

Espectroscopia de Ressonância Magnética Nuclear (RMN):

Vídeo 1: Fundamentos da técnica

Prof^a. Dr^a. Patrícia Bulegon Brondani
(@patyqmc)

Ressonância Magnética Nuclear

Principal aplicação: determinar o esqueleto carbono-hidrogênio de uma molécula

- ✓ Análise química.
- ✓ Estrutura de biomoléculas complexas.
- ✓ Mapeamento da distribuição eletrônica em moléculas.
- ✓ Cinética de transformações químicas.
- ✓ Imagem de órgãos internos do corpo humano de maneira não-destrutiva.

Propriedades do núcleo do átomo

Spin Nuclear (I)

É expresso em múltiplos de $1/2$ (+ ou -): $I = 0, 1/2, 1, 3/2, \text{etc}$;

- Número de Prótons e Nêutrons for par: spin = zero;
- Número de Prótons e Nêutrons for ímpar: spin = inteiro;
- Número de Prótons par, Nêutrons ímpar: spin = fracionário;
- Número de Prótons ímpar, Nêutrons par: spin = fracionário;

^{14}N : 7 prótons e 7 neutrons, **$I = 1$**

^{10}B : 5 prótons e 5 neutrons, **$I = 3$**

^1H : 1 prótons e 0 neutrons, **$I = 1/2$**

^{13}C : 6 prótons e 7 neutrons, **$I = 1/2$**

^{12}C : 6 prótons e 6 neutrons, **$I = 0$**

Propriedades do núcleo do átomo

Número de estados de spins permitidos: $2I + 1$ variando de $+I$ a $-I$

The image shows two sticky notes with handwritten calculations. The left note is yellow and contains the following text: ${}^1\text{H}, I = 1/2$, $2(1/2) + 1 = 2$, and $-1/2 \text{ e } +1/2$. A pink arrow points to the first line. The right note is green and contains: ${}^{35}\text{Cl}, I = 3/2$, $2(3/2) + 1 = 4$, and $-3/2, -1/2, +1/2 \text{ e } +3/2$. Both notes are secured with orange corner tabs.

Núcleos com $I > 0$, possuem momento angular (P)

A pink arrow points to a white box containing the equation:
$$P = \sqrt{I(I+1)} \cdot \frac{h}{2\pi}$$

Núcleos: momento angular intrínseco

Propriedades do núcleo do átomo

Quando $I = 0$, não há momento magnético

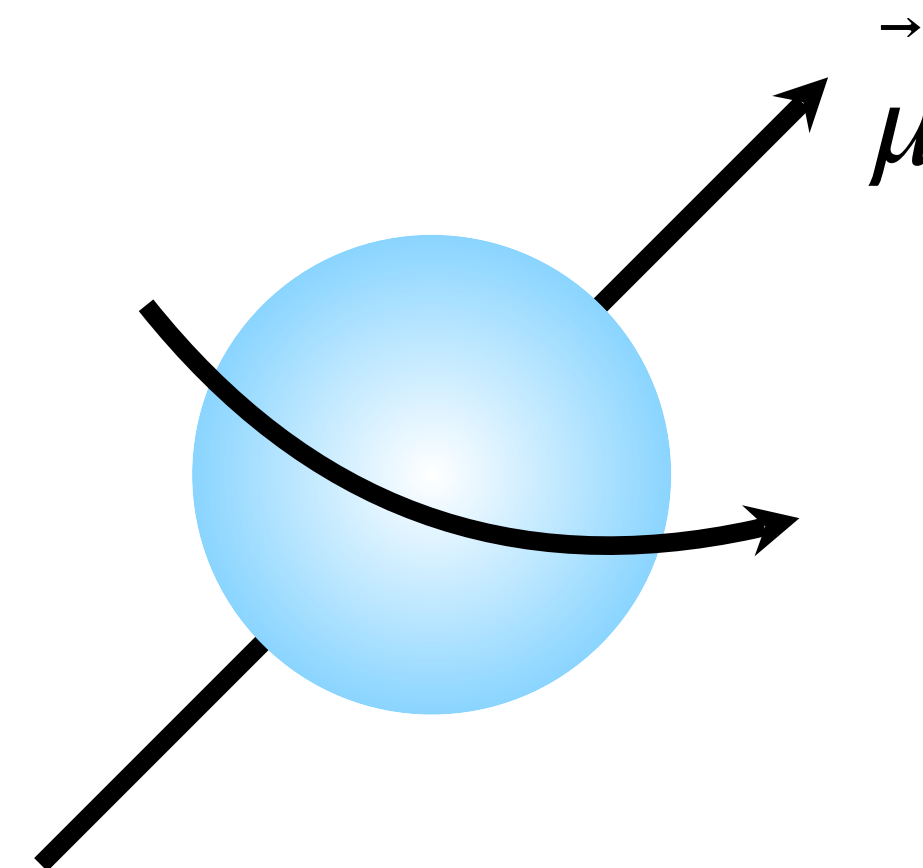
Quando $I > 0$, há momento magnético resultante

O momento magnético nuclear (μ) é proporcional ao spin nuclear (I):

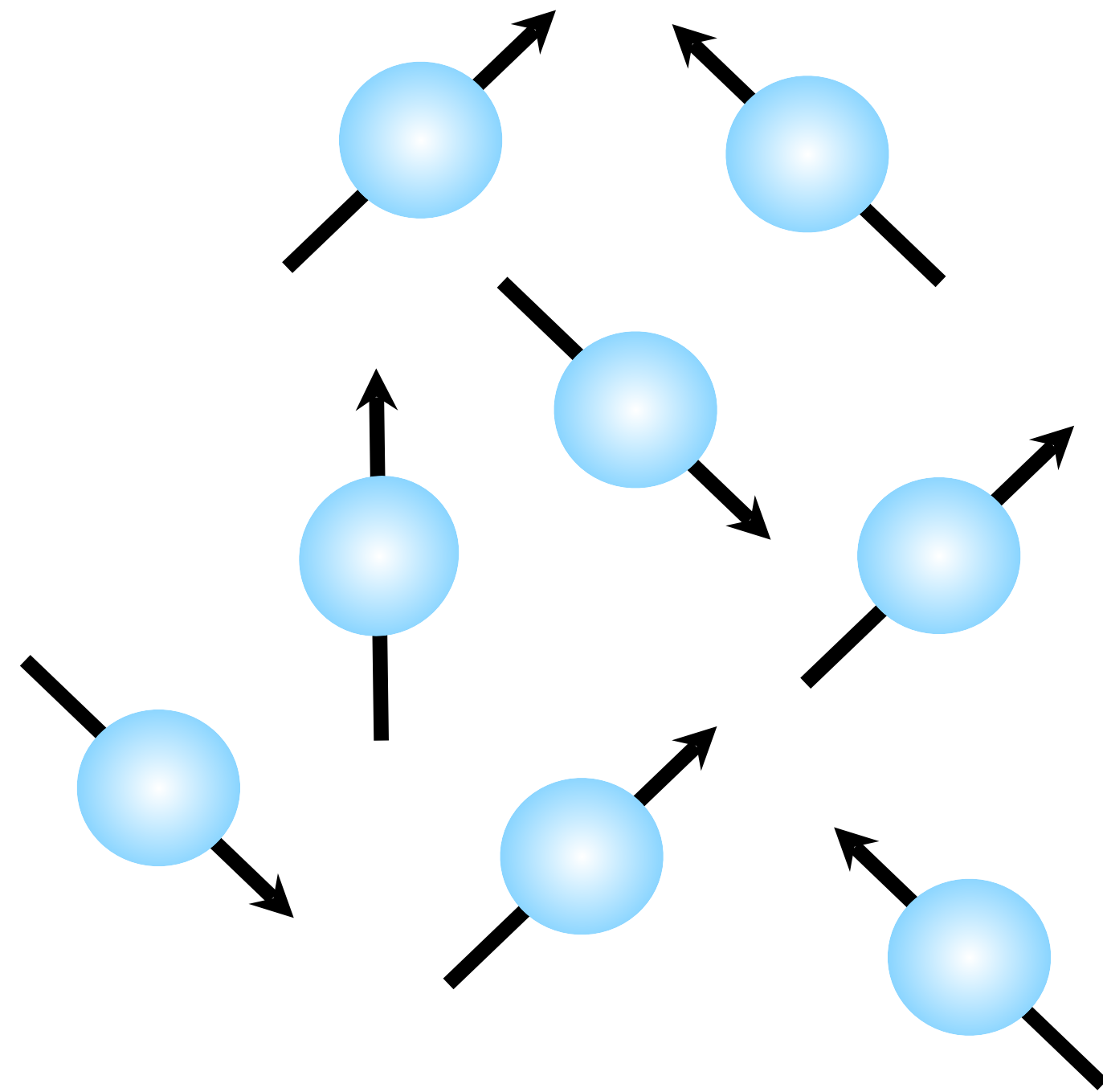
$$\mu = \gamma \hbar I$$

Razão Magnetogírica

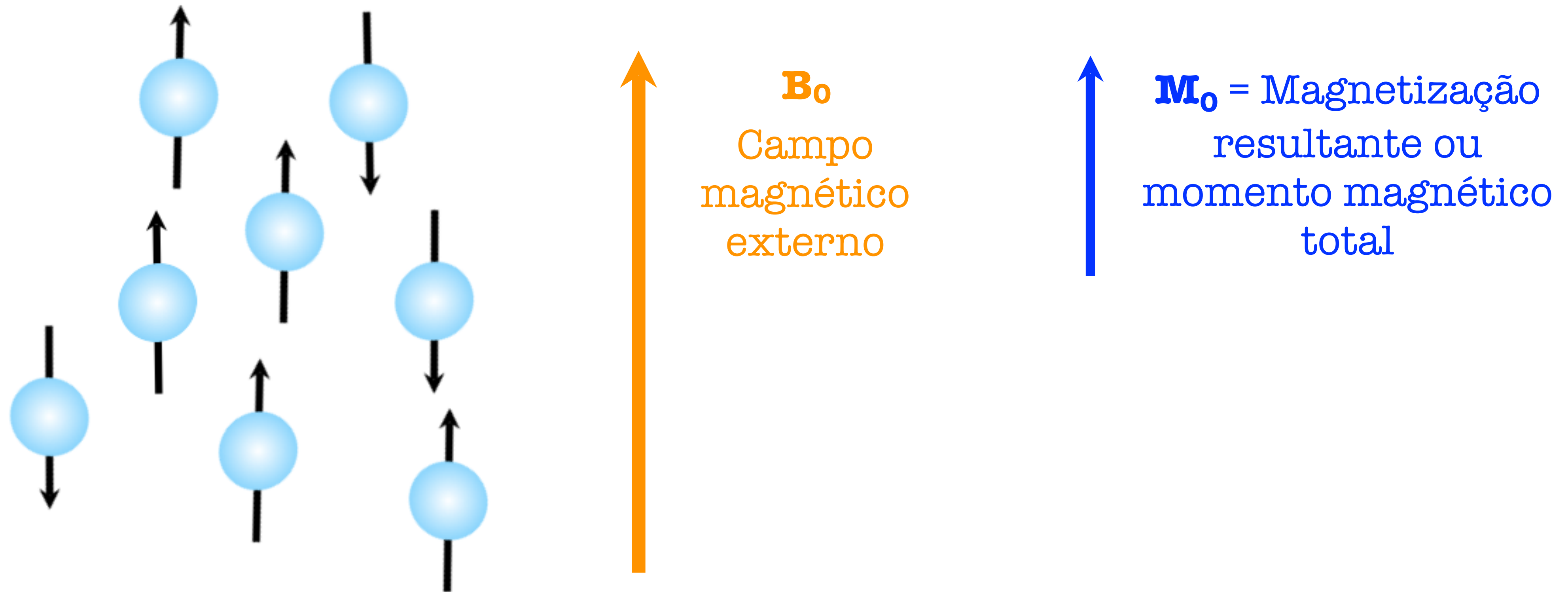
$$\gamma = \frac{\mu}{P}$$



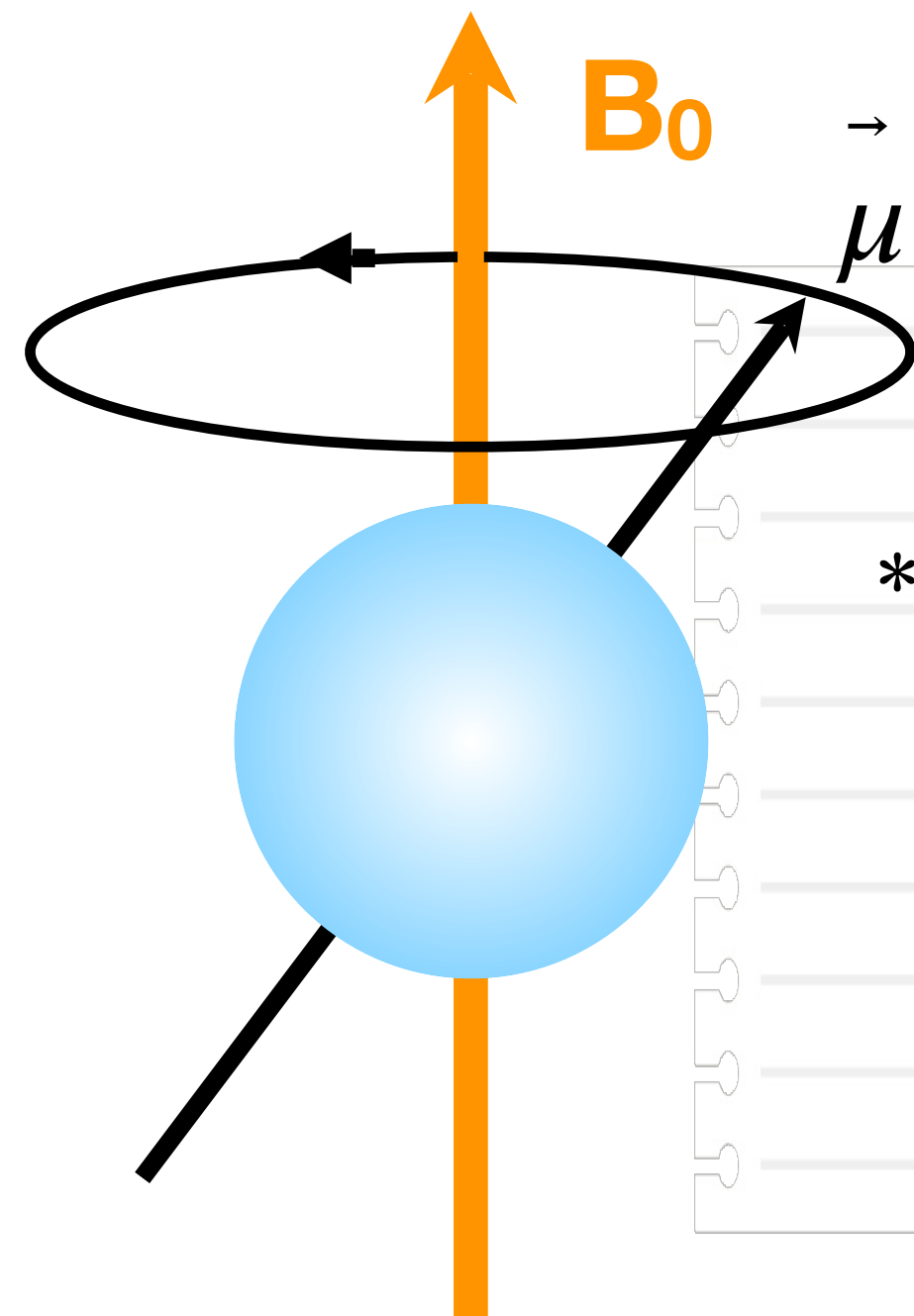
Efeito do campo magnético sobre o spin nuclear



Efeito do campo magnético sobre o spin nuclear



Efeito do campo magnético sobre o spin nuclear

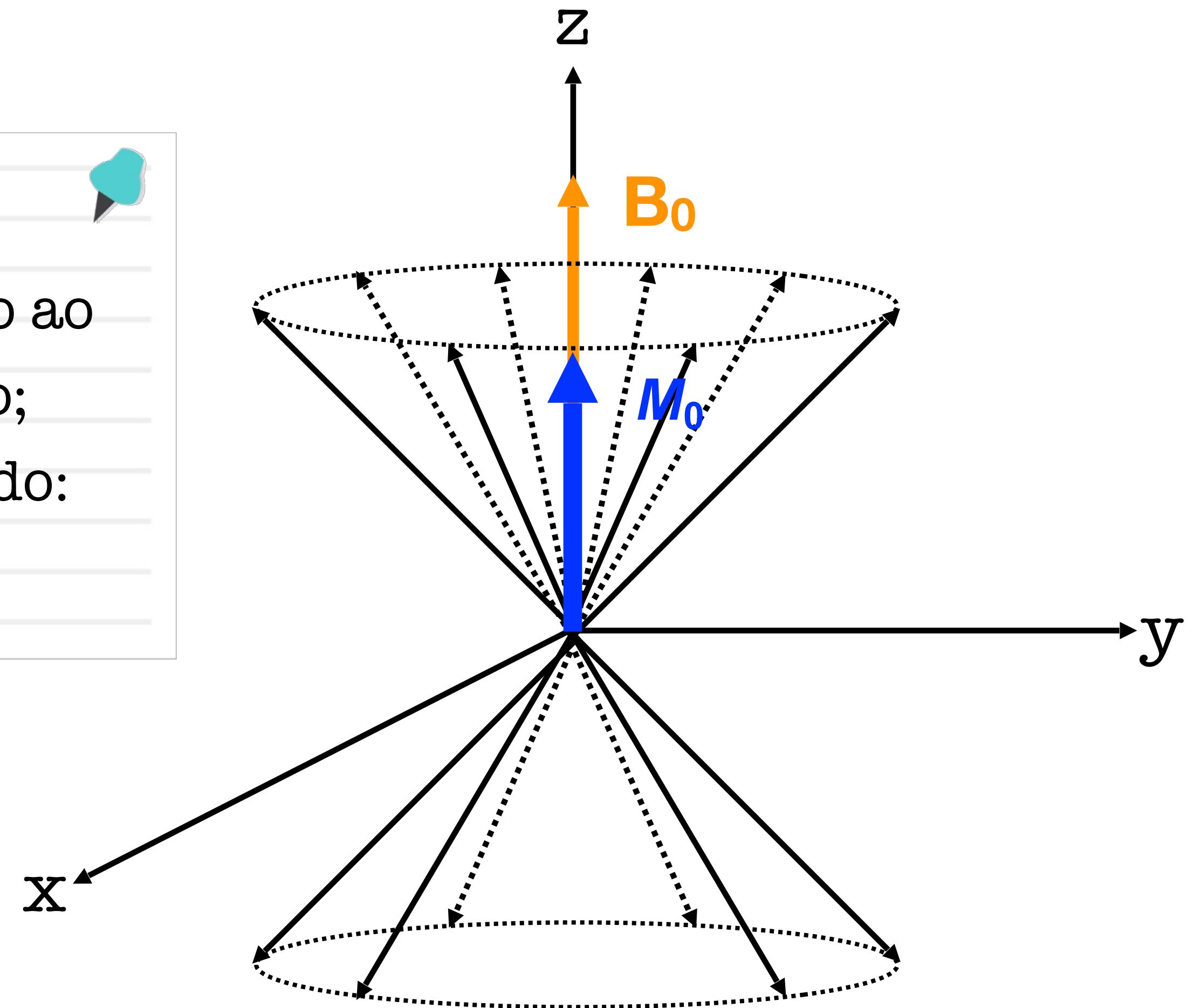


Frequência de Larmor

* Eixo de precessão paralelo ao campo magnético externo;

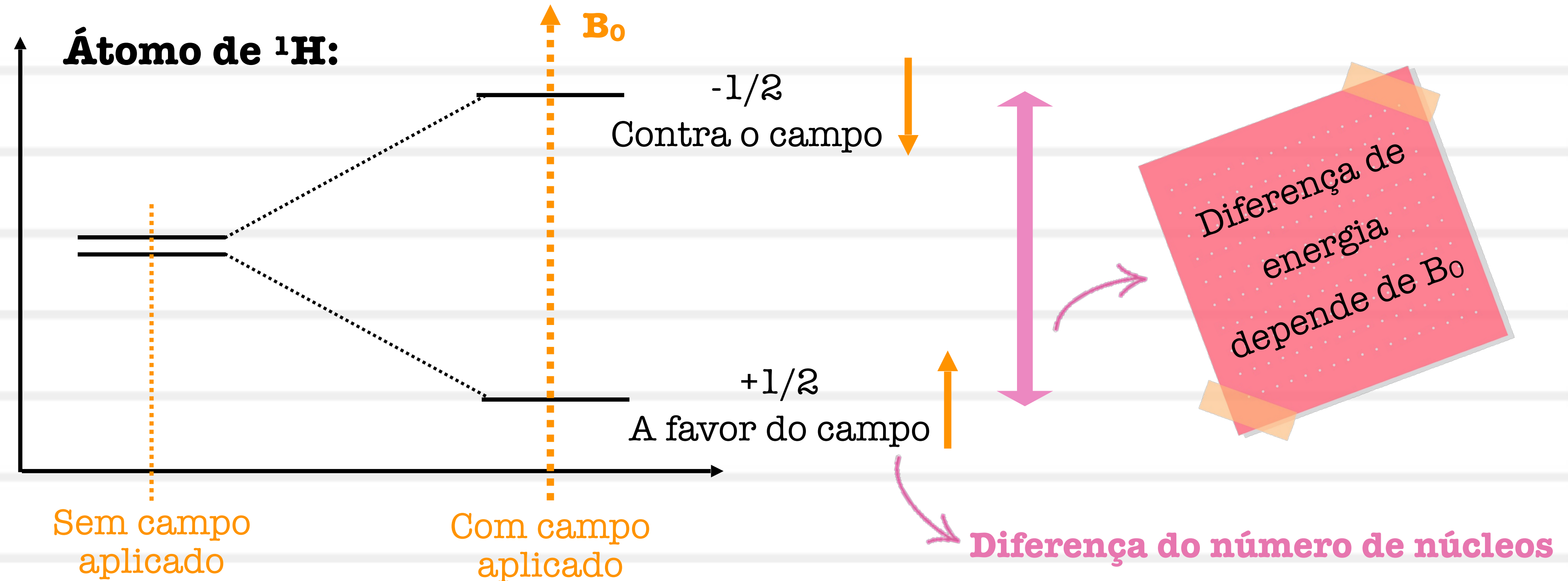
* Proporcional ao B_0 aplicado:

$$\omega = \gamma B_0$$



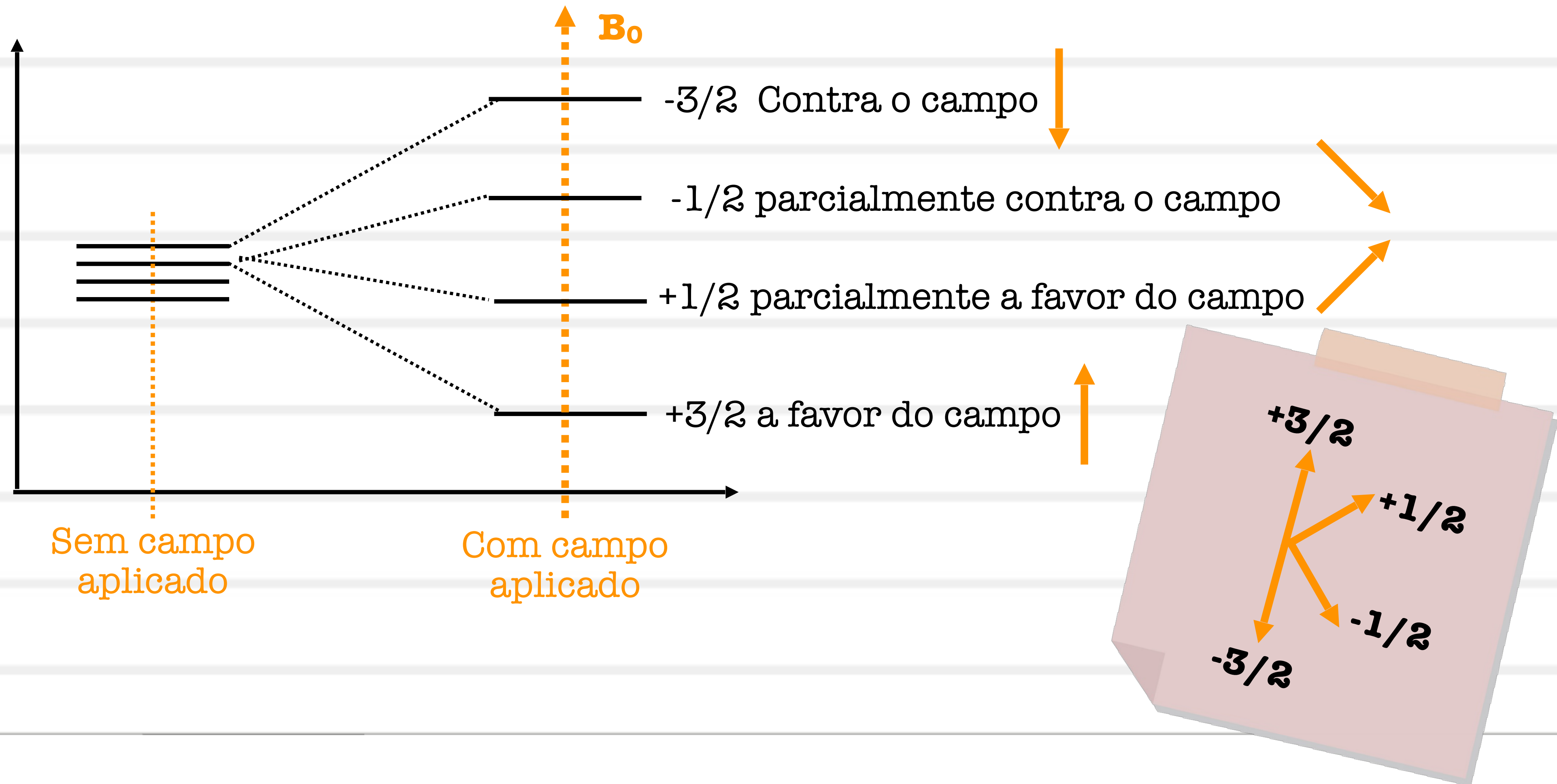
Estados de spin dos núcleos

- Ausência de campo magnético aplicado: Estados de I tem a mesma energia;
- Com campo magnético aplicado: Estados de I possuem energia diferente;

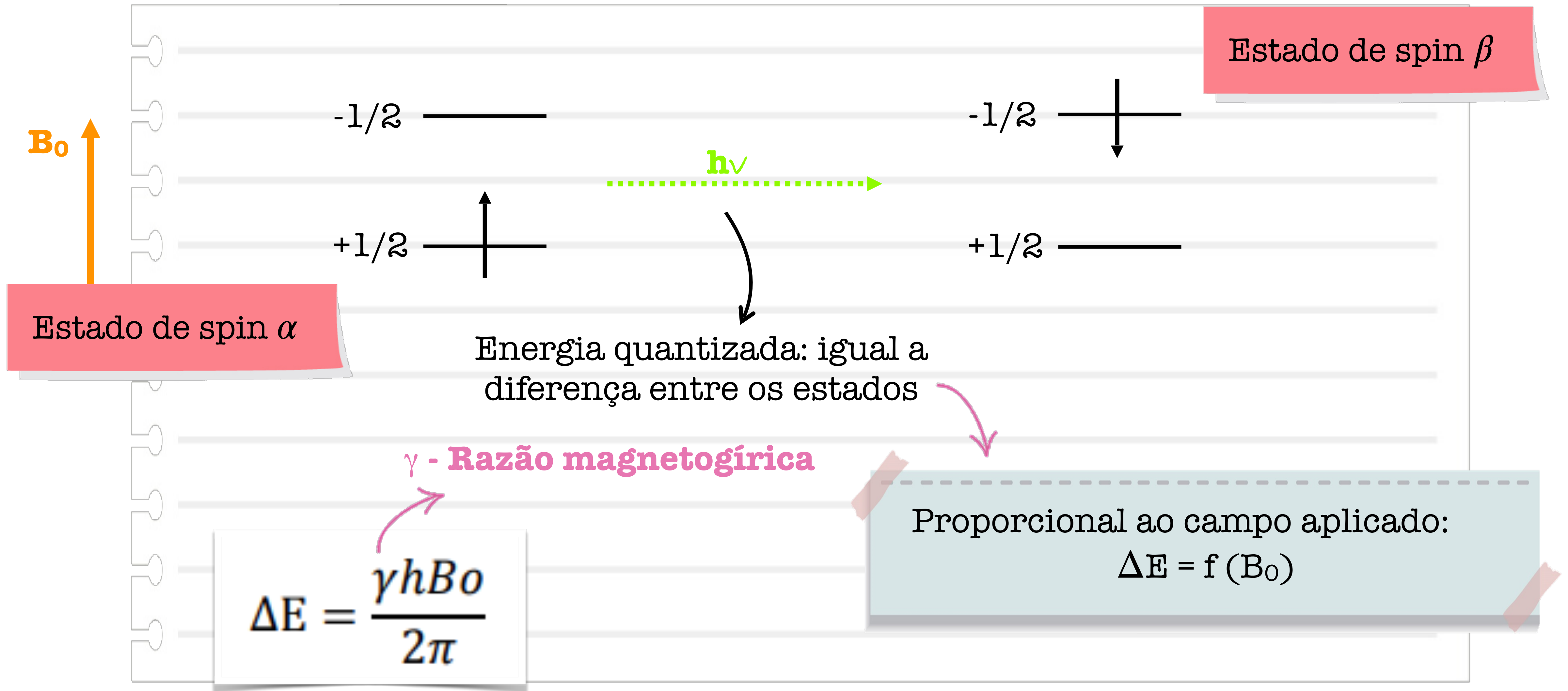


Estados de spin dos núcleos

Para o átomo de cloro:



Absorção de energia



Absorção de energia

$$\Delta E = \gamma \left(\frac{h}{2\pi} \right) B_0 = h\nu$$

TABLE 3.2
FREQUENCIES AND FIELD STRENGTHS AT WHICH SELECTED
NUCLEI HAVE THEIR NUCLEAR RESONANCES

Isotope	Natural Abundance (%)	Field Strength, B_0 (Tesla ^a)	Frequency, ν (MHz)	Magnetogyric Ratio, γ (radians/Tesla)
¹ H	99.98	1.00	42.6	267.53
		1.41	60.0	
		2.35	100.0	
		4.70	200.0	
		7.05	300.0	
² H	0.0156	1.00	6.5	41.1
¹³ C	1.108	1.00	10.7	67.28
		1.41	15.1	
		2.35	25.0	
		4.70	50.0	
		7.05	75.0	
¹⁹ F	100.0	1.00	40.0	251.7
³¹ P	100.0	1.00	17.2	108.3

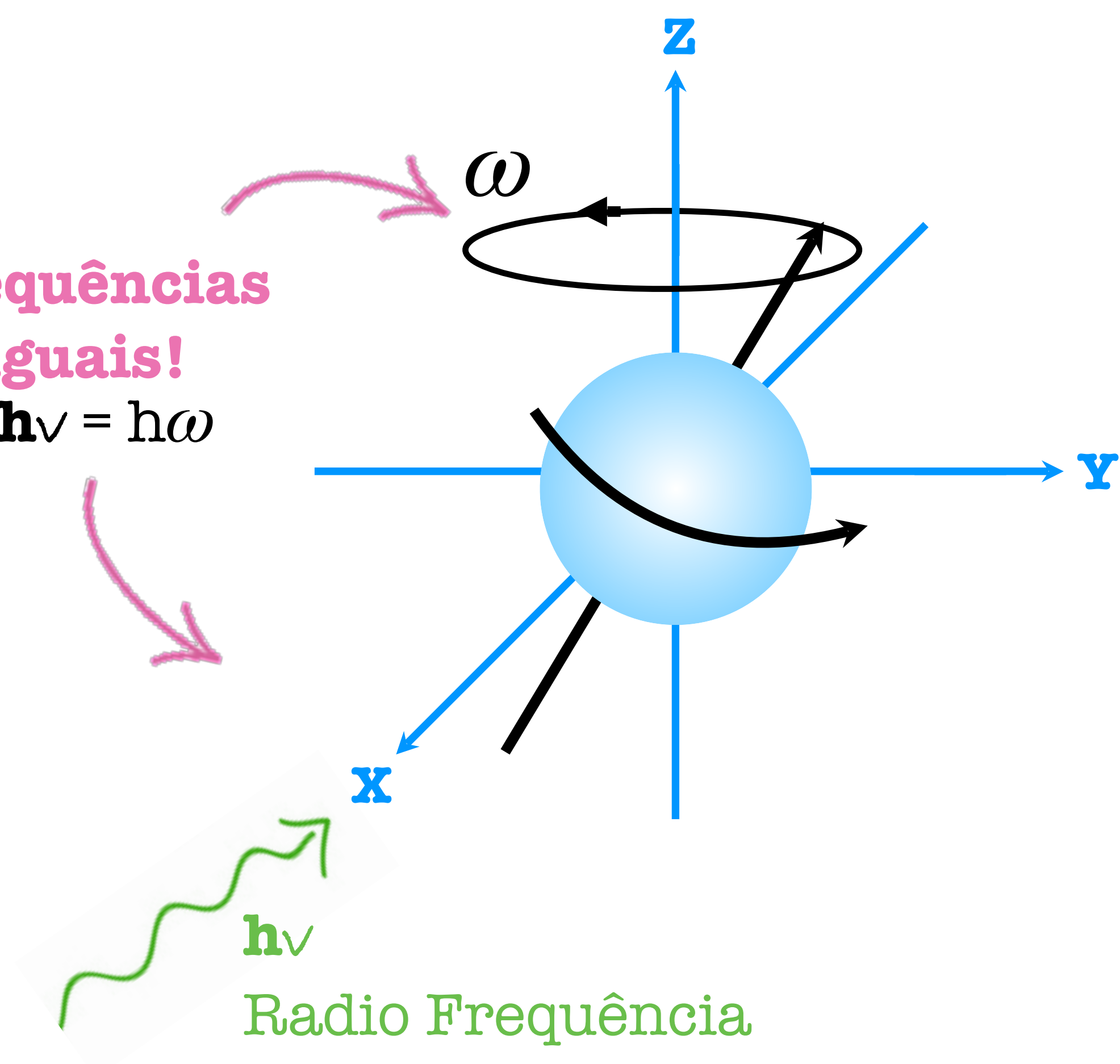
^a 1 Tesla = 10,000 Gauss.

Absorção de energia

B_0



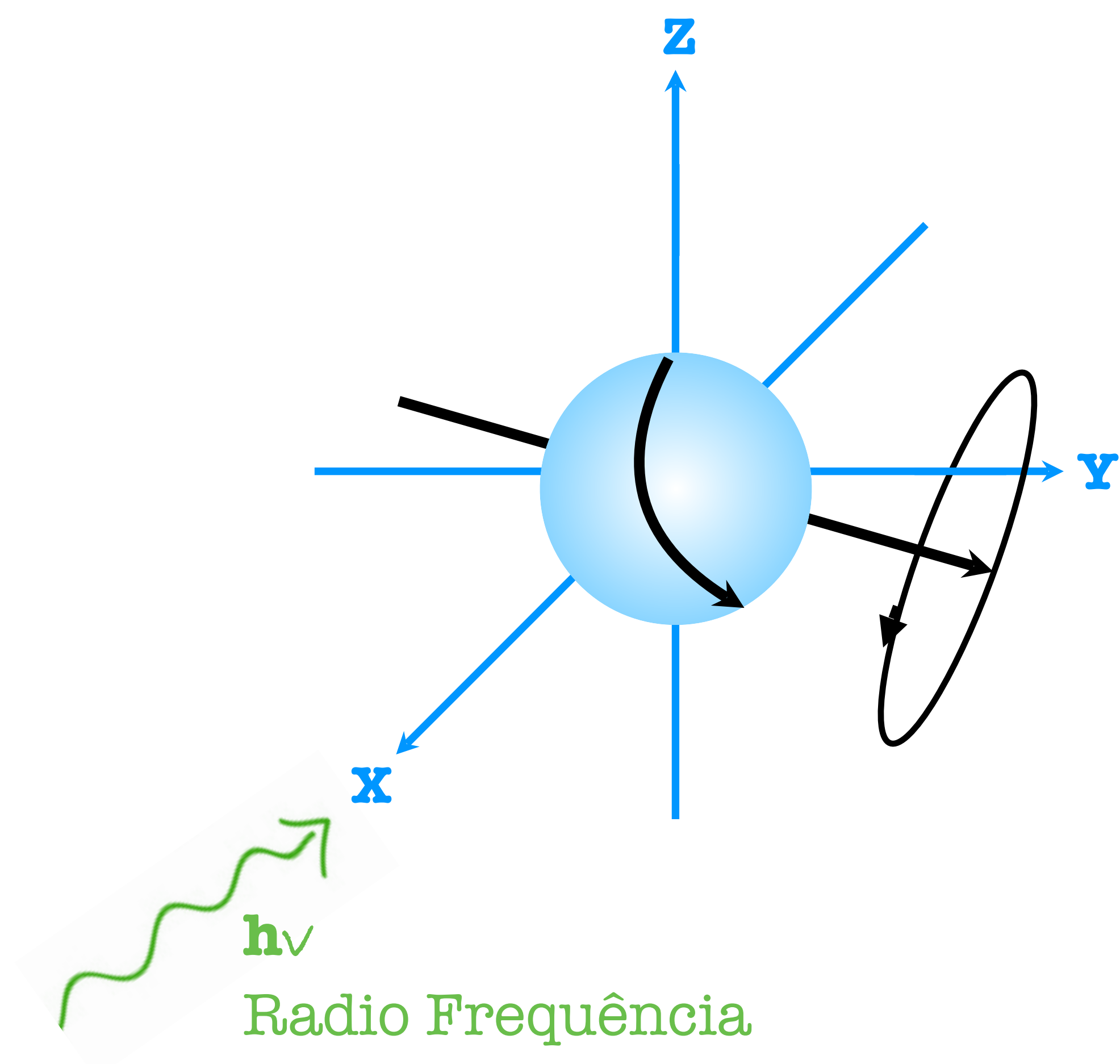
Frequências iguais!
 $h\nu = h\omega$



Absorção de energia
Mudança de spin
Ressonância

Absorção de energia

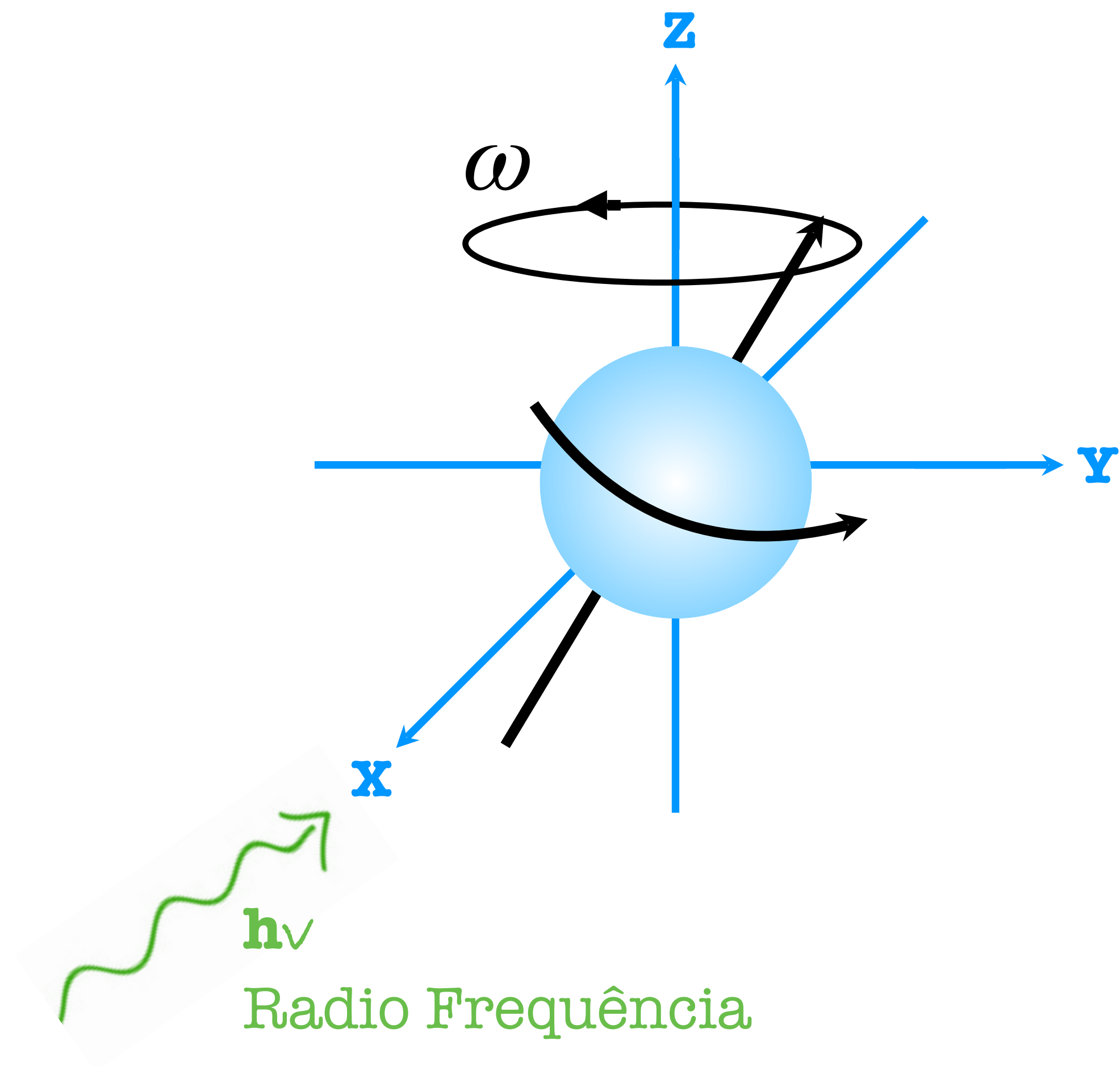
B_0



Absorção de energia
Mudança de spin
Ressonância

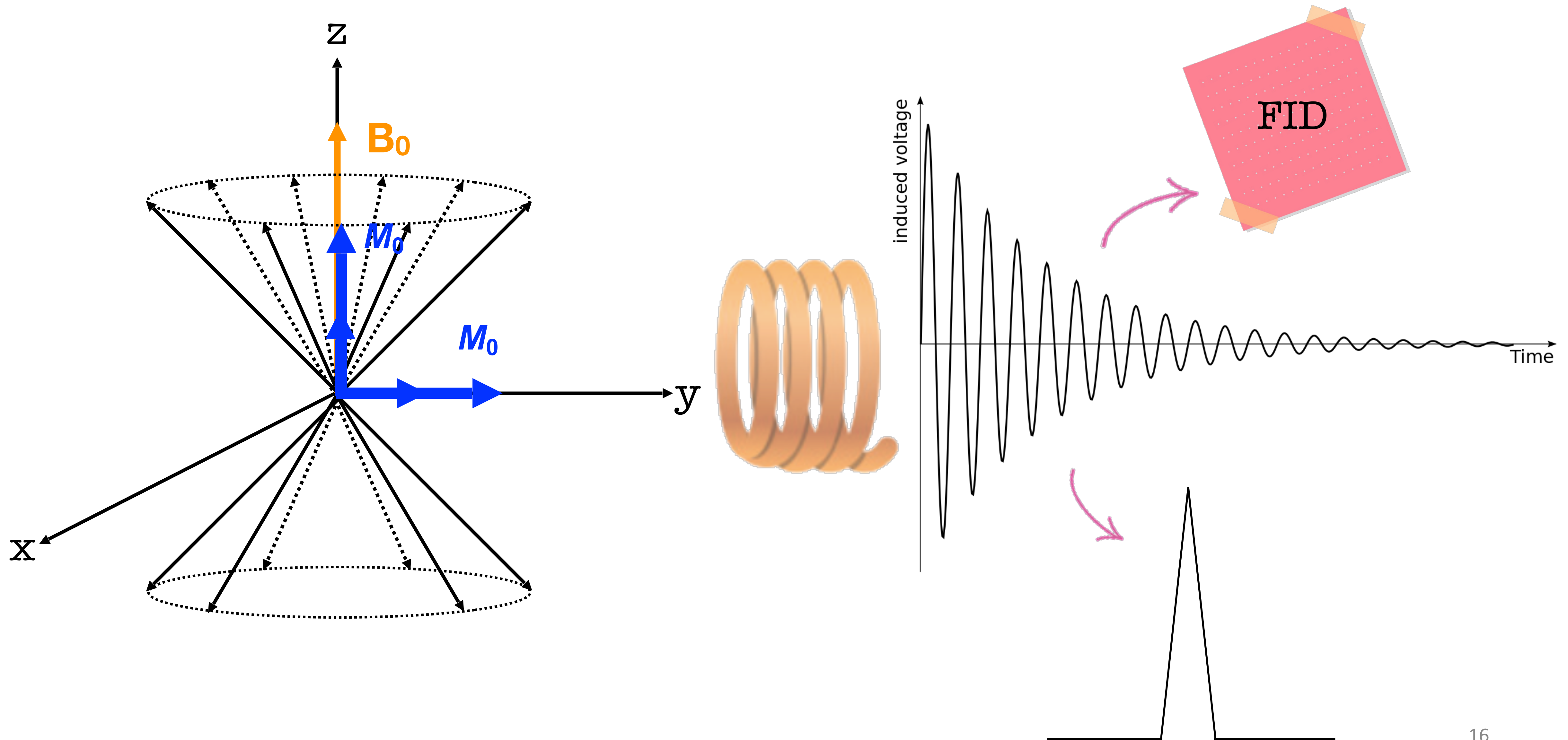
Absorção de energia

B_0

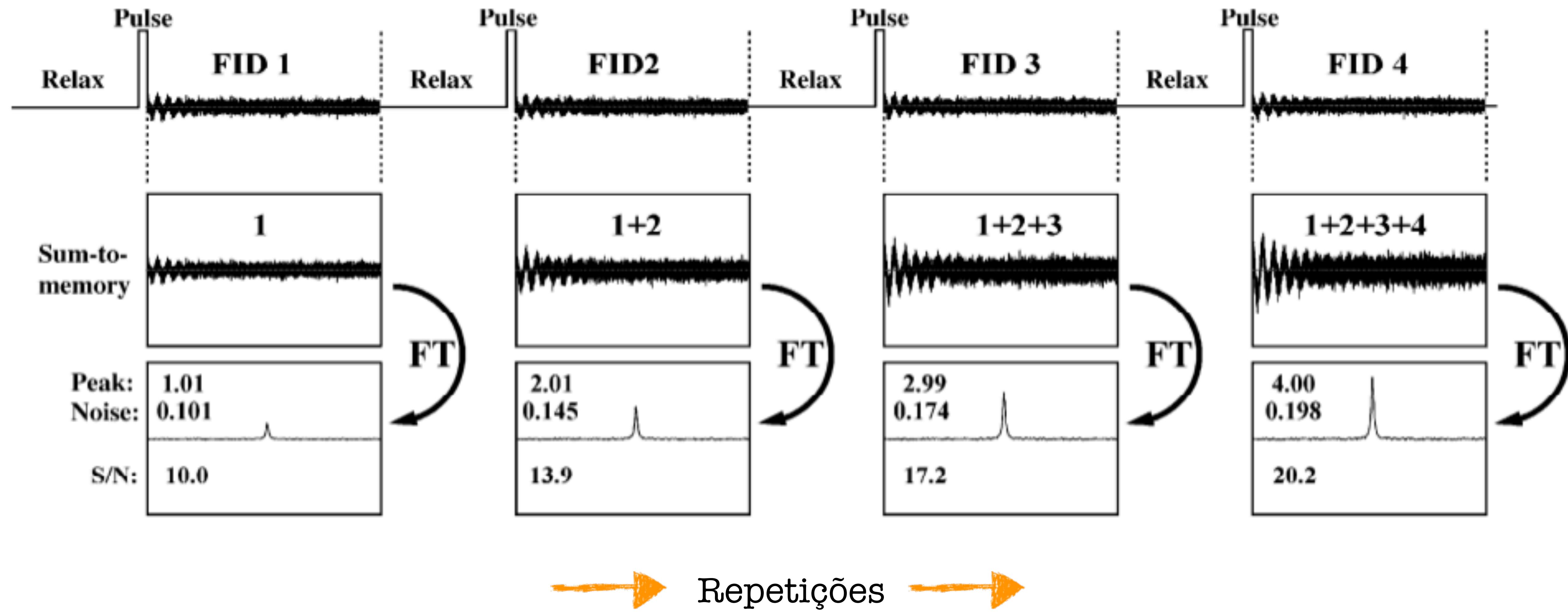


Absorção de energia
Mudança de spin
Ressonância

Absorção de energia, Relaxação e Detecção



Absorção de energia, Relaxação e Detecção



Densidades populacionais

Maior população no estado α é necessária;

Saturação não gera sinal;

B_0 mais fortes geram sinais melhores;

Distribuição de Boltzmann:

$$N_{\beta}/N_{\alpha} = e^{-\Delta E/KT} = e^{-h\nu/KT}$$

ΔE = Diferença de energia entre os estados;

K = Constante de Boltzmann

h = Constante de Planck

ν = Frequência de operação

$T = 298 \text{ K (} 25 \text{ }^{\circ}\text{C)}$

Frequência do experimento

B_0 (Tesla)	ν (MHz)	N^α / N^β
1,41	60	9
2,35	100	16
4,7	200	32
7,05	300	48
9,4	400	64
14,1	600	96



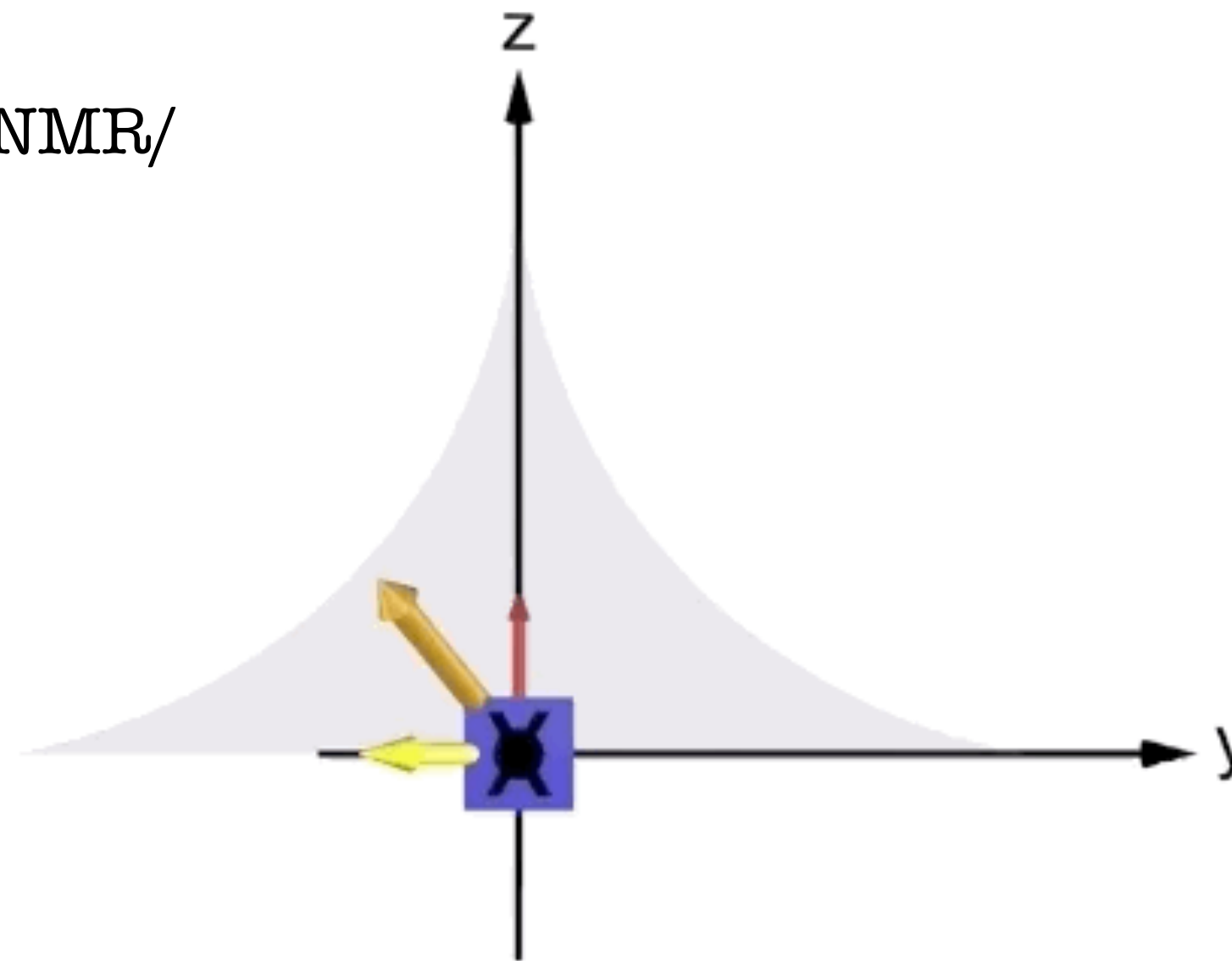
<https://www.jeol.co.jp/en/products/detail/JNM-ECZR.html>



<https://www.birmingham.ac.uk/facilities/nmr/index.aspx>

Relaxação

<https://www.imaios.com/br/e-Cursos/e-MRI/NMR/Relaxation-nmr>



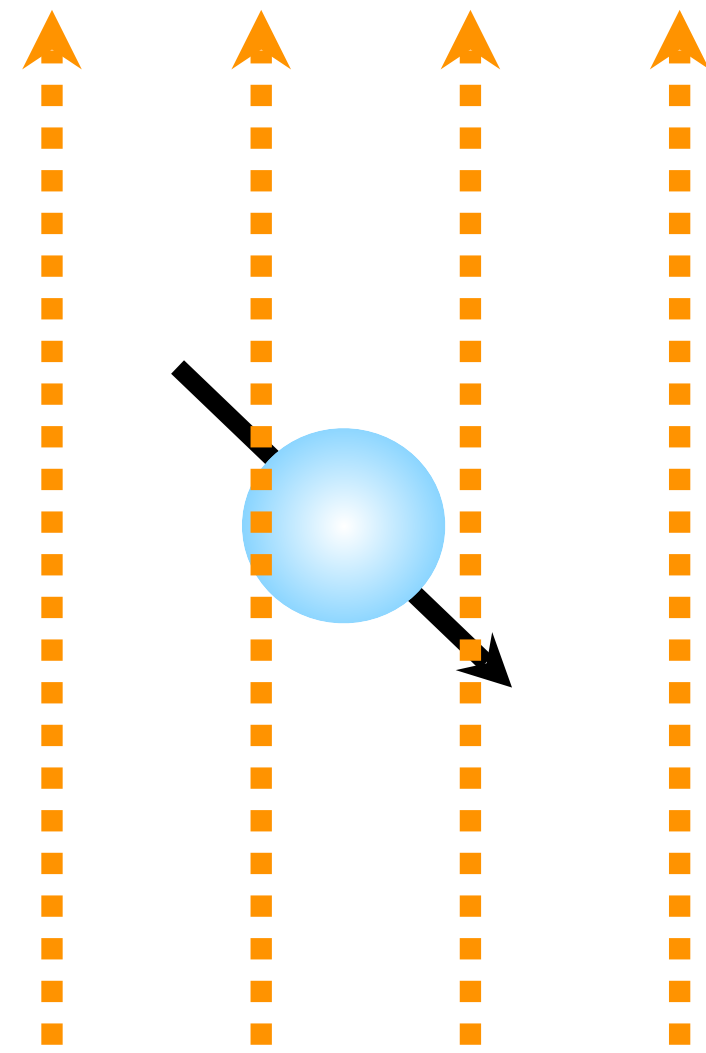
T1 → Relaxação spin-lattice ou longitudinal

- Transferência de energia para o solvente com decaimento exponencial;
- Resulta em pequeno aumento de temperatura da amostra.

T2 → Relaxação spin-spin ou transversal

- Troca de energia entre os núcleos excitados e os em estado de menor energia;
- Spins e momentos magnéticos ficam randômicos.

