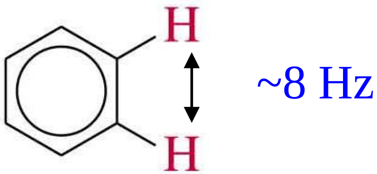
# QFL-1221

## RMN

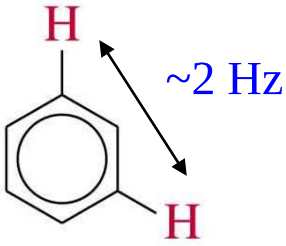
## RMN de $^{13}C$

10 de julho - 2020

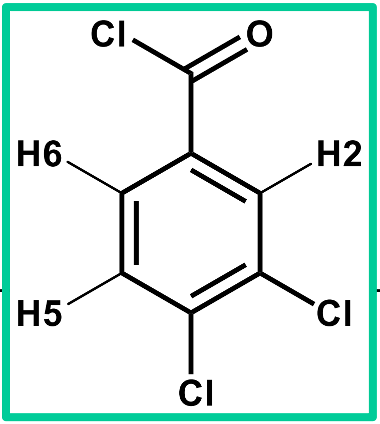
# Qual o padrão de substituição do anel aromático para o cloreto de ácido de fórmula $C_7H_3Cl_3O$?



(ortho)



(meta)

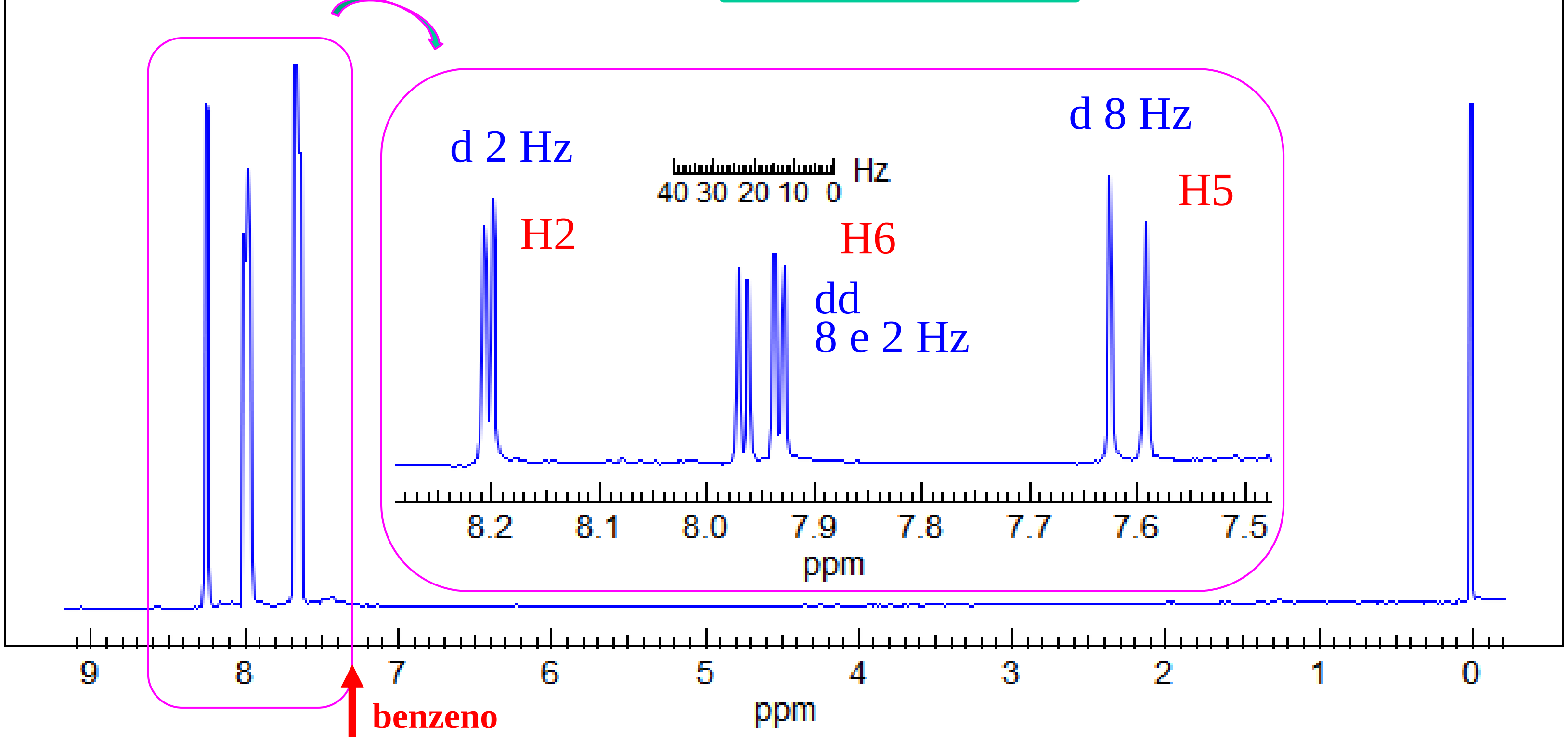


H2 acopla em meta (d, 2,0 Hz) com H6.

H5 acopla em orto (d, 8,0 Hz) com H6.

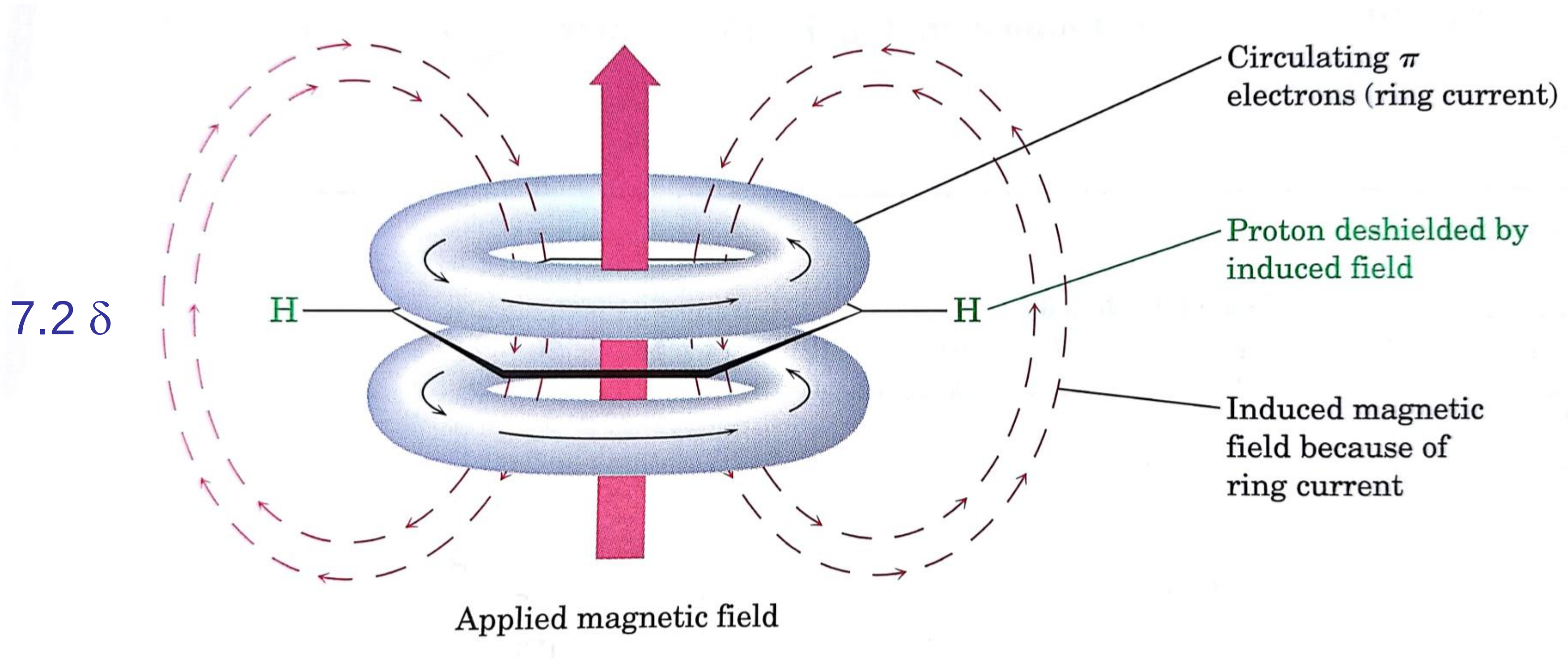
H6 acopla em orto (d, 8,0 Hz) com H6 e em meta com H2 (d, 2,0 Hz) formando um duplo-dubleto.

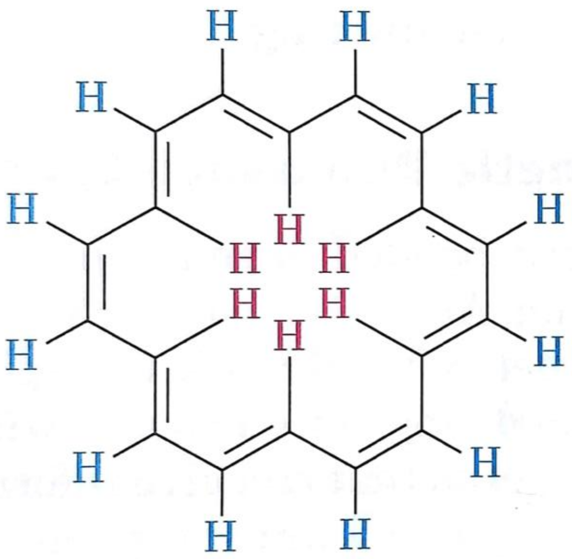
R-19M $C_7H_3Cl_3O$
270 MHz $^1$H NMR Spectrum ($CDCl_3$)



# Desproteção dos hidrogênios de aneis aromáticos pelo campo magnético induzido causado pela corrente de elétrons π

7.2 δ

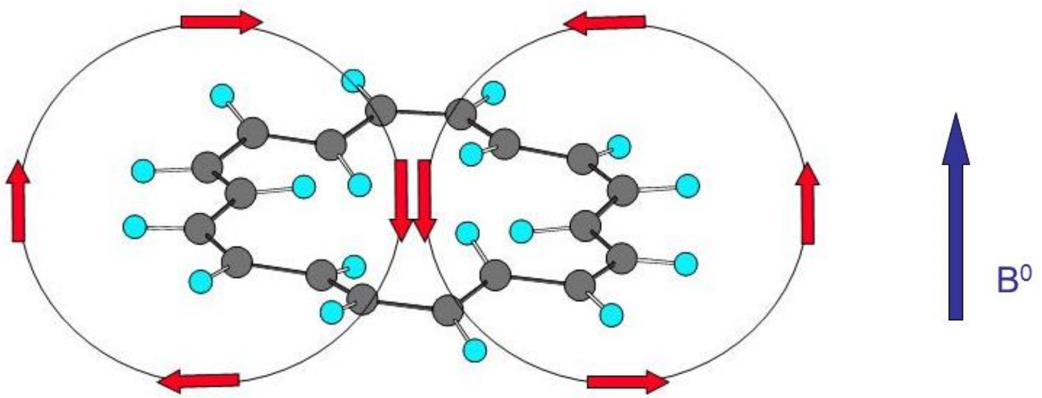




**[18]Annulene**

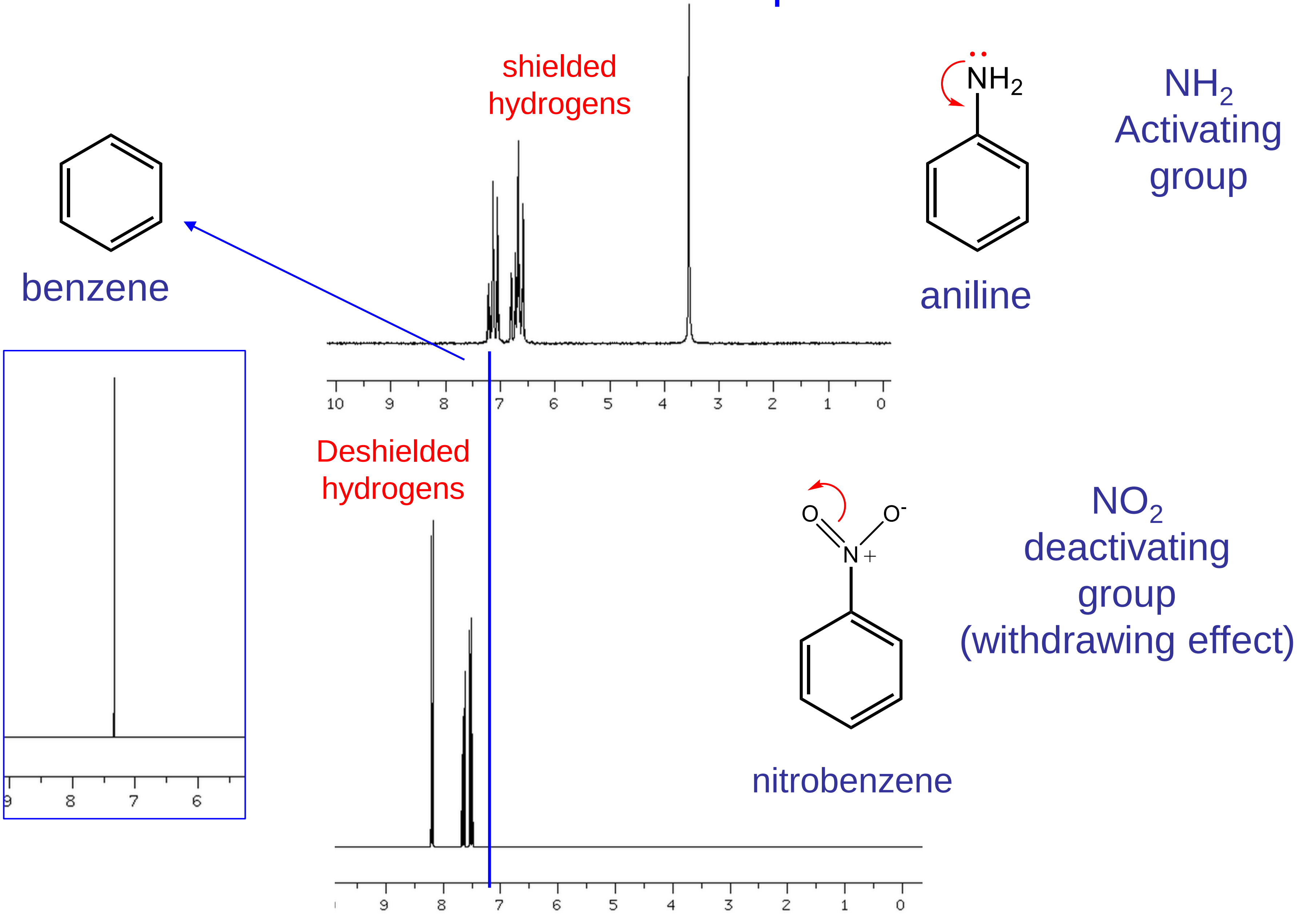
Inside H: −3.0 δ

Outside H: 9.3 δ



Direction of
magnetic field

# Substituent Effects on aromatic compounds: $^1$H NMR data



shielded hydrogens

Deshielded hydrogens

benzene

aniline

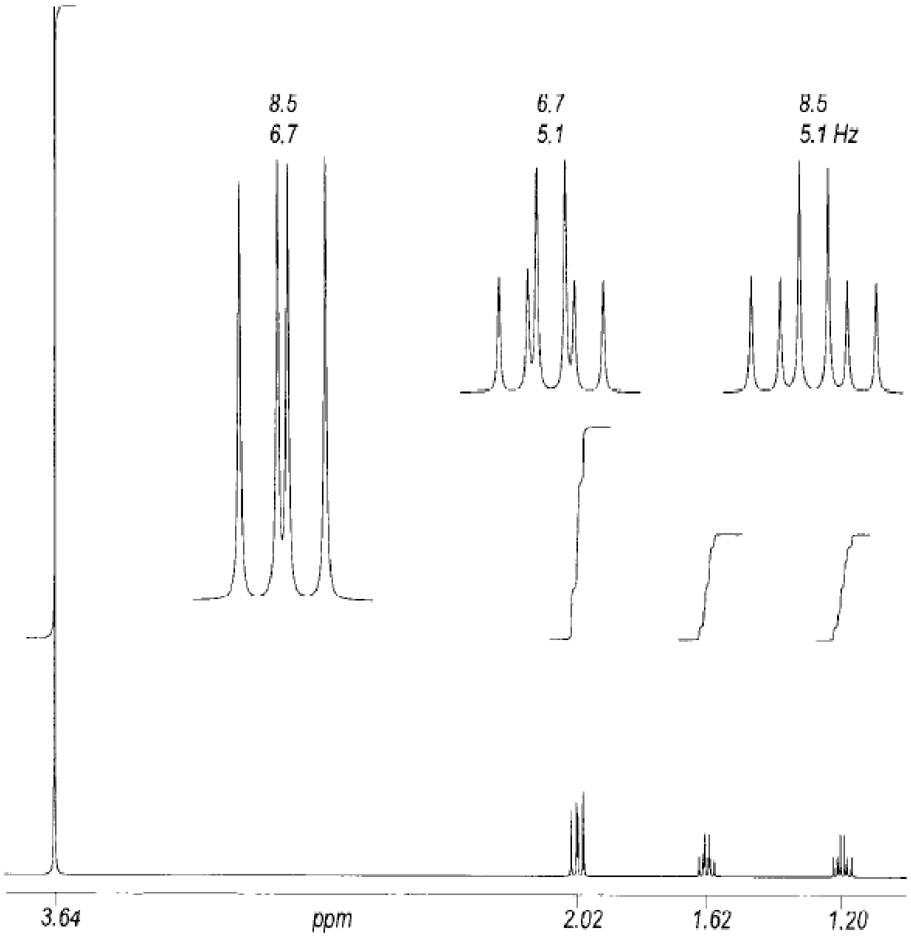
$NH_2$ Activating group

nitrobenzene

$NO_2$ deactivating group (withdrawing effect)

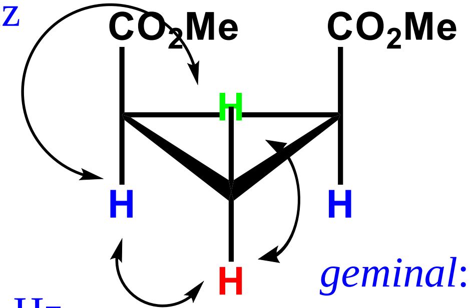
**NMR spectra of benzenoid compounds**

# Espectro de RMN de $^1$H obtido para o ciclopropanocarboxilato de dimetila. Esse é o isômero *cis* ou *trans*?



CDCl$_3$, 25 °C, 400 MHz

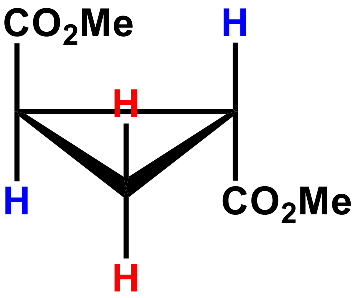
# *cis* e *trans* - ciclopropanocarboxilato de dimetila



*trans* : 4 – 8 Hz

*cis* : 6 – 12 Hz

*geminal*: 5 – 6 Hz

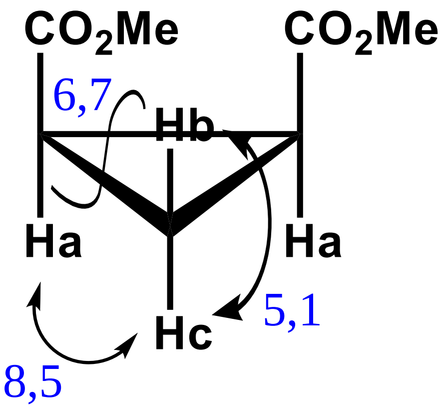


Quantos hidrogênios diferentes temos em cada caso?

2H - 1H - 1H

Somente dois hidrogênios diferentes (azul e vermelho)

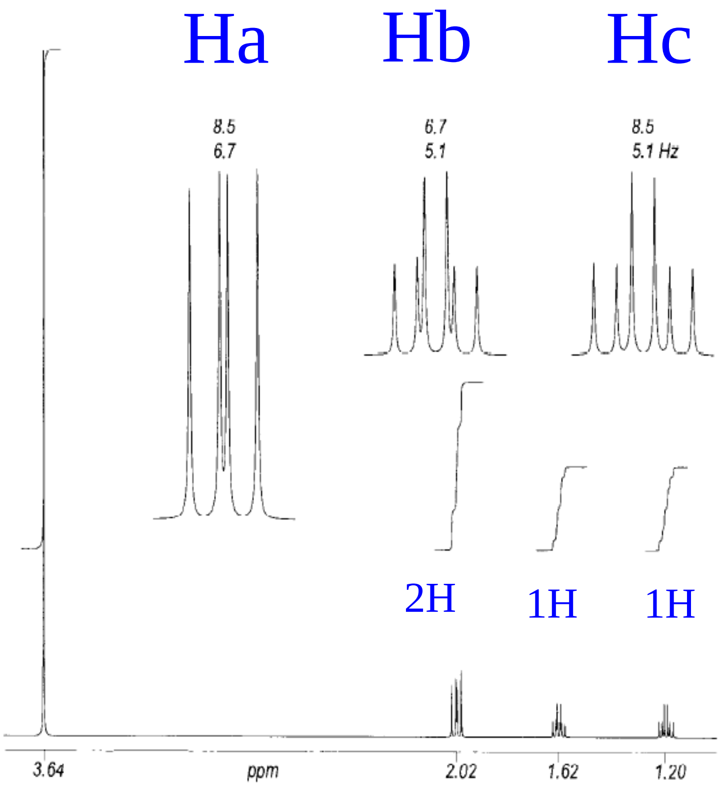
# *Cis*-ciclopropanodicarboxilato de dimetila



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

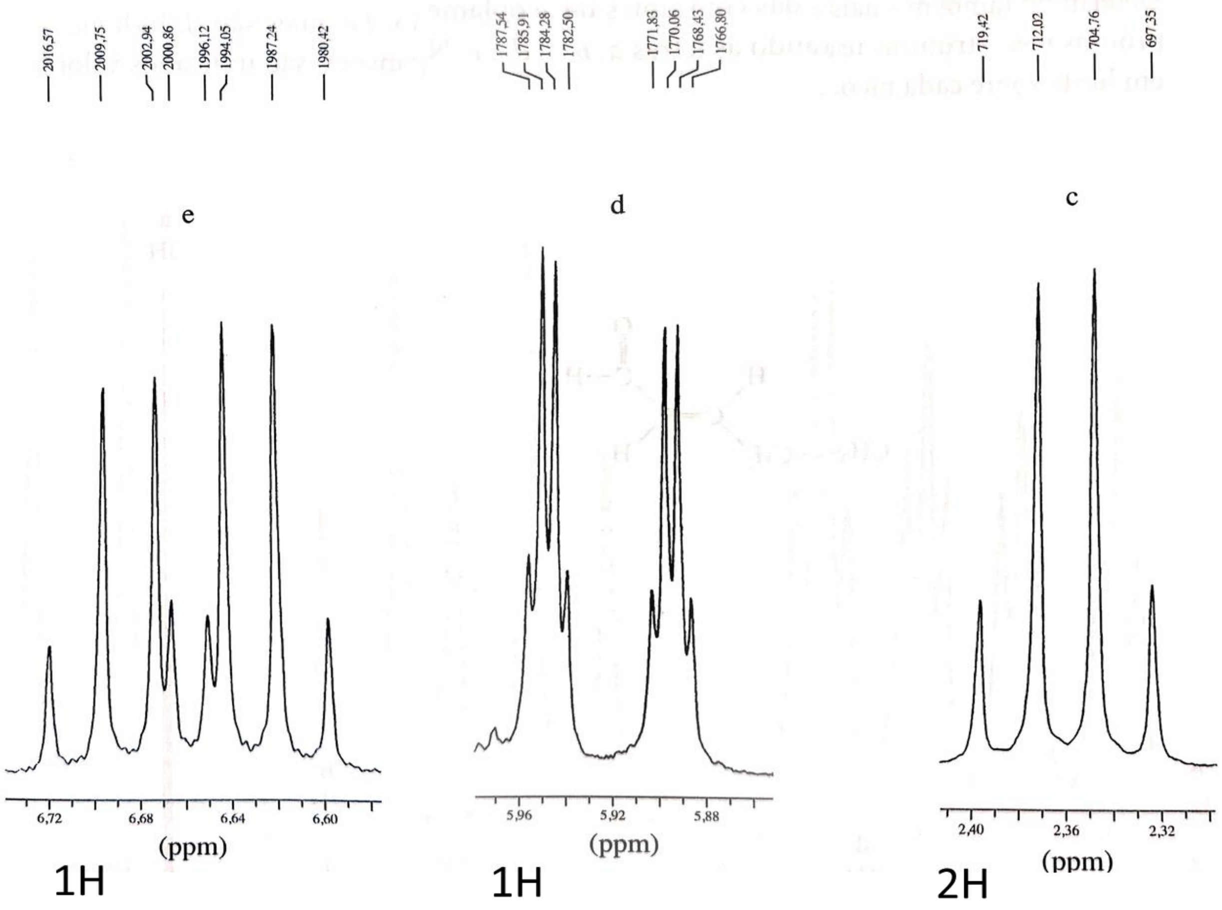
Hb (1H): td 6,7 e 5,1 Hz

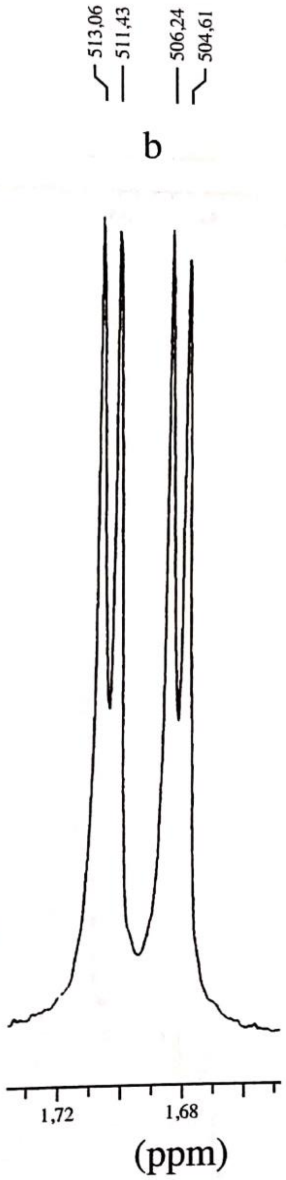
Hc (1H): td 8,5 e 5,1 Hz



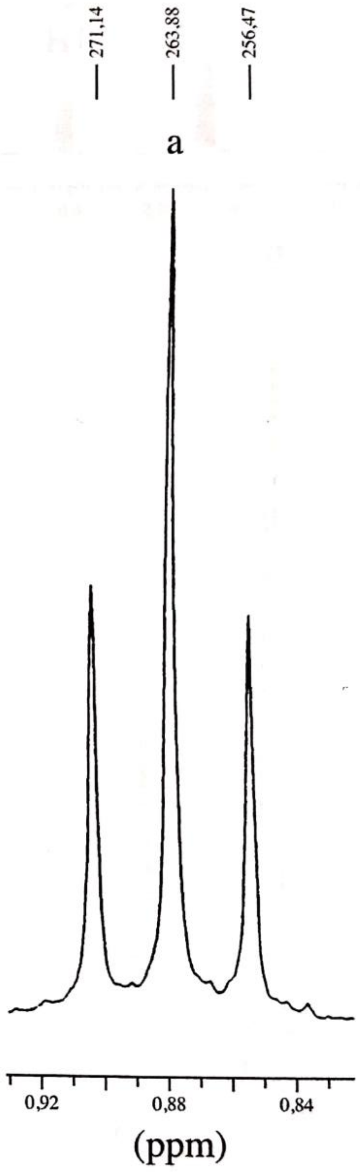
Os Hb e Hc são triplo dubletos (td), pois acoplam com dois Ha formando um tripleto (6,7 e 8,5 Hz, respectivamente). Esses são desdobrados pelo acoplamento geminal (5,1 Hz). O acoplamento maior é especificado primeiro por isso é um triplo dubleto. Caso contrário, no caso do dubleto ser maior, seria um duplo tripleto.

**Lista 12, 1)** O espectro de RMN de $^1H$ é da substância de fórmula molecular $C_6H_{10}O$. A substância apresentou um máximo no UV em 227 nm. Calcule o IDH. Para se obter as constantes de acoplamento, defina a multiplicidade e subtraia os valores que estão dados em Hertz. A diferença corresponde ao acoplamento do sinal. Por exemplo, o pico **e** (abaixo) é um duplo quadrupleto (dq, 15,8 e 6,8 Hz).




513,06
511,43
506,24
504,61
b
1,72
1,68
(ppm)

3H


271,14
263,88
256,47
a
0,92
0,88
0,84
(ppm)

3H

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

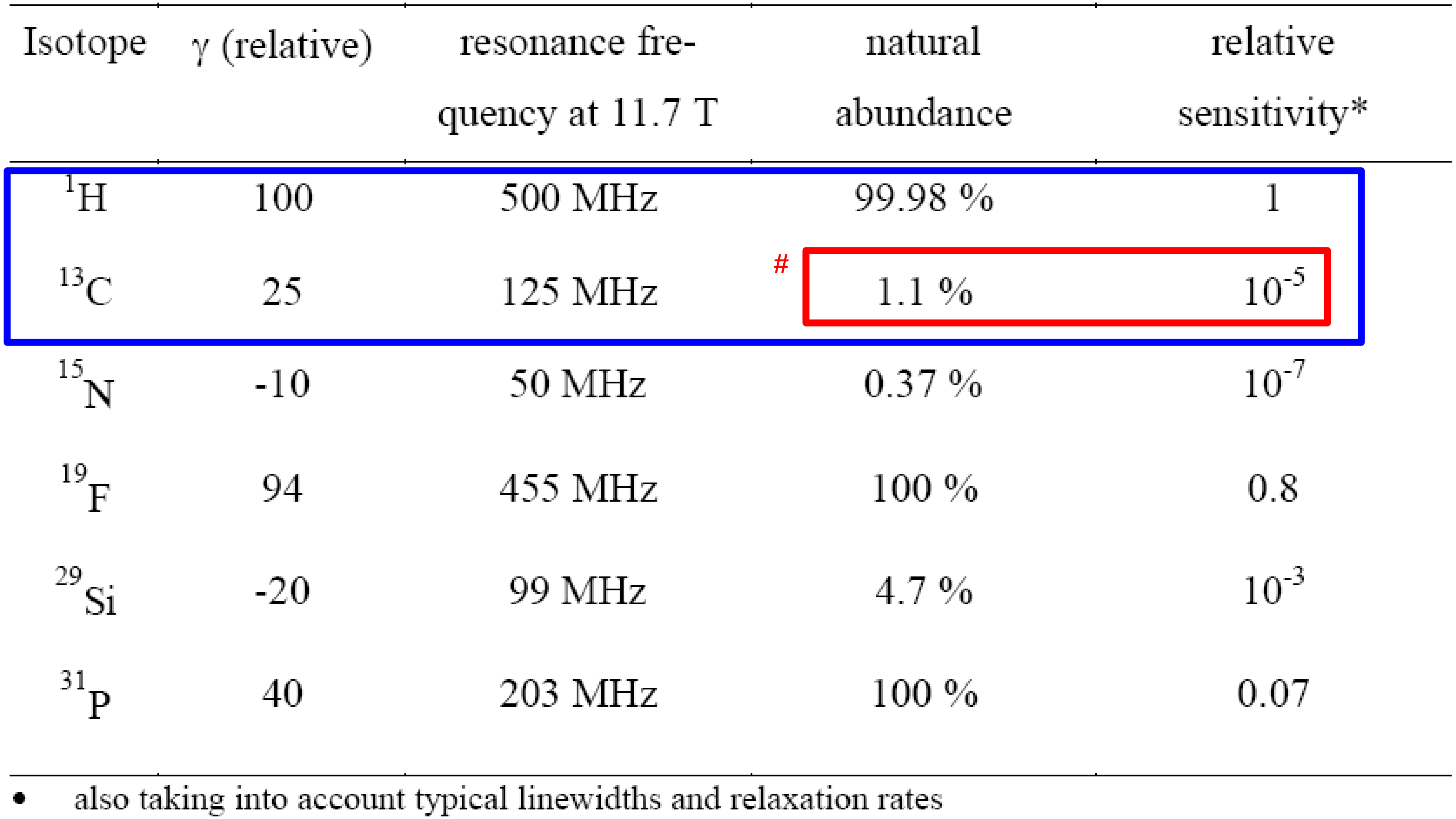
1) Posição de absorção (deslocamento químico em δ - ppm);

2) Tipo de carbono ($CH_3$, $CH_2$, CH, C);

3) Proporção de carbono (quase não se usa);

4) Podem ser 2D [COSY (H acoplados); HSQC (C-H diretamente ligados; HMBC (C-H a 2-4 ligações); outras]

# Características de alguns núcleos ativos em RMN

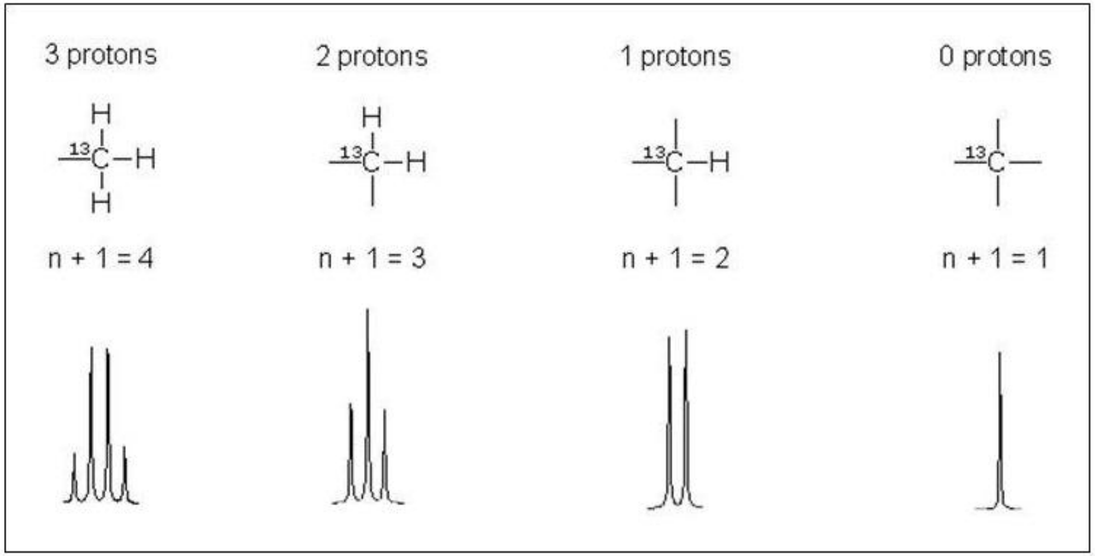


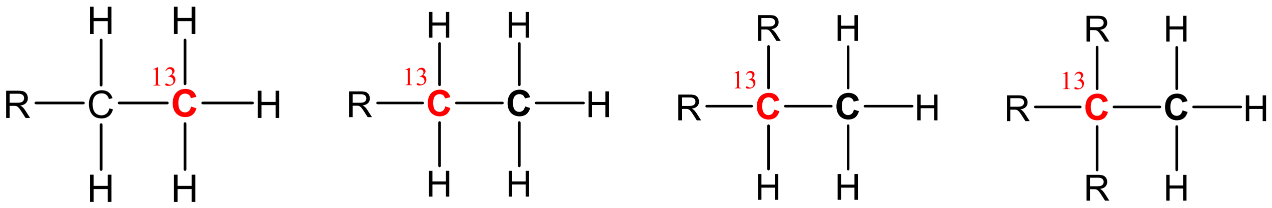
| Isotope | γ (relative) | resonance frequency at 11.7 T | natural abundance | relative sensitivity* |
|---|---|---|---|---|
| $^{1}$H | 100 | 500 MHz | 99.98 % | 1 |
| $^{13}$C | 25 | 125 MHz | # 1.1 % | $10^{-5}$ |
| $^{15}$N | -10 | 50 MHz | 0.37 % | $10^{-7}$ |
| $^{19}$F | 94 | 455 MHz | 100 % | 0.8 |
| $^{29}$Si | -20 | 99 MHz | 4.7 % | $10^{-3}$ |
| $^{31}$P | 40 | 203 MHz | 100 % | 0.07 |

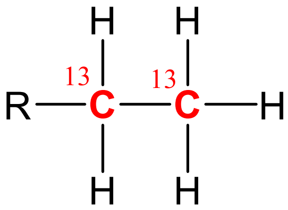
- also taking into account typical linewidths and relaxation rates

**$^{\#}$Parâmetros que tornam a detecção de sinais de $^{13}$C bem mais difícil do que os de $^{1}$H**

**Abundância natural de $^{13}C$ 1,11%**







1/10.000 moléculas

**A técnica INADEQUATE permite obter informações sobre os acoplamentos C-C**

# $^{13}C$ Coupling Constants

## *$^{13}C$—H couplings*

**$^{1}J_{CH}$ -one bond $^{13}C$ - $^{1}H$ coupling**

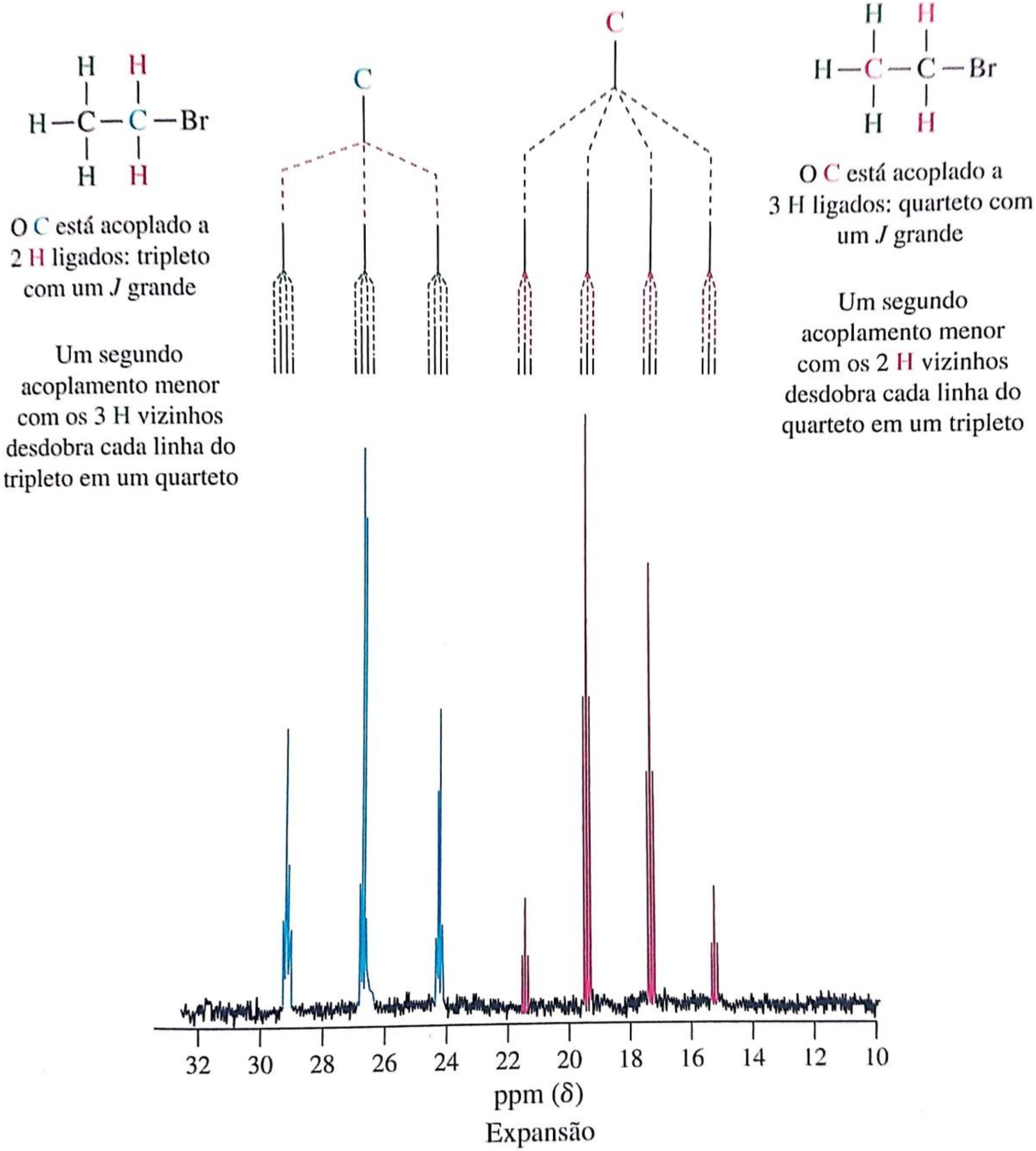
range from 120-320 $H_z$ and increases linearly with increasing carbon '**s**'-character.

| | $CH_3$-$CH_3$ | $CH_2$=$CH_2$ | $C_6H_6$ | HC≡CH |
|---|---|---|---|---|
| % s-character: | 25% | 33% | 33% | 50% |
| $^{1}J_{CH}$ ($H_z$): | 125 | 156 | 159 | 249 |

**$^{1}J_{CH}$ = 5 x ( % s) $H_z$.**

**$^{2}J_{CH}$-two bond ($^{13}C$-C-$^{1}H$) coupling constants**

$^{2}J_{CH}$, are between 5 and 60 $H_z$ but usually *ca*. 12 $H_z$.



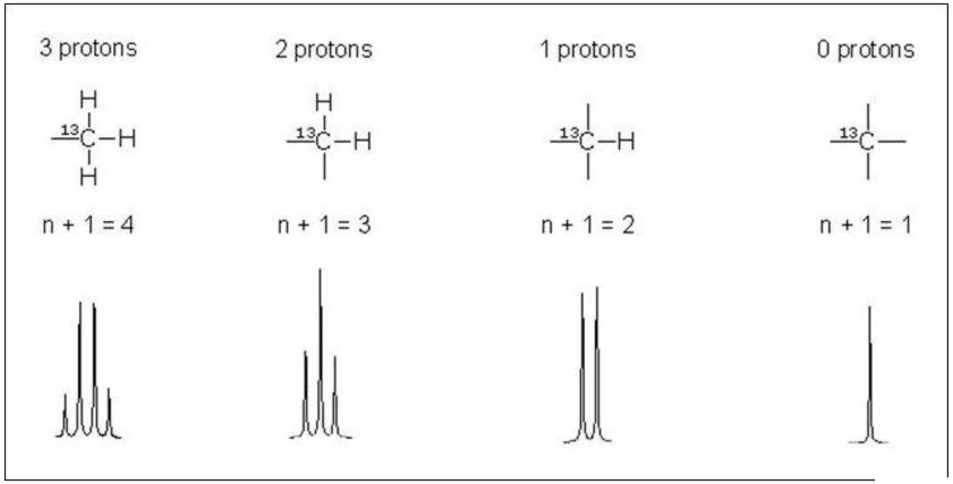
O C está acoplado a 2 H ligados: tripleto com um *J* grande

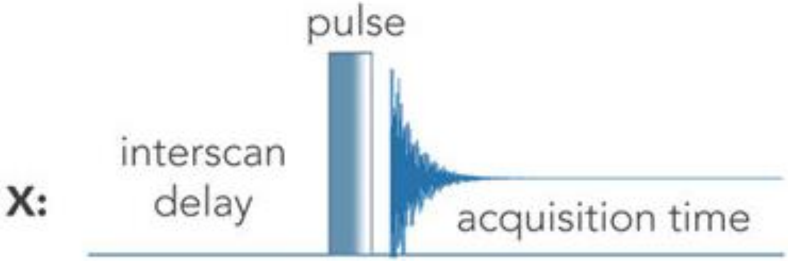
Um segundo acoplamento menor com os 3 H vizinhos desdobra cada linha do tripleto em um quarteto

O C está acoplado a 3 H ligados: quarteto com um *J* grande

Um segundo acoplamento menor com os 2 H vizinhos desdobra cada linha do quarteto em um tripleto

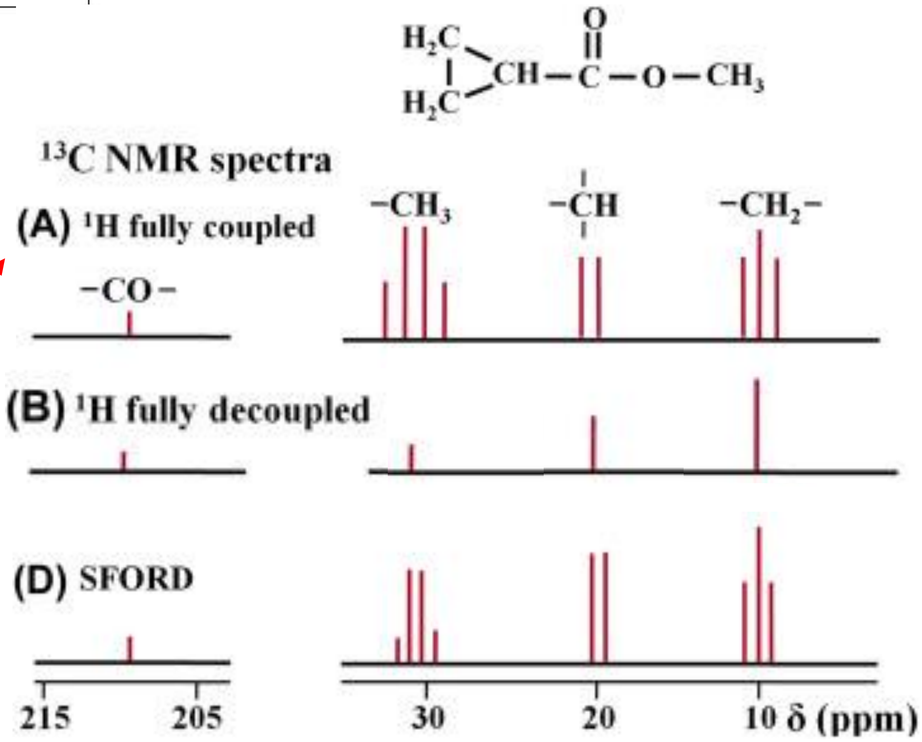
# Abundância natural de $^{13}C$ 1,11%



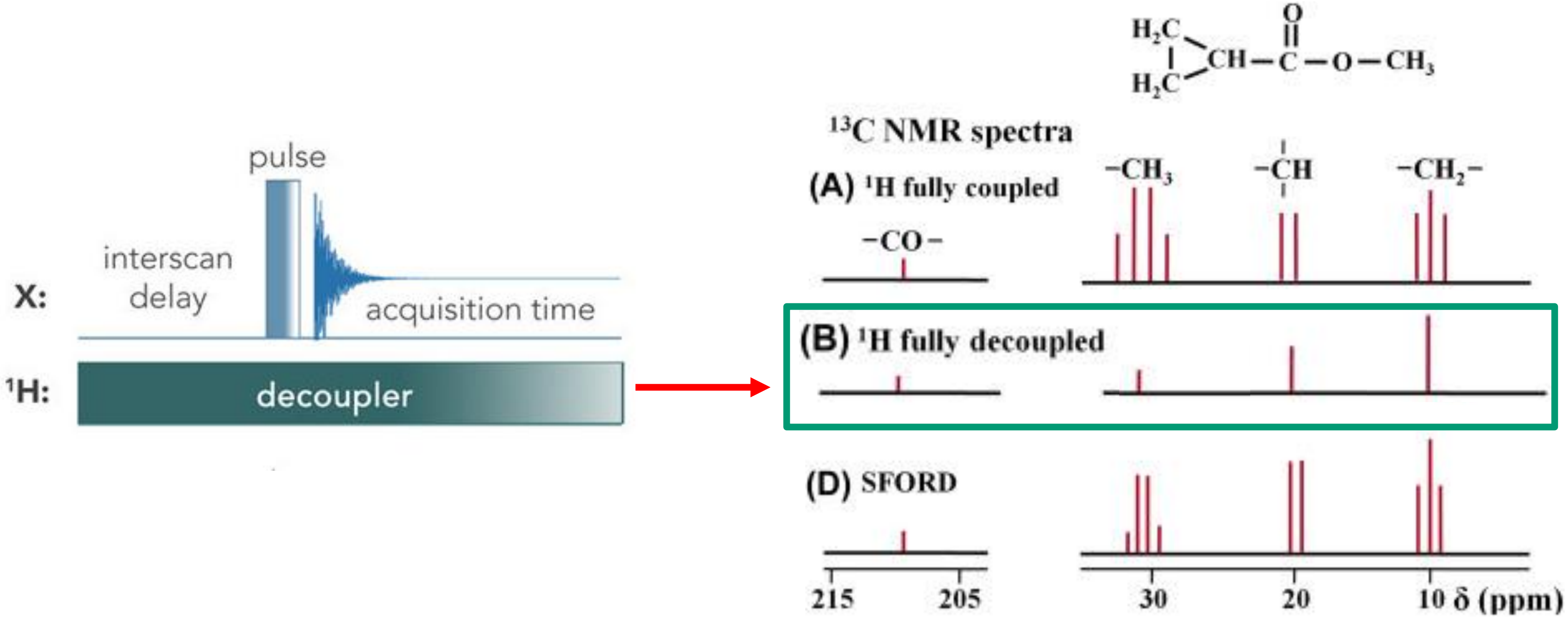


$^{1}H$: **desacoplador desligado**

**ou fora da frequencia de ressonância do $^{1}H$**



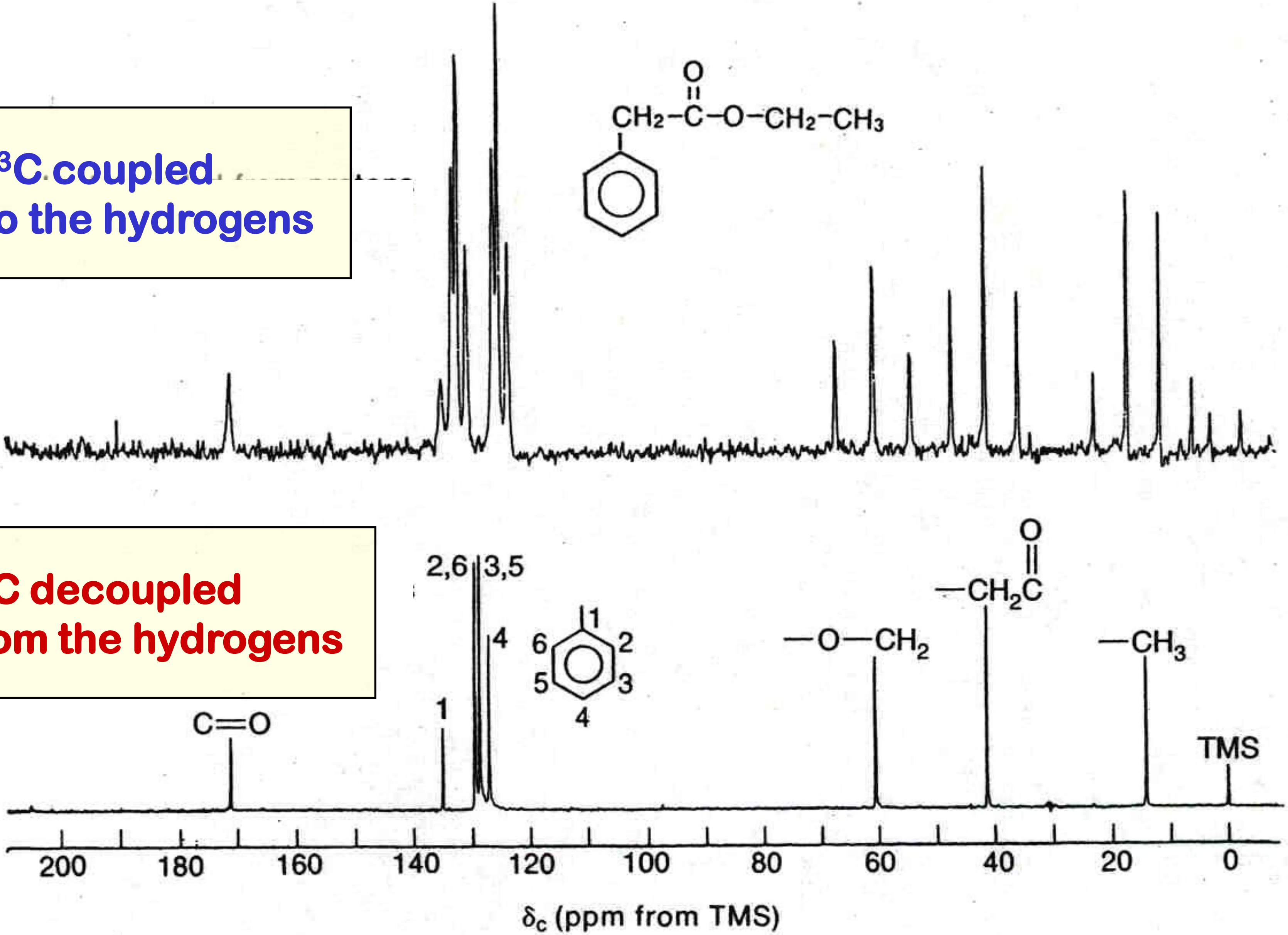
# Espectros de RMN de $^{13}C$ normalmente são totalmente desacoplados de $^1H$ (proton noise decoupled or fully decoupled)



# ETHYL PHENYLACETATE

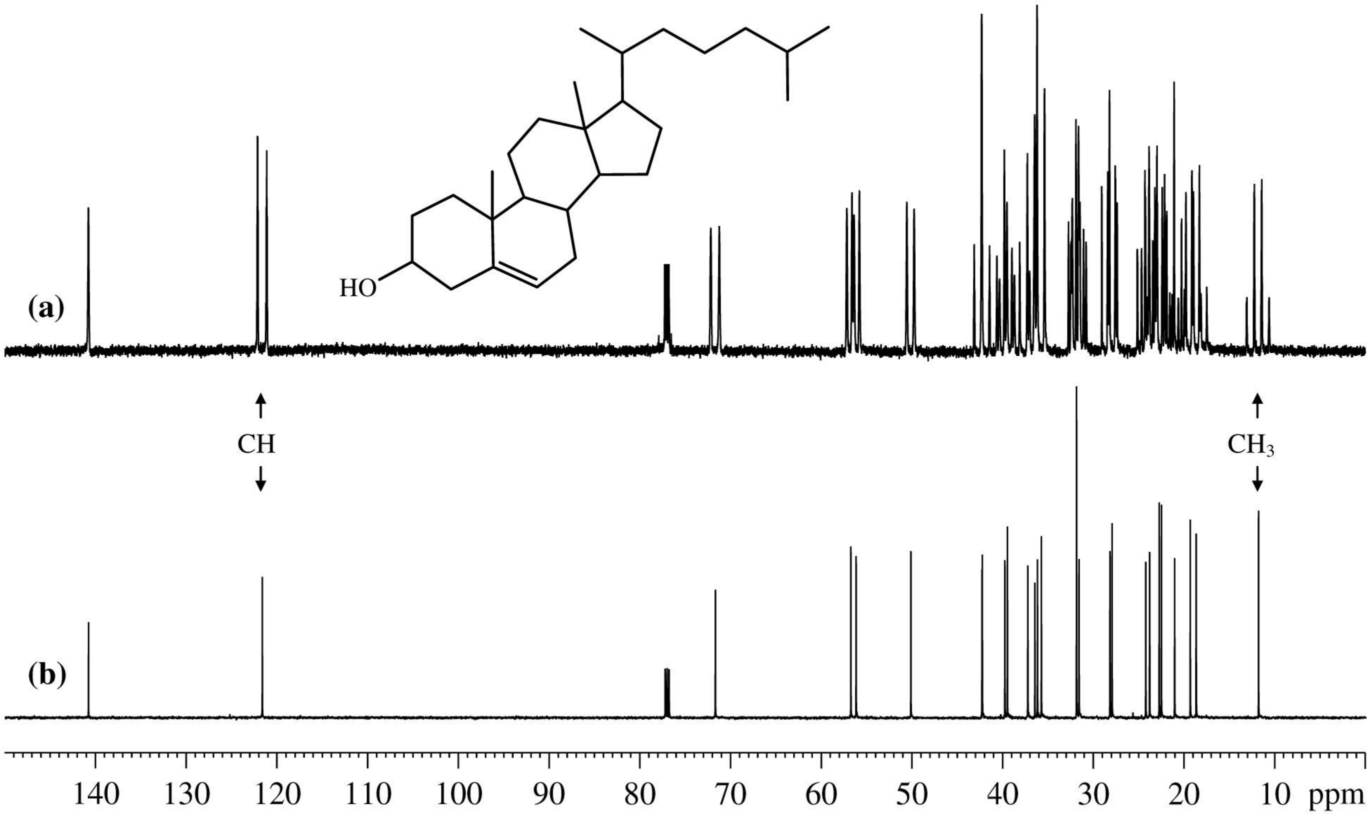
$^{13}$C coupled
to the hydrogens

$^{13}$C decoupled
from the hydrogens



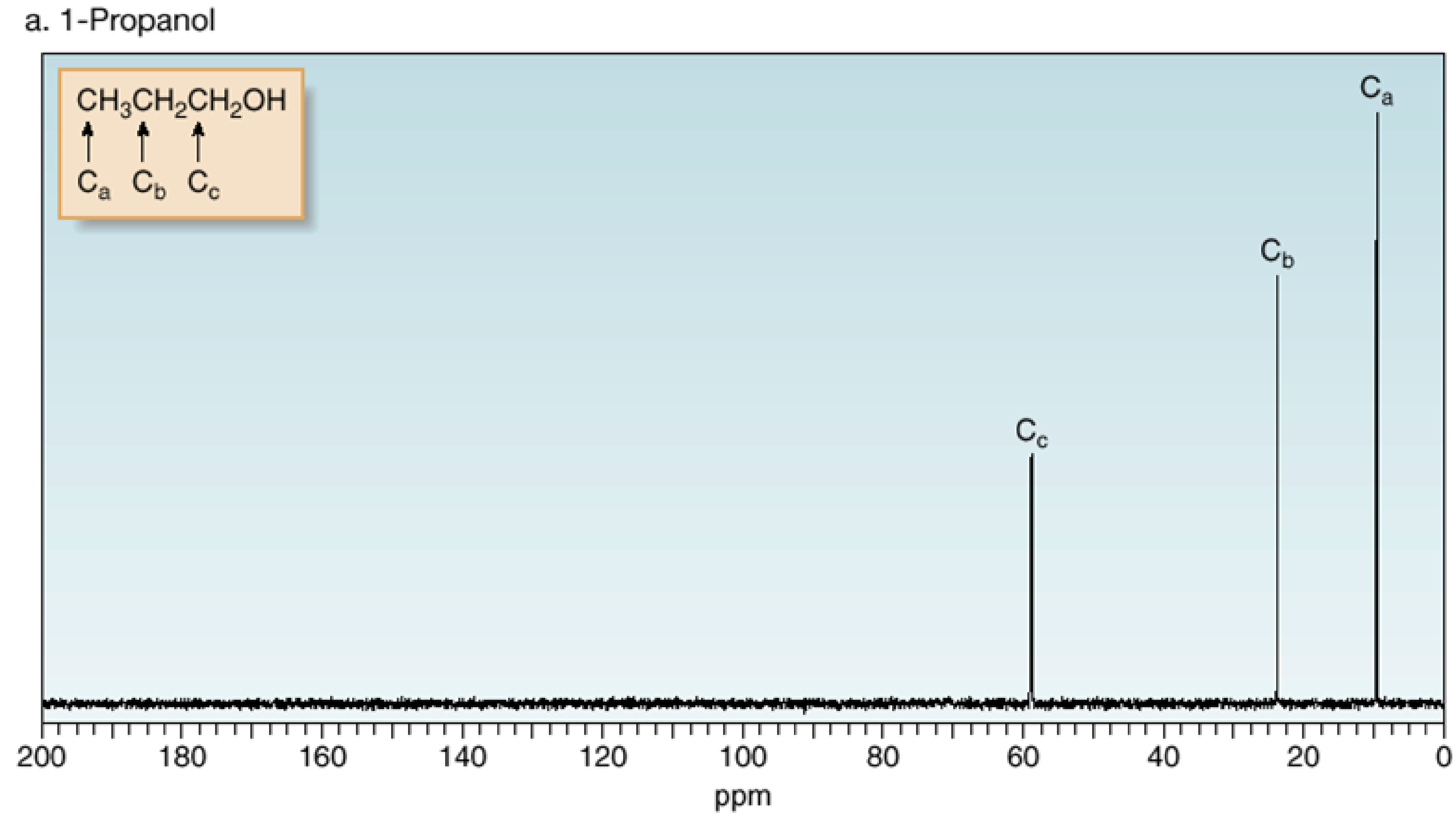
# Espectros de RMN de $^{13}C$ parcialmente acoplados

Valores de J para C-H ~110-300 Hz (C-C-H and C-C-C-H are 0-60Hz)



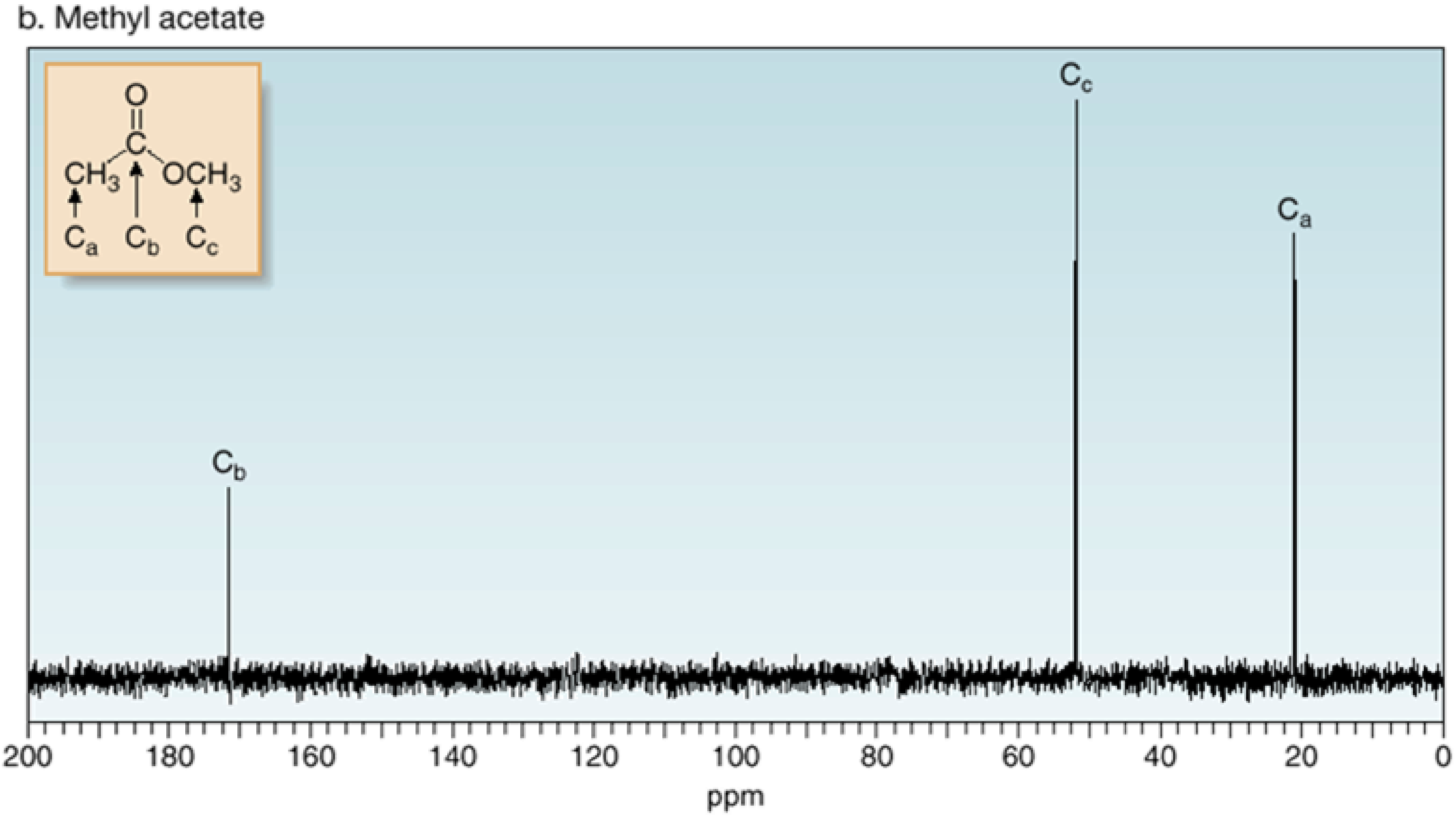
# Ressonância magnética nuclear de 13C

**O espectro mais simples apresenta sinais bem definidos que representam pelo menos um átomo de carbono.**



Os deslocamentos químicos estão associados densidade de elétrons dos carbonos.

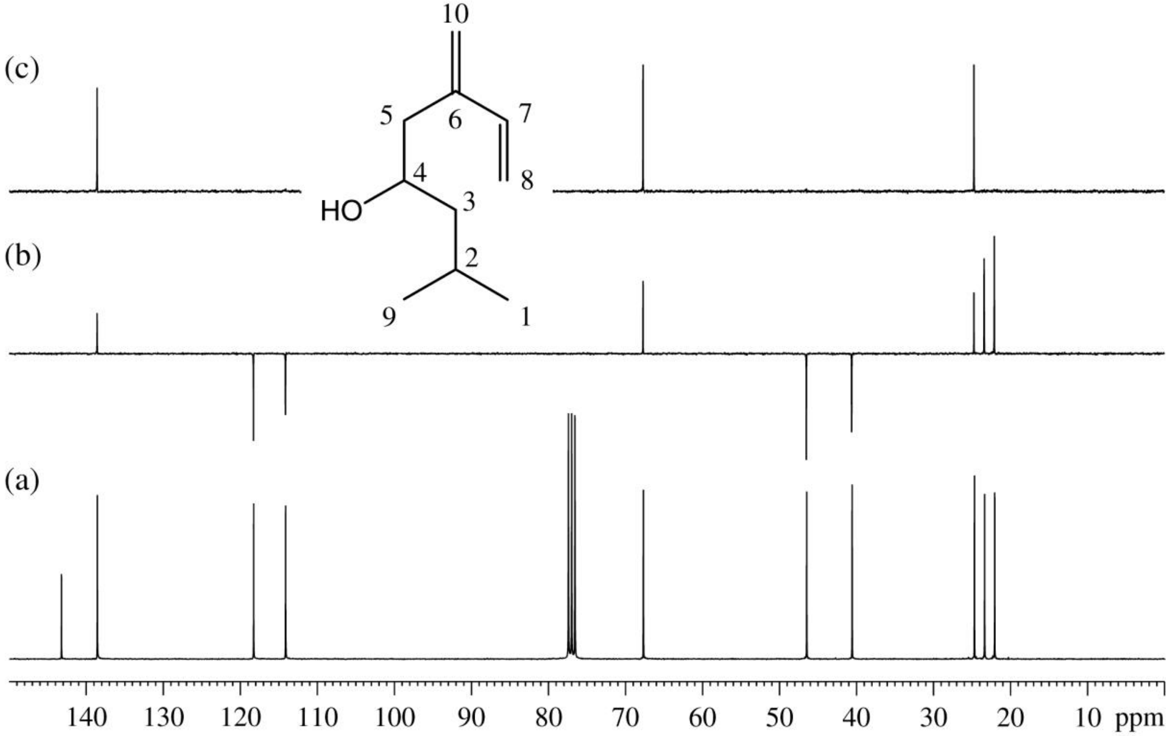
# Espectro de RMN de $^{13}$C ao acetato de metila



# Espectros DEPT

## (Distortionless Enhancement by Polarization Transfer (DEPT)

Baseado em sequencias de pulsos que resultam em diferentes fases para diferentes carbonos.



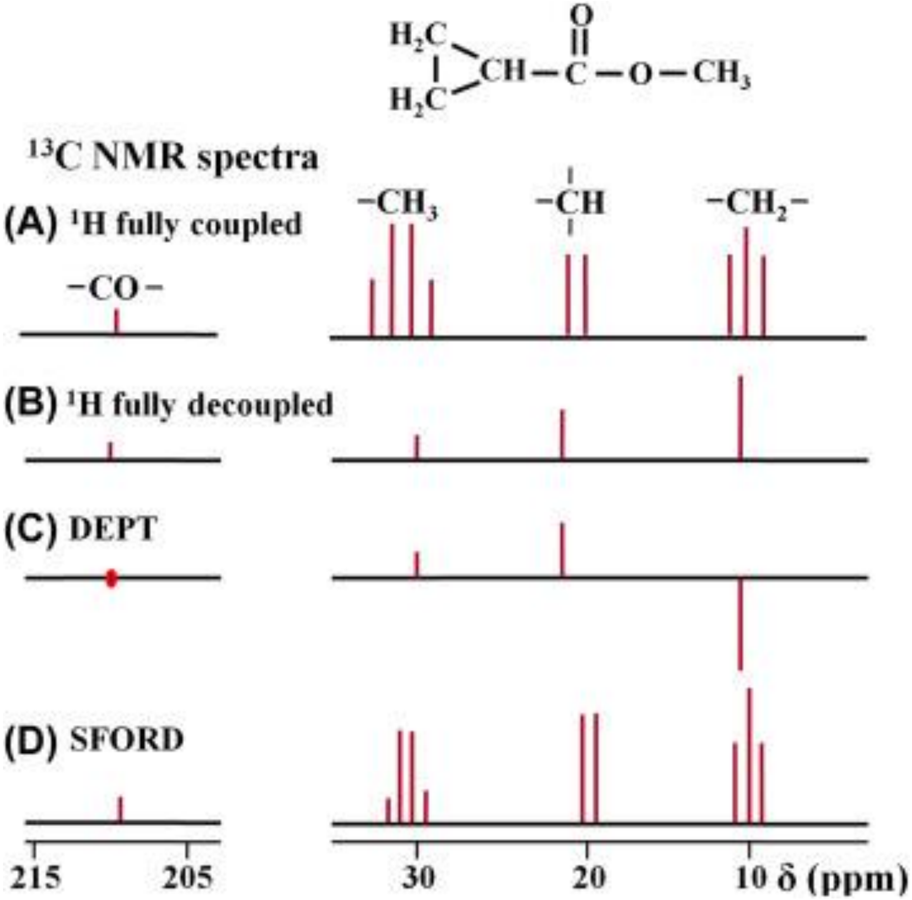
DEPT 90
apenas CH

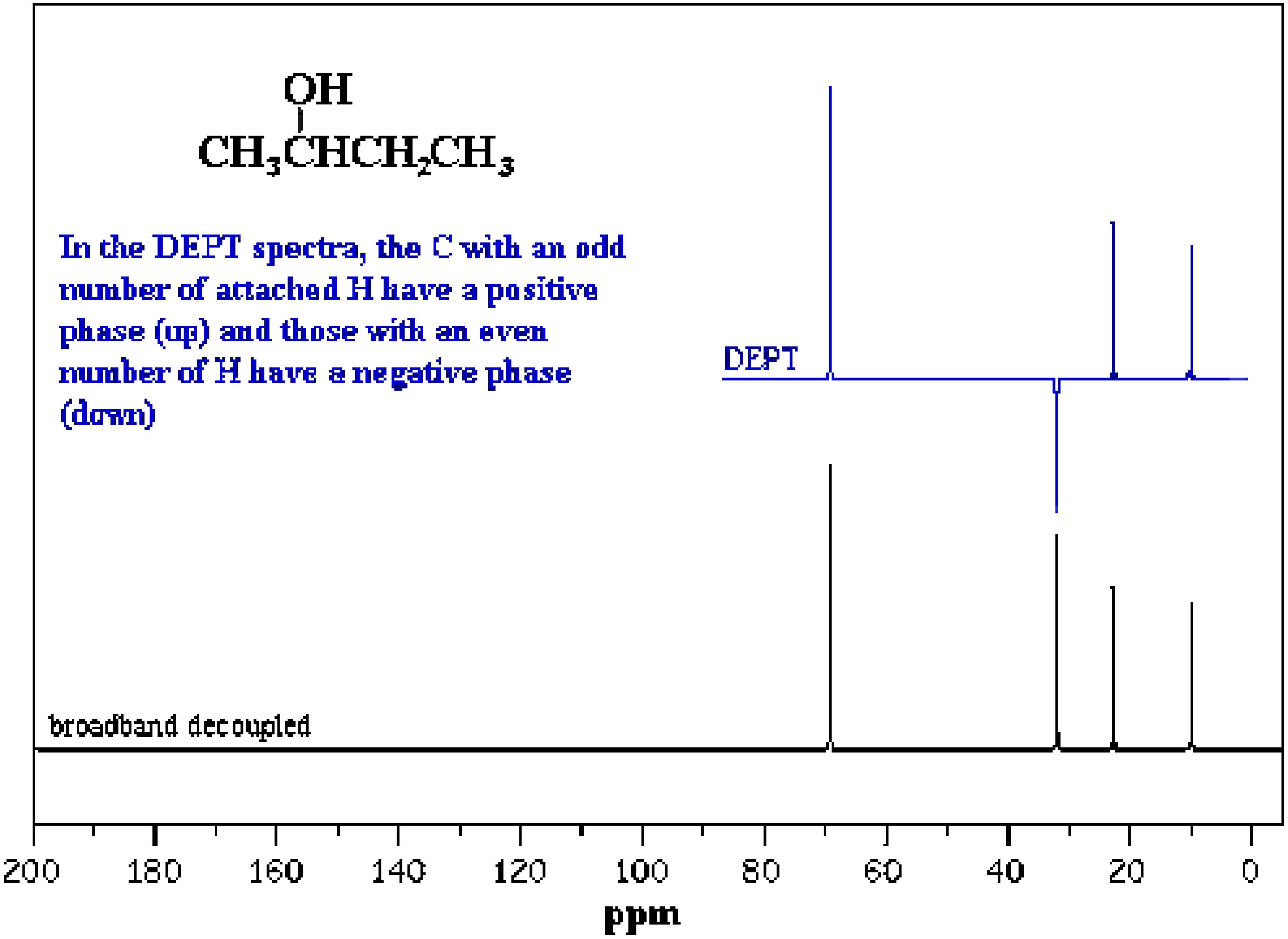
DEPT 135
CH &CH3 para cima,
CH2 para baixo

Espectro de 13C
normal

DEPT é bastante útil para se caracterizar os diferentes carbonos.

# A informação sobre o tipo de carbono (C, CH, CH2 e CH3) são atualmente obtidos por DEPT (Distortionless Enhancement by Polarization Transfer)

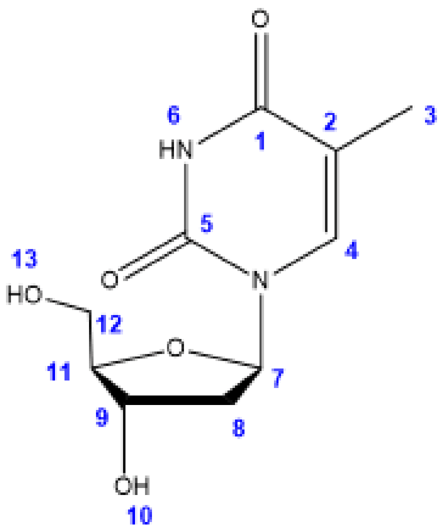




$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$

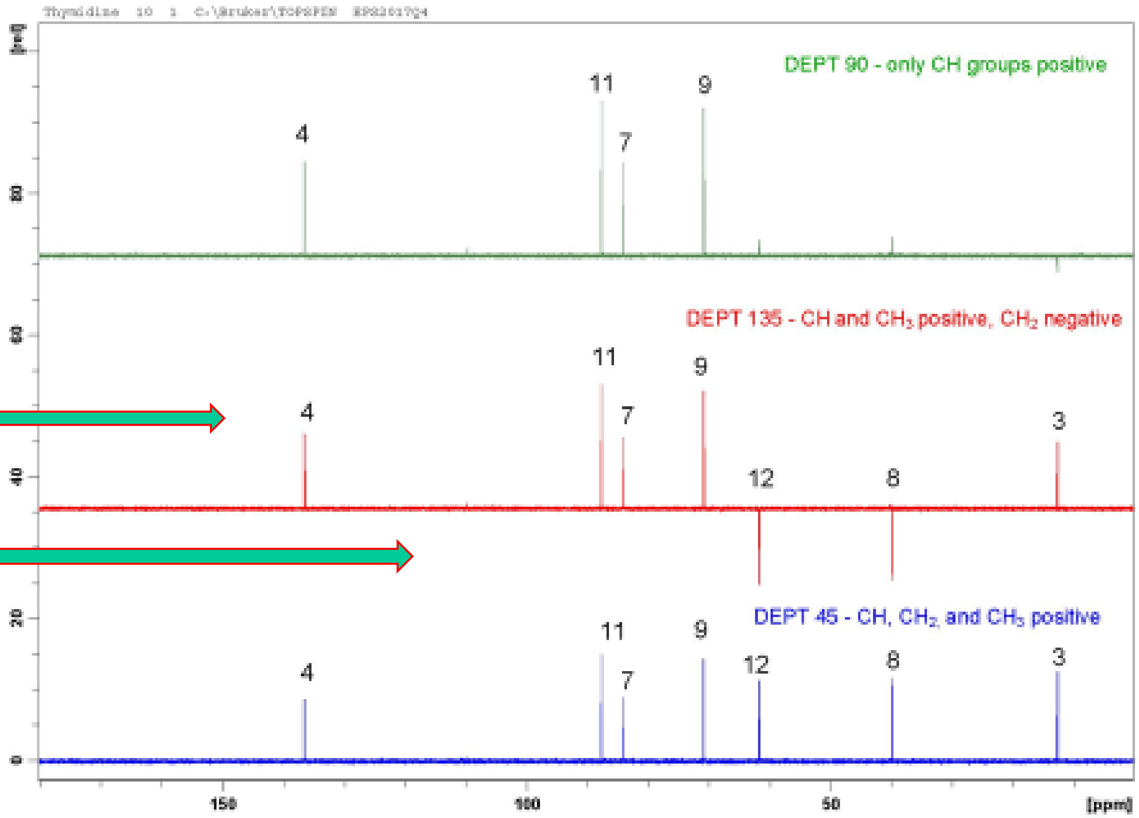
In the DEPT spectra, the C with an odd number of attached H have a positive phase (up) and those with an even number of H have a negative phase (down)

# Espectro DEPT para a timidina

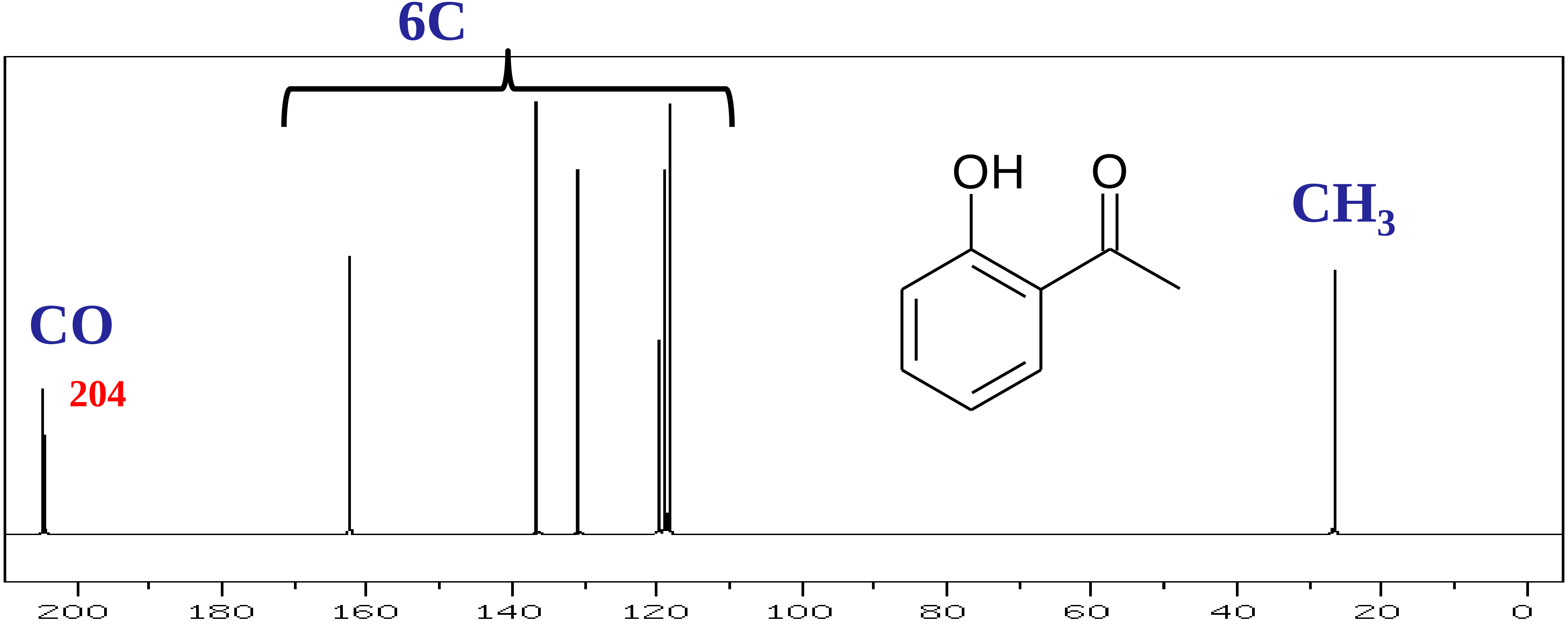


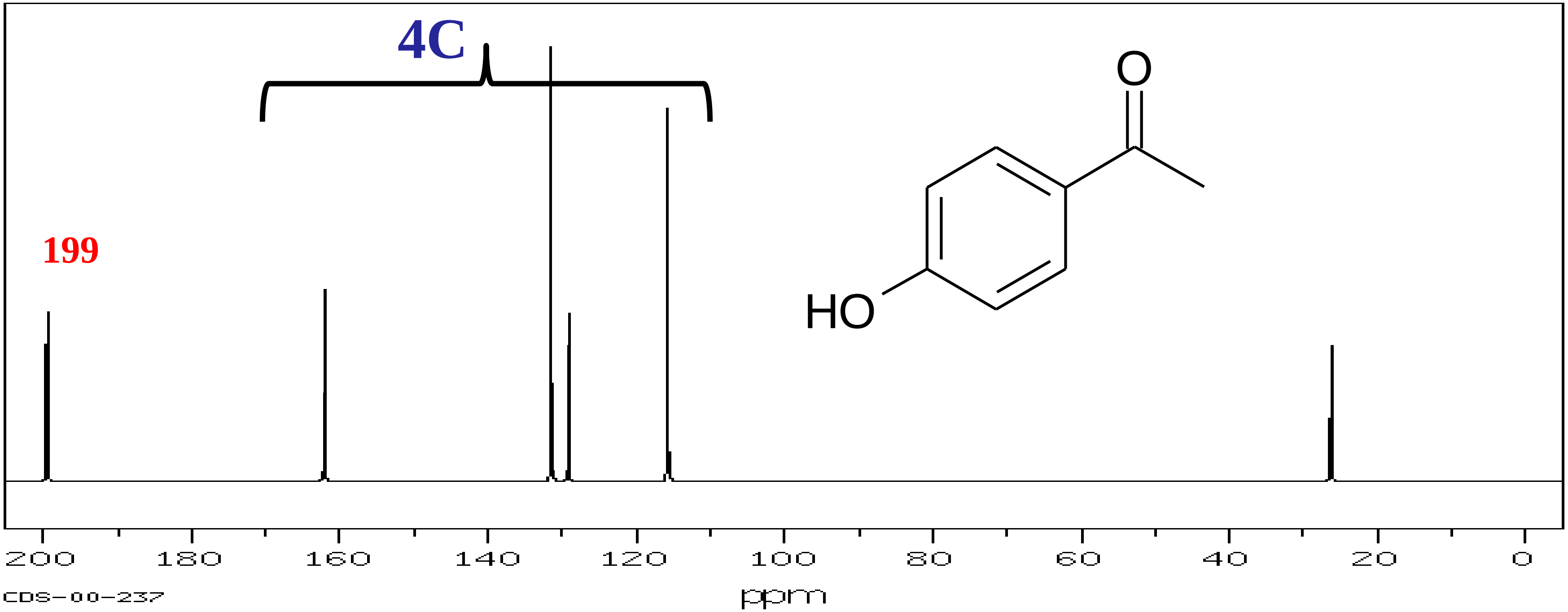
**sinais de CH e $CH_3$ positivos**

**sinais de $CH_2$ negativos**

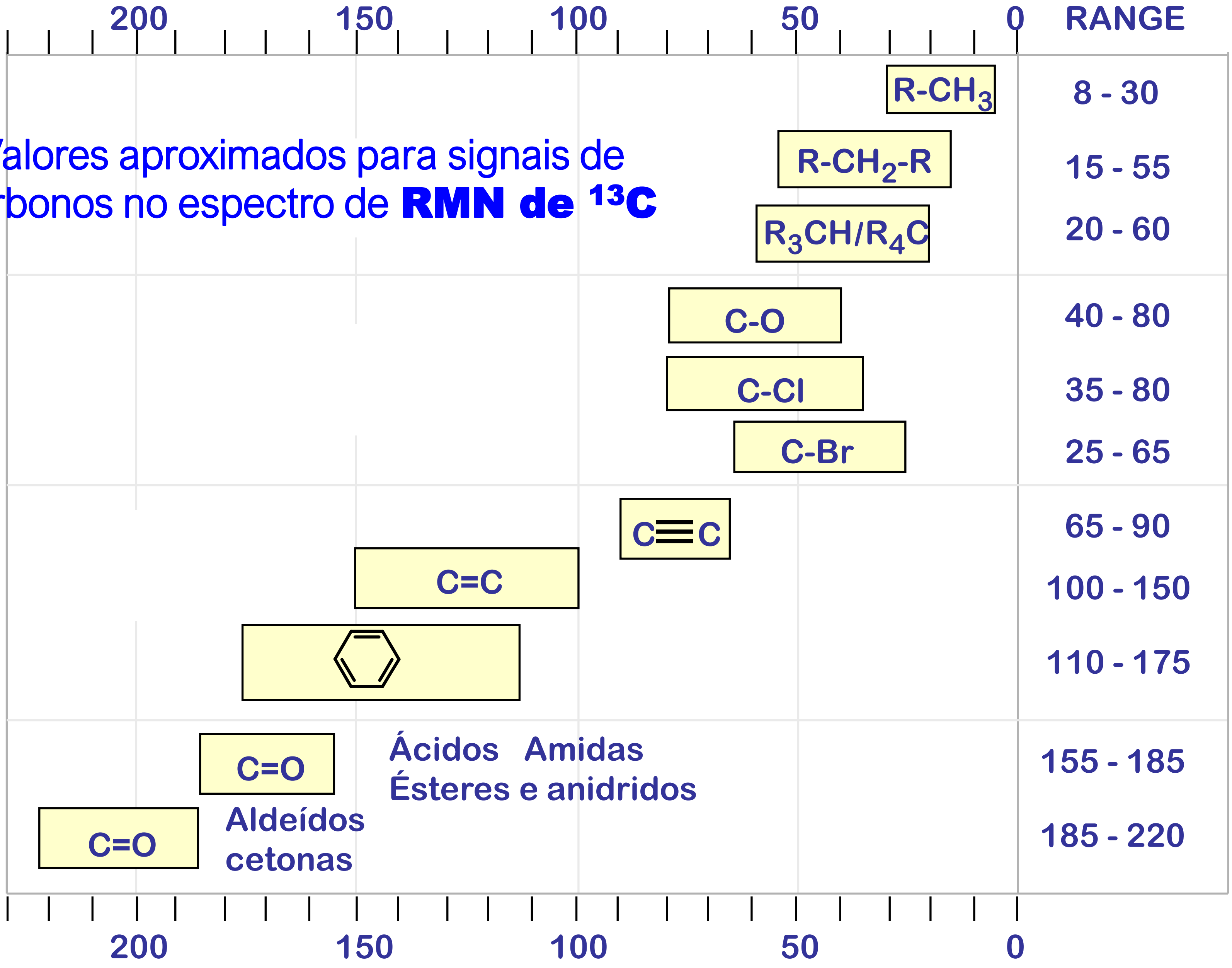


| Experiment | C | CH | $CH_2$ | $CH_3$ |
|---|---|---|---|---|
| **DEPT-45** | not visible | positive | positive | positive |
| **DEPT-90** | not visible | positive | not visible | not visible |
| **DEPT-135** | not visible | positive | negative | positive |


6C
CO
204
OH
O
CH$_3$
200
180
160
140
120
100
80
60
40
20
0

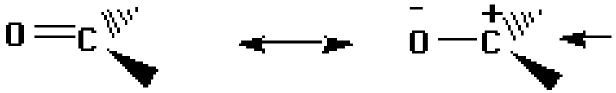

4C
O
199
HO
200
180
160
140
120
100
80
60
40
20
0
CDS-00-237
ppm

# Valores aproximados para signais de carbonos no espectro de **RMN de $^{13}$C**

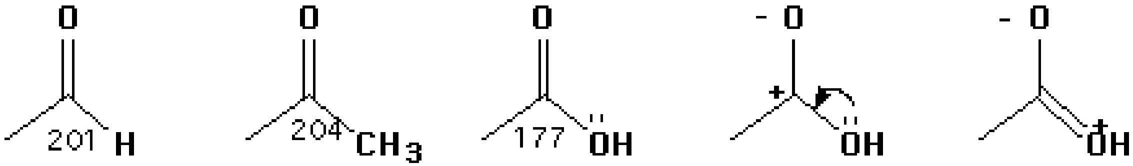


|  | RANGE |
|---|---|
| $R\text{-}CH_3$ | 8 - 30 |
| $R\text{-}CH_2\text{-}R$ | 15 - 55 |
| $R_3CH/R_4C$ | 20 - 60 |
| C-O | 40 - 80 |
| C-Cl | 35 - 80 |
| C-Br | 25 - 65 |
| C≡C | 65 - 90 |
| C=C | 100 - 150 |
|  | 110 - 175 |
| C=O Ácidos Amidas Ésteres e anidridos | 155 - 185 |
| C=O Aldeídos cetonas | 185 - 220 |

# Fatores que afetam o deslocamento químico de $^{13}C$

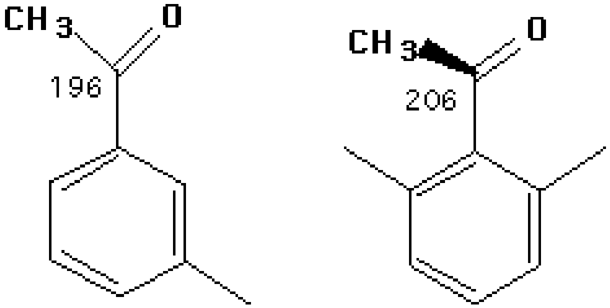


conjugação



conjugação por mesomeria

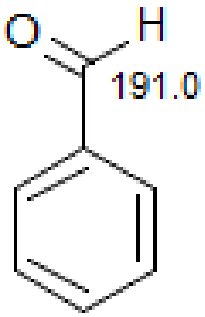
conjugação

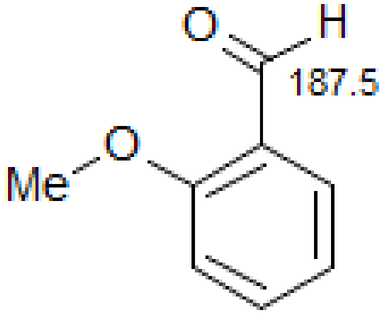


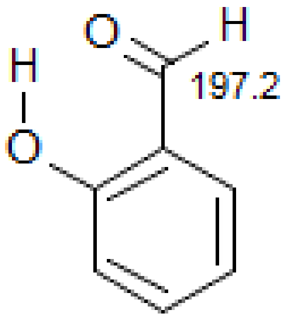
inibição da conjugação por impedimento estérico

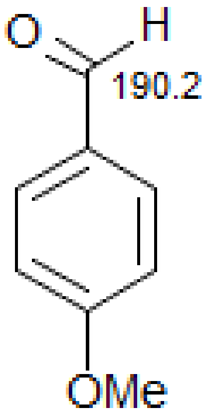
# Fatores que afetam o deslocamento químico de $^{13}C$

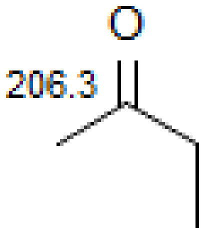
## ligação de hidrogênio e desproteção







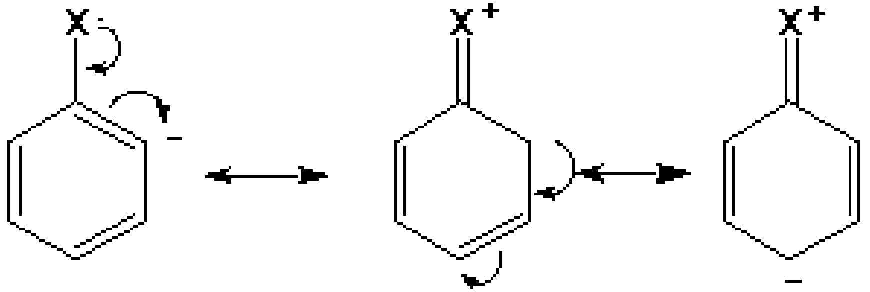




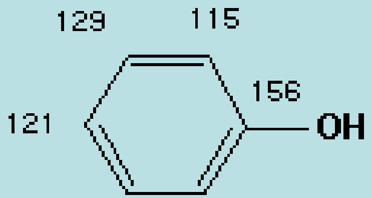
# Factors affecting chemical shifts

## Delocalisation in aromatics

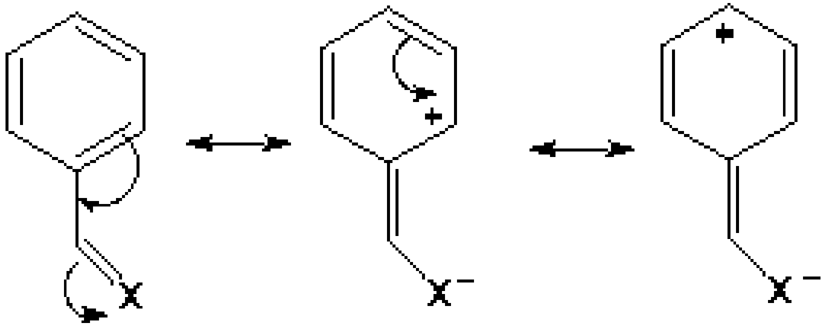
$+M$



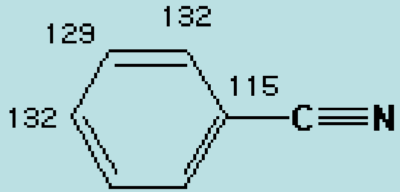
e.g.



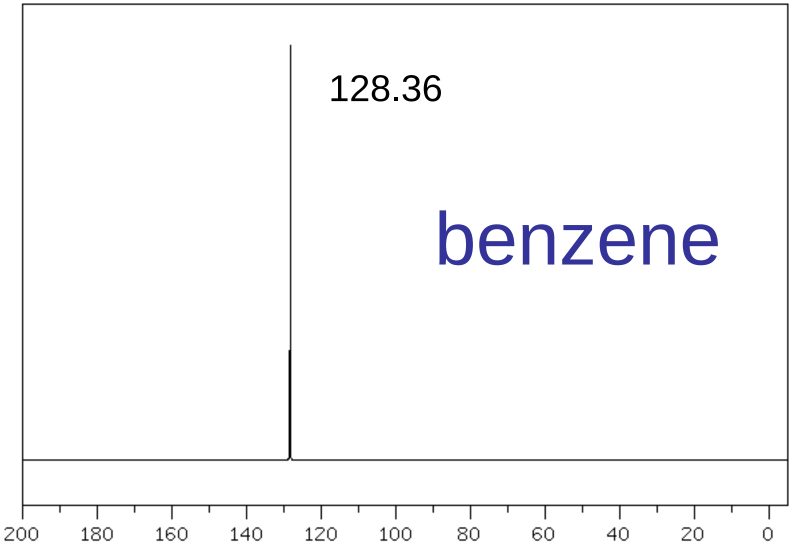
$-M$

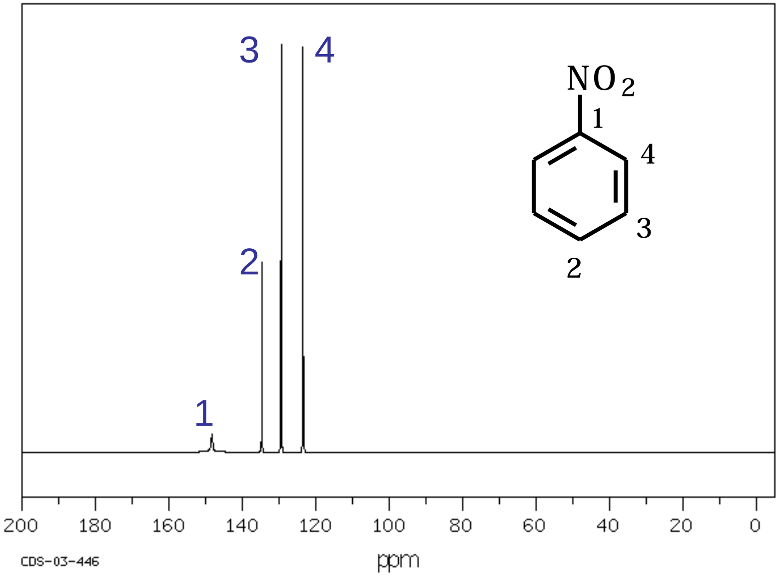


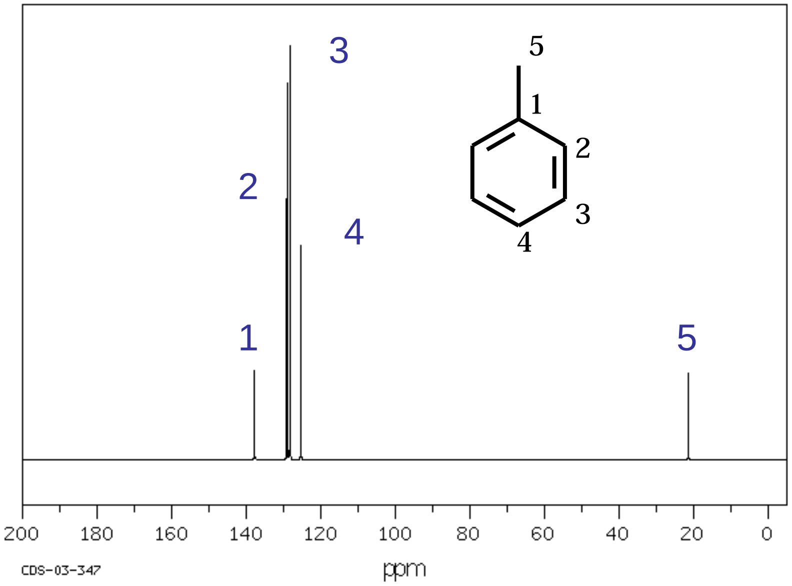
e.g.

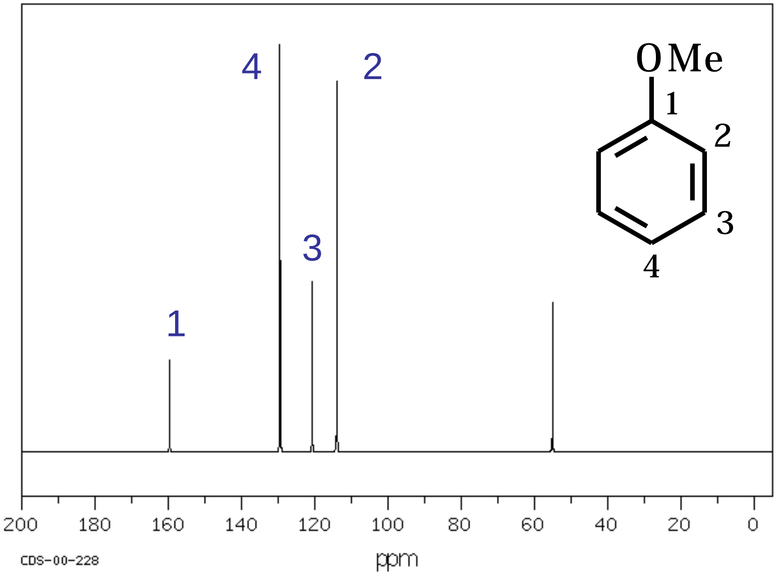


# NMR $^{13}$C of benzene derivatives

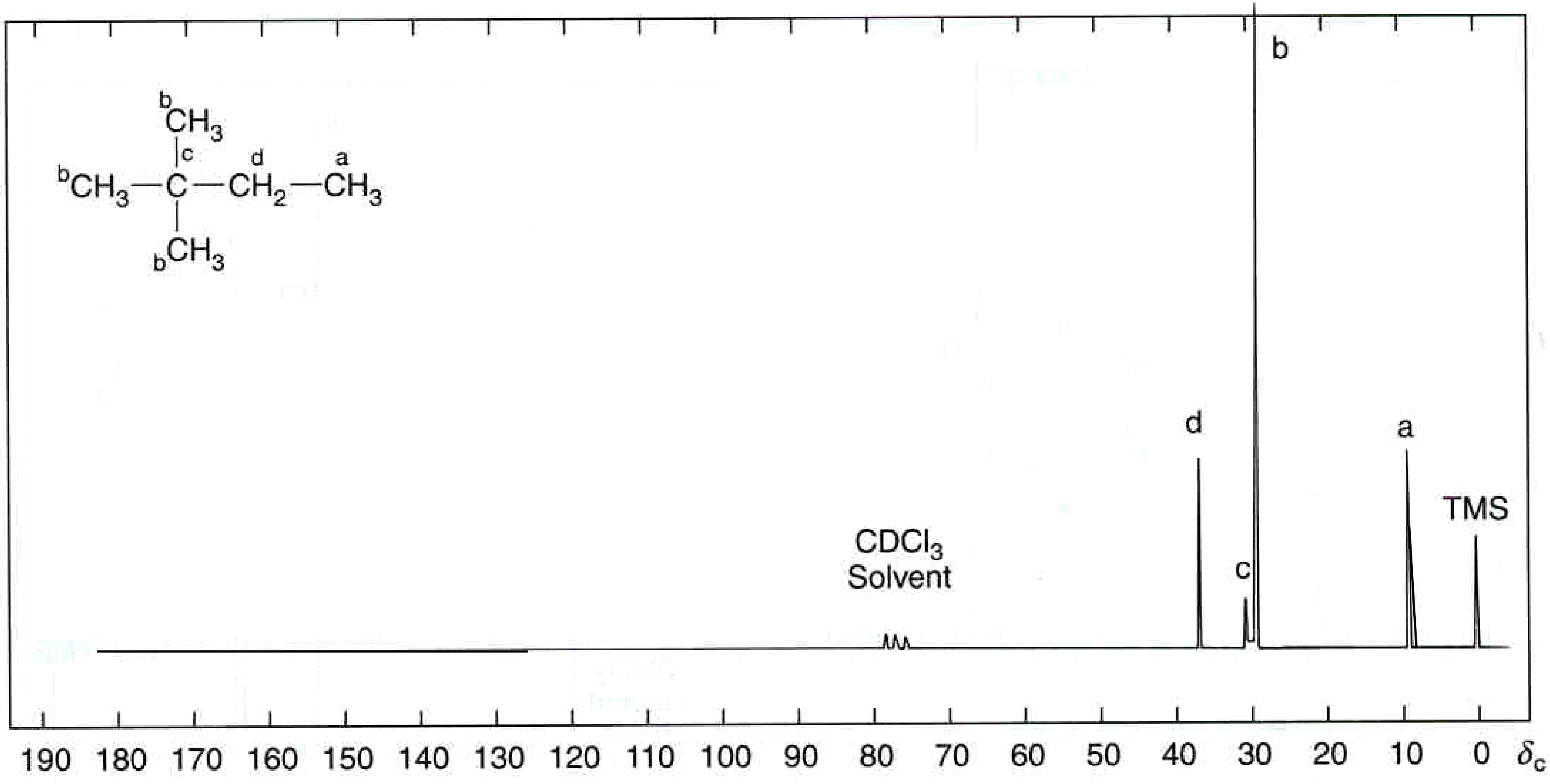




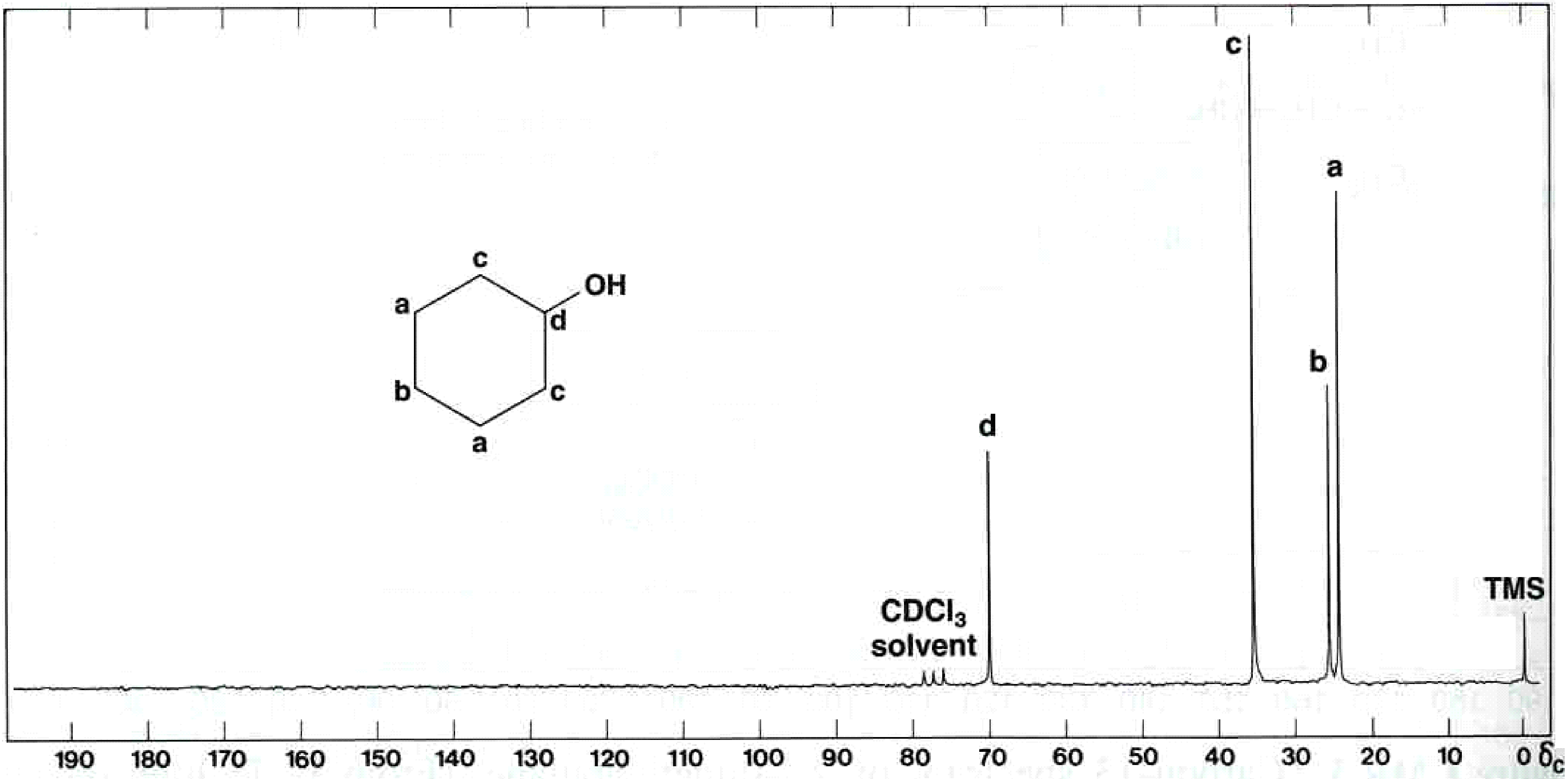




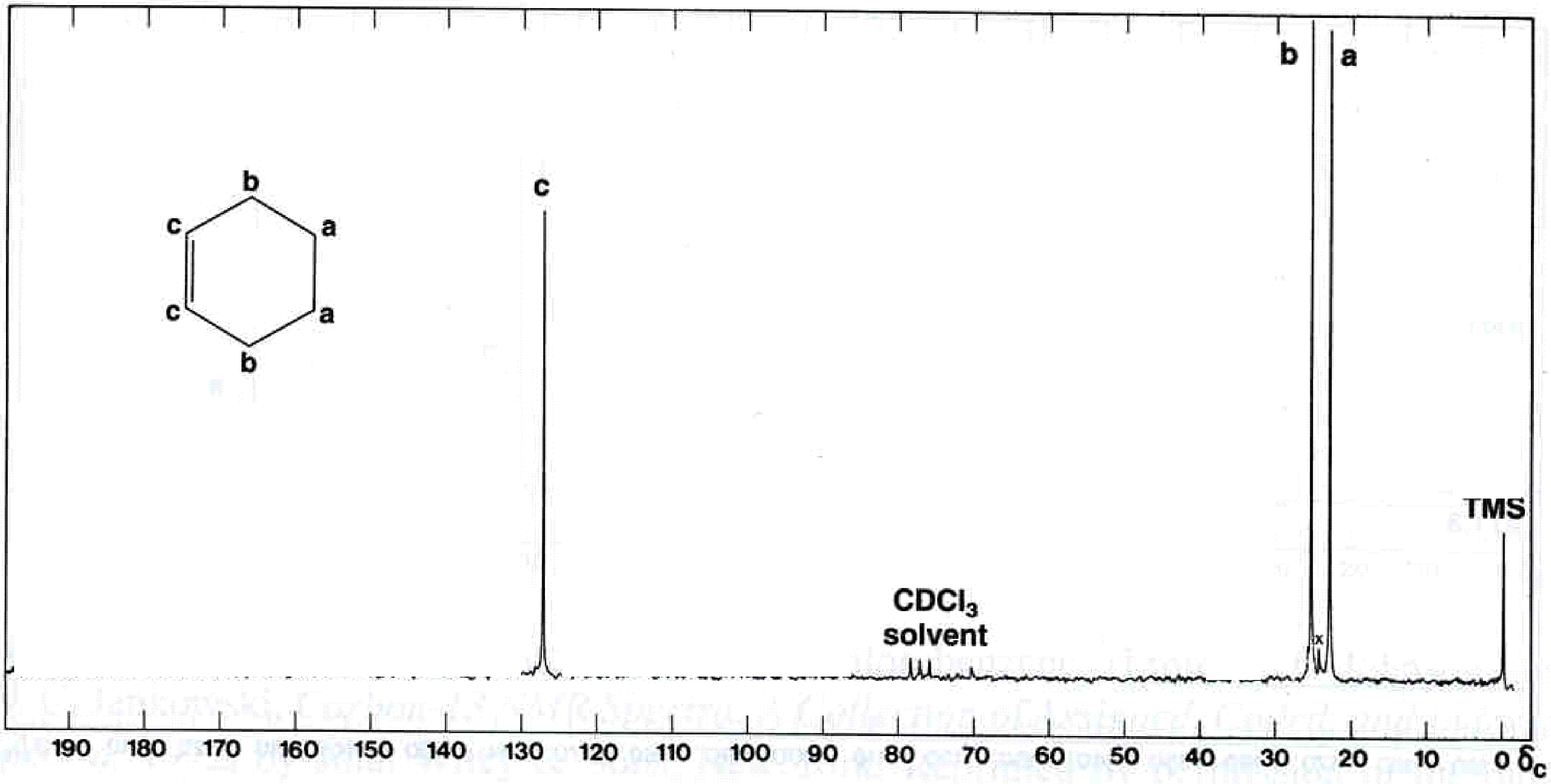
# 2,2-DIMETILBUTANO



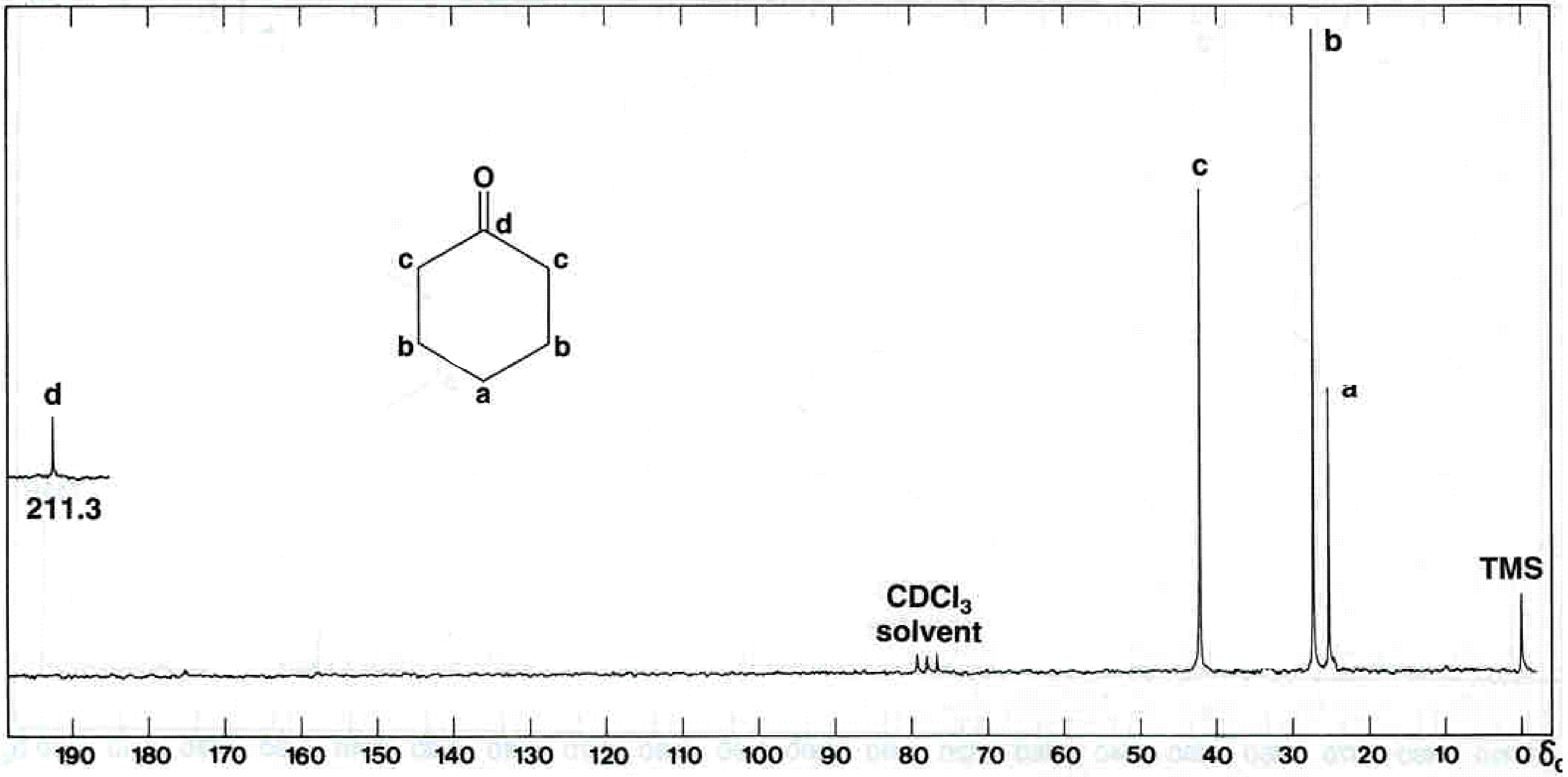
# CICLOHEXANOL



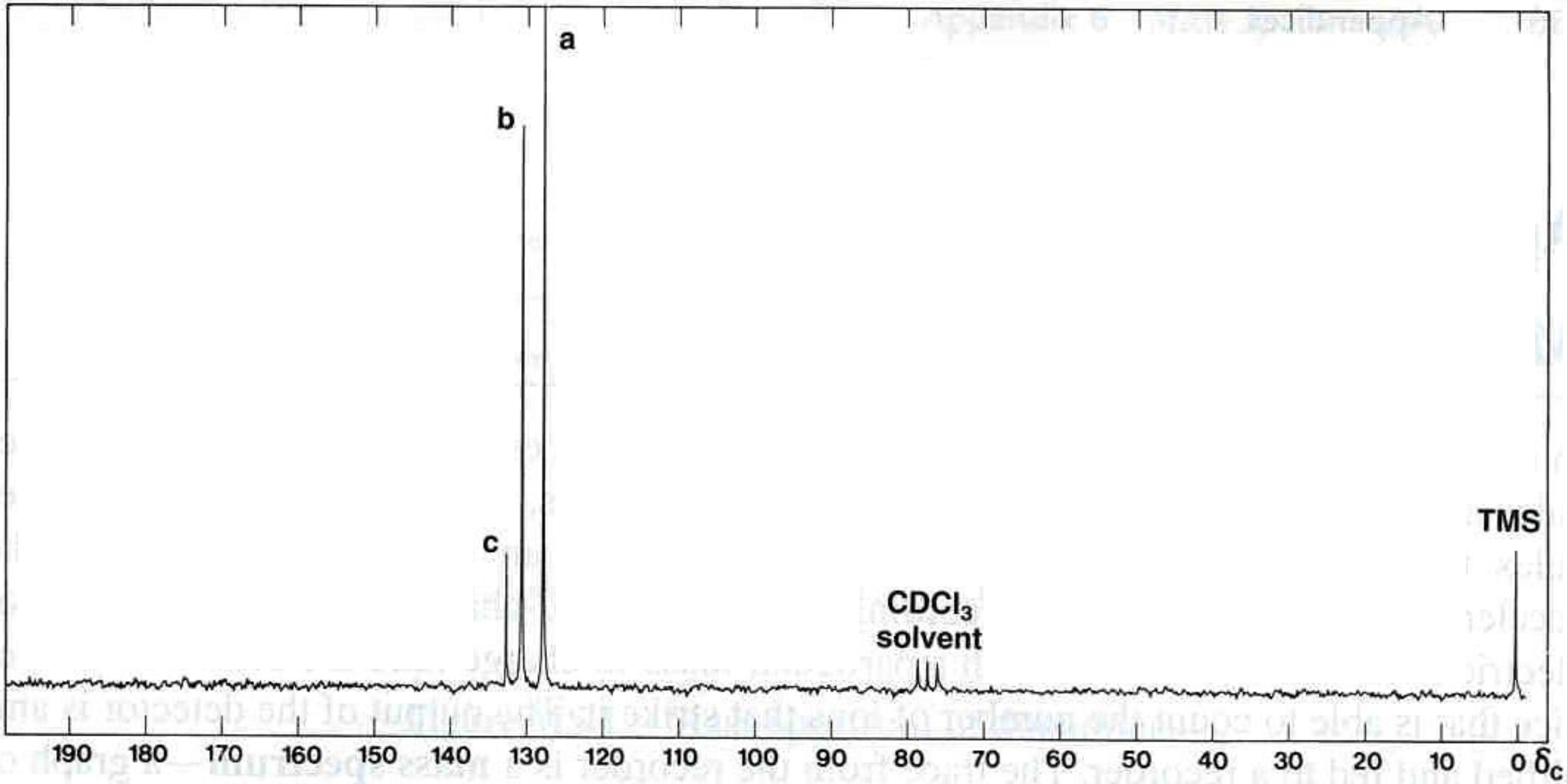
# CICLOHEXENO



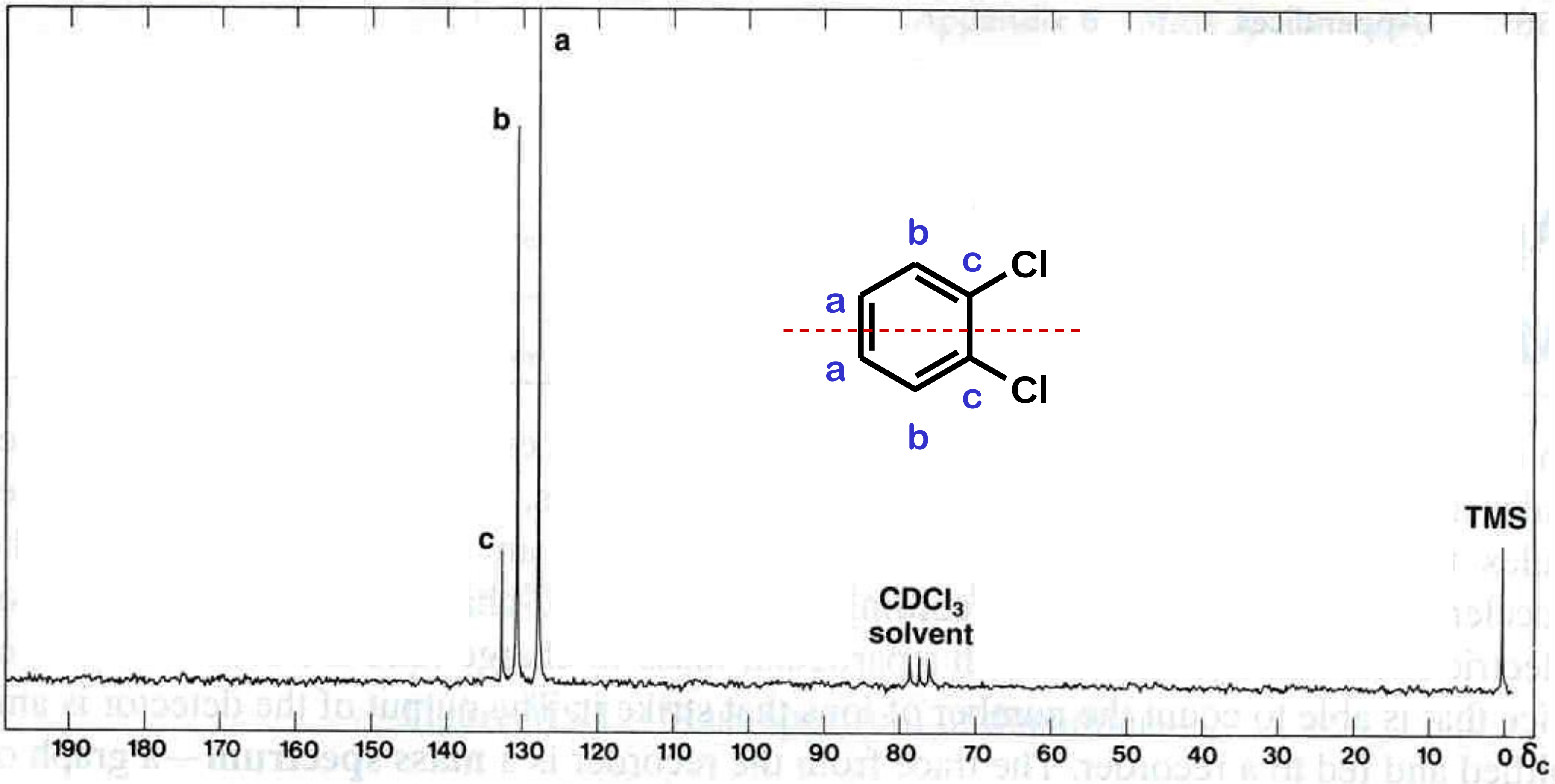
# CICLOHEXANONA



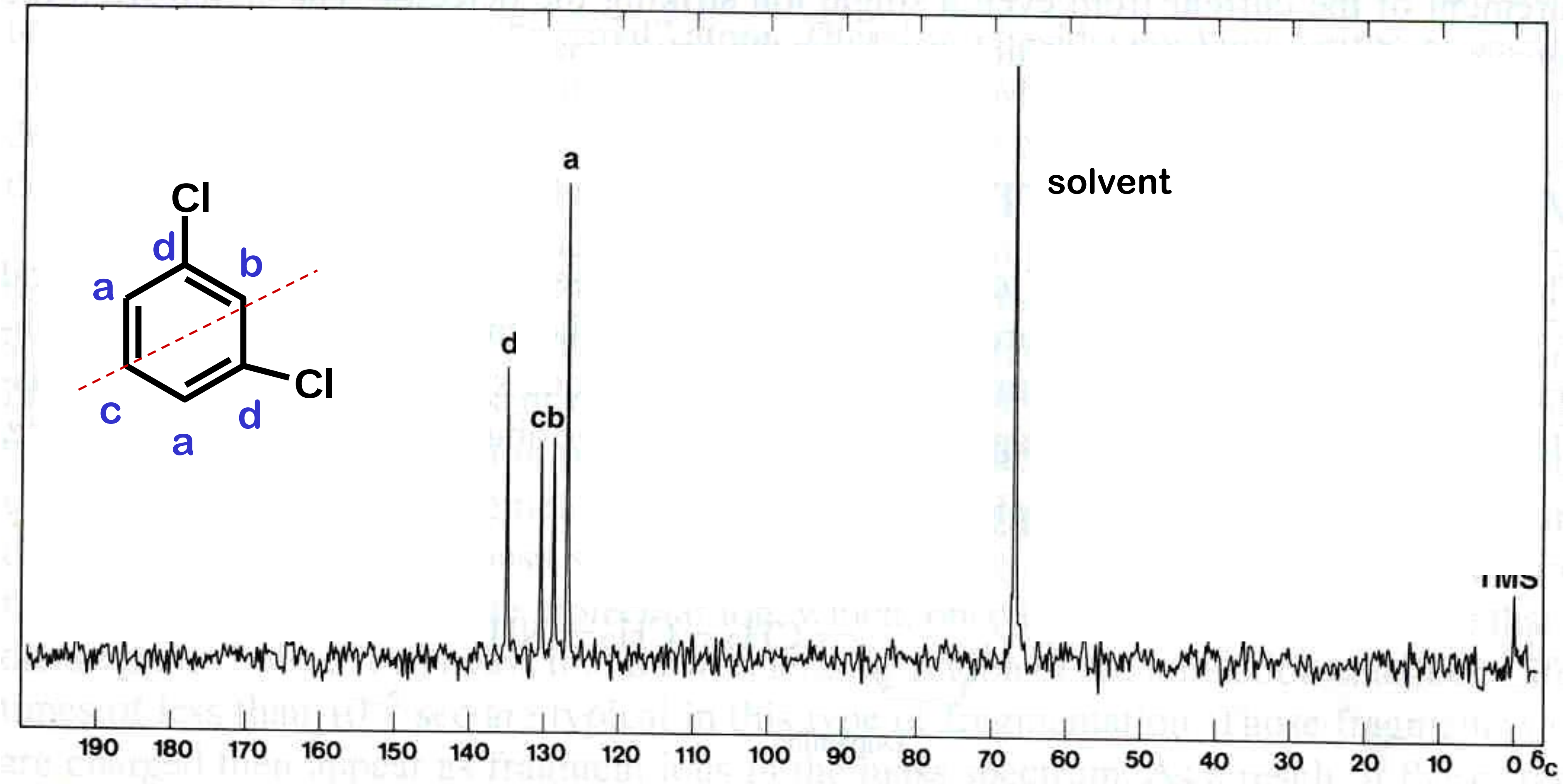
# Qual diclorobenzeno?



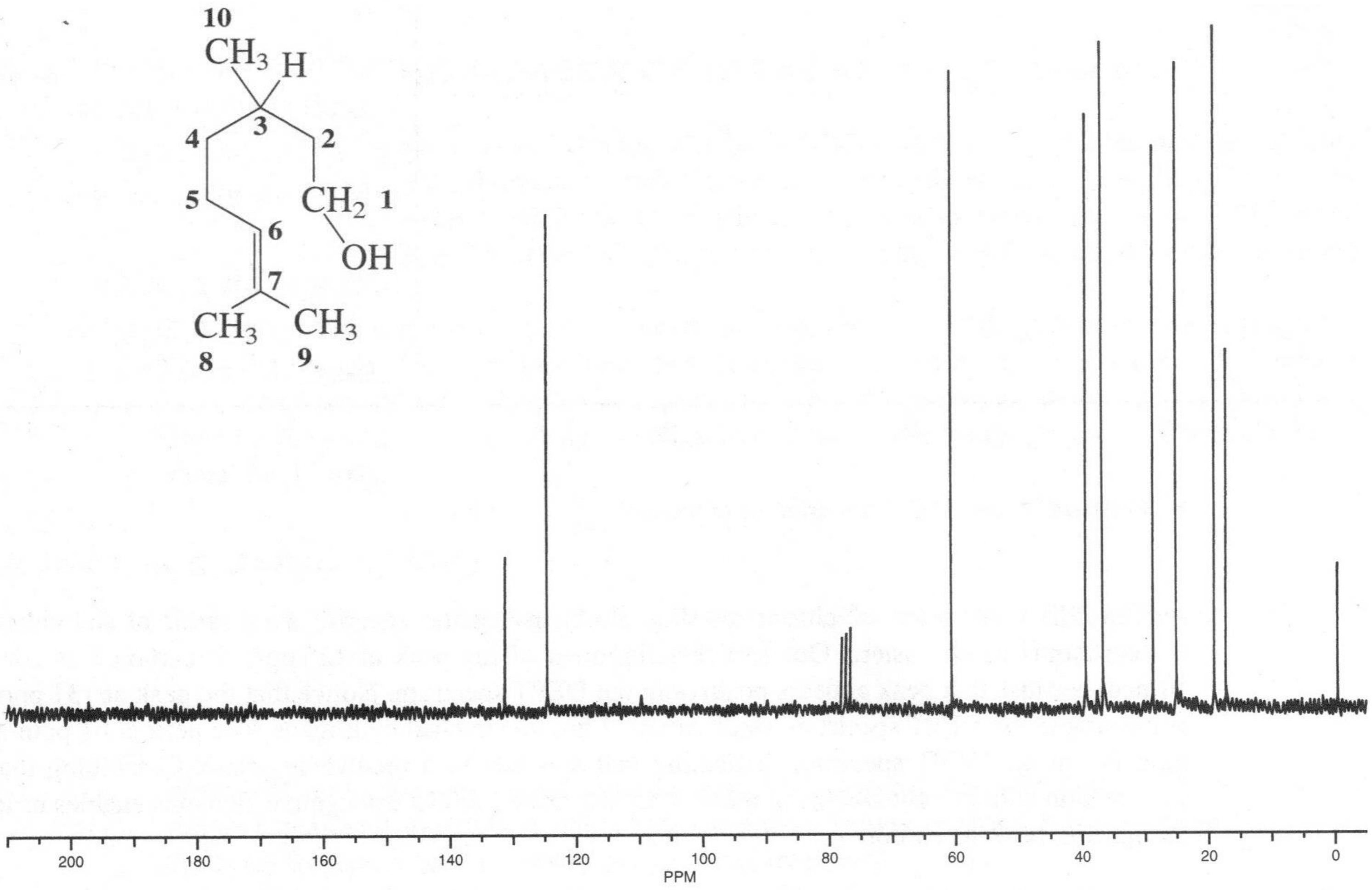
# 1,2-DICLOROBENZENO



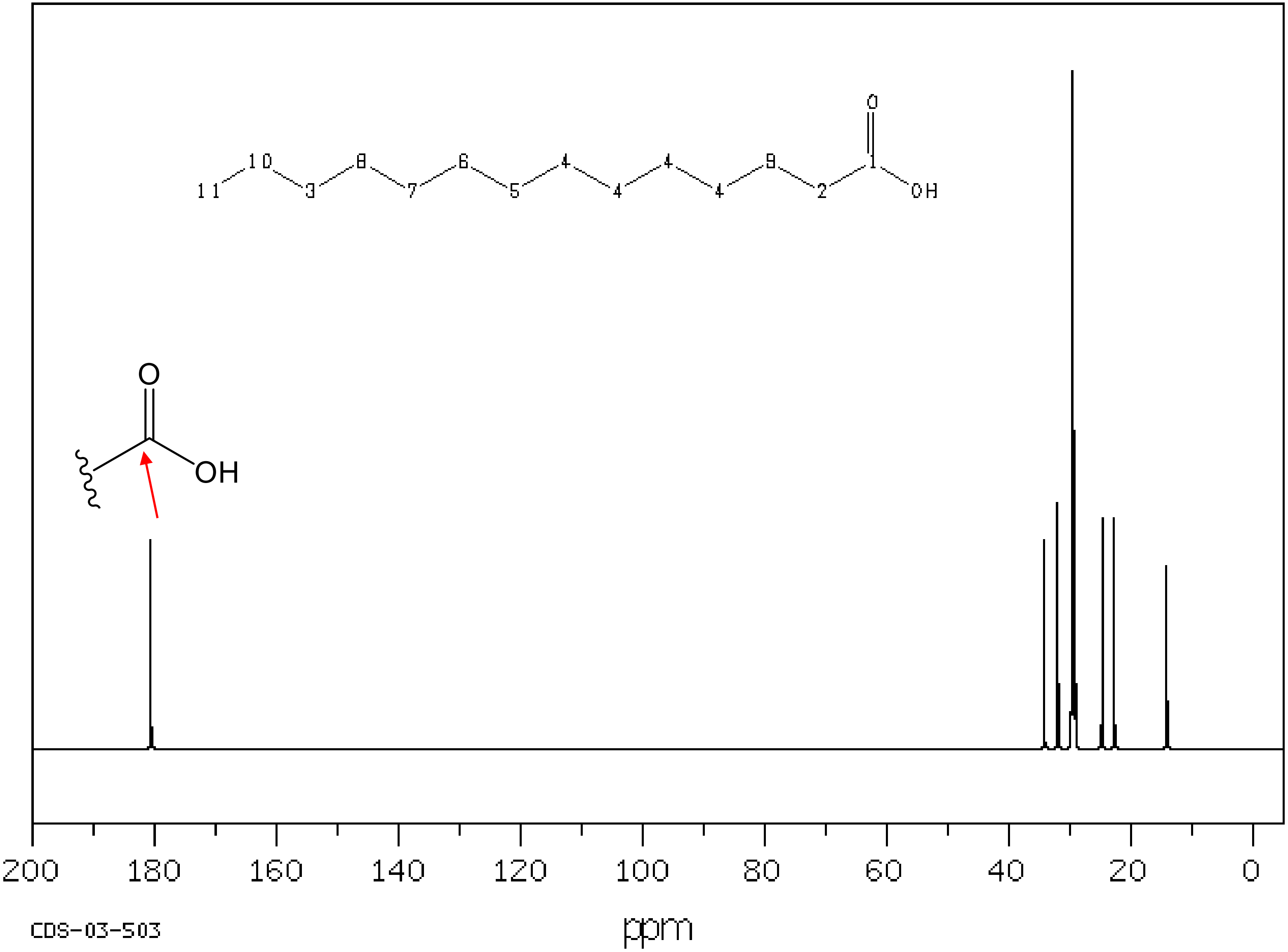
# 1,3-DICLOROBENZENO

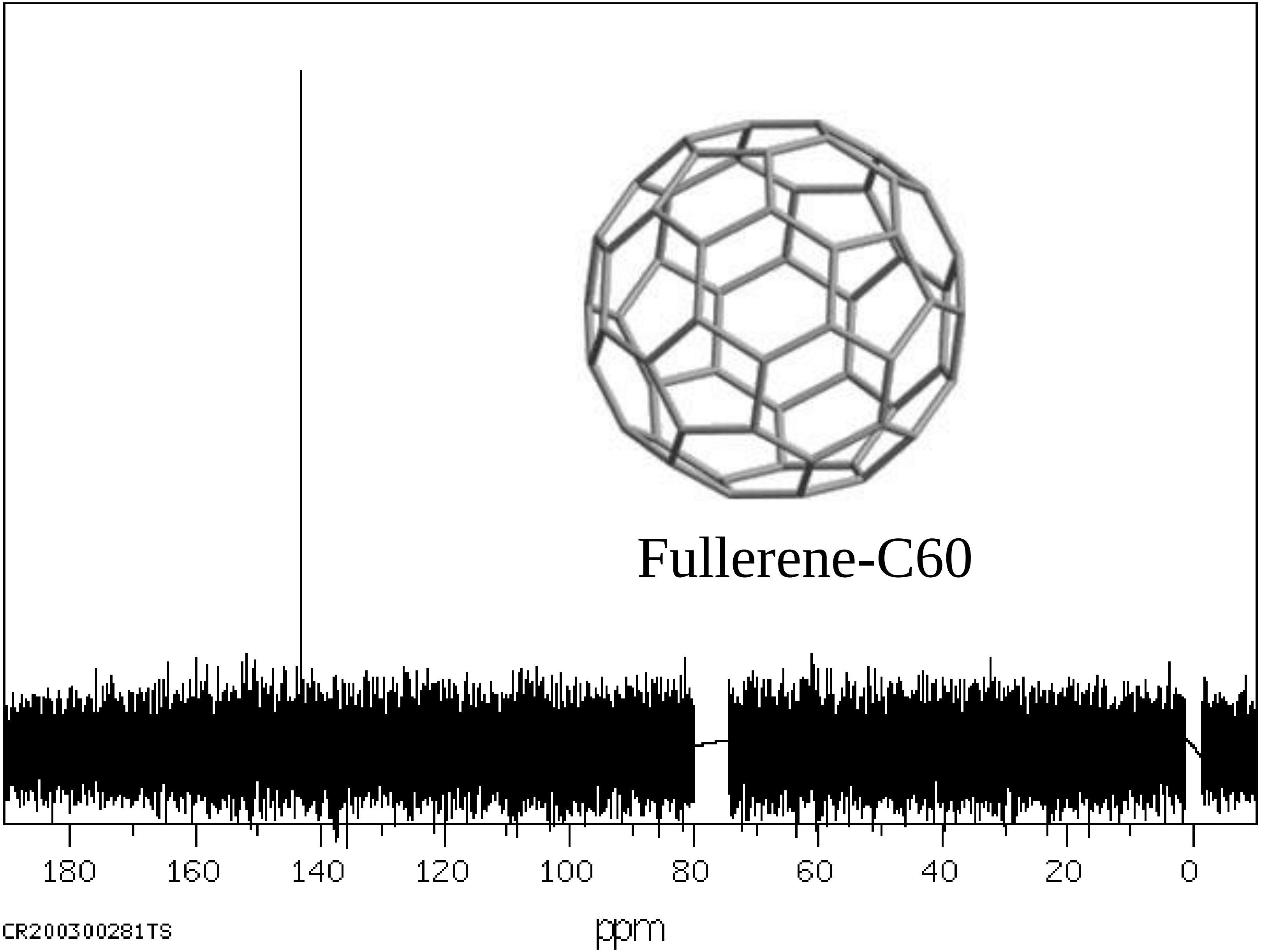


# Espectro de RMN de $^{13}$C do citronelol



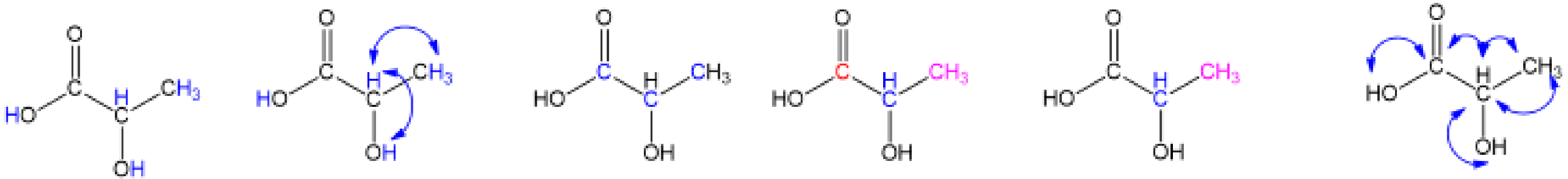
# Espectro de RMN de $^{13}$C do ácido miristico




Fullerene-C60
180
160
140
120
100
80
60
40
20
0
ppm
CR200300281TS

# Sequencia de experimentos em RMN

**RMN 1D** $^{1}$H-NMR → **RMN 2D** $^{1}$H-$^{1}$H COSY → **RMN 1D** $^{13}$C-NMR → **RMN 1D** DEPT → **RMN 2D** $^{1}$H-$^{13}$C HSQC → **RMN 2D** $^{1}$H-$^{13}$C HMBC



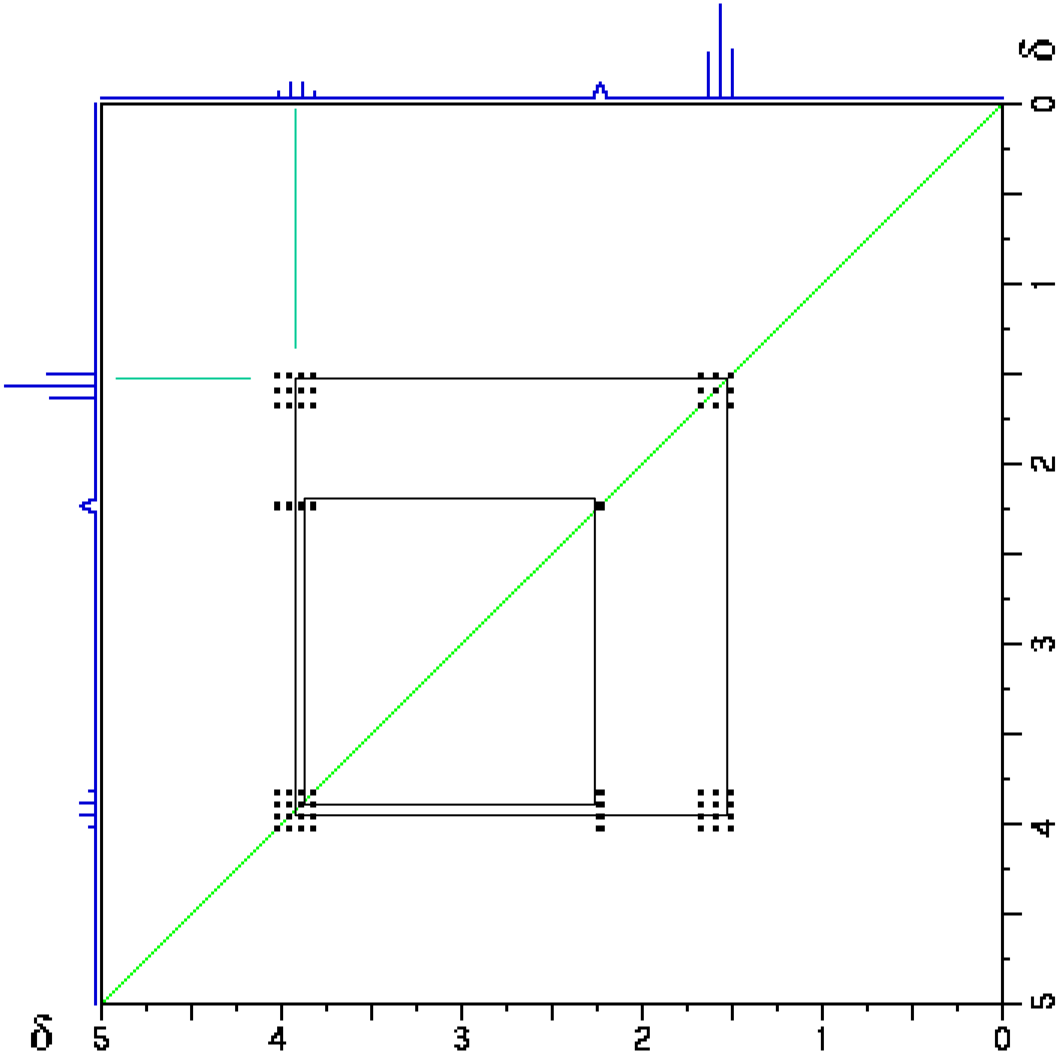
atribui os H baseados no deslocamento químico, padrão e constante de acoplamento

Determina o número de H ligados a cada carbono (C, CH, $CH_2$ e $CH_3$)

Determina quais H estão ligados a quais carbonos

Determina a conectividade entre H e os carbonos (3-4 ligações)

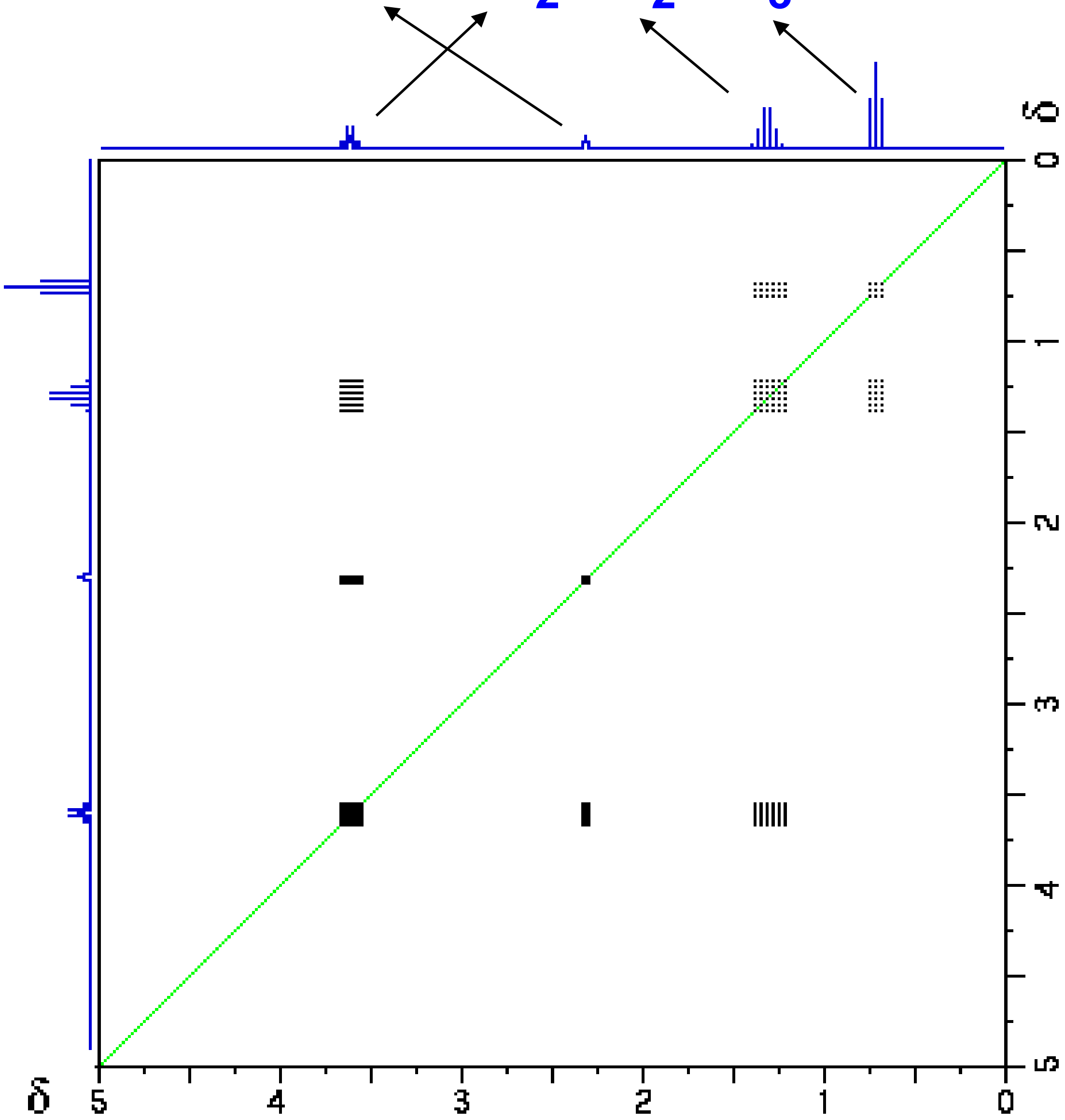
# Espectro de COSY $^1H$-$^1H$ para o etanol



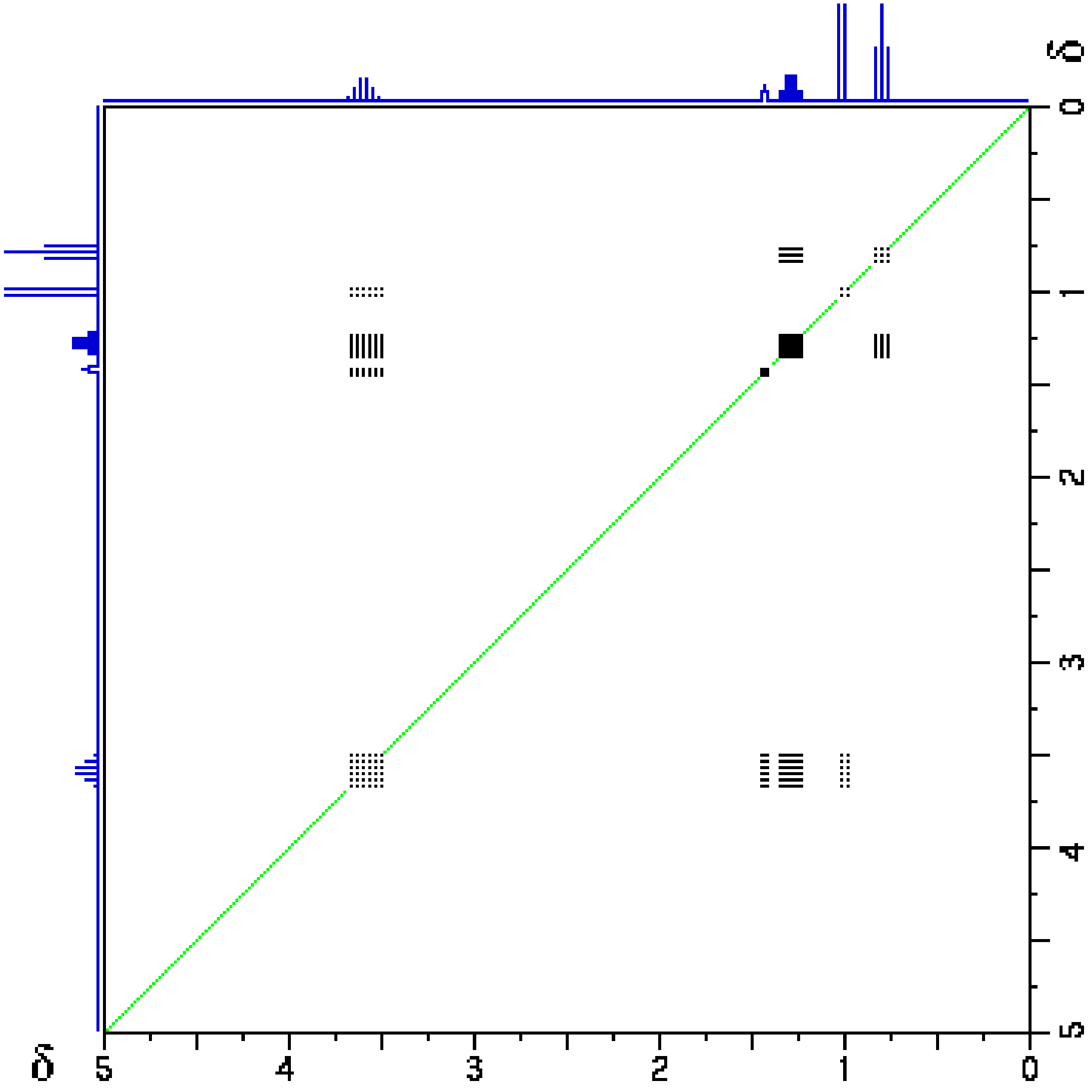
COSY: Correlational spectroscopy

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

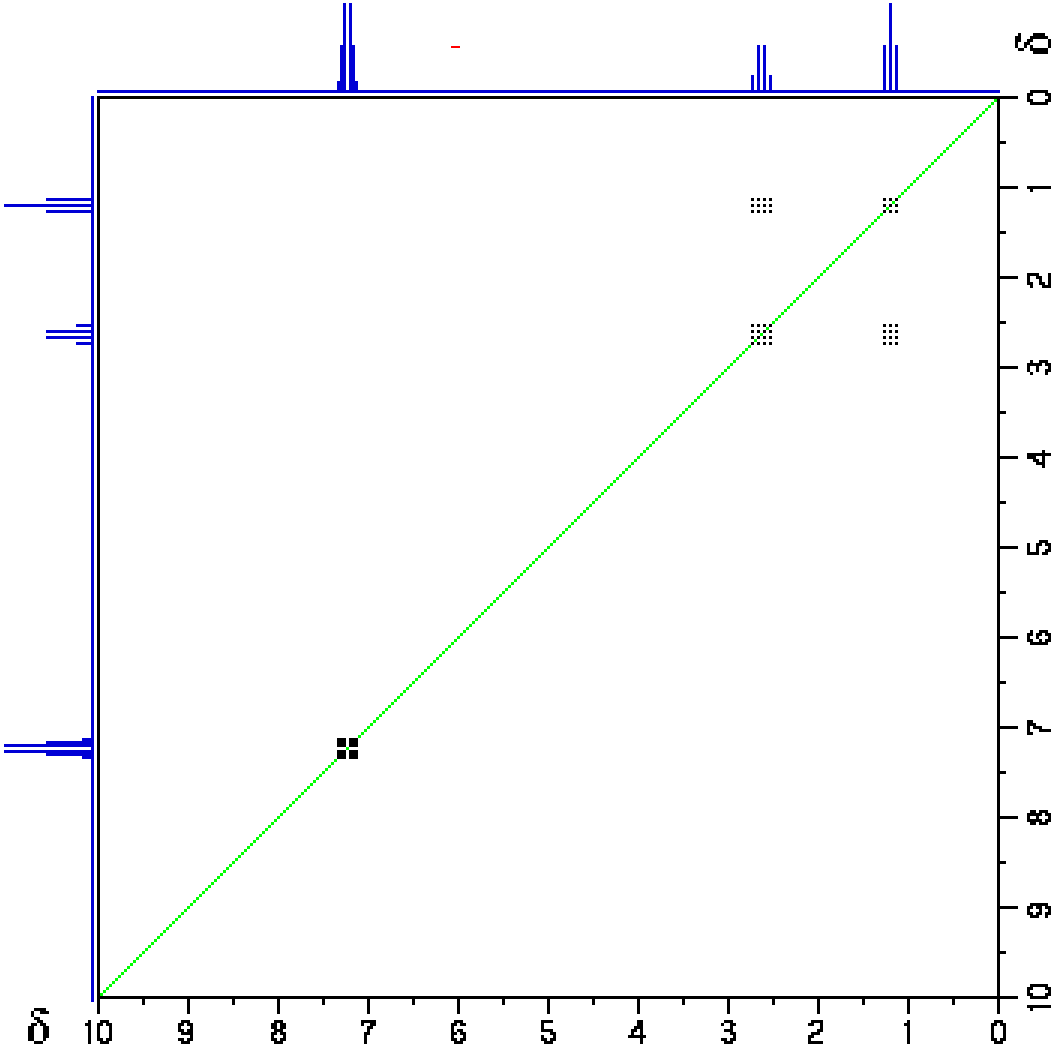
**$HOCH_2CH_2CH_3$**



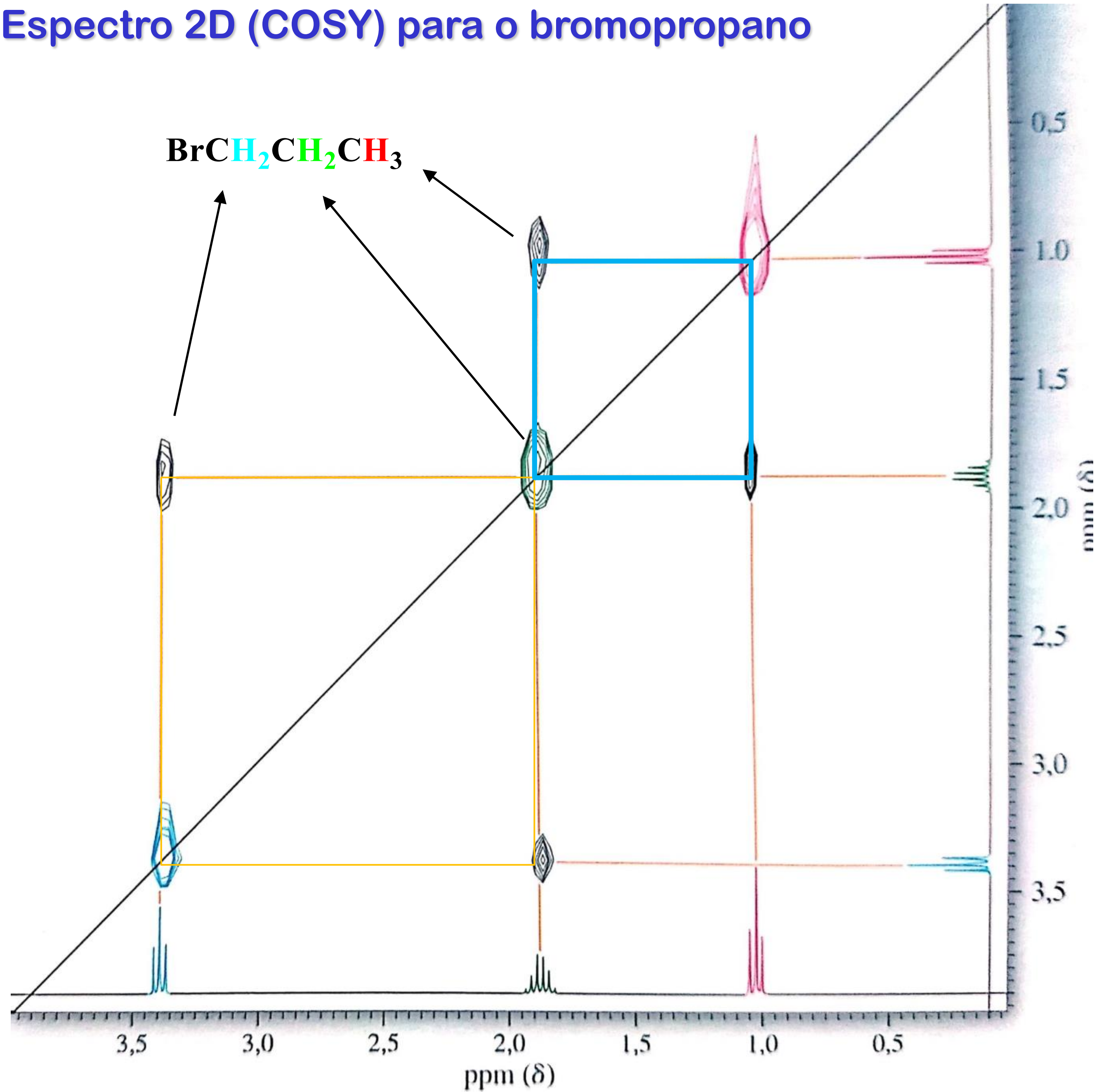
# Espectro de COSY $^1H$-$^1H$ para 2-butanol



# Espectro de COSY $^1$H-$^1$H para o etilbenzeno



# Espectro 2D (COSY) para o bromopropano



# Espectro 2D (HETCOR) para o bromopropano

**C-H diretamente ligados:**

**HETCOR**
**HMQC**
**HSQC**

**técnicas que se equivalem**