

COSTANTI DI ACCOPPIAMENTO

- ❑ L'accoppiamento è sempre reciproco:
se H_A è accoppiato con H_X anche H_X è accoppiato con H_A e $J_{AX} = J_{XA}$
- ❑ Le costanti di accoppiamento sono misurate in Hz
- ❑ I valori delle costanti di accoppiamento sono indipendenti da B_0 . L'accoppiamento spin-spin è un'interazione tra i momenti magnetici nucleari, che sono indipendenti dal campo magnetico applicato (dipendono da γ e da I)

COSTANTI DI ACCOPPIAMENTO H-H

DIPENDONO DA

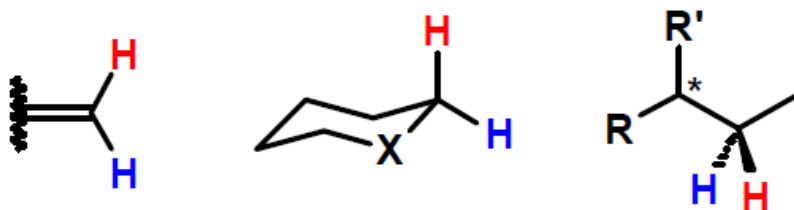
- 1. Ibridazione degli atomi di carbonio**
- 2. Angolo di legame e angolo torsionale**
- 3. Lunghezza di legame**
- 4. Presenza di doppi legami vicini**
- 5. Effetto di lone pair adiacenti**
- 6. Effetto di sostituenti**

¹J	positiva
²J	solitamente negativa
³J	positiva
⁴J	Positiva/negativa

ACCOPPIAMENTO GEMINALE ²J

²J H-H osservata fra protoni di un gruppo CH₂ quando essi sono chimicamente non equivalenti, cioè in tre casi principali:

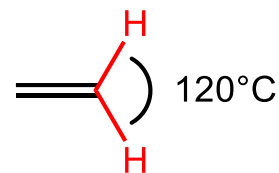
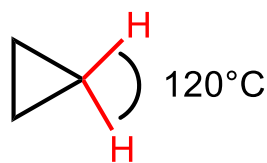
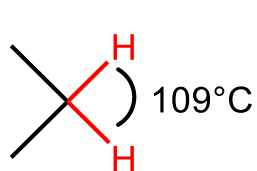
1. CH₂ olefinici
2. CH₂ inseriti in una struttura rigida che impedisce la libera rotazione
3. CH₂ diastereotopici per la presenza di un centro stereogenico



Le costanti geminali possono variare in un range piuttosto ampio (-17 +40 Hz). I fattori che principalmente influenzano questo tipo di costante sono:

-  **L'angolo di legame H-C-H**
-  **L'ibridazione del carbonio**
-  **Sostituenti**

Dipendenza dall'angolo di legame e dall'ibridazione



Maggiore l'angolo
maggiore la J

2J (Hz)

-12.4

- 3.9

+2.5

Aumento del carattere s

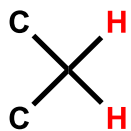
2J : può essere negativa o positiva

$|^2J| \approx 12-15 \text{ Hz se } Csp^3; 2-4 \text{ Hz se } Csp^2$

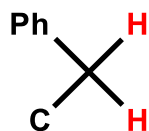
Dipendenza dai sostituenti

Ibridazione sp^3 : valori molto variabili $^2J = -23 \div +43$ Hz

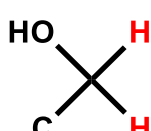
casi più comuni: $^2J = 10 \div 15$ Hz



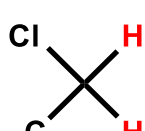
-12.4



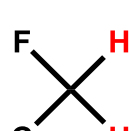
-14.5



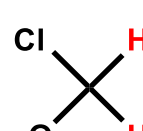
-10.8



-10.8



-9.6



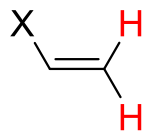
-7.5

Sostituenti elettronegativi in α : aumento della 2J (*diminuzione in valore assoluto*)

