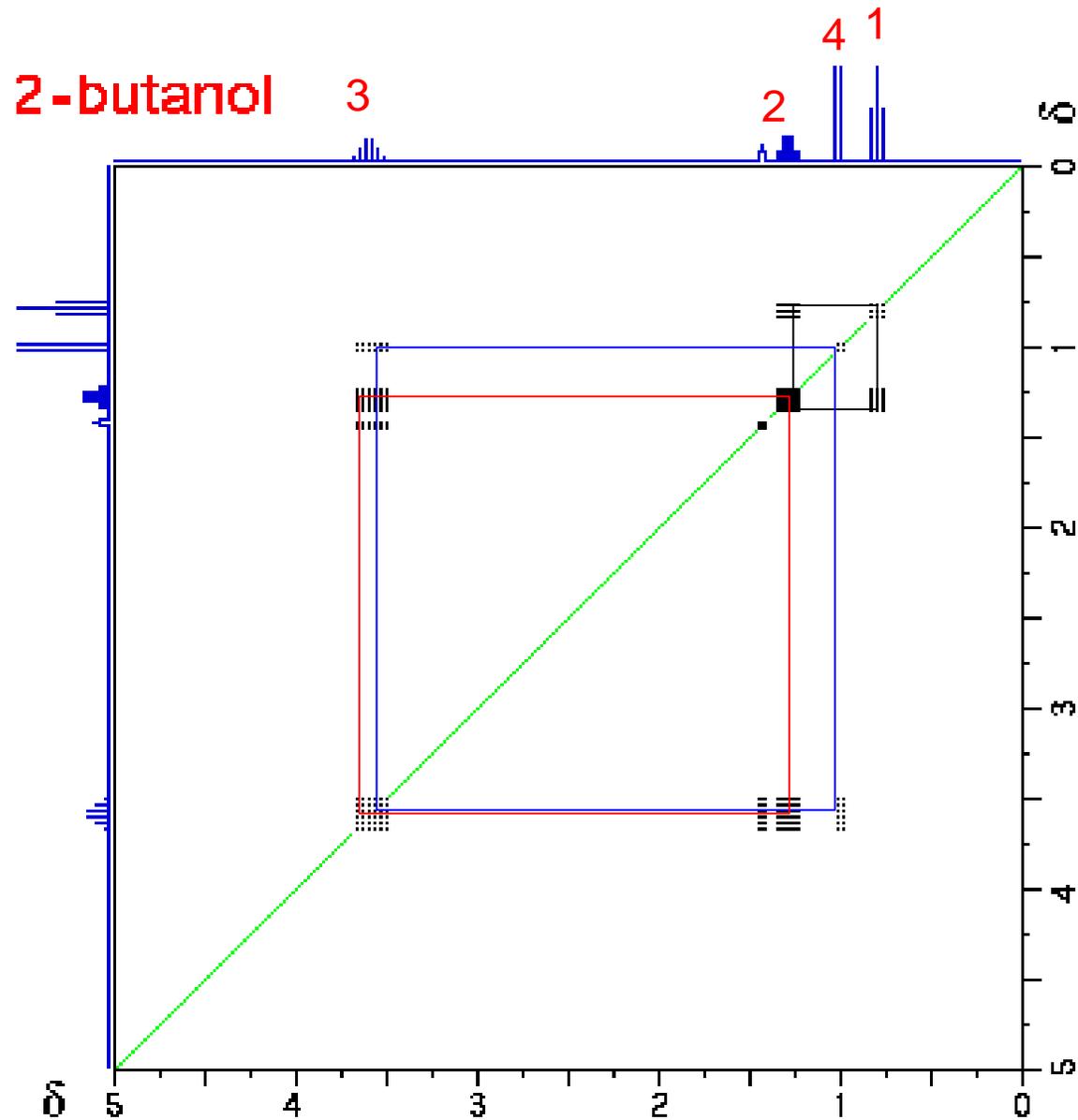
Espectro de TOCSY ^1H - ^1H para o 1-propanol



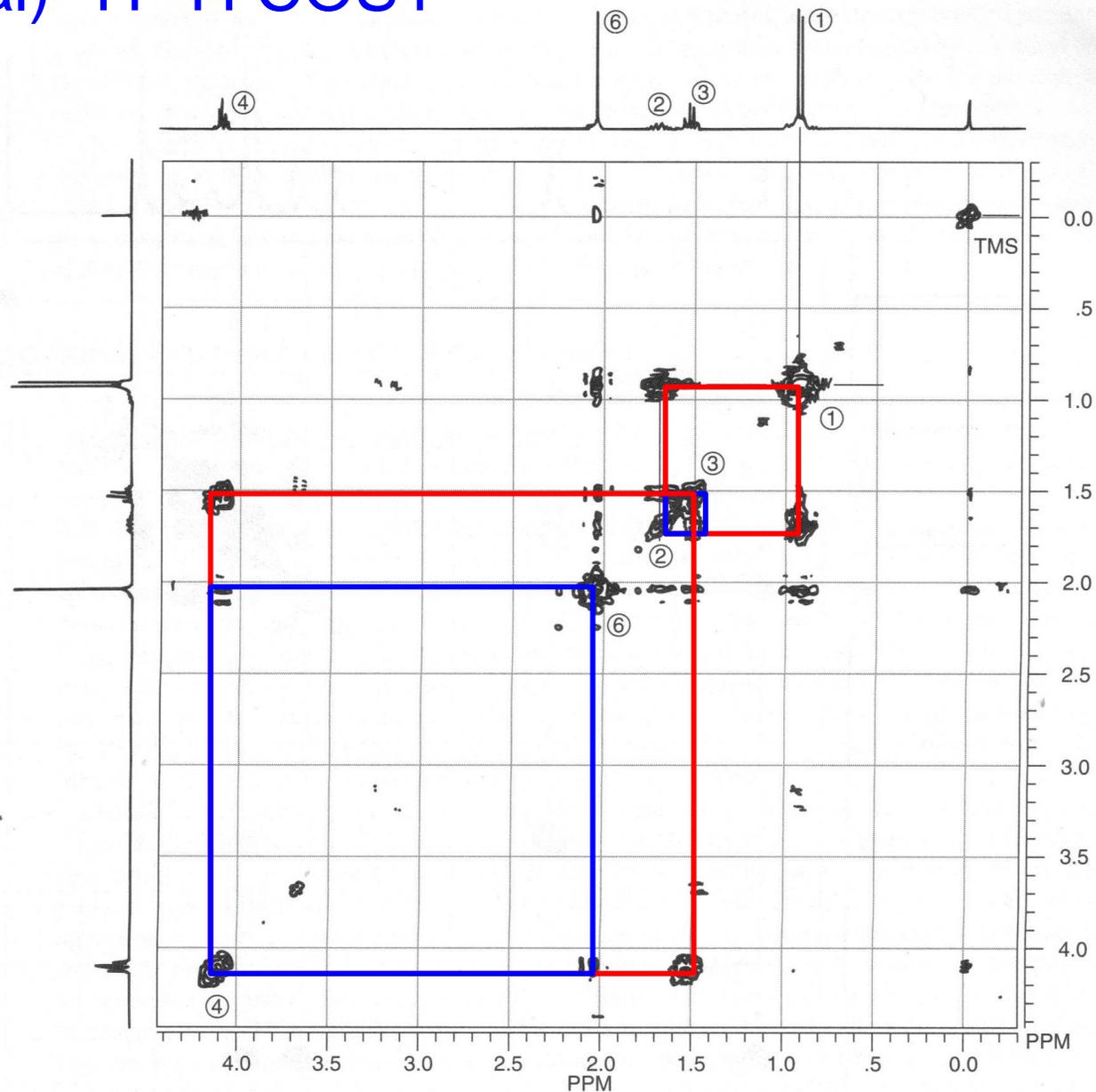
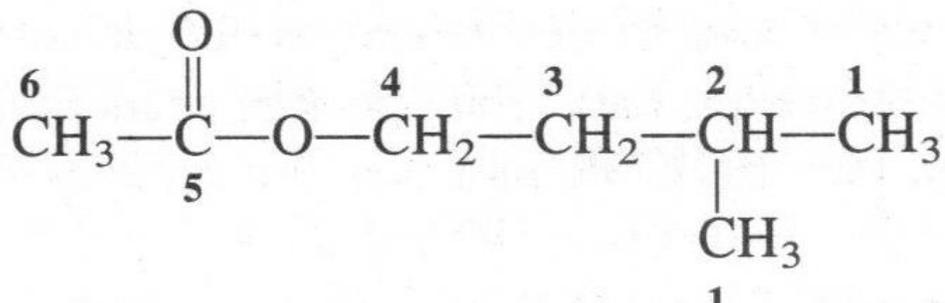
Espectros de RMN de ^1H e DEPT 135,
do composto com fórmula molecular $\text{C}_4\text{H}_9\text{Cl}$



