INSTITUT FÜR
ORGANISCHE CHEMIE
UNIVERSITÄT REGENSBURG

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Sommersemester

Seminar zum OC I Praktikum

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1. Spektroskopie (Übersicht)
2. Strukturaufklärung
3. Stereochemie
4. Isomerie
5. Mobile Proton

Übersicht

University of California, Irvine
Understanding NMR Spectroscopy

James Keeler, *University of Cambridge*

http://www-keeler.ch.cam.ac.uk/lectures/Irvine/

NMR spectra:

\\TITAN-DPS009.ur.de\DPS009\CHEMIE\ZA\nmrspec\Ava400Stud

(Help:
https://www.uni-regensburg.de/rechenzentrum/support/netzlaufwerke-und-dateidienste/index.html)

TopSpin
http://www-oc.chemie.uni-regensburg.de/za/nmr/software/software_d.html

https://www.uni-regensburg.de/rechenzentrum/software/softwarekatalog/index.html

http://www-oc.chemie.uni-regensburg.de/za/nmr/software/software_d.html

auf 15 Jahre befristete, Lizenzserver unabhängige Software:

TOPSPIN (Windows, Mac, Linux): TopSpin Version herunterladbar bei der Firma Bruker Bio-Spin GmbH mit einer 15 Jahre gültigen Lizenz (Anleitung).

TopSpin 3.2

NMR-Spektroskopie

http://www-oc.chemie.uni-regensburg.de/za/nmr/diverses/diverses_d.html

„VERSCHIEDENES“:

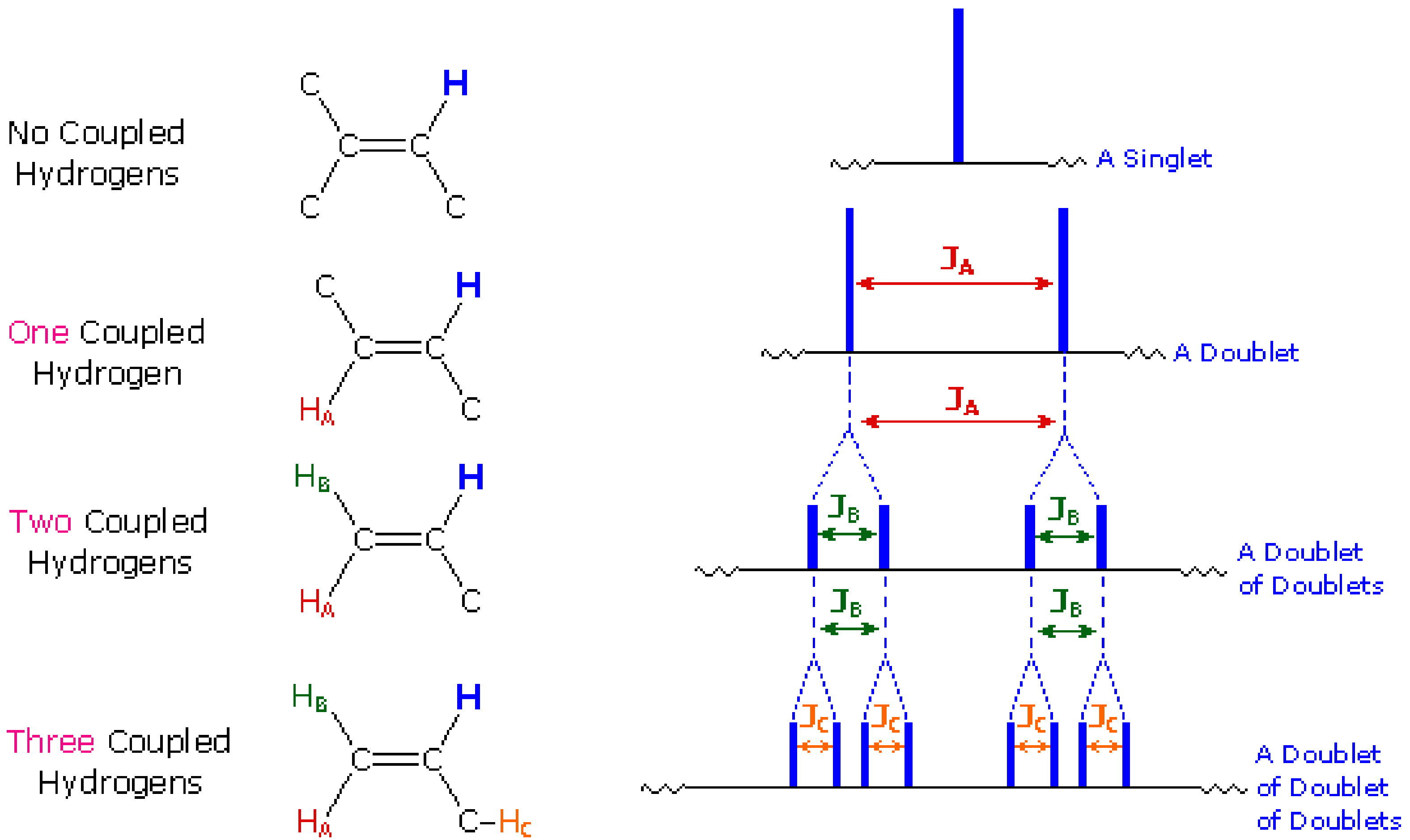
NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities

Organometallics **2010**, 29, 2176-2179 (**DOI:** 10.1021/om100106e)

Table 1. ^{1}H NMR Data[a]

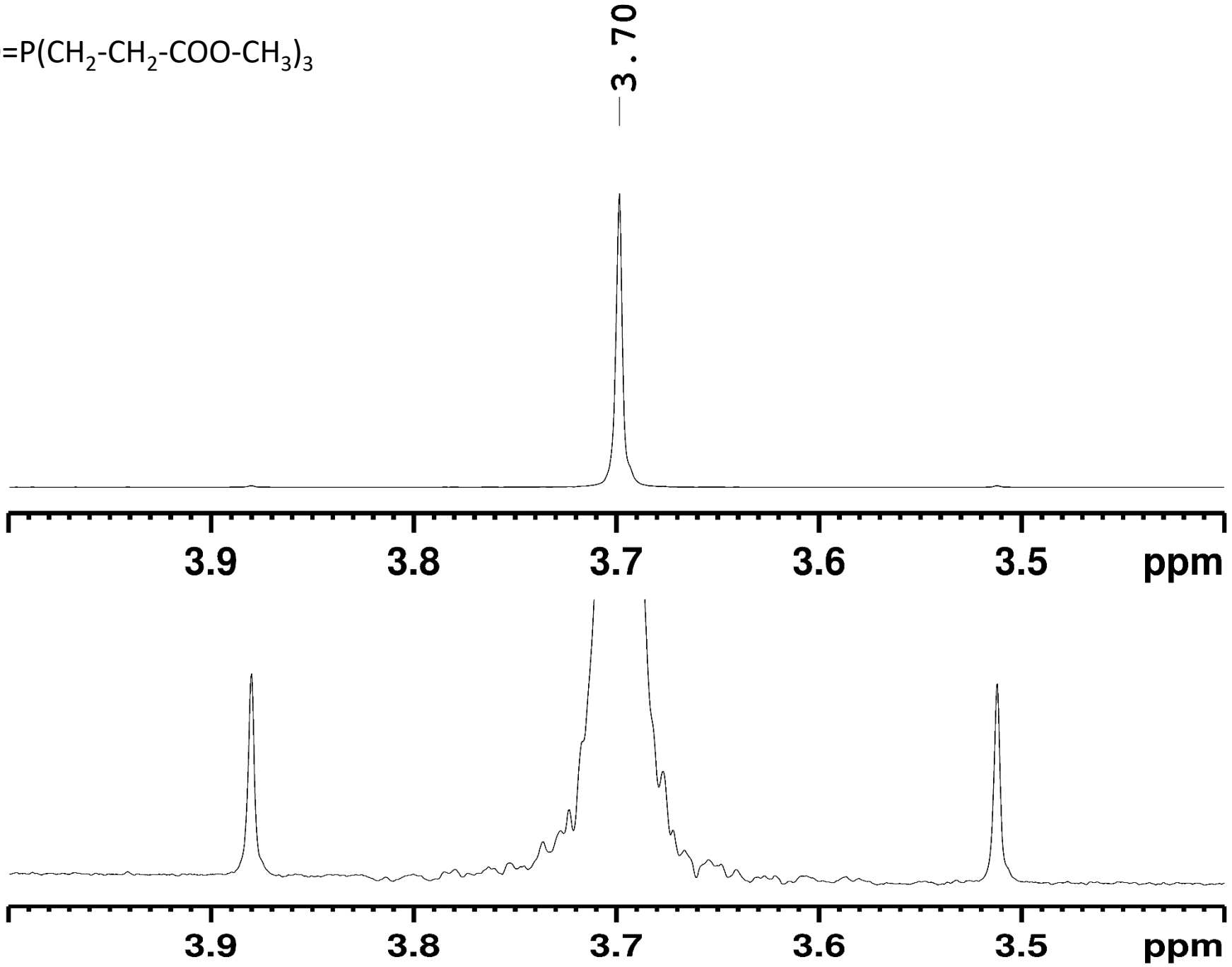
	proton	mult	THF-d_8	CD_2Cl_2	$CDCl_3$	toluene-d_8	C_6D_6	C_6D_5Cl	$(CD_3)_2CO$	$(CD_3)_2SO$	CD_3CN	TFE-d_3	CD_3OD	D_2O
solvent residual signals			1.72 3.58	5.32	7.26	2.08 6.97 7.01 7.09	7.16	6.96 6.99 7.14	2.05	2.50	1.94	5.02 3.88	3.31	4.79
water	OH	s	2.46	1.52	1.56	0.43	0.40	1.03	2.84[b]	3.33[b]	2.13	3.66	4.87	
acetic acid	CH_3	s	1.89	2.06	2.10	1.57	1.52	1.76	1.96	1.91	1.96	2.06	1.99	2.08
acetone	CH_3	s	2.05	2.12	2.17	1.57	1.55	1.77	2.09	2.09	2.08	2.19	2.15	2.22
acetonitrile	CH_3	s	1.95	1.97	2.10	0.69	0.58	1.21	2.05	2.07	1.96	1.95	2.03	2.06
benzene	CH	s	7.31	7.35	7.36	7.12	7.15	7.20	7.36	7.37	7.37	7.36	7.33	
tert -butyl alcohol	CH_3	s	1.15	1.24	1.28	1.03	1.05	1.12	1.18	1.11	1.16	1.28	1.40	1.24
	OH	s[c]	3.16			0.58	0.63	1.30		4.19	2.18	2.20		
chloroform	CH	s	7.89	7.32	7.26	6.10	6.15	6.74	8.02	8.32	7.58	7.33	7.90	

J-coupling



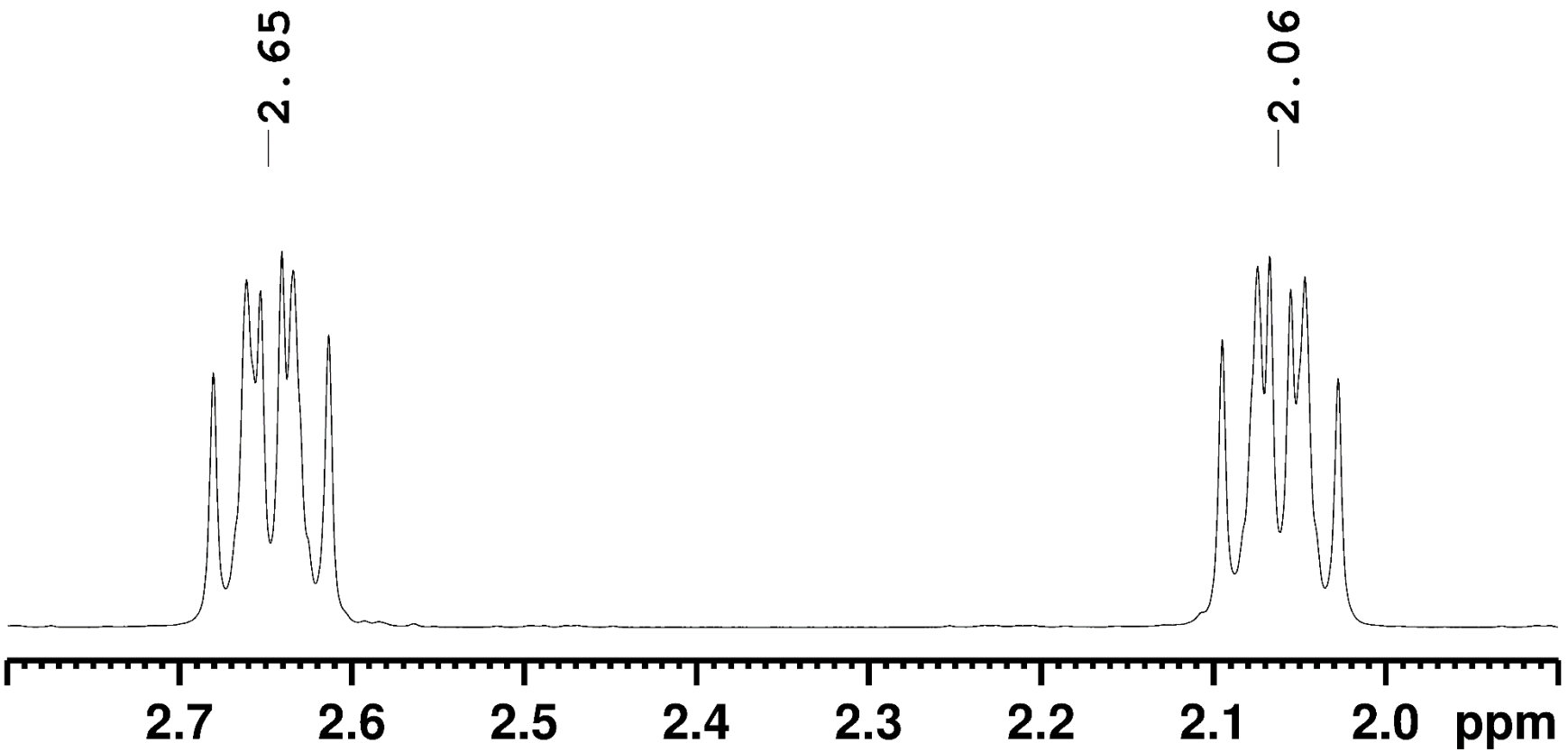
https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm

$O=P(CH_2\text{-}CH_2\text{-}COO\text{-}CH_3)_3$



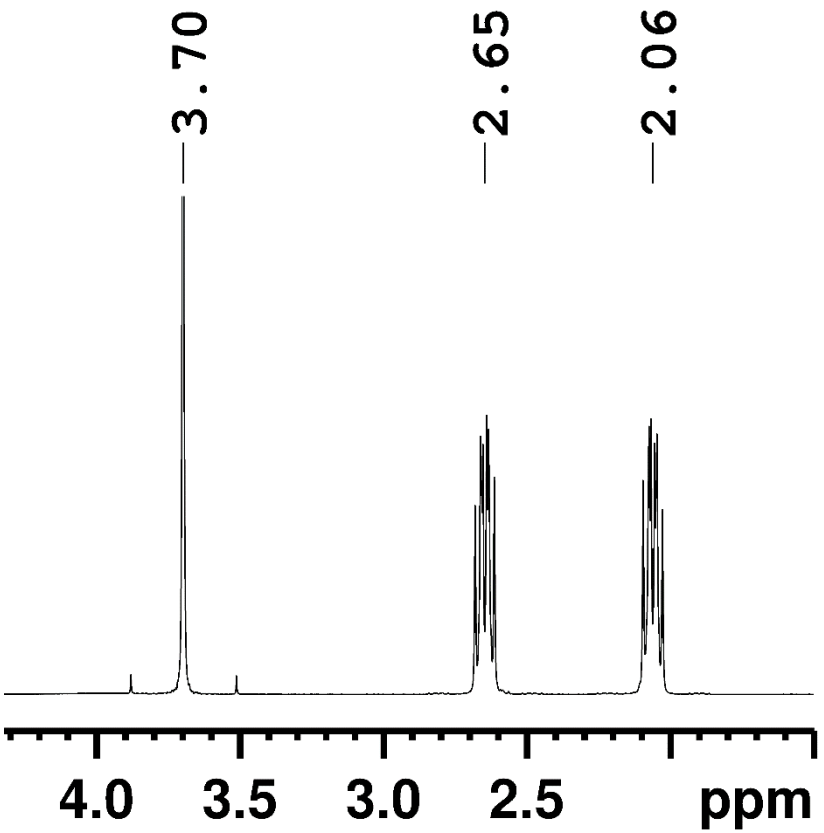
$O=P(CH_2\text{-}CH_2\text{-}COO\text{-}CH_3)_3$

2.06 ppm **2.65 ppm**



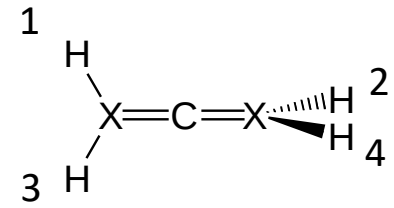
$O=P(CH_2\text{-}CH_2\text{-}COO\text{-}CH_3)_3$

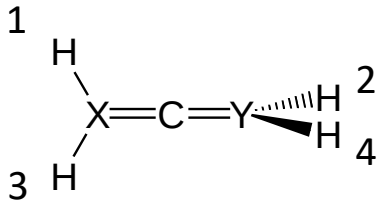
Spectrum 20

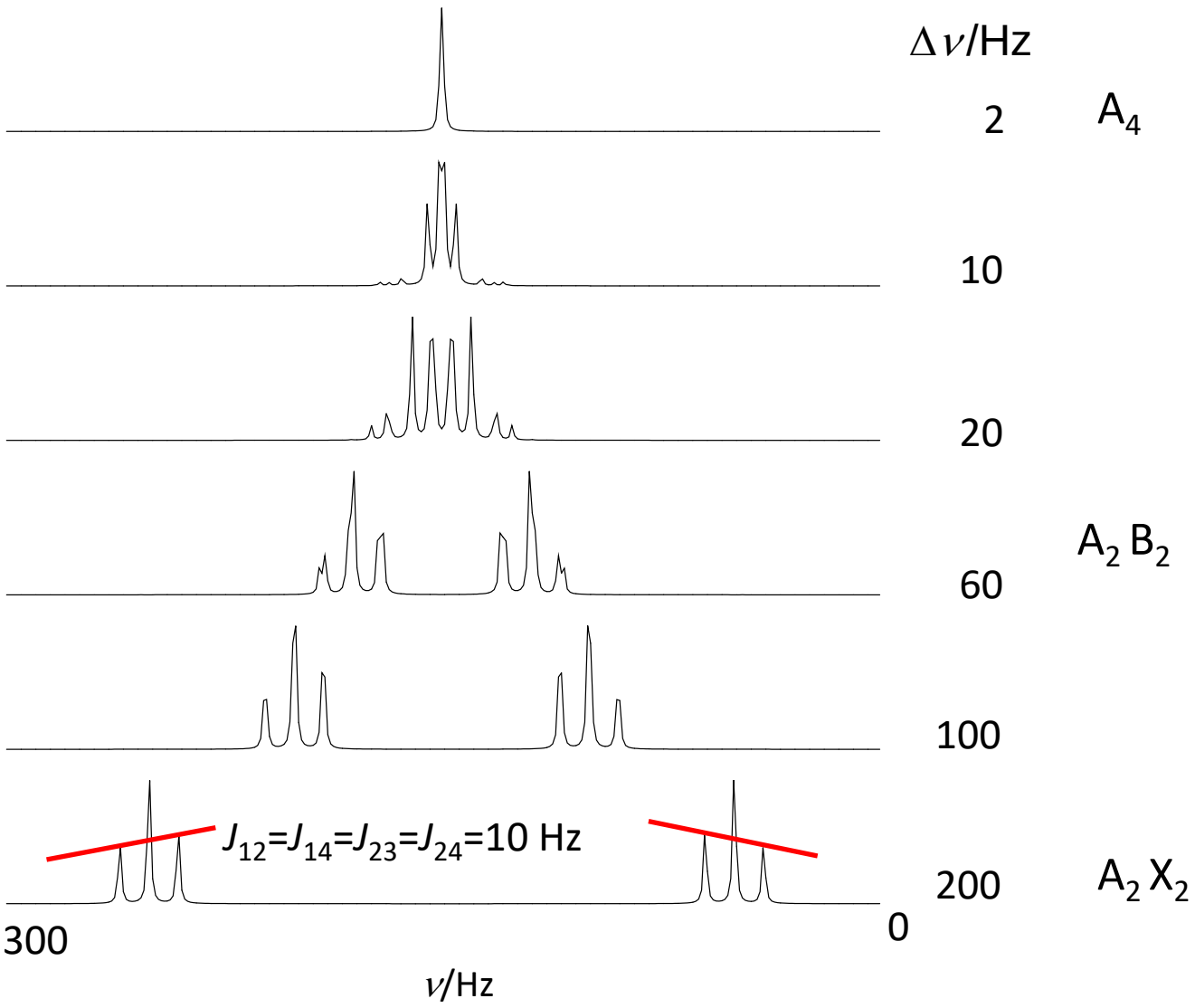


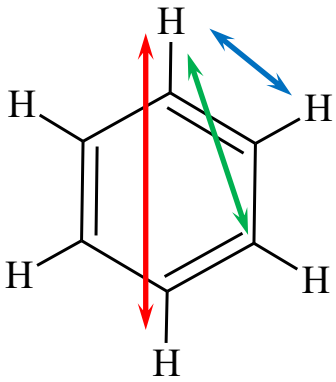
TopSpin
Analyse→Simulate →1D
Incl. 31P
2 spins 2.647 ppm
2 spins 2.0615 ppm
3J(HH) ≈ 7.8 Hz
2J(PH) ≈ 11.0 Hz
3J(PH) ≈ 11.0 Hz
Sim

Dacheffekte

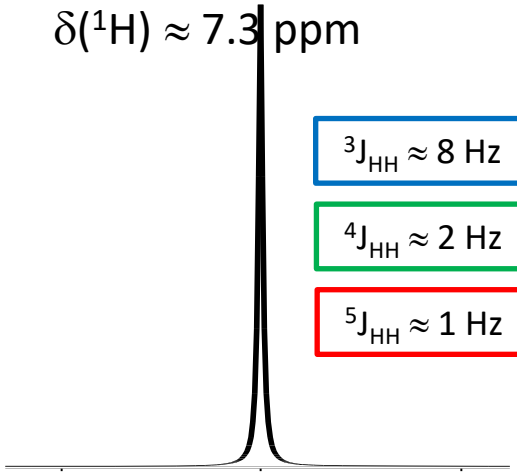








$\delta(^1H) \approx 7.3$ ppm



$^3J_{HH} \approx 8$ Hz

$^4J_{HH} \approx 2$ Hz

$^5J_{HH} \approx 1$ Hz

AA‘MM‘X

$\delta(^1H) \approx 8.6$ ppm

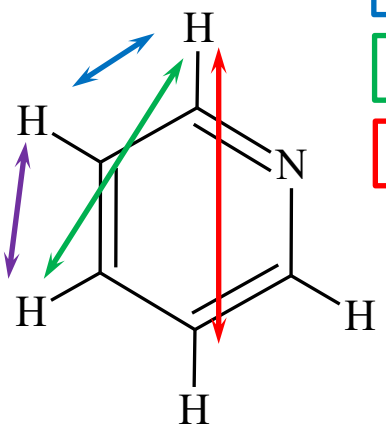
$^3J_{HH} \approx 5$ Hz

$^4J_{HH} \approx 2$ Hz

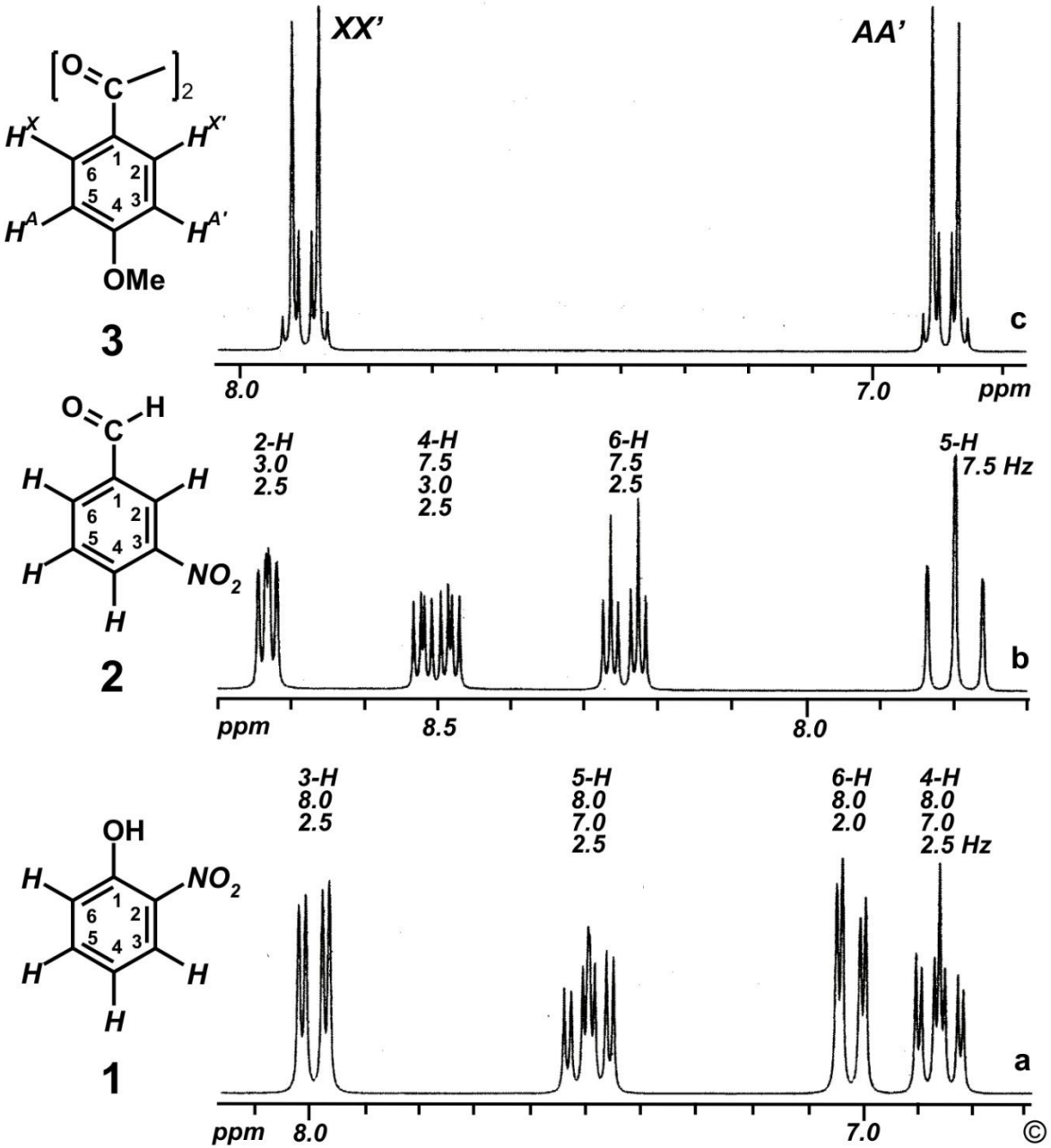
$^5J_{HH} \approx 1$ Hz

$^3J_{HH} \approx 8$ Hz

$\delta(^1H) \approx 7.2$ ppm

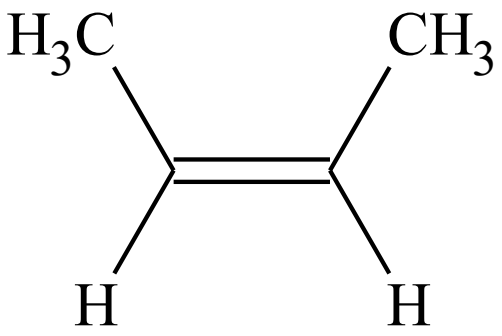


$\delta(^1H) \approx 7.6$ ppm

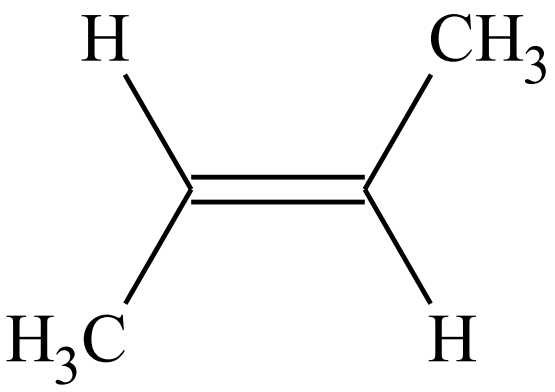


^{1}H-NMR-Spektren disubstituierter Benzen-Ringe ($CDCl_3$, 25°C, 200 MHz.
(a) o-Nitrophenol (1); (b) m-Nitrobenzaldehyd (2); (c) 4,4'-Dimethoxybenzil (3)

Stereochemie und NMR



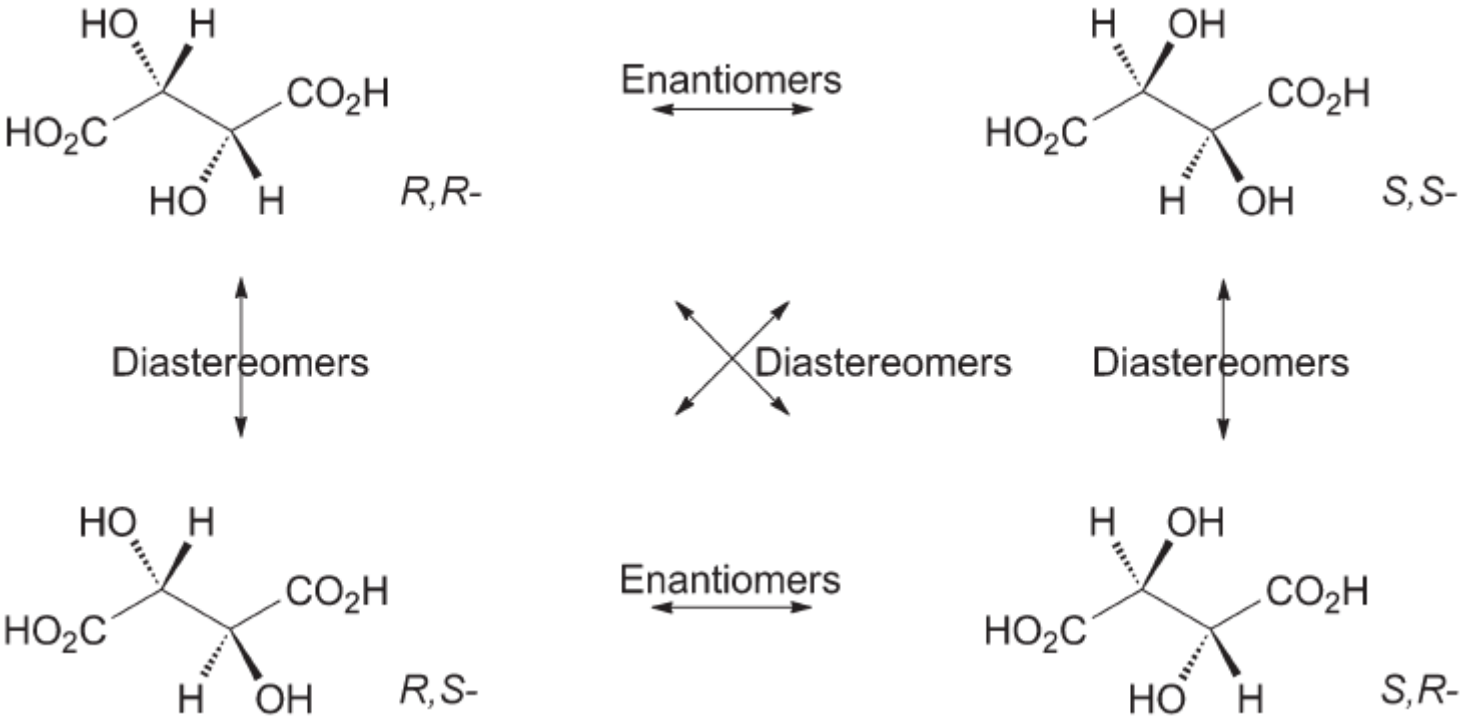
cis-2Buten



trans-2Buten

^{1}H NMR

Stereochemie und NMR



Isomere der Weinsäure

R,R- & *S,S-*	^{13}C, ppm
C=O	175.3
C(H)OH	72.7
R,S- & *S,R-*	^{13}C, ppm
C=O	174.8
C(H)OH	73.3

NMR Spektrum:

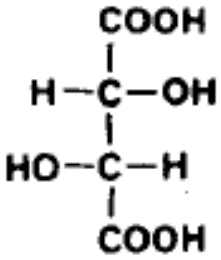
Diastereomer 1 ≠ Diastereomer 2

Enantomer 1 = Enantomer 2

Chirale Lösungsmitteln:

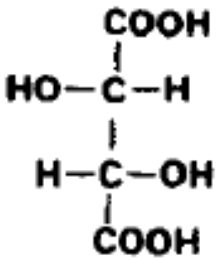
Enantomer 1 ≠ Enantomer 2

Stereochemie und NMR



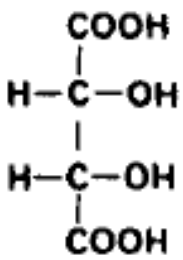
1

(+)-(2*R*,3*R*)-Weinsäure



1′

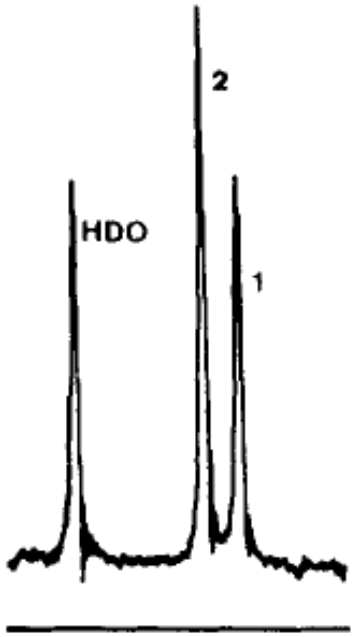
(−)-(2*S*,3*S*)-Weinsäure



2

meso-Weinsäure

ohne $EuCl_3$



mit 0,35 Mol-Äquiv. $EuCl_3$

NMR Spektrum:

Diastereomer 1 ≠ Diastereomer 2

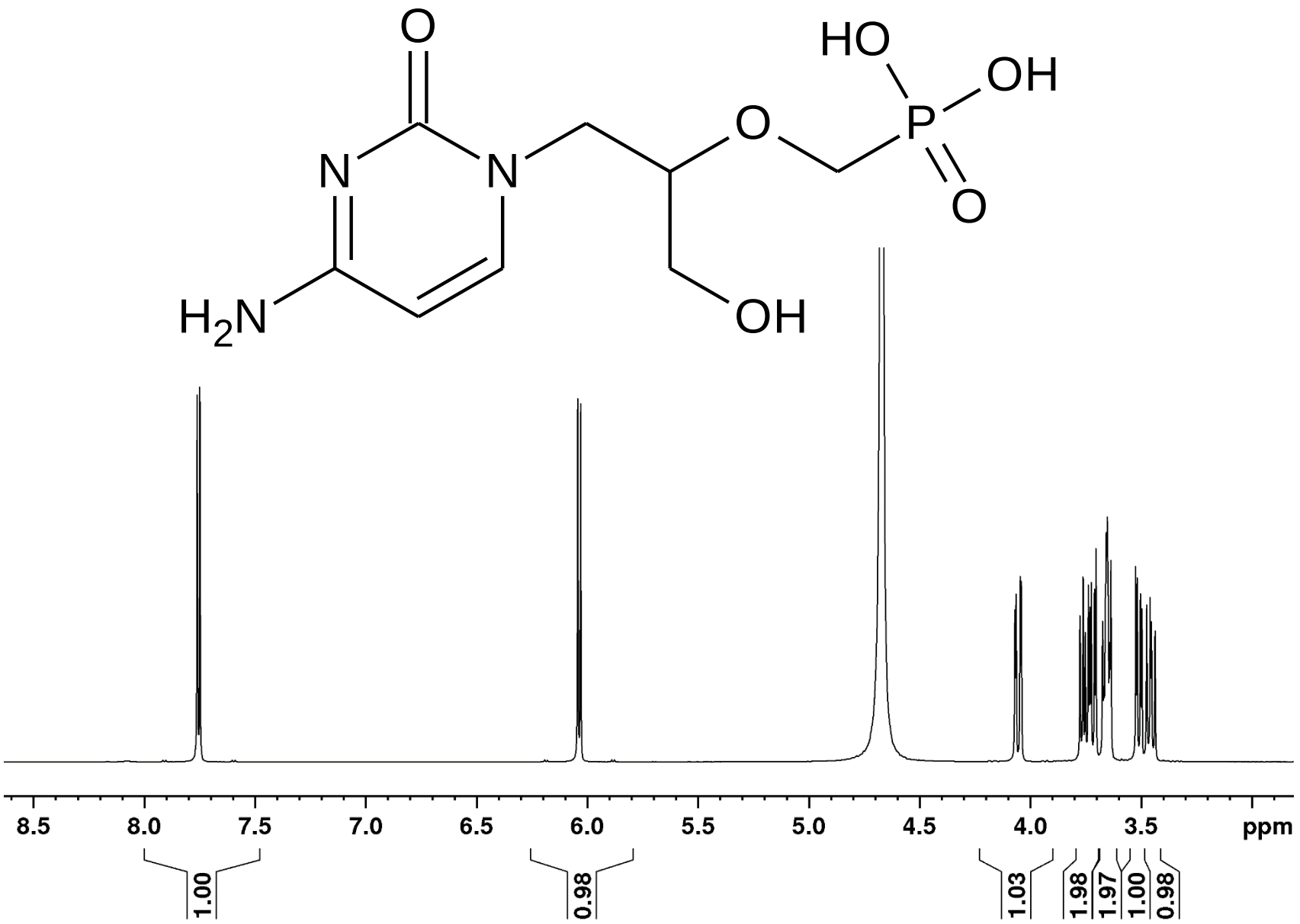
Enantomer 1 = Enantomer 2

Chirale Lösungsmitteln:

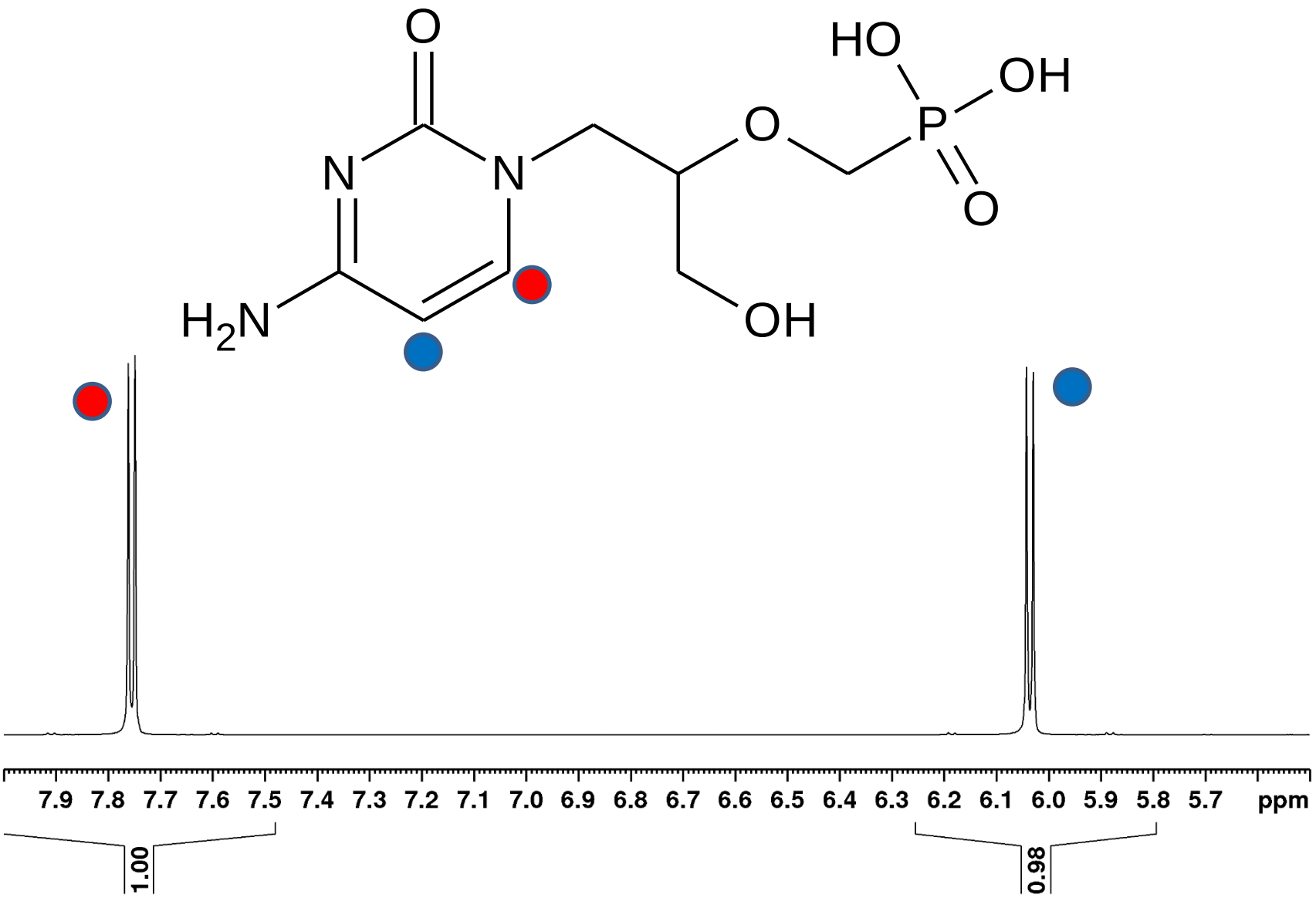
Enantomer 1 ≠ Enantomer 2

A. Pfenninger, A. Hochrainer
Helvetica Chimica Acta
1981, *64* 1558.

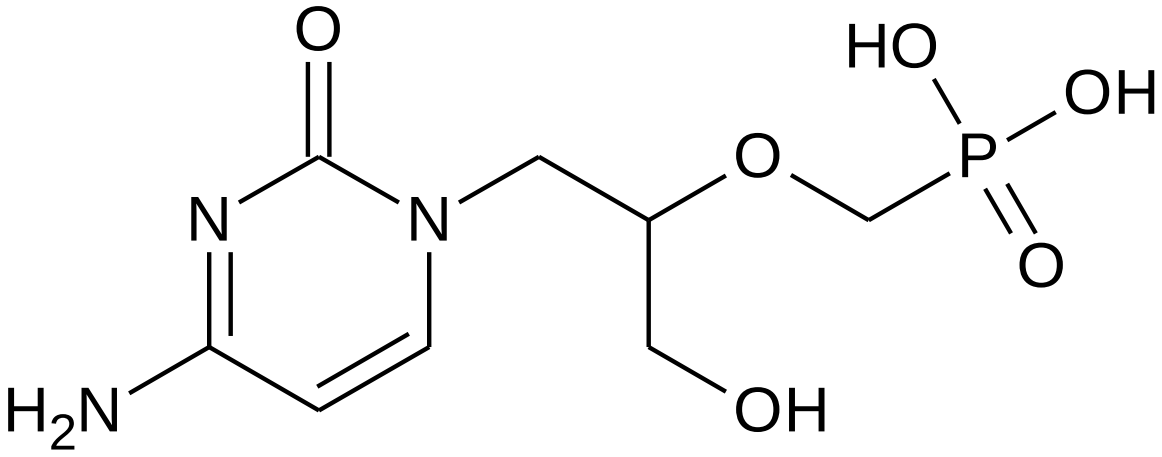
Stereochemie und NMR

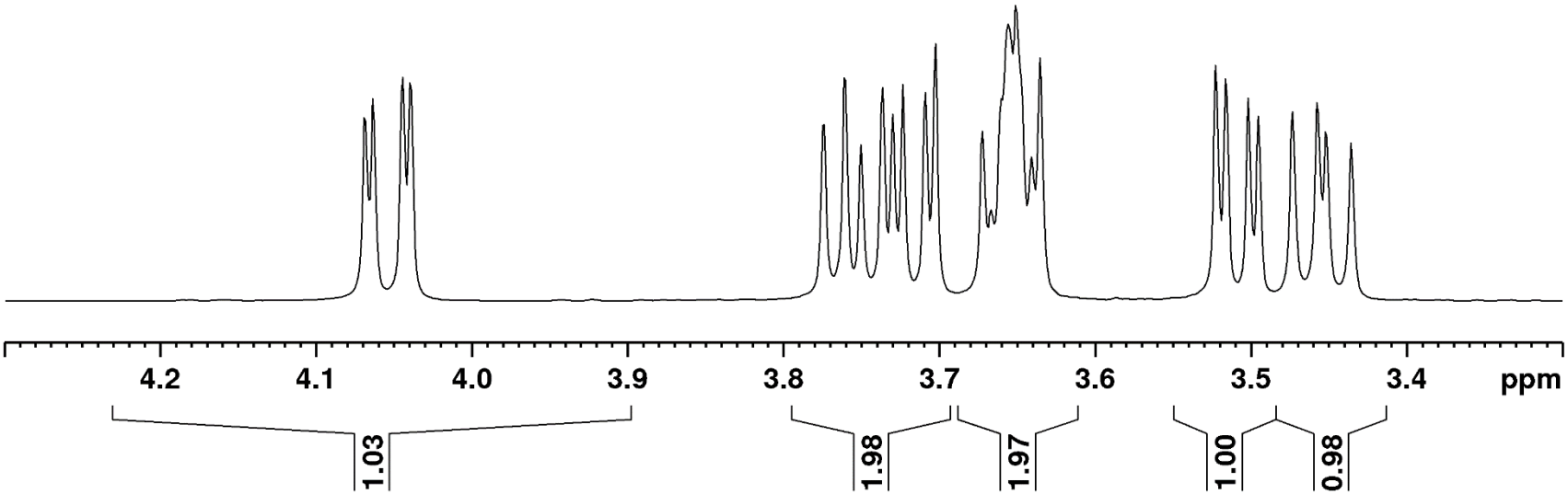


Stereochemie und NMR

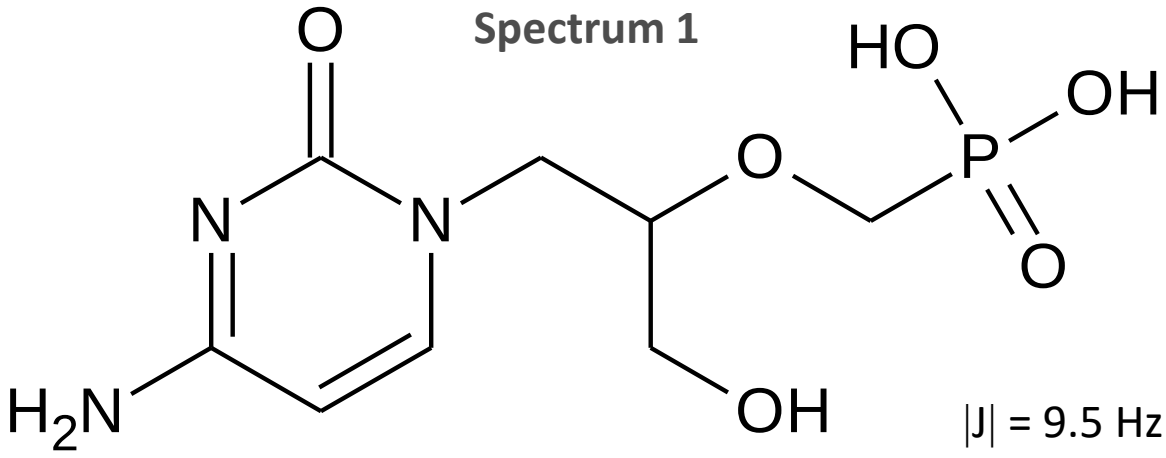


Stereochemie und NMR





Stereochemie und NMR



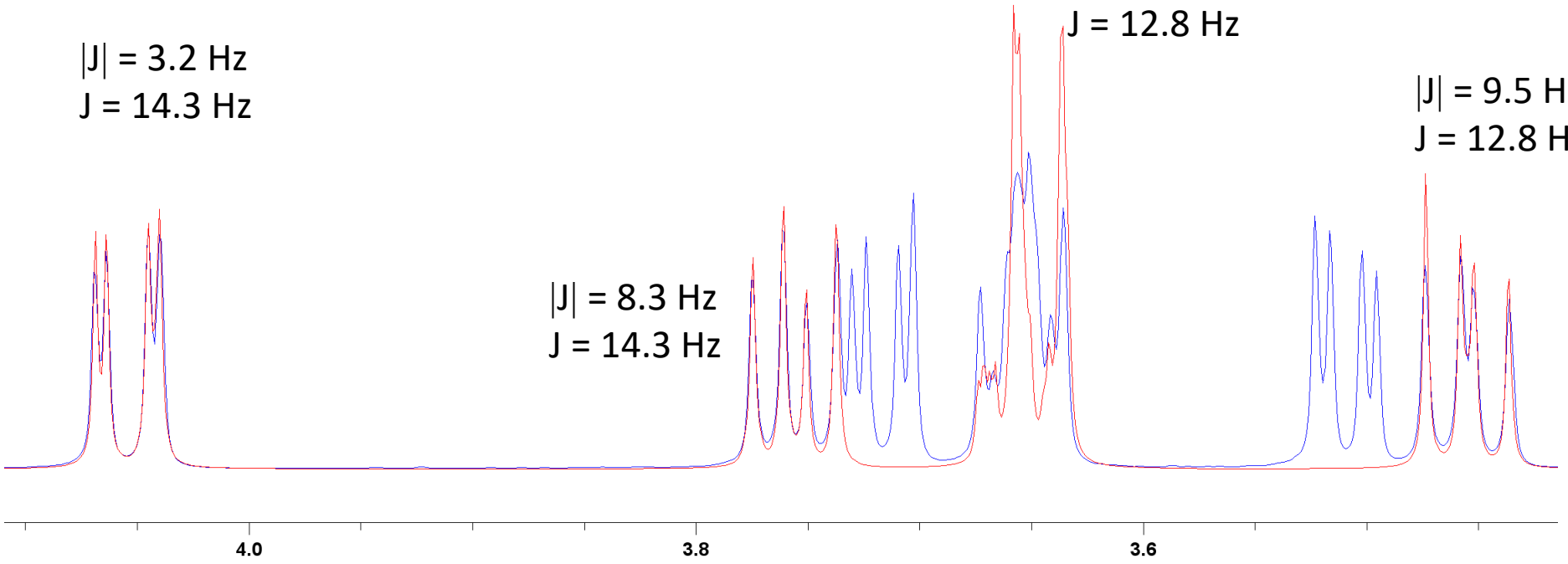
Spectrum 1

|J| = 9.5 Hz
|J| = 8.3 Hz
|J| = 3.2 Hz
J = 12.8 Hz

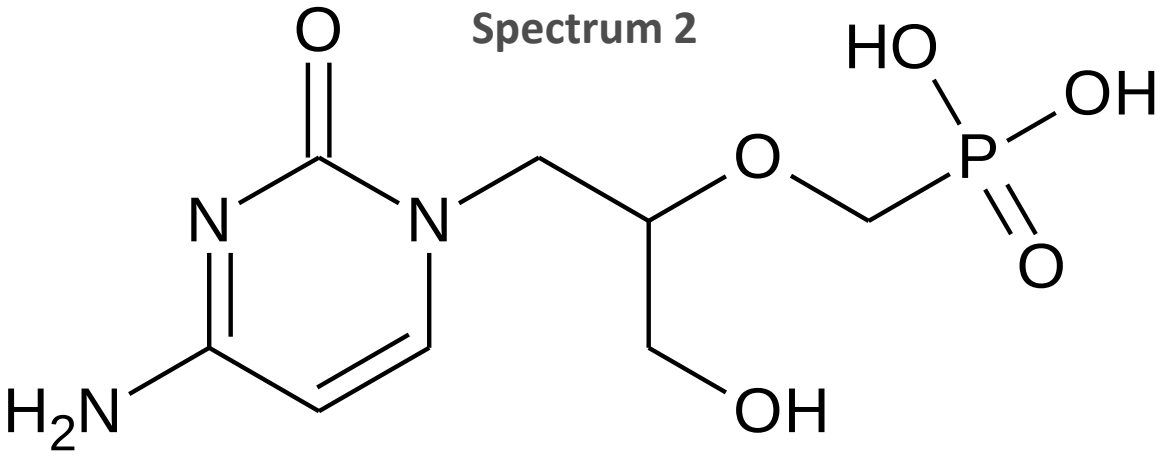
|J| = 3.2 Hz
J = 14.3 Hz

|J| = 9.5 Hz
J = 12.8 Hz

|J| = 8.3 Hz
J = 14.3 Hz



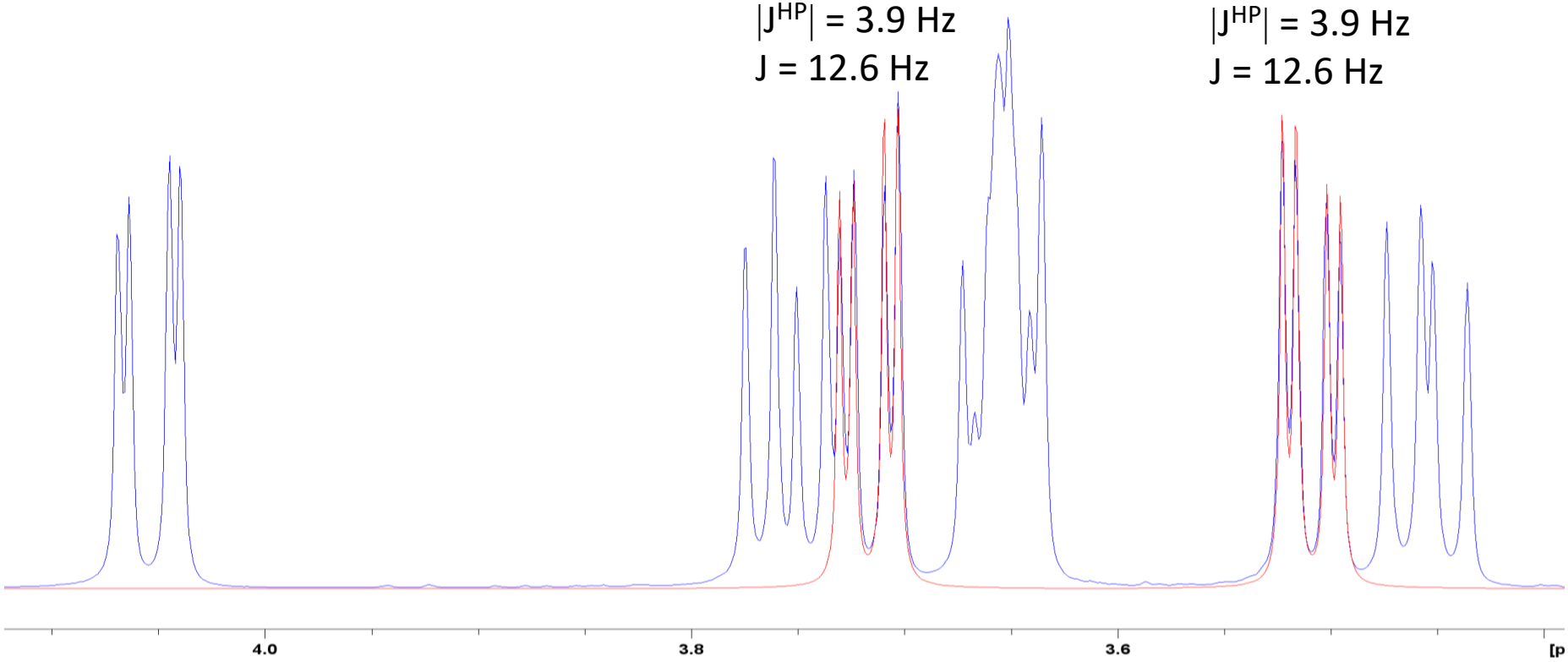
Stereochemie und NMR



Spectrum 2

$|J^{HP}|$ = 3.9 Hz
J = 12.6 Hz

$|J^{HP}|$ = 3.9 Hz
J = 12.6 Hz



Stereochemie und NMR

$\delta_{axial}(^{13}C) \approx \delta_{equatorial}(^{13}C) - 5$ ppm

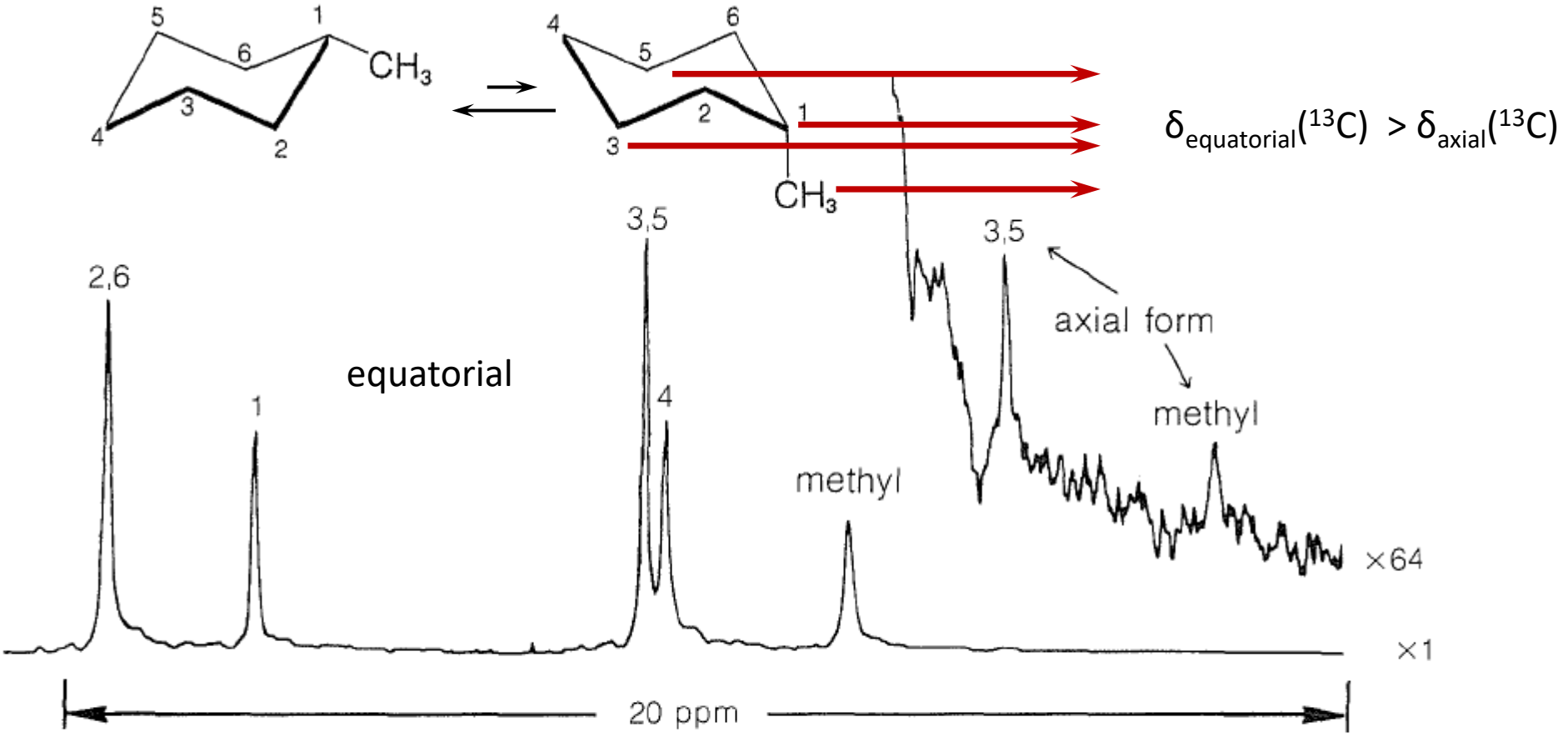
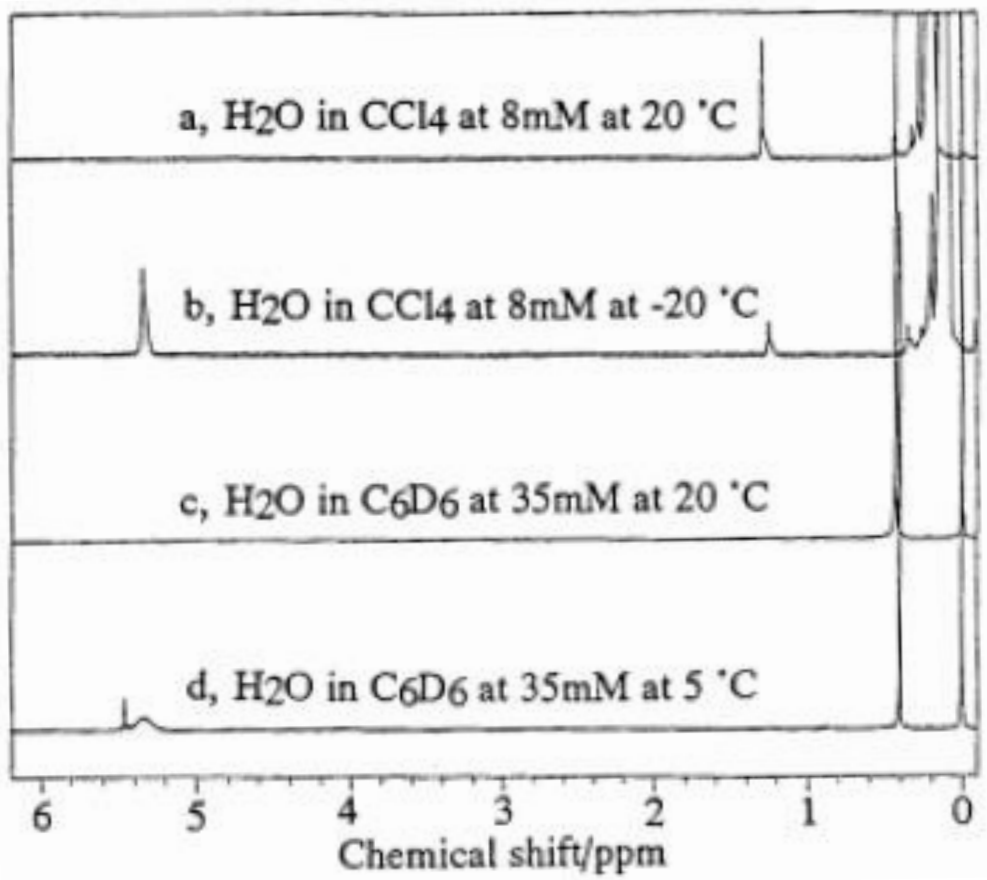


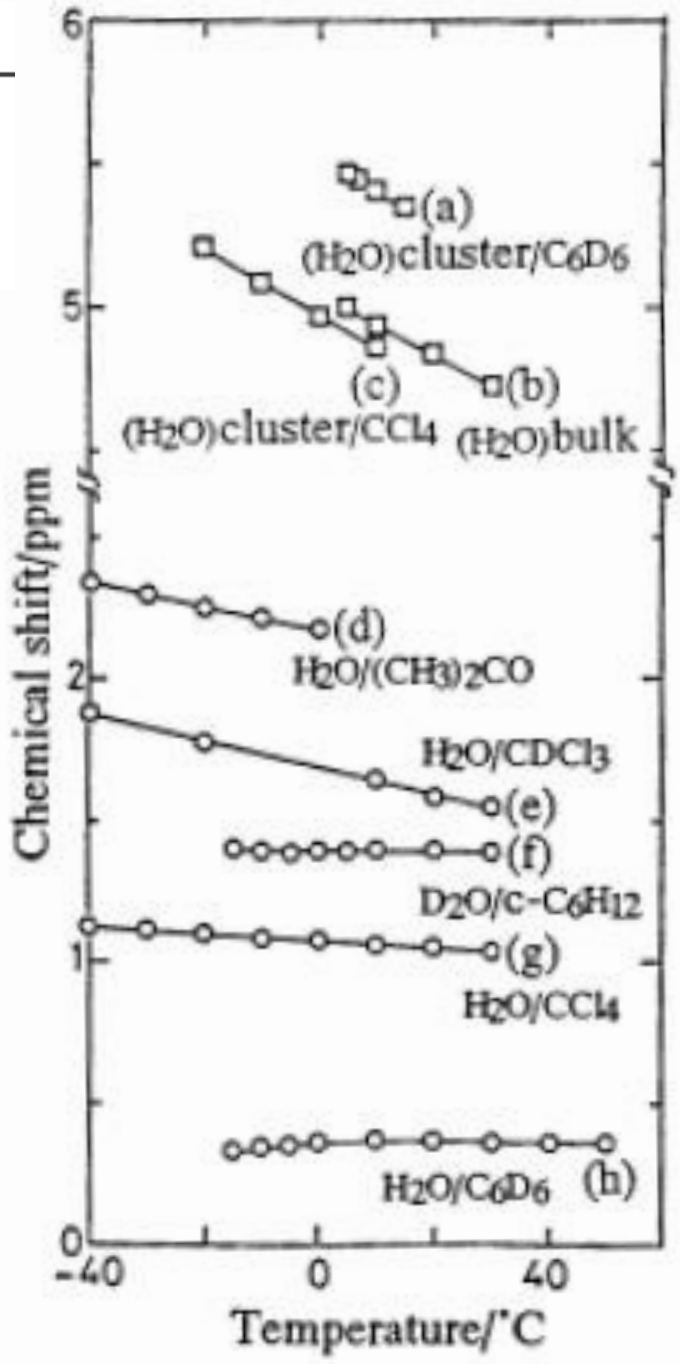
Figure 12-12 Proton-decoupled, 63.1 MHz, ^{13}C spectrum of methylcyclohexane at −110°. The upper right curve was taken with the signal sensitivity control turned up by a factor of 64. (Courtesy of Dr. F. A. L. Anet.)

