C8953
NMR strukturní analýza
seminář
NOESY

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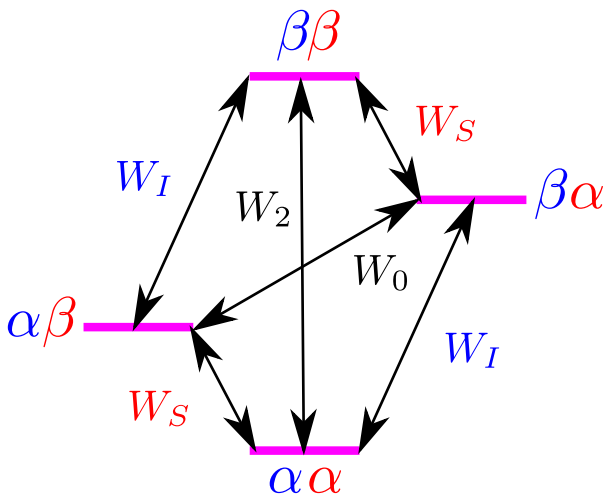
NOESY - introduction

Nuclear Overhauser effect

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

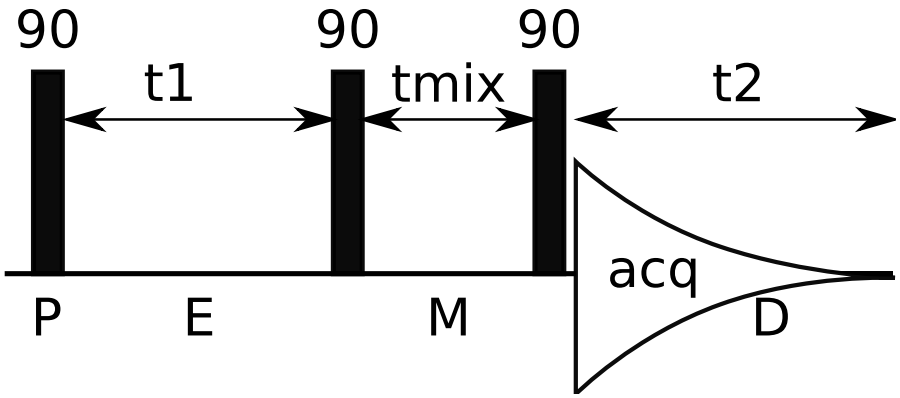
NOESY

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



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

