تفريغ تحليل آلي

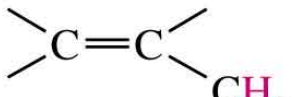
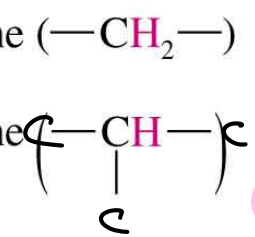
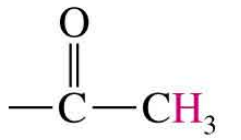
اسم الموضوع: NMR part2

إعداد الصيدلاني/ـة: نور منصور

Seul Academy

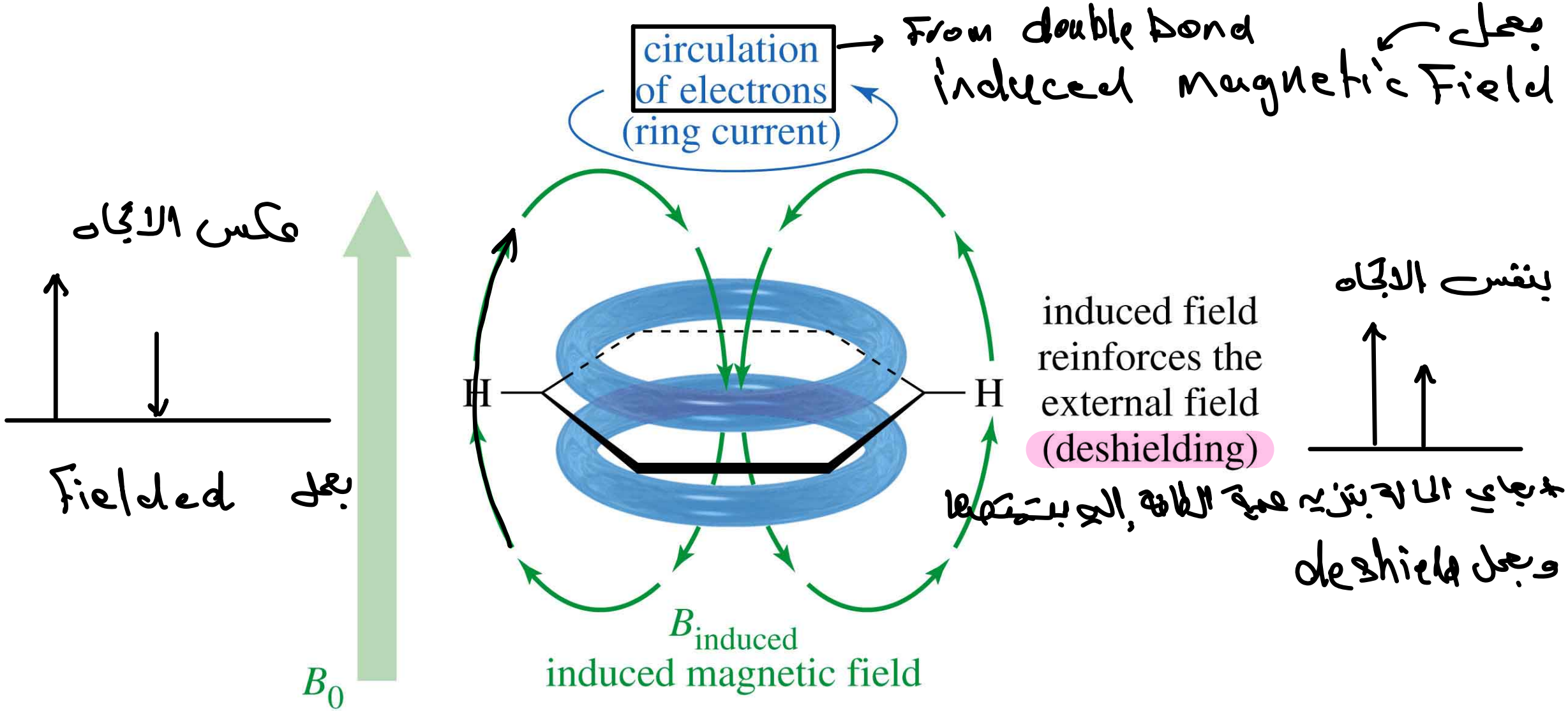
لجان الدُفعات

Typical Values

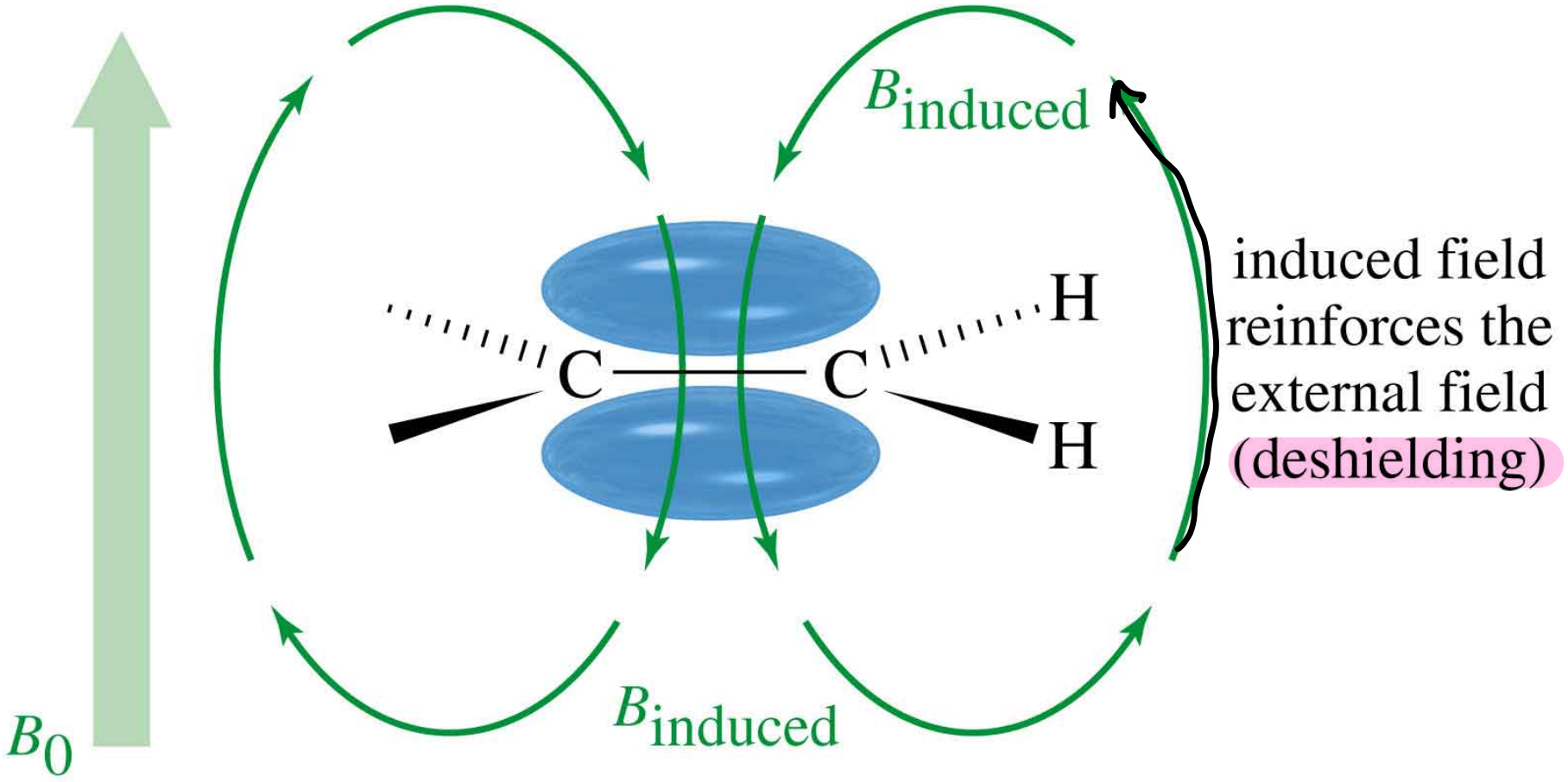
Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane (—CH_3)	0.9		1.7
alkane (—CH_2—)	1.3	Ph—H	7.2
alkane 	1.4	Ph—CH_3	2.3
	2.1	R—CHO	9–10
—C≡C—H	2.5	R—COOH	10–12
R—CH_2—X (X = halogen, O)	3–4	R—OH	variable, about 2–5
	5–6	Ar—OH	variable, about 4–7
		R—NH_2	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

