JS Organic Practical Course

Additional NMR spectra to aid structural determination

Four types of data are supplied :

- -2D homonuclear correlation spectra (HH COSY- TOCSY)
- -2D heteronuclear correlation spectra (CH COSY - HSQC)
- -2D Long range heteronuclear correlation spectra (HMBC)
- -1D Nuclear Overhauser spectra (NOE)

Additional Data is supplied for experiments :

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

Additional material for 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

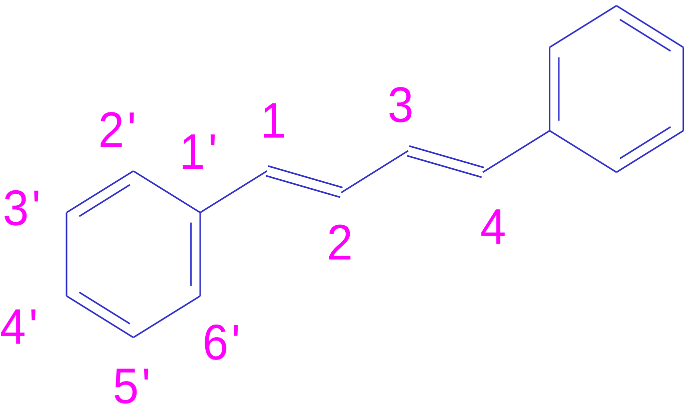
  often can correlate several protons to a carbon

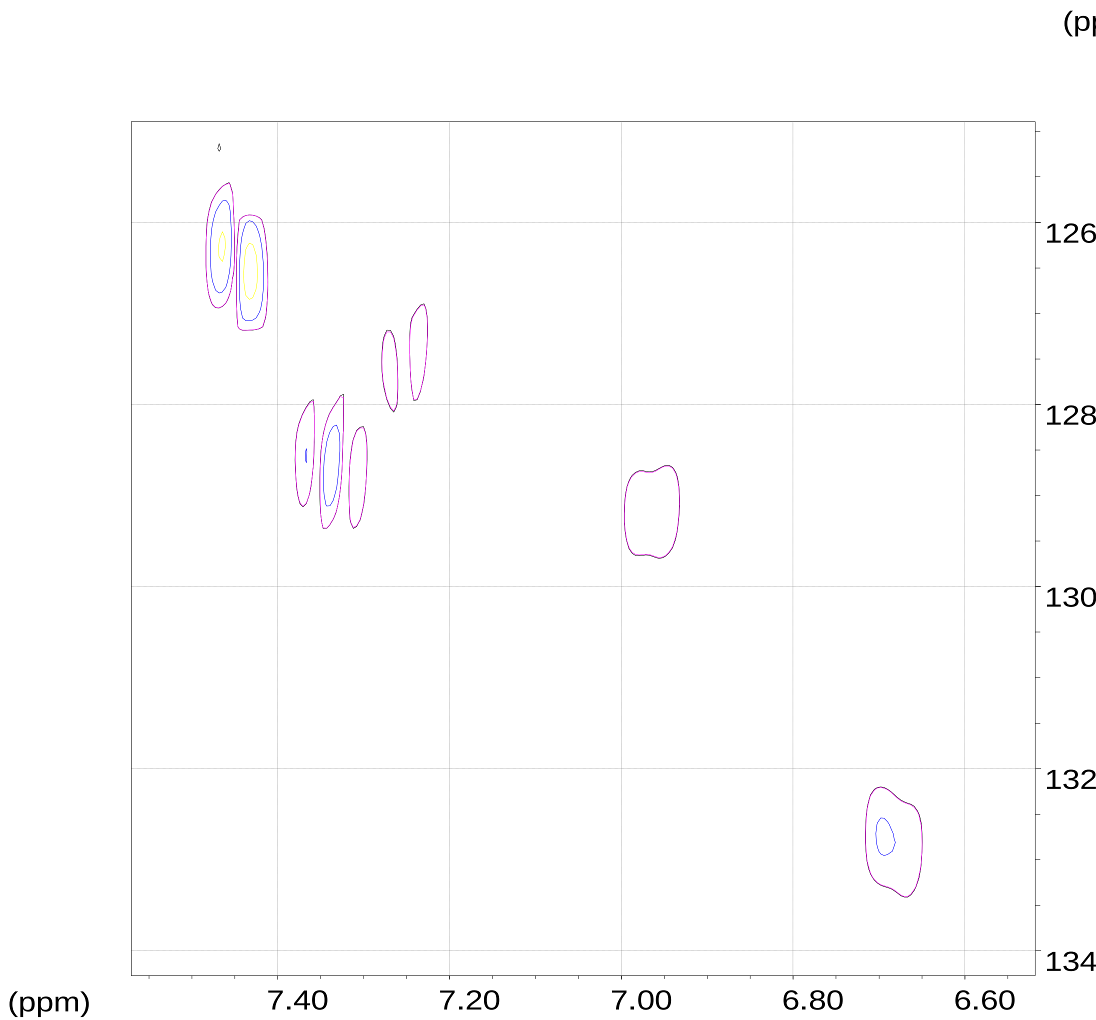
  (or *vice versa* - whichever is most appropriate)

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

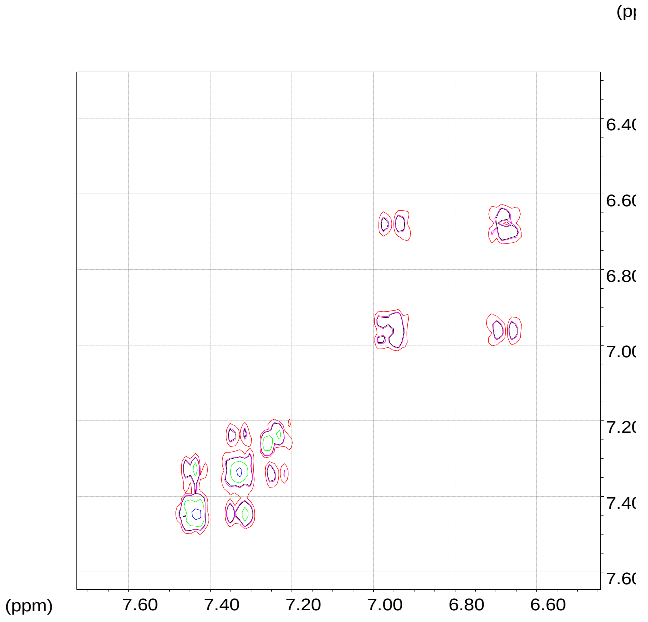
2B CH COSY (E,E)-1,4-Diphenyl-1,3-butadiene

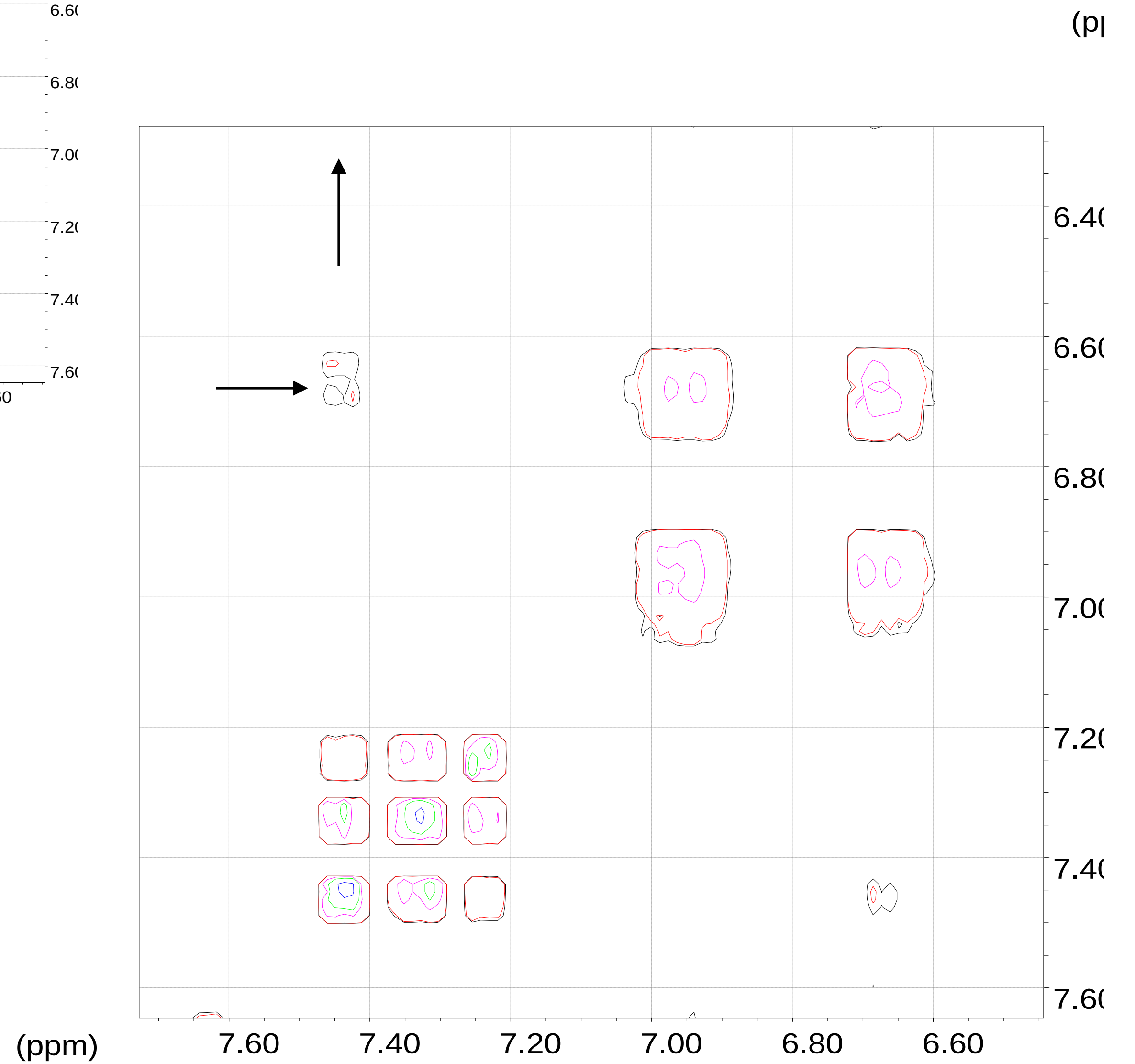
Direct correlation of *hydrogen* to *carbon* resonances





2B HH COSY (E,E)-1,4-Diphenyl-1,3-butadiene

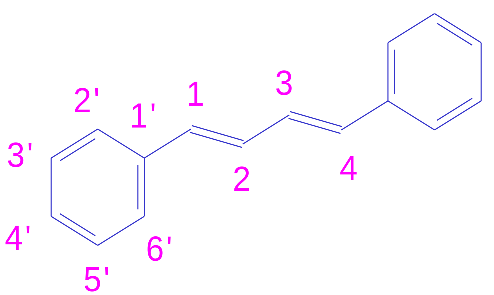




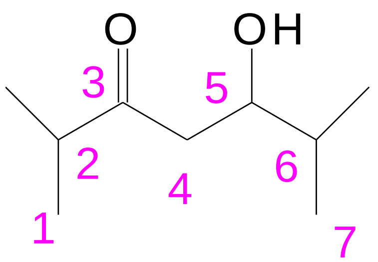
Diagonal contains the 1D spectrum

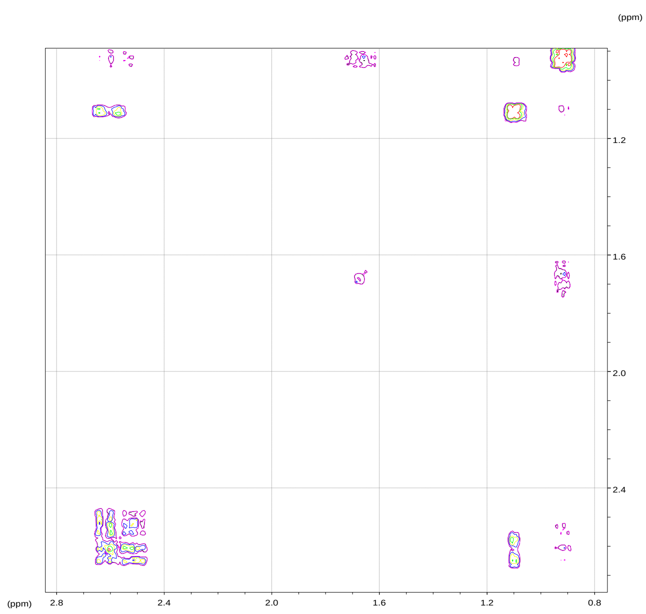
Connections between hydrogens are symmetrical about the diagonal

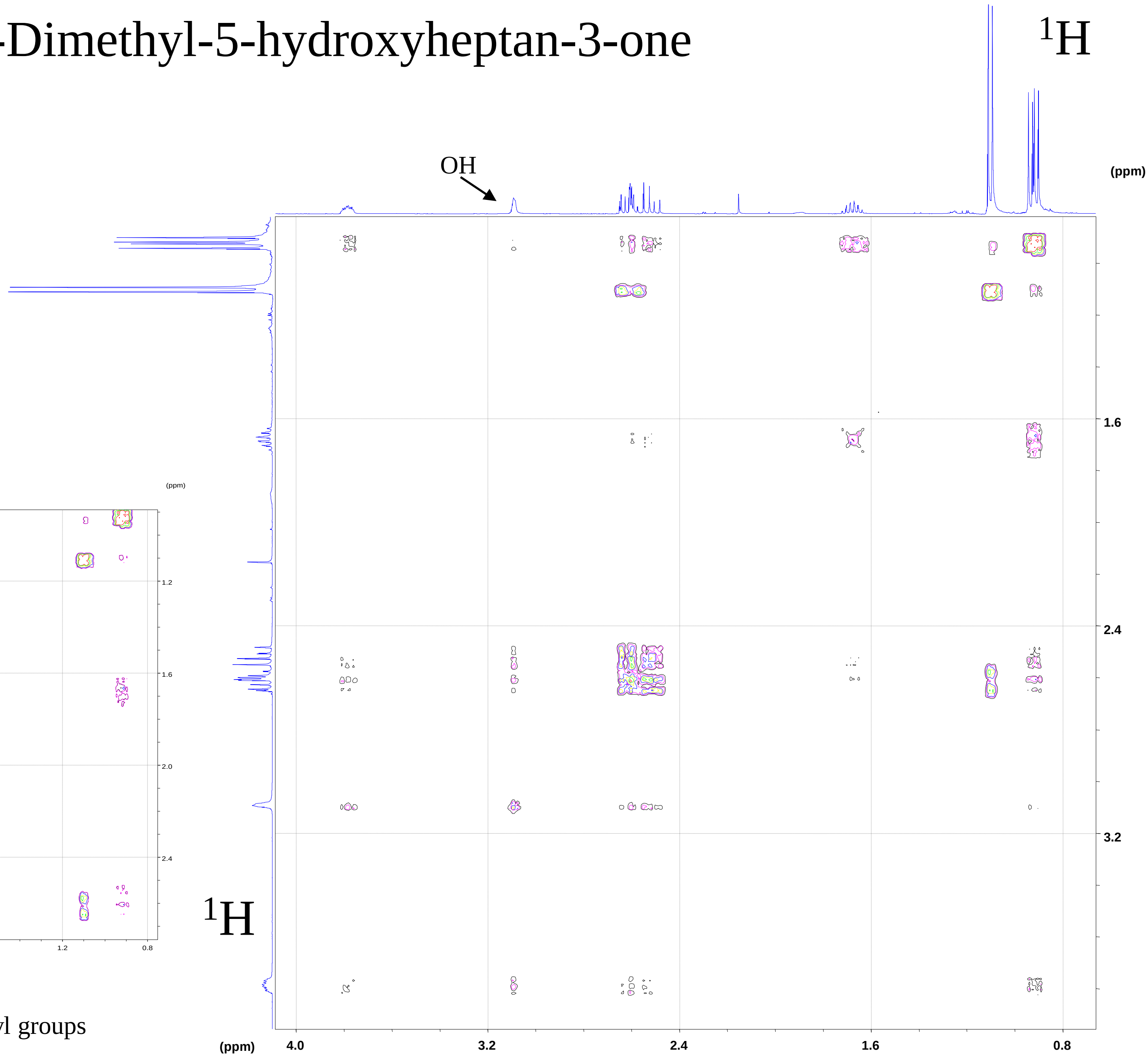
Generally, the higher the contour the stronger the connection



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

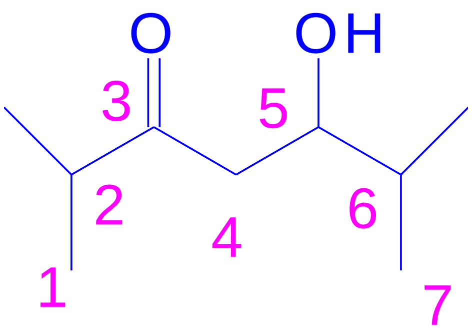


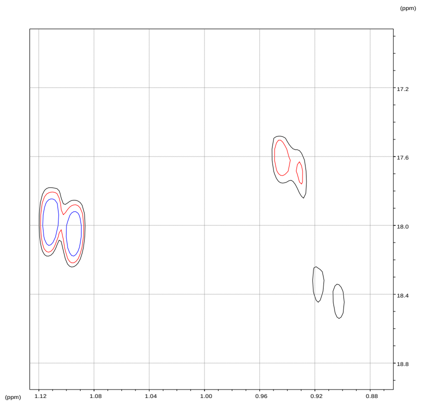




Identify the two isopropyl groups

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





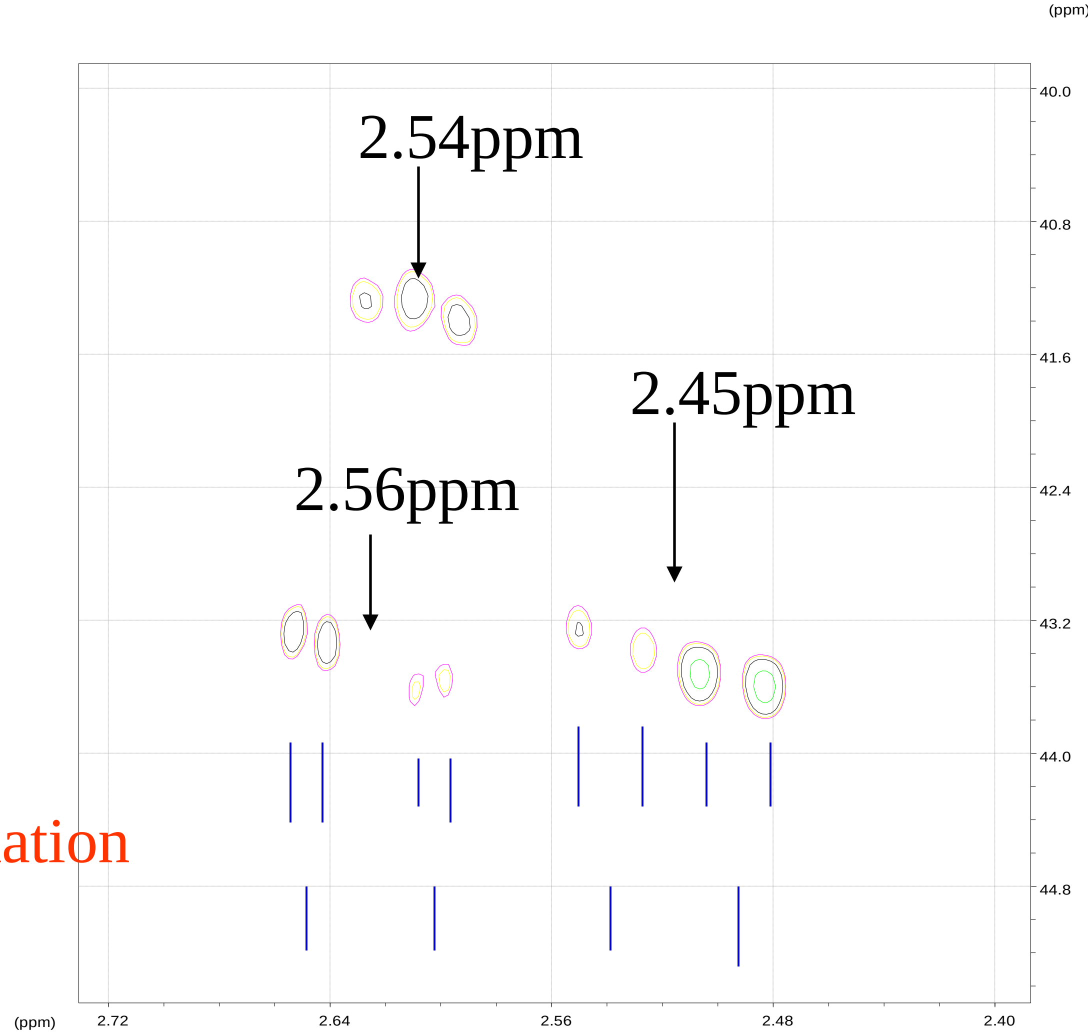
Methyl region

4 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)

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

Notice CH correlations to :

- a longer range

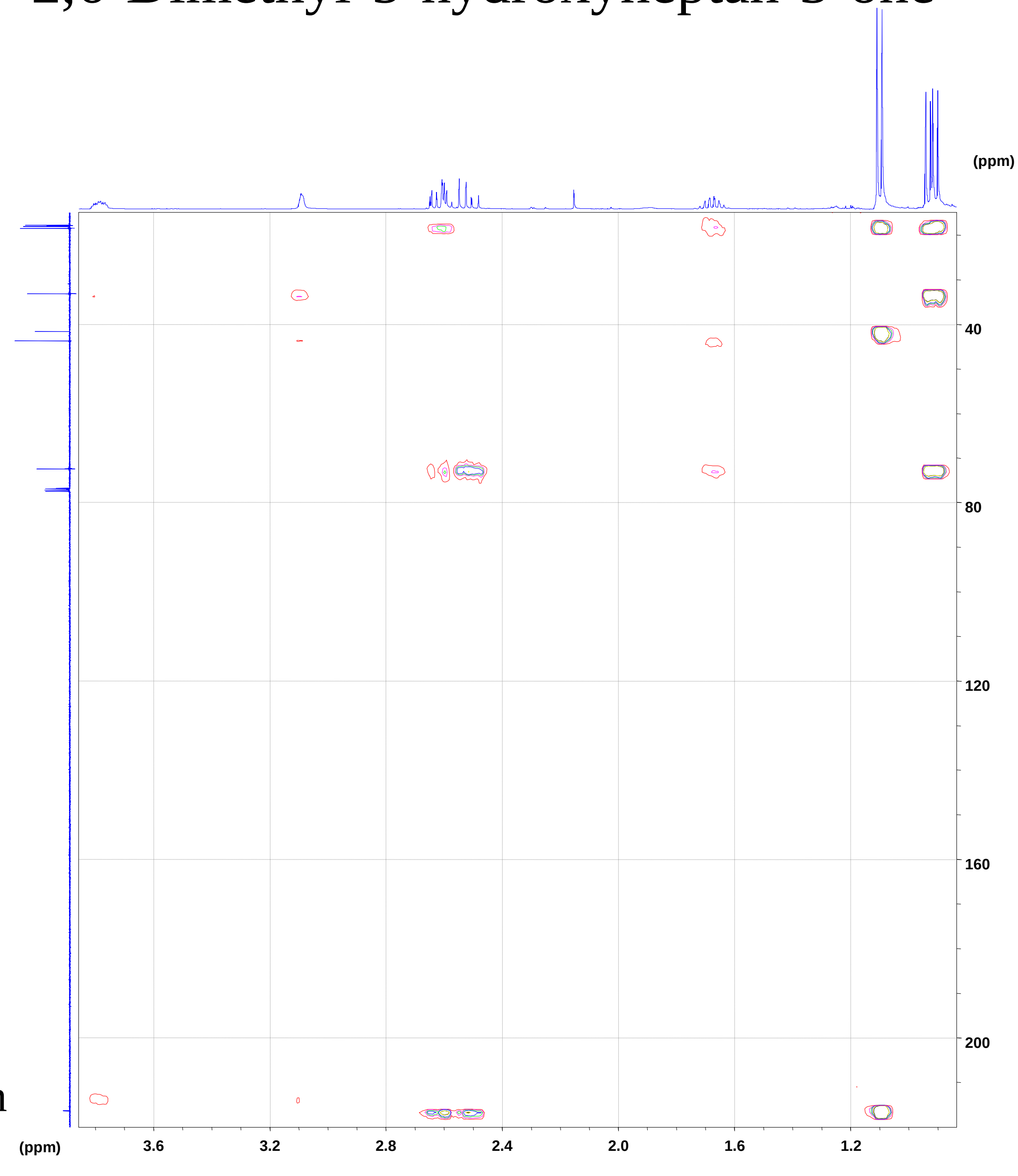
  i.e. two or more bonds for a CH correlation

