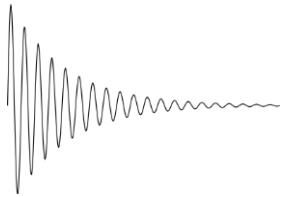
UNIVERSITY OF TARTU
1632

LOKT.06.014

Analüütiline keemia II



Tuumamagnetresonantsspektroskoopia (TMR)

seminar

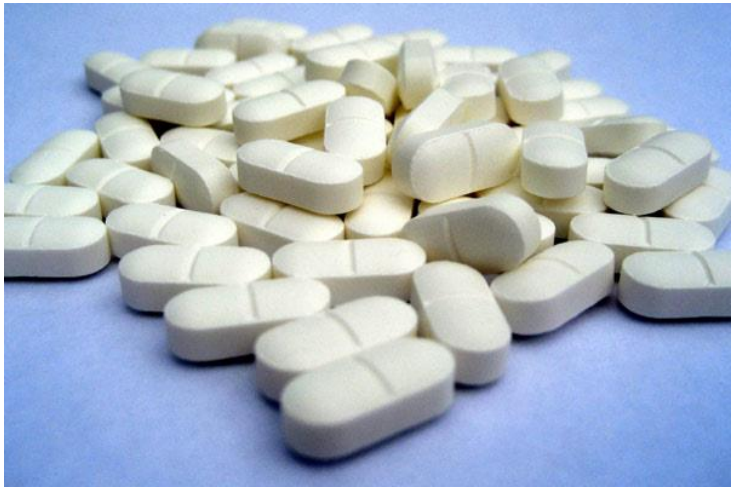
2015-04-28

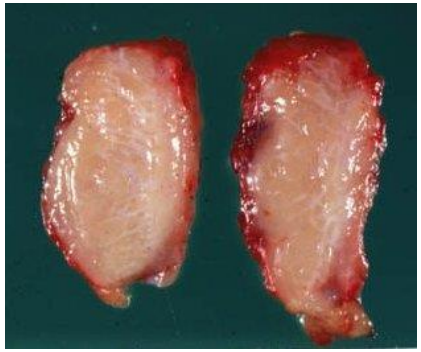
Lauri Toom

lauri.toom@ut.ee

http://kodu.ut.ee/~laurit/AK2/

Proov





Mõned TMR-spektroskoopia rakendusvaldkonnad

Orgaanilises ja analüütilises keemias:

- *orgaaniliste ühendite struktuuri määramine,*
- *orgaaniliste reaktsioonide produktide puhtuse ja saagiste määramine toorsegus,*
- *reaktsioonide kineetika ja mehhanismide uurimine, termodünaamiliste parameetrite määramine,*
- *ühendite happelisuse või aluselisuse määramine.*

Bioloogilistes süsteemides:

- *peptiidide struktuuri määramine ja dünaamilise käitumise uurimine lahusefaasis,*
- *ensüüm-substraadi reaktsioonide kineetika uurimine,*
- *diffusiooniprotsesside uurimine lahustes,*
- *reaktsioonide mehhanismide uurimine,*
- *metaboliitide määramine,*
- *looduslikest materjalidest ekstraheeritud (või muul moel eraldatud) ainete analüüs ja kvantifitseerimine,*
- *bioaktiivsete ainete läbisõelumine (screening),*
- *rakumembraaniproteiinide ja biopsia proovide uurimine HR-MAS-iga.*

Materjaliteaduses, arheoloogias, geoloogias:

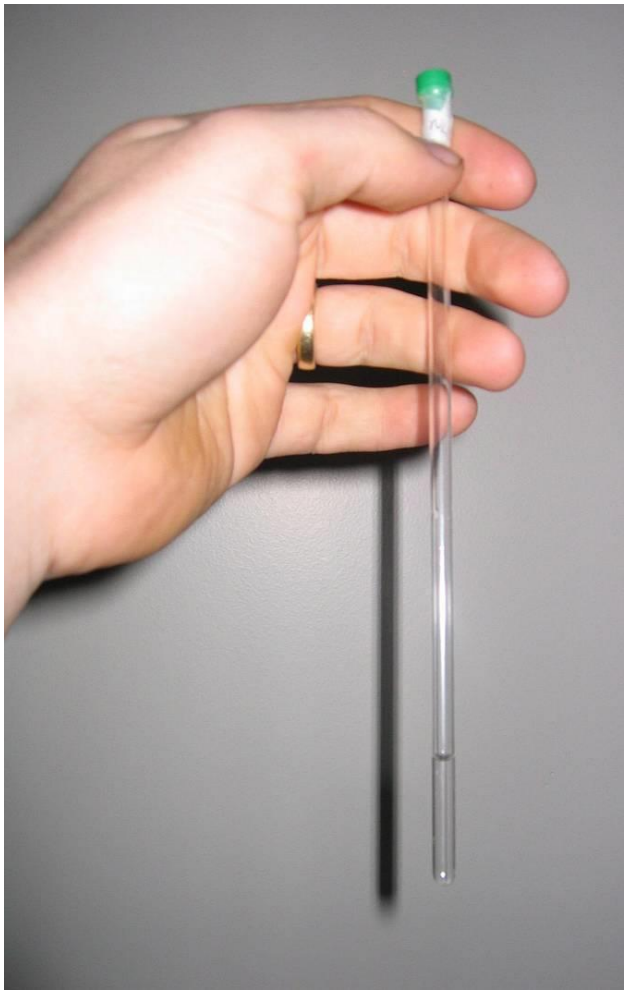
- *polümeeride ja mineraalide uurimine.*

Proovi valmistamine TMR-analüüsiks

Uuritav proov

TMR katseklaasid
(tuubid)

→



Lahusti (deutereeritud)

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TMR spektromeetrid Tartus

200 MHz

(4,7 T, 46975 G magnet)

Chemicumis

400 MHz

(9,4 T, 93980 G magnet)

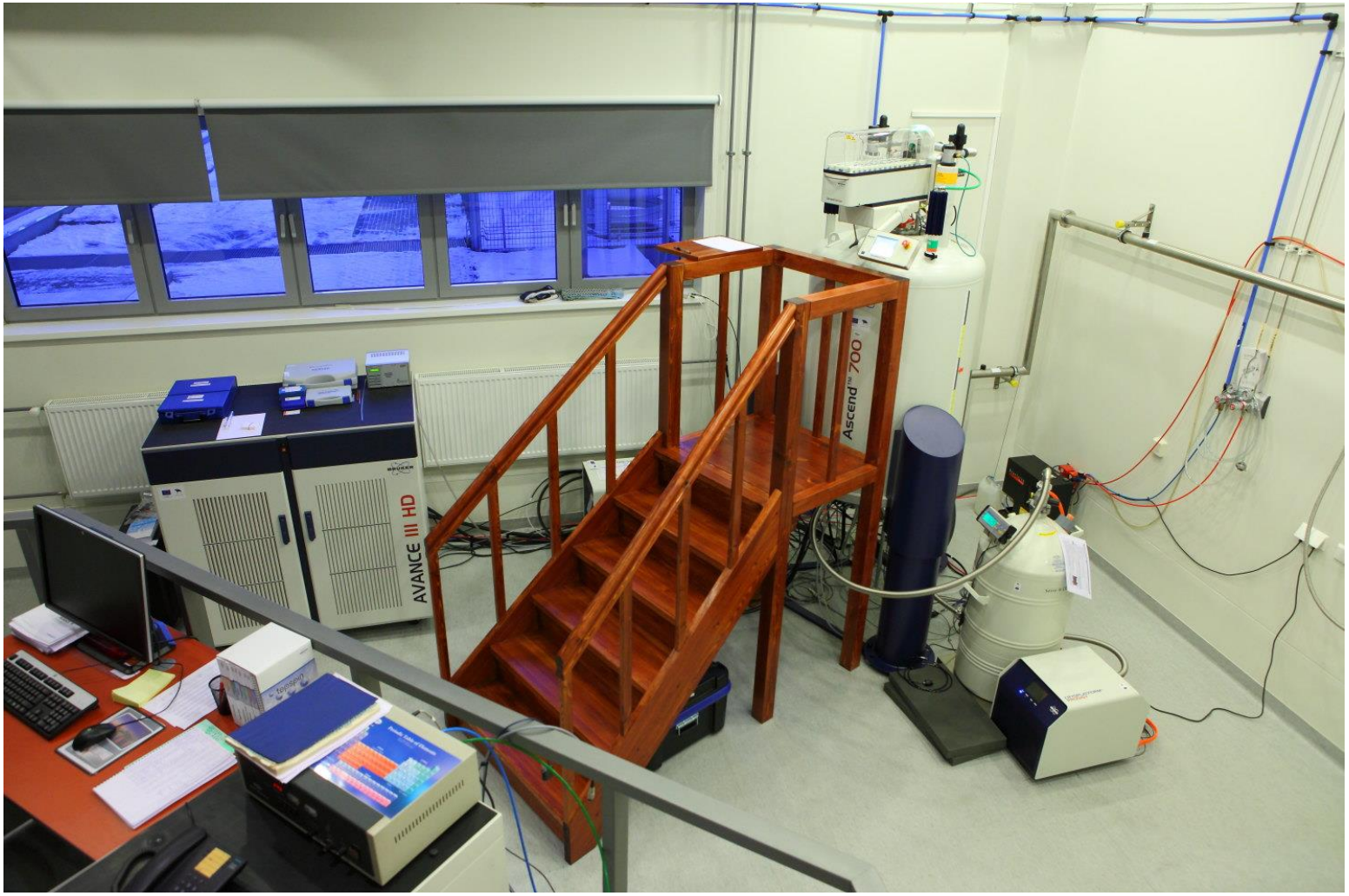
Tehnoloogiainstituudis

700 MHz

(16,4 T, 164400 G magnet)

Chemicumis

TMR spektromeetrid Tartus

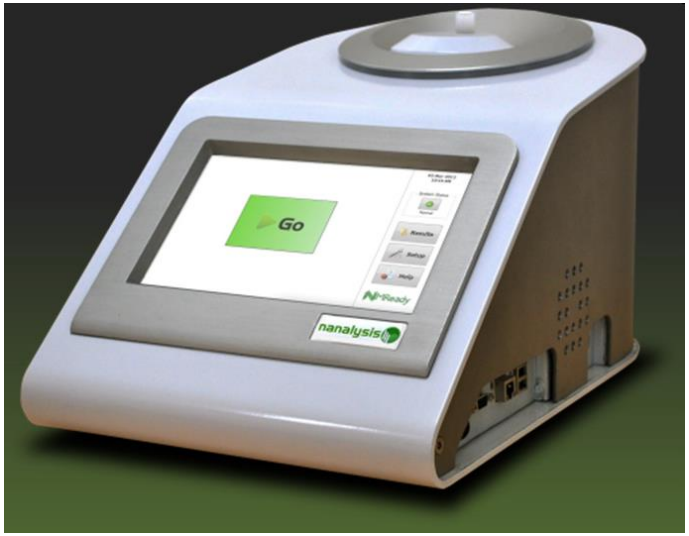


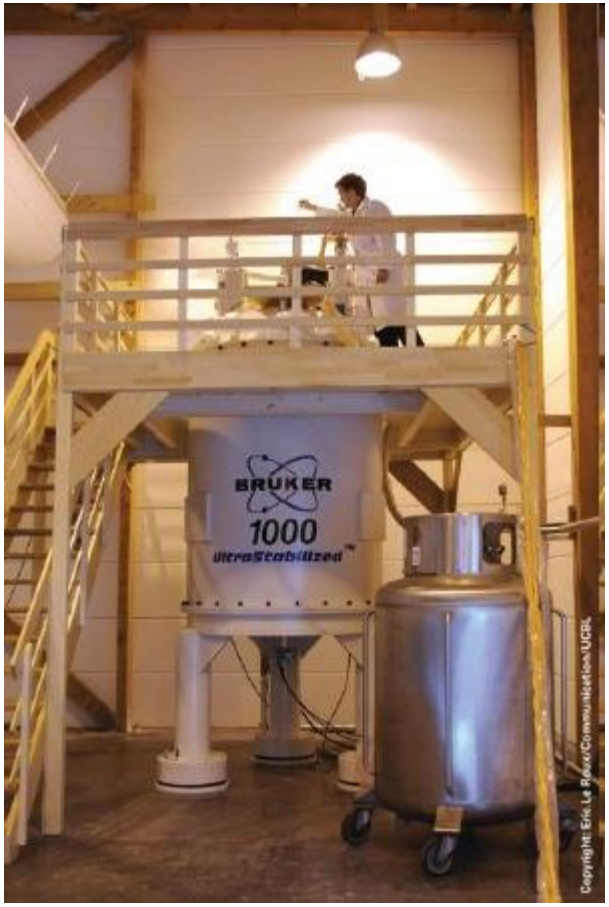
16,44 T (164400 G) magnet

Muud saadaolevad TMR spektromeetrid

picoSpin-45

NMReady 60P





Bruker 1,0 GHz magnet

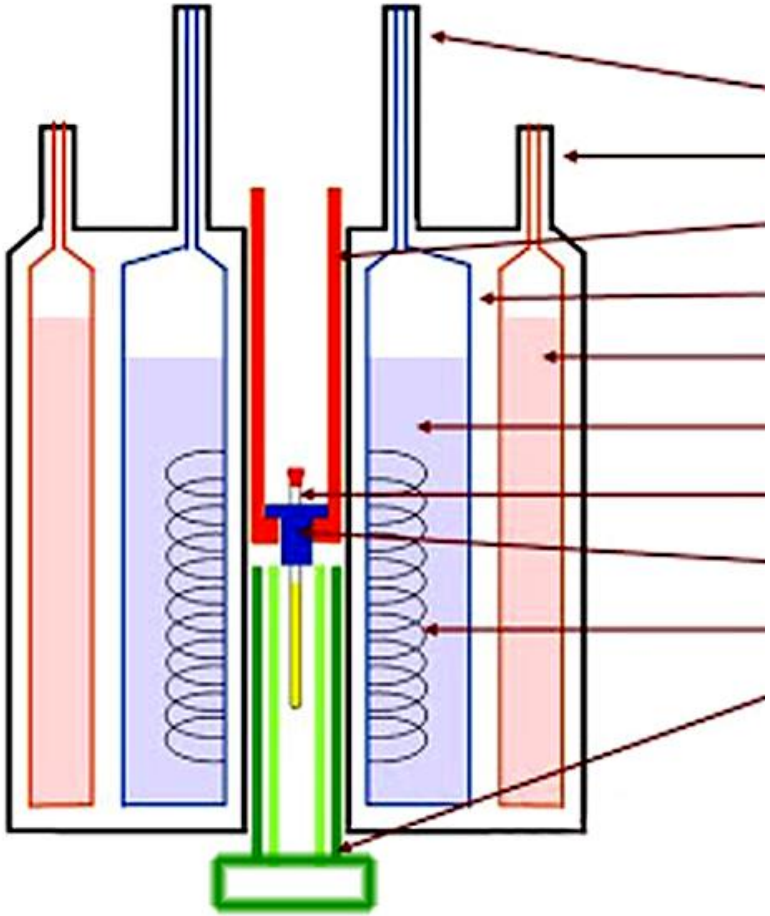
TMR spektromeetri põhikomponendid

Magnet
(töökorras)

Magnet
(siin lahtilõigatud näidis)

TMR spektromeetri põhikomponendid

Magneti skeem



vedela heeliumi (4 K) lisamiseks

vedela lämmastiku (77 K) lisamiseks

proovi vahetamise komponendid

vaakum ja isolatsioon

vedela lämmastiku (77 K, -196 °C) reservuaar

vedela heeliumi (4 K, -269 °C) reservuaar

uuritav proov

turbiin

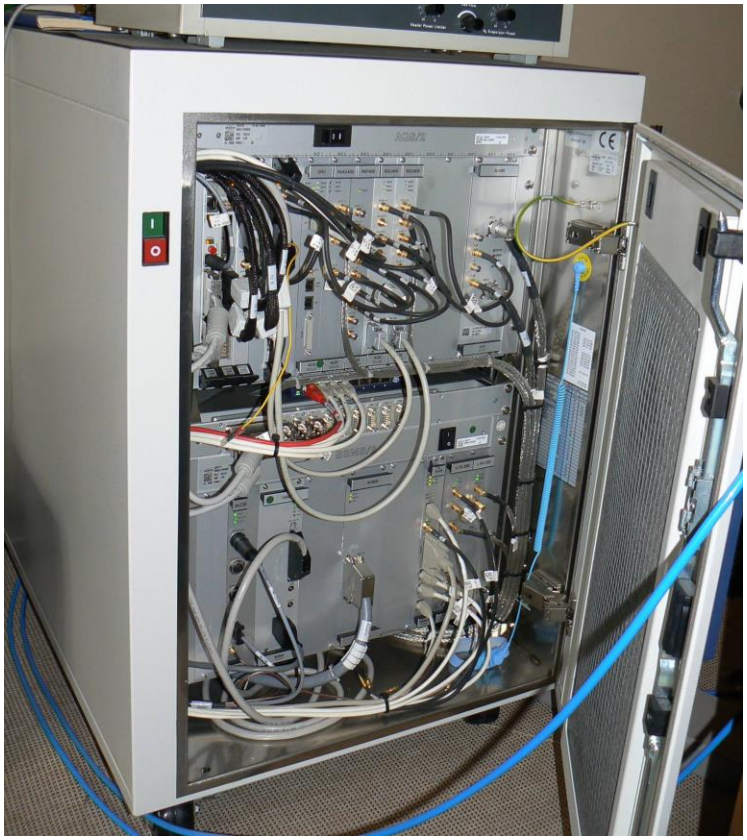
ülijuhtiva magneti (Nb_3Sn) mähised

mõõtepea

TMR spektromeetri põhikomponendid

Mõõtepead

TMR spektromeetri põhikomponendid



Konsoolid

TMR spektromeetri põhikomponendid

Temperatuurikontroller

Proovivahetaja

Perioodilisustabel

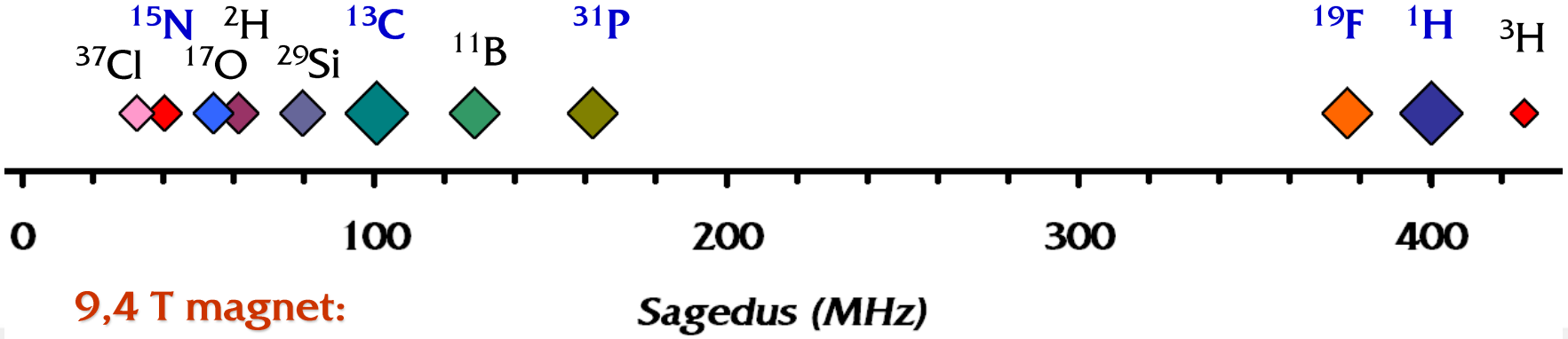
Group	I	II		IIIa	IVa	Va	VIa	VIIa	VIIIa	VIIIb	VIIIc	IB	IIB	III	IV	V	VI	VII	VIII
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanides			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinides			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Nuclear Spins	1/2	1	3/2	5/2	7/2	9/2

Kõige huvipakkuvamad TMR-aktiivsed isotoobid

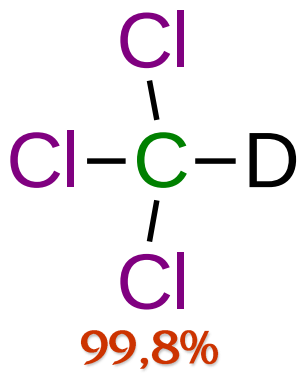
^{1}H, ^{13}C, ^{15}N, ^{19}F ja ^{31}P on 5 kõige tähtsamat TMR-aktiivset tuuma:

- ^{1}H – kõrge tundlikkuse ja laialdase esinemise tõttu orgaanilistes ühendites;
- ^{13}C – esinemise tõttu orgaanilistes ühendites, hoolimata sellest, et seda on võrreldes süsiniku peamise ^{12}C isotoobiga vähe (1,1%);
- ^{15}N – kuna N esineb sagedasti paljudes orgaanilistes ühendites, on tähtsal kohal sellistes biomolekulides nagu proteiinid ja DNA;
- ^{19}F – kõrge tundlikkuse tõttu;
- ^{31}P – orgaanilistes ühendites sagedase esinemise ja keskmise tundlikkuse tõttu.

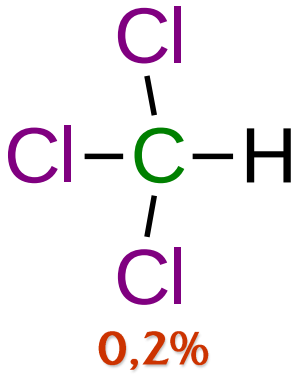


Näide: 99,8%D $CDCl_3$

Deutereeritud triklorometaan - üks tavalisemaid lahusteid, mida TMR-spektroskoopia proovide jaoks kasutatakse.



99,8%

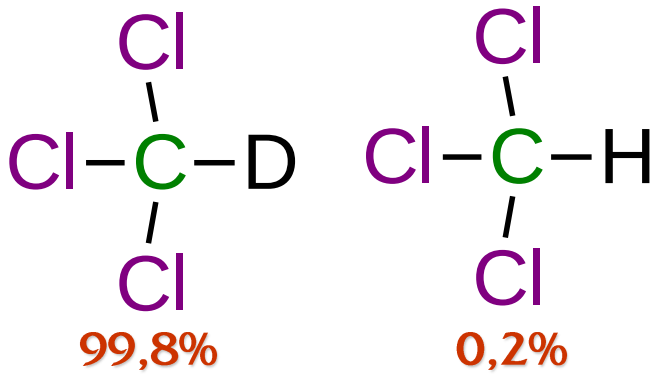


0,2%

Lisaks sisaldub seal väike kogus vett.

Hind on umbes 200 EUR liiter
(tavaline deutereerimata kloroform G.R. puhtusega maksab alla 10 EUR liiter).

Näide: 99,8%D $CDCl_3$



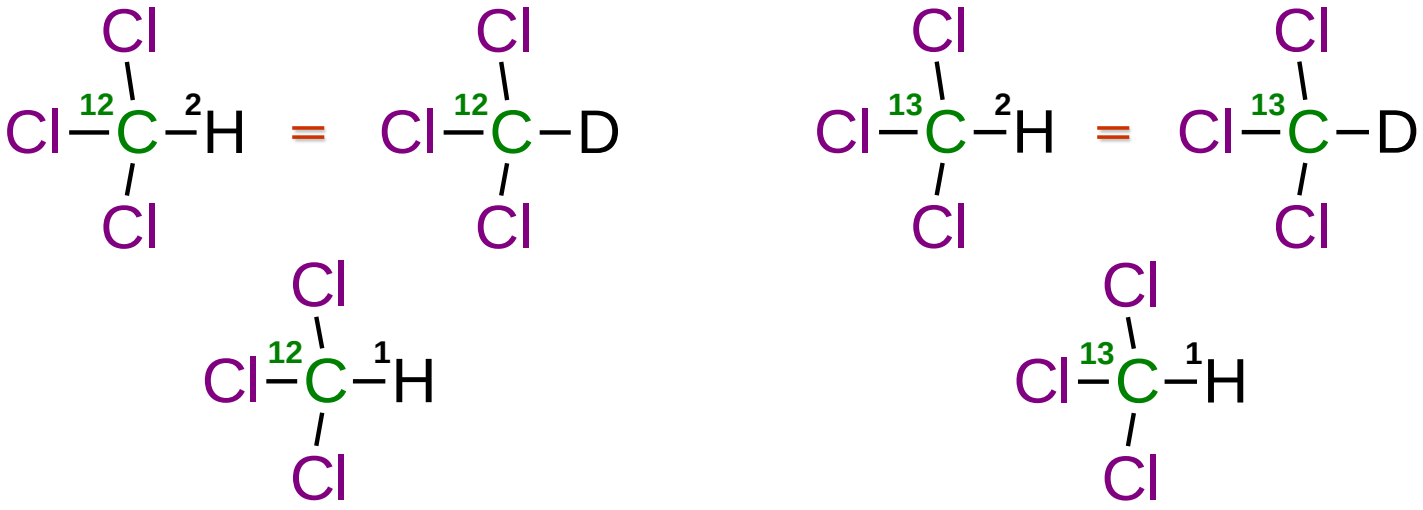
Isotoopide jaotus looduses:

Vesinik: ^{1}H – 99.99%
^{2}H – 0.01%

Süsinik: ^{12}C – 98.9%
^{13}C – 1.1%

Kloor: ^{35}Cl – 75.8%
^{37}Cl – 24.2%

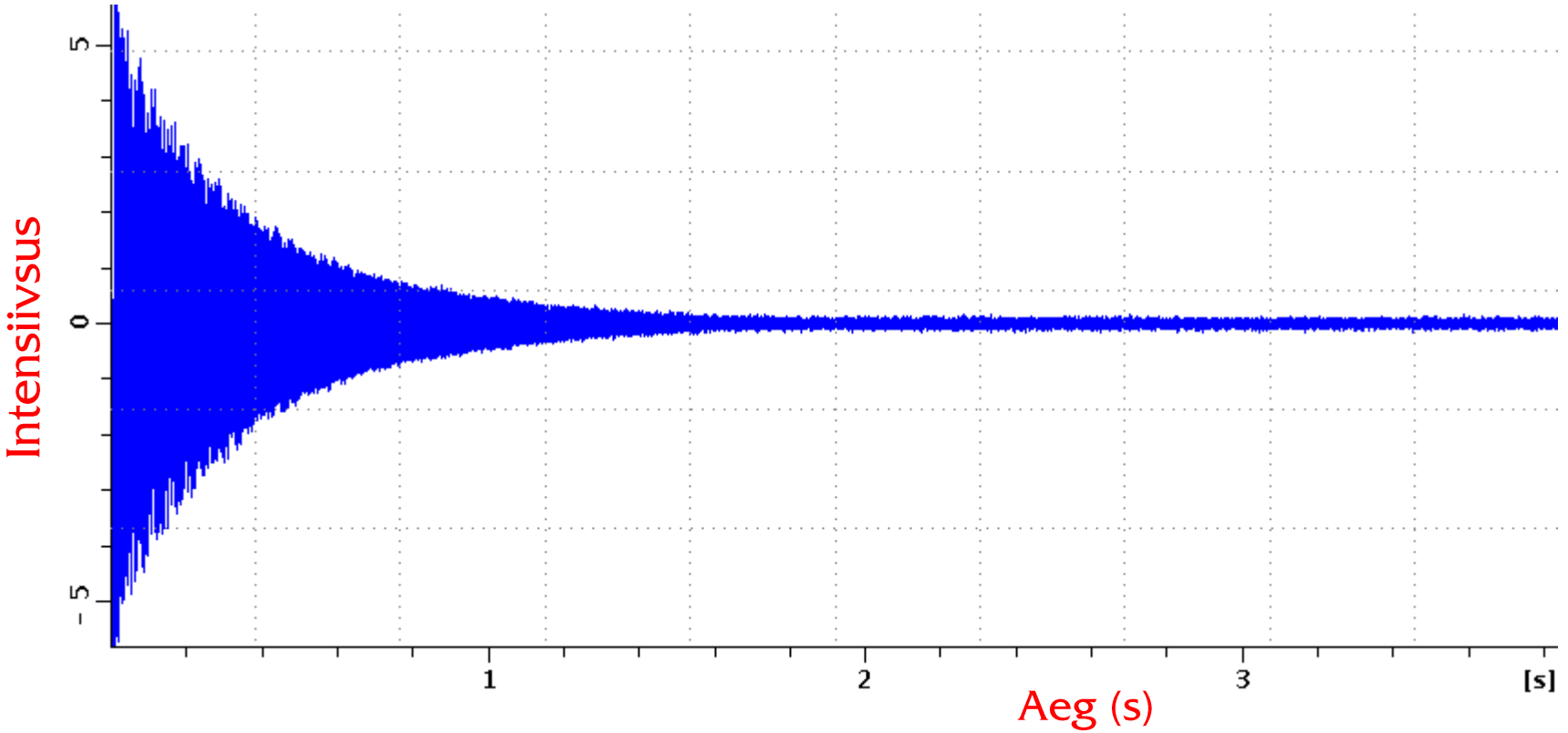
Põhilised isotopomeerid:



Lisaks Cl-isotoopidest ^{35}Cl ja ^{37}Cl tulenevad isotopomeerid.

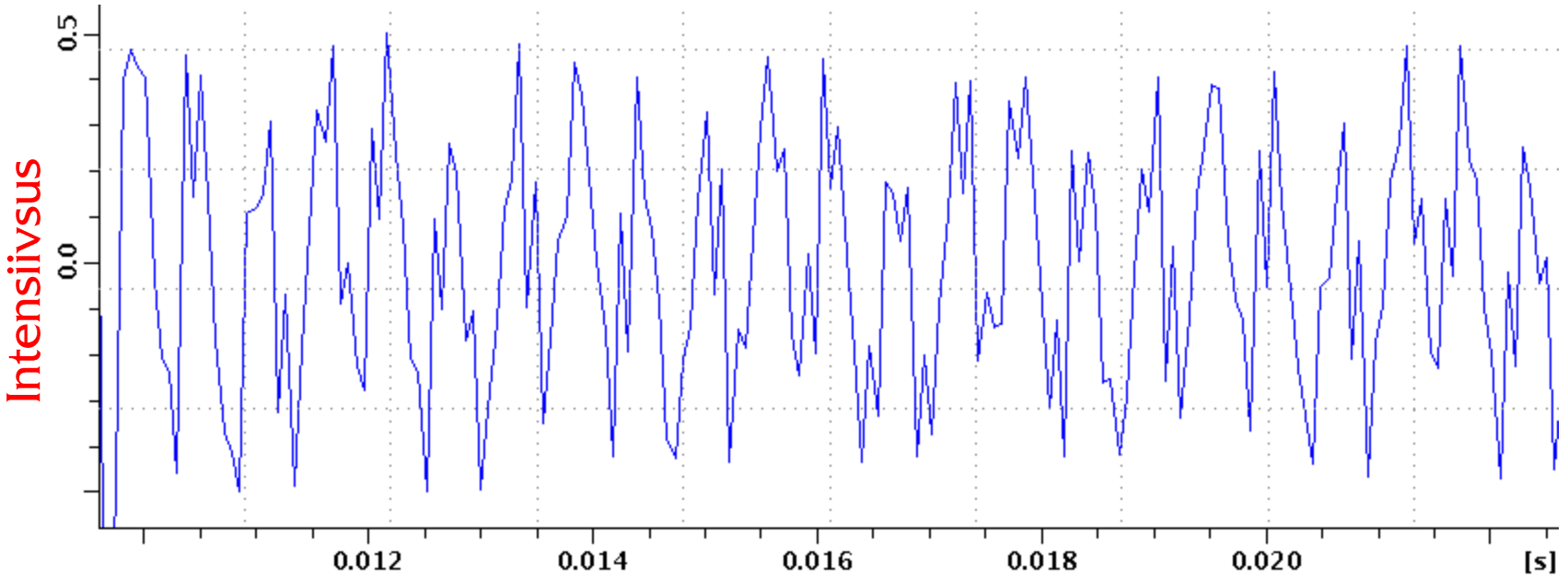
Näide: 99,8%D $CDCl_3$

^{1}H TMR fid (400,1 MHz)



* *fid* - free induction decay ("vaba induktsiooni hääbumine"), aeg/intensiivsus spekter

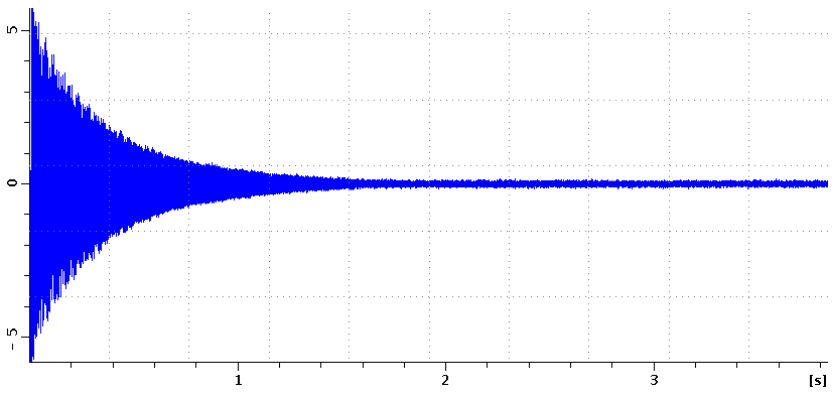
^{1}H TMR fid (400,1 MHz), suurendus:



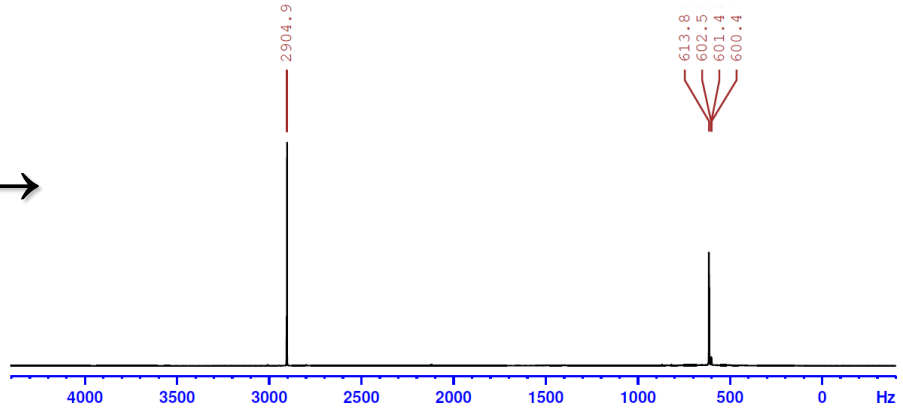
^{1}H TMR fid (400,1 MHz), suurendus, numbrilisel kujul:

…; 12670; 12019; 10628; 8987; 7635; 6934; 6909; 7237; 7392; 6884; 5497; 3392; 1043; -971; -2224; -2621; -2428; -2136; -2228; -2963; -4263; -5759; -6957; -7454; -7097; -6025; -4595; -3208; -2155; -1507; -1125; -751; -158; 726; 1756; 2617; 2938; 2457; 1147; -729; -2684; -4151; -4675; -4077; -2502; -363; 1829; 3648; 4894; 5595; 5913; 5968; 5719; 4945; 3376; 905; -2234; -5427; -7853; -8792; -7967; -5726; -2976; -848; -240; -1425; -3910; -6617; -8323; -8154; -5927; -2198; 2016; 5668; 8080; 9132; 9166; 8703; 8117; …

FID → Spekter + töötlemine

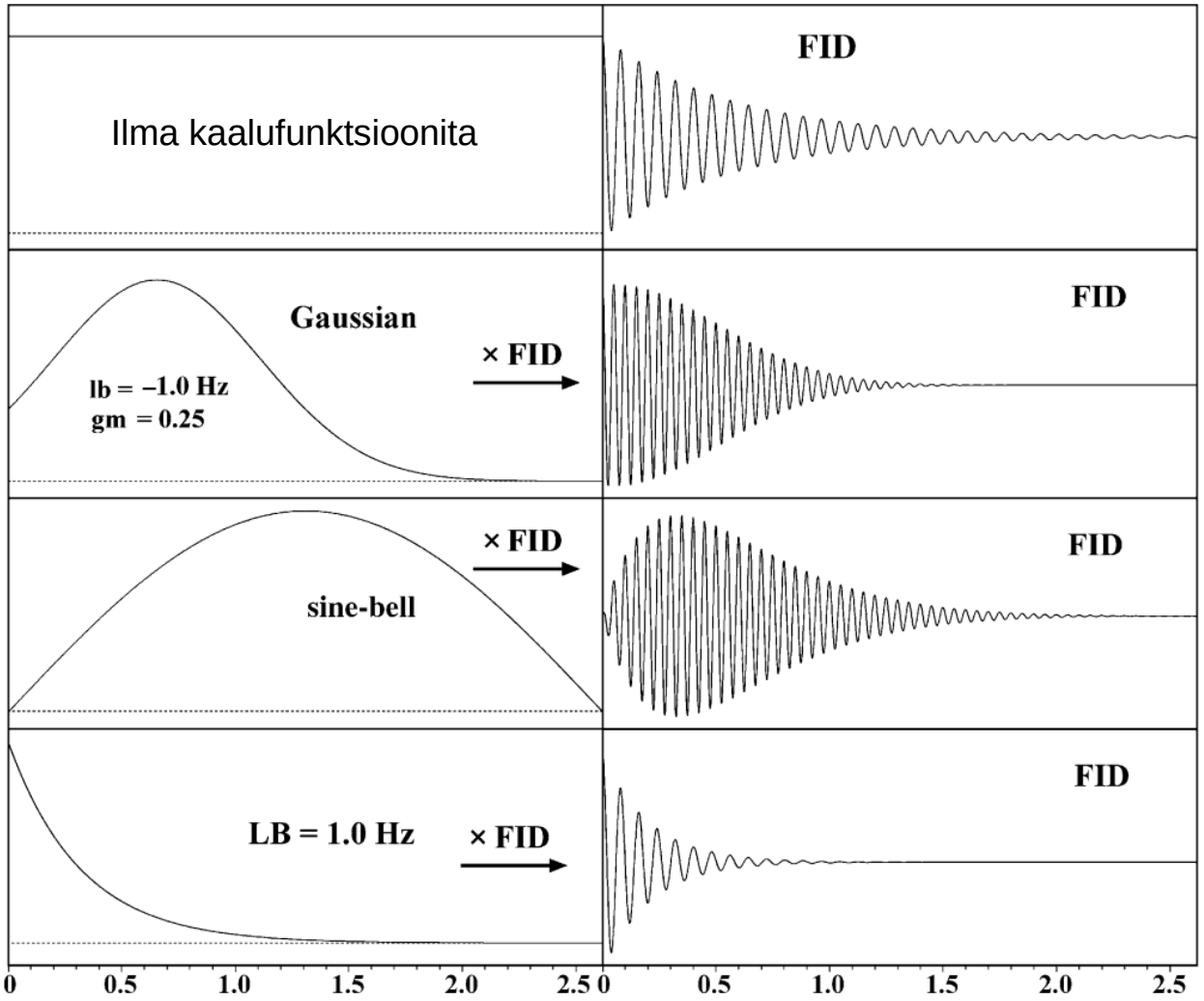


→

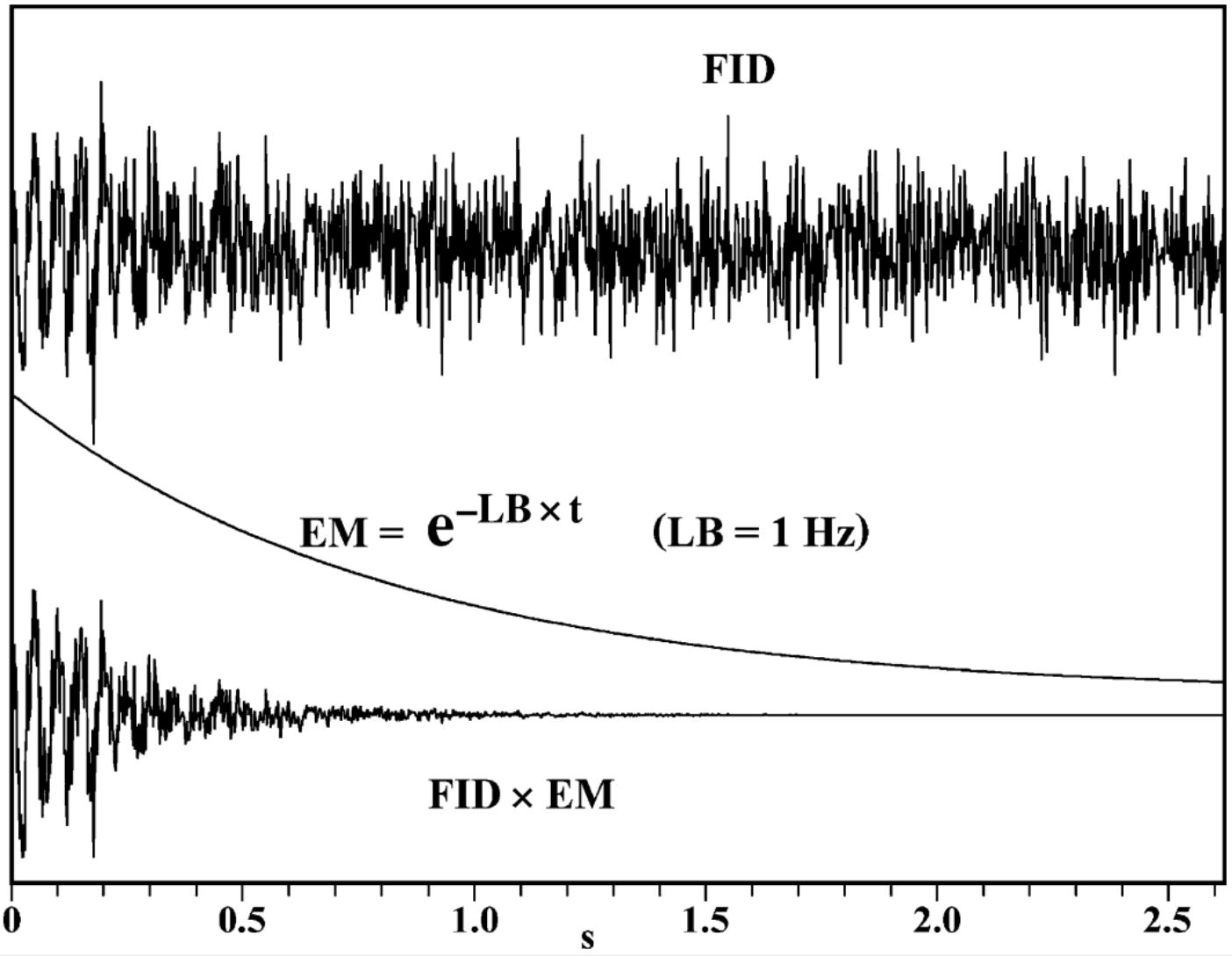


1) FID suuruse muutmine (punktide lisamine, eemaldamine, tuletamine).
2) Matemaatilise kaalufunktsiooniga läbikorrutamine (*inglise k. apodization*).
3) Fourier' teisendus.
4) Faseerimine.
5) Baasjoone korrektsioon.
6) Referentspunkti märkimine.
7) Signaalide integreerimine.

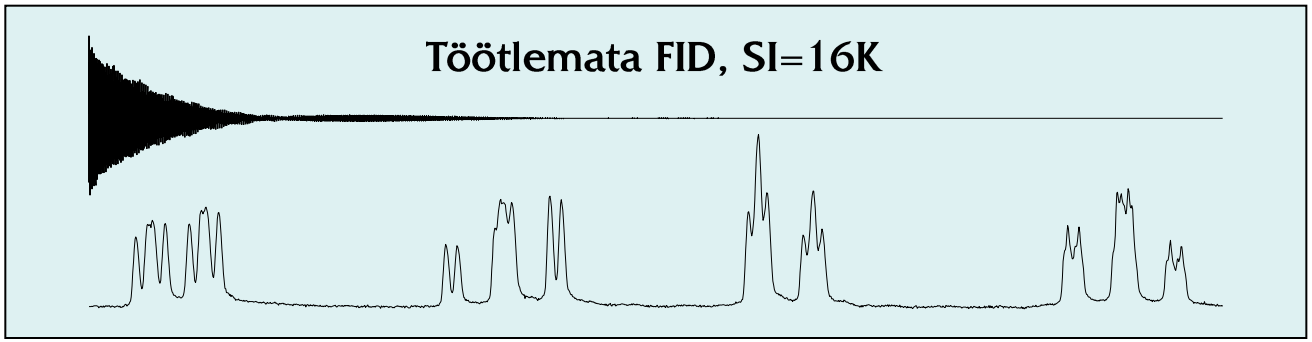
Matemaatilise kaalufunktsiooniga läbikorrutamine

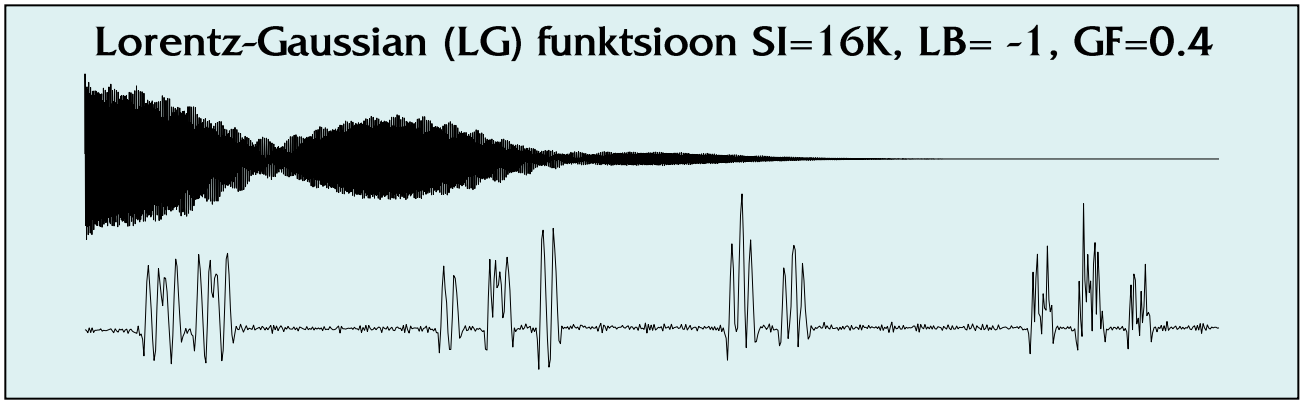


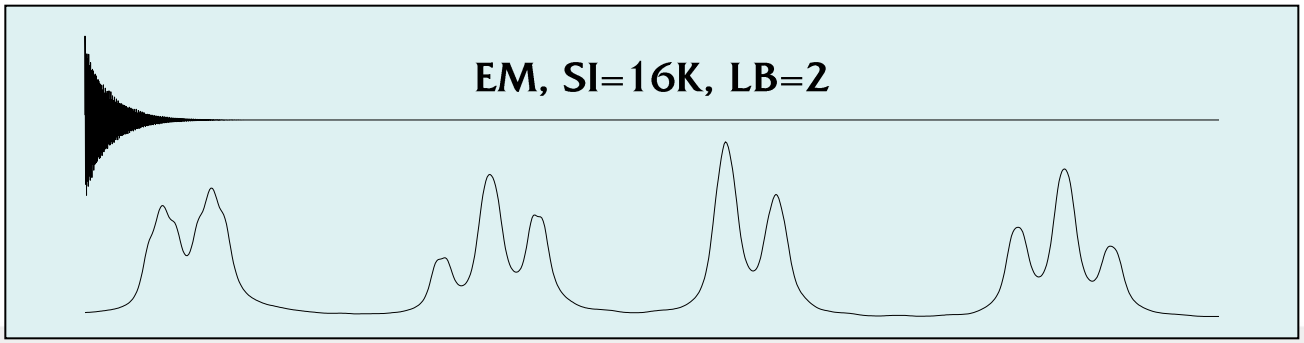
Matemaatilise kaalufunktsiooniga läbikorrutamine



Matemaatilise kaalufunktsiooniga läbikorrutamine



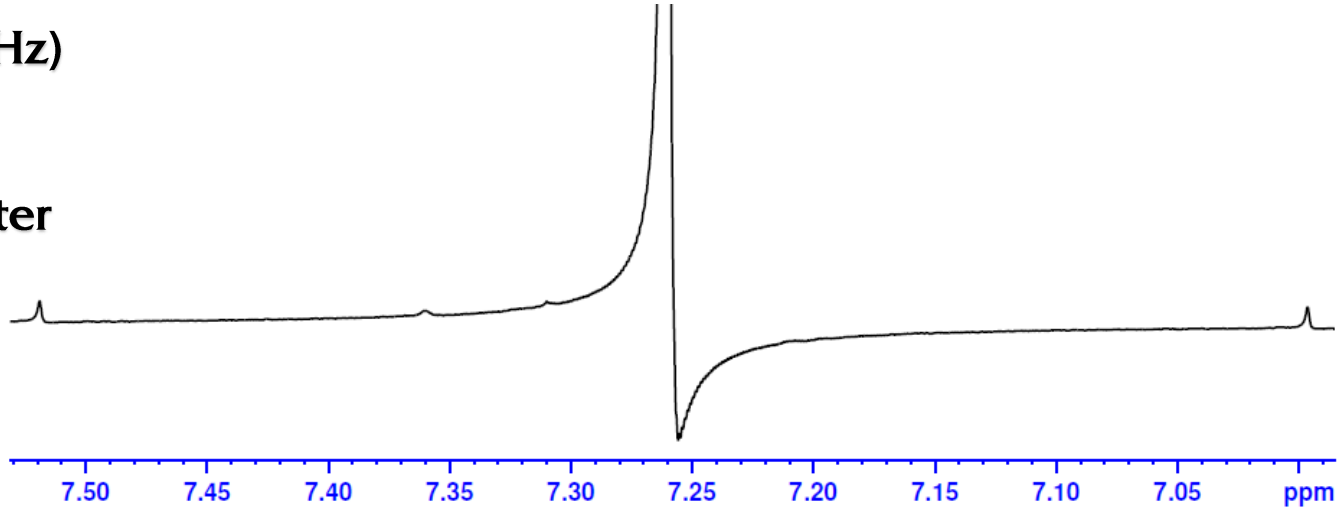




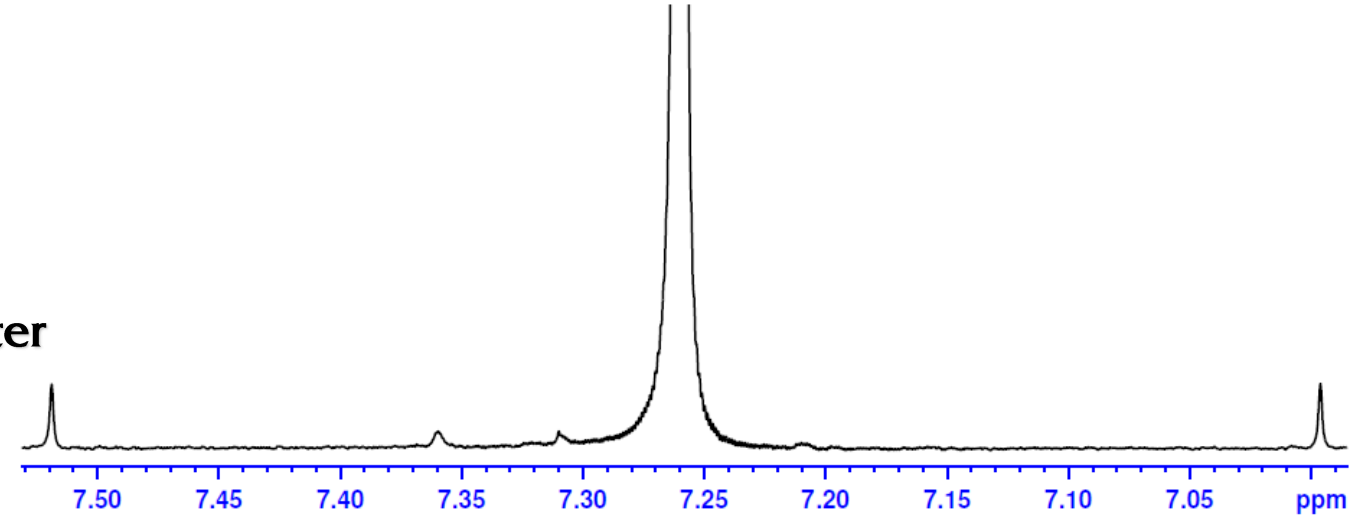
Spektri faseerimine

^{1}H TMR (400,1 MHz)
99,8%D $CDCl_3$

Faseerimata spekter



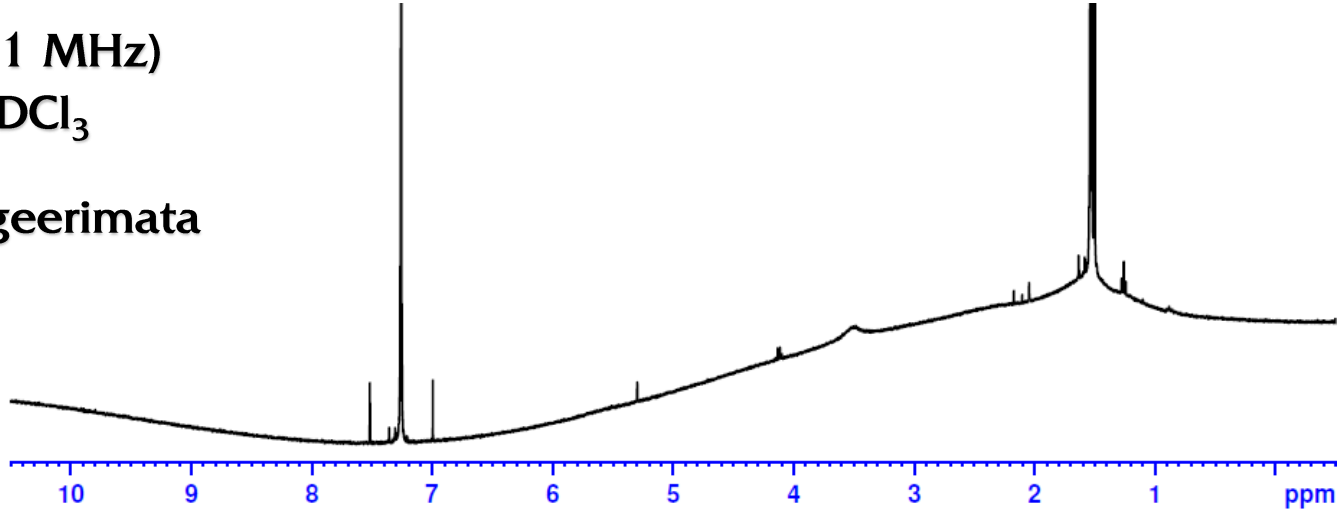
Faseeritud spekter



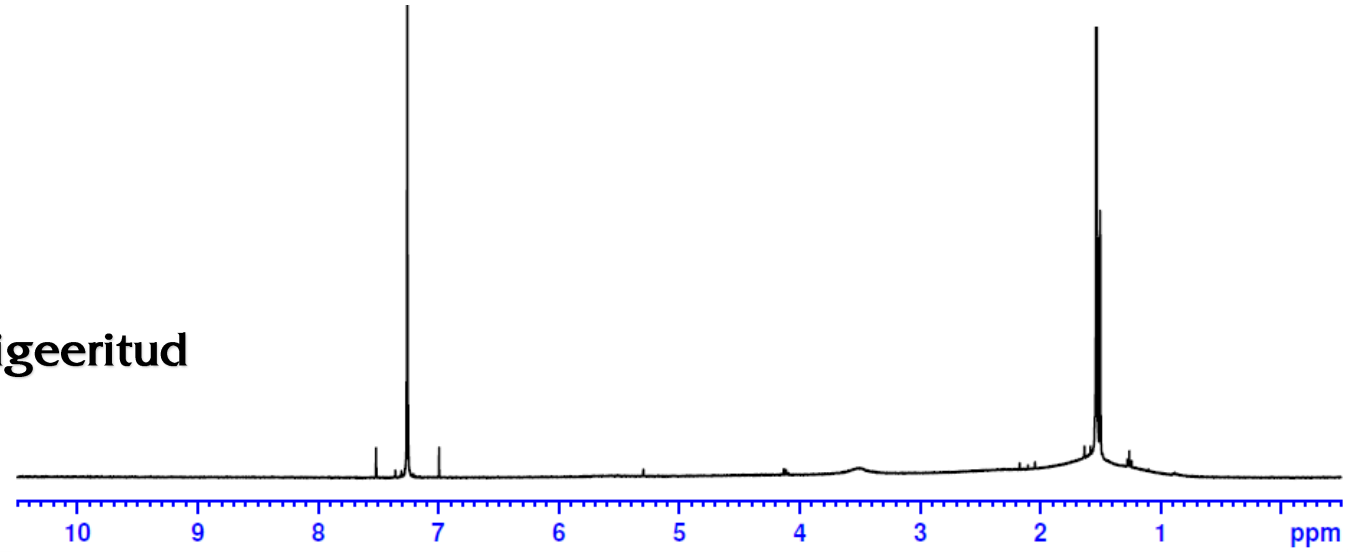
Baasjoone korrektsioon

^{1}H TMR (400,1 MHz)
99,8%D $CDCl_3$

Baasjoon korrigeerimata

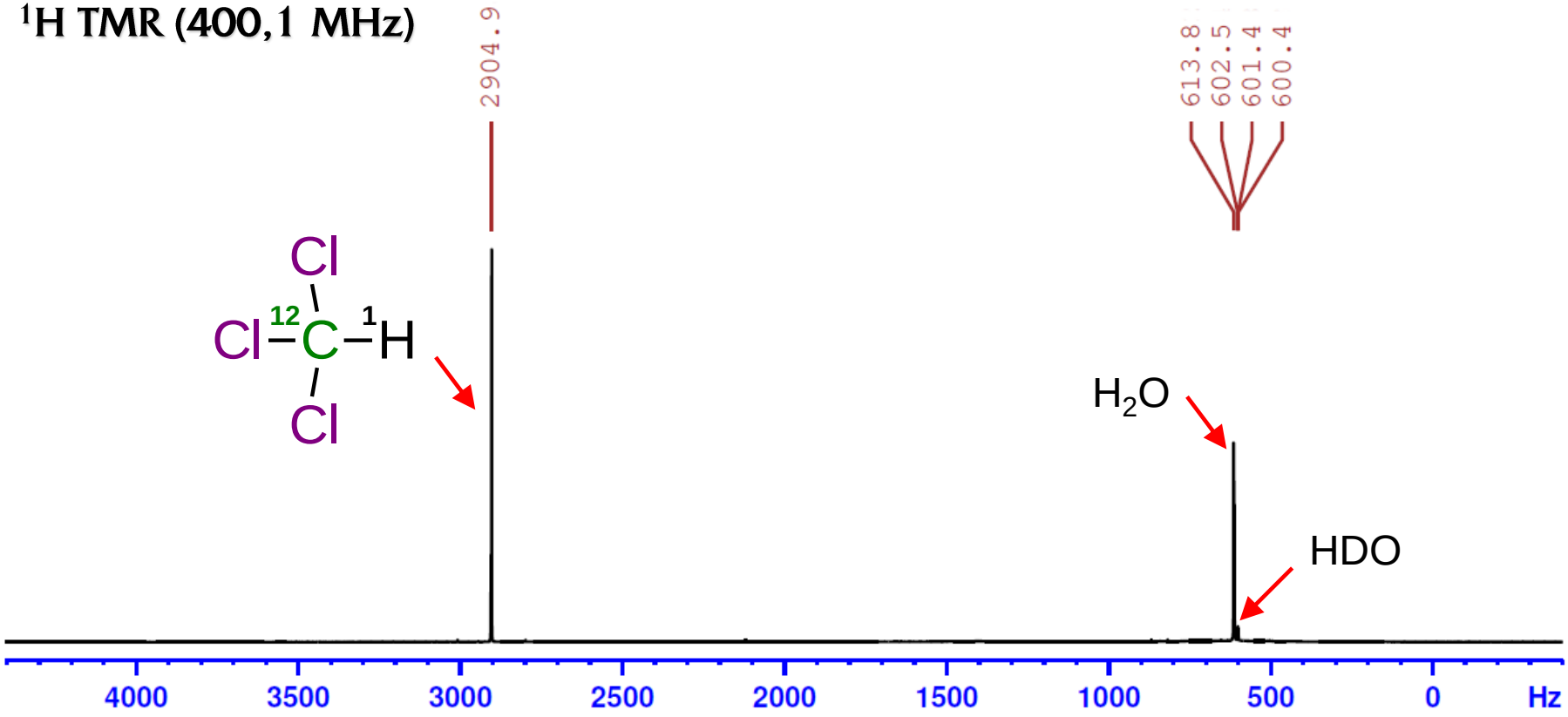


Baasjoon korrigeeritud



Näide: 99,8%D $CDCl_3$

^{1}H TMR (400,1 MHz)

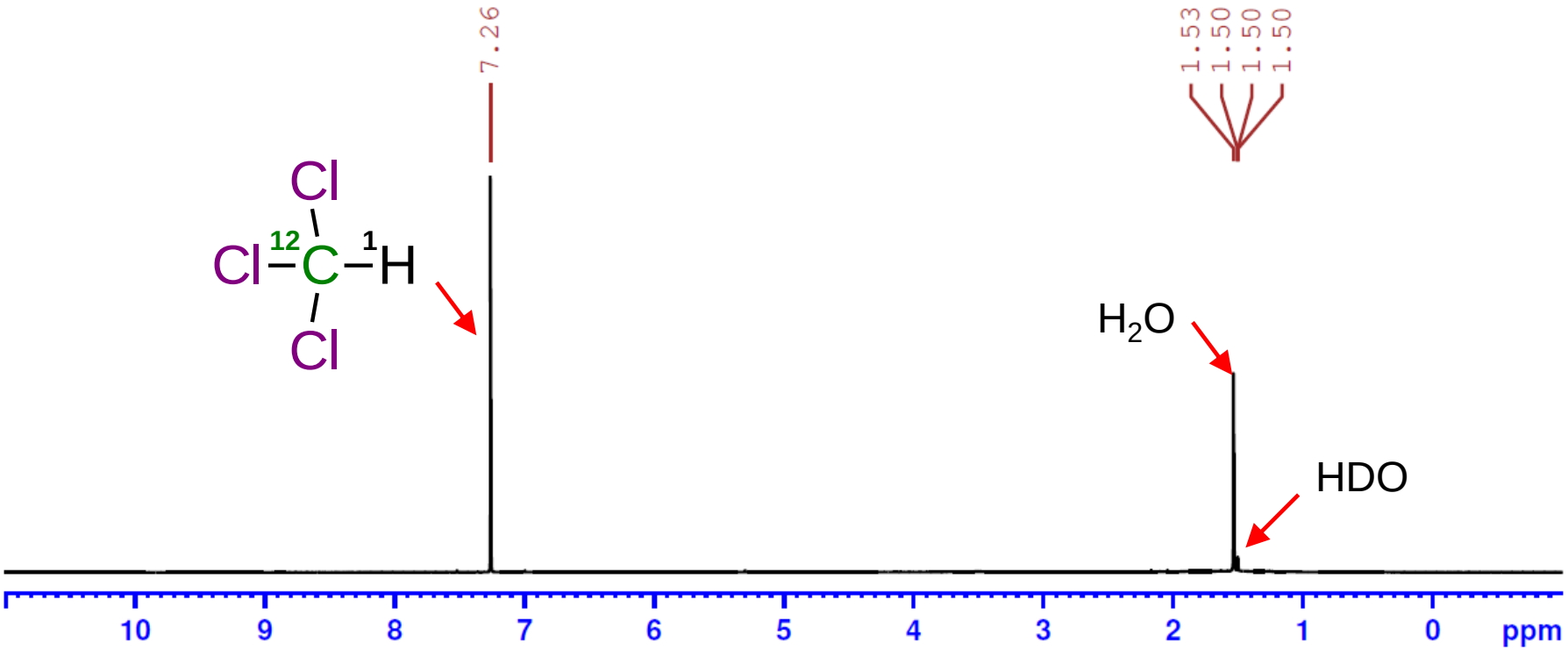


Skaala on hertsides!

ppm skaalasse teisendamine: $\delta = \dfrac{\nu - \nu_{ref}}{\text{spektromeetri sagedus}}$

Näide: 99,8%D $CDCl_3$

^{1}H TMR (400,1 MHz)



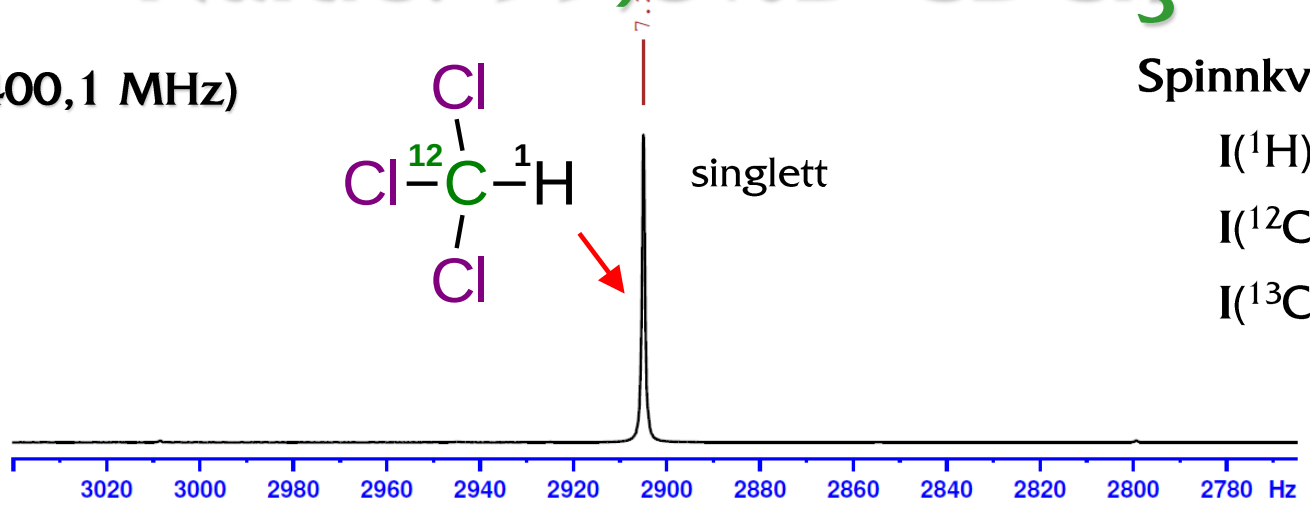
Skaala on ppm-ides!

$$\delta = \frac{\nu - \nu_{ref}}{\text{spektromeetri sagedus}}$$

Vahemik suurusega 1 ppm on vastavuses spektromeetri sagedusega:
näiteks praegusel spektril 1 ppm = 400,1 Hz

Näide: 99,8%D $CDCl_3$

^{1}H TMR (400,1 MHz)



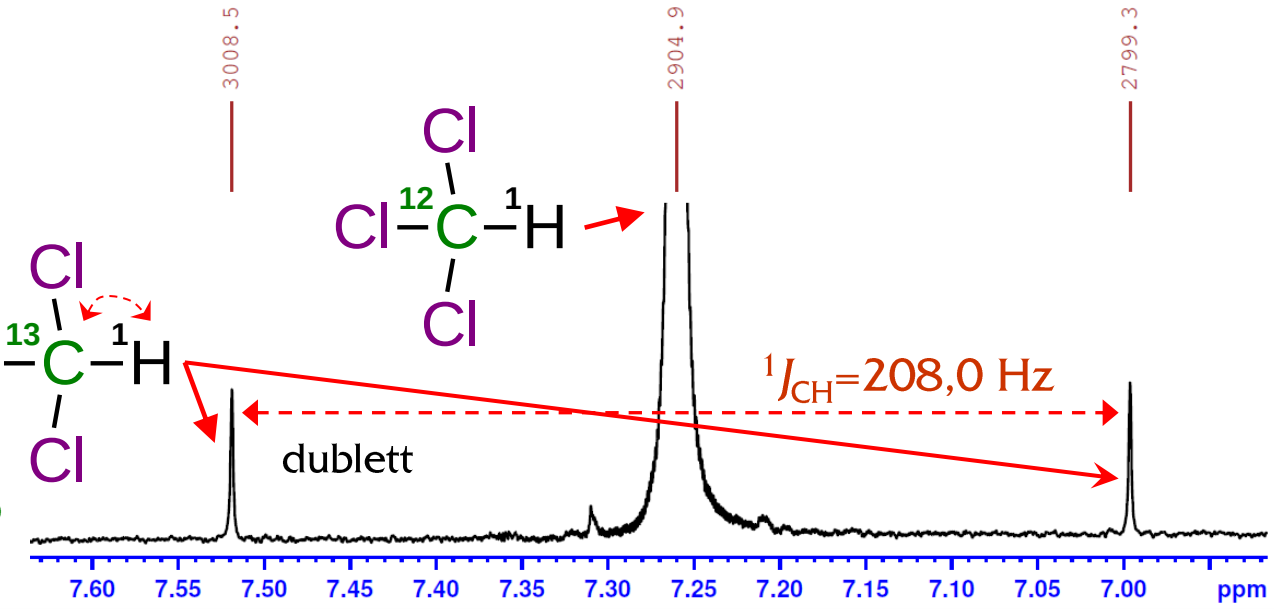
Spinnkvantarvud:

$I(^1H) = ½$

$I(^{12}C) = 0$

$I(^{13}C) = ½$

↑ ×64



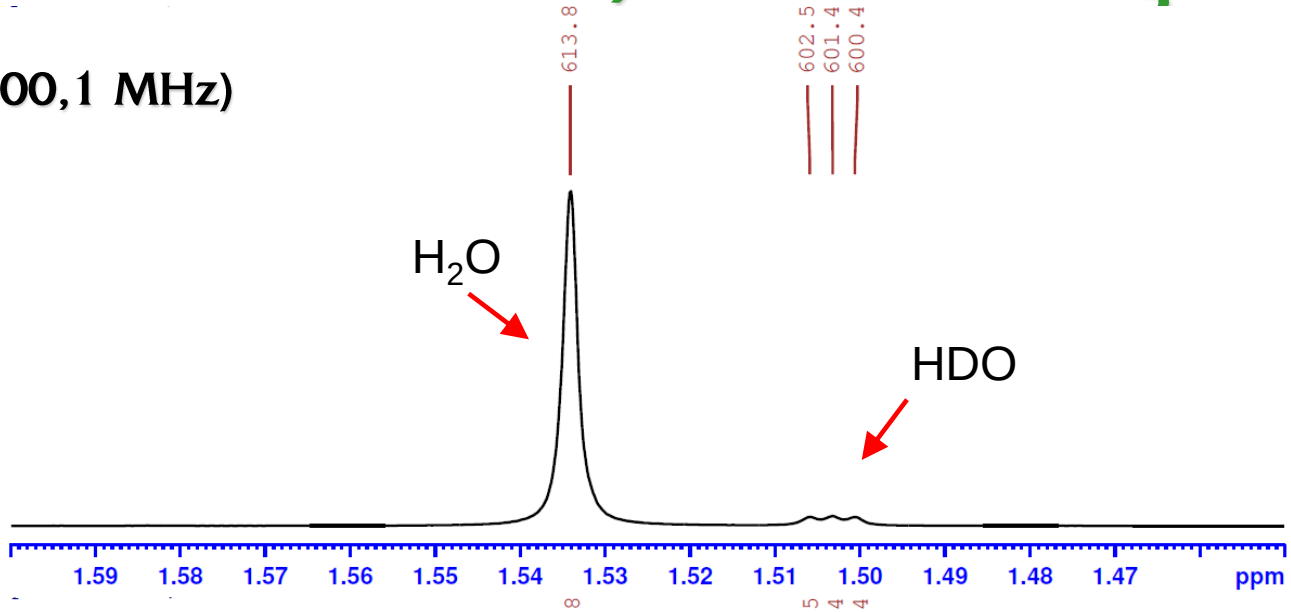
Süsinik:

^{12}C – 98.9%

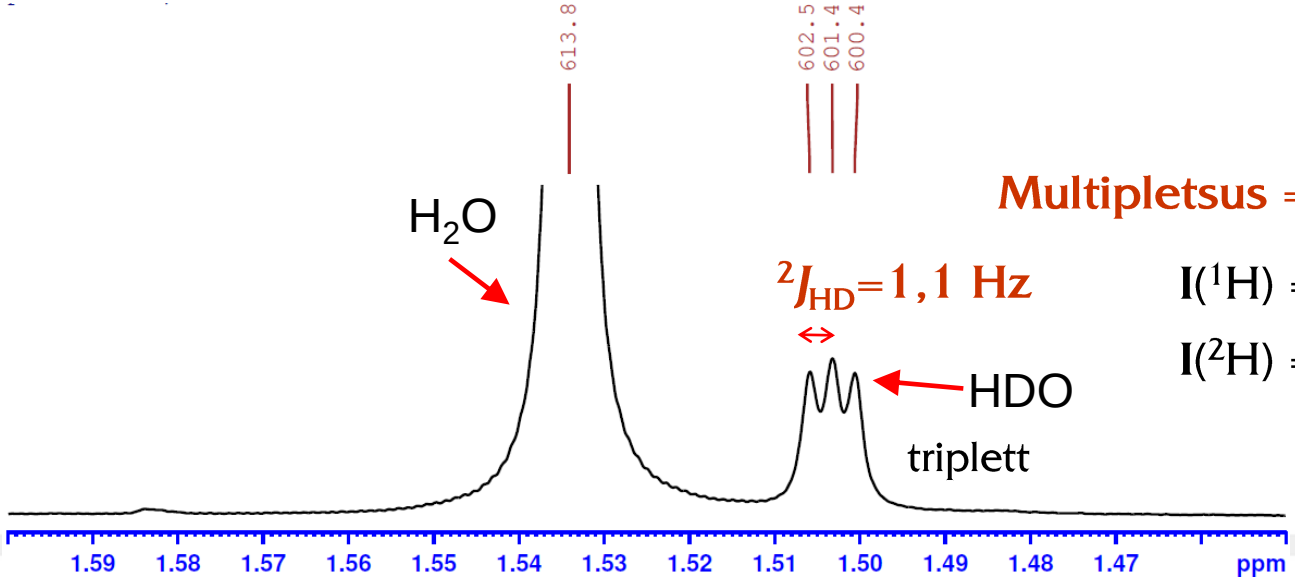
^{13}C – 1.1%

Näide: 99,8%D $CDCl_3$

^{1}H TMR (400,1 MHz)



↑ ×16



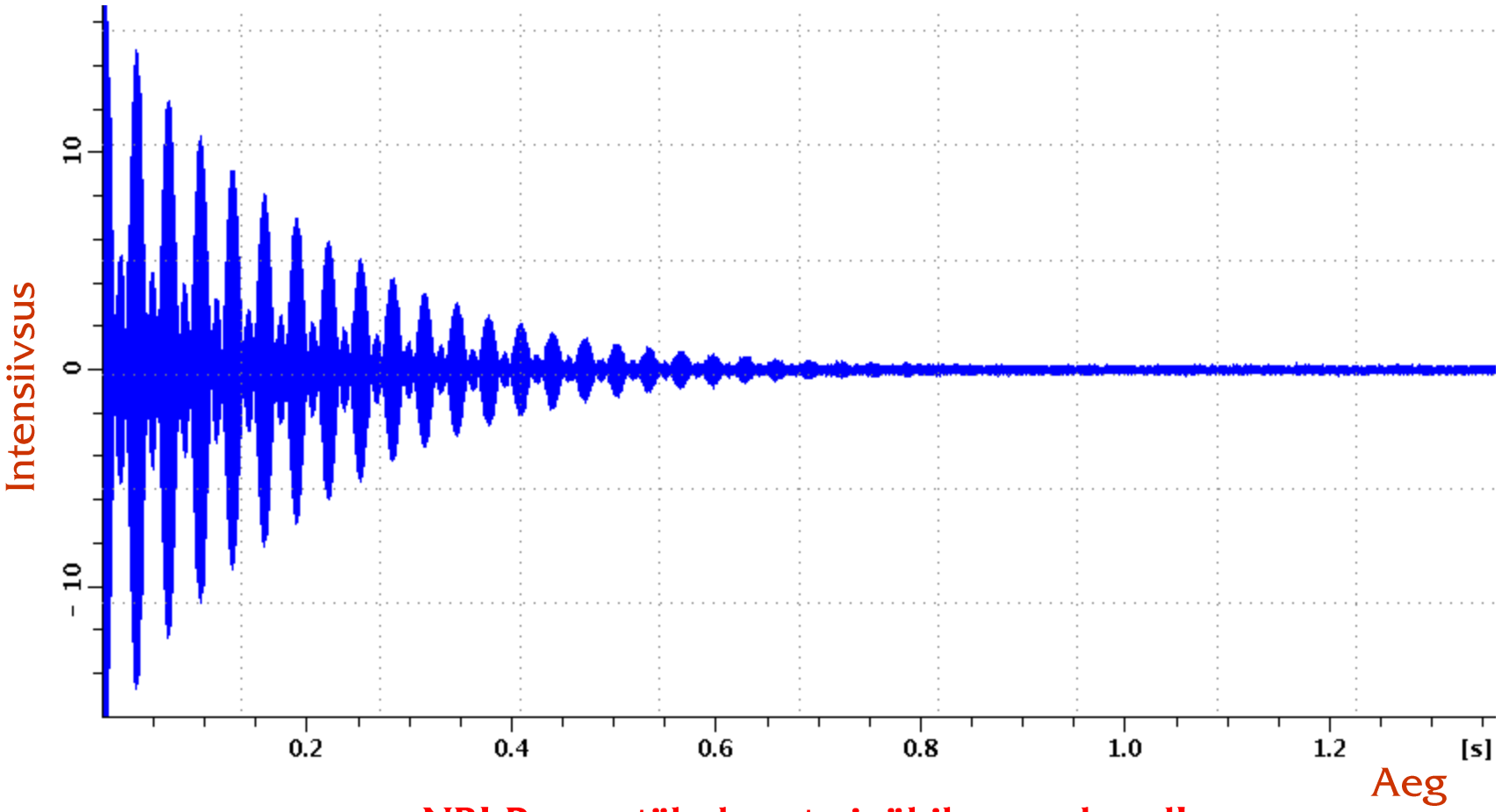
Multipletsus = 2·n·I + 1

I(^{1}H) = ½

I(^{2}H) = 1

Näide: 99,8%D $CDCl_3$

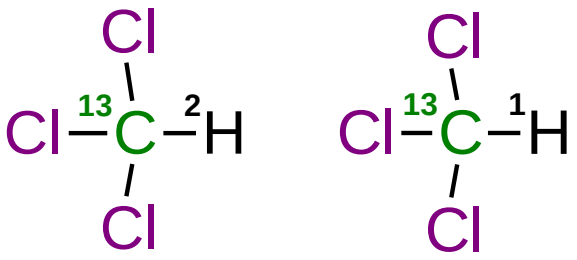
^{13}C TMR fid (100,6 MHz)



NB! Pange tähele, et ajaühik on sekund!

Näide: 99,8%D $CDCl_3$

^{13}C TMR (100,6 MHz)



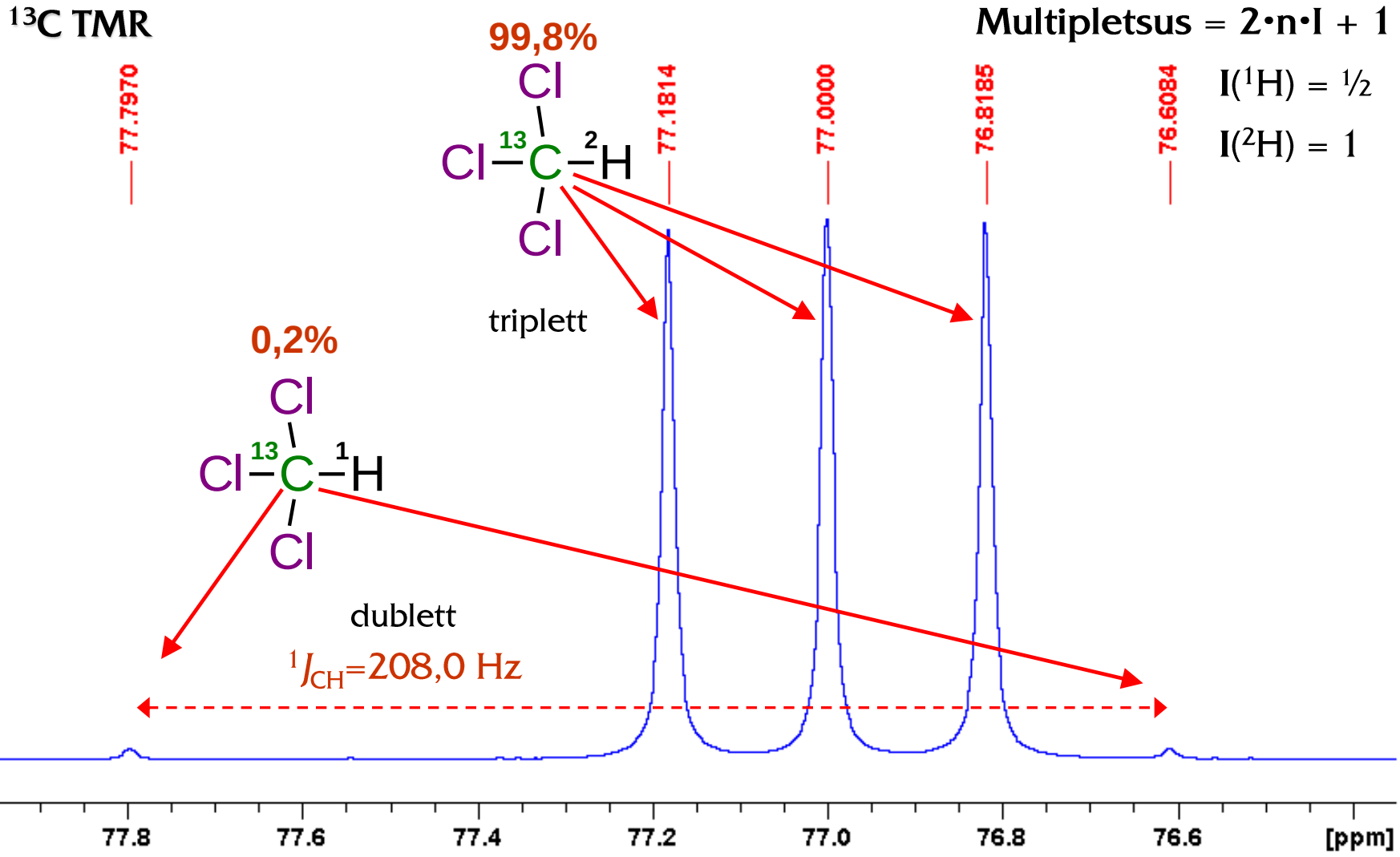
Spinnkvantarvud:

$I(^{12}C) = 0$

$I(^{13}C) = ½$

Skaala on ppm-ides!

Näide: 99,8%D $CDCl_3$



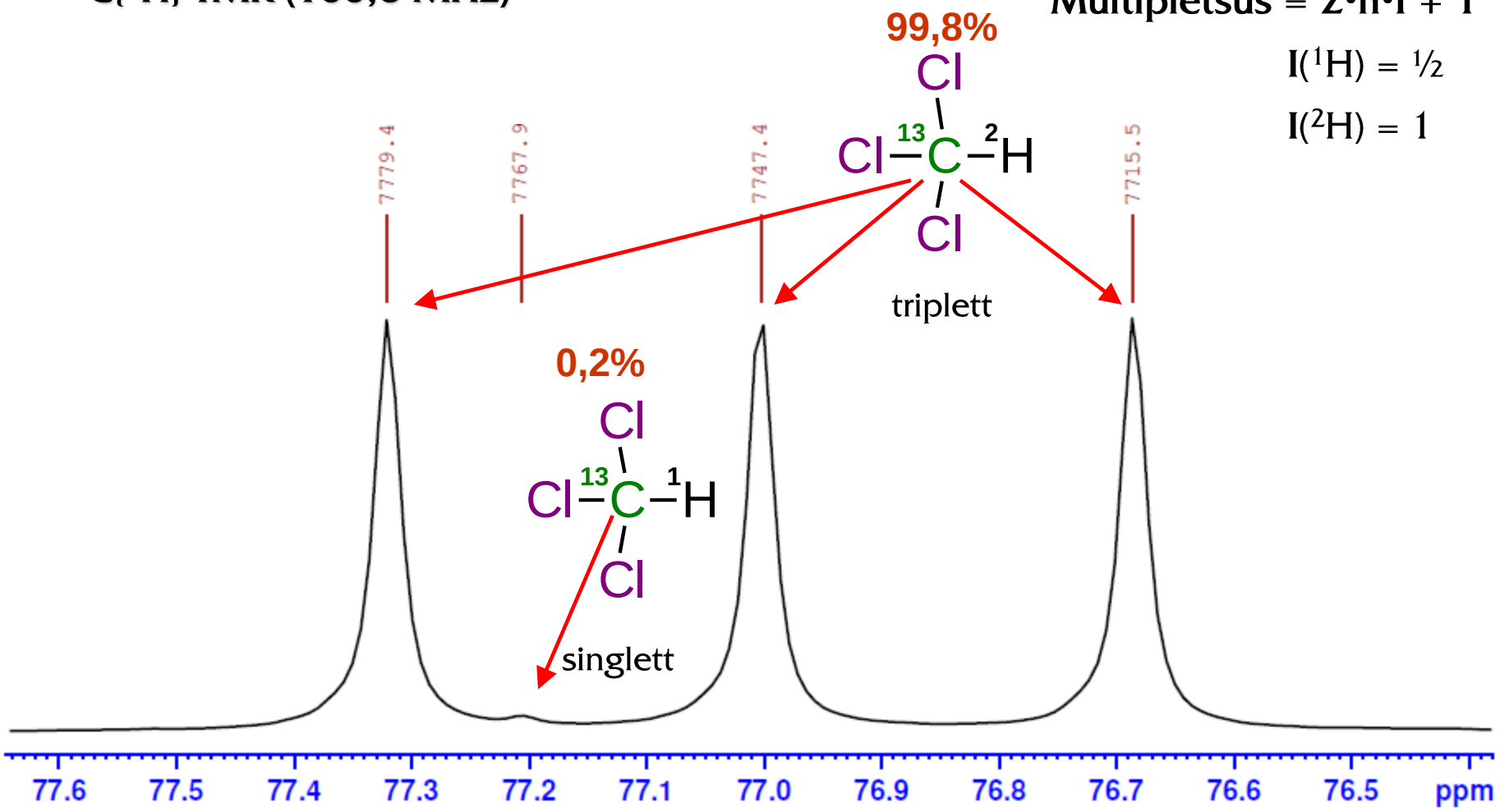
Näide: 99,8%D $CDCl_3$

$^{13}C\{^{1}H\}$ TMR (100,6 MHz)

Multipletsus = 2·n·I + 1

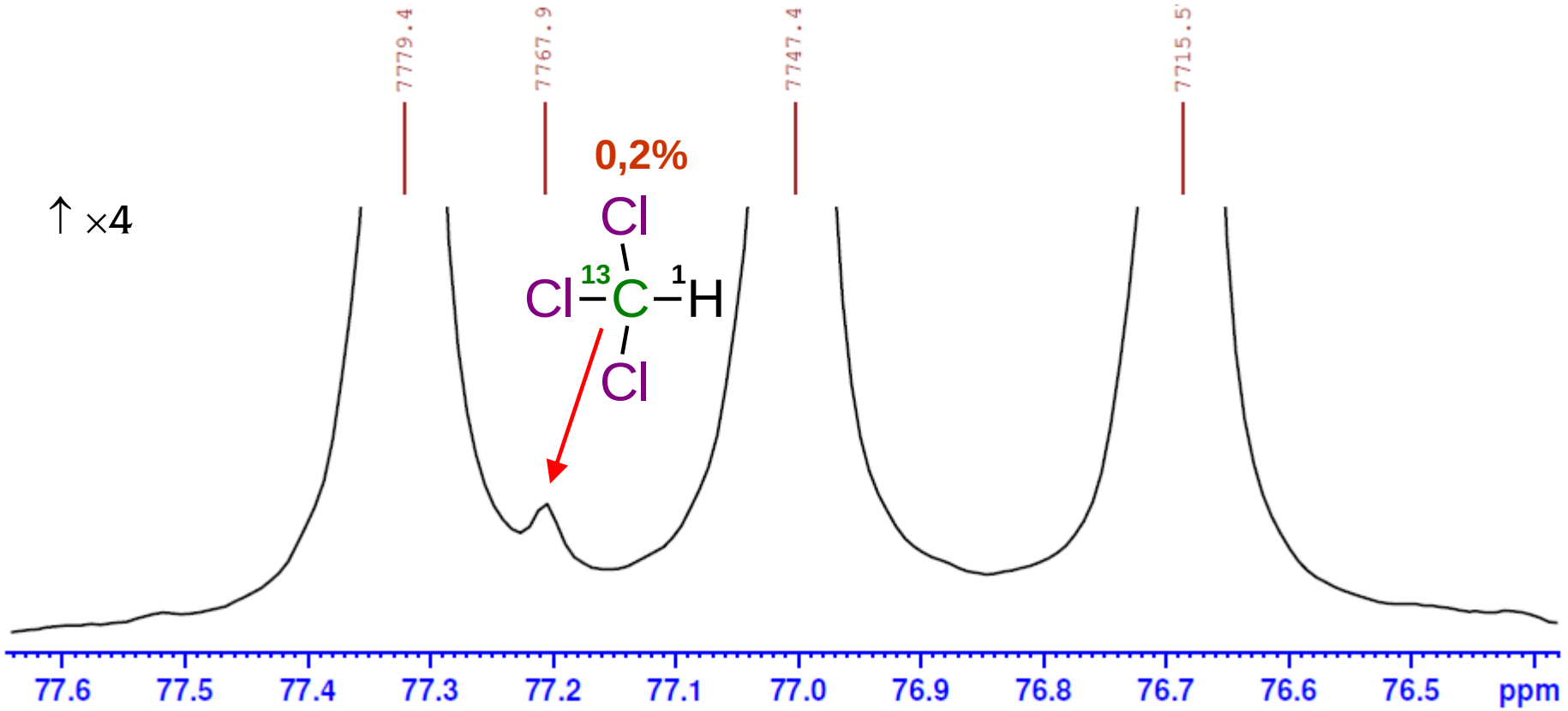
$I(^{1}H) = ½$

$I(^{2}H) = 1$



Näide: 99,8%D $CDCl_3$

$^{13}C\{^{1}H\}$ TMR (100,6 MHz)

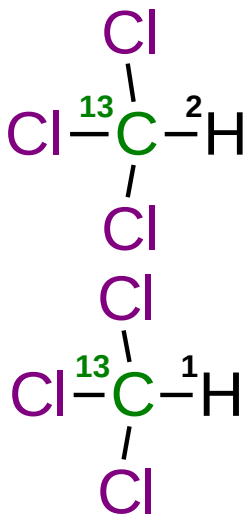


Spektrijoonte lõhenemine

Multipletsus = 2 × n × I + 1
n = naabertuumade arv
I = spinnkvantarv

$I(^1H) = ½$
$I(^2H) = 1$
$I(^{13}C) = ½$

Kui **I=½,** *siis*
Multipletsus = n + 1



NB! Sidestuskonstantide (*J*) väärtused esitatakse hertsides täpsusega 1 kümnendkoht!

Multipletsuse valem!

Lihtsamate (1. järku) signaalide puhul kehtib signaali lõhenemise hindamiseks ja ennustamiseks järgnev valem:

Signaali multipletsus = 2·n·I + 1

kus:

n – ekvivalentsete tuuma signaali lõhestavate naabertuumade arv

I – uuritava tuuma signaali lõhestavate naabertuuma spinnkvantarv

Kui I=½, siis: Signaali multipletsus = n+1 Nt: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P

Kui I=1, siis: Signaali multipletsus = 2·n+1 Nt: ^{2}H, ^{6}Li, ^{14}N

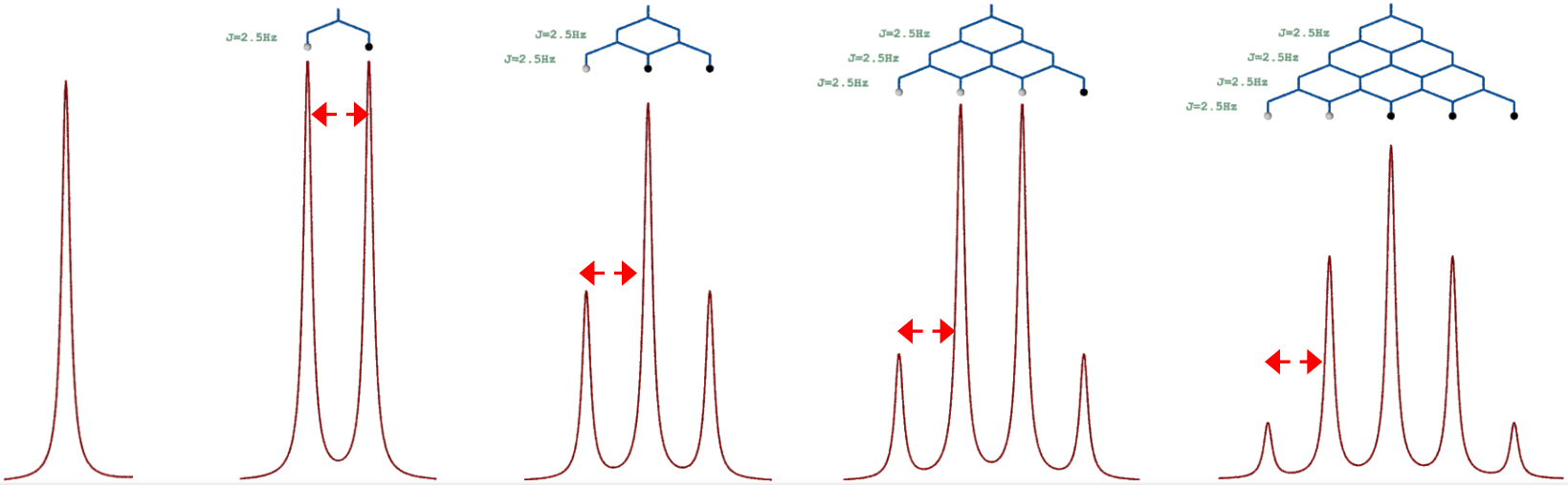
Pascali kolmnurk (kui spinnkvantarv I=½, nt. ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P)

Signaali multipletsus = n+1

n=0	1	Singlett (s)
n=1	1 1	Dublett (d)
n=2	1 2 1	Triplett (t)
n=3	1 3 3 1	Kvartett (q)
n=4	1 4 6 4 1	Kvintett (quint)

Signaali komponentide intensiivsuste suhted

Singlett (s) Dublett (d) Triplett (t) Kvartett (q) Kvintett



TMR multipletid erinevate naabertuumade poolt põhjustatud lõhestamiste korral

Kui uuritavat signaali lõhestavad mitmed erinevad tuumad, siis:

$$\text{Signaali multipletsus} = \sum(2 \cdot n \cdot I + 1)$$

kus:

n – ekvivalentsete tuuma signaali lõhestavate naabertuumade arv

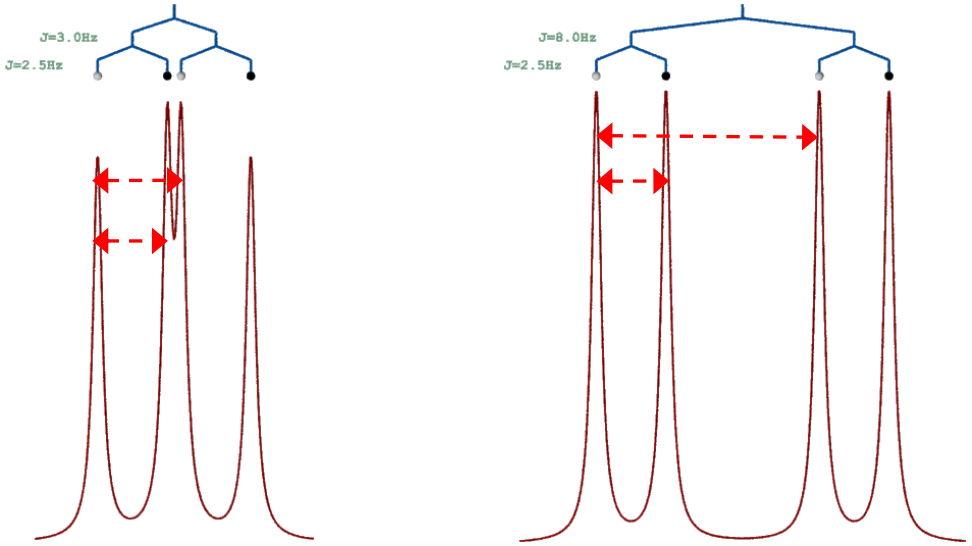
I – uuritava tuuma signaali lõhestavate naabertuuma spinnkvantarv

Tekivad lõhenemiste kombinatsioonid: dubleti dubletid, dubleti tripletid jne.

Näiteks:

Dubleti dubletid (dd)

Kummagi lõhenemise jaoks on vaja mõõta oma sidestuskonstant!



Pascali kolmnurk (kui spinnkvantarv I=1, nt. ^{2}H, ^{6}Li, ^{14}N)

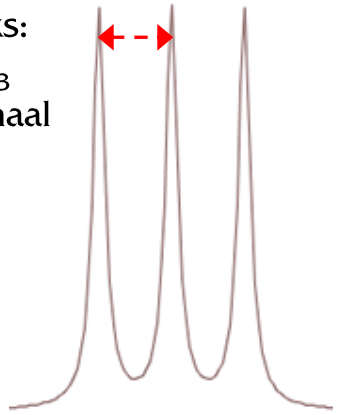
Signaali multipletsus = 2·n+1

n=0				1				Singlett (s)
n=1			1	1	1			Triplett (t)
n=2		1	2	3	2	1		Kvintett (quint)
n=3	1	3	6	7	6	3	1	Septett (sept)

Signaali komponentide intensiivsuste suhted

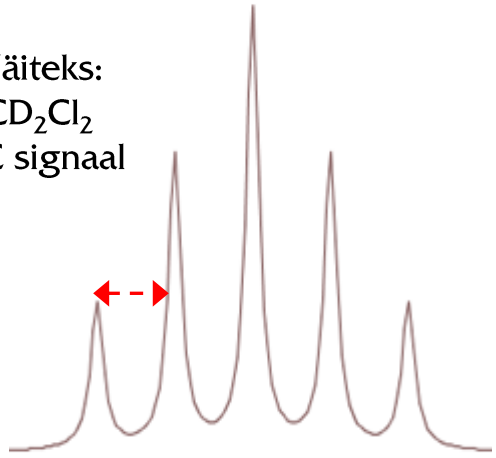
Triplett (t)

Näiteks:
$CDCl_3$
^{13}C signaal



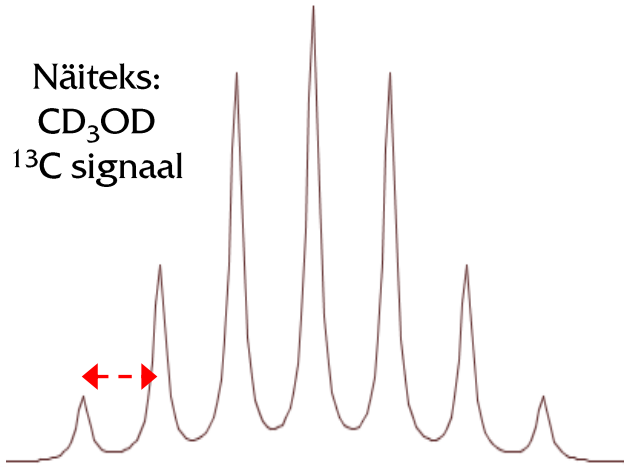
Kvintett (quint)

Näiteks:
CD_2Cl_2
^{13}C signaal

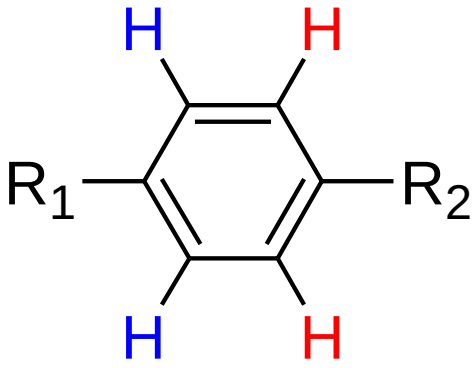


Septett (sept)

Näiteks:
CD_3OD
^{13}C signaal



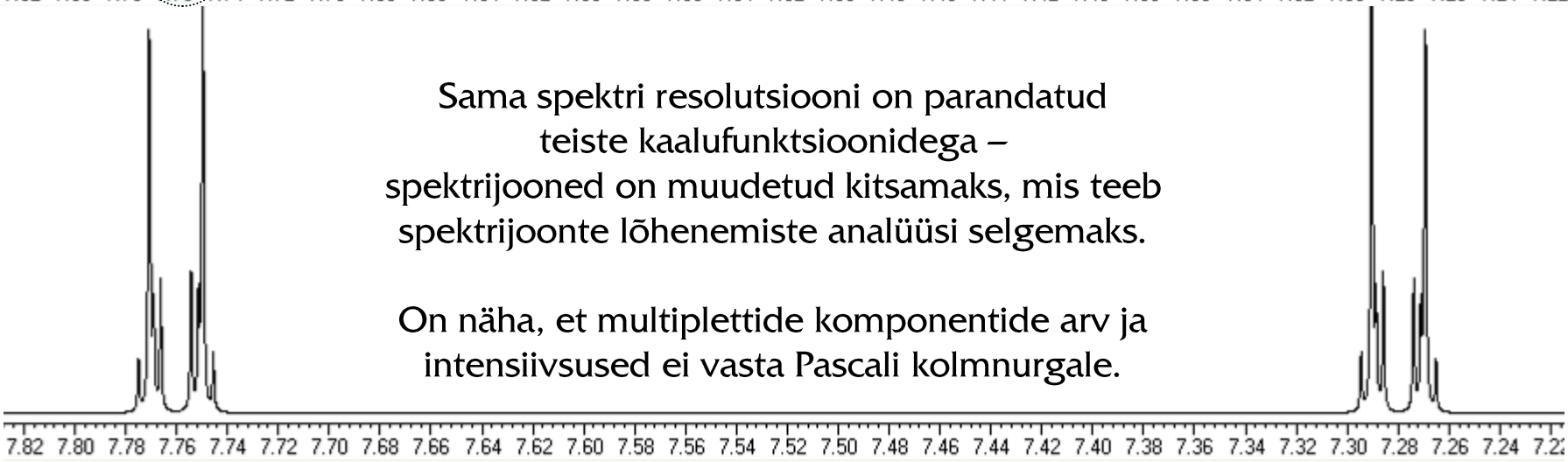
Näide: kõrgemat järku TMR multipletid



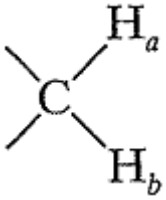
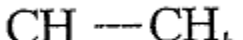
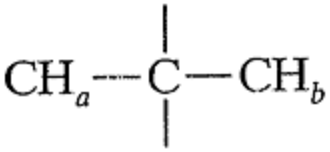
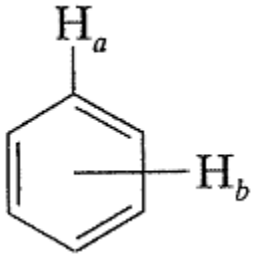
Eksponentsiaalne kaalufunktsioon parameetriga LB=0,3

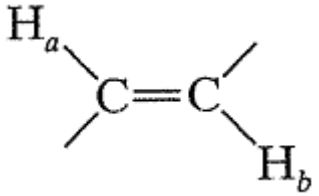
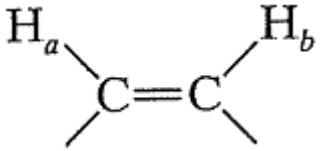
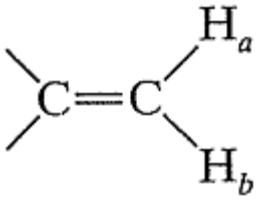
Sama spektri resolutsiooni on parandatud teiste kaalufunktsioonidega – spektrijooned on muudetud kitsamaks, mis teeb spektrijoonte lõhenemiste analüüsi selgemaks.

On näha, et multiplettide komponentide arv ja intensiivsused ei vasta Pascali kolmnurgale.

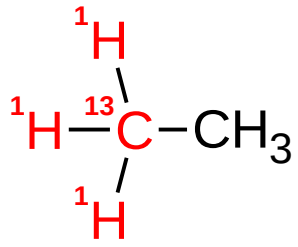


^{1}H-^{1}H sidestuskonstandid ($^{n}J_{HH}$)

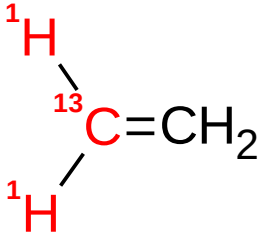
	$^{n}J_{HH}$ (Hz)	$^{n}J_{HH}$ (Hz) *tüüpiliselt*
	0–30	12–15
	6–8	7
	0–1	0
	*J* (ortho) 6–10 *J* (meta) 1–3 *J* (para) 0–1	9 3 ~0

	$^{n}J_{HH}$ (Hz)	$^{n}J_{HH}$ (Hz) *tüüpiliselt*
	12–18	17
	6–12	10
	0–3	0–2

^{1}H-^{13}C sidestuskonstandid ($^{n}J_{CH}$)

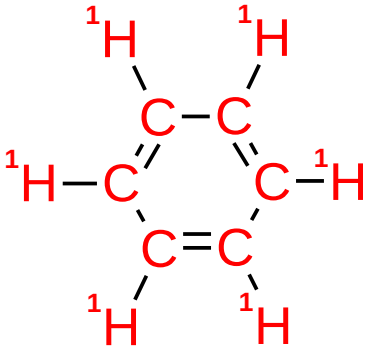


$^{1}J_{CH}$ = 124,9 Hz

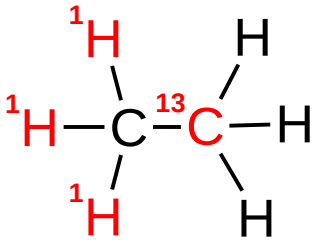


$^{1}J_{CH}$ = 156,4 Hz

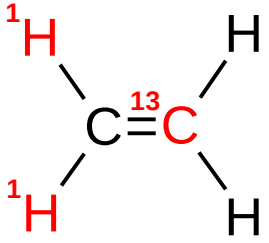
$^{1}J_{CH}$ = 249,0 Hz



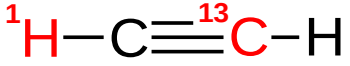
$^{1}J_{CH}$ = 158,4 Hz



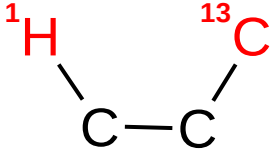
$^{2}J_{CH}$ = -4,5 Hz



$^{2}J_{CH}$ = -2,4 Hz



$^{2}J_{CH}$ = 49,6 Hz



$^{3}J_{CH}$ < 15 Hz

Muud sidestuskonstandid ($^{n}J_{XY}$)

Mõned näited:

$^{1}J_{CC}$ = 30-180 Hz

$^{1}J_{CF}$ = 150-280 Hz

$^{2}J_{CF}$ ~ 10-40 Hz

$^{1}J_{CP}$ = 50-70 Hz

$^{1}J_{FP}$ ~ 1000 Hz

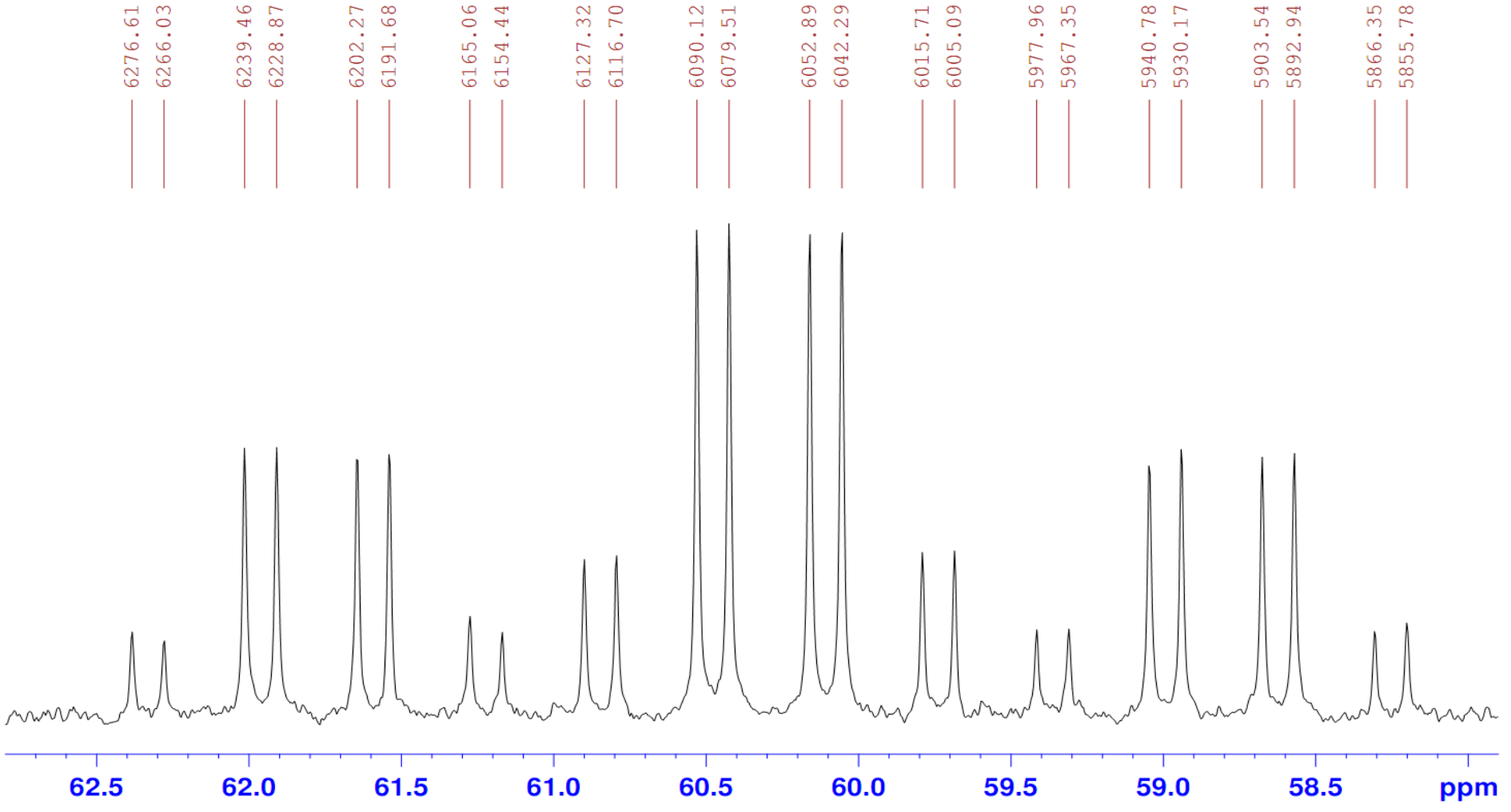
$^{1}J_{HN}$ = 50-140 Hz

$^{2}J_{HN}$ = 0-16 Hz

$^{3}J_{HN}$ = 0-11 Hz

Ülesanne

- ***Kirjeldage ära slaidil olev TMR-signaal (keemiline nihe, multipletsus, sidestuskonstandid).***
- ***Mis sagedusel on spekter mõõdetud? Mis tuuma spektriga võiks olla tegu?***
- ***Mida saate järeldada signaali lõhenemiste põhjal?***



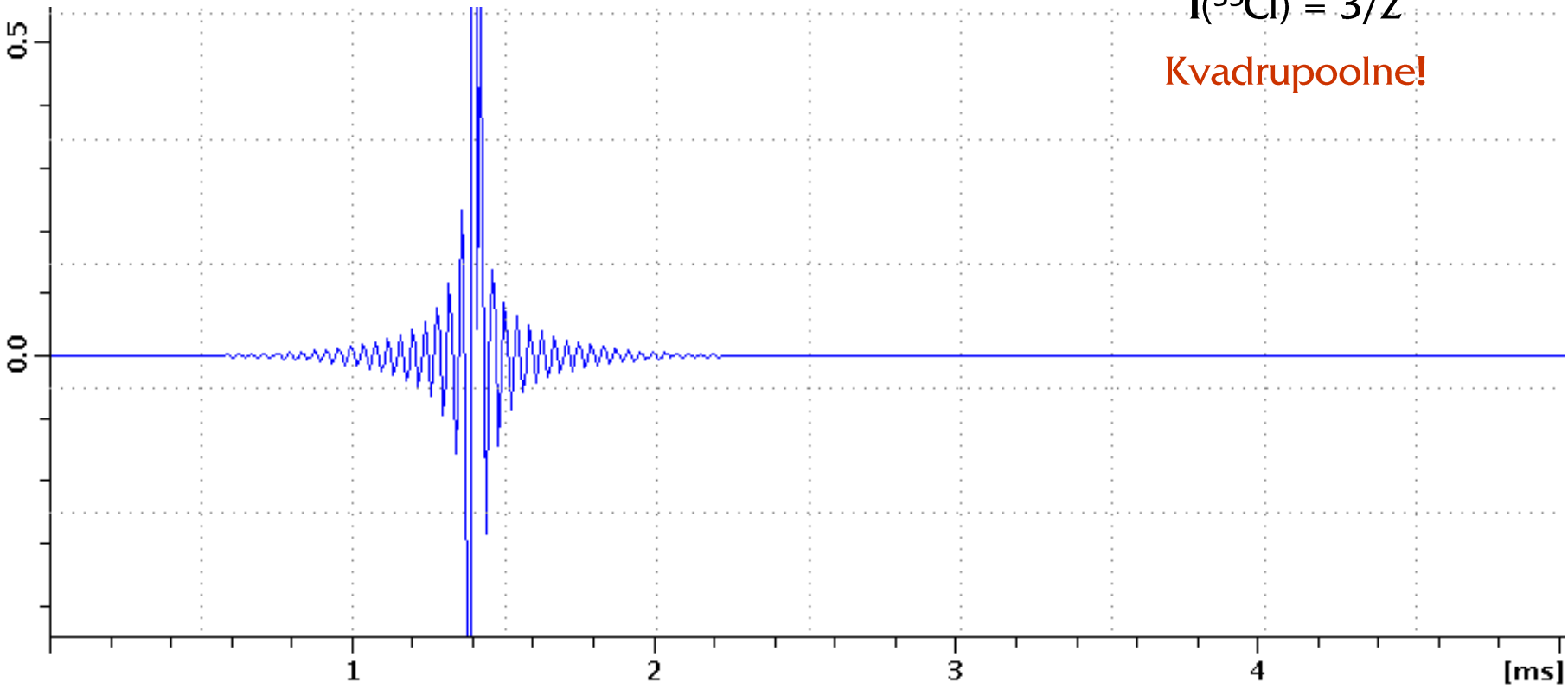
Näide: 99,8%D $CDCl_3$

^{35}Cl TMR fid (39,2 MHz)

Spinnkvantarv:

$I(^{35}Cl) = 3/2$

Kvadrupoolne!



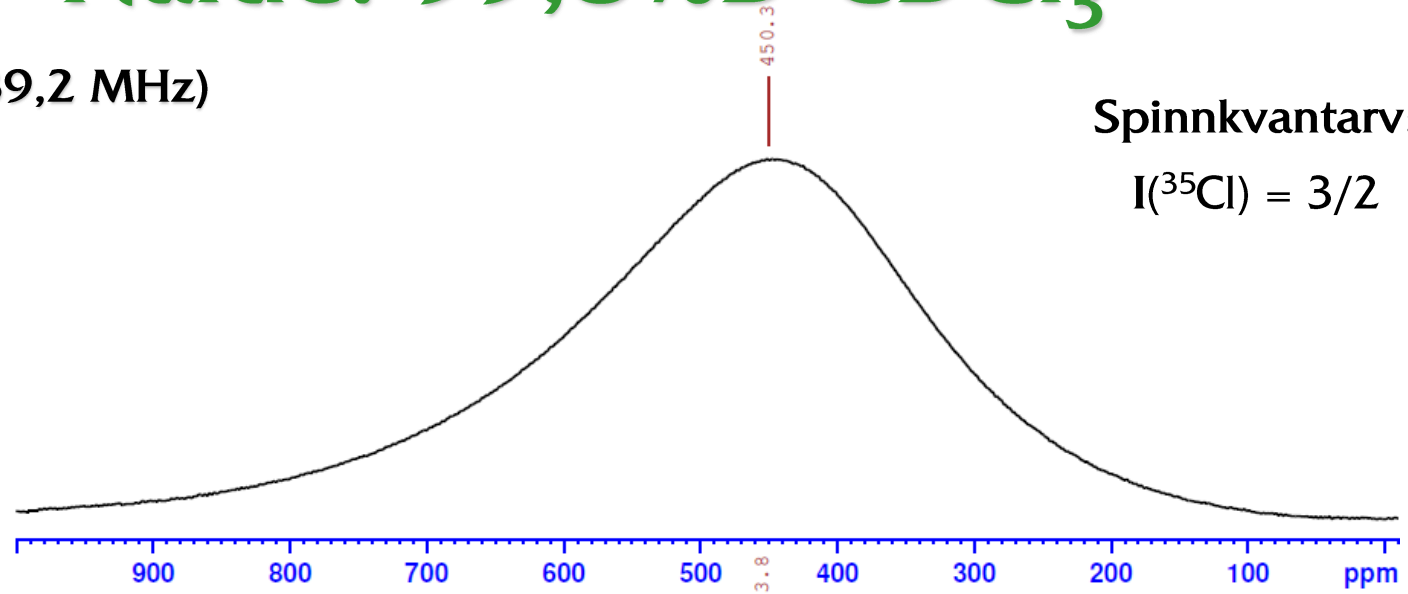
NB! Pange tähele, et ajaühik on seekord sekundi asemel millisekund!

Näide: 99,8%D $CDCl_3$

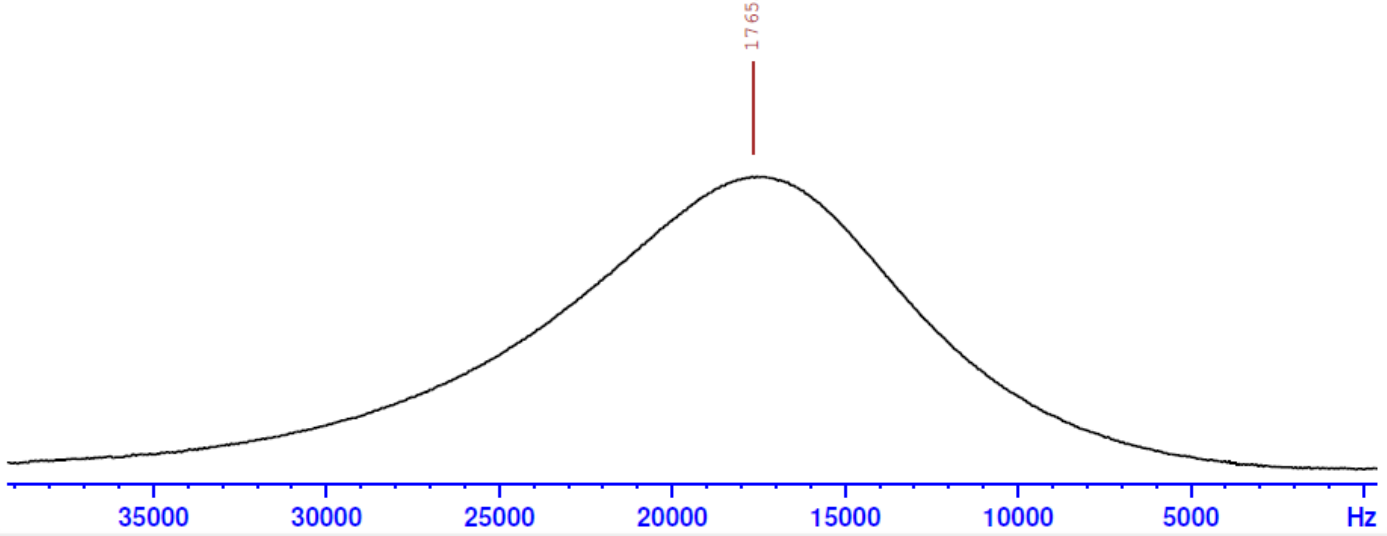
^{35}Cl TMR (39,2 MHz)

Spinnkvantarv:

I(^{35}Cl) = 3/2



ppm skaala



Hz skaala

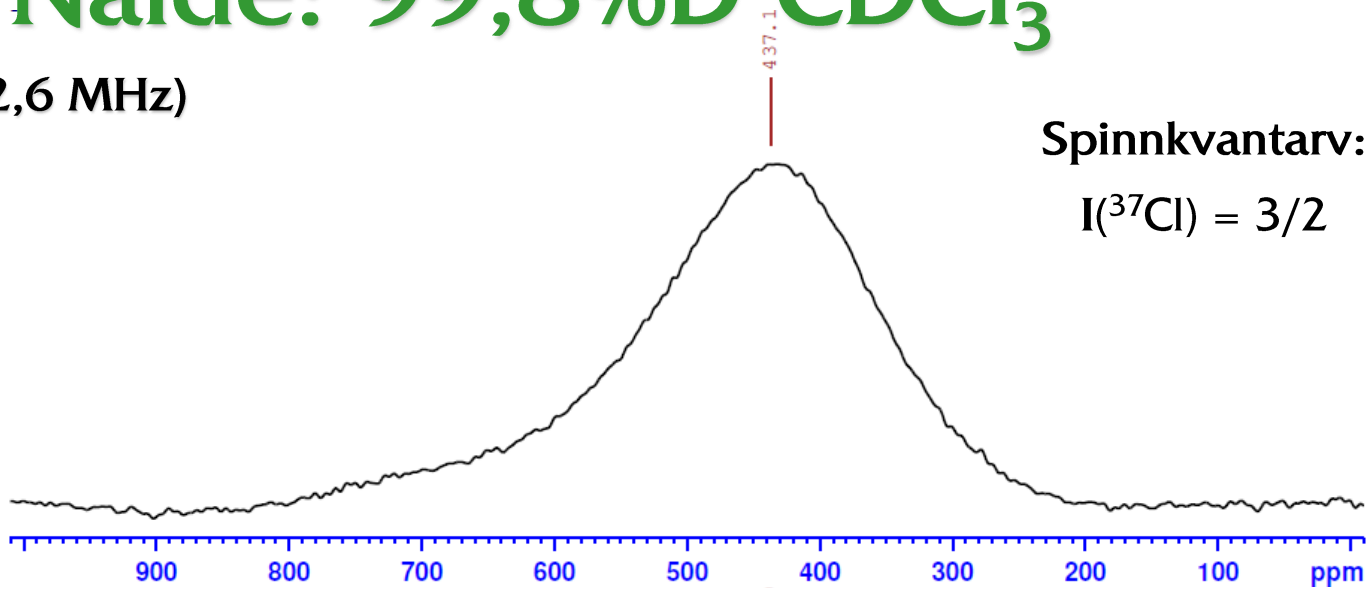
Näide: 99,8%D $CDCl_3$

^{37}Cl TMR (32,6 MHz)

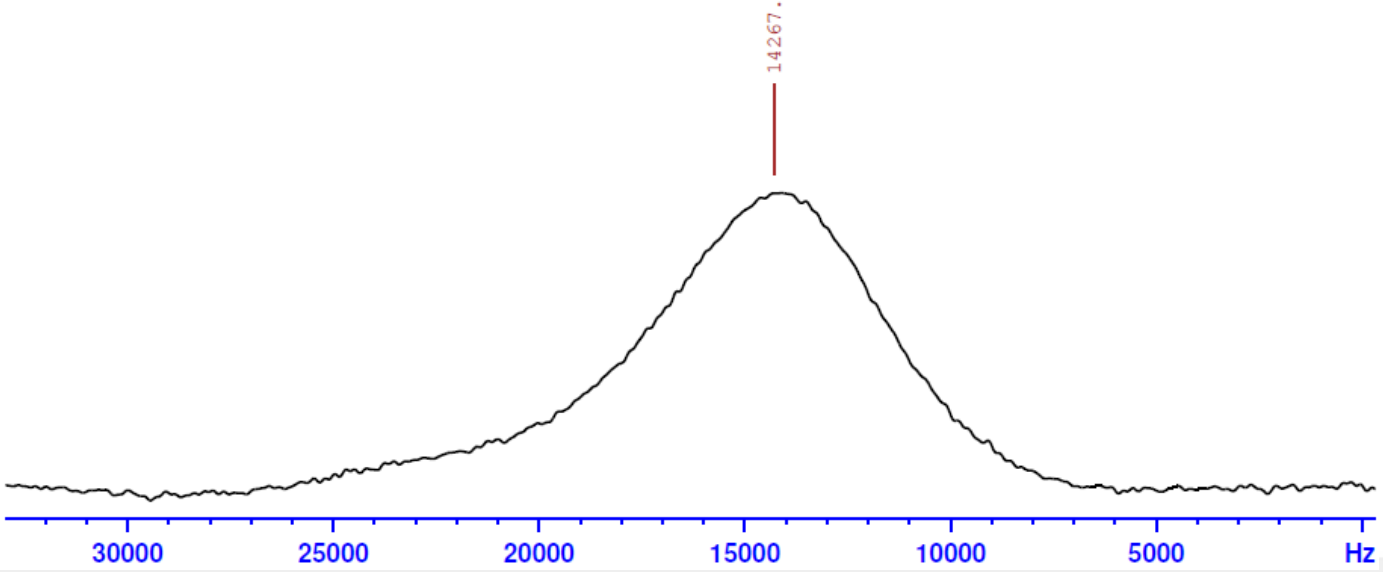
Spinnkvantarv:

I(^{37}Cl) = 3/2

ppm skaala



Hz skaala



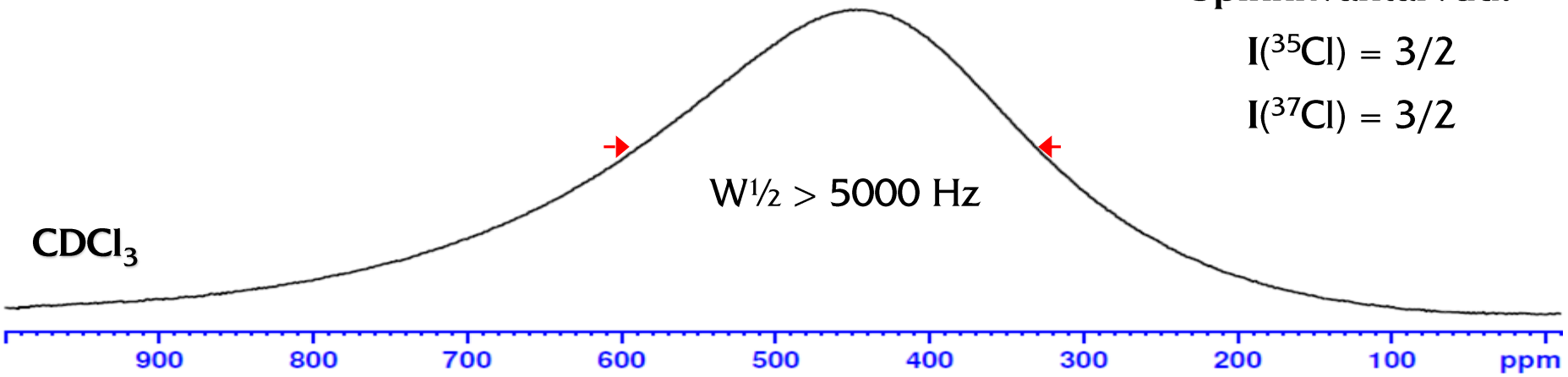
Miks kloori TMR spektreid väga harva mõõdetakse?

^{35}Cl TMR (39,2 MHz):

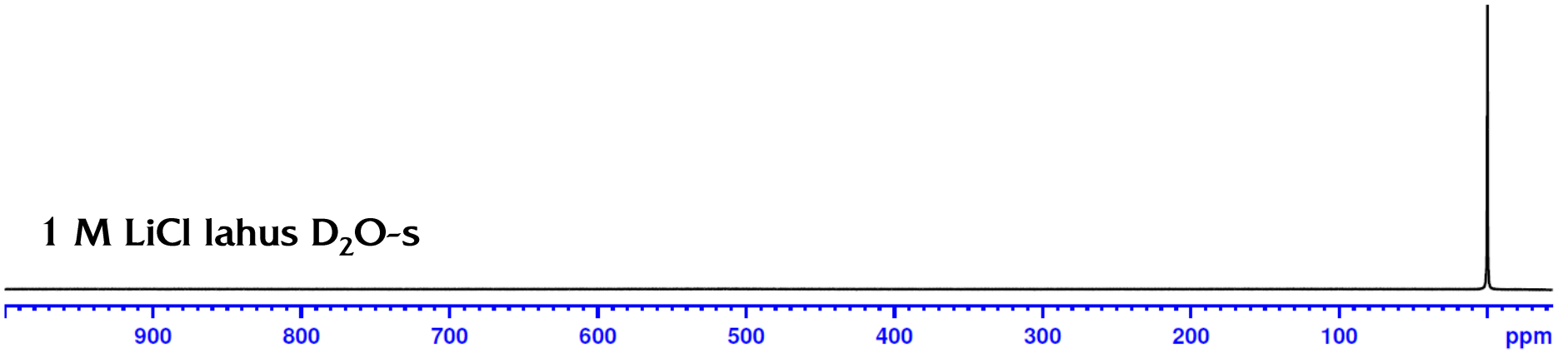
Spinnkvantarvud:

I(^{35}Cl) = 3/2

I(^{37}Cl) = 3/2



1 M LiCl lahus D_2O-s



Skaala ulatus on sama, aga Cl^--iooni signaali laius on palju väiksem kui $CDCl_3$ puhul. Mida keerulisem molekul, seda laiemad on signaalid.

Kvadrupoolsete tuumade TMR (I>½)

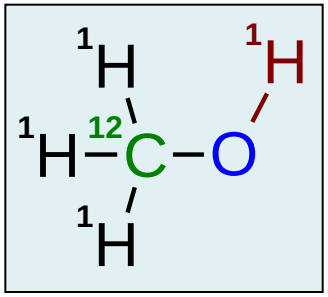
Laengujaotus sfäärilise ja mitte-sfäärilise tuumasümmeetria korral.

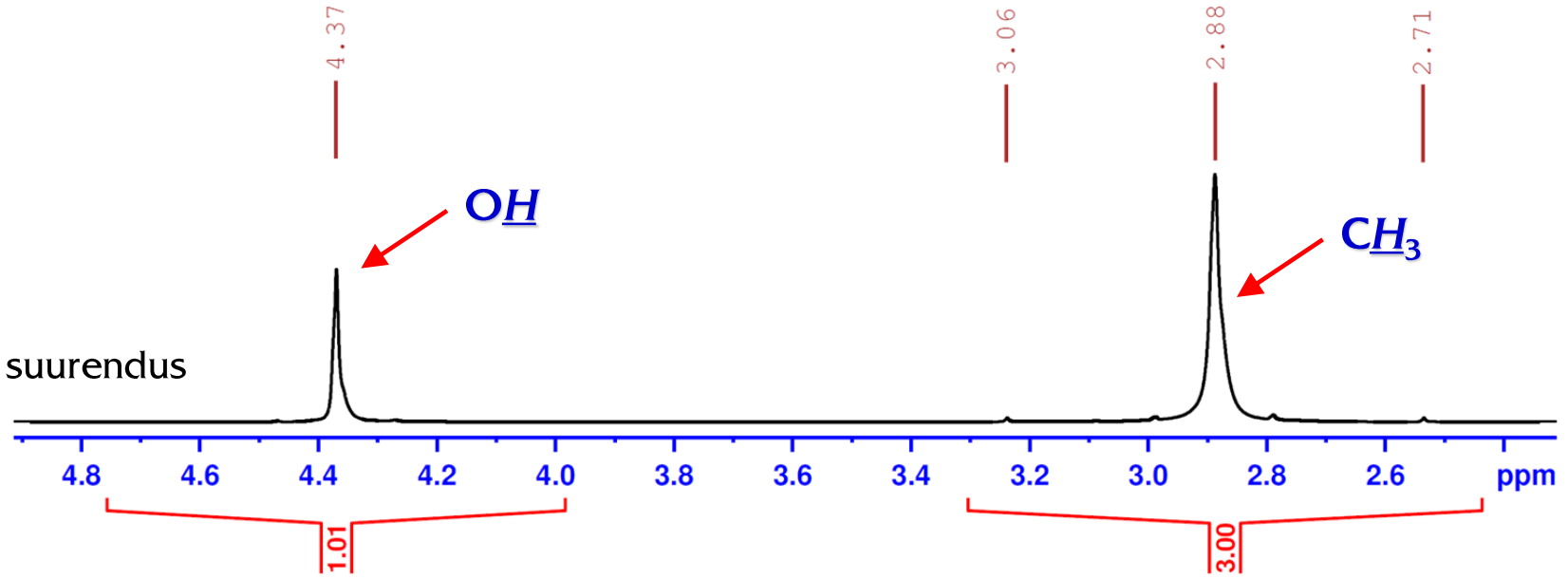
- Mida kiiremini signaal ära kustub, seda laiem on spektrijoon.
- Kui signaal kustub ära liiga kiiresti (kiiremini kui 1/J), siis see tuum teise tuuma signaali ei lõhestagi.
  Näiteks, kui signaal kustub ära 0,01 s jooksul, peaks temast tingitud lõhenemine olema >100 Hz, et seda lõhenemist spektris veel näha oleks.

Näide: MeOH (LC-MS puhtusega)

^{1}H TMR spekter:

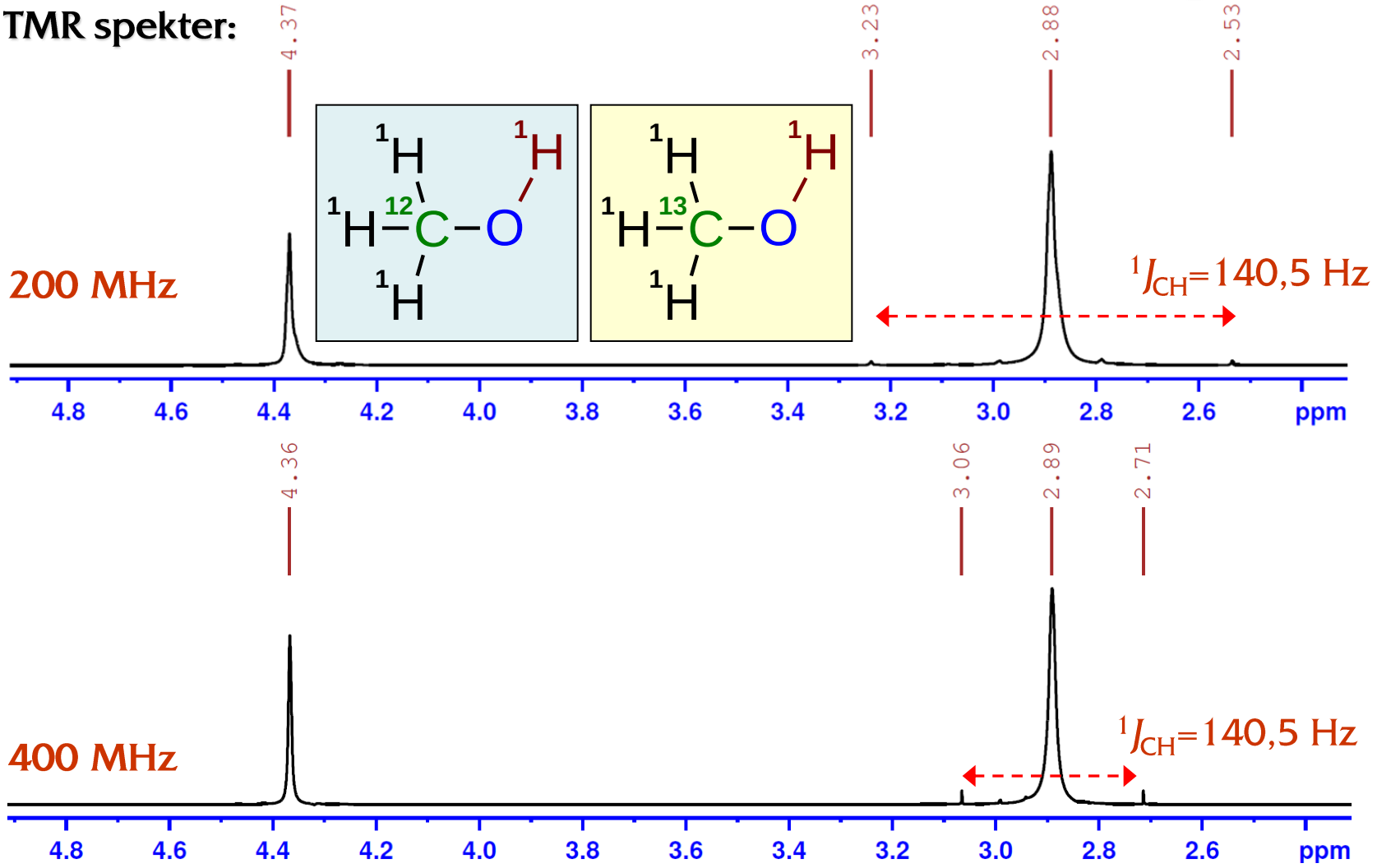
200 MHz





Näide: MeOH (LC-MS puhtusega)

^{1}H TMR spekter:



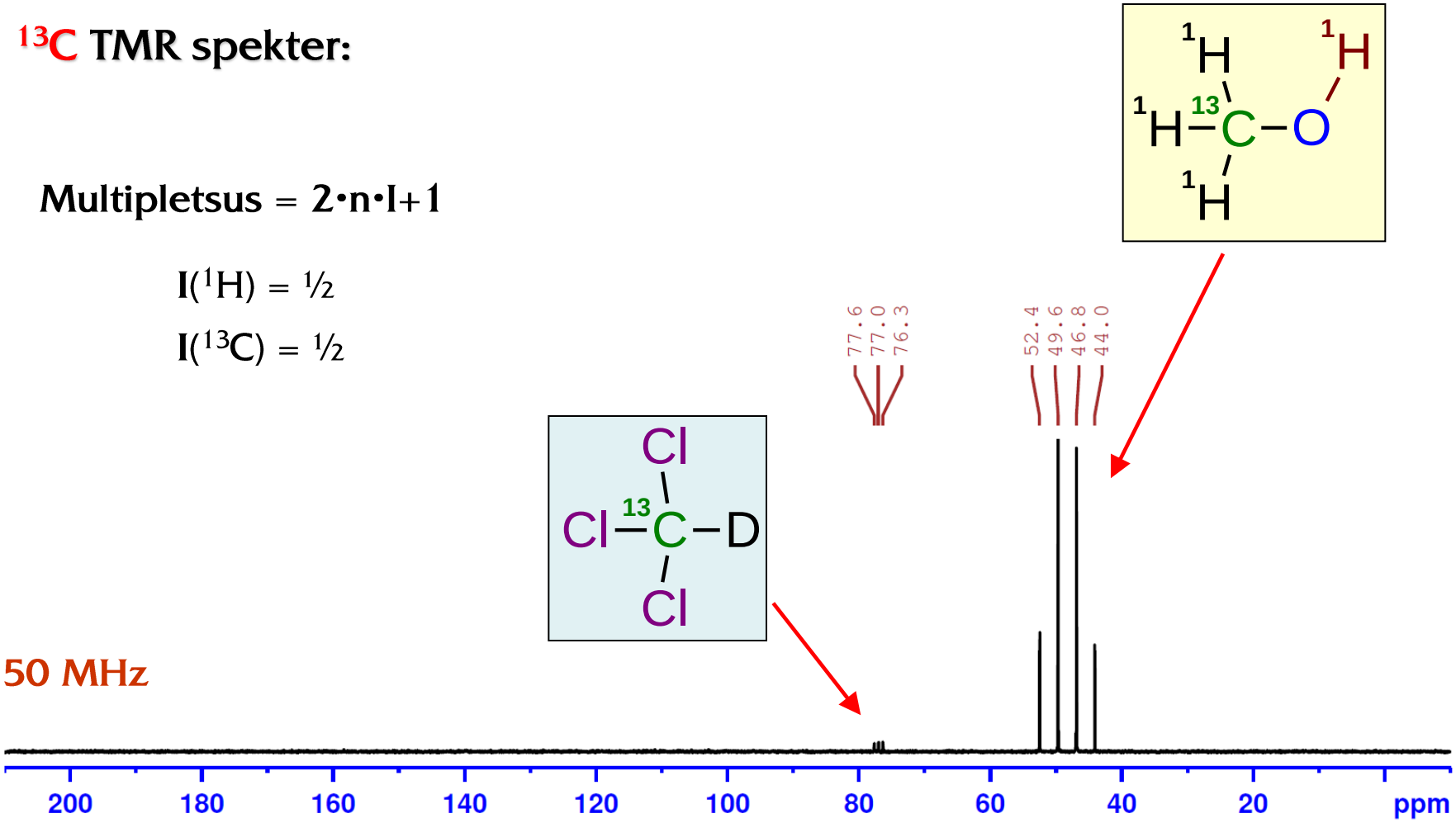
Näide: MeOH (LC-MS puhtusega)

^{13}C TMR spekter:

Multipletsus = 2·n·I+1

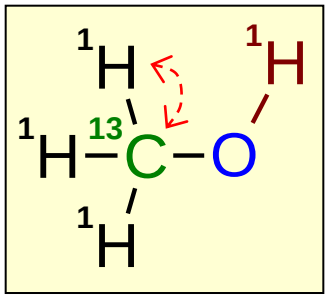
I(^{1}H) = ½

I(^{13}C) = ½



Näide: MeOH (LC-MS puhtusega)

^{13}C TMR spekter:



50 MHz

$^{1}J_{CH}$=140,5 Hz

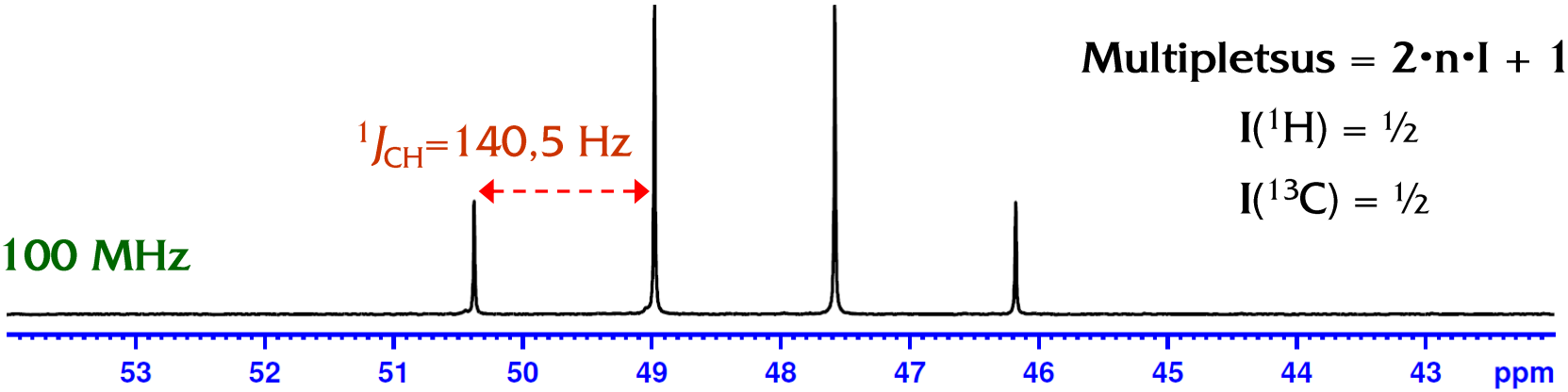
$^{1}J_{CH}$=140,5 Hz

Multipletsus = 2·n·I + 1

I(^{1}H) = ½

I(^{13}C) = ½

100 MHz

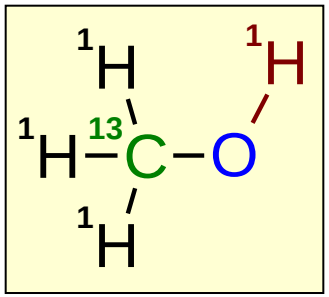


NB! *J*-väärtused ja keemiline nihe ei sõltu kasutatavast magnetväljast (spektromeetrist).

Näide: MeOH (LC-MS puhtusega)

^{13}C TMR spekter:

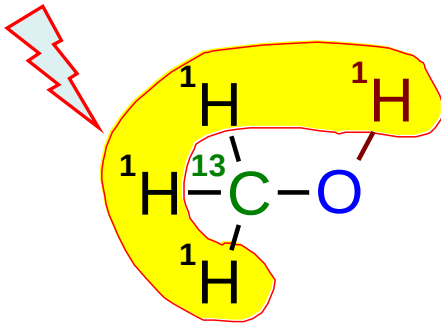
100 MHz



^{13}C{^{1}H} TMR spekter:

100 MHz

Samal ajal, kui kogutakse ^{13}C sagedust, kiiritatakse proovi ^{1}H sagedusega (400 MHz).

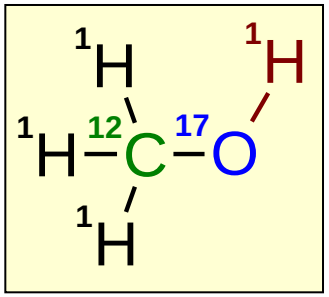


Osa infot (*J*-väärtused) läheb kaduma, aga spekter lihtsustub ja signaalid muutuvad intensiivsemaks.

Näide: MeOH (LC-MS puhtusega)

^{17}O TMR spekter:

54 MHz



Isotoopide jaotus looduses:

^{16}O – 99.76%

^{17}O – 0.04%

^{18}O – 0.20%

Spinnkvantarvud:

I(^{16}O) = 0

I(^{17}O) = 5/2

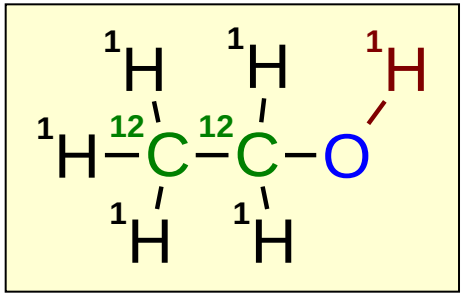
I(^{18}O) = 0

^{17}O TMR spektrite kogumine on väga ajamahukas ja signaalide suure laiuse tõttu väheinformatiivne.

Näide: EtOH (piiritus)

^{1}H TMR spekter:

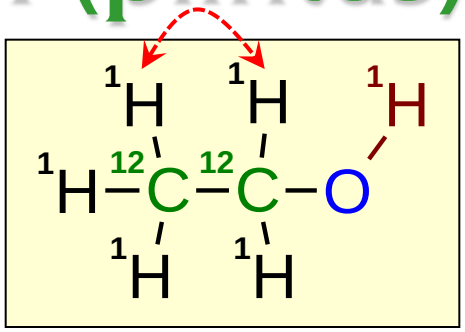
400 MHz



Näide: EtOH (piiritus)

^{1}H TMR spekter:

400 MHz

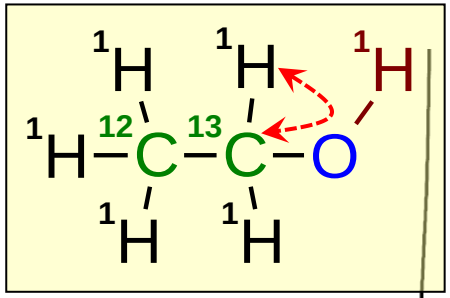


suurendused

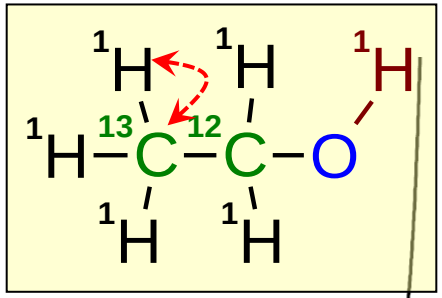
Süsinik:

^{12}C – 98.9%

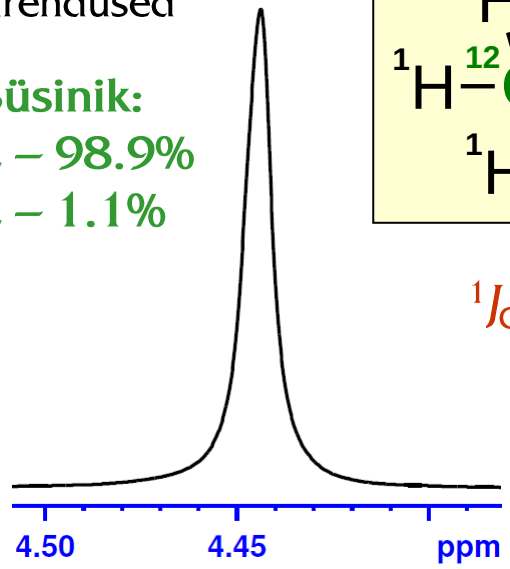
^{13}C – 1.1%

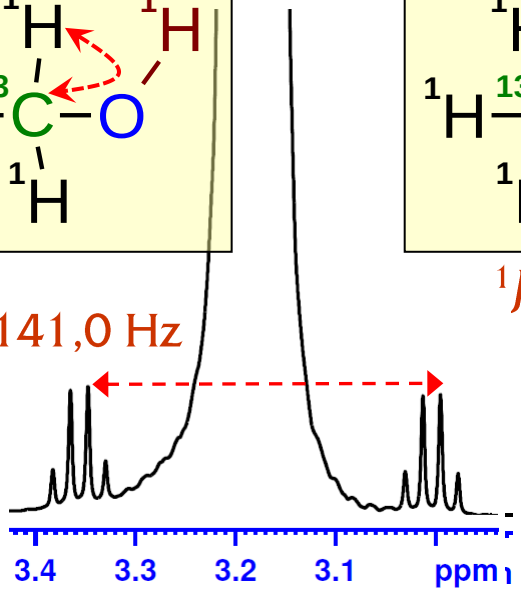


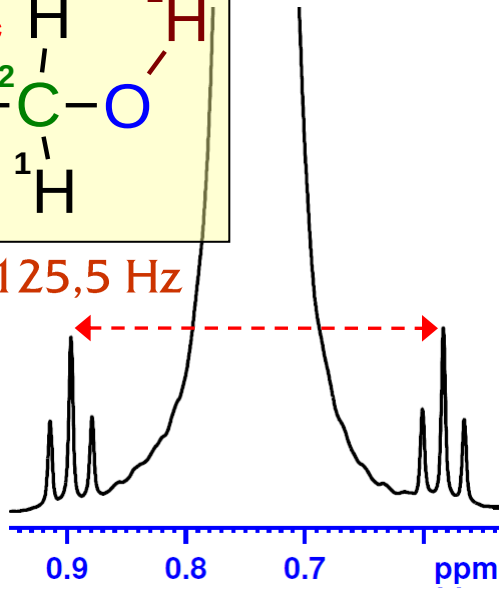
$^{1}J_{CH}$=141,0 Hz



$^{1}J_{CH}$=125,5 Hz



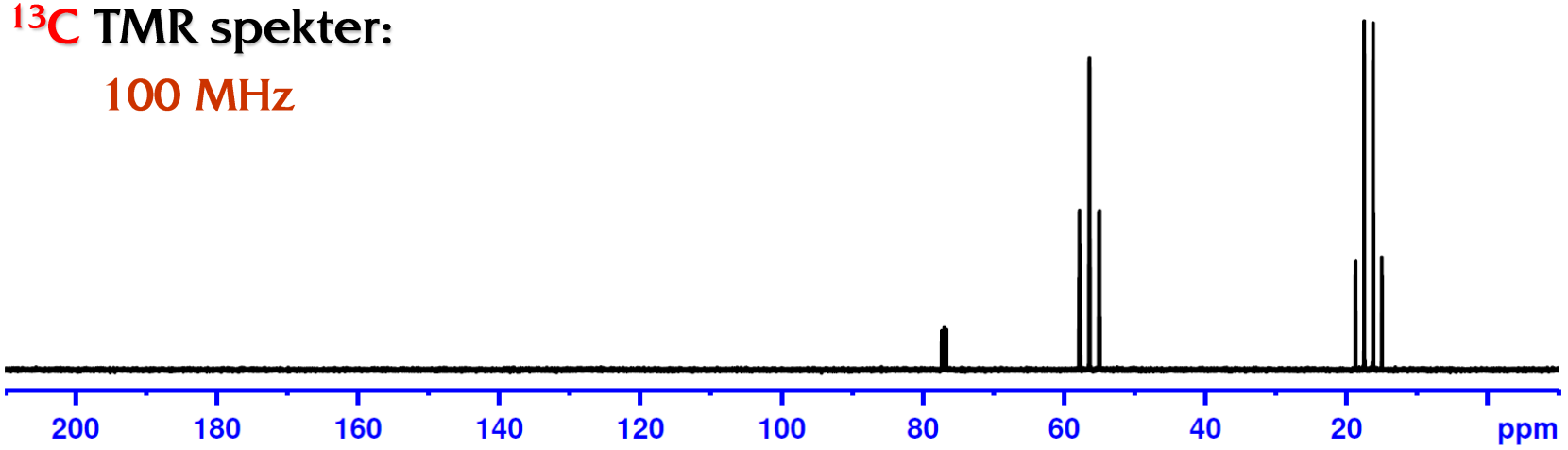


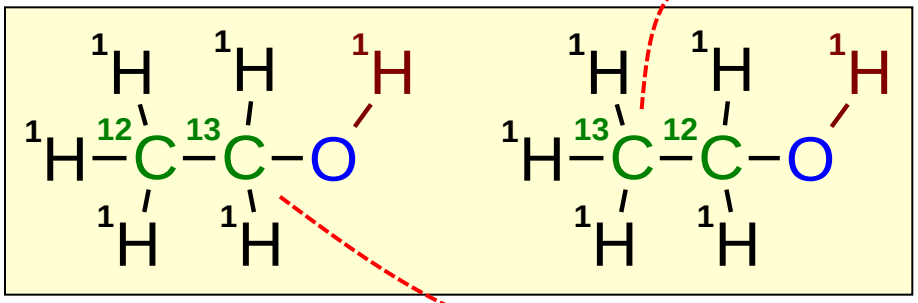


Näide: EtOH (piiritus)

^{13}C TMR spekter:

100 MHz





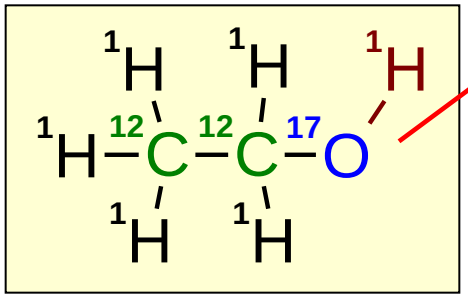
$^{13}C\{^{1}H\}$ TMR spekter:

Näide: EtOH (piiritus)

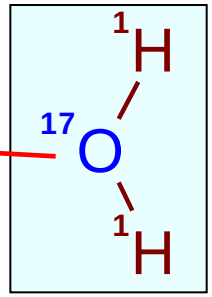
^{17}O TMR spekter:

54 MHz

Pange tähele signaali laiust!



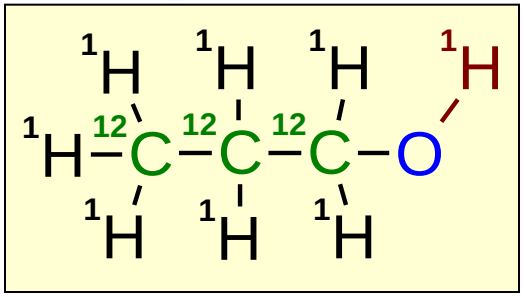
W½=230 Hz

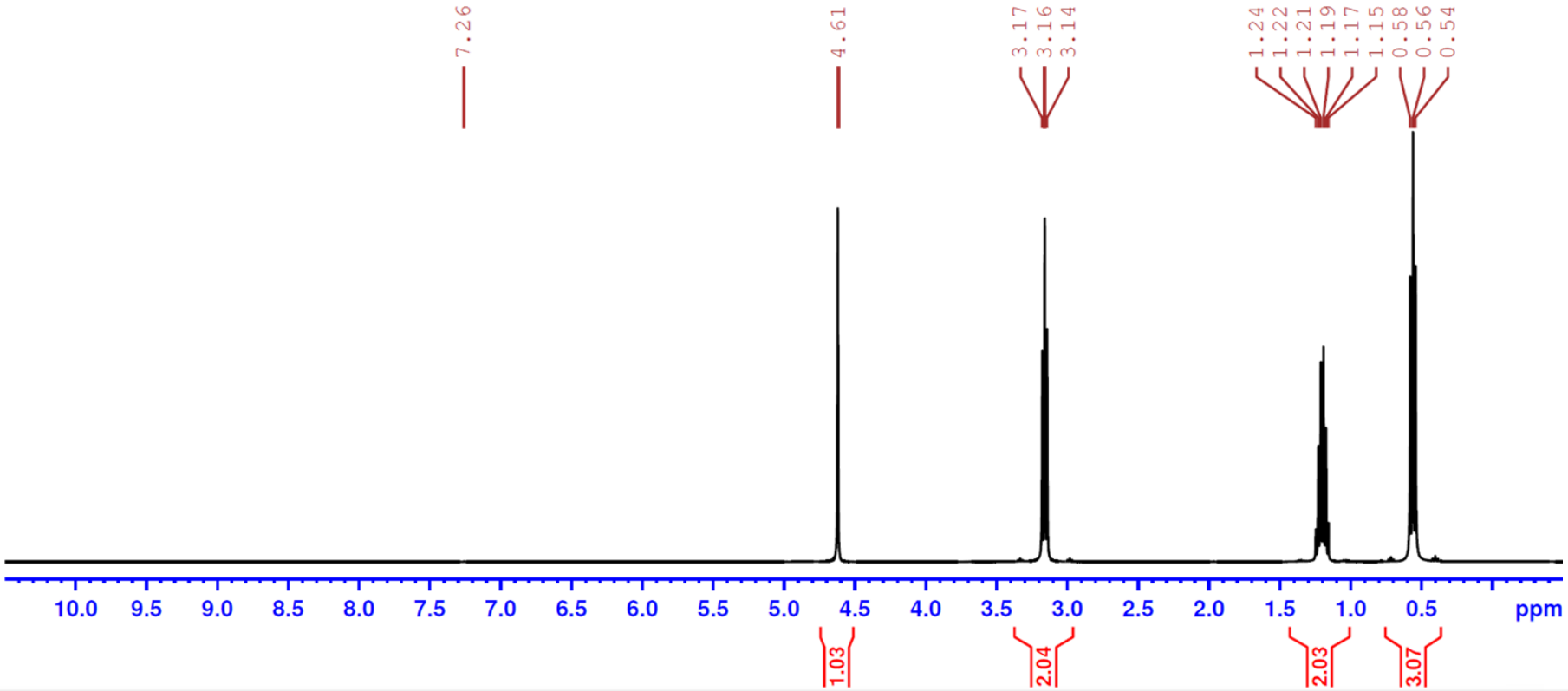


Näide: Propanool (99% puhtusega)

^{1}H TMR spekter:

400 MHz

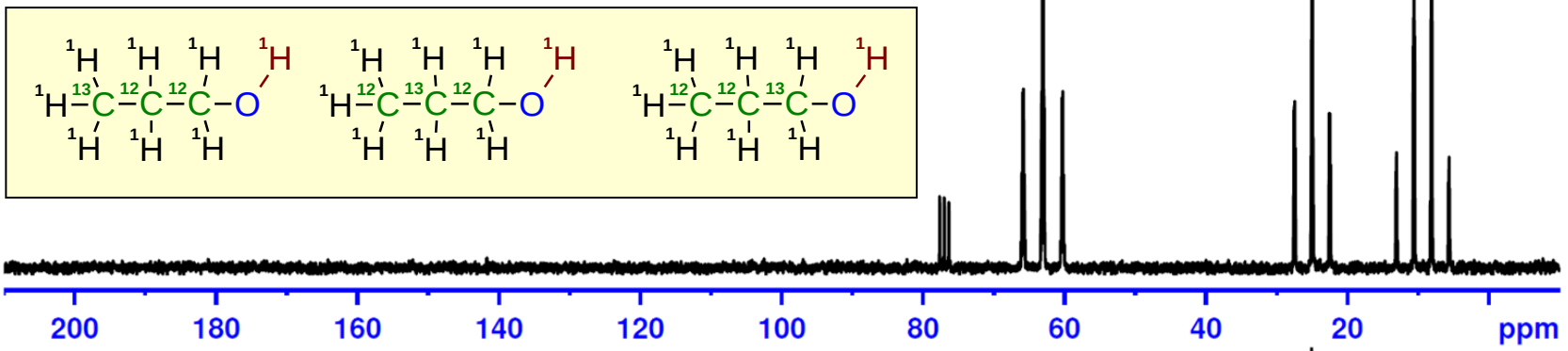




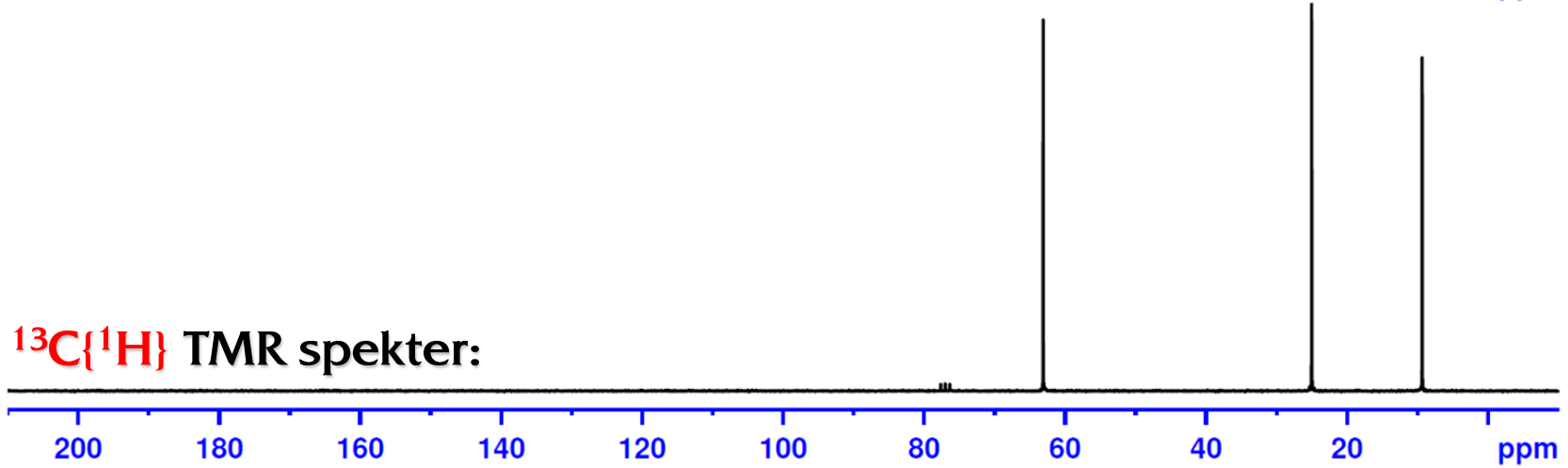
Näide: Propanool (99% puhtusega)

^{13}C TMR spekter:

50 MHz



$^{13}C\{^{1}H\}$ TMR spekter:



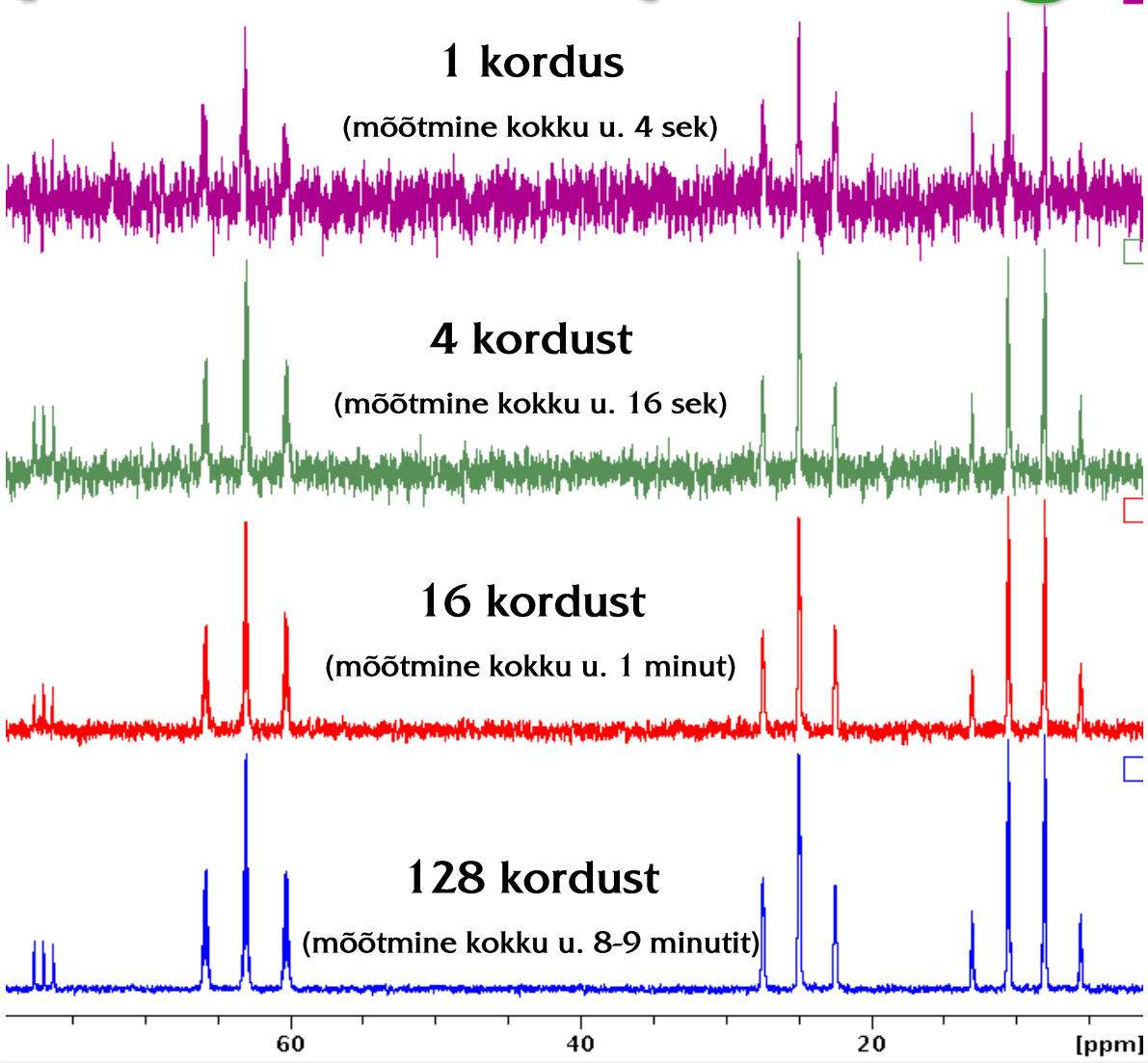
Näide: Propanool (99% puhtusega)

^{13}C TMR spekter:

50 MHz

Signaal-müra paraneb, kui *fid*'e koguda korduvalt ja need summeerida!

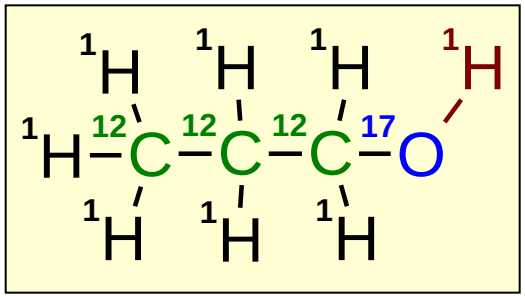
Kuidas veel signaal-müra suhet parandada saab?



Näide: Propanool (99% puhtusega)

^{17}O TMR spekter:

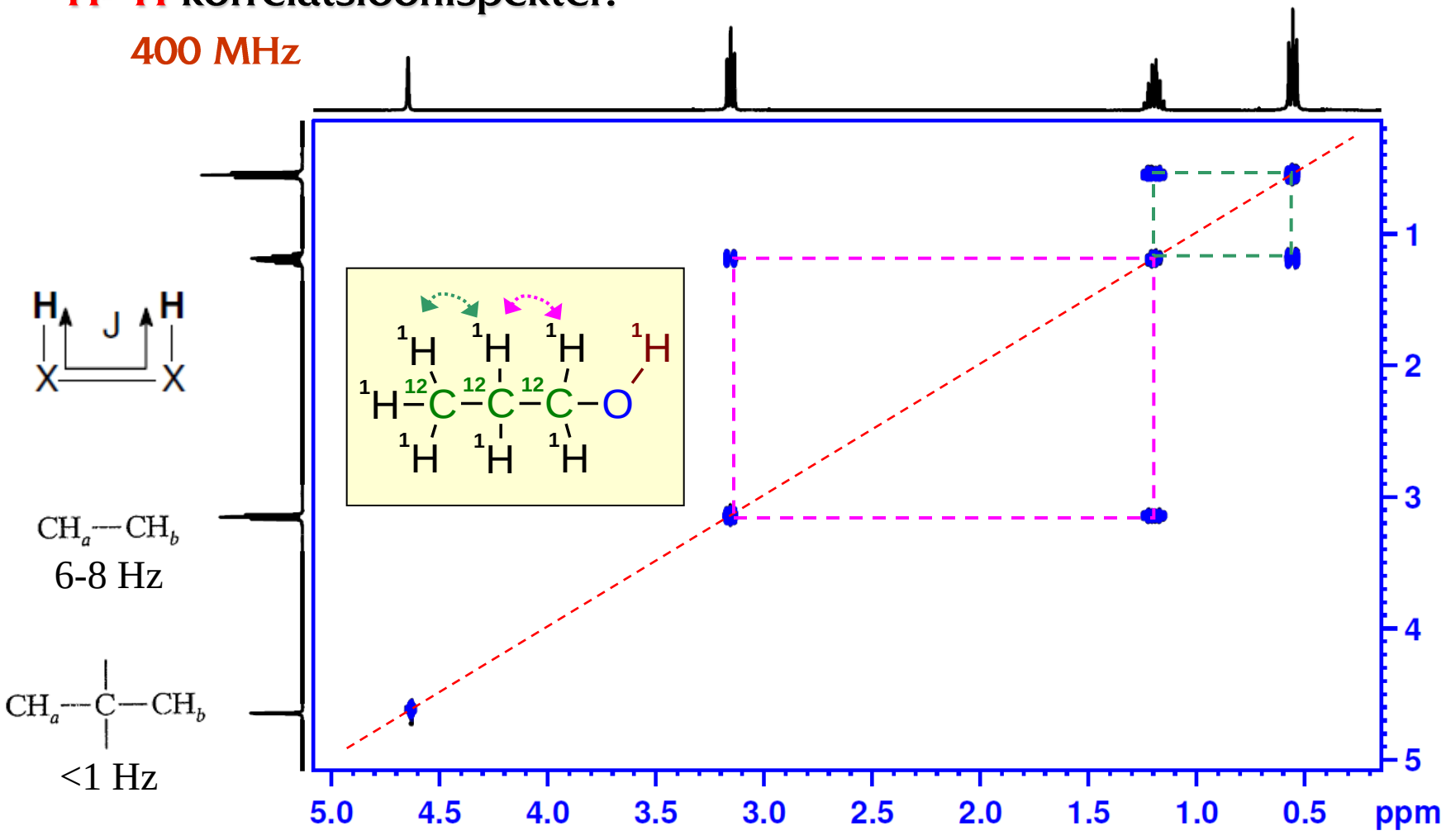
54 MHz



Näide: Propanool (99% puhtusega)

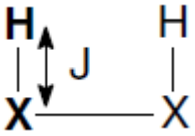
^{1}H-^{1}H korrelatsioonispekter:

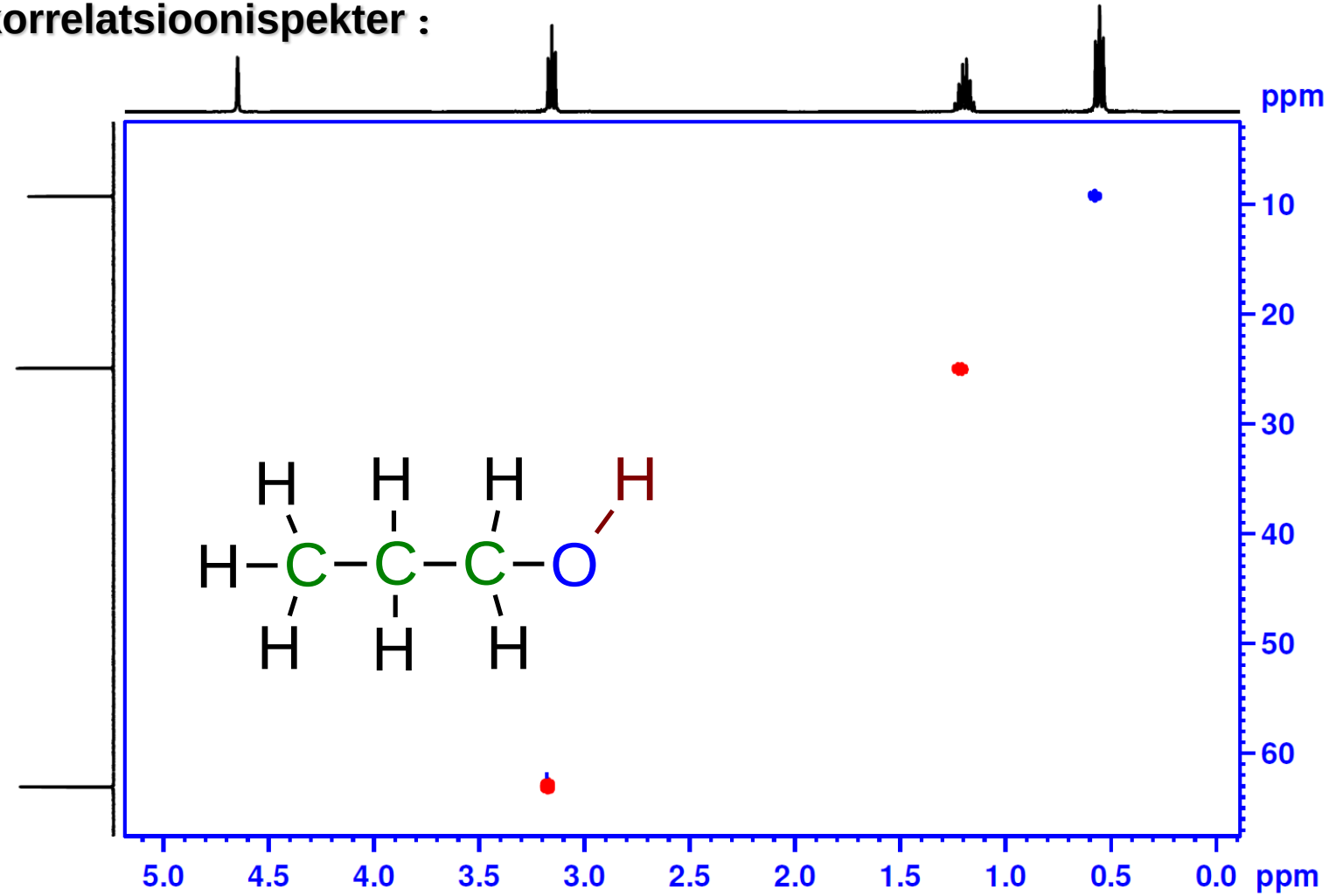
400 MHz



Näide: Propanool (99% puhtusega)

^{1}H-^{13}C korrelatsioonispekter :

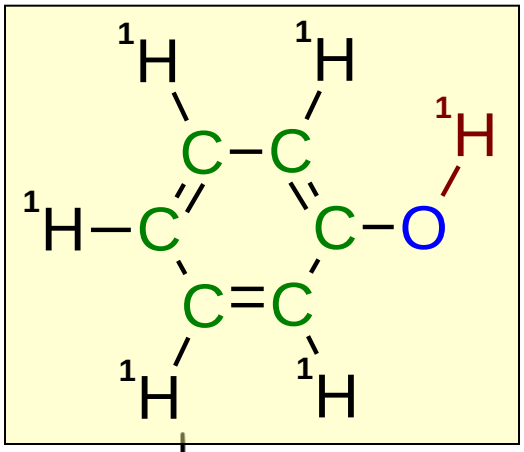




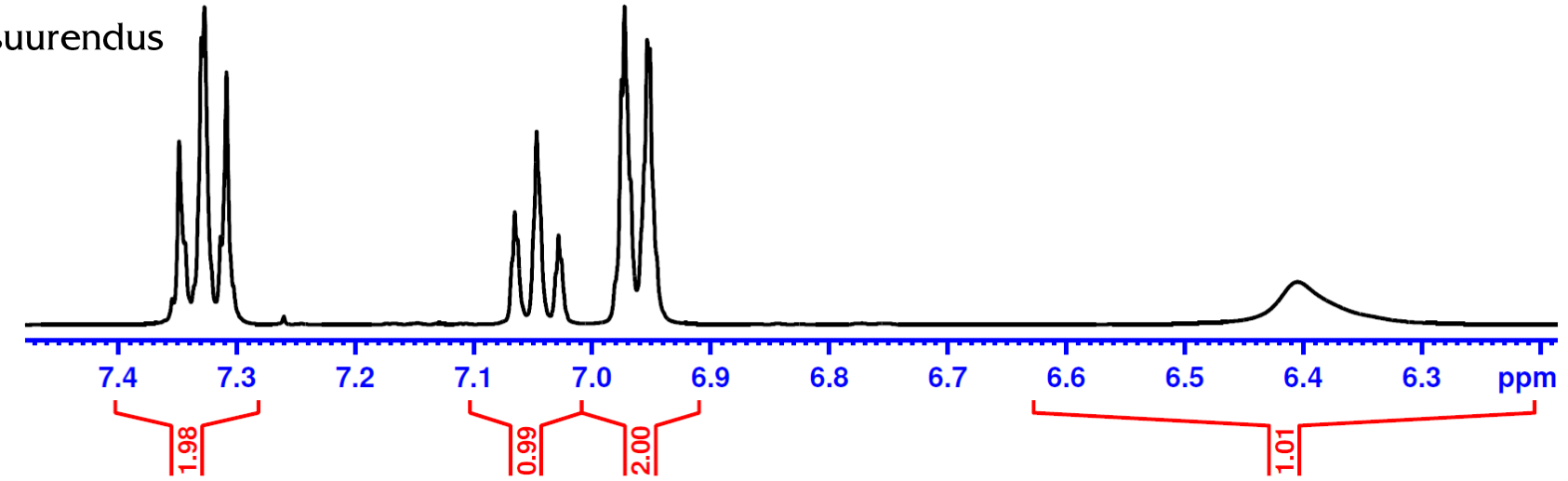
Näide: Fenool (98% puhtusega)

^{1}H TMR spekter:

400 MHz



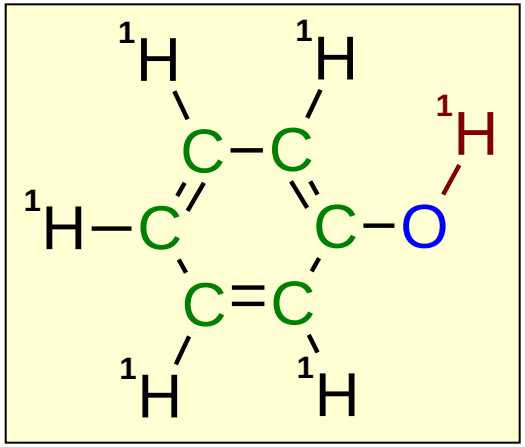
suurendus



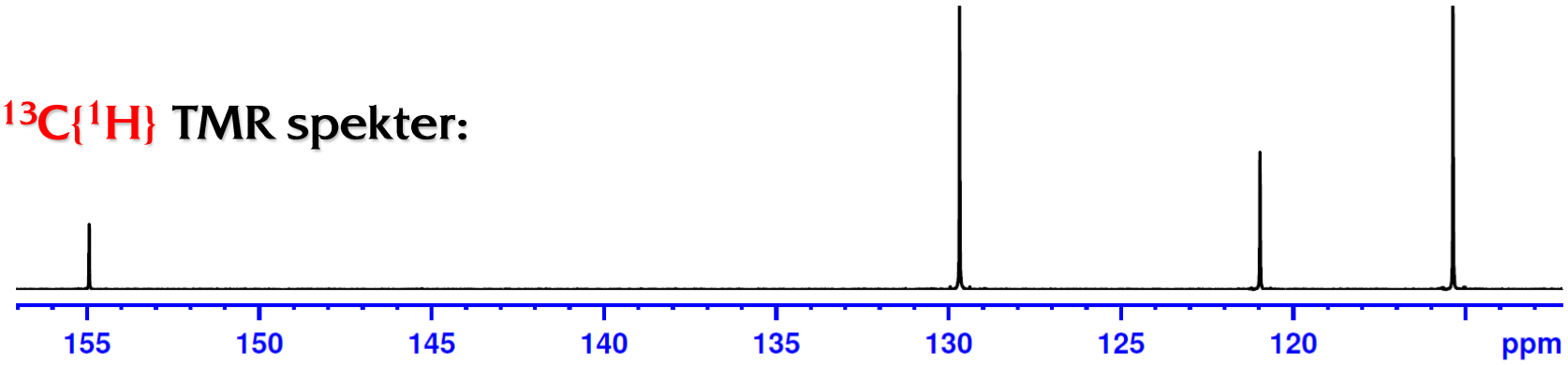
Näide: Fenool (98% puhtusega)

^{13}C TMR spekter:

100 MHz



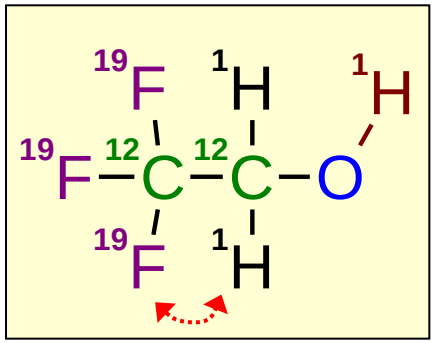
^{13}C{^{1}H} TMR spekter:



Näide: CF_3CH_2OH (99% puhtusega)

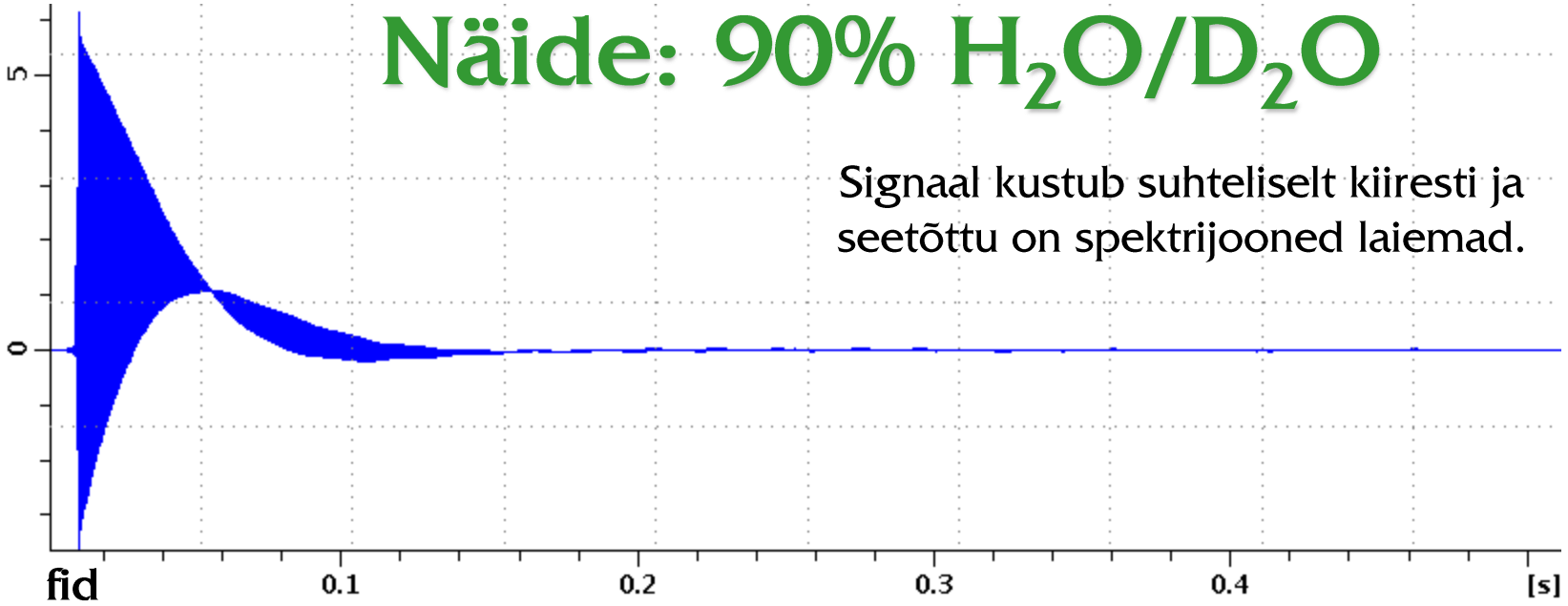
^{19}F TMR spekter:

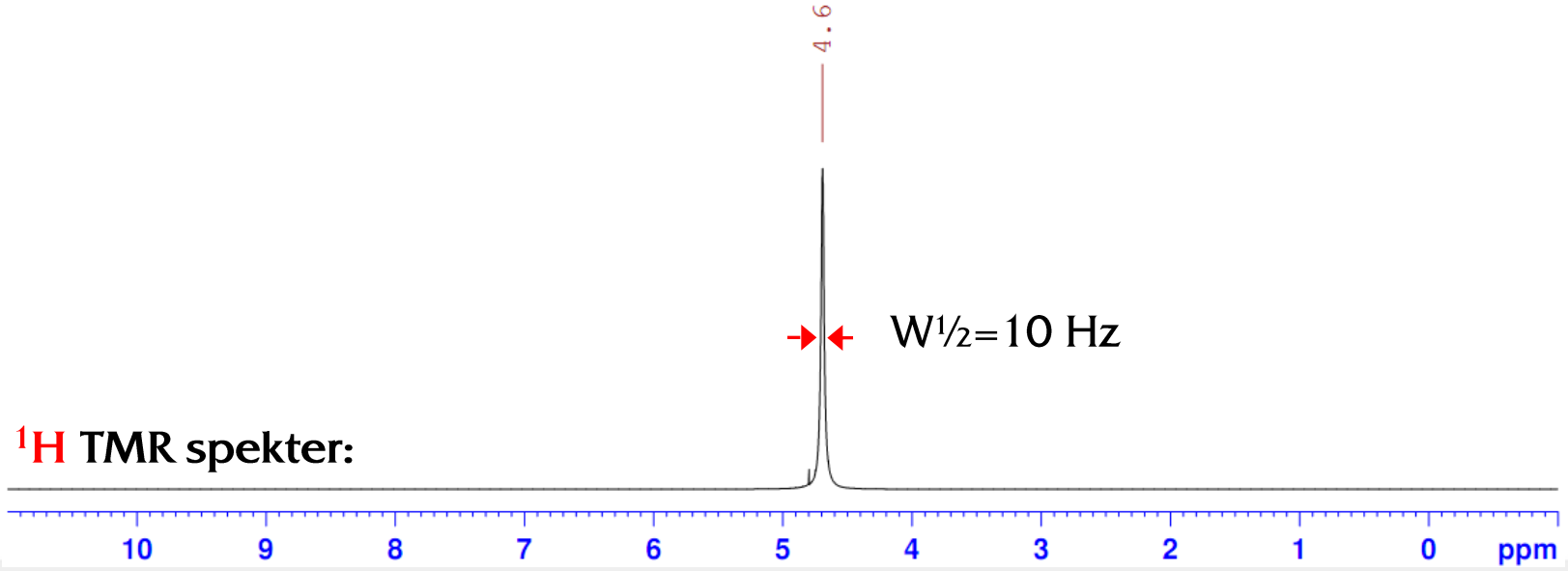
188.3 MHz



Näide: 90% H_2O/D_2O

Signaal kustub suhteliselt kiiresti ja seetõttu on spektrijooned laiemad.

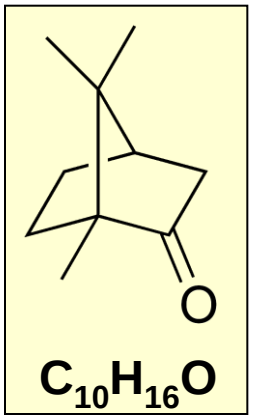




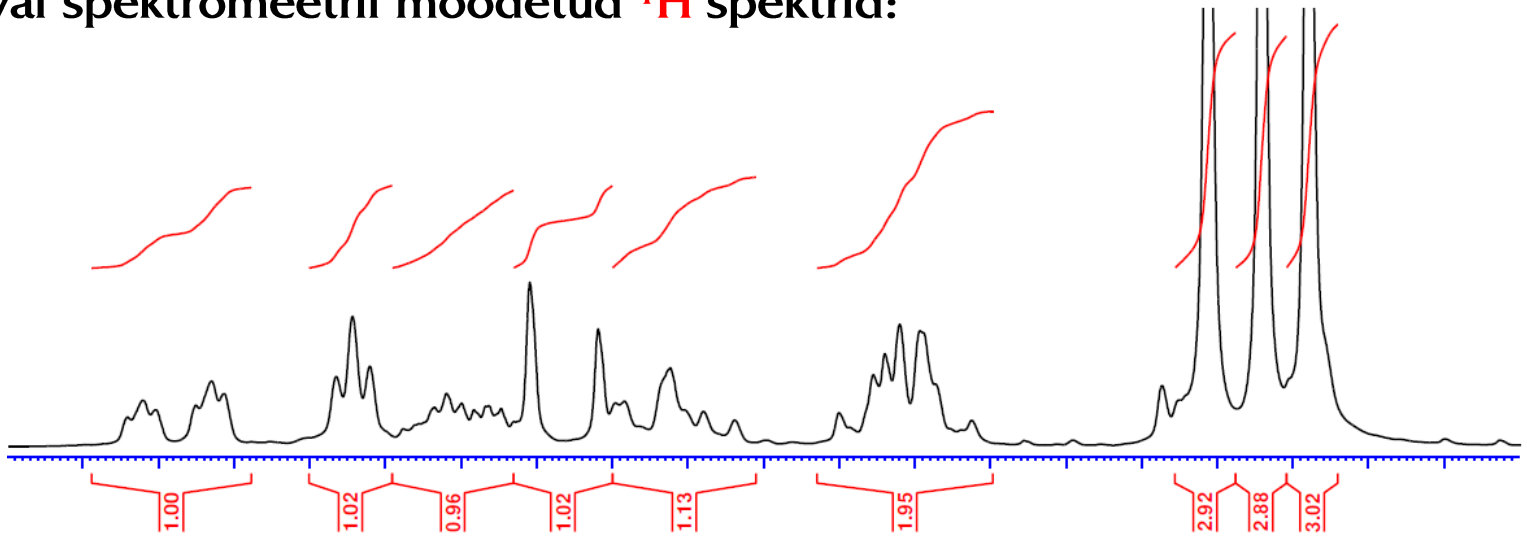
^1H TMR spekter:

Keerulisem näide: Kamper

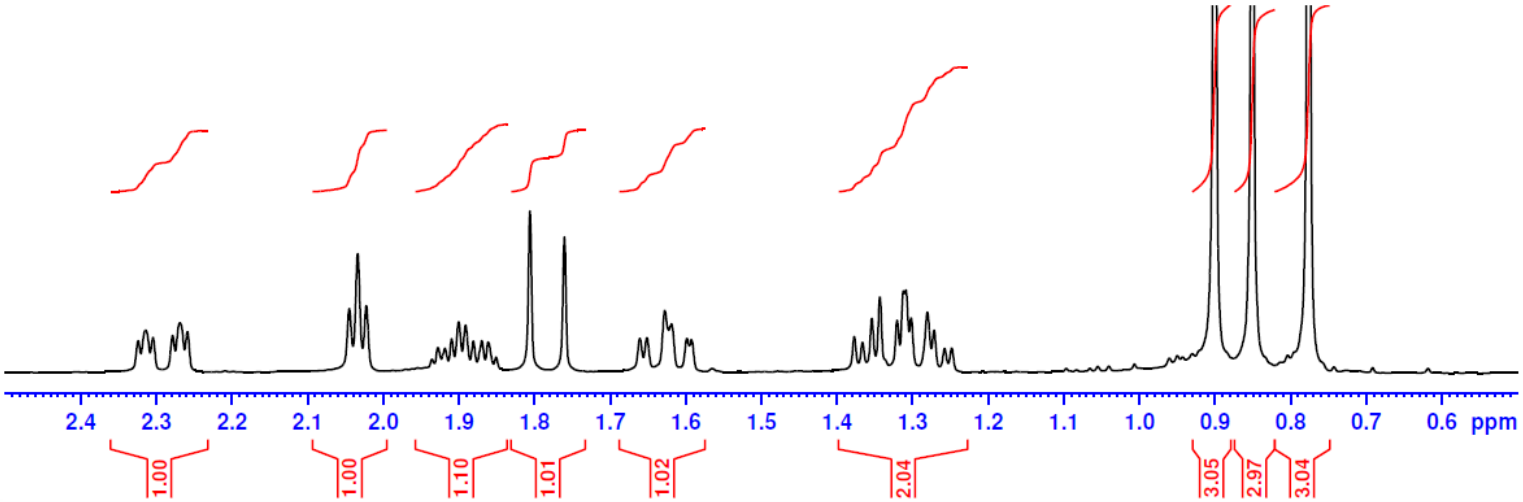
Kahel erineval spektromeetril mõõdetud ^{1}H spektrid:



200 MHz:



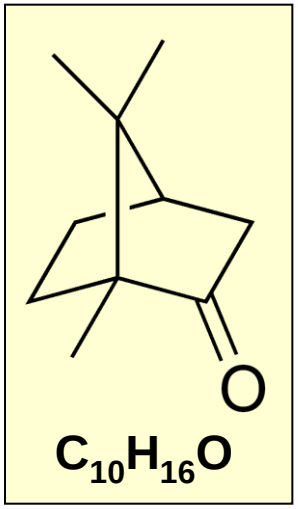
400 MHz:



Näide: Kamper

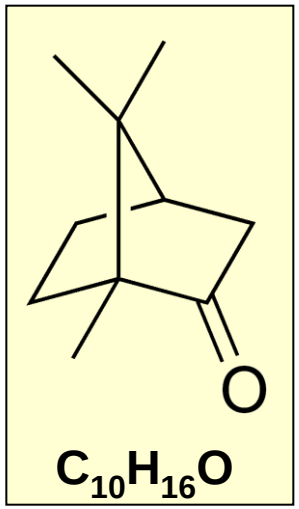
^{13}C TMR spekter:

100 MHz

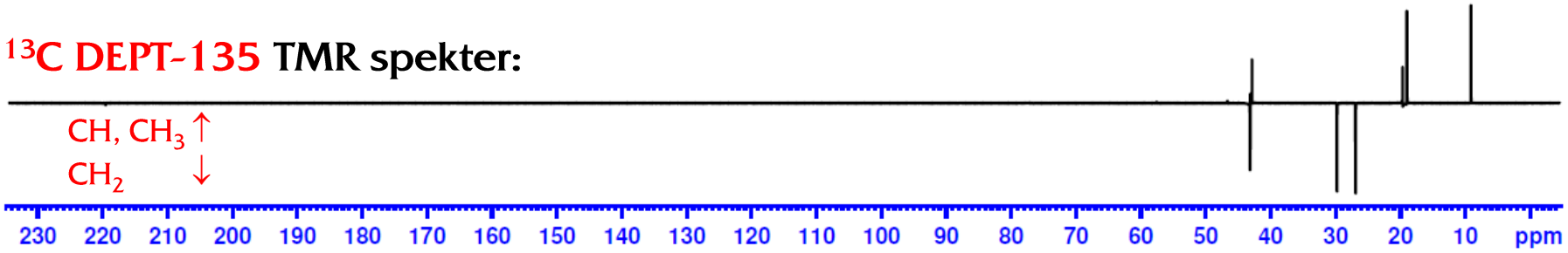


Näide: Kamper

$^{13}C\{^{1}H\}$ TMR spekter:



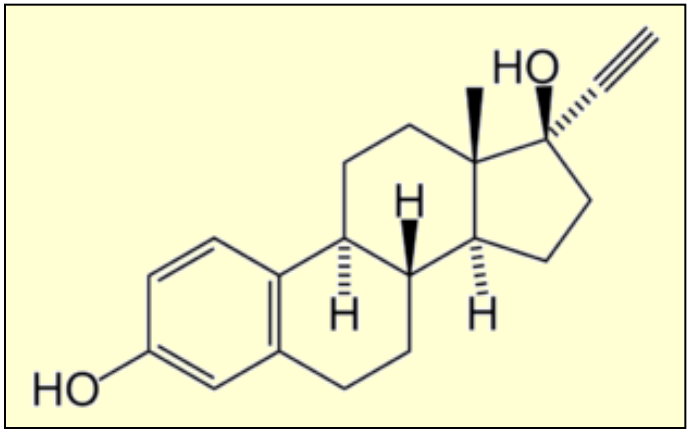
^{13}C DEPT-135 TMR spekter:



Etünüülestradiool (1,0 mg $CDCl_3$-s)

^{1}H TMR spekter:

400 MHz

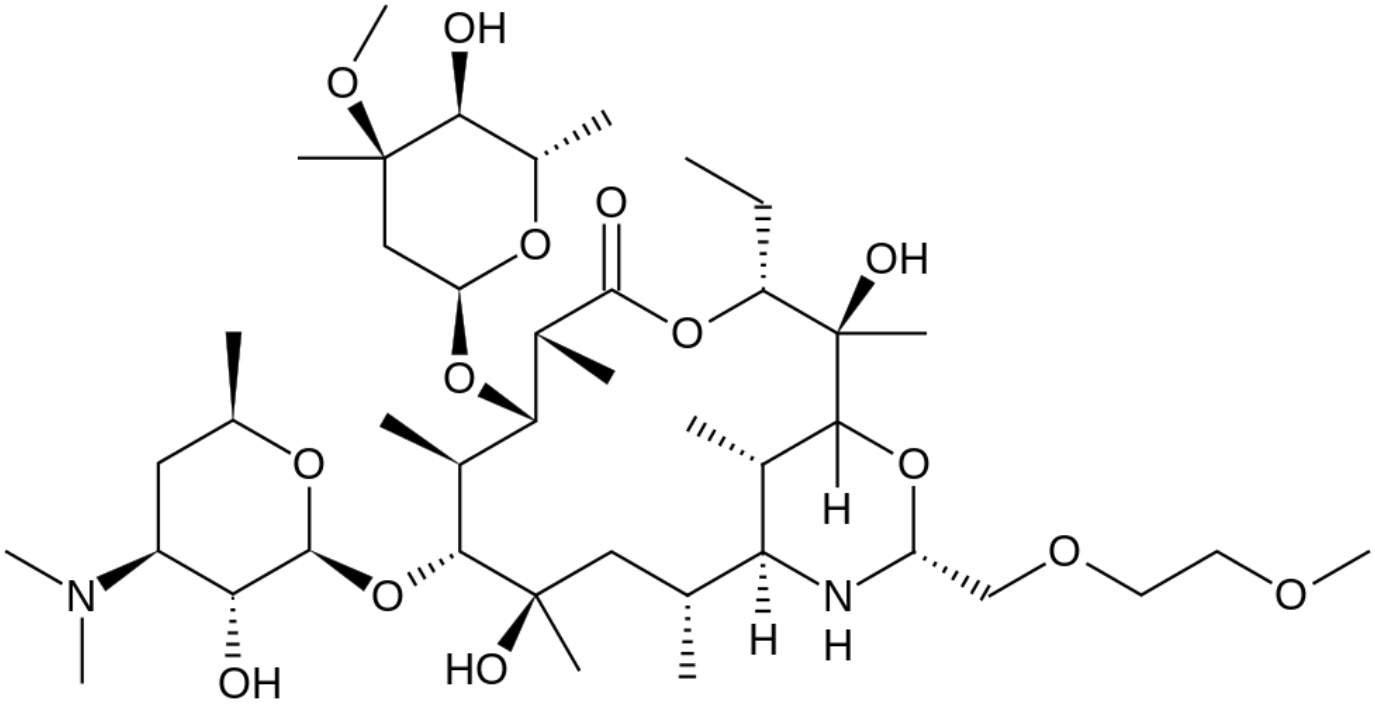


Näide: diritromütsiini spektrid

$C_{42}H_{78}N_2O_{14}$

Molaarmass: 835,1 g/mol

Kontsentratsioon: 2,0 mg/ml ehk 2,4 mM

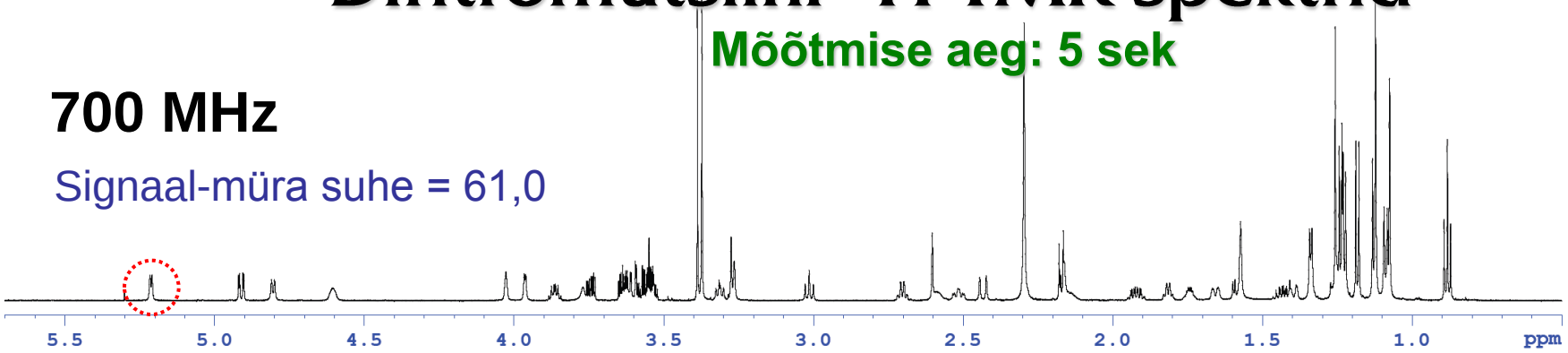


Diritromütsiini ^{1}H TMR spektrid

Mõõtmise aeg: 5 sek

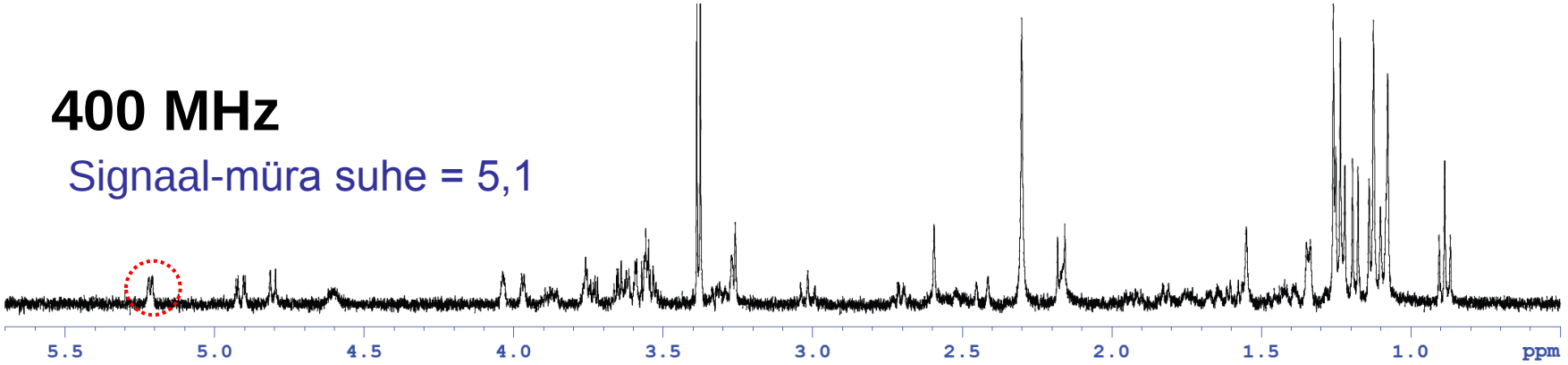
700 MHz

Signaal-müra suhe = 61,0



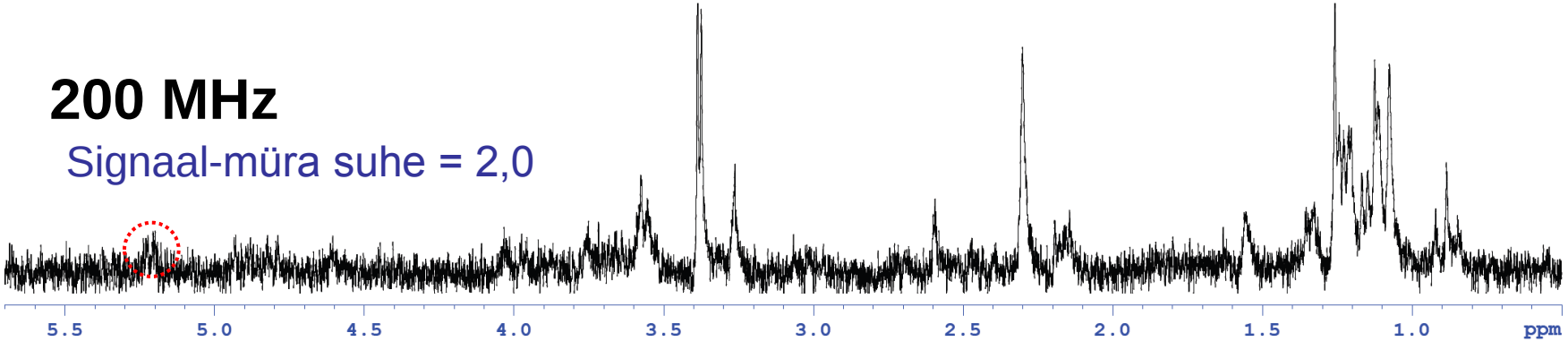
400 MHz

Signaal-müra suhe = 5,1



200 MHz

Signaal-müra suhe = 2,0

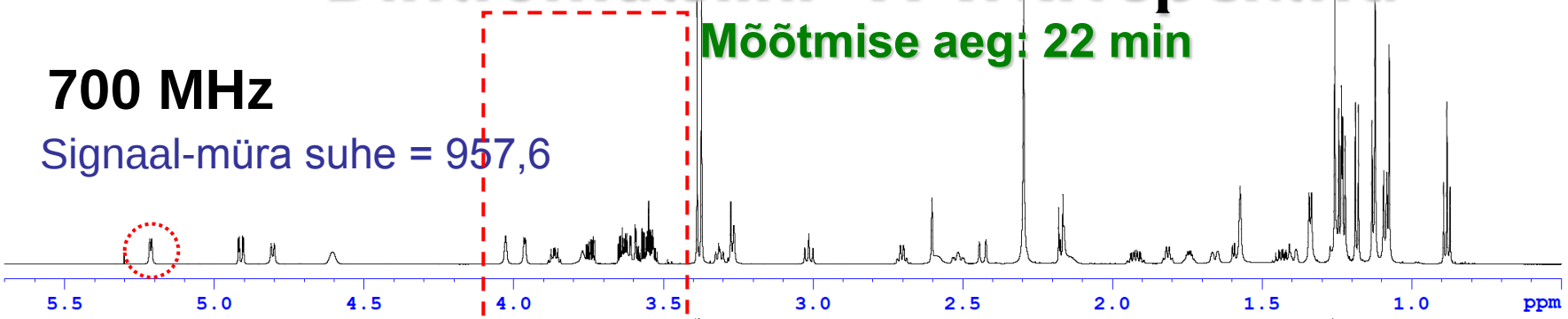


Diritromütsiini ^{1}H TMR spektrid

Mõõtmise aeg: 22 min

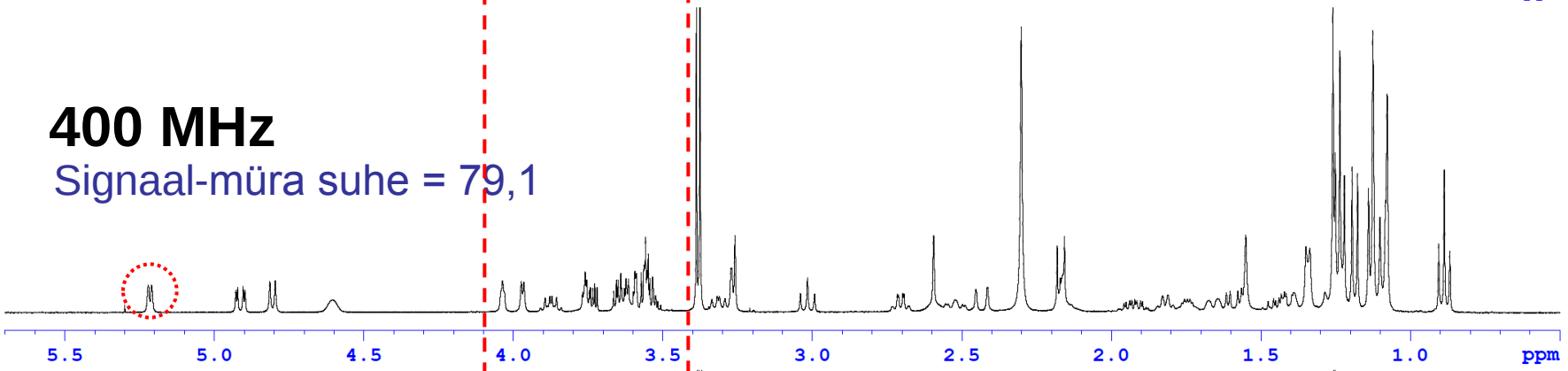
700 MHz

Signaal-müra suhe = 957,6



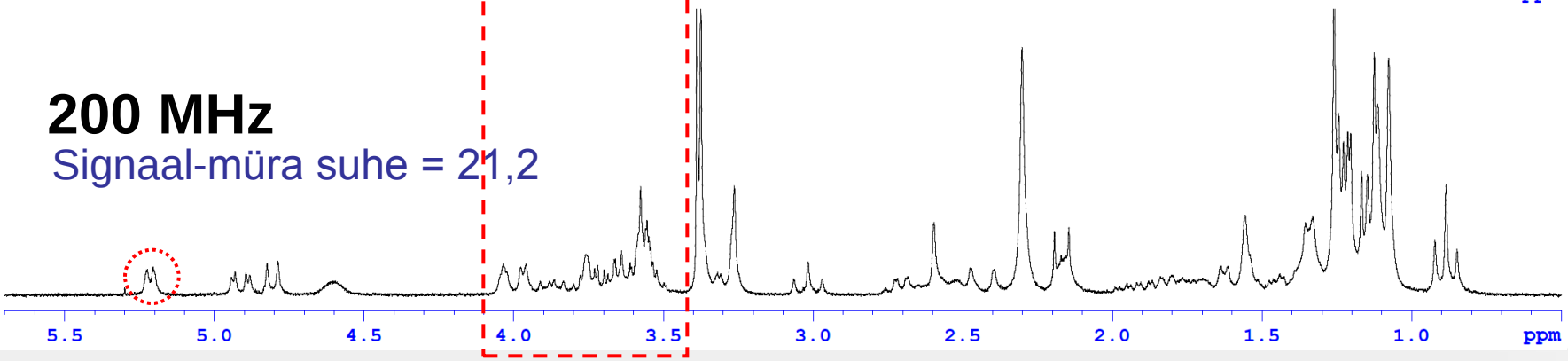
400 MHz

Signaal-müra suhe = 79,1



200 MHz

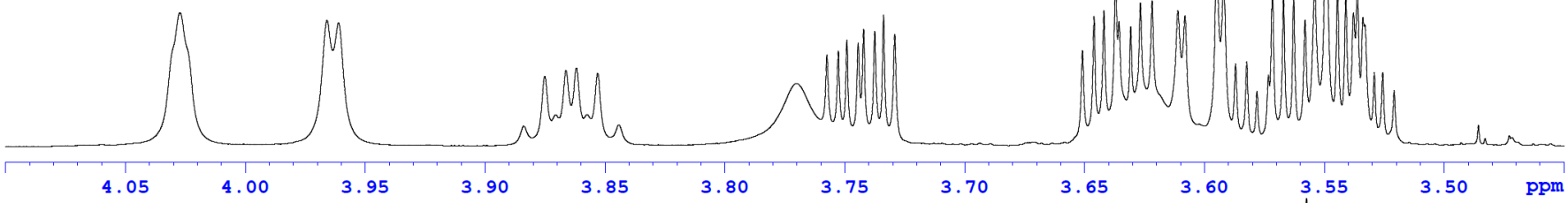
Signaal-müra suhe = 21,2



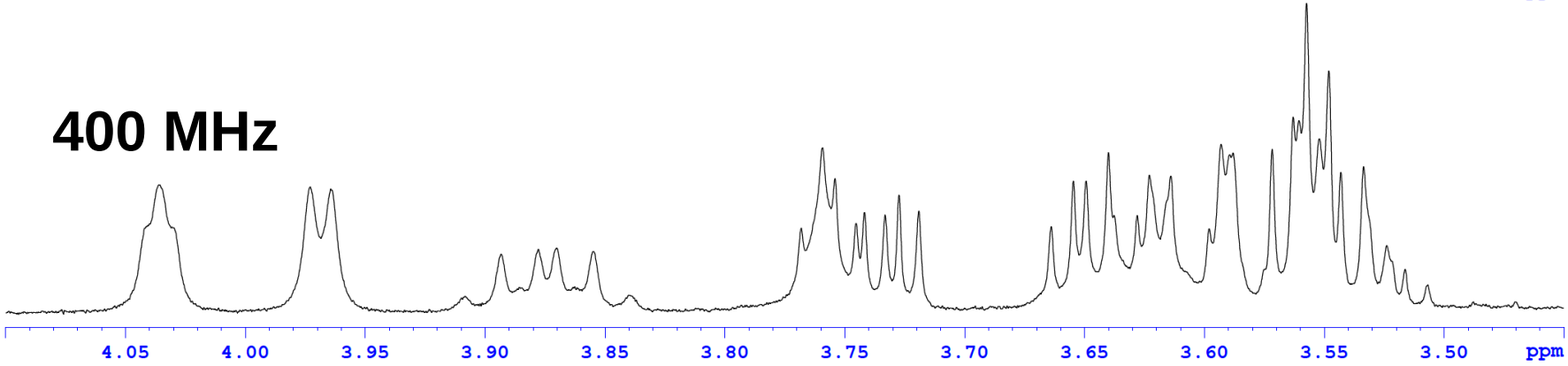
Diritromütsiini ^{1}H TMR spektrid

Suurendus

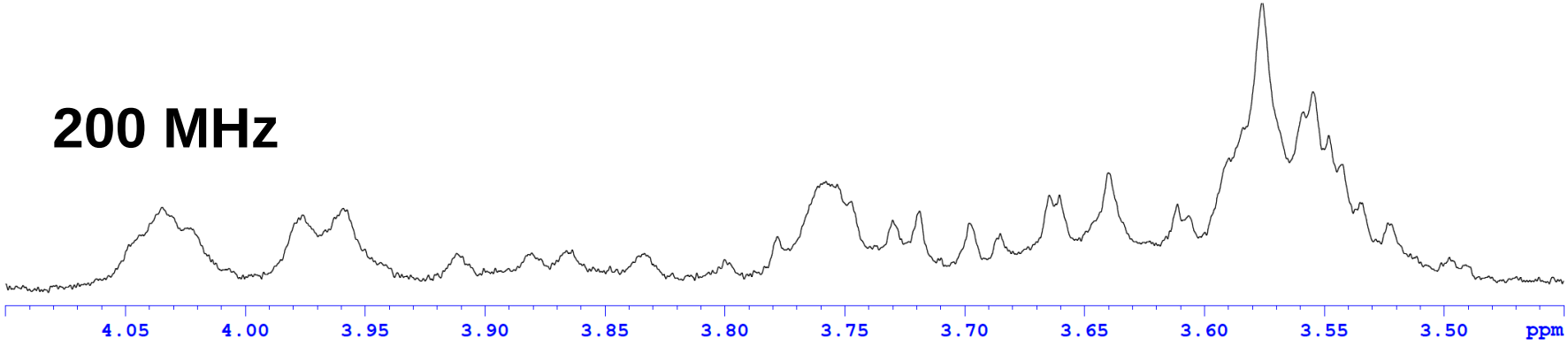
700 MHz



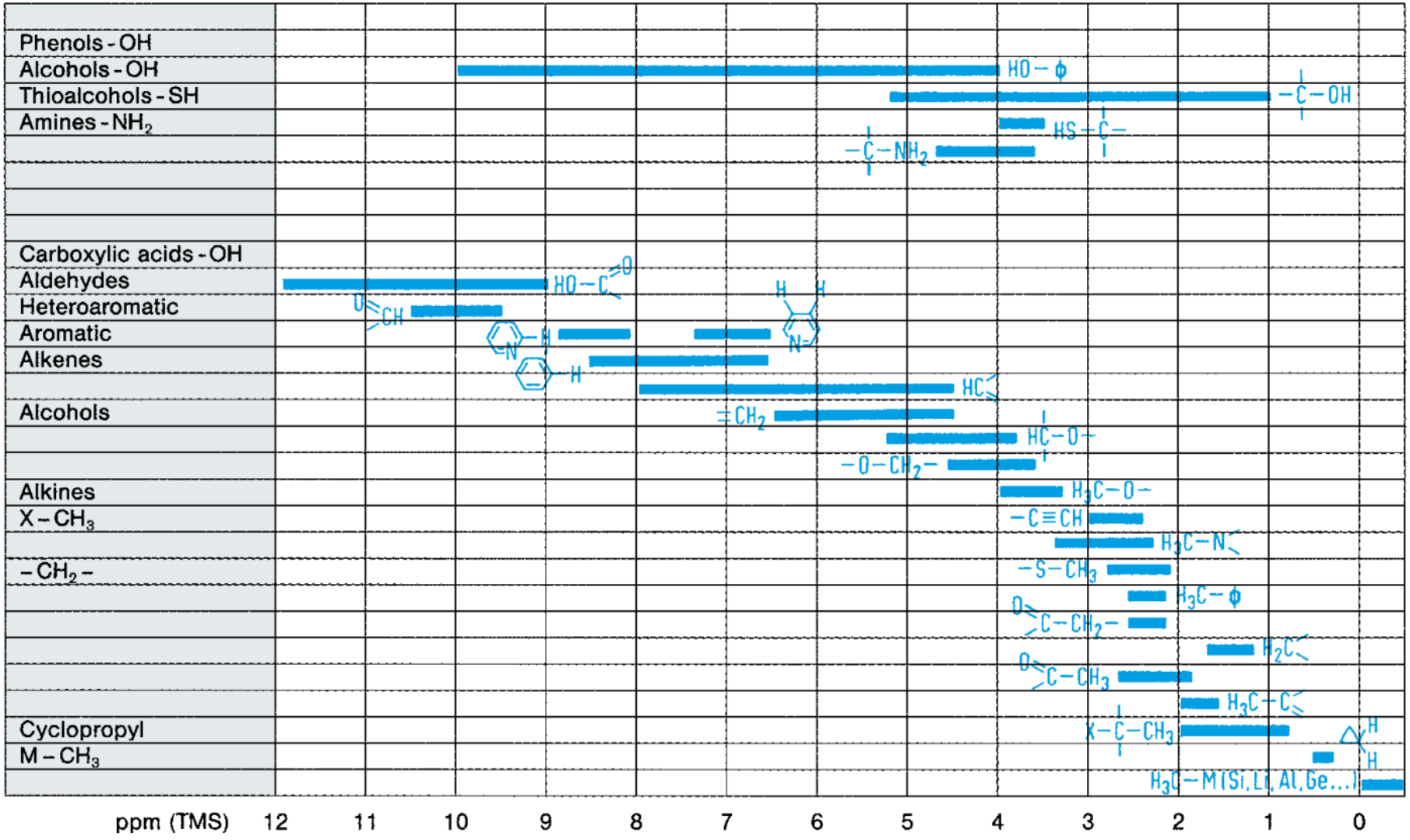
400 MHz



200 MHz



^{1}H TMR keemiliste nihete korrelatsioonitabel



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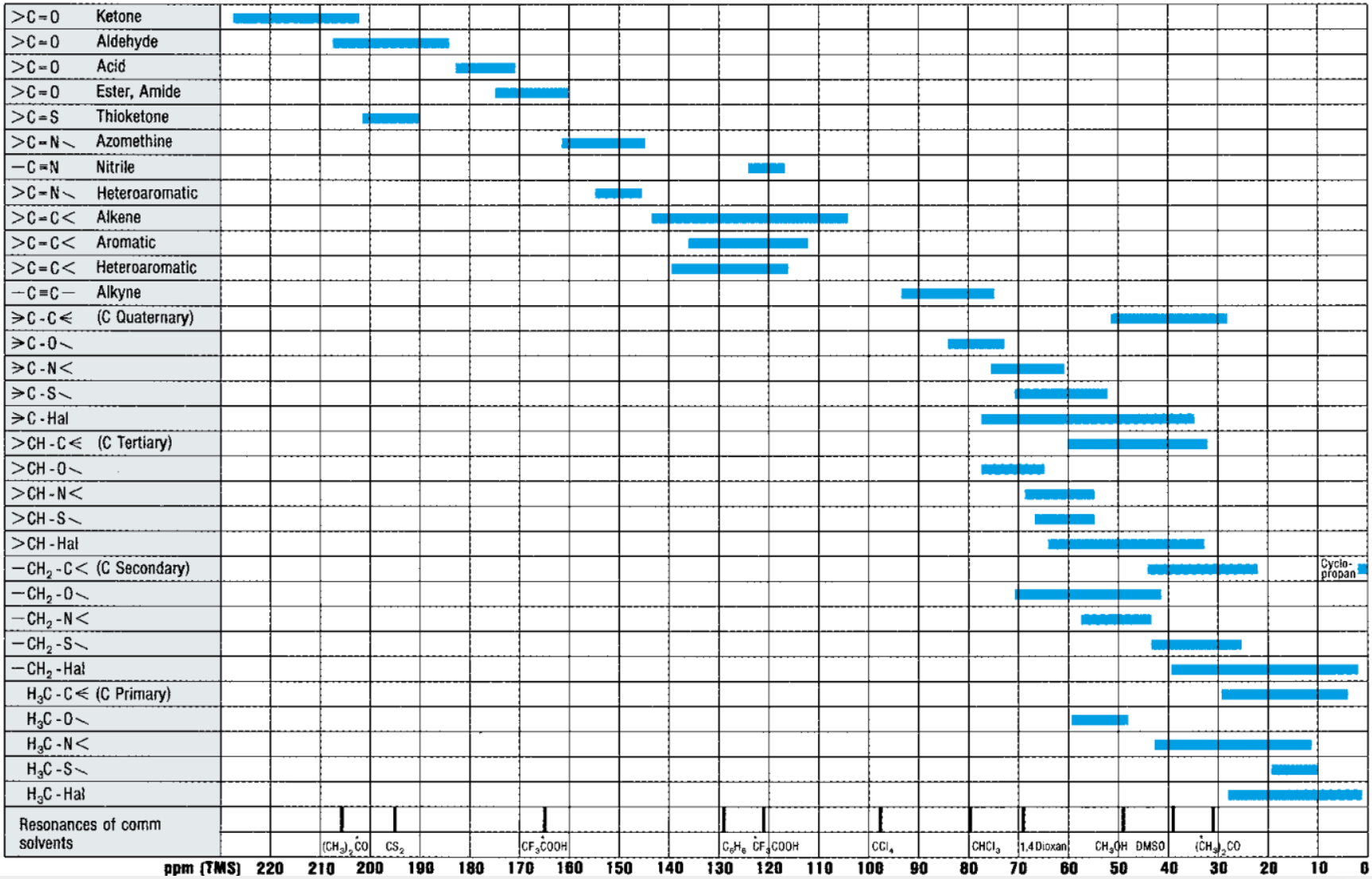
1632

^{13}C TMR keemiliste nihete korrelatsioonitabel



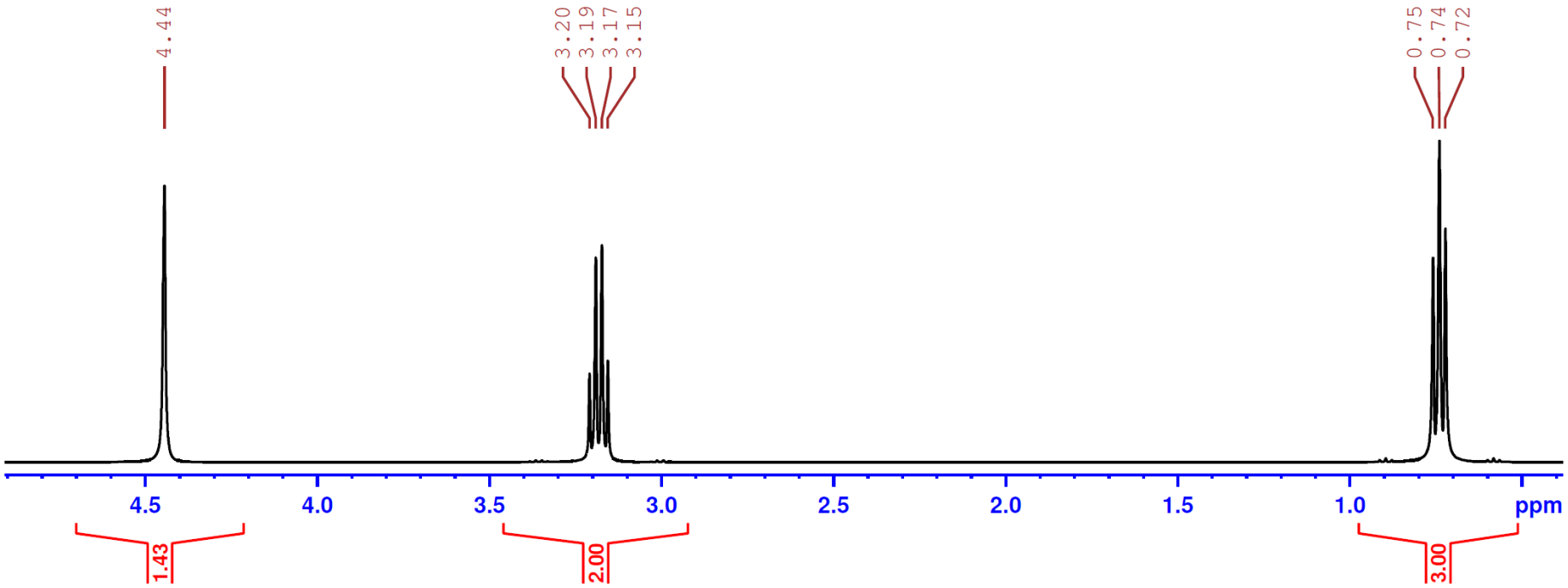
Keemilise nihke tabelid

G. Fulmer, *et al.* "NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist." *Organometallics*, **2010**, *29*, 2176-9.

Table 1. ^{1}H NMR Data[a]

	proton	mult	THF-d_8	CD_2Cl_2	$CDCl_3$	toluene-d_8	C_6D_6	C_6D_5Cl	$(CD_3)_2CO$	$(CD_3)_2SO$	CD_3CN	TFE-d_3	CD_3OD	D_2O
solvent residual			1.72	5.32	7.26	2.08	7.16	6.96	2.05	2.50	1.94	5.02	3.31	4.79
signals			3.58			6.97		6.99				3.88		
						7.01		7.14						
						7.09								
water	OH	s	2.46	1.52	1.56	0.43	0.40	1.03	2.84[b]	3.33[b]	2.13	3.66	4.87	
acetic acid	CH_3	s	1.89	2.06	2.10	1.57	1.52	1.76	1.96	1.91	1.96	2.06	1.99	2.08
acetone	CH_3	s	2.05	2.12	2.17	1.57	1.55	1.77	2.09	2.09	2.08	2.19	2.15	2.22
acetonitrile	CH_3	s	1.95	1.97	2.10	0.69	0.58	1.21	2.05	2.07	1.96	1.95	2.03	2.06
benzene	CH	s	7.31	7.35	7.36	7.12	7.15	7.20	7.36	7.37	7.37	7.36	7.33	
tert -butyl alcohol	CH_3	s	1.15	1.24	1.28	1.03	1.05	1.12	1.18	1.11	1.16	1.28	1.40	1.24
	OH	s[c]	3.16			0.58	0.63	1.30		4.19	2.18	2.20		
chloroform	CH	s	7.89	7.32	7.26	6.10	6.15	6.74	8.02	8.32	7.58	7.33	7.90	
18-crown-6	CH_2	s	3.57	3.59	3.67	3.36	3.39	3.41	3.59	3.51	3.51	3.64	3.64	3.80
cyclohexane	CH_2	s	1.44	1.44	1.43	1.40	1.40	1.37	1.43	1.40	1.44	1.47	1.45	
1,2-dichloroethane	CH_2	s	3.77	3.76	3.73	2.91	2.90	3.26	3.87	3.90	3.81	3.71	3.78	
dichloromethane	CH_2	s	5.51	5.33	5.30	4.32	4.27	4.77	5.63	5.76	5.44	5.24	5.49	
diethyl ether	CH_3	t, 7	1.12	1.15	1.21	1.10	1.11	1.10	1.11	1.09	1.12	1.20	1.18	1.17
	CH_2	q, 7	3.38	3.43	3.48	3.25	3.26	3.31	3.41	3.38	3.42	3.58	3.49	3.56
diglyme	CH_2	m	3.43	3.57	3.65	3.43	3.46	3.49	3.56	3.51	3.53	3.67	3.61	3.67
	CH_2	m	3.53	3.50	3.57	3.31	3.34	3.37	3.47	3.38	3.45	3.62	3.58	3.61
	OCH_3	s	3.28	3.33	3.39	3.12	3.11	3.16	3.28	3.24	3.29	3.41	3.35	3.37
dimethylformamide	CH	s	7.91	7.96	8.02	7.57	7.63	7.73	7.96	7.95	7.92	7.86	7.97	7.92
	CH_3	s	2.88	2.91	2.96	2.37	2.36	2.51	2.94	2.89	2.89	2.98	2.99	3.01
	CH_3	s	2.76	2.82	2.88	1.96	1.86	2.30	2.78	2.73	2.77	2.88	2.86	2.85
1,4-dioxane	CH_2	s	3.56	3.65	3.71	3.33	3.35	3.45	3.59	3.57	3.60	3.76	3.66	3.75
DME	CH_3	s	3.28	3.34	3.40	3.12	3.12	3.17	3.28	3.24	3.28	3.40	3.35	3.37
	CH_2	s	3.43	3.49	3.55	3.31	3.33	3.37	3.46	3.43	3.45	3.61	3.52	3.60
ethane	CH_3	s	0.85	0.85	0.87	0.81	0.80	0.79	0.83	0.82	0.85	0.85	0.85	0.82
ethanol	CH_3	t, 7	1.10	1.19	1.25	0.97	0.96	1.06	1.12	1.06	1.12	1.22	1.19	1.17
	CH_2	q, 7[d]	3.51	3.66	3.72	3.36	3.34	3.51	3.57	3.44	3.54	3.71	3.60	3.65
	OH	s[c,d]	3.30	1.33	1.32	0.83	0.50	1.39	3.39	4.63	2.47			

^{1}H TMR spektri raporteerimine

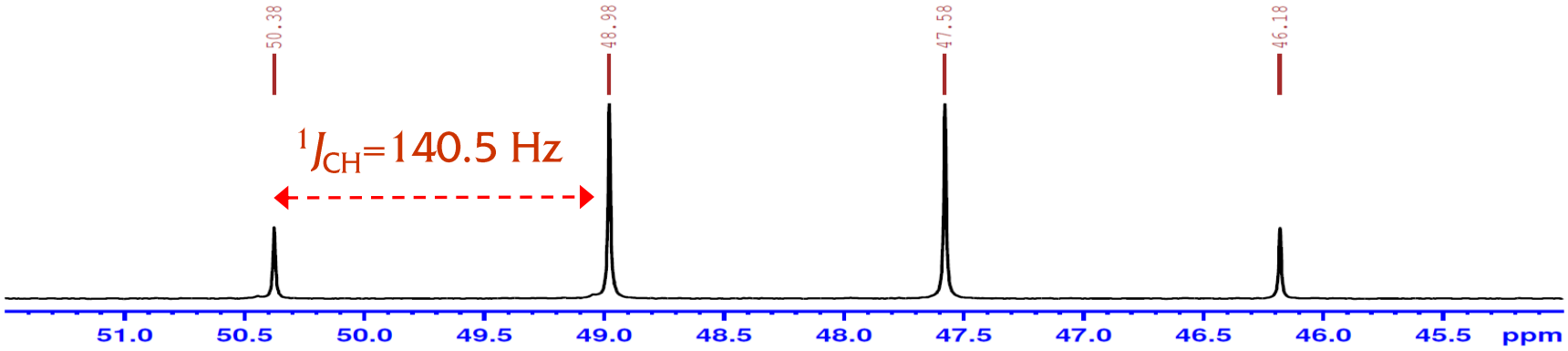


^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ: 4.44 (s, 1H, O*H*); 3.18 (q, $^3J_{HH}$=7.1 Hz, 2H, C*H*$_2$); 0.74 (t, $^3J_{HH}$=7.1 Hz, 3H, C*H*$_3$).

NB! Keemilise nihke (*δ*) väärtused esitatakse ^{1}H spektrite puhul ppm-ides täpsusega 2 kümnendkohta!

NB! Sidestuskonstantide (*J*) väärtused esitatakse hertsides täpsusega 1 kümnendkoht!

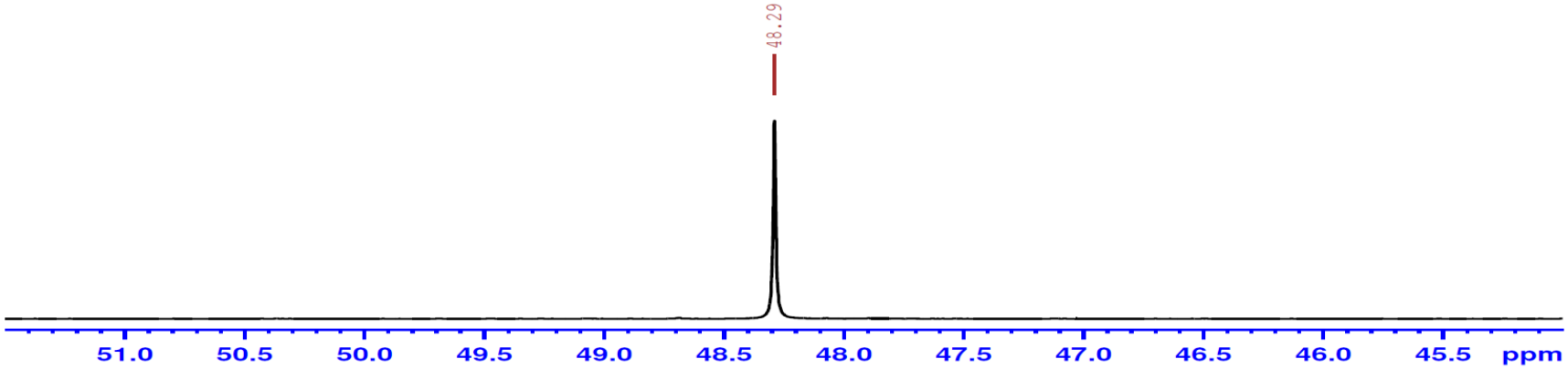
^{13}C TMR spektri raporteerimine



^{13}C TMR (100.6 MHz, $CDCl_3$, 25 °C) δ: 48.3 (q, $^{1}J_{CH}$ = 140.5 Hz, $\underline{C}H_3$);

NB! Sidestuskonstantide (*J*) väärtused esitatakse hertsides täpsusega 1 kümnendkoht!

NB! Keemilise nihke (*δ*) väärtused esitatakse ^{13}C spektrite puhul ppm-ides enamasti täpsusega 1 kümnendkoht!



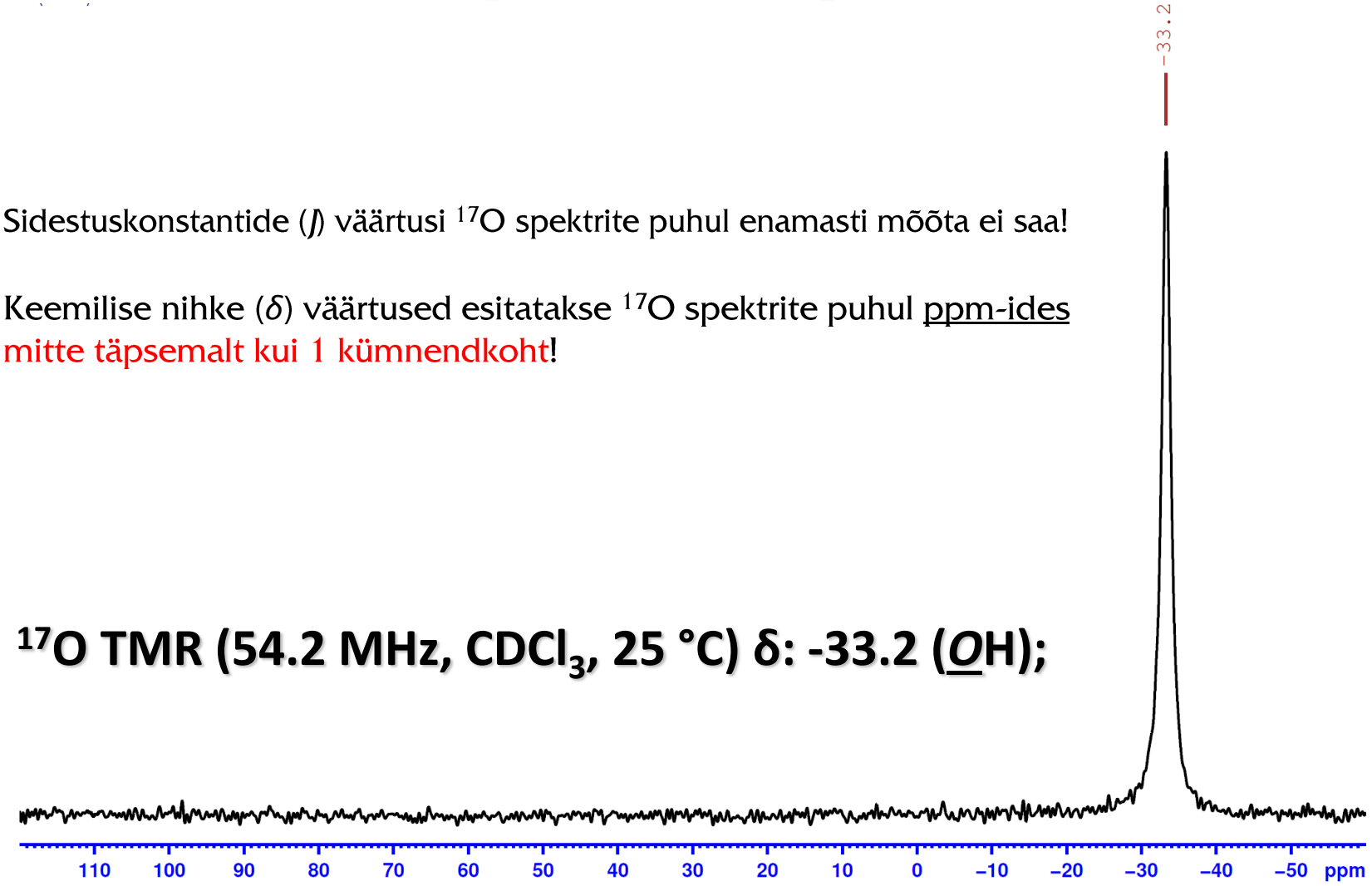
^{13}C{^{1}H} TMR (100.6 MHz, $CDCl_3$, 25 °C) δ: 48.3 ($\underline{C}H_3$);

^{17}O TMR spektri raporteerimine

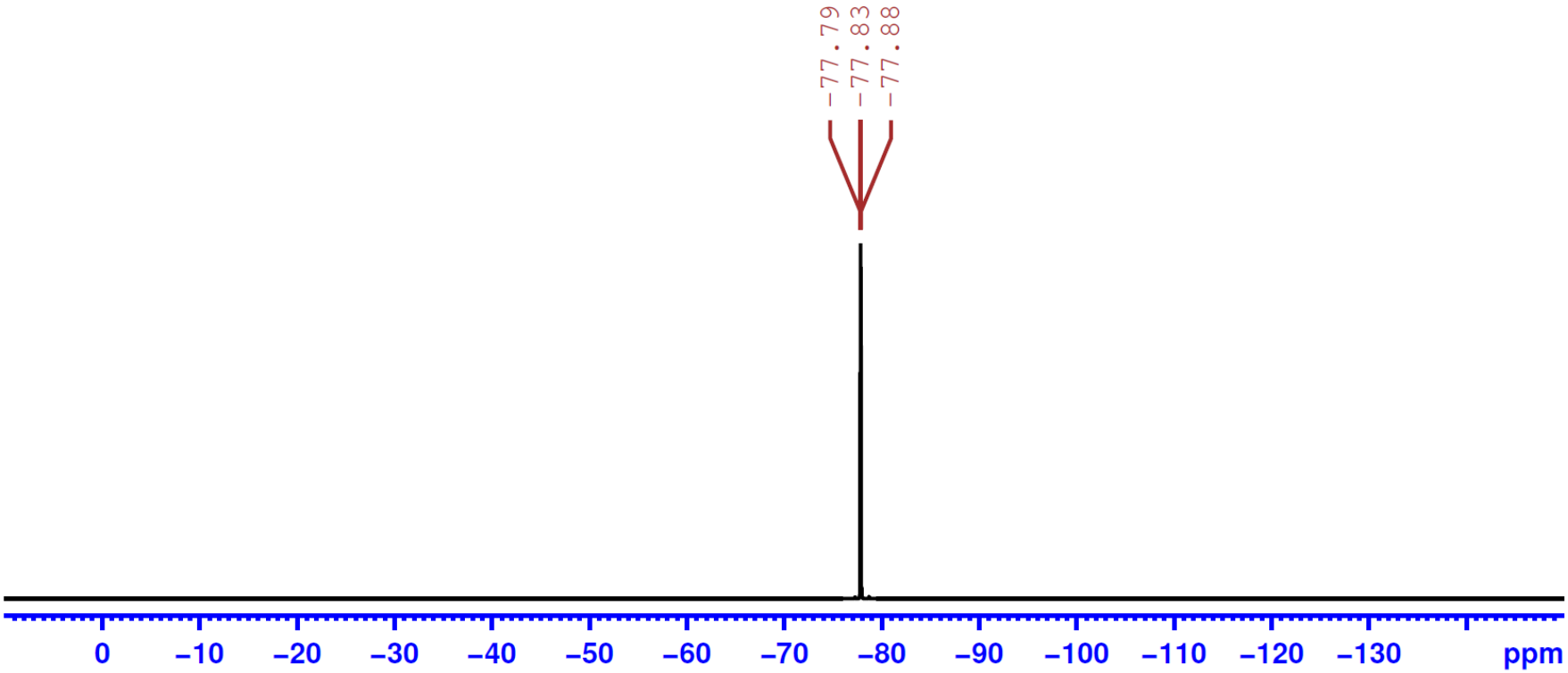
Sidestuskonstantide (*J*) väärtusi ^{17}O spektrite puhul enamasti mõõta ei saa!

Keemilise nihke (*δ*) väärtused esitatakse ^{17}O spektrite puhul ppm-ides mitte täpsemalt kui 1 kümnendkoht!

^{17}O TMR (54.2 MHz, $CDCl_3$, 25 °C) δ: -33.2 (*O*H);



^{19}F TMR spektri raporteerimine



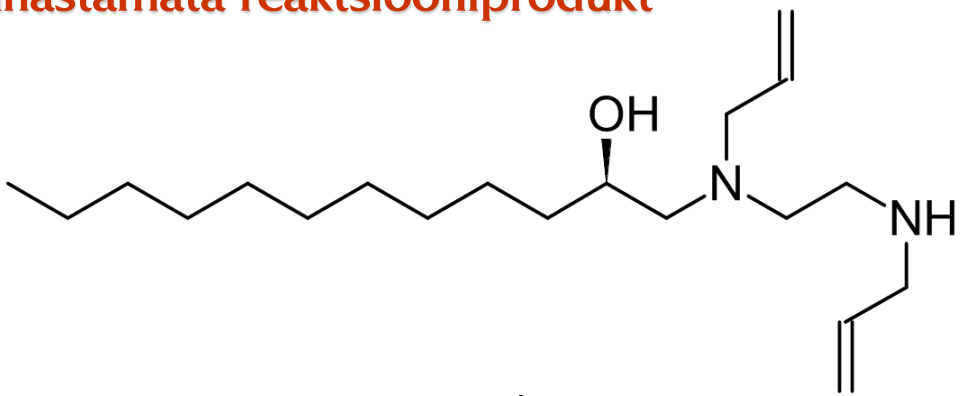
^{19}F TMR (188.3 MHz, $CDCl_3$, 25 °C) δ: -77.8 (t, $^3J_{FH}$ = 8.5 Hz, 3F, C$\underline{F}_3$);

^{19}F andmed (keemilised nihked ja sidestuskonstandid) esitatakse sarnaselt ^{1}H TMR spektriandmetele!

Aine puhtuse hindamine

^{1}H TMR spekter:

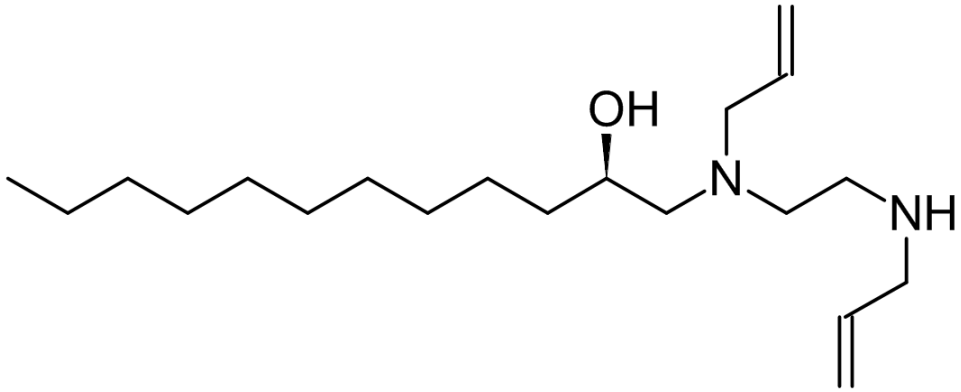
Puhastamata reaktsiooniprodukt



Sünteesiprodukt ($CDCl_3$-s)

^{1}H TMR spekter:

Puhastatud reaktsiooniprodukt



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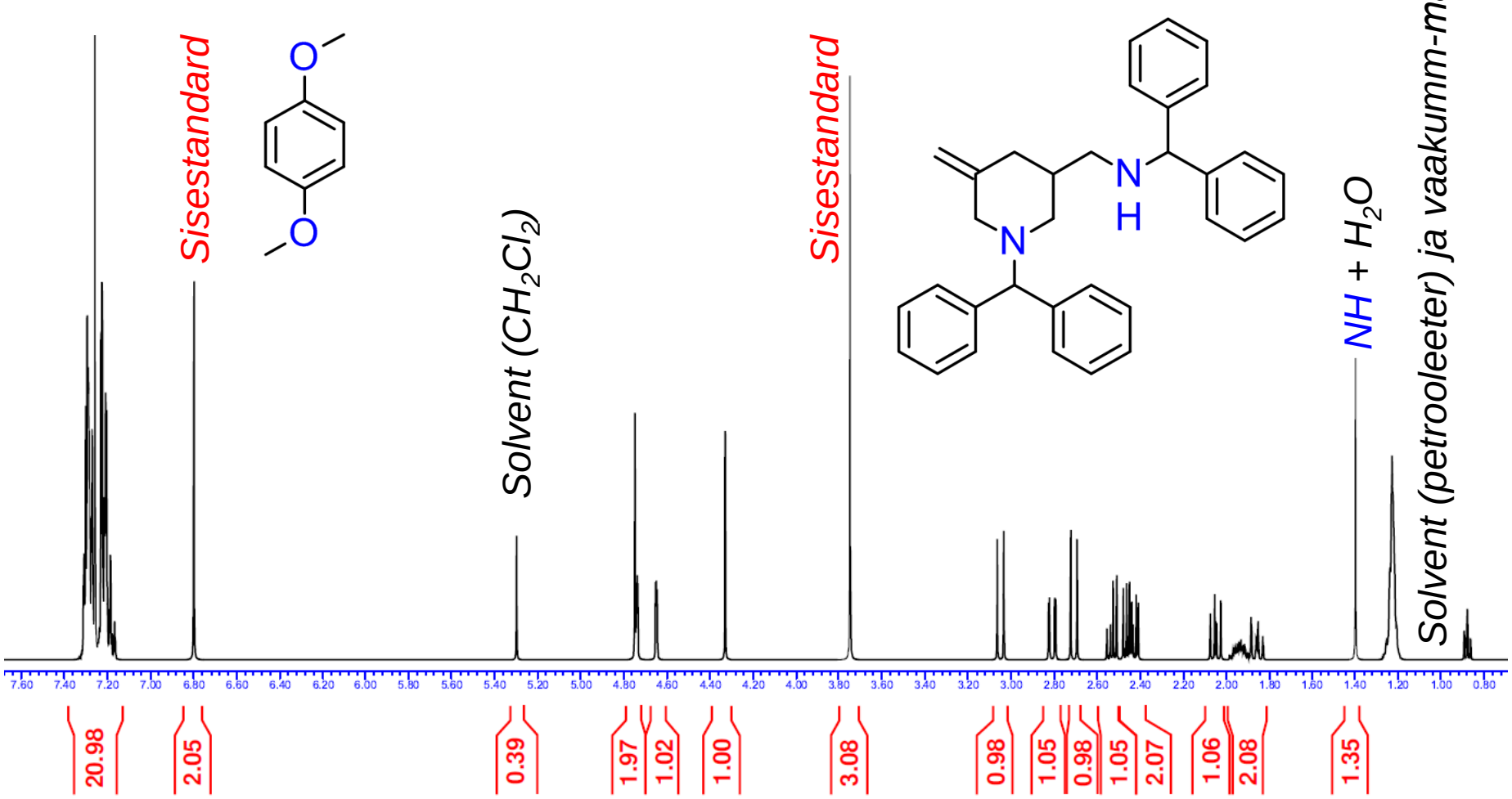
Kontsentratsiooni ja puhtuse määramine sisestandardi abil



Kontsentratsiooni ja puhtuse määramine sisestandardi abil

1) Kaalutakse uuritav aine;

2) lisatakse kindel kaalutis sisestandardit:

- võimalikult puhas (puhtus on teada, nt. 99,5%),
- pole lenduv, ei lagune ega reageeri,
- täielikult lahustuv kasutatavas solvendis,
- piisavalt suure molekulmassiga,
- lihtne spekter, signaalid ei kattu uuritava aine ega lisandite signaalidega.

3) lisatakse solvent, milles nii uuritav aine kui ka sisestandard täielikult lahustuvad;

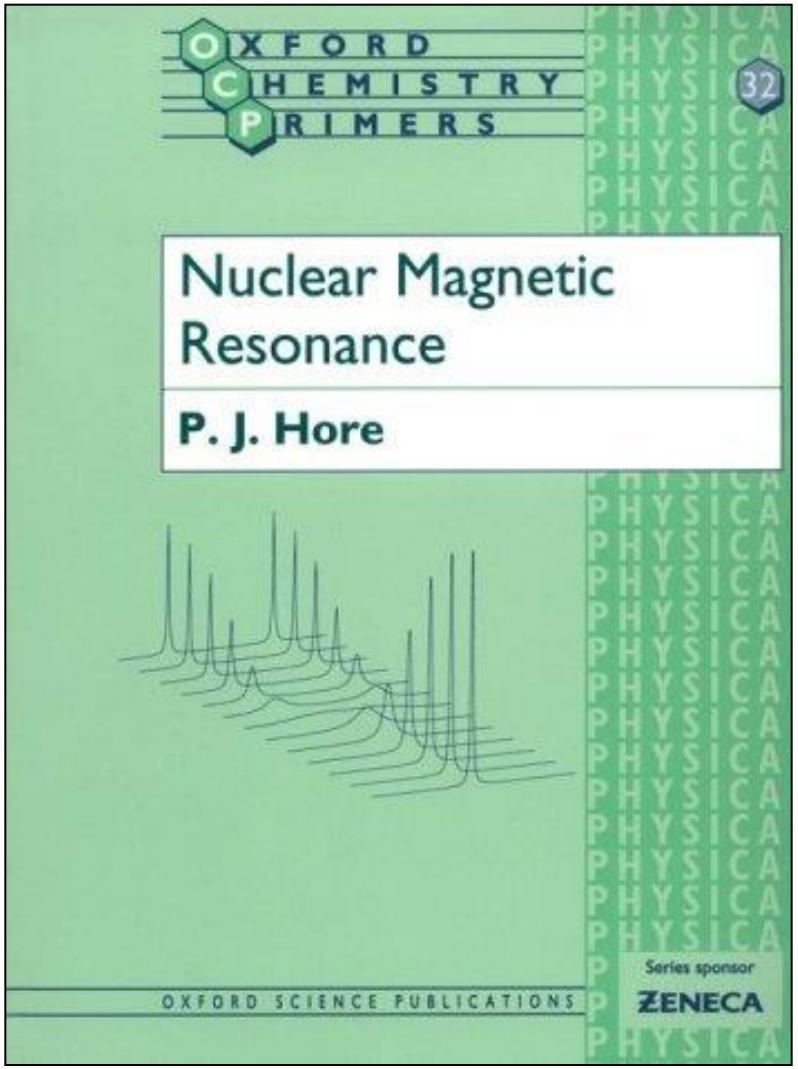
4) mõõdetakse korraliku signaal-müra suhtega TMR spekter;

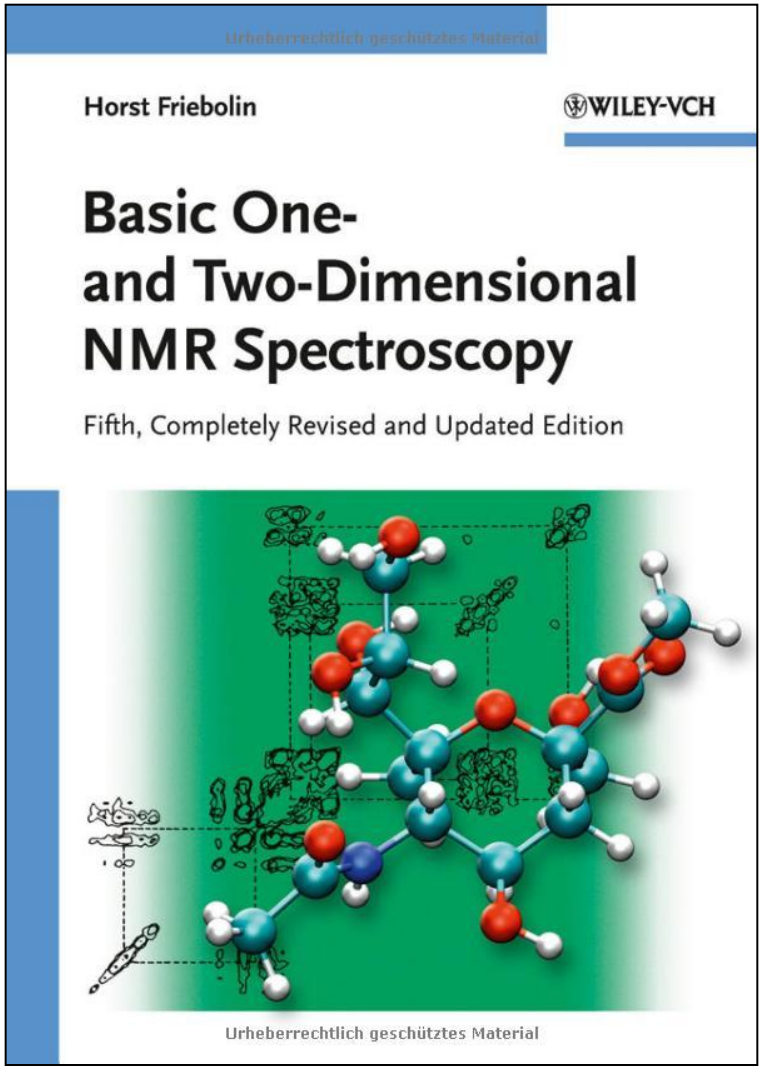
5) spektrilt mõõdetakse ära nii uuritava aine signaalide kui ka standardaine signaalide integraalid;

6) teades, mitmele vesinikule molekulvalemis need signaalid vastavad, võib arvutada uuritava aine puhtuse (*viga üldiselt kuni 5%*).

Huvilistele lisalugemiseks: T. Rundlöf *et al. Journal of Pharmaceutical and Biomedical Analysis* **2010**, *52*, 645-651.

Lisalugemist:





http://kodu.ut.ee/~laurit/AK2/

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