C8953
NMR structural analysis - seminar
Vector model & edited ^{13}C NMR spectra

Jan Novotný
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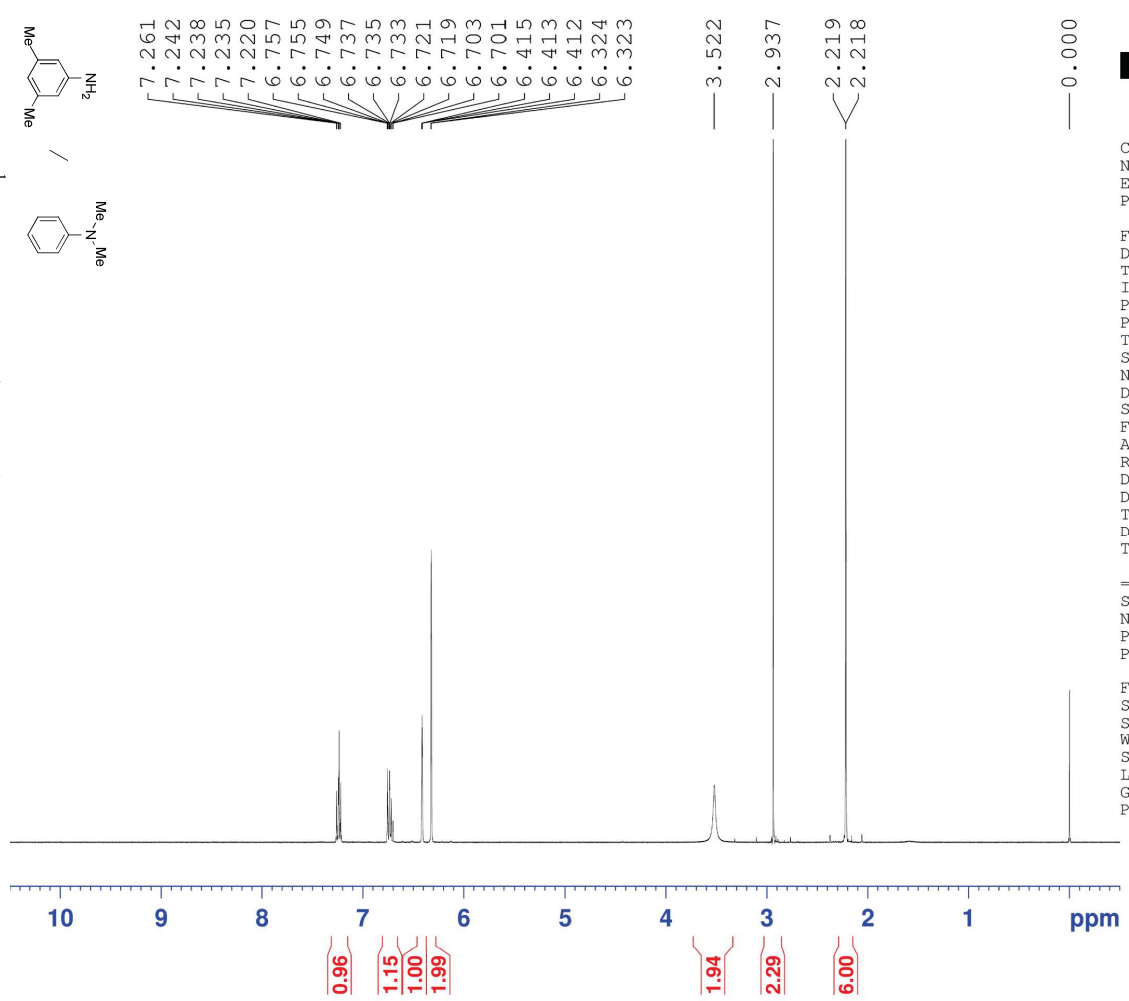
March 8, 2023

Determine percentage of dominant regioisomer in attached ^{1}H spectrum:



Spectrum S-23: ^{1}H NMR spectrum from Table 3.

BRUKER

```
Current Data Parameters
NAME         DALO-V-108R
EXPNO                  1
PROCNO                 1

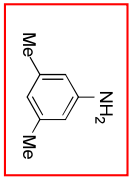
F2 - Acquisition Parameters
Date_           20131026
Time               13.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     1
DS                     0
SWH             5597.015 Hz
FIDRES          0.085404 Hz
AQ              5.8545995 sec
RG                 87.49
DW                89.333 usec
DE                 6.50 usec
TE                298.1 K
D1           30.00000000 sec
TD0                    1

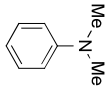
======== CHANNEL f1 ========
SFO1         400.2224013 MHz
NUC1                   1H
P1                 16.00 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.2200196 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

Determine percentage of dominant regioisomer in attached ^{1}H spectrum:

72%





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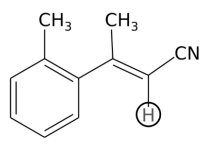
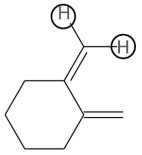
```

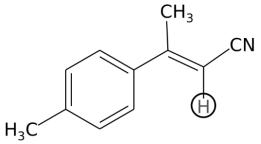
Assign correct value of chemical shift to labelled NMR active atoms[1]:

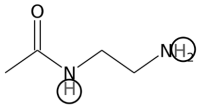


5.22 5.46

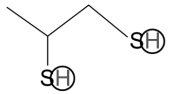


4.64 4.92

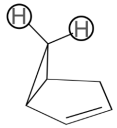




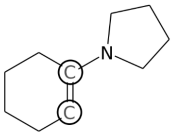
1.5 7.0



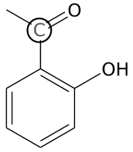
1.65(t) 1.85(d)

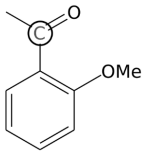


-0.17 0.73



93 142





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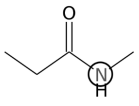

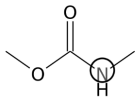

[1] http://www.chem.wisc.edu/areas/reich/chem605/

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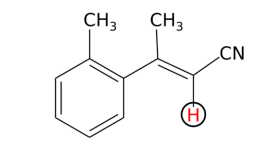

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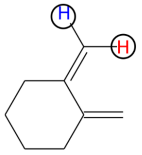

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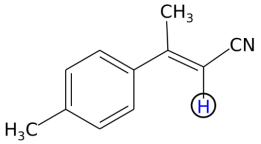

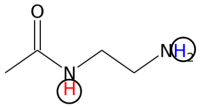

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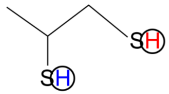

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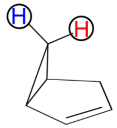

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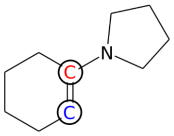

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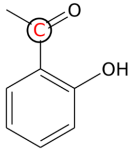

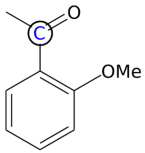

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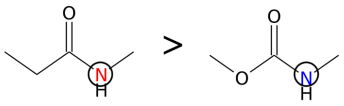
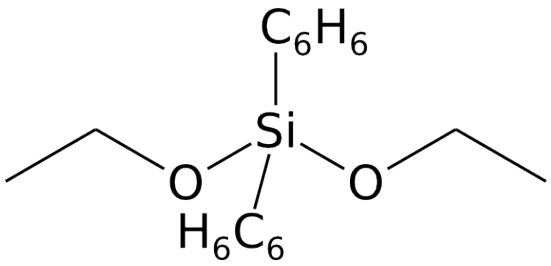
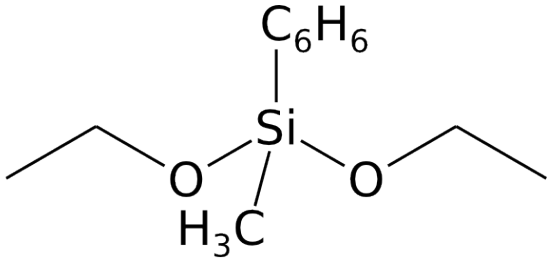
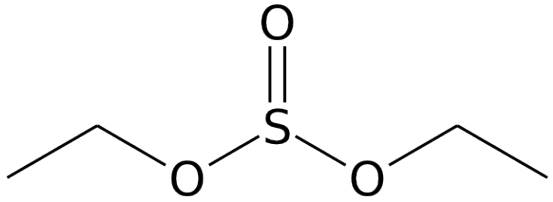


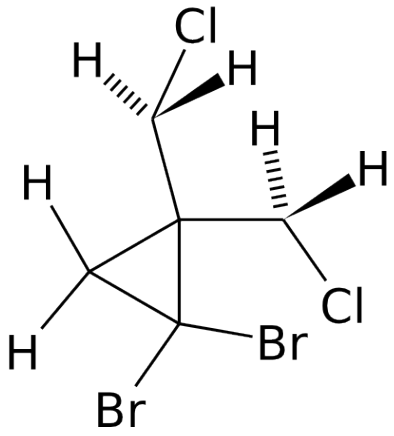
[1] http://www.chem.wisc.edu/areas/reich/chem605/

