

1. The HMQC (HETCOR-equivalent) spectrum below belongs to a compound  $C_{10}H_{18}O$ .  $U = 2$

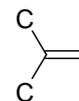
a) (2 points) Why is there no correlation for the  $^1H$  signal at 2.2 ppm? Which structural feature follows from this observation?

**molecular formula has "O" which is not part of a C=O (all C signals below 150 ppm); signal integrates for 1 H; no C-H coupling**



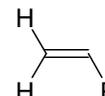
b) (2 points) Why is there no correlation for the  $^{13}C$  signal at 130 ppm? Which structural feature follows from this observation?

**$U = 2$ , 130 ppm: suggests C=C (not an aromatic system!); no coupling suggests C must be fully substituted**



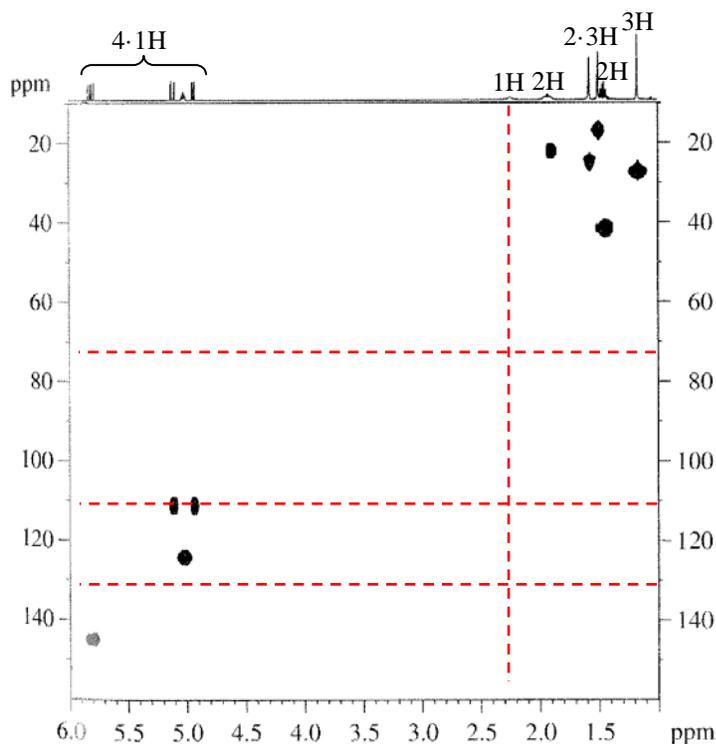
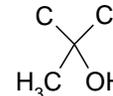
c) (2 points) What can you conclude for the connectivity (and corresponding structural feature) for the  $^{13}C$  signal at 110 ppm?

**110 ppm: suggests C=C; correlates with two  $^1H$  signals integrating for 1 H (so chemically not identical): both are bound to that carbon atom**



d) (2 points) The  $^{13}C$  signal at 73 ppm also does not show a correlation peak. Why? With this information, the information from a), its chemical shift and the integrations given, provide a guess for the partial structural information for this carbon atom.

**73 ppm: suggests OH substitution; no coupling suggests C must be fully substituted (quaternary); fourth substituent most likely  $CH_3$  (at 1.2 ppm)**



only the correlations (or lack thereof) addressed above are graphically evaluated here; normally you would do the full graphical analysis

2 C=C

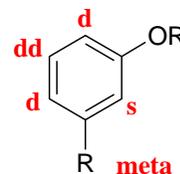
2. The data below (expansions of the aromatic region of a  $^1\text{H}$  NMR spectrum at 600 MHz, and a COSY spectrum) belong to a di-substituted aromatic compound.

a) (6 points) From the  $^1\text{H}$  NMR signals, determine all coupling constants. Then, to determine the “smoothed” signal multiplicity, ignore 1 Hz and 2 Hz couplings.

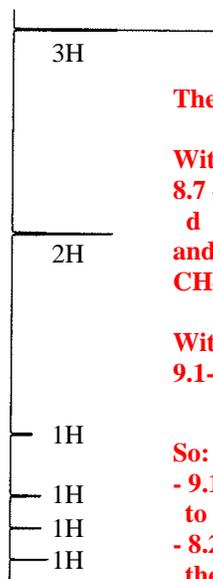
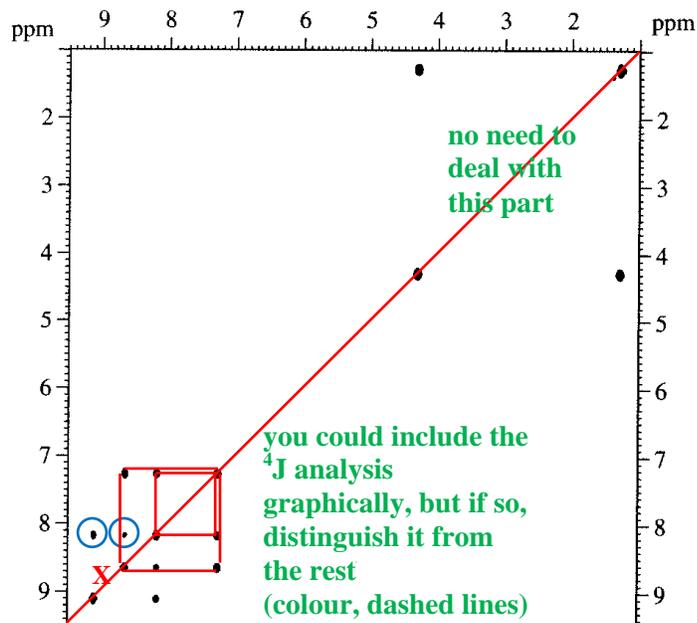
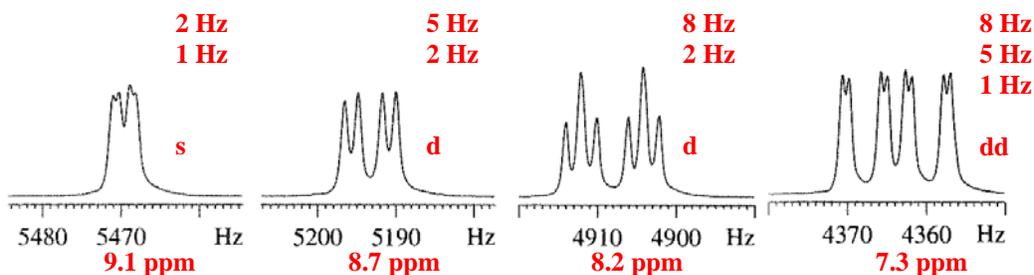
b) (1 points) From the “smoothed” signals from a), determine the substitution pattern: o, m or p.

c) (5 points) From the COSY, it is obvious that “1.3 ppm couples with 4.3 ppm”, and from that the connectivity is  $\text{CH}_3\text{--CH}_2$ . In a similar fashion, determine the connectivity in the aromatic system. The connectivity should fit your result from b). (Hint: When you determine the coupling, keep in mind the “smoothed” signals that you determined in a), i.e., initially ignore the long-range couplings –the smaller dots–, then put them back into the analysis.)

d) Study the COSY again. Did you really need the  $^1\text{H}$  expansions to determine the substitution pattern?



with what you know now, your answer might be ‘no’



There seem to be two smaller cross peaks.

Without the 2 Hz coupling, starting at X:  
8.7 – 7.3 – 8.2 ppm; 9.1 ppm does not couple  
d – dd – d; s  
and obviously (just not informative)  
CH–CH–CH; CH

With the 2 Hz coupling:  
9.1---8.2---8.7  
7.3 – 8.7 ppm

So:

- 9.1 ppm: the “s”  $^1\text{H}$  sees one of the  $^1\text{H}$  meta to it ( $^4\text{J}$ ), leading to the larger d splitting  
- 8.2 ppm: the “d”  $^1\text{H}$  sees the  $^1\text{H}$  at 9.1 and the other “d” at 8.7 ppm ( $^4\text{J}$ , both accidentally the same), leading to the smaller triplet splitting (dt)

Analysis fits with the m-substitution pattern.