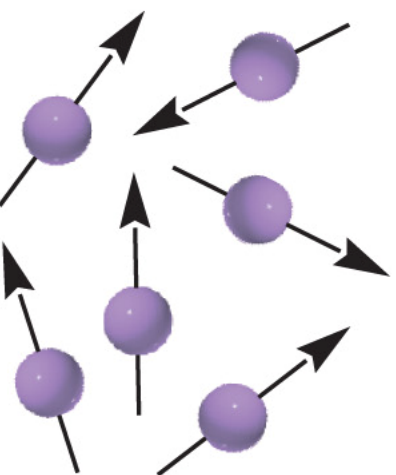
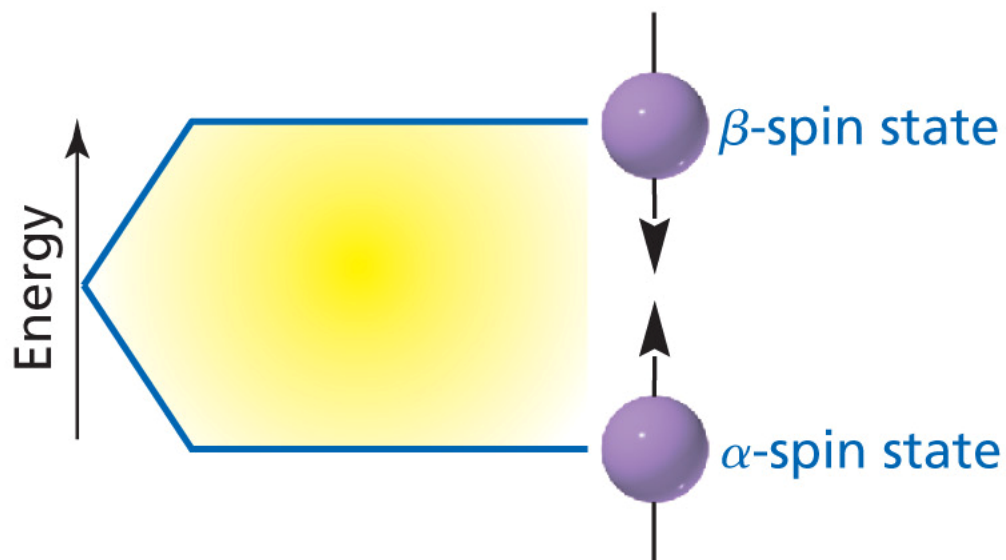


1-Nitropropane

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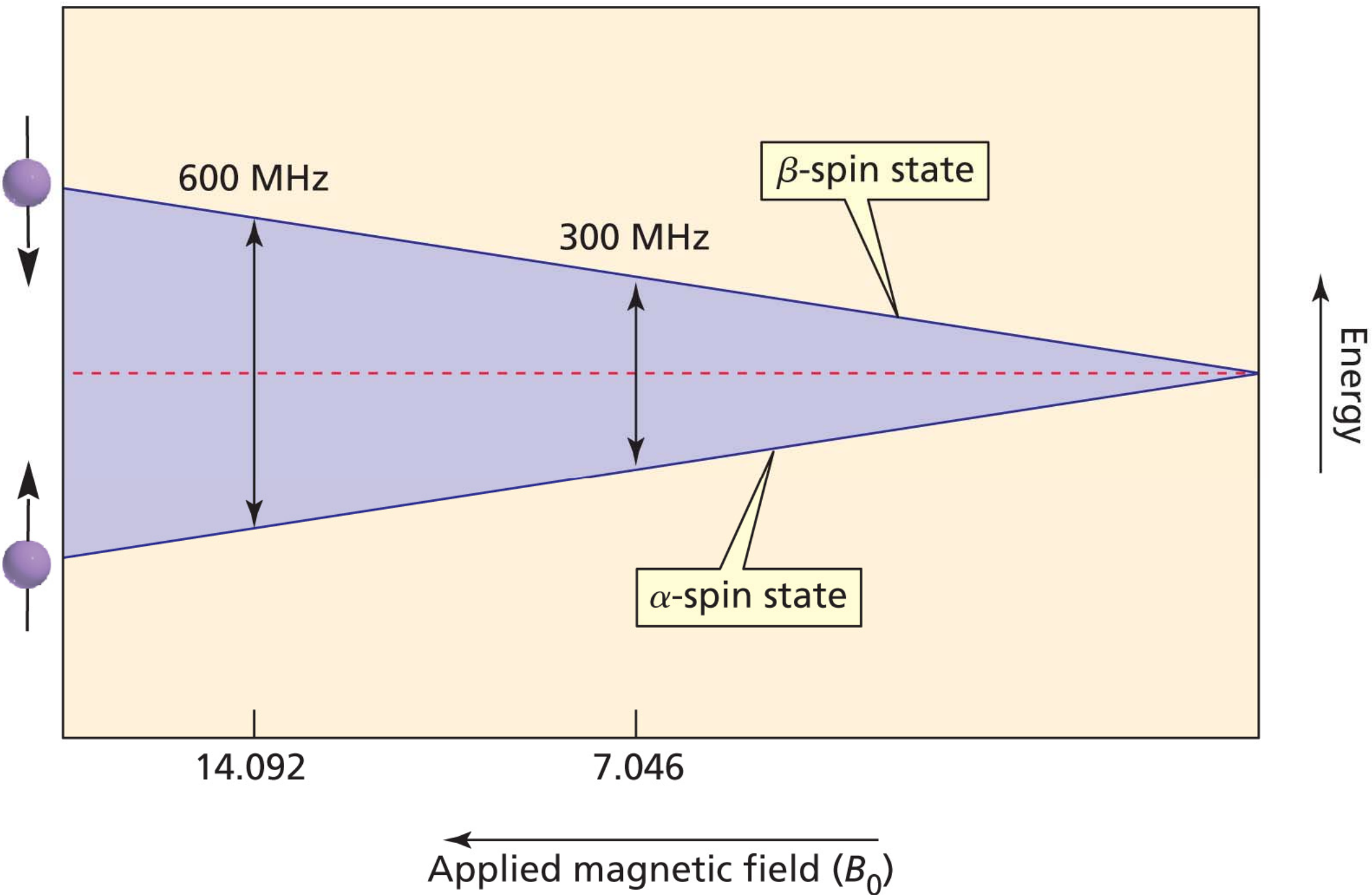


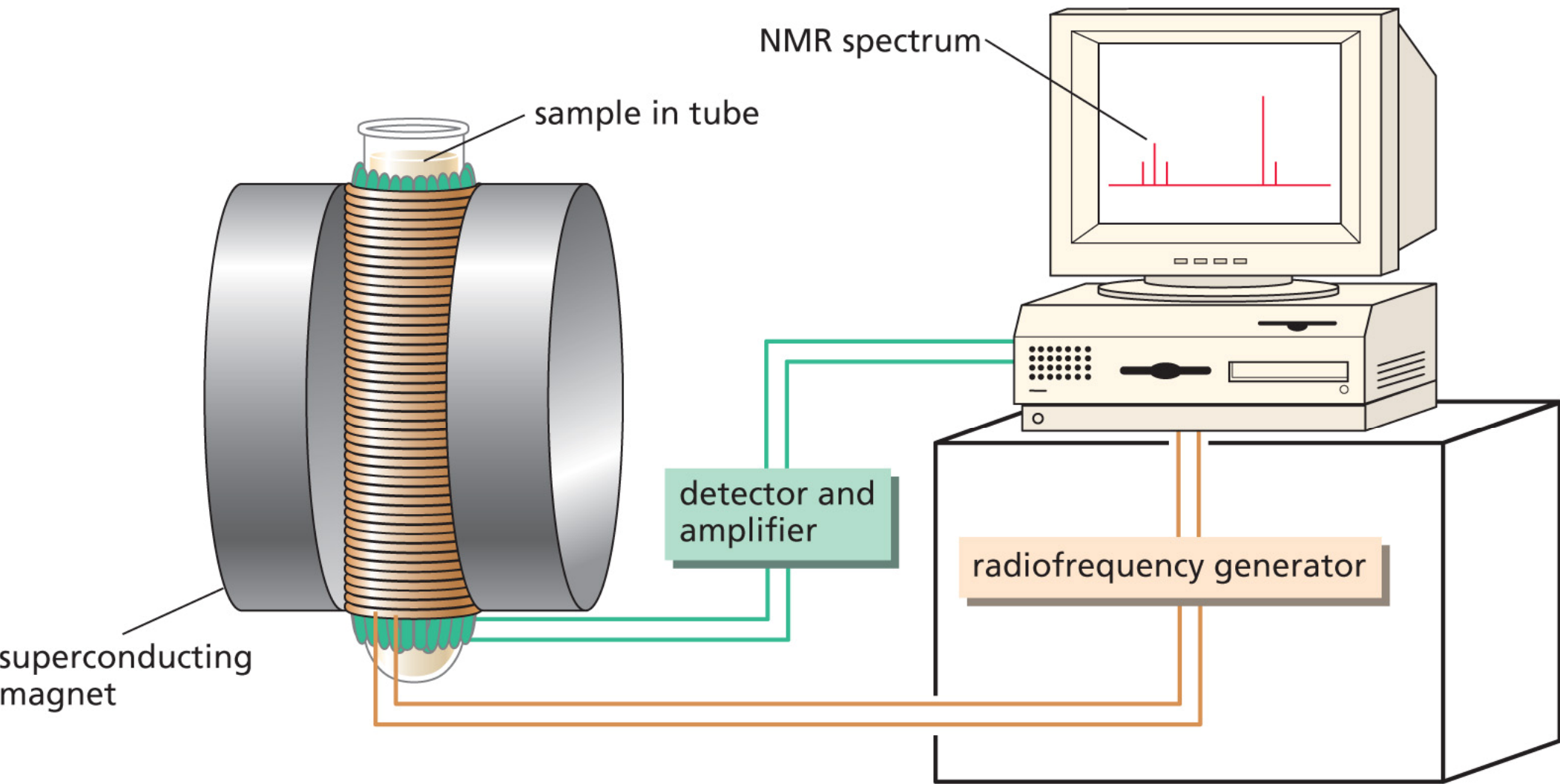
**no applied
magnetic field**

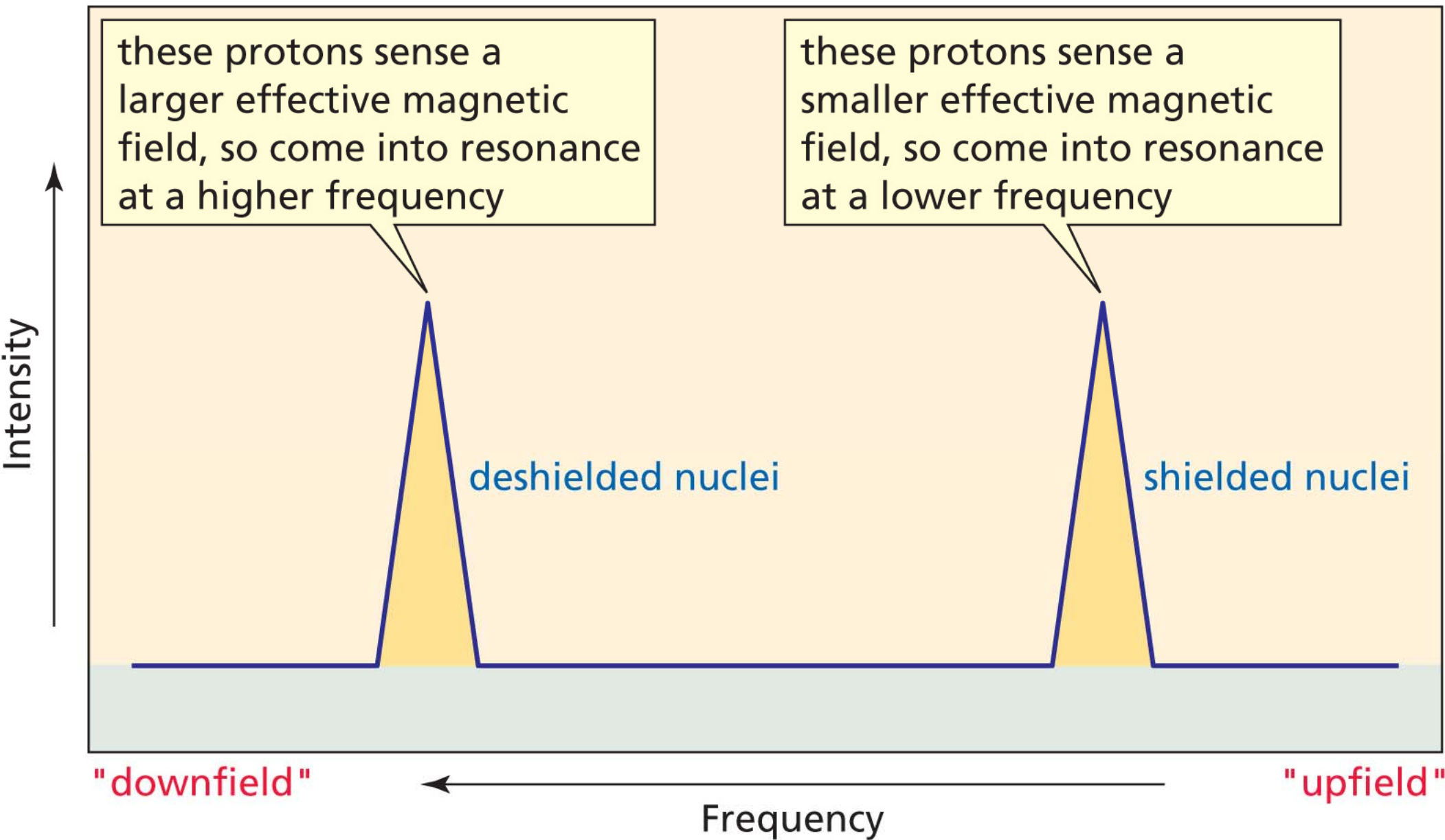


magnetic field is applied

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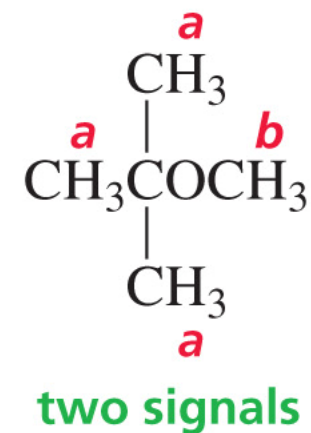
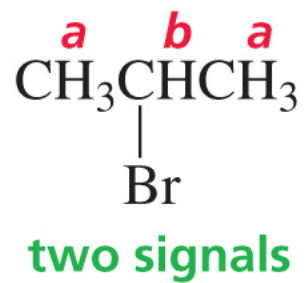


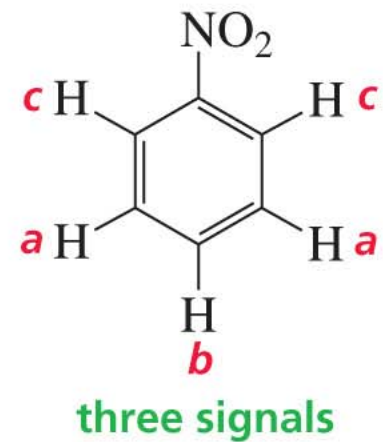
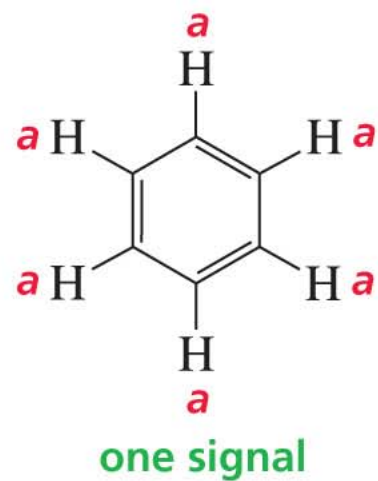
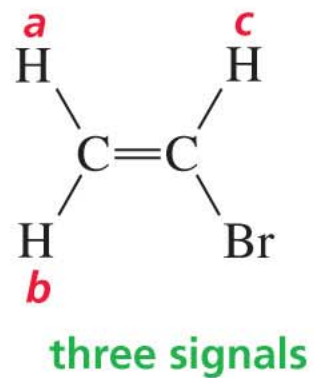
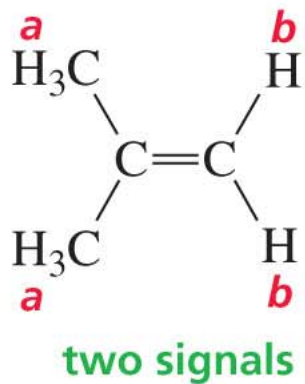
chemically
equivalent
protons



