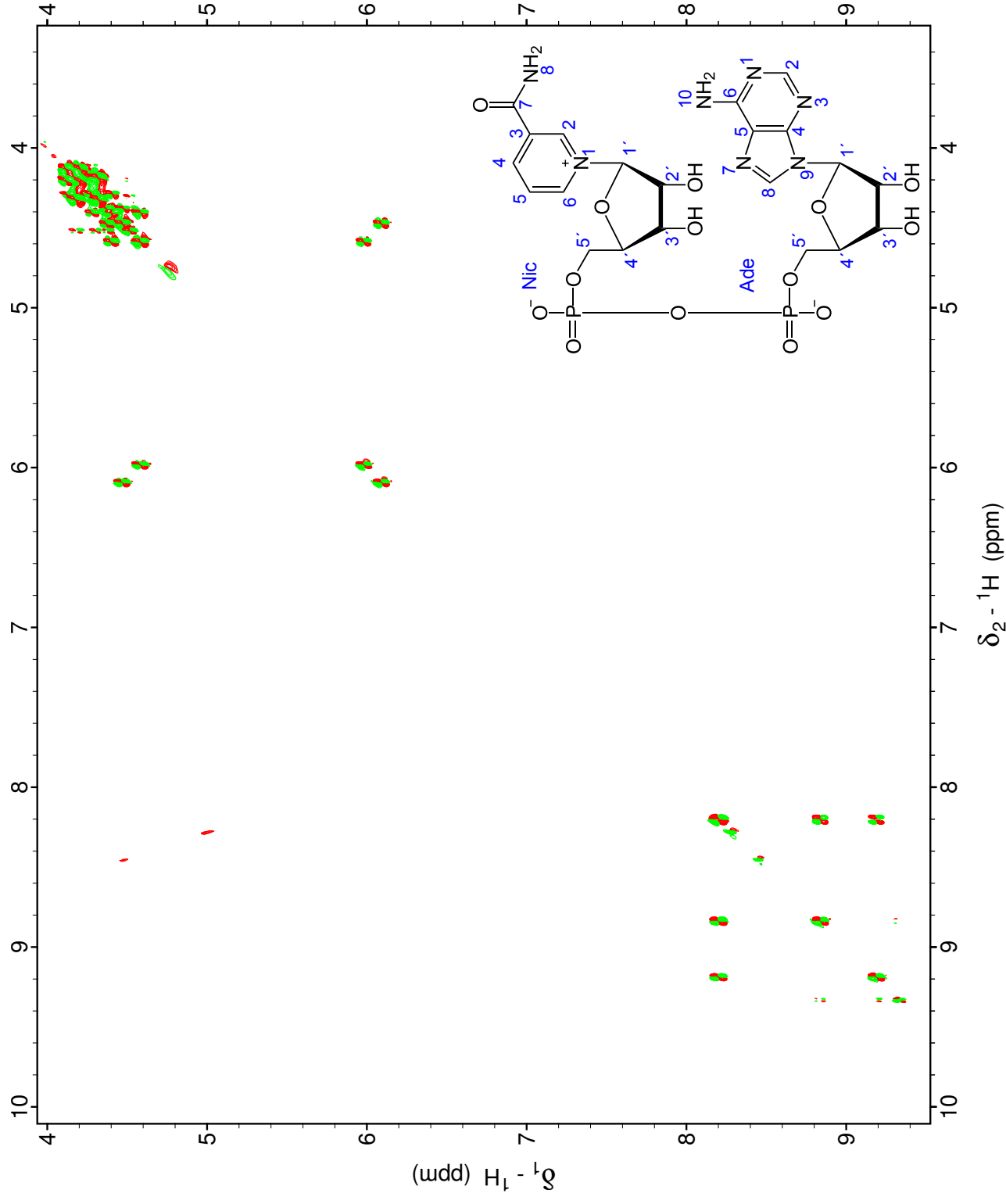


C8953
NMR structural analysis
seminar
COSY + NOESY

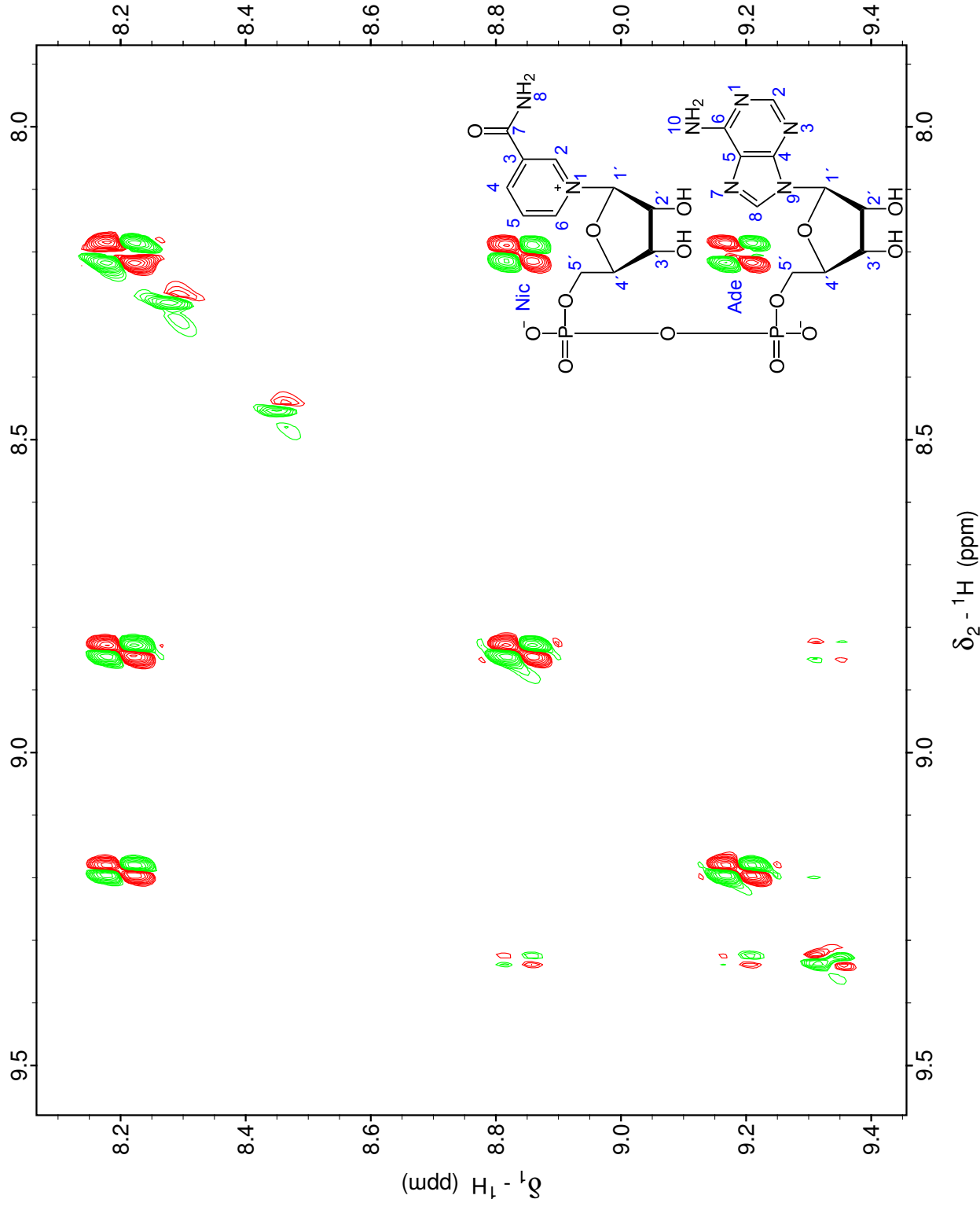
Jan Novotný
novotnyjan@mail.muni.cz

March 19, 2015

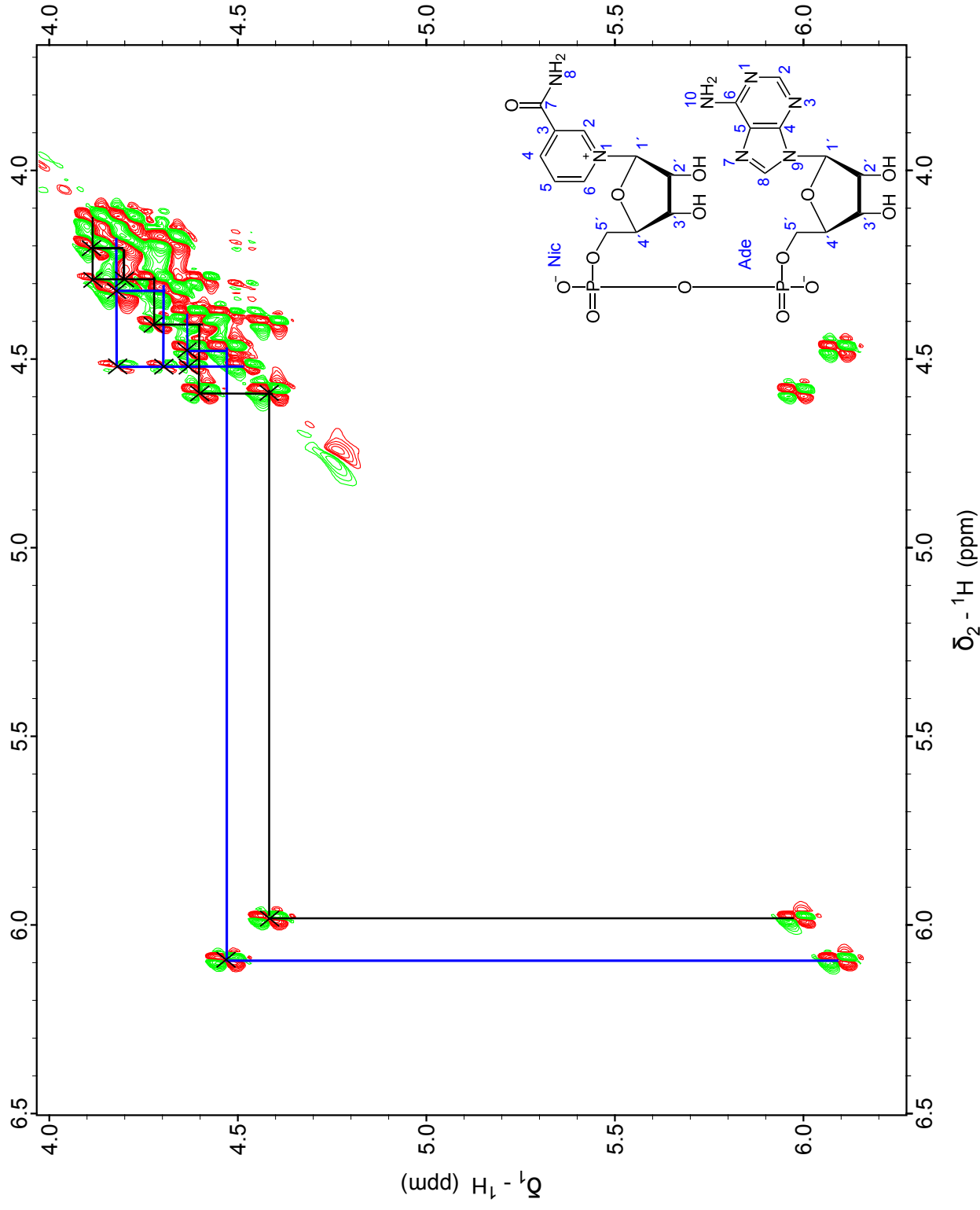
