C8953
NMR strukturní analýza
seminář

Identification of an unknown compound

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April 18, 2018

Task 0: **Classification of an unknown substance**

Assign the general name to displayed substances:

CARBOHYDRATE

PEPTIDE

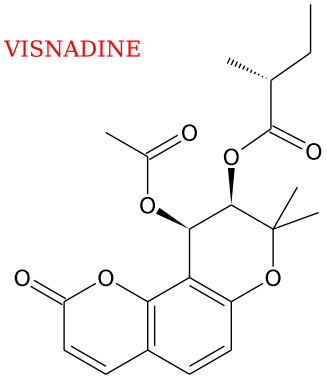
STEROID

TERPENE

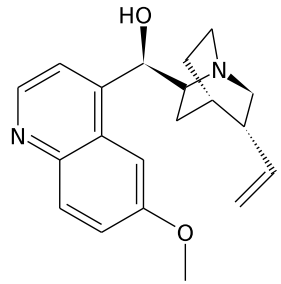
ALKALOID

COUMARINE

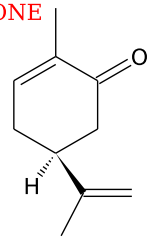
VISNADINE



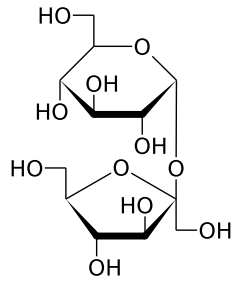
QUININE



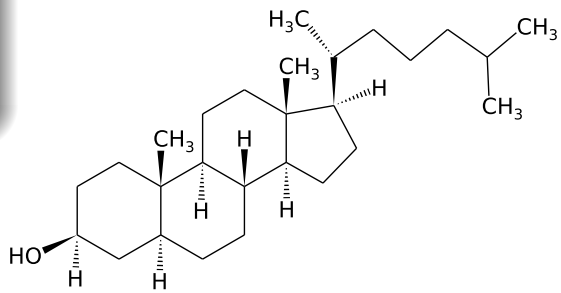
CARVONE



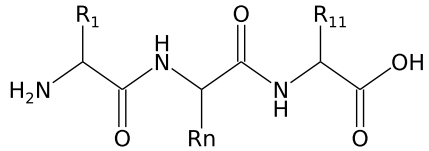
SACHAROSA



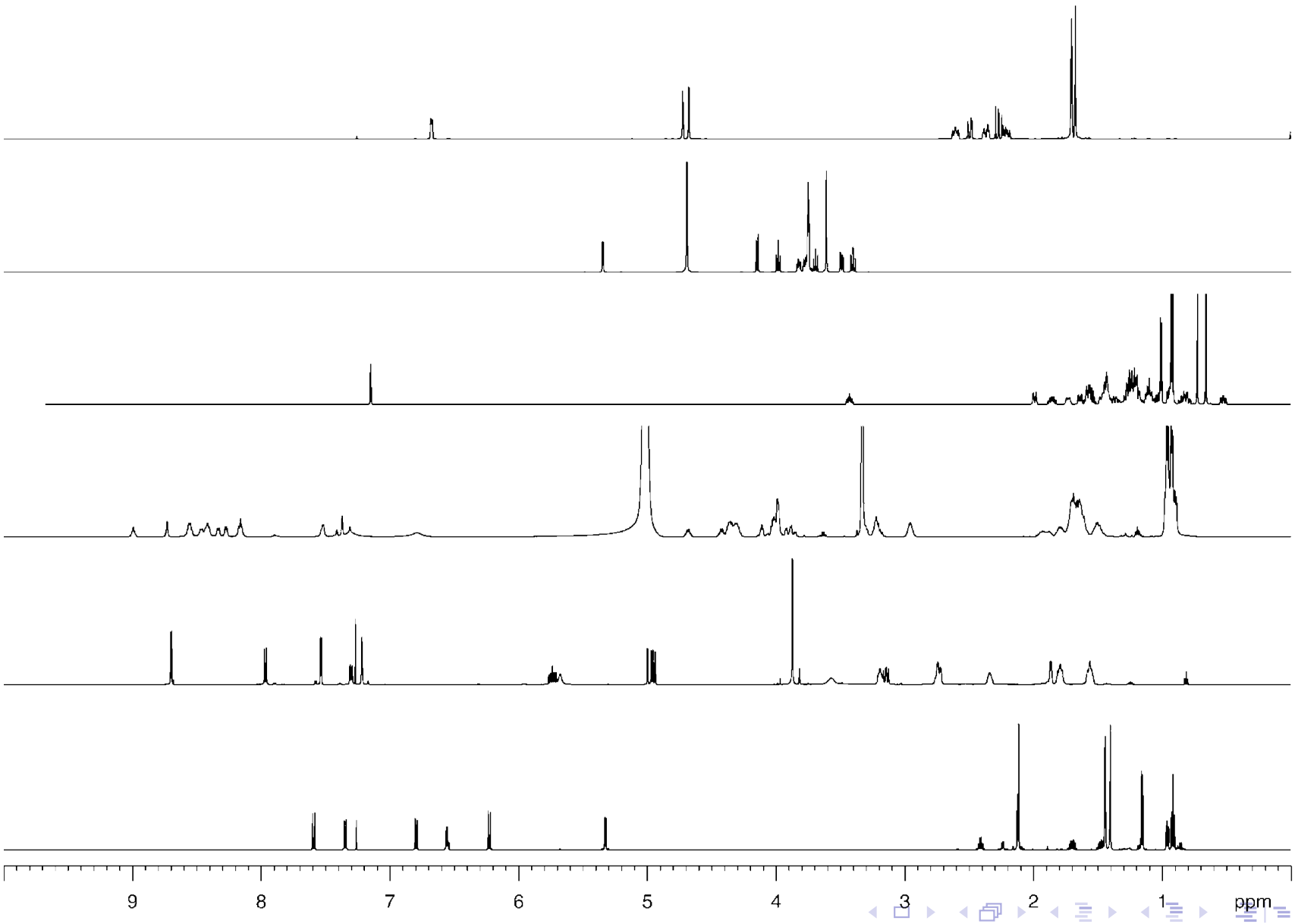
DIHYDROCHOLESTEROL



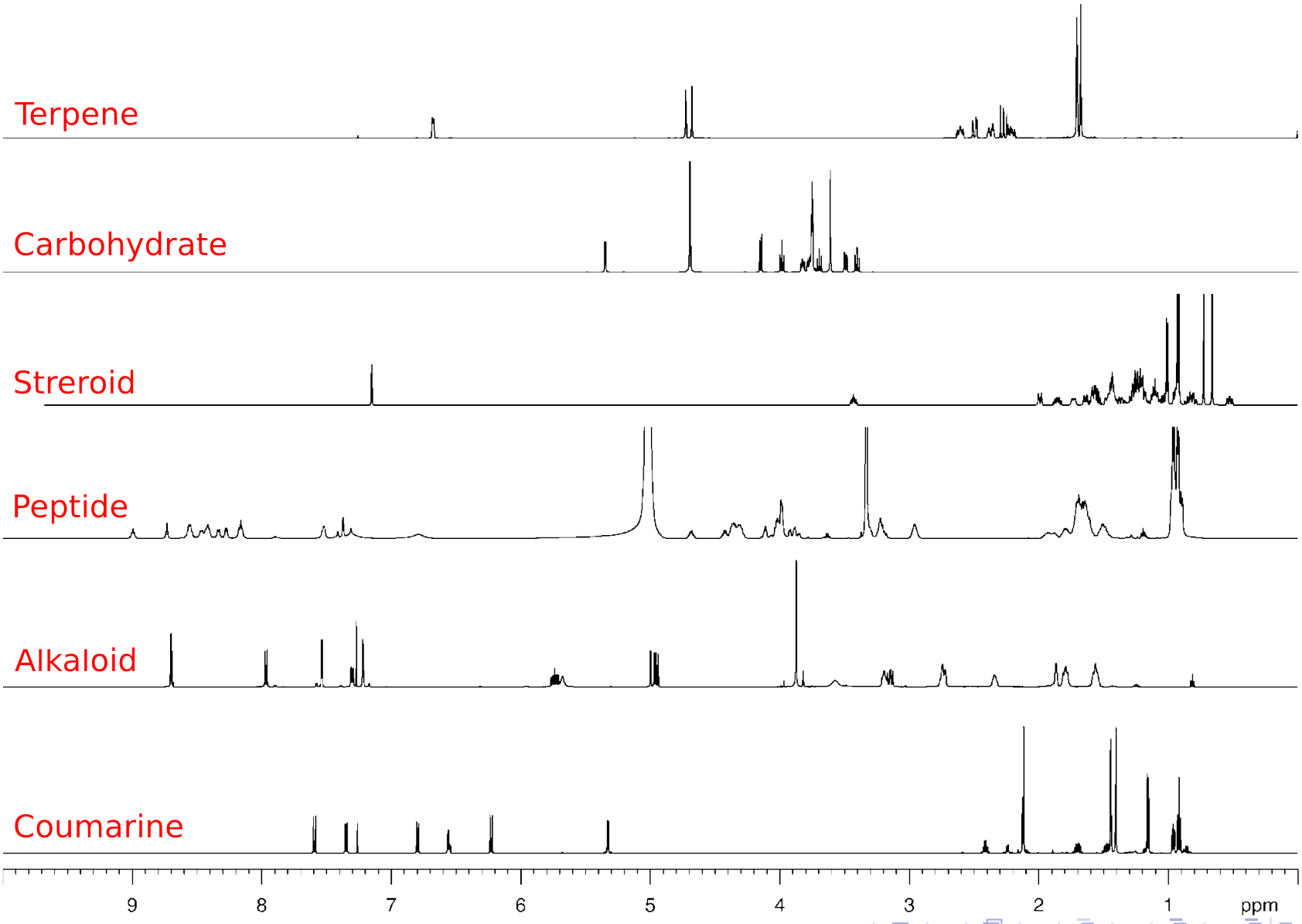
SGGLRLHLGLS



Task 0: **Classification of an unknown substance**



Task 0: **Classification of an unknown substance**



Task 1: $C_{10}H_{13}NO$

δ[ppm]	Multiplicity	Integral
1.05	triplet	3
1.75	singlet	3
3.70	quartet	2
7-7.60	complex multiplet	5