Diastereotopicity[1] Determine the equivalency of geminal protons









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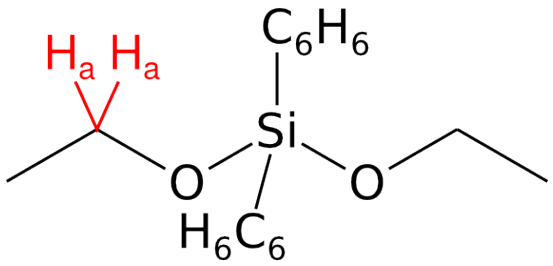

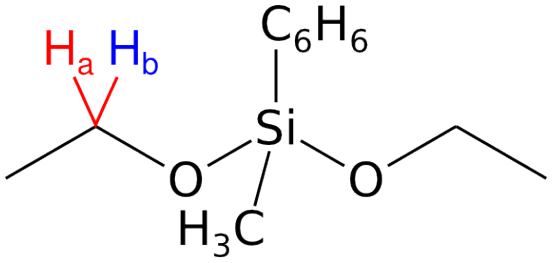

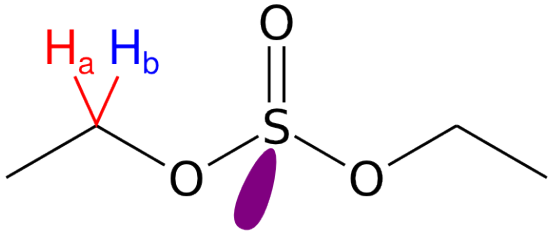

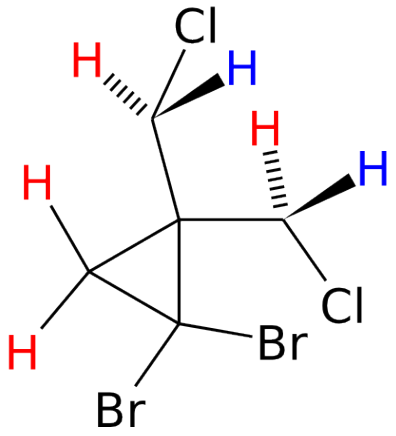

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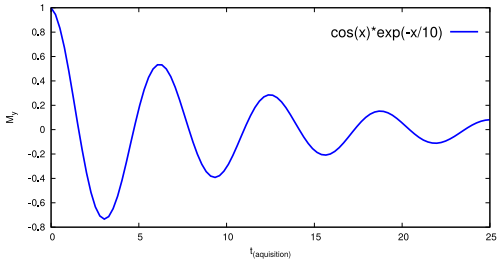
Values of chemical shift of important solvents

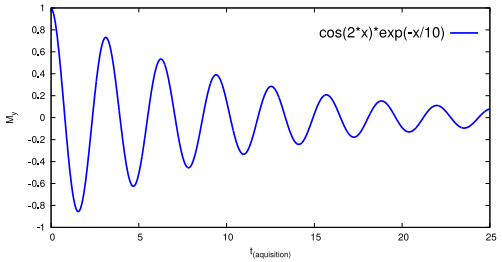
Abbr.	Formula	^{1}H	^{13}C
ACN	CH_3CN	1.9	118
Benzene	C_6H_6	7.2	128
	$CHCl_3$	7.2	77
DCM	CH_2Cl_2	5.3	54
DMF	$(CH_3)_2NCHO$	2.9, 8.0	32, 163
DMSO	$(CH_3)_2SO$	2.5	40
MeOH	CH_3OH	3.3, 4.8	49
Water	H_2O	**4.8**	-

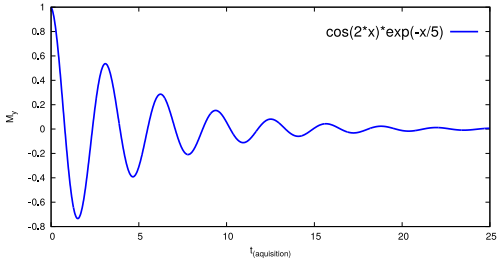
EXPLAIN effect of solvent on the position of residual ^{1}H water signal:

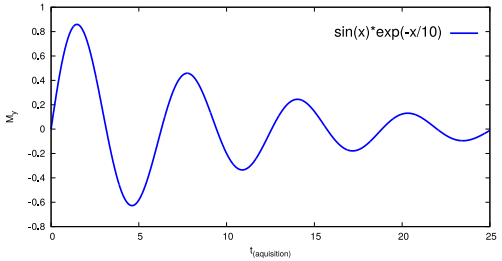
$CHCl_3$ - **1.6**, ACN - **2.1**, DMSO - **3.3**, MeOH - **4.9**

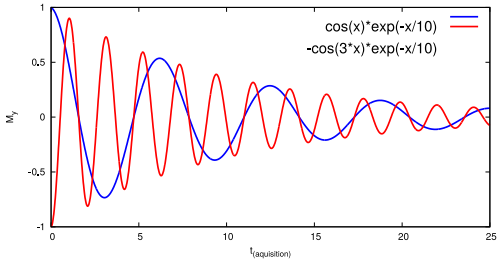
Processing simulated NMR signal:











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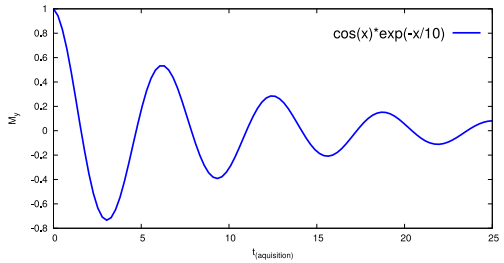
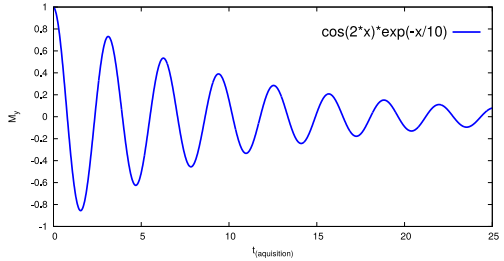
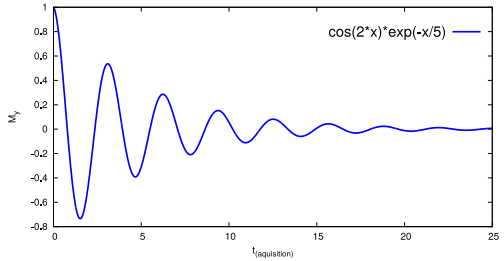
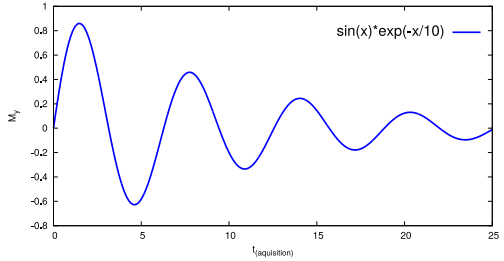
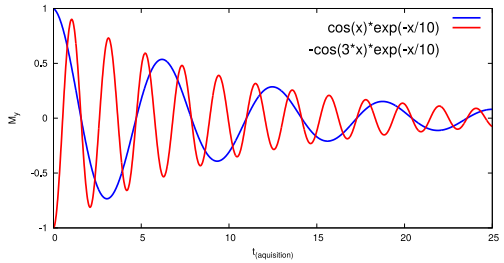
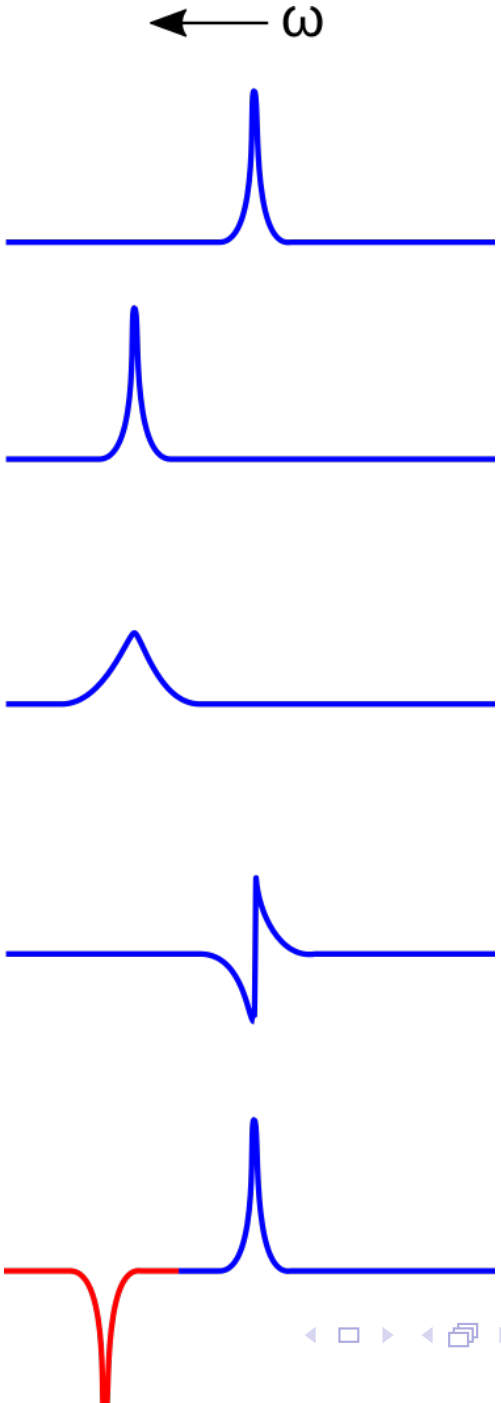






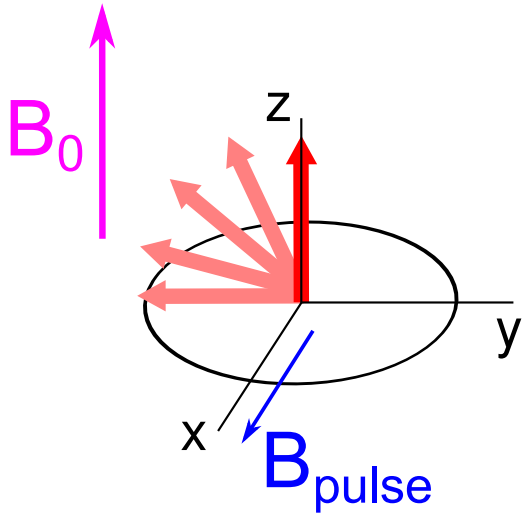






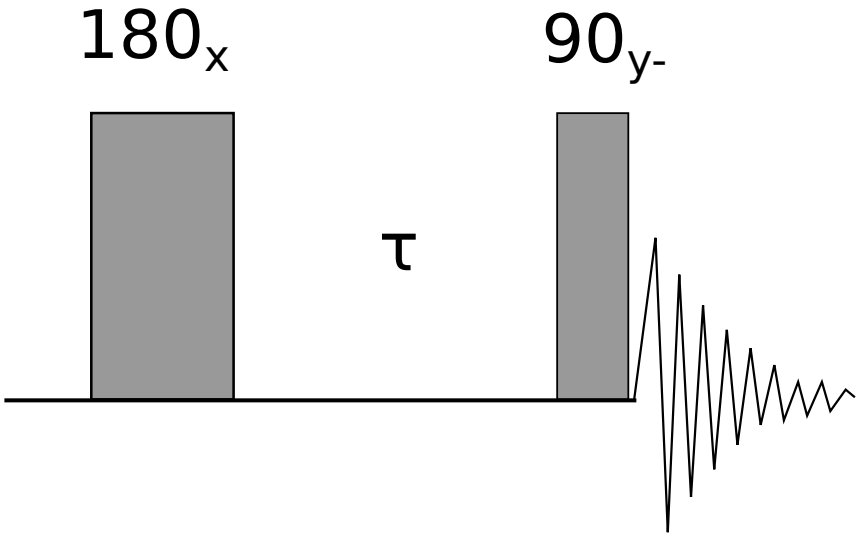
Analysis of simple pulse sequences using vector model

- simple model based on rotation of the vector of bulk magnetization in the plane perpendicular to the vector of magnetic field, direction is determined by the "right-hand rule"
- NMR signal is detectable only as coherent magnetization oscillating in *xy* plane
- the free precession ω (due to the B_0) of magnetization vector is eliminated by introducing rotating frame $\omega_0 \Rightarrow$ magnetic field of excitation pulses (B_1) is motionless and the individual resonance frequencies differs in so called offset $\Omega_i = \omega_i - \omega_0$
- applicability of vector model is rather limited to simple single-quantum experiments without transfer of polarisation



T_1 relaxation

Apply following sequence (inversion recovery) to isolated spin characterized by **a)** $\tau = 2 * T_1$ and **b)** $\tau = 0.2 * T_1$. Draw semi-quantitatively resulting spectrum.



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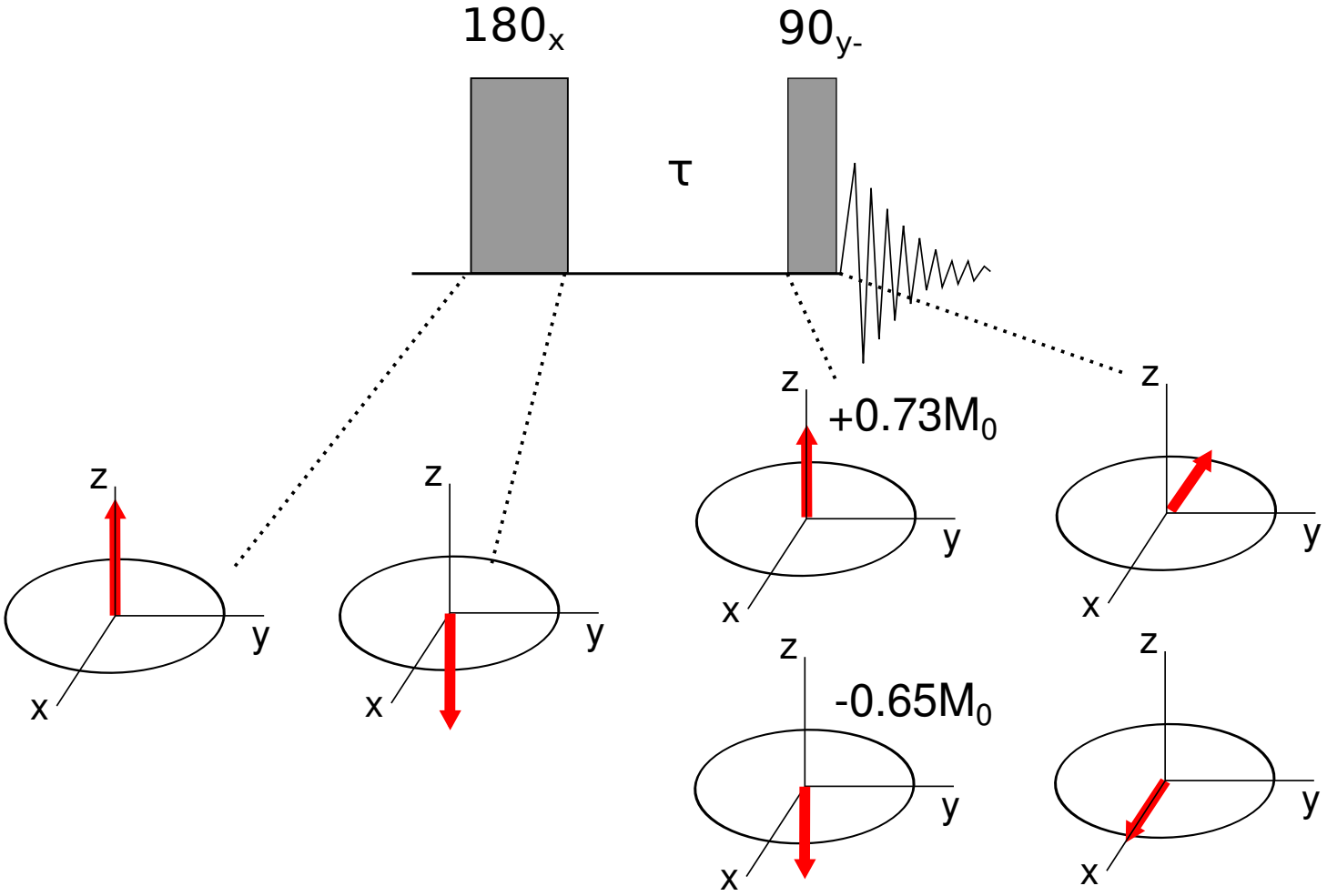
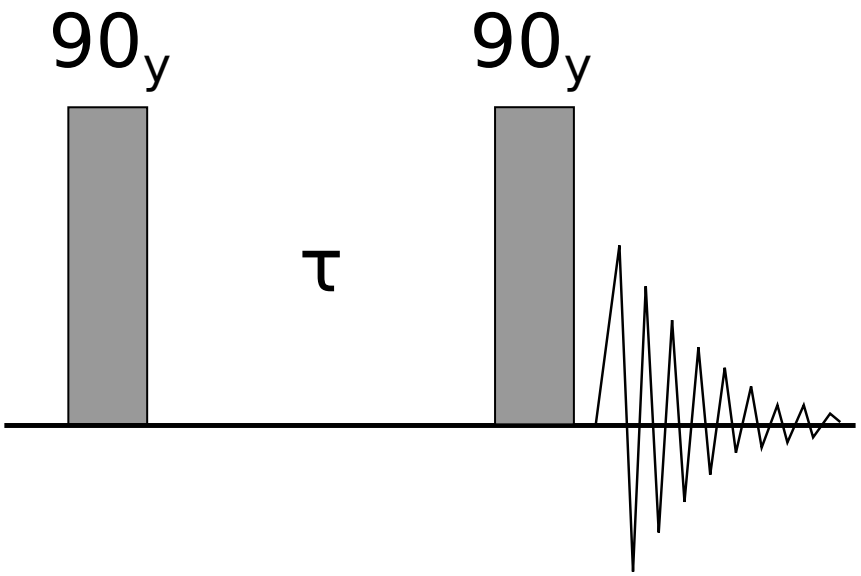


1-$\bar{1}$ sequence

Draw the evolution of macroscopic magnetization through the sequence:
90(y) - τ - 90(y) - aq
Consider the evolution of an isolated spin due to the chemical shift.

1. How does the result differ for the following offsets: $\Omega\tau = 0, \pi/2, \pi$.
2. Draw lineshapes of resulting signal assuming the a) $y+$ b) $x+$ corresponds to zero phase of receiver (prior phase correction).



1-$\bar{1}$ sequence

Draw the evolution of macroscopic magnetization through the sequence:
90(y) - τ - 90(y) - aq
Consider the evolution of an isolated spin due to the chemical shift.

1. How does the result differ for the following offsets: $\Omega\tau = 0, \pi/2, \pi$.
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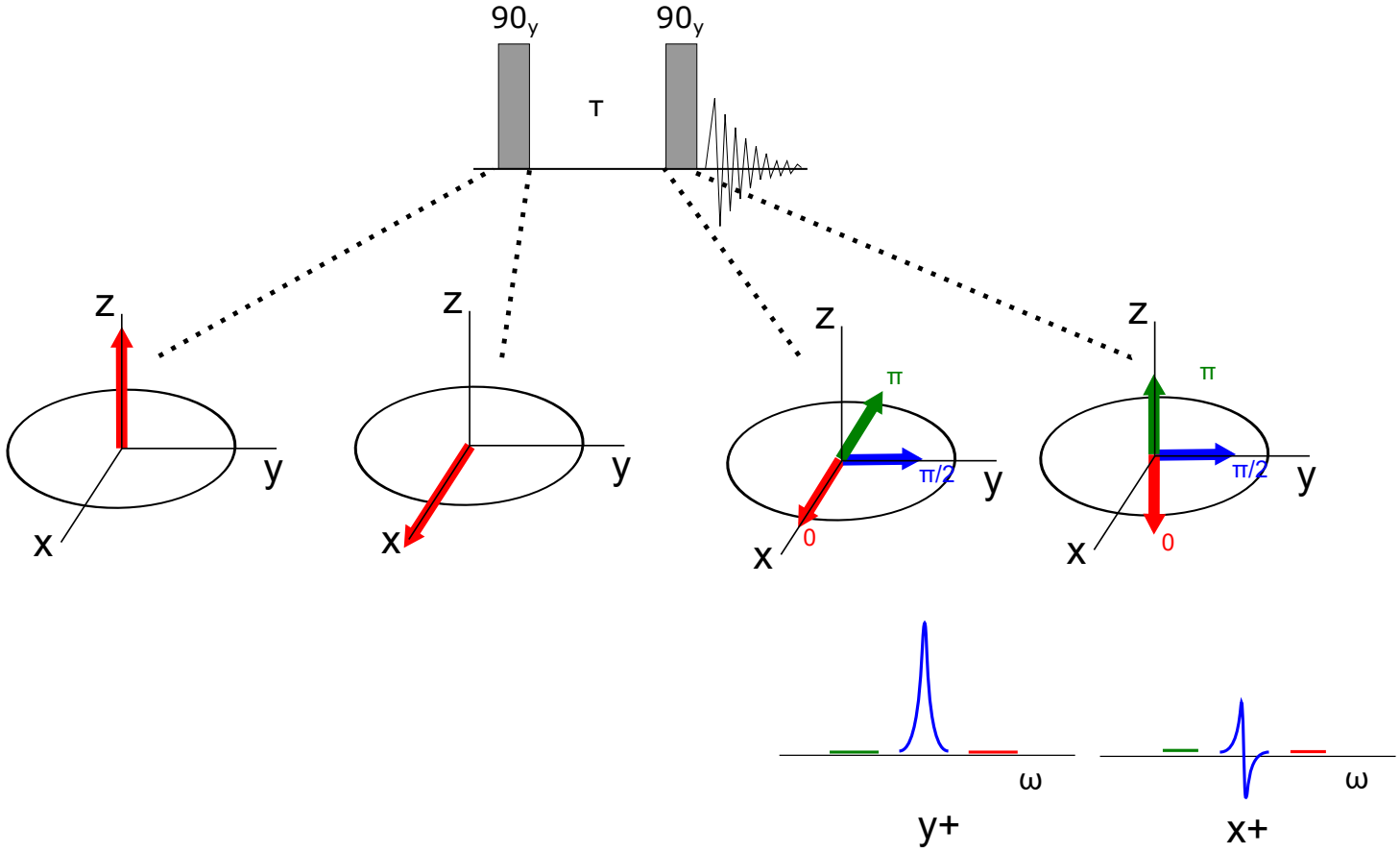
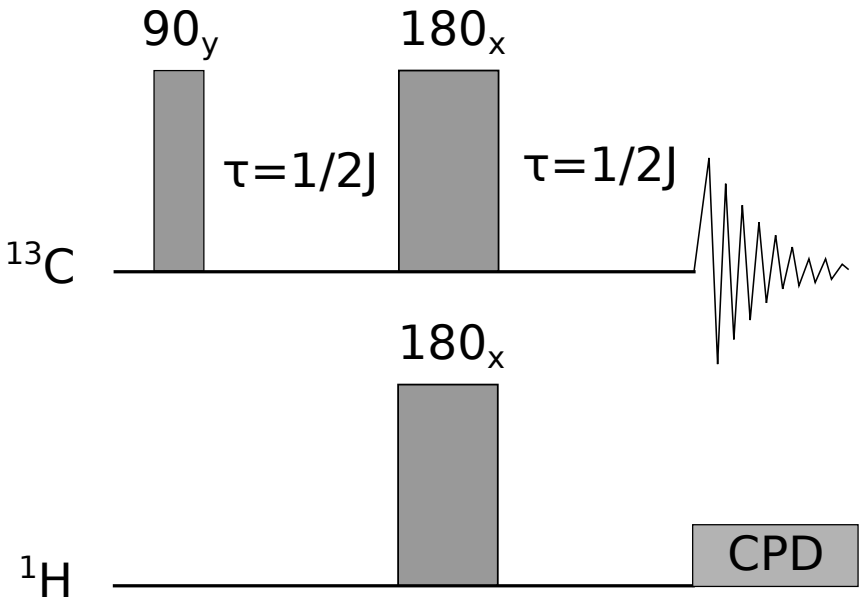


Heteronuclear spin echo

By using vector diagrams determine the result of attached pulse sequence.

1. **Ignore 180 pulse** in hydrogen channel for isolated spin systems **a)** ^{13}C-^{1}H and **b)** ^{13}C-$^{1}H_2$. Explain the role of CPD block.
2. Lets consider **the complete sequence** and isolated spin systems **a)** ^{13}C-^{1}H and **b)** ^{13}C-$^{1}H_2$.



