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

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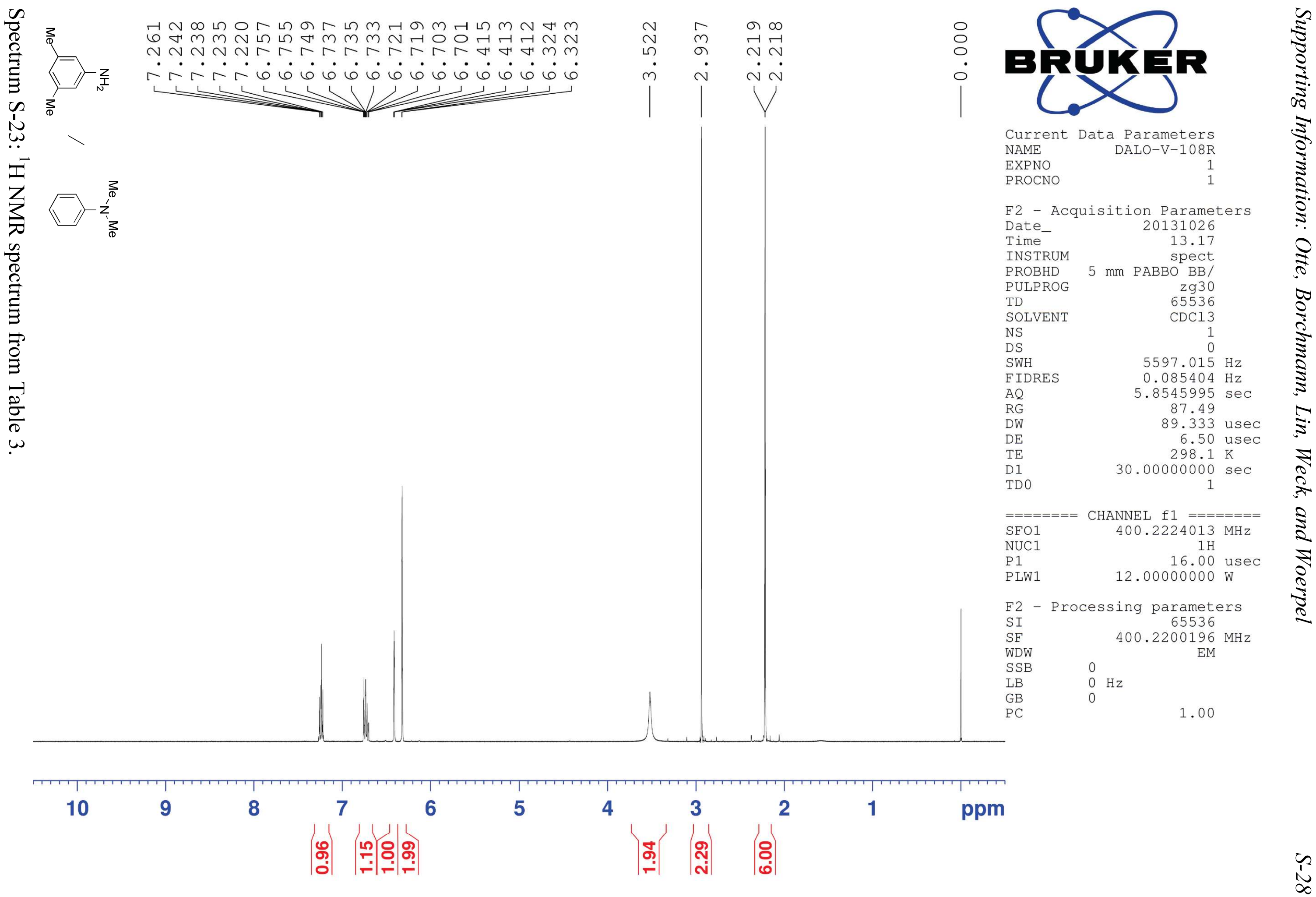
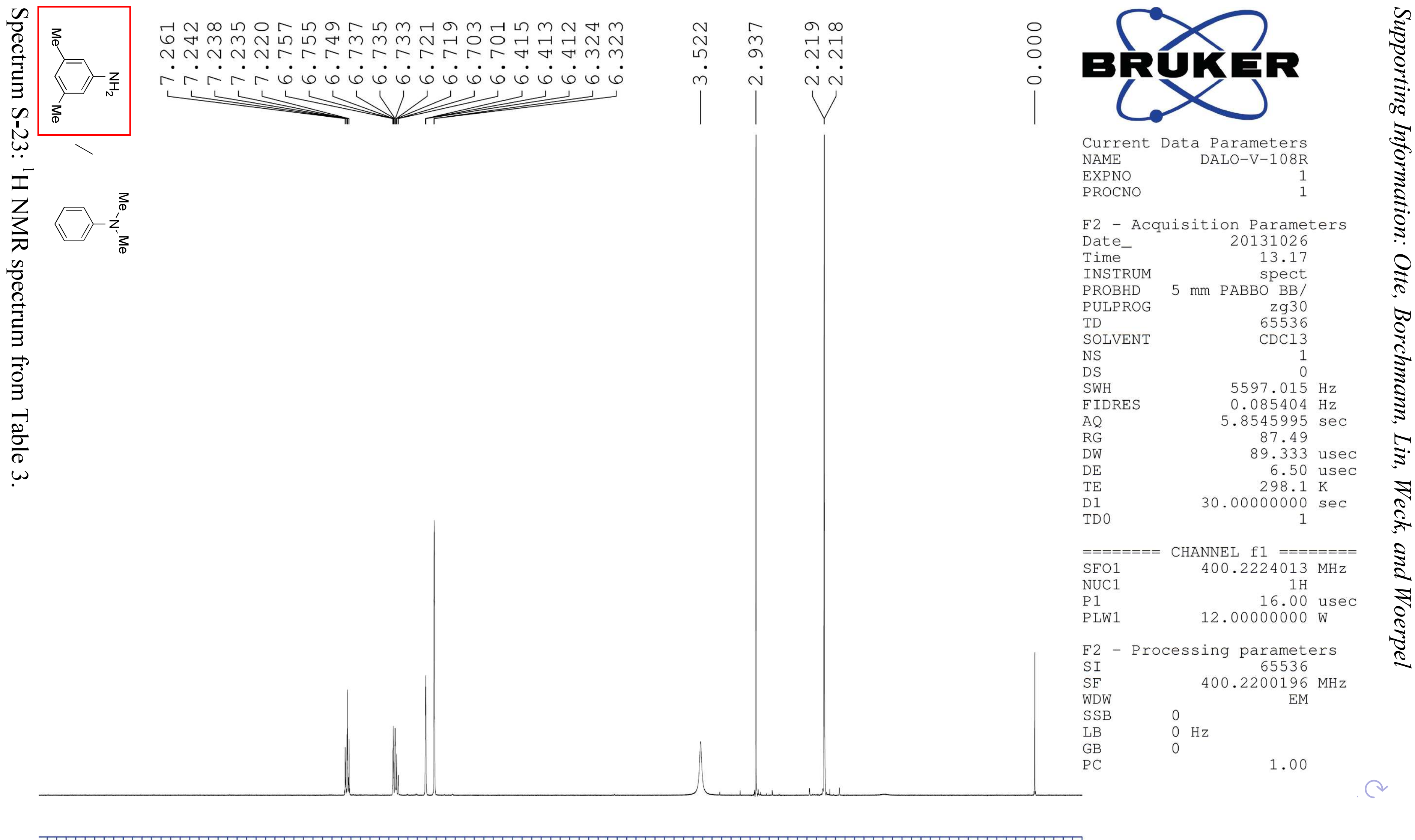
March 13, 2024

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

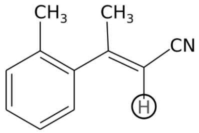


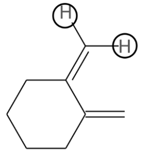
# Determine percentage of dominant regioisomer in attached $^{1}$H spectrum:

72%



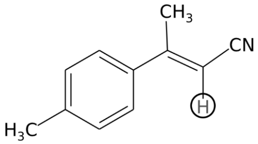
# Assign correct value of chemical shift to labelled NMR active atoms[1]:

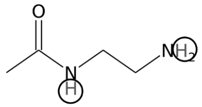


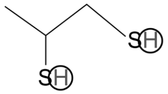

4.64 4.92

5.22 5.46

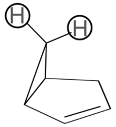


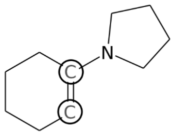

1.5 7.0




1.65(t) 1.85(d)




-0.17 0.73

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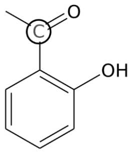


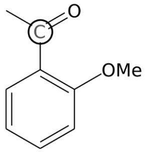


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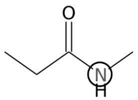
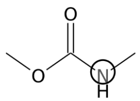
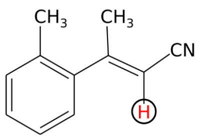