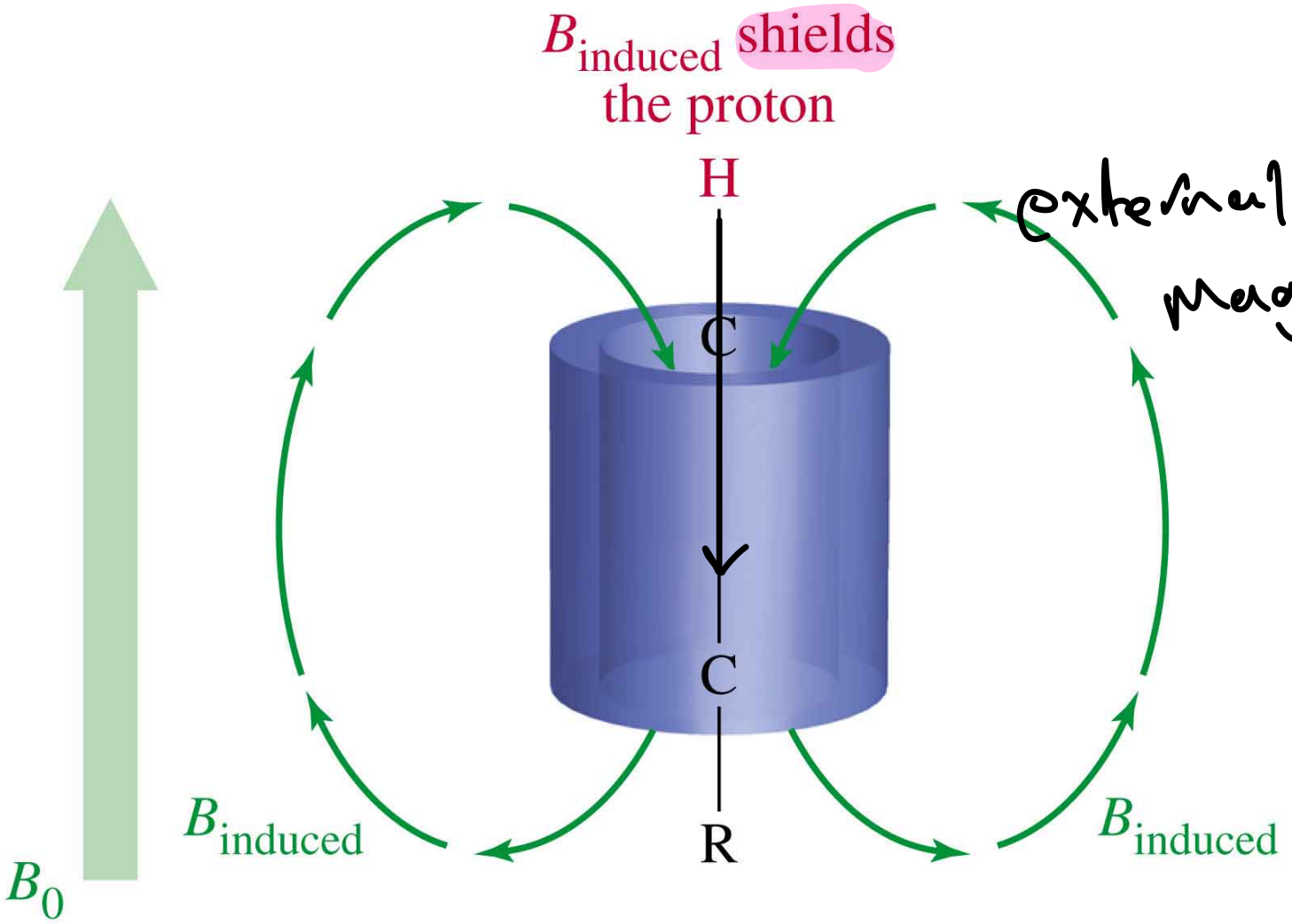
Aromatic Protons, § 7-§ 8



Vinyl Protons, δ 5-δ 6

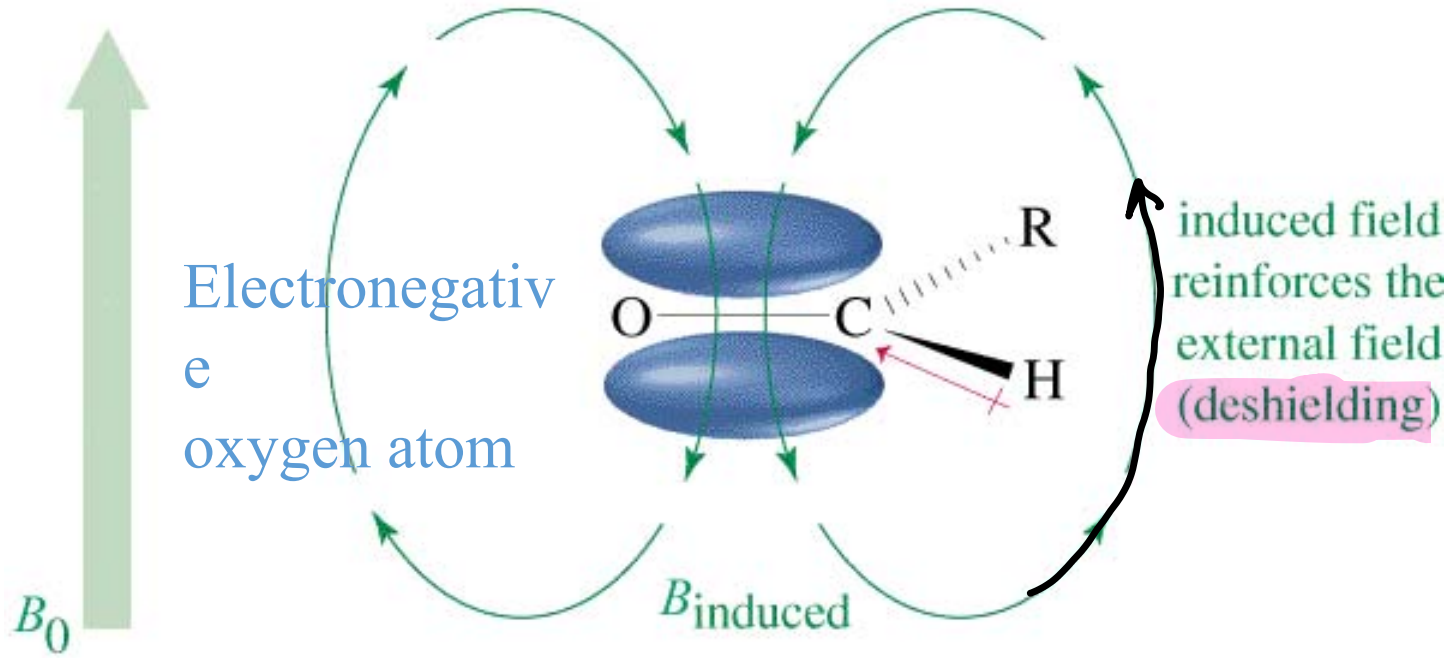


Acetylenic Protons, δ 2.5



external coils induced magnetic Field

Aldehyde Proton, δ 9-δ10

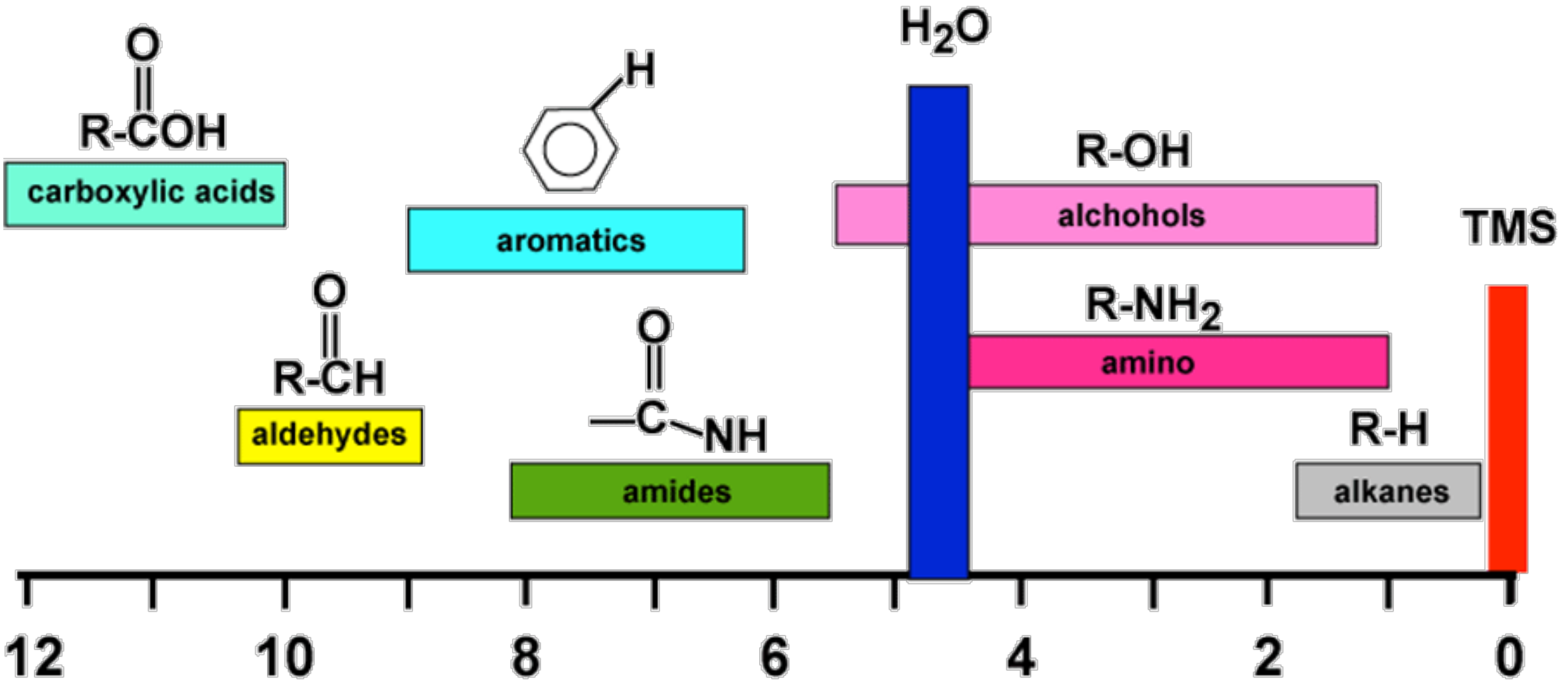


O-H and N-H Signals

- Chemical shift depends on concentration.