Dipendenza dai sostituenti

Ibridazione sp^2 : ${}^2J = 0 \div 4$ Hz

Sostituenti elettronegativi in β : diminuzione della J

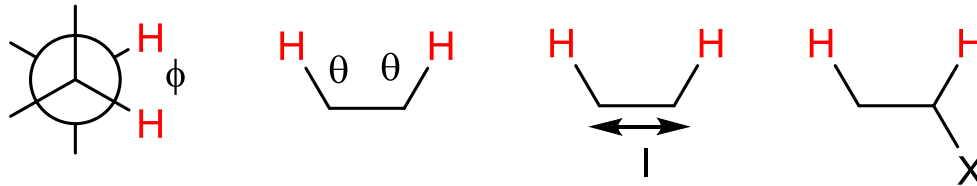


X	2J	E
Li	+7.1	1.0
H	+2.5	2.2
Cl	-1.4	3.0
OR	-2.0	3.5
F	-3.2	4.0

ACCOPPIAMENTO VICINALE $^3J(\text{H,H})$

La costante vicinale è influenzata da:

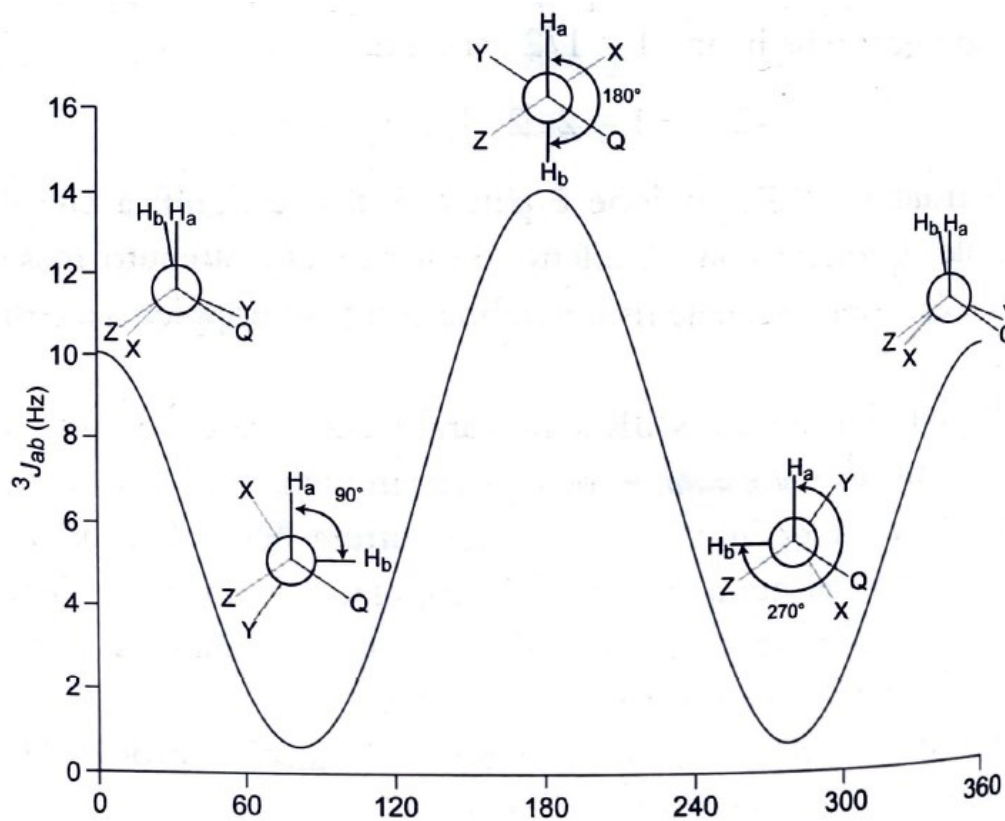
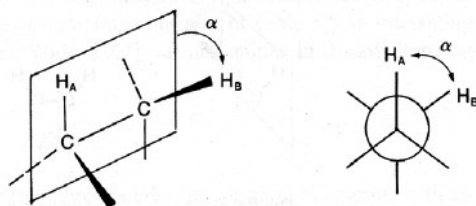
- Angolo diedro ϕ (Legge di Karplus)
- Sostituenti X
- Angolo di legame θ
- Lunghezza di legame l



