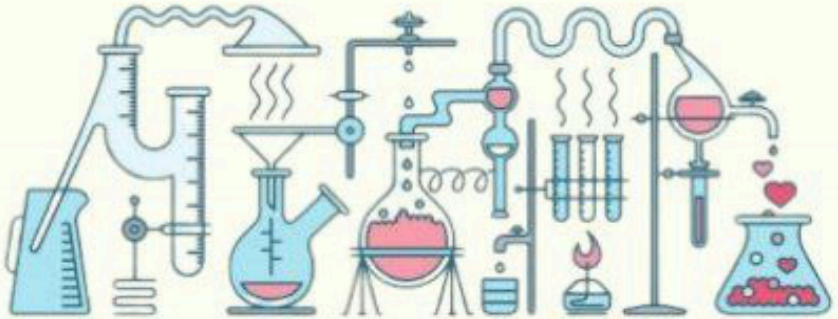
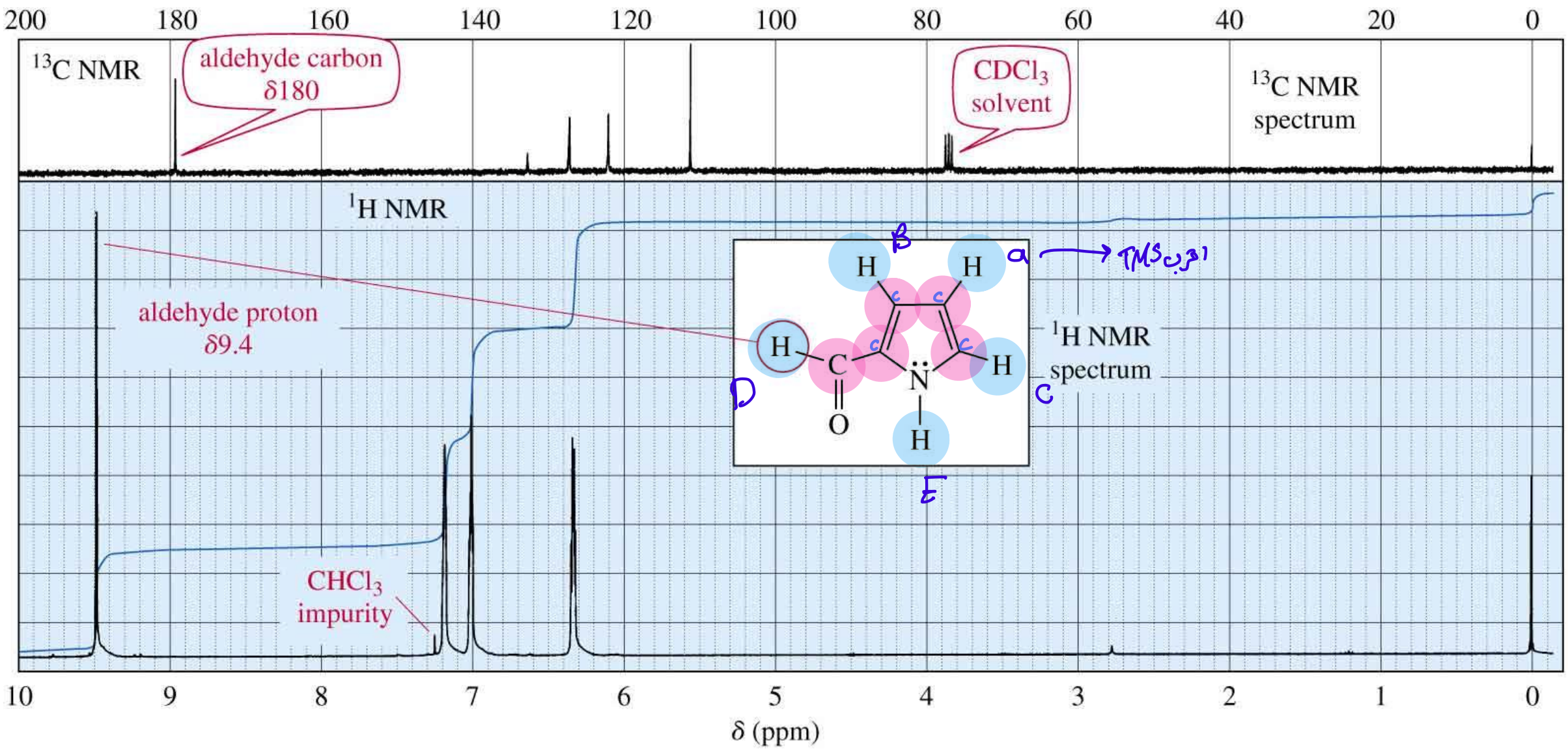
تفريغ تحليل آلي