RMN 2D (bidimensional) ^1H - ^1H COSY

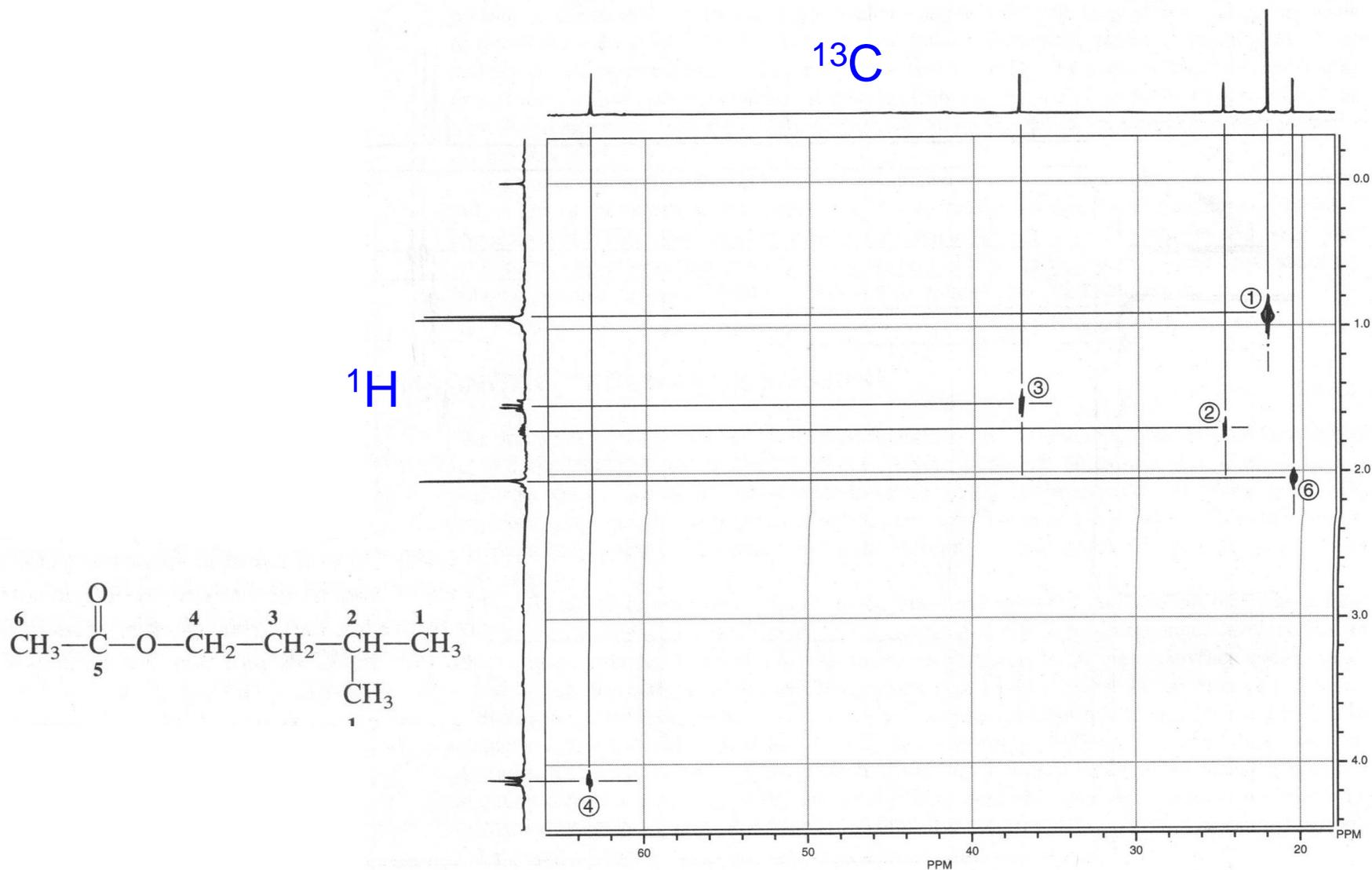


RMN 2D (bidimensional) ^1H - ^1H COSY



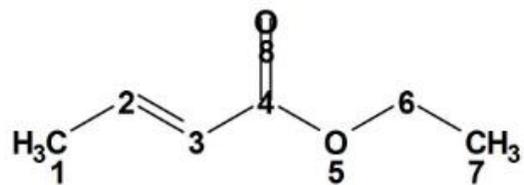
► **FIGURE 9.13** COSY spectrum of isopentyl acetate.

RMN 2D (bidimensional) ^1H - ^{13}C (HETCOR)



► **FIGURE 9.16** HETCOR spectrum of isopentyl acetate.