Deslocamento Químico

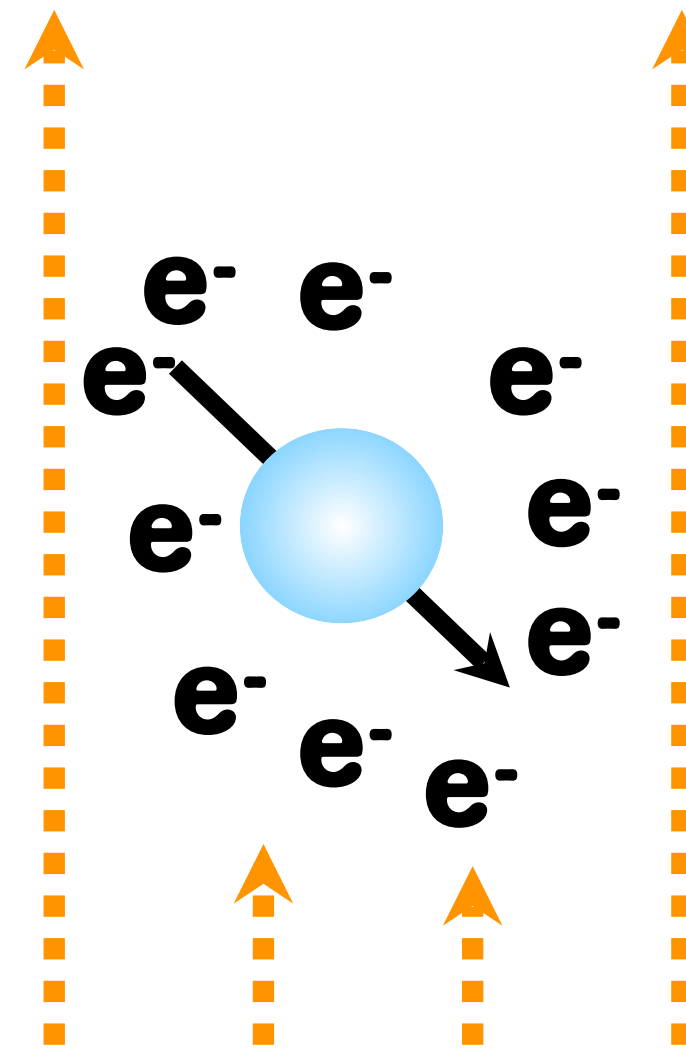


B_0

Campo magnético externo

$$B_{\text{efetivo}} = B_{\text{aplicado}} - 0$$

$$B_{\text{efetivo}} = B_{\text{aplicado}}$$



B_0

Campo magnético externo

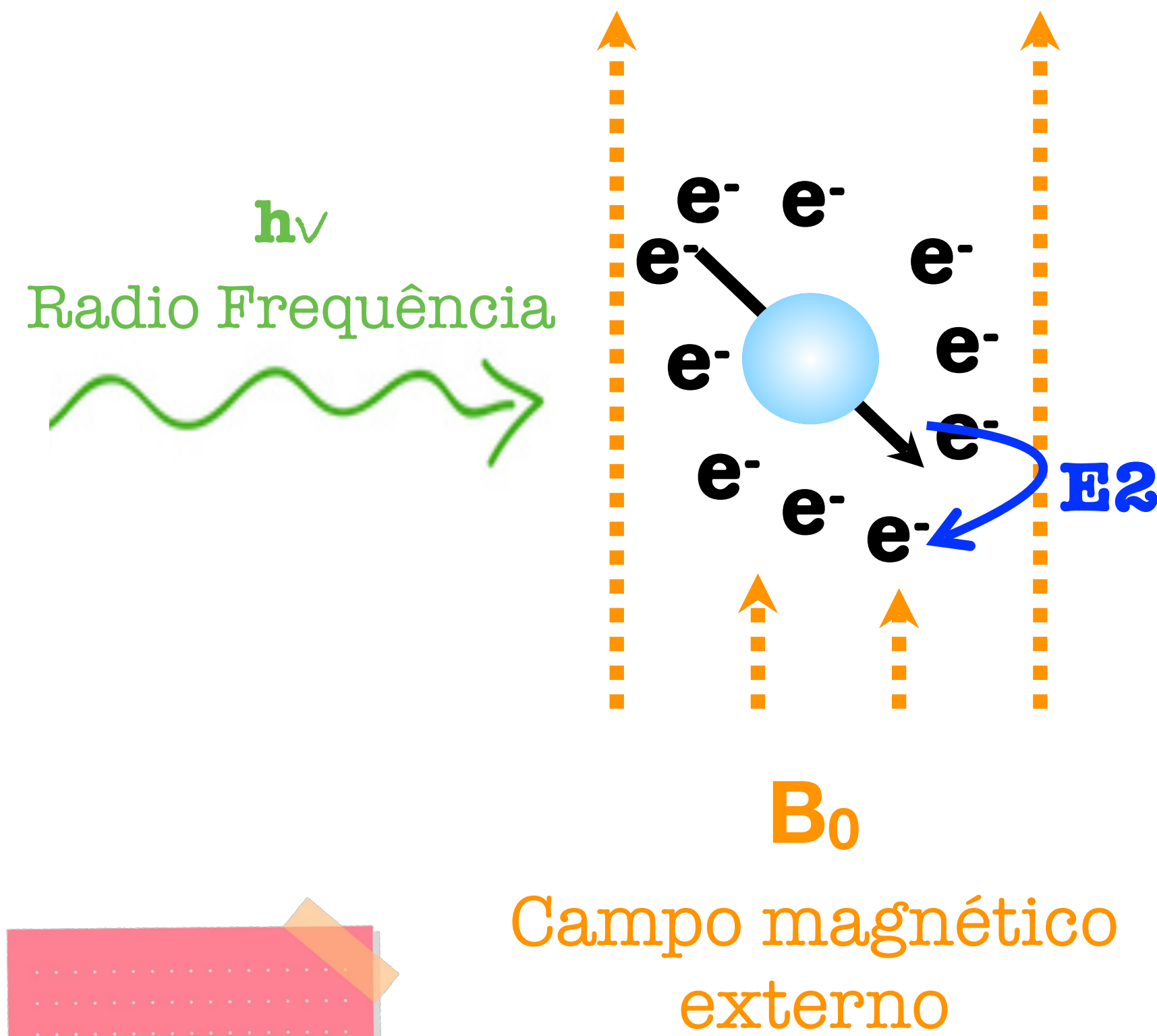
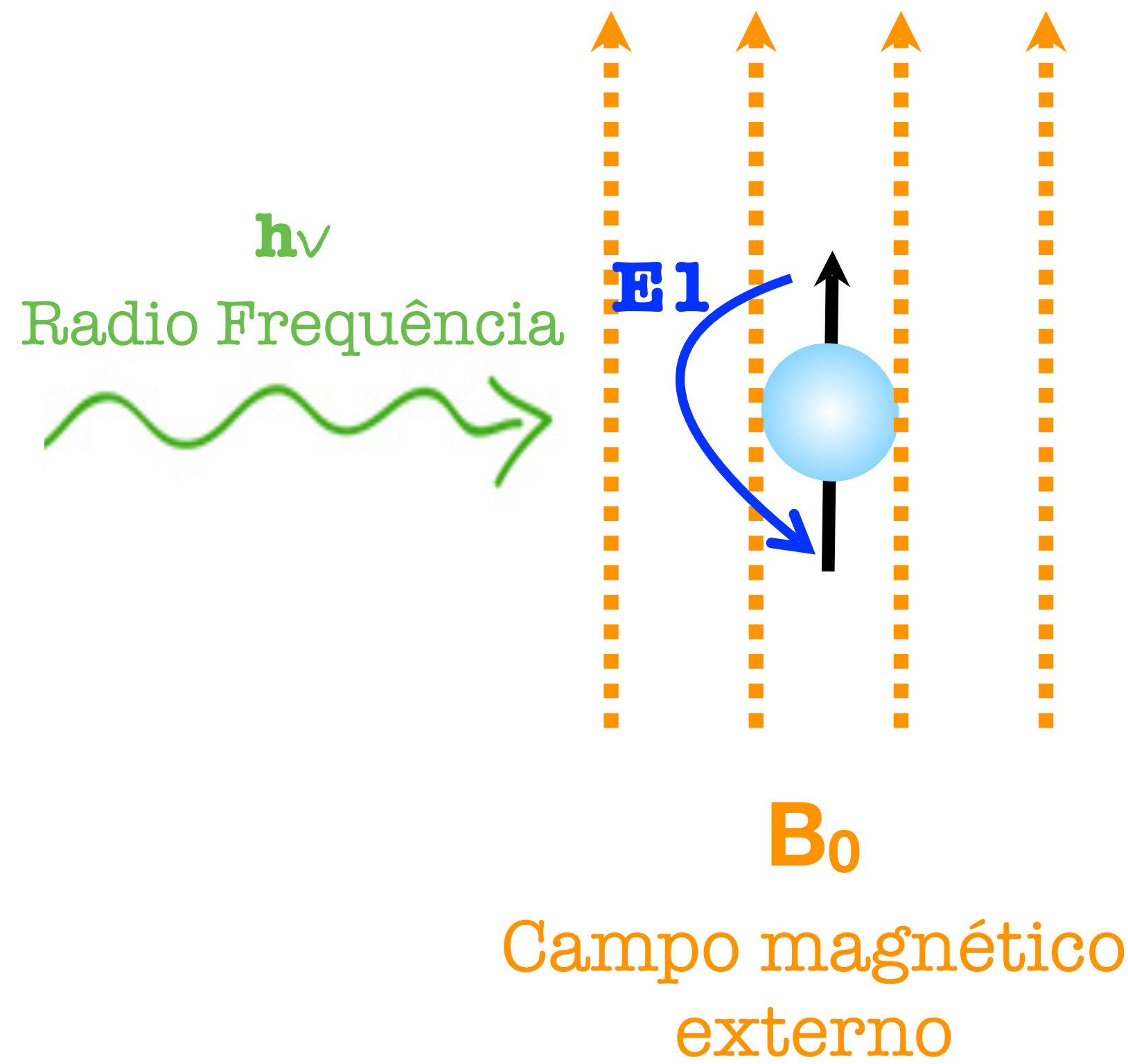
$$B_{\text{efetivo}} = B_{\text{aplicado}} - (>0)$$

$$B_{\text{efetivo}} < B_{\text{aplicado}}$$

Núcleos em ambientes químicos diferentes levam a sinais diferentes

$$B_{\text{efetivo}} = B_{\text{aplicado}} - B_{\text{local}}$$

Deslocamento Químico

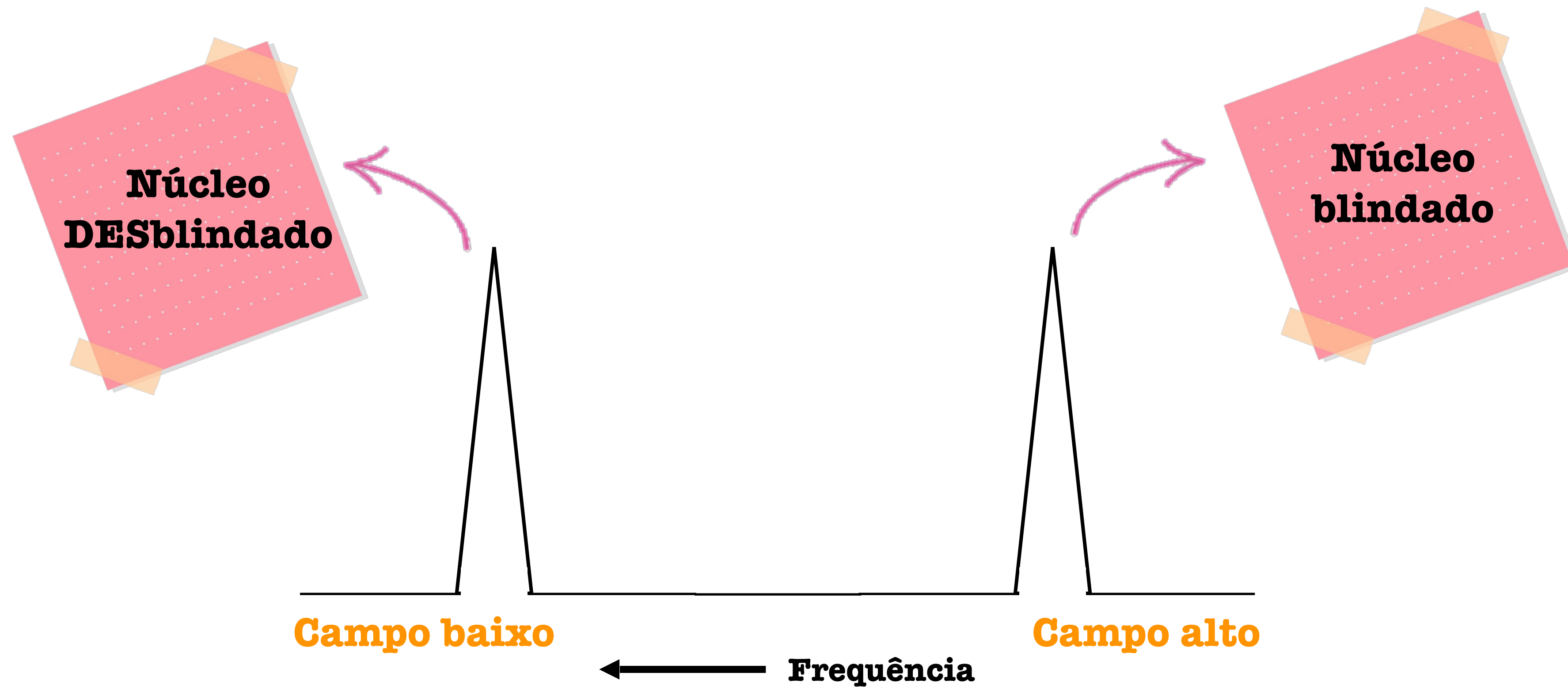


E1 > E2

Núcleos em ambientes químicos diferentes levam a sinais diferentes

Prótons blindados precisam de menor energia para entrar em ressonância

Deslocamento Químico



Esquema simplificado de um espectro de RMN

Deslocamento Químico


	Frequência	Eletronegatividade do halogênio
CH_3I	ν_i	2,66
CH_3Br	$\nu_i + 53 \text{ Hz}$	2,96
CH_3Cl	$\nu_i + 90 \text{ Hz}$	3,16
CH_3F	$\nu_i + 211 \text{ Hz}$	3,98

Grupos eletronegativos diminuem a densidade eletrônica em volta do núcleo (desblindam)




Deslocamento Químico

Efeito maior para maior número de átomos eletronegativos



CHCl_3	CH_2Cl_2	CH_3Cl	
7,27	5,30	3,05	(ppm)

Efeito diminui com a distância



RCH_2Br	$\text{RCH}_2\text{CH}_2\text{Br}$	$\text{RCH}_2\text{CH}_2\text{CH}_2\text{Br}$	
3,30	1,69	1,25	(ppm)

Deslocamento Químico

Deslocamento Químico (δ)

Posição de um sinal em relação a uma referência

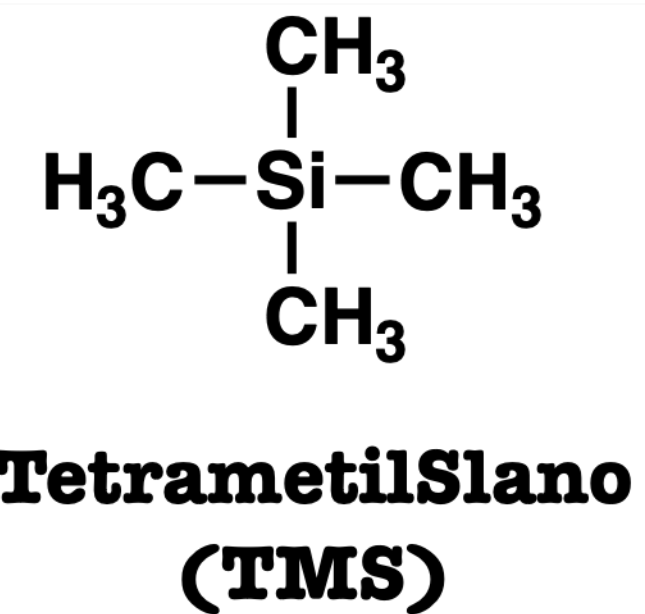
Gera somente um sinal no espectro (simétrico)

Sinal muito blindado (zero da escala)

Volátil

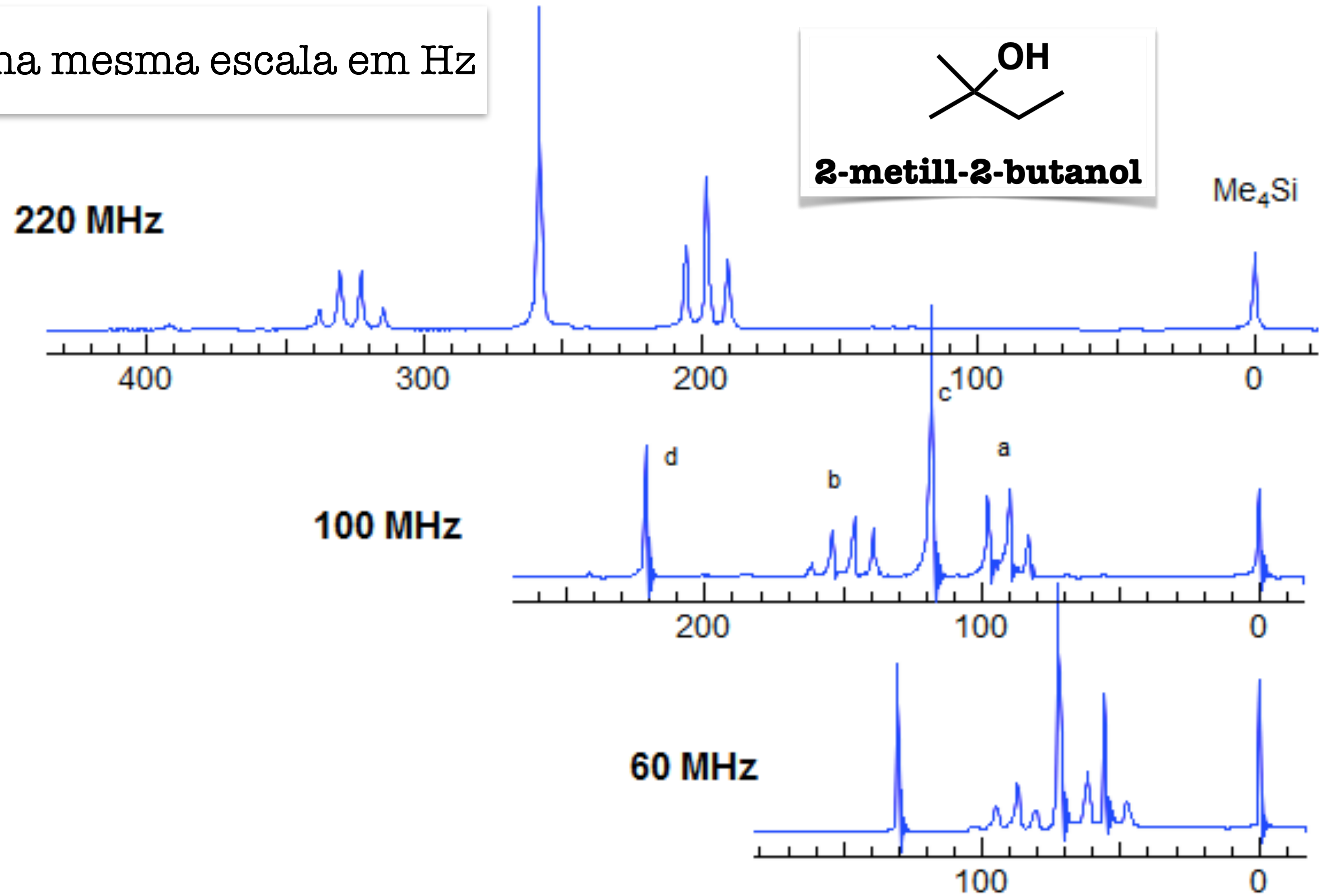
Solúvel na maioria dos solventes

Quimicamente inerte



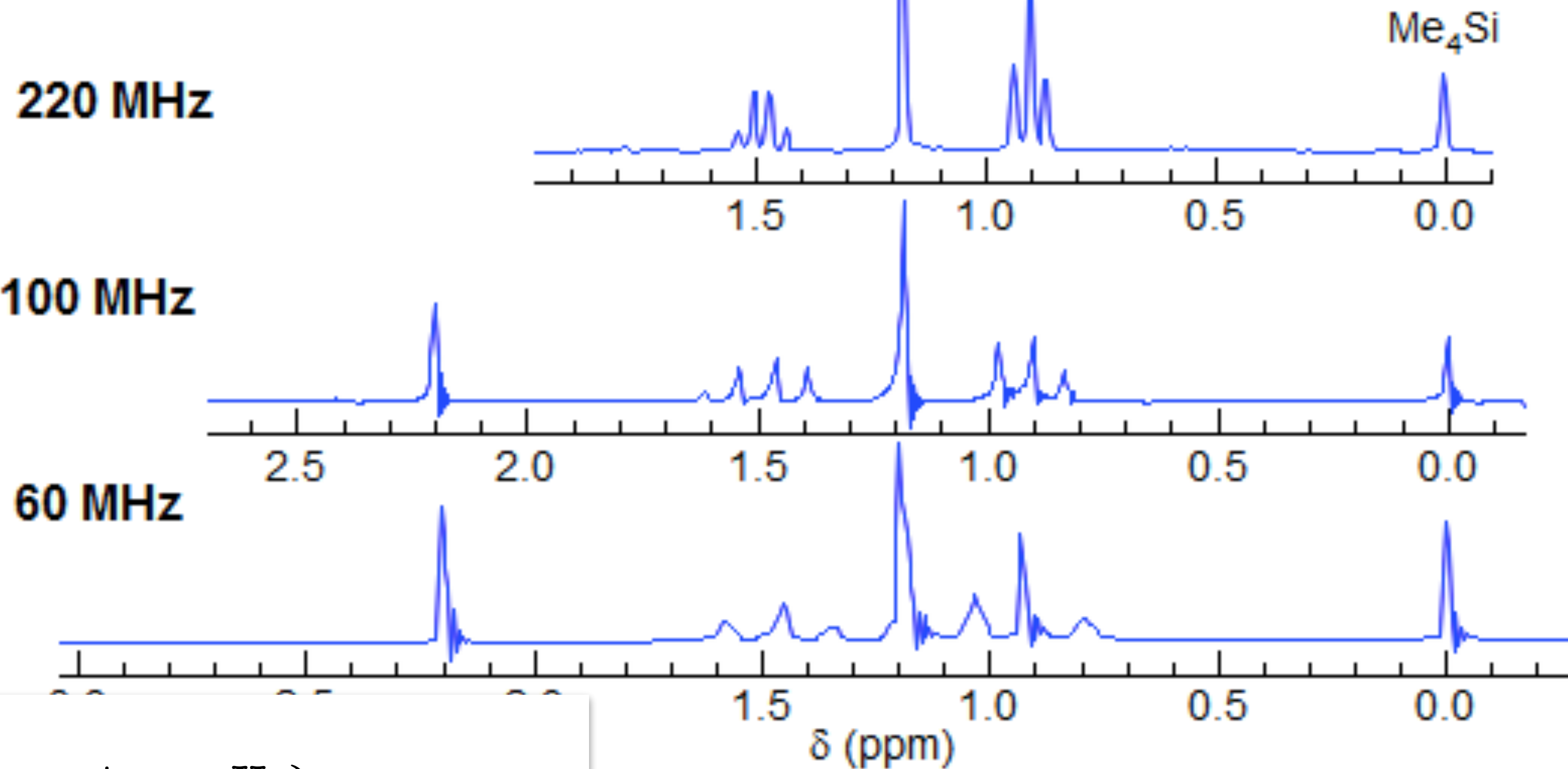
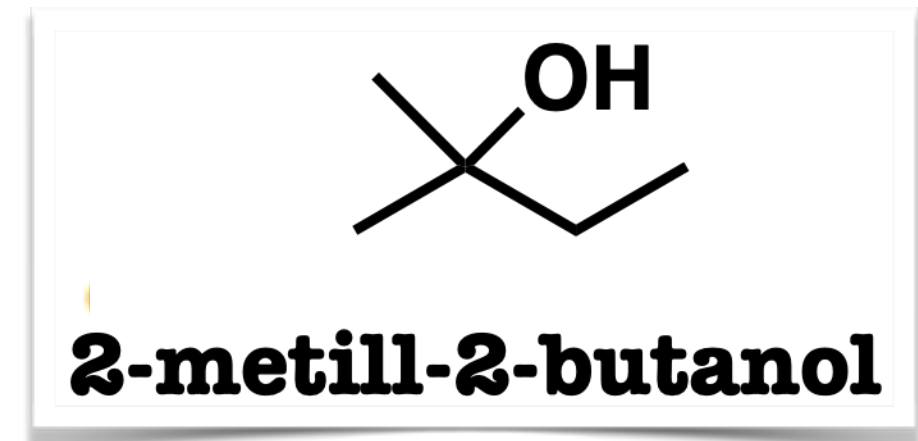
Deslocamento Químico

Espectros plotados na mesma escala em Hz



Deslocamento Químico

Espectros plotados na mesma escala em **ppm**

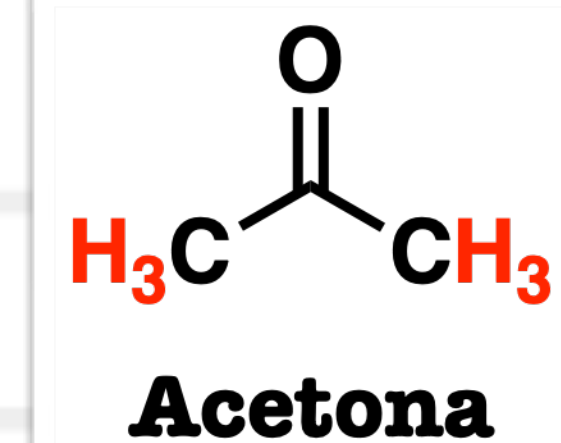
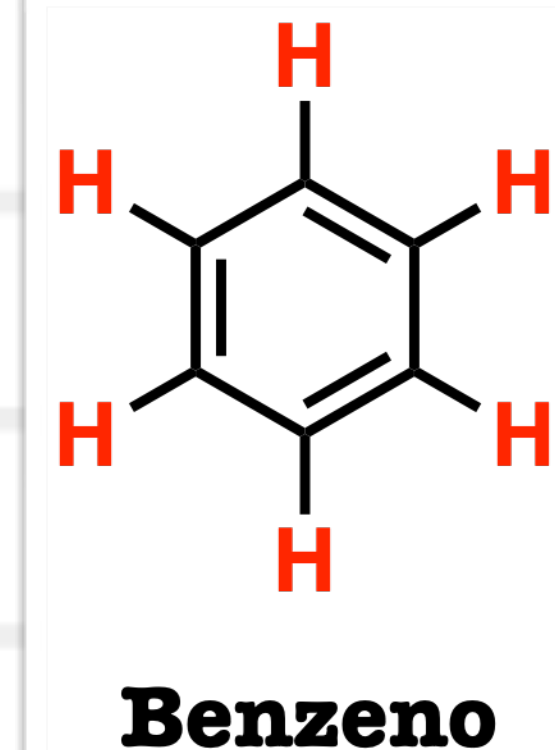
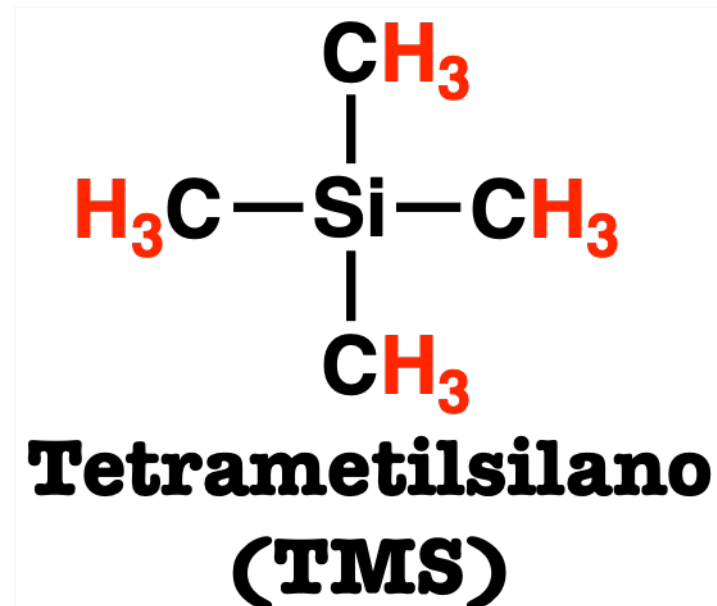


$$\delta = \frac{\text{(Deslocamento em Hz)}}{\text{(Frequência do Espectrômetro em MHz)}}$$

Equivalência Química

Prótons em ambientes quimicamente idênticos dentro de uma molécula
são **QUIMICAMENTE EQUIVALENTES**;

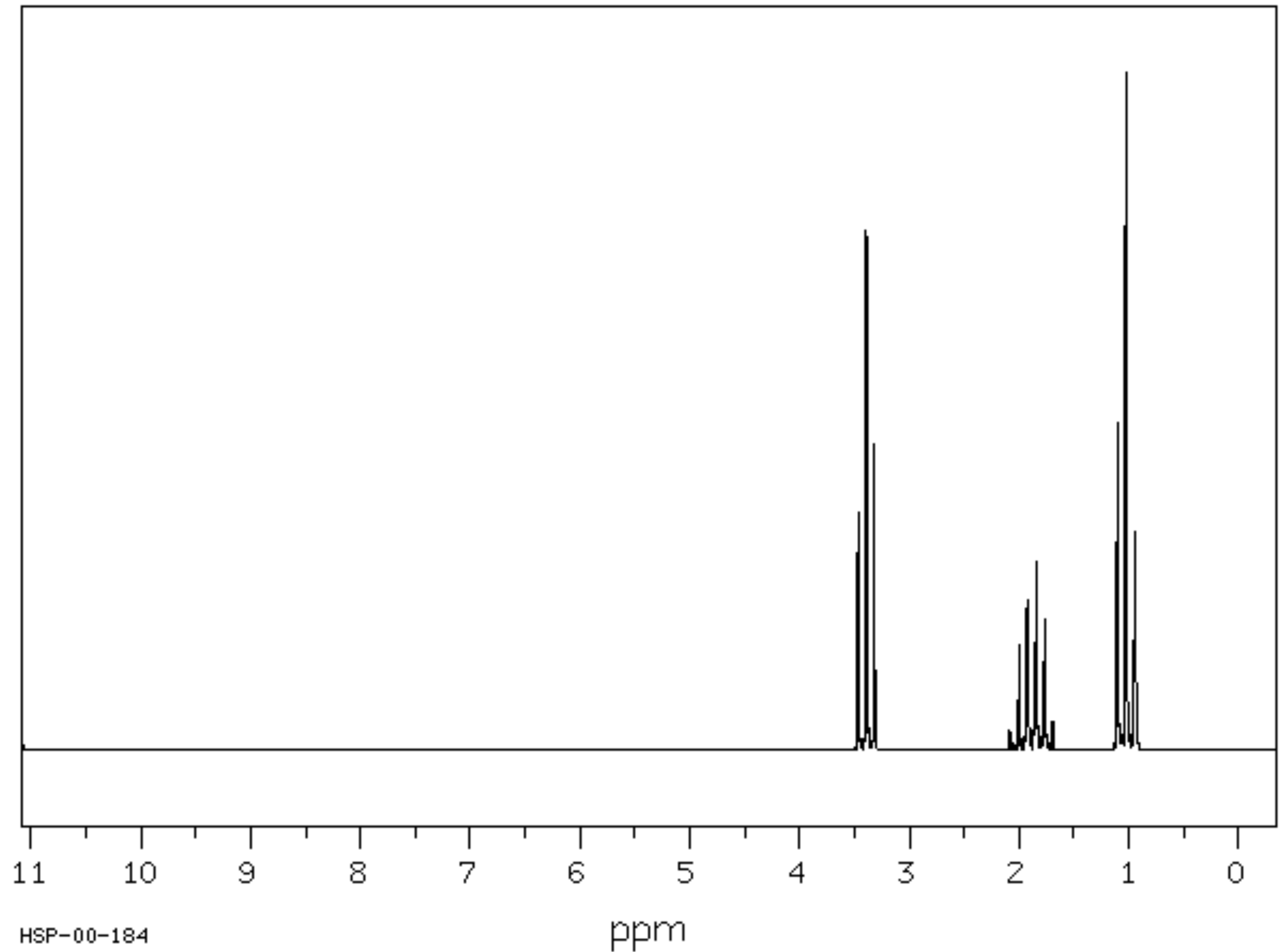
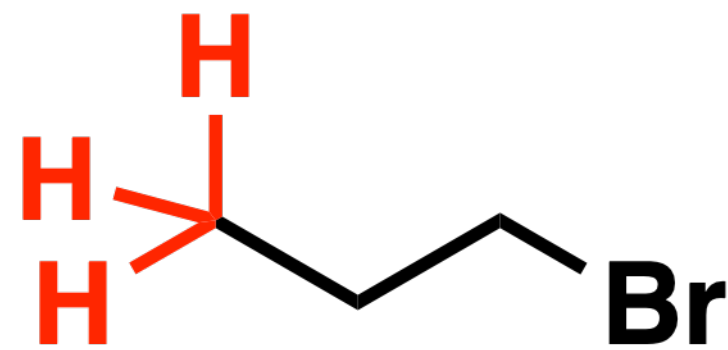
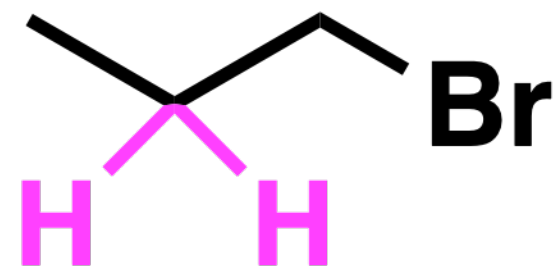
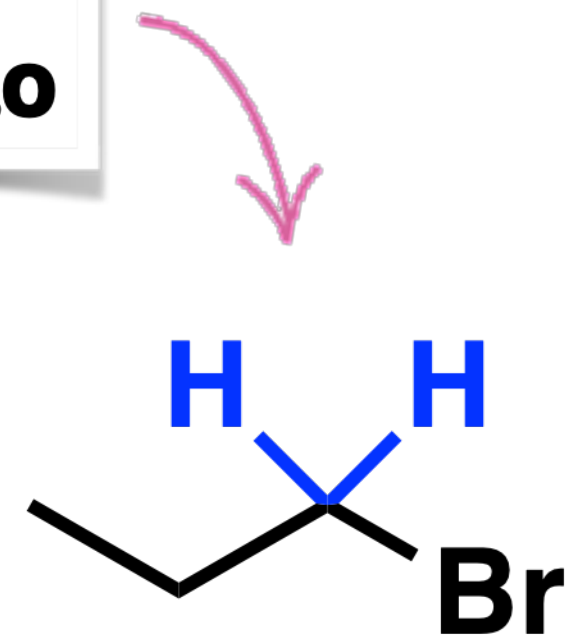
Exibem o mesmo deslocamento químico.



12 hidrogênios e um único
sinal no espectro de RMN ¹H!

Equivalência Química

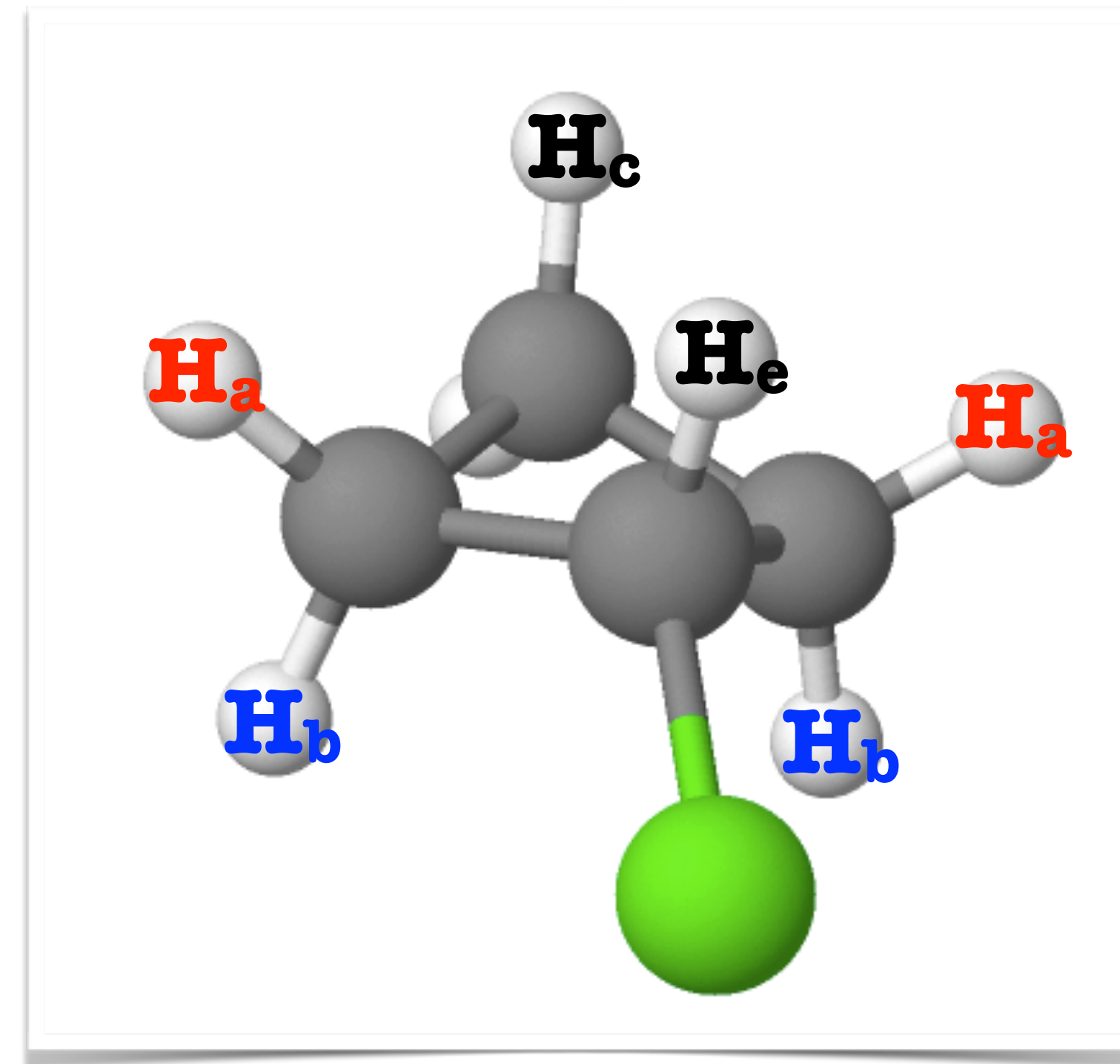
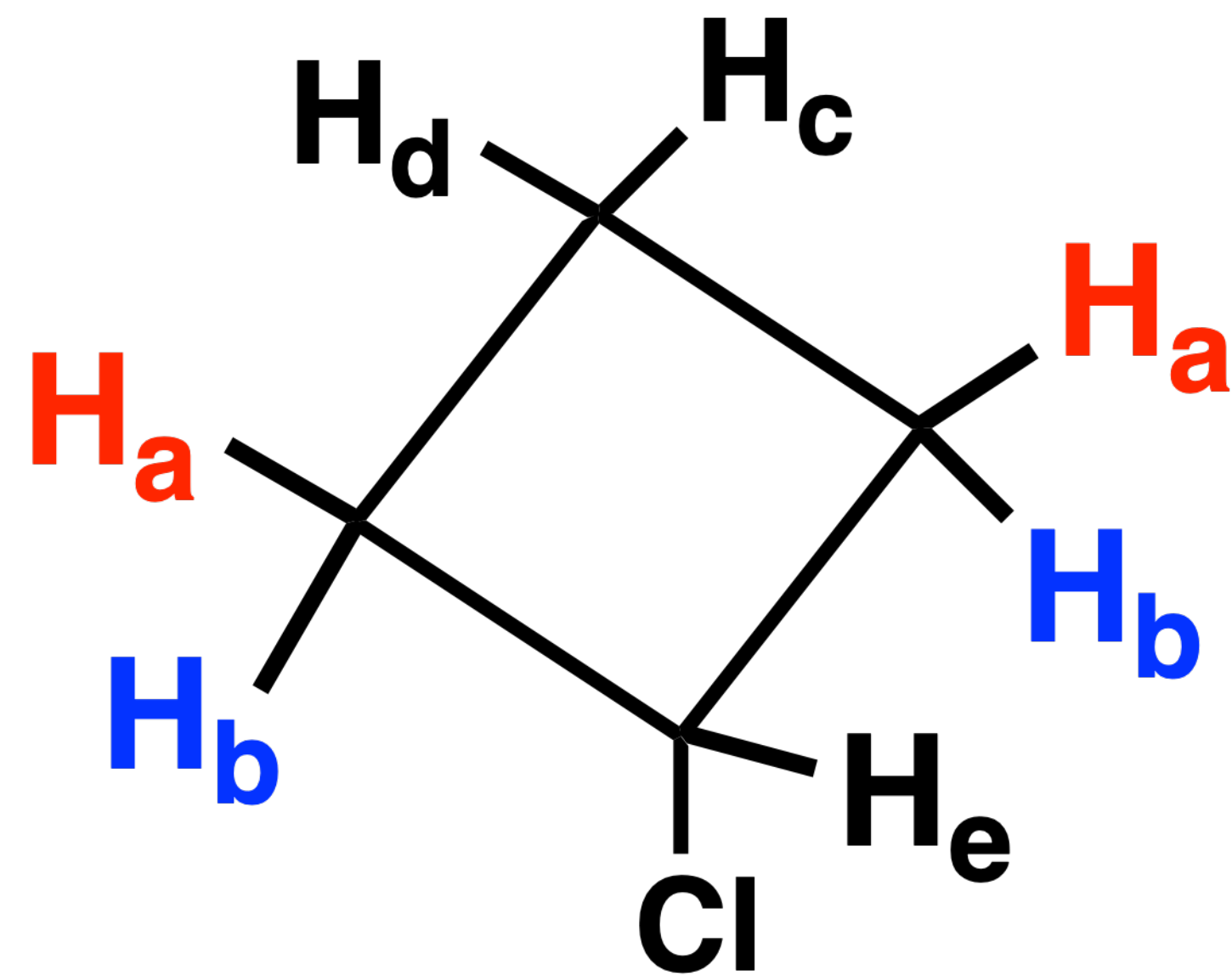
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
1-Bromopropano



Espectro de RMN ^1H do 1-bromopropano.

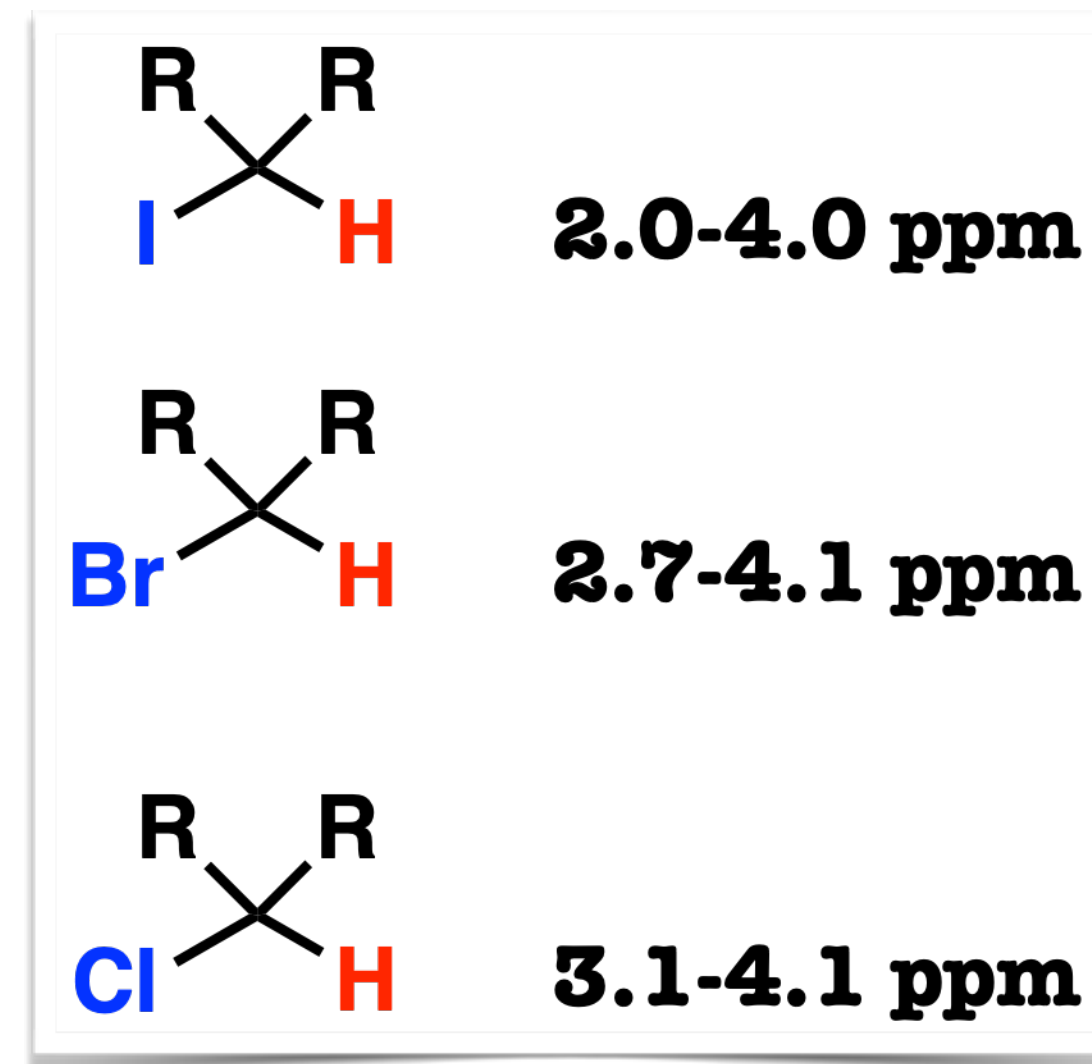
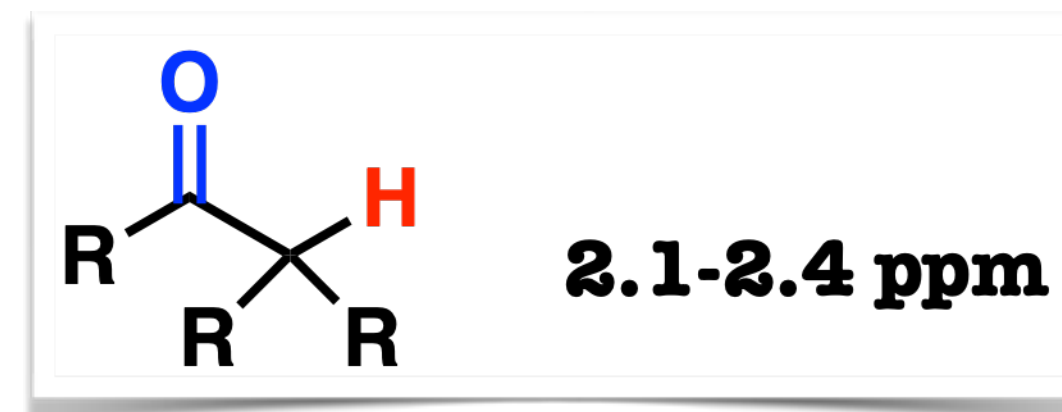
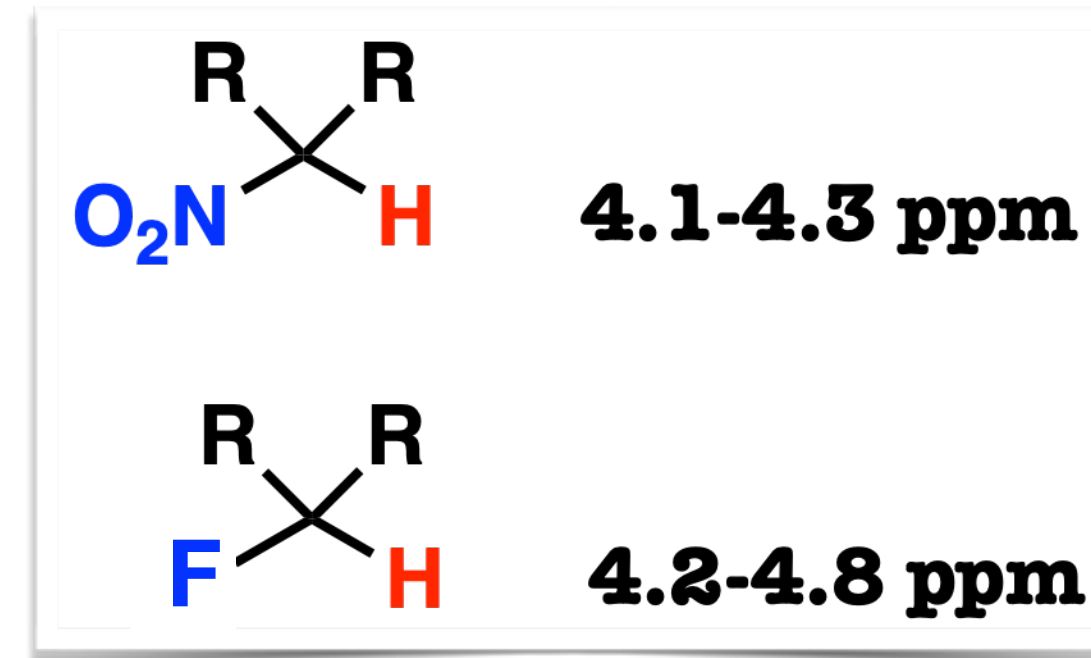
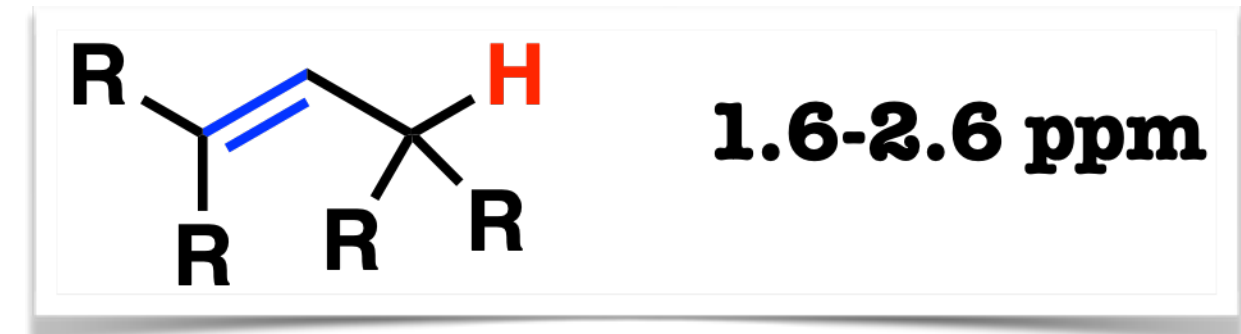
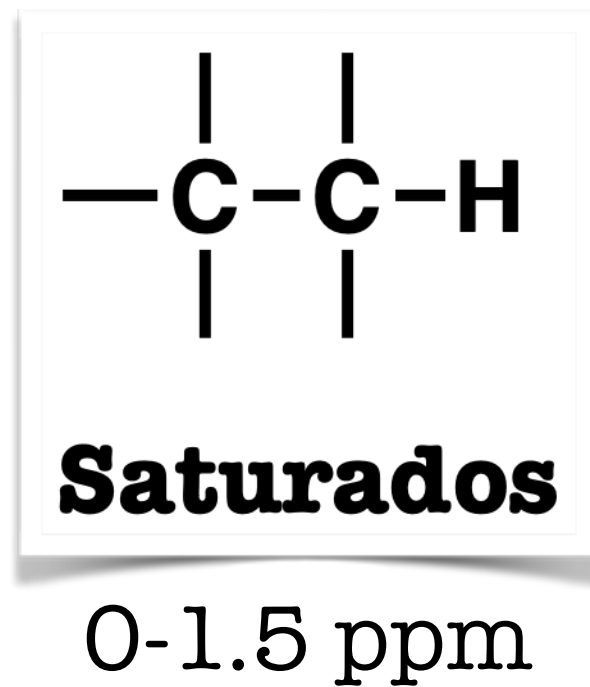
Equivalência Química

ATENÇÃO: nem sempre estar ligado ao mesmo carbono faz dos prótons equivalentes!!!!

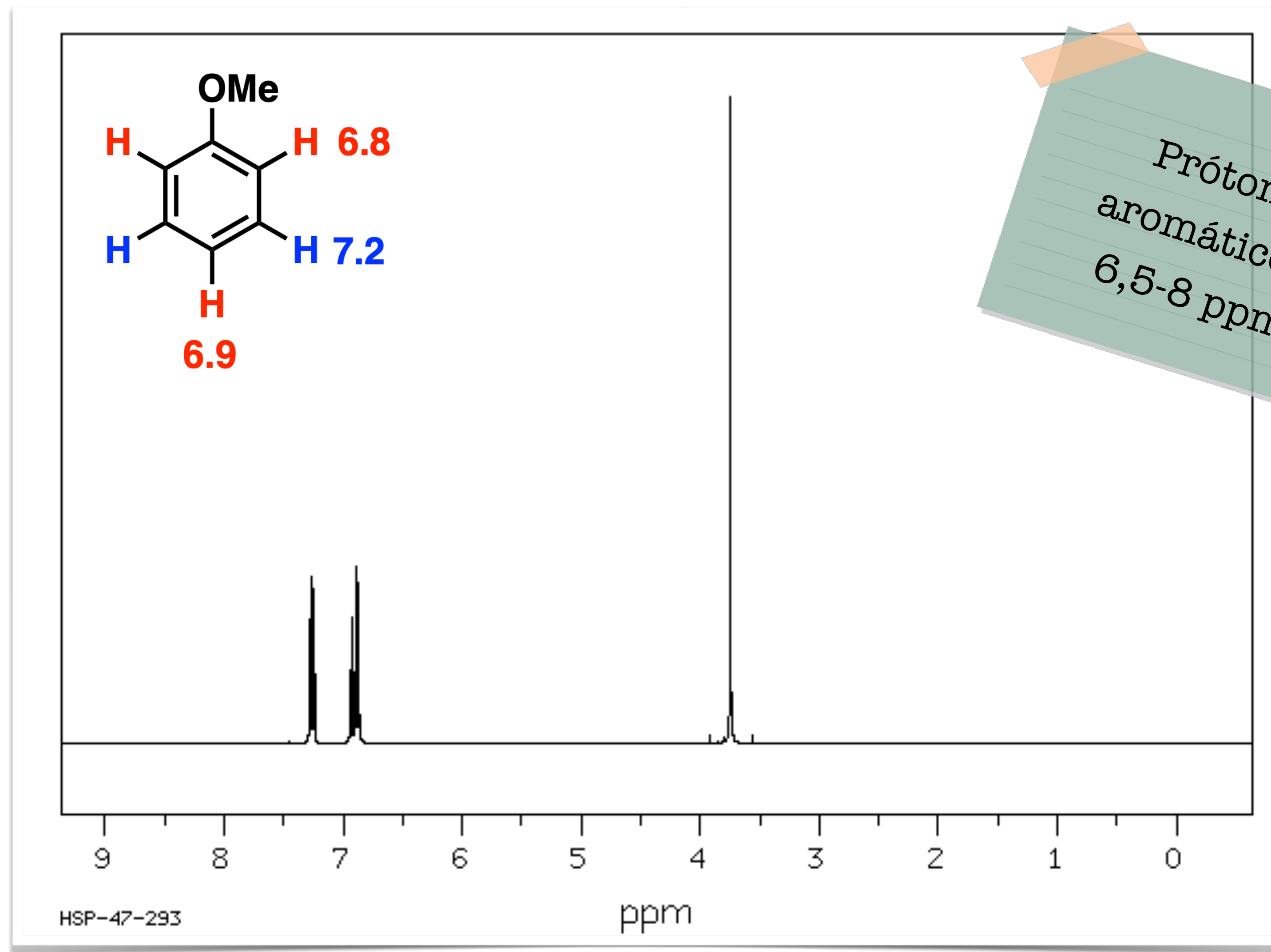


Deslocamento: Efeito retirador

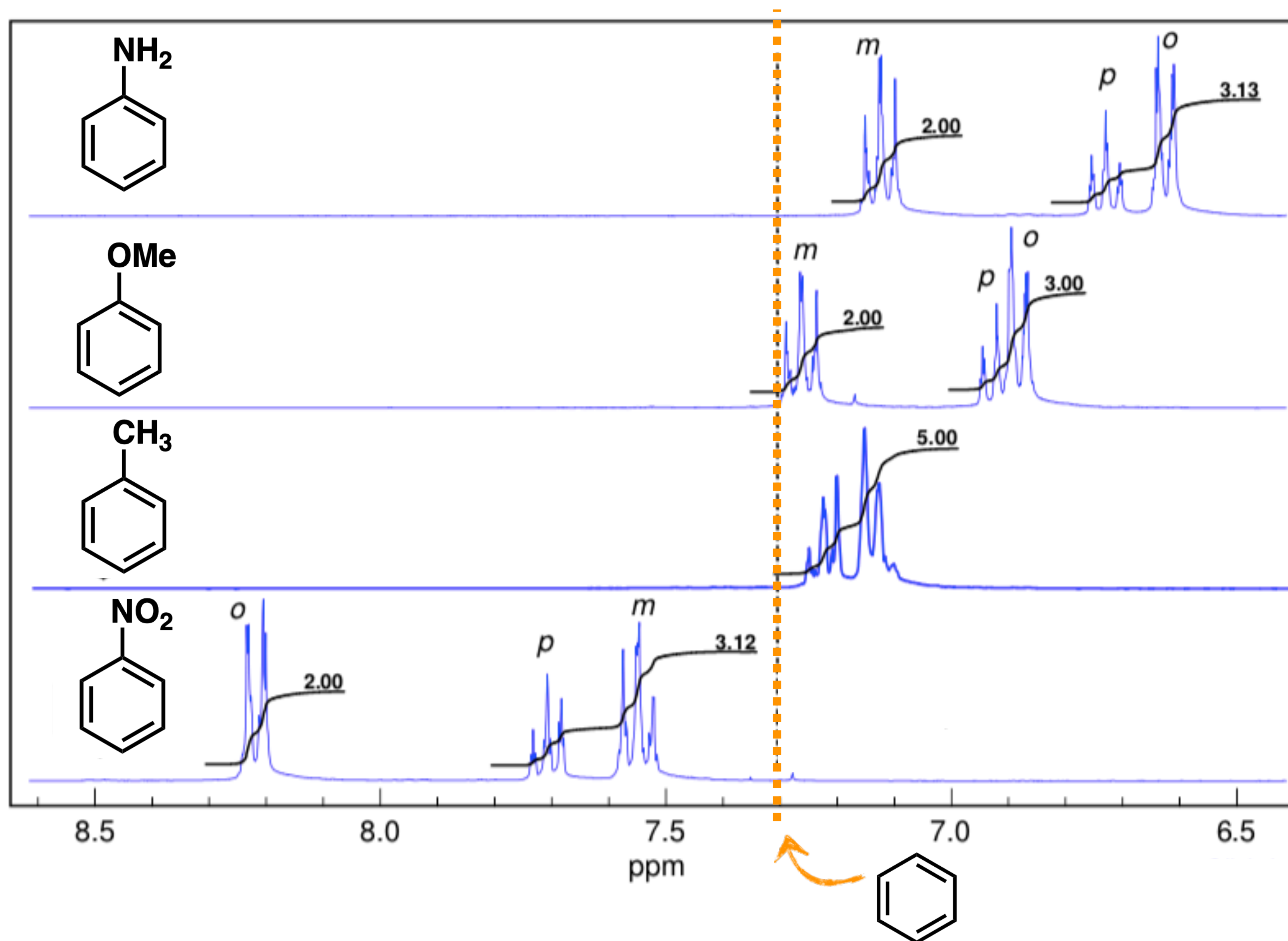
Grupos retiradores diminuem a blindagem nas proximidades do próton.



Deslocamento: Efeito doador



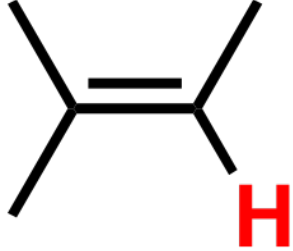

Deslocamento: Comparação de efeitos



Deslocamento: Hibridização

Quanto maior o caráter s, mais eletronegativo é o carbono:



	Deslocamento (δ) Aproximado		Deslocamento (δ) Aproximado
Alcanos		Alquenos	
—CH ₃	0,9		5-6
—CH ₂ —	1,3	Alquinos	
—CH— 	1,4		2-3 ?

Outro efeito atuando:
Anisotropia

Deslocamento: Anisotropia diamagnética

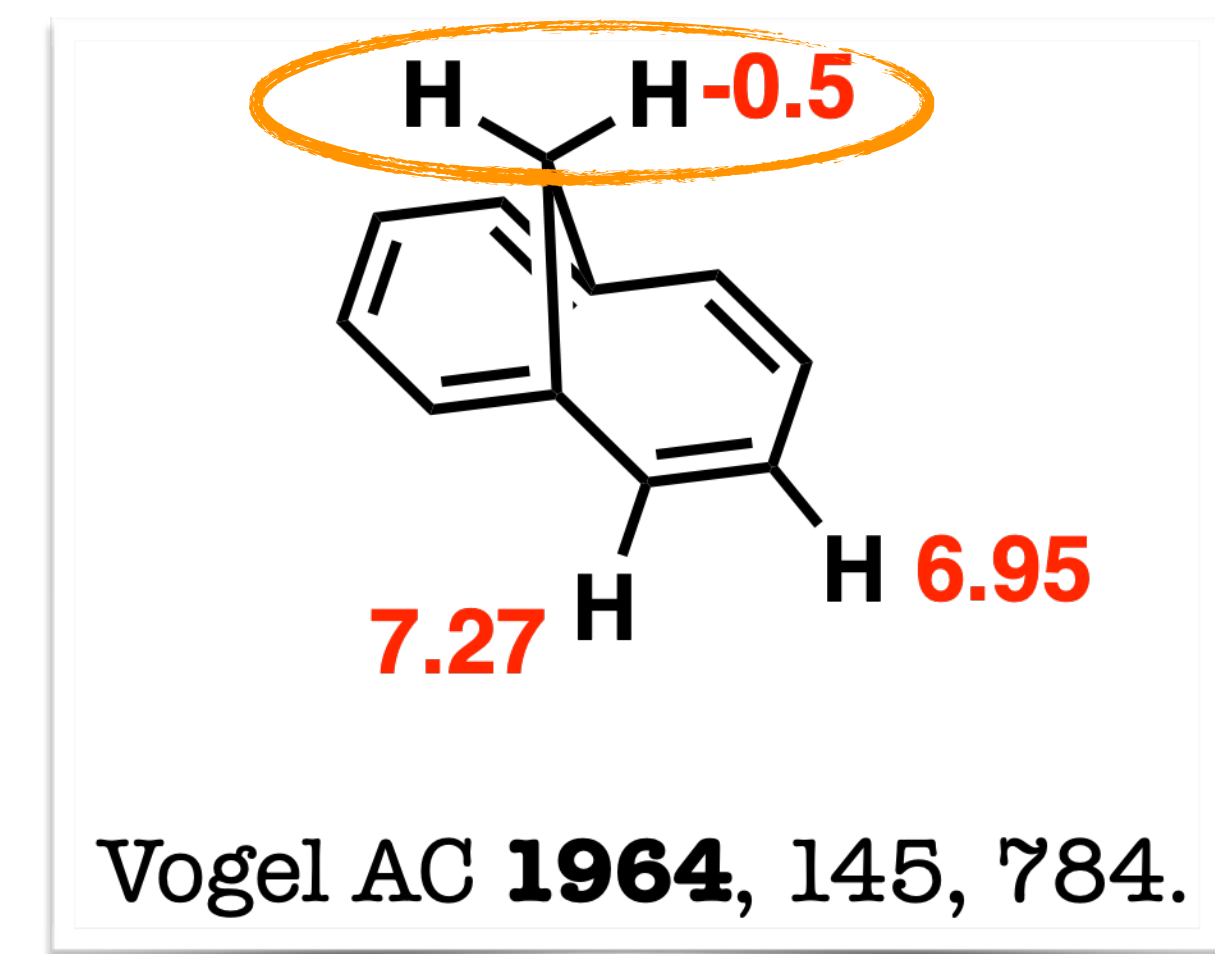
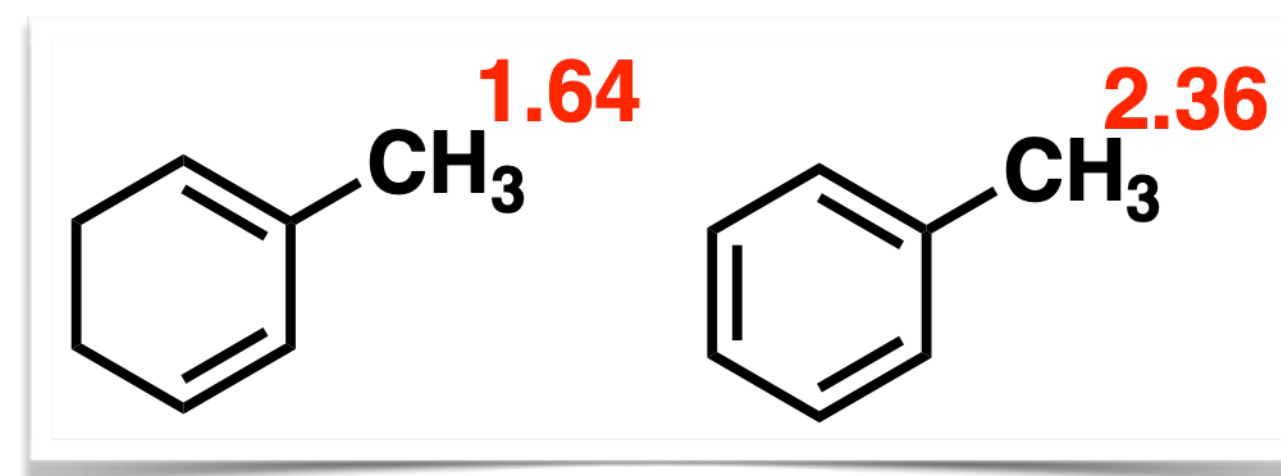
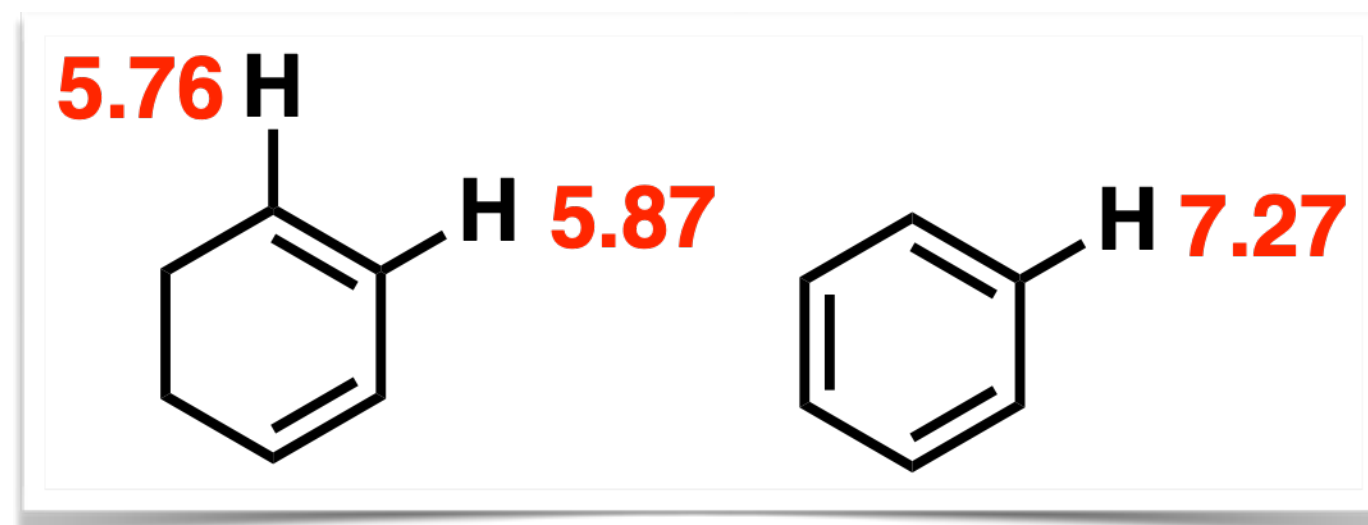
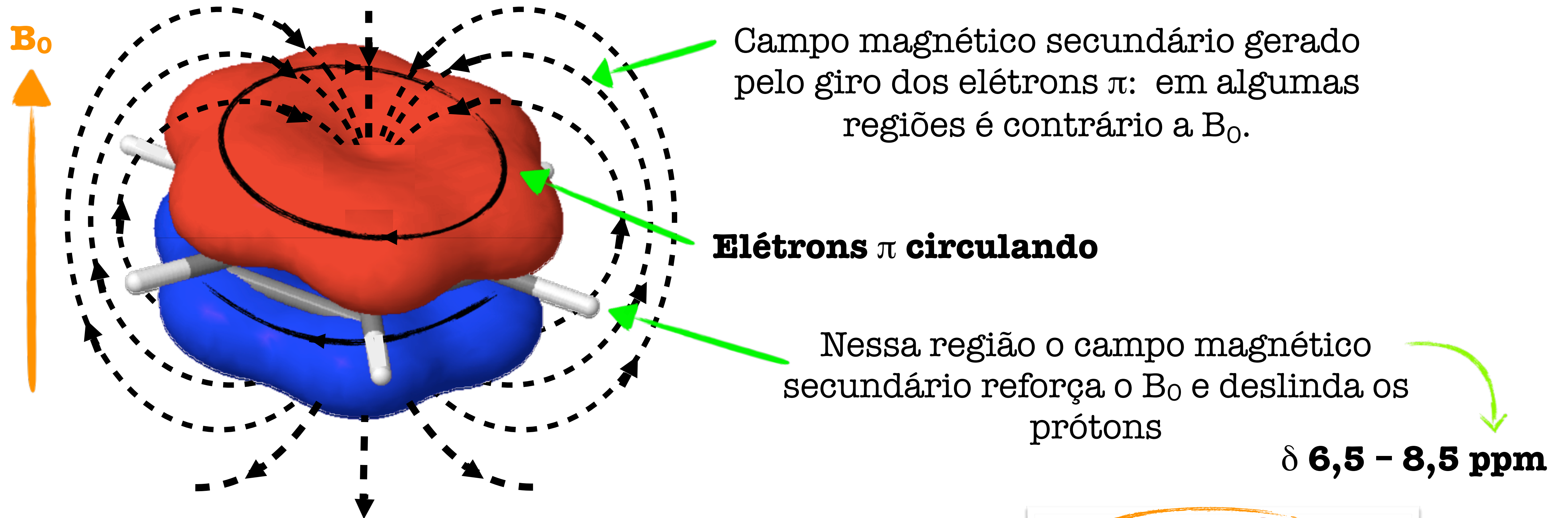
Deslocamentos não explicados pela eletronegatividade dos grupos

???

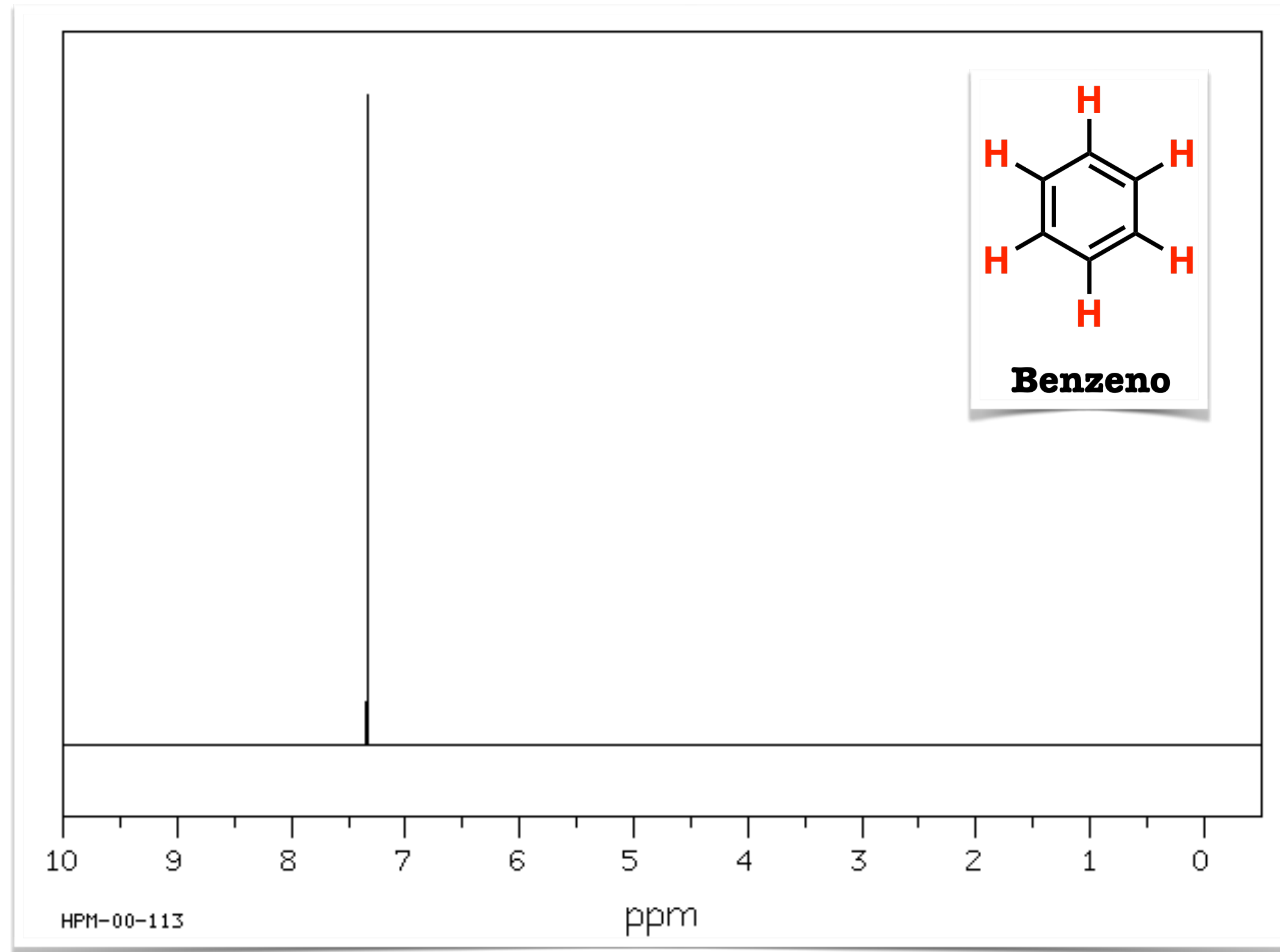
Elétrons π ficam
mais livres para
se mover em
resposta a B_0

- ✓ Provocado pela corrente dos elétrons π no sistema molecular C=C; C=O; C \equiv C...;
- ✓ Blindagem e a desblindagem dependem da orientação do próton em relação ao campo local e a B_0 .

Deslocamento: Anisotropia diamagnética



Deslocamento: Anisotropia diamagnética



https://sdfs.db.aist.go.jp/sdfs/cgi-bin/direct_frame_top.cgi

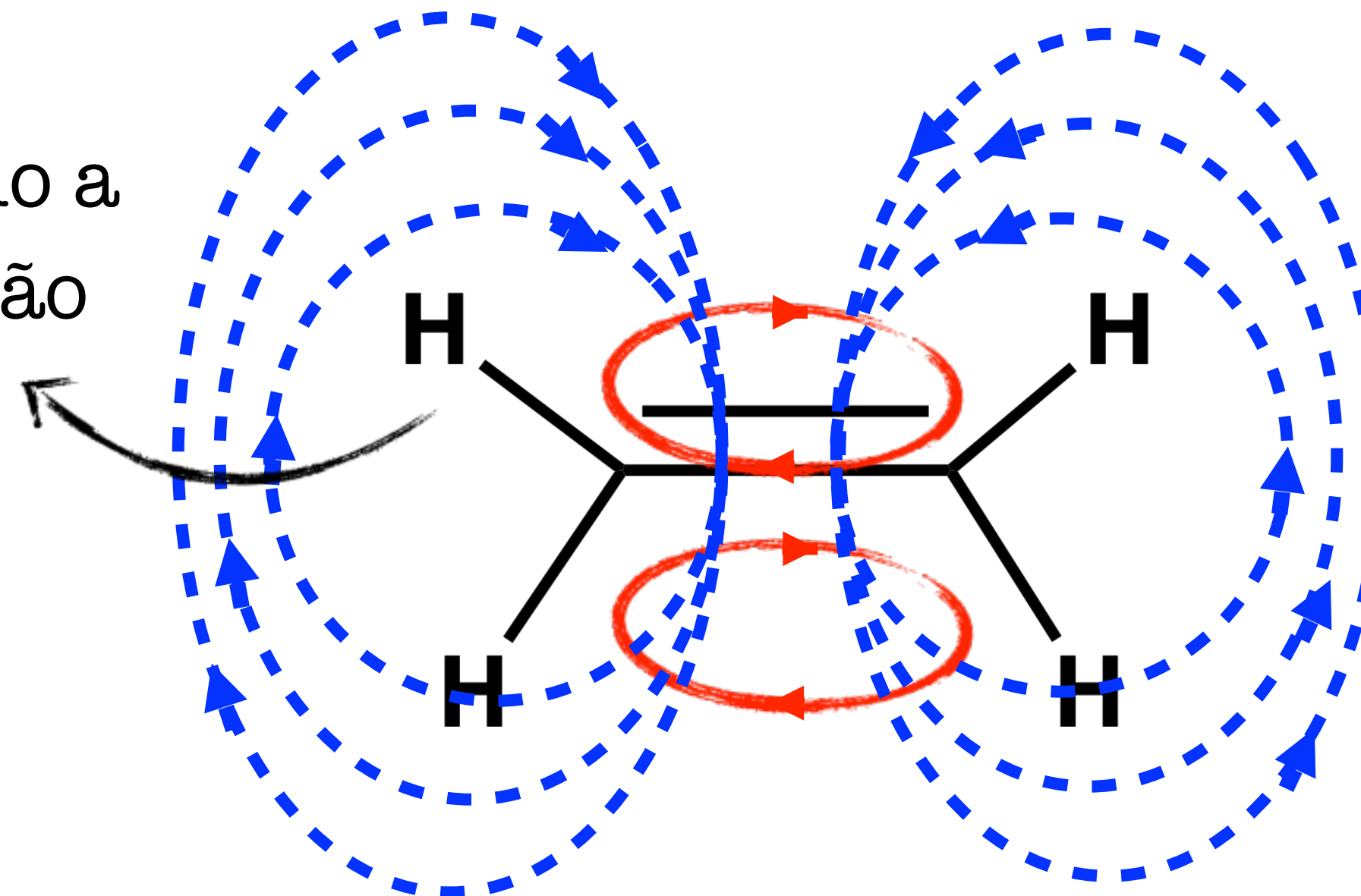
Deslocamento: Anisotropia diamagnética

B_0

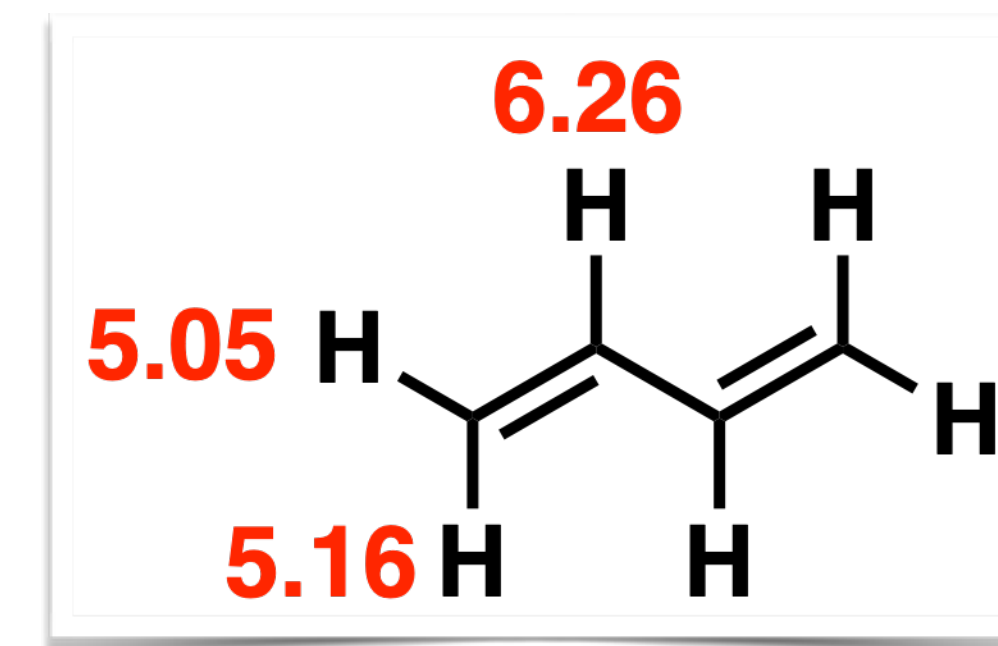
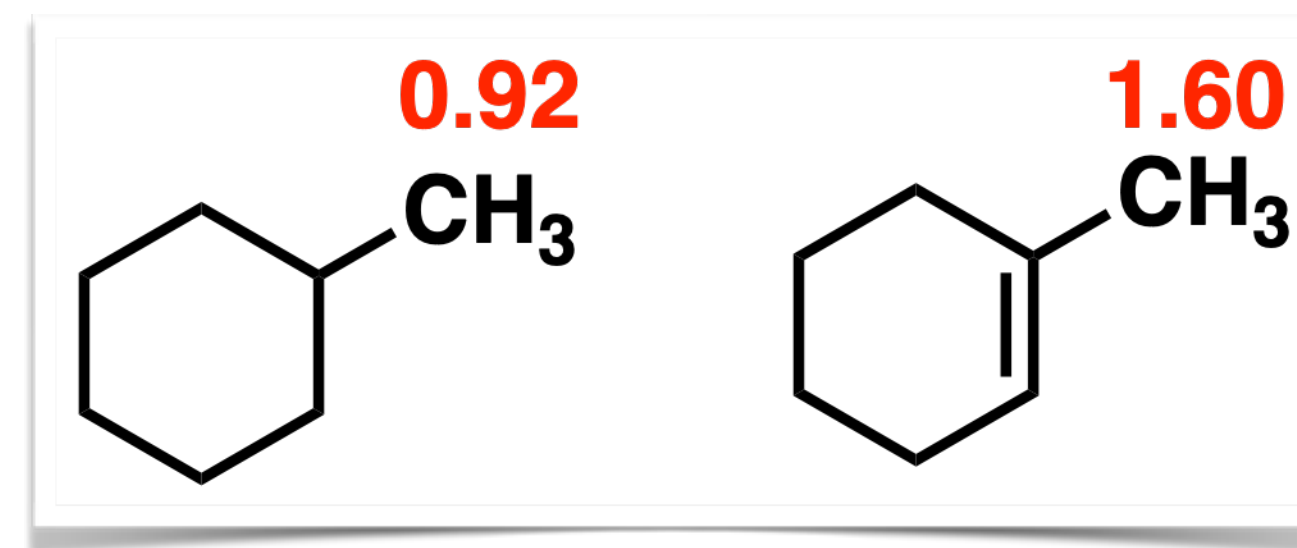
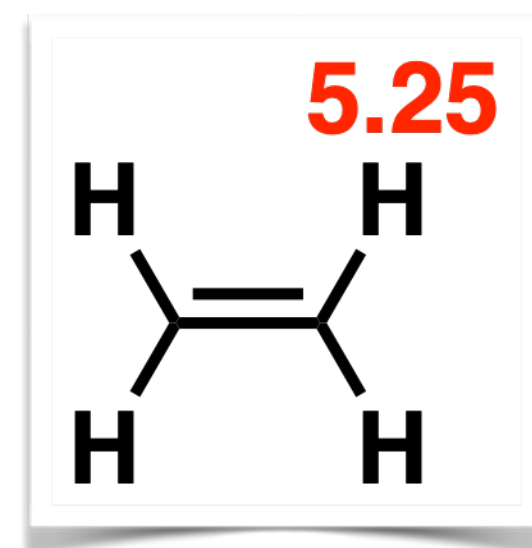


Desblindados devido a região de localização

δ 4-6 ppm



Campo magnético secundário causado pelos elétrons π

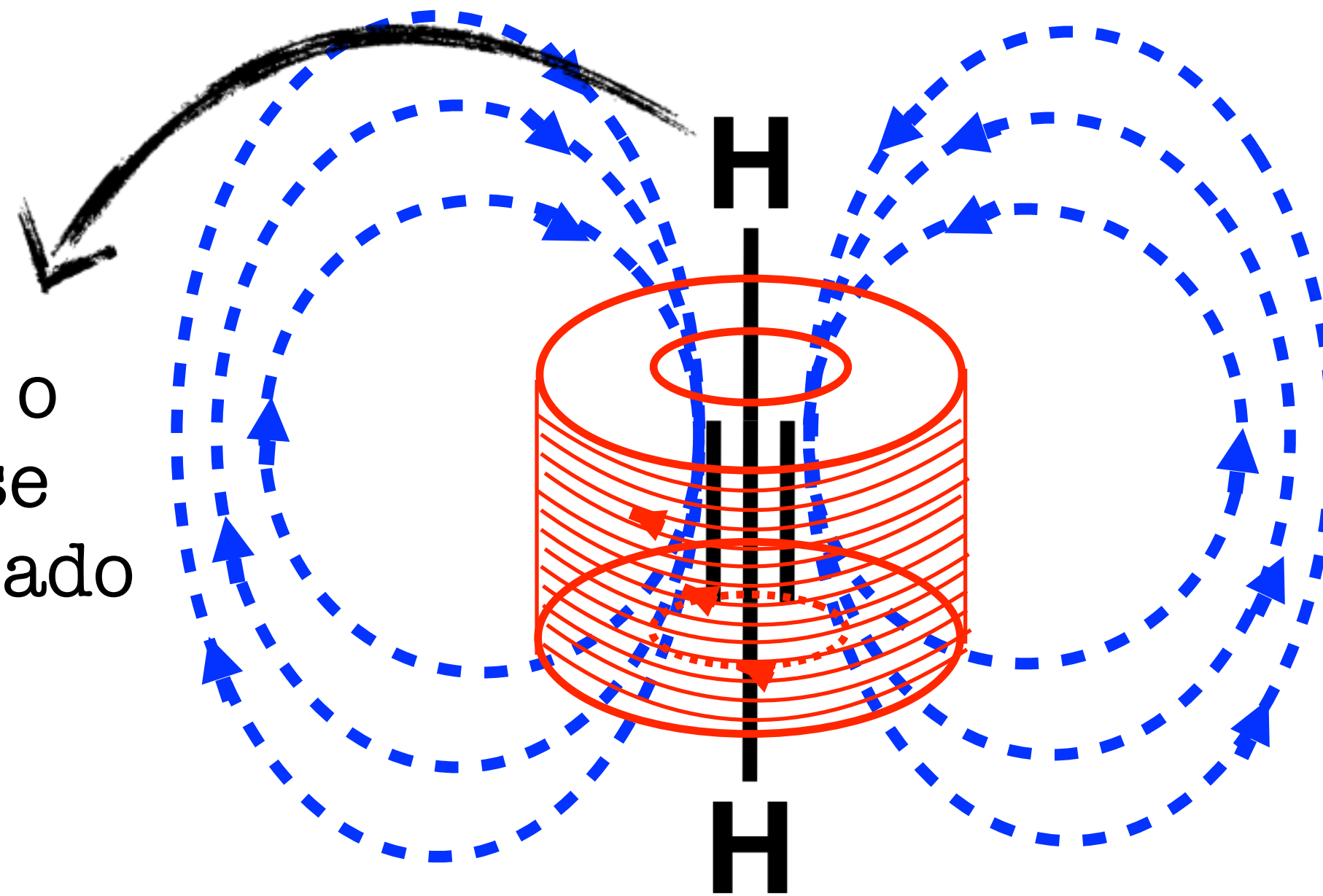


Deslocamento: Anisotropia diamagnética



Blindado
Está na região onde o campo secundário se opõem ao campo aplicado

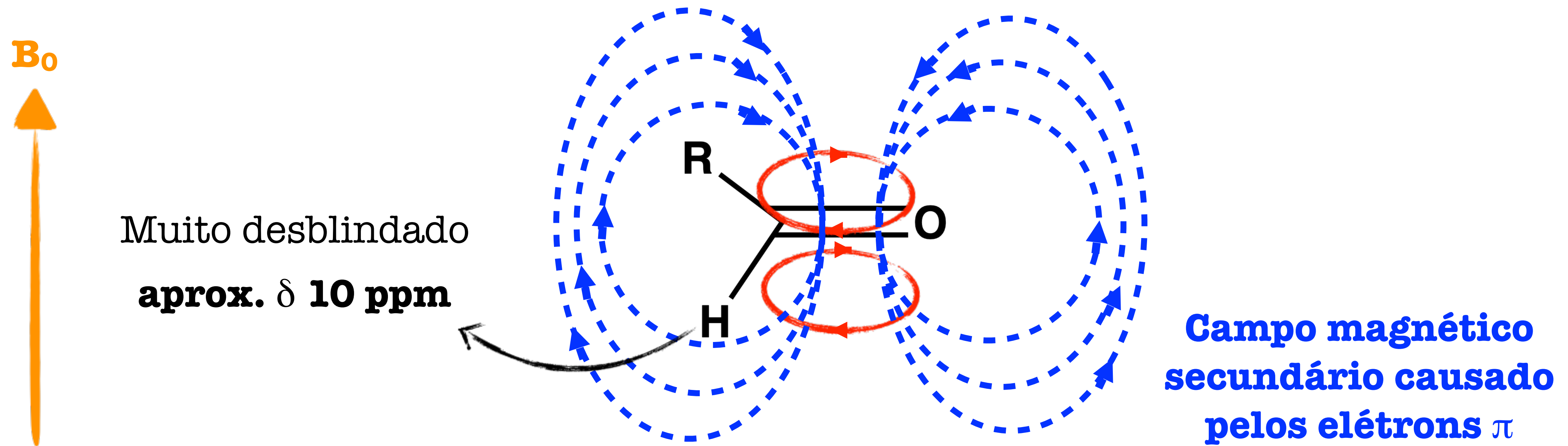
δ **1,5 - 3 ppm**



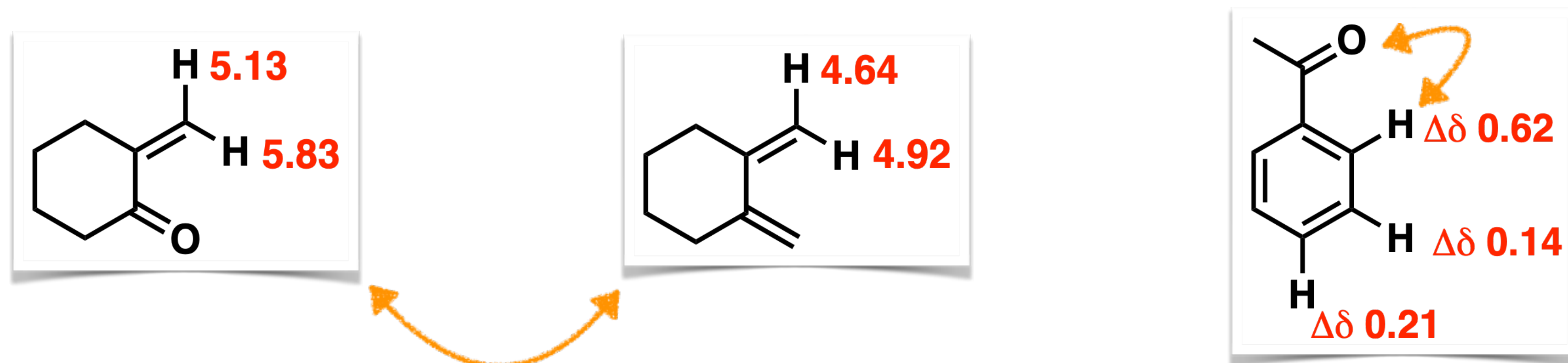
Campo magnético secundário (anisotrópico)



Deslocamento: Anisotropia diamagnética

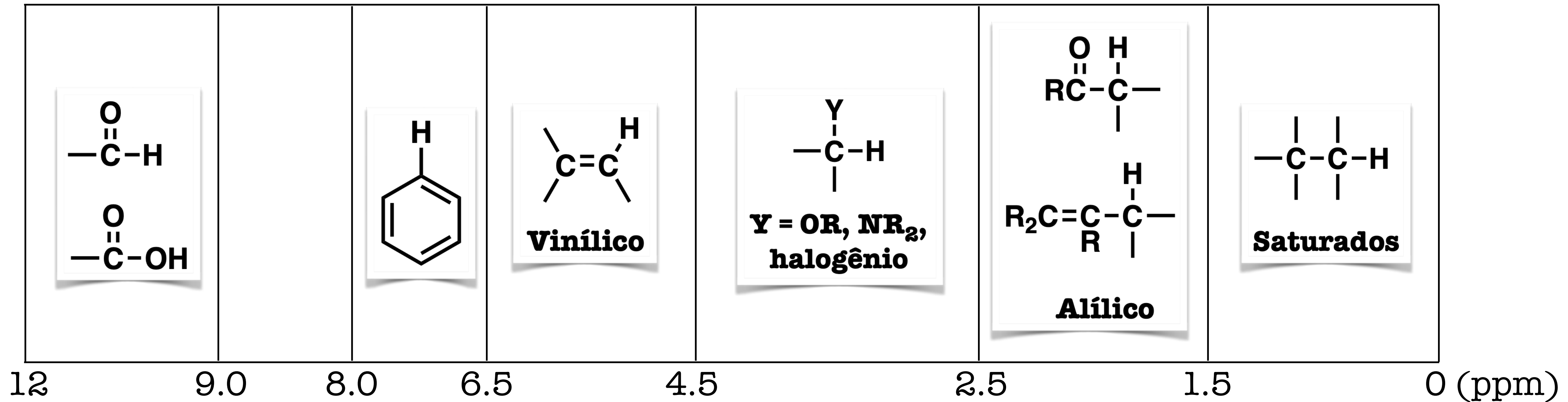


Tudo que estiver no plano é desblindado, claro que se diretamente ligado a carbonila é mais



Deslocamentos: Faixas

RMN ^1H



Deslocamentos: Tabelas

DESLOCAMENTOS QUÍMICOS EM ANÉIS ALICÍCLICOS E APÊNDICE C HETEROCÍCLICOS

TABELA C.1 Deslocamentos Químicos em Anéis Alicíclicos.









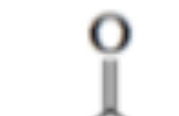

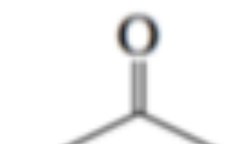
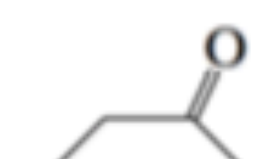
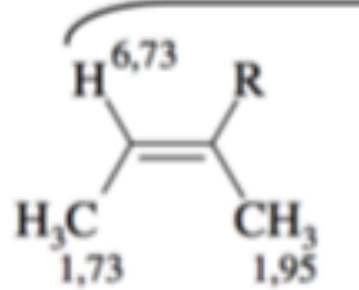
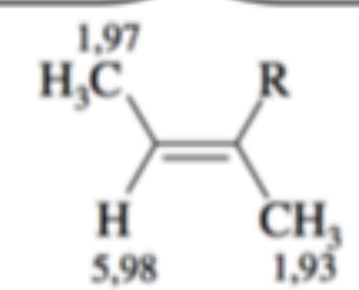
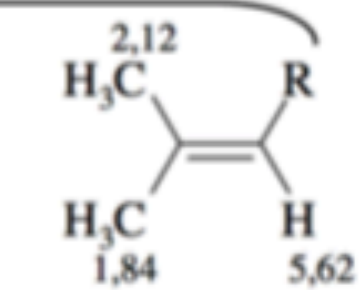
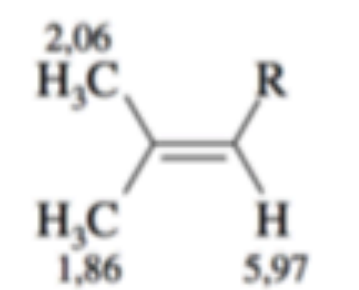
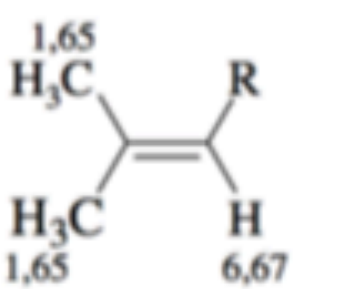
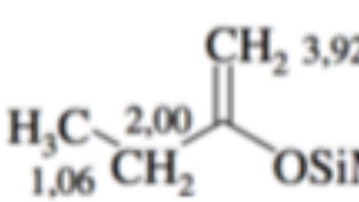
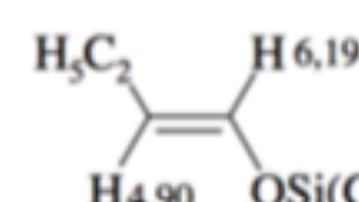
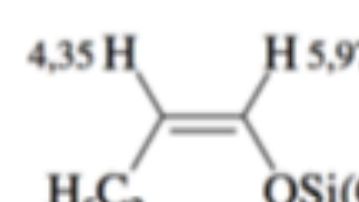
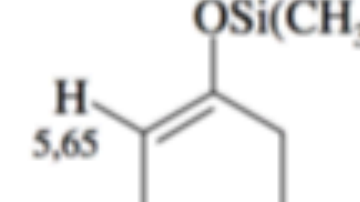
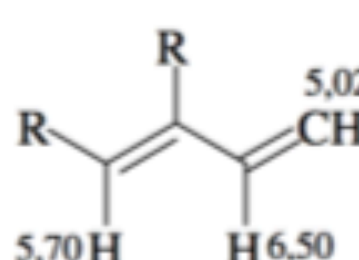
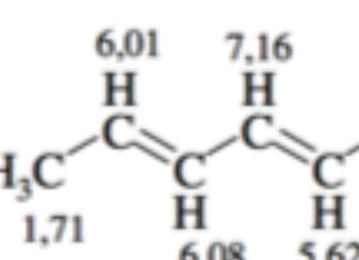
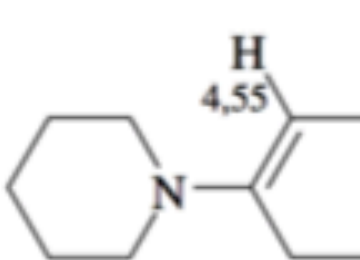
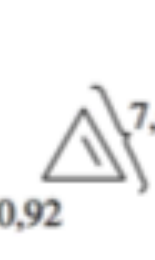
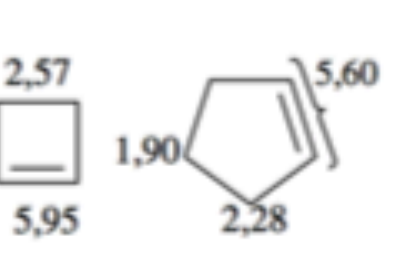
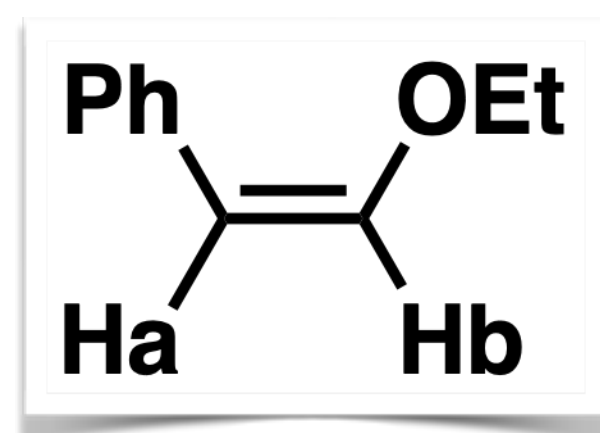
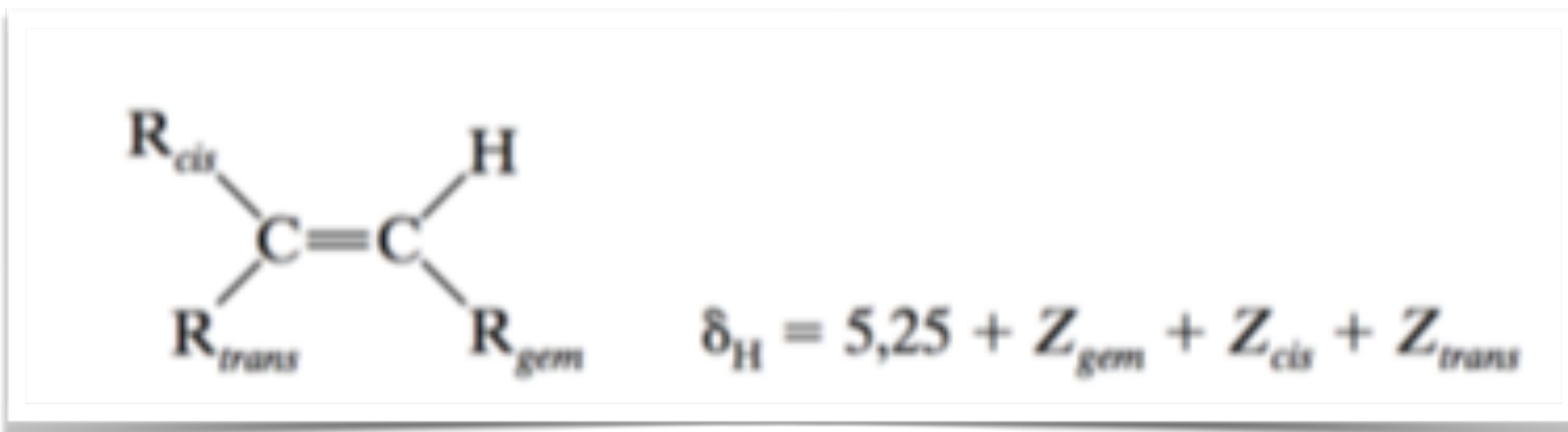
					
0,22	1,96	1,51	1,44	1,54	1,78
					
1,65	1,96 3,03	2,06 2,02	2,22 ~1,8	2,38 ~1,8	2,30 ~1,52 ~1,52

TABELA D.2 Deslocamentos Químicos de Diversos Alquenos.

R = C(=O)OCH ₃			R = C(=O)CH ₃	R = OC(=O)CH ₃
				
				
				

Deslocamentos: Tabelas



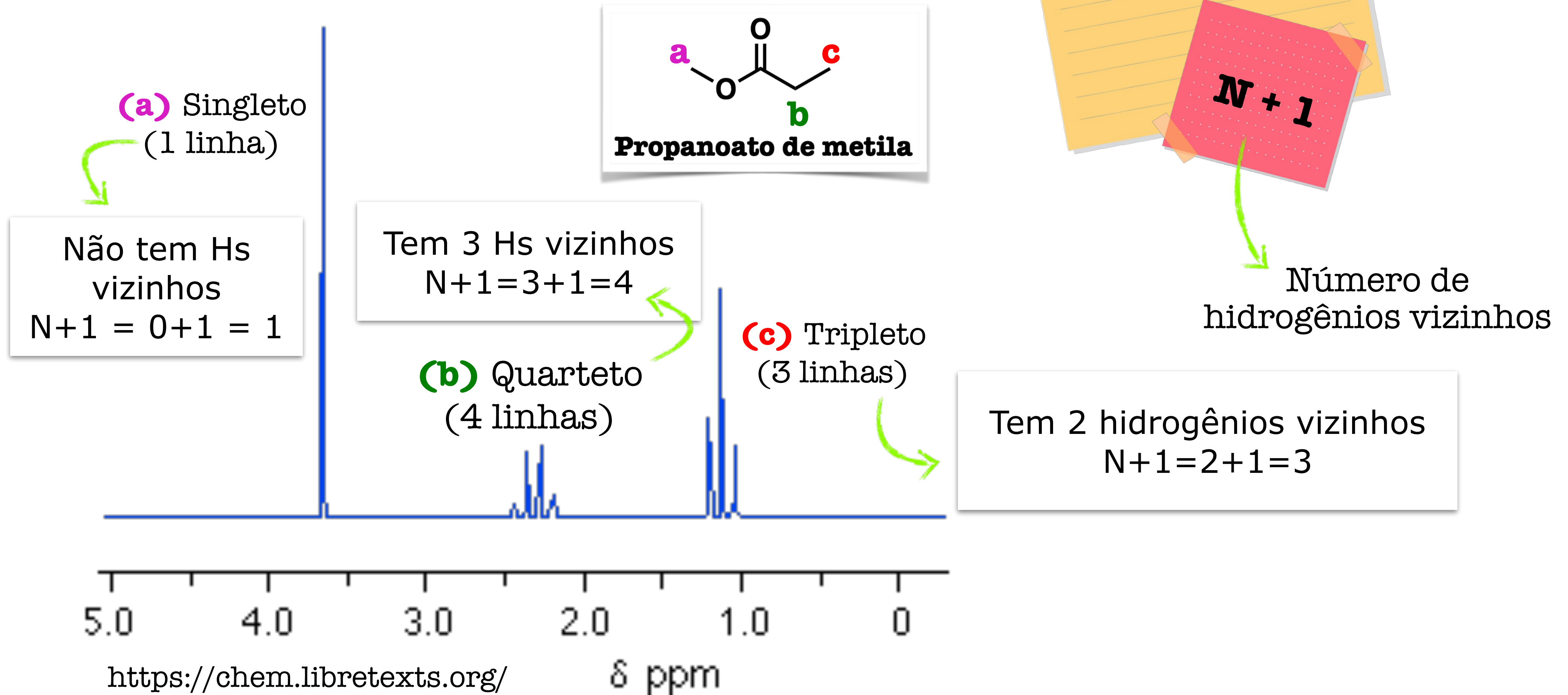
$$\begin{aligned}
 \delta_{\text{Ha}} &= 5,25 \\
 &+ 1,35 \\
 &- 1,28 \\
 \hline
 &5,32 \text{ ppm}
 \end{aligned}$$

TABELA D.1 Constantes de Substituição (Z) para os Deslocamentos Químicos de Etilenos Substituídos.

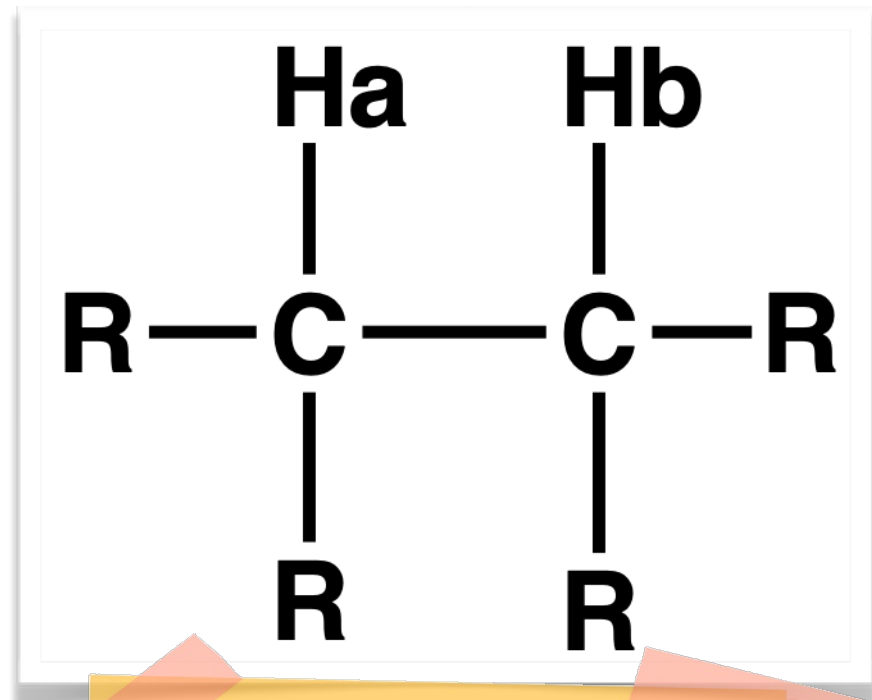
Substituinte R	Z			Substituinte R	Z		
	gem	cis	trans		gem	cis	trans
—H	0	0	0		1,03	0,97	1,21
—Alquila	0,44	—0,26	—0,29		1,37	0,93	0,35
—Alquila-anel ^a	0,71	—0,33	—0,30		1,10	1,41	0,99
—CH ₂ O, —CH ₂ I	0,67	—0,02	—0,07	—OR, R: alifático	1,18	—1,06	—1,28
—CH ₂ S	0,53	—0,15	—0,15	—OR, R: conjugado ^b	1,14	—0,65	—1,05
—CH ₂ Cl, —CH ₂ Br	0,72	0,12	0,07	—OCOR	2,09	—0,40	—0,67
—CH ₂ N	0,66	—0,05	—0,23	—Aromático	1,35	0,37	—0,10
—C≡C	0,50	0,35	0,10	—Cl	1,00	0,19	0,03
—C≡N	0,23	0,78	0,58	—Br	1,04	0,40	0,55
—C=C	0,98	—0,04	—0,21		0,69	—1,19	—1,31
—C=C conjugado ^b	1,26	0,08	—0,01		2,30	—0,73	—0,81
—C=O	1,10	1,13	0,81	—SR	1,00	—0,24	—0,04
—C=O conjugado ^b	1,06	1,01	0,95	—SO ₂	1,58	1,15	0,95
—COOH	1,00	1,35	0,74				
—COOH conjugado ^b	0,69	0,97	0,39				
—COOR	0,84	1,15	0,56				
—COOR conjugado ^a	0,68	1,02	0,33				

Desdobramento spin-spin

Os sinais de RMN ^1H podem se **desdobrar** em duas ou mais linhas.

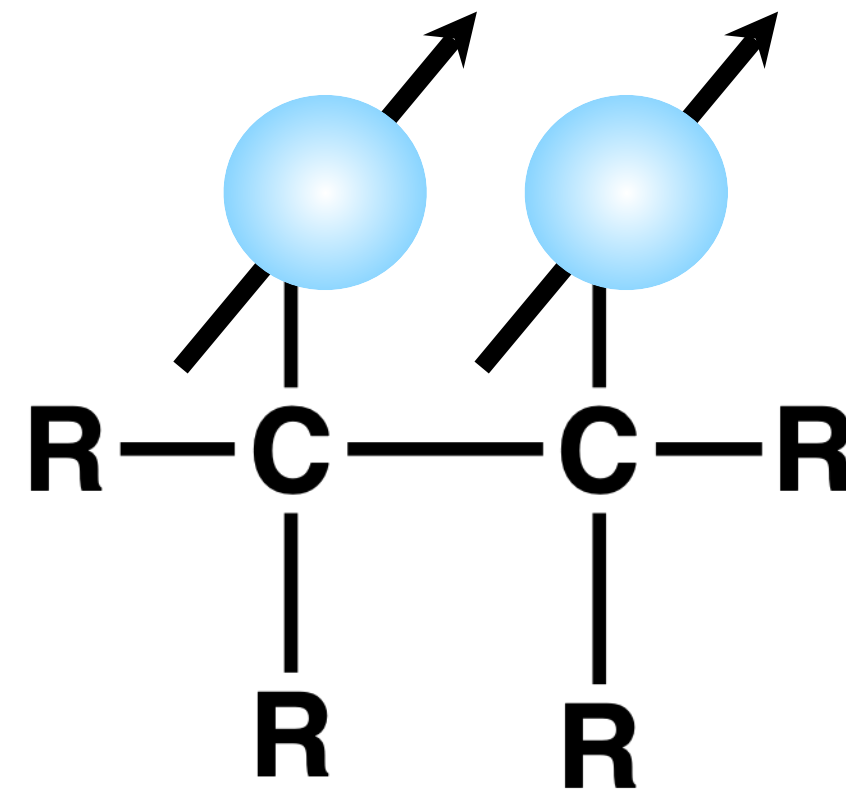


Desdobramento spin-spin



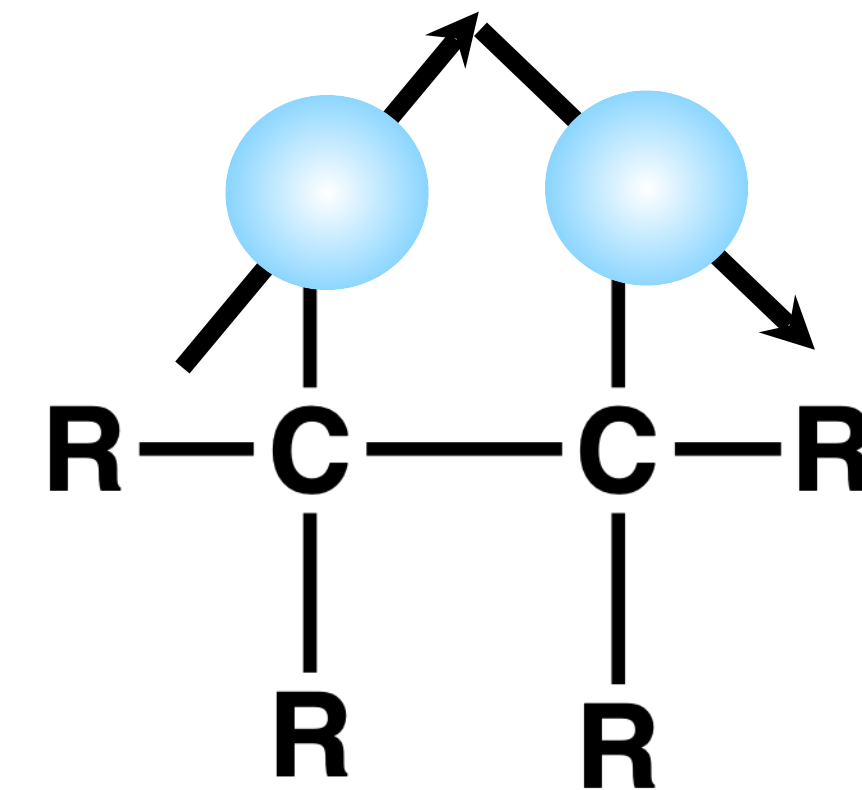
**Ha e Hb são
NÃO
equivalentes**

Sinal do Ha é um dubleto ou duplete: dois sinais de mesma magnitude



Hb com spin alinhado ao campo aplicado causa desblindagem

Ha entra em ressonância a um campo efetivo maior
 $H_{\text{efetivo}} = H_{\text{aplicado}} + H_{\text{induzido}}$



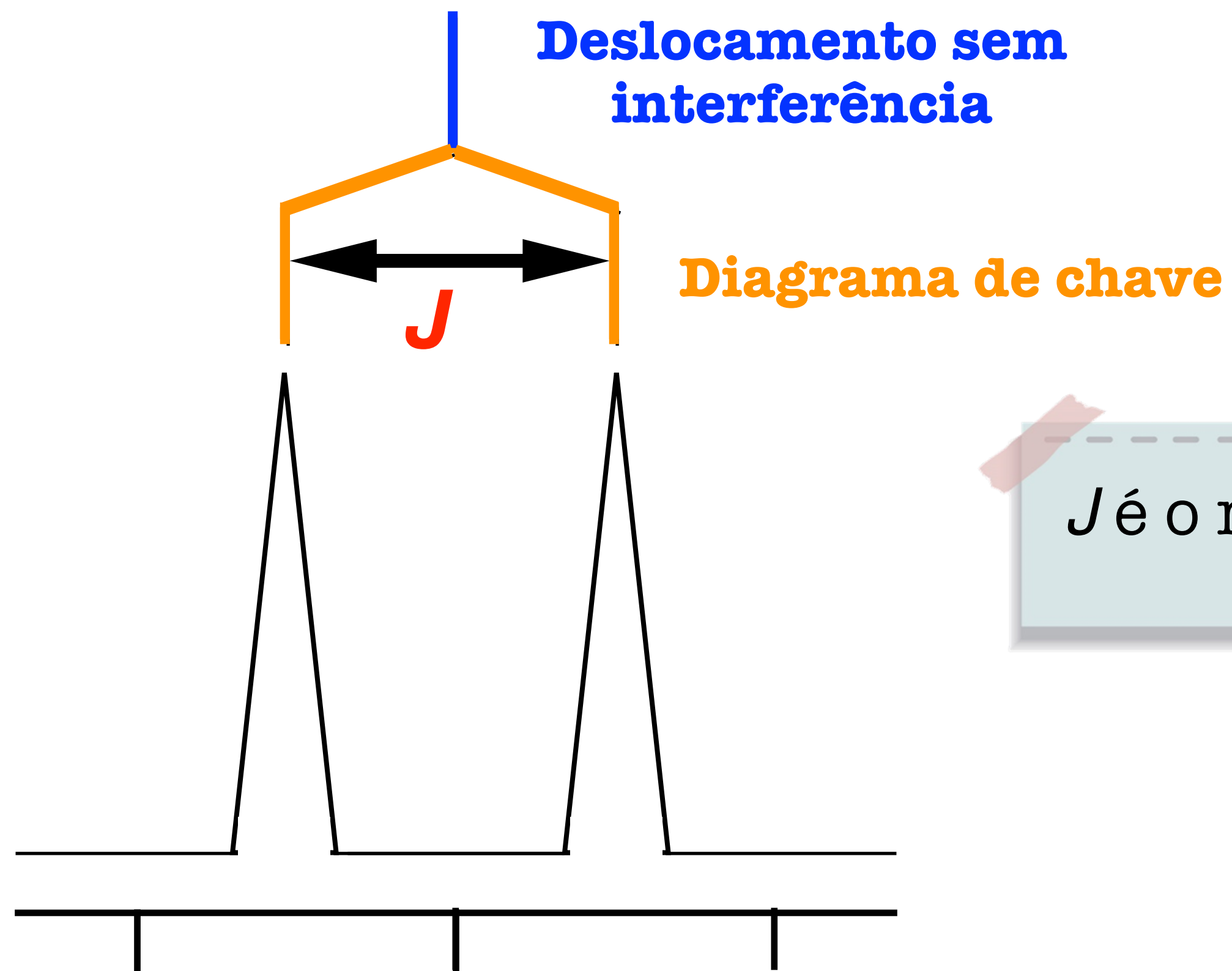
Hb com spin oposto ao campo aplicado causa blindagem

Ha entra em ressonância a um campo efetivo menor
 $H_{\text{efetivo}} = H_{\text{aplicado}} - H_{\text{induzido}}$

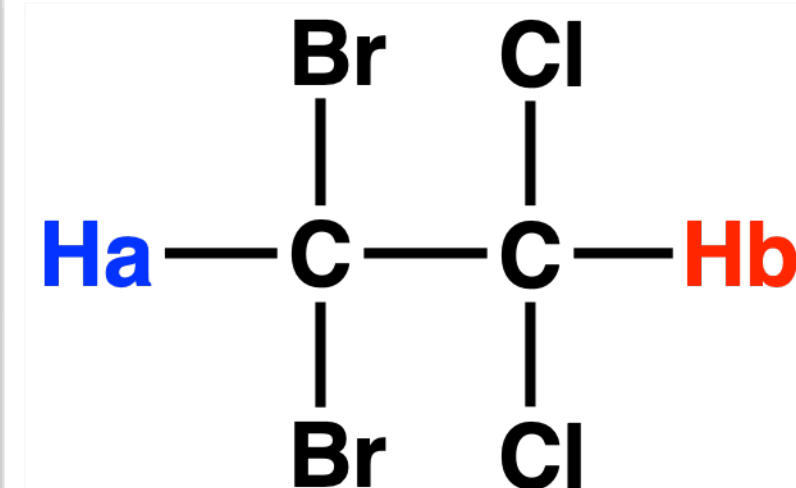
Sinal do Ha sem o efeito do vizinho

Desdobramento spin-spin

- ✓ A separação entre os dois sinais do dubleto (Hz) traduz a intensidade do acoplamento;
- ✓ Este valor é chamado de **constante escalar de acoplamento**, e é simbolizada pela letra J .

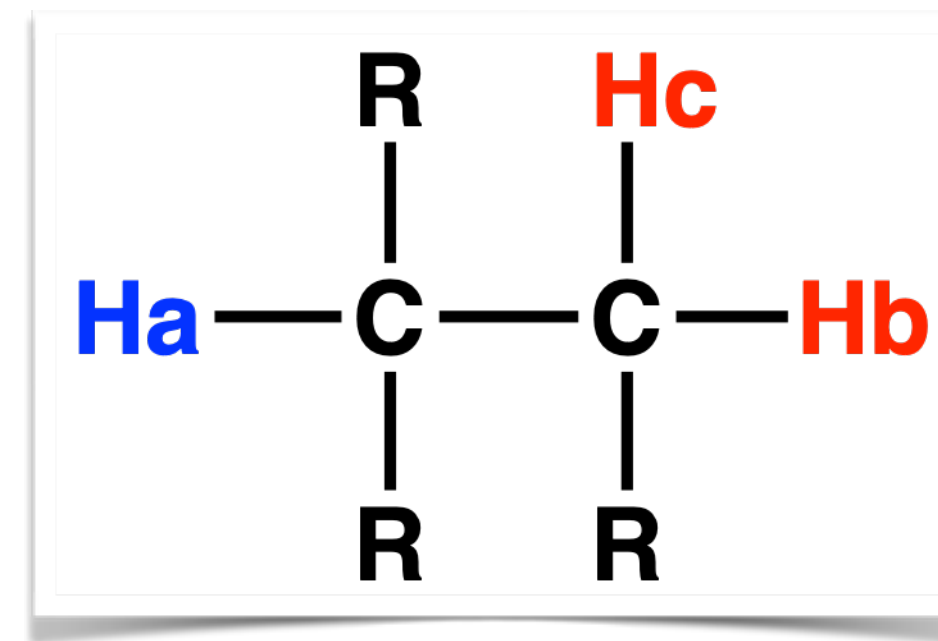
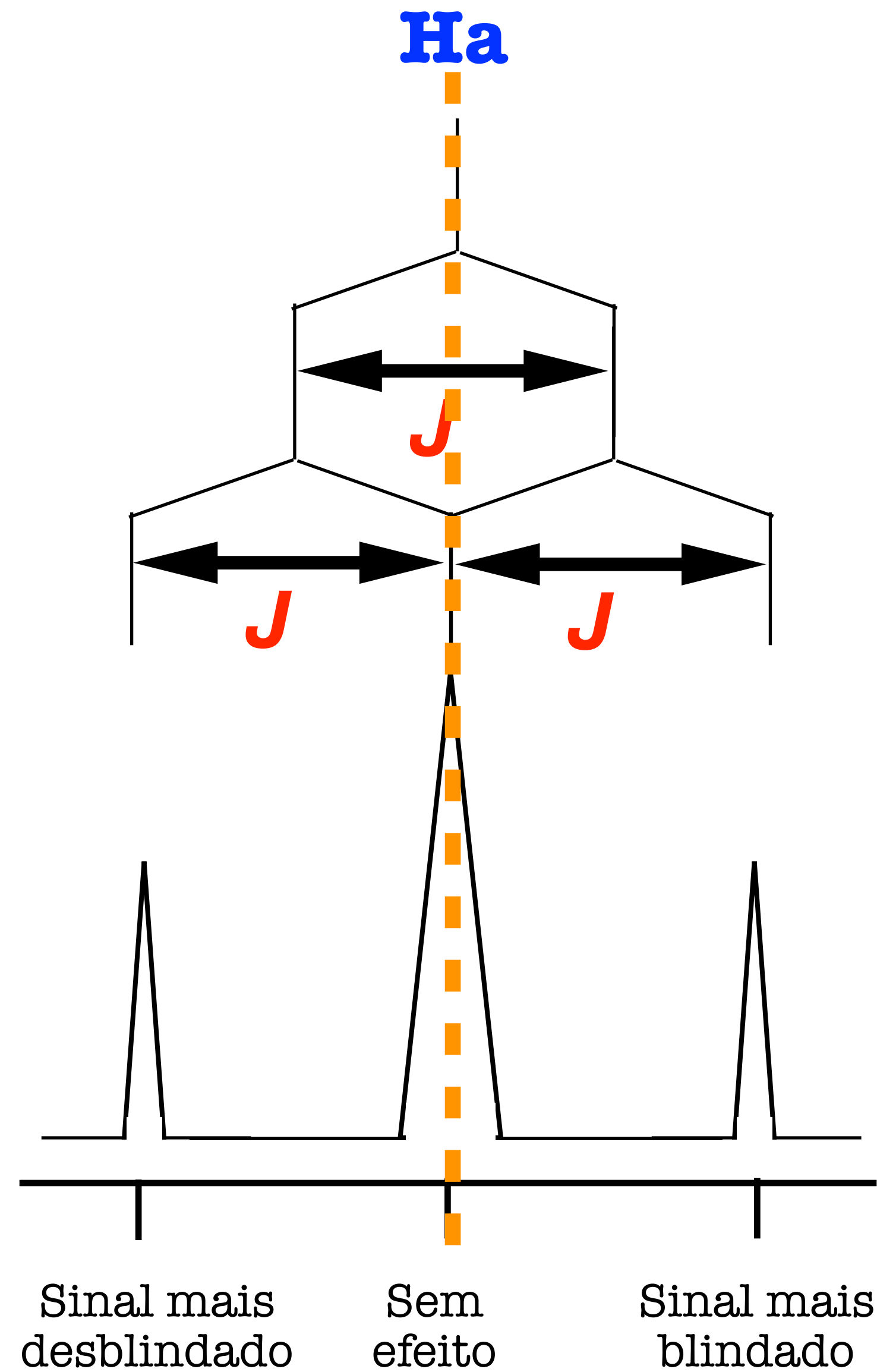


J é o mesmo de H_a para H_b e de H_b para H_a .

