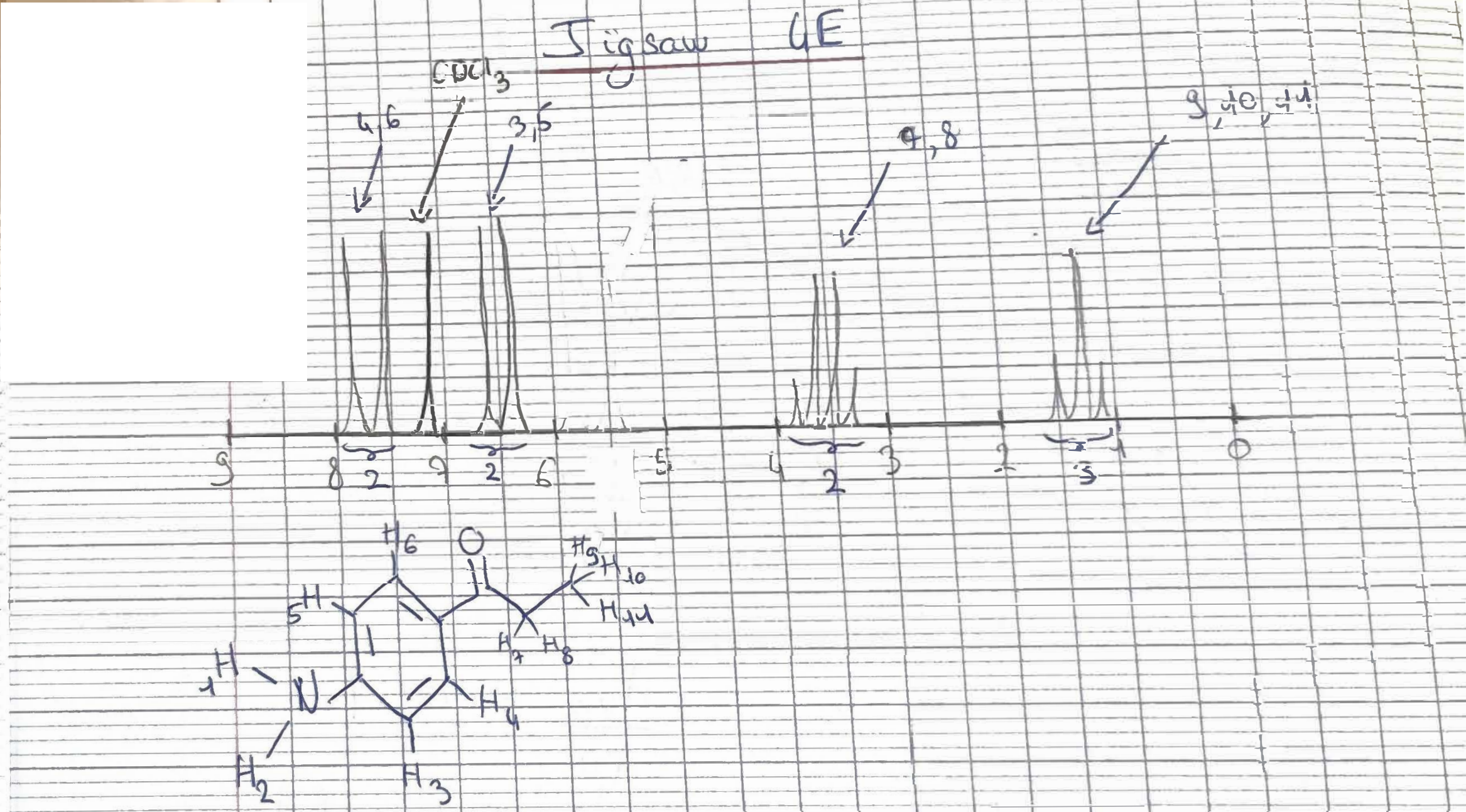
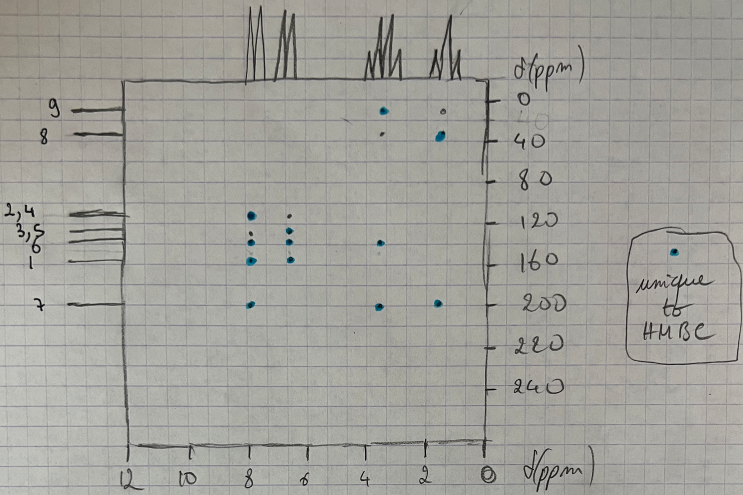
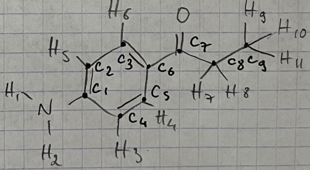
Jigsaw 4E


CDCl3
4,6
3,6
7,8
9,10,11
9
8
2
7
2
6
5
4
2
3
2
1
3
0
H6
O
H9
H10
H11
5H
H7
H8
1H
N
H4
H2
H3


δ(ppm)
0
40
80
120
160
200
220
240
9
8
2,4
3,5
6
1
7
12
10
8
6
4
2
0
δ(ppm)
unique to HMBC

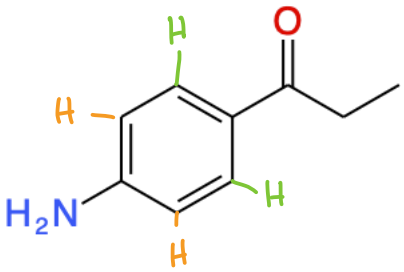

H6
O
H9
H10
H5
C2
C3
C6
C7
C8
C9
H11
H1
C1
C5
H7
H8
N
C4
H4
H2
H3

Clarice Mihalache
Diego Meraldi
Witek Huguenin
Sidène Croome
Elodie-Angélique Lendi

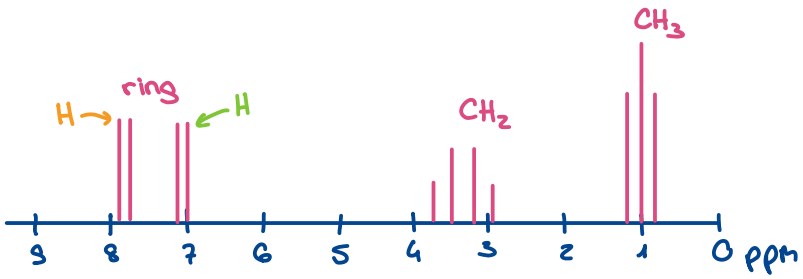
CH-314 Structural Analysis
ruben.rodriguezmadrid@epfl.ch
ray.cowen@epfl.ch

Jigsaw 4E

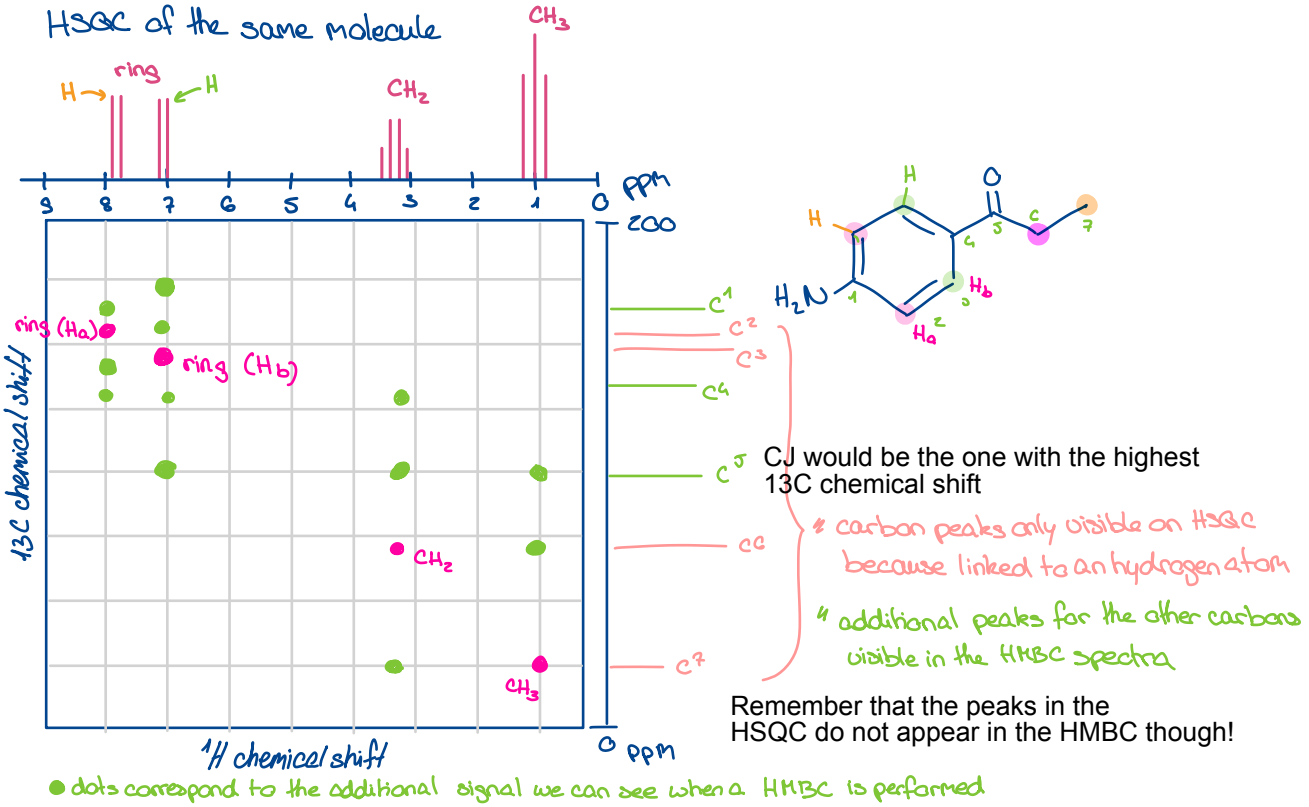
2D NMR: HSQC and HMBC



1. [From past exam] Draw schematically the solution state ^1H spectrum of the molecule in $CDCl_3$ and label the peaks. Use qualitative estimates for the expected chemical shifts. Consider only $^3J_{HH}$ couplings.



2. [From past exam] Draw schematically the ^1H-^{13}C HMBC and HSQC spectra on the same plot. Assume the HMBC spectrum shows connectivity through up to three bonds. Circle the peaks unique to the HMBC spectrum.

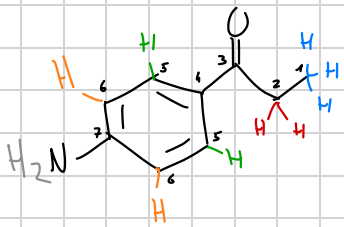


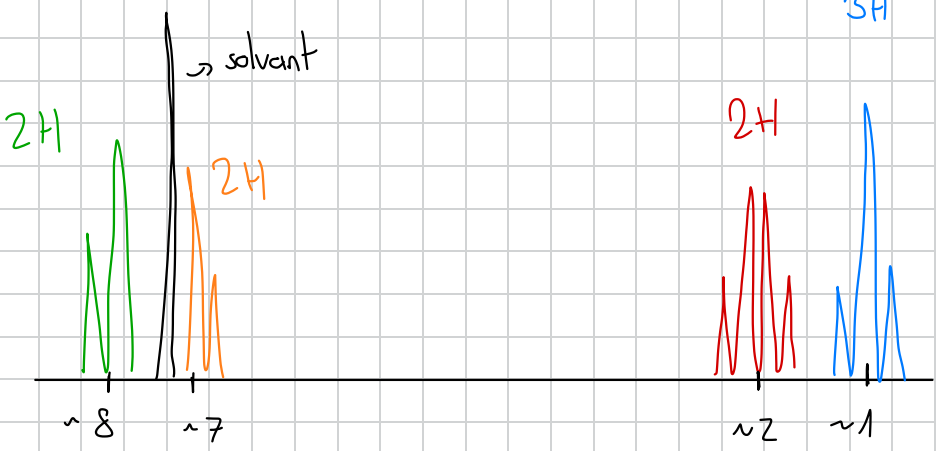
Demierre Jérémy, Wininger Quentin, Dubois Aurèle,
Danilko Arsenijs, Elkaim Robin, HANS HENRIK GJERULDSEN

10.11.2025

Jigsaw 4E

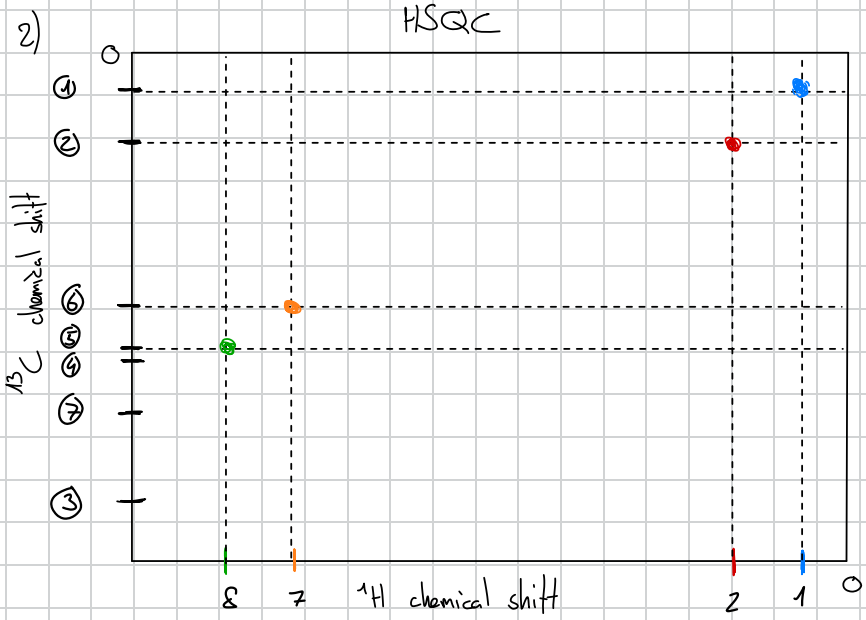
1)

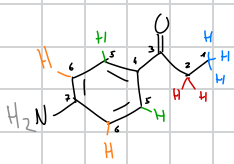


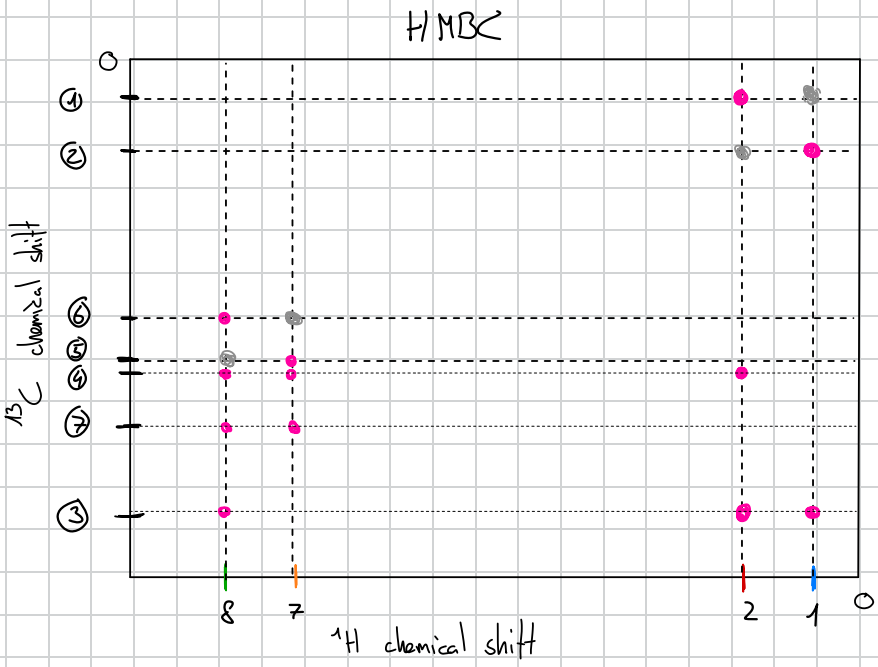


The H from H_2N group are exchanged with the deuterium of the solvant, vanishing the peak of the NH_2 group.

2)





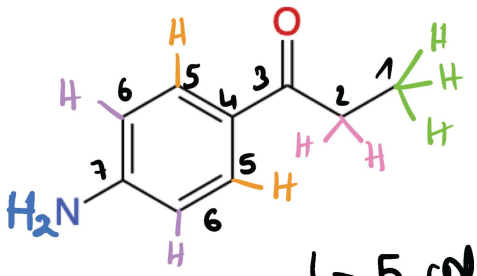


The pink point correspond to the points that are only in HMBC.

Lucas Eichenberger
Marcin Desgeans
Julian Barth
Laura Fréry
Aloïsse Dantant-Cochet

Jigsaw 4E

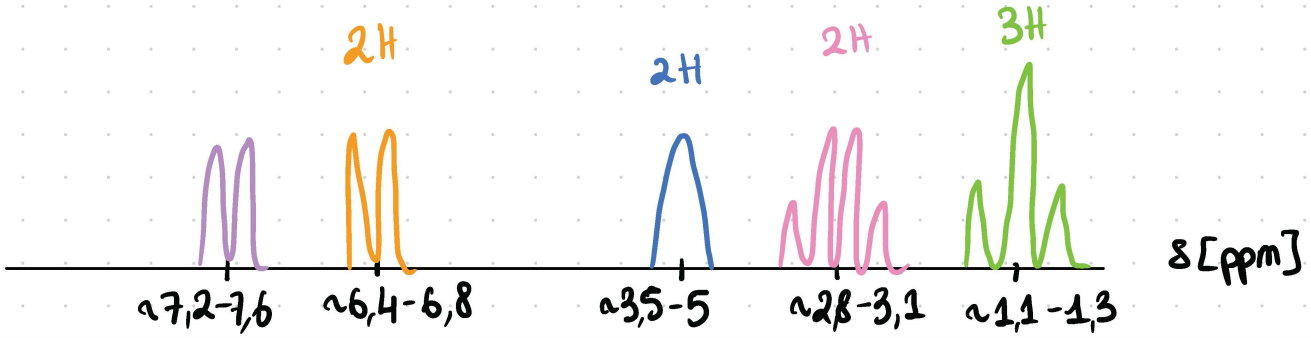
1. [From past exam] Draw schematically the solution state ^1H spectrum of the molecule in $CDCl_3$ and label the peaks. Use qualitative estimates for the expected chemical shifts. Consider only $^3J_{HH}$ couplings.



{ each color means that the protons are equivalent

↳ 5 colors = 5 different signals

Scheme of ^1H NMR spectrum



explanations

↳ CH_3 : located at the end of the alkyl chain, so these protons are relatively shielded → signal around 1,2 ppm

they are coupled only to the two protons of the adjacent CH_2 group ⇒ we have a triplet.

↳ CH_2 : positioned between a carbonyl group (strongly deshielding) and a methyl group (weakly deshielding) so these protons appear further downfield around 3,0 ppm

coupled to the 3 protons of the CH_3 group ⇒ quartet

↳ aromatic protons : because the ring is para-substituted, the molecule has a symmetry plane, leading to 2 sets of equivalent aromatic protons.

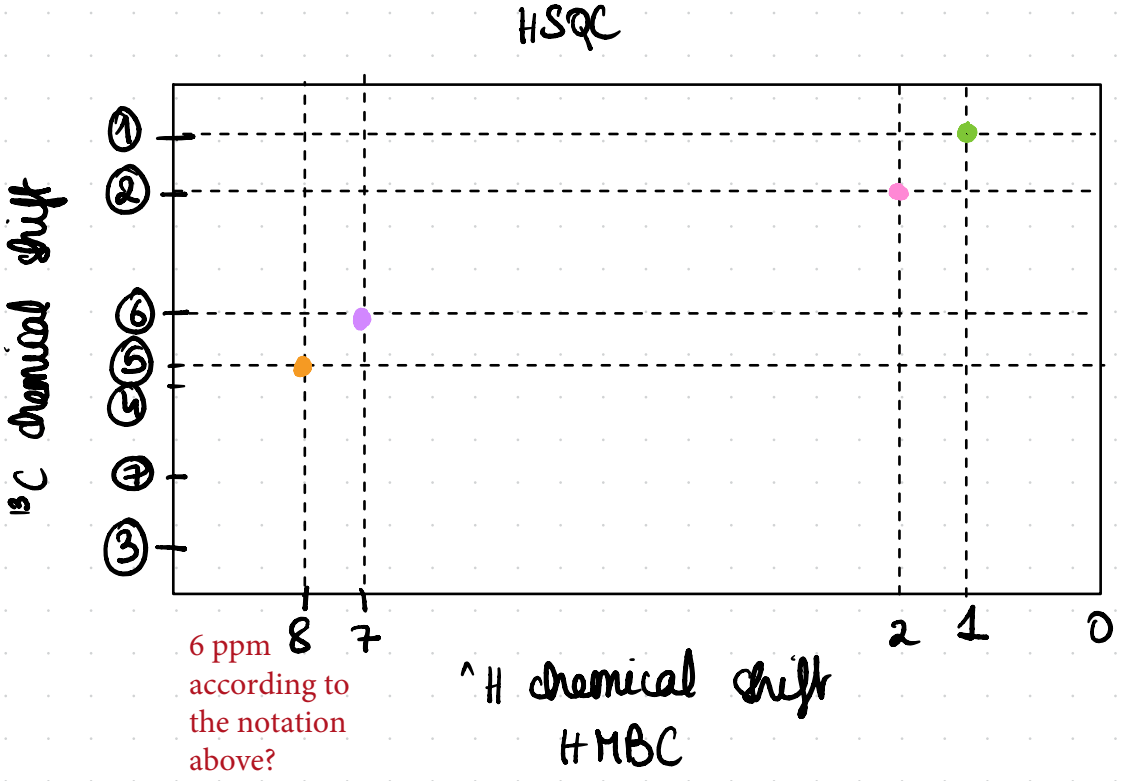
↳ Hs : ortho to the electron donating NH_2 group ⇒ more shielded so around 6,5-6,7 ppm

↳ H_5 : ortho to the electron - withdrawing carbonyl group → more deshielded → around 7,3 - 7,5 ppm