RMN 2D (bidimensional) COSY



Ethyl crotonate

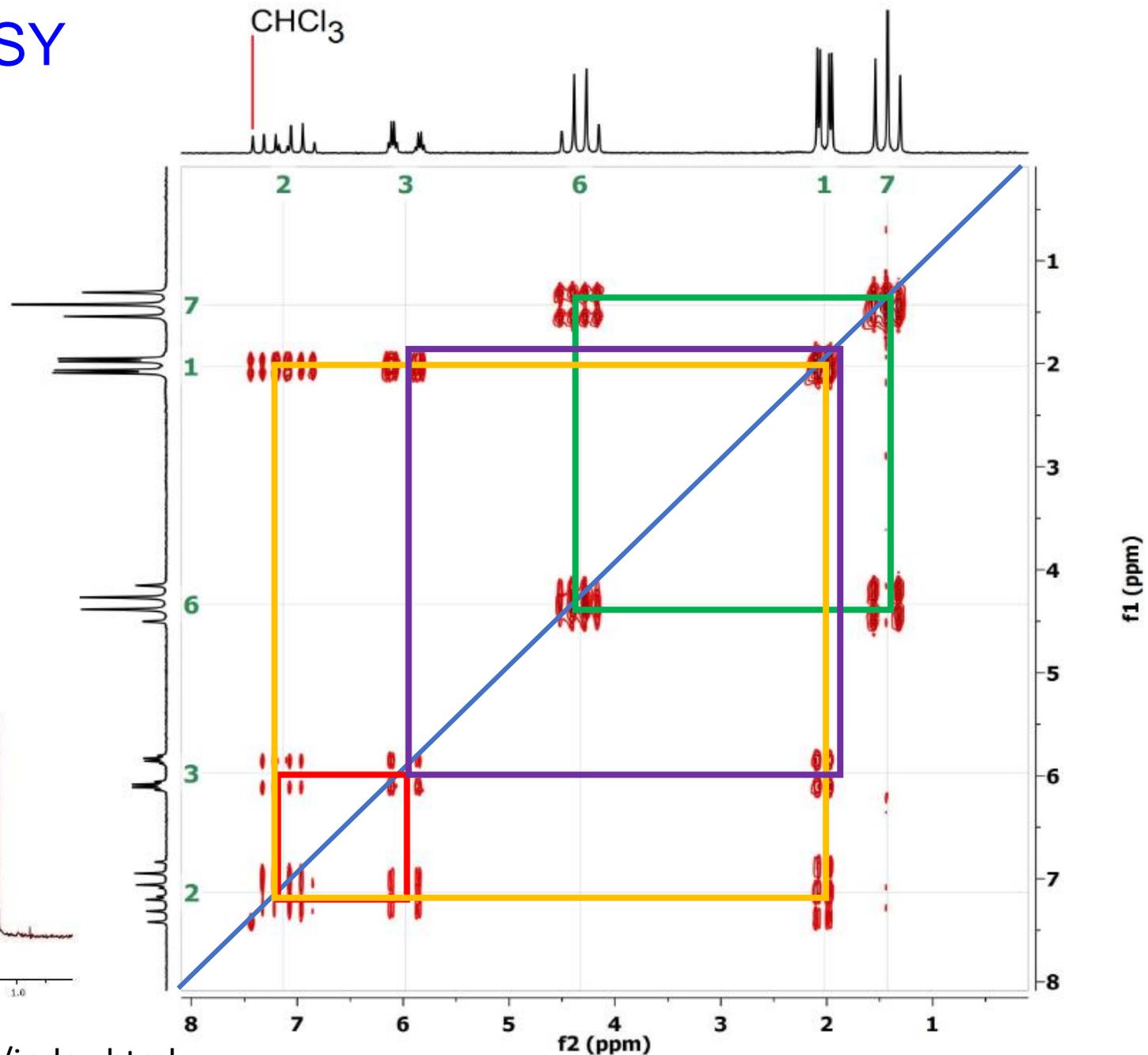
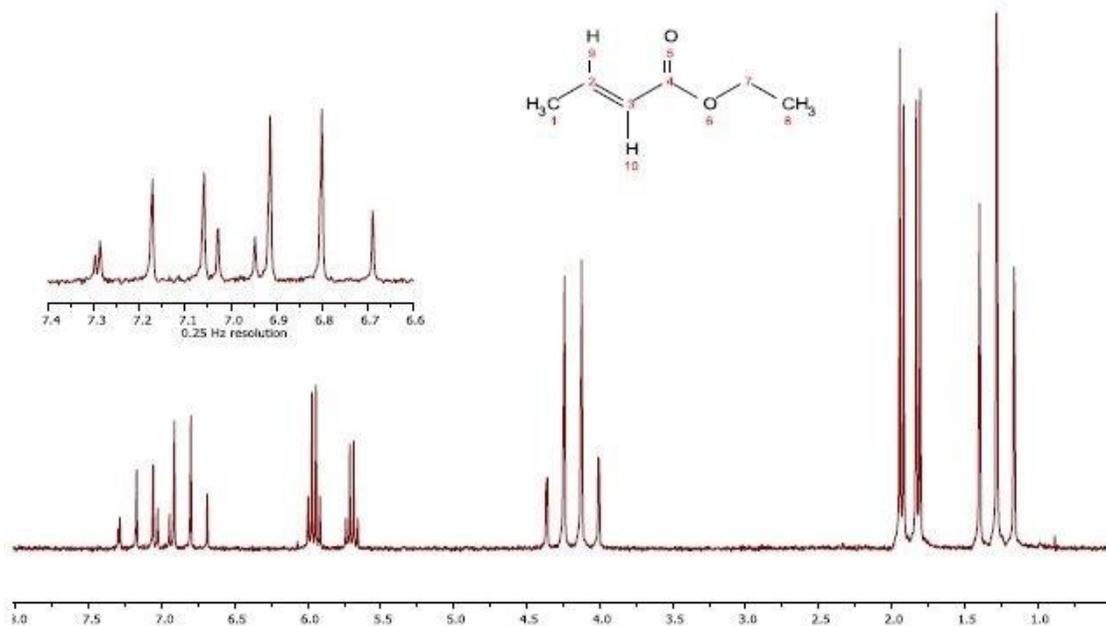
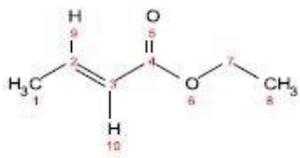
Solvent = CDCl₃

Concentration = 250 mM

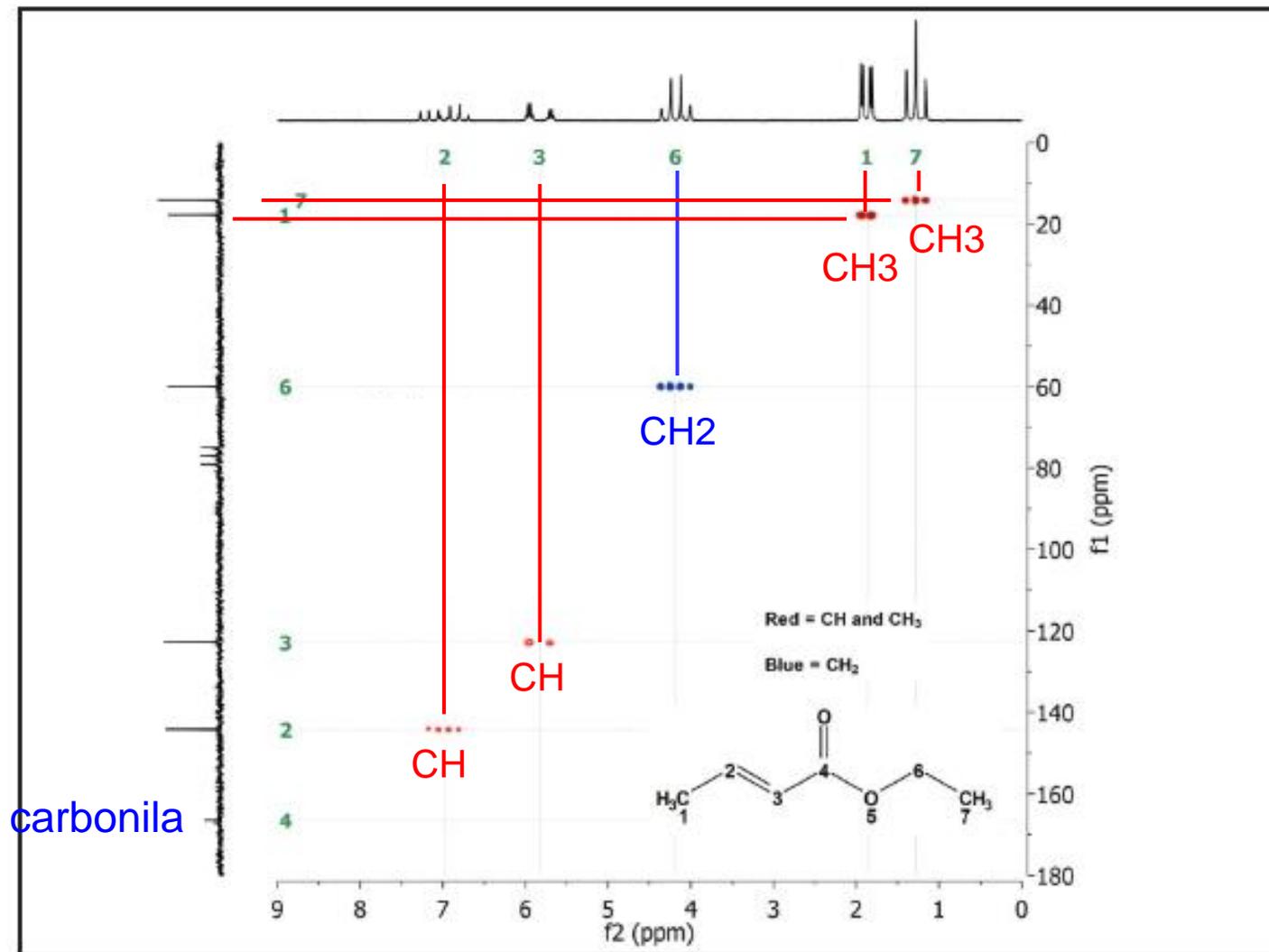
Number of scans = 1

Total experimental time = 10 min

EB-60 single scan
0.15 Hz Resolution



RMN 2D (ed-HSQC) do crotonato de etila (carbonos e hidrogênios diretamente ligados)



RMN 2D (HMBC) do crotonato de etila

Ethyl crotonate

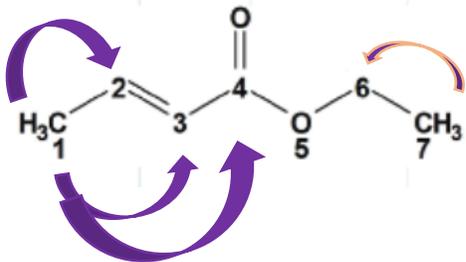
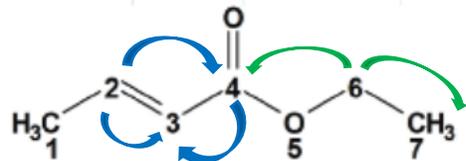
Solvent = CDCl₃

Concentration = 1 M

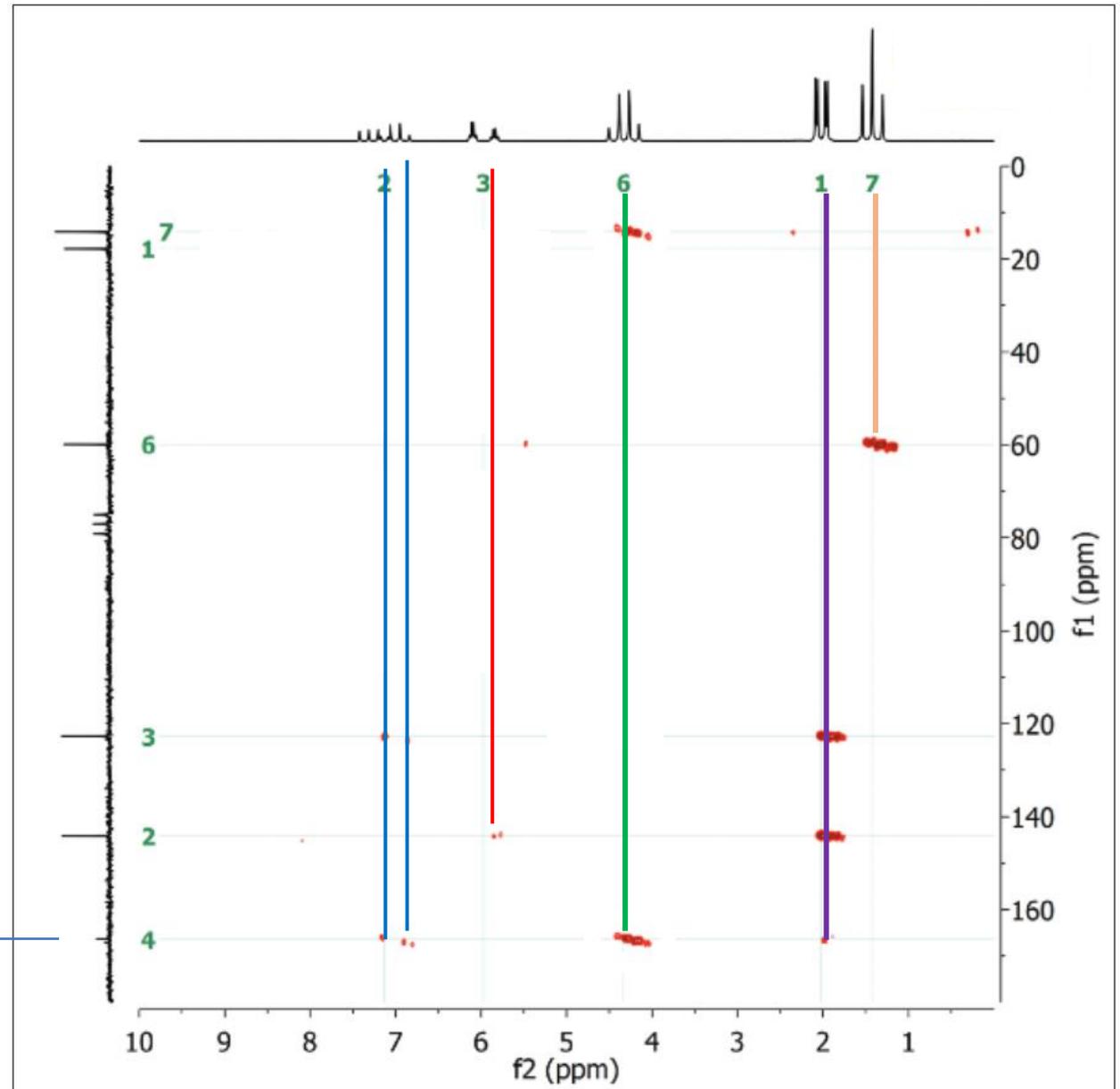
Number of scans = 16

Repetition time = 2 s

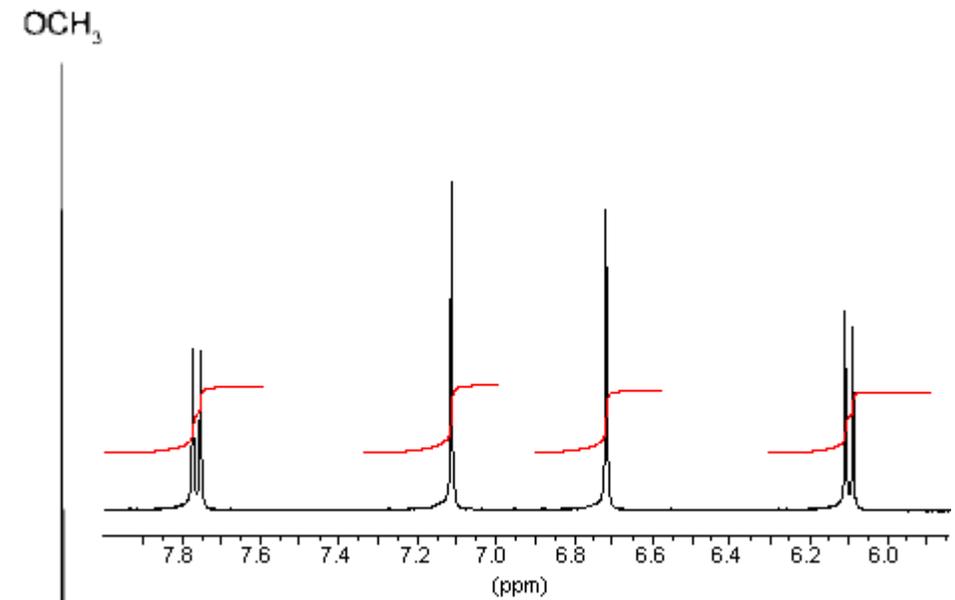
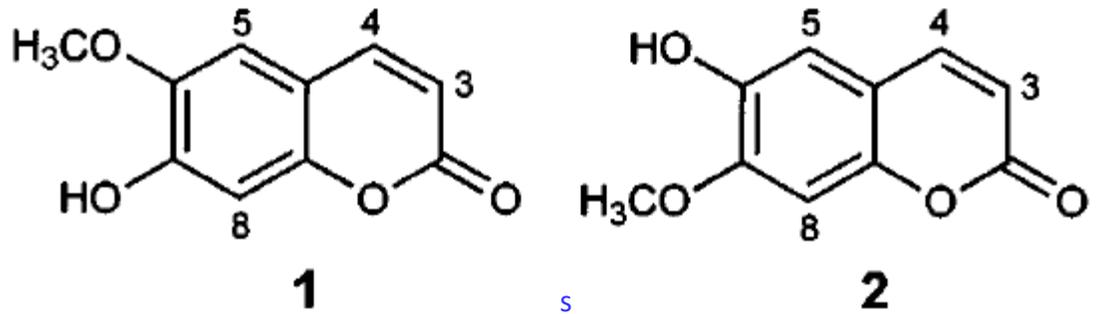
Total experimental time = 69 min



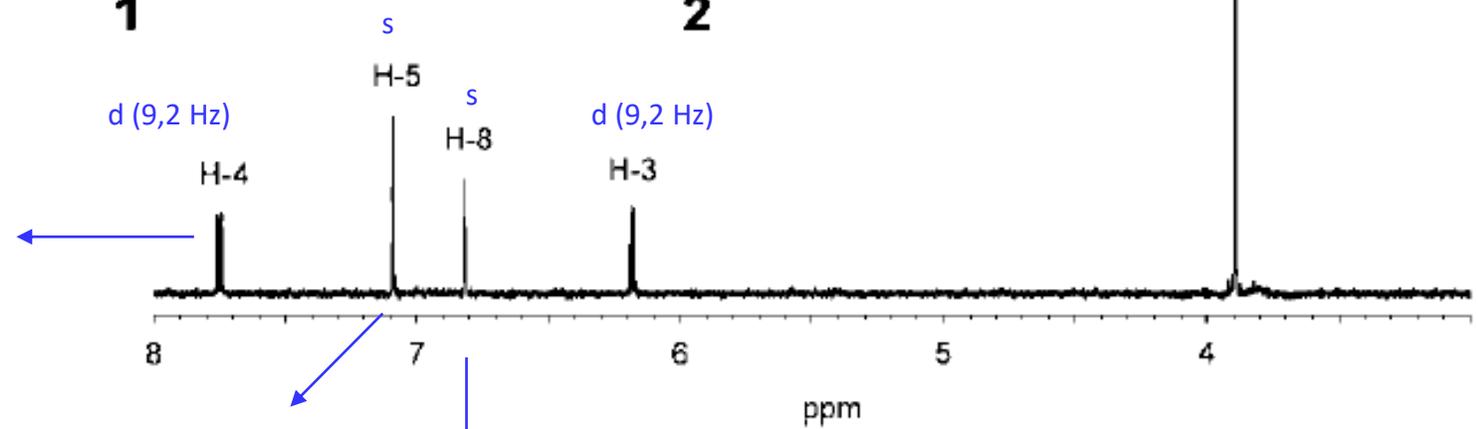
carbonila ←



Qual isômero é responsável pelo espectro abaixo?



