C8953
NMR strukturní analýza
seminář

TOCSY & ROESY

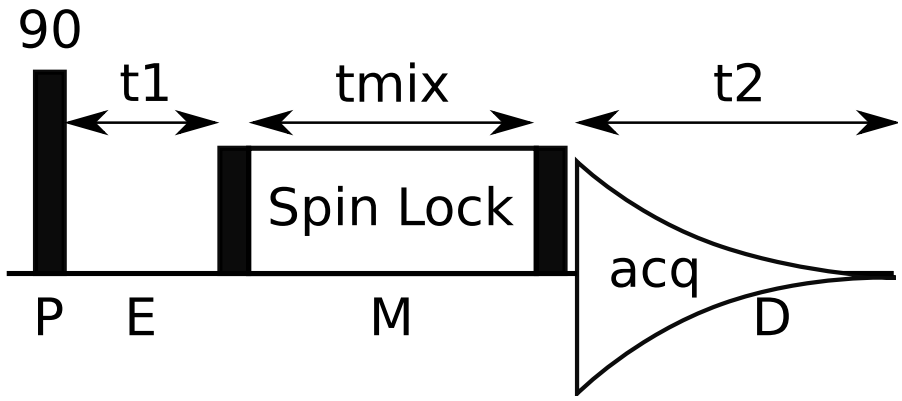
Jan Novotný
176003@is.muni.cz

April 3, 2019

TOCSY (TOtal Correlation SpectroscopY)

spin lock - isotropic mixing

- series of short 180° 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)



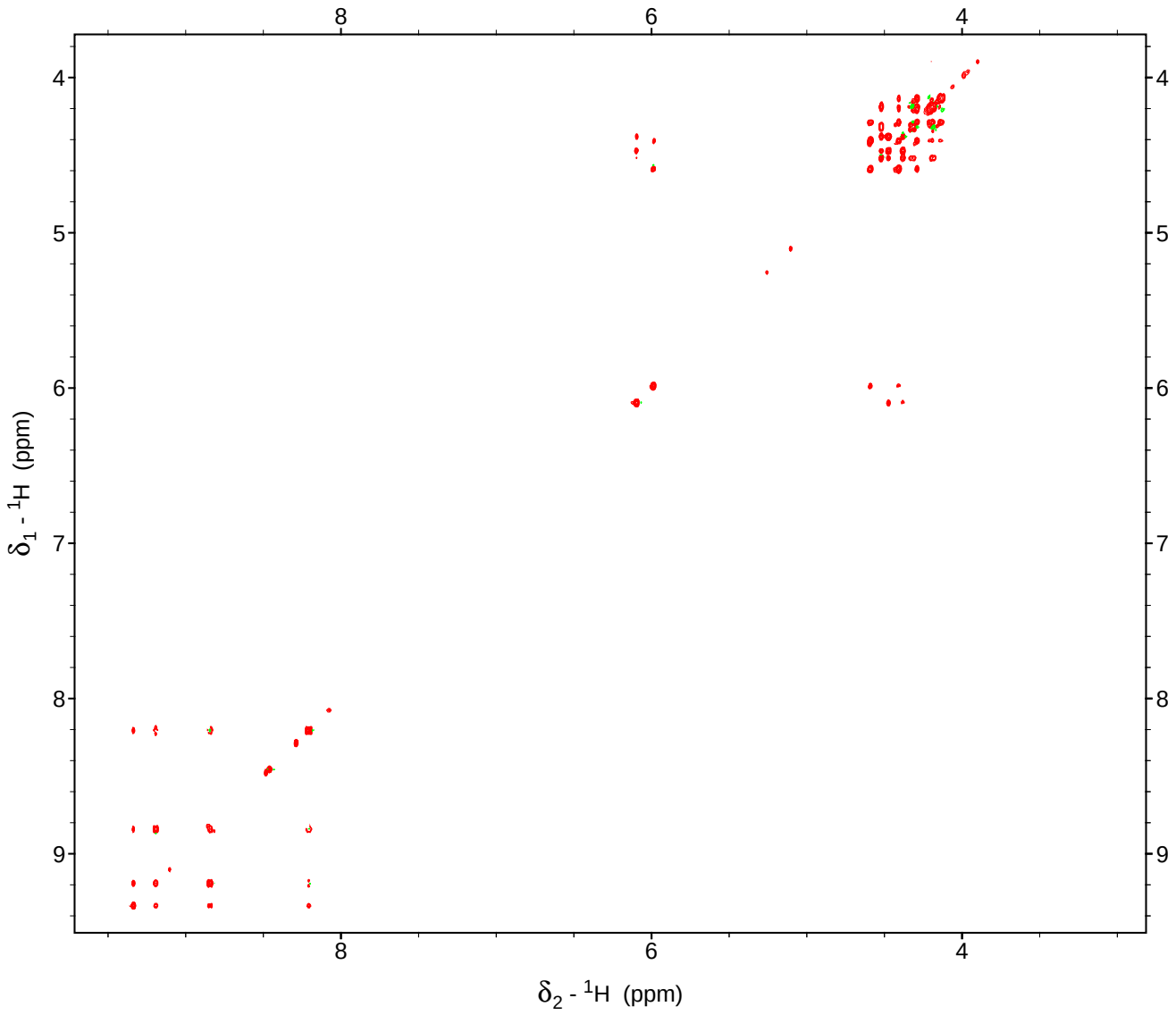
TOCSY (TOtal Correlation SpectroscopY)