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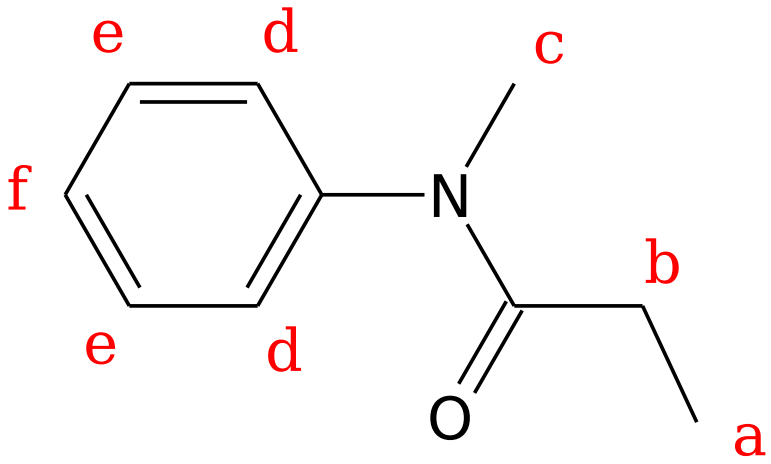
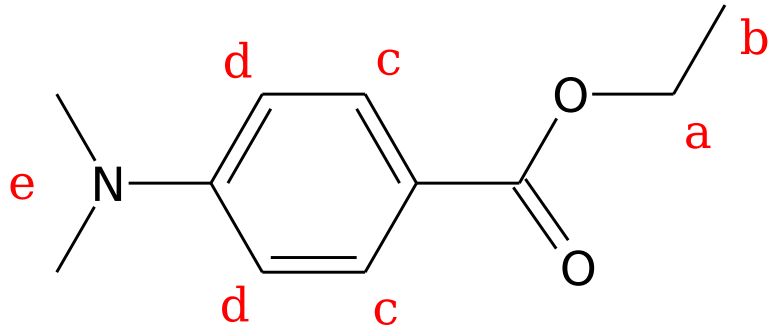


Task 2: $\mathbf{C_{11}H_{15}NO_2}$

δ[ppm]	Multiplicity	J(Hz)	Integral
1.30	triplet	7	3
3.00	singlet	-	6
4.25	quartet	7	2
6.65	dublet	8	2
7.80	dublet	8	2

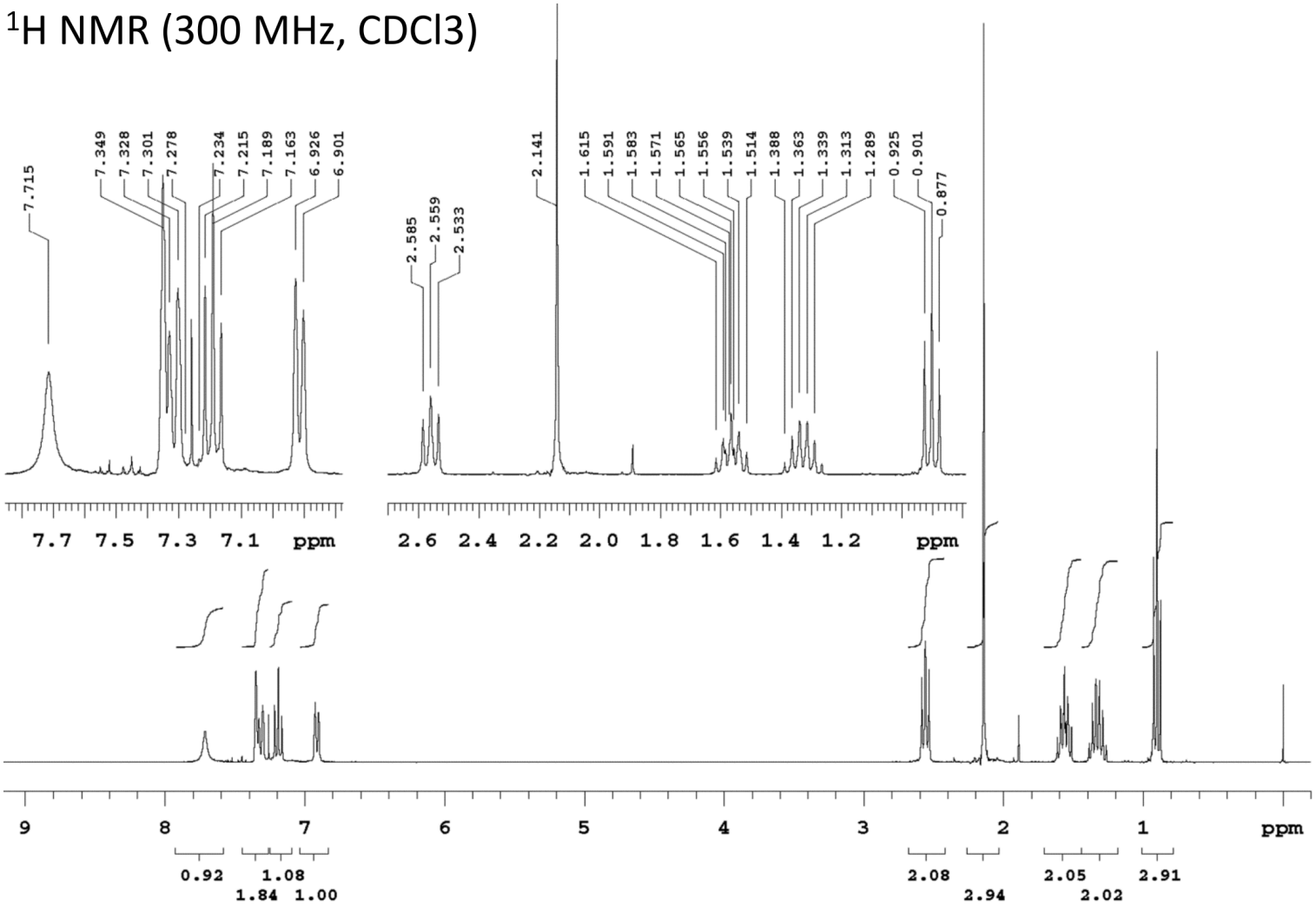
Task 2: $C_{11}H_{15}NO_2$

δ[ppm]	Multiplicity	J(Hz)	Integral
1.30 b	triplet	7	3
3.00 e	singlet	-	6
4.25 a	quartet	7	2
6.65 d	dublet	8	2
7.80 c	dublet	8	2



Task 3: $\mathbf{C_{12}H_{17}NO}$ - ^{1}H/COSY

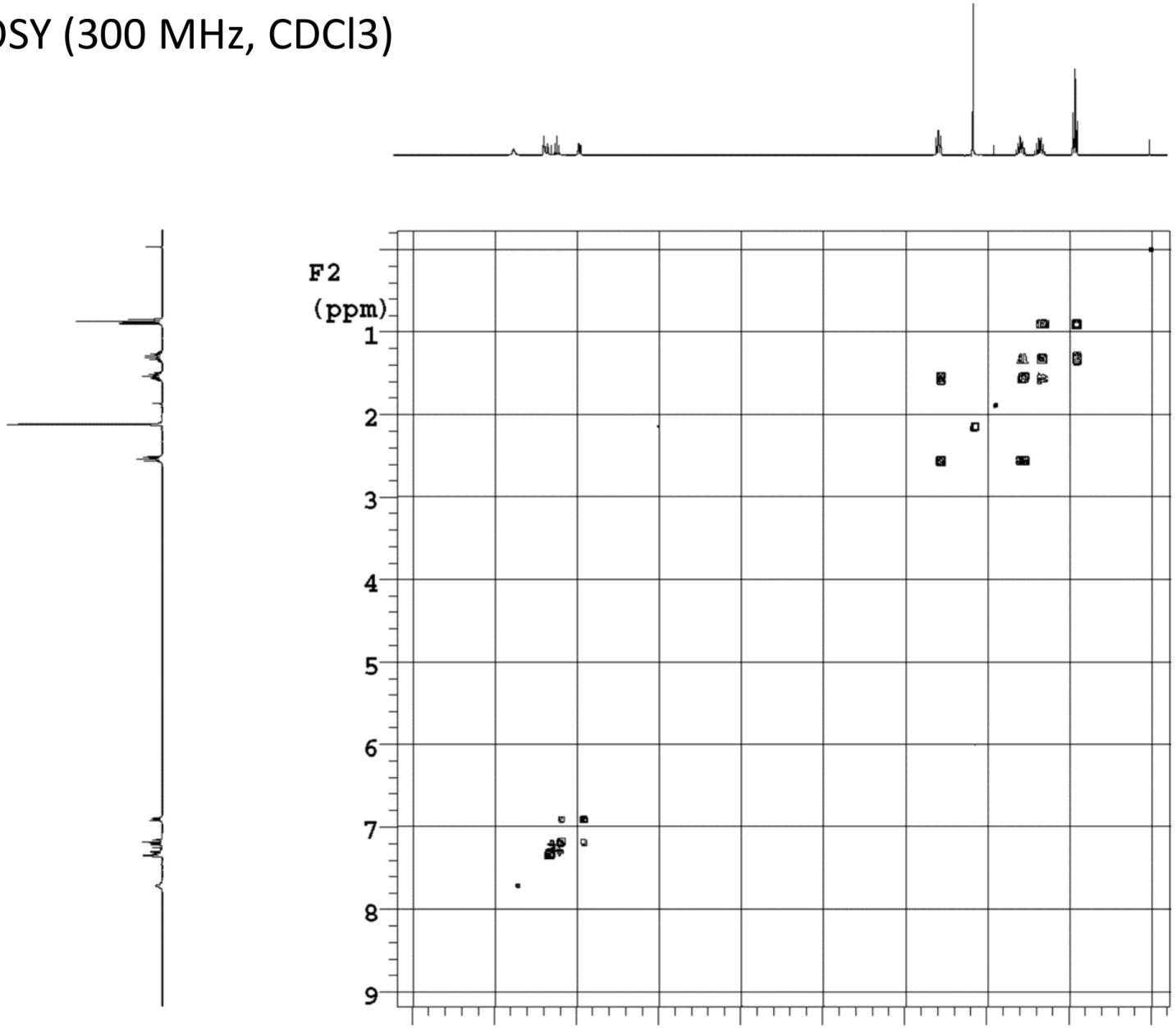
^{1}H NMR (300 MHz, CDCl3)



