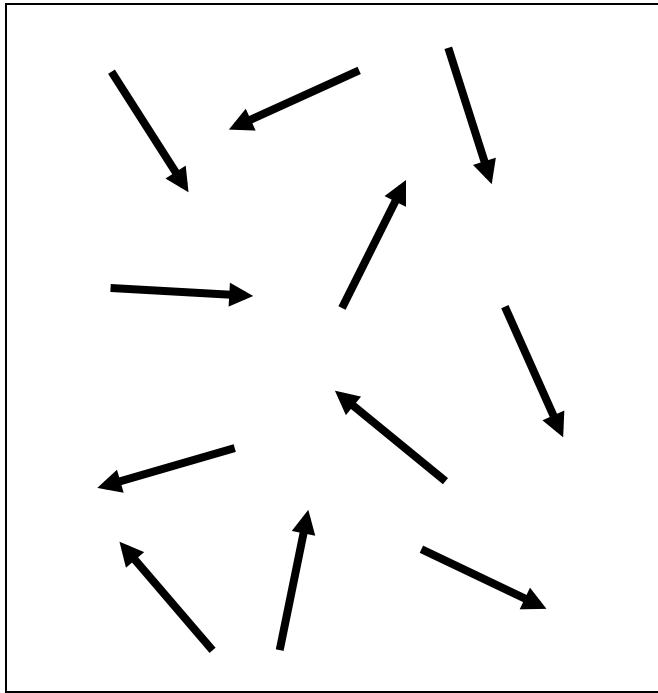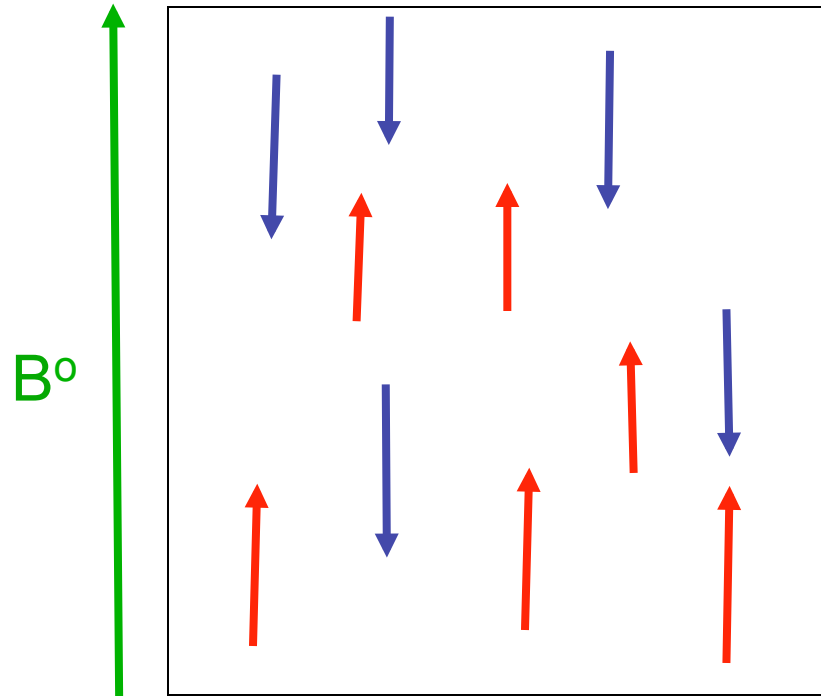Yale Chemistry 800 MHz
Supercooled Magnet

# *Nuclear Magnetic Resonance*
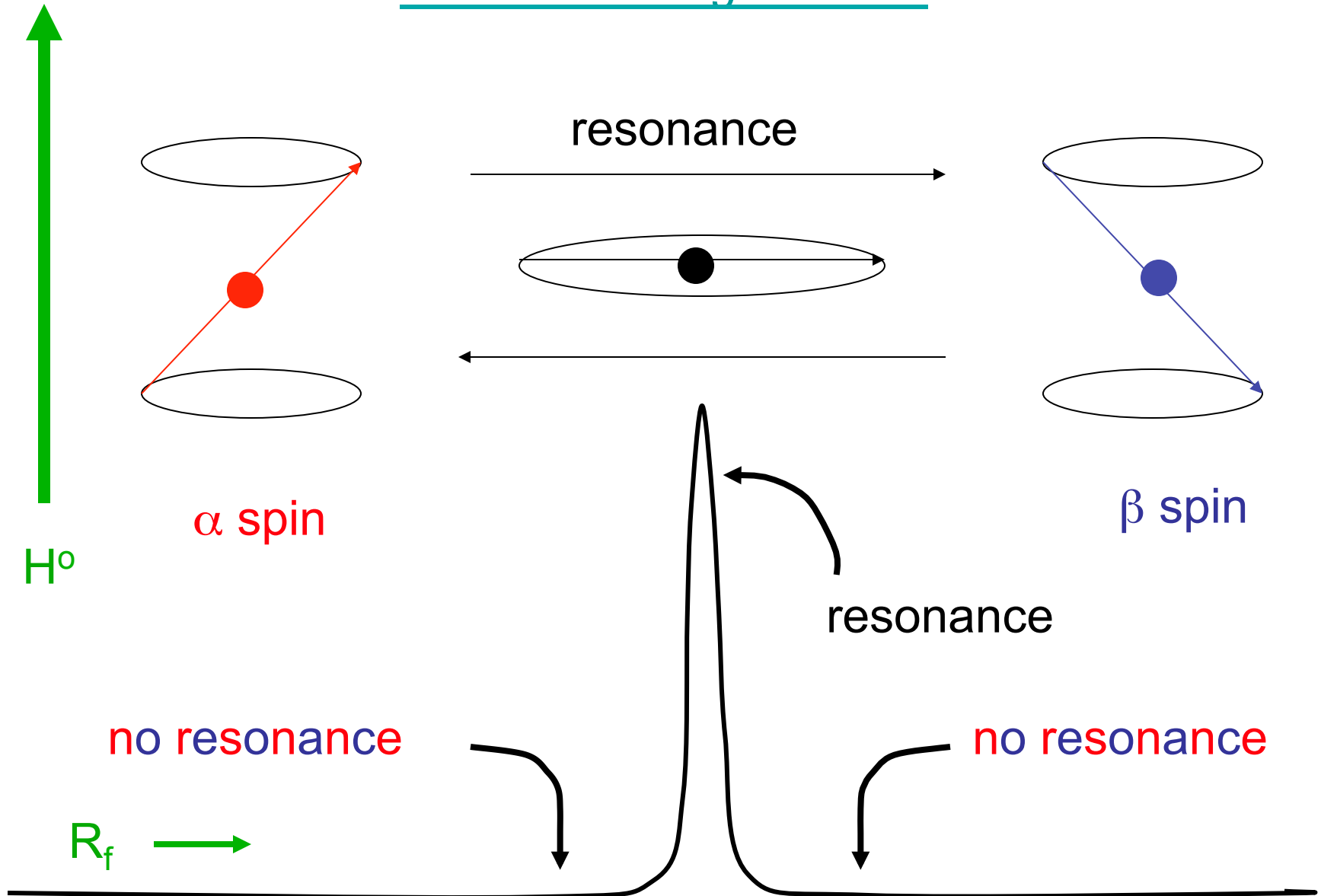
Atomic nuclei in
The absence of
a magnetic field

Atomic nuclei in the presence
of a magnetic field
$\alpha$ spin - with the field
$\beta$ spin - opposed to the field

# *The Precessing Nucleus*

resonance

resonance

α spin

β spin

H°

resonance

no resonance

no resonance

R$_f$

*The Precessing Nucleus Again*

*The Continuous Wave Spectrometer*

*The Fourier Transform Spectrometer*

## *Observable Nuclei*

- Odd At. Wt.; s = ±1/2

| Nuclei | $^1H_1$ | $^{13}C_6$ | $^{15}N_7$ | $^{19}F_9$ | $^{31}P_{15}$ .... |
|---|---|---|---|---|---|
| Abundance (%) | 99.98 | 1.1 | 0.385 | 100 | 100 |

- Odd At. No.; s = ±1

Nuclei    $^2H_1$    $^{14}N_7$ …

- Unobserved Nuclei

$^{12}C_6$    $^{16}O_8$    $^{32}S_{16}$…

- $\Delta E = h\nu$         h = Planck's constant: $1.58 \times 10^{-37}$ kcal-sec

- $\Delta E = \gamma h / 2\pi (B^o)$    $\gamma$ = Gyromagnetic ratio: sensitivity of nucleus to the magnetic field. $^1H = 2.67 \times 10^4$ rad sec$^{-1}$ gauss$^{-1}$

- Thus:      $\nu = \gamma / 2\pi (B^o)$
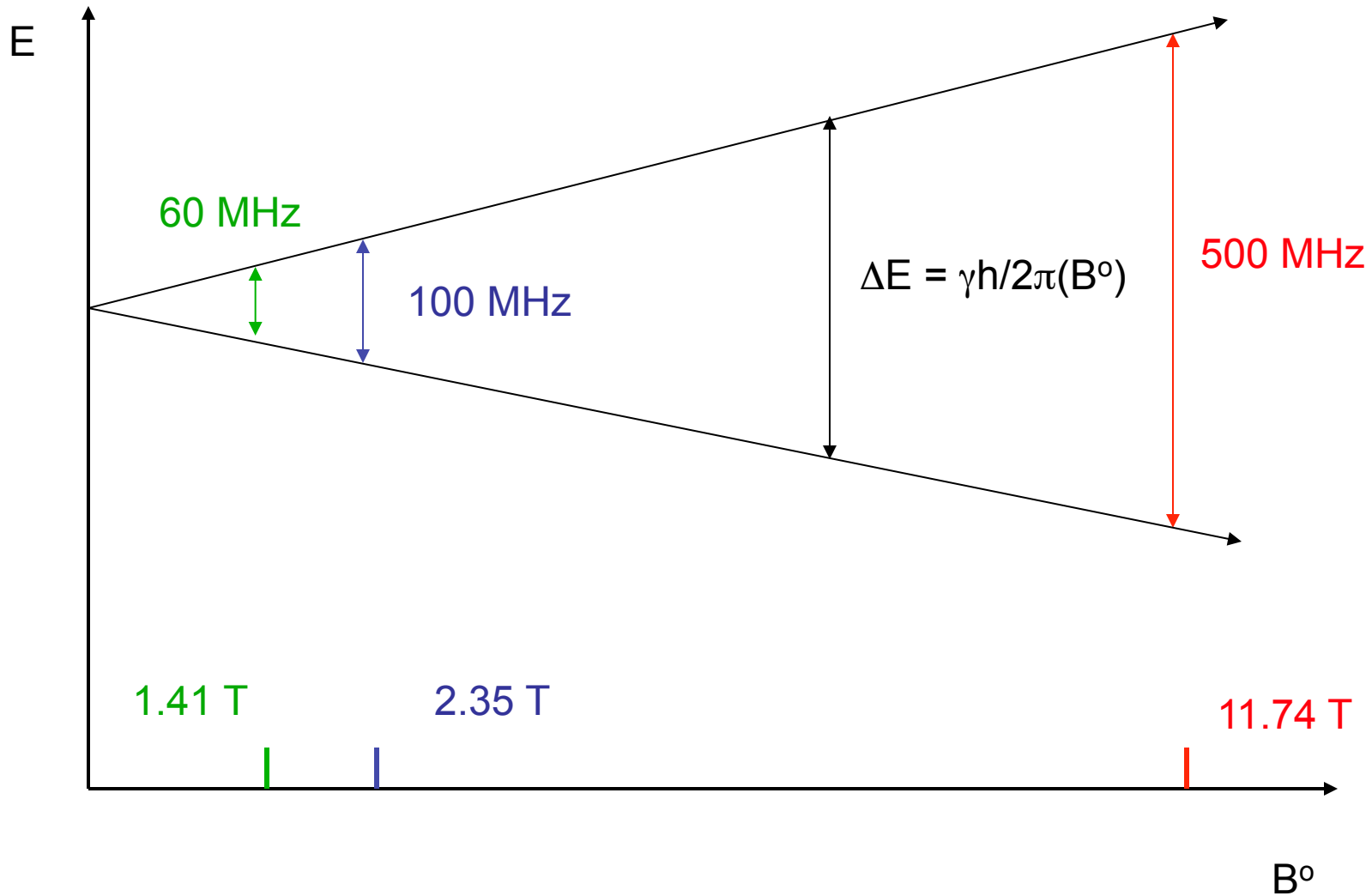
- For a proton,

if $B^o$ = 14,092 gauss (1.41 tesla, 1.41 T),
$\nu = 60 \times 10^6$ cycles/sec = 60 MHz

and

- $\Delta E_N = Nh\nu = 0.006$ cal/mole

*R_f Field vs. Magnetic Field for a Proton*

## $R_f$ Field /Magnetic Field for Some Nuclei

| Nuclei | $R_f$ (MHz) | $B^o$ (T) | $\gamma/2\pi$ (MHz/T) |
|---|---|---|---|
| $^1H$ | 500.00 | 11.74 | 42.58 |
| $^{13}C$ | 125.74 | 11.74 | 10.71 |
| $^2H$ | 76.78 | 11.74 | 6.54 |
| $^{19}F$ | 470.54 | 11.74 | 40.08 |
| $^{31}P$ | 202.51 | 11.74 | 17.25 |

