

C8953
NMR strukturní analýza
seminář
NOESY

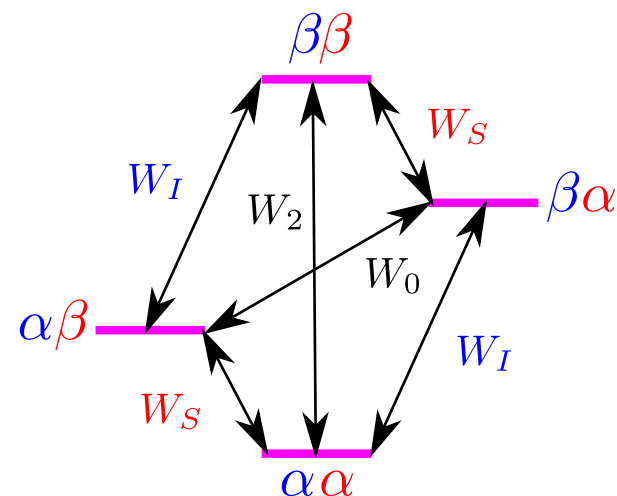
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NOESY - introduction

Nuclear Overhauser effect

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

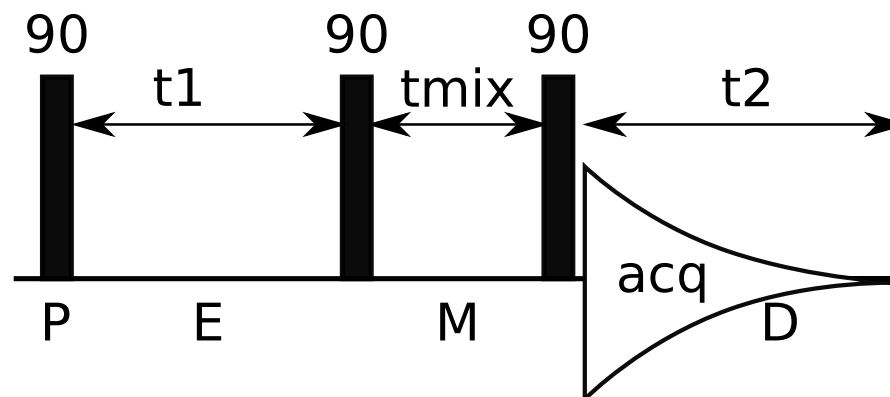


$$\frac{d\Delta I_z}{dt} = -\rho_I(I_z - I_z^0) - \sigma_{IS}(S_z - S_z^0)$$

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

NOESY

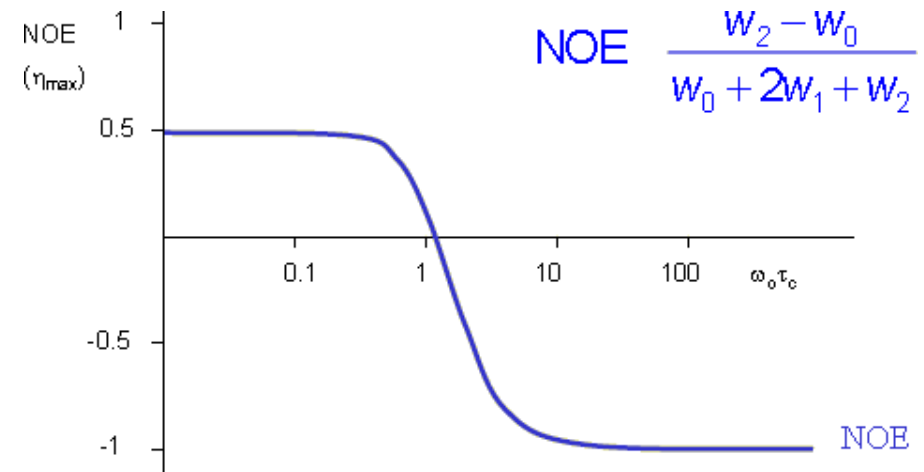
- ▶ correlates nuclei if their distance is **smaller than 5 Å**



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 ≈ 0 - no crosspeaks
 - ▶ ROESY



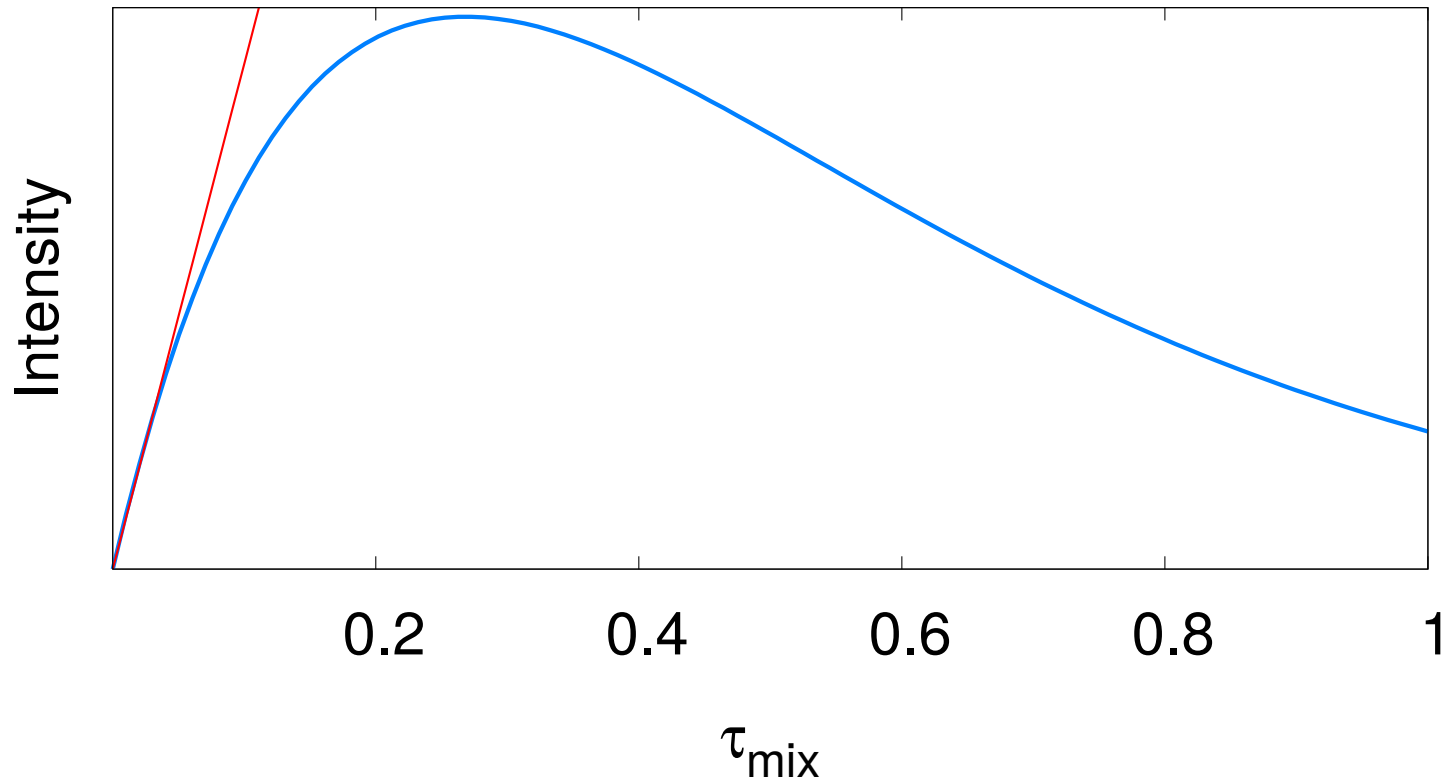
Application of NOESY

Mixing time τ_{mix}

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

approximative determination of interatomic distances ($< 5 \text{ \AA}$)

