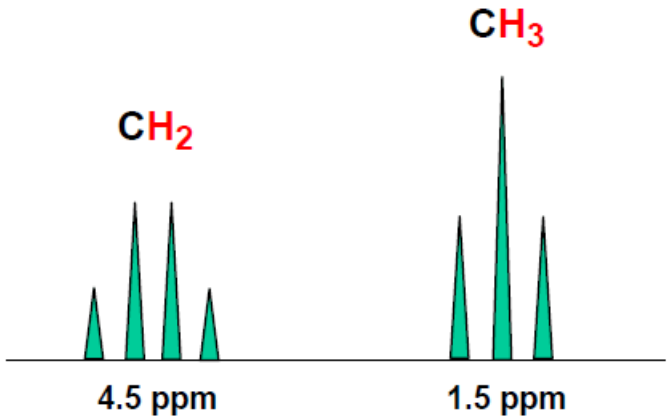
Σύζευξη πρώτης τάξης μεταξύ χημικά ισοδύναμων πρωτονίων

Στο φάσμα ^{1}H NMR της ένωσης $CH_3CH_2NO_2$ παρατηρούμε:

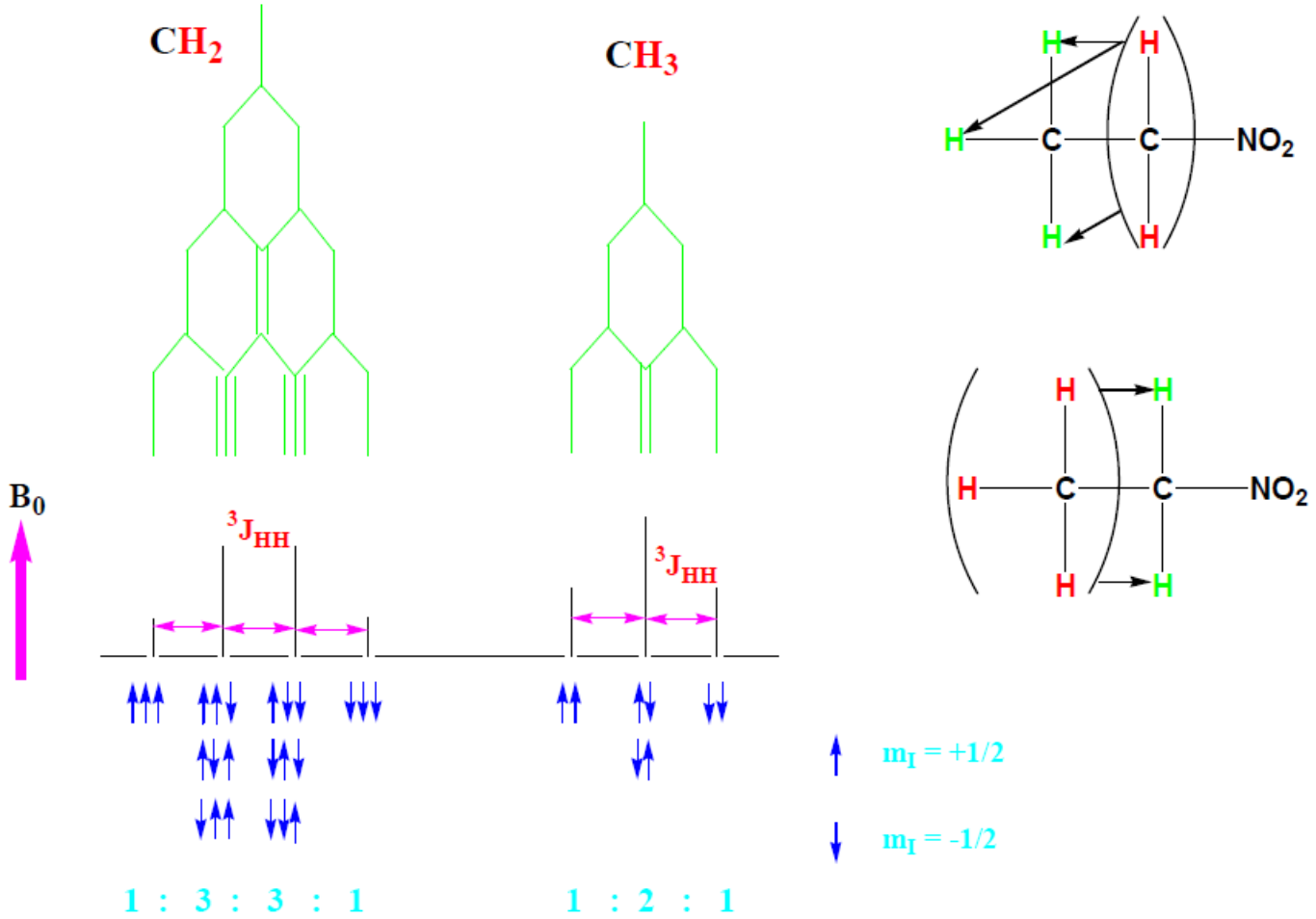
Μια τετραπλή κορυφή, η οποία οφείλεται στα δύο χημικά ισοδύναμα πρωτόνια CH_2 και μια τριπλή κορυφή, η οποία οφείλεται στα τρία χημικά ισοδύναμα πρωτόνια CH_3.

Η σχετική ένταση των κορυφών στα 4.5 ppm είναι 1:3:3:1, ενώ η σχετική ένταση των κορυφών στα 1.5 ppm είναι 1:2:1.

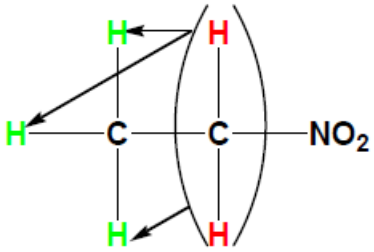
Οι συνιστώσες κορυφές σε κάθε πολλαπλή κορυφή ισαπέχουν. Η απόσταση αυτή είναι ίση με τα σταθερά σύζευξης.



Σύζευξη πρώτης τάξης

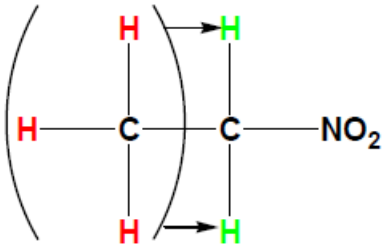


Σύζευξη πρώτης τάξης (συνέχεια)



Το σχάσιμο της κορυφής ενός πρωτονίου λόγω σύζευξης με N γειτονικά πρωτόνια, ακολουθεί το γενικό κανόνα

$$N + 1$$

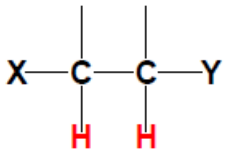


Ο αριθμός των συνιστωσών κορυφών ονομάζεται πολλαπλότητα

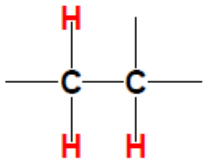
Τα CH_3 έχουν δύο γειτονικά πρωτόνια, επομένως η πολλαπλότητα είναι 2 + 1 = 3 (τριπλή κορυφή).