Chemistry Letters pp 809-812 1992

Monomeric and Cluster States of Water Molecules in Organic Solvent

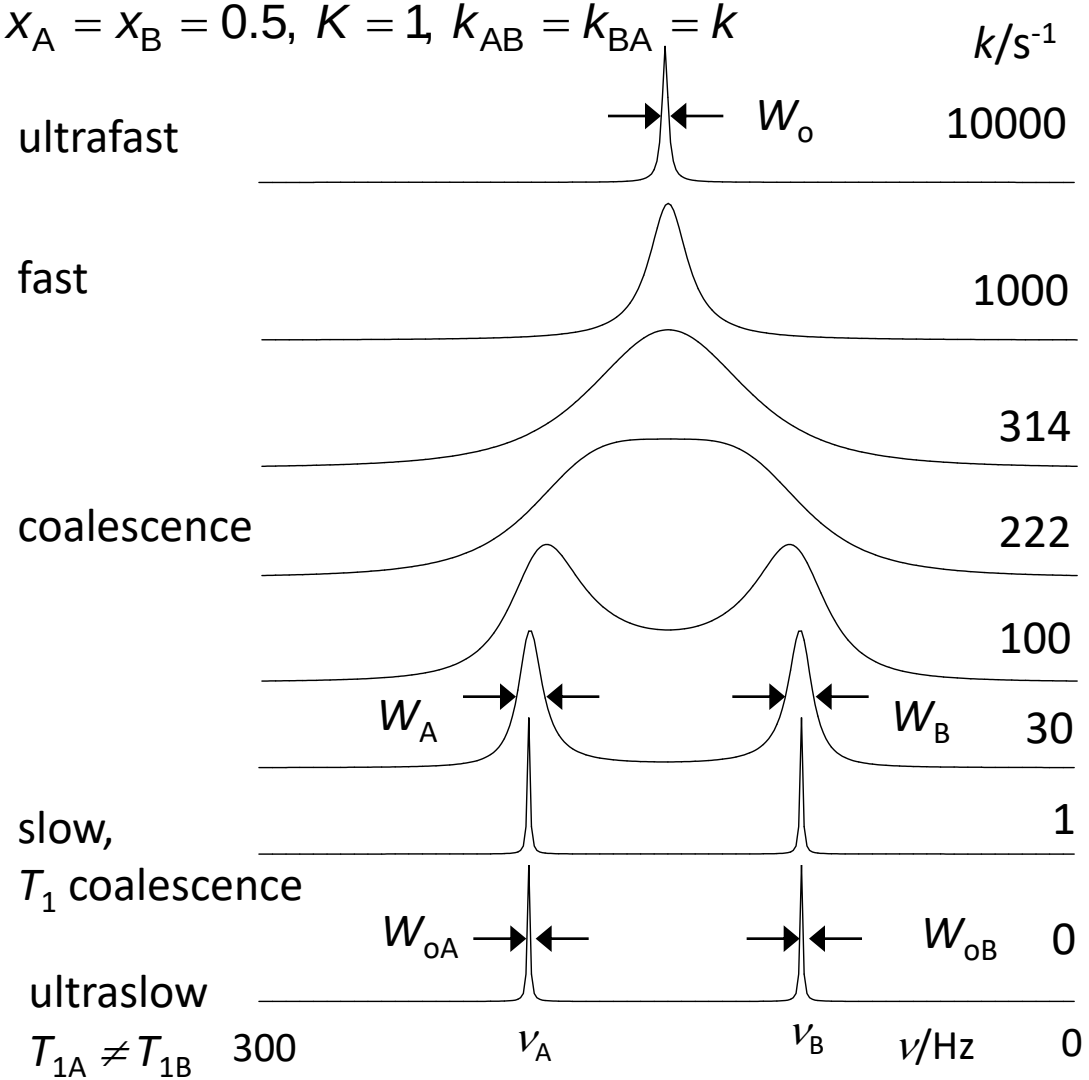
Masaru NAKAHARA and Chihiro WAKAI





NMR of a symmetric two-site exchange system

$x_A = x_B = 0.5,\ K = 1,\ k_{AB} = k_{BA} = k$



$$A \underset{k}{\overset{k}{\rightleftharpoons}} B$$

$$k = \frac{\pi \Delta \nu^2}{2(W - W_o)}$$

$$k = \pi \Delta \nu$$

$$k = \frac{\pi \Delta \nu}{\sqrt{2}}$$

$$k = \pi (W_B - W_{oB})$$

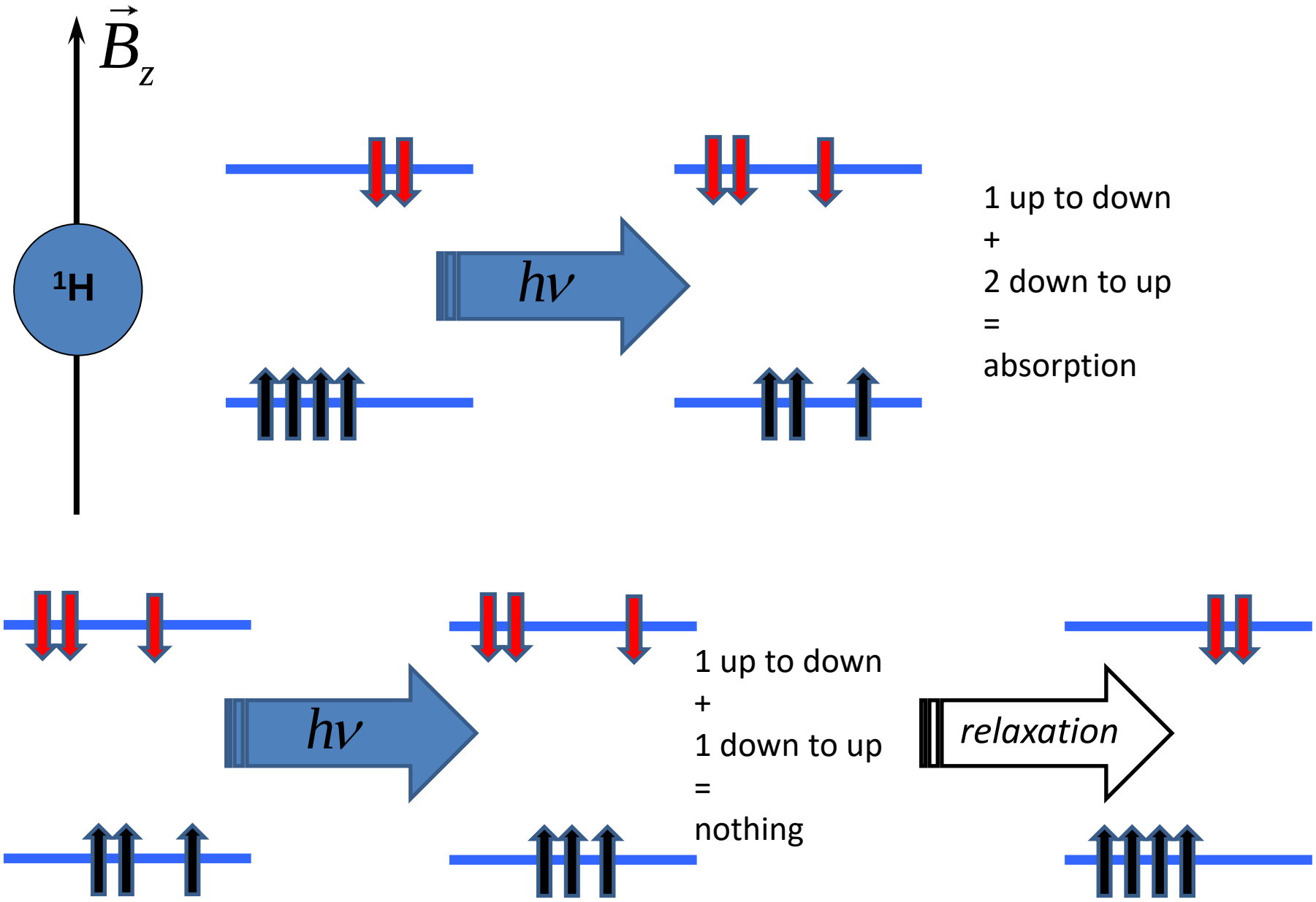
$$\frac{1}{T_1} = \frac{0.5}{T_{1A}} + \frac{0.5}{T_{1B}}$$

$$k << 1/T_{1A},\ k << 1/T_{1B}$$

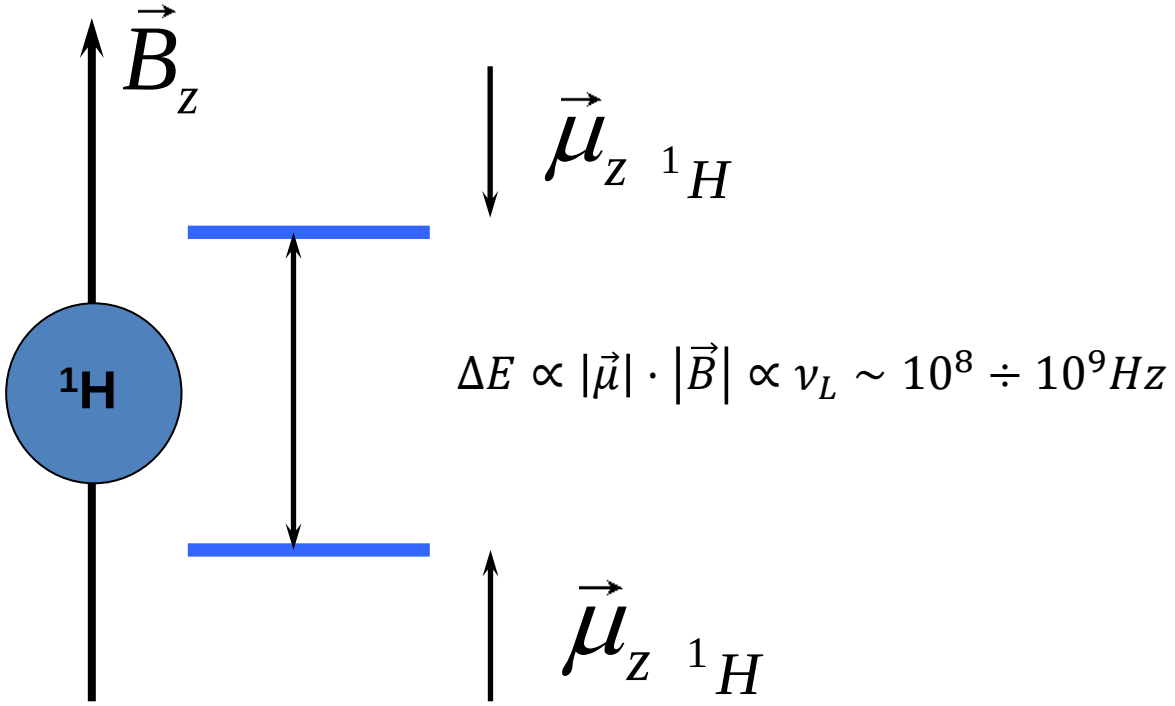
$$W_o = \frac{1}{\pi T_2}$$

$$\Delta \nu = \nu_A - \nu_B = 100 \text{ Hz}$$

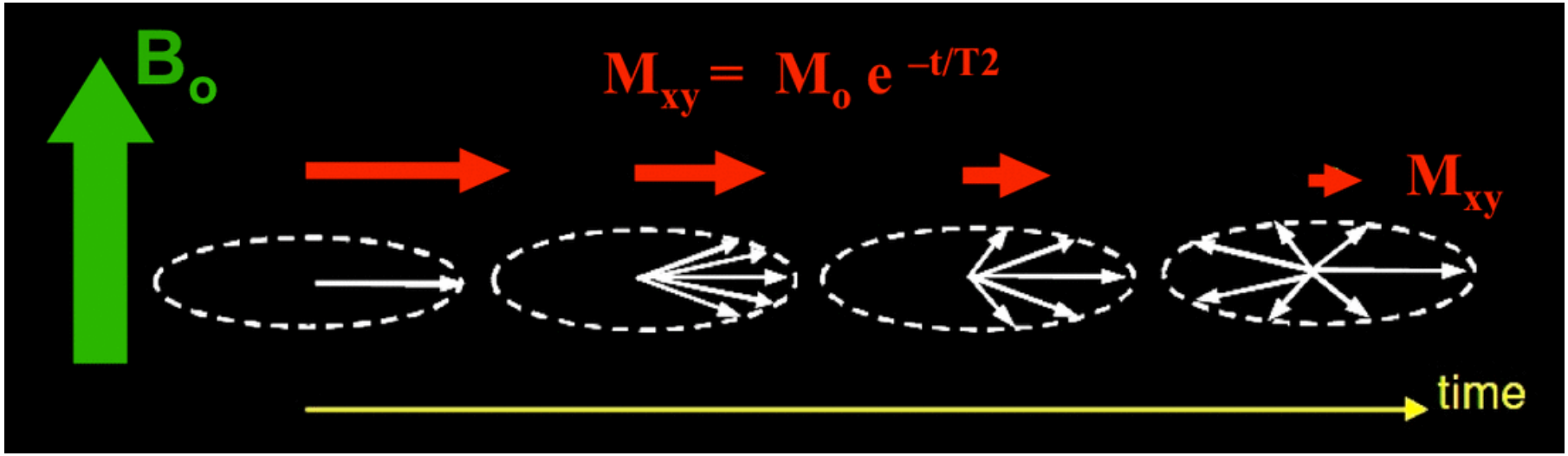
$T_2 \approx T_1$ for fluid liquids


$\vec{B}_z$
^{1}H
hν
1 up to down
+
2 down to up
=
absorption
hν
1 up to down
+
1 down to up
=
nothing
relaxation

T_1 ≡ spin-lattice relaxation

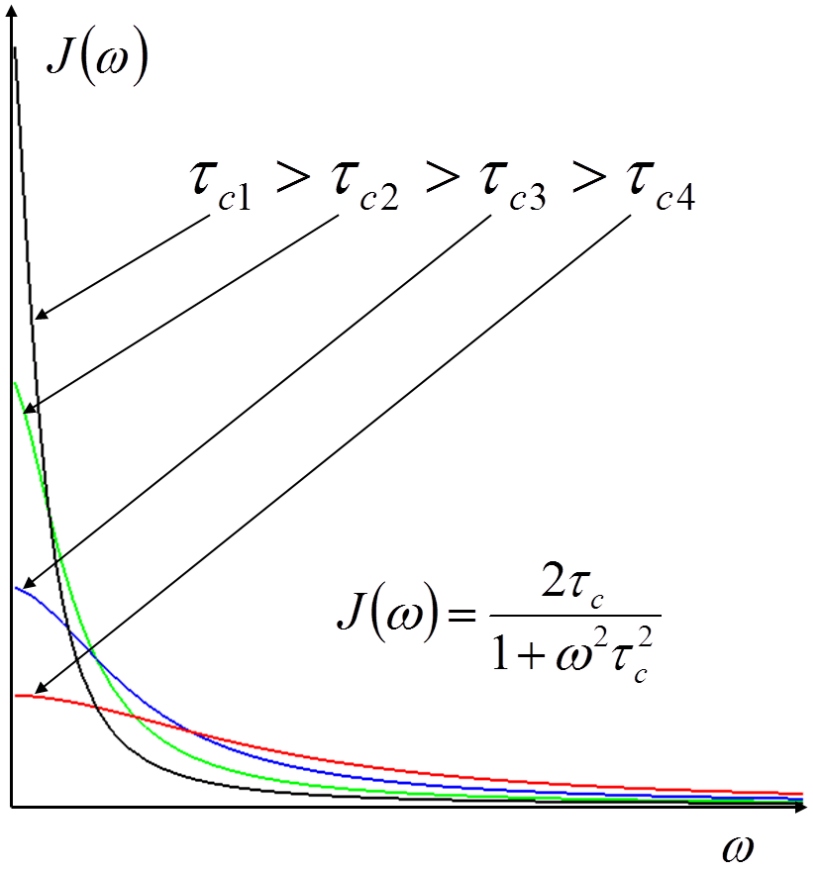


T_2 ≡ spin-spin relaxation

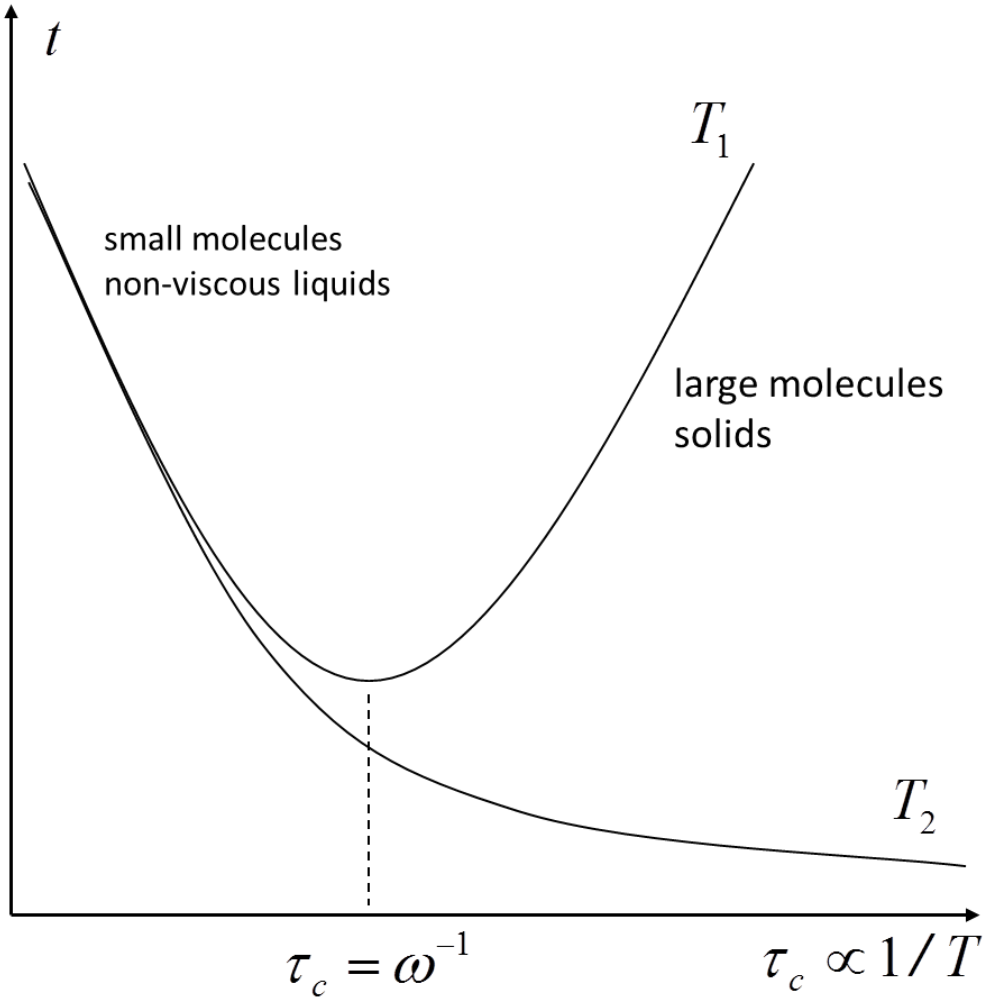


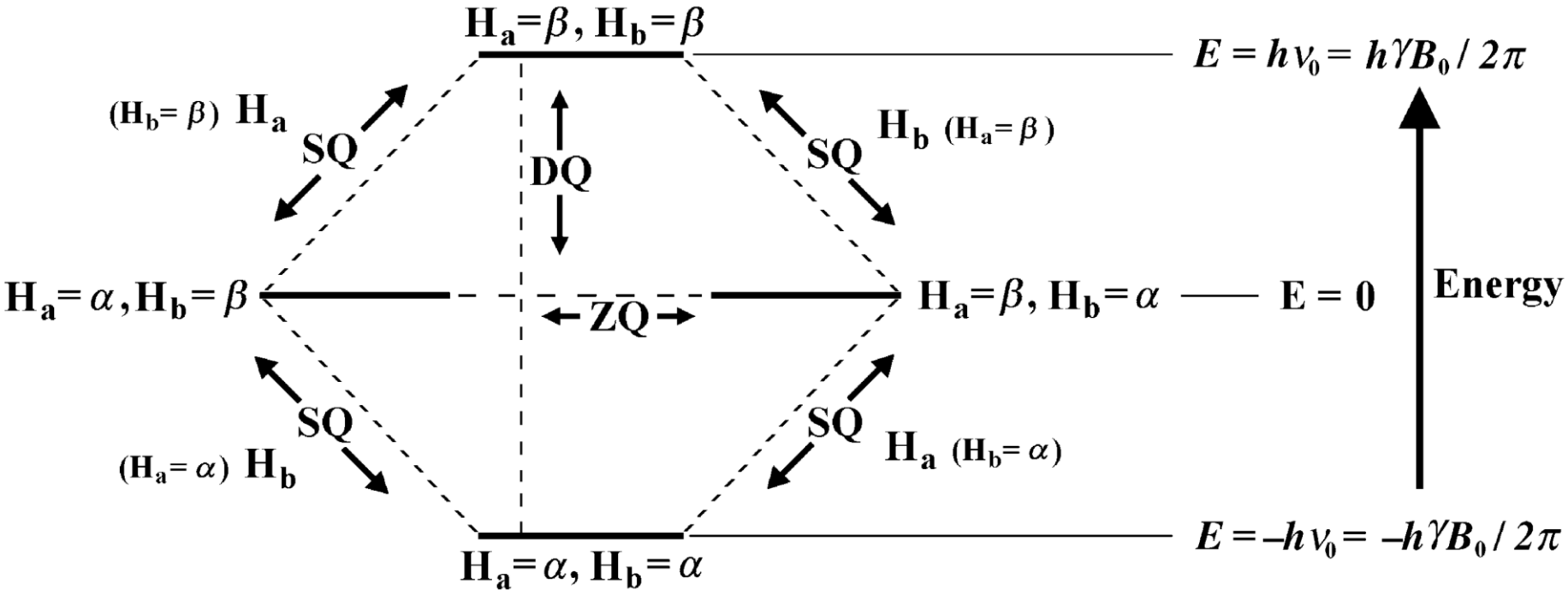
$$\nu \sim 1 \div 100Hz$$

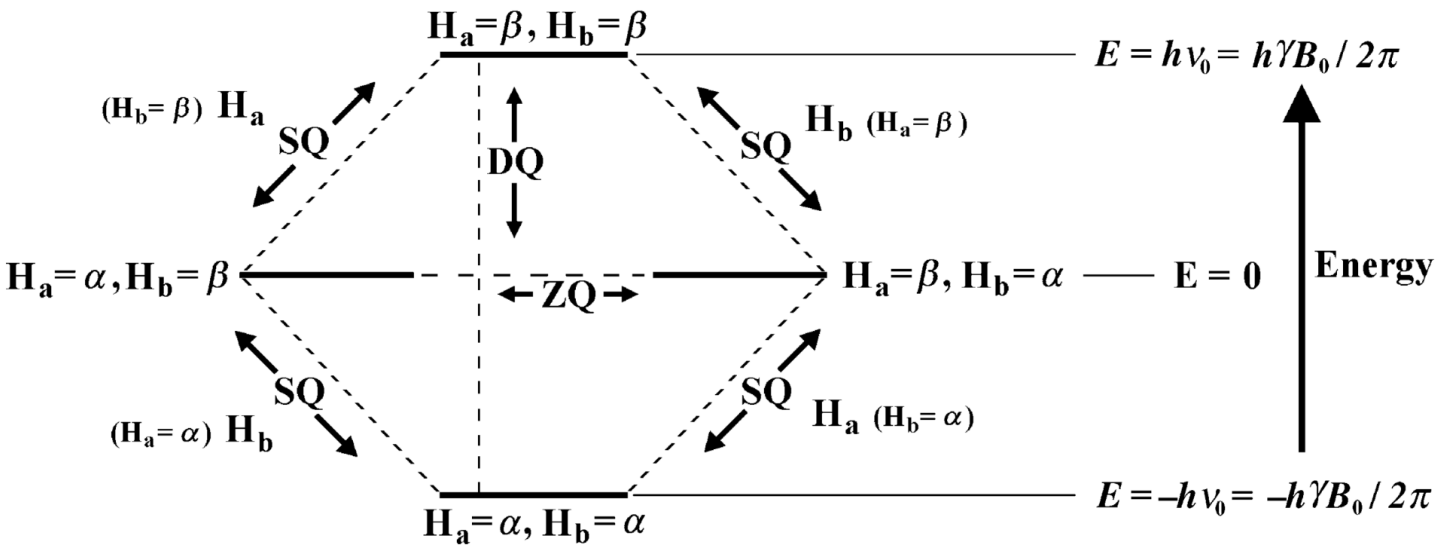
Spectral density of noises

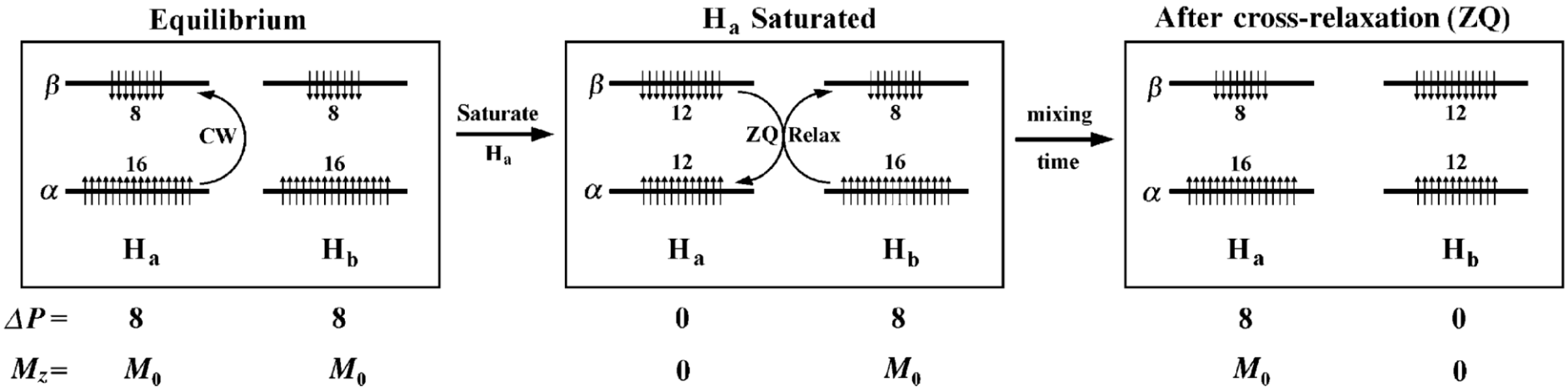


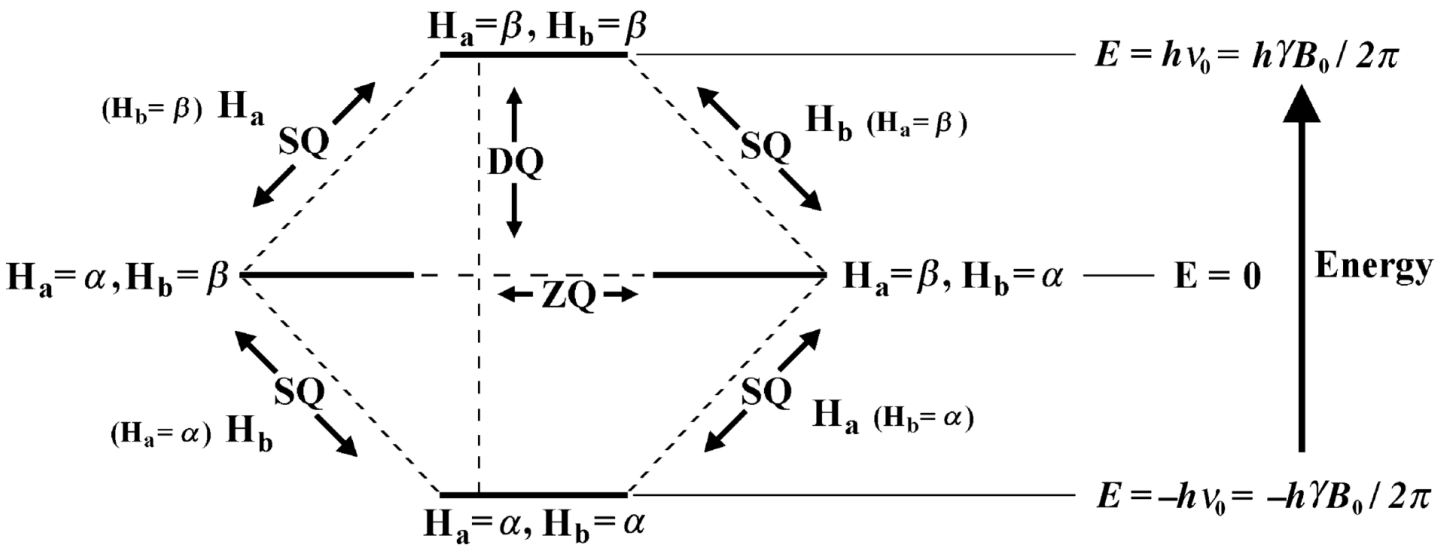
T_1 and T_2 curves

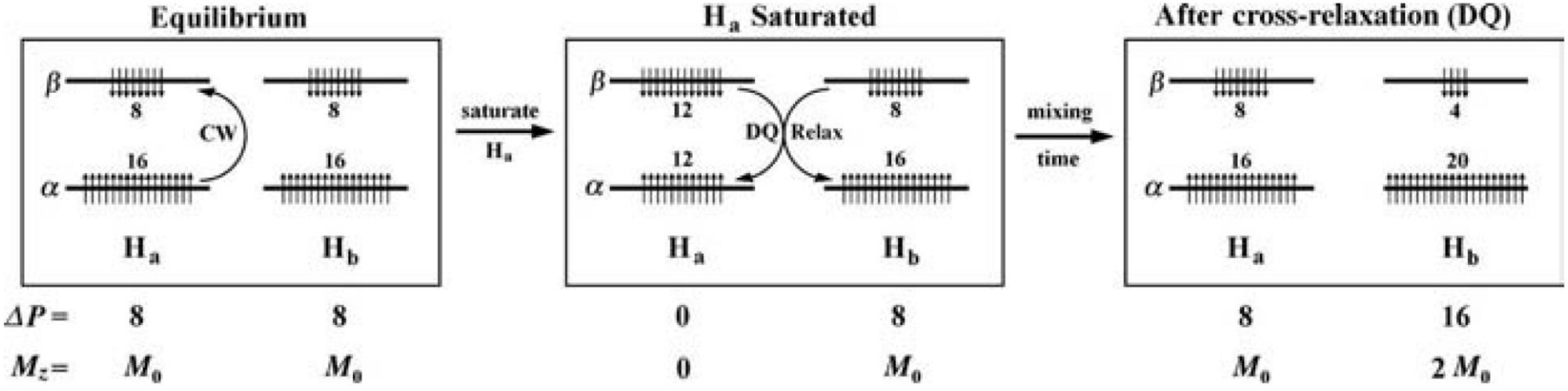


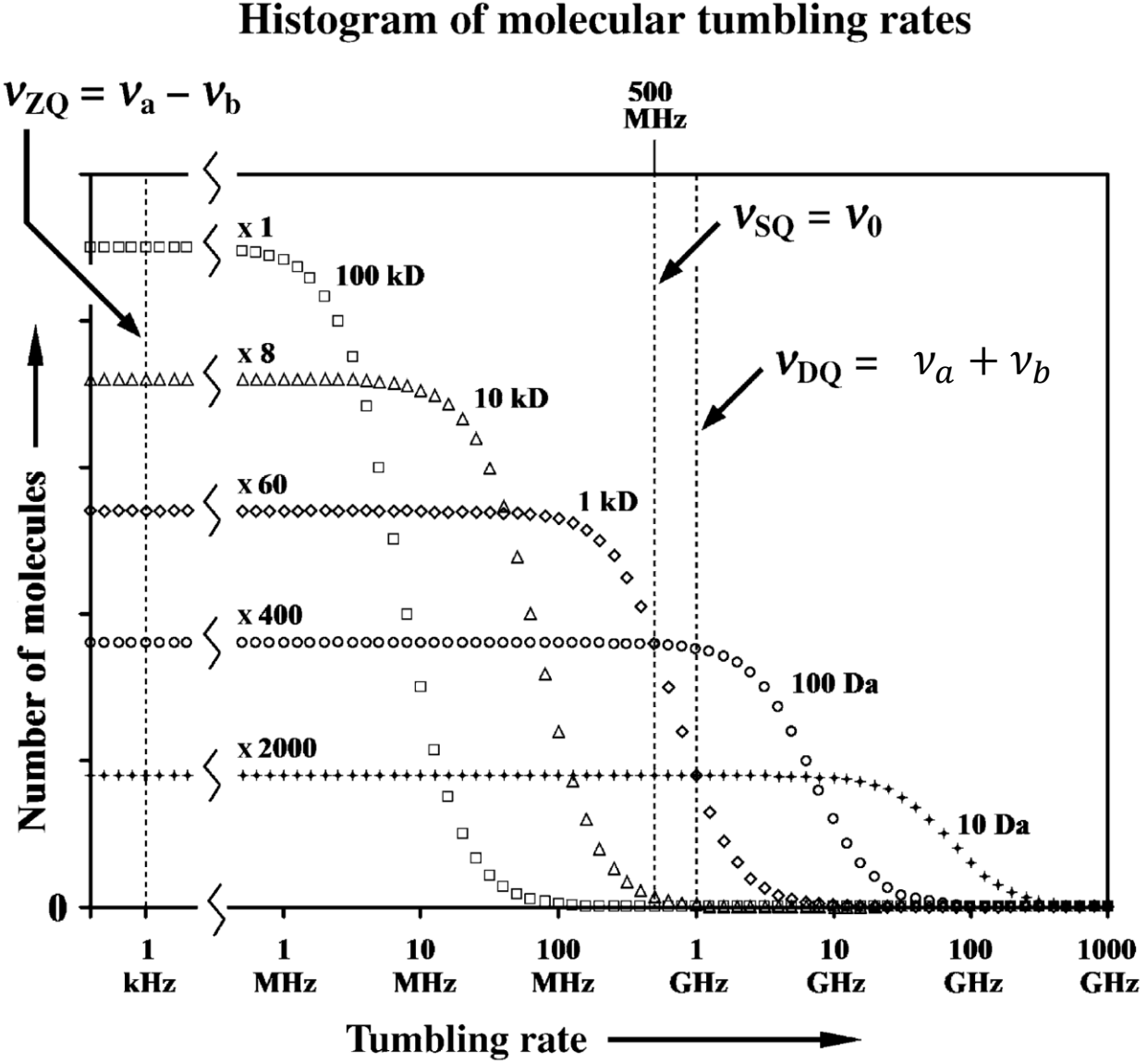

$H_a=\beta, H_b=\beta$
$E = h\nu_0 = h\gamma B_0 / 2\pi$
$(H_b=\beta)$ H_a
SQ
DQ
SQ
H_b $(H_a=\beta)$
$H_a=\alpha, H_b=\beta$
ZQ
$H_a=\beta, H_b=\alpha$
E = 0
Energy
SQ
$(H_a=\alpha)$ H_b
SQ
H_a $(H_b=\alpha)$
$E = -h\nu_0 = -h\gamma B_0 / 2\pi$
$H_a=\alpha, H_b=\alpha$