# *Fortunately, all protons are not created equal!*

at 1.41 T

60 MHz
60,000,000 Hz

60,000,600 Hz

downfield ←

deshielded

60 Hz

upfield →

shielded

Me$_4$Si

240 Hz

| 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 | δ scale (ppm) |

at 500 MHz →

500 Hz
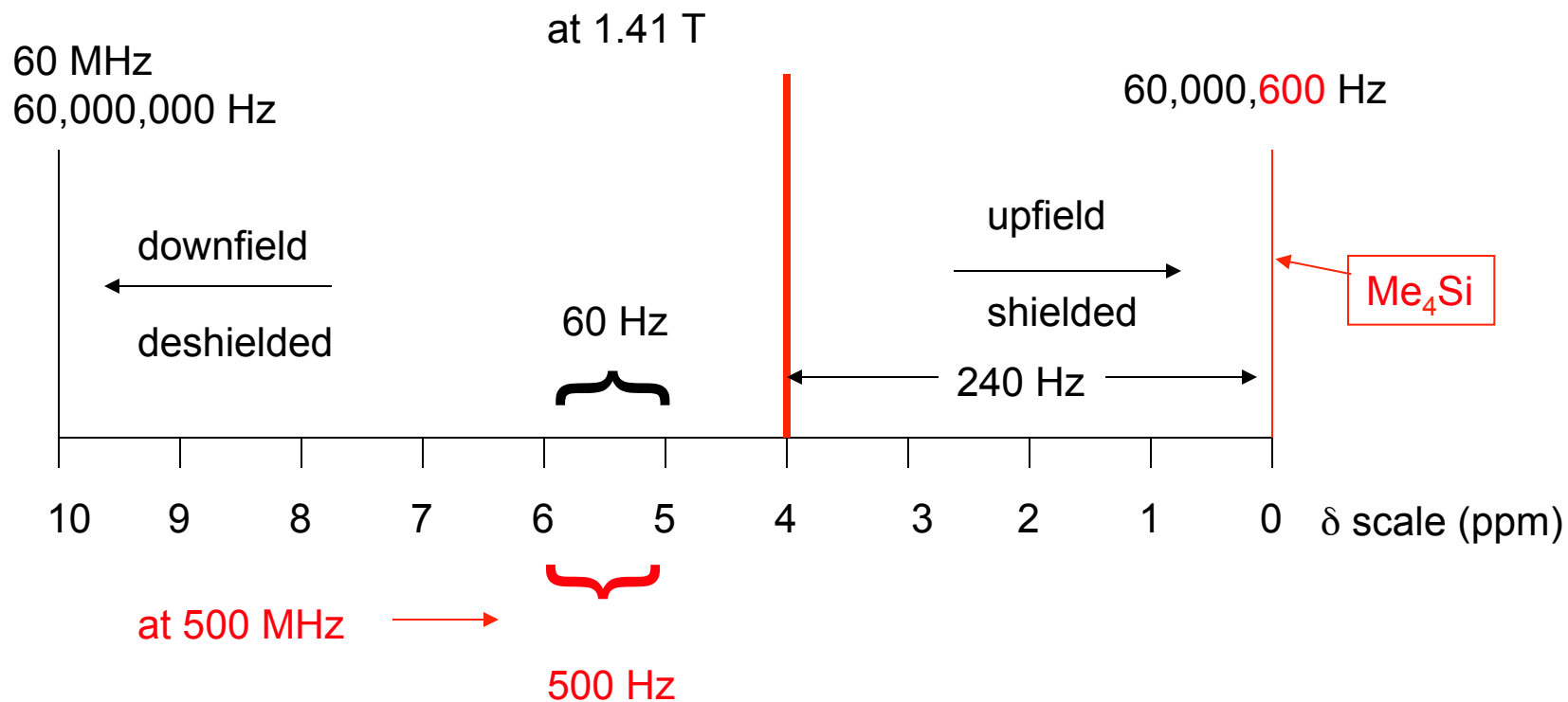
chemical shift

$$\delta = (\nu_{obs} - \nu_{TMS})/\nu_{inst(MHz)} = (240.00 - 0)/60 = 4.00$$

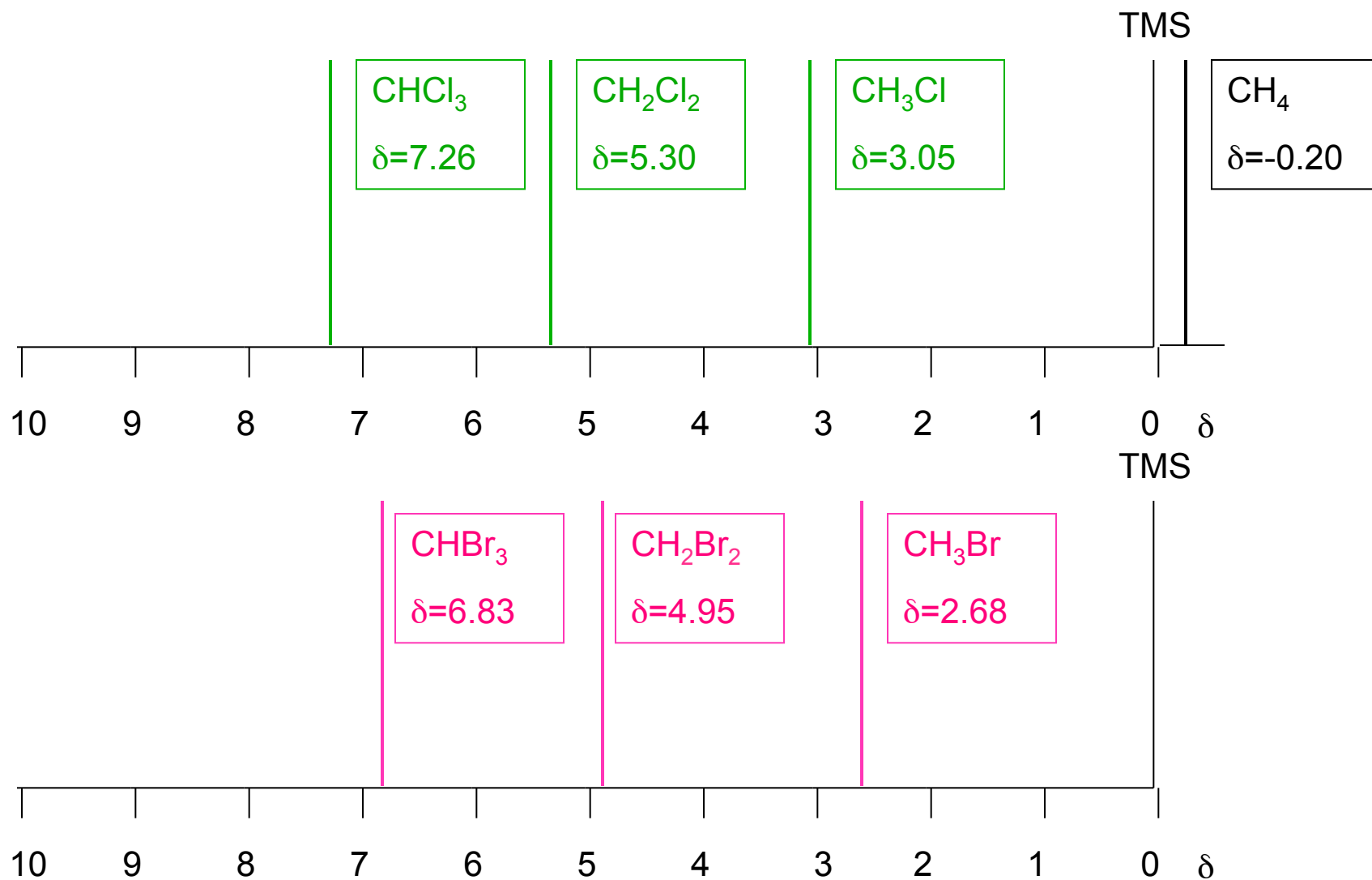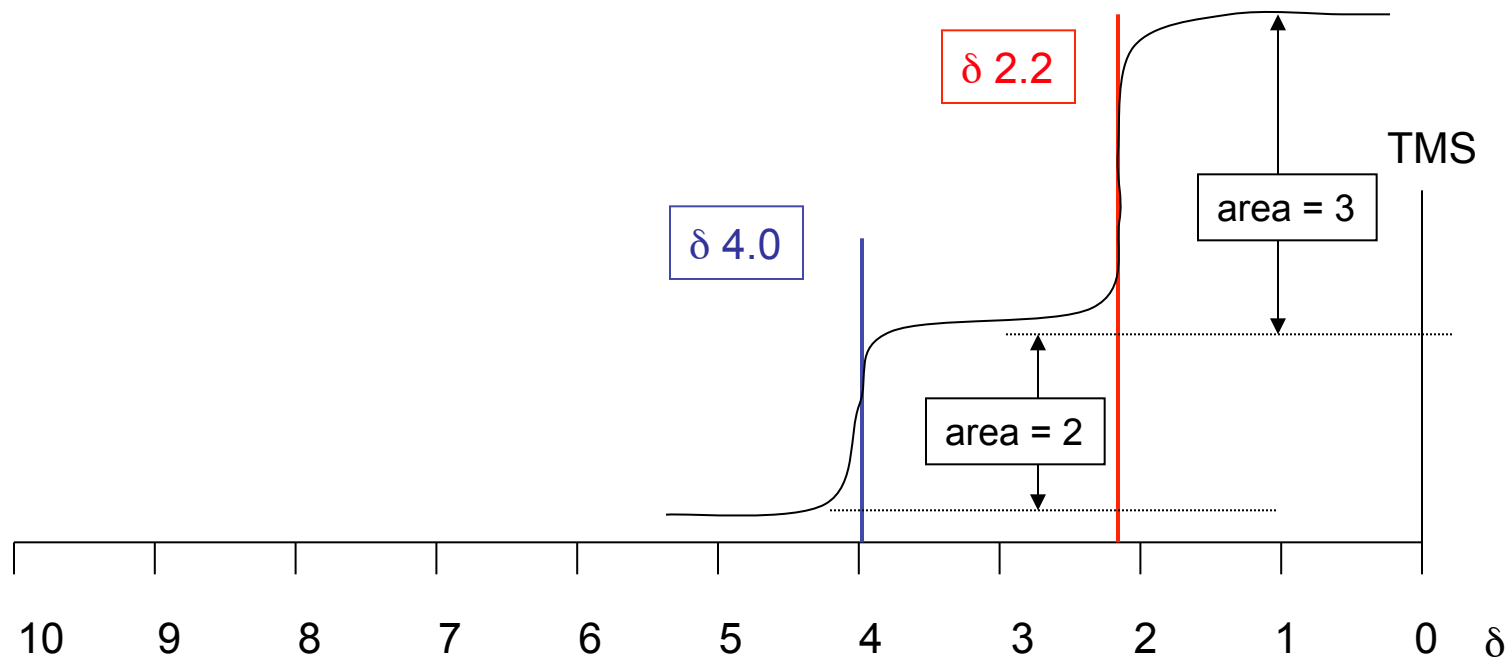# *Where Nuclei Resonate at 11.74T*
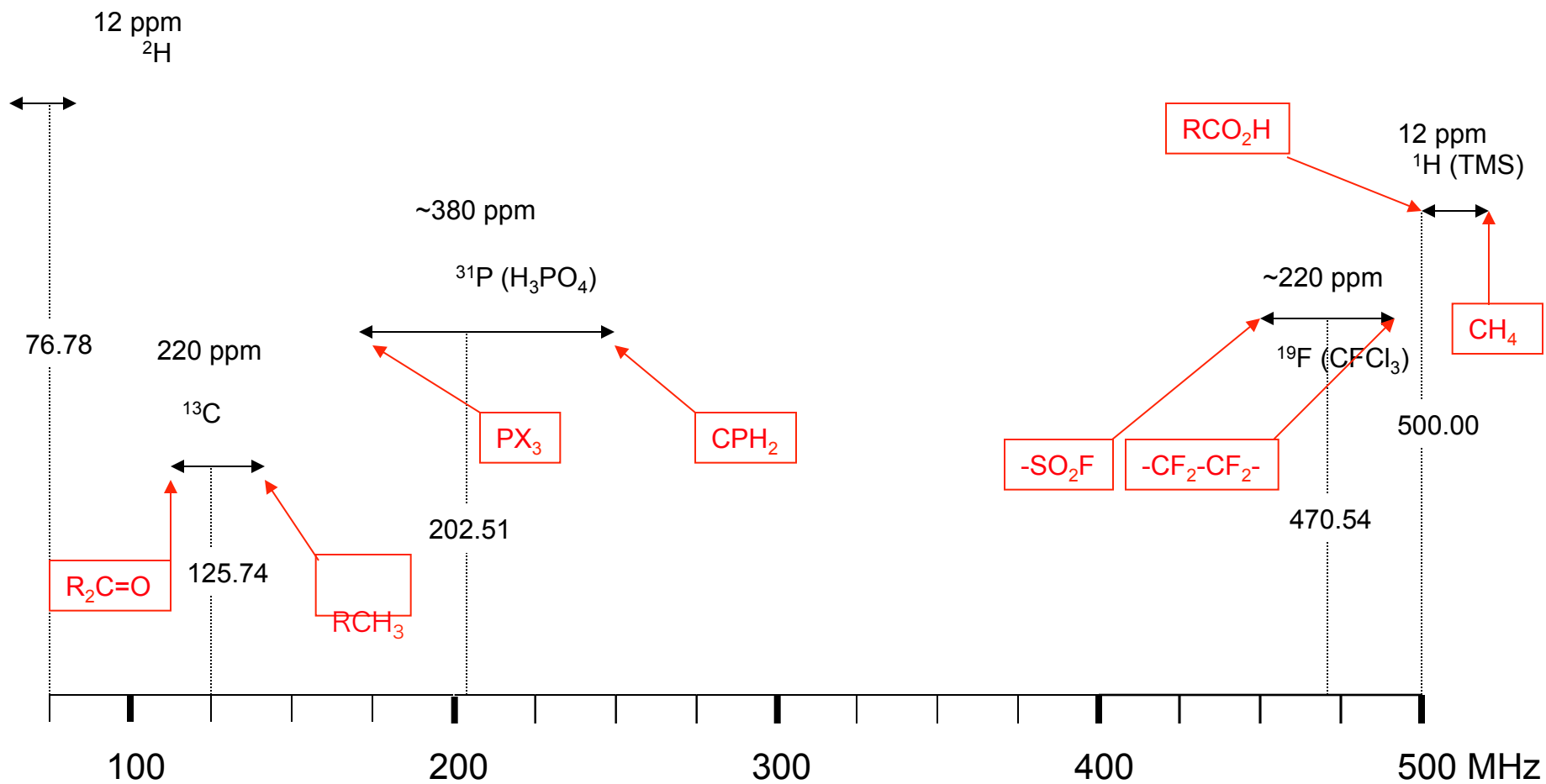
# *Chemical Shifts of Protons*

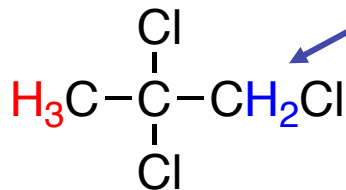# The Effect of Electronegativity on Proton Chemical Shifts
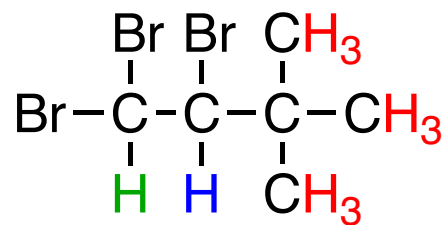
# Chemical Shifts and Integrals

