QFL-1345

RMN
Constantes de acoplamento

14 de junho de 2023

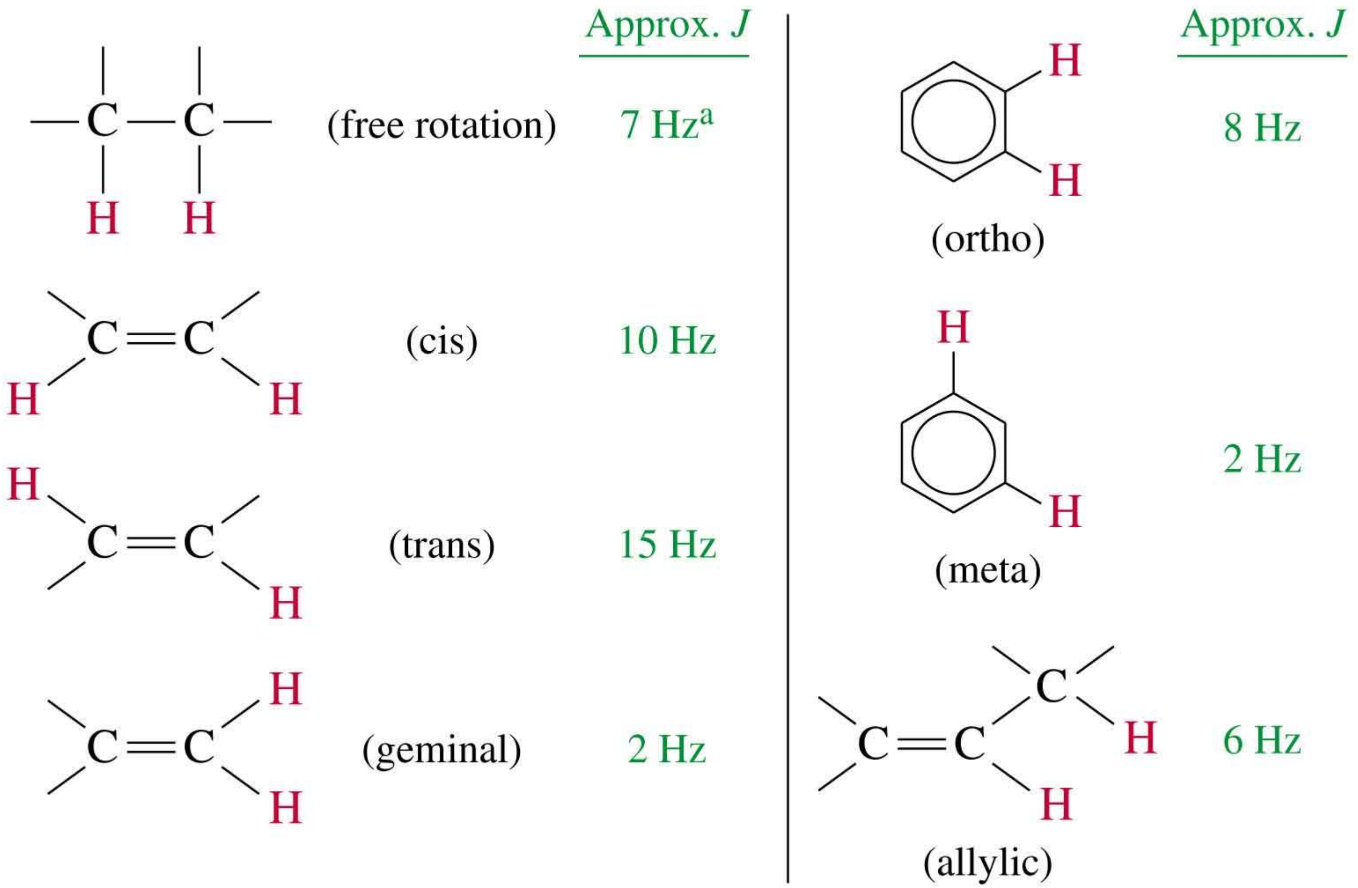
Informações obtidas de um espectro de RMN de ^{1}H:

1) Deslocamentos químicos (δ - ppm);

2) Integração (nº relativo de Hs);

3) Constantes de acoplamento (J em Hertz);

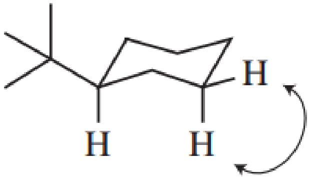
A magnitude das constantes de acoplamento podem ser utilizadas para se definir as relações de distâncias e espaciais entre os hidrogênios envolvidos



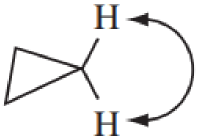
		Approx. *J*		Approx. *J*	
^3J	(free rotation)	7 Hz[a]	(ortho)	8 Hz	^3J
^3J	(cis)	10 Hz	(meta)	2 Hz	^4J
	(trans)	15 Hz			
^2J	(geminal)	2 Hz	(allylic)	6 Hz	^3J

[a] The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

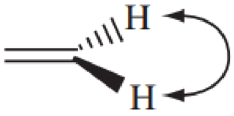
O acoplamento geminal ^{2}J é inversamente proporcional ao ângulo



$\alpha \cong 109^\circ$
$^2J_{HH} \cong 12-18$ Hz



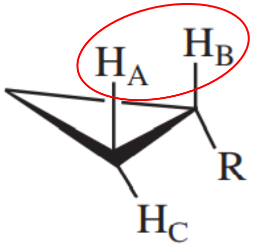
$\alpha \cong 118^\circ$
$^2J_{HH} \cong 5$ Hz



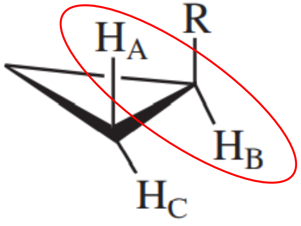
$\alpha \cong 120^\circ$
$^2J_{HH} \cong 0-3$ Hz

Acoplamento vicinal ^{3}J em ciclopropanos

cis



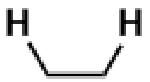
$^3J_{AB} = 6-12$ Hz
$\alpha = \sim 0^\circ$



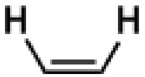
trans

$^3J_{AB} = 2-9$ Hz
$\alpha = \sim 120^\circ$

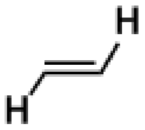
^{3}J



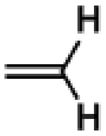
alkane
6-8 Hz



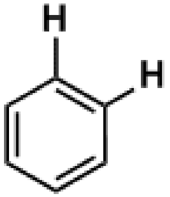
cis 6-15 Hz



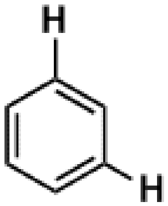
trans 11-18 Hz



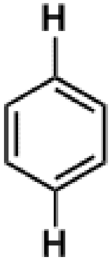
geminal 0-5 Hz



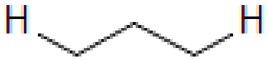
ortho 7-10 Hz



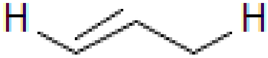
meta 2-3 Hz



para 0-1 Hz



W-Coupling
^{4}J = -1 to +3 Hz



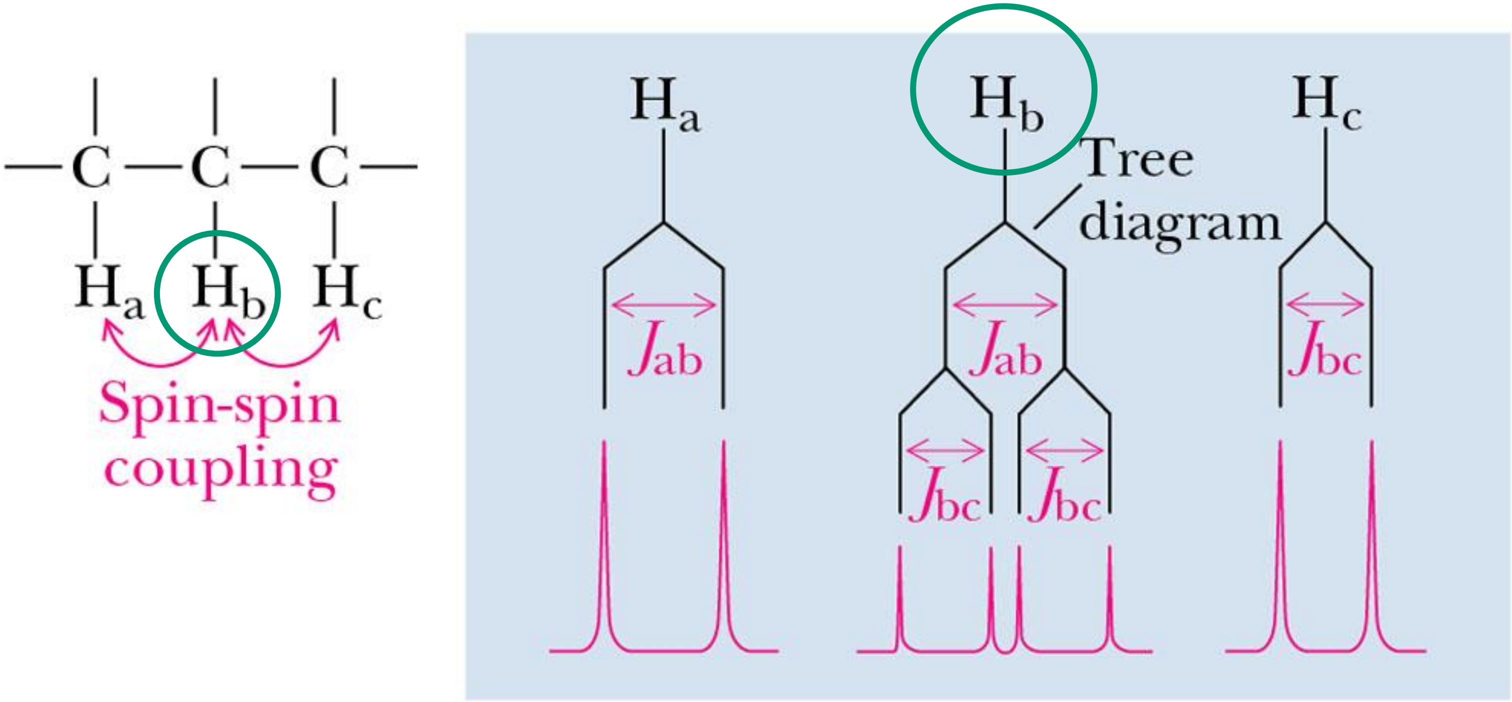
Allylic
^{4}J = -3 to +3 Hz

^{3}J ^{4}J ^{5}J ^{4}J

Padrões de acoplamentos mais complexos

Padrões mais complexos são observados quando um conjunto de H acoplam com mais de um hidrogênio.