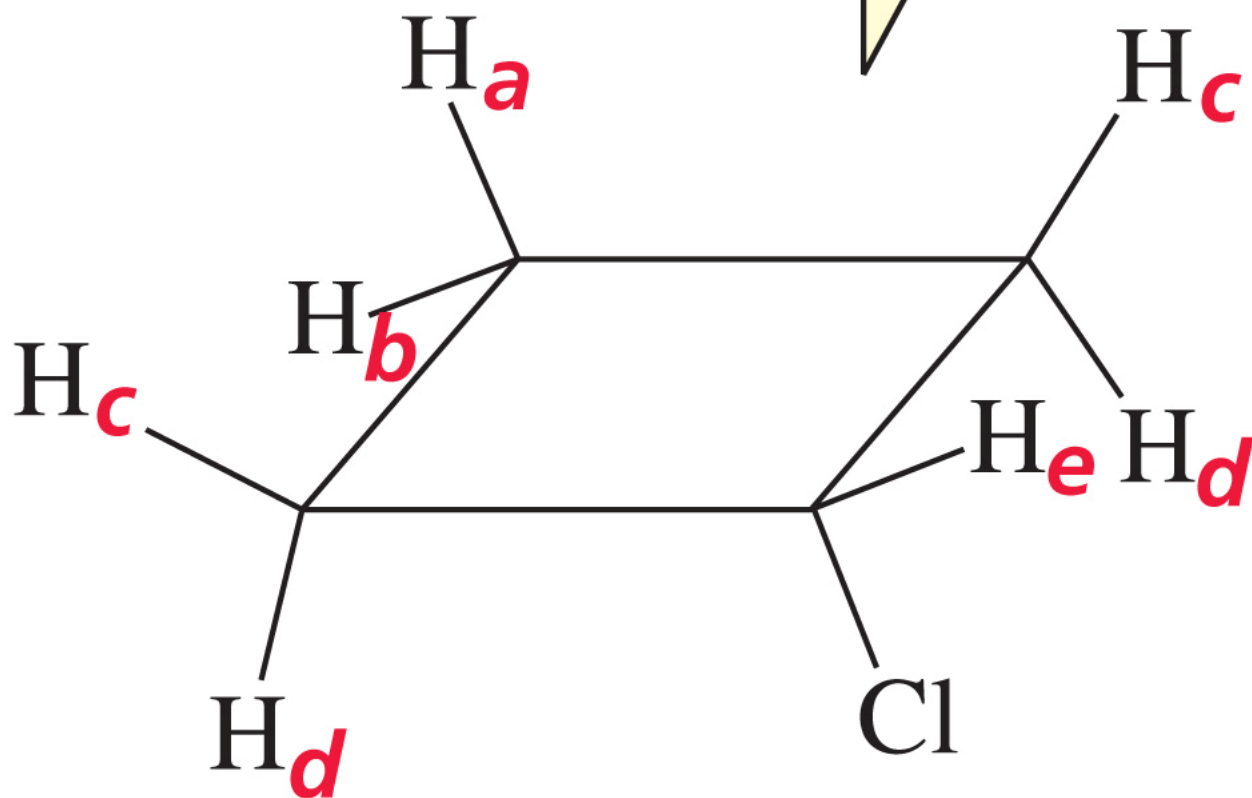
chemically
equivalent
protons

chemically
equivalent
protons





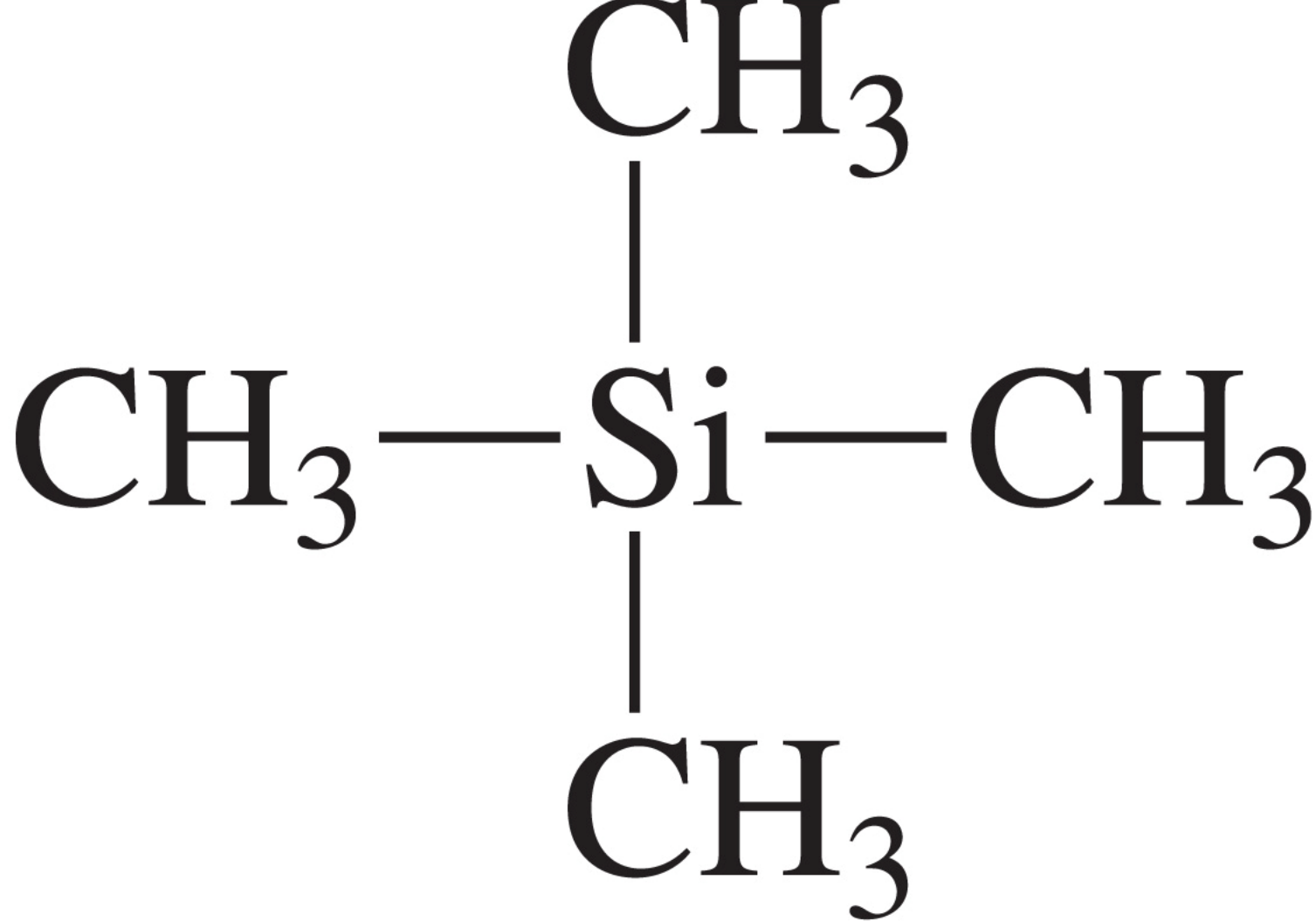
its ^1H NMR spectrum
has five signals



chlorocyclobutane

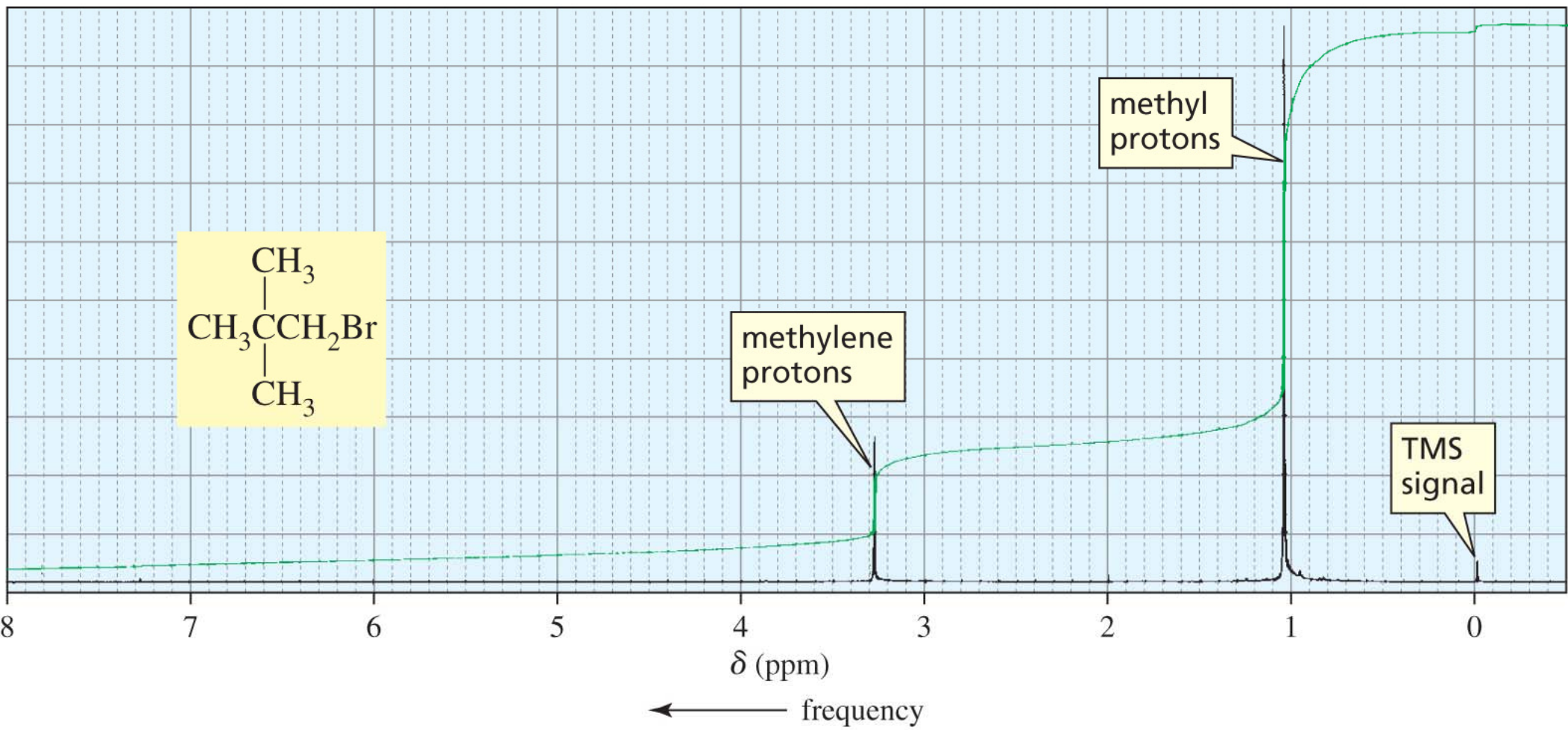
H_a and H_b are not equivalent

H_c and H_d are not equivalent



tetramethylsilane

TMS



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protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

← δ ppm

← frequency

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1.04 ppm

2.07 ppm

4.37 ppm



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4.50 ppm



3.50 ppm

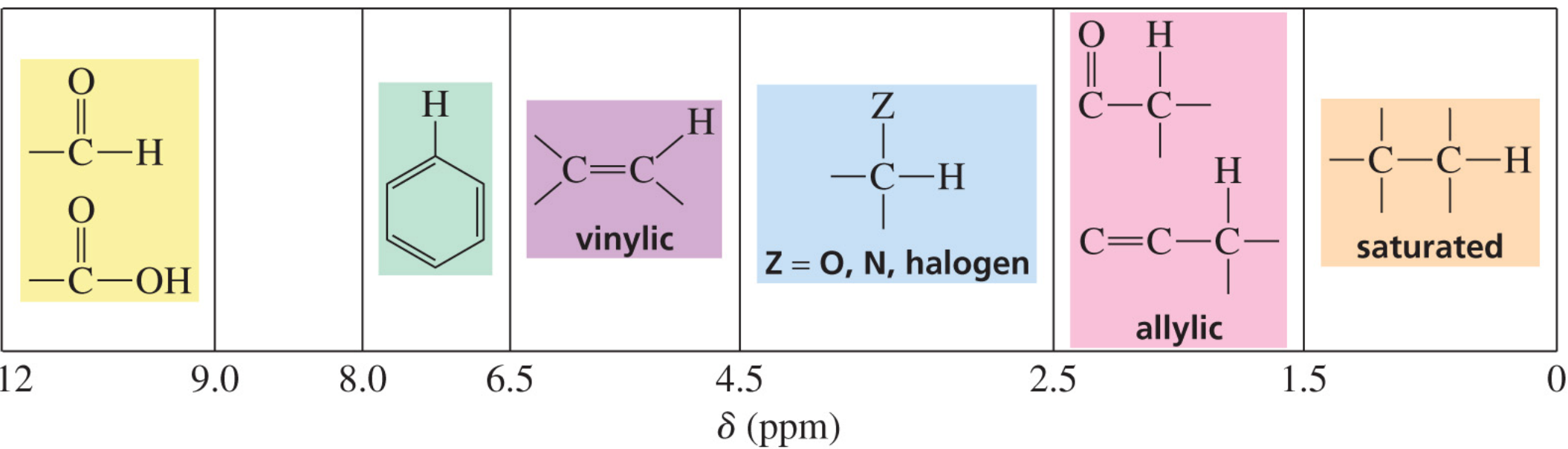


3.40 ppm



3.20 ppm

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methine

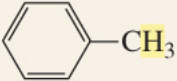
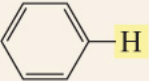


methylene

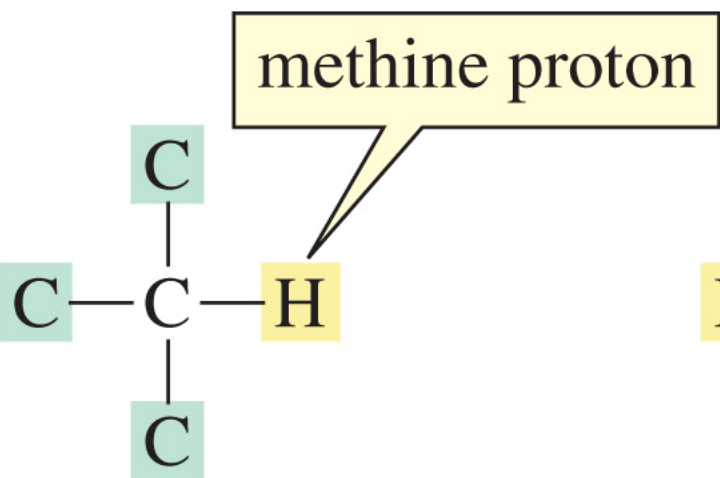


methyl

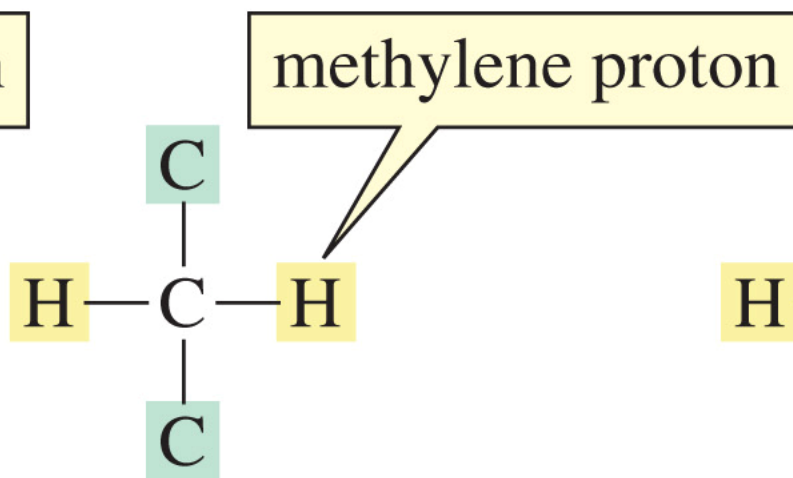
Table 13.1 Approximate Values of Chemical Shifts for ^1H NMR^a

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$-\text{CH}_3$	0.85	$\text{I}-\text{C}-\text{H}$	2.5–4
$-\text{CH}_2-$	1.20	$\text{Br}-\text{C}-\text{H}$	2.5–4
$-\text{CH}-$	1.55	$\text{Cl}-\text{C}-\text{H}$	3–4
$-\text{C}=\text{C}-\text{CH}_3$	1.7	$\text{F}-\text{C}-\text{H}$	4–4.5
$-\text{C}(=\text{O})-\text{CH}_3$	2.1	RNH_2	Variable, 1.5–4
	2.3	ROH	Variable, 2–5
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ArOH	Variable, 4–7
$\text{R}-\text{O}-\text{CH}_3$	3.3		6.5–8
$\text{R}-\text{C}(\text{R})=\text{CH}_2$	4.7	$-\text{C}(=\text{O})-\text{H}$	9.0–10
$\text{R}-\text{C}(\text{R})=\text{C}(\text{R})-\text{H}$	5.3	$-\text{C}(=\text{O})-\text{OH}$	Variable, 10–12
		$-\text{C}(=\text{O})-\text{NH}_2$	Variable, 5–8

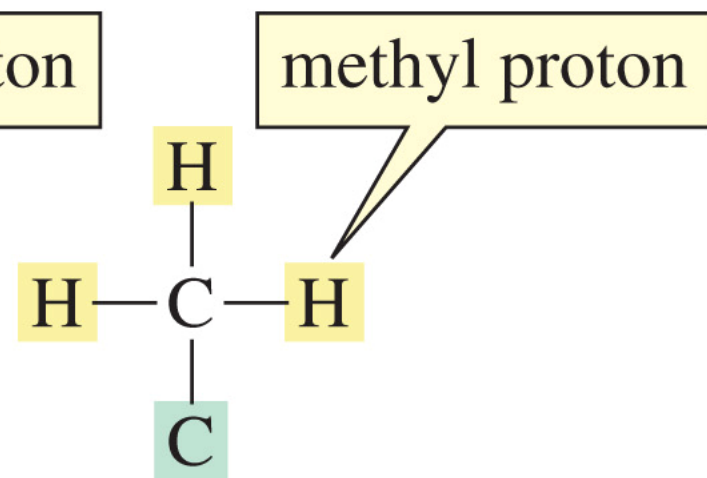
^aThe values are approximate because they are affected by neighboring substituents.



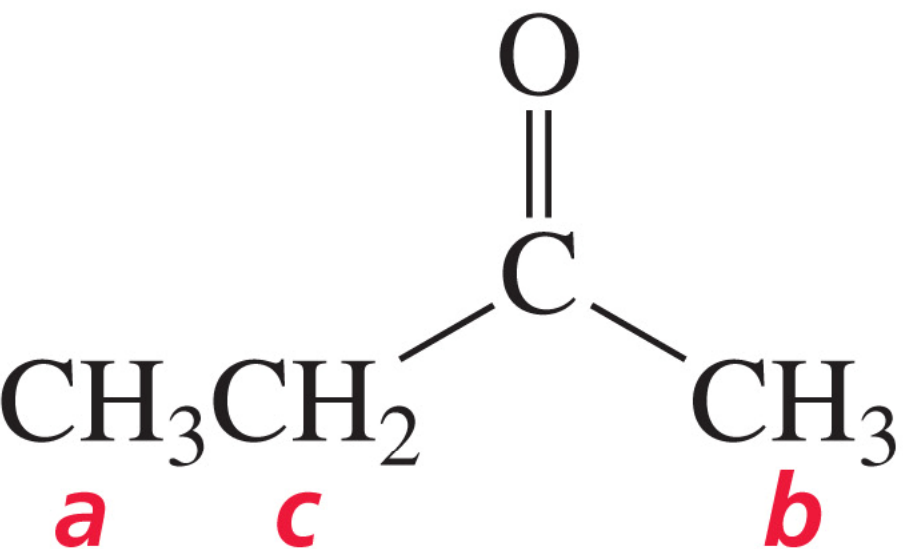
1.55 ppm



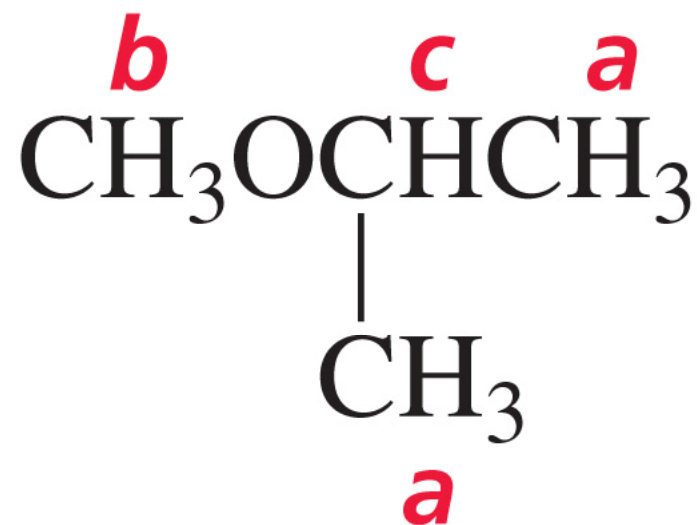
1.20 ppm



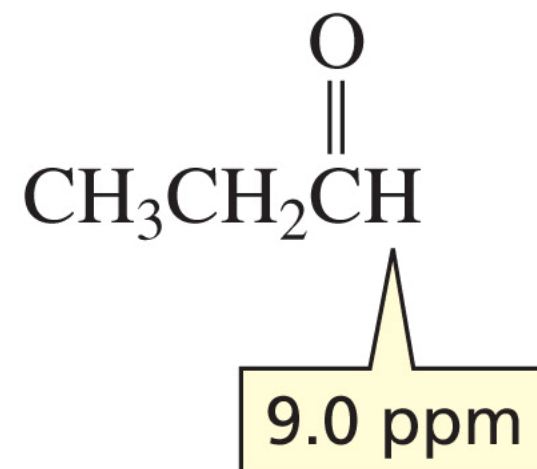
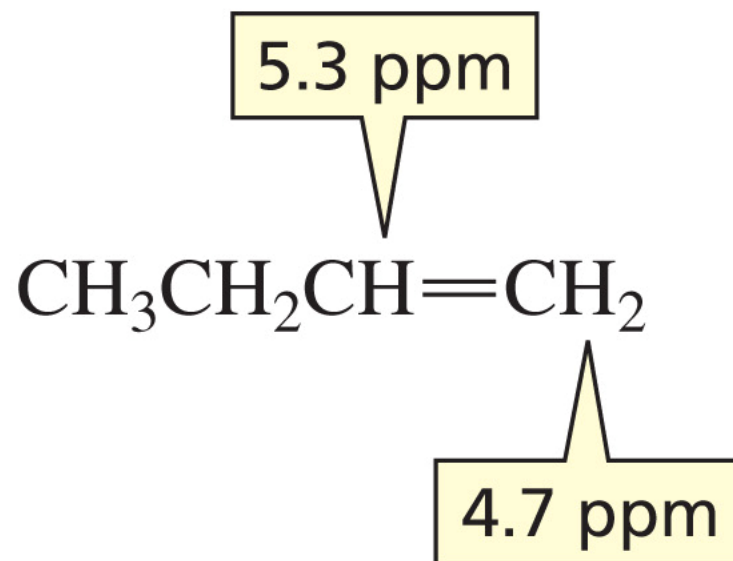
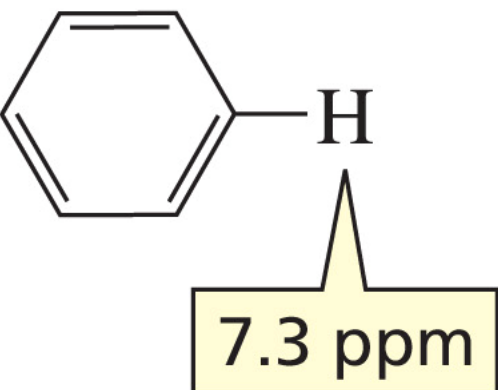
0.85 ppm

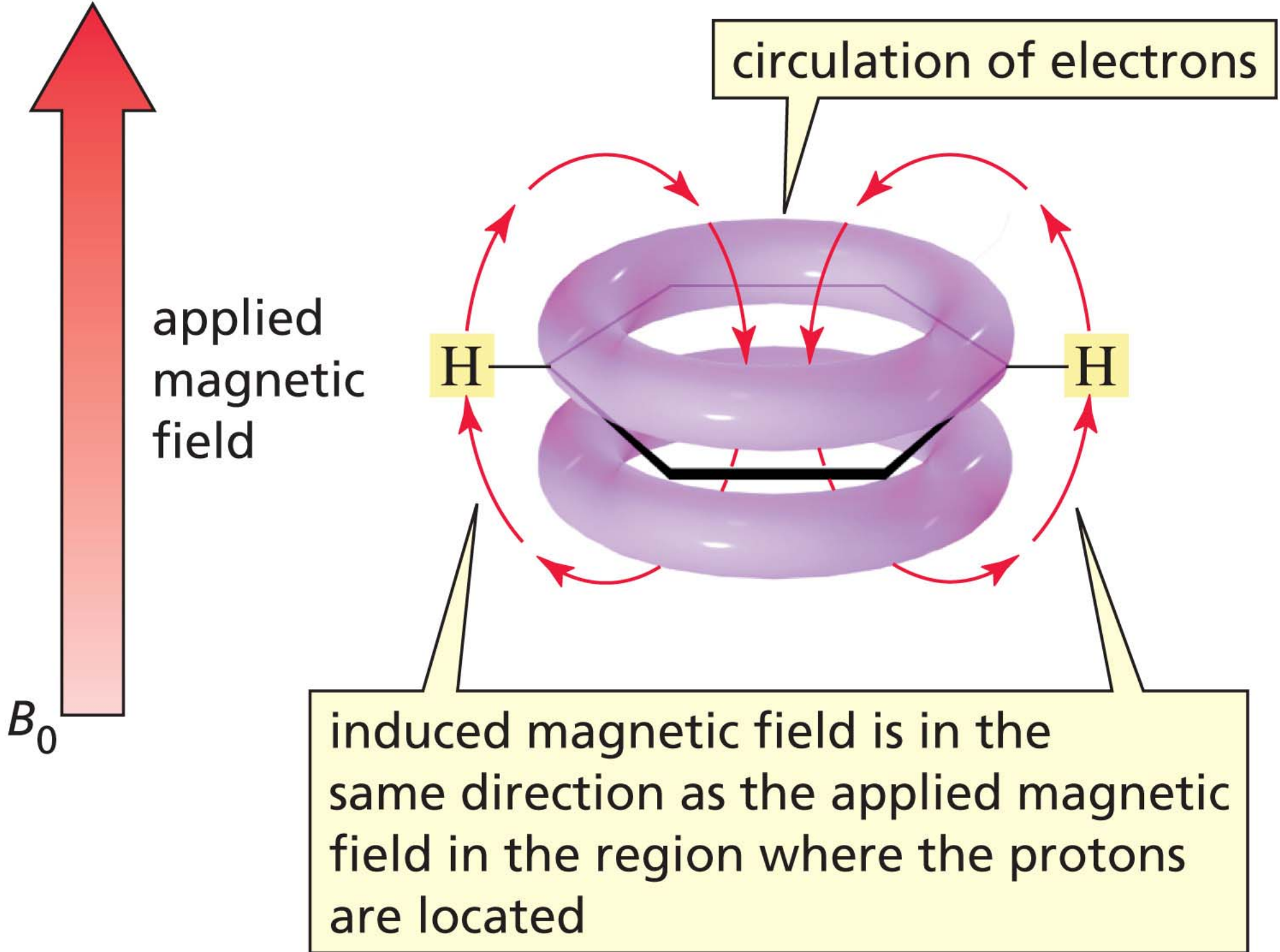


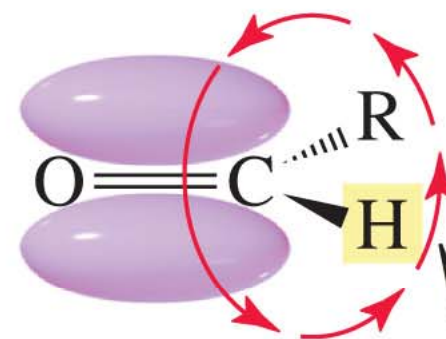
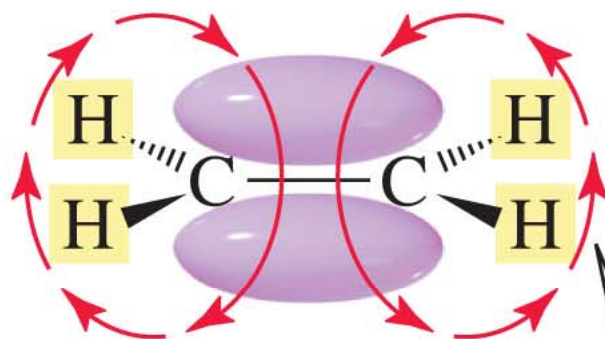
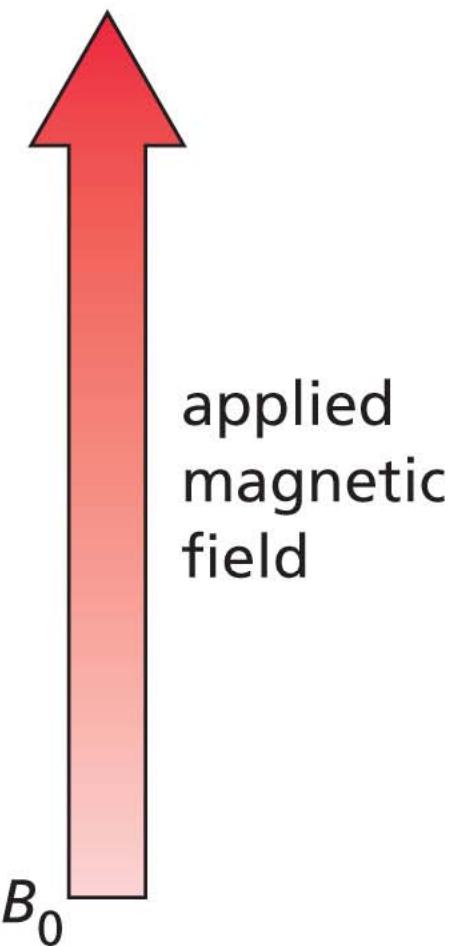
butanone