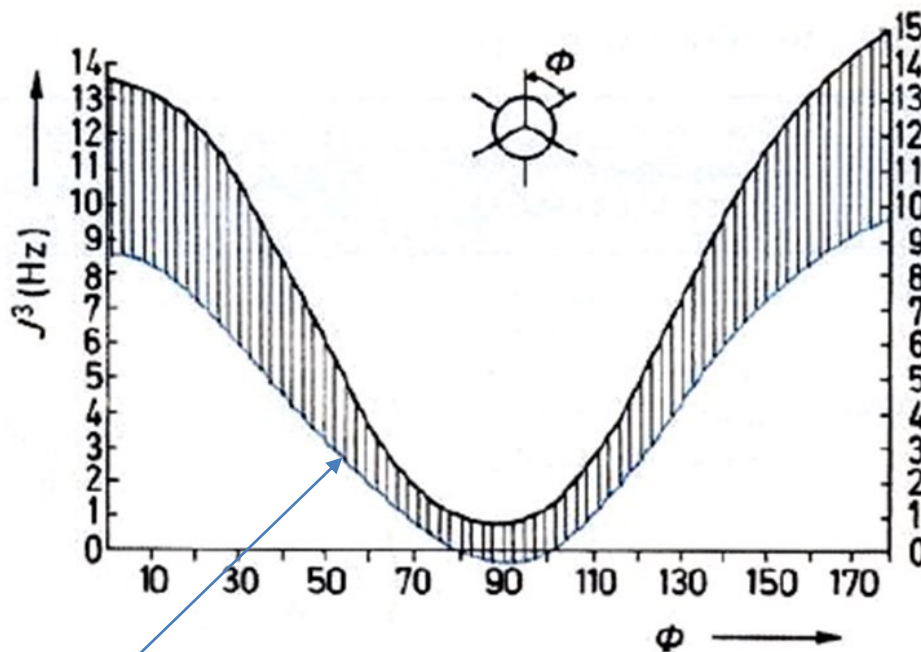
Dipendenza dall'angolo diedro LEGGE DI KARPLUS

$$^3J = A + B\cos\phi + C\cos^2\phi$$

A, B, C costanti empiriche



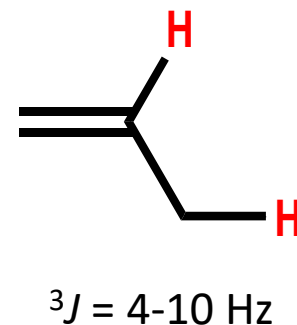
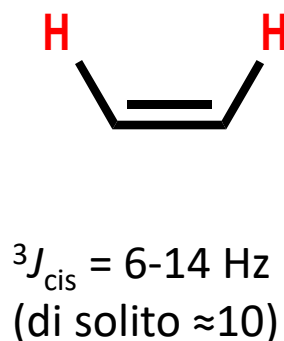
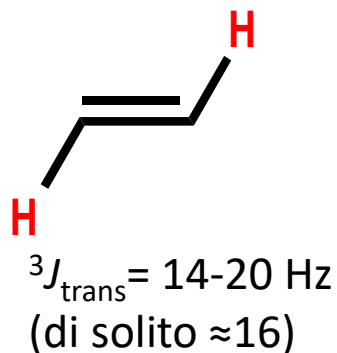
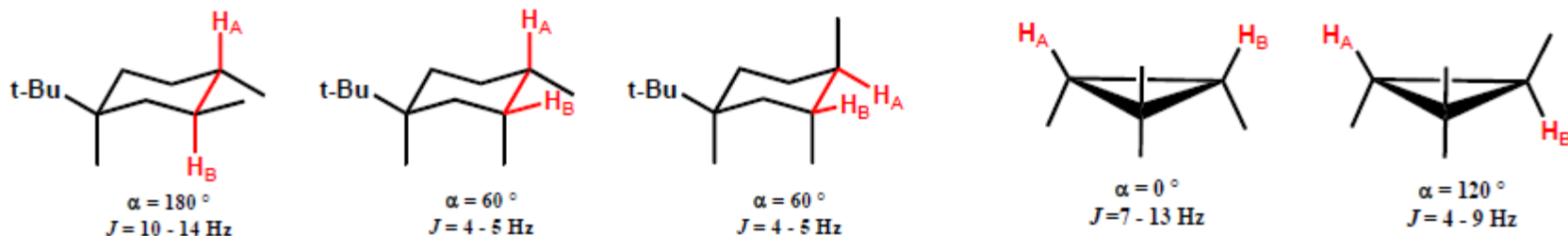
Dipendenza dall'angolo diedro LEGGE DI KARPLUS



