

C8953

# NMR structural analysis - seminar

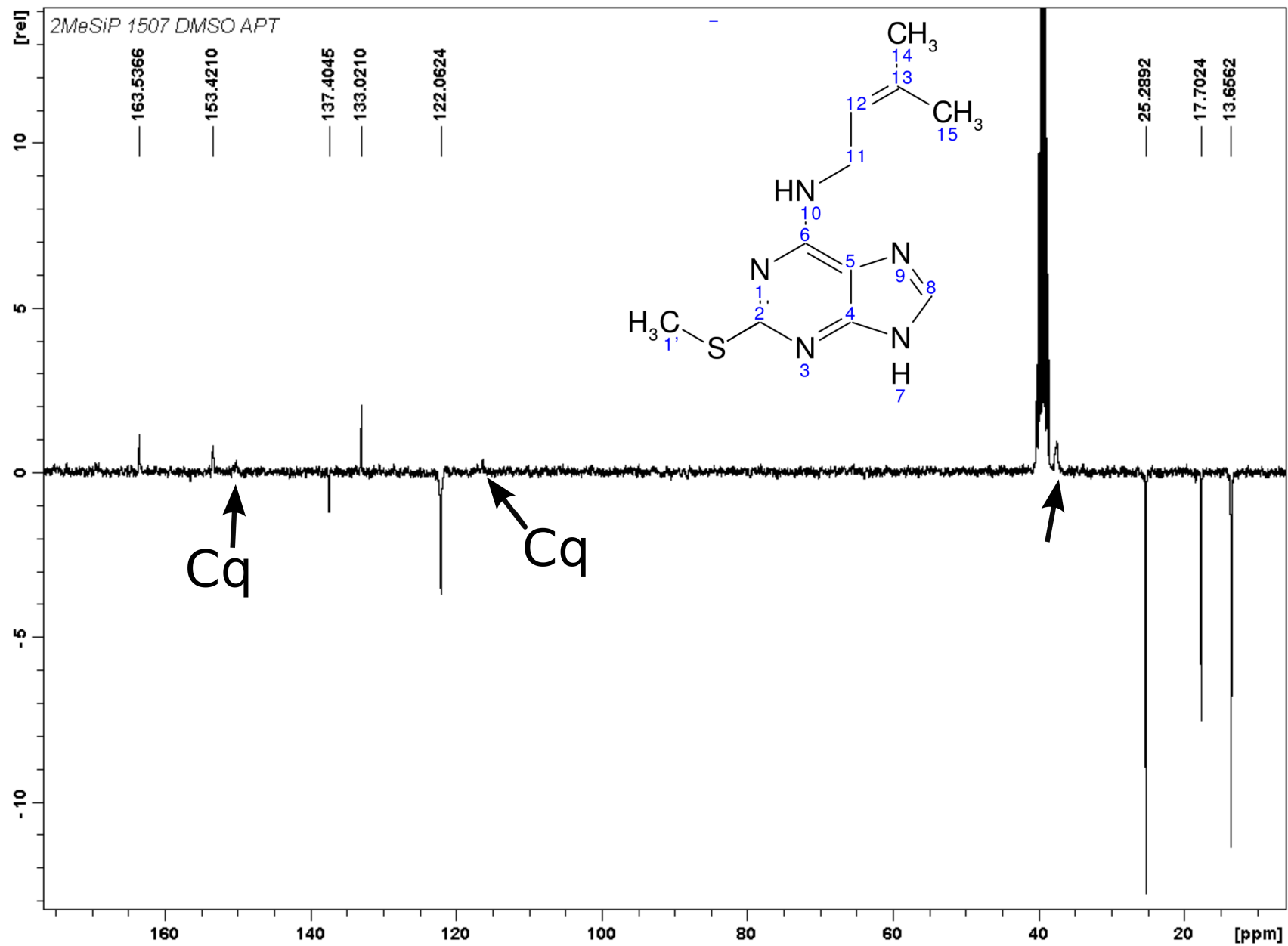
2D NMR spectra, COSY+TOCSY

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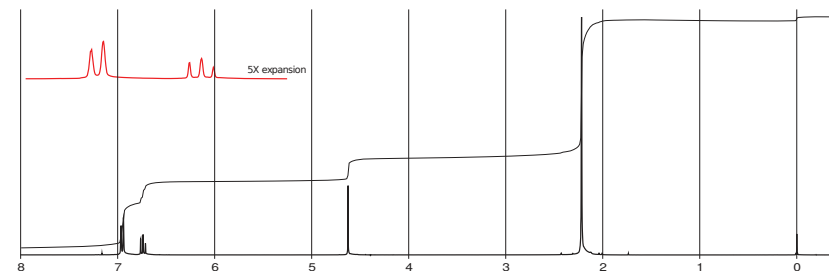
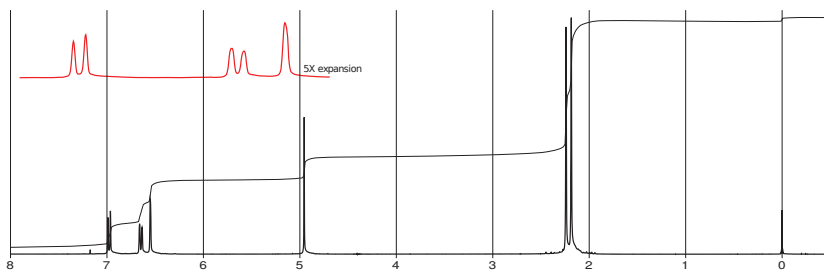
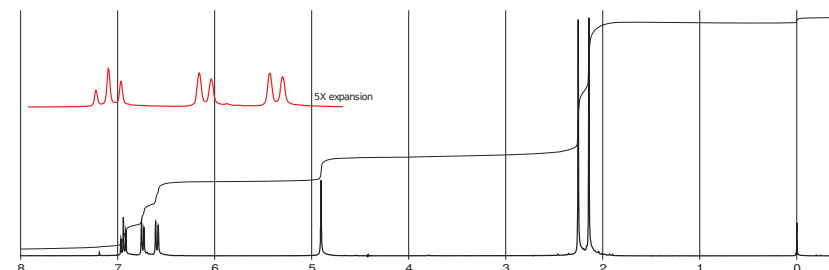
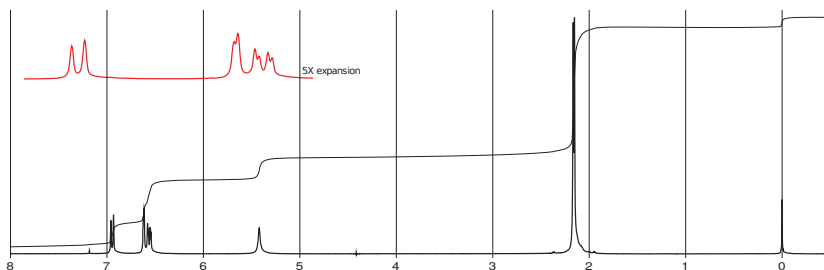
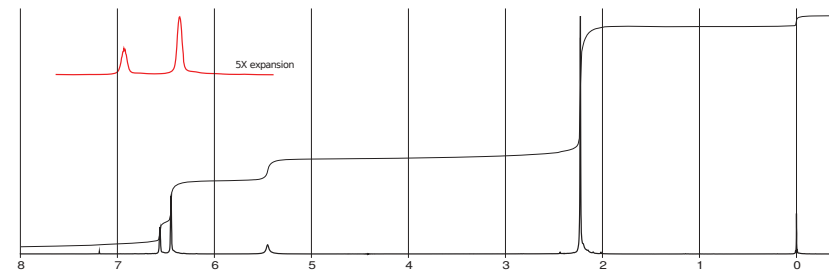
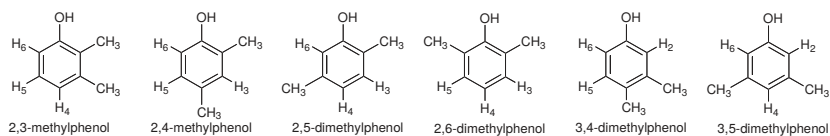
March 31, 2021