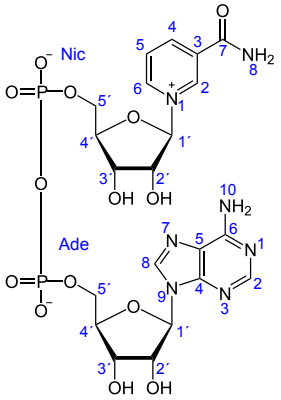
correlation based on J

- mutual correlation of all protons in one spin system
- $\tau_{mix} \approx$ 20 - 120ms
- crosspeak intensity depends on τ_{mix} a J value

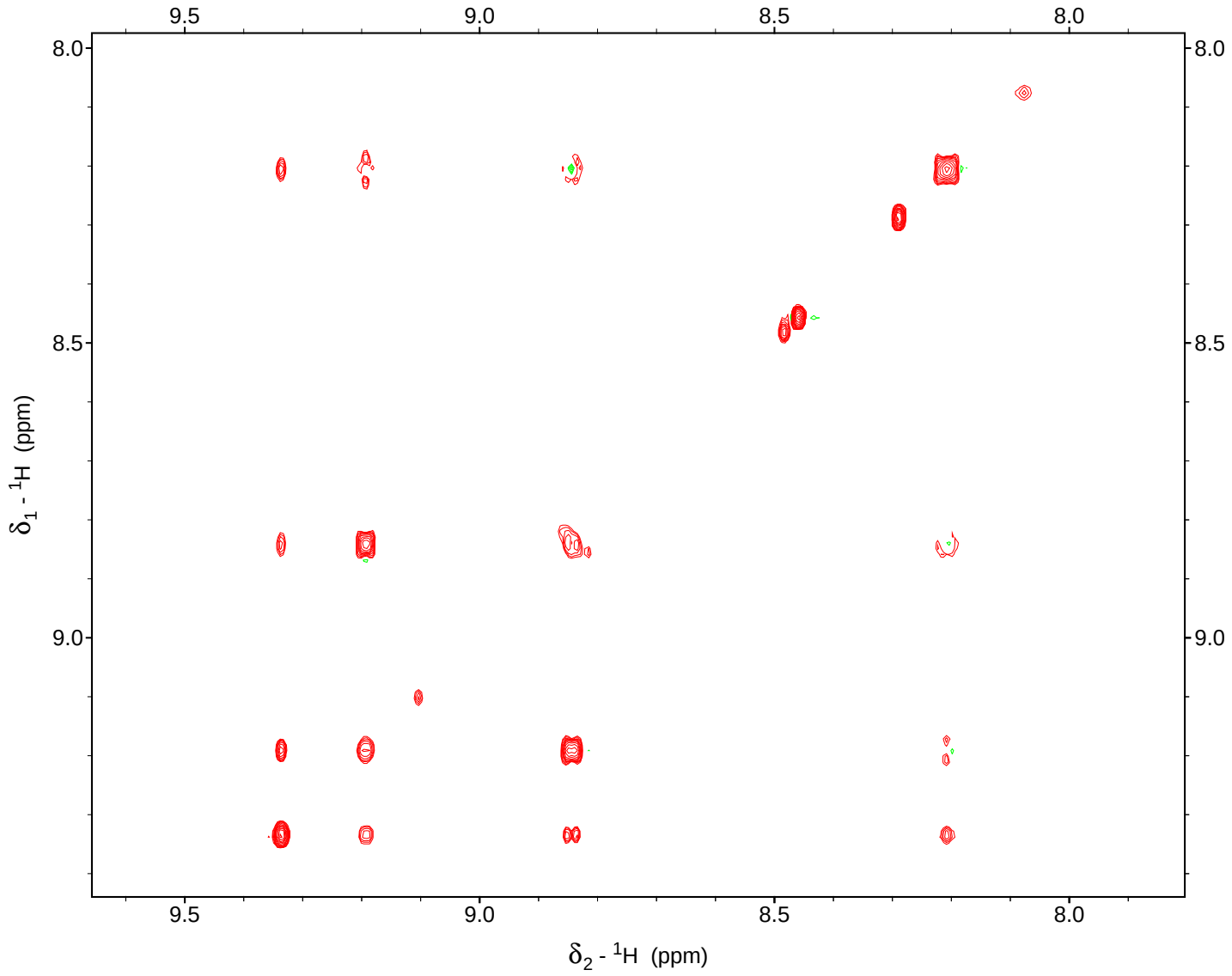
$$H_A \overset{J_{AB}}{\Longleftrightarrow} H_B \overset{J_{BC}}{\Longleftrightarrow} H_C \overset{J_{CD}}{\Longleftrightarrow} H_D$$