$H_a=\beta, H_b=\beta$
$E = h\nu_0 = h\gamma B_0 / 2\pi$
$(H_b=\beta)$ H_a
SQ
DQ
SQ
H_b $(H_a=\beta)$
$H_a=\alpha, H_b=\beta$
ZQ
$H_a=\beta, H_b=\alpha$
E = 0
Energy
SQ
SQ
$(H_a=\alpha)$ H_b
H_a $(H_b=\alpha)$
$H_a=\alpha, H_b=\alpha$
$E = -h\nu_0 = -h\gamma B_0 / 2\pi$


Equilibrium
H_a Saturated
After cross-relaxation (ZQ)
β
α
8
16
CW
Saturate
H_a
12
ZQ Relax
mixing
time
H_a
H_b
$\Delta P =$ 8 8 0 8 8 0
$M_z =$ M_0 M_0 0 M_0 M_0 0


$H_a=\beta, H_b=\beta$
$E = h\nu_0 = h\gamma B_0 / 2\pi$
$(H_b=\beta)$ H_a
SQ
DQ
SQ
H_b $(H_a=\beta)$
$H_a=\alpha, H_b=\beta$
ZQ
$H_a=\beta, H_b=\alpha$
E = 0
Energy
SQ
SQ
$(H_a=\alpha)$ H_b
H_a $(H_b=\alpha)$
$H_a=\alpha, H_b=\alpha$
$E = -h\nu_0 = -h\gamma B_0 / 2\pi$


Equilibrium
H_a Saturated
After cross-relaxation (DQ)
β
α
8
16
CW
H_a
H_b
saturate
H_a
12
DQ
Relax
mixing
time
4
20
$\Delta P =$ 8 8 0 8 8 16
$M_z =$ M_0 M_0 0 M_0 M_0 2 M_0

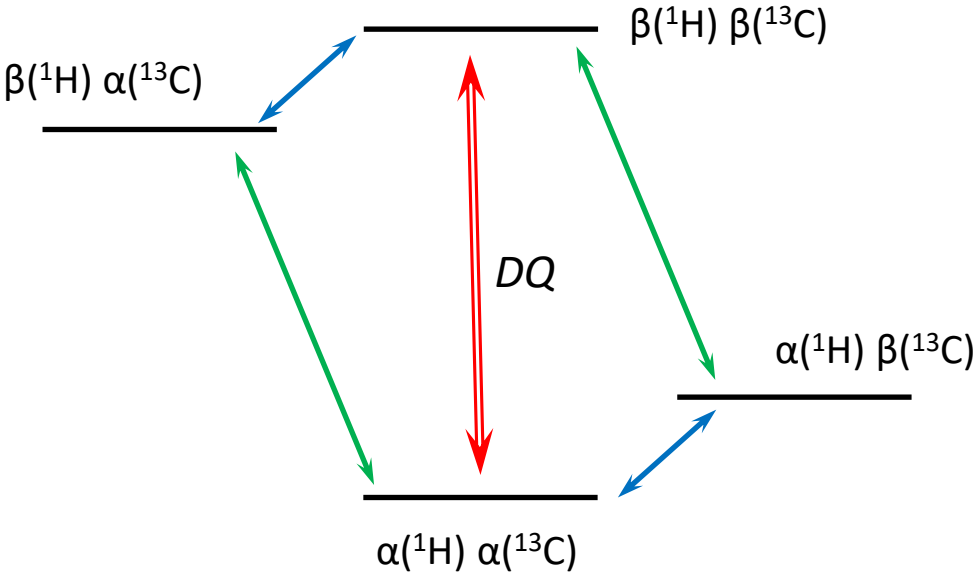


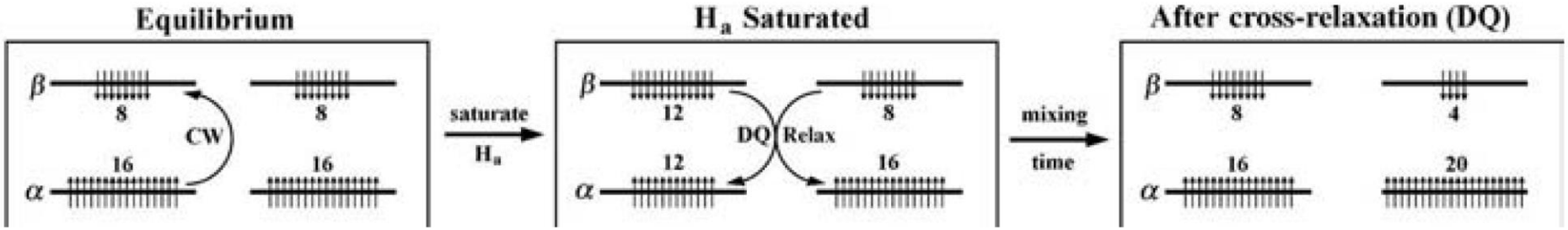
Relaxation efficiency

	$ZQ = \nu_a - \nu_b$	$SQ = \nu_a$	$DQ = \nu_a + \nu_b$
Small molecule ($\omega_0\tau_c \ll 1$)	2	3	12
Large molecule ($\omega_0\tau_c \gg 1$)	2	<<1	<<1

Relaxation efficiency

	ZQ: $\alpha\beta \Longrightarrow \beta\alpha$	SQ: $\alpha \Longrightarrow \beta$	DQ: $\alpha\alpha \Longrightarrow \beta\beta$
Small molecule ($\omega_0\tau_c \ll 1$)	2	3	12
Large molecule ($\omega_0\tau_c \gg 1$)	2	<<1	<<1

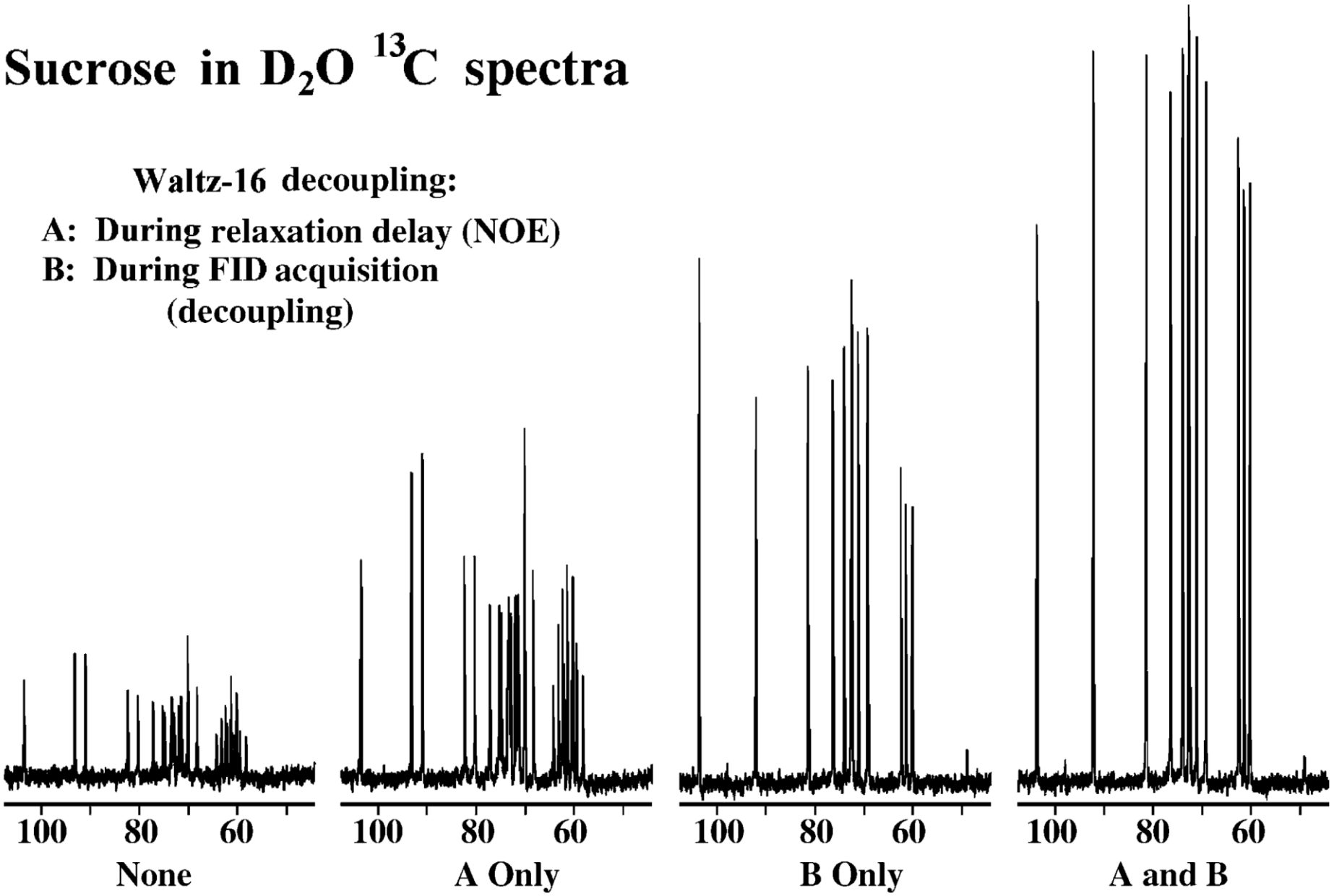




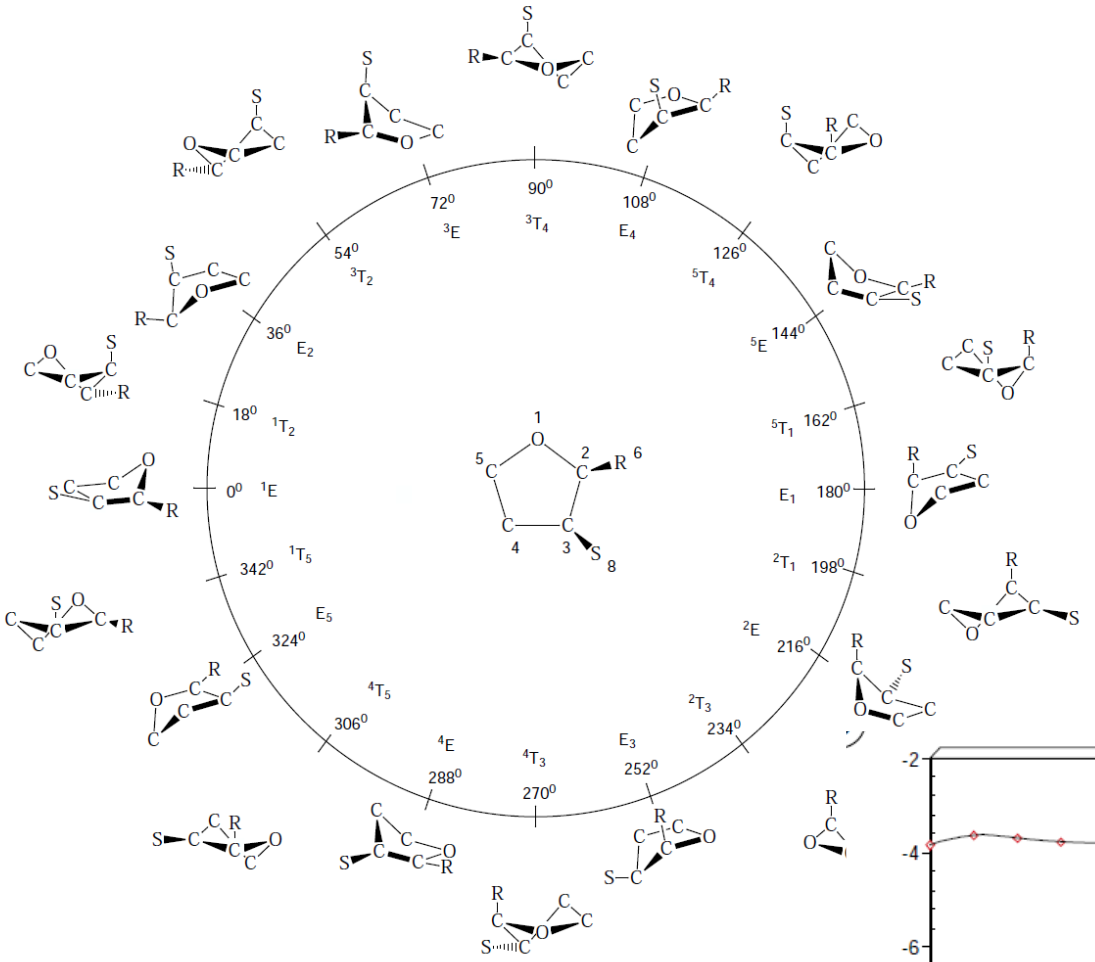
Sucrose in D_2O ^{13}C spectra

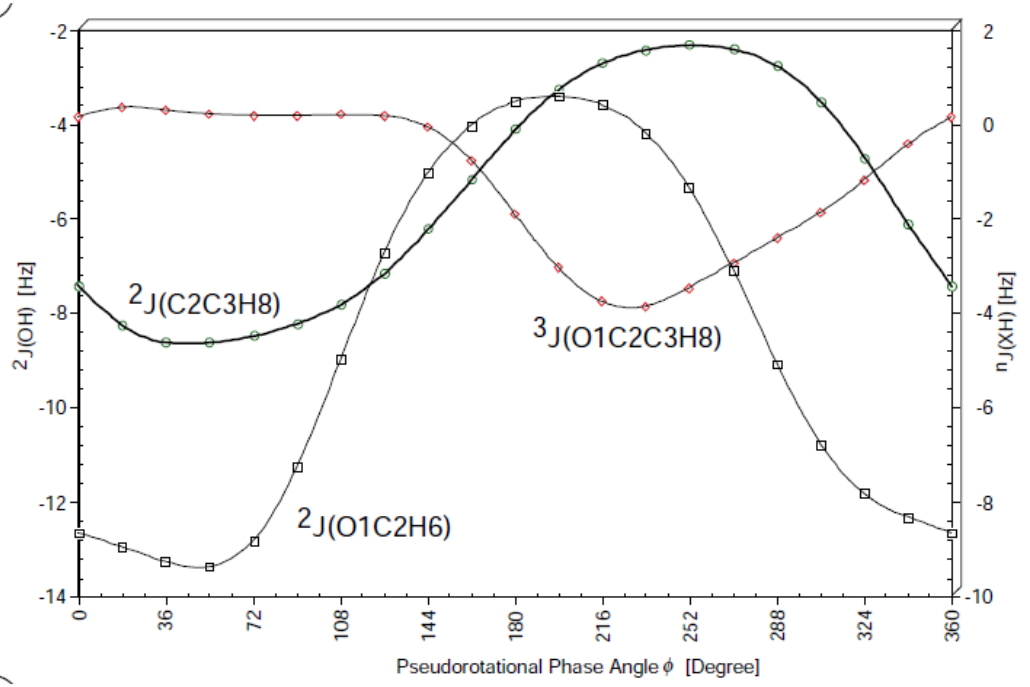
Waltz-16 decoupling:

A: During relaxation delay (NOE)
B: During FID acquisition (decoupling)



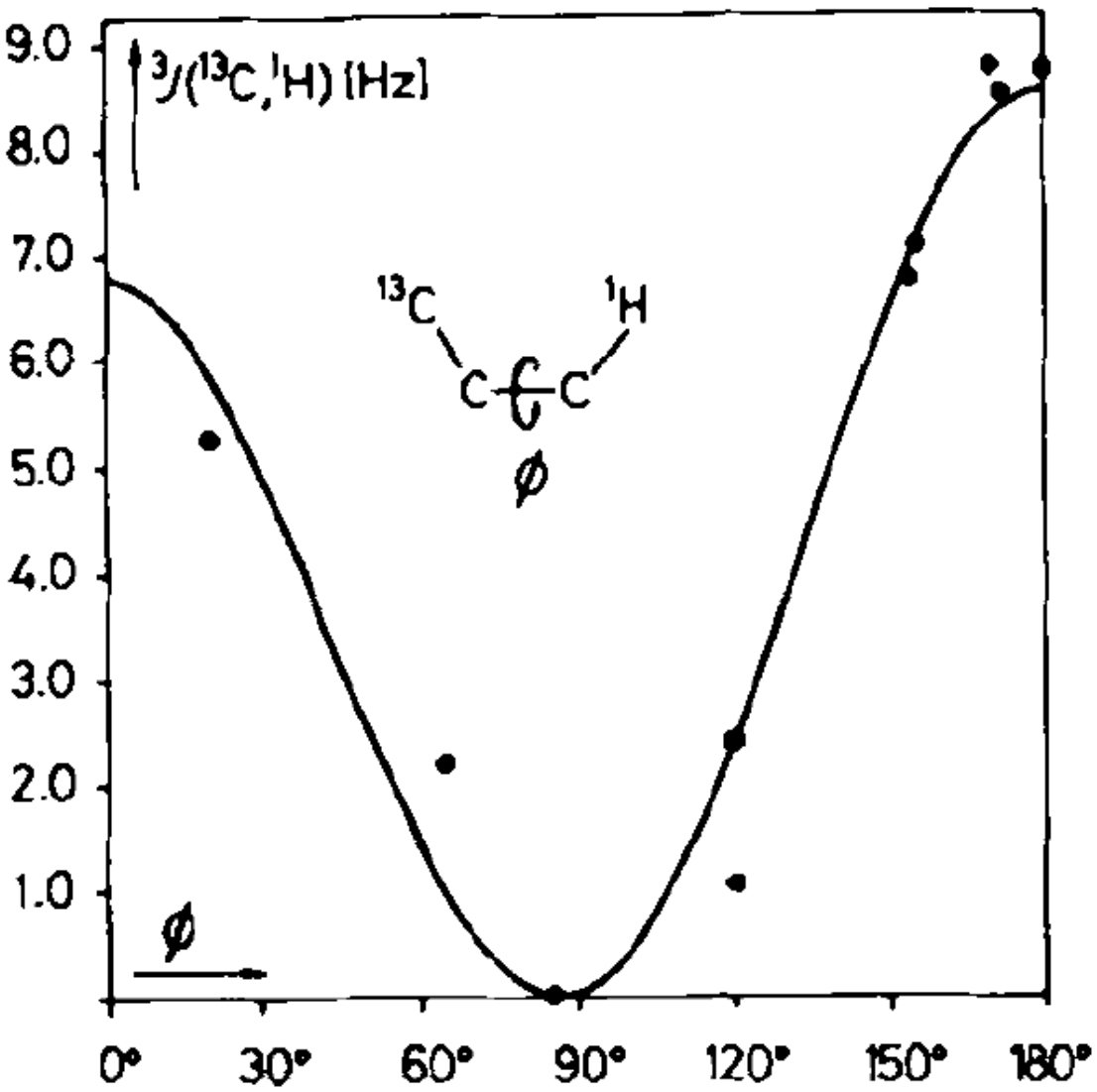
HMBC NMR



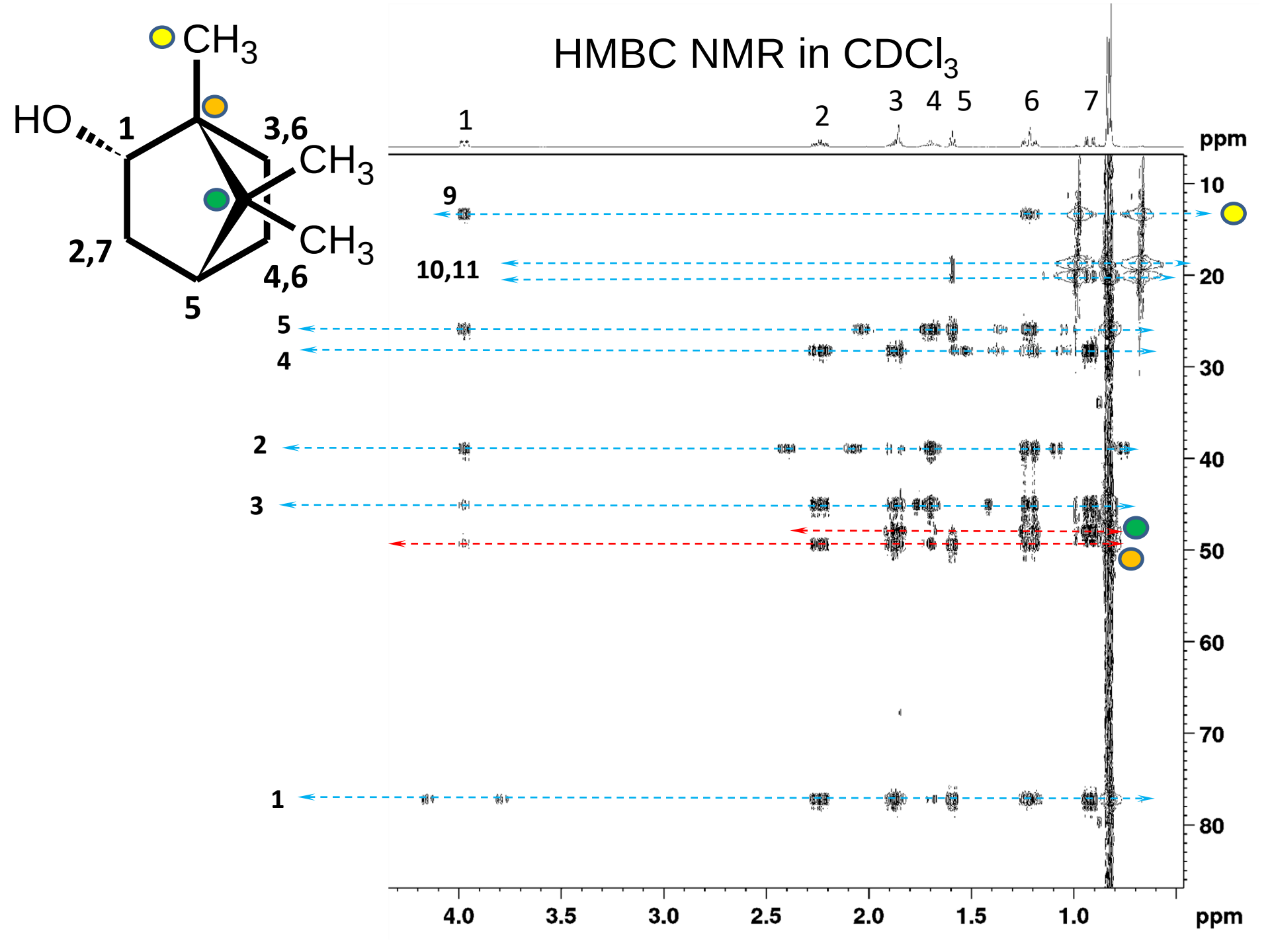


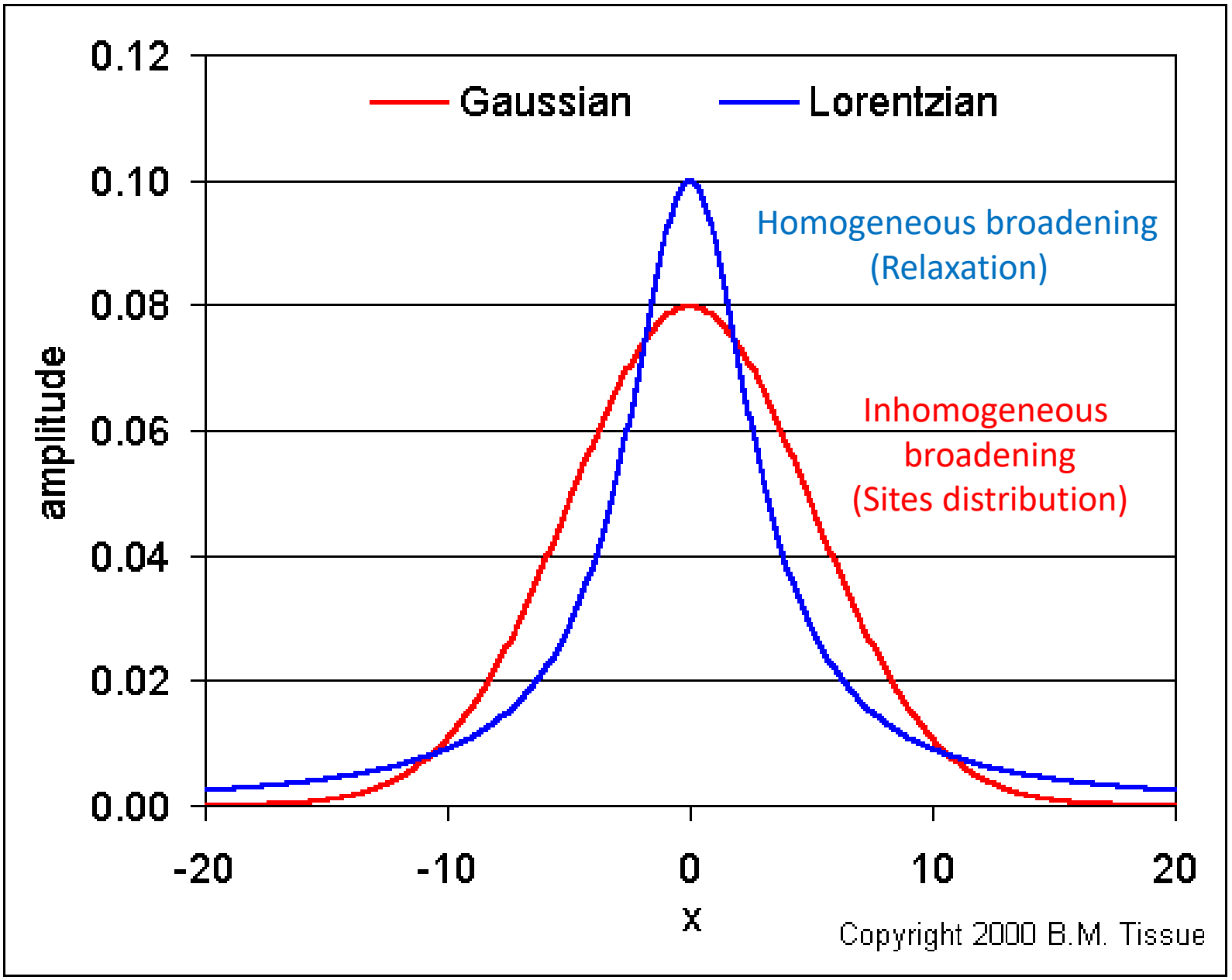
Wu, A.; Cremer, D.
Int. J. Mol. Sci. **2003**, *4*, 158.

HMBC NMR



Aydin, R.; Loux, J.-P.; Günther, H. *Angew. Chem.* **1982**, *94*, 451


HMBC NMR in CDCl3
CH3
HO
1
3,6
CH3
CH3
2,7
4,6
5
1
2
3 4 5
6
7
ppm
9
10,11
5
4
2
3
1
10
20
30
40
50
60
70
80
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


0.12
0.10
0.08
0.06
0.04
0.02
0.00
amplitude
Gaussian
Lorentzian
Homogeneous broadening
(Relaxation)
Inhomogeneous
broadening
(Sites distribution)
-20
-10
0
10
20
x
Copyright 2000 B.M. Tissue

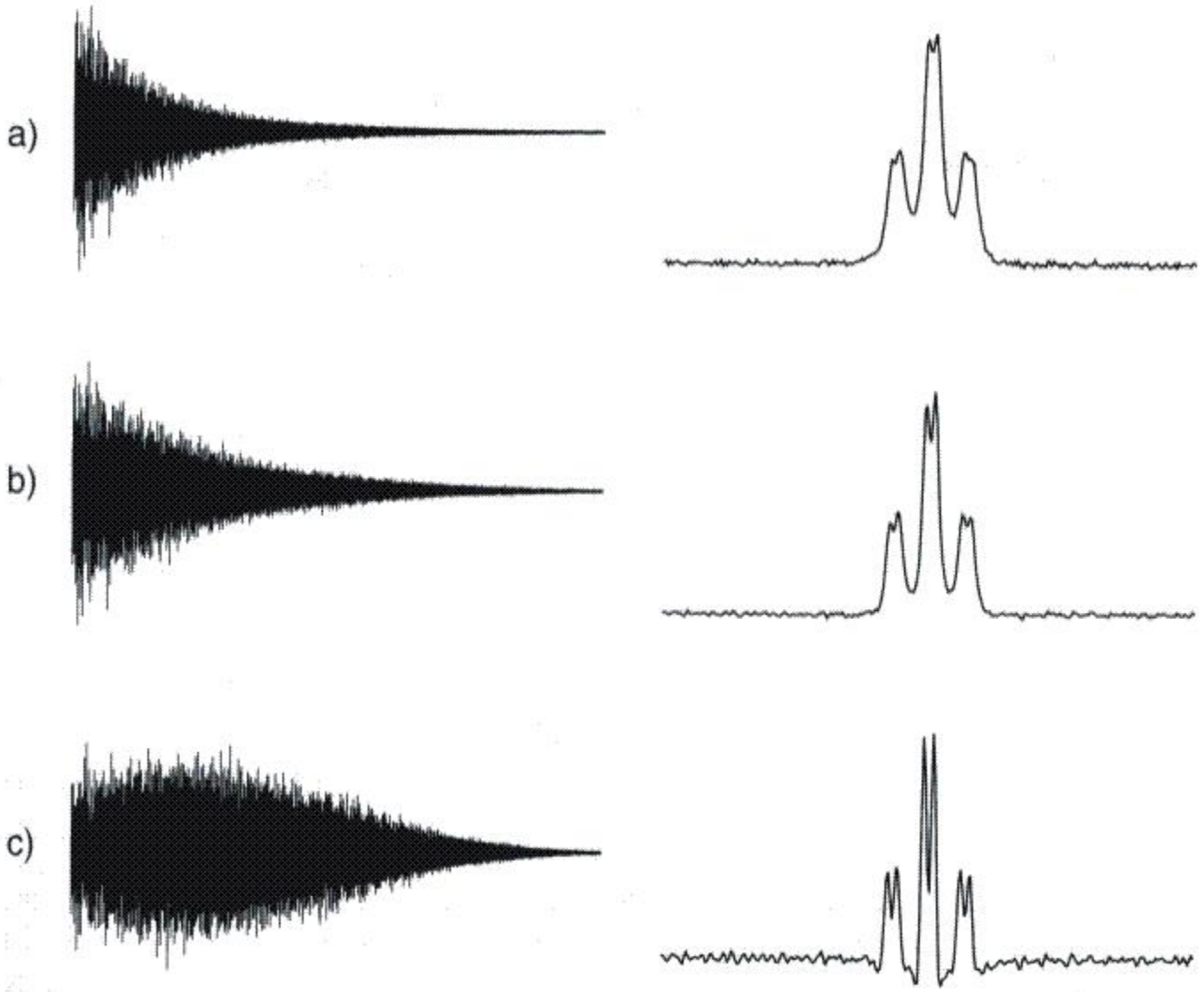
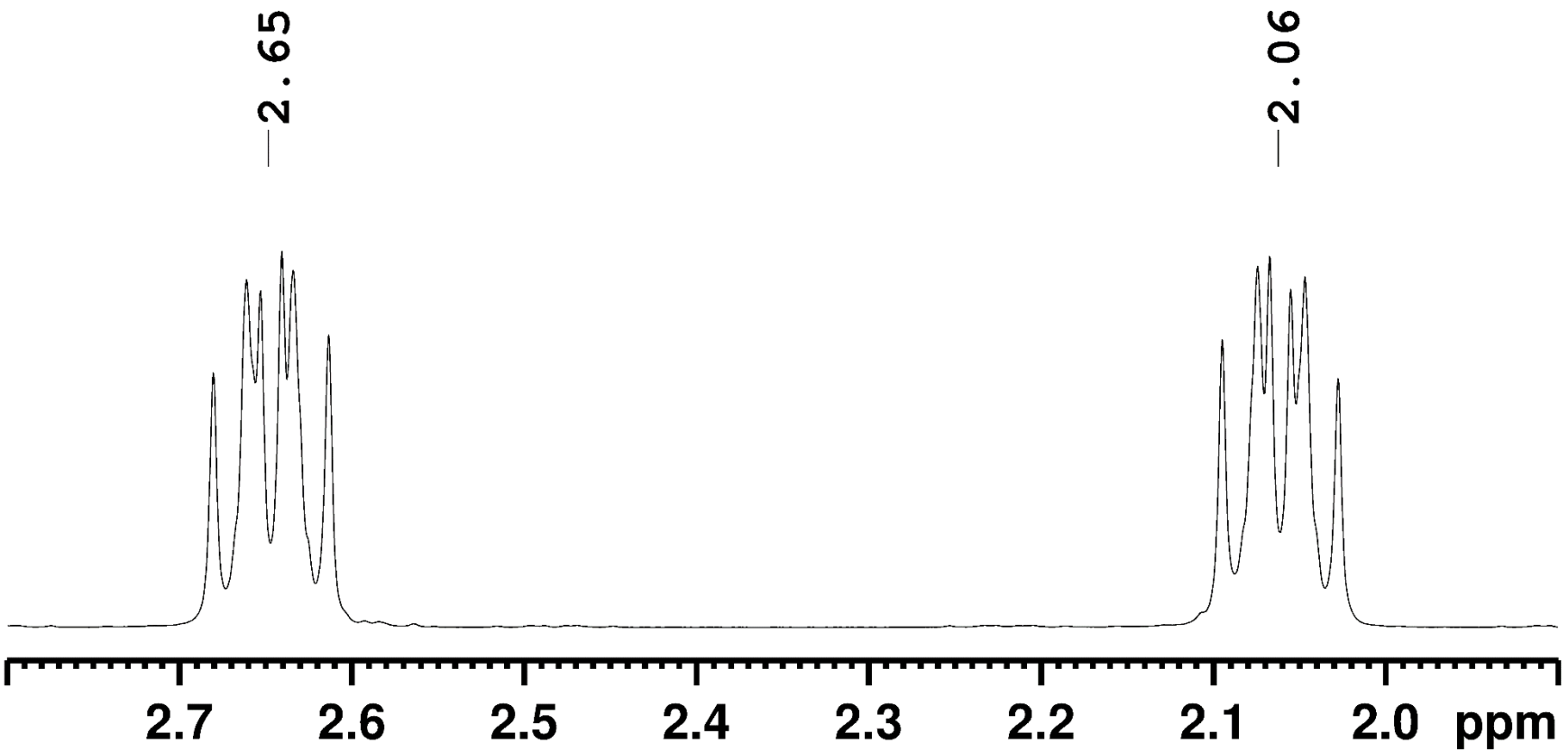


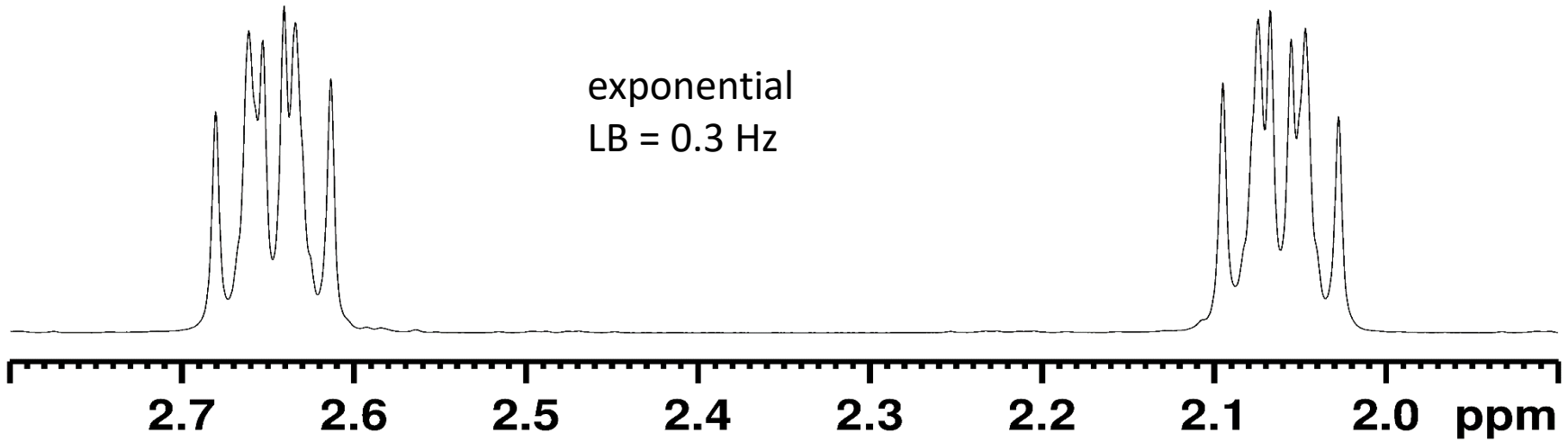
Fig. 3.37. The Lorentz-Gauss transformation ("Gaussian multiplication") can be used to improve resolution. (A) RAW FID and spectrum following Fourier transformation and results after the L-G transformation with (b) lb = 1 Hz. gb = 0,2 and (c) lb = -3Hz and gb = 0.2.