اسم الموضوع: NMR Carbon 13

إعداد الصيدلاني/ـة: Sara Jaber

Combined ^{13}C and ^{1}H Spectra



A	B	D
C	E	

ندرس طاقة 150 MHz

Carbon 13

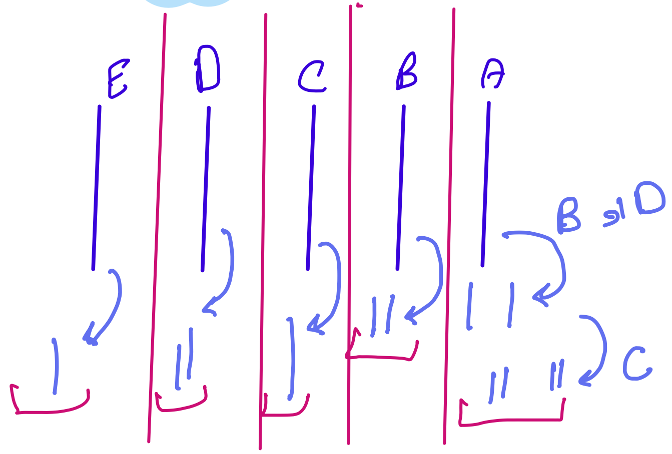
1.1 %

ندرس طاقة = 60 MHz

^{1}H Proton

Proton

99.1 %



عندي جزيء molecules تكون موجودة ويتخطى بالجهاز

فيه كذا ^{13}C وتحلل

فاحتمال انه يكون واحد منهم

وأحوال العقل مصقول الرقي النفس

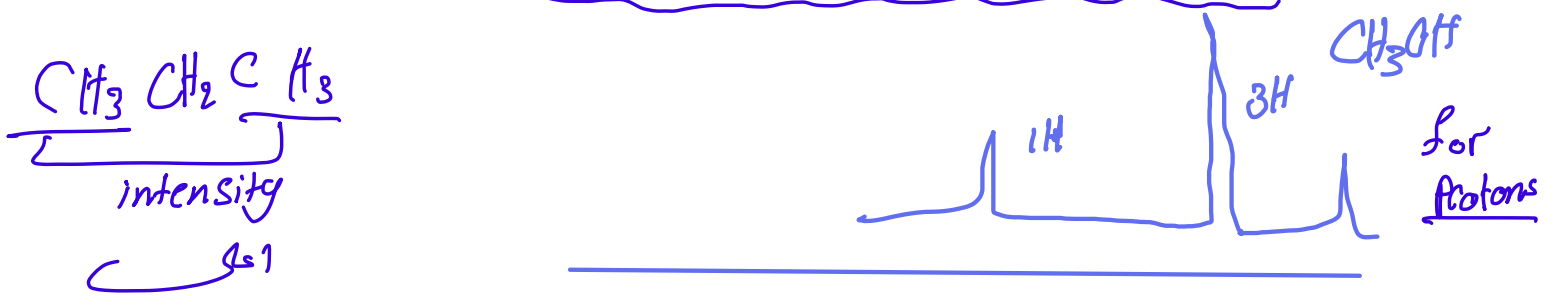
مجال النفس تسدد السهم

فأصرار مرمى تحيله

بقوة ارتي المعتز

Differences in ^{13}C Technique

- Resonance frequency is ~ one-fourth, 15.1 MHz instead of 60 MHz. → in proton
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.



Spin-Spin Splitting

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.

- ^{13}C will magnetically couple with attached protons and adjacent protons.

- These complex splitting patterns are difficult to interpret.

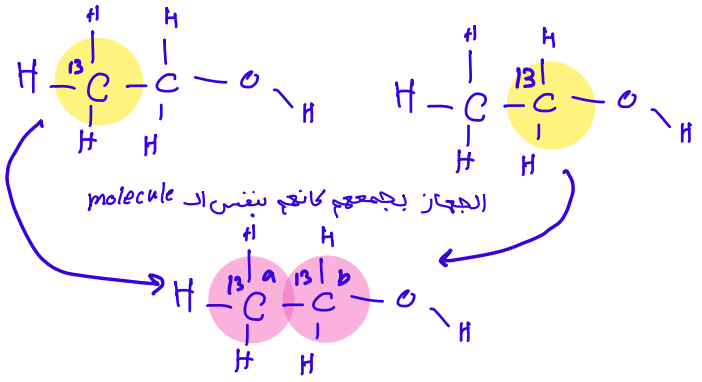
Proton Spin Decoupling

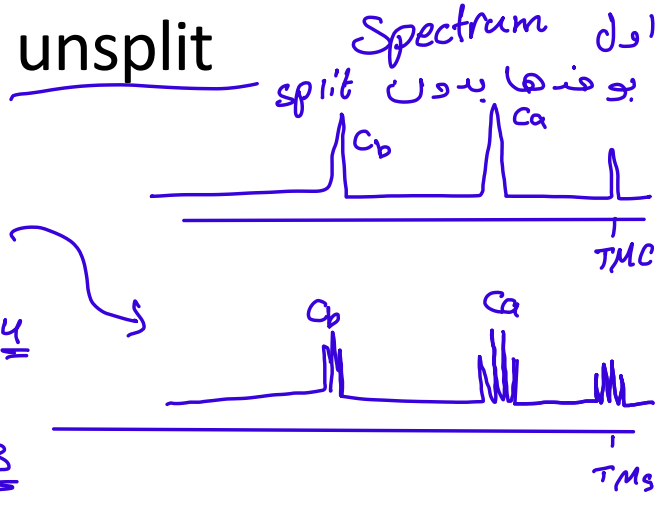
- To simplify the spectrum, protons are continuously irradiated with "noise," so they are rapidly flipping.