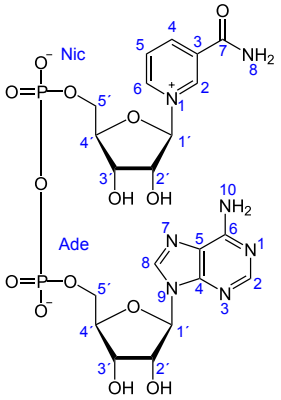
NAD^+: TOCSY (40ms)



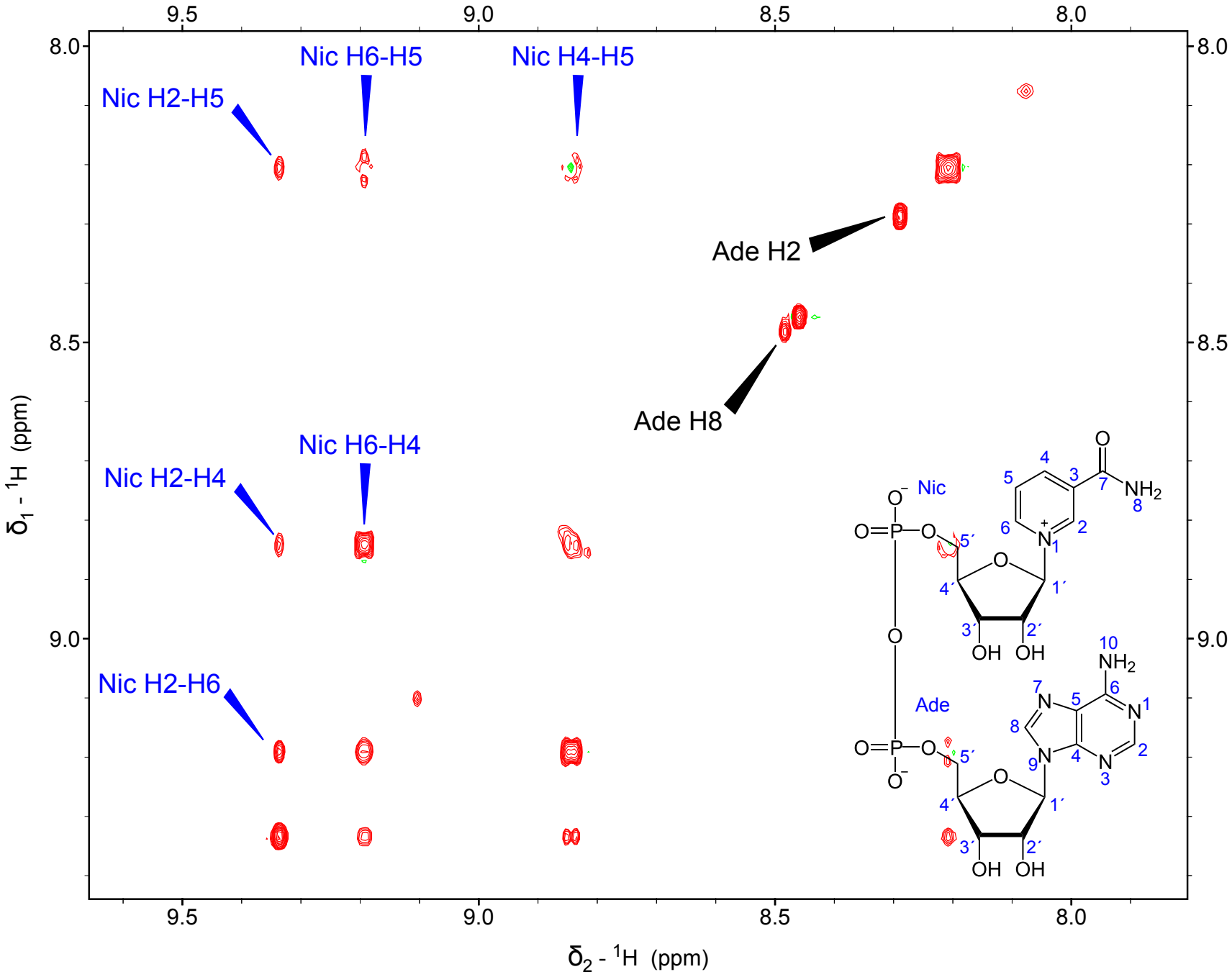


NAD^+: TOCSY (40ms), detail of aromatics

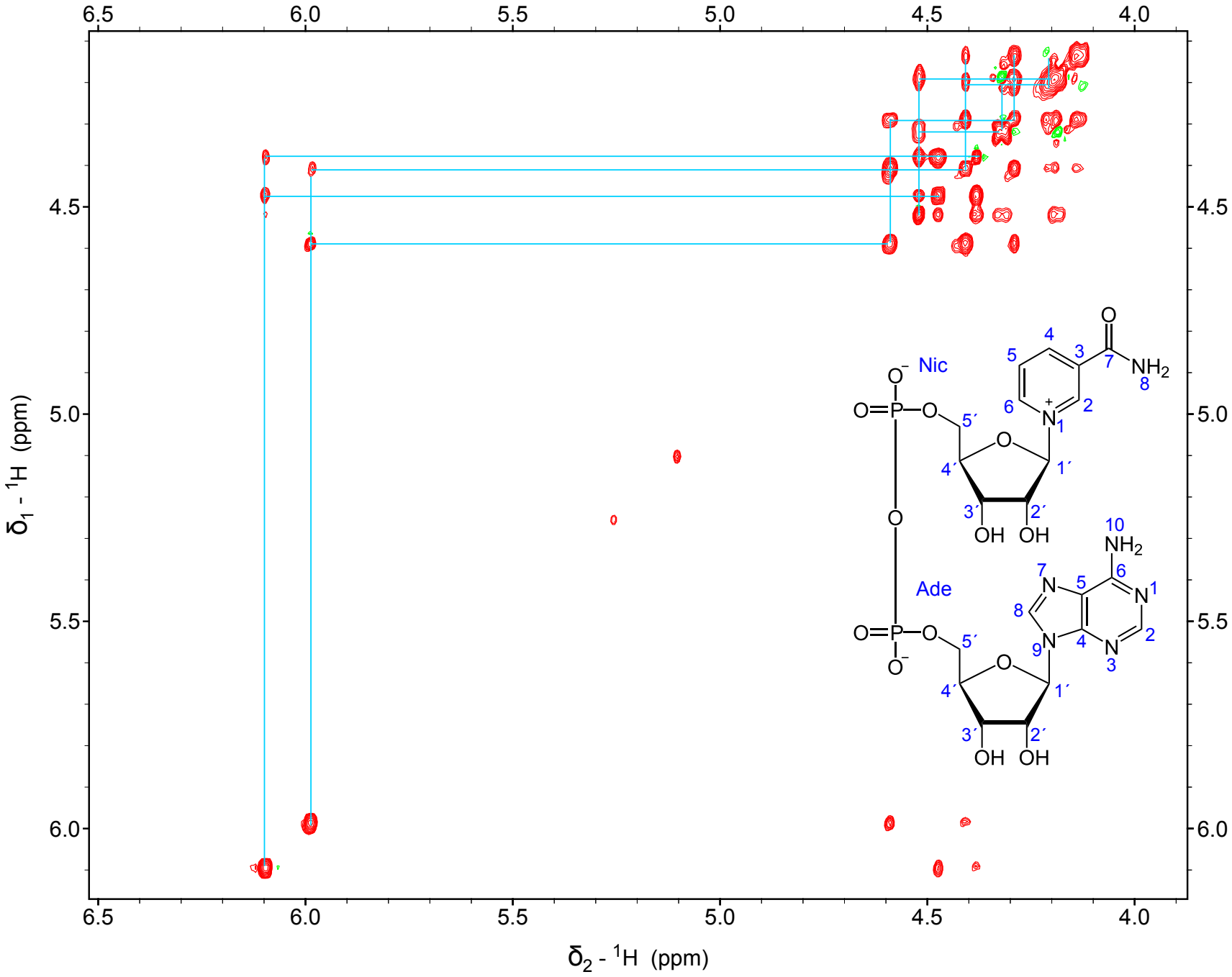




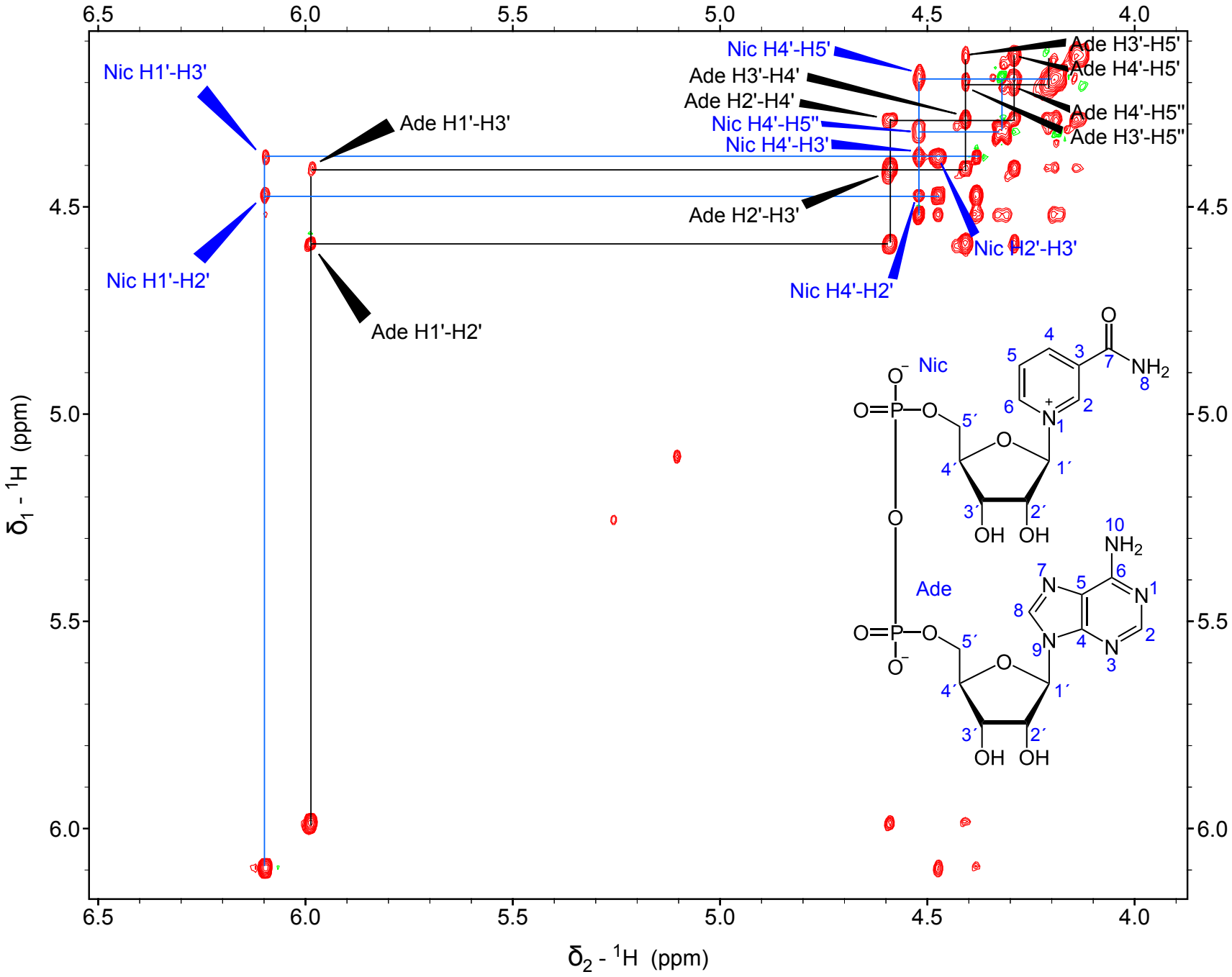
NAD^+: TOCSY (40ms), detail of aromatics



NAD^+: TOCSY (40ms), detail of aliphatics



NAD^+: TOCSY (40ms), detail of aliphatics



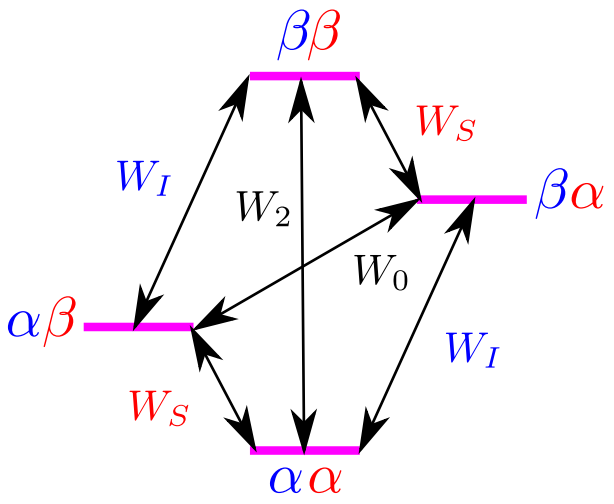
NOESY - introduction

Nuclear Overhauser effect

- dipol-dipol interaction
- magnetisation transfer TROUGH SPACE as a consequence of cross-relaxation

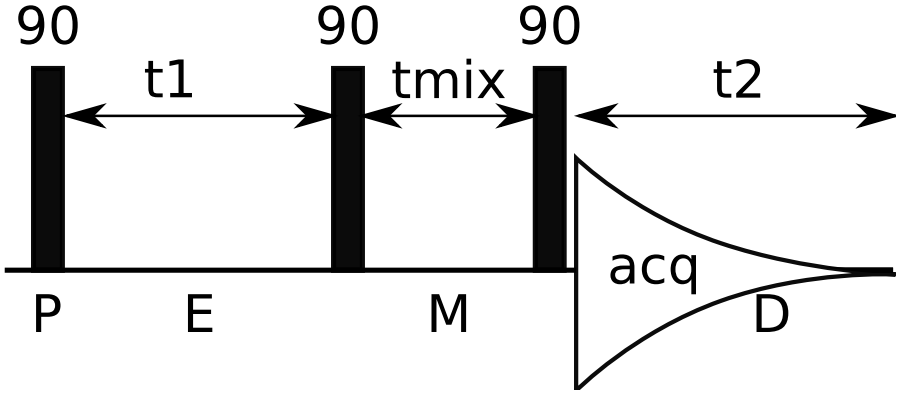
NOESY

- correlates nuclei if their distance is **smaller than 5 Å**



$$\frac{\mathrm{d}\Delta I_z}{\mathrm{d}t} = -\rho_I(I_z - I_z^0) - \sigma_{IS}(S_z - S_z^0)$$

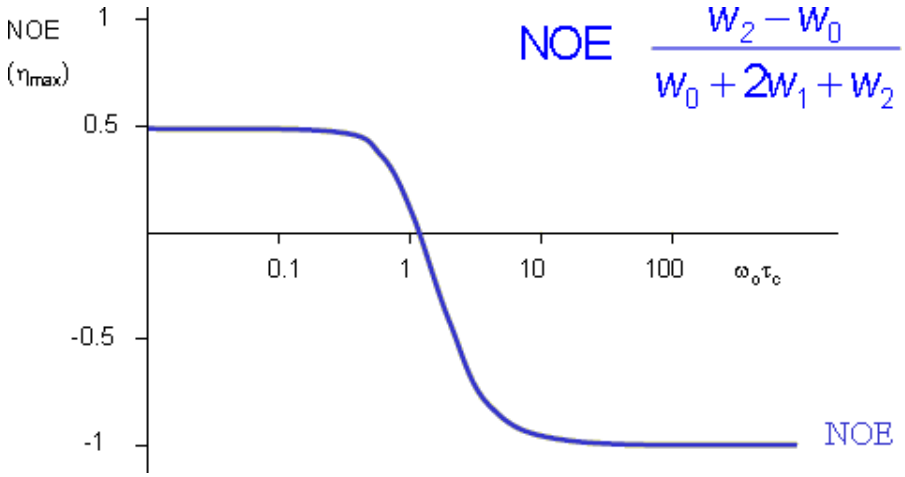
$$\sigma_{IS} = W_2 - W_0$$



NOE vs. size of a molecule

Correlation time τ_c

- $\omega_0\tau_c < 1 \Leftrightarrow \omega_0 \frac{1}{f} < 1 \Leftrightarrow \omega_0 < f$ (small molecules $\ll$ 1 kDa)
  - **fast molecular motion**, $\beta\beta \rightarrow \alpha\alpha$ dominates $\Rightarrow W_2 > W_0$
  - positive NOE
  - crosspeaks have opposite phase relative to diagonal
- $\omega_0\tau_c > 1$ (large molecules $\gg$ 1 kDa)
  - **slow molecular motion**, $\alpha\beta \rightarrow \beta\alpha$ dominates $\Rightarrow W_0 > W_2$
  - negative NOE
  - crosspeaks have the same phase
- $\omega_0\tau_c \approx 1$ (cca 1 kDa)
  - NOE$\approx$0 - no crosspeaks
  - ROESY



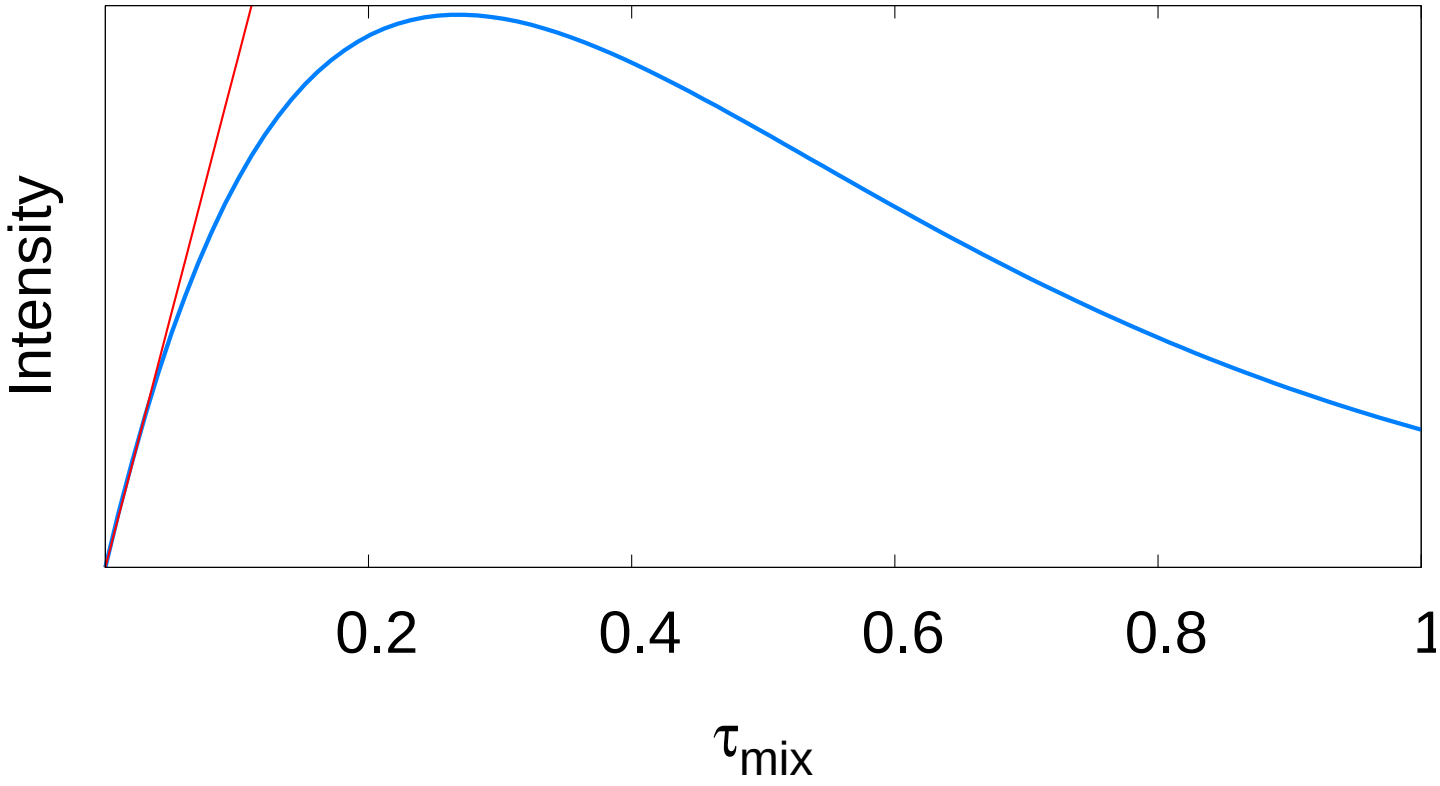
Application of NOESY

Mixing time τ_{mix}

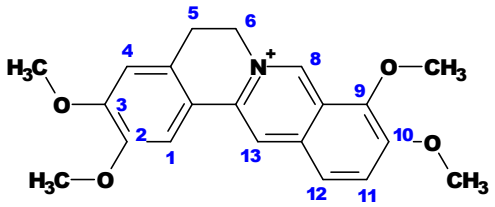
- small molecules $\tau_{mix} \approx 500 - 800\,ms$
- biomolecules $\tau_{mix} \approx 50 - 300\,ms$

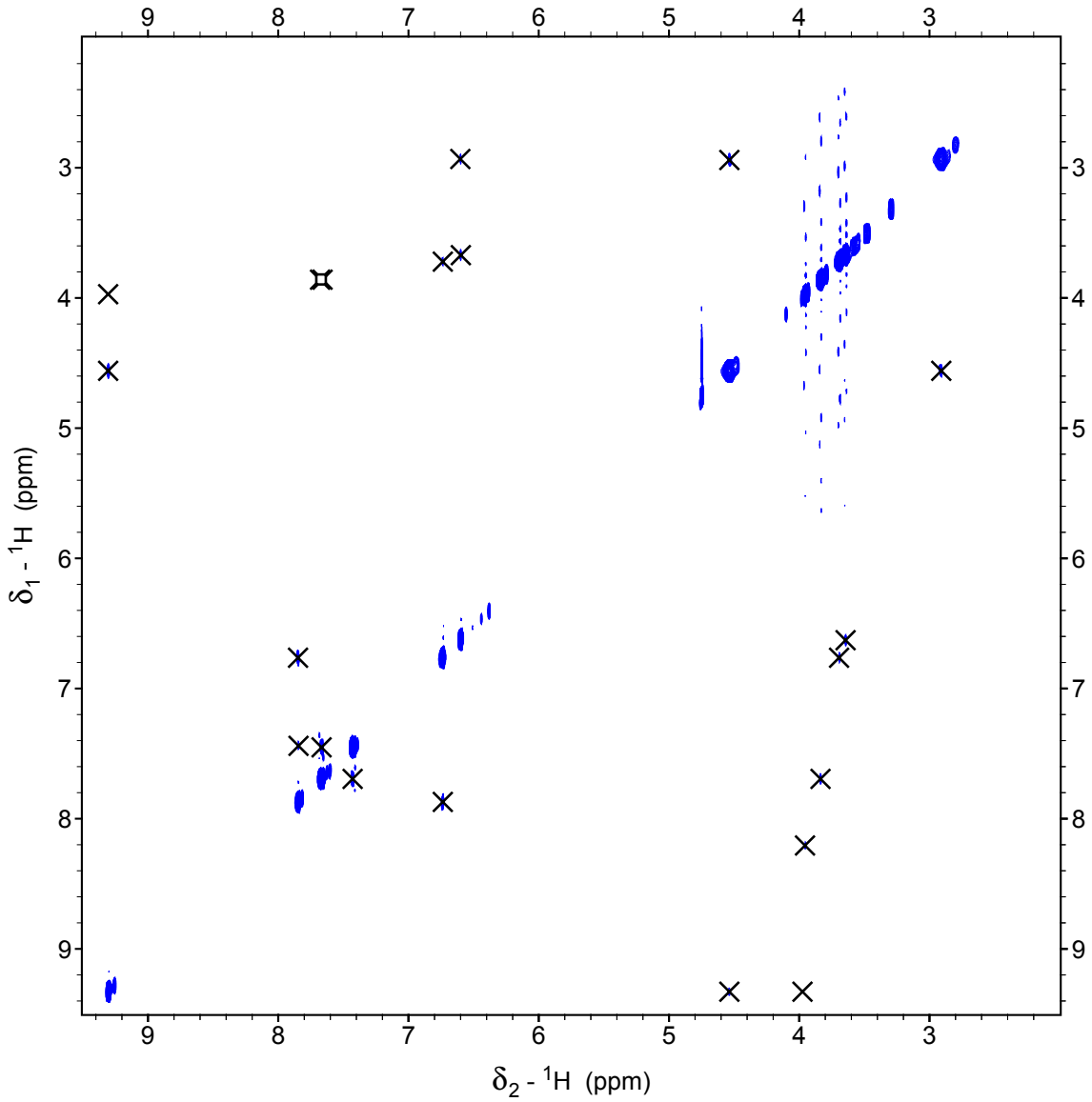
approximative determination of interatomic distatces ($< 5\,Å$)

- at short τ_{mix}
- $r_{ij} \approx A \times I_{ij}$

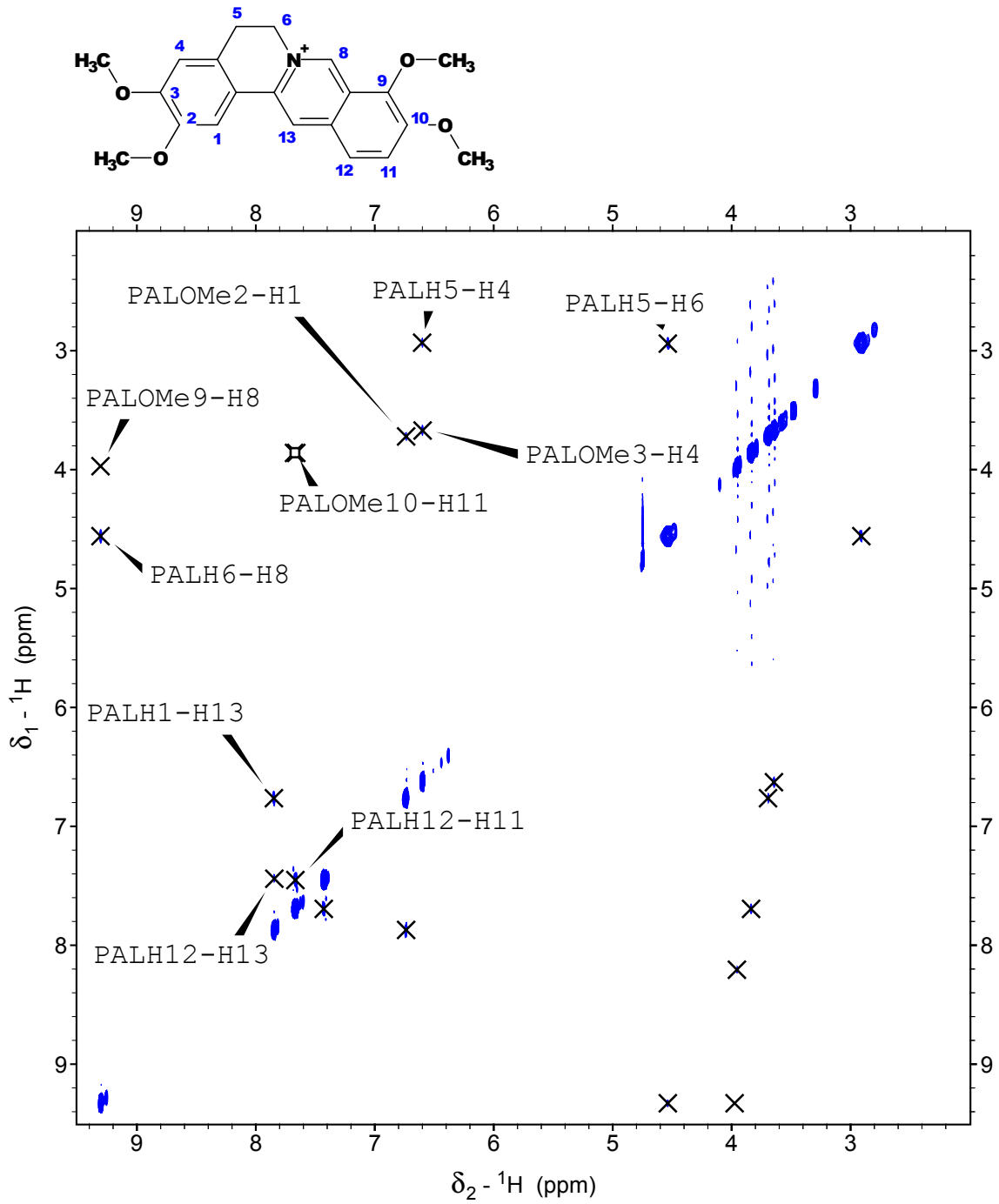


NOESY - Palmatine





NOESY - Palmatine



ROESY - Glutathione