# C8953
# NMR strukturní analýza
# seminář

## Identification of an unknown compound

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

**Assign the general name to displayed substances:**

CARBOHYDRATE

PEPTIDE

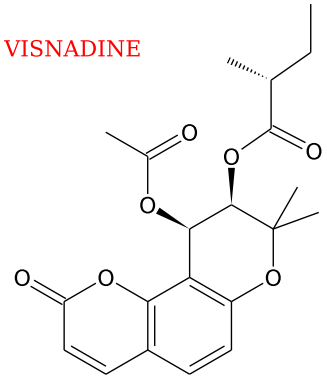
STEROID

TERPENE

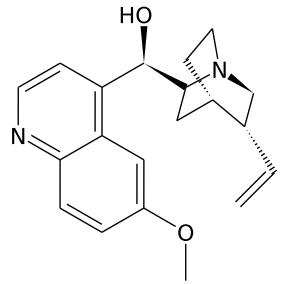
ALKALOID

COUMARINE

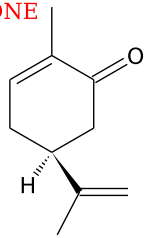
VISNADINE



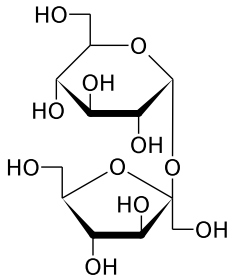
QUININE



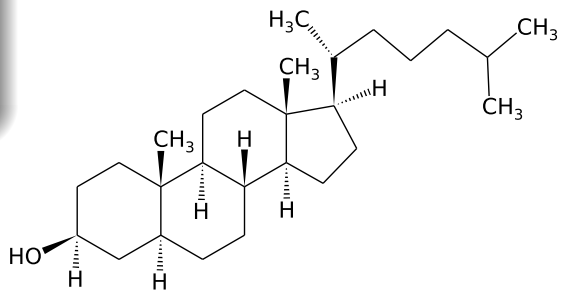
CARVONE



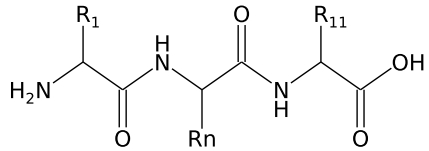
SACHAROSA



DIHYDROCHOLESTEROL



SGGLRLHLGLS



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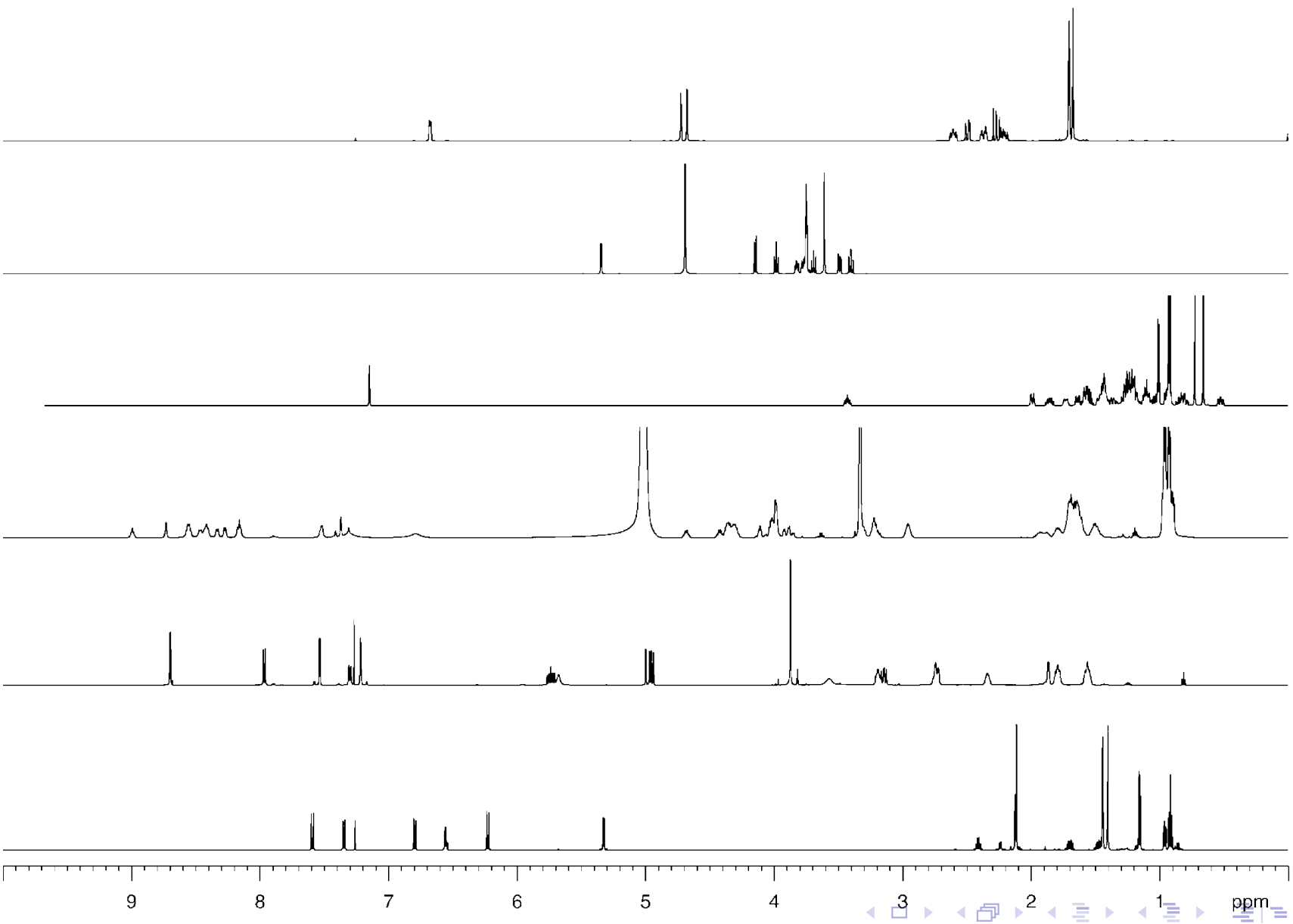

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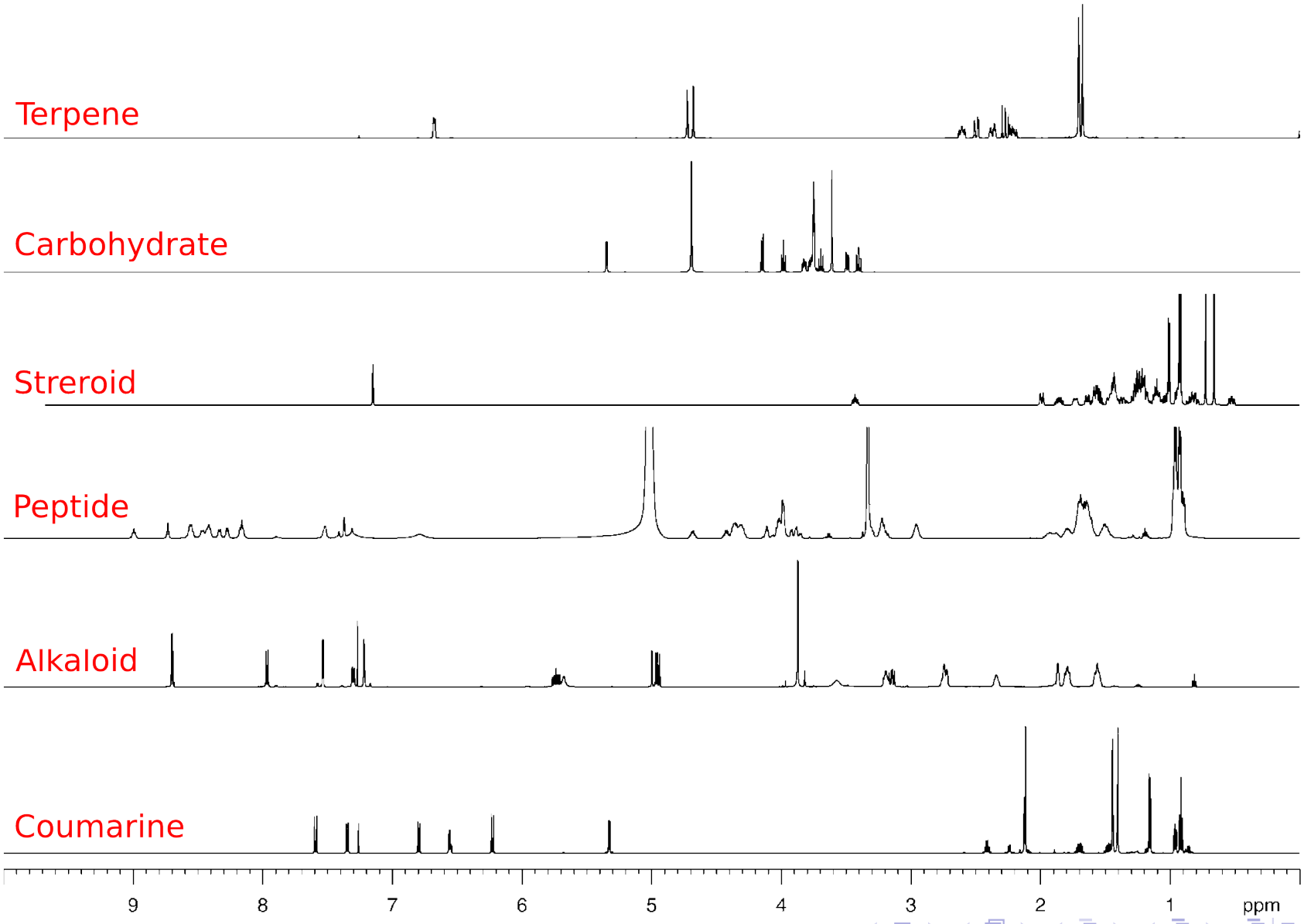

# Task 1: $C_{10}H_{13}NO$

| $\delta$[ppm] | Multiplicity | Integral |
|---|---|---|
| 1.05 | triplet | 3 |
| 1.75 | singlet | 3 |
| 3.70 | quartet | 2 |
| 7-7.60 | complex multiplet | 5 |

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

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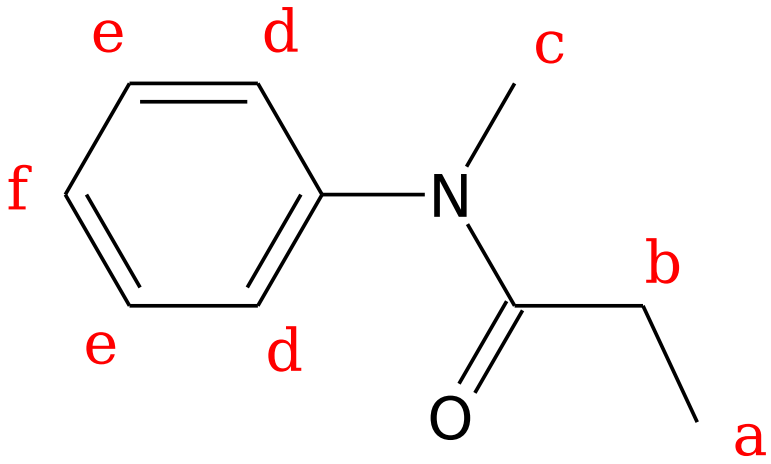
| 1.75 c | singlet | 3 |
| 3.70 b | quartet | 2 |
| 7-7.60 d-f | complex multiplet | 5 |

