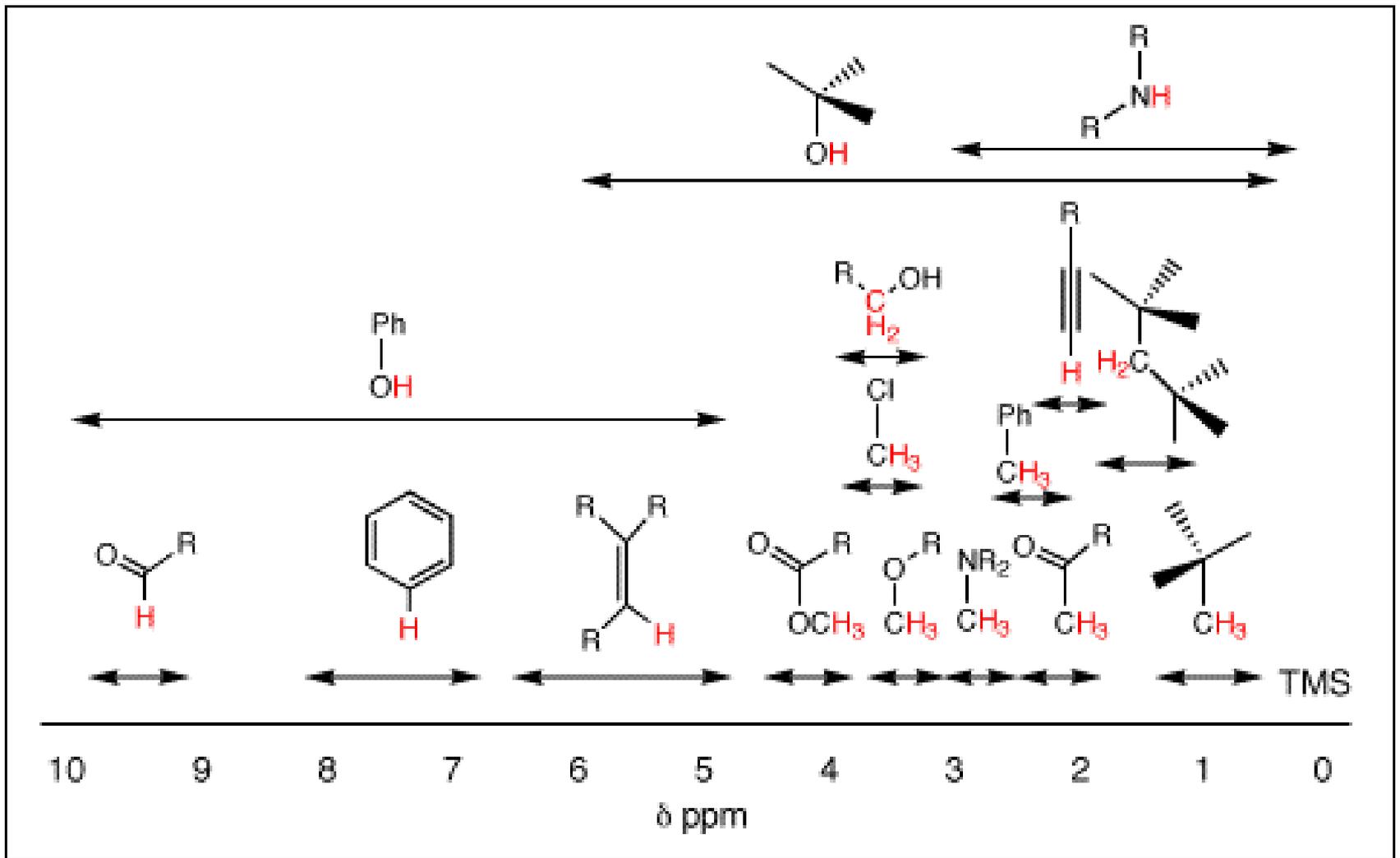


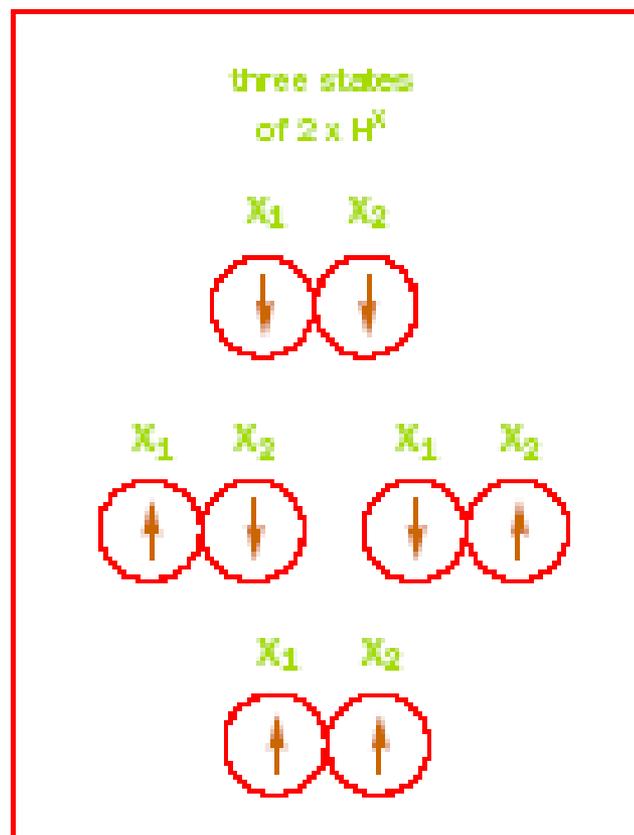
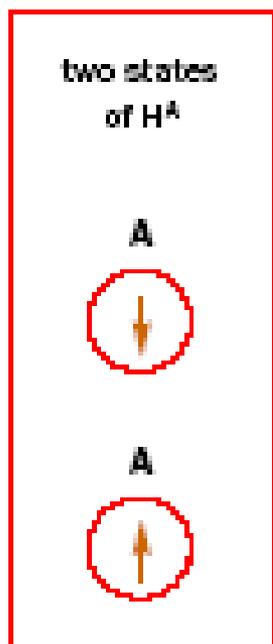
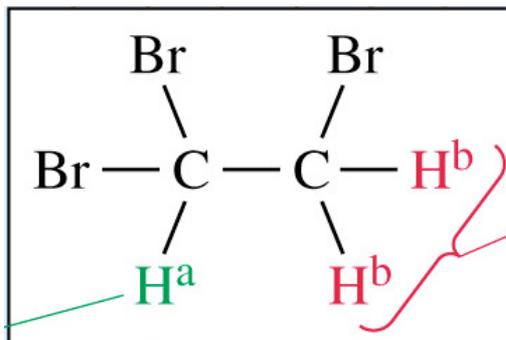
Tema 1

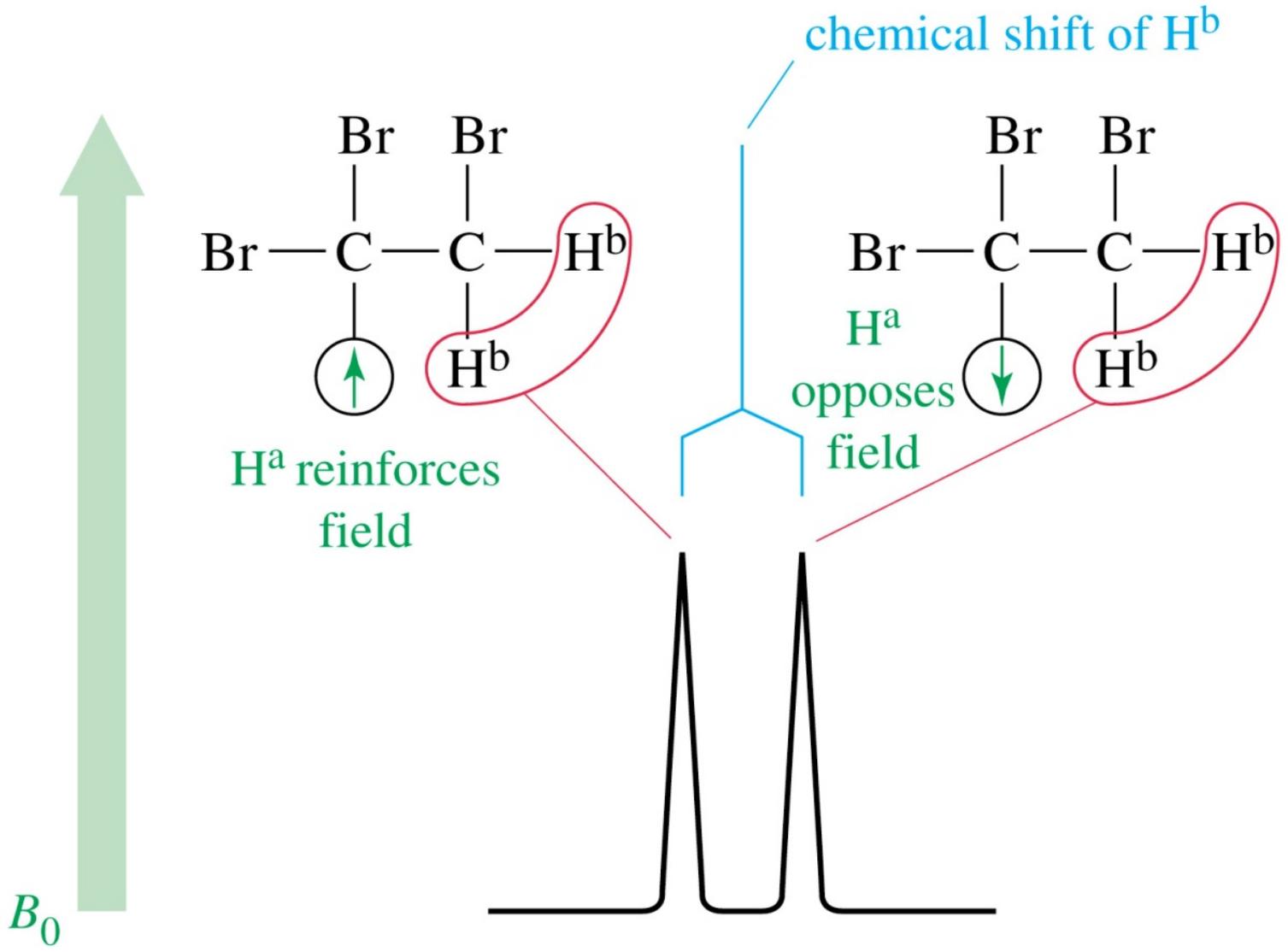
Parte II

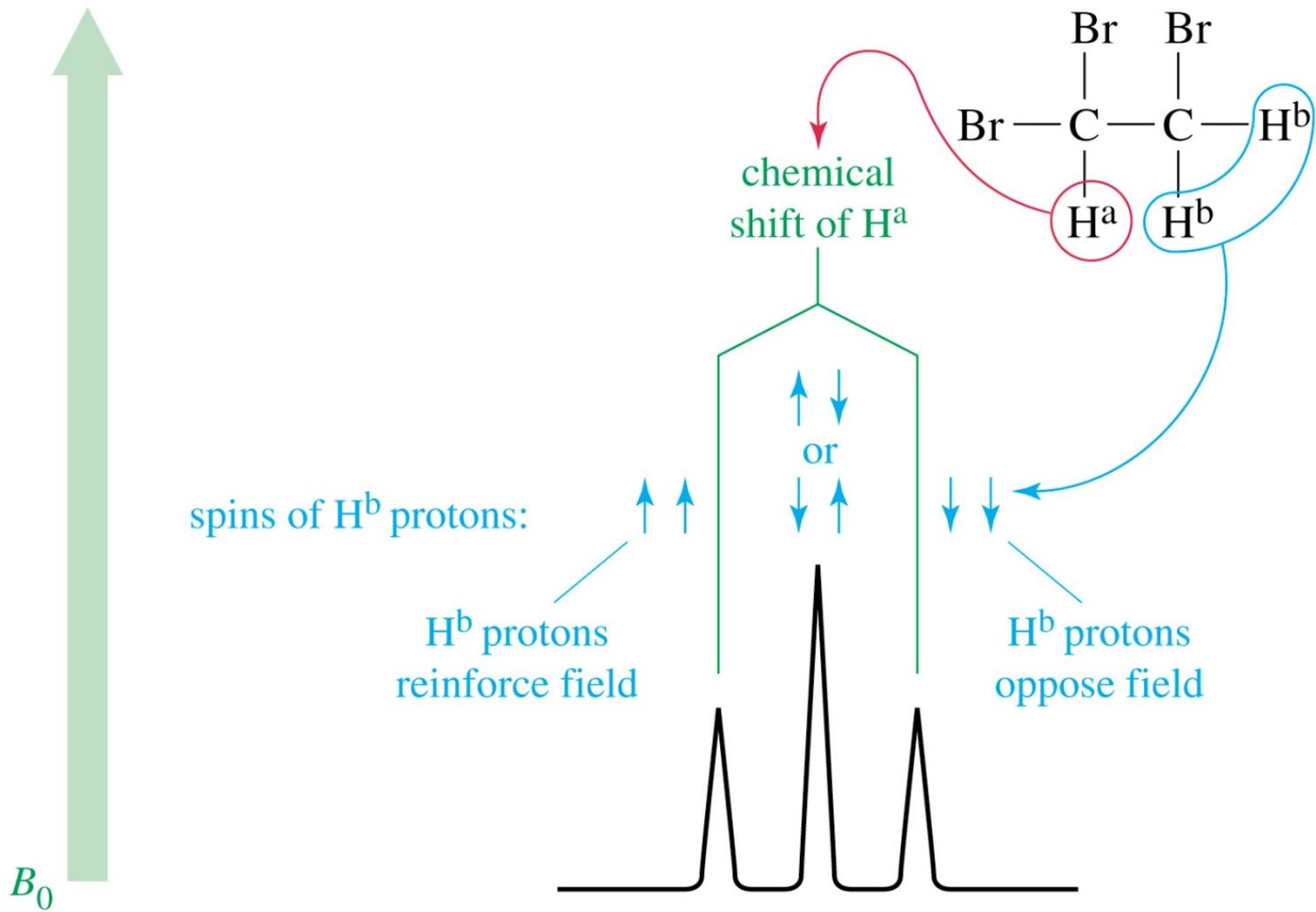
Introducción al empleo de técnicas espectrométricas en la elucidación de estructuras orgánicas.

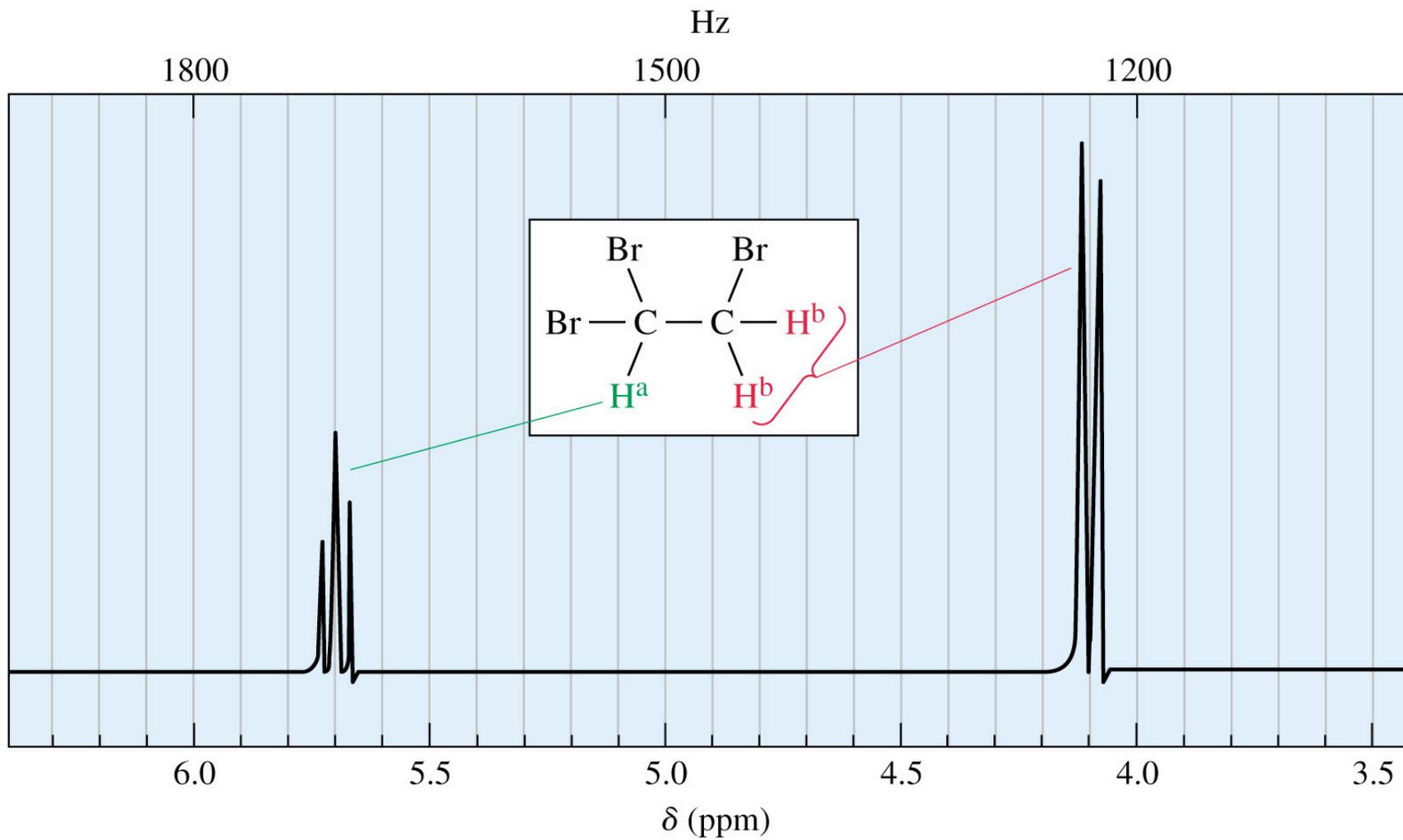


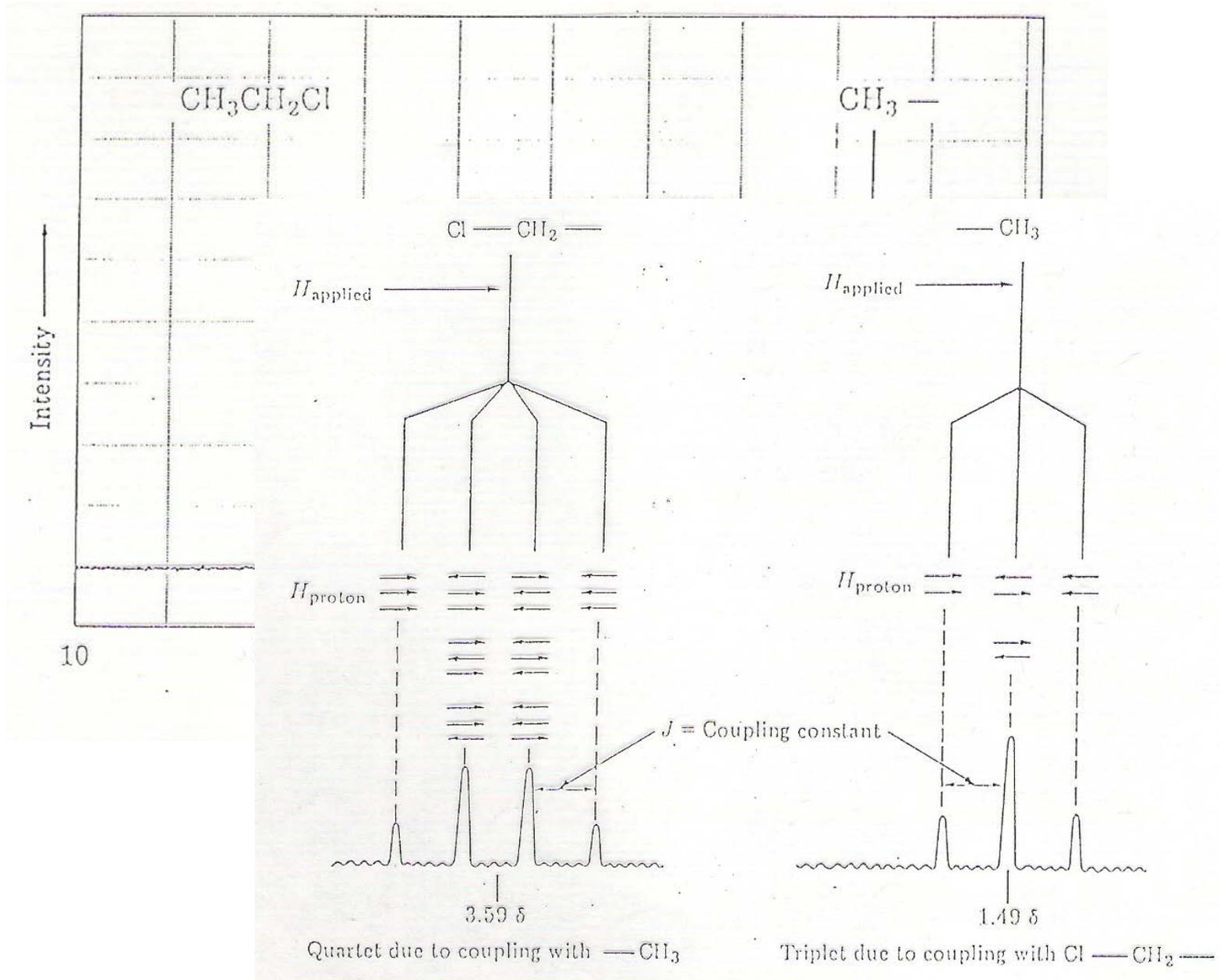




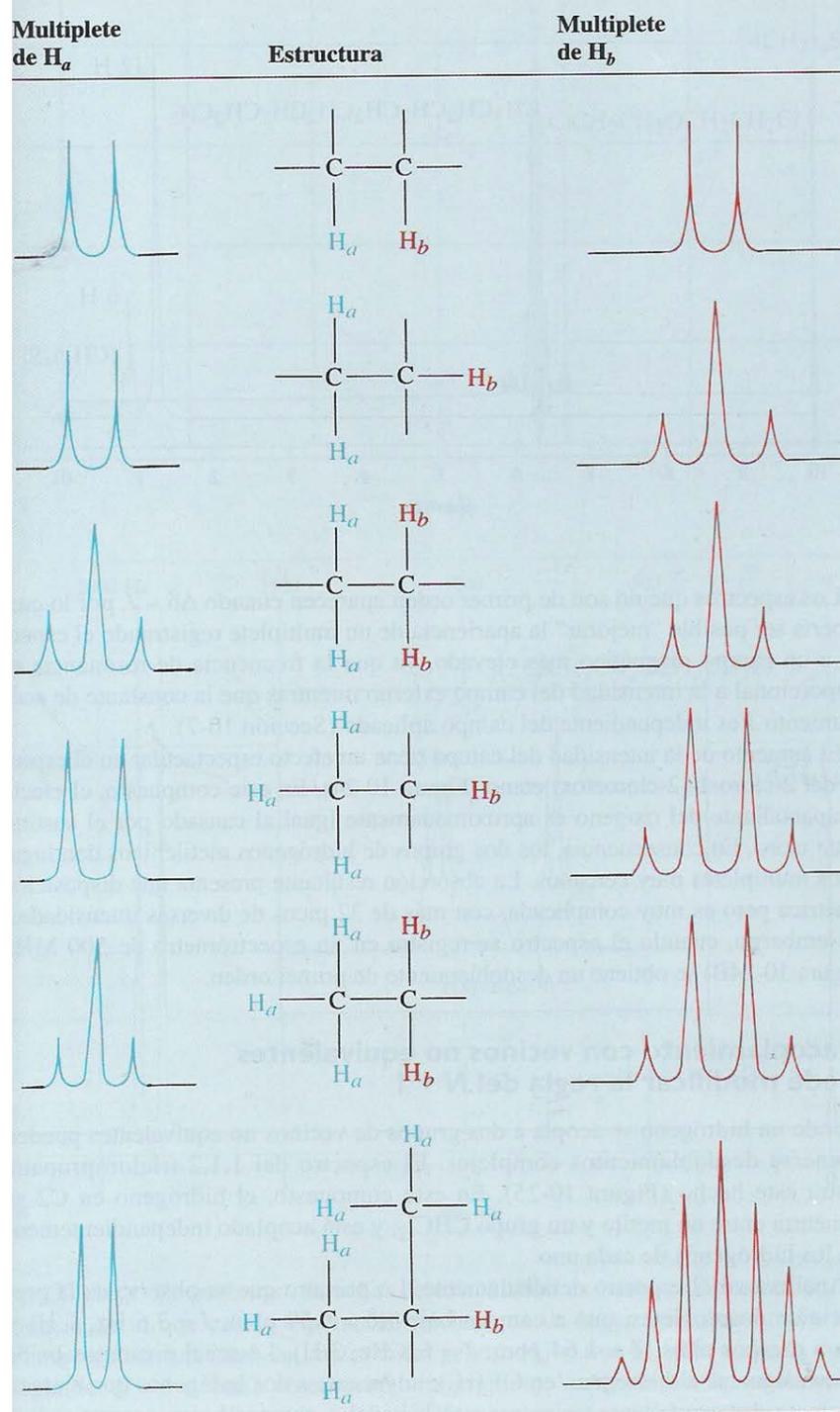




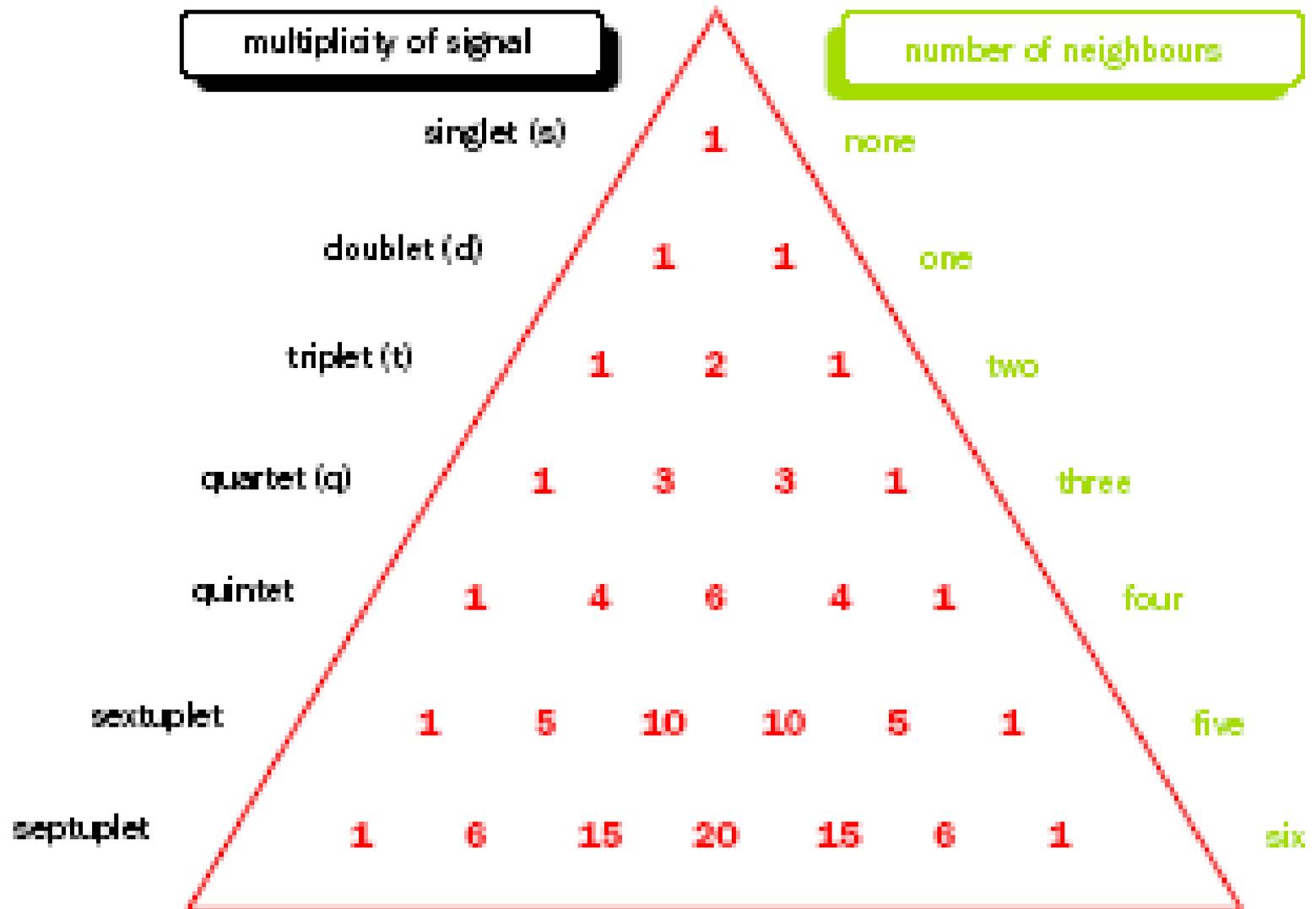




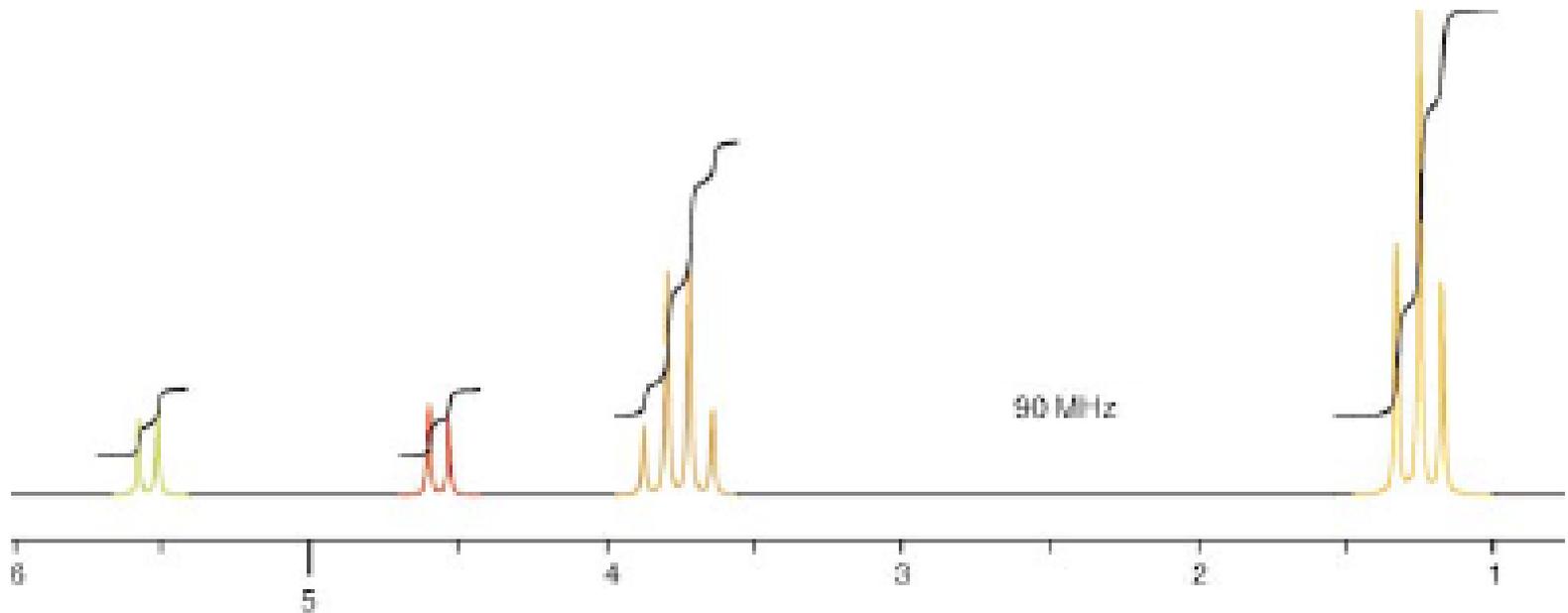
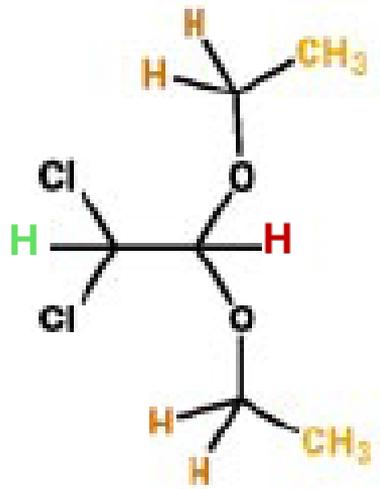
Desdoblamientos frecuentes en grupos alquilo



Pascal's triangle



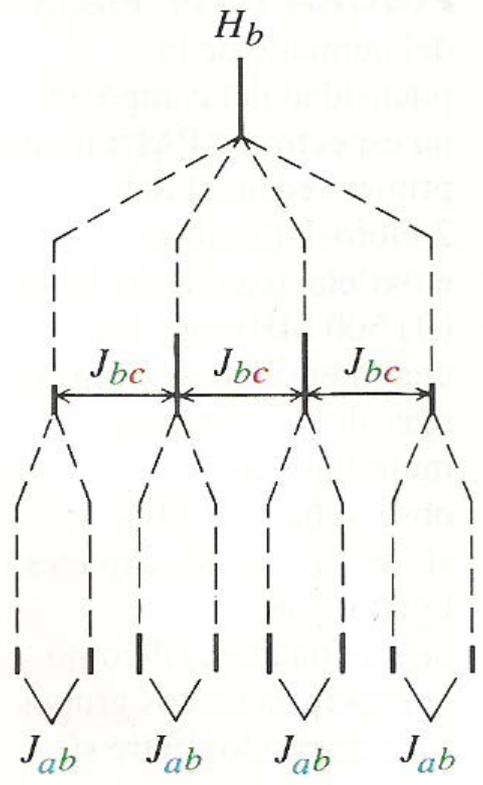
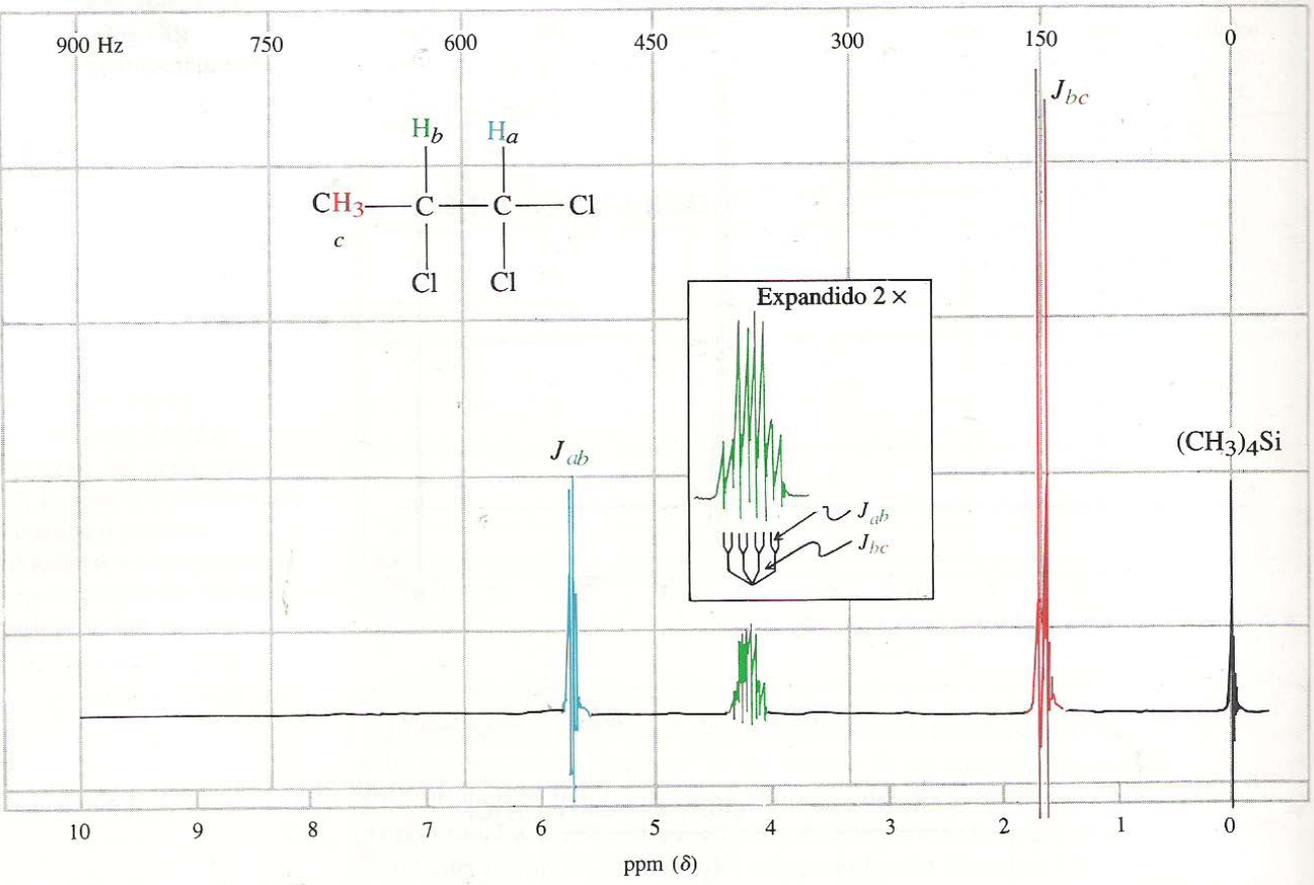
$$\text{multiplicidad} = 2n + 1$$

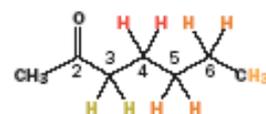
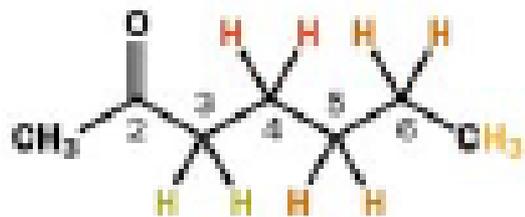


Inicio del barrido

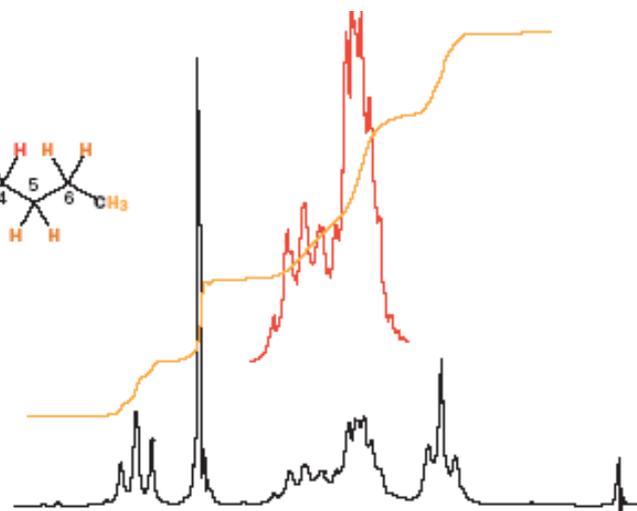
← H →

Final del barrido

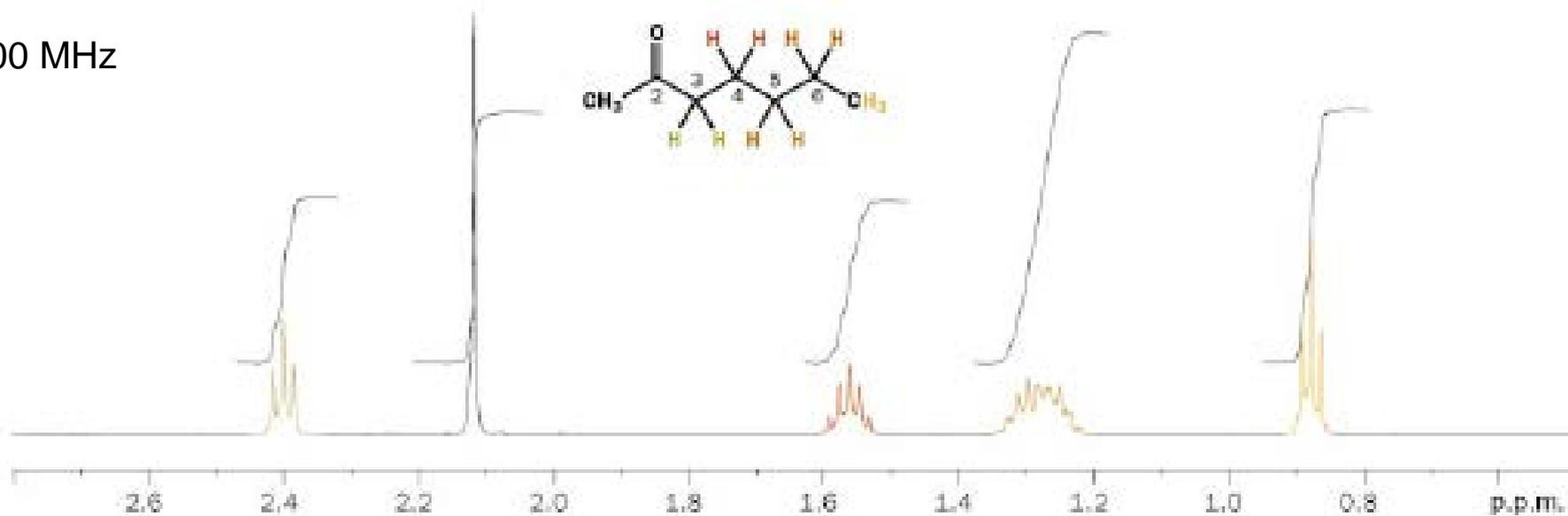
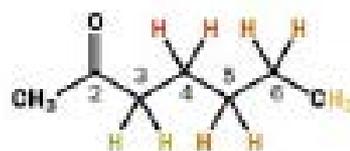




90 MHz

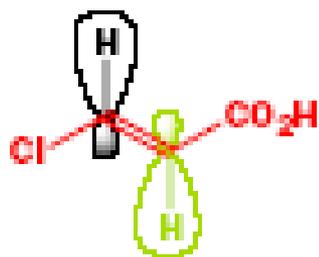


500 MHz

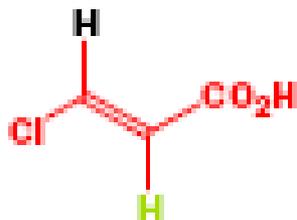


Las constantes de acoplamiento dependen de tres factores

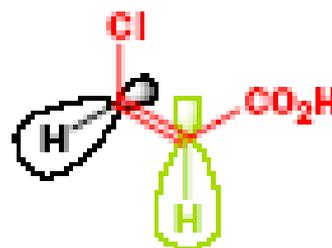
- La distancia de enlace entre los núcleos de hidrógeno
- El ángulo entre los dos enlaces C-H
- La electronegatividad de los sustituyentes



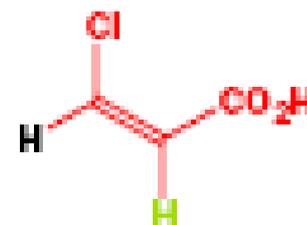
H atoms distant
orbitals parallel



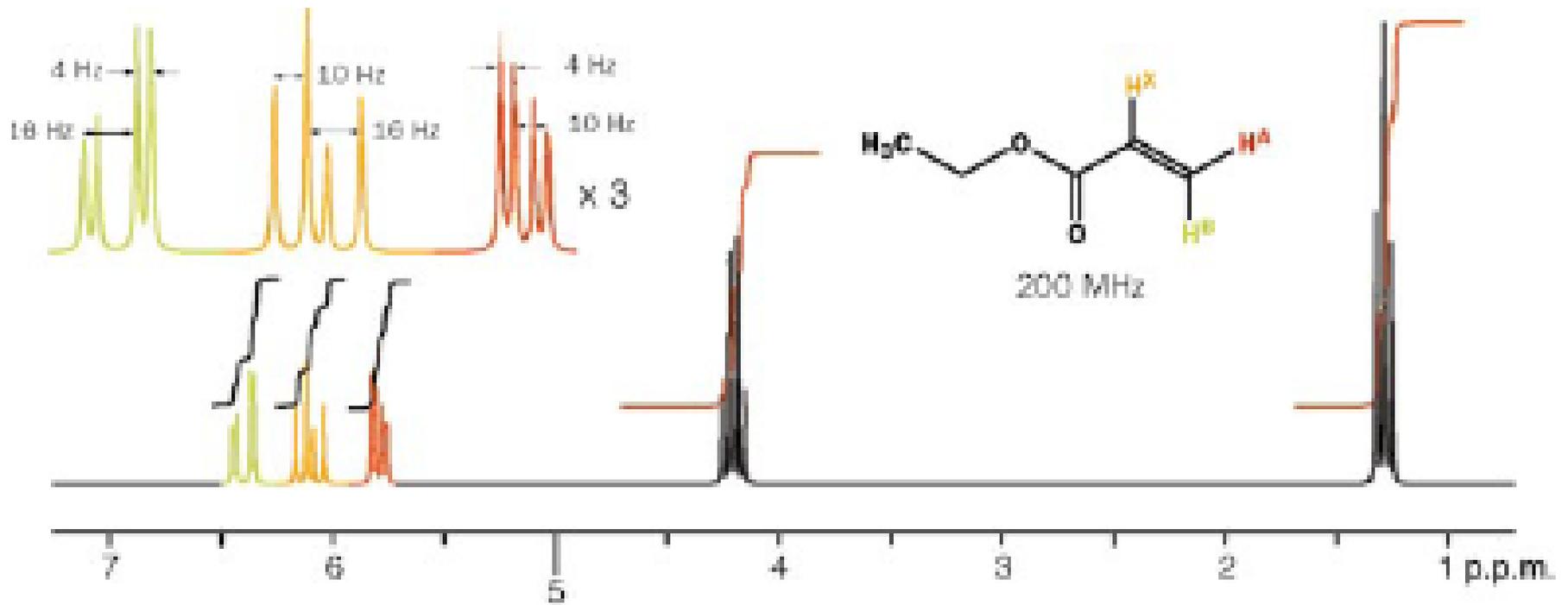
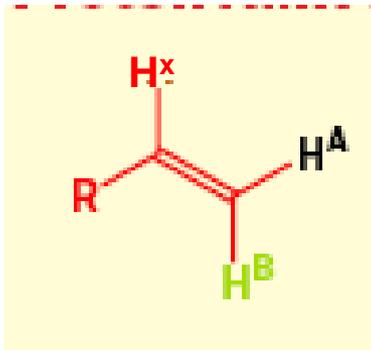
hydrogens are trans
 $J = 15$ Hz



H atoms close
orbitals not parallel



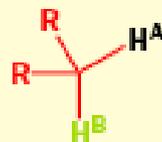
hydrogens are cis
 $J = 9$ Hz



Typical coupling constants

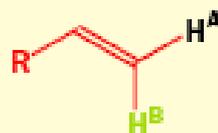
Geminal $^2J_{HH}$

saturated



10–16 Hz

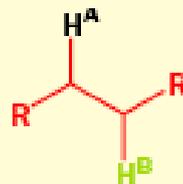
unsaturated



0–3 Hz

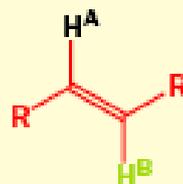
Vicinal $^3J_{HH}$

saturated



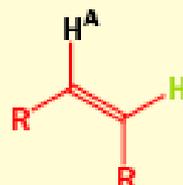
6–8 Hz

unsaturated *trans*



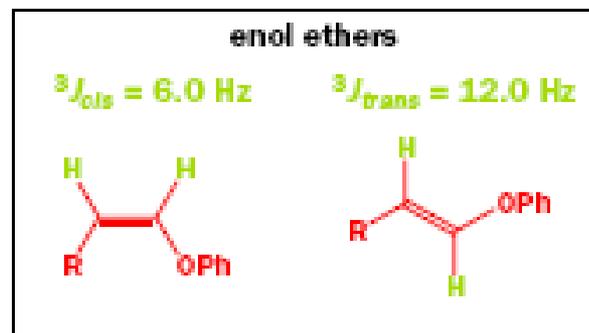
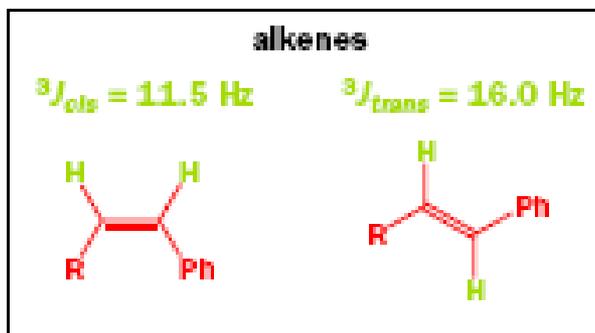
14–16 Hz

unsaturated *cis*



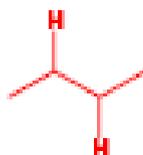
8–11 Hz

effect of electronegative substituents on $^3J_{\text{HH}}$ – alkenes and enol ethers



$^3J_{\text{HH}}$ coupling constants

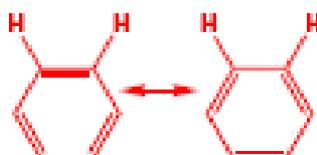
open chain
single bond



free rotation

$J = 7 \text{ Hz}$

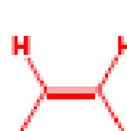
benzene ring
longer bond (0.5π bond)



60° angle

J 8-10 Hz

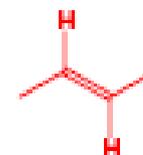
cis alkene
double bond



60° angle

J 10-12 Hz

trans alkene
double bond

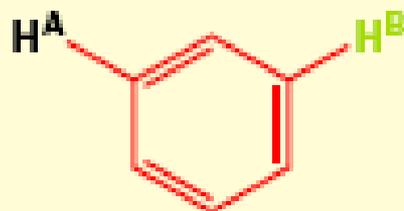


180° angle

J 14-18 Hz

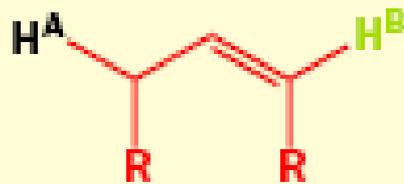
Long-range ${}^4J_{\text{HH}}$

meta

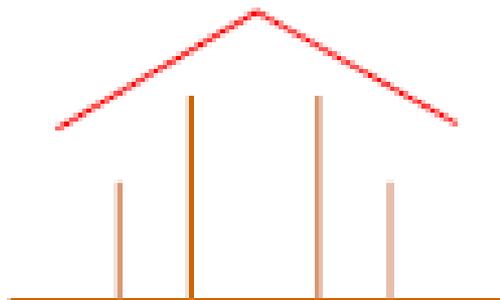


1–3 Hz

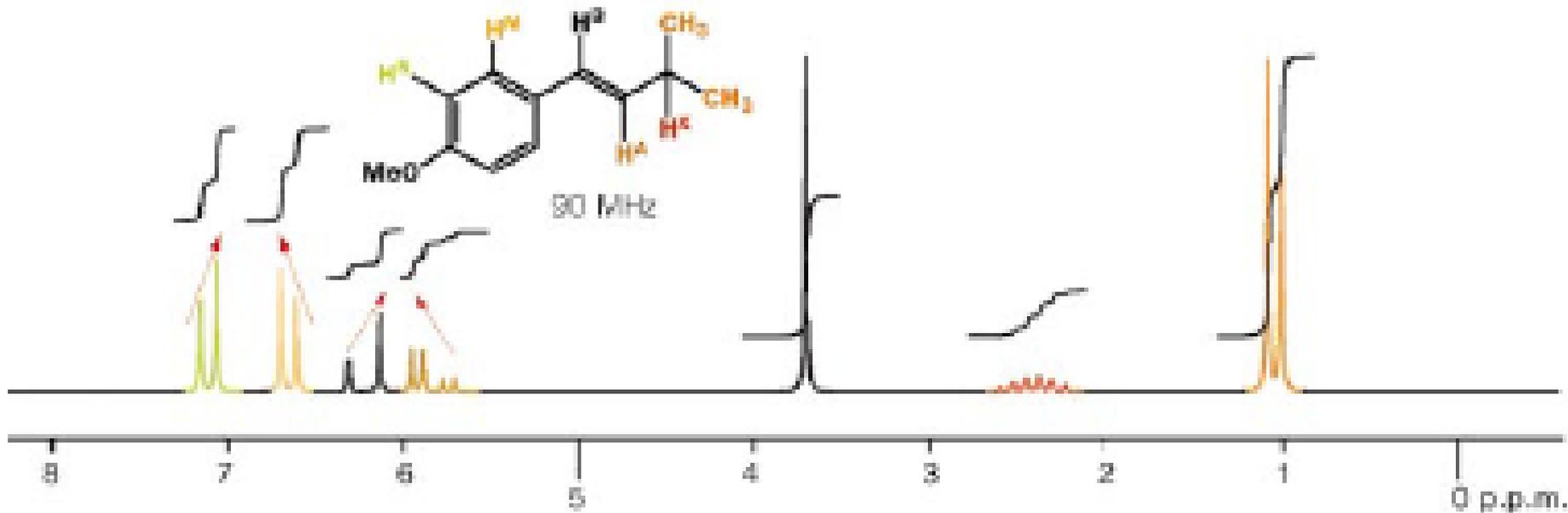
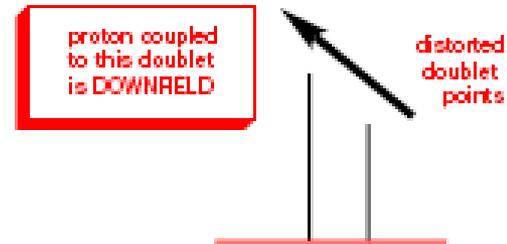
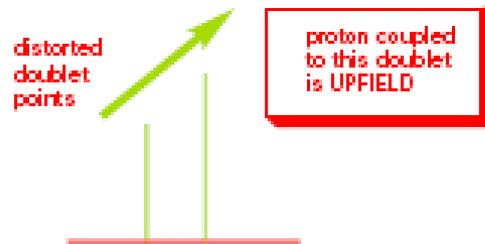
allylic



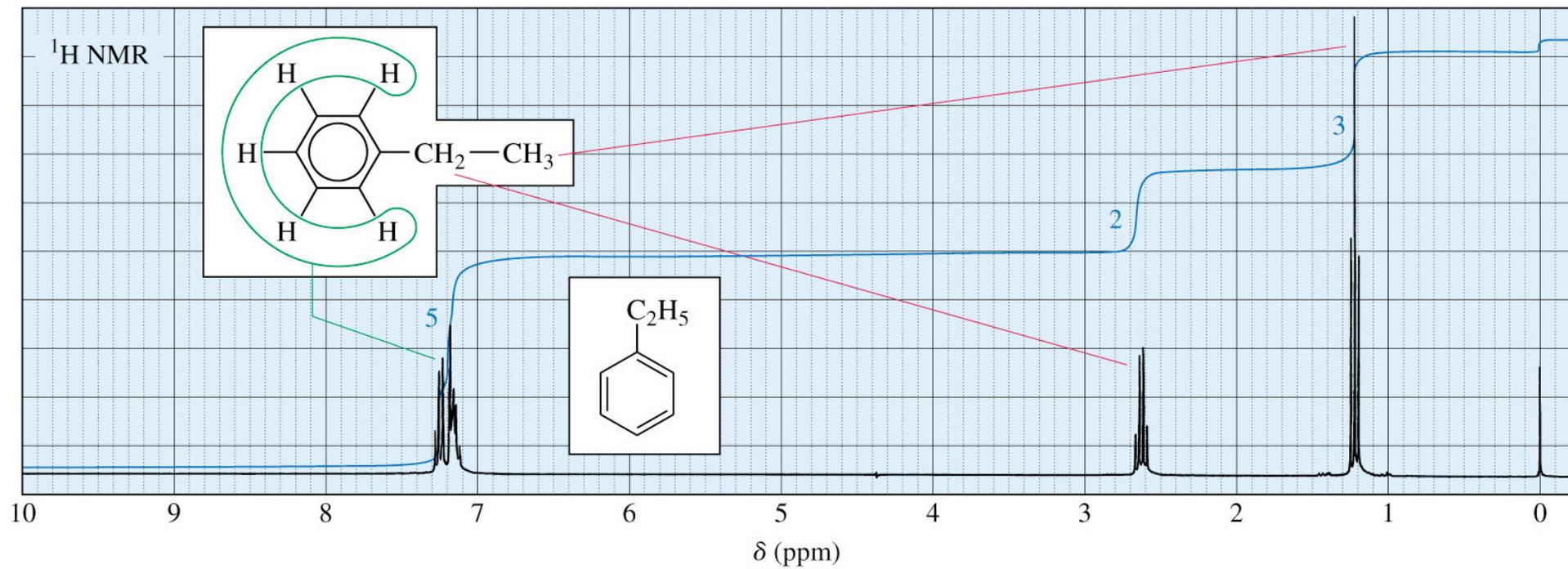
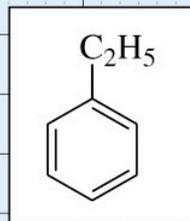
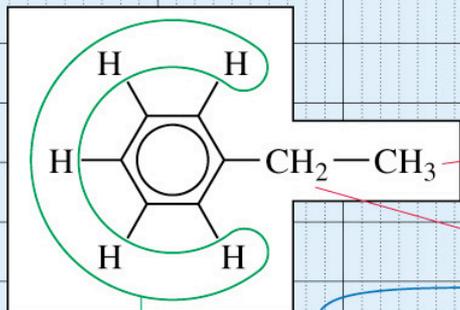
1–2 Hz

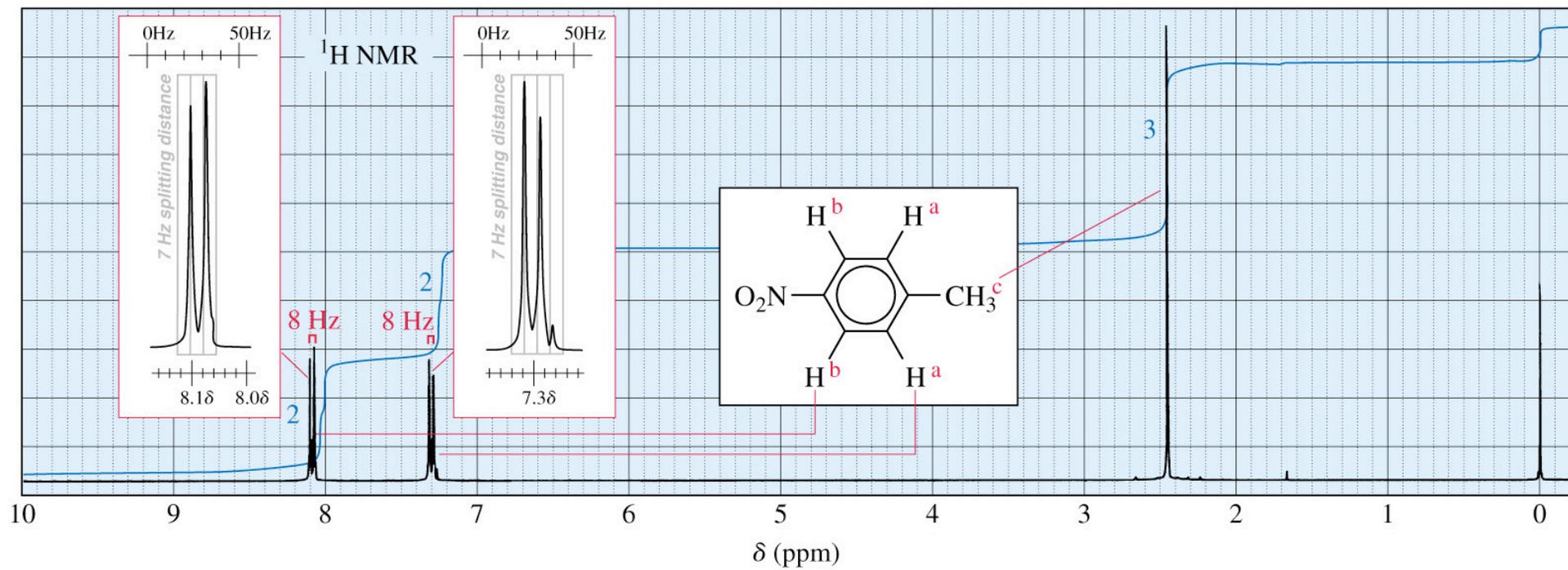
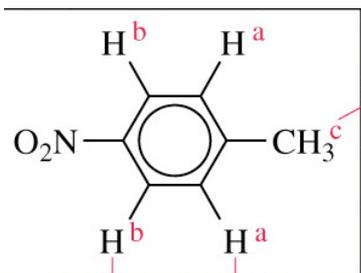


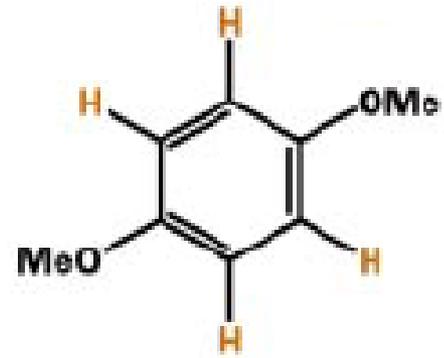
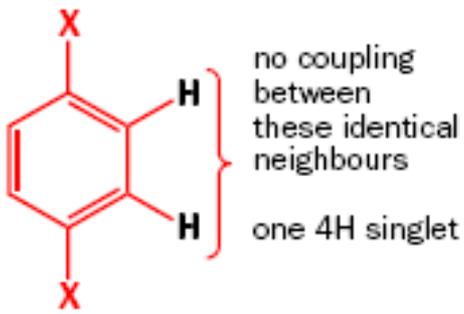
Efecto tejado



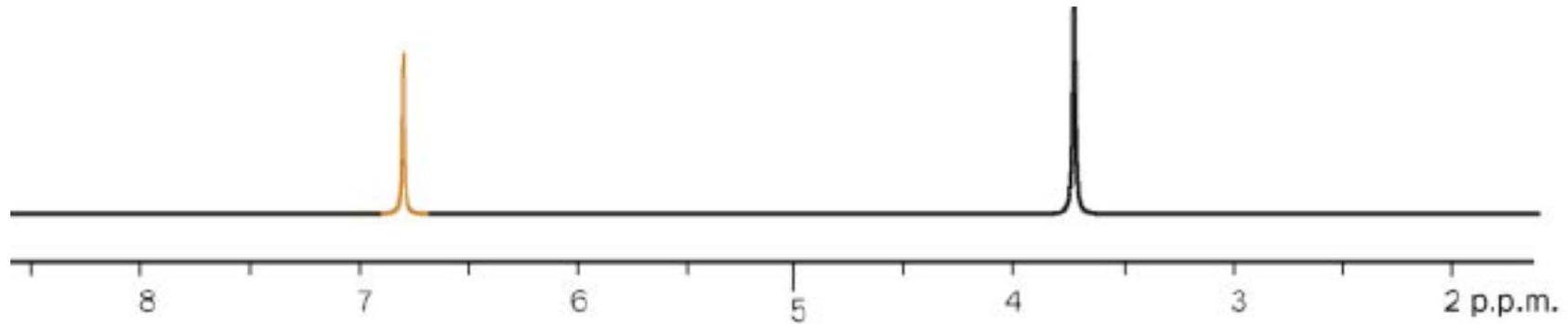
^1H NMR

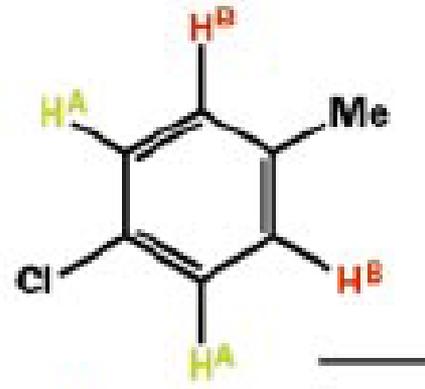
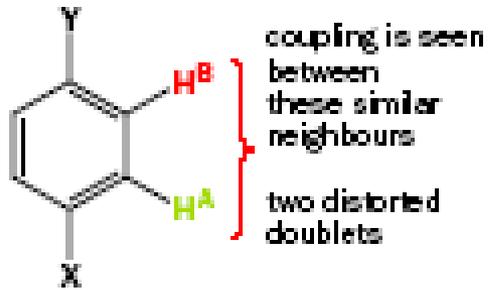






$\Delta\delta = 0$





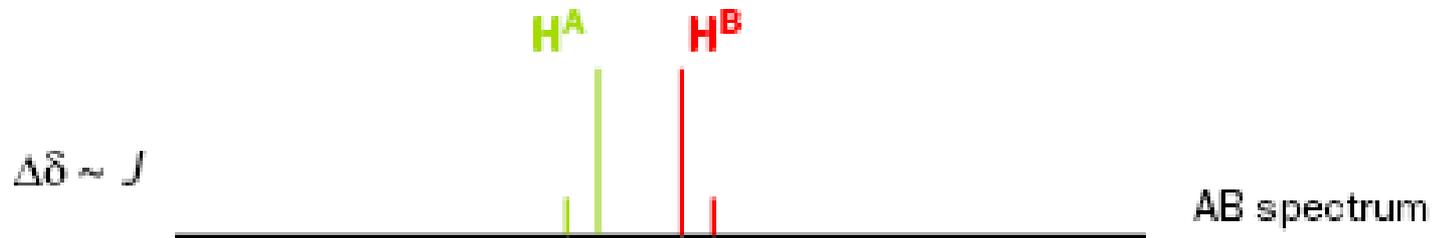
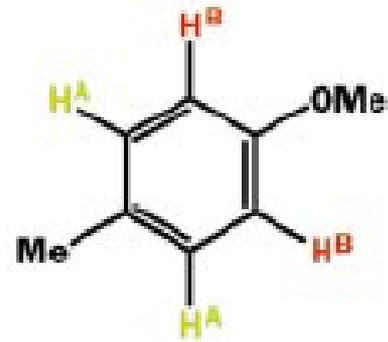
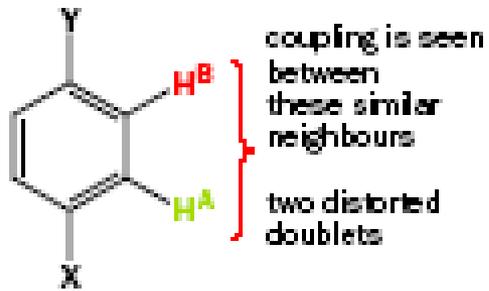
$$\Delta\delta < J$$

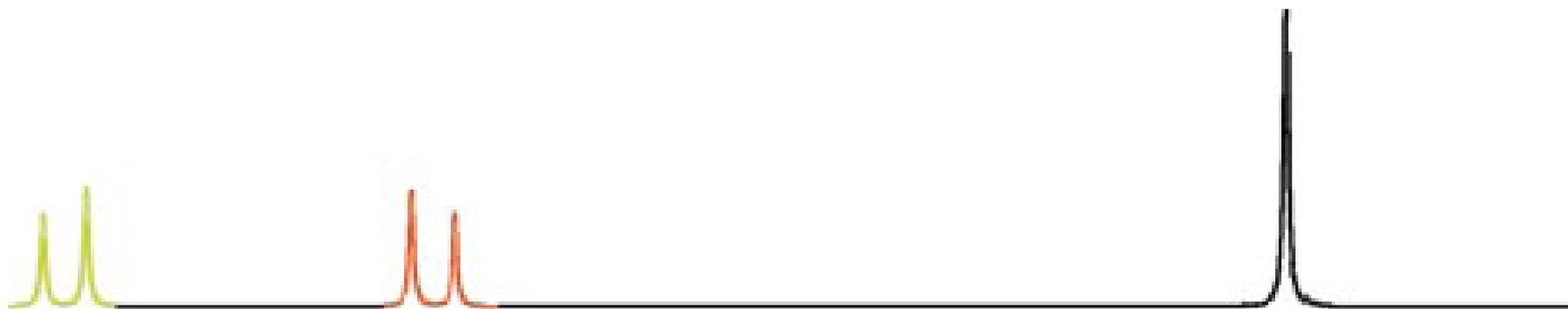
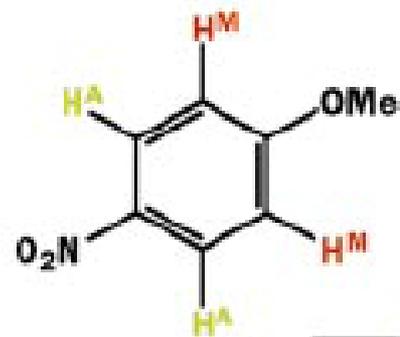
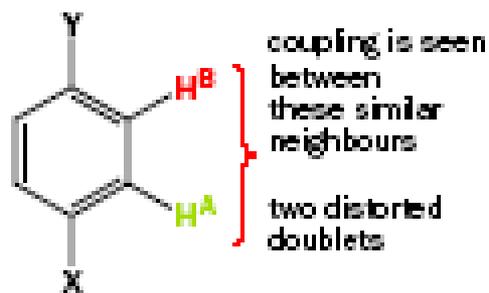
H^A H^B

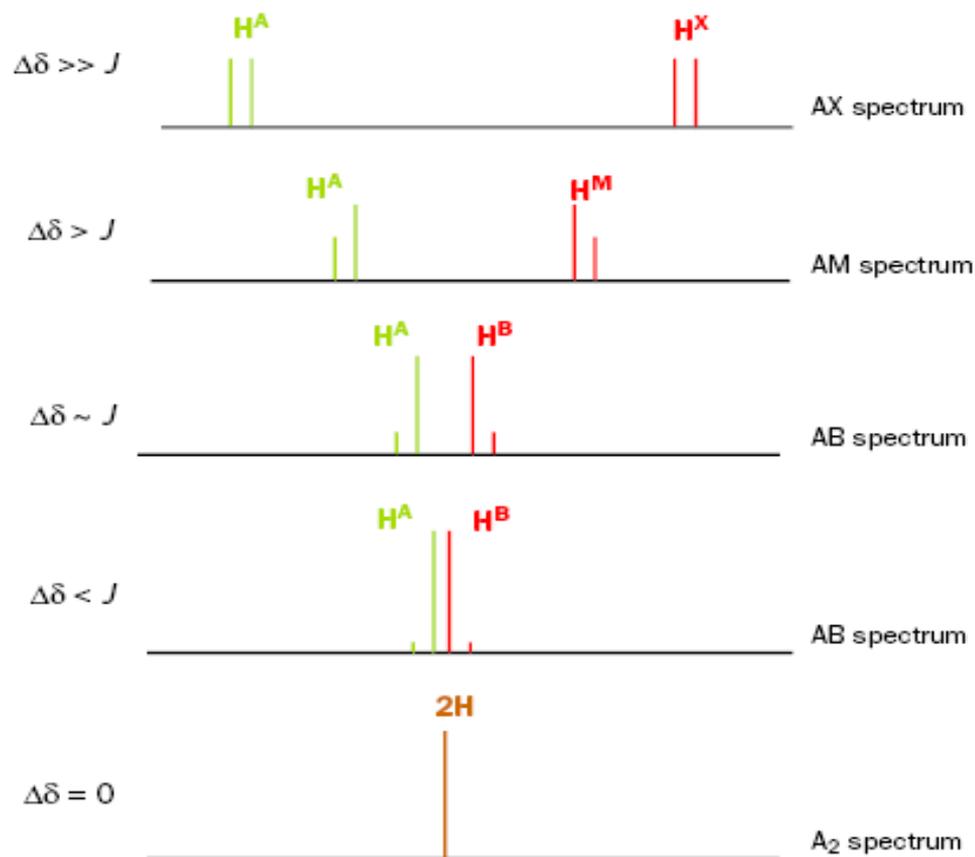
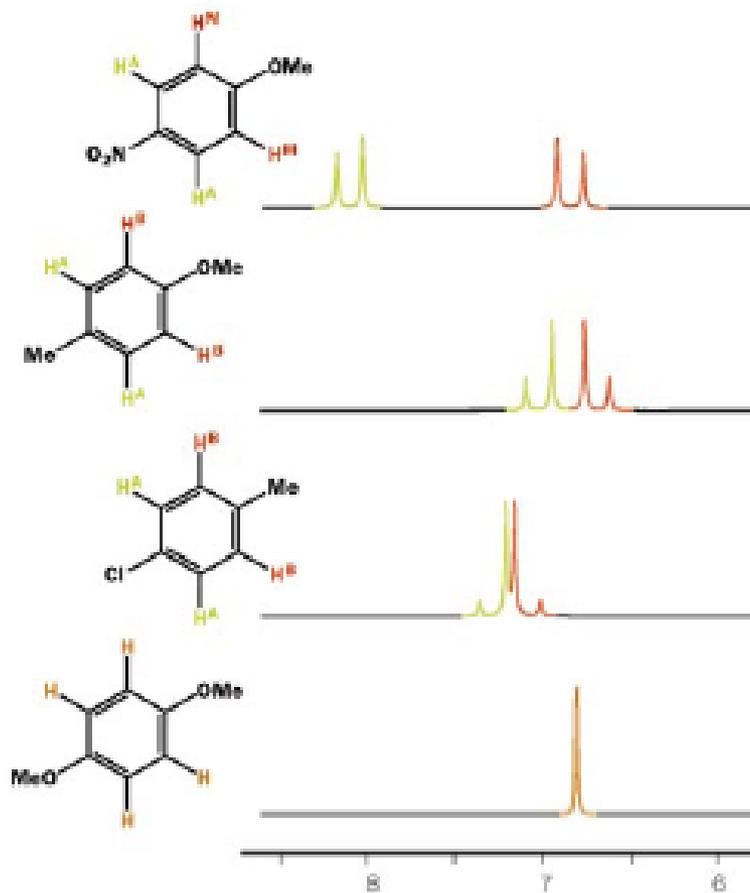
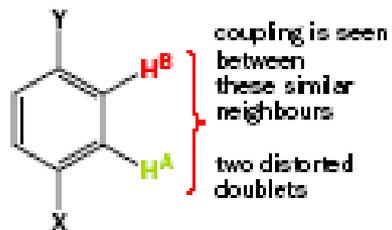


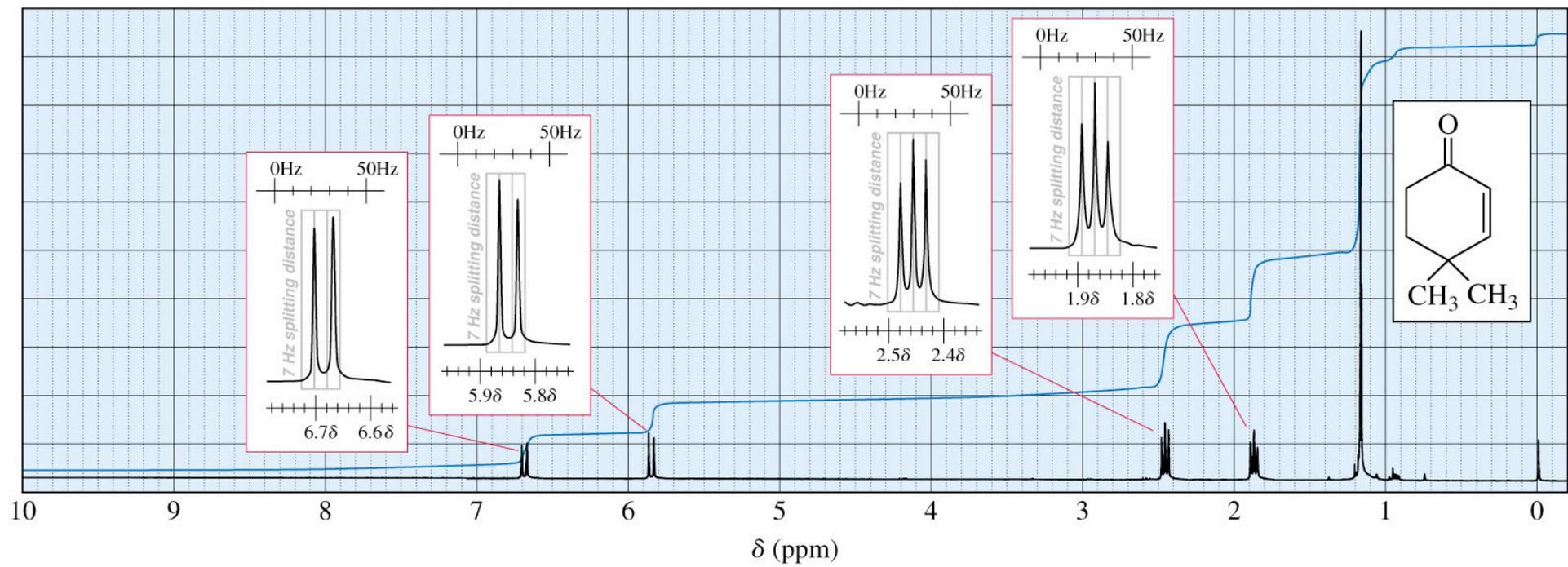
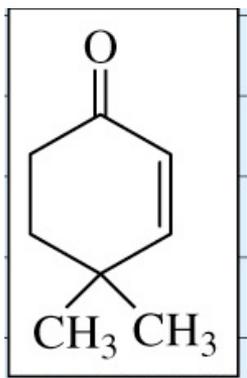
AB spectrum











Los disolventes que se utilizan en espectroscopia RMN son líquidos orgánicos de baja viscosidad con buenas propiedades de solubilidad.

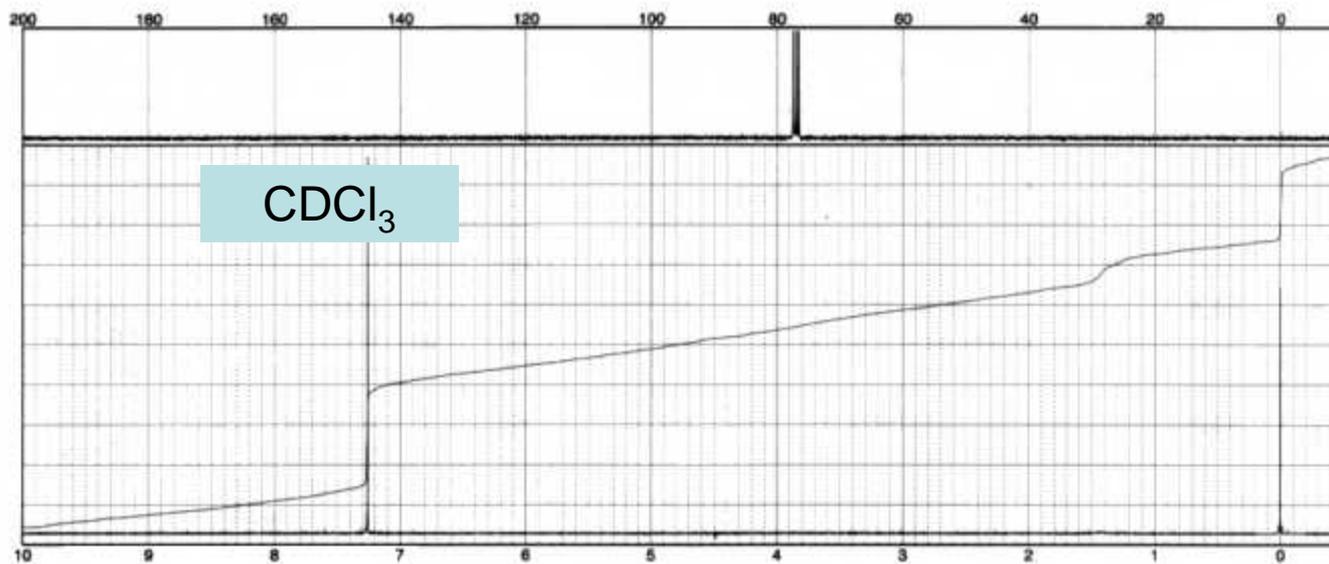
Para prevenir el solapamiento de las señales intensas del disolvente en espectroscopía ^1H -RMN, los protones se sustituyen por deuterios.



- Acetone- d_6
- Acetonitrile- d_3
- Benzene- d_6
- Chloroform- d_1
- Cyclohexane- d_{12}
- Deuterium oxide
- Dichloromethane- d_2
- DMF- d_7
- DMSO- d_6
- Fluorodichloromethane- d
- Formic acid- d_2
- Methanol- d_4
- Methylphthalene- d_{10}
- Nitrobenzene- d_5
- Nitromethane- d_3
- Pyridine- d_5
- Tetrachloroethane- d_2
- THF- d_8
- Toluene- d_8
- Trifluoroacetic acid- d

Deuterocloroformo $\text{CDCl}_3\text{-d}_1$

^{13}C 77.0 ppm
 $^1\text{J}(\text{C},\text{D})$ 32.0 Hz



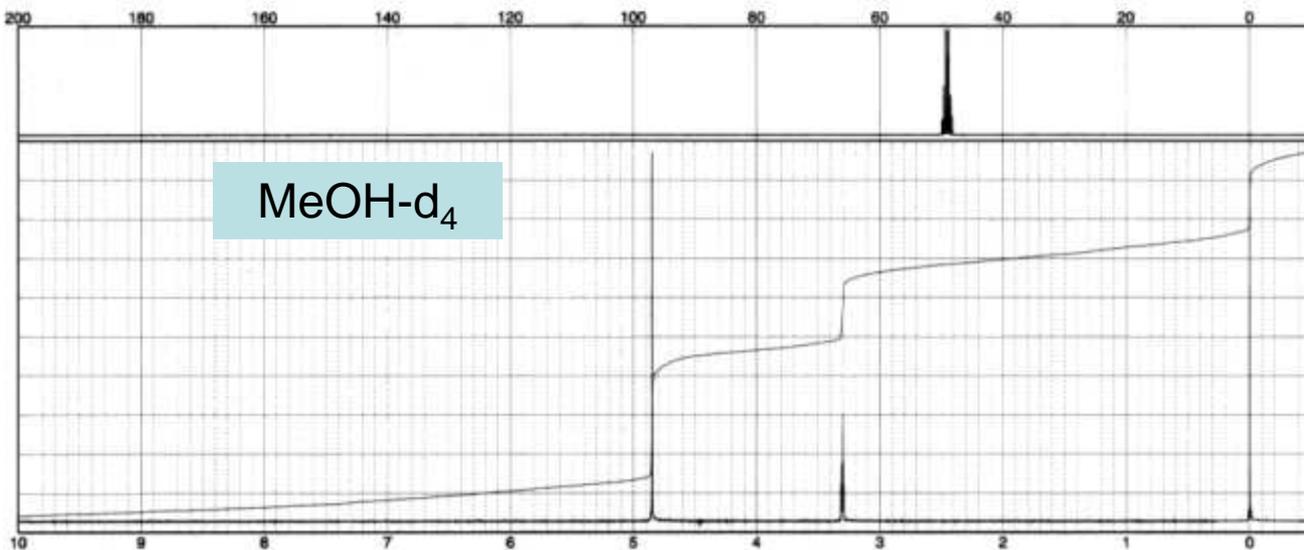
^1H 7.26 ppm

Metanol deuterado MeOH-d₄

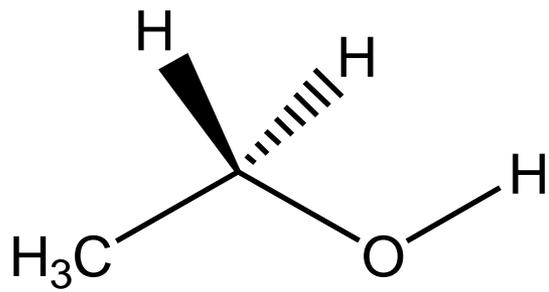
¹³C 49.0 ppm

¹J(C,D) 21.0 Hz

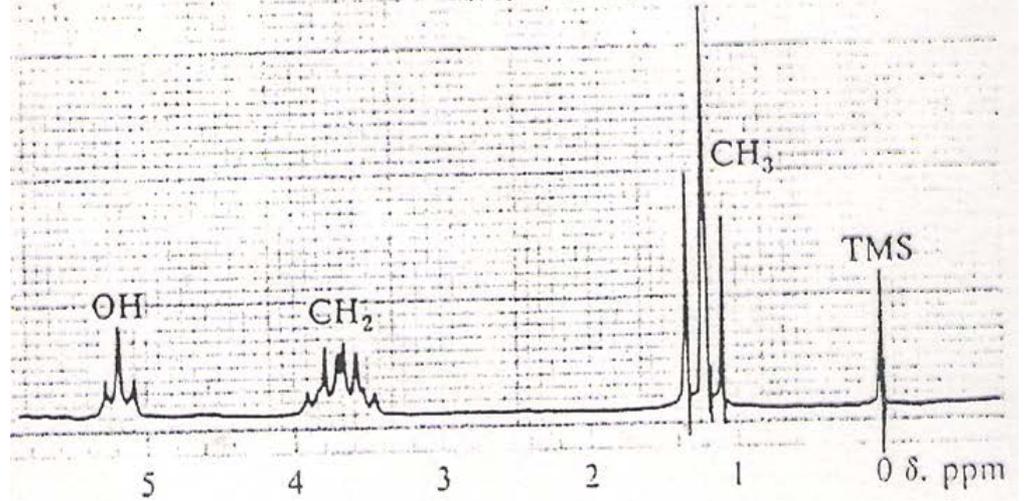
²J(H,D) 1.6 Hz



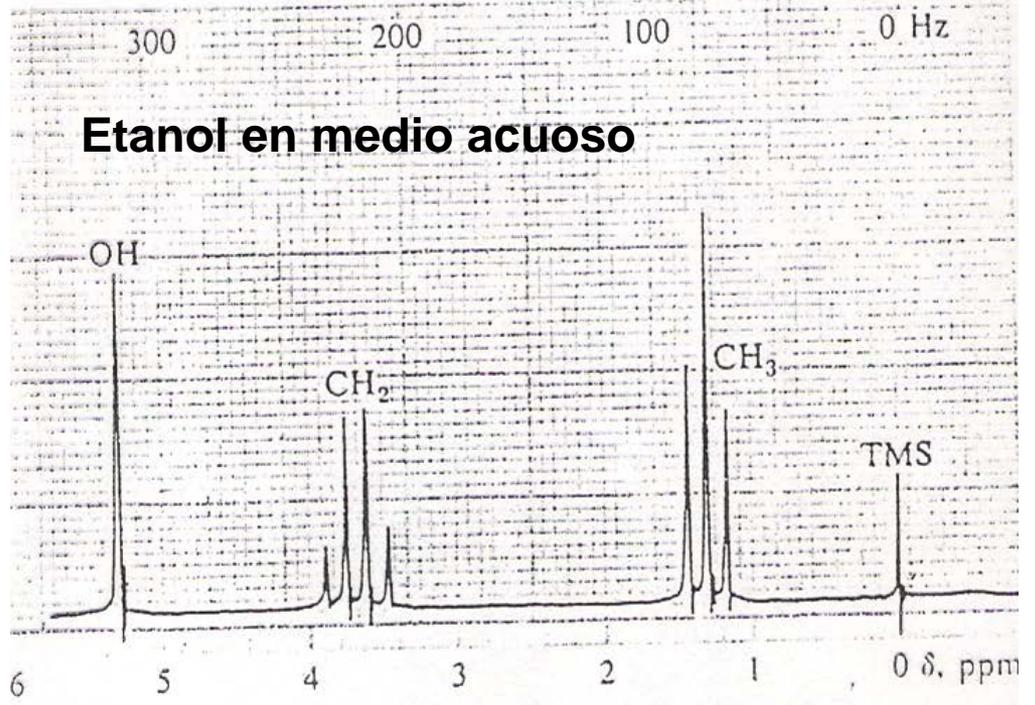
¹H 4.79 ppm
3.31 ppm



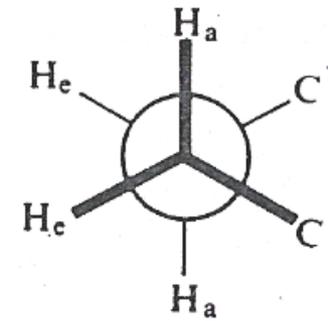
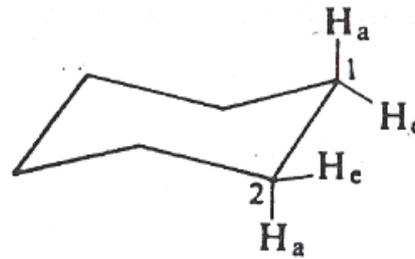
Etanol absoluto



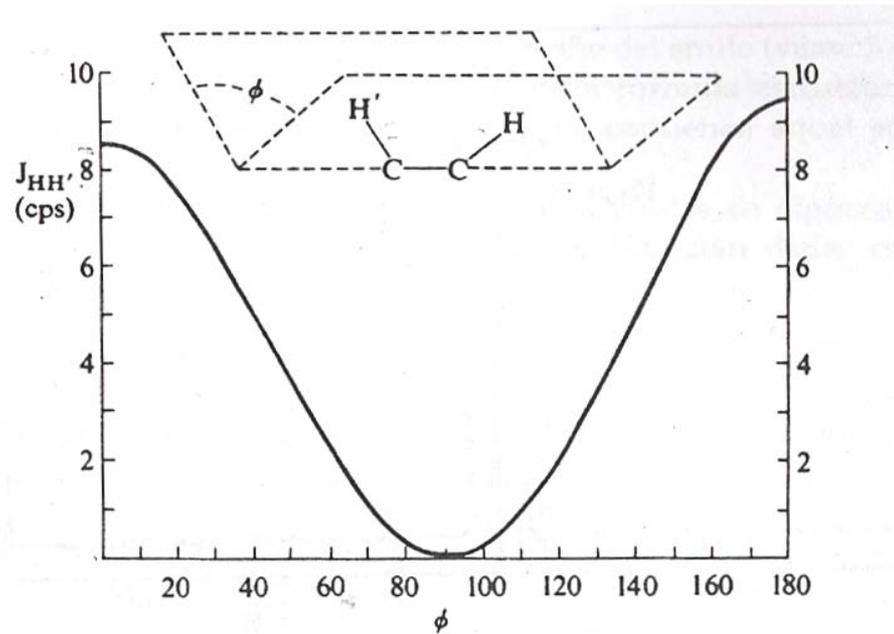
Etanol en medio acuoso



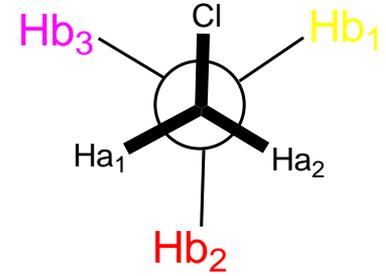
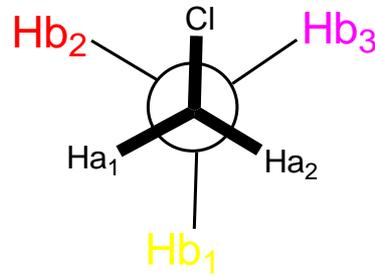
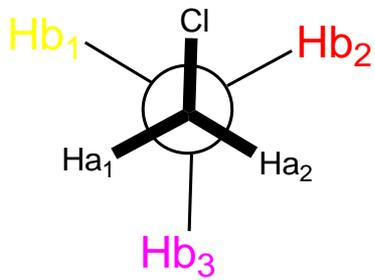
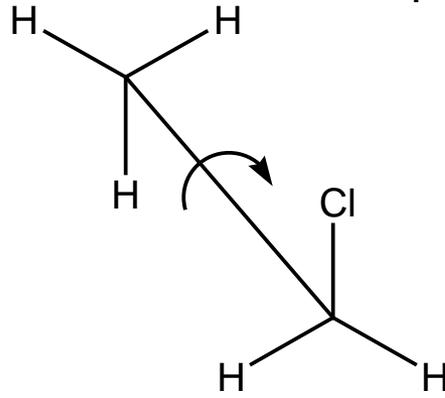
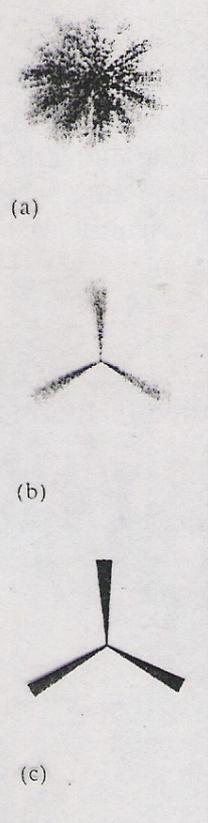
Constantes vecinales 3J Variación con el ángulo diedro



$$^3J = 4.22 - 0,5 \cos\phi + 4.5 \cos 2\phi$$

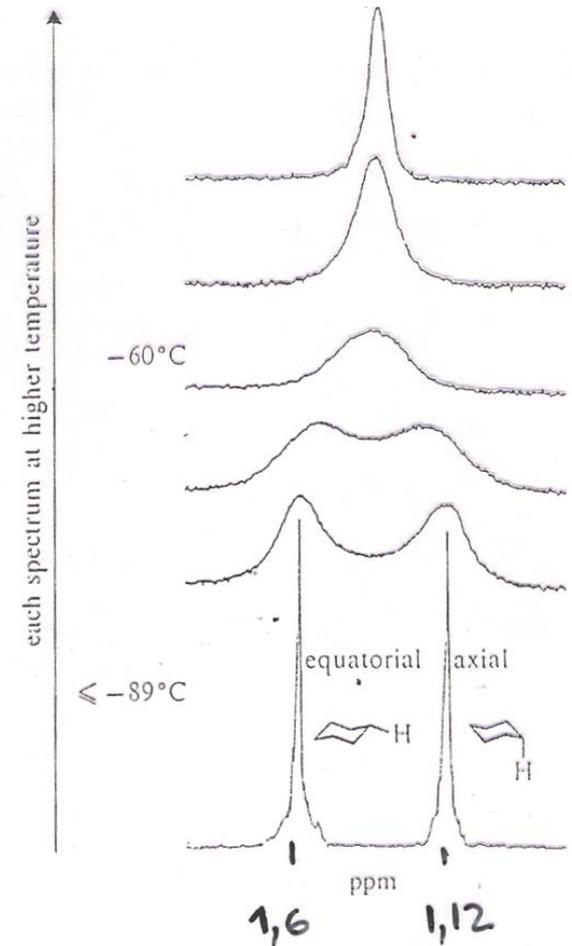
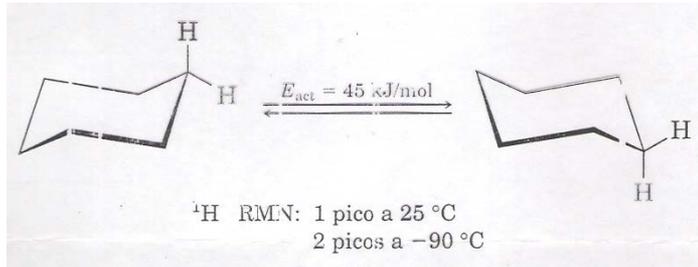


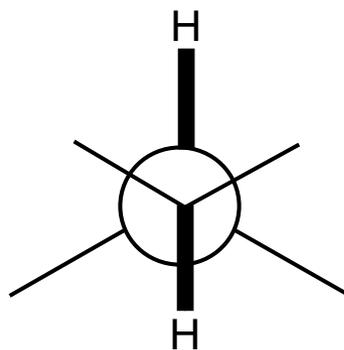
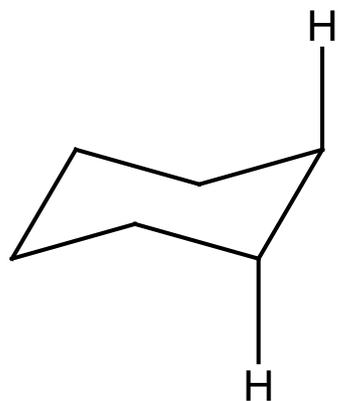
Espectroscopía de sistemas dinámicos



1 señal para H_b

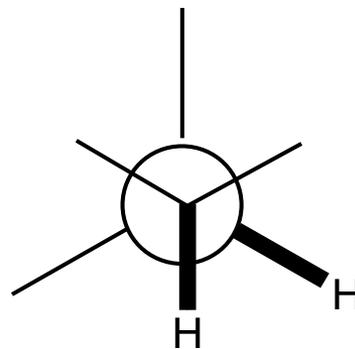
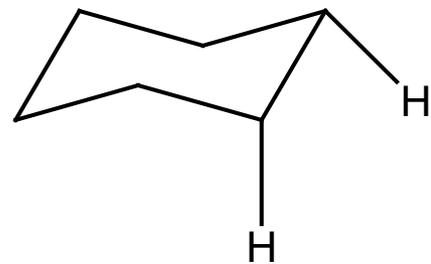
Espectroscopía de sistemas dinámicos





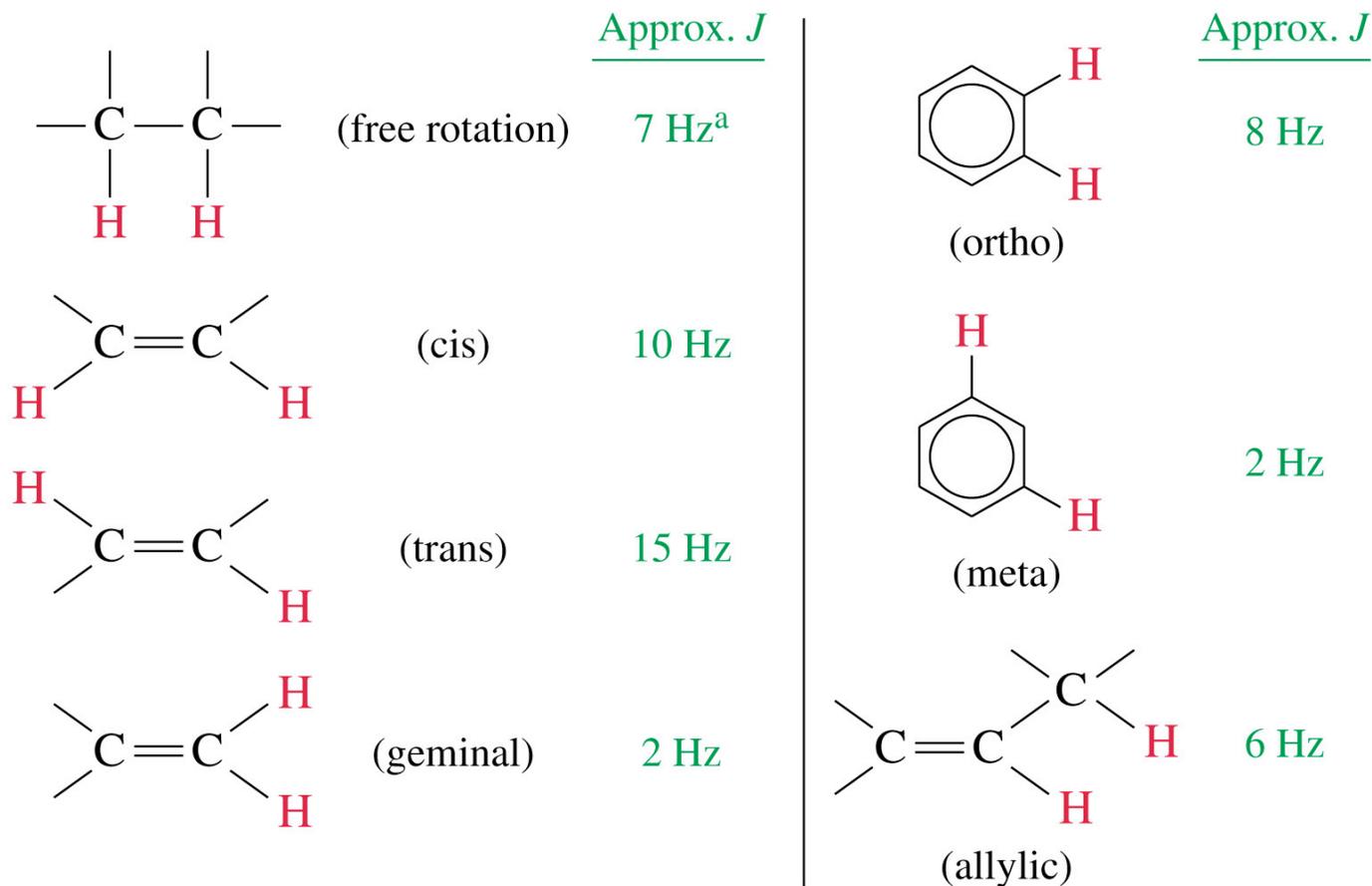
$$\phi = 180^\circ$$

$$J = 10 \text{ Hz}$$



$$\phi = 60^\circ$$

$$J = 3 \text{ Hz}$$



^aThe 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.

¿En qué se diferencian los espectros ^1H RMN de la piridina y benceno?

Ambos compuestos son aromáticos, y sus señales de H del anillo se presentan a campos bajos.

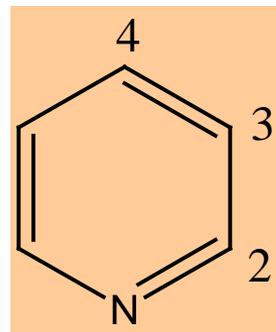
Como todos los hidrógenos del benceno son iguales, se observa una señal.

La piridina da tres señales (con acoplamientos espín–espín):

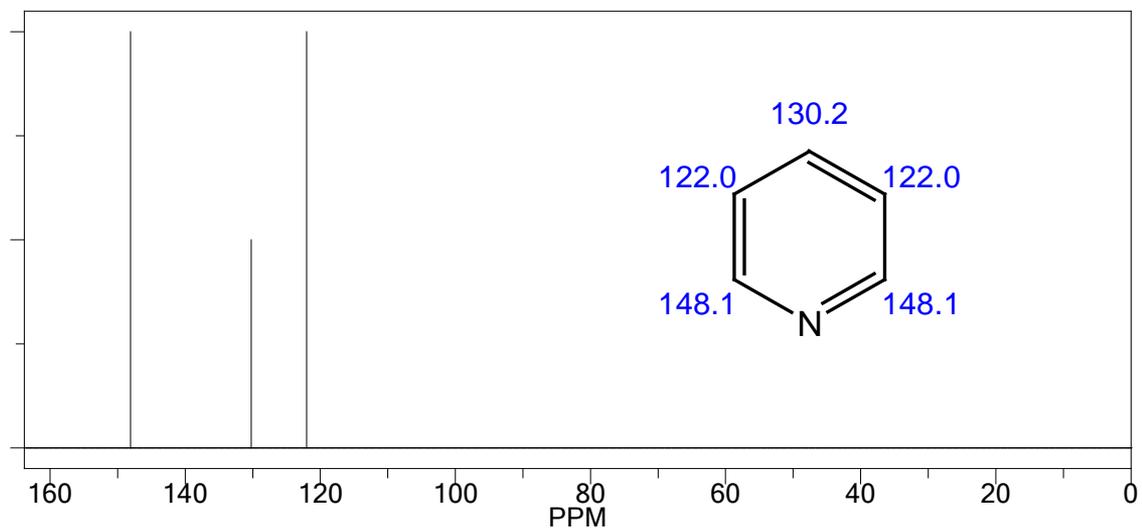
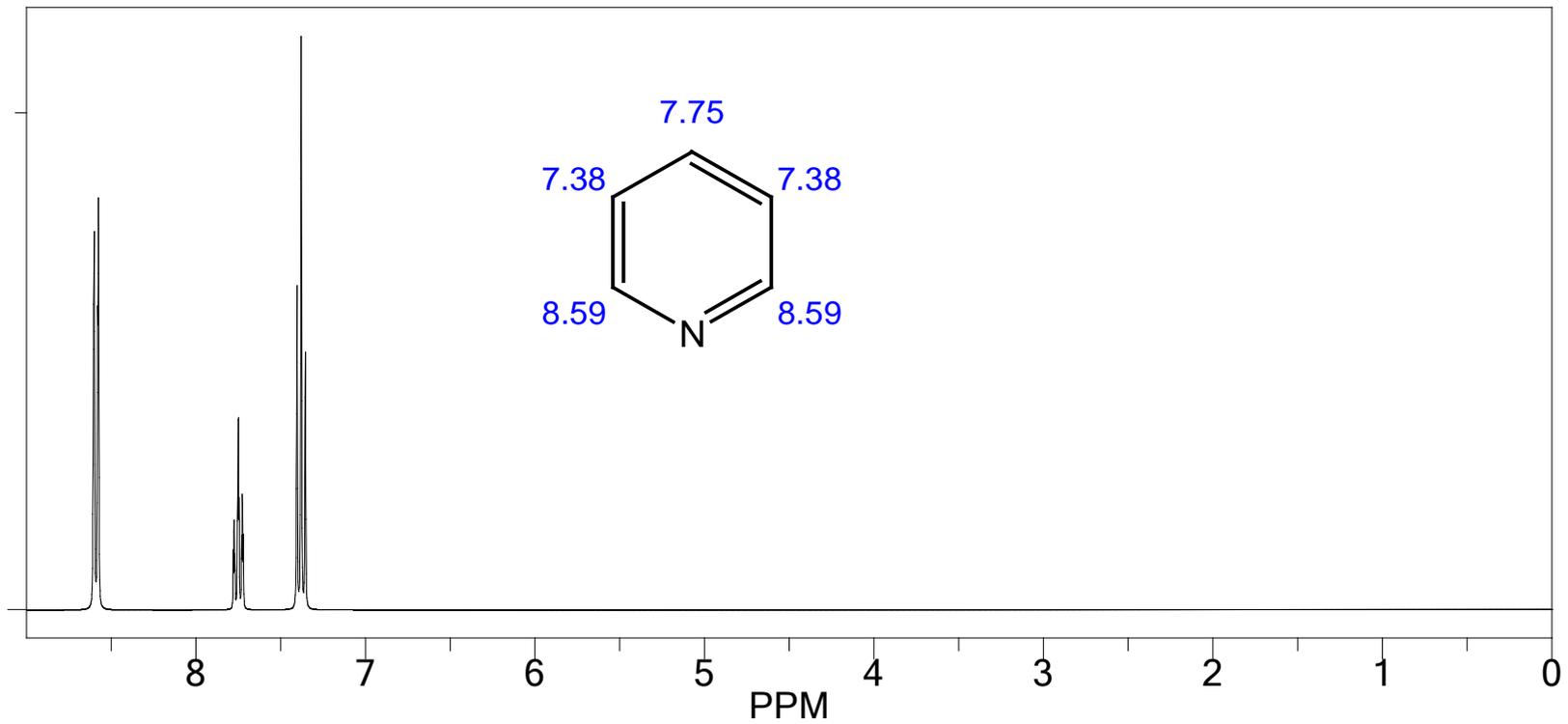
$\delta = 8,5$ (dos H, C²),

$\delta = 7,06$ (dos H, C³) y

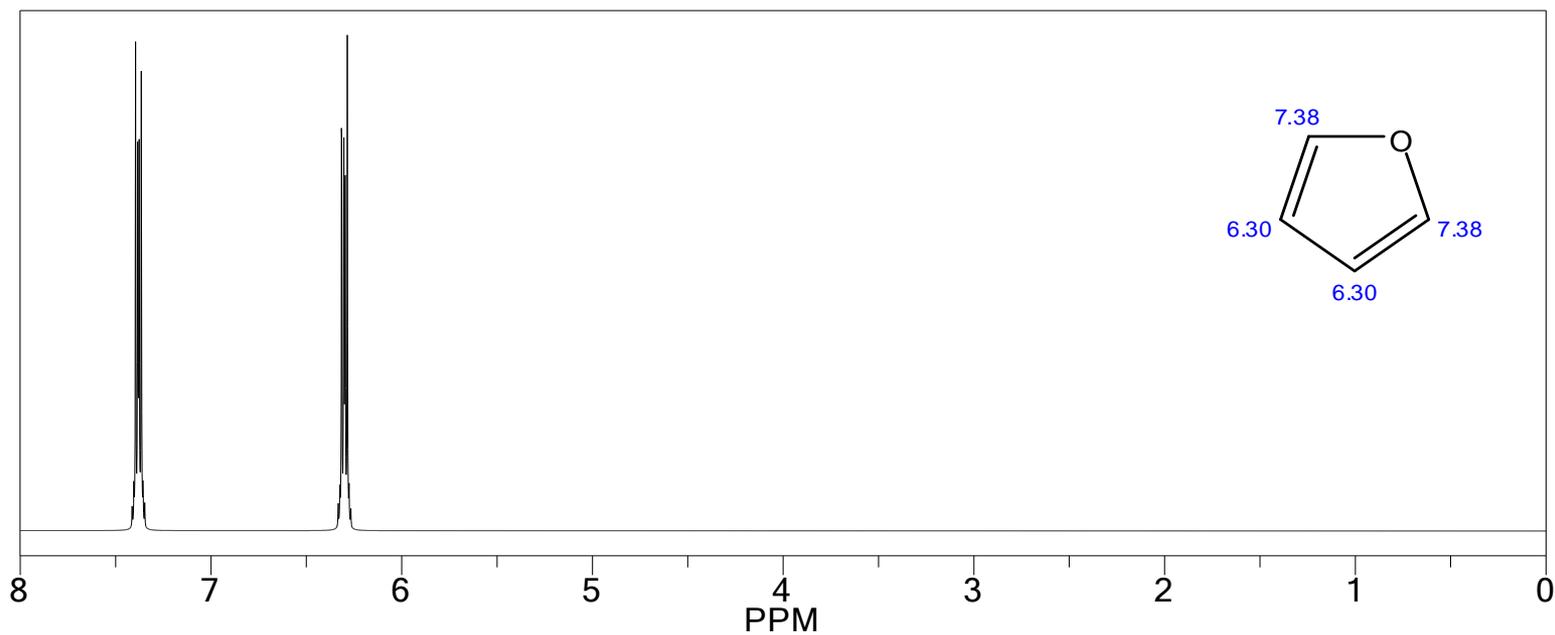
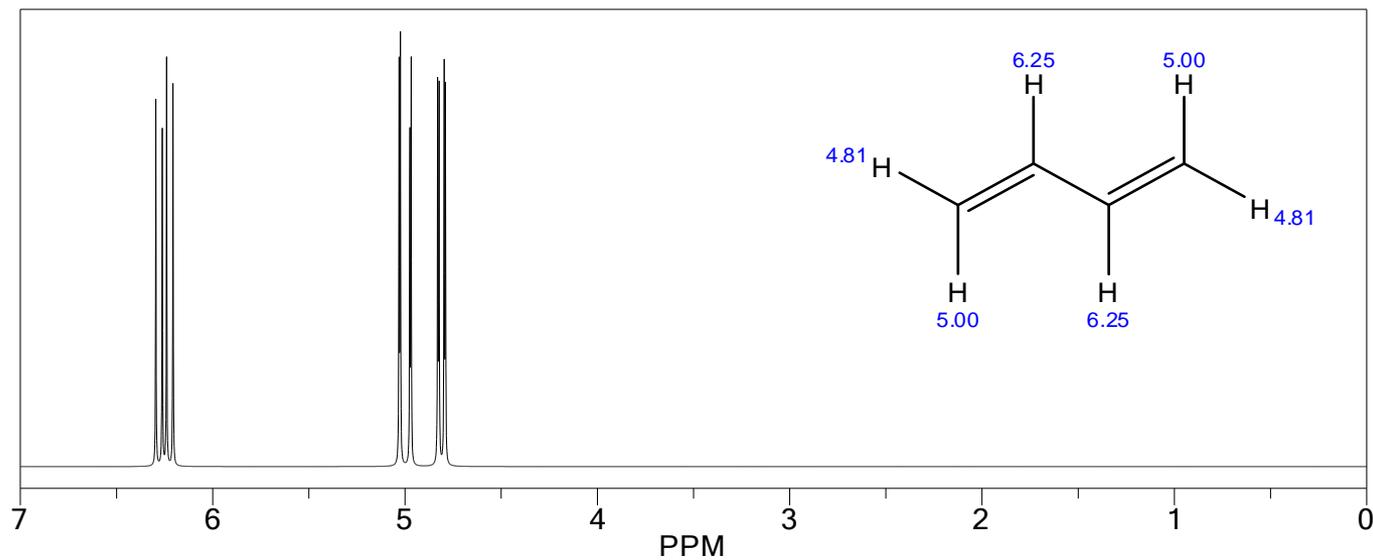
$\delta = 7,46$ (un H, C⁴).

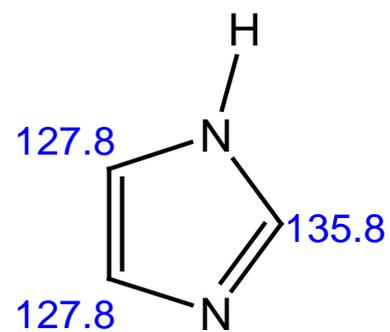
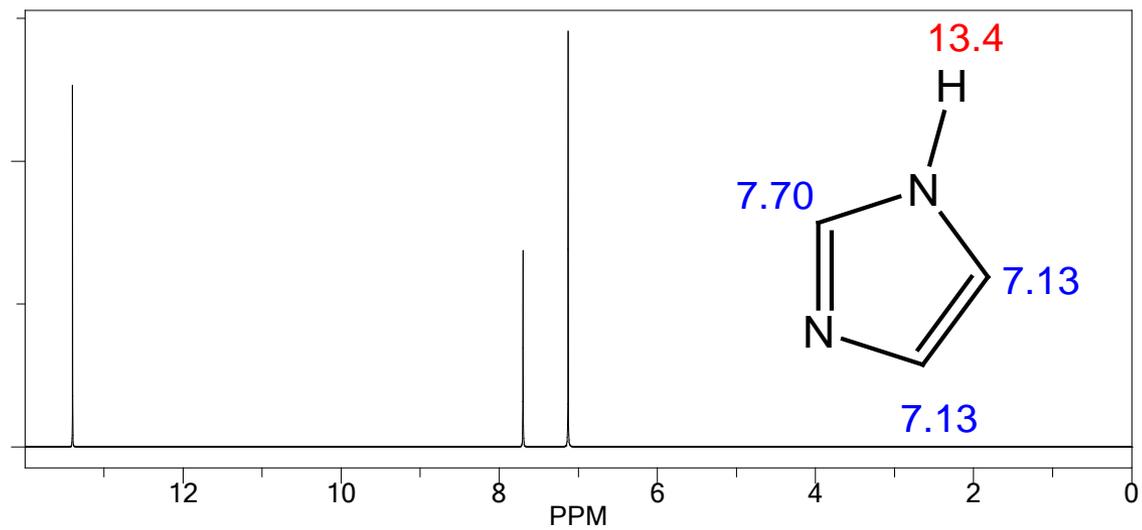
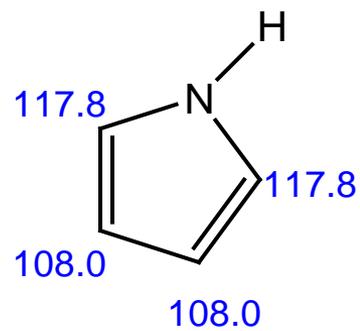
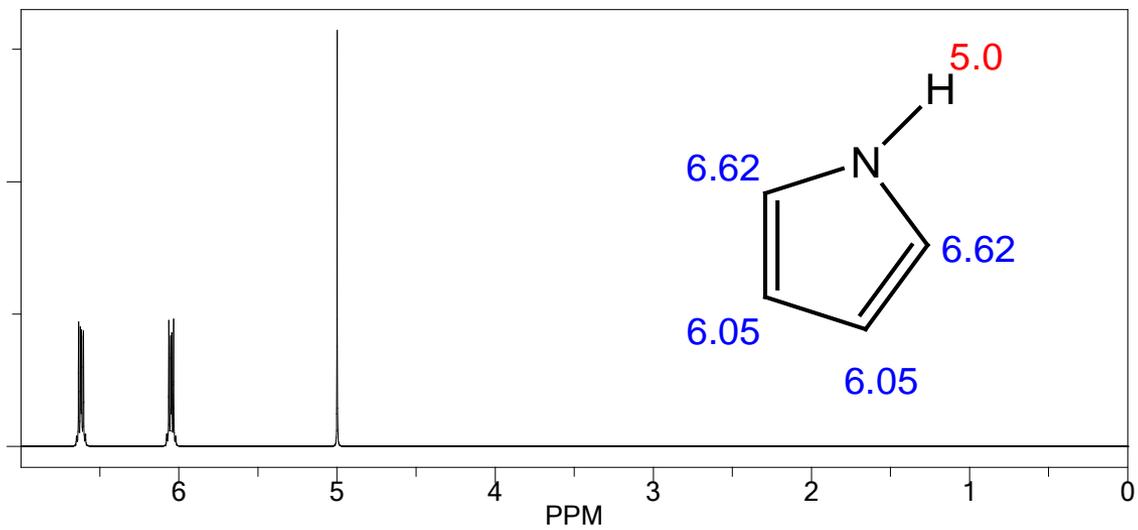


Obsérvese que la señal del H, C² es la de campo más bajo ya que el N es atractor de electrones y menos apantallante.



^1H -RMN de un dieno conjugado y un anillo heterocíclico pentatómico aromático





^1H RMN

^{13}C RMN

<https://aceochem.wordpress.com/tag/chemical-shift/>

<https://es.khanacademy.org/test-prep/mcat/physical-processes/proton-nuclear-magnetic-resonance/v/proton-nmr-practice-2>