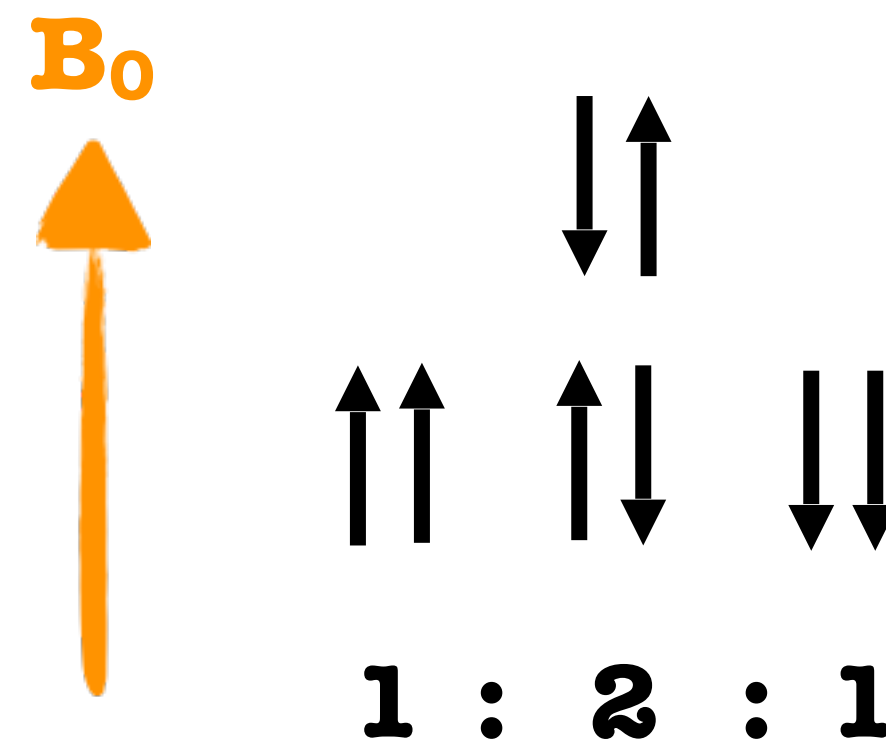


$$\begin{aligned} J_{a-b} &= 7\text{Hz} \\ J_{b-a} &= 7\text{Hz} \end{aligned}$$

Desdobramento spin-spin



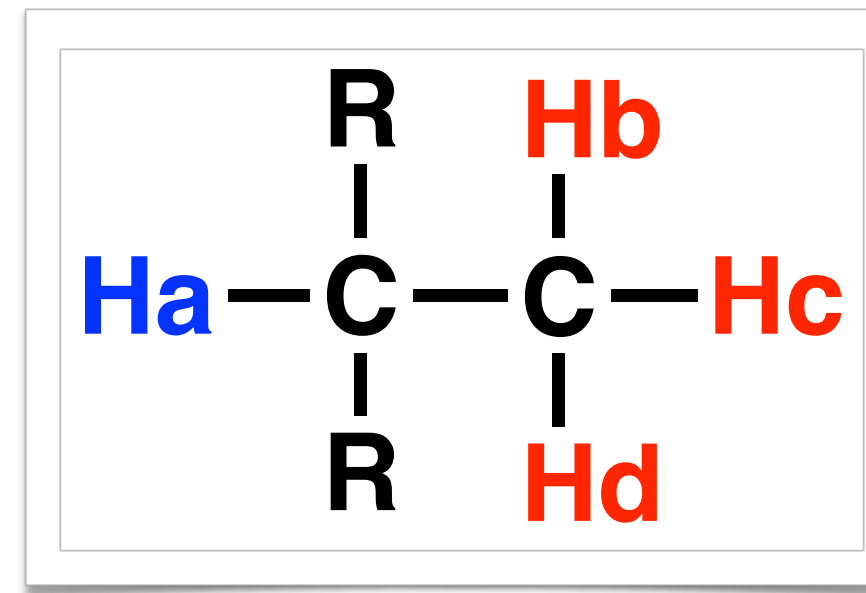
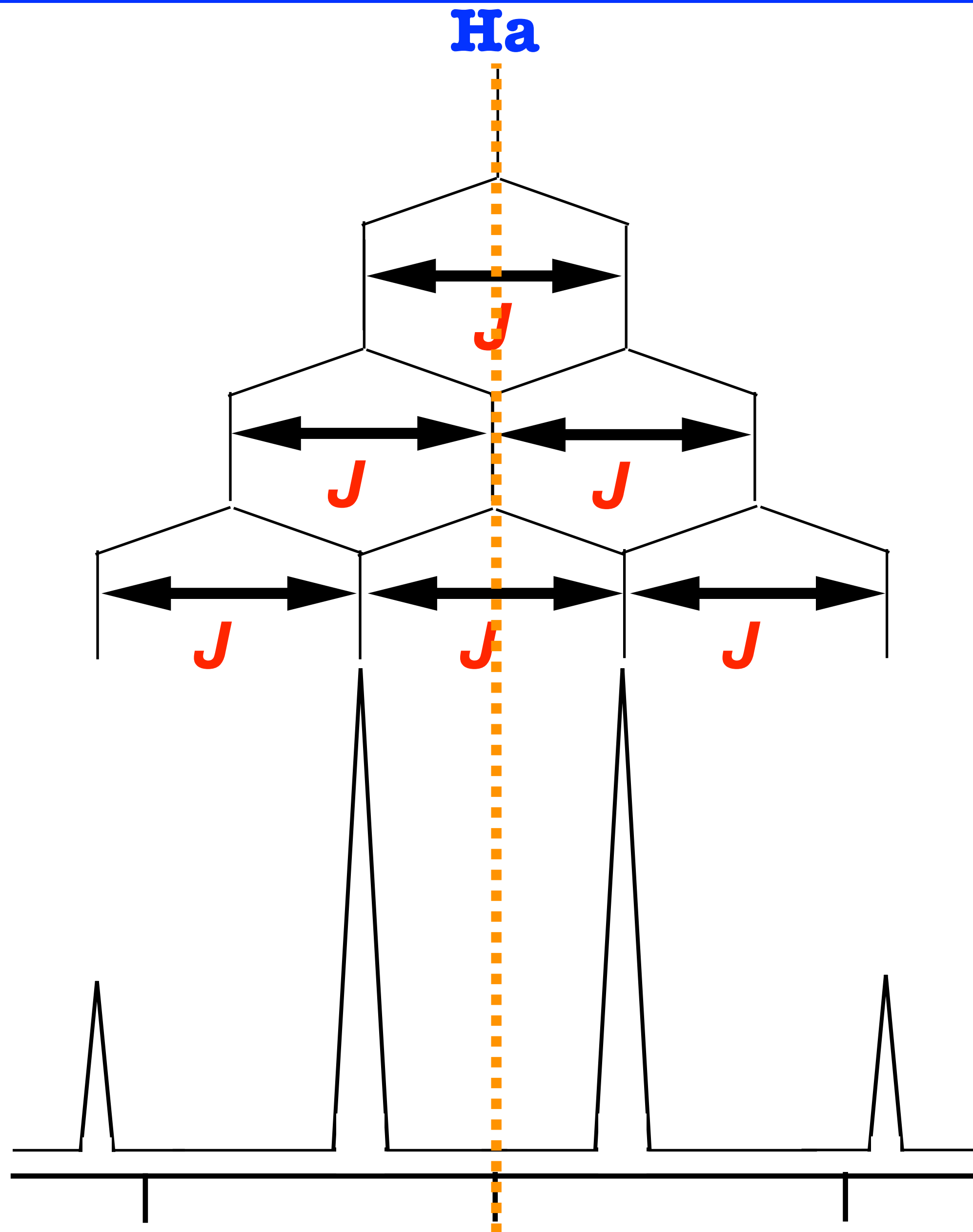
E quando há dois hidrogênios no carbono vizinho?



$$N+1 = 2+1=3$$

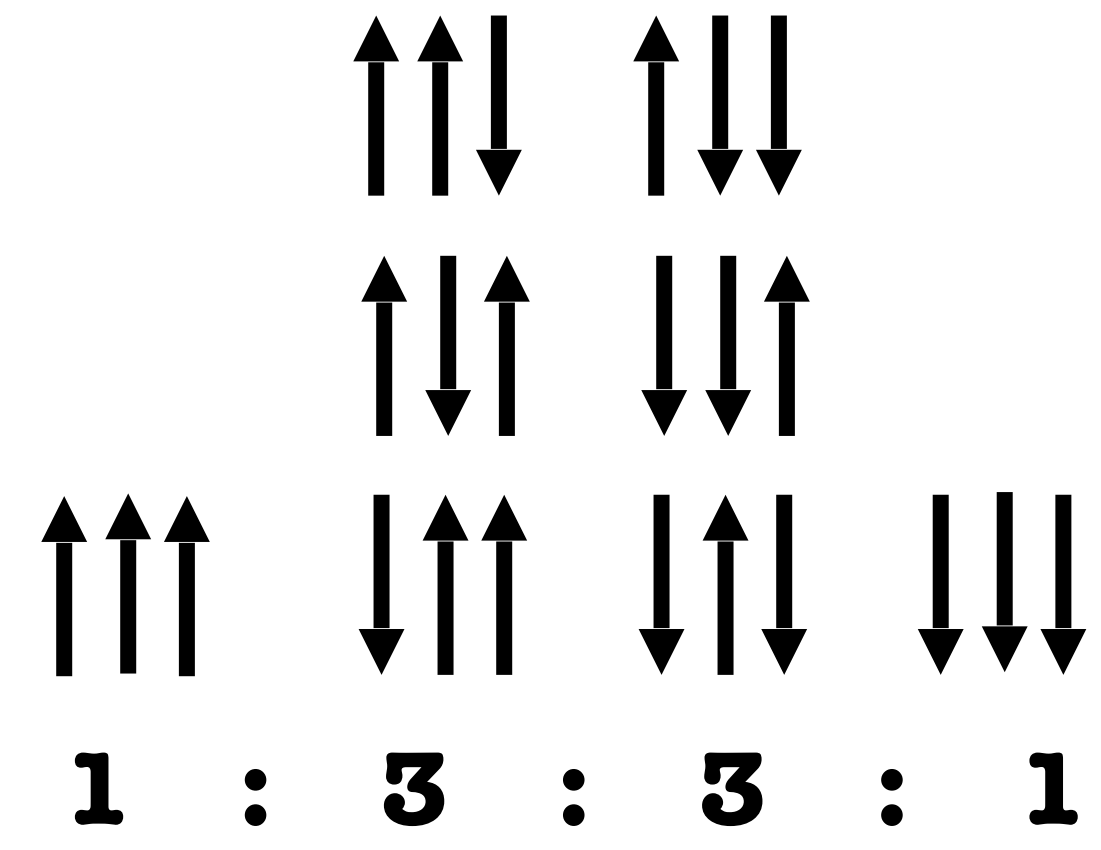
Tripleto

Desdobramento spin-spin



Três hidrogênios:
 $N+1 = 3+1 = 4$
(Quarteto ou Quadrupletto)

B_0



Desdobramento spin-spin

Triângulo de Pascal

N Multiplicidade Intensidade Relativa

0 Singleto (s)

1 Duplete (d)

2 Tripleto (t)

3 Quarteto (qua)

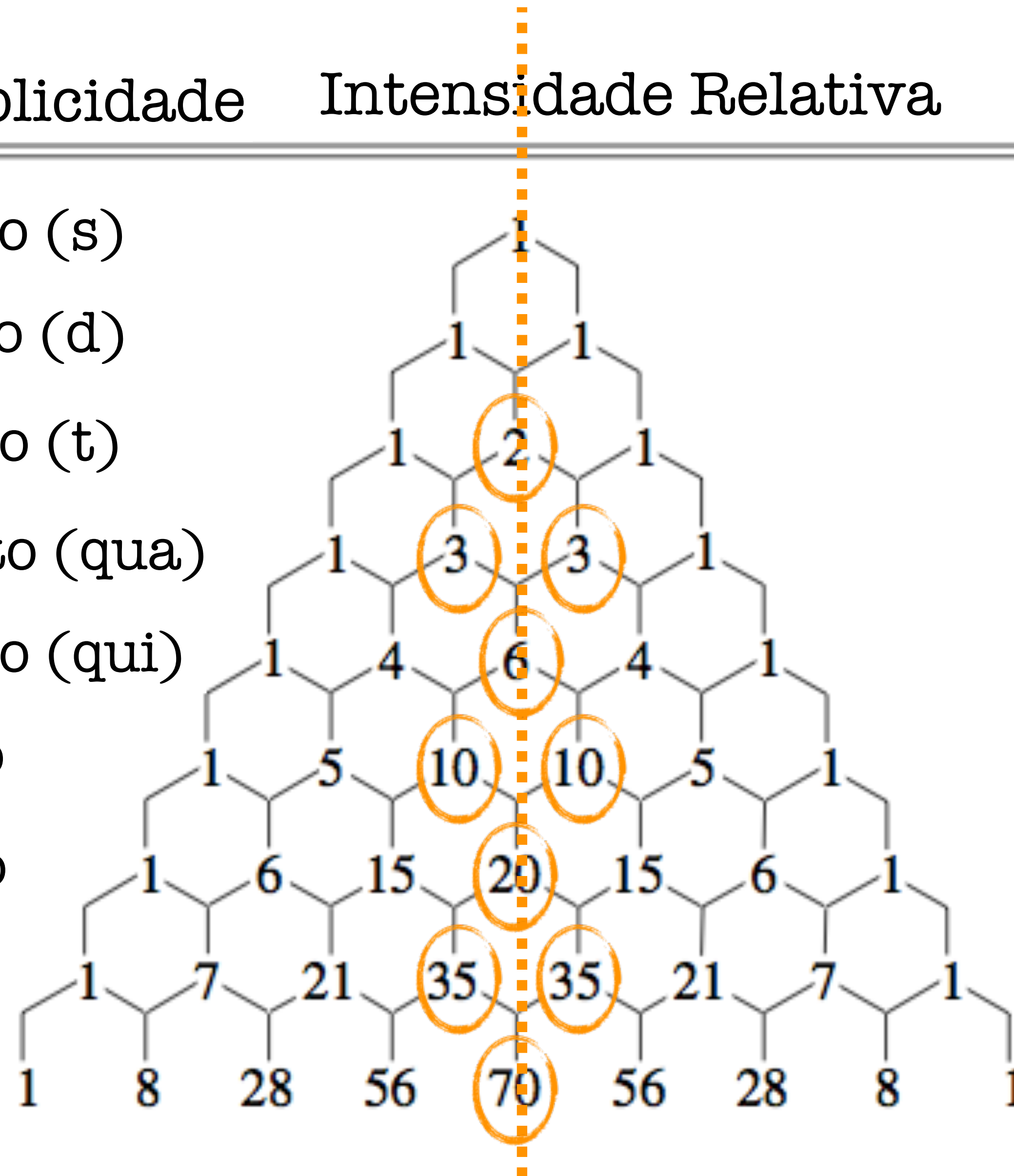
4 Quinteto (qui)

5 Sexteto

6 Septeto

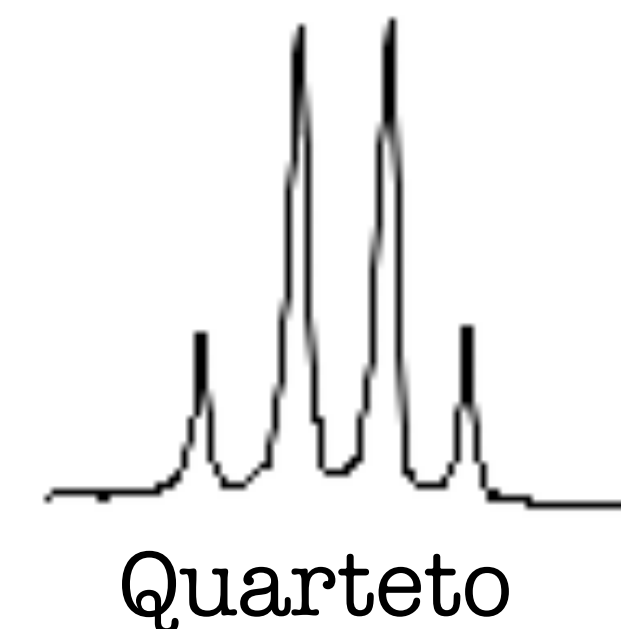
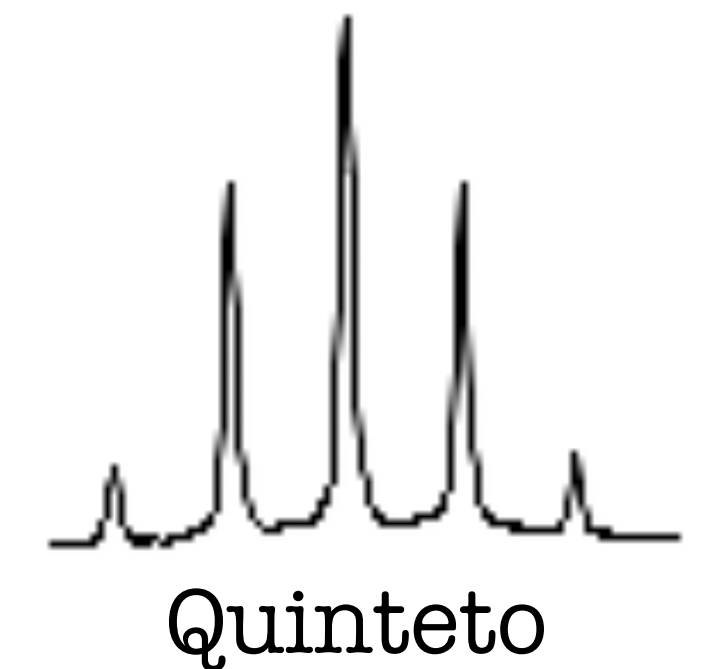
7 Octeto

8 Noneto



$N+1$

N = número de núcleos equivalentes com spin $1/2$



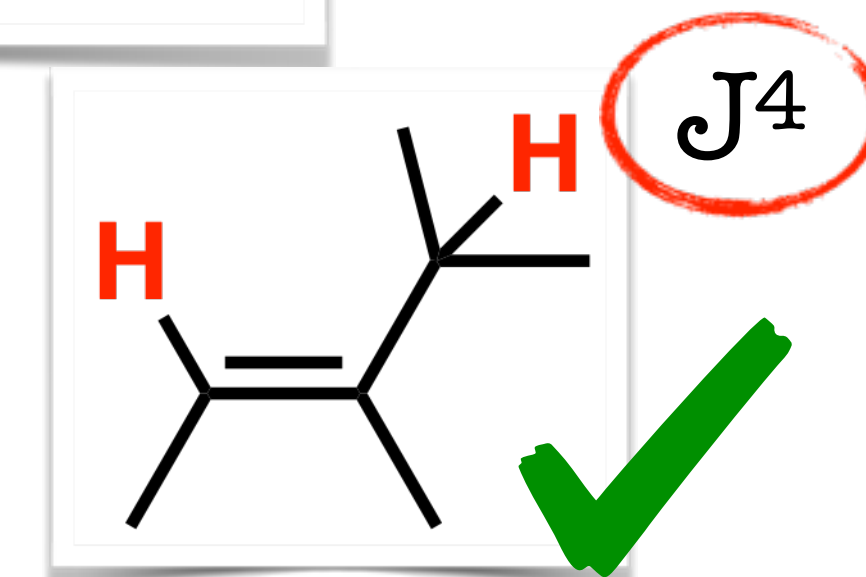
Desdobramento spin-spin

J depende da distância
entre os núcleos

J^2
H-C-H ocorre acoplamento se forem quimicamente
e magneticamente distintos

H-C-C-H
 J^3

H-C-C-C-H Geralmente, não ocorre acoplamento

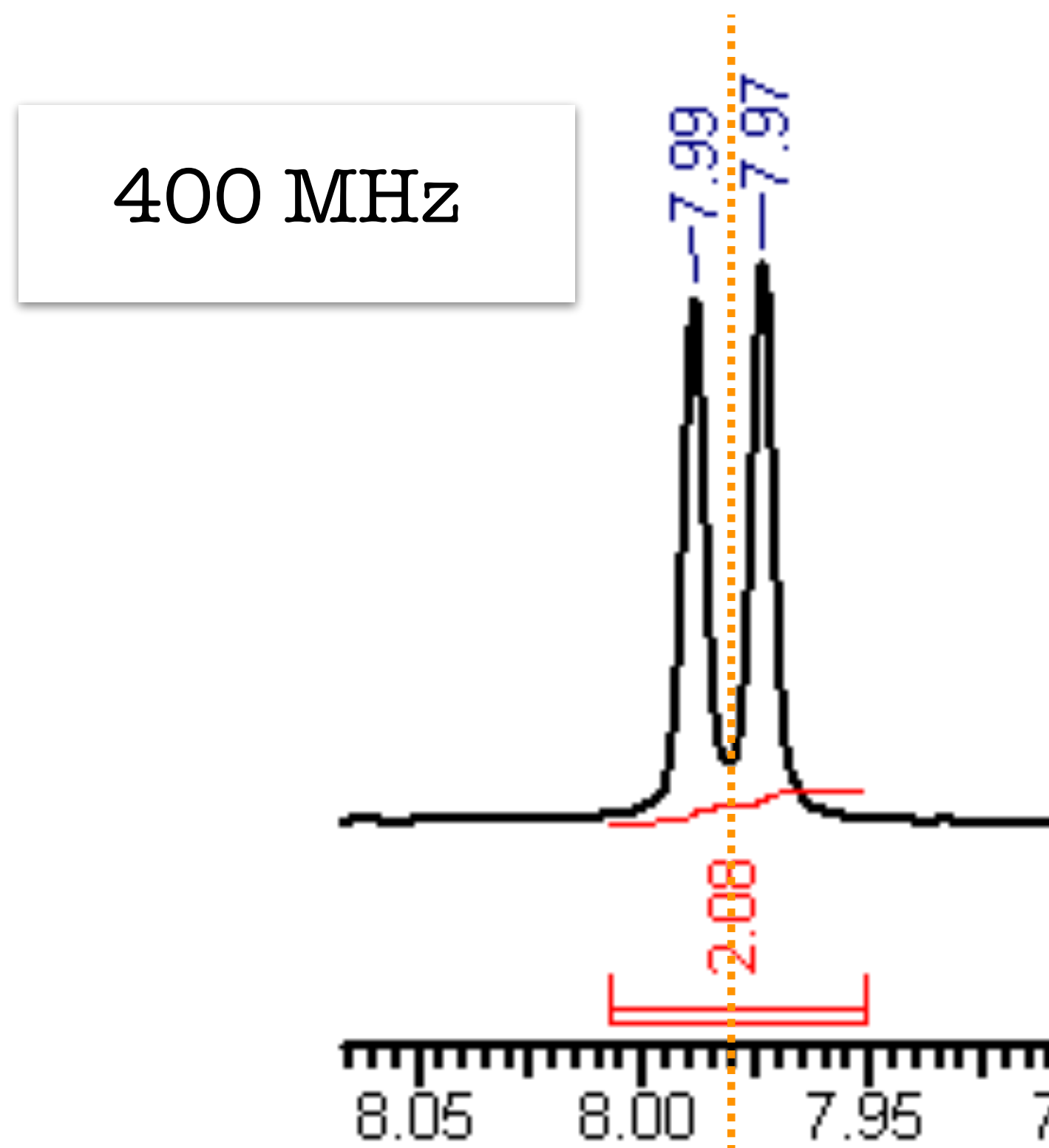


Ocorre!

...e da
densidade
eletrônica

Constante de acoplamento

- ✓ Distância entre duas linhas de um sinal: Constante de acoplamento (J em Hz);
- ✓ Distância entre as linhas (em ppm) multiplicada pela frequência do espectrômetro (em MHz).

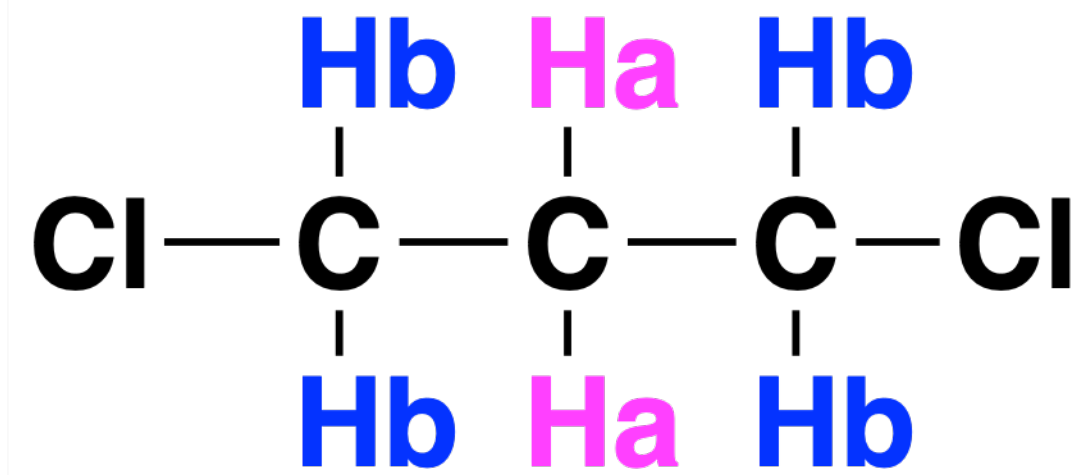


$$J = (7,99 - 7,97) \times 400 = 8,0 \text{ Hz}$$

Os sinais de Hs que acoplam entre si têm J iguais.

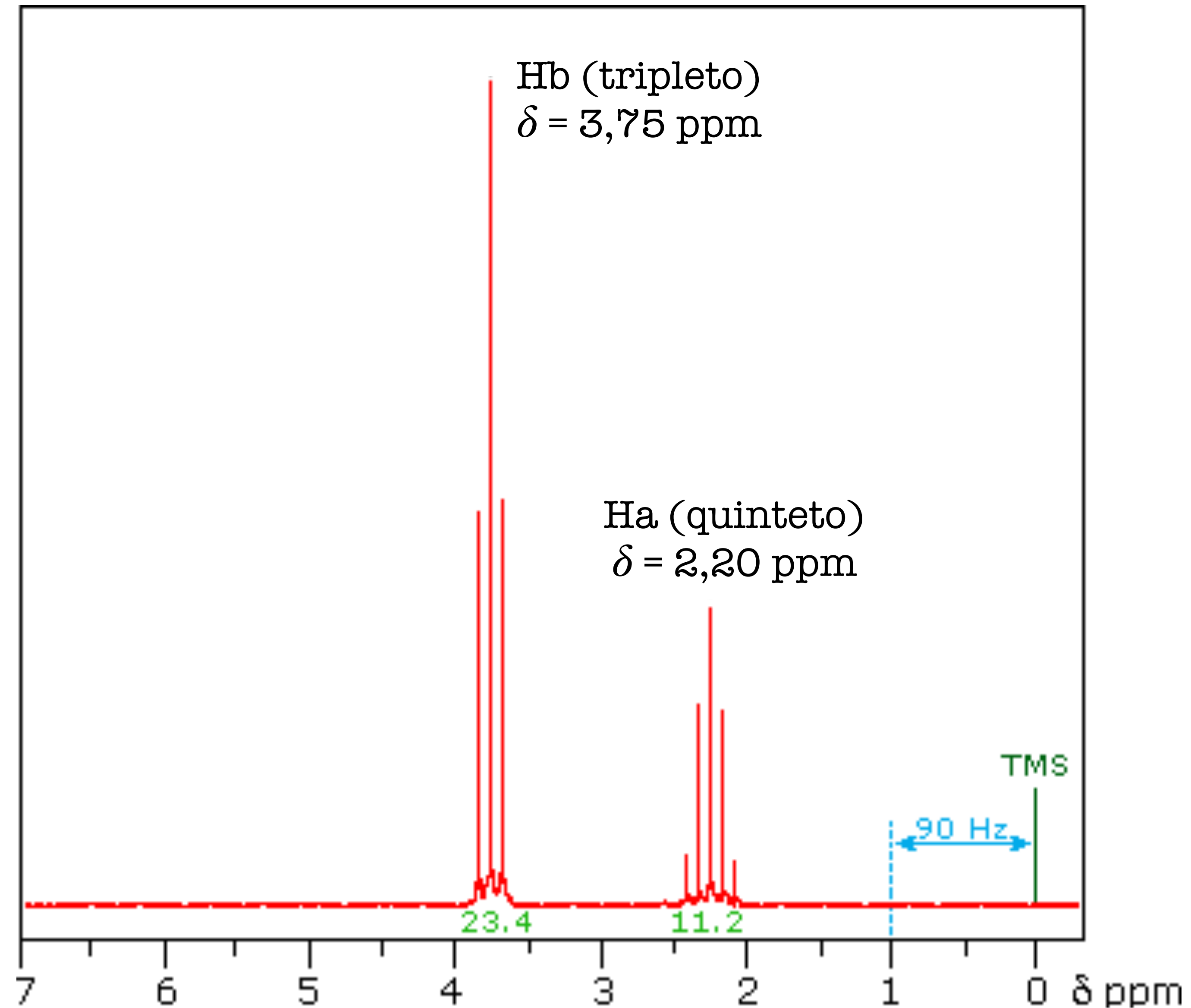
Deslocamento químico do sinal $\delta = 7,98$ ppm

Constante de acoplamento

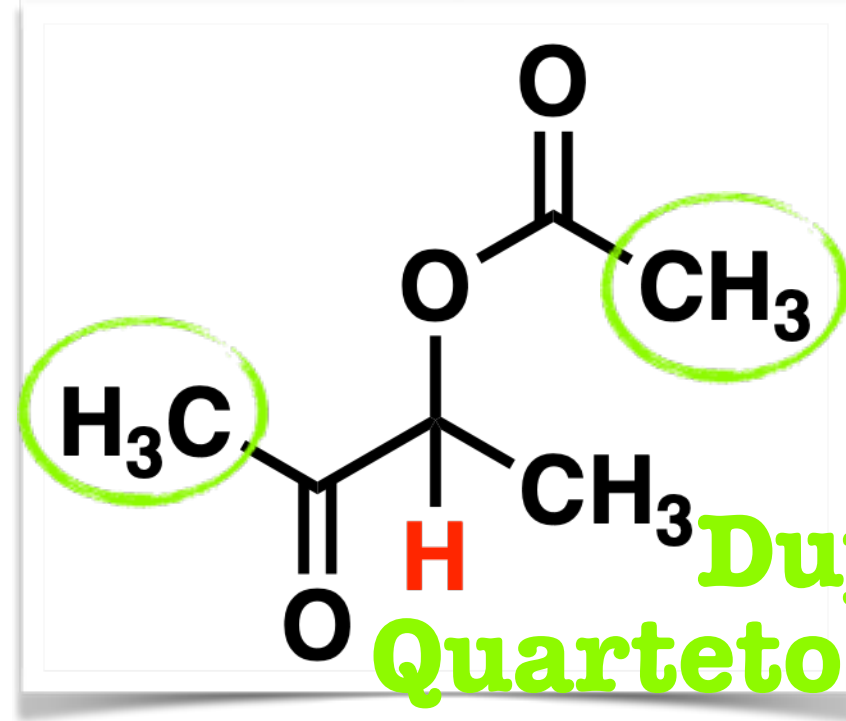


$$J_{a-b} = 6,2 \text{ Hz}$$

$$J_{b-a} = 6,2 \text{ Hz}$$



Constante de acoplamento



3-acetóxi-2-butanona

RMN ¹H 300 MHz

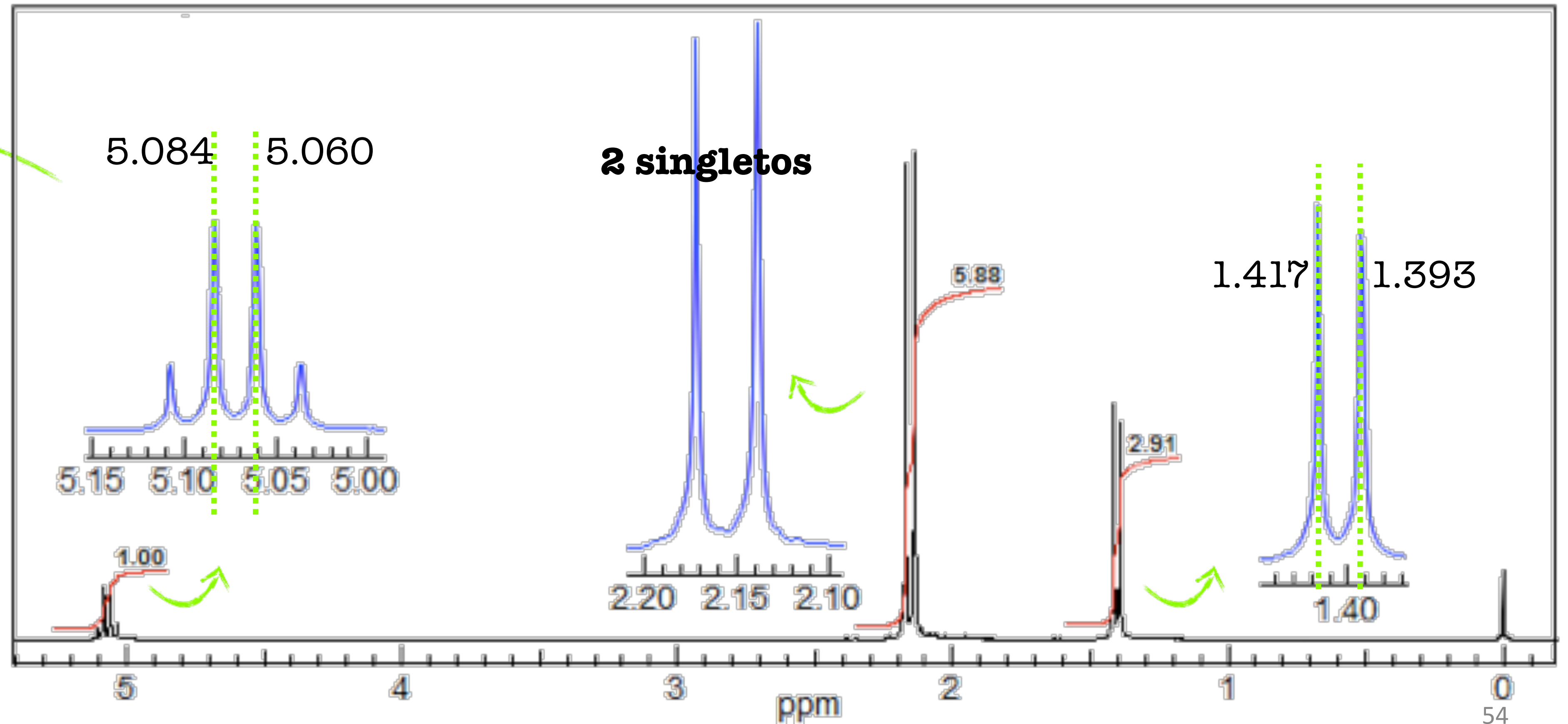
Fonte: Coleção de espectro Sigma-Aldrich

$$J = 5,084 - 5,060$$

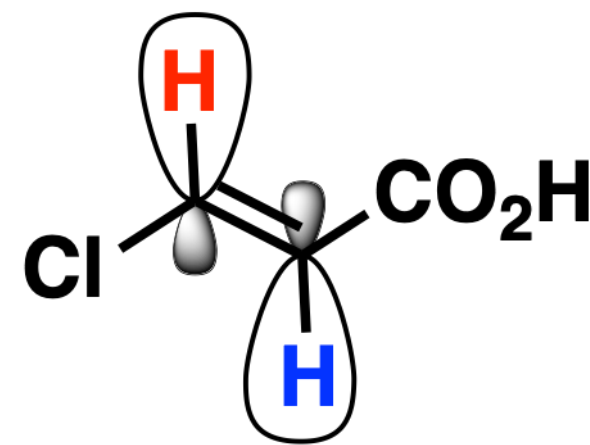
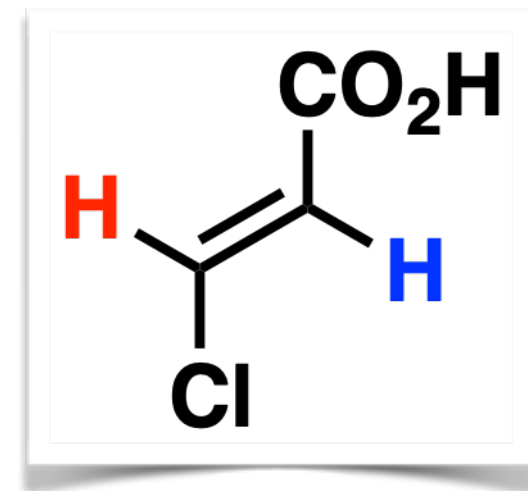
$$= 0,024 \times 300$$

$$J_{H-Me} = 7,2 \text{ Hz}$$

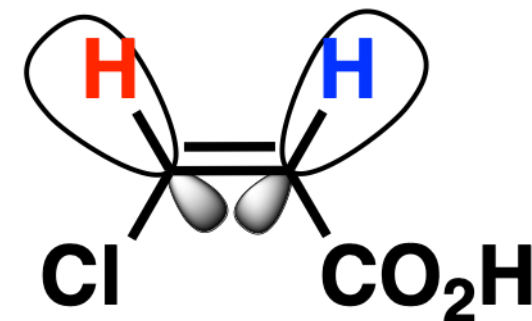
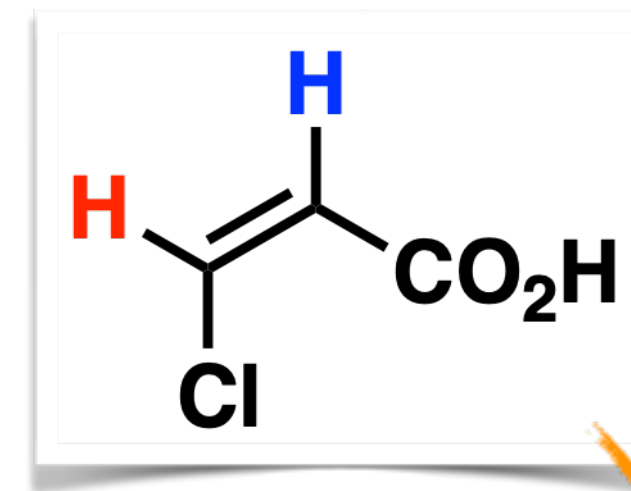
$$J_{Me-H} = 7,2 \text{ Hz}$$



Constante de acoplamento



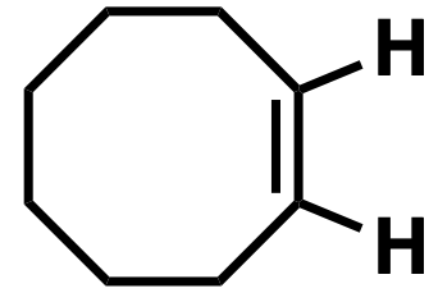
Átomos mais distantes
Orbitais paralelos
J = 15 Hz



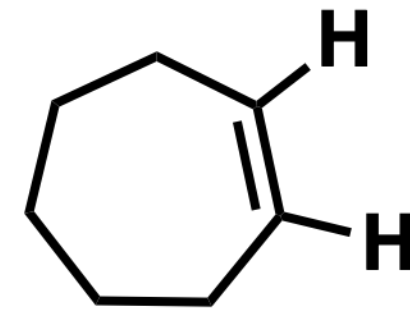
Átomos mais próximos
Orbitais NÃO paralelos
J = 9 Hz

Constantes de acoplamento diferentes para Cis e Trans

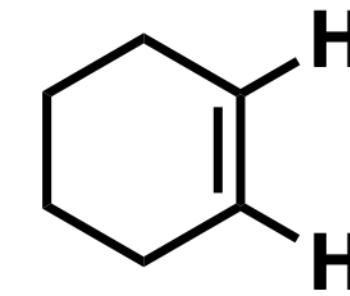
Constante de acoplamento



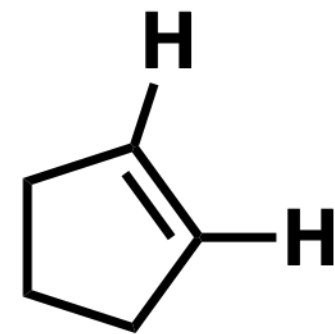
$J = 10.4 \text{ Hz}$
(varia de 11.8 a 12.8)



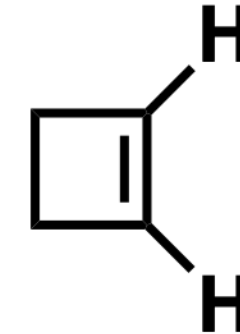
$J = 11.0 \text{ Hz}$
(varia de 9.7 a 12.5)



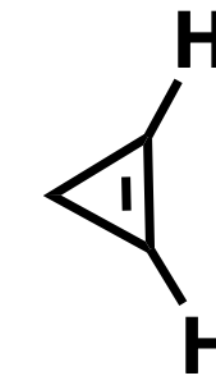
$J = 10.1 \text{ Hz}$
(varia de 8.8 a 10.5)



$J = 5.6 \text{ Hz}$
(varia de 5.1 a 7.0)



$J = 2.9 \text{ Hz}$
(varia de 3.0 a 3.5)

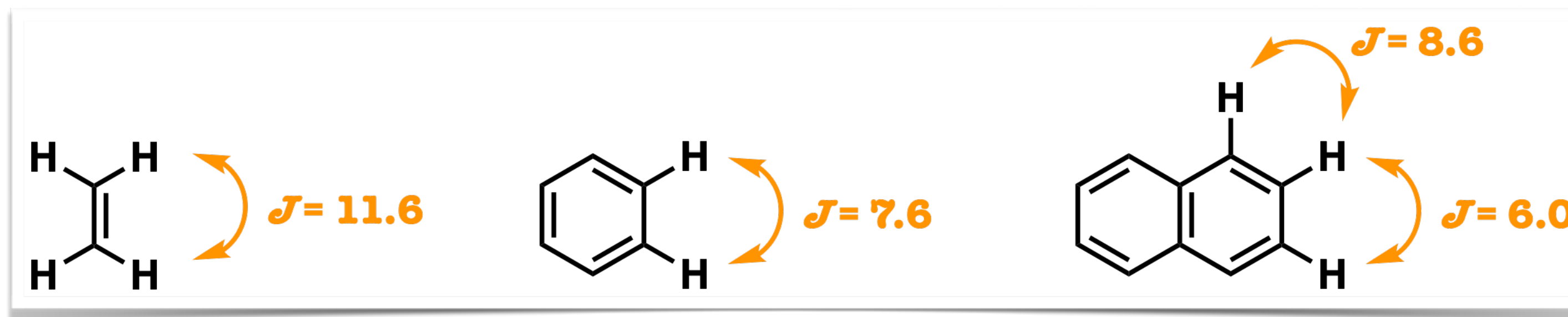


$J = 1.3 \text{ Hz}$
(varia de 0 a 1.3)

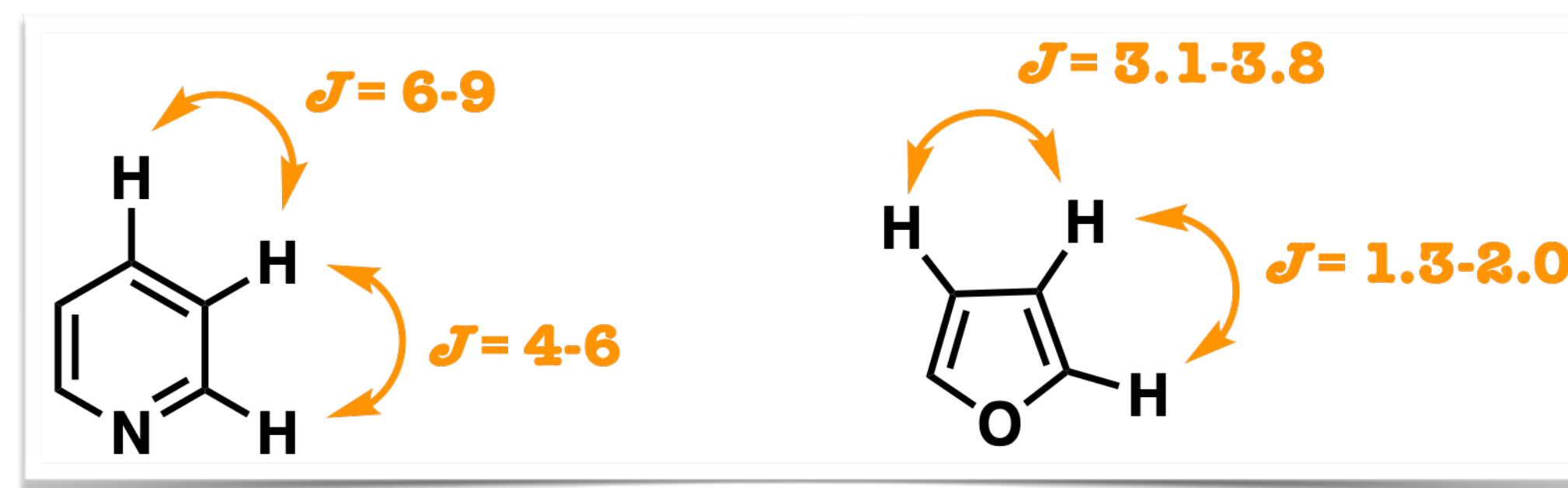
Cicloalquenos menores que o ciclohexeno mostram J reduzidos.

Constante de acoplamento

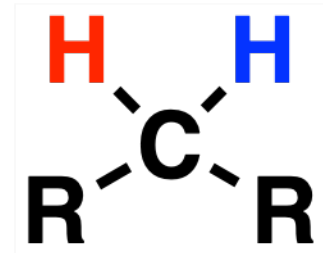
Aromáticos tem J menores que alquenos:



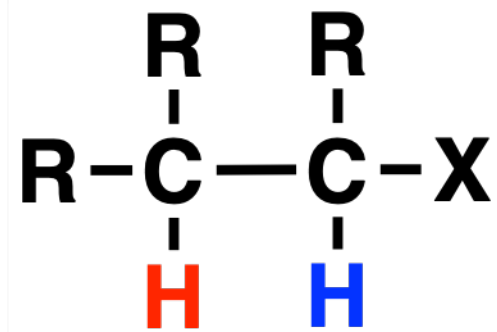
E heterociclos tem J menores que sistemas hidrocarbônicos



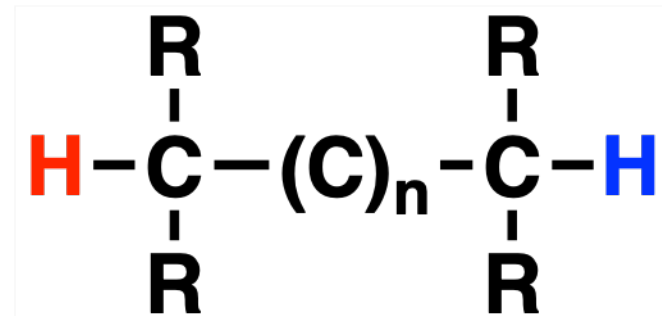
Constante de acoplamento



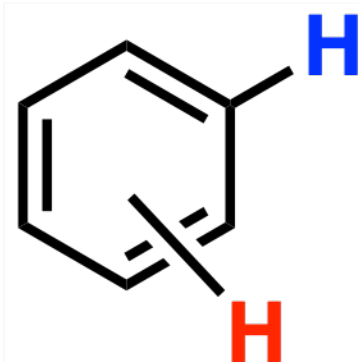
$J = 12-15$
(precisam ser diastereotópicos)



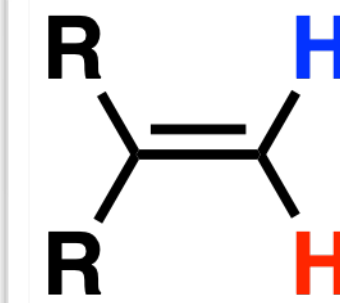
$J = 6-8$ Hz



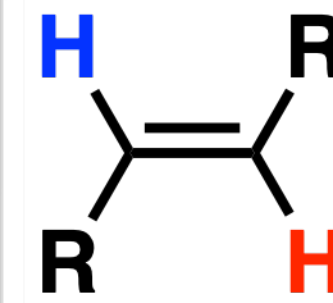
$J = 0$ Hz
(a menos que seja uma orientação rígida e ideal)



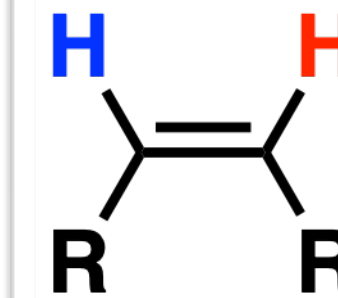
$J_{orto} = 6 - 9$ Hz
 $J_{meta} = 1-3$ Hz
 $J_{para} = 0-1$



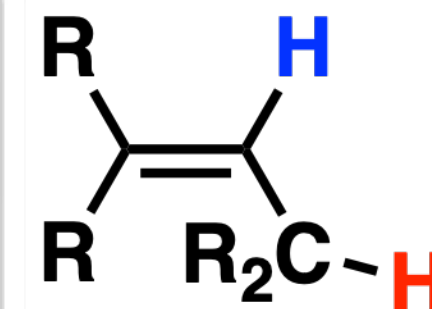
$J = 0.5 - 3$ Hz



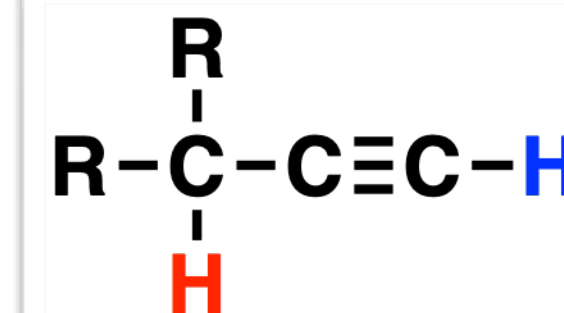
$J = 12 - 18$ Hz



$J = 7 - 12$ Hz



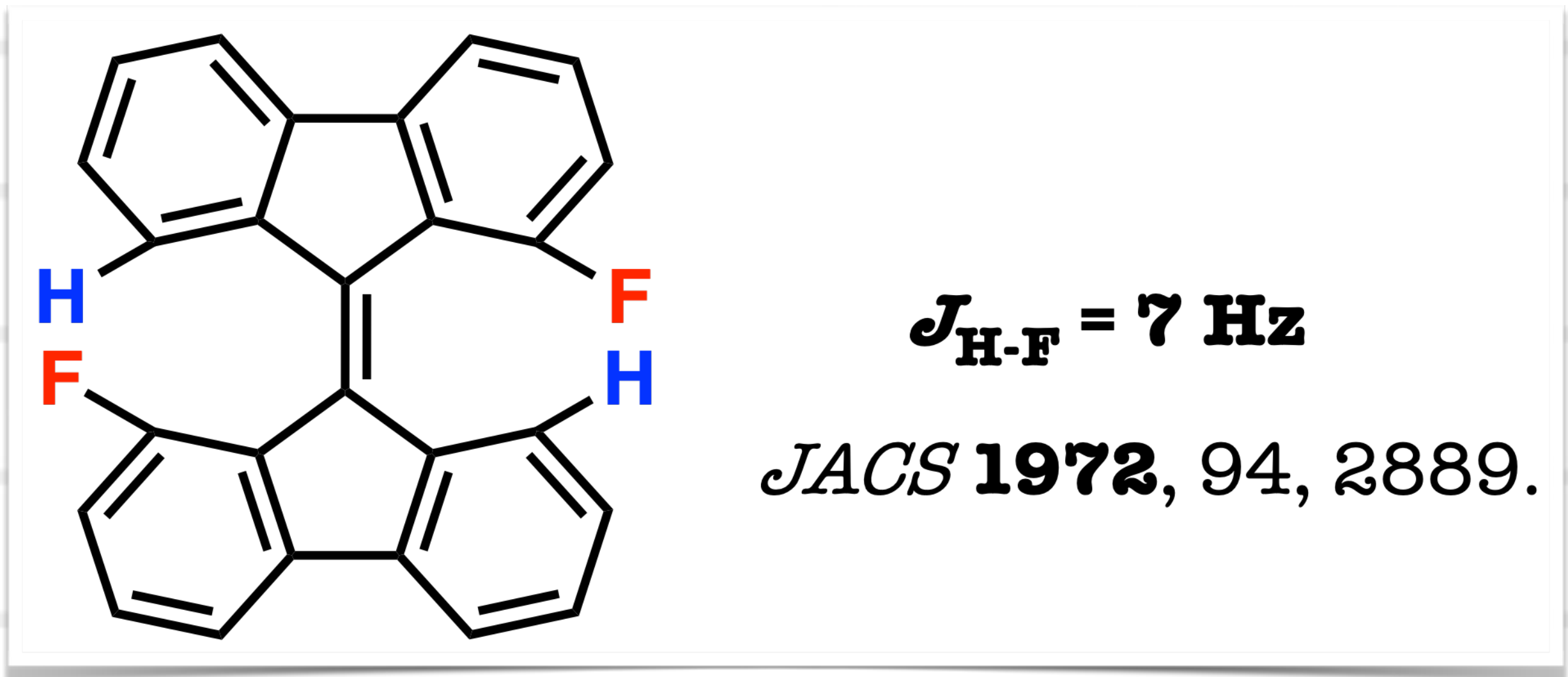
$J = 3 - 11$ Hz



$J = 2 - 3$ Hz

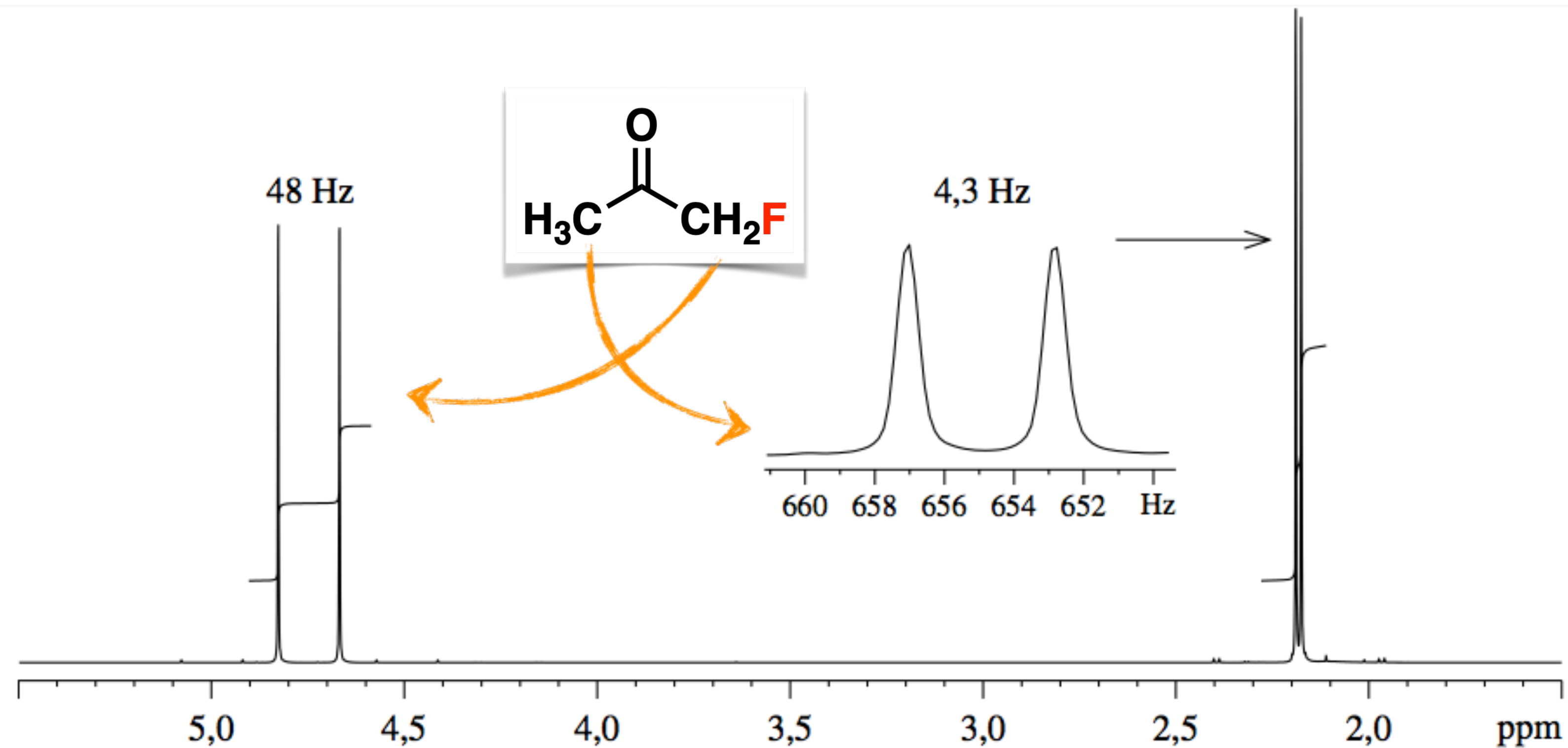
Constante de acoplamento

- ✓ O Acoplamento, geralmente, ocorre através de ligações;
- ✓ Mas, em alguns casos, pode ocorrer através do espaço devido a proximidade;
- ✓ Ocorre na maioria das vezes entre dois núcleos de ^1H , mas pode ocorrer com outros núcleos (ex: ocorre entre ^1H e ^{19}F).



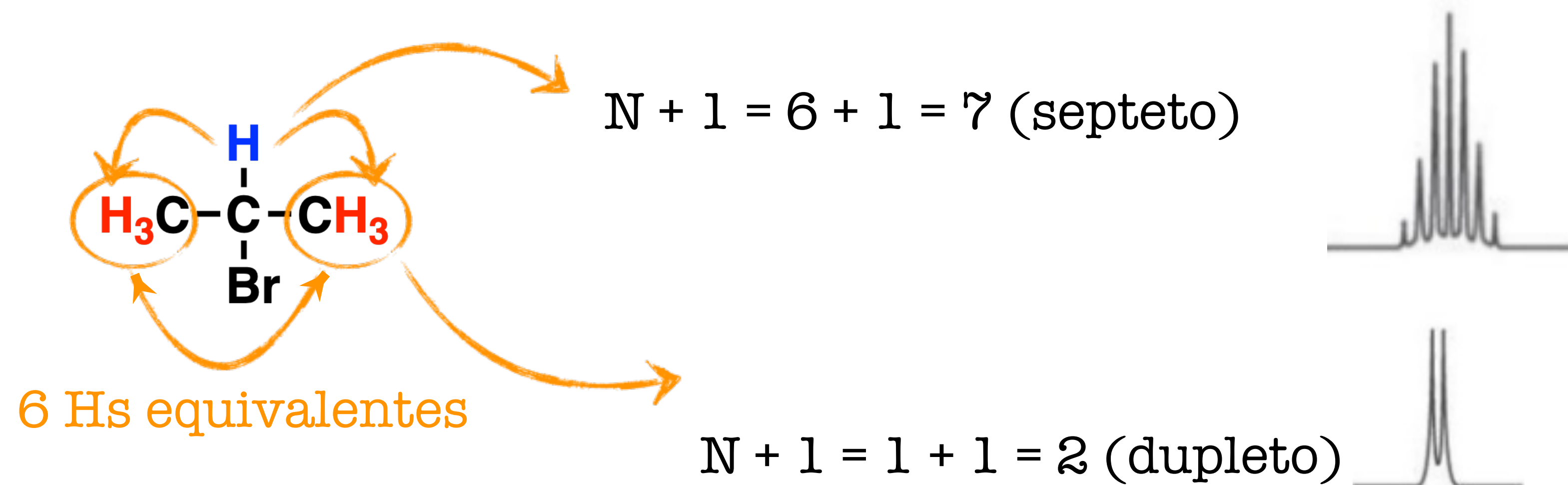
Acoplamento com ^{19}F

- ✓ ^{19}F tem número de spin igual a $1/2$, os acoplamentos H-F e H-H obedecem as mesmas regras de multiplicidade.
- ✓ $J_{\text{H-F}} > J_{\text{H-H}}$
- ✓ Acoplamento de longa distância de H-F é mais importante.



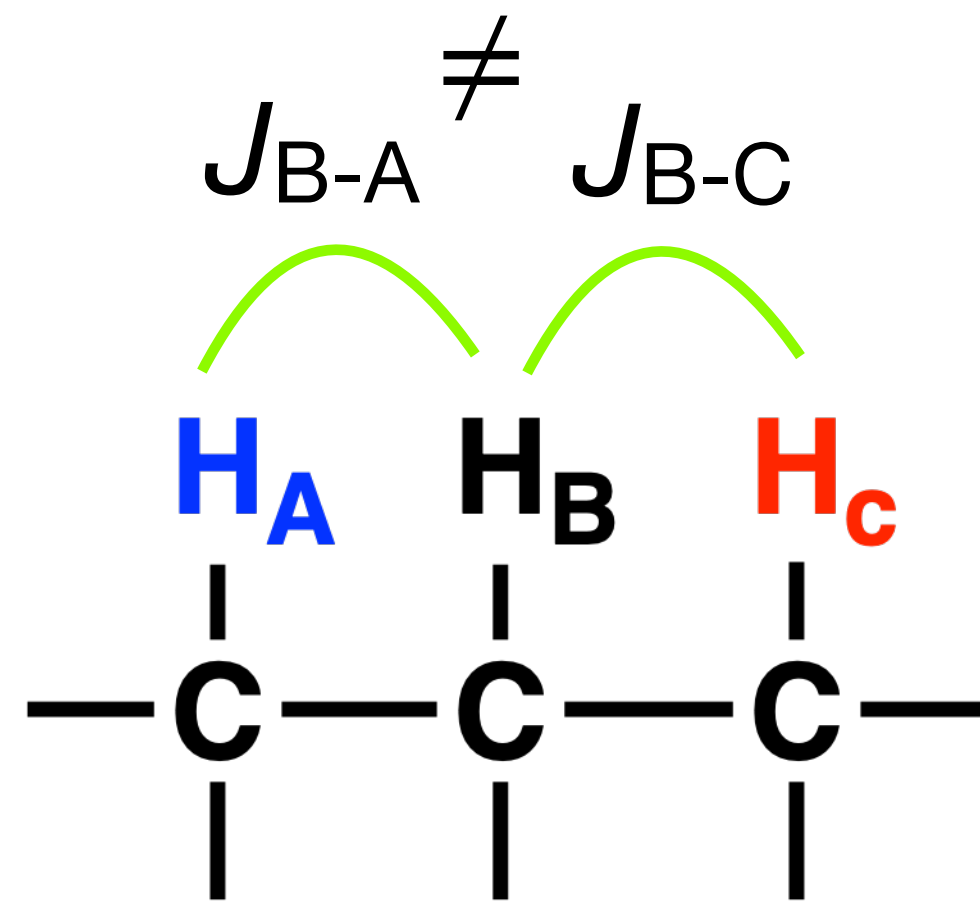
Espectro gerado em equipamento de 300 MHz

Desdobramento spin-spin

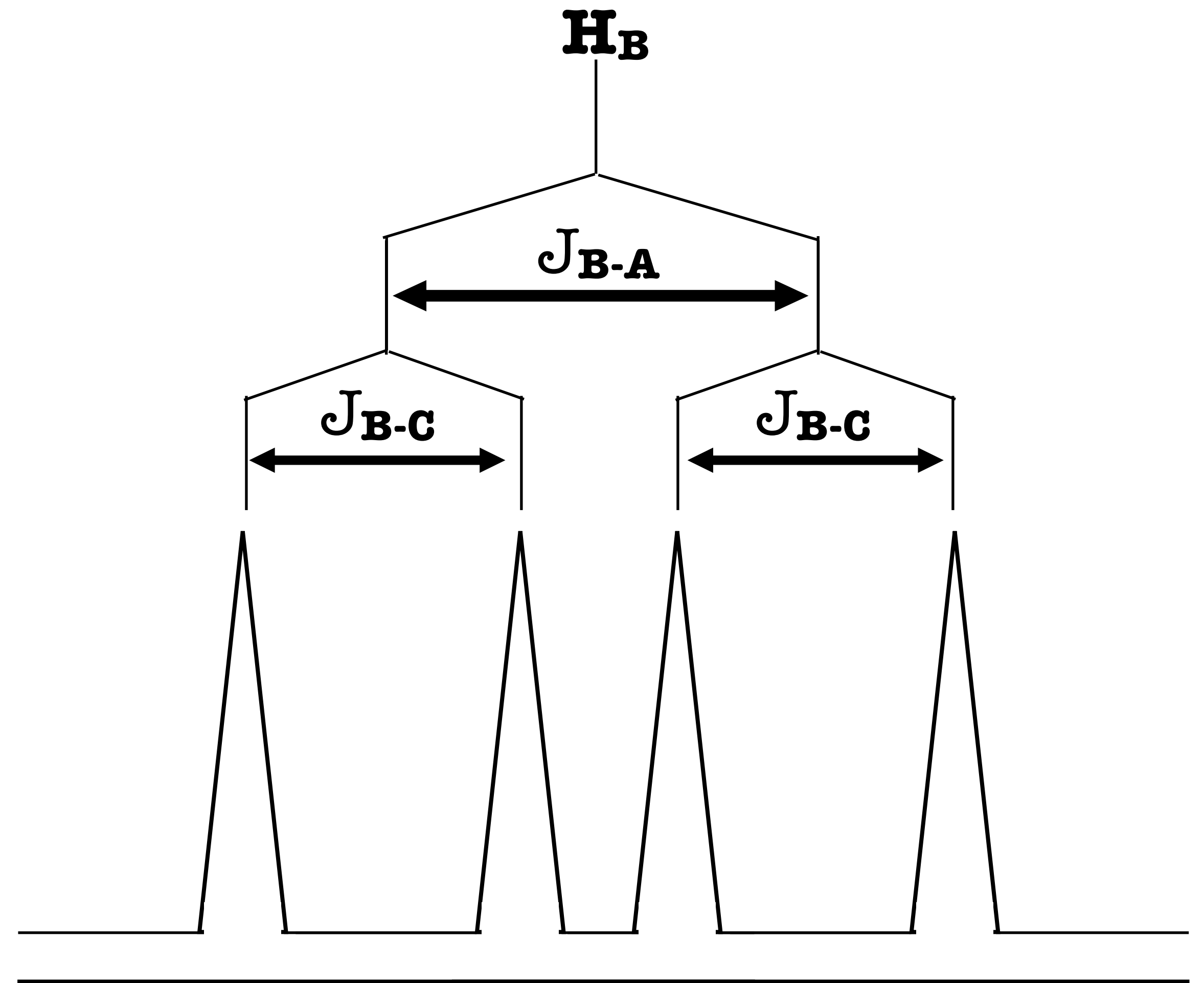


E quando o acoplamento ocorre com hidrogênios não equivalentes?

Desdobramento spin-spin



O desenho do sinal deve ser iniciado pela maior constante de acoplamento!