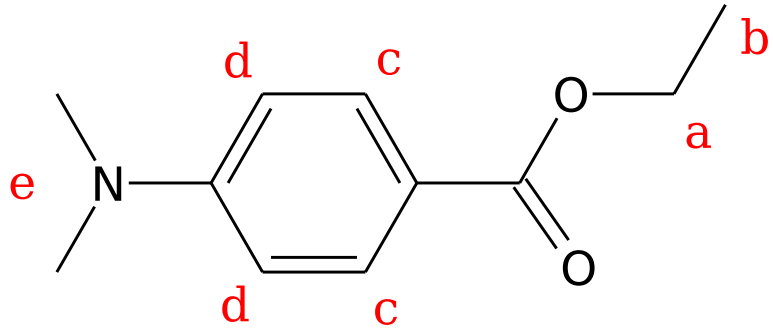


# Task 2: $\mathbf{C_{11}H_{15}NO_2}$

| $\delta$[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 |

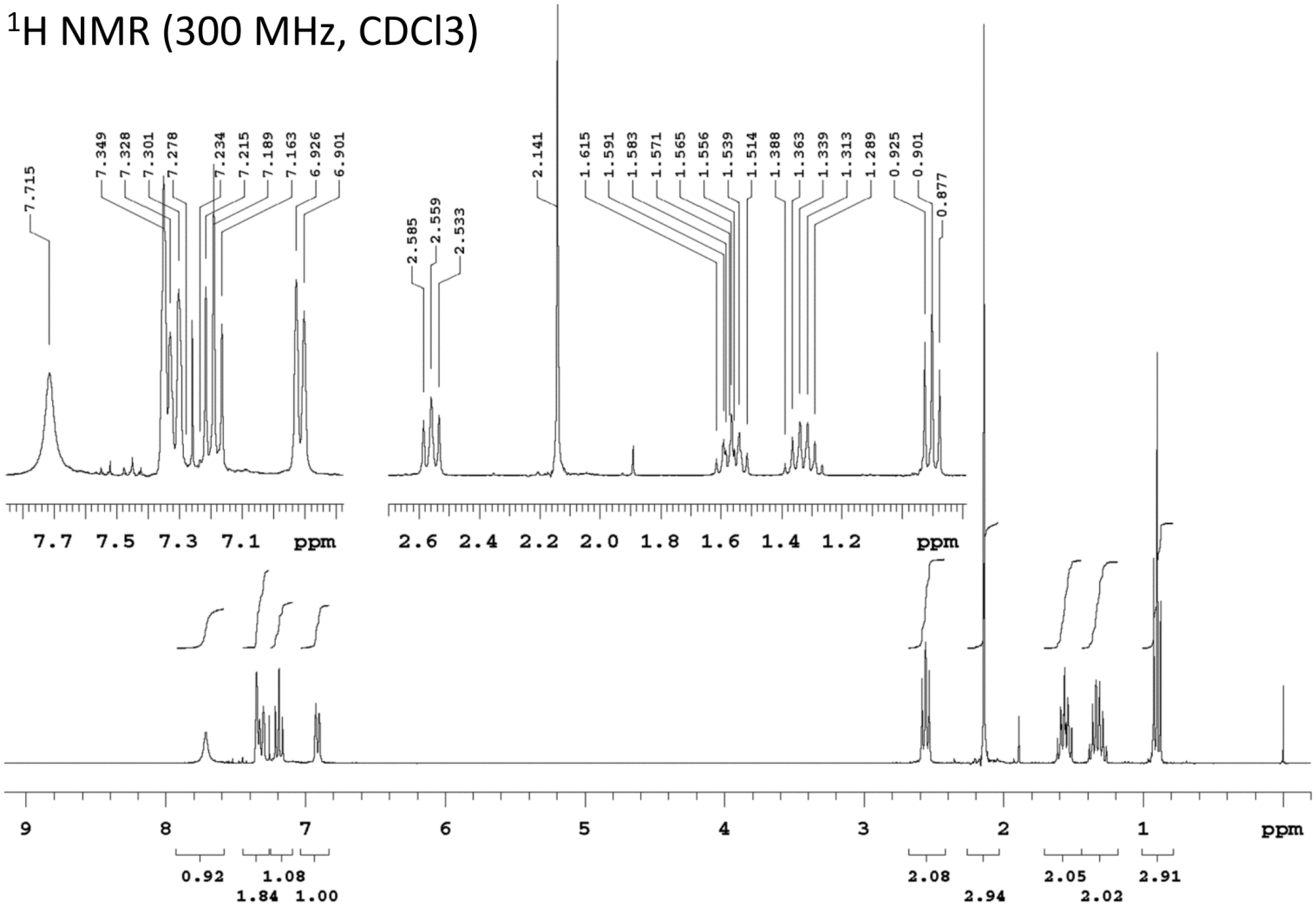
# Task 2: $C_{11}H_{15}NO_2$

| $\delta$[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: $C_{12}H_{17}NO$ - $^1H$/COSY

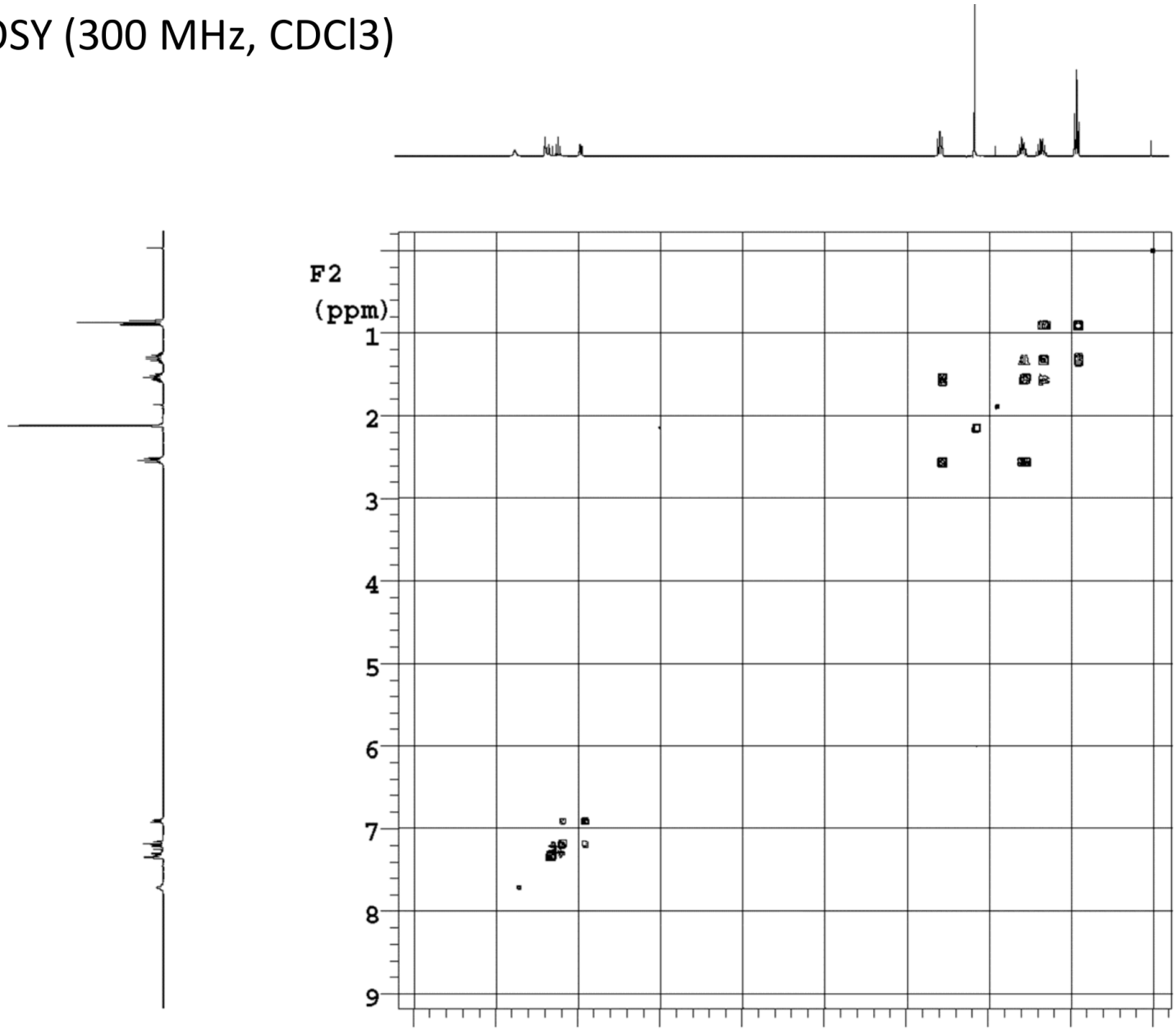
$^1H$ NMR (300 MHz, CDCl3)




SOLUTION

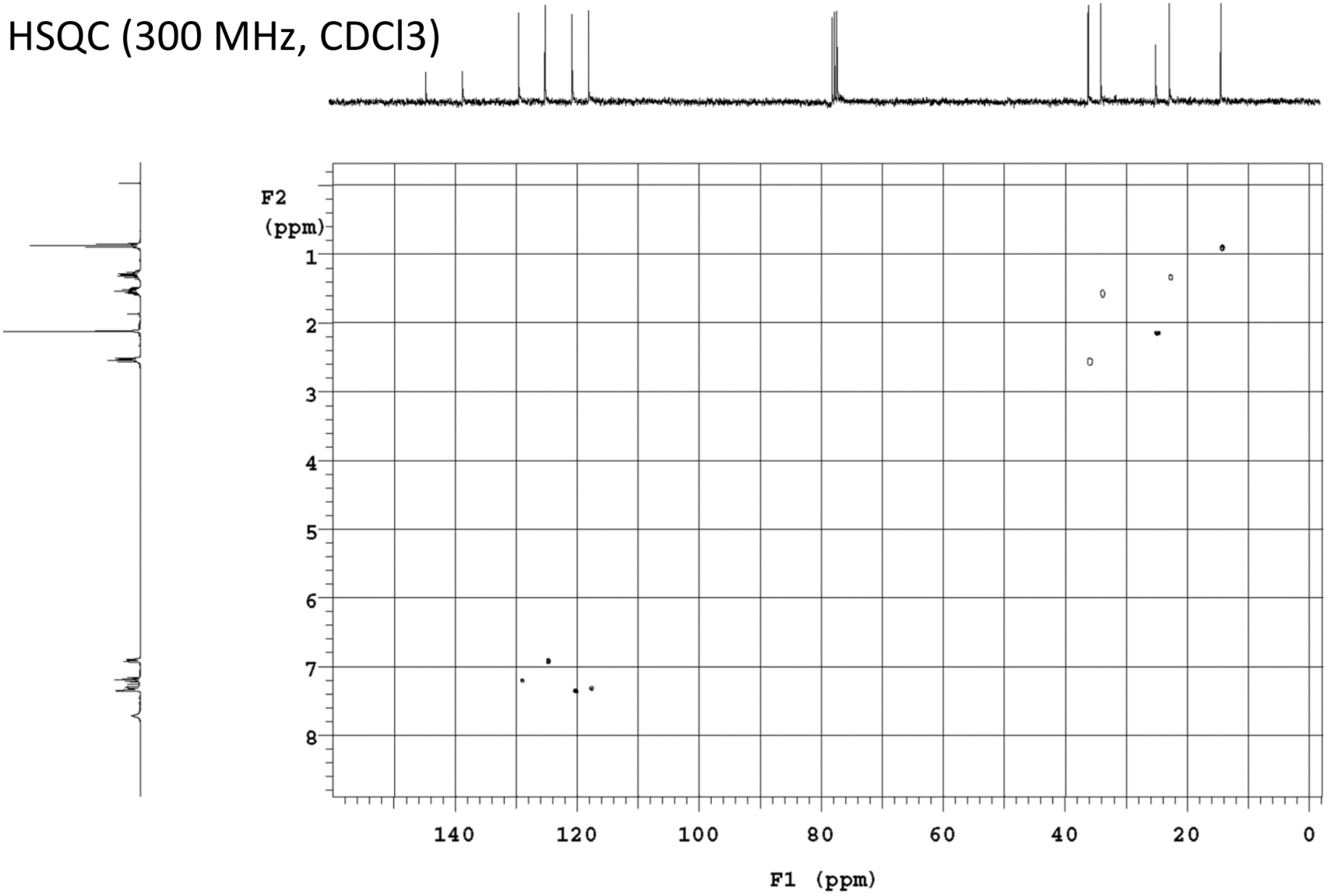
# Task 3: $\mathbf{C_{12}H_{17}NO}$ - $^{1}$H/COSY

COSY (300 MHz, CDCl3)