$$^3J = A + B\cos\phi + C\cos^2\phi$$

Dipendenza dall'angolo diedro

Andamenti costanti previsti dalla legge di Karplus



Dipendenza dai sostituenti

Per catene alchiliche in libera rotazione la J vicinale dipende dall'elettronegatività di X secondo la seguente equazione empirica

$$^3J(\text{H,H}) = 8.0 - 0.8(E_X - E_H)$$

X-CH ₂ -CH ₃		
X	3J	E
Li	8.4	1.0
H	8.0	2.2
Ph	7.6	
CH ₃	7.3	2.5
Cl	7.2	3.0
OR	7.0	3.5

1. Trend: sostituenti elettronegativi riducono la $^3J(\text{H,H})$ ma non di molto

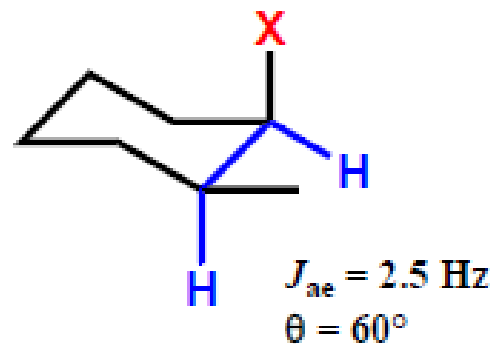
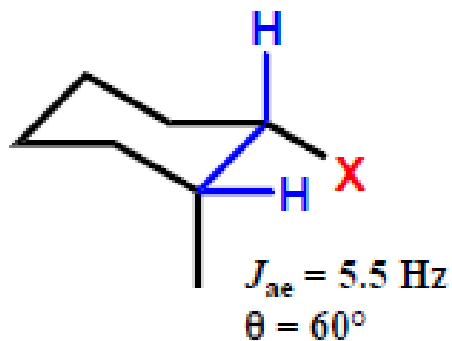
2. Attenzione: Si osserva sempre una J mediata su tutte le conformazioni!

 R-CH₂-CH₃ $^3J = 7.1 - 7.3$
DA RICORDARE

$$^3J = \frac{^3J(60^\circ) + ^3J(180^\circ) + ^3J(300^\circ)}{3} \approx 7.0 \text{ Hz}$$

Dipendenza dai sostituenti

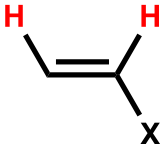
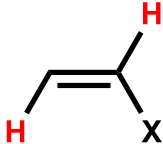
Nei sistemi ciclici c'è una dipendenza dall'orientazione

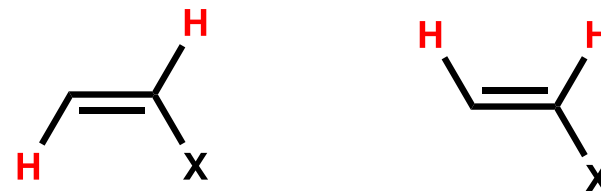


X= OH, OAc, Br

Dipendenza dai sostituenti

Negli alcheni

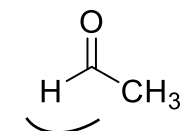
			
X	$^3J_{\text{cis}}$	$^3J_{\text{trans}}$	E
Li	19.3	23.9	1.0
H	11.6	19.1	2.2
Cl	7.3	14.6	3.0
OR	7.1	15.2	3.5
F	4.7	12.8	4.0



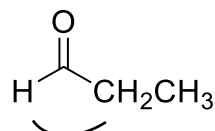
$$^3J_{\text{cis}} = 11.7-4.7 (E_X-E_H)$$

$$^3J_{\text{trans}} = 19.0-3.3 (E_X-E_H)$$

Nelle aldeidi



$$^3J = 2.9$$

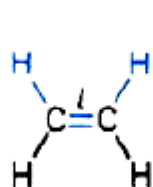
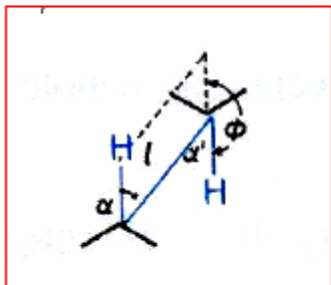


$$^3J = 1.4$$

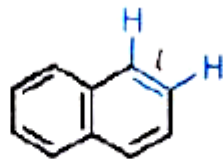
Nelle aldeidi le J vicinali sono molto piccole, spesso = 0

Dipendenza dalla lunghezza di legame e dall'angolo di legame

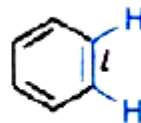
- Angolo di legame
- Lunghezza di legame



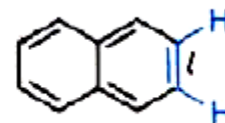
3J : 11,6 Hz



8,3 Hz



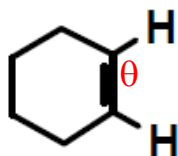
7,54 Hz



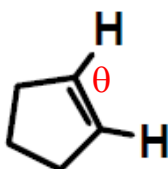
6,9 Hz

————— distanza l crescente
(ordine di legame π decrescente) —————>

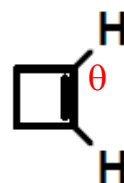
Dipendenza dagli angoli di legame



8.8-10.5 Hz



5.1-7.0 Hz



2.4-4.0 Hz



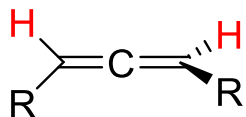
0.5-2.0 Hz

—————> Angolo crescente

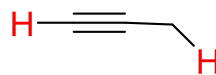
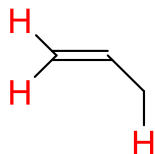
Long range coupling

4J

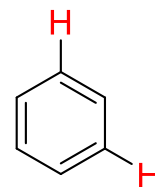
Sistemi insaturi



$^4J = 3 \text{ Hz}$ allenica

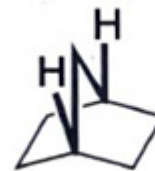
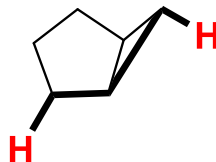
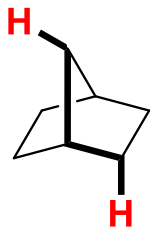
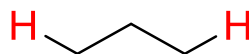


$^4J = 0-3 \text{ Hz}$ alilica e propargilica



$^4J = 1-3 \text{ Hz}$ meta

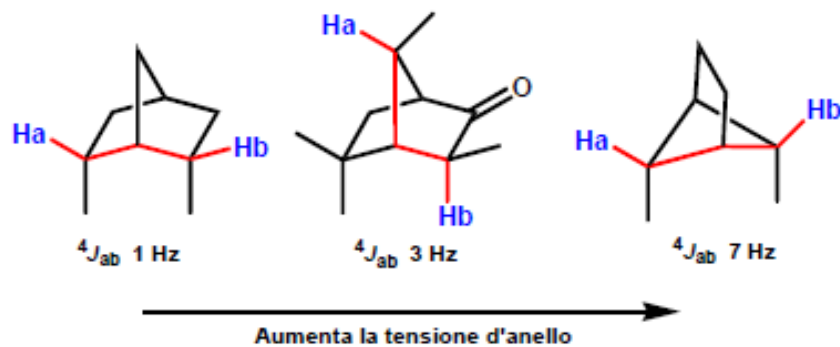
Sistemi saturi rigidi a W



$^4J = 0-3 \text{ Hz}$

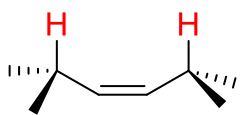
Long range coupling

Sistemi saturi: a W

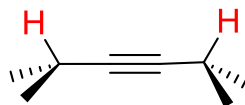
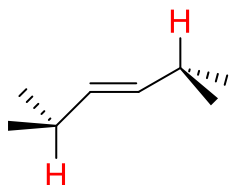


Long range coupling

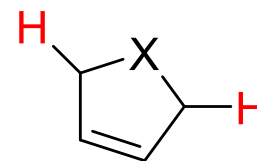
5J



$$^5J = 0-2 \text{ Hz}$$

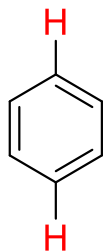


$$^5J = 2.6 \text{ Hz}$$

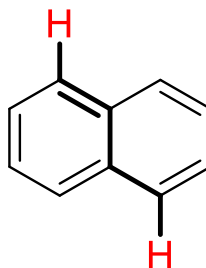


$$^5J \text{ fino a } 7\text{Hz}$$

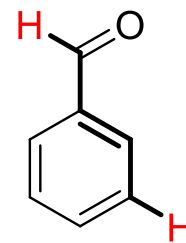
Omoallilica



$$^5J = 0-1 \text{ Hz} \quad \text{para}$$



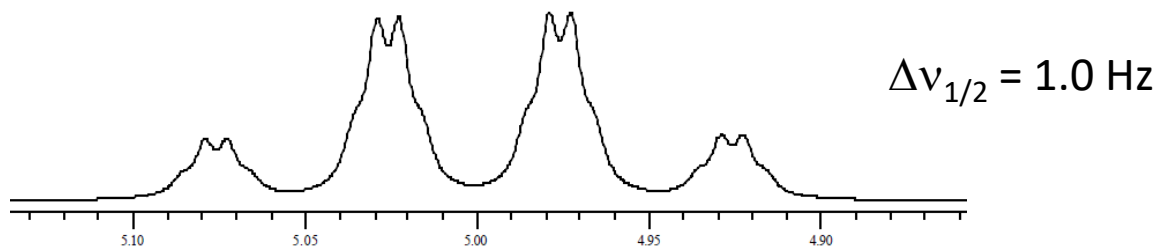
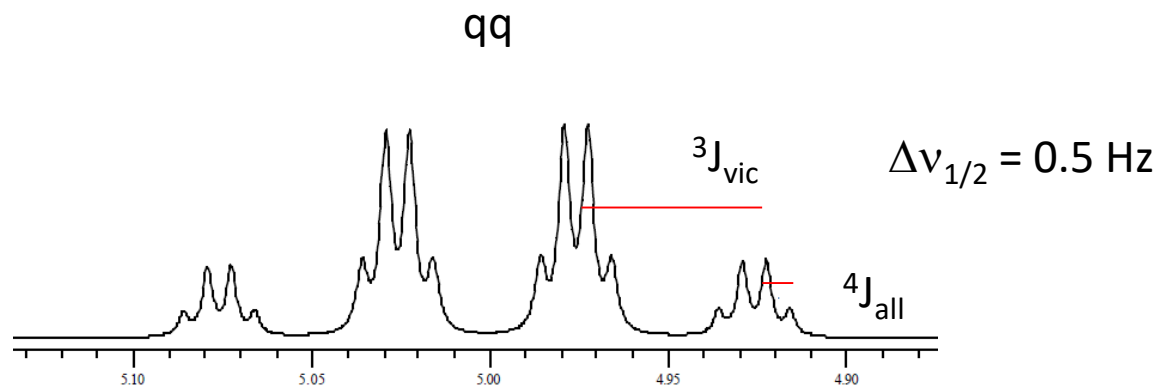
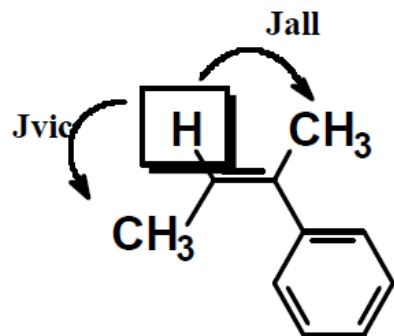
$$^5J = 0.8 \text{ Hz}$$



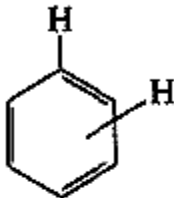
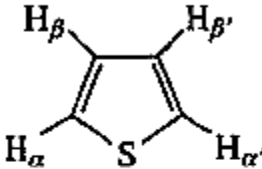
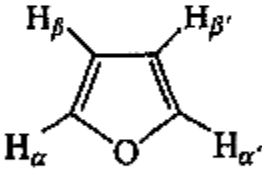
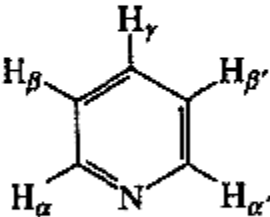
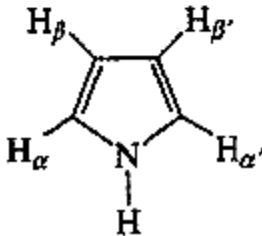
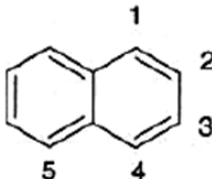
$$^5J = 0.4 \text{ Hz}$$

$4J$, $5J$

Richiedono grande risoluzione



ACCOPPIAMENTI AROMATICI ED ETEROAROMATICI

Type		Typical Value (Hz)	Range (Hz)	Type		Range (Hz)
	3J <i>ortho</i> 4J <i>meta</i> 5J <i>para</i>	8 3 <1	6-10 1-4 0-2		3J $\alpha\beta$ 4J $\alpha\beta'$ 4J $\alpha\alpha'$ 3J $\beta\beta'$	4.6-5.8 1.0-1.5 2.1-3.3 3.0-4.2
	3J $\alpha\beta$ 4J $\alpha\beta'$ 4J $\alpha\alpha'$ 3J $\beta\beta'$		1.6-2.0 0.3-0.8 1.3-1.8 3.2-3.8		3J $\alpha\beta$ 4J $\alpha\gamma$ 5J $\alpha\beta'$ 4J $\alpha\alpha'$ 3J $\beta\gamma$ 4J $\beta\beta'$	4.9-5.7 1.6-2.0 0.7-1.1 0.2-0.5 7.2-8.5 1.4-1.9
	3J $\alpha\beta$ 4J $\alpha\beta'$ 4J $\alpha\alpha'$ 3J $\beta\beta'$		2.0-2.6 1.0-1.5 1.8-2.3 2.8-4.0			

$$^3J_{1,2} = 8.3 - 9.1 \text{ Hz}$$

$$^3J_{2,3} = 6.1 - 6.9 \text{ Hz}$$

$$^4J_{1,3} = 1.2 - 1.6 \text{ Hz}$$

$$^5J_{1,4} = 0 - 1.0 \text{ Hz}$$

$$^5J_{1,5} = 0 - 1.5 \text{ Hz}$$