بالمركب بكون عندي وحدة ^{13}C والي
جنبها بتكون ^{12}C لانه نسبة الوفرة = ١.١٪

- The carbon nuclei see an average of all the possible proton spin states.

- Thus, each different kind of carbon gives a single, unsplit peak.





Off-Resonance Decoupling

- ^{13}C nuclei are split only by the protons attached directly to them.

- The *N* + 1 rule applies: a carbon with *N* number of protons gives a signal with *N* + 1 peaks.

Interpreting ^{13}C NMR

- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon.

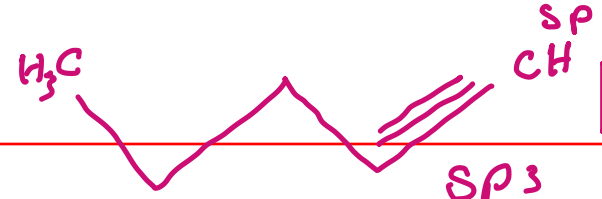
^{13}C Chemical Shifts

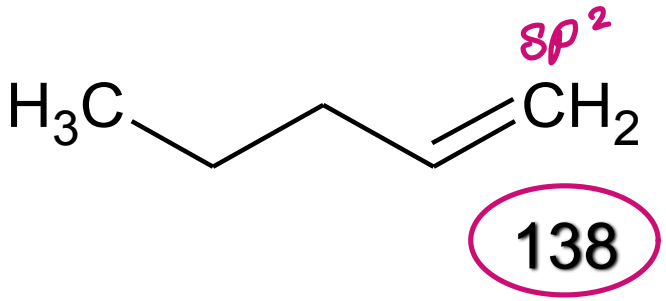
are measured in ppm (δ) from the carbons of TMS

^{13}C Chemical shifts are most affected by:

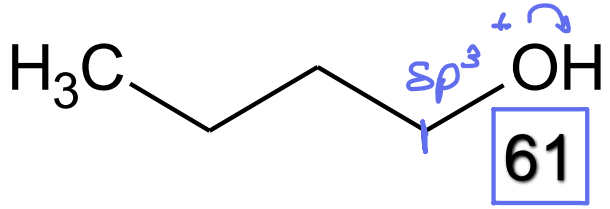
- hybridization state of carbon $\quad \delta\uparrow \quad sp^2 > sp > sp^3 \quad \delta\downarrow$
- electronegativity of groups attached to carbon $\quad C\text{-}O > C\text{-}C$ ($\delta\uparrow$ $\quad$ $\delta\downarrow$)

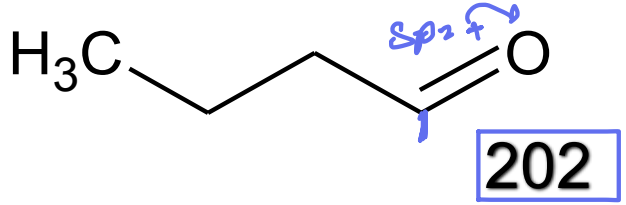
Examples (chemical shifts in ppm from TMS)



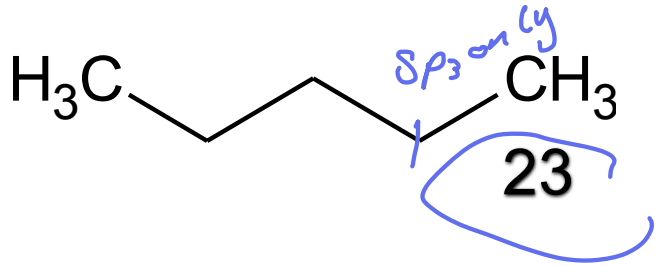


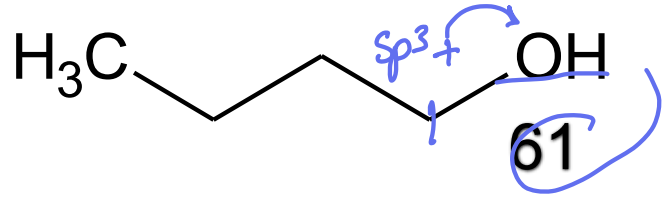
sp³ hybridized carbon is more shielded than sp²



