JS Organic Practical Course

Additional NMR spectra to aid structural determination

Three types of data are supplied :

- -2D homonuclear corelation spectra (HH COSY)
- -2D heteronuclear corelation spectra (CH COSY)
- -1D Nuclear Overhauser spectra (NOE)

Data is supplied for experiments :

- -2 (Benzoin), 3b (1,4-Diphenyl-1,3- butadiene)
- -5 (2,6-Dimethyl-3-heptan-5-one)
- -6a (1-Phenylbutane-1,4-diol)
- -6b (γ-Phenyl-γ-butyrolactone)
- -7 (*cis*-Caran-*trans*-4-ol)

Additional NMR analysis
connections through bonds and space

- Correlation Spectra (COSY) – through bond connections
  - HH COSY - connections of proton spins through bonds
  - CH COSY- direct link of carbon to proton(s)
  - Long range CH COSY
- Connections through space
  - Nuclear Overhauser (NOE) experiments
    - 1D : Difference NOE, DPFGSE-NOE
    - 2D : NOESY, ROESY

How to read a COSY

- HH COSY

  diagonal is the 1D spectrum

  off diagonal signal(s) display the connections of the spins

  true signal *must* have mirror image across the diagonal

- CH COSY

  signals are the direct correlation between the C and H

- Long range CH COSY

  often can correlate several protons to a carbon

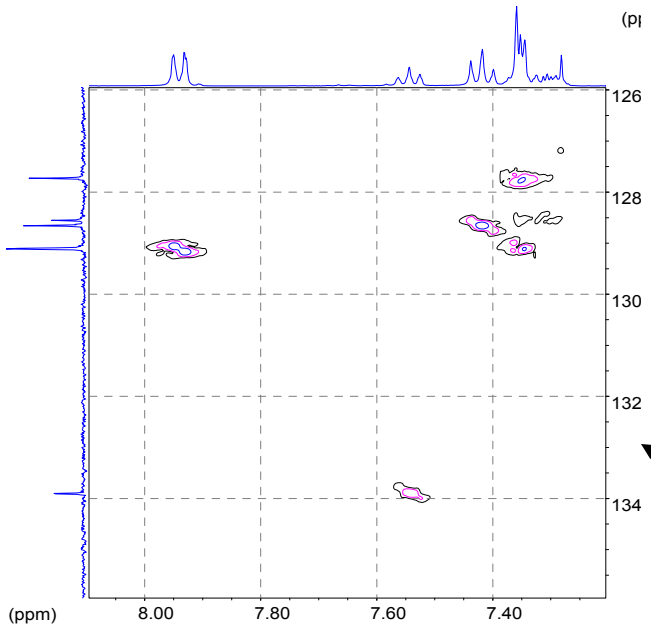
  (or *vice versa* - whichever is most appropriate)