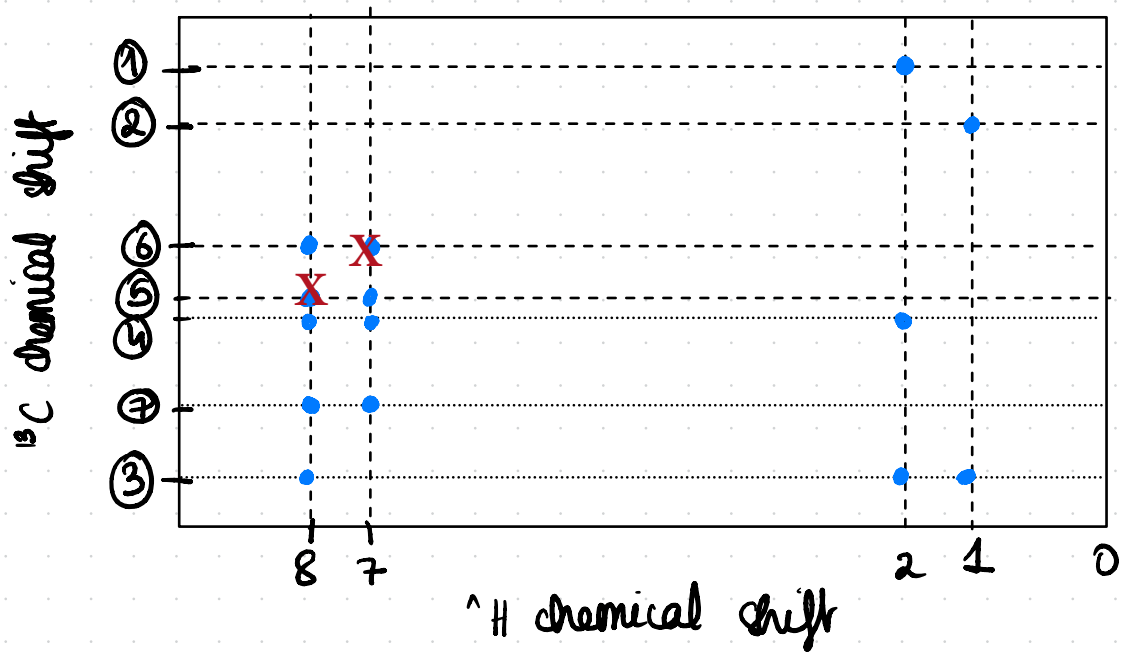
↳ H_s from NH_2 : exchangeable protons that undergo fast exchange with traces of water or acid in the solvent → the signal appears broad, around 3,5 and 5 ppm

because of the fast exchange, scalar couplings are usually not observed, so the signal appears as a broad singlet.

2. [From past exam] Draw schematically the ^{1}H-^{13}C HMBC and HSQC spectra on the same plot. Assume the HMBC spectrum shows connectivity through up to three bonds. Circle the peaks unique to the HMBC spectrum.



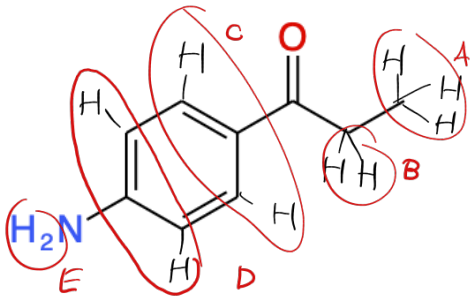
6 ppm according to the notation above?



CH-314 Structural Analysis
ruben.rodriguezmadrid@epfl.ch
ray.cowen@epfl.ch

Jigsaw 4E

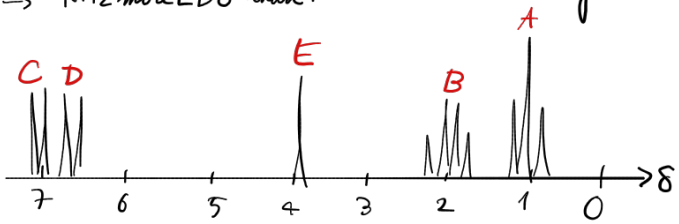
2D NMR: HSQC and HMBC



1. [From past exam] Draw schematically the solution state ^1H spectrum of the molecule in $CDCl_3$ and label the peaks. Use qualitative estimates for the expected chemical shifts. Consider only $^3J_{HH}$ couplings.

