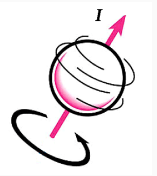

Ressonância Magnética Nuclear - RMN

Espectroscopia

Lucas Colucci Ducati

22 de maio de 2018

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Sumário

Constante de Acoplamento Indireta Spin-Spin J - Continuação

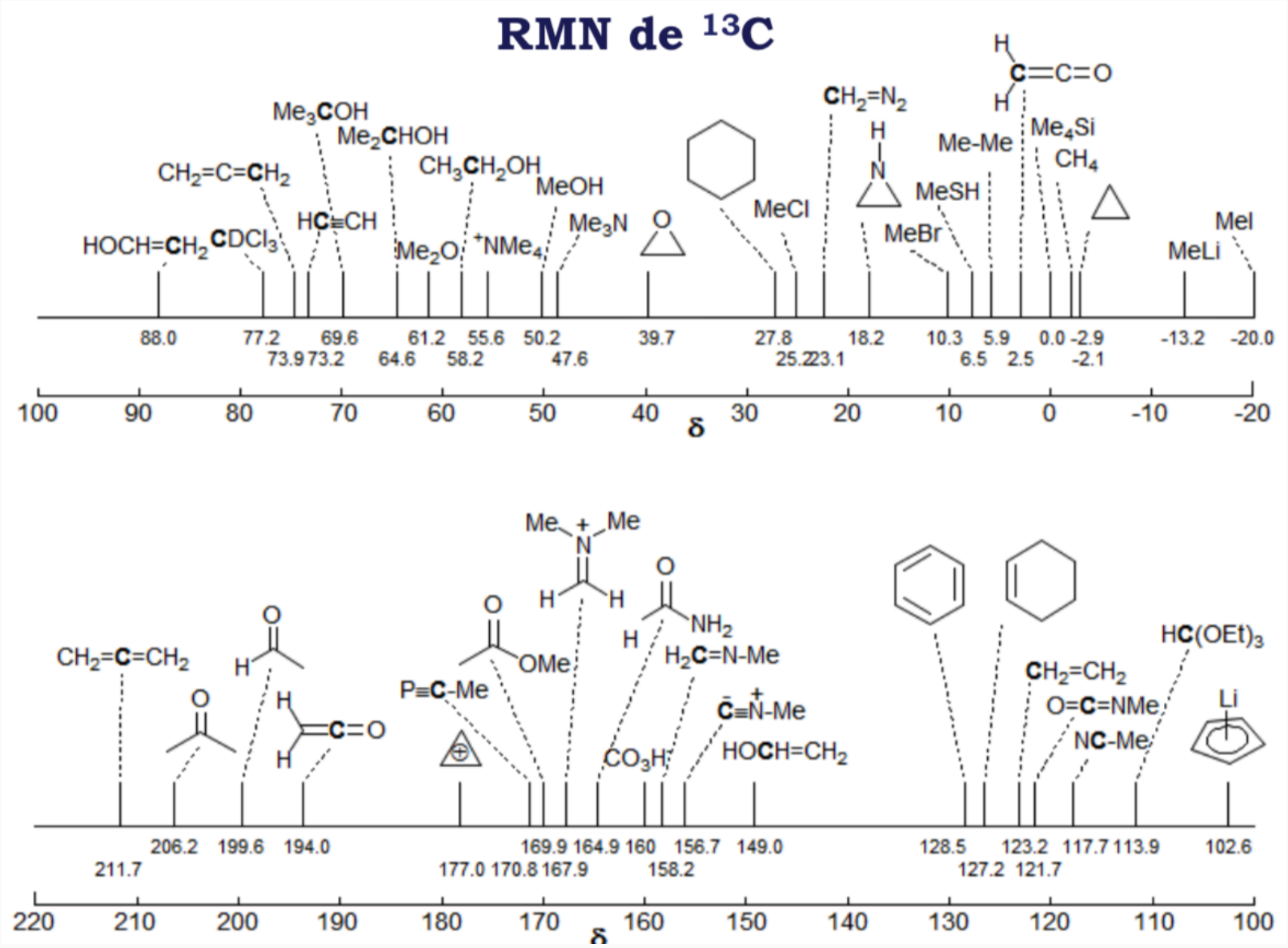
RMN de ^{13}C

Características dos núcleo de ^{13}C e ^{1}H

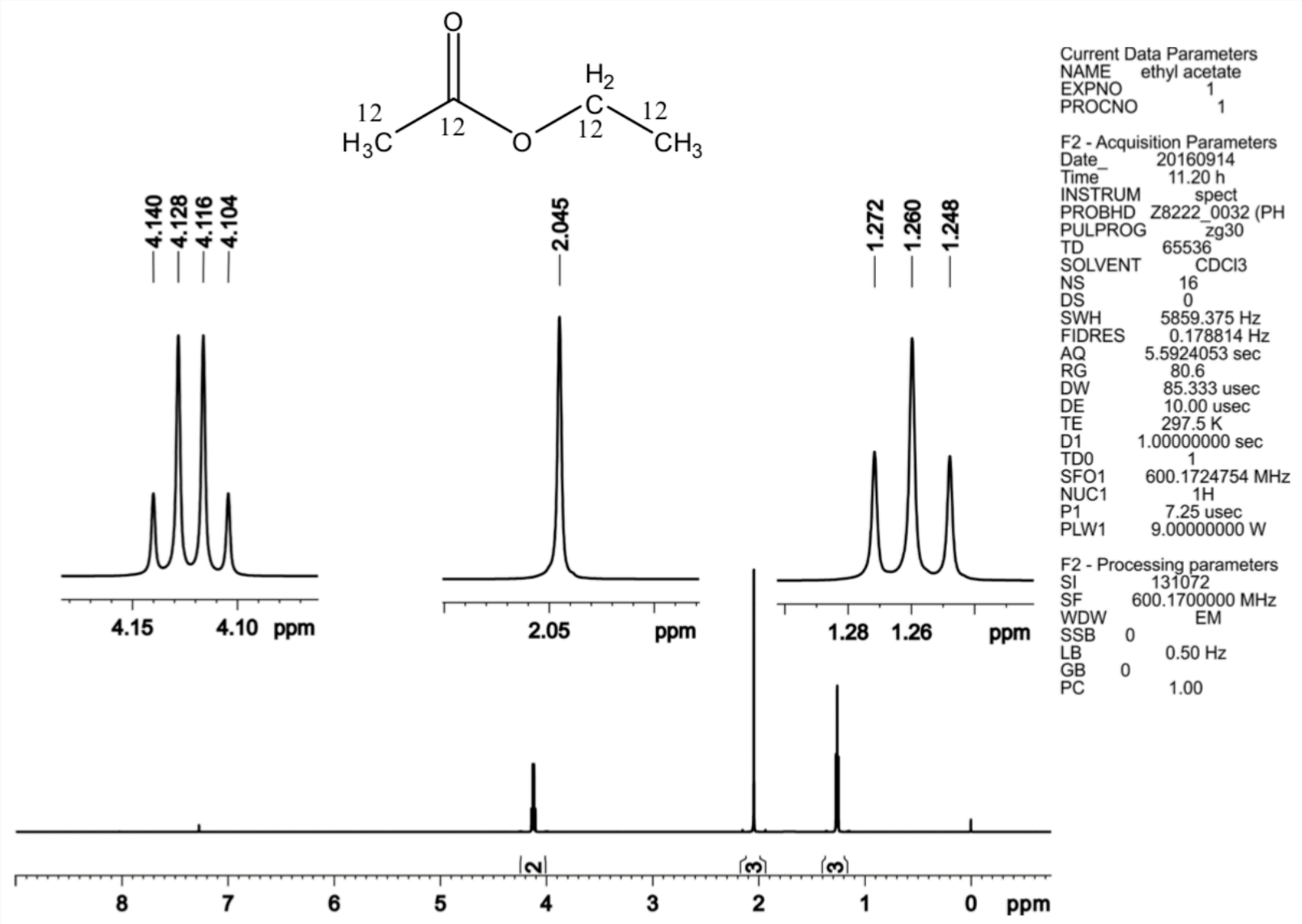
Tabela 1: Propriedades do núcleo de ^{13}C e ^{1}H

	^{13}C	^{1}H
Abundância natural	1%	99,99%
Spin ($\boldsymbol{I}$)	$1/2$	$1/2$
Sensibilidade	1	$5,87 \times 10^{3}$
Razão magnetogírica (γ / rad s^{-1} T^{-1})	$6,7 \times 10^{7}$	$26,7 \times 10^{7}$
Frequência (7,04 T)	75 MHz	300 MHz

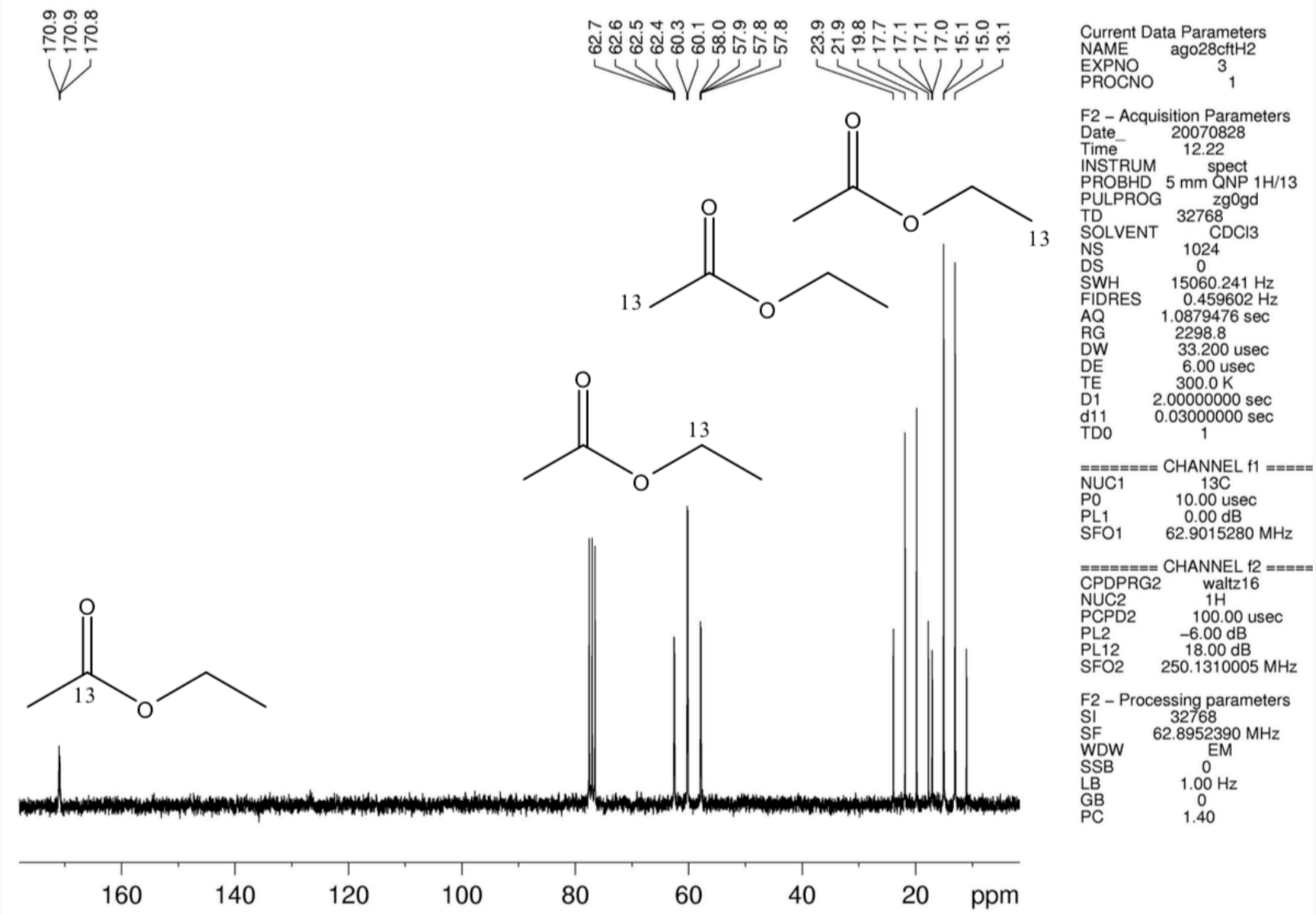
Escala de Deslocamento Químico de ^{13}C



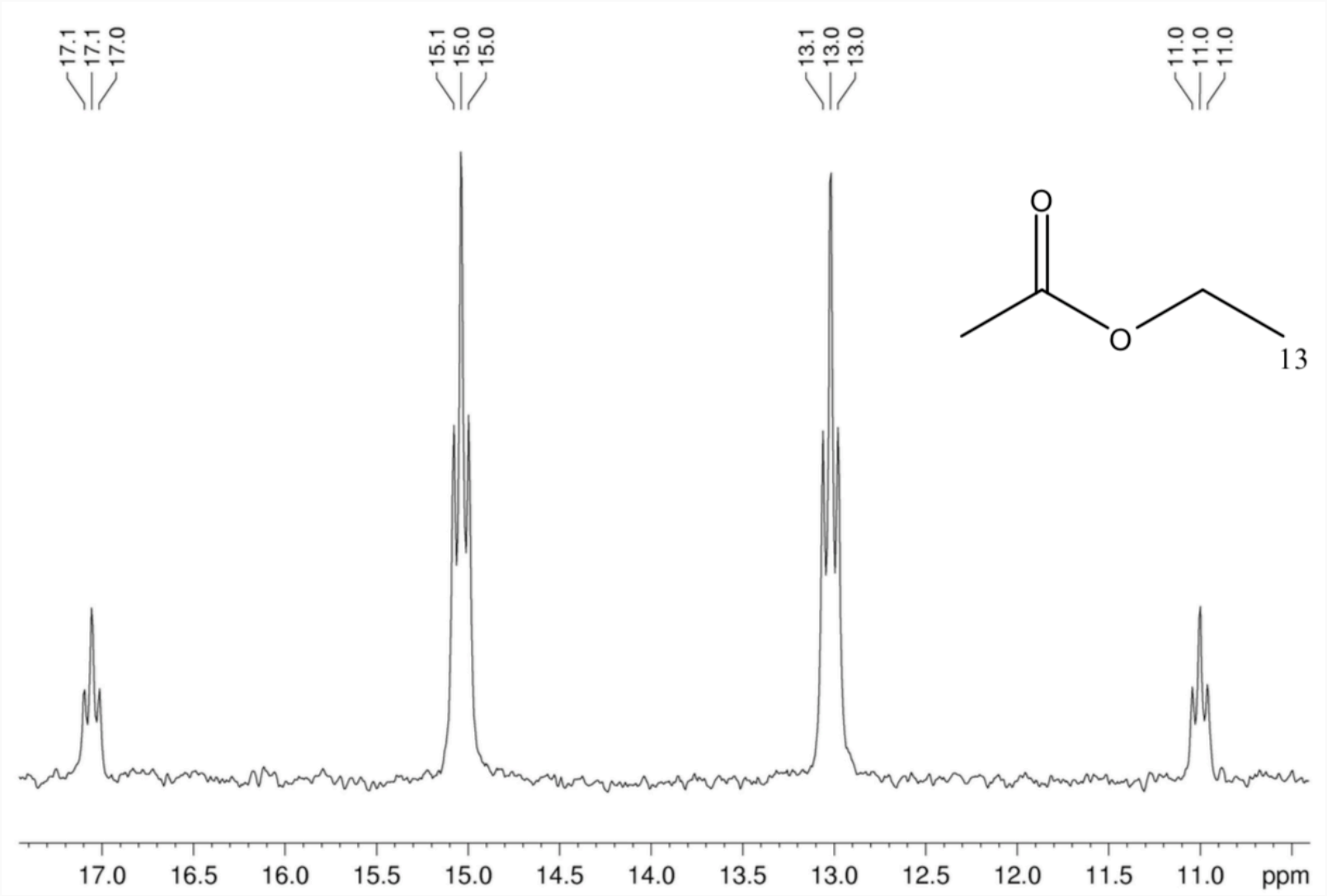
Espectro de ^{1}H do Acetato de Etila



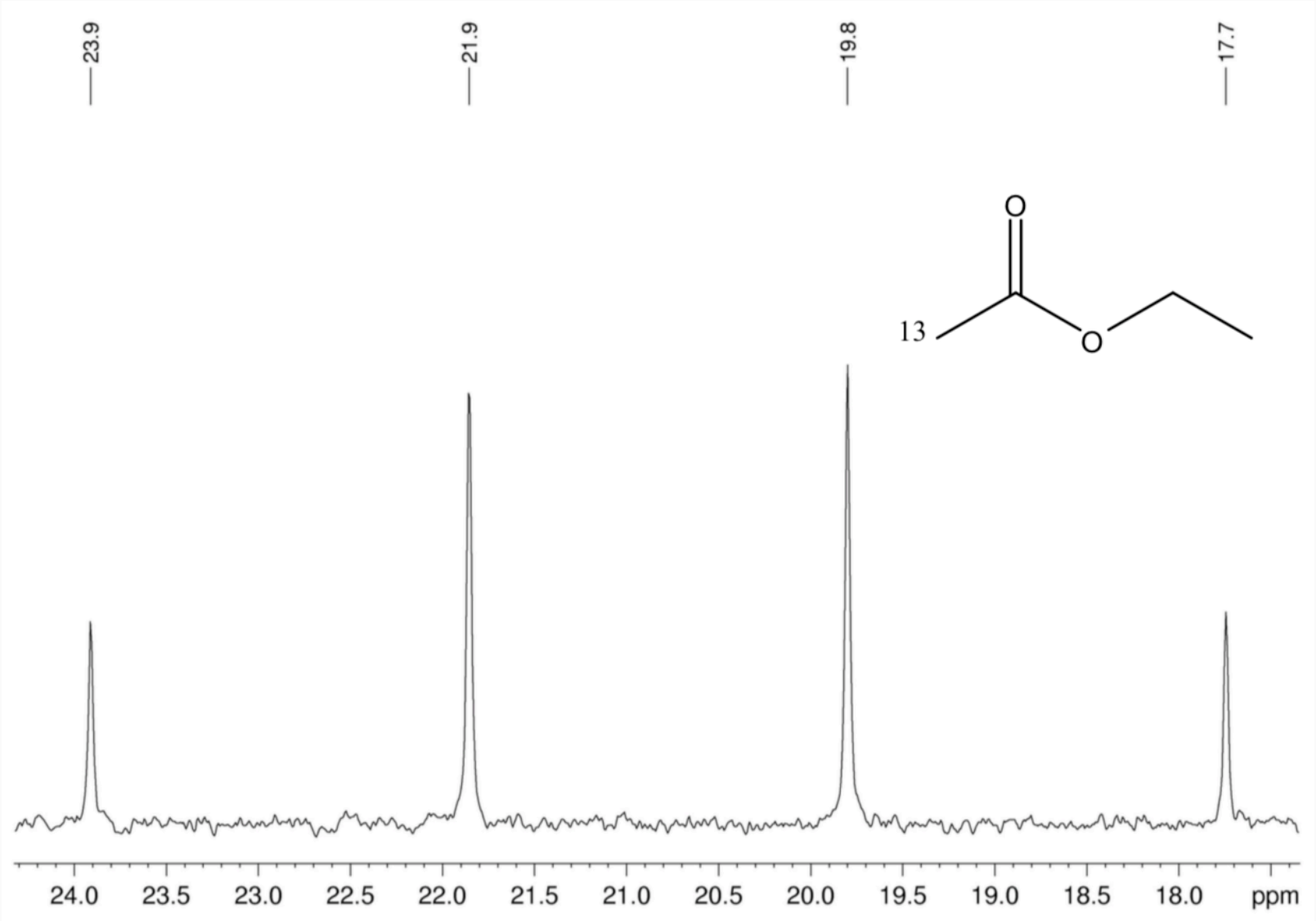
Espectro de ^{13}C Acoplado (de ^{1}H) do Acetato de Etila



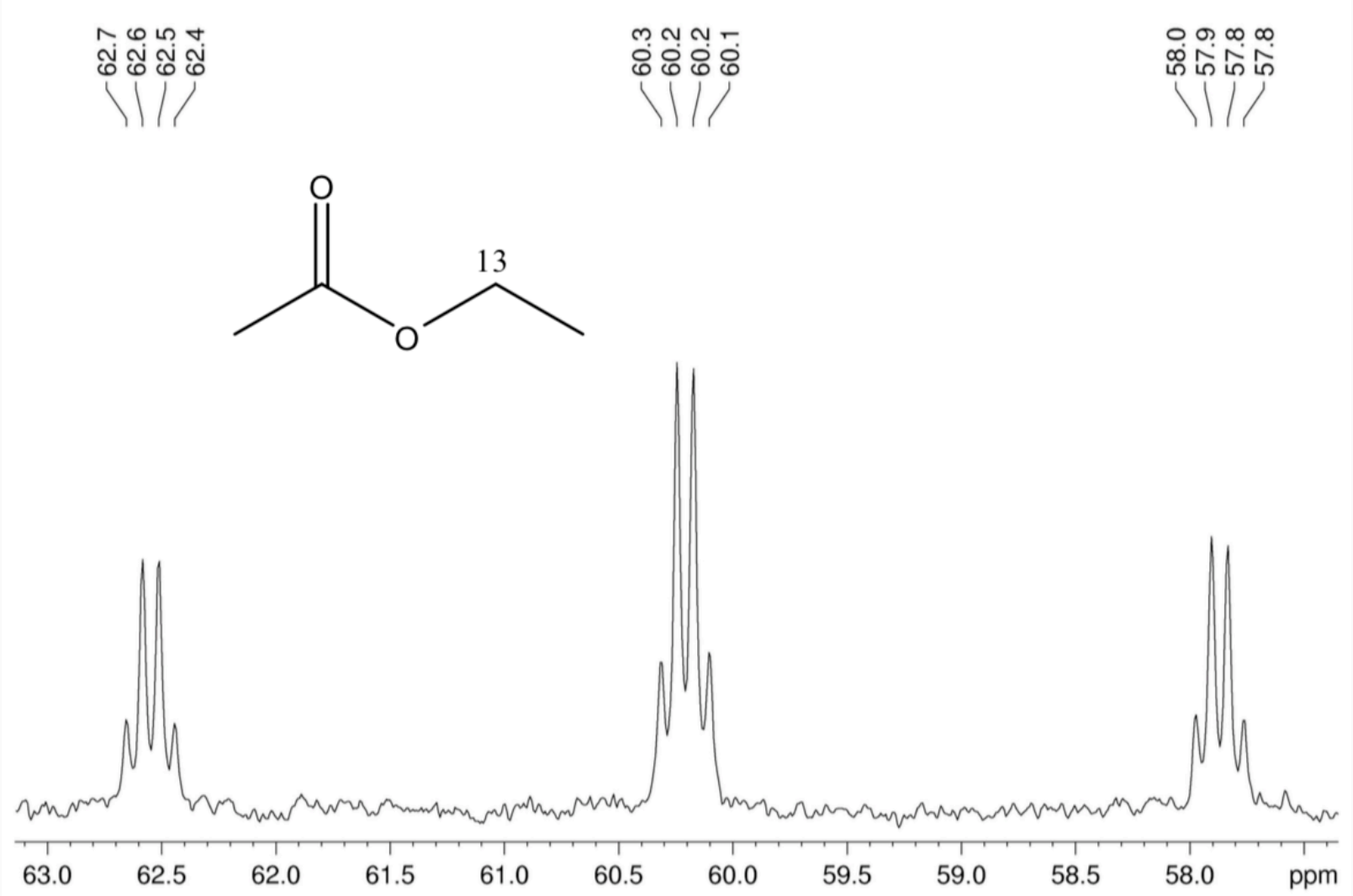
Espectro de ^{13}C Acoplado (de ^{1}H) do Acetato de Etila



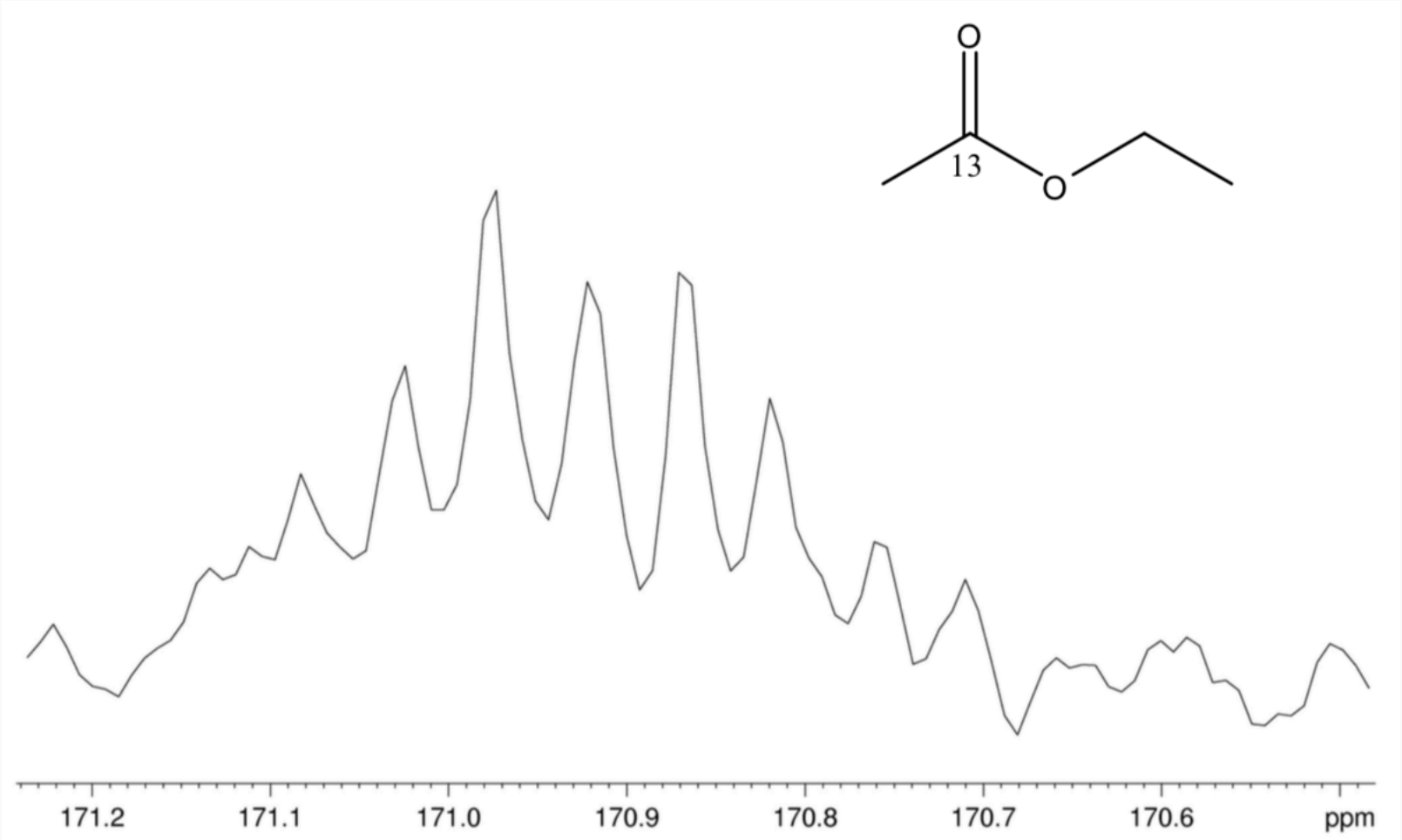
Espectro de ^{13}C Acoplado (de ^{1}H) do Acetato de Etila



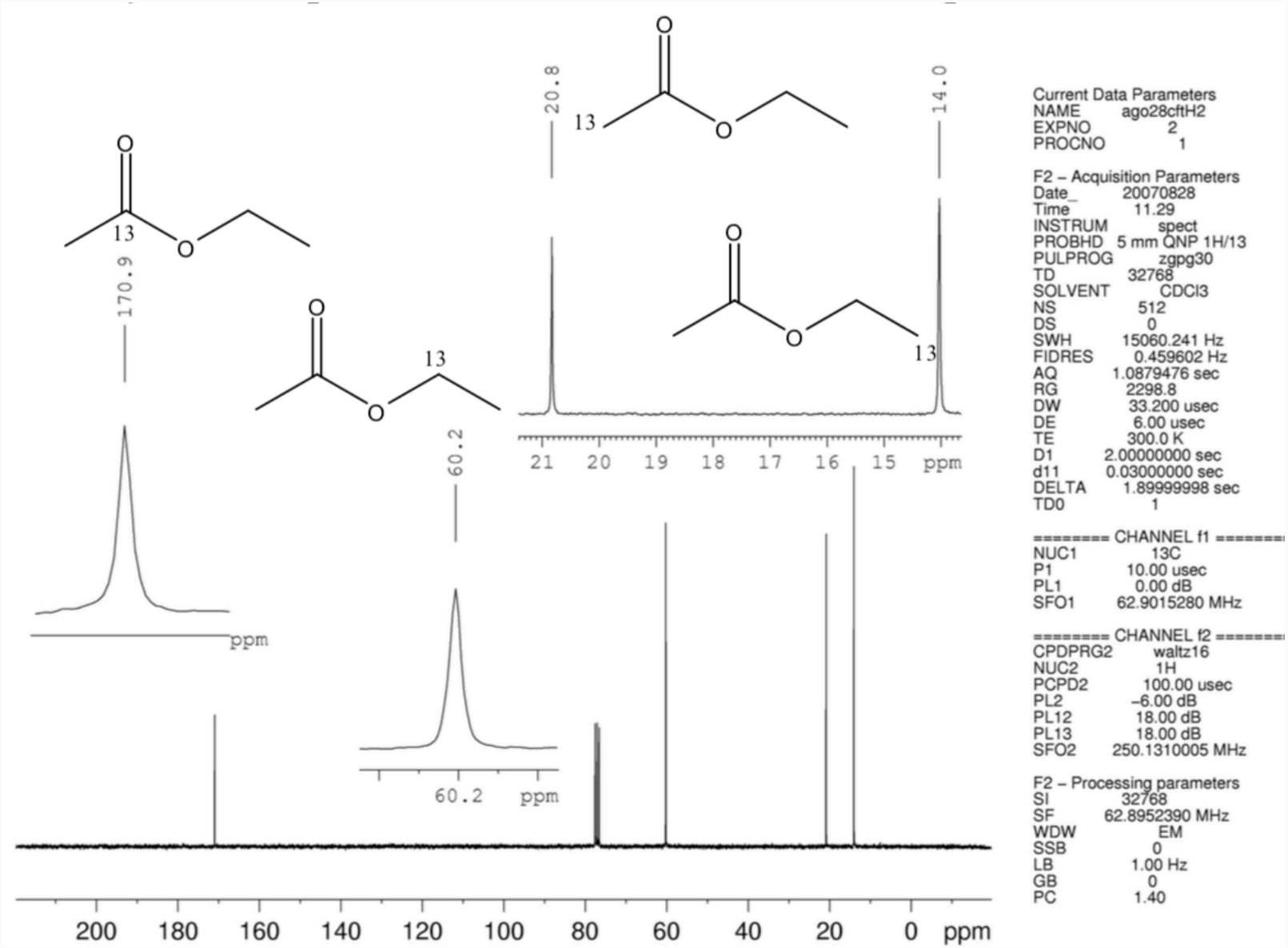
Espectro de ^{13}C Acoplado (de ^{1}H) do Acetato de Etila



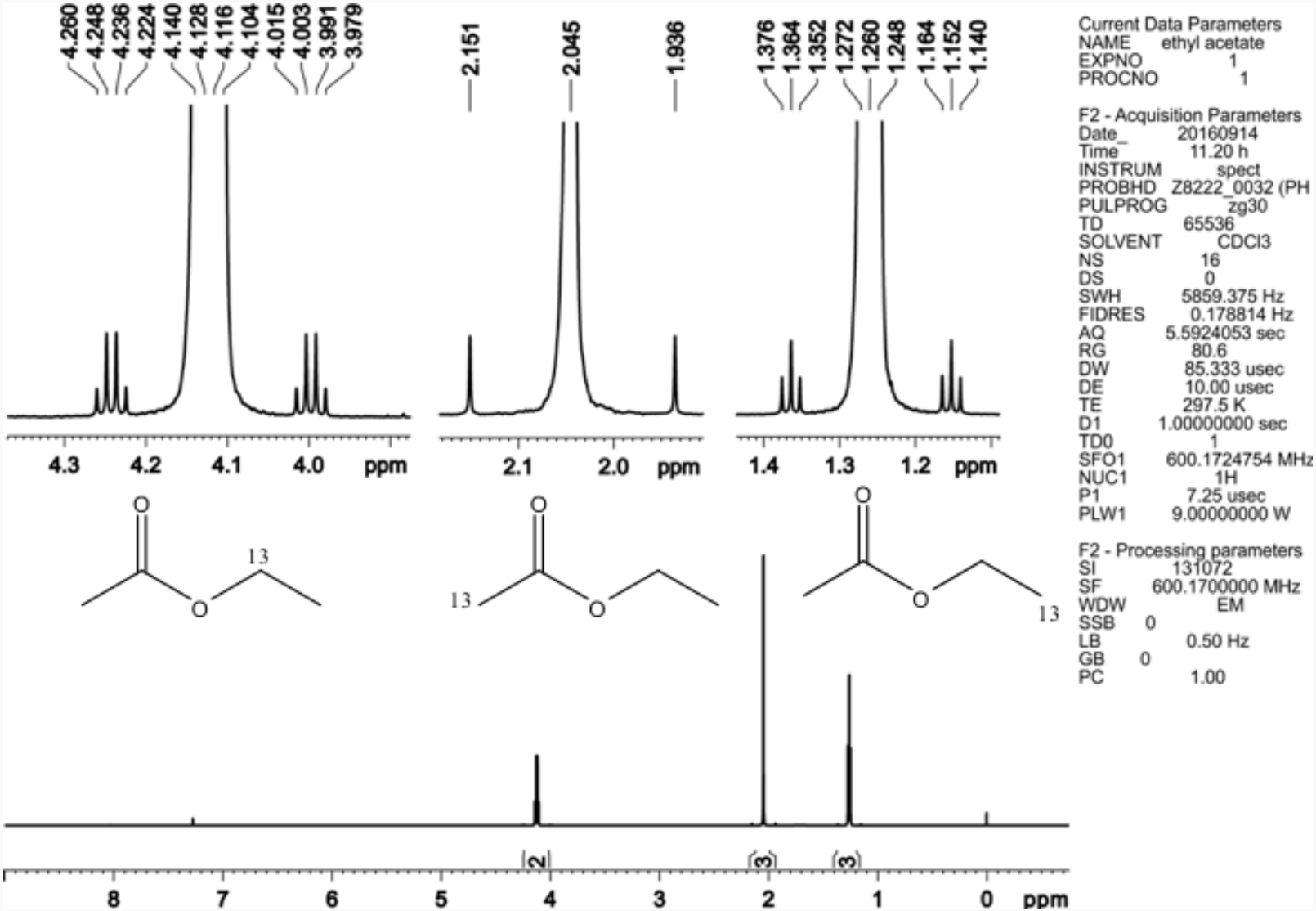
Espectro de ^{13}C Acoplado (de ^{1}H) do Acetato de Etila



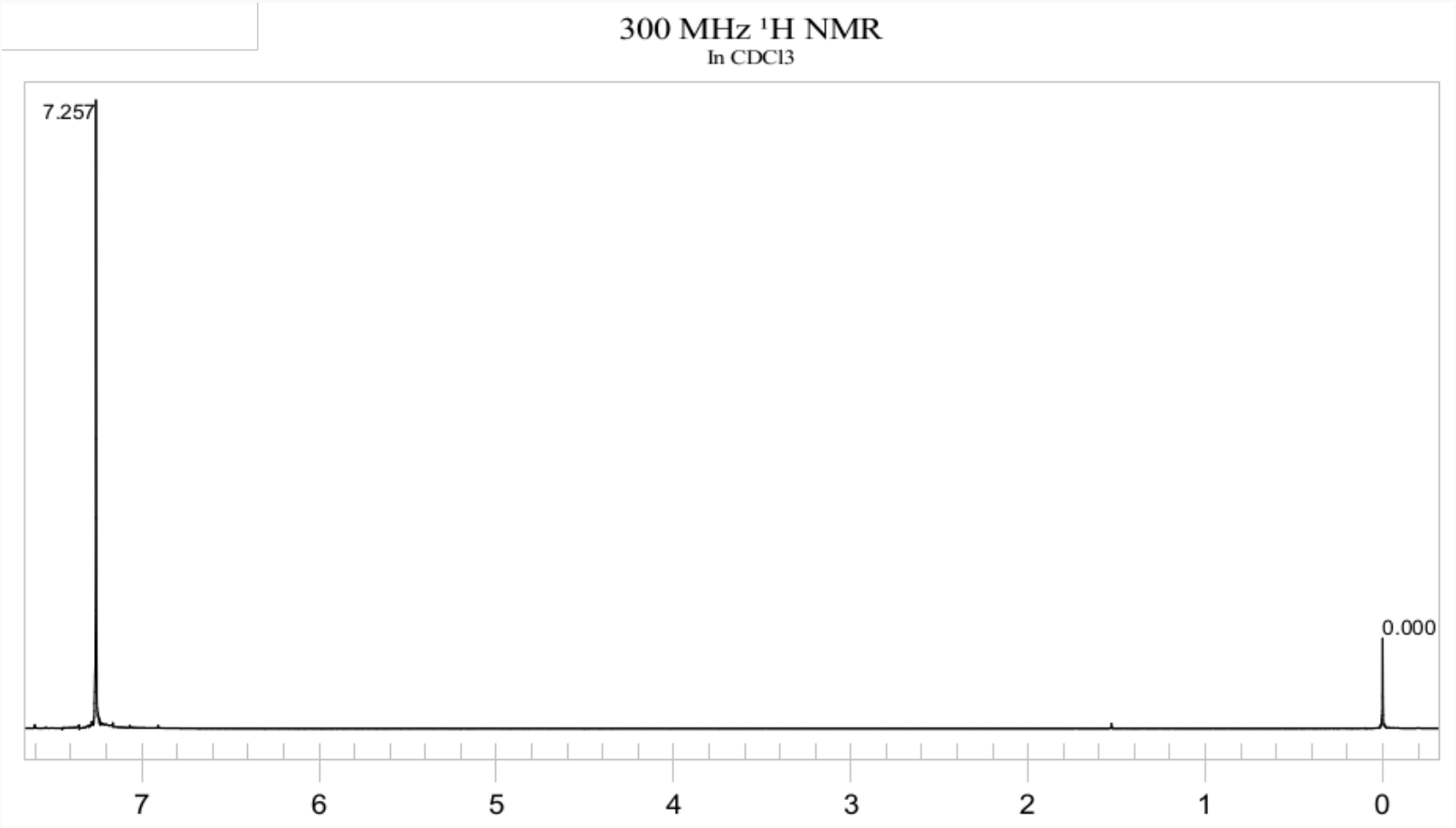
Espectro de ^{13}C Desacoplado (de ^{1}H) do Acetato de Etila



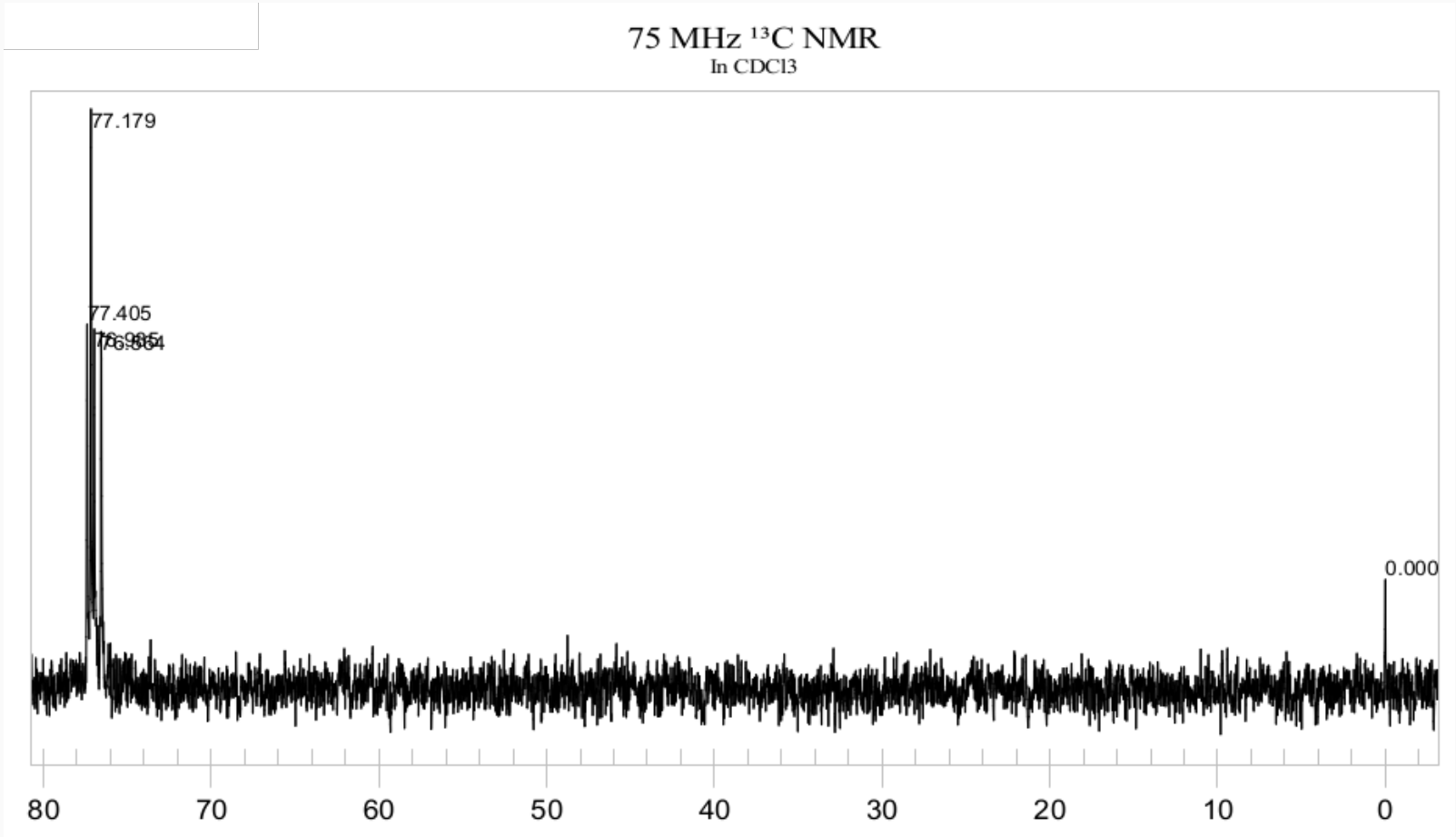
Espectro de ^{1}H do Acetato de Etila - Picos Satélites



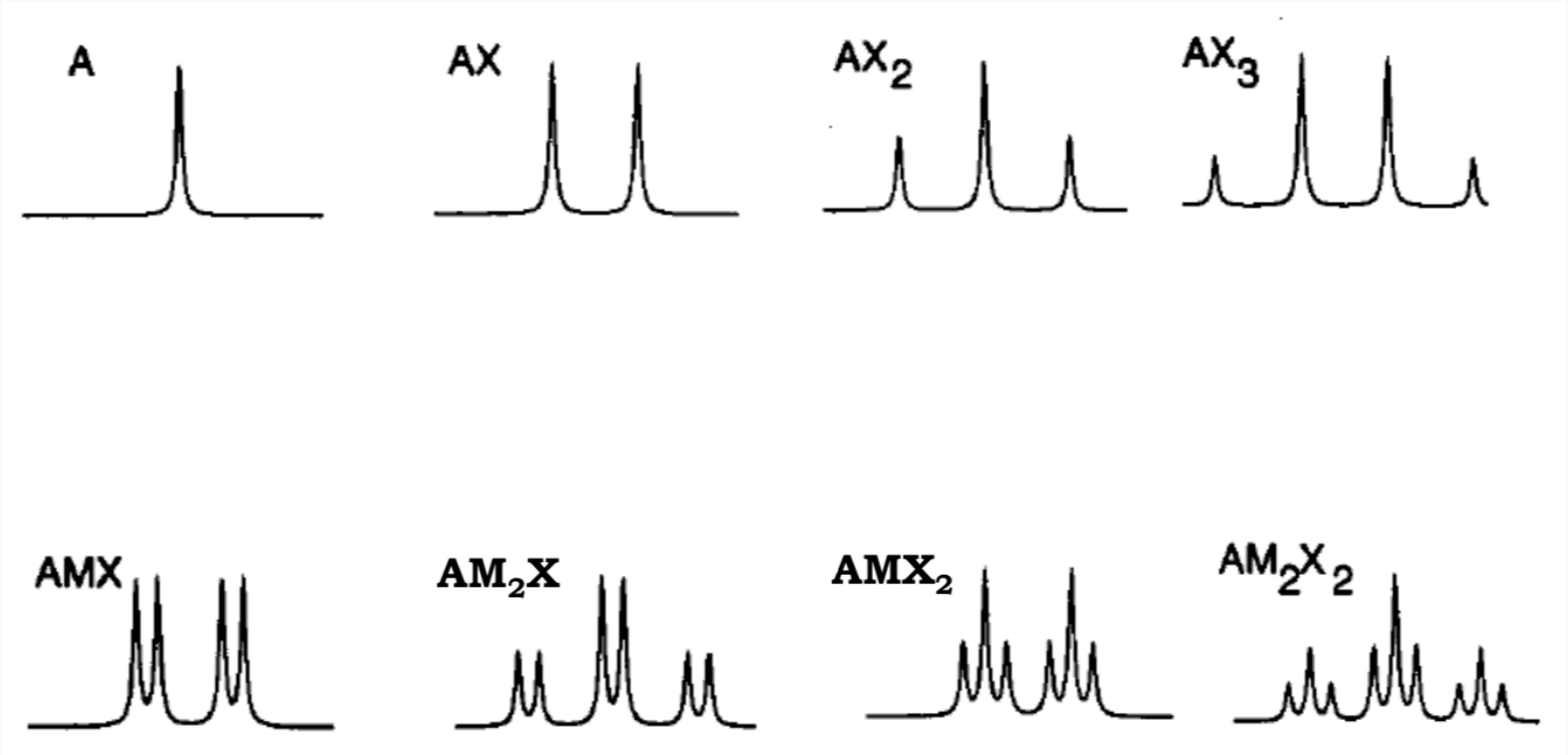
Solventes no Espectro de ^{1}H - $CDCl_3$ + $CHCl_3$



Solventes no Espectro de ^{13}C - $CDCl_3$ + $CHCl_3$



Padrão dos Acoplamentos



Mecanismo do Acoplamento Spin-Spin

- Como se dá a transmissão do acoplamento?
  - via elétrons da ligação
  - há 4 contribuições não relativísticas: FC, SD, PSO e DSO
  - mais importante é o contato de Fermi (FC) para ^{1}H e ^{13}C
- Contato de Fermi (FC)
  - interação nuclear de spins entre A e B envolve elétrons da ligação A$-$B
  - atualmente não precisa haver uma ligação formal
  - há mecanismos através de ligações e espaço
- Considerando a ligação H$-$C e $\boldsymbol{H}_0 \Uparrow$
  - sendo $\boldsymbol{\mu}_H \uparrow$:
  - o elétron $\bar{e}$ da ligação σ próximo de H terá $\boldsymbol{\mu}_{\bar{e}} \downarrow$
  - o elétron vizinho ao C terá $\boldsymbol{\mu}_{\bar{e}} \uparrow$ (*Princípio de Pauli*)
  - logo $\boldsymbol{\mu}_C$ será $\downarrow$:
- $\boldsymbol{\mu}_H$ e $\boldsymbol{\mu}_C$ são antiparalelos $\rightarrow J > 0$
- $^{1}J_{\mathrm{CH}}$ é sempre positivo!

Interação Spin-Spin através dos elétrons da ligação C–H

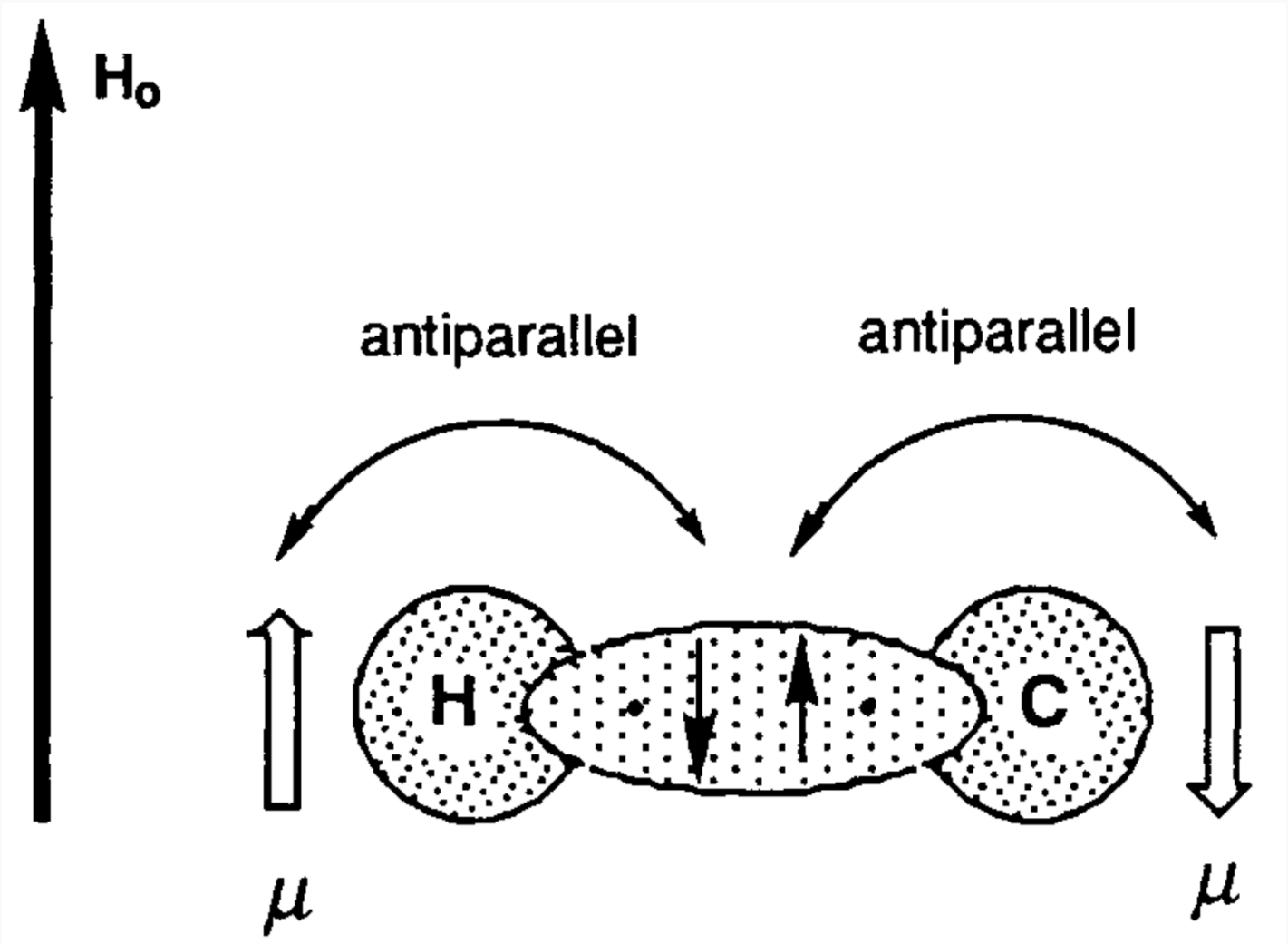


Figura 1: Representação da interação spin-spin para o acoplamento $^{1}J_{CH}$.

Mecanismo do Acoplamento Spin-Spin

- Acoplamento a 2 ligações geminal metilênico H_A-C-H_B e $\boldsymbol{H}_0 \Uparrow$
  - hidrogênios de grupo $R-CH_2-R'$
- Racionalizamos com a mesma analogia, por exemplo:
  - sendo $\boldsymbol{\mu}_{H_A} \uparrow$:
  - o elétron $\bar{e}$ da ligação σ próximo de H terá $\boldsymbol{\mu}_{\bar{e}} \downarrow$
  - o elétron vizinho ao C, nesta mesma ligação terá $\boldsymbol{\mu}_{\bar{e}} \uparrow$
  - o elétron da ligação gemial perto do C terá $\boldsymbol{\mu}_{\bar{e}} \uparrow$
  - o elétron vizinho próximo ao H_B terá $\boldsymbol{\mu}_{\bar{e}} \downarrow$
  - logo $\boldsymbol{\mu}_{H_B}$ será $\uparrow$
- $\boldsymbol{\mu}_{H_A}$ e $\boldsymbol{\mu}_{H_B}$ são paralelos $\rightarrow J < 0$
- Acoplamento geminal é negativo para metilênico

Interação Spin-Spin para hidrogênios geminais R–CH_2–R'

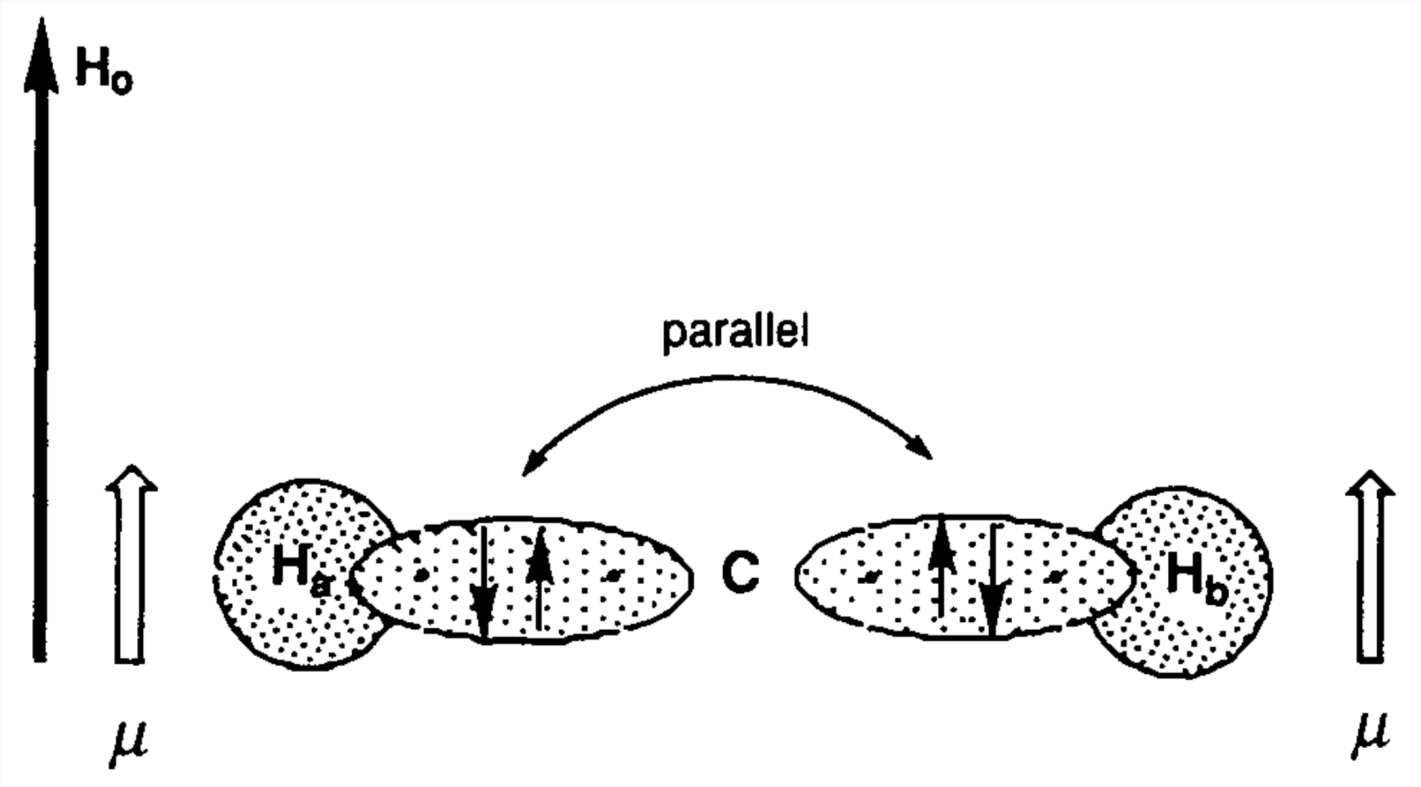
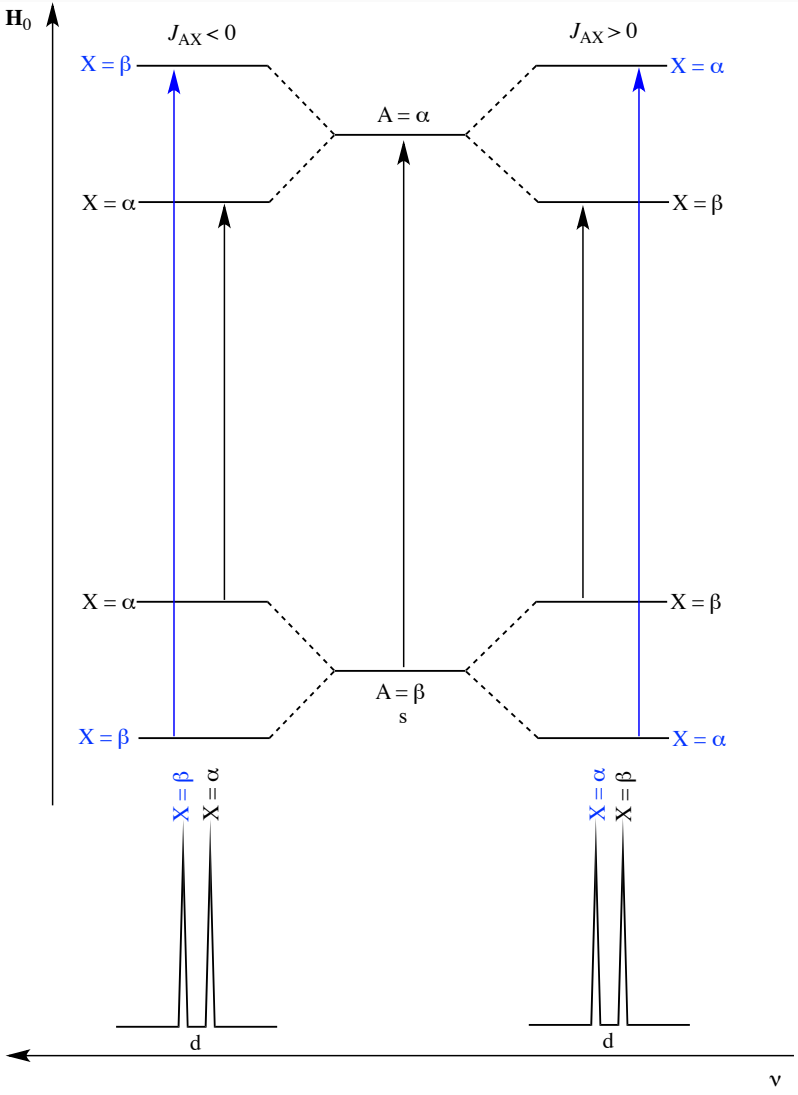


Figura 2: Representação da interação spin-spin para o $^2J_{HH}$ geminal.

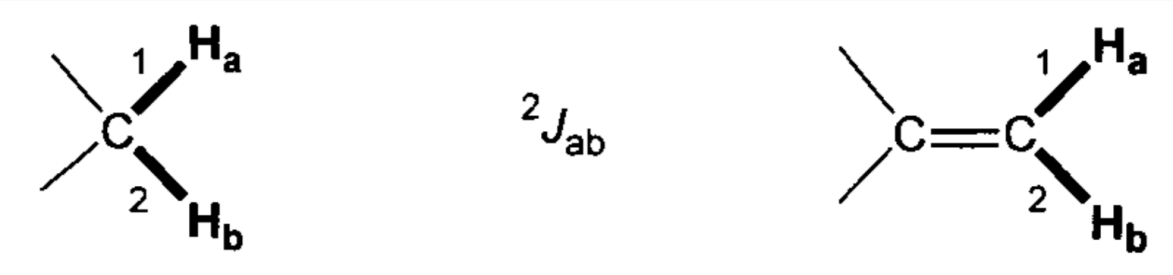
Sinal do Acoplamento Spin-Spin



- Sinais de J são consistentes:
- ${}^{1}J_{CH} > 0$ - $\alpha\beta < \alpha\alpha$
- ${}^{1}J_{XY}$ dependerá de X e Y
- ${}^{2}J_{HH} < 0$ para C_{sp3}
- ${}^{2}J_{HH} > 0$ para C_{sp2}
- ${}^{3}J_{HH}$ é *sempre* positivo

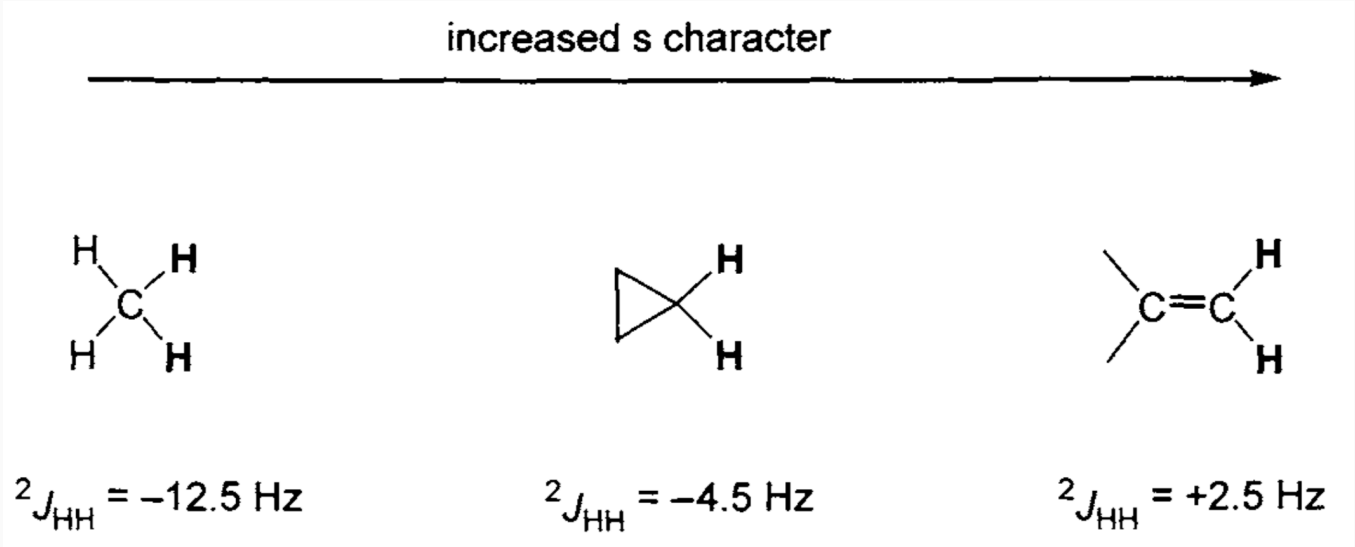
Tipos de Acoplamentos $^{n}J_{HH}$ entre núcleos de ^{1}H

- $n = 1$
  - existe em uma única molécula (H_2)
  - $^{1}J_{HH} = 280$ Hz
  - interessante para teóricos
- $n = 2$
  - acoplamento geminal
  - observado em ^{1}Hs quimicamente não equivalentes do grupo CH_2
  - $^{2}J_{HH} > 0$ ou $^{2}J_{HH} < 0$
  - depende da hibridização do C e dos substituintes
  - dependência com ângulo $H-C-H$



Efeitos em Acoplamentos Geminais - $^2J_{HH}$

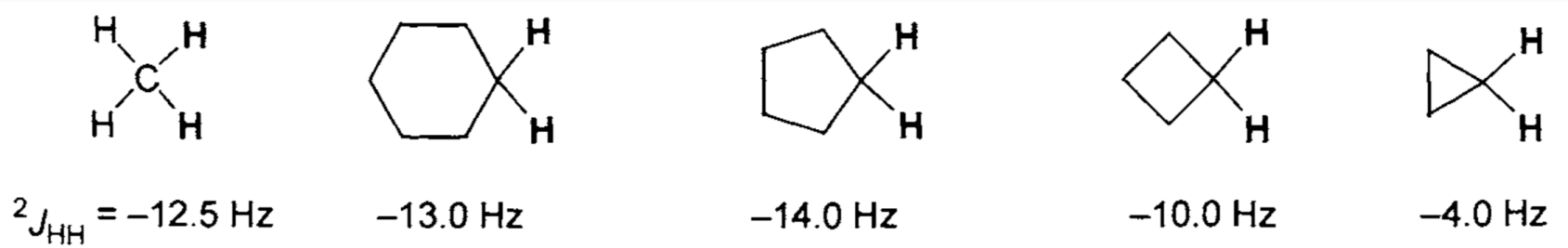
Efeito do Caráter 's' do C



Efeito da Eletronegatividade de $H_2C{=}X$, , $X{=}CH_2$ e O

Efeitos em Acoplamentos Geminais - $^2J_{HH}$

Efeito do Ângulo H−C−H

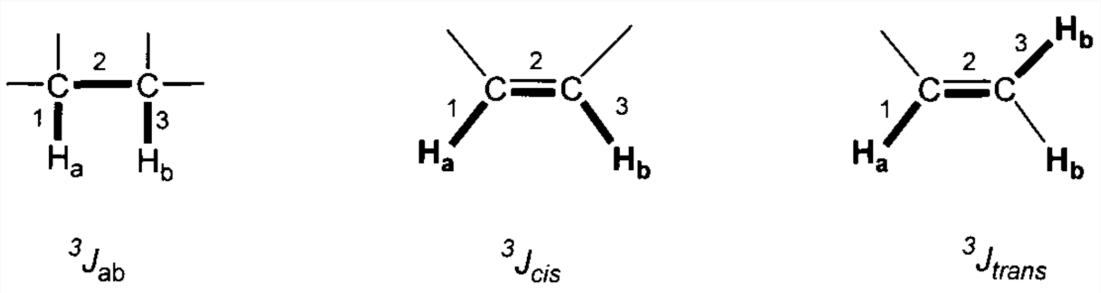


$^2J_{HH}$ = −12.5 Hz −13.0 Hz −14.0 Hz −10.0 Hz −4.0 Hz

$\uparrow$ tensão no anel $\longrightarrow \uparrow$ ângulo H−C−H $\longrightarrow \uparrow {}^2J_{HH}$

Acoplamentos Vicinais - $^3J_{HH}$

- $n = 3$
  - acoplamento vicinal
  - ocorre entre ^{1}Hs adjacentes
  - mais útil e informativo
  - depende do ângulo diedro H−C−C−H
  - depende do ângulo C−C−H
  - depende de R_{C-C}
  - depende da eletronegatividade dos substituintes



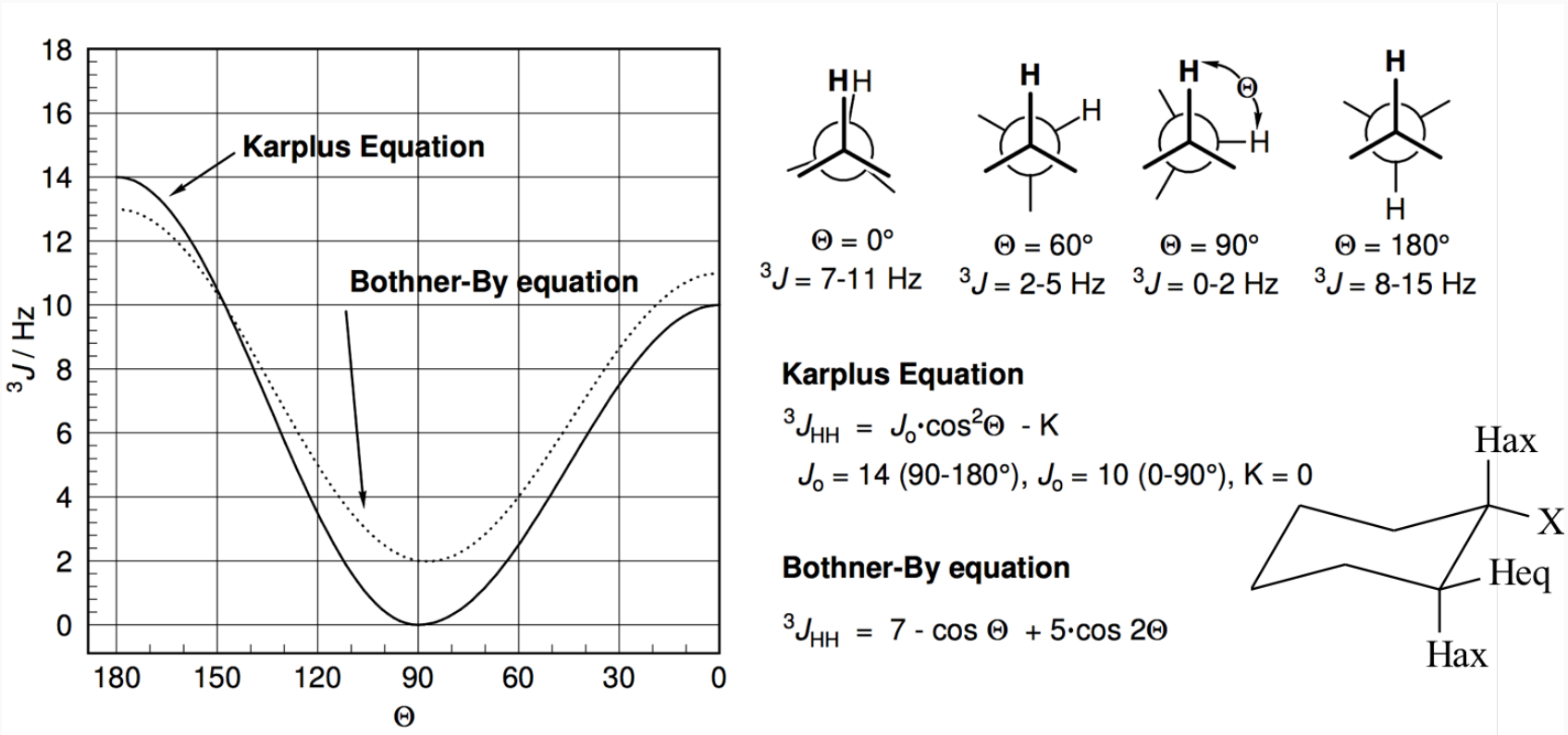
Efeitos em Acoplamentos Vicinais - $^3J_{HH}$

Tipos de $^3J_{HH}$ no Cicloexano

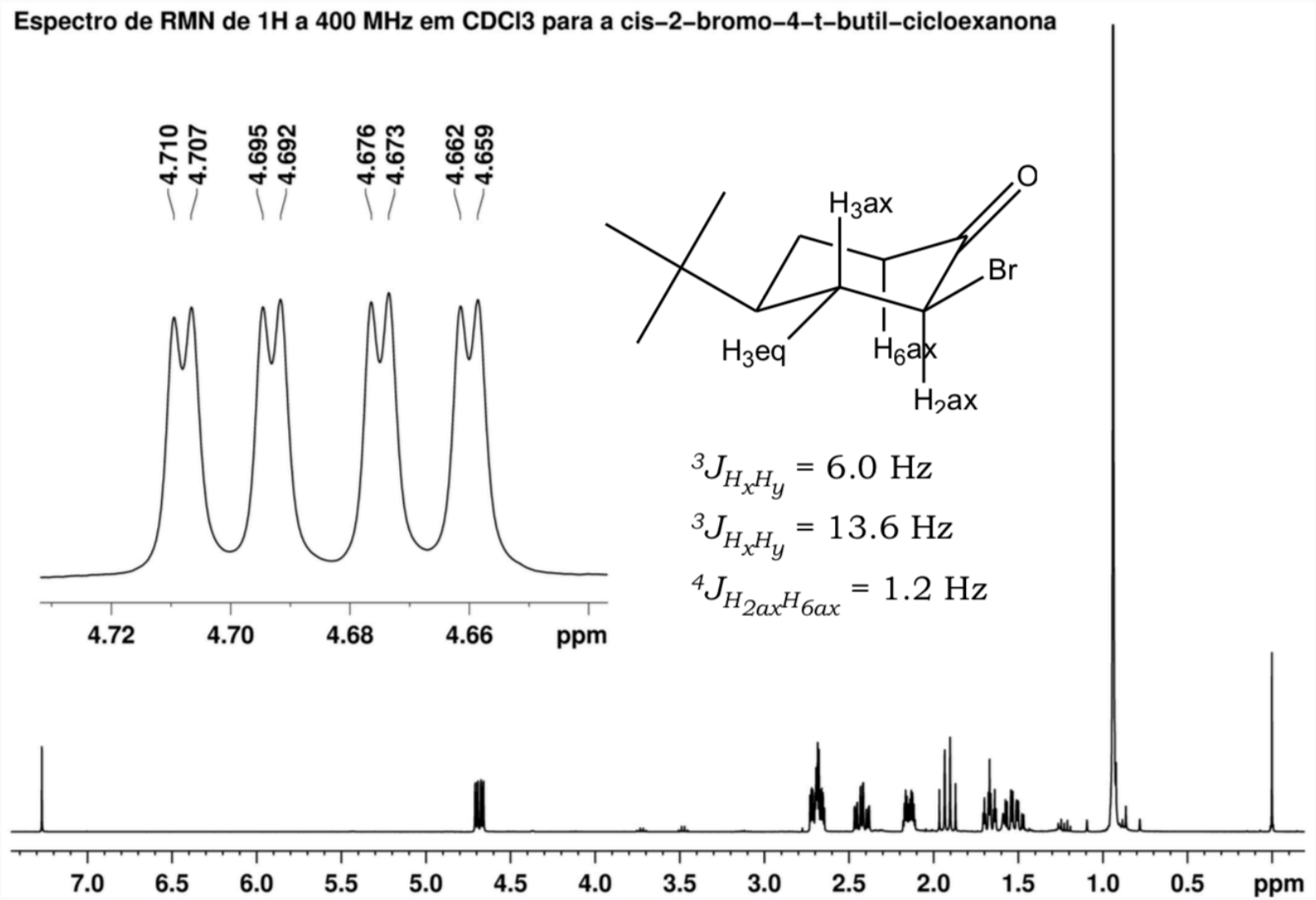
- ^3J axial-axial $\rightarrow^3 J_{aa} = 8,0 - 13,0$ Hz
- ^3J axial-equatorial $\rightarrow^3 J_{ae} = 2,0 - 5,0$ Hz
- ^3J equatorial-equatorial $\rightarrow^3 J_{ee} = 2,0 - 5,0$ Hz

Efeitos em Acoplamentos Vicinais - $^3J_{HH}$

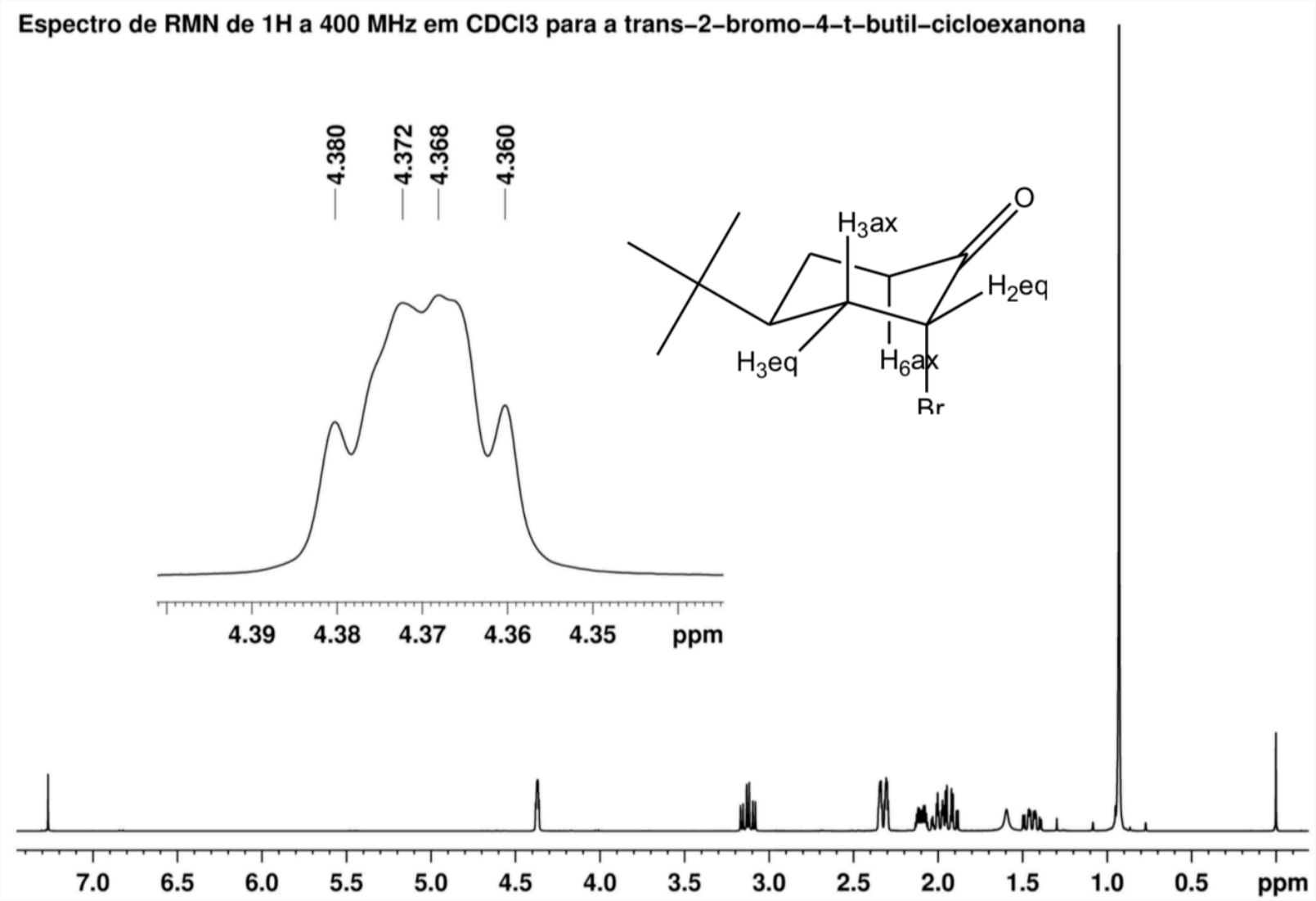
Curva de Karplus - $^3J_{HH}$ *vs* diedro H−C−C−H



Exemplo da Aplicação da Curva de Karplus para $^3J_{HH}$

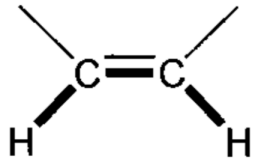


Exemplo da Aplicação da Curva de Karplus para $^3J_{HH}$

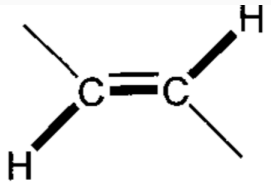


Efeitos em Acoplamentos Vicinais - $^3J_{HH}$

Acoplamento em Olefinas - $^3J_{HH}$ *cis vs trans*



J_{cis} = 7.0–10.0 Hz



J_{trans} = 12.0–18.0 Hz

Acoplamento em Ciclo Alcanos - $^3J_{HH}$

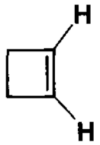
J_{cis} = 5.0–10.0 Hz
J_{trans} = 5.0–10.0 Hz

J_{cis} = 4.0–12.0 Hz
J_{trans} = 2.0–10.0 Hz

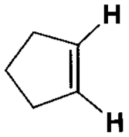
J_{cis} = 7.0–13.0 Hz
J_{trans} = 4.0–9.0 Hz

Dependência com o Ângulo H−C−C - $^3J_{HH}$

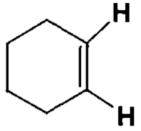
0.5 – 2.0 Hz



2.5 – 4.0 Hz



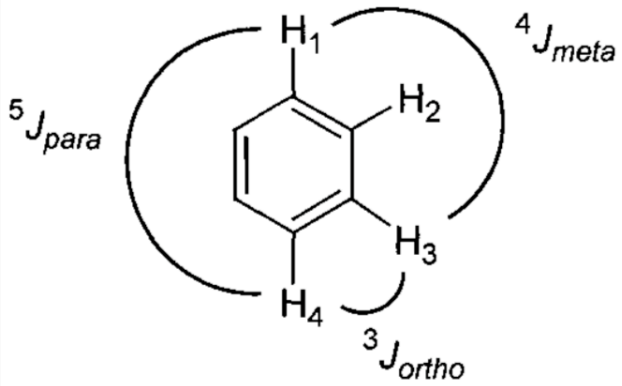
5.1 – 7.0 Hz



8.8 – 10.5 Hz

Acoplamentos Vicinais em Aromáticos - $^3J_{HH}$

Acoplamento em Benzeno Substituidos - $^3J_{HH}$, $^4J_{HH}$ e $^5J_{HH}$

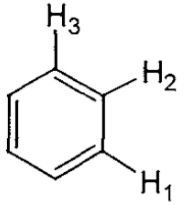


$^3J_{12} = {}^3J_{ortho} = 6.0 – 10.0$ Hz

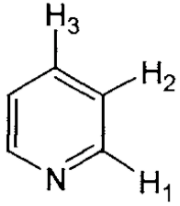
$^4J_{13} = {}^4J_{meta} = 1.0 – 3.0$ Hz

$^5J_{15} = {}^5J_{para} = 0.0 – 1.0$ Hz

Acoplamento em Heterociclos Aromáticos - $^3J_{HH}$



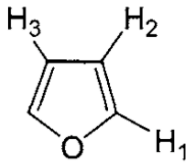
$^3J_{12} = 8.0$ Hz



82

$^3J_{12} = 4.88$ Hz

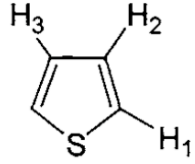
$^3J_{12} = 7.67$ Hz



83

$^3J_{12} = 1.75$ Hz

$^3J_{12} = 3.30$ Hz



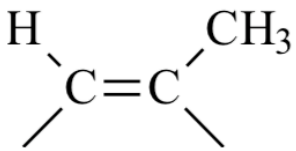
84

$^3J_{12} = 5.0$ Hz

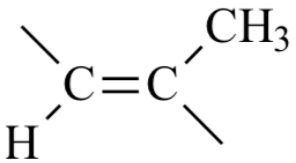
$^3J_{12} = 3.5$ Hz

Acoplamentos Alílicos - $^{3}J_{HH}$ e $^{4}J_{HH}$

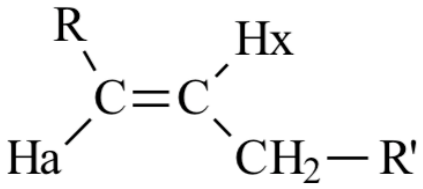
Acoplamentos alílicos ($^{3}J_{HH}$ e $^{4}J_{HH}$)

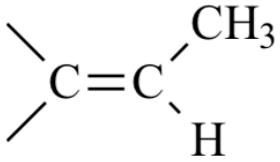


1,0 a 2,0 Hz



0,4 a 1,7 Hz





4,0 a 10,0 Hz

Exemplo de Estudo de Acoplamentos Vicinal - $^3J_{HF}$

Trabalho Recente Publicado - PCCP, 2016, 18, 24119

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NMR spin–spin coupling constants: bond angle dependence of the sign and magnitude of the vicinal $^3J_{HF}$ coupling†

Renan V. Viesser,[a] Lucas C. Ducati,*[b] Jochen Autschbach*[c] and Cláudio F. Tormena[a]

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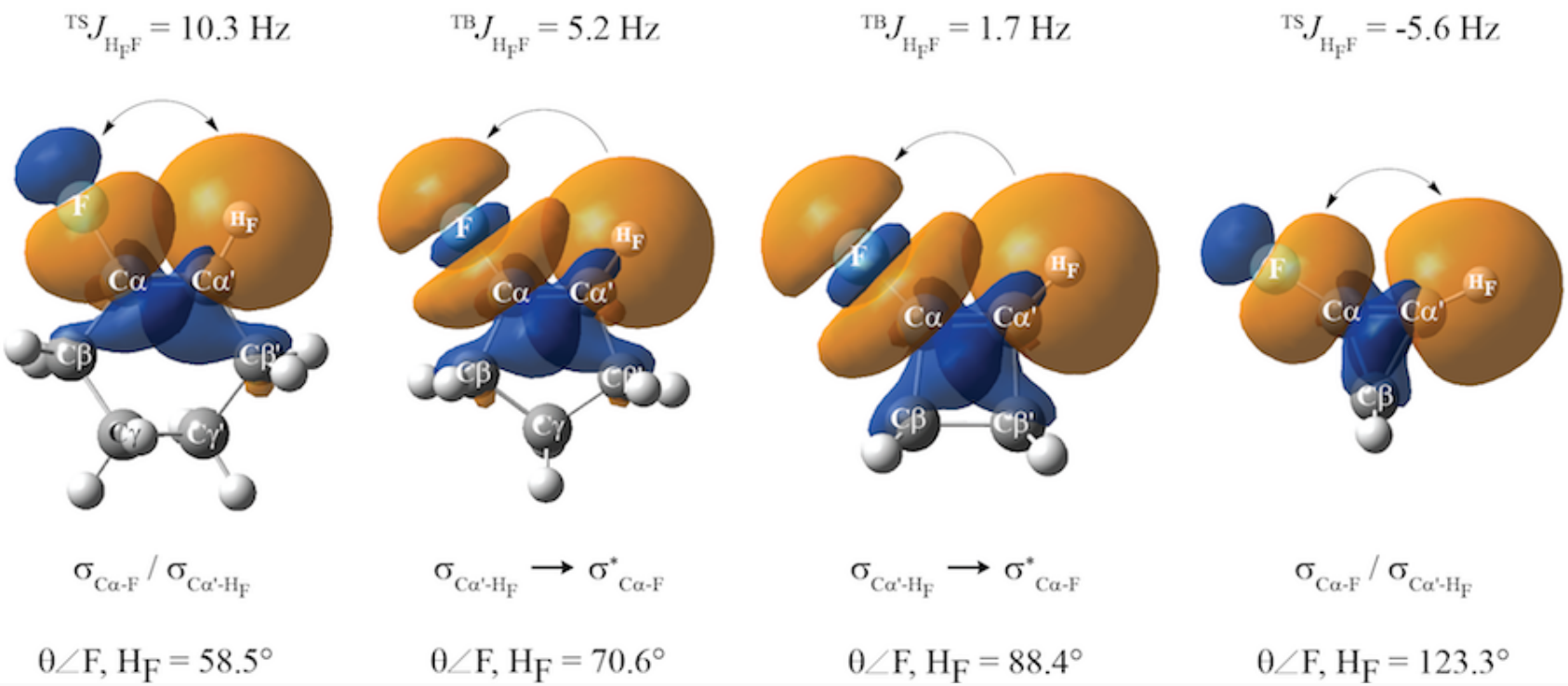
The dependence of the magnitude and sign of $^3J_{H_FF}$ on the bond angle in fluoro-cycloalkene compounds is evaluated by electronic structure calculations using different levels of theory, *viz.* DFT, SOPPA(CCSD) and SOPPA(CC2). Localized molecular orbital contributions to $^3J_{H_FF}$ are analyzed to assess which orbitals are responsible for $^3J_{H_FF}$ and which are the most important coupling transmission mechanisms for each compound. Fluoro-ethylene is used as a model system to evaluate the dependence of the $^3J_{H_FF}$ coupling constant on the angle between the $\sigma_{C\alpha-F}$ and $\sigma_{C\alpha'-H_F}$ vectors. Through-space and hyperconjugative transmission pathways and ring strain are identified as responsible for the opposite trend between $^3J_{H_FF}$ and bond angle, and for the negative signs obtained for the two molecules, respectively. One of the fluorine lone pairs, $\sigma_{C\alpha'-H_F}$, $\sigma_{C\alpha-F}$, $\sigma_{C\alpha'-C\beta'}$ bonding orbitals and the $\sigma^*_{C\alpha-F}$ antibonding orbital are involved in the *J*-coupling pathways, according to analyses of pairwise-steric and hyperconjugative energies.

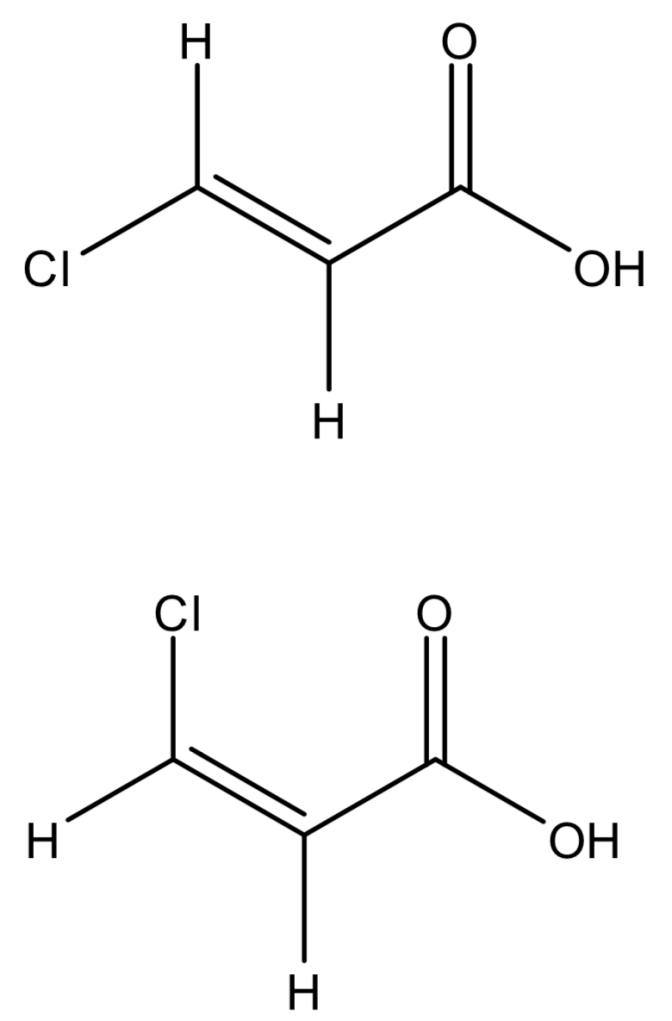
Exemplo de Estudo de Acoplamentos Vicinal - $^{3}J_{HF}$

Caminhos da Transmissão do Acoplamento - PCCP, 2016, 18, 24119



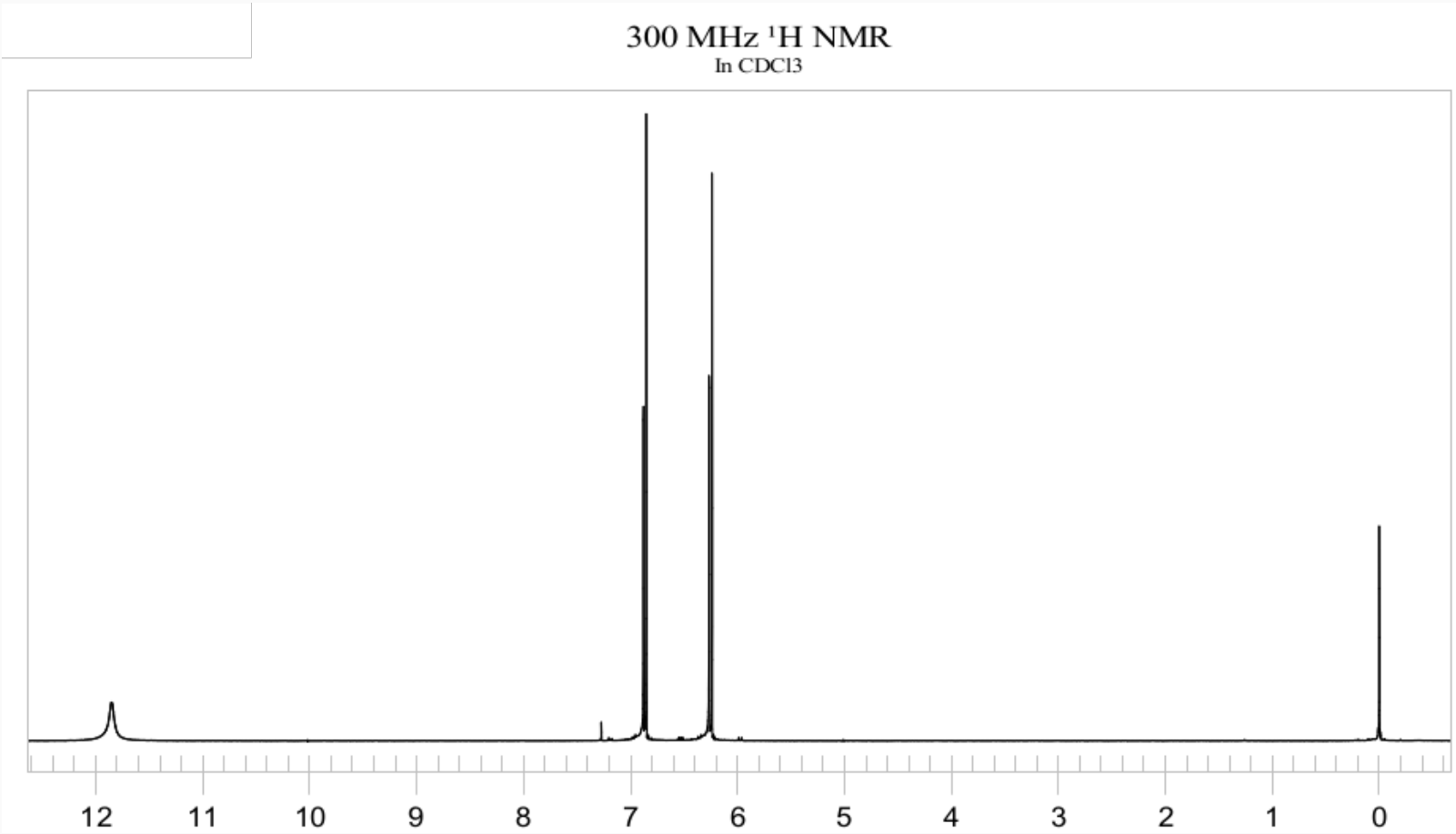
Espectros de ^{1}H com Acoplamentos ^{2}J e ^{3}J

Estruturas do Ácido Cloro Acrílico - cis ou trans?

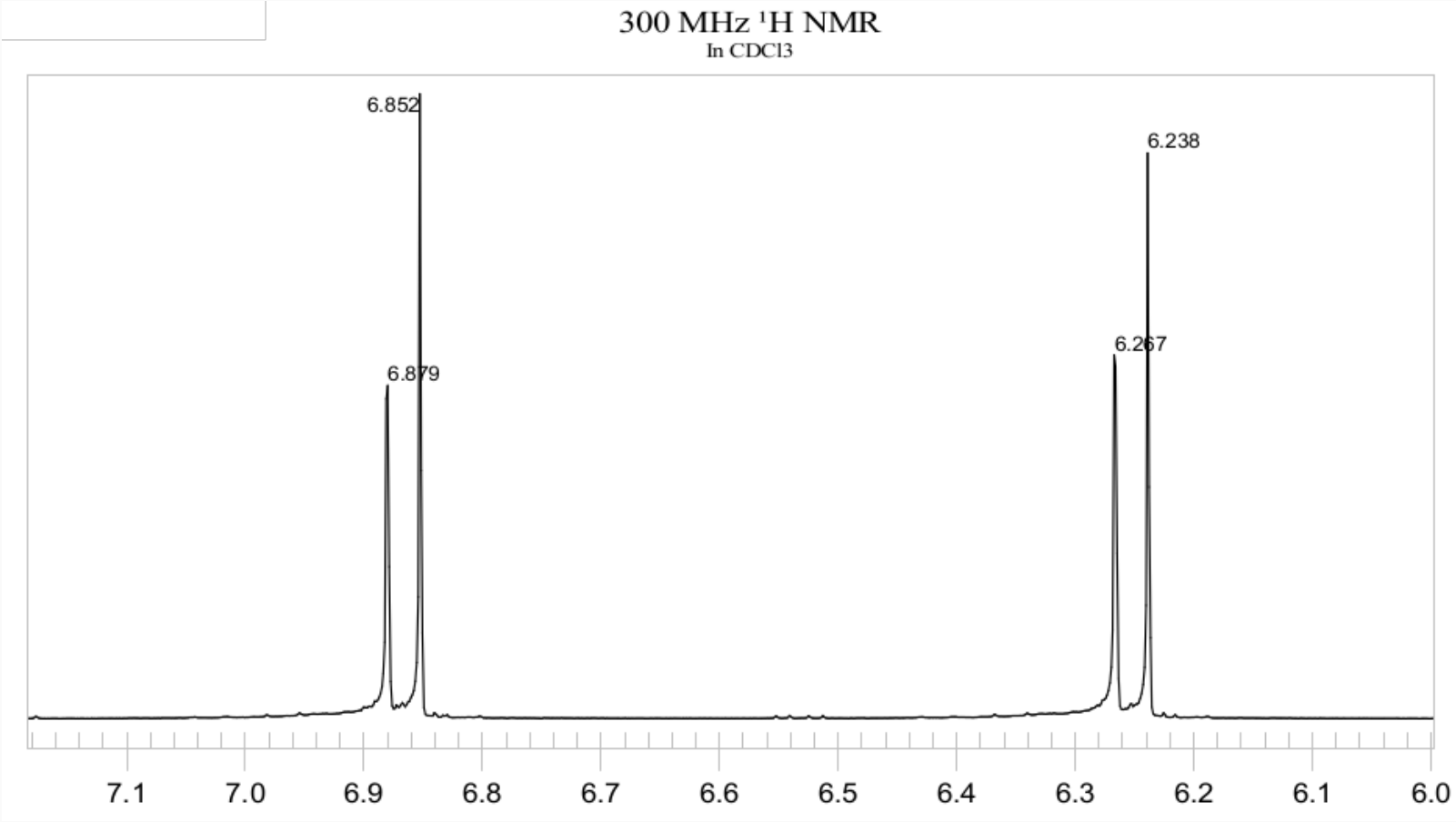


- Teremos para esse espectro de ^{1}H 3 sinais sendo eles:
- 1 H da OH como um singleto
- 2 dubletos de Hs da olefina
- Curva de Karplus: $^{3}J_{\text{HHtrans}} > {}^{3}J_{\text{HHcis}}$

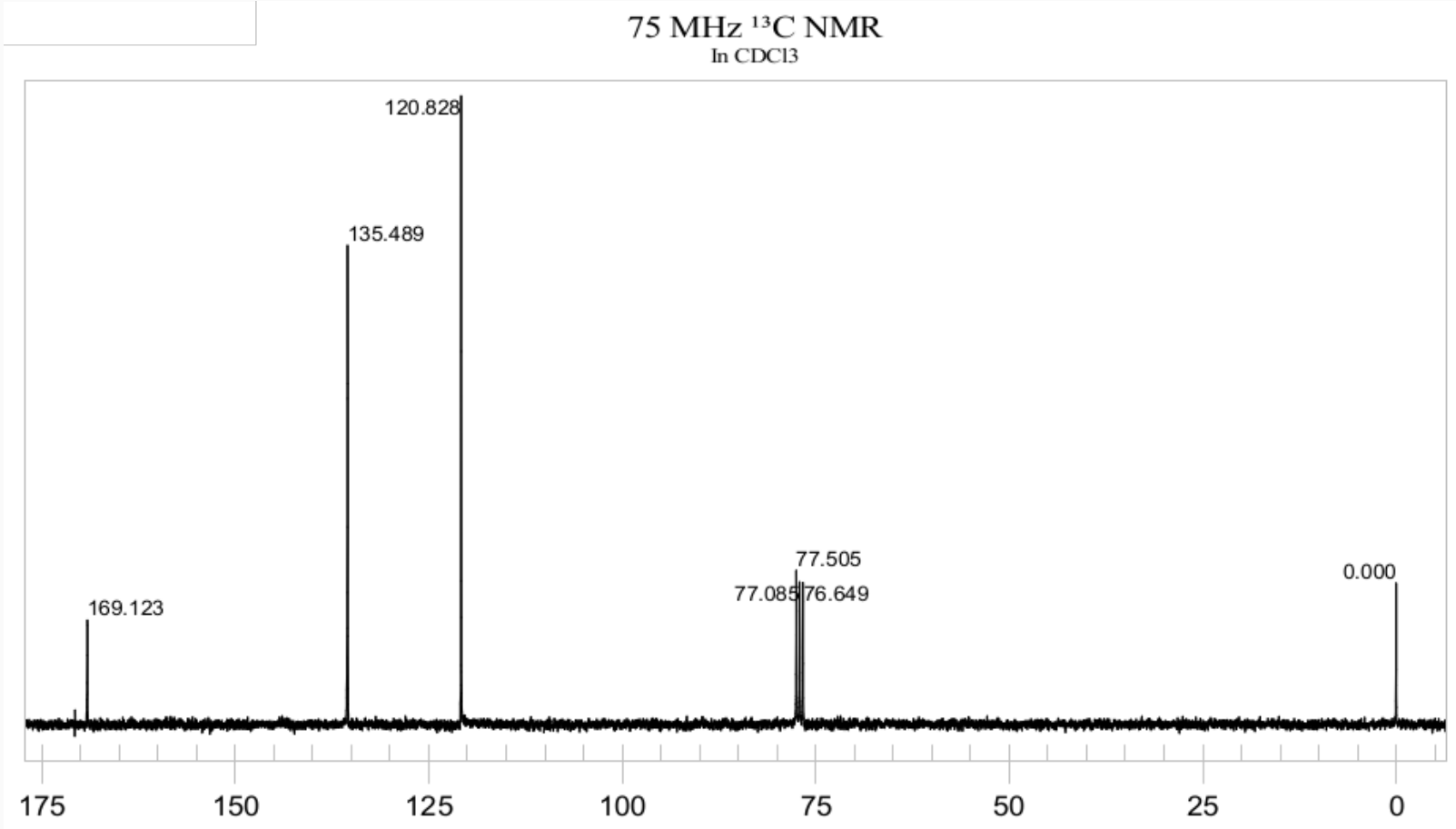
Espectro de ^{1}H do Ácido Cloro Acrílico - cis ou trans?



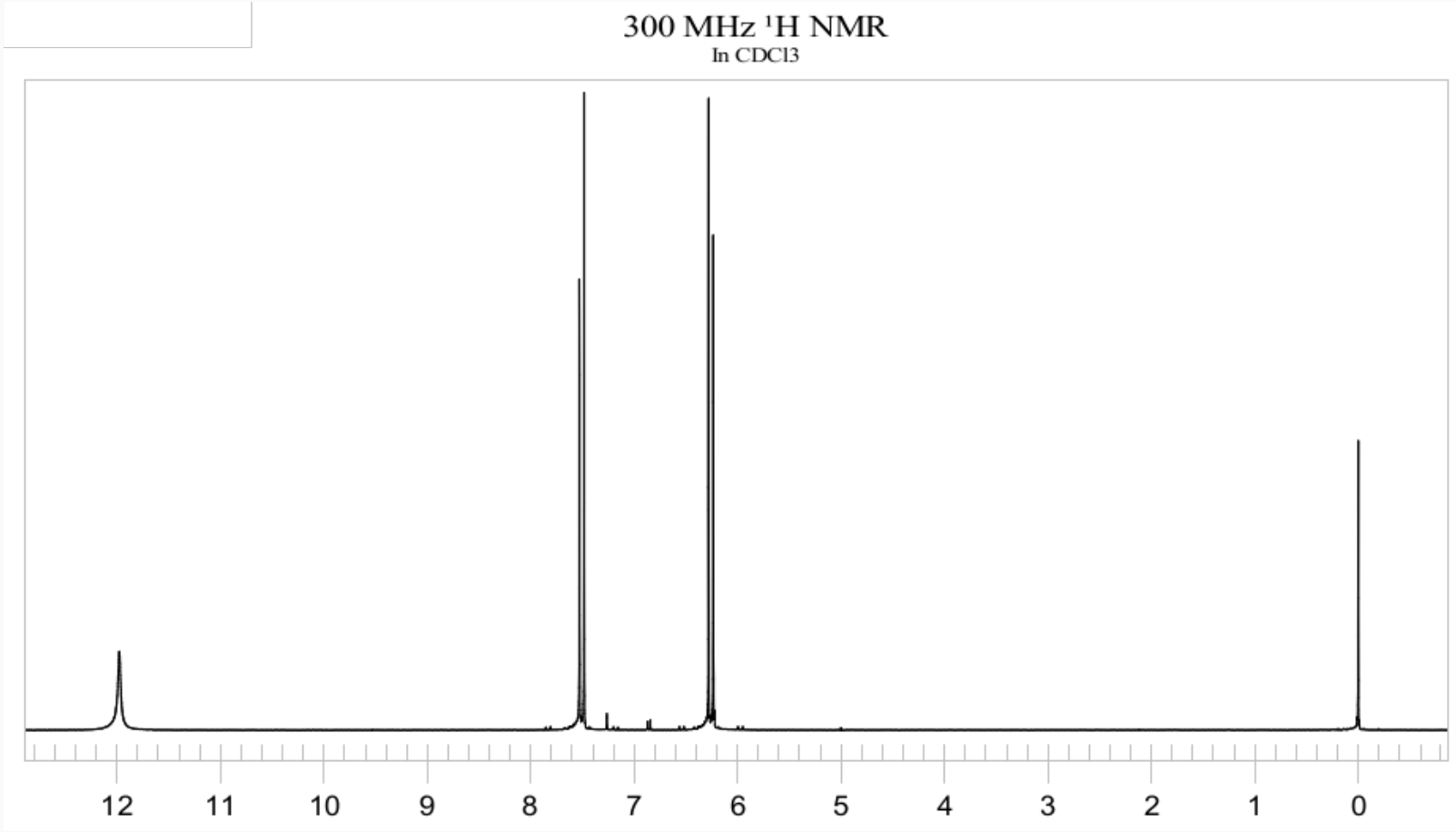
Espectro de ^{1}H do Ácido Cloro Acrílico - cis ou trans?



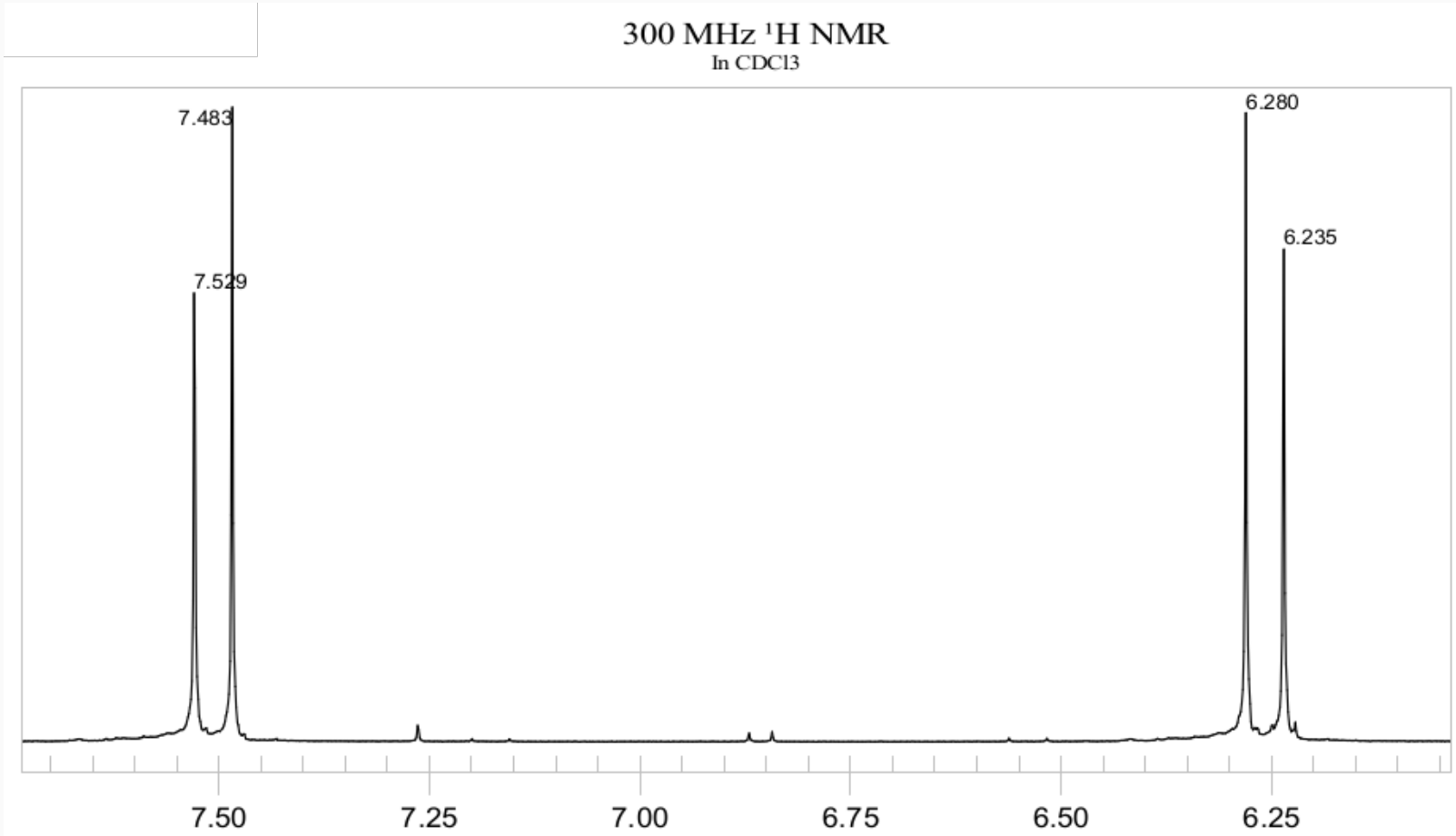
Espectro de ^{13}C do Ácido Cloro Acrílico - cis ou trans?



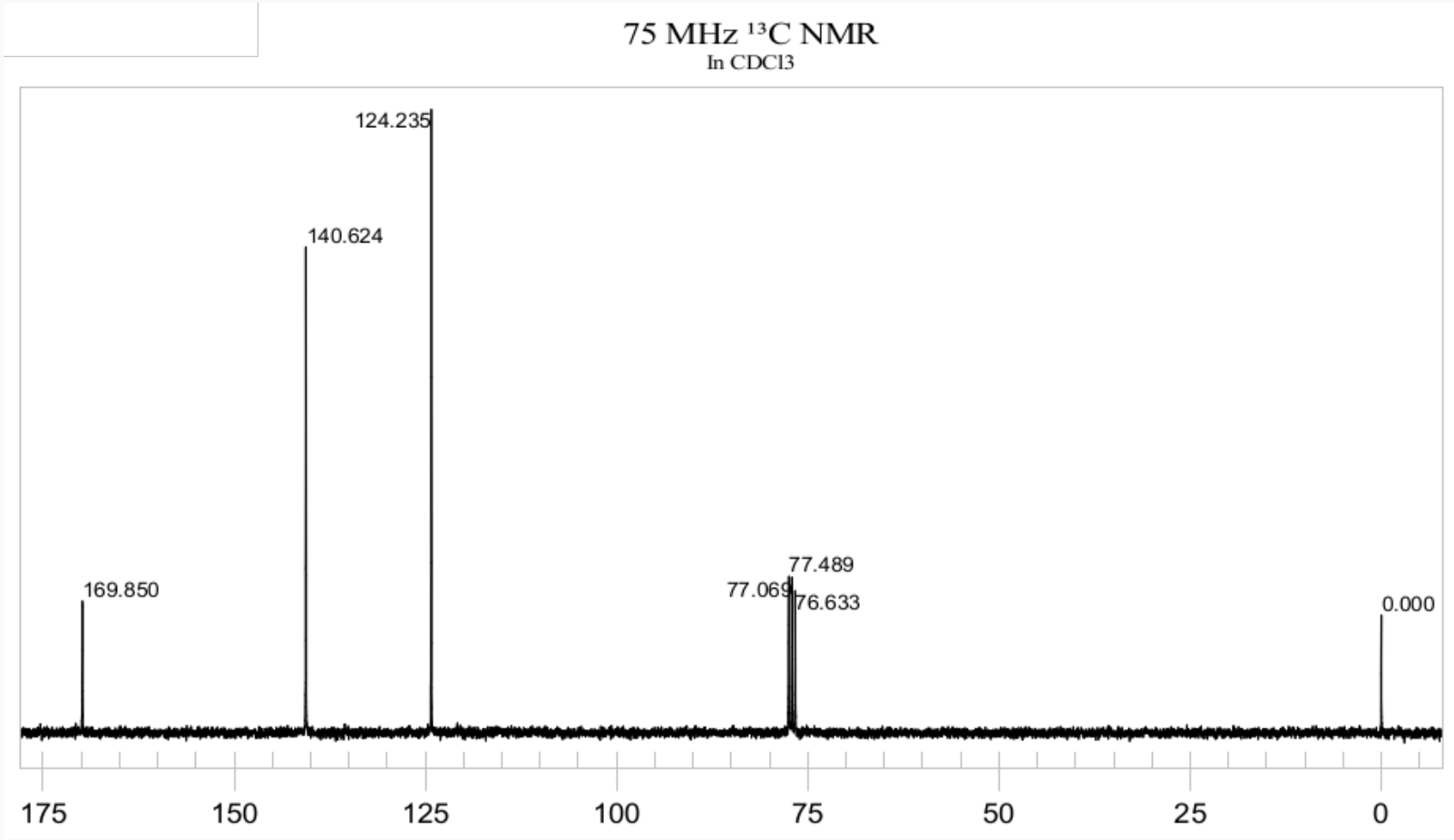
Espectro de ^{1}H do Ácido Cloro Acrílico - cis ou trans?



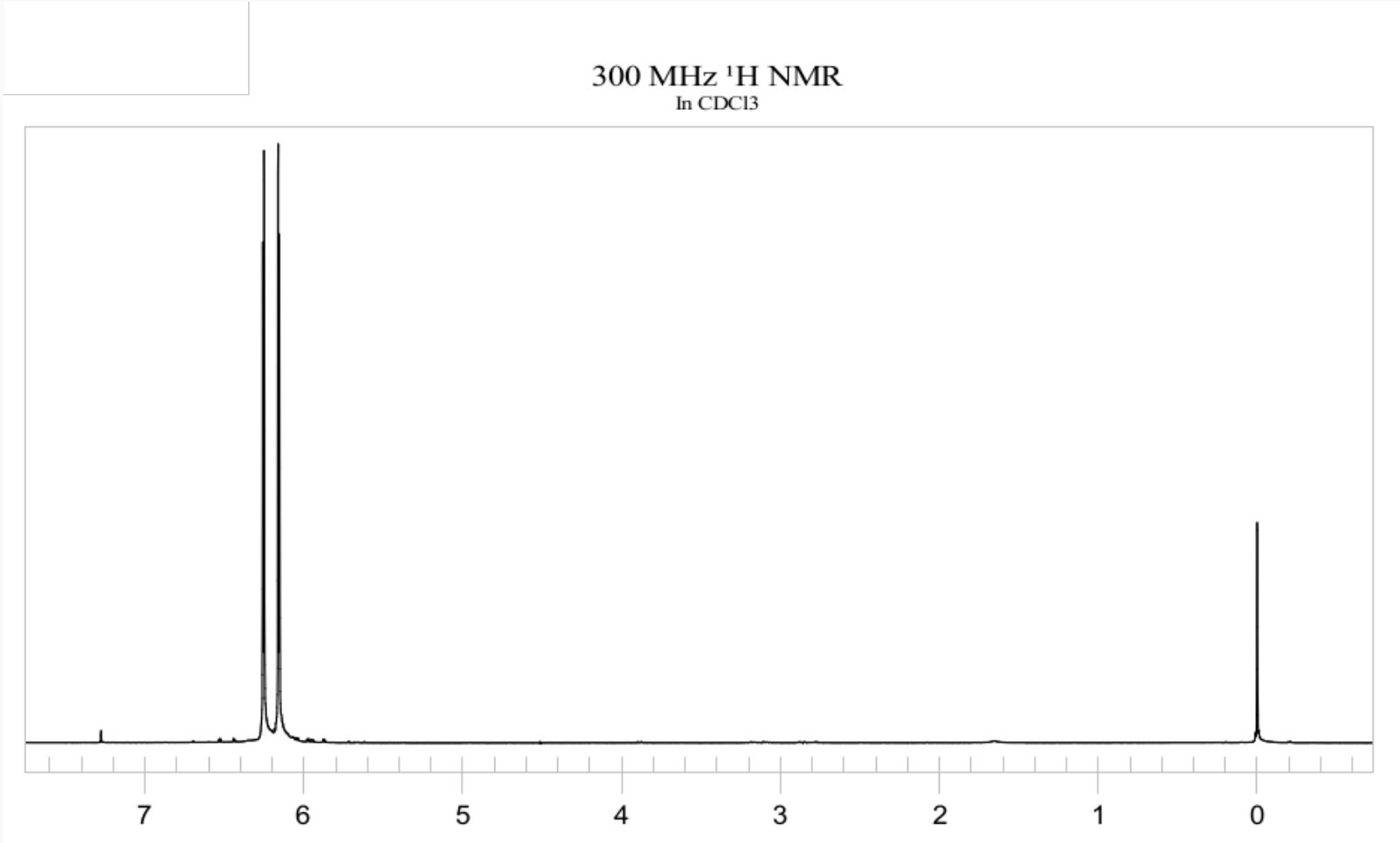
Espectro de ^{1}H do Ácido Cloro Acrílico - cis ou trans?



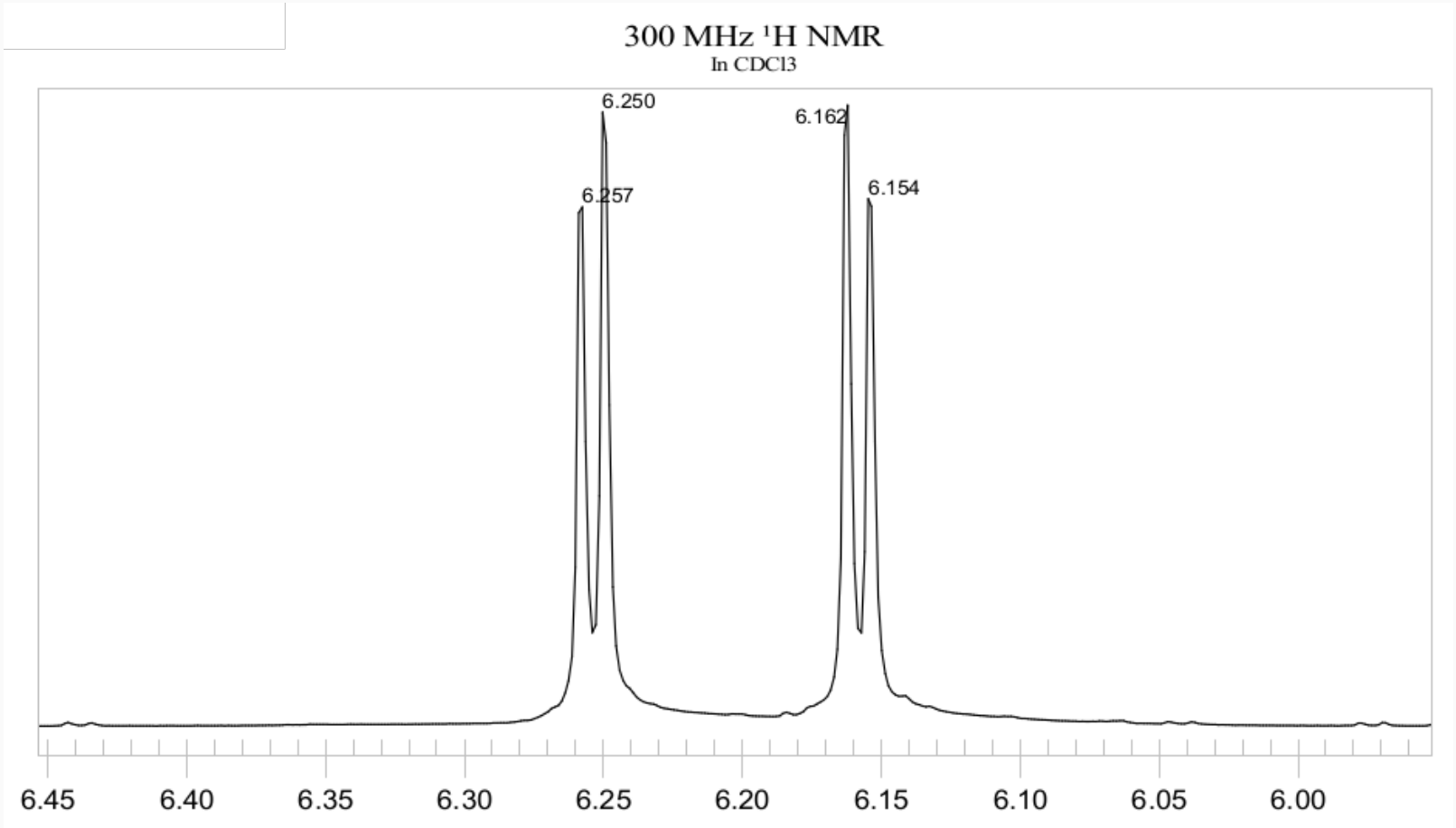
Espectro de ^{13}C do Ácido Cloro Acrílico - cis ou trans?



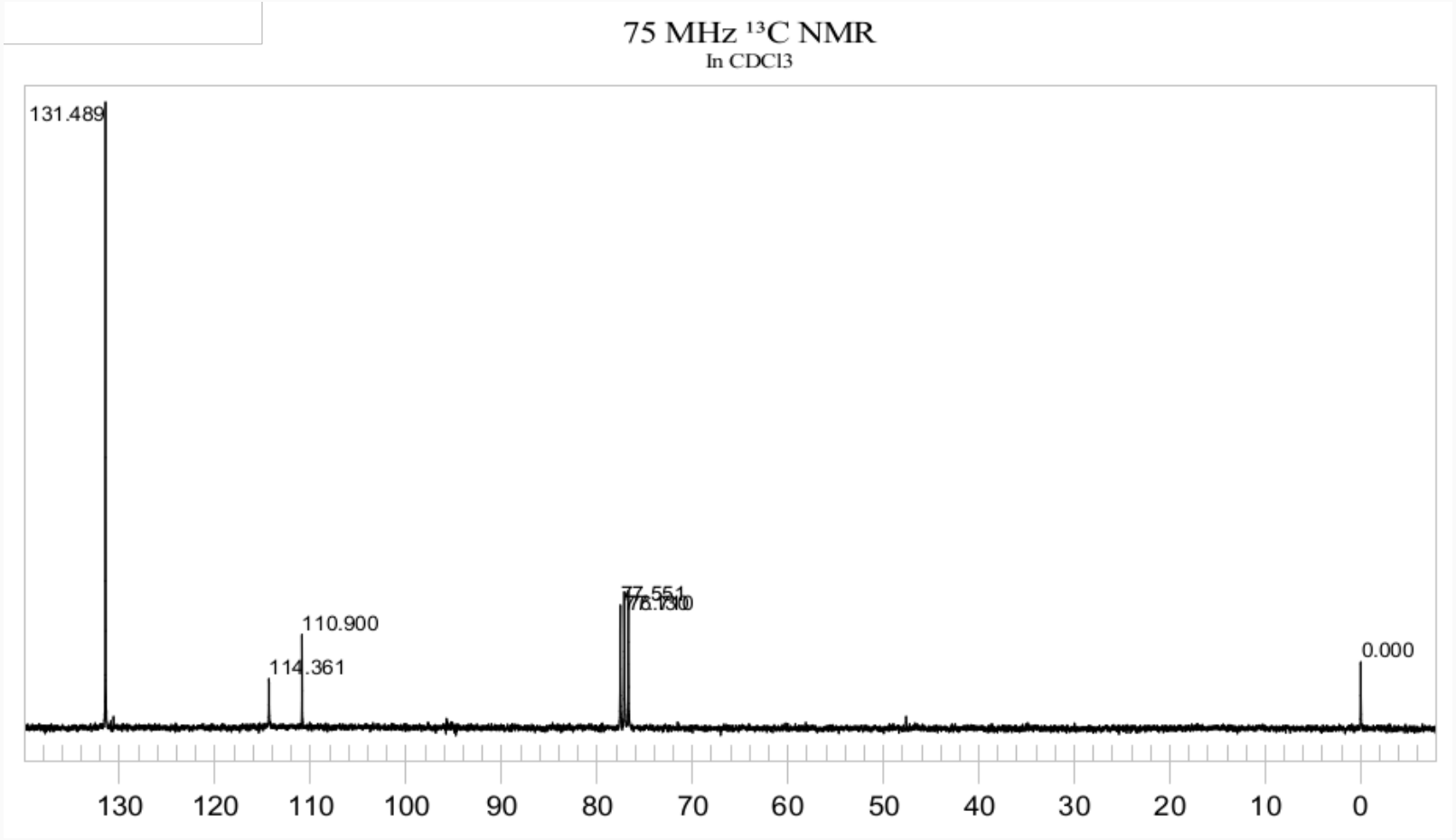
Espectro de ^{1}H do 2-Cloro Acrilonitrila - $CH_2{=}CClCN$



Espectro de ^{1}H do 2-Cloro Acrilonitrila - $CH_2{=}CClCN$

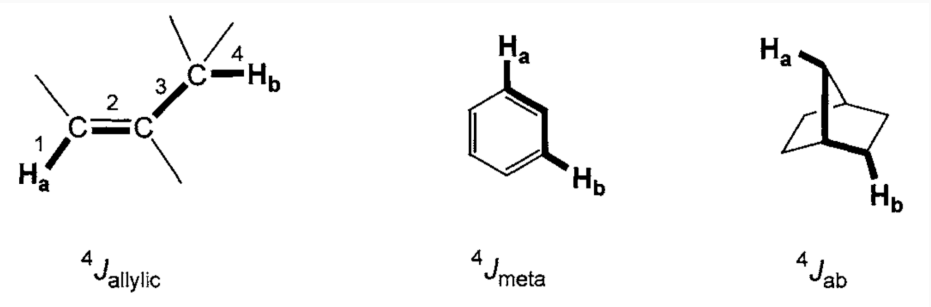


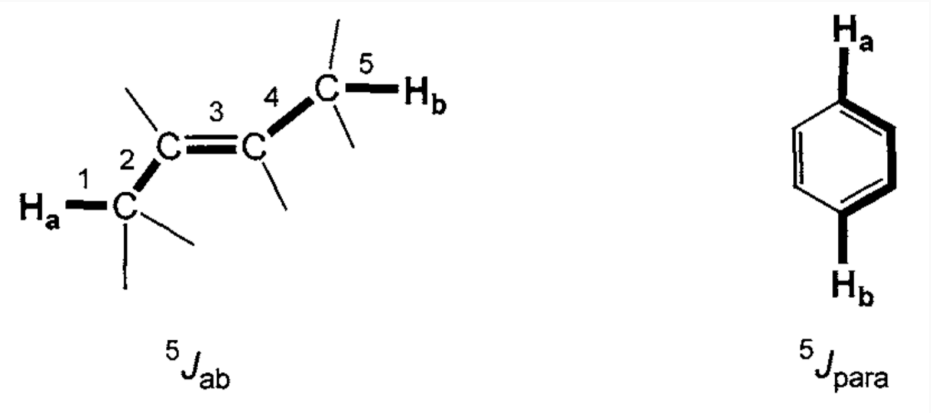
Espectro de ^{13}C do 2-Cloro Acrilonitrila - $CH_2{=}CCICN$



Acoplamentos de Longo Alcance - $^{n}J_{HH}, n > 3$

- Acoplamento de longo alcance quando $n > 3$
- $n = 4$
  - observado em compostos cíclicos saturados em especial biciclos
  - ocorre em sistemas alílicos e aromáticos
- $n = 5$
  - observado em sistemas aromáticos e homo alílicos

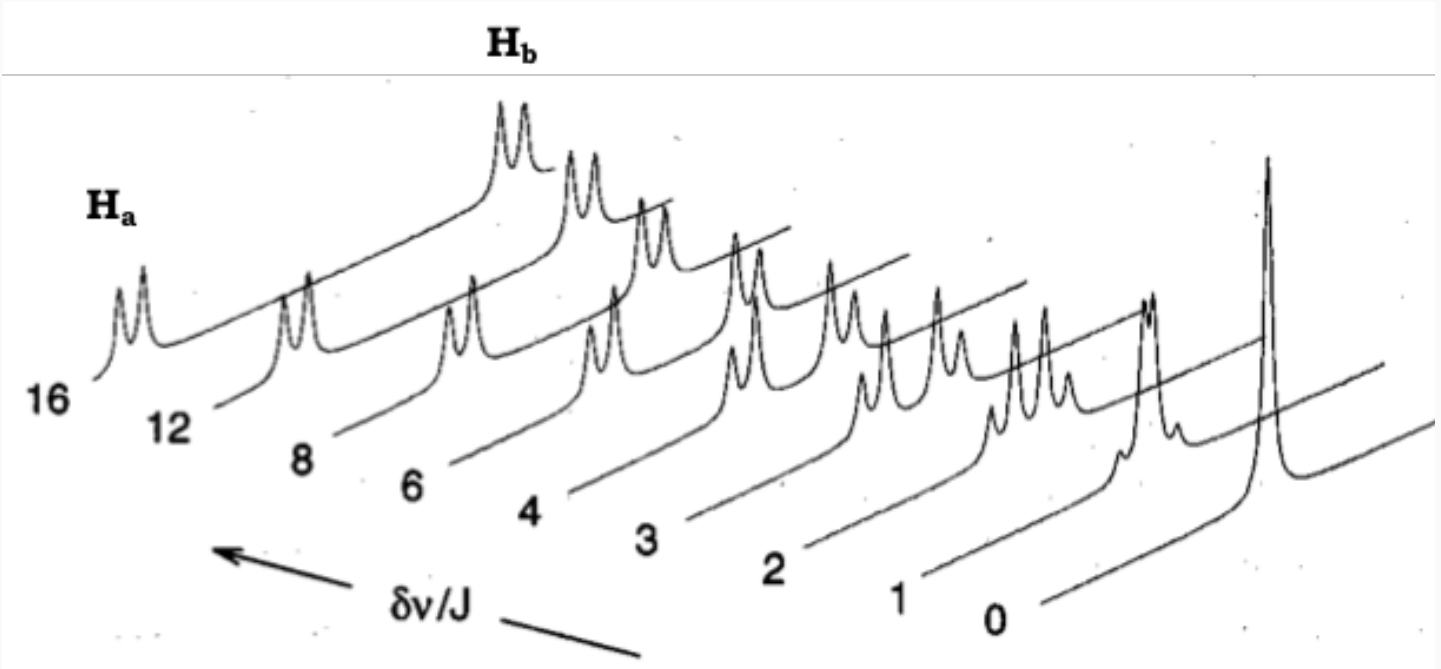




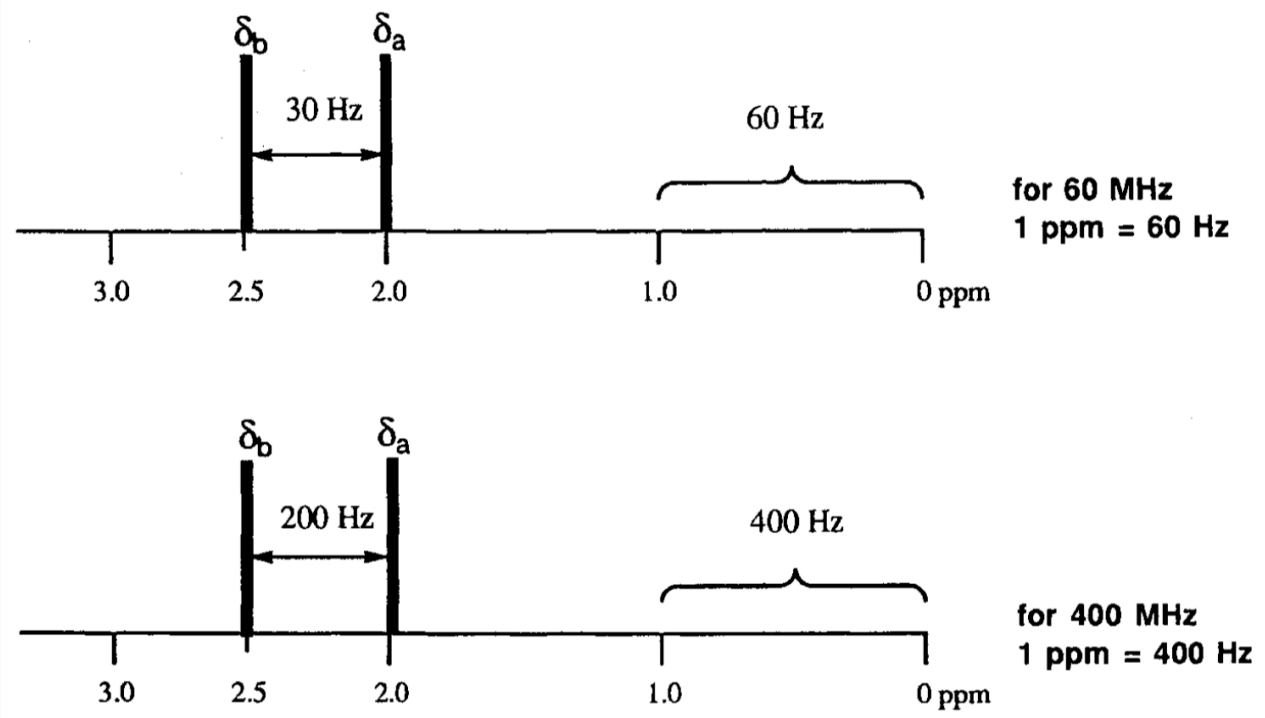
Espectros de 1° e 2° ordem

- Se H_a acopla com H_b e H_c sendo equivalentes ou não
  - usamos a regra da multiplicidade e triângulo de Pascal para intensidades
  - $\Delta\delta$ em Hz é bem maior que J_{ab}
  - $J_{ab} = J_{ac}$
- $\dfrac{\delta H_a - \delta H_b}{J_{ab}} \geqslant 10$ em Hertz
  - espectro de 1° ordem
  - mutiplicidade e intensidade comportadas
  - dubleto, tripleto, quarteto, $\cdots$
- $\dfrac{\delta H_a - \delta H_b}{J_{ab}} < 10$ em Hertz
  - espectro de 2° ordem
  - mutiplicidade e intensidade não seguem as regras anteriores
  - desdobramentos são chamados de multipletos

Espectros de 1° e 2° ordem

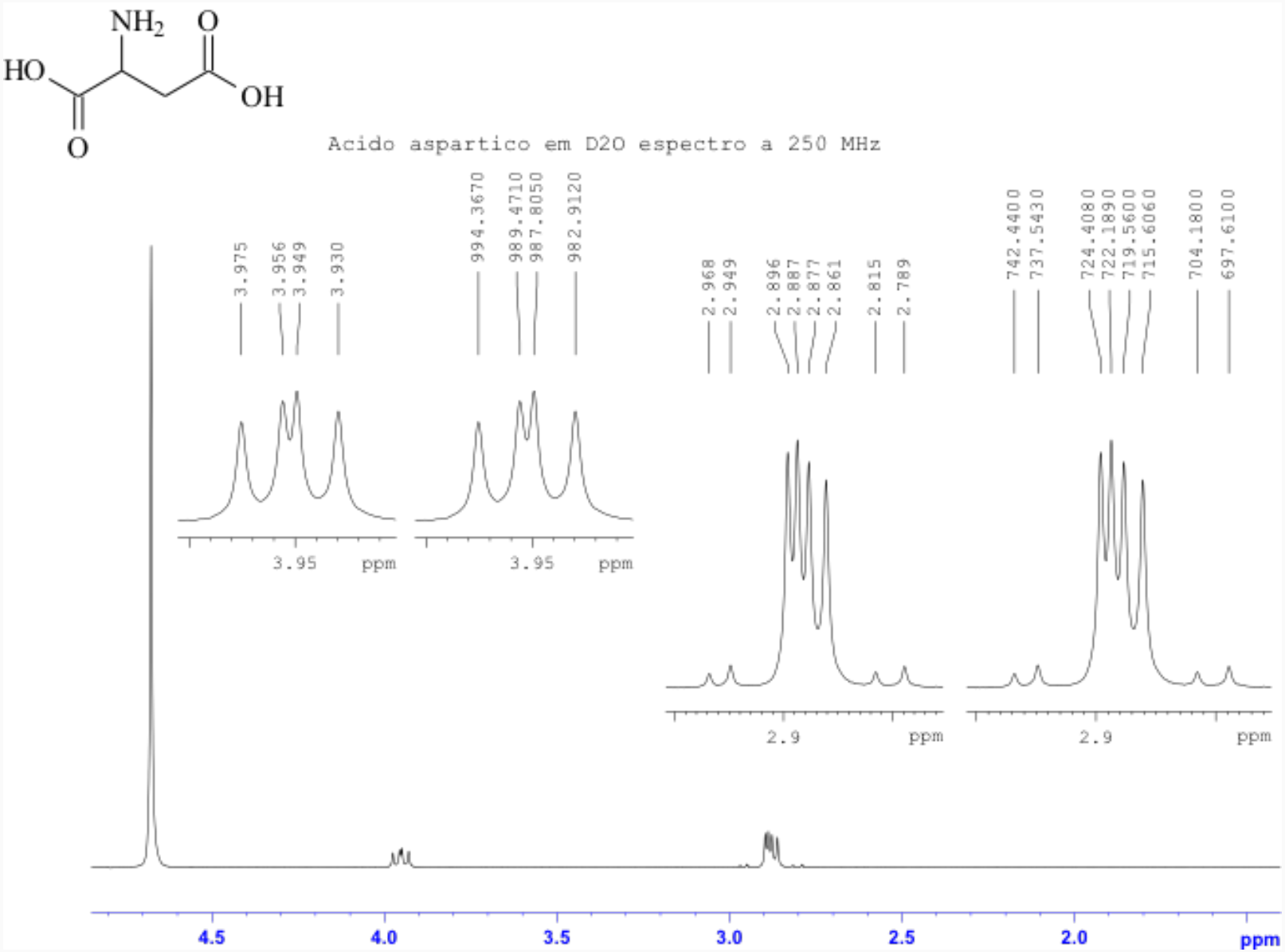


Espectros de 1° e 2° ordem

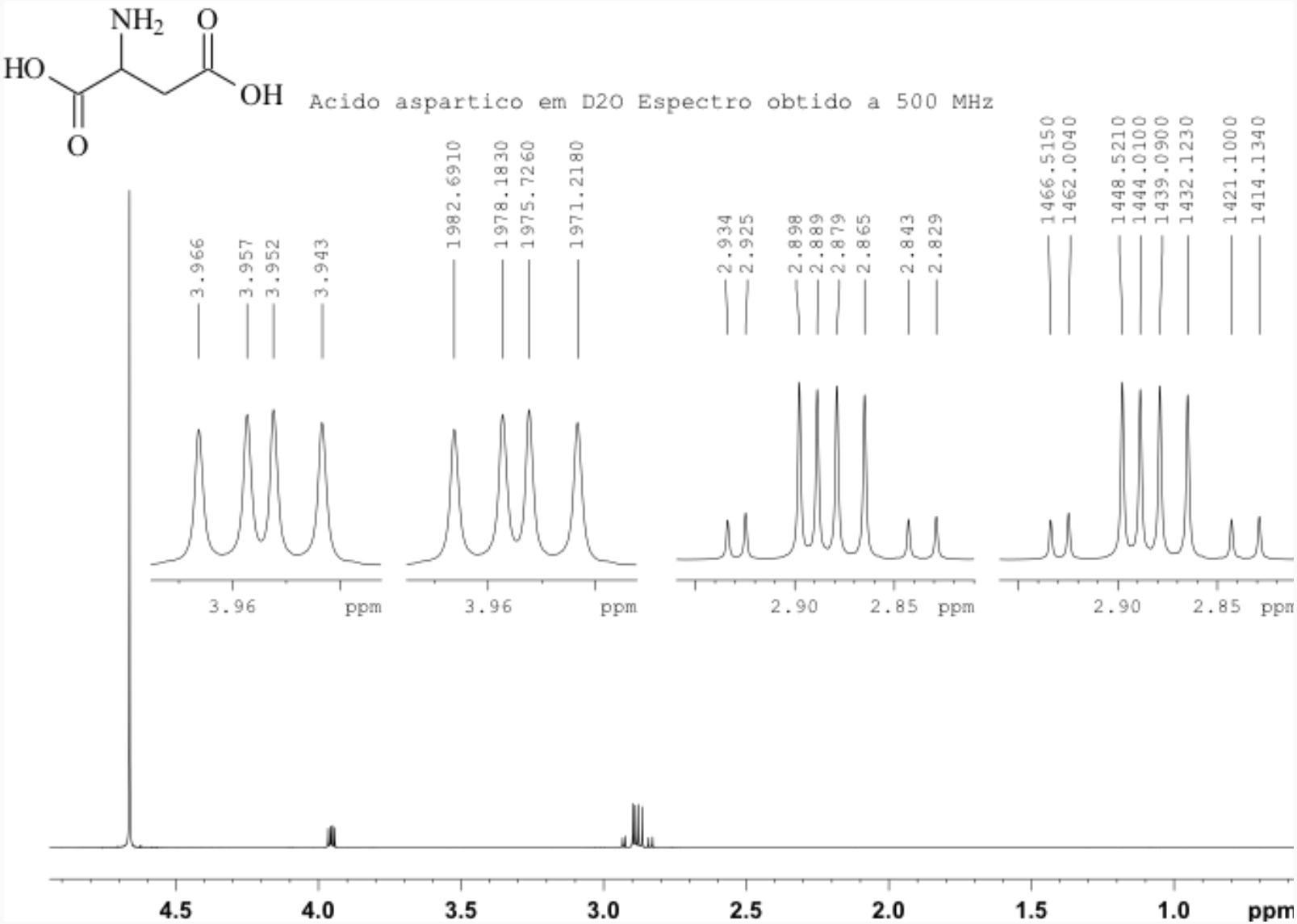


- 60 MHz: $\Delta\delta_{H_aH_b} = 0,5$ ppm e $J_{ab} = 10$ Hz
  - $\frac{(0,5 \times 60)}{10} = 3 \rightarrow$ espectro de 2° ordem
- 400 MHz: $\Delta\delta_{H_aH_b} = 0,5$ ppm e $J_{ab} = 10$ Hz
  - $\frac{(0,5 \times 400)}{10} = 20 \rightarrow$ espectro de 1° ordem

Espectros de ^{1}H do Ácido Aspartico a 250 MHz

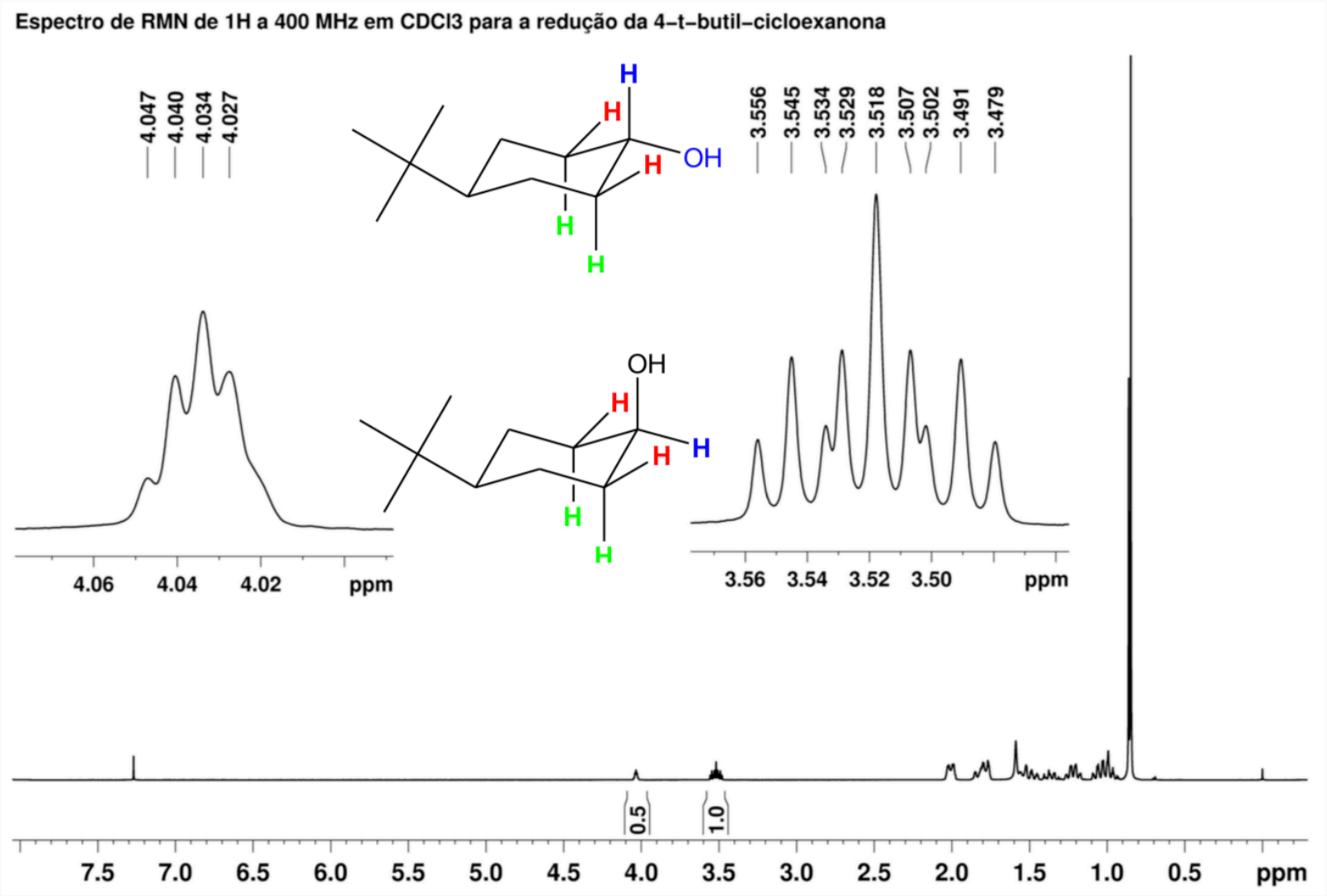


Espectros de ^{1}H do Ácido Aspartico a 500 MHz



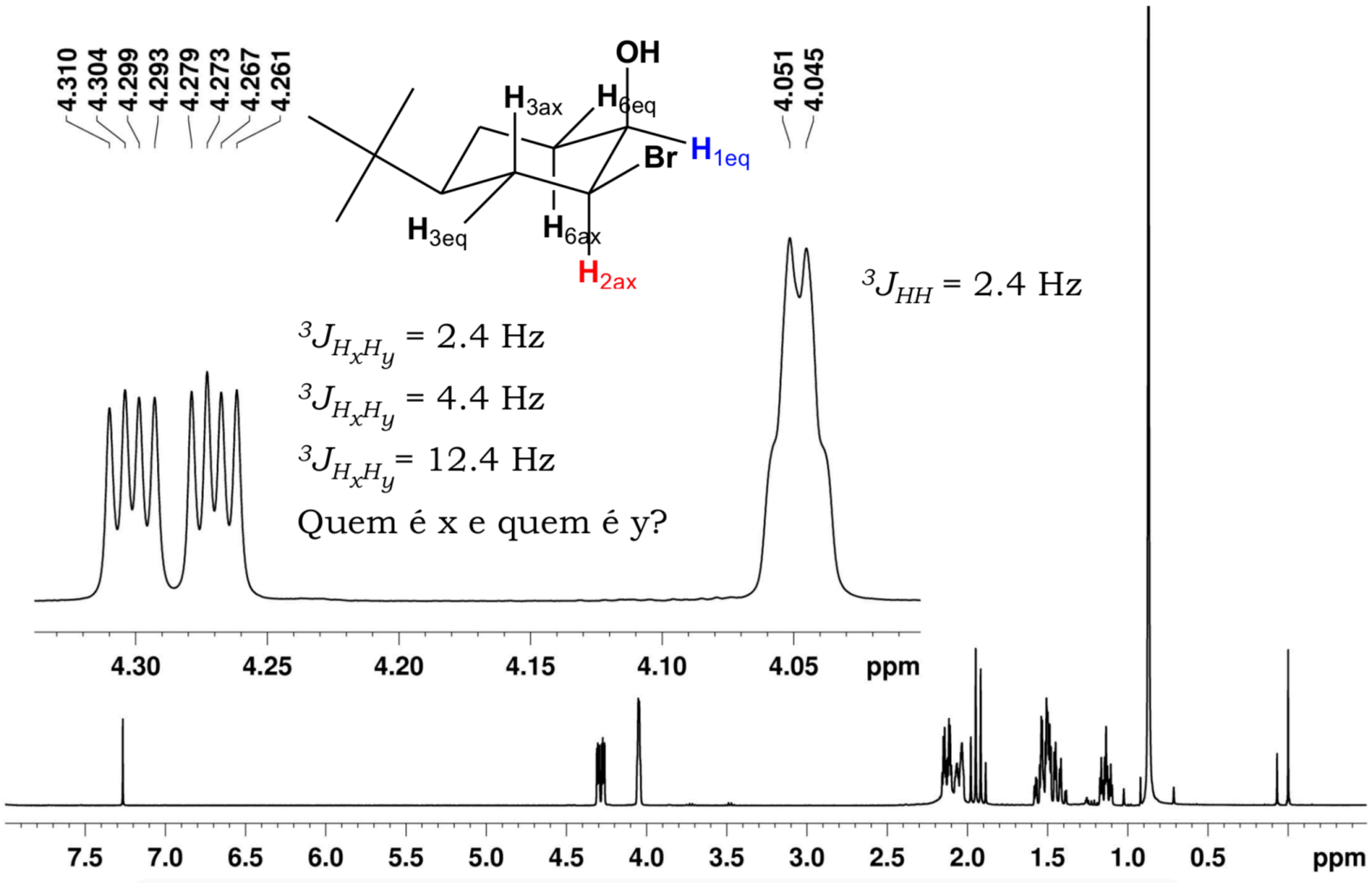
Exercícios

Ex.1: Mistura de Produtos de Reação

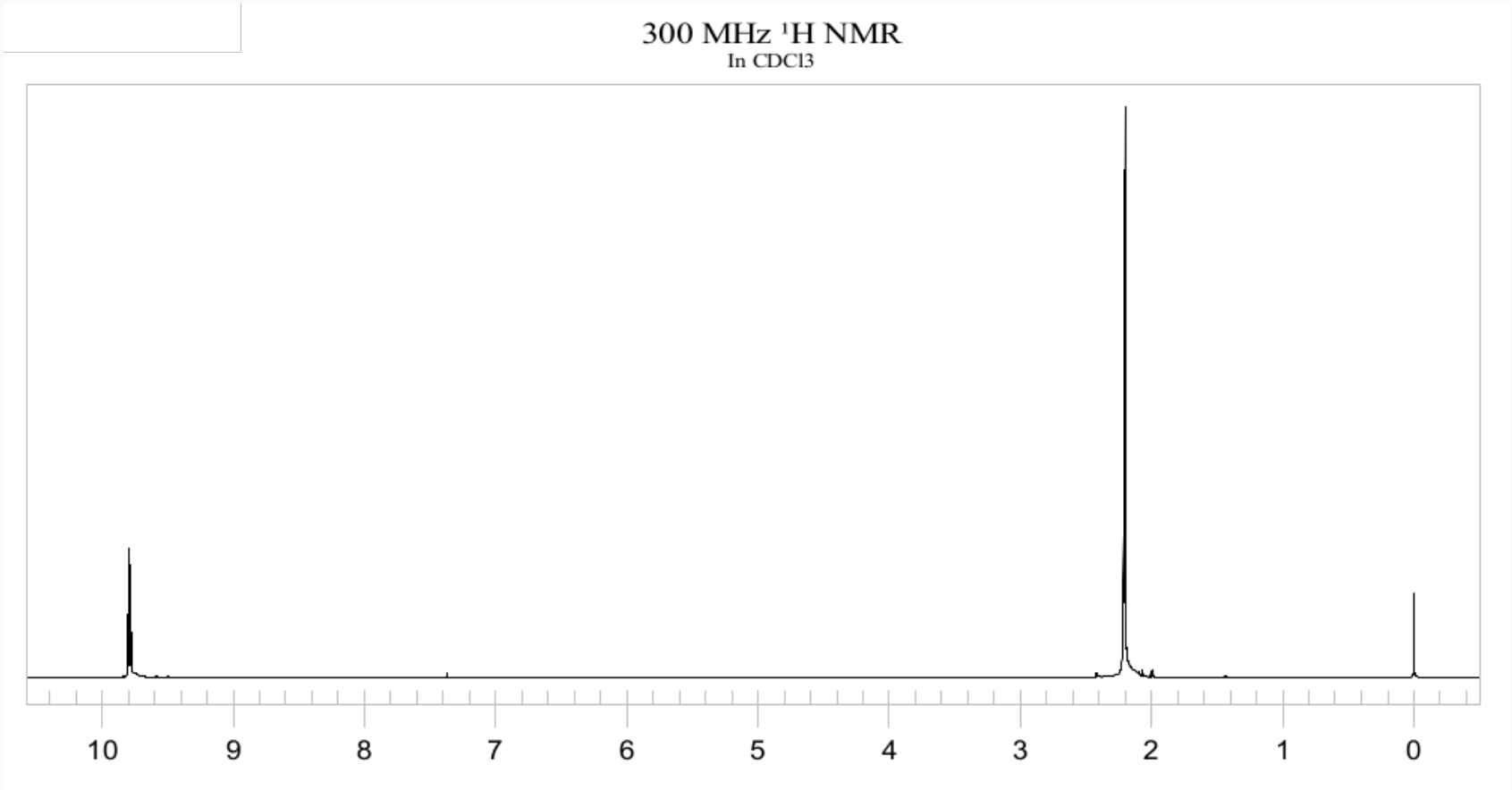


Ex. 2: Espectro de ^{1}H da cis-2-Bromo-4-T-butil-cicloexanona

Espectro de RMN de ^{1}H a 400 MHz para o produto da redução da *cis*-2-bromo-4-t-butyl-cicloexanona.



Ex. 3: Espectro de ^{1}H do C_2H_4O



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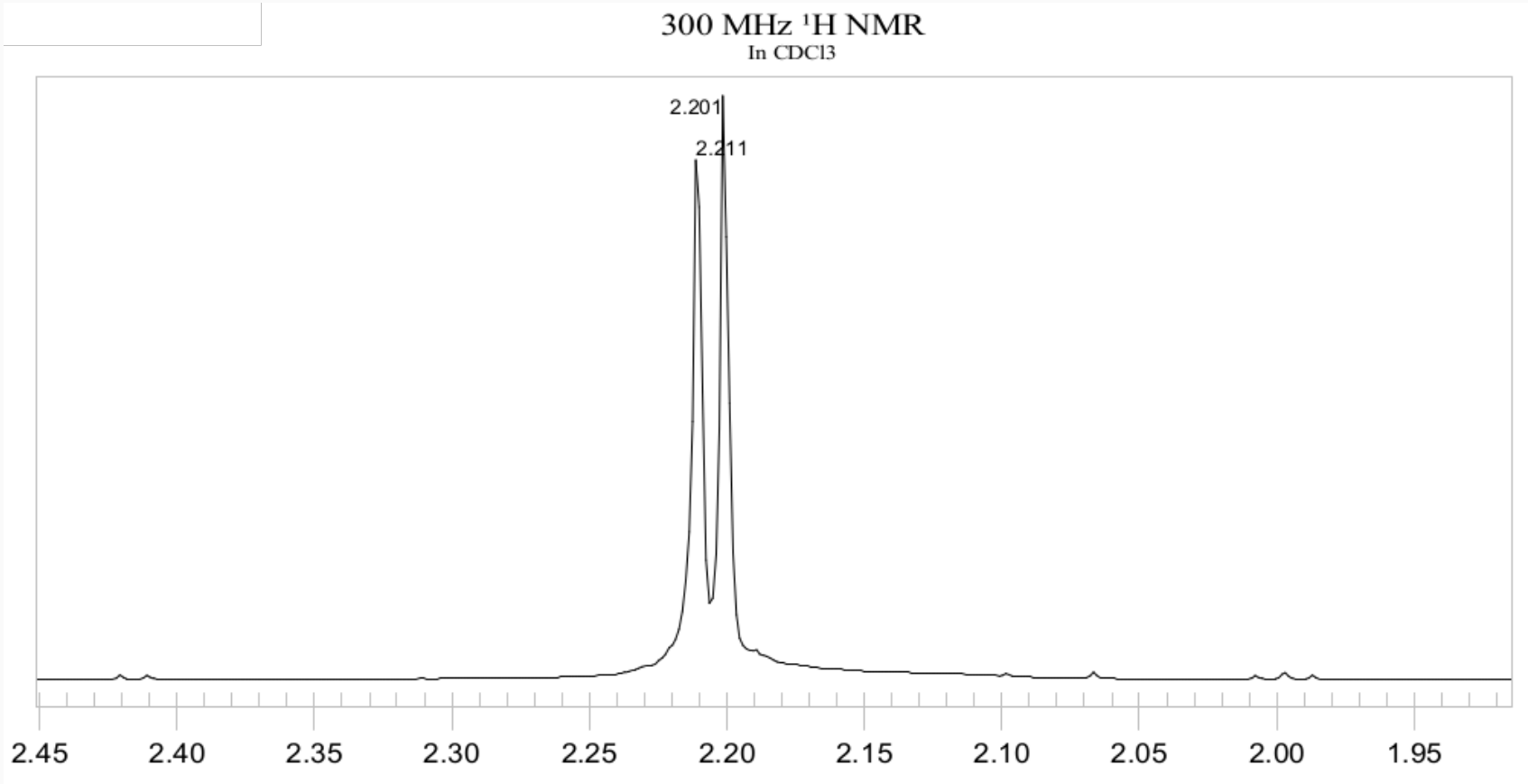

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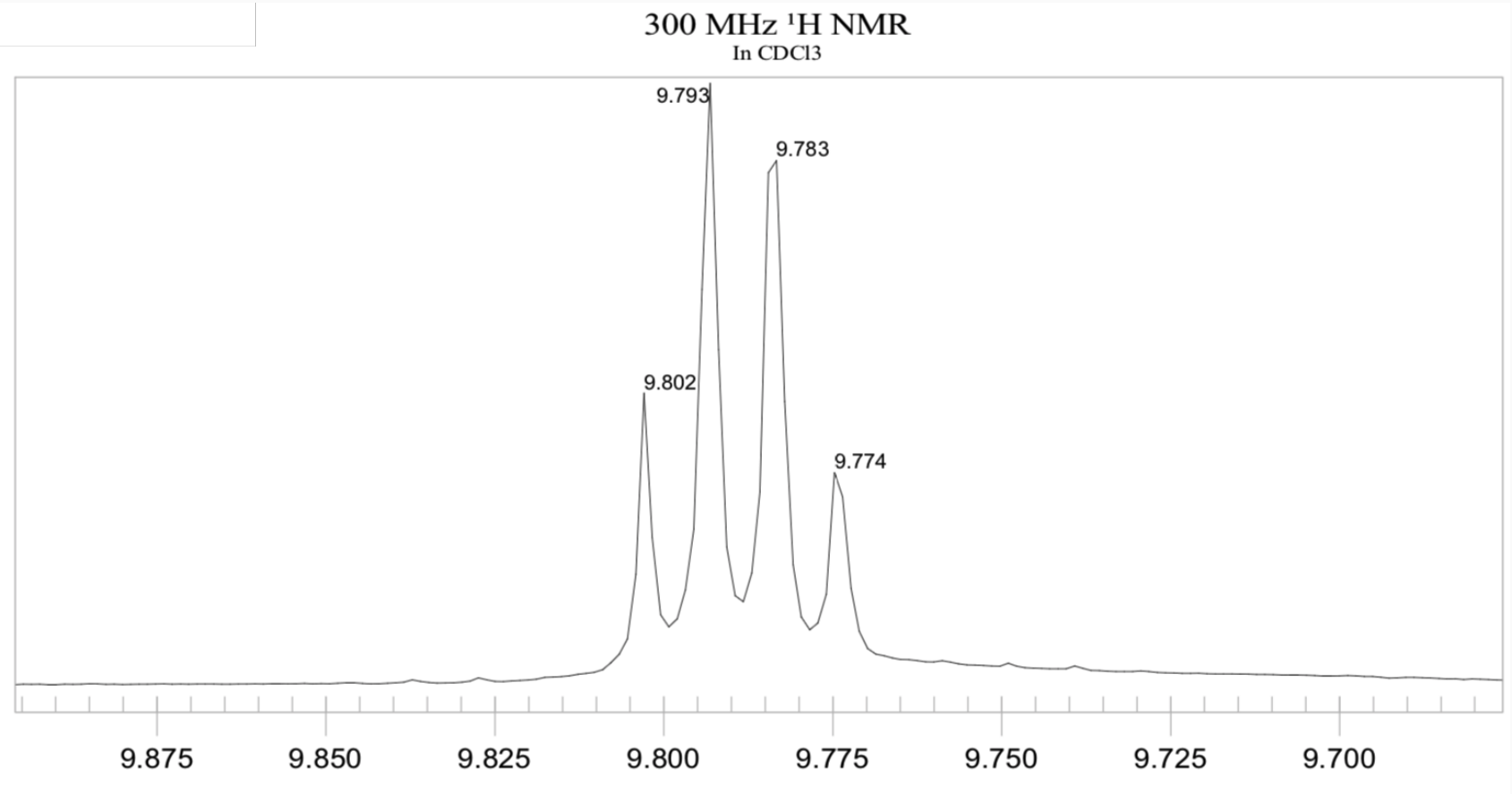
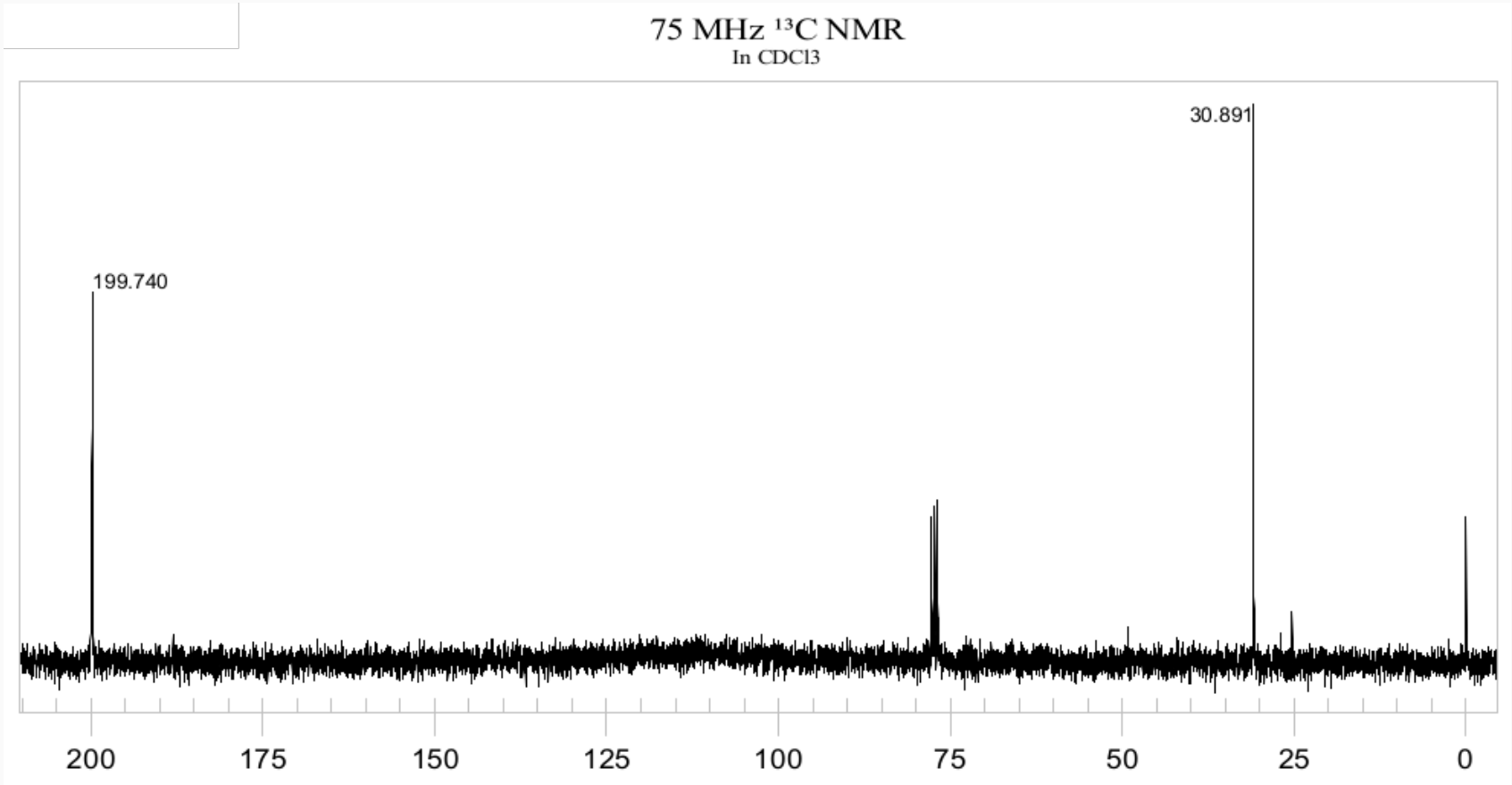
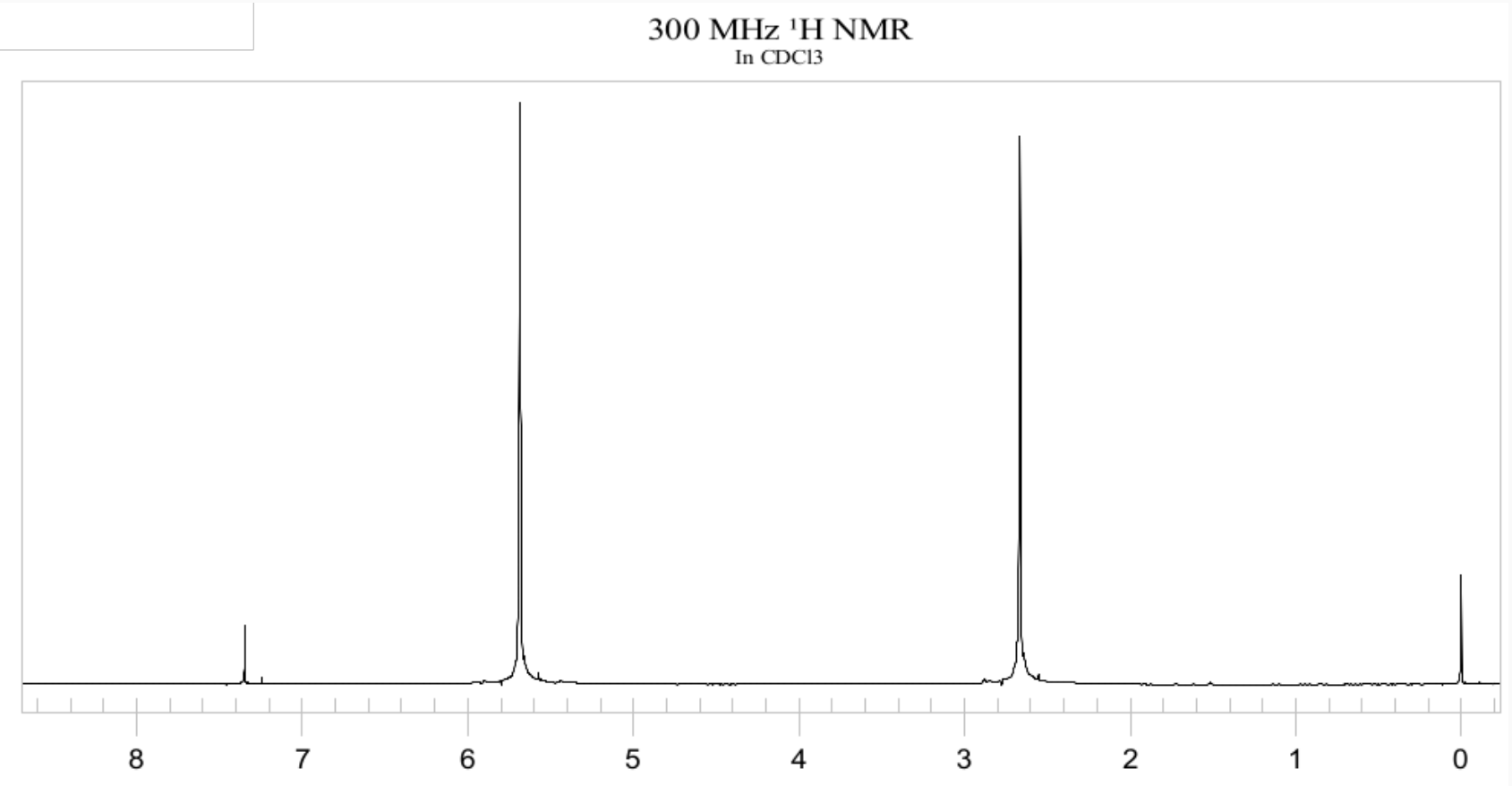


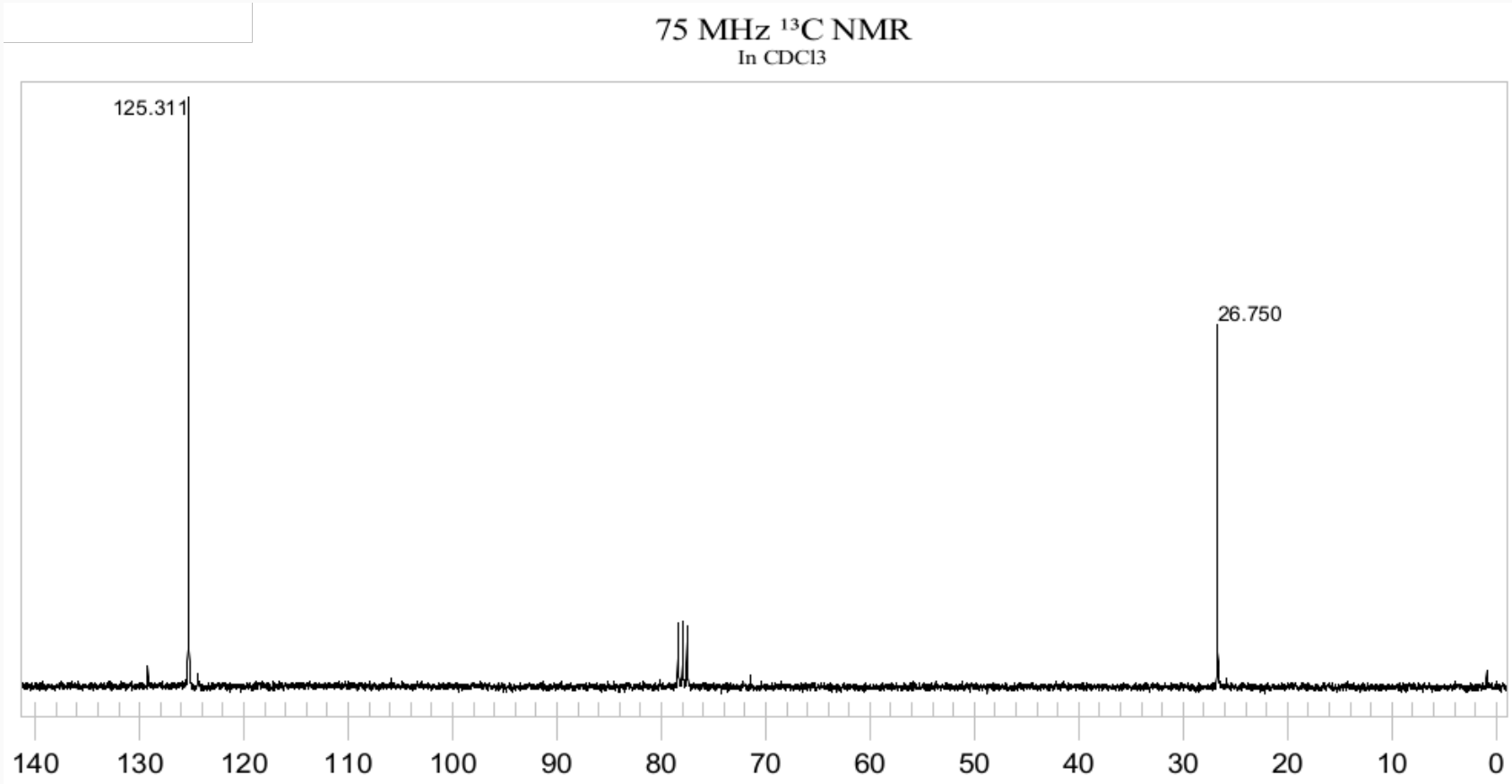
Ex. 3: Espectro de ^{13}C do C_2H_4O



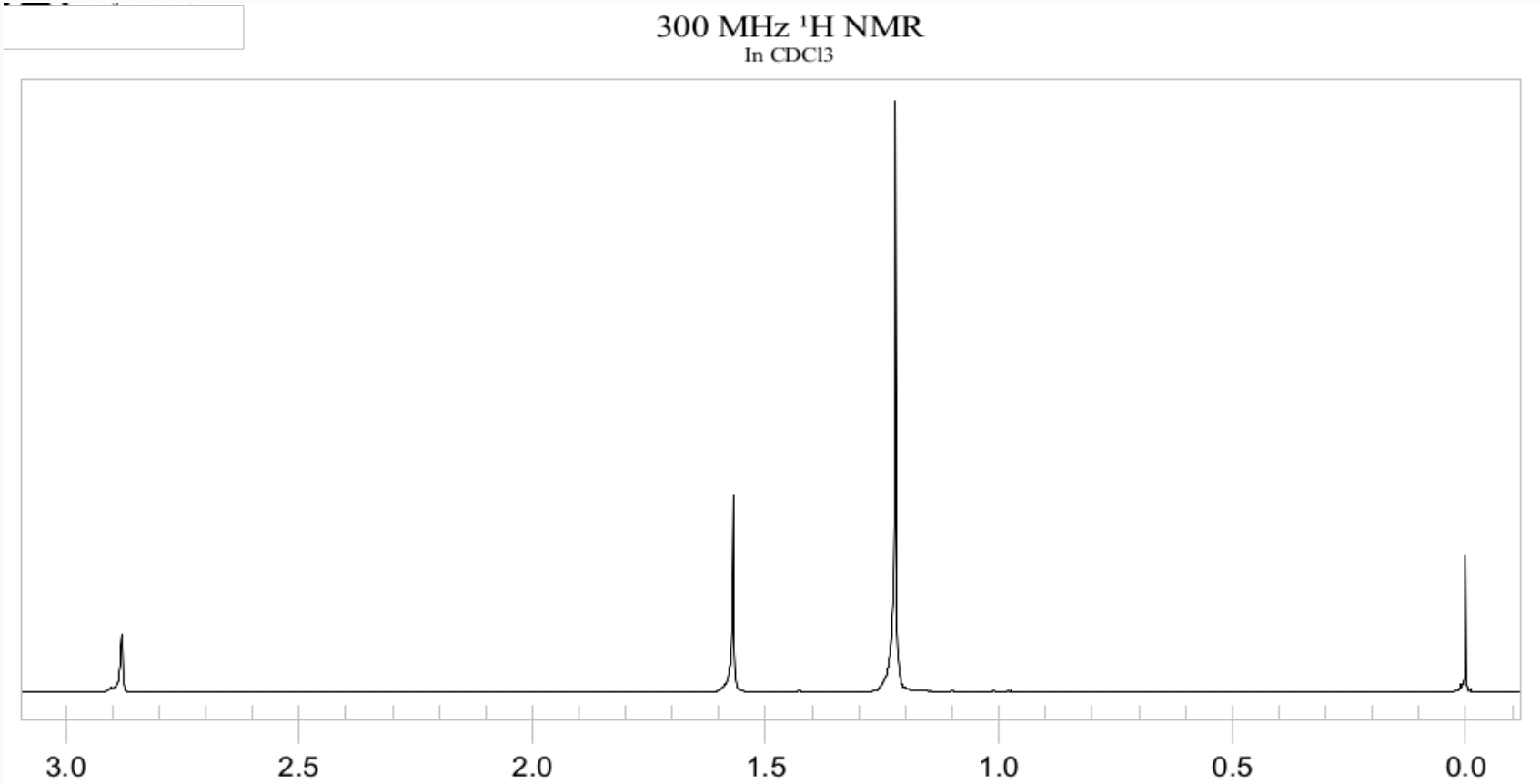
Ex. 4: Espectro de ^{1}H do C_6H_8



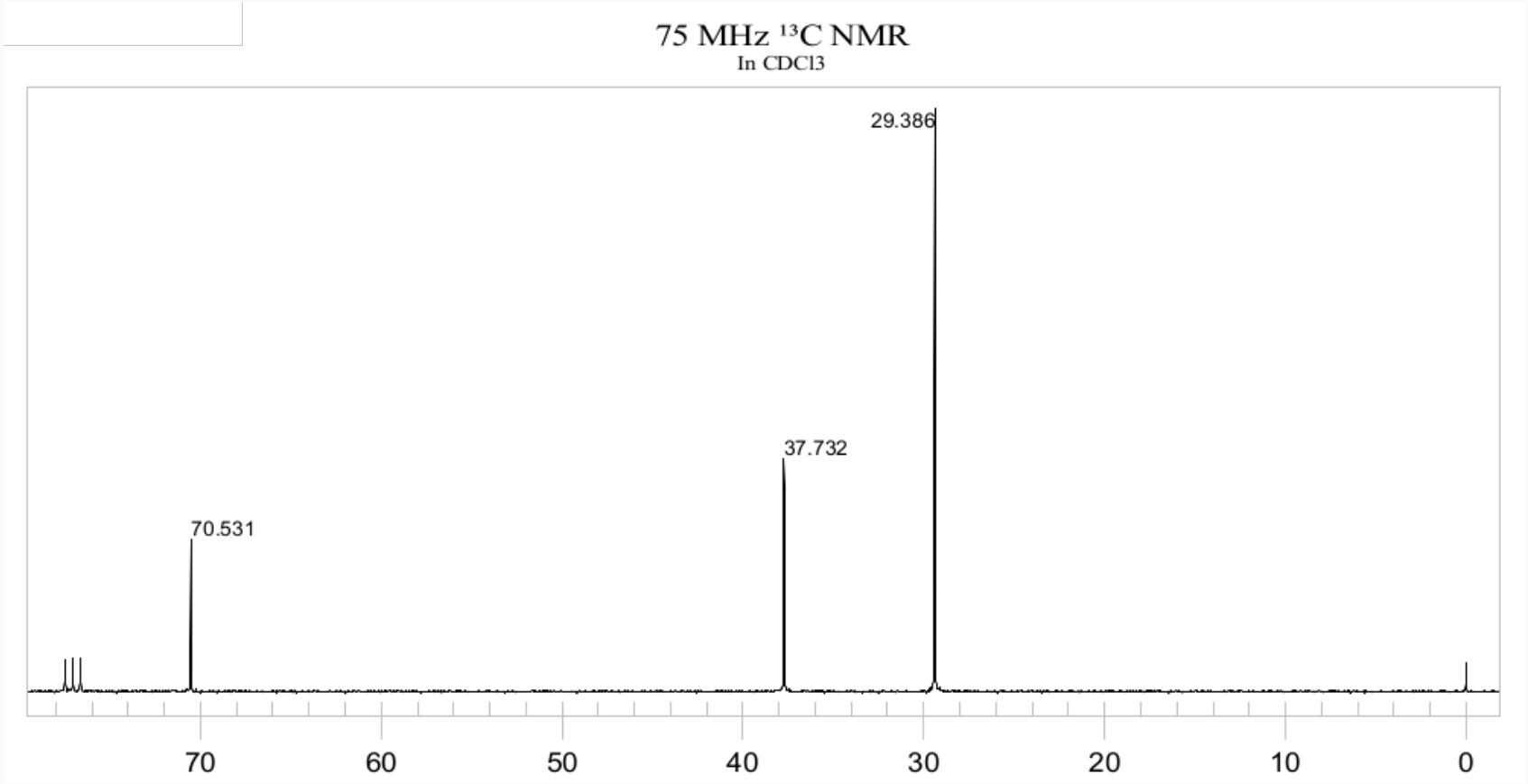
Ex. 4: Espectro de ^{13}C do C_6H_8



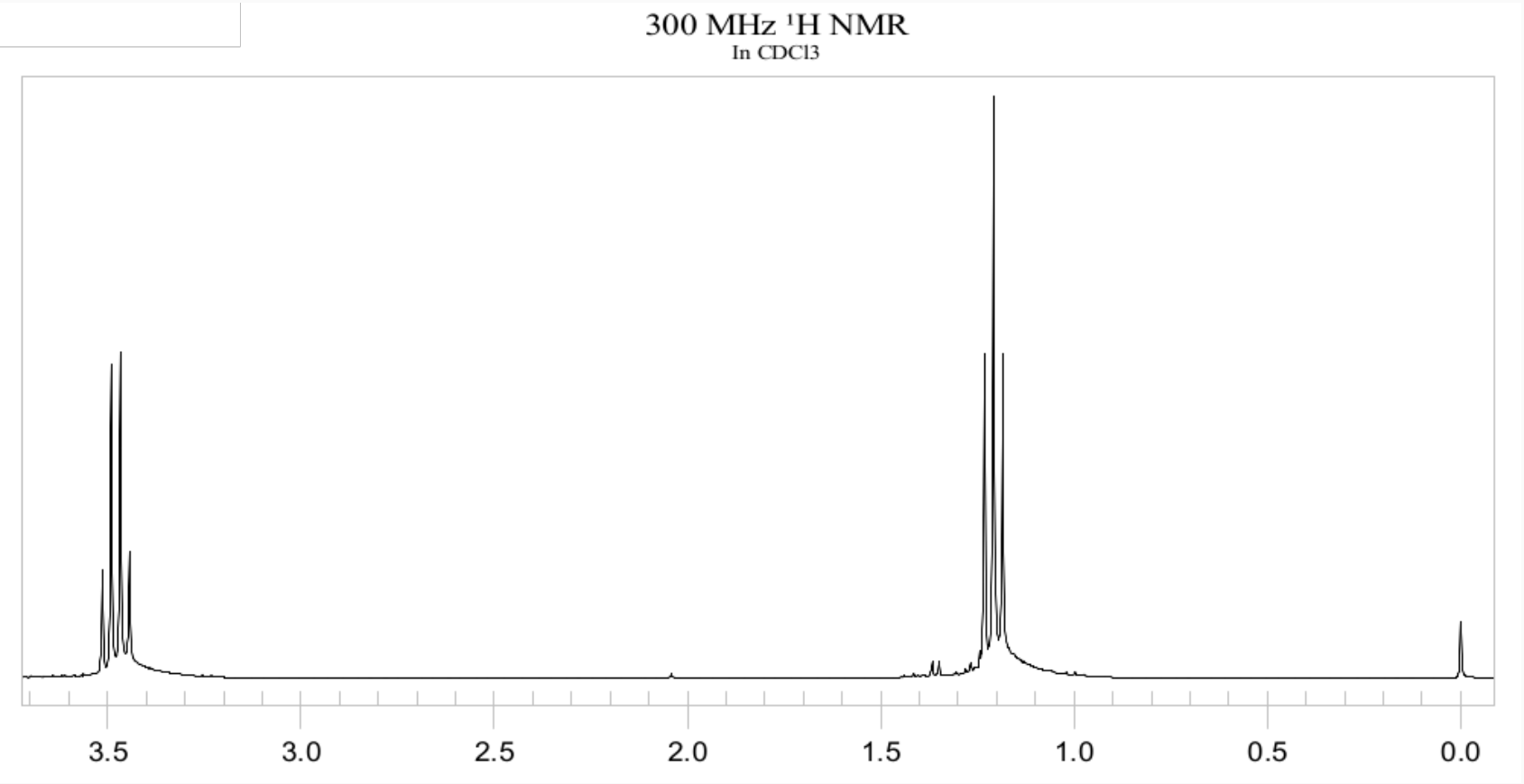
Ex. 5: Espectro de ^{1}H do $C_8H_{18}O_2$



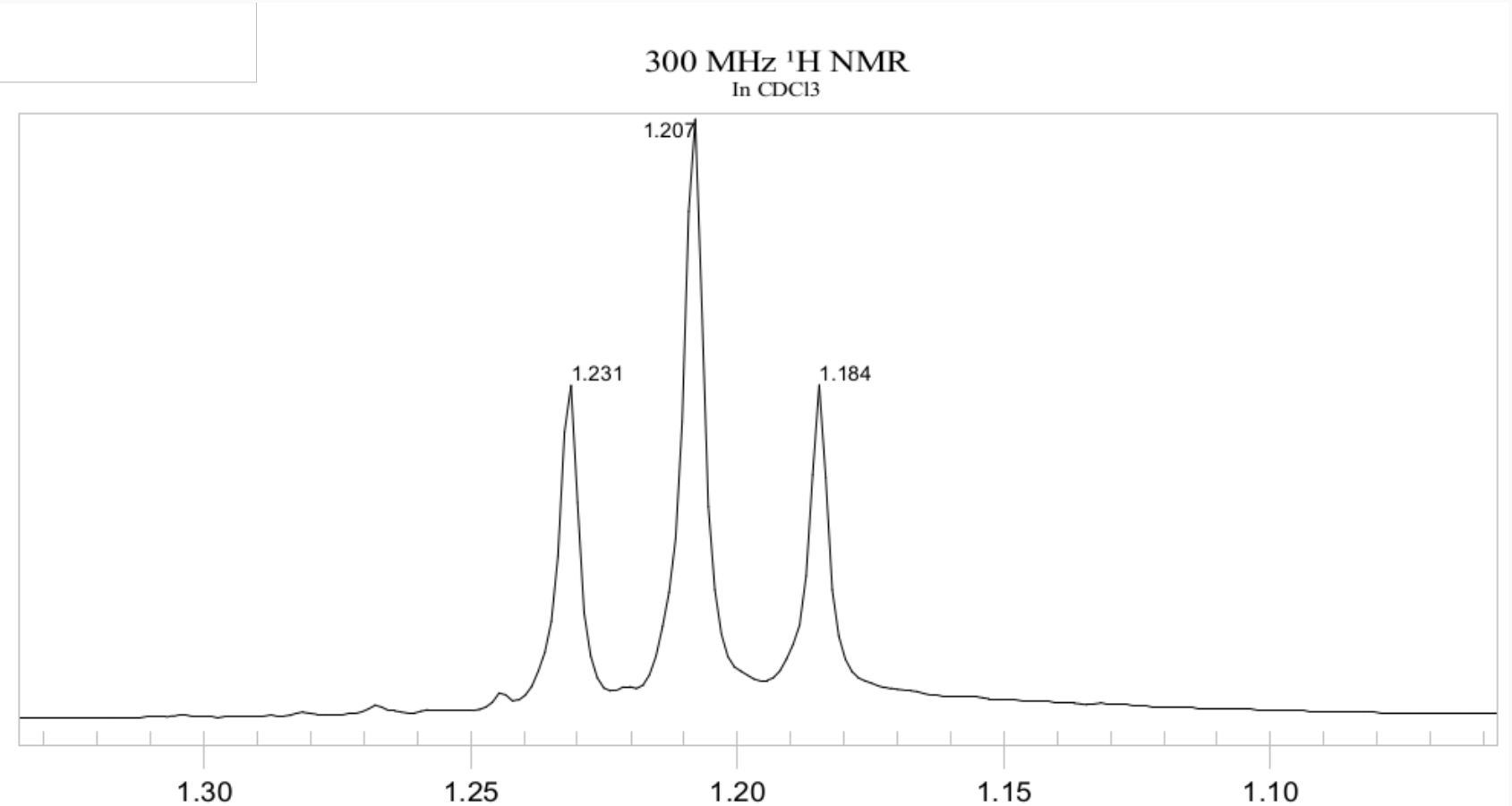
Ex. 5: Espectro de ^{13}C do $C_8H_{18}O_2$



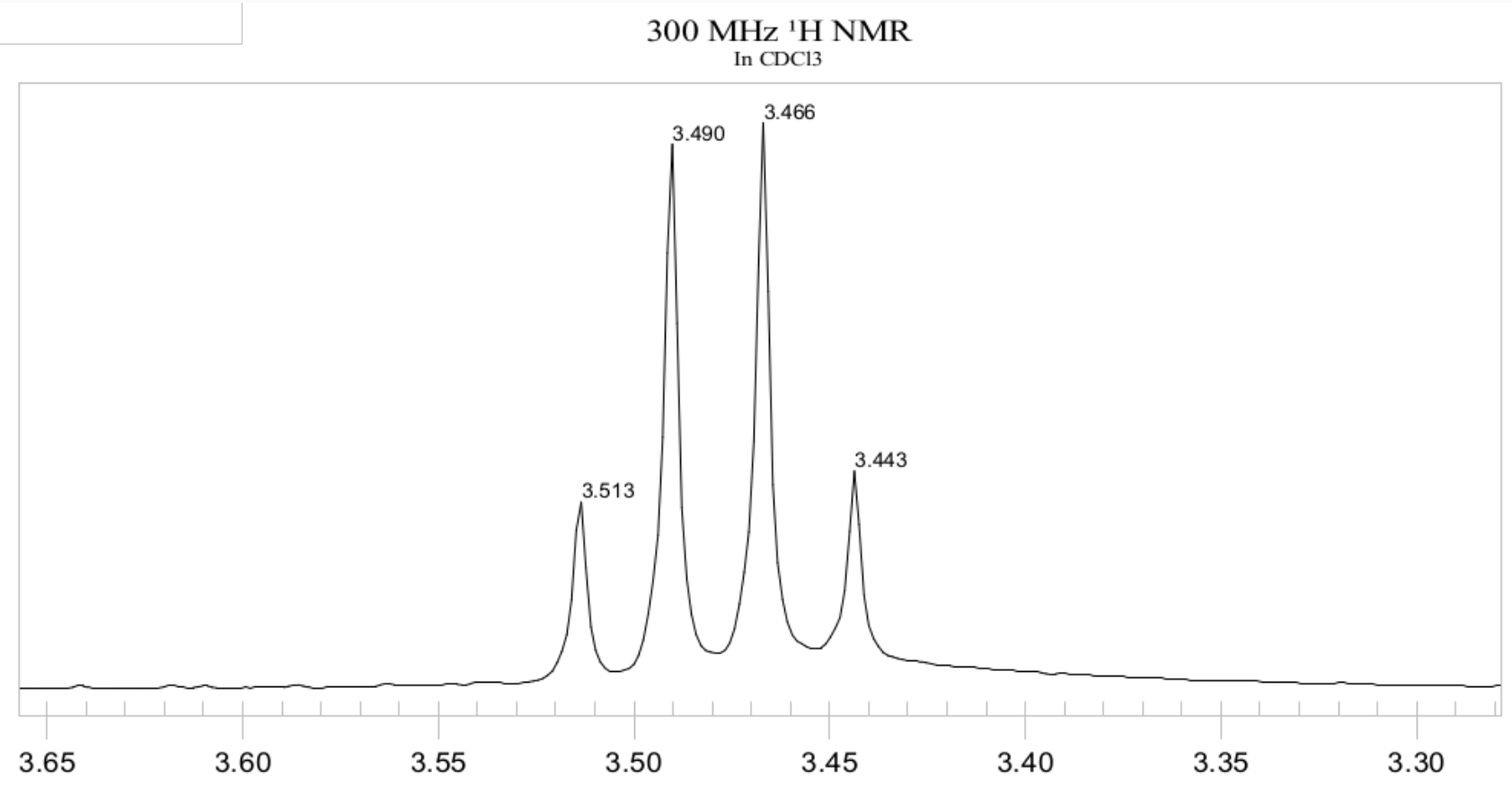
Ex. 6: Espectro de ^{1}H do $C_4H_{10}O$



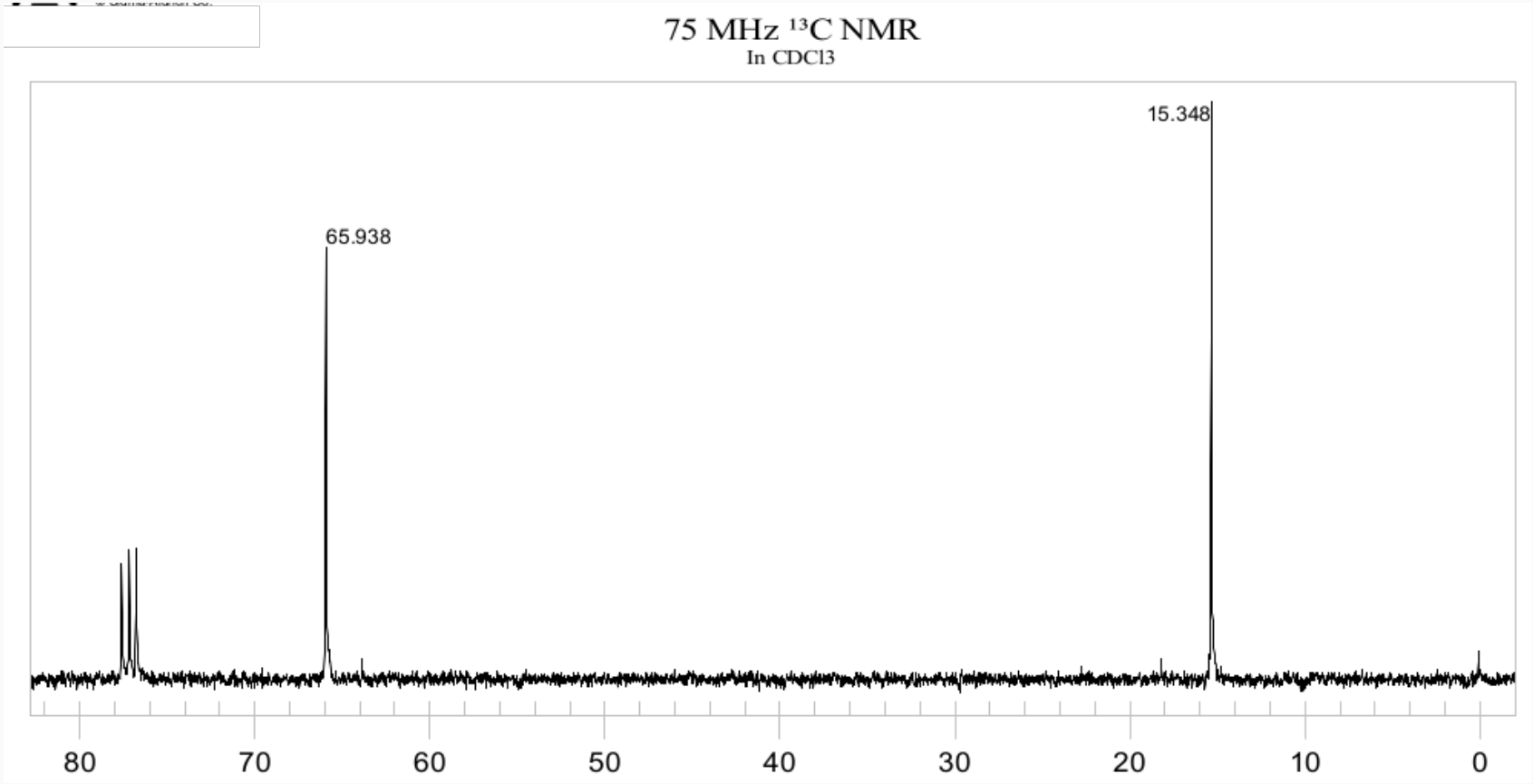
Ex. 6: Espectro de ^{1}H do $C_4H_{10}O$



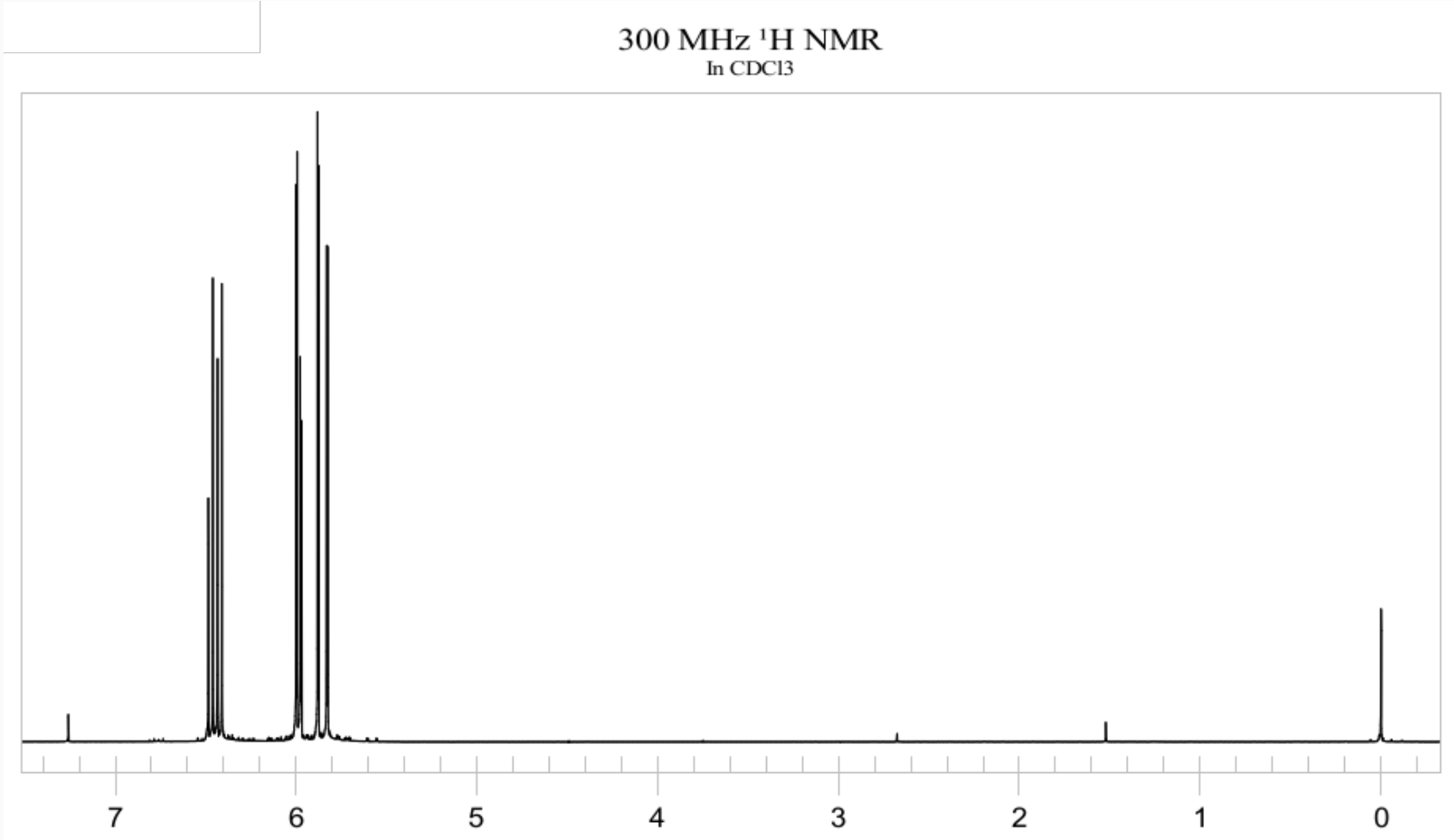
Ex. 6: Espectro de ^1H do $C_4H_{10}O$



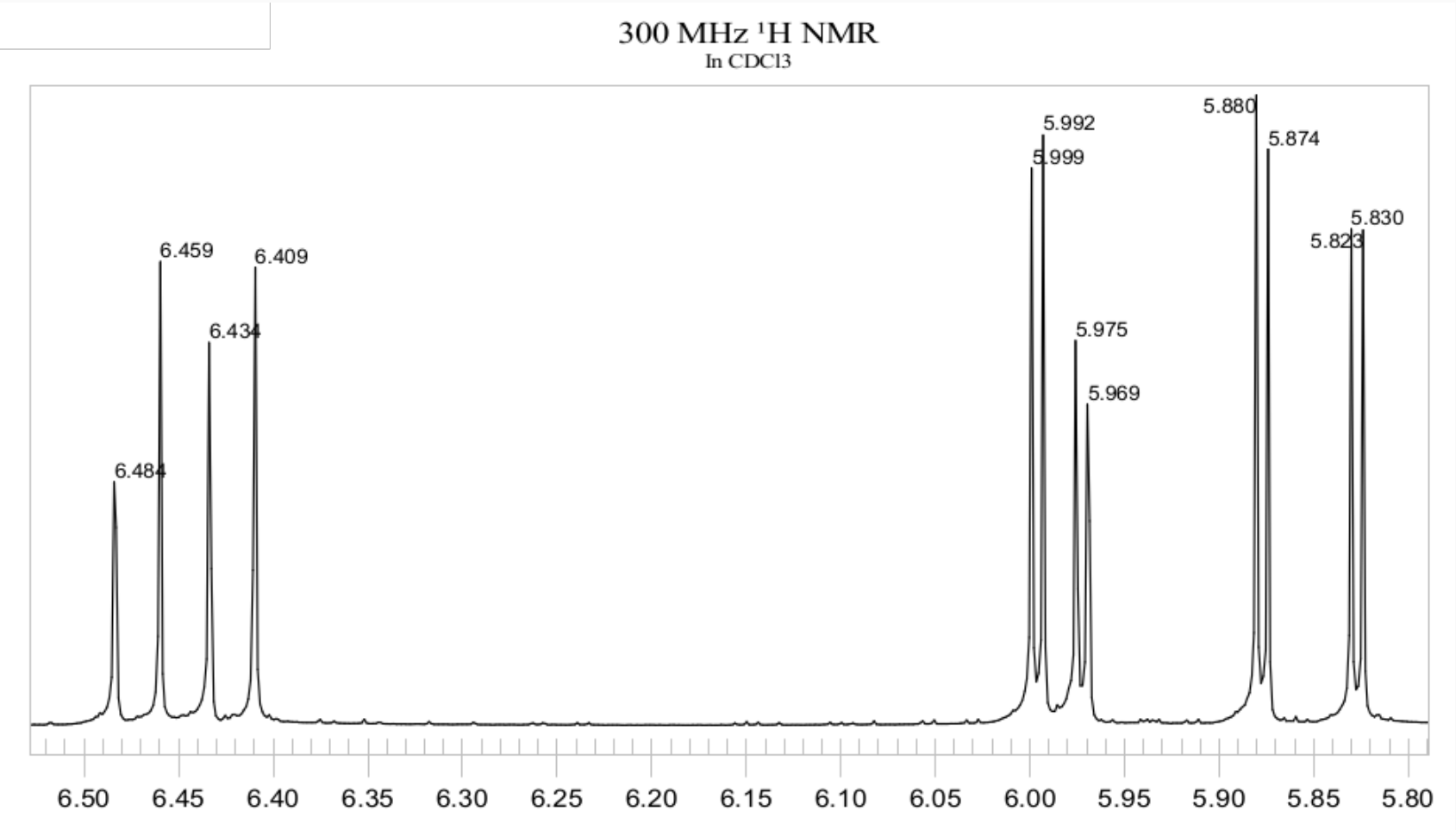
Ex. 6: Espectro de ^{13}C do $C_4H_{10}O$



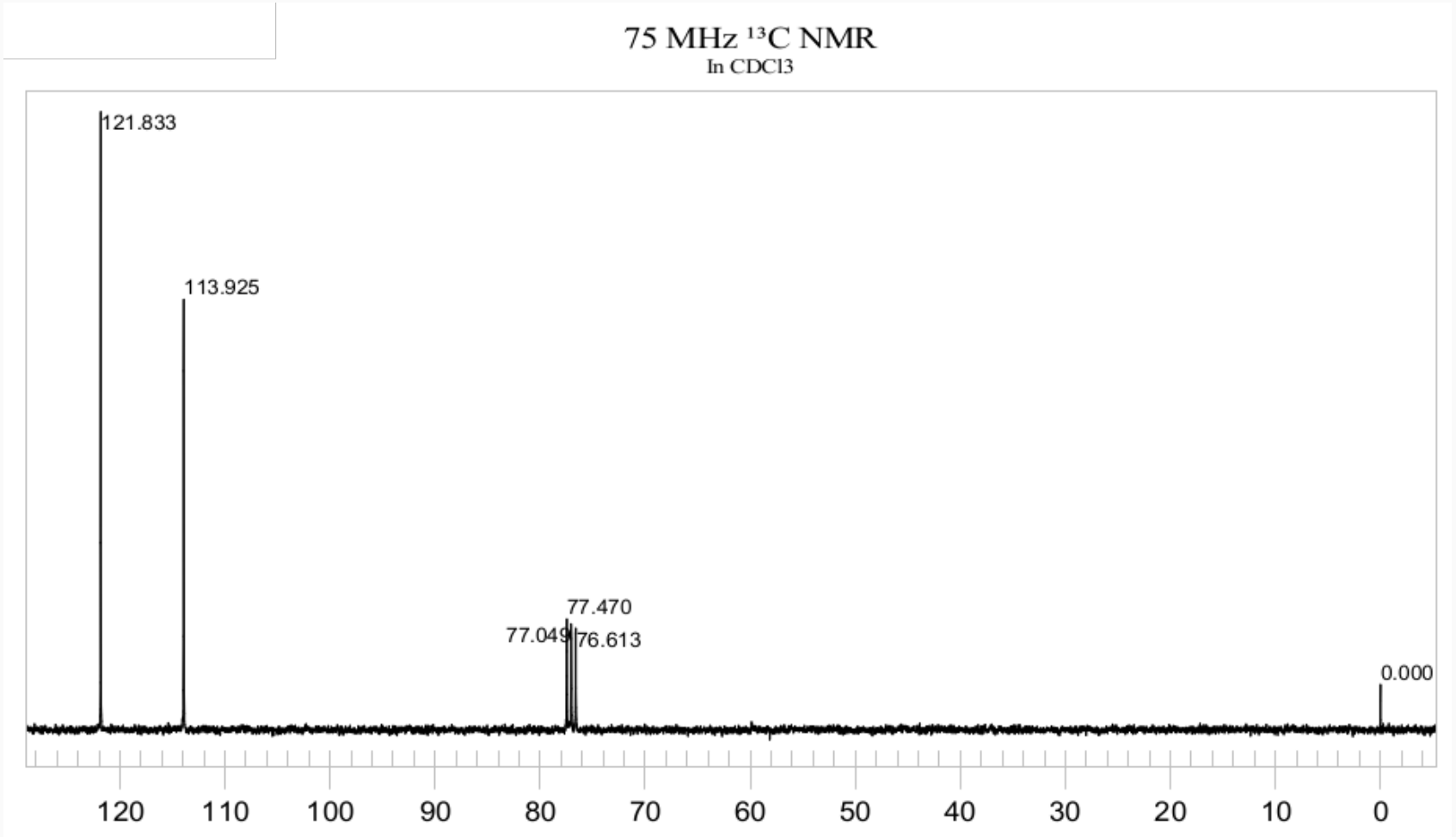
Ex. 7: Espectro de ^{1}H do C_2H_3Br



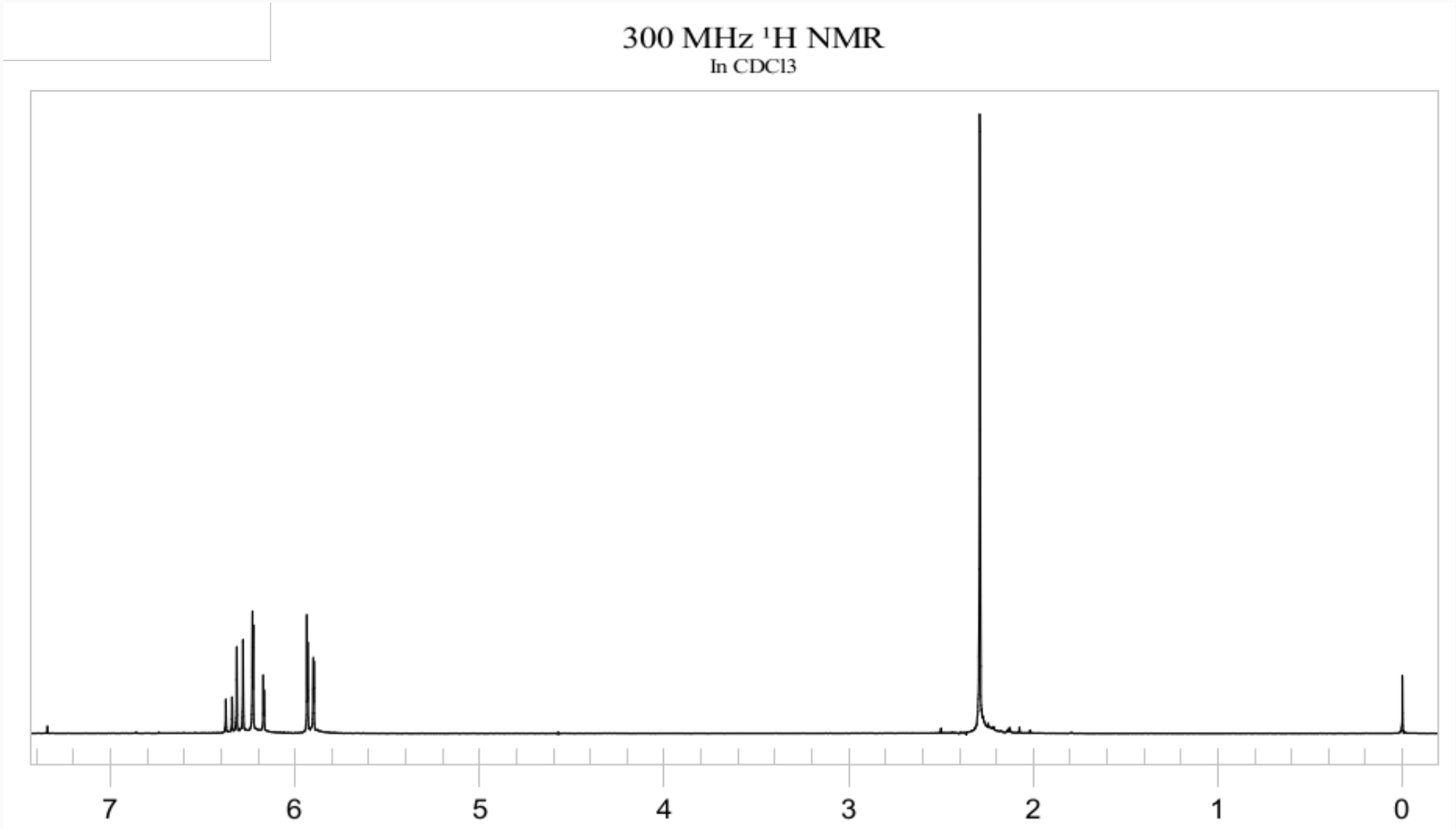
Ex. 7: Espectro de ^{1}H do C_2H_3Br



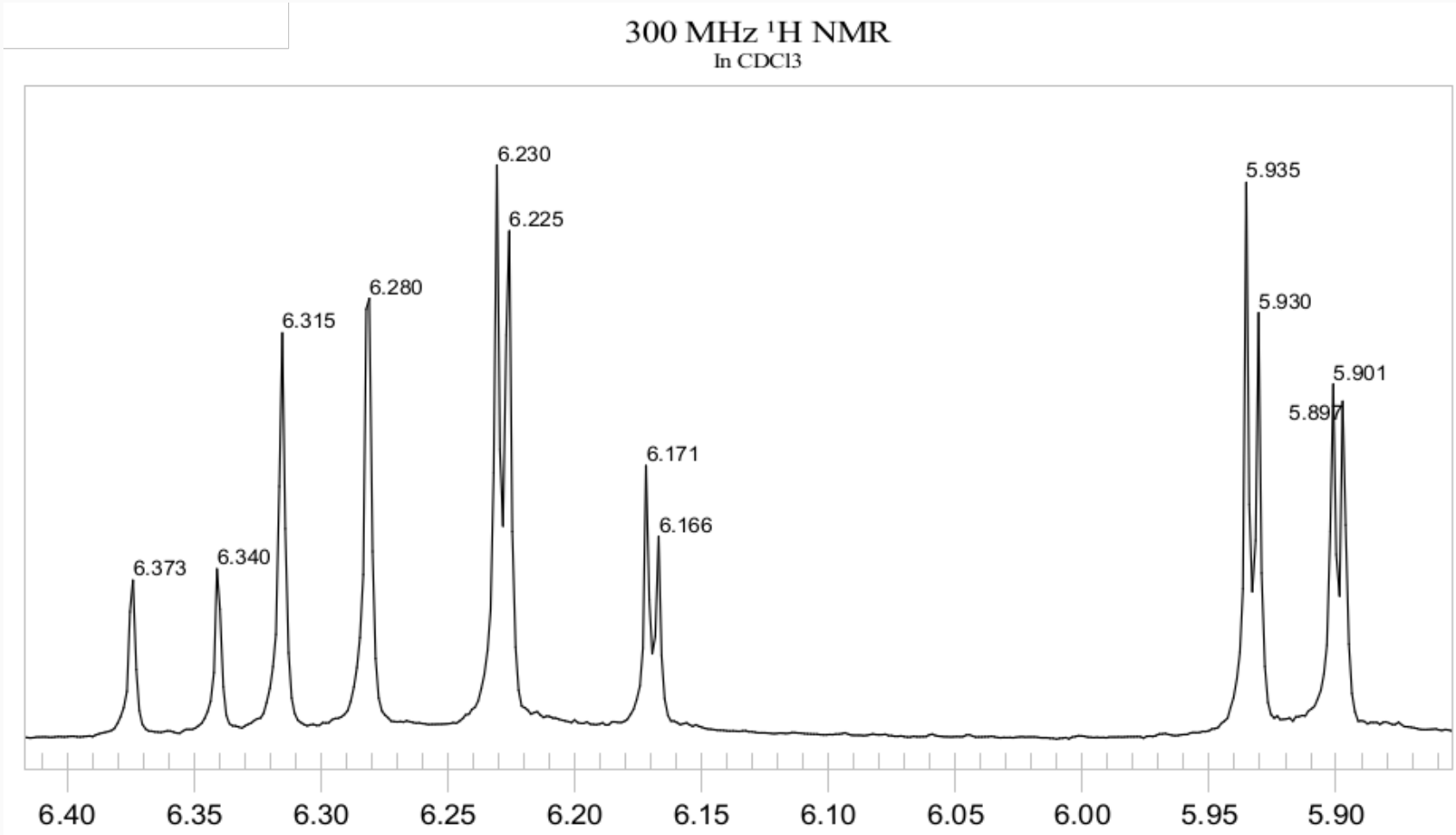
Ex. 7: Espectro de ^{13}C do C_2H_3Br



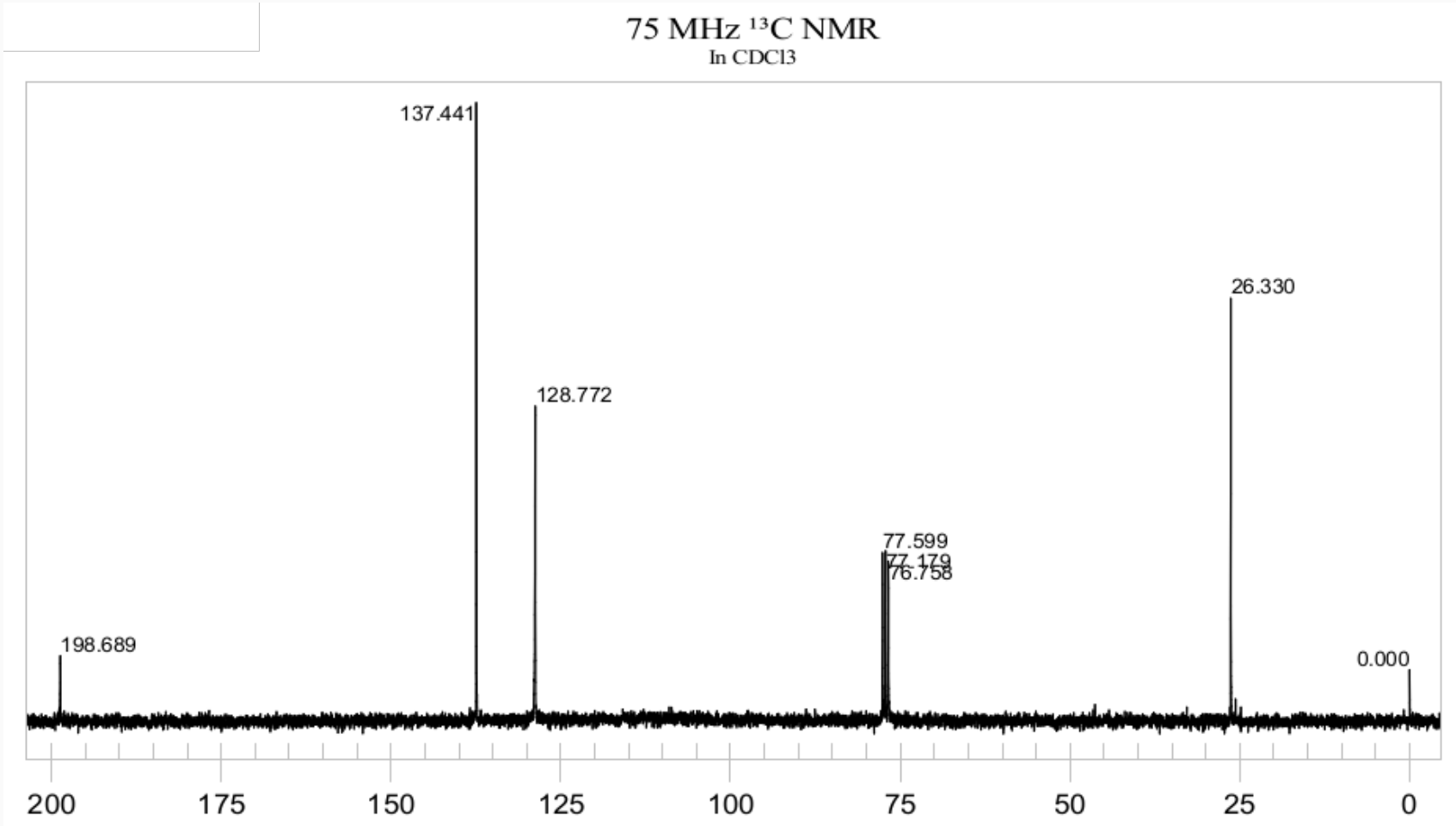
Ex. 8: Espectro de ^{1}H do C_4H_6O



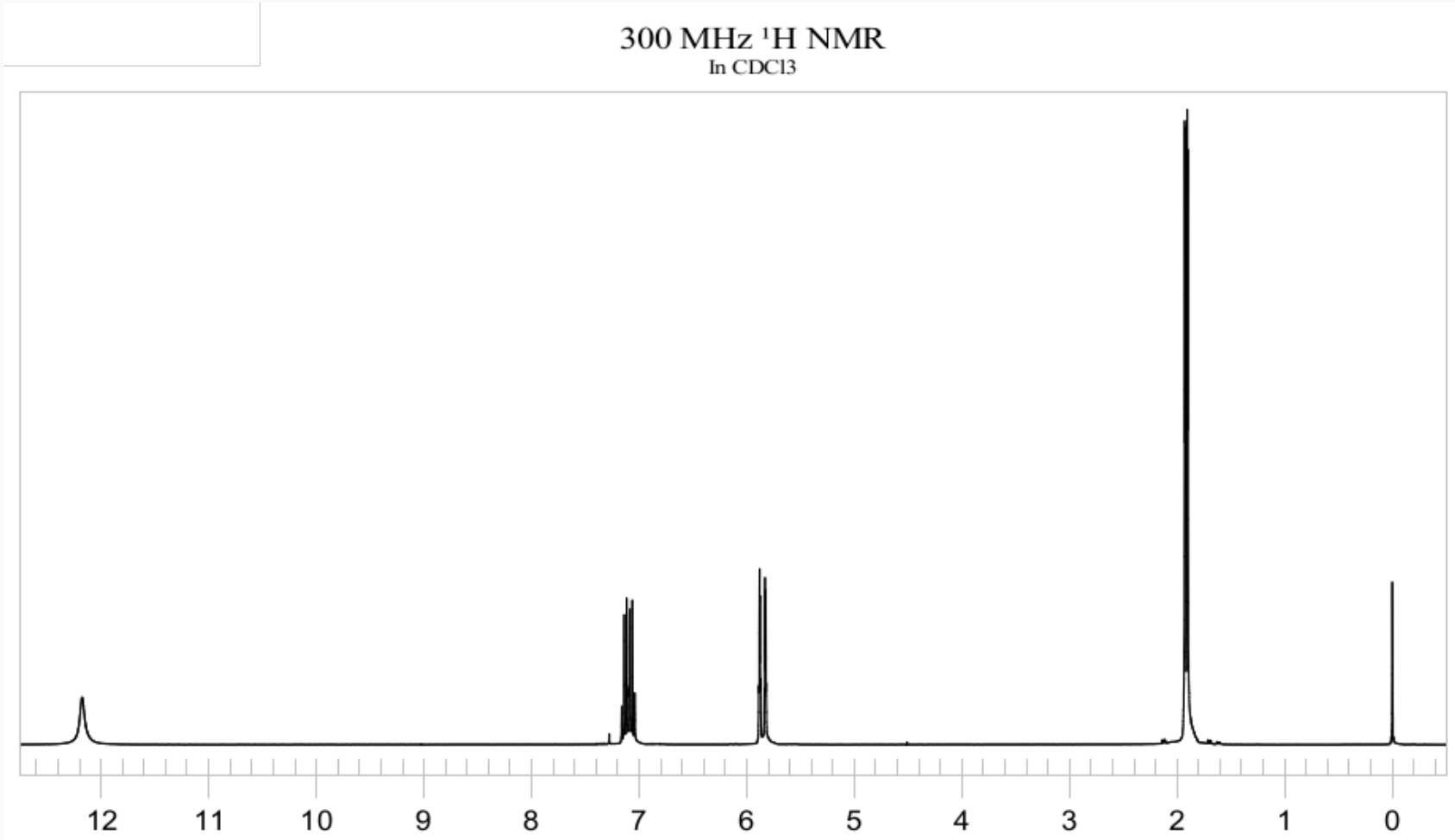
Ex. 8: Espectro de ^{1}H do C_4H_6O



Ex. 8: Espectro de ^{13}C do C_4H_6O



Ex. 9: Espectro de ^{1}H do $C_4H_6O_2$



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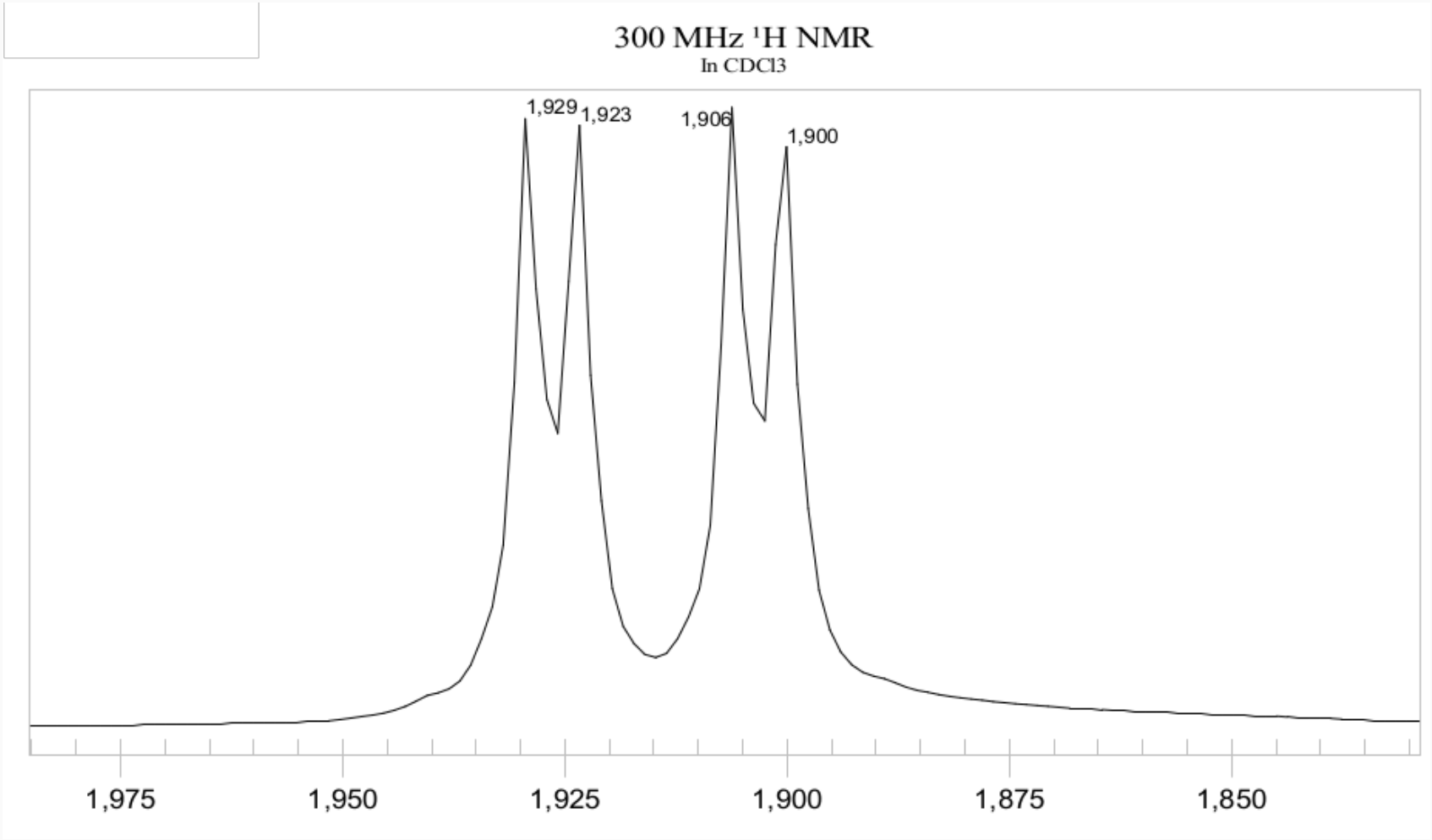

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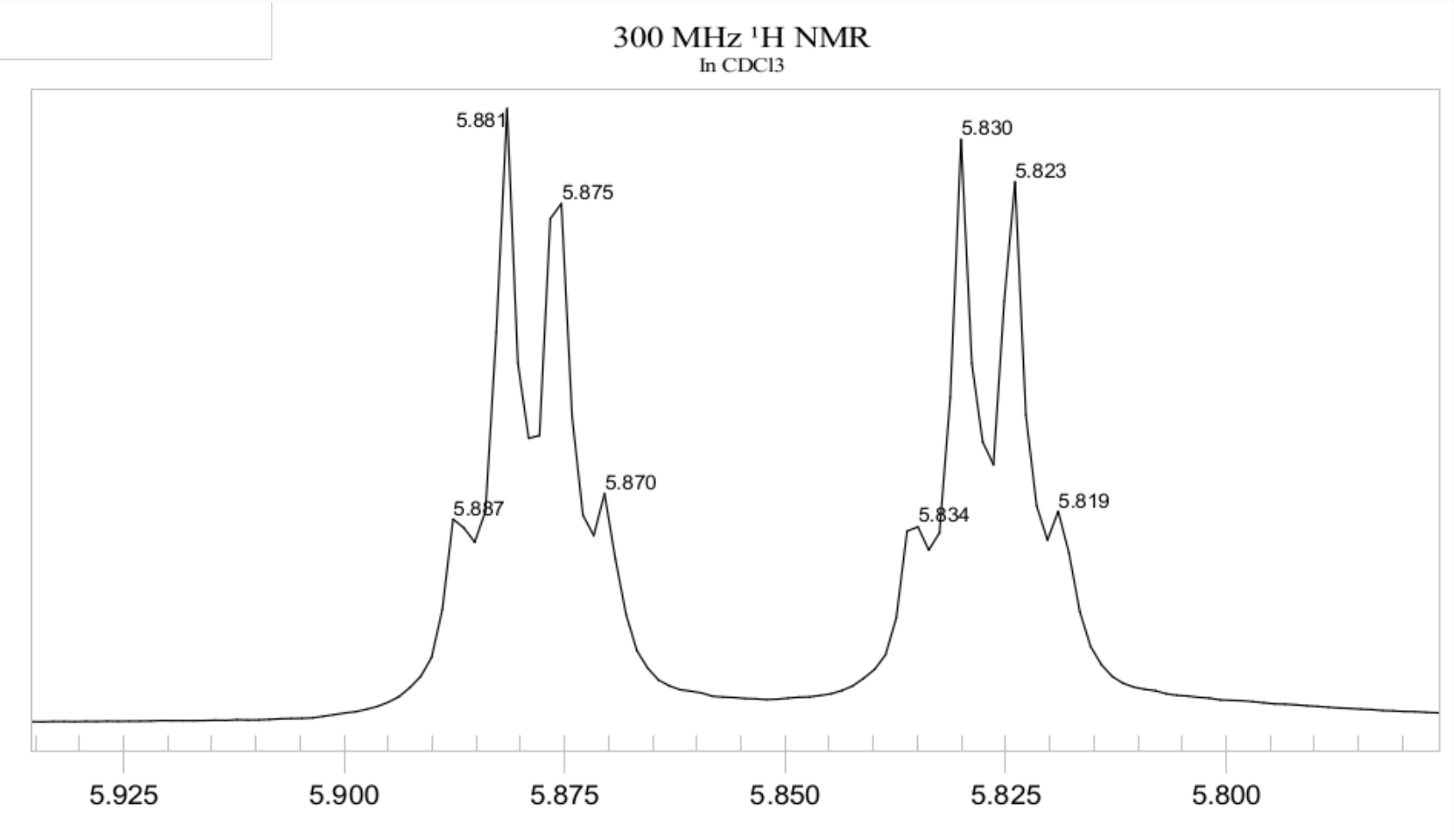
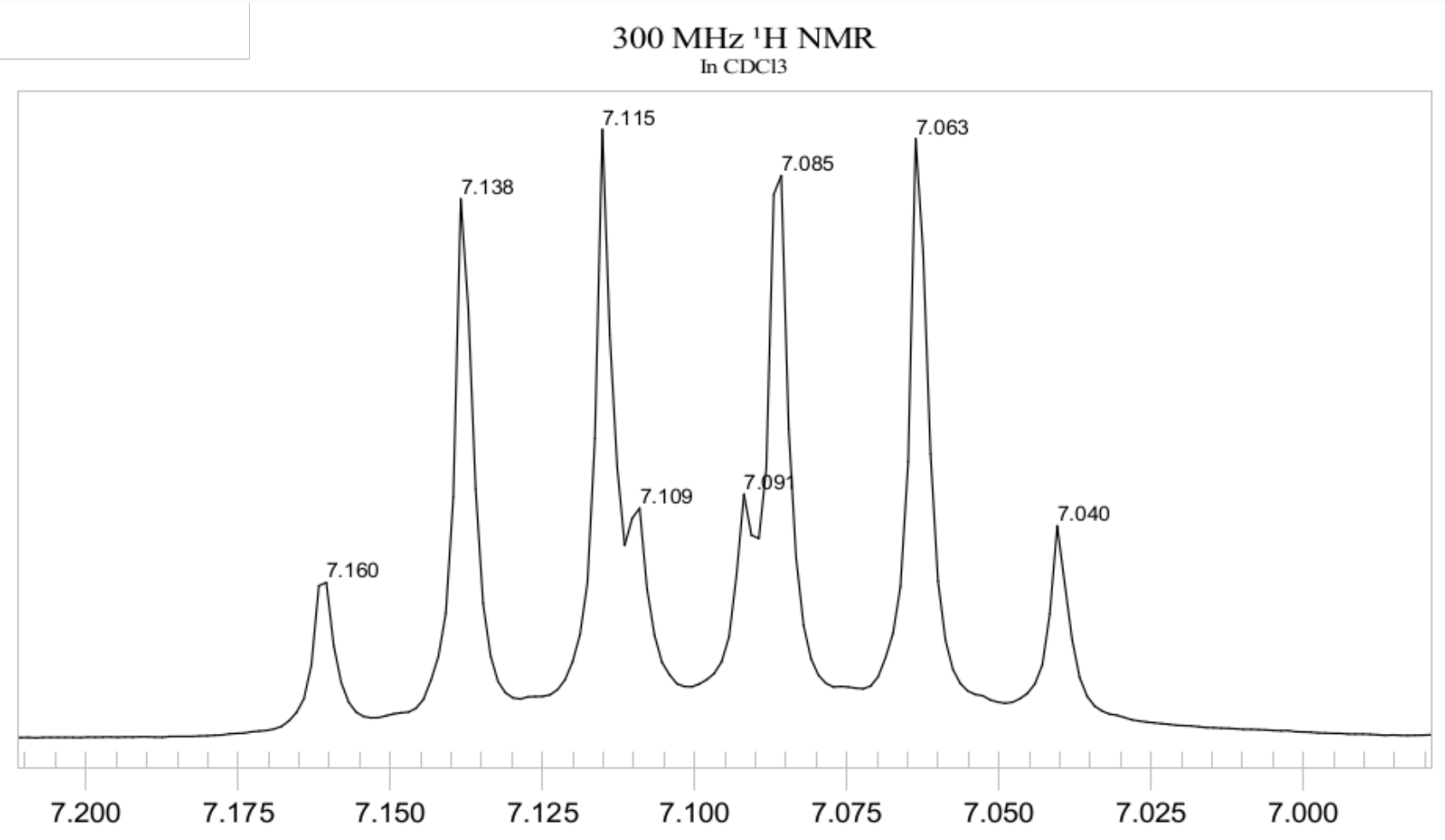
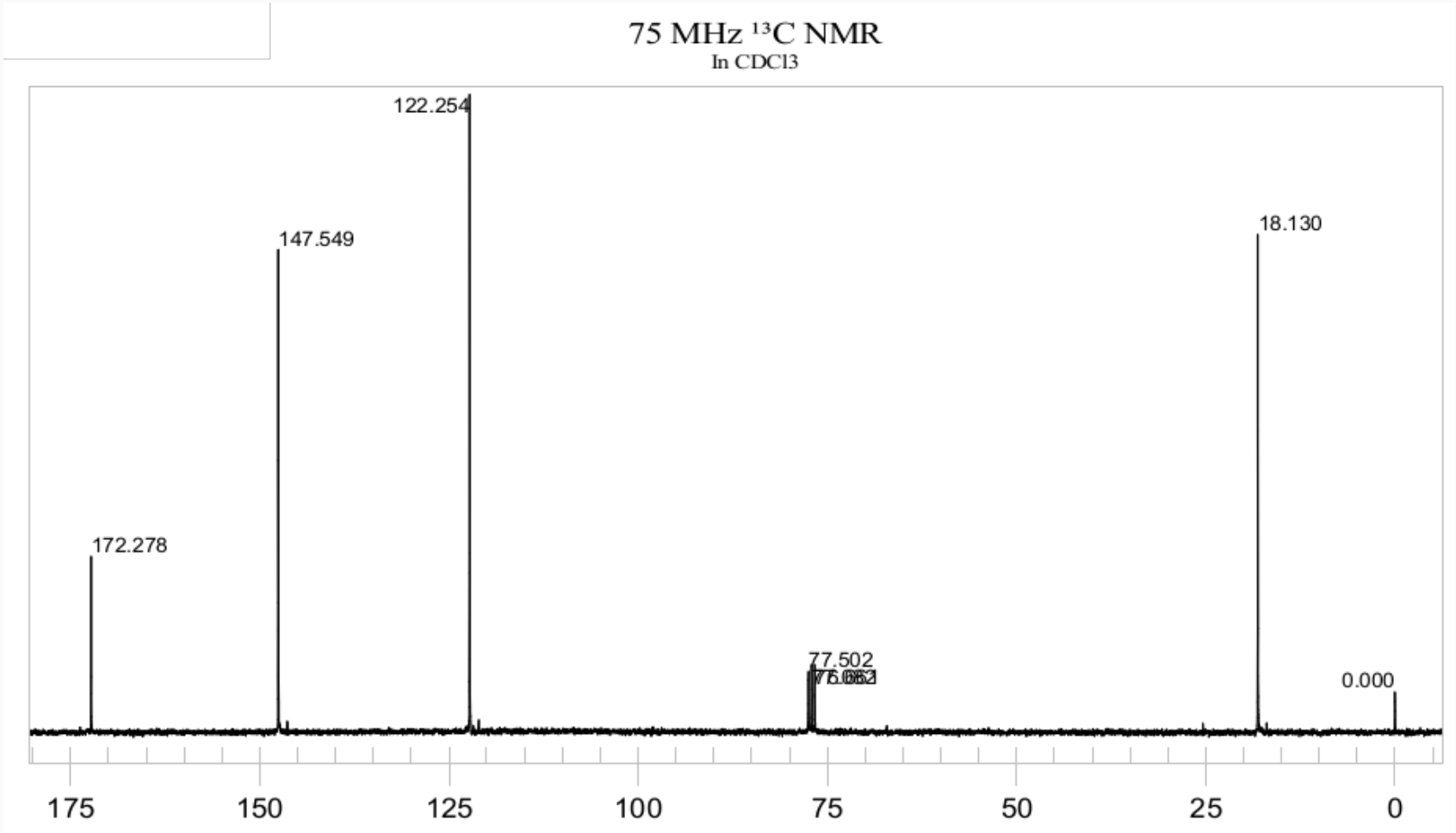


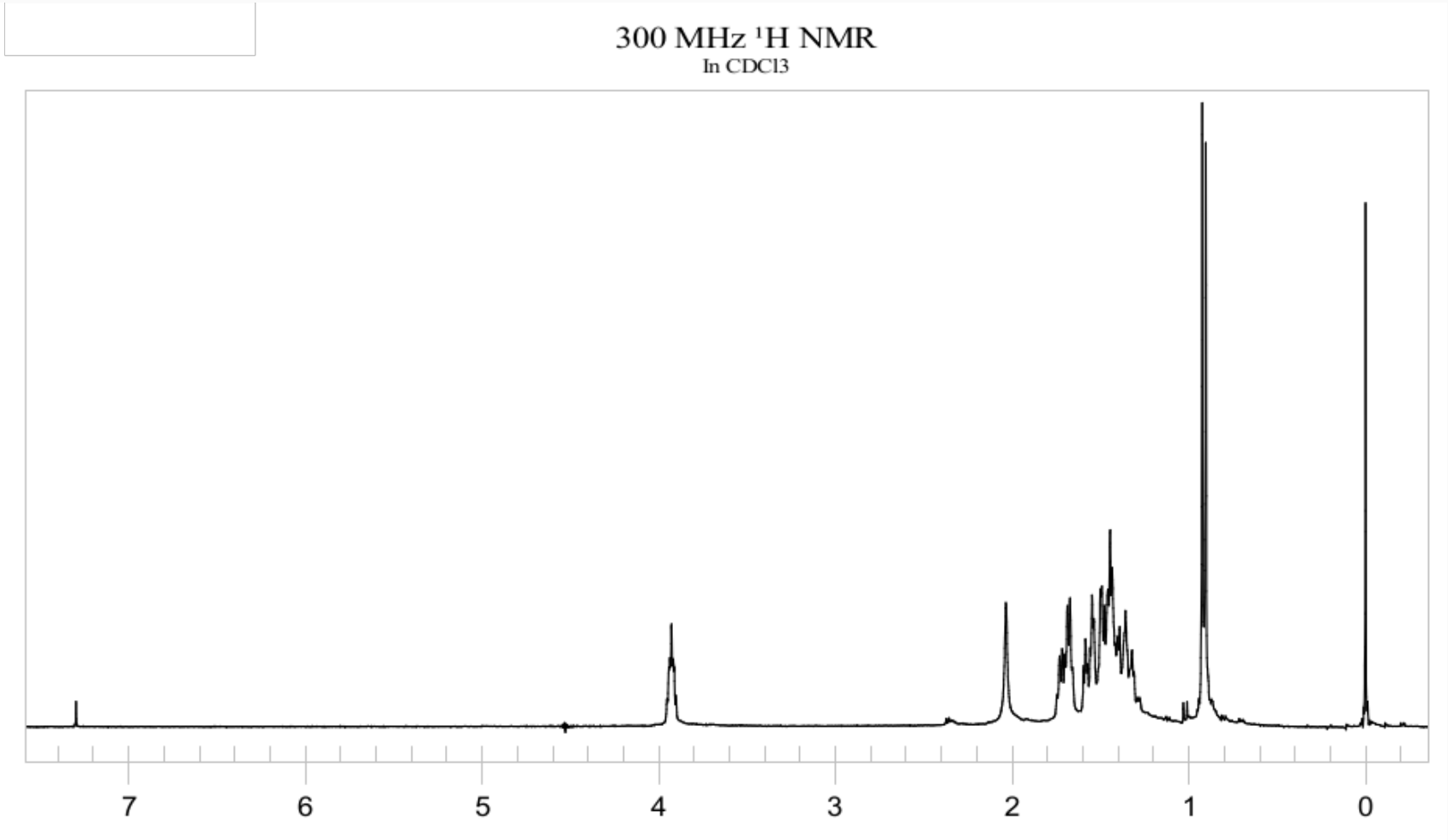
Ex. 9: Espectro de ^{13}C do $C_4H_6O_2$



Ex. 9: Espectro de ^{13}C do $C_4H_6O_2$



Ex. 10: Espectro de ^{1}H do $C_7H_{14}O$ - Isômero A



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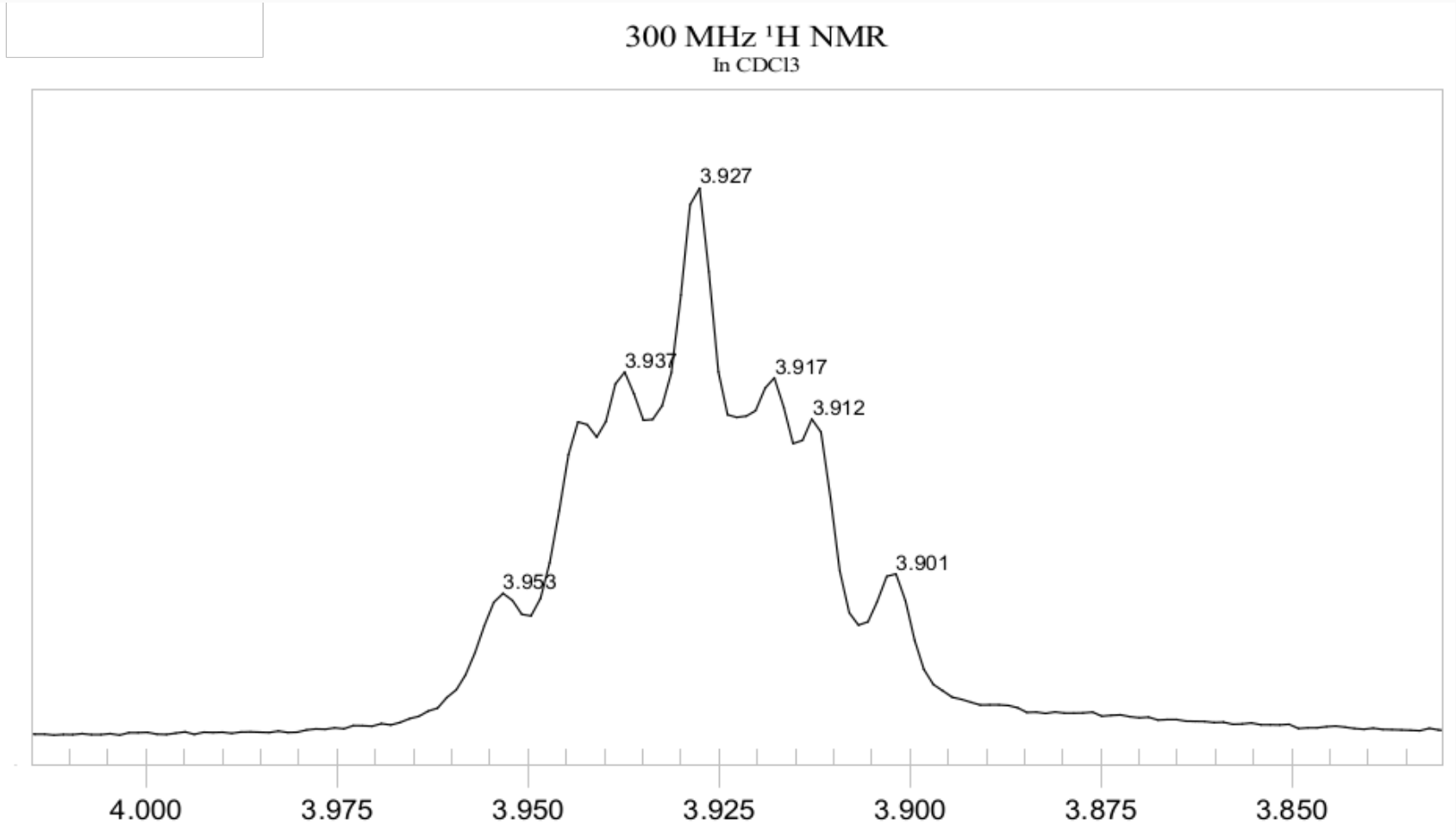

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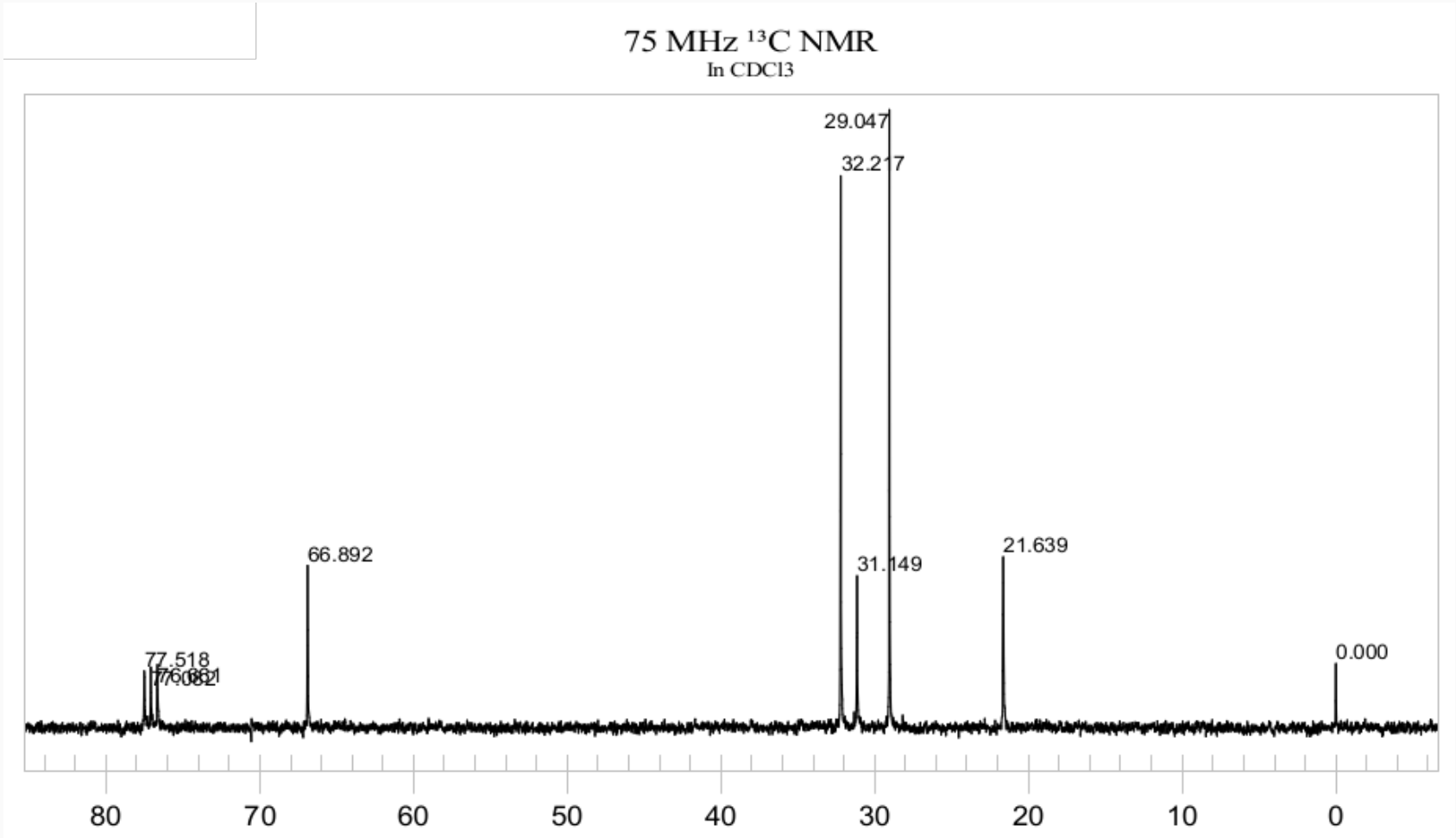
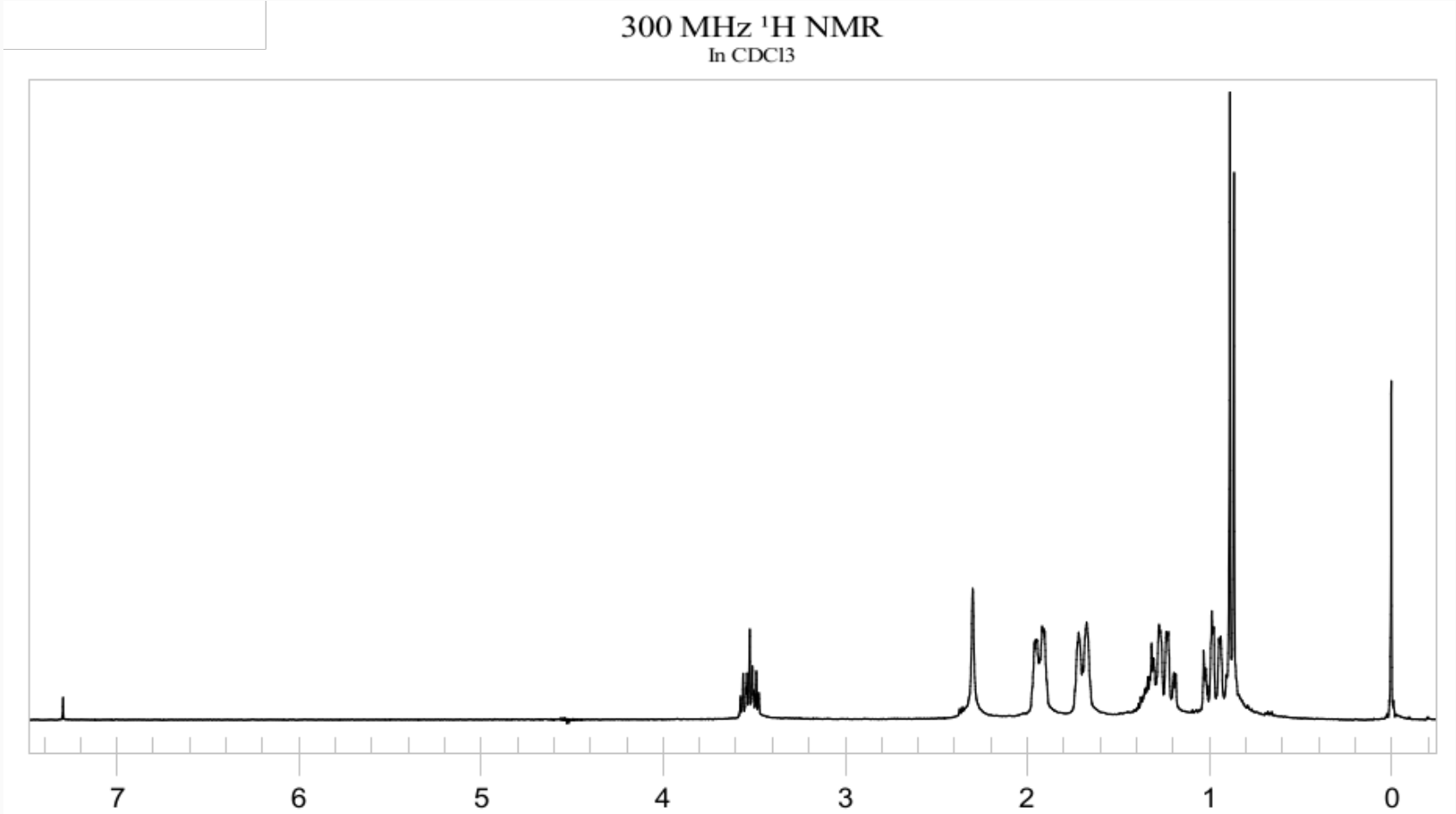
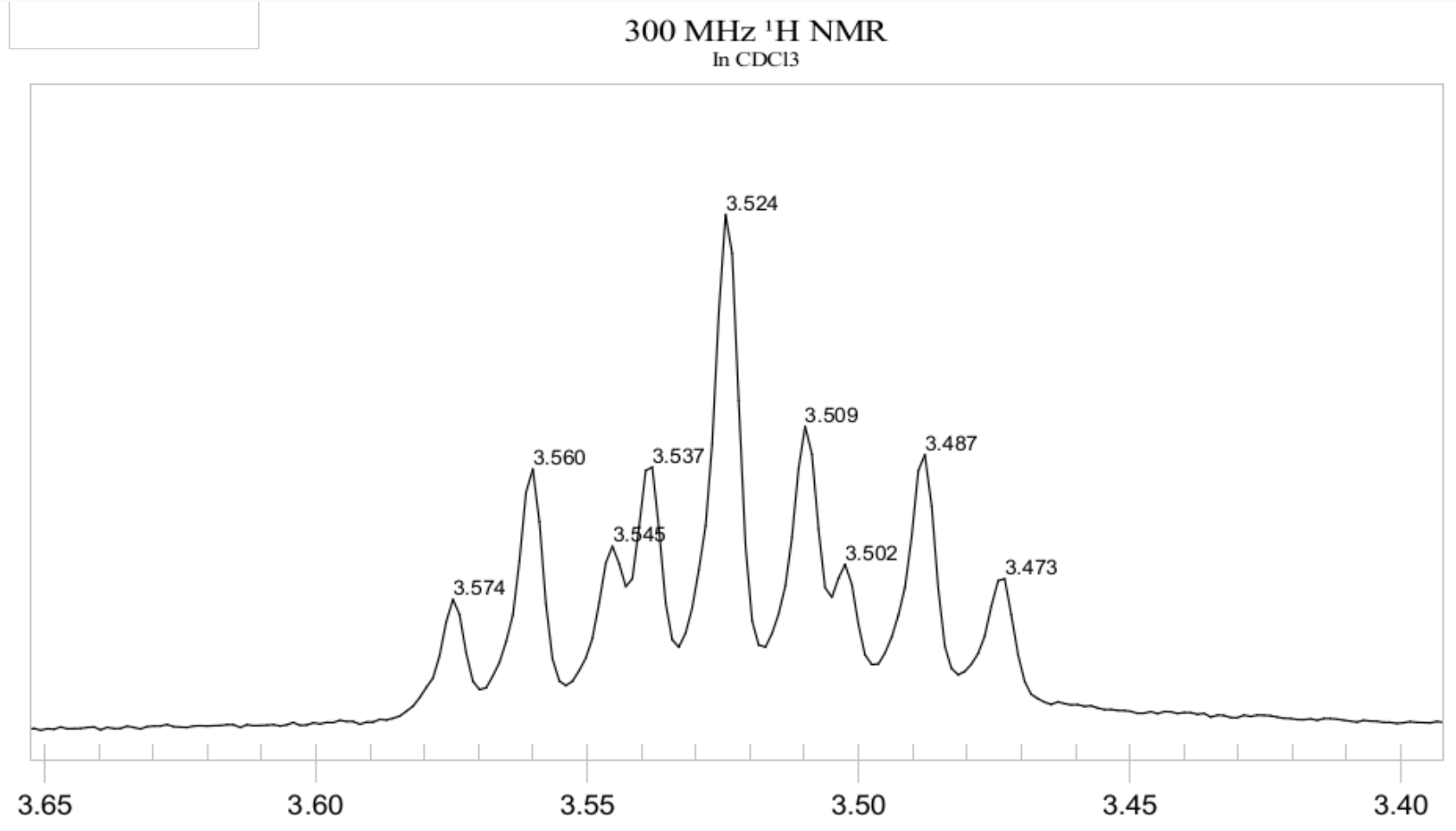


Ex. 10: Espectro de ^{1}H do $C_7H_{14}O$ - Isômero B



Ex. 10: Espectro de ^{1}H do $C_7H_{14}O$ - Isômero B



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