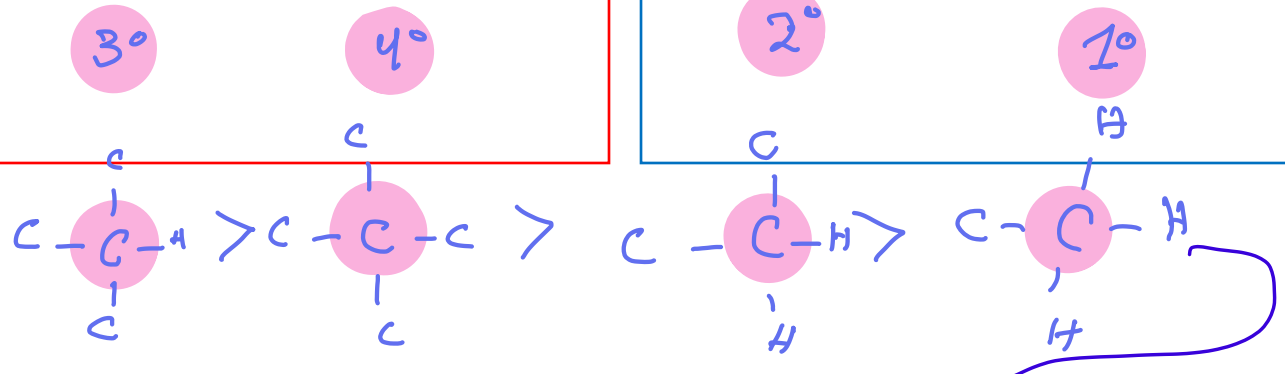


sp³ hybridized carbon is more shielded than sp²

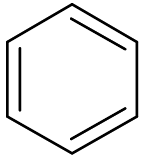




an electronegative atom deshields the carbon to which it is attached

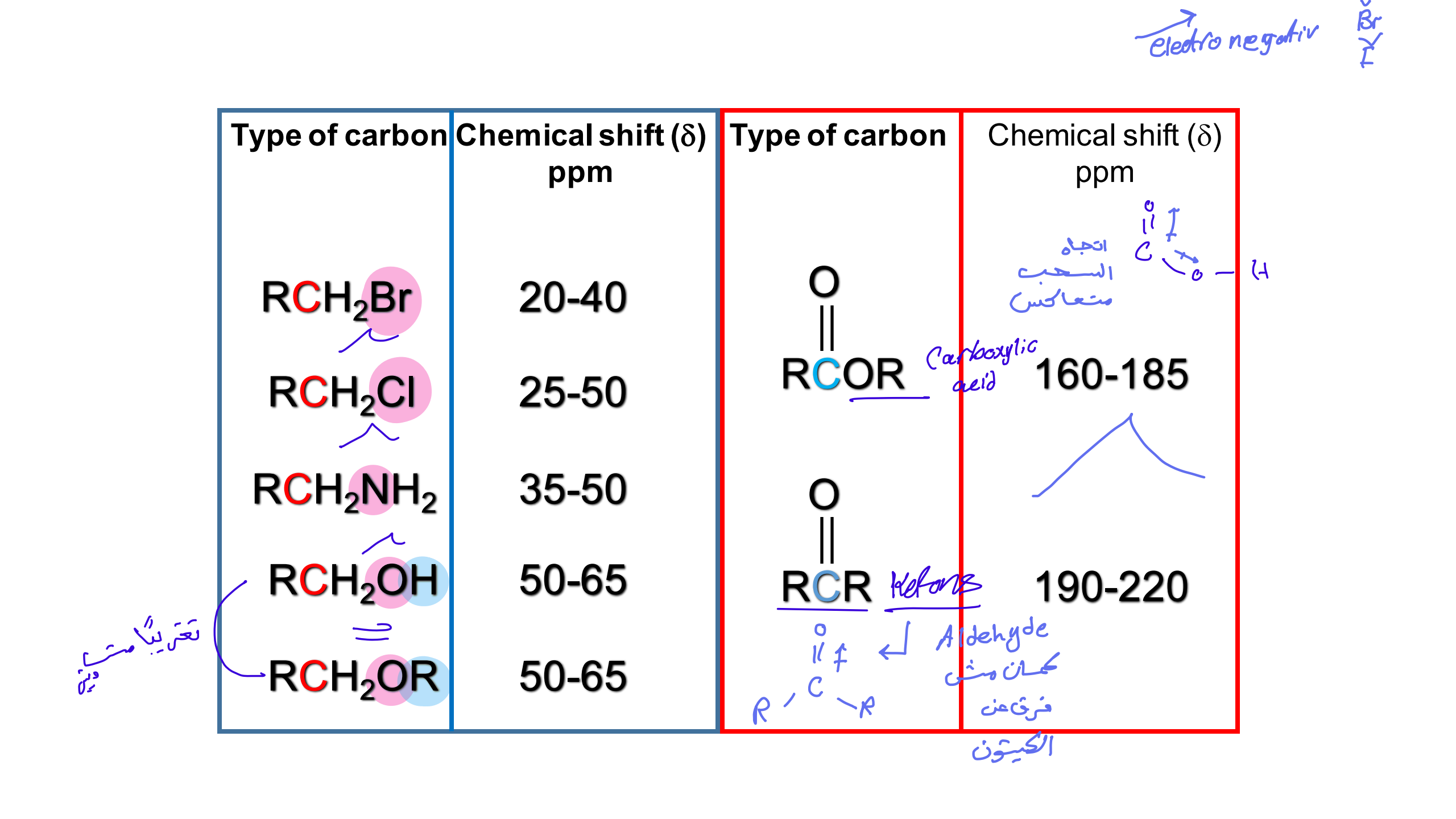


كلهم sp^3 وروابطهم σ