	N_H = intensity	adj. H	^3J	δ
A	3	2	t	~1
B	2	3	q	~2
C	2	1	d	~7
D	2	1	d	~6.5
E	2	0	s	~4

→ NH_2 more EDG than Ph → more shielding

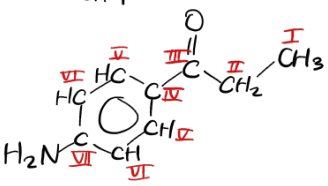


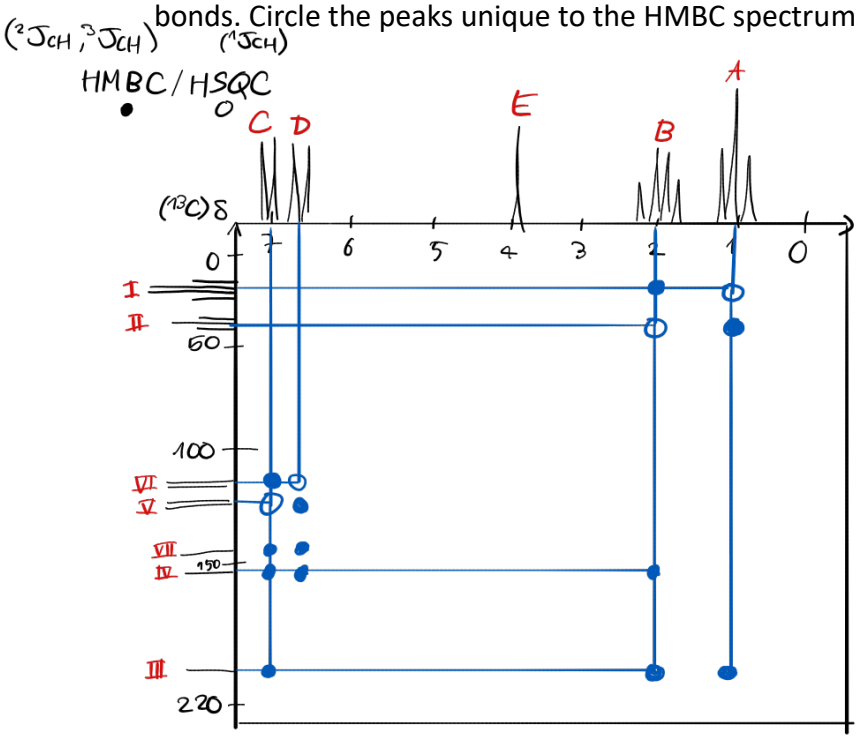
2. [From past exam] Draw schematically the ^1H-^{13}C HMBC and HSQC spectra on the same plot. Assume the HMBC spectrum shows connectivity through up to three bonds. Circle the peaks unique to the HMBC spectrum.

($^2J_{CH}$, $^3J_{CH}$) ($^1J_{CH}$)

HMBC / HSQC

We consider $^1J_{CH}$ for ^{13}C NMR.





	^1J	type	δ	
I	q	CH_3	~20	RCH_3
II	t	CH_2	~40	$R-CH_2-X$, $X=C=O$
III	s	C	~210	R(CO)R
IV	s	C	~150	near C=O, EWG
V	d	CH	~125	
VI	d	CH	~120	
VII	s	C	~145	near NH_2, EDG

rel. intensity: $C < CH < CH_2 < CH_3$

NOTE: Mainly in the 13C NMR we use 1H decoupling so we would get rid of the multiplicities.