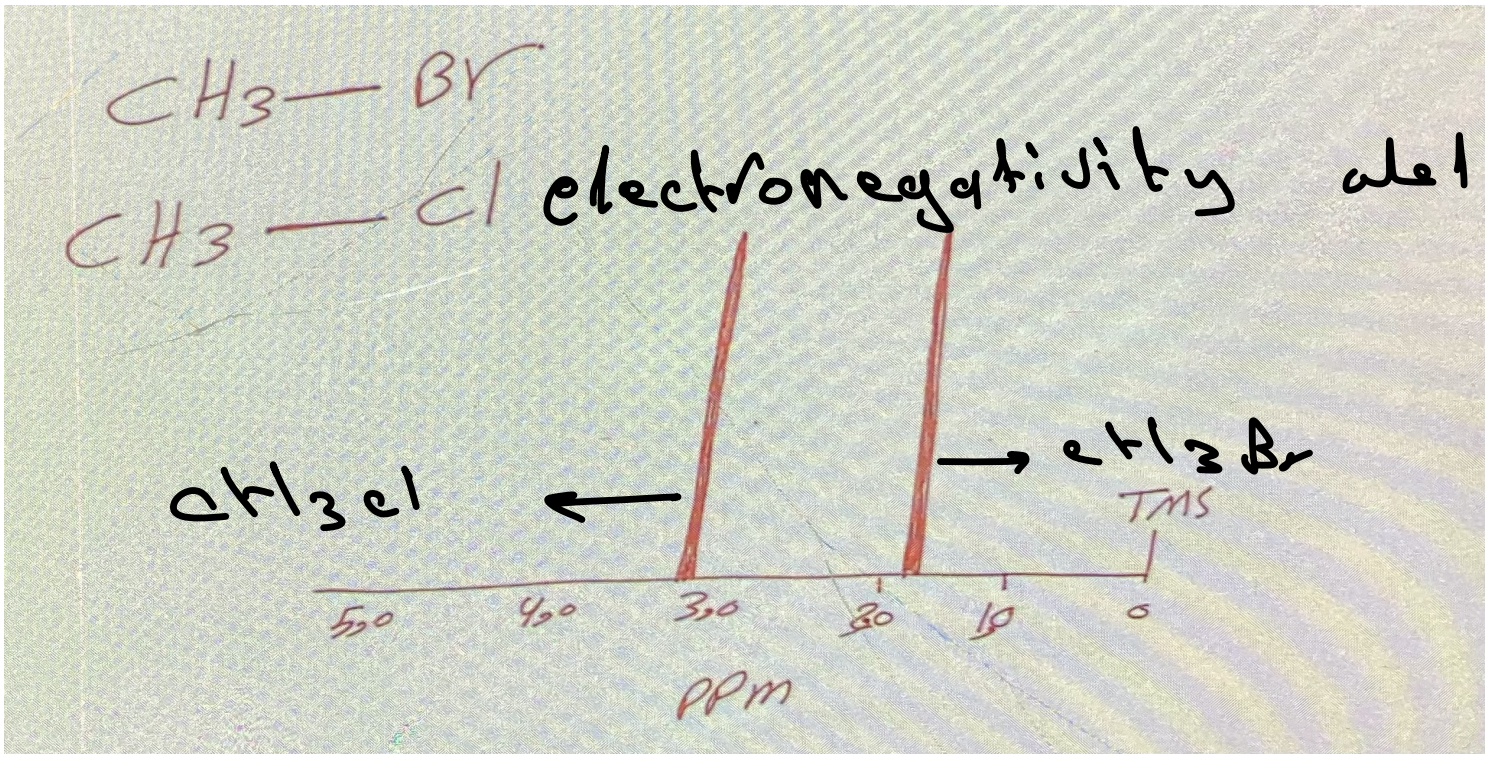
- Hydrogen bonding in concentrated solutions deshield the protons, so signal is around δ 3.5 for N-H and δ 4.5 for O-H.

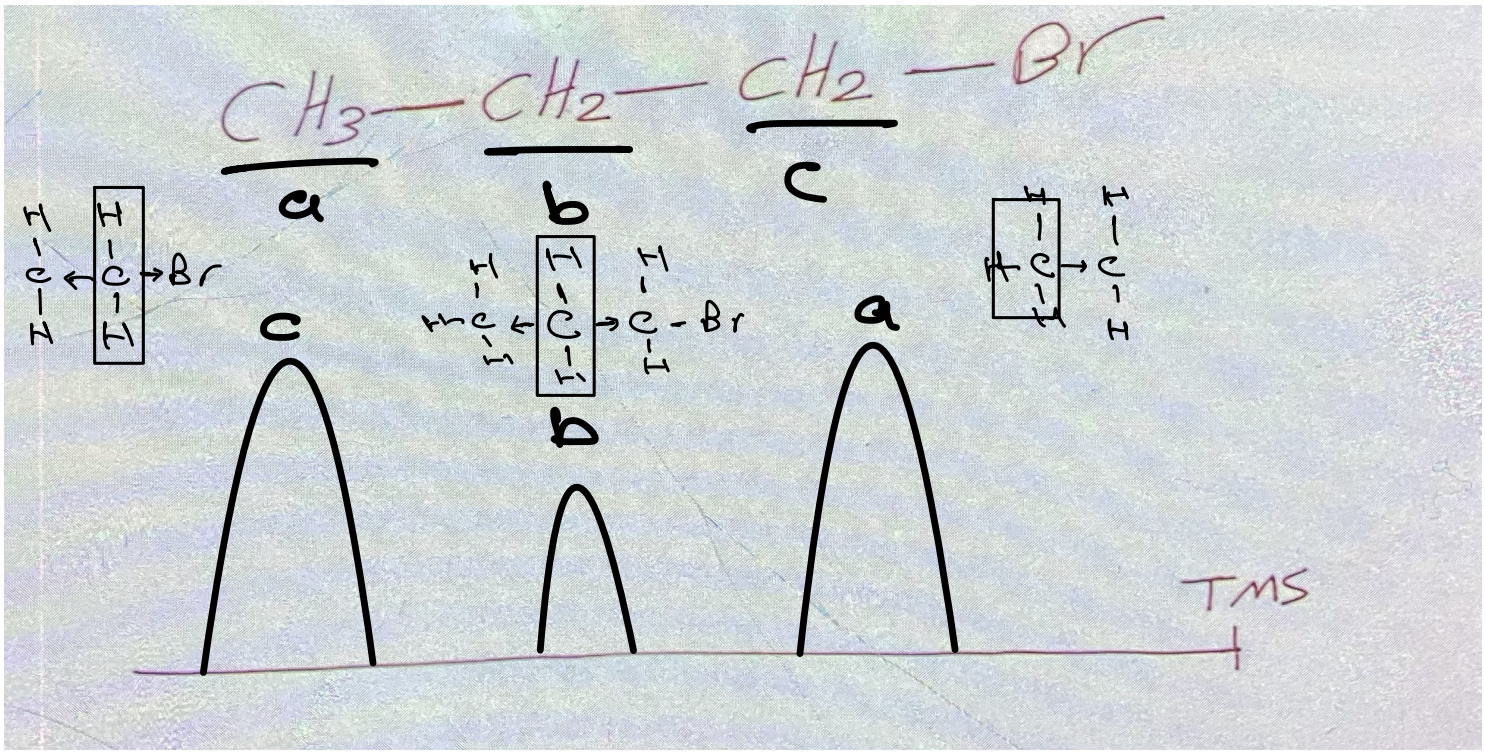
- Proton exchanges between the molecules broaden the peak.