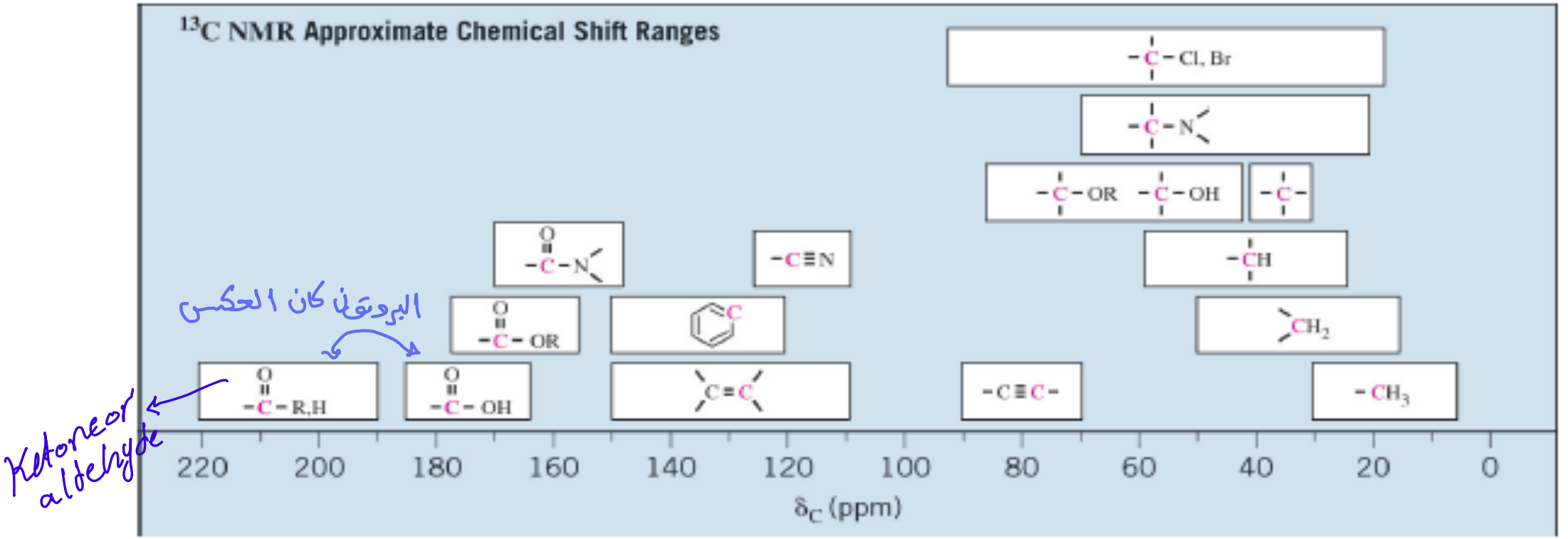
Type of carbon	Chemical shift (δ) ppm	Type of carbon	Chemical shift (δ) ppm
1° carbon RCH_3	0-35	$RC\equiv CR$	65-90
2° carbon R_2CH_2	15-40	$R_2C=CR_2$	100-150
3° carbon R_3CH	25-50	 Benzen Ring	110-175
4° carbon R_4C	30-40		

$sp^2 > sp > sp^3$

B < C < N < O < F

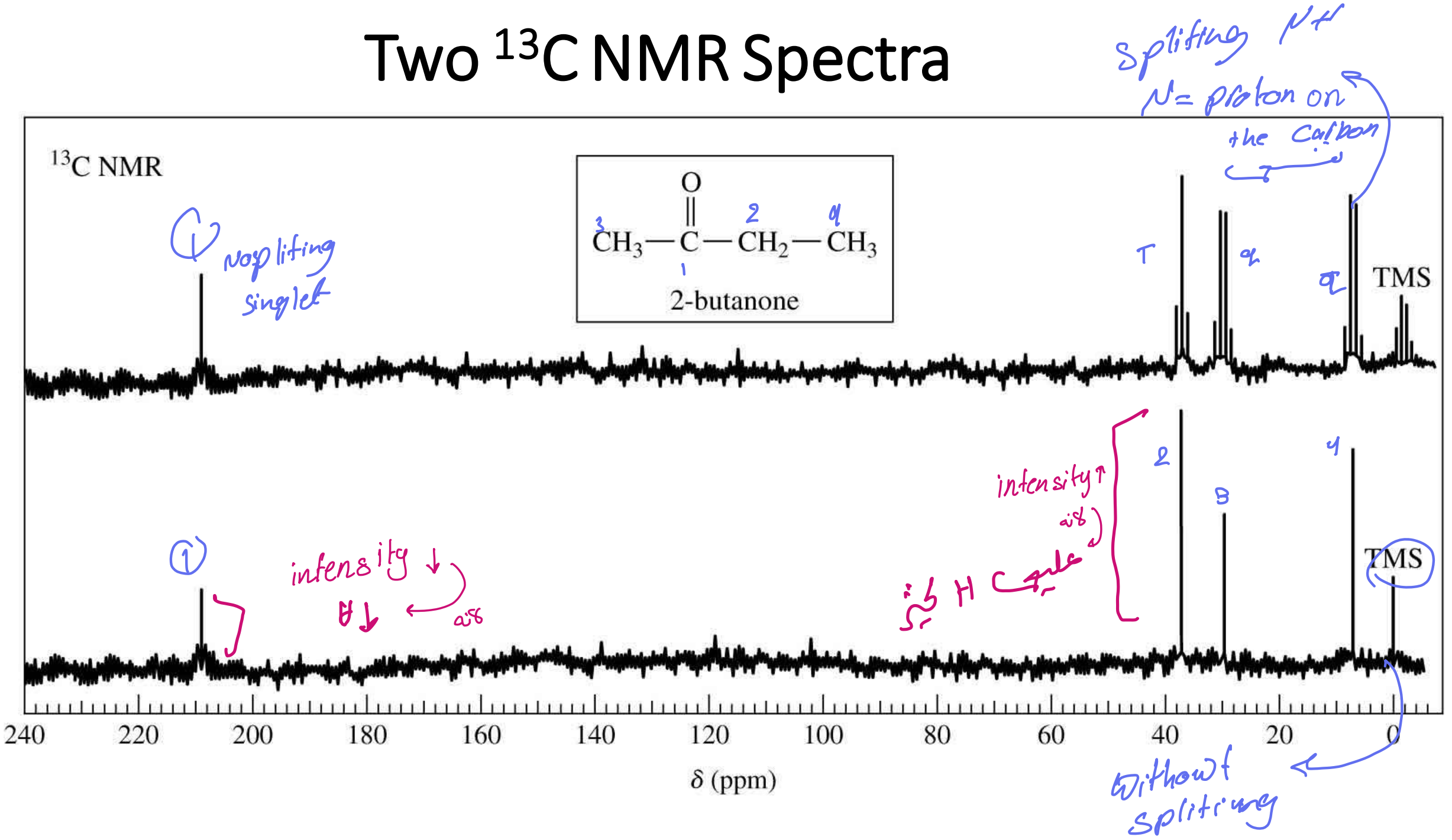

Electro negativ
Br
I
Type of carbon
Chemical shift (δ) ppm
RCH2Br
20-40
RCH2Cl
25-50
RCH2NH2
35-50
RCH2OH
50-65
RCH2OR
50-65
Type of carbon
Chemical shift (δ) ppm
RCOR
Carboxylic acid
160-185
RCR
Ketone
190-220
Aldehyde
اتجاه السحب متعاكس
تعتبر متشابهة
محمان مش فرق عن الكيتون

- **^{13}C Chemical Shifts**
  - ➔ Just as in ^{1}H NMR spectroscopy, chemical shifts in ^{13}C NMR depend on the electron density around the carbon nucleus
    - Decreased electron density causes the signal to move downfield (*desheilding*)
    - Increased electron density causes the signal to move upfield (*sheilding*)