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

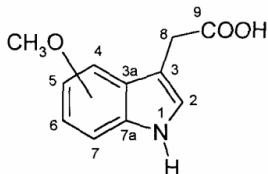


NOE differential experiment

PROBLEM 4

NOE- Difference Spectroscopy

Figure 4.1 shows the ^1H NMR and a ^1H NOE difference spectrum of a 3-indolylacetic acid derivative **13** bearing a methoxy group at the benzenoic ring.



What is the position of the methoxy group?

(400 MHz ^1H)

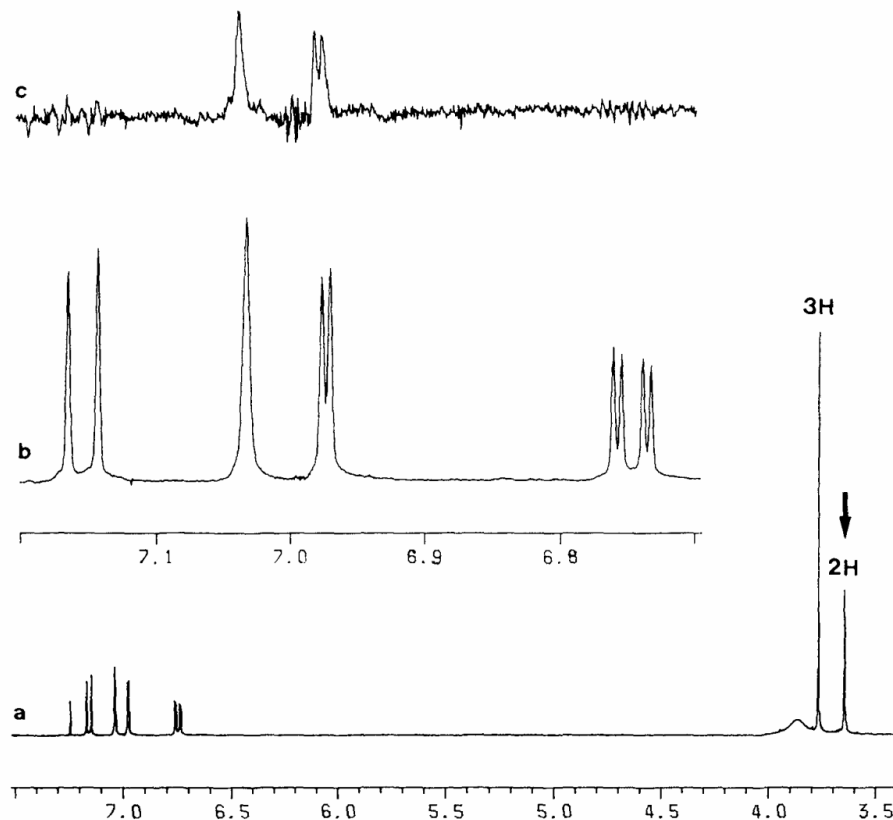


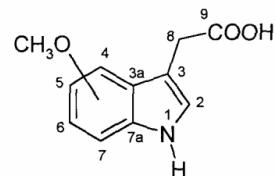
Fig. 4.1. 400 MHz ^1H NMR spectrum of **13** in a mixture of CDCl_3 and CD_3OD . **a** Full spectrum; **b** expanded section of the aromatic proton signals; **c** ^1H NOE difference spectrum, same section as in **b**, irradiation position at $\delta = 3.64$.

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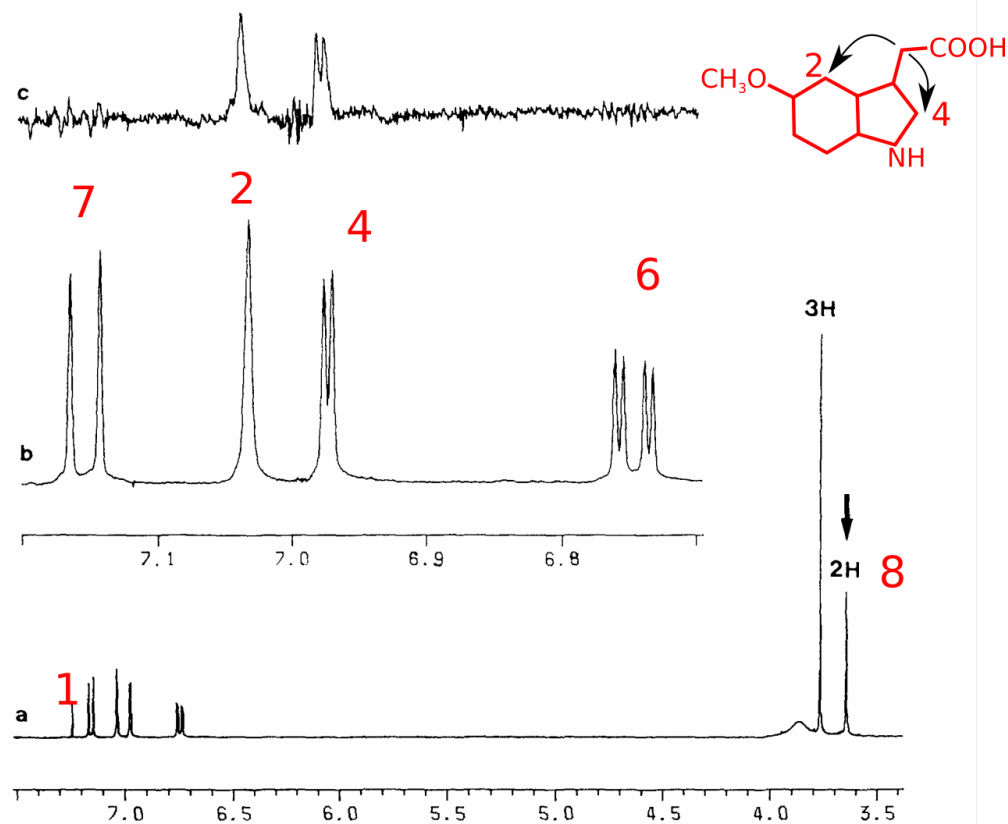
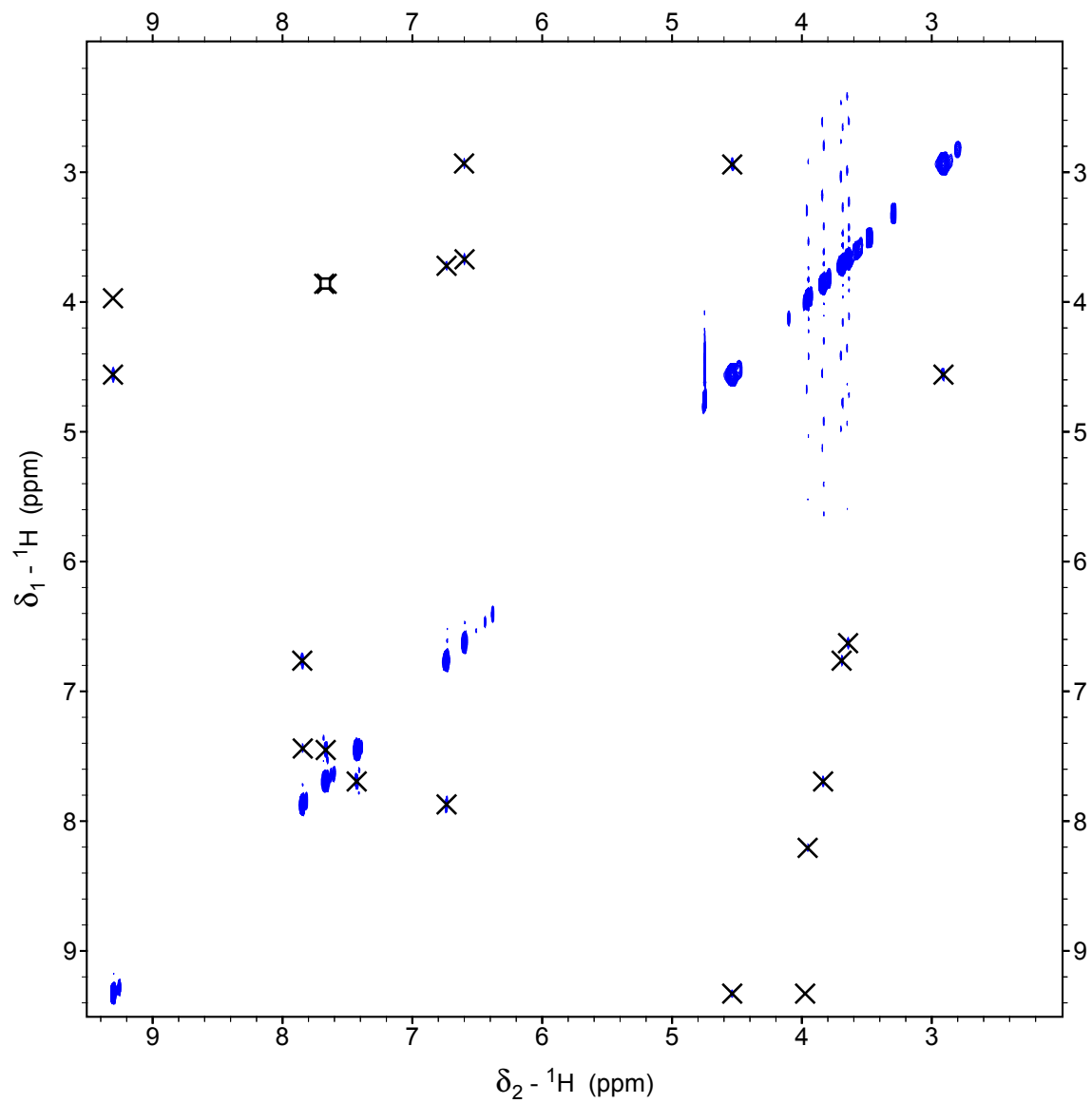
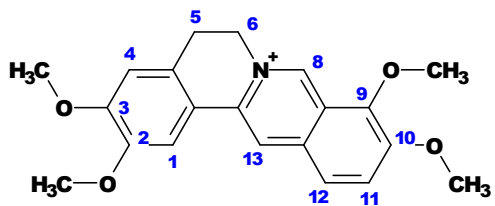
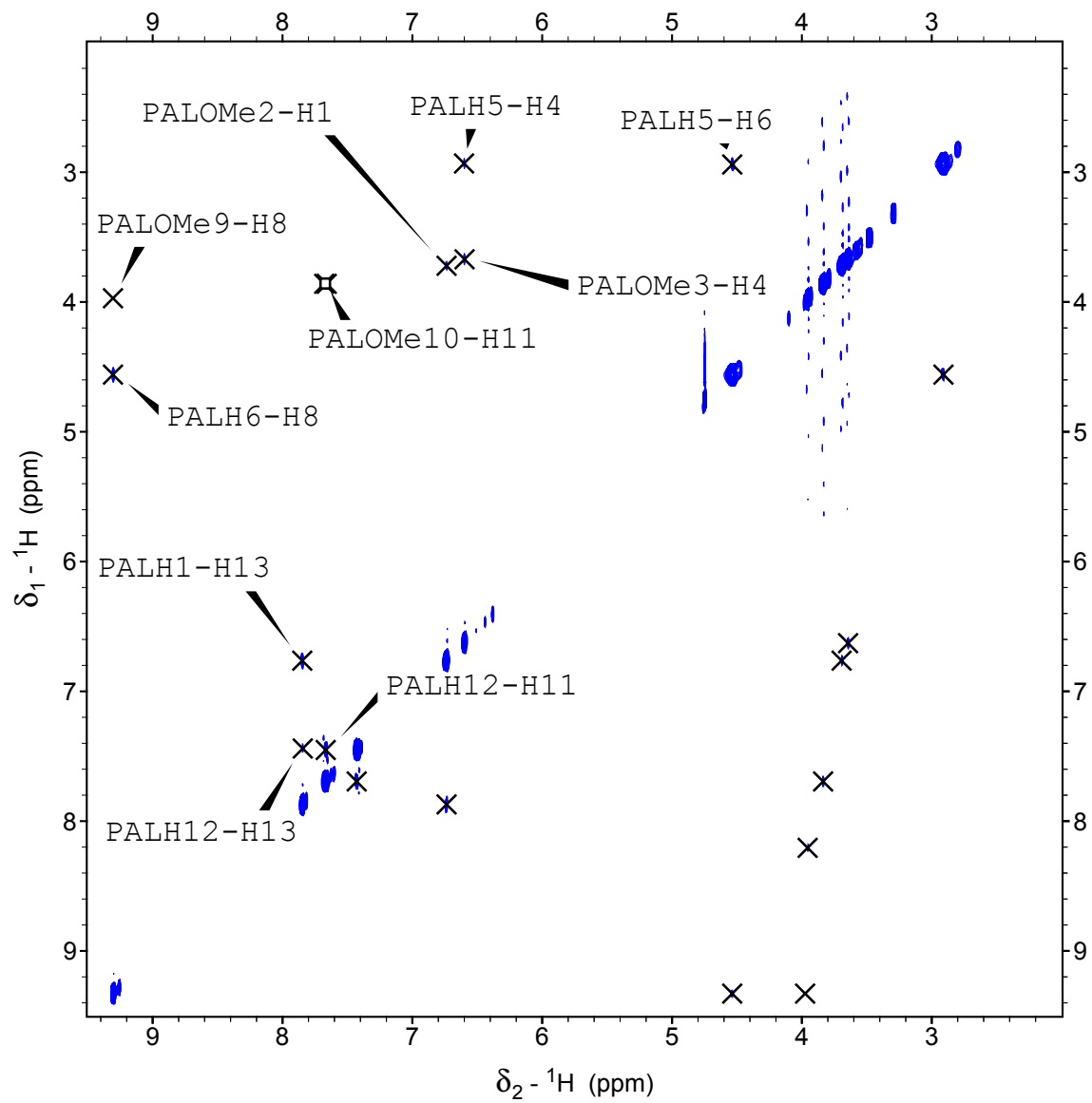
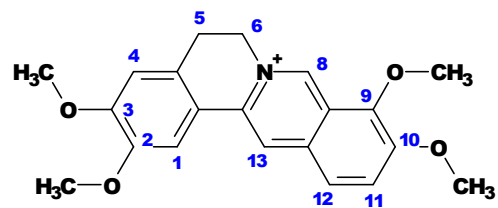


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NOESY - Palmatine

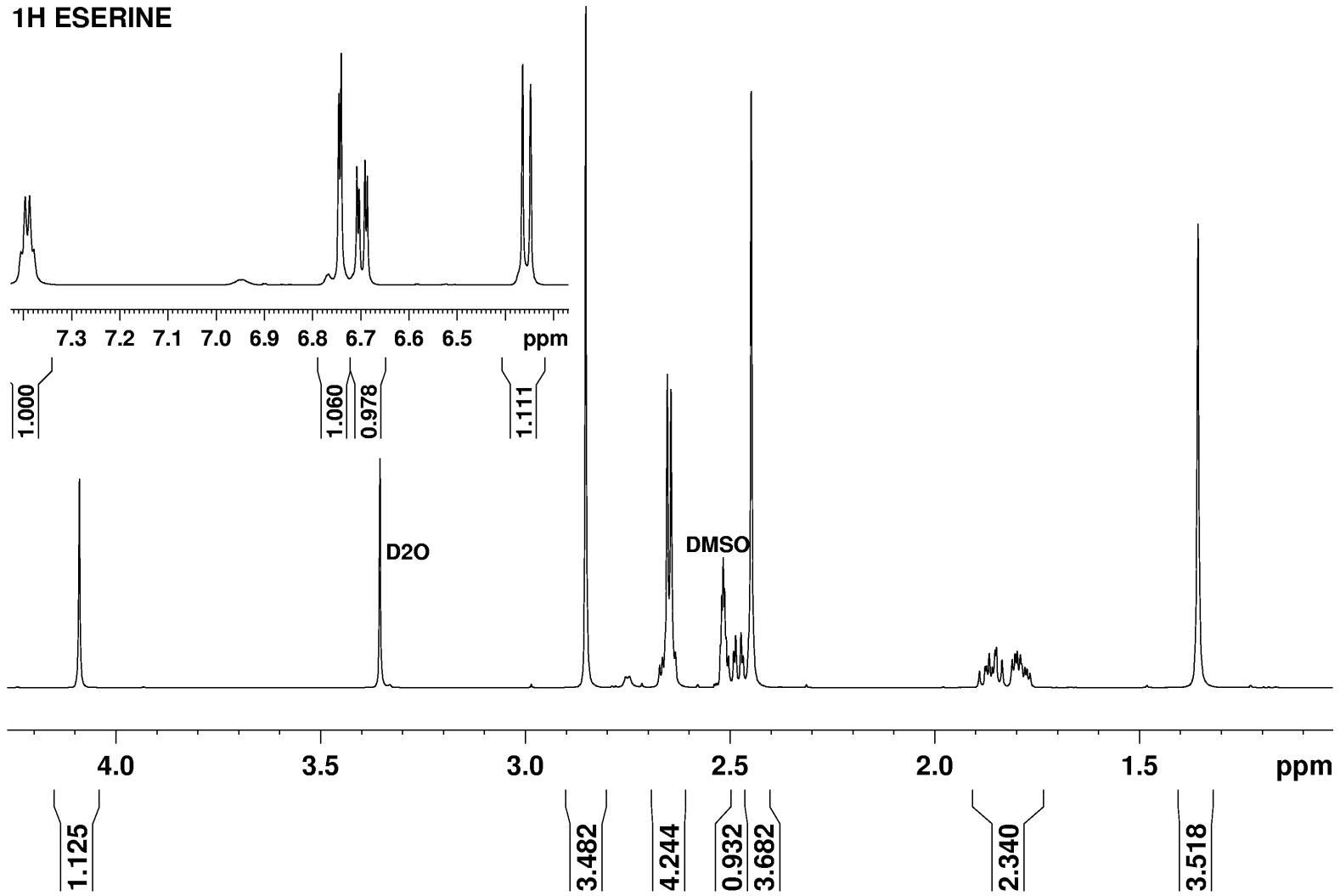


NOESY - Palmatine