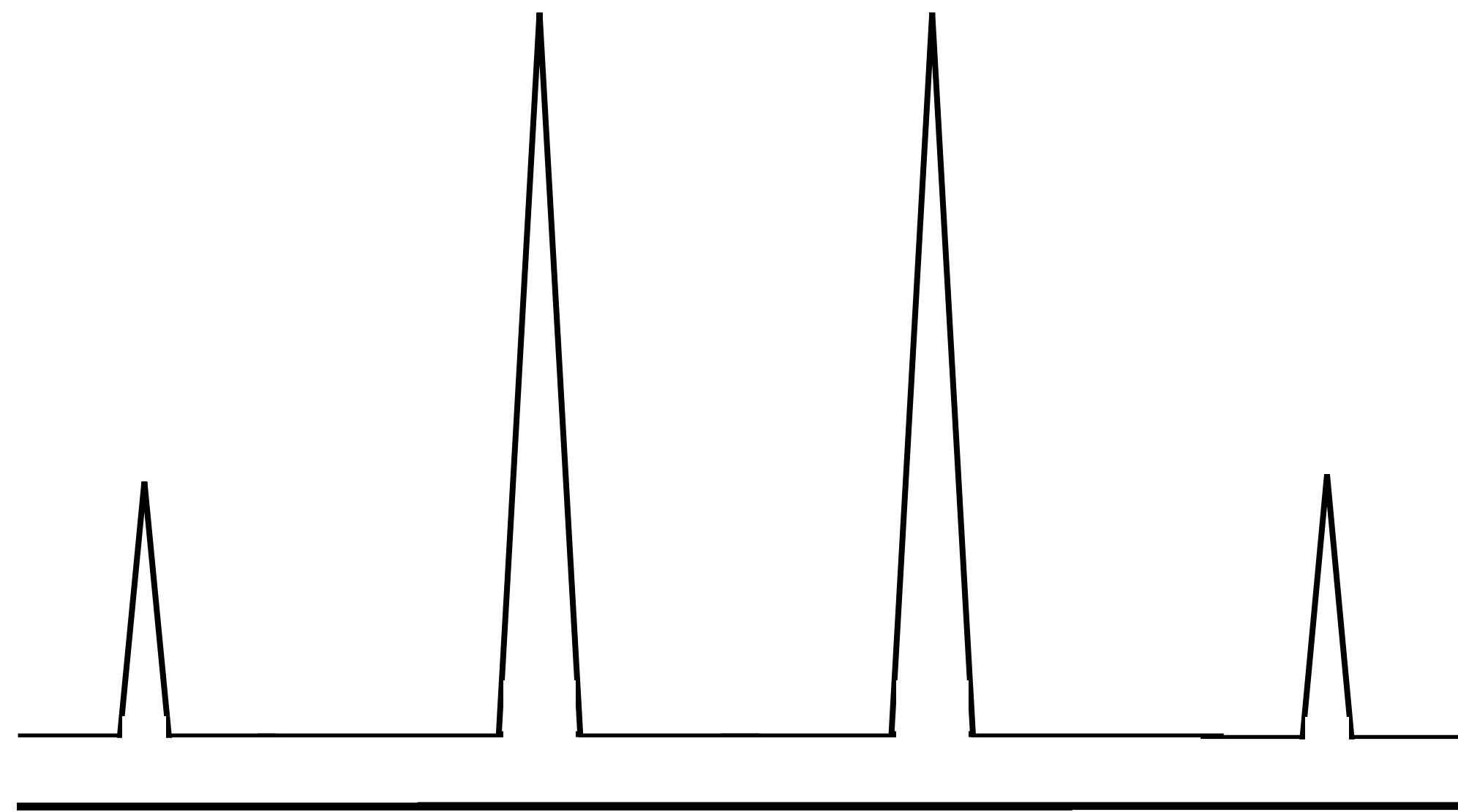


Dupleto de dupletos ou duplo dupleto

Desdobramento spin-spin

✓ Gerado pelo acoplamento com 3 núcleos equivalentes ($N+1 = 3+1 = 4$)

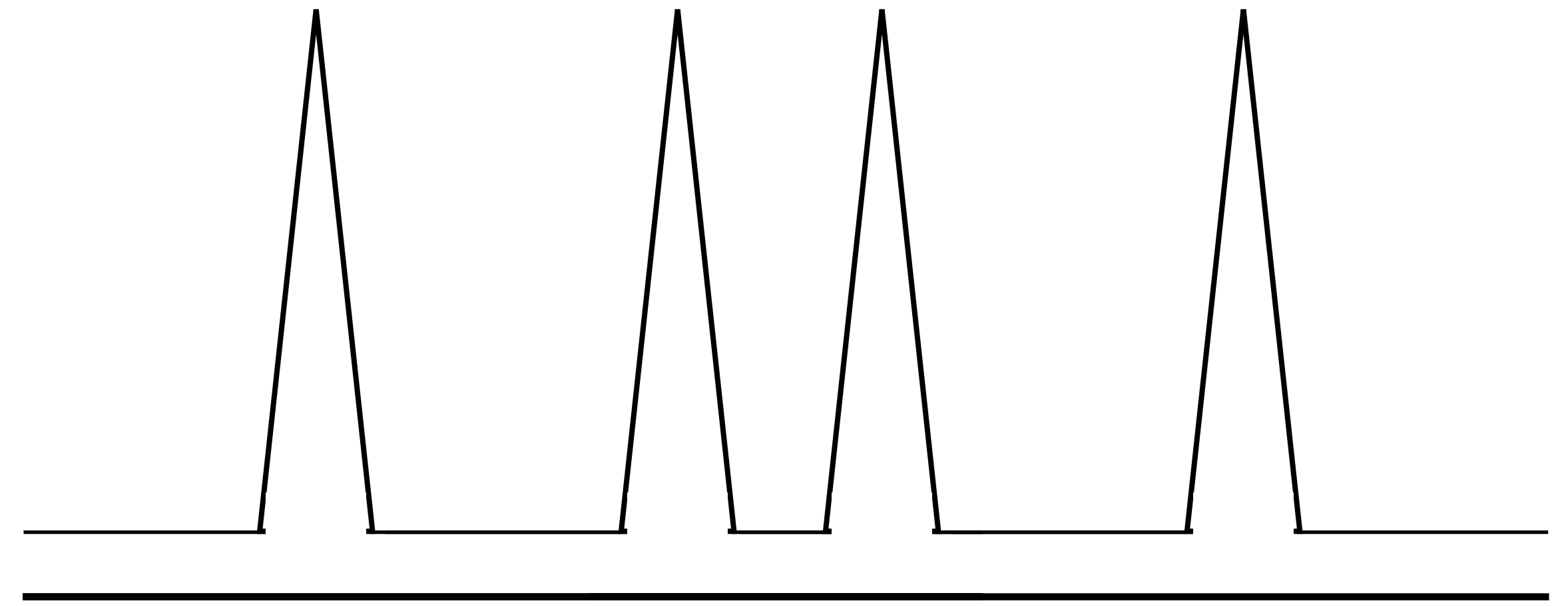
✓ Intensidades de linhas diferentes (1 : 3 : 3 : 1)



Quarteto

✓ Gerado pelo acoplamento com 2 núcleos **não** equivalentes

✓ Intensidades de linhas iguais

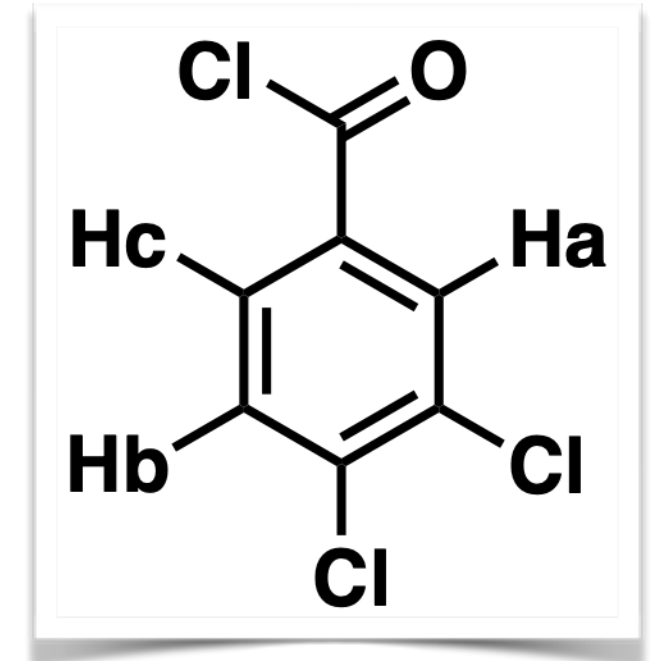
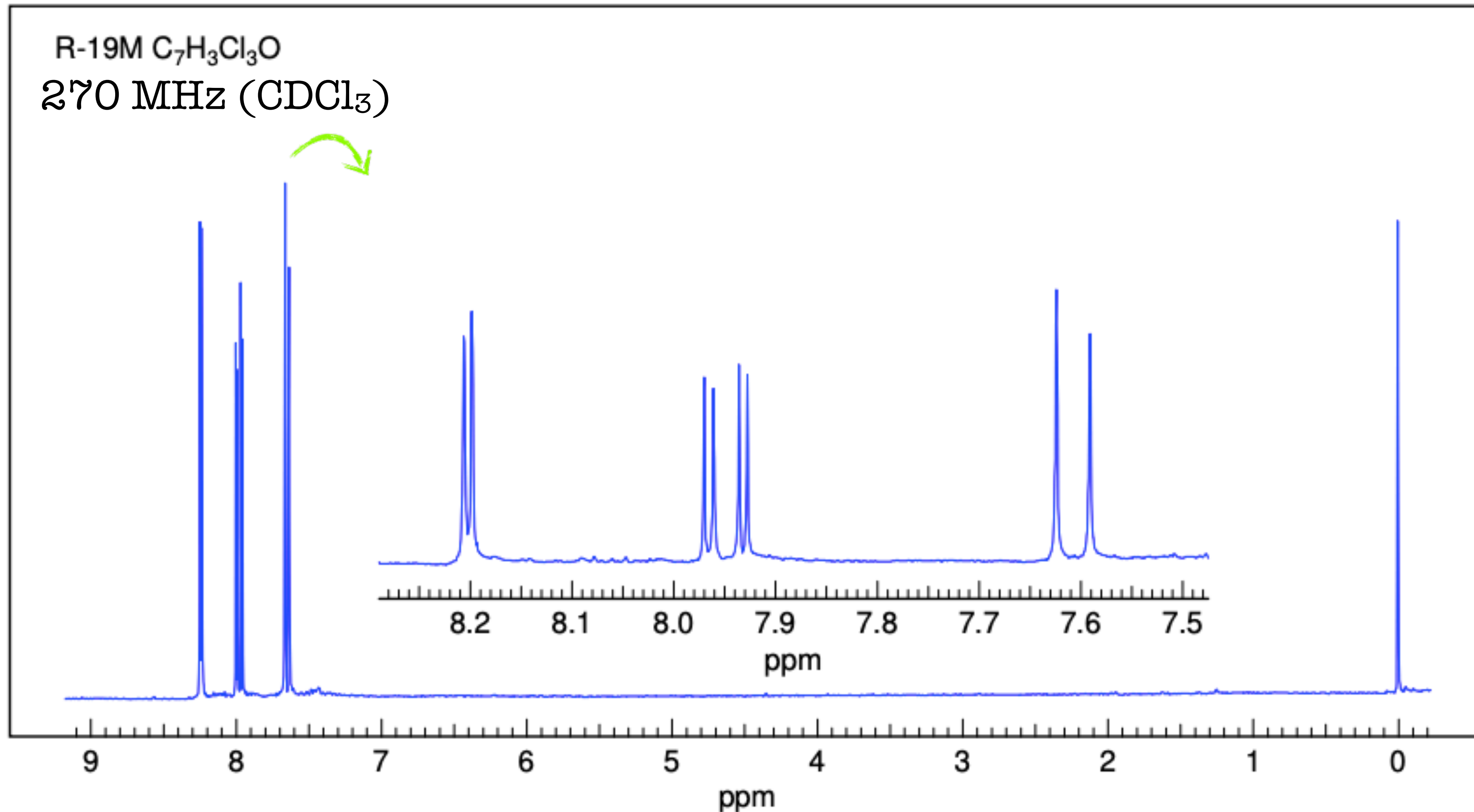


Dupleto de dupletos ou duplo dupleto

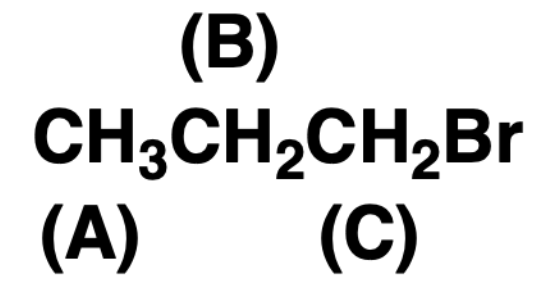
Desdobramento spin-spin

Valores típicos para o benzeno:

Hs orto $\rightarrow J = 7-9$ Hz Hs meta $\rightarrow J = 2-3$ Hz Hs para $\rightarrow J = < 1$ Hz

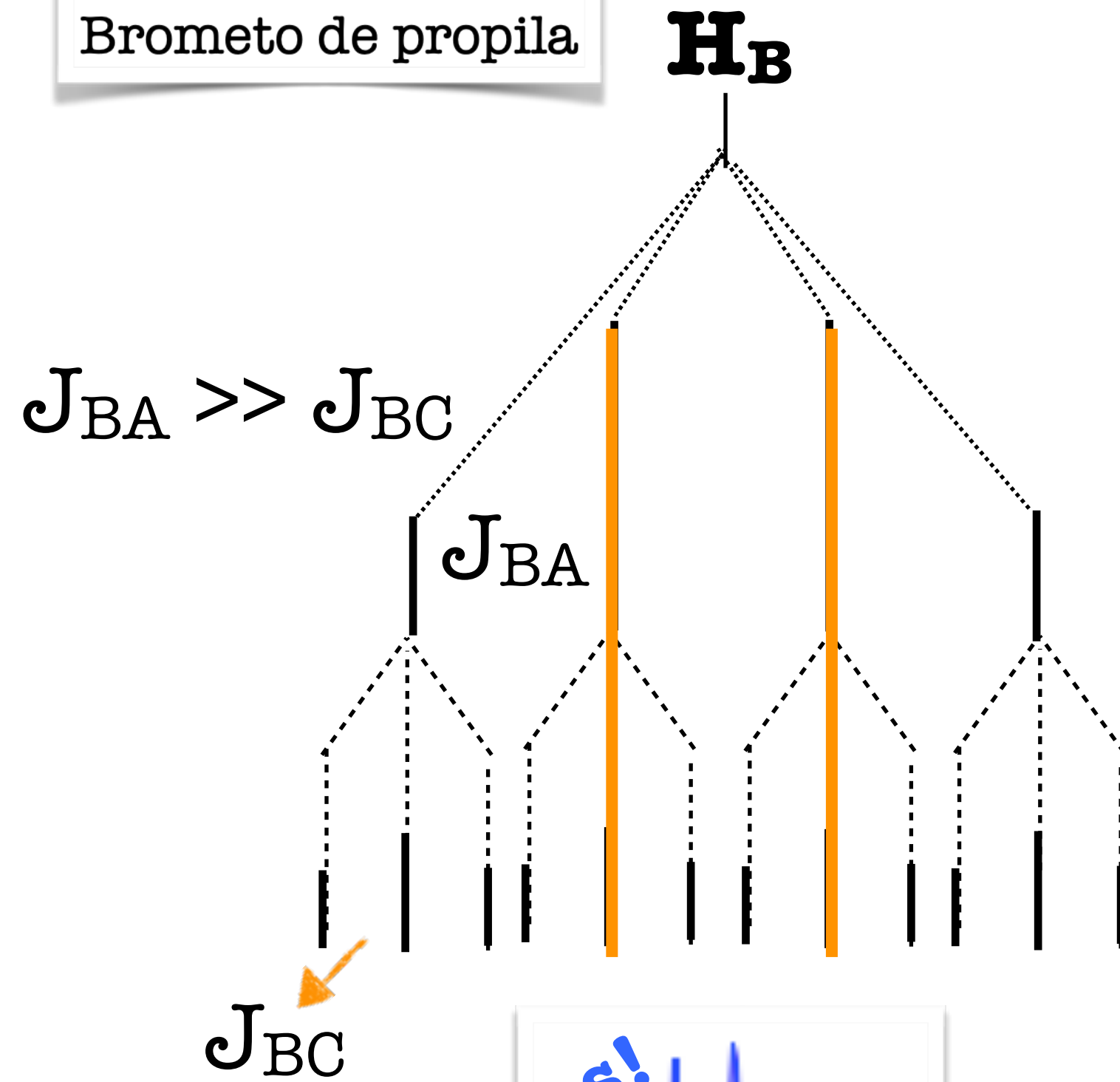


Desdobramento spin-spin

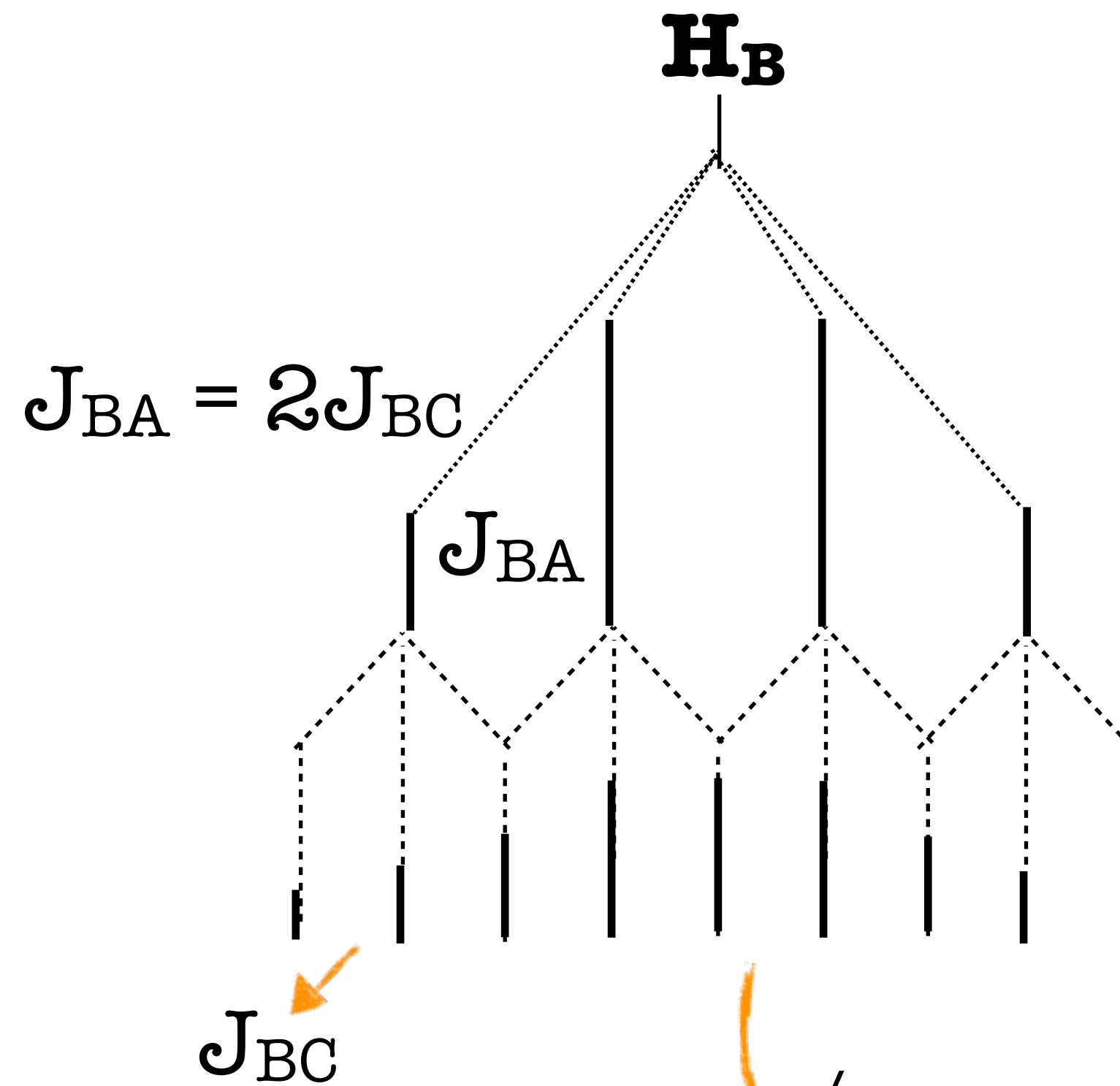
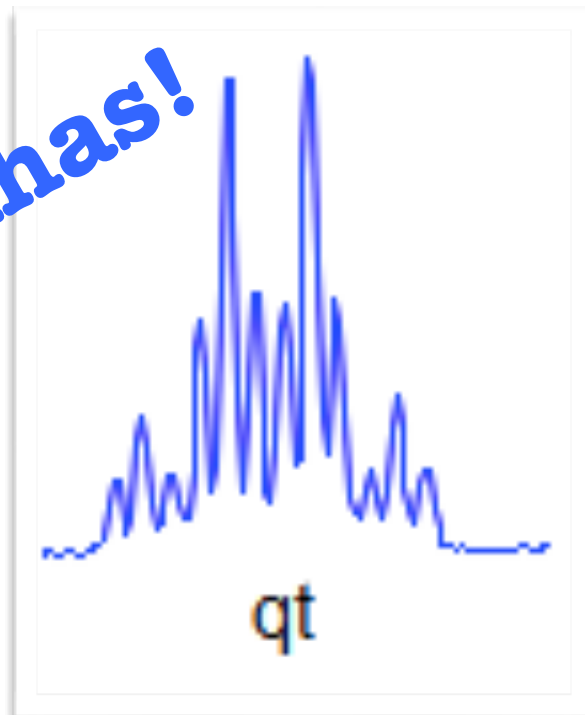


Brometo de propila

Quarteto de tripletes



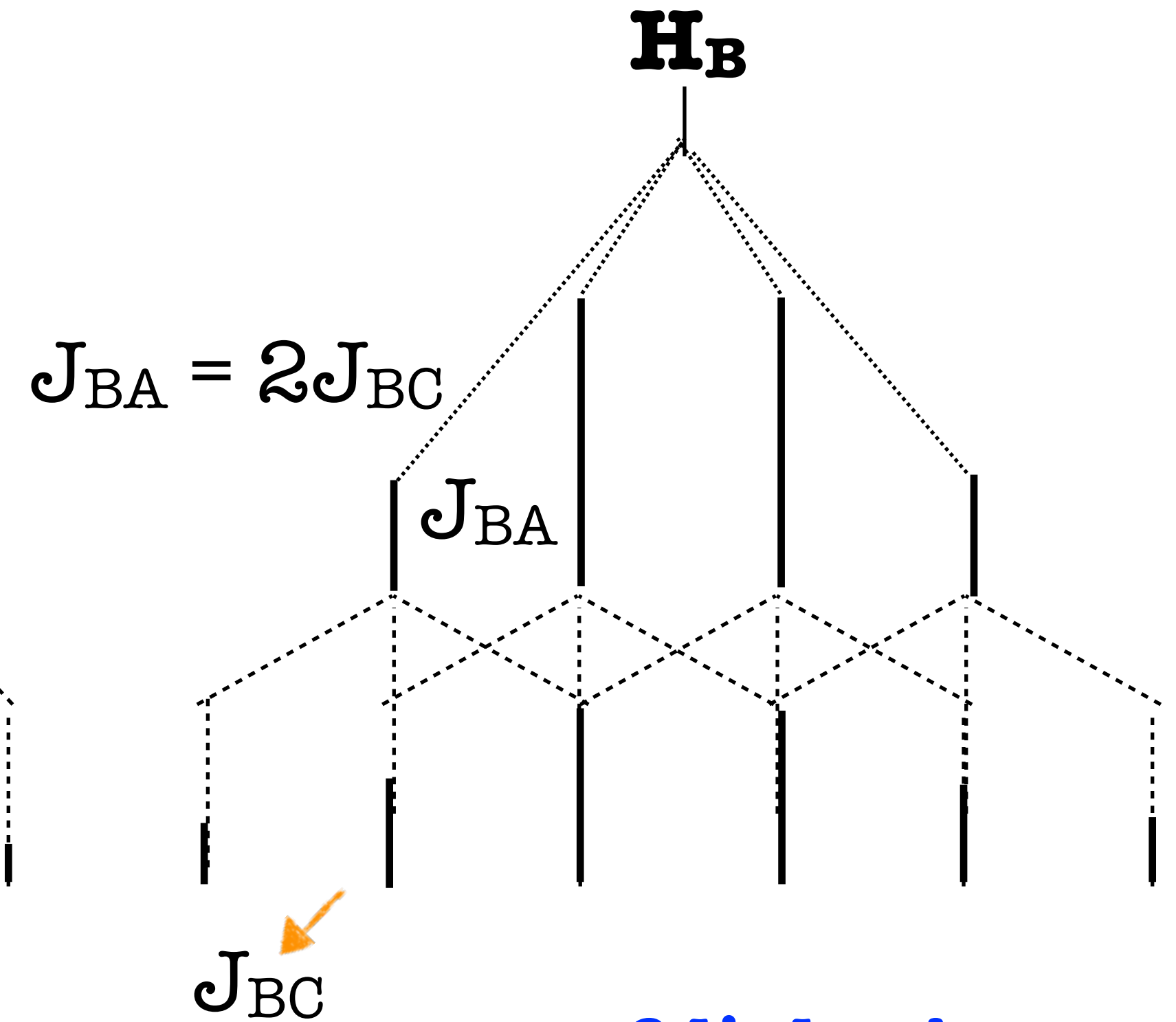
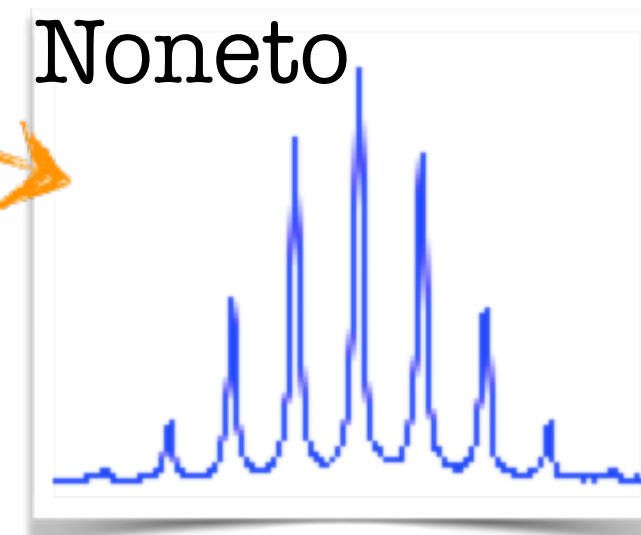
12 linhas!



9 linhas!

\neq

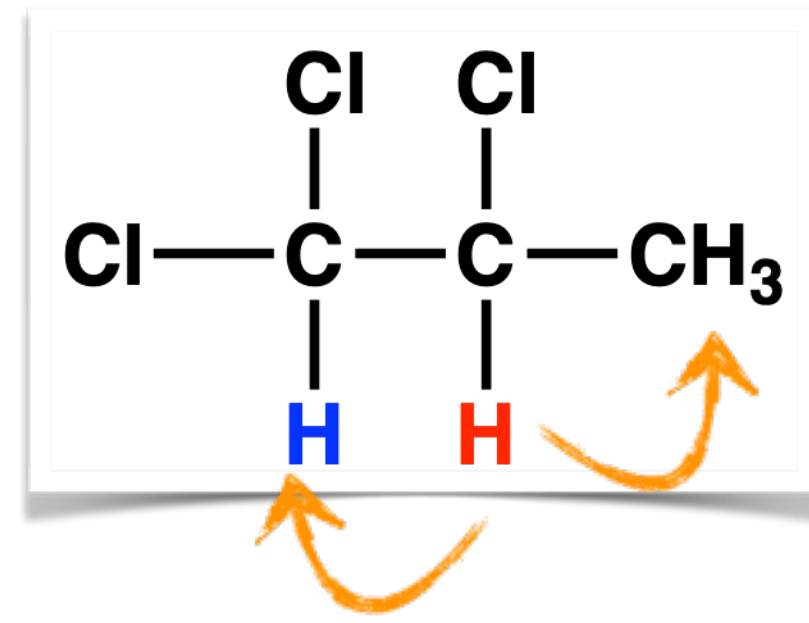
Noneto



6 linhas!

Fica muito similar
a um sexteto!

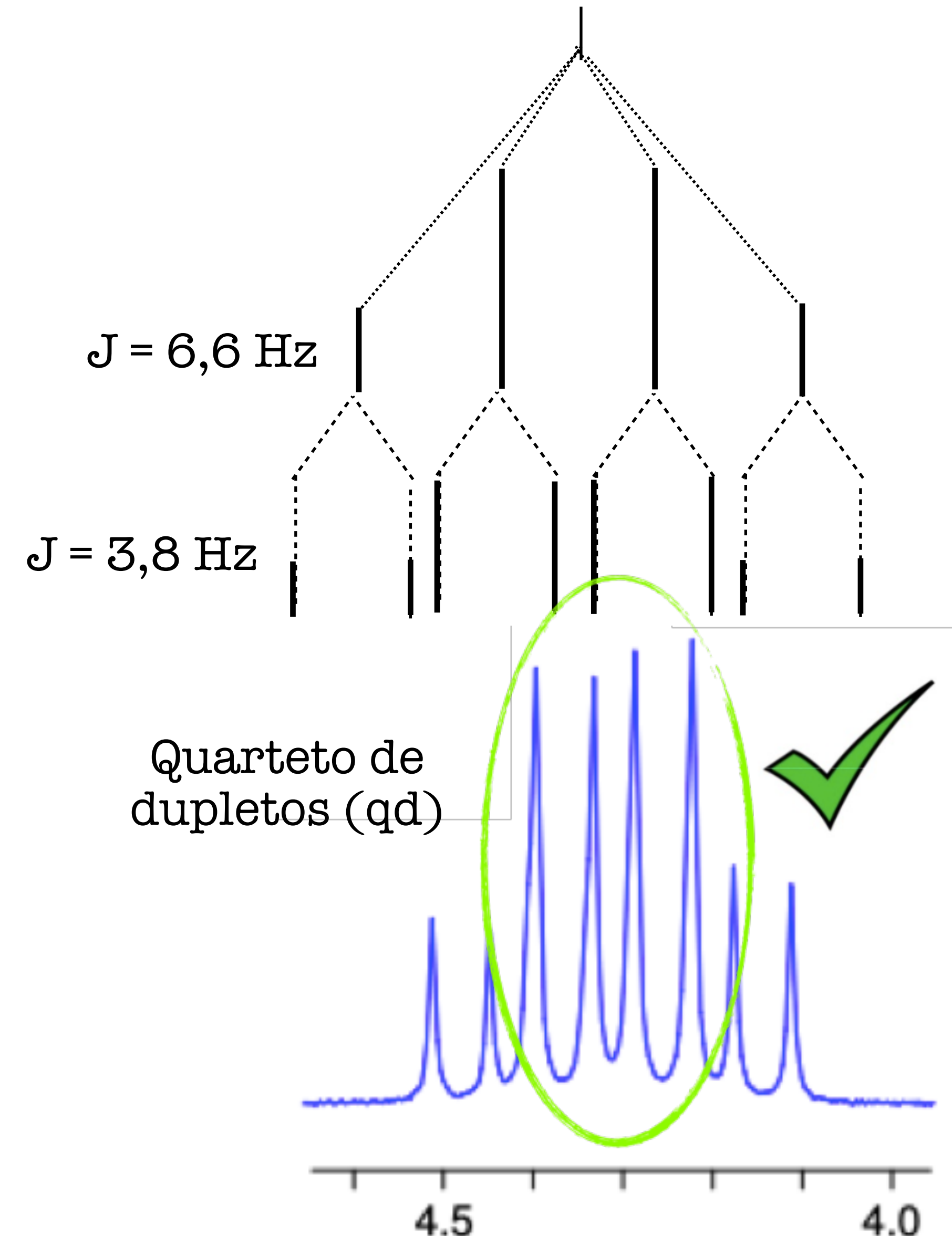
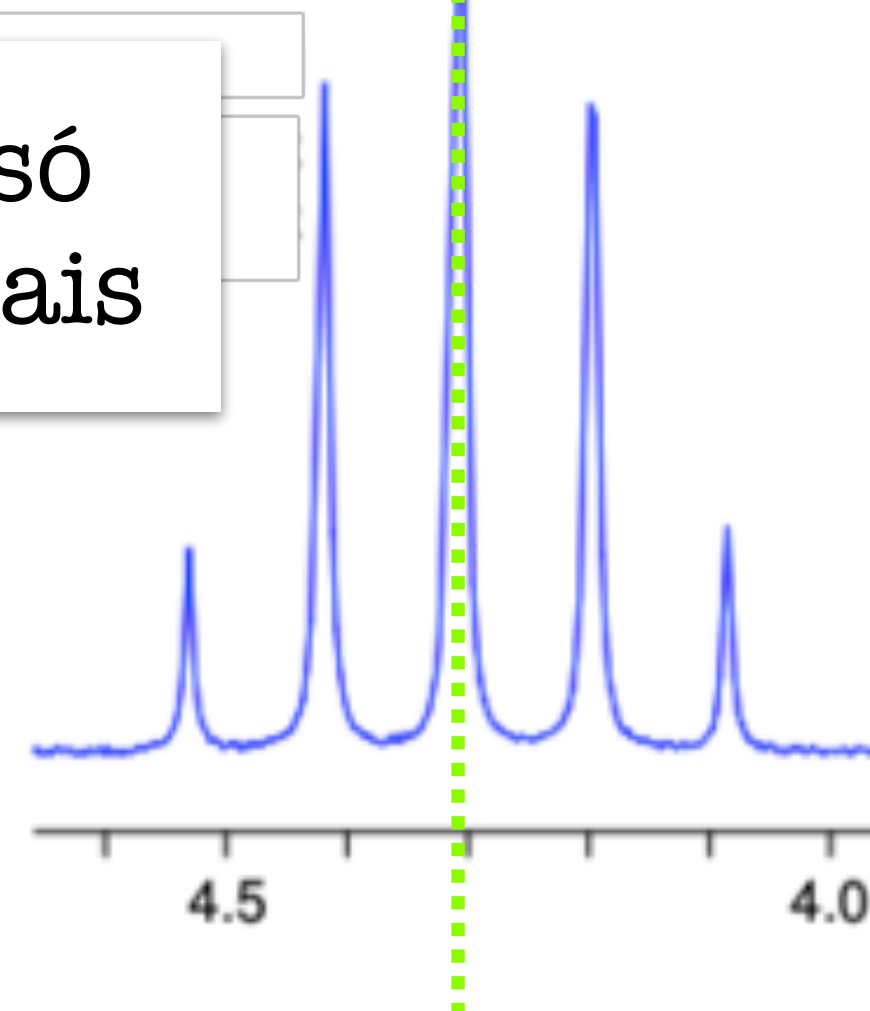
Desdobramento spin-spin



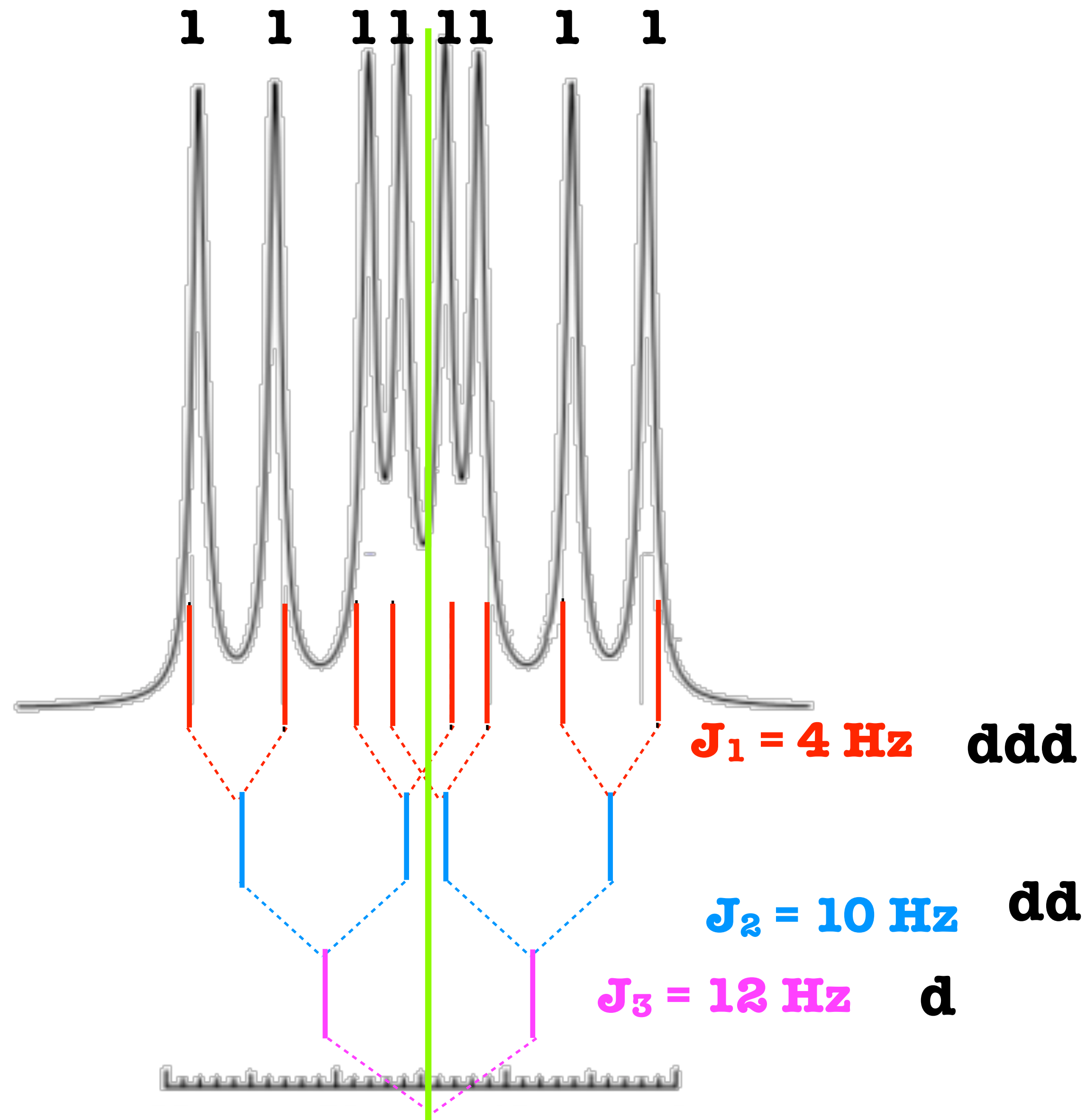
Constantes de acoplamentos diferentes

Centrosimétrico

X Penteto: só para J iguais



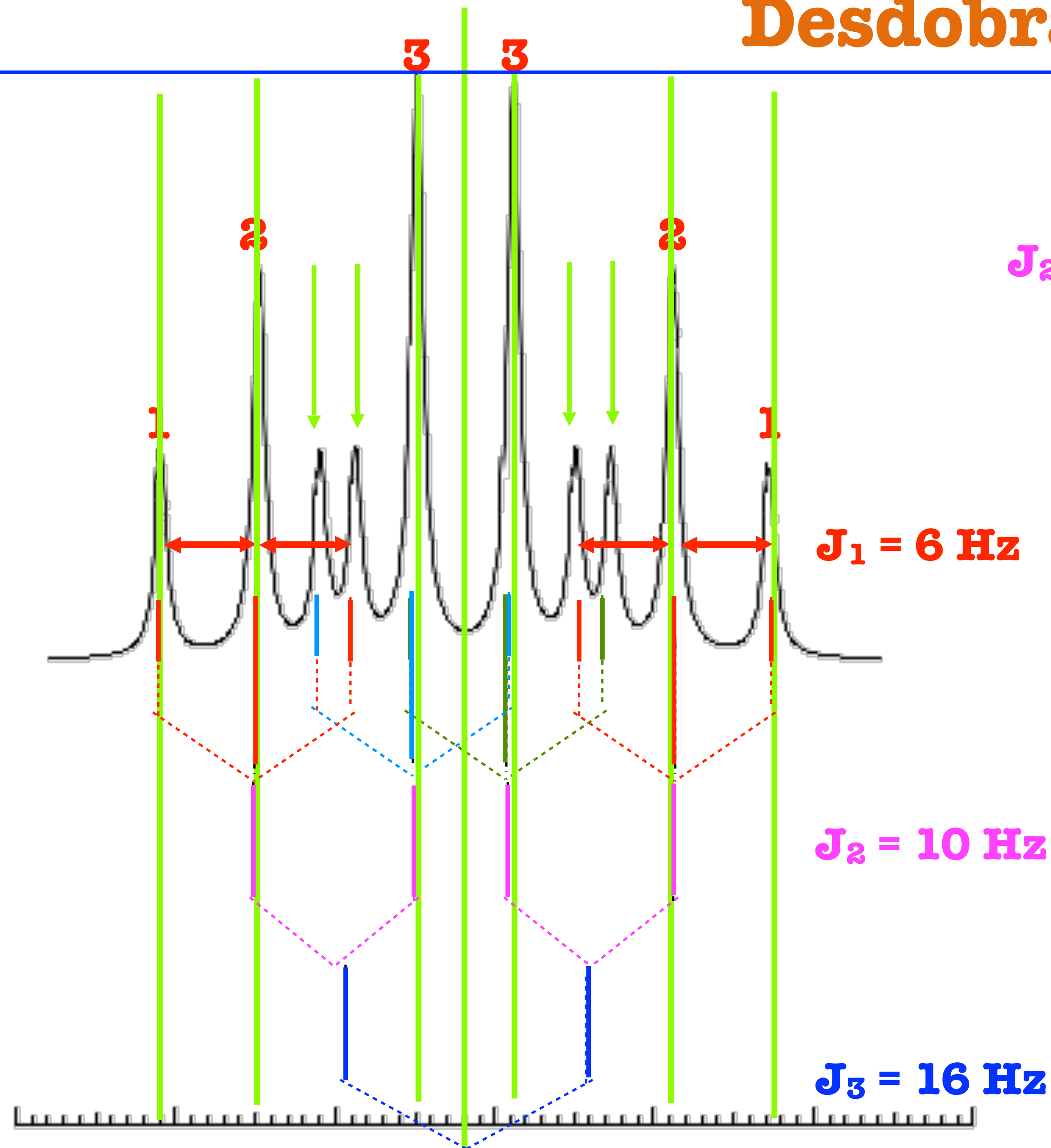
Desdobramento spin-spin



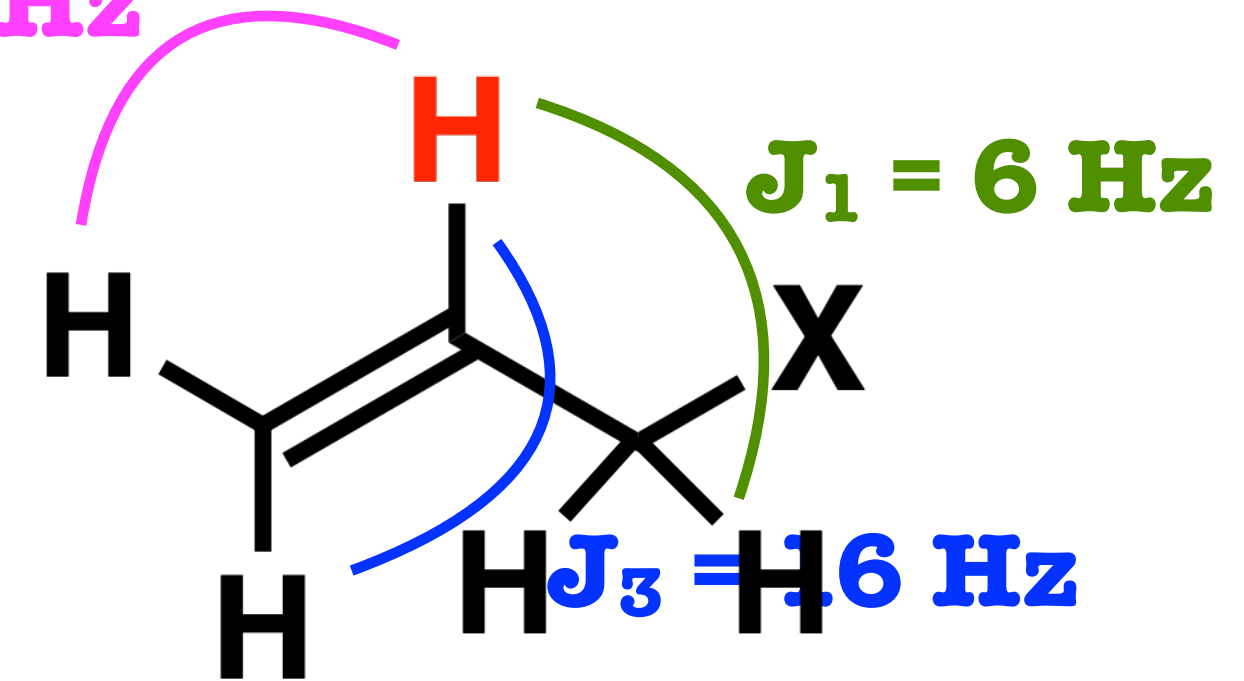
Obter o esquema de
chaves e verificar a
multiplicidade a
partir do sinal.

Importante para
realizar o cálculo do
J corretamente e
reportar os dados de
RMN corretamente.

Desdobramento spin-spin



$J_2 = 10 \text{ Hz}$



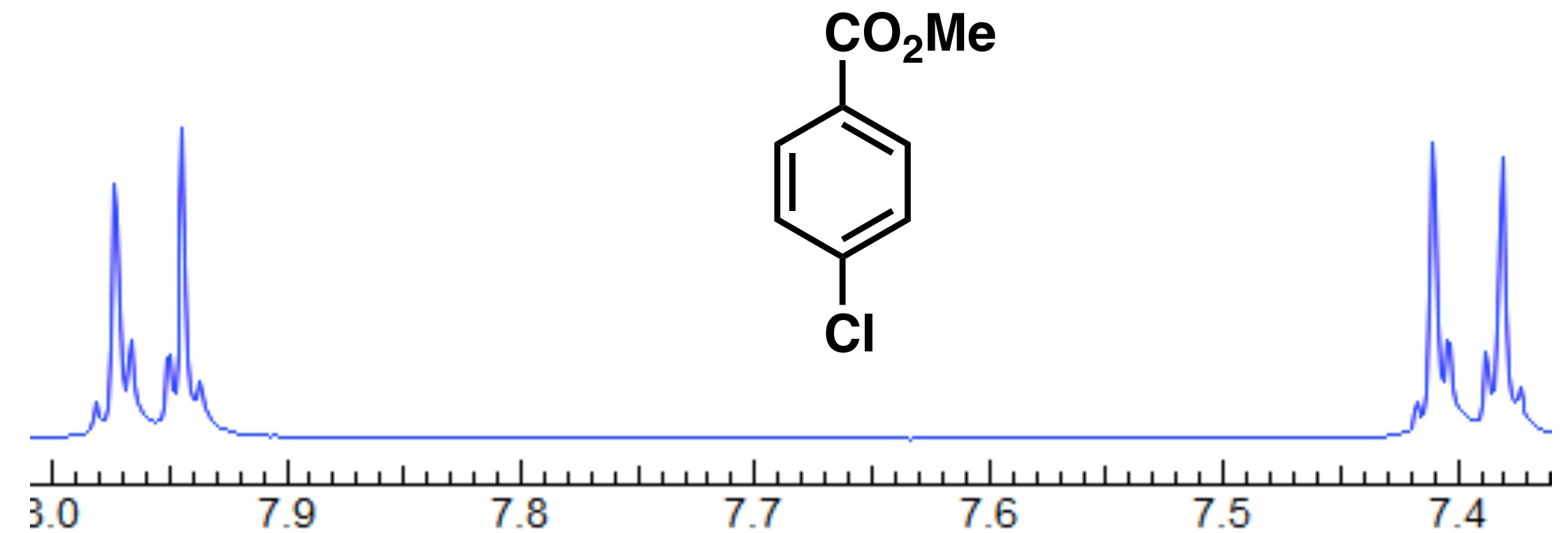
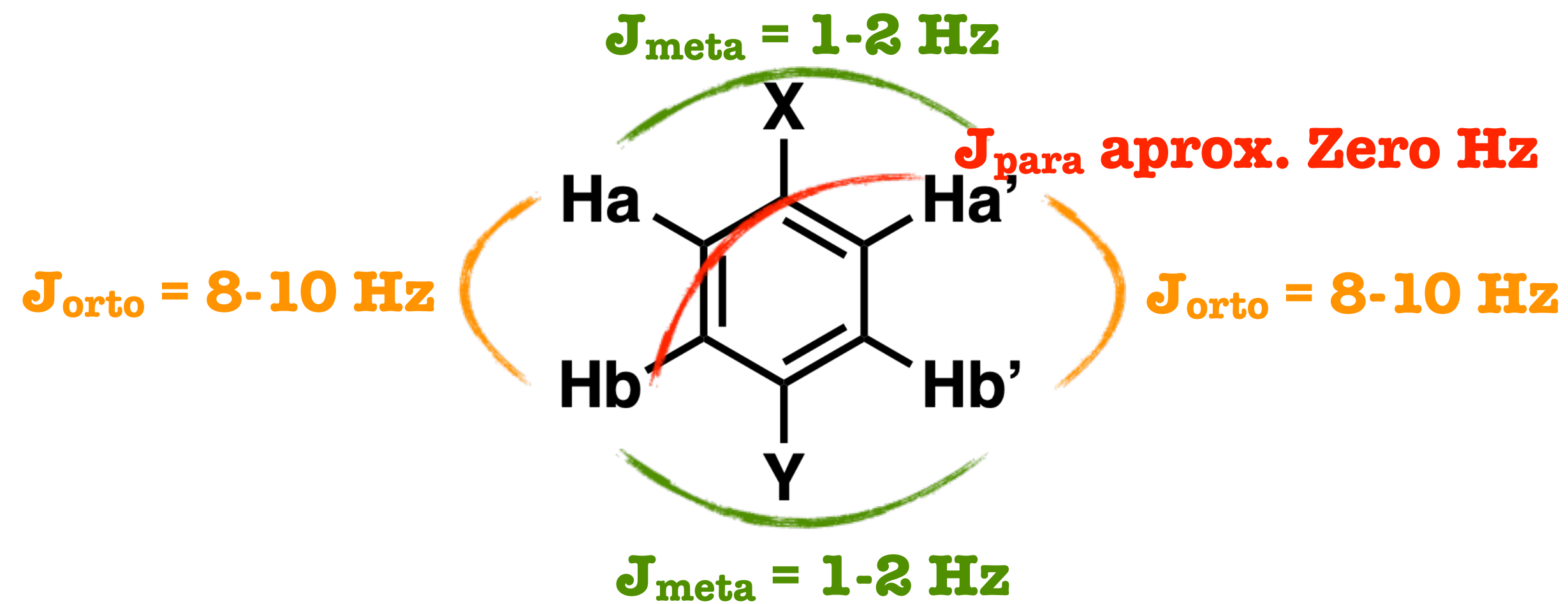
$J_1 = 6 \text{ Hz}$

$J_2 = 10 \text{ Hz}$

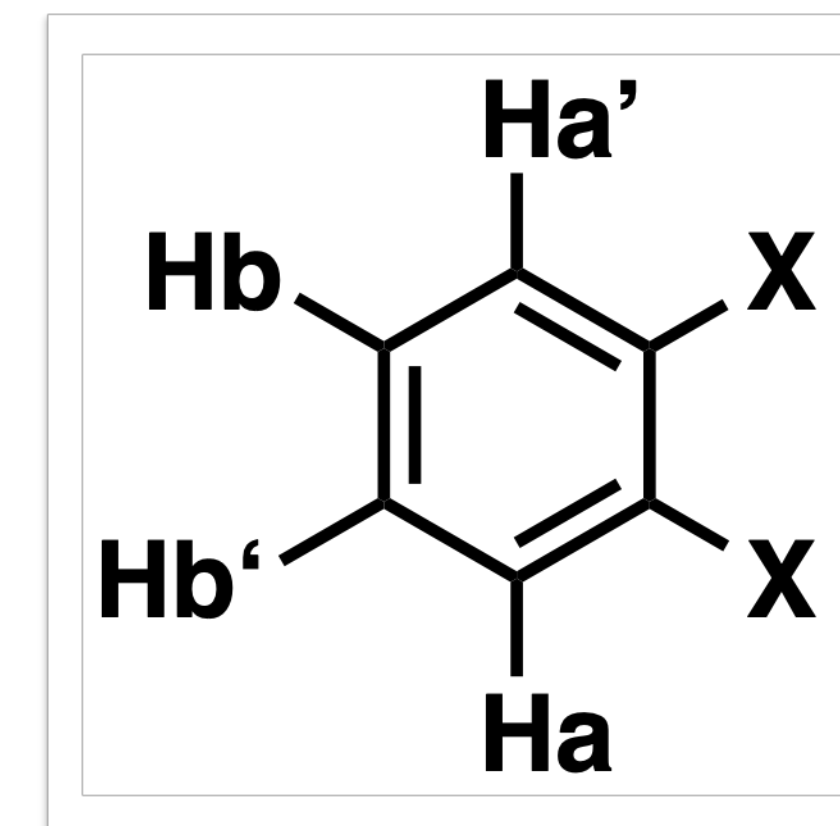
$J_3 = 16 \text{ Hz}$

Equivalência Química x Equivalência Magnética

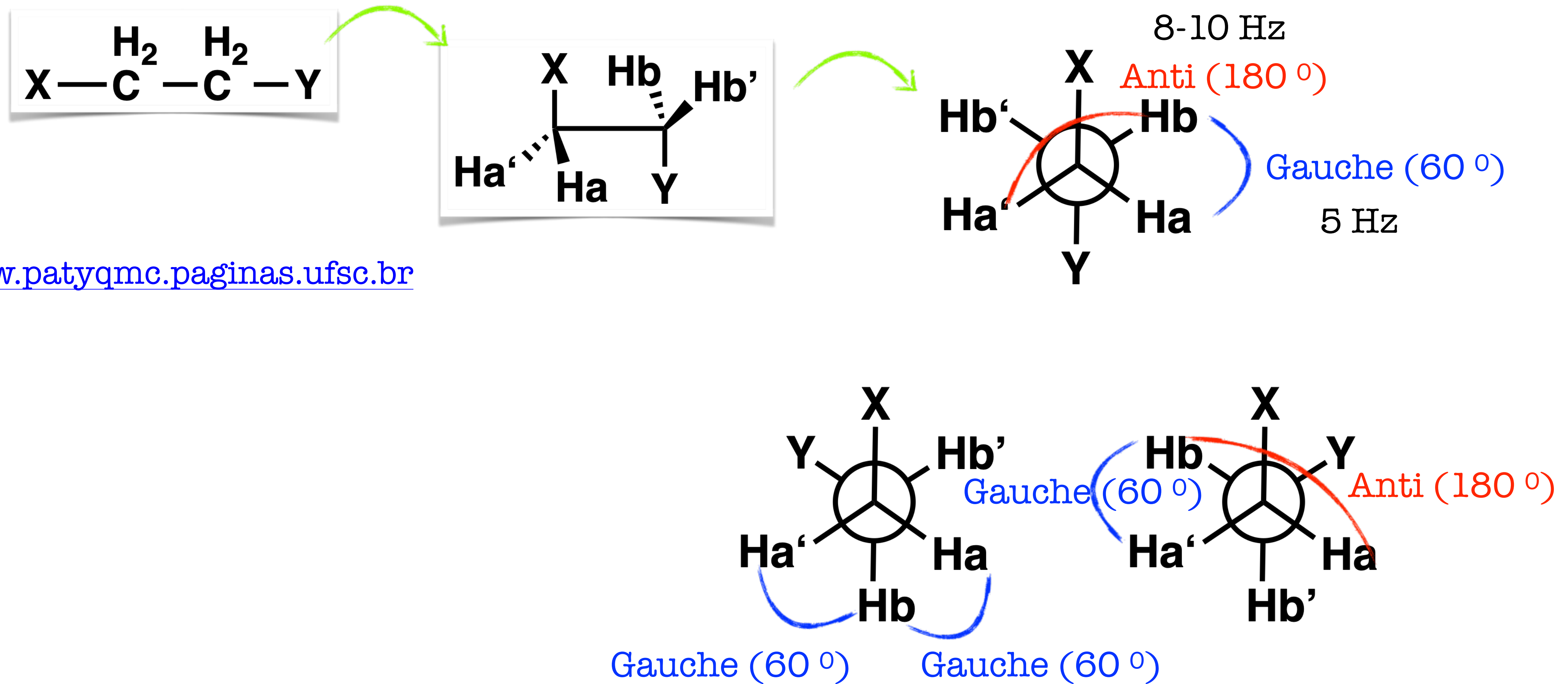
Mesmo deslocamento químico mas diferentes Js com outros prótons da molécula



Magneticamente não equivalentes!