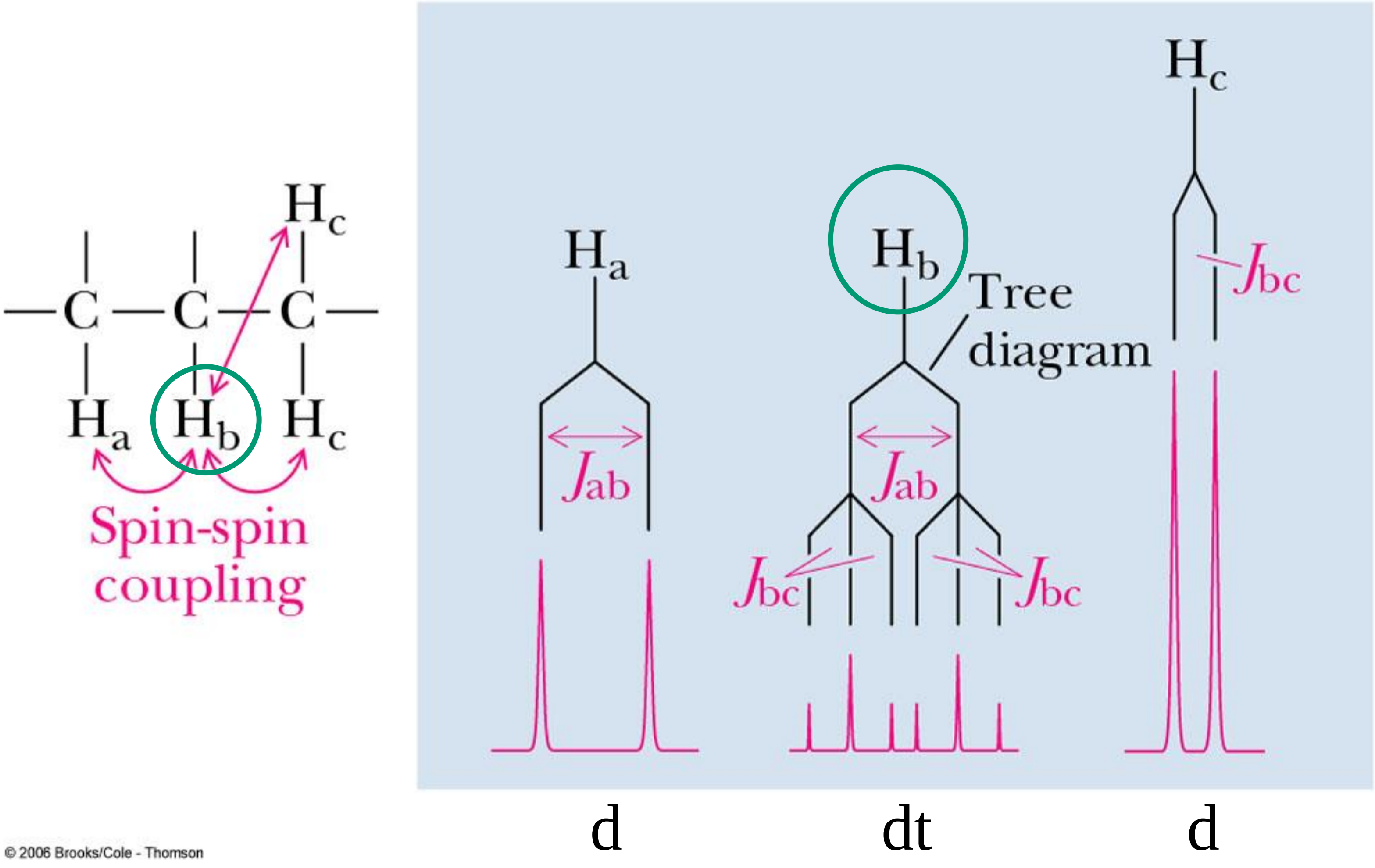
Quando um H_b está adjacente a H_a e H_c, forma-se um duplo-dubleto ($J_{ab} > J_{bc}$)



d dd d

Padrões de acoplamentos mais complexos

Se H_c = 2 hidrogênios, observa um padrão de duplo tripletos.



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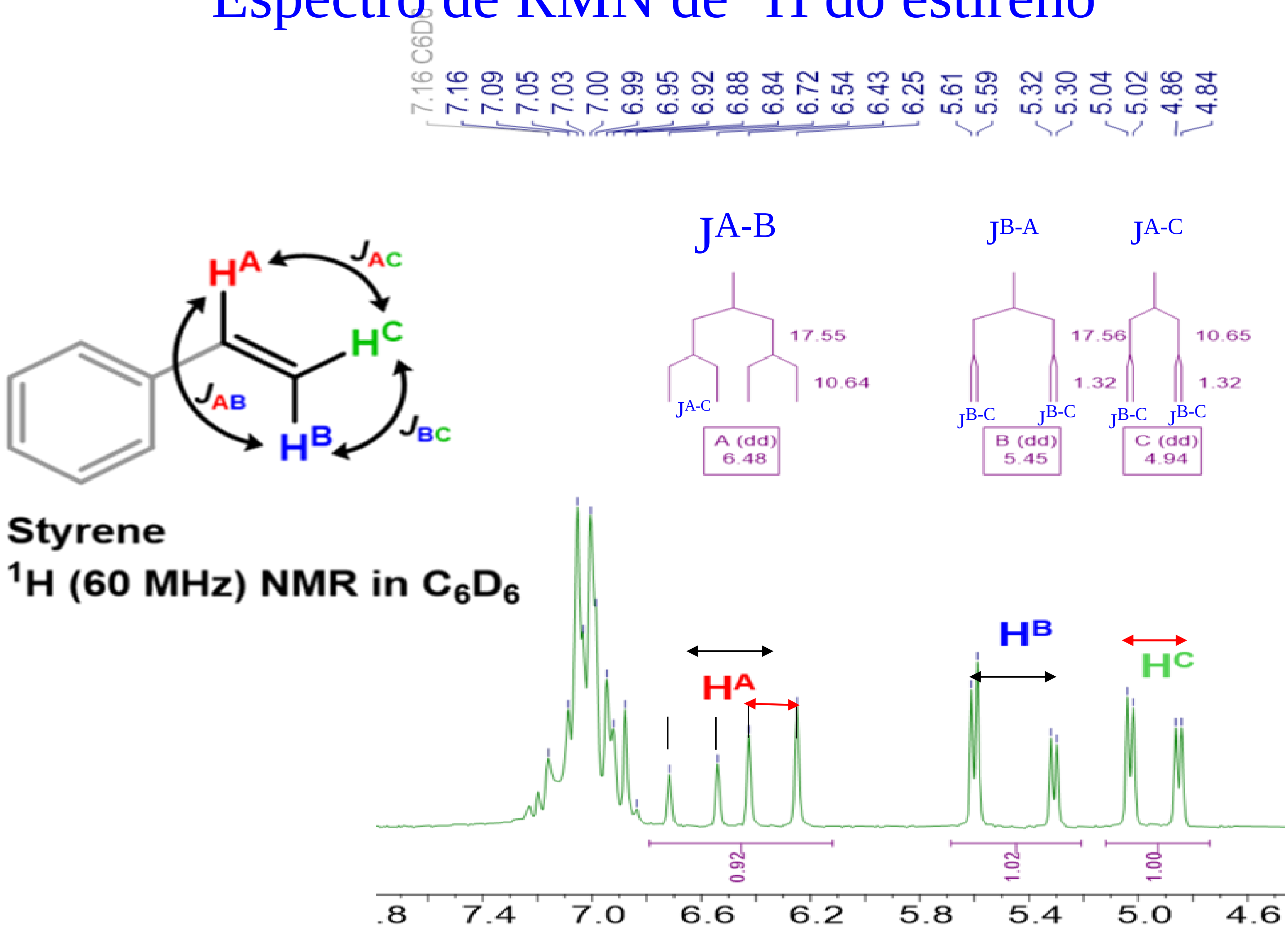
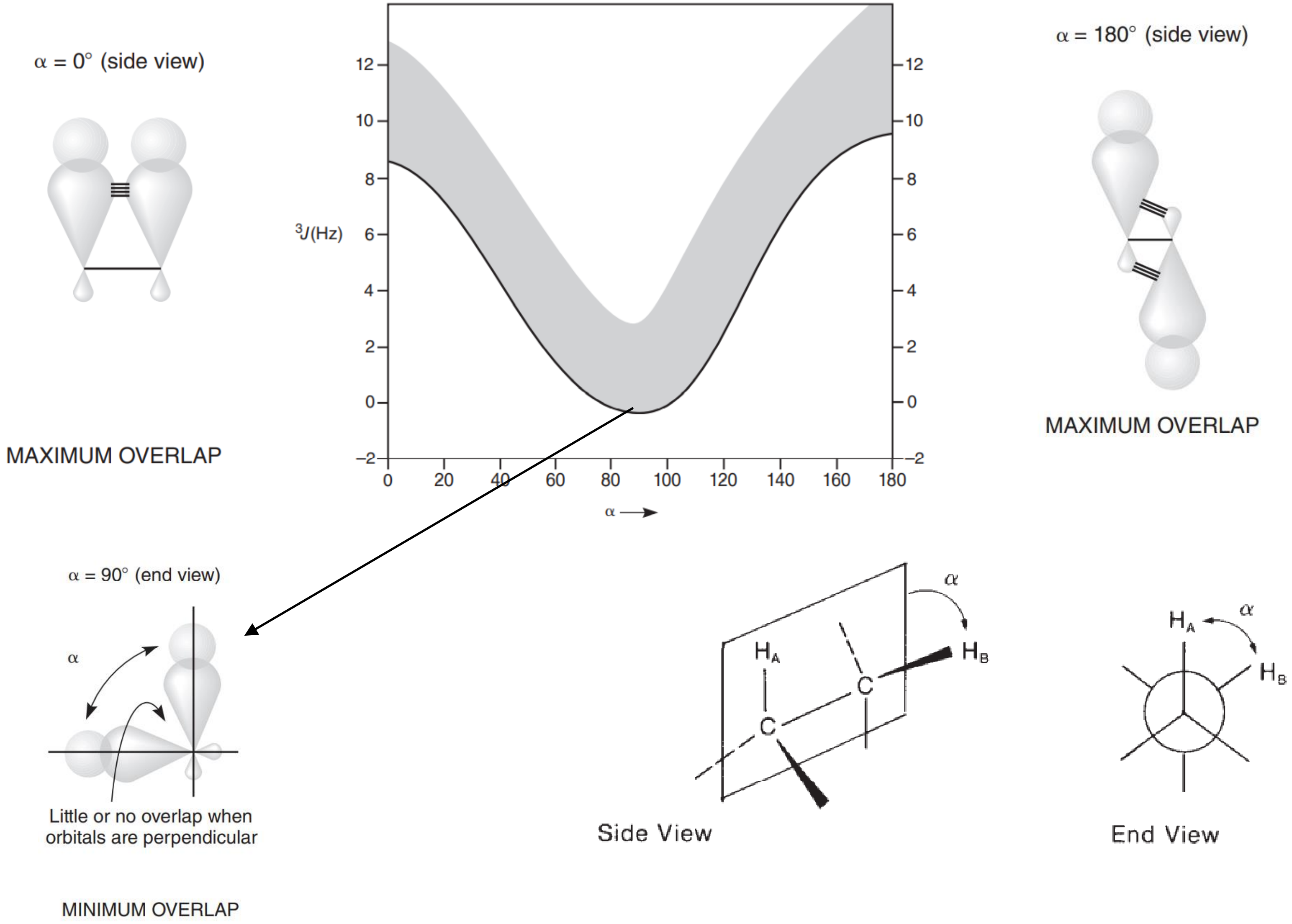
Espectro de RMN de ^{1}H do estireno



Styrene

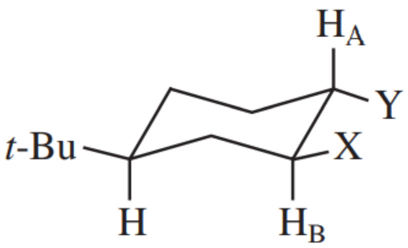
^{1}H (60 MHz) NMR in C_6D_6

Correlação de Karplus—variação da constante De acoplamento ^3J com o ângulo diedro α



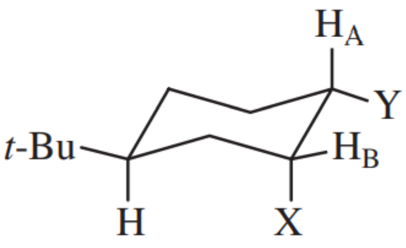
Acoplamentos vicinais ^3J em ciclohexanos

a,a



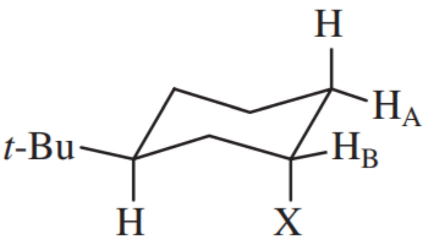
$J_{AB} = 10\text{–}14$ Hz
$\alpha = 180°$

a,e



$J_{AB} = 2\text{–}6$ Hz
$\alpha = 60°$

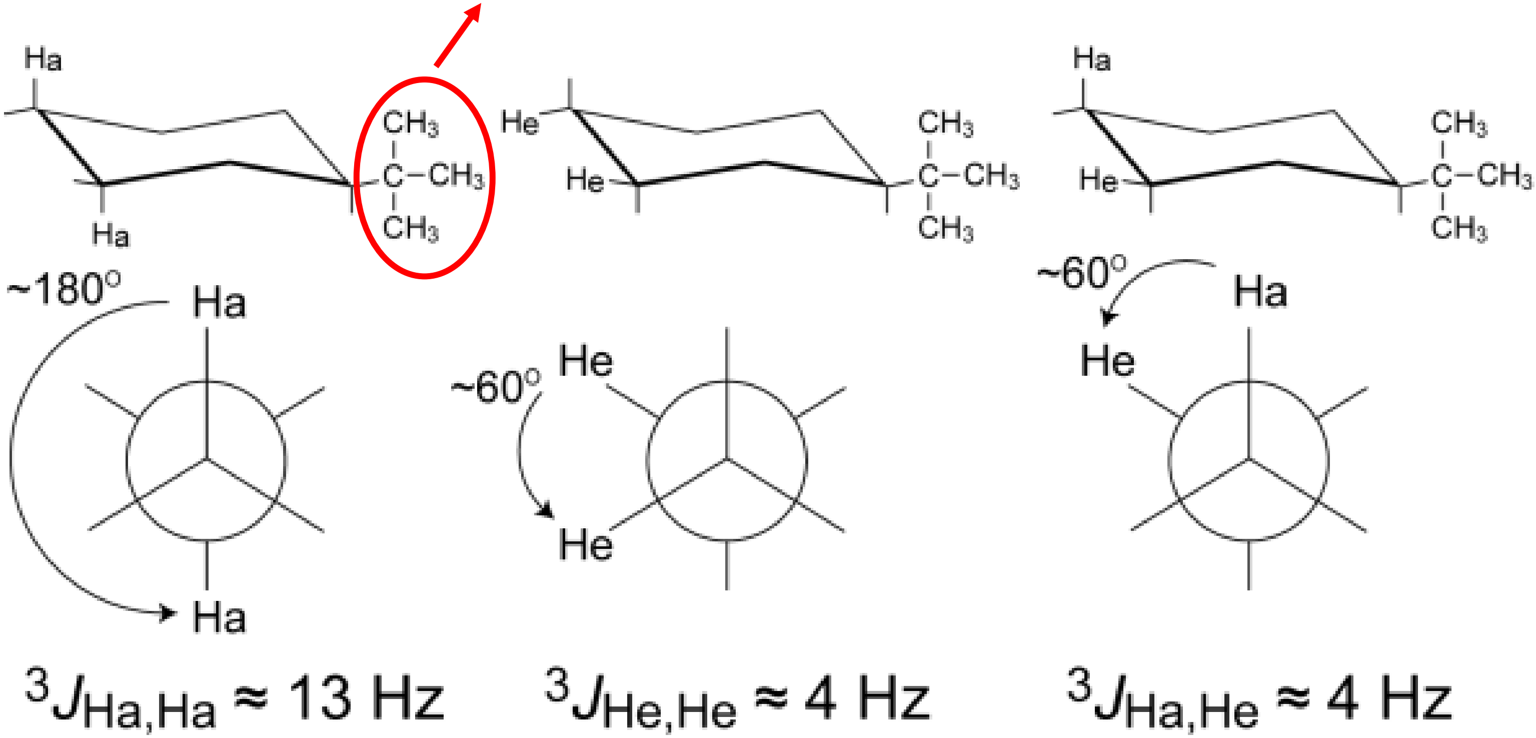
e,e



$J_{AB} = 2\text{–}5$ Hz
$\alpha = 60°$

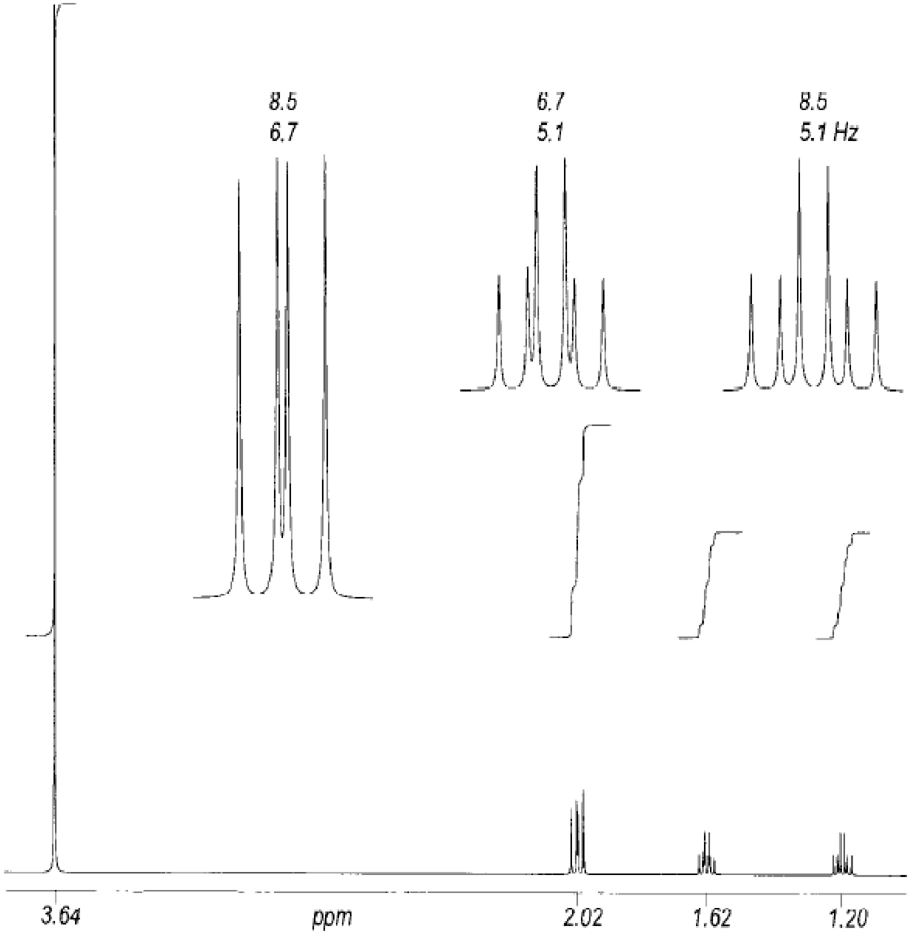
Use of coupling constant and Karplus relationship to assign cyclohexane derivatives

tert-butyl group in the equatorial position

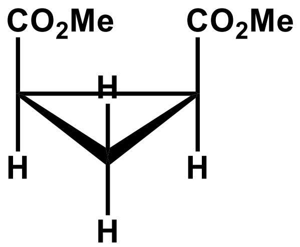


Espectro de RMN de ^1H do dimetilciclopropano dicarboxilato de dimetila.

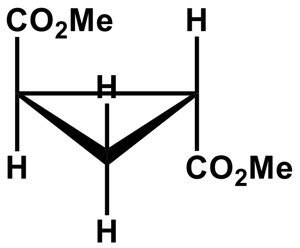
Qual a configuração?



cis

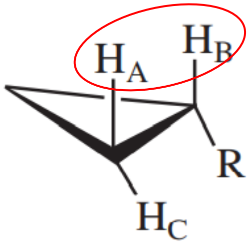


trans

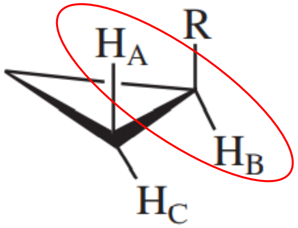


Acoplamento vicinal ^{3}J em ciclopropanos

cis



$$^3J_{AB} = 6–12 \text{ Hz}$$
$$\alpha = \sim 0°$$



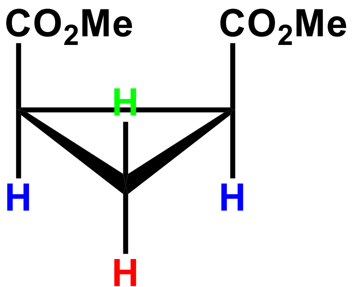
trans

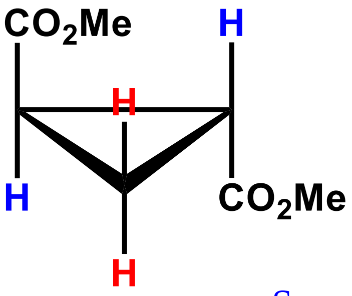
$$^3J_{AB} = 2–9 \text{ Hz}$$
$$\alpha = \sim 120°$$

Ciclopropano dicarboxilato de dimetila

Quantos hidrogênios diferentes temos em cada caso?

cis

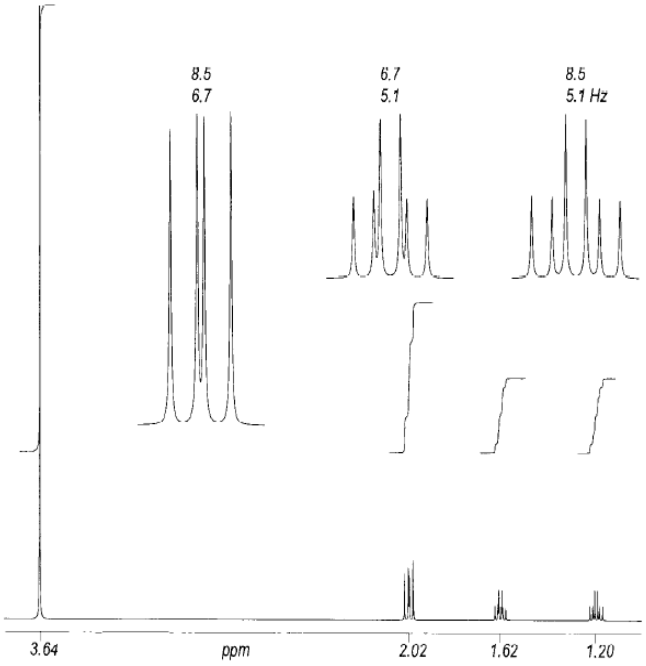




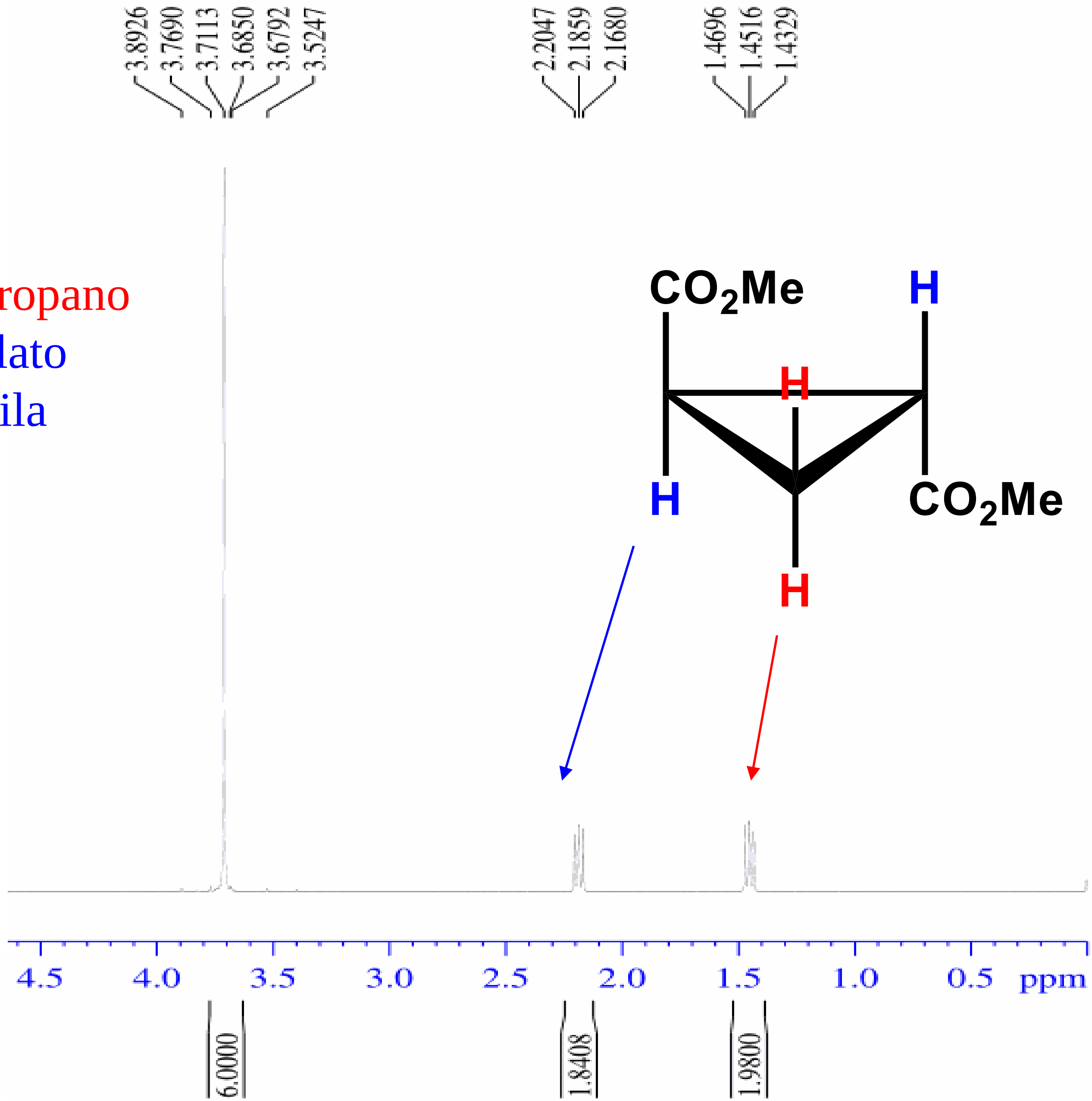
trans

Três hidrogênios diferentes
(2H - 1H - 1H)

Somente dois hidrogênios
diferentes (2H e 2H)



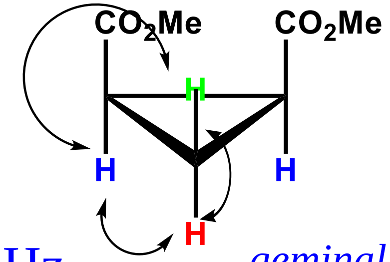
Trans-ciclopropano dicarboxilato de dimetila



cas 826-35-7

CDCl3 400 MHZ

Ciclopropano dicarboxilato de dimetila

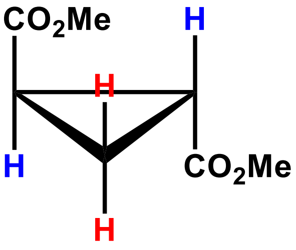


trans : 2 – 9 Hz

cis : 6 – 12 Hz

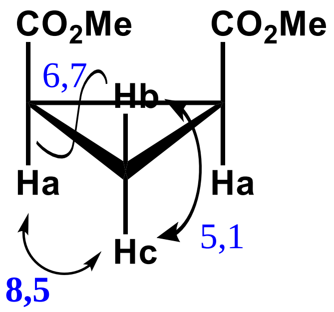
geminal: 5 – 6 Hz

cis



trans

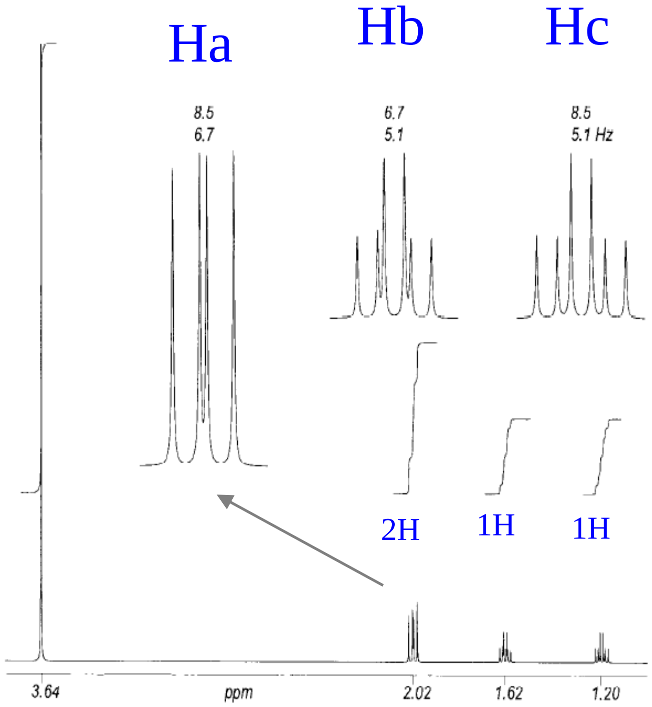
Cis-ciclopropano dicarboxilato de dimetila



Ha **(2H)**: dd 8,5 e 6,7

Hb (1H): td 6,7 e 5,1 Hz

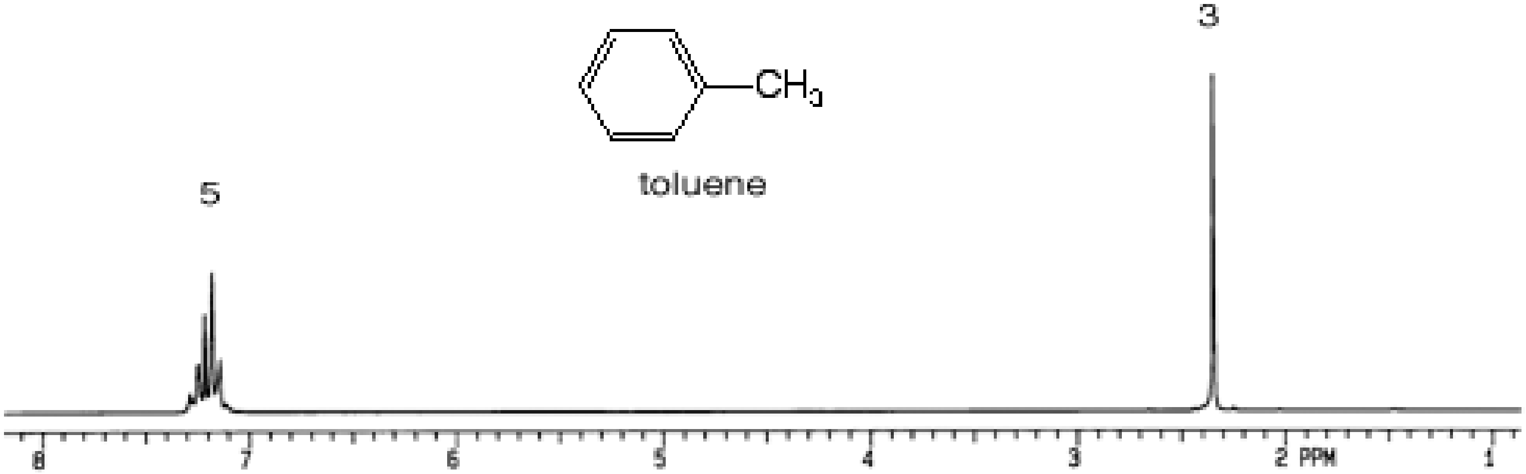
Hc (1H): td 8,5 e 5,1 Hz



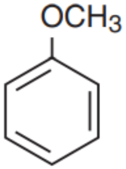
Os Hb e Hc são **triplo dubletos** (td), pois acoplam com dois Ha formando um tripleto (6,7 e 8,5 Hz, respectivamente). Esses são desdobrados pelo acoplamento geminal (5,1 Hz).

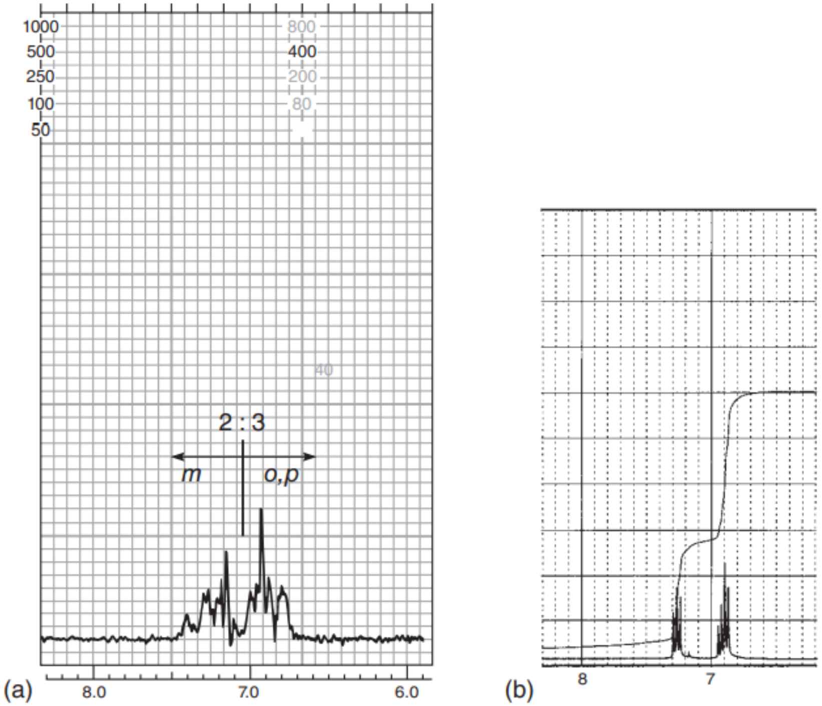
O acoplamento maior é especificado primeiro por isso é um **triplo** dubleto.
Caso contrário, no caso do J do dubleto ser maior, seria um **duplo** tripleto.

RMN de ^{1}H
Padrão de substituição em aneis benzênicos



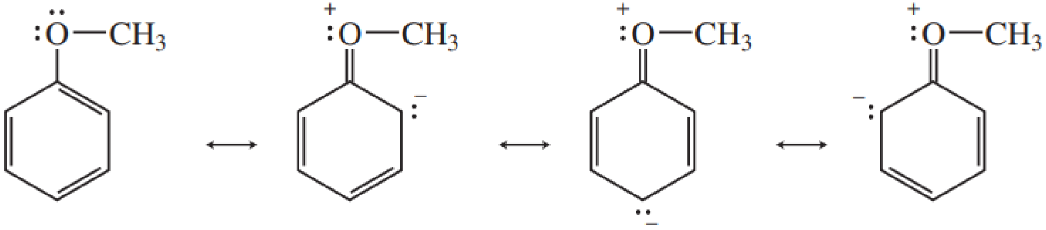
The aromatic ring portions of the ^1H NMR spectrum of anisole



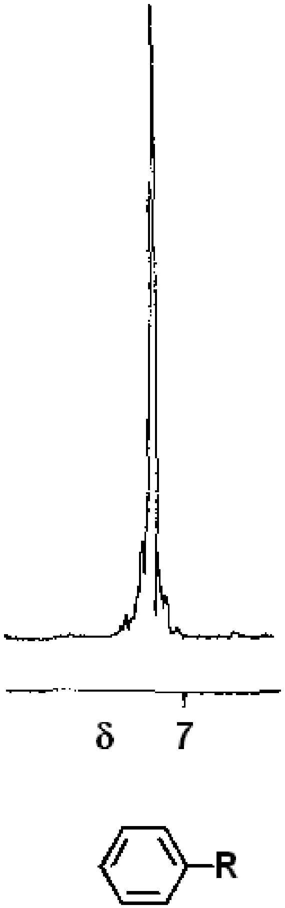


(a) 60 MHz

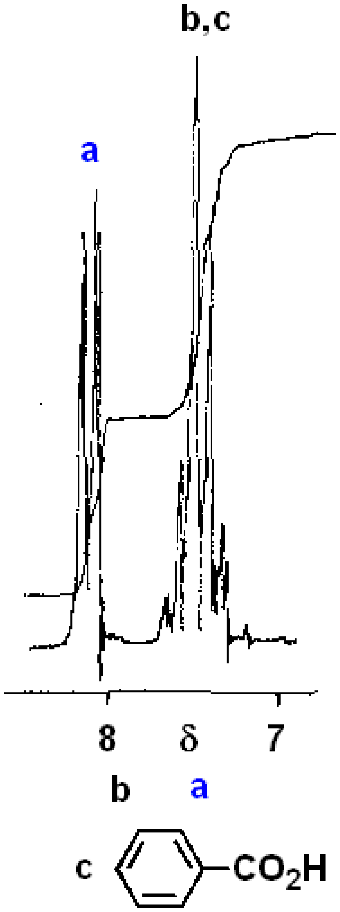
(b) 300 MHz



Aneis benzênicos monossubstituidos

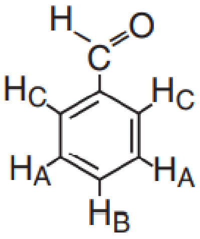


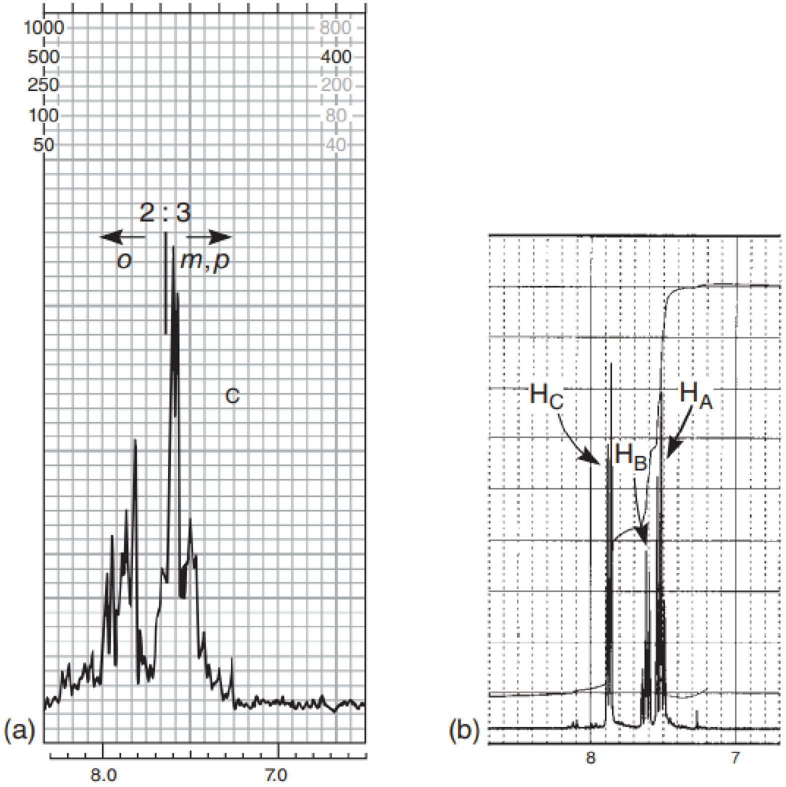
Proteção dos hidrogênios
orto e *para* do fenol
por ressonância

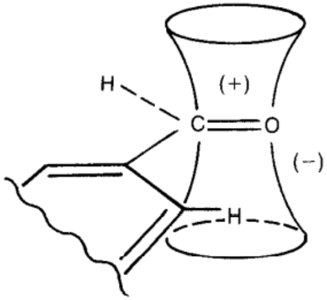


Desproteção dos hidrogênios *orto*
do ácido benzoico
por anisotropia

Aneis benzênicos monossubstituidos

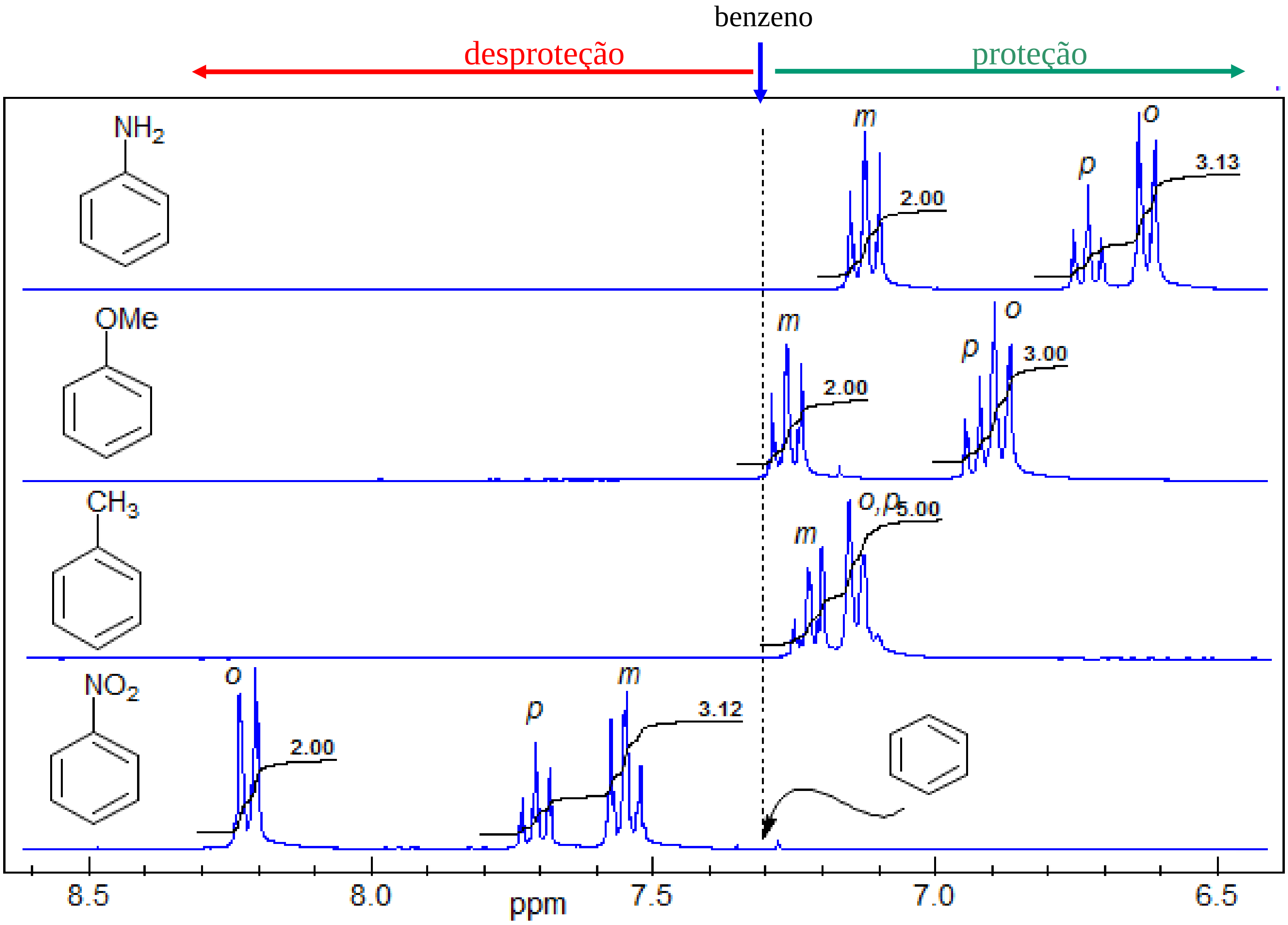






Desproteção anisotrópica dos hidrogênios *orto* do benzaldeido

Efeito de substituíntes nos δ de hidrogênios benzênicos monossubstituidos



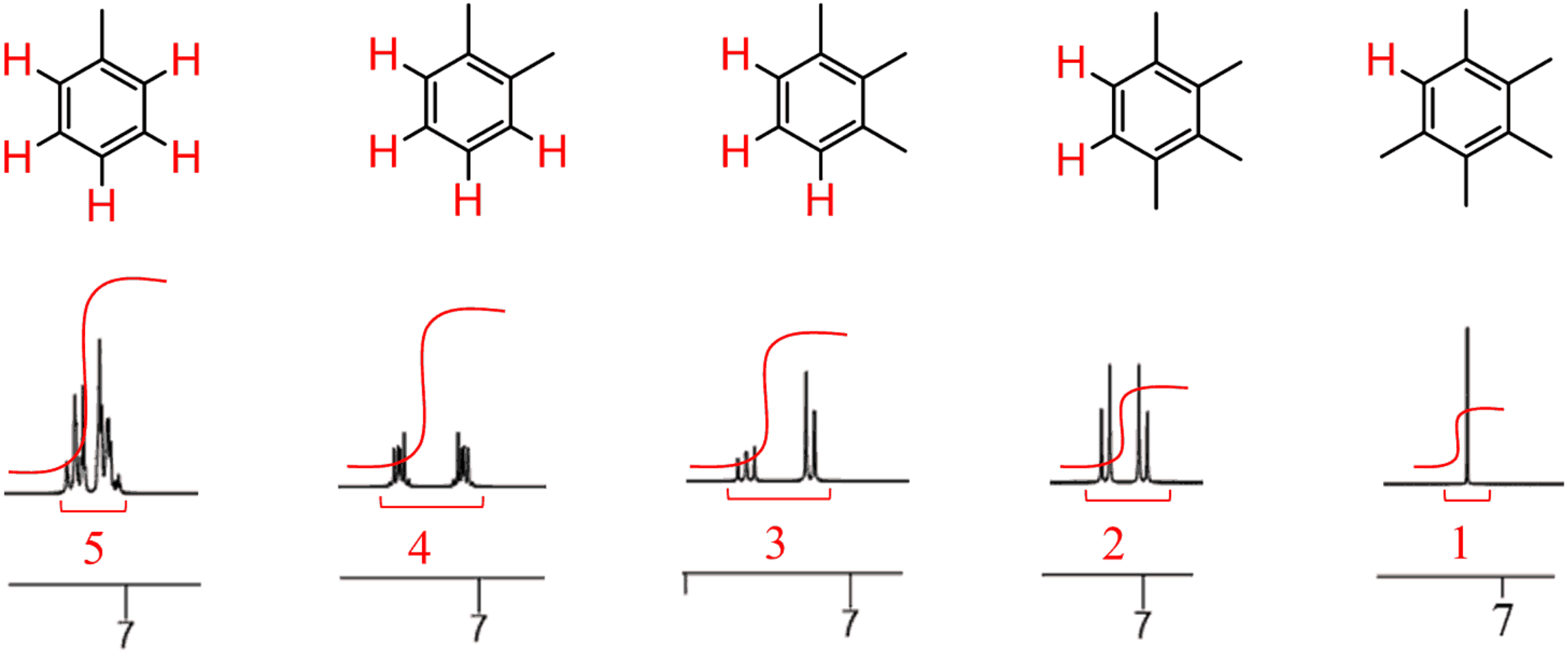
benzeno

desproteção

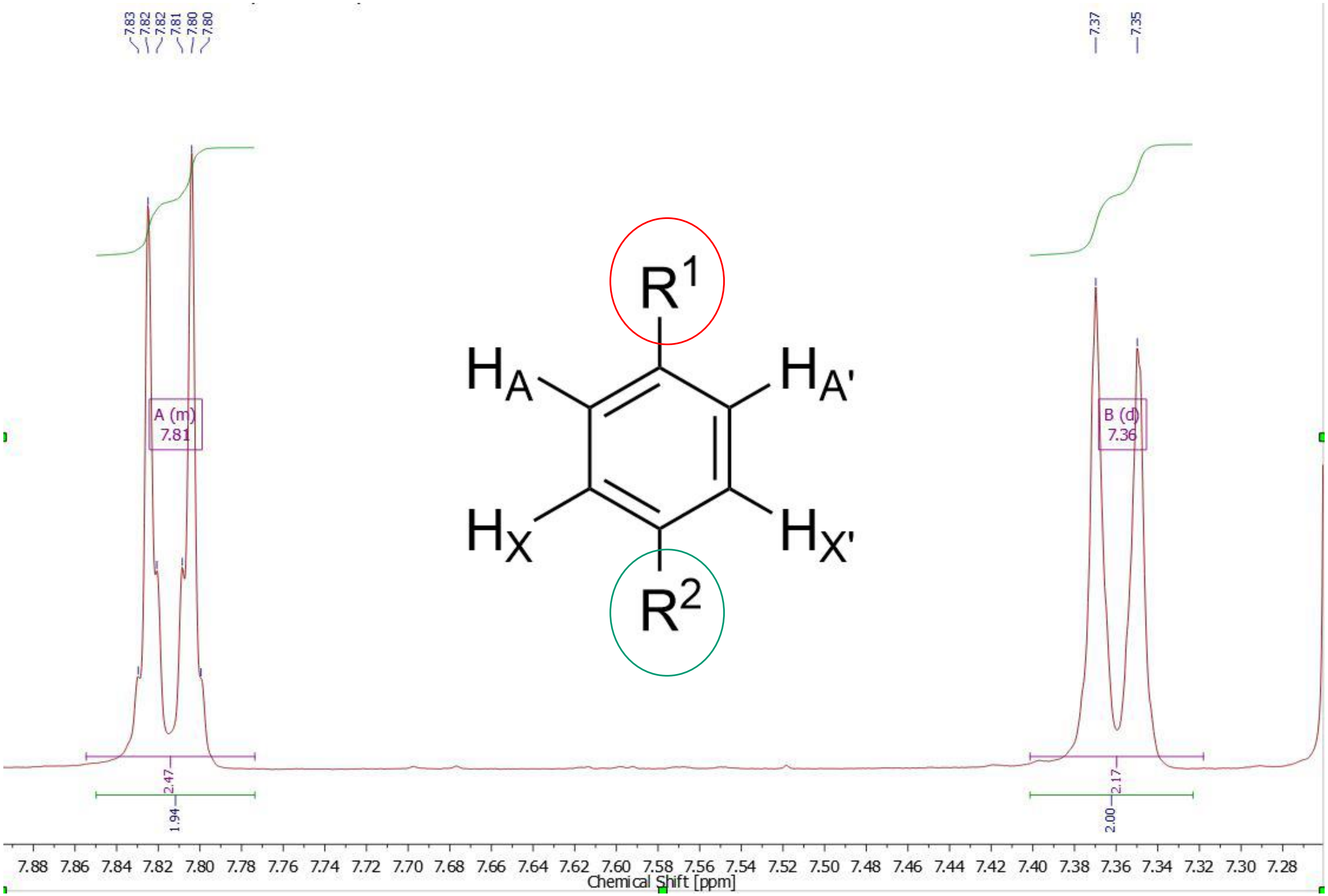
proteção

RMN de ^{1}H

Padrão de substituição em aneis benzênicos



Aneis benzênicos *p*-dissubstituidos

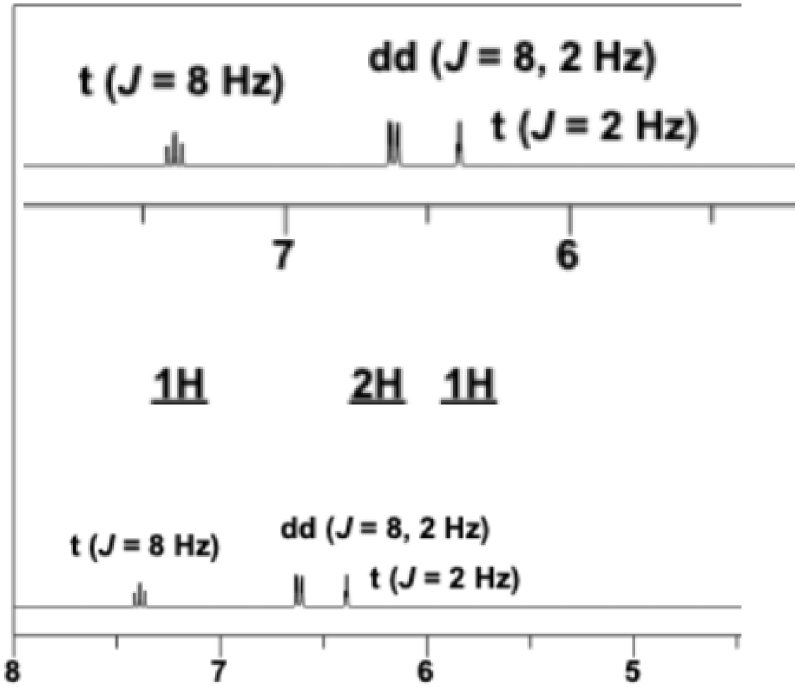


Qual das estruturas é a mais compatível com o espectro apresentado?