2-methoxypropane

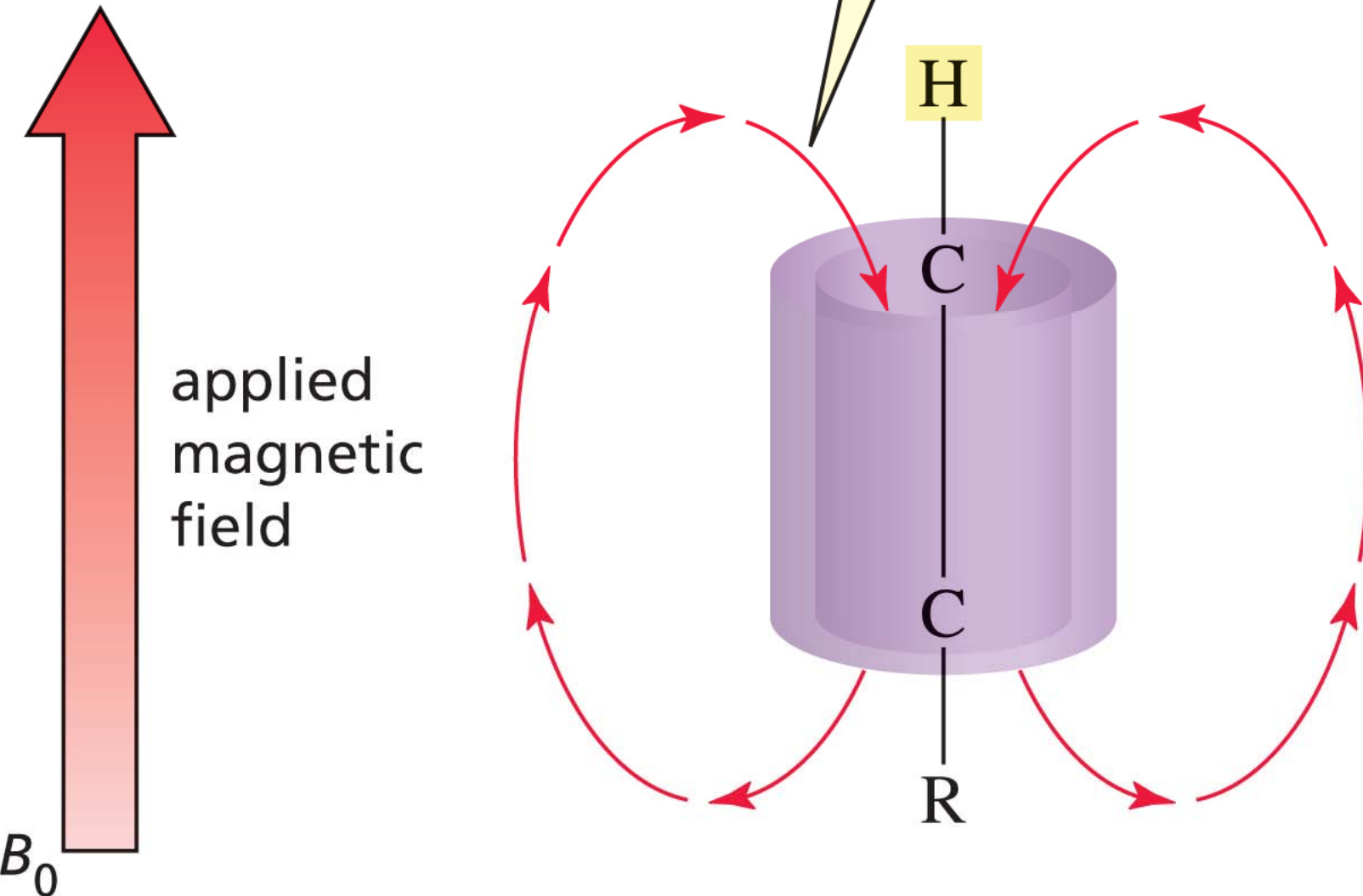


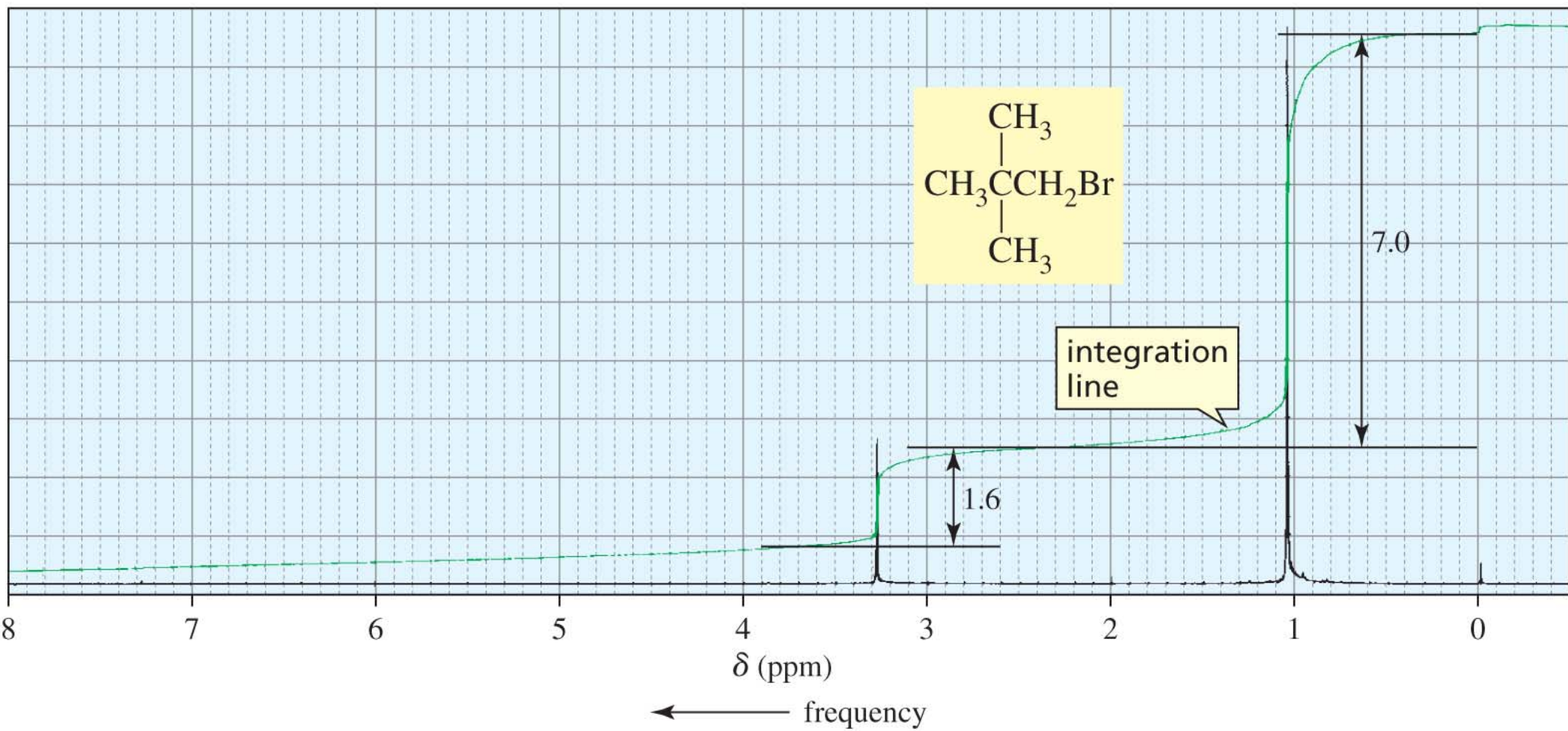




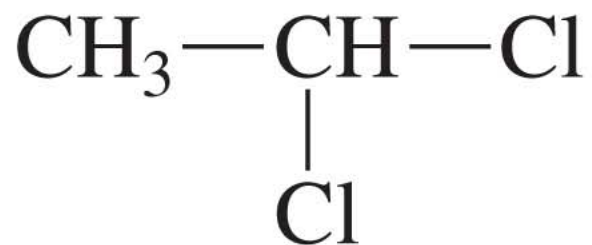
induced magnetic field is in the same direction as the applied magnetic field in the region where the proton is located

induced magnetic field is in the direction opposite to that of the applied magnetic field in the region where the proton is located



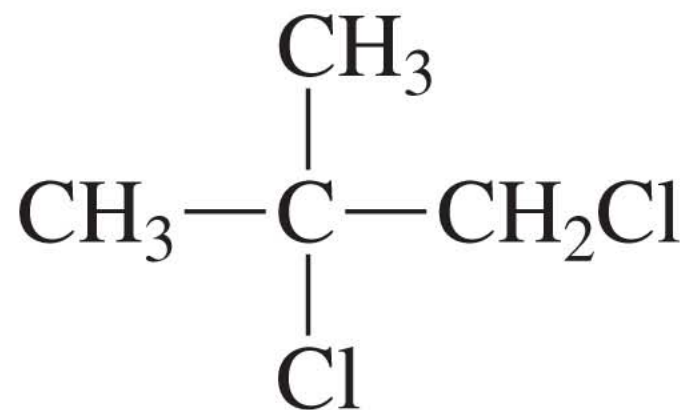


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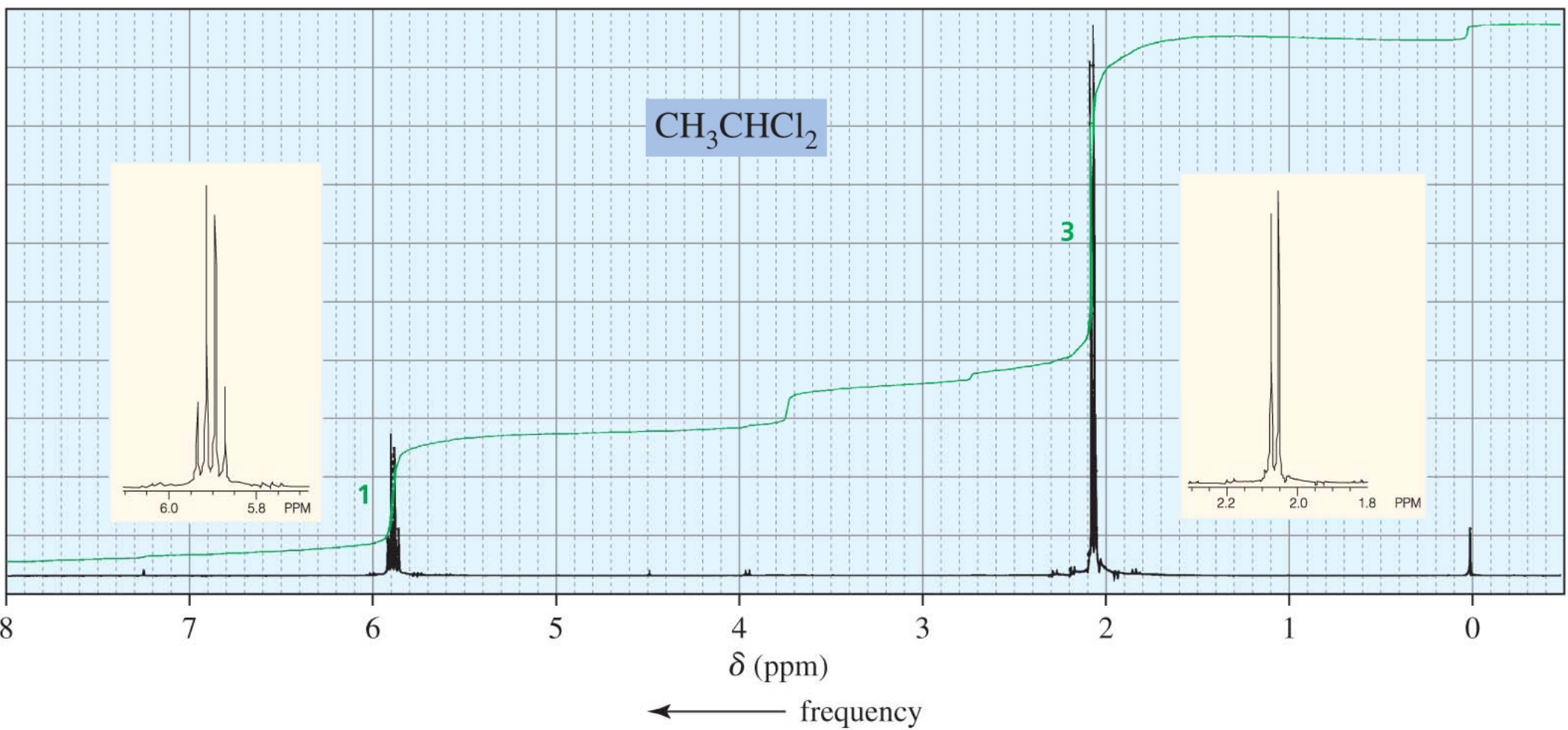
1,1-dichloroethane

ratio of protons = 1:3



1,2-dichloro-2-methylpropane

ratio of protons 2:6 = 1:3



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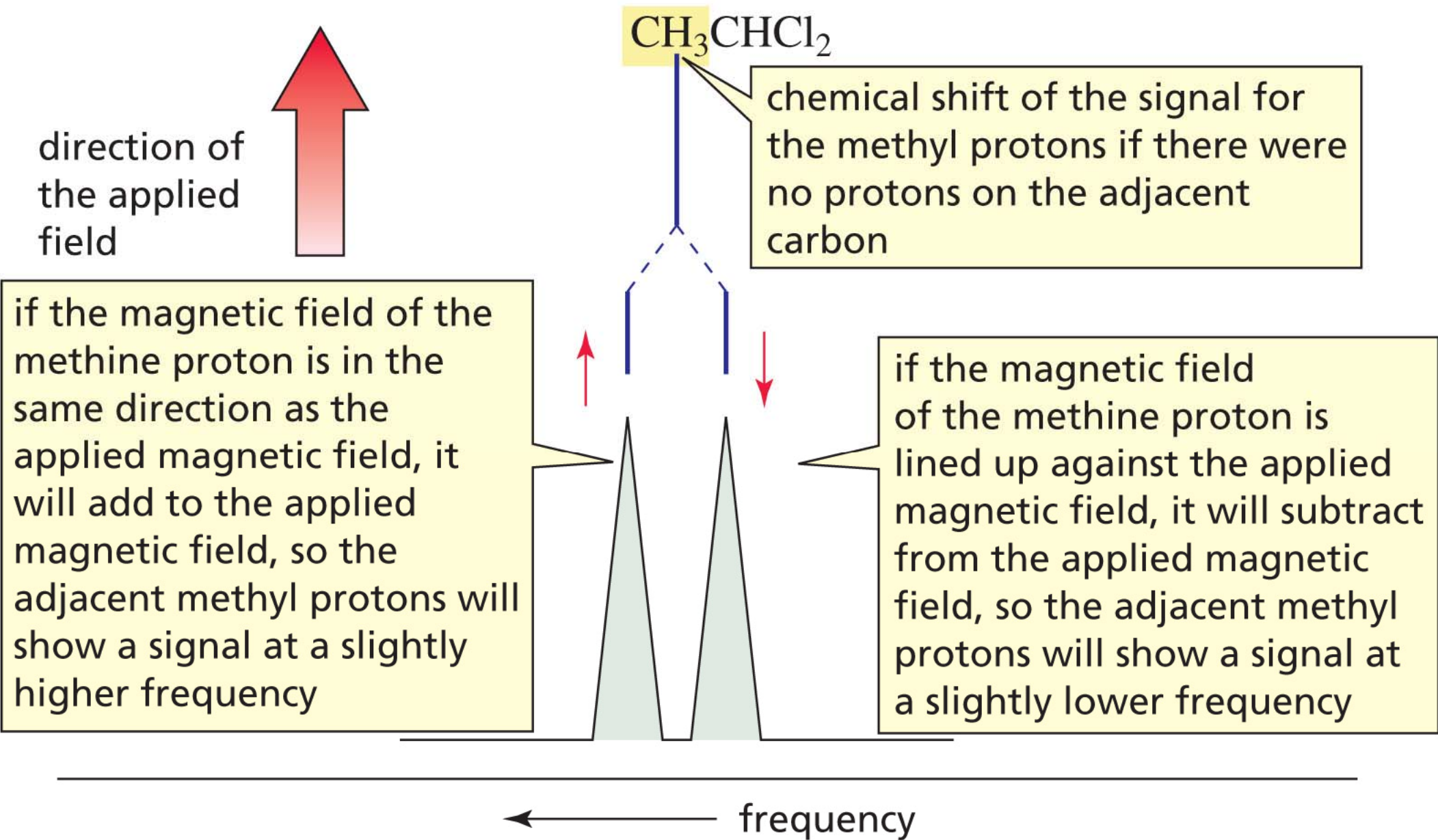


bromomethane



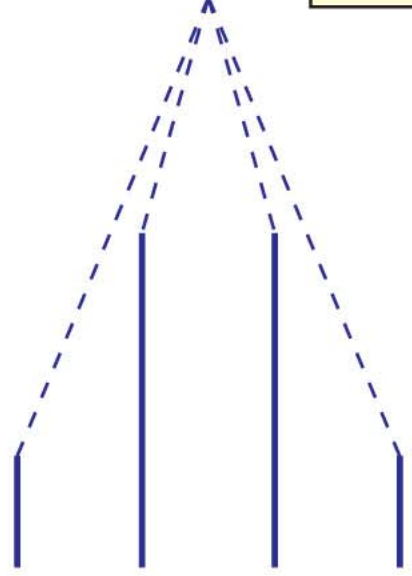
1,2-dichloroethane

each compound has an NMR spectrum that shows one singlet because equivalent protons do not split each other's signals

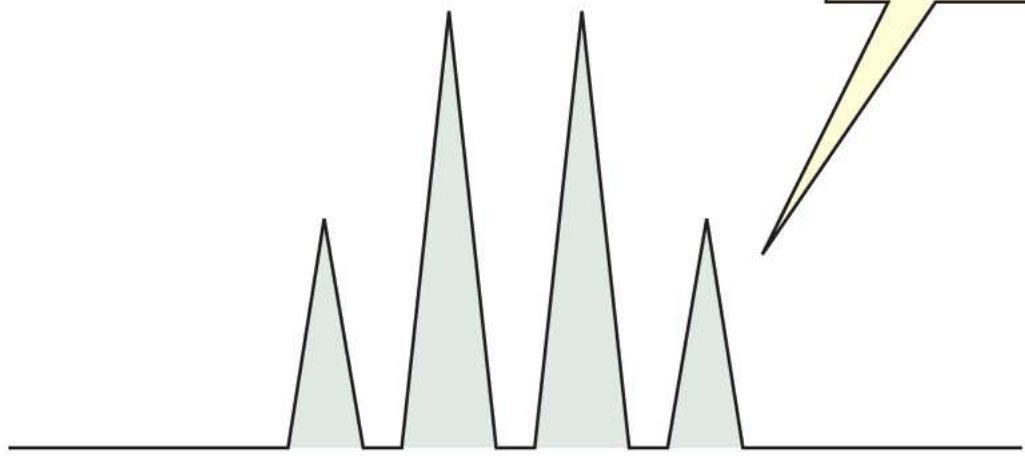




chemical shift of the methine proton if there were no protons on the adjacent carbon



signal for the methine proton is split into a quartet

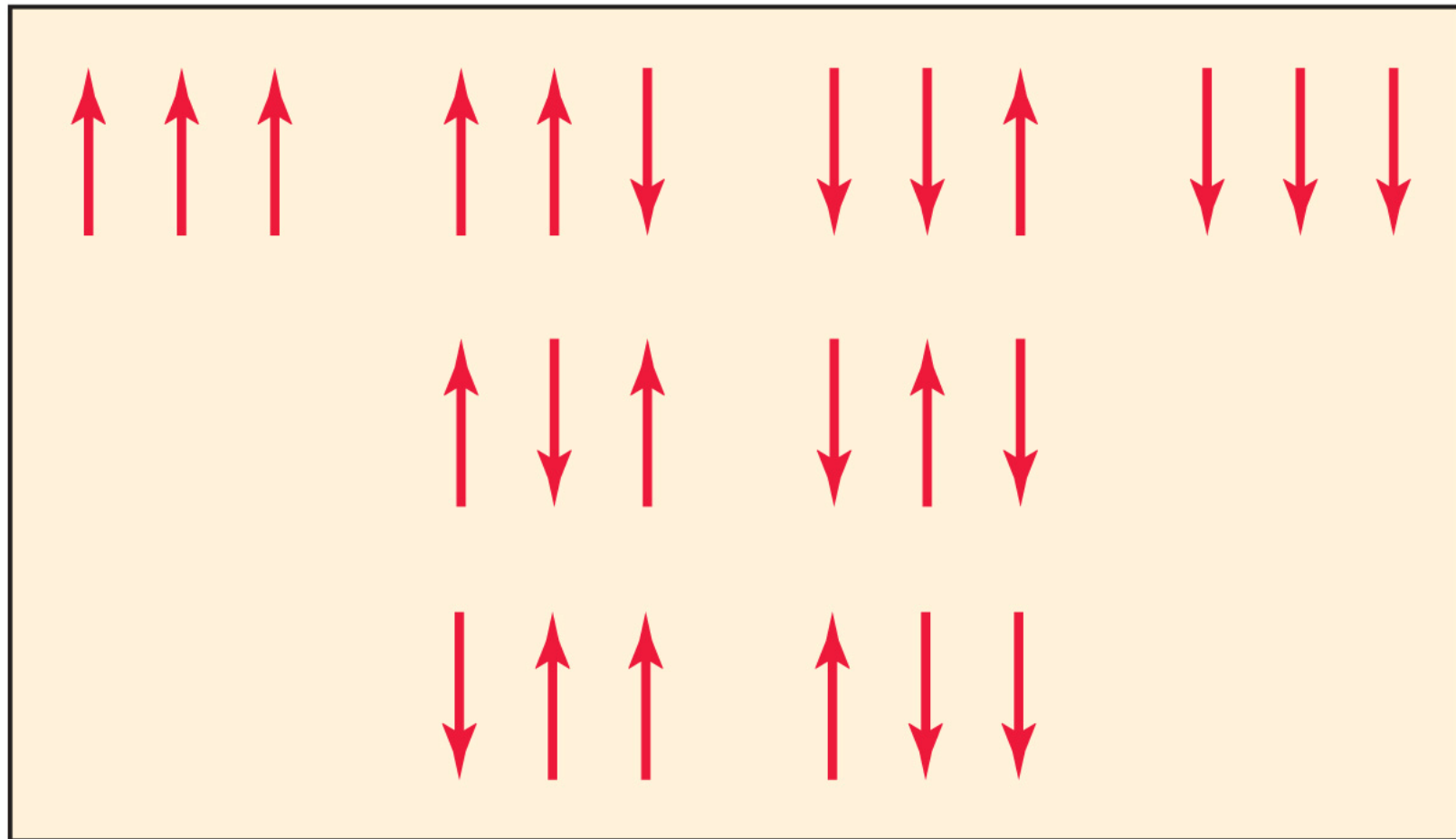


← frequency

all with



all against

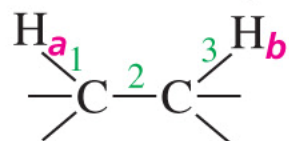


2 with
and
1 against

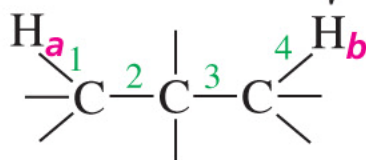


2 against
and
1 with

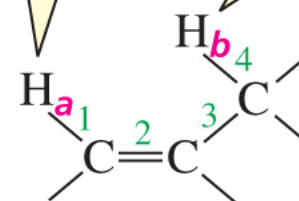
H_a and H_b split each other's signal because they are separated by three σ bonds