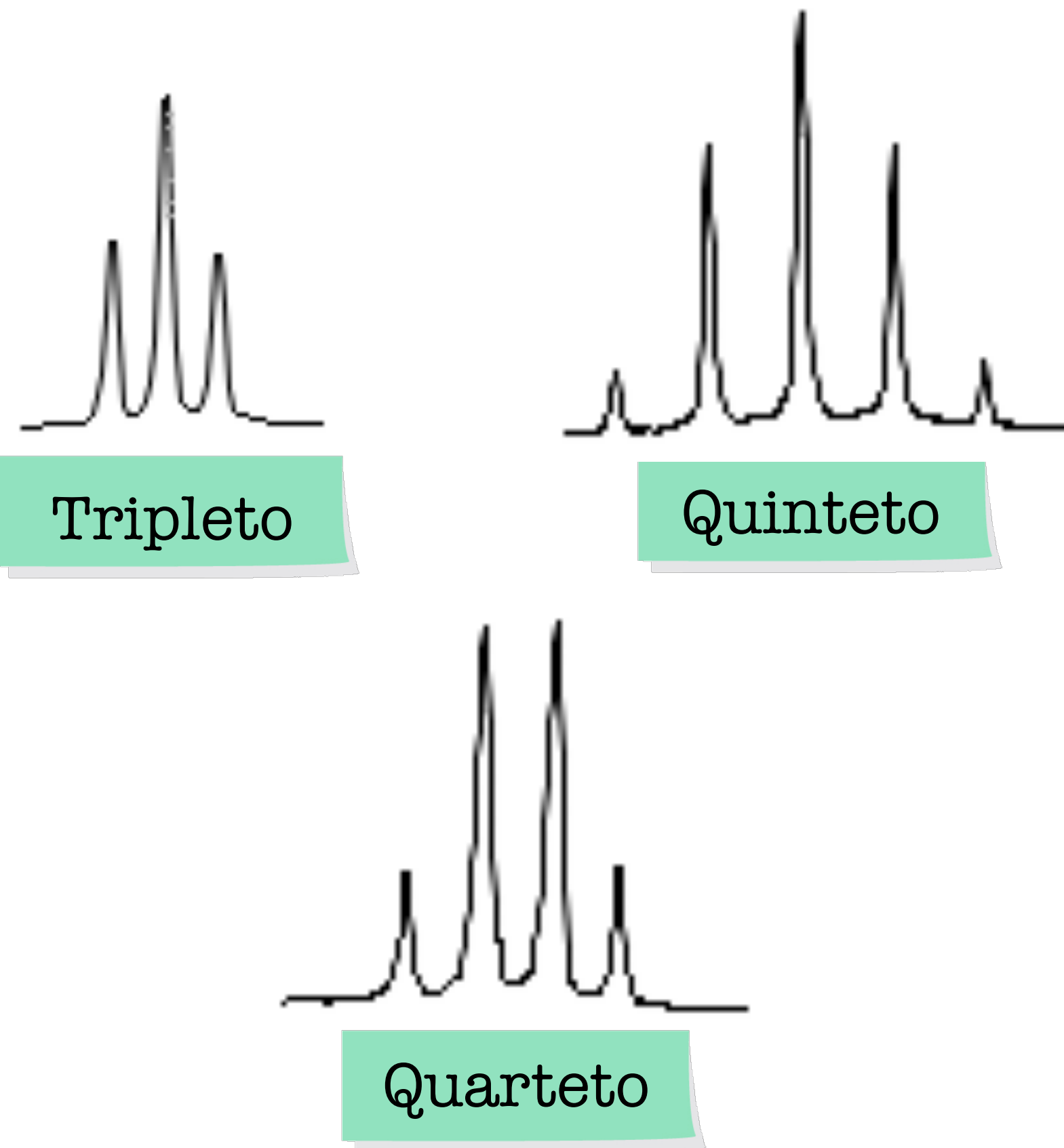


Equivalência Química x Equivalência Magnética

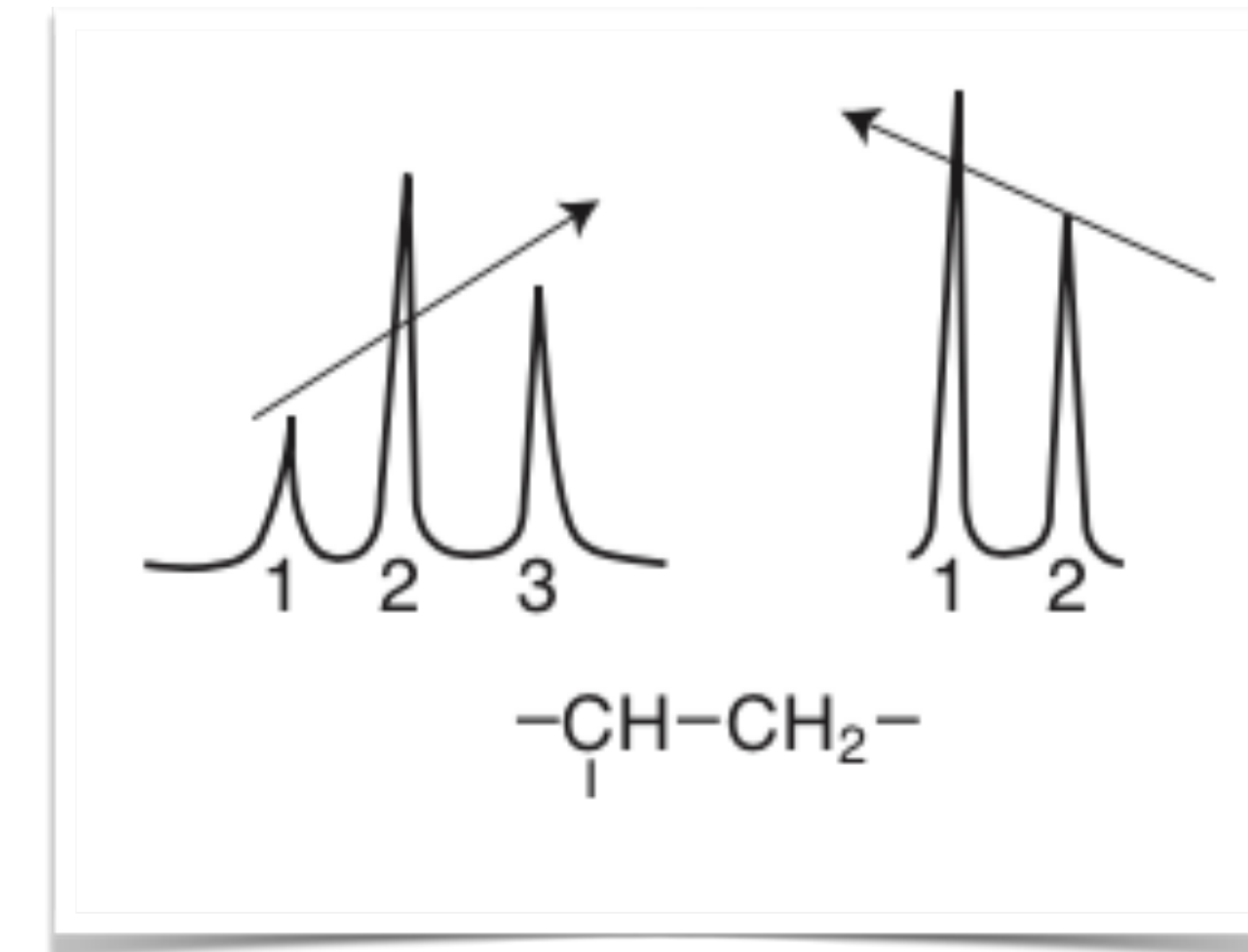


www.patyqmc.paginas.ufsc.br

Distorção de multipletos

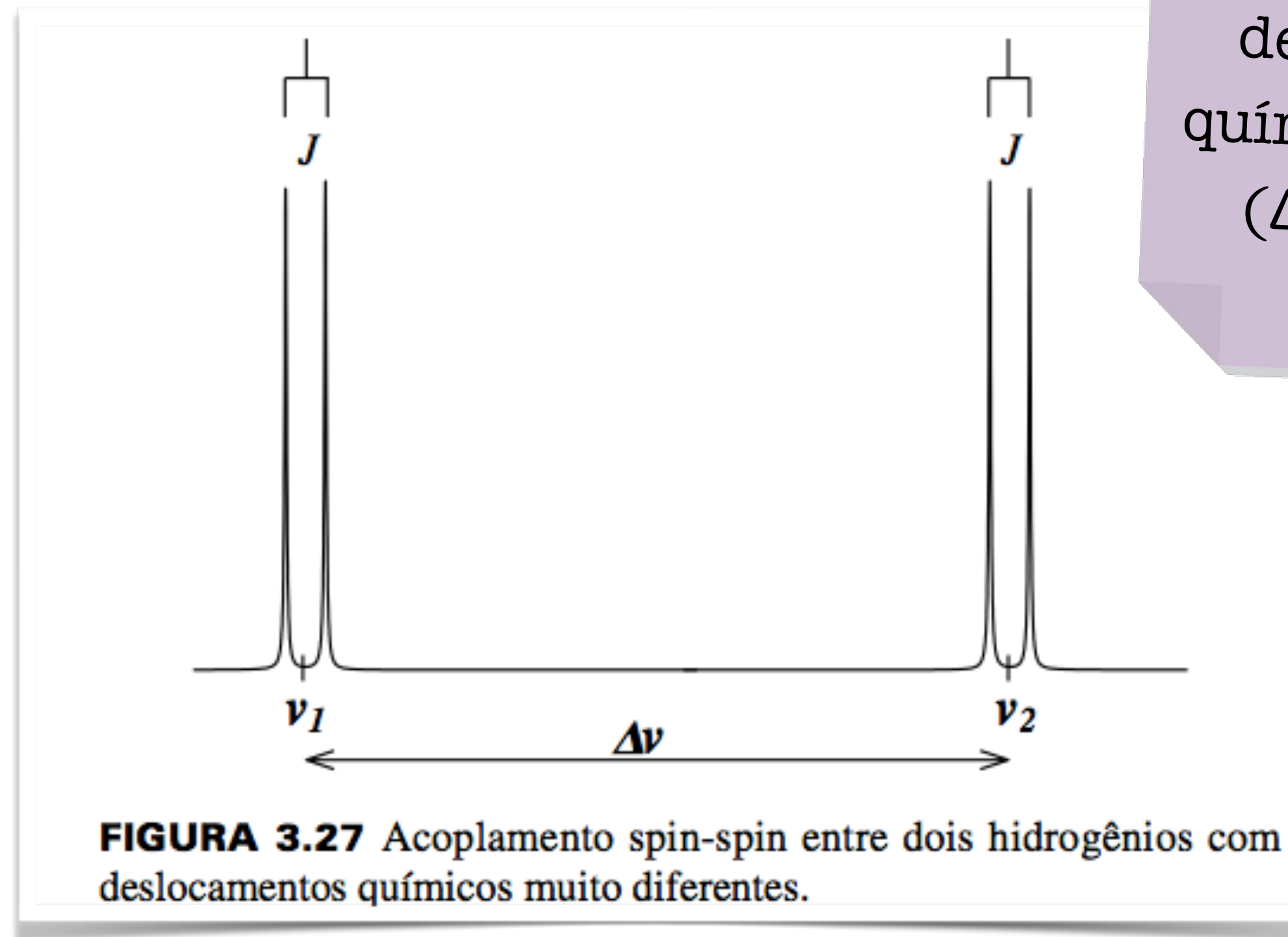


Linhas mais exteriores ficam com alturas não equivalentes

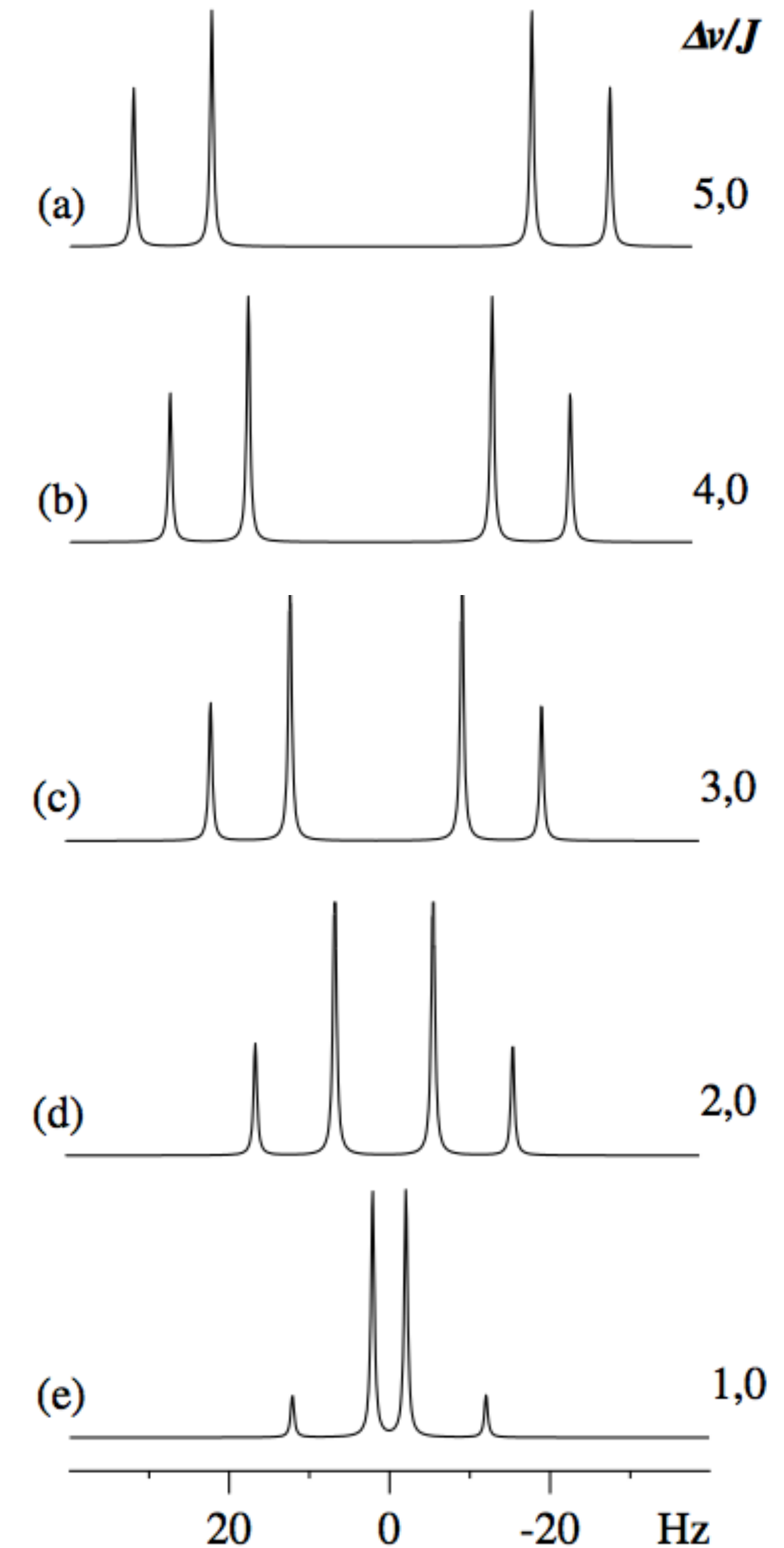


Pode refletir proximidade estrutural

Distorção de multipletos

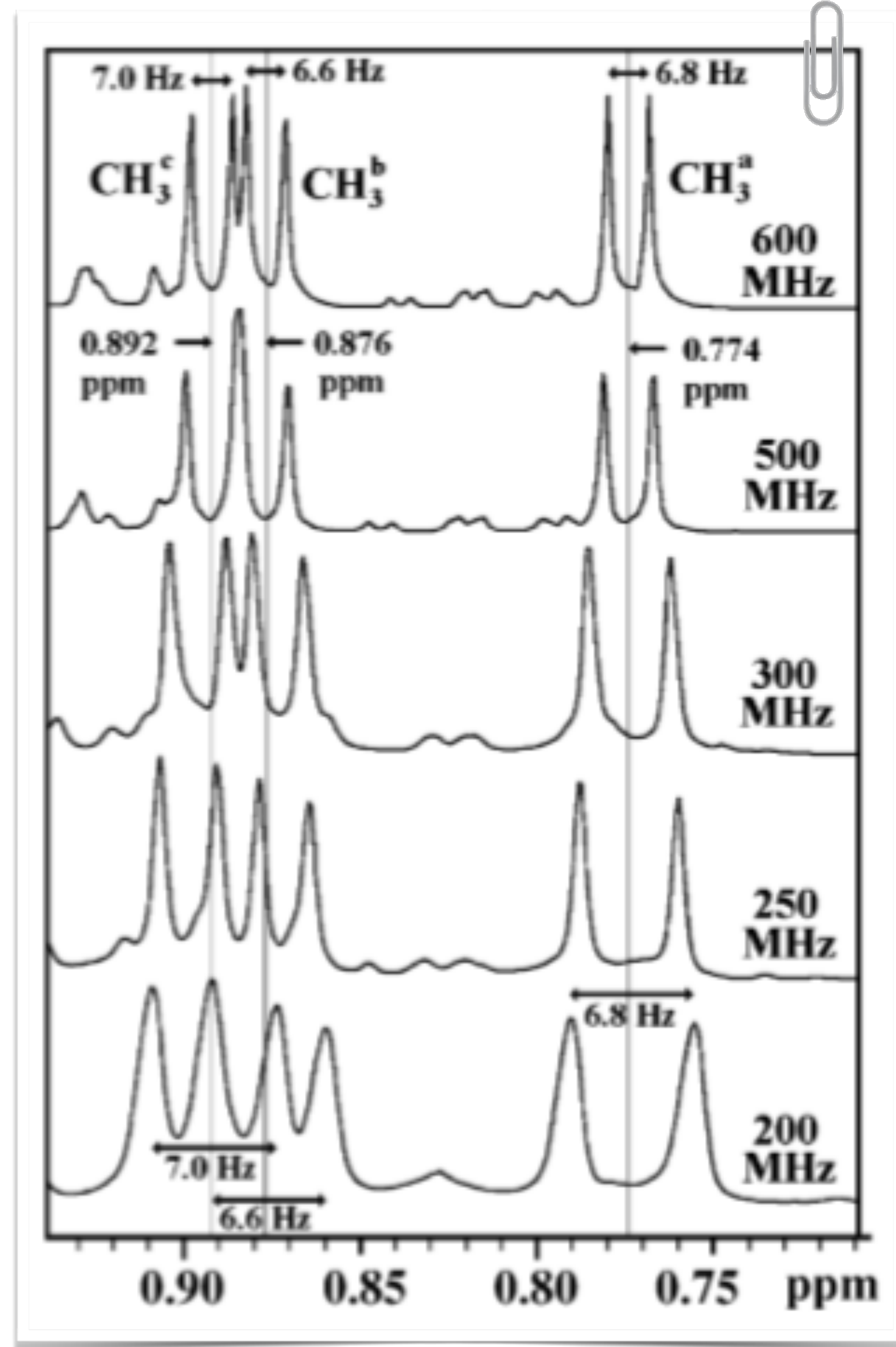


Quando a diferença de deslocamento químico ($\Delta\nu$) $\gg J$ ($\Delta\nu/J > 8$): 2 dubletos.



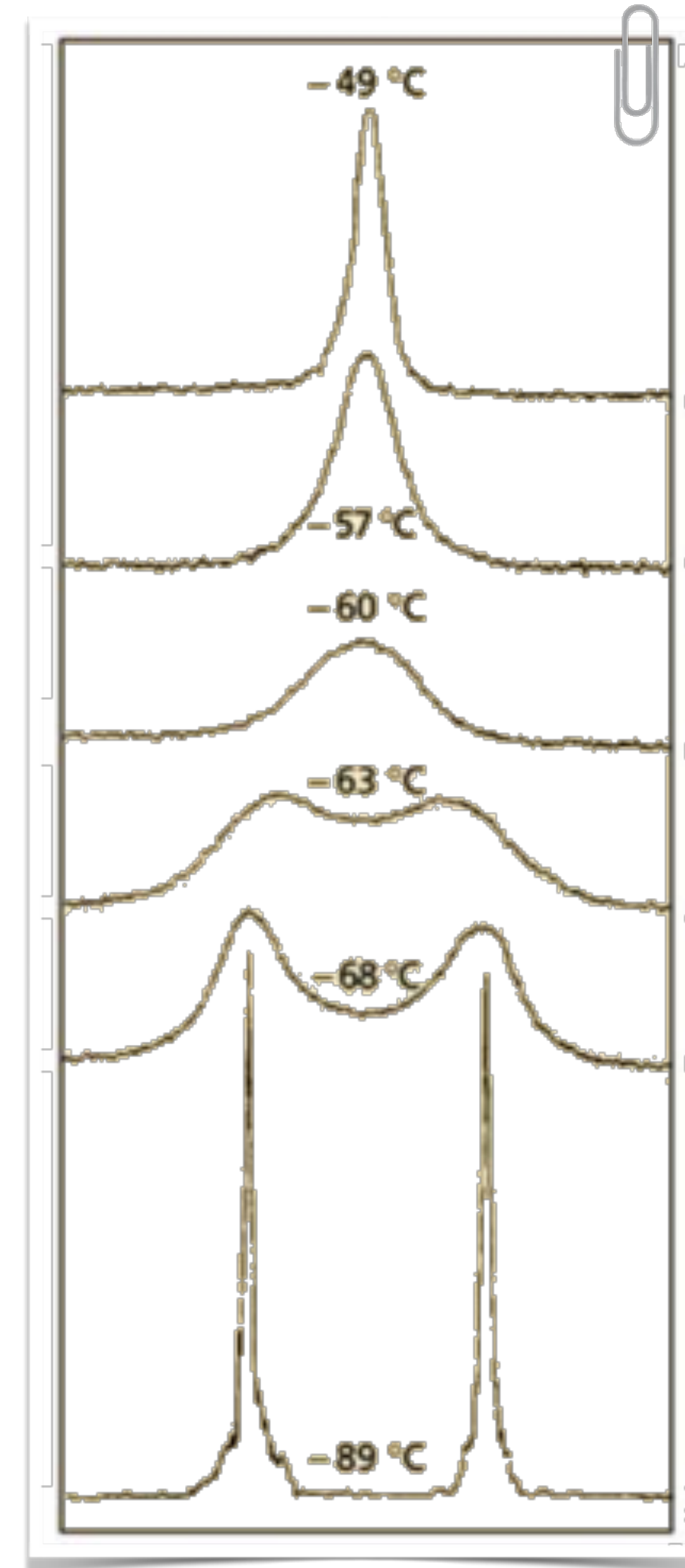
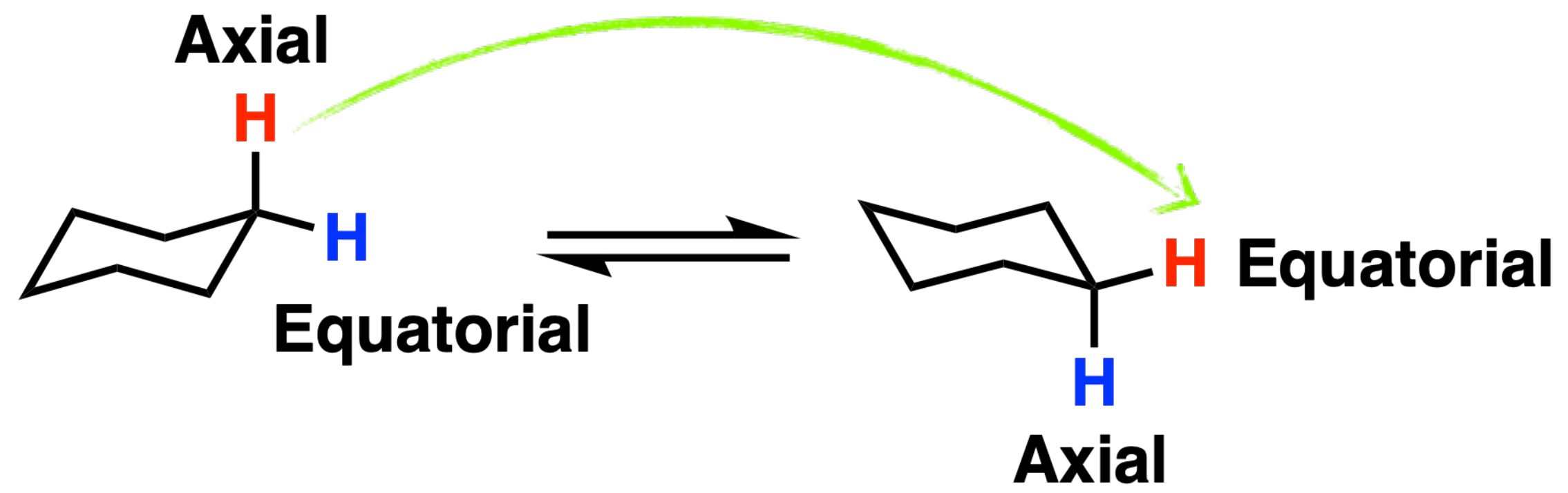
Pavia, D. L; Lampman, G. M; Kriz, G. S;
Vyvyan, J. Introduction to spectroscopy,
5 ed., 2015, Cengage Learning

Definição do sinal



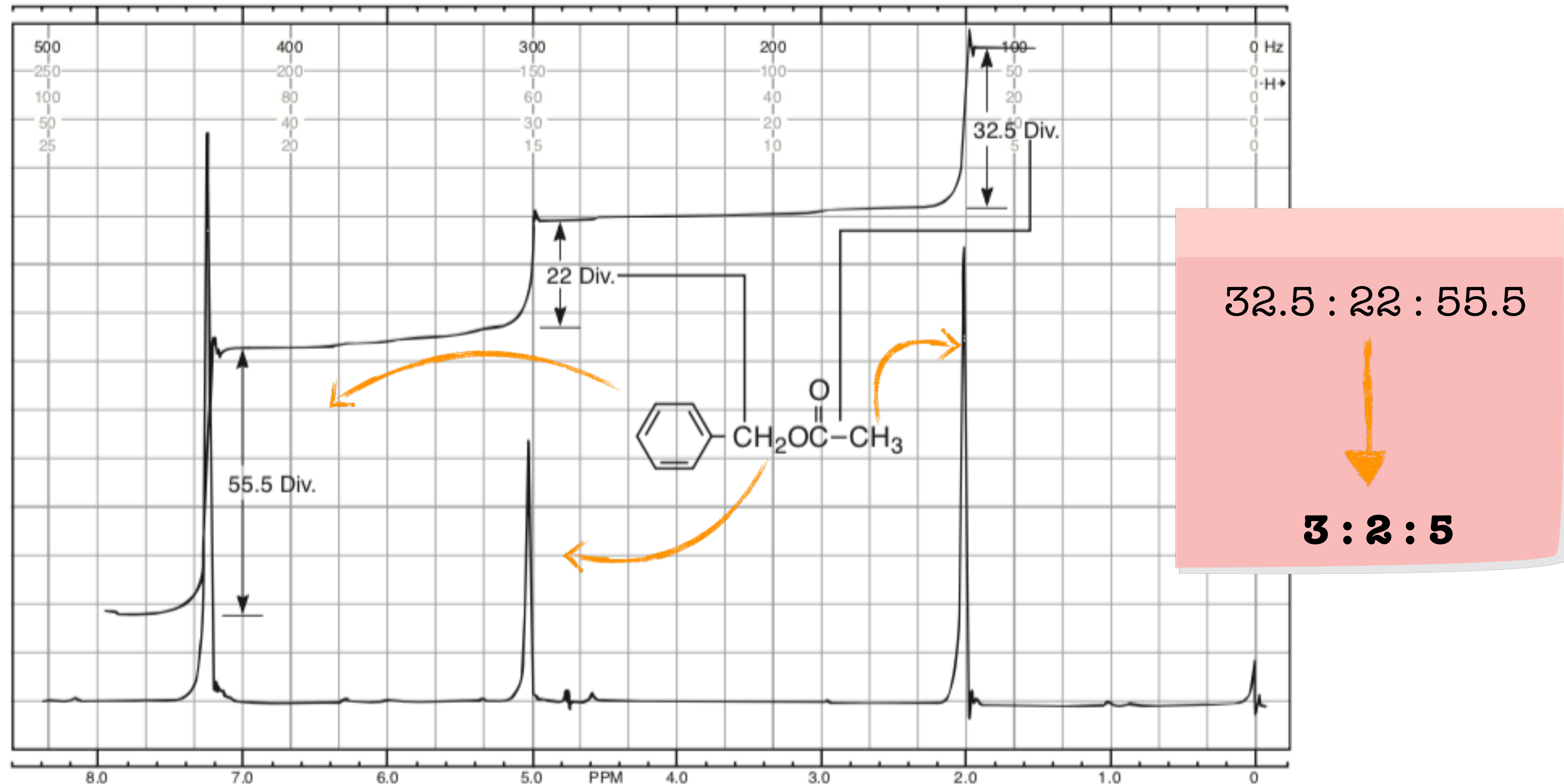
NMR SPECTROSCOPY EXPLAINED,
Neil E. Jacobsen, Wiley, **2007**.

Ciclohexanos

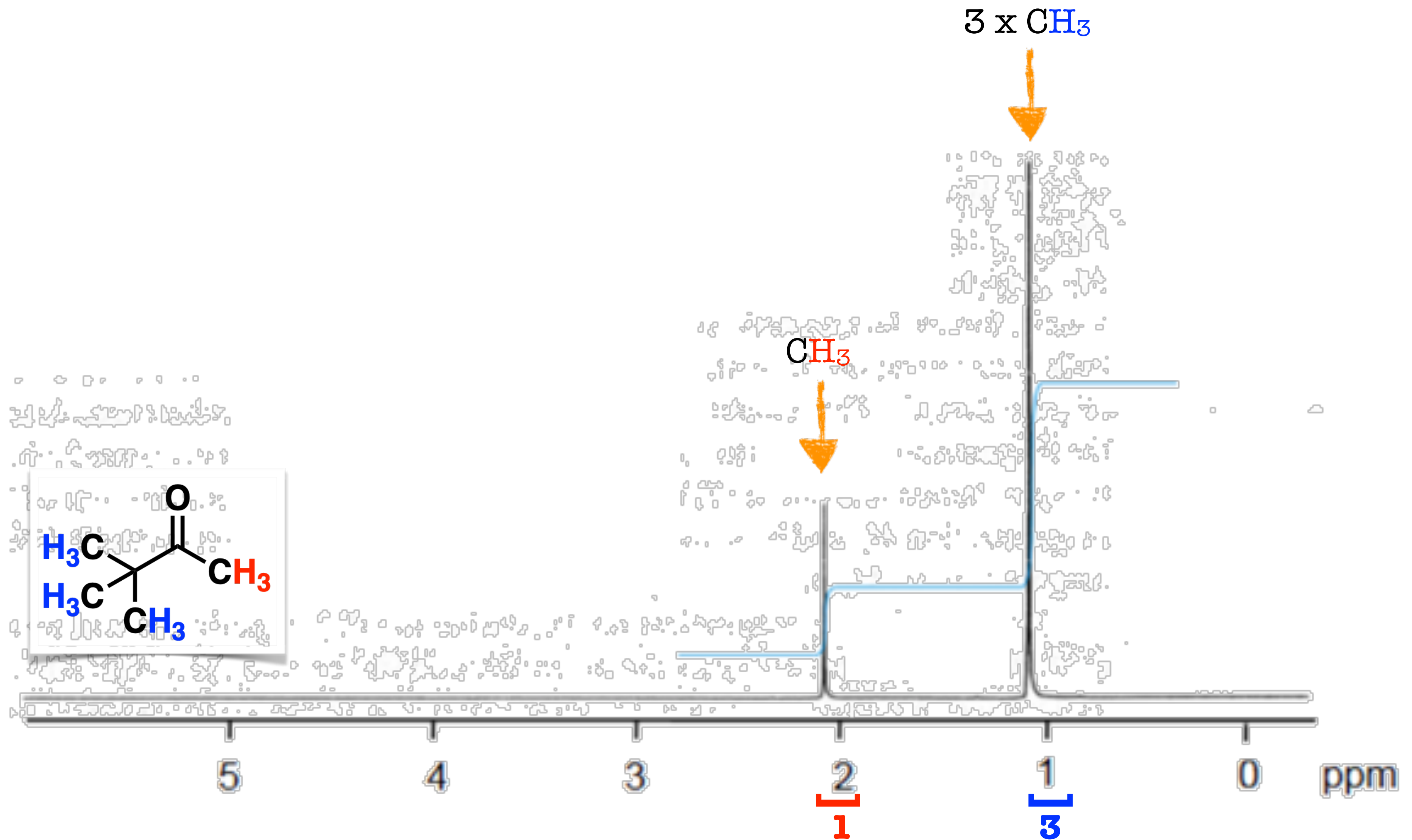


Integração dos sinais

A área de cada sinal pode ser integrada para dar a informação de quantos prótons geraram determinado sinal.



Integração dos sinais

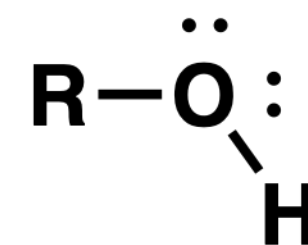


Ligação de Hidrogênio

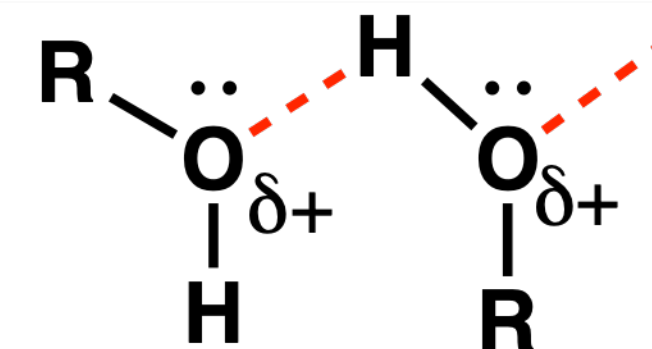
Localização do sinal varia muito!

OH e NH

- ✓ Deslocamentos variam: estrutura do composto, solvente usado na amostra, temperatura e concentração da amostra;
- ✓ Mais desblindados em amostras mais concentradas;



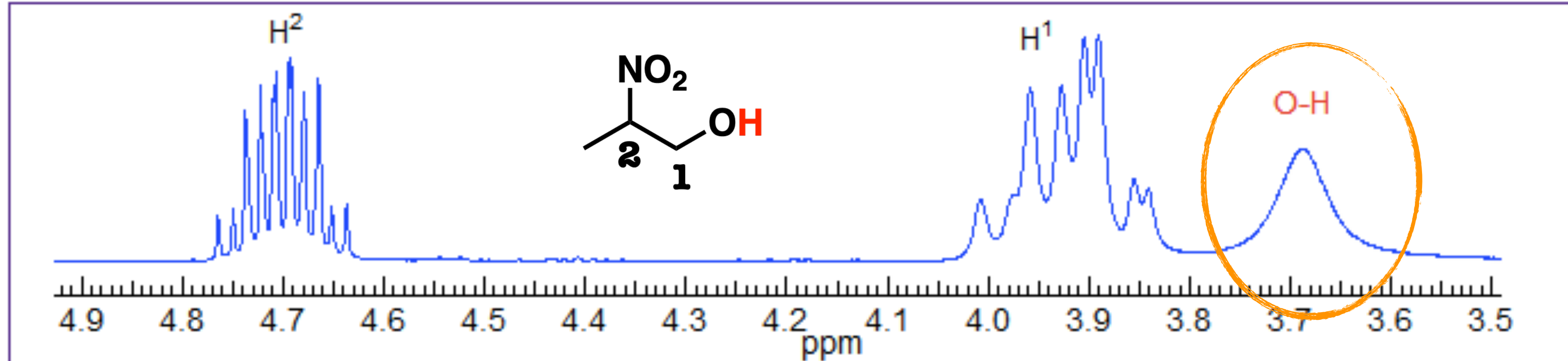
Solução diluída
(Livre)



Solução concentrada
(Em ligação de hidrogênio)

Prótons intercambiáveis

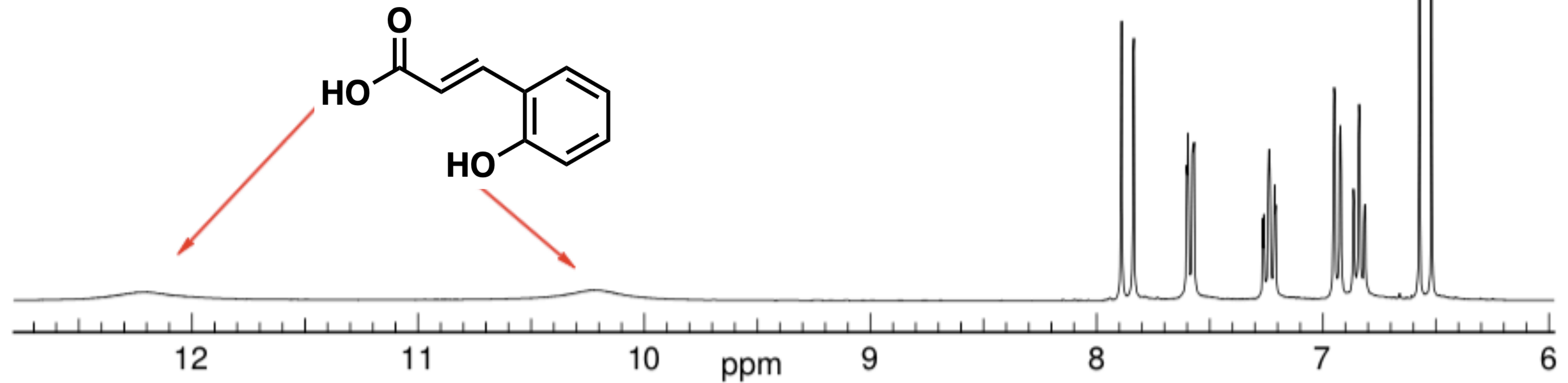
- ✓ Trocam de lugar com prótons do solvente: sinal alargado!
- ✓ Não acoplam com H vizinhos;
- ✓ Desaparecem do espectro caso gotas de D₂O sejam adicionadas a amostra.



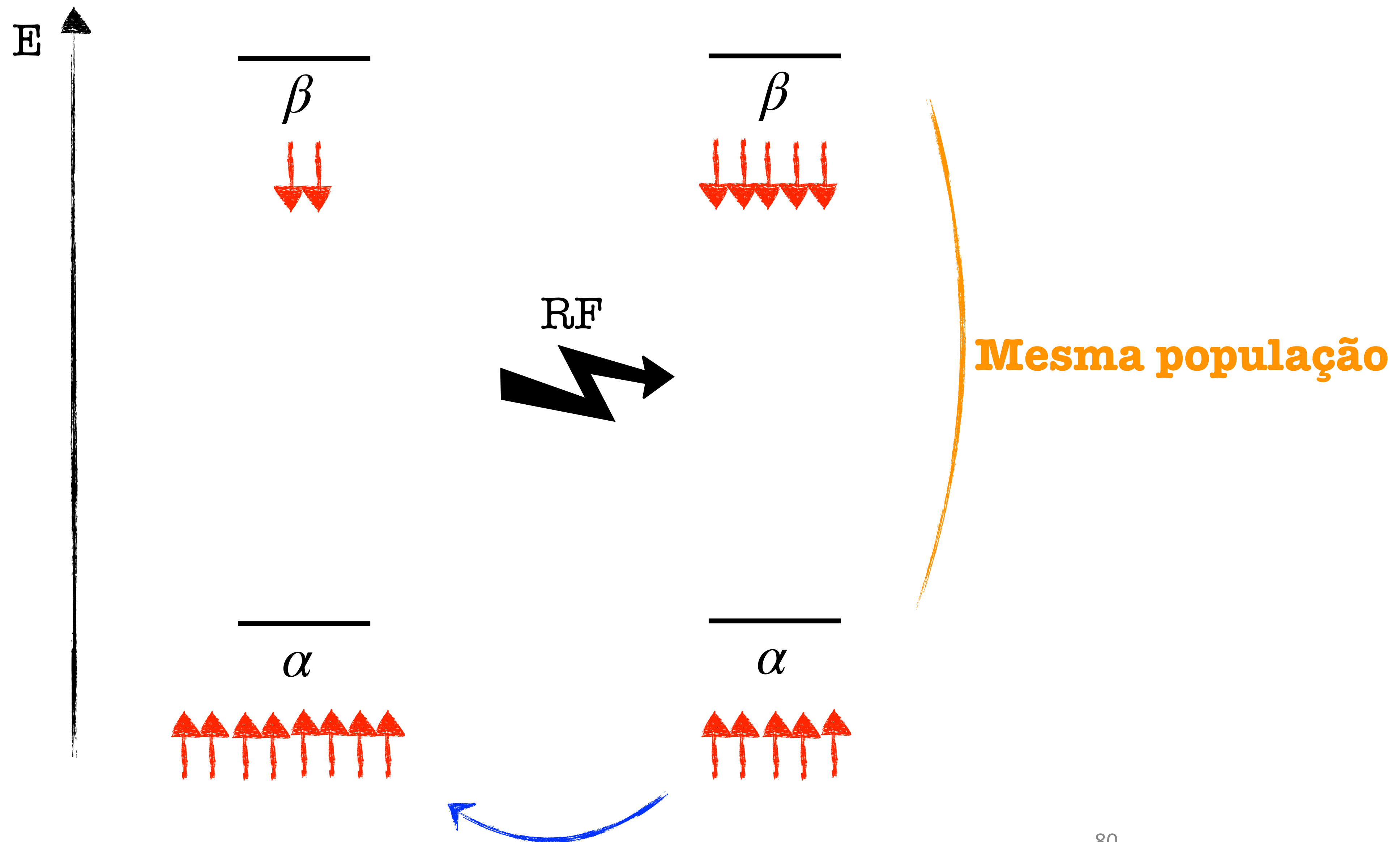
Prótons intercambiáveis

Mais desblindados em grupos mais ácidos

300 MHz RMN ^1H em DMSO- D_6
Fonte: Biblioteca Sigma-Aldrich

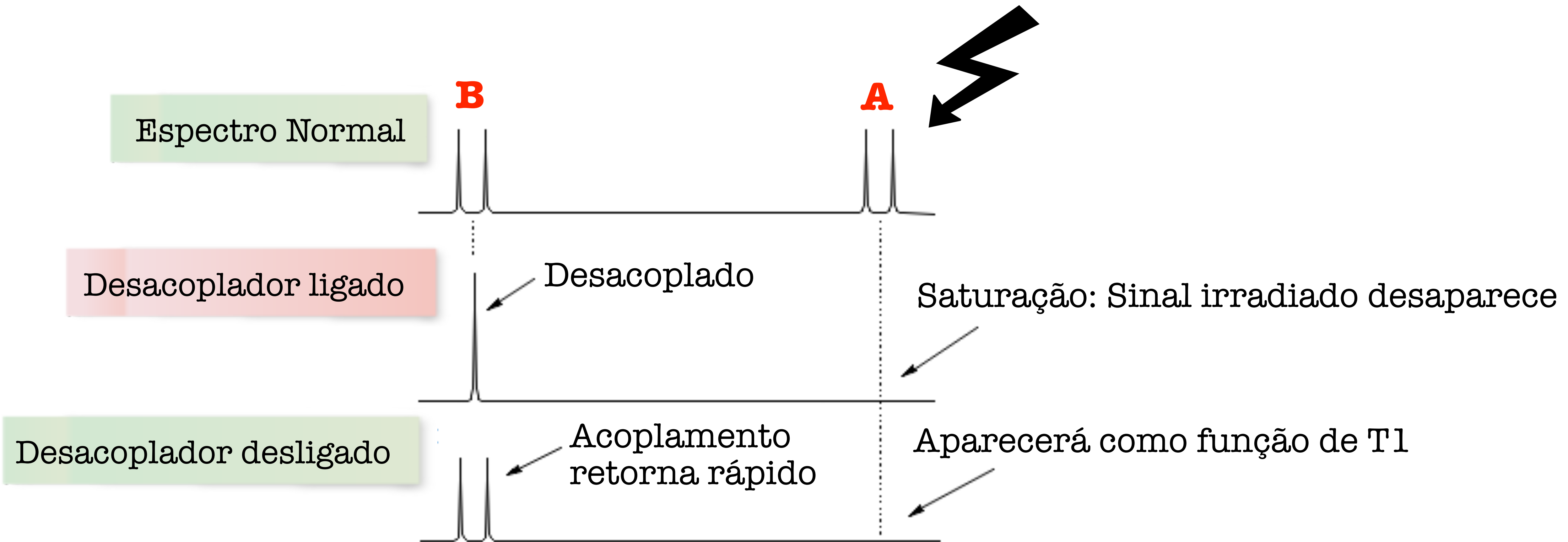


Saturação

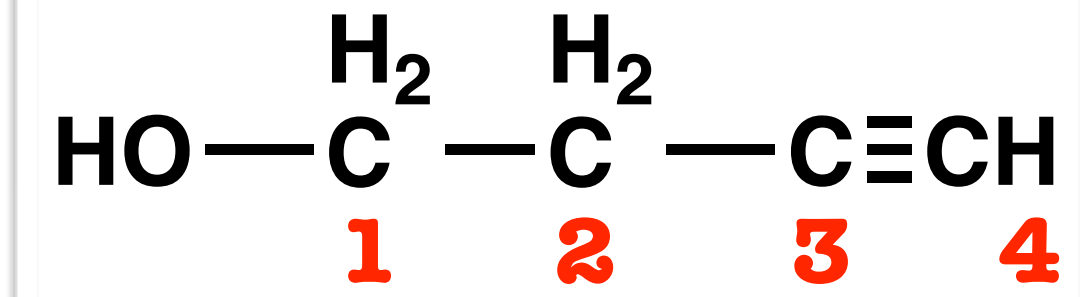
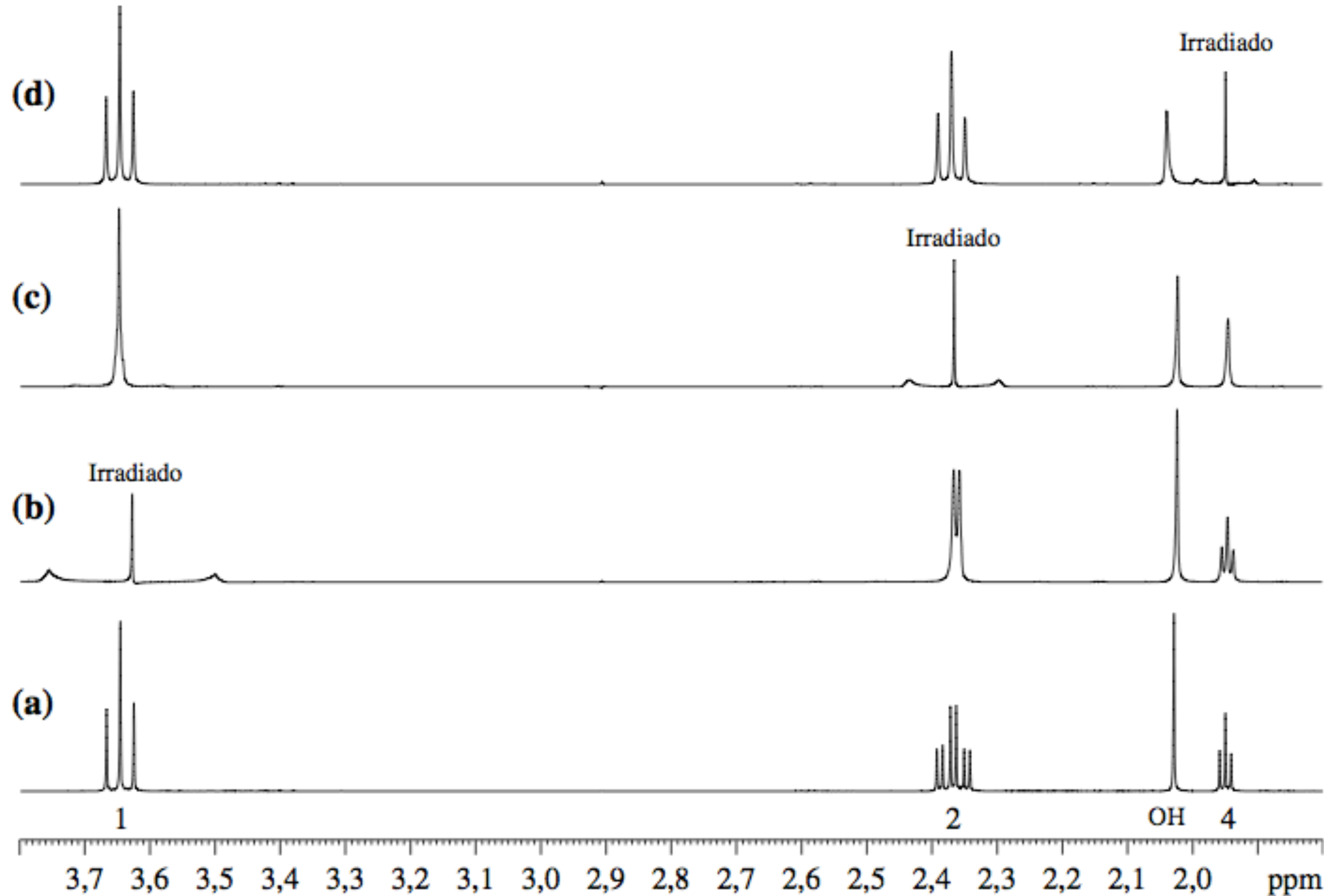


Desacoplamento Homonuclear de spins

- ✓ Segundo campo de RF que causa a saturação de um núcleo
- ✓ Sinal desaparece



Desacoplamento de spins



Pavia, D. L; Lampman, G. M; Kriz, G. S; Vyvyan, J. Introduction to spectroscopy, 5 ed., 2015, Cengage Learning

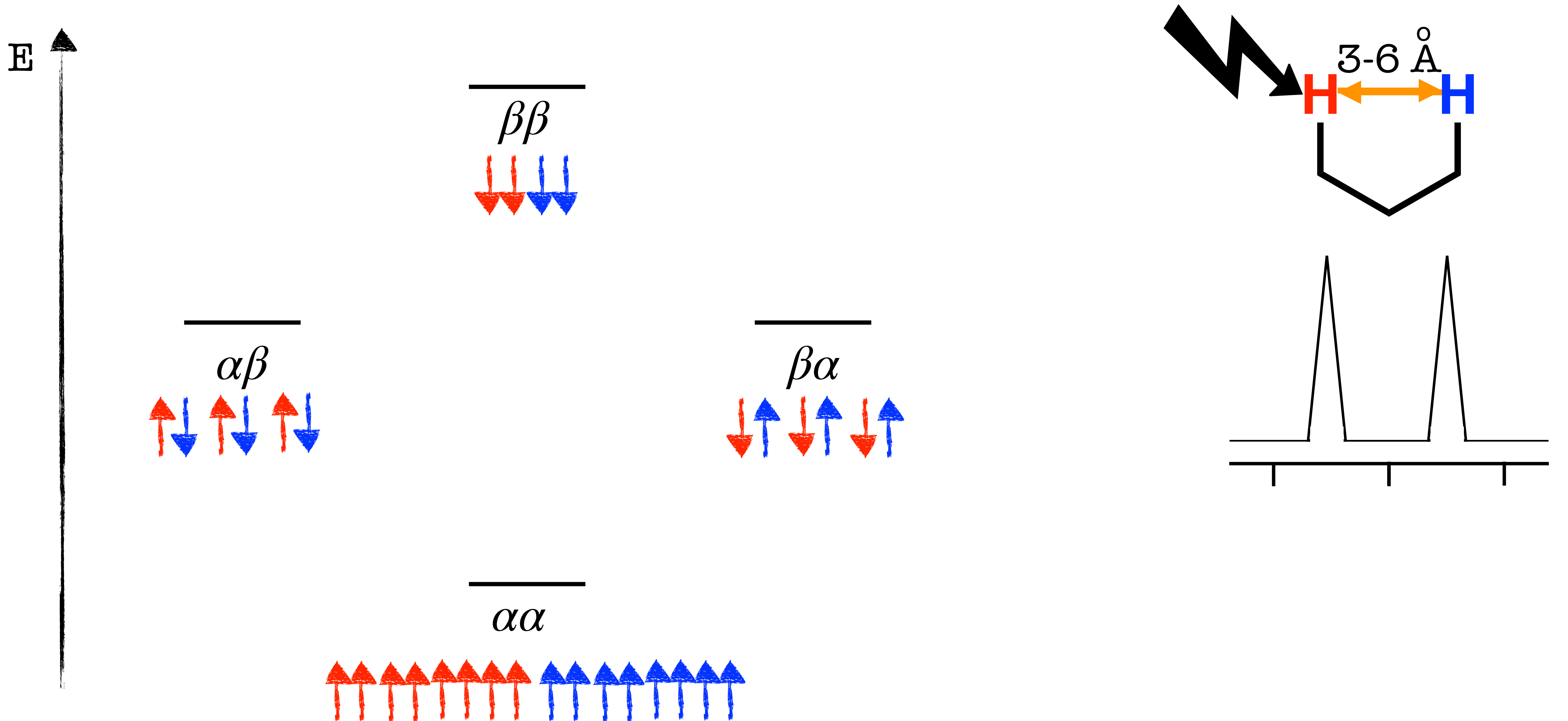
NOE: Nuclear Overhauser Effect

Mudança da intensidade de um sinal referente a um núcleo, quando outro núcleo vizinho é saturado por irradiação

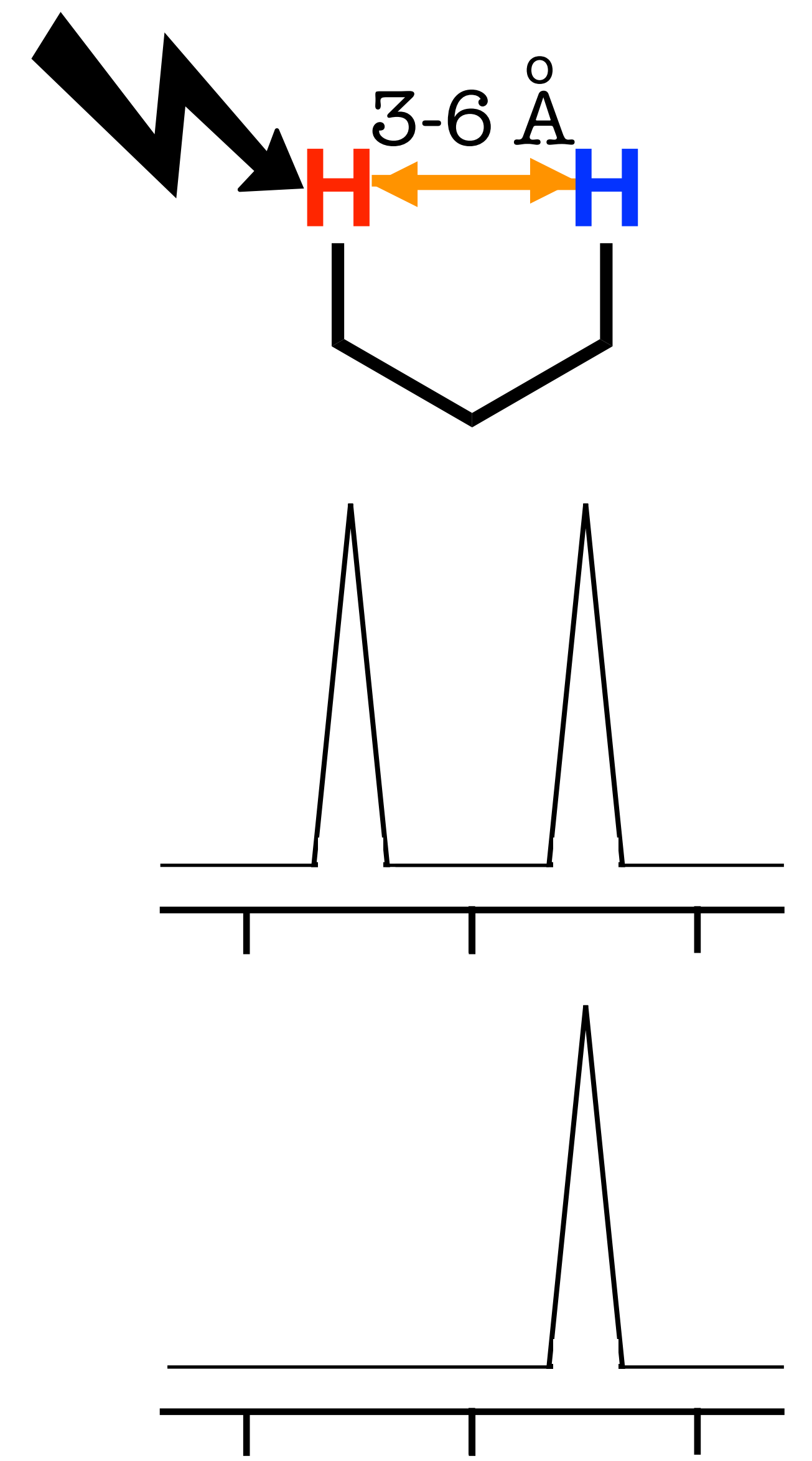
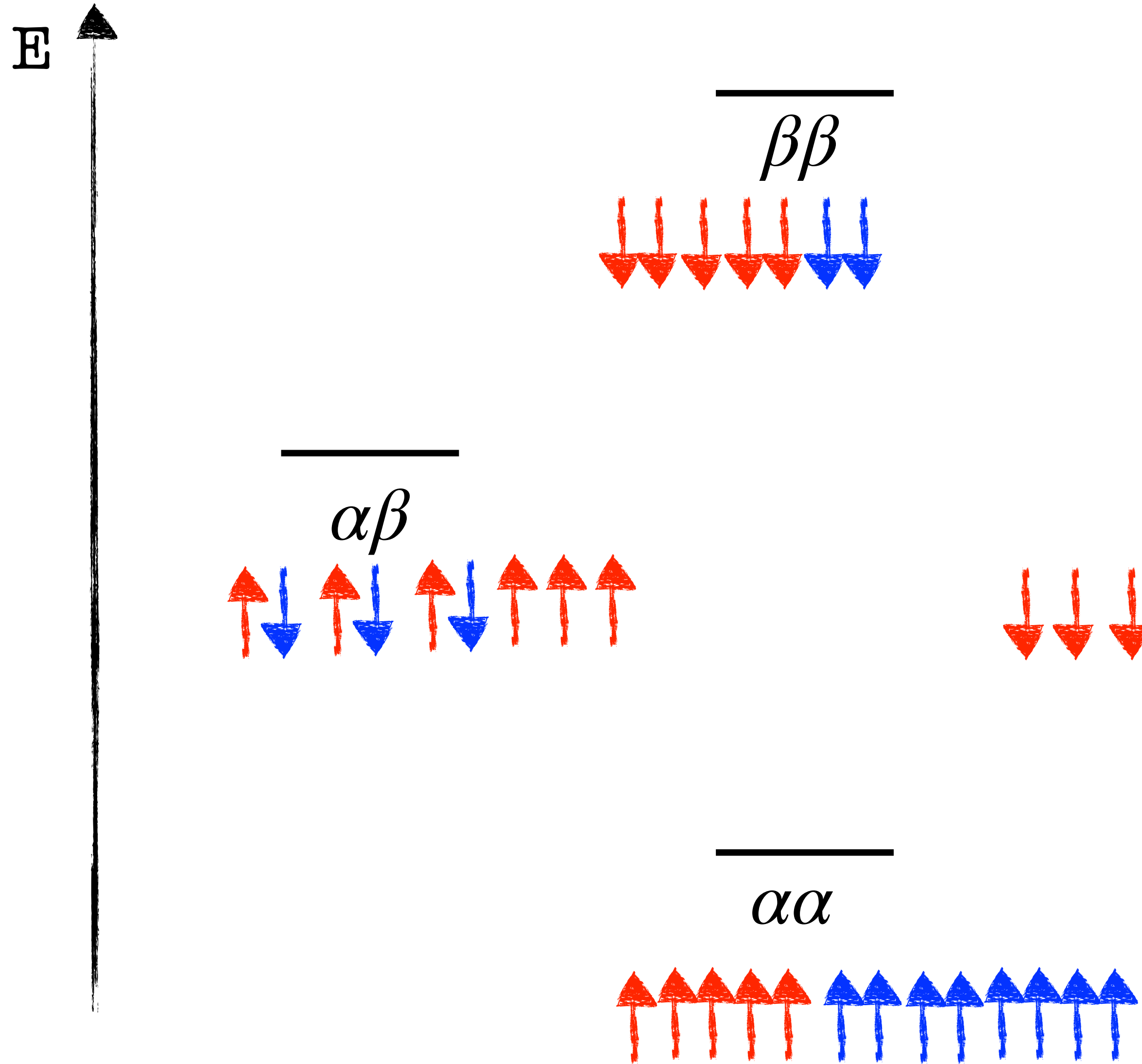
A diferença de intensidade é proporcional a proximidade espacial dos núcleos.