- a carbonyl resonance

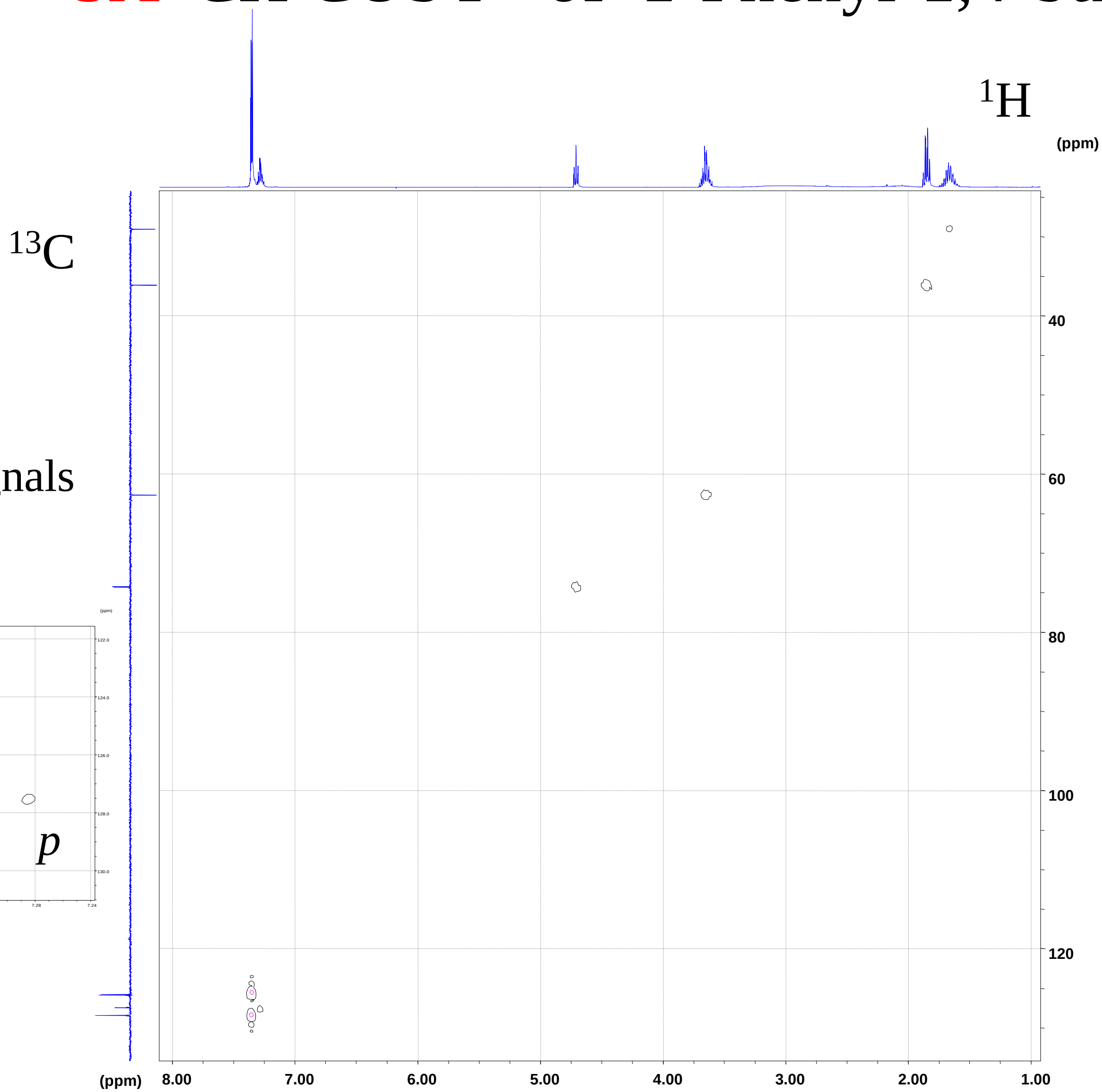
  i.e. a quaternary peak

- a hydroxyl peak

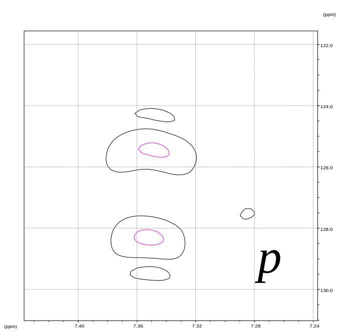
Keto Carbon 216 ppm

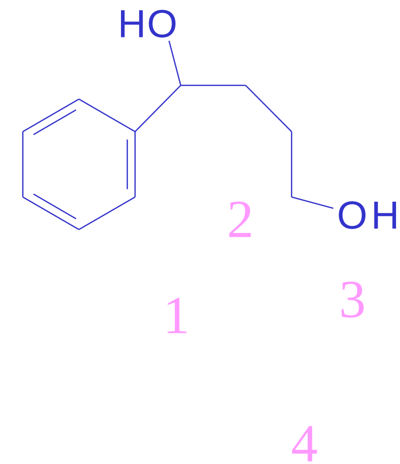


5A CH COSY of 1-Phenyl-1,4-butanediol

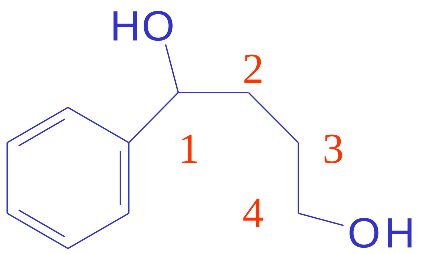


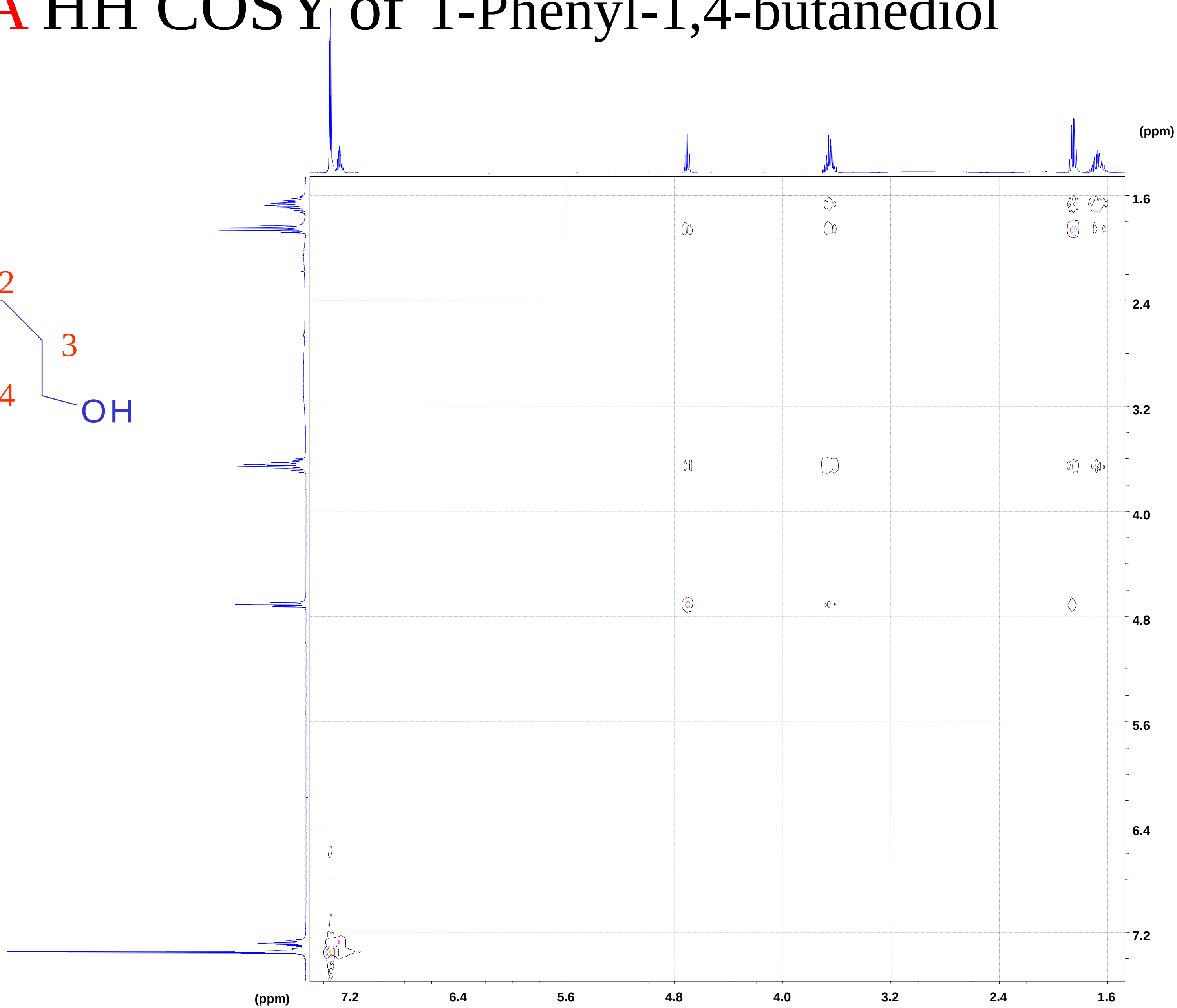
o,m ^{1}H signals overlap



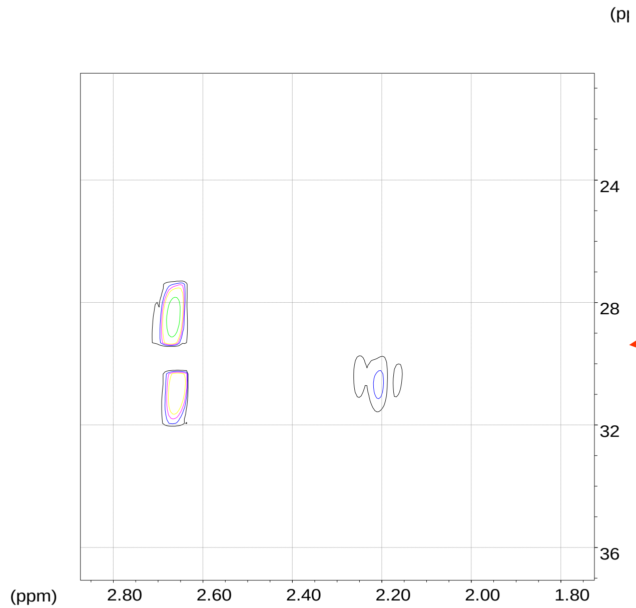