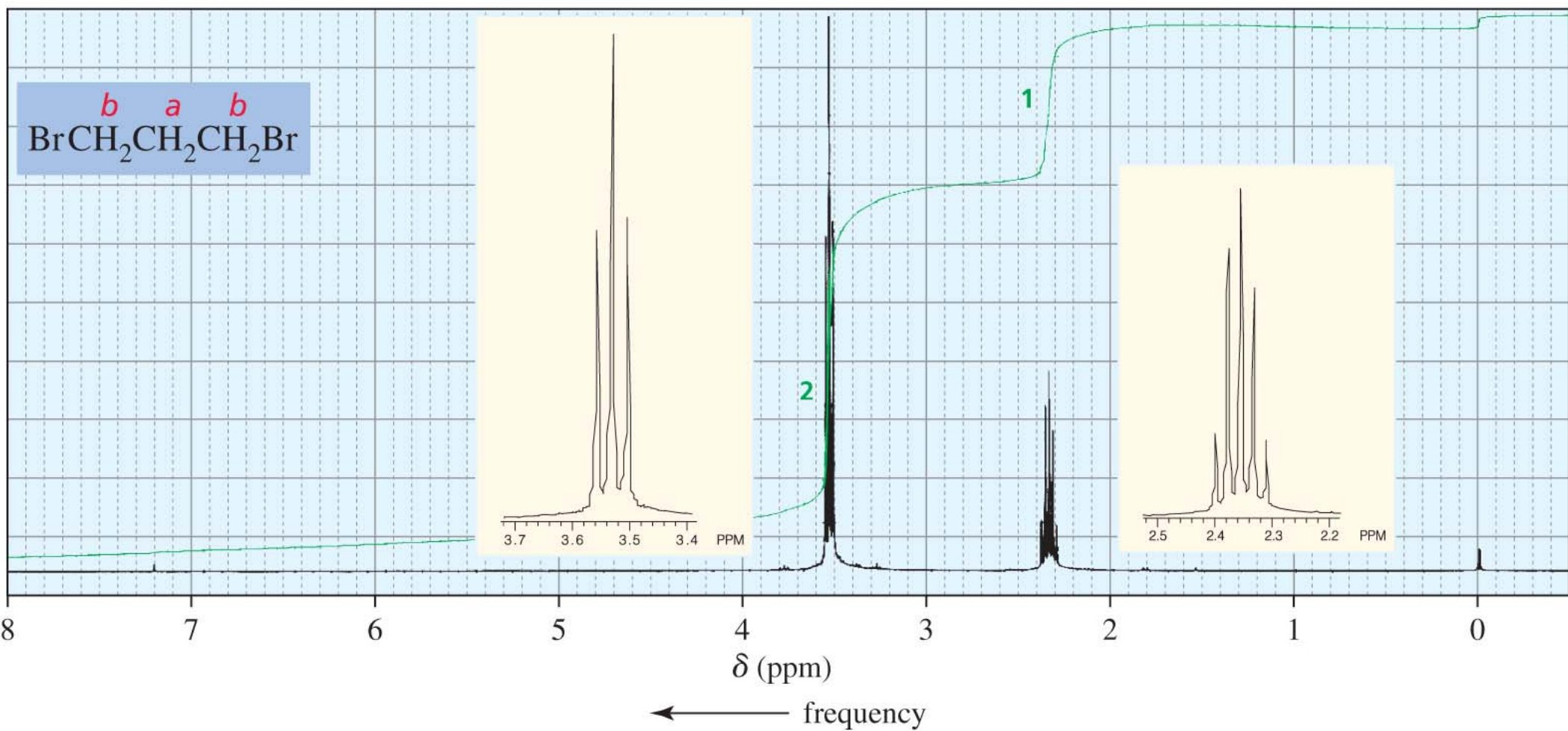


H_a and H_b do not split each other's signal because they are separated by four σ bonds

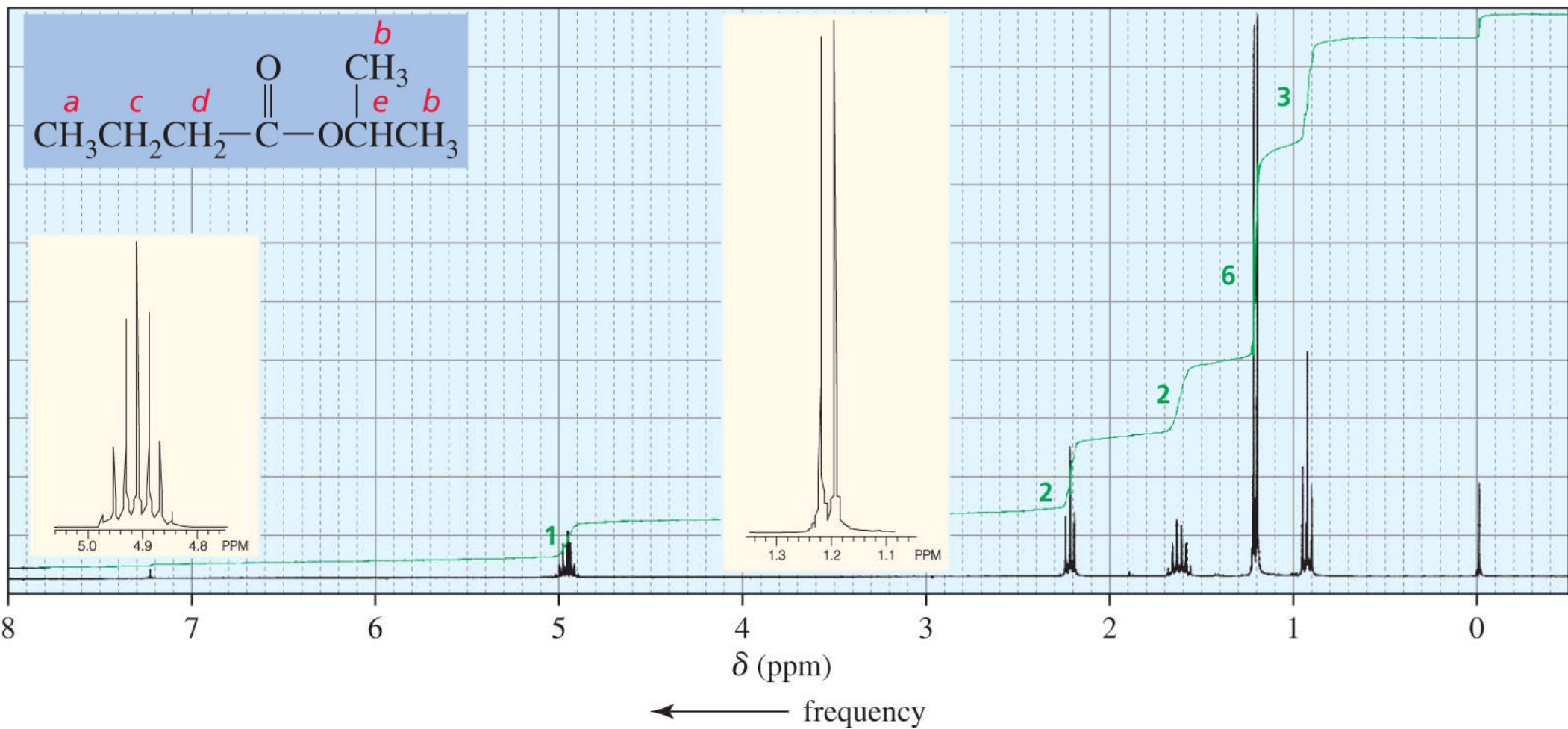


H_a and H_b may split each other's signal because they are separated by four bonds one of which is a double bond

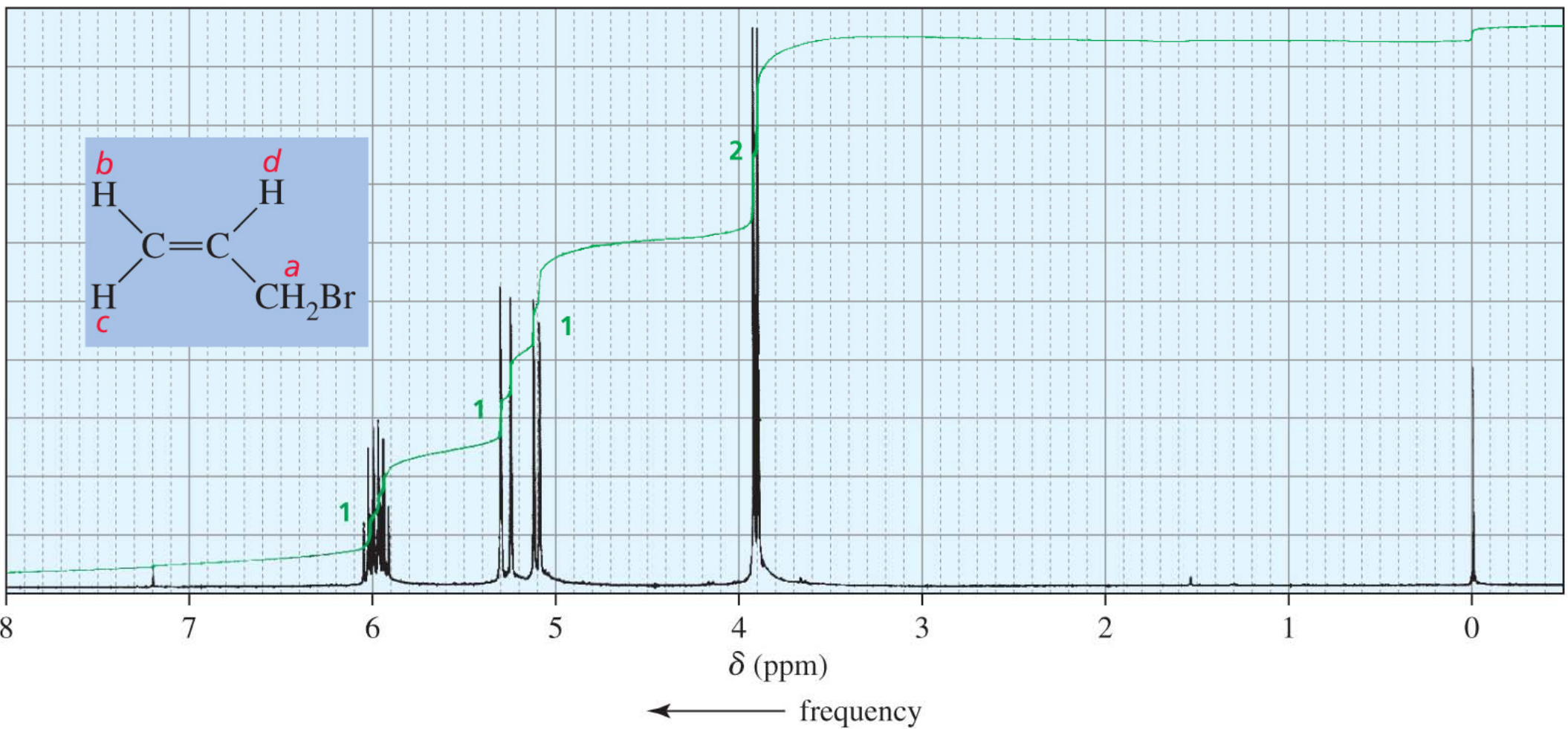




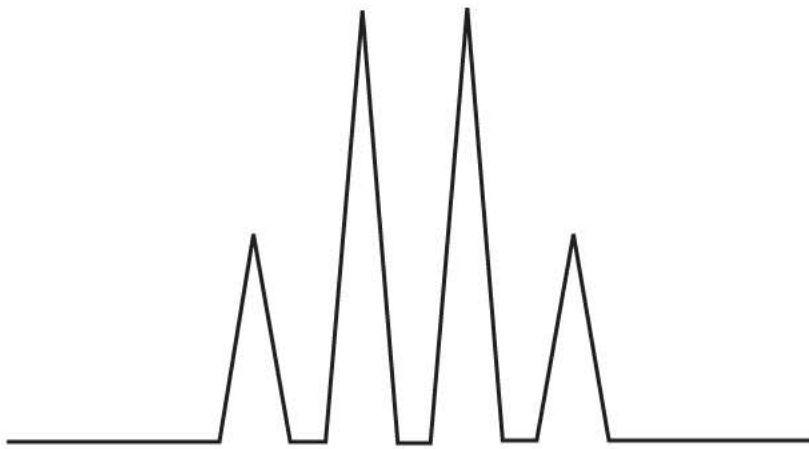
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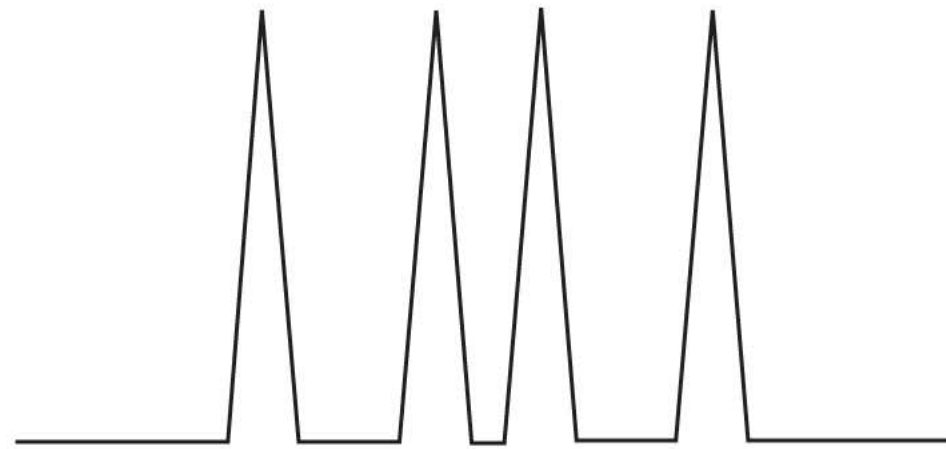


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a quartet

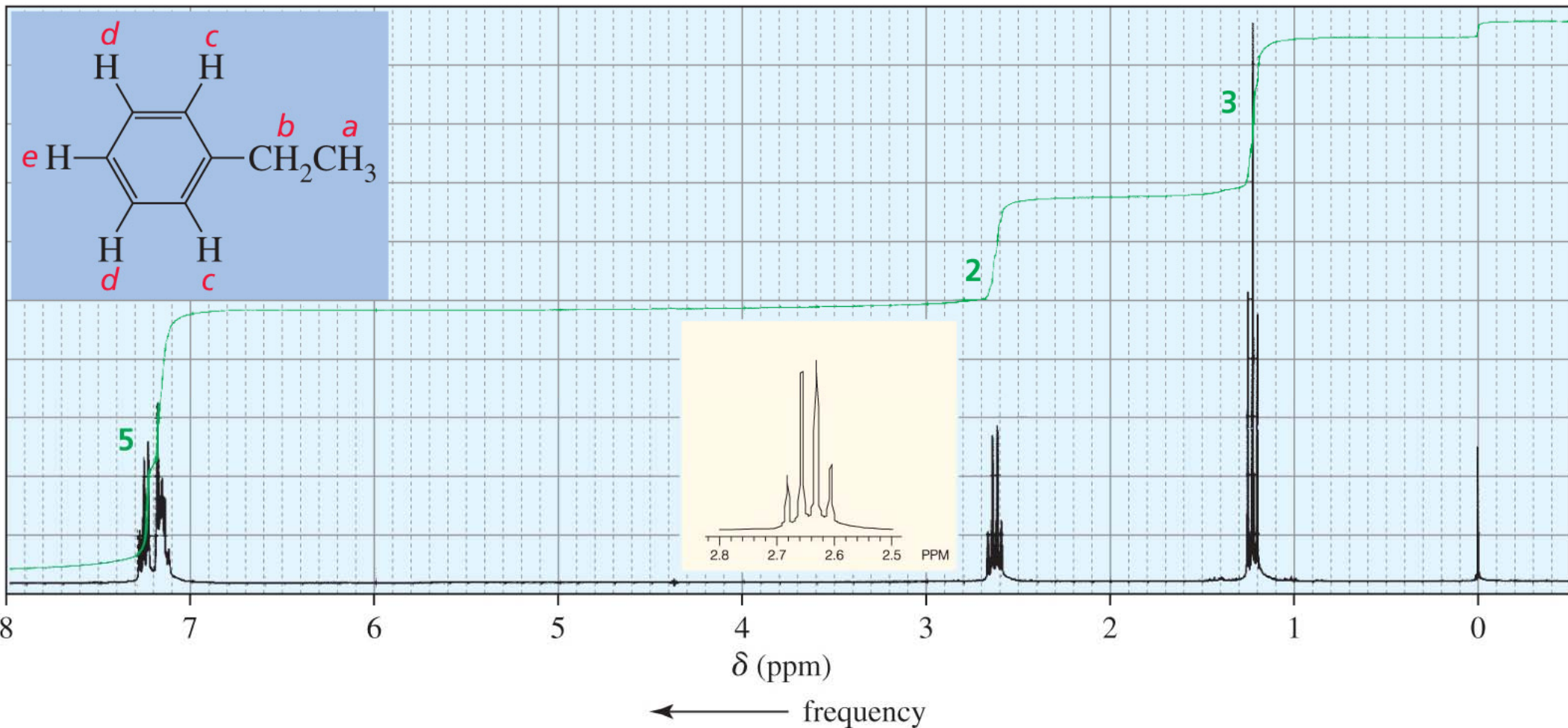
relative intensities: 1 : 3 : 3 : 1



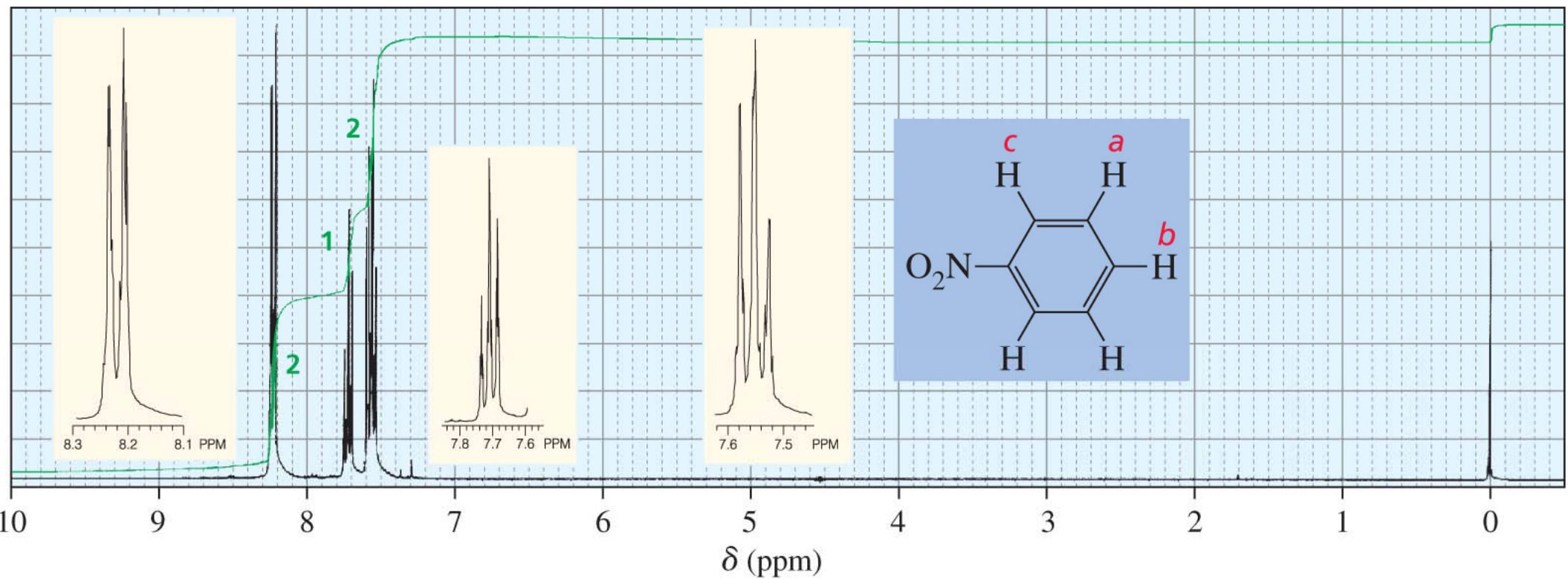
a doublet of doublets

relative intensities: 1 : 1 : 1 : 1

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← frequency

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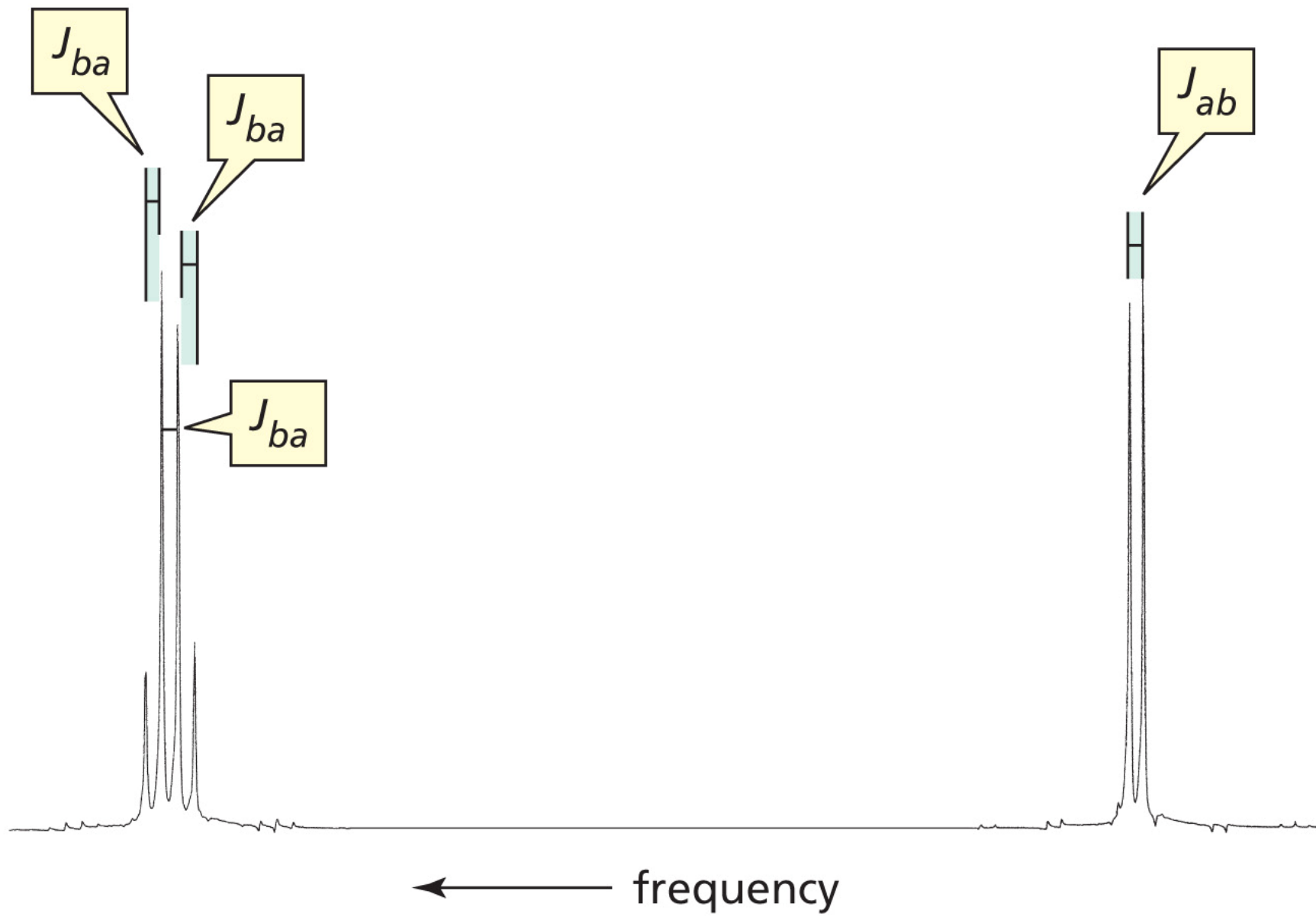
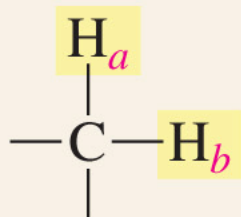


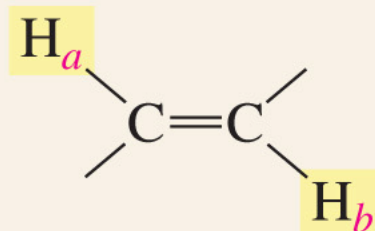
Table 13.3 Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)

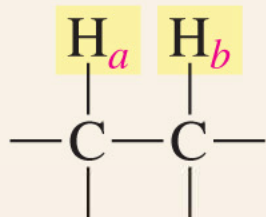
Approximate value of J_{ab} (Hz)



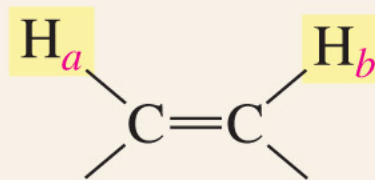
12



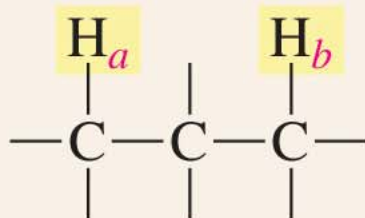
15 (trans)



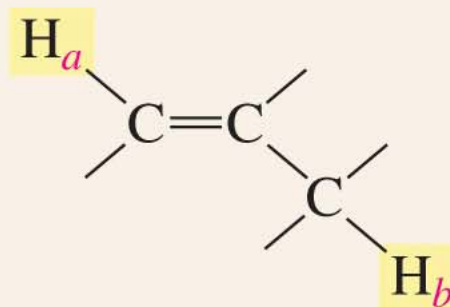
7



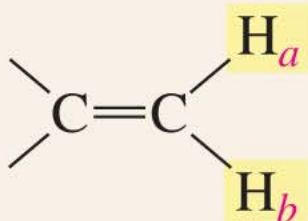
10 (cis)



0

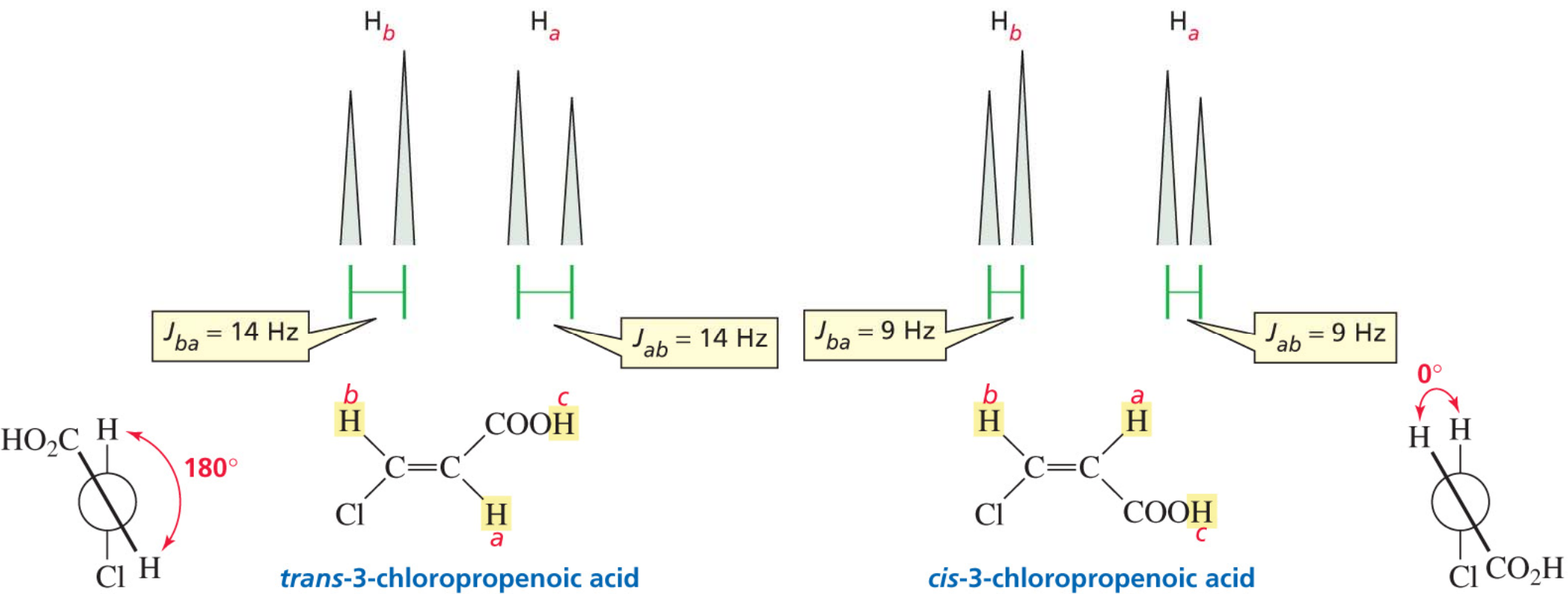


1
(long-range
coupling)

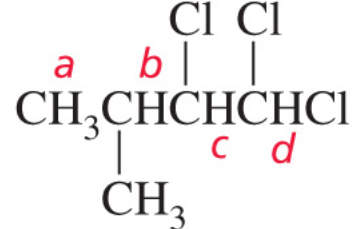


2

(geminal coupling)

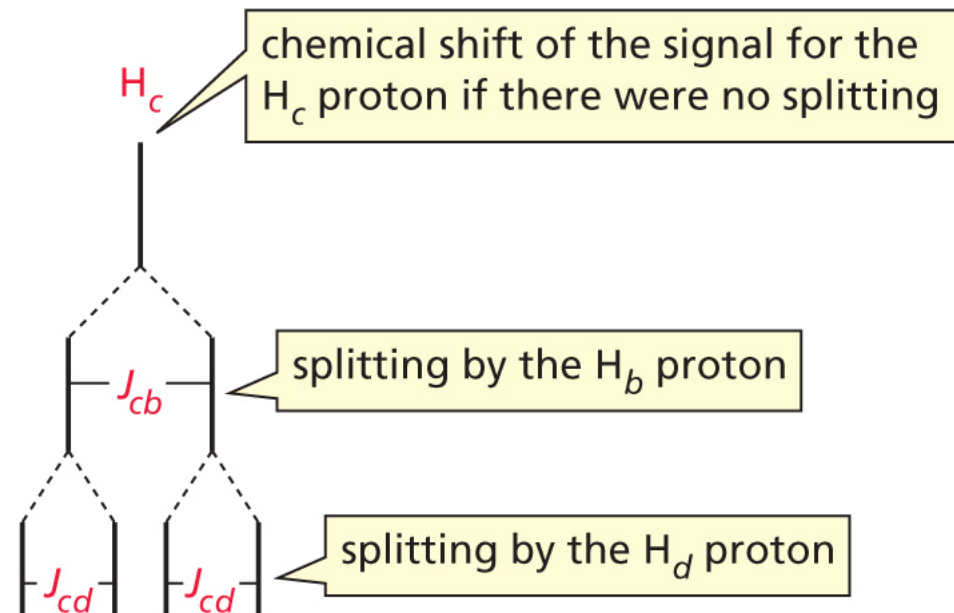


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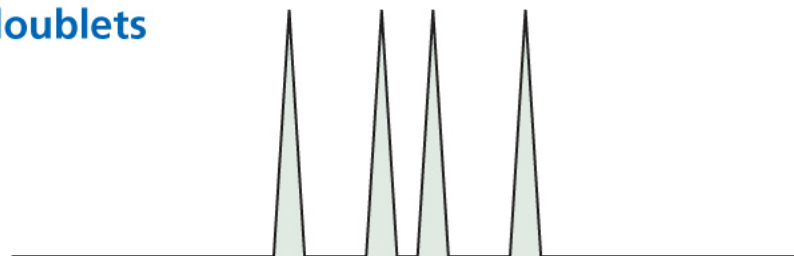


1,1,2-trichloro-3-methylbutane

a splitting diagram



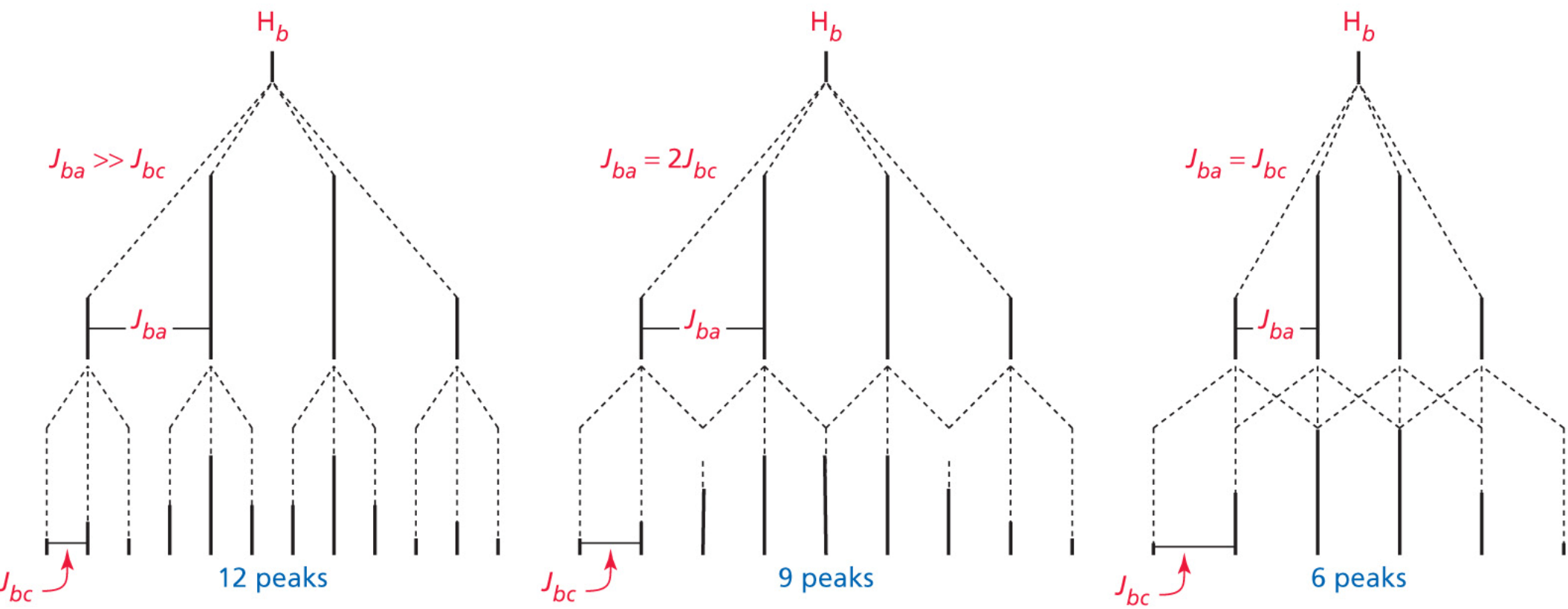
a doublet of doublets

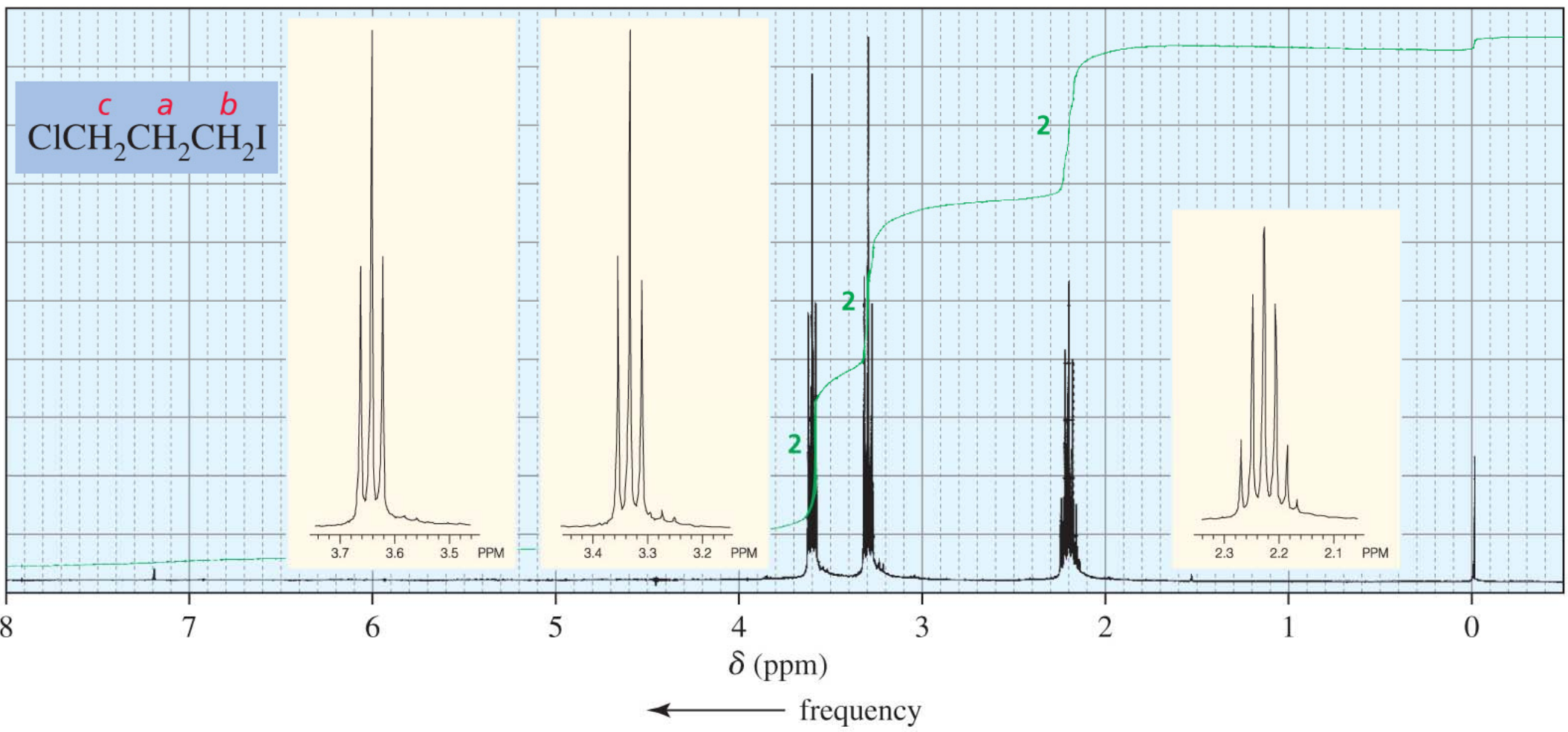
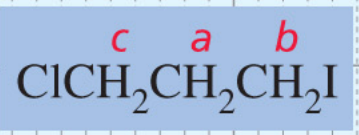


← frequency

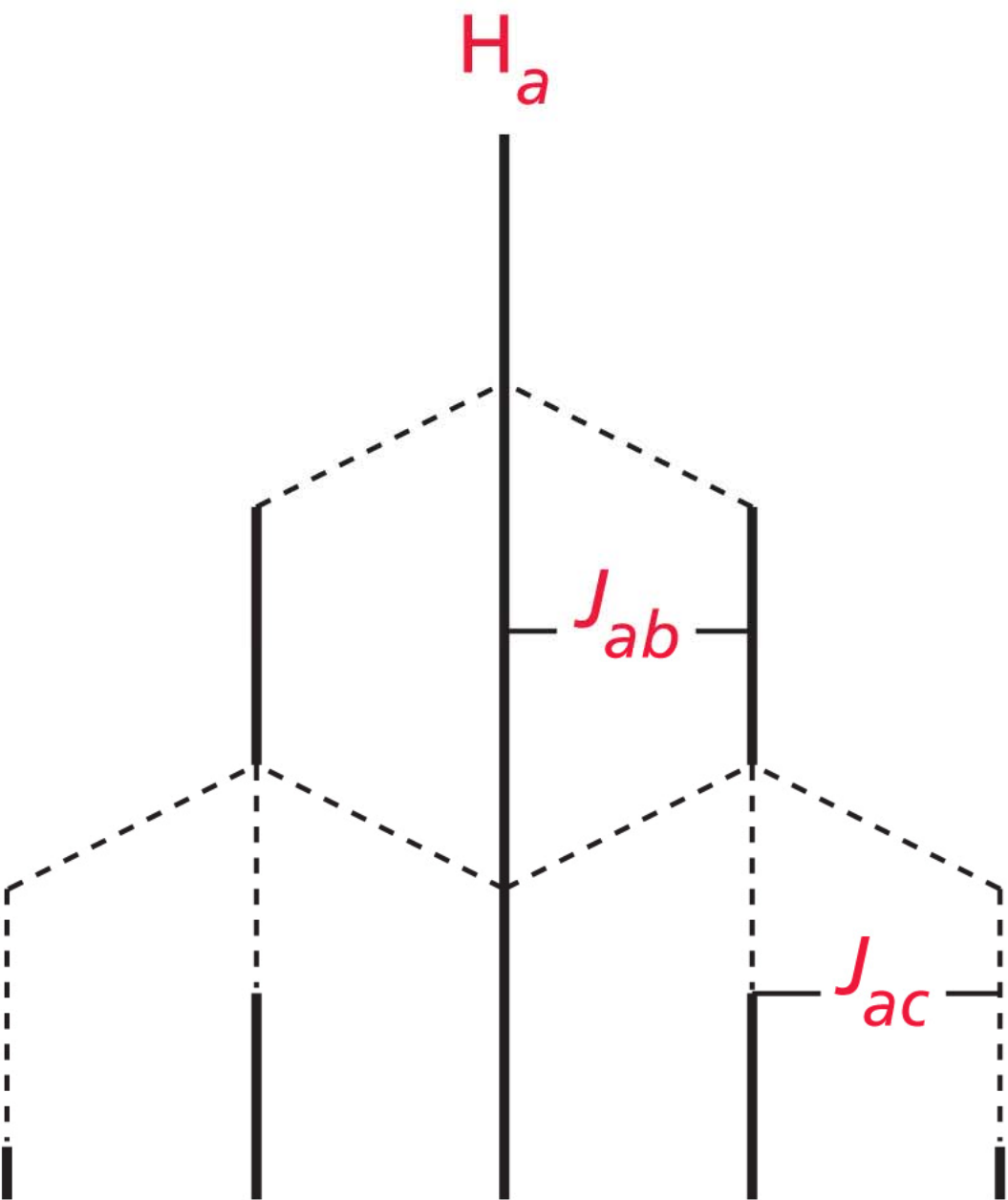


1-bromopropane

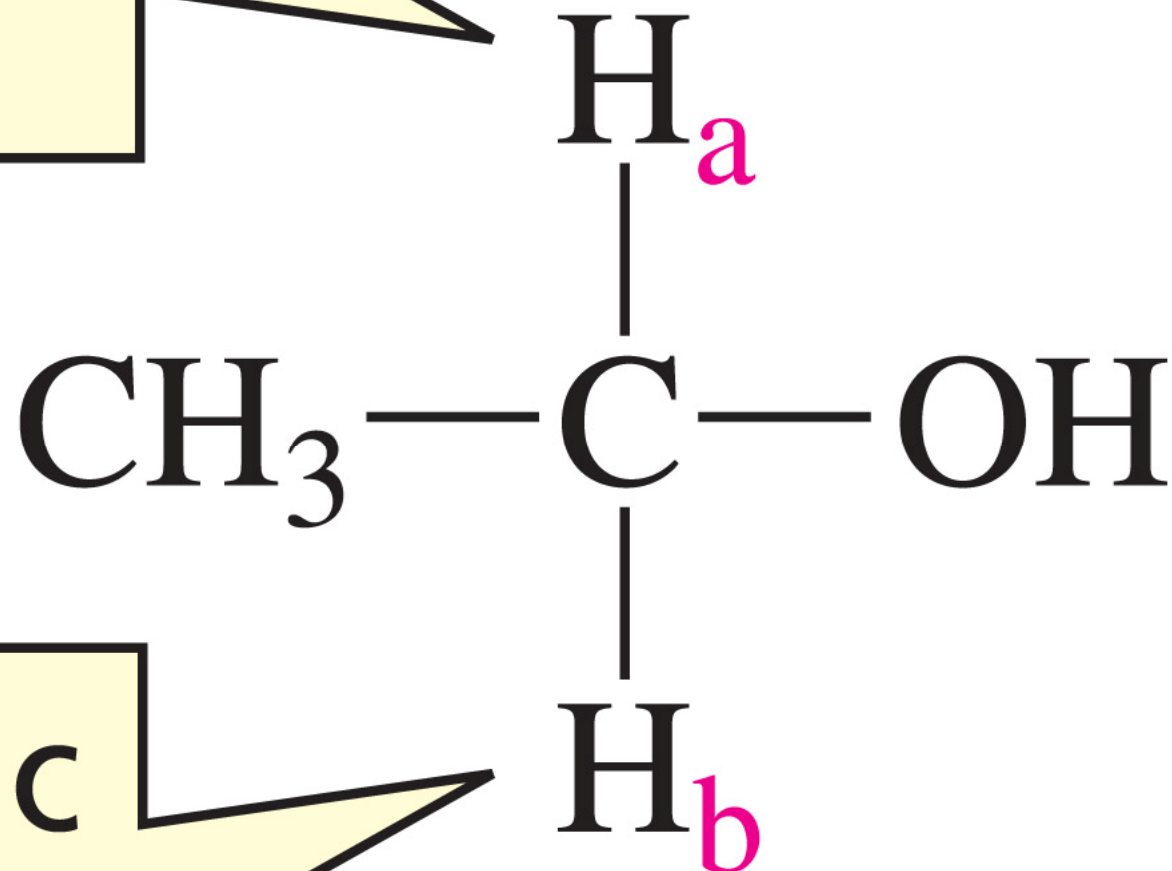




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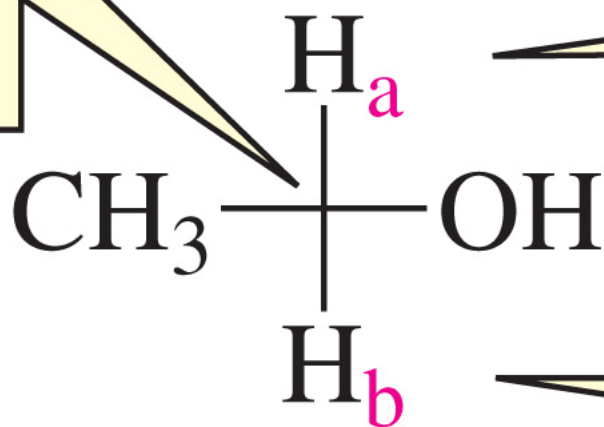


enantiotopic
hydrogen



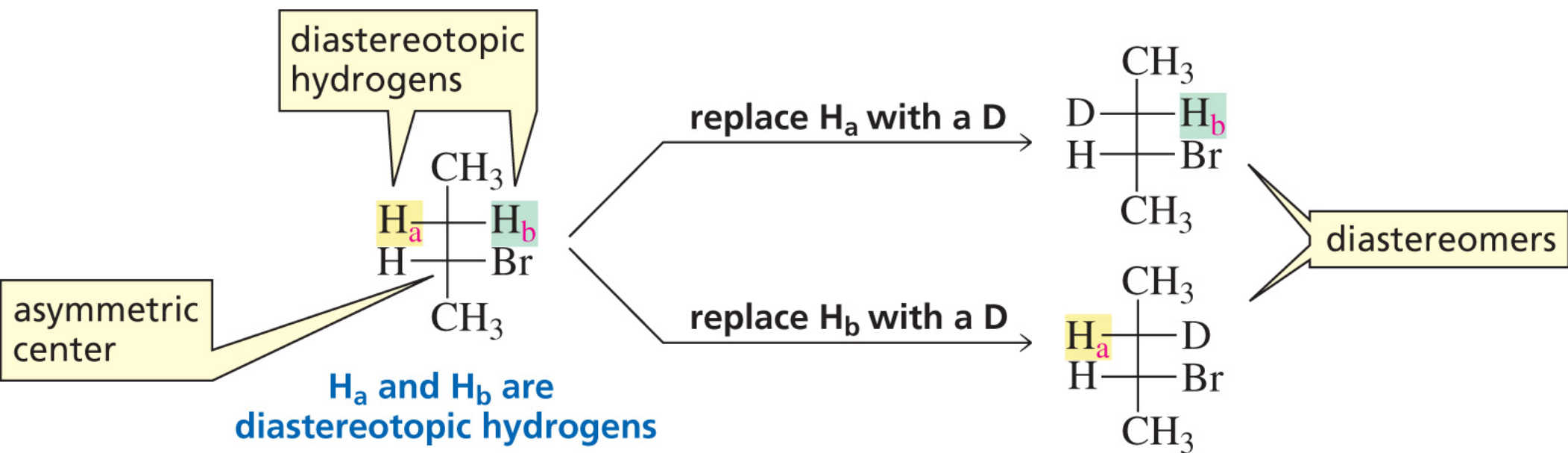
enantiotopic
hydrogen

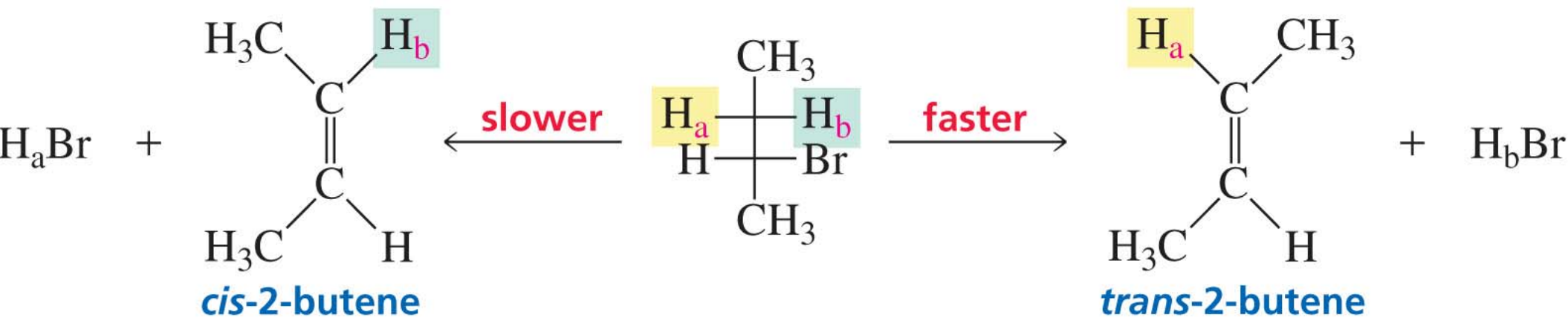
prochiral
carbon



pro-*R*-hydrogen

pro-*S*-hydrogen



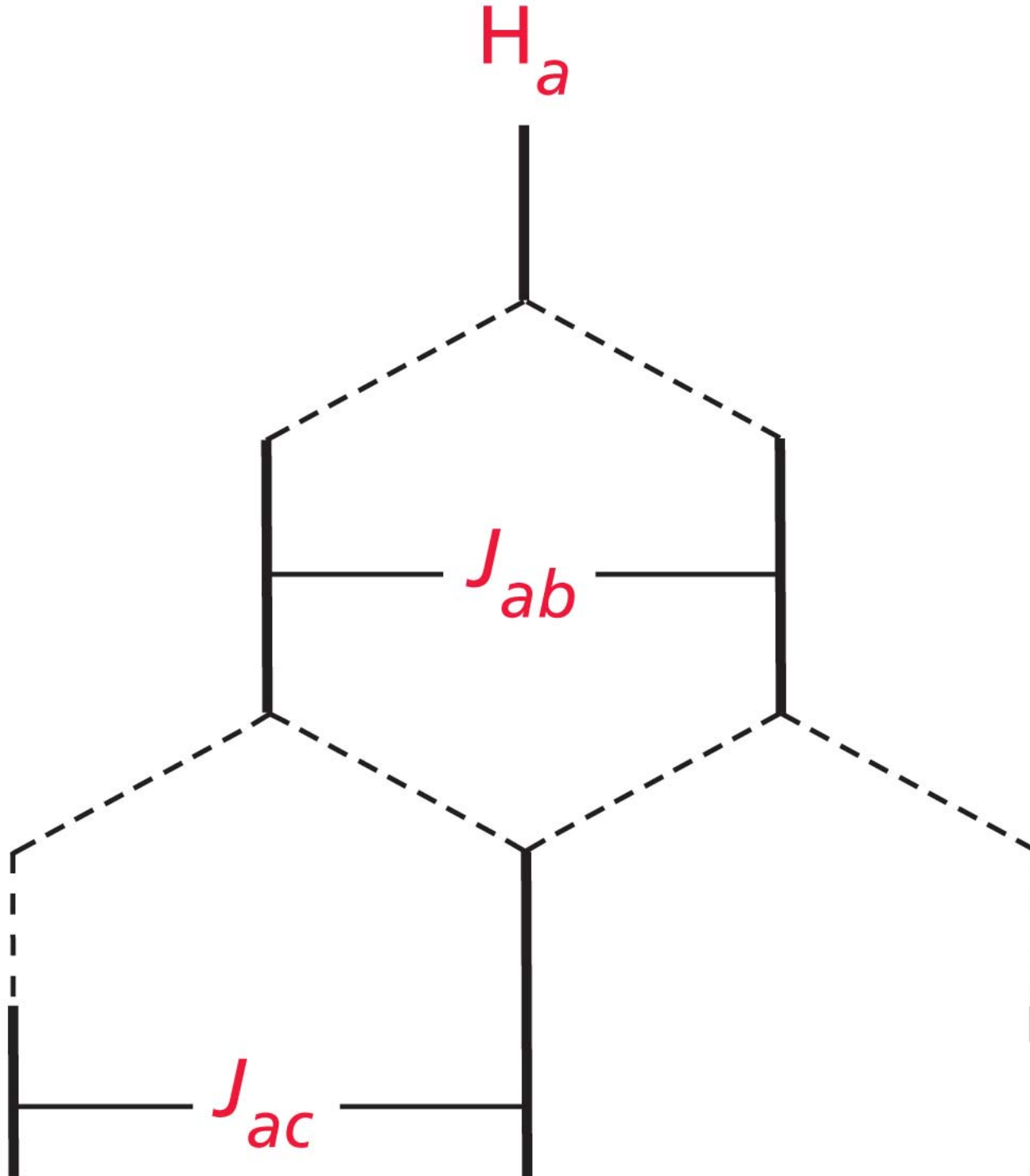


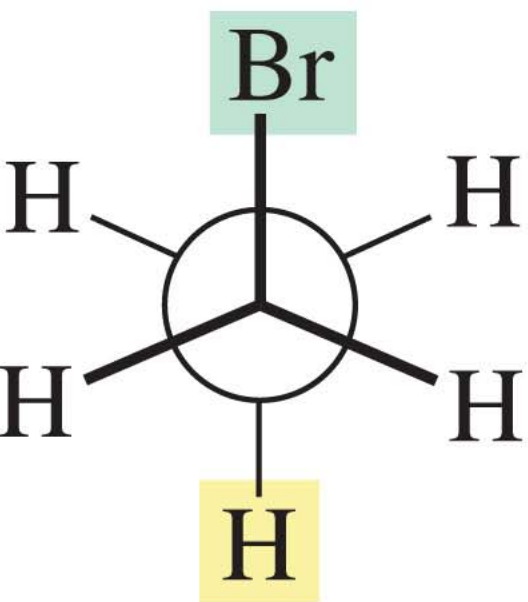
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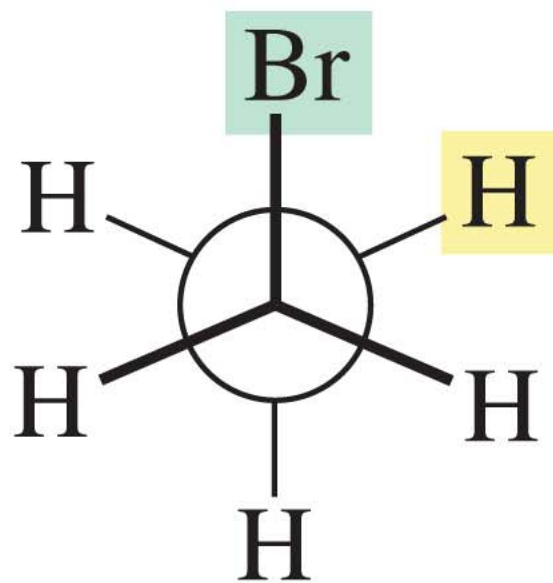
nonequivalent diastereotopic hydrogens

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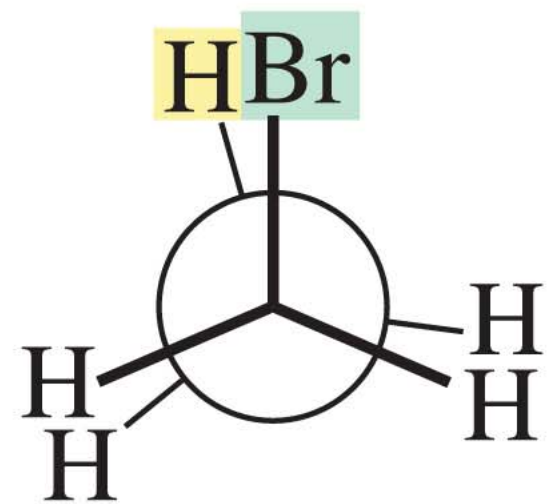