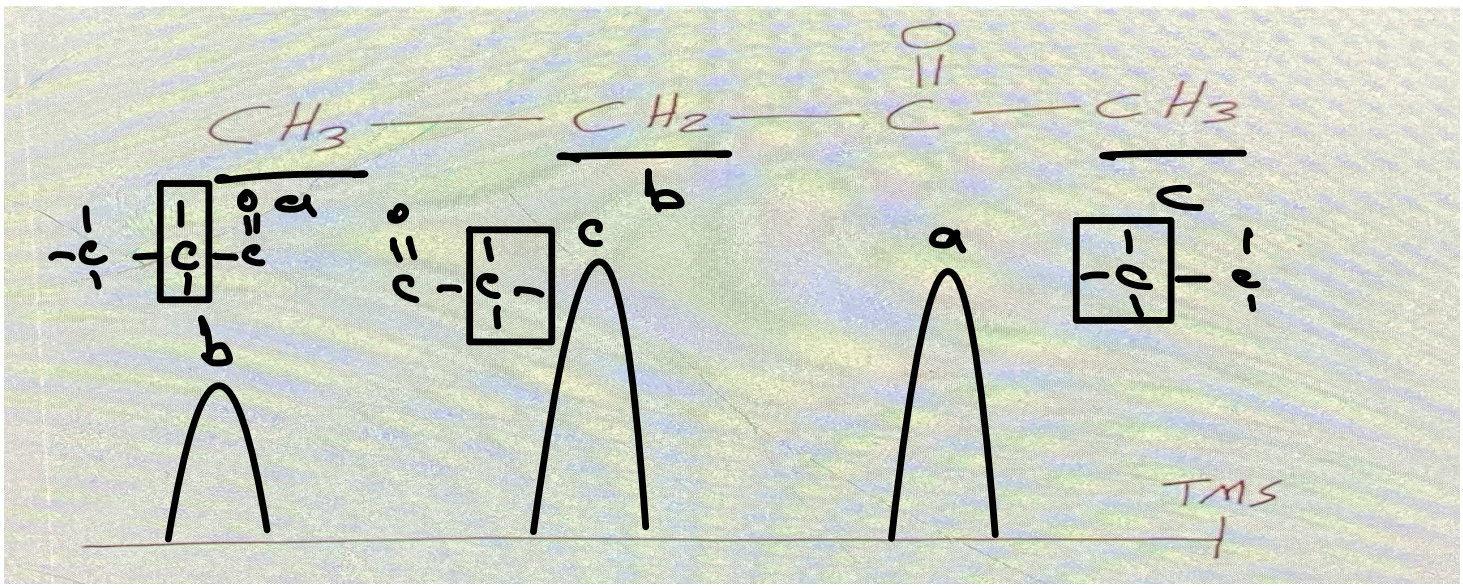


electronegativity

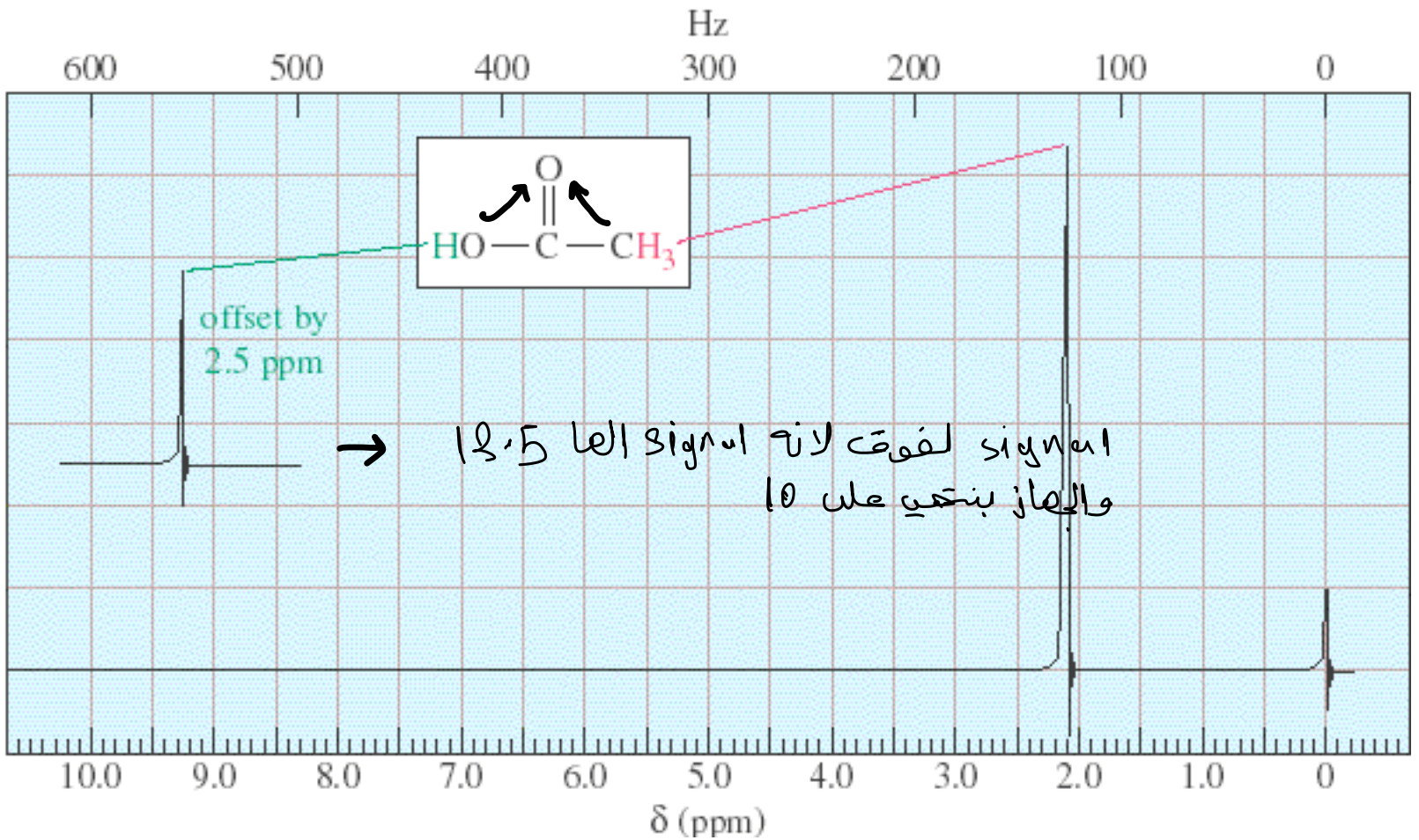
carboxylic acids > aldehyde > aromatic > amides > H_2O > alkohol > amino > alkanes > TMS