δ 2.2
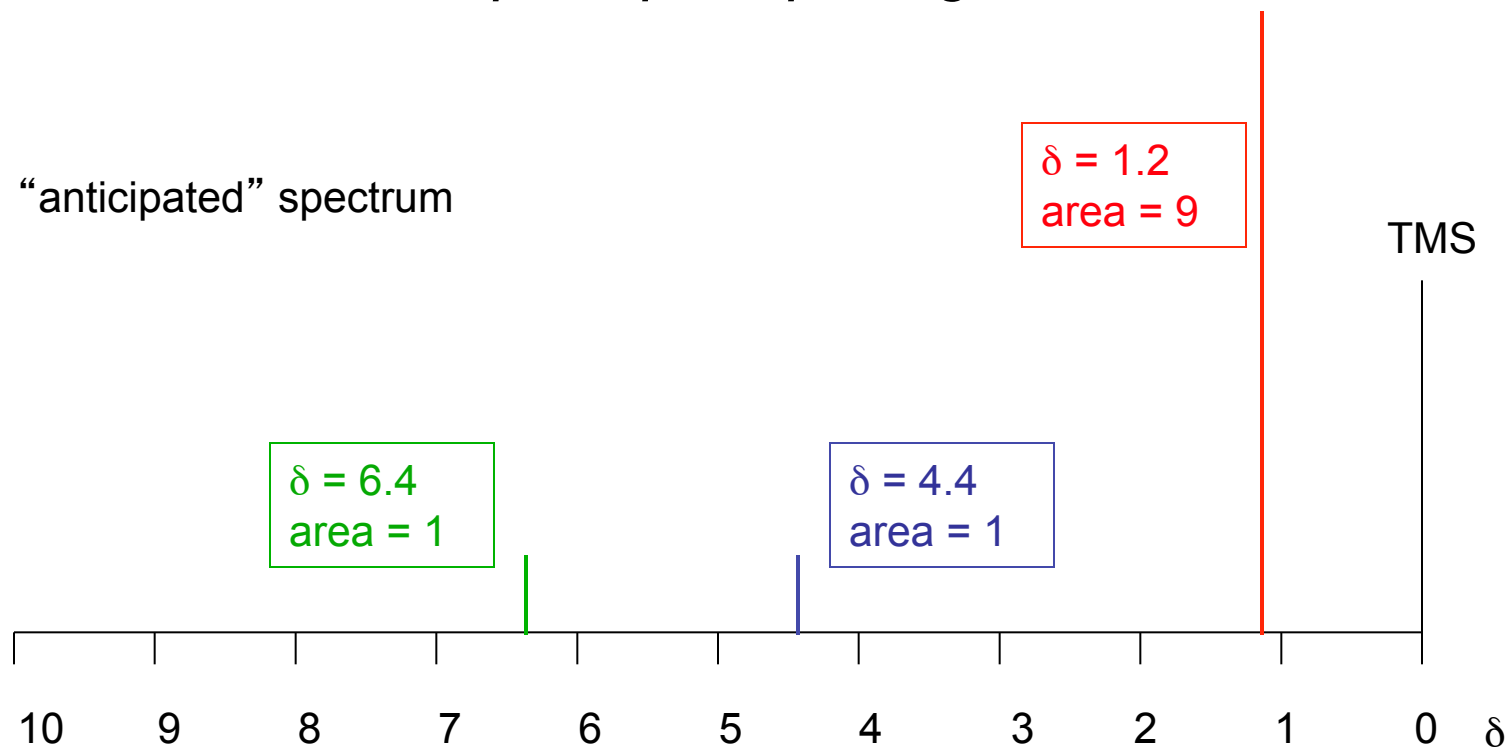
TMS

area = 3

δ 4.0

area = 2

| 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 | δ |

homotopic protons: chemically and magnetically equivalent

enantiotopic protons: chemically and magnetically equivalent

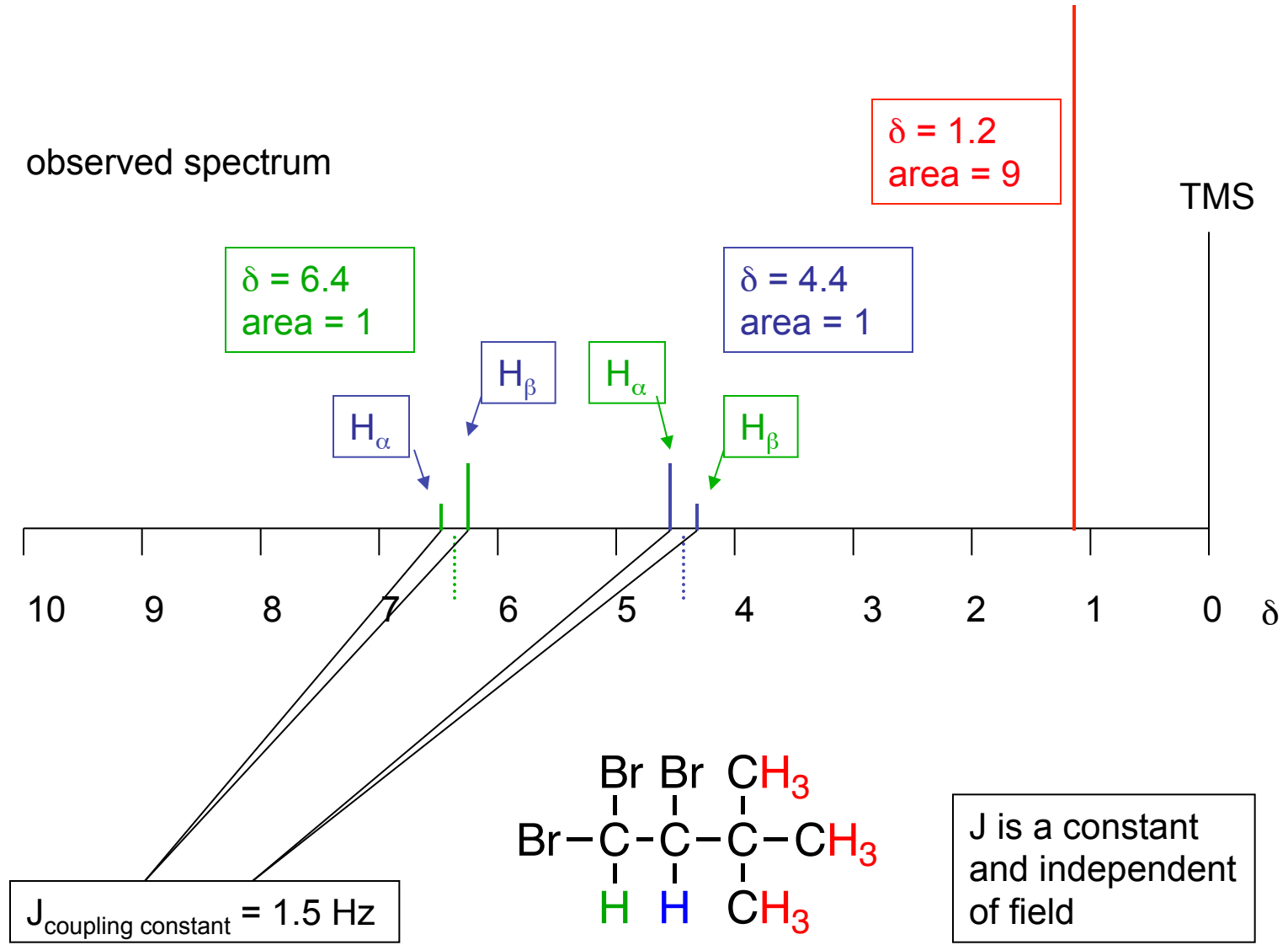$$H_3C-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_2Cl$$

# *Spin-Spin Splitting*

"anticipated" spectrum

$\delta = 6.4$
area = 1

$\delta = 4.4$
area = 1

$\delta = 1.2$
area = 9

TMS

10   9   8   7   6   5   4   3   2   1   0   $\delta$

Br  Br  C$H_3$
Br—C—C—C—C$H_3$
H   H   C$H_3$

# *Spin-Spin Splitting*

observed spectrum

δ = 1.2
area = 9

TMS

δ = 6.4
area = 1

δ = 4.4
area = 1

H$_\beta$

H$_\alpha$

H$_\alpha$

H$_\beta$

10   9   8   7   6   5   4   3   2   1   0   δ

J$_{coupling\ constant}$ = 1.5 Hz

Br  Br  CH$_3$

Br—C—C—C—CH$_3$

H   H   CH$_3$

J is a constant
and independent
of field

# Spin-Spin Splitting

δ = 6.4
J = 1.5 Hz

δ = 4.4
J = 1.5 Hz

$H_\beta$

$H_\alpha$

$H_\alpha$
$\nu_{local}$

$H_\beta$
$\nu_{local}$

$\nu_{observed}$

$\nu_{observed}$

$\nu_{observed}$

8          7          6          5          4          3    δ

$\nu_{applied}$

$\nu_{applied}$
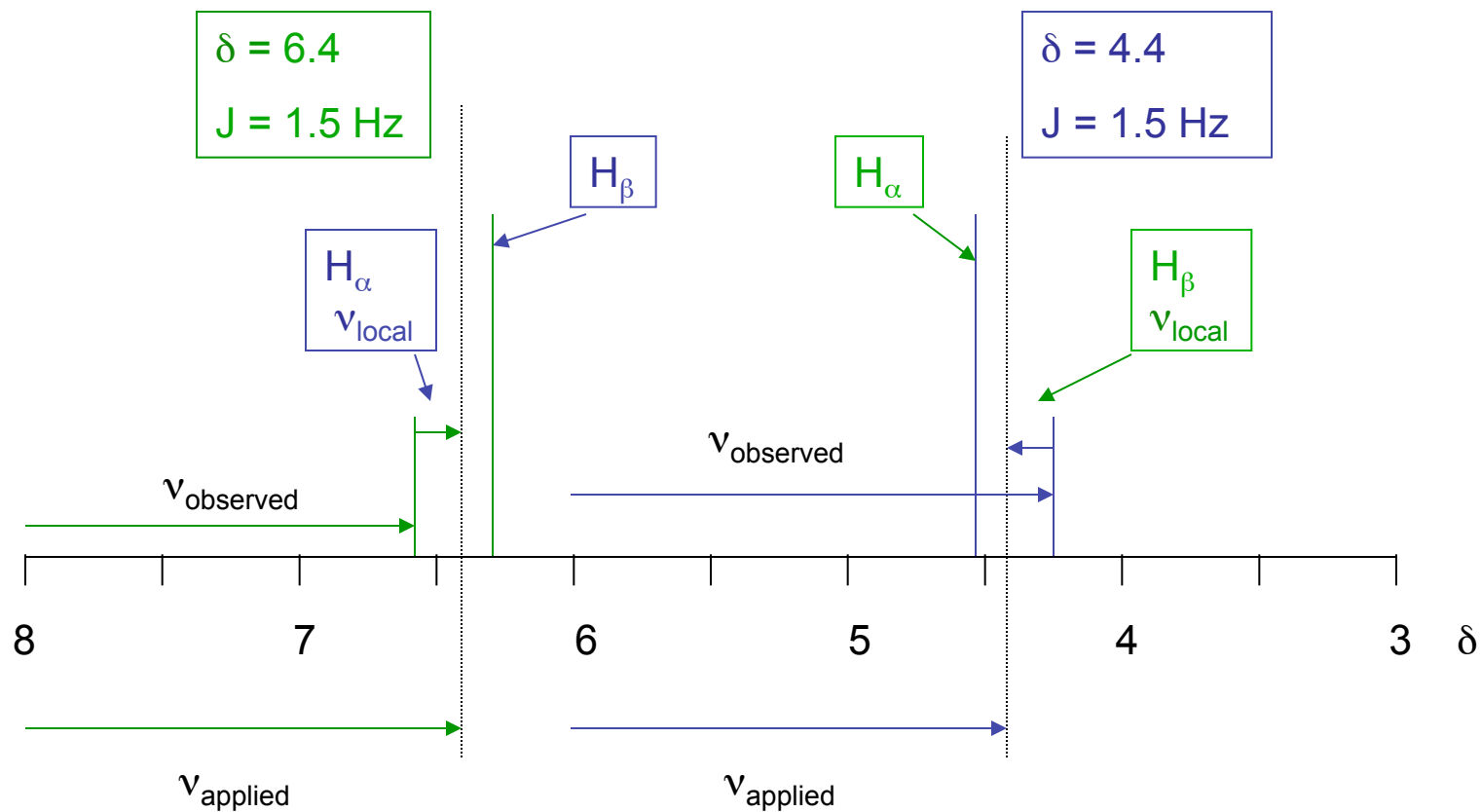
This spectrum is not recorded at ~6 MHz!

δ and J are not to scale.

Br  Br  C$H_3$
Br—C—C—C—C$H_3$
H   H   C$H_3$
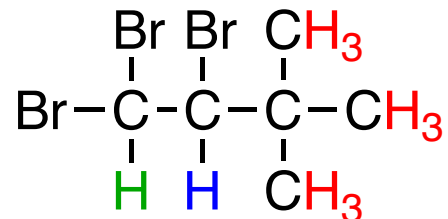
# *Multiplicity of Spin-Spin Splitting for s = ±1/2*

multiplicity (m) = $2\Sigma s + 1$

| # equiv. neighbors | spin (1/2) | multiplicity | pattern $(a + b)^n$ | symbol |
|---|---|---|---|---|
| 0 | 0 | 1 | 1 | singlet (s) |
| 1 | 1/2 | 2 | 1:1 | doublet (d) |
| 2 | 2/2 = 1 | 3 | 1:2:1 | triplet (t) |
| 3 | 3/2 | 4 | 1:3:3:1 | quartet (q) |
| 4 | 4/2 = 1 | 5 | 1:4:6:4:1 | quintet (qt) |

# $^1H$ NMR of Ethyl Bromide (90 MHz)

CH$_3$CH$_2$Br

for H spins

ααβ  αββ

αβα  βαβ

ααα  βαα  ββα  βββ

1    3    3    1

for H spins

αβ

αα  βα  ββ

1    2    1

δ = 1.68
area = 3

δ = 3.43
area = 2

90 Hz/46 pixels
= 3J/12 pixels
: J= 7.83 Hz

Pixels
50    100    150    200

Pixels
50    100    150    200

11   10   9   8   7   6   5   4   3   2   1   0

# *¹H NMR of Isopropanol (90 MHz)*

(CH₃)₂CHOH



1H septuplet; no coupling to OH

6H, d, J = 7.5 Hz

(4.25-3.80)x90/6 = 7.5 Hz

1H, s

δ4.25

δ3.80

4

3
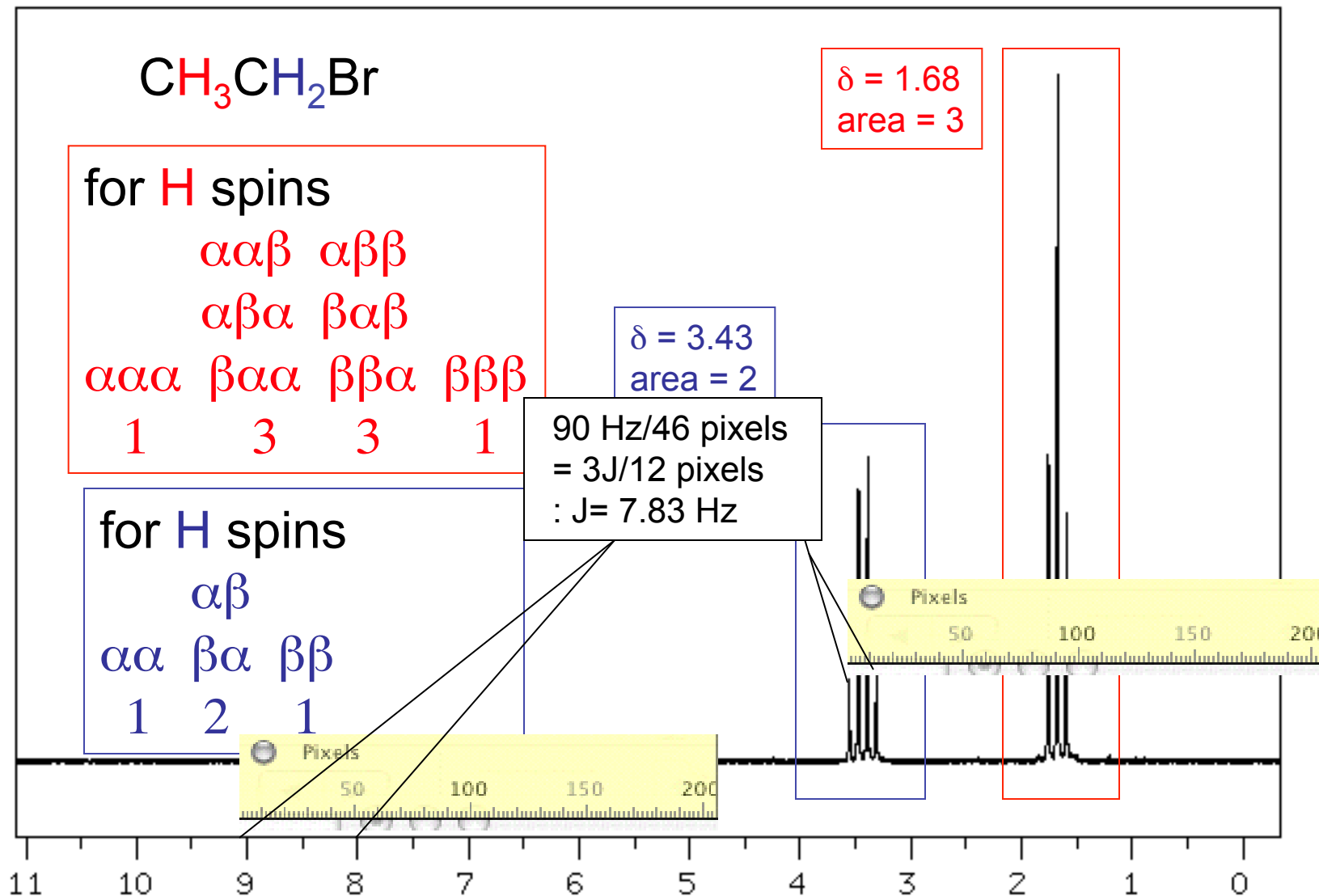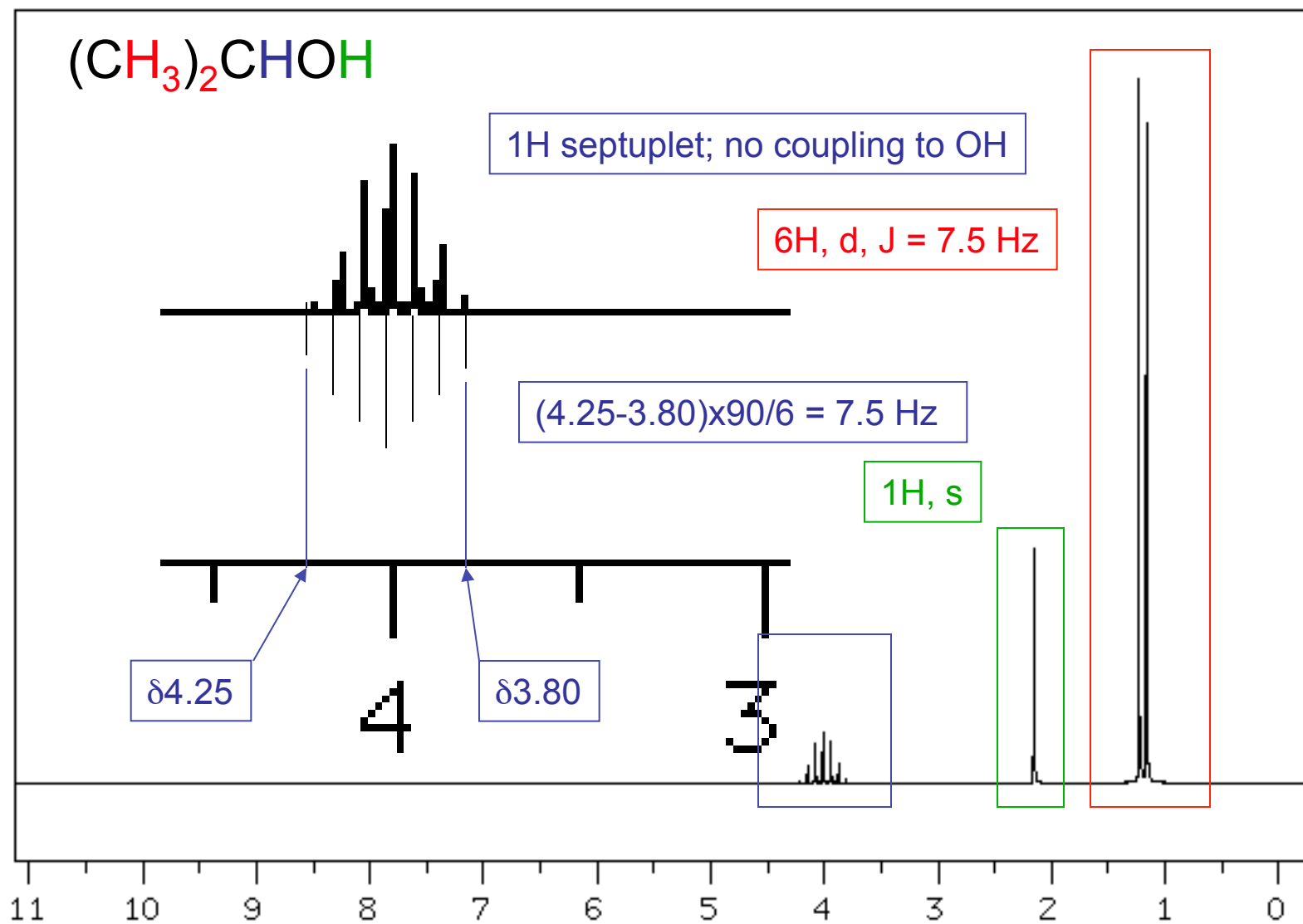
Proton Exchange of Isopropanol (90 MHz)

$(CH_3)_2CHOH + D_2O \longrightarrow (CH_3)_2CHOD$
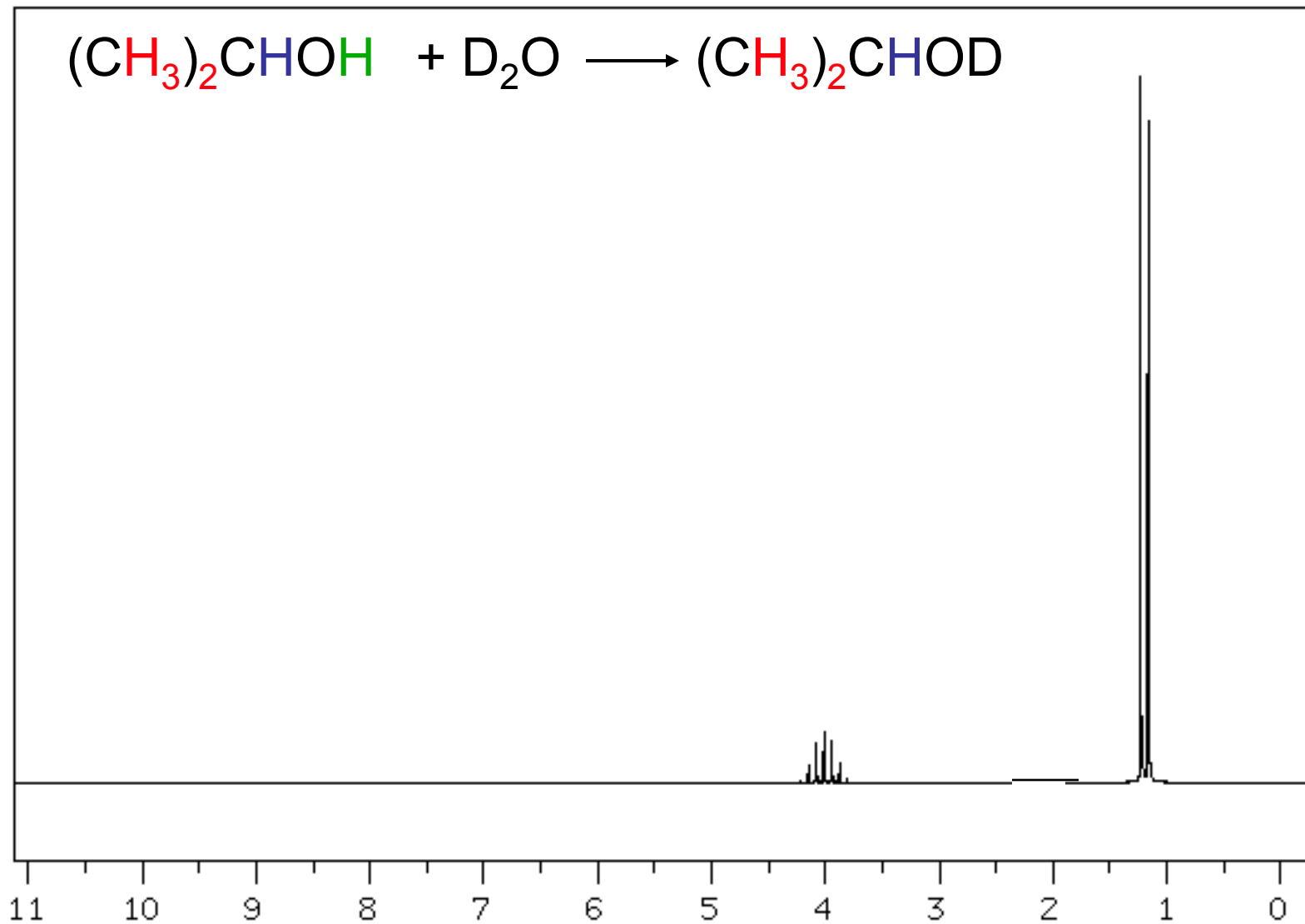
# Diastereotopic Protons: 2-Bromobutane
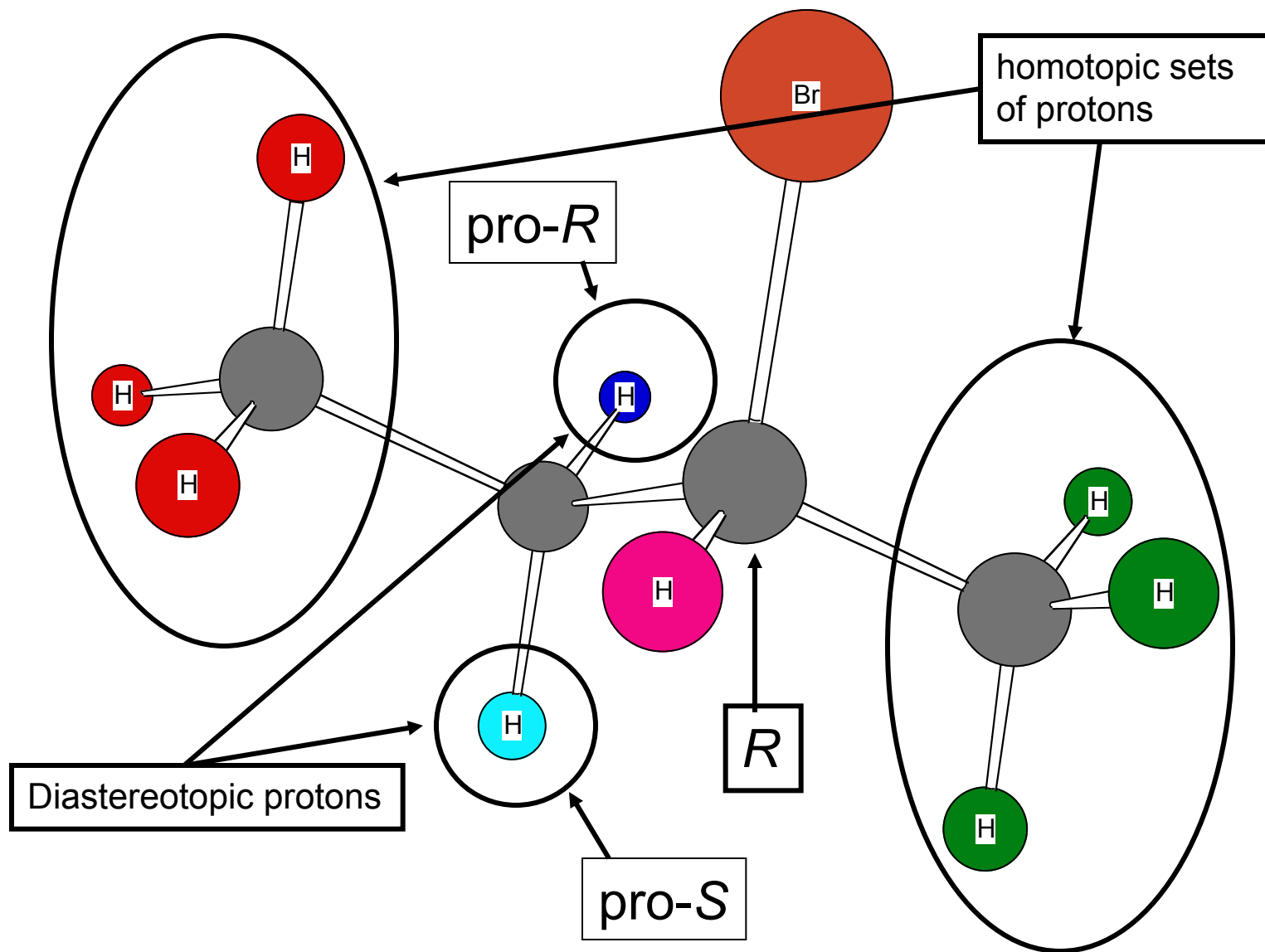
# Diastereotopic Protons: 2-Bromobutane at 90MHz



$\delta$1.03 (3H, t)

$\delta$1.70 (3H, d)

$\delta$1.82 (1H, m)

$\delta$1.84 (1H, m)

$\delta$4.09 (1H, m (sextet?))

# $^1H$ NMR of Propionaldehyde: 300 MHz

$\delta$1.13 (3H, t, J = 7.3 Hz)

$\delta$9.79 (1H, t, J = 1.4 Hz)

Is this pattern at $\delta$2.46 a pentuplet given that there are two different values for J?

No!

# $^1H$ NMR of Propionaldehyde: 300 MHz



δ2.46

7.3 Hz  7.3 Hz  7.3 Hz

1.4 Hz

7.3 Hz

quartet of doublets

7.3 Hz

δ9.79 (1H, t, J = 1.4 Hz)
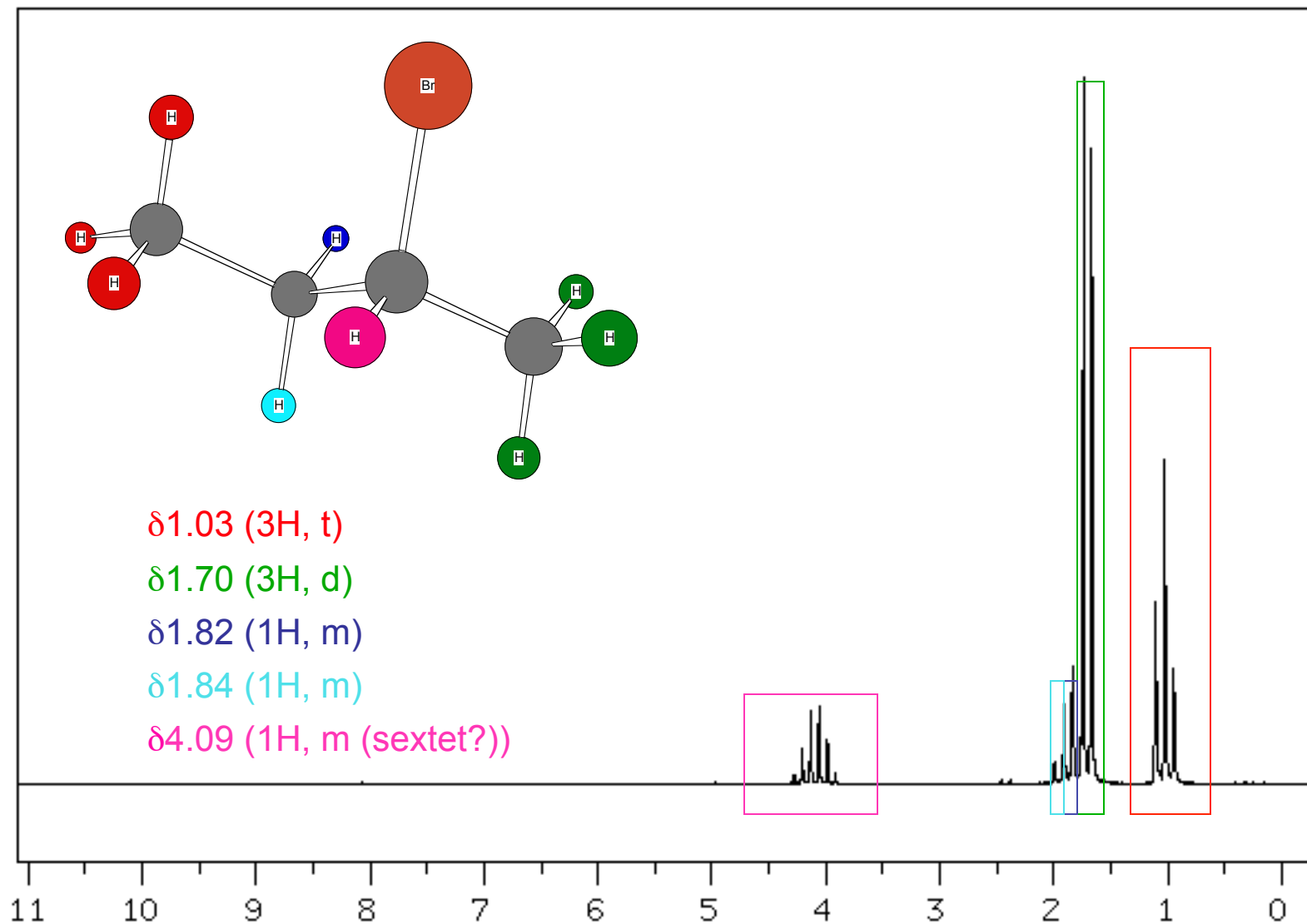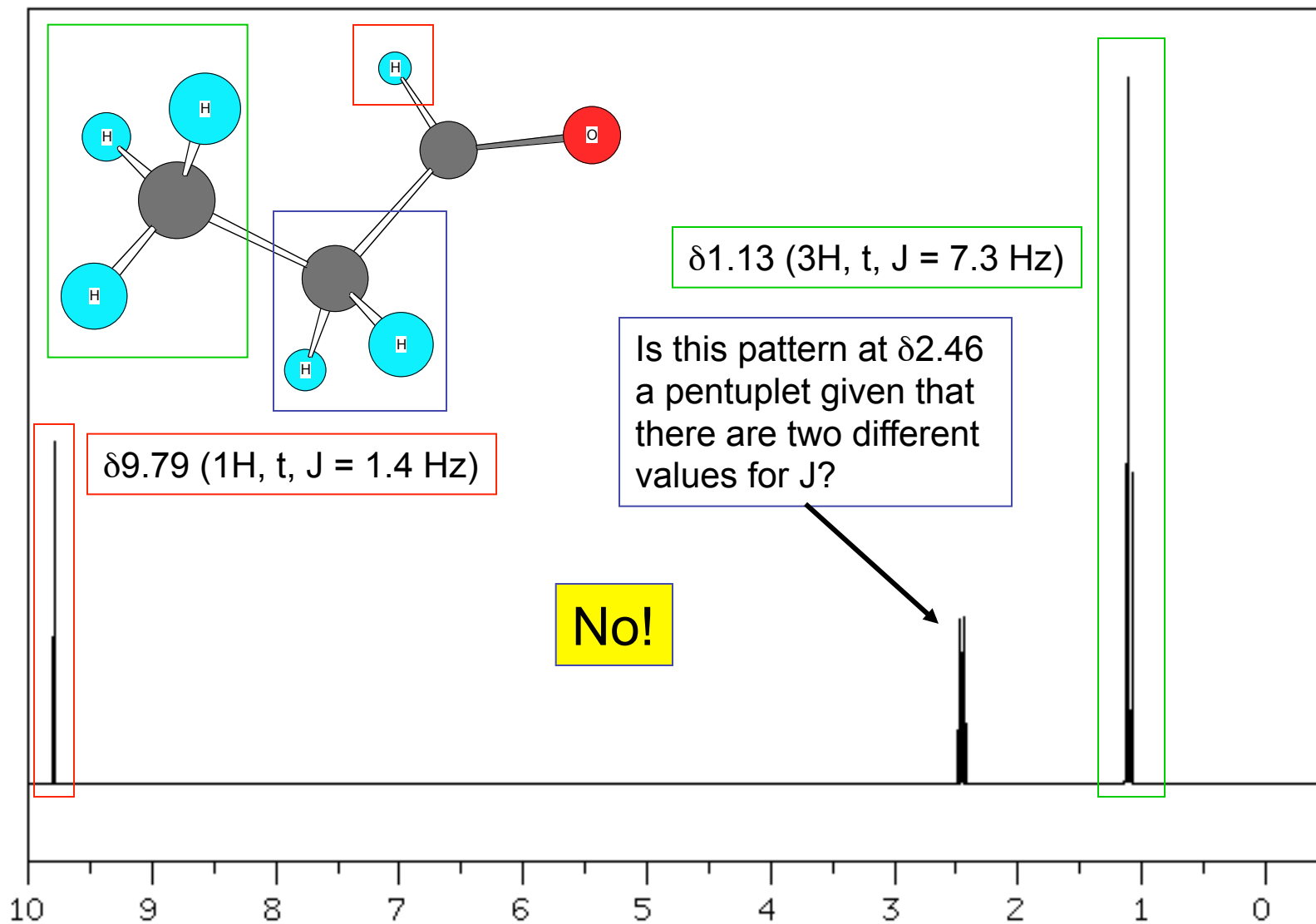
δ1.13 (3H, t, J = 7.3 Hz)
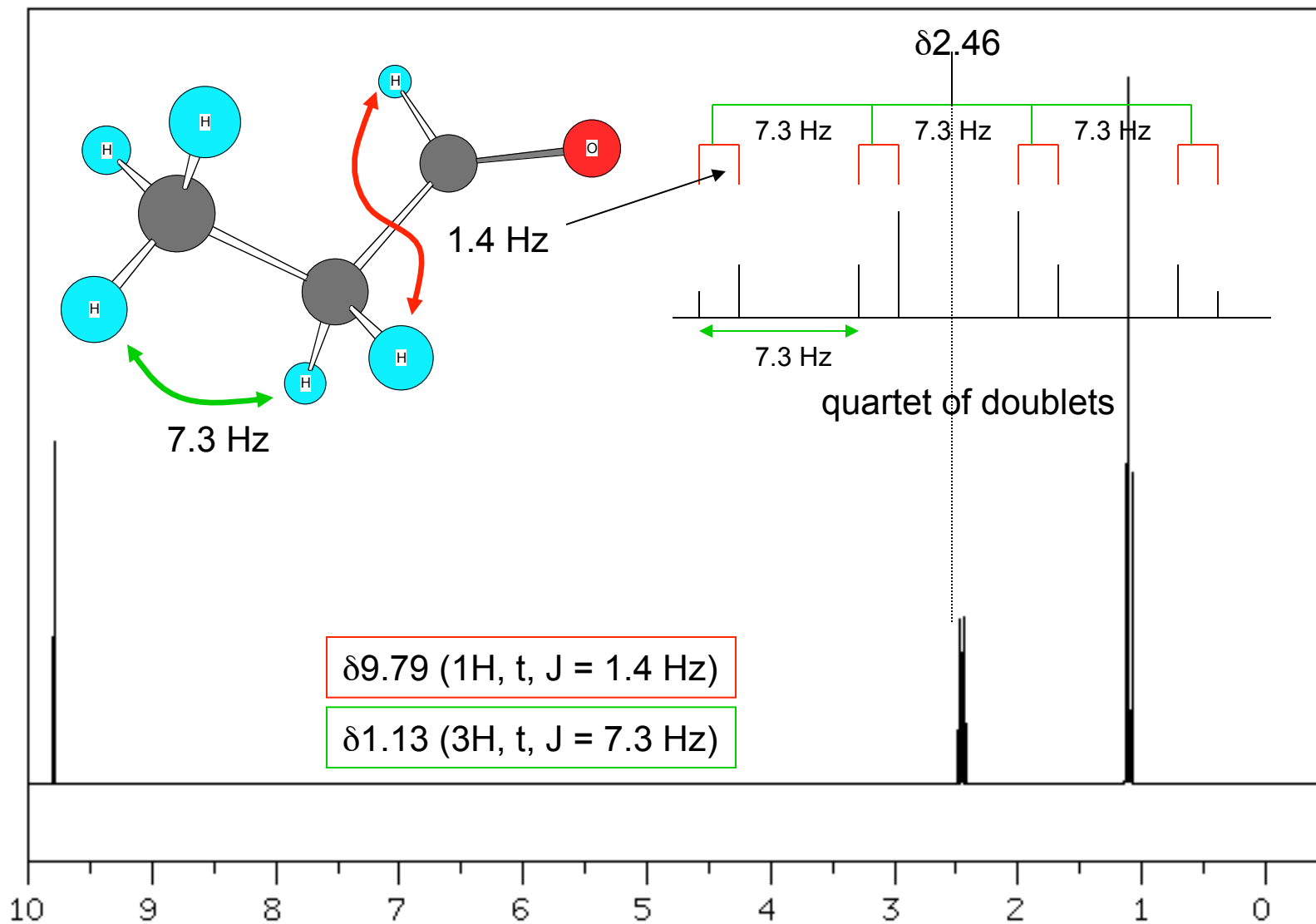
# $^1$H NMR of Ethyl Vinyl Ether: 300 MHz



J● ●= 14.4 Hz

J● ●= 1.9 Hz

J● ●= 6.9 Hz

3H, t, J = 7.0 Hz

2H, q, J = 7.0 Hz

δ3.96 (1H, dd, J = 6.9, 1.9 Hz)

δ4.17 (1H, dd, J = 14.4, 1.9 Hz)
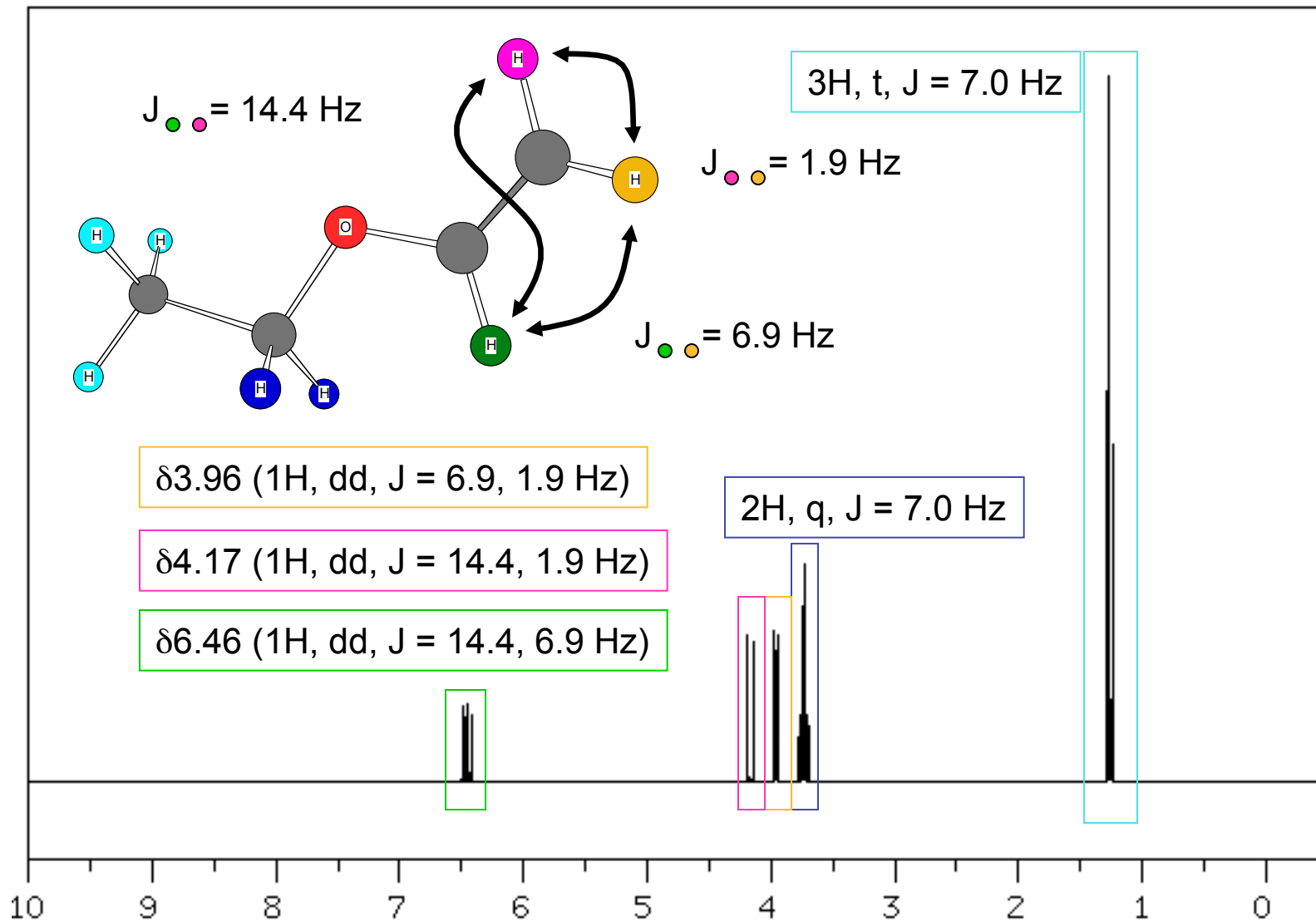
δ6.46 (1H, dd, J = 14.4, 6.9 Hz)