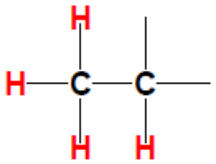
Τα CH_2 έχουν τρία γειτονικά πρωτόνια, επομένως η πολλαπλότητα είναι 3 + 1 = 4 (τετραπλή κορυφή).

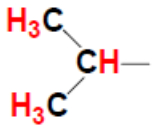
Σύζευξη πρώτης τάξης (…)

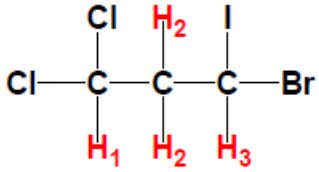
διπλή  διπλή

$X \neq Y$

διπλή  τριπλή

διπλή  τετραπλή

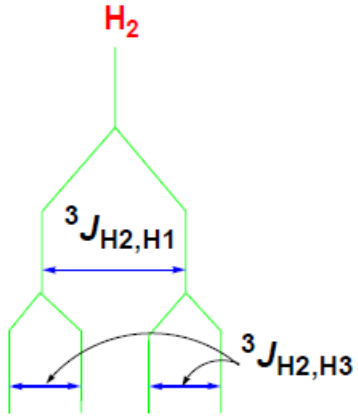
διπλή  επταπλή



H_1 $2 + 1 = 3$ (τριπλή κορυφή)

H_3 $2 + 1 = 3$ (τριπλή κορυφή)

H_2 $(1 + 1)(1 + 1)$ (διπλή της διπλής)

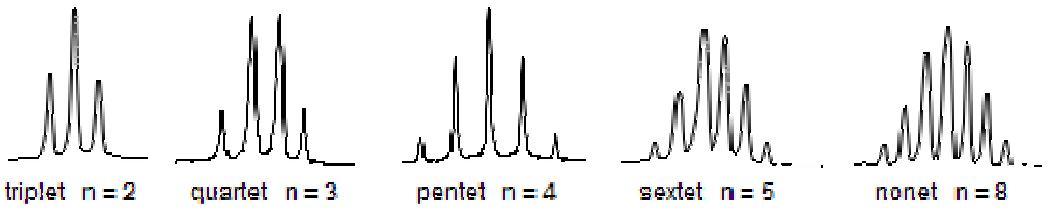


Πολλαπλότητα = $(N_1 + 1)(N_2 + 1)$ …

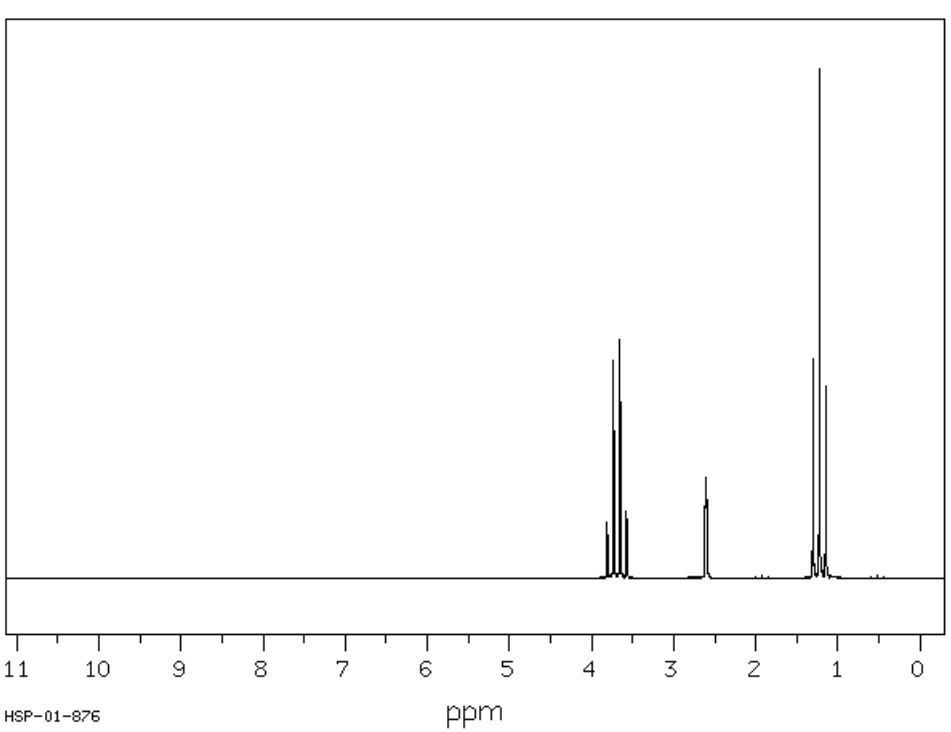
Σύζευξη πρώτης τάξης (…)

Σχετική ένταση συνιστωσών κορυφών σε μια πολλαπλή κορυφή για πυρήνες με I = 1/2 δίνεται από το τρίγωνο του Pascal.

N	Ενταση κορυφών	Πολλαπλότητα	Πολλαπλή κορυφή
0	1	1	απλή
1	1 : 1	2	διπλή
2	1 : 2 : 1	3	τριπλή
3	1 : 3 : 3 : 1	4	τετραπλή
4	1 : 4 : 6 : 4 : 1	5	πενταπλή
5	1 : 5 : 10 : 10: 5 : 1	6	εξαπλή
6	1 : 6 : 15 : 20 : 15 : 6 : 1	7	επταπλή



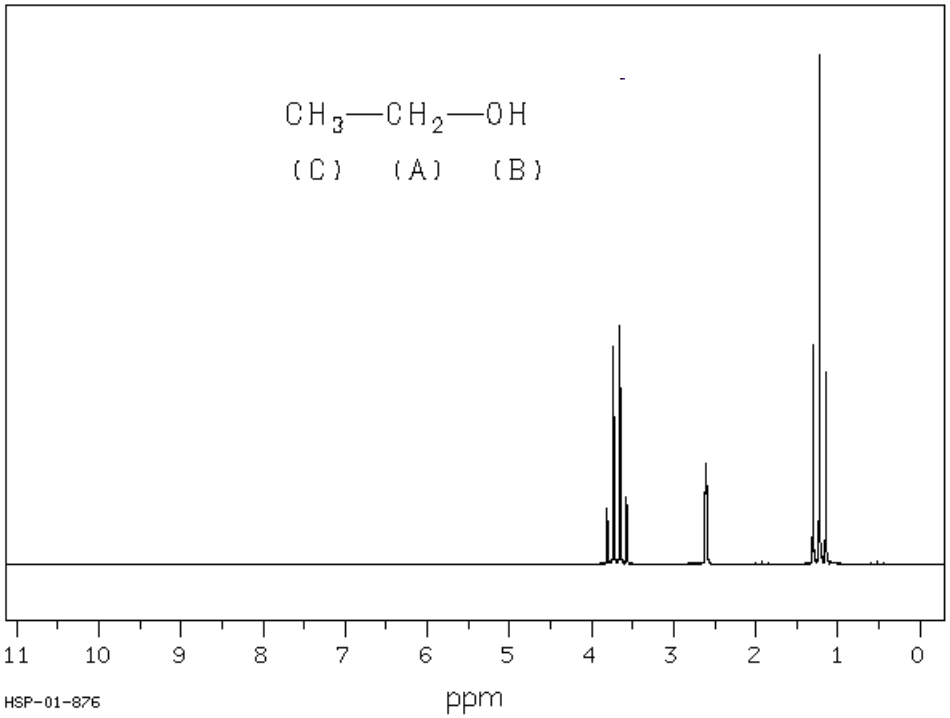
Homonuclear coupling



$CH_3—CH_2—OH$

(C) (A) (B)

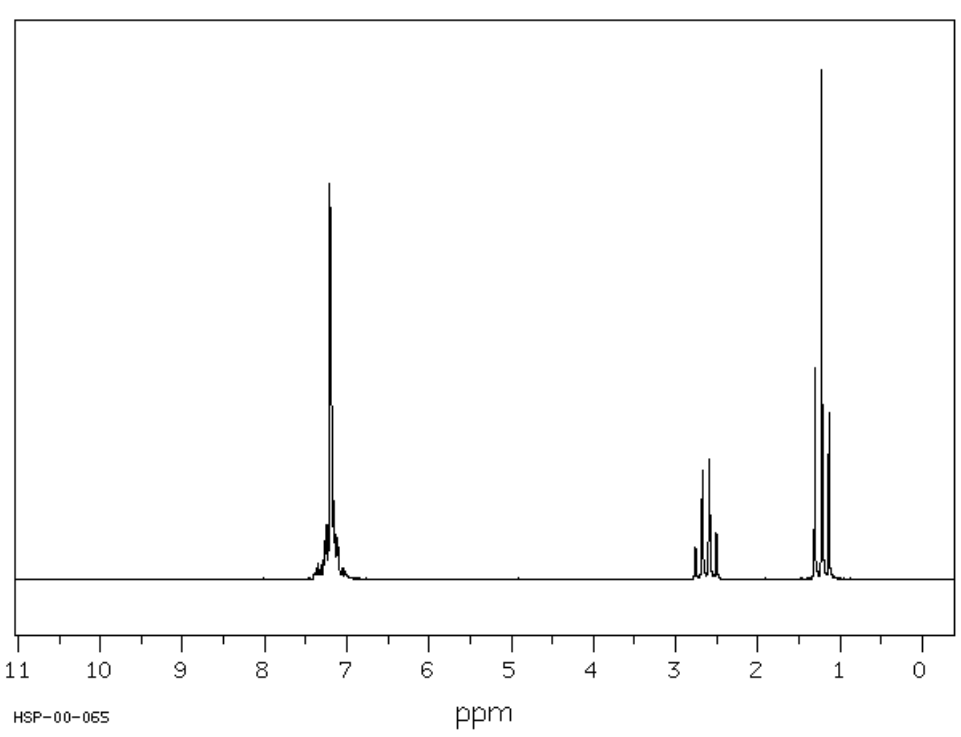
Homonuclear coupling

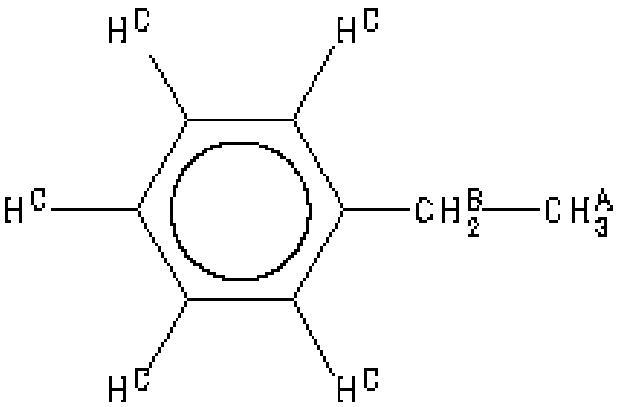


Assign.	Shift(ppm)
A	3.687
B	2.61
C	1.226

singlet				1			
doublet			1		1		
triplet		1		2		1	
quartet	1		3		3		1
quintet		1		4		6	
sextet	1		5		10		