Atribuição de proximidade espacial entre núcleos em moléculas bastante complexas

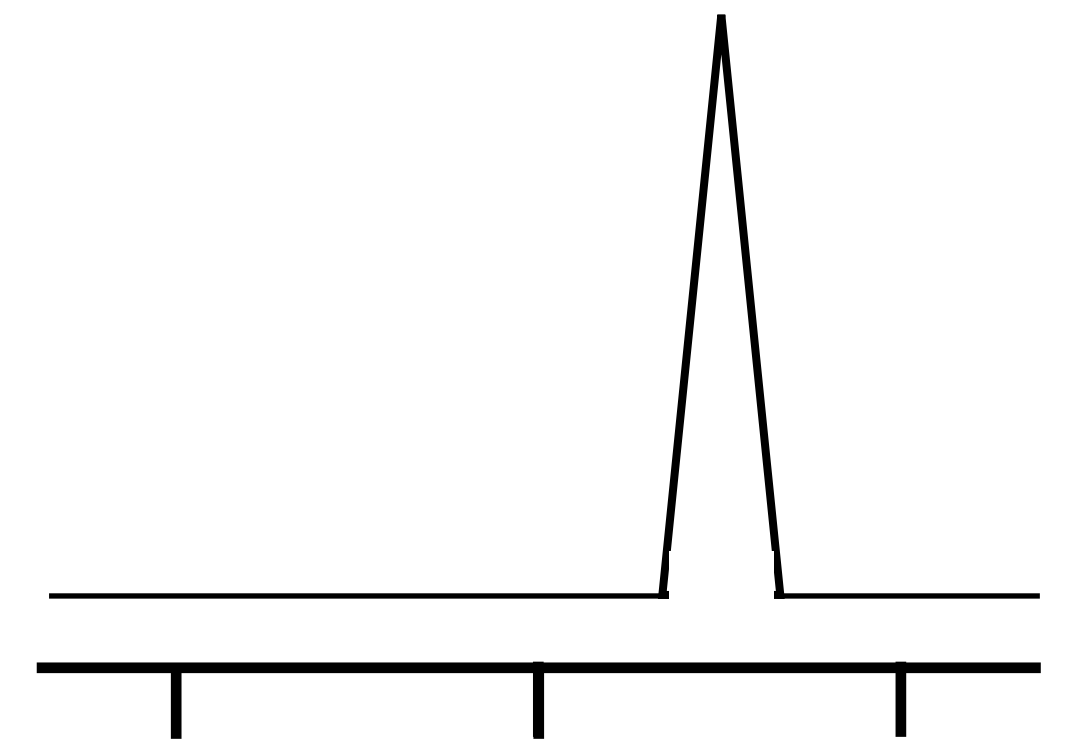
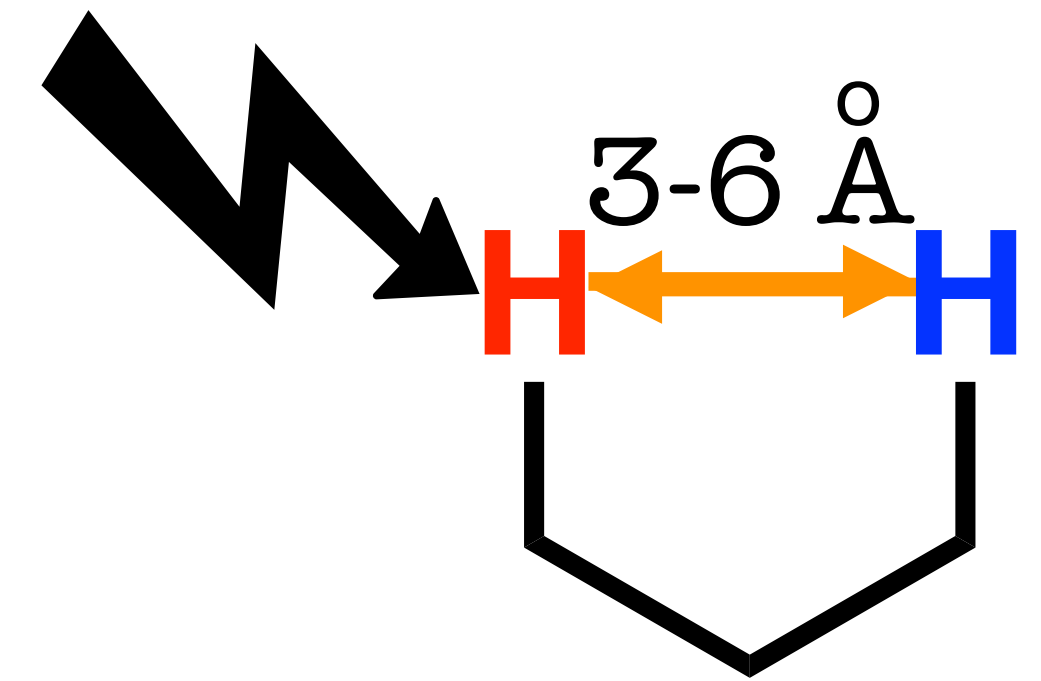
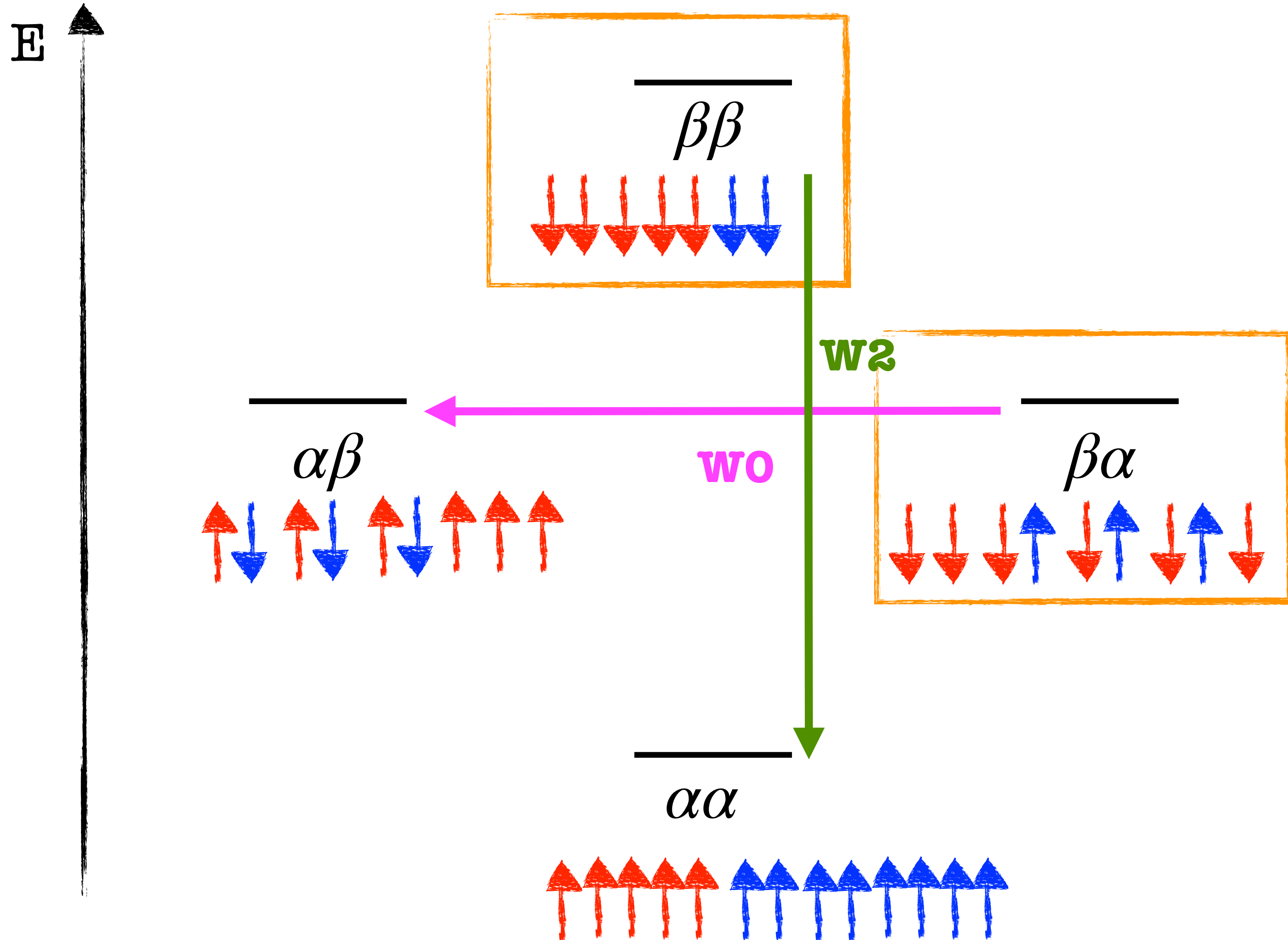
NOE: Nuclear Overhauser Effect



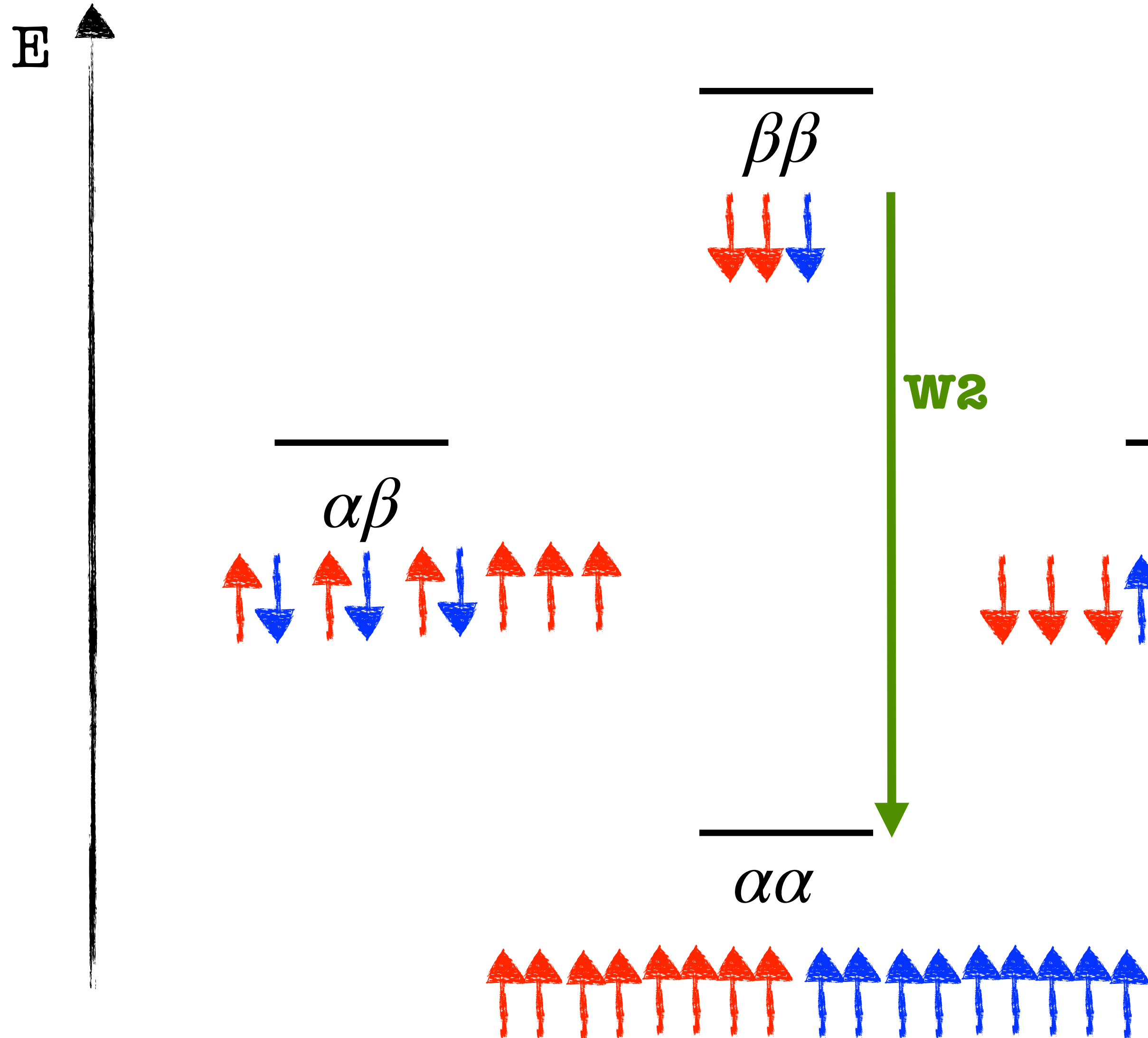
NOE: Nuclear Overhauser Effect



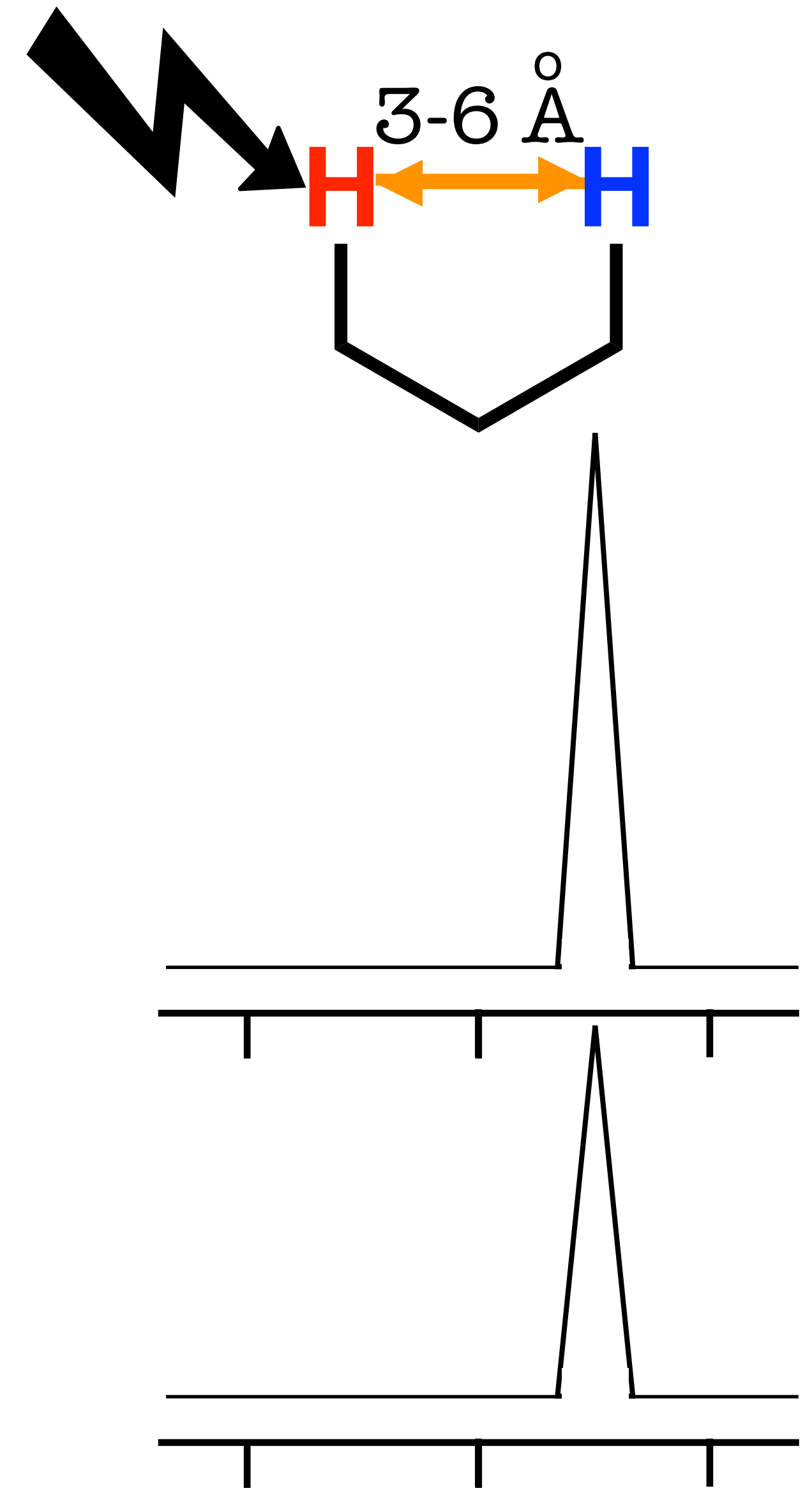
NOE: Nuclear Overhauser Effect



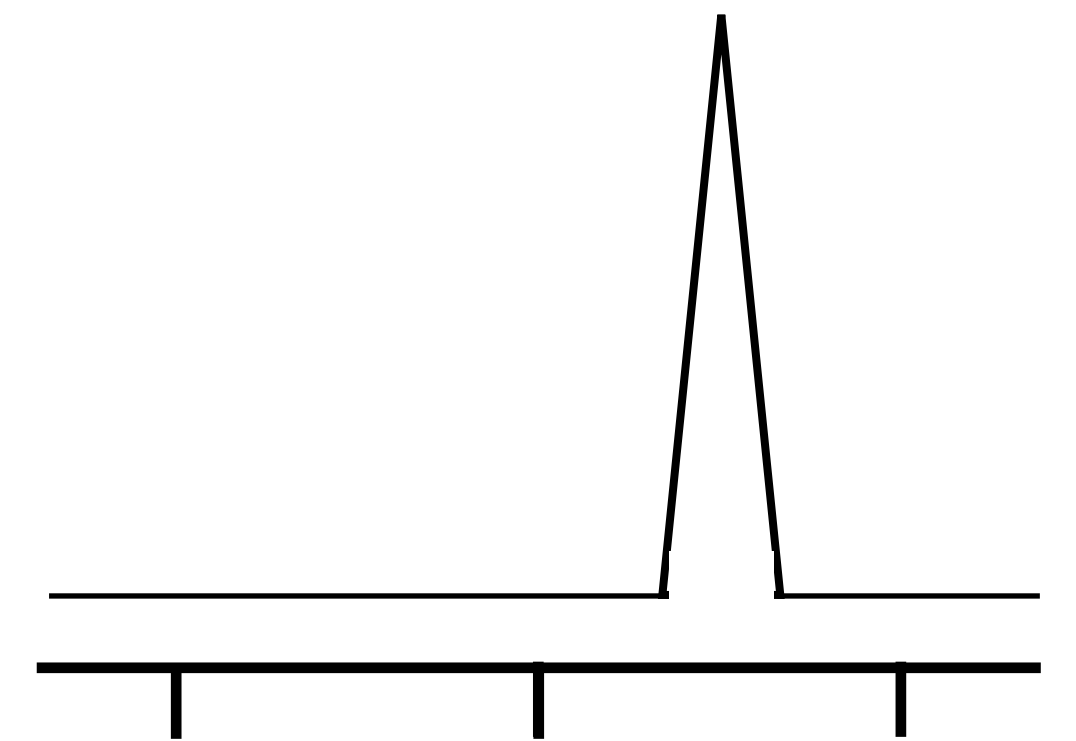
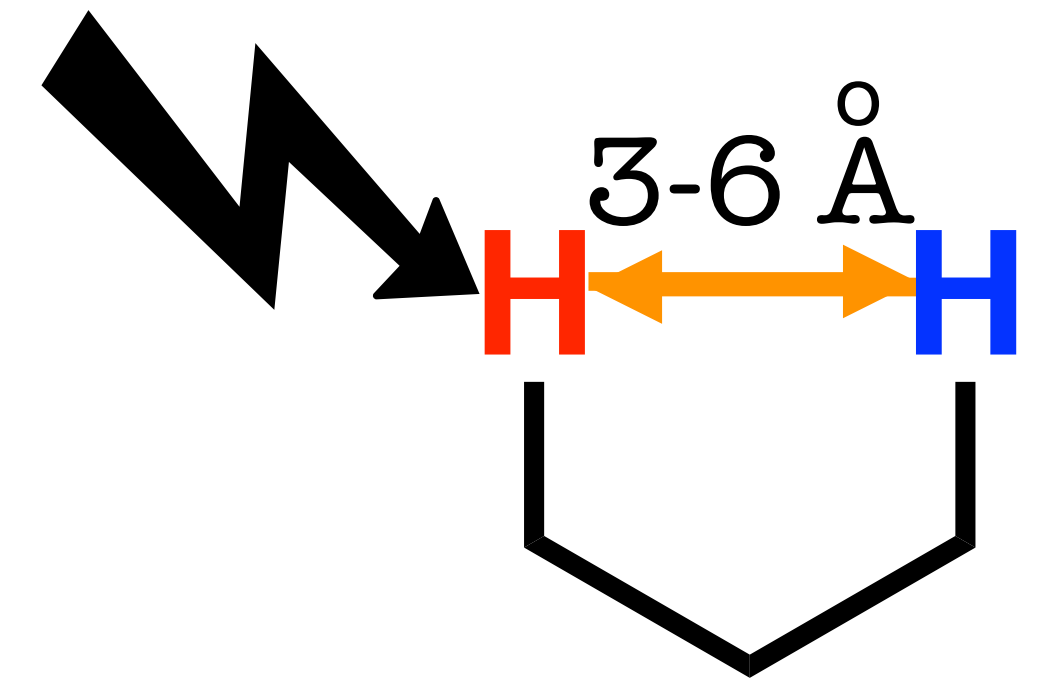
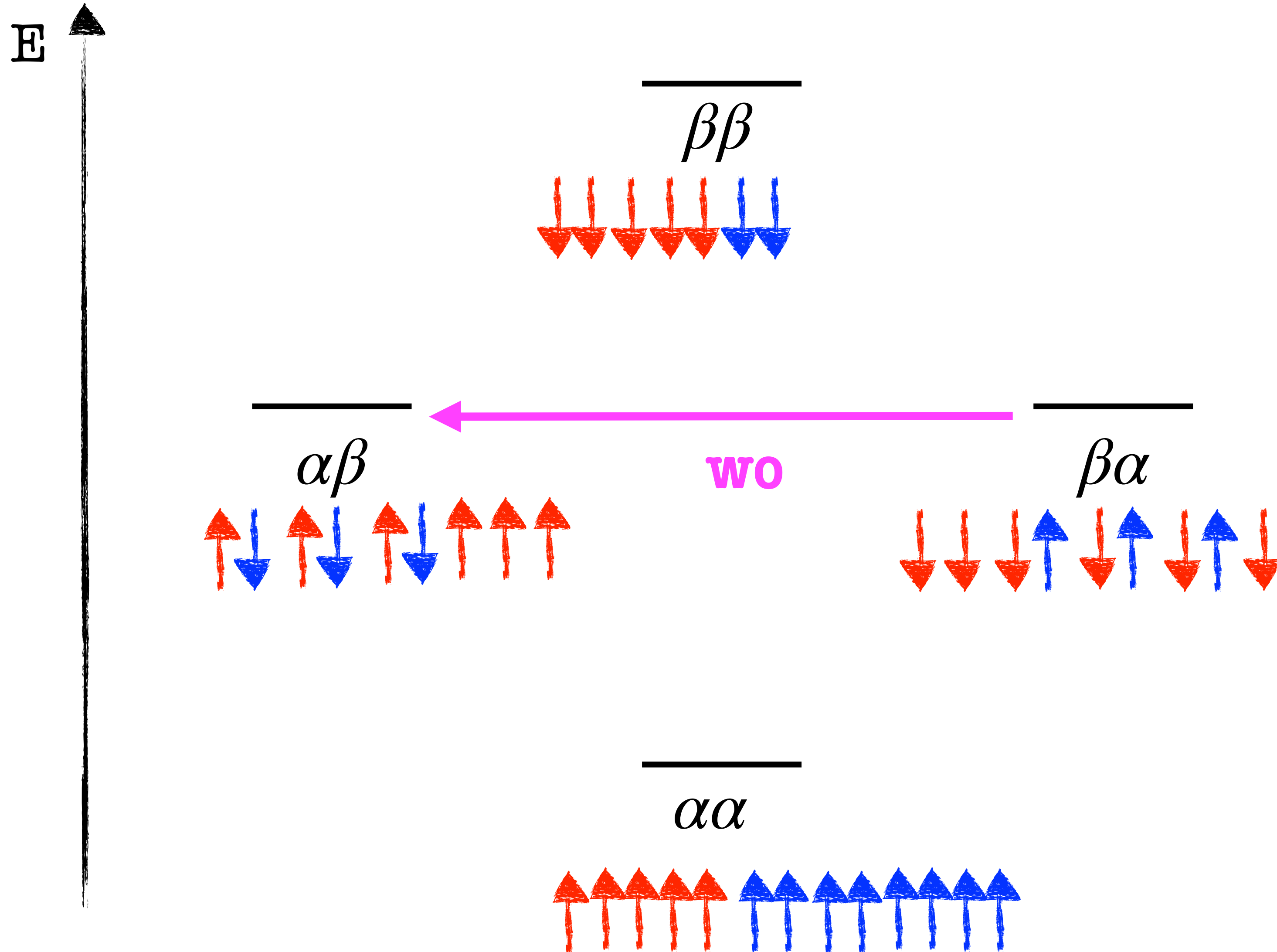
NOE: Nuclear Overhauser Effect



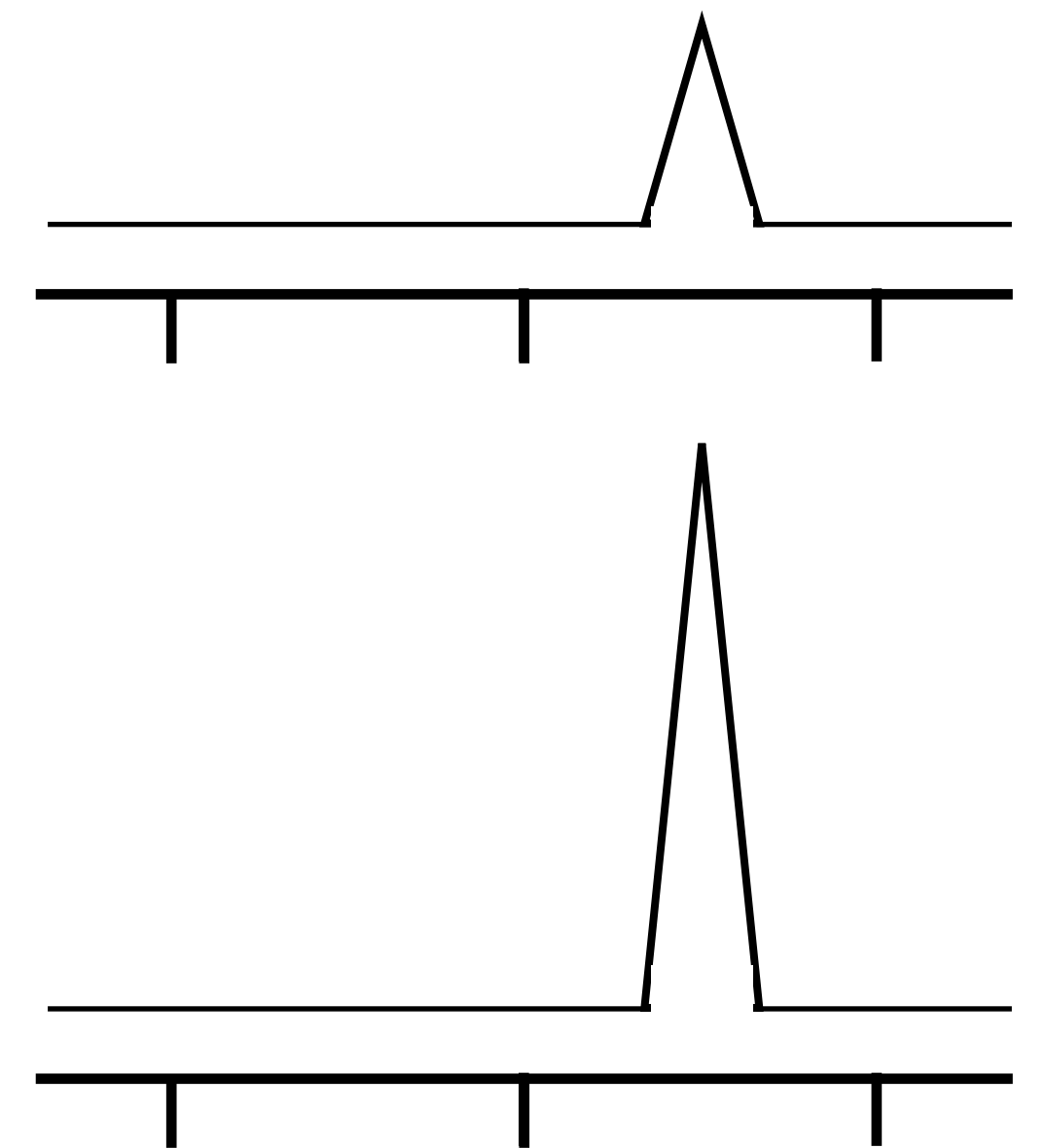
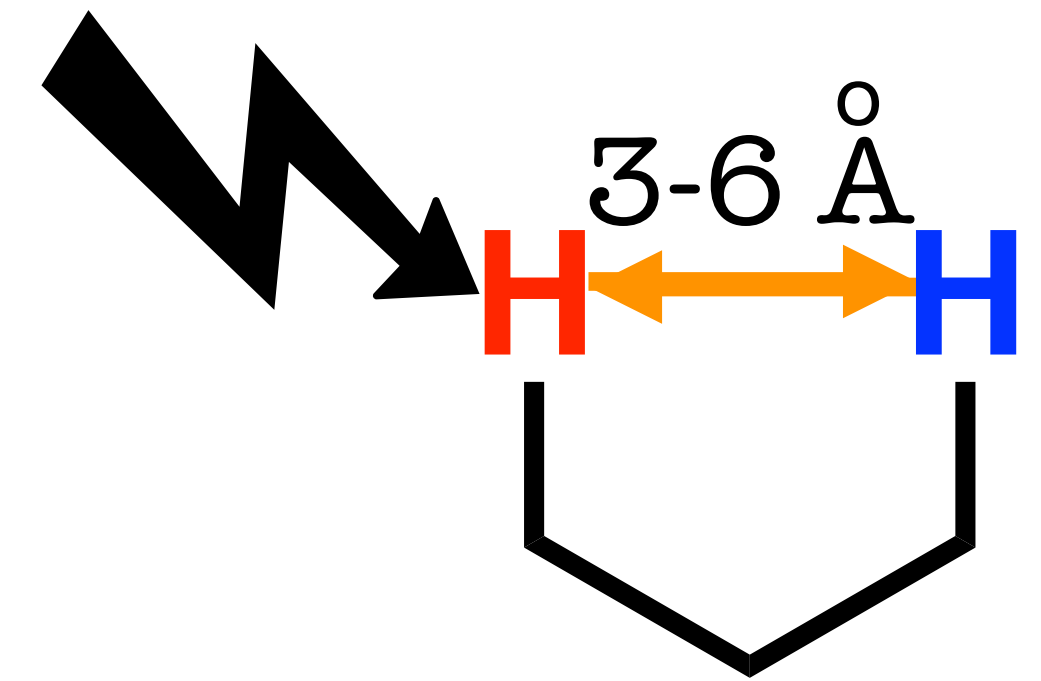
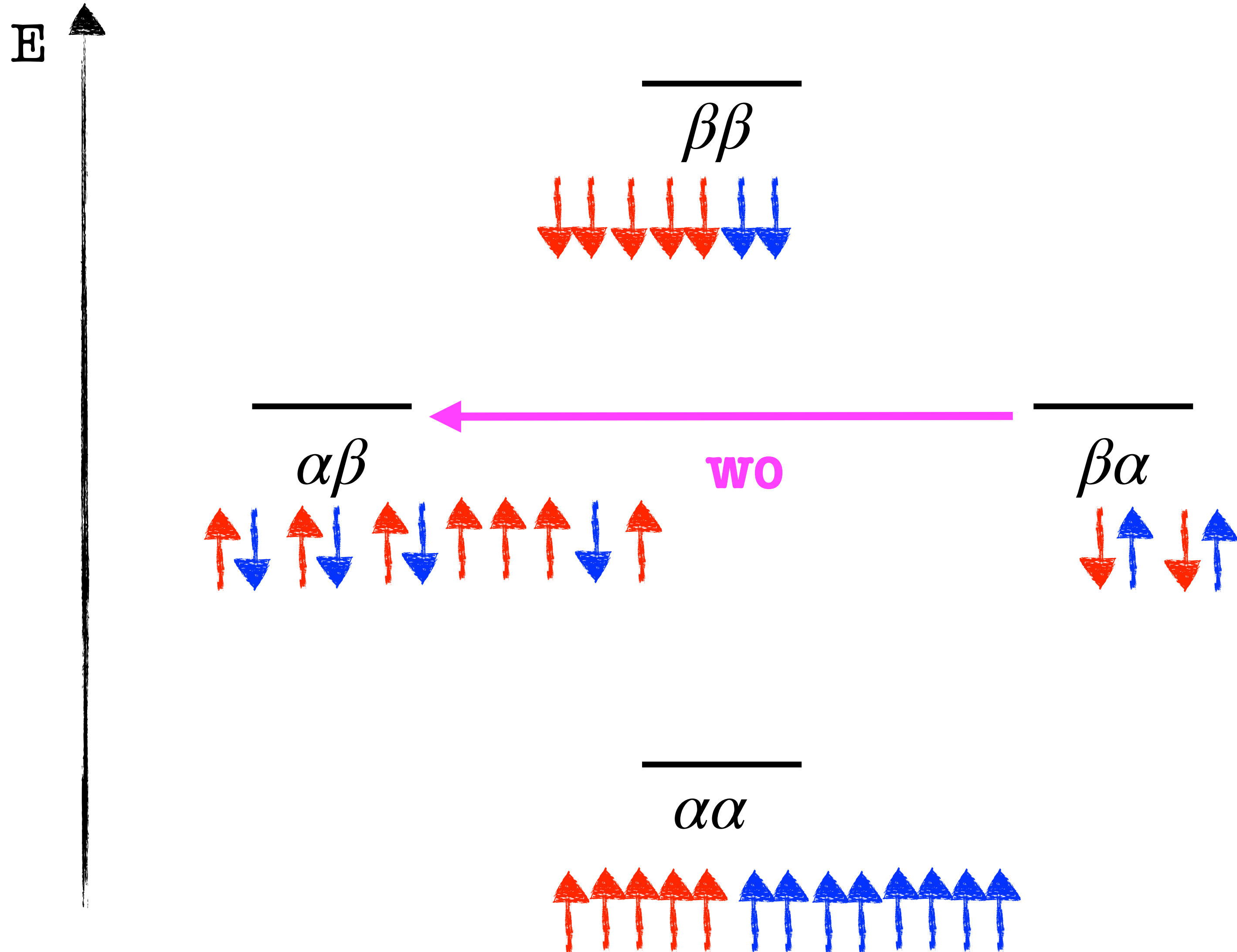
Aumentou o excesso de núcleo azul aqui!



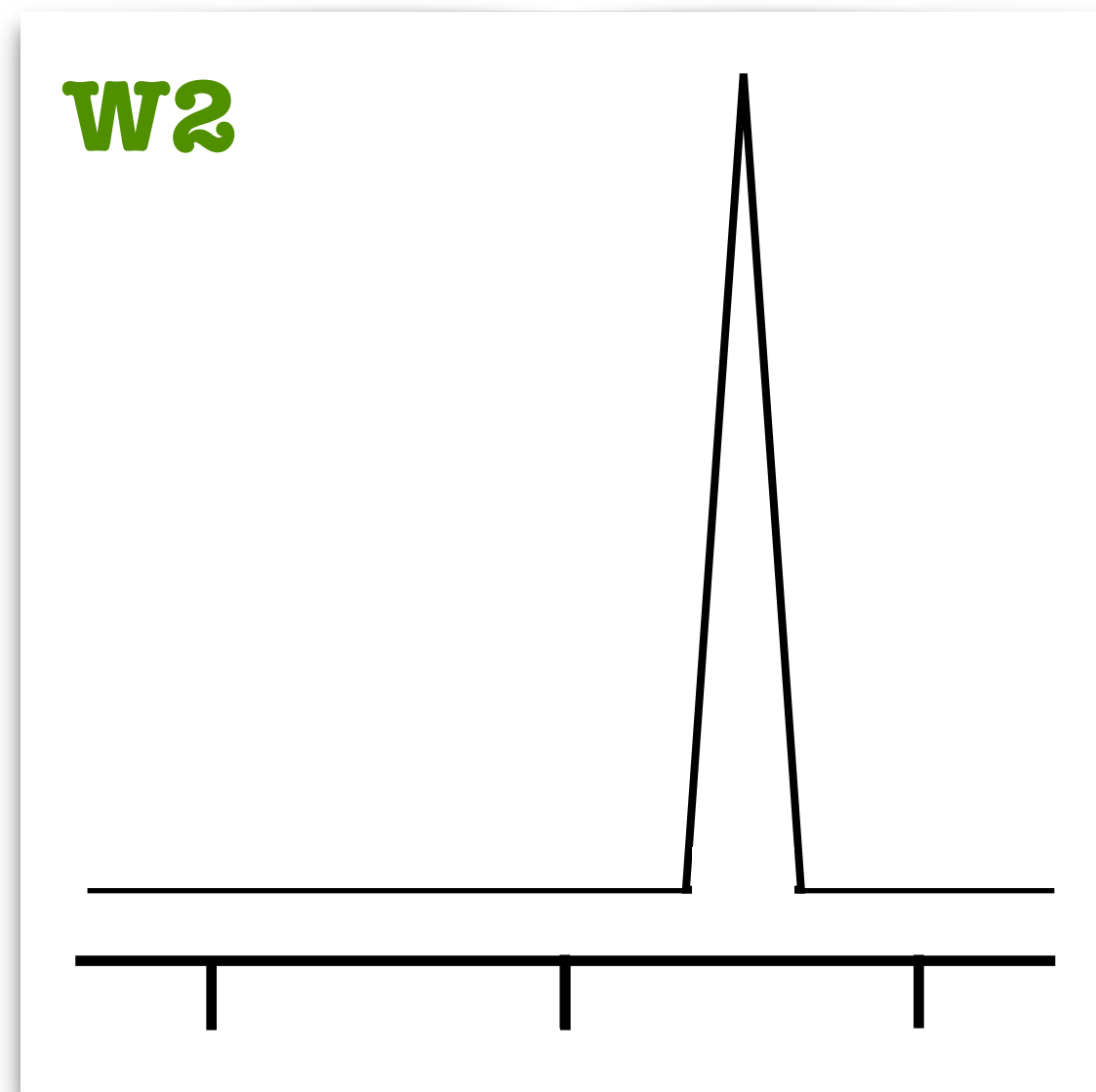
NOE: Nuclear Overhauser Effect



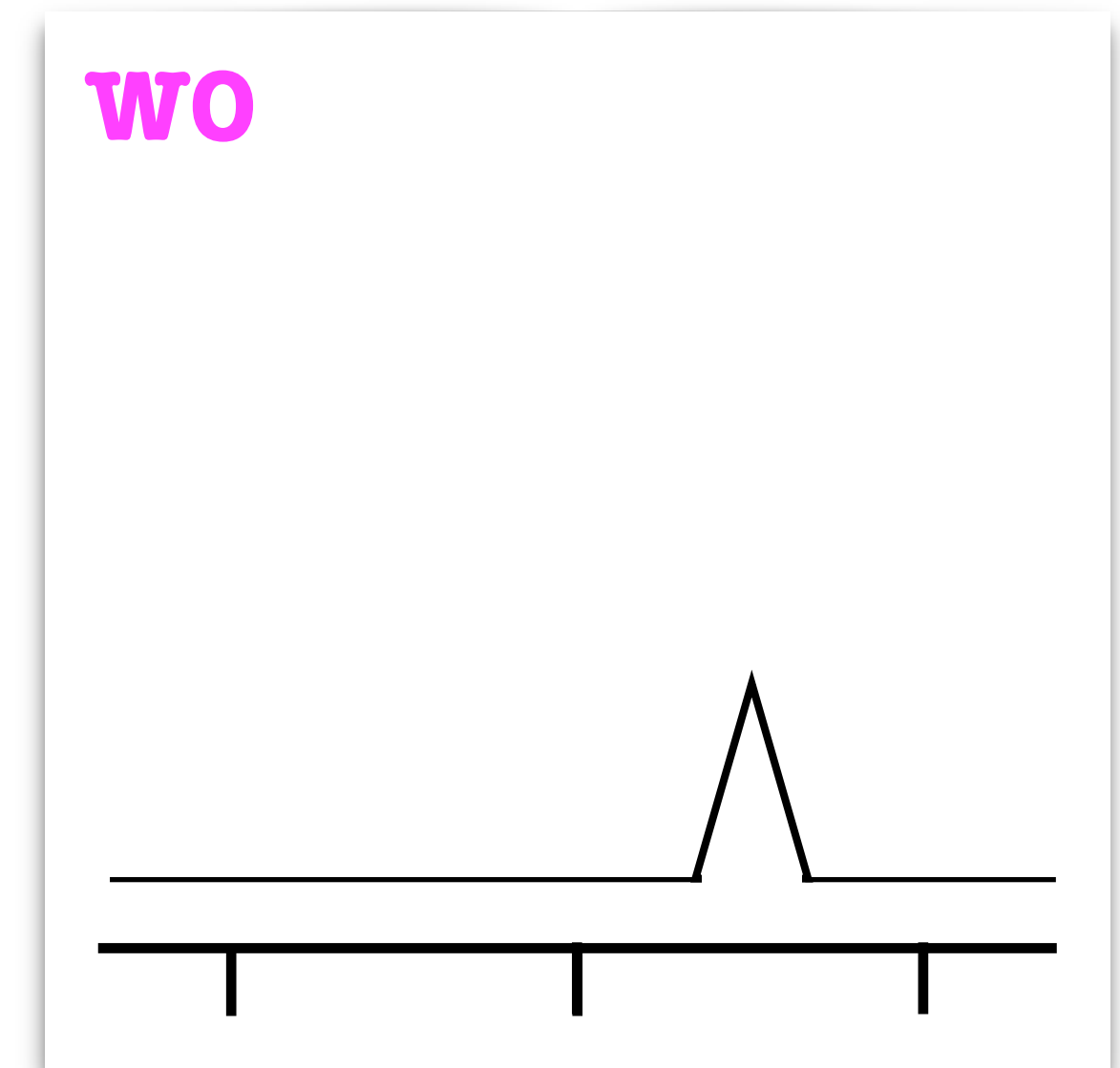
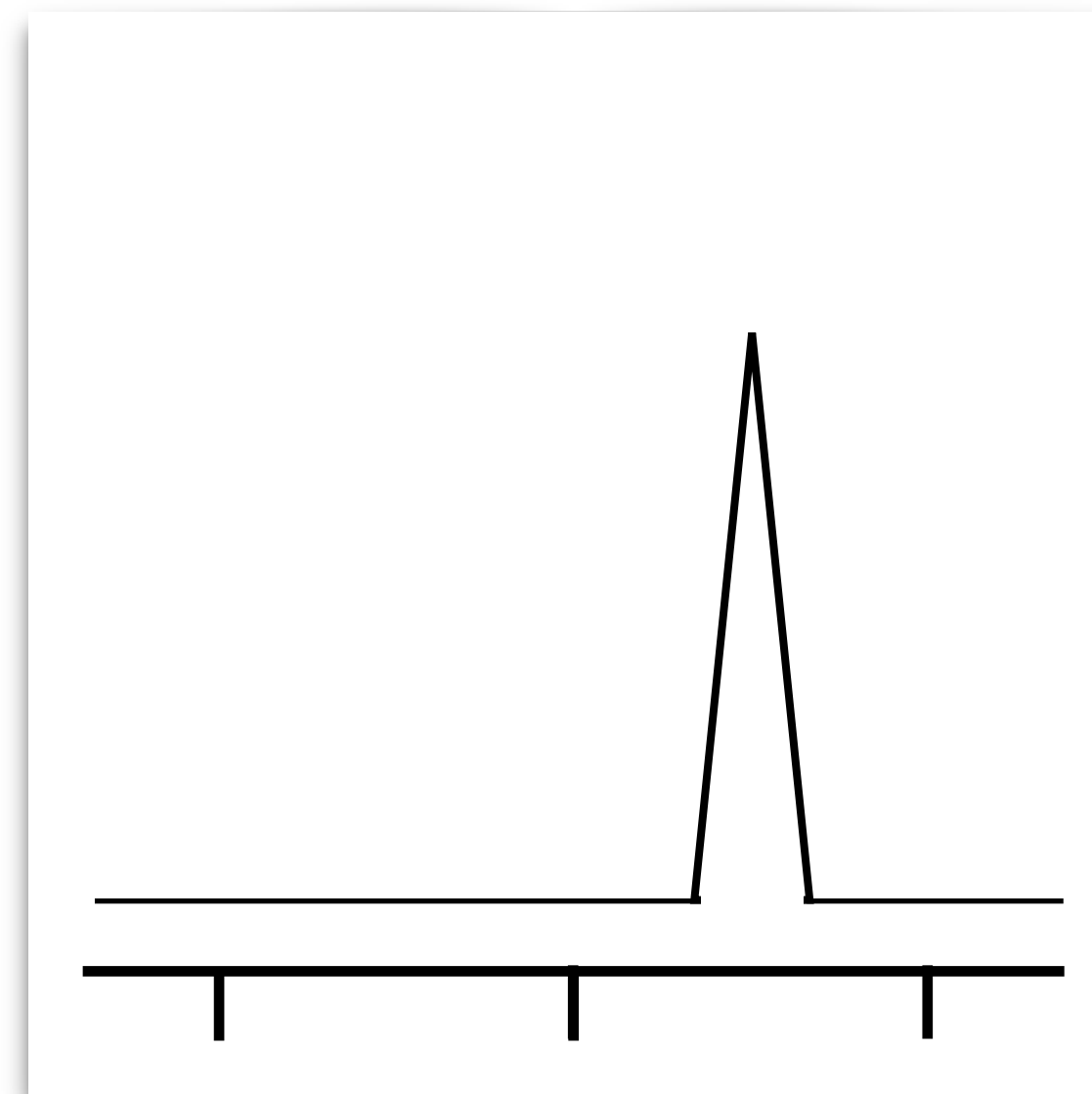
NOE: Nuclear Overhauser Effect



NOE: Nuclear Overhauser Effect



Moléculas pequenas
(menores que 1000 Da)



Moléculas Grandes
(ex: proteínas)

RMN ^{13}C

Abundância natural do ^{13}C = 1,11%

**Amostra
muito mais
concentrada**

Pode haver
acoplamento
 ^{13}C - ^1H

**Ausência de
acoplamento
 ^{13}C - ^{13}C**

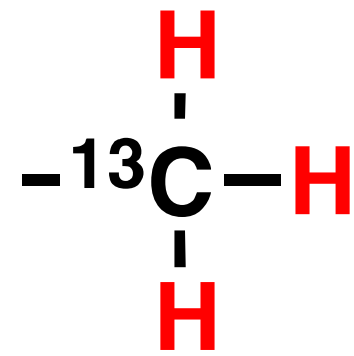
(pouco provável
haver dois ^{13}C
adjacentes)

Faixa de **deslocamentos químicos:**
0 - 220 ppm

Mesmo campo aplicado: frequência de
ressonância diferente

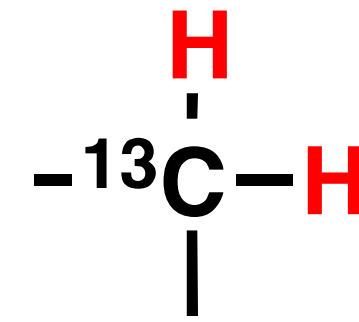
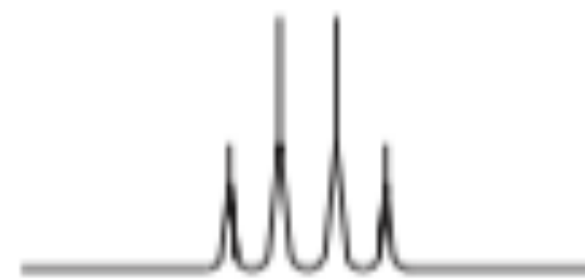
^1H	100.0	200.0	300.0	360.0	500.0	600.0 MHz
^{13}C	25.14	50.28	75.4	90.5	125.7	150.8 MHz

Técnica de ^{13}C com acoplamento



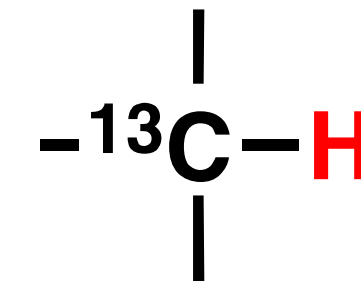
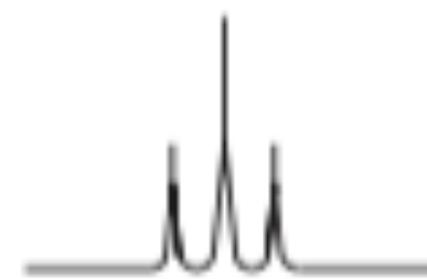
3 prótons

$$N + 1 = 3 + 1 = 4 \\ \text{(quarteto)}$$



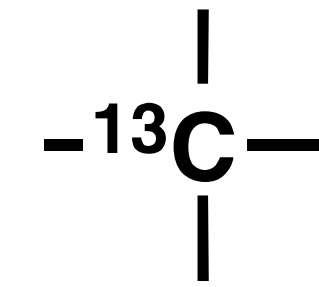
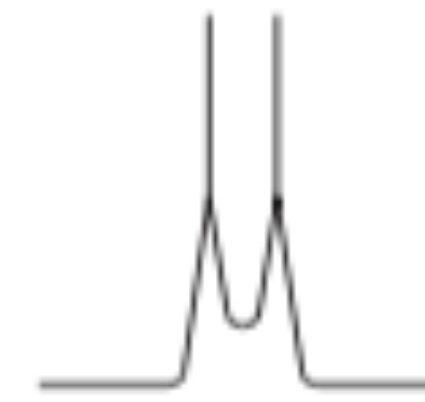
2 prótons

$$N + 1 = 2 + 1 = 3 \\ \text{(triplete)}$$



1 próton

$$N + 1 = 1 + 1 = 2 \\ \text{(dubleto)}$$

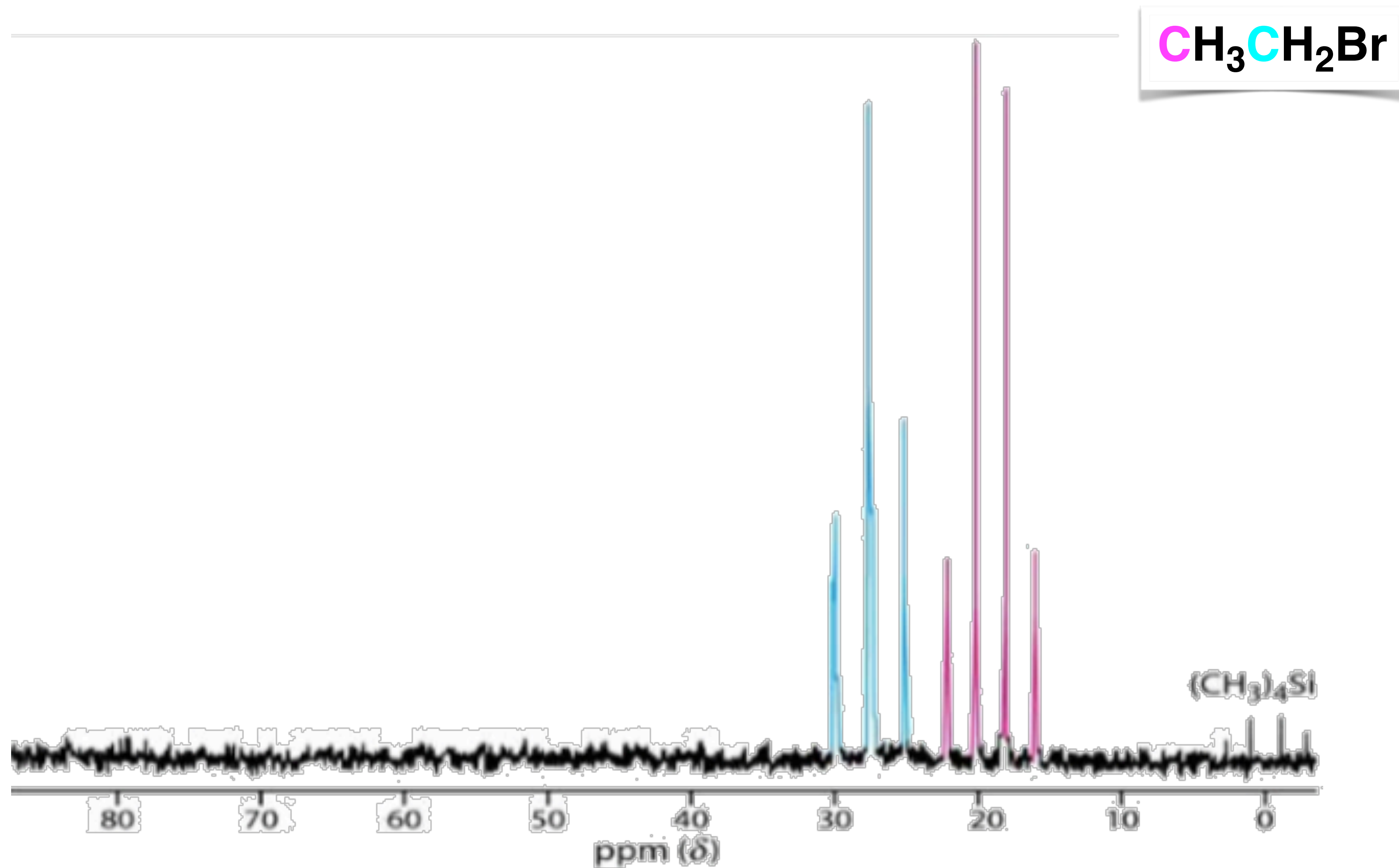


Nenhum próton

$$N + 1 = 0 + 1 = 1 \\ \text{(singleto)}$$

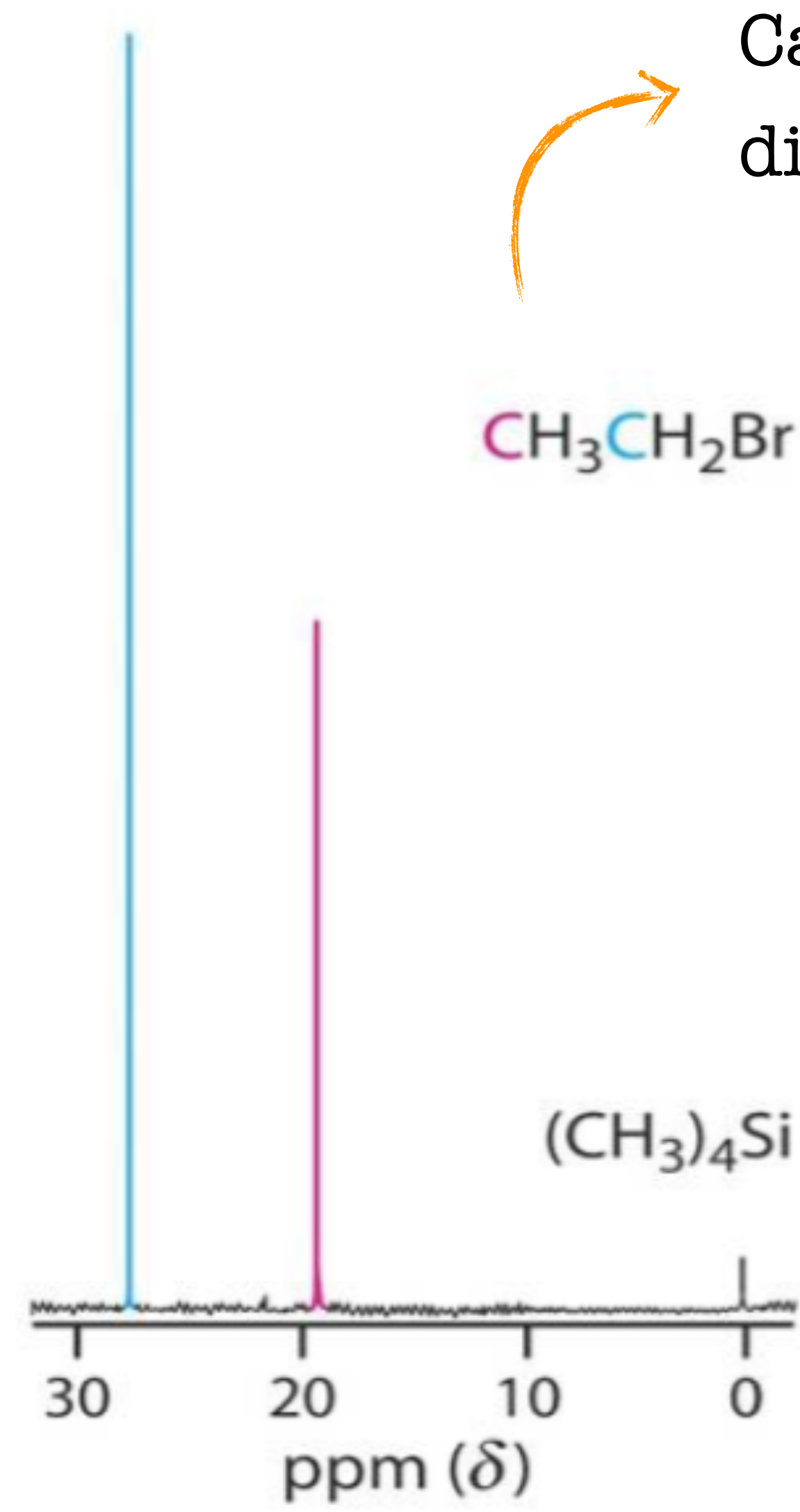


Técnica de ^{13}C com acoplamento



Técnica de ^{13}C desacoplado

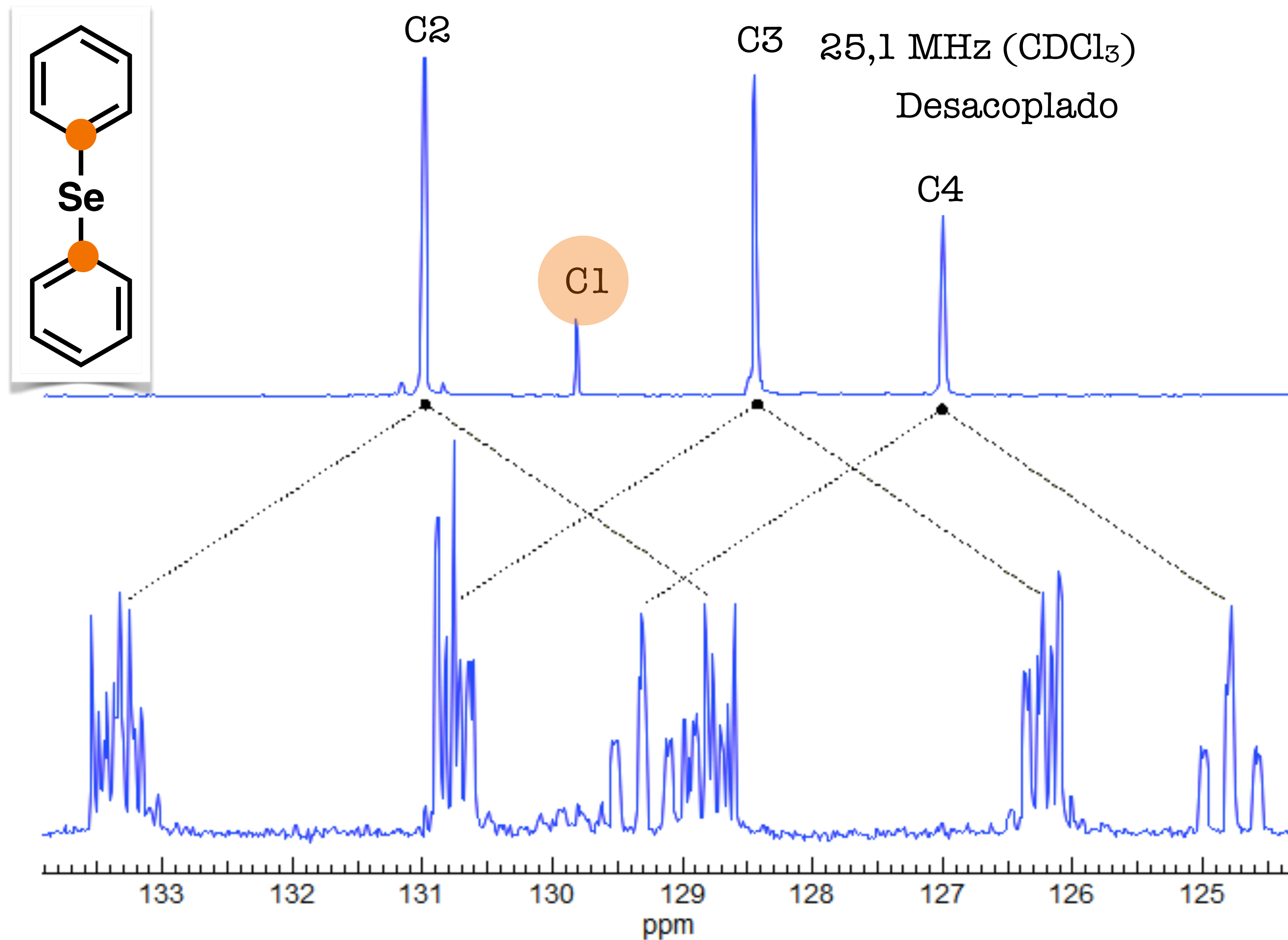
Aplicada uma 2ª frequência que “impede” o acoplamento $^{13}\text{C}-^1\text{H}$



Cada sinal representa um tipo de carbono diferente \rightarrow todos os sinais são singletos

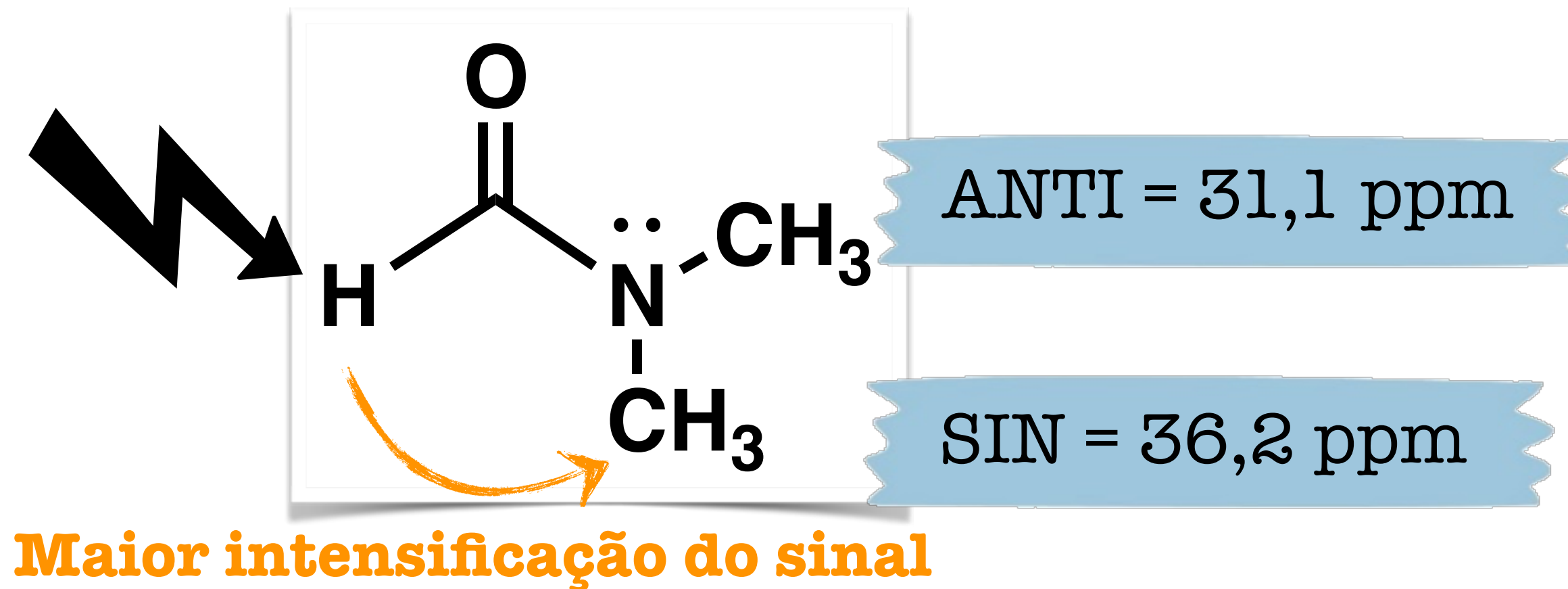
Sinais não integráveis

Técnica de ^{13}C desacoplado

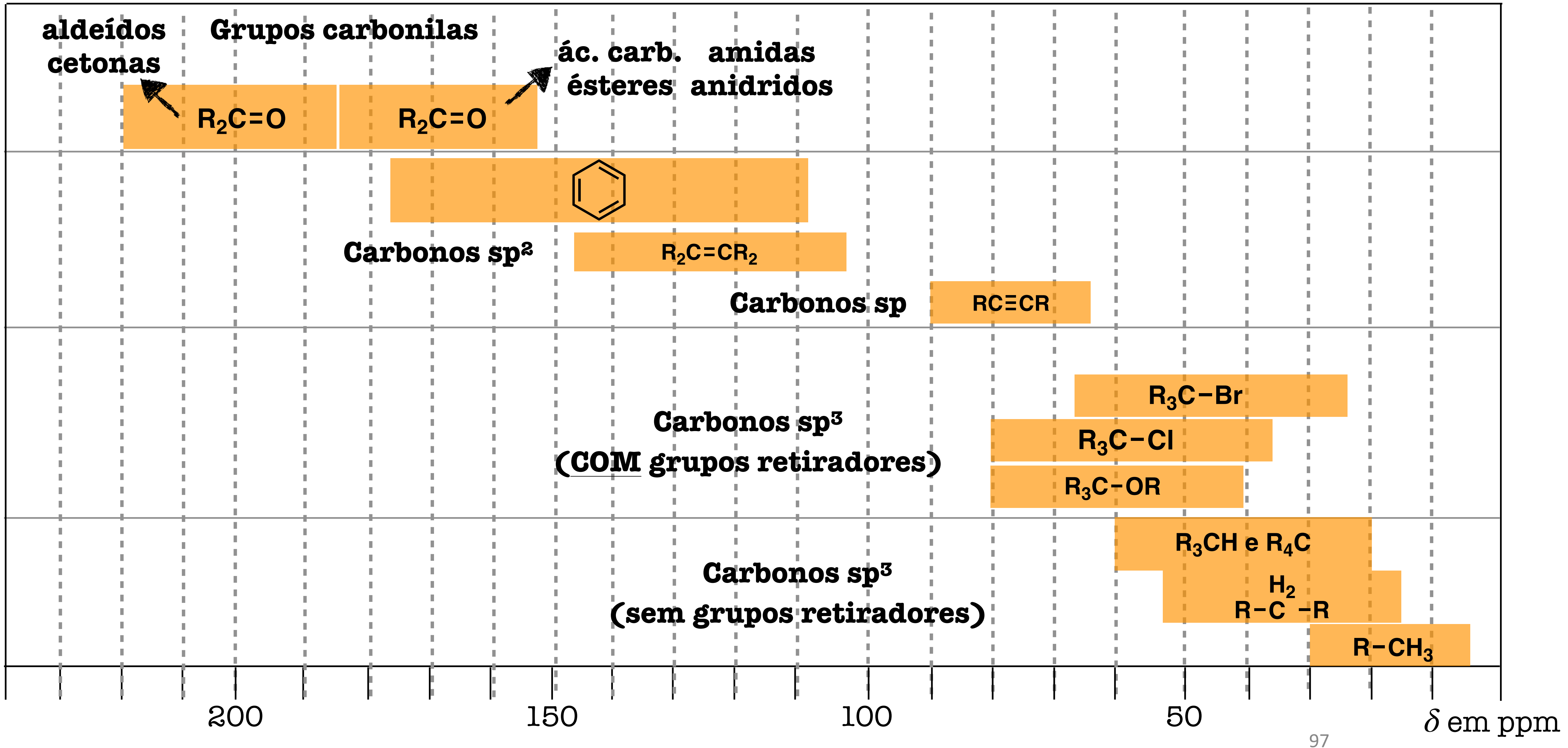


Técnica de ^{13}C desacoplado

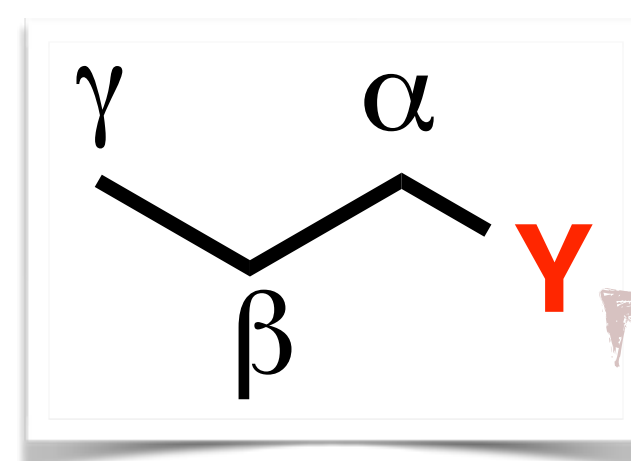
NOE → Pode ser usado para verificar atribuição de picos
(o efeito é maior nos carbonos mais próximos)



RMN ¹³C: deslocamento

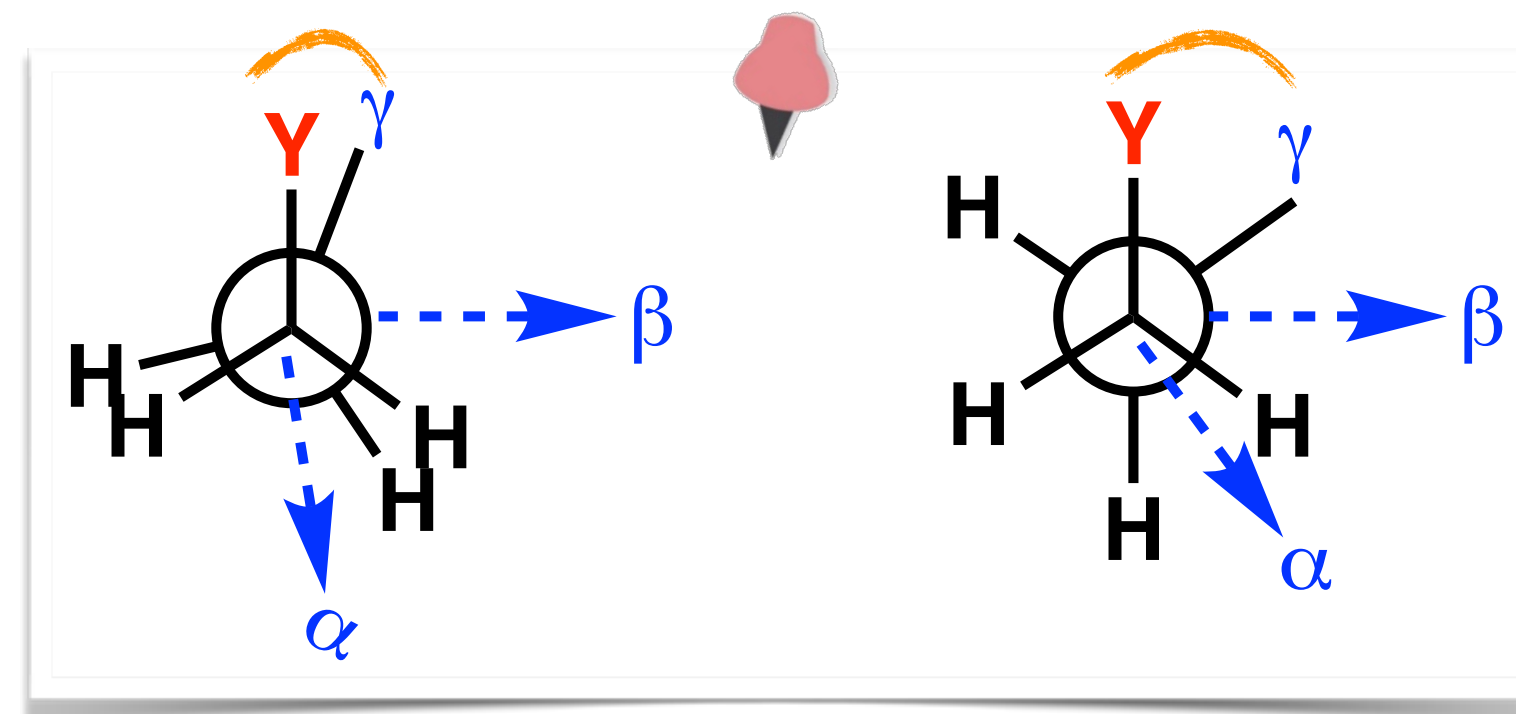


RMN ^{13}C : deslocamento (Csp^3)



Grupos eletronegativos

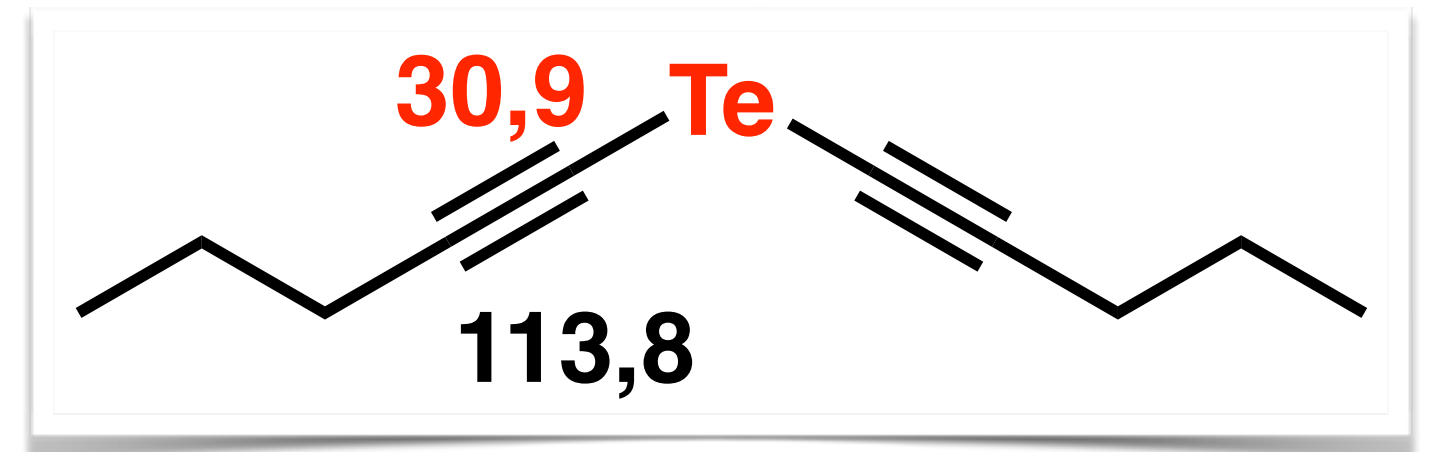
- O carbono diretamente ligado ao grupo (carbono α) sofre grande efeito de desblindagem;
- Há também desblindagem do carbonos β (menor intensidade);
- Há uma blindagem do carbono γ !!!!



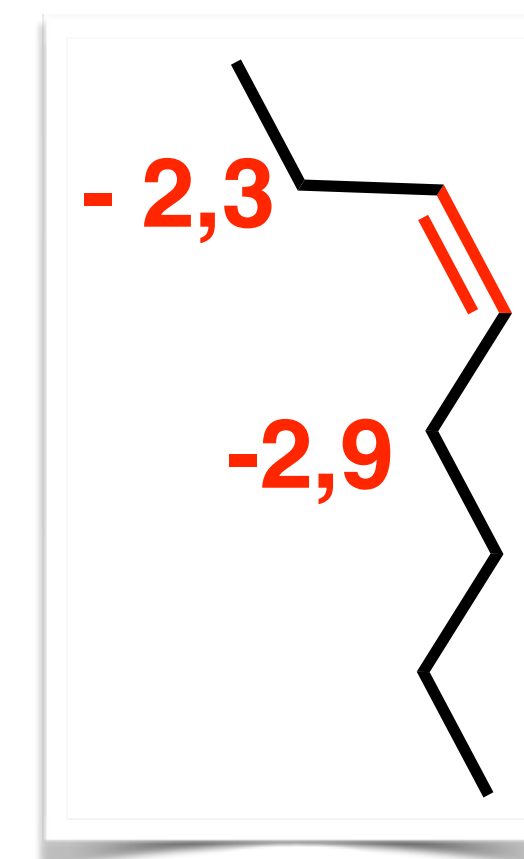
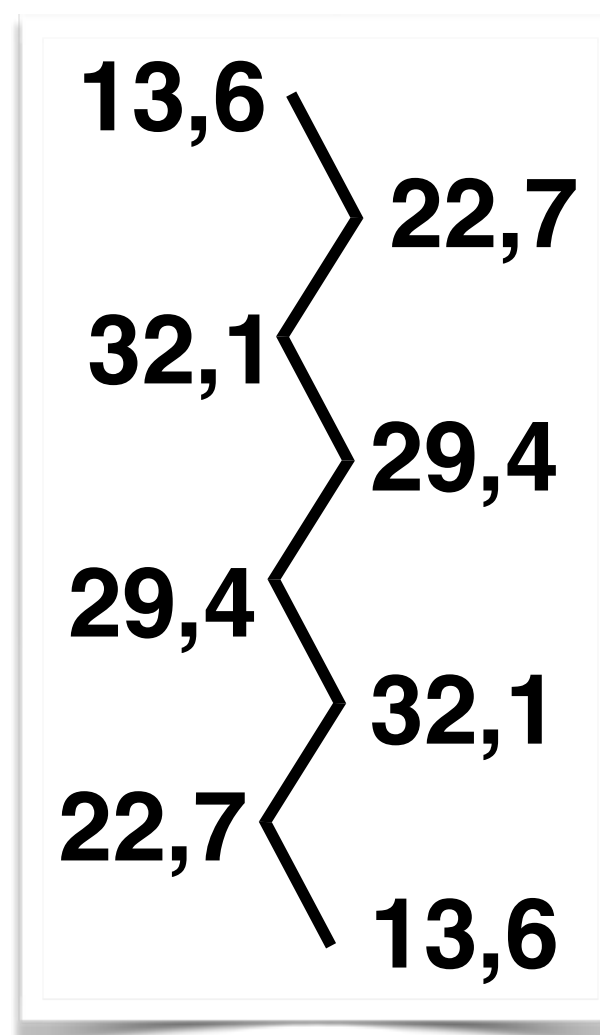
Necessidade de consultar tabelas!

RMN ^{13}C : deslocamento (Csp^3 efeito α)

Efeito do átomo pesado: vai contra a eletronegatividade (**blinda**)

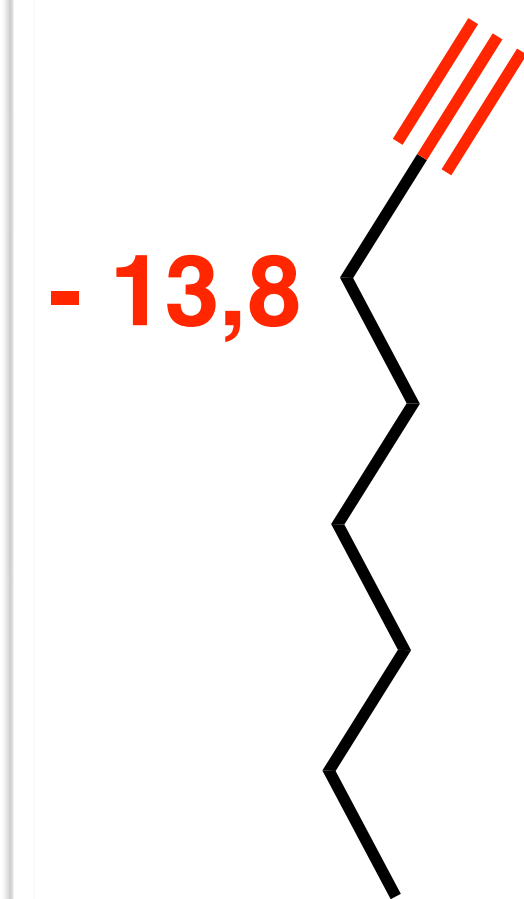
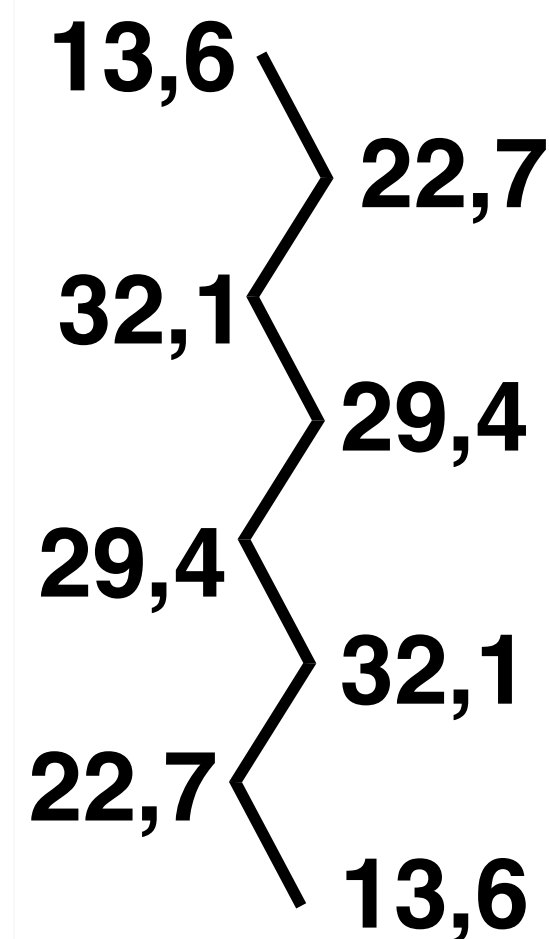


Efeito da ligação dupla: pequeno!
Comparação C-Csp^3 x C-Csp^2 ($\text{C}=\text{C}$)



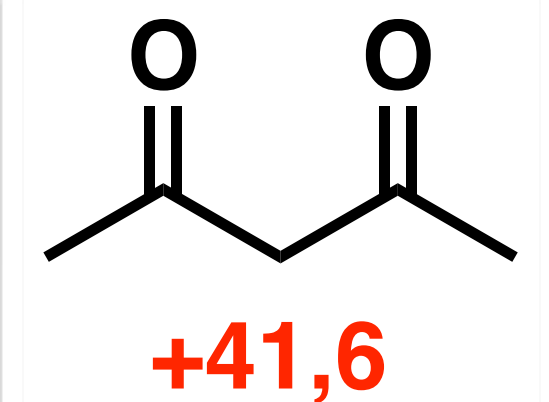
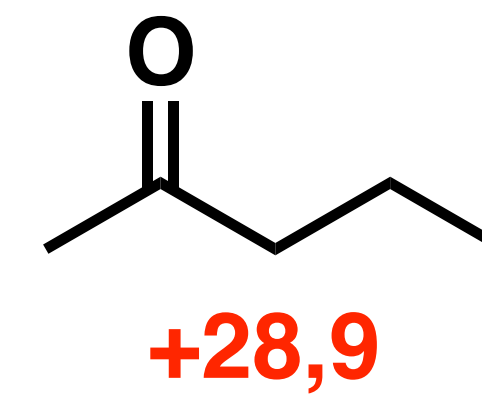
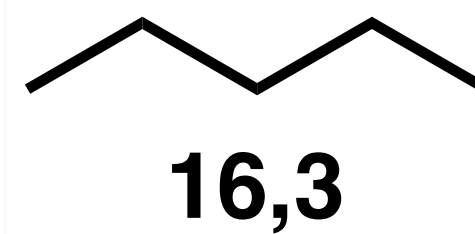
RMN ^{13}C : deslocamento (Csp^3 efeito α)

Efeito da tripla: efeito de blindagem no carbono diretamente ligado



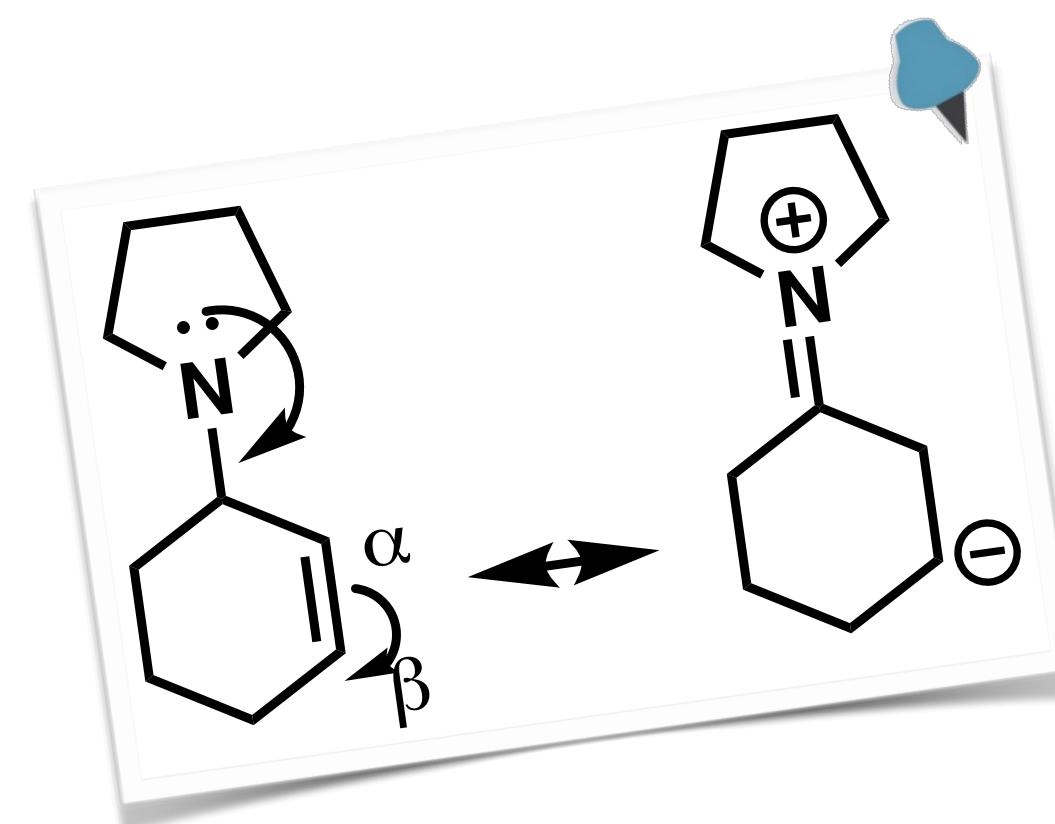
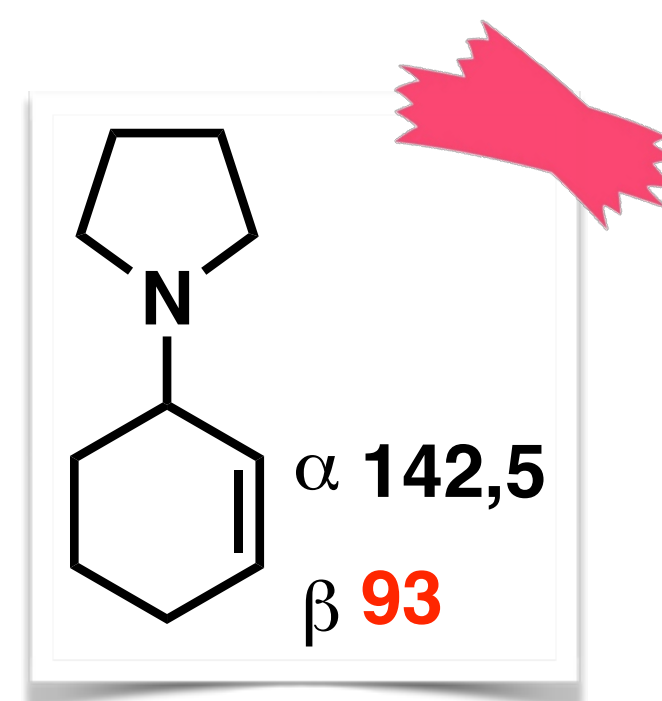
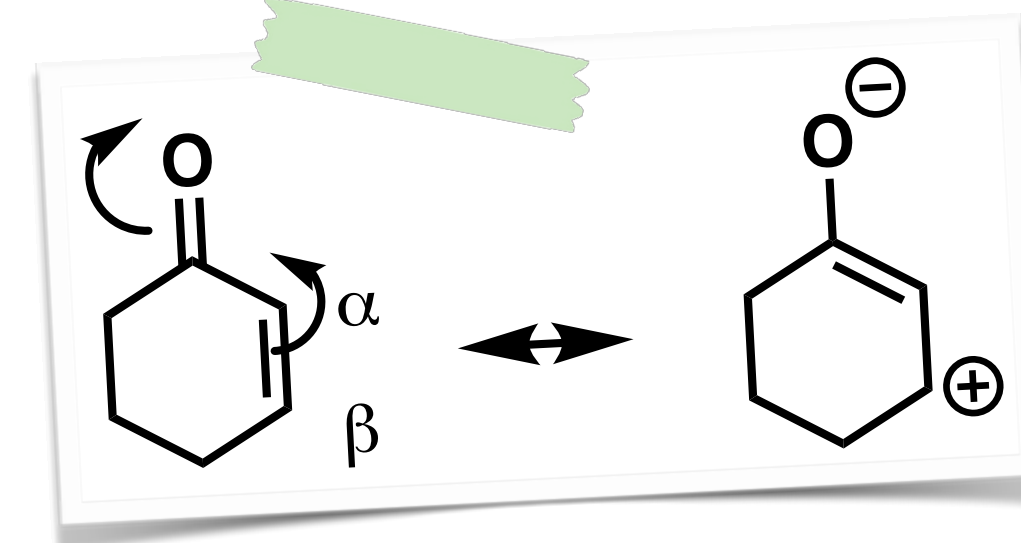
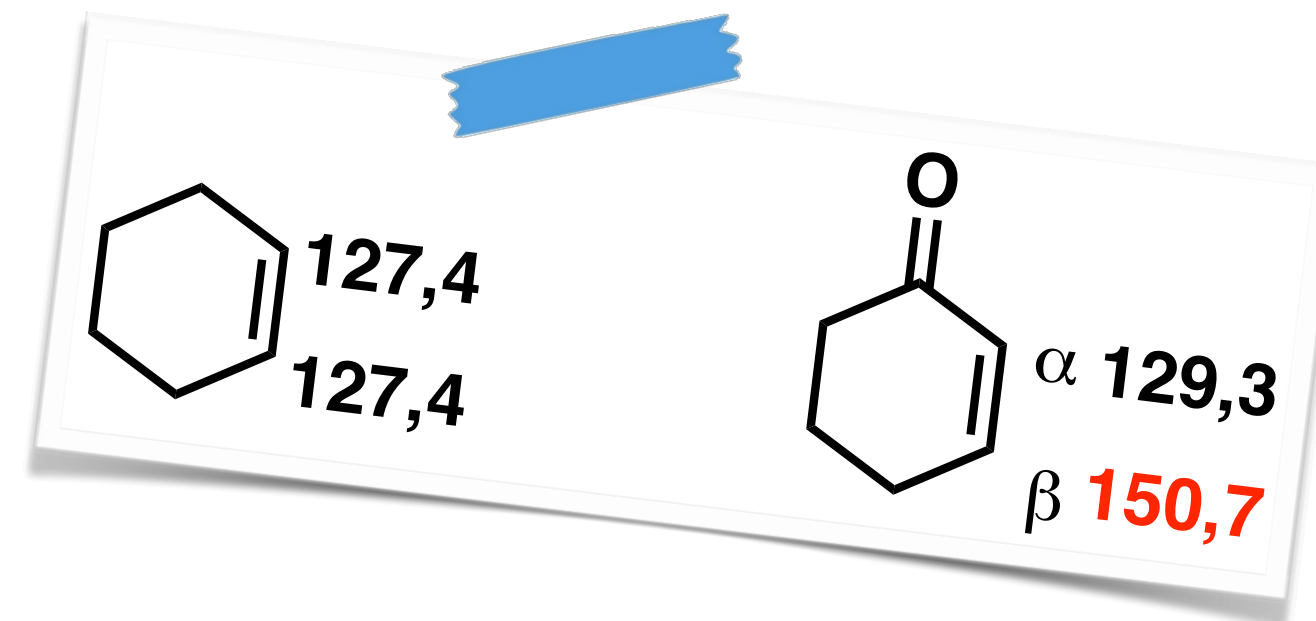
Substituintes contendo carbonila:

Efeito grande de desblindagem!

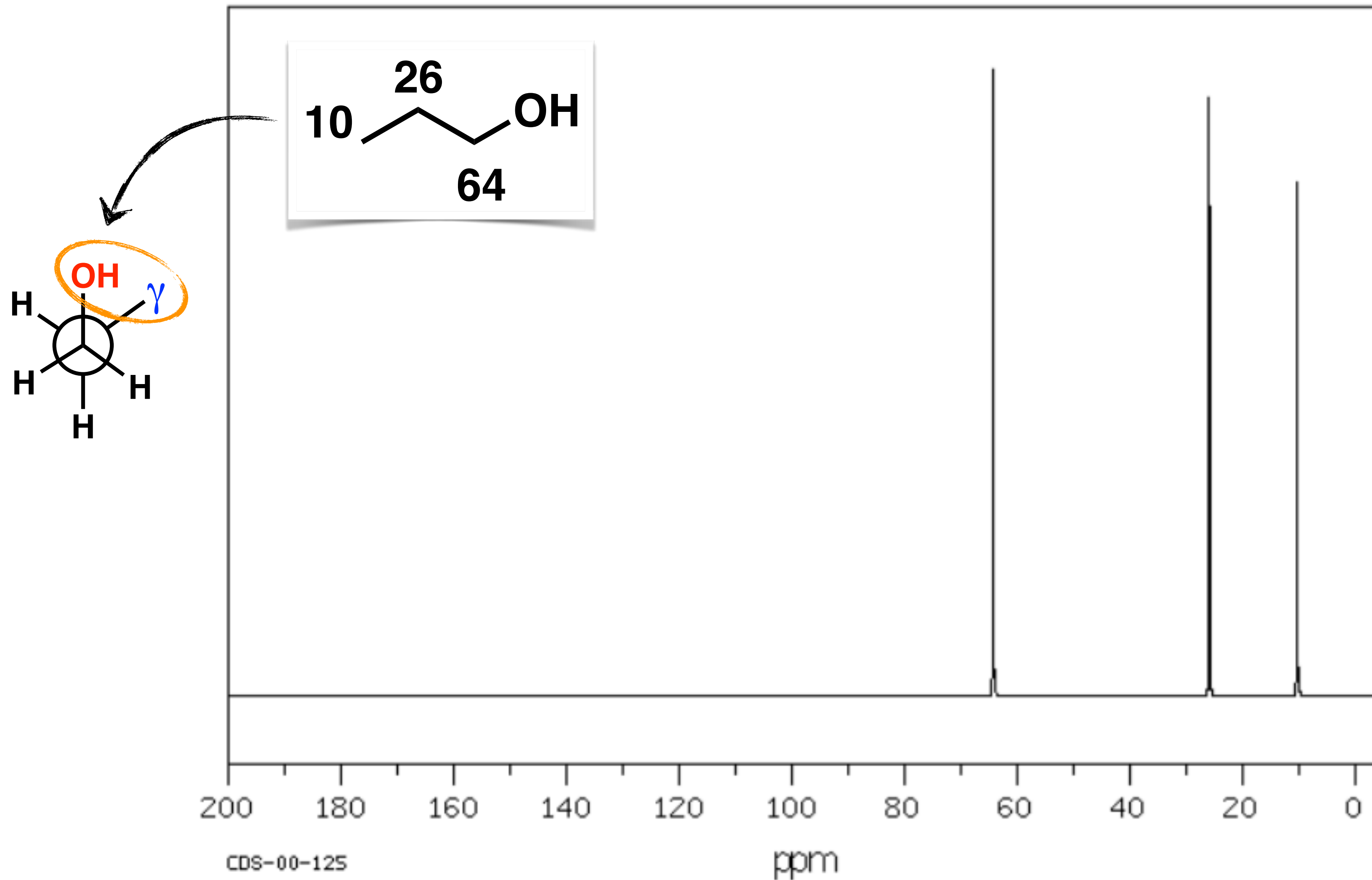


RMN ^{13}C : deslocamento (Csp^2/Csp efeito α)

Devido ao poder de conjugação, sofrem grande efeito com grupos de efeito mesomérico (doador ou retirador).

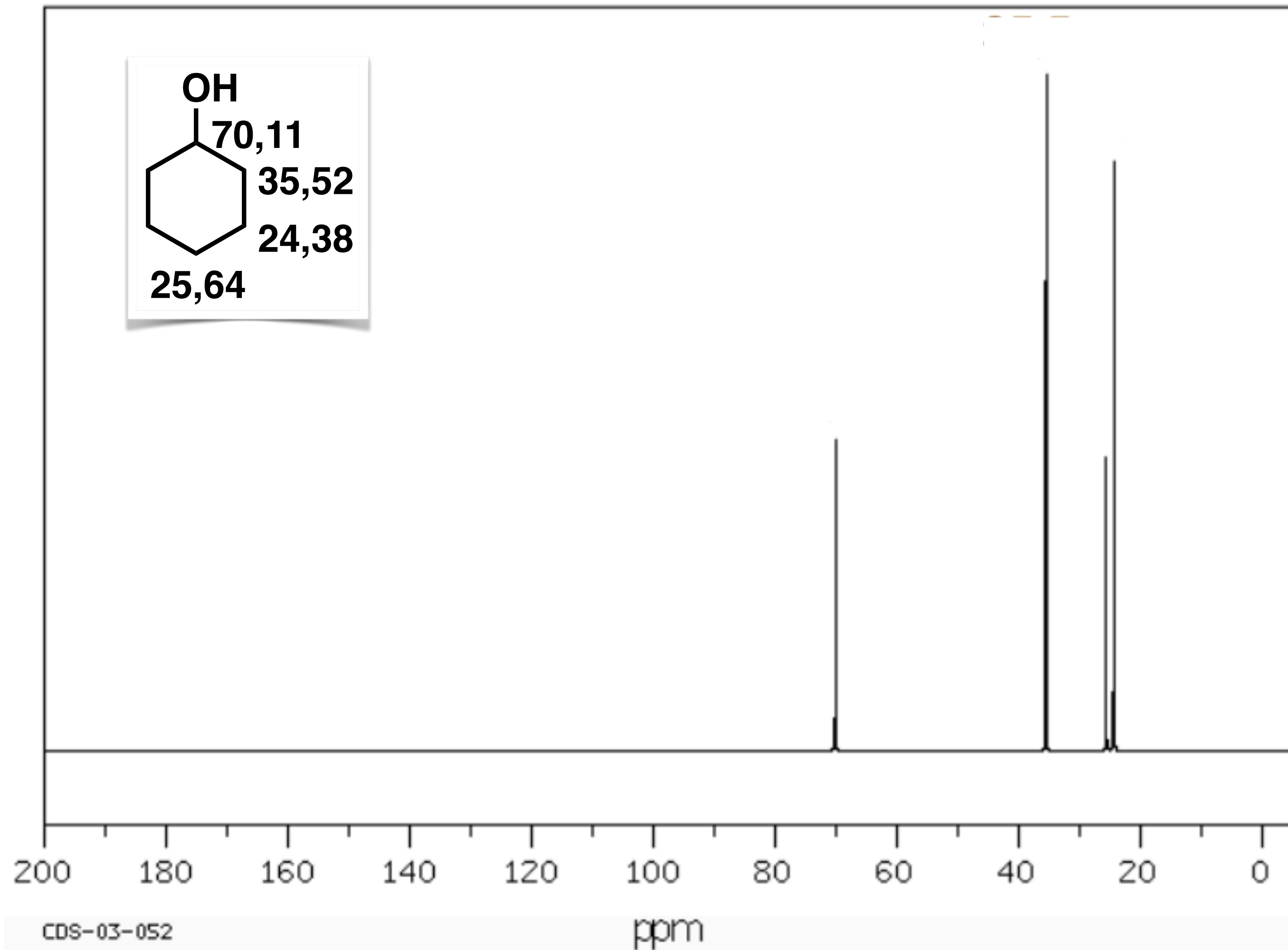


Espectros de RMN ¹³C

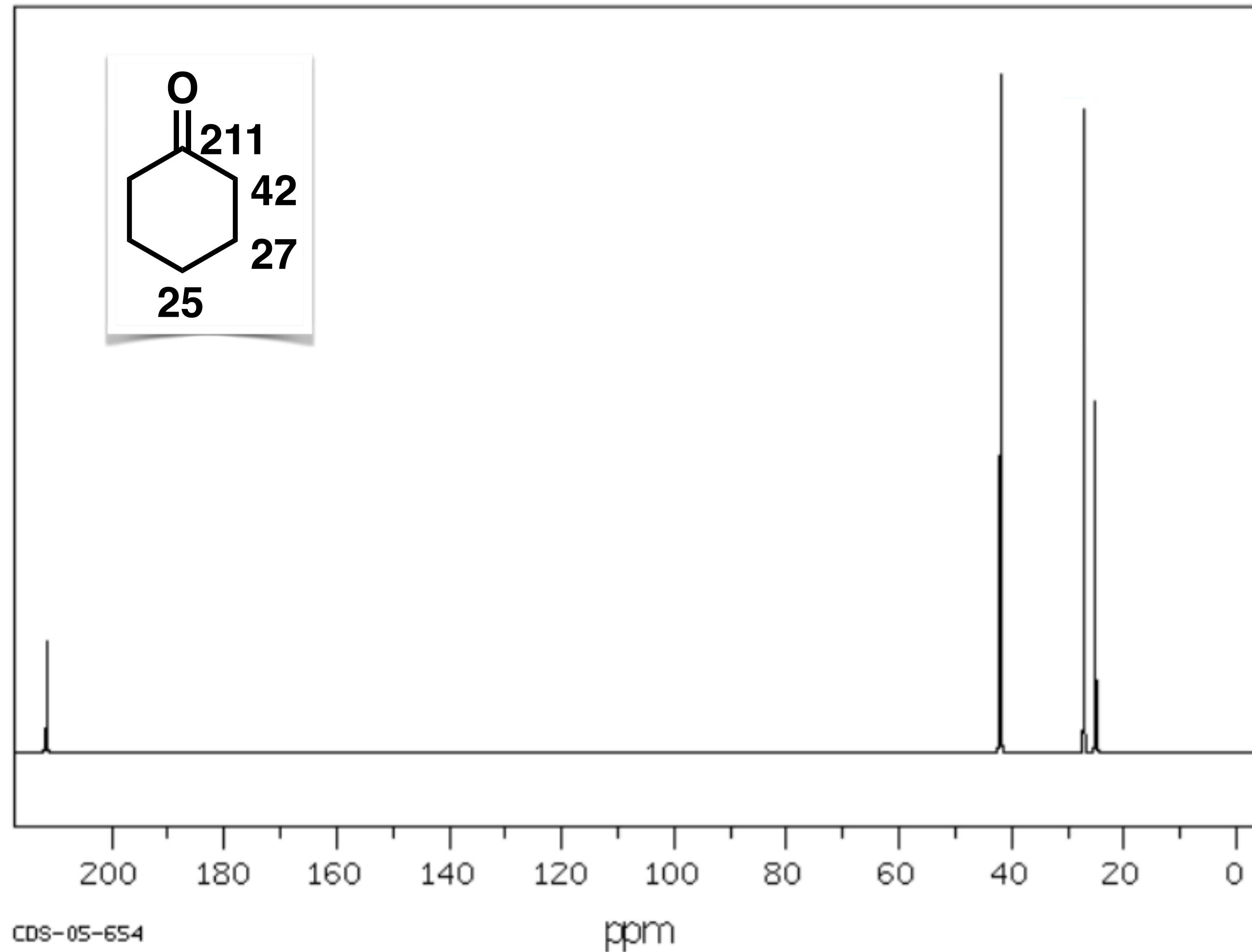


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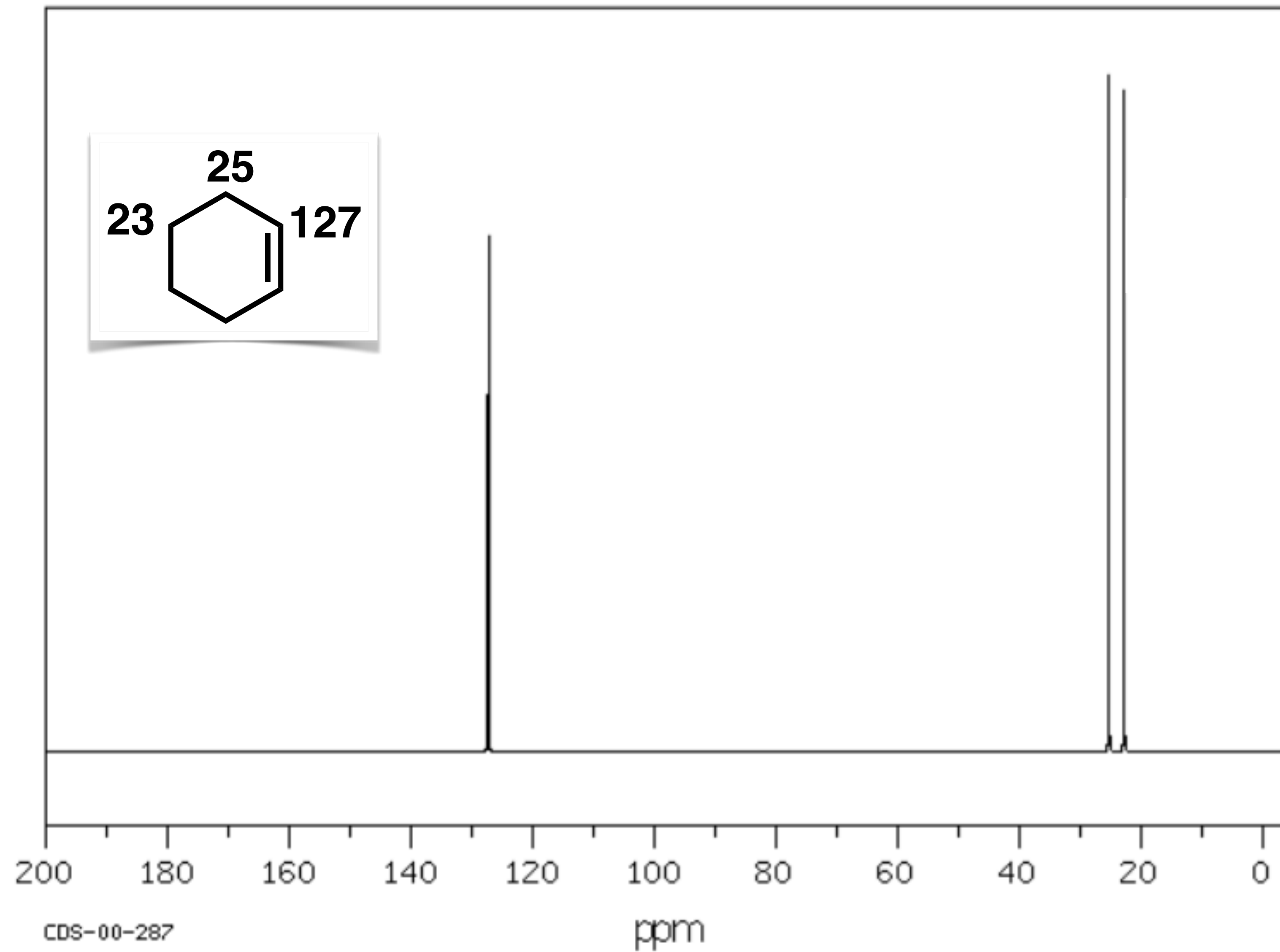
Espectros de RMN ^{13}C



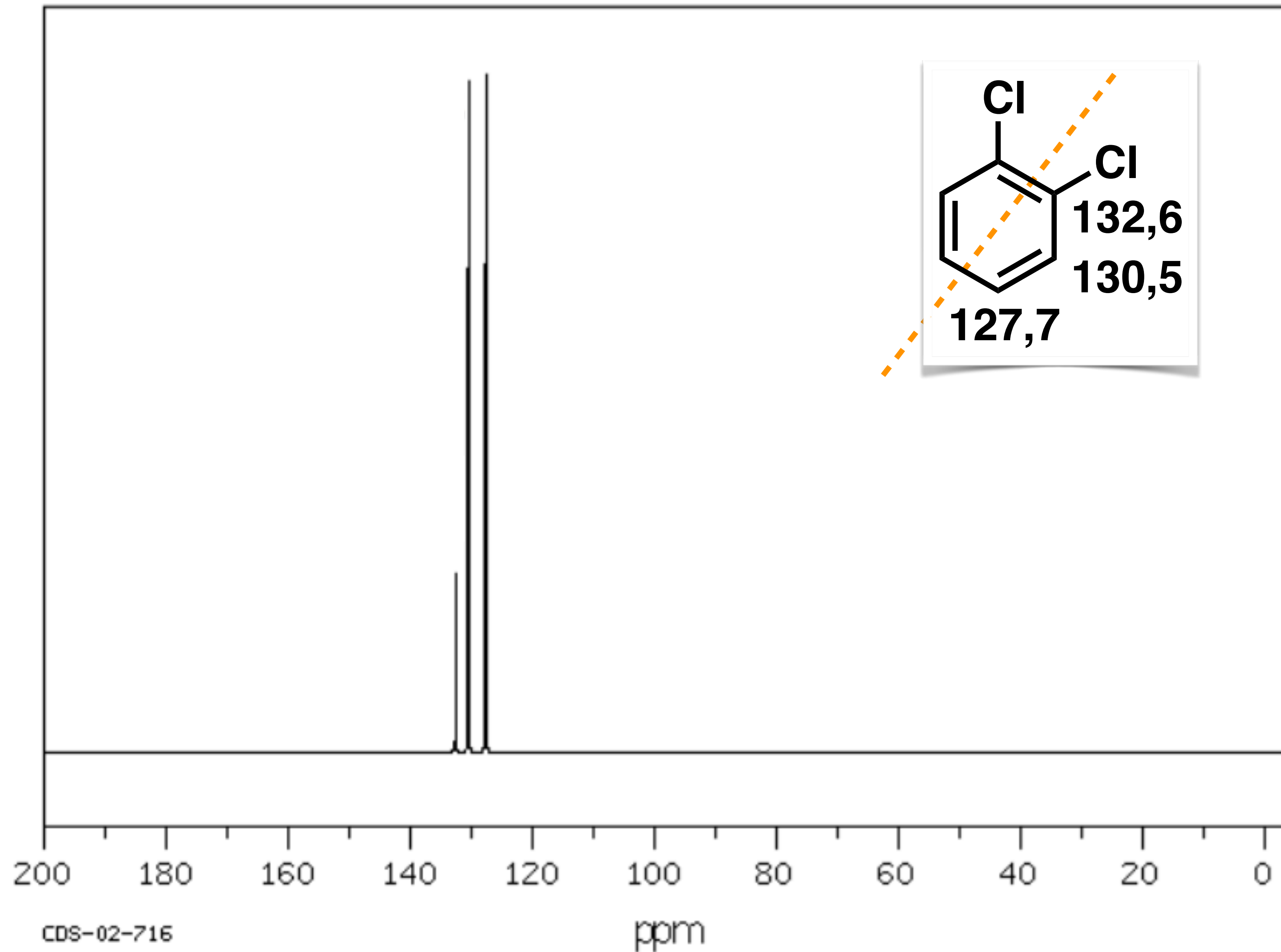
Espectros de RMN ^{13}C



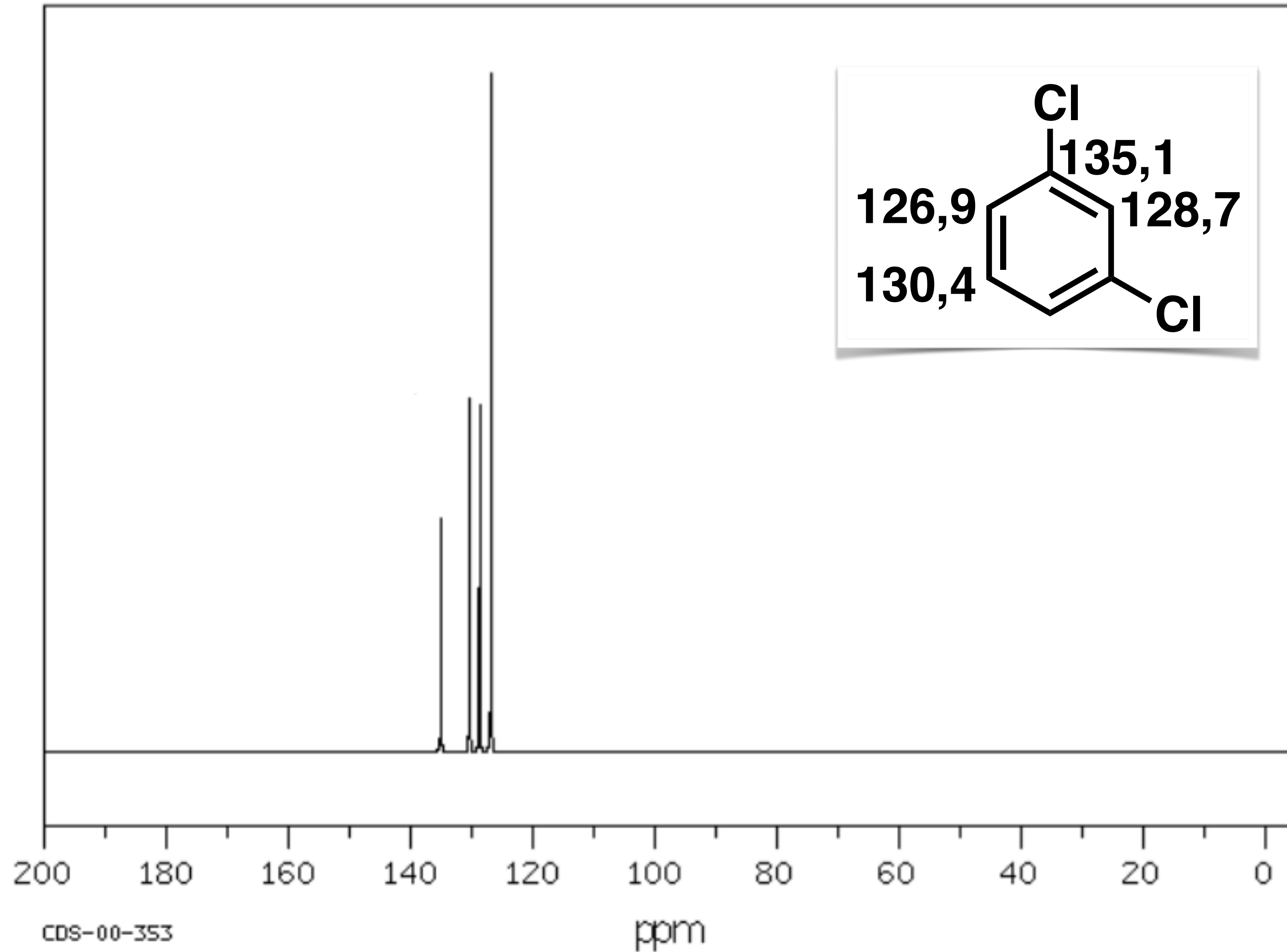
Espectros de RMN ^{13}C



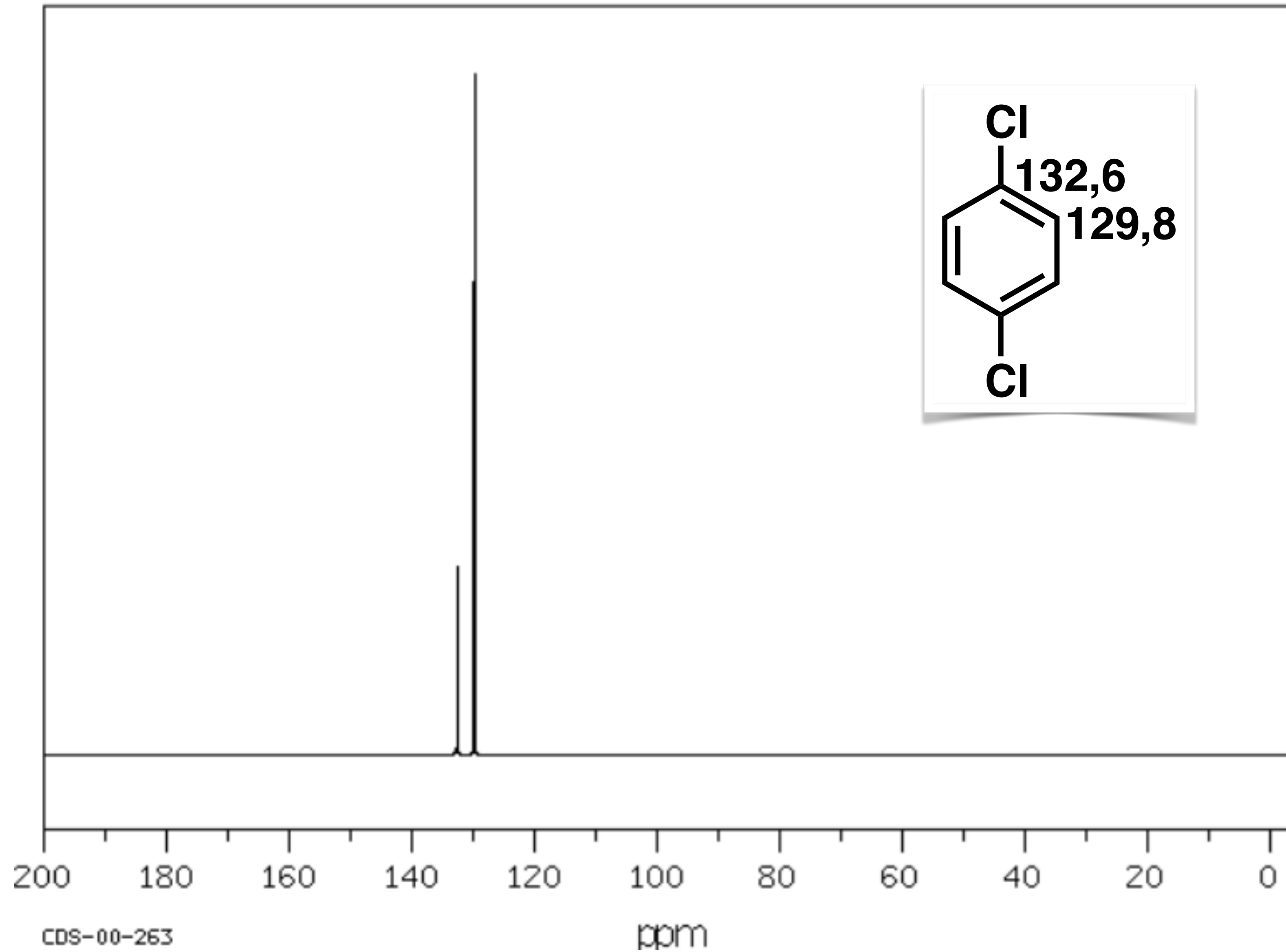
Espectros de RMN ^{13}C



Espectros de RMN ^{13}C



Espectros de RMN ^{13}C



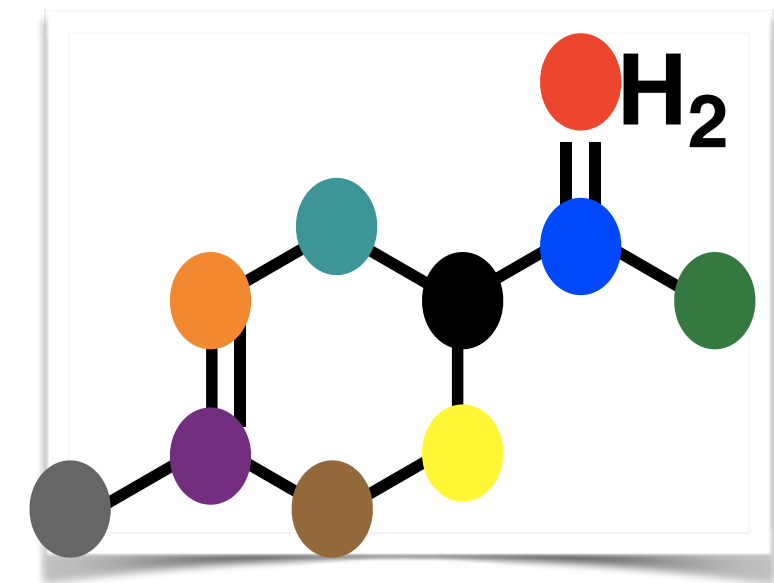
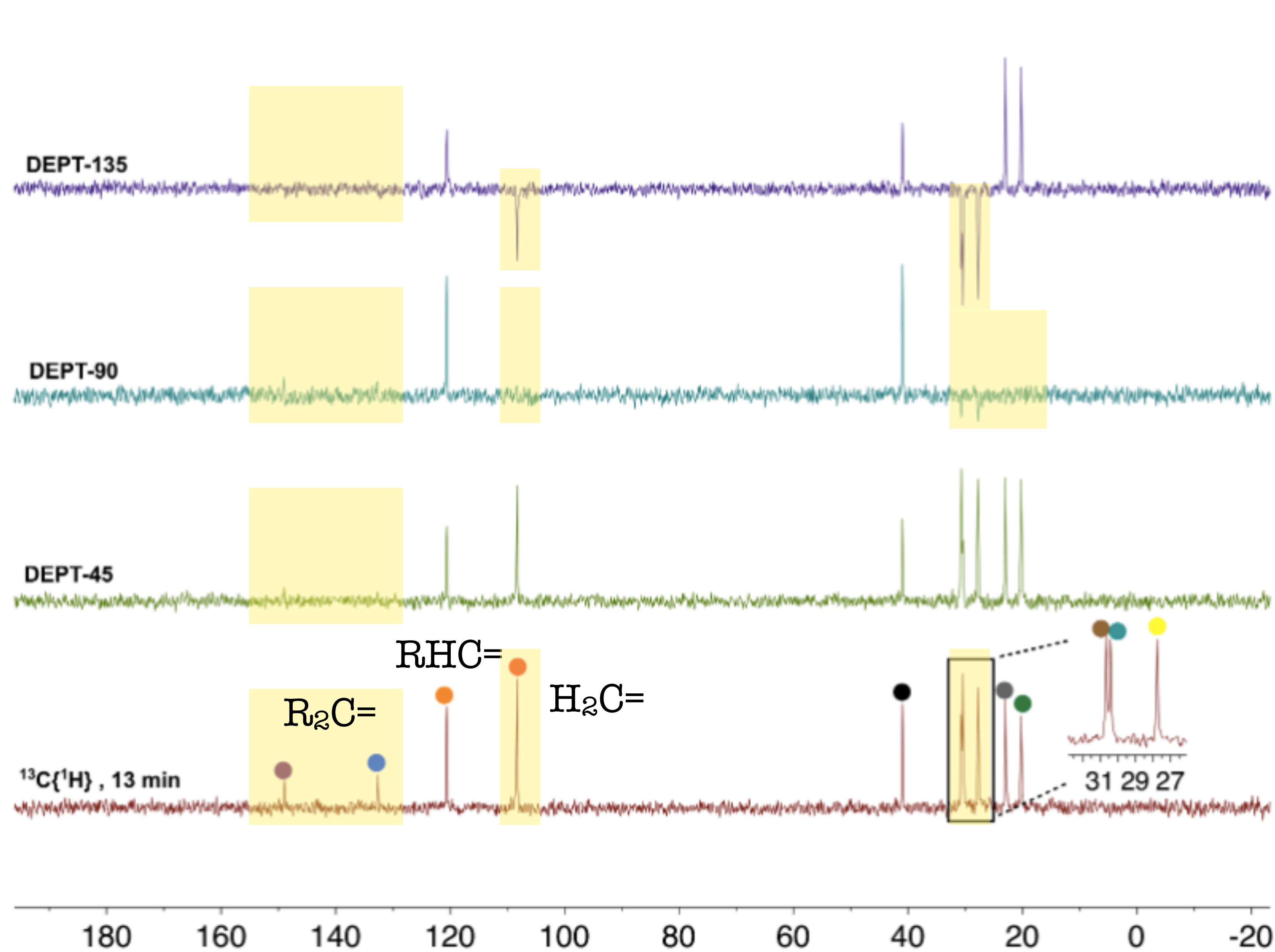
DEPT (Distortionless Enhanced Polarization Transfer)

"Intensificação da Distorção por Transferência de Polarização"

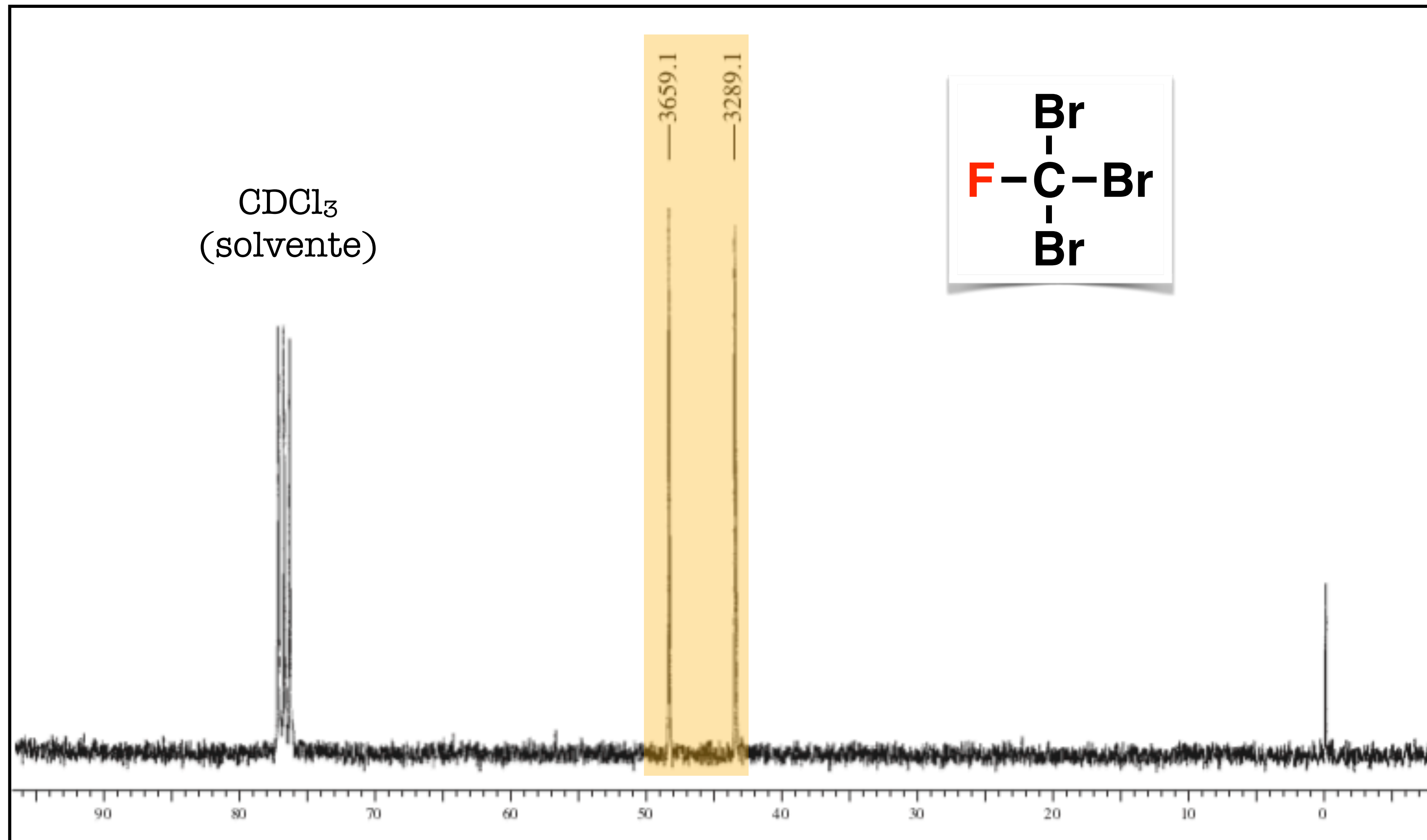
✓ Determina o número de H diretamente ligado ao átomo de ^{13}C

- DEPT **45**: Só aparecem sinais de carbonos ligados a hidrogênio
- DEPT **90**: Só aparece os **CH**
- DEPT **135**: **CH₃** e **CH** para cima e **CH₂** para baixo

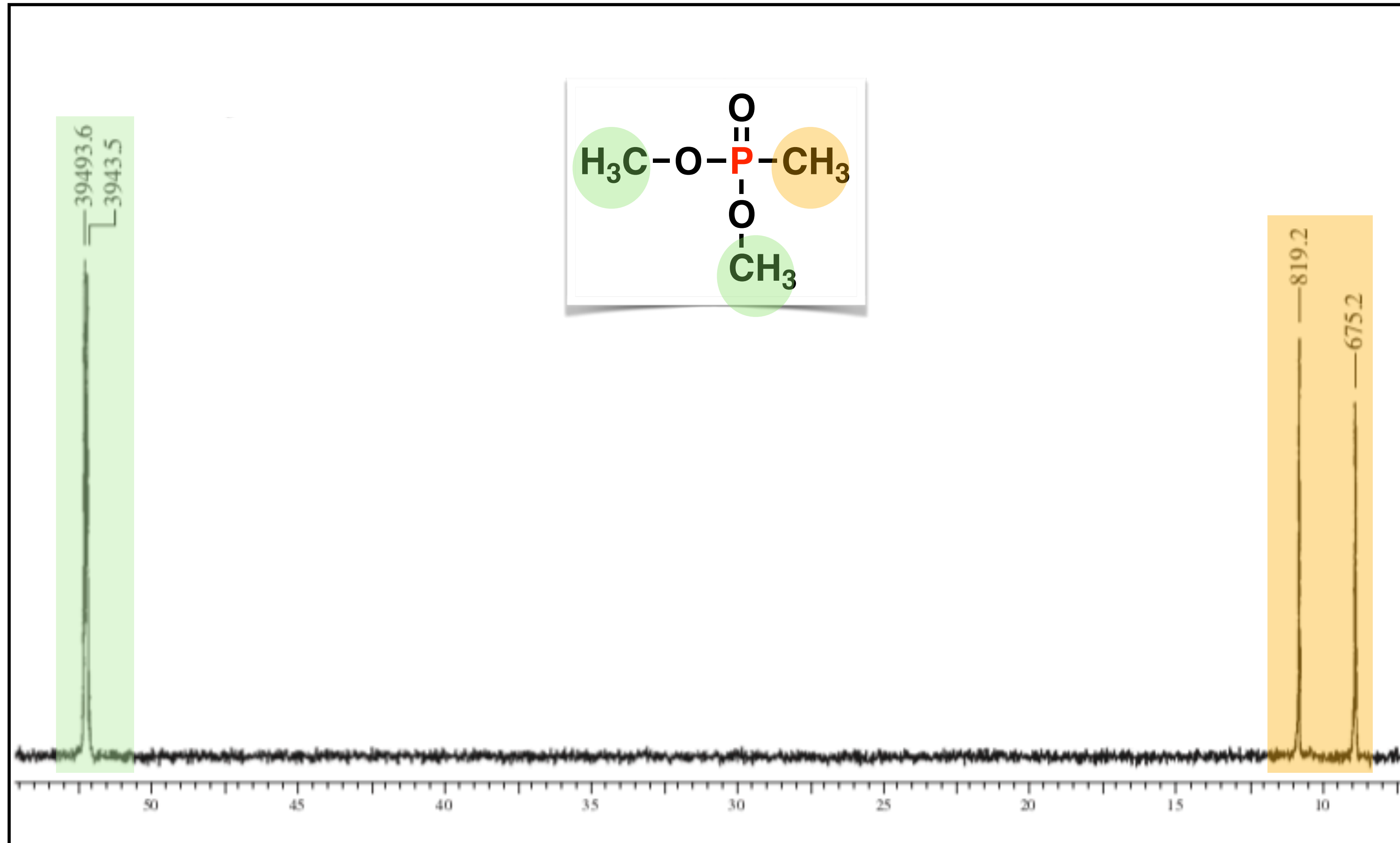
DEPT (Distortionless Enhanced Polarization Transfer)



Acoplamento Heteronuclear ^{13}C e ^{19}F



Acoplamento Heteronuclear ^{13}C e ^{31}P



Acoplamento Heteronuclear ^{13}C e $^{10}\text{B}/^{11}\text{B}$

^{10}B : 19%, $I=3$

^{11}B : 81%, $I=3/2$

Espectro retirado da coleção Aldrich (75 MHz ^{13}C RMN em DMSO- d_6)

