

C8953
NMR strukturní analýza
seminář
TOCSY & NOESY

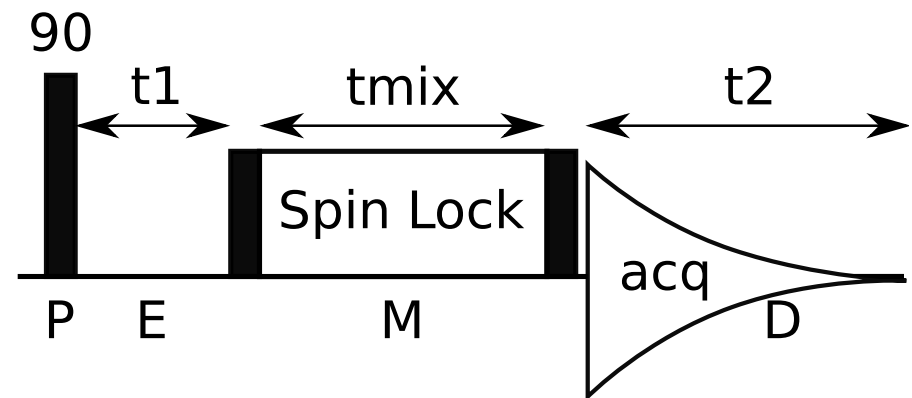
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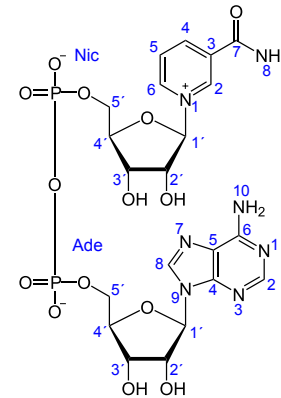
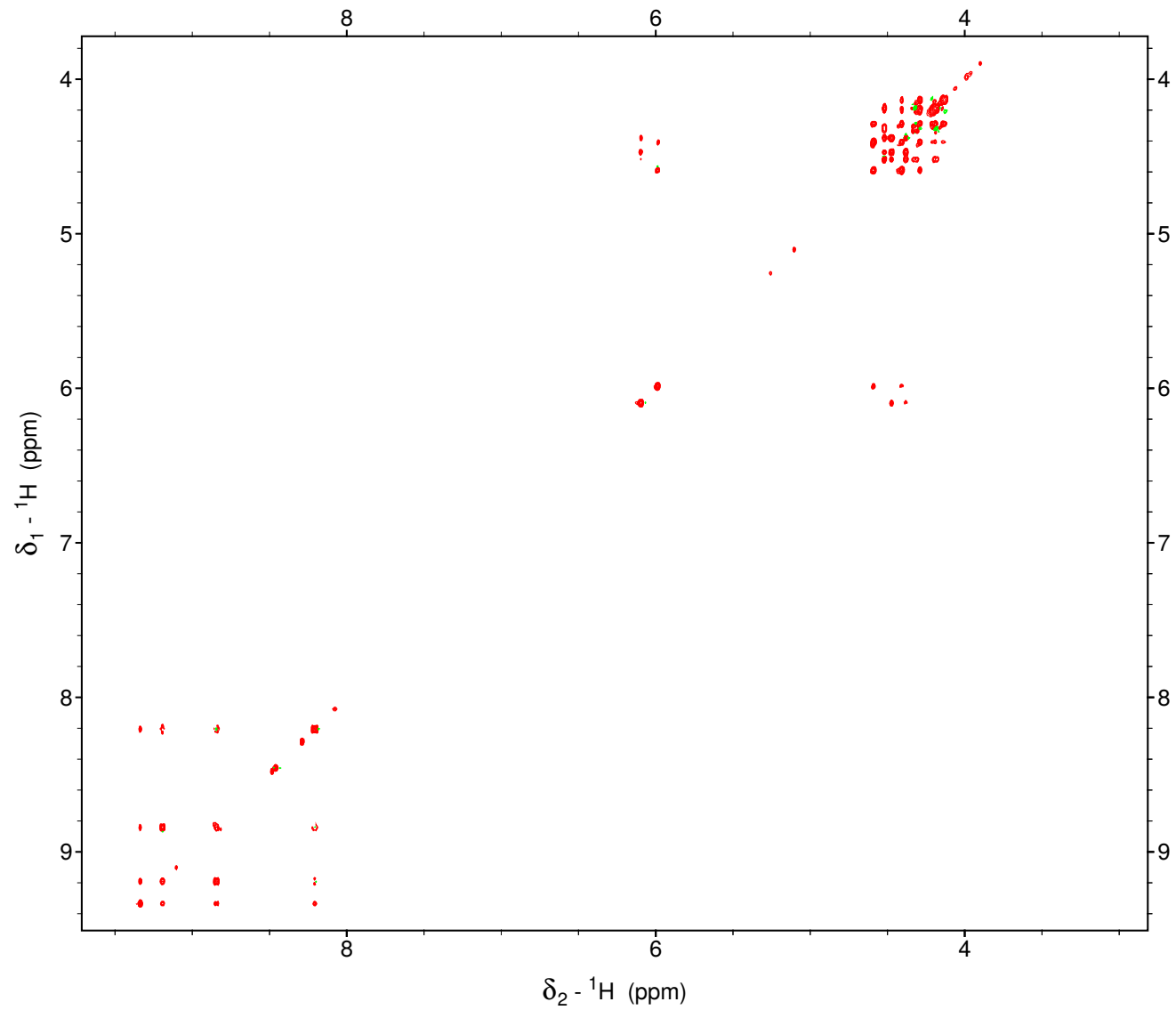
TOCSY (TOtal Correlation SpectroscopY)

spin lock - isotropic mixing

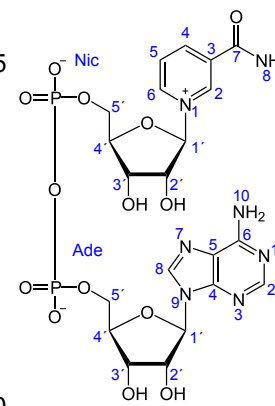
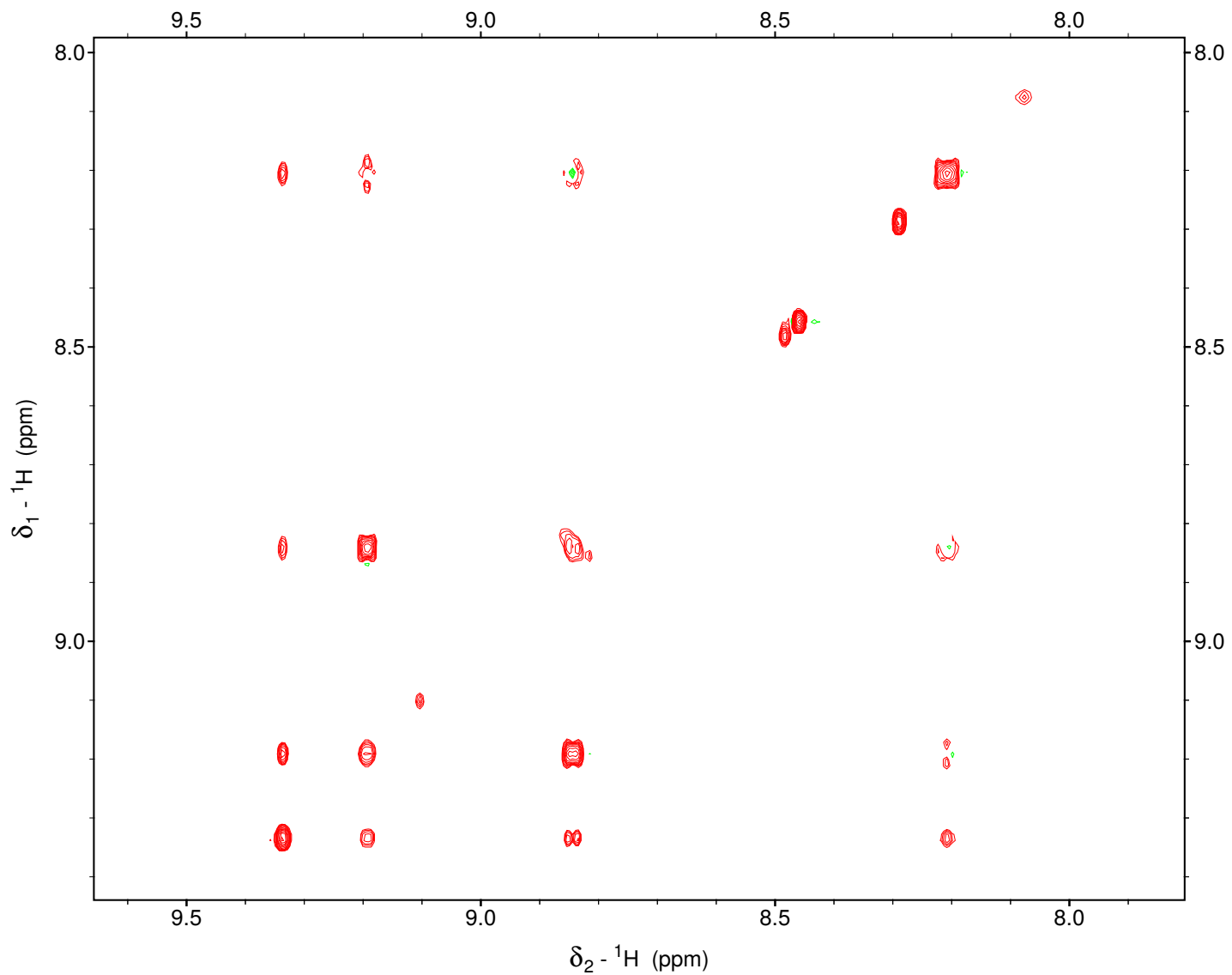
- ▶ series of short 180° pulses
- ▶ "lock-in" of spins in transversal plane
- ▶ higher power in case of TOCSY, offset set into the middle (on resonance)
- ▶ smaller power in case of ROESY, offset set into the edge (off resonance)
- ▶ crosstalk (ROE transfer in TOCSY, J -coupling in ROESY)



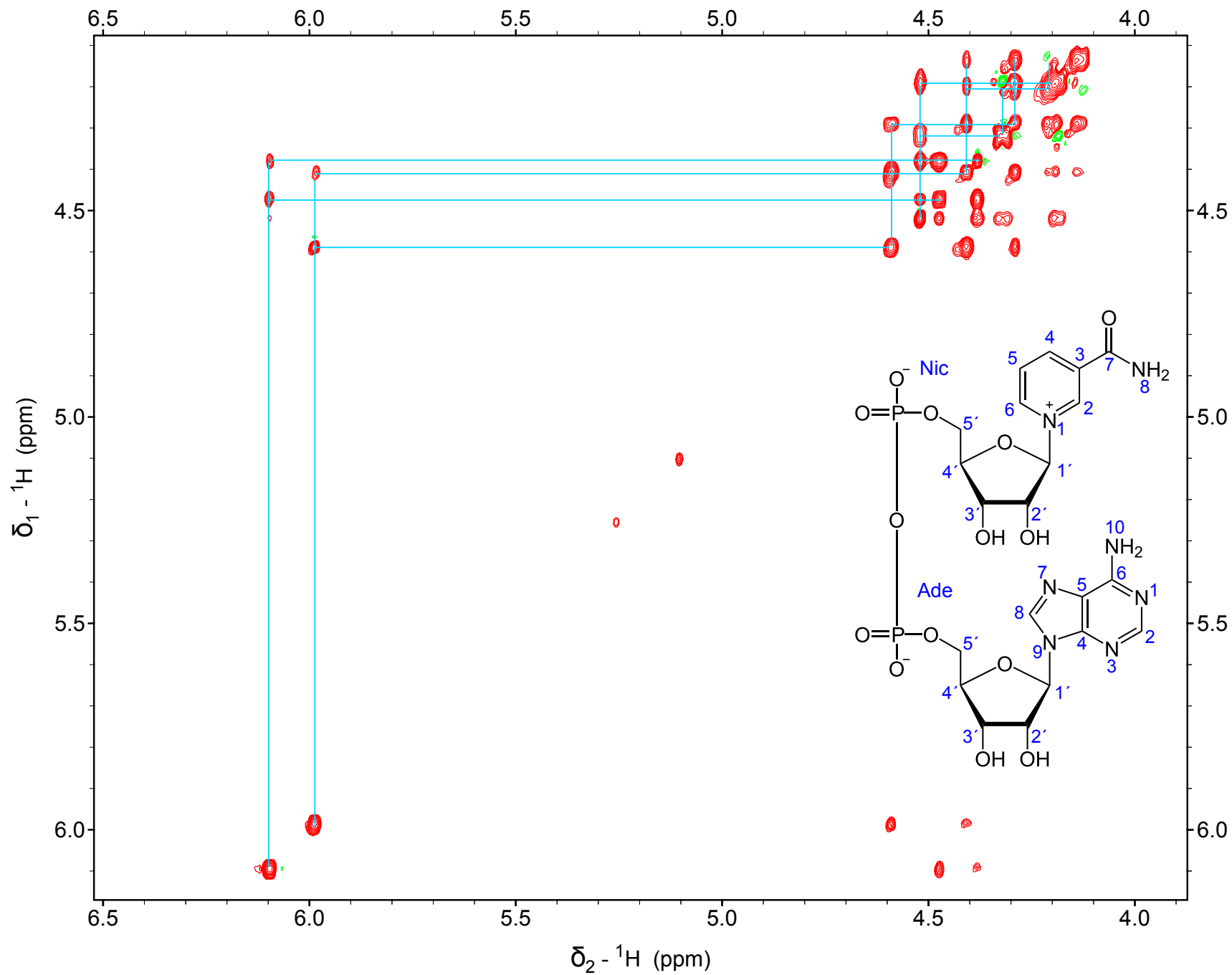
NAD⁺: TOCSY (40ms)



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



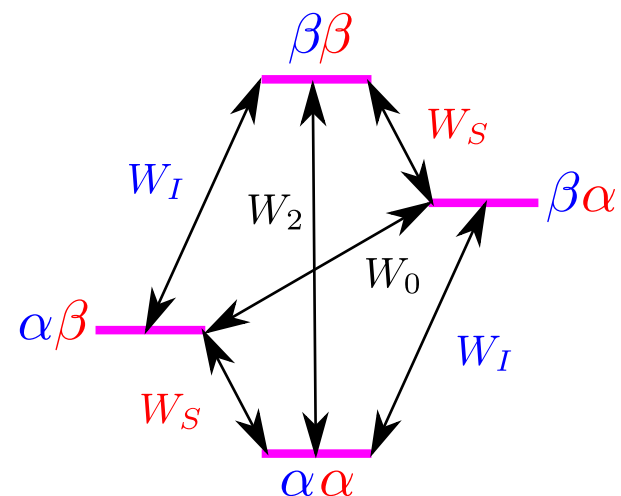
NAD⁺: TOCSY (40ms), detail of aliphatics



NOESY - introduction

Nuclear Overhauser effect

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

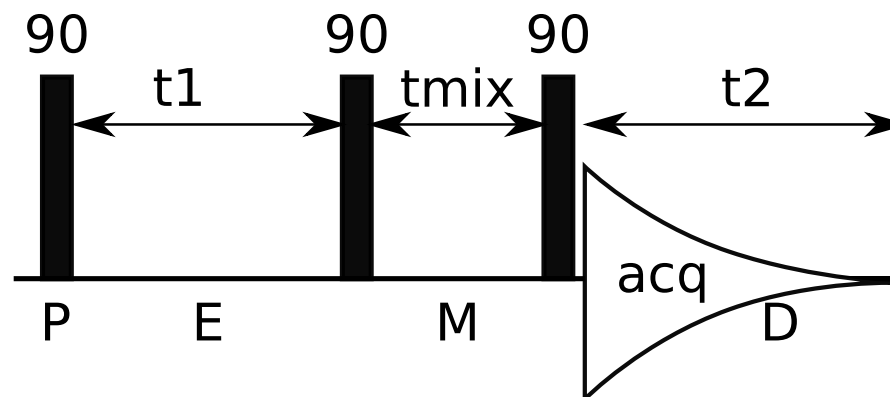


$$\frac{d\Delta I_z}{dt} = -\rho_I(I_z - I_z^0) - \sigma_{IS}(S_z - S_z^0)$$

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

NOESY

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

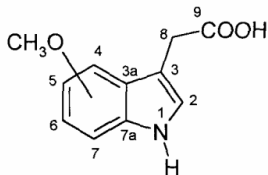


NOE differential experiment

PROBLEM 4

NOE- Difference Spectroscopy

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



What is the position of the methoxy group?

(400 MHz ^1H)

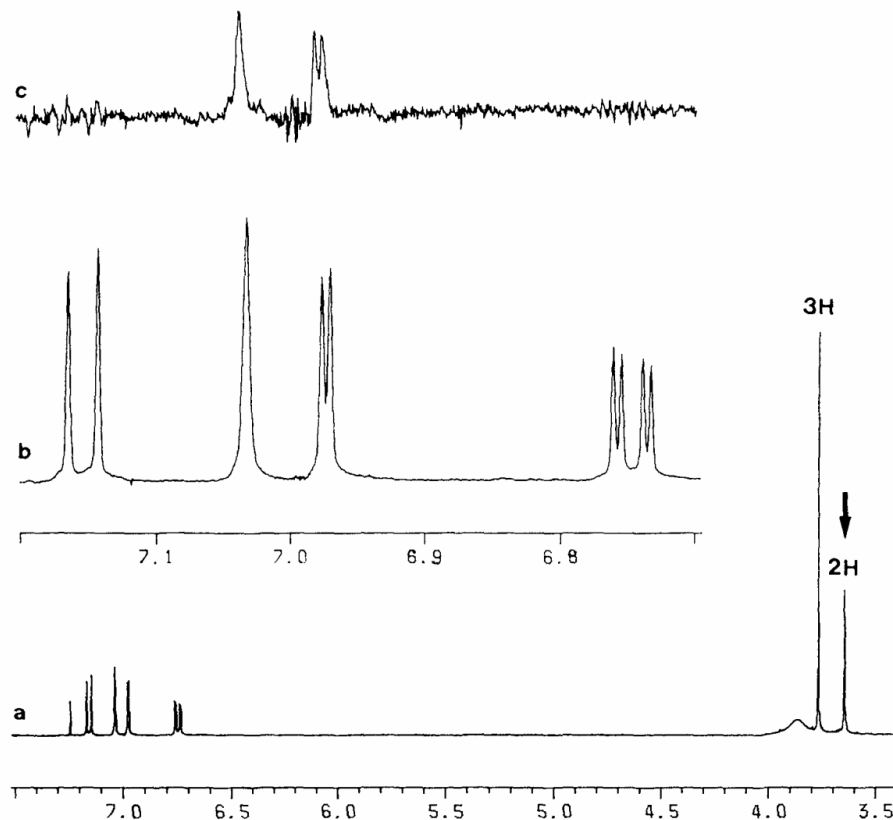
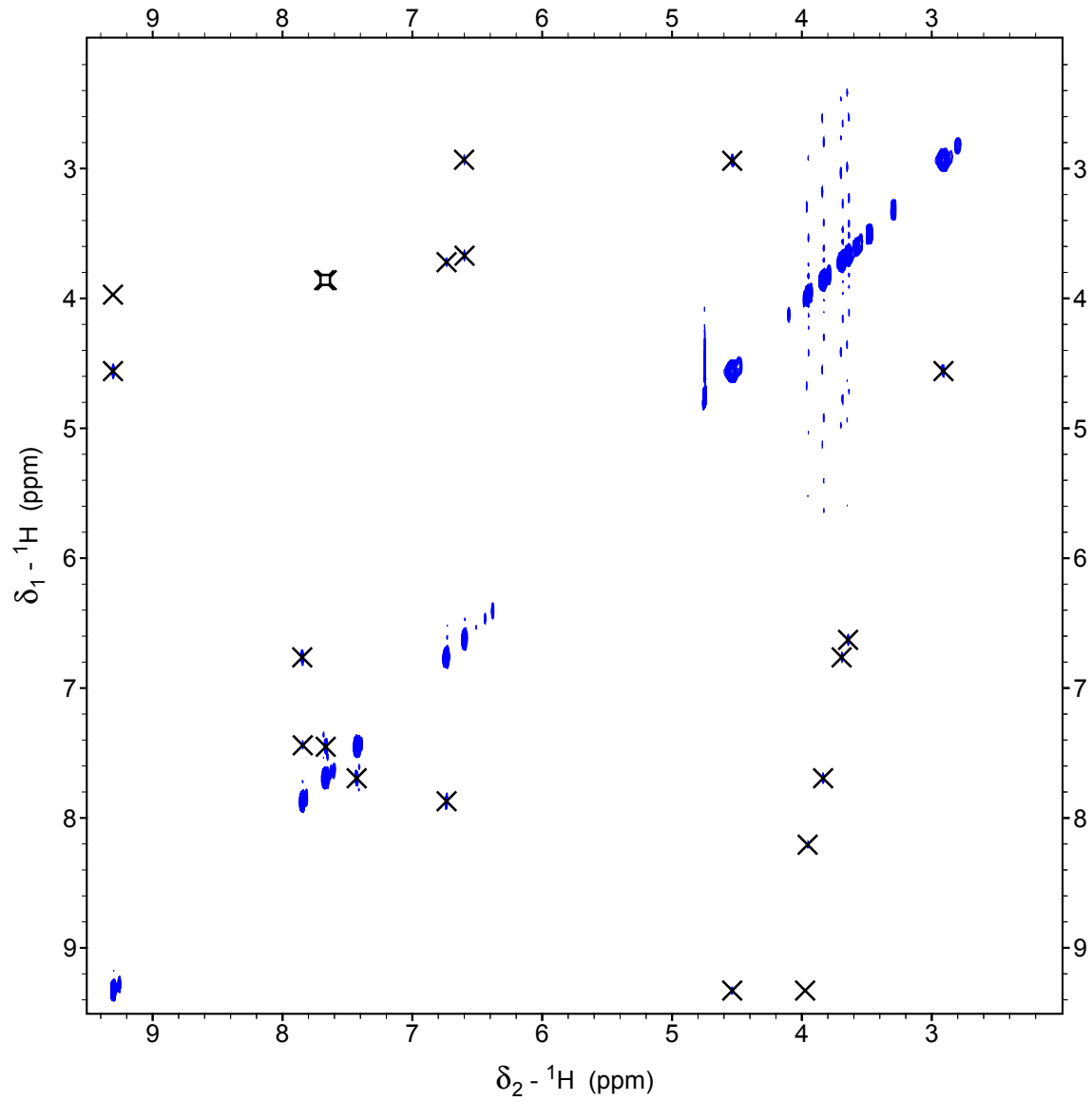
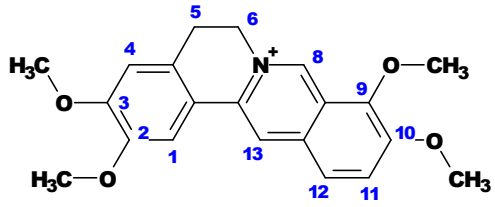


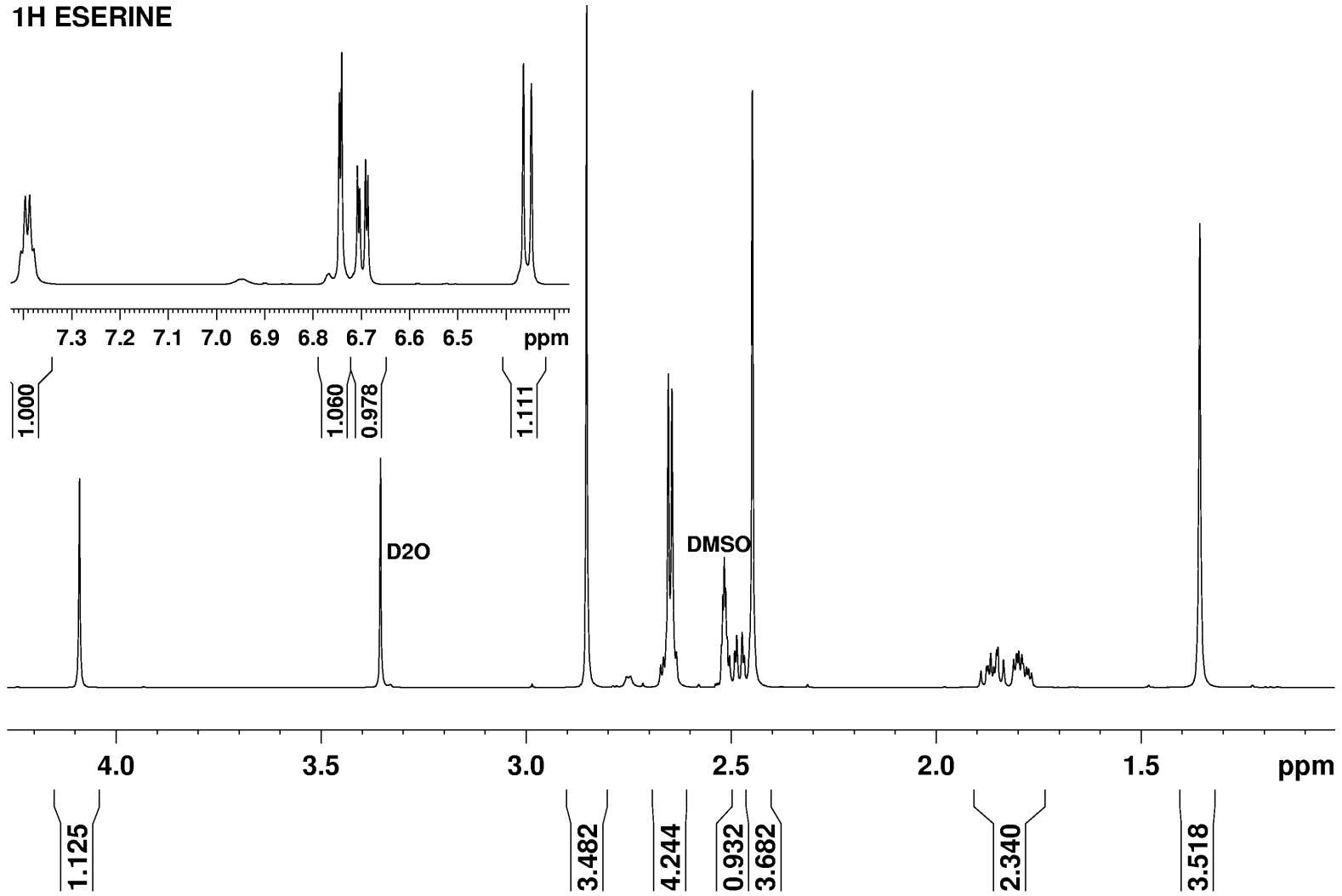
Fig. 4.1. 400 MHz ^1H NMR spectrum of **13** in a mixture of CDCl_3 and CD_3OD . **a** Full spectrum; **b** expanded section of the aromatic proton signals; **c** ^1H NOE difference spectrum, same section as in **b**, irradiation position at $\delta = 3.64$.

NOESY - Palmatine

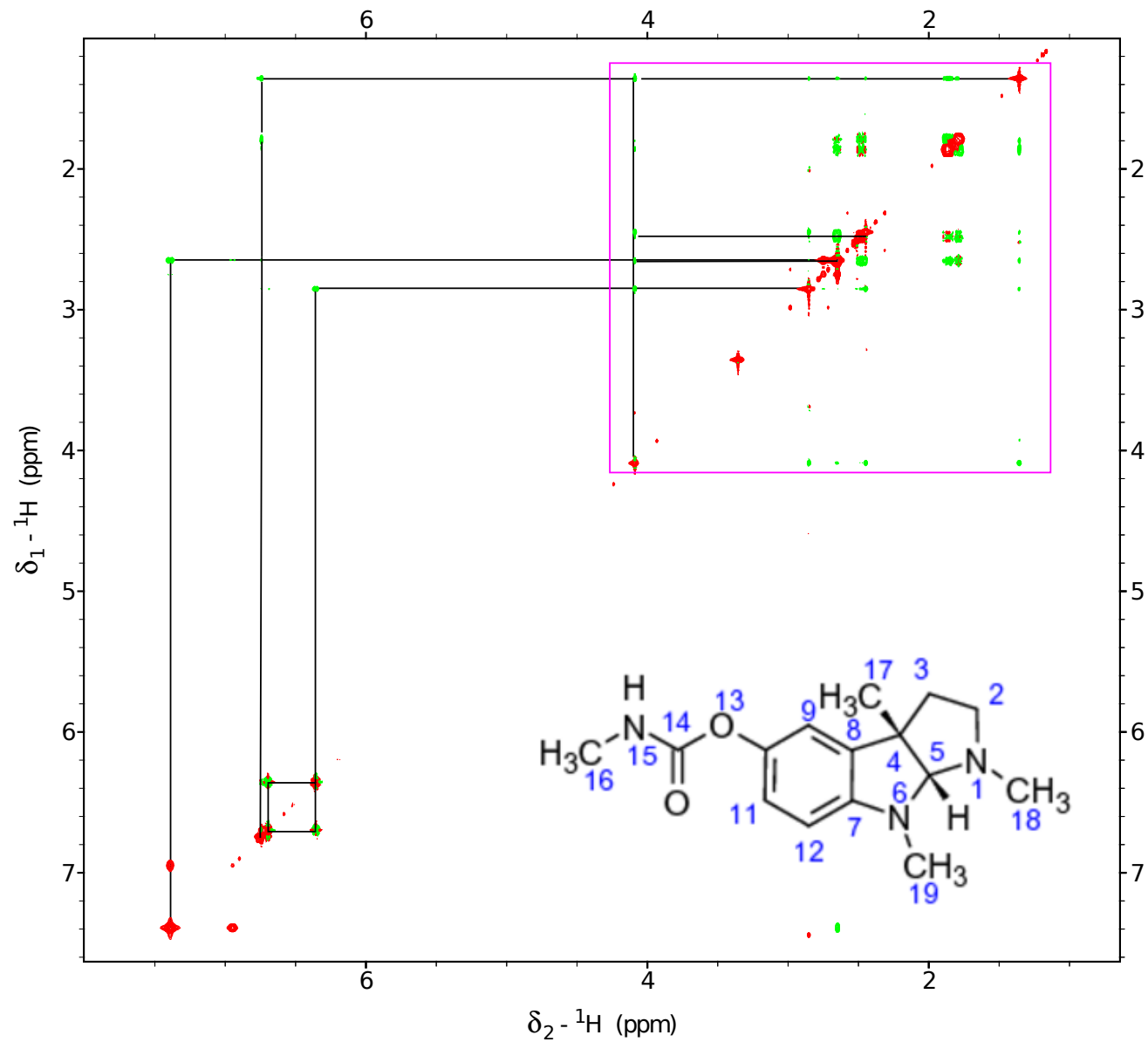


Eserine ¹H

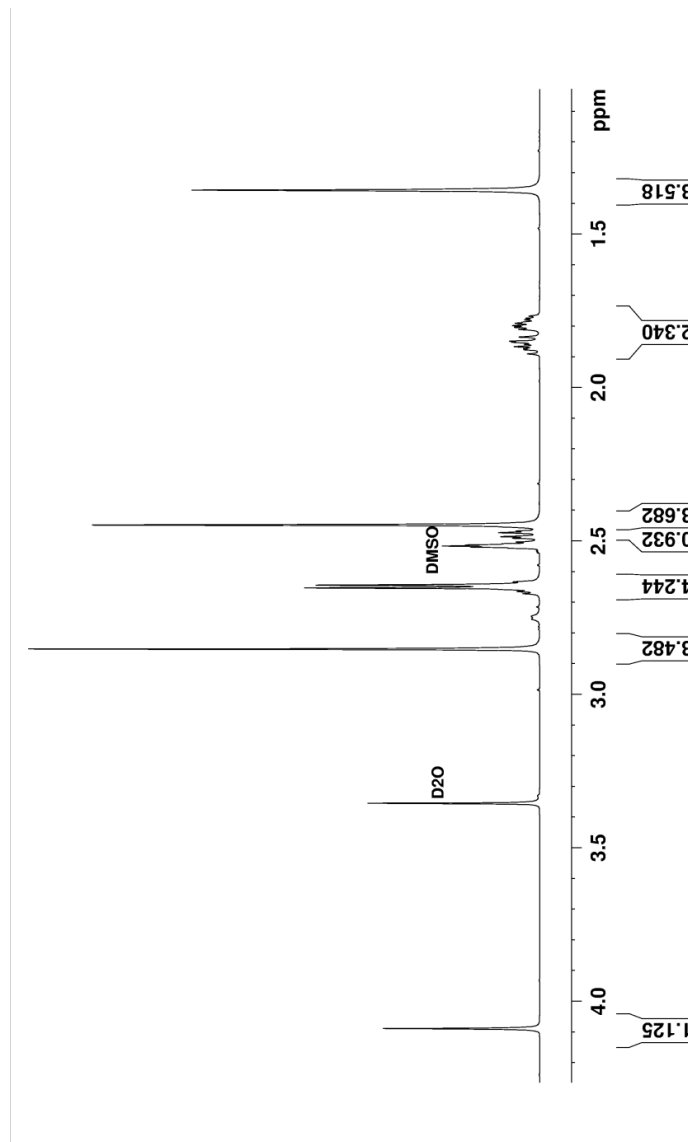
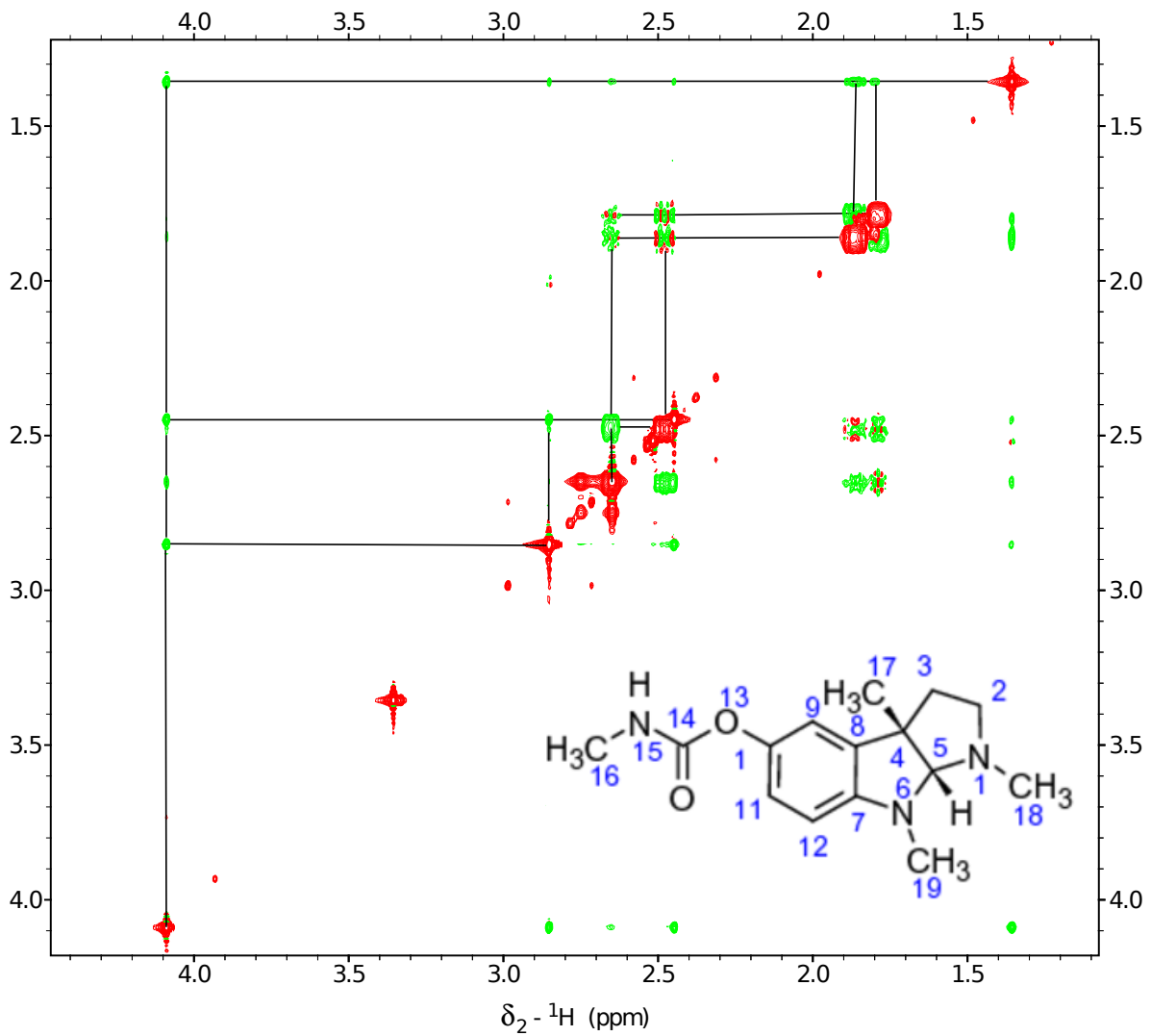
1H ESERINE



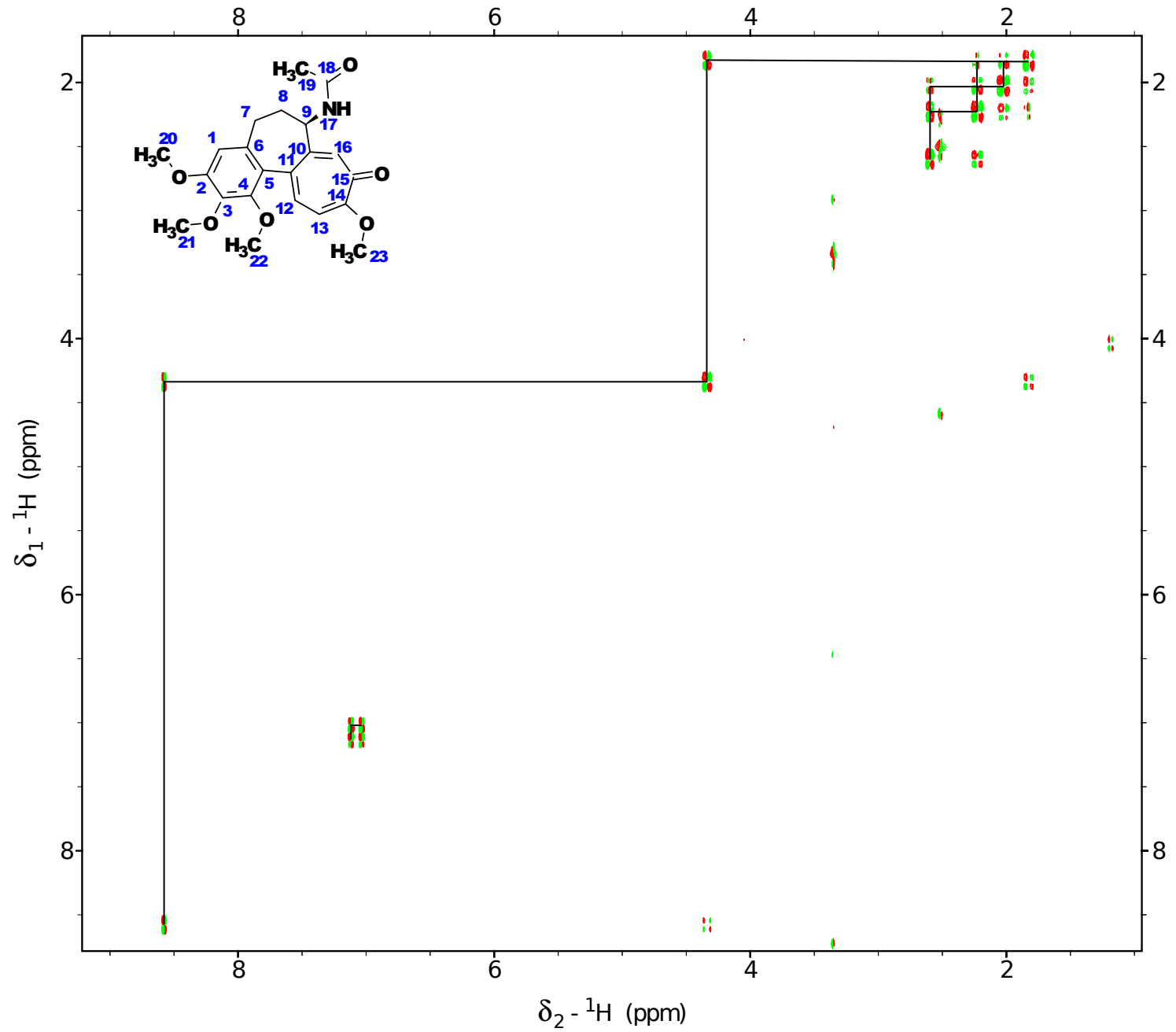
NOESY - Eserine in DMSO



NOESY - Eserine



Colchicine - DQF-COSY



Colchicine - NOESY