# *ABX Coupling in Ethyl Vinyl Ether*

δ6.46

δ4.17

1.9 → 14.4

δ3.96 (1H, dd, J = 6.9, 1.9 Hz)

δ4.17 (1H, dd, J = 14.4, 1.9 Hz)

δ6.46 (1H, dd, J = 14.4, 6.9 Hz)

δ3.96

1.9 → 6.9
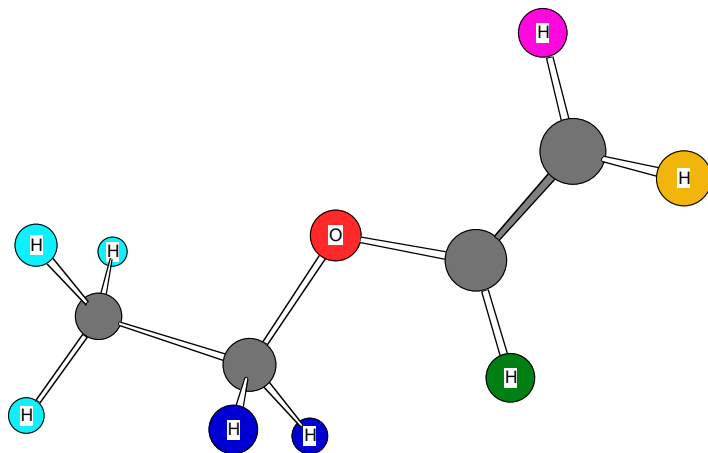
Another example
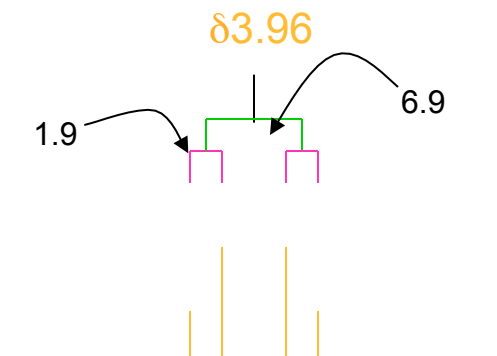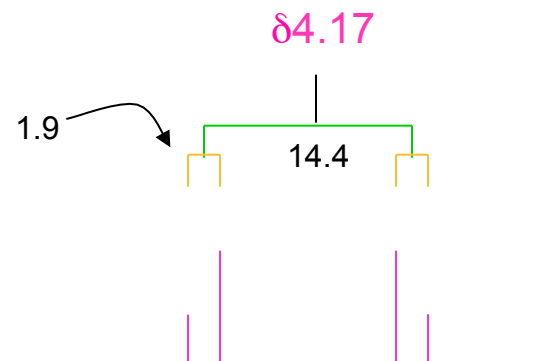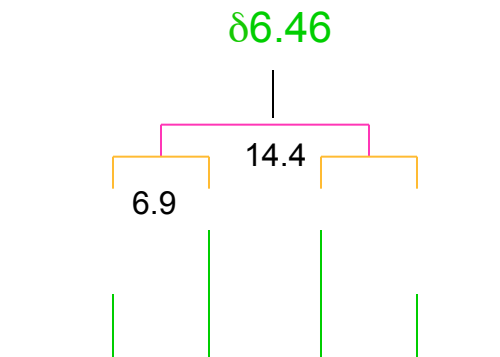
# Dependence of J on the Dihedral Angle

## The Karplus Equation

# $^1$H NMR (400 MHz): cis-4-*t*-Butylcyclohexanol



triplet of triplets
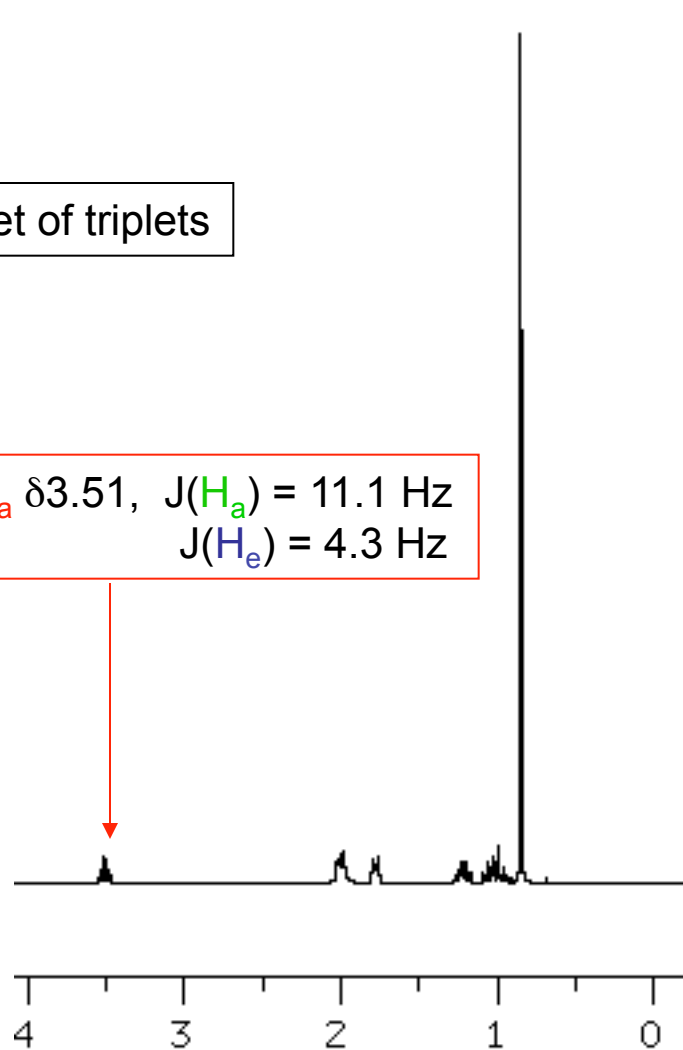
$H_e$

3.0    3.0

2.7    2.7

11.4 Hz

$H_e$ δ 4.03,  J($H_a$) = 3.0 Hz

J($H_e$) = 2.7 Hz

400 Hz
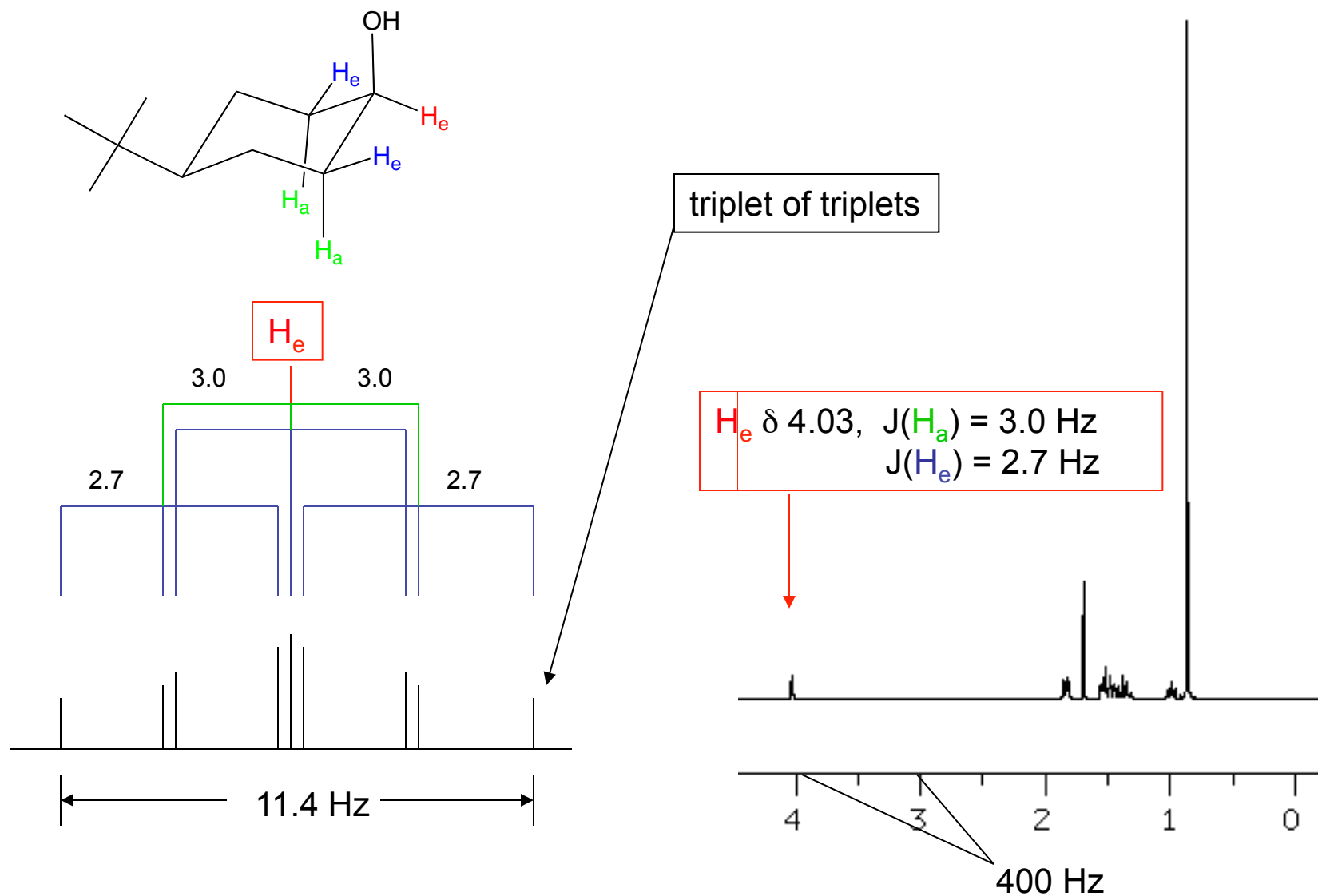
# ¹H NMR (400 MHz): trans-4-*t*-Butylcyclohexanol
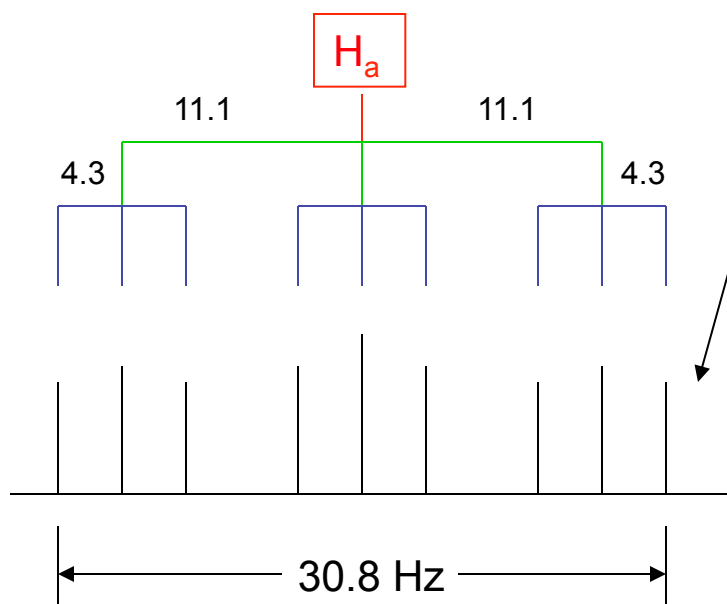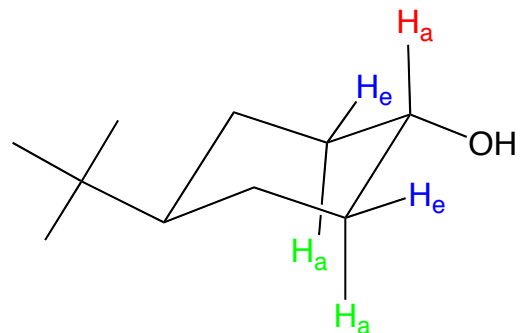


triplet of triplets

$H_a$

11.1   11.1

4.3   4.3

30.8 Hz

$H_a$ δ3.51,  J($H_a$) = 11.1 Hz
J($H_e$) = 4.3 Hz
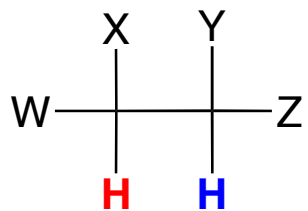
*Peak Shape as a Function of Δδ vs. J*

Δδ >> J

Δδ

J

10  9  8  7  6  5  4  3  2  1  0  δ

Δδ ~= J

10  9  8  7  6  5  4  3  2  1  0  δ

Δδ = 0

10  9  8  7  6  5  4  3  2  1  0  δ

*Magnetic Anisotropy*

Downfield shift for aromatic protons ($\delta$ 6.0-8.5)
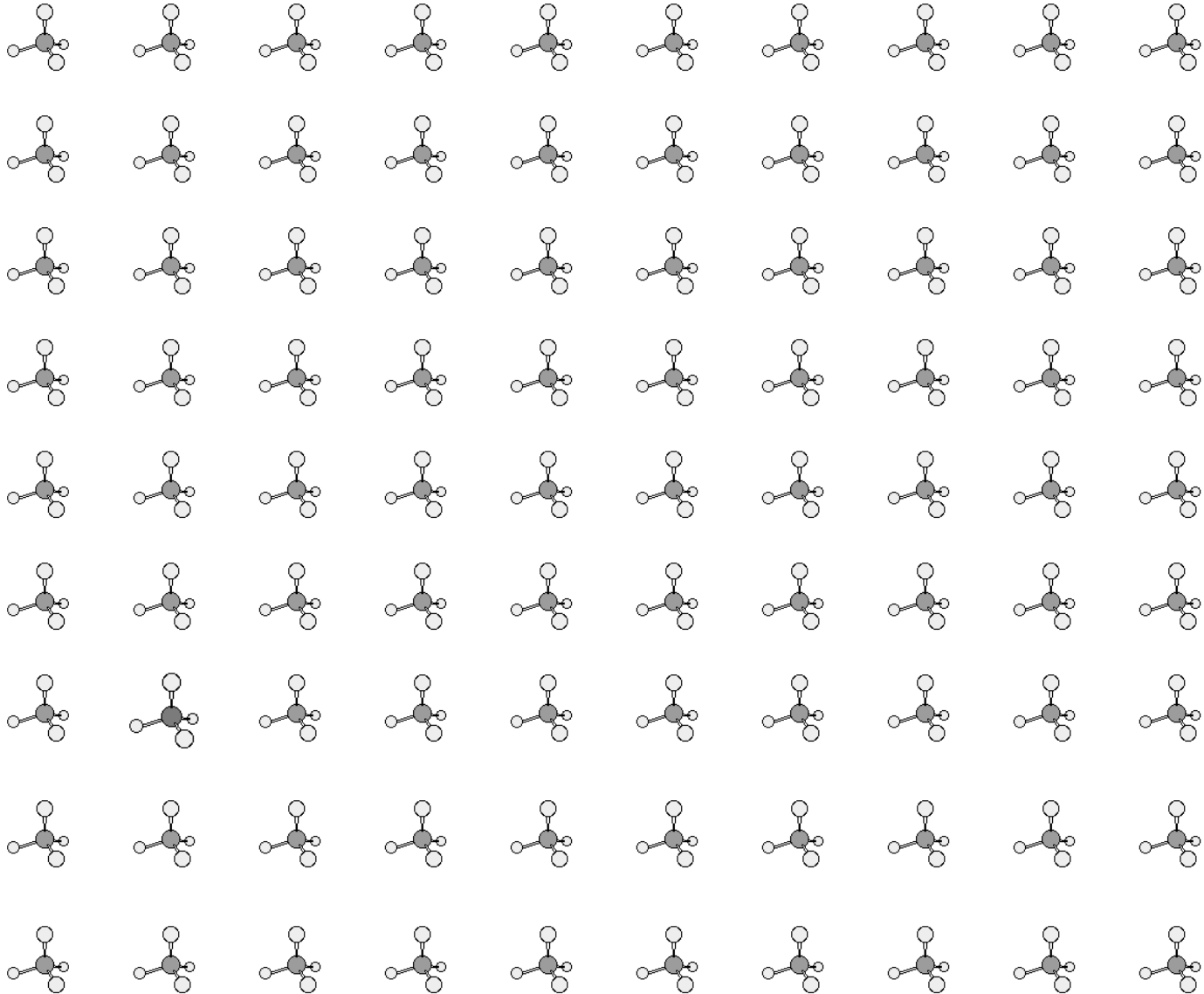
$B^o$

*Magnetic Anisotropy*

R

C

C

H

B$^o$
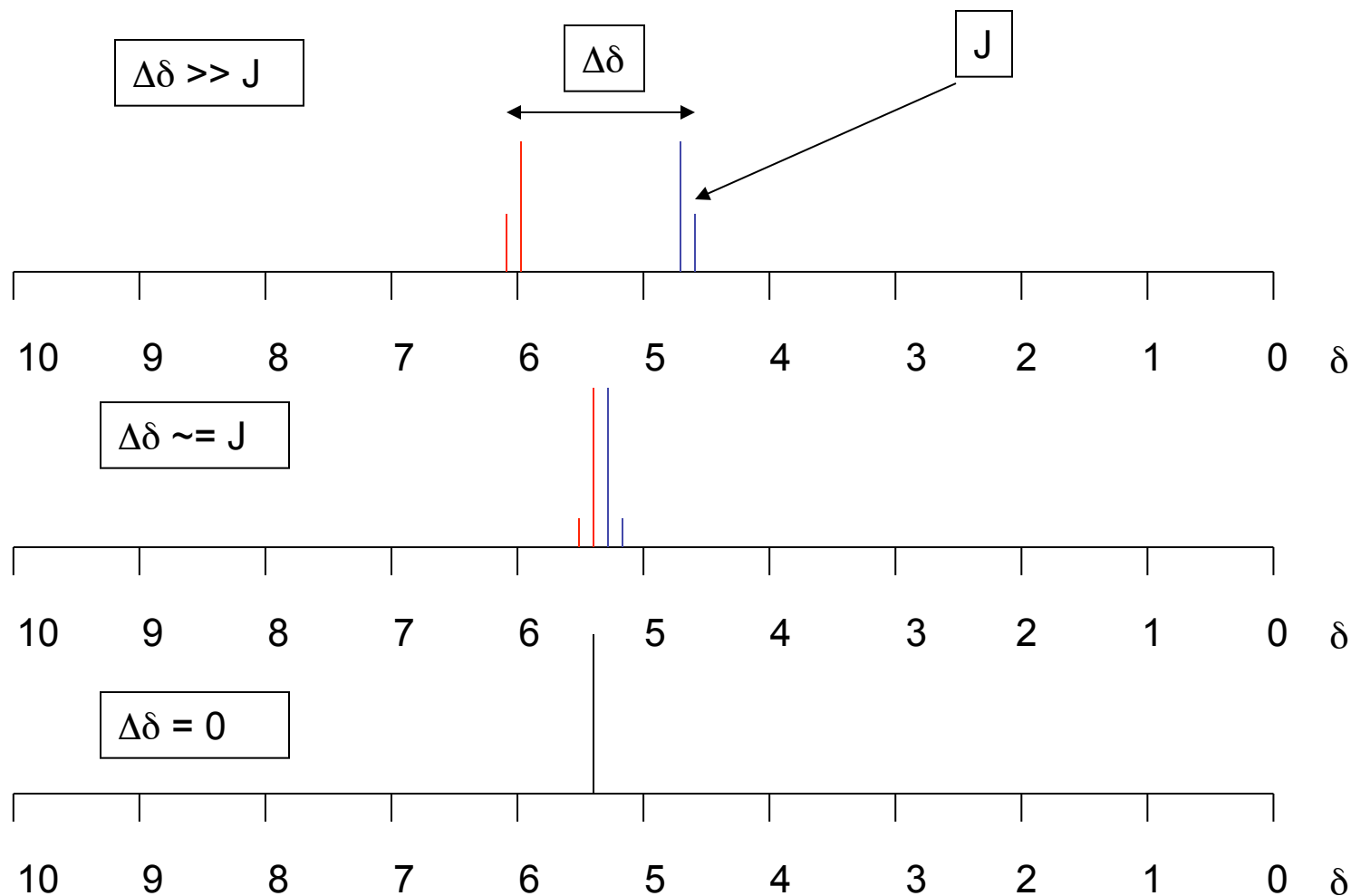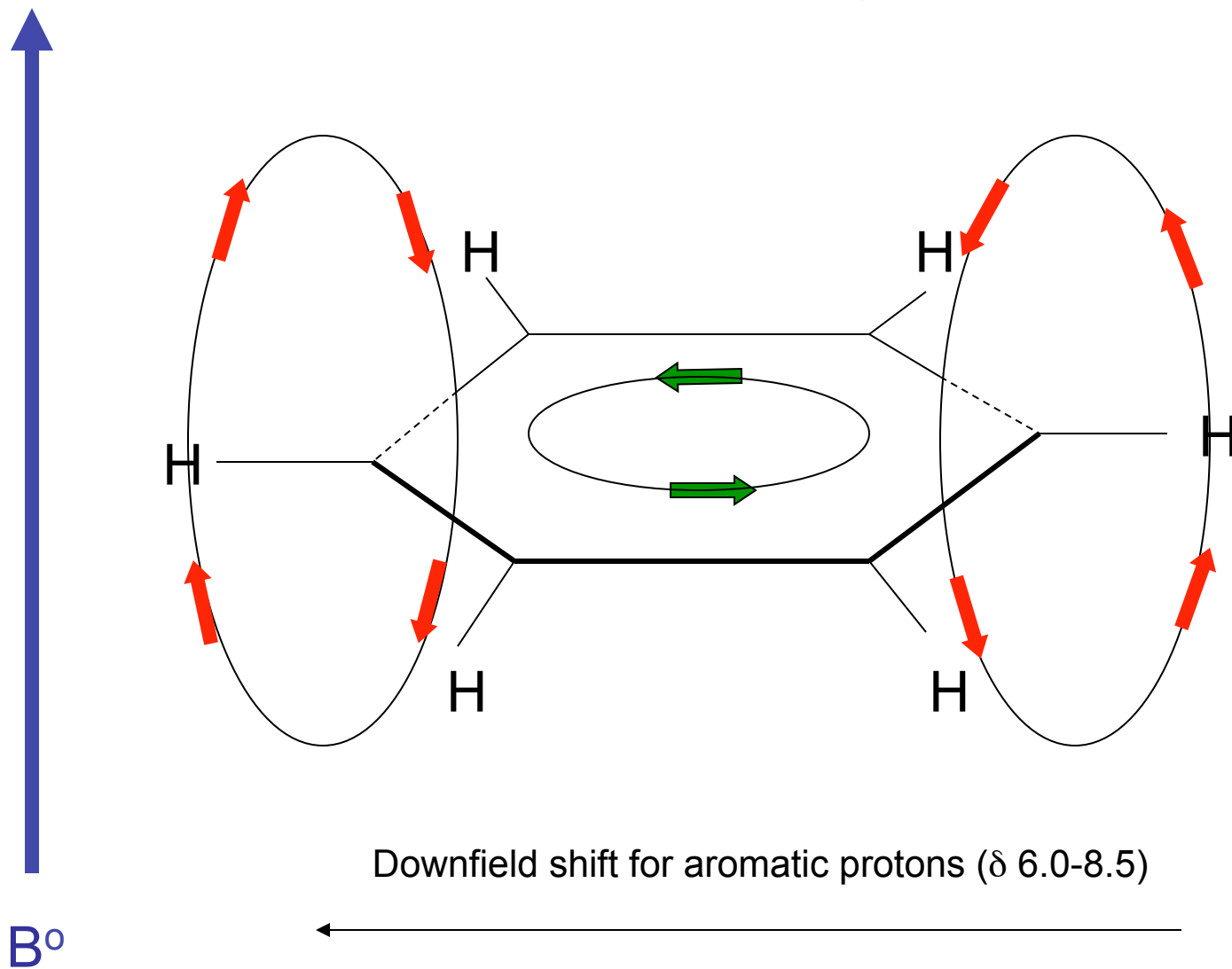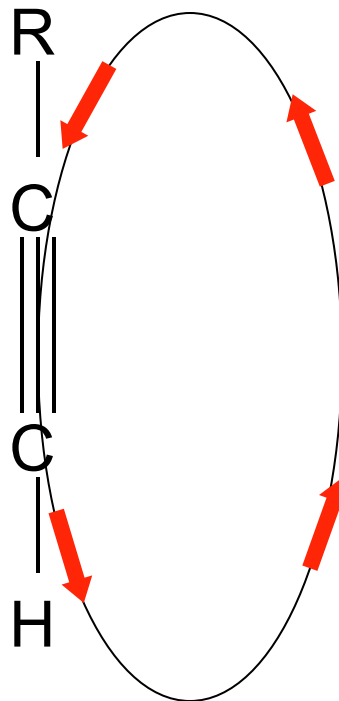
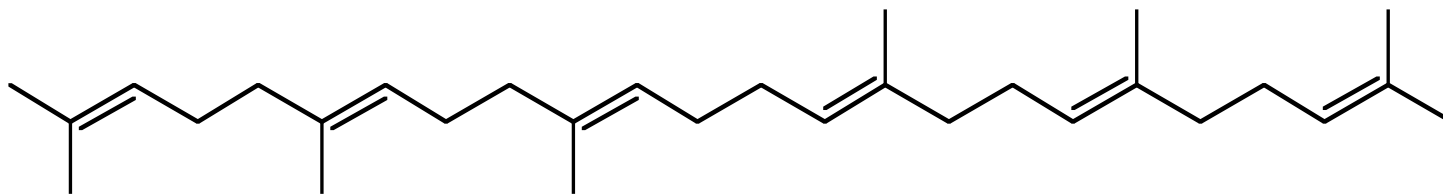Upfield shift for alkyne protons ($\delta$ 1.7-3.1)
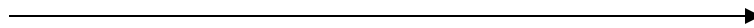
# $^{13}C$ Nuclear Magnetic Resonance
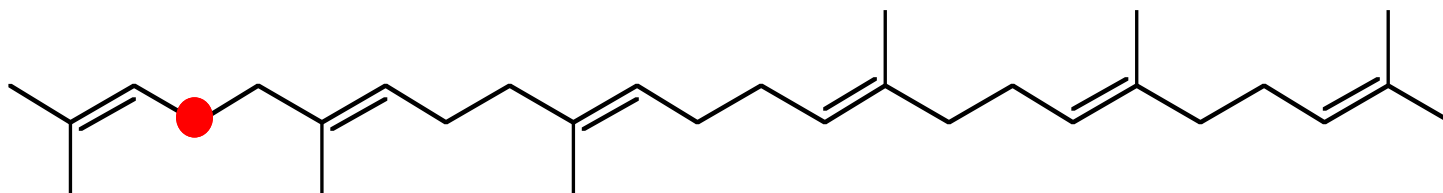
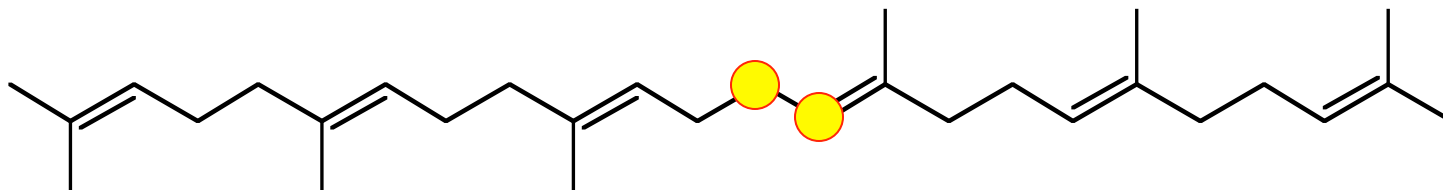## $^{13}C$ Chemical Shifts