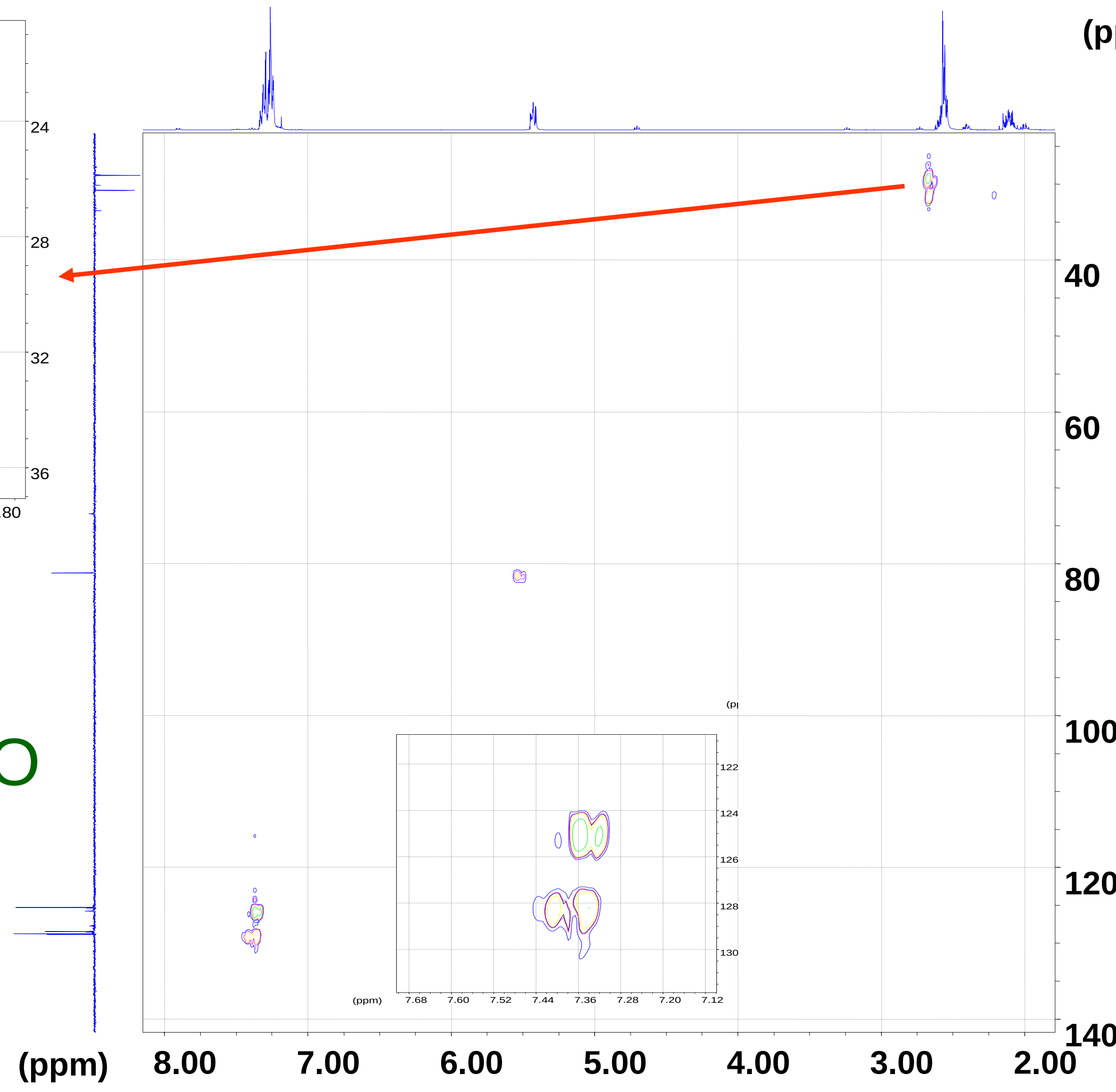
5A HH COSY of 1-Phenyl-1,4-butanediol

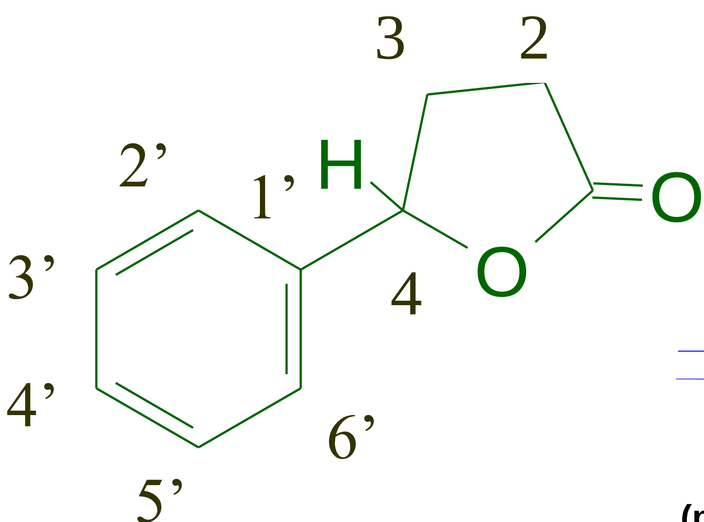




5B CH COSY γ-Phenyl-γ-butyrolactone







6 *cis*-caran-*trans*-4-ol

The proton NMR is complex - a number of features can be ascertained from the spectrum

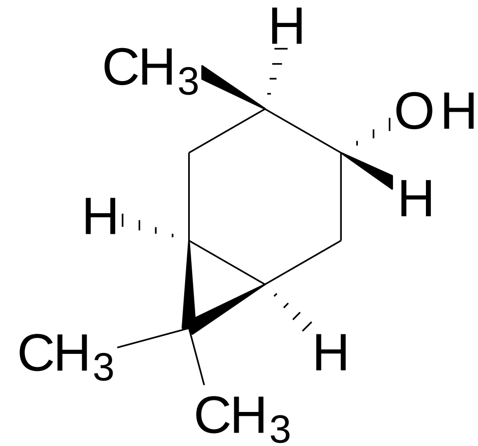
Carbon-13 and Carbon DEPT 135° and 90° spectra provide clearer information on the structure - match the data to the formula

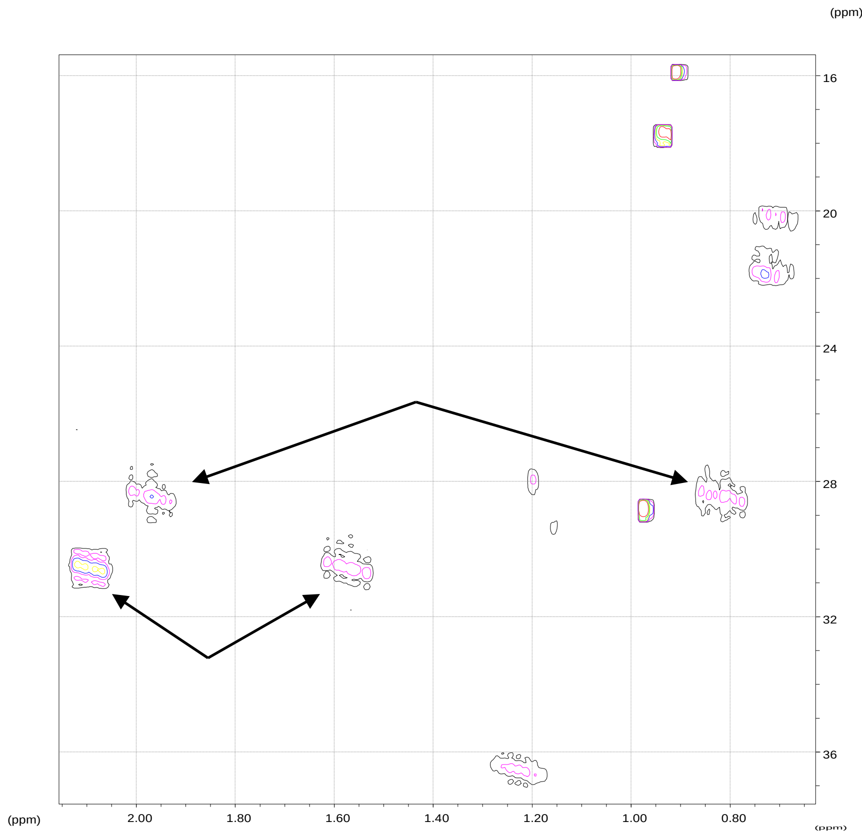
The CH COSY provides the solution to the proton resonance positions
Assign most of the cyclohexyl ring structure from the HH COSY

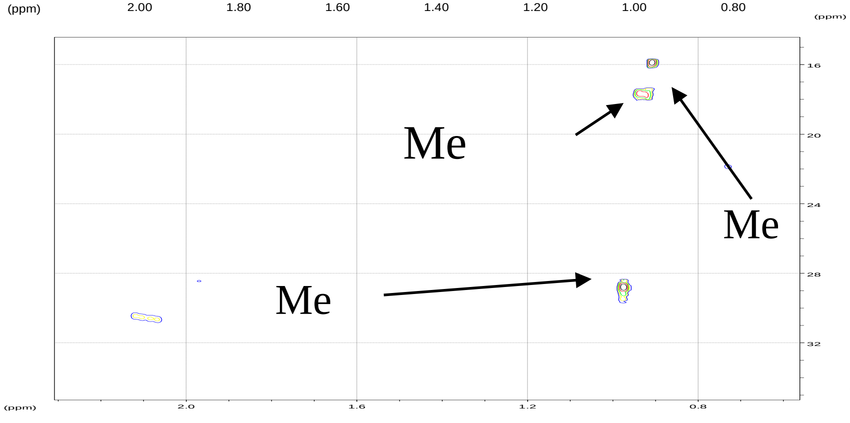
from the Long range CH COSY - the riung assigment can be solved

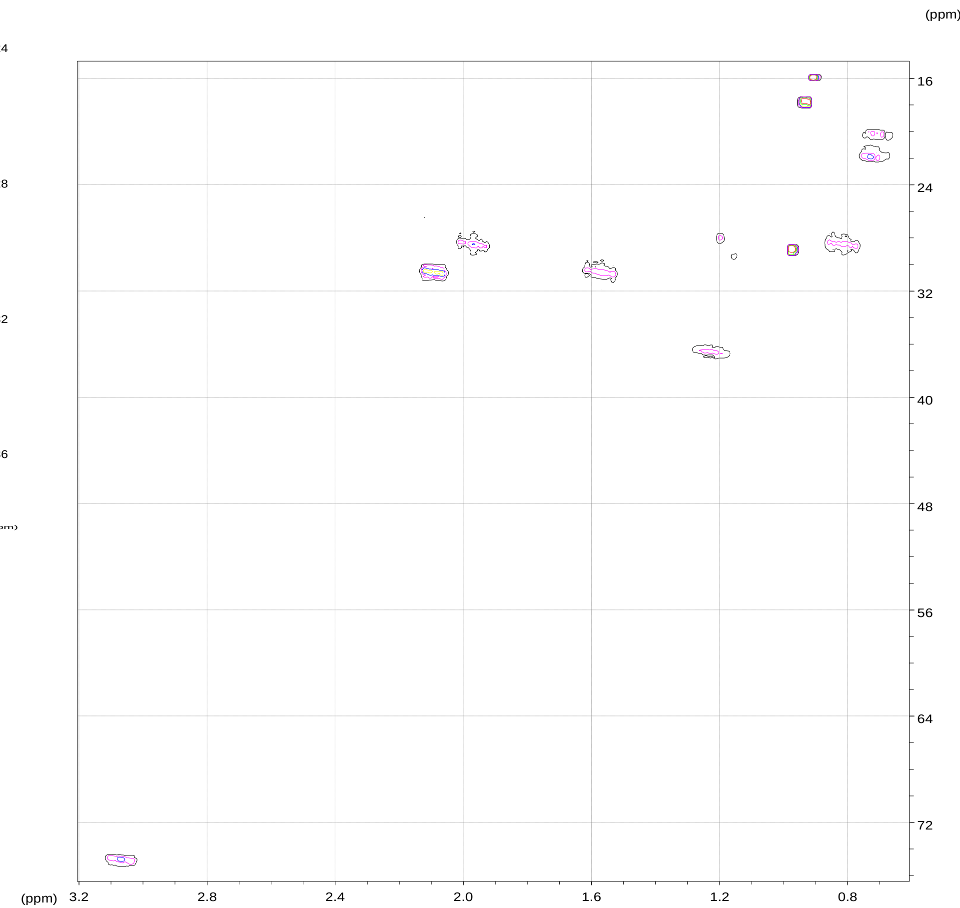
from the NOE data a key conformational feature can be confirmed

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

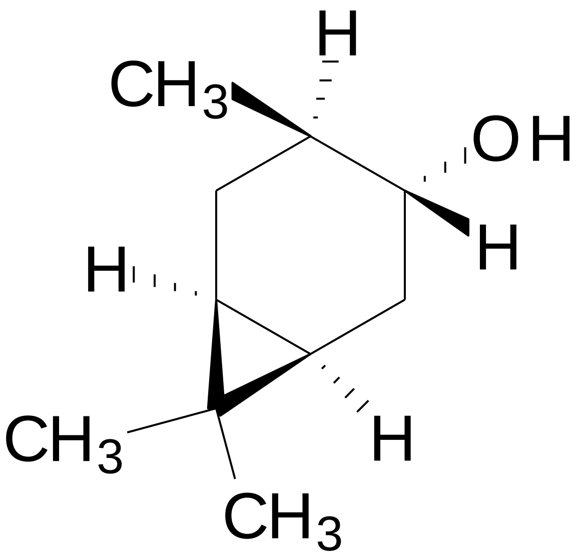


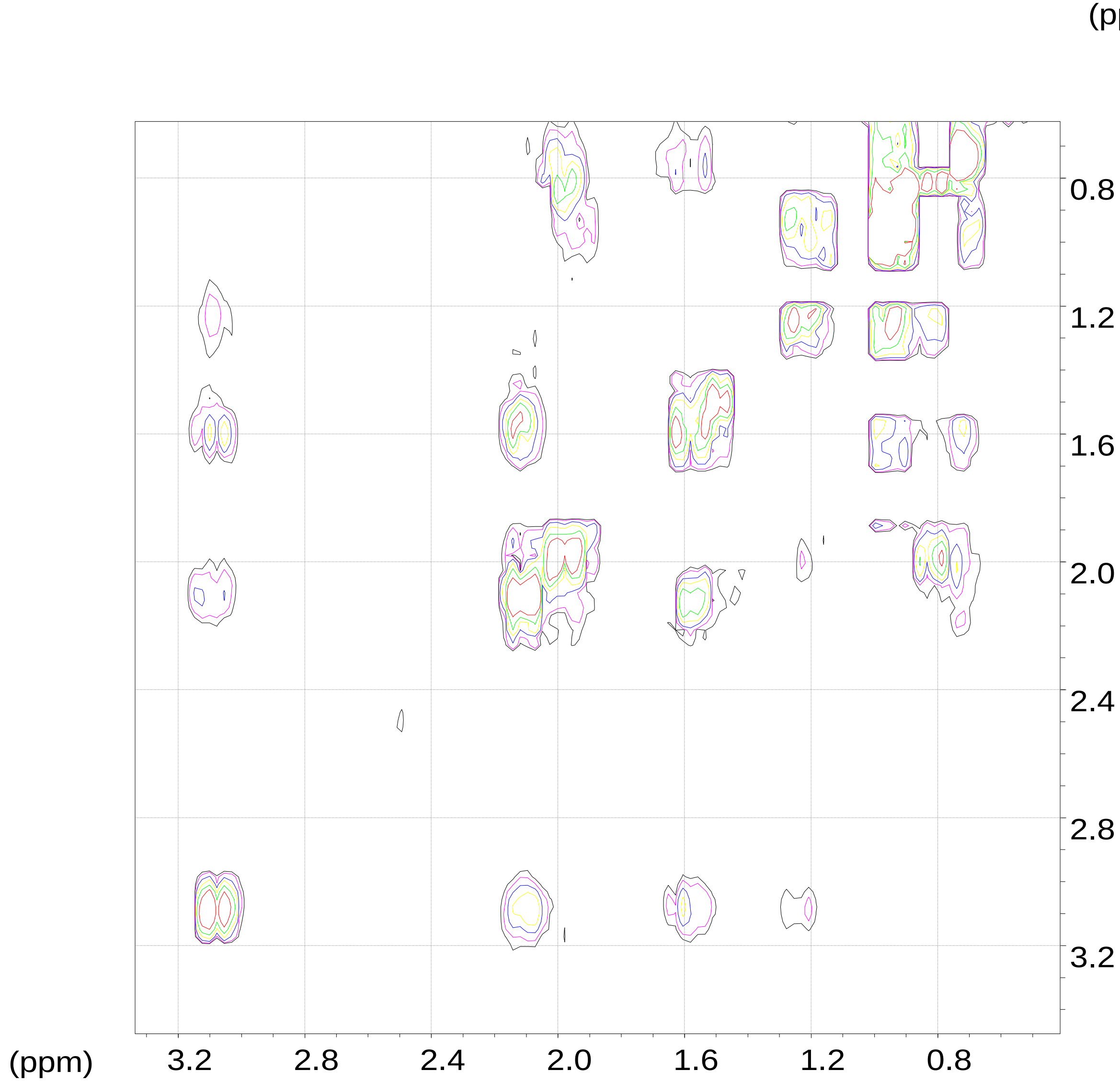






6 HH COSY *cis*-caran-*trans*-4-ol





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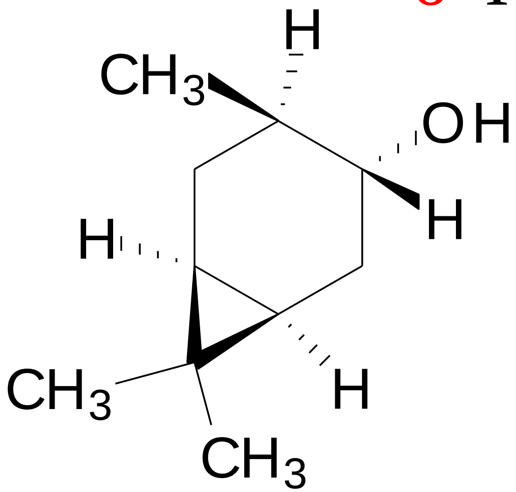
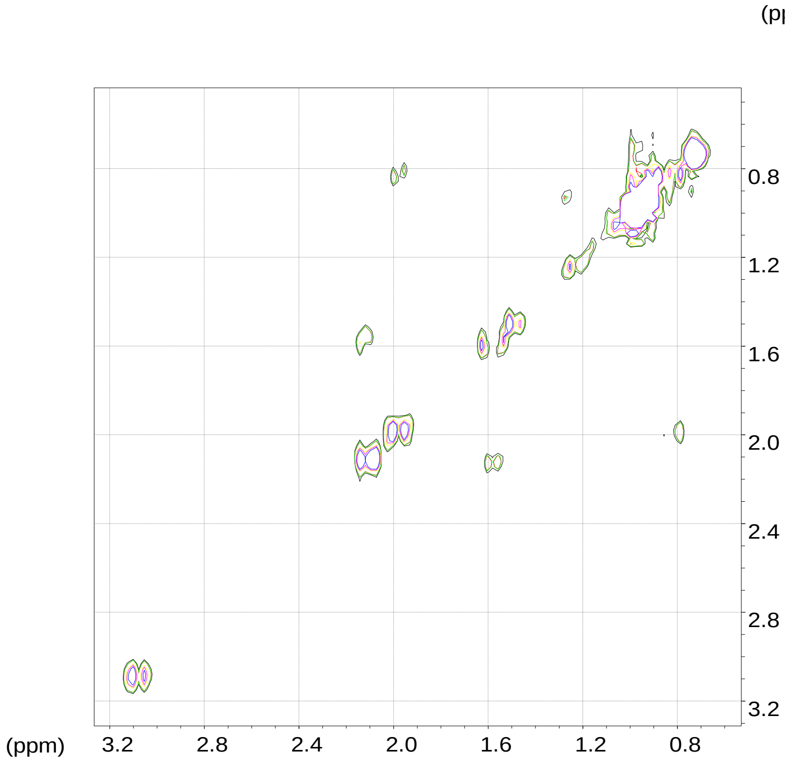
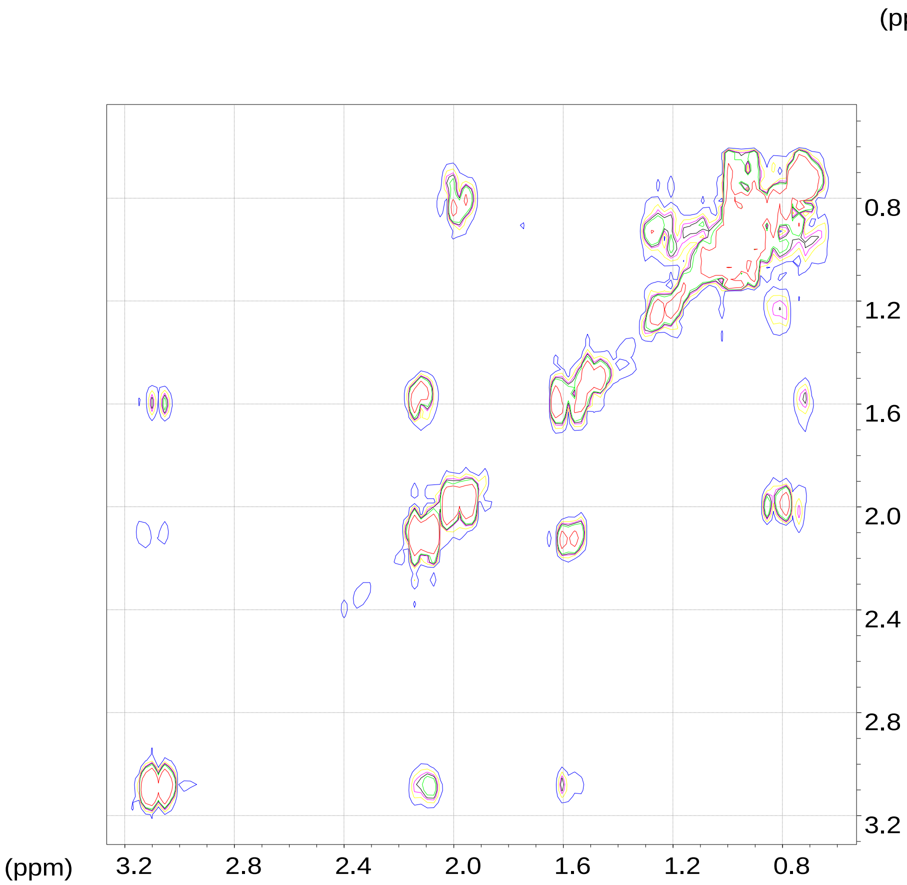






high contour levels - confirms the methylene proton positions