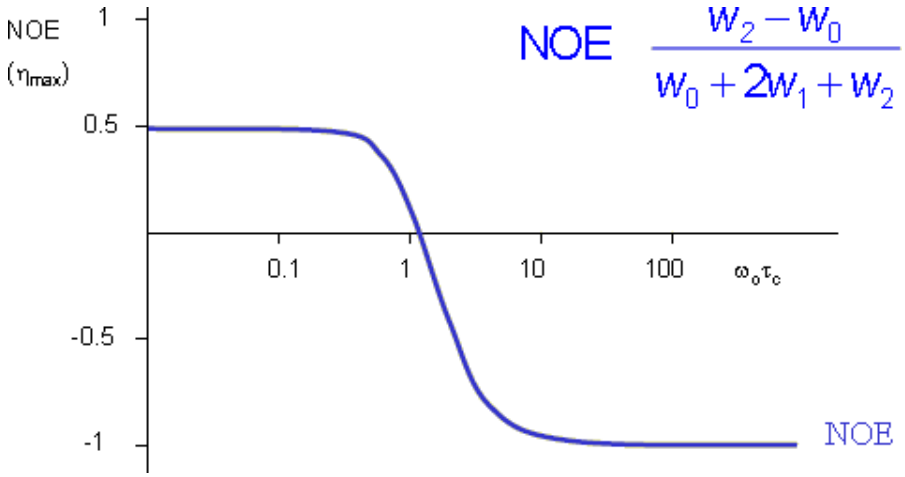
$$\sigma_{IS} = W_2 - W_0$$



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



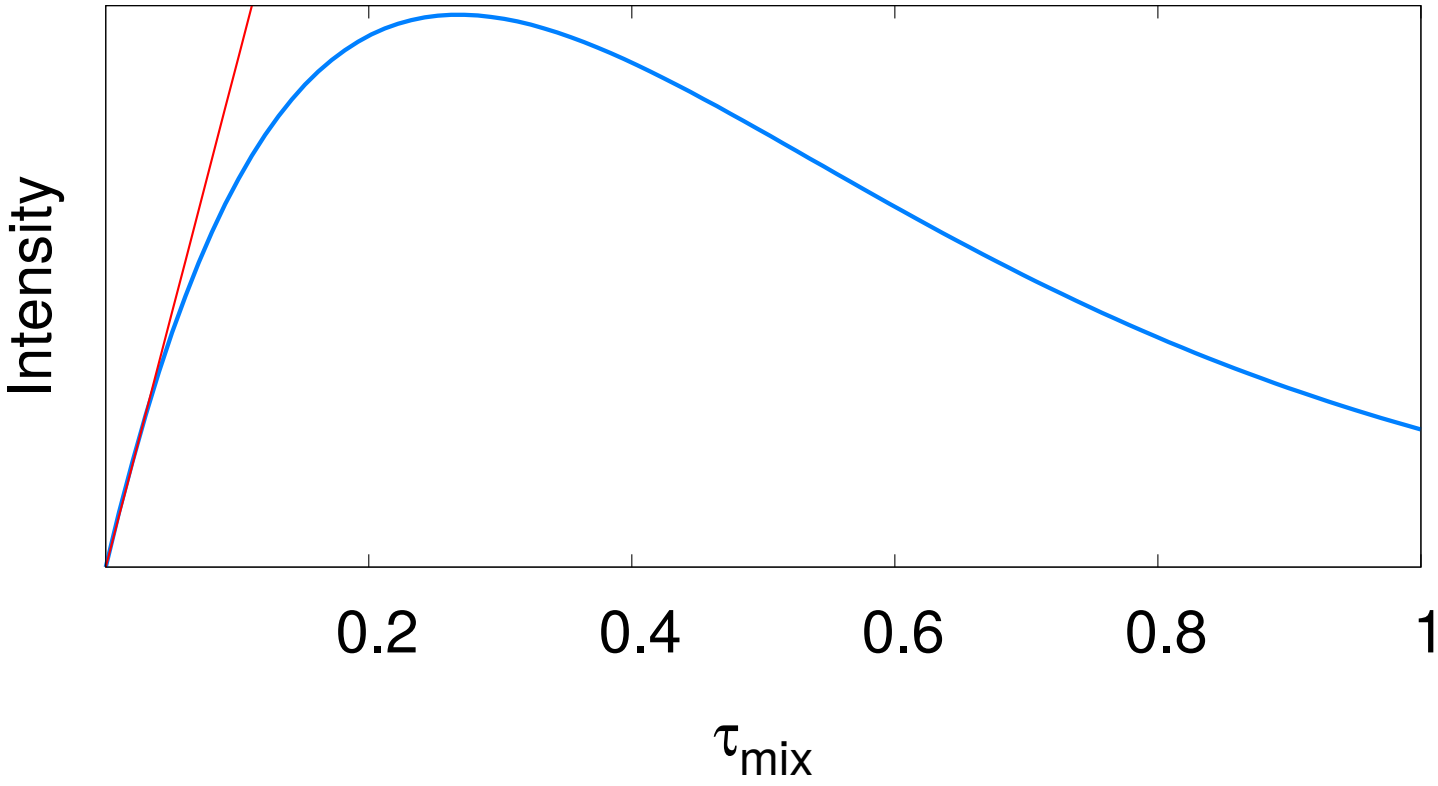
Application of NOESY

Mixing time τ_{mix}

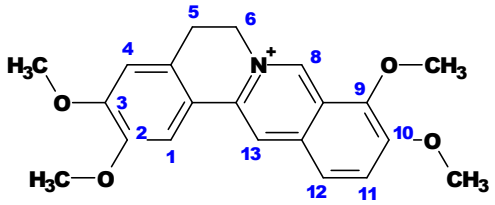
- small molecules $\tau_{mix} \approx 500 - 800\,ms$
- biomolecules $\tau_{mix} \approx 50 - 300\,ms$