  e.g. links carbon signals with NO protons directly attached

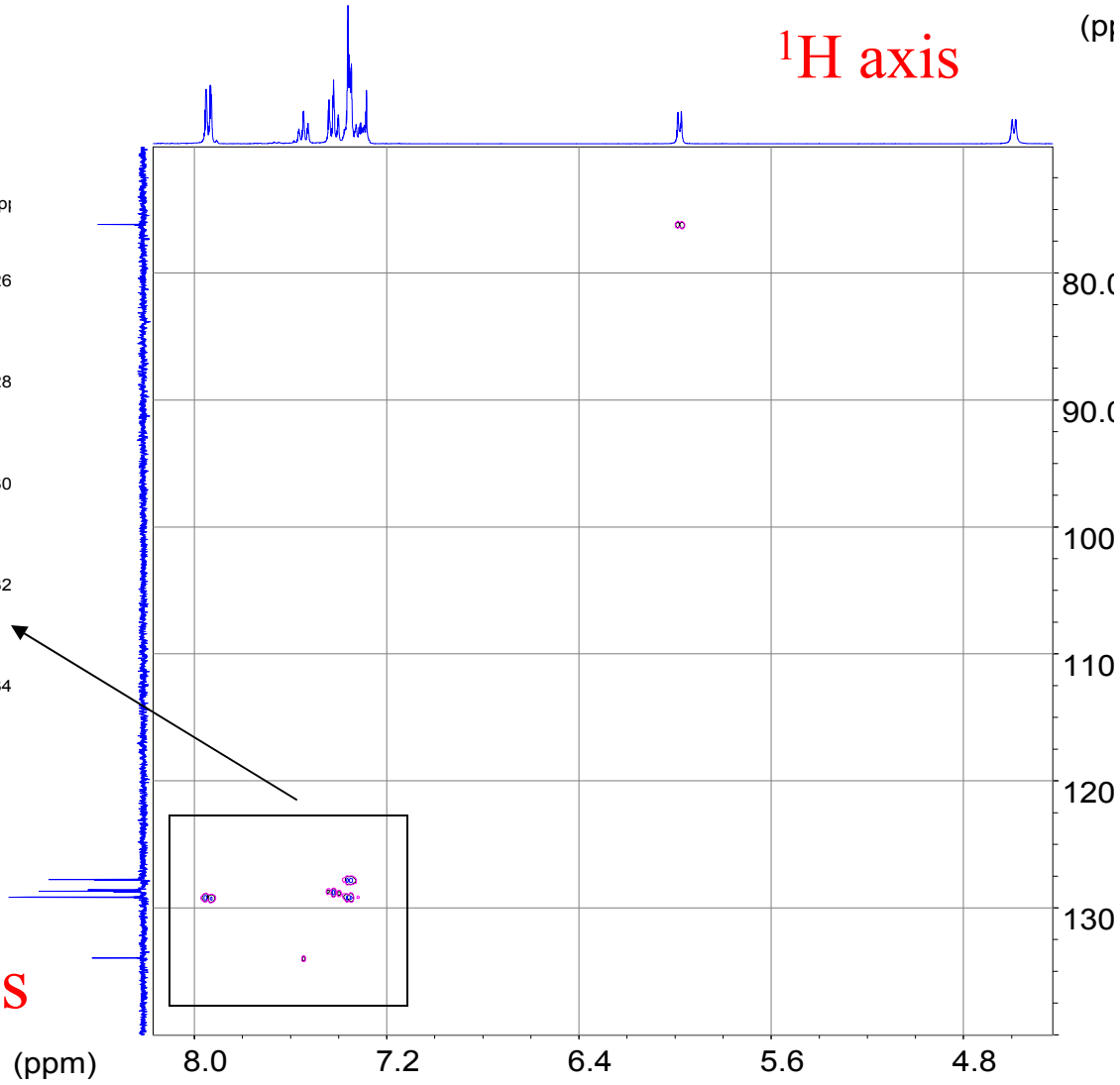
2 CH COSY Benzoin

Direct correlation of

hydrogen to *carbon* resonances



Expansion of aromartic region

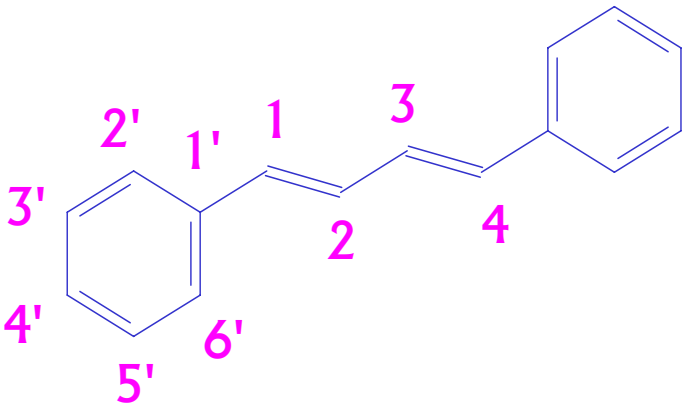


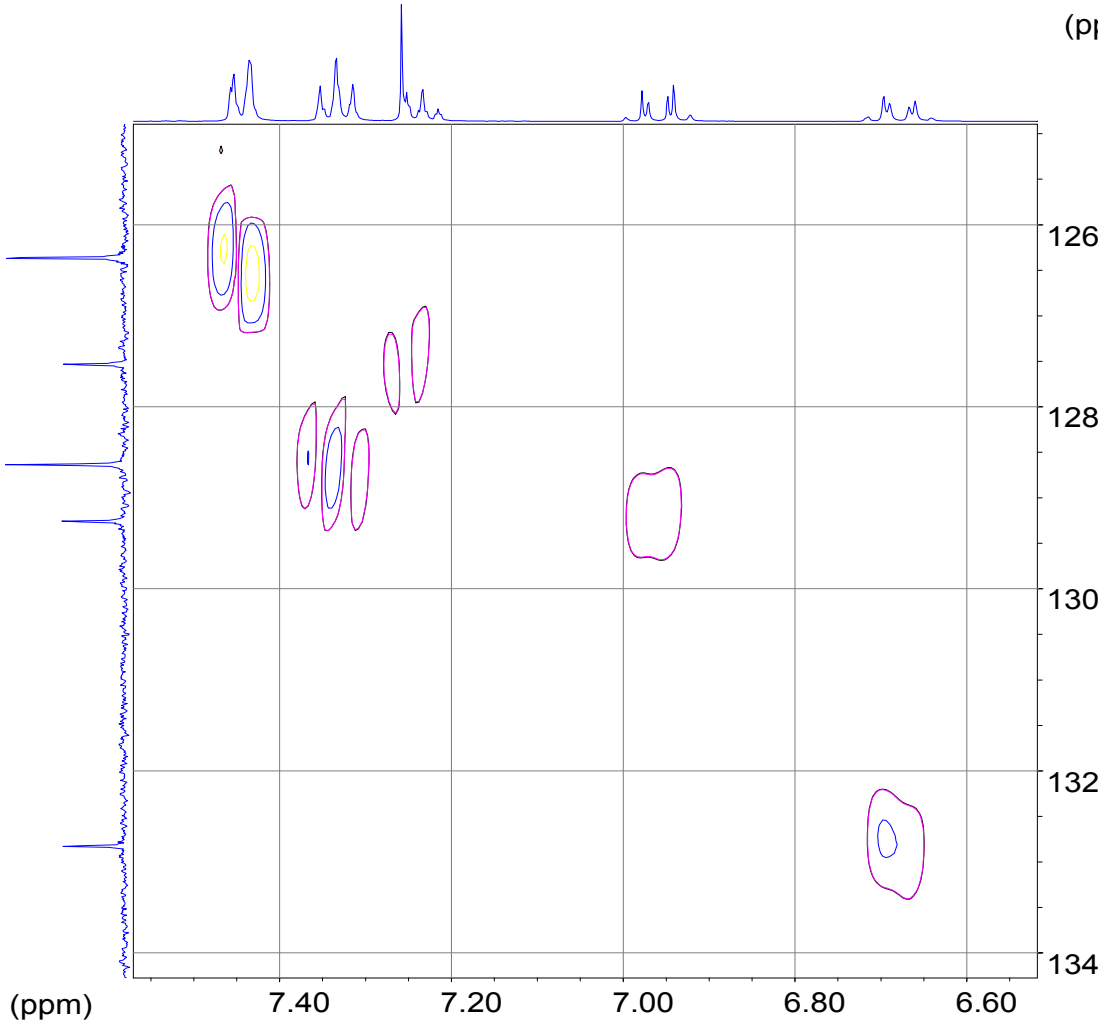
^{1}H axis

^{13}C axis

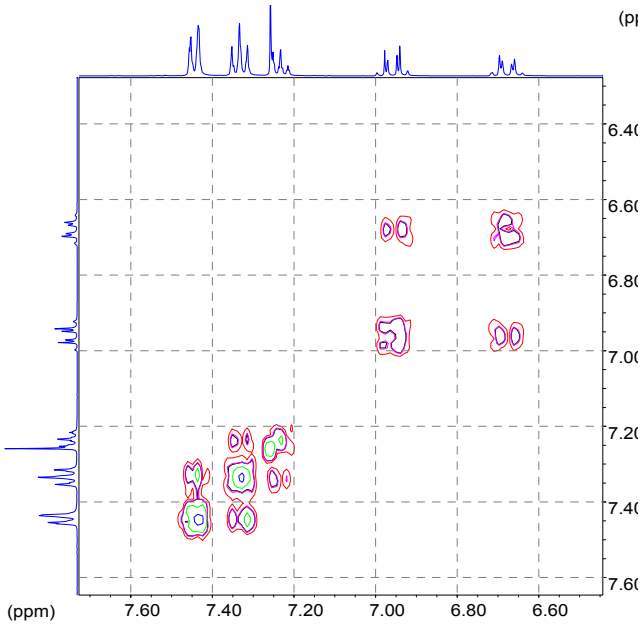
3B CH COSY (E,E)-1,4-Diphenyl-1,3-butadiene

Direct correlation of
hydrogen to *carbon* resonances





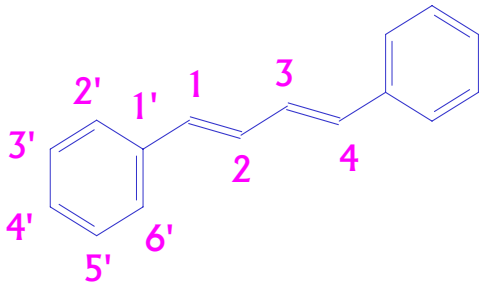
3B HH COSY (E,E)-1,4-Diphenyl-1,3-butadiene

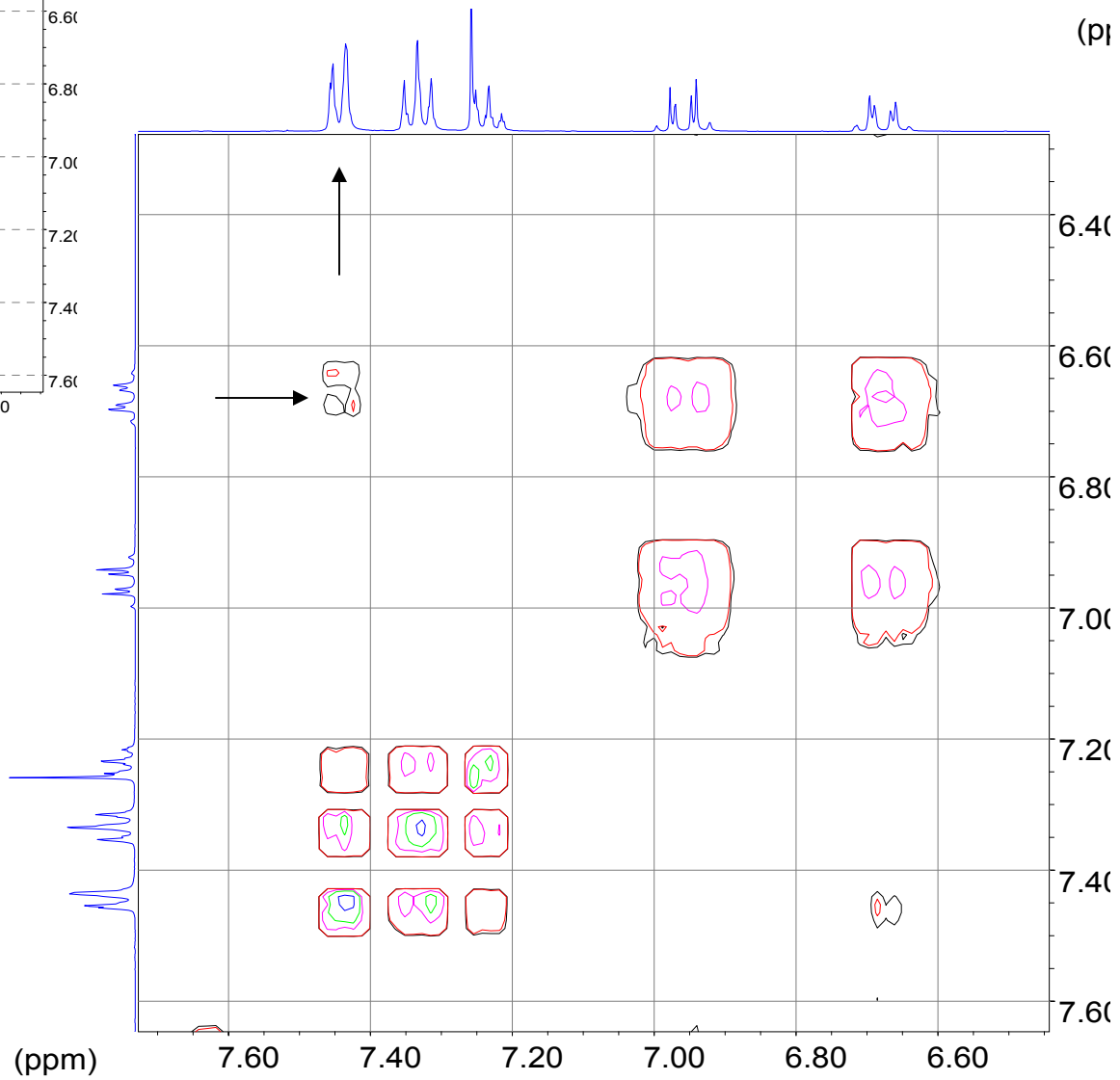


Diagonal contains the 1D spectrum

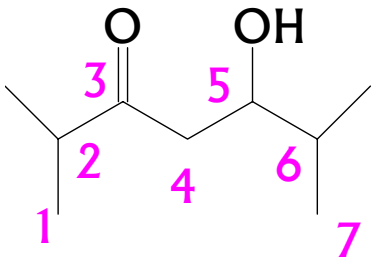
Connections between atoms are symmetrical about the diagonal

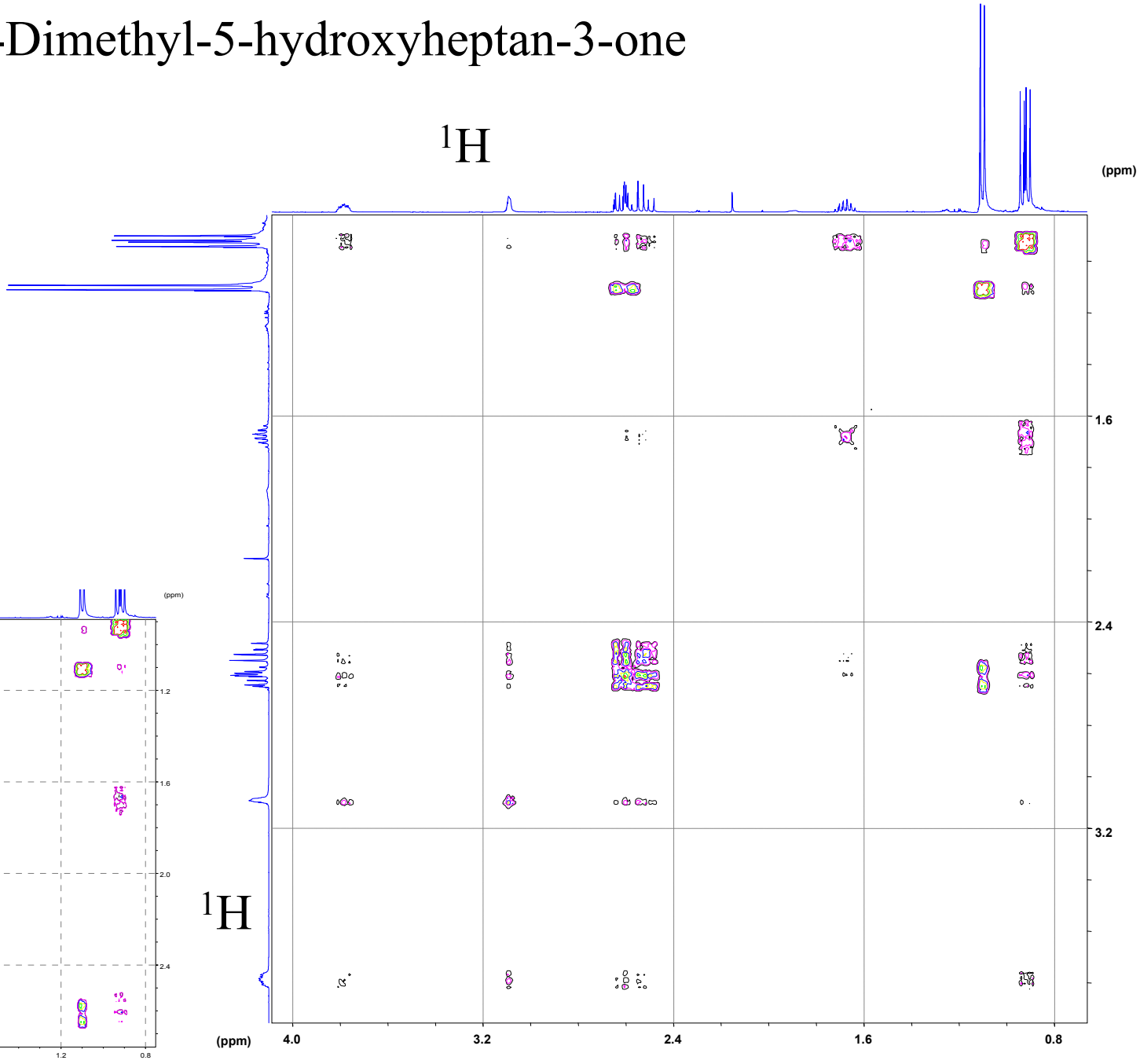
Generally, the higher the contour the stronger the connection

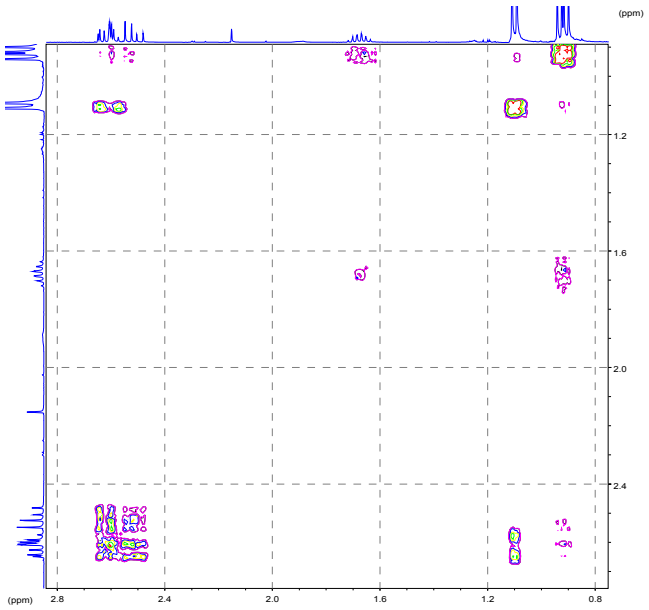




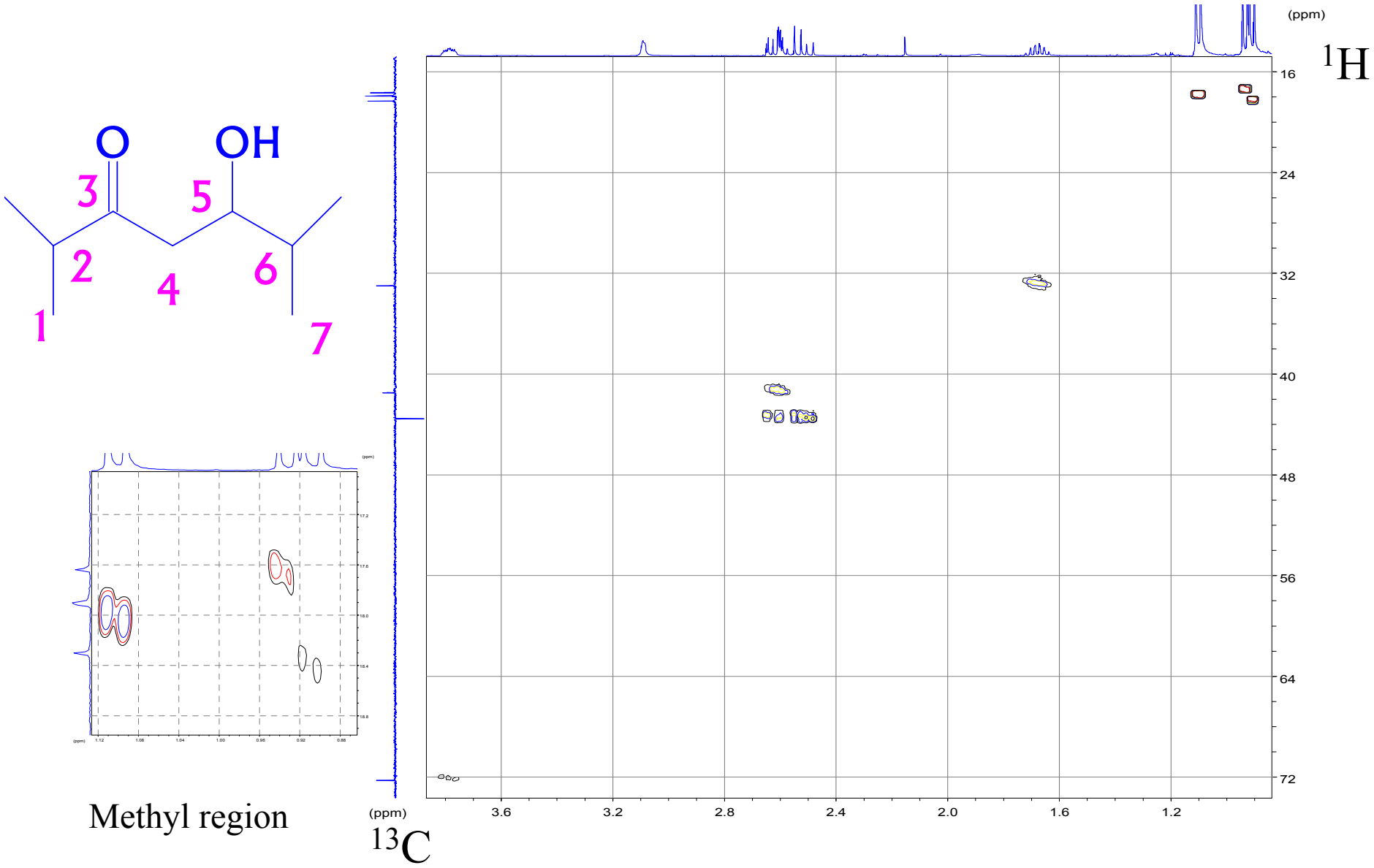
5 HH COSY 2,6-Dimethyl-5-hydroxyheptan-3-one





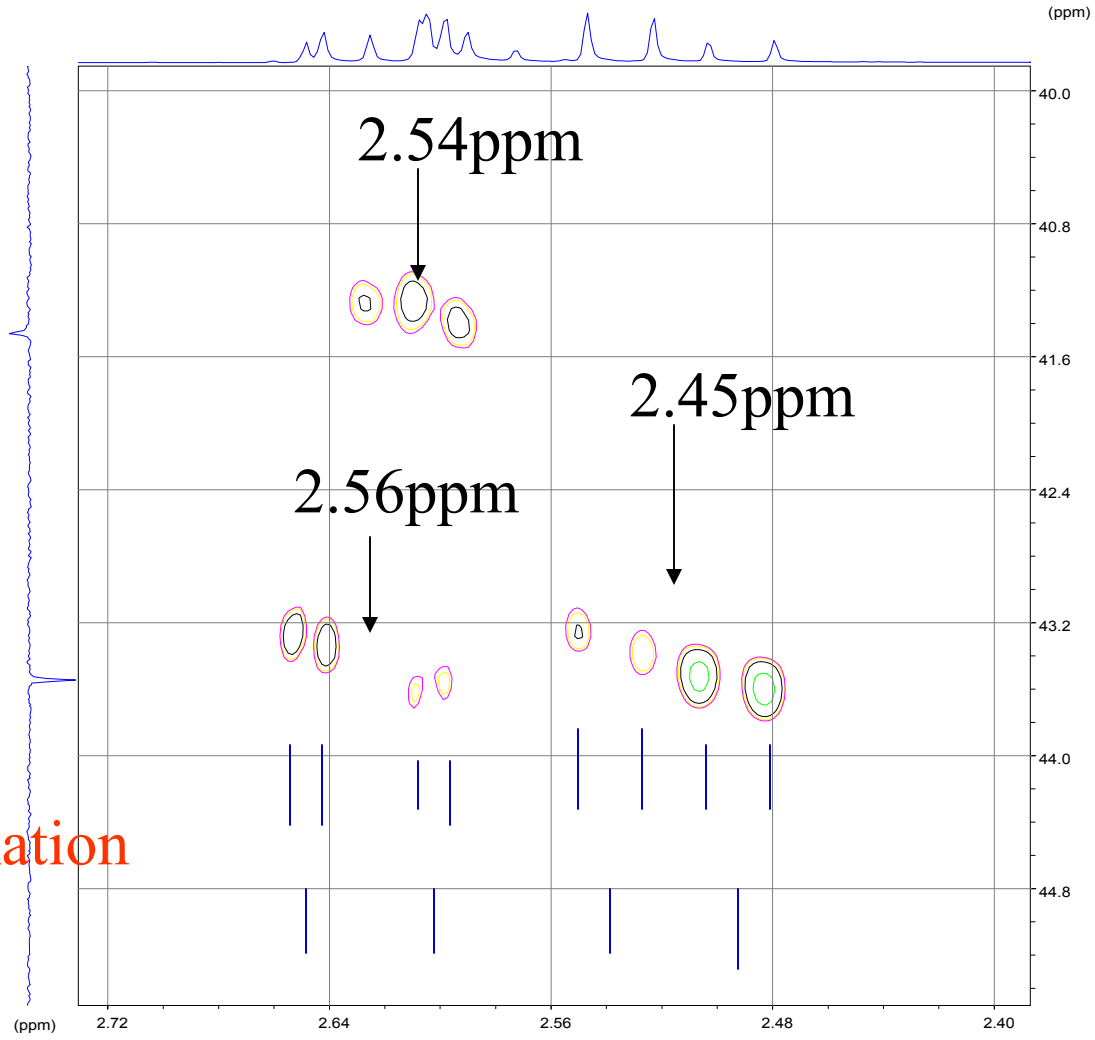


5 CH COSY 2,6-Dimethyl-5-hydroxyheptan-3-one



5 CH COSY 2,6-Dimethyl-5-hydroxy-heptan-3-one

Expansion of the 2.40-2.75ppm region



CH →

-CH_2- →

Spin-Spin Coupling information from the CH_2 (Hz)

5 Long Range CH COSY 2,6-Dimethyl-5-hydroxyheptan-3-one

Notice CH correlations to :

- a longer range

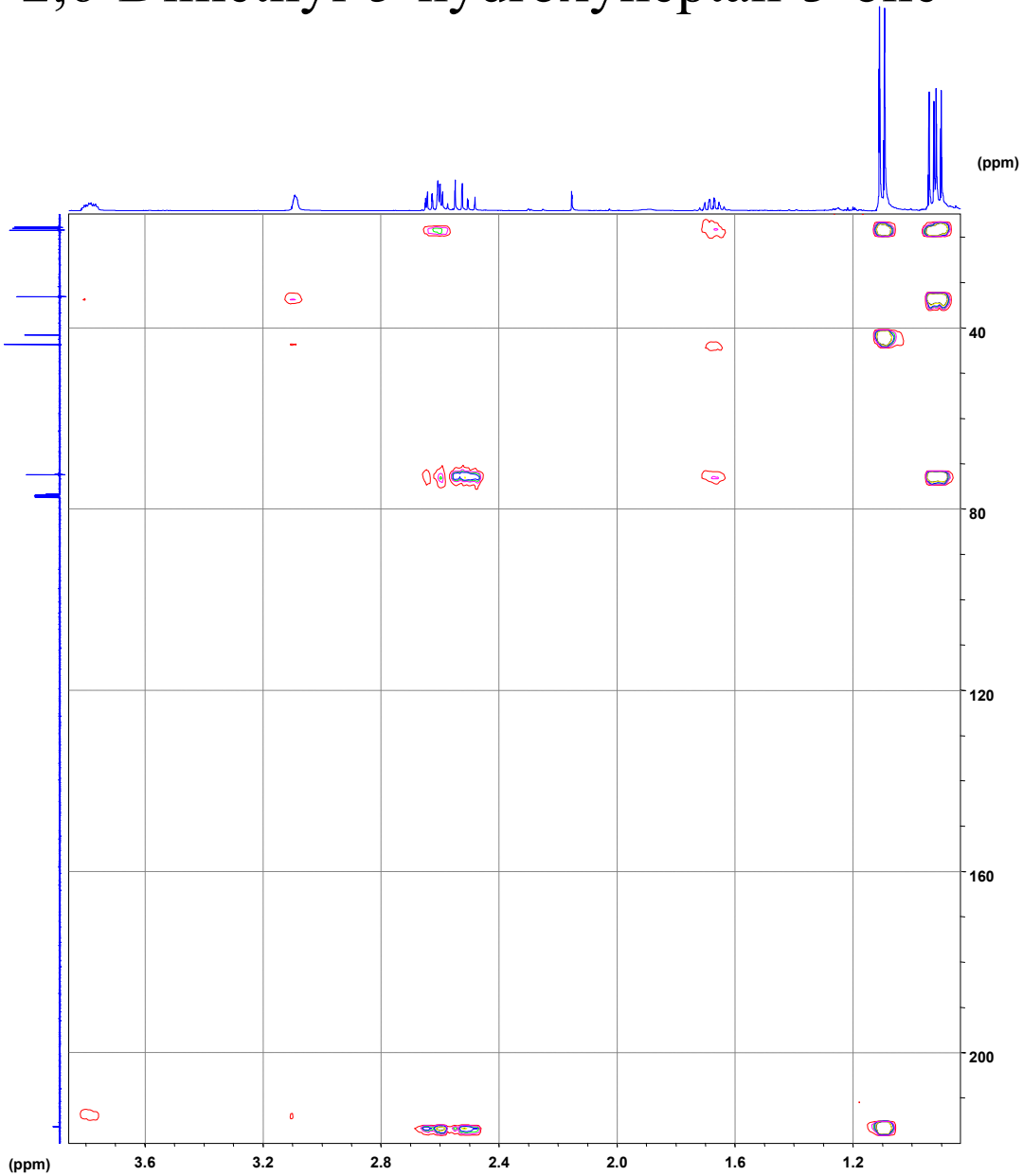
  i.e. two or more bonds for a CH correlation

- a carbonyl resonance

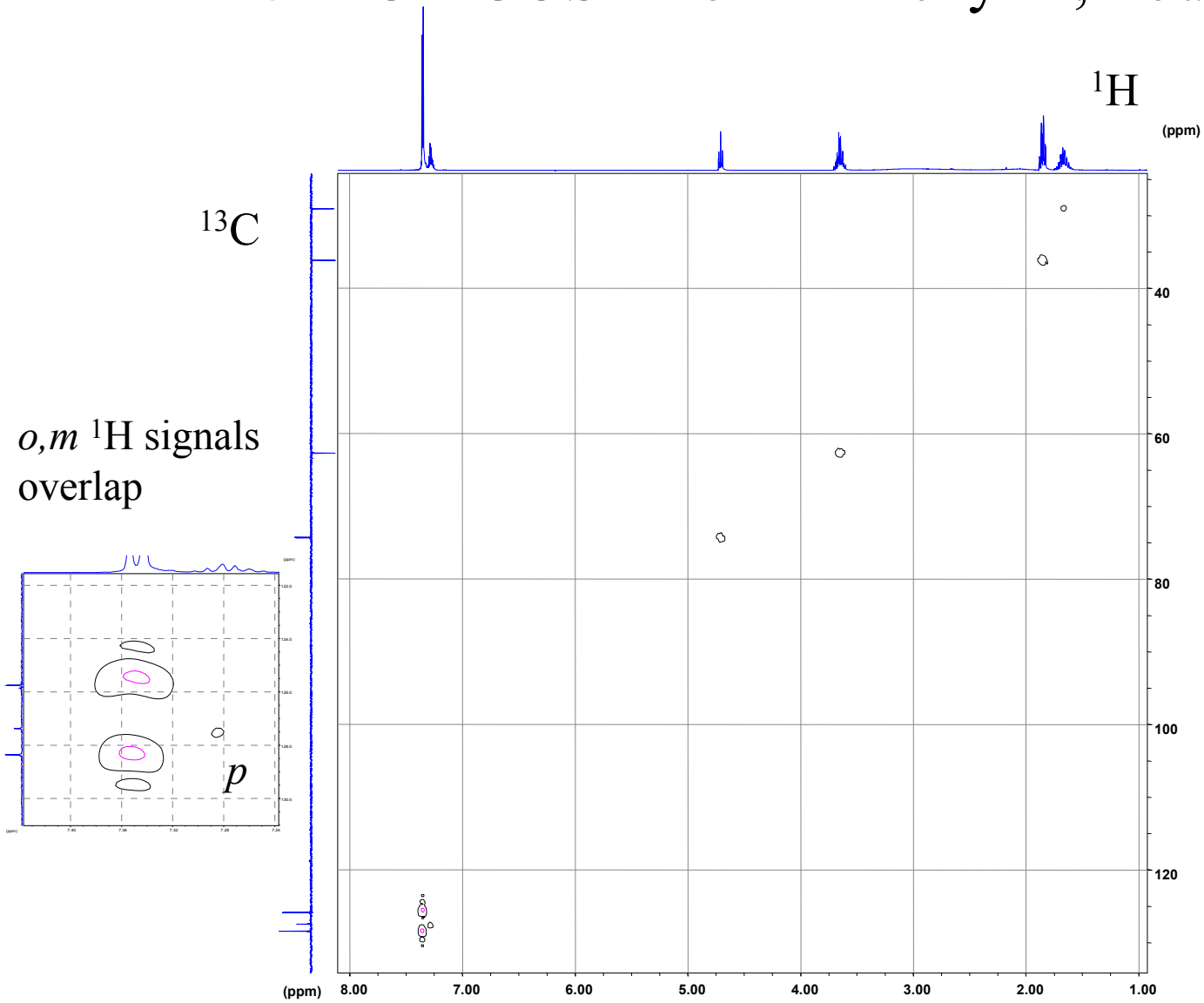
  i.e. a quaternary peak

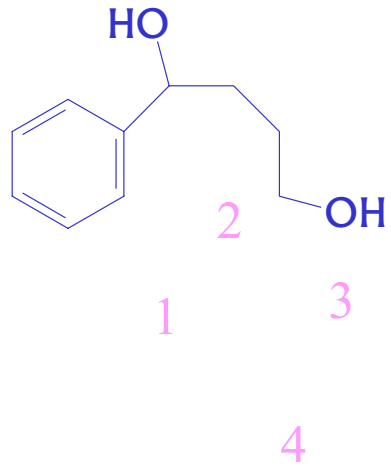
- a hydroxyl peak

Keto Carbon 216 ppm

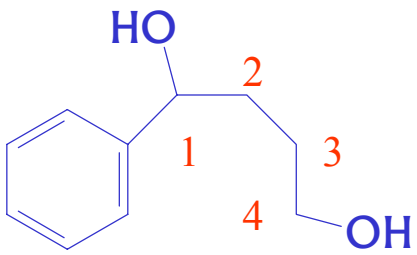


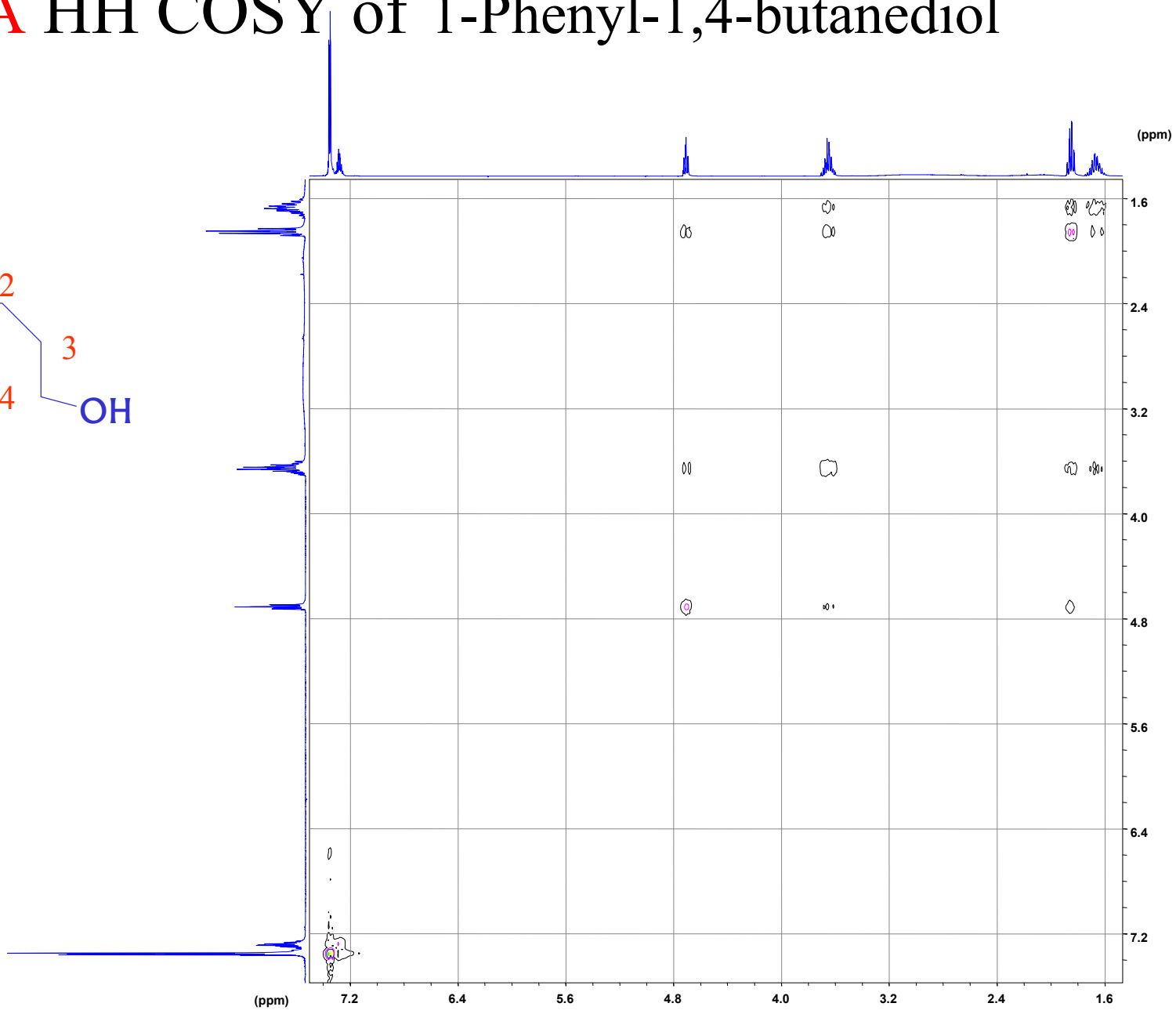
6A CH COSY of 1-Phenyl-1,4-butanediol



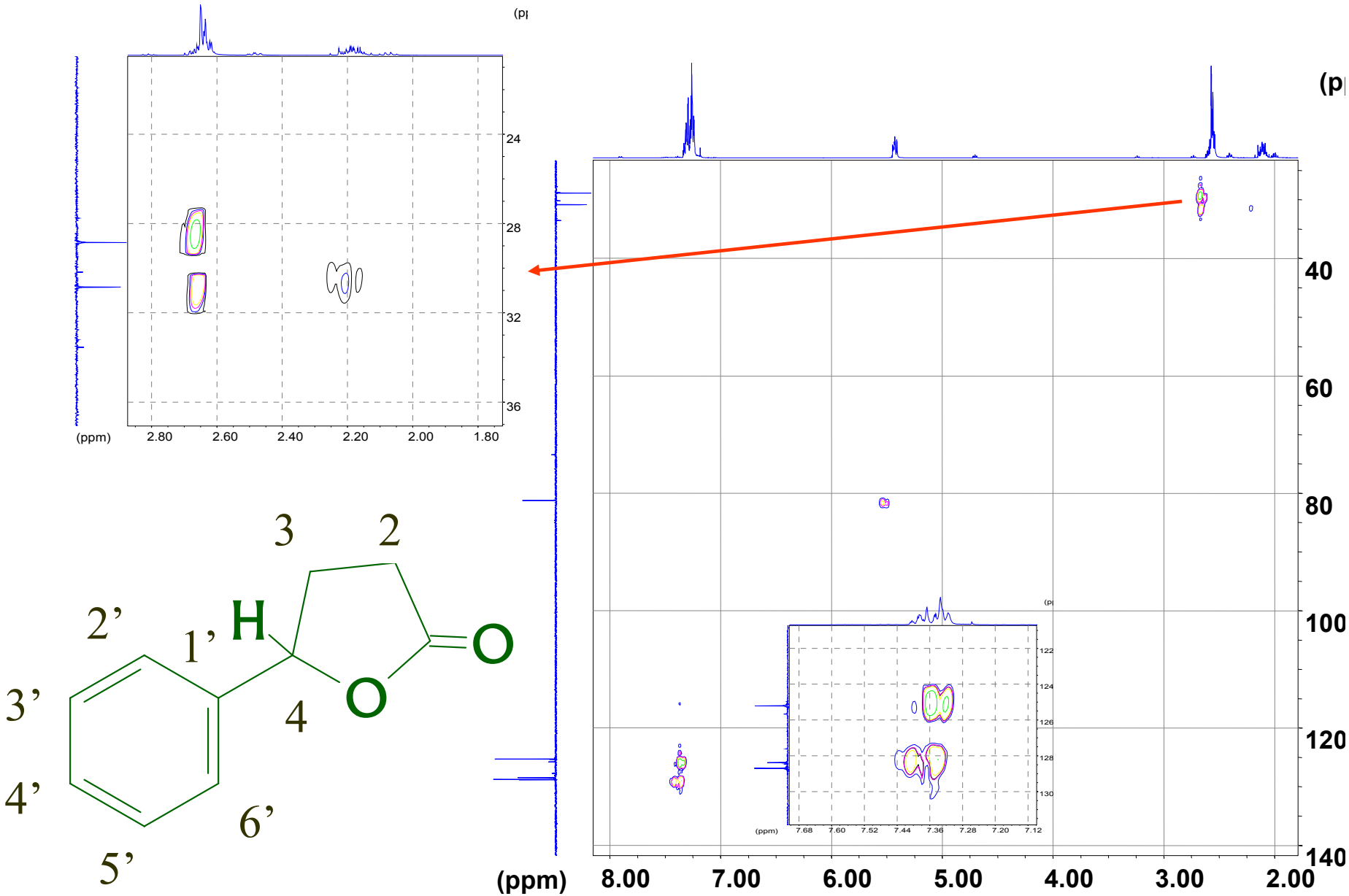


6A HH COSY of 1-Phenyl-1,4-butanediol

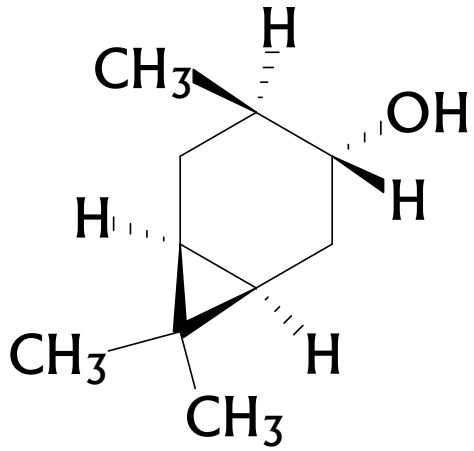


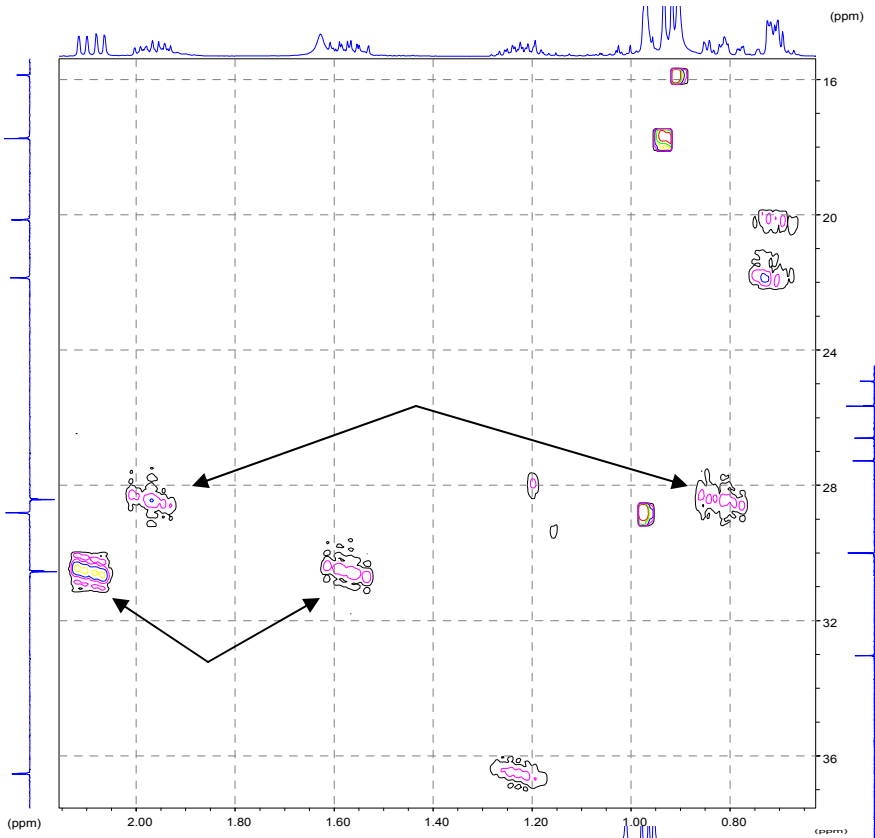


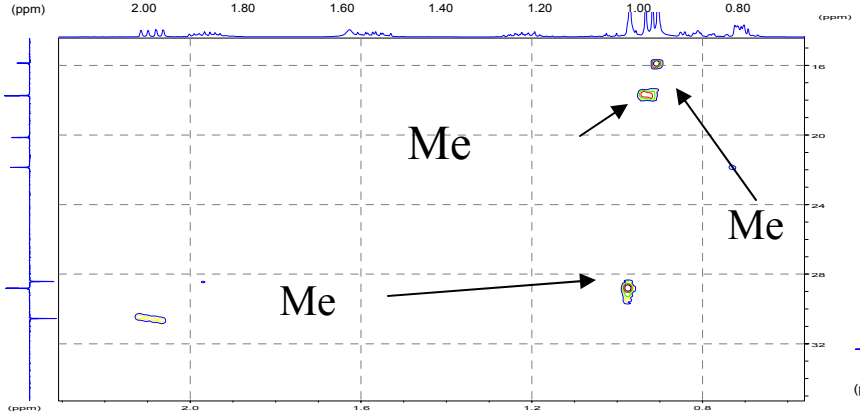
6B CH COSY γ-Phenyl-γ-butyrolactone

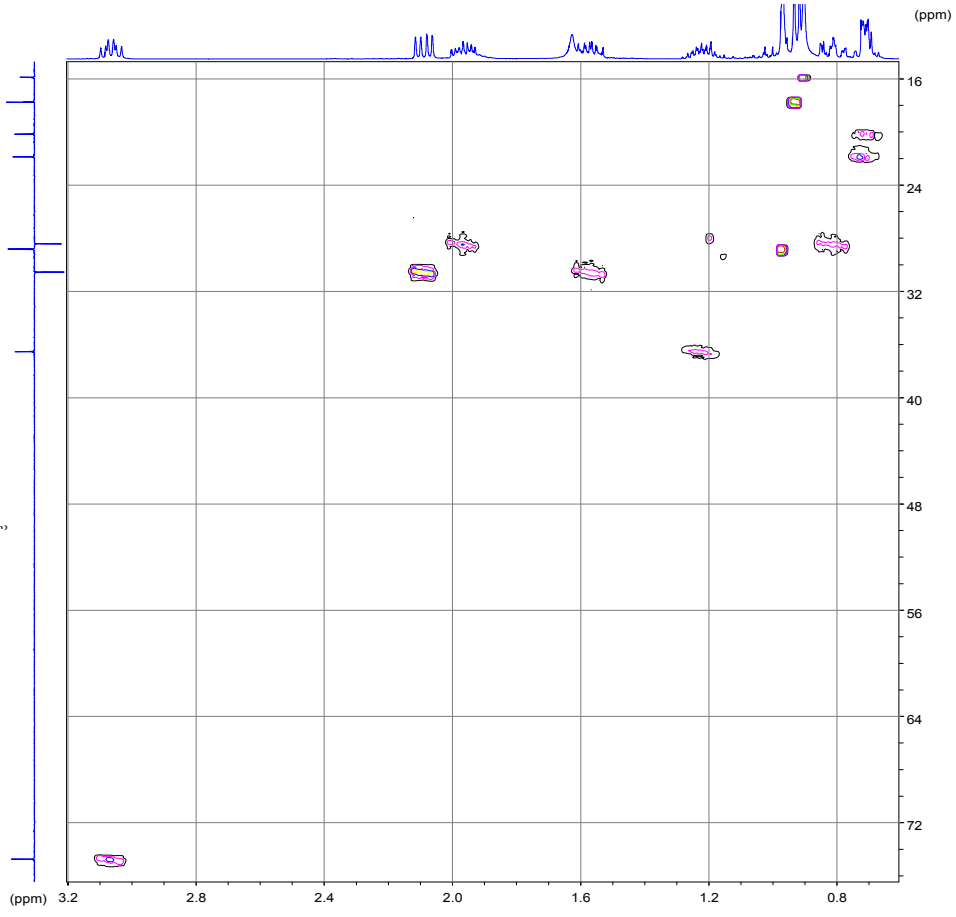


7 CH COSY *cis*-caran-*trans*-4-ol

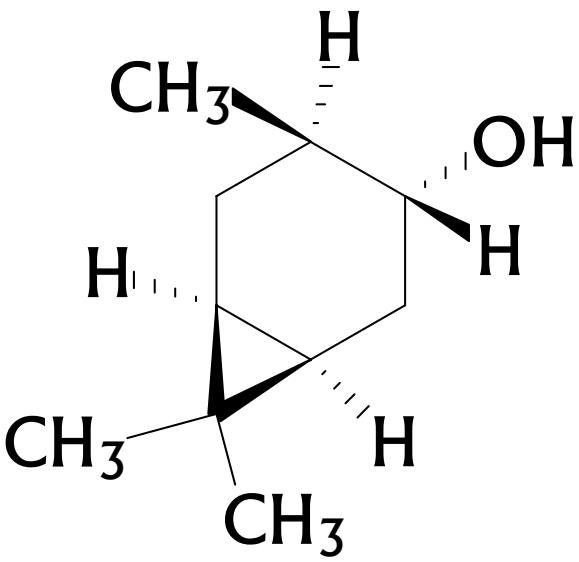


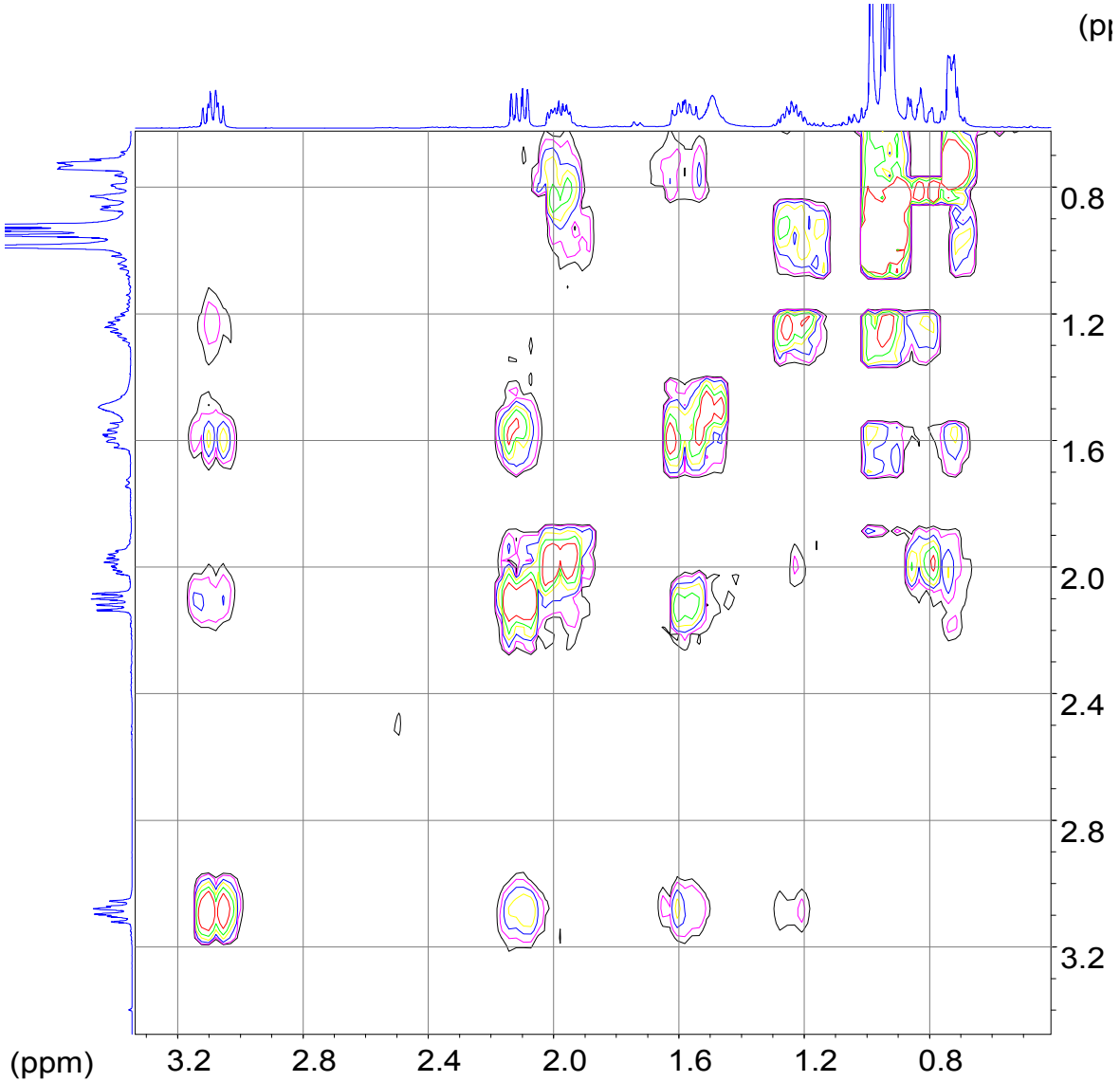




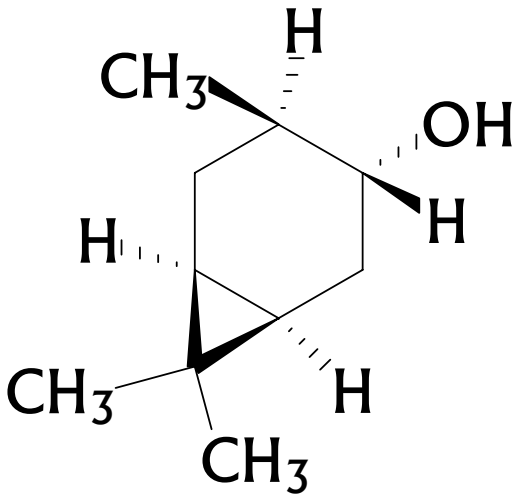


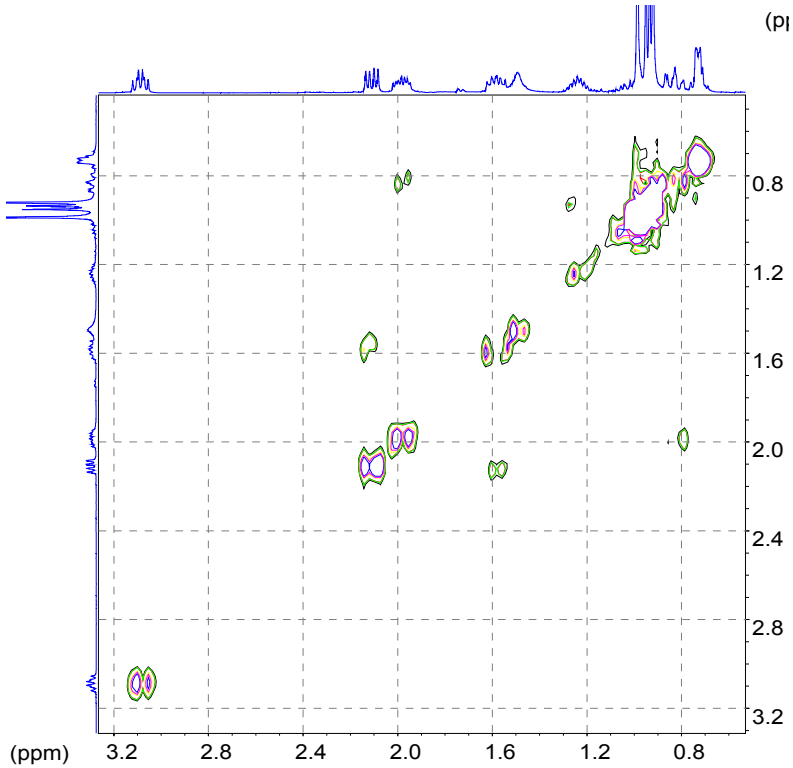
7 HH COSY *cis*-caran-*trans*-4-ol

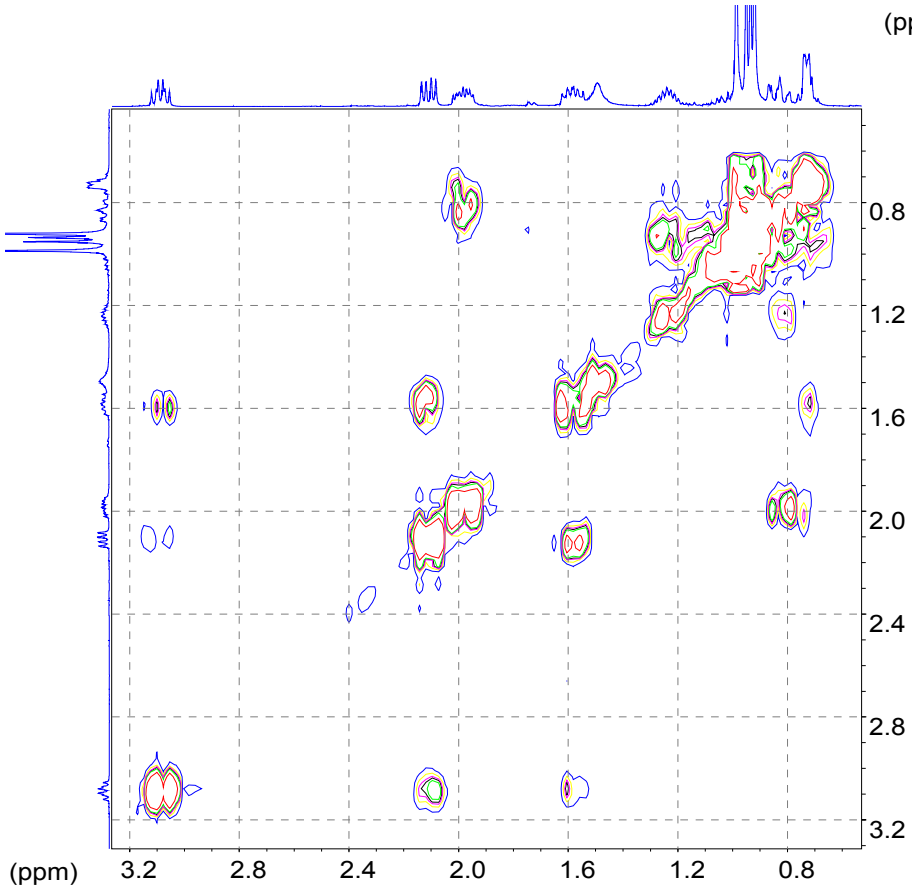




7 HH COSY *cis*-caran-*trans*-4-ol







More complex NMR experiments to detemine the configuration of the *cis*-Caran-*trans*-ol

Long range CH COSY

used to find correlations to proton(s) other than those directly attached to a carbon
used to establish links to hydroxy groups and 'quaternary' carbon peaks

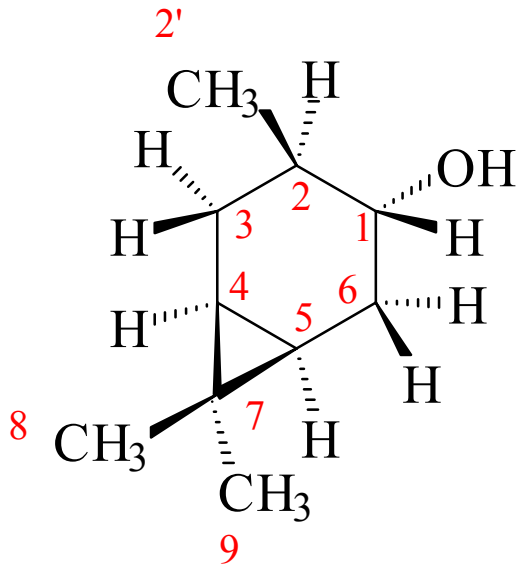
Nuclear Overhauser Effect (NOE)

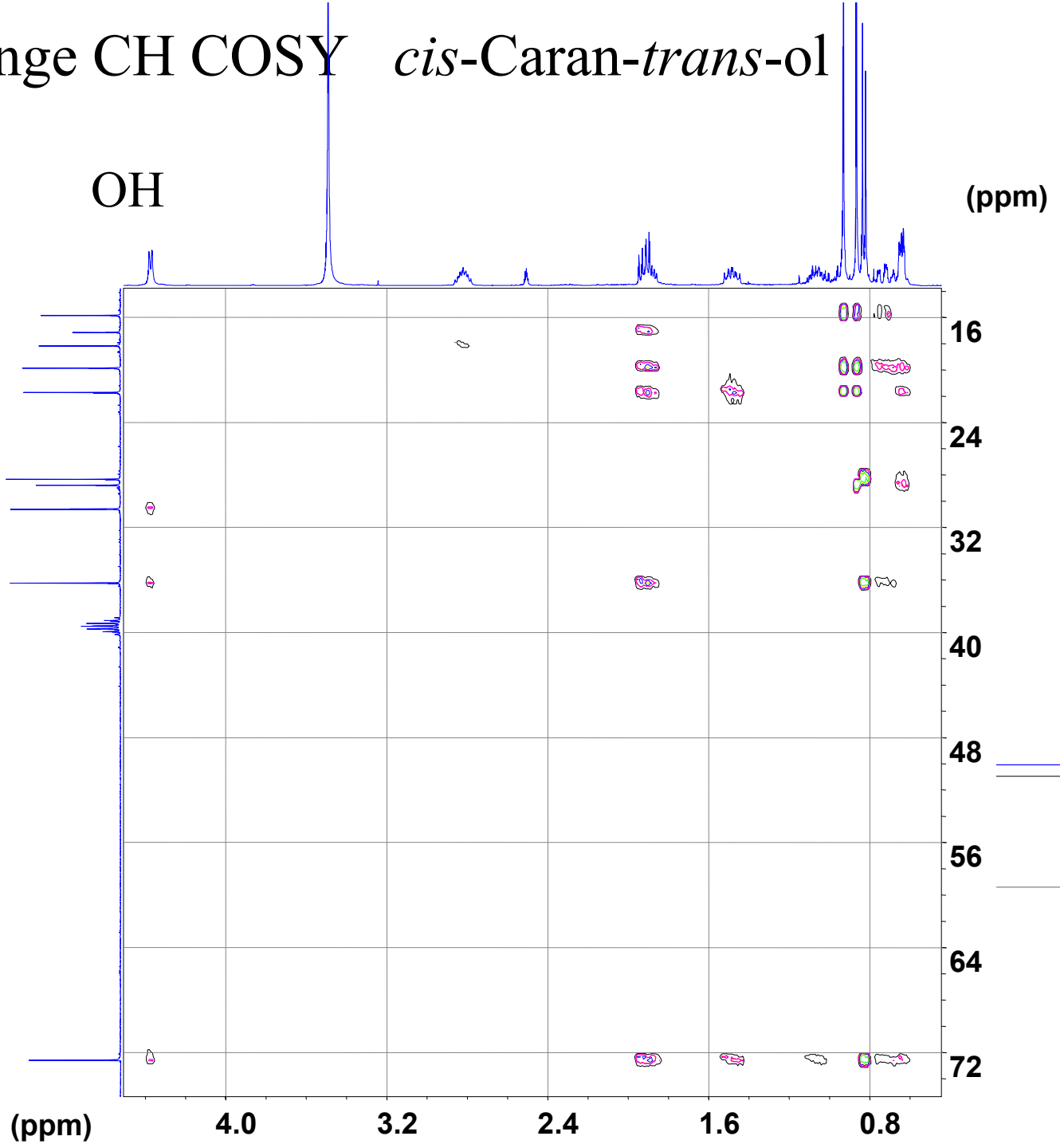
This will etablish interactions of the spins through **SPACE**

Difference NOE experiment – irradiate a specific proton and observe any changes
(a normal spectrum is subtracted from the irradiated spectrum to give the DIFFERENCE spectrum

expect to differentiate between the two *methyl peaks* on the *cyclopropyl* ring
one should be lying in the same plane as the two *cis* protons on the ring

7 Long range CH COSY *cis*-Caran-*trans*-ol





Solvent DMSO-d6

7 Difference NOE NMR *cis*-Caran-*trans*-4-ol