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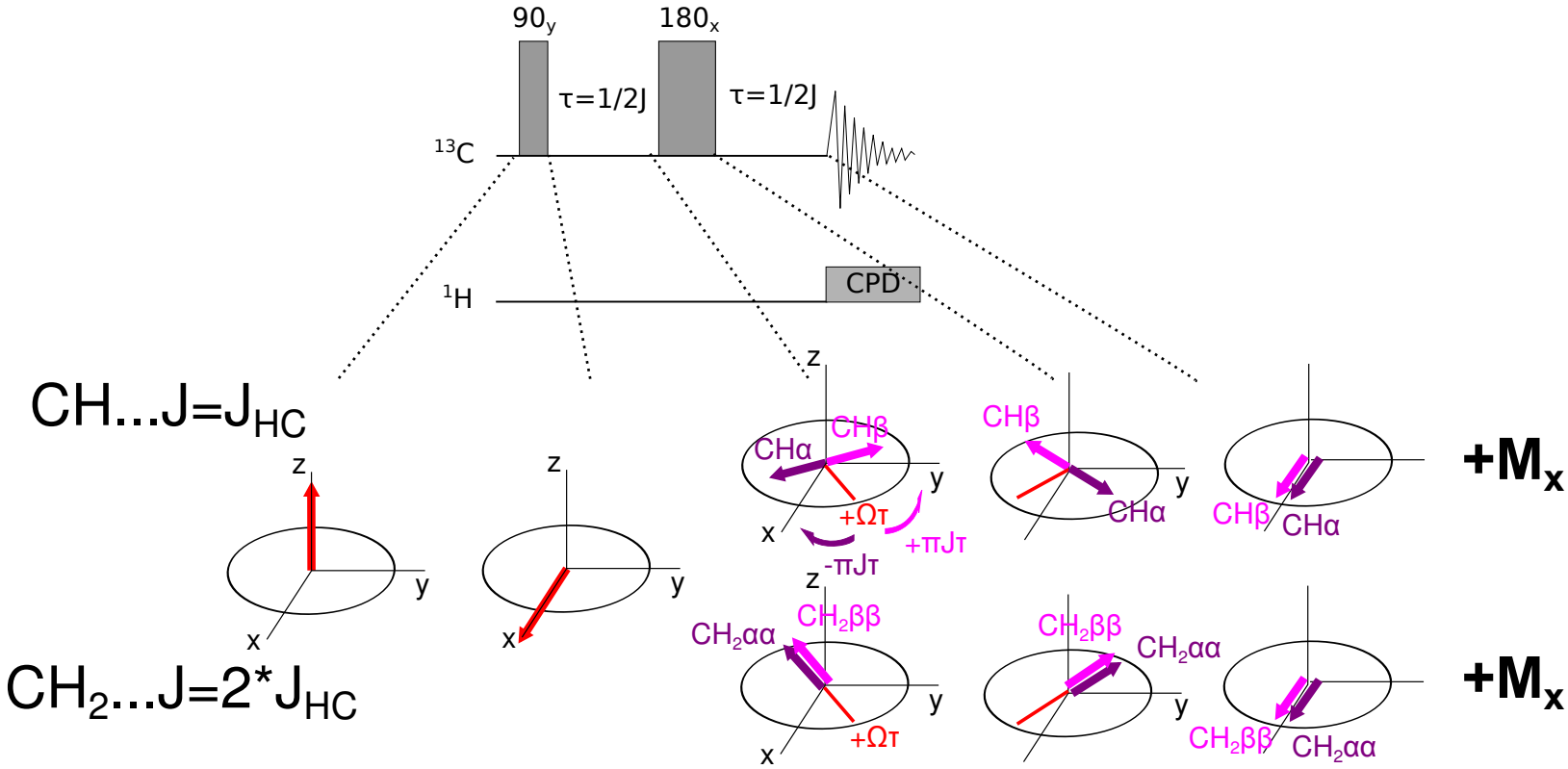

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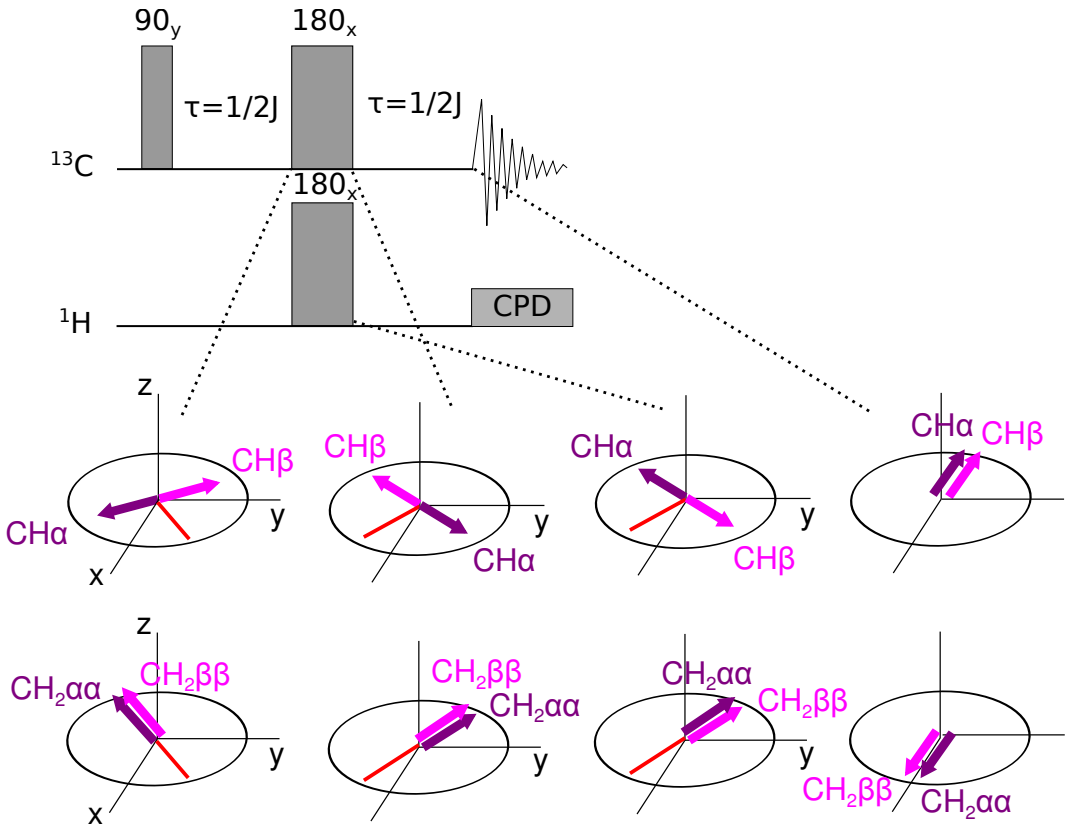


$CH...J=J_{HC}$

$CH_2...J=2*J_{HC}$

APT - Attached Proton Test

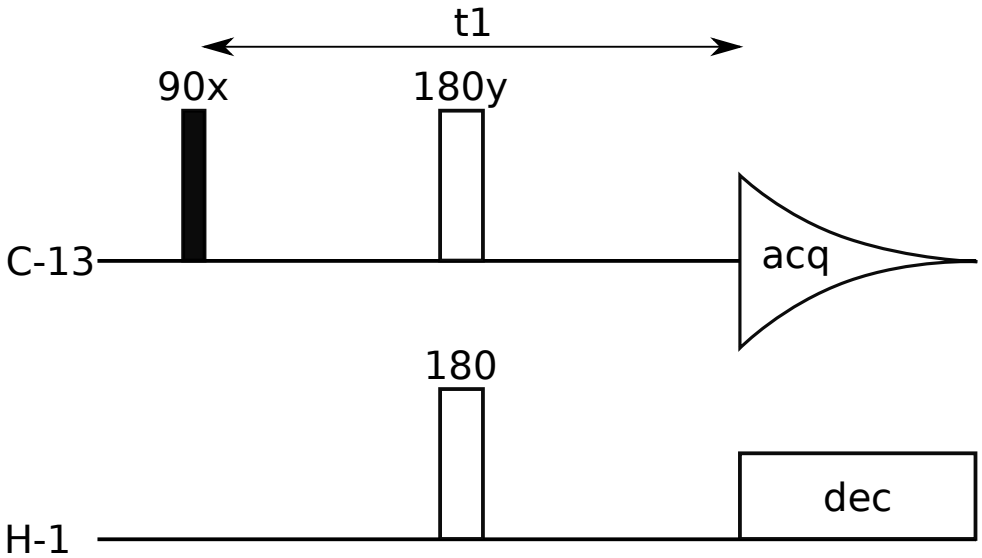
based on heteronuclear spin-echo

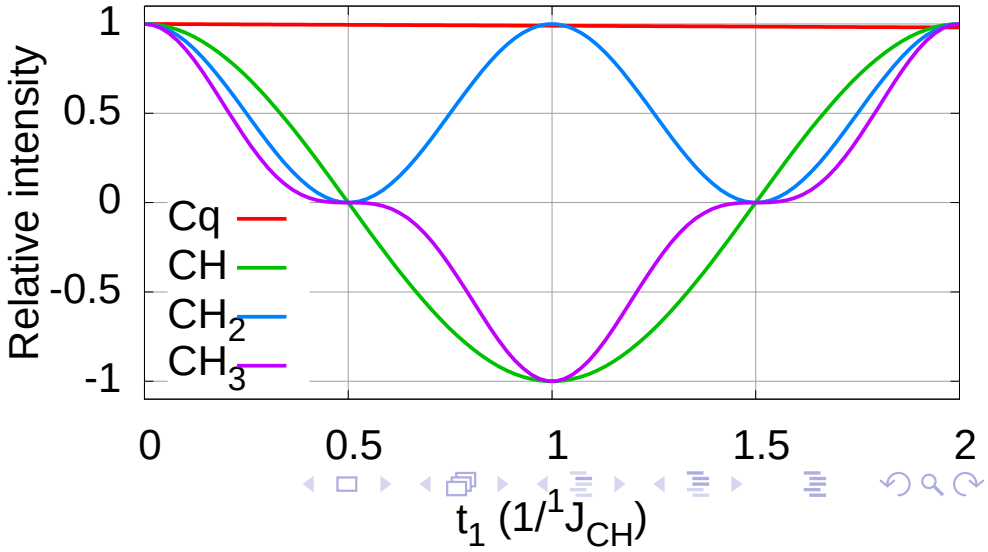
- $t_1 = 1/{}^1J_{CH}$

phase of ^{13}C signals resolved according to number of attached ^1H

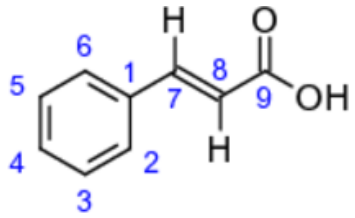
- Cq, CH_2 positive
- CH, CH_3 negative

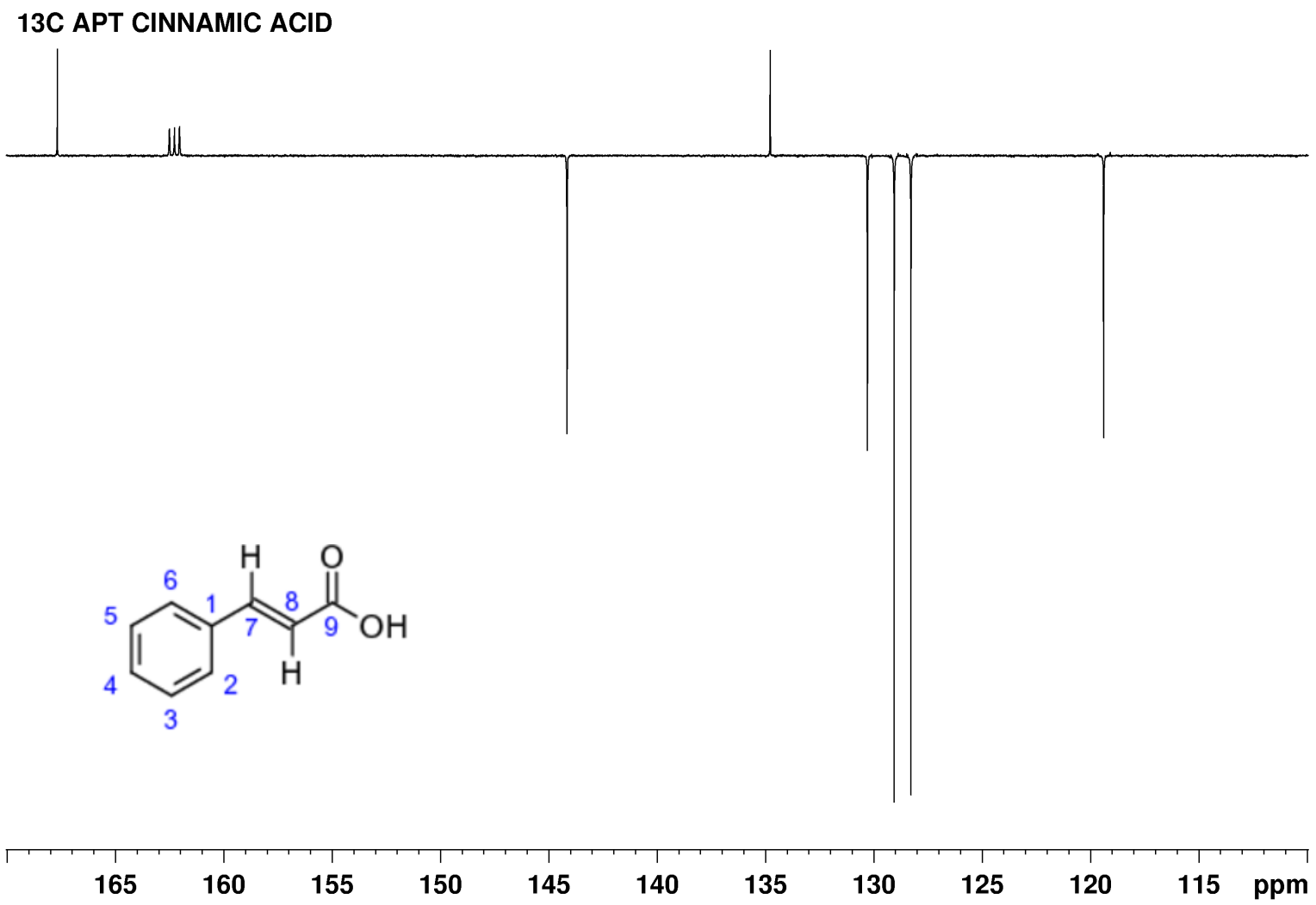
Different $^1J_{CH} \Longrightarrow$ different intensities





^{13}C APT Cinnamic acid





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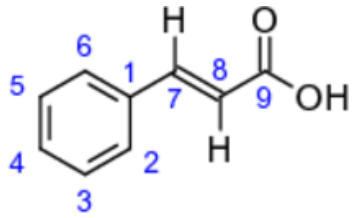
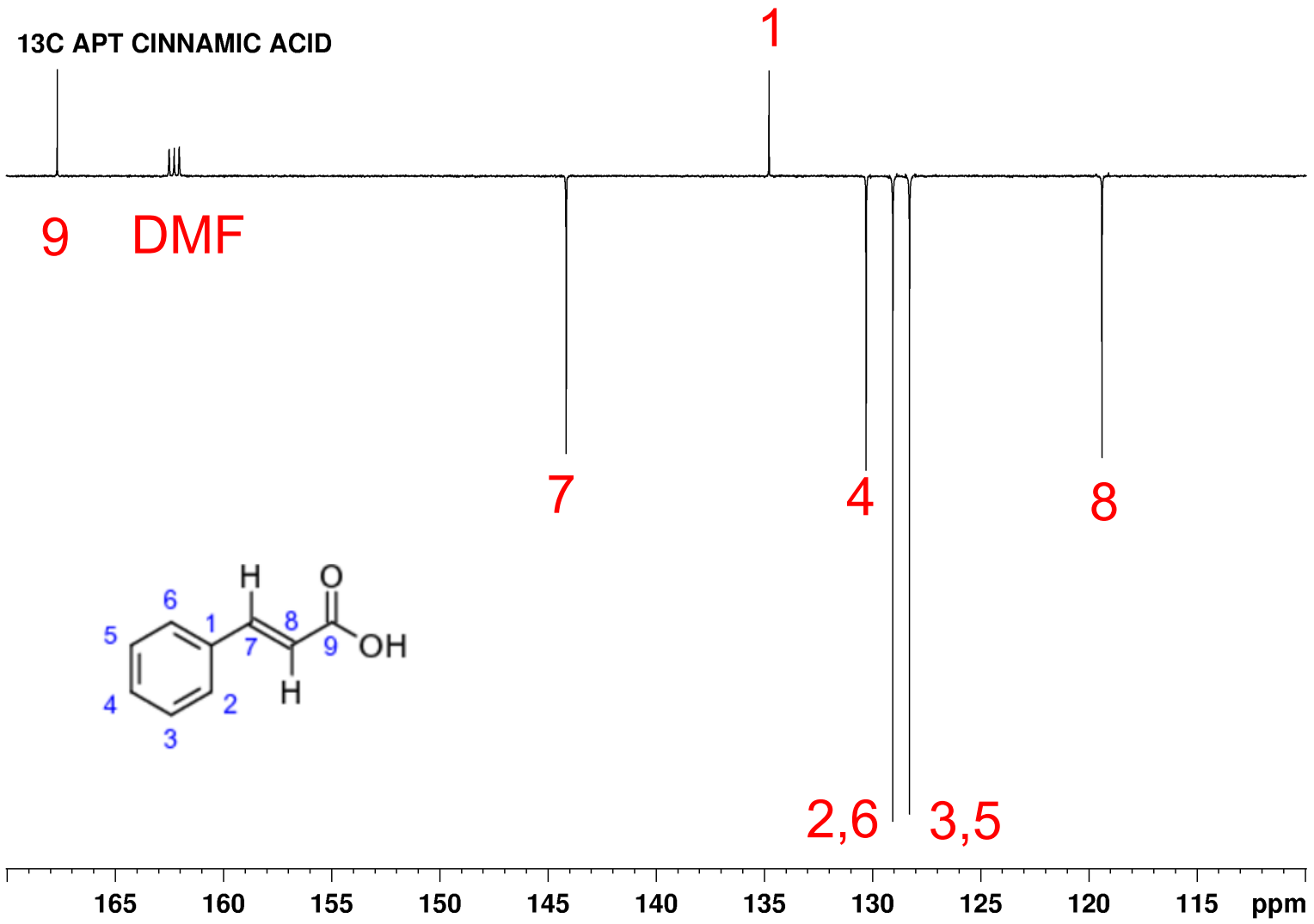
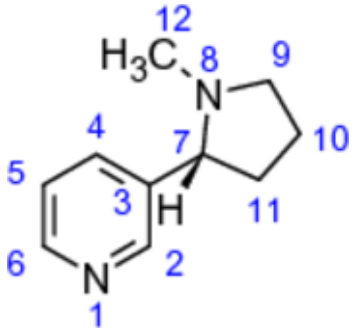
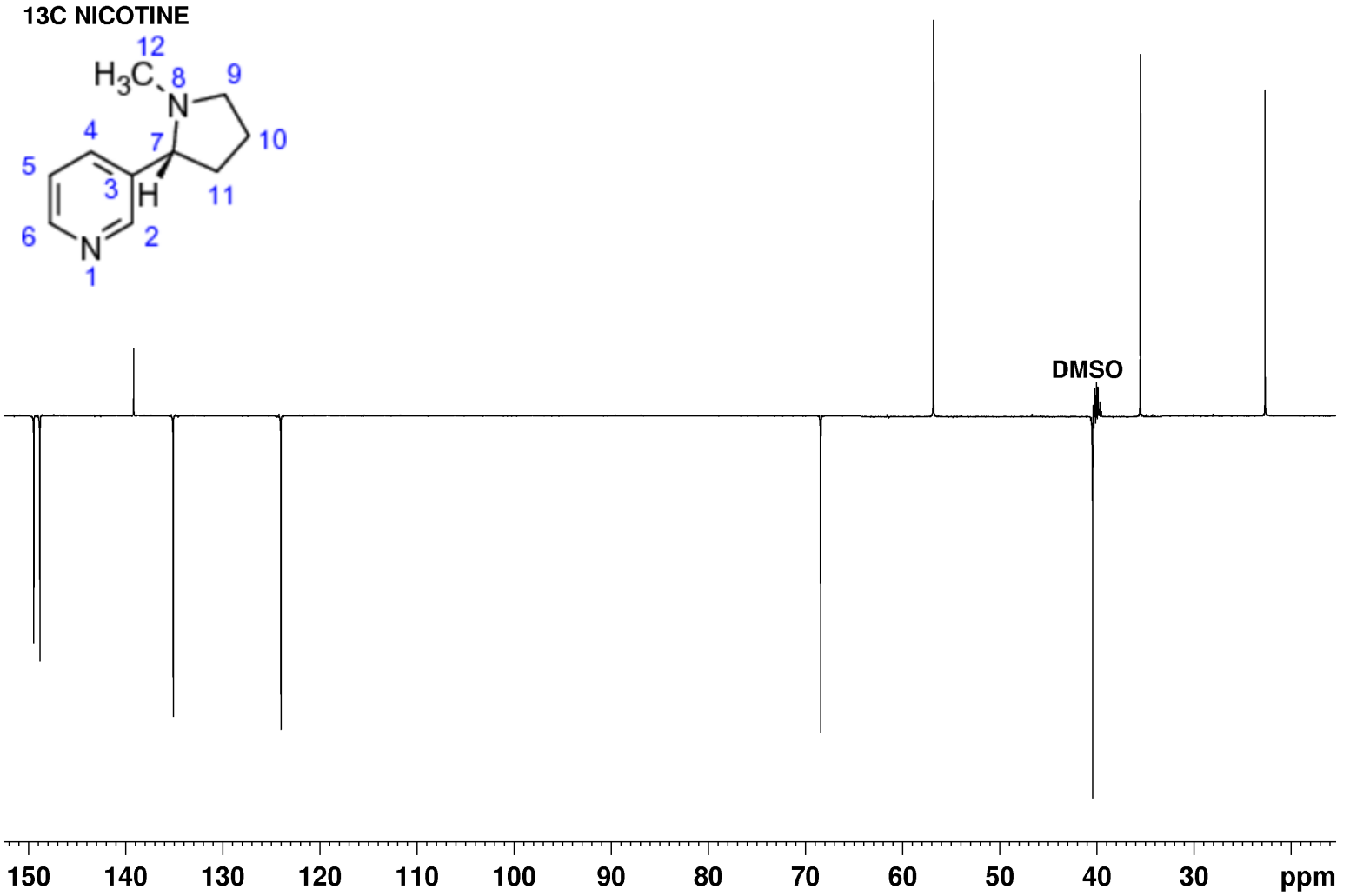




^{13}C APT Nicotine





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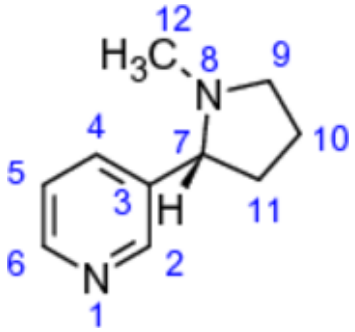
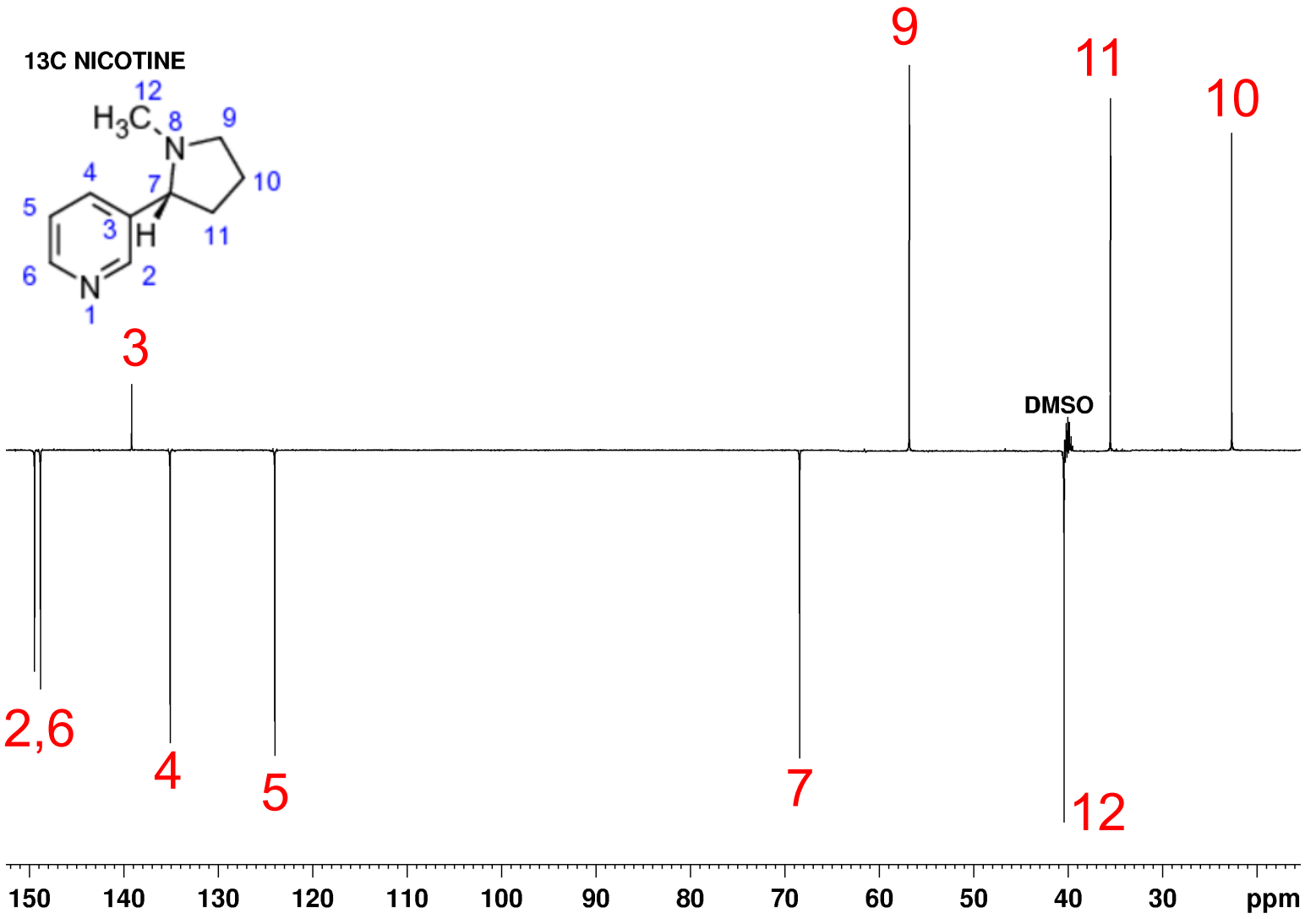
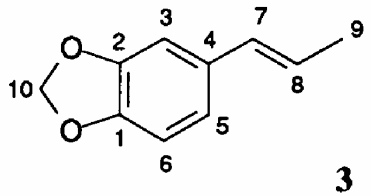




DEPT experiment



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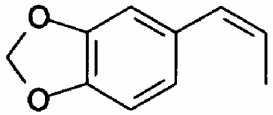


4

Which is the major product? Assign the signals as far as possible. Why does the signal at $\delta = 100.8$ exist in the spectrum 3.3.c, although its intensity should be zero?

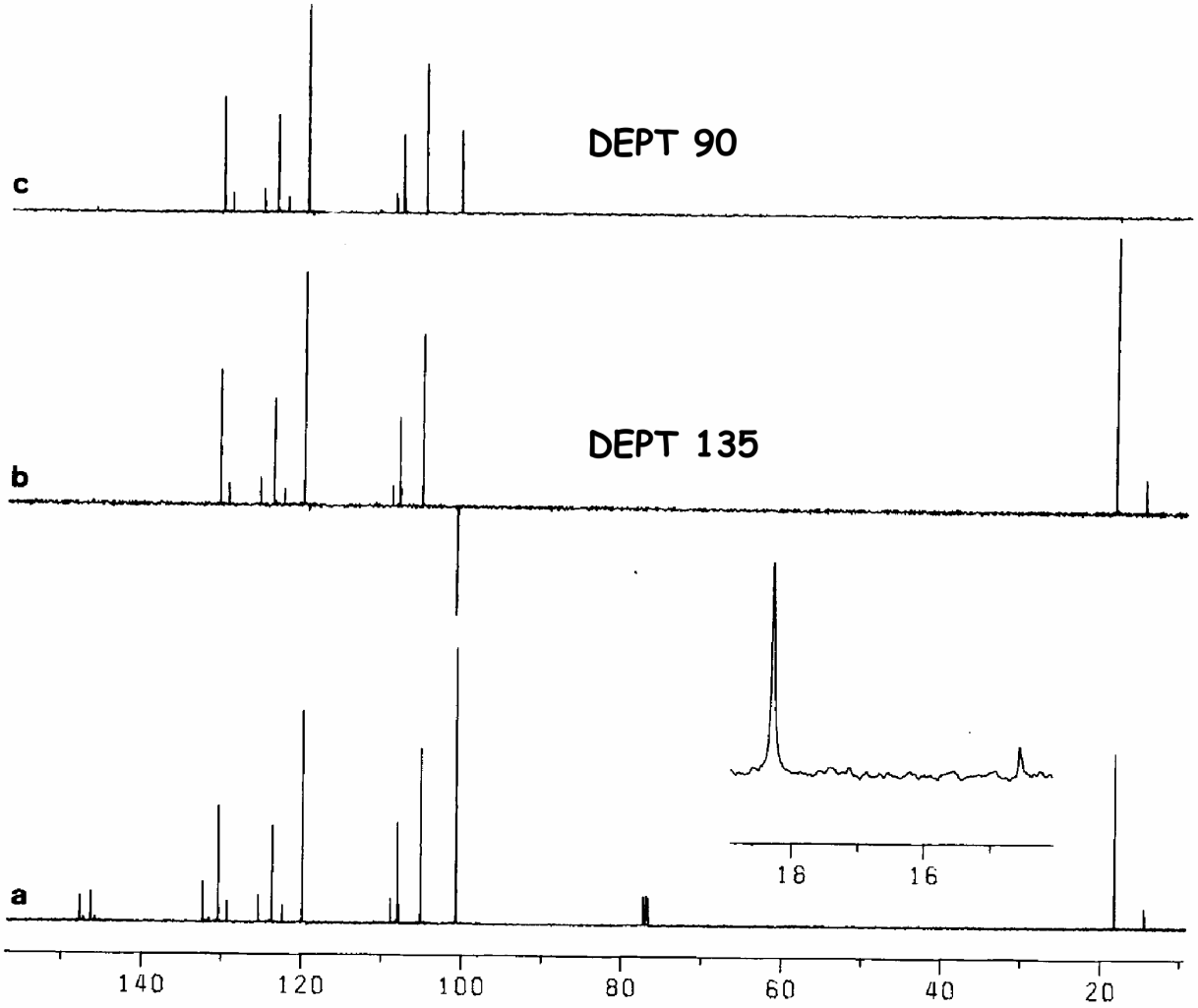
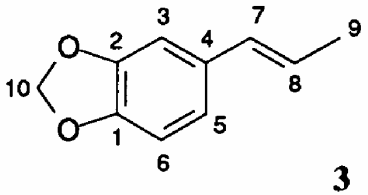
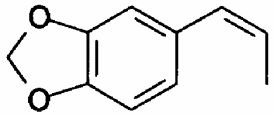


Fig. 3.3. (a) ^{1}H broad-band decoupled ^{13}C NMR spectrum of a mixture of **3** and **4** in $CDCl_3$. Traces (b) and (c) are DEPT spectra

DEPT experiment



3



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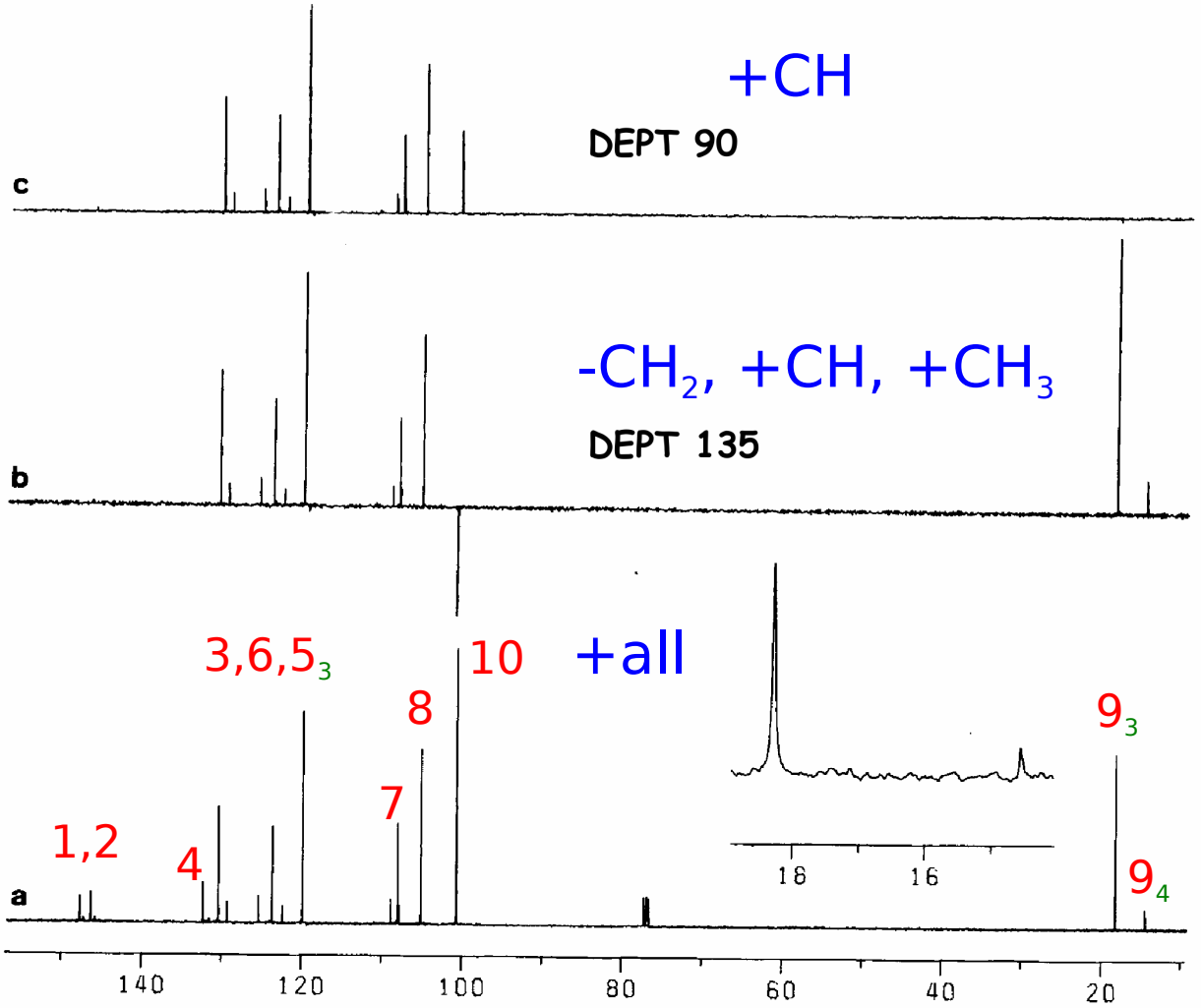

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Next topic

2D NMR - homonuclear experiments