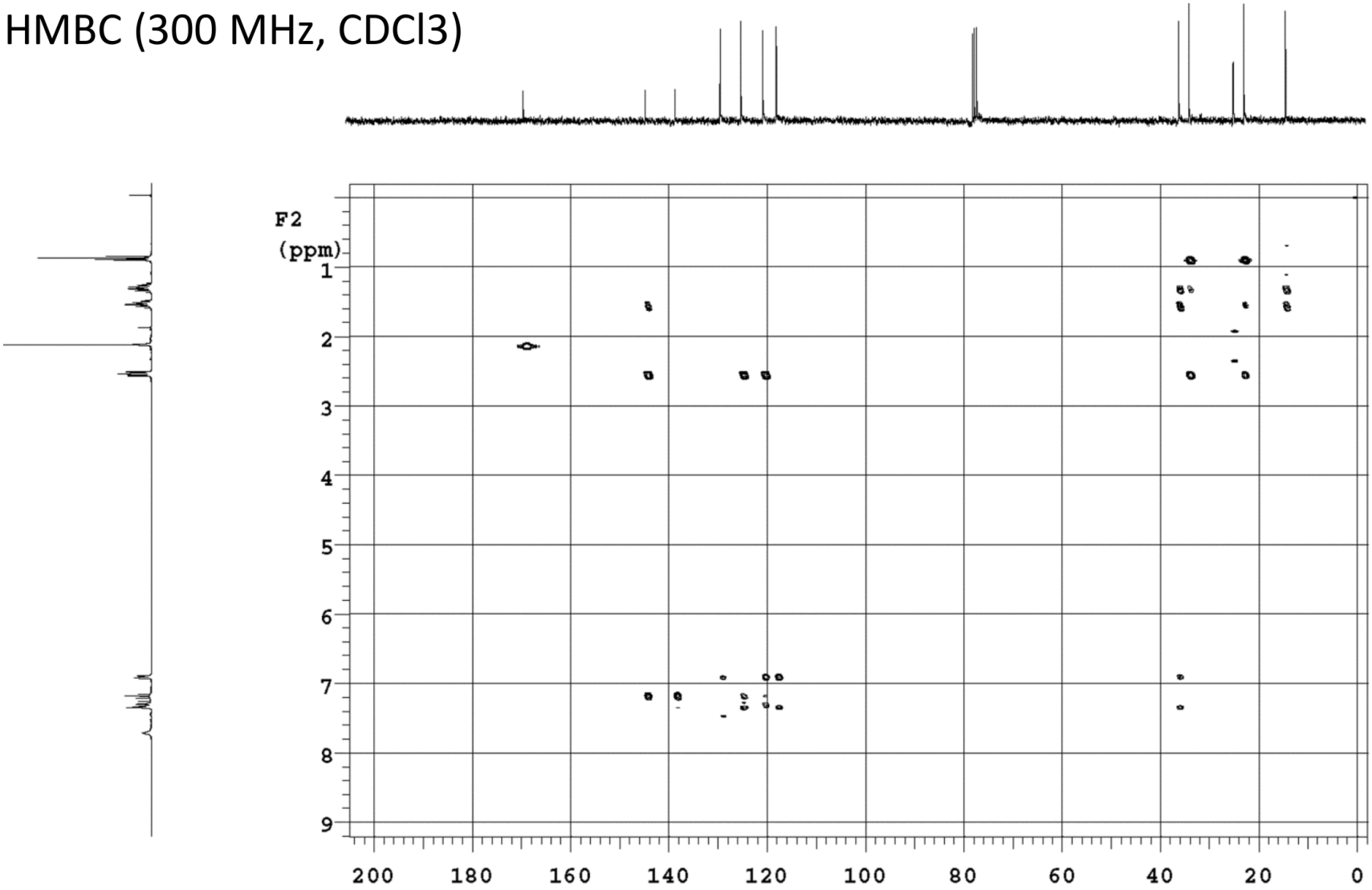
# Task 3: $\mathbf{C_{12}H_{17}NO}$ - $^{1}$H-$^{13}$C/HSQC,HMBC

HSQC (300 MHz, CDCl3)

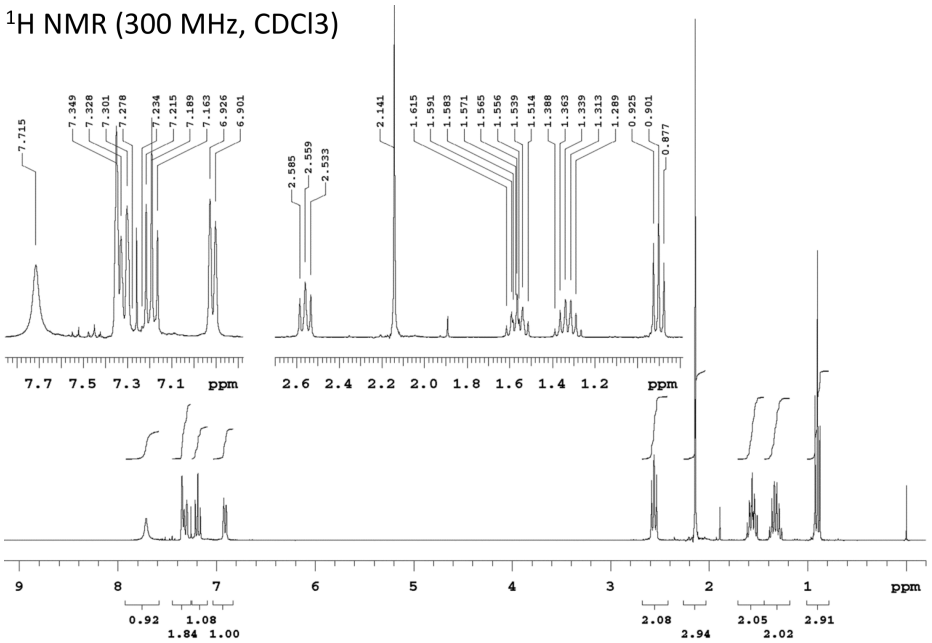


# Task 3: $\mathbf{C_{12}H_{17}NO}$ - $^{1}$H-$^{13}$C/HSQC,HMBC

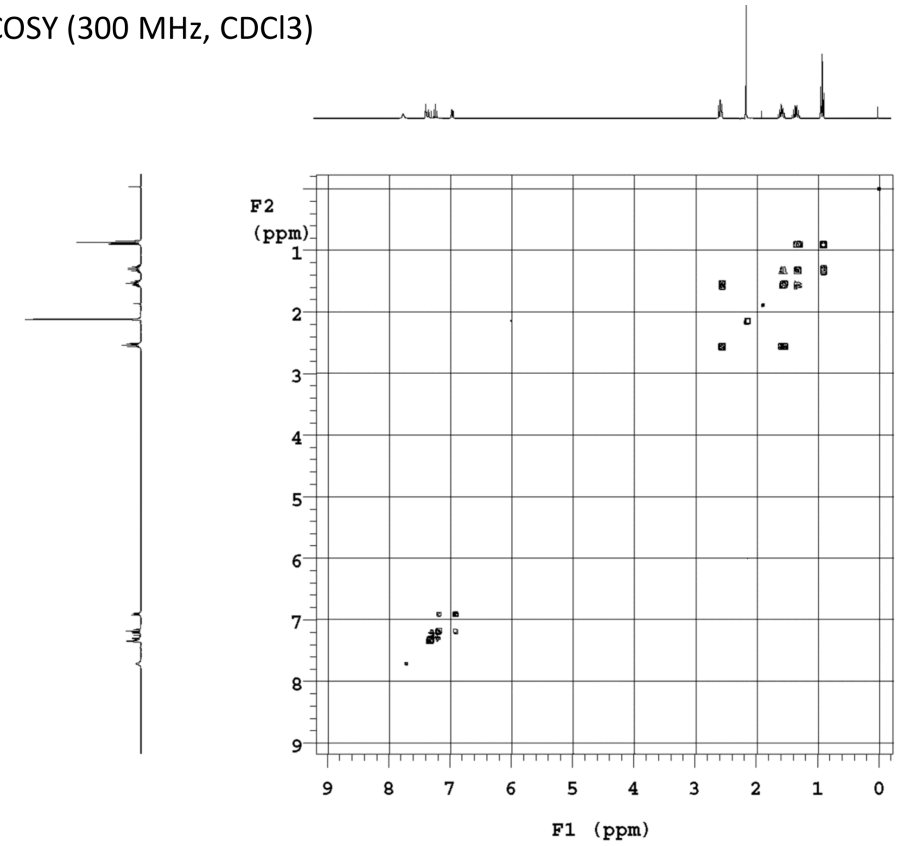
HMBC (300 MHz, CDCl3)

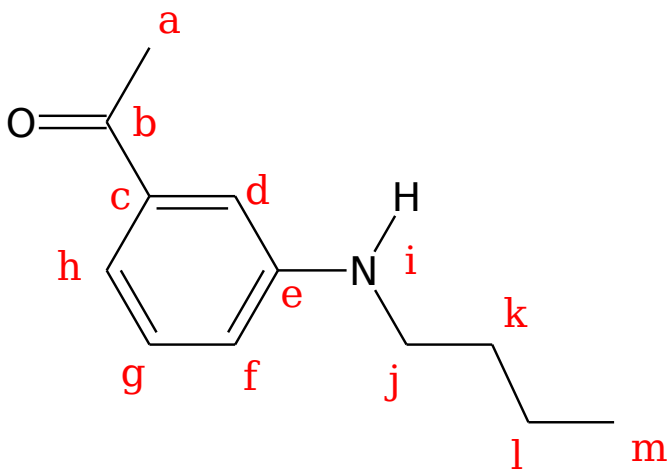


$^1$H NMR (300 MHz, CDCl3)




COSY (300 MHz, CDCl3)



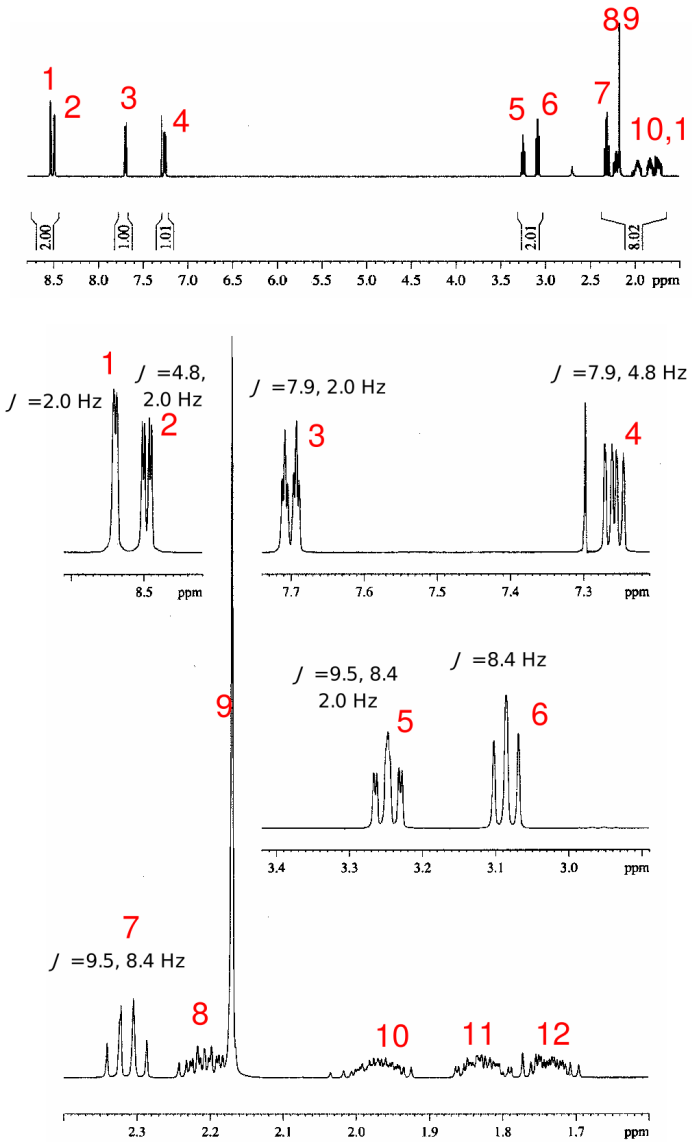



# General comments

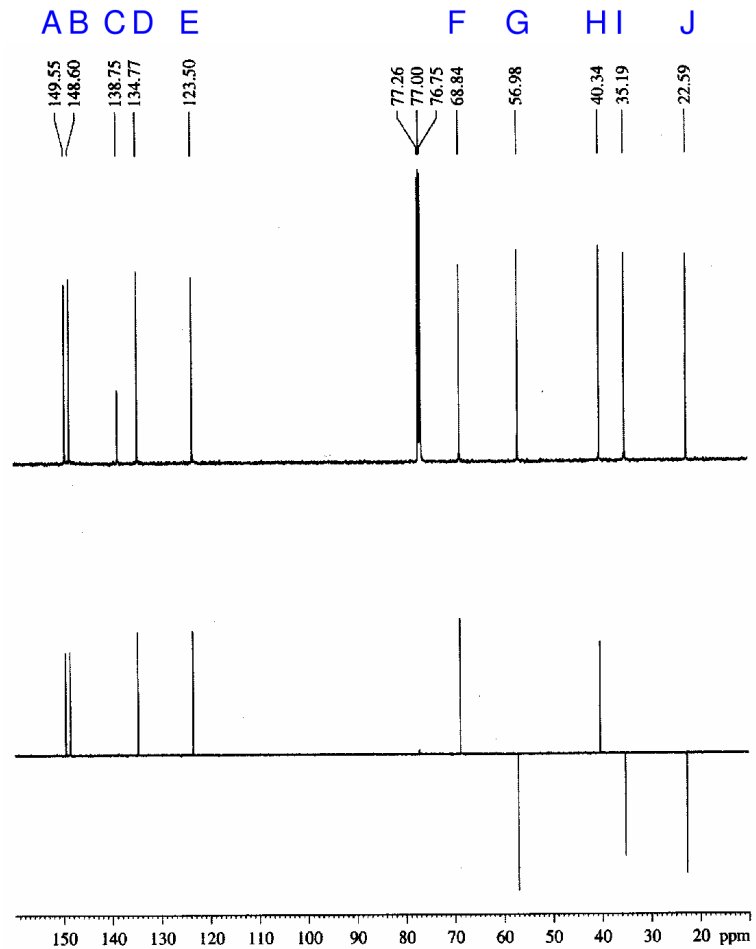
- inspect molecular formula $\mathrm{C_mH_hO_oN_nX_x}$:
  Degree of unsaturation $\mathbf{m + 1 - 0.5(h + x - n)}$
- identify signals of $CH_3$ and exchangeable protons in 1D $^1$H sectrum
- arbitrary numbering (e.g., from lower to higher value of chemical shift) of resolved resonances in all spectra
- 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