SOLUTION

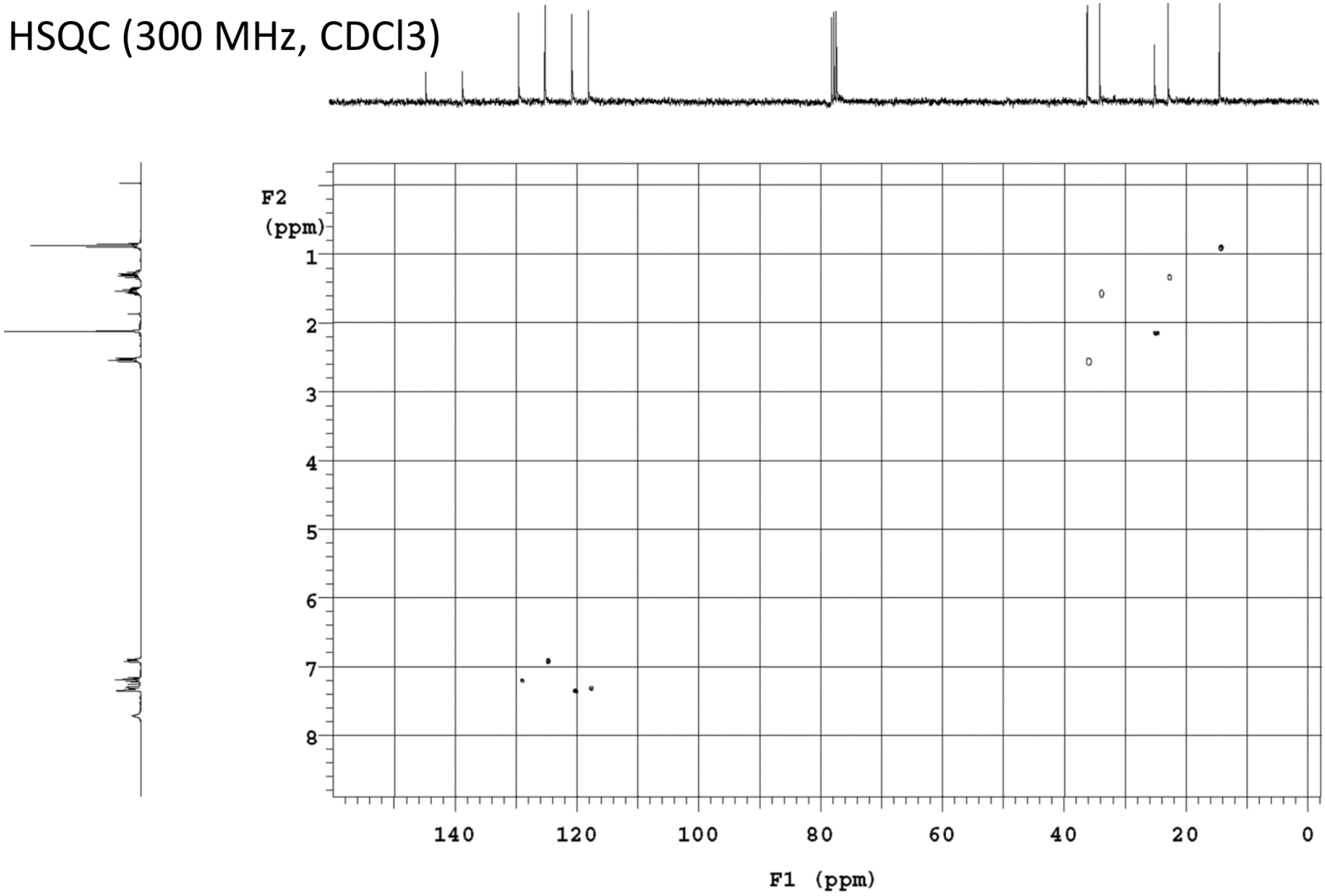
Task 3: $C_{12}H_{17}NO$ - ^1H/COSY

COSY (300 MHz, CDCl3)



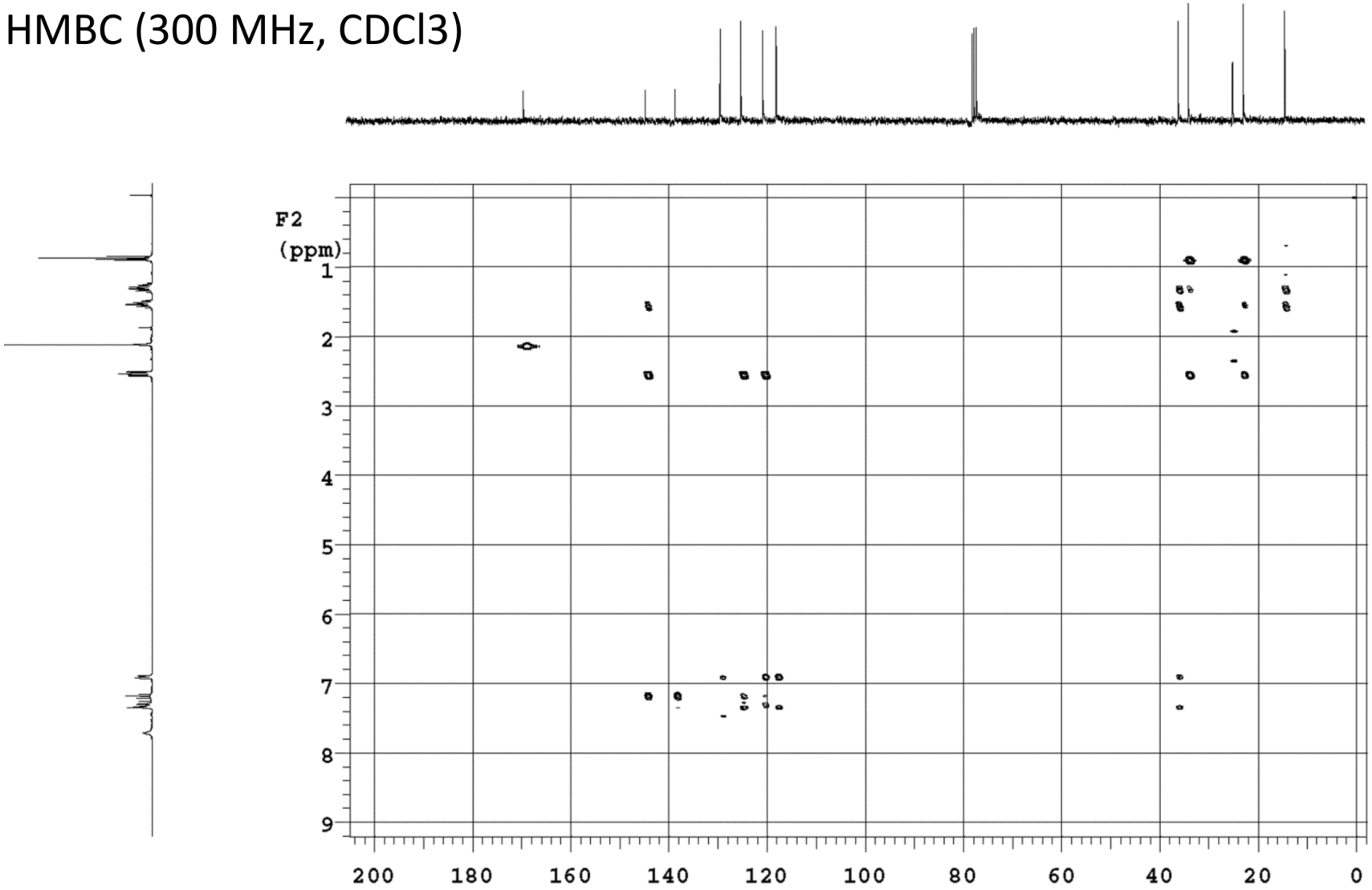
Task 3: $\mathbf{C_{12}H_{17}NO}$ - ^{1}H-^{13}C/HSQC,HMBC

HSQC (300 MHz, CDCl3)

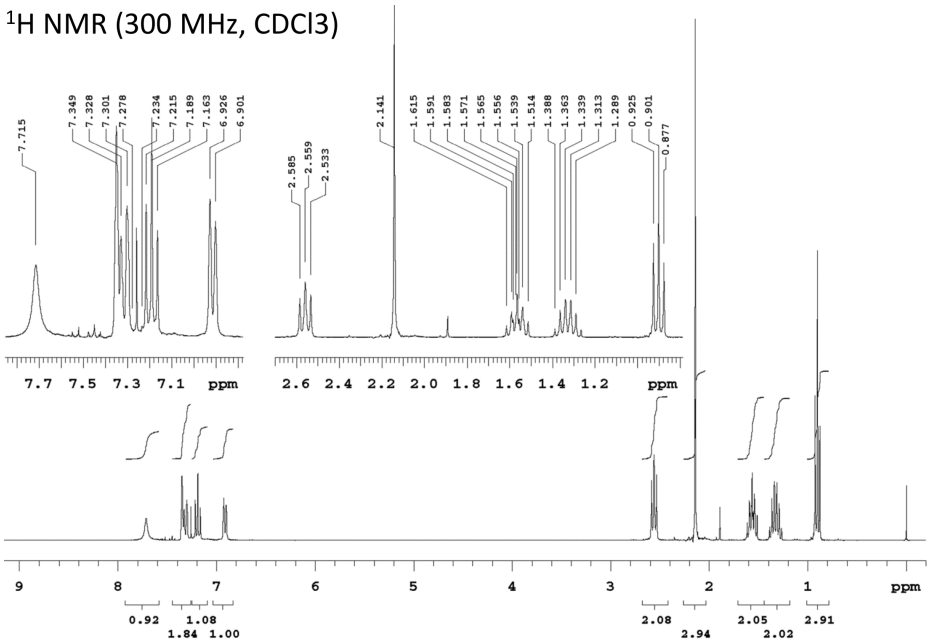


Task 3: $\mathbf{C_{12}H_{17}NO}$ - ^{1}H-^{13}C/HSQC,HMBC

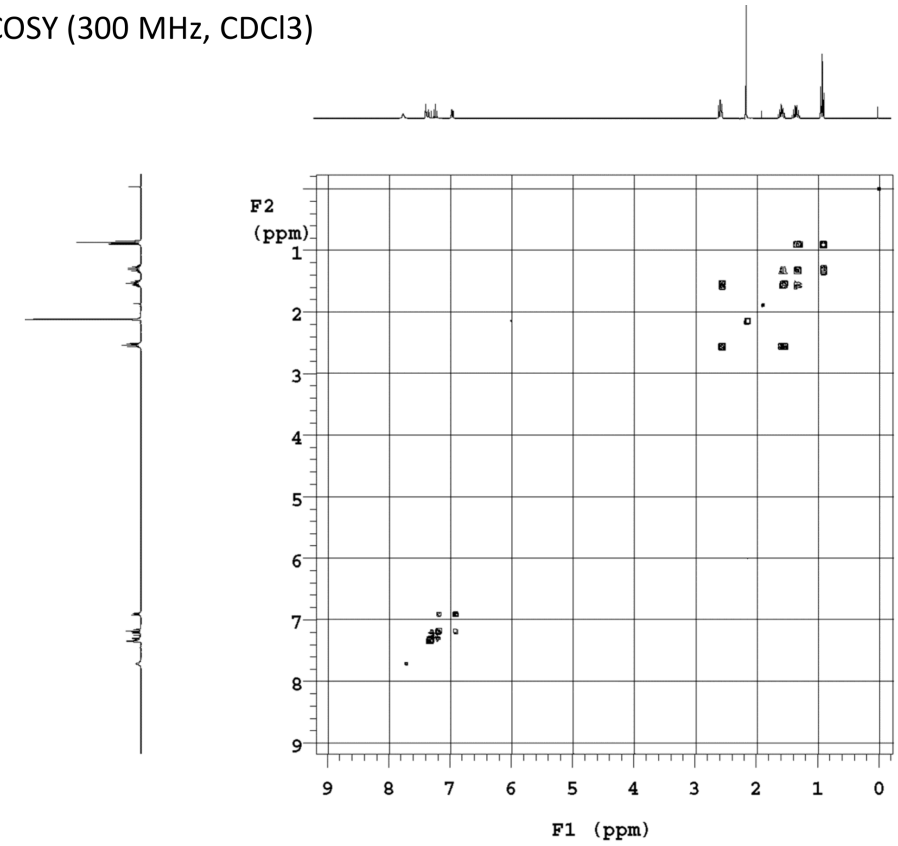
HMBC (300 MHz, CDCl3)