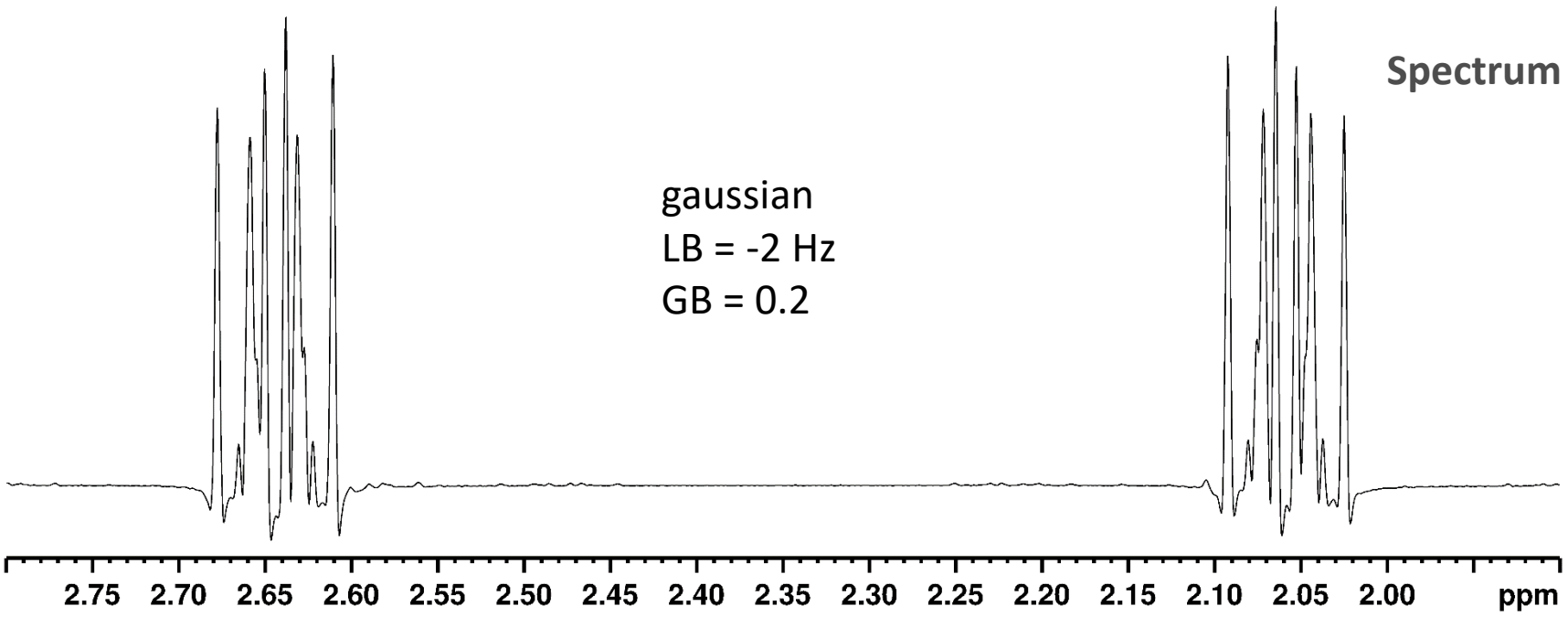
$O=P(CH_2\text{-}CH_2\text{-}COO\text{-}CH_3)_3$

2.06 ppm **2.65 ppm**



$O=P(CH_2\text{-}CH_2\text{-}COO\text{-}CH_3)_3$





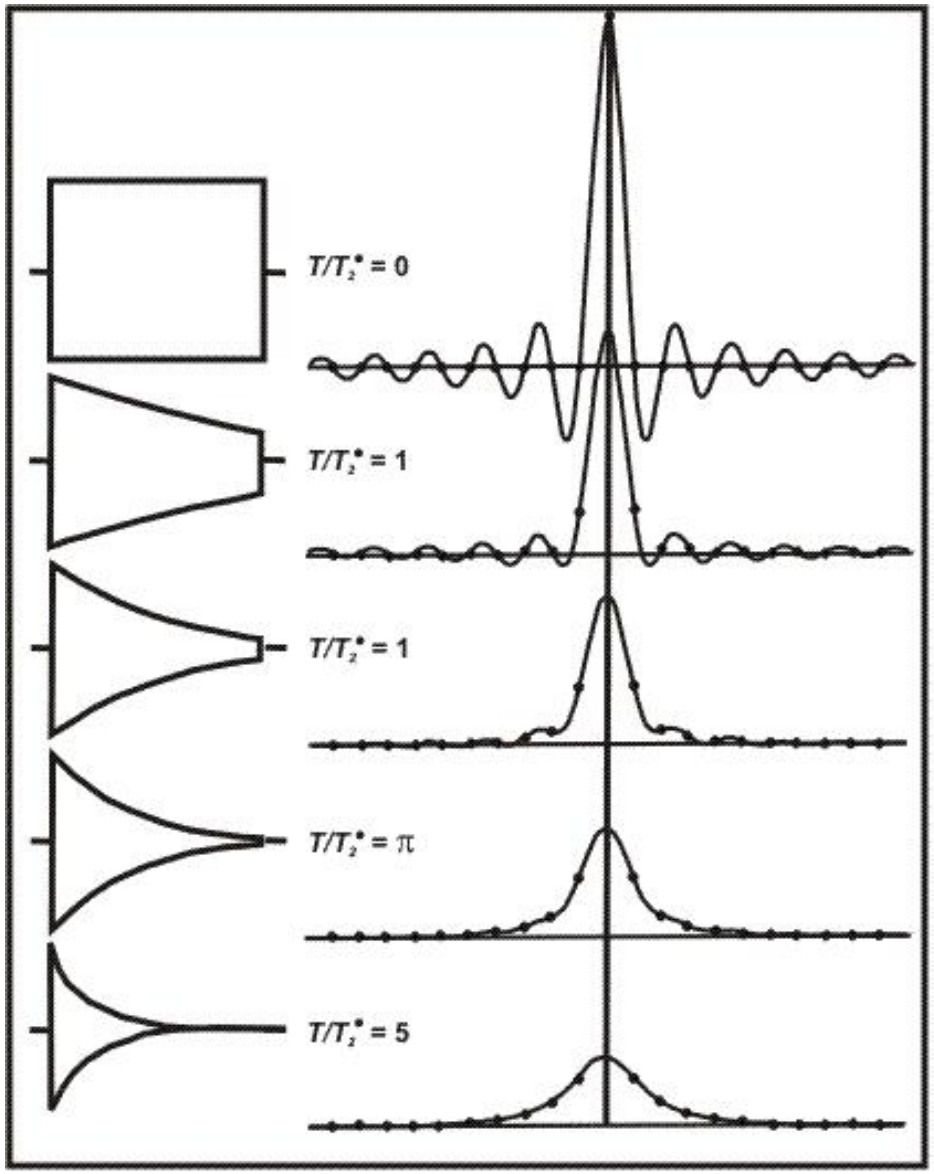


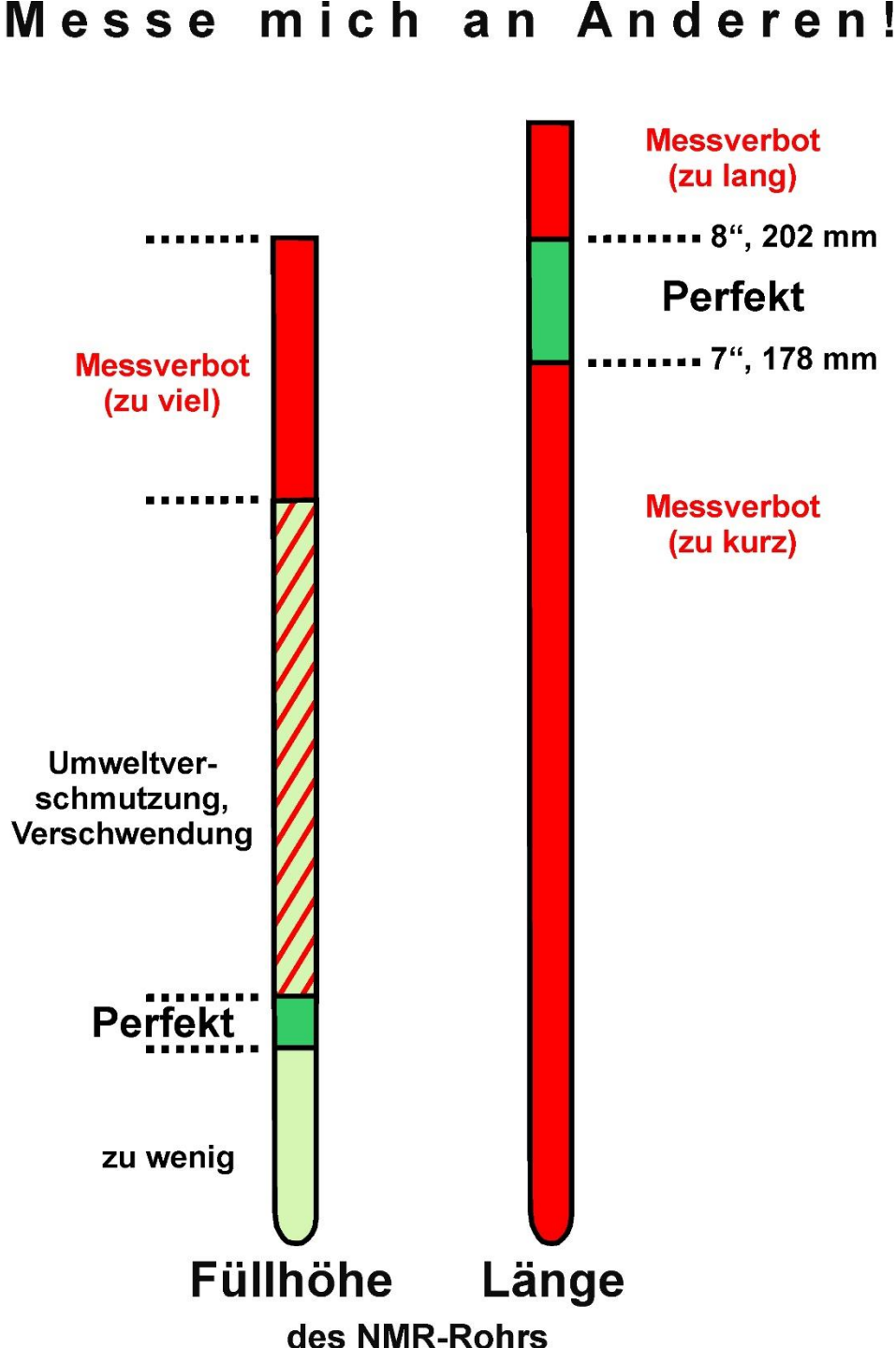
FIG. 4.1.4 Lineshapes obtained by Fourier transformation of truncated free inductiondecays of lenght $t_{max} = T$. (a) No decay of the signal ($T_2^* = \infty$): the full width at half-height of the central lobe is $\Delta f = 0.604/t_{max}$.(b) to (e): Signals with increasing decayrates $T_2^* = T$, $T/2$, T/π, *and* $T/5$. Note that the ripple amplitude decreases. If the free induction signal is extended by unrestricted zero-filling, the continuos curve is approached. If the signal is only extended by a factor two by zero-filling, the Fouriertransformation gives the sampling points indicated by dots. A Fourier transform of the truncated signal without zero-filling only gives a sampling point for every second dot. (Adapted from Ref. 4.27.)

http://www-oc.chemie.uni-regensburg.de/za/nmr/service/service_d.html

Anmerkung: Für eine rasche Erledigung von Aufträgen sind folgende Substanzmengen wünschenswert:

^{1}H: 0.03 mmol
^{13}C: 0.1 mmol
^{31}P: 0.1 mmol

Diese Mengen müssen sich in 0.6 ml des gewünschten Lösungsmittels lösen. Bitte überprüfen Sie die Löslichkeit!

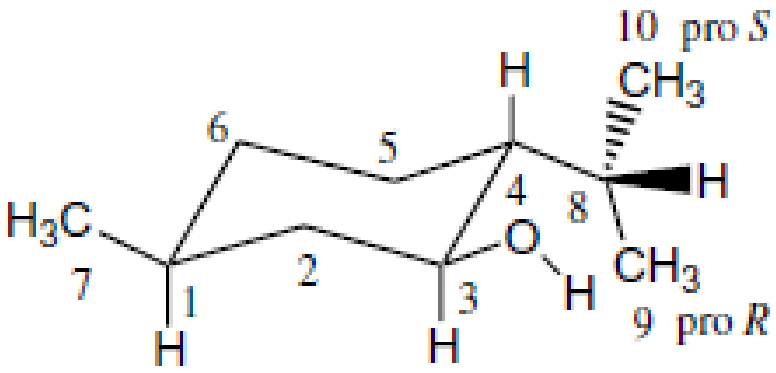


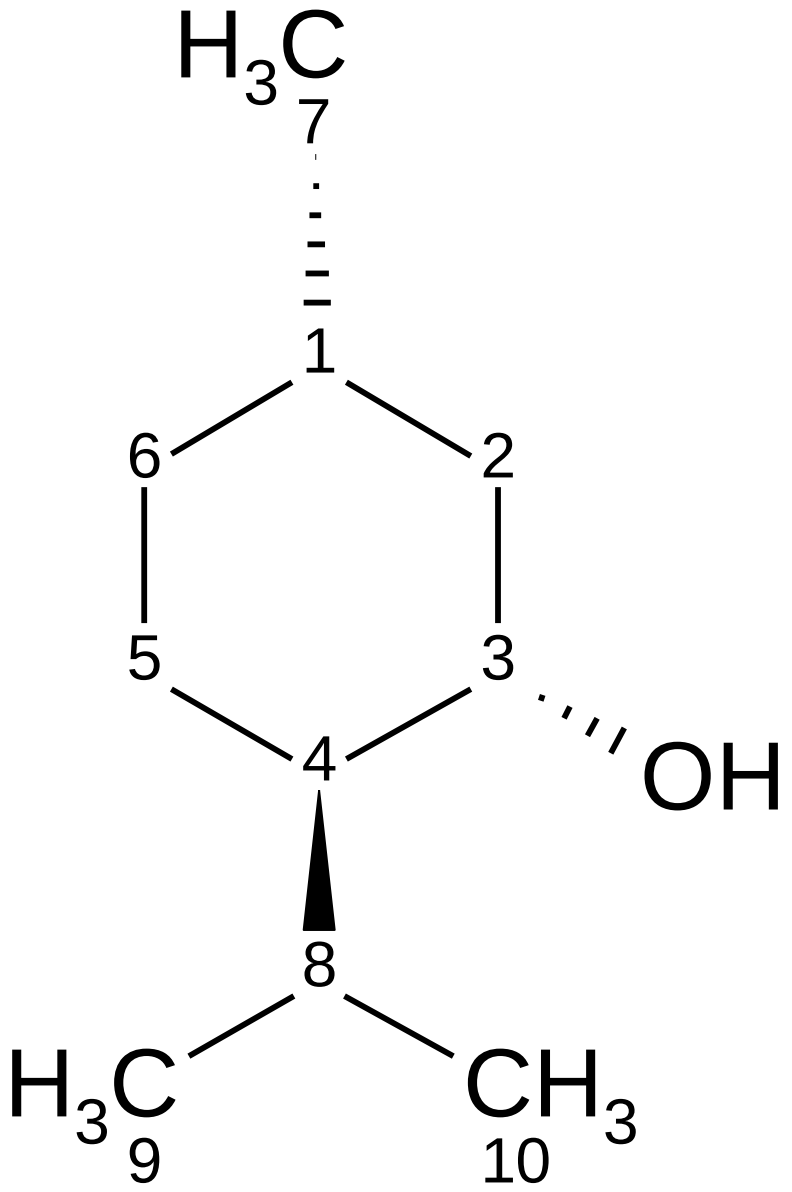
Strukturaufklärung

D-Menthol

(+) Menthol

^1H: 1_{ax}, 3_{ax}, 4_{ax},)





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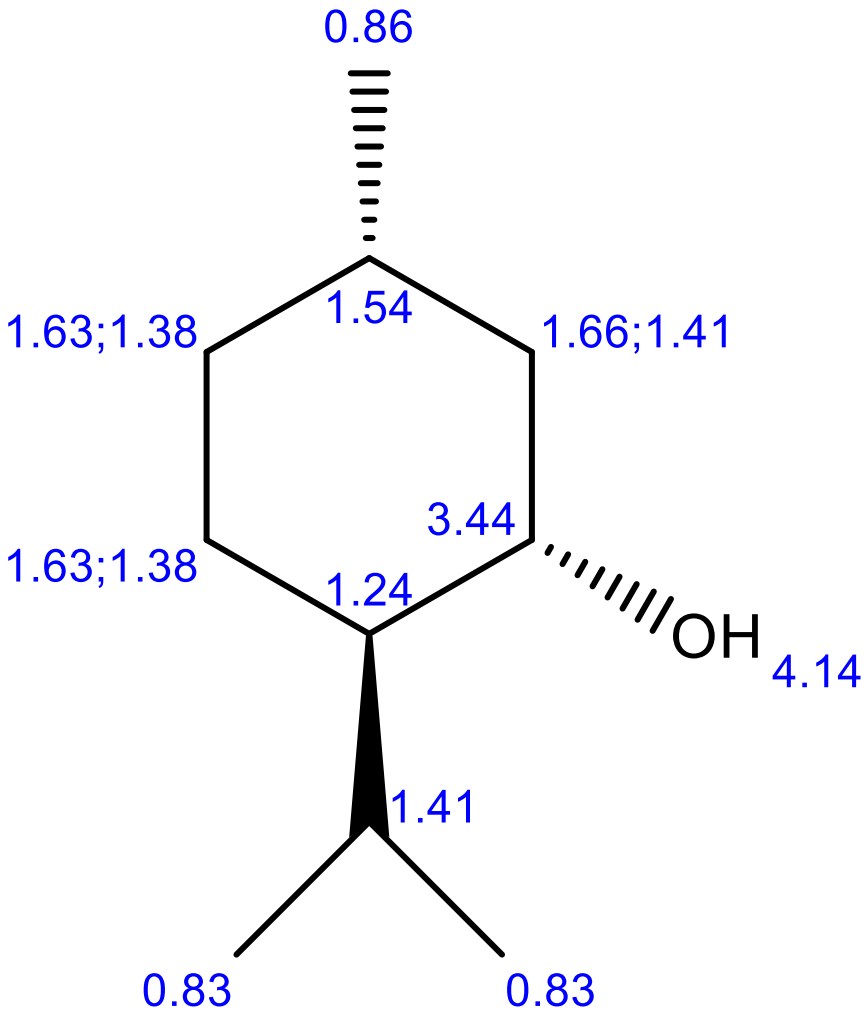
D-Menthol

(+) Menthol

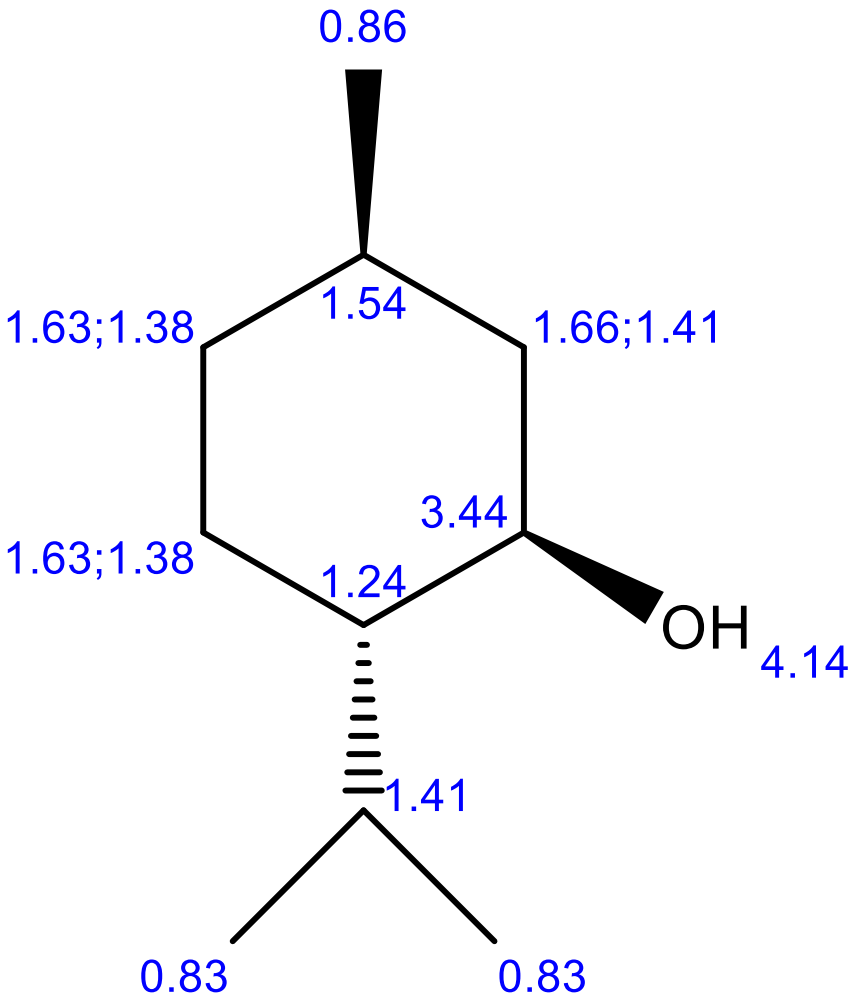
^{1}H: 1_{ax}, 3_{ax}, 4_{ax})



L-Menthol

(-) Menthol

^{1}H: 1_{ax}, 3_{ax}, 4_{ax})

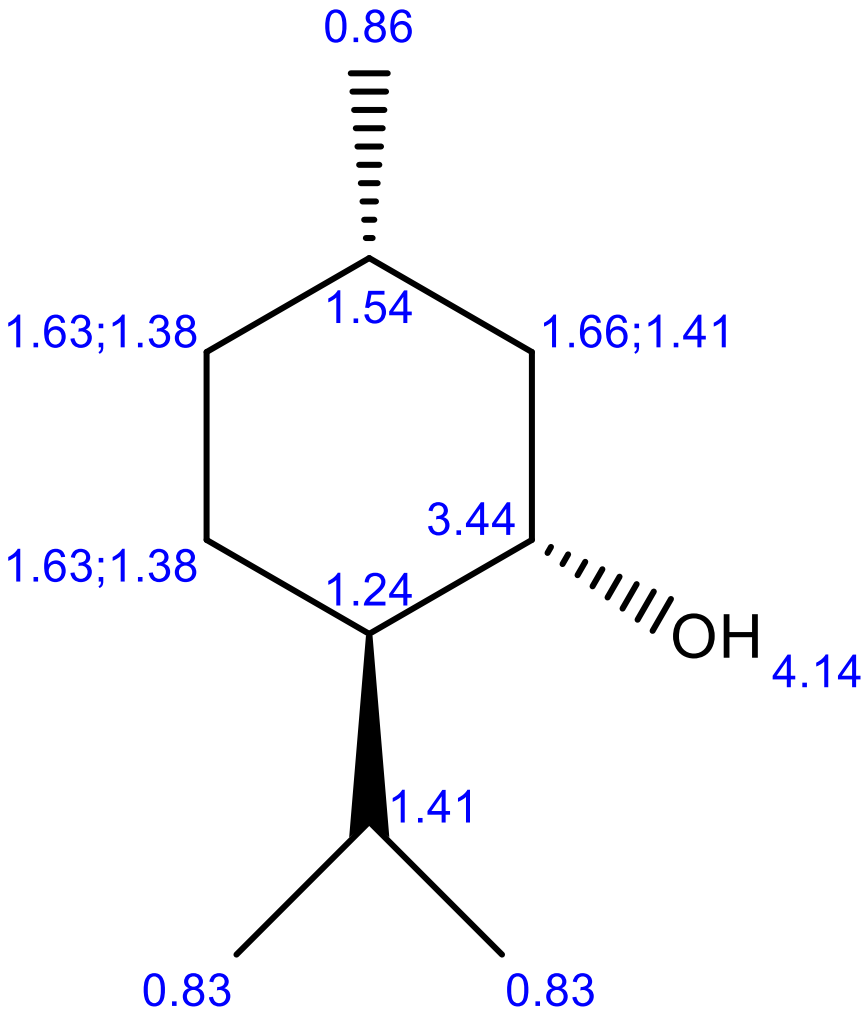


ChemDraw Professional

D-Menthol

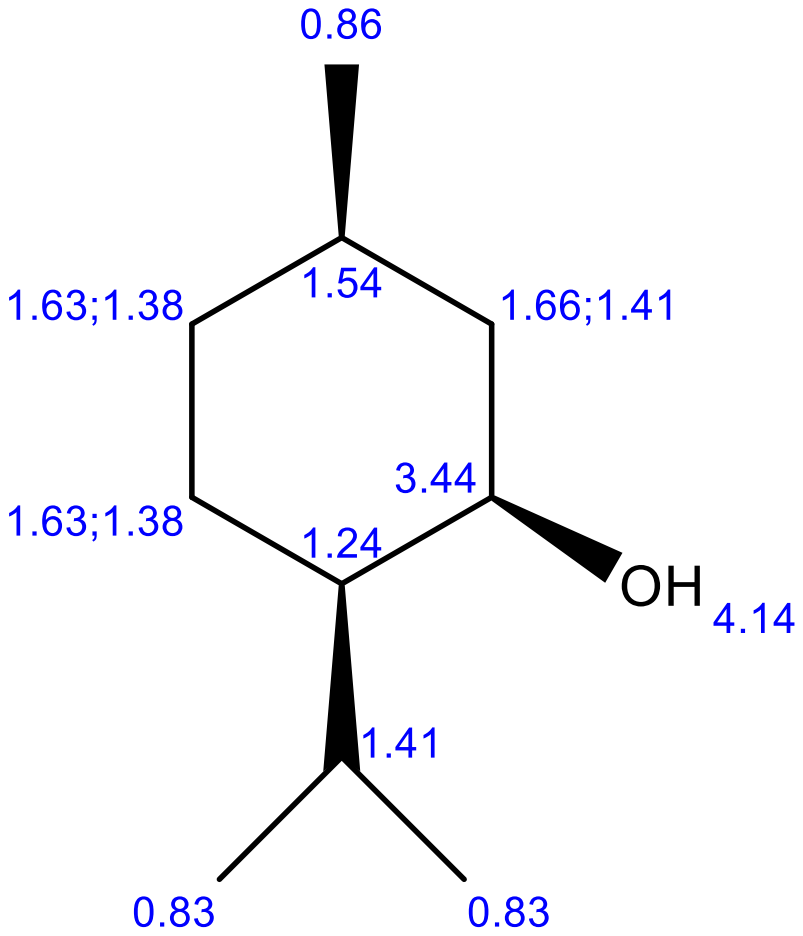
(+) Menthol

^1H: 1_{ax}, 3_{ax}, 4_{ax})



(+) Neisomenthol

^1H: 1_{ax}, 3_{ax}, 4_{eq})

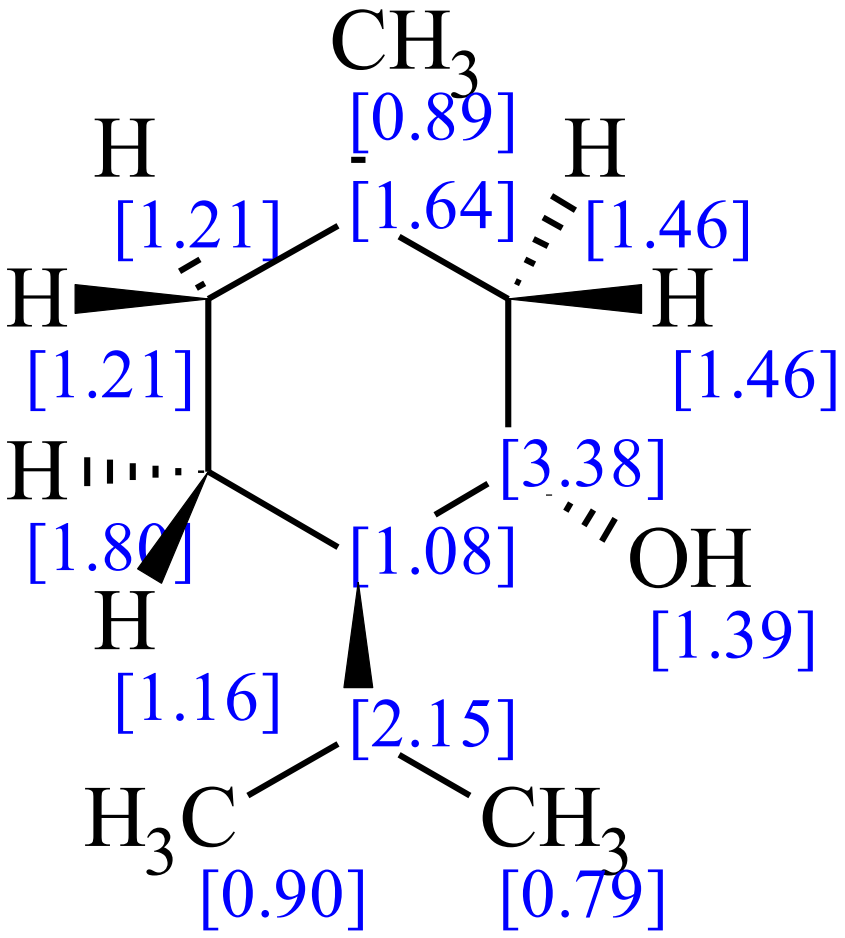


ACD/Labs

D-Menthol

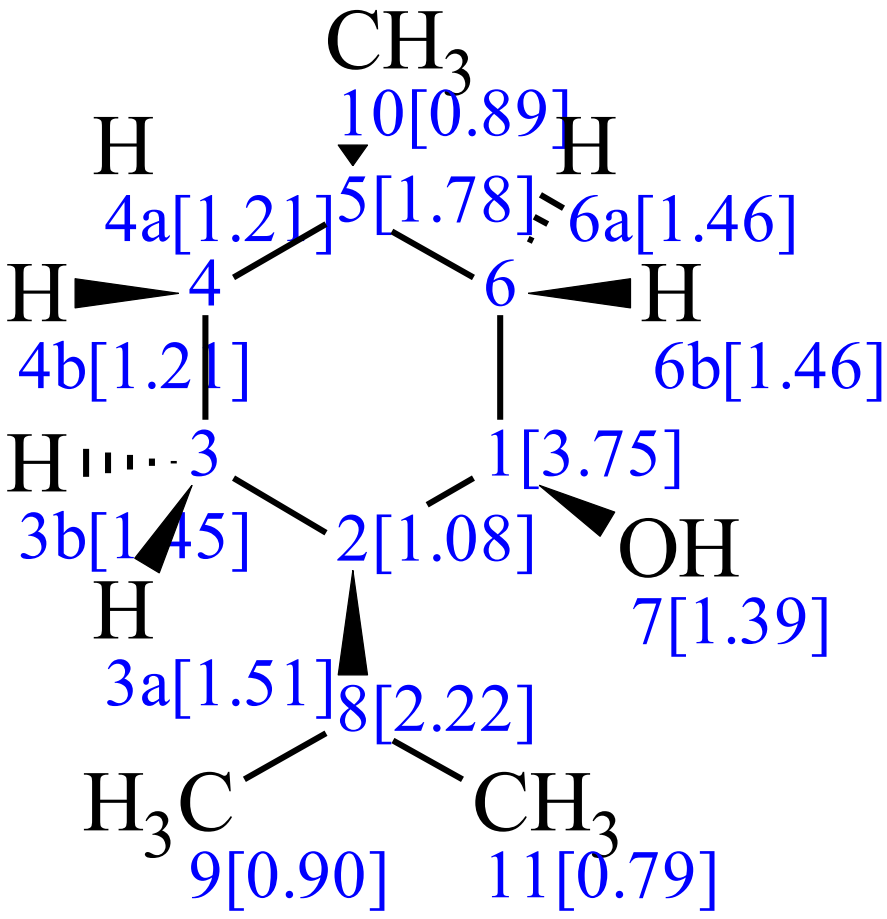
(+) Menthol

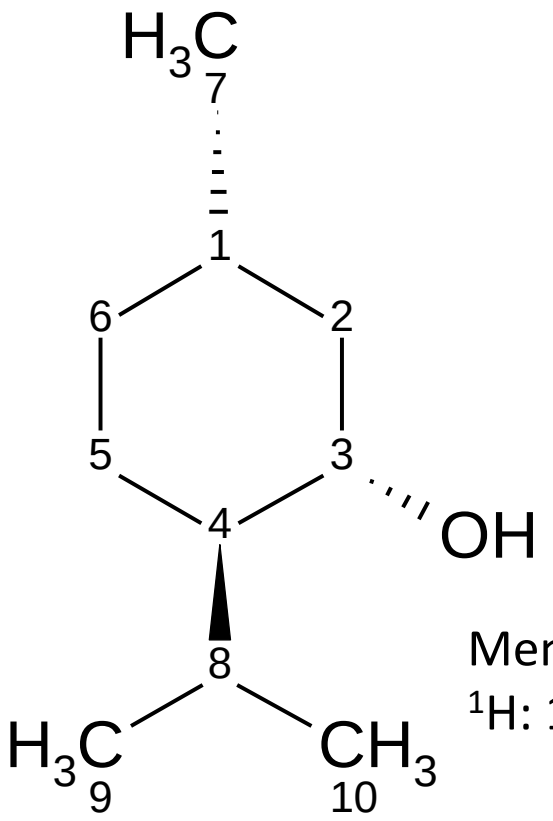
^1H: 1_{ax}, 3_{ax}, 4_{ax})



(+) Neisomenthol

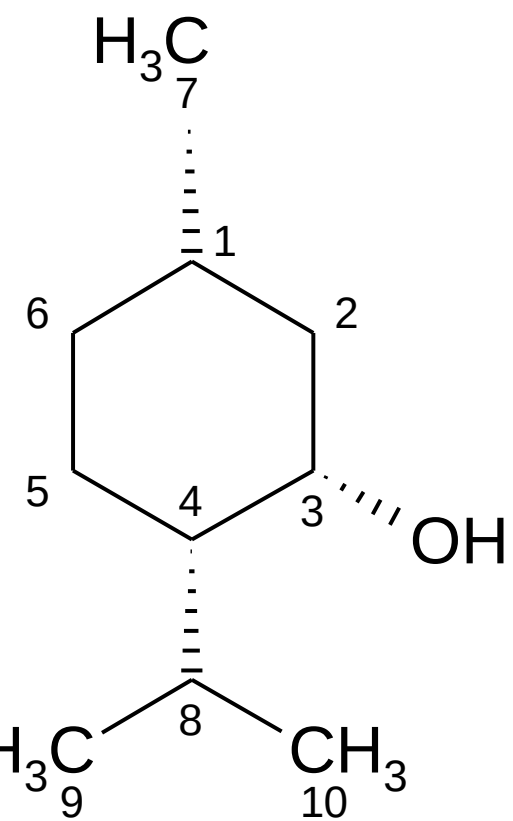
^1H: 1_{ax}, 3_{ax}, 4_{eq})





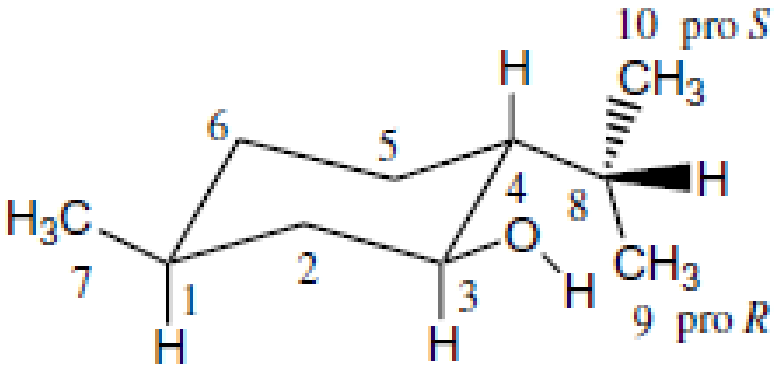
Menthol

^{1}H: 1_{ax}, 3_{ax}, 4_{ax}



Neisomenthol

^{1}H: 1_{ax}, 3_{ax}, 4_{eq}



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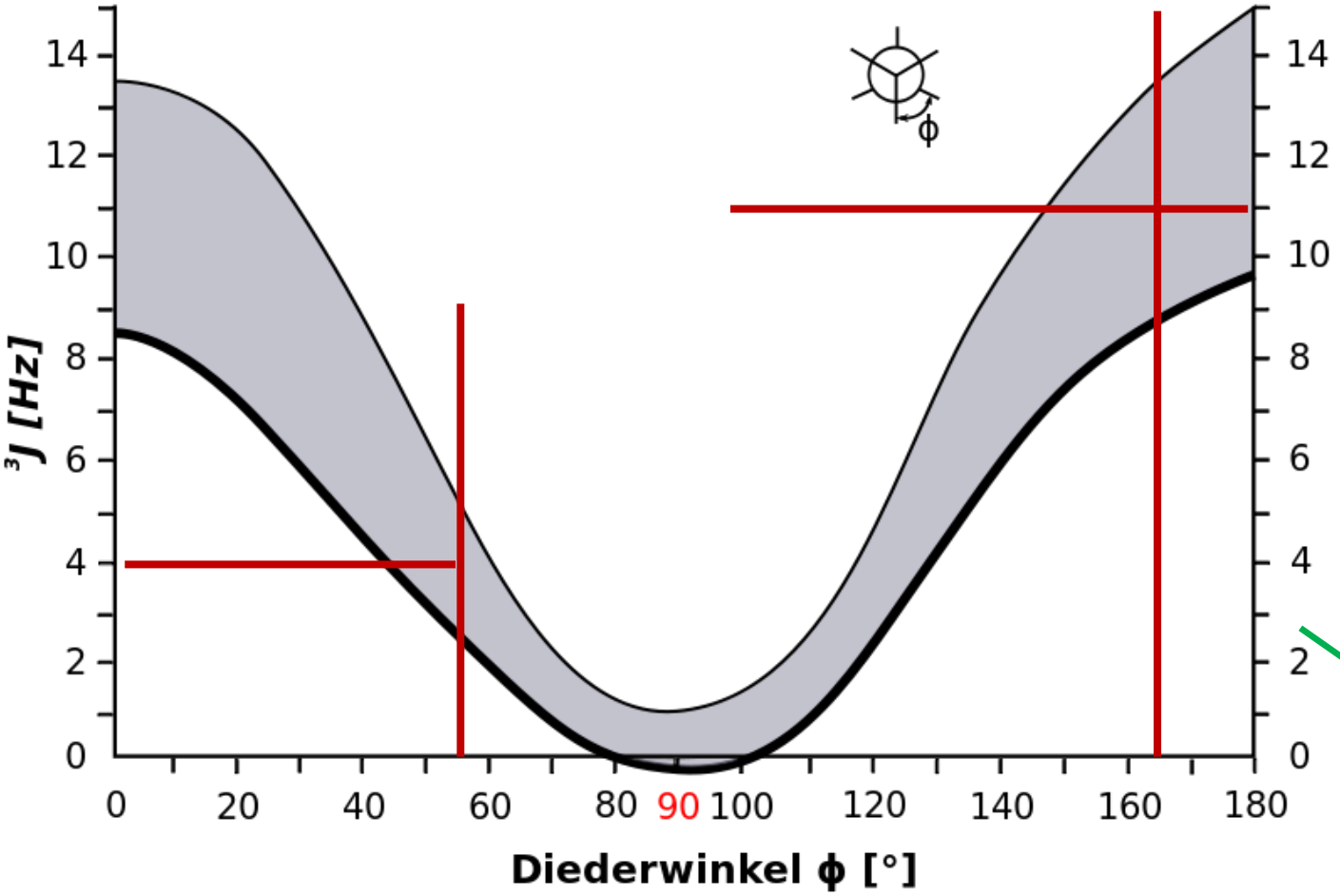
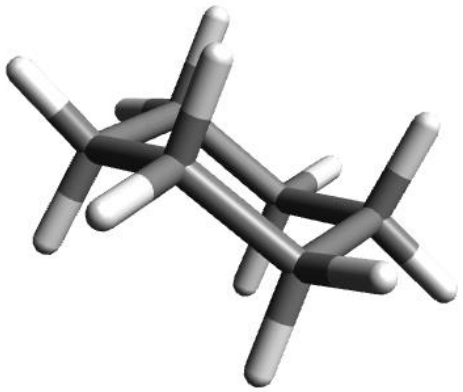
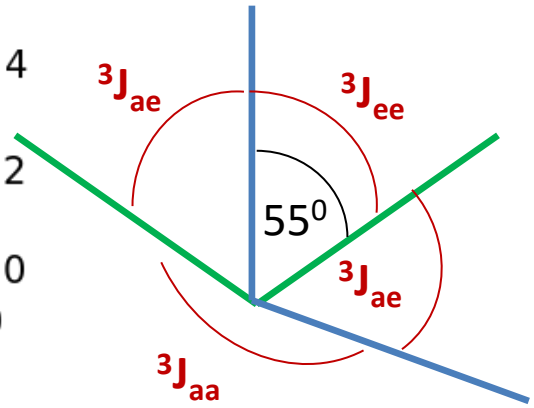
Karplus-Beziehung

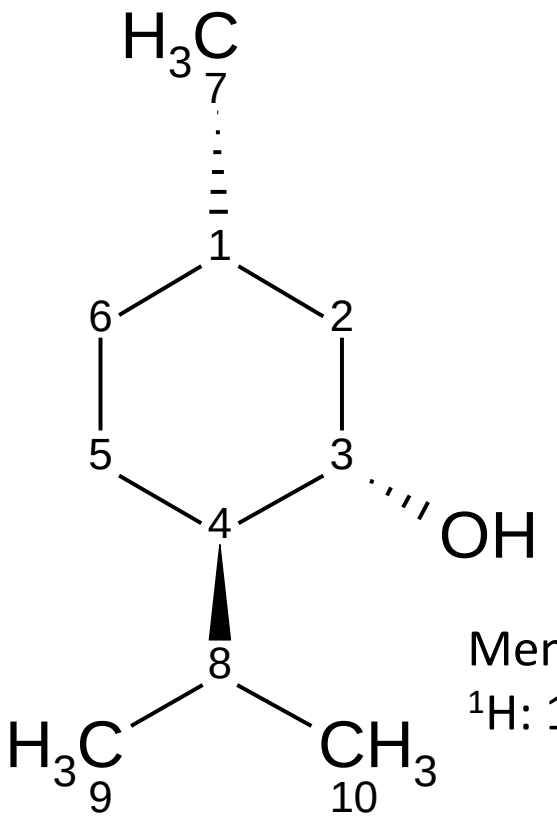


Cyclohexan



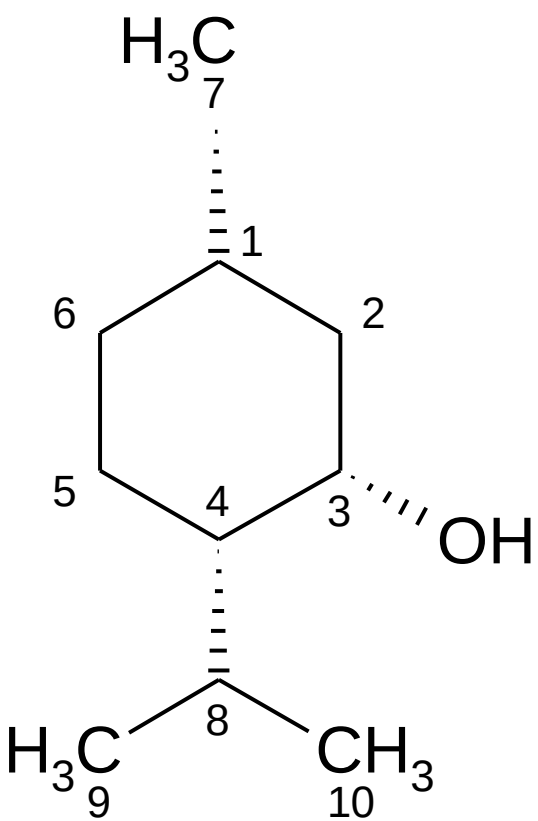


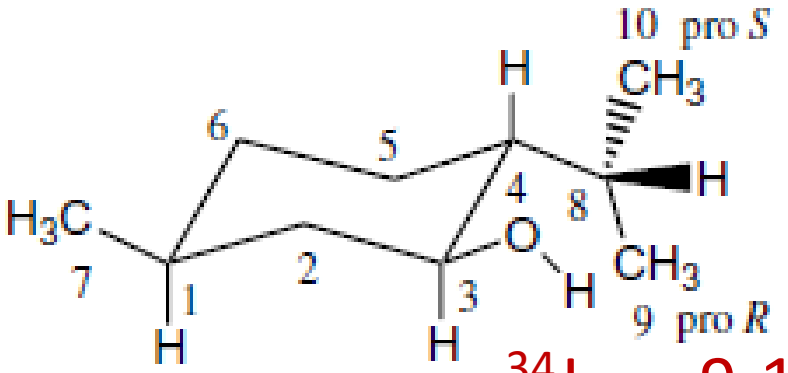
$^2J_{HH} \approx 11\text{-}13$ Hz, $^3J_{aa} \approx 9\text{-}13$ Hz, $^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz



Menthol

^{1}H: 1_{ax}, 3_{ax}, 4_{ax}





$^{34}J_{aa} \approx 9\text{-}13$ Hz

Neisomenthol

^{1}H: 1_{ax}, 3_{ax}, 4_{eq}

$^{34}J_{ae} \approx 3\text{-}4$ Hz

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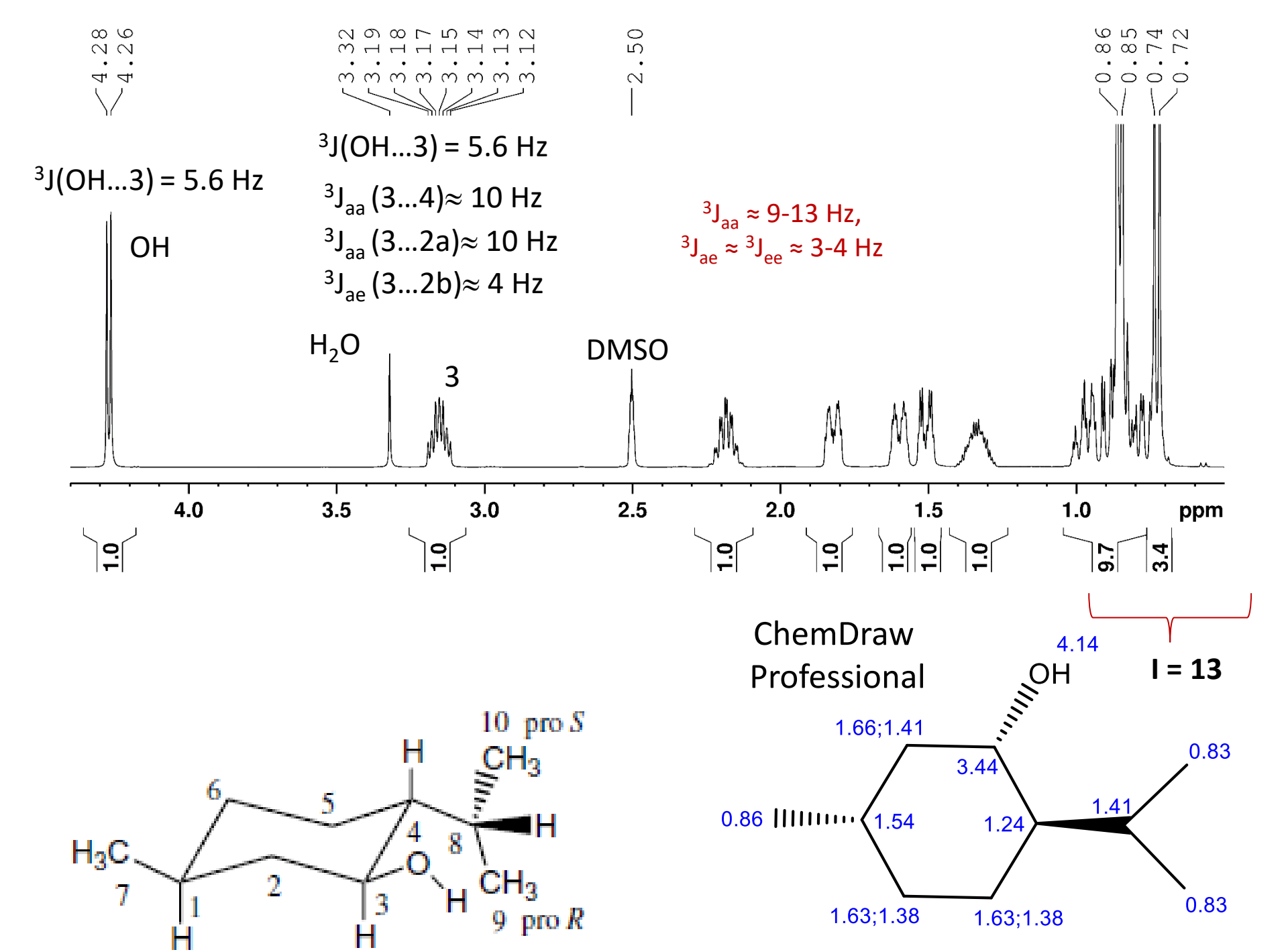
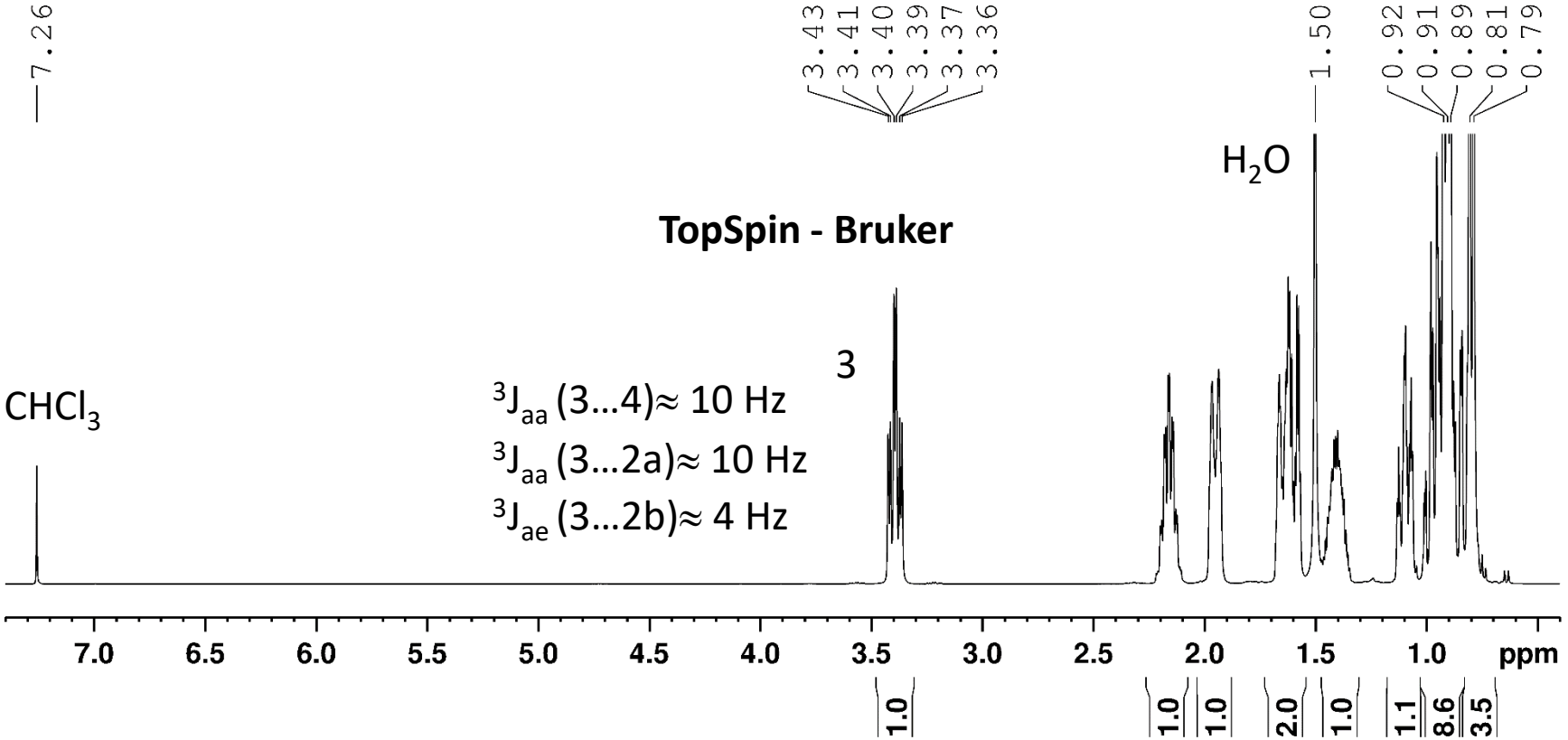
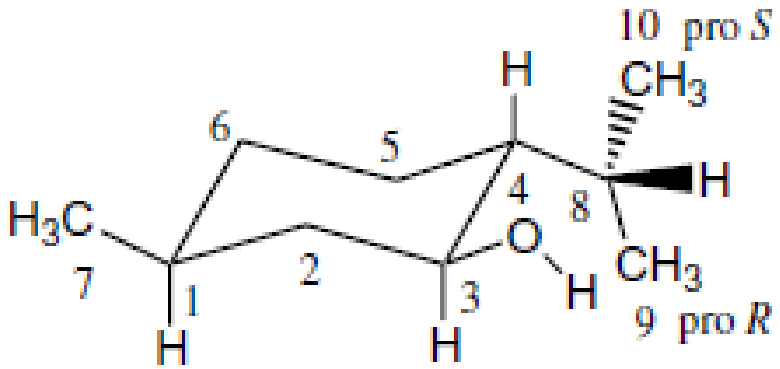


ChemDraw Professional





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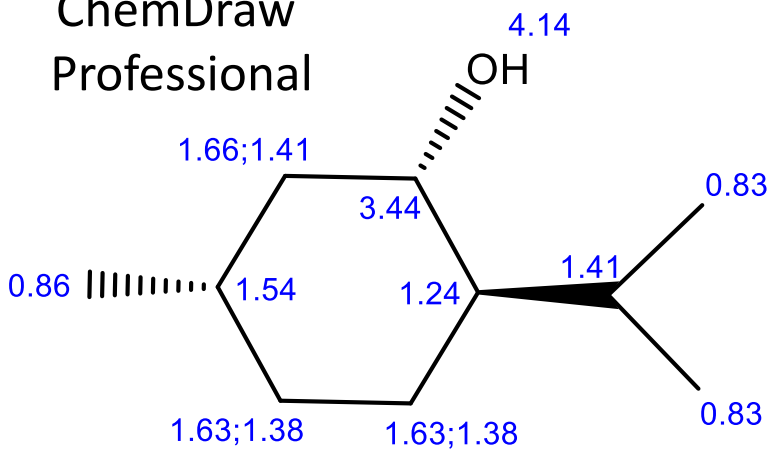
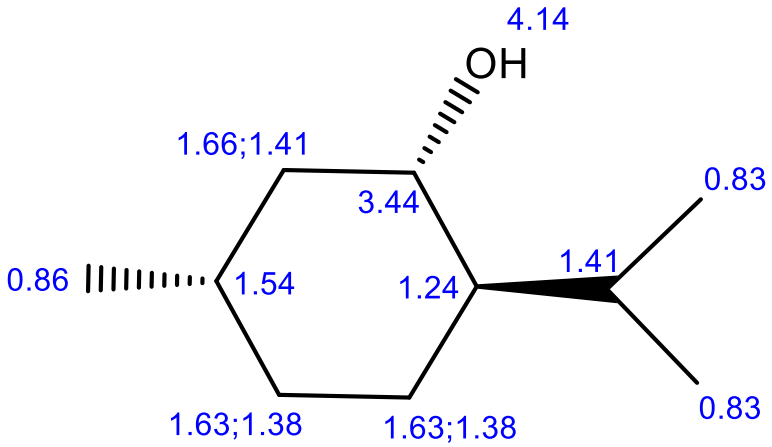




δ (OH) = 4.2705 ppm

δ = 3.1540 ppm

$^3J_{aa} \approx 10.5$ Hz

$^3J_{aa} \approx 9.5$ Hz

$^3J_{ae} \approx 4.4$ Hz

DMSO

δ = 3.3937 ppm

$^3J_{aa} \approx 10.5$ Hz

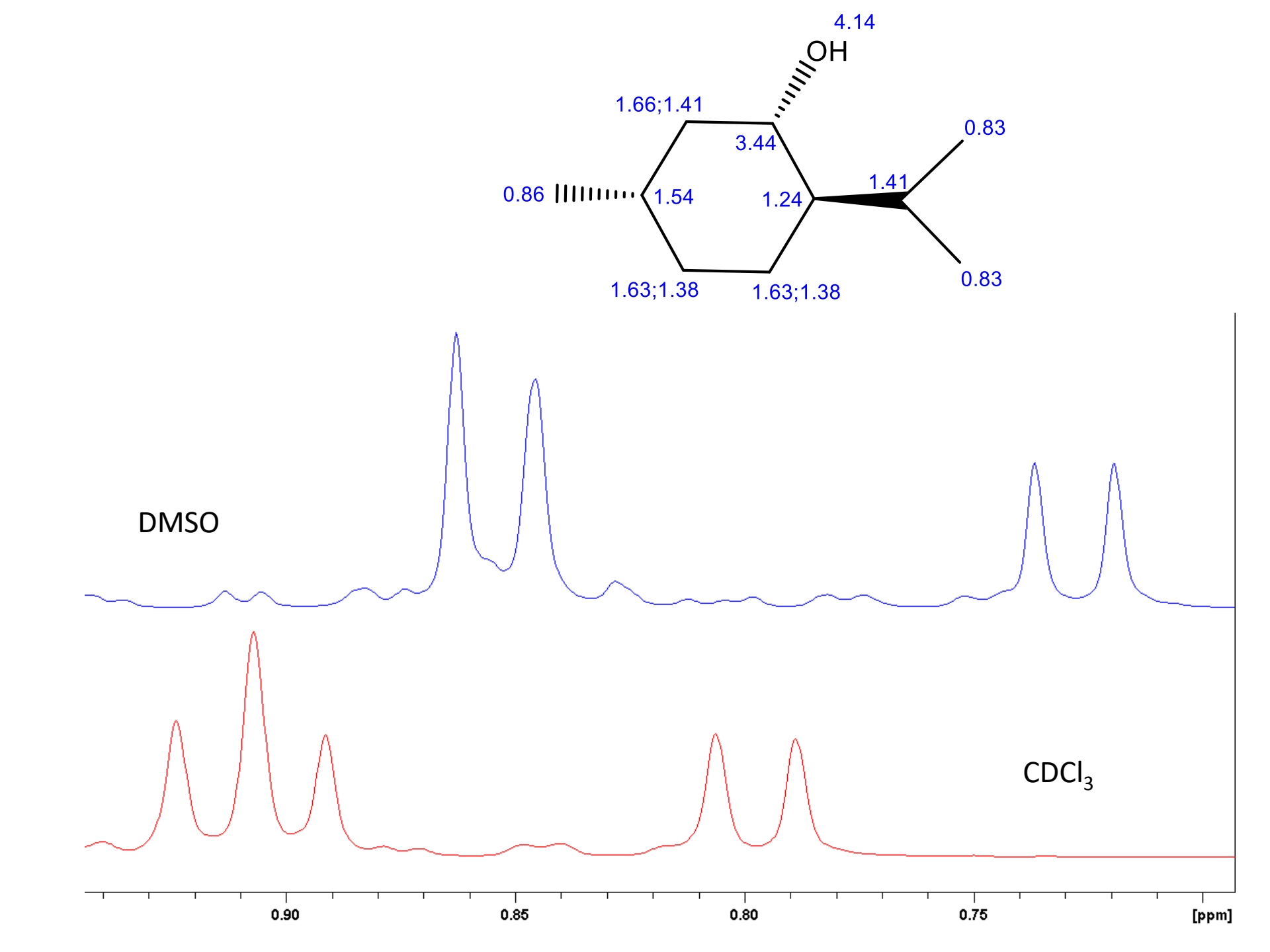
$^3J_{aa} \approx 10.5$ Hz

$^3J_{ae} \approx 4.0$ Hz

δ (OH) = 1.50 ppm

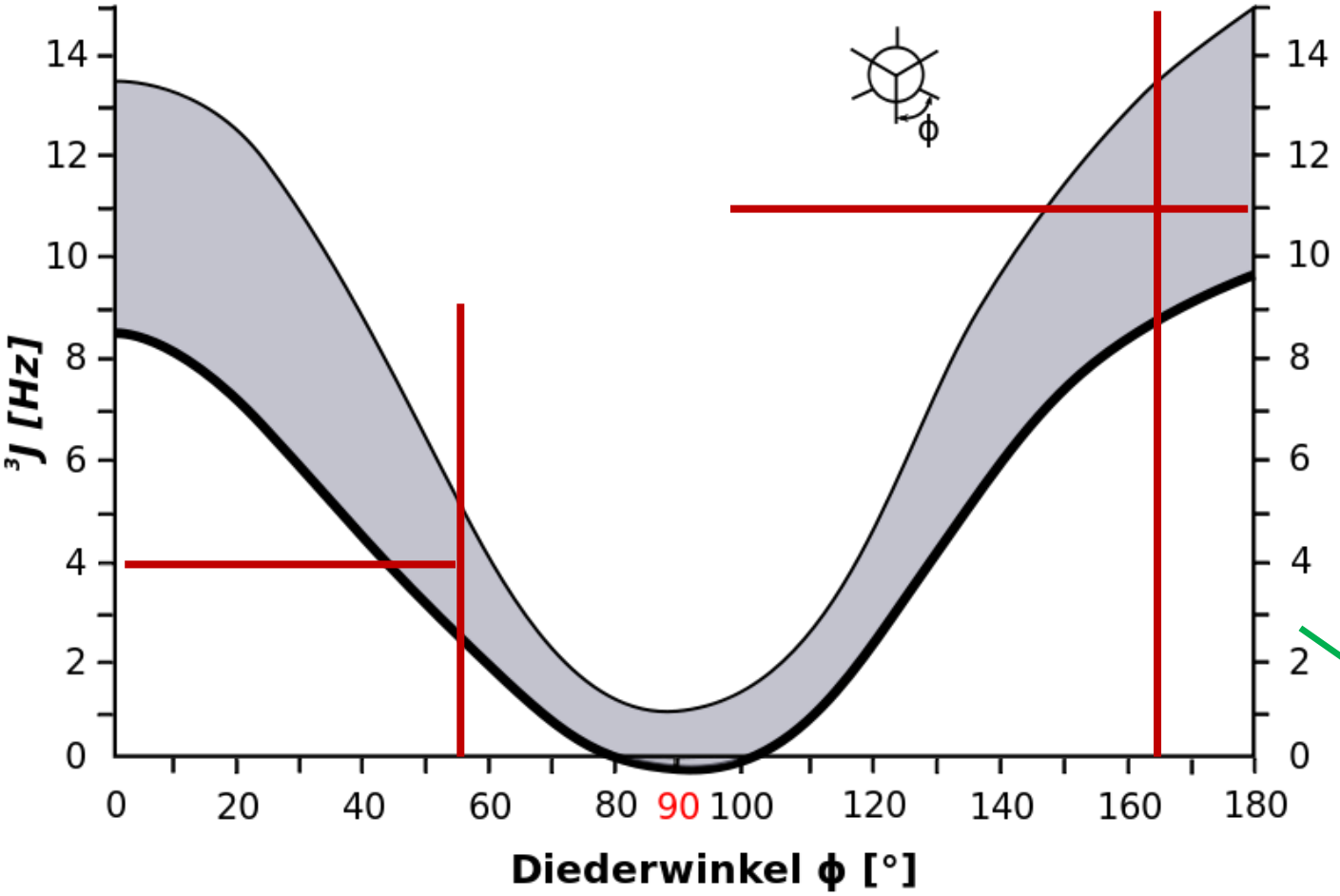
$CDCl_3$

3.4 3.3 3.2 3.1 [ppm]

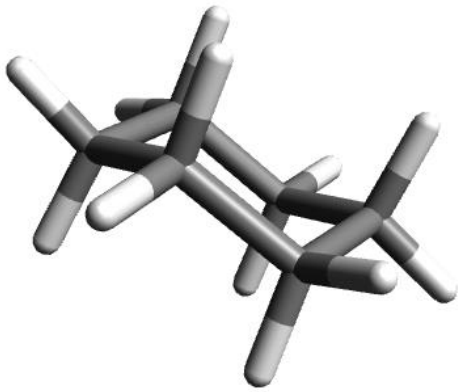

4.14
OH
1.66;1.41
0.83
3.44
1.41
0.86
1.54
1.24
0.83
1.63;1.38
1.63;1.38
DMSO
CDCl3
0.90
0.85
0.80
0.75
[ppm]

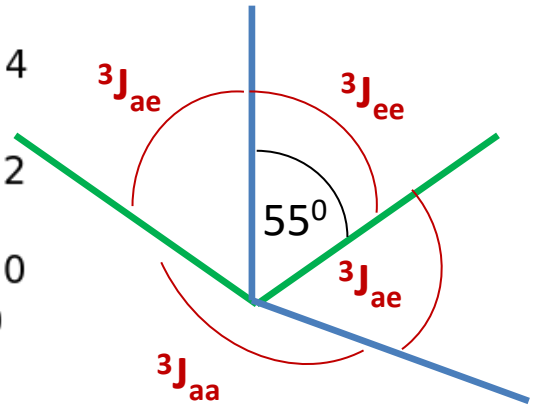
Stereochemie

Karplus-Beziehung



Cyclohexan

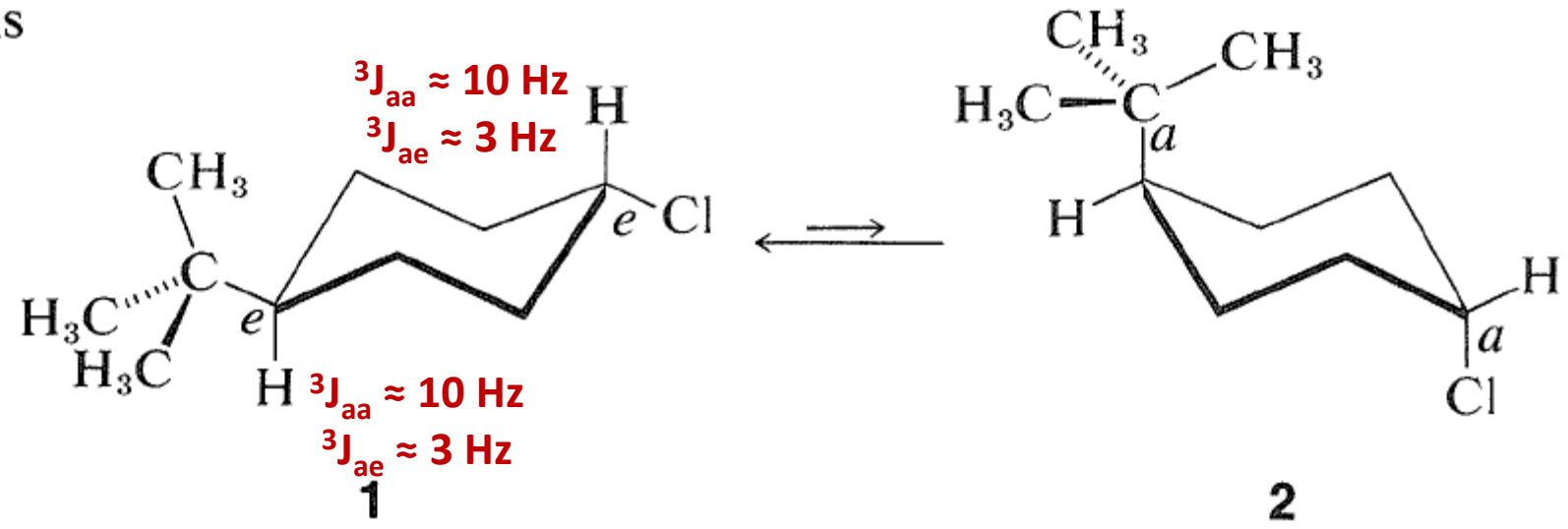




$^2J_{HH} \approx 11\text{-}13$ Hz, $^3J_{aa} \approx 9\text{-}13$ Hz, $^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz

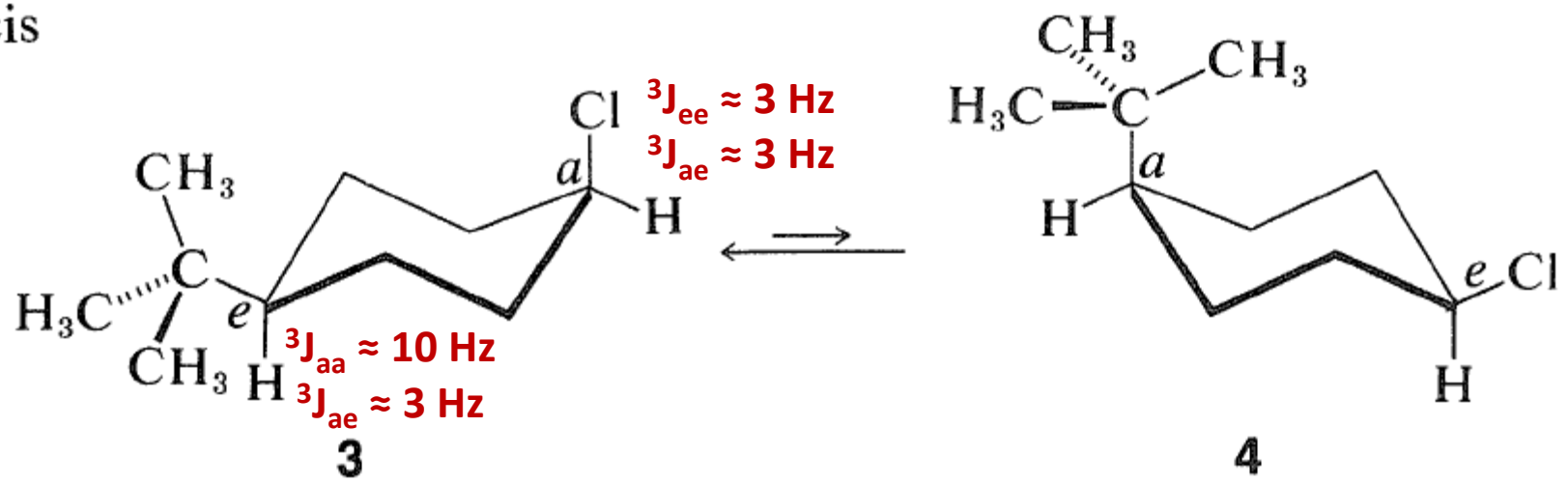
Karplus-Beziehung

trans



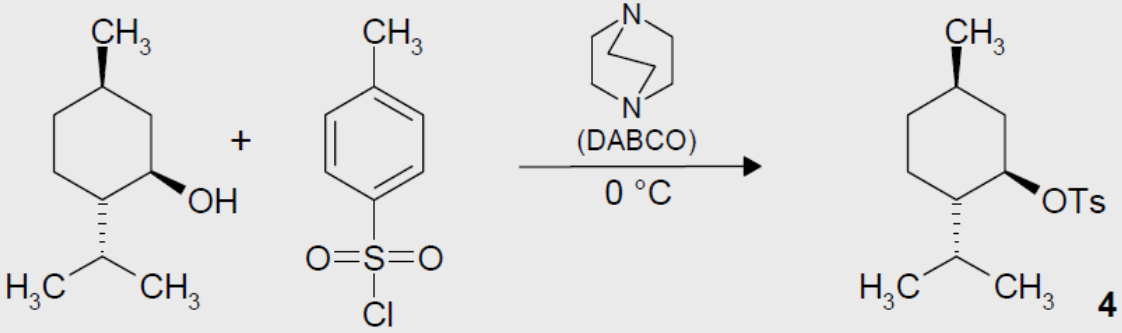
1 2

cis

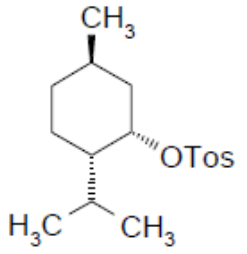


3 4

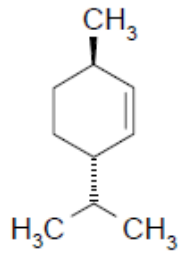
1.2.4 Veresterung von (–)-Menthol mit 4-Toluolsulfonsäurechlorid (Tosylchlorid) zu (–)-Menthyltosylat (4)



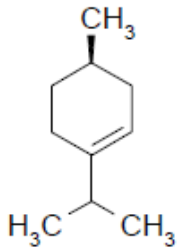
Weitere denkbare Reaktionsprodukte:



A



B

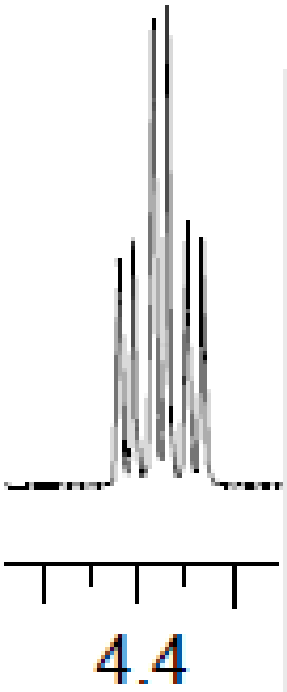


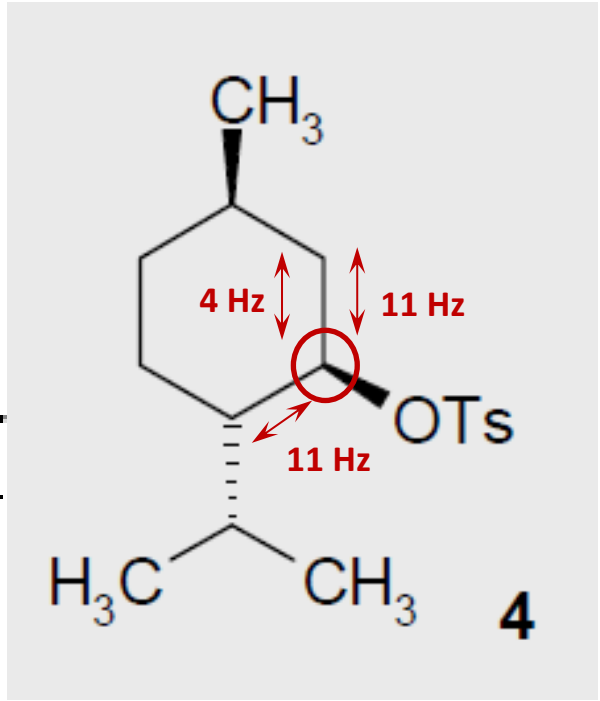
C

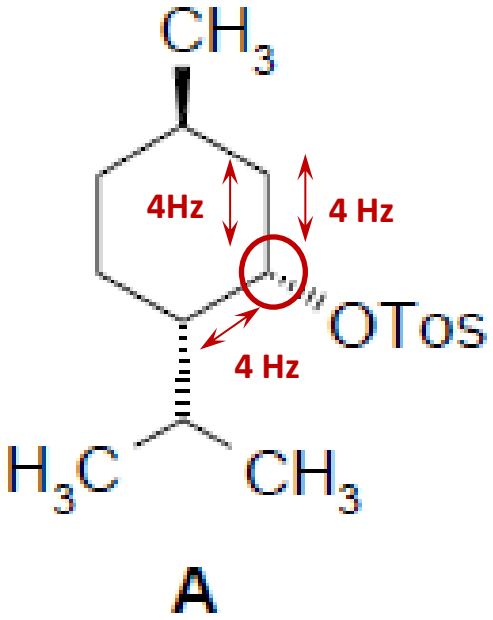
$^2J_{HH} \approx 11\text{-}13$ Hz

$^3J_{aa} \approx 9\text{-}13$ Hz,

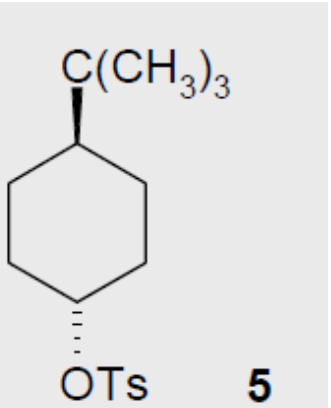
$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz

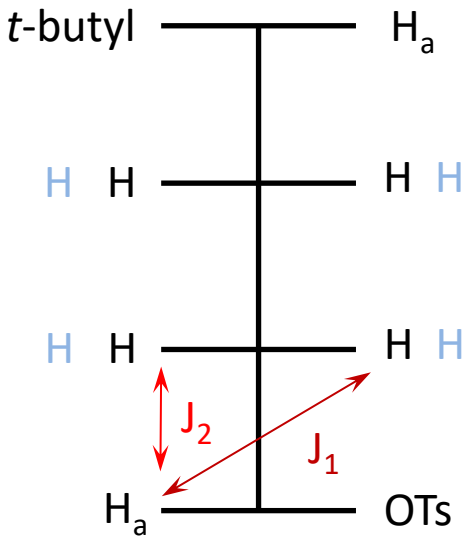




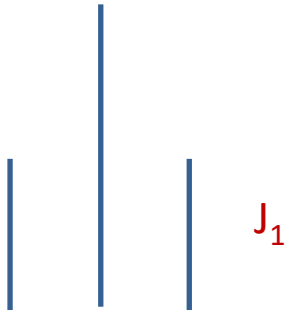


A





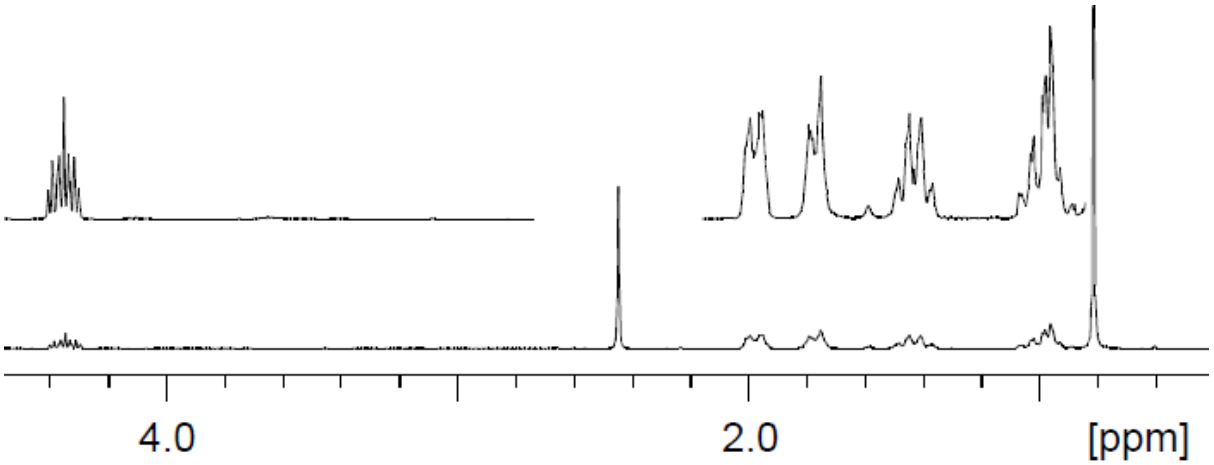
$J_1 > J_2$

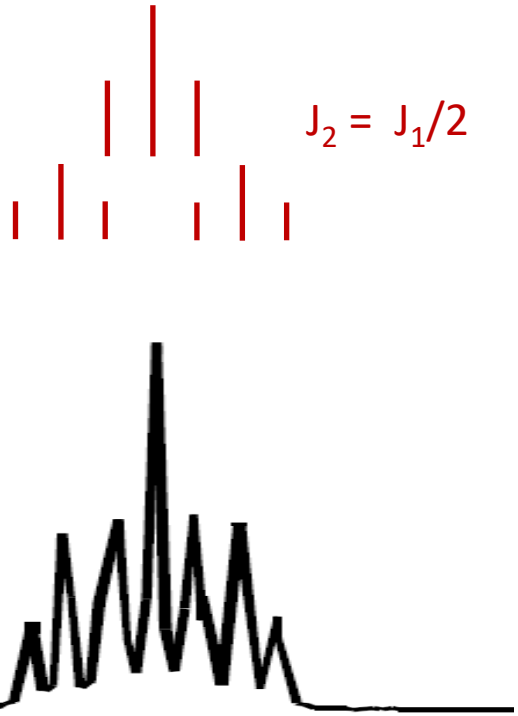


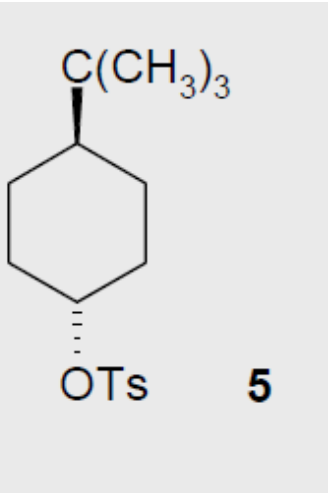
$^2J_{HH} \approx 11\text{-}13$ Hz

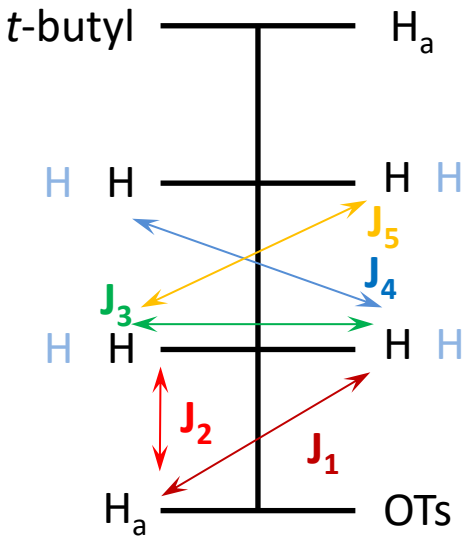
$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz









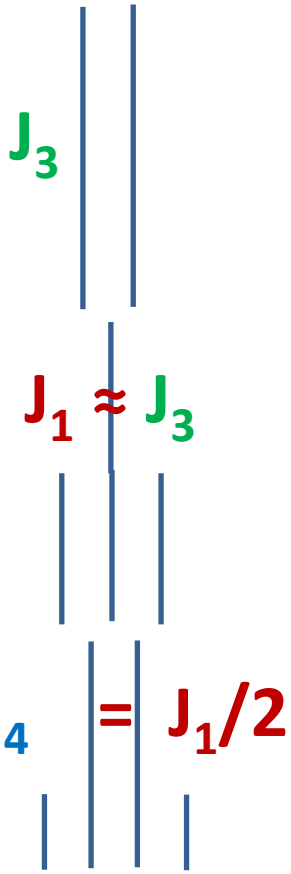
$J_2 = J_1/2$

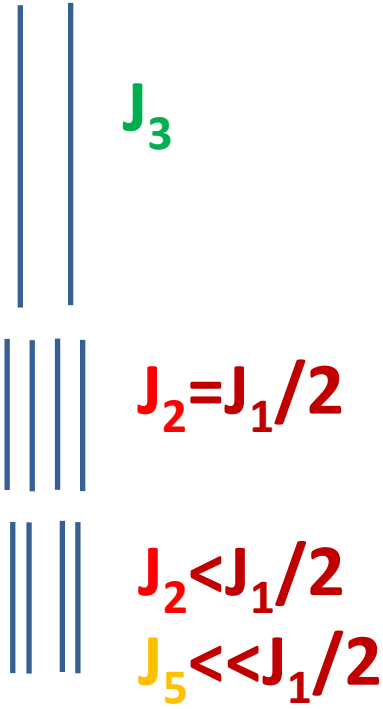
$J_1 \approx J_3$

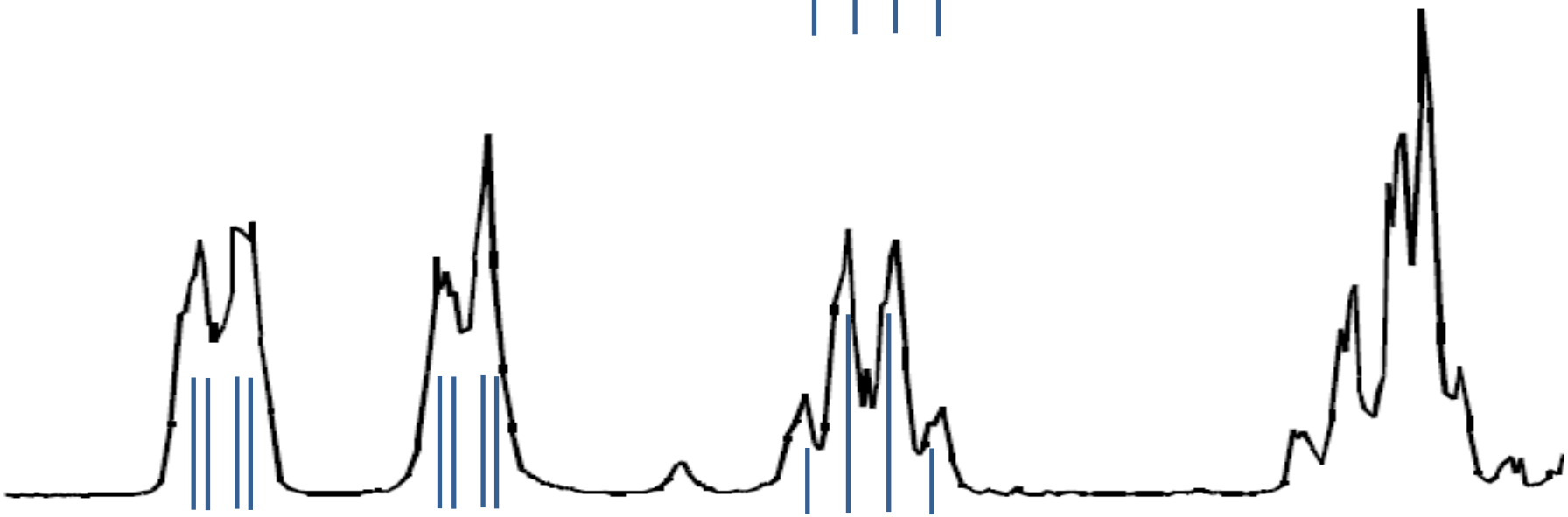
$^2J_{HH} \approx 12\text{-}13$ Hz

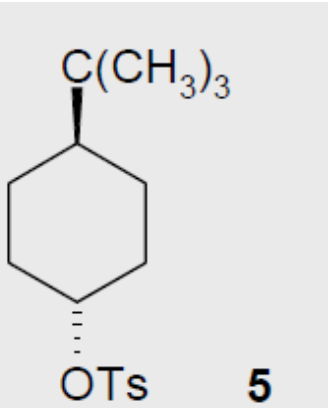
$^3J_{aa} \approx 9\text{-}13$ Hz,

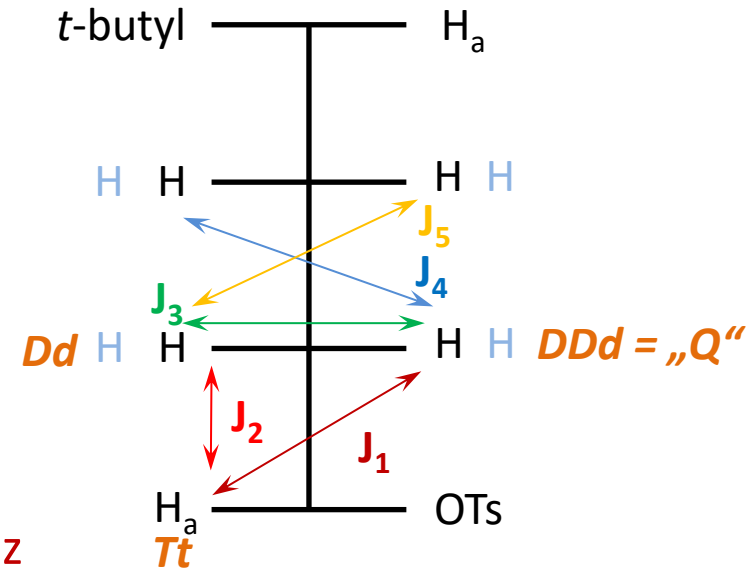
$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz











$J_2 < J_1/2$

$J_3 \approx J_1$

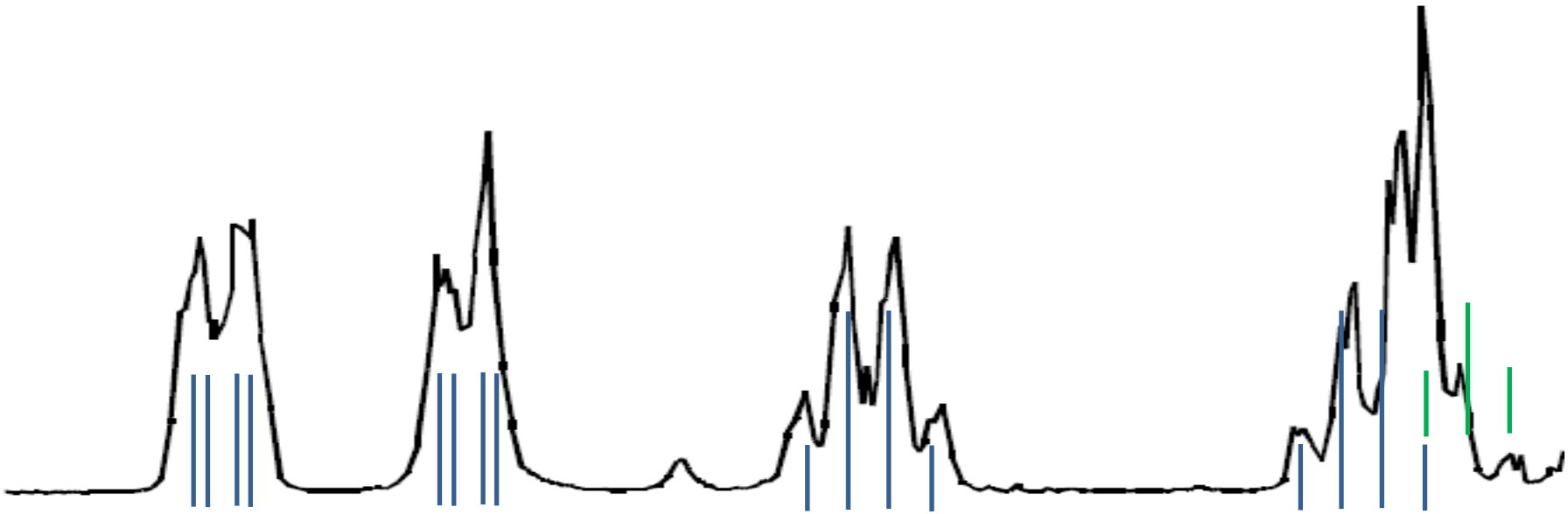
$J_4 = J_1/2$

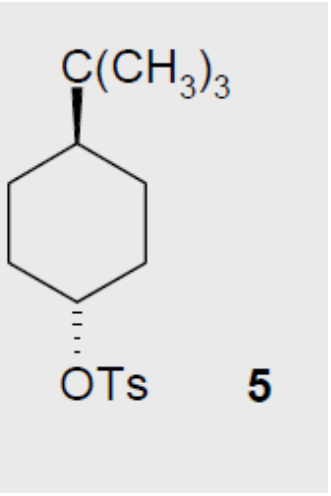
$J_5 << J_1/2$

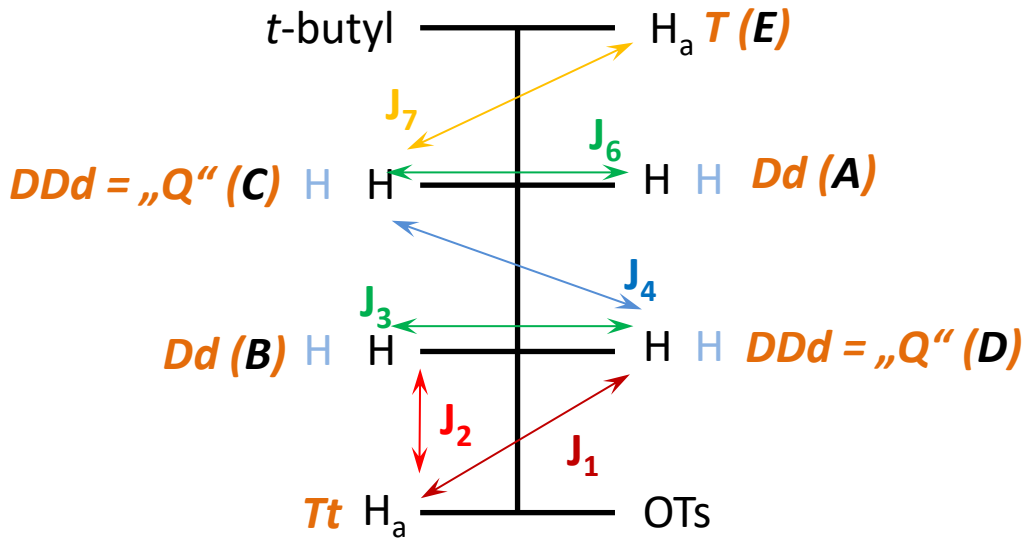
$^2J_{HH} \approx 11\text{-}13$ Hz

$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz







$J_2 < J_1/2$

$J_3 \approx J_1$

$J_4 = J_1/2$

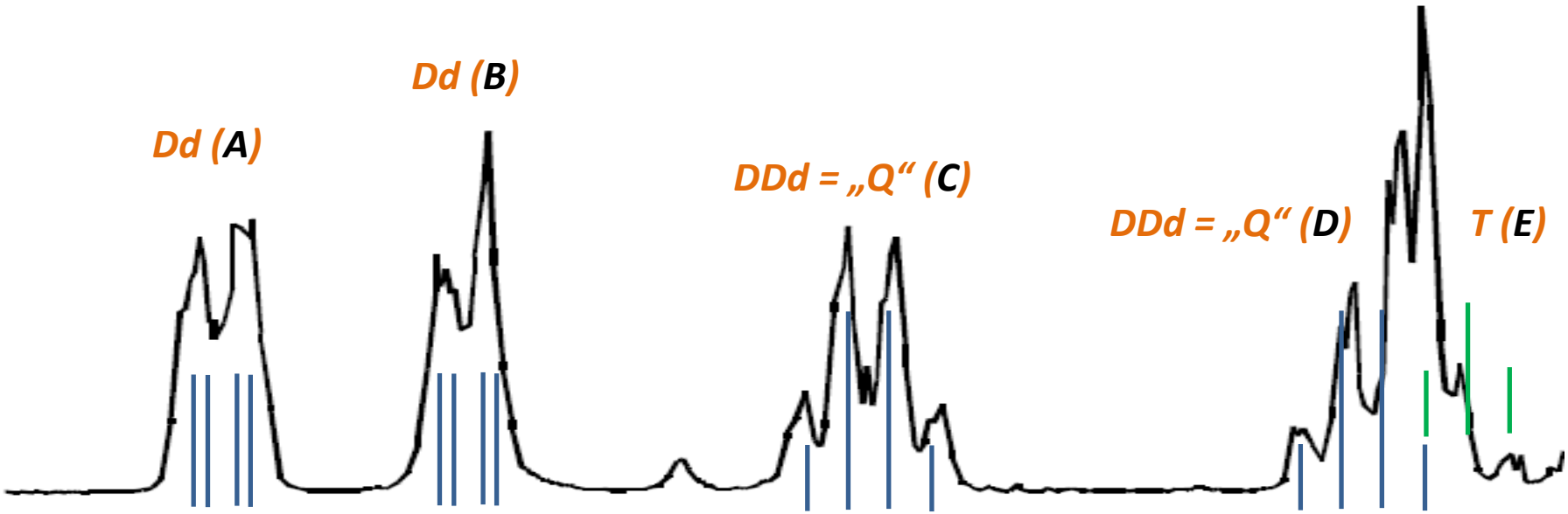
$J_6 \approx J_3$

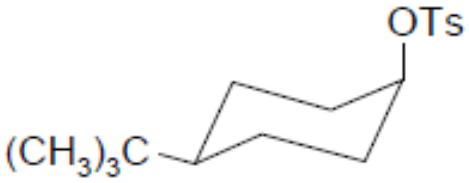
$J_7 \approx J_1$

$^2J_{HH} \approx 11\text{-}13$ Hz

$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz



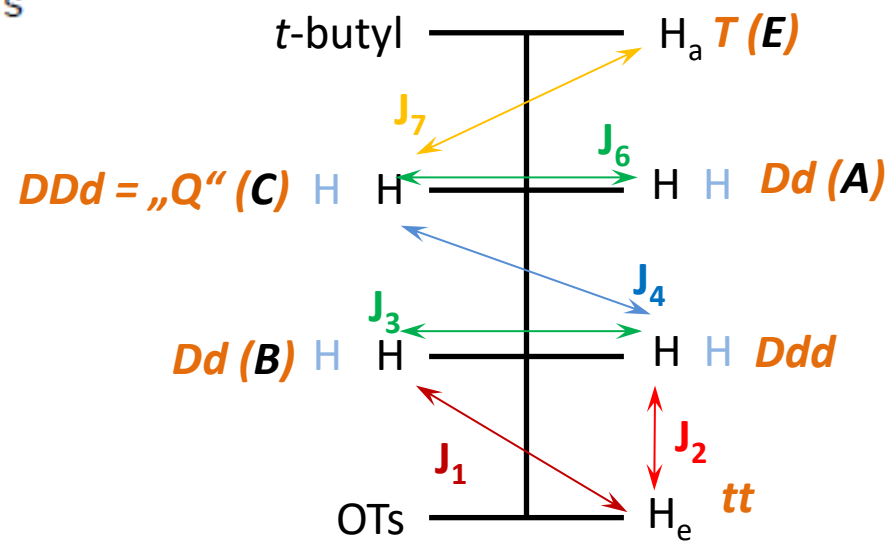


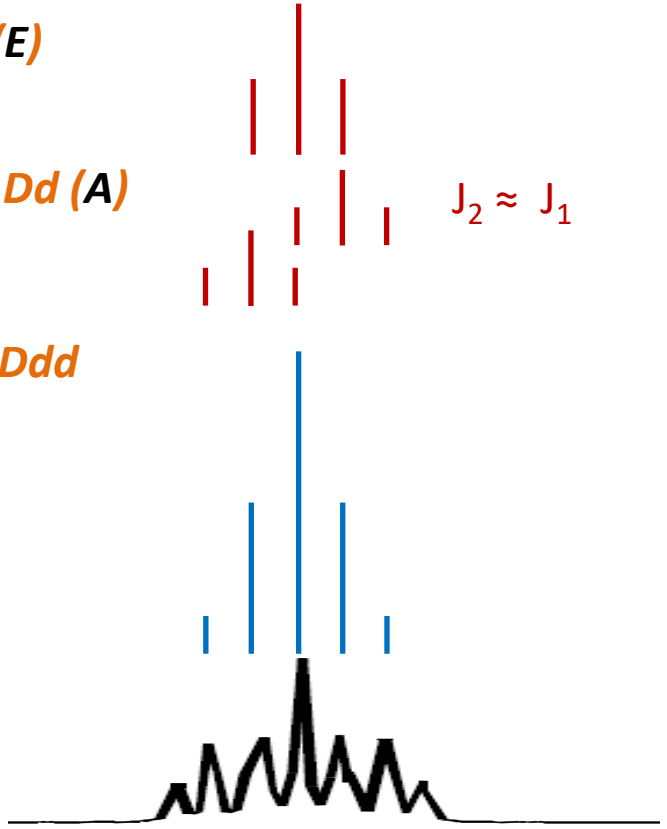
B

$^2J_{HH} \approx 11\text{-}13$ Hz

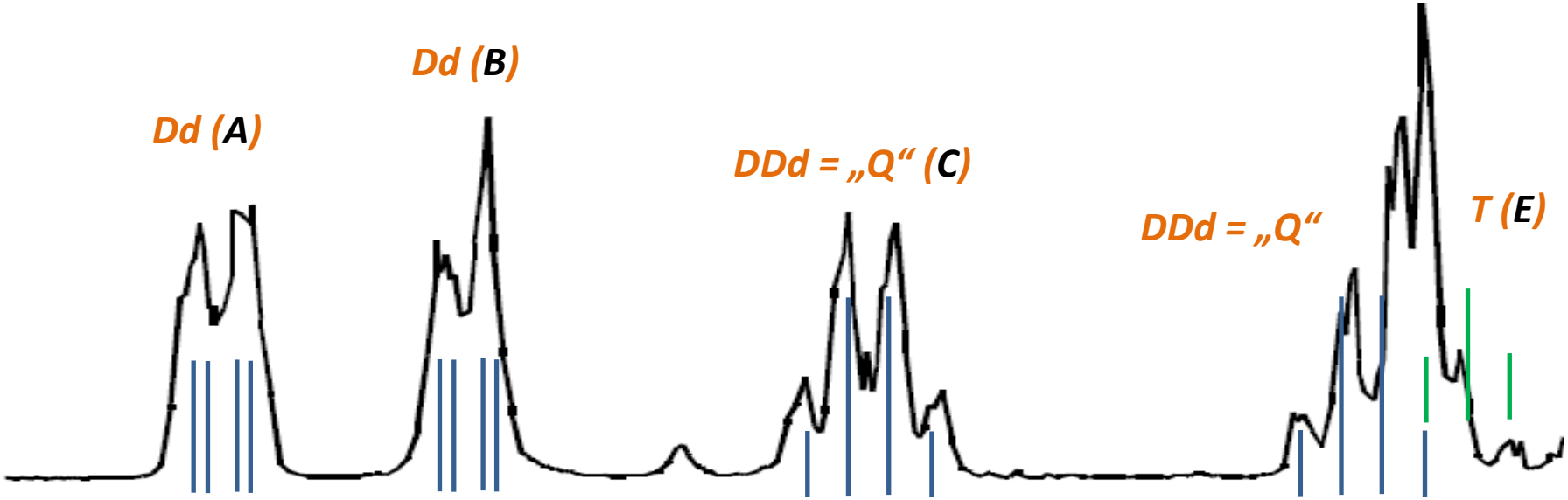
$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz

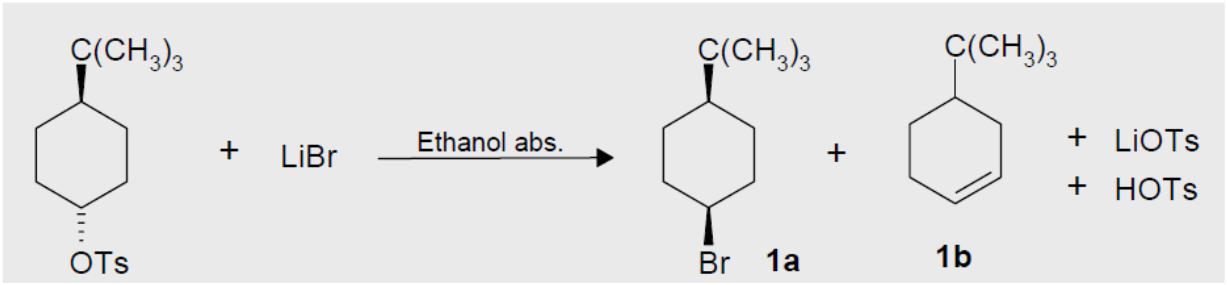




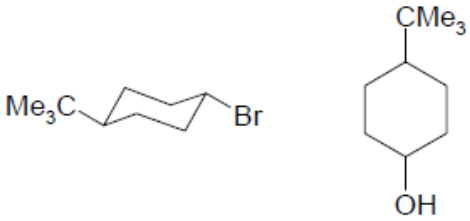
$$J_2 \approx J_1 ; J_3 \approx 3J_1 ; J_4 \approx J_1 ; J_6 \approx J_3 ; J_7 \approx 3J_1$$



1.4.1 Umsetzung von *trans*-4-*tert*-Butylcyclohexyltosylat mit Lithiumbromid zu *cis*-4-*tert*-Butylcyclohexylbromid (1a) und 4-*tert*-Butylcyclo-1-hexen (1b)



Weitere denkbare Reaktionsprodukte:



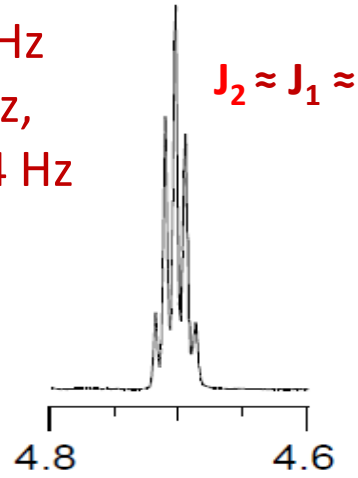
A B

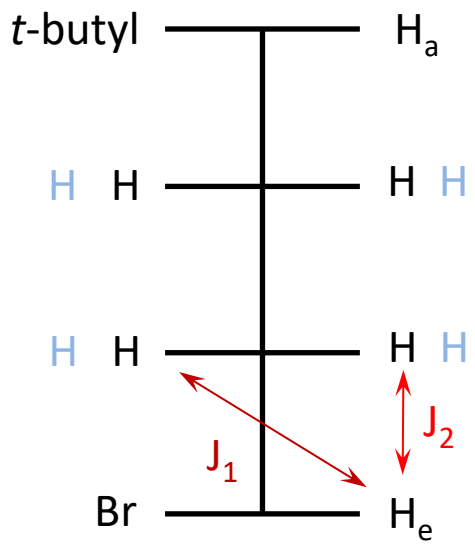
$^2J_{HH} \approx 11\text{-}13$ Hz

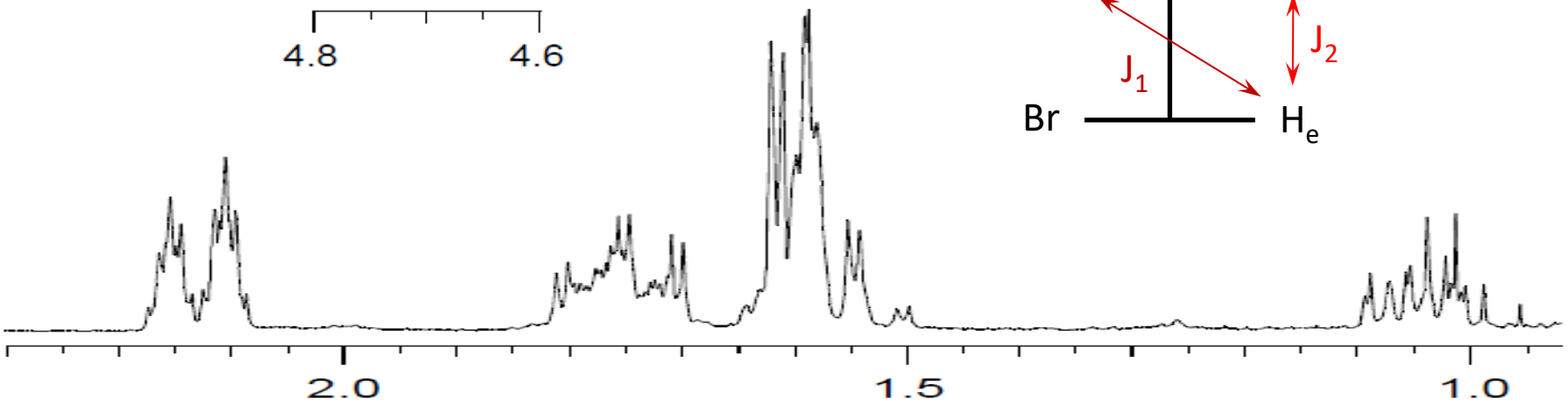
$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz

$J_2 \approx J_1 \approx 3$ Hz



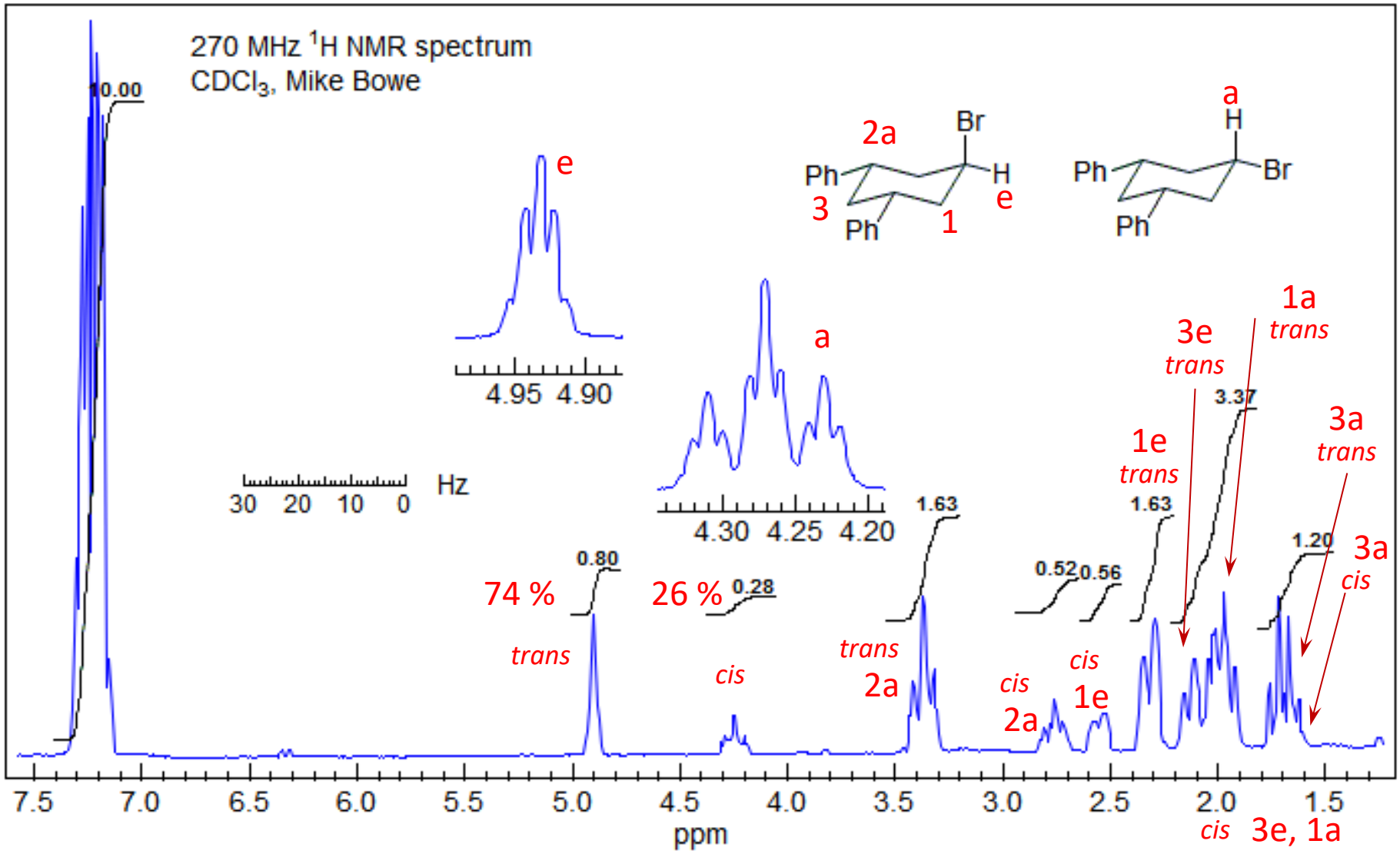




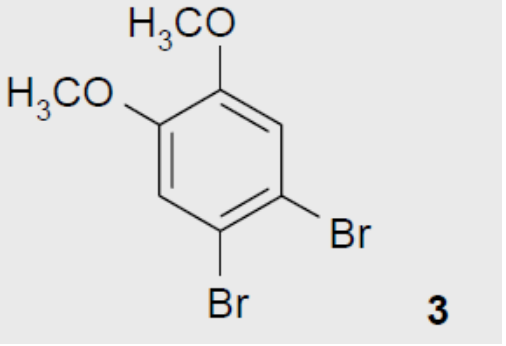
$^2J_{HH} \approx 11\text{-}13$ Hz

$^3J_{aa} \approx 9\text{-}13$ Hz,

$^3J_{ae} \approx {}^3J_{ee} \approx 3\text{-}4$ Hz



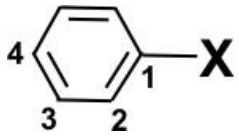
Isomerie



3

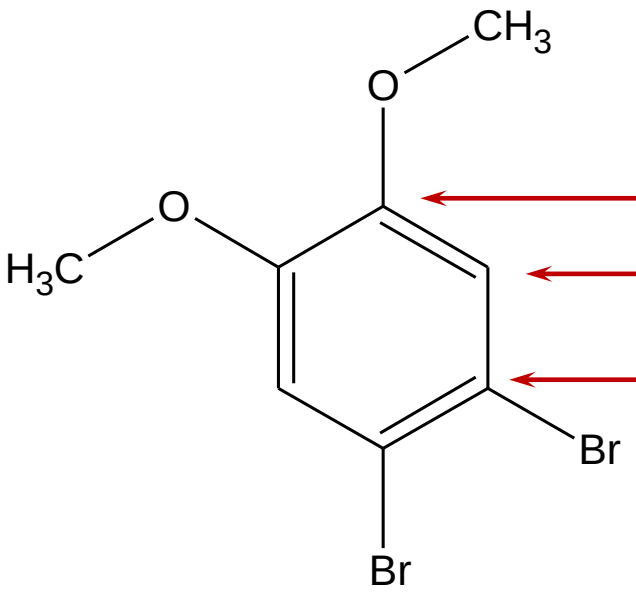
^{13}C-NMR Spektrum von **3** (62.9 MHz, $CDCl_3$):

δ = 56.33 (CH_3), 114.86 (C), 116.25 (CH), 149.09 (C).



$\delta_{C_i} = 128.5 + Z_i$

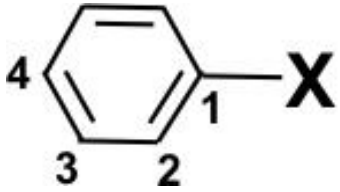
Substituent X		Z_1	Z_2	Z_3	Z_4
A	—Br	–5.4	3.3	2.2	–1.0
O	—OCH_3	30.2	–14.7	0.9	–8.1



30 – 15 + 2 – 1 = 16 (145 ppm)

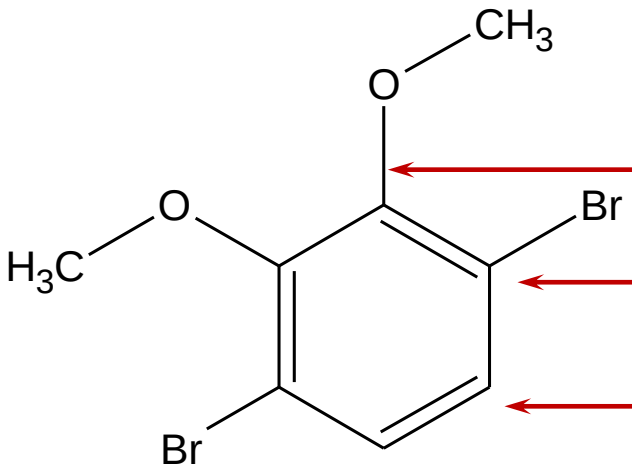
– 15 + 1 + 3 + 2 = - 9 (120 ppm)

1 – 8 - 5 + 3 = - 9 (120 ppm)



$$\delta_{C_i} = 128.5 + Z_i$$

Substituent X	Z_1	Z_2	Z_3	Z_4
A —Br	–5.4	3.3	2.2	–1.0
O —OCH_3	30.2	–14.7	0.9	–8.1

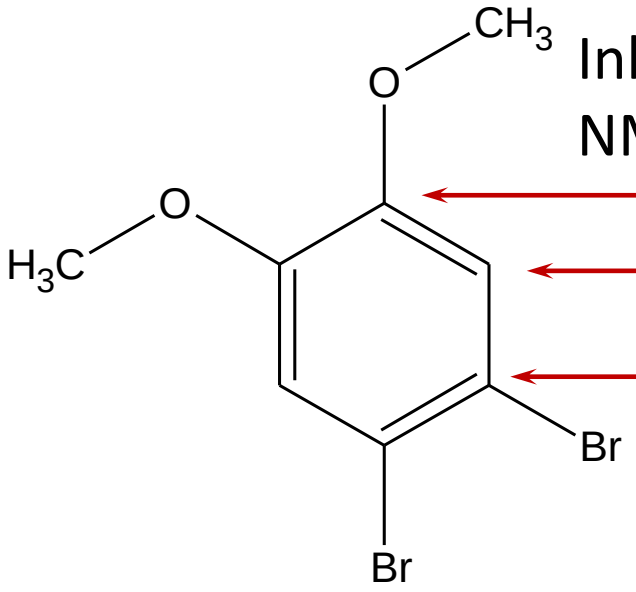


30 – 15 + 3 + 2 = 20 (149 ppm)

– 15 + 1 - 5 - 1 = - 20 (109 ppm)

1 – 8 + 3 + 2 = 12 (141 ppm)

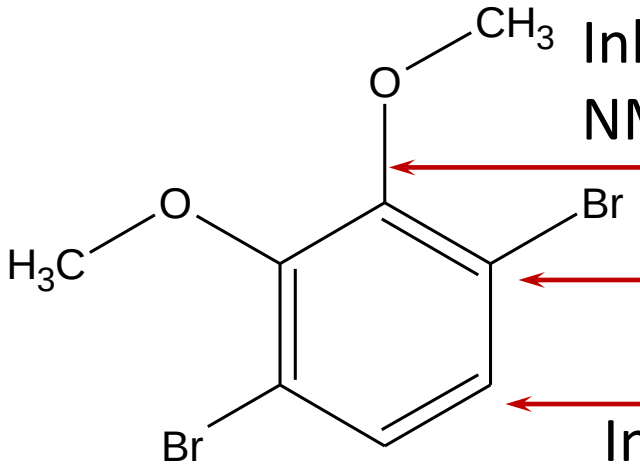
^{13}C-NMR Spektrum 114.86 (C), 116.25 (CH), 149.09 (C).



Inkrementsystem: 145 ppm
NMR-Prädiktor: 149 ppm

Inkrementsystem: 120 ppm
NMR-Prädiktor: 119 ppm

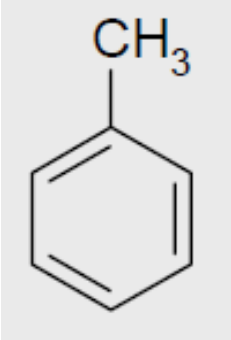
Inkrementsystem: 120 ppm
NMR-Prädiktor: 117 ppm



Inkrementsystem: 149 ppm
NMR-Prädiktor: 146 ppm

Inkrementsystem: 109 ppm
NMR-Prädiktor: 120 ppm

Inkrementsystem: 141 ppm
NMR-Prädiktor: 130 ppm

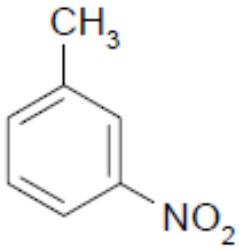


2.27 ppm

7.03 ppm

7.14 ppm

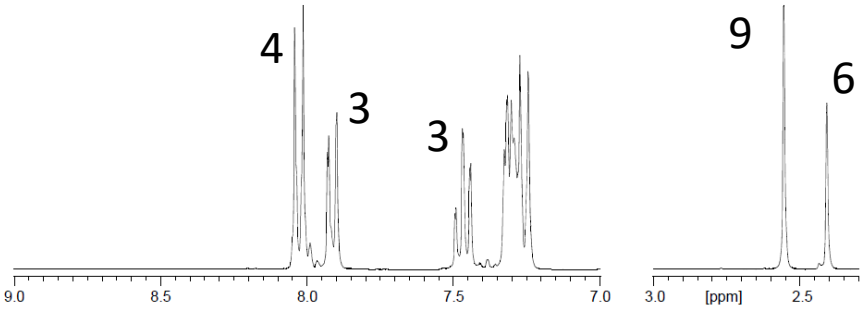
7.06 ppm



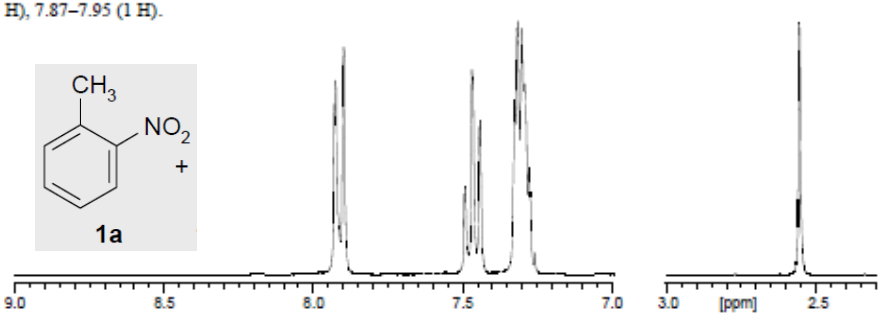
falsche Spektrum!

1a:1b = 3:2

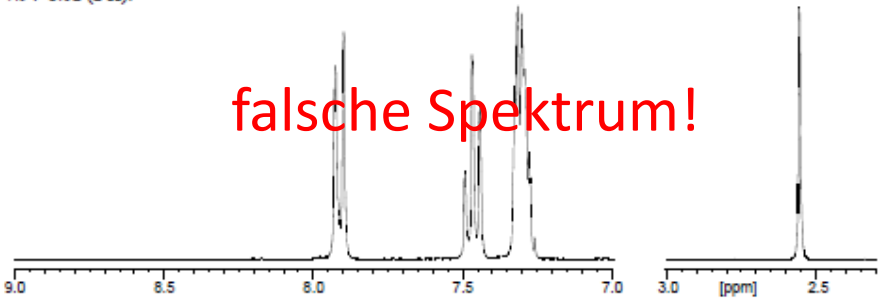
^{1}**H-NMR-Spektrum** des **Destillats** (300 MHz, $CDCl_3$): δ = 2.56 , 2.41, Integral ca. 3:2.



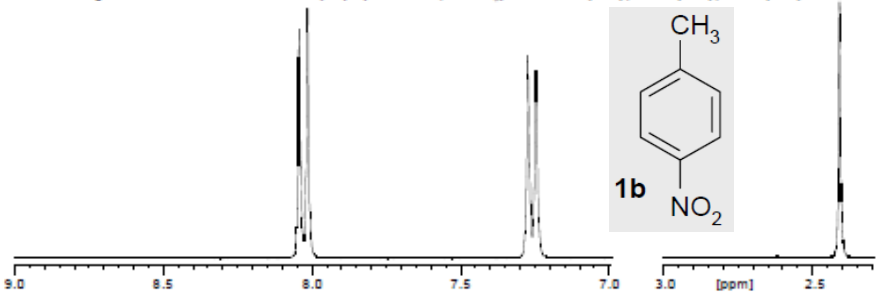
^{1}**H-NMR-Spektrum** von **2-Nitrotoluol (1a)** (300 MHz, $CDCl_3$): δ = 2.56 (3 H), 7.26–7.35 (2 H), 7.42–7.51 (1 H), 7.87–7.95 (1 H).



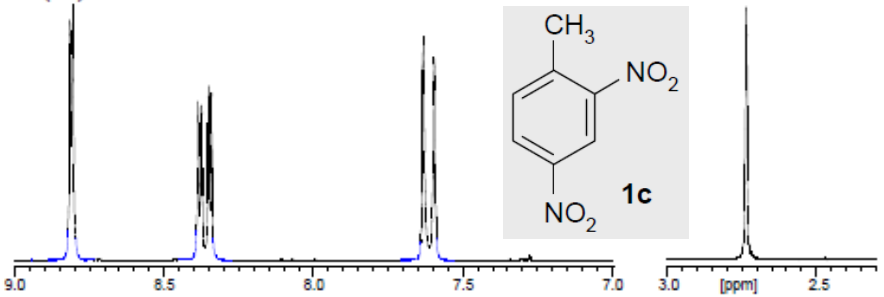
^{1}**H-NMR-Spektrum** von **3-Nitrotoluol** (300 MHz, $CDCl_3$): δ = 2.43 (3 H), 7.34–7.42 (1 H), 7.44–7.52 (1 H), 7.94–8.02 (2 H).



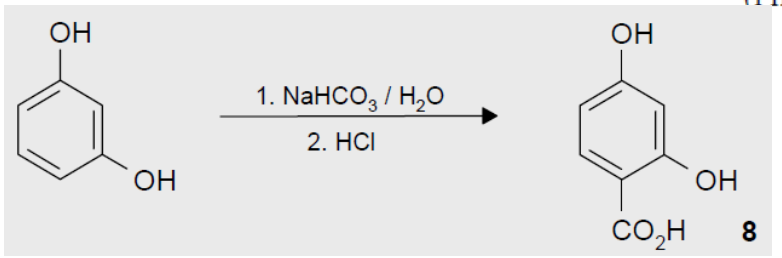
^{1}**H-NMR-Spektrum** von **4-Nitrotoluol (1b)**: (300 MHz, $CDCl_3$): δ = 2.41 (3 H), 7.26 (2 H), 8.03 (2 H).



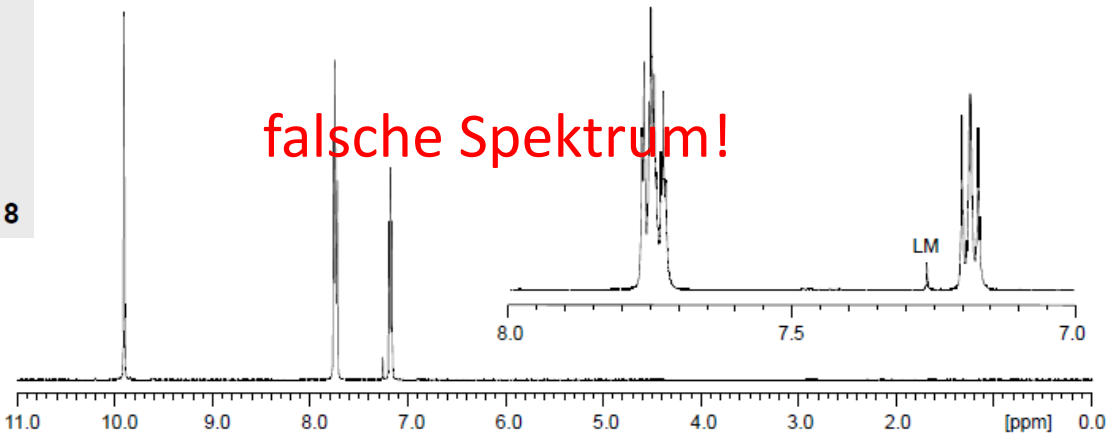
^{1}**H-NMR-Spektrum** von **2,4-Dinitrotroluol (1c)**: (300 MHz, $CDCl_3$): δ = 2.73 (3 H), 7.61 (1 H), 8.36 (1 H), 8.81 (1 H).



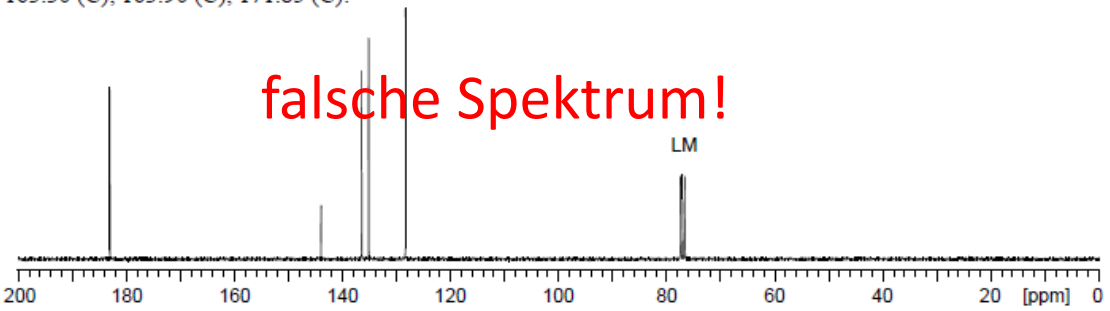
7.3.8 Carboxylierung von 1,3-Dihydroxybenzol (Resorcin) zu 2,4-Dihydroxybenzoesäure (8)

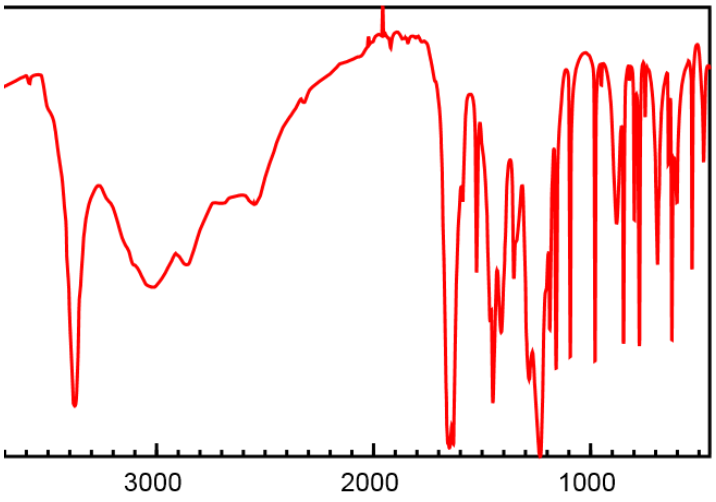


^{1}H-NMR-Spektrum von **8** (300 MHz, DMSO-d_6): δ = 6.27 (1 H), 6.34 (1 H), 6.62 (1 H), 10.37 (1 H), 11.45 (1 H), 13.25 (1 H).



^{13}C-NMR Spektrum von **8** (75.5 MHz, DMSO-d_6): δ = 102.14 (CH), 104.19 (C), 107.85 (CH), 131.81 (CH), 163.30 (C), 163.90 (C), 171.85 (C).





IR-Spektrum von **8** (KBr):