NAD⁺ - DQF-COSY in D₂O



NAD⁺ - DQF-COSY in D₂O



NAD⁺ - DQF-COSY in D₂O



NOESY - theoretical background

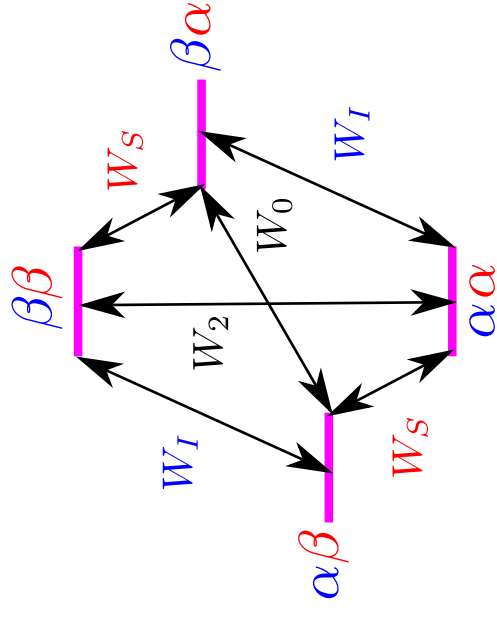
Nuclear Overhauser Effect

- ▶ consequence of **dipol-dipol interaction** via space:

$$E_{DD} \propto \frac{\mu_I \mu_S (3 \cos^2 \theta - 1)}{r_{IS}^3}$$

- ▶ relaxation of a perturbed spin modulates the population of close spins = **cross-relaxation**