Conjugados à carbonila

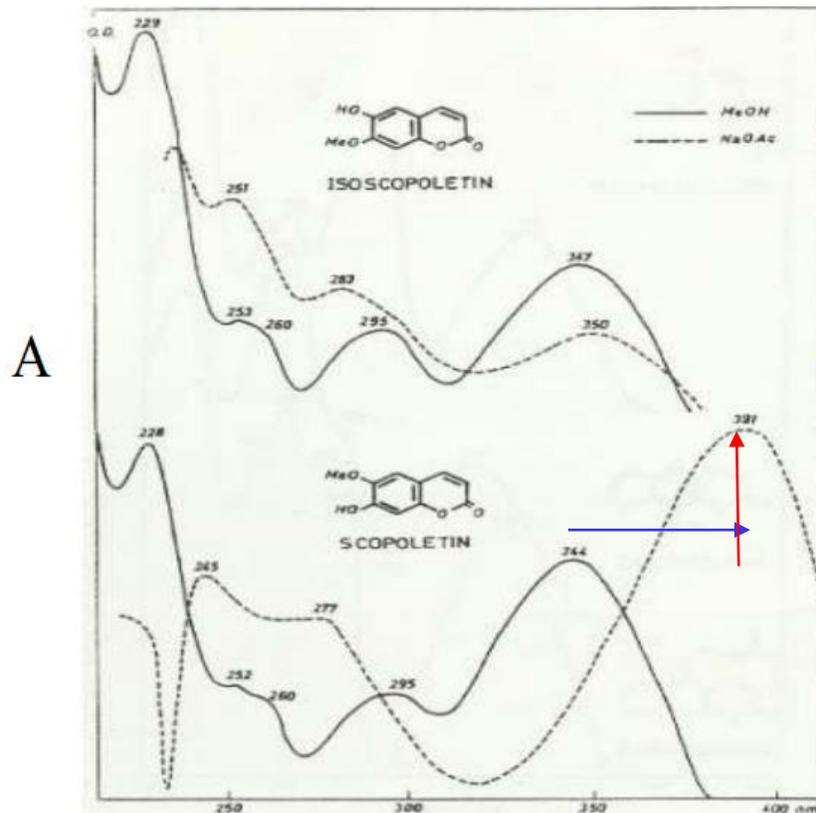


Conjugado à carbonila (mais desblindado do que H8)

orto a dois oxigênios (é mais blindado do que o H5)

TABLE III
THE DATA FROM UV SPECTRUM OF STANDARD SCOPOLETIN [6], [7]
AND ISOLATED COMPOUND

Sample	λ max (nm)		
	Me OH	After additional NaOAc	After additional NaOH
Standard Scopoletin	344.40 295 252 228	391 277	390.29
Isolated Compound	345 295.80 252 228.80	391.40 276.60	391.60

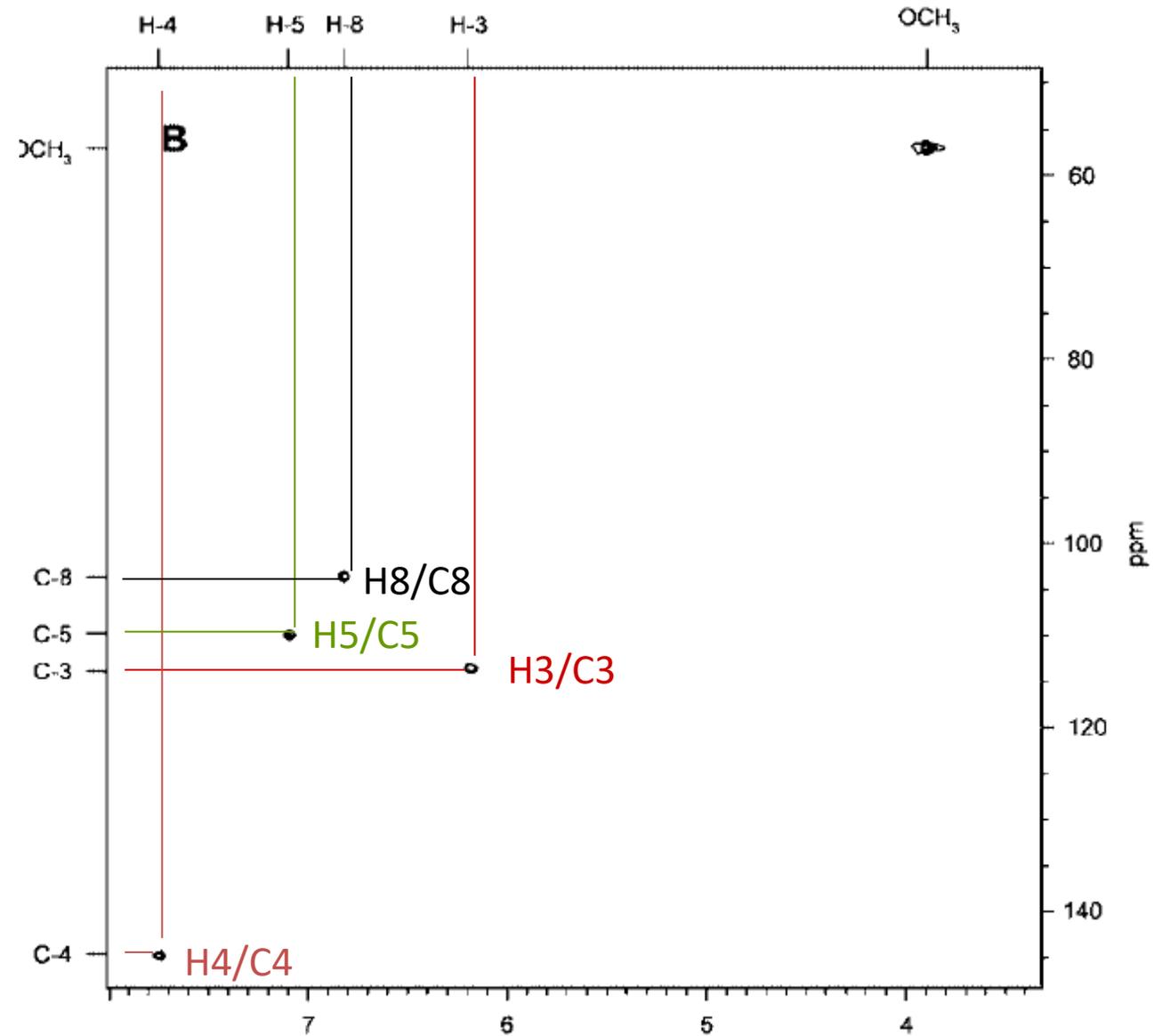
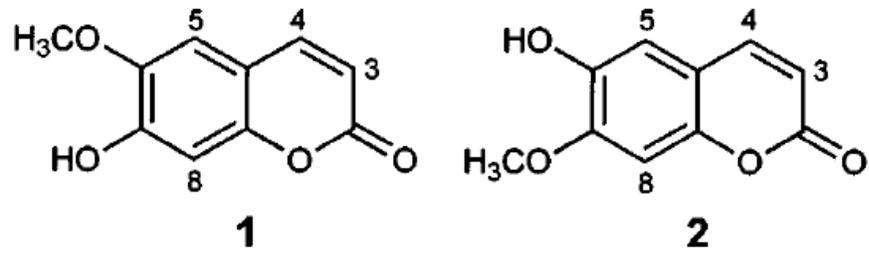


Espectro no UV da isoescopoletina e escopoletina em MeOH e NaOAc

Deslocamento batocrômico
e hiperacrômico

Esse efeito da basificação só é observado para a escopoletina indicando que a hidroxila se encontra conjugada à carbonila