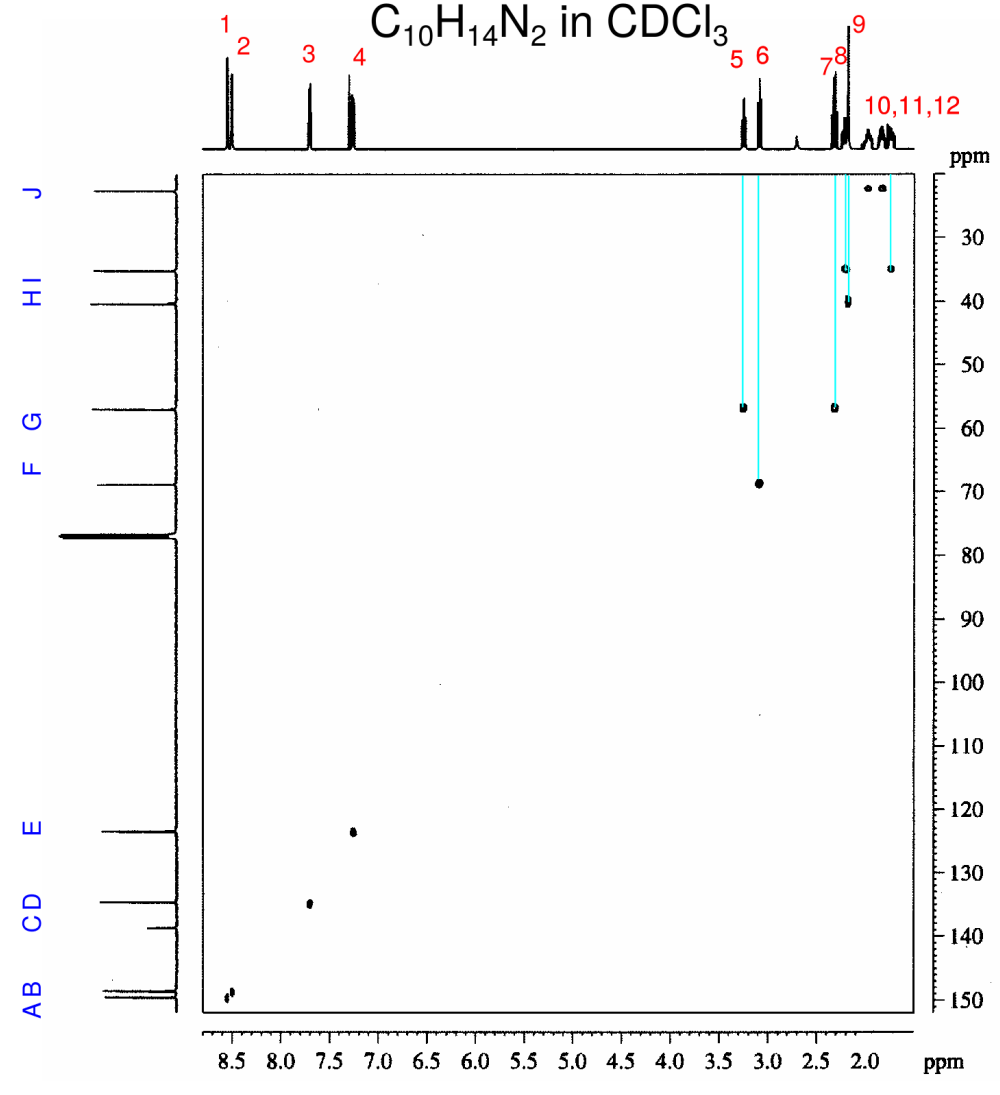
# $C_{10}H_{14}N_2$ in $CDCl_3$



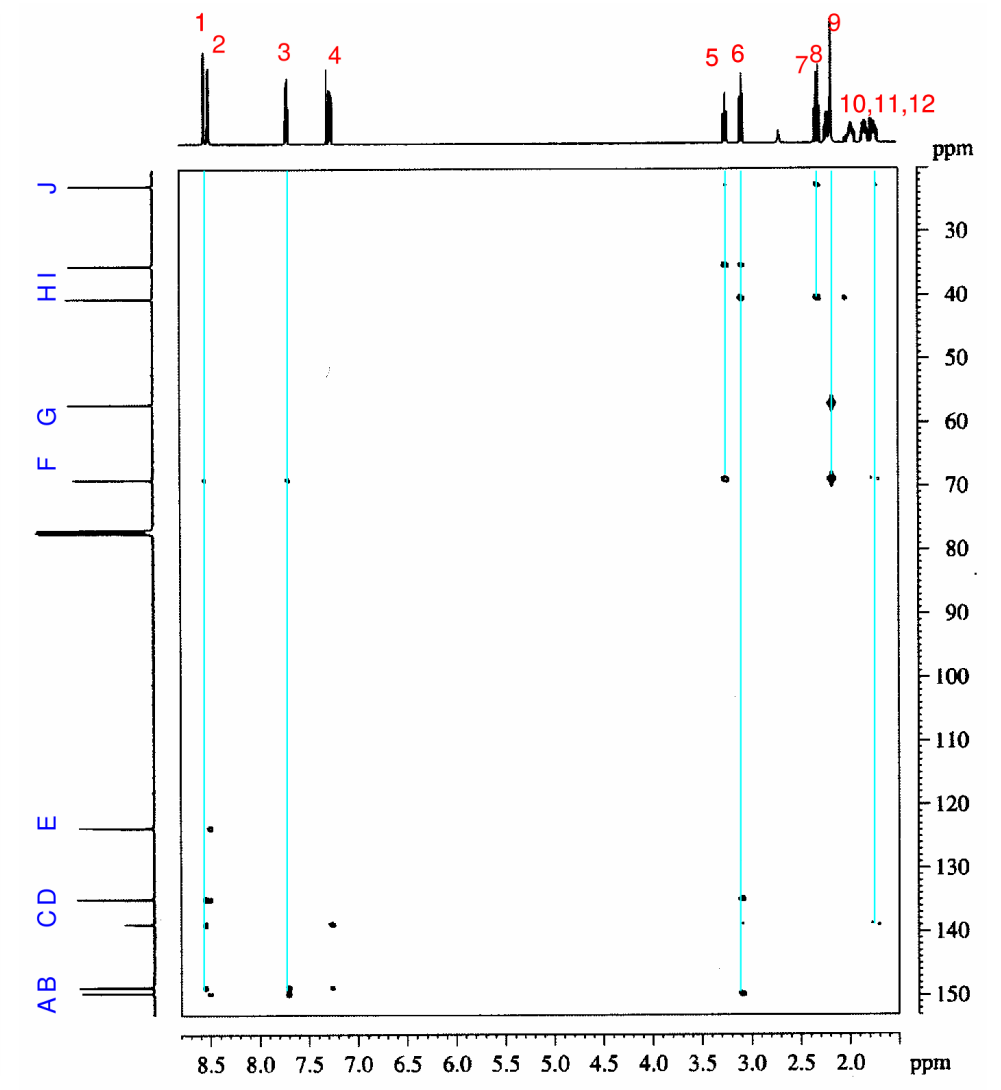

**$^1$H NMR**



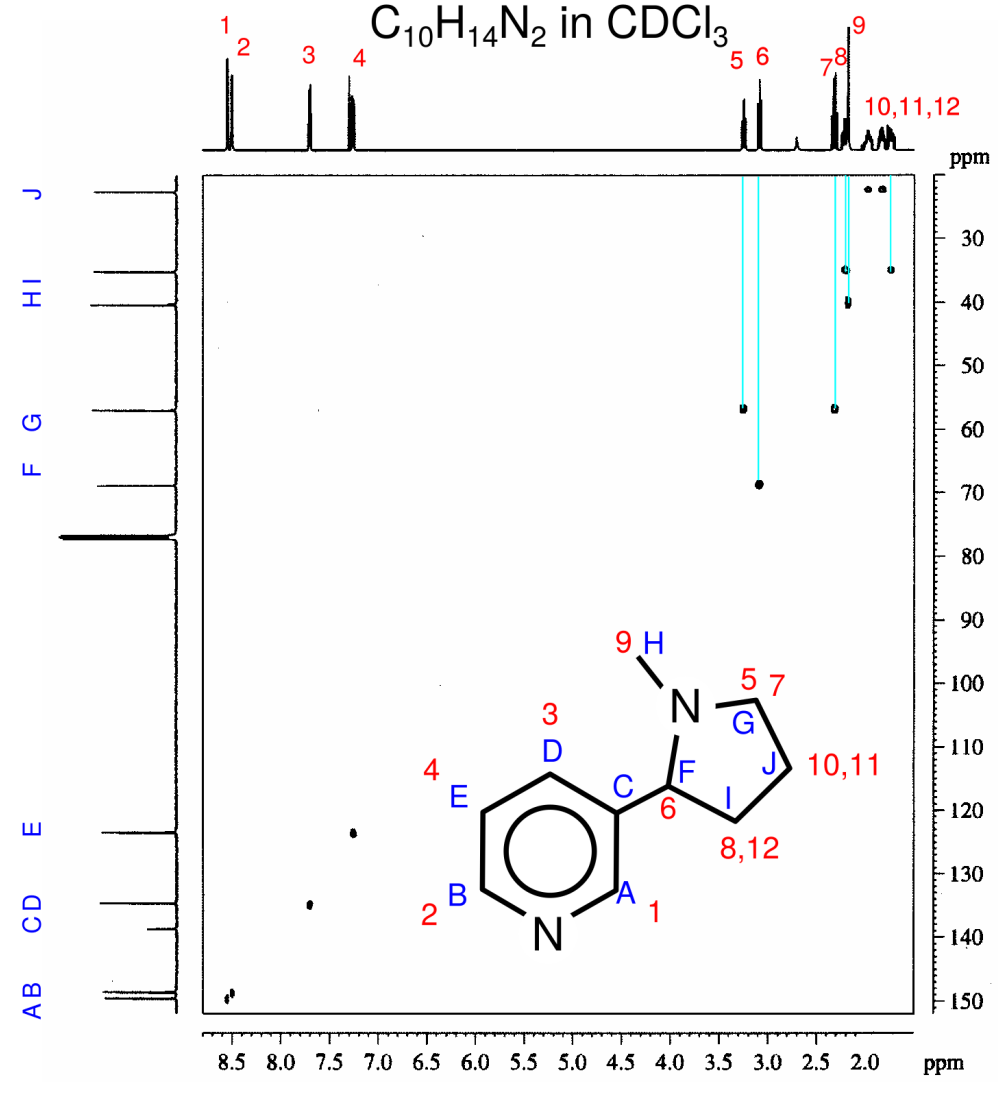

**$^{13}$C NMR**



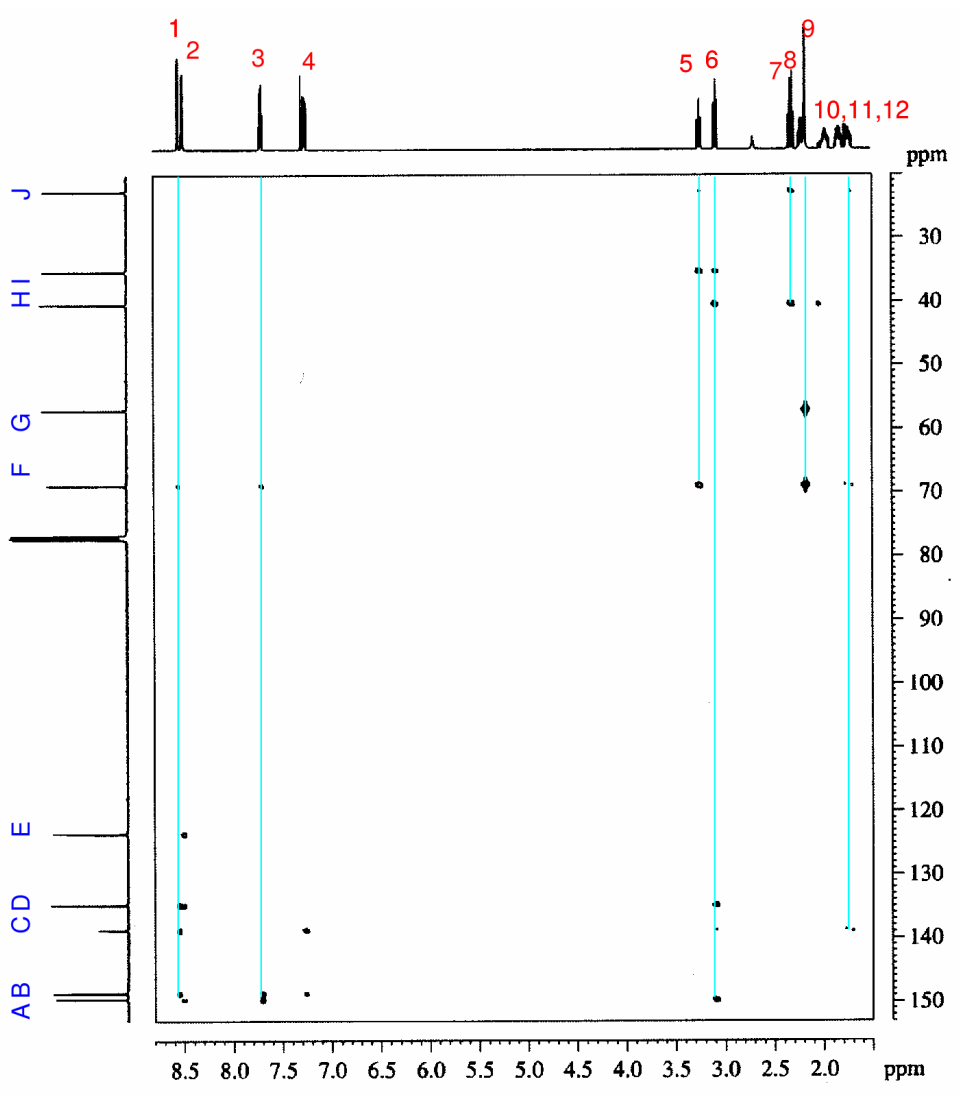

$^{13}C, ^{1}H$ HSQC




$^{13}C, ^{1}H$ HMBC

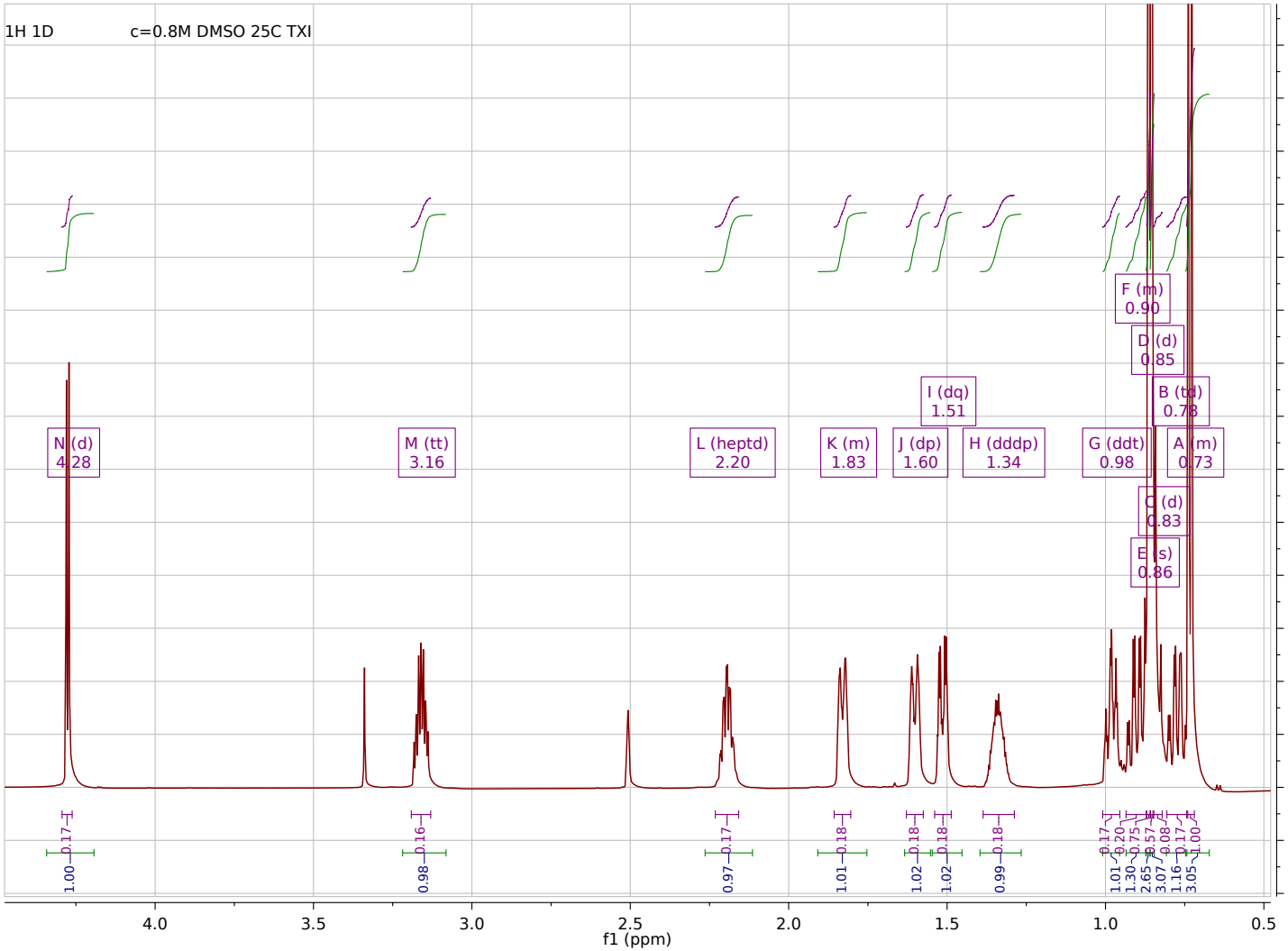



$^{13}C, ^{1}H$ HSQC



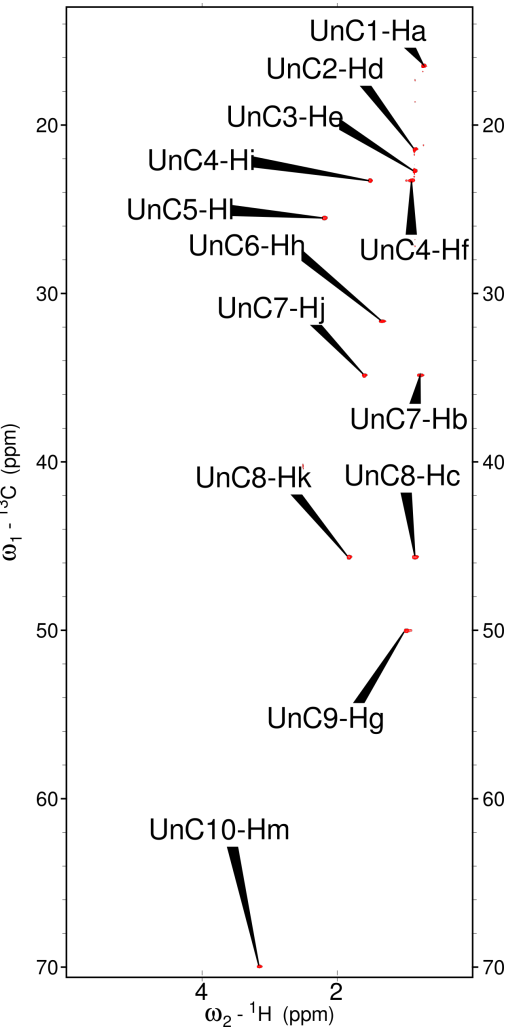

$^{13}C, ^{1}H$ HMBC

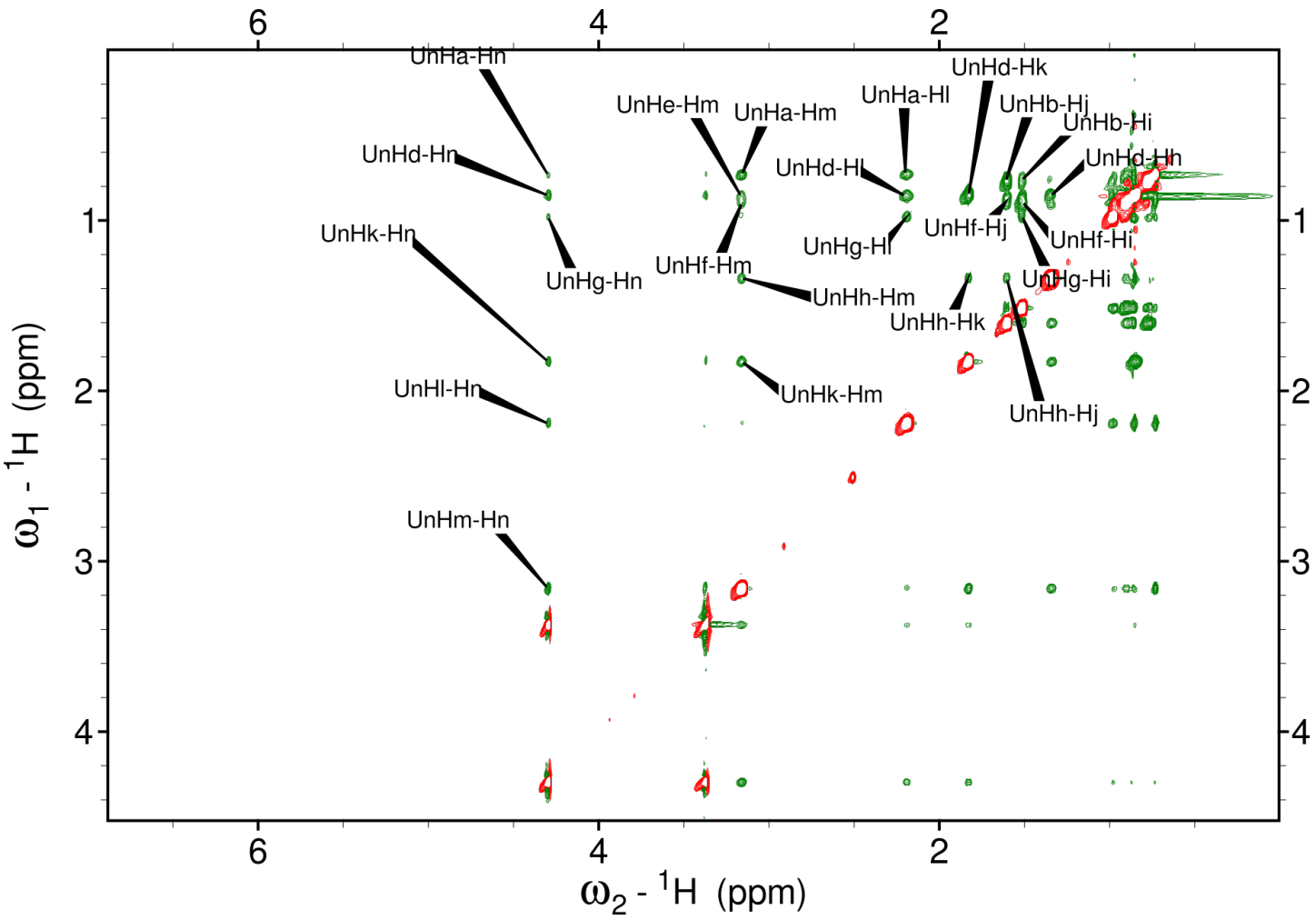
# 1D $^{1}$H of $C_{10}H_{20}O$



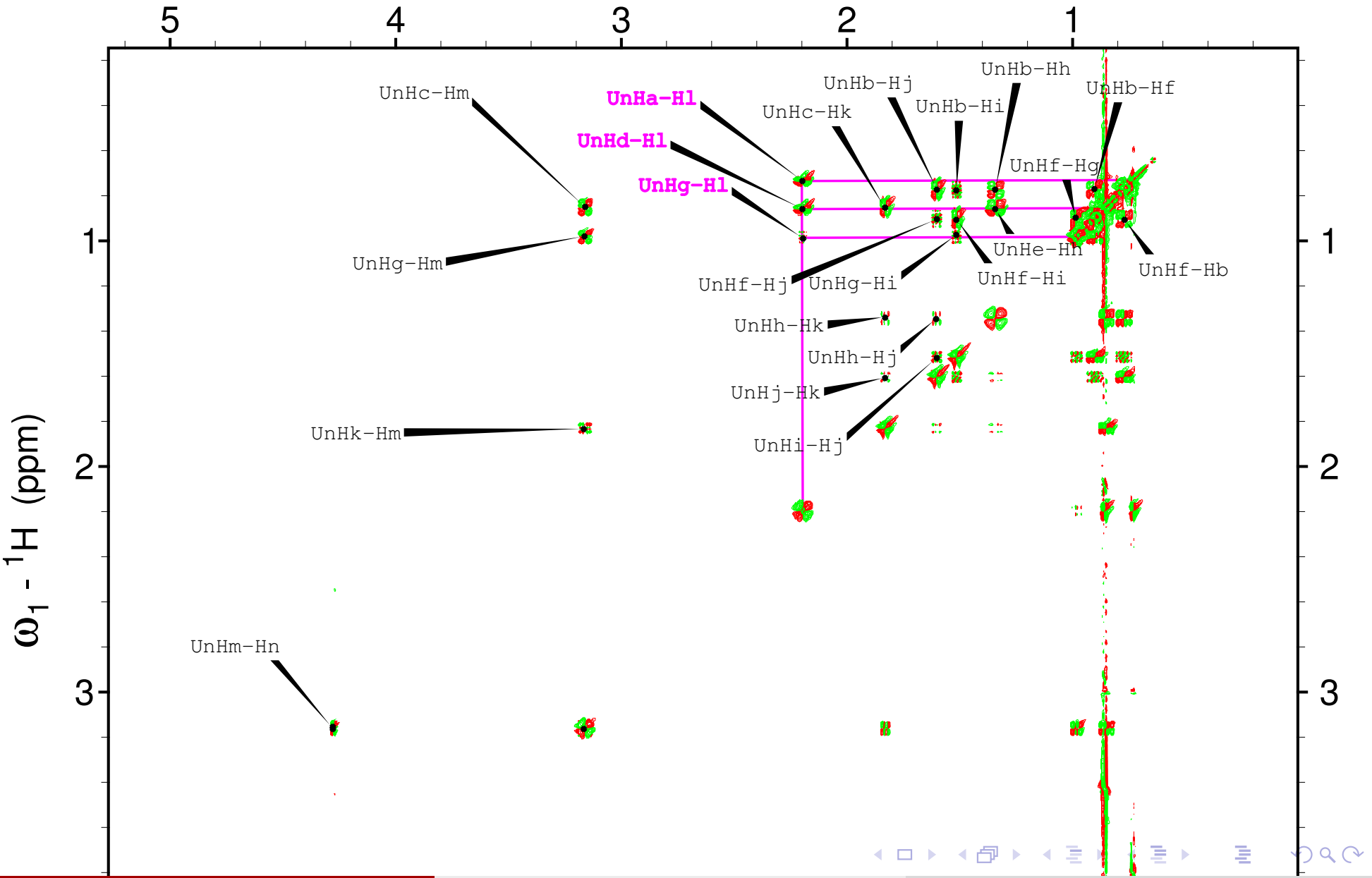

1H 1D
c=0.8M DMSO 25C TXI
G (ddt)
0.98
F (m)
0.90
E (s)
0.86
D (d)
0.85
C (d)
0.83
B (td)
0.78
A (m)
0.73
1.01
0.17
1.30
0.20
2.65
0.75
3.07
0.57
0.08
1.16
0.17
1.00
3.05
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
0.70
0.68
f1 (ppm)

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



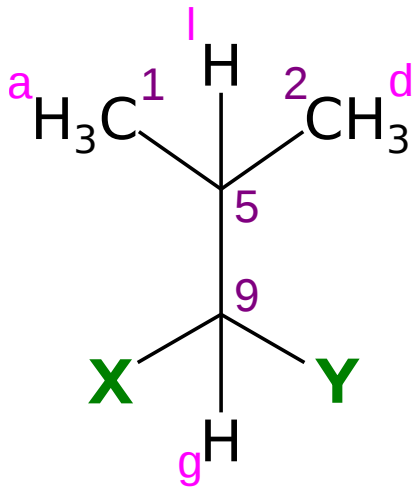



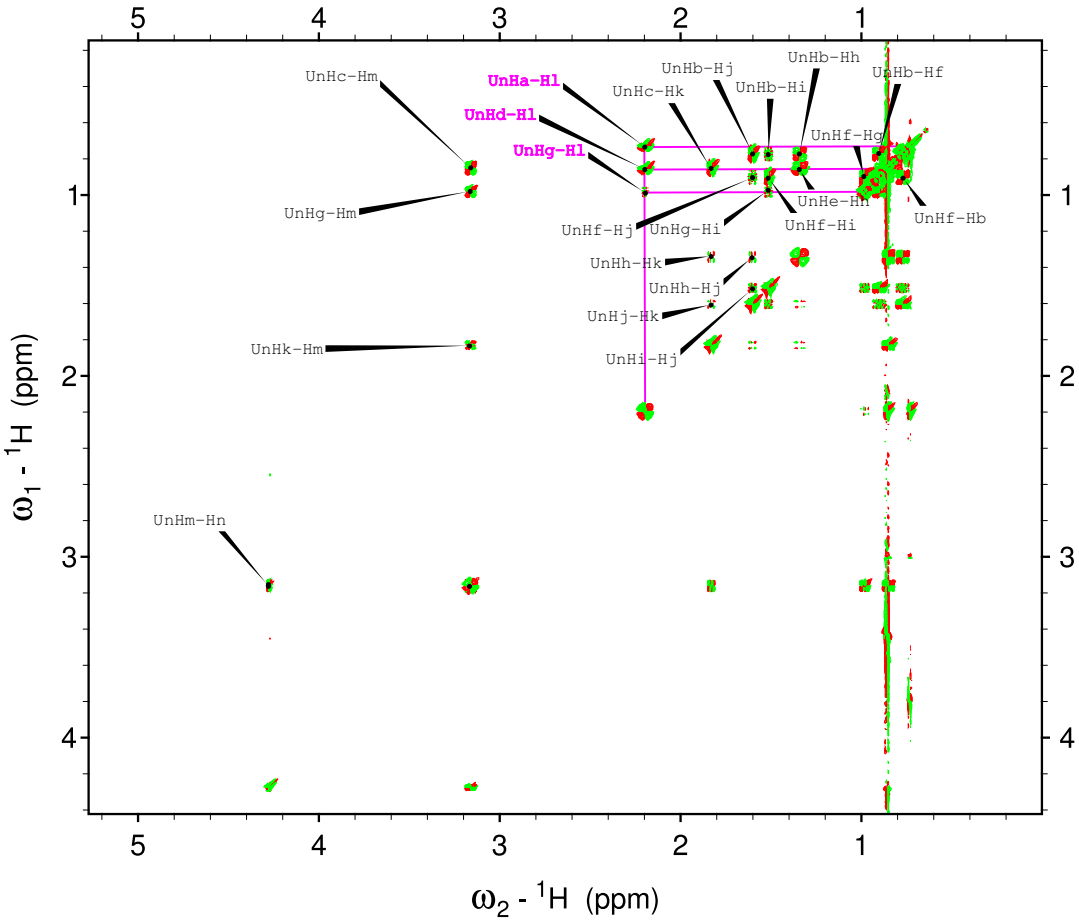
# Task 1: *J*-connectivity of $C_{10}H_{20}O$



# 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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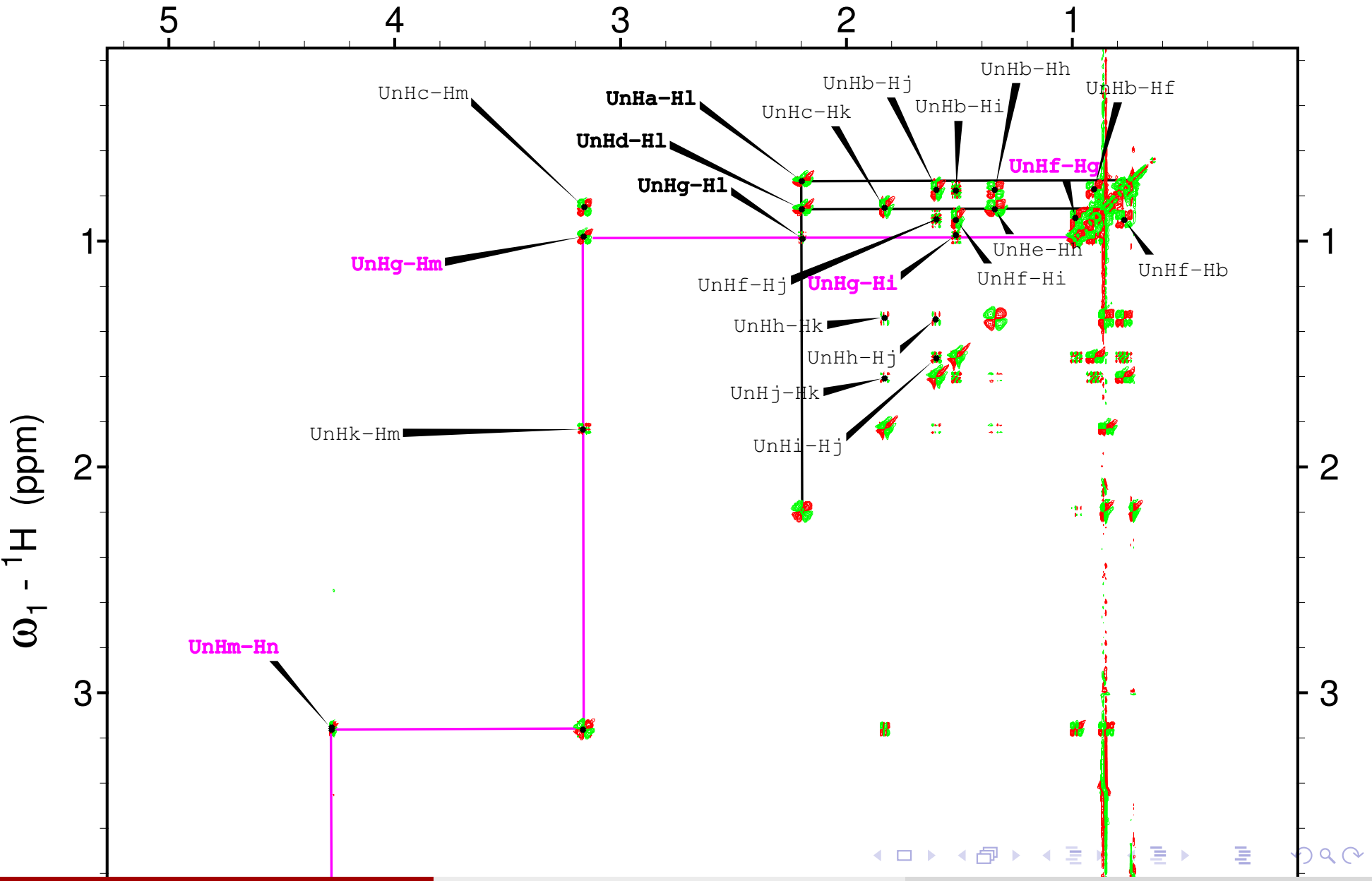
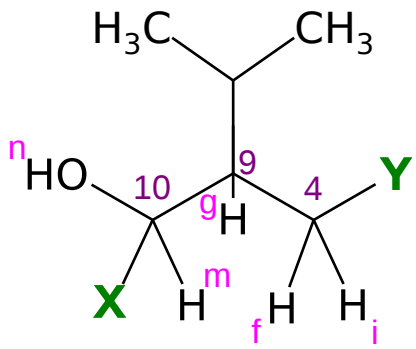
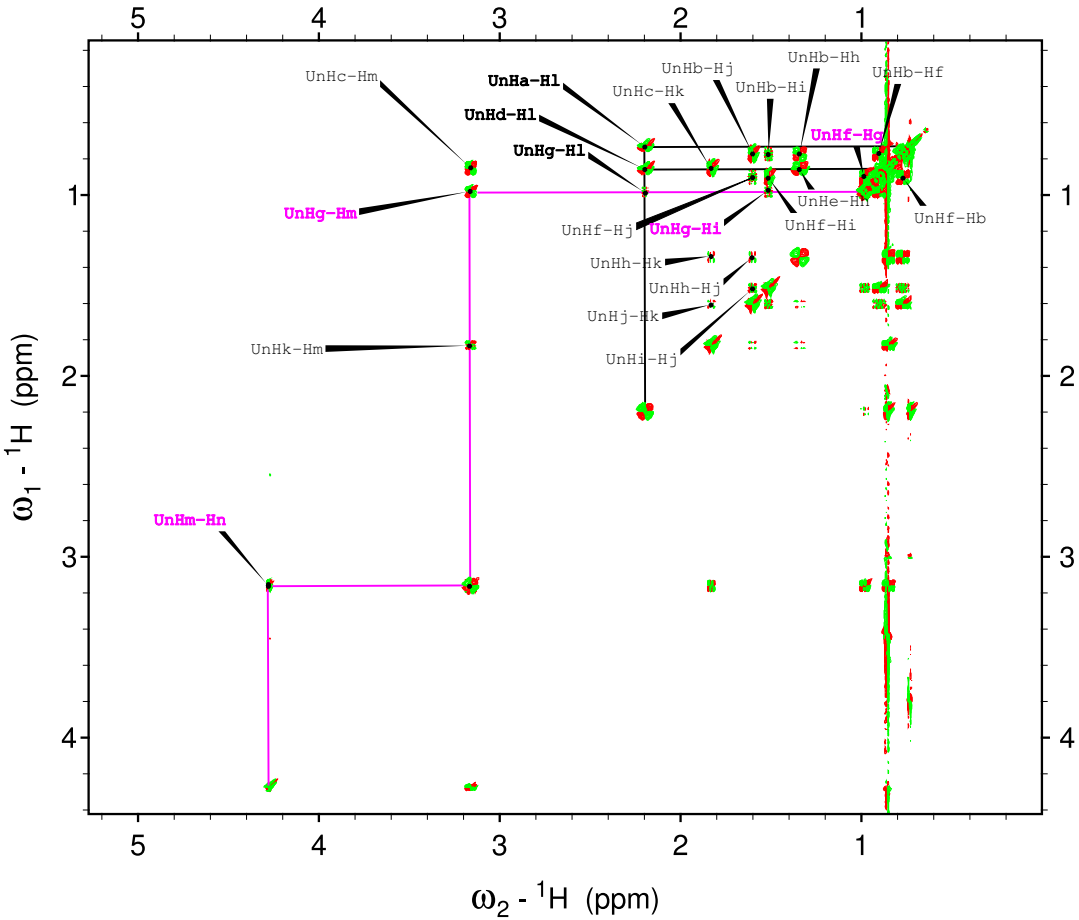