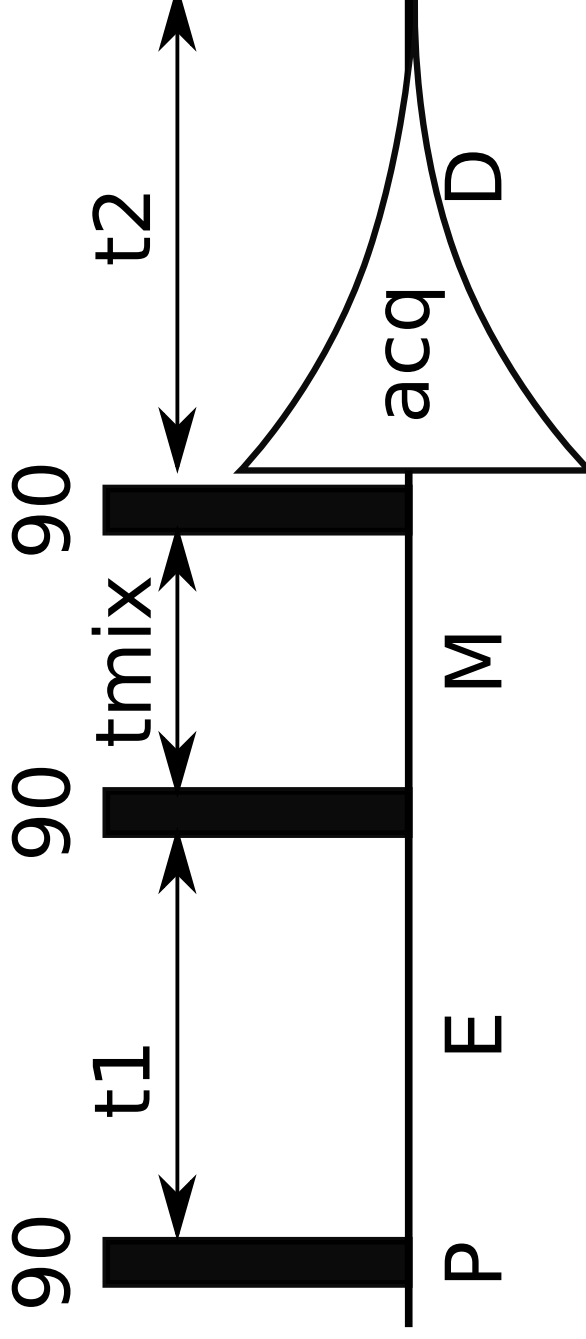
$$R_{DD} \propto \gamma_I^2 \gamma_S^2 \frac{\tau_c}{r_{IS}^6}$$



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

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

2D-NOESY

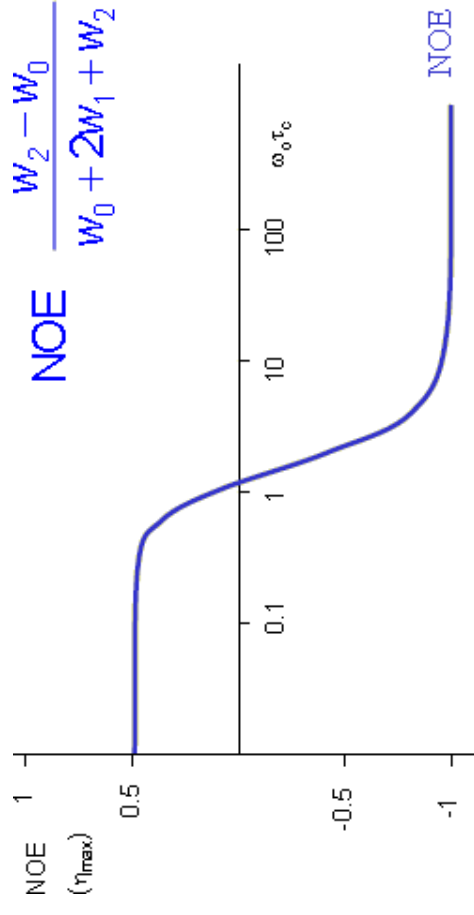


- ▶ correlates nuclei in the proximity of cca 5 Å
- ▶ **P:** excitation of spins by $\pi/2$ pulse
- ▶ **E:** evolution of magnetization during $t_1 \Rightarrow$ encoding of magnetization by its own frequency
- ▶ **M:** $\pi/2$ pulse: rotation of transversal magnetization into z -axis \Rightarrow transfer of magnetization via cross-relaxation during t_{mix}
- ▶ **D:** $\pi/2$ pulse \Rightarrow acquisition (t_2) of signal whose amplitude is modulated by frequency of interacting spins

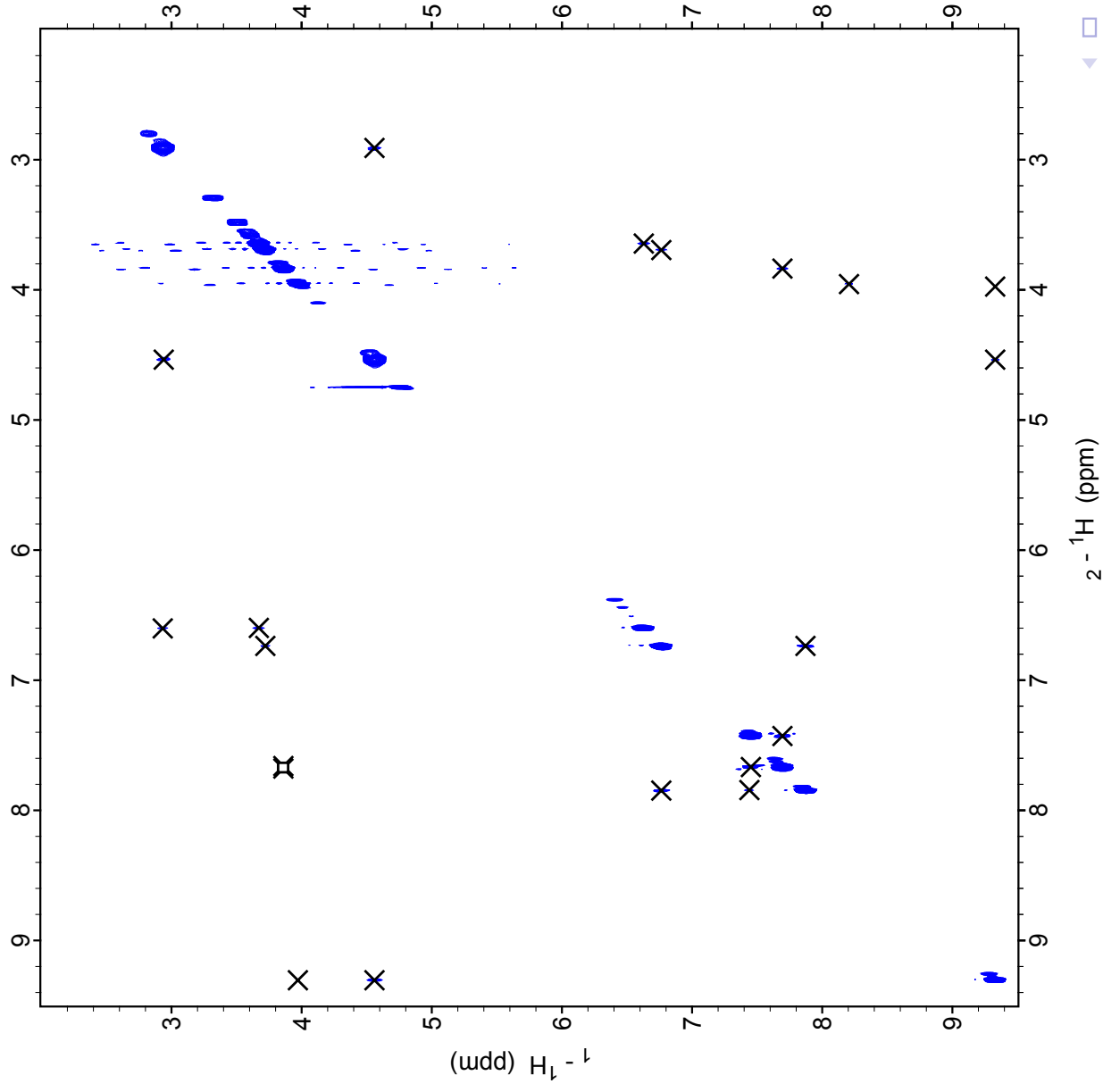
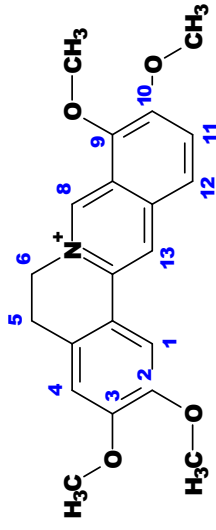
NOE vs. size of the molecule

Correlation time τ_c

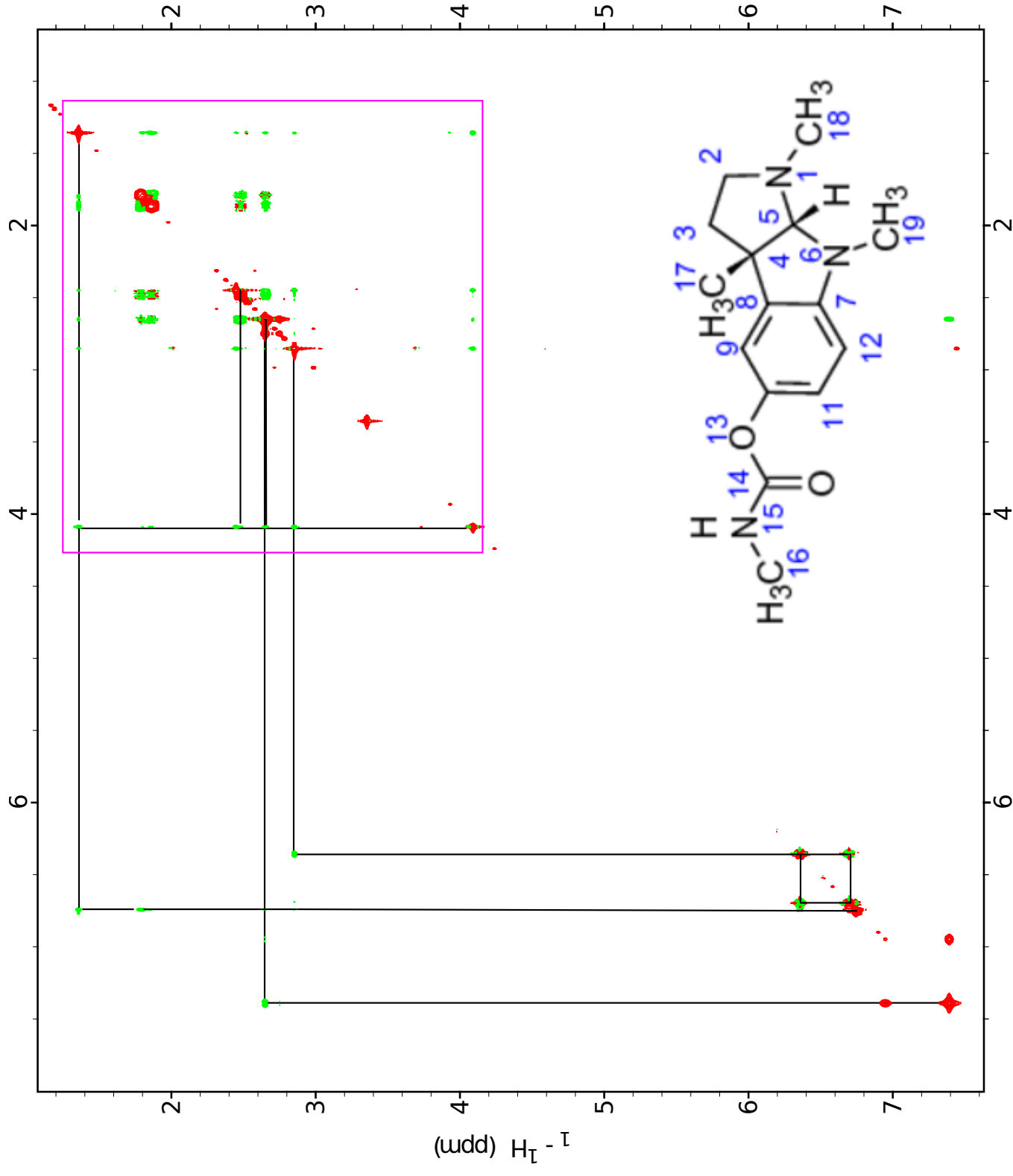
- ▶ the average time it takes the molecule to rotate through one radian $\tau_c = \frac{1 \text{ rad}}{\omega_{mol}}$
 \Rightarrow ratio of ω_{mol} and carrier frequency ω_0 :
- ▶ $\omega_0 \tau_c < 1$ (small molecules)
 - ▶ positive NOE ($W_2 > W_0$)
 - ▶ slow relaxation \Rightarrow long mixing period
 - ▶ in NOESY spectrum crosspeaks of opposite phase relative to diagonal ones
- ▶ $\omega_0 \tau_c > 1$ (large molecules)
 - ▶ negative NOE ($W_2 < W_0$)
 - ▶ fast relaxation \Rightarrow shorter mixing period
 - ▶ crosspeaks of the same phase as the diagonal
- ▶ $\omega_0 \tau_c \approx 1$ (cca 1 kDa)
 - ▶ $\text{NOE} \approx 0$
 - ▶ no crosspeaks \Rightarrow Rotating frame nOE Spectroscopy (ROESY)



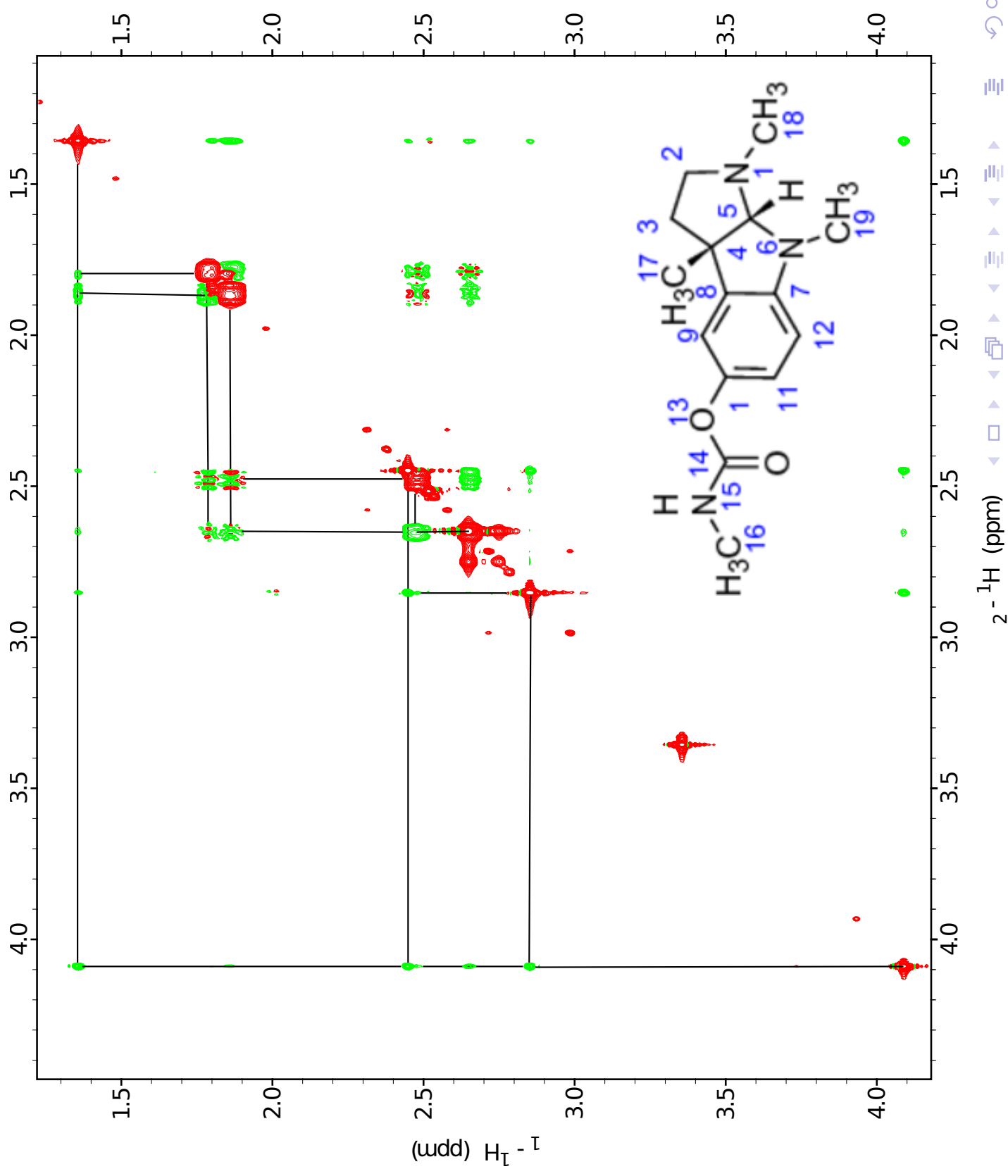
NOESY - Palmatine in DMSO-d6



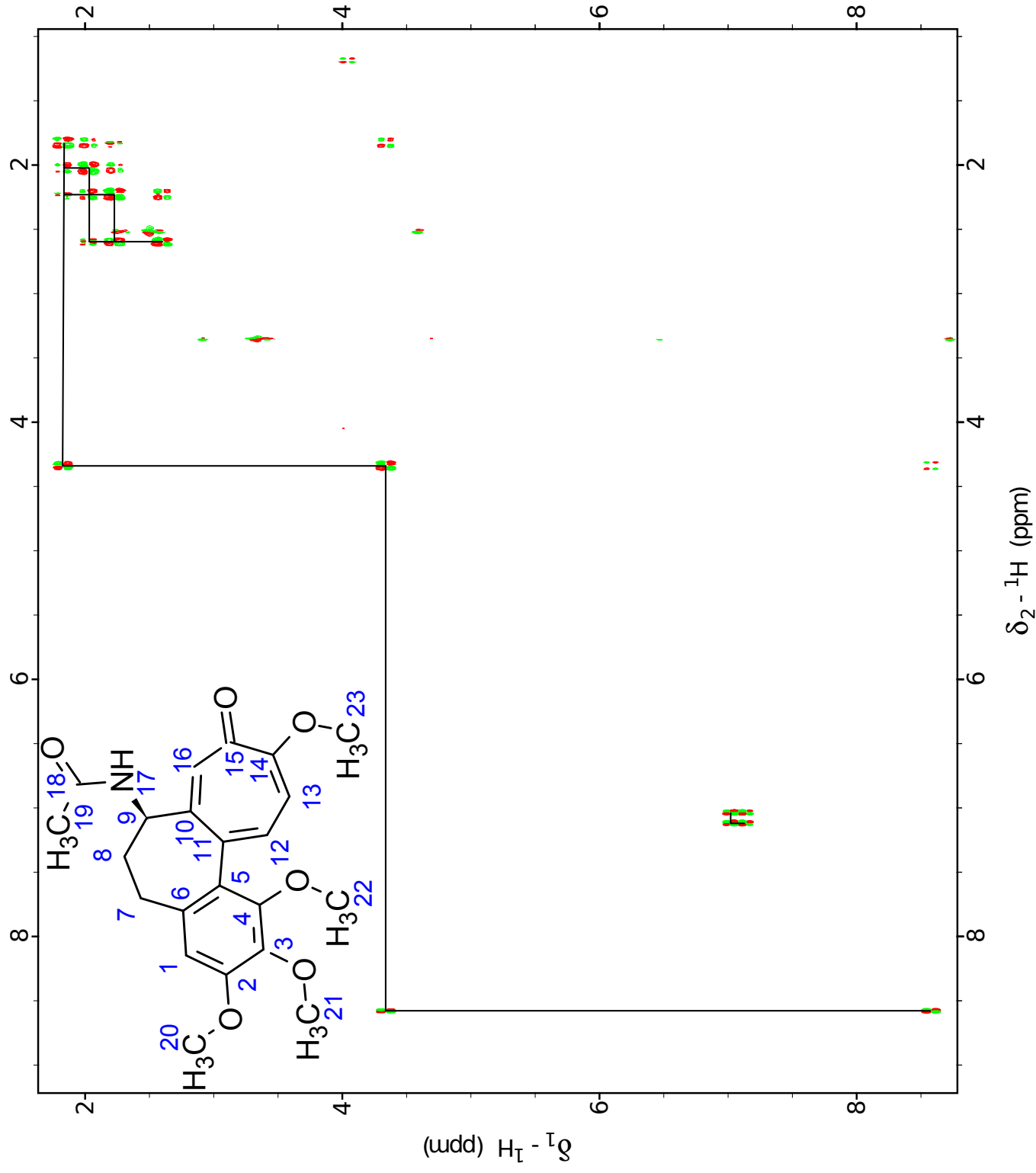
NOESY 600ms - Eserine in DMSO-d6



NOESY 600ms - Eserine in DMSO-d6



DQ-COSY - Colchicine in DMSO-d6



NOESY 600ms - Colchicine in DMSO-d6