Toluene





Assign.	Shift(ppm)
A	1.22
B	2.63
C	7.0 to 7.45

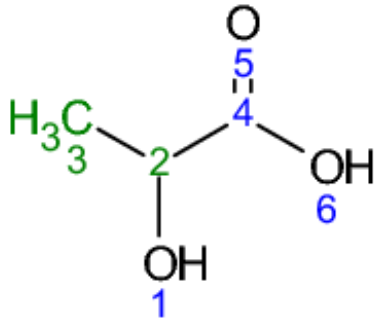
Lactic acid

HMDB00190

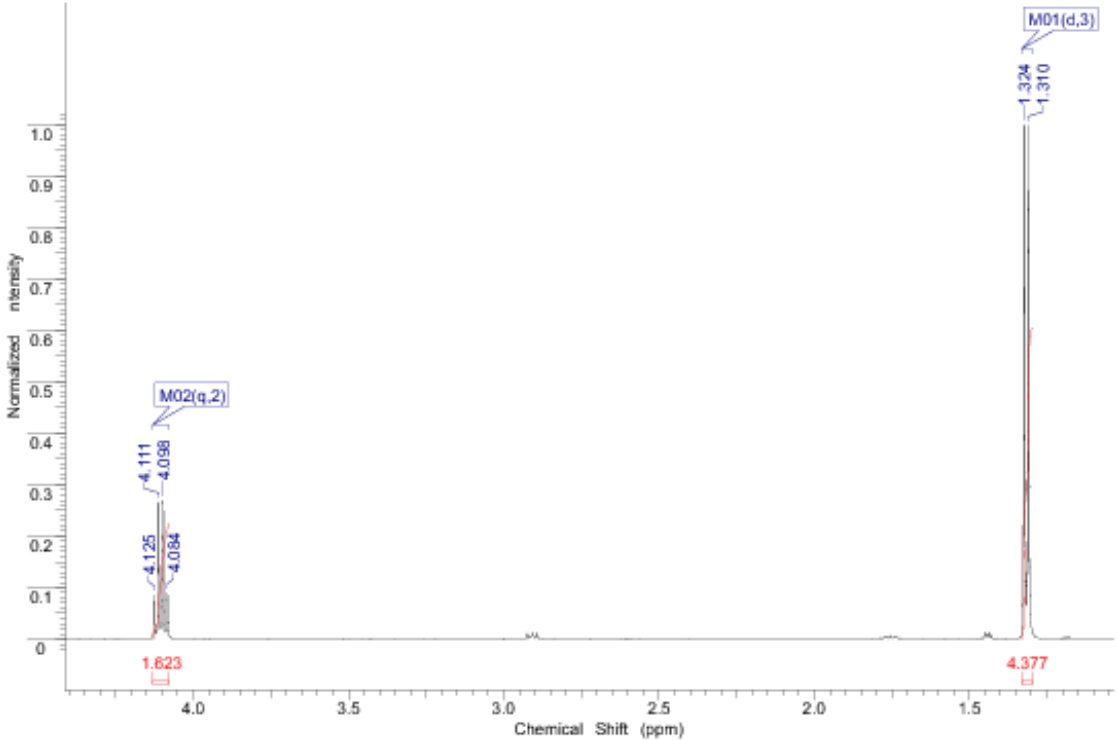
^{1}H NMR Spectrum: 500 Mhz $_2$0n H

Sample: 50 mM at pH 7.0

Referenced to DSS



Zoomed ^{1}H NMR spectrum

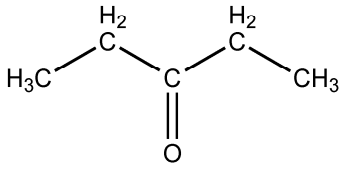


singlet						1					
doublet					1		1				
triplet				1		2		1			
quartet			1		3		3		1		
quintet		1		4		6		4		1	
sextet	1		5		10		10		5		1

3-pentanone
c6d6
c115a

Solvent: Benzene
Temp. 27.0 C / 300.1 K
File: c115a

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 12.0 degrees
Acq. time 5.972 sec
Width 2614.9 Hz
Single scan
OBSERVE H1, 299.8882477 MHz
DATA PROCESSING
FT size 32768
Total time 1 minute

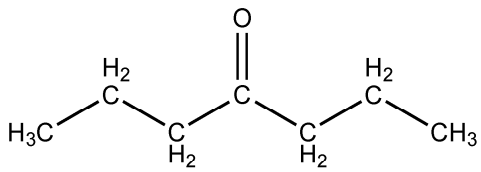


3-Pentanone

4-heptanone
c6d6
f13a

Solvent: Benzene
Temp. 27.0 C / 300.1 K
File: f13a

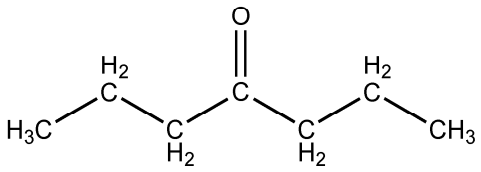
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 12.0 degrees
Acq. time 5.978 sec
Width 2596.1 Hz
Single scan
OBSERVE H1, 299.8882475 MHz
DATA PROCESSING
FT size 32768
Total time 1 minute



4-Heptanone

4-heptanone
c6d6
f13a
 Solvent: Benzene
 Temp. 27.0 C / 300.1 K
File: f13a

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 12.0 degrees
 Acq. time 5.978 sec
 Width 2596.1 Hz
 Single scan
OBSERVE   H1, 299.8882475 MHz
DATA PROCESSING
FT size 32768
Total time 1 minute

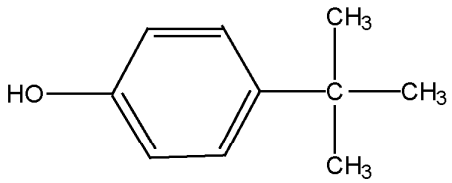


4-Heptanone

4-t-Butylphenol
DMSO-d6
Shoulders
e21a

Solvent: DMSO
Temp. 27.0 C / 300.1 K
File: e21a

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 12.0 degrees
Acq. time 5.980 sec
Width 3087.8 Hz
Single scan
OBSERVE H1, 299.8896532 MHz
DATA PROCESSING
FT size 65536
Total time 1 minute



