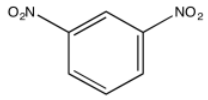
5.7: 2D NMR Solutions

Exercise 5.1.1:

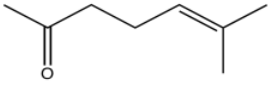
ethyl butanoate

Exercise 5.1.2:

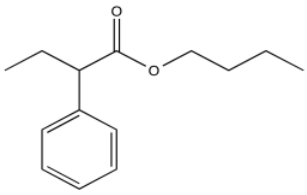


Exercise 5.1.3:

6-methylhept-5-en-2-one

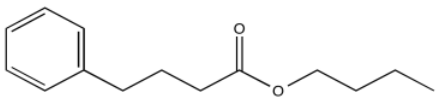


Exercise 5.1.4:



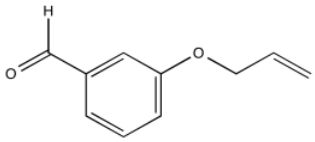
butyl 2-phenylbutanoate

Exercise 5.1.5:



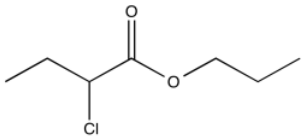
butyl 4-phenylbutanoate

Exercise 5.1.6:

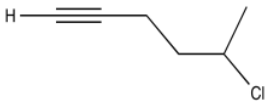


3-(allyloxy)benzaldehyde

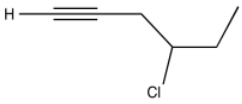
Exercise 5.1.7:



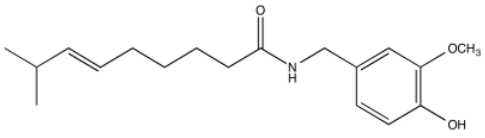
Exercise 5.1.8:



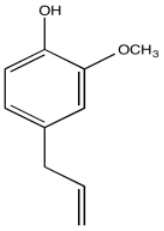
Exercise 5.1.9:



Exercise 5.1.10:

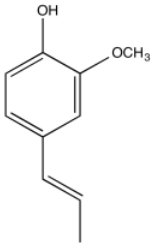


Exercise 5.1.11:



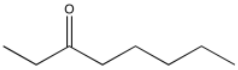
eugenol

Exercise 5.1.12:

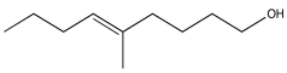


isoeugenol

Exercise 5.2.1:

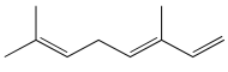


Exericse 5.2.2:

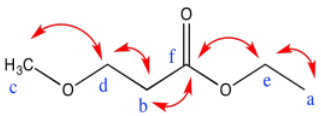


Exercise 5.2.3:

Ocimene

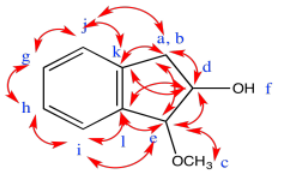


Exercise 5.3.1:



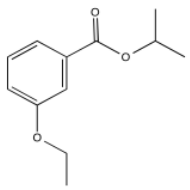
	^{1}H	^{13}C	HMBC
a	1.1	15	e
b	2.4	32	d, f
c	3.2	58	d
d	3.7	63	b, c
e	4.0	69	a, f
f	-	172	b, e

Exercise 5.3.2:

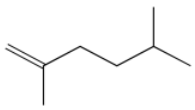


	^{1}H	^{13}C	HMBC
a	2.8	38	d, e, j, k
b	3.2		
c	3.2	57	e
d	4.4	78	a/b, e, k, l
e	4.7	92	a/b, c, d, i, l
f	5.0	-	-
g	7.1	127	h, i, j, k, l
h	7.2	127	g, i, j, k, l
i	7.3	126	e, g, h, j, k, l
j	7.4	129	a/b, g, h, i, k, l
k	-	140	a/b, d, g, h, i, j, l
l	-	142	d, e, g, h, i, j, k

Exercise 5.3.3:

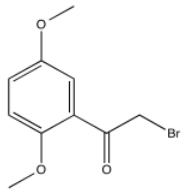


Exercise 5.3.4:

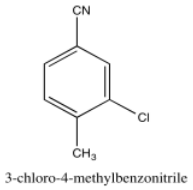


2,5-dimethylhex-1-ene

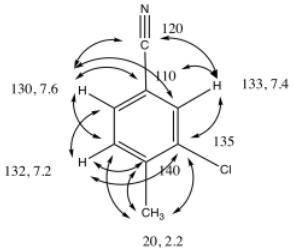
Exercise 5.3.5:



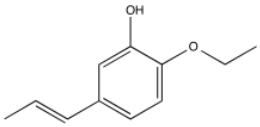
Exercise 5.3.6:



3-chloro-4-methylbenzonitrile

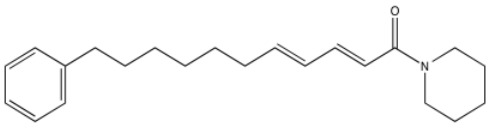


Exercise 5.3.7:

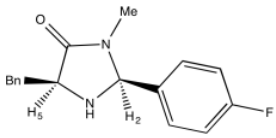


(*E*)-2-ethoxy-5-(prop-1-en-1-yl)phenol

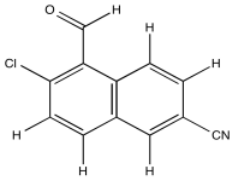
Exercise 5.3.8:



Exercise 5.4.1:



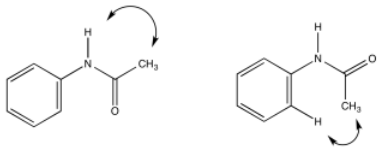
Exercise 5.4.2:



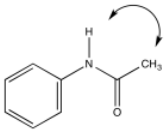
Exercise 5.4.3:

a) Due to resonance, there is substantial pi character to the amide bond which restricts free rotation around that bond.

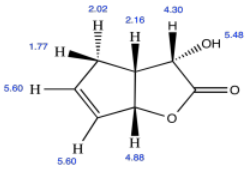
b)



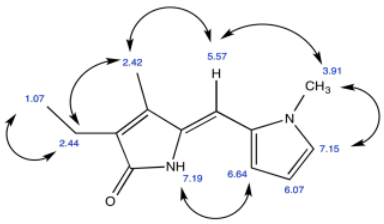
c)



Exercise 5.4.4:

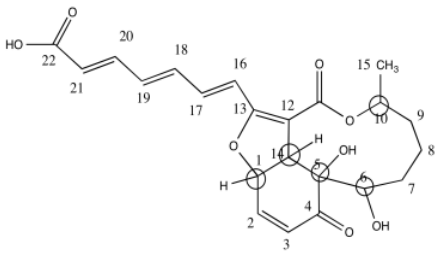


Exercise 5.4.5:

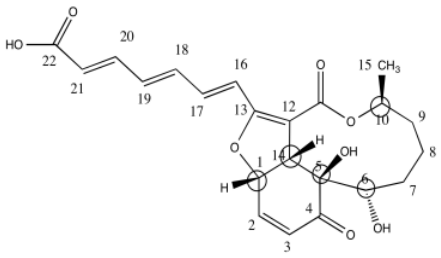


Exercise 5.4.6:

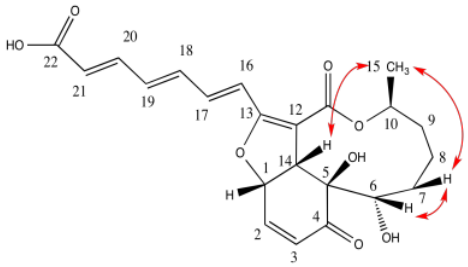
a)



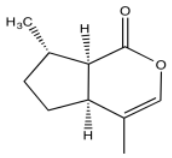
b)



c)

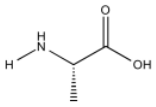


Exercise 5.4.7:



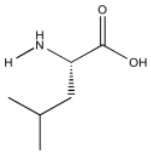
Catnip (nepetalactone)

Exercise 5.5.1:



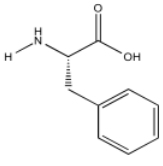
Alanine

Exercise 5.5.2:



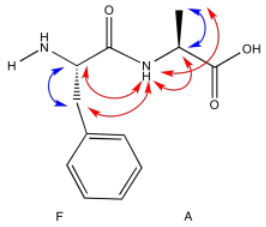
Leucine

Exercise 5.5.3:

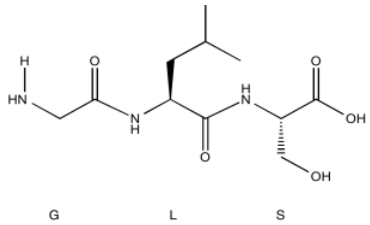


Phenylalanine

Exercise 5.5.4:



Exercise 5.5.5:



Exercise 5.6.1:

^{1}H NMR

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
5.54	2H	multiplet	C**H**=C (x 2)
4.17	2H	doublet	O-C**H**$_2$-CH
2.08	2H	quintet	CH-C**H**$_2$-CH$_3$
1.47	1H	boad singlet	OH
0.95	3H	triplet	CH$_2$-C**H**$_3$

* total # H: 10

^{13}C NMR

Chemical shift (ppm)	Type of carbon
134	sp^2
128	sp^2
58	sp^3-O
21	sp^3
14	sp^3

*total # C: 5

COSY

Assignment	^{1}H	COSY
A	0.95	2.08
B	2.08	0.95, 5.54
C	4.17	5.54
D	5.54	2.08

E	5.54	4.17

*HMQC indicates two hydrogens at 5.54 are in two different environments

HMQC

Assignment	**^{13}C**	**^{1}H**
A	14	0.95
B	21	2.08
C	58	4.17
D	128	5.54
E	134	5.54

Formula:

$C_5H_{10}O$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $5 \times 12) + (10 \times 1) + (1 \times 16) = 86$

Compare C_5H_{10} ratio to C_5H_{12} in hydrocarbon

Degrees of unsaturation = \(\frac{(2 \times 5) + 2 - 10}{2} = 1 unit (1 double bond)

The data tables should be consitent with this structure:

pent-2-en-1-ol (could be *cis* or *trans* based on this analysis)

Exercise 5.6.2:

^{1}H NMR:

Chemical shift (ppm)	**Integration**	**Multiplicity**	**Partial structure**
4.7	5H	singlet	solvent
3.93	1H	triplet	CH_2-C**H**-N
2.40	2H	multiplet	CH_2-C**H_2**?
2.09	2H	multiplet	C**H_2**-CH_2?
1.4	9H	singlet	C(C**H_3**)$_3$

*Total number of H: 19 H

^{13}C NMR:

Chemical shift (ppm)	**Type of carbon**
170	sp^2 (C=O)
80	sp^3 (C-O)
52	sp^3 (C-N)
32	sp^3
28	sp^3
26	sp^3

*Total number of C: 6 apparent, but two more suggested by symmetry (3 methyl groups in ^{1}H NMR) for 8 C; a third extra suggested by MW fit for 9 C

COSY:

Assignment	^{1}H	COSY
Solvent	4.7	--
B	3.93	2.40
D	2.40	2.09
C	2.09	2.40, 2.09
A	1.4	--

Formula:

$C_9H_{18}O_3N_2$ (extra O indicated from shift in ^{13}C, ^{1}H NMR; second O suggested by C=O in ^{13}C NMR; additional CO needed to fit MW)

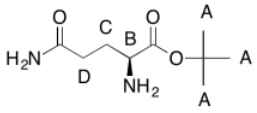
FW = $(9 \times 12) + (18 \times 1) + (3 \times 16) + (2 \times 14) = 202$

FW = ((9 \times 12) + (18 \times 1) + (3 \times 16) + (2 \times 14) = 202\)

Compare C_9H_{18} to C_9H_{22} for the corresponding hydrocarbon corrected for two nitrogens (therefore two extra hydrogens)

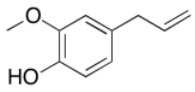
Degrees of unsaturation = $\frac{(2\times9)+2+2-10}{2} = 2$ units (2 double bonds)

The data tables should be consistent with this structure:



Exercise 5.6.3:

The data should be consistent with this structure:



Exercise 5.6.4:

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
4.71	--	singlet	solvent
4.17	1H	doublet?	CO-C**H**-N
3.75	3H	singlet	O-C**H**$_3$
2.25	1H	multiplet	CH-C**H**-(CH$_3$)$_2$
0.92	6H	triplet?	2 x C**H**$_3$

^{13}C NMR:

Chemical shift (ppm)	Type of carbon
170	sp^2 C=O

60	sp^3 C-N
52	sp^3 C-O
30	sp^3 C
19	sp^3 C

COSY:

Assignment	**^{1}H**	**COSY**
A	4.17	2.25
B	3.75	--
C	2.25	4.17
D	0.92	2.25

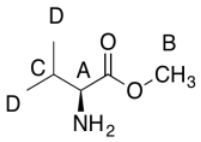
Formula:

$C_6H_{13}O_2N$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $(6 \times 120 + (13 \times 1) + (2 \times 16) + (1 \times 14) = 131$

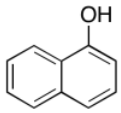
Degrees of unsaturation = $\frac{(2\times6)+2+1-13}{2} = 1$ unit (1 double bond)

The data should be consistent with this structure:



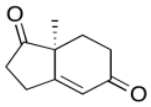
Exercise 5.6.5:

The data should be consistent with this structure:



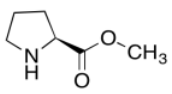
Exercise 5.6.6:

The data should be consistent with this structure:



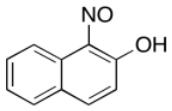
Exercise 5.6.7:

The data should be consistent with this structure:



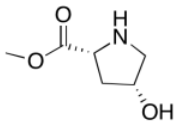
Exercise 5.6.8:

The data should be consistent with this structure:



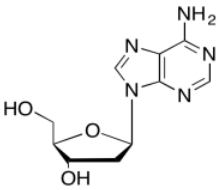
Exercise 5.6.9:

The data should be consistent with this structure:



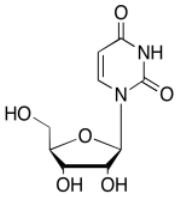
Exercise 5.6.10:

The data should be consistent with this structure:



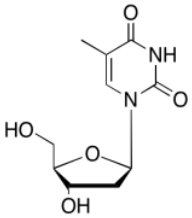
Exercise 5.6.11:

The data should be consistent with this structure:



Exercise 5.6.12:

The data should be consistent with this structure:



Exercise 5.6.13:

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial structure
5.7	1H	singlet	C=C**H**-CO
2.77	1H	multiplet	CH_2-C**H**-CO
2.62	1H	multiplet	C-C**H**-C
2.39	1H	multiplet	C-C**H**-C

2.05	1H	doublet?	C-C**H**-CH?
1.96	3H	singlet	C-C$\mathbf{H}_3$
1.48	3H	singlet	C-C$\mathbf{H}_3$
0.98	3H	singlet	C-C$\mathbf{H}_3$

^{13}C NMR:

Chemical shft (ppm)	**Type of carbon**
204	sp^2 C=O
170	sp^2
121	sp^2
59	sp^3
55	sp^3
50	sp^3
41	sp^3
28	sp^3
24	sp^3
22	sp^3

COSY:

Assignment	**^{1}H**	**COSY**
1	2.39	2.77, 2.62?
3	5.7	2.05?
5	2.62	2.62?
7a	2.77	2.05
7b	2.05	2.77
8	1.48	--
9	0.98	--
10	1.96	--

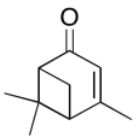
Formula:

$C_{10}H_{14}O$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $(10 \times 12) + (14 \times 1) + (1 \times 16) = 150$

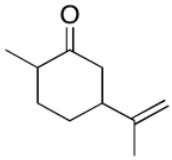
Degrees of unsaturation = \(\frac{(2 \times 10) + 2 - 14}{2} = 4 units (e.g. 2 rings, 2 double bonds)

The data should be consistent with this structure:



Exercise 5.6.14:

The data should be consistent with this structure:



Exercise 5.6.15:

The data should be consistent with this structure: