

Avance I Solid State NMR

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Applications

Bruker Biospin Billerica, USA

DAY 1

- Introduction
- Basic setup procedures
- Productivity tools

DAY 2

- Setup Cross Polarization Experiments
- CP Pulse programs, include and protection files

DAY 3

- Various basic CP experiments
- Relaxation experiments with CP
- Other spin 1/2 X - nuclei than ^{13}C

DAY 4

- Quadrupolar nuclei, solidsecho and mqmas
- Advanced NMR experiments

NMR: Tool for structural analysis

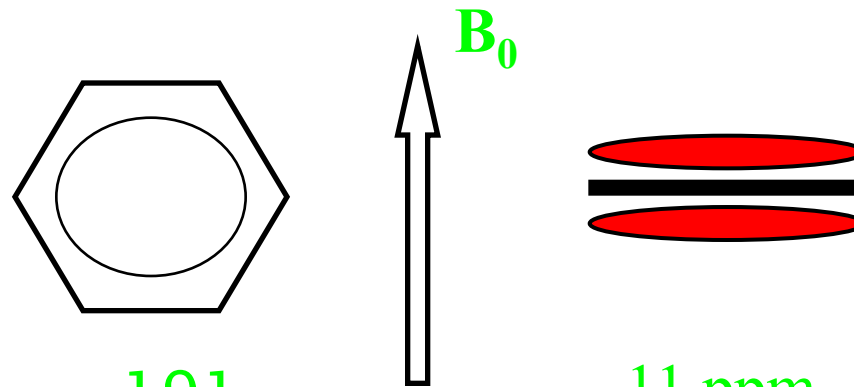
NMR in liquids:

- Tools for structure determination:
 - Chemical Shift (CS) for distinction of electronic environment.
 - J coupling for identification of spin system - creation of coherence
 - NOE for distance constraints (dipole dipole interaction)
 - Weakly aligned systems (direct dipole - interaction)

NMR in Solids

- All interactions are present full structural information available
 - Dipole Dipole interaction (DD)
 - Chemical Shift Anisotropy (CSA) and isotropic Chemical Shift (CS)
 - Quadrupole interaction (Q) for spin $> 1/2$
 - J-interaction (very weak)
- Problem: Entanglement of the information
- Solution: Average as many interactions as possible by tailoring the interaction Hamiltonian through:
 - Sample rotation at the magic angle: Magic Angle Spinning (MAS)
 - Heteronuclear decoupling schemes: continuous wave (cw) or time proportional phase modulation (TPPM) technique, etc
 - Combination of heteronuclear decoupling and sample rotation
 - ...etc...

Chemical Shift Anisotropy CSA



^{13}C chemical shift:

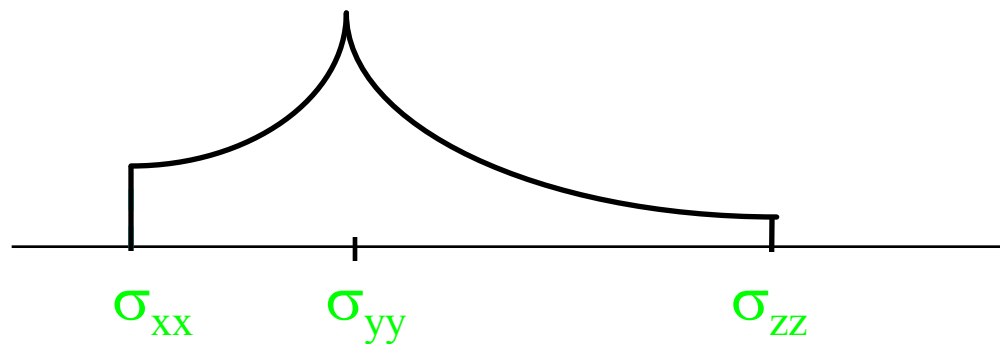
$$\sigma_{xx} = 191$$

11 ppm

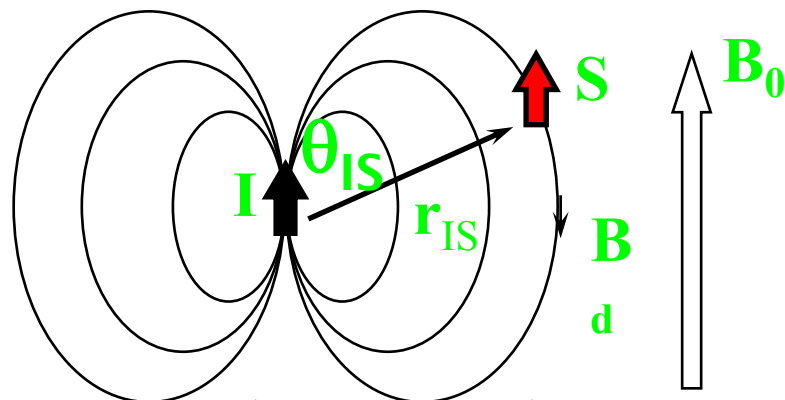
Powder pattern:

ppm

three principal components σ_{xx} , σ_{yy} , σ_{zz} .



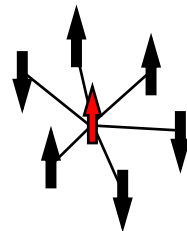
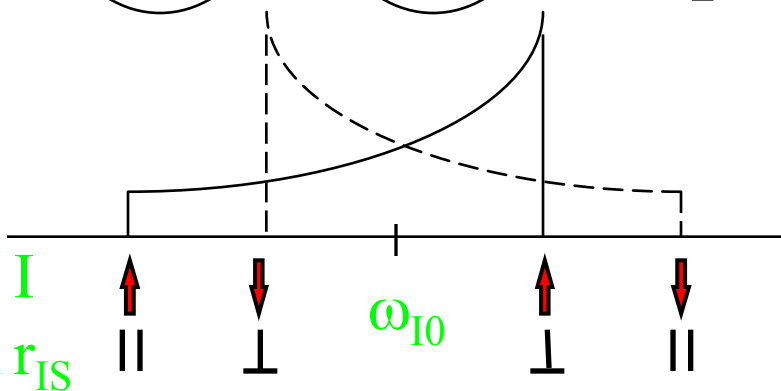
Dipole Dipole Interaction DD



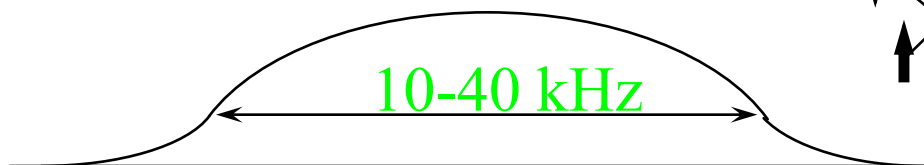
Local field B_{loc} at spin S:
Vector sum of Zeeman field B_0 and dipolar field B_d generated by spin I.

$$D_{IS} \approx \frac{\gamma_I \gamma_S}{r_{IS}^3} (3 \cos^2(\theta_{IS}) - 1)$$

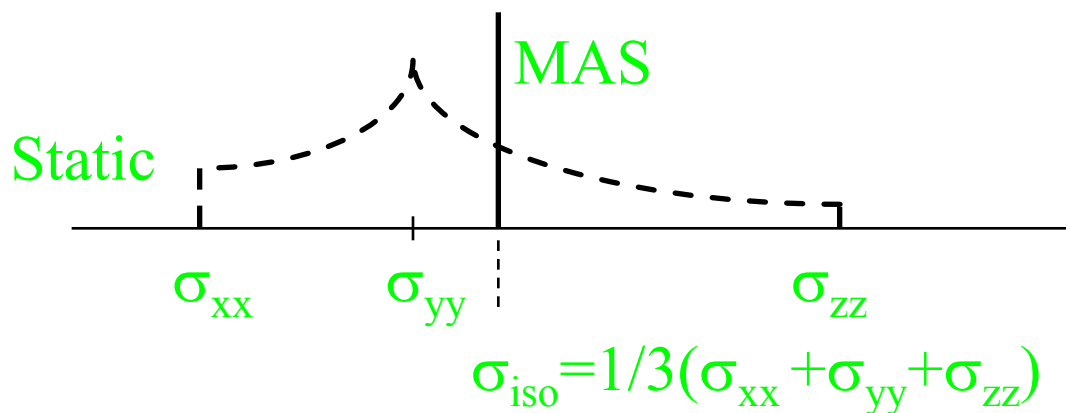
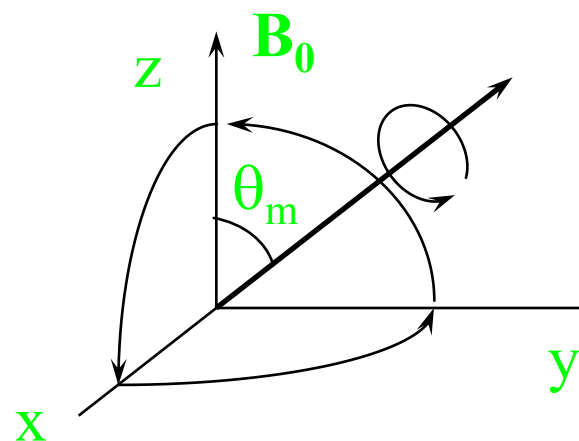
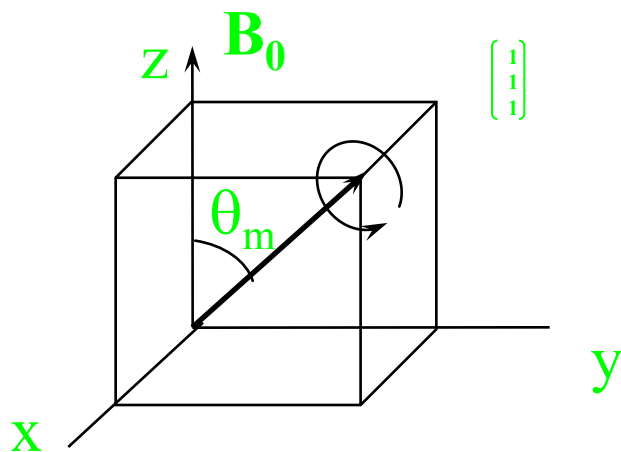
Single Spin pair: Pake doublet



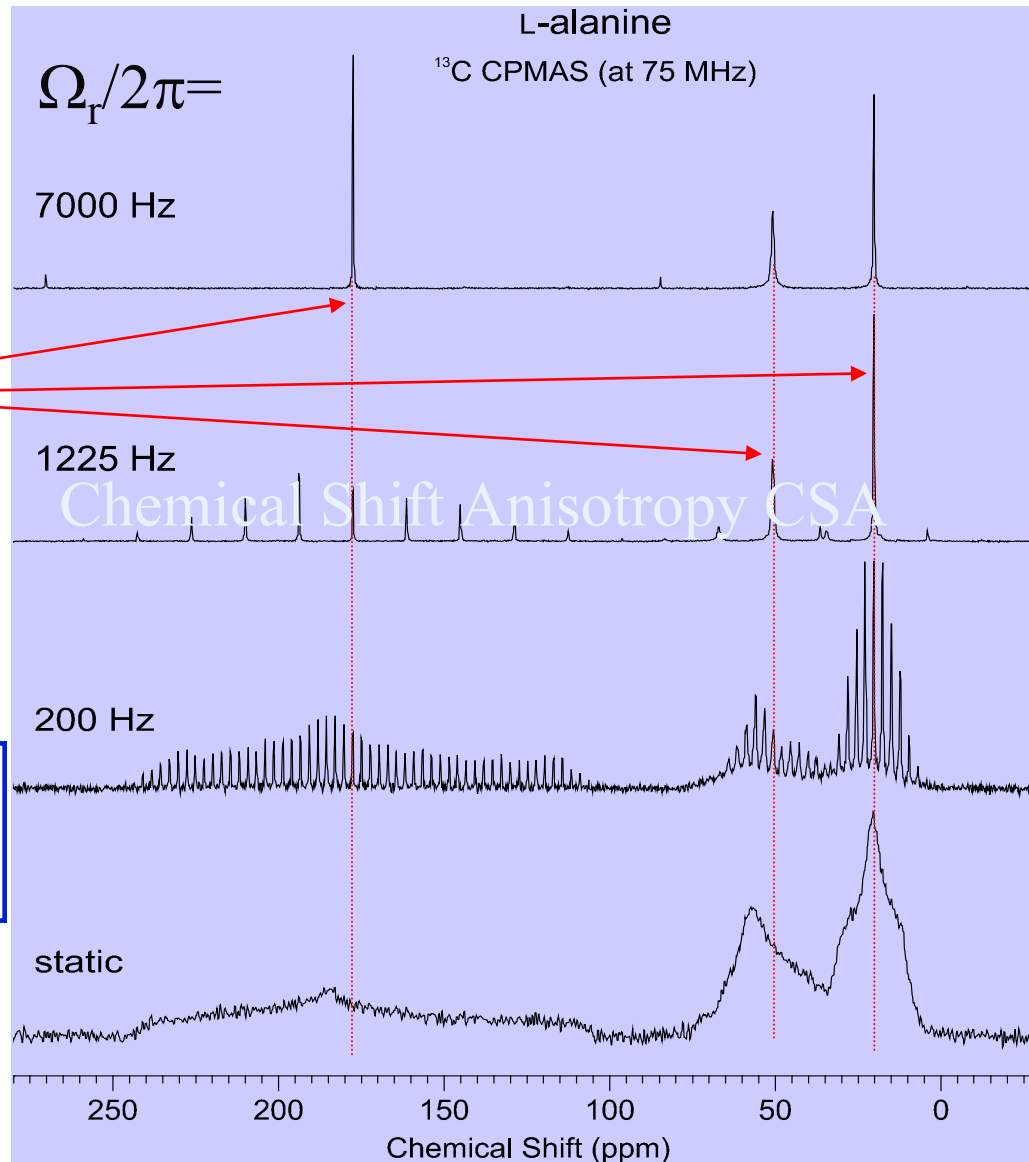
Multiple spin couplings: broad featureless hump.



Magic Angle Spinning



Averaging CSA powder pattern



Note!
CS position
Not
necessarily at
extremum of
CSA powder
pattern

$$\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$$

Averaging DD powder pattern



Adamantane
1H spectra
increasing spinning speed



Current Data Parameters
NAME Adamantane
EXPNO 1
PROCNO 1

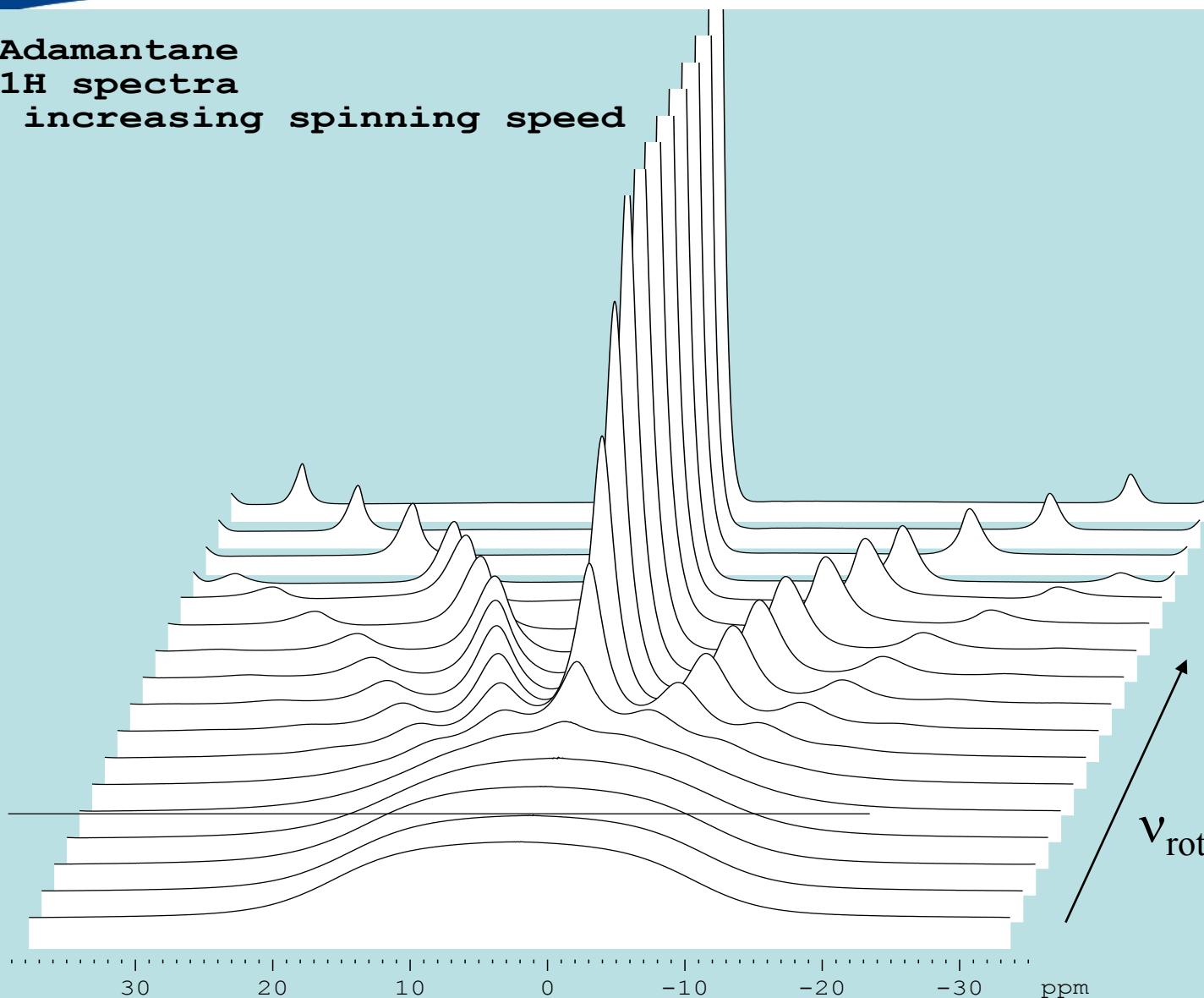
F2 - Acquisition Parameters

Date_ 20021005
Time 10.50
INSTRUM spect
PROBHD 4 mm MAS 1H H1
PULPROG zg
TD 2048
SOLVENT chcl3
NS 32
DS 0
SWH 35714.285 Hz
FIDRES 17.438616 Hz
AQ 0.0287360 sec
RG 8
DW 14.000 usec
DE 6.00 usec
TE 373.0 K
D1 2.5000000 sec

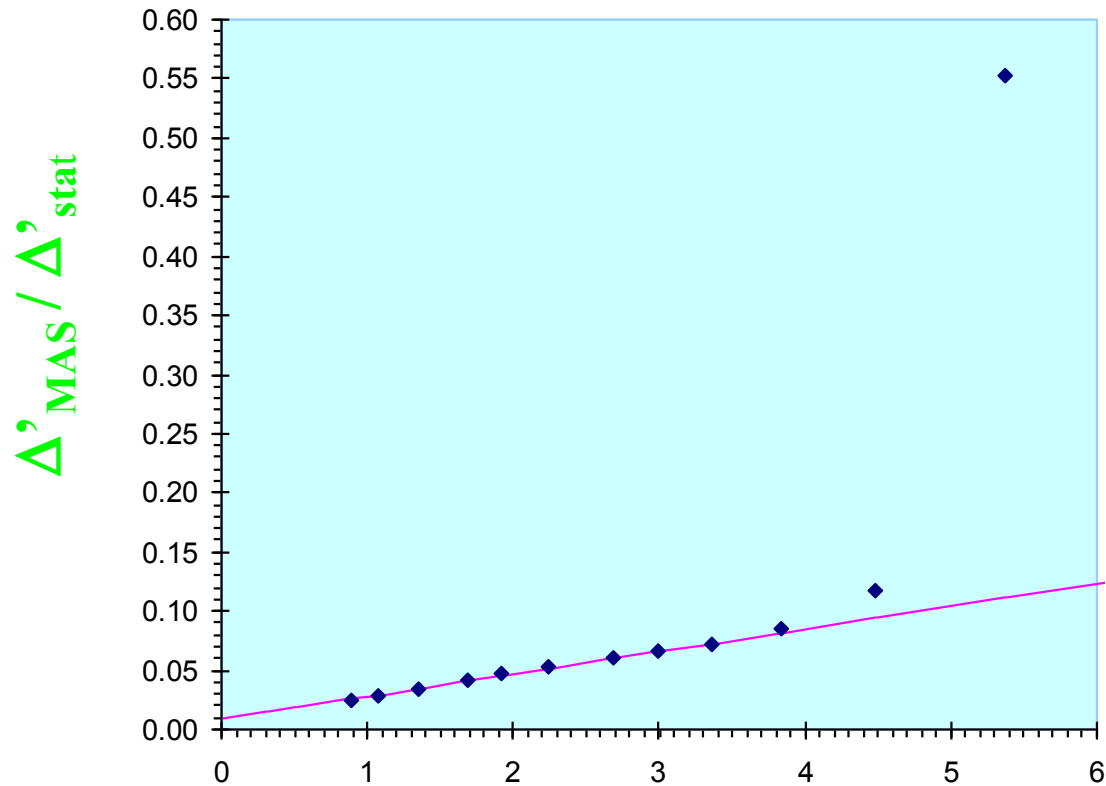
==== CHANNEL f1 =====
NUC1 1H
P1 1.70 usec
PL1 1.00 dB
SFO1 499.5509991 MHz

F2 - Processing parameters

SI 2048
SF 499.5500000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



Averaging DD interactions



Δ'_{stat} static linewidth

Δ'_{MAS} linewidth at ν_R

ν_R Spinning speed

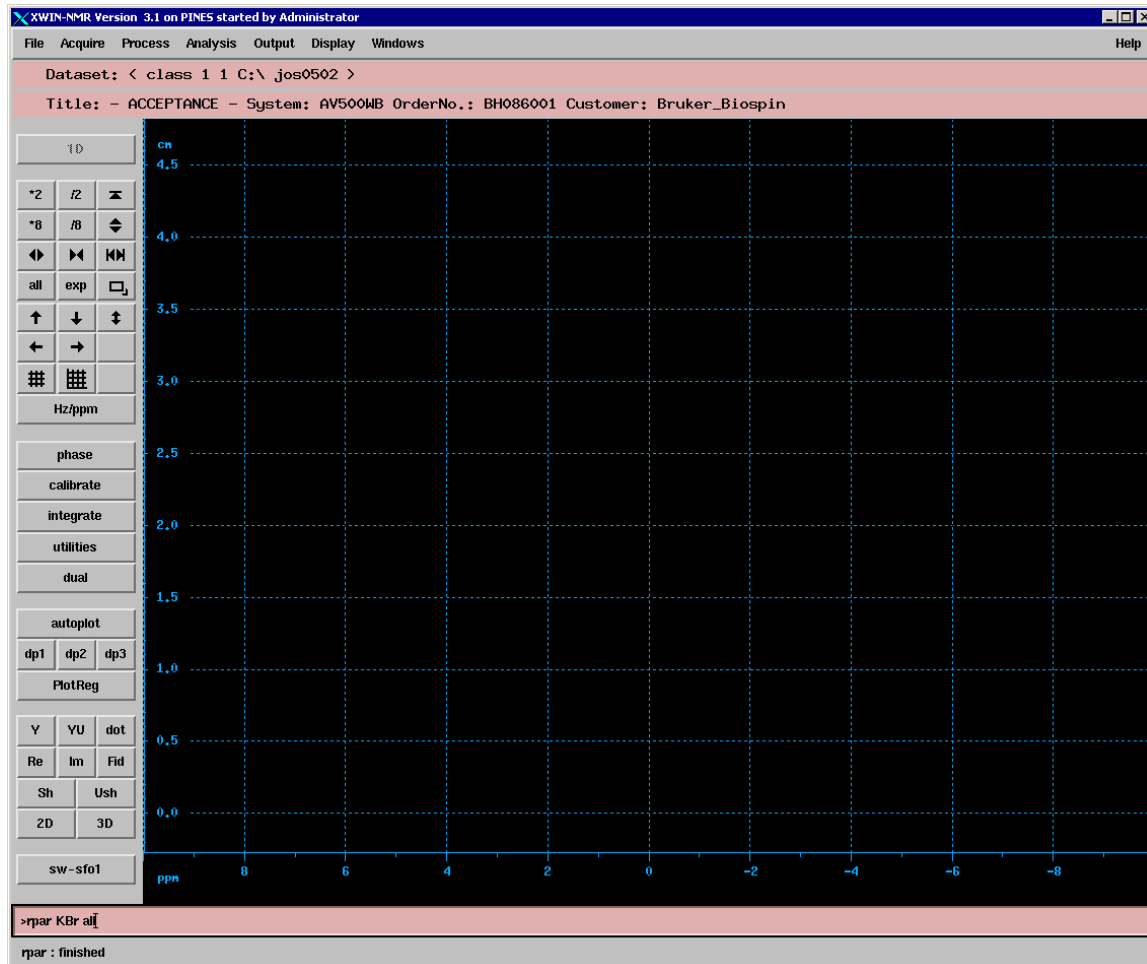
Δ'_{stat} / ν_R

←
Increasing spinning speed

Magic Angle Setup



- Use KBr sample,
- Call parameter set **KBr** by typing rpar **KBr**



Magic Angle Setup

Check or set routing using edasp:

	frequency		logical channel	amplifier	High/Low Power Stage	preamplifier
BF1	125.1469980 MHz		NUC 1			
SFO1	125.1520039 MHz		F1	FCU1	X	
OFSX1	5005.880 Hz		79Br		X 1000 W	1H LNA
					300.0 W	XBB19F 2HS
BF2	499.5000000 MHz		NUC 2		H	2H
SFO2			F2	FCU2	H/F 1000 W	HPHP 19F/1H
			off		150.0 W	HPHP XBB31P
BF3	499.5000000 MHz		NUC 3		X 300.0 W	
SFO3			F3	FCU3		
			off			

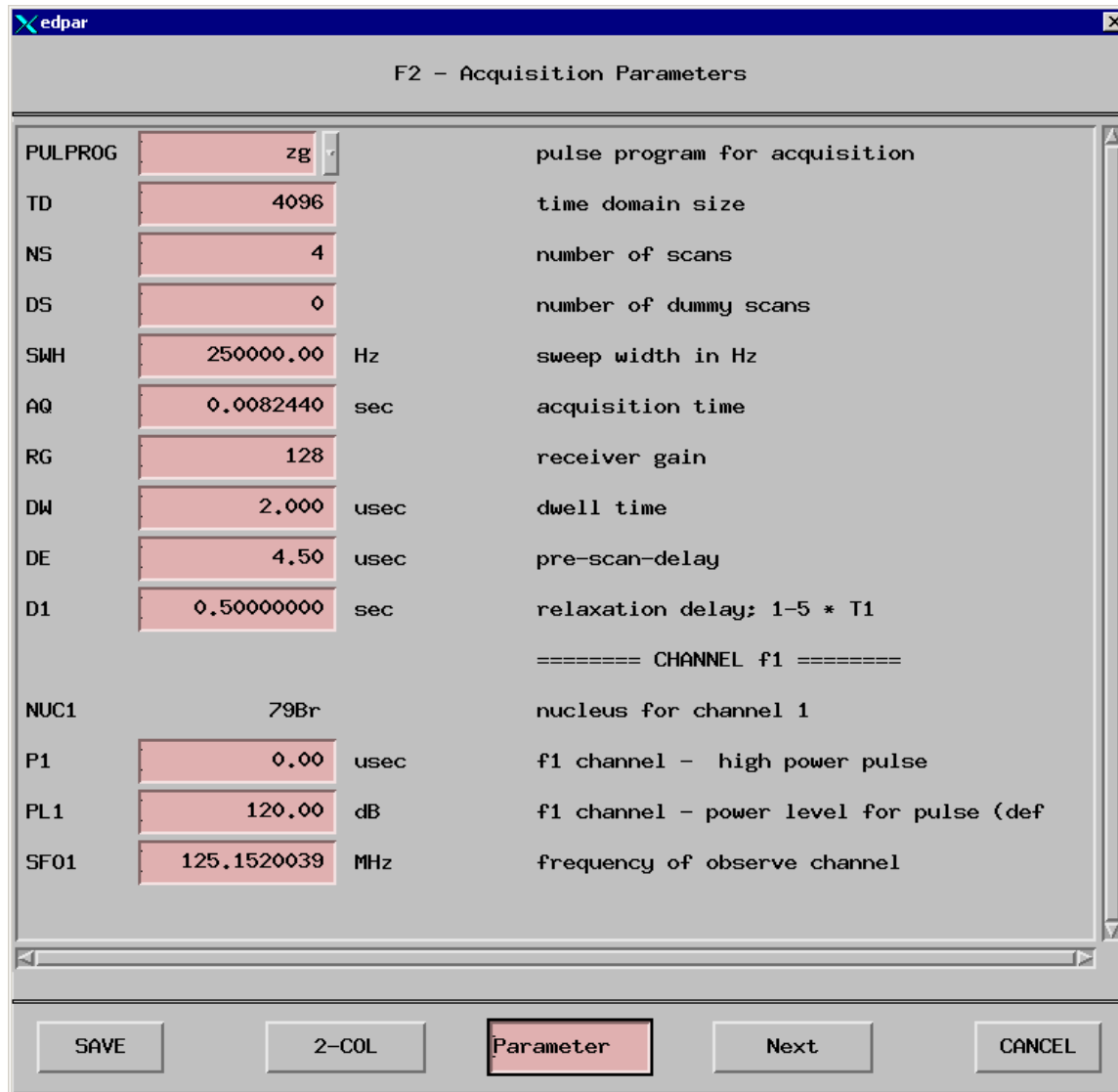
Preferred output for 19F :

- 19F
- X

SAVE SWITCH F1/F2 SWITCH F1/F3 DEFAULT CANCEL PARAM

Magic Angle Setup

- Check parameters in the used:



edpar

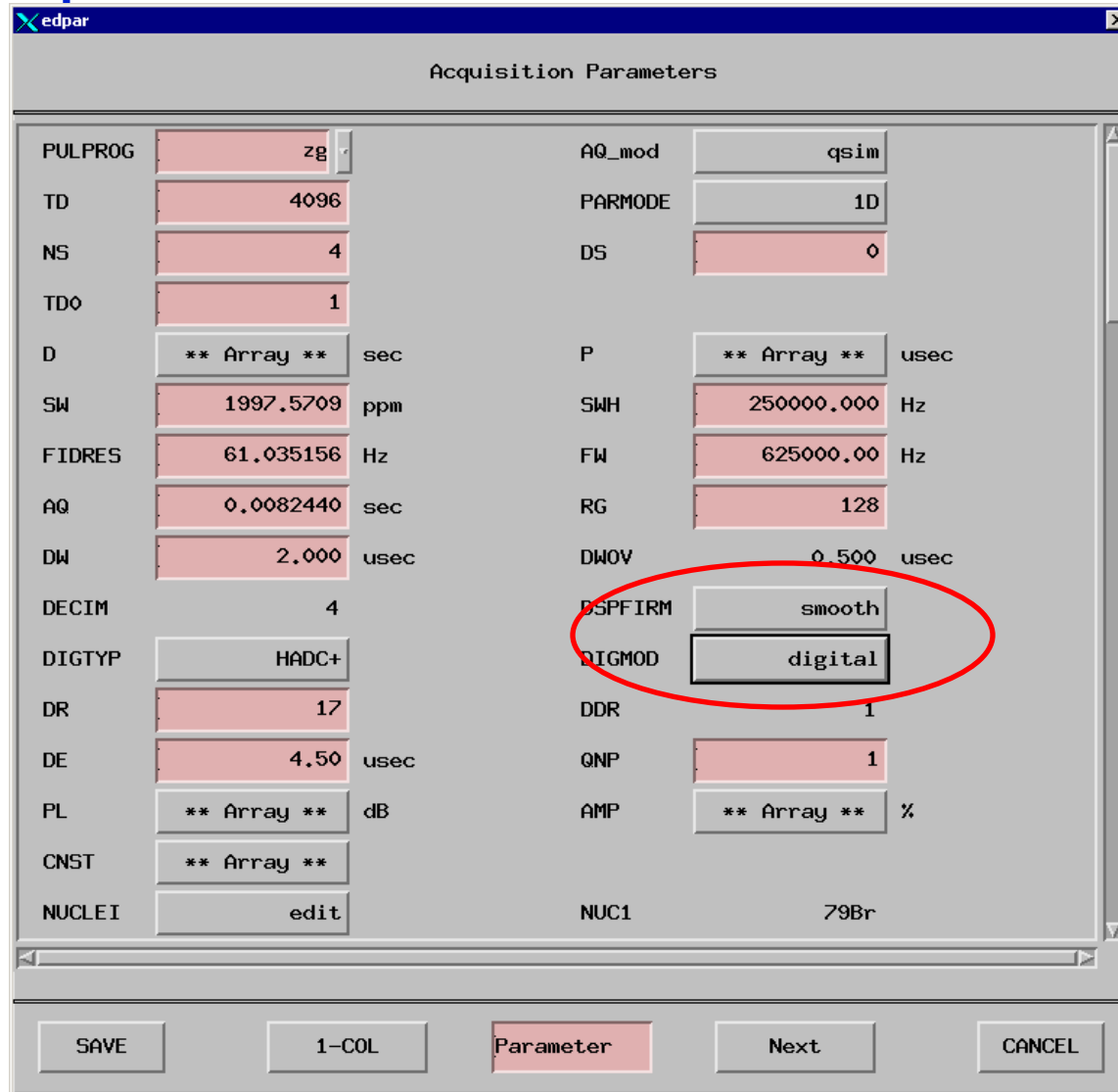
F2 - Acquisition Parameters

PULPROG	zg		pulse program for acquisition
TD	4096		time domain size
NS	4		number of scans
DS	0		number of dummy scans
SWH	250000.00	Hz	sweep width in Hz
AQ	0.0082440	sec	acquisition time
RG	128		receiver gain
DW	2.000	usec	dwel time
DE	4.50	usec	pre-scan-delay
D1	0.50000000	sec	relaxation delay: 1-5 * T1
===== CHANNEL f1 =====			
NUC1	79Br		nucleus for channel 1
P1	0.00	usec	f1 channel - high power pulse
PL1	120.00	dB	f1 channel - power level for pulse (def
SF01	125.1520039	MHz	frequency of observe channel

SAVE 2-COL **Parameter** Next CANCEL

Magic Angle Setup

- Check parameters in the eda:



The screenshot shows the 'edpar' window with the title 'Acquisition Parameters'. The parameters are arranged in two columns. The 'DIGMOD' parameter is highlighted with a red circle. The parameters and their values are as follows:

Parameter	Value	Unit
PULPROG	zg	
TD	4096	
NS	4	
TD0	1	
D	** Array **	sec
SW	1997.5709	ppm
FIDRES	61.035156	Hz
AQ	0.0082440	sec
DW	2.000	usec
DECIM	4	
DIGTYP	HADC+	
DR	17	
DE	4.50	usec
PL	** Array **	dB
CNST	** Array **	
NUCLEI	edit	
AQ_mod	qsim	
PARMODE	1D	
DS	0	
P	** Array **	usec
SWH	250000.000	Hz
FW	625000.00	Hz
RG	128	
DW0V	0.500	usec
DSPFIRM	smooth	
DIGMOD	digital	
DDR	1	
QNP	1	
AMP	** Array **	%
NUC1	79Br	

At the bottom of the window, there are five buttons: SAVE, 1-COL, Parameter (highlighted), Next, and CANCEL.

Magic Angle Setup

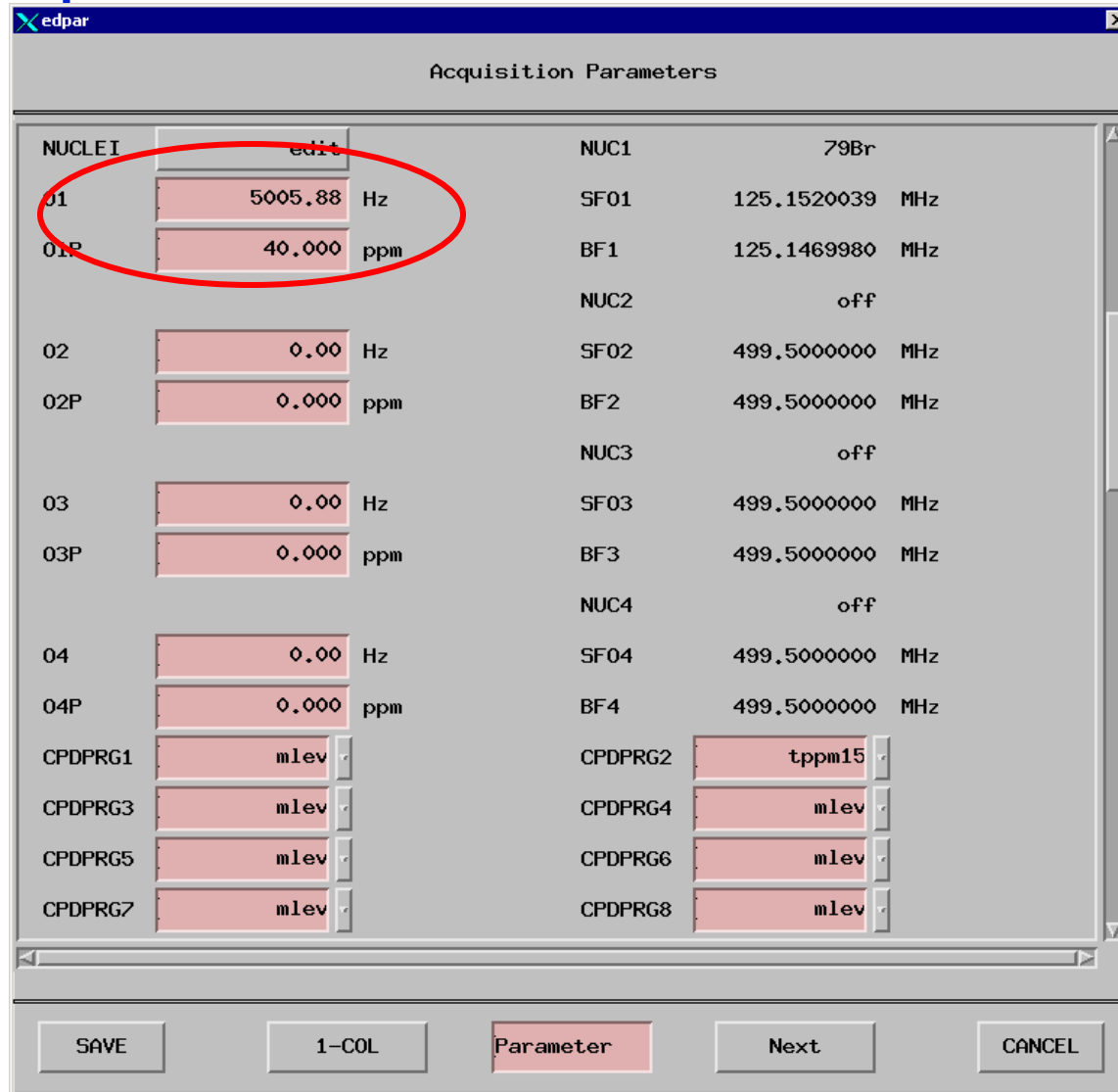


- Alternative choice of parameters:
- Check parameters in the eda:
 - Use: DIGMOD = analog and
SW = 100000 Hz



Magic Angle Setup

- Check parameters in the eda:

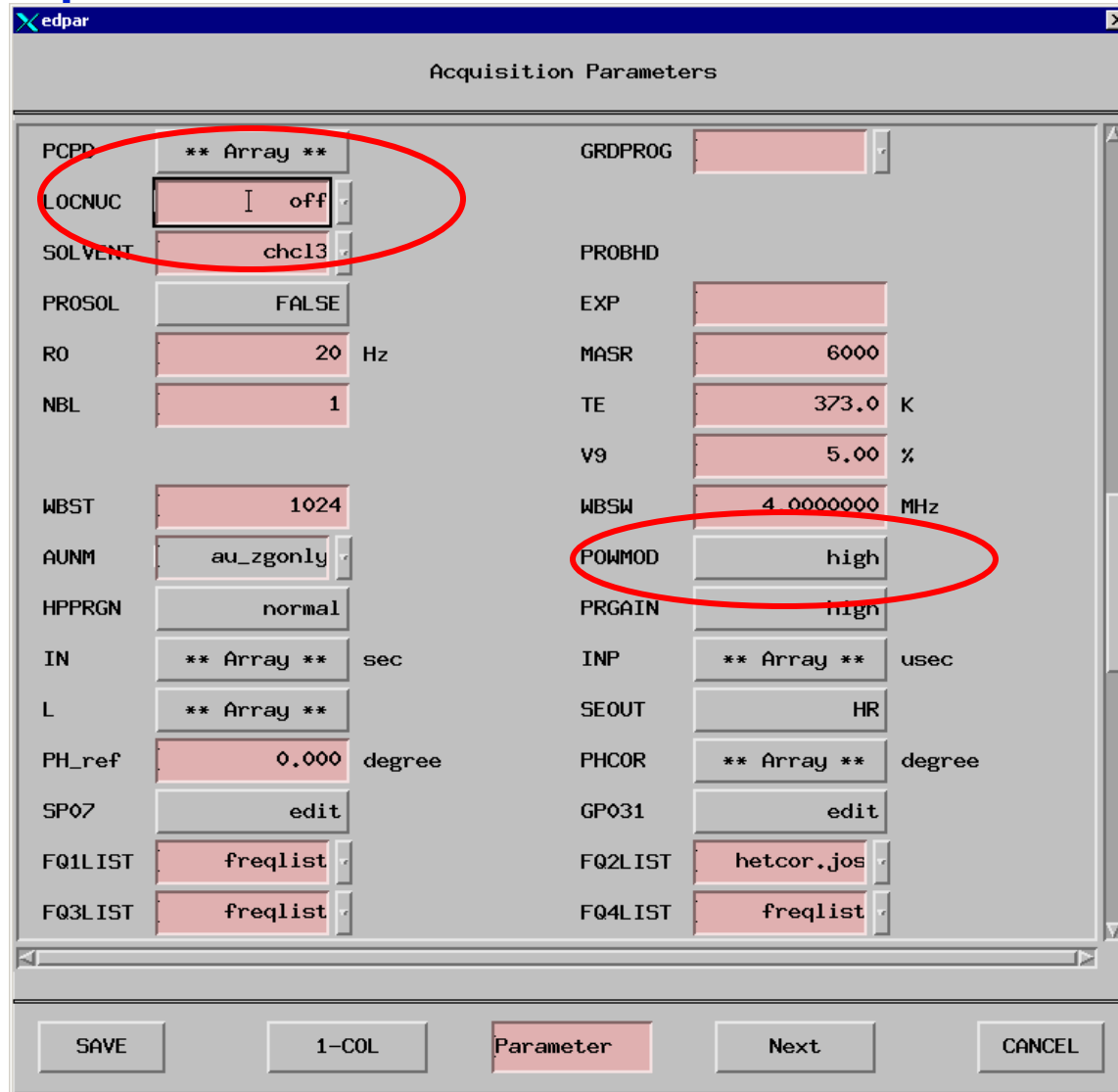


The screenshot shows the 'edpar' window with the title 'Acquisition Parameters'. The parameters are organized into two columns. The left column contains NUCLEI, J1, Q1P, Q2, Q2P, Q3, Q3P, Q4, Q4P, CPDPRG1, CPDPRG3, CPDPRG5, and CPDPRG7. The right column contains NUC1, SF01, BF1, NUC2, SF02, BF2, NUC3, SF03, BF3, NUC4, SF04, BF4, CPDPRG2, CPDPRG4, CPDPRG6, and CPDPRG8. The J1 and Q1P parameters are circled in red. The bottom of the window has buttons for SAVE, 1-COL, Parameter, Next, and CANCEL.

Parameter	Value	Unit
NUCLEI	edit	
J1	5005.88	Hz
Q1P	40.000	ppm
Q2	0.00	Hz
Q2P	0.000	ppm
Q3	0.00	Hz
Q3P	0.000	ppm
Q4	0.00	Hz
Q4P	0.000	ppm
CPDPRG1	mlev	
CPDPRG3	mlev	
CPDPRG5	mlev	
CPDPRG7	mlev	
NUC1	79Br	
SF01	125.1520039	MHz
BF1	125.1469980	MHz
NUC2	off	
SF02	499.5000000	MHz
BF2	499.5000000	MHz
NUC3	off	
SF03	499.5000000	MHz
BF3	499.5000000	MHz
NUC4	off	
SF04	499.5000000	MHz
BF4	499.5000000	MHz
CPDPRG2	tppm15	
CPDPRG4	mlev	
CPDPRG6	mlev	
CPDPRG8	mlev	

Magic Angle Setup

- Check parameters in the eda:



edpar

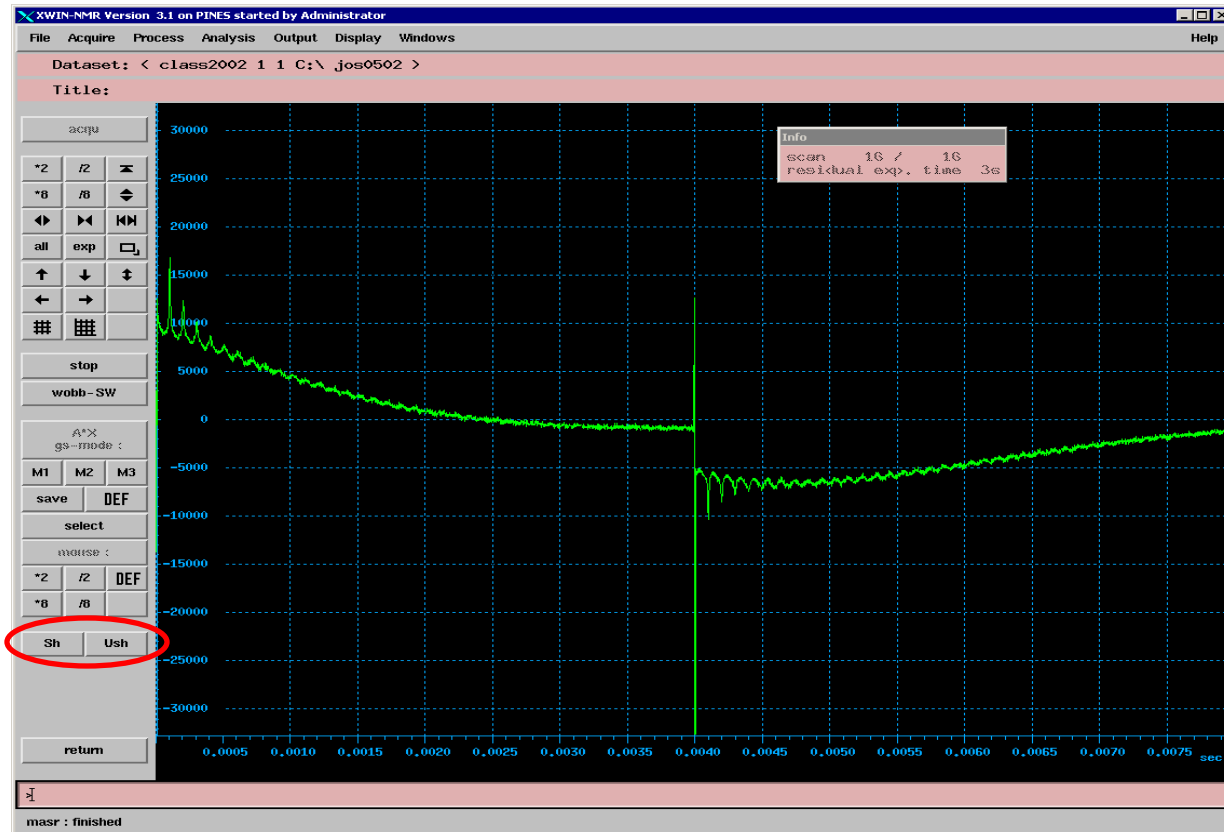
Acquisition Parameters

PCPD	** Array **	GRDPROG	
LOCNUC	off	PROBH	
SOLVENT	chc13	EXP	
PROSOL	FALSE	MASR	6000
R0	20 Hz	TE	373.0 K
NBL	1	V9	5.00 %
WBST	1024	WBSW	4.0000000 MHz
AUNM	au_zgonly	POWMOD	high
HPPRGN	normal	PRGAIN	high
IN	** Array ** sec	INP	** Array ** usec
L	** Array **	SEOUT	HR
PH_ref	0.000 degree	PHCOR	** Array ** degree
SP07	edit	GP031	edit
FQ1LIST	freqlist	FQ2LIST	hetcor.jos
FQ3LIST	freqlist	FQ4LIST	freqlist

SAVE 1-COL Parameter Next CANCEL

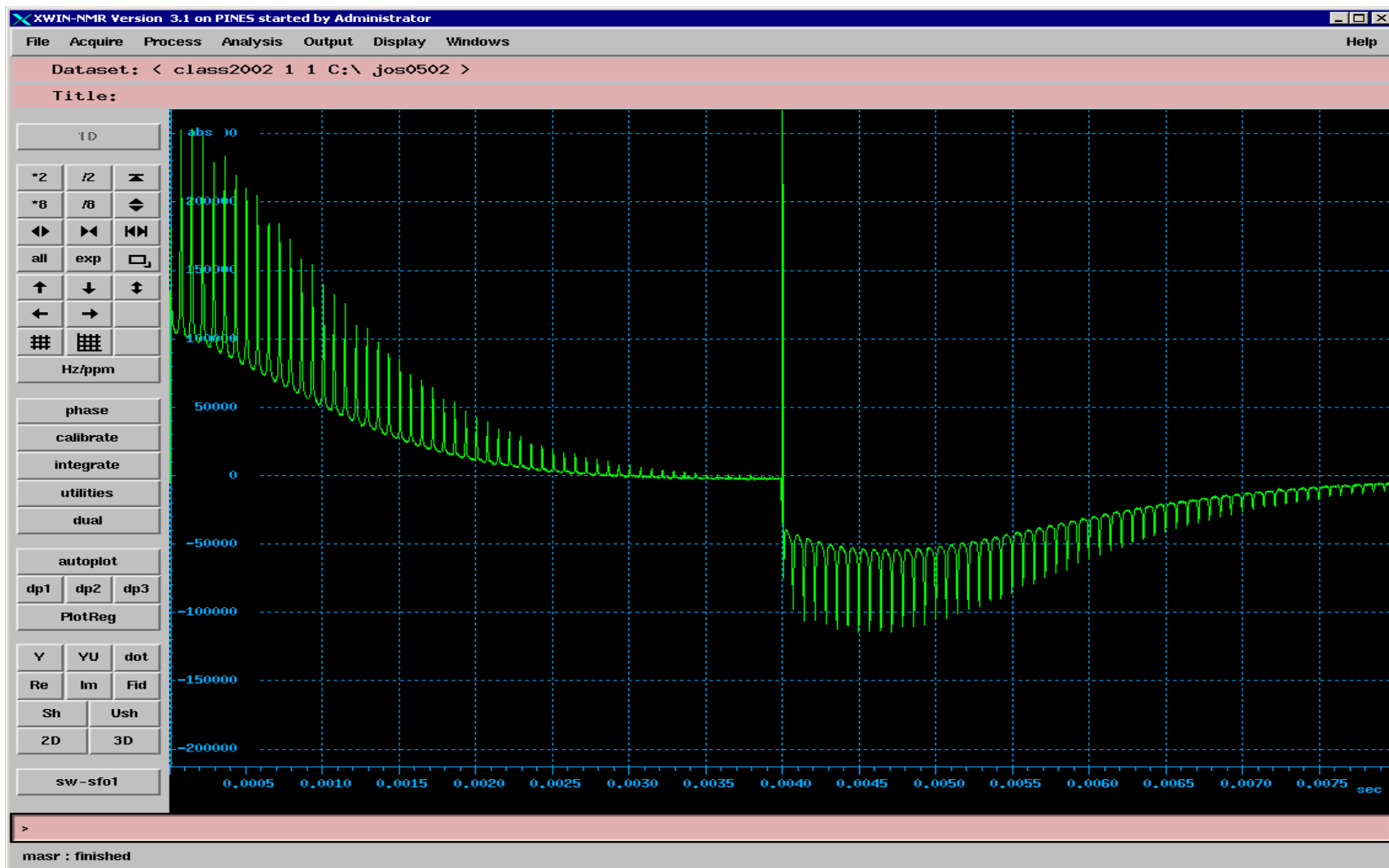
Magic Angle Setup

- Match and tune probe
- Enter value for power level p1 and pulse width p1 into ased
- Open the acquisition window and type gs:



Magic Angle Setup

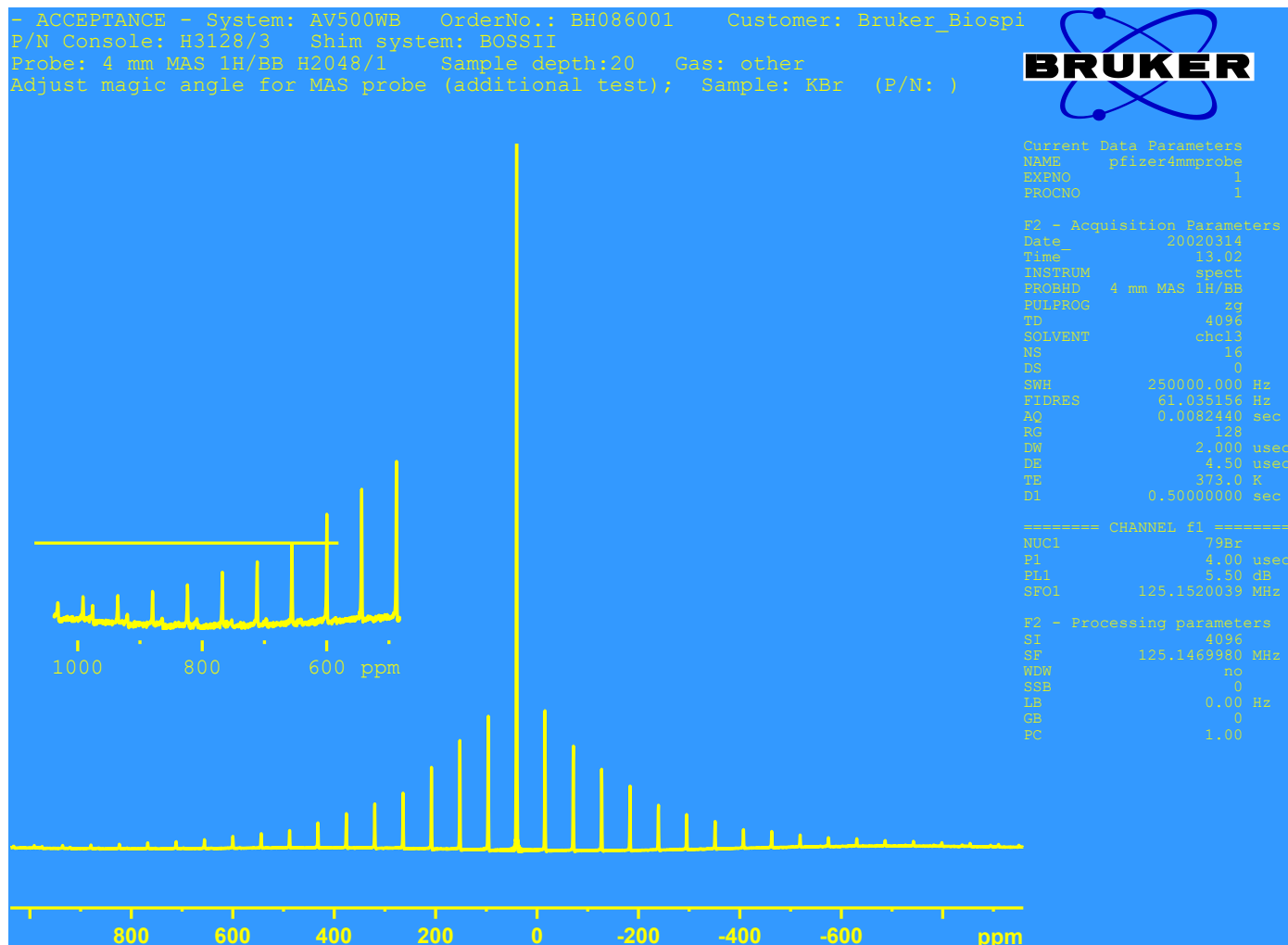
- Optimize rotation echos by changing the magic angle adjustment: goal:



Magic Angle Setup



- Acquired KBr spectrum:



Parameter optimization



- Optimize pulse width:
 - Set power level and optimize pulse width
 - Set pulse width and optimize power level
- Use **POPT**

Parameter Optimization Setup

Store as 2D data (ser file)

The AU program specified in AUNM will be executed

Run optimization in background

Info:
Each line in the table below describes a single parameter.
If the checkbox of a parameter is off, the parameter will be ignored in the AU program.
During save, it will be saved as comment with the prefix 'Off'.
If option INC is not zero and option VARMOD is 'LIN', the experiment number NEXP will be ignored. You can omit it in this case.

Dataset: C:/Bruker/XWIN-NMR/data/jos/nmr/bl4.atptest/2/

On/Off	Parameter	OPTIMUM	STARTVAL	ENDVAL	NEXP	VARMOD	INC
<input checked="" type="checkbox"/>	p1	POSMAX	1	16		LIN	1

Start Halt Read protocol Add parameter Copy parameters Save Restore Update Exit

Status: There are unsaved parameters.

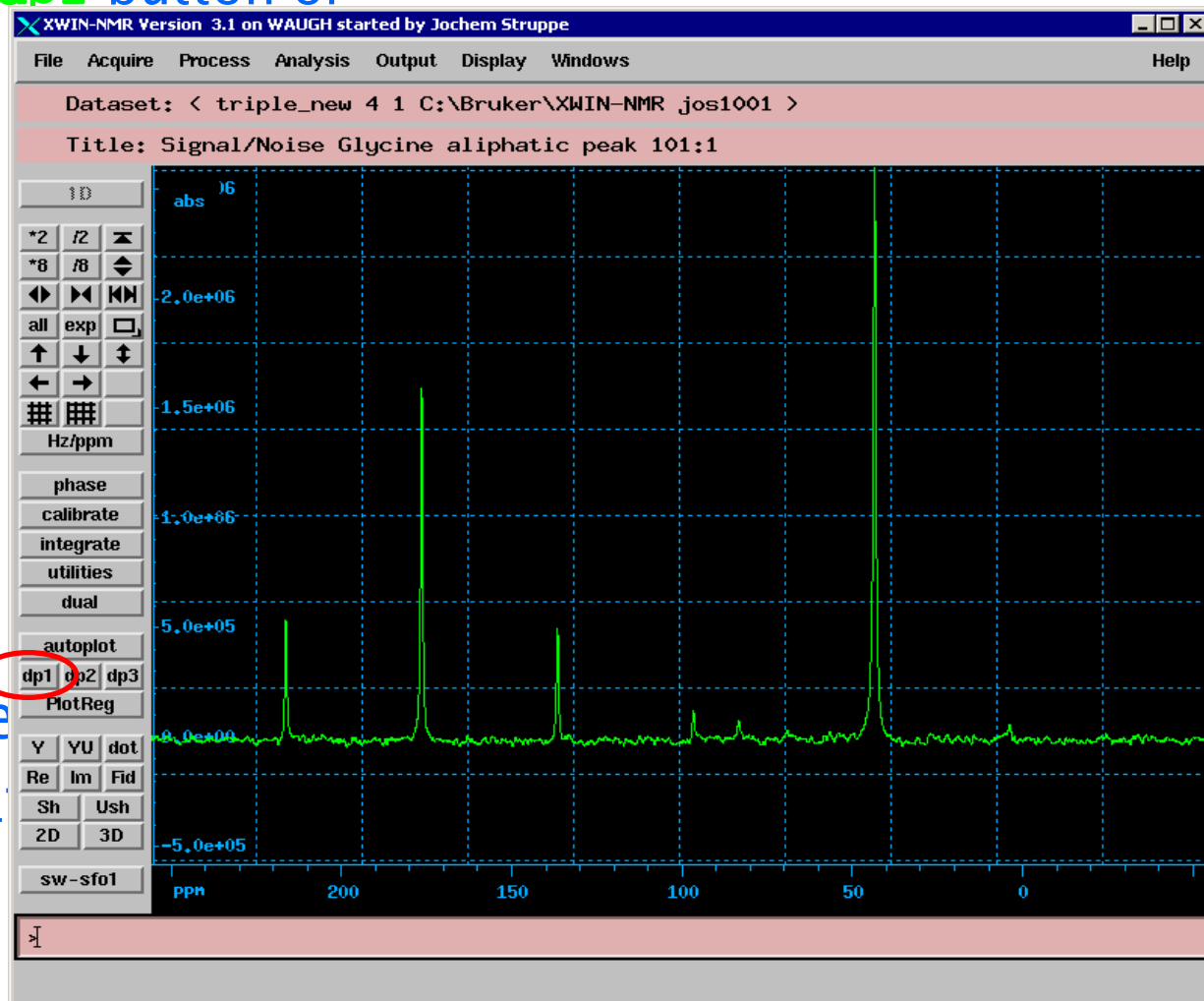


Parameter optimization



- Before starting **POPT**:
- set spectral region parameters
 - Either by clicking **dp1** button or
 - Enter parameter **F1P, F2P**

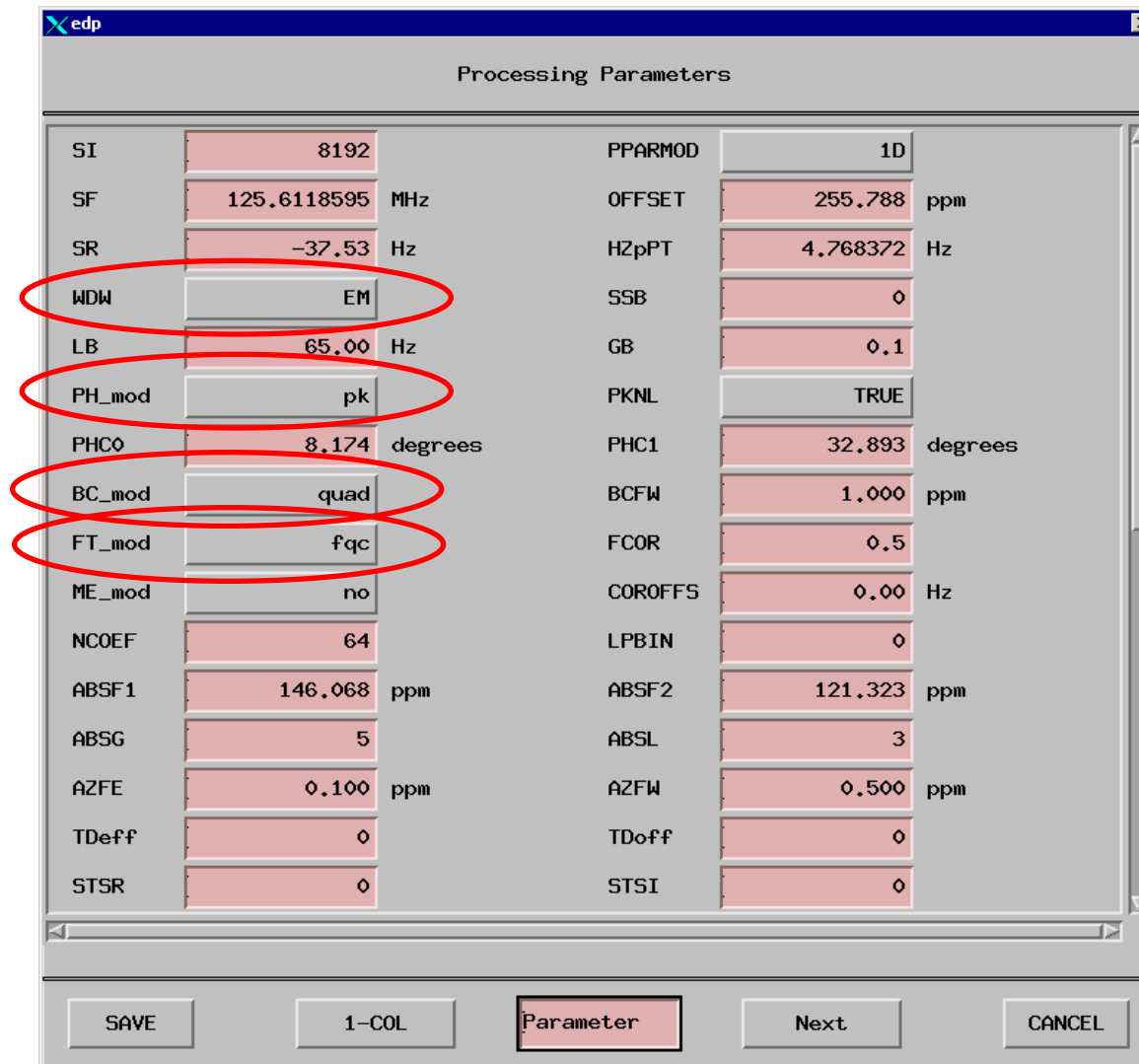
- make sure processing parameters are set for processing data using **trf**



Parameter optimization

trf - uses processing instruction
parameters

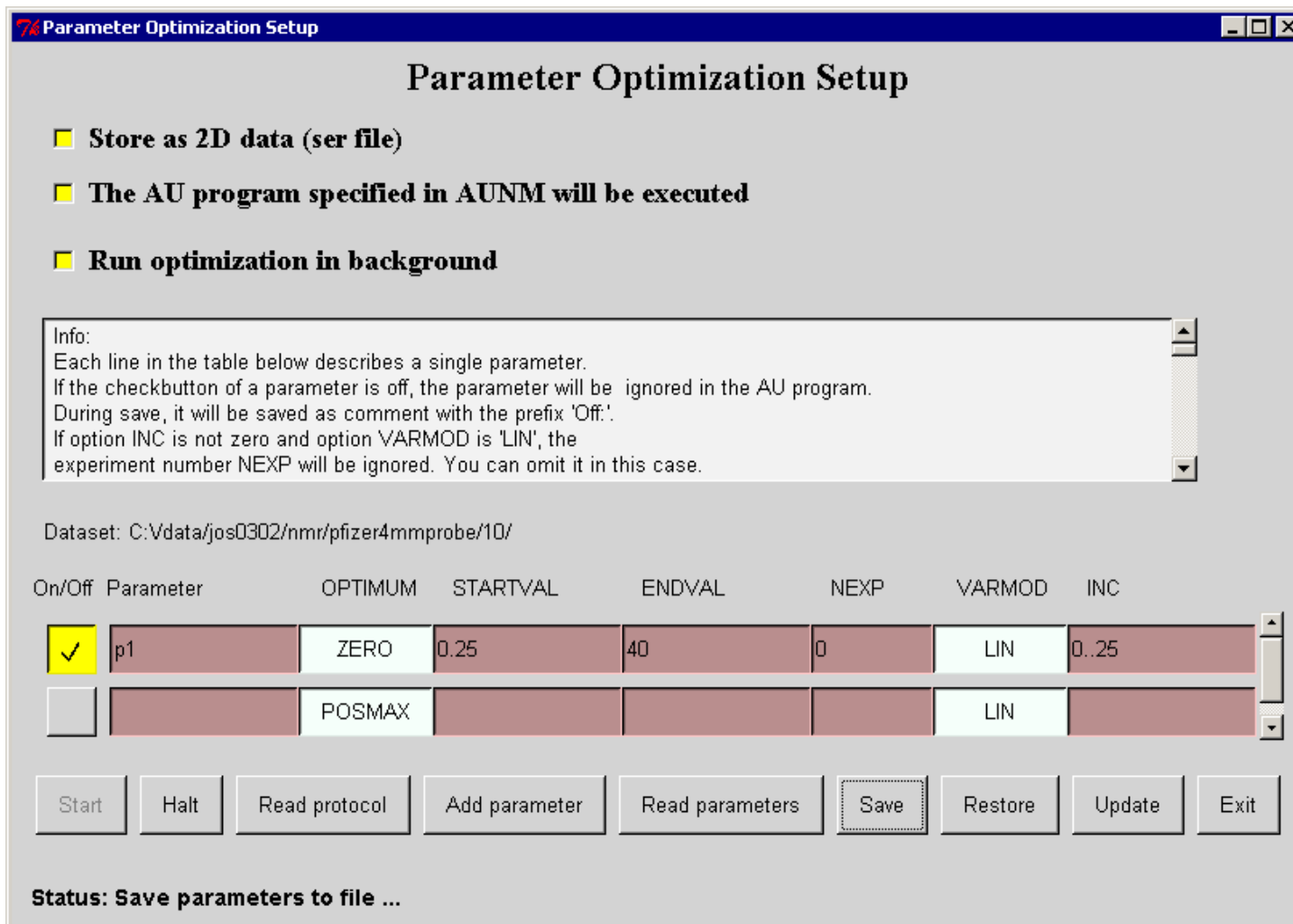
- **WDW**
- **Ph_mod**
- **BC_mod**
- **FT_mod**



Parameter	Value	Unit
SI	8192	
SF	125.6118595	MHz
SR	-37.53	Hz
WDW	EM	
LB	65.00	Hz
PH_mod	pk	
PHC0	8.174	degrees
BC_mod	quad	
FT_mod	fqc	
ME_mod	no	
NCOEF	64	
ABSF1	146.068	ppm
ABSG	5	
AZFE	0.100	ppm
TDeff	0	
STSR	0	
PPARMOD	1D	
OFFSET	255.788	ppm
HZpPT	4.768372	Hz
SSB	0	
GB	0.1	
PKNL	TRUE	
PHC1	32.893	degrees
BCFW	1.000	ppm
FCOR	0.5	
COROFFS	0.00	Hz
LPBIN	0	
ABSF2	121.323	ppm
ABSL	3	
AZFW	0.500	ppm
TDoff	0	
STSI	0	

Parameter optimization

- Everything set up - start **popt**:



Parameter Optimization Setup

- Store as 2D data (ser file)**
- The AU program specified in AUNM will be executed**
- Run optimization in background**

Info:
Each line in the table below describes a single parameter.
If the checkbox of a parameter is off, the parameter will be ignored in the AU program.
During save, it will be saved as comment with the prefix 'Off'.
If option INC is not zero and option VARMOD is 'LIN', the experiment number NEXP will be ignored. You can omit it in this case.

Dataset: C:\vdata\jos0302/nmr/pfizer4mmprobe/10/

On/Off	Parameter	OPTIMUM	STARTVAL	ENDVAL	NEXP	VARMOD	INC
<input checked="" type="checkbox"/>	p1	ZERO	0.25	40	0	LIN	0.25
<input type="checkbox"/>		POSMAX				LIN	

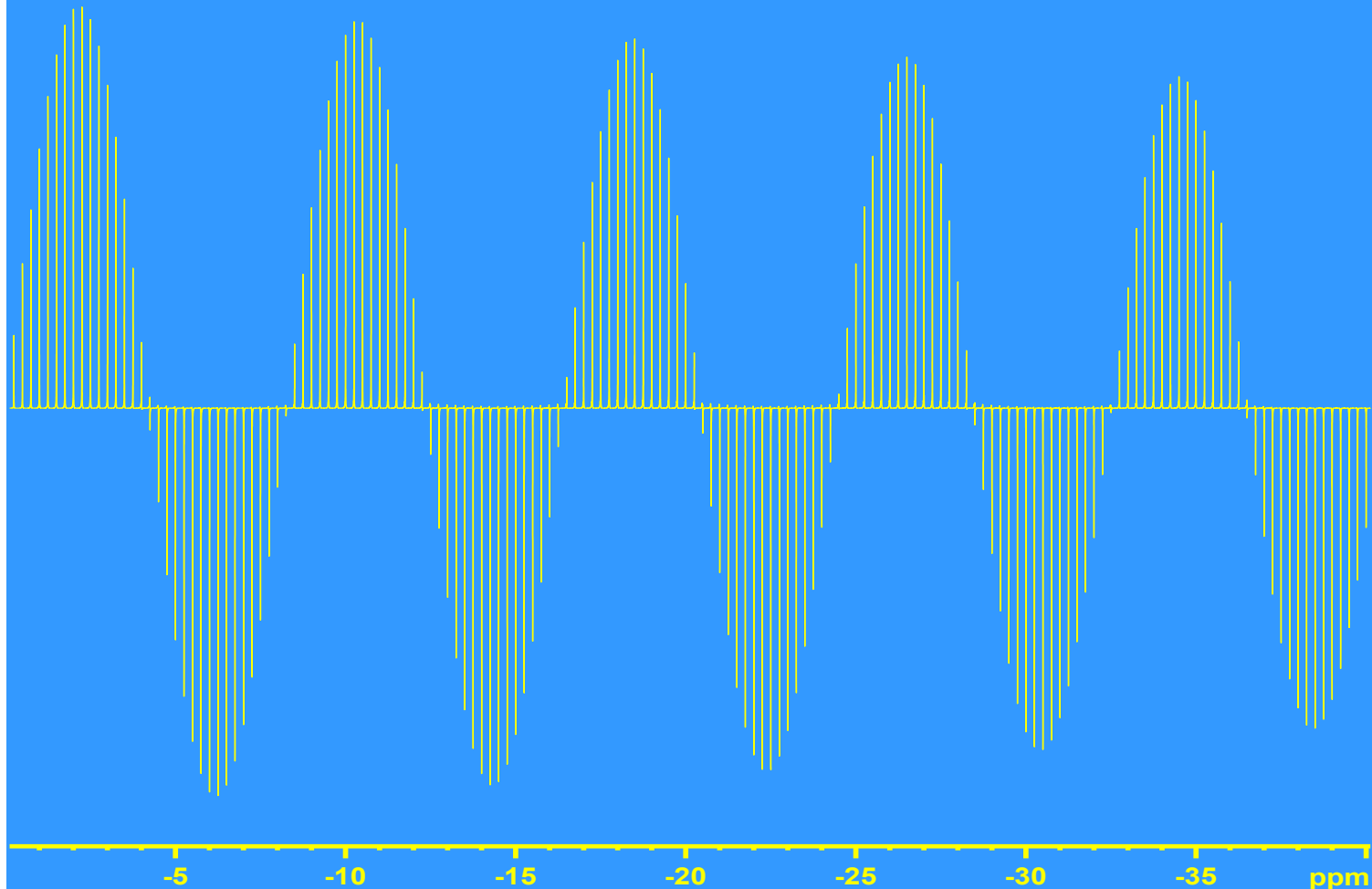
Start Halt Read protocol Add parameter Read parameters Save Restore Update Exit

Status: Save parameters to file ...

Parameter optimization

poptau for p1 finished.
ZERO at experiment 16.749563: p1 = 4.187391

NEXP=160



- If result not satisfying - pulse width too large or too small:
 - Use au program **PULSE** to calculate correct pulse
 - Verify calculation with **POPT**
- Use of **Pulse: xau pulse**

```
< pulse.exe >
bl4.atptest 2 1 C:/Bruker/XWIN-NMR jos

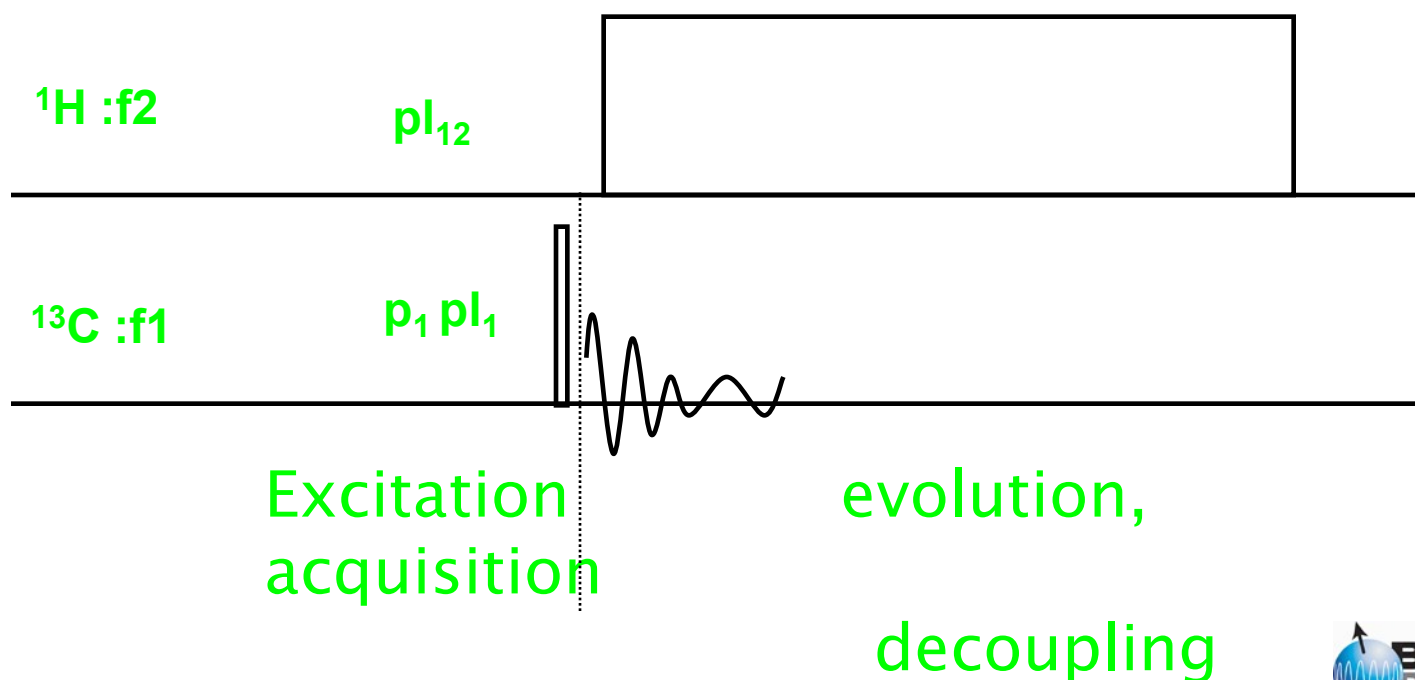
Calculation of pulse attenuation values
length frequency atten
i ref: 2.8 us 90909 Hz 3.0 dB
calc: 4.0 us 62500 Hz 6.3 dB
      3.9 us 64359 Hz 6 dB
```

Seen

Setup Direct Polarization Experiments



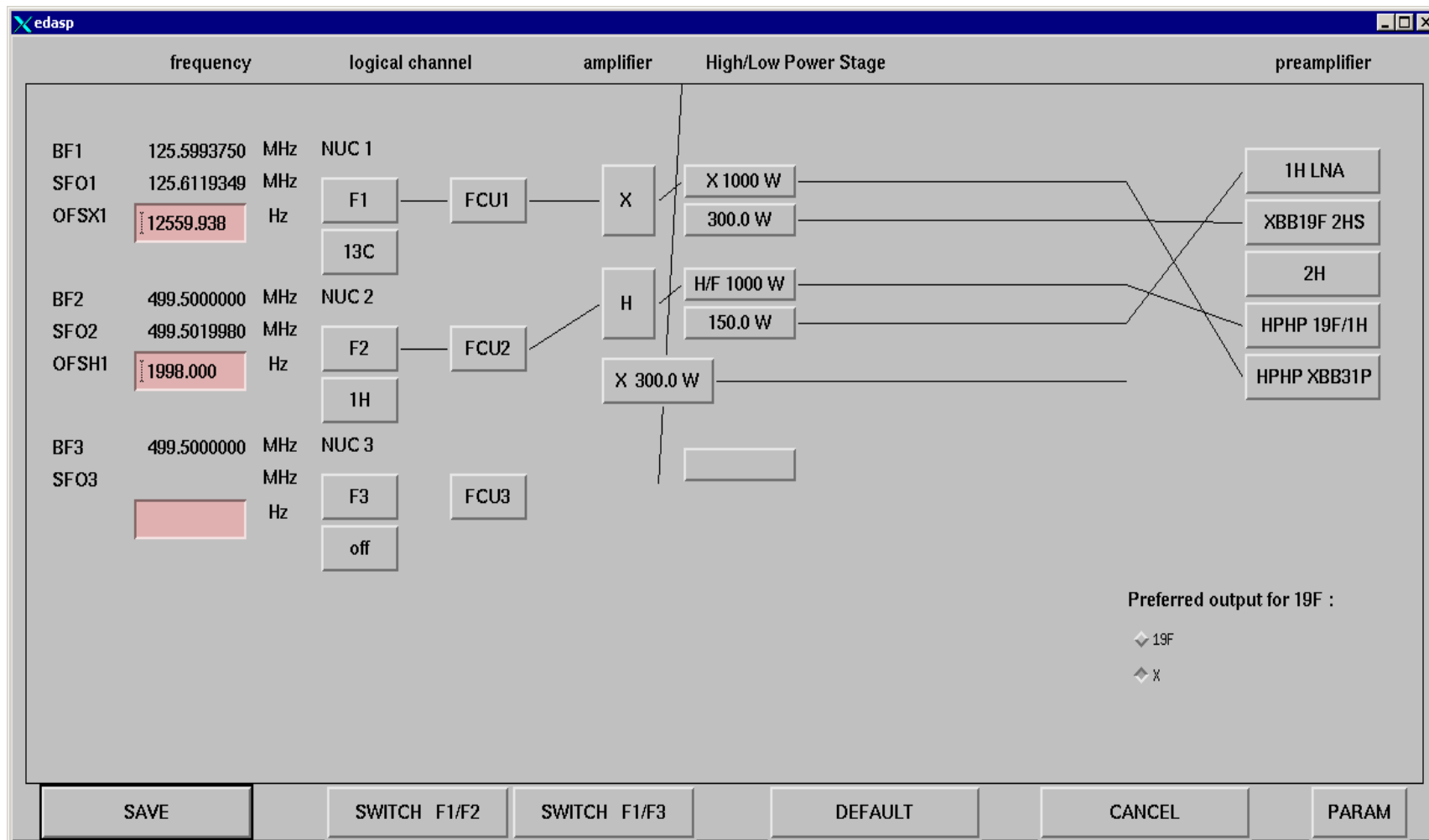
- Direct Polarization ^{13}C for pulse power measurement:
 - Parameter file: C13SOL
 - Pulse program: hpdec.av
 - See header in pulse program.
 - Edit pulse program with: edcpul <pp-name>
 - Setting of decoupling program by pulse decoupling dprg2



Setup Direct Polarization Experiments



- EDASP display:



Setup Direct Polarization Experiments



- EDA cpdprg2:

Parameter	Value	Unit	Parameter	Value	Unit
03	0.00	Hz	SF03	499.5000000	MHz
03P	0.000	ppm	BF3	499.5000000	MHz
			NUC4	off	
04	0.00	Hz	SF04	499.5000000	MHz
04P	0.000	ppm	BF4	499.5000000	MHz
CPDPRG1	mlev		CPDPRG2	I cw	
CPDPRG3	mlev		CPDPRG4	mlev	
CPDPRG5	mlev		CPDPRG6	mlev	
CPDPRG7	mlev		CPDPRG8	mlev	
PCPD	** Array **		GRDPROG		
LOCNUC	off		PROBHD		
SOLVENT	chc13		EXP		
PROSOL	FALSE		MASR	15000	
R0	20	Hz	TE	373.0	K
NBL	1		V9	5.00	%

Parameter



- Pulse program:

```
;hpdec.av
```

```
1 ze ;set RCU to replace mode
2 d1 do:f2 ;recycle delay
   (p1 ph1):f1 ;pulse on F1; power level p11
   1u cpds2:f2 ;use cpdprg2 cw or tppm at p112
   go=2 ph31 ;adc is finished,
   1m do:f2 ;turn decoupling off
   wr #0 ;save data in current data set
exit
ph0= 0 ;constant phase for acquisition
ph1= 0 1 2 3 ;simple pulse phase list
ph31=0 1 2 3 ;signal routing corresponds to
;pulse phase list
```

- Decoupling program:

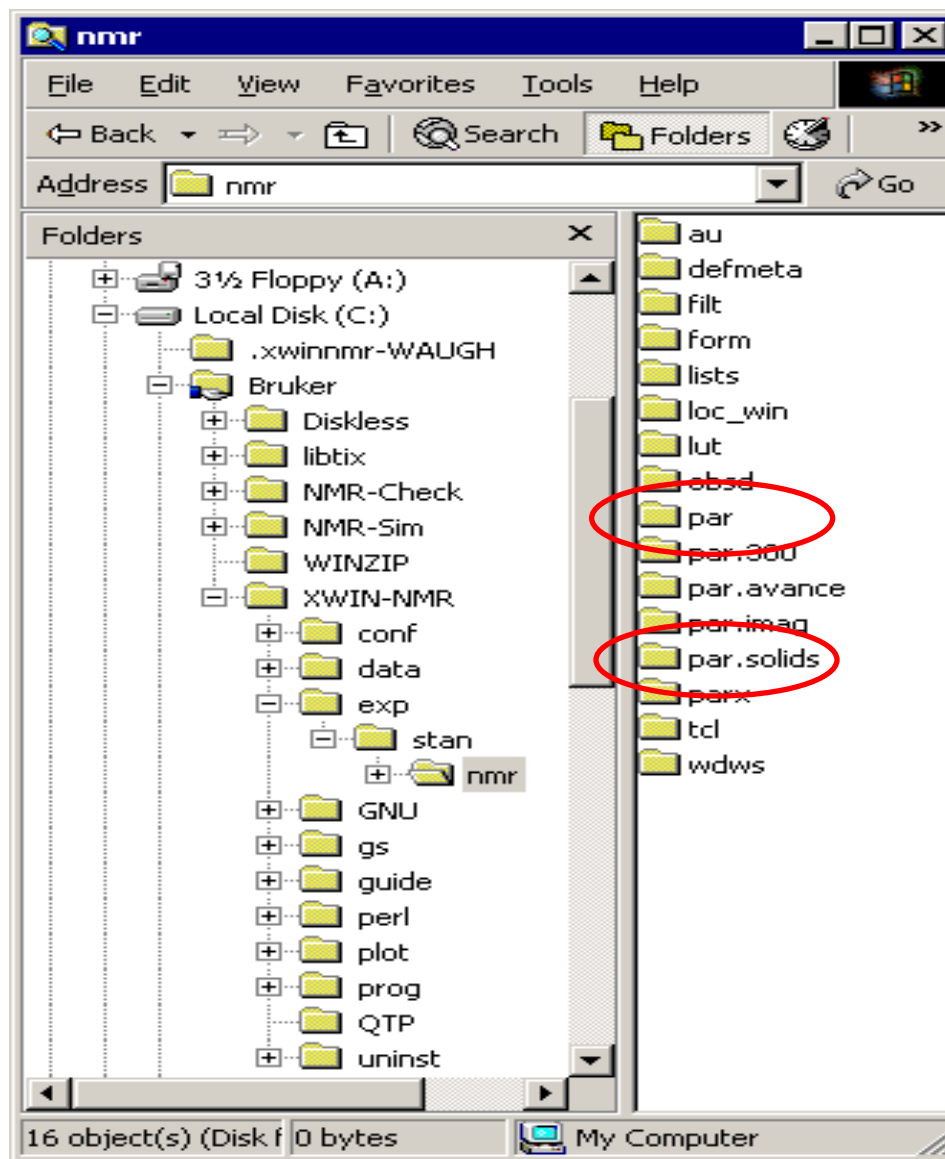
```
0.5u p1=p112
```

```
1 100up:0 fq=cnst21
```

```
jump to 1
```

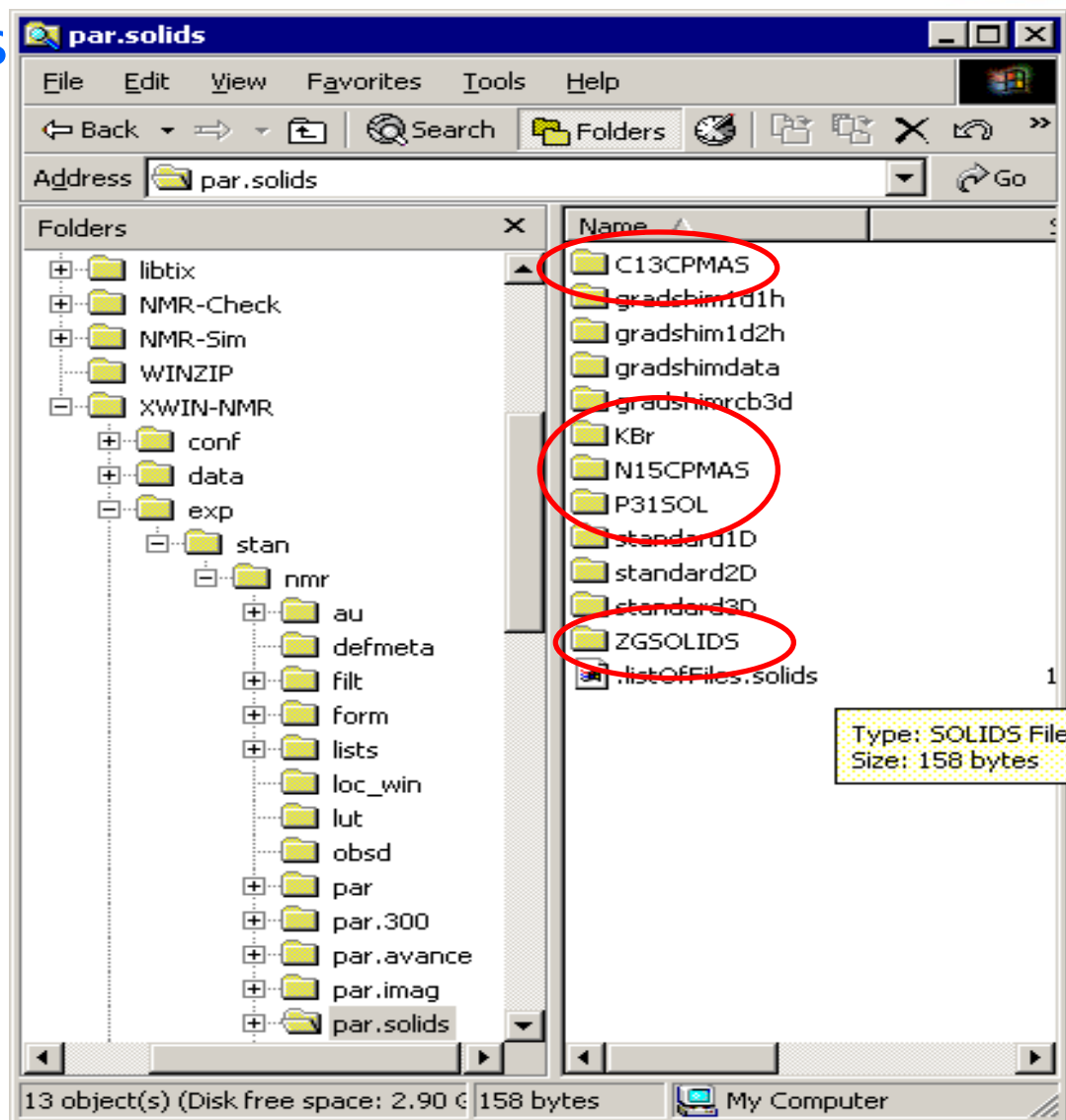
Productivity Tools

- Location of parmeter sets



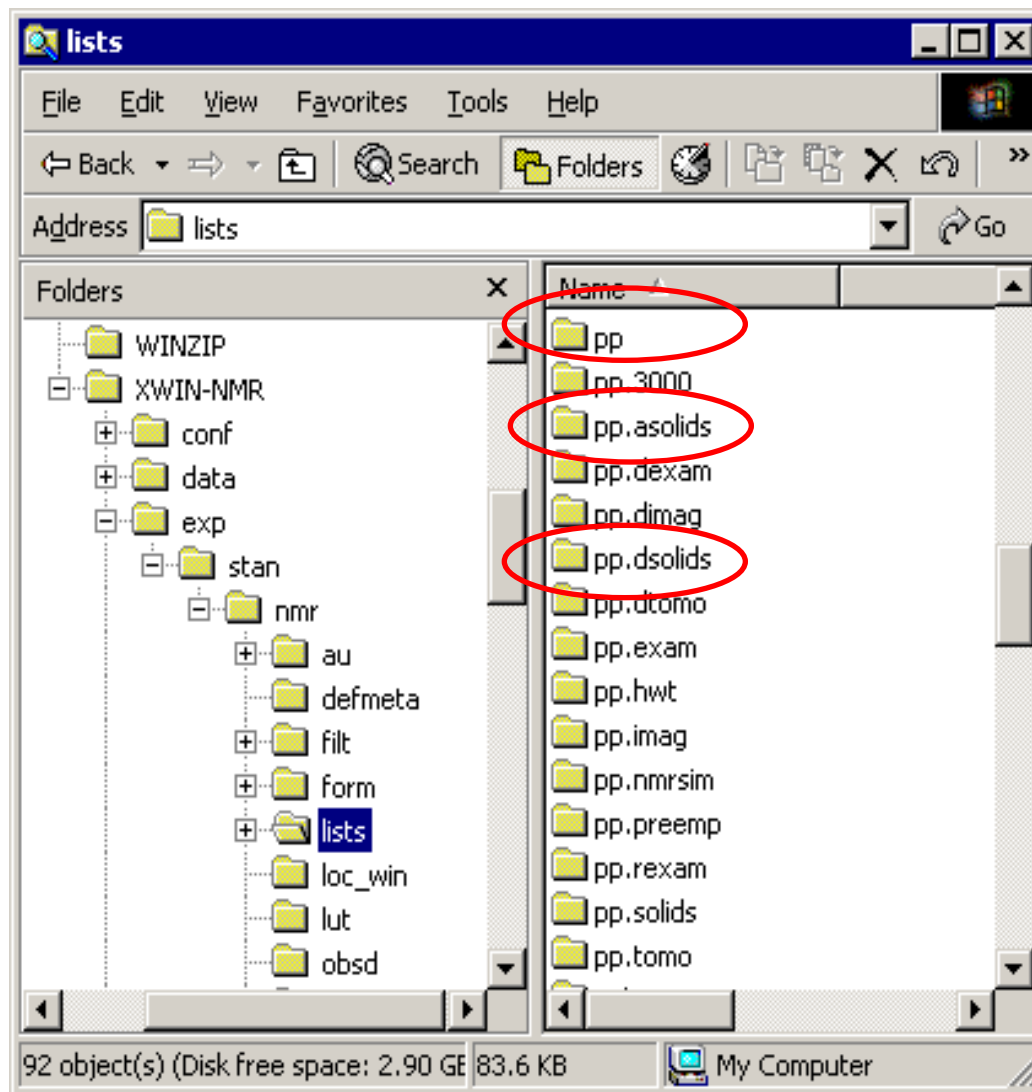
Productivity Tools

- Parmeter sets



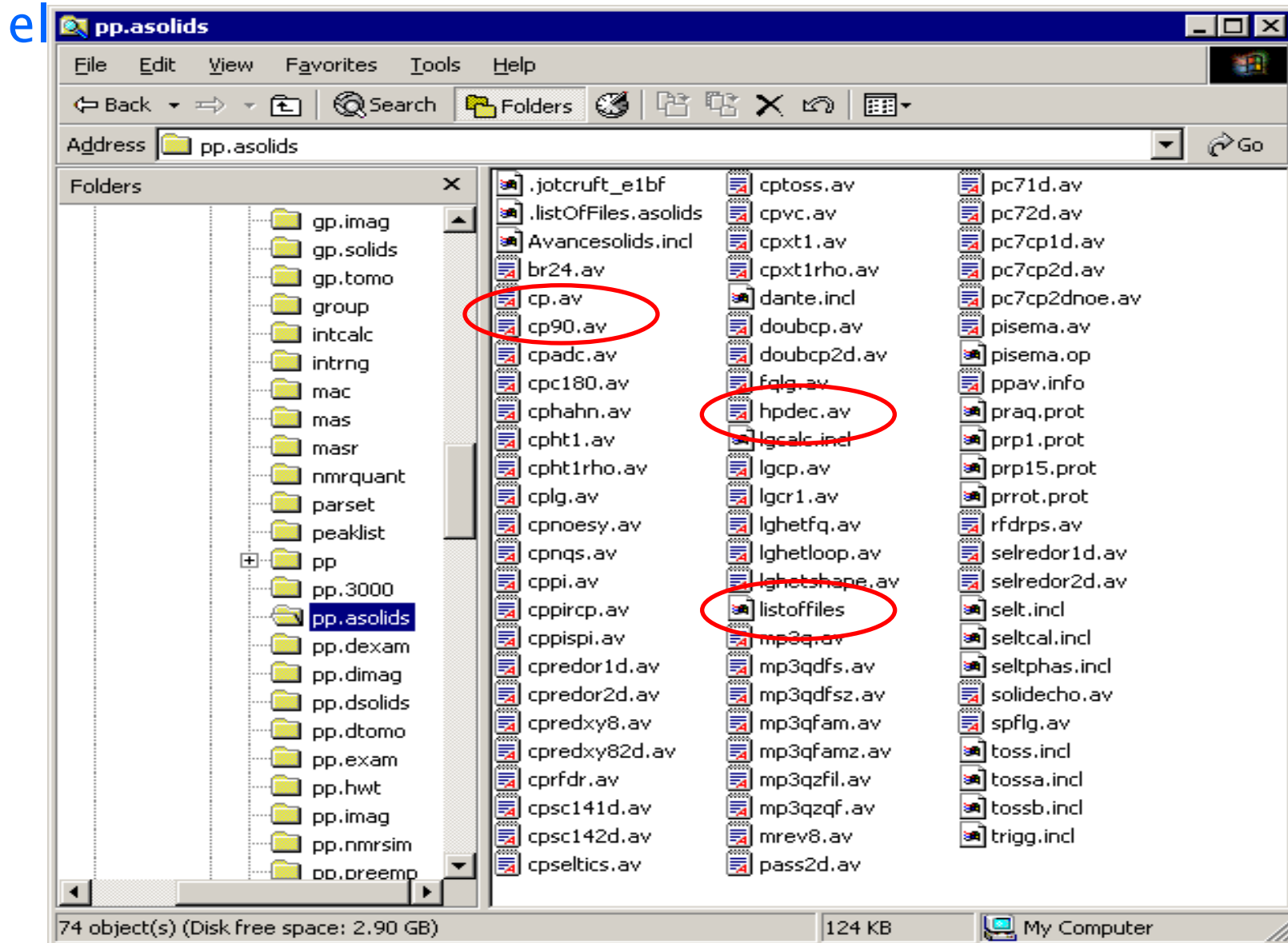
Productivity Tools

- Pulse Programs, etc



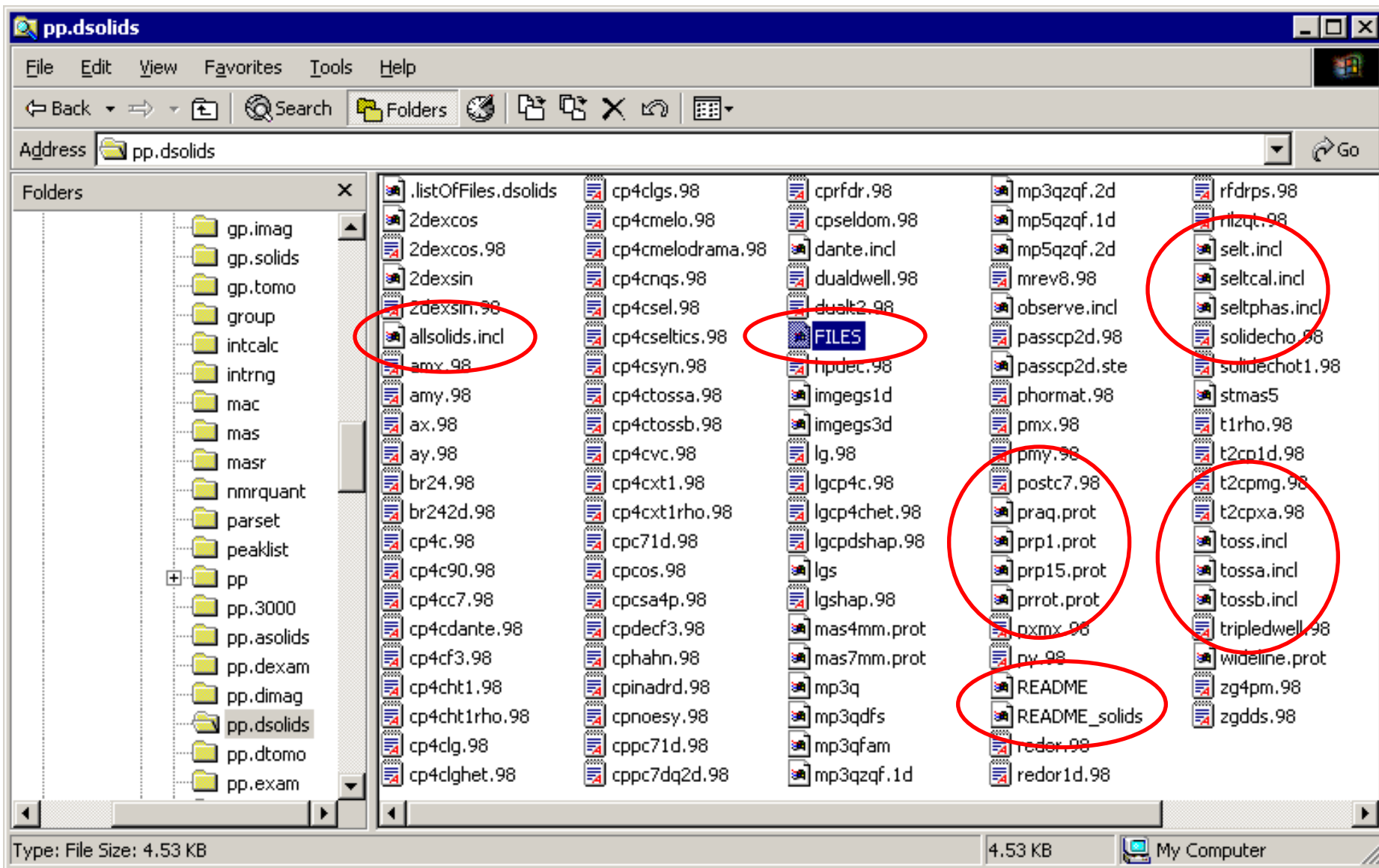
Productivity Tools

- Pulse Programs for consoles with AQS (SGU)



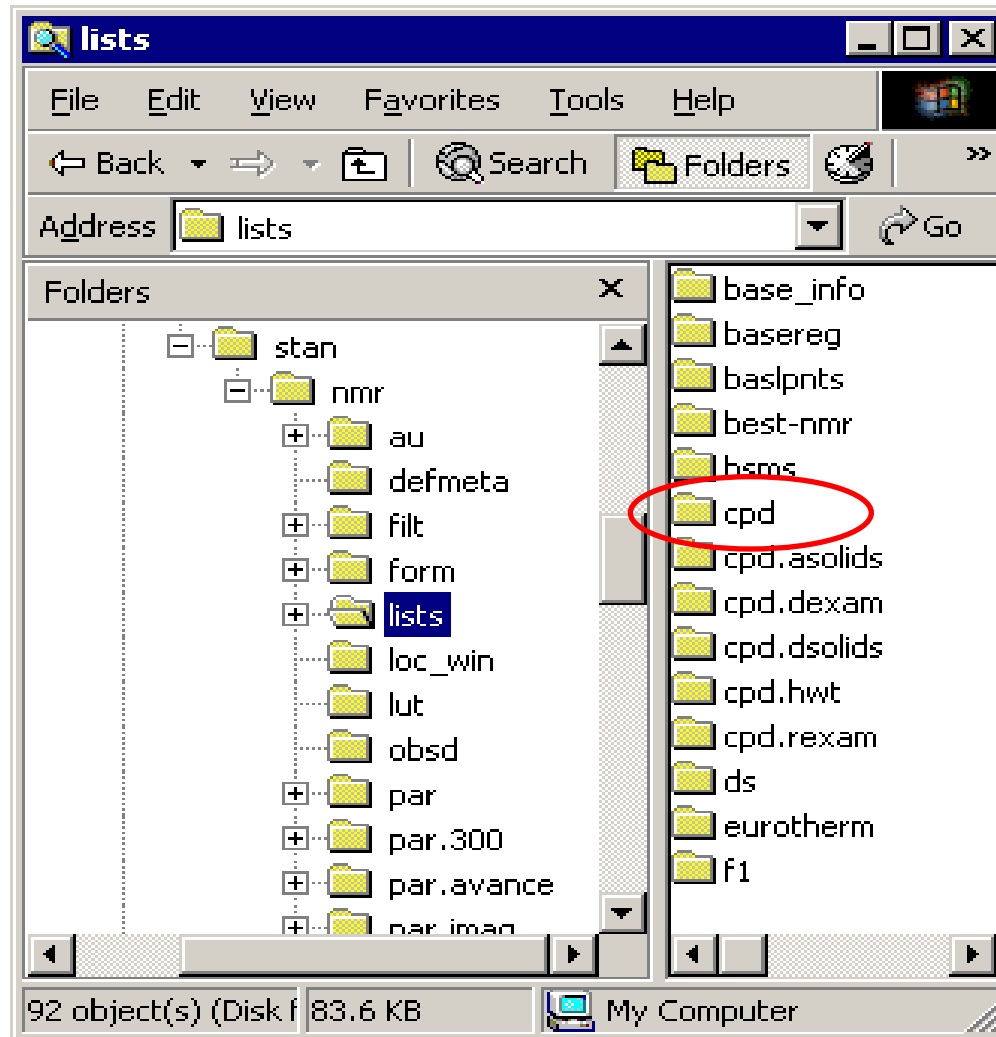
Productivity Tools

- Pulse Programs for consoles with AQX electronic



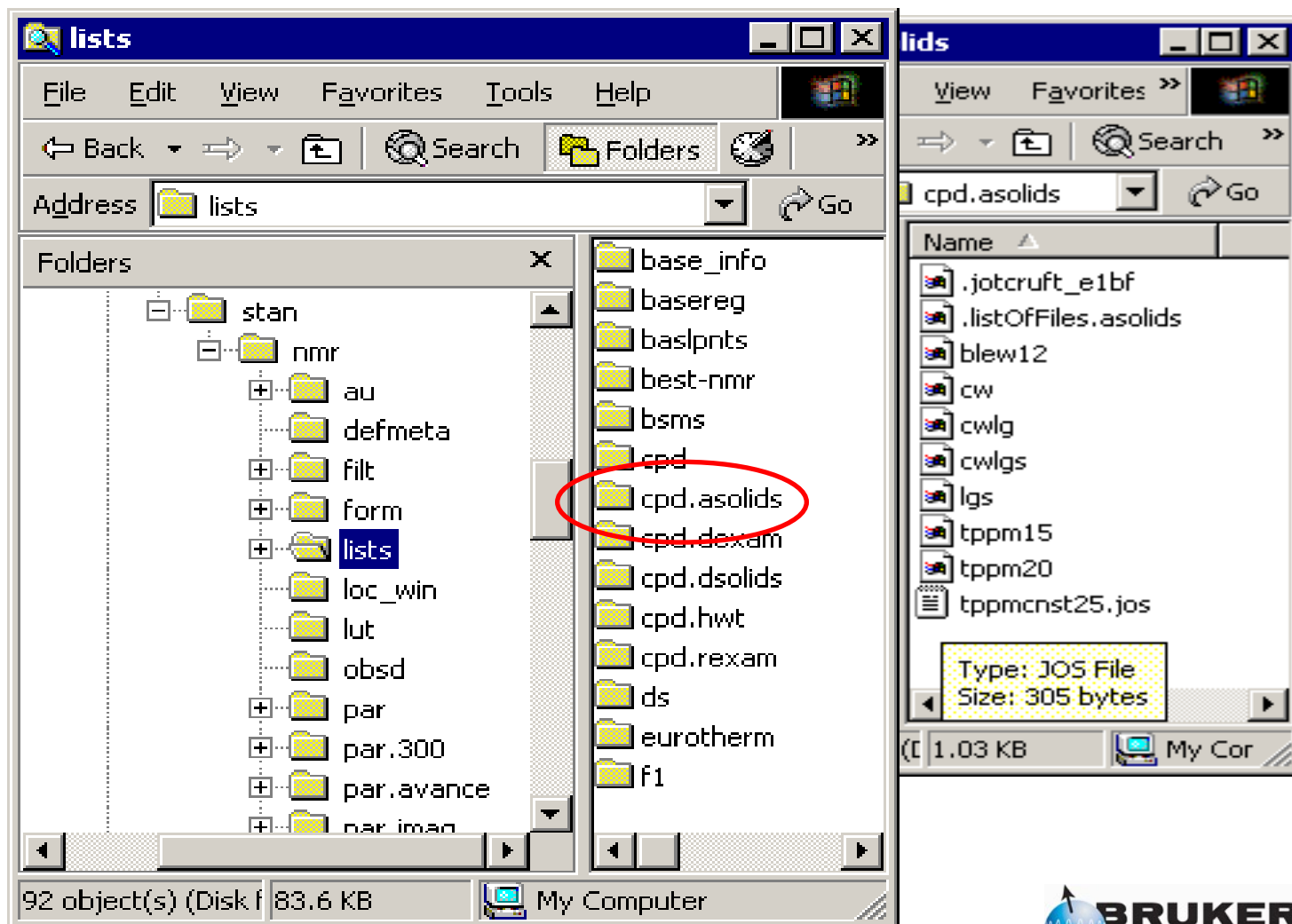
Productivity Tools

- Composit Pulse Decoupling (CPD) Programs



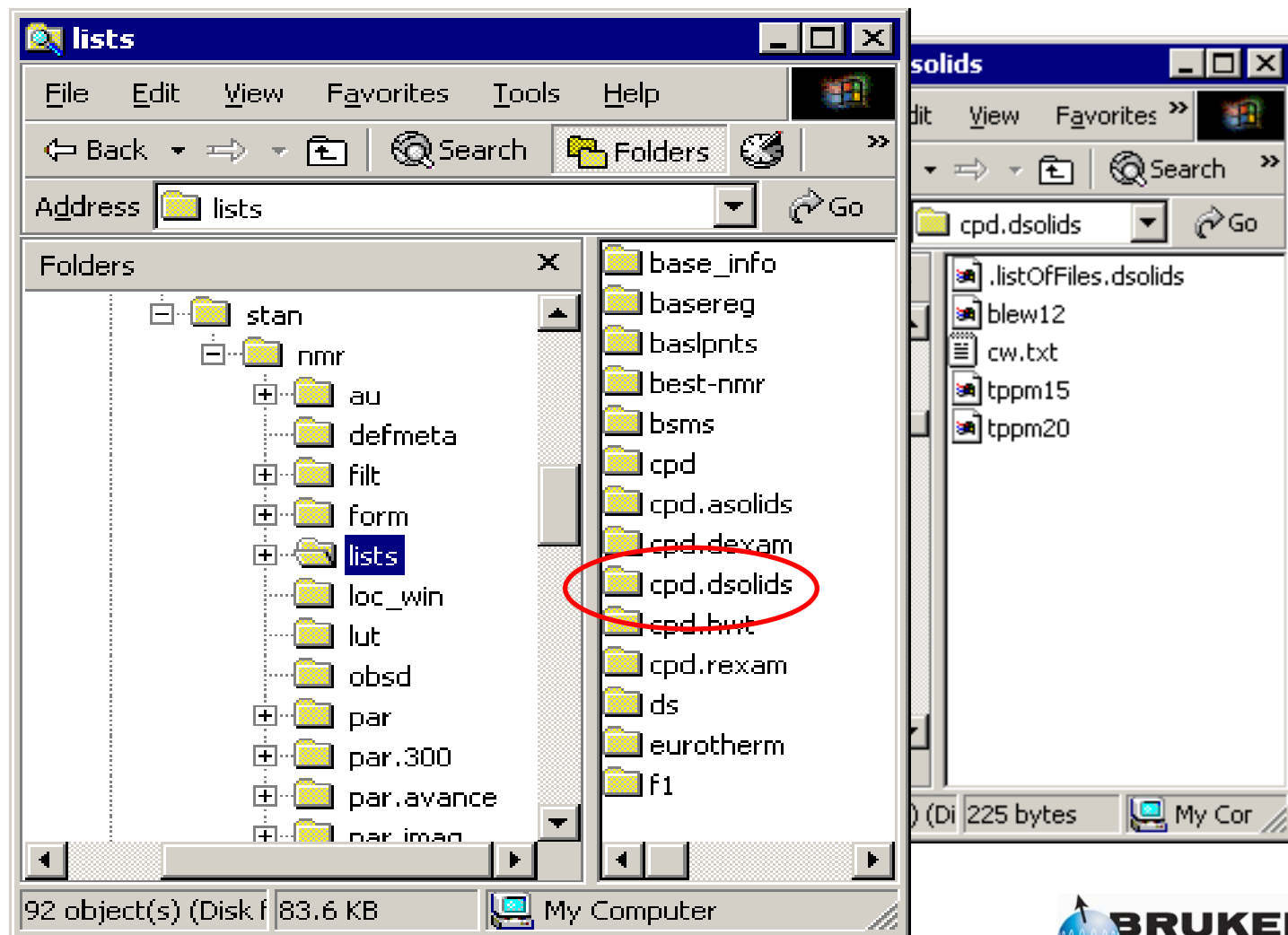
Productivity Tools

- Composit Pulse Decoupling (CPD) Programs



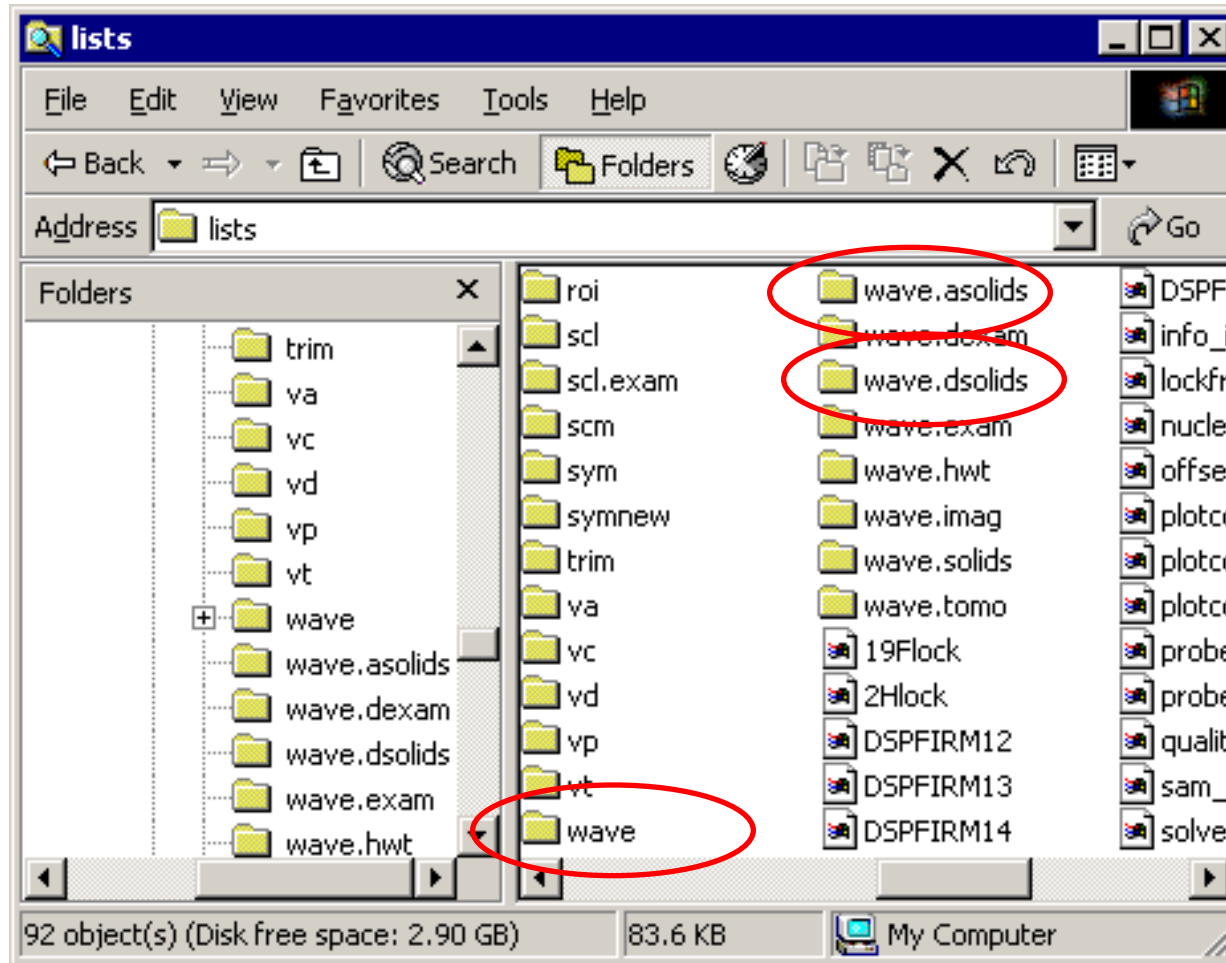
Productivity Tools

- Composit Pulse Decoupling (CPD) Programs

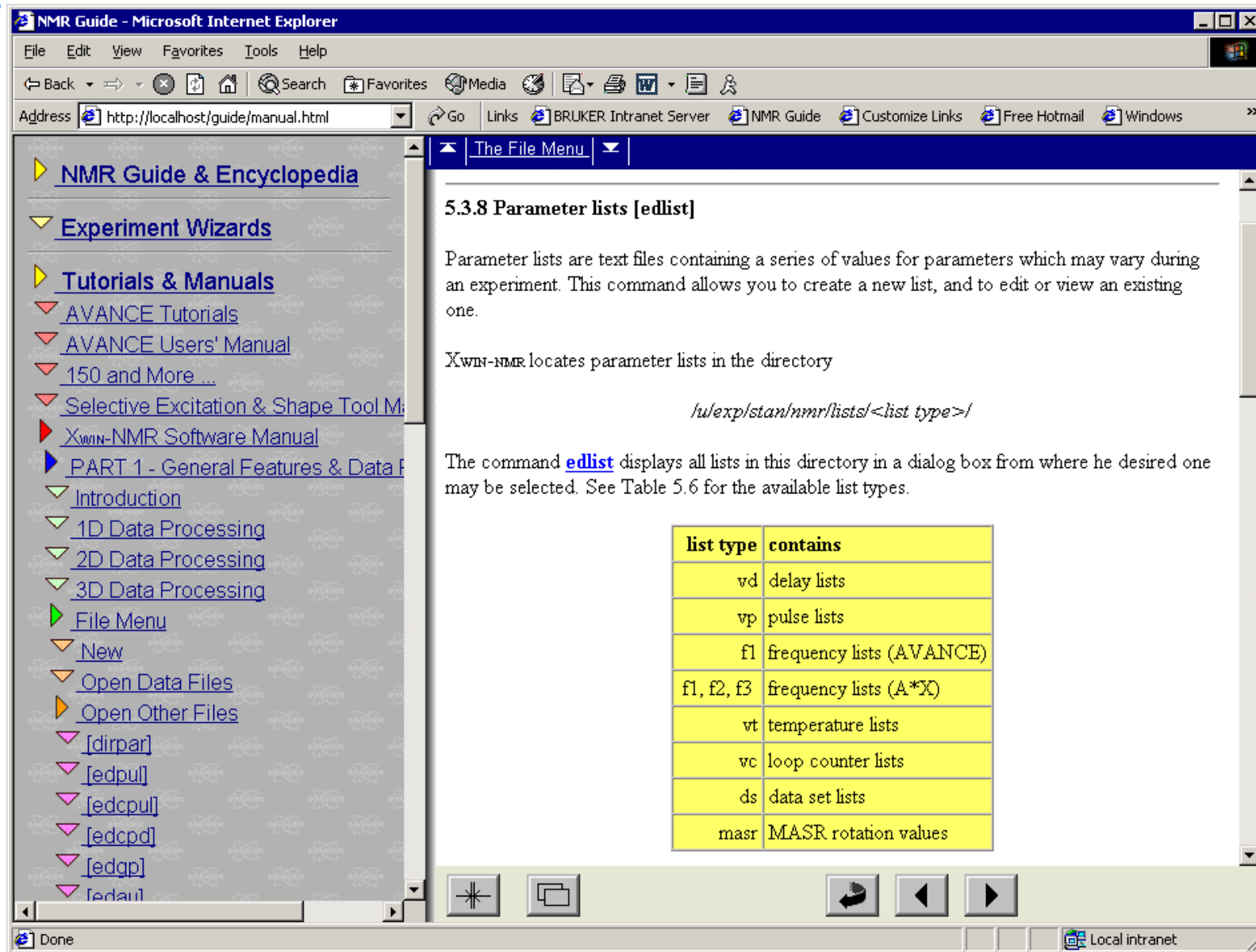


Productivity Tools

- Shape Files (CPD)



- Lists



5.3.8 Parameter lists [edlist]

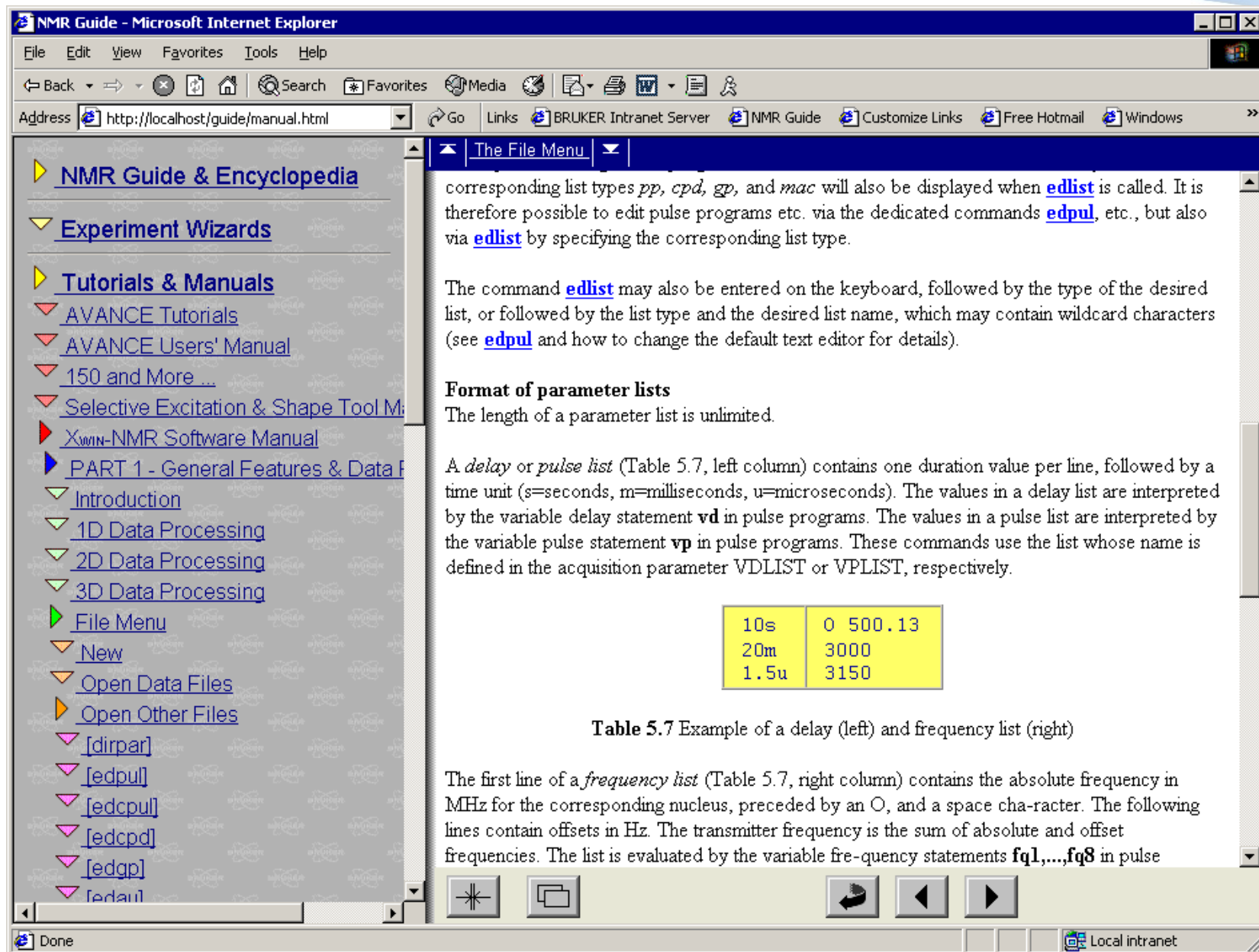
Parameter lists are text files containing a series of values for parameters which may vary during an experiment. This command allows you to create a new list, and to edit or view an existing one.

XWIN-NMR locates parameter lists in the directory

```
/u/exp/stan/nmr/lists/<list type>/
```

The command [edlist](#) displays all lists in this directory in a dialog box from where he desired one may be selected. See Table 5.6 for the available list types.

list type	contains
vd	delay lists
vp	pulse lists
f1	frequency lists (AVANCE)
f1, f2, f3	frequency lists (A*XX)
vt	temperature lists
vc	loop counter lists
ds	data set lists
masr	MASR rotation values



The screenshot shows a Microsoft Internet Explorer browser window titled "NMR Guide - Microsoft Internet Explorer". The address bar shows "http://localhost/guide/manual.html". The left sidebar contains a navigation menu with the following items:

- NMR Guide & Encyclopedia
- Experiment Wizards
- Tutorials & Manuals
 - AVANCE Tutorials
 - AVANCE Users' Manual
 - 150 and More ...
 - Selective Excitation & Shape Tool M...
 - XWIN-NMR Software Manual
 - PART 1 - General Features & Data F
 - Introduction
 - 1D Data Processing
 - 2D Data Processing
 - 3D Data Processing
 - File Menu
 - New
 - Open Data Files
 - Open Other Files
 - [dirpar]
 - [edpul]
 - [edcpul]
 - [edcpd]
 - [edgp]
 - [edaul]

The main content area is titled "The File Menu" and contains the following text:

corresponding list types *pp*, *cpd*, *gp*, and *mac* will also be displayed when [edlist](#) is called. It is therefore possible to edit pulse programs etc. via the dedicated commands [edpul](#), etc., but also via [edlist](#) by specifying the corresponding list type.

The command [edlist](#) may also be entered on the keyboard, followed by the type of the desired list, or followed by the list type and the desired list name, which may contain wildcard characters (see [edpul](#) and how to change the default text editor for details).

Format of parameter lists

The length of a parameter list is unlimited.

A *delay* or *pulse list* (Table 5.7, left column) contains one duration value per line, followed by a time unit (*s*=seconds, *m*=milliseconds, *u*=microseconds). The values in a delay list are interpreted by the variable delay statement **vd** in pulse programs. The values in a pulse list are interpreted by the variable pulse statement **vp** in pulse programs. These commands use the list whose name is defined in the acquisition parameter VDLIST or VPLIST, respectively.

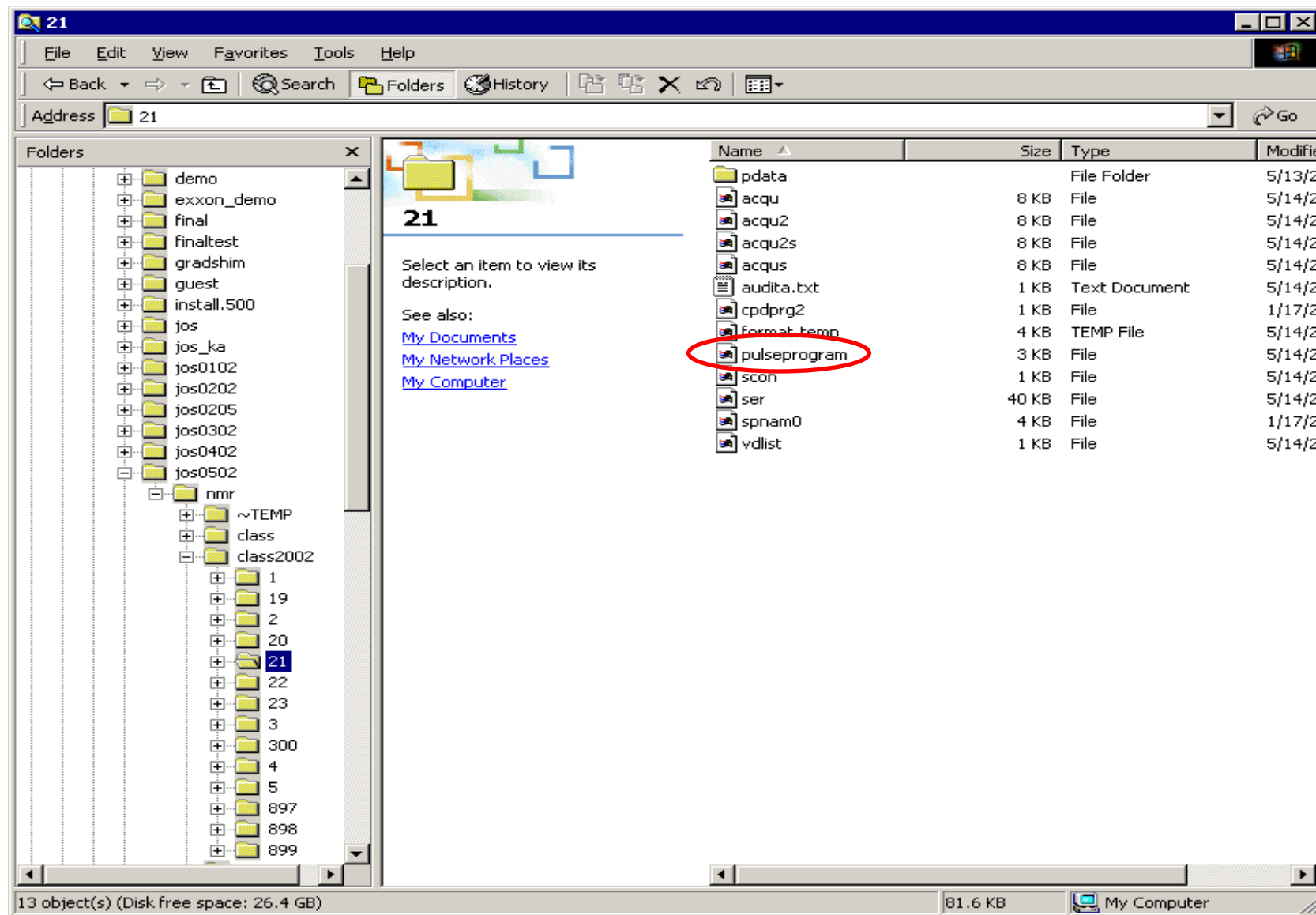
10s	0 500.13
20m	3000
1.5u	3150

Table 5.7 Example of a delay (left) and frequency list (right)

The first line of a *frequency list* (Table 5.7, right column) contains the absolute frequency in MHz for the corresponding nucleus, preceded by an O, and a space character. The following lines contain offsets in Hz. The transmitter frequency is the sum of absolute and offset frequencies. The list is evaluated by the variable frequency statements **fq1**, ..., **fq8** in pulse

Productivity Tools

- Information in stored data sets



The screenshot shows a Windows Explorer window titled '21'. The address bar shows the path '21'. The left pane shows a folder tree with '21' selected. The right pane shows a list of files and folders. The 'pulseprogram' file is circled in red.

Name	Size	Type	Modified
pdata		File Folder	5/13/2
acqu	8 KB	File	5/14/2
acqu2	8 KB	File	5/14/2
acqu2s	8 KB	File	5/14/2
acqu	8 KB	File	5/14/2
audita.txt	1 KB	Text Document	5/14/2
cpdprg2	1 KB	File	1/17/2
format_temp	4 KB	TEMP File	5/14/2
pulseprogram	3 KB	File	5/14/2
scon	1 KB	File	5/14/2
ser	40 KB	File	5/14/2
spnam0	4 KB	File	1/17/2
vdlist	1 KB	File	5/14/2

13 object(s) (Disk free space: 26.4 GB) 81.6 KB My Computer

Productivity Tools



- Information in stored data sets

21

Select an item to view its description.

See also:
[My Documents](#)
[My Network Places](#)
[My Computer](#)

Name	Size	Type	Modified
pdata		File Folder	5/13/2
acqu	8 KB	File	5/14/2
acqu2	8 KB	File	5/14/2
acqu2s	8 KB	File	5/14/2
acqu	8 KB	File	5/14/2
audita.txt	1 KB	Text Document	5/14/2
cpdprg2	1 KB	File	1/17/2
format.temp	4 KB	TEMP File	5/14/2
pulseprogram	3 KB	File	5/14/2
scon	1 KB	File	5/14/2
ser	40 KB	File	5/14/2
spnam0	4 KB	File	1/17/2
vulist	1 KB	File	5/14/2

13 object(s) (Disk free space: 26.4 GB) 81.6 KB My Computer

Productivity Tools



- Information in stored data sets

21

File Edit View Favorites Tools Help

Back Search Folders History

Address 21 Go

Folders

- demo
- exxon_demo
- final
- finaltest
- gradshim
- guest
- install.500
- jos
- jos_ka
- jos0102
- jos0202
- jos0205
- jos0302
- jos0402
- jos0502
- nmr
 - ~TEMP
 - class
 - class2002
 - 1
 - 19
 - 2
 - 20
 - 21
 - 22
 - 23
 - 3
 - 300
 - 4
 - 5
 - 897
 - 898
 - 899

21

Select an item to view its description.

See also:
[My Documents](#)
[My Network Places](#)
[My Computer](#)

Name	Size	Type	Modified
pdata		File Folder	5/13/2
acqu	8 KB	File	5/14/2
acqu2	8 KB	File	5/14/2
acqu2s	8 KB	File	5/14/2
acqu	8 KB	File	5/14/2
audita.txt	1 KB	Text Document	5/14/2
cpdprg2	1 KB	File	1/17/2
format.temp	4 KB	TEMP File	5/14/2
pulseprogram	3 KB	File	5/14/2
scon	1 KB	File	5/14/2
ser	40 KB	File	5/14/2
spnam0	4 KB	File	1/17/2
vdlst	1 KB	File	5/14/2

13 object(s) (Disk free space: 26.4 GB) 81.6 KB My Computer

Productivity Tools



- Information in stored data sets

The screenshot shows a Windows Explorer window titled '21'. The address bar shows the path '21'. The left pane shows a folder tree with '21' selected. The right pane shows a list of files and folders. The file 'audita.txt' is circled in red.

Name	Size	Type	Modified
pdata		File Folder	5/13/2
acqu	8 KB	File	5/14/2
acqu2	8 KB	File	5/14/2
acqu2s	8 KB	File	5/14/2
acquc	8 KB	File	5/14/2
audita.txt	1 KB	Text Document	5/14/2
cpdprg2	1 KB	File	1/17/2
format.temp	4 KB	TEMP File	5/14/2
pulseprogram	3 KB	File	5/14/2
scon	1 KB	File	5/14/2
ser	40 KB	File	5/14/2
spnam0	4 KB	File	1/17/2
vdlist	1 KB	File	5/14/2

13 object(s) (Disk free space: 26.4 GB) 81.6 KB My Computer

- Audit trail:

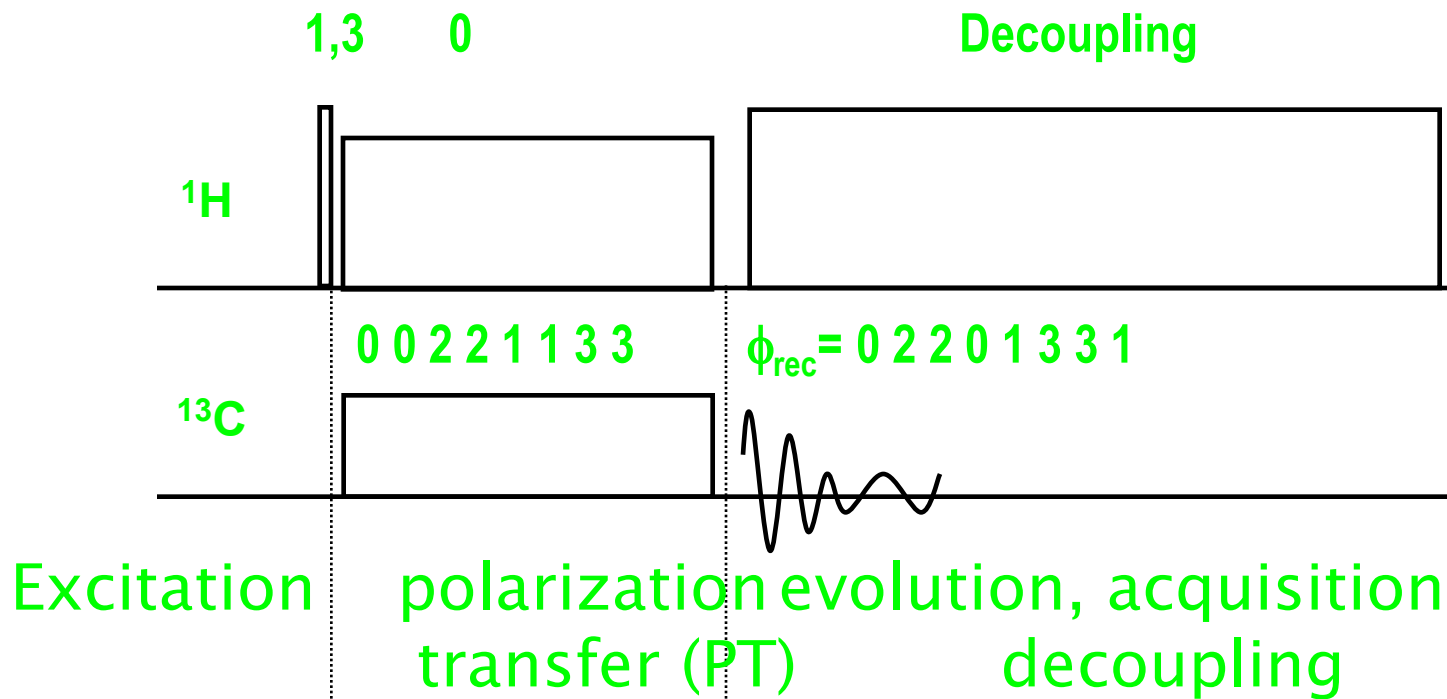
```
##TITLE= Audit trail, XWIN-NMR           Version 3.1
##JCAMPDX= 5.01
##ORIGIN= Bruker Analytik GmbH
##OWNER= Administrator
$$ C:\data\jos0502\nmr\class2002\21\audita.txt
##AUDIT TRAIL= $$ (NUMBER, WHEN, WHO, WHERE, WHAT)
( 1,<2002-05-14 14:05:23.73 -400>,<Administrator>,<PINES>,
  <created by zg
    data hash MD5: 1K * 10
    CC B6 7F 0A F5 94 FA F5 9F C6 50 C4 BD 68 5B 33>)
##END=

$$ hash MD5
$$ BF 3A 92 C9 76 50 C1 F1 D3 0F 62 F4 28 A3 46 19
```


Setup Cross Polarization Experiments



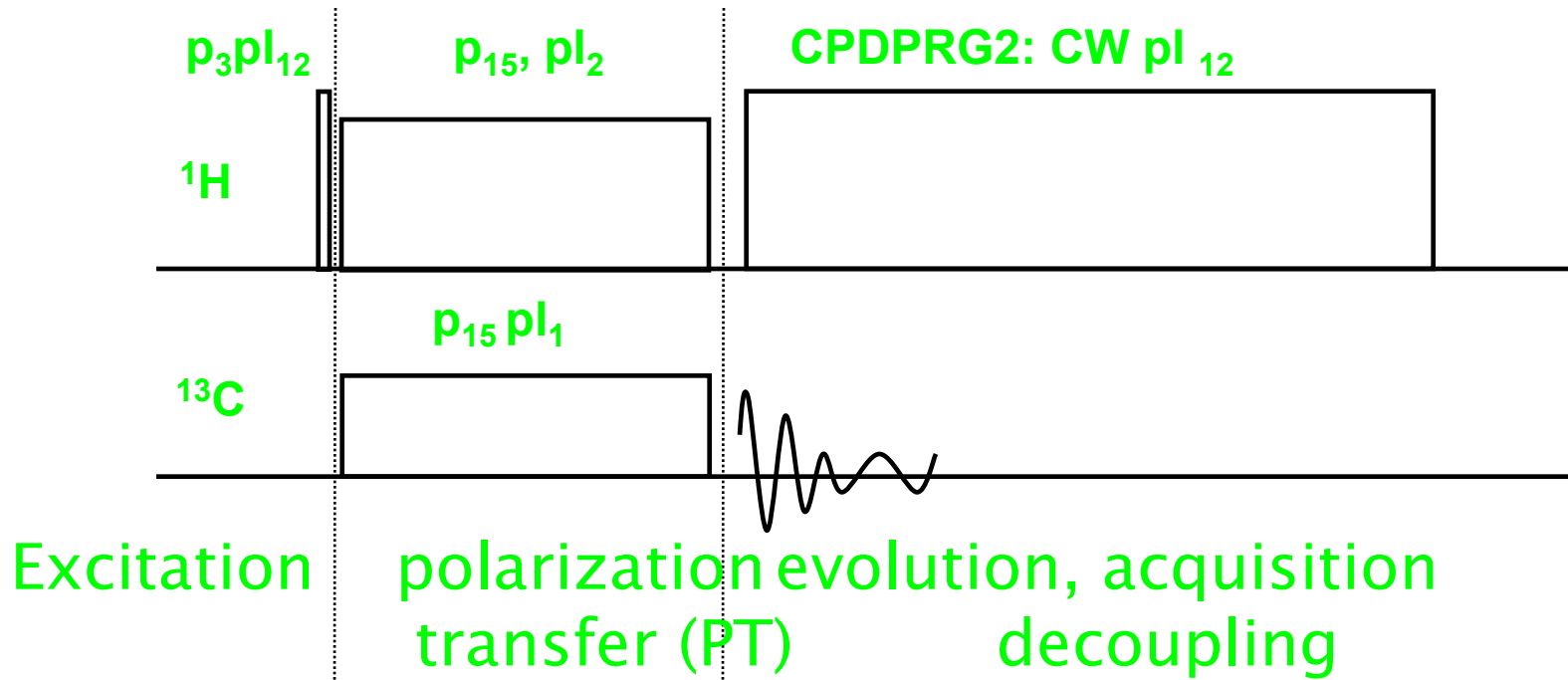
- General setup for cross polarization cp experiment
 - Parameter set: **C13CPMAS**
 - Pulse program: **cp.av** or **cp90.av**
 - See header in pulse program.
 - Edit pulse program with: **edcpul <pp-name>**



Setup Cross Polarization Experiments



- General setup for cross polarization cp experiment
 - Conventions in solids CPMAS release pulse programs:



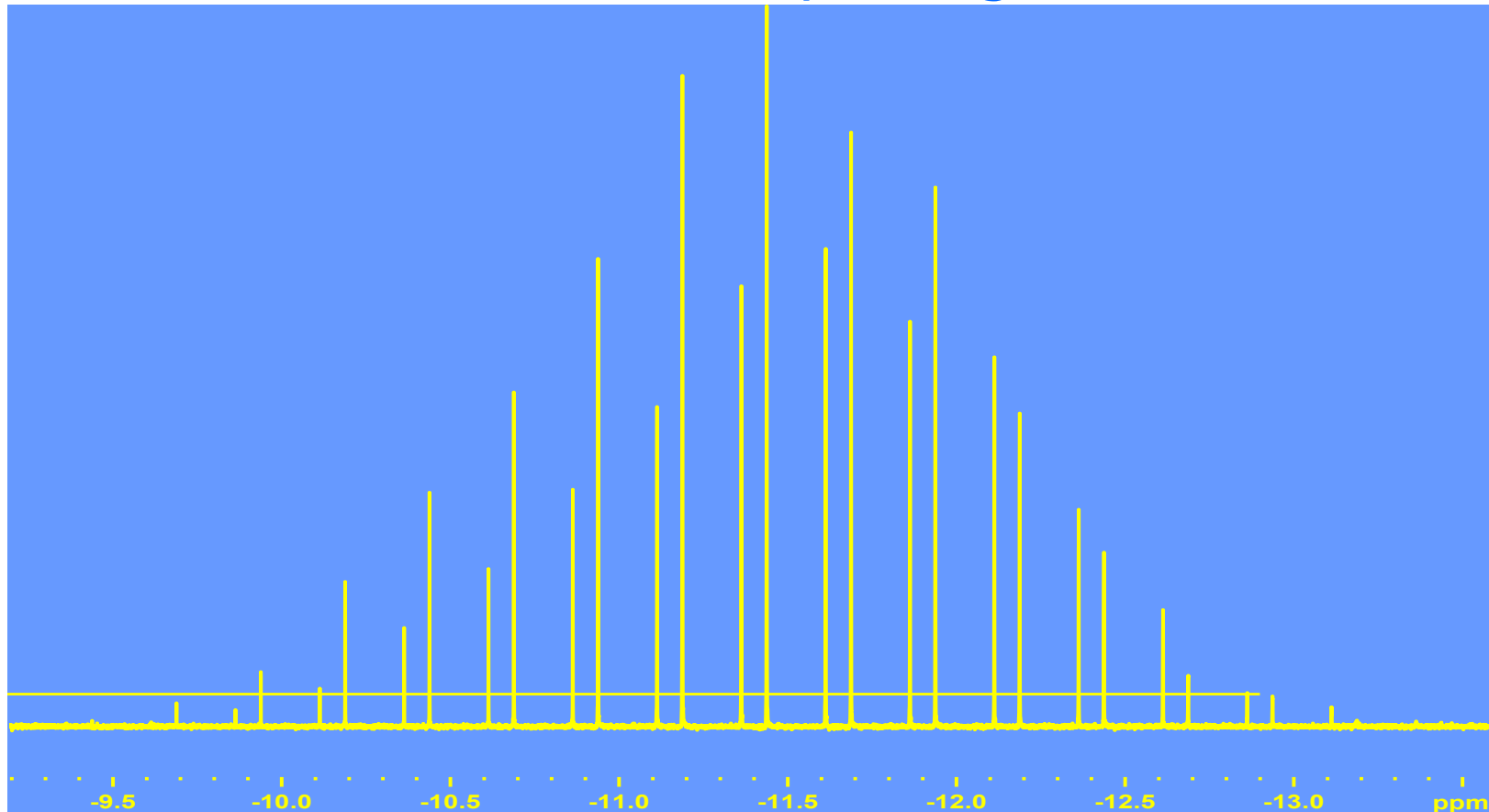
- Conventions in release pulse programs:
 - f2 - ^1H channel, f1 - ^{13}C channel (observe)
 - f1 channel: **p11** for contact, **p111** for pulses etc after CP
 - f2 channel: **p12** for contact, **spnam0** for shape, **p3** at **p112** for excitation and heteronuclear decoupling, **p113** for homonuclear FSLG/PMLG decoupling, **p15** for contact pulse width.
 - Other parameters: see header in pulse program.
 - Edit pulse program with: **edcpul <pp-name>**

- Setup from scratch:
 - Set the magic angle with KBr
 - Measure ^1H 4us pulse width on adamantane - spin as fast as probe permits.
 - Measure ^{13}C 4us pulses on adamantane with direct polarization using high power decoupling experiment with parameter set **C13SOL**, pulse program **hpdec.av** (spin 2 -3 kHz)
 ^1H decoupling **p1 2=pl(4us)+3dB** permits $50\text{ms} < aq < 0.5\text{s}$.
 - Use obtained power levels and pulses for CP experiment load pulse program **cp.av** or **cp90.av**.
Set **p1 5=3-4ms**
 - Optimize HH match with POPT on p1 or p2

Setup Cross Polarization Experiments



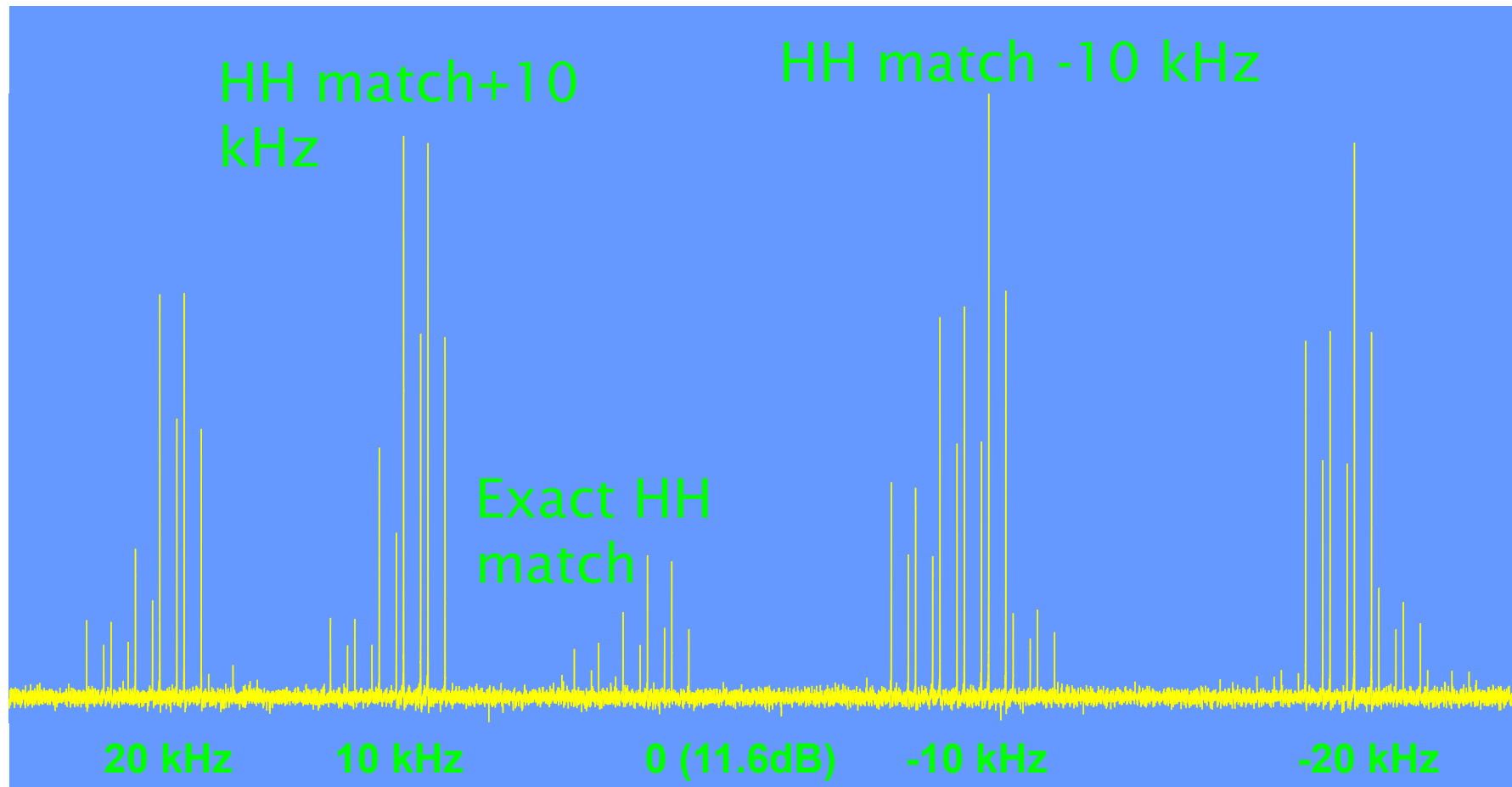
- HH matching profile using POPT
 - Adamantane, 2 kHz spinning.



Setup Cross Polarization Experiments



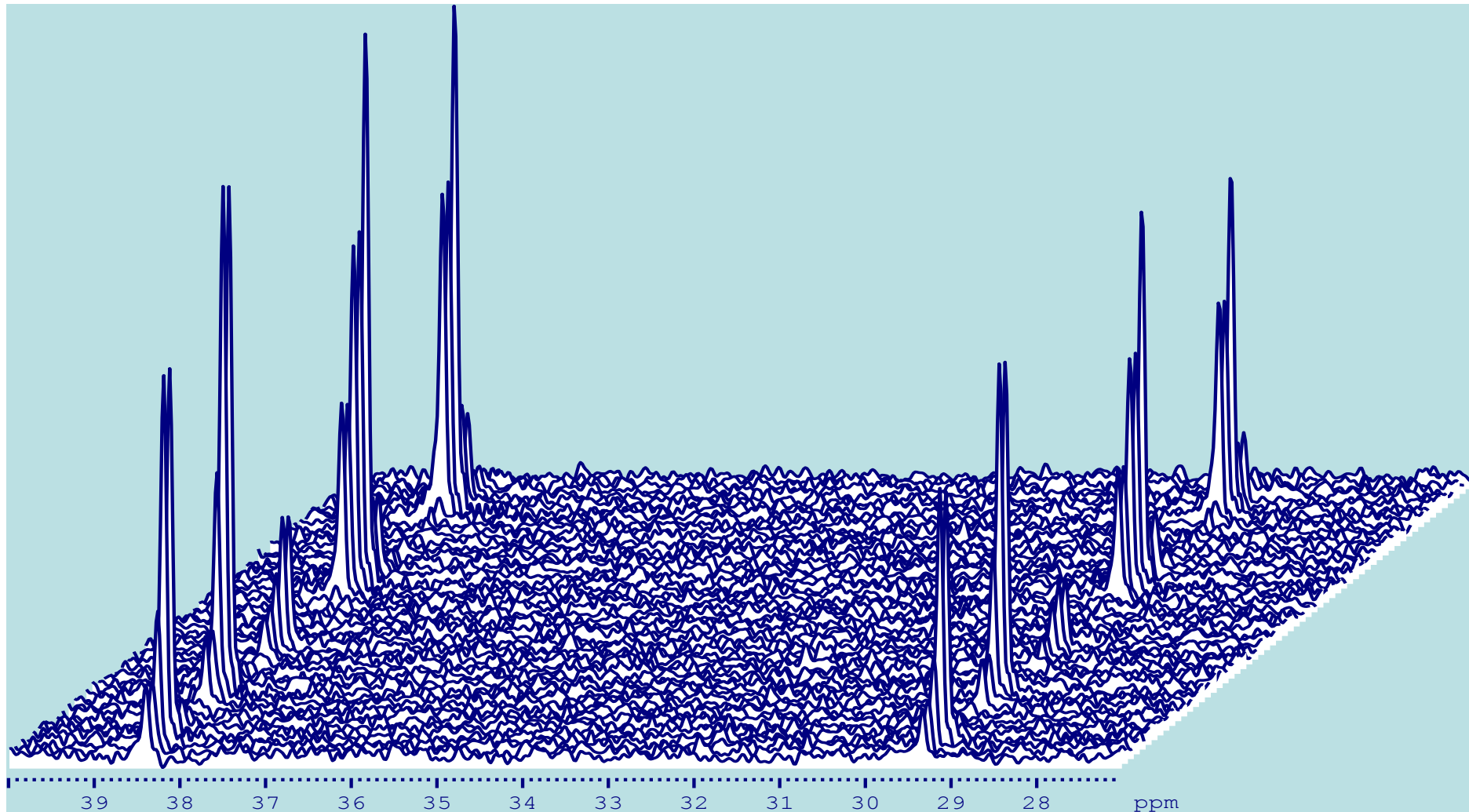
- HH matching profile using POPT
 - Adamantane, 10 kHz spinning.



Setup Cross Polarization Experiments

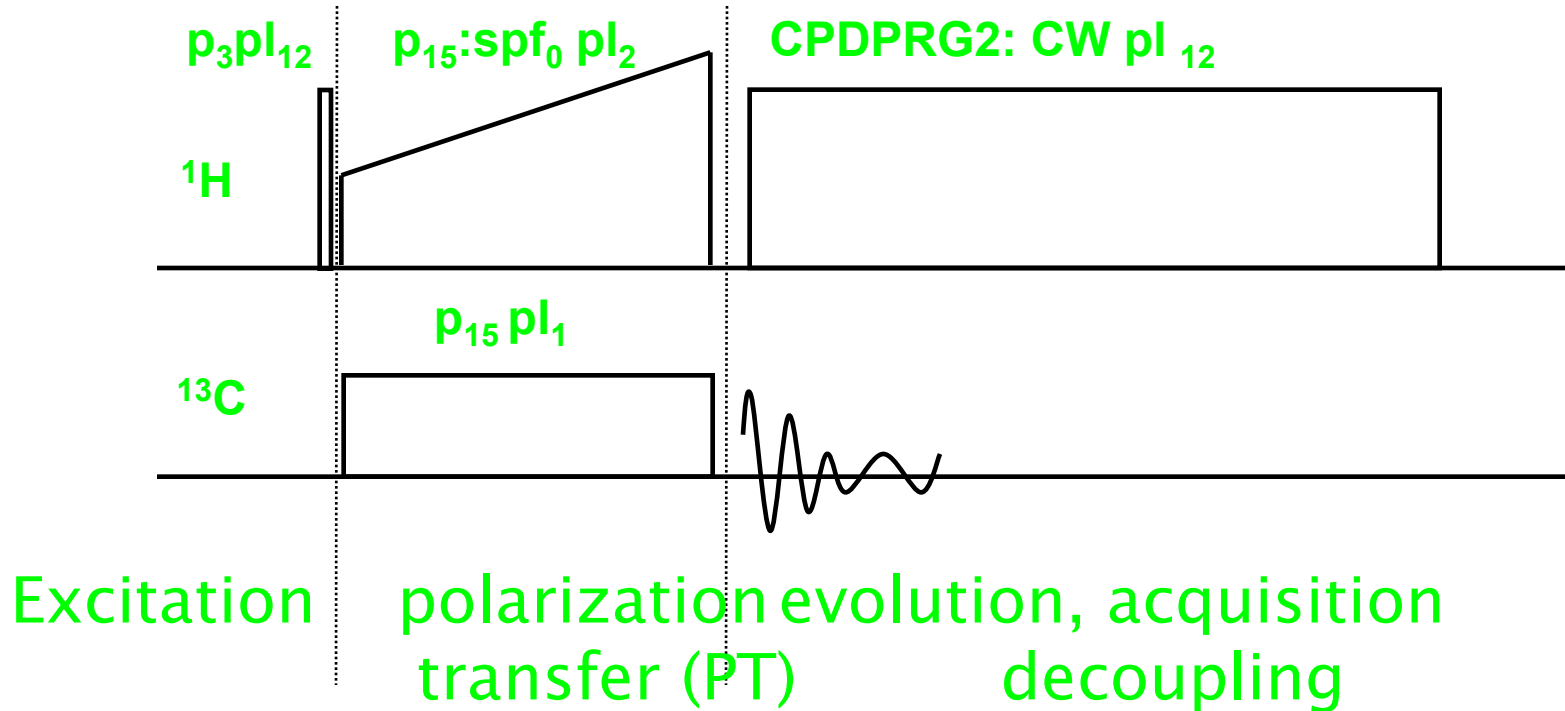


- HH matching profile from pseudo 2D data (POPT)



Setup Cross Polarization Experiments

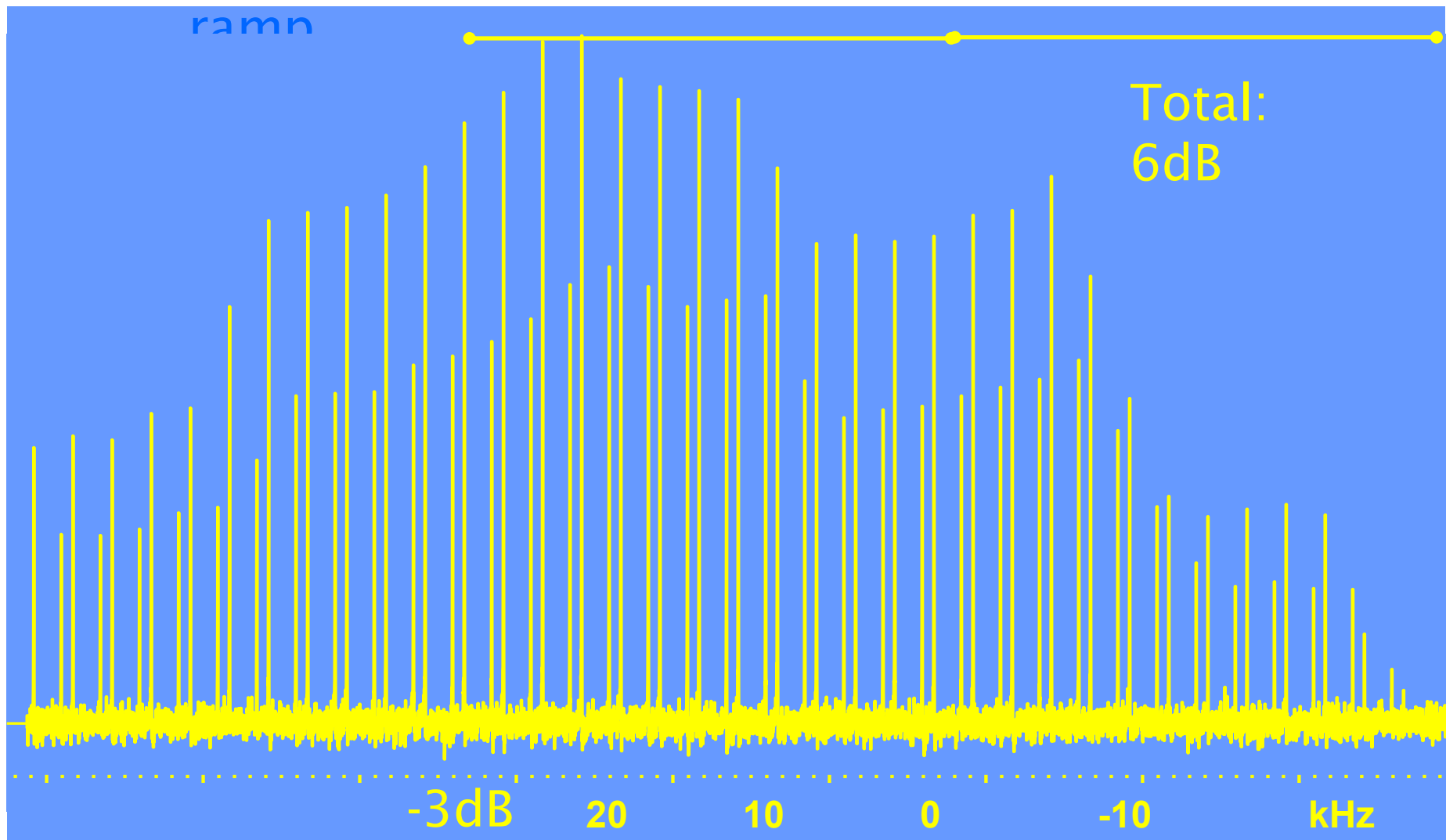
- CP experiment using ramped rf-field during contact



Setup Cross Polarization Experiments



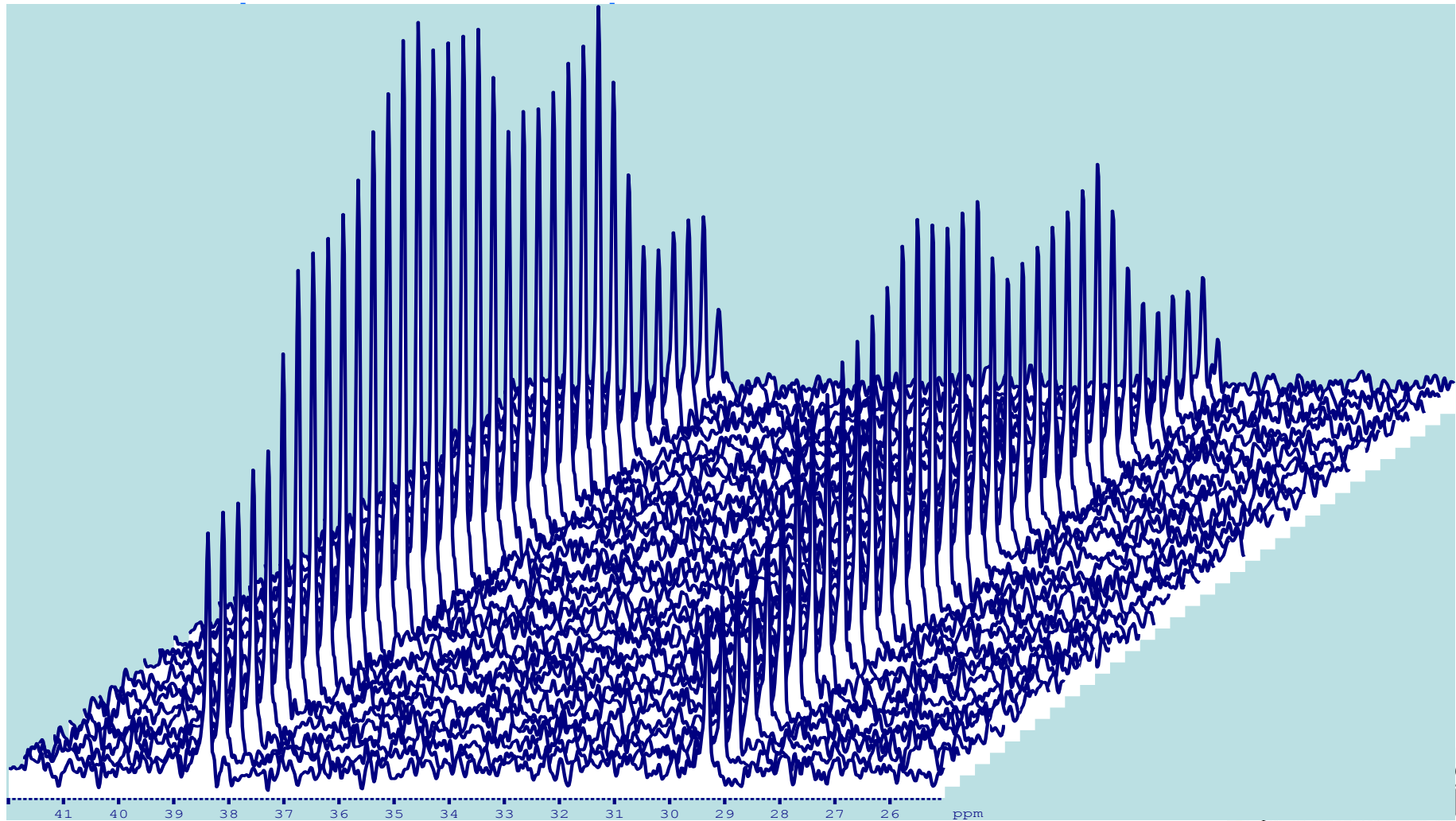
- HH matching profile from POPT
 - Adamantane, 10 kHz spinning, with 50%



Setup Cross Polarization Experiments



- HH matching profile from pseudo 2D data (POPT)



- General parameter optimization after initial setup with adamantane:
 - Determine HH match on glycine: load parameter set **C13CPMAS**
 - Measure p3 at pl12 (choose **pl12 = pl2**, if pl2 is the power level for a 4us pulse)
 - For following steps with high decoupling power, use protection scheme to avoid acquisition time, $aq > 50\text{ms}$.
 - Calculate required pulse width for maximum decoupling field in kHz
 - Calculate pl12 for p3=2.5us using au-program **pulse** on dummy experiment.
 - Verify that calculated pl12 gives p3 = 2.5us with **POPT**.
 - Optimize decoupling on Glycine - use **POPT** for proton carrier frequency **o2**, use steps $\leq 500\text{ Hz}$

Decoupling, general remarks

- High power decoupling in solids is done by strong continuous on resonance rf irradiation.
- Decoupling becomes better with higher rf field strength.
 - Power limitations of high power decoupling
 - Sample heating
 - Probe arcing, probe destruction
- Decoupling is optimized if rf carrier is set on resonance

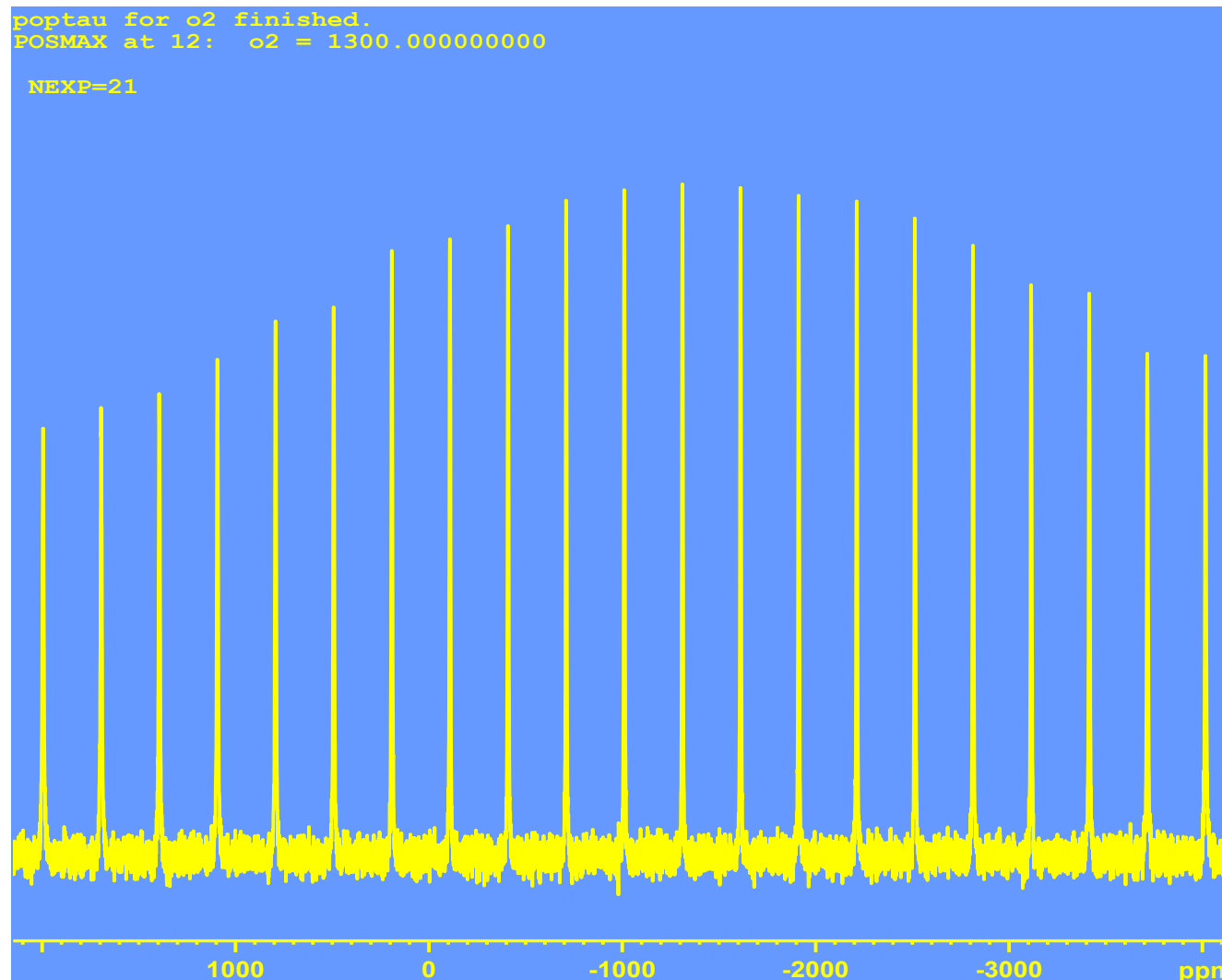
Setup Cross Polarization Experiments



Glycine, decoupling O2 dependence, aliphatic peak displayed in the POPT window:

```
poptau for o2 finished.  
POSMAX at 12: o2 = 1300.000000000
```

```
NEXP=21
```



- Calculate maximum decoupling power

- Get specification sheet, e.g. for widebore probes: 2.5mm 150kHz; 4mm 100 kHz; 7mm 70 kHz

- e.g. max decoupling field is given $100\text{kHz} \cdot p_3 = \frac{1}{4 \cdot 100\text{kHz}} = 2.5\mu\text{s}$

- Set power level 3 dB below that maximum and approach maximum slowly (1 dB steps watching for arcing) (important if probe has not been used for a while).

- Use maximum decoupling power for Glycine setup

- Problems of high power cw decoupling
 - cw irradiation has poor bandwidth
 - Particularly problematic at higher fields - CS dispersion
 - Power limitations
- Alternative decoupling schemes needed for more bandwidth and less power

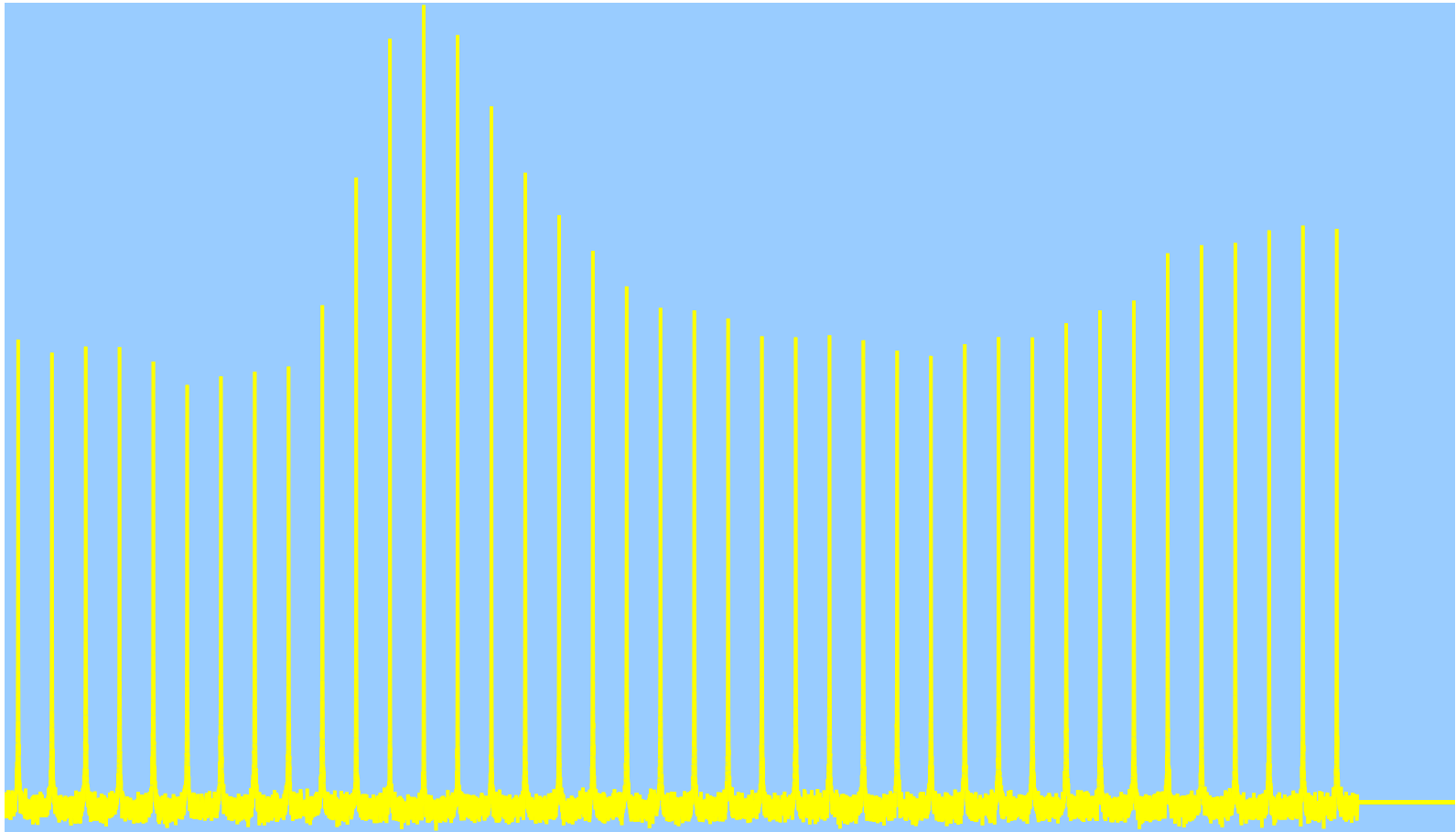
- For spectrometers of 400MHz and higher, improved heteronuclear decoupling is achieved by:
 - Time proportional phase modulation (TPPM)
 - Phase toggling for constant length with certain phase steps

- e.g. CPD program TPPM15:

```
0.3u fq=cnst21
0.5u p1=p112
1 p31:0
p31:15
p31:0
.
p31:0
p30:15
jump to 1
```

- Tip: **p31** is approximately 180° pulse, e.g. for 100 kHz decoupling, $p3 = 2.5 \mu\text{s}$, $p31 \sim 4.8 \mu\text{s}$

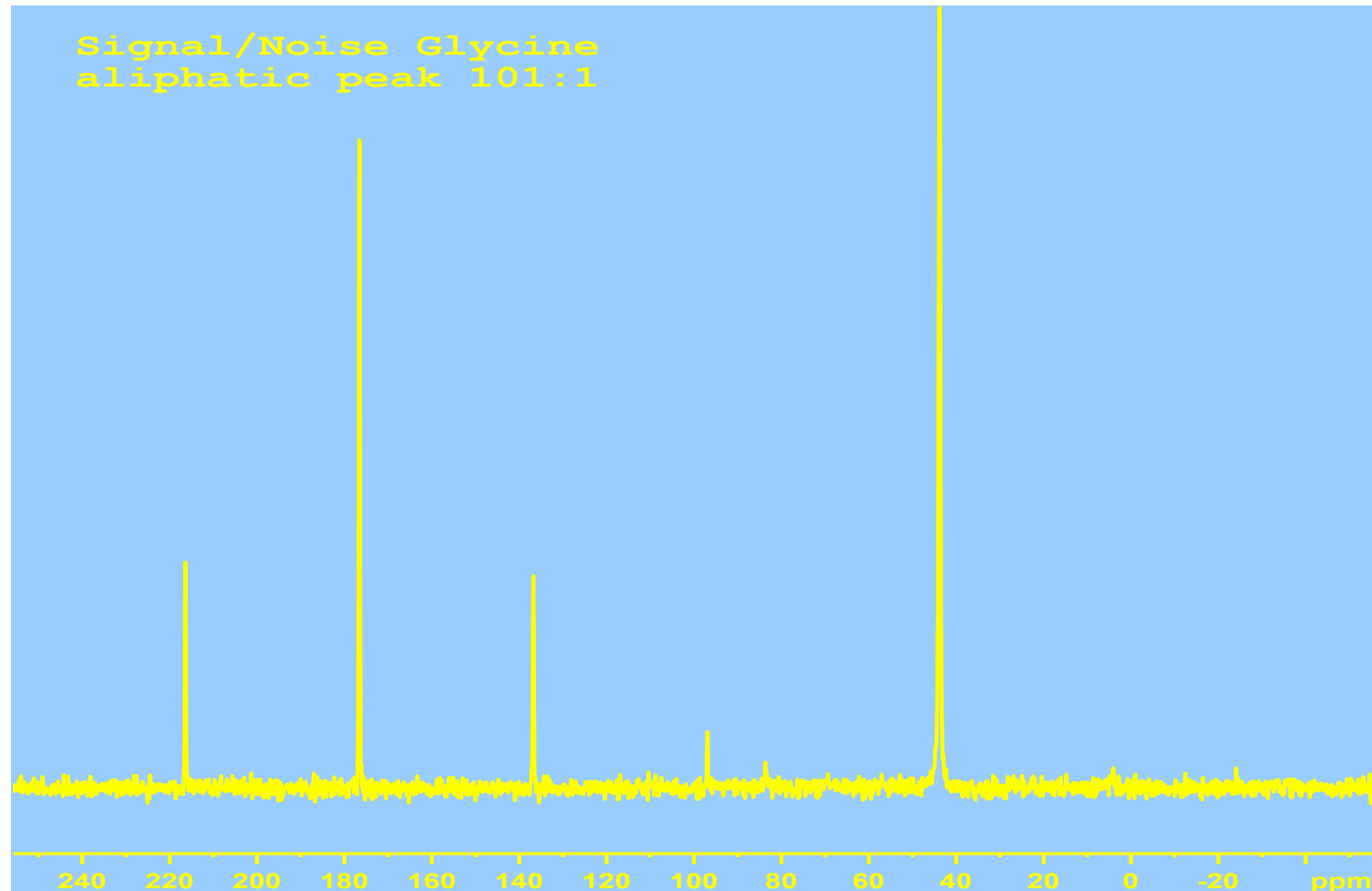
- Optimize heteronuclear decoupling (TPPM)



Setup Cross Polarization Experiments



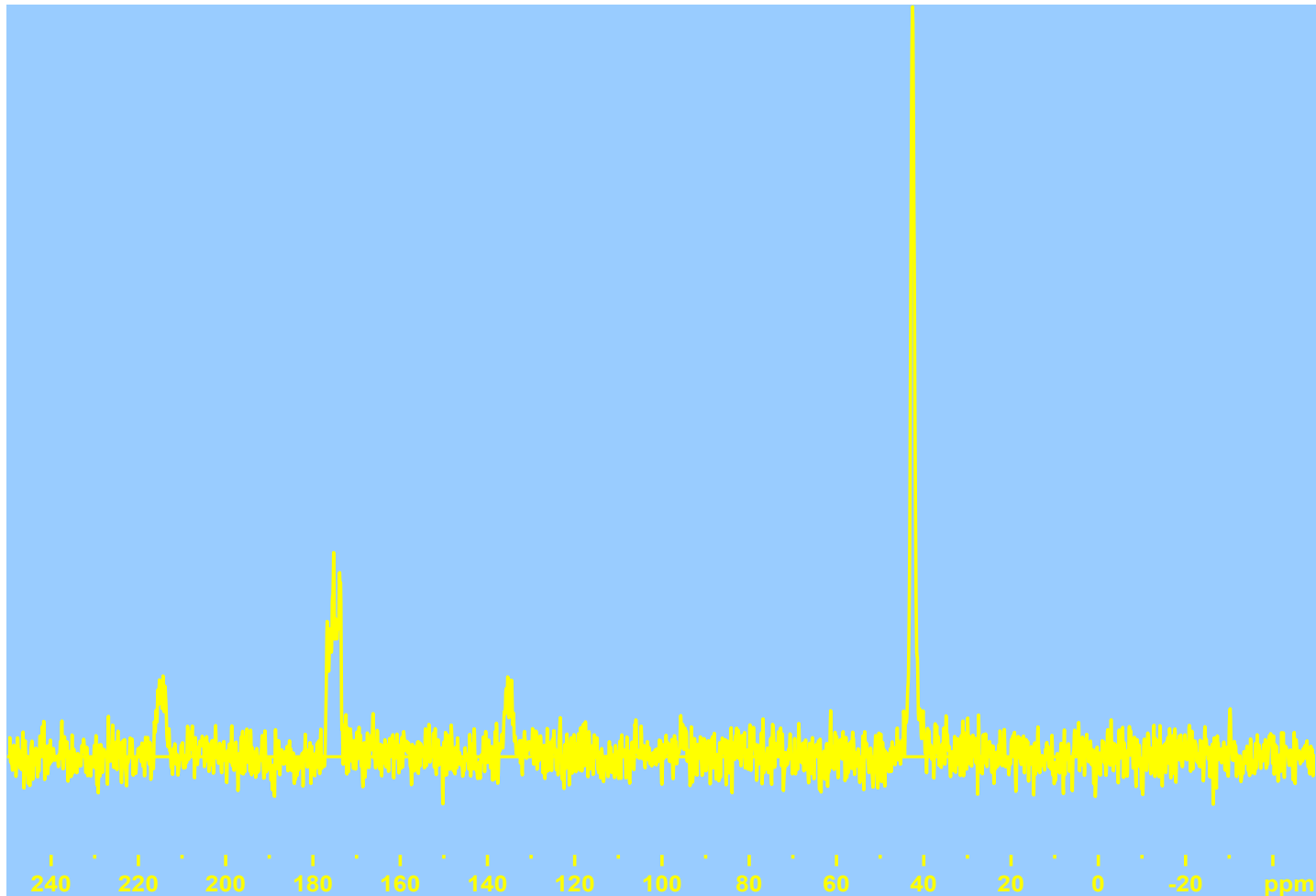
Sensitivity measurement on glycine



Setup Cross Polarization Experiments



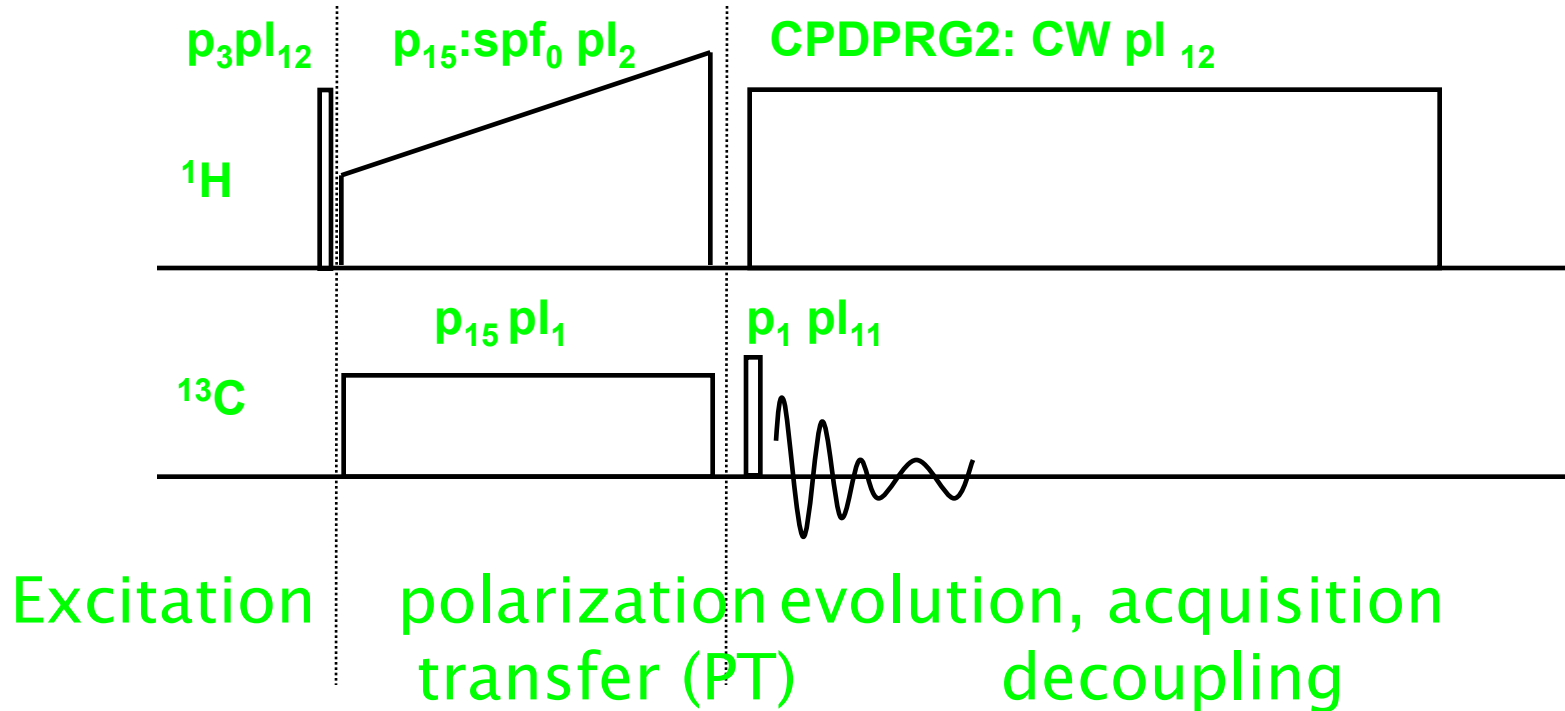
Glycine Magic Angle $> 1^\circ$ off.



Setup Cross Polarization Experiments



- Measuring pulse widths after polarization transfer
 - Pulse program `cp90.av`



Setup Cross Polarization Experiments



- Measure ^{13}C pulse p_1 with POPT: note a 90 degree pulse after CP with a phase orthogonal to the phase of the contact pulse results in $\pm z$ -magnetization!
- Therefore: Optimize for Zero signal.

Parameter Optimization Setup

Store as 2D data (ser file)

The AU program specified in AUNM will be executed

Run optimization in background

Info:
Each line in the table below describes a single parameter.
If the checkbox of a parameter is off, the parameter will be ignored in the AU program.
During save, it will be saved as comment with the prefix 'Off'.
If option INC is not zero and option VARMOD is 'LIN', the experiment number NEXP will be ignored. You can omit it in this case.

Dataset: C:\Vdata\jos0502\nmr\class2002\5/

On/Off	Parameter	OPTIMUM	STARTVAL	ENDVAL	NEXP	VARMOD	INC
<input type="checkbox"/>	p2	POSMAX	6	16	0	LIN	0.5
<input type="checkbox"/>	p3	POSMAX	0.5	16	0	LIN	0.5
<input checked="" type="checkbox"/>	p1	ZERO	0	16	0	LIN	0.4

Start Halt Read protocol Add parameter Read parameters Save Restore Update Exit

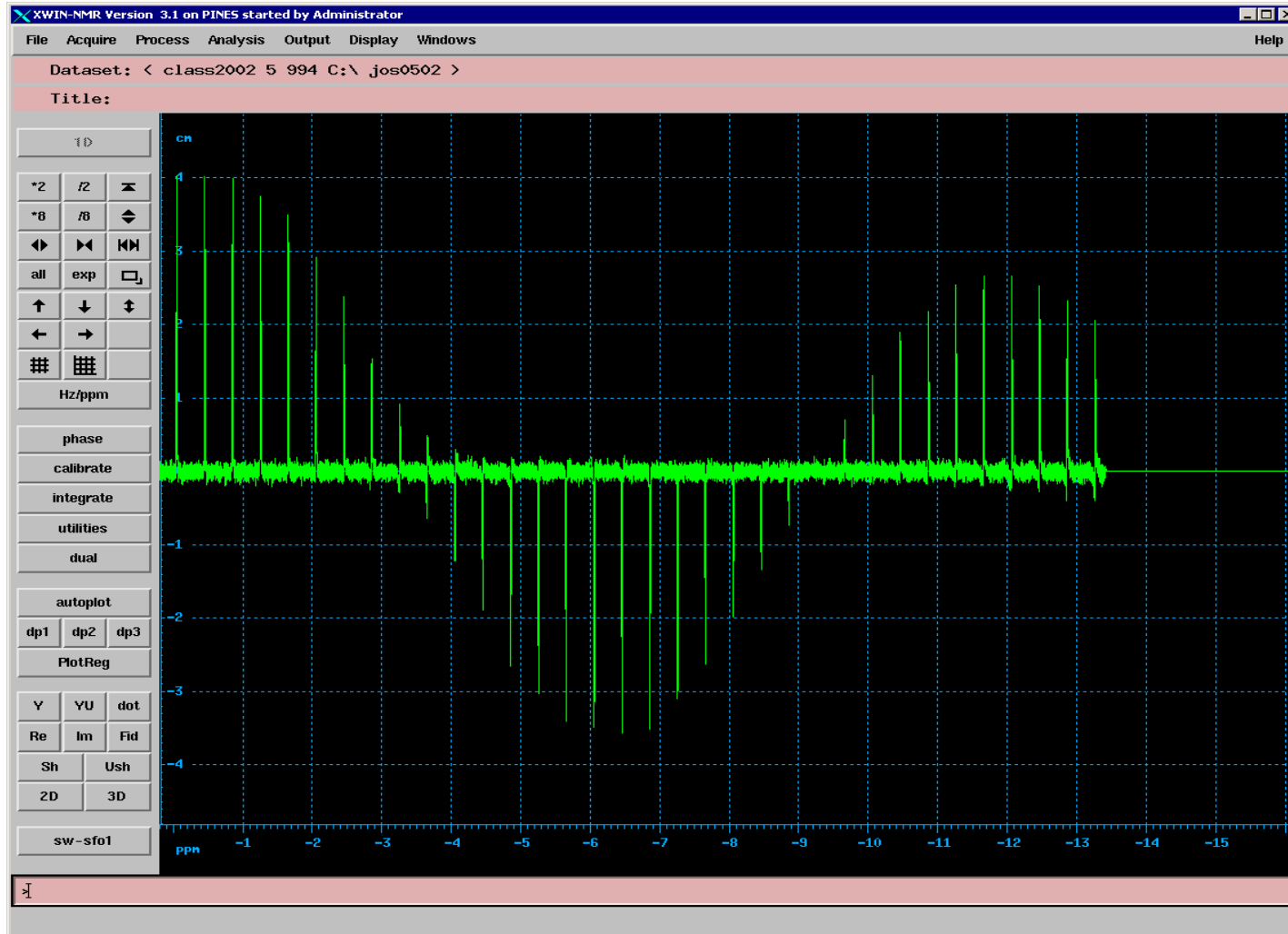
Status: Parameter optimization started ...



Setup Cross Polarization Experiments



- POPT result,



- Pulse programming:

```
;cp.av basic cp experiment
;written by HF 1.3.2001
;set: p3 proton 90 at power level p112
;cpdprg2 cw, tppm (at p112), or lgs, cwlg. Cwlg
    ;(LG-decouplinghere p113 is used instead of p112)
```

```
;d1 :recycle delay
;p3 :f2 90 deg pulse at p112
;p15 :contact time at p11 (f1) and p12 (f2)
;p31 :pulse interval for CPD
;p11 :f1 power level for CP
;p12 :f2 power level for CP
;p112 :f2 power level for 90 deg + decoupling
;p113 :f2 power level in case of LG decoupling
;cnst20 :decoupling RF field in Hz
;cnst24 :additional LG-offset
```

- Pulse programming:

```
#include <lgcalc.incl>
"p30=p31-0.4u"
#include <trigg.incl>
;10 usec trigger pulse at TCU connector I cable 6

#include <Avancesolids.incl>

1 ze          ;accumulate into an empty memory
2 d1 do:f2    ;recycle delay, decoupler off
  #include <prp15.prot>
              ;make sure p15 does not exceed 10 msec
  #include <praq.prot>
              ;allows max. 50 msec acquisition time, nmrsu
;may change to max. 1s at less than 5 % duty cycle
;and reduced decoupling field
```


- Pulse programming:

```
1u fq=cnst21:f2
```

```
10u pl12:f2 pl1:f1 ;pl12 for F2, pl1 for F1
```

```
trigg ;trigger for scope, 10 usec
```

```
p3:f2 ph1 ;proton 90 pulse
```

```
0.3u
```

```
(p15 ph2):f1 (p15:spf0 pl2 ph10):f2
```

```
;contact pulse with square or ramp
```

```
;shape on F2, at pl2 proton power level
```

```
1u cpds2:f2
```

```
;pl12 is used here with tppm, pl13 with cwlg, cwlg
```

```
go=2 ph31
```

```
1m do:f2 ;decoupler off
```

```
wr #0 ;save data to disk
```

```
HaltAcqu, 1m ;jump address for protection files
```

```
exit ;quit
```

- Protection schemes:

```
#include <prp15.prot>
```

```
    ;make sure p15 does not exceed 10 msec
```

```
#include <praq.prot>
```

```
    ;allows max. 50 msec acquisition time, nmrsu
```

```
    ;may change to max. 1s at less than 5 % duty cycle
```

```
    ;and reduced decoupling field
```

```
wr #0
```

```
    ;save data to disk
```

```
HaltAcqu, 1m
```

```
    ;jump address for protection files
```

```
exit
```

```
    ;quit
```

- Protection schemes:

```
#include <prp15.prot>
                ;make sure p15 does not exceed 10 msec
#include <praq.prot>
;allows max. 50 msec acquisition time, nmrsu
;may change to max. 1s at less than 5 % duty cycle
;and reduced decoupling field

wr #0                ;save data to disk
HaltAcqu, 1m        ;jump address for protection files
exit                ;quit
```

- Protection schemes:

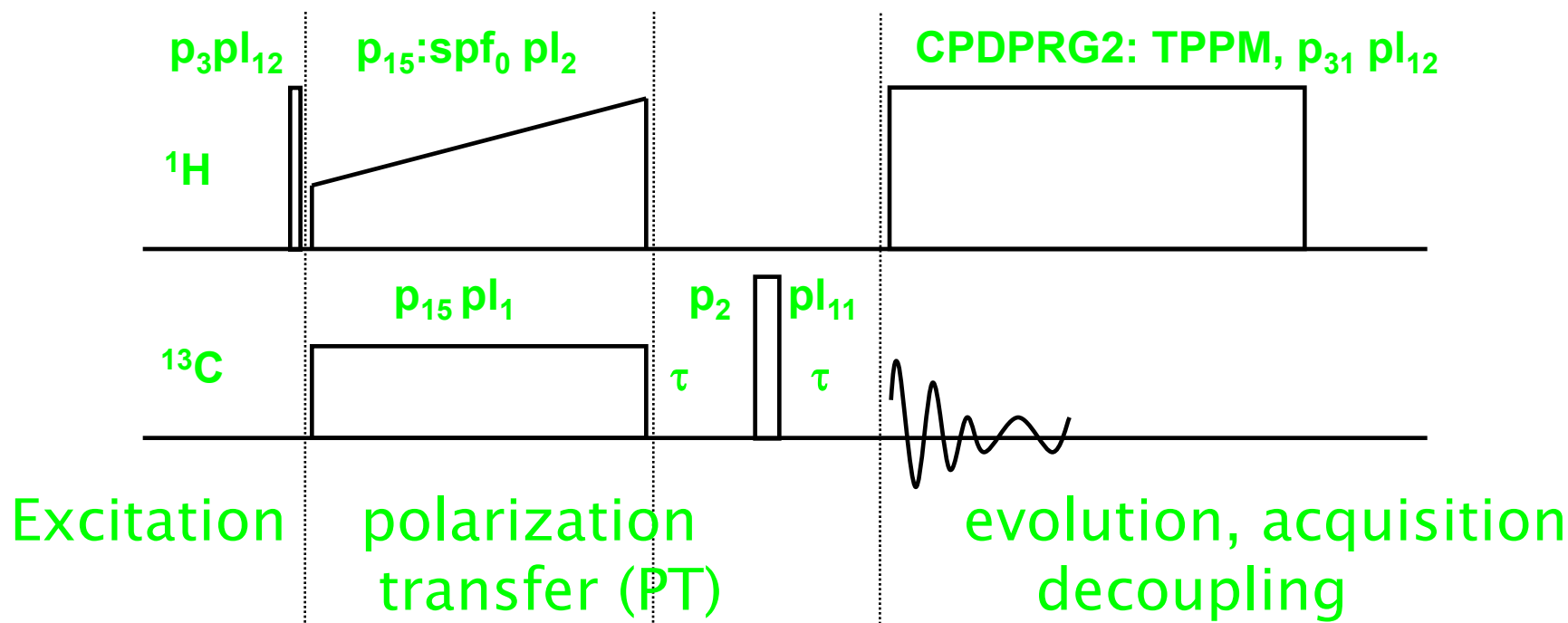
```
#include <prp15.prot>
    ;make sure p15 does not exceed 10 msec
#include <praq.prot>
    ;allows max. 50 msec acquisition time, nmrsu
;may change to max. 1s at less than 5 % duty cycle
;and reduced decoupling field
```

```
wr #0
HaltAcqu, 1m
exit
    ;save data to disk
    ;jump address for protection files
    ;quit
```

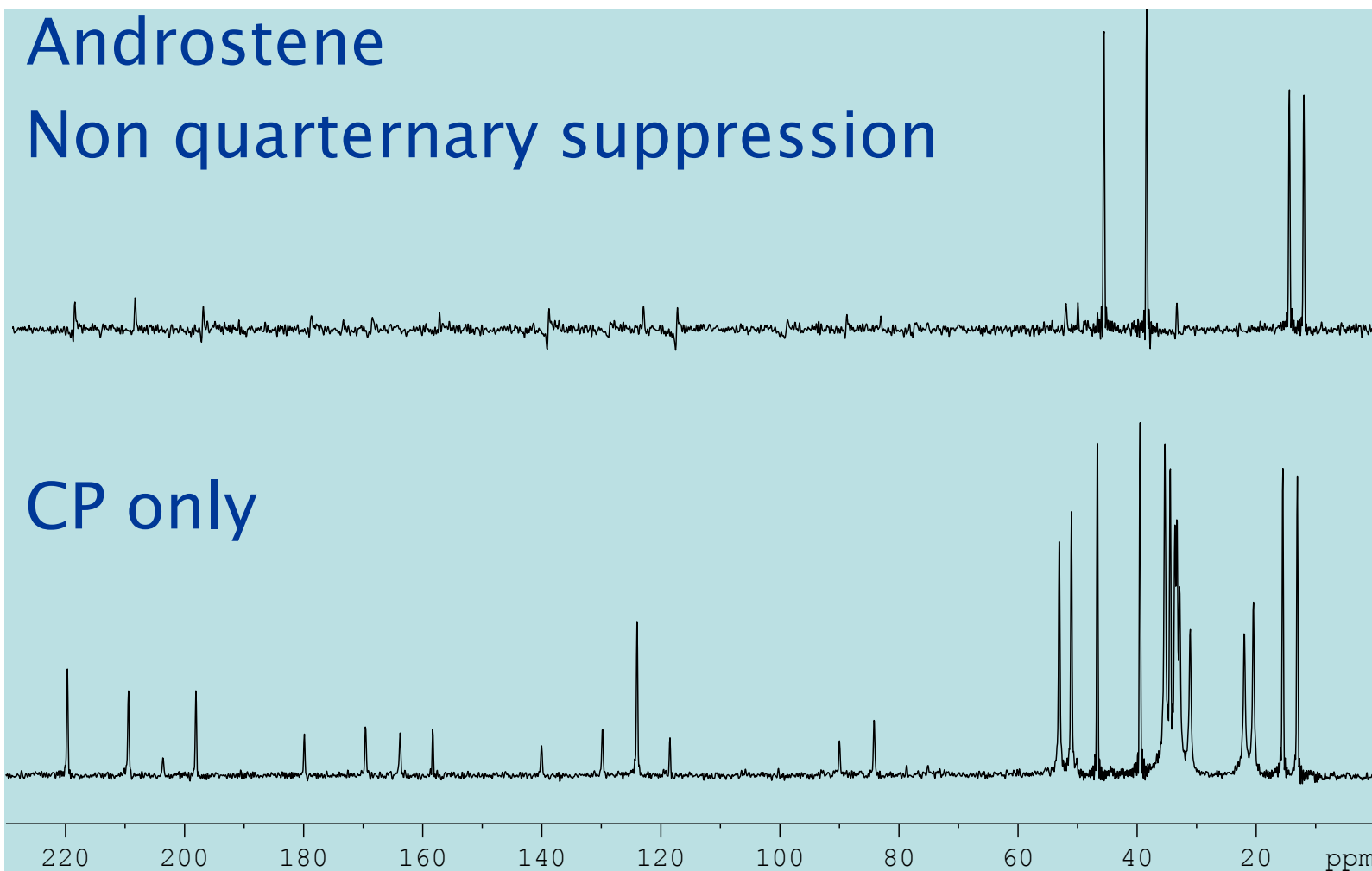
END first day

- Various experiments:
 - Variable spinning speed experiments
 - Use au program: [multimas](#)
 - Variable Contact time experiments
 - Pulse sequence: [cpvc.av](#) or [cp4cvc.98](#)
 - Spinning sideband suppression:
 - Pulse sequences: [cptoss.av](#) or [cp4ctossa.98](#),
[cptossb.98](#)
[cpseltics.av](#) or [cp4cseltics.98](#)
 - Non Quarternary suppression:
 - Pulse sequence: [cpnqs.av](#) or [cp4cnqs.98](#)

- Non quaternary suppression or dipolar dephasing experiment

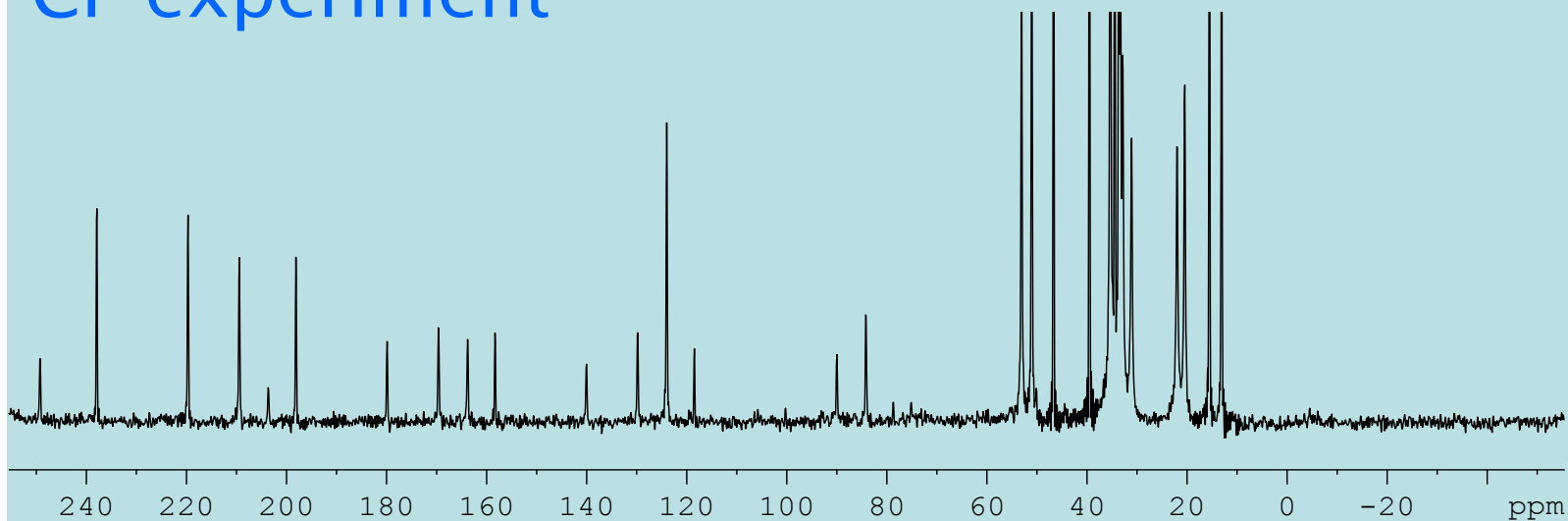


- Androstene
Non quarternary suppression

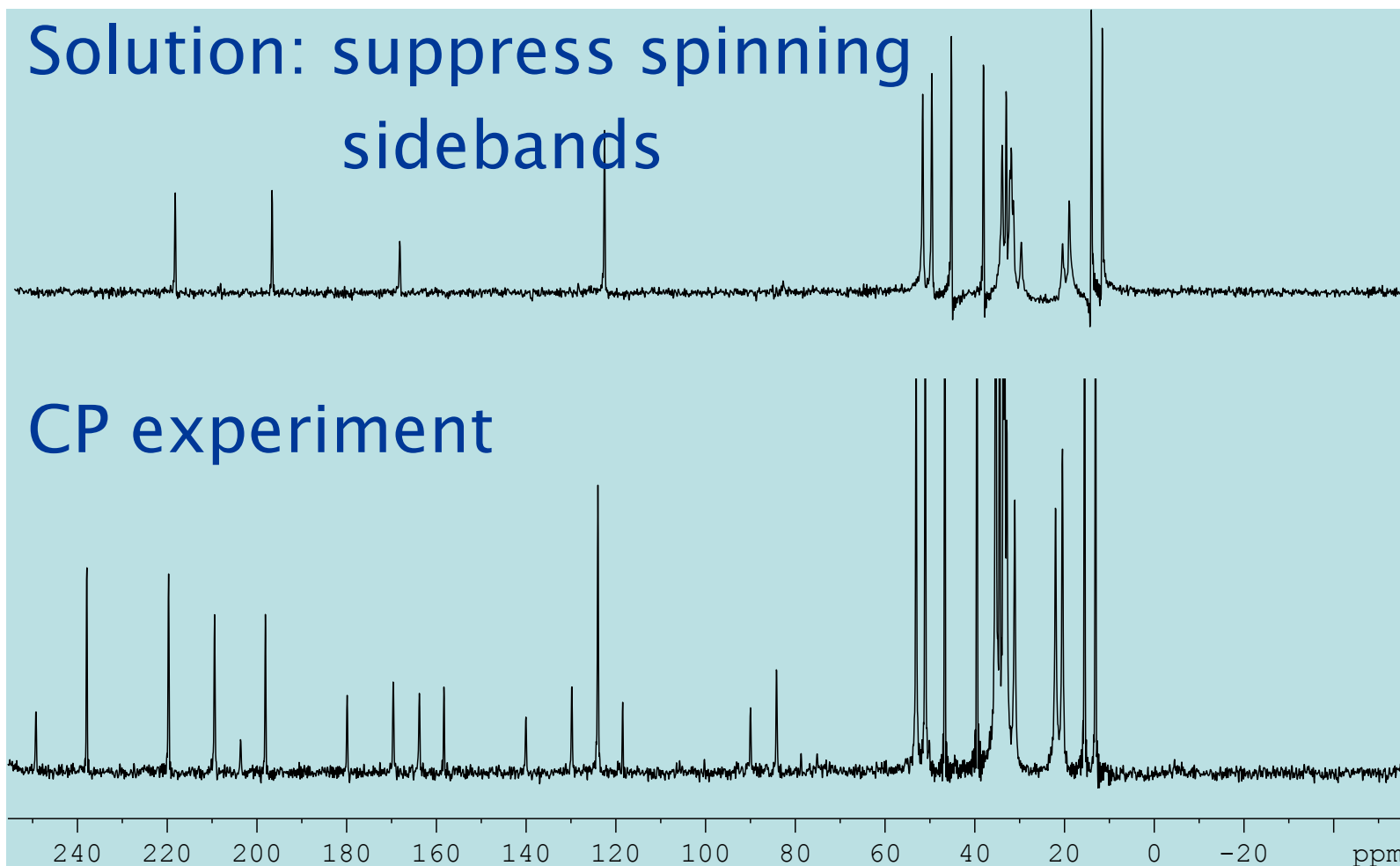


- Problem: through spinning sidebands too crowded spectra:

