NTNU – Trondheim
Norwegian University of
Science and Technology

Department of Chemistry

Examination paper for KJ3021 – NMR

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- approved calculator
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Prof. Finn Aachmann

Date Signature

Notes:

- *In some of multiple choice questions more than one answer can be correct.*
- *Circle letter(s) before the correct answer(s)*

Problem 1.

Which processes are responsible for the NOE effect? (6 p)

a. single-quantum relaxation processes
b. zero-quantum relaxation processes
c. double-quantum relaxation processes
d. non-dipolar relaxation processes

Problem 2.

a) Draw an energy level scheme for a homonuclear AX spin system (I=1/2).

(5 p)

b) Mark on the scheme the allowed transitions by quantum mechanical rules.

(3 p)

Problem 3.

Draw a scheme for the pulsed gradient spin-echo pulse sequence and explain its effect on a macroscopic magnetization by using the vector model.

(10 p)

Problem 4.

A) Draw a scheme (vector model) for the experiment for determination of T_1 by observing disappearance of the signal. Explain it shortly.

(8 p)

B) Describe an experiment for suppression of water signal in a 1D ^{1}H-experiment for small organic molecules, based on difference in τ_{null} between water and the sample.

(8 p)

Problem 5.

The phase correction is, in other words:

a) improving signal-to-noise ratio
b) tuning and matching on the sample
c) removal of dispersion component of the signal
d) correction of magnetic field inhomogeneities
e) determination of pulse with (pulse calibration)
f) spectrum calibration.

(5 p)

Problem 6.

In a 2D TOCSY experiment:

A) Observing nucleus is:

i) ^{1}H
ii) ^{13}C

B) Available information is:

i) ^{1}H, ^{1}H coupling constants
ii) ^{1}H, ^{13}C coupling constants
iii) distinction of spin systems
iv) long range ^{1}H-^{13}C correlations
v) one-bond ^{1}H-^{13}C correlations
vi) through-space direct correlation between nuclei
vii) chemical shifts.

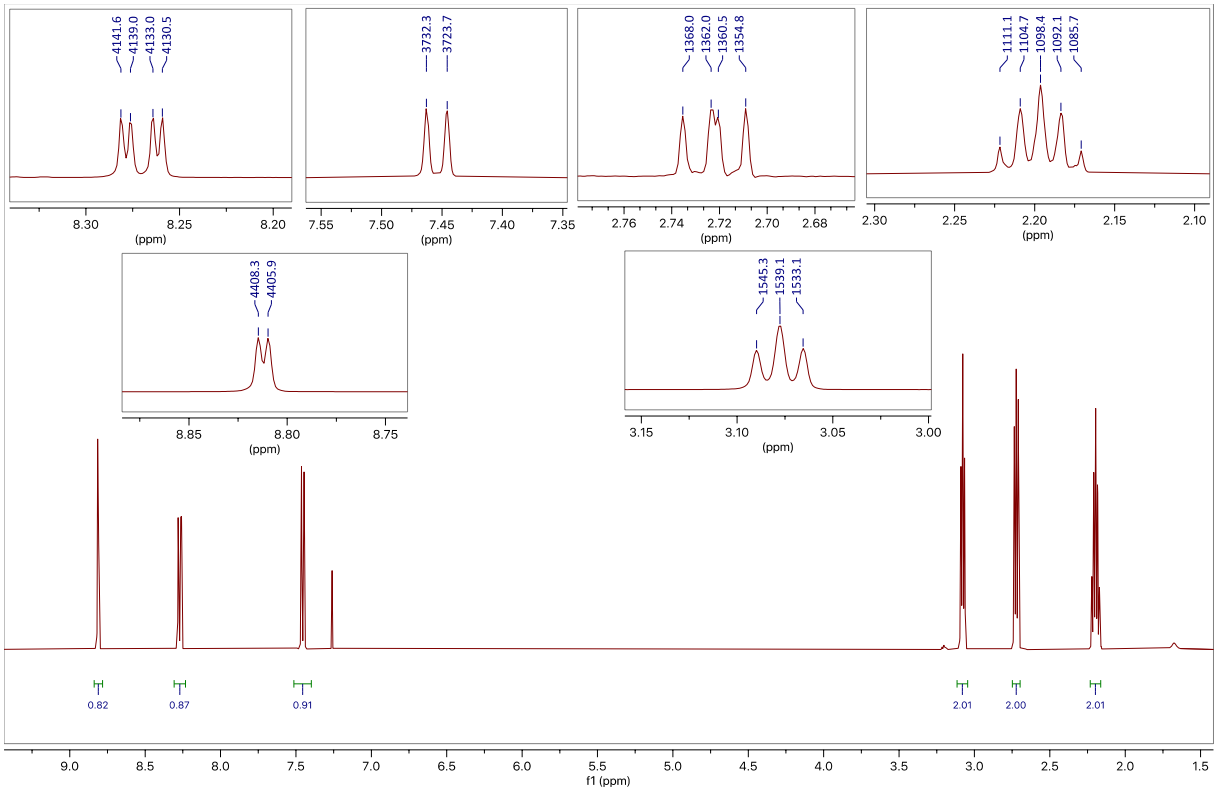
(9 p)

Problem 7.

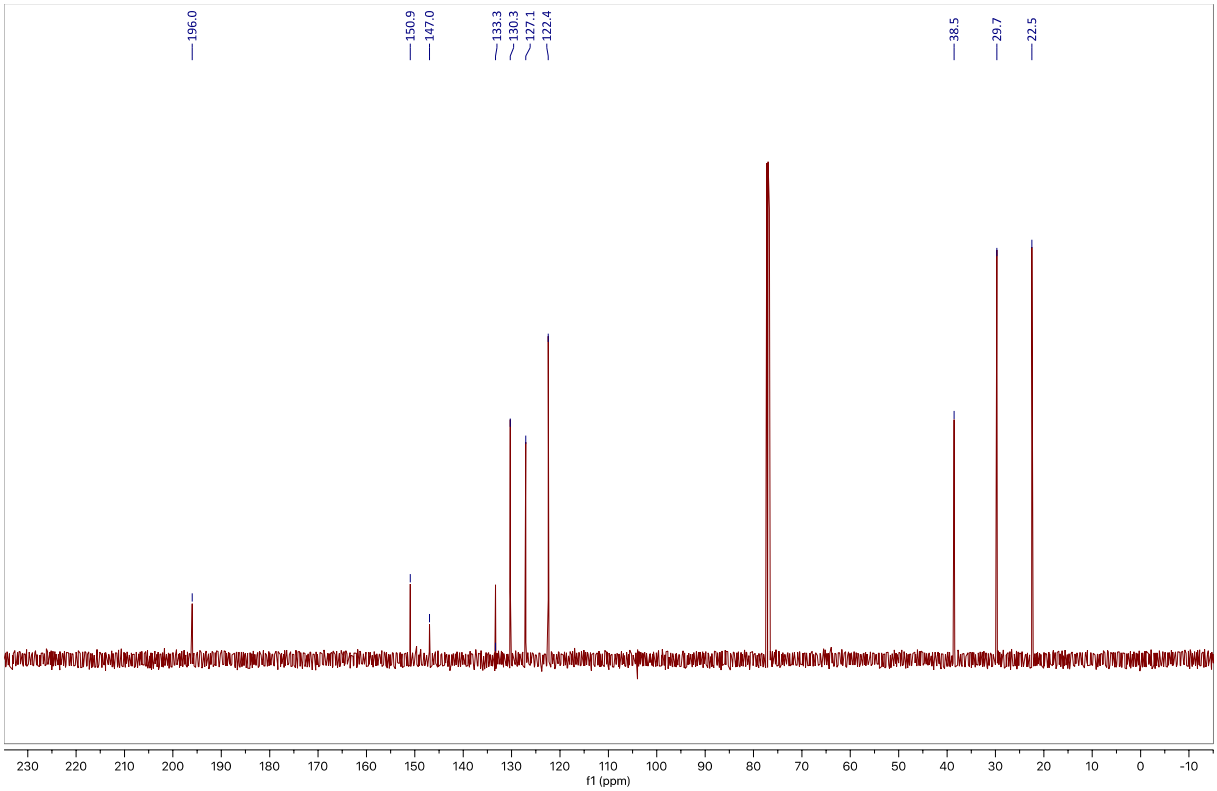
1D and 2D NMR spectra (500 MHz, $CDCl_3$) of an unknown compound are shown on pages 3-5. Its molecular formula is $C_{10}H_9NO_3$. Elucidate the structure and assign all ^{1}H and ^{13}C shifts.

(24 p)

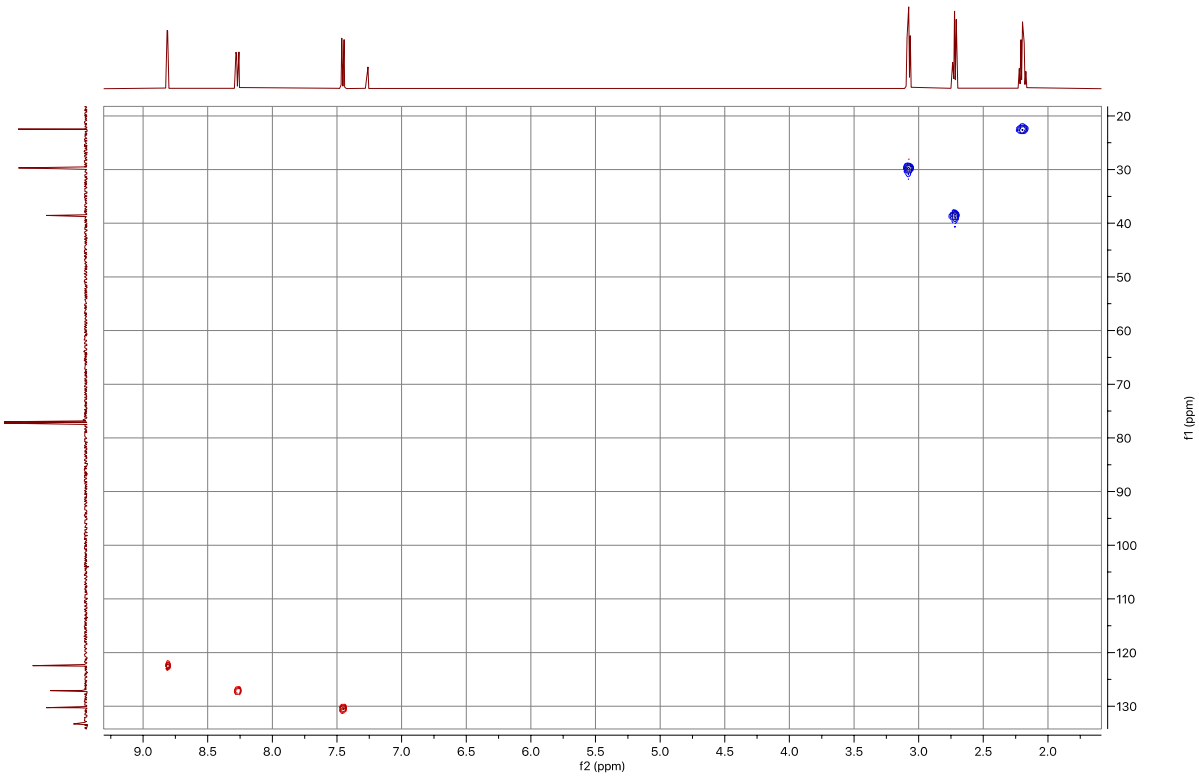
^{1}H spectrum



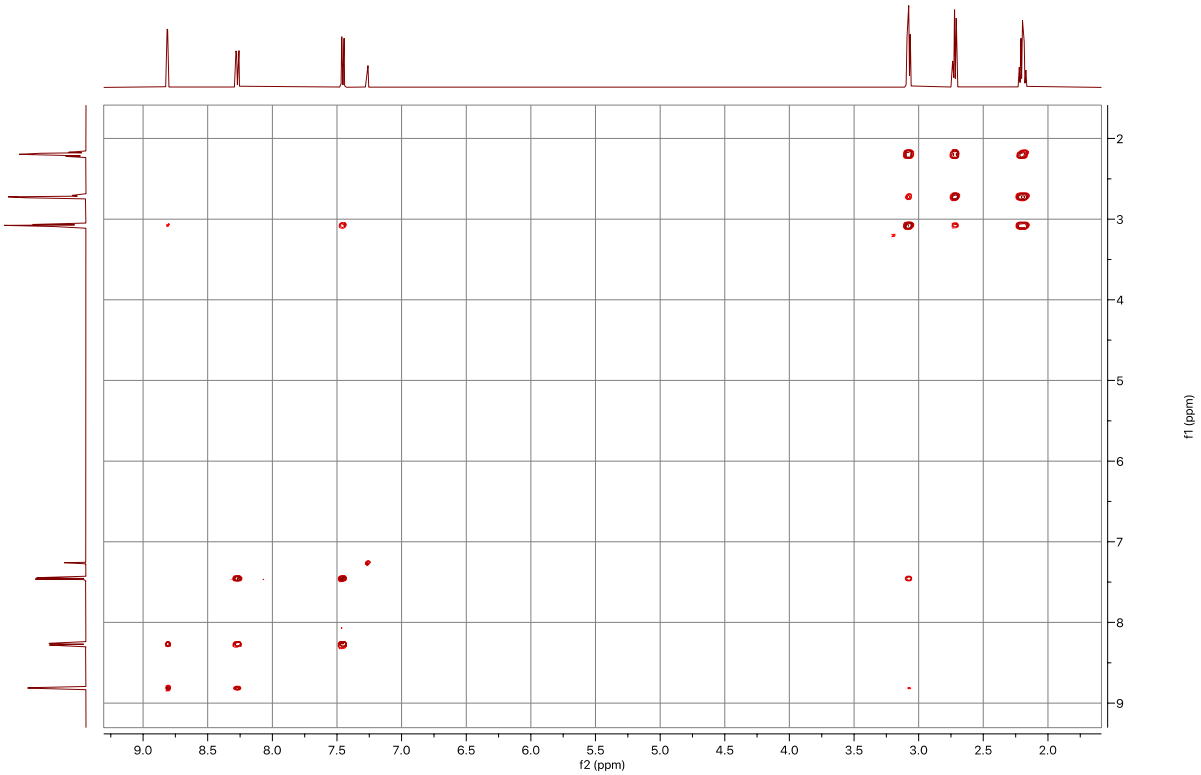
^{13}C spectrum



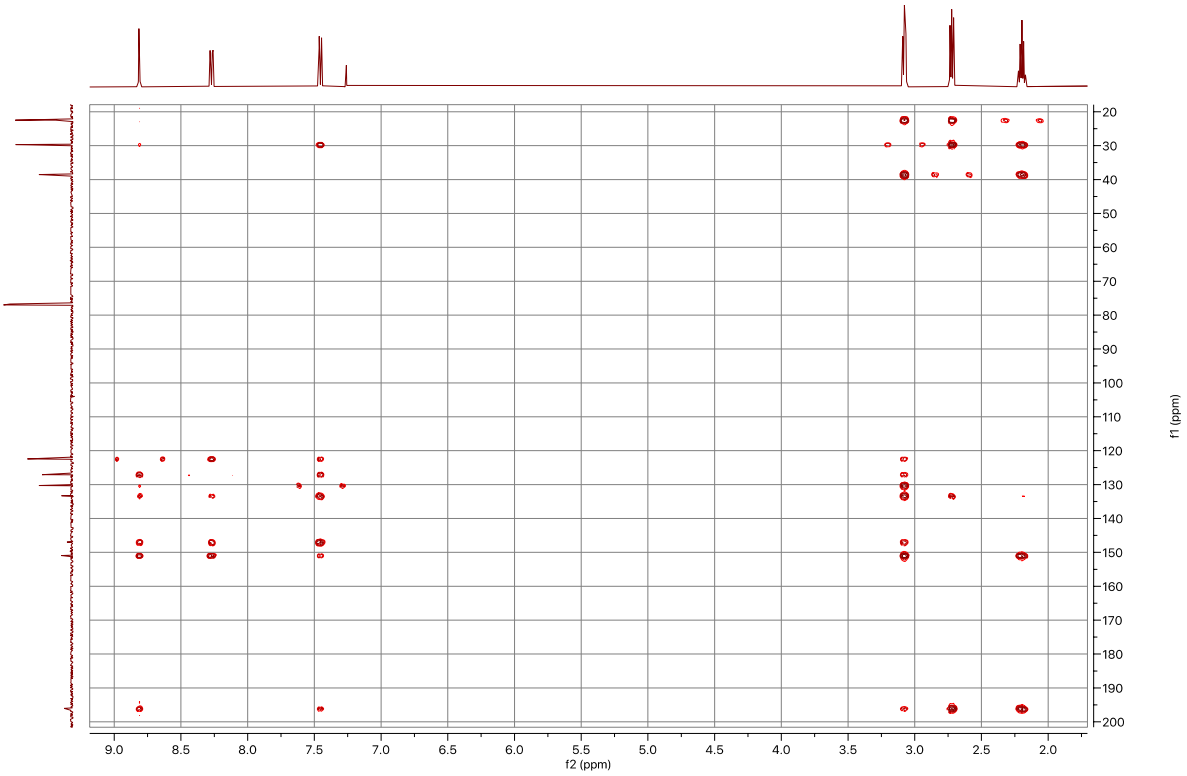
HSQC (red – positive phase, blue – negative phase signal**)**



COSY



HMBC



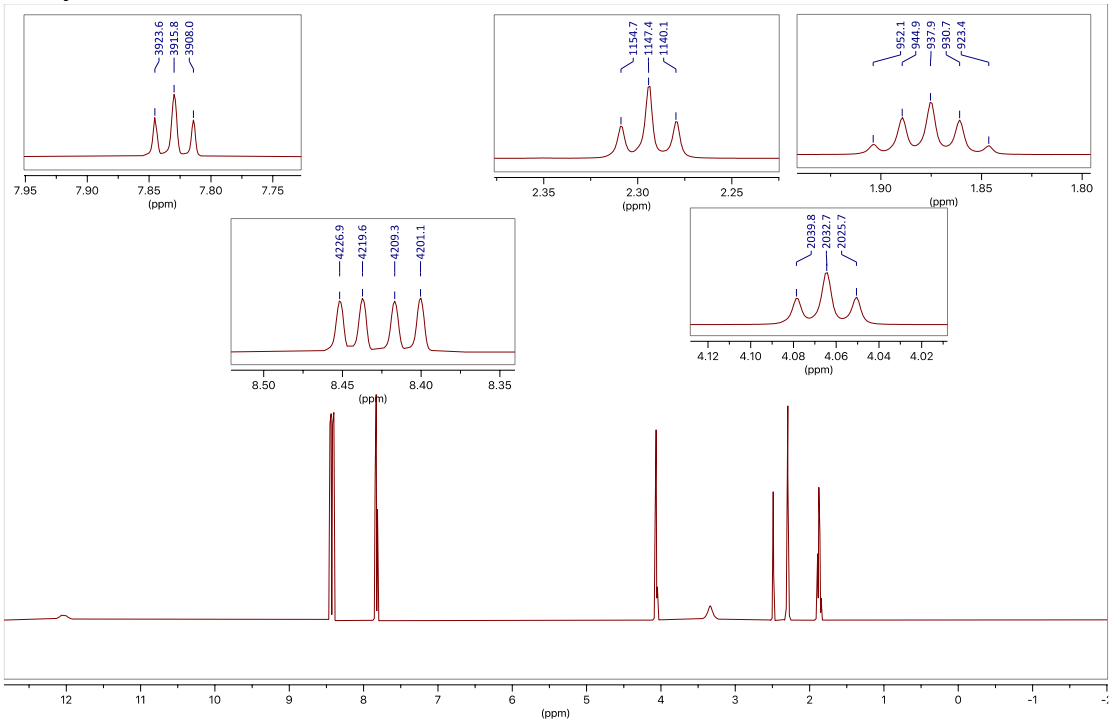
Problem 8.

A set of 1D and 2D NMR spectra (500 MHz, DMSO-d6) shown on pages 6-8, belongs to the compound **1** (page 8).

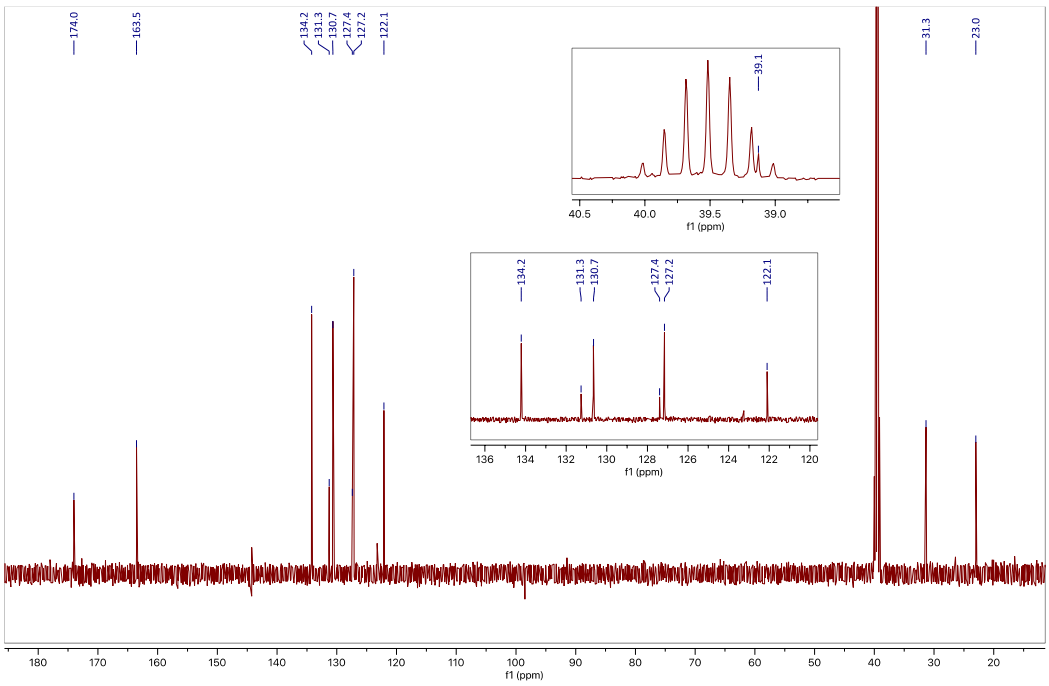
Assign all ^{1}H and a ^{13}C resonances of that compound, except O**H** proton. Write the shifts in the table on page 8.

(22 p)

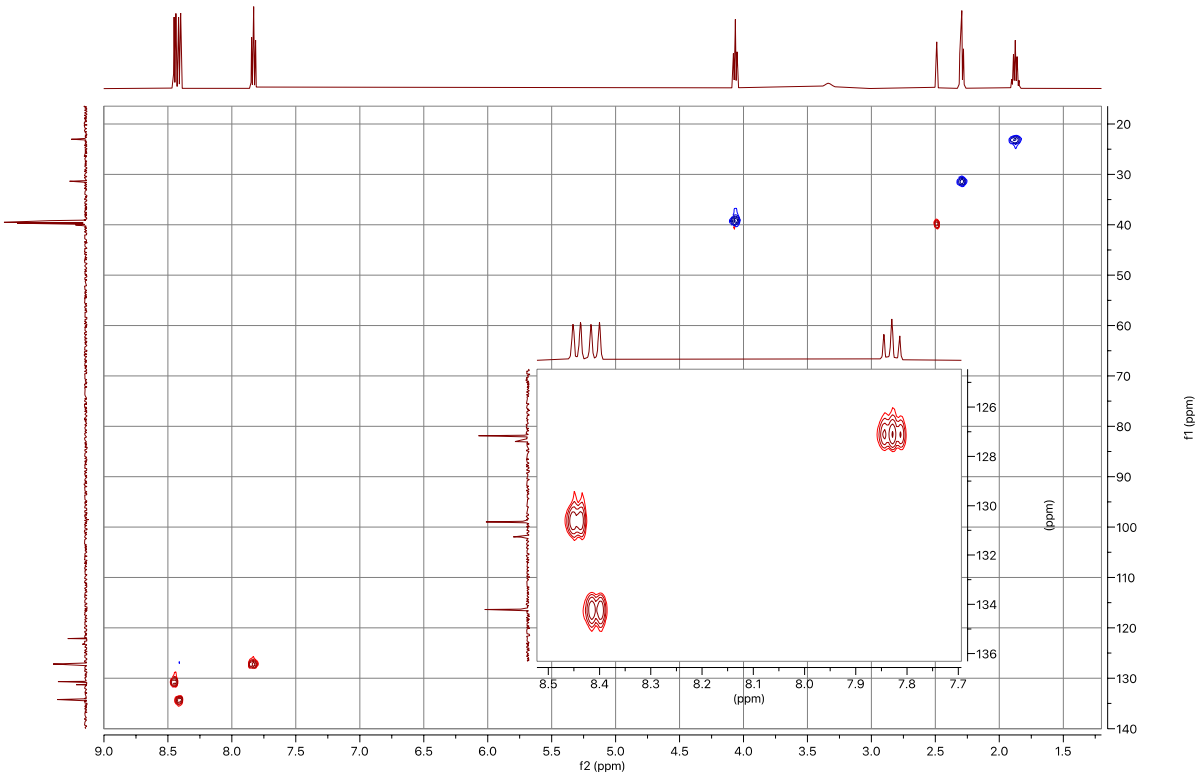
Proton spectrum



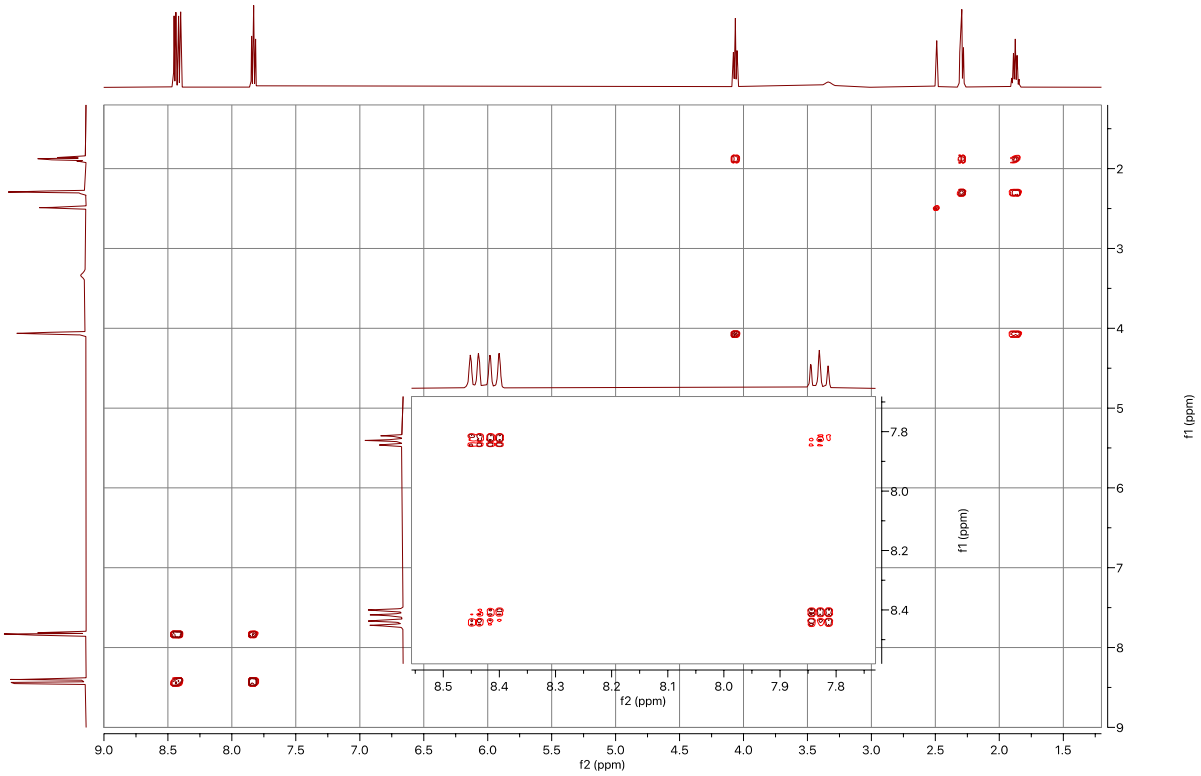
^{13}C spectrum



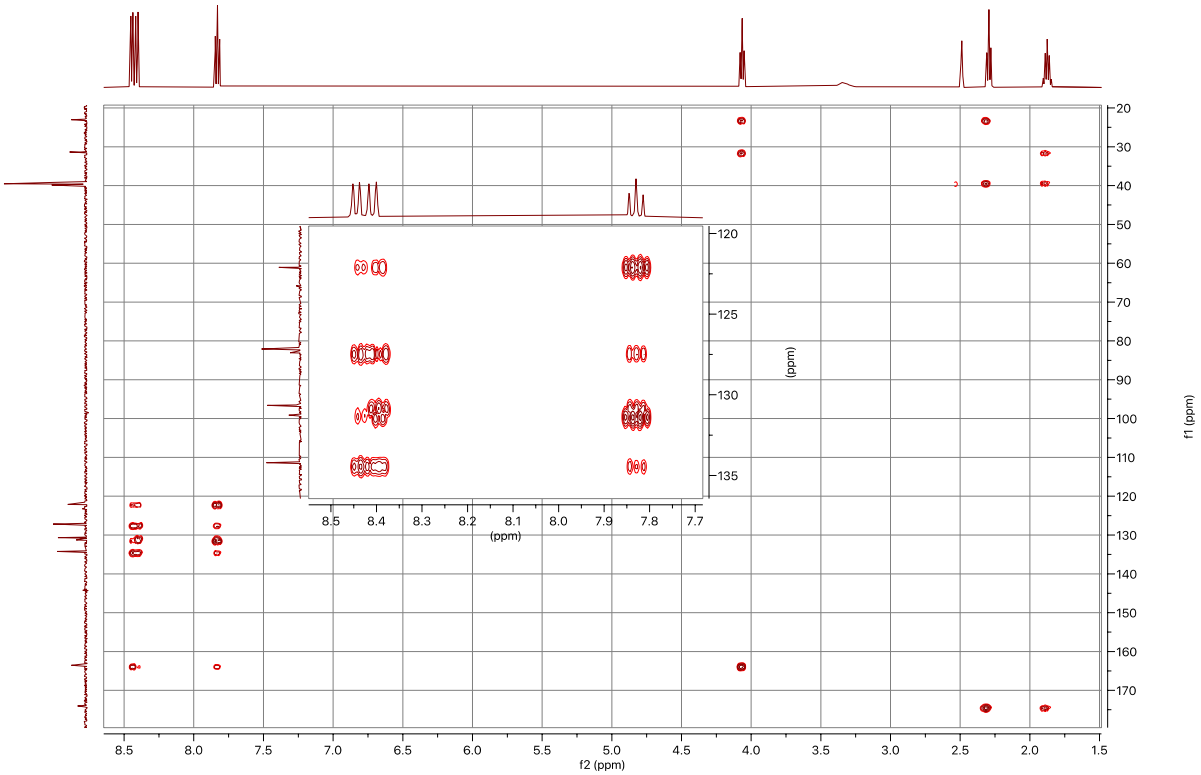
HSQC spectrum (red – positive phase, blue – negative phase signal)

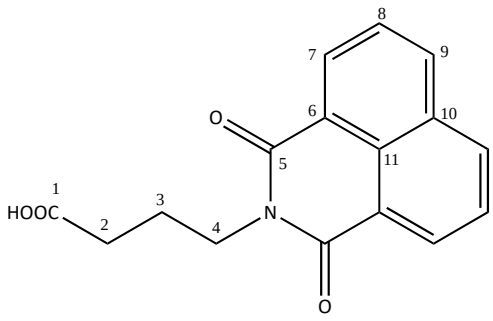


COSY spectrum



HMBC





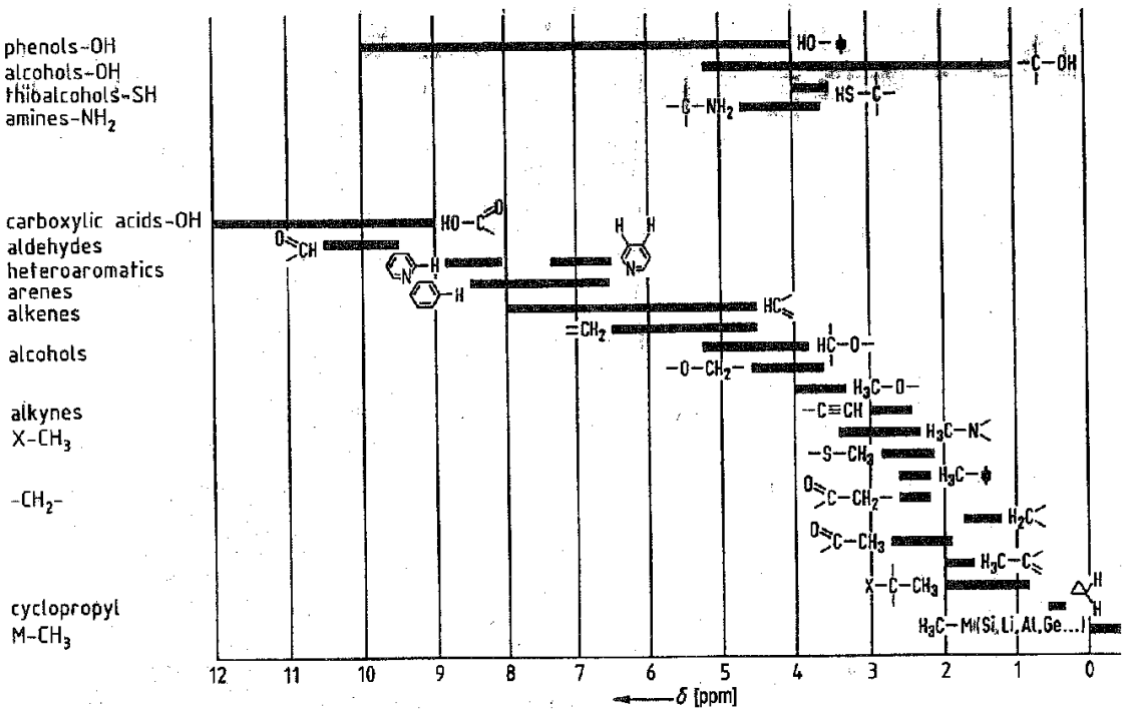
1

Figure 1. Structure of the compound **1**

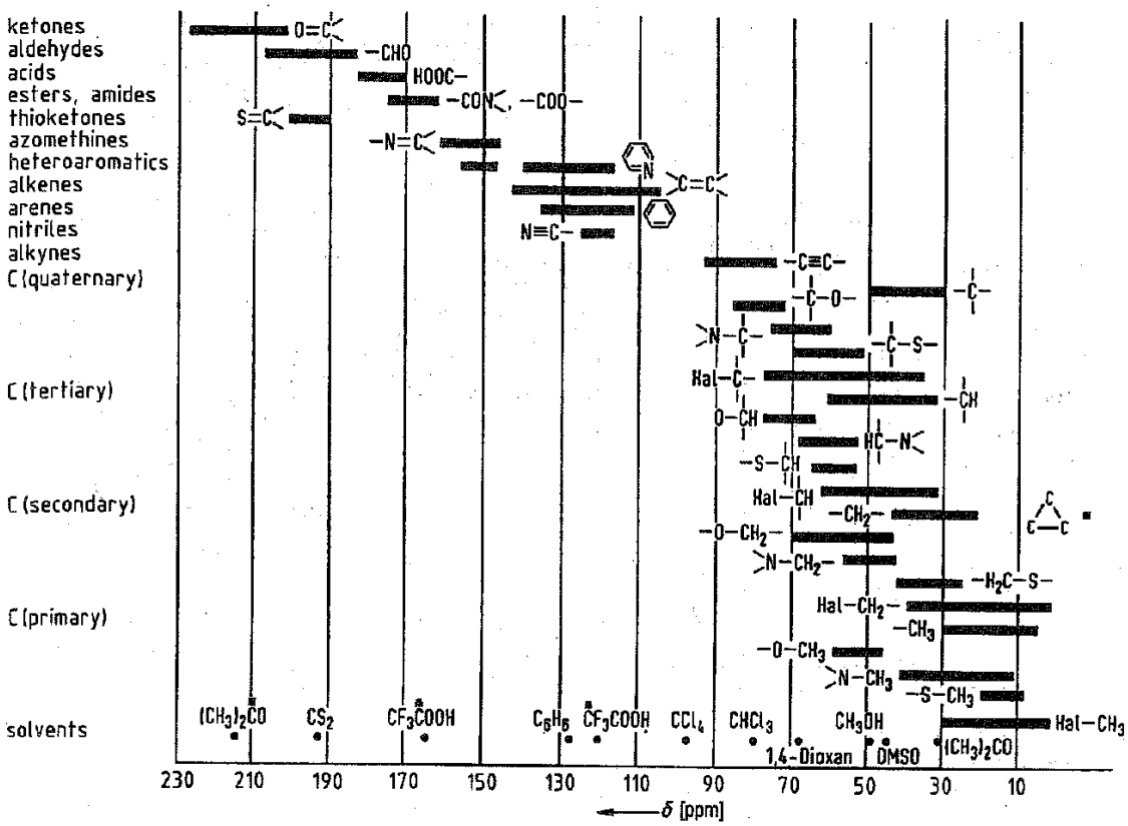
Shift assignments for **1**

Carbon no.	δ ^{13}C (ppm)	δ ^{1}H (ppm)
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		

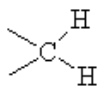
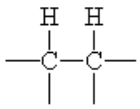
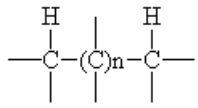
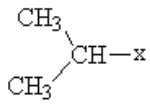
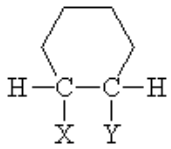
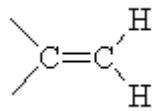
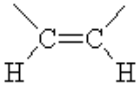
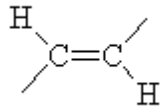
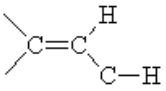
Proton shifts for common organic compounds

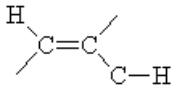
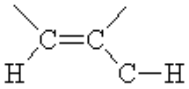
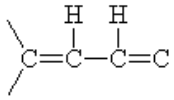
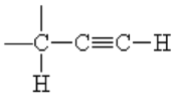
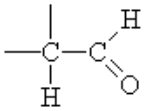
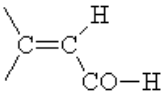
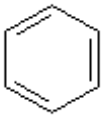
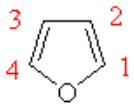
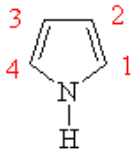
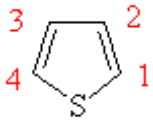
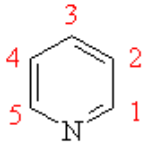
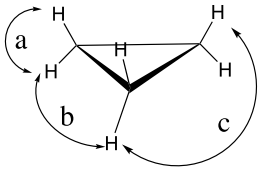


^{13}C shifts for common organic compounds



^{1}H, ^{1}H Coupling constants for common organic compounds

Type	J (Hz)	Type	J (Hz)
	12-15		2-9
	0		6.5- 7.5
	5.5- 7.0		• aa 5-8 • ae 2-4 • ee 2-4
	0.5- 3		7-12
	13-18		4-10

	0.5- 2.5		0
	9- 13		2- 3
	1- 3		2- 4
	• o 6- 9 • m 1- 3 • p 0- 1		• 1-2 1.6-2.0 • 1-3 0.6-1.0 • 1-4 1.3-1.8 • 2-3 3.2-3.8
	• 1-2 2.0-2.6 • 1-3 1.5-2.2 • 1-4 1.8-2.3 • 2-3 2.8-4.0		• 1-2 4.6-5.8 • 1-3 1.0-1.8 • 1-4 2.1-3.3 • 2-3 3.0-4.2
	• 1-2 4.9-5.7 • 1-3 1.6-2.6 • 1-4 0.7-1.1 • 1-5 0.2-0.5 • 2-3 7.2-8.5 • 2-4 1.4-1.9		a) 4.5 (gem) b) 6-10 (cis) c) 3-6 (trans)

$_1$H shifts

relativ to TMS	12	11	10	9	8	7	6	5	4	3	2	1	0	-1
H_3C-Alkyl													■	■
H_3C-C-Hal												■		
H_3C-C=C												■		
H_3C-CC												■		
H_3C-Aryl,-Heteroaryl											■			
H_3C-CO											■	■		
H_3C-S-											■			
H_3C-SO_2-										■	■			
H_3C-N										■	■			
H_3C-O-Alkyl										■				

H_3C-O-Aryl, -O-CO-										■				
C-CH_2-Alkyl												■		
Cyclopropane													■	■
C-CH_2-CO											■	■		
C-CH_2-O-									■	■				
C-CH_2-S										■				
C-CH_2-NO_2									■					
C-CH_2-N										■	■			
C=C-CH_2-C=C											■			
N-CH_2-CO-									■	■	■			
-O-CH_2-CO-								■	■					
-O-CH_2-O-, -Aryl								■	■					

	12	11	10	9	8	7	6	5	4	3	2	1	0	-1
CH-Alkyl												■		
CH-Hal								■	■					
C-CH-O-									■	■				
C-CH-N									■	■	■			
CO-CH-C=C									■	■				
CH-Aryl,-NR-,-O-							■	■	■	■				
-CCH Alkine										■				
CH=C-						■	■	■	■					
Ar-H					■	■	■							

	12	11	10	9	8	7	6	5	4	3	2	1	0	-1
Alkyl-, Aryl-CHO			■	■										
Alkyl-OH										■	■	■		
Aryl-OH						■	■	■	■	■				
R-COOH	■	■	■	■										
Alkyl-SH										■	■	■		
Aryl-SH									■	■				
Alkyl-NH_2, Alkyl$_2$-NH											■	■		
Aryl-NH_2, Aryl$_2$-NH								■	■	■				
R-CO-NH-				■	■	■	■							
-CO-NH-CO			■	■										

^{13}C Chemical Shifts

relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20
H_3C-C- primary										■	■		
H_3C-S-										■	■		
H_3C-N									■	■			
H_3C-O-									■				
-H_2C-C secondary									■	■			
Cyclopropanes											■	■	
-H_2C-S-									■	■			
-H_2C-N									■				
-H_2C-O-								■	■				

-H_2C-Hal			F	Cl	Br	I
>CH-C- tertiary				Cl	Br	
>CH-S-						
>CH-N						
>CH-Hal		F	Cl	Br	I	
C-C quarternary						
C-S-						
C-N						
C-O-						
C-Hal			Cl	Br	I	

relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20
Alkines							■	■					
C=C=C Allenes							■	■					
C=C Alkenes				■	■	■	■						
Aromatic Compounds				■	■	■							
Heteroaromatic Compounds				■	■	■							
-S-CN Rhodanides						■							
-N=C=S Isothiocyanates					■								
-O-CN				■									
-N=C=O					■								
-CN					■	■							
-NC			■	■									
>C=N- Azomethines			■	■									
$(-CO)_2O$ Anhydrides			■	■									
-COOR			■	■									
-CONHR			■	■									
$-(CO)_2NR$ Imides			■										
-COOH		■	■										
-COCl			■										
-CHO	■	■	■	■									
>C=O	■	■											
relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20

Residual ^{1}H and ^{13}C NMR shifts of common organic NMR solvents

Solvent	^{1}H Chemical Shift (ppm from TMS) (multiplicity)	JHD (Hz)	Carbon-13 Chemical Shift (ppm from TMS) (multiplicity)	JCD (Hz)	^{1}H Chemical Shift of HOD (ppm from TMS)
Acetic Acid-d_4	11.65 (1) 2.04 (5)	2.2	178.99 (1) 20.0 (7)	20	11.5
Acetone-d_6	2.05 (5)	2.2	206.68 (1) 29.92 (7)	0.9 19.4	2.8
Acetonitrile-d_3	1.94 (5)	2.5	118.69 (1) 1.39 (7)	21	2.1
Benzene-d_6	7.16 (1)		128.39 (3)	24.3	0.4
Chloroform-d	7.24 (1)		77.23 (3)	32.0	1.5
Cyclohexane-d_{12}	1.38 (1)		26.43 (5)	19	0.8
Deuterium Oxide	4.80 (DSS) 4.81 (TSP)		NA	NA	4.8
N, N-Dimethyl -formamide-d_7	8.03 (1) 2.92 (5) 2.75 (5)	1.9 1.9	163.15 (3) 34.89 (7) 29.76 (7)	29.4 21.0 21.1	3.5
Dimethyl Sulfoxide-d_6	2.50 (5)	1.9	39.51 (7)	21.0	3.3
1,4-Dioxane-d_8	3.53 (m)		66.66 (5)	21.9	2.4
Ethanol-d_6	5.19 (1) 3.56 (1) 1.11 (m)		56.96 (5) 17.31 (7)	22 19	5.3
Methanol-d_4	4.78 (1) 3.31 (5)	1.7	49.15 (7)	21.4	4.9
Methylene Chloride-d_2	5.32 (3)	1.1	54.00 (5)	27.2	1.5
Pyridine-d_5	8.74 (1) 7.58 (1) 7.22 (1)		150.35 (3) 135.91 (3) 123.87 (3)	27.5 24.5 25	5
1,1,2,2-Tetrachloroethane-d_2	6.0		73.78 (3)		
Tetrahydrofuran-d_8	3.58 (1) 1.73 (1)		67.57 (5) 25.37 (5)	22.2 20.2	2.4-2.5
Toluene-d_8	7.09 (m) 7.00 (1) 6.98 (5) 2.09 (5)	2.3	137.86 (1) 129.24 (3) 128.33 (3) 125.49 (3) 20.4 (7)	23 24 24 19	0.4
Trifluoroacetic Acid-d	11.50 (1)		164.2 (4) 116.6 (4)		11.5
Trifluoroethanol-d_3	5.02 (1) 3.88 (4x3)	2(9)	126.3 (4) 61.5 (4x5)	22	5