# Where's Waldo?

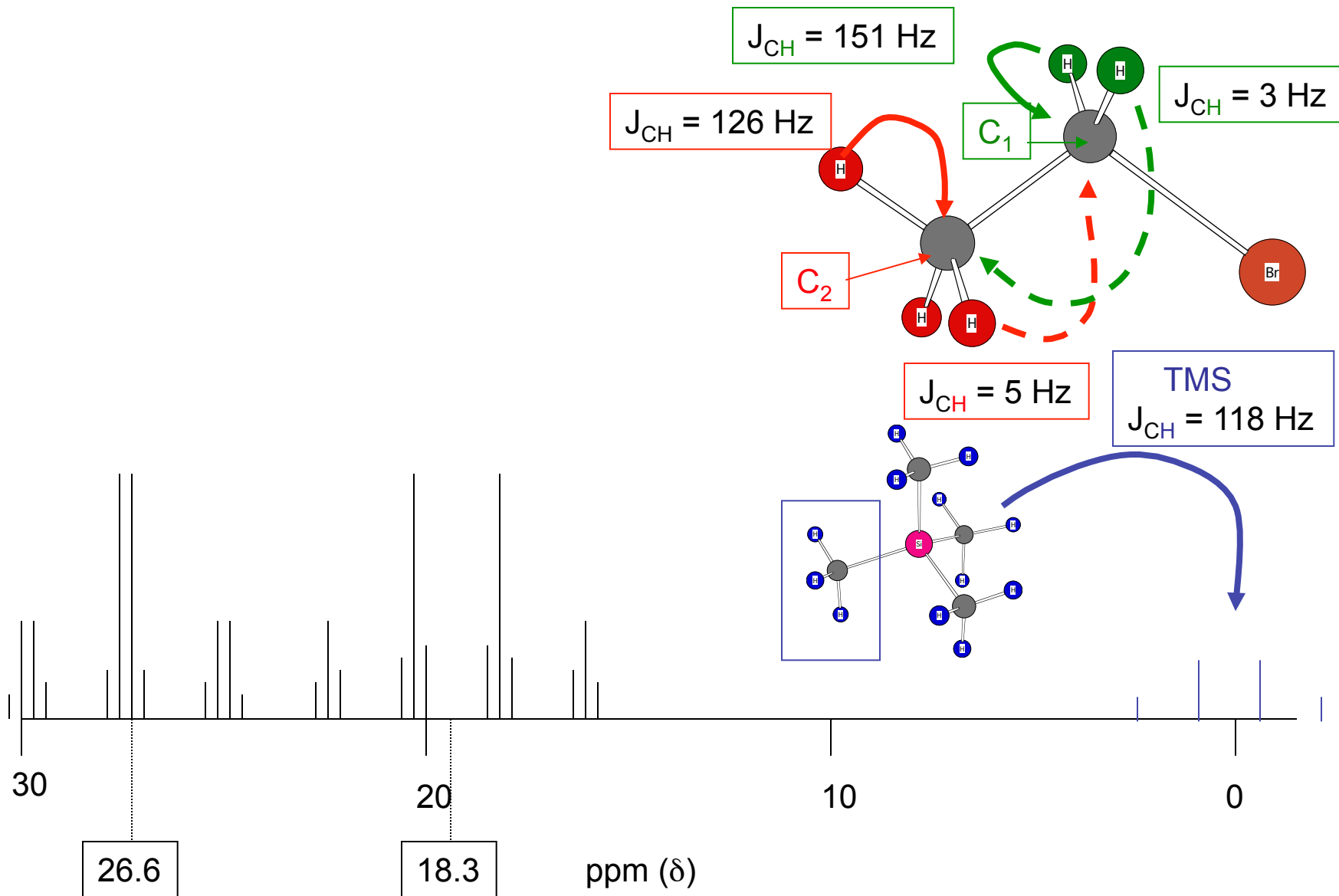One carbon in 3 molecules of squalene is $^{13}C$

What are the odds that two $^{13}C$ are bonded to one another?
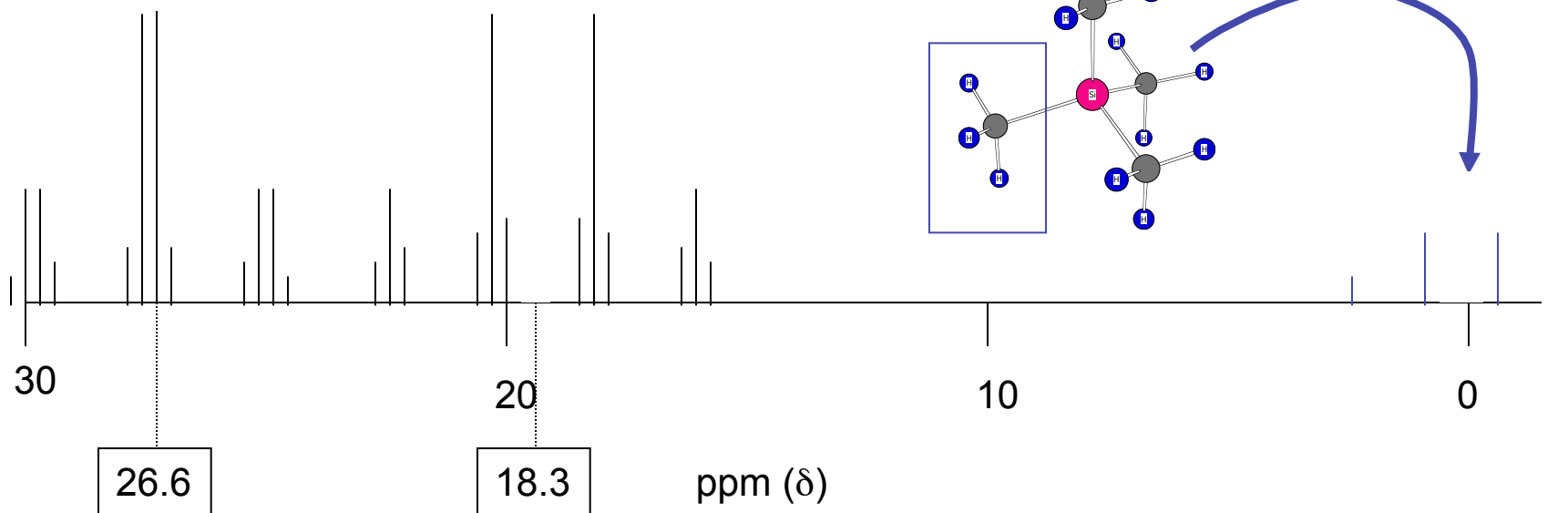
~10,000 to 1

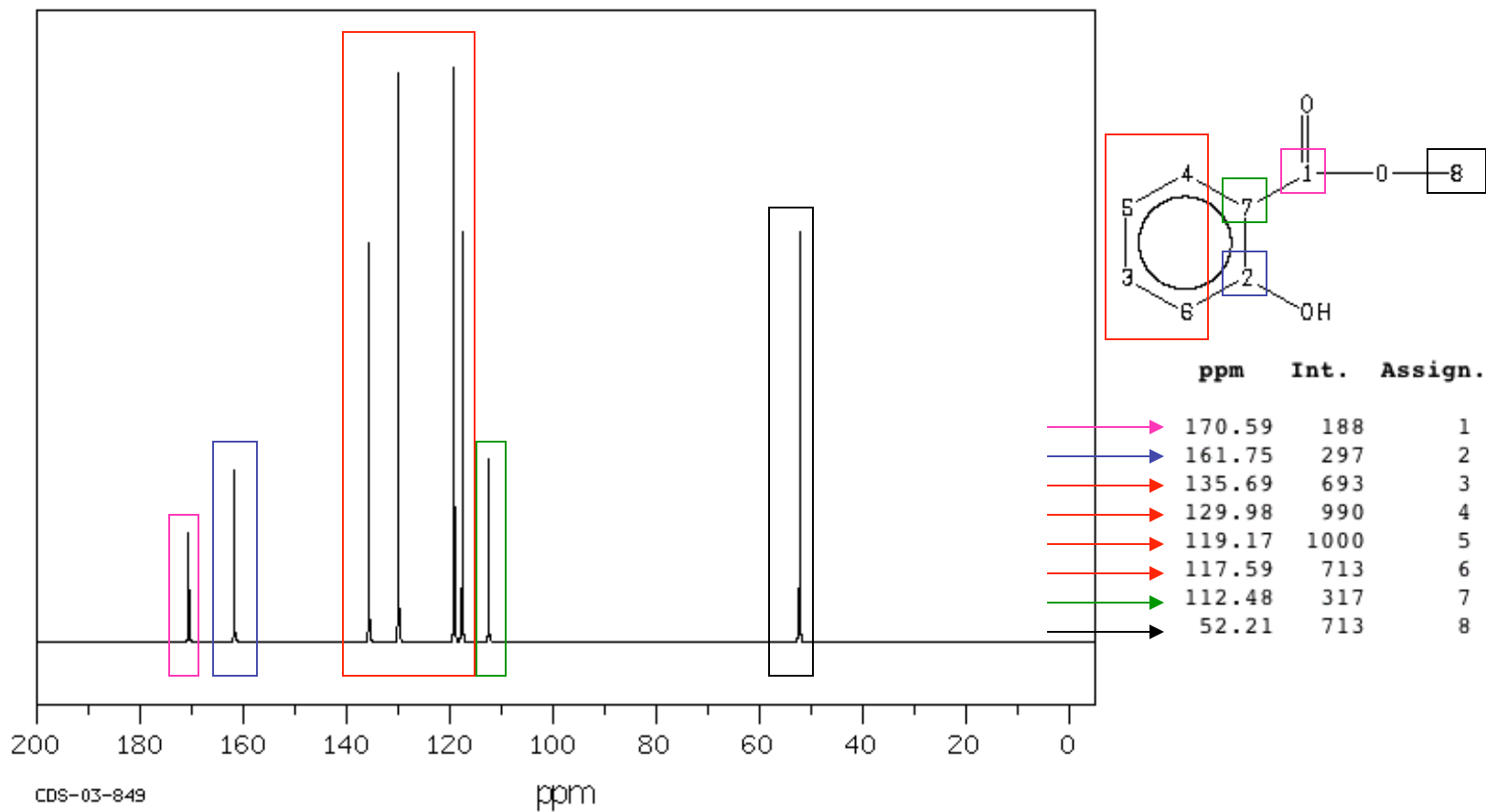# $^{13}C$ NMR Spectrum of Ethyl Bromide at 62.8 MHz

# $^{13}C$ NMR Spectrum of Ethyl Bromide at 62.8 MHz

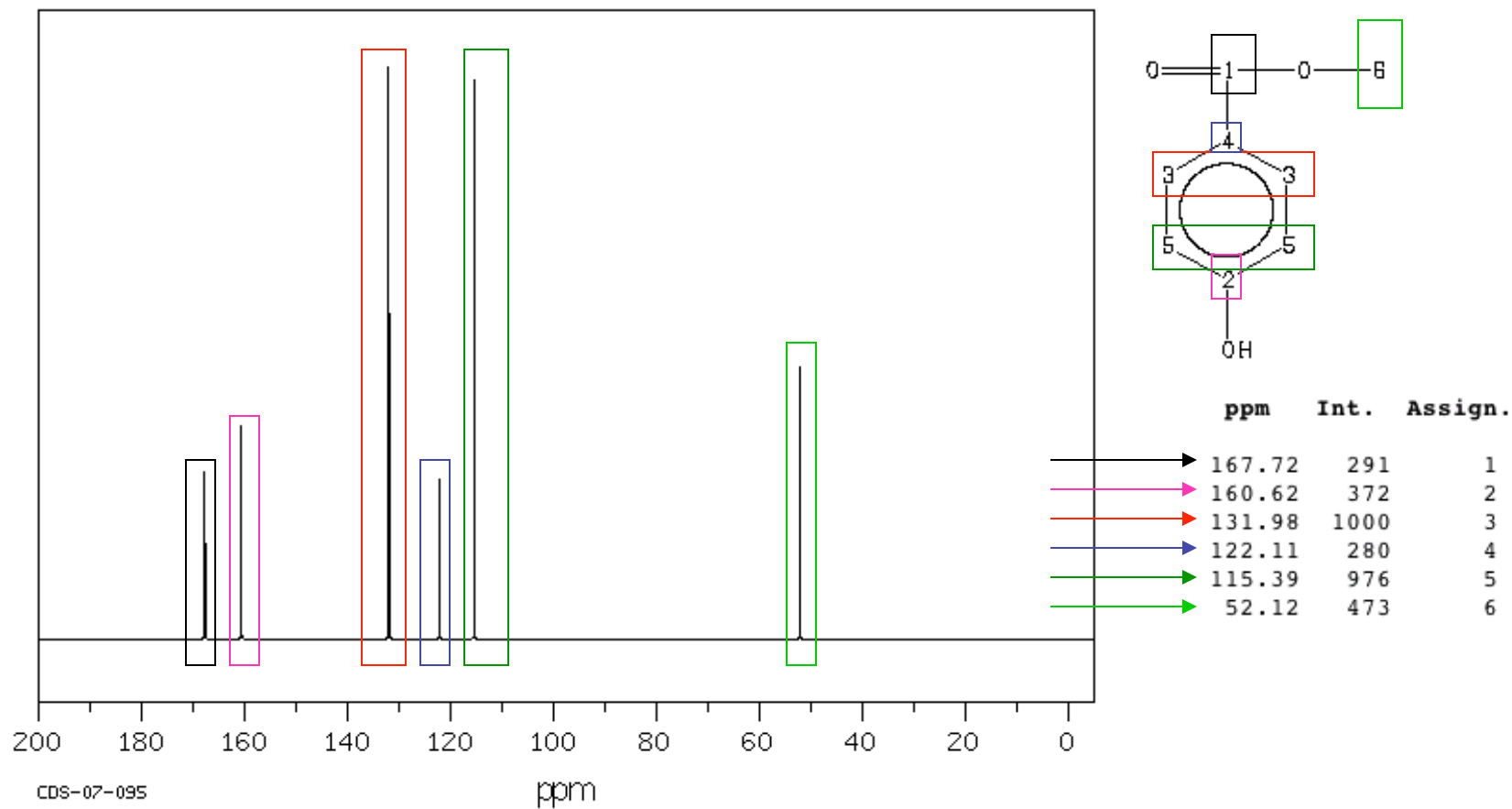Off resonance decoupling of the $^{1}H$ region removes small C-H coupling.

Broadband decoupling removes all C-H coupling.

$J_{CH} = 151$ Hz

$J_{CH} = 126$ Hz

$J_{CH} = 3$ Hz

$C_1$

$C_2$

Br

$J_{CH} = 5$ Hz

TMS
$J_{CH} = 118$ Hz



30

20

10

0

26.6

18.3

ppm ($\delta$)

# $^{13}C$ Spectrum of Methyl Salicylate
## (Broadband Decoupled)

| ppm | Int. | Assign. |
|---|---|---|
| 170.59 | 188 | 1 |
| 161.75 | 297 | 2 |
| 135.69 | 693 | 3 |
| 129.98 | 990 | 4 |
| 119.17 | 1000 | 5 |
| 117.59 | 713 | 6 |
| 112.48 | 317 | 7 |
| 52.21 | 713 | 8 |

CDS-03-849

# $^{13}C$ Spectrum of Methyl p-Hydroxybenzoate
## (Broadband Decoupled)



| ppm | Int. | Assign. |
|---|---|---|
| 167.72 | 291 | 1 |
| 160.62 | 372 | 2 |
| 131.98 | 1000 | 3 |
| 122.11 | 280 | 4 |
| 115.39 | 976 | 5 |
| 52.12 | 473 | 6 |

CDS-07-095

ppm

# *The $^{13}$C Spectrum of Camphor*

# *The End*