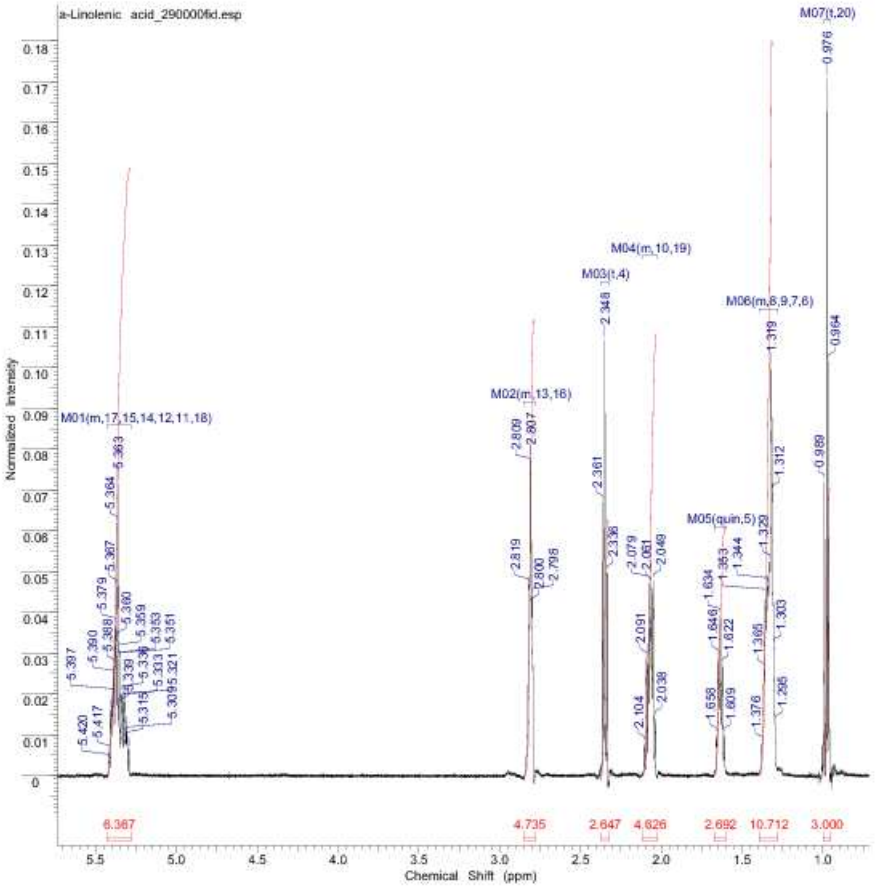
4-t-Butylphenol

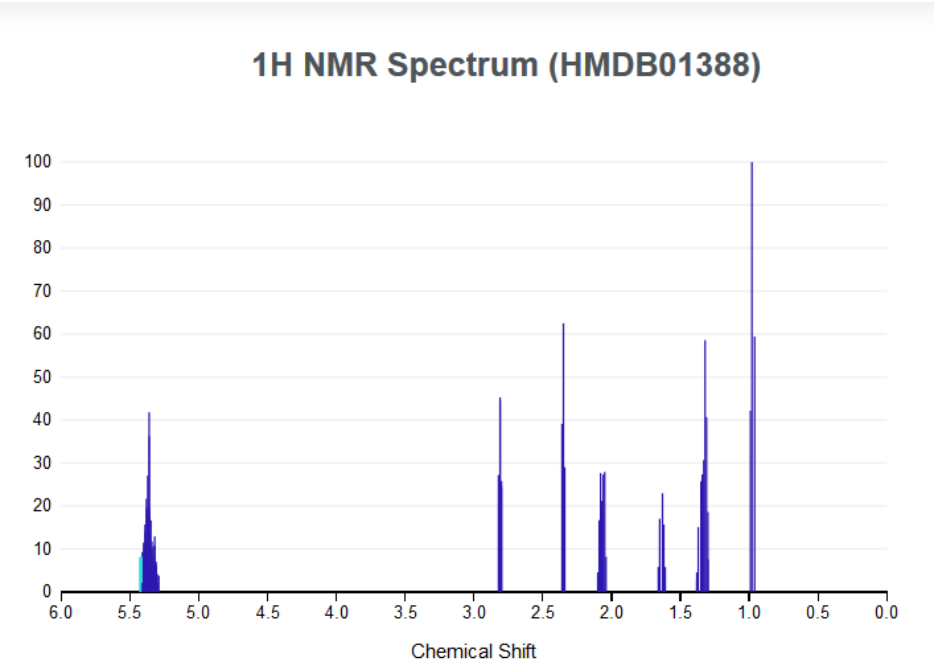
a-Linolenic acid (HMDB01388)

1H NMR spectrum: 600 MHz in $_3$CDCl

Sample:50 mM

Referenced to TMS





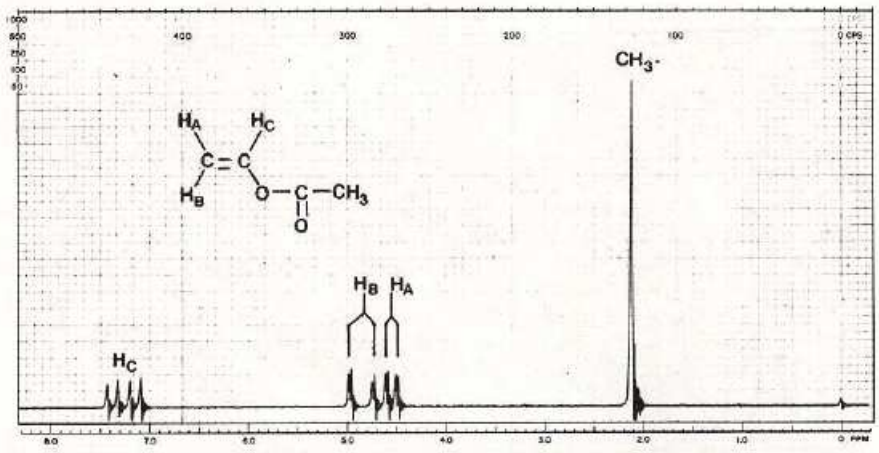


FIGURE 4–12 The NMR Spectrum of Vinyl Acetate

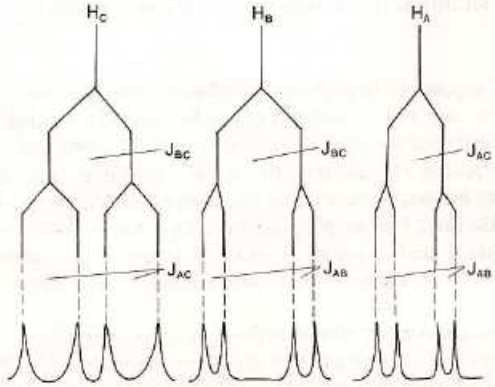
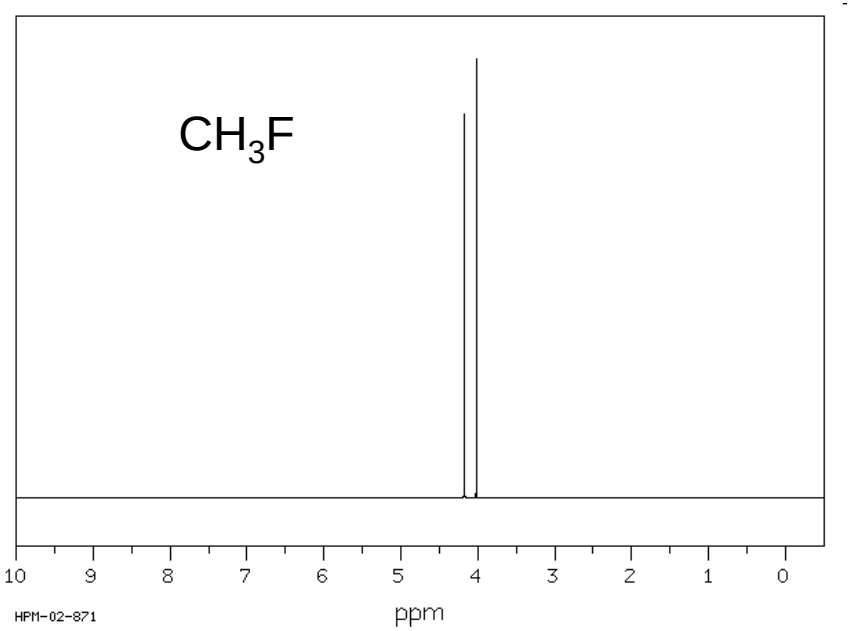
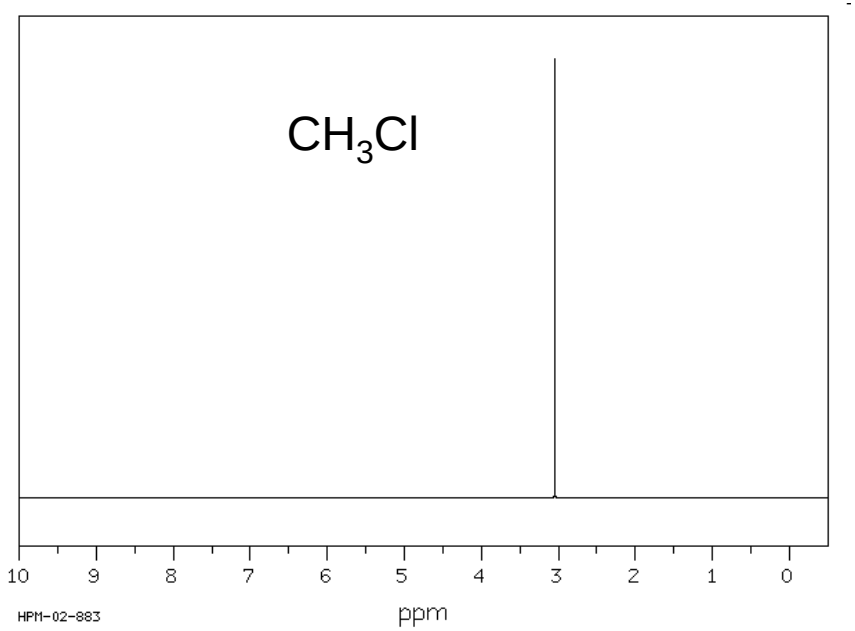


