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

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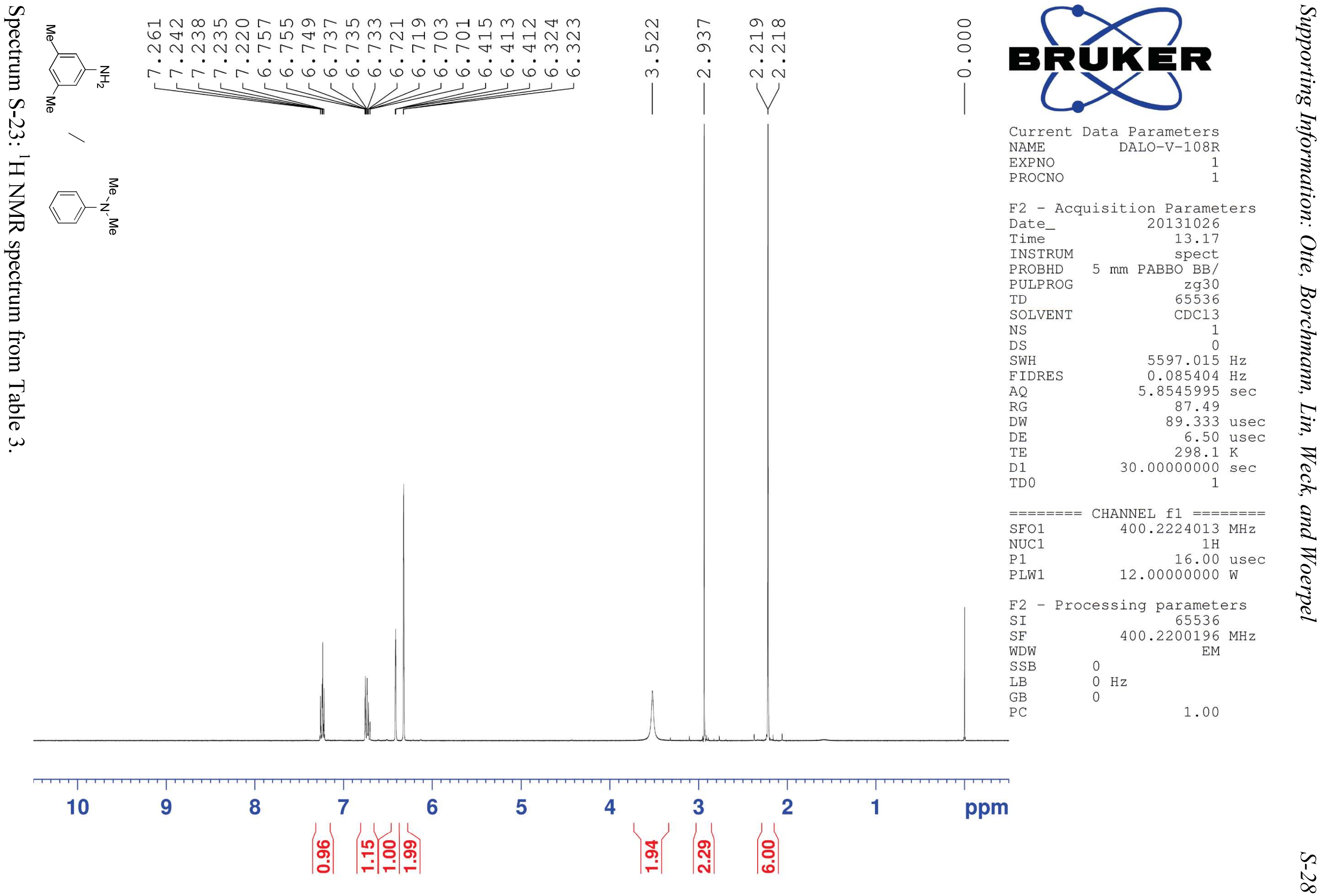
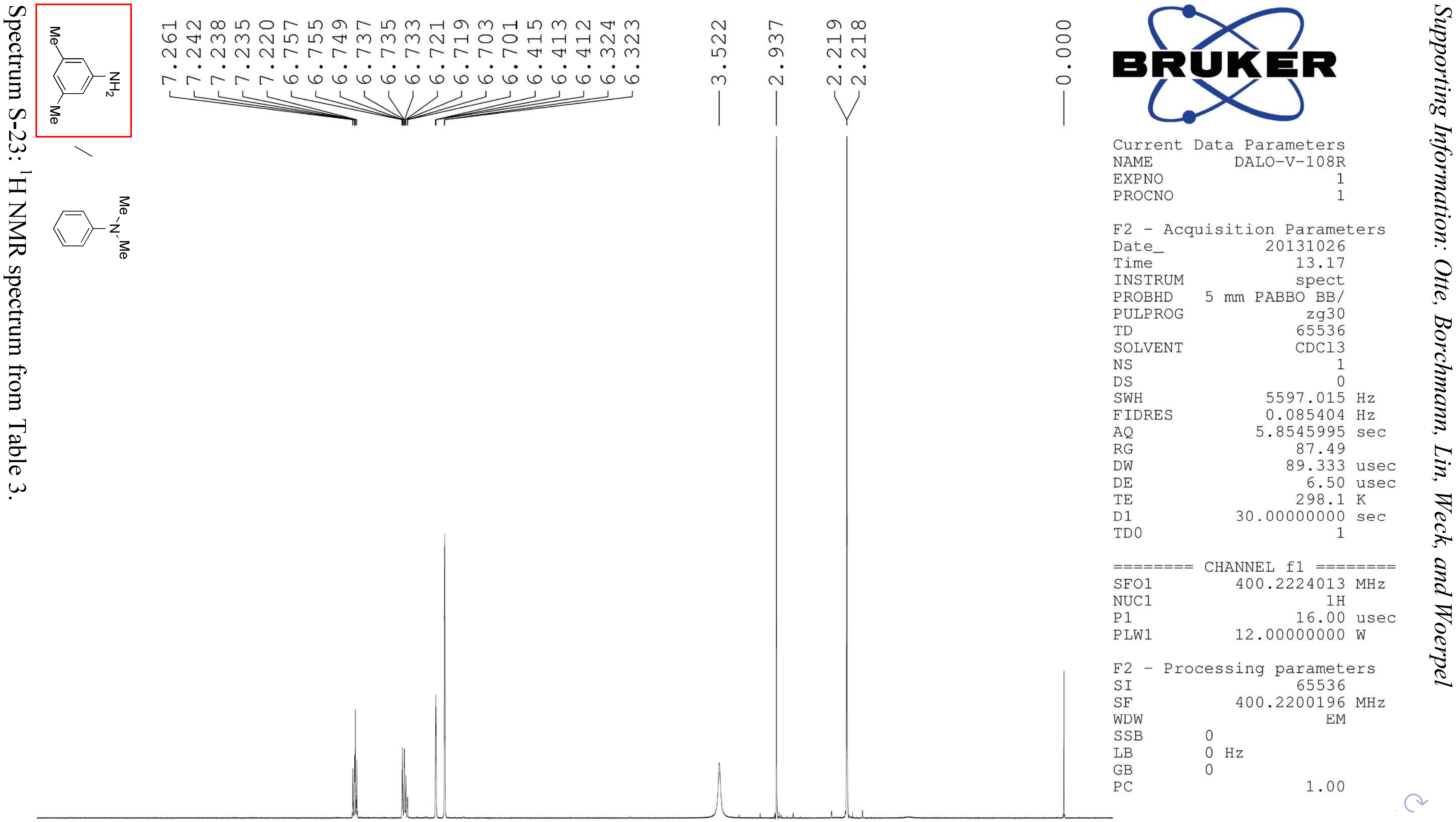
March 9, 2022