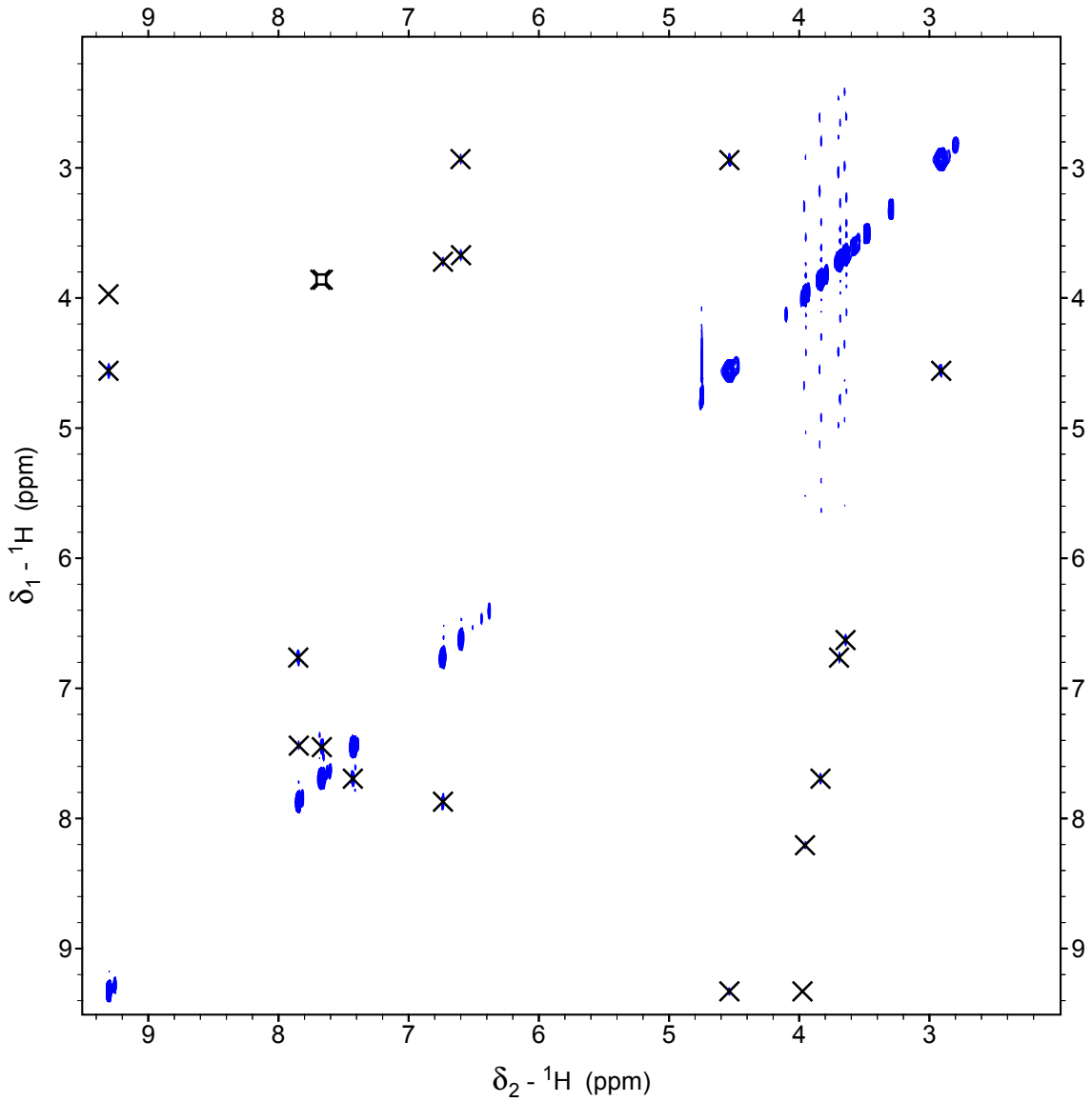
approximative determination of interatomic distatces ($< 5\,Å$)

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

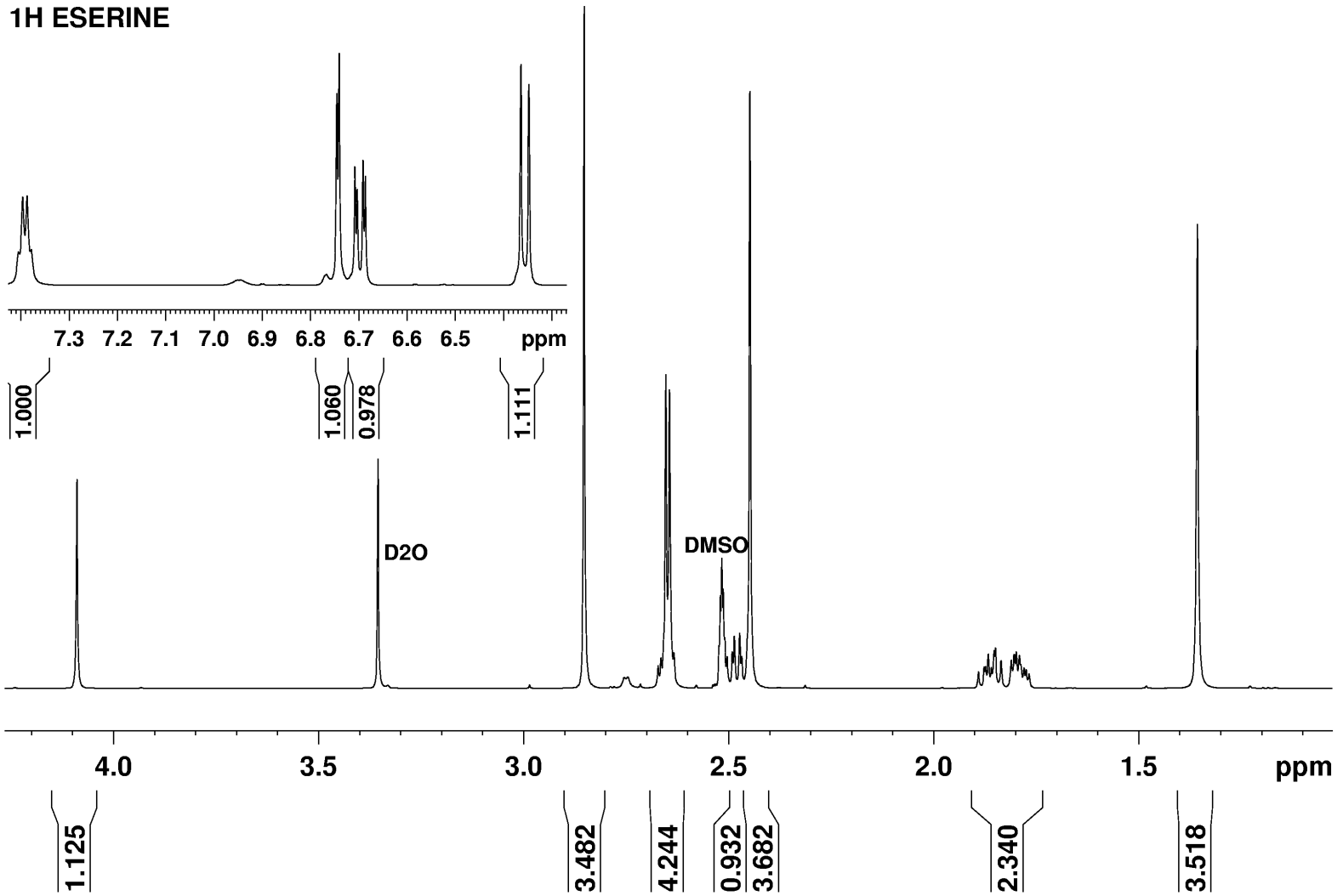


NOESY - Palmatine

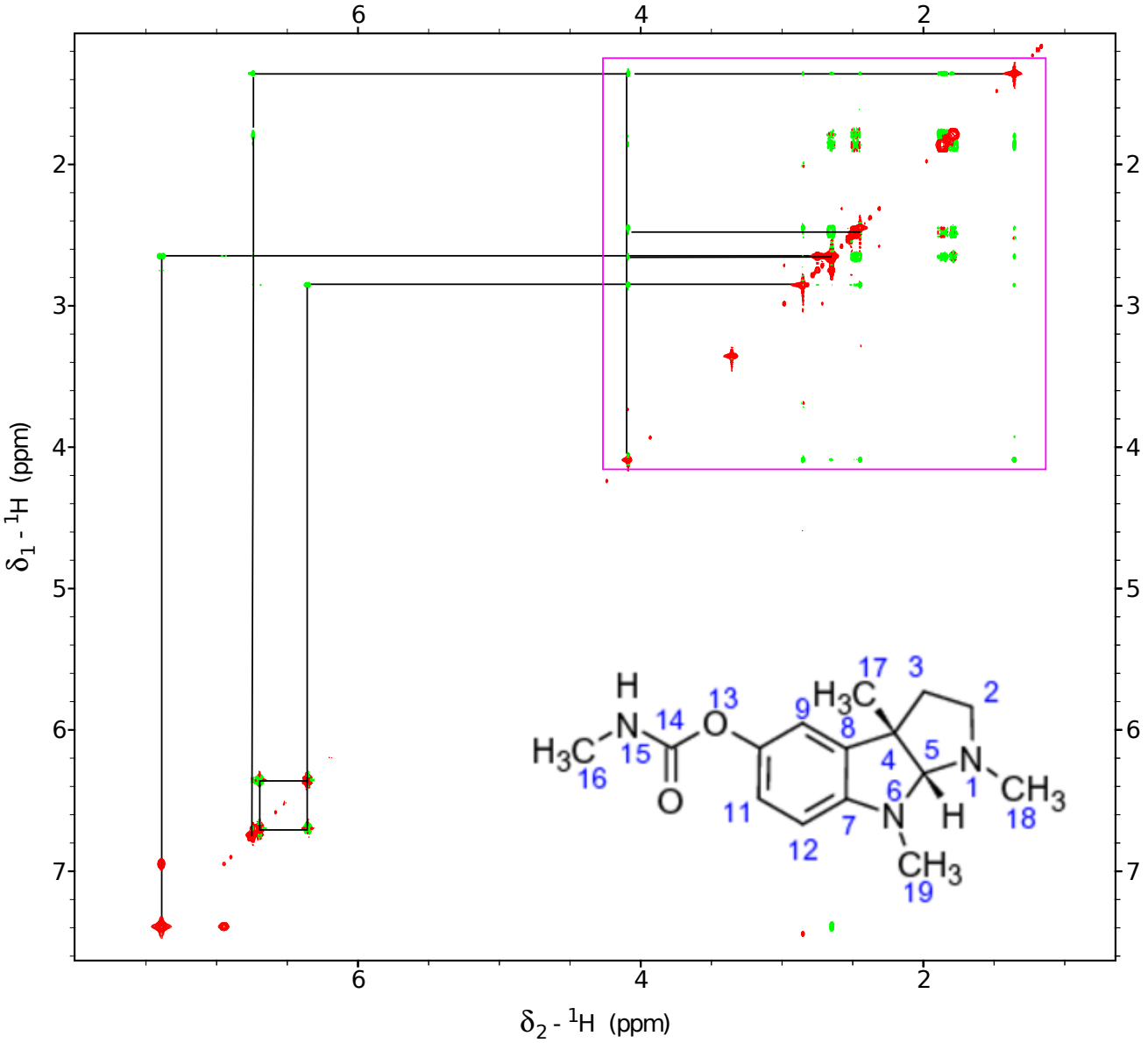




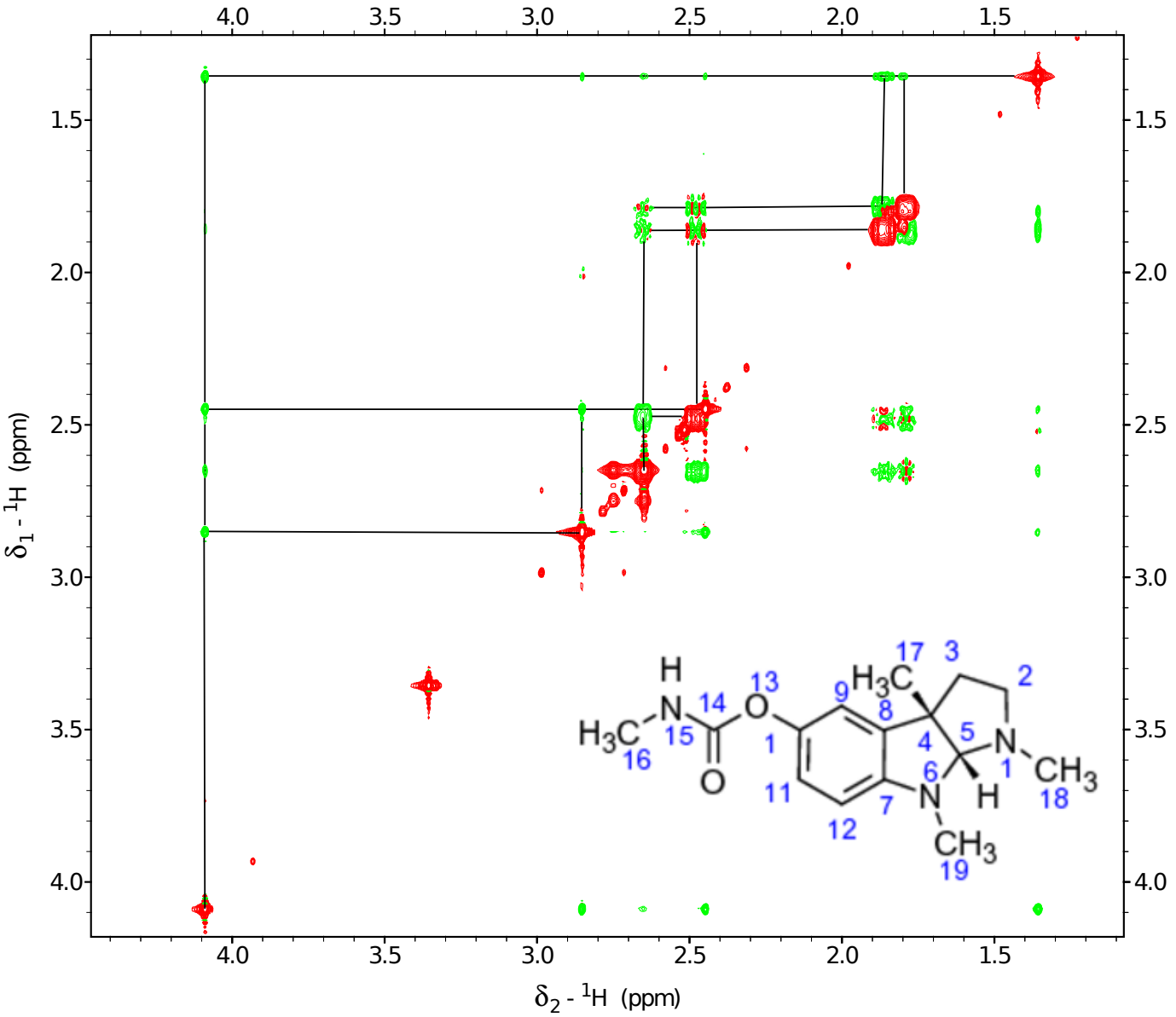
Eserine ^{1}H


1H ESERINE
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
1.000
1.060
0.978
1.111
D2O
DMSO
4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.125
3.482
4.244
0.932
3.682
2.340
3.518

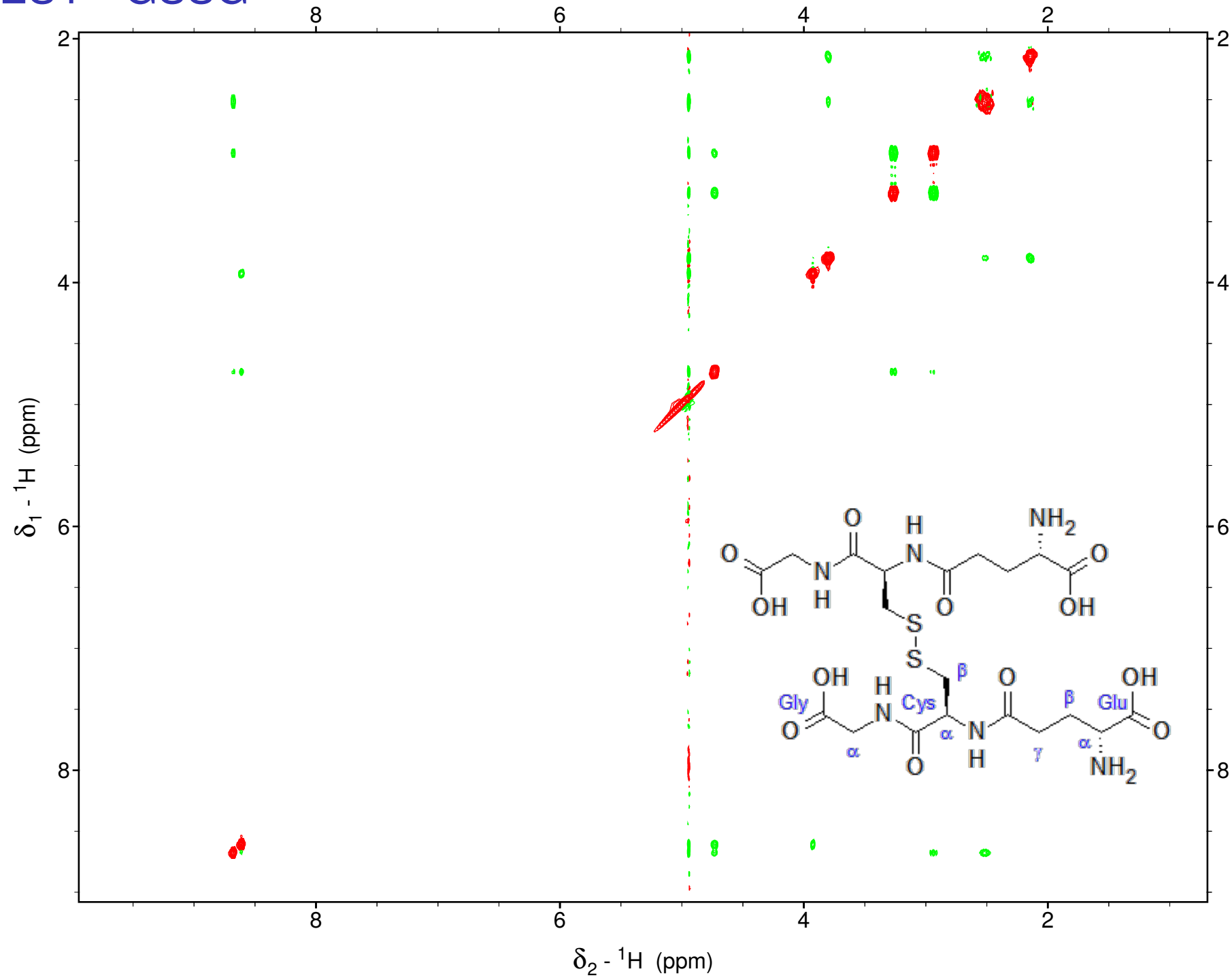
NOESY - Eserine



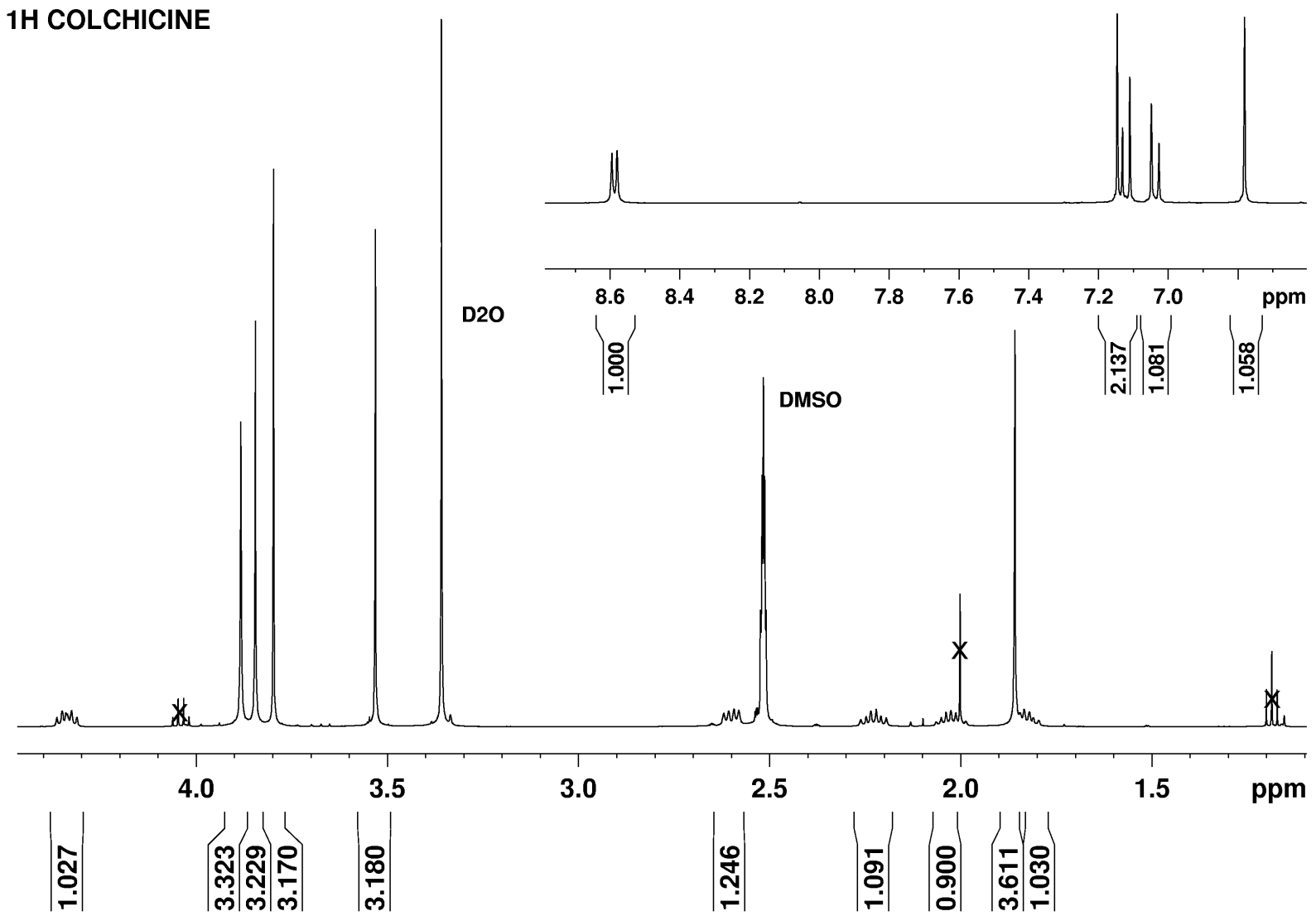
NOESY - Eserine