CH3—Br
CH3—Cl
electronegativity ale1
CH3Cl
CH3Br
TMS
5,0
4,0
3,0
2,0
1,0
0
ppm


CH3—CH2—CH2—Br
a
b
c
c
b
a
TMS

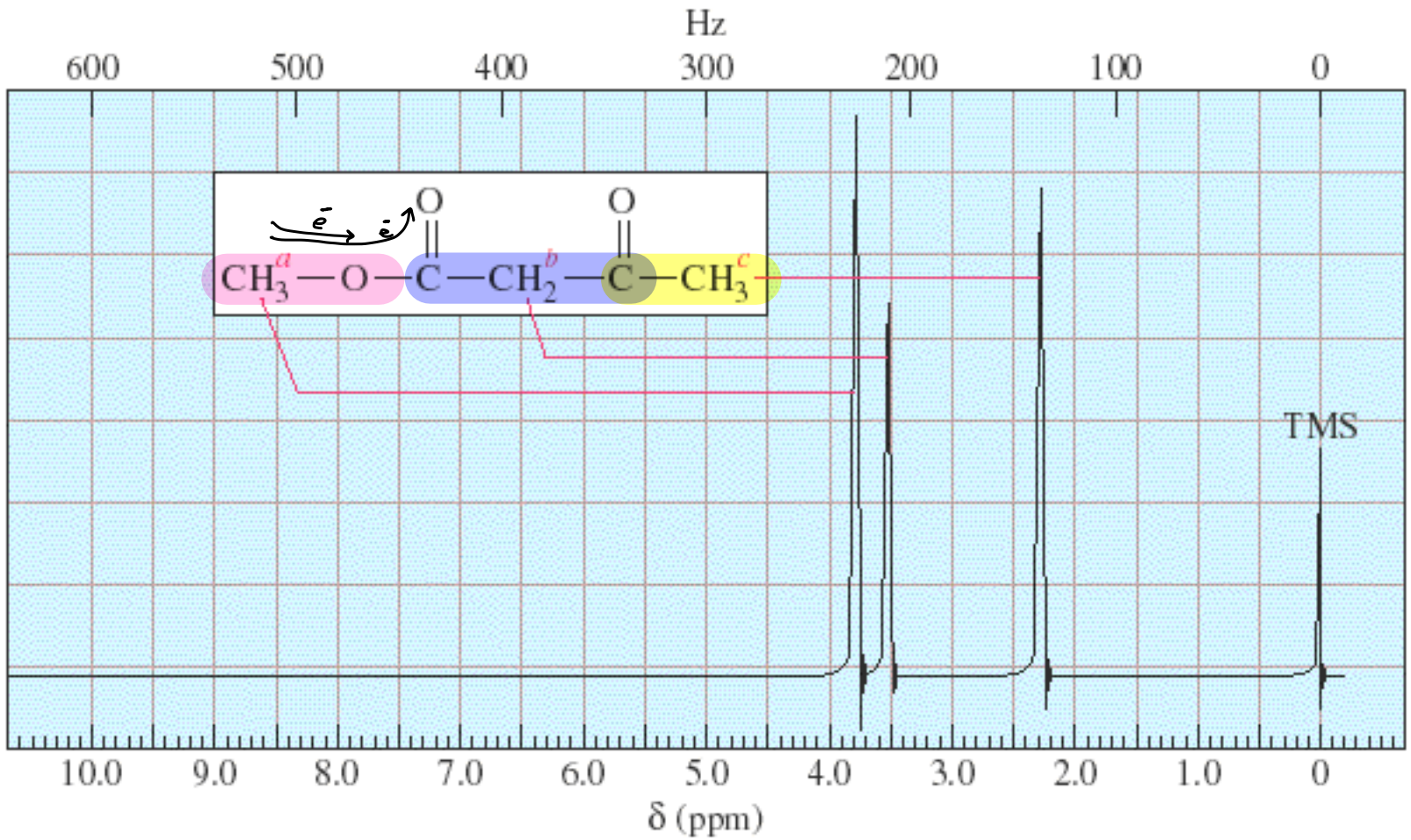

CH3—CH2—C—CH3
a
b
c
b
c
a
TMS

Carboxylic Acid Proton, □10+



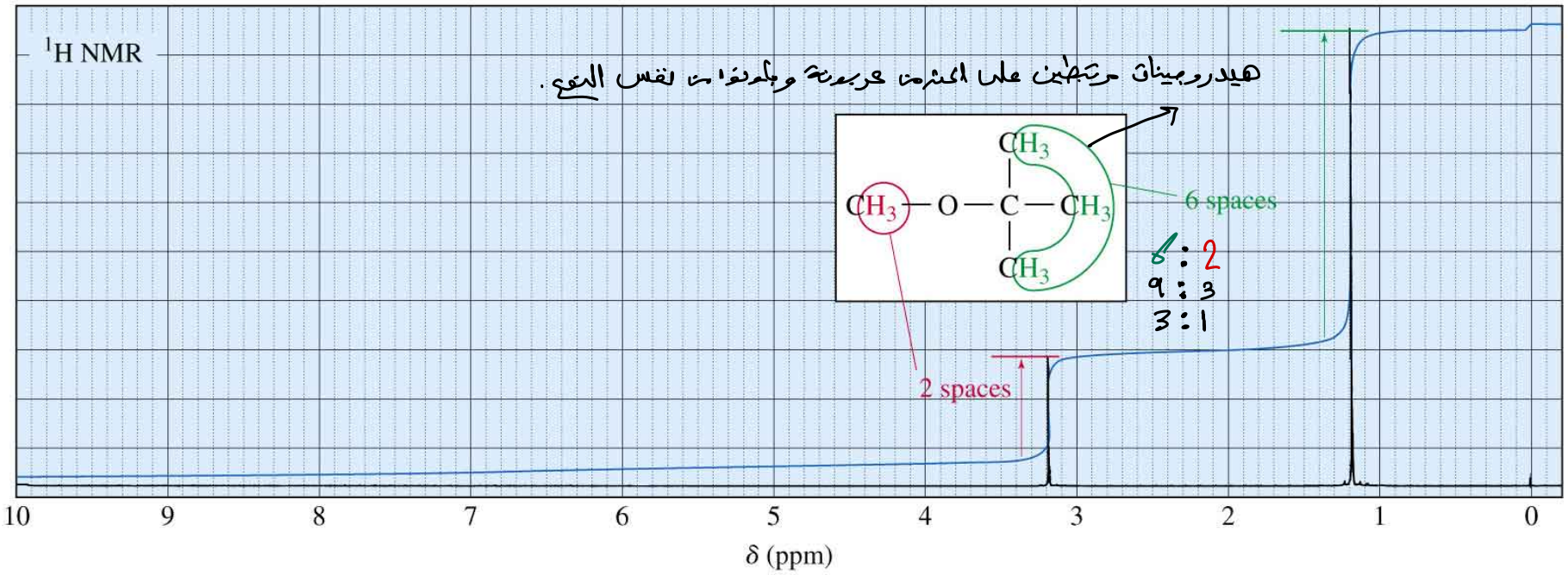
Number of Signals

Equivalent hydrogens have the same chemical shift.



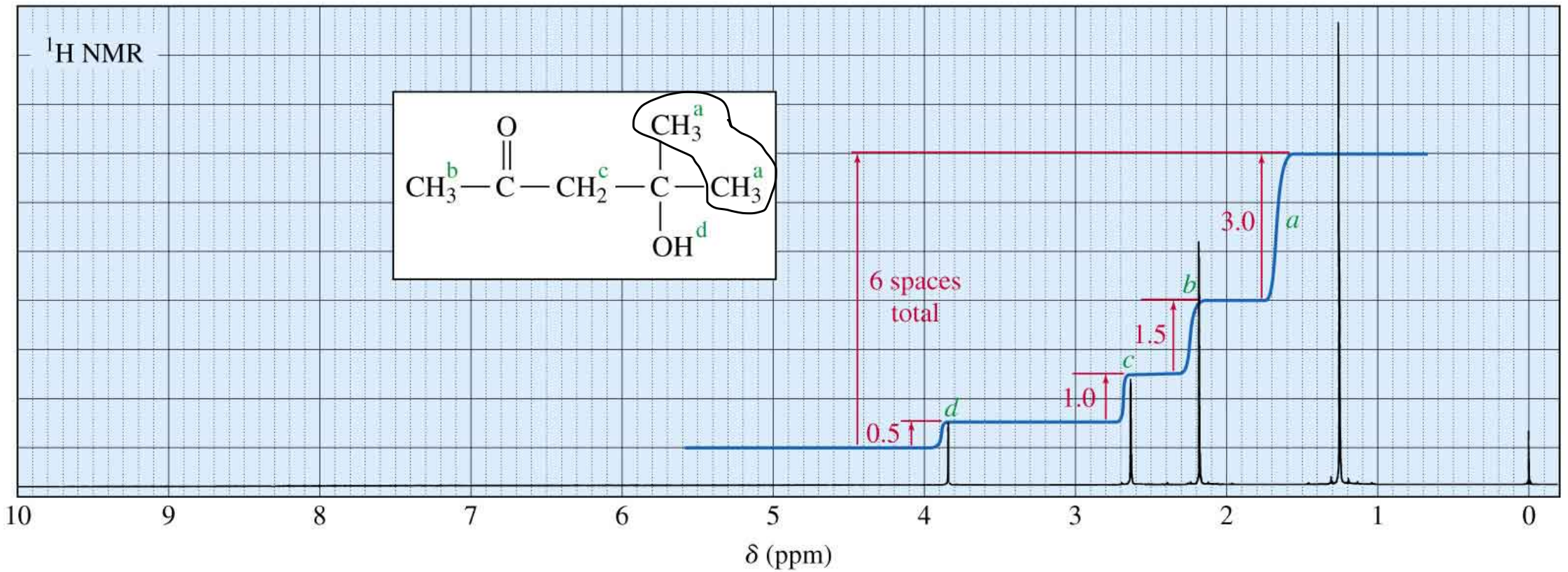
Intensity of Signals

- The area under each peak is proportional to the number of protons.
- Shown by integral trace.



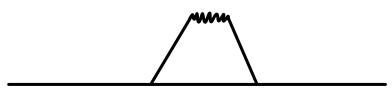
How Many Hydrogens?

When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.



The $N + 1$ Rule

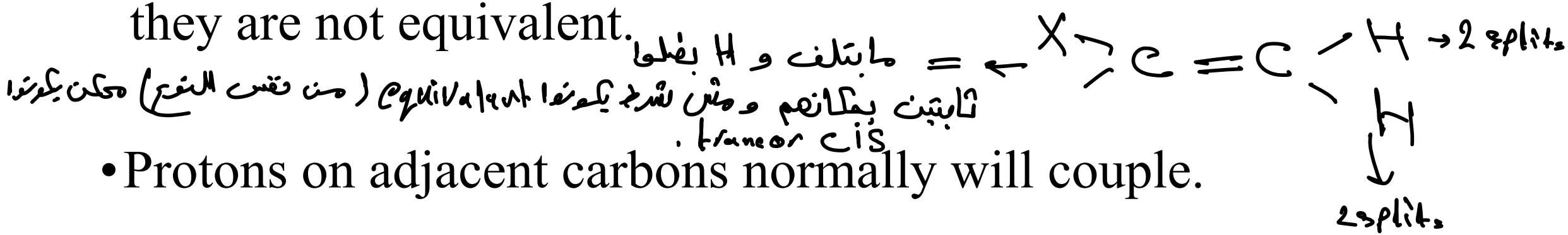
If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.



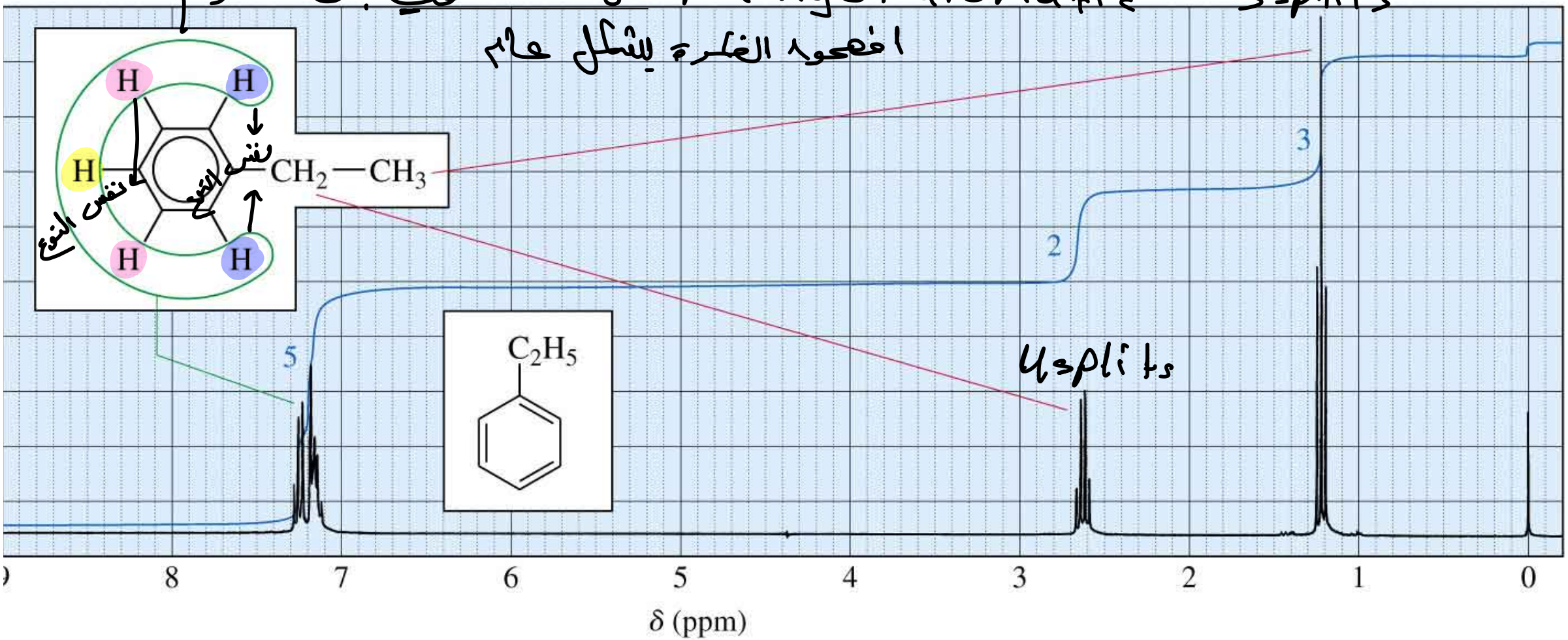
Relative Peak Intensities of Symmetric Multiplets		
Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

Range of Magnetic Coupling

- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other only if they are not equivalent.
- Protons on adjacent carbons normally will couple.
- Protons separated by four or more bonds will not couple.