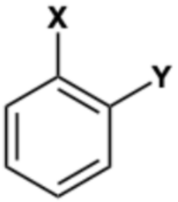
7,40 (t, 8,0 Hz)

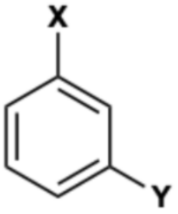
6,62 (dd, 8,0, 2,1 Hz)

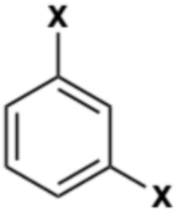
6,40 (t, 2,1 Hz)

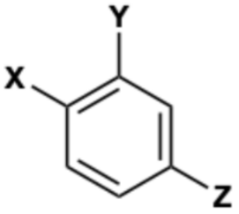


Integrais = 1H 2H 1H

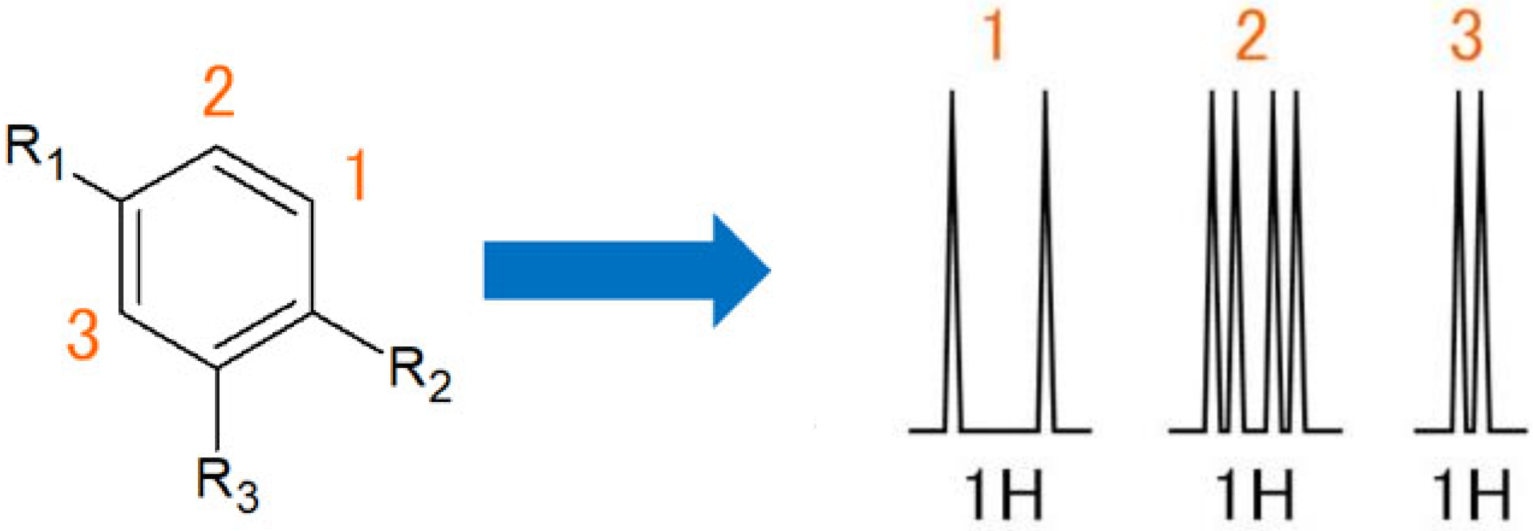




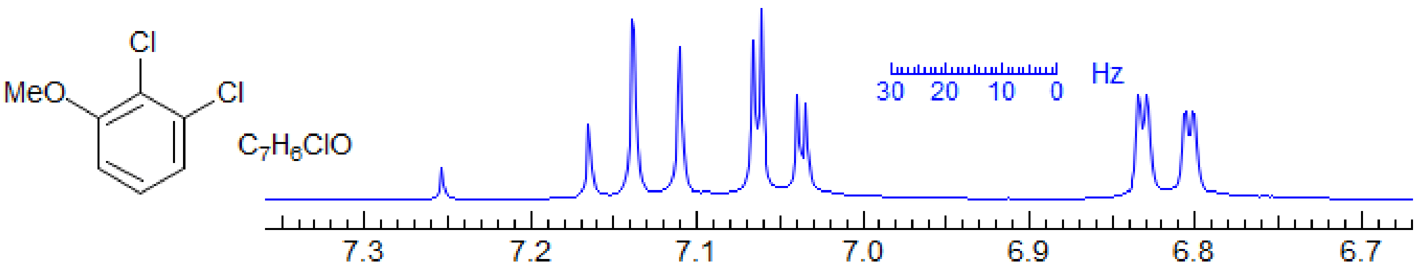


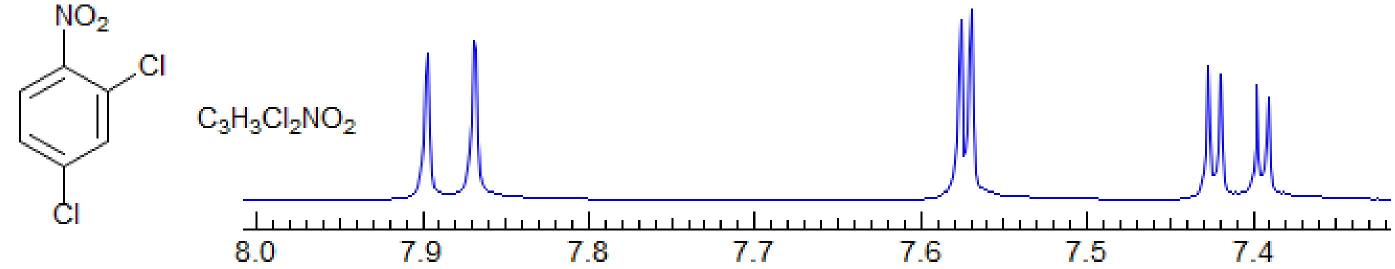


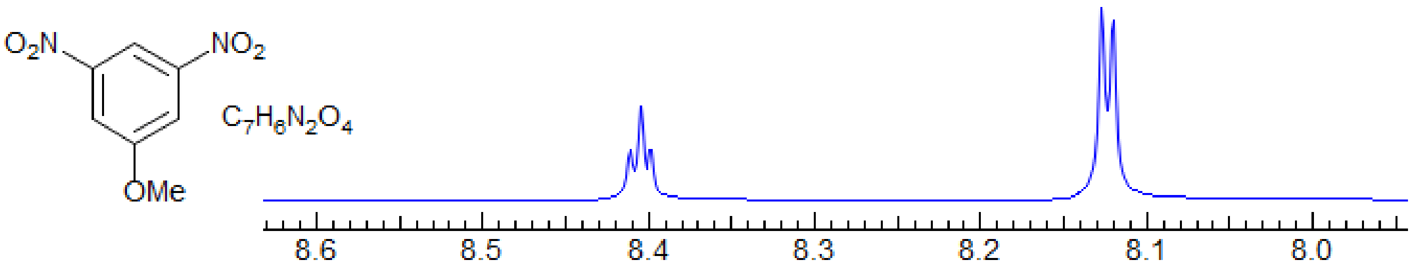
Aneis benzênicos trissubstituidos

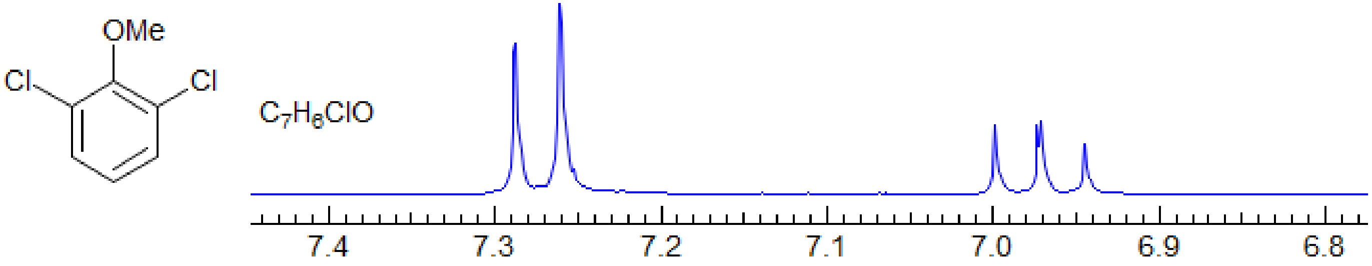


Aneis benzênicos trissubstituidos

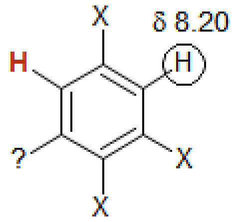








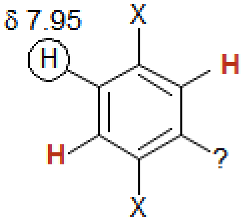
J^4



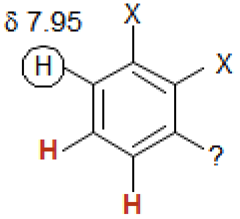
A

J ca 2 Hz
one meta H only

J^3 e J^4



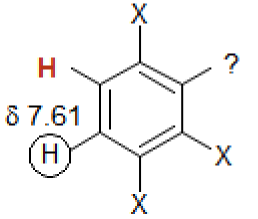
B



C

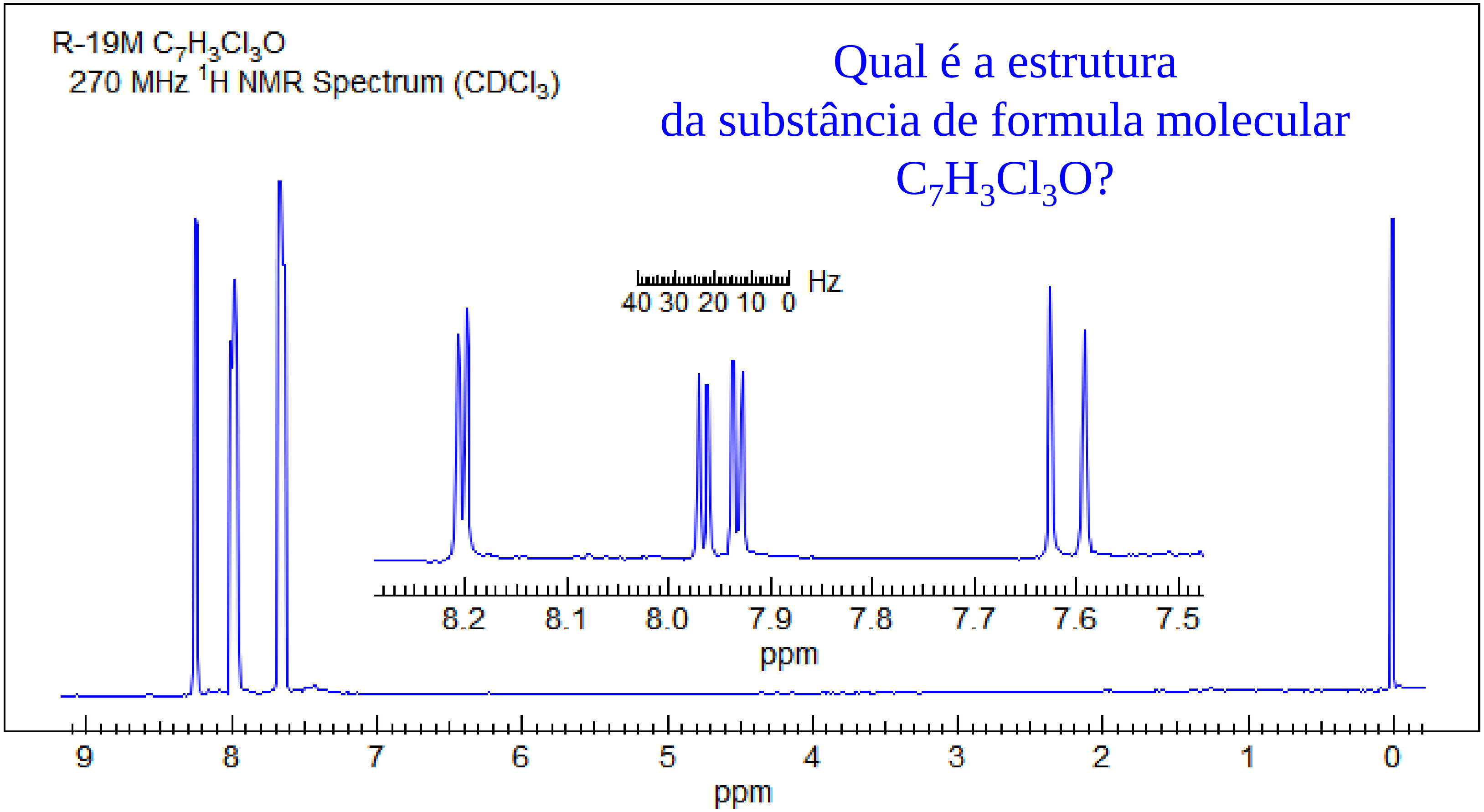
J ca 2 and 8 Hz
one ortho and one meta H

J^3



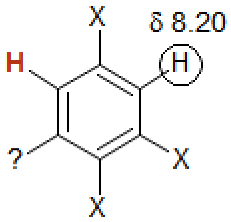
D

J = 8 Hz
one ortho H



Qual é a estrutura
da substância de formula molecular
$C_7H_3Cl_3O$?

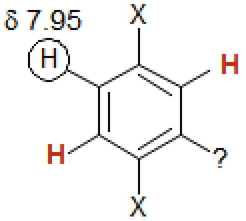
J^4



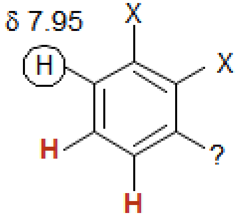
A

J ca 2 Hz
one meta H only

J^3 e J^4



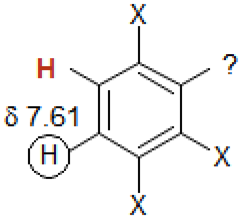
B



C

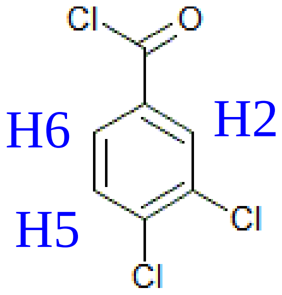
J ca 2 and 8 Hz
one ortho and one meta H

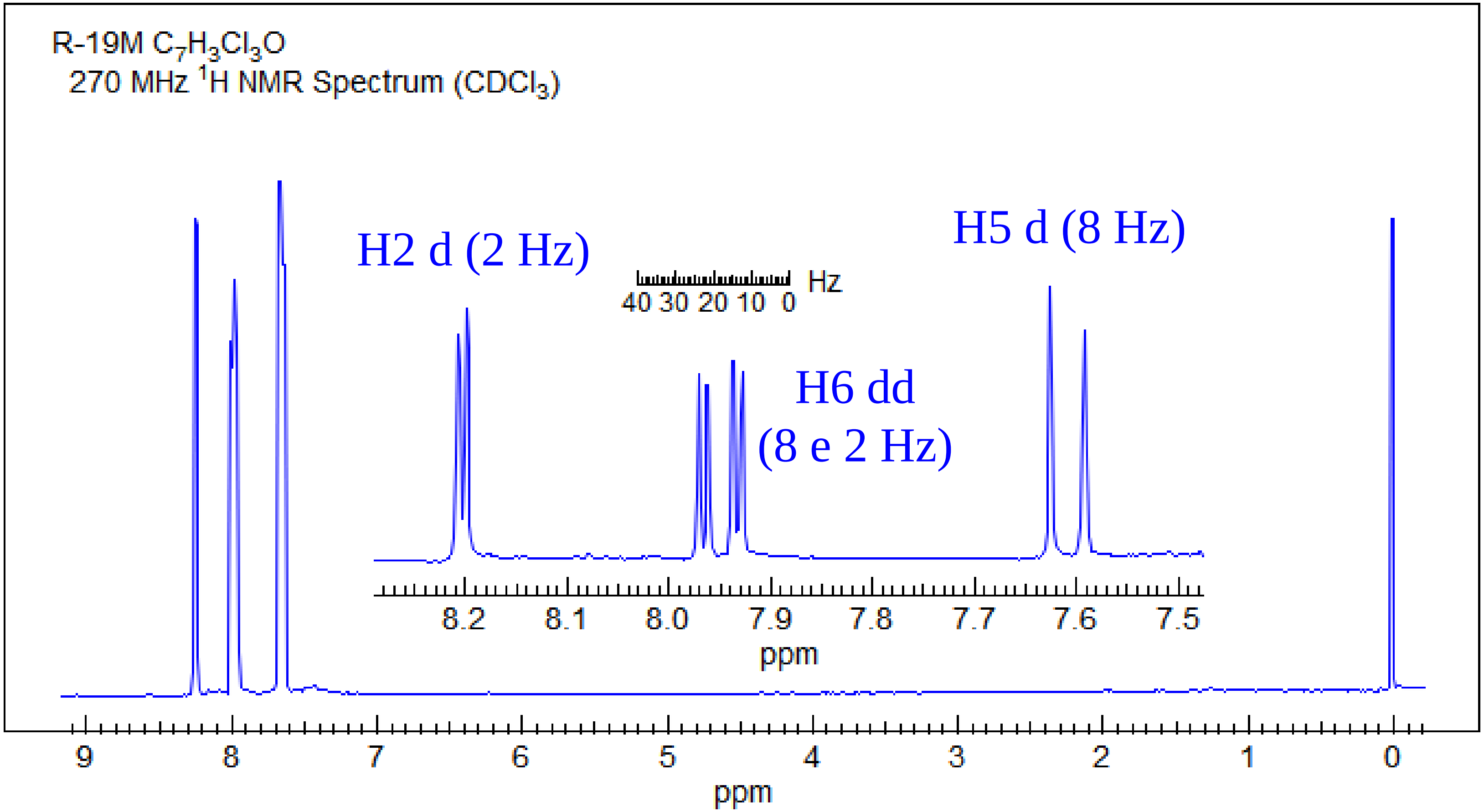
J^3



D

J = 8 Hz
one ortho H



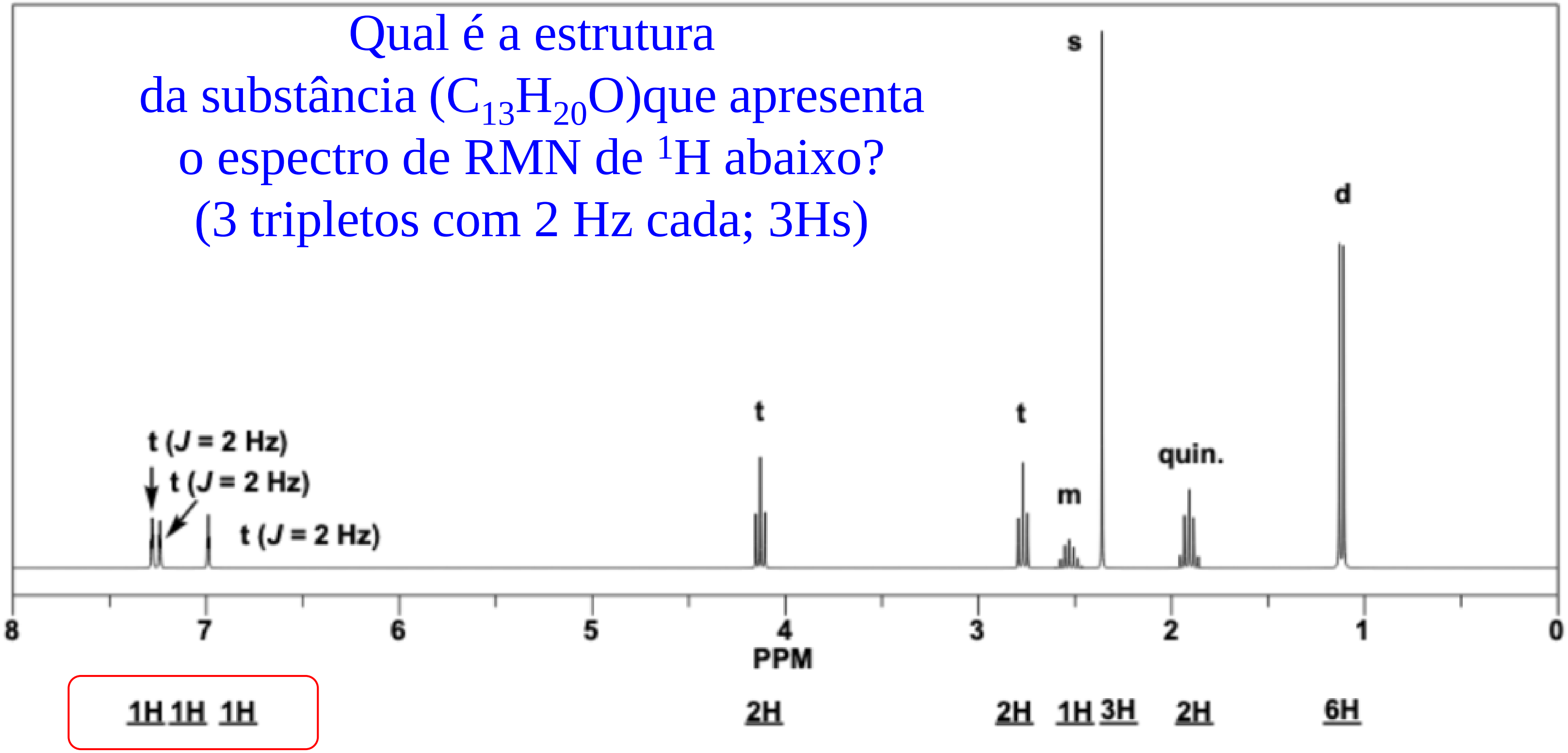

R-19M $C_7H_3Cl_3O$
270 MHz ^{1}H NMR Spectrum ($CDCl_3$)

H2 d (2 Hz)

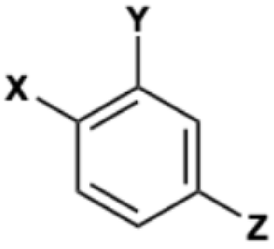
H6 dd
(8 e 2 Hz)

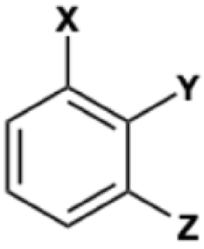
H5 d (8 Hz)

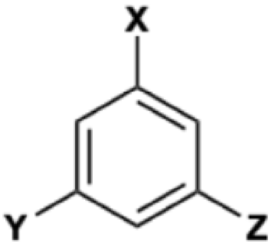
Aneis benzênicos trissubstituidos

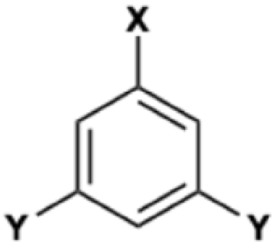


Qual é a estrutura
da substância ($C_{13}H_{20}O$)que apresenta
o espectro de RMN de ^1H abaixo?
(3 tripletos com 2 Hz cada; 3Hs)

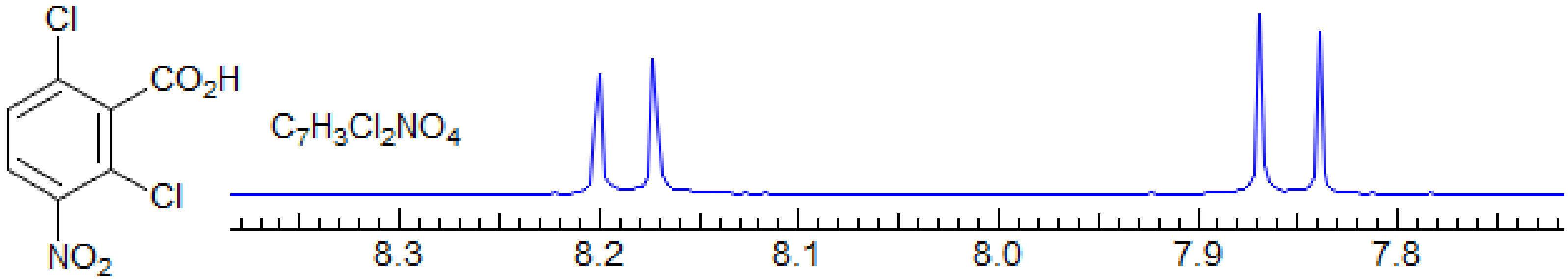




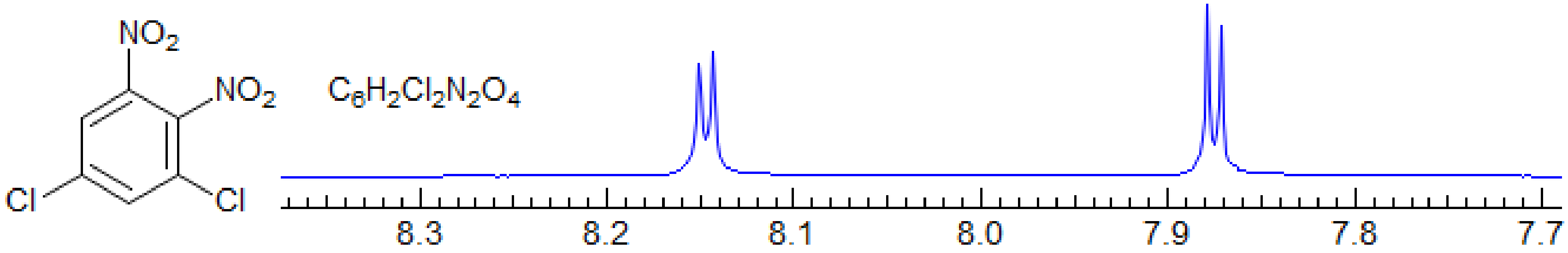




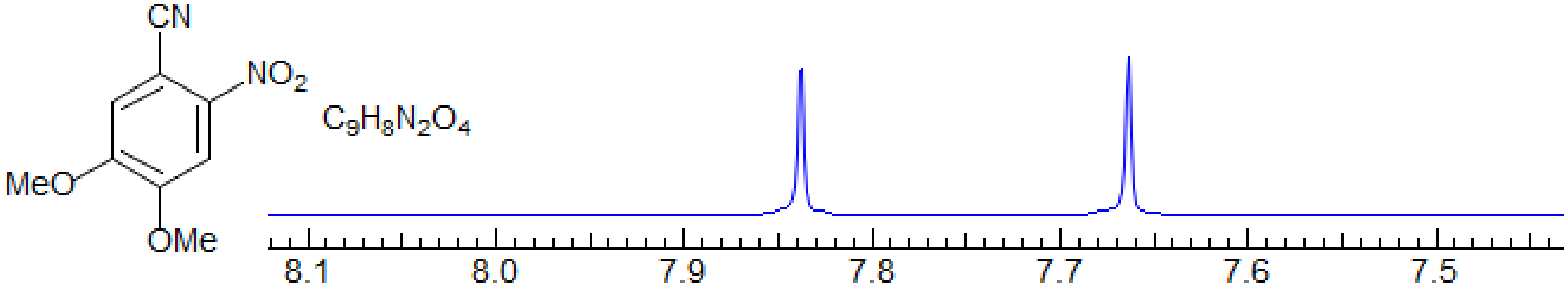
Aneis benzênicos tetrassubstituidos



$C_7H_3Cl_2NO_4$

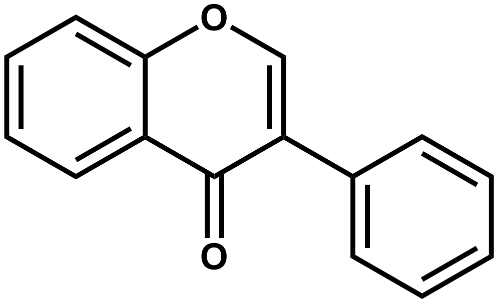


$C_6H_2Cl_2N_2O_4$

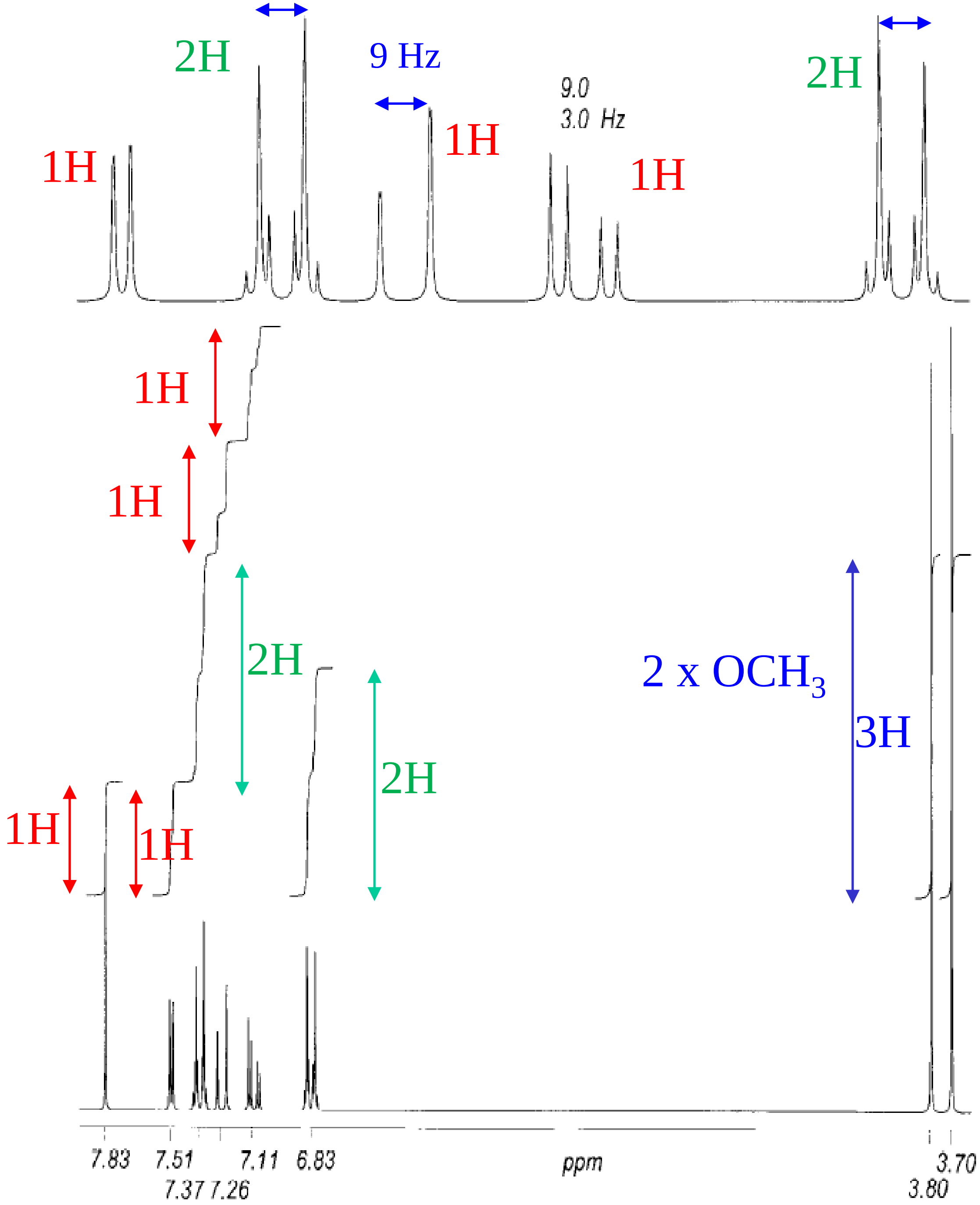


$C_9H_8N_2O_4$

Qual a estrutura da isoflavona?

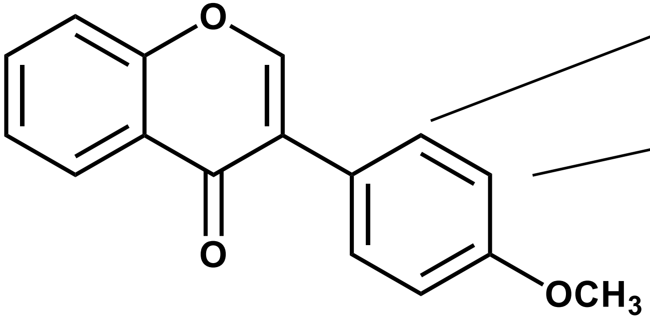


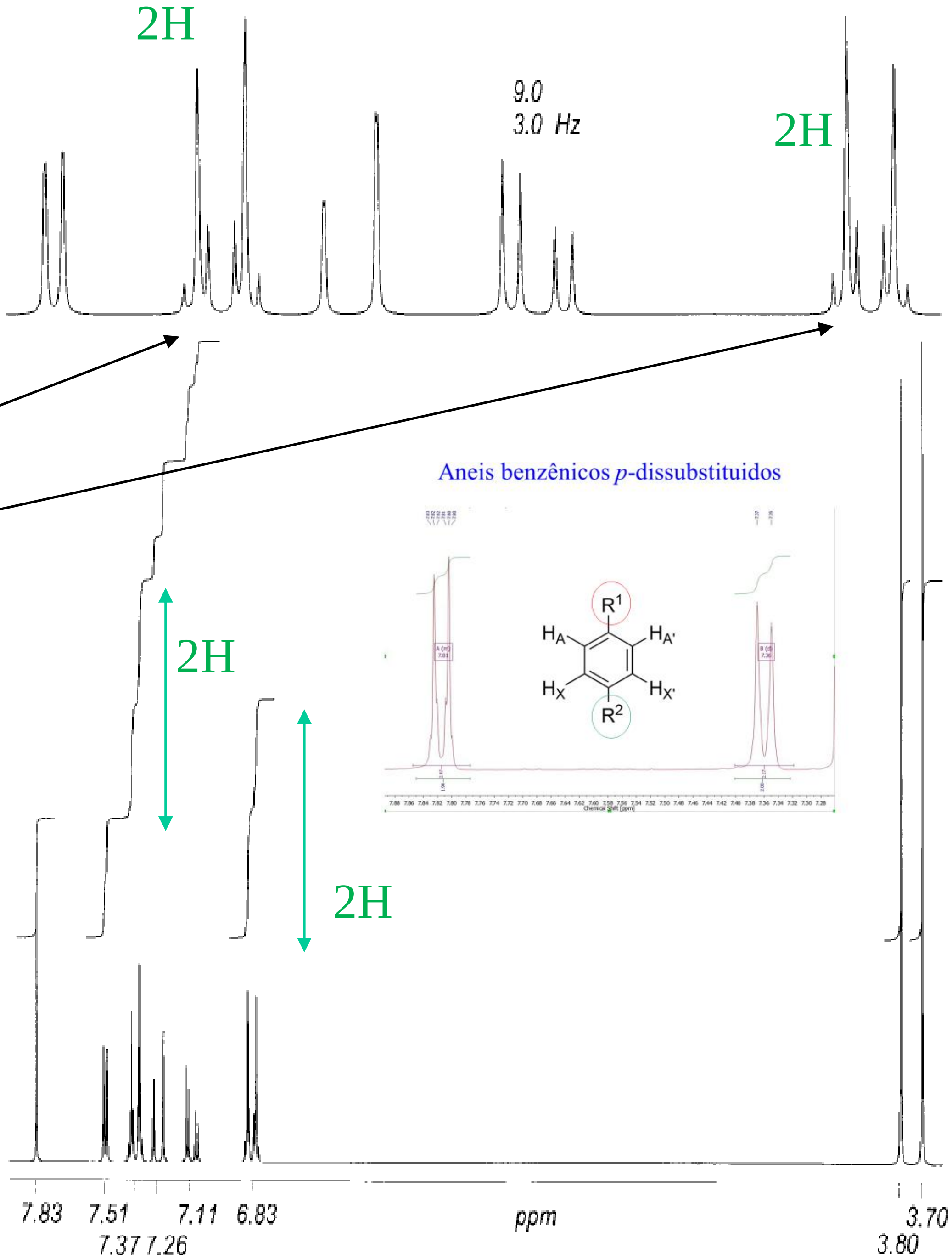
$C_{17}H_{14}O_4$



Espectro obtido em $CDCl_3$, 25 ºC, 200 MHz. Os valores de contantes de acoplamento são dados em Hertz.

Qual a estrutura da isoflavona?





$C_{17}H_{14}O_4$

Espectro obtido em $CDCl_3$, 25 °C, 200 MHz. Os valores de contantes de acoplamento são dados e Hertz.

onde colocar a outra metoxila no anel A?

Experimente colocar em cada uma das 4 posições disponiveis e analise o que esperaria em termos de multiplicidade. Compare com os sinais do espectro.