# $^{13}\text{C}$ APT



# Determination of regioisomers - note number of signals, splitting and $\delta$

300 MHz  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$

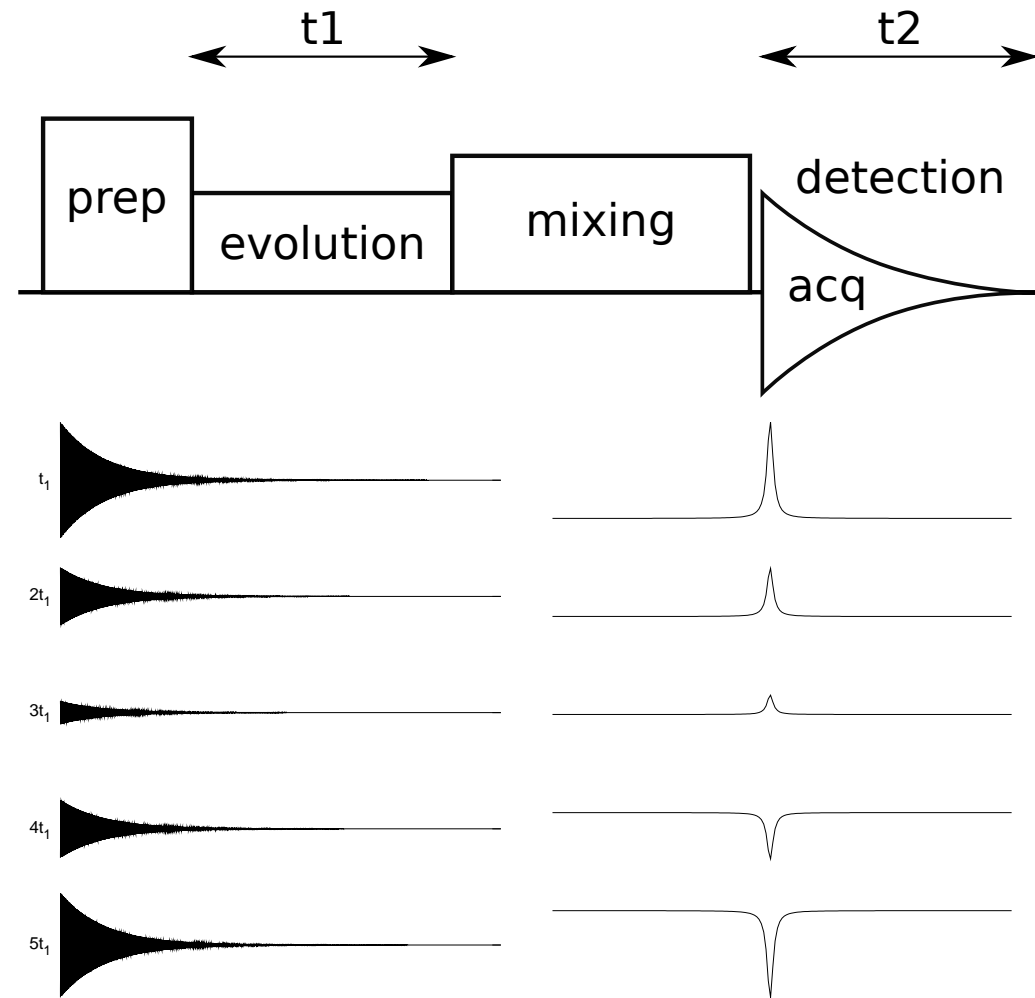


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# 2D NMR

## Second dimension $f_1$

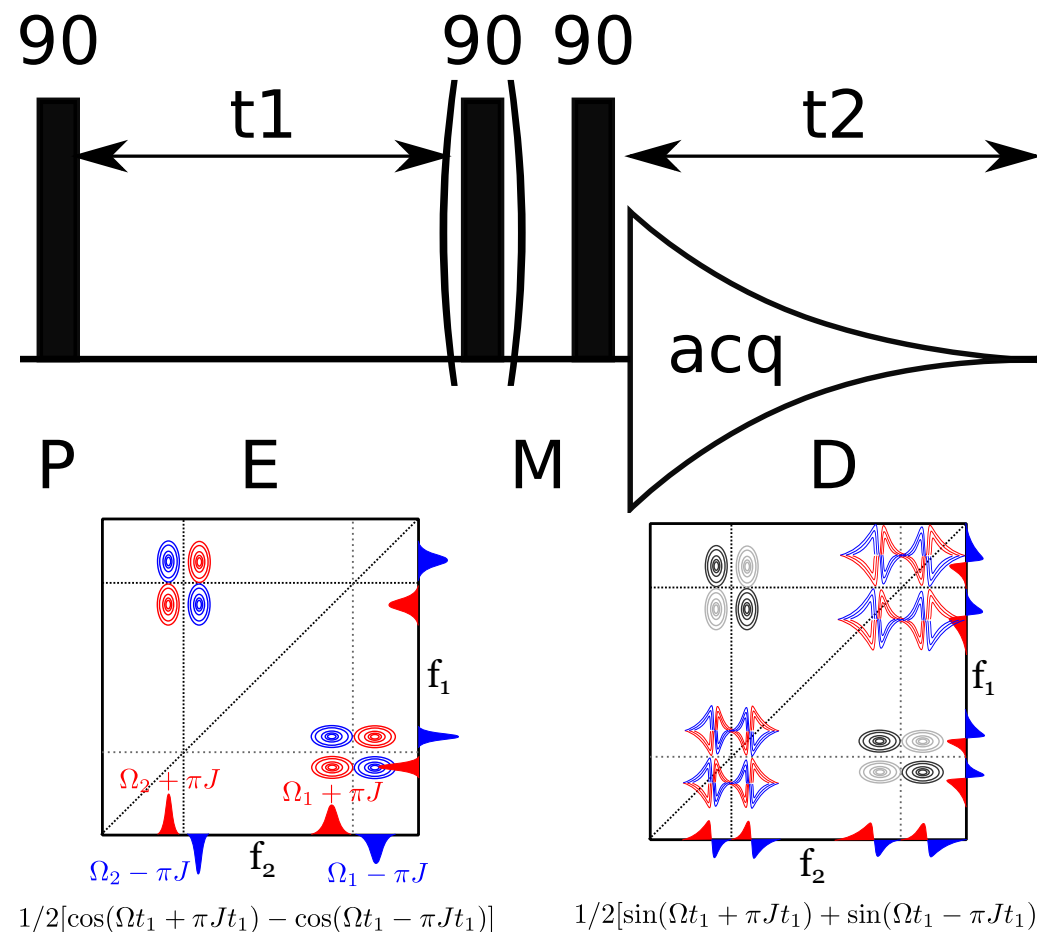
- ▶ preparation period  
⇒ coherence
- ▶ evolution period  
 $t_1 \xrightarrow{\text{FT}} f_1$ 
  - ▶ increments
  - ▶ evolution of coherence
- ▶ mixing period
  - ▶ transfer of encoded magnetisation
  - ▶ measurable signal
- ▶ detection of signal  
 $t_2 \xrightarrow{\text{FT}} f_2$