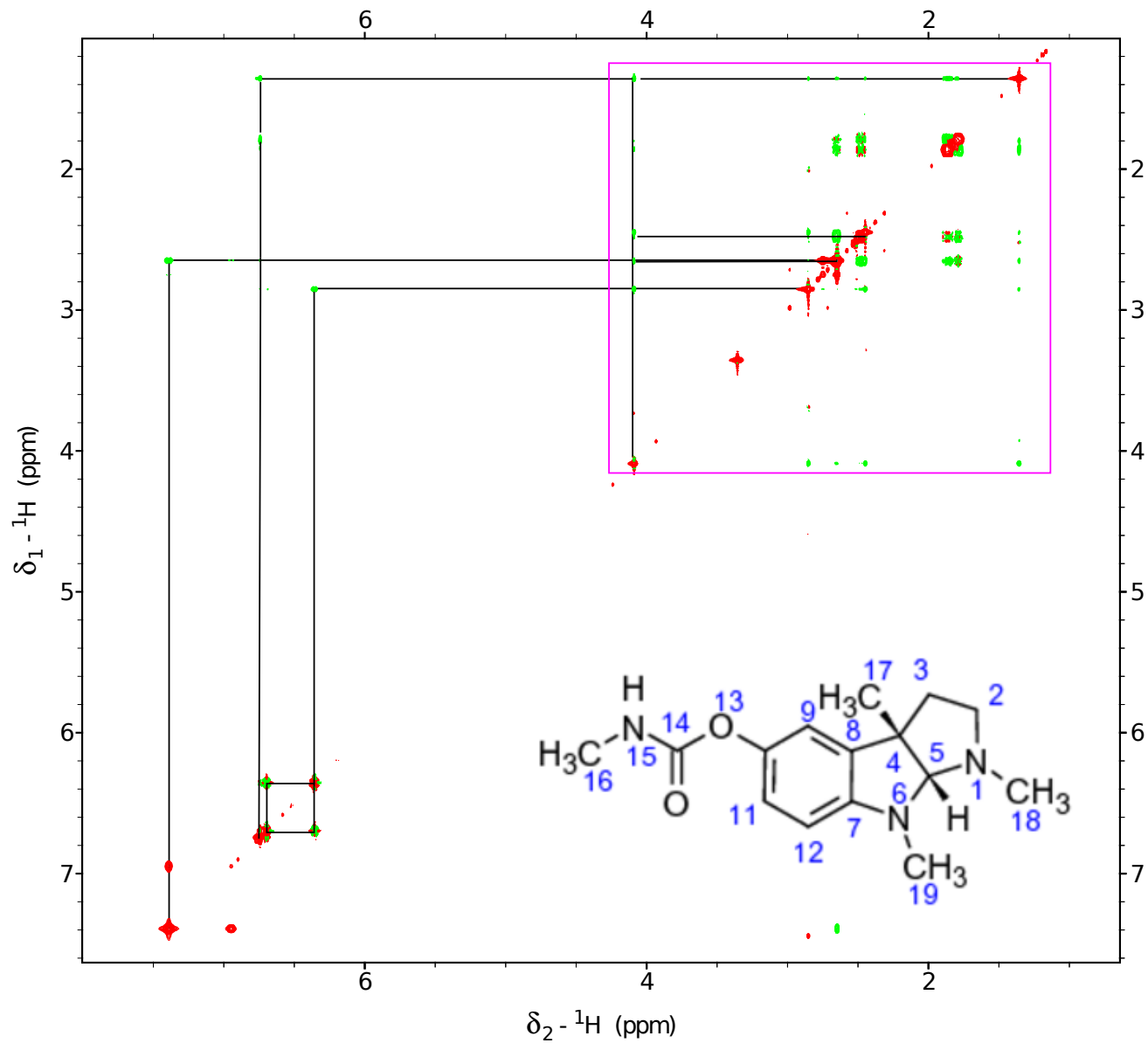


Eserine ¹H

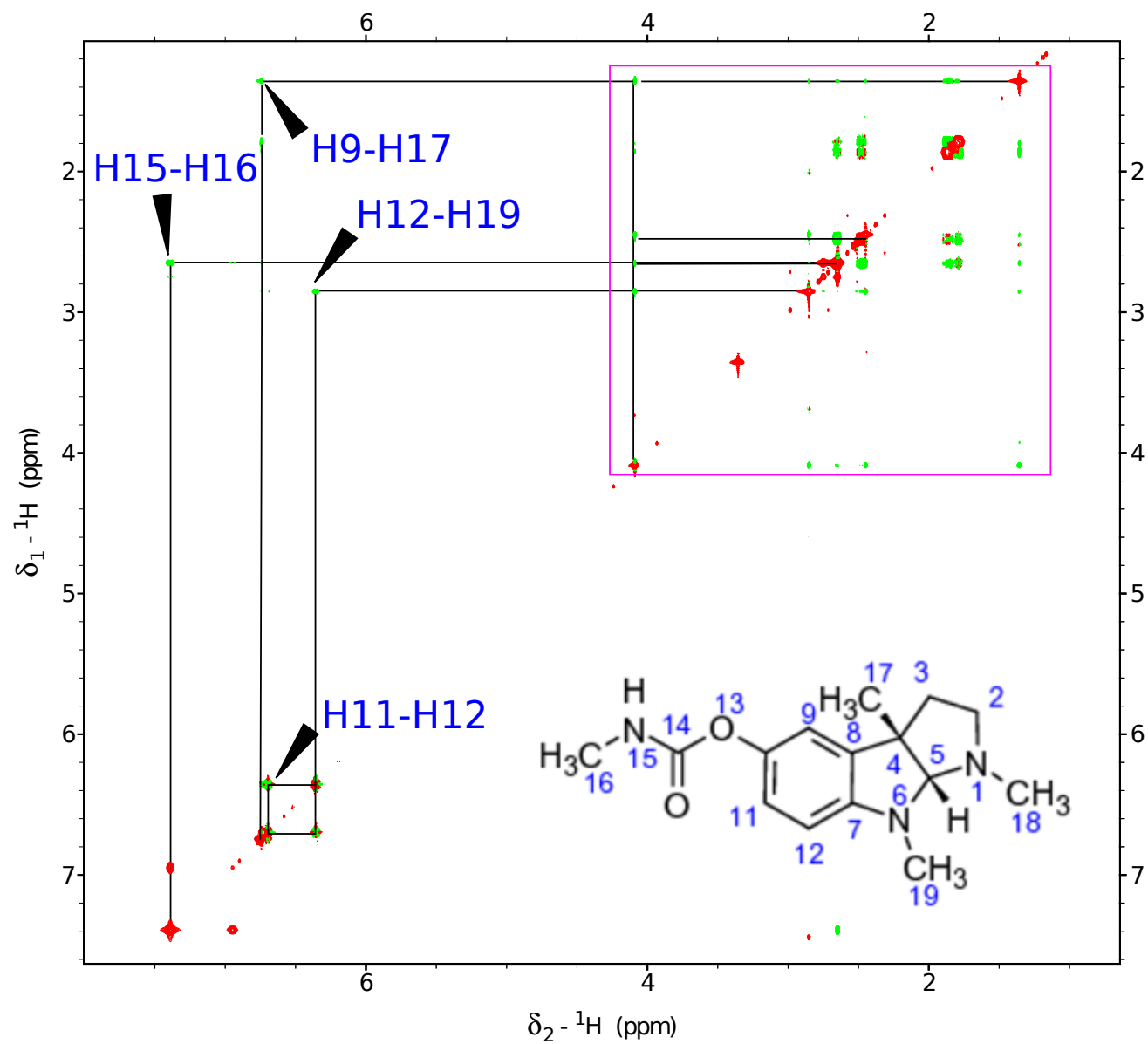
1H ESERINE



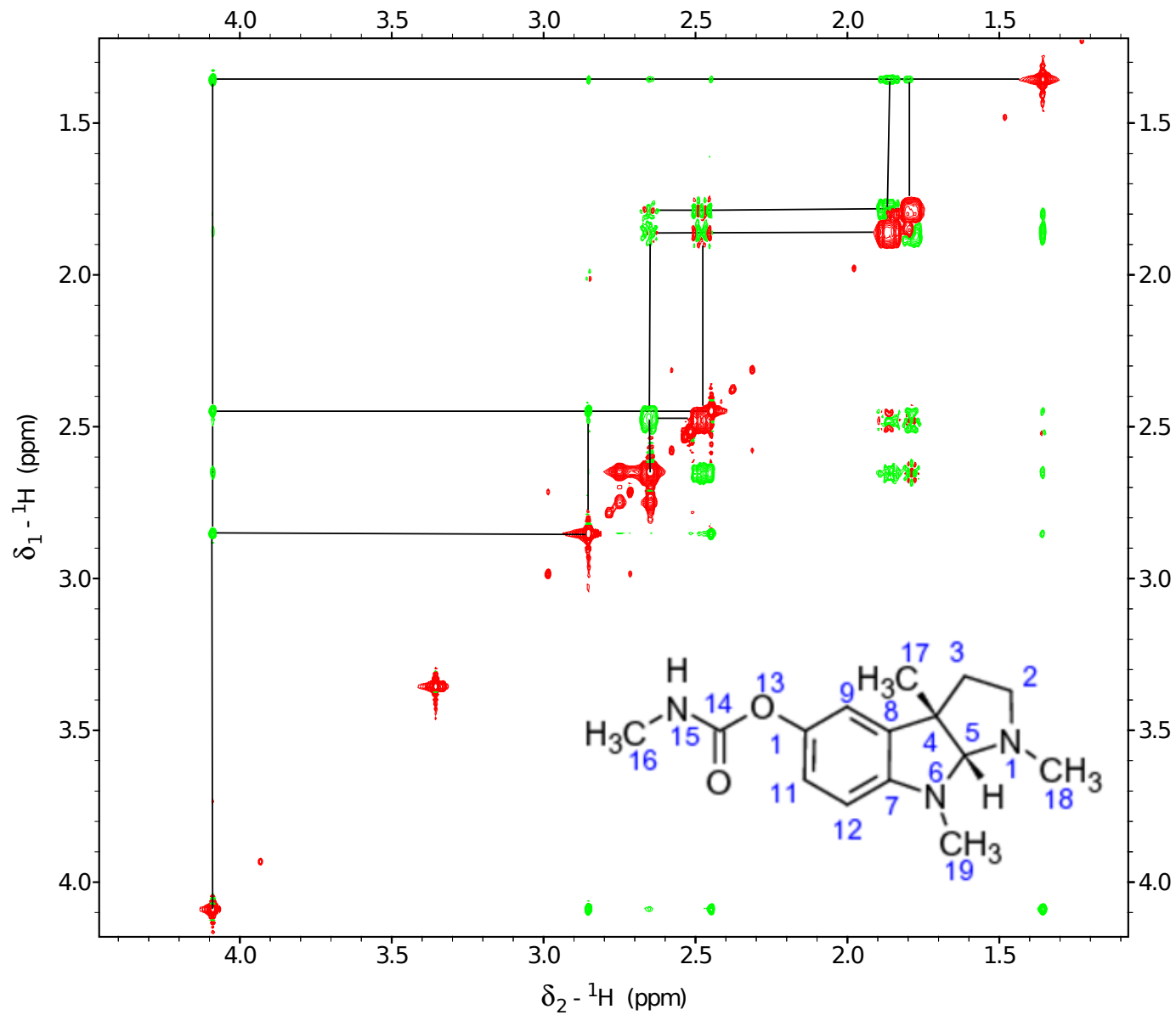
NOESY - Eserine



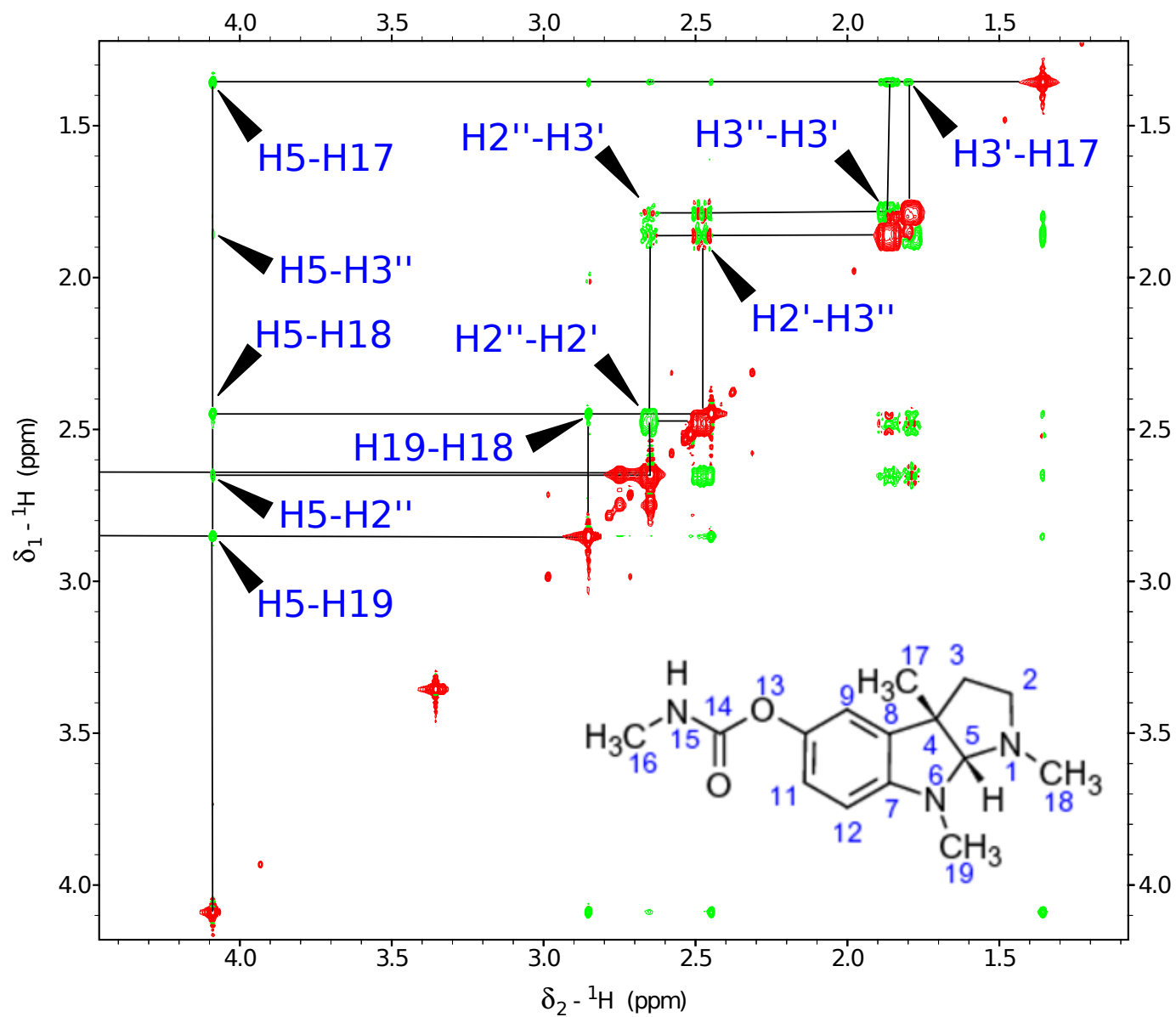
NOESY - Eserine



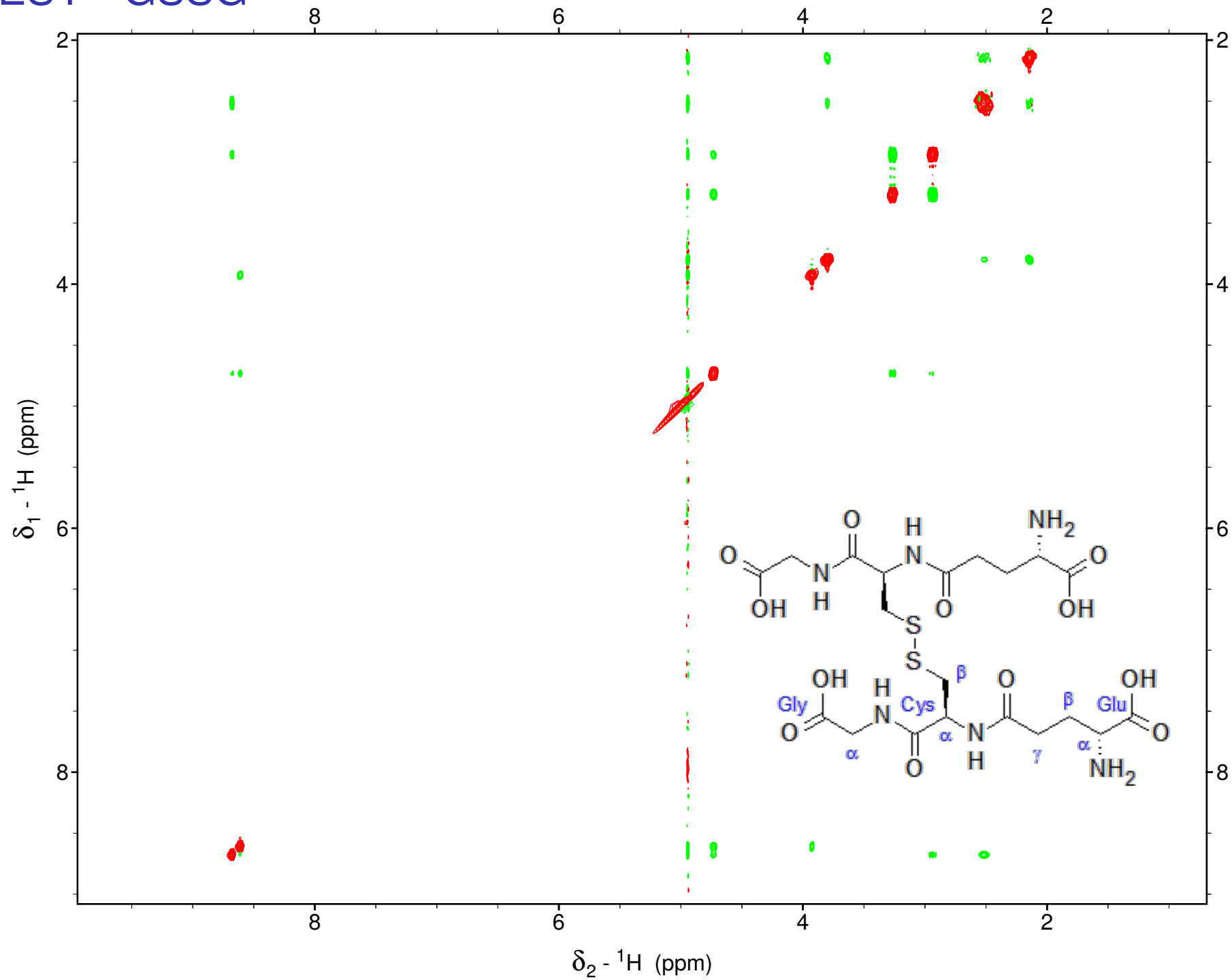
NOESY - Eserine



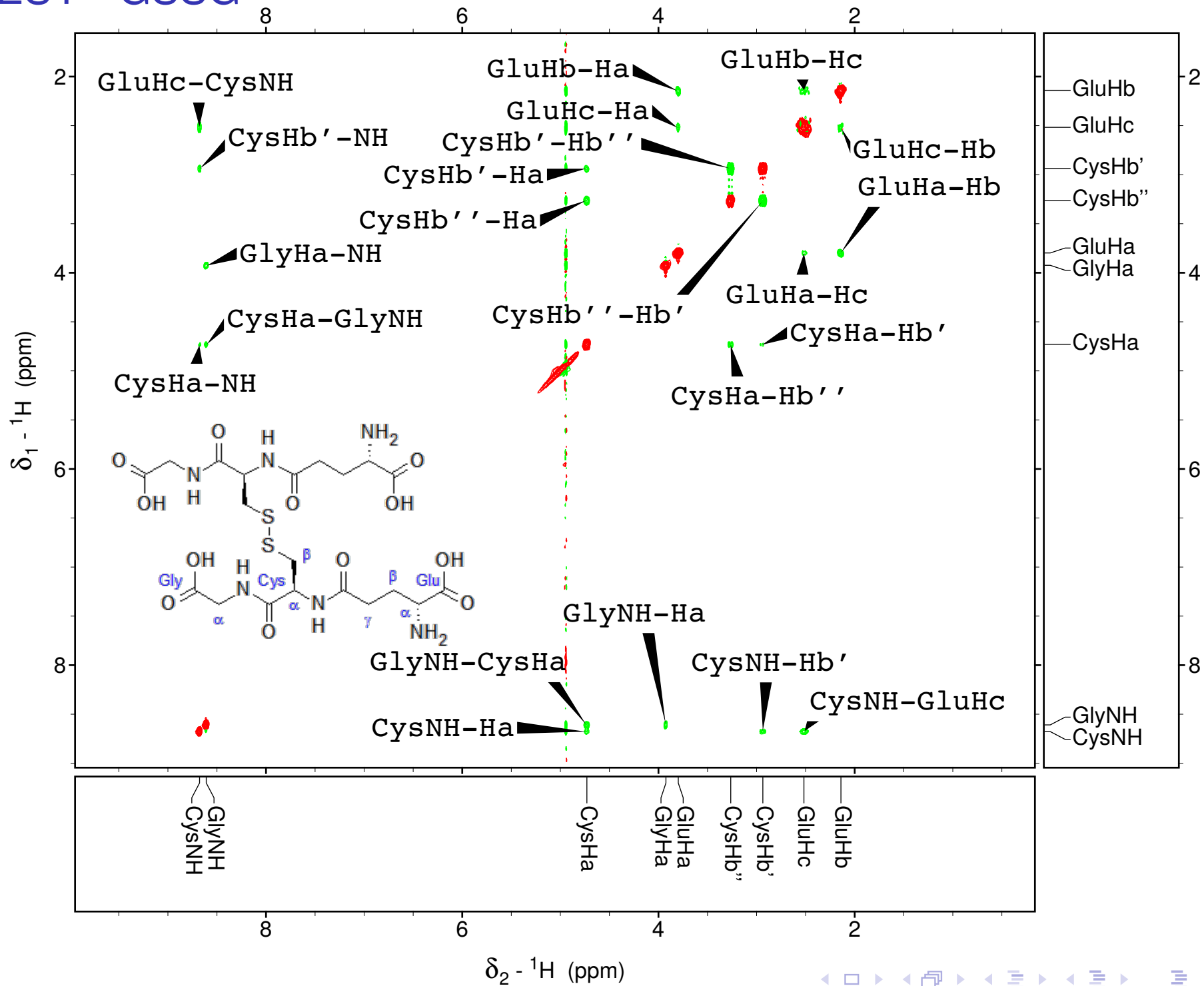
NOESY - Eserine



ROESY - GSSG

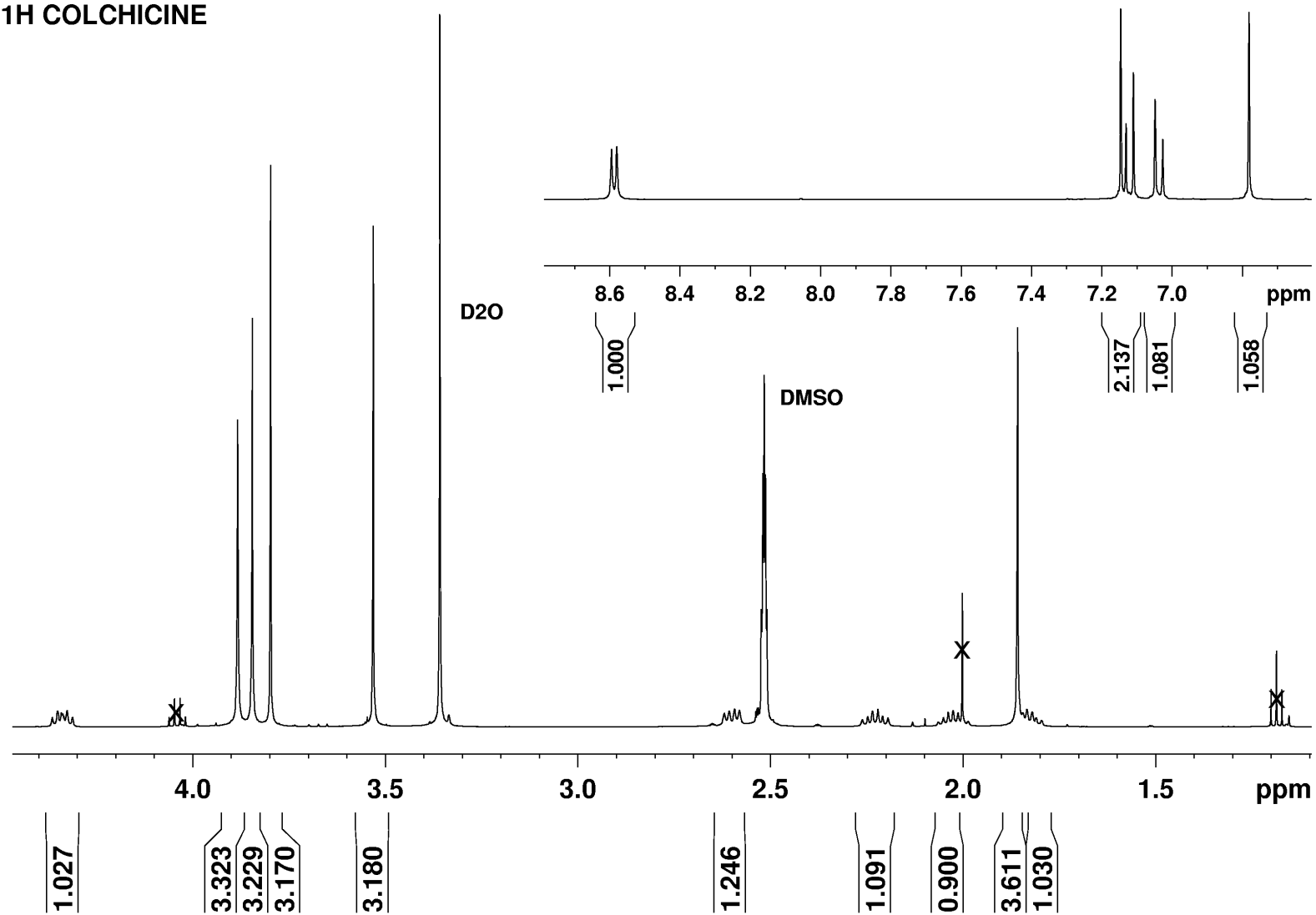


ROESY - GSSG

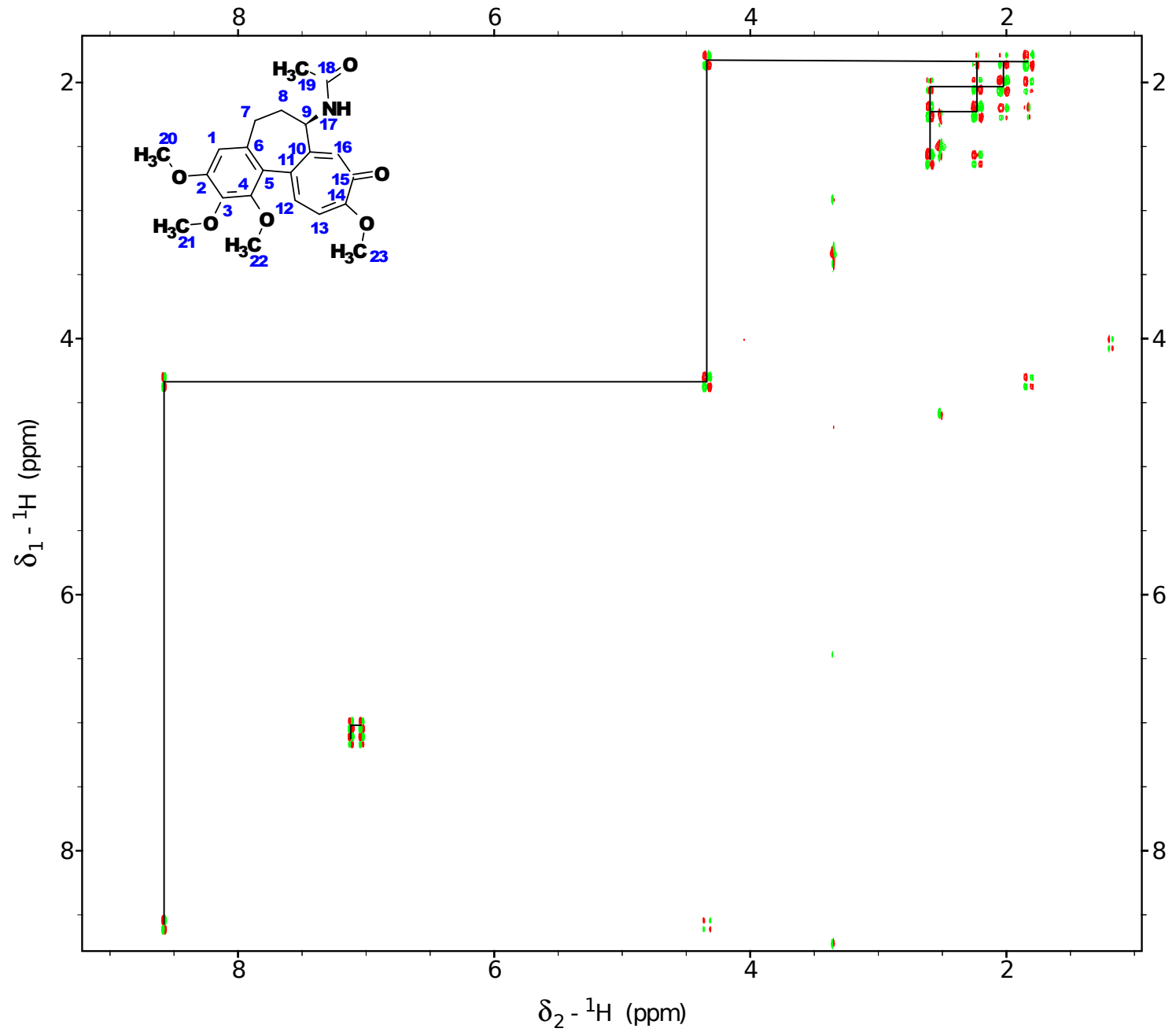


Colchicine 1D-¹H

1H COLCHICINE



Colchicine - DQF-COSY



Colchicine - NOESY