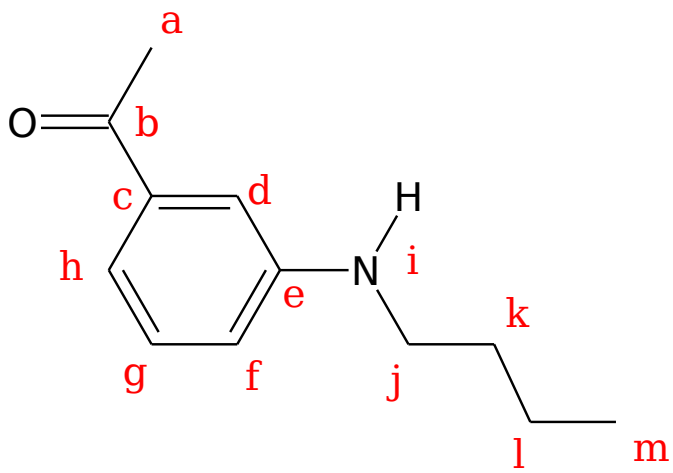


^{1}H NMR (300 MHz, CDCl3)



COSY (300 MHz, CDCl3)



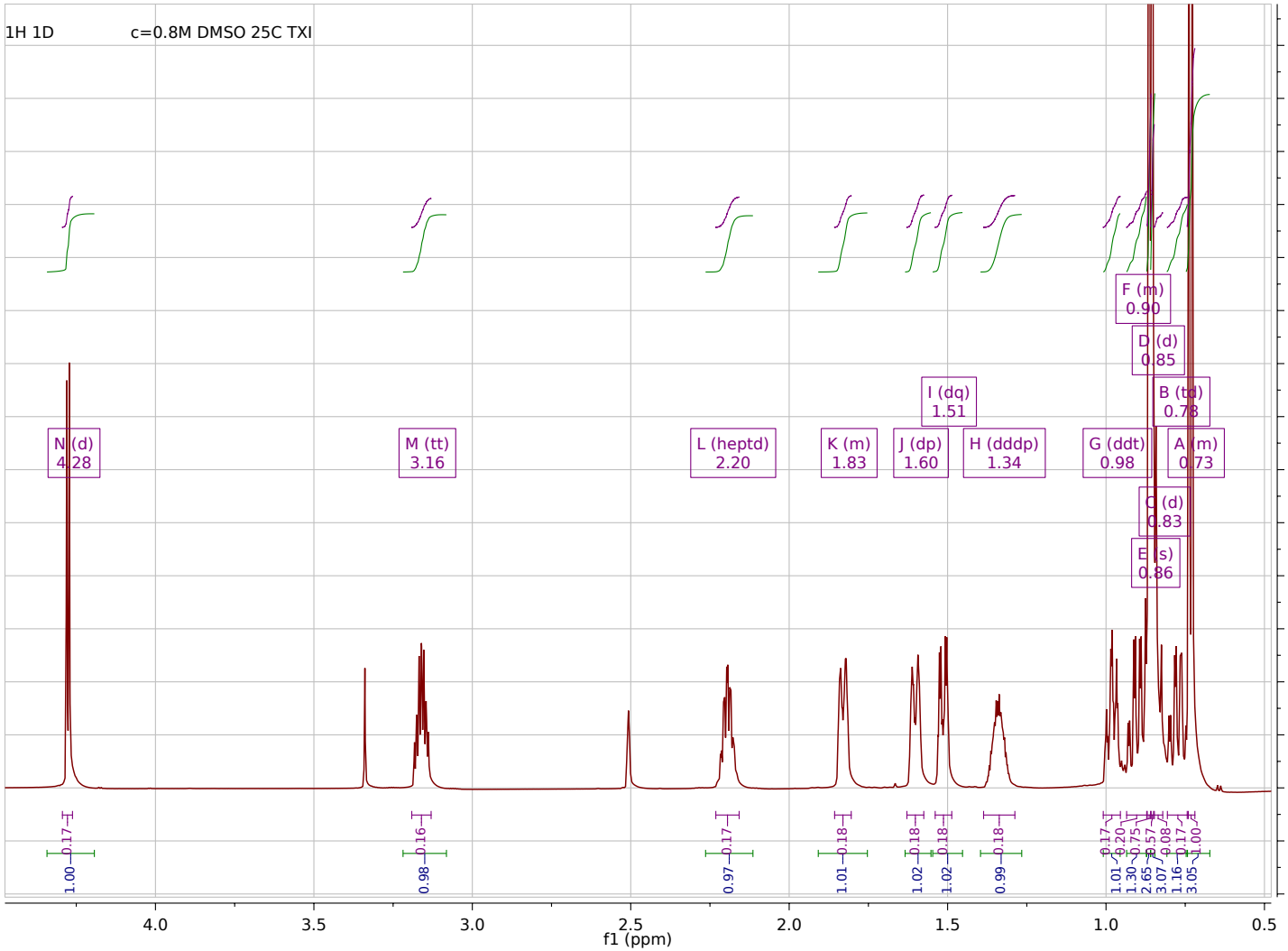


General comments

- inspect molecular formula $\mathrm{C_mH_hO_oN_nX_x}$:
  Degree of unsaturation $\mathbf{m + 1 - 0.5(h + x - n)}$
- identify signals of CH_3 and exchangeable protons in 1D ^{1}H sectrum
- arbitrary numbering (e.g., from lower to higher value of chemical shift) of resolved resonances in all spectra
- identification of the individual spin systems using DQF-COSY
- resolve geminal protons using HSQC
- connect molecular fragments/isolated spins using HMBC, NOESY
- specify the stereochemistry (relative configuration) by means of $J-$ and NOE interaction

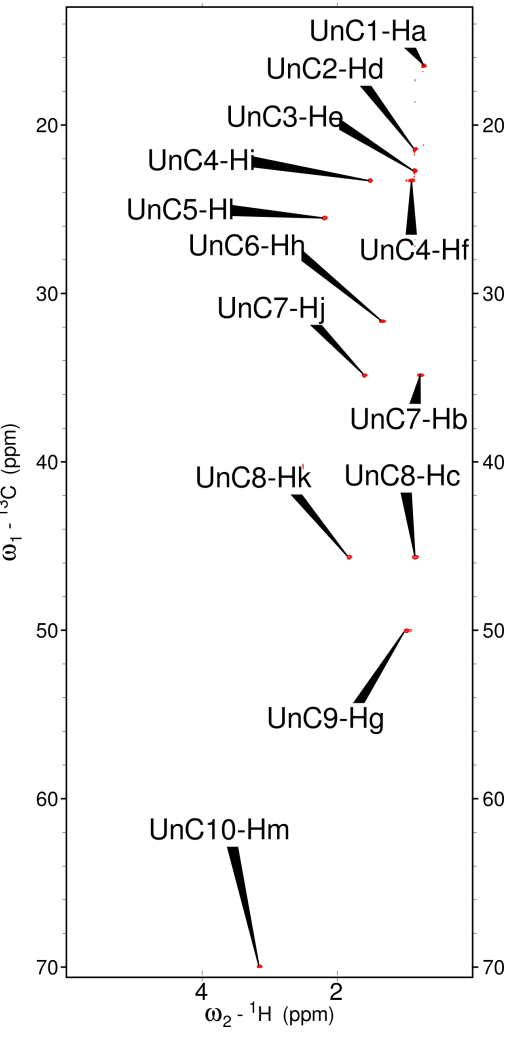
- in 1D spectrum bottom blue numbers are integrals, labels in violet frames contains the arbitrary label (A-N), multiplet specification (use with caution, automatically determined), and position of a signal in ppm
- UnHa-UnHb in 2D reffers to correlation of protons *a* and *b* of unknown compound Un

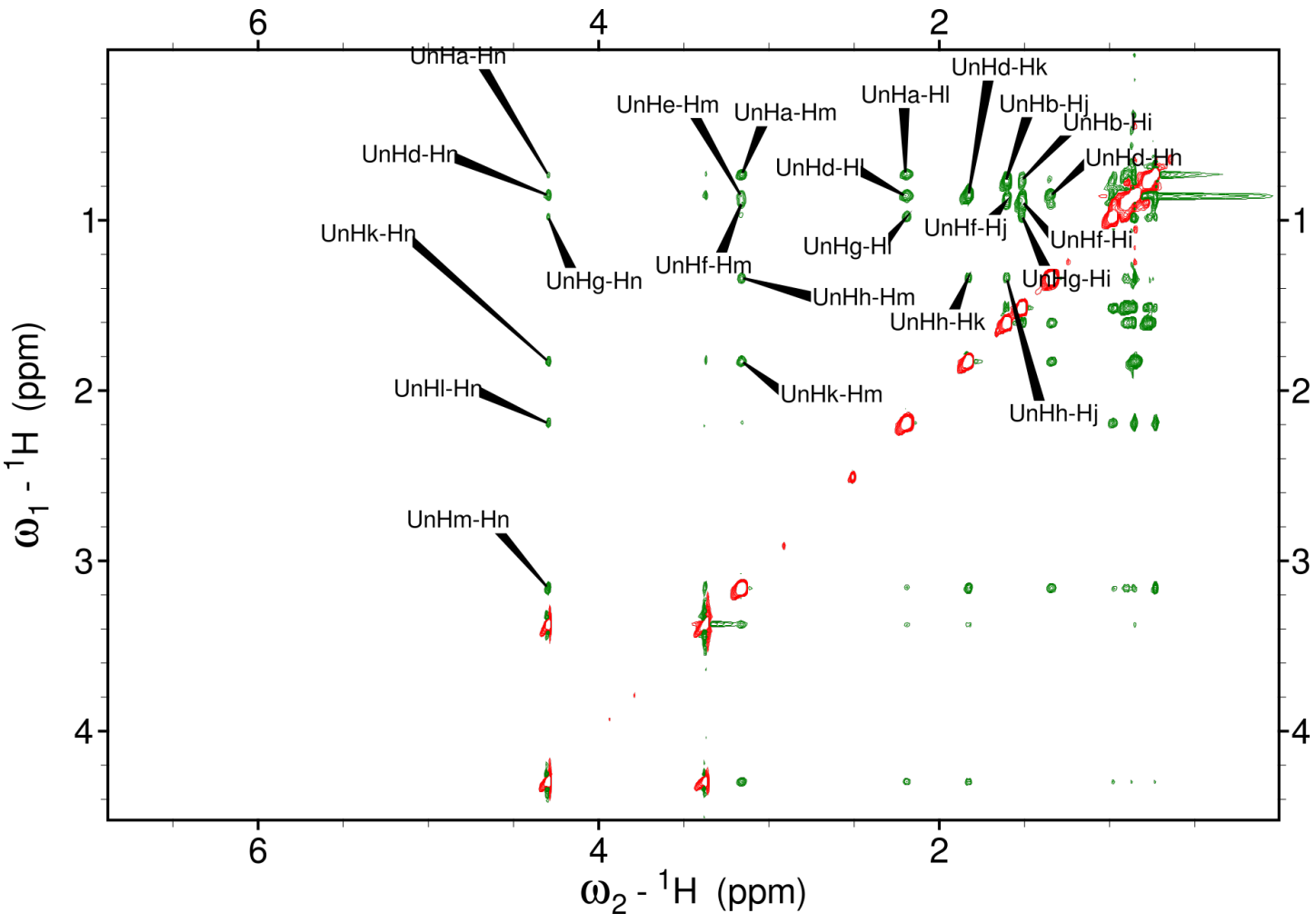
1D ^{1}H of $C_{10}H_{20}O$



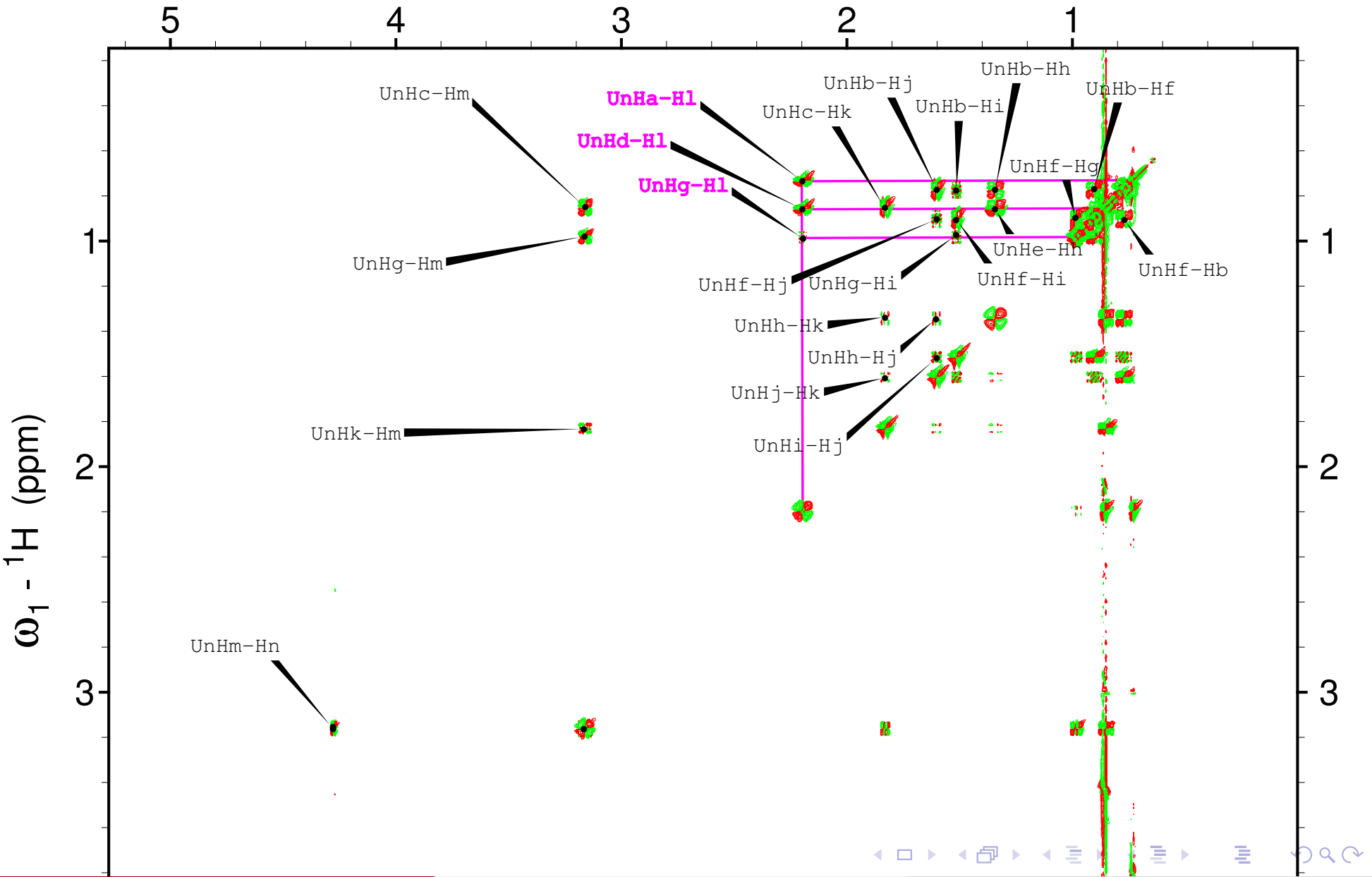
1H 1D
c=0.8M DMSO 25C TXI
G (ddt)
0.98
F (m)
0.90
E (s)
0.86
D (d)
0.85
C (d)
0.83
B (td)
0.78
A (m)
0.73
1.01
0.17
1.30
0.20
2.65
0.75
3.07
0.57
0.08
1.16
0.17
1.00
3.05
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
0.70
0.68
f1 (ppm)

^{1}H-^{13}C HSQC and NOESY



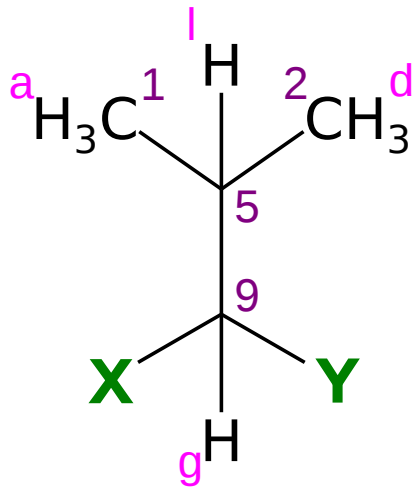


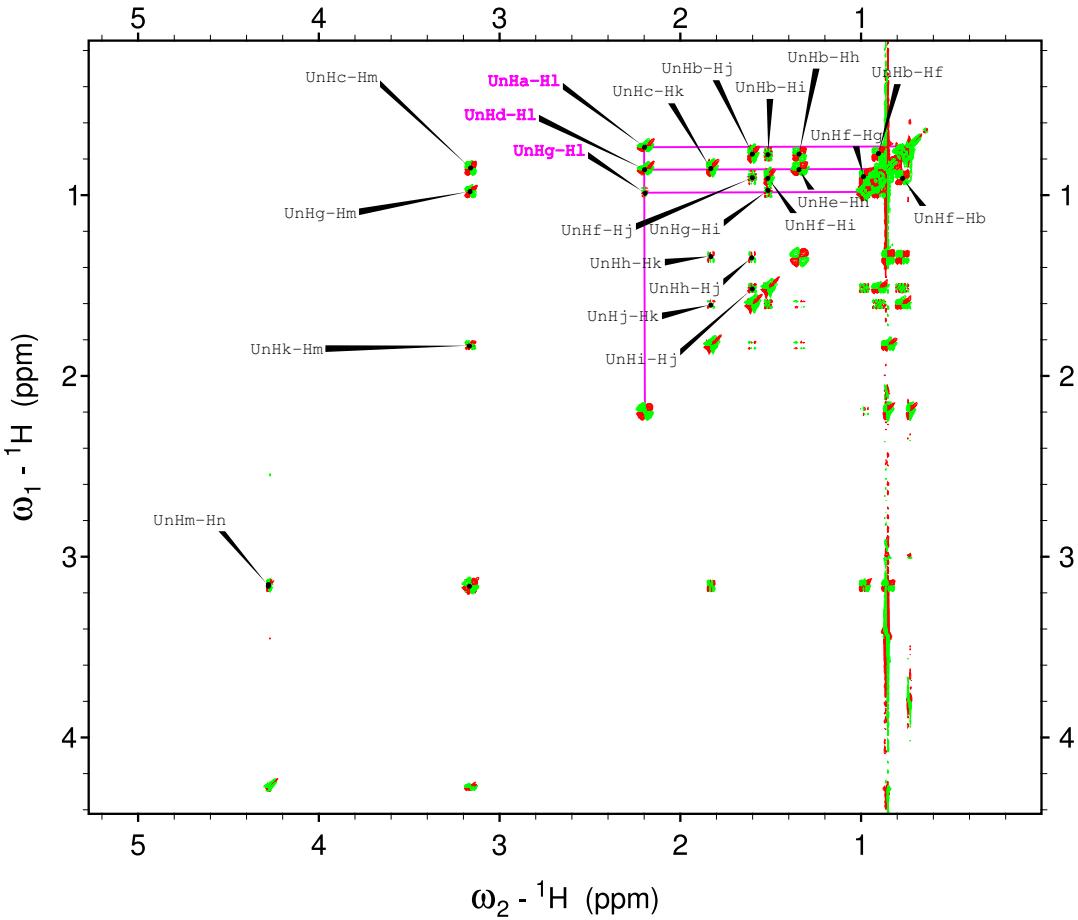
Task 1: *J*-connectivity of $C_{10}H_{20}O$



Task 1: *J*-connectivity of $C_{10}H_{20}O$

- methyls **1a,2d** connected to CH **5l**
- remaining crosspeak of CH **5l** to CH **9g**
- methyls 1a,2d diastereotopic ⇒ chiral carbon 9





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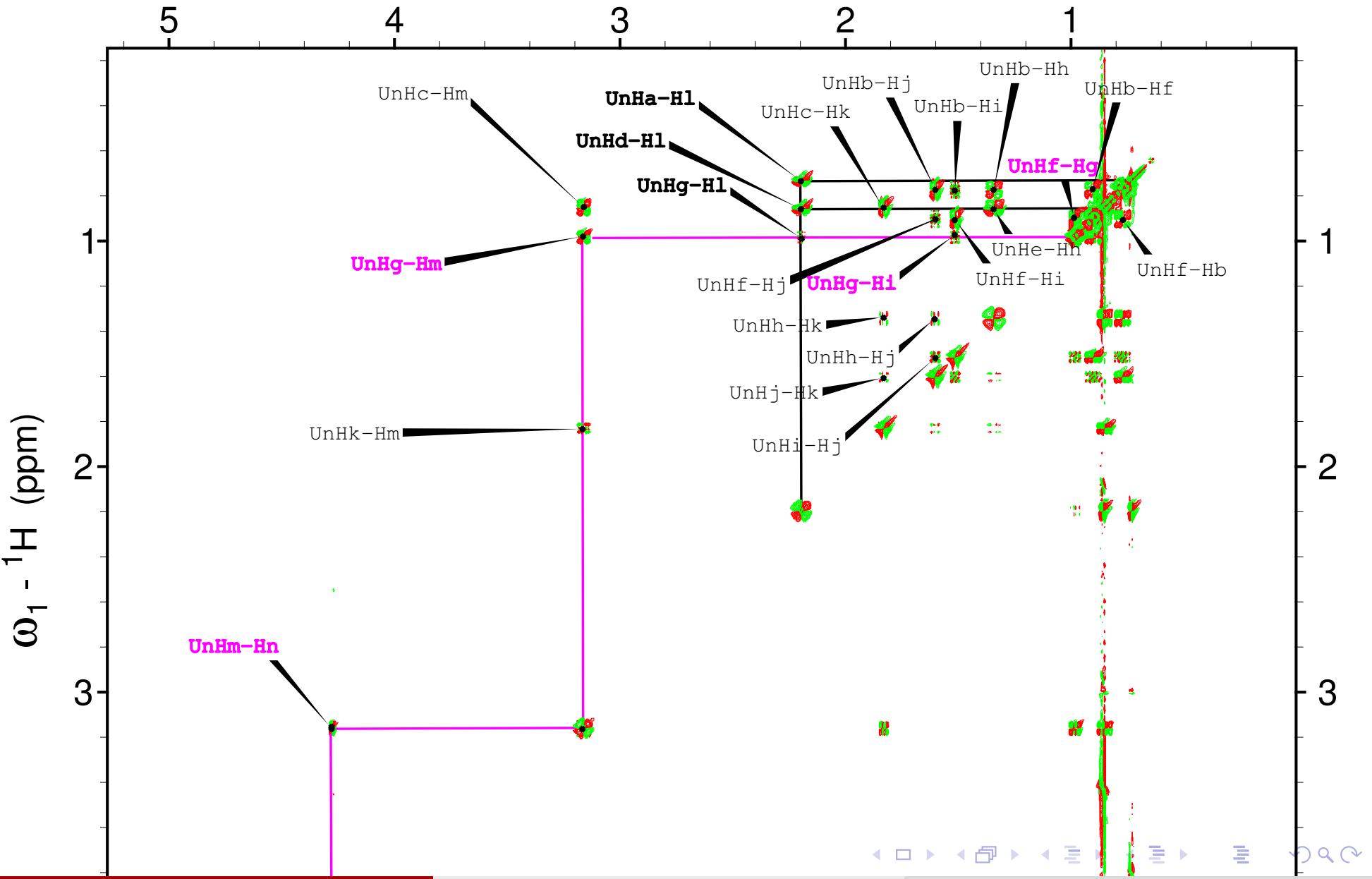
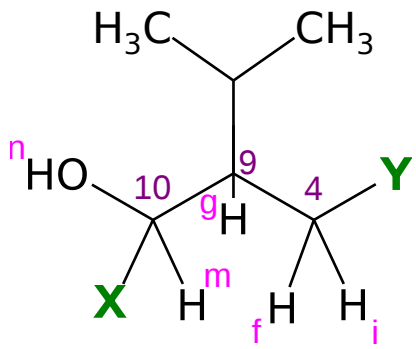
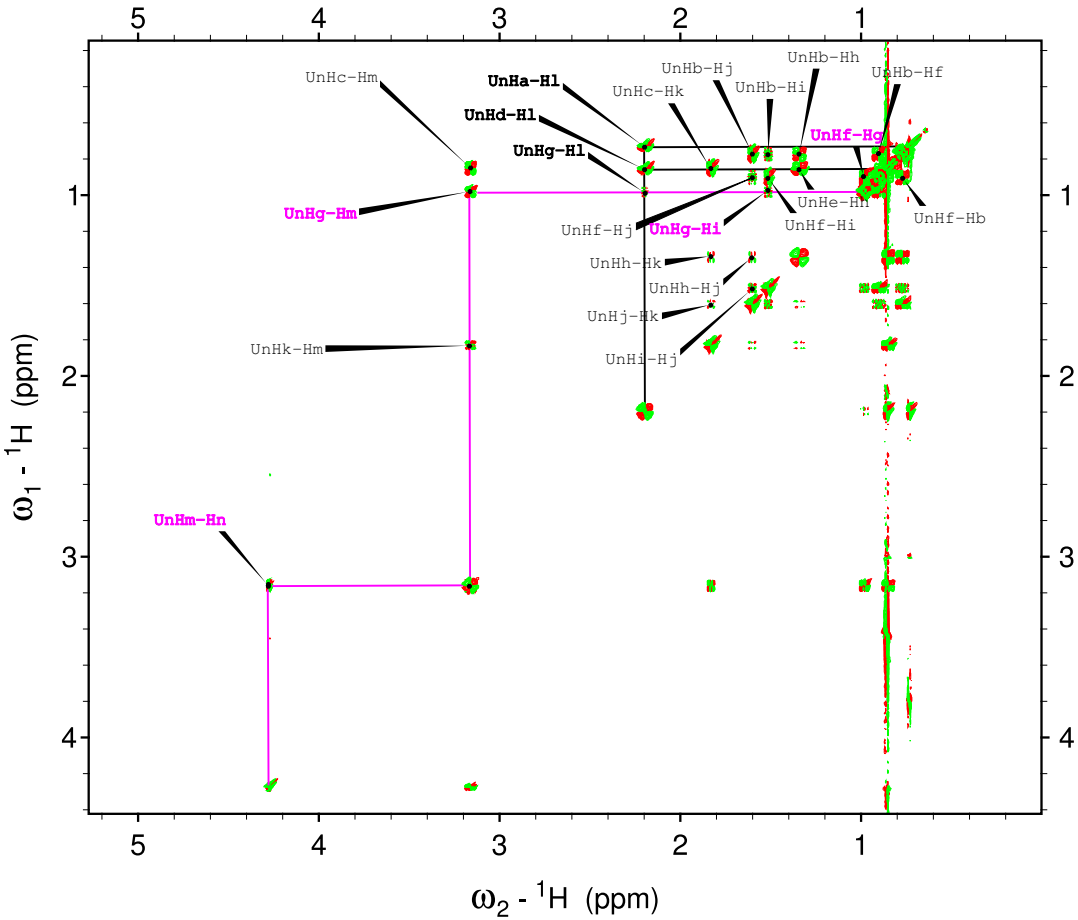


Task 1: *J*-connectivity of $C_{10}H_{20}O$

- CH **9g** has crosspeaks with deshielded **10m** $\Rightarrow$ OH group (**n**)
- CH **9g** has two crosspeaks with diastereotopic protons **4if**





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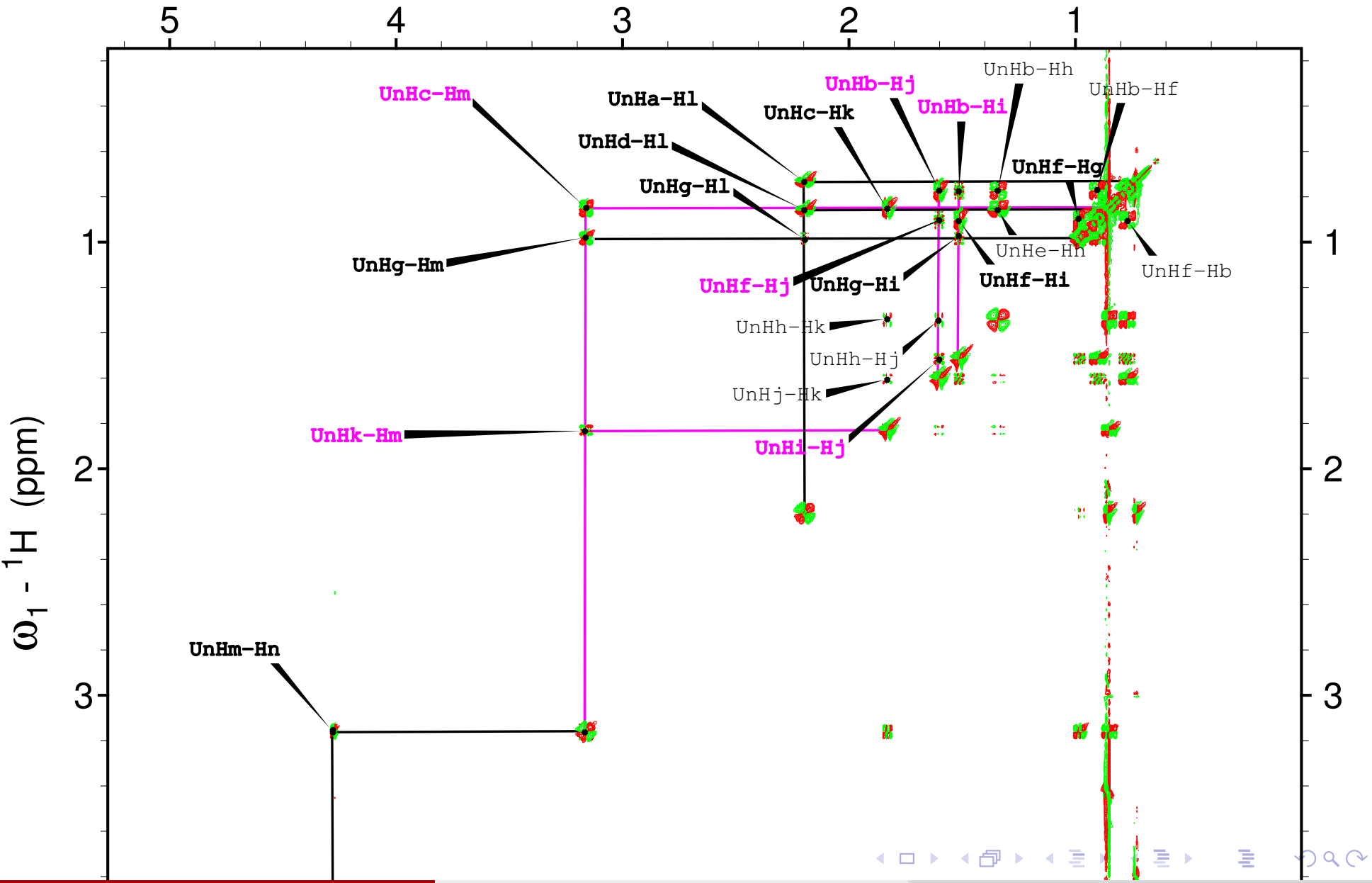
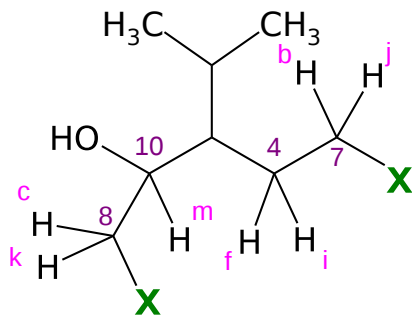
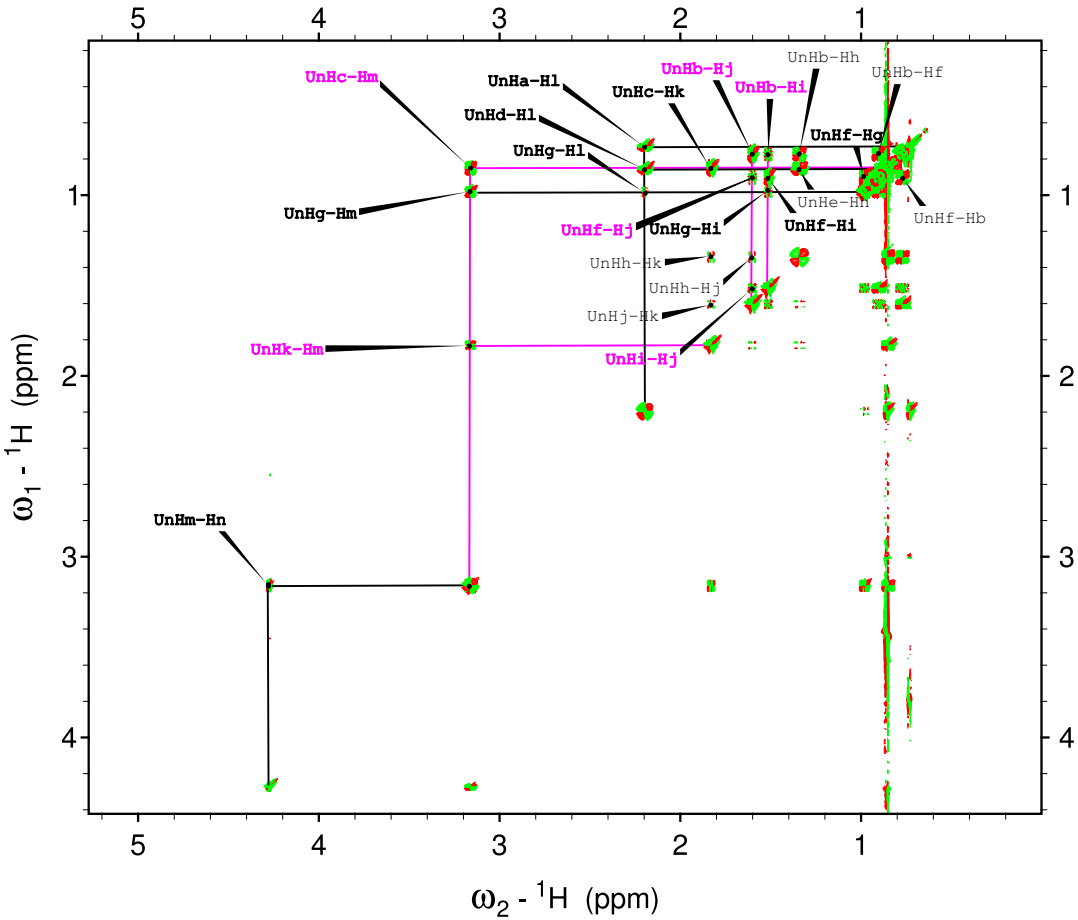


Task 1: *J*-connectivity of $C_{10}H_{20}O$

- CH **10m** connected with CH_2 **8ck**
- CH_2 **4if** connected with CH_2 **7bj**





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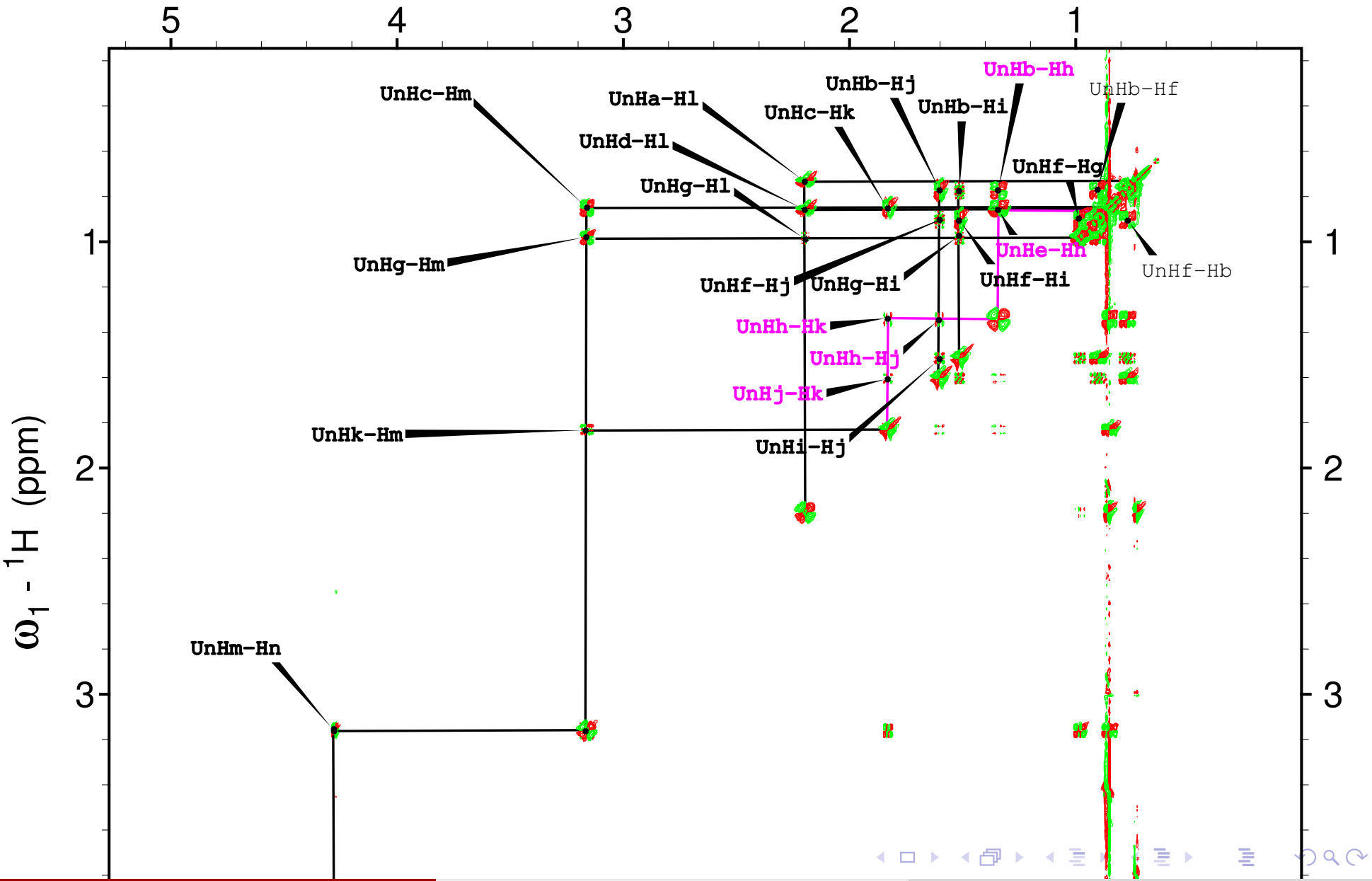
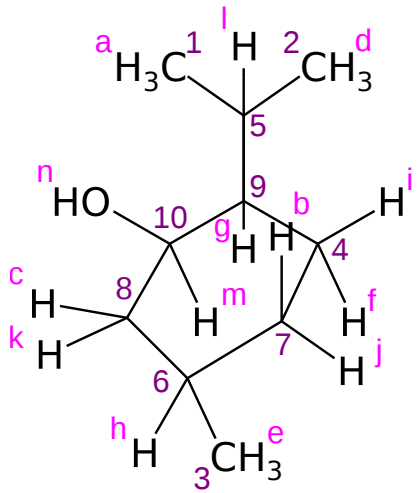
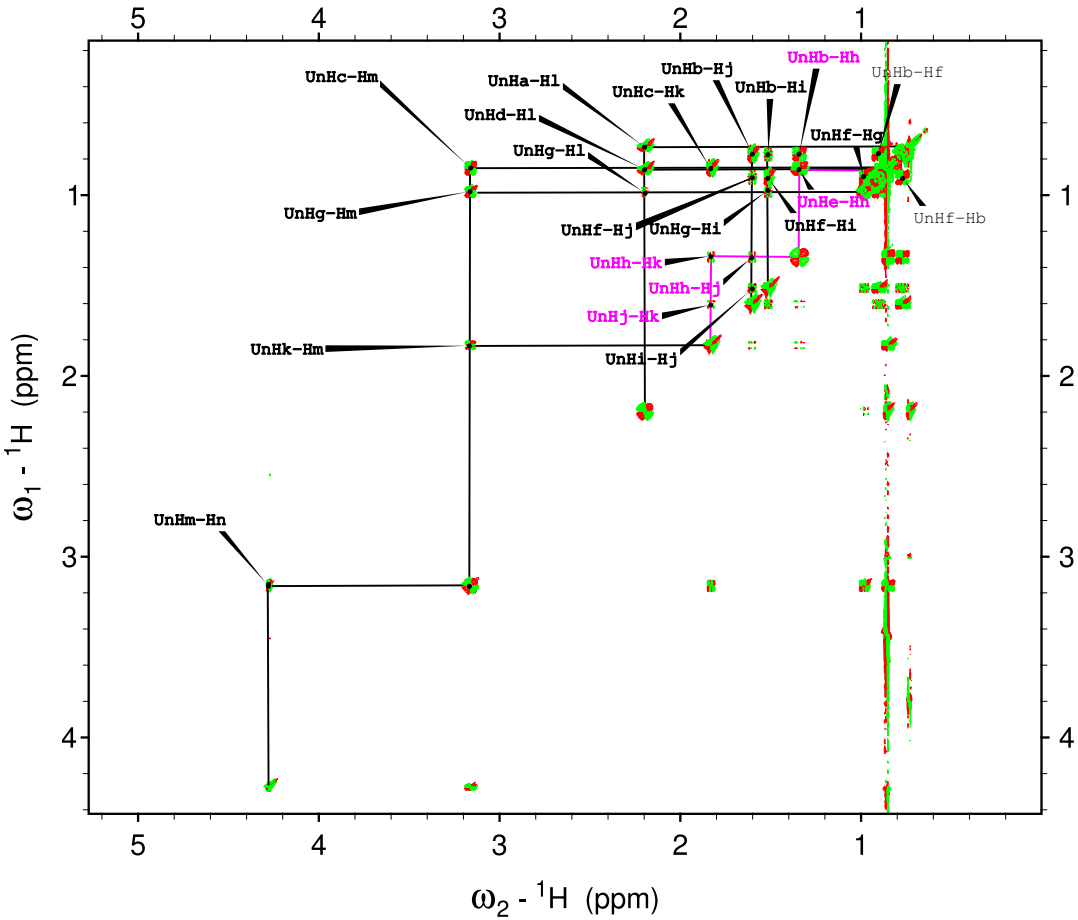


Task 1: *J*-connectivity of $C_{10}H_{20}O$

- CH_2 **8ck** weakly coupled with CH_2 **7bj** $\Rightarrow$ closing ring
- protons **b** and **k** coupled to CH **6h** which is connected to methyl **3e**
- other expected crosspeaks in DQ-COSY crowded/overlapped, found topology confirmed in HMBC ($^{3/4}J_{HC}$)





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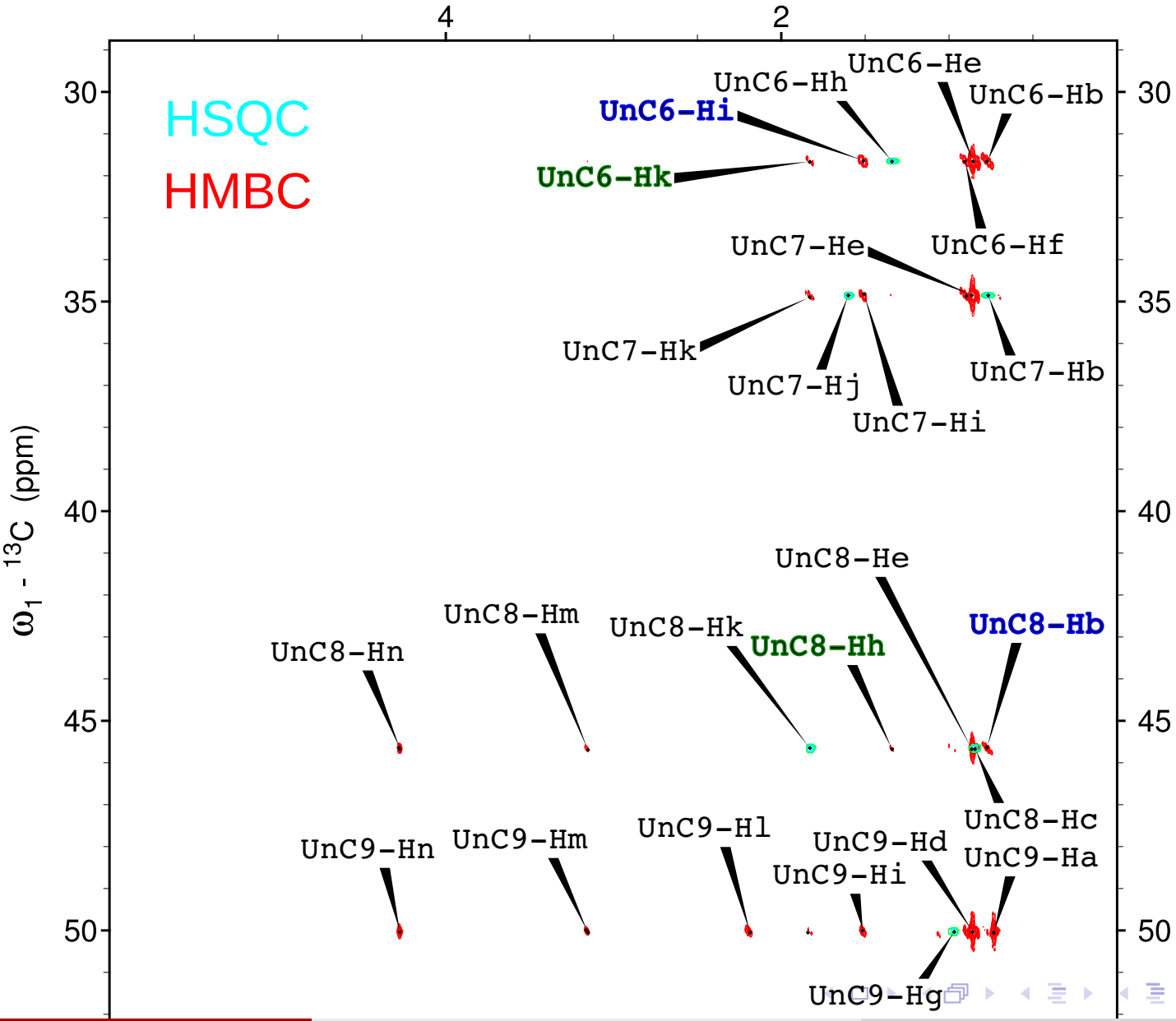

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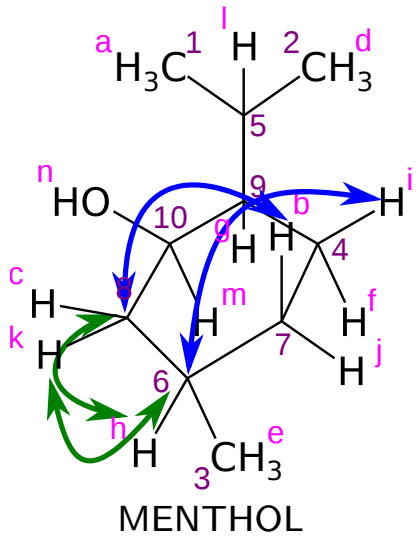
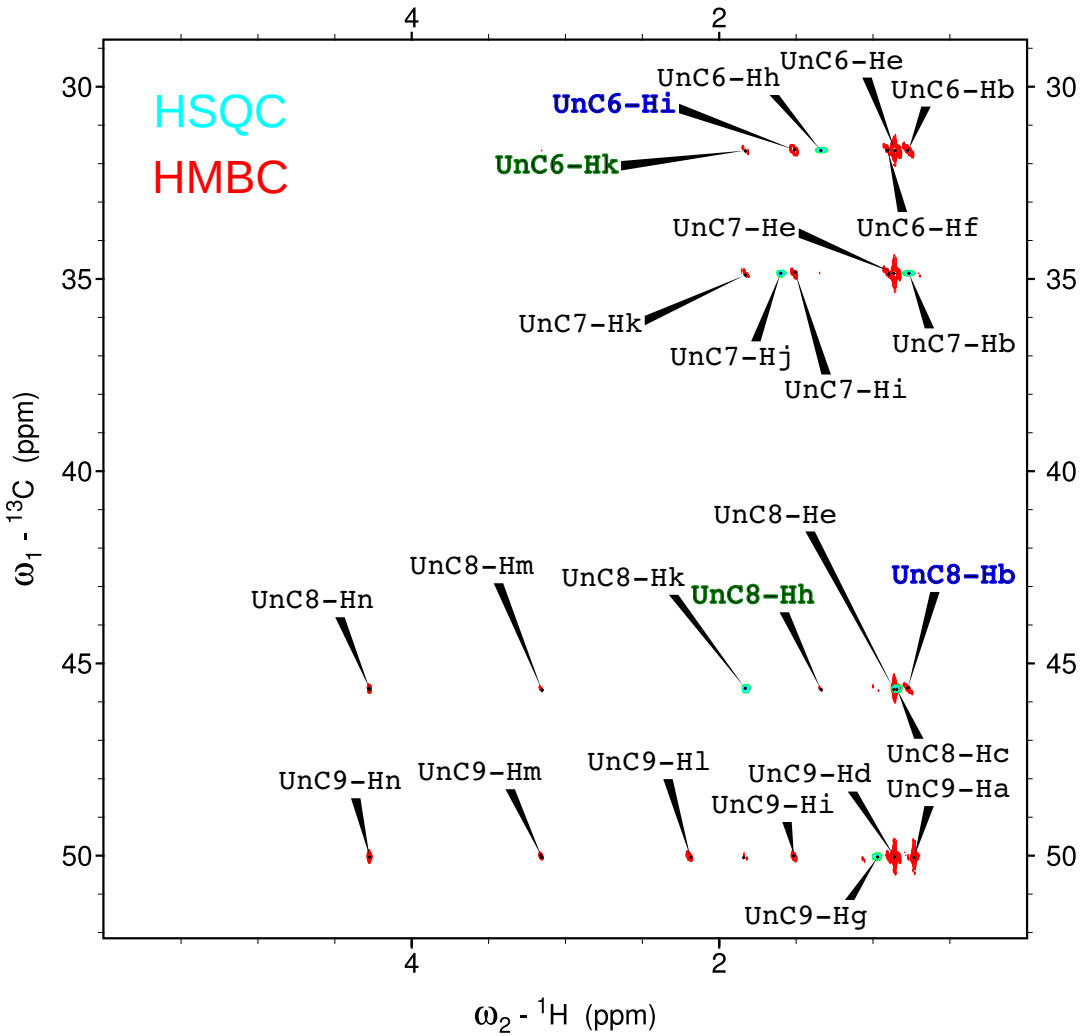
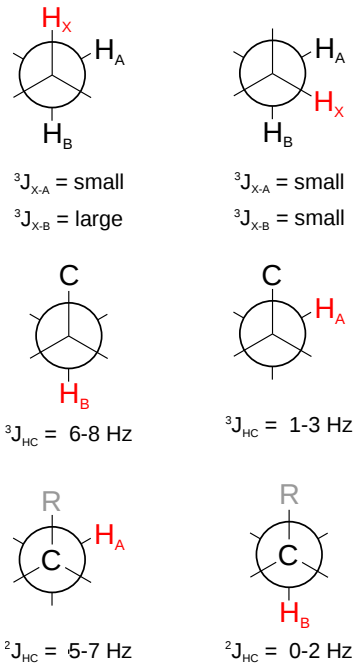


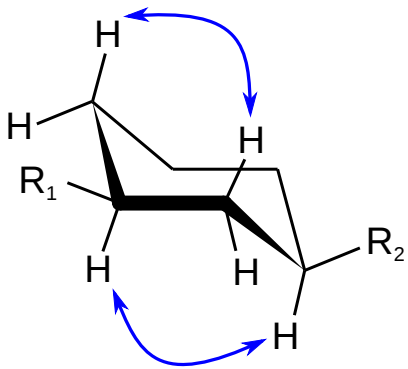
MENTHOL



Task 1:
Stereochemistry of menthol $C_{10}H_{20}O$

- 1↔2: homonuclear/heteronuclear couplings
  - large couplings preserved in 1D slices of HSQC: axial H - 2 visible interactions (geminal and vicinal) × equatorial H - only geminal
  - 1D TOCSY: selective decoupling ⇒ simplification of complex multiplets
  - DQF-COSY: analysis of phase sensitive spectrum
- 1↔3: NOE contacts (axial strong)





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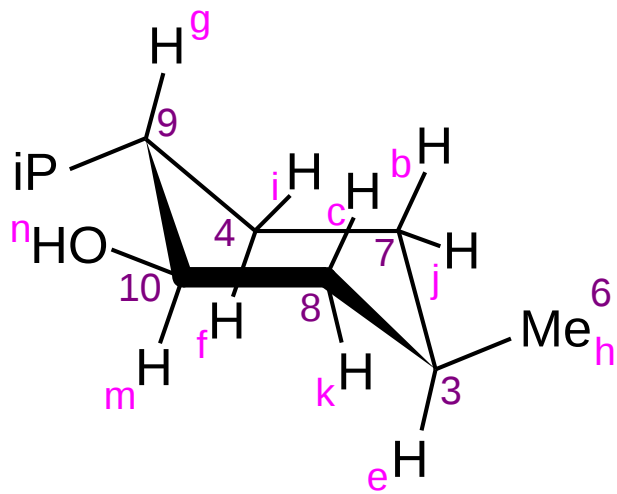
Stereochemistry of menthol $C_{10}H_{20}O$

- 1↔2: homonuclear/heteronuclear couplings
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