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

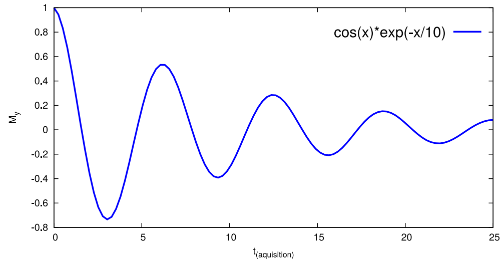


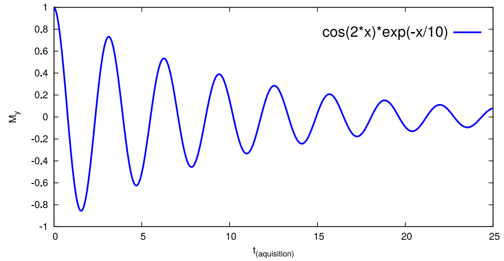
Determine percentage of dominant regioisomer in attached ^{1}H spectrum:

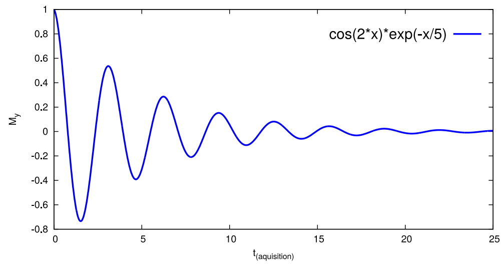
72%

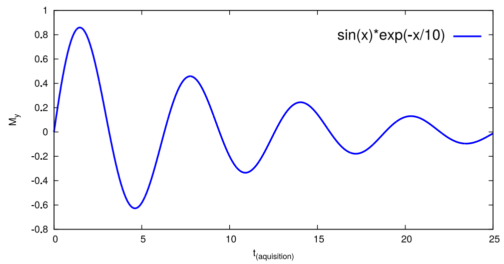


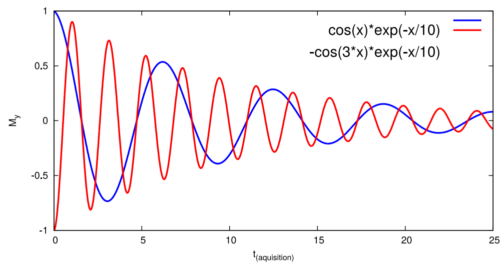
Processing simulated NMR signal:











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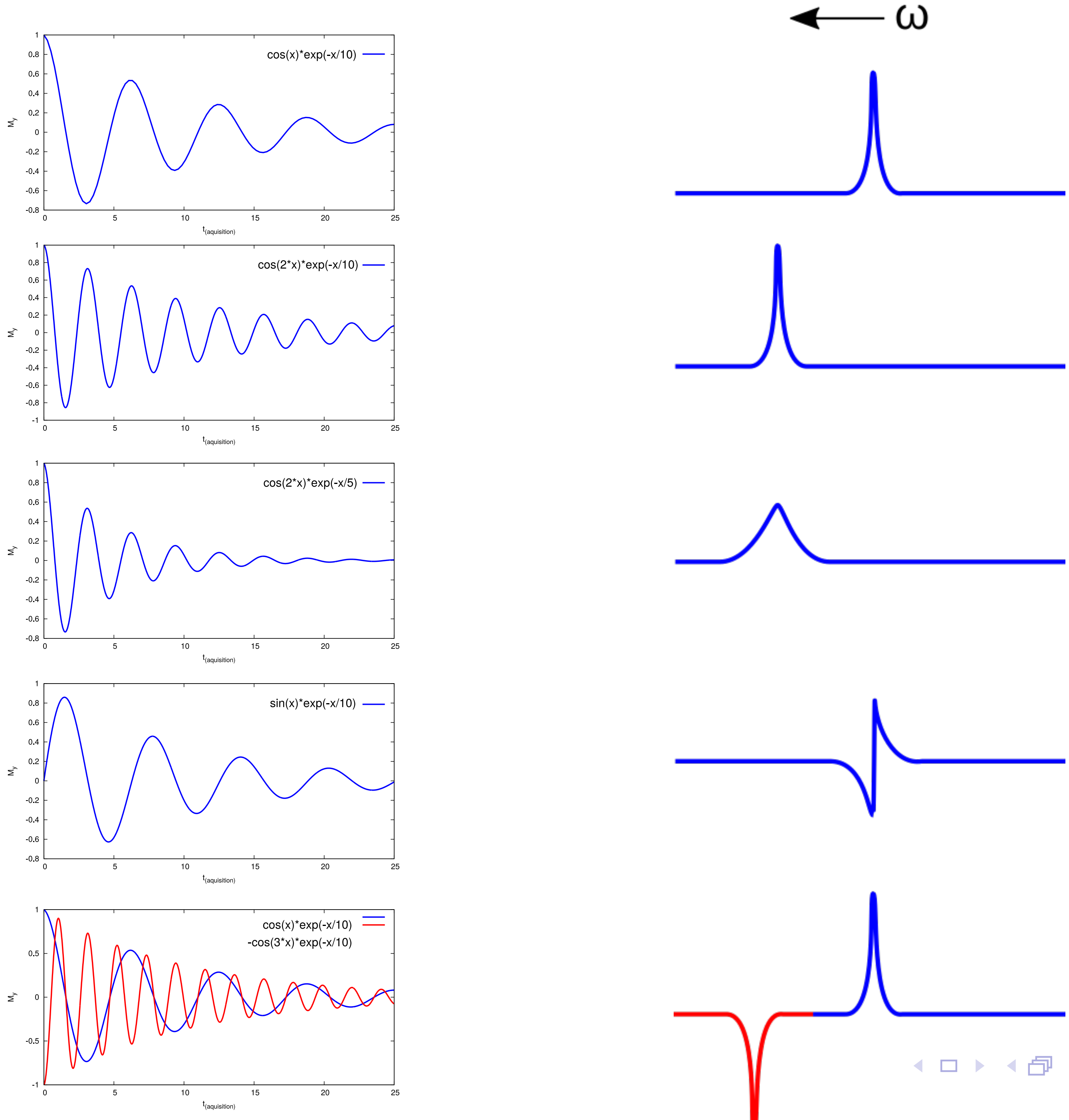
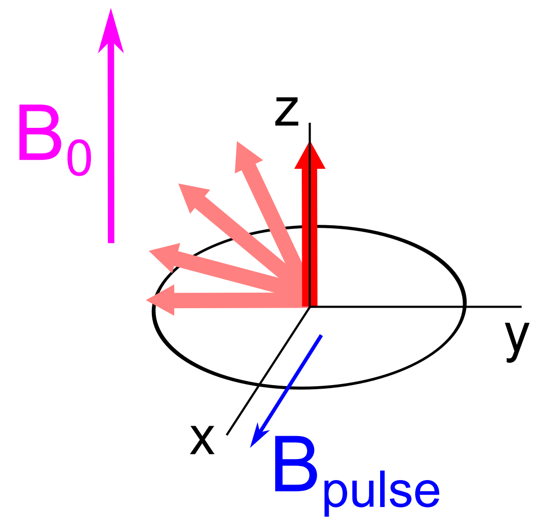


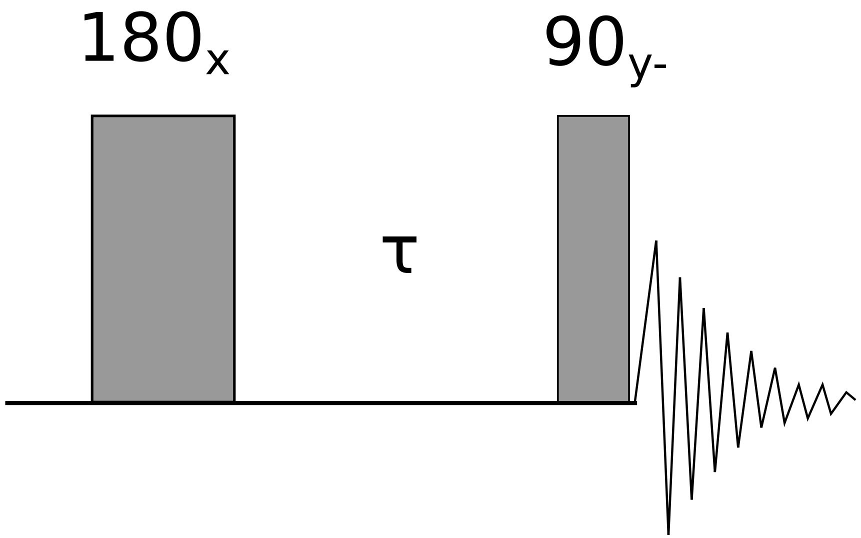
Analysis of simple pulse sequences using vector model

- 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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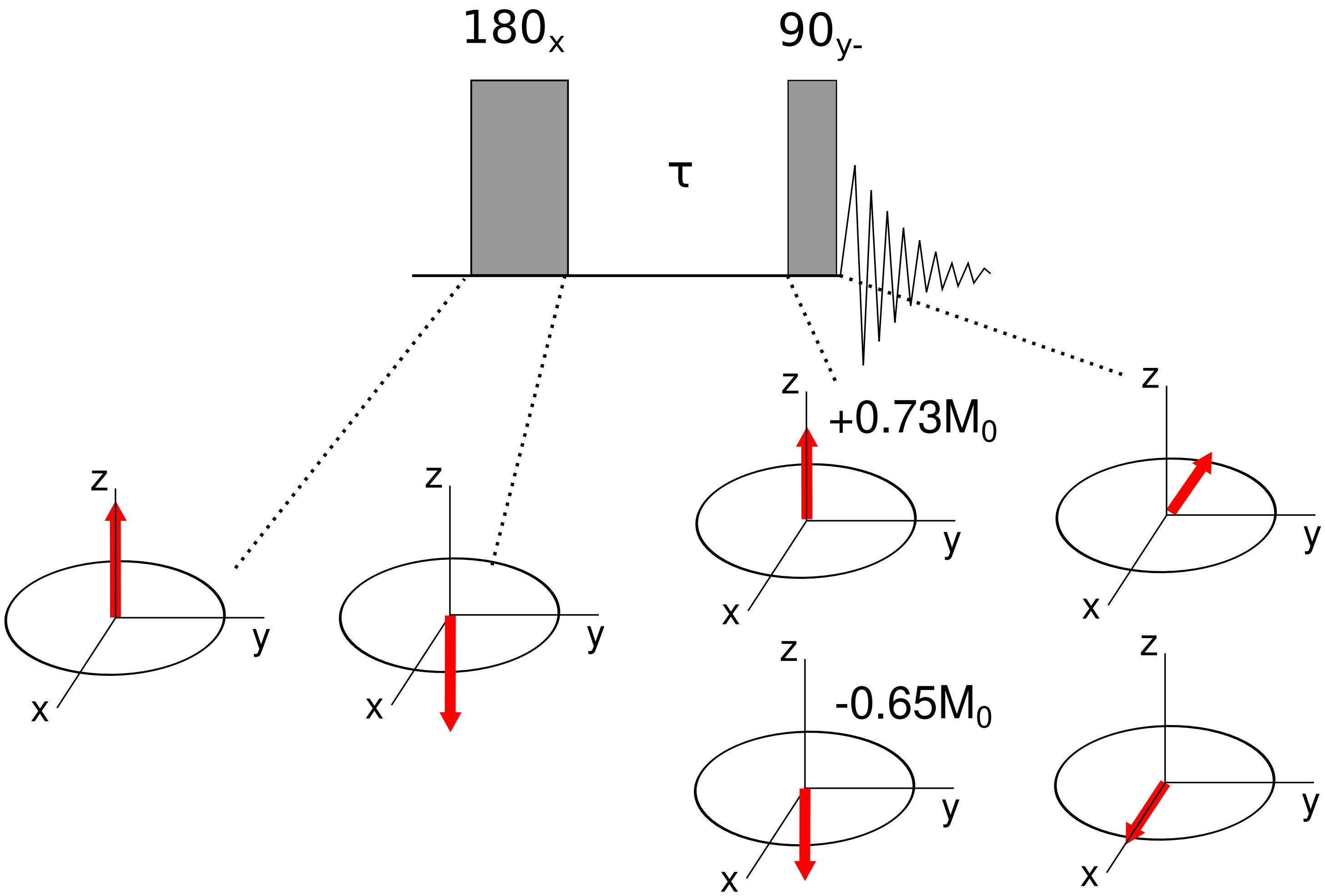
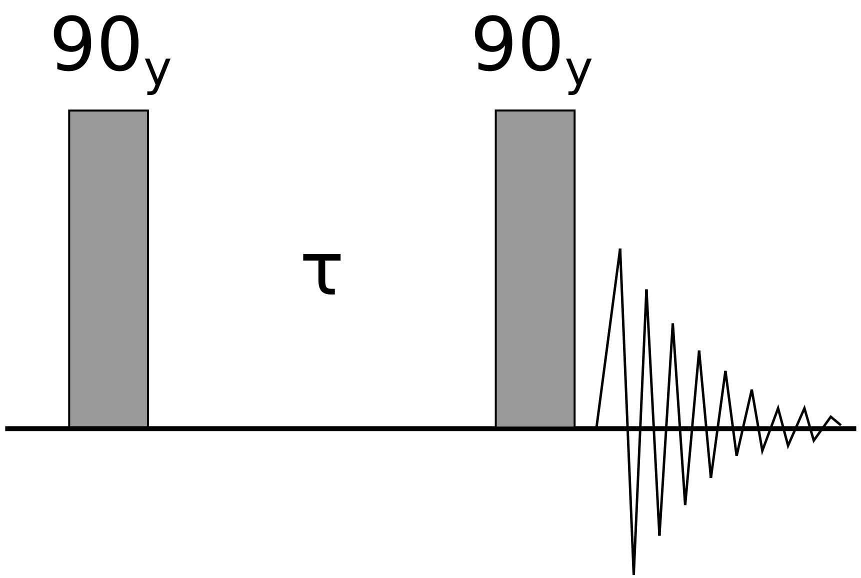


1-$\overline{1}$ sequence

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).



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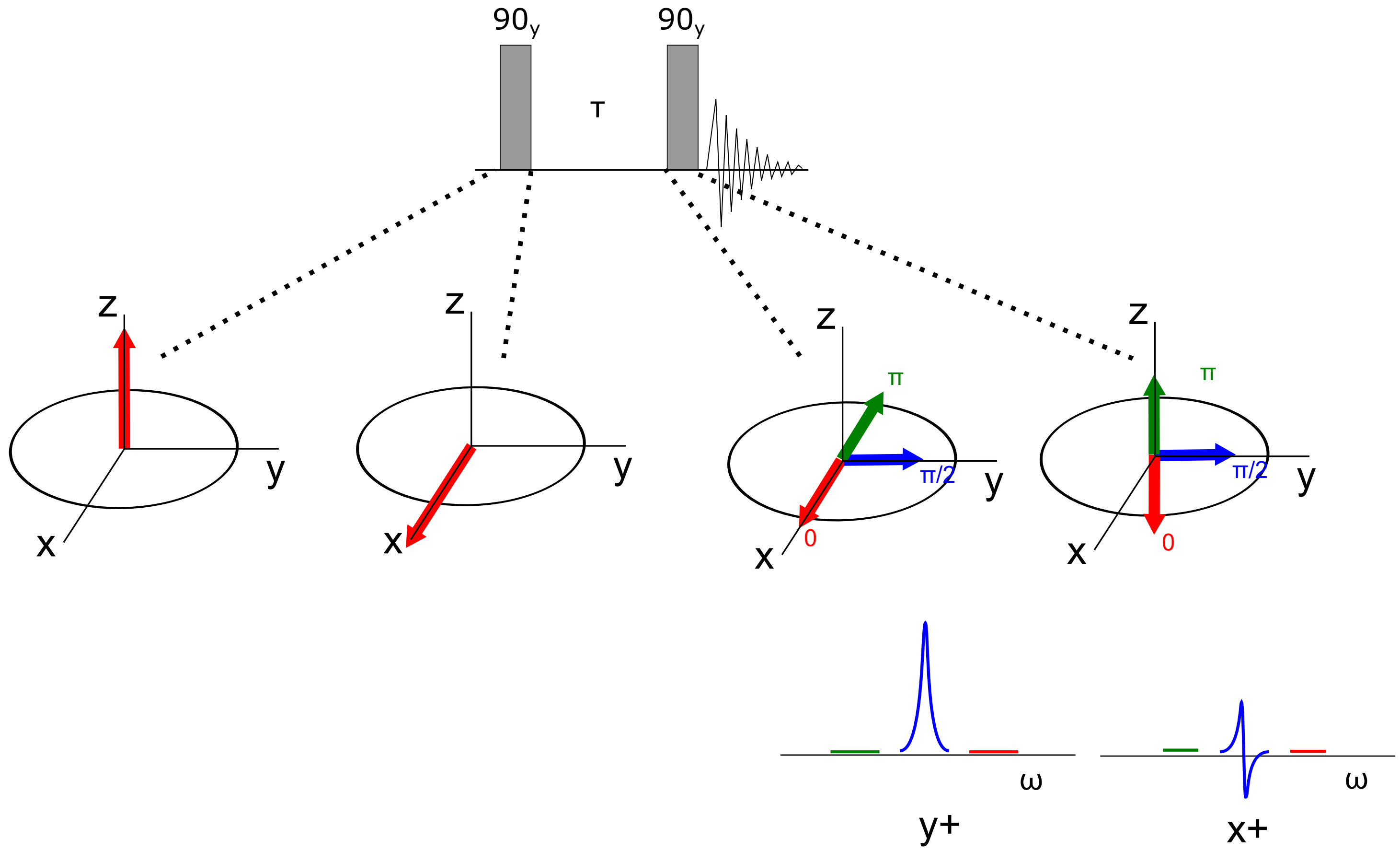
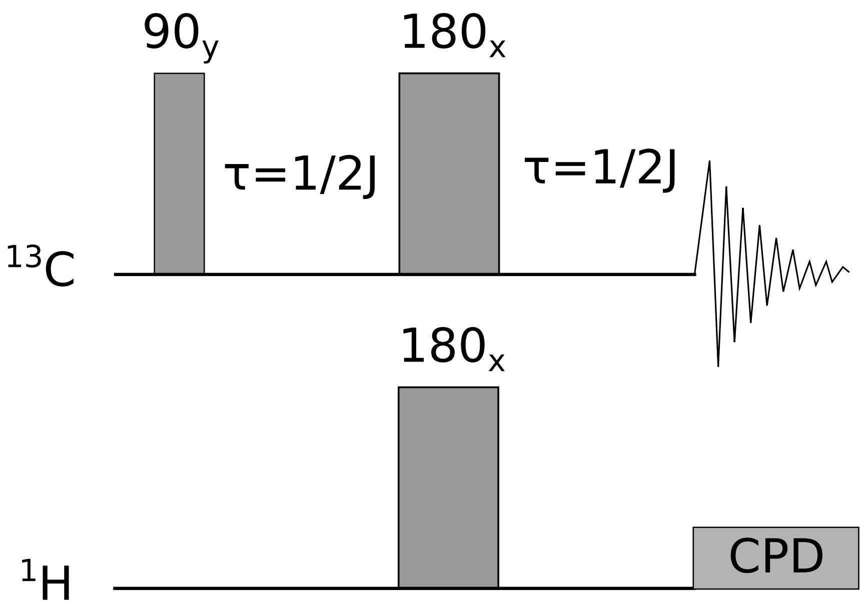


Heteronuclear spin echo

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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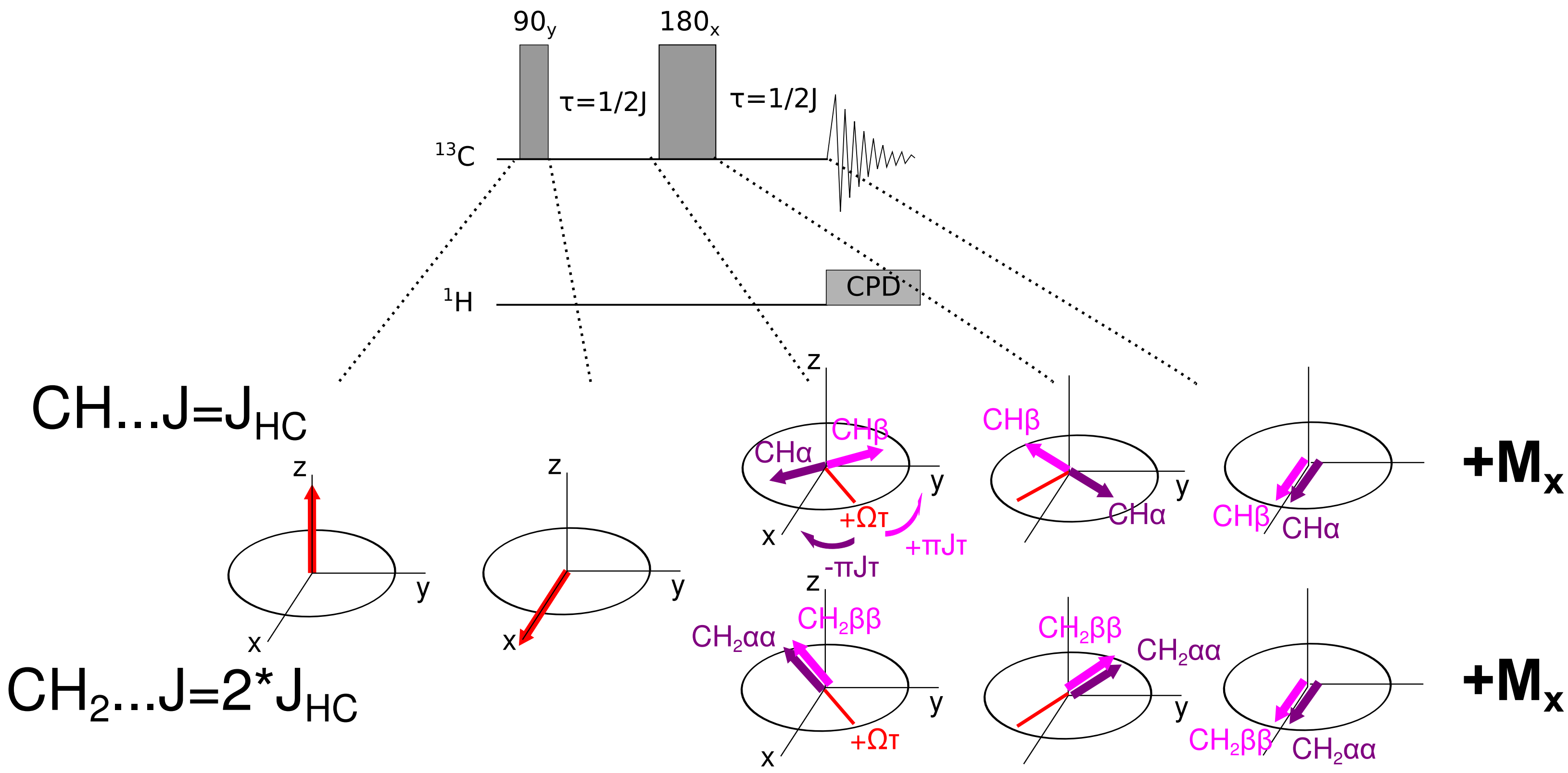

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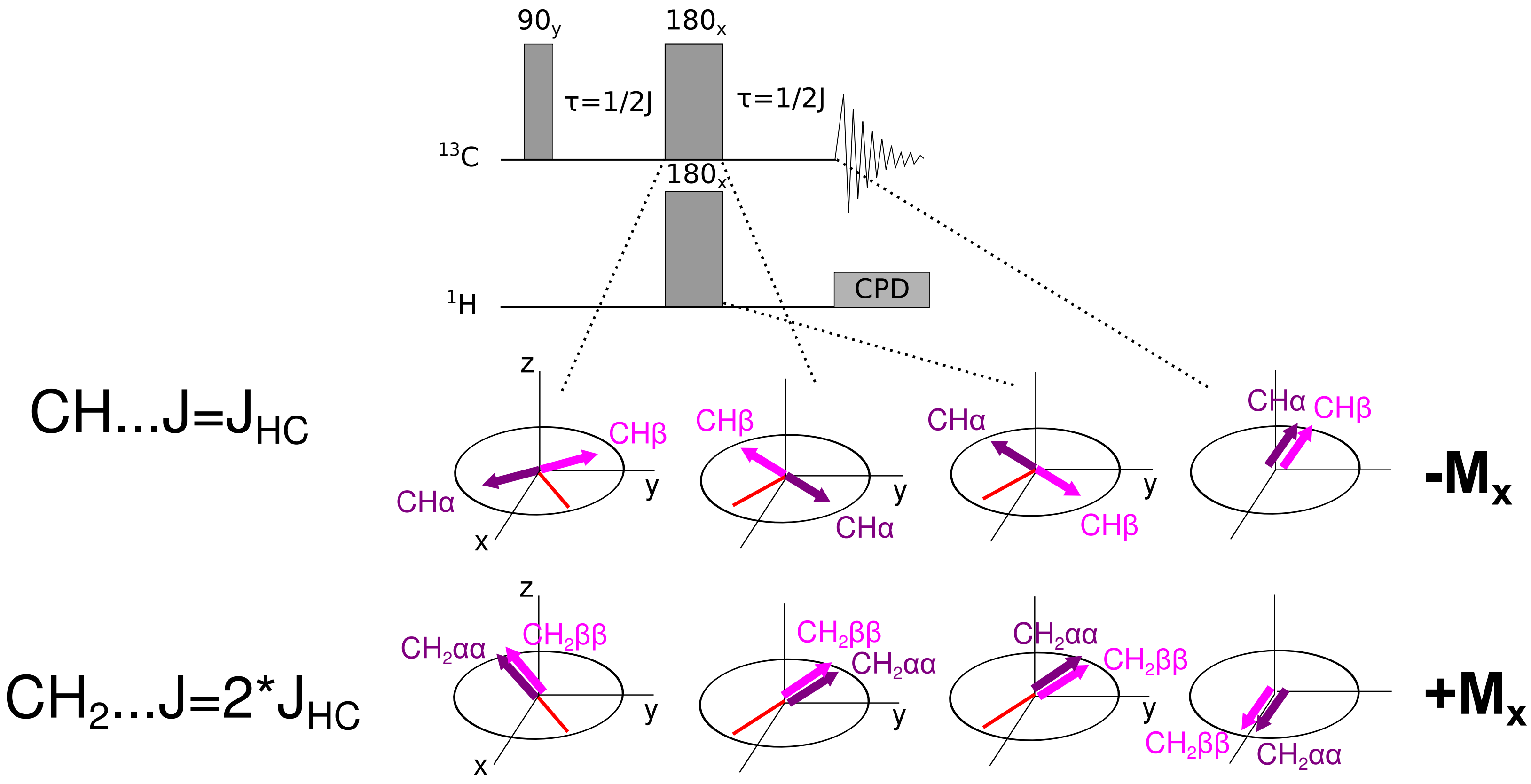


APT - Attached Proton Test

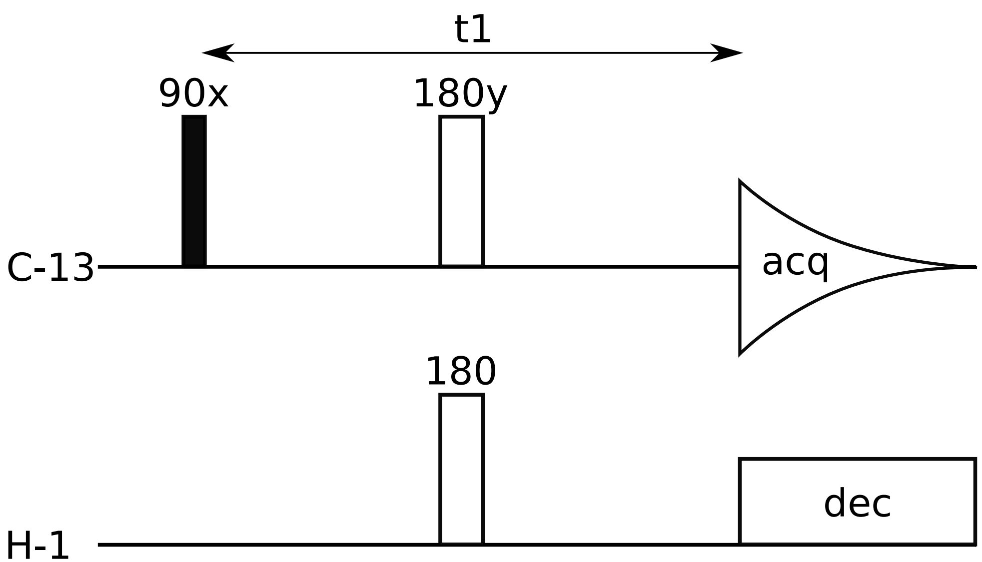
based on heteronuclear spin-echo

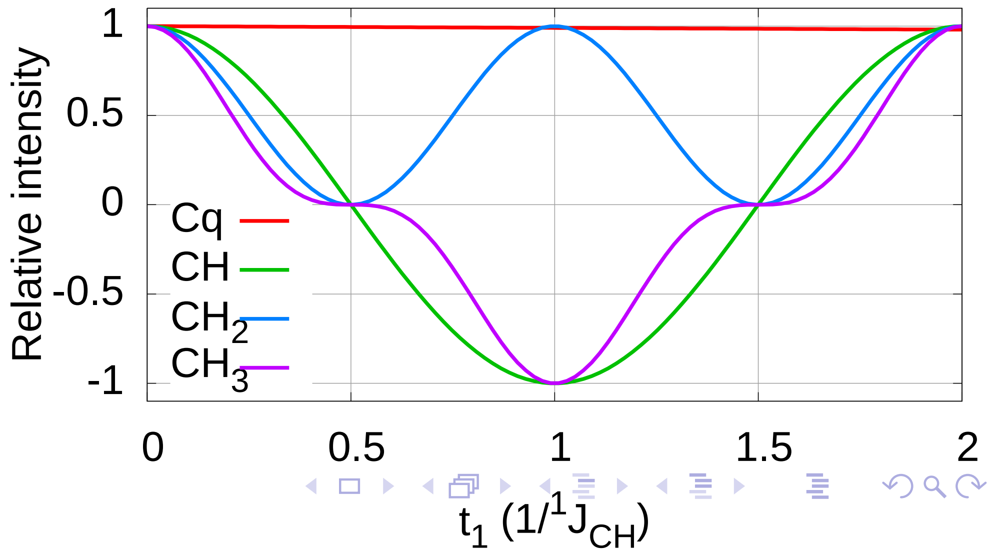
- $t_1 = 1/{}^1J_{CH}$

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

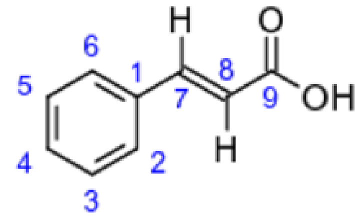
- Cq, CH_2 positive
- CH, CH_3 negative

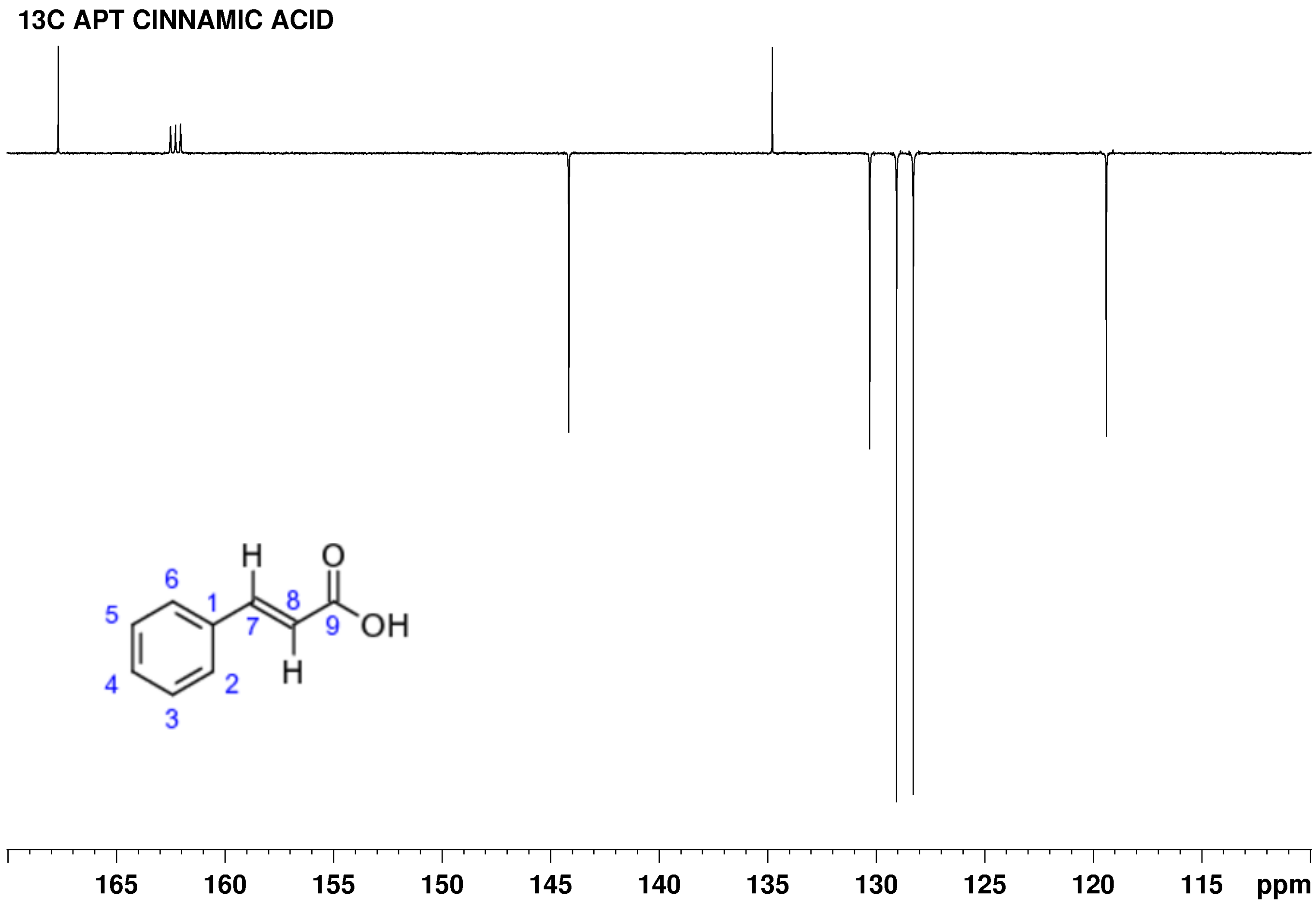
Different $^1J_{CH} \Longrightarrow$ different intensities





^{13}C APT Cinnamic acid





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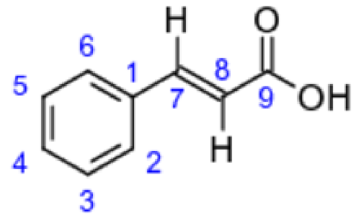
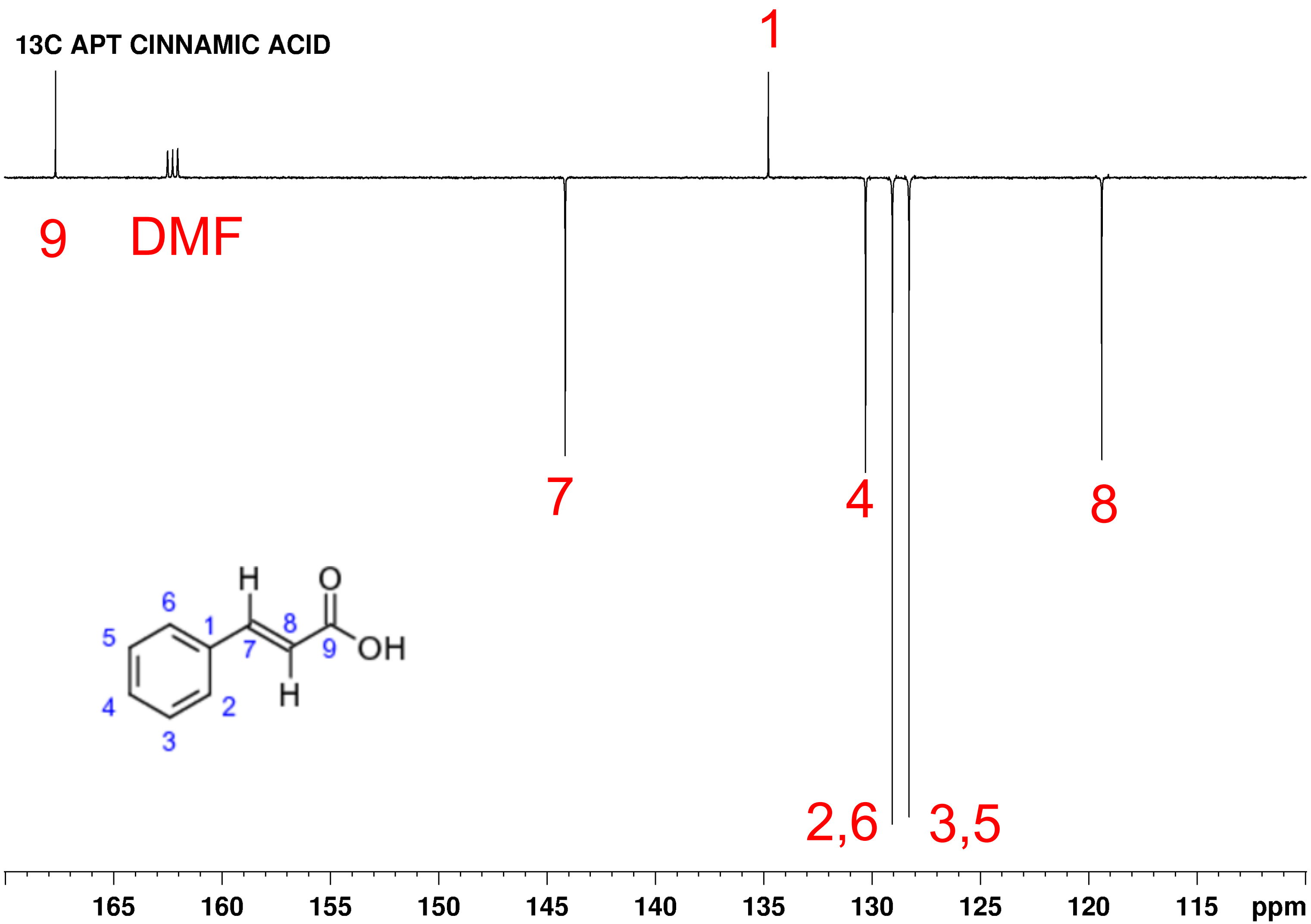
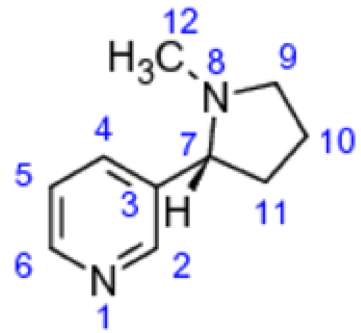
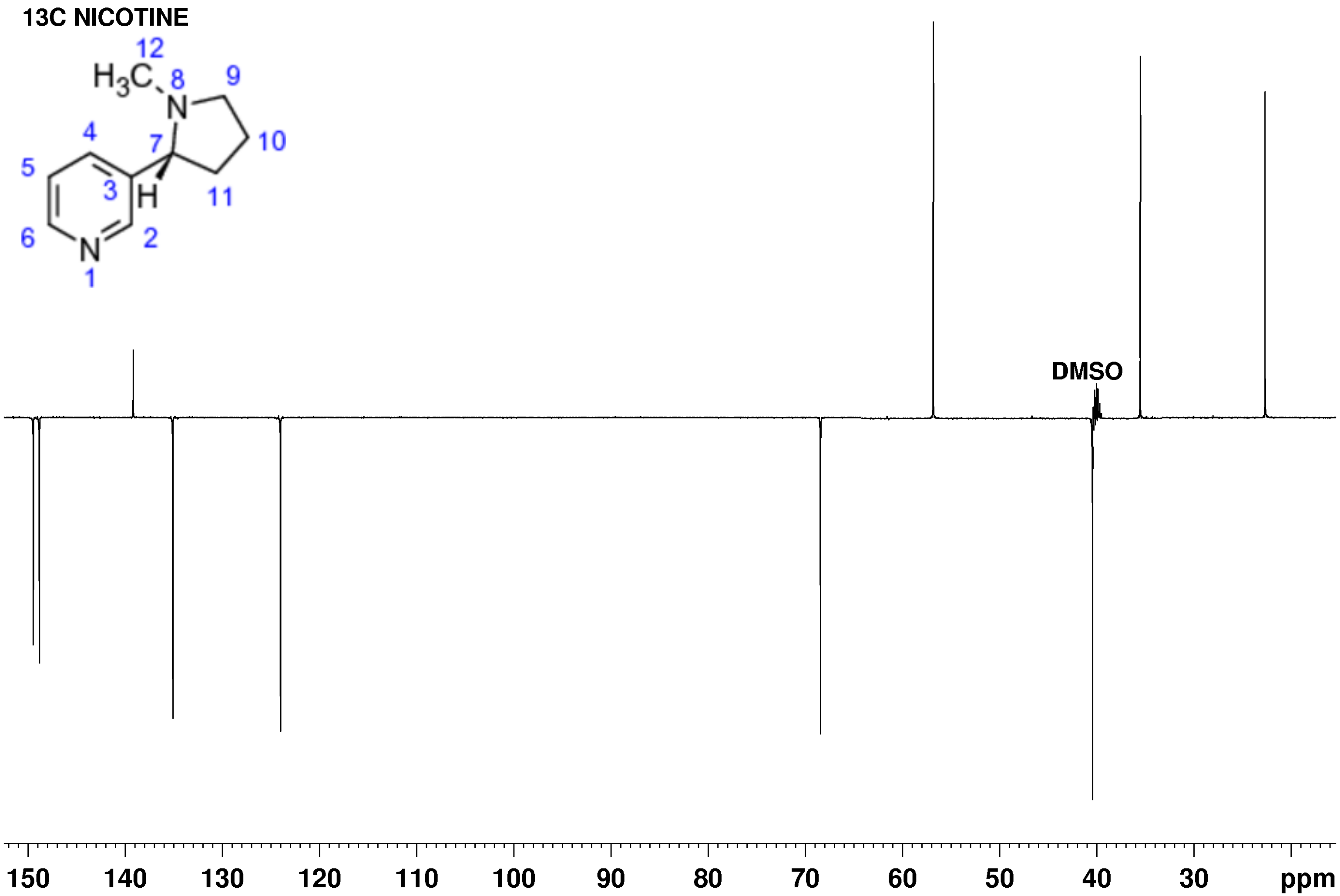




^{13}C APT Nicotine





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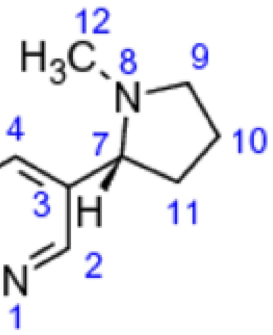
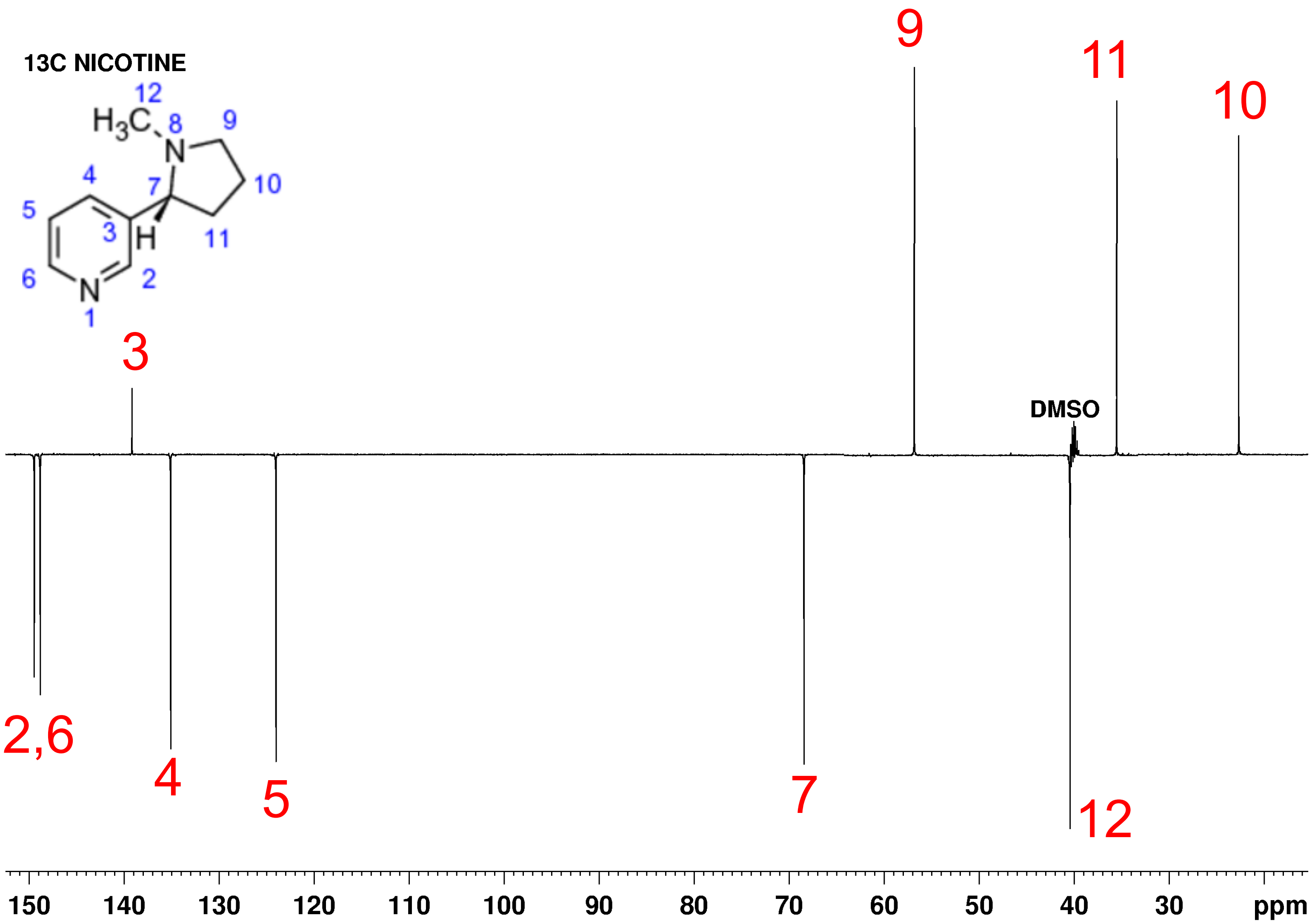
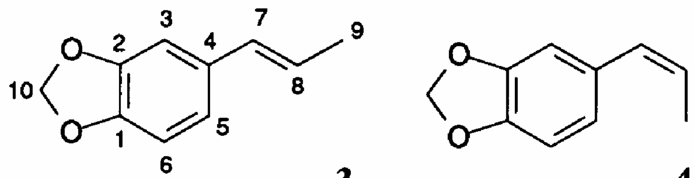




DEPT experiment



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?

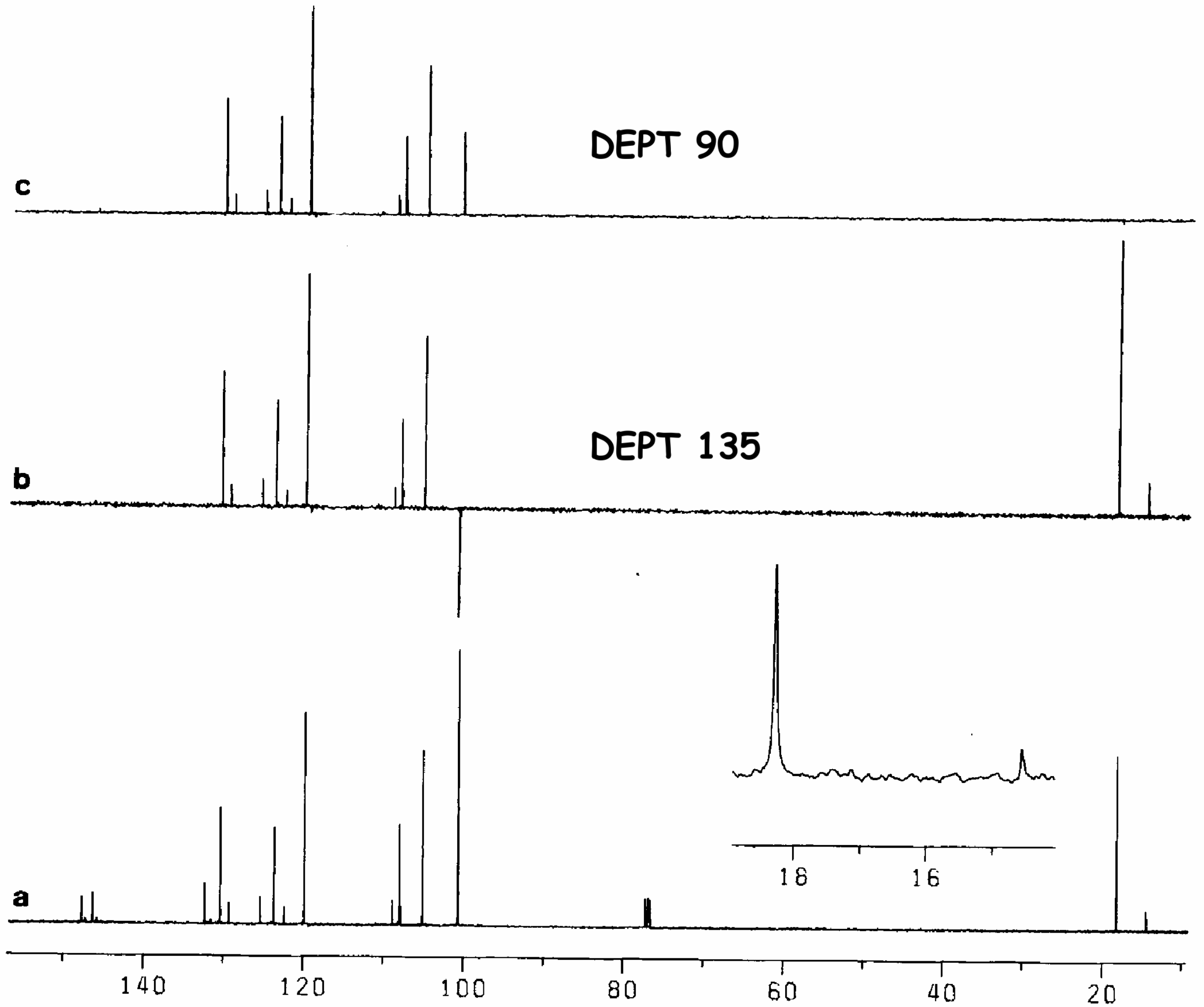


Fig. 3.3. (a) ^{1}H broad-band decoupled ^{13}C NMR spectrum of a mixture of **3** and **4** in $CDCl_3$. Traces (b) and (c) are DEPT spectra

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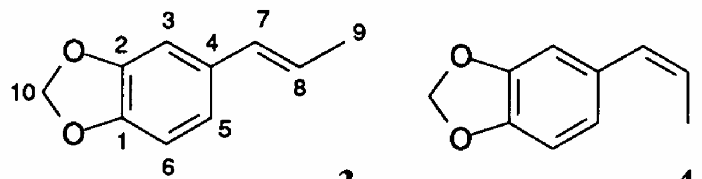

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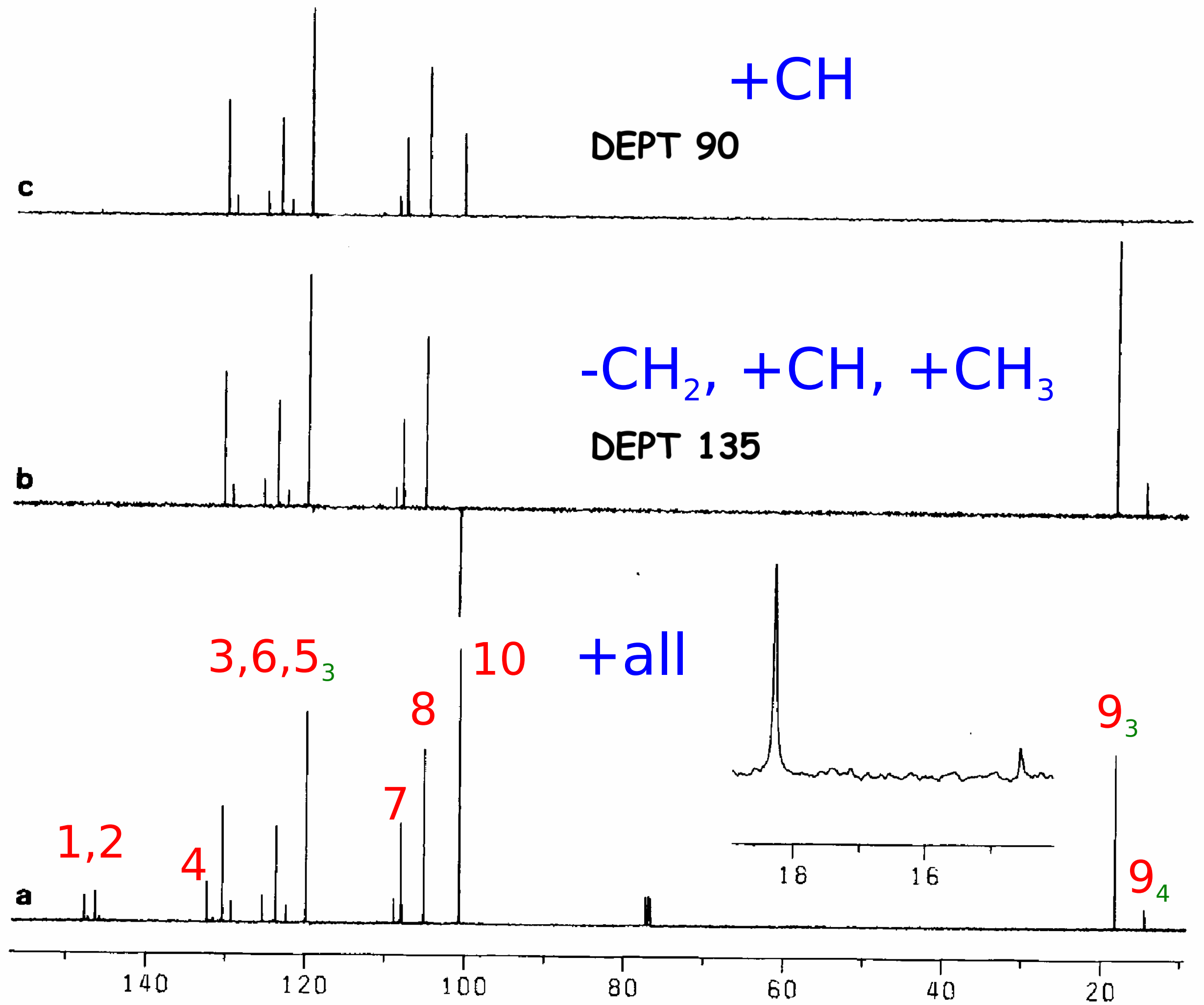

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Next topic

2D NMR - homonuclear experiments