FIGURE 4–13 A Graphical Analysis of the Splittings in Vinyl Acetate

Heteronuclear coupling





singlet			1			
doublet			1		1	
triplet		1		2		1
quartet		1		3		3		1
quintet	1		4		6		4		1
sextet	1		5		10		10		5		1

1.1.1
Proton NMR Spectrum of the Model Compound 1

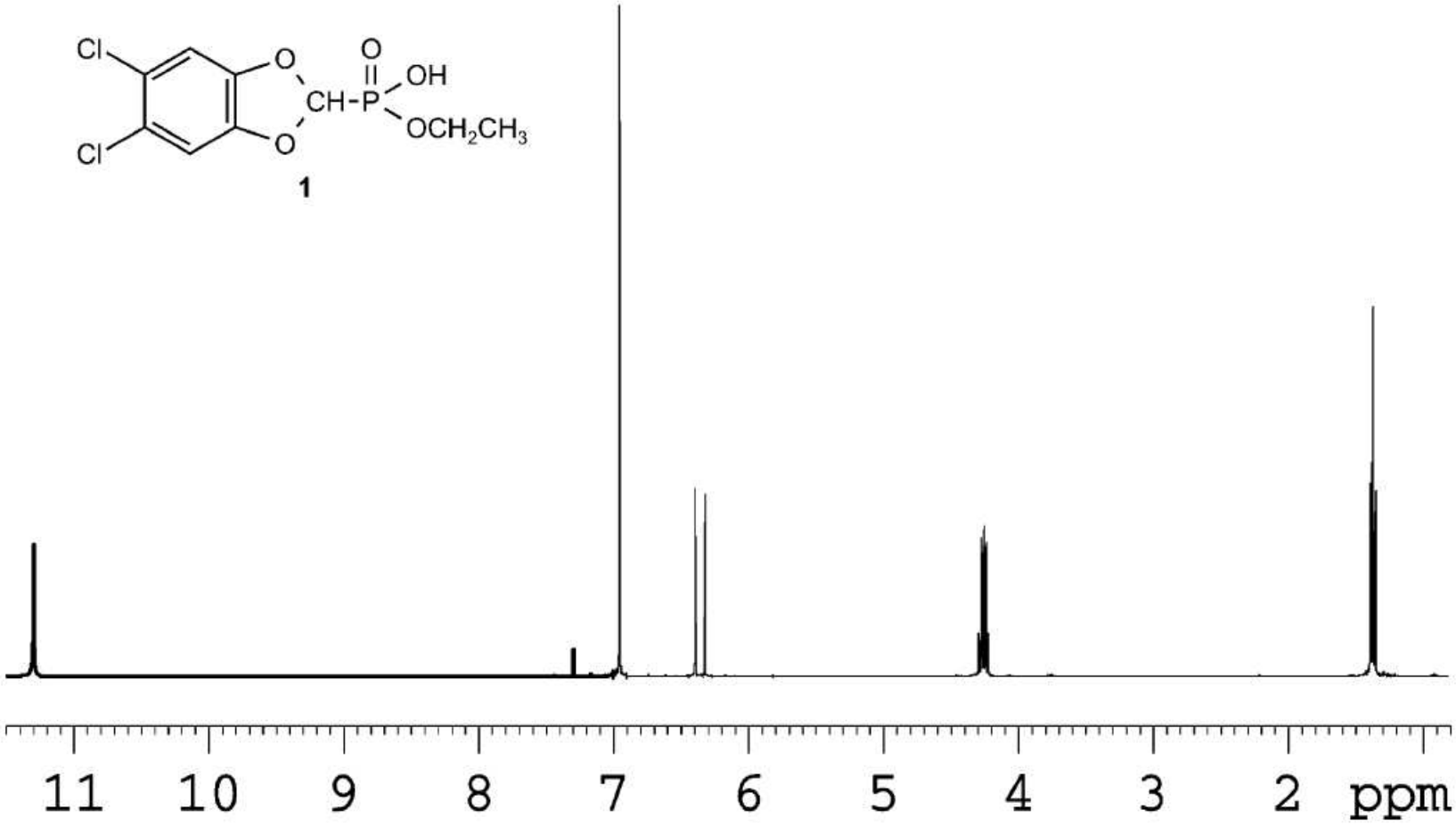


Fig. 1 Proton spectrum of compound **1** at 200 MHz. Signal assignment (from *left to right*): OH proton (singlet), aromatic protons (singlet), methine proton (doublet), OCH_2 protons (*apparently* a quintet), CH_3 protons, triplet. The small signal at 7.24 ppm is due to $CHCl_3$

Table 1 Result of a prediction compared with the actual values

Chemical shift (ppm)	J_{HP} (Hz)	Chemical shift (calc.)	J_{HP} (calc.)	Assignment
11.58	0	10.6	0	OH
6.92	not observed	7.0	0.3	CH_{arom}
6.32	28.7	6.6	16.9	CH-P
4.20	8.0	4.2	8.4	CH_2
1.33	0.6	1.3	1.0	CH_3