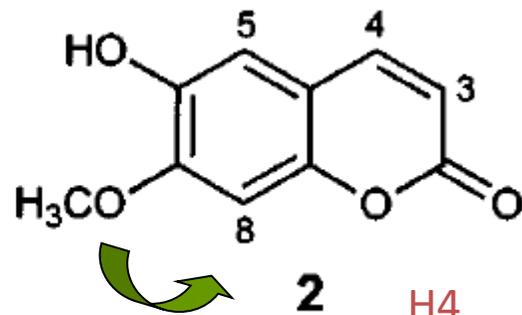
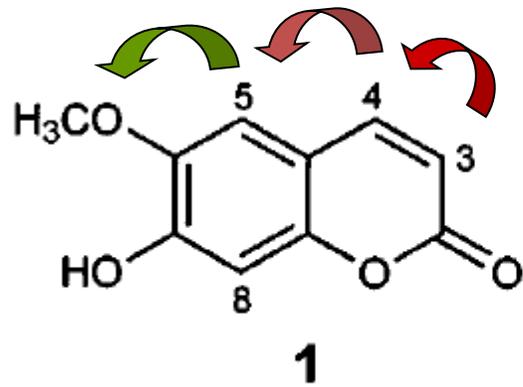
Espectro de HSQC da cumarina



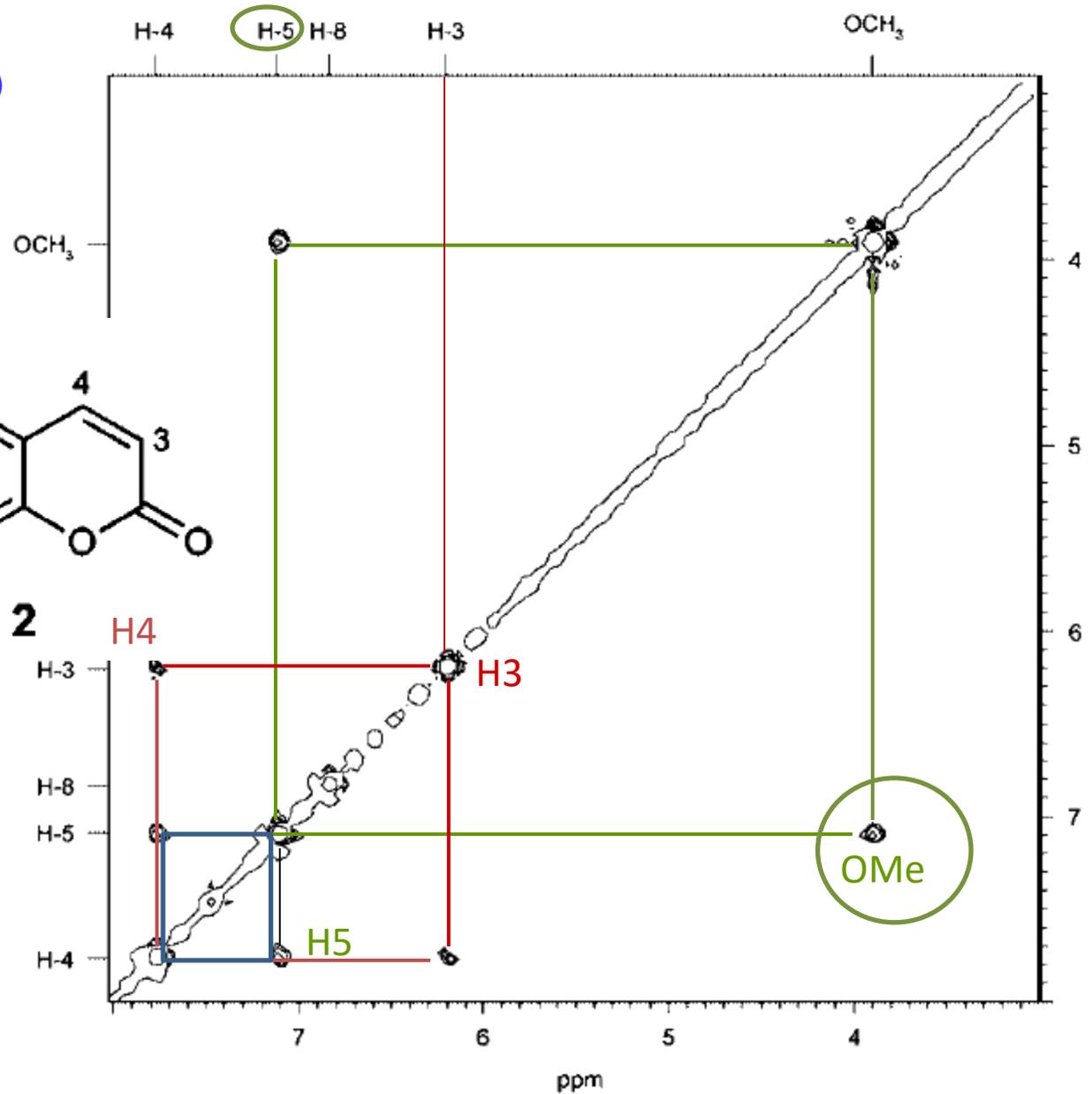
Espectro de RMN 2D (NOESY) de uma cumarina

NOESY (nuclear Overhauser Spectroscopy: interações espaciais)

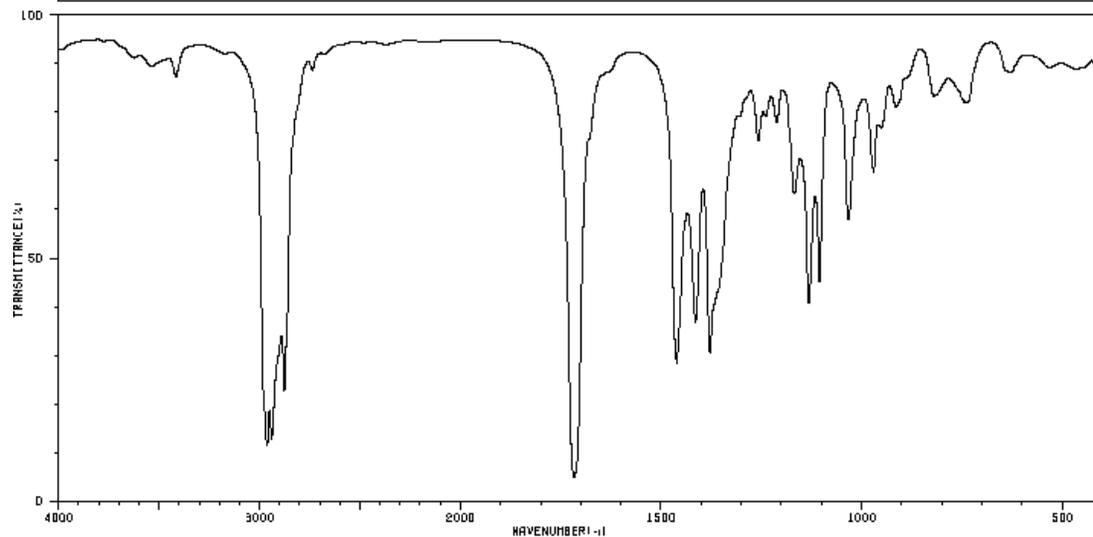
Correlação Observada!!!



Correlação esperada

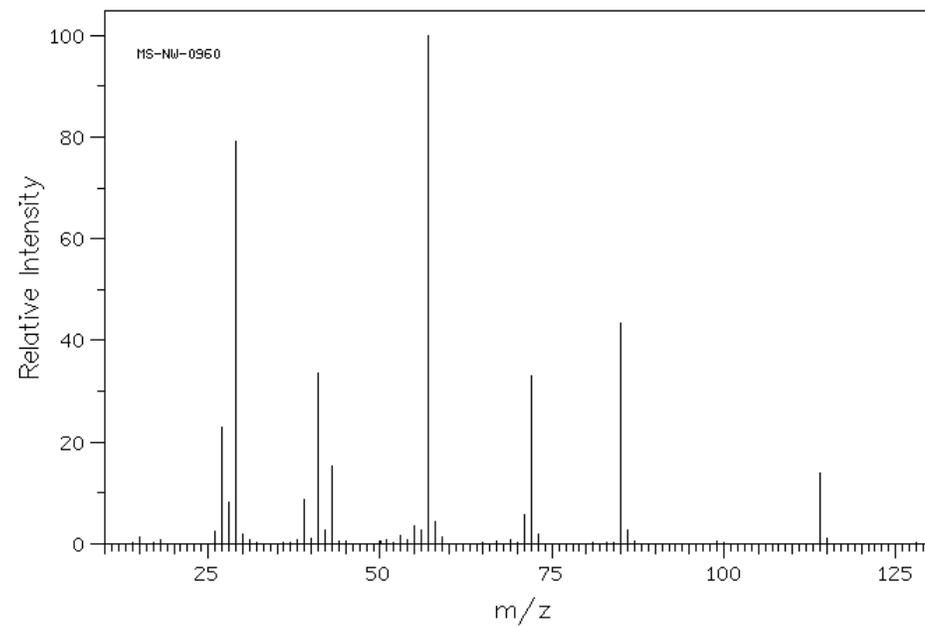


HIT-NO=1140	SCORE= ()	SDBS-NO=704	IR-NIDA-01521 : LIQUID FILM
3-HEPTANONE			
C ₇ H ₁₄ O			

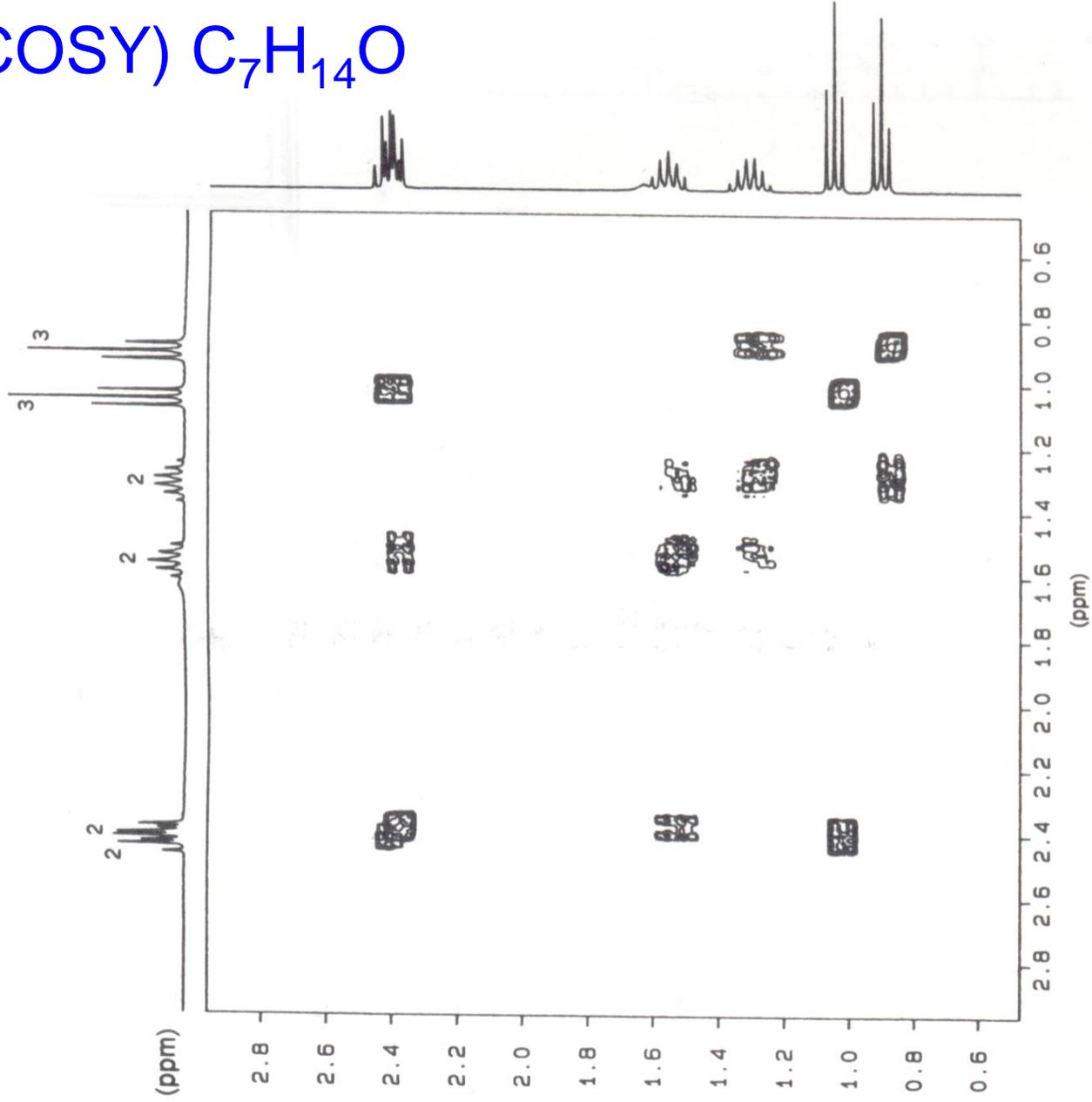
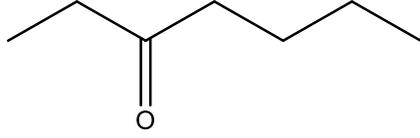


3638	86	1461	28	1105	43	807	81
3415	84	1414	35	1033	55	747	79
2962	10	1378	29	970	84	741	79
2939	12	1268	70	958	74	641	84
2876	21	1212	74	915	79	632	84
2756	84	1168	60	821	79		
1716	4	1131	39	816	79		

Problema 4



Problema 4 (COSY) C₇H₁₄O



^1H - ^1H COSY $\text{C}_7\text{H}_{14}\text{O}$

Ethyl crotonate

Solvent = CDCl_3

Concentration = 1 M

Number of scans = 16

Repetition time = 2 s

Total experimental time = 69 min