Splitting for Ethyl Groups



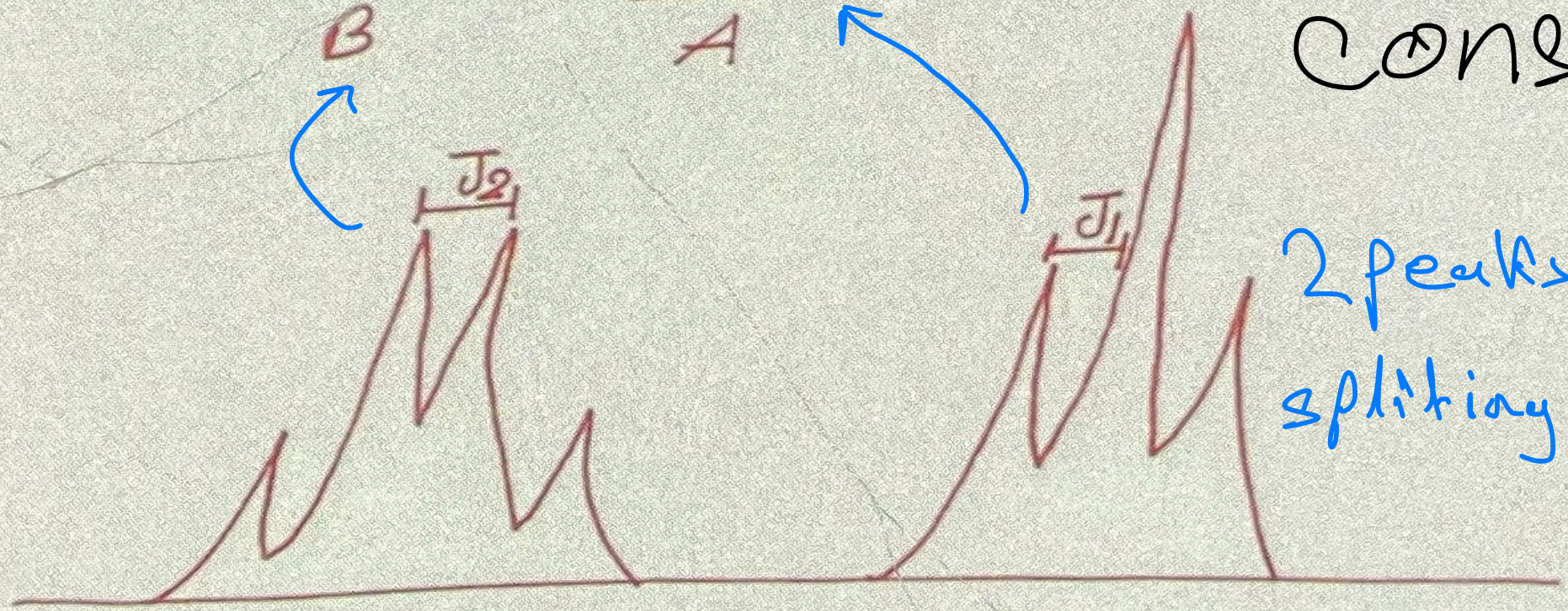
وحدة قياسها Hz

$Cl-\underset{B}{CH_2}-\underset{A}{CH_3}$

Coubling constant

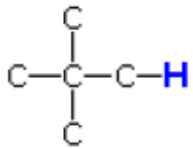
↓

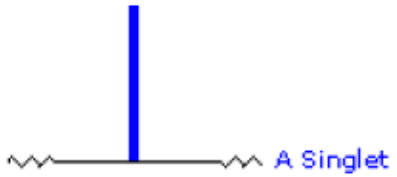
المسافة بين 2 peaks splitting الي هحولهم



إذا كانت $J_1 = J_2$ يعني H_A و H_B متجاورين

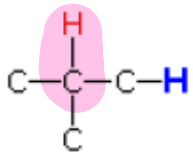
No Coupled Hydrogens

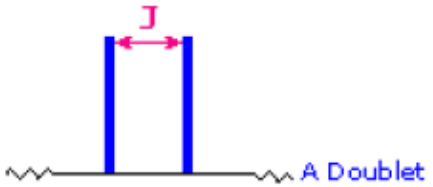




0 + 1 = 1

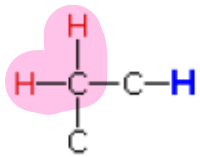
One Coupled Hydrogen

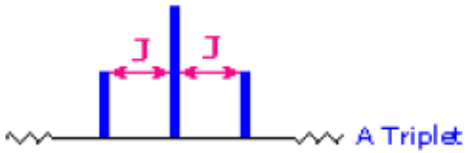




1 + 1 = 2

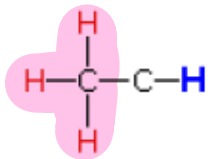
Two Coupled Hydrogens

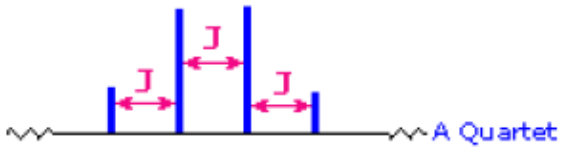




2 + 1 = 3

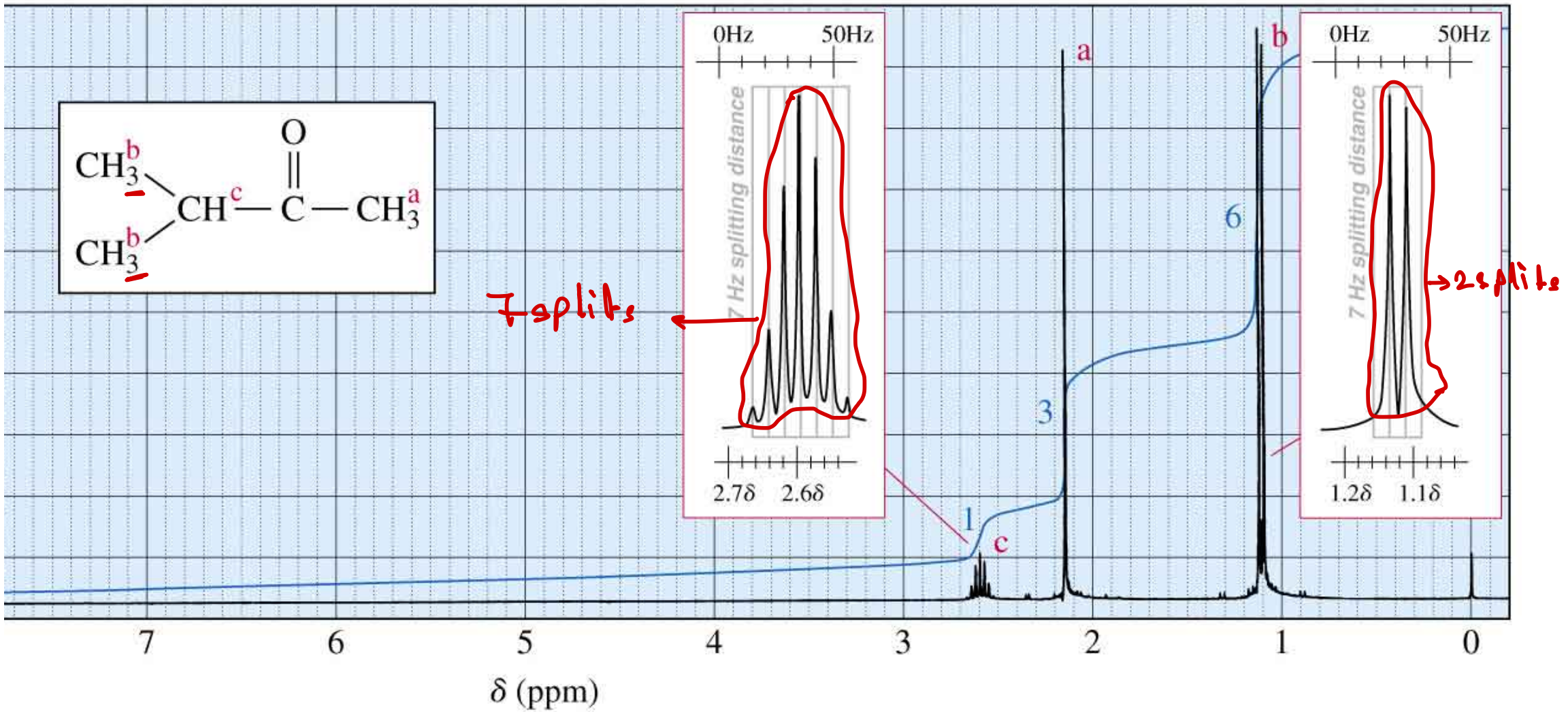
Three Coupled Hydrogens



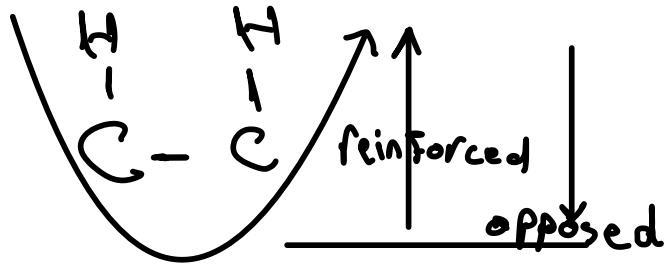


3 + 1 = 4

Splitting for Isopropyl Groups



Spin-Spin Splitting

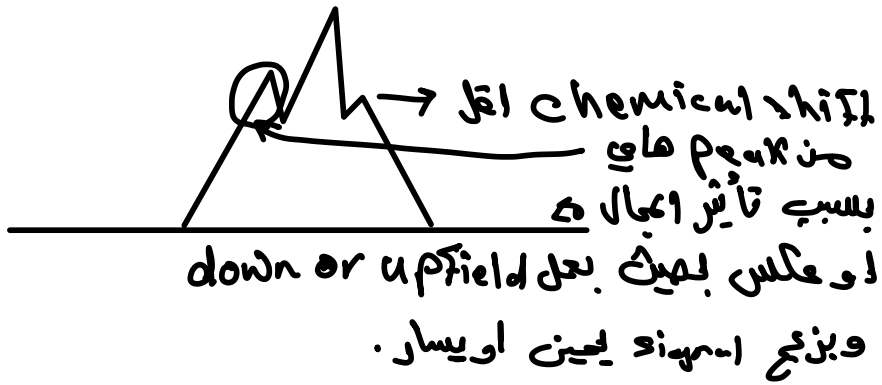


- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.

- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.

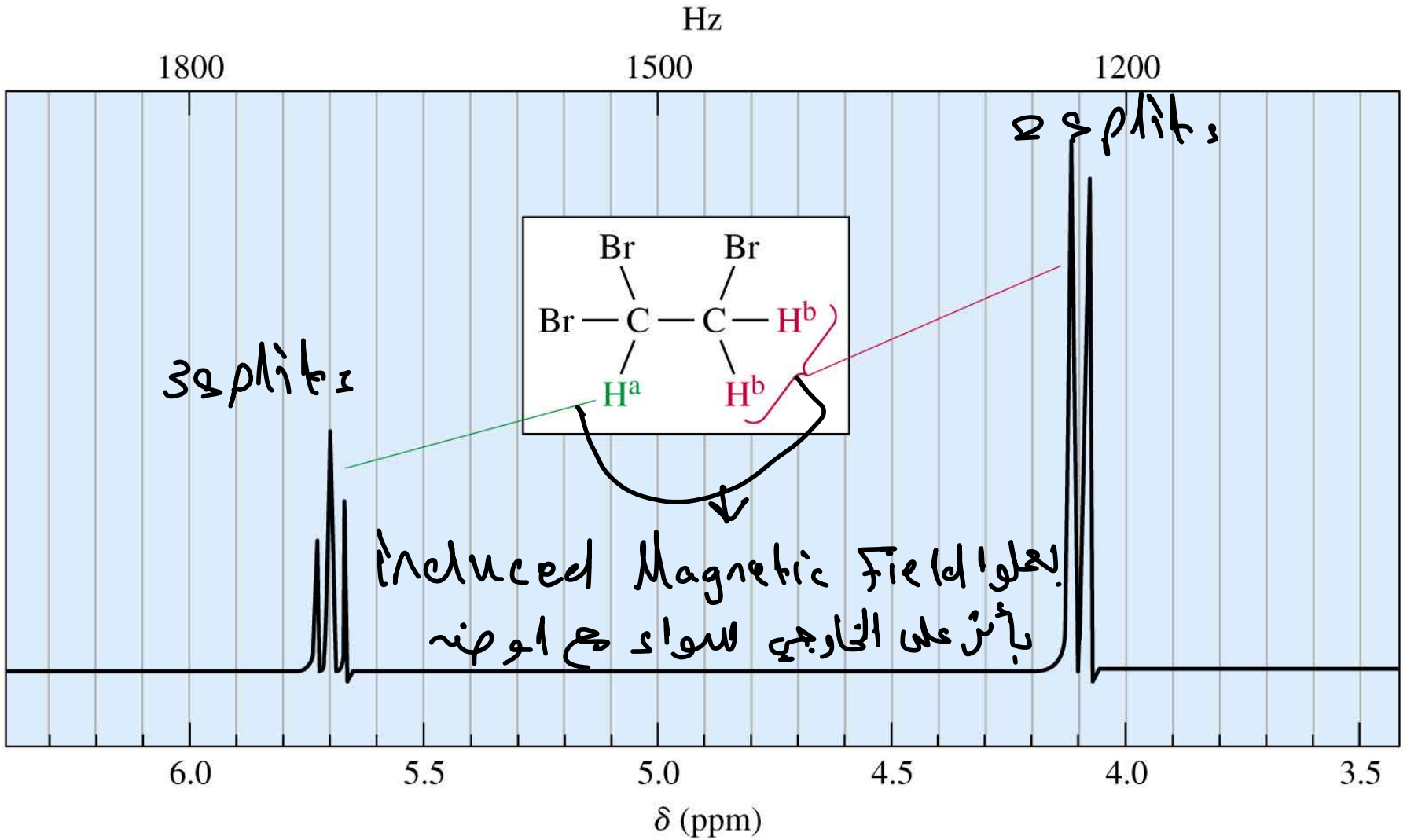
اقلل المجال المغناطيسي الخارجي، لانه صار مدعوم من مجال مغناطيسي يعوض الي صار induced

- All possibilities exist, so signal is split.