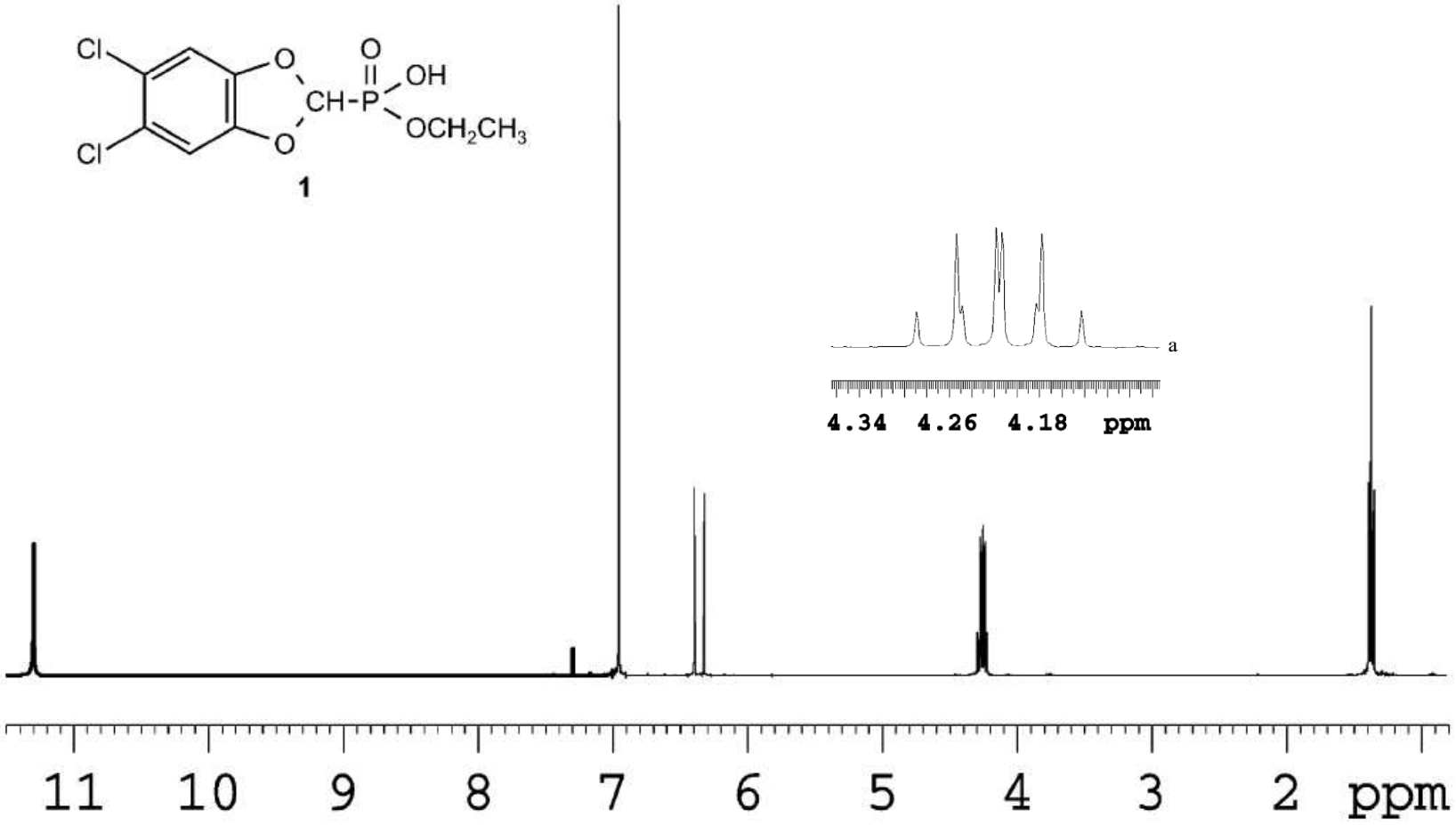
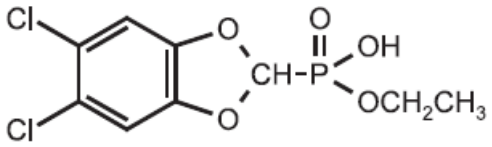
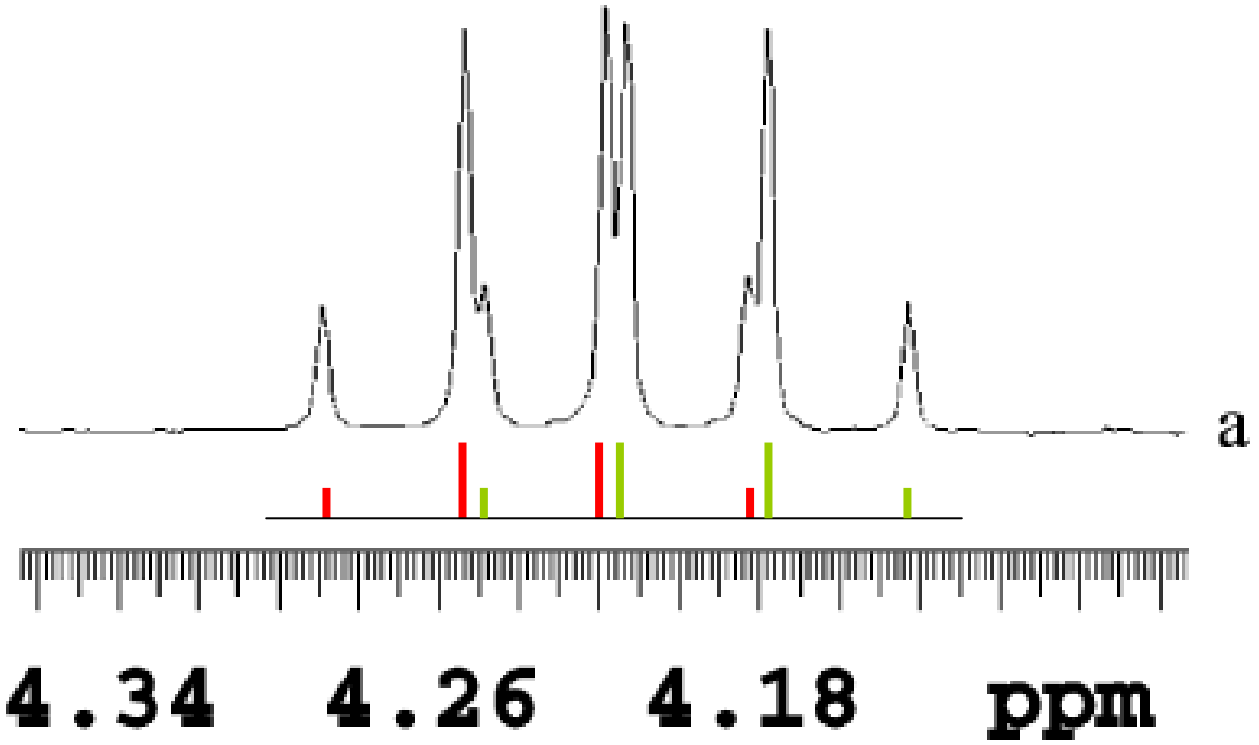


Fig. 1 Proton spectrum of compound **1** at 200 MHz. Signal assignment (from *left to right*): OH proton (singlet), aromatic protons (singlet), methine proton (doublet), OCH_2 protons (*apparently* a quintet), CH_3 protons, triplet. The small signal at 7.24 ppm is due to $CHCl_3$



1



Heterodecoupling
^{31}P

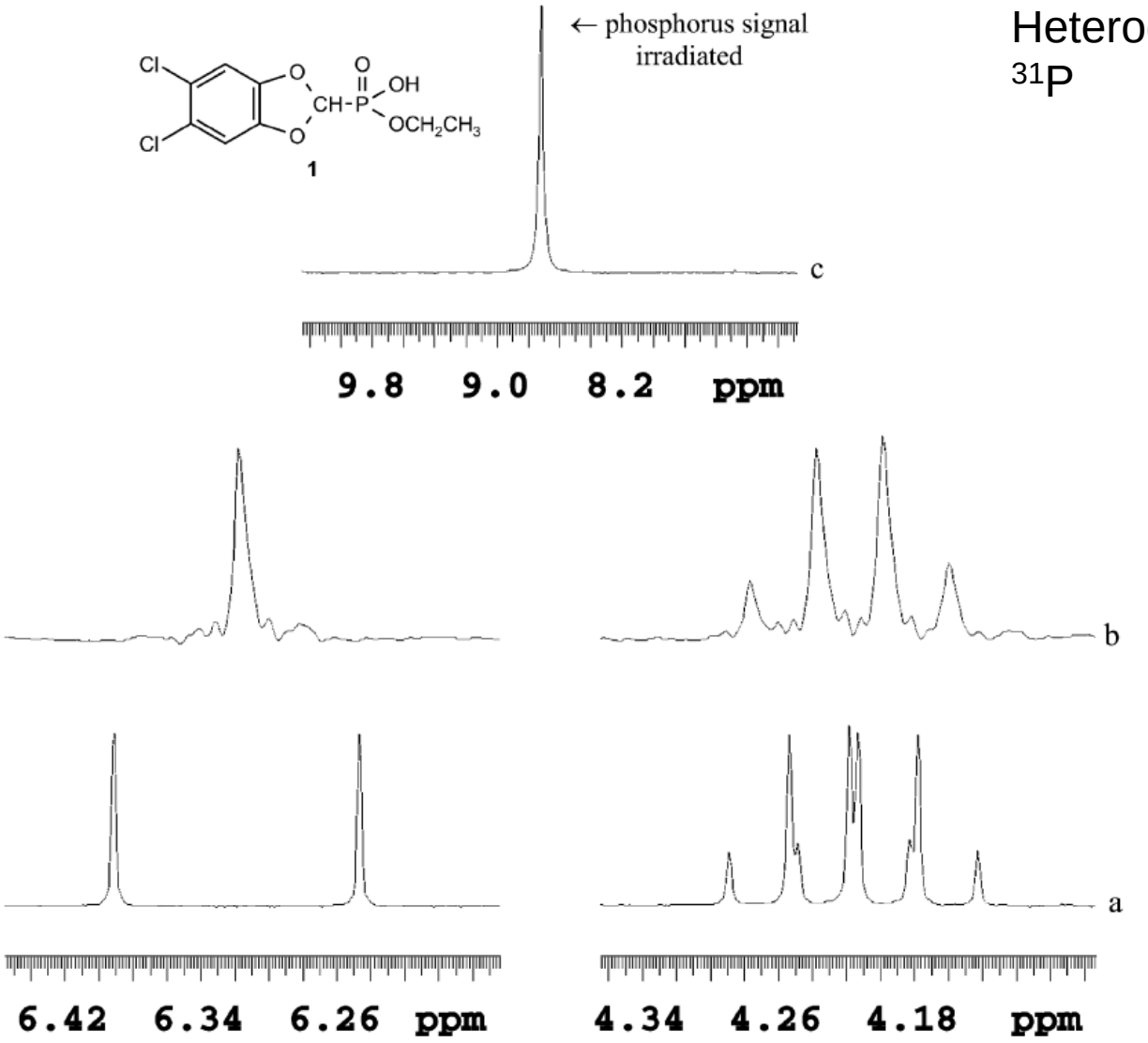


Fig. 2a–c Heterodecoupling experiment on compound 1 (at 200 MHz). a Undecoupled methine and methylene signals; b signals after decoupling of the phosphorus. c ^{31}P spectrum, showing the signal which is irradiated using the decoupling channel (channel 2)

Homodecoupling
^1H

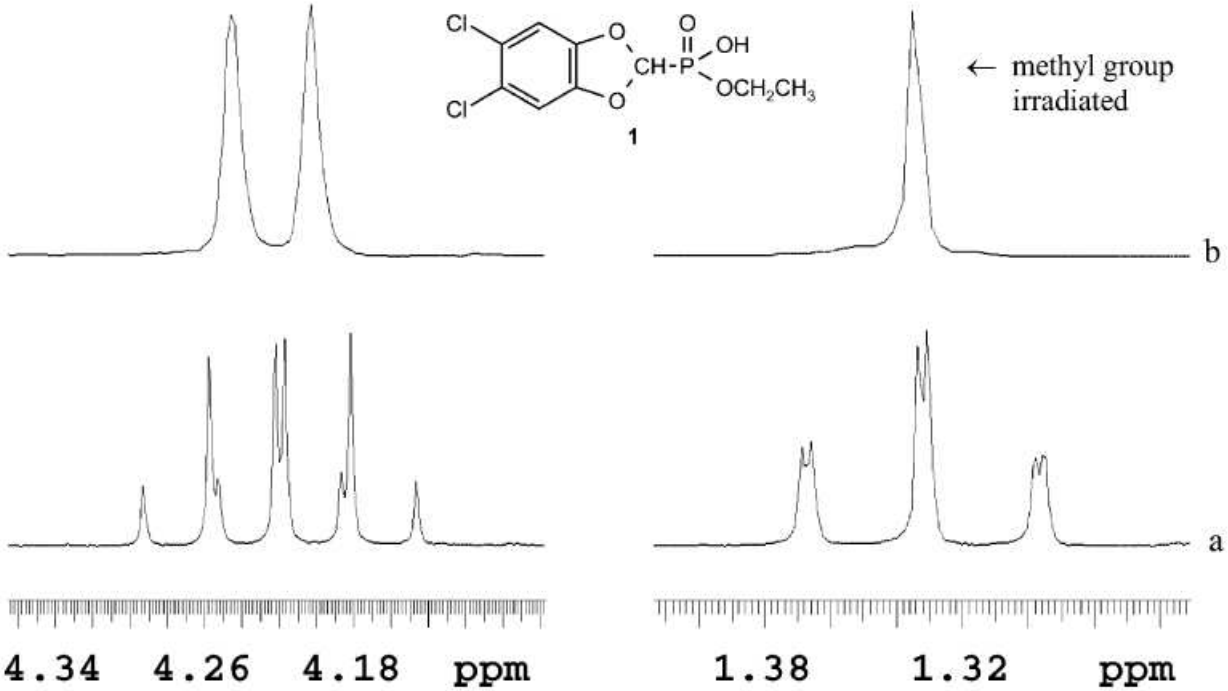


Fig. 3a,b Homodecoupling experiment on compound 1 (at 200 MHz). a Undecoupled methylene and methyl signals; b signals after irradiation of the methyl group