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 establish interactions of the spins through **SPACE**

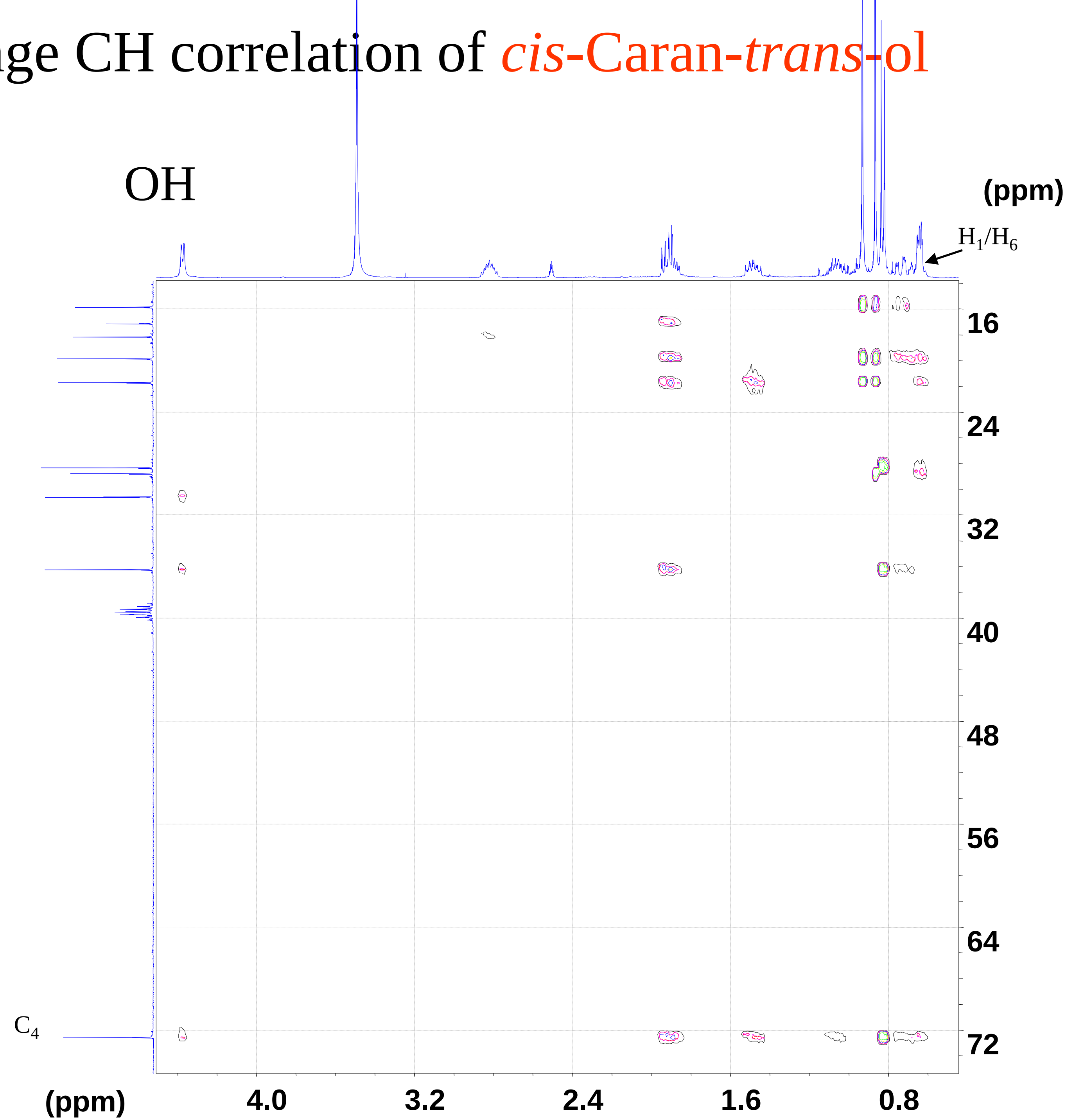
Difference NOE experiment – irradiate a specific proton and observe any changes

(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

6 Long range CH correlation of *cis*-Caran-*trans*-ol



Solvent is DMSO-*d6*

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