# COSY

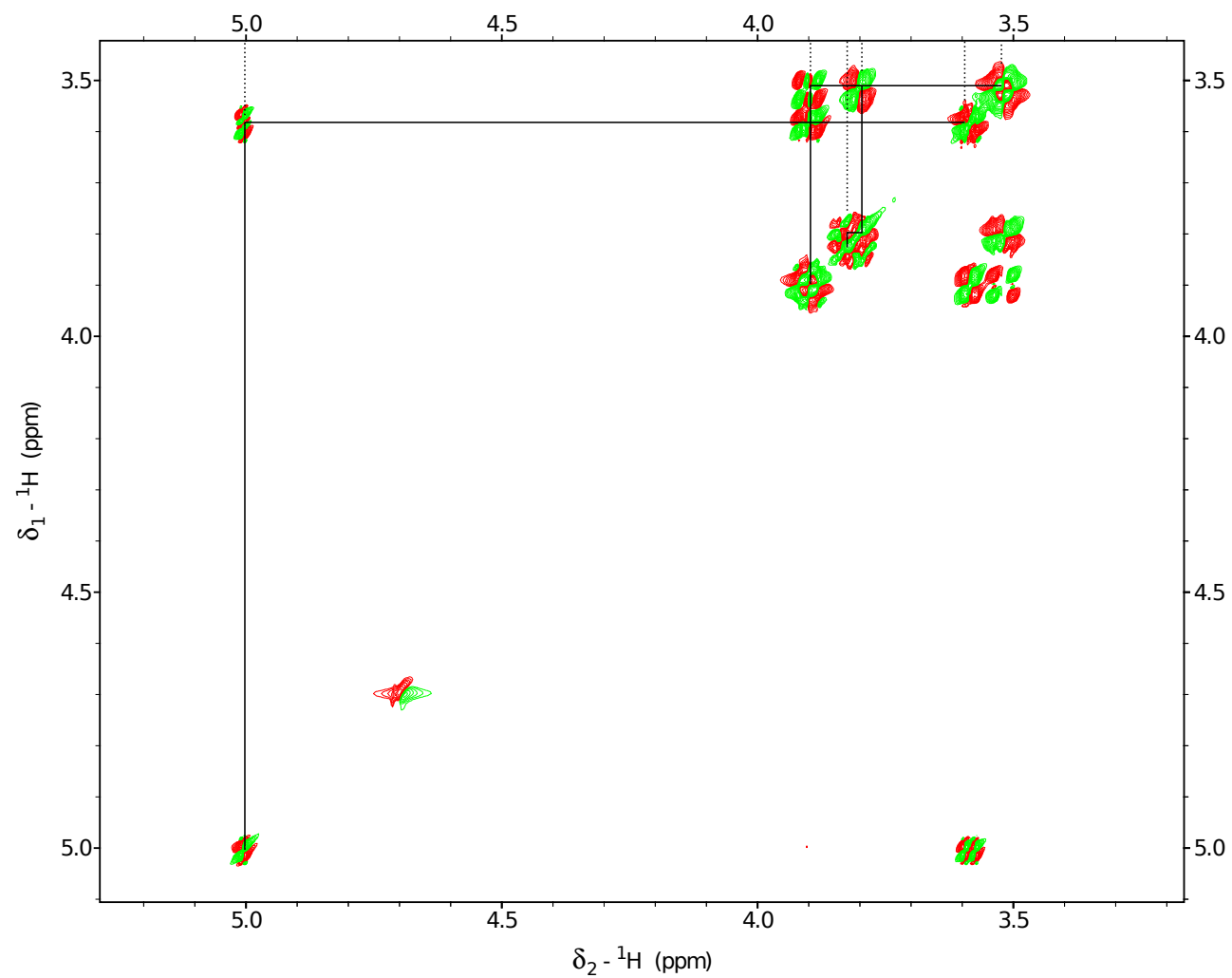
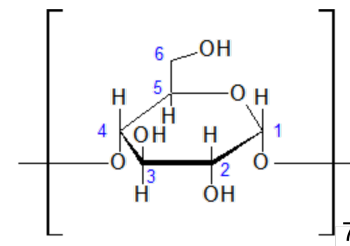
- ▶ easiest 2D experiment
- ▶ **correlates H nuclei based on  $^2/3 J$  coupling**
- ▶ through 2, 3, (4) bonds
- ▶ antiphase off-diagonal crosspeak between coupled atoms
- ▶ DQF-COSY - modification of basic sequence, diagonal crosspeaks in absorption phase



# Hints for beginners

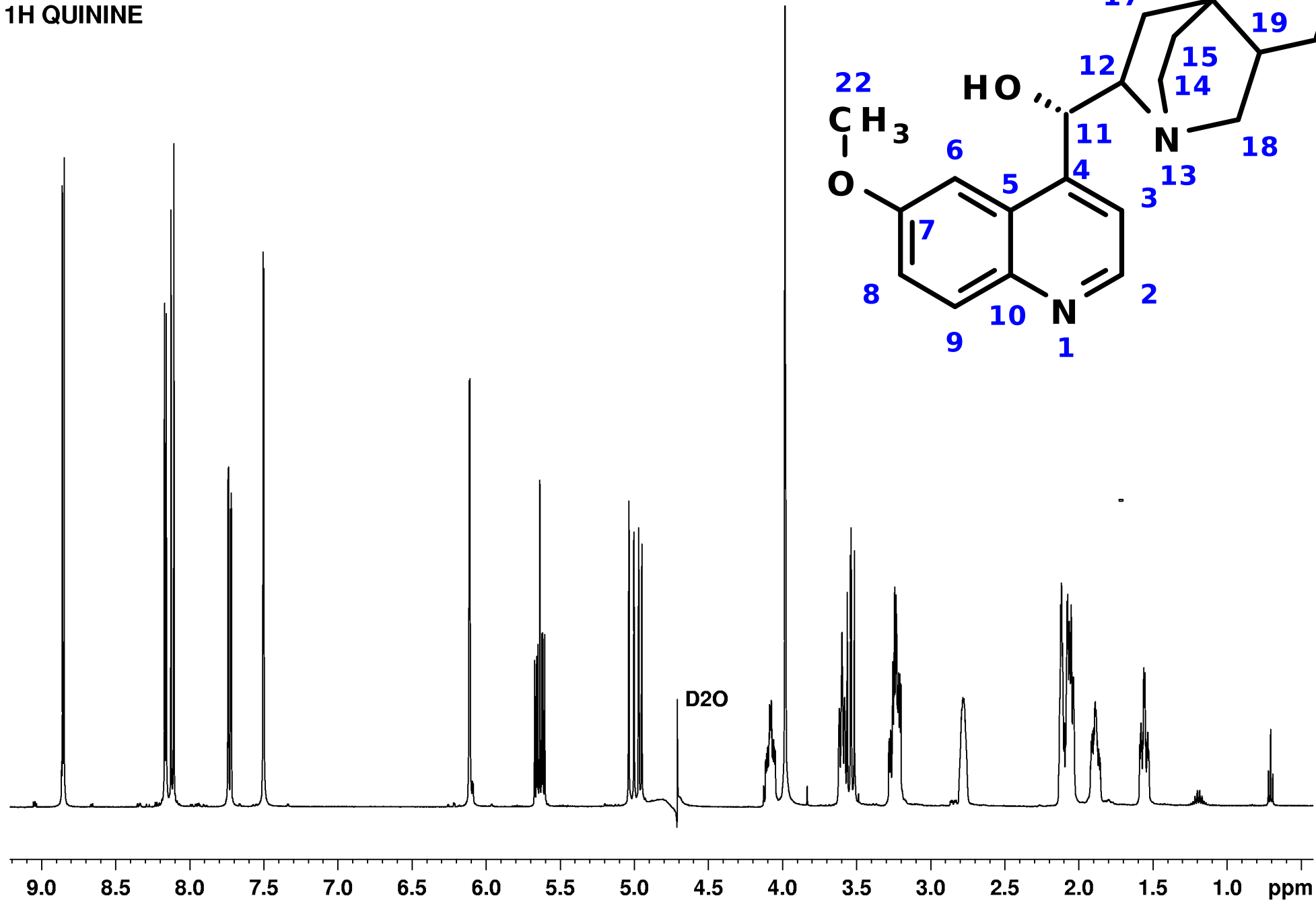
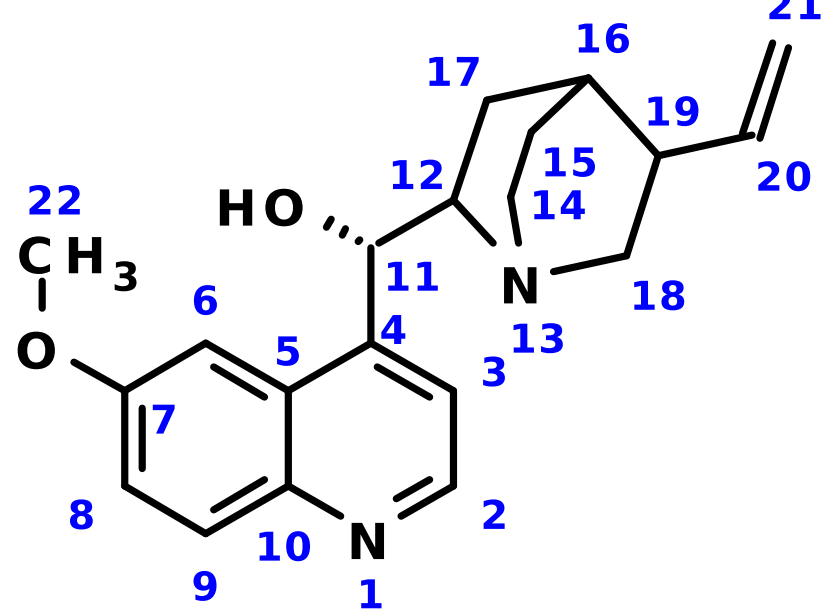
- ▶ Determination of **individual spin systems** - sharing **off-diagonal crosspeaks**
- ▶ Isolated protons - only diagonal crosspeak
- ▶ Already known rules: symmetry, diastereotopicity, most shielded/deshielded atoms etc.

# COSY : $\beta$ -cyclodextrine

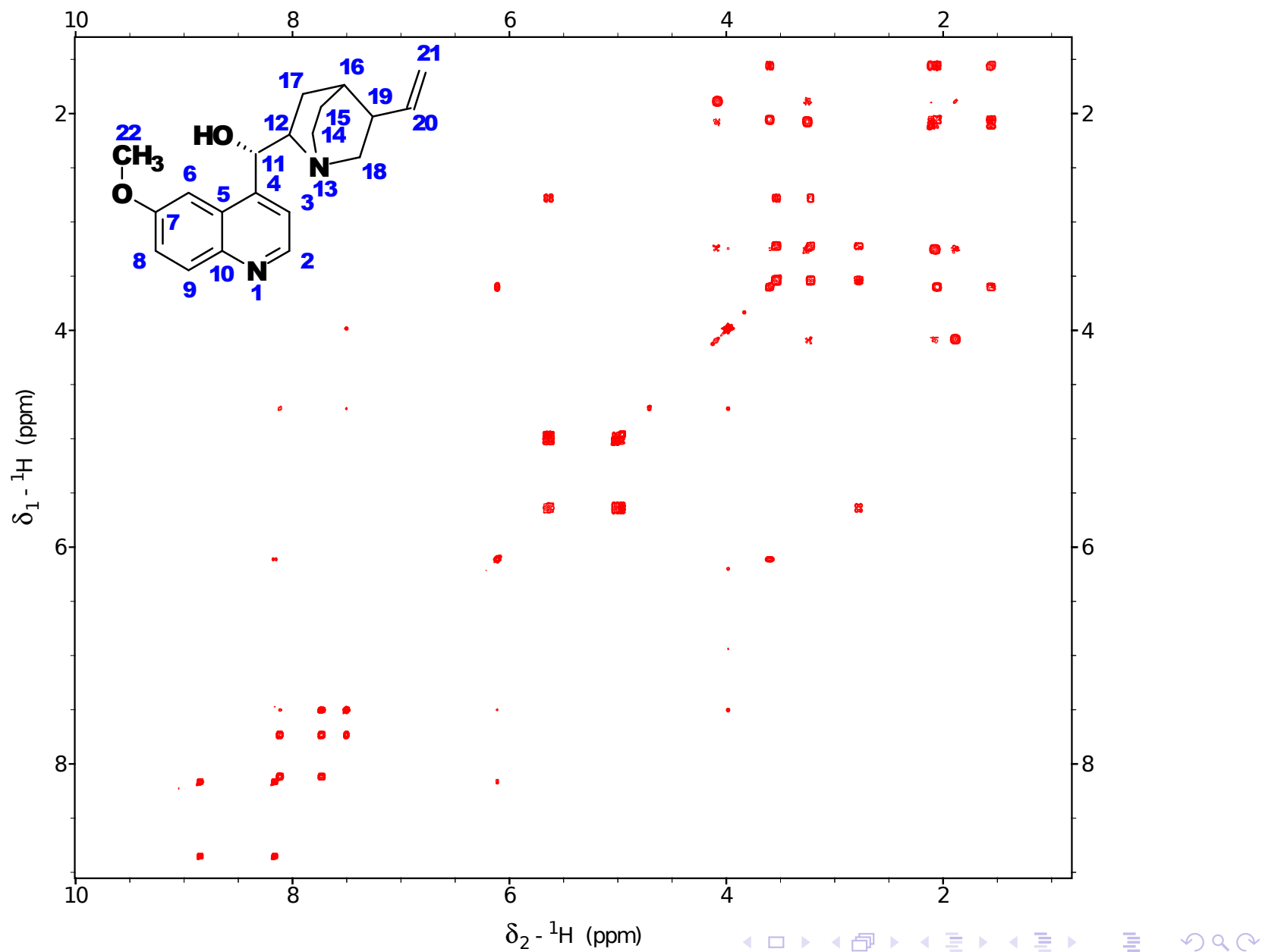




# 1H QUININE



# COSY - Chinin

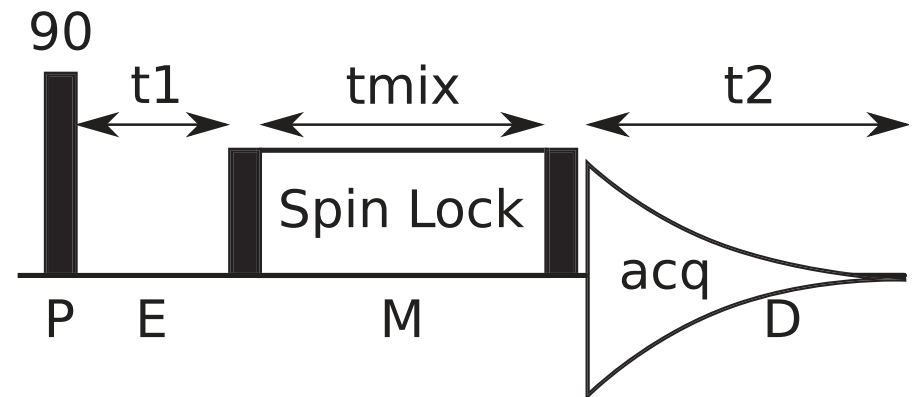




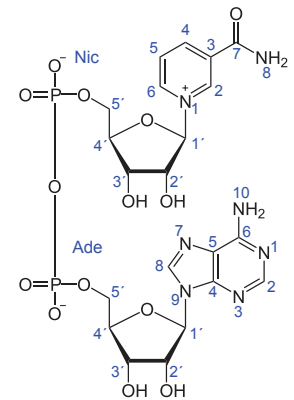
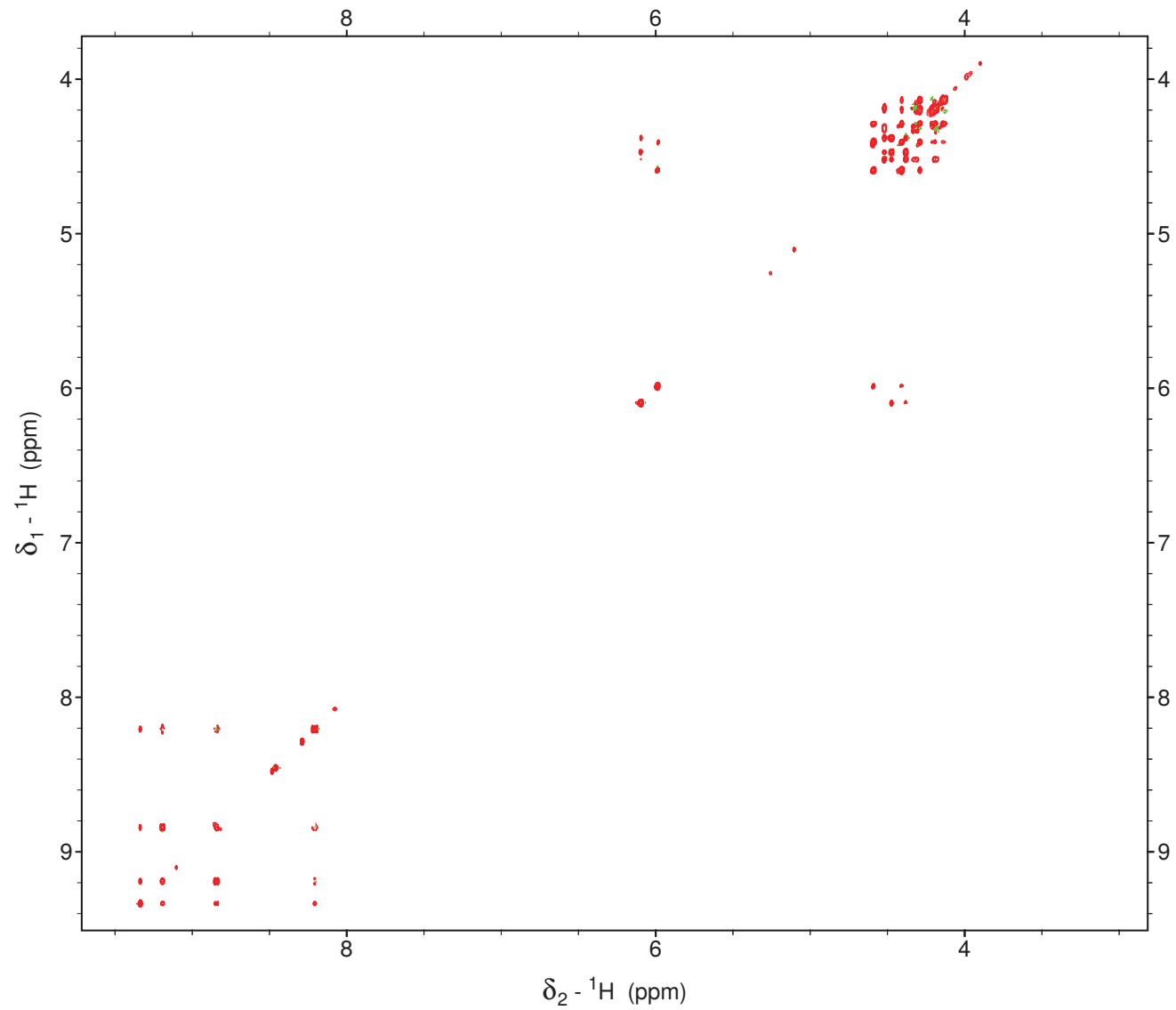
# TOCSY (TOtal Correlation SpectroscopY)

spin lock - isotropic mixing

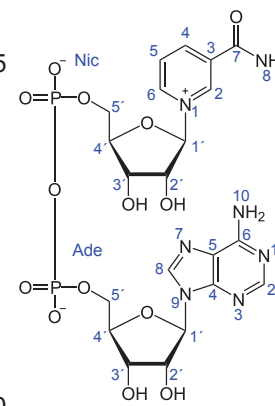
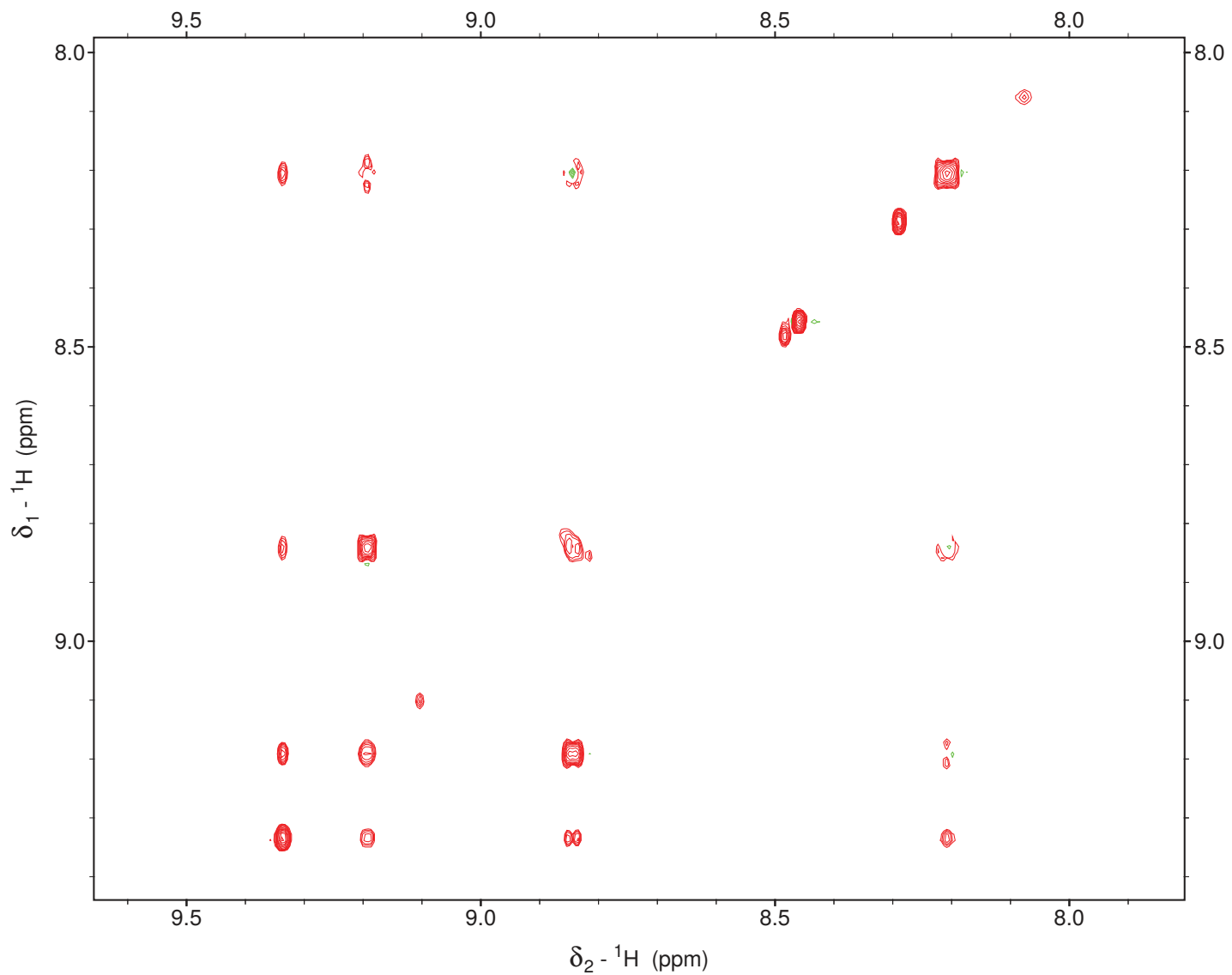
- ▶ series of short  $180^\circ$  pulses
- ▶ "lock-in" of spins in transversal plane
- ▶ higher power in case of TOCSY, offset set into the middle (on resonance)
- ▶ smaller power in case of ROESY, offset set into the edge (off resonance)
- ▶ crosstalk (ROE transfer in TOCSY,  $J$ -coupling in ROESY)



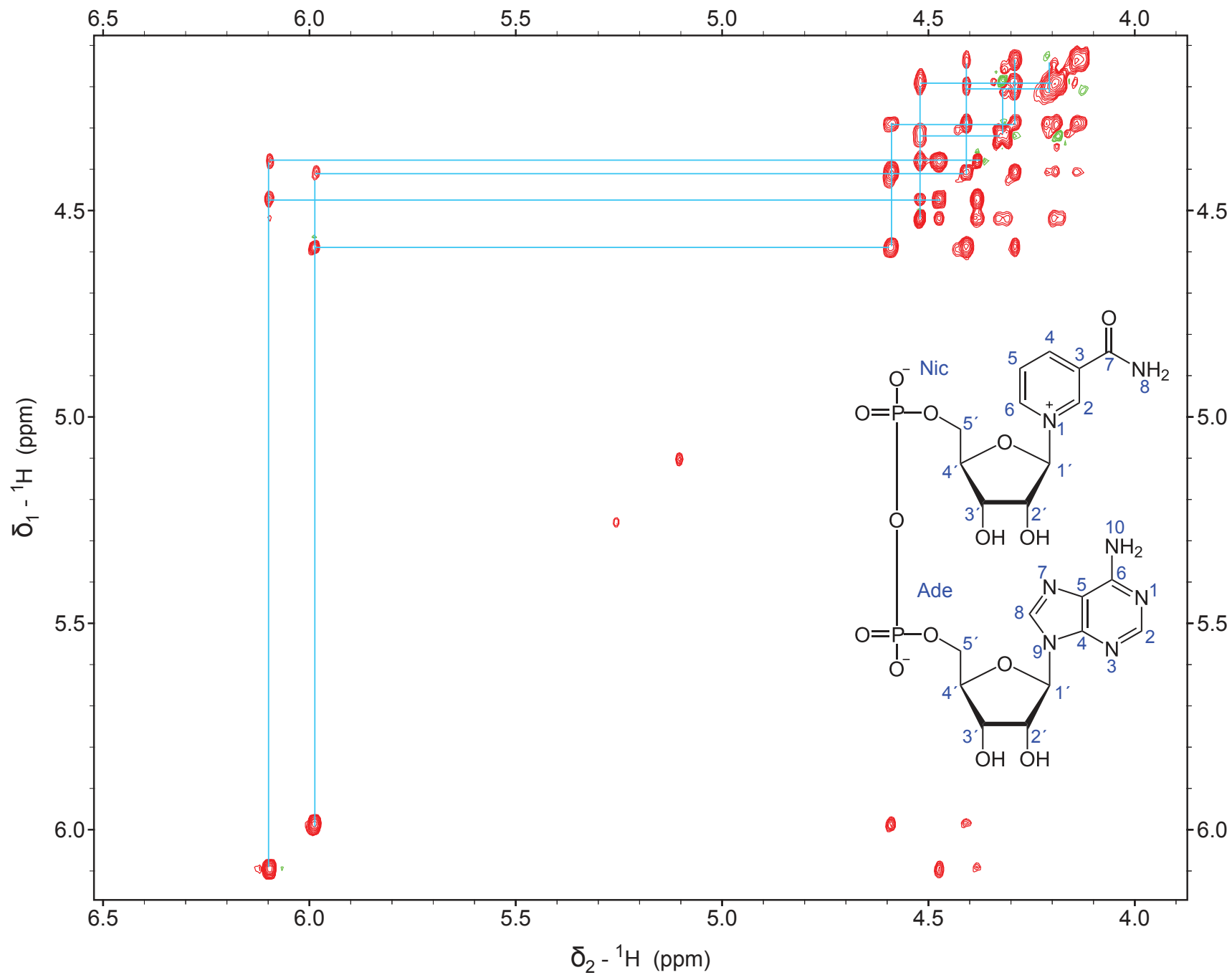
# NAD<sup>+</sup>: TOCSY (40ms)



# NAD<sup>+</sup>: TOCSY (40ms), detail of aromatics



# NAD<sup>+</sup>: TOCSY (40ms), detail of aliphatics



# Next topic

$^1\text{H}$ - $^1\text{H}$  through space correlations (NOESY, ROESY)