[1] http://www.chem.wisc.edu/areas/reich/chem605/

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

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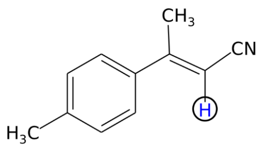


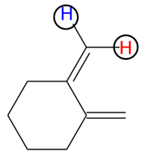


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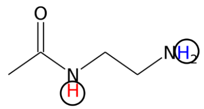


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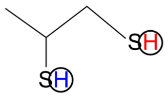


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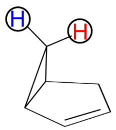


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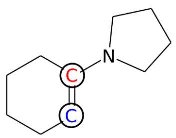


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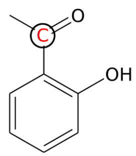


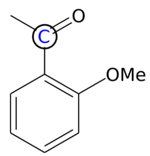


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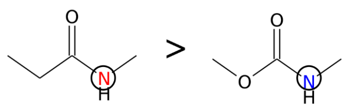


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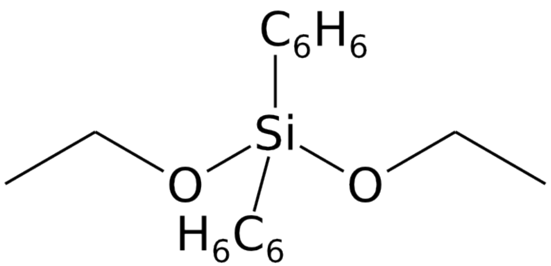
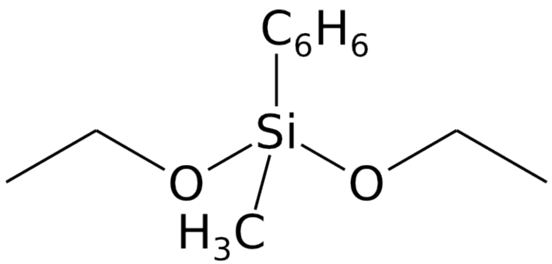
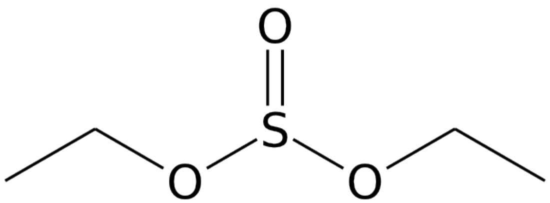
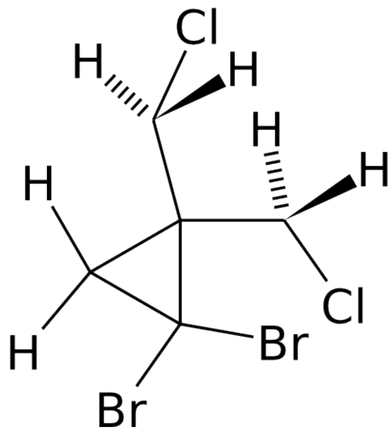
# Diastereotopicity[1] Determine the equivalency of geminal protons

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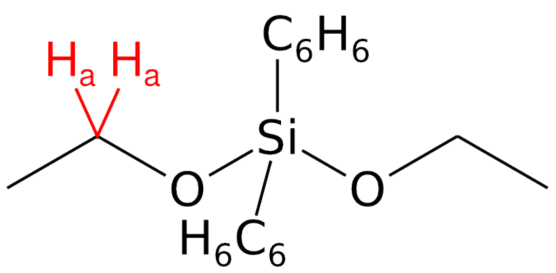


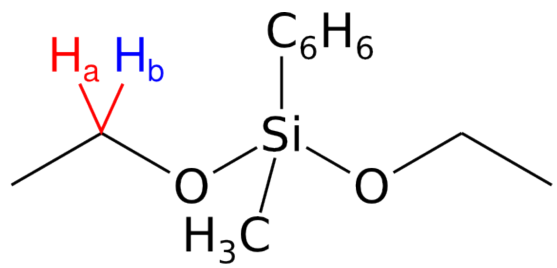


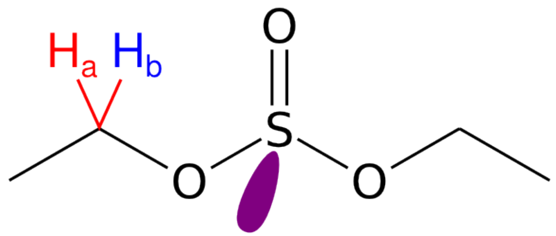


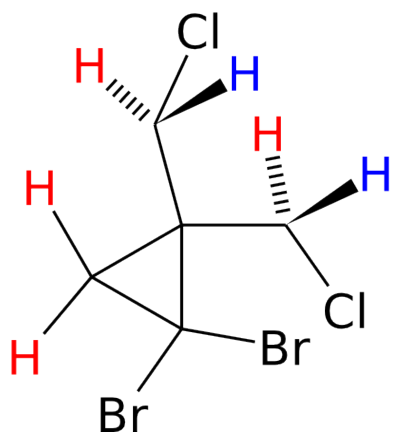


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# Values of chemical shift of important solvents

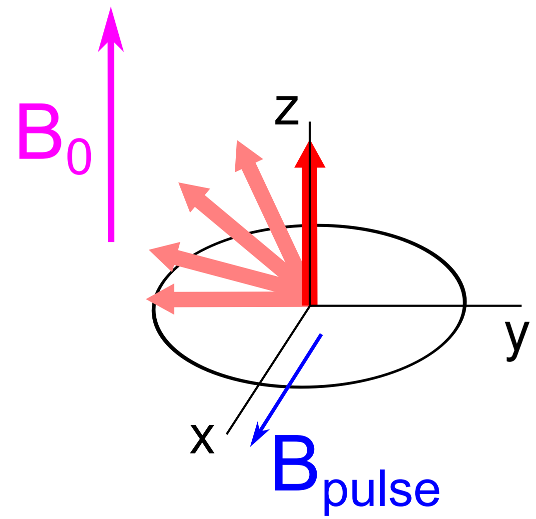
| Abbr. | Formula | $^1H$ | $^{13}C$ |
| --- | --- | --- | --- |
| **ACN** | $CH_3CN$ | 1.9 | 118 |
| **Benzene** | $C_6H_6$ | 7.2 | 128 |
| | $CHCl_3$ | 7.2 | 77 |
| **DCM** | $CH_2Cl_2$ | 5.3 | 54 |
| **DMF** | $(CH_3)_2NCHO$ | 2.9, 8.0 | 32, 163 |
| **DMSO** | $(CH_3)_2SO$ | 2.5 | 40 |
| **MeOH**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

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

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

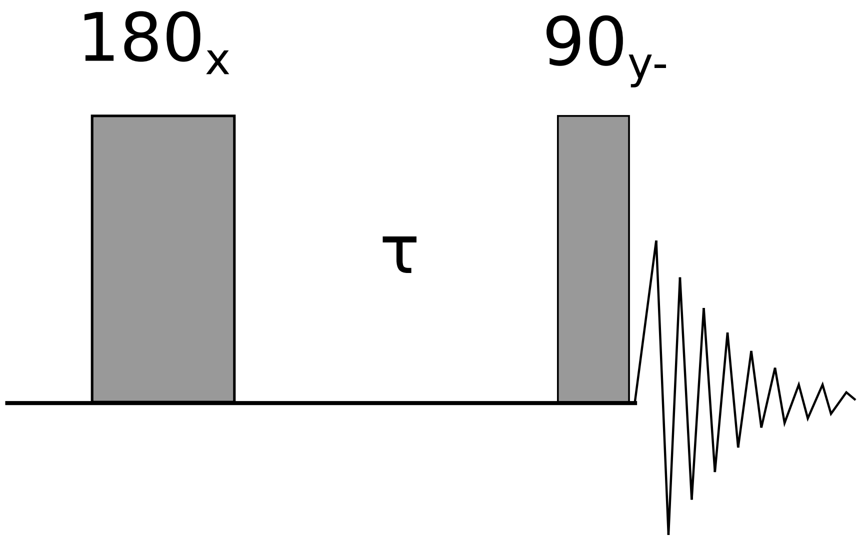
# Analysis of simple pulse sequences using vector model

- 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 $\omega$ (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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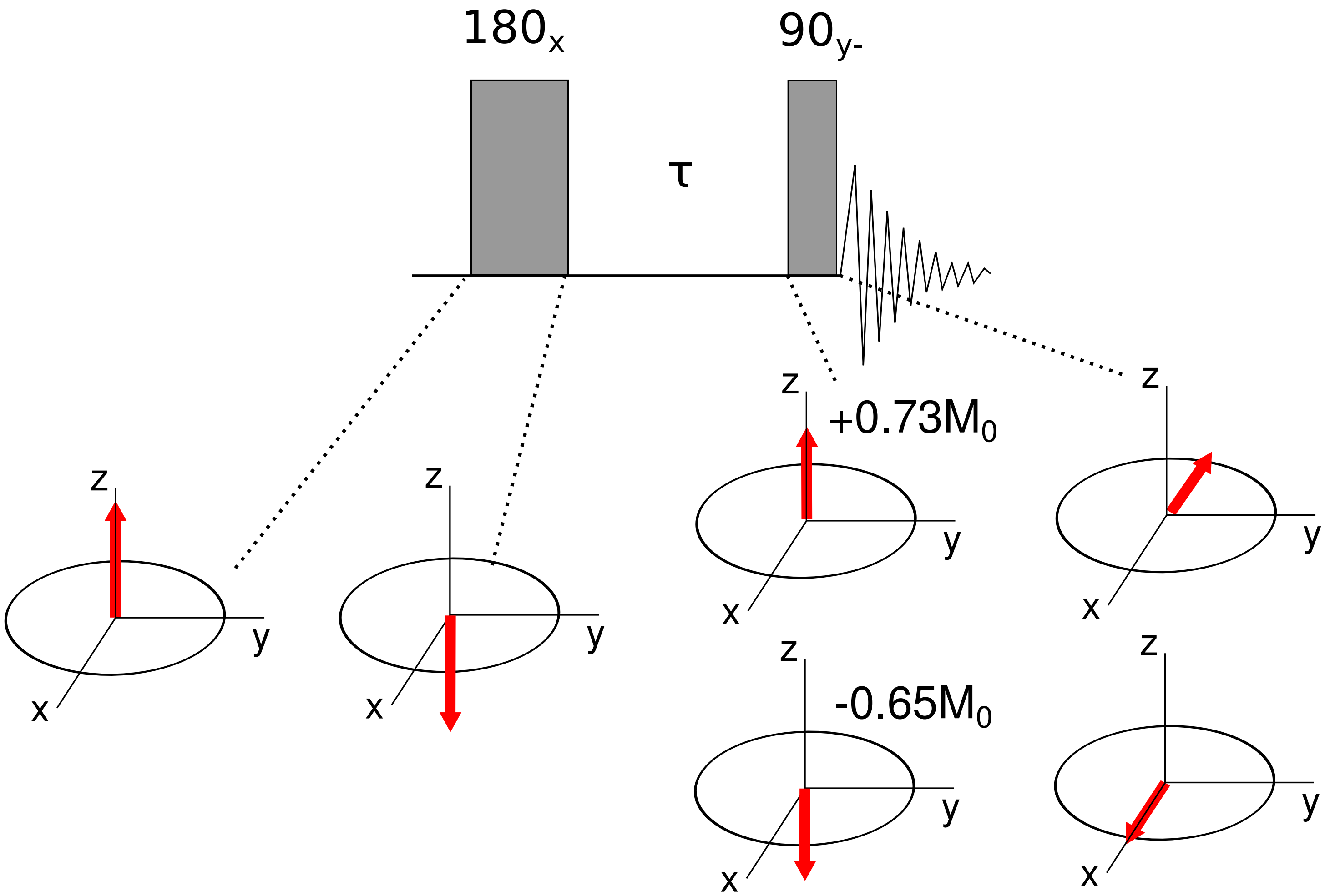
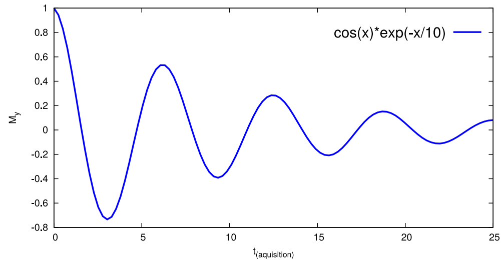
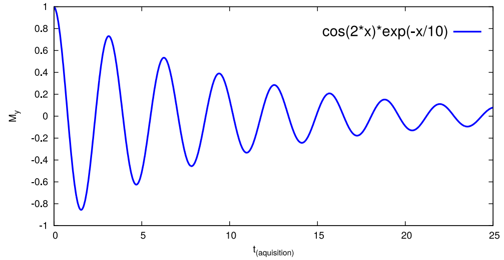
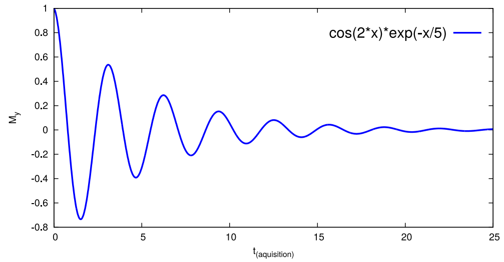
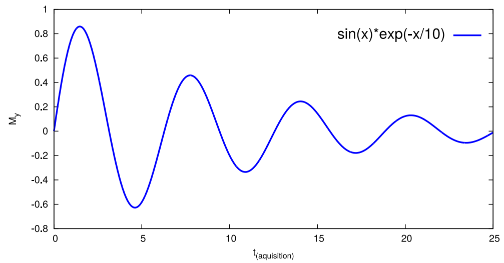


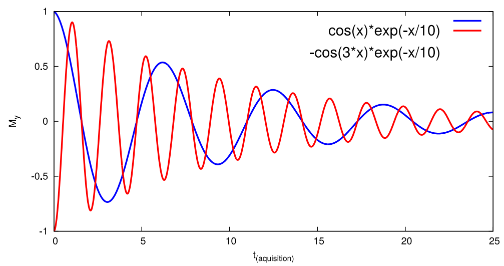
# Processing simulated NMR signal:



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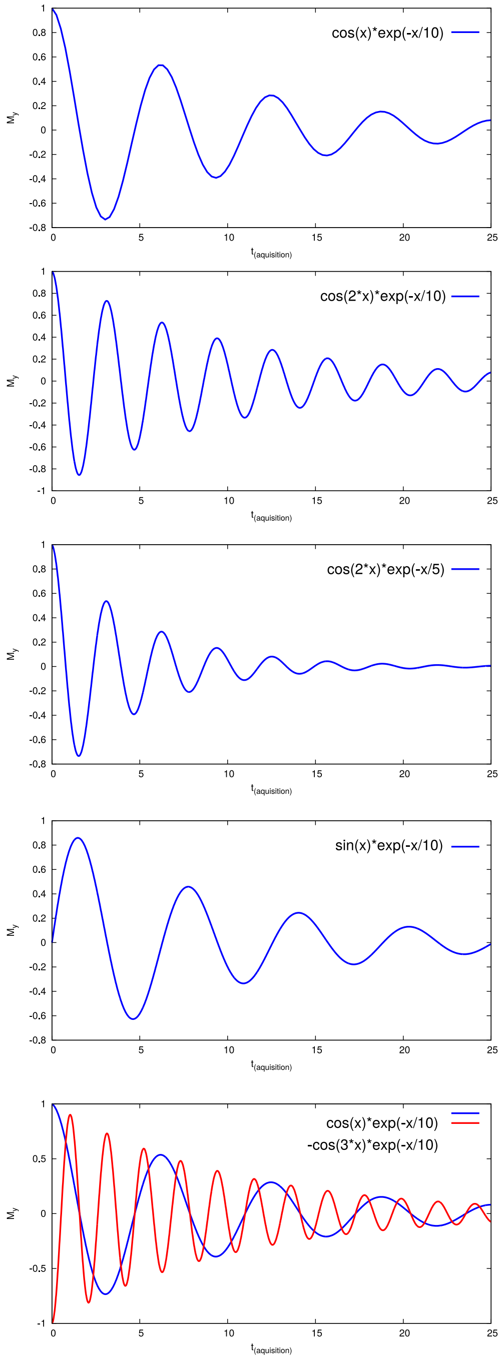
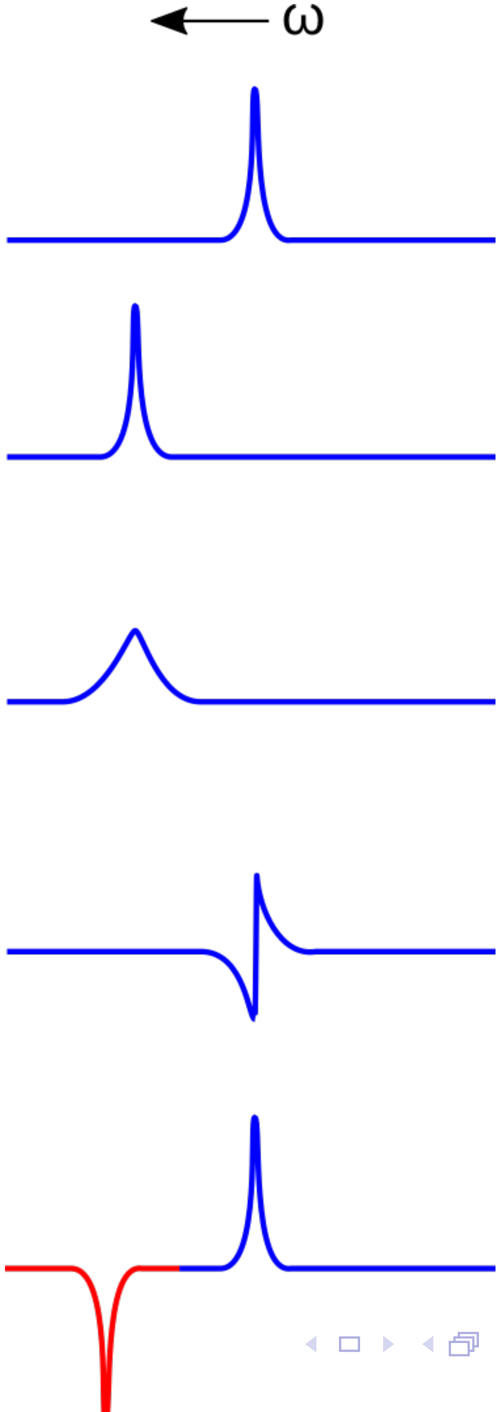
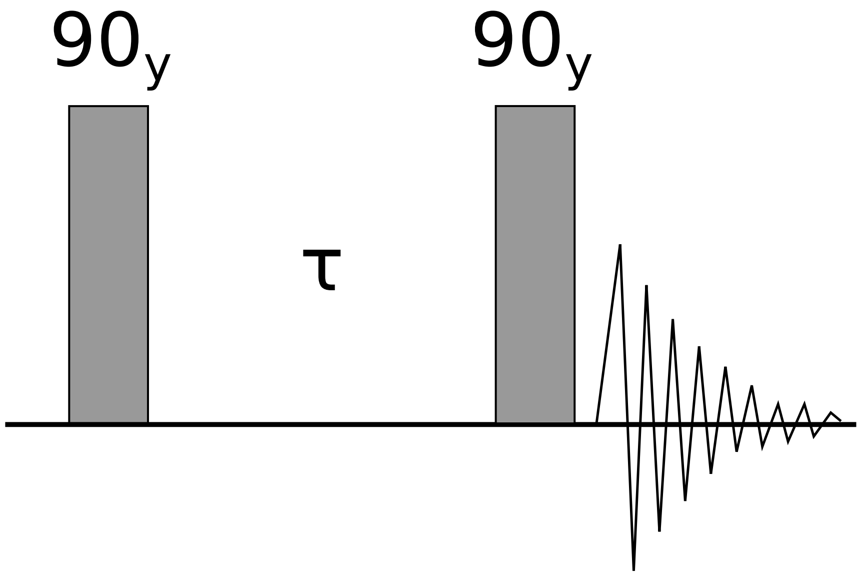


# 1-$\bar{1}$ sequence

Draw the evolution of macroscopic magnetization through the sequence:
**90(y) - $\tau$ - 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).



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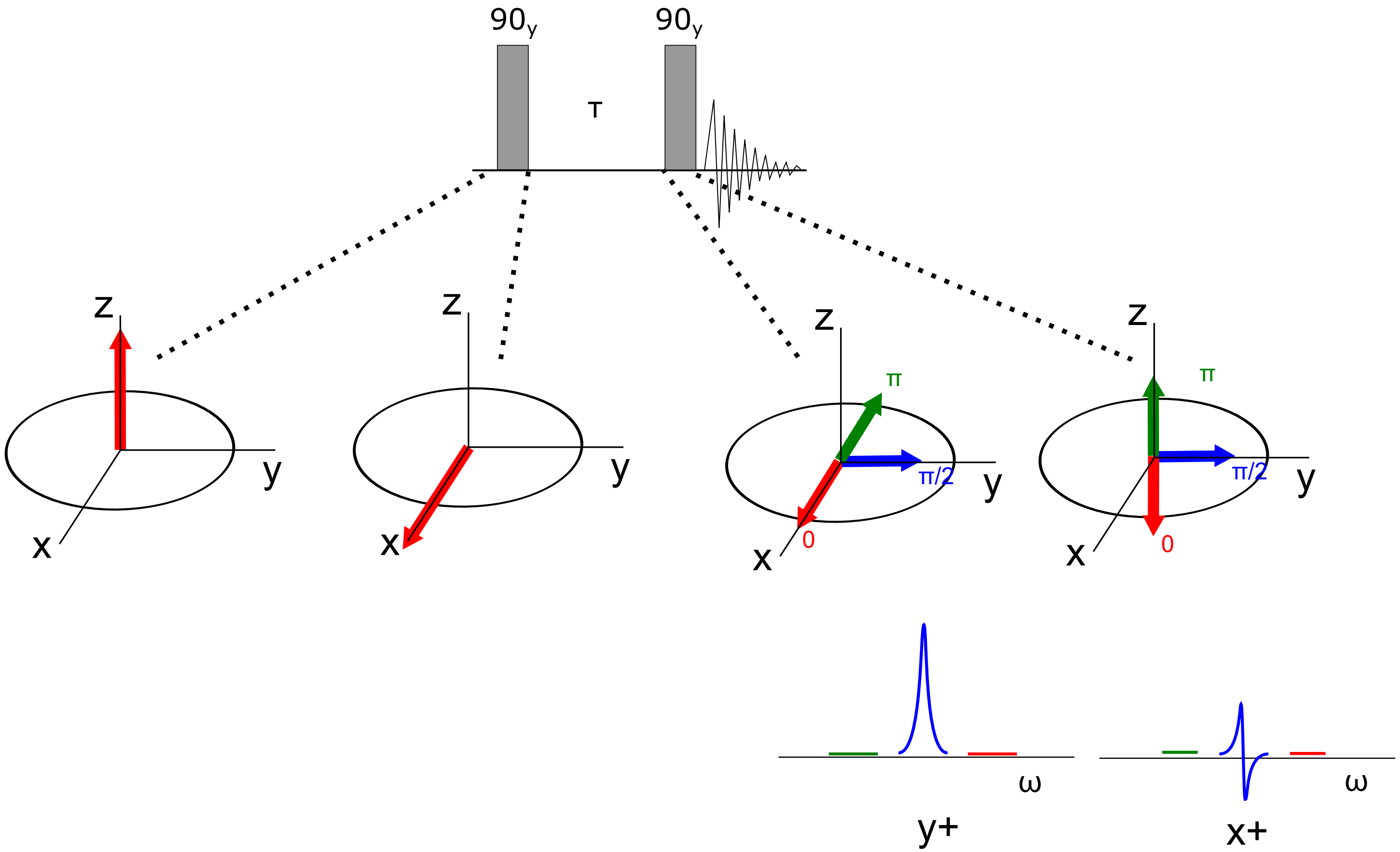
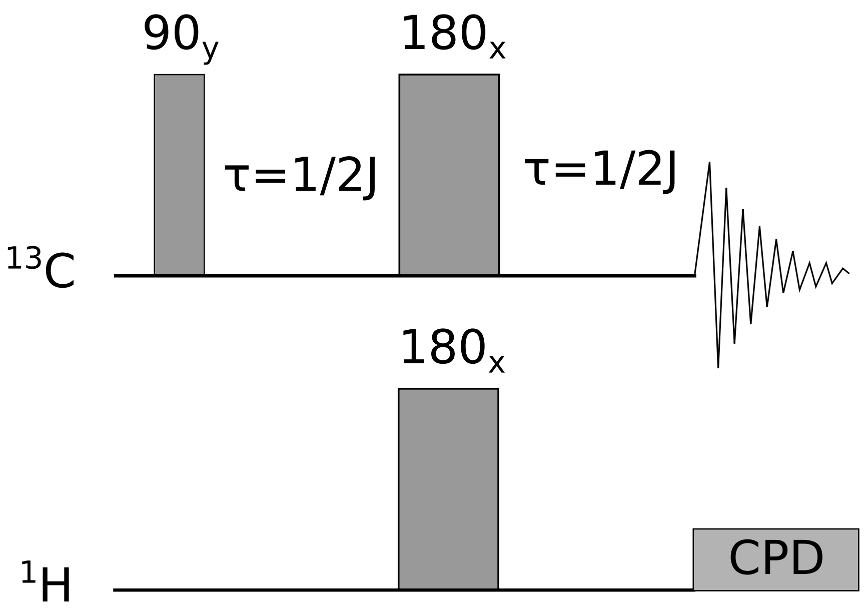


# Heteronuclear spin echo

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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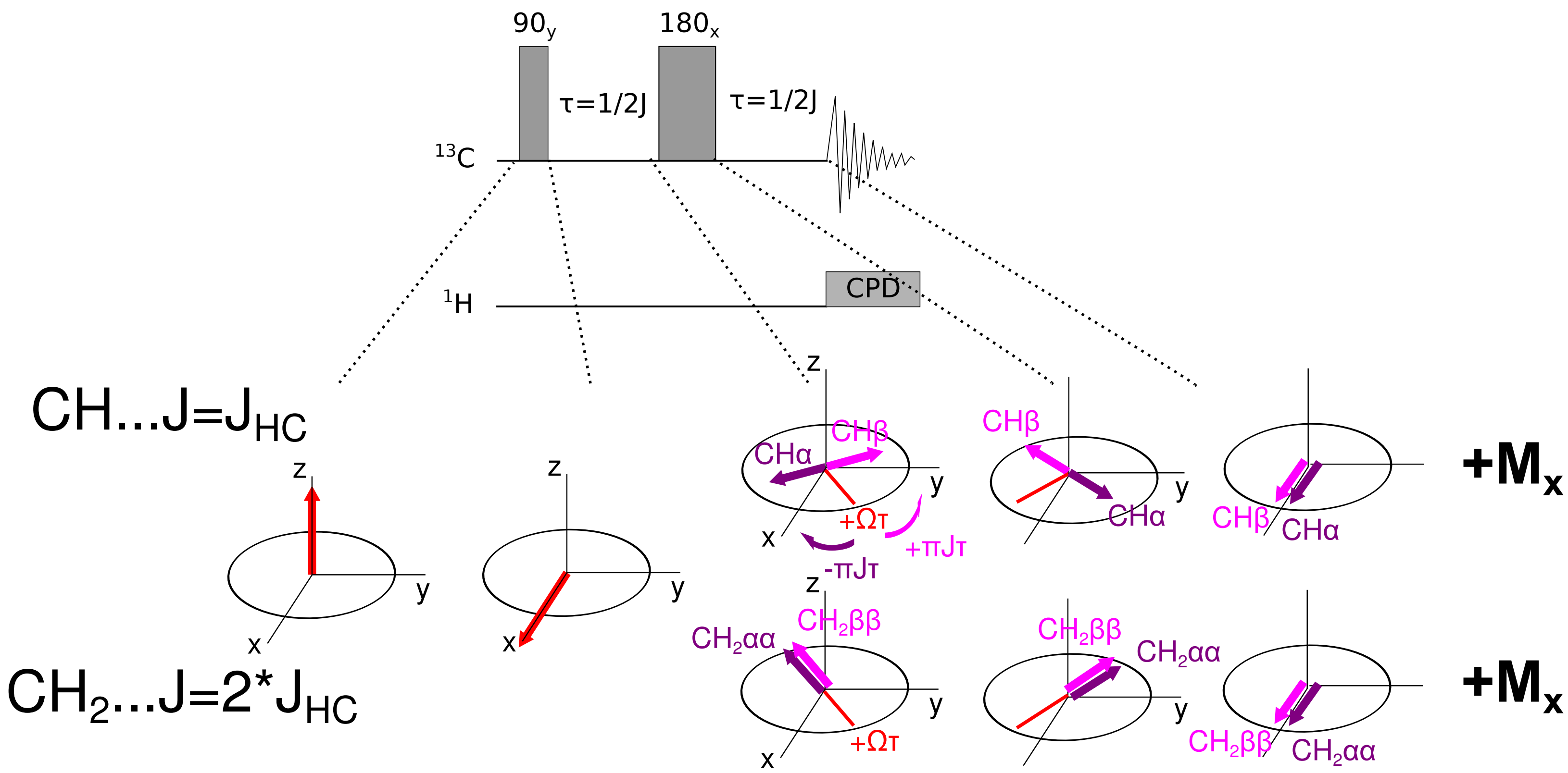

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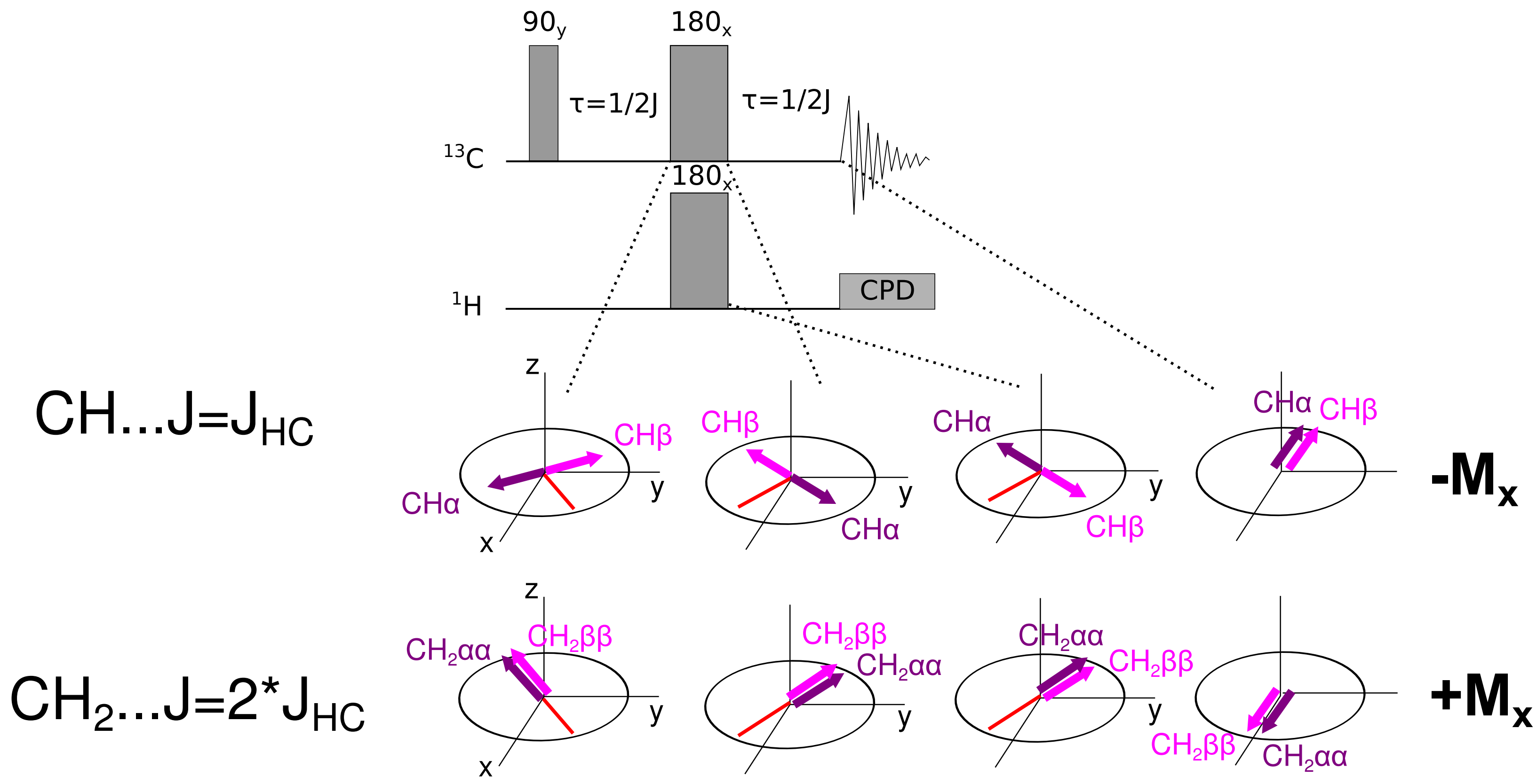


# APT - Attached Proton Test

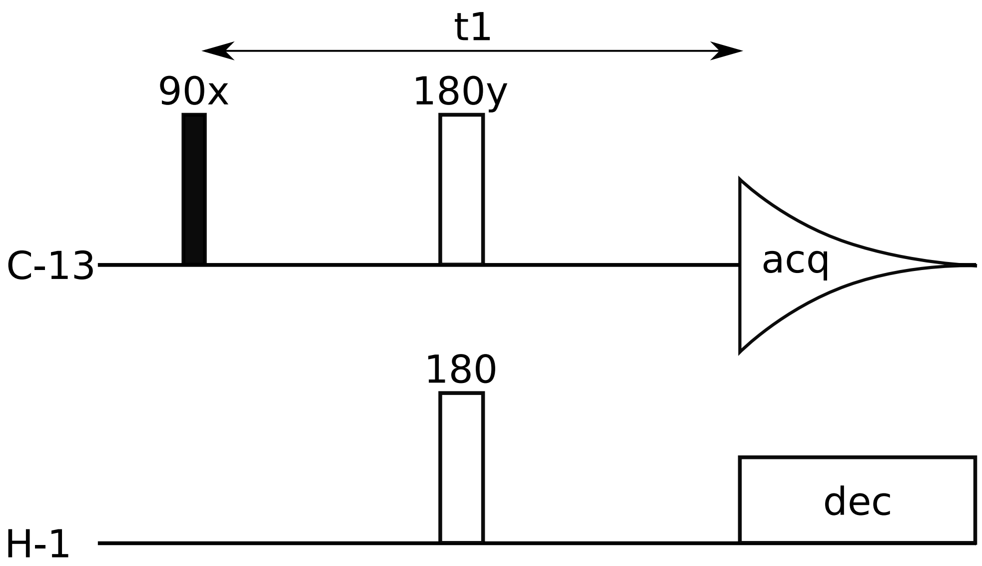
based on heteronuclear spin-echo

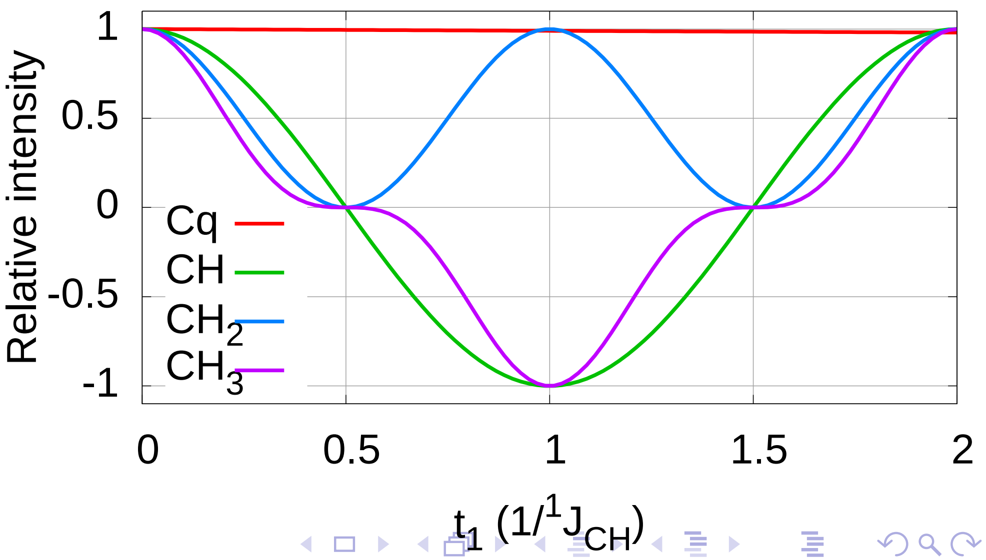
- $t_1 = 1/^1J_{CH}$

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

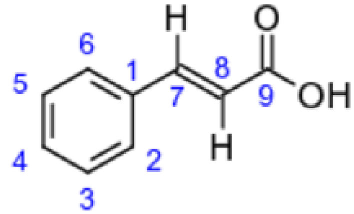
- Cq, $CH_2$ positive
- CH, $CH_3$ negative

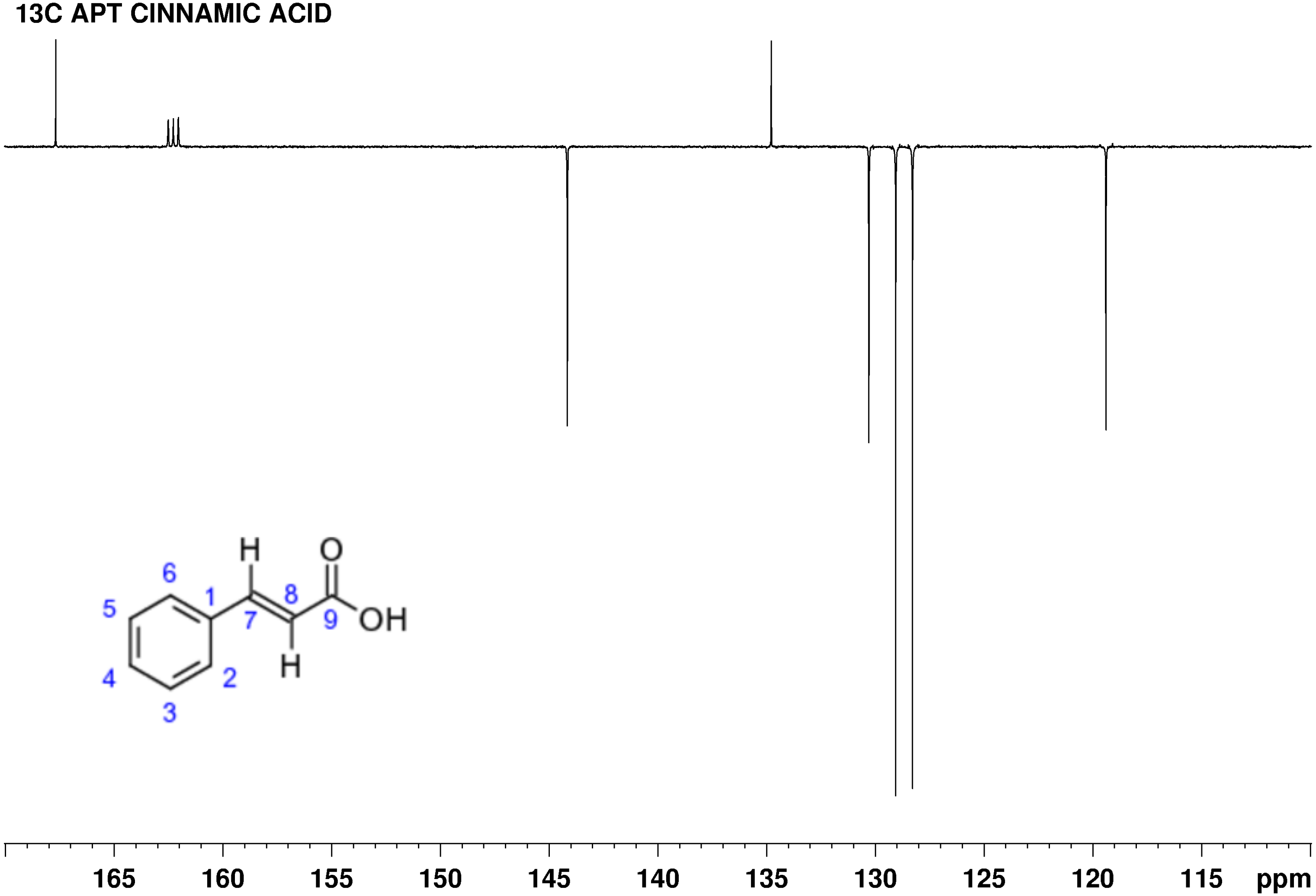
Different $^1J_{CH} \implies$ different intensities



# $^{13}$C APT Cinnamic acid



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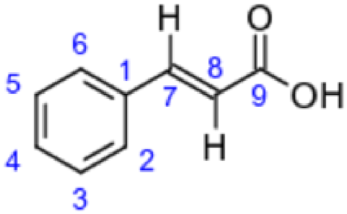
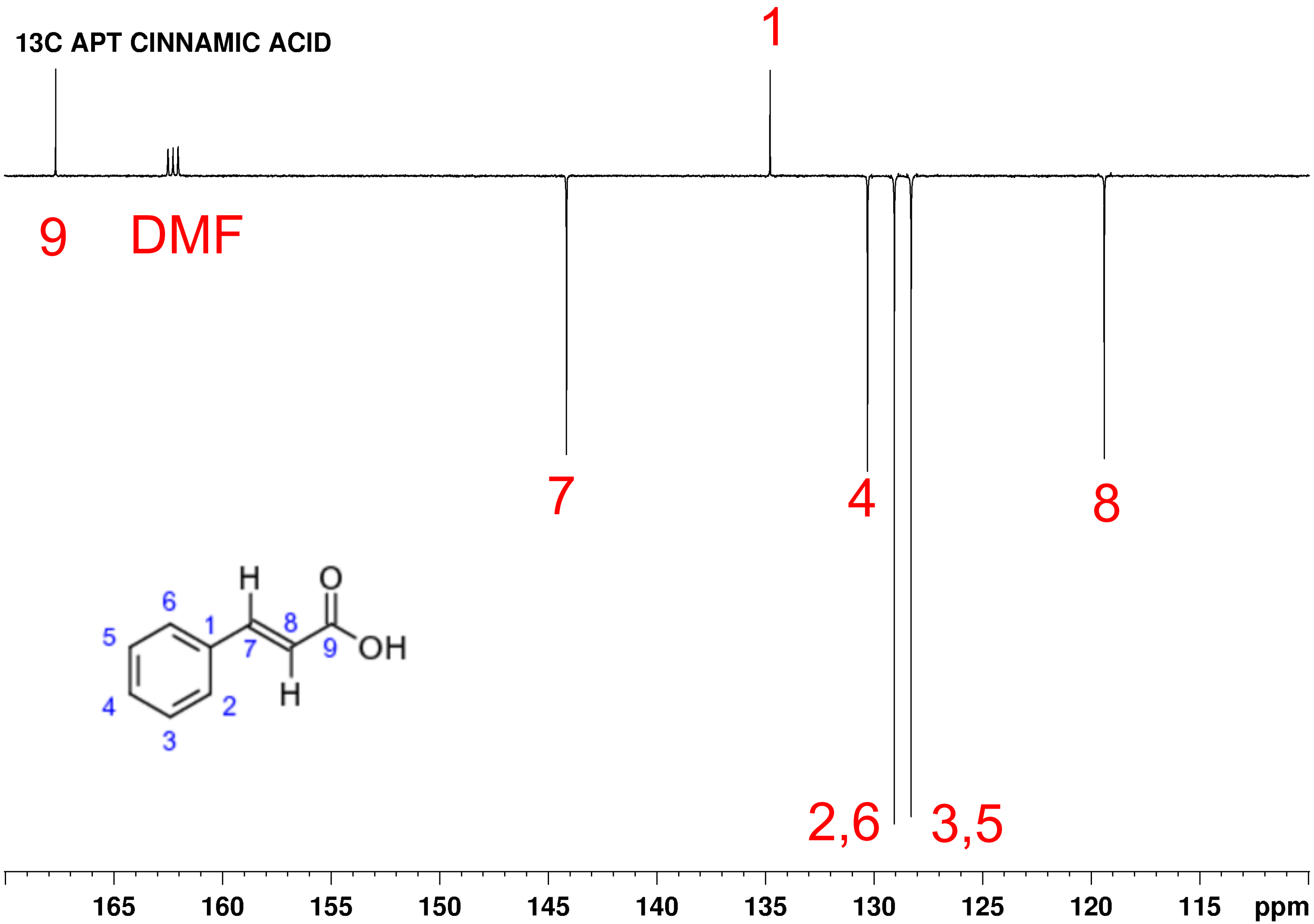
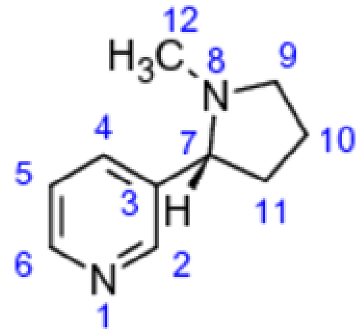
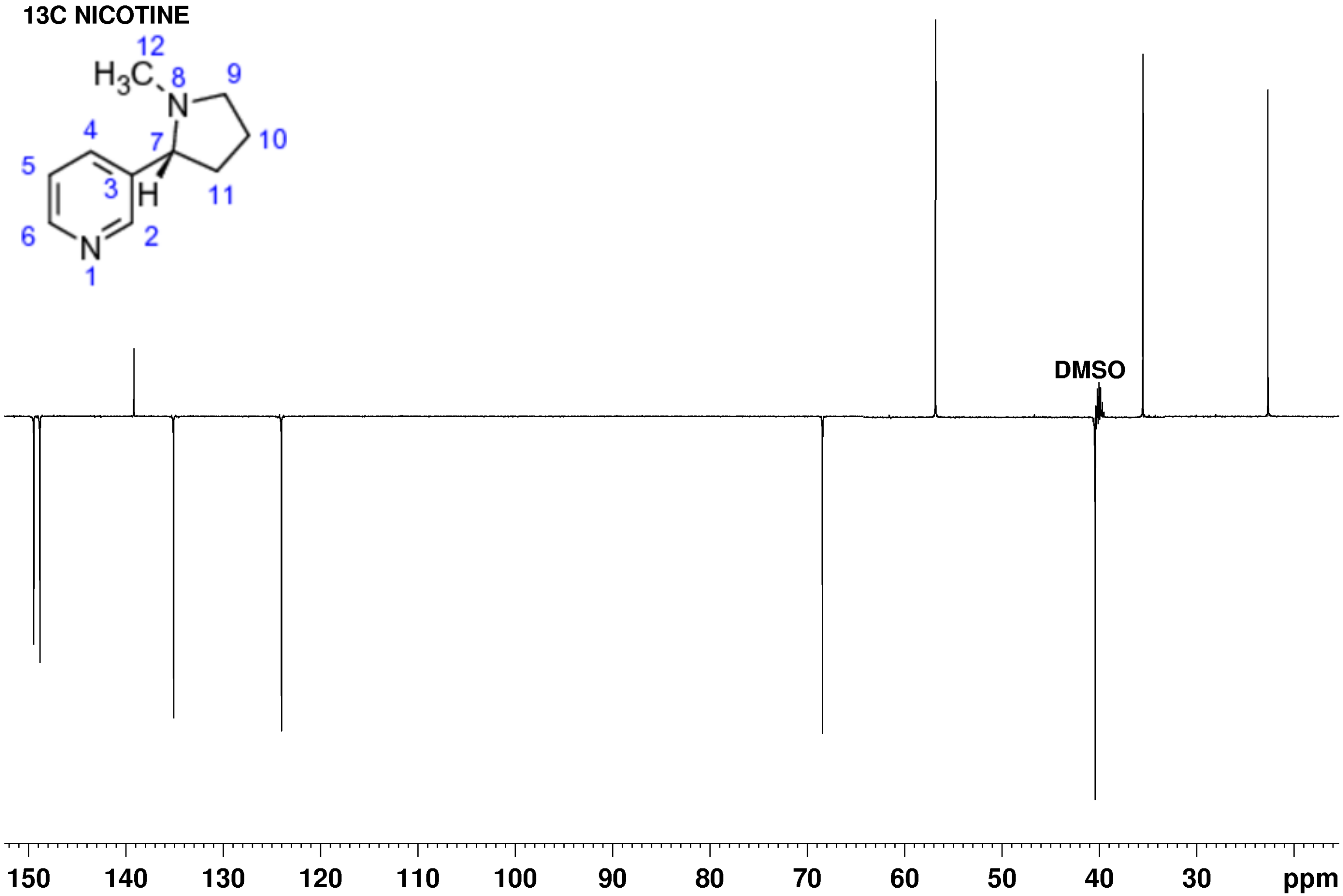


# $^{13}C$ APT Nicotine



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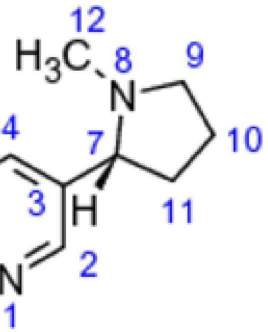
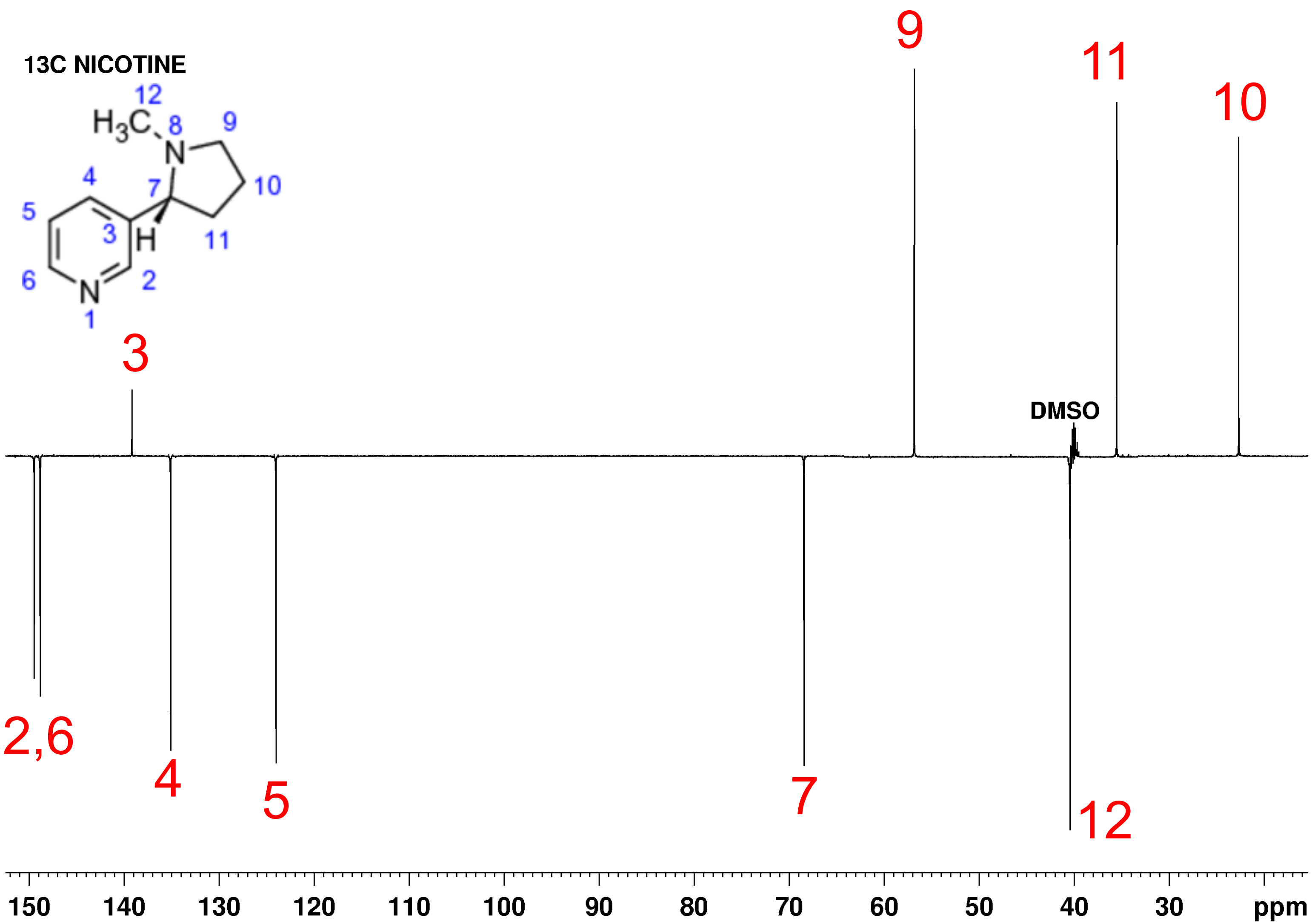
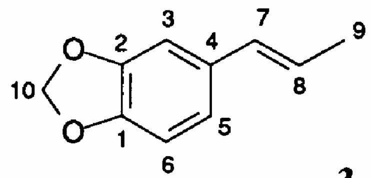
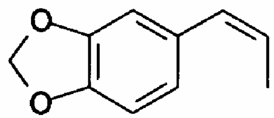


# DEPT experiment




3




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?

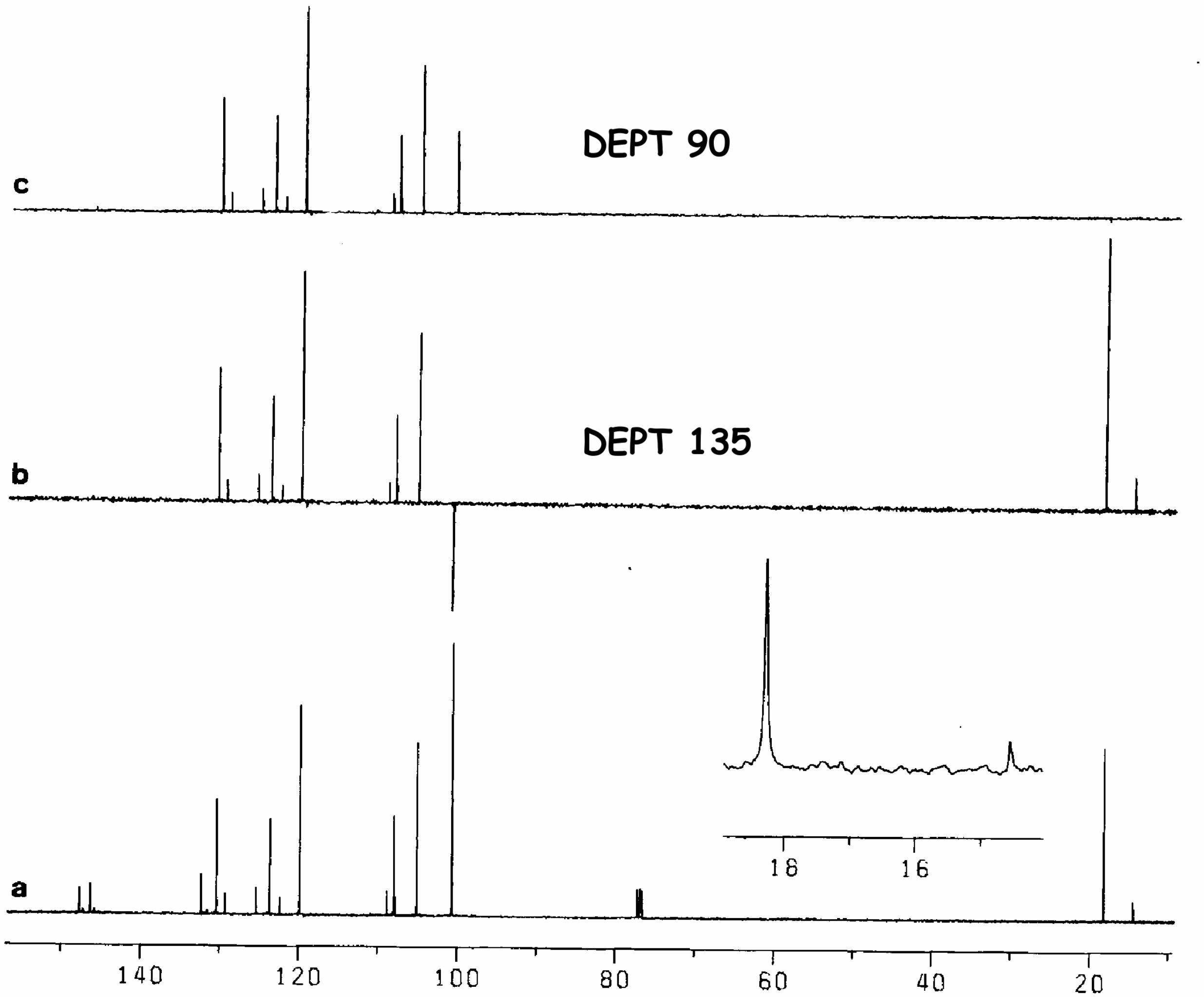



**Fig. 3.3.** (a) $^{1}H$ broad-band decoupled $^{13}C$ NMR spectrum of a mixture of **3** and **4** in $CDCl_3$. Traces (b) and (c) are DEPT spectra.

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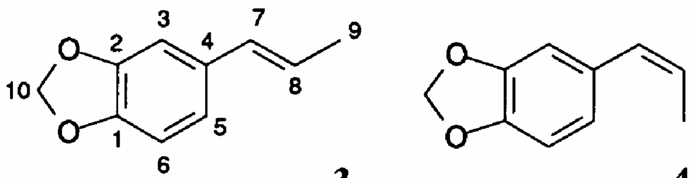


**3** **4**

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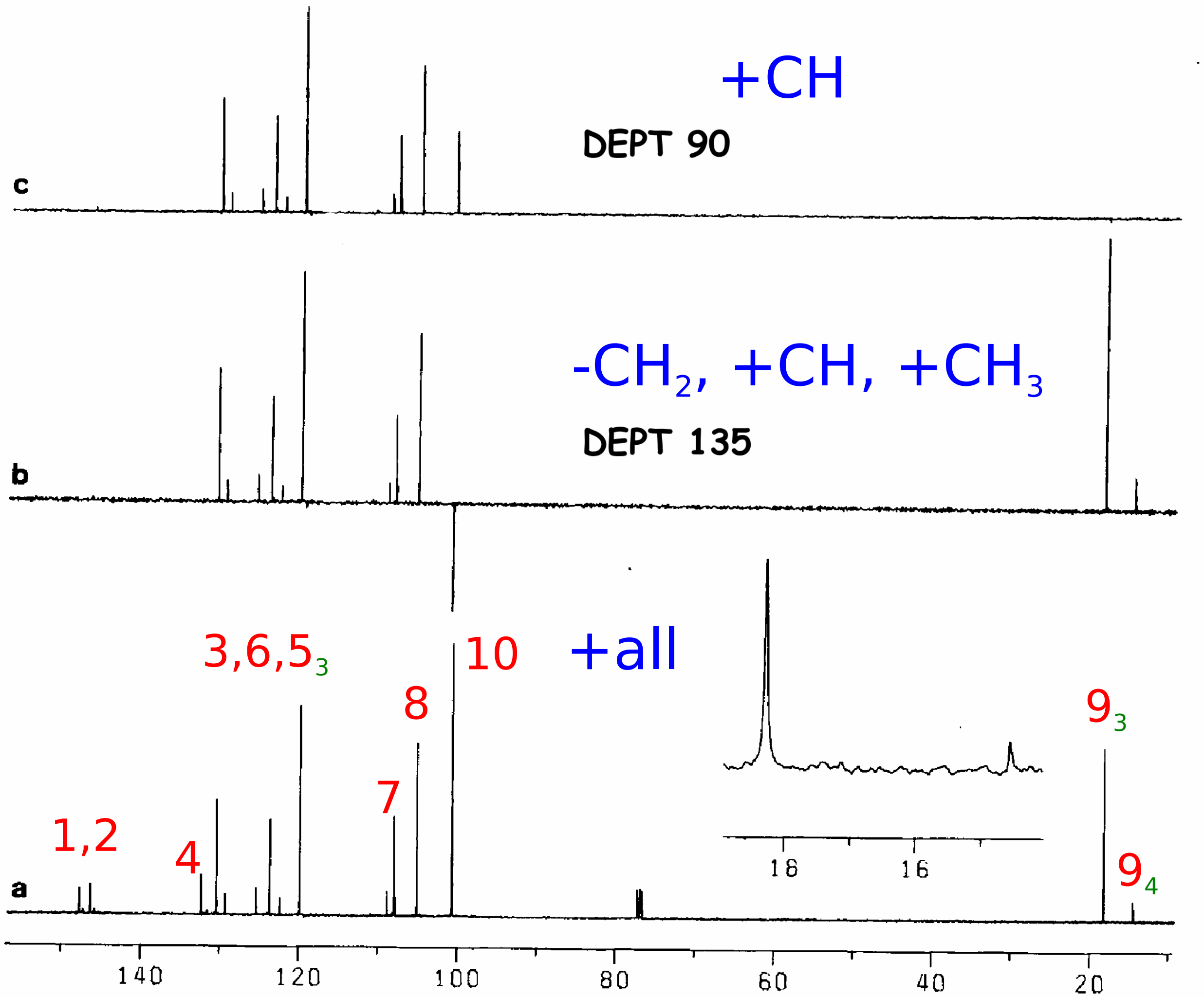


**Fig. 3.3.** (a) [1]H broad-band decoupled [13]C NMR spectrum of a mixture of **3** and **4** in $CDCl_3$. Traces (b) and (c) are DEPT spectra.

# Next topic

2D NMR - homonuclear experiments