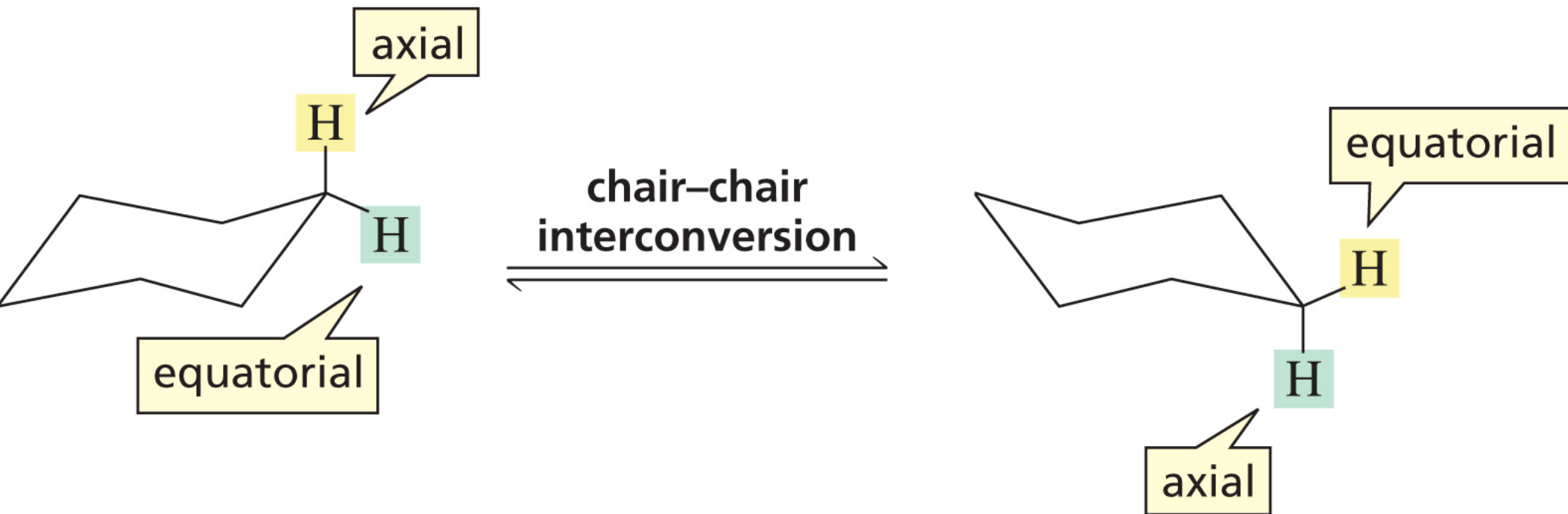
anti



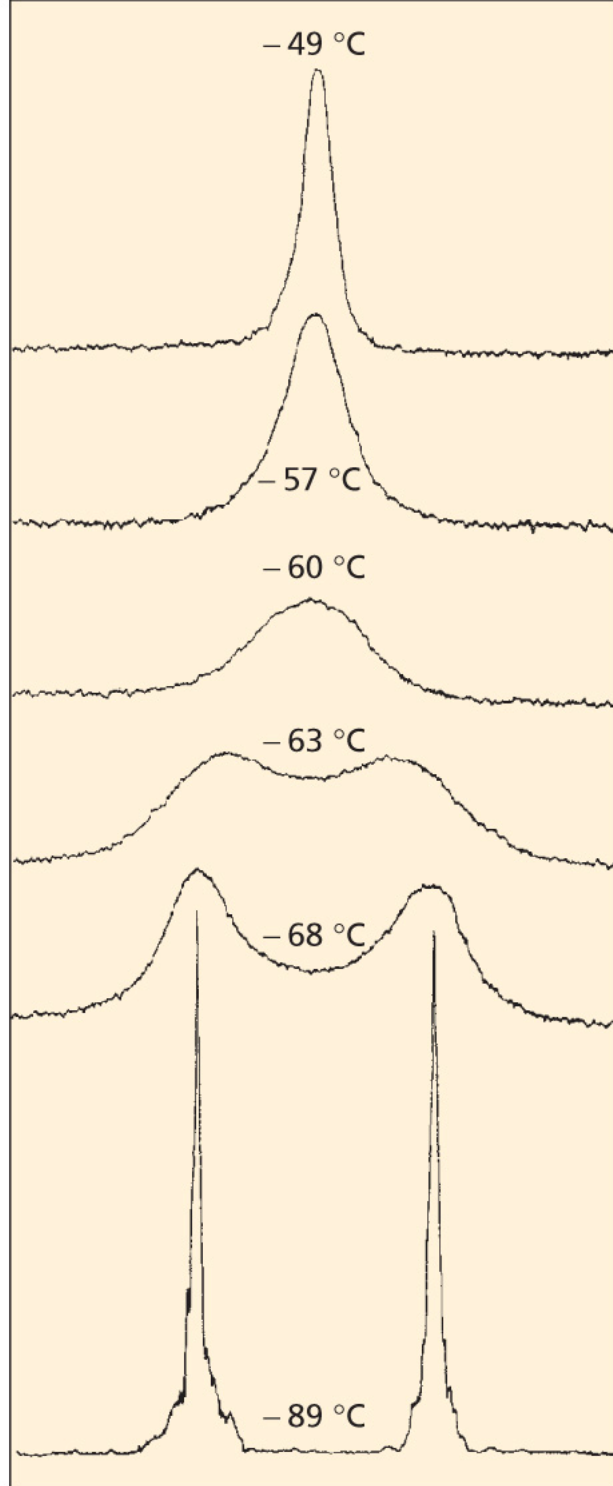
gauche



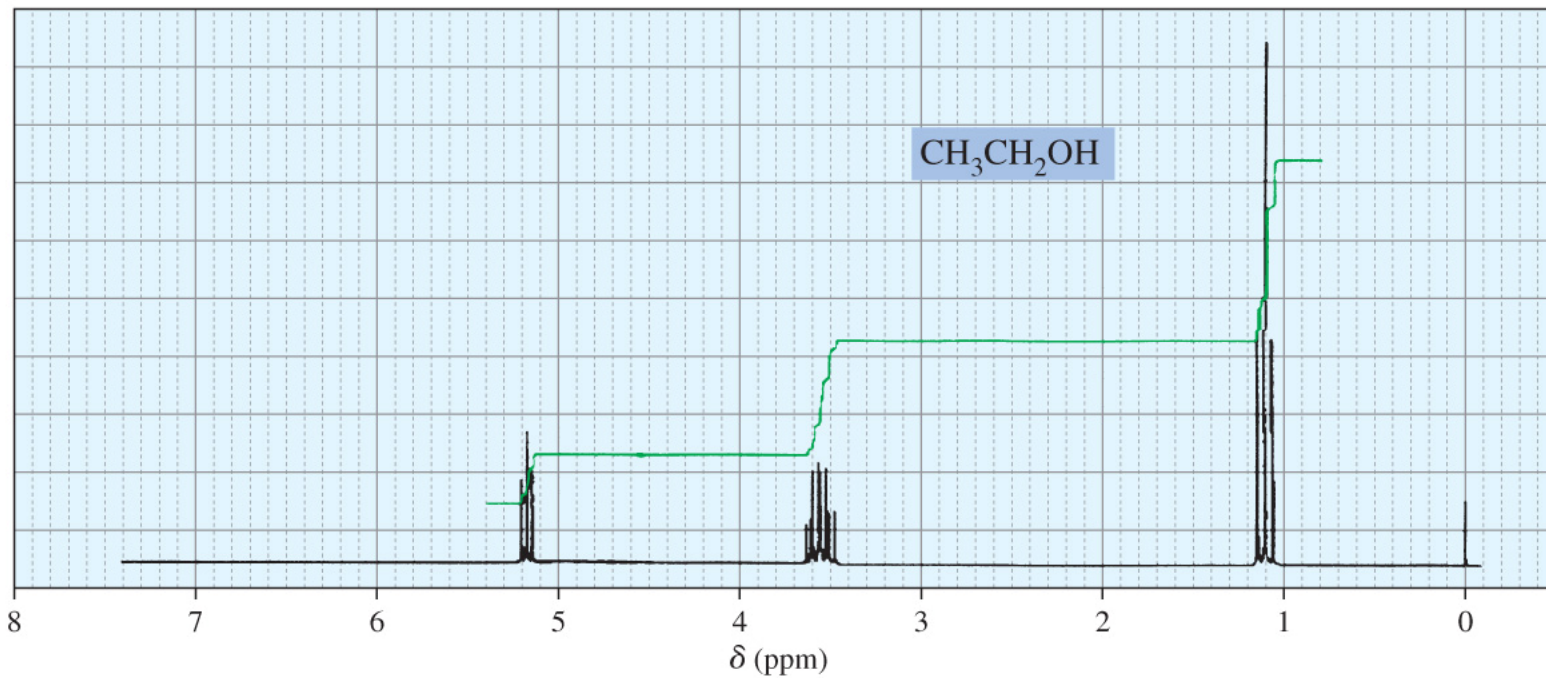
eclipsed



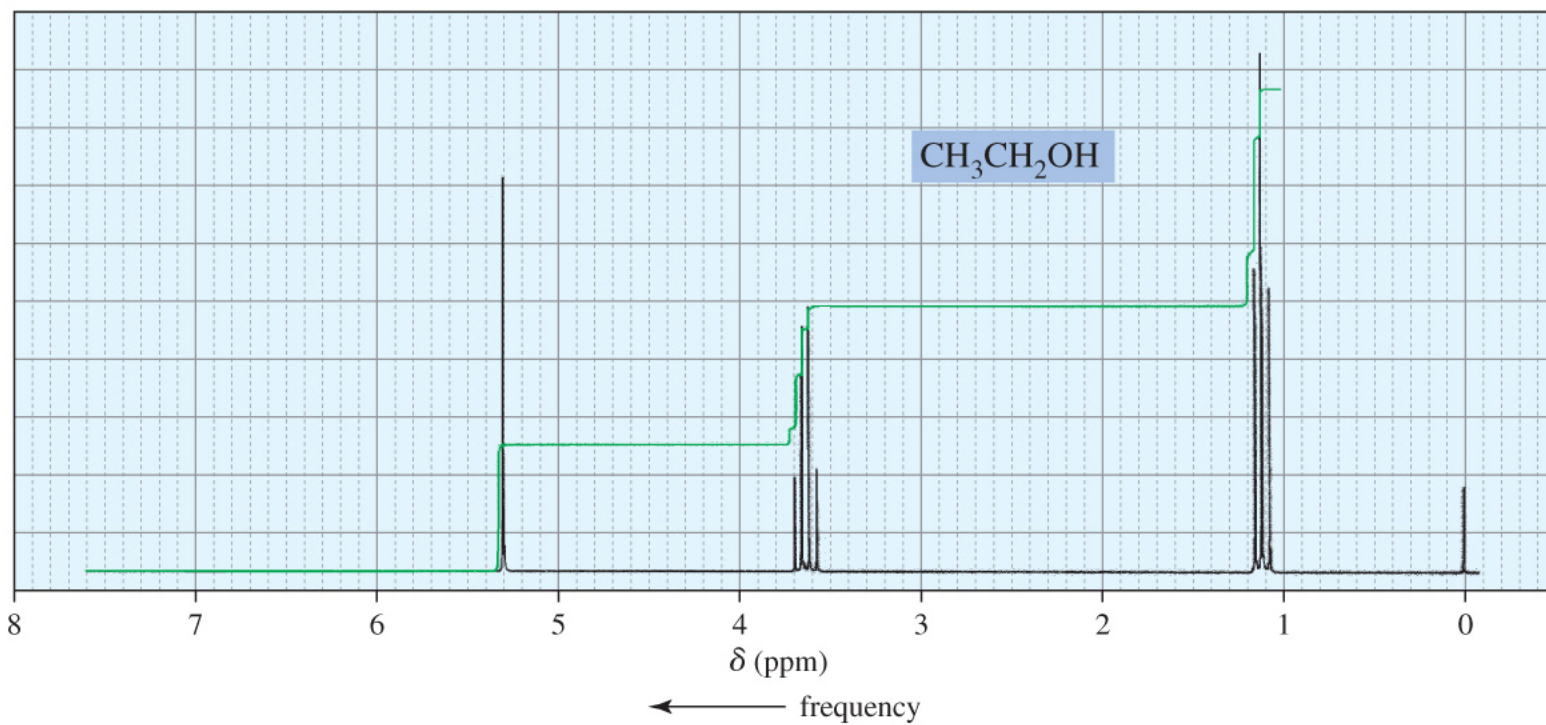
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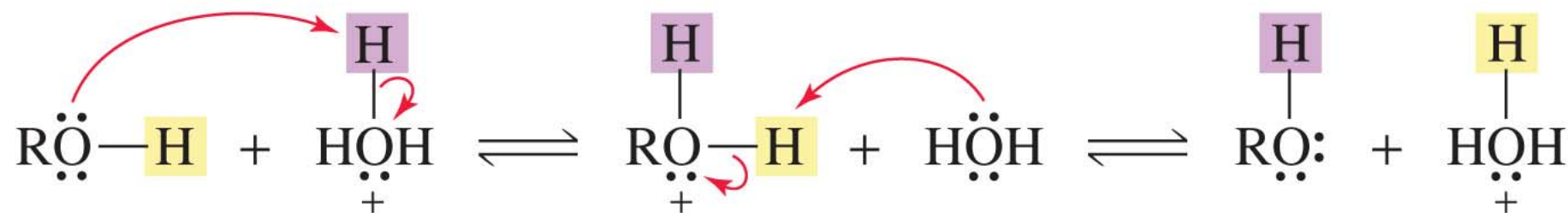
a.



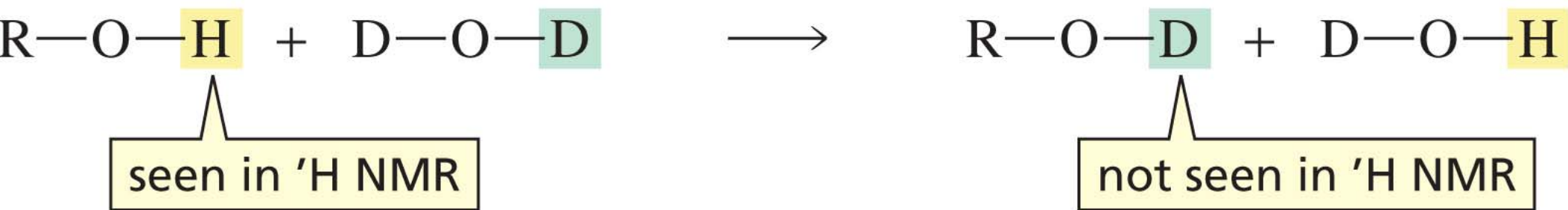
b.



Mechanism for acid-catalyzed proton exchange

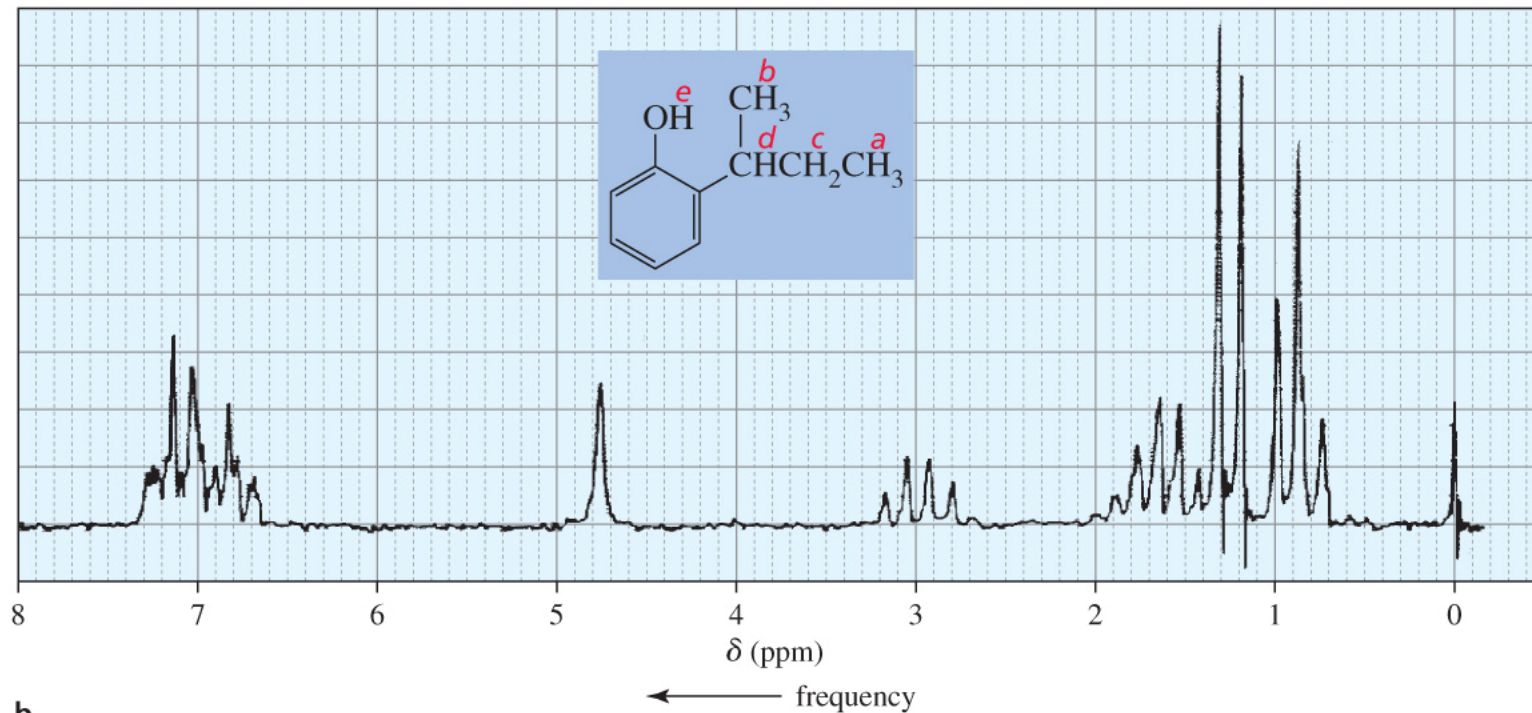


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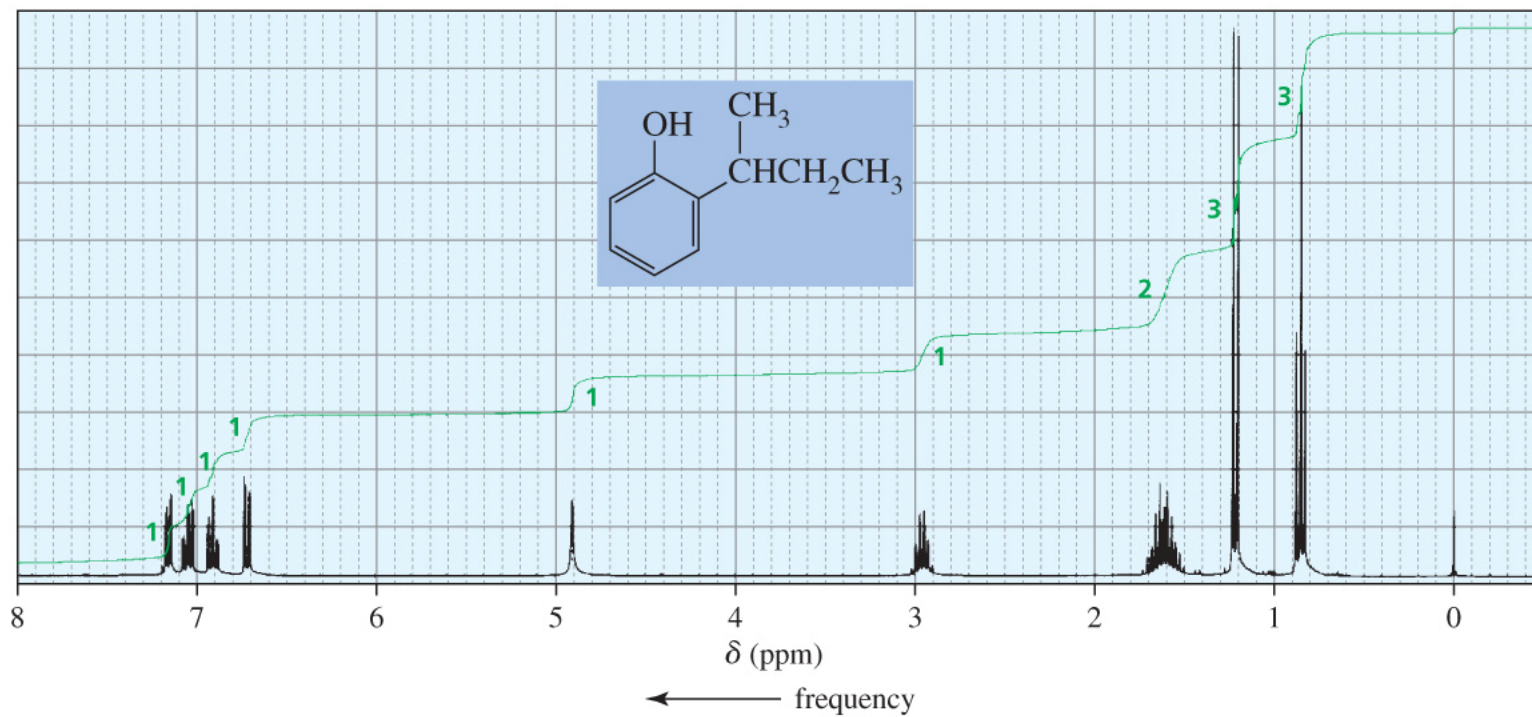


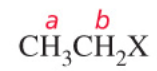
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a.

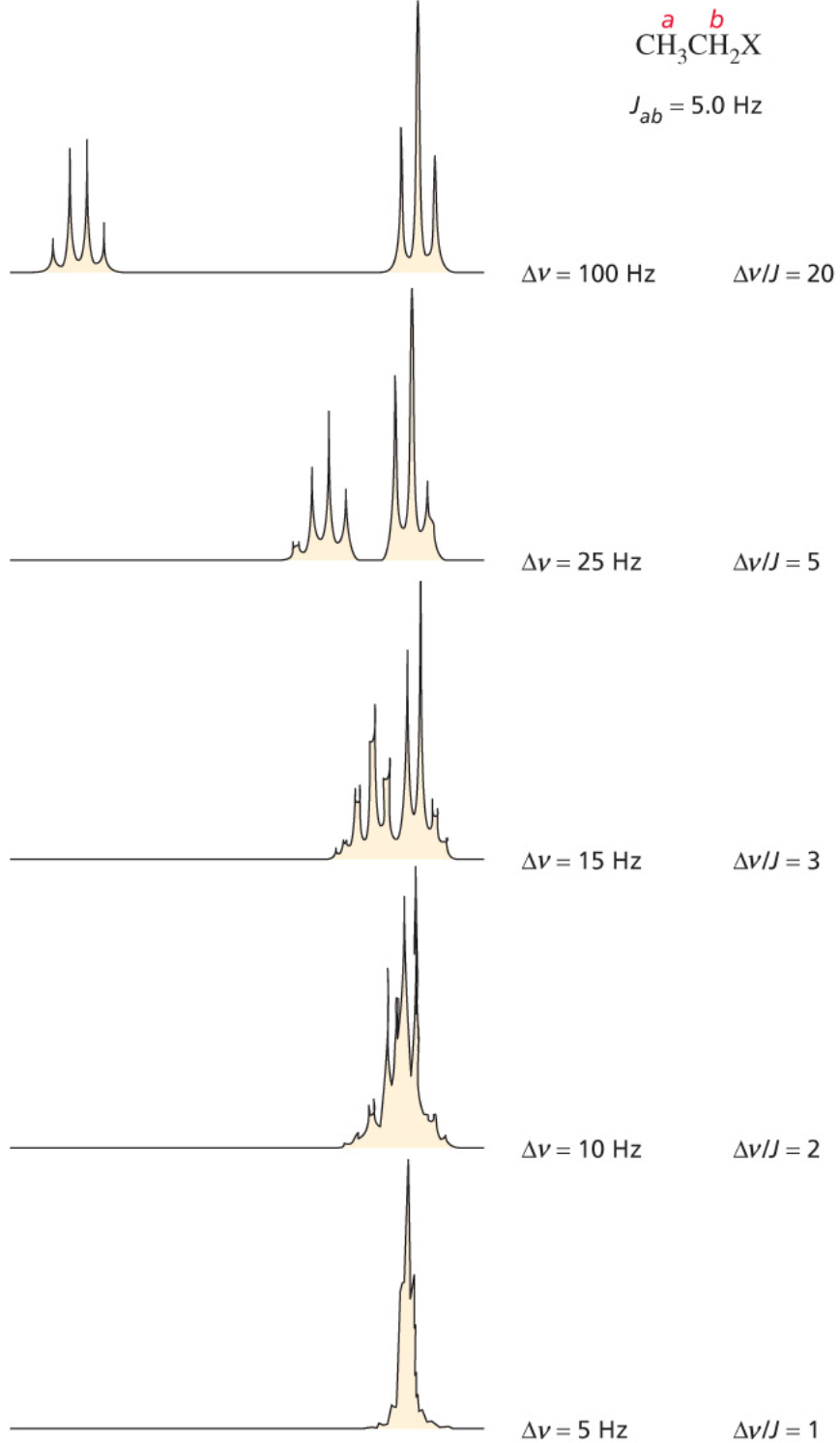


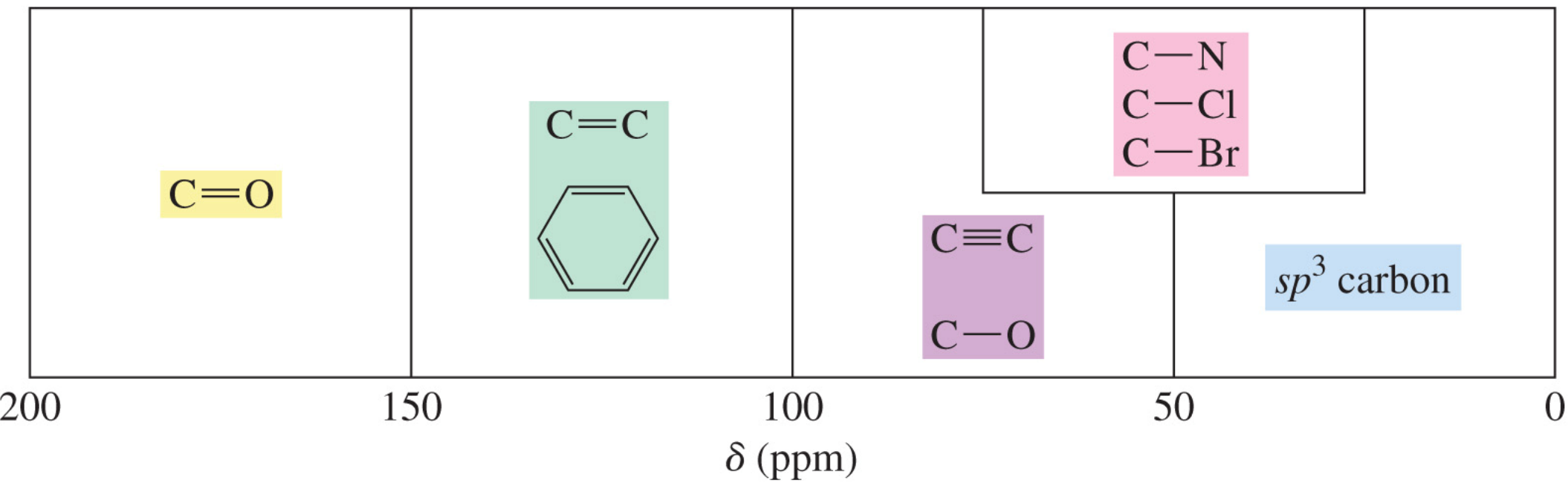
b.





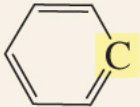
$J_{ab} = 5.0 \text{ Hz}$

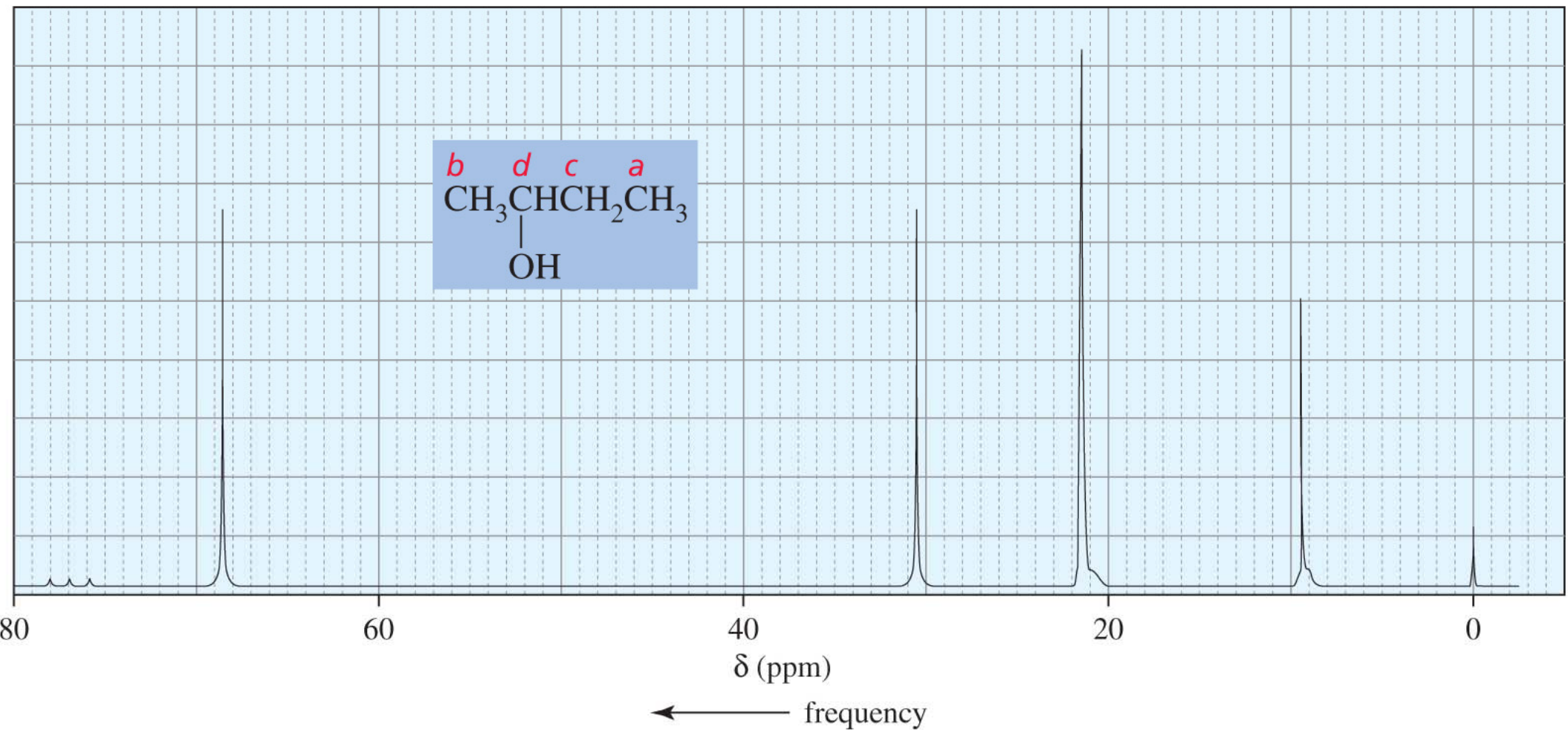




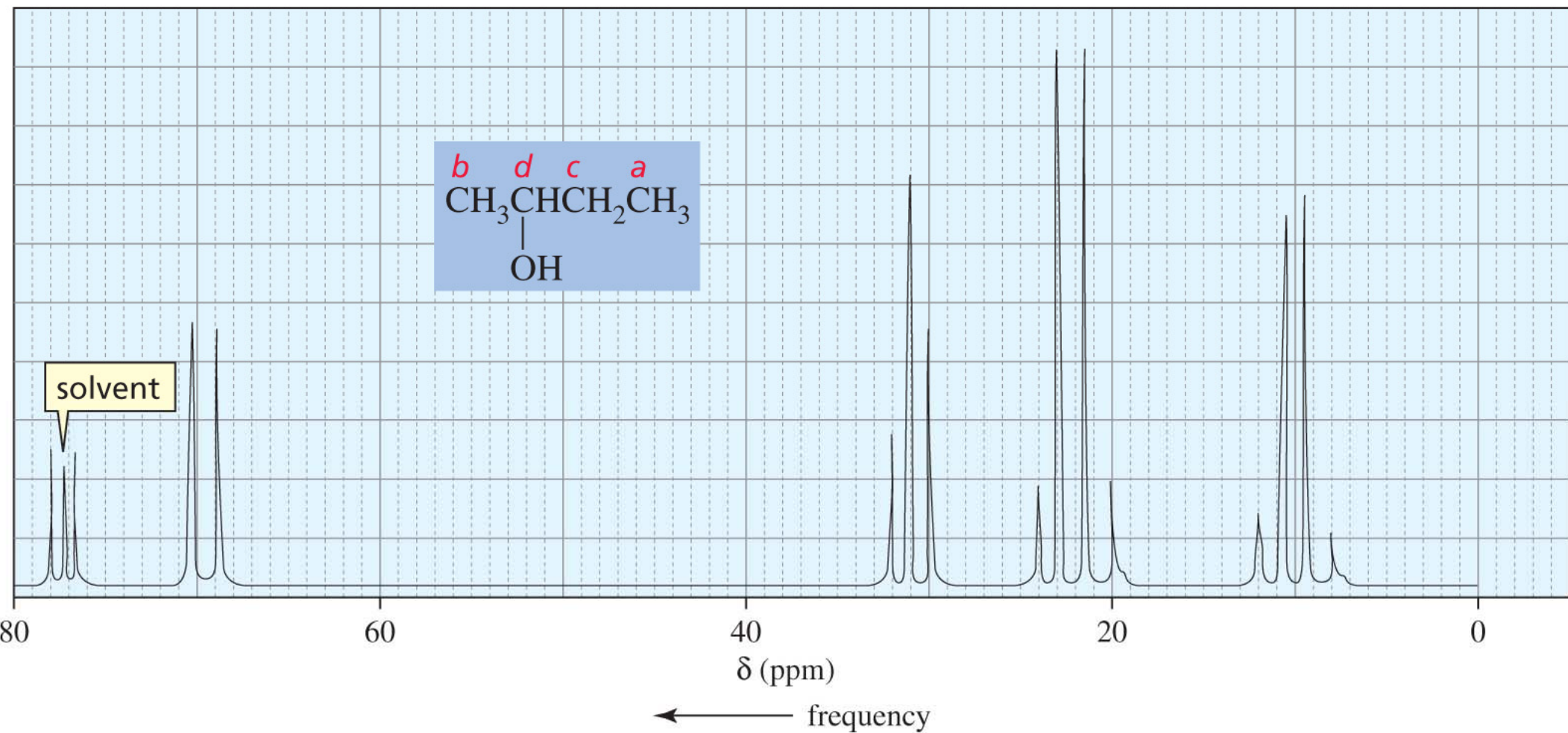
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Table 13.4 Approximate Values of Chemical Shifts for ^{13}C NMR

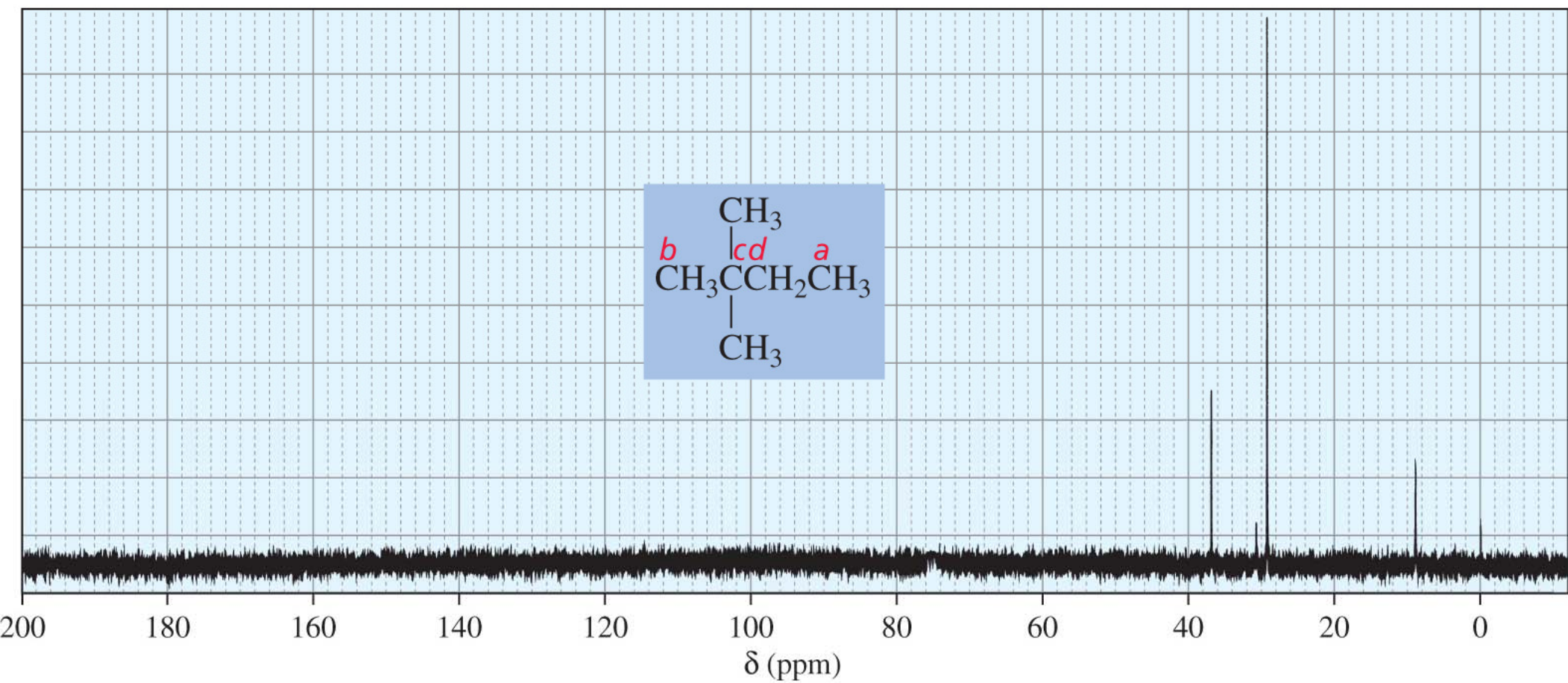
Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}-\text{I}$	0–40
$\text{R}-\text{CH}_3$	8–35	$\text{C}-\text{Br}$	25–65
$\text{R}-\text{CH}_2-\text{R}$	15–50	$\text{C}-\text{Cl}$	35–80
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{R} \end{array}$	20–60	$\text{C}-\text{N}$	40–60
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30–40	$\text{C}-\text{O}$	50–80
$\equiv\text{C}$	65–85	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{N} \\ \end{array}$	165–175
$=\text{C}$	100–150	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{RO} \end{array}$	165–175
	110–170	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$	175–185
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$	190–200
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$	205–220



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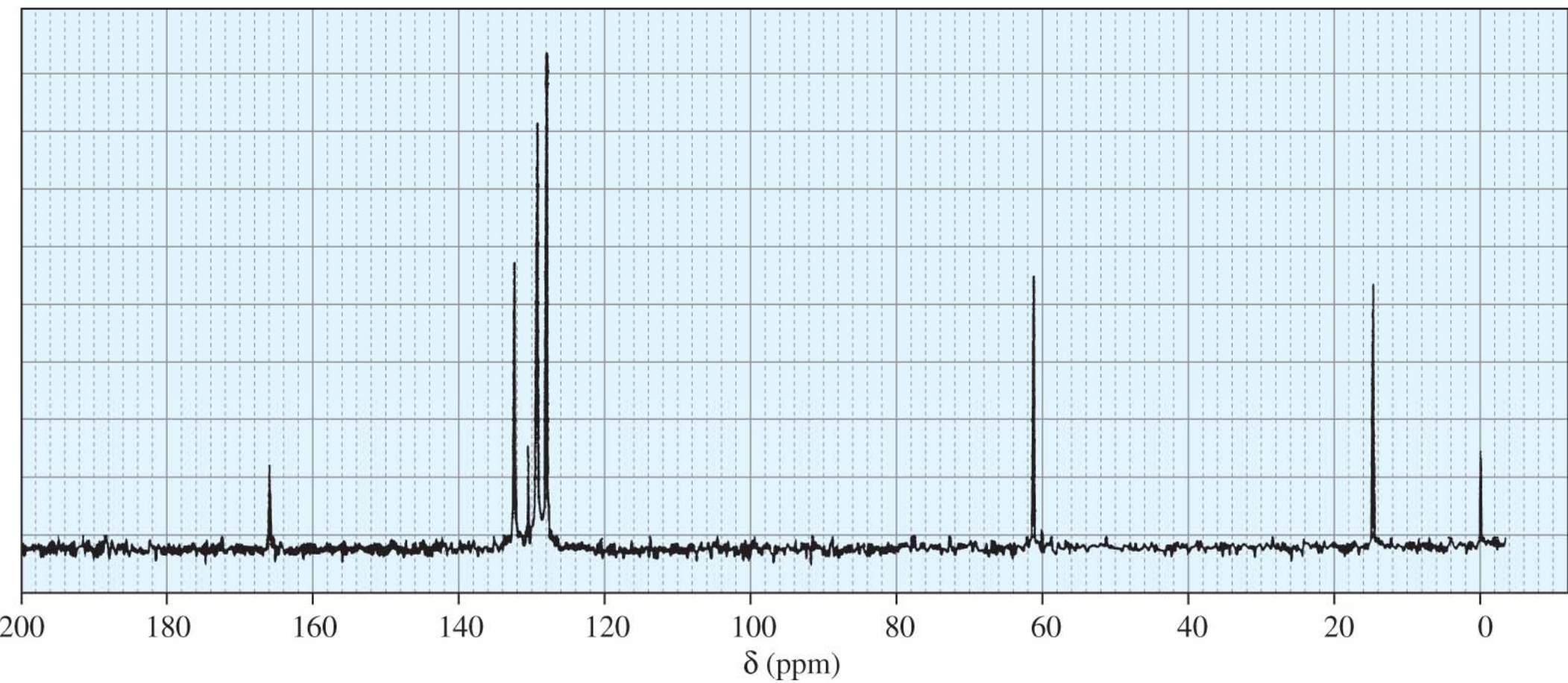


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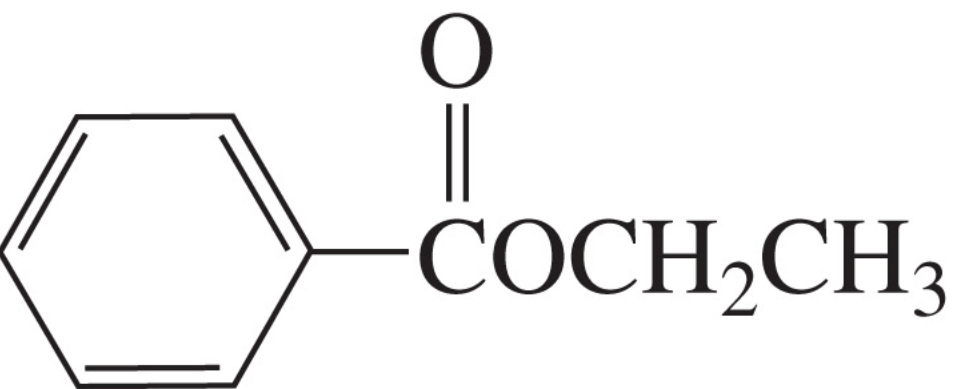
← frequency

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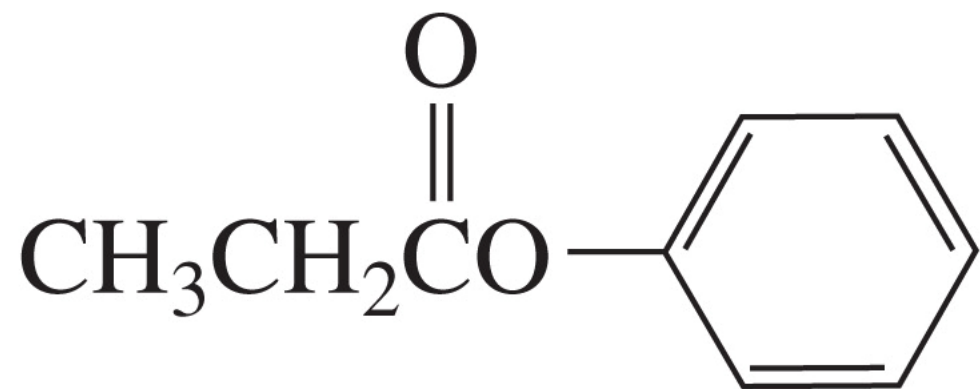


← frequency

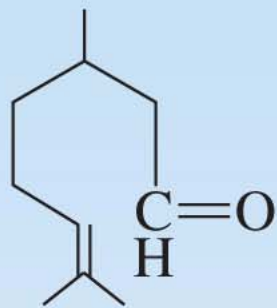
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ethyl benzoate



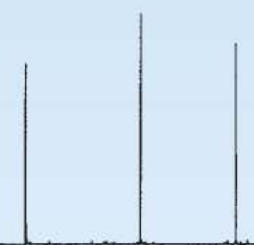
phenyl propanoate



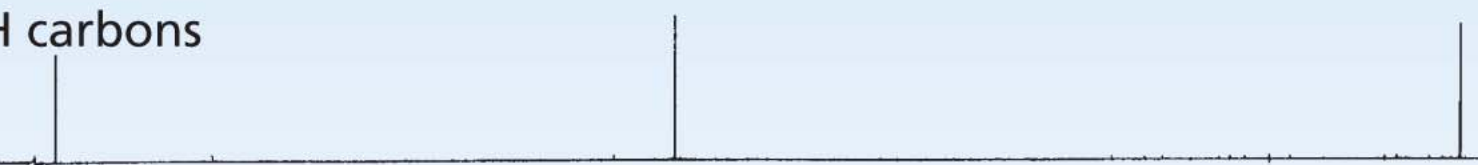
CH₃ carbons



CH₂ carbons



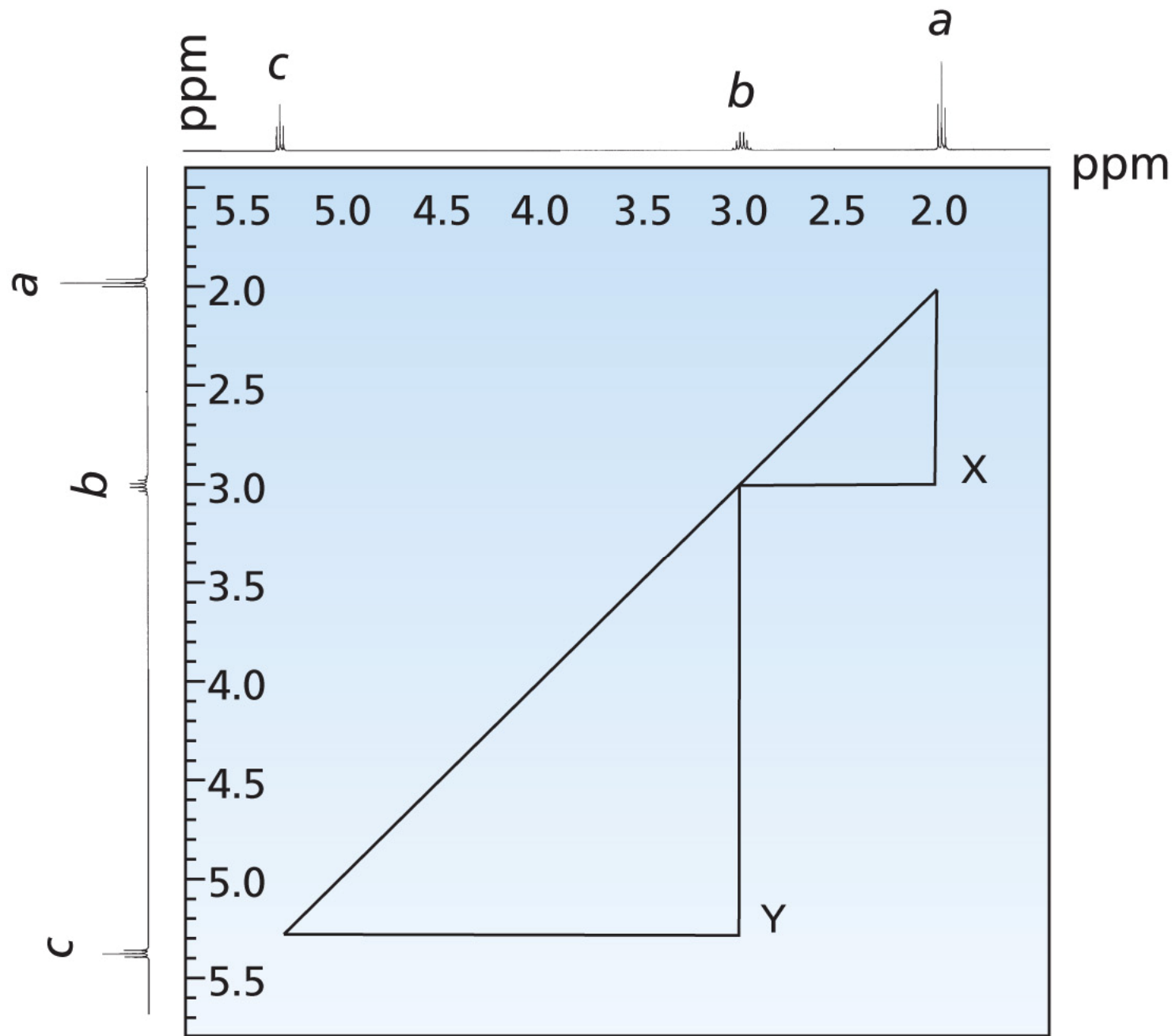
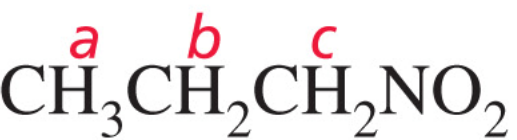
CH carbons



all carbons



200 180 160 140 120 100 80 60 40 20 0 ppm



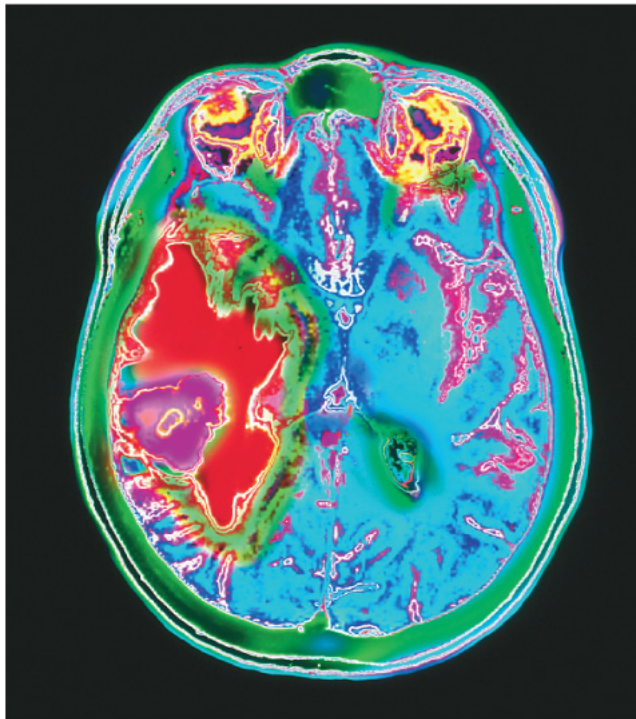
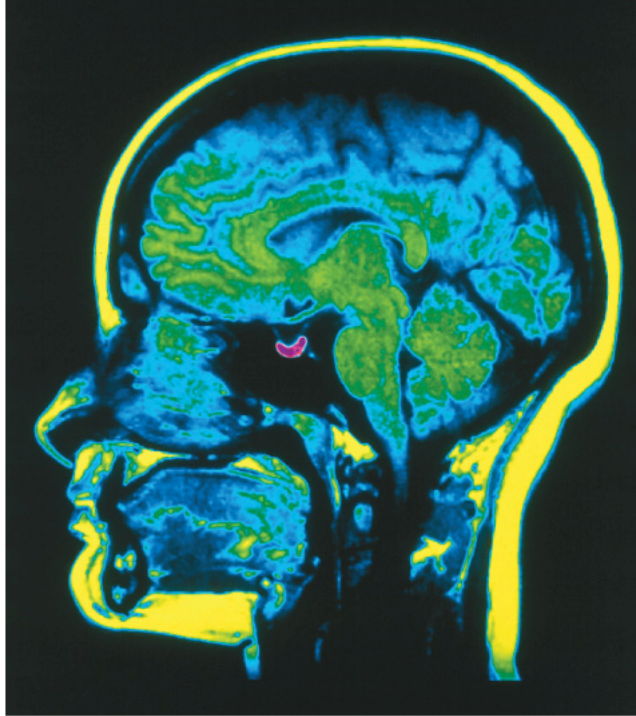


Table 13.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet	1
1	doublet	1 : 1
2	triplet	1 : 2 : 1
3	quartet	1 : 3 : 3 : 1
4	quintet	1 : 4 : 6 : 4 : 1
5	sextet	1 : 5 : 10 : 10 : 5 : 1
6	septet	1 : 6 : 15 : 20 : 15 : 6 : 1