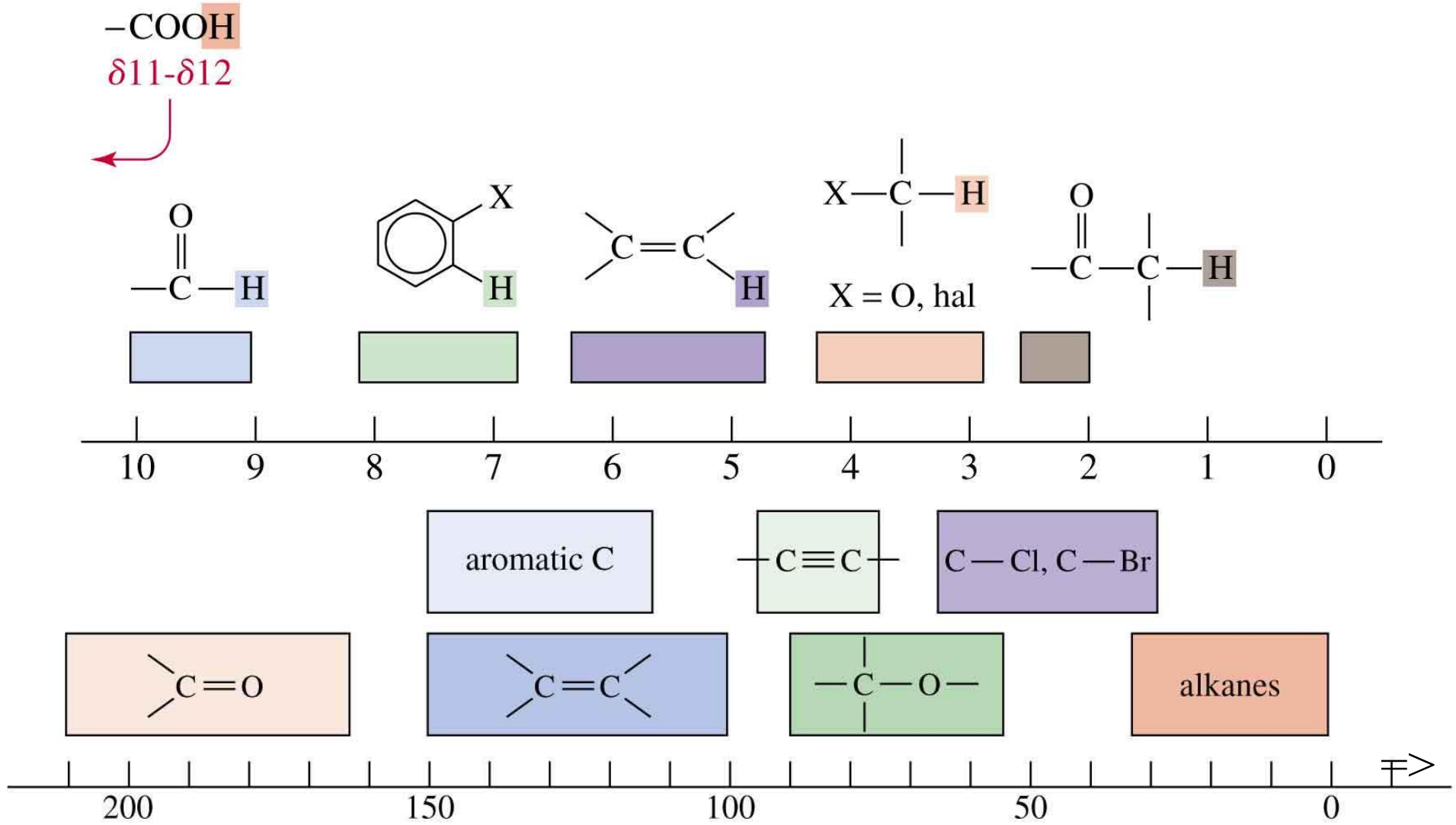


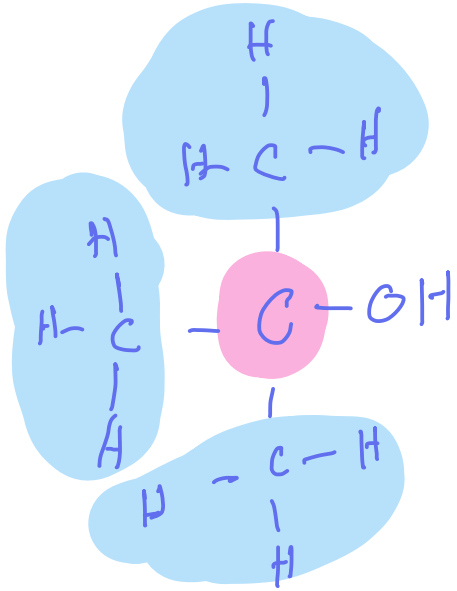
  - ➔ Because of the wide range of chemical shifts, it is rare to have two ^{13}C peaks coincidentally overlap
  - ➔ A group of 3 peaks at δ 77 comes from the common NMR solvent deuteriochloroform and can be ignored

Two ^{13}C NMR Spectra

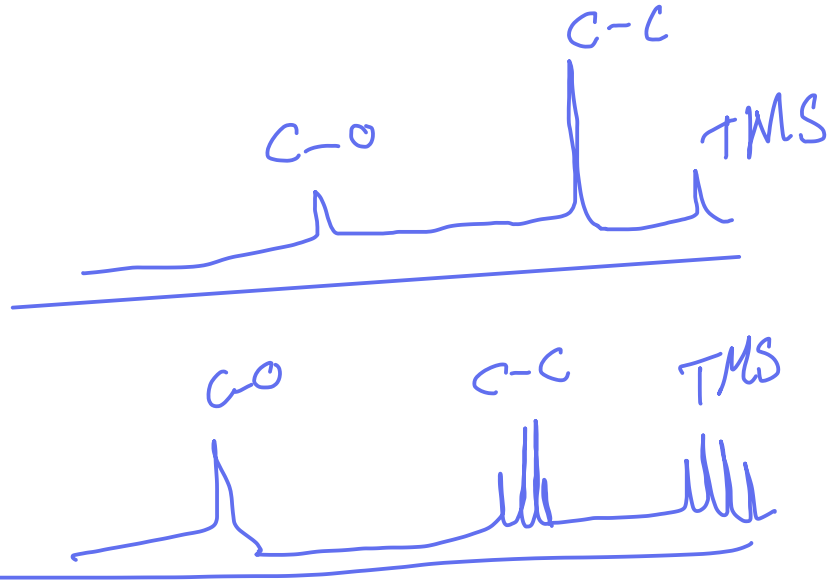


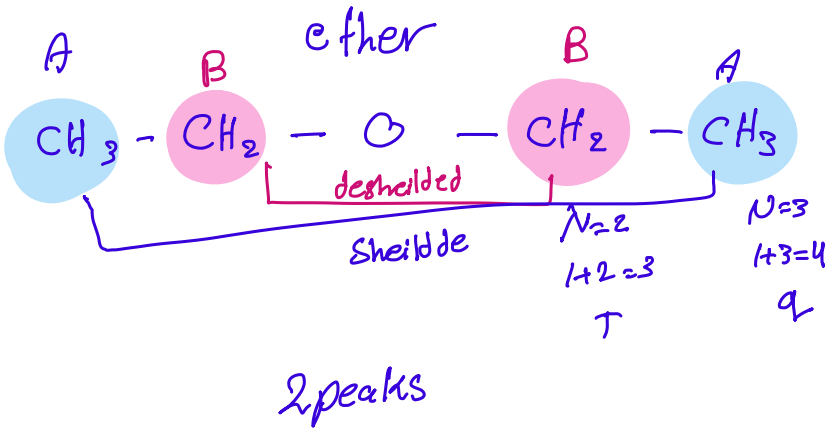
Hydrogen and Carbon Chemical Shifts



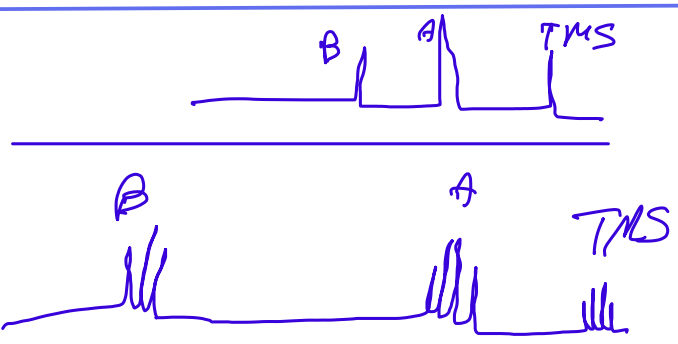


2peaks

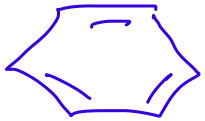




2peaks

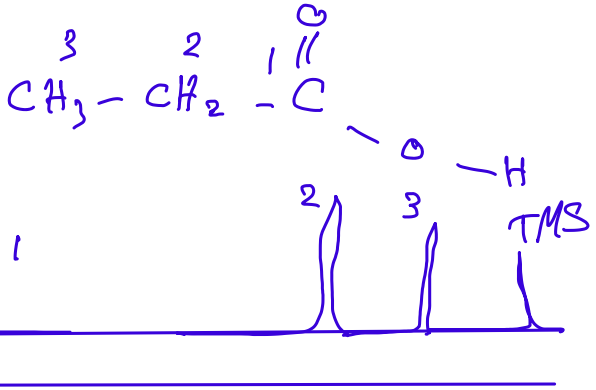


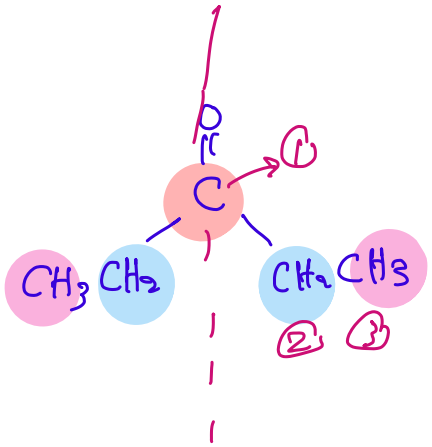
one peak



one peak

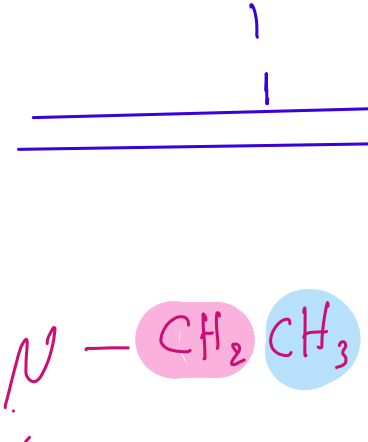
+ مثل داخل

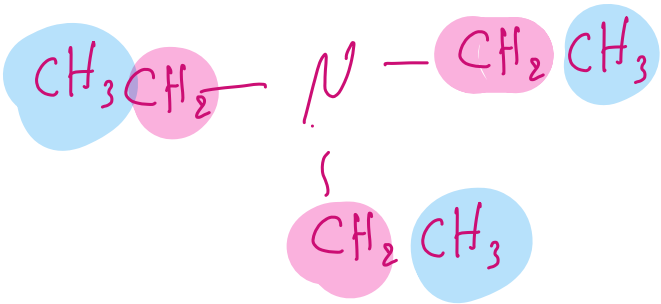




Symmetric

3 peaks





2 peaks