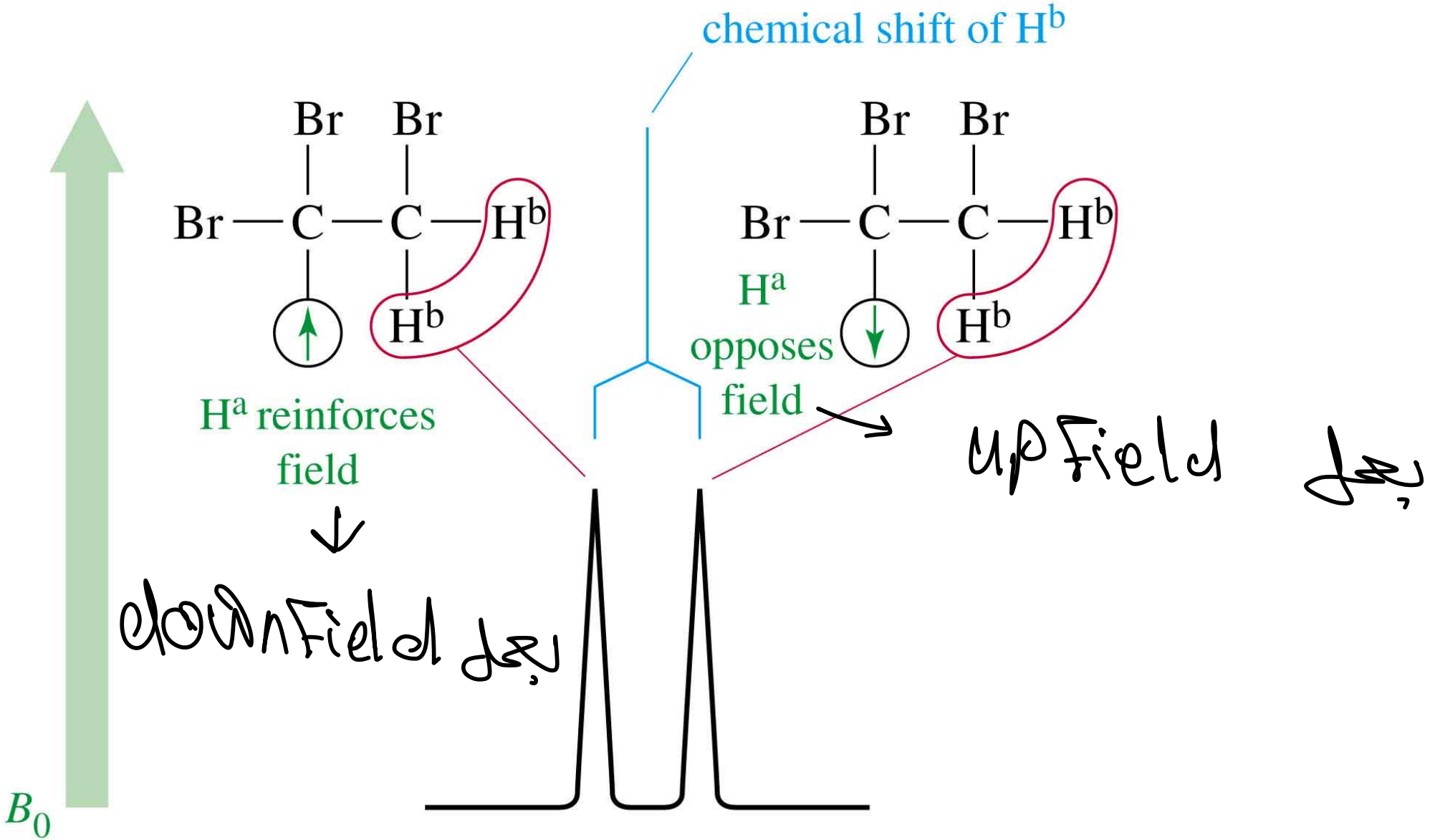


1,1,2-Tribromoethane

Nonequivalent protons on adjacent



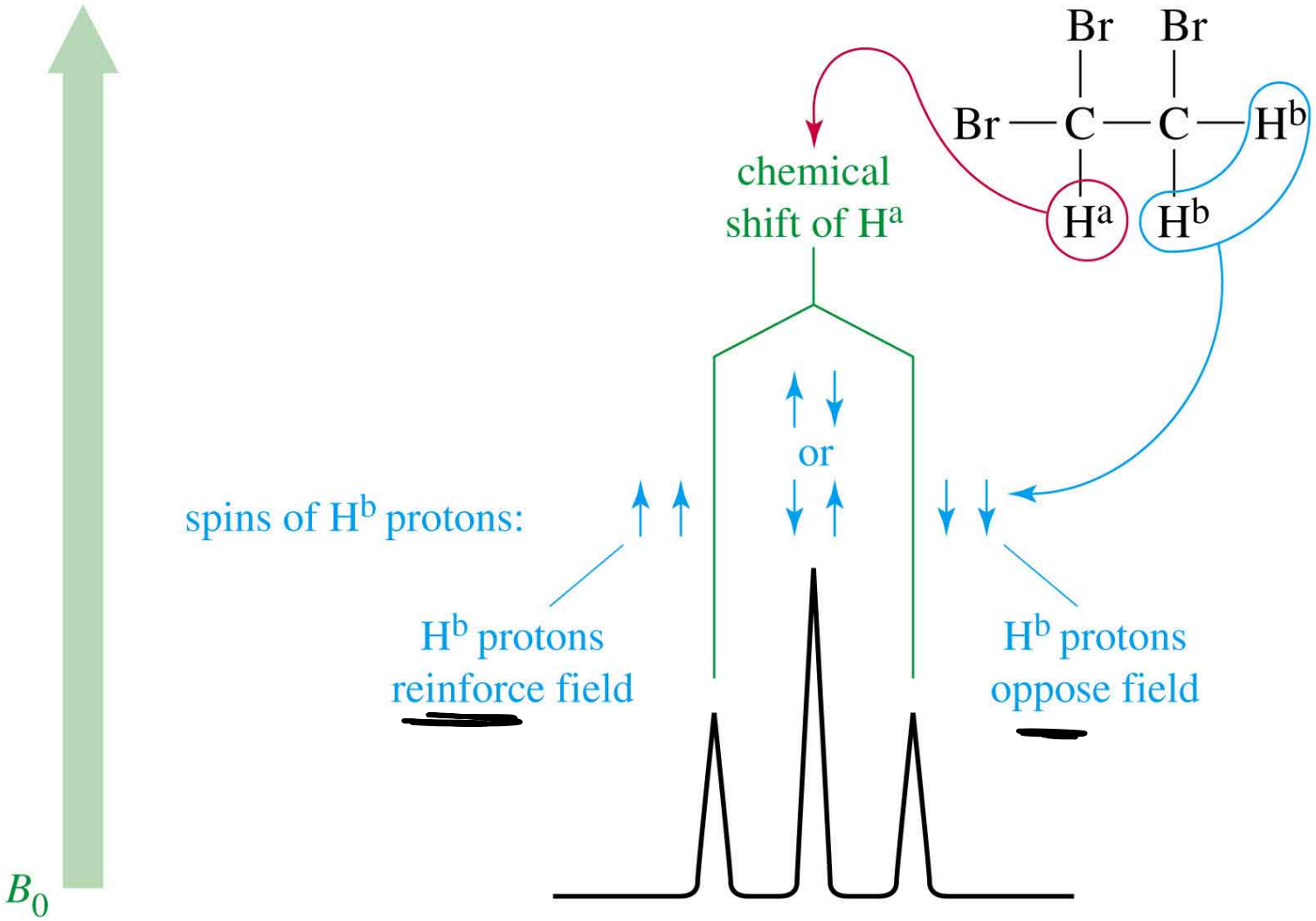
Doublet: 1 Adjacent Proton



downfield جهة

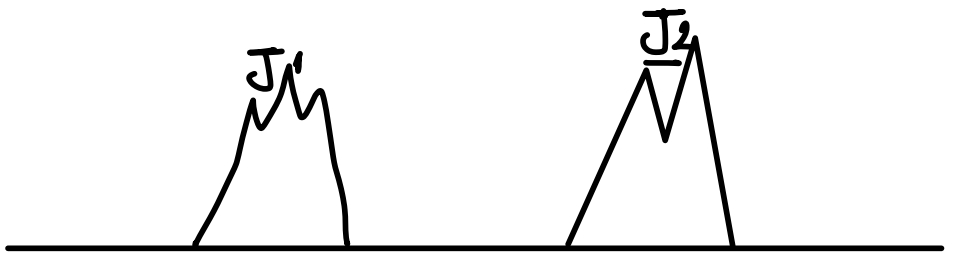
upfield جهة

Triplet: 2 Adjacent Protons



Coupling Constants

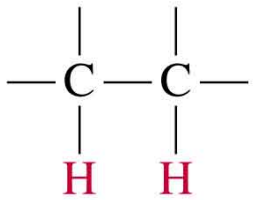
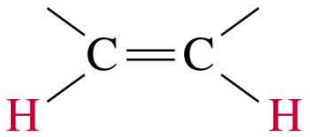
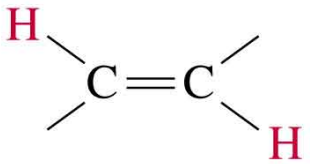
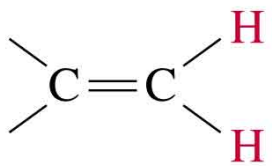
- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field يعتمد على Induced Field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

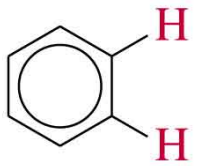
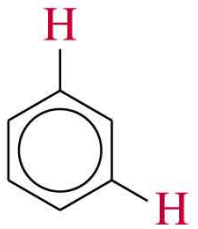
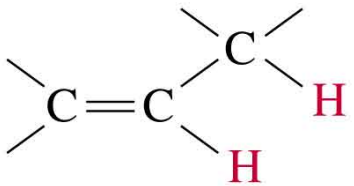


$J_1 = J_2$
* يعني انهم متجاوران

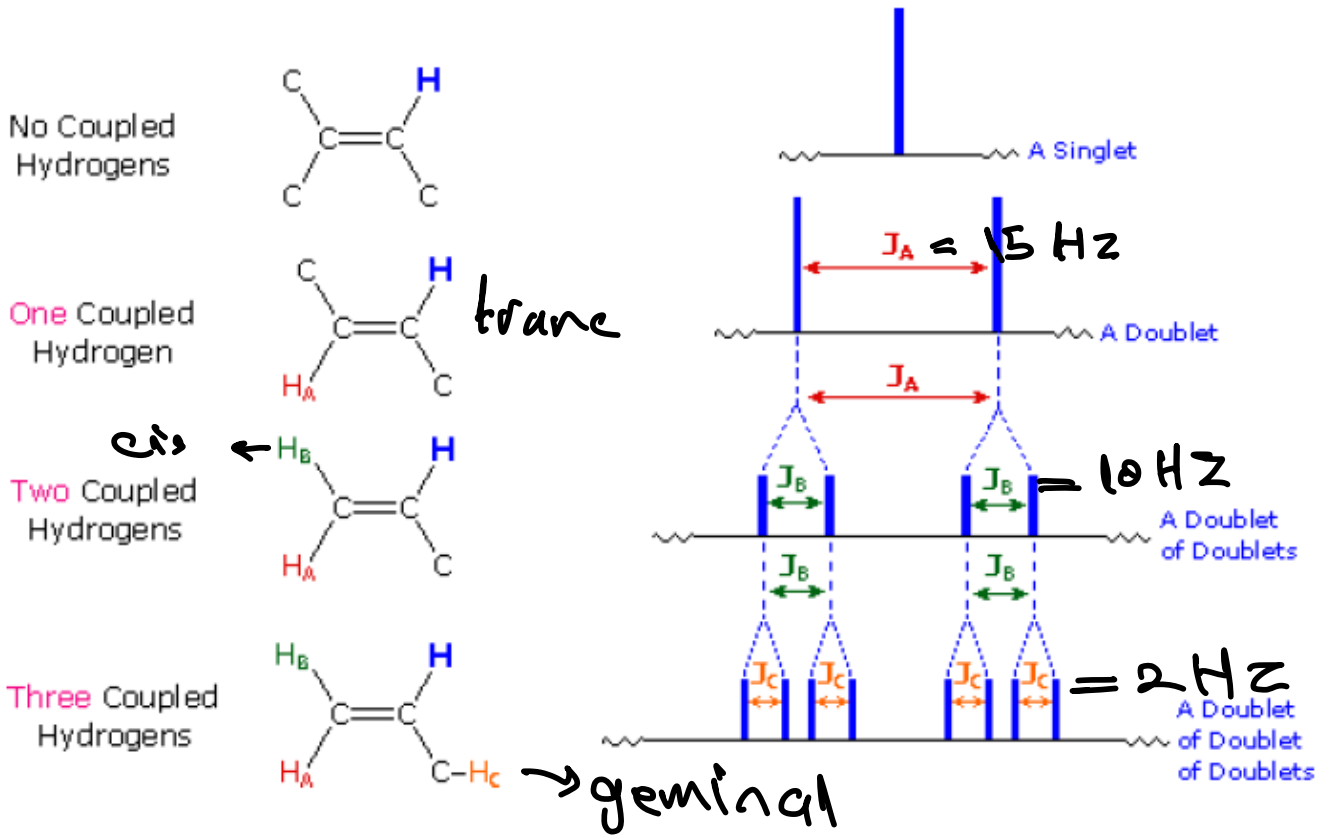
Values for Coupling Constants

القيم حفظ

		Approx. J
	(free rotation)	7 Hz[a]
	(cis)	10 Hz
	(trans)	15 Hz
	(geminal)	2 Hz

	Approx. J
 (ortho)	8 Hz
 (meta)	2 Hz
 (allylic)	6 Hz

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


No Coupled Hydrogens
One Coupled Hydrogen
Two Coupled Hydrogens
Three Coupled Hydrogens
trans
cis
gemingl
A Singlet
A Doublet
A Doublet of Doublets
A Doublet of Doublet of Doublets
= 10 Hz
= 2 Hz