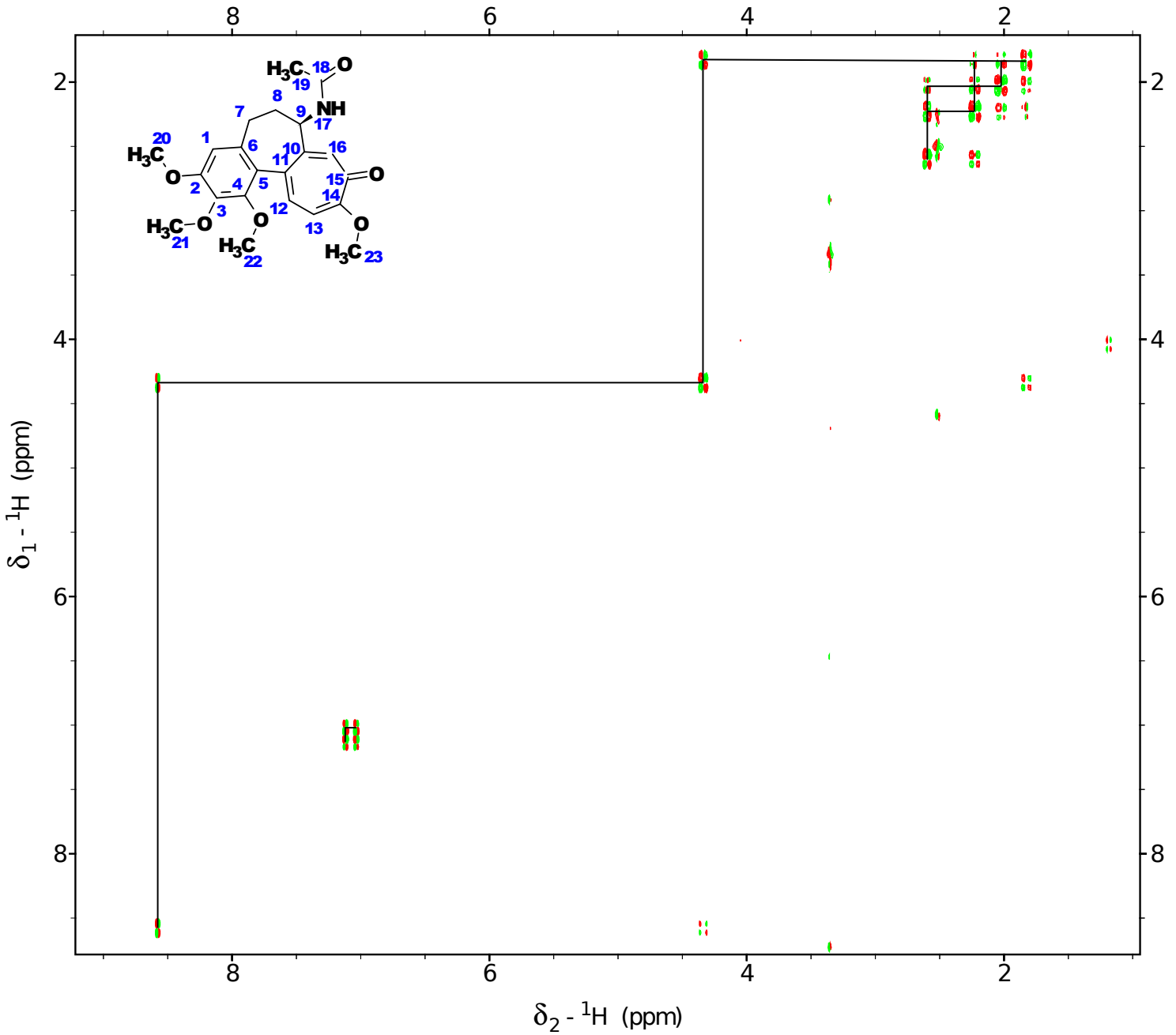
ROESY - GSSG



Colchicine 1D-^{1}H



Colchicine - DQF-COSY



Colchicine - NOESY