# Task 1: *J*-connectivity of $C_{10}H_{20}O$

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



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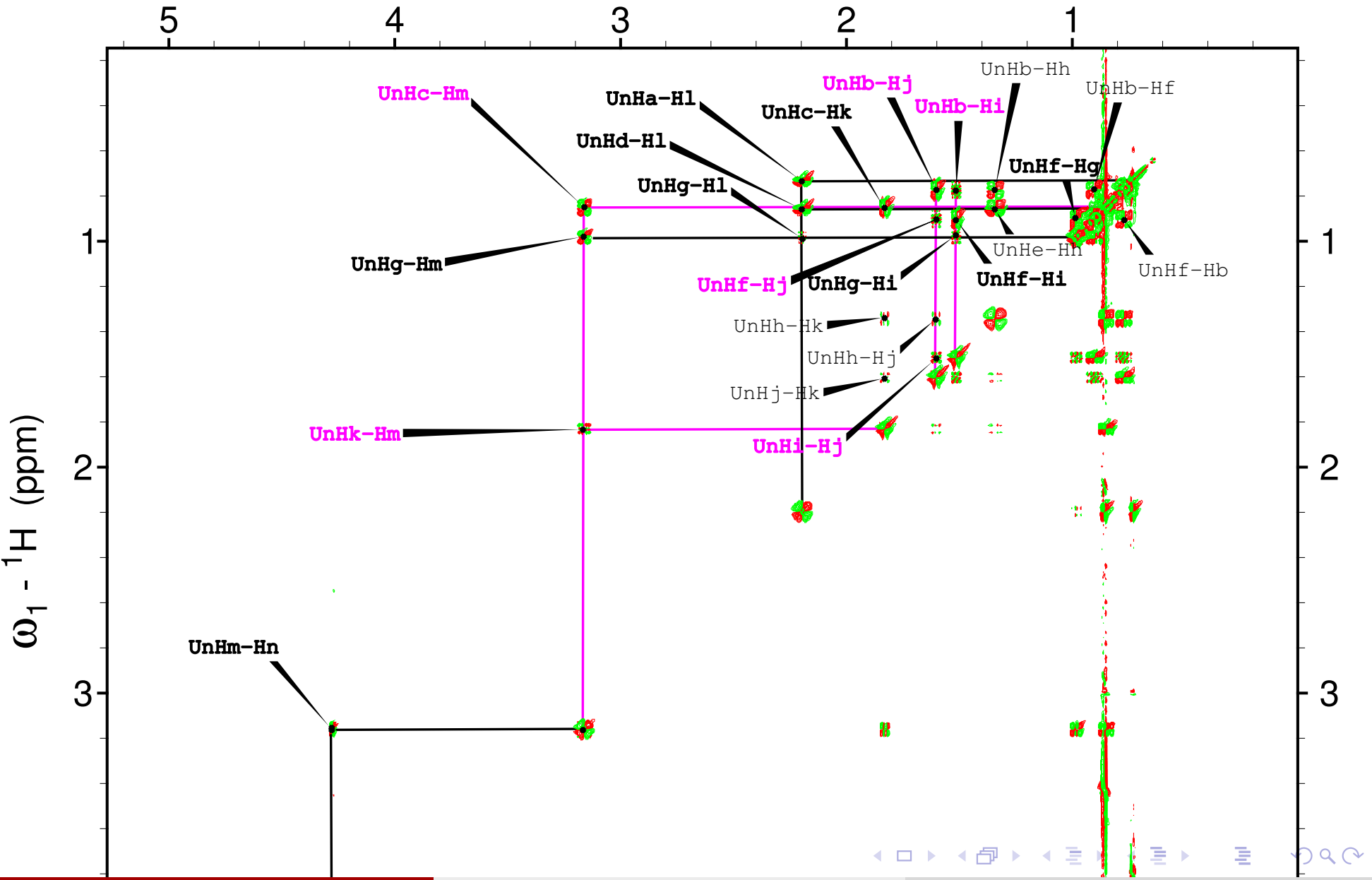
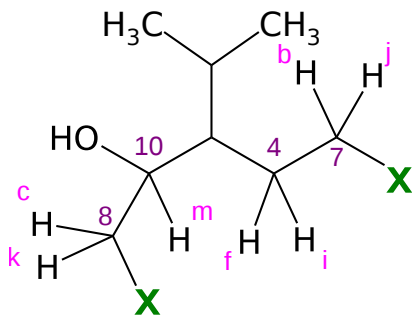
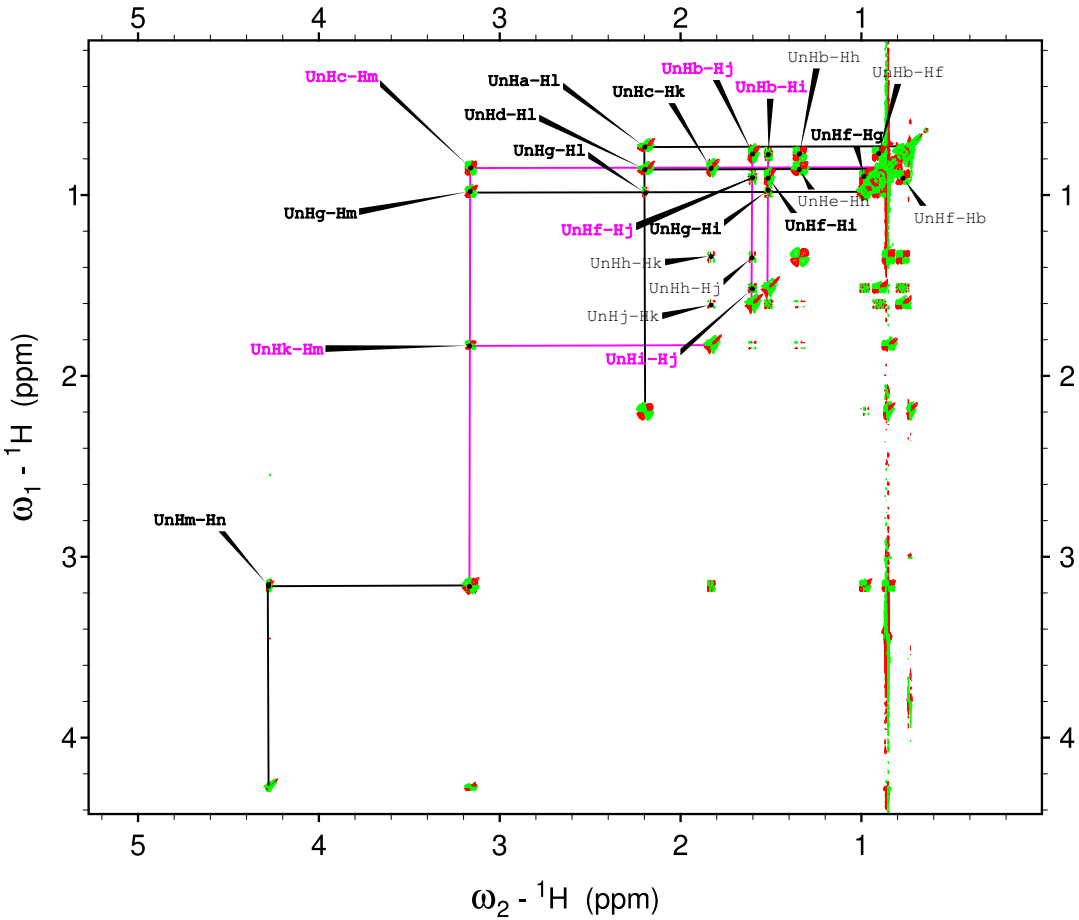


# Task 1: *J*-connectivity of $C_{10}H_{20}O$

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



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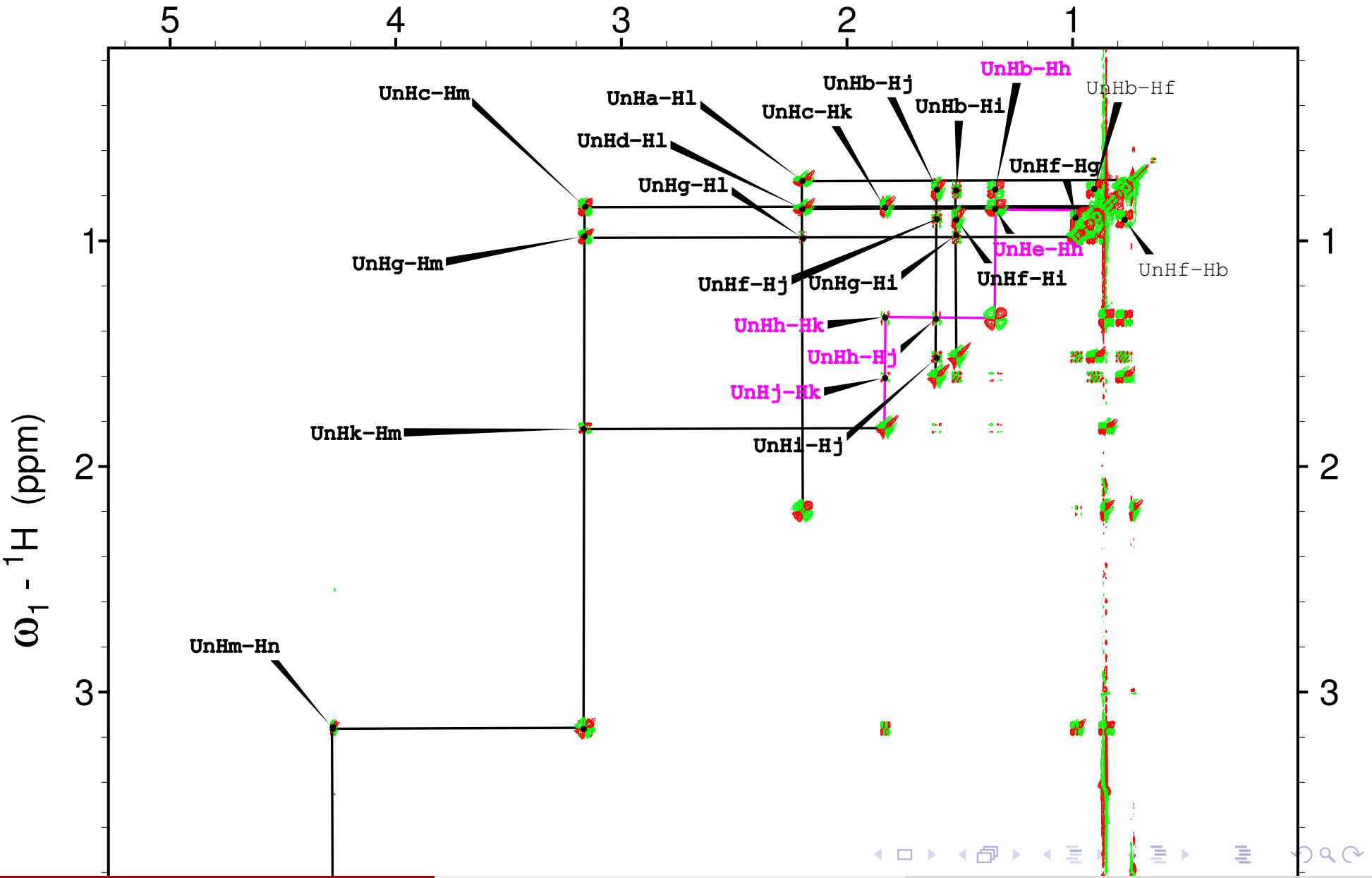
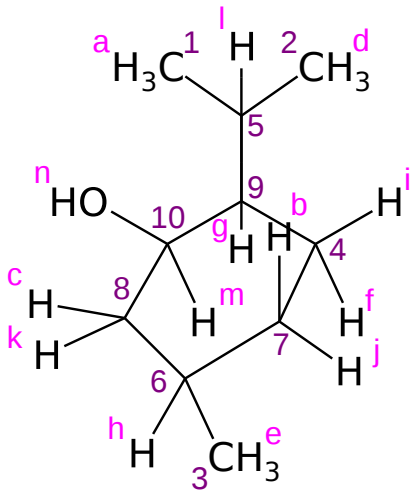
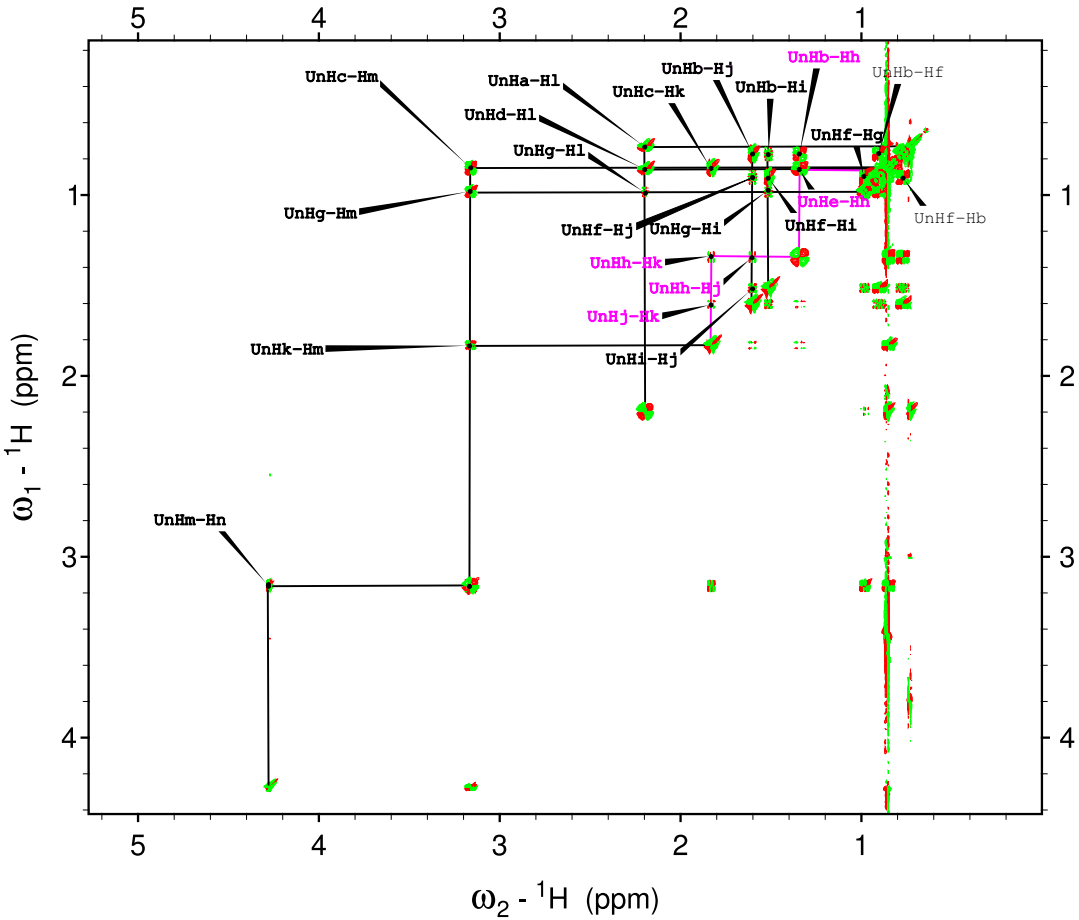


# Task 1: *J*-connectivity of $C_{10}H_{20}O$

- $CH_2$ **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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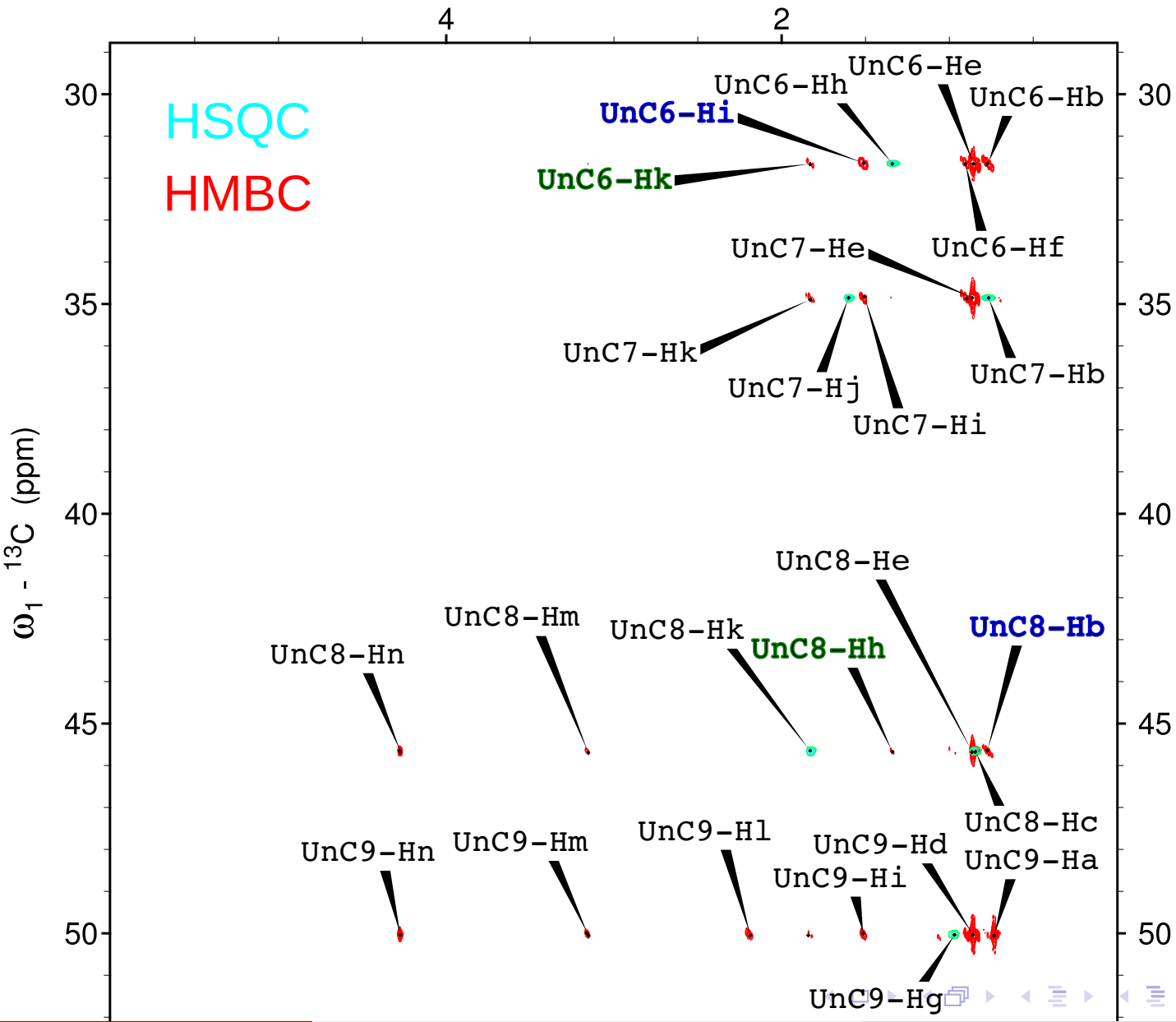

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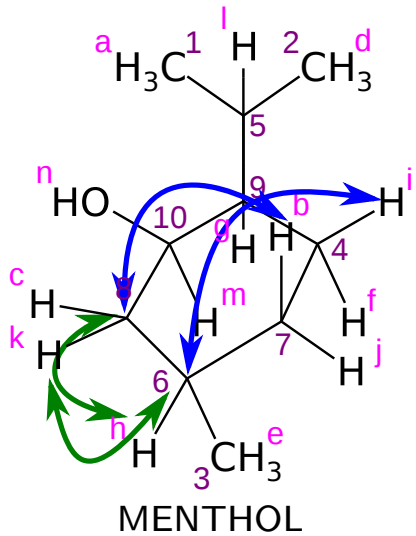
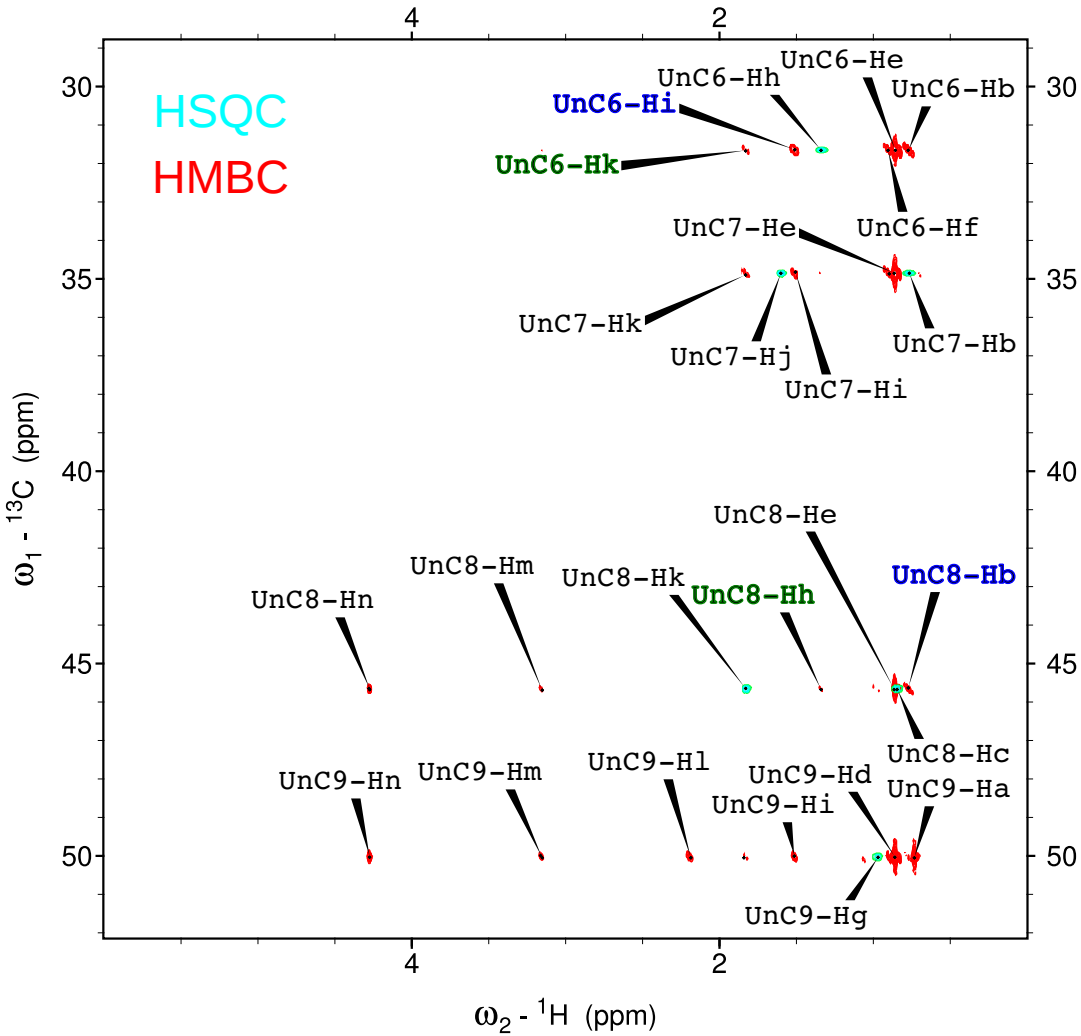
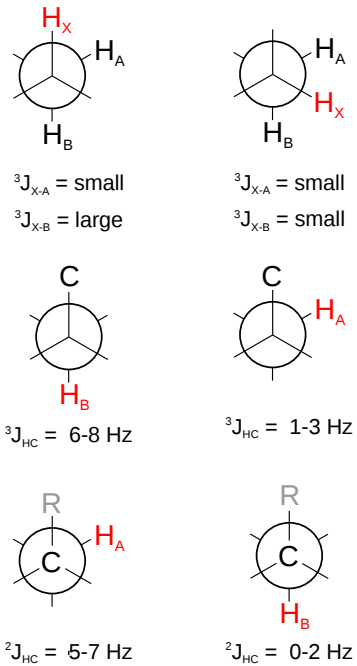


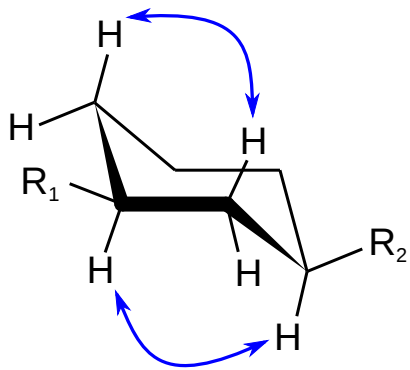
MENTHOL



# 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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