

# Notation for Spin Systems

Capital letters A, B, C, M, A, X, Y, .....

➤ Same letter = same chemical shift ( $A_3, B_2, X_6, \dots$ )

➤ Different letters = different chemical shifts

Letters close in the alphabet (A, B, C, ...)

J [Hz] of the same magnitude as  $\Delta\nu$  [Hz]

Letters separated in the alphabet (A, M, X, ...)

large separation of chemical shifts

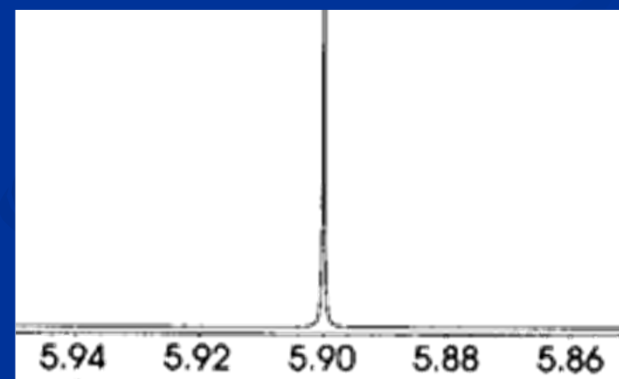
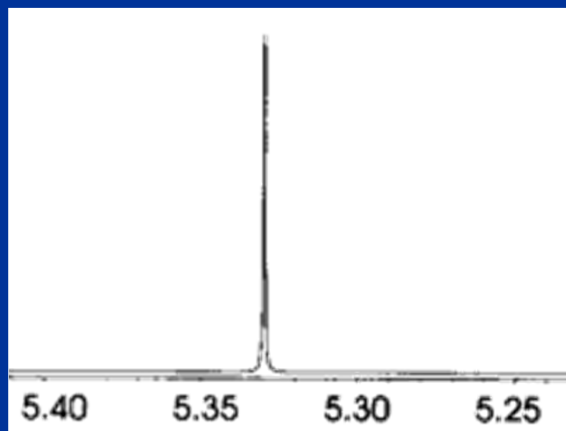
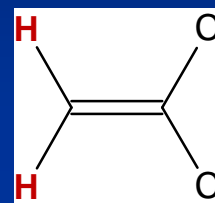
-different nuclei ( $^1\text{H}, ^{31}\text{P}, ^{195}\text{Pt}, \dots$ )

-same nuclei but  $\Delta\nu$  [Hz] much larger than J

!!  $\Delta\nu$  [Hz] depends on  $B_0$  !!

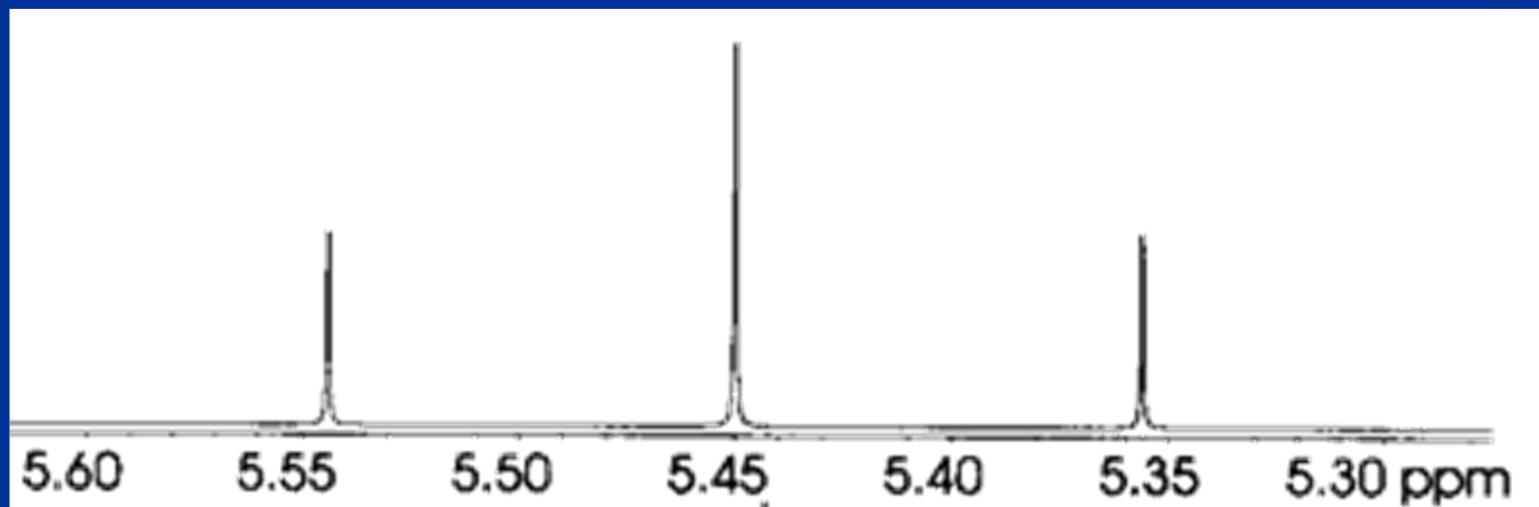
# Notation for Spin Systems

➤ Same letter = same chemical shift ( $A_3$ ,  $B_2$ ,  $X_6$ , ...)



# Notation for Spin Systems

➤ Different letters = different chemical shifts



# Notation for Spin Systems

Two situations:

a) Complete equivalence =

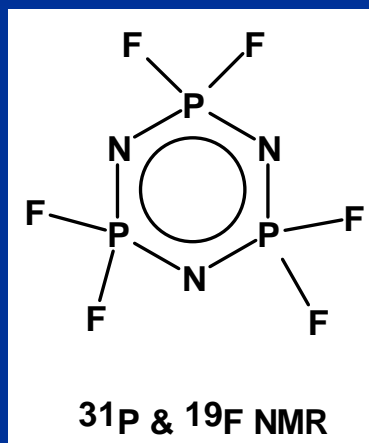
Chemical shift equivalence (isochronous nuclei)  
+ magnetic (spin-coupling) equivalence (isotachous)

Magnetic equivalence = **each member of one group of spins is coupled equally to all members of any other group**

$A_2B_2, A_2X_2, \dots$

# Notation for Spin Systems

b) Chemical shift equivalence, magnetic **INEquivalence**  
 $AA'BB'$ ,  $AA'XX'$ ,  $AA'A''XX'X''$ , ....



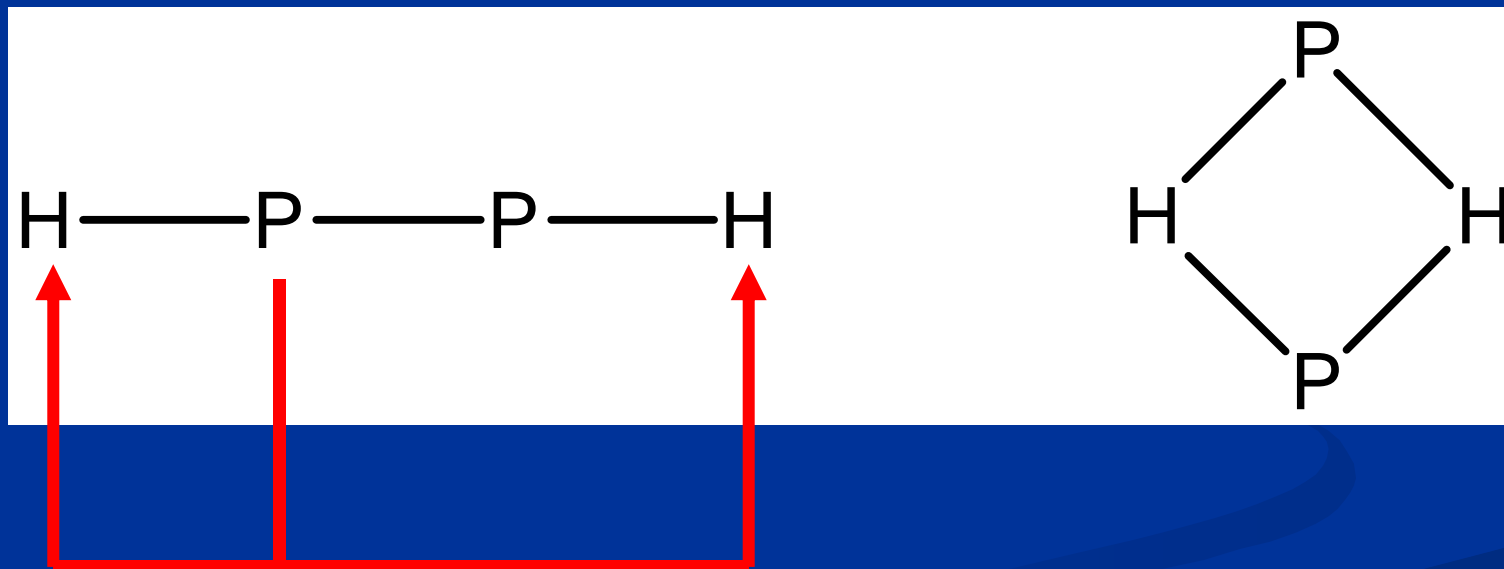
$AA'A''XX'X''X'''X^4X^5$

$[A[X]_2]_3$

# Magnetic Inequivalence

$AA'XX'$

$A_2X_2$



# Prime vs. Bracket Notation

$AA'BB'$

$[AB]_2$

$A_2B_2$

$[A_2B_2]$

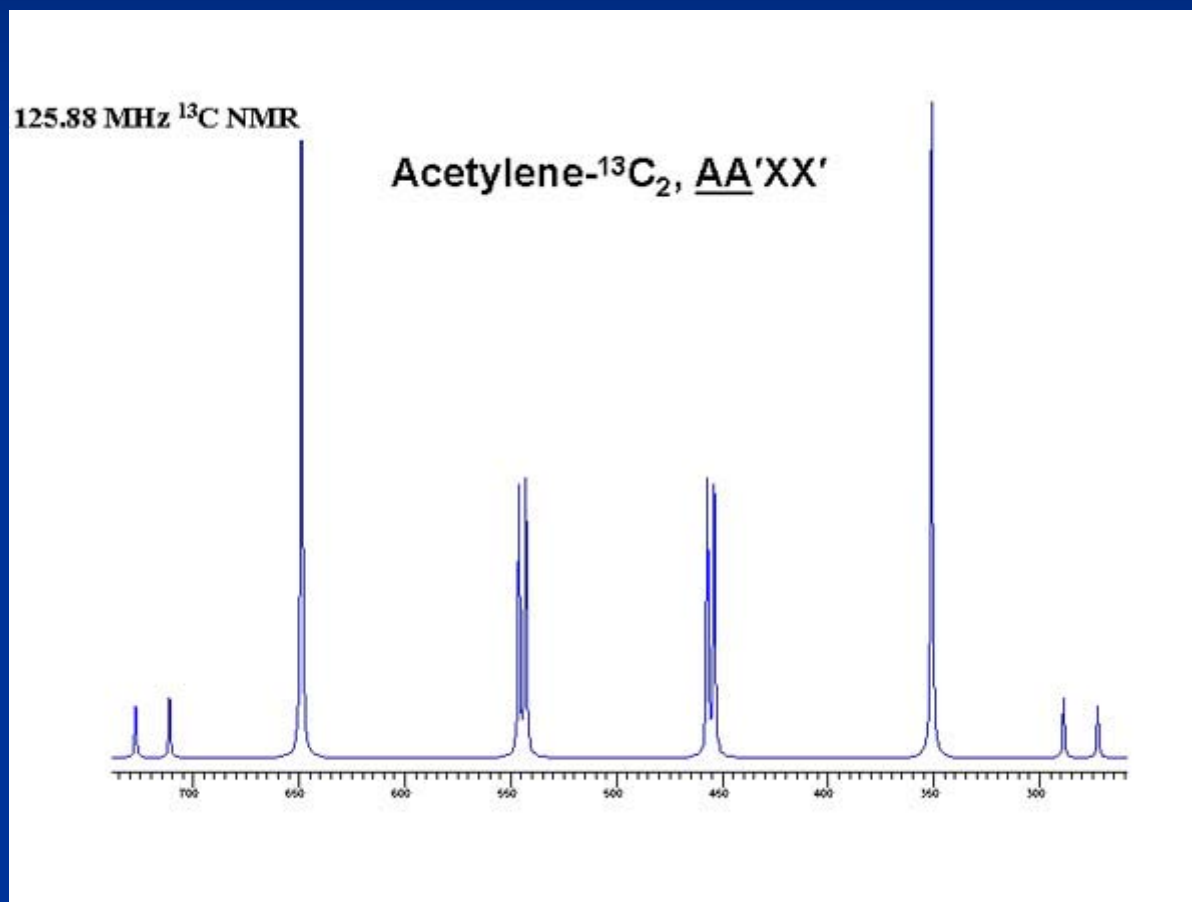
$AA'BXX'$

$[AX]_2B$

$AA'X_3X_3'$

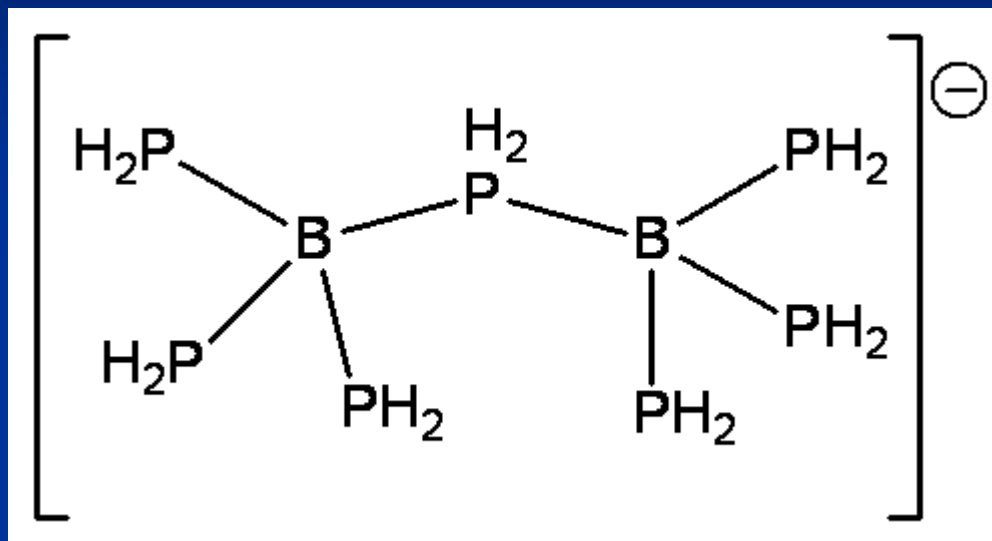
$[AX_3]_2$

# Magnetic Inequivalence





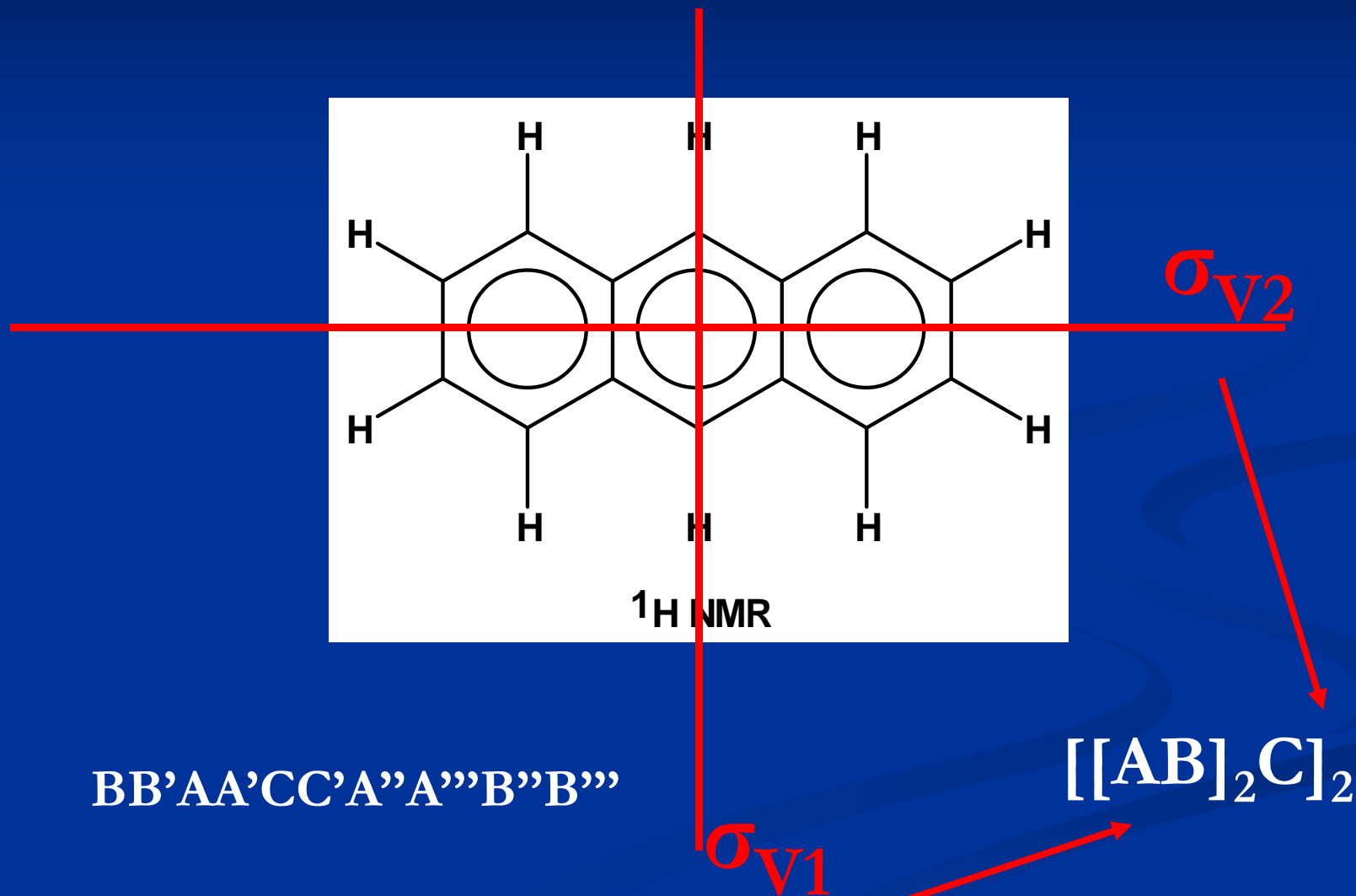
# Magnetic Inequivalence



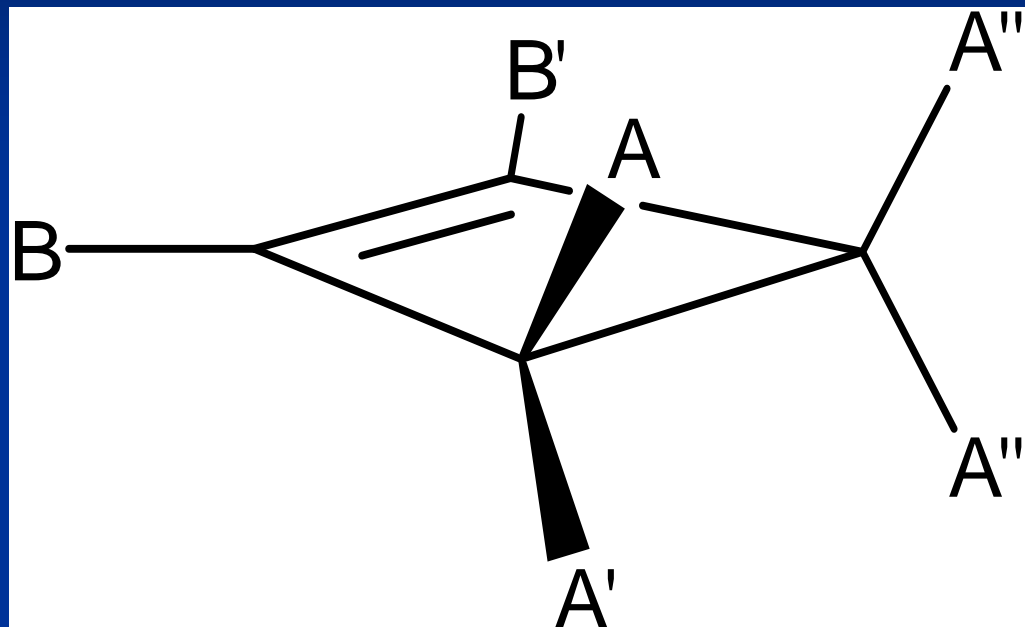
# Bracket Notation

- Square brackets with subscript indicate repeated symmetry-related magnetically inequivalent groups of nuclei, e.g.  $[AB]_2$
- Square bracket without subscript indicate magnetic equivalence of isochronous nuclei inside, e.g.  $[A_6]$
- Each bracket represents a specific symmetry operation (see anthracene)
- Append a point group symbol to avoid ambiguity
- Free rotation – apply Mortimer rule = the most symmetrical conformer

# Notation for Spin Systems



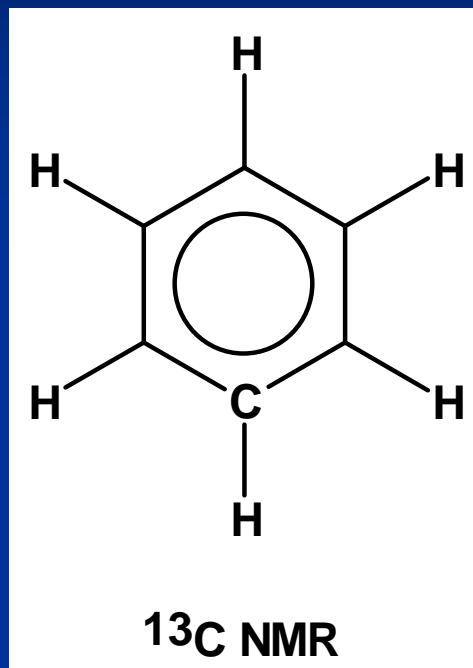
# Notation for Spin Systems



Ring plane

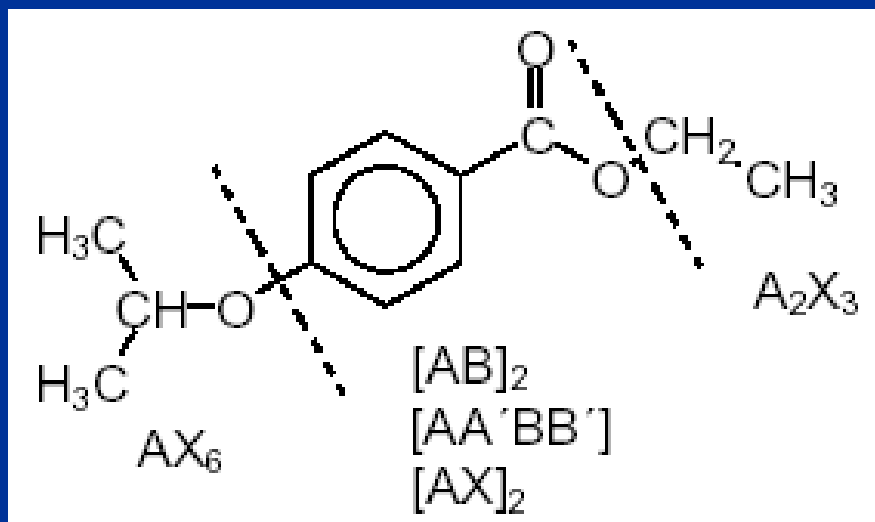
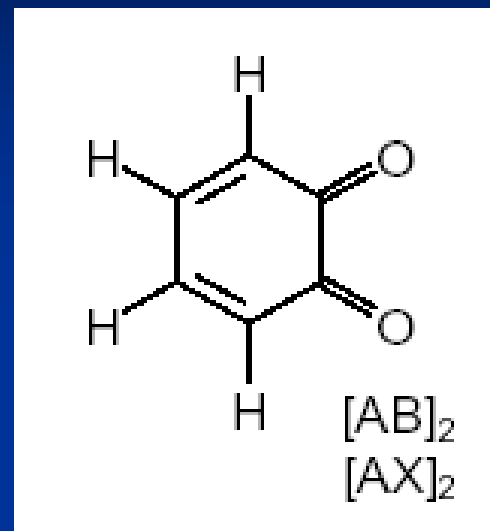
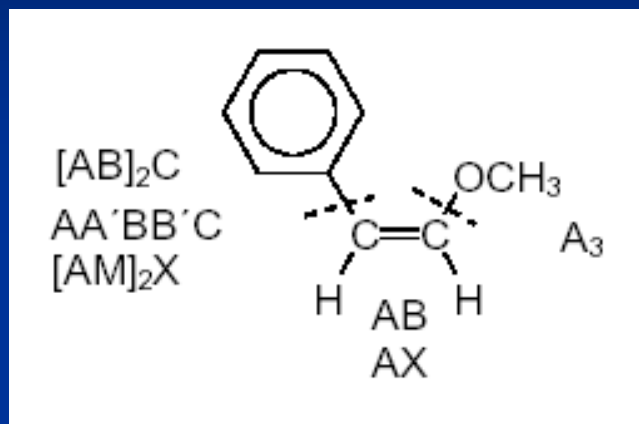
Plane perpendicular to ring

# Notation for Spin Systems



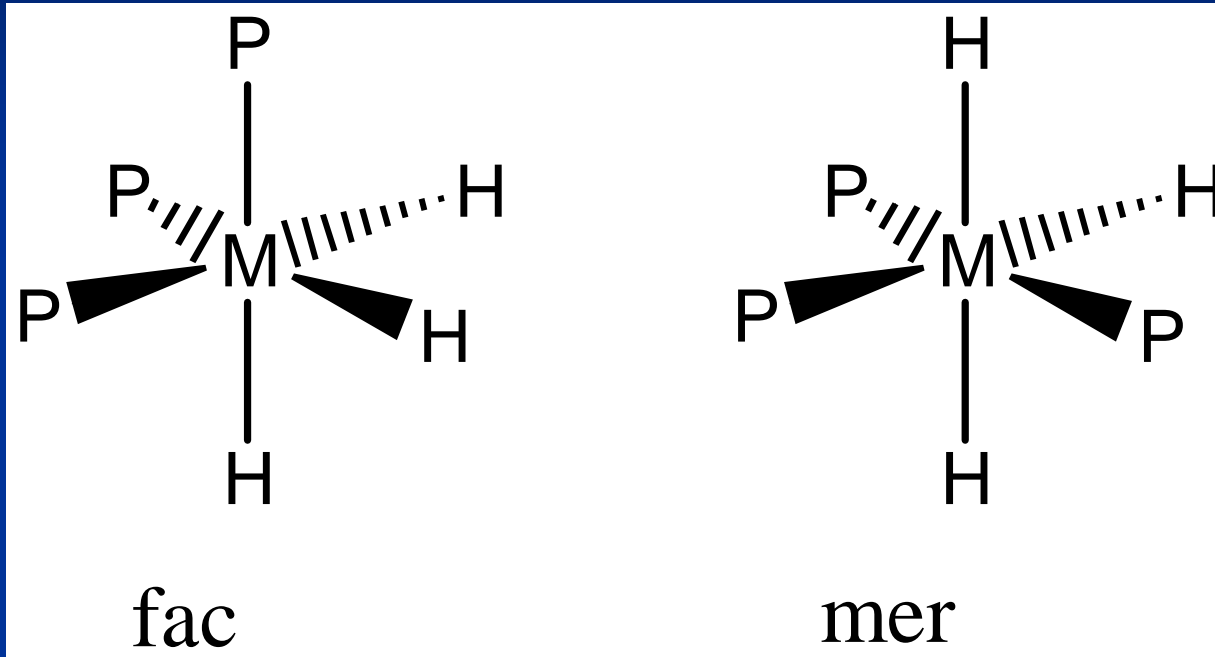
considering isotope shift:  $A[BC]_2DX$

# Spin Systems in $^1\text{H}$ NMR



When separated by more than 3 bonds, the spin systems can be considered separately (with exceptions)

# Spin Systems



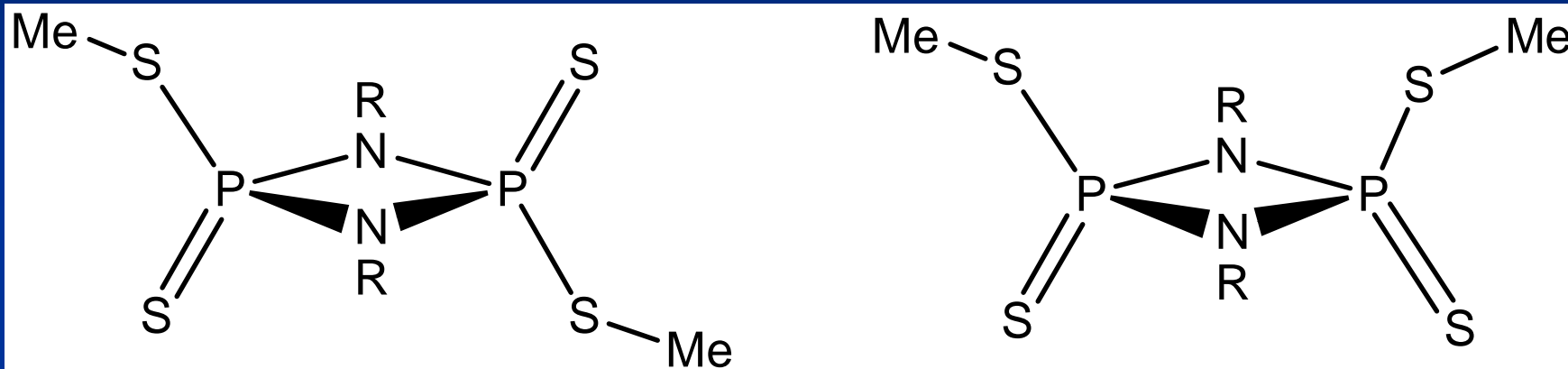
AA'A''XX'X''

AB<sub>2</sub>XY<sub>2</sub>

$${}^3J_{\text{PH}}(\text{cis}) = 10 - 40 \text{ Hz}$$

$${}^3J_{\text{PH}}(\text{trans}) = 80 - 150 \text{ Hz}$$

# Spin Systems

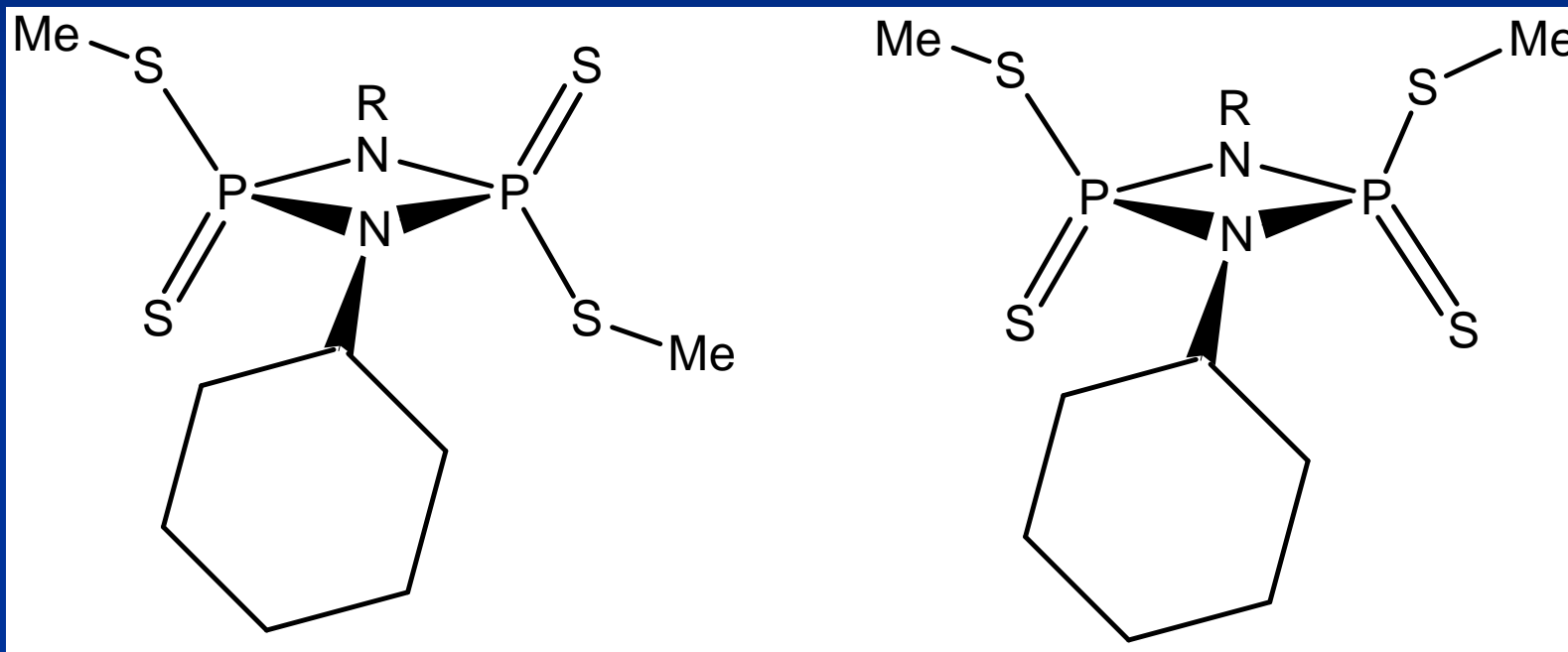


$^1\text{H}, ^{31}\text{P}$

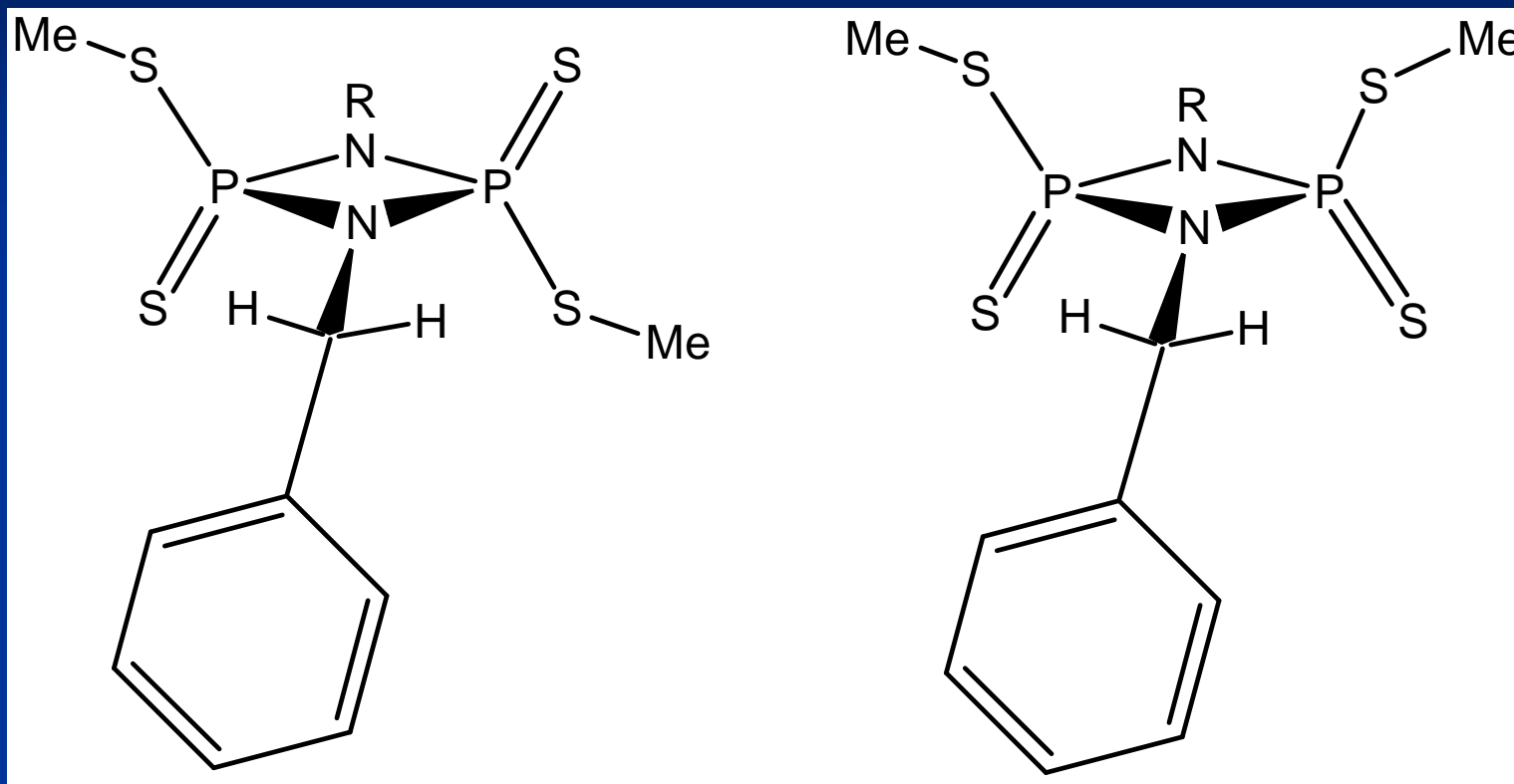
$^{13}\text{C}, ^{31}\text{P}$



# Spin Systems



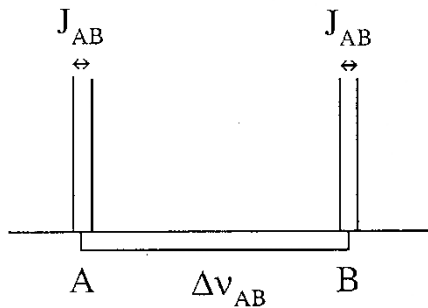
# Spin Systems



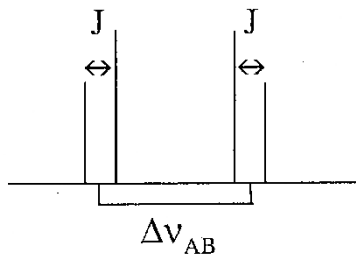
$^1\text{H}$ ,  $^{31}\text{P}$

# AB System

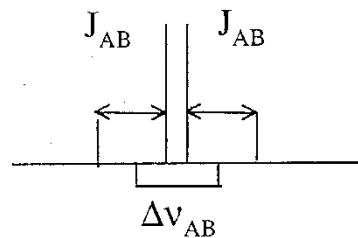
## Spin-spin coupling



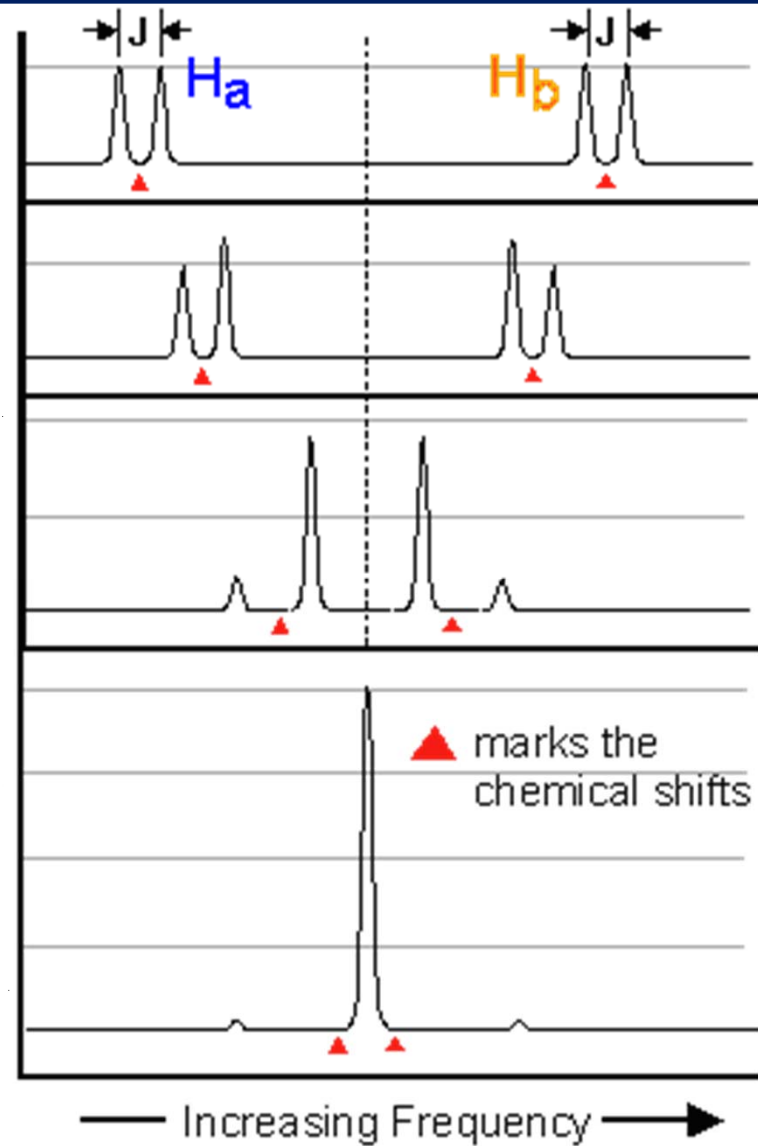
$$\frac{\Delta v_{AB}}{J_{AB}} \gg 1$$



$$\frac{\Delta v}{J} > 1$$



$$\frac{\Delta v}{J} < 1$$



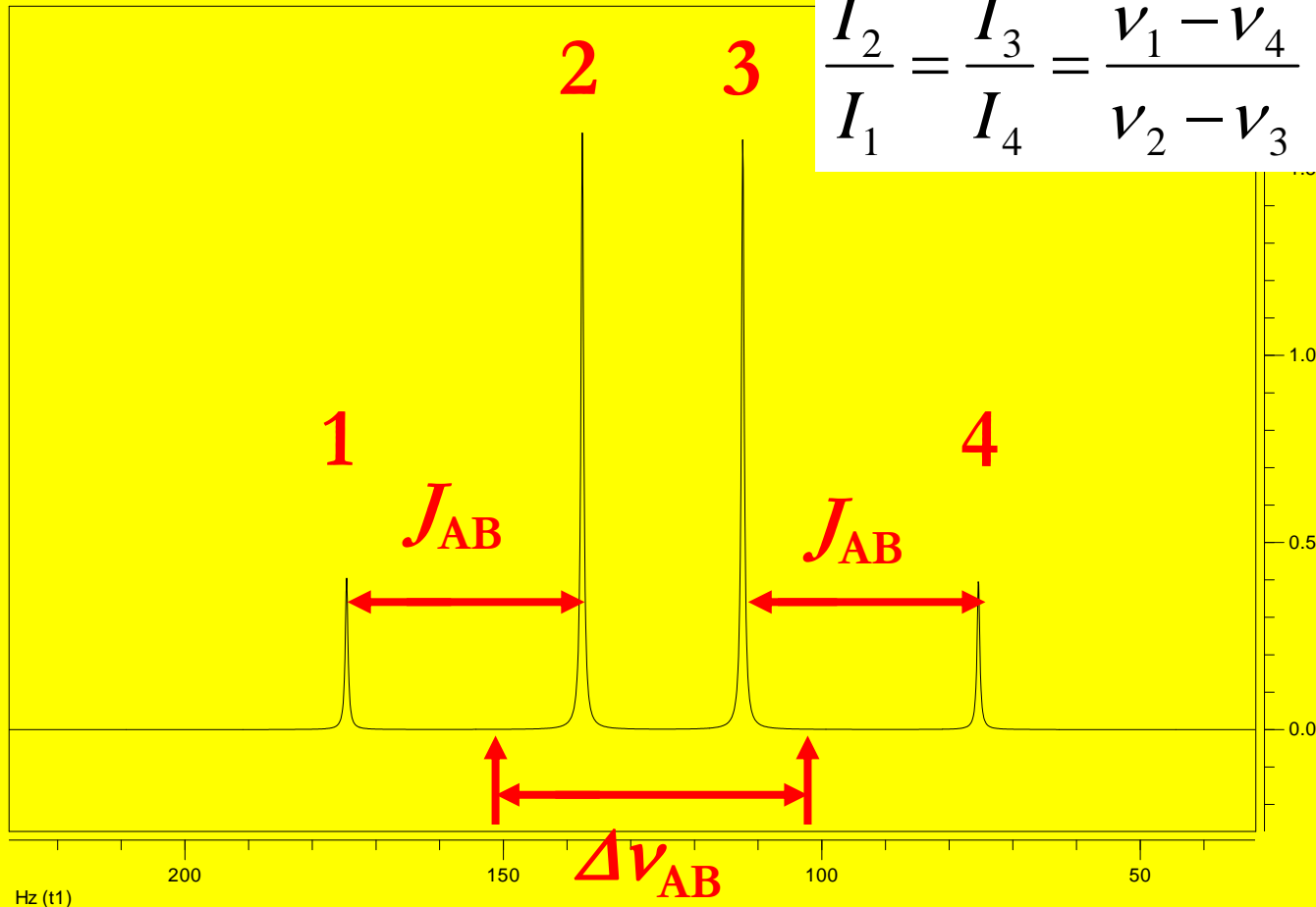
# AB System

The simplest higher-order spin system

$$J_{AB} = \nu_1 - \nu_2 = \nu_3 - \nu_4$$

$$\Delta\nu_{AB} = \nu_A - \nu_B = \sqrt{(\nu_1 - \nu_4)(\nu_2 - \nu_3)}$$

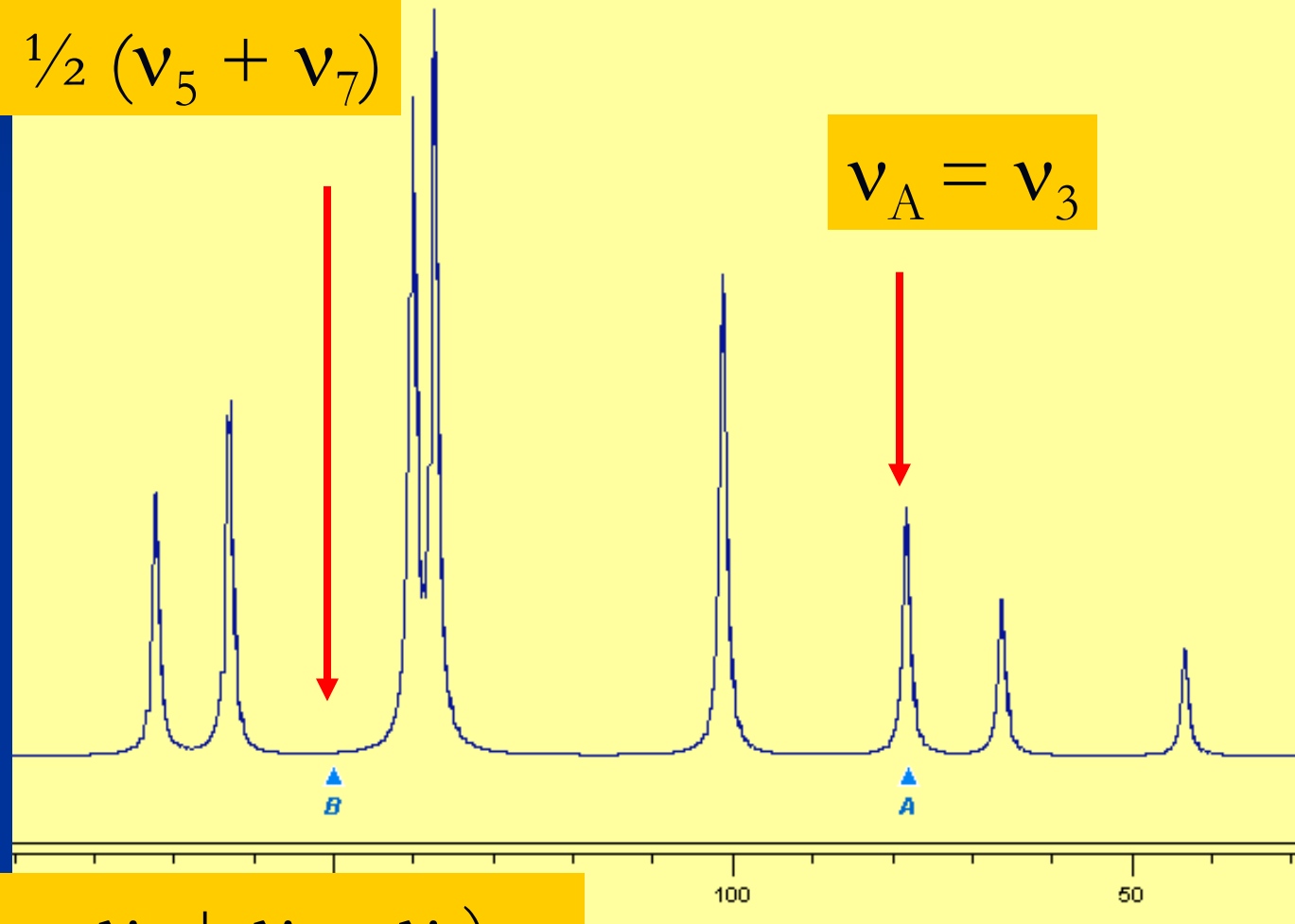
$$\frac{I_2}{I_1} = \frac{I_3}{I_4} = \frac{\nu_1 - \nu_4}{\nu_2 - \nu_3}$$



# AB<sub>2</sub> Spin System

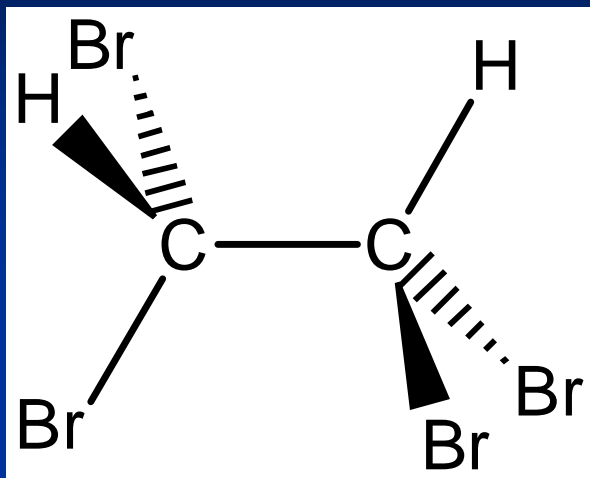
$$\nu_B = \frac{1}{2} (\nu_5 + \nu_7)$$

$$\nu_A = \nu_3$$

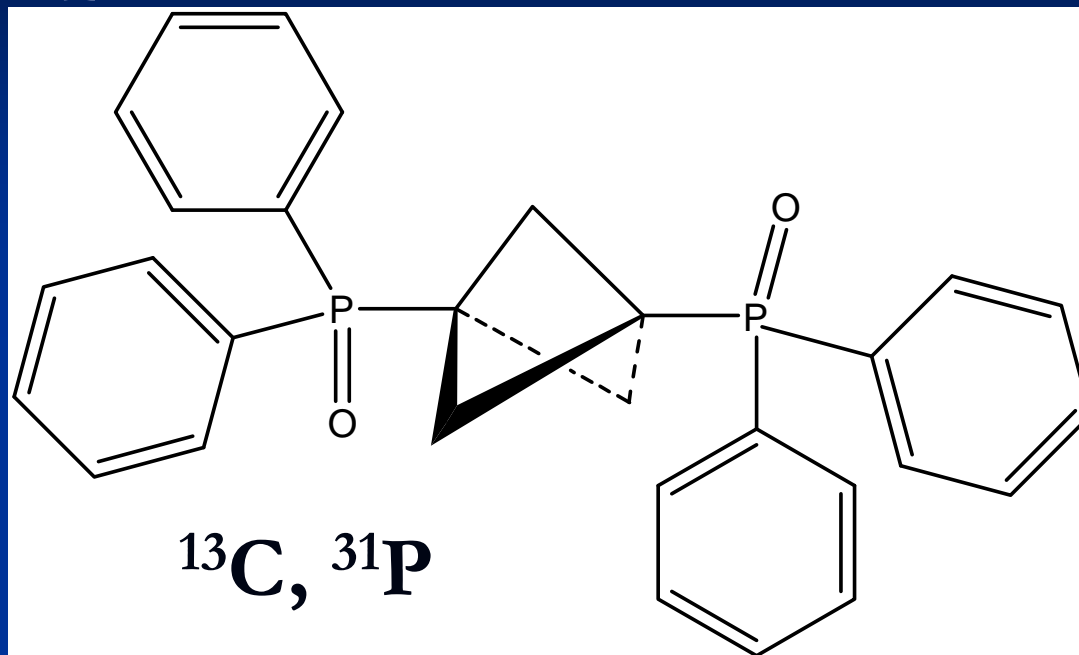


$$J_{AB} = \frac{1}{3}(\nu_1 - \nu_4 + \nu_6 - \nu_8)$$

# ABX Spin System



$^1\text{H}, ^{13}\text{C}$

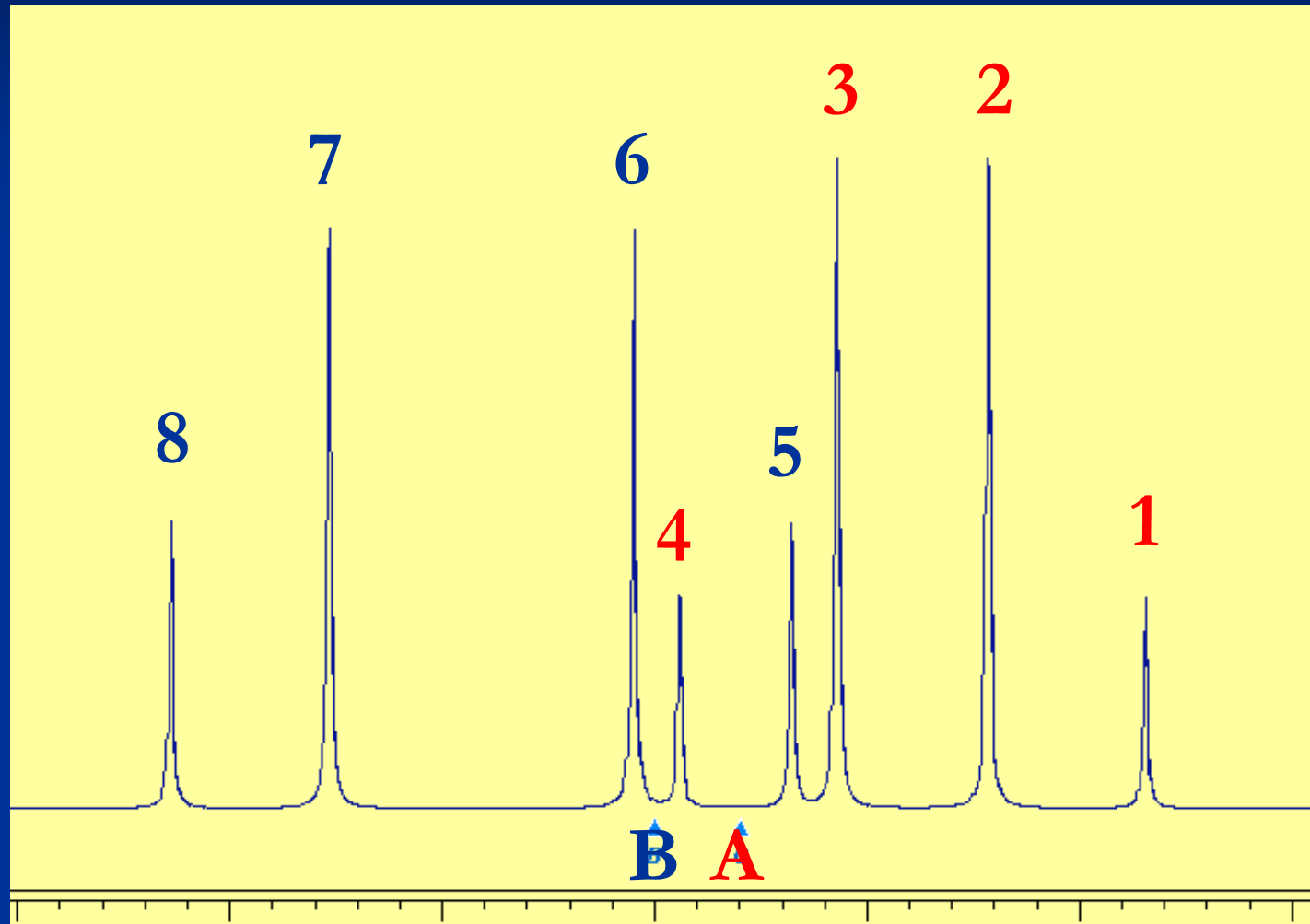


$^{13}\text{C}, ^{31}\text{P}$

AB part = 2 AB pseudoquartets = 8 lines

X part = 6 lines

# AB Part of the ABX Spin System



# ABX Spin System

$$J_{AB} = \nu_2 - \nu_1 = \nu_4 - \nu_3 = \nu_6 - \nu_5 = \nu_8 - \nu_7$$

$$J_{AX} + J_{BX} = \nu_{12} - \nu_9$$

$$\Delta \nu_{AB} = \nu_A - \nu_B$$

$$L = \frac{1}{2} (J_{AX} - J_{BX})$$

$$N = \frac{1}{2} (J_{AX} + J_{BX})$$

$$\Delta \nu_{AB}^{RED} = \Delta \nu_{AB} + L = \sqrt{(\nu_4 - \nu_1)(\nu_3 - \nu_2)}$$

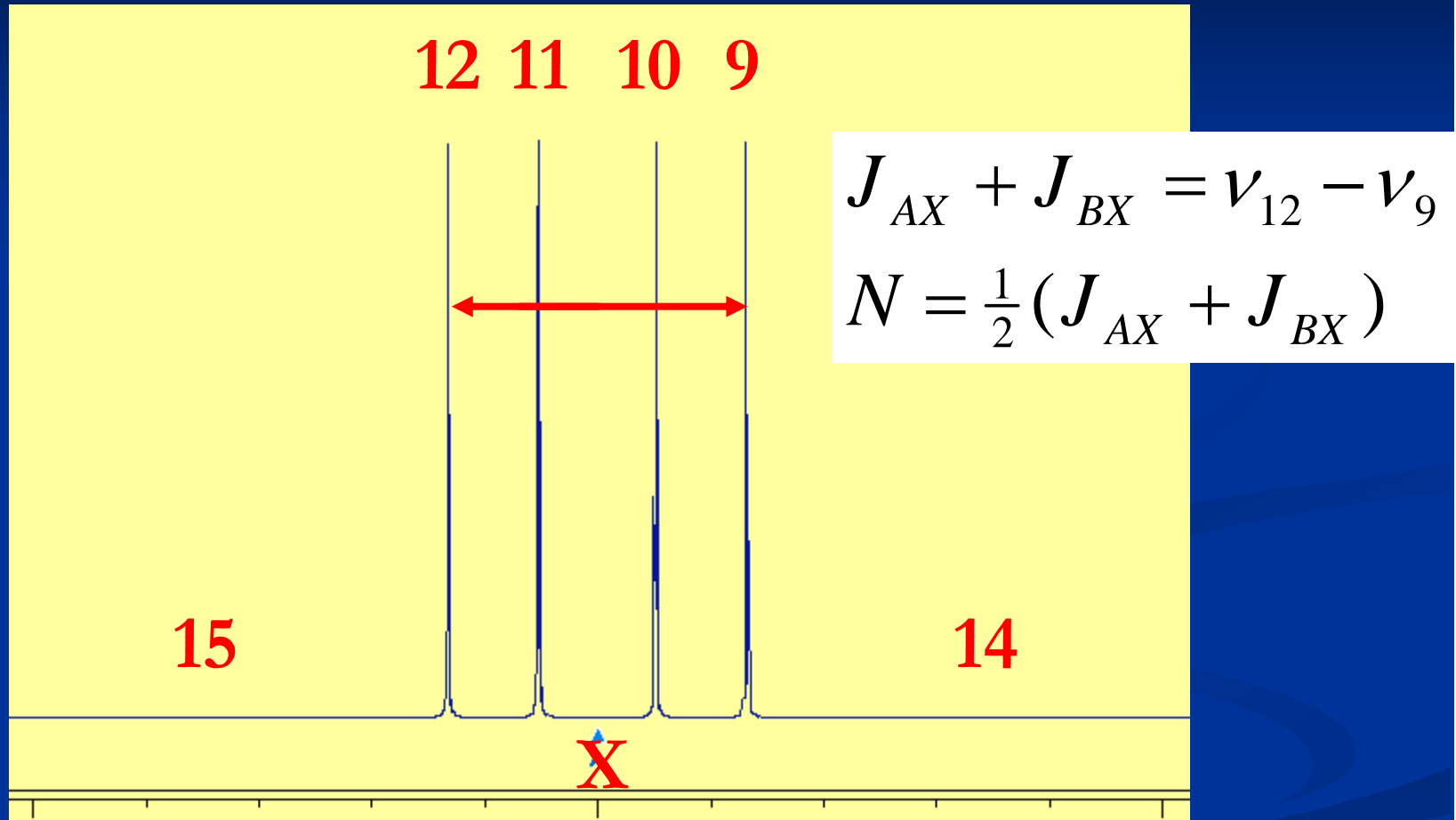
$$Midp = \frac{1}{2} (\nu_A + \nu_B) + \frac{1}{2} N$$

$$\Delta \nu_{AB}^{BLUE} = \Delta \nu_{AB} - L = \sqrt{(\nu_8 - \nu_5)(\nu_7 - \nu_6)}$$

$$Midp = \frac{1}{2} (\nu_A + \nu_B) - \frac{1}{2} N$$



# X Part of the ABX Spin System

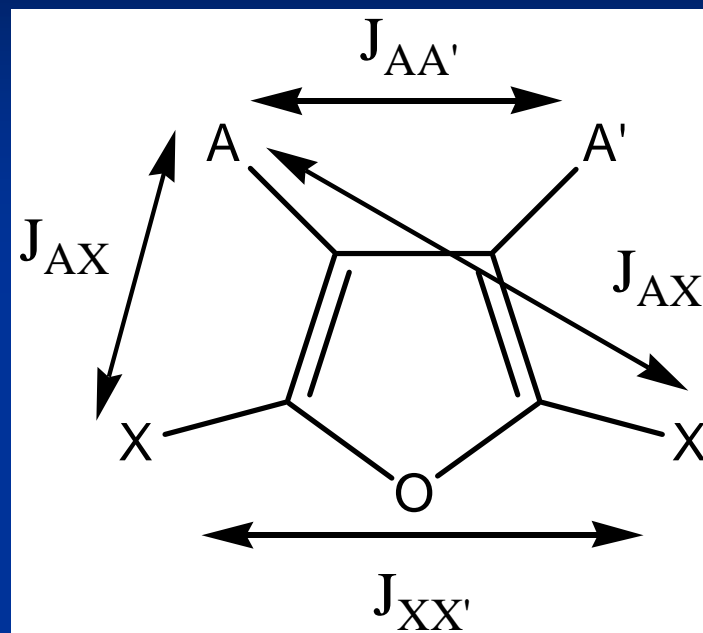


# AA'XX' Spin System

4 coupling constants

Both part A and part X feature the same multiplet symmetrical about  $\nu_A$  or  $\nu_X$

Both parts have 12 lines with a center of symmetry at  $\nu_A$  or  $\nu_X$



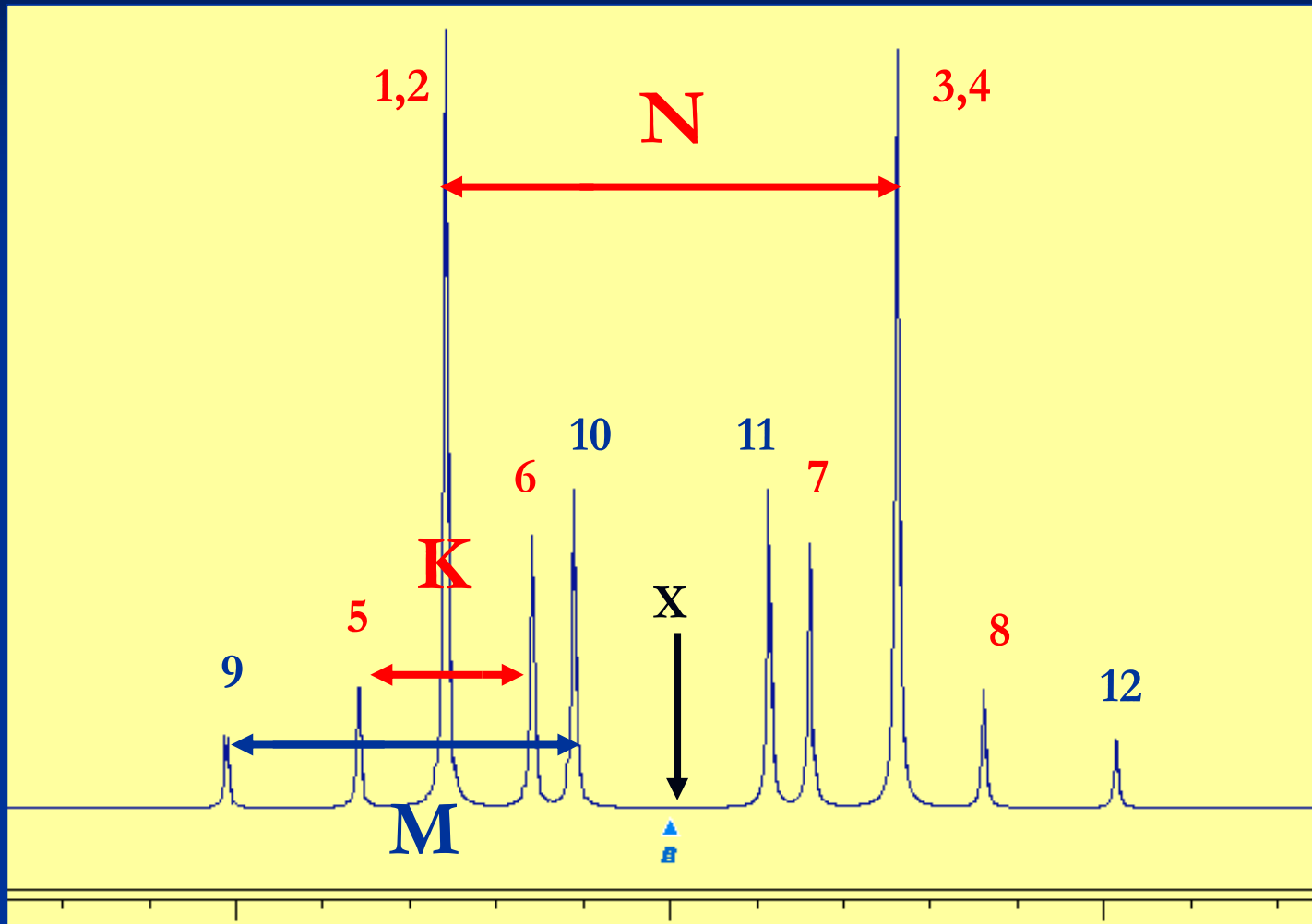
$$K = J_{AA'} + J_{XX'}$$

$$M = J_{AA'} - J_{XX'}$$

$$N = J_{AX} + J_{AX'}$$

$$L = J_{AX} - J_{AX'}$$

# AA'XX' Spin System



# AA'XX' Spin System

$$|N| = \nu_{1,2} - \nu_{3,4} = |J_{AX} + J_{AX'}|$$

$$|K| = \nu_5 - \nu_6 = \nu_7 - \nu_8 = |J_{AA'} + J_{XX'}|$$

$$|M| = \nu_9 - \nu_{10} = \nu_{11} - \nu_{12} = |J_{AA'} - J_{XX'}|$$

$$|L| = \sqrt{(\nu_6 - \nu_7)(\nu_5 - \nu_8)} = \sqrt{(\nu_9 - \nu_{12})(\nu_{10} - \nu_{11})} = |J_{AX} - J_{AX'}|$$

$$I_{1,2} = I_{3,4} = I_{5+6+7+8} = I_{9+10+11+12}$$

$$\frac{I_9}{I_{10}} = \frac{I_{12}}{I_{11}} = \frac{\nu_{10} - \nu_{11}}{\nu_9 - \nu_{12}}$$

$$\frac{I_5}{I_6} = \frac{I_8}{I_7} = \frac{\nu_6 - \nu_7}{\nu_5 - \nu_8}$$

# AA'X<sub>n</sub>X<sub>n</sub>' Spin System

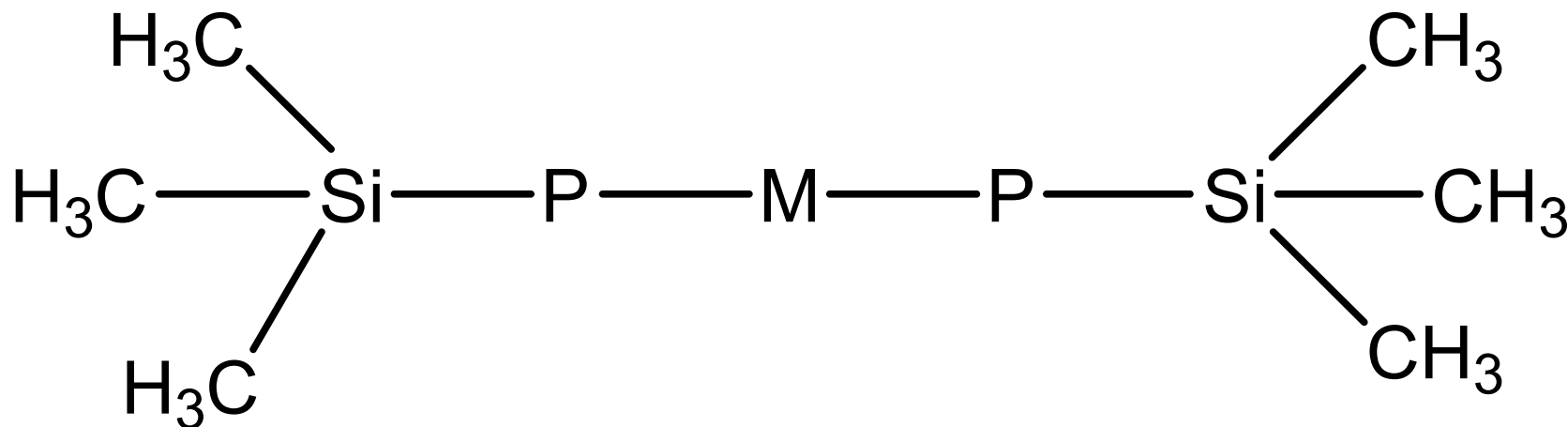
<sup>1</sup>H and <sup>31</sup>P

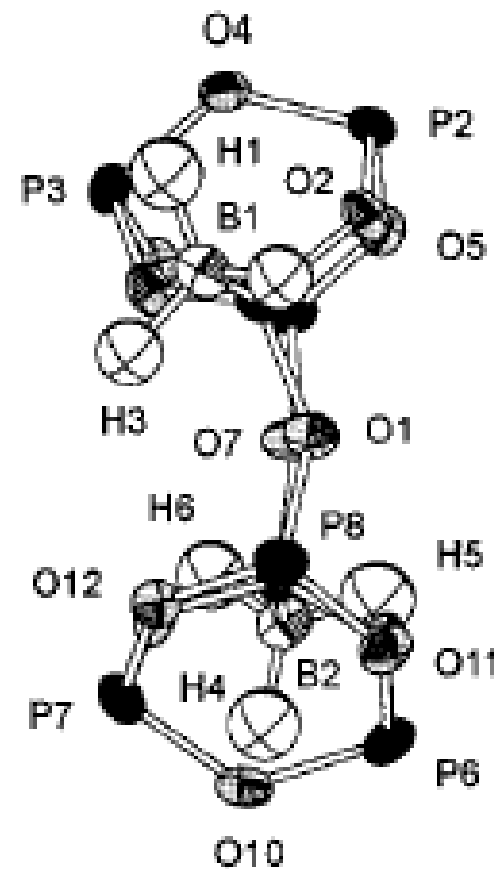
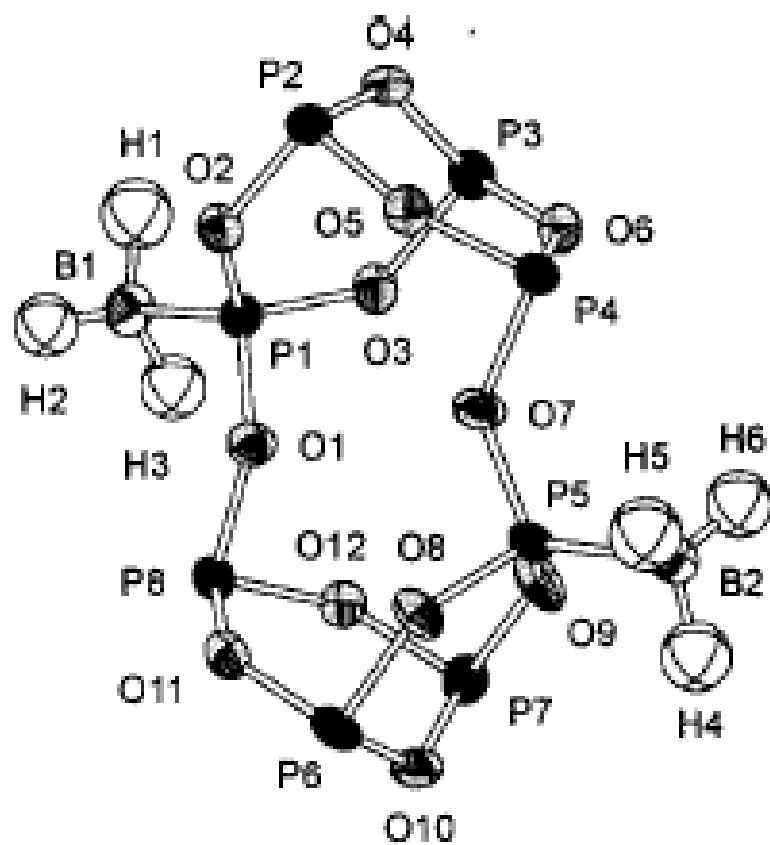
AA'X<sub>3</sub>X<sub>3</sub>'

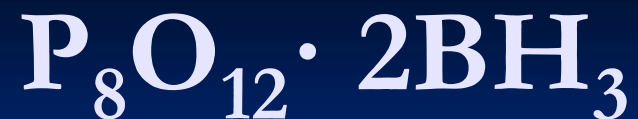


<sup>1</sup>H and <sup>31</sup>P

AA'X<sub>9</sub>X<sub>9</sub>'







$C_{2h}$  Molecular symmetry

$^{31}\text{P}$  Spin system

AA'BB'B''B'''XX'

Nuclei

$\text{P}_A$ : P4, P8

$\text{P}_B$ : P2, P3, P6, P7

$\text{P}_X$ : P1, P5

H

$\delta$  [ppm]

82.65

80.95

70.5

0.8

Coupling constants

[Hz]

$^2J_{AB}$ :  $J_{2-4}, J_{3-4}, J_{6-8}, J_{7-8}$

29.2

$^2J_{BX}$ :  $J_{1-2}, J_{1-3}, J_{5-6}, J_{5-7}$

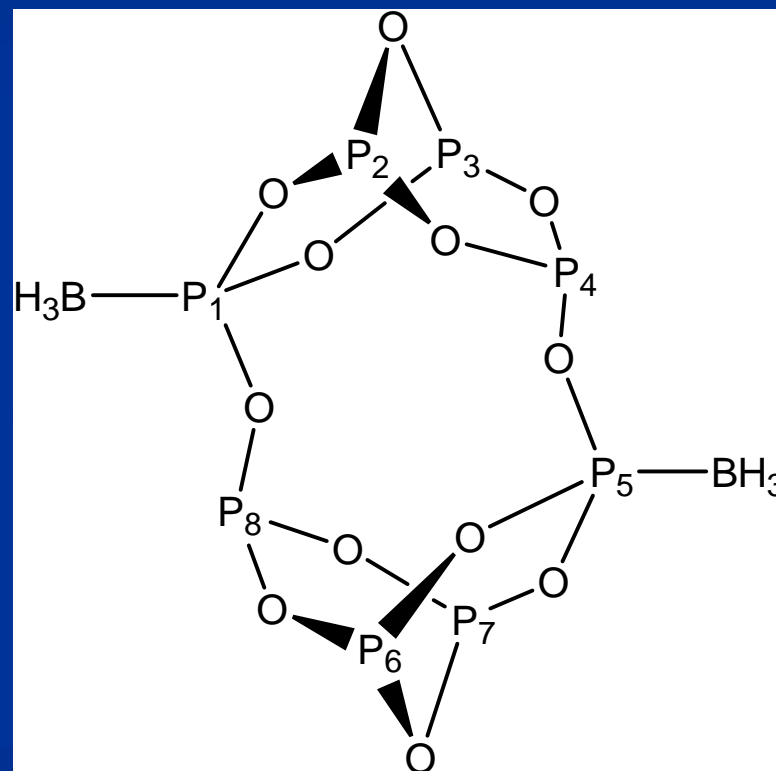
24.0

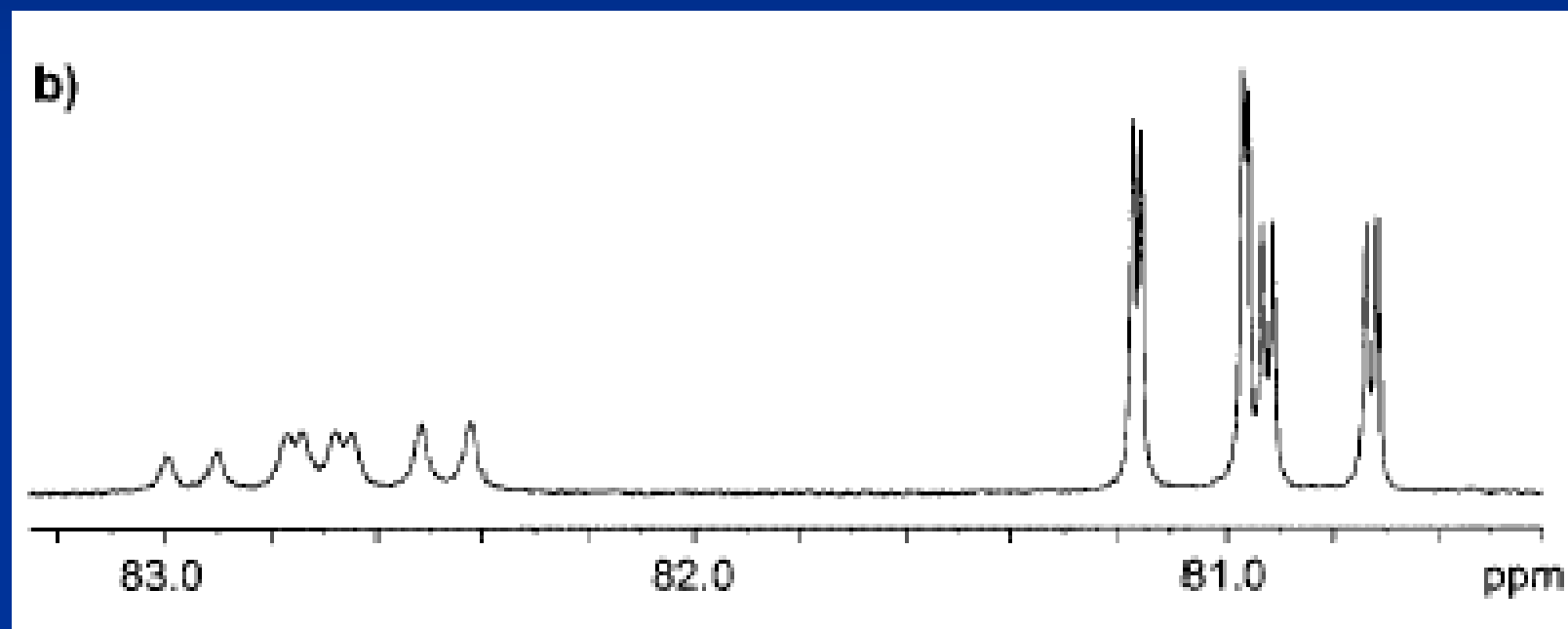
$^2J_{AX}$ :  $J_{1-8}, J_{4-5}$

11.4

$J_{AH}$ :  $J_{4-H}, J_{8-H}$

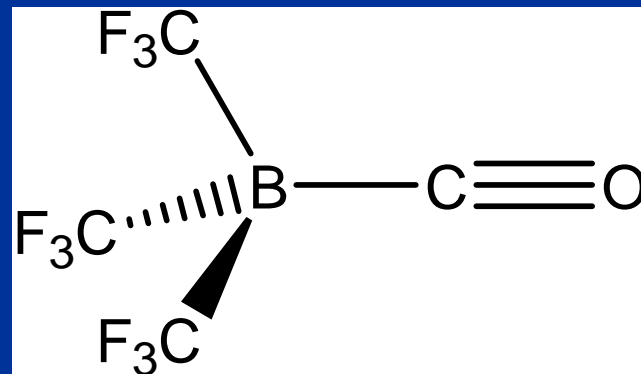
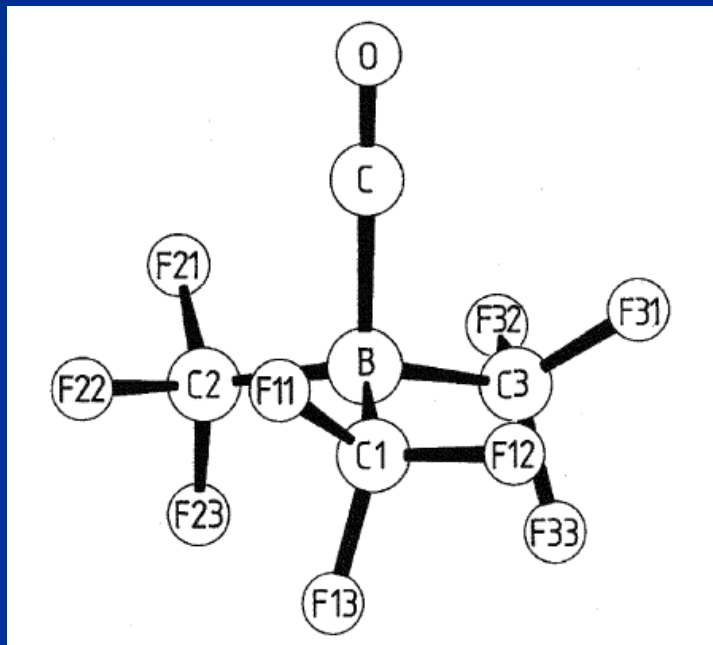
7.5

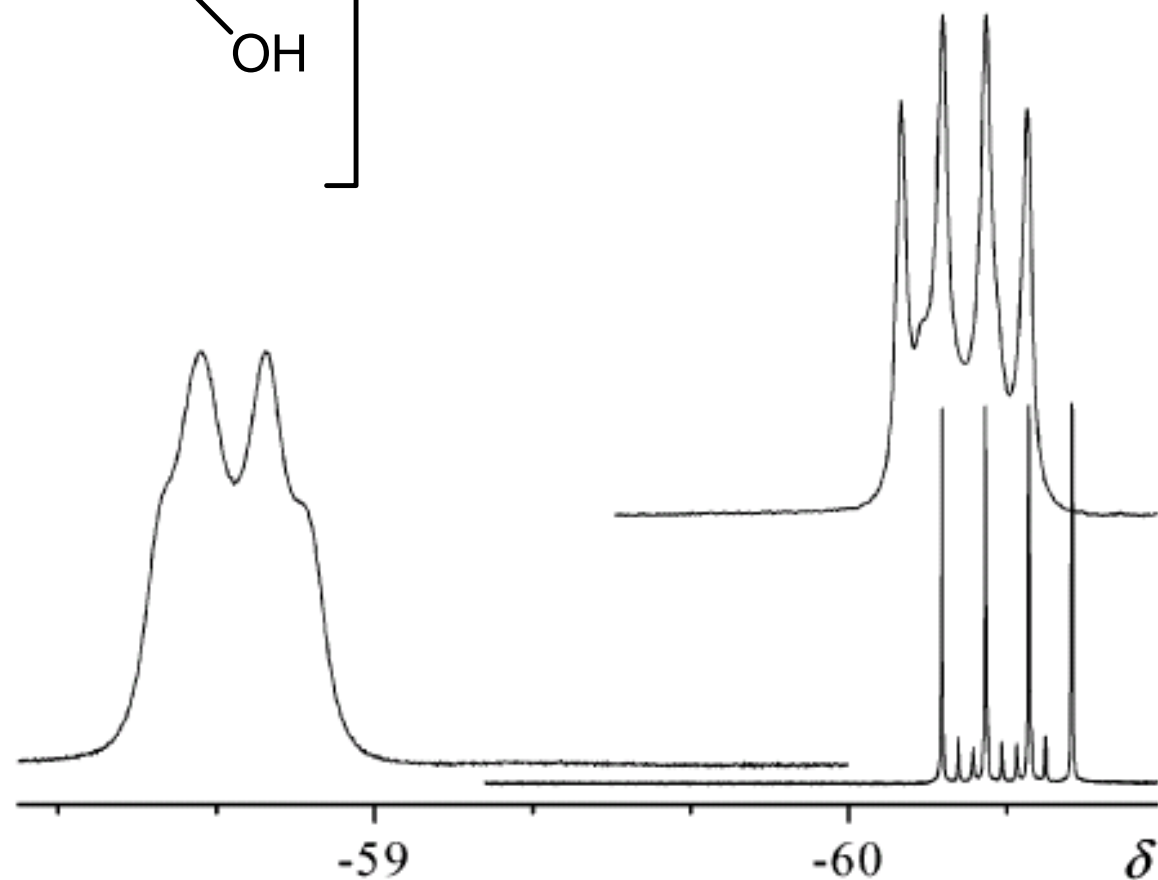
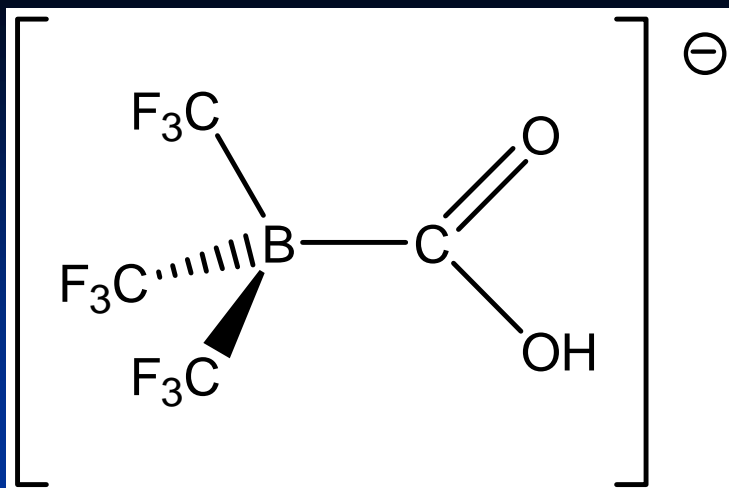




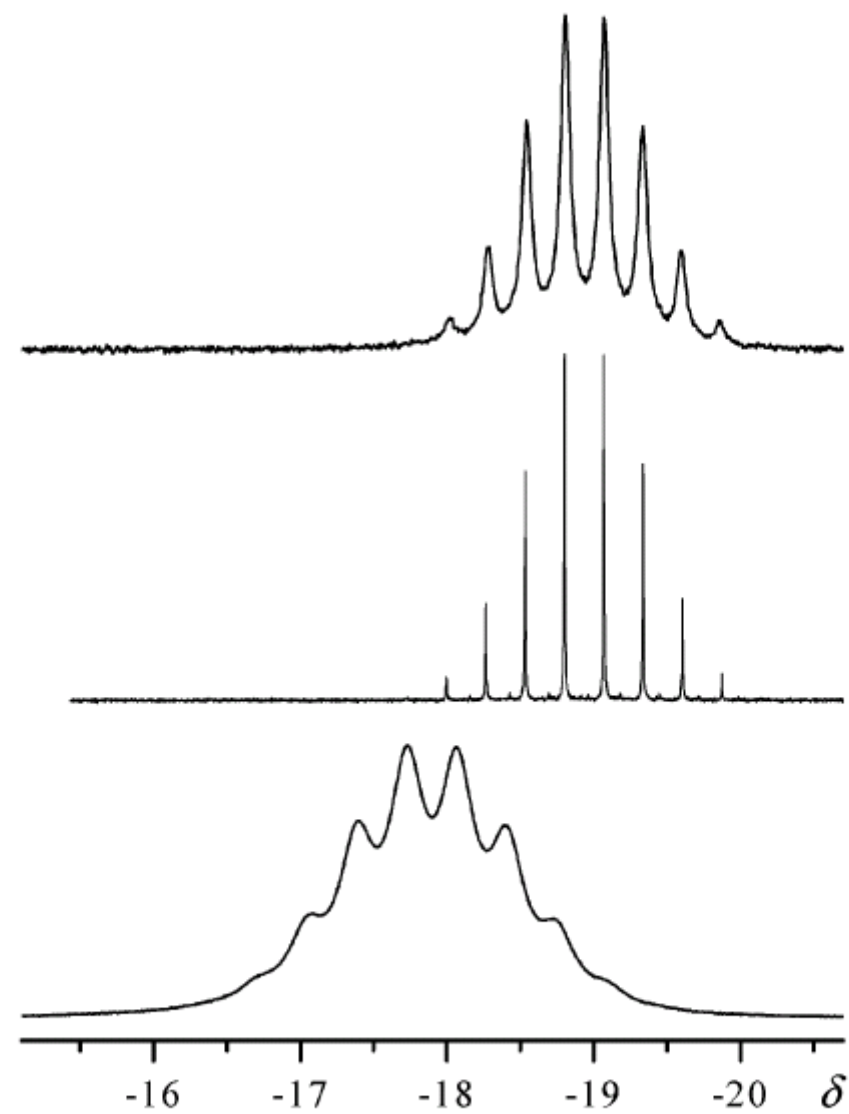


# Coupling Patterns

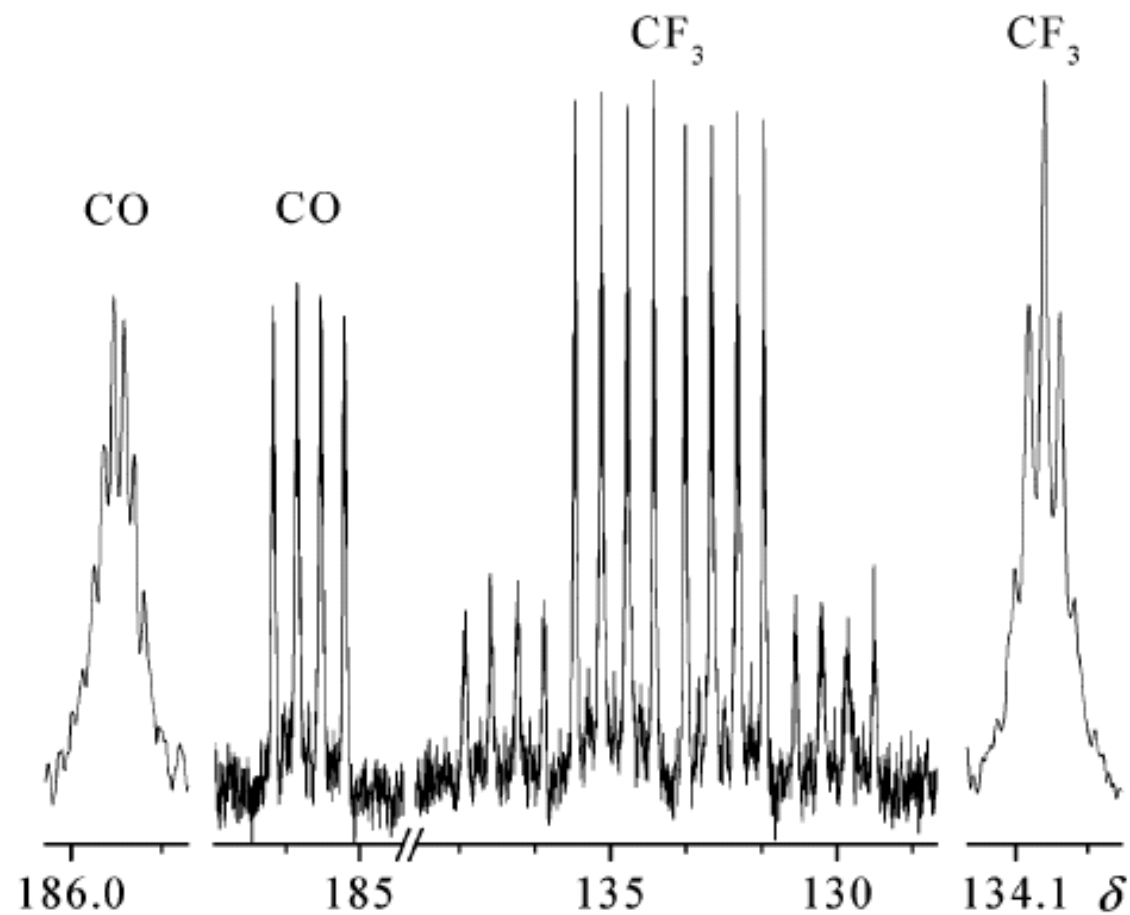




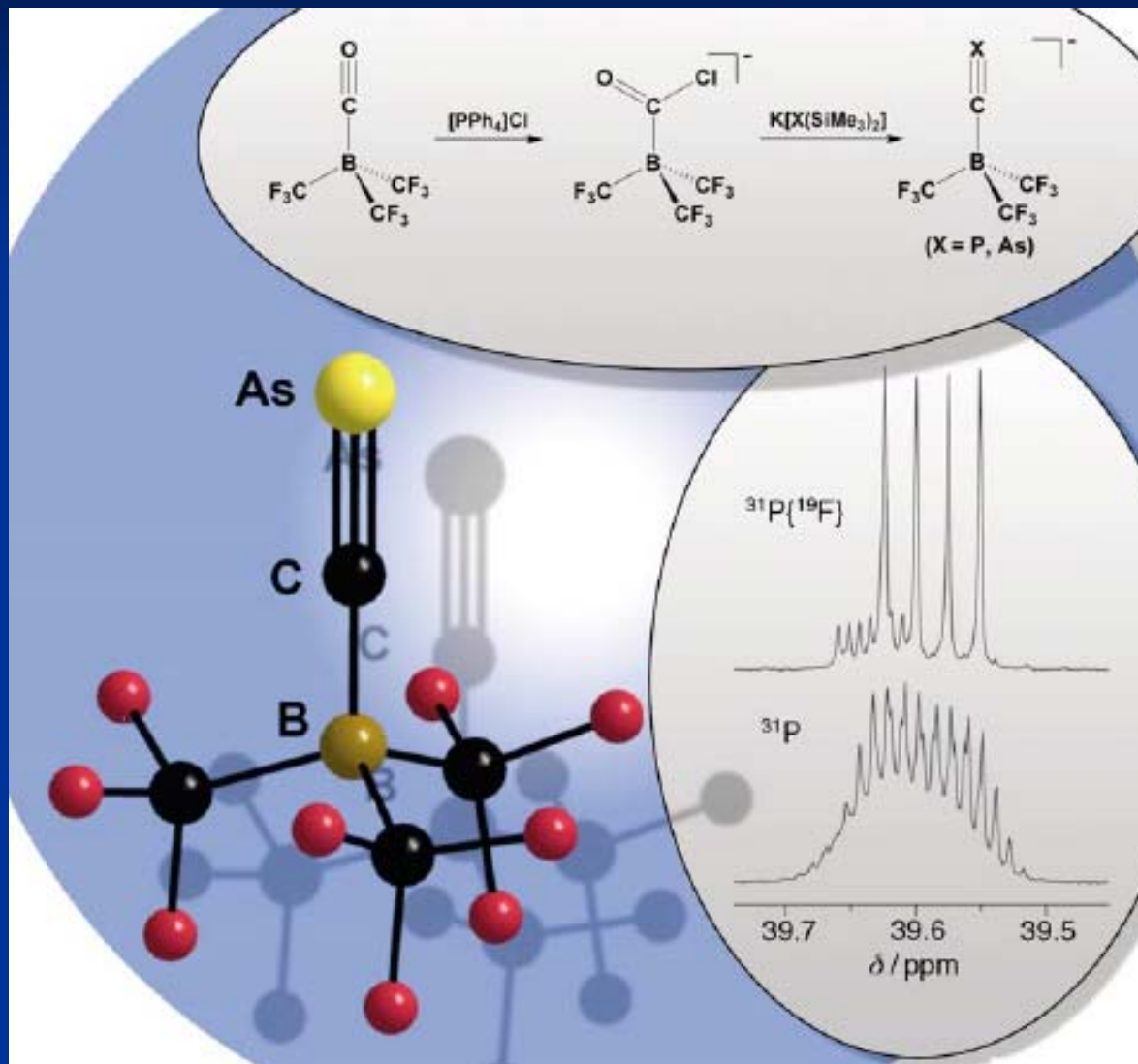
**Figure 7.**  $^{19}\text{F}$  NMR spectra of  $(\text{CF}_3)_3\text{BCO}$  (left),  $[(\text{CF}_3)_3\text{BC}(\text{O})\text{OH}]^-$  (right) and  $[(\text{CF}_3)_3\text{BCO}_2]^{2-}$  (top).

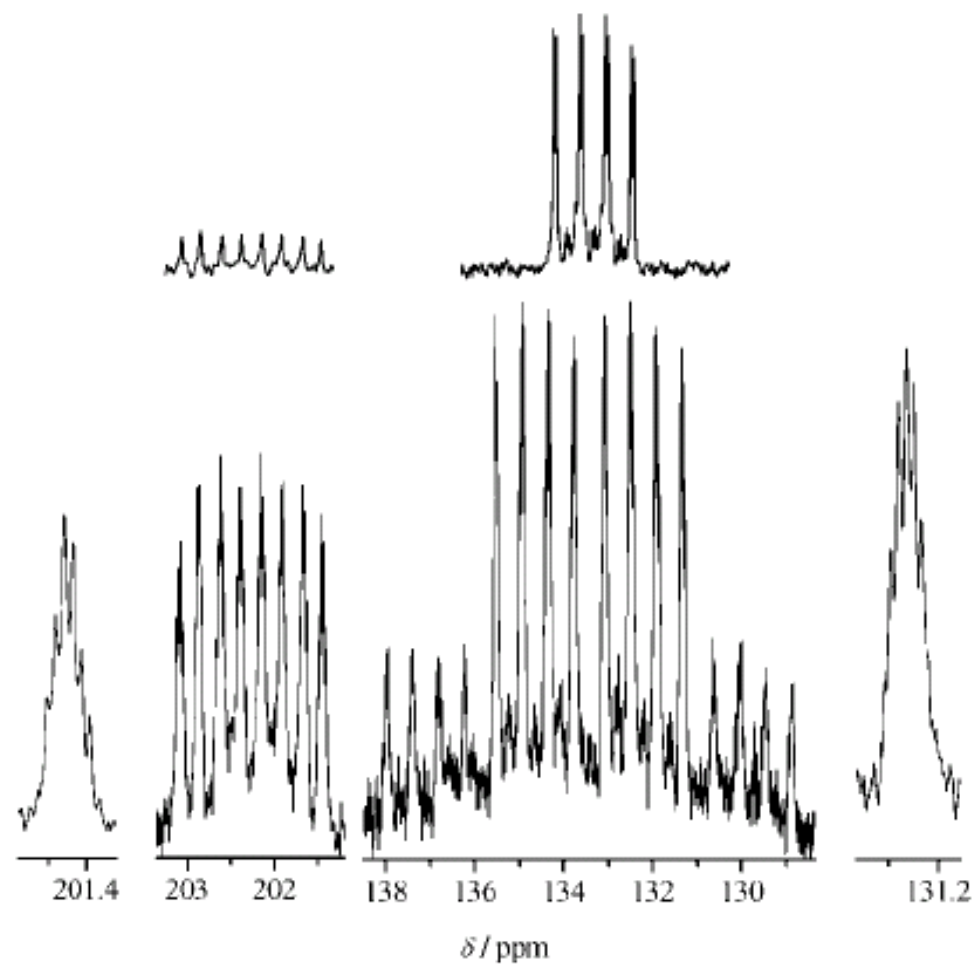


**Figure 8.**  $^{11}\text{B}$  NMR spectra of  $(\text{CF}_3)_3\text{BCO}$  (bottom),  $[(\text{CF}_3)_3\text{BC}(\text{O})\text{OH}]^-$  (middle) and  $[(\text{CF}_3)_3\text{BCO}_2]^{2-}$  (top).

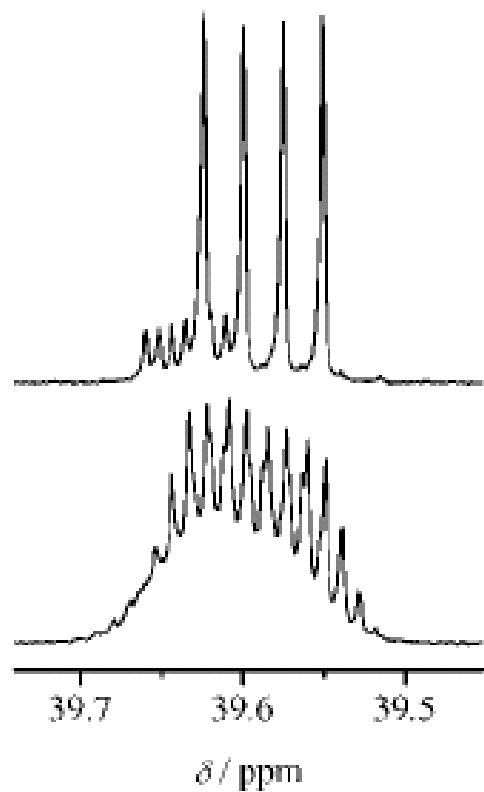


**Figure 10.**  $^{13}\text{C}$  NMR spectrum of  $[(\text{CF}_3)_3\text{BC}(\text{O})\text{OH}]^-$ . The expanded sections of the two signals show the  $^3J(^{13}\text{C}, ^{19}\text{F})$  coupling patterns.

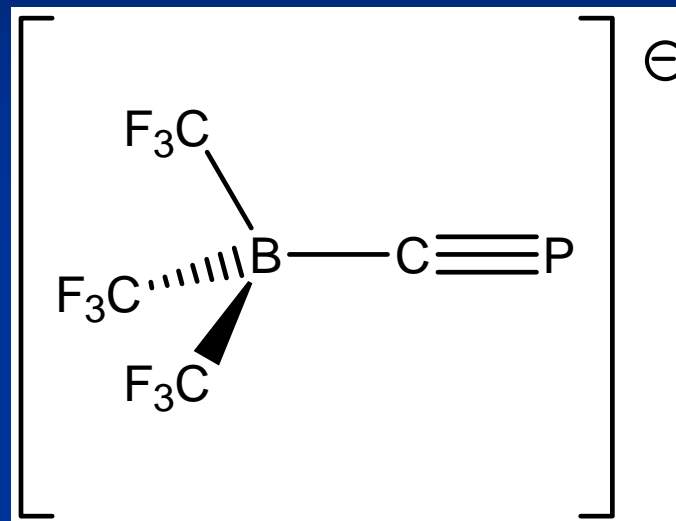




**Figure 1.**  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectrum (top) and  $^{13}\text{C}$  NMR spectrum (bottom) of  $[(\text{CF}_3)_3\text{BCP}]^-$  in  $\text{CD}_3\text{CN}$  solution.



**Figure 3.**  $^{31}\text{P}$   $\{^{19}\text{F}\}$  NMR spectrum (top) and the  $^{31}\text{P}$  NMR spectrum (bottom) of  $[(\text{CF}_3)_3\text{BCP}]^-$  in  $\text{CD}_3\text{CN}$  solution.



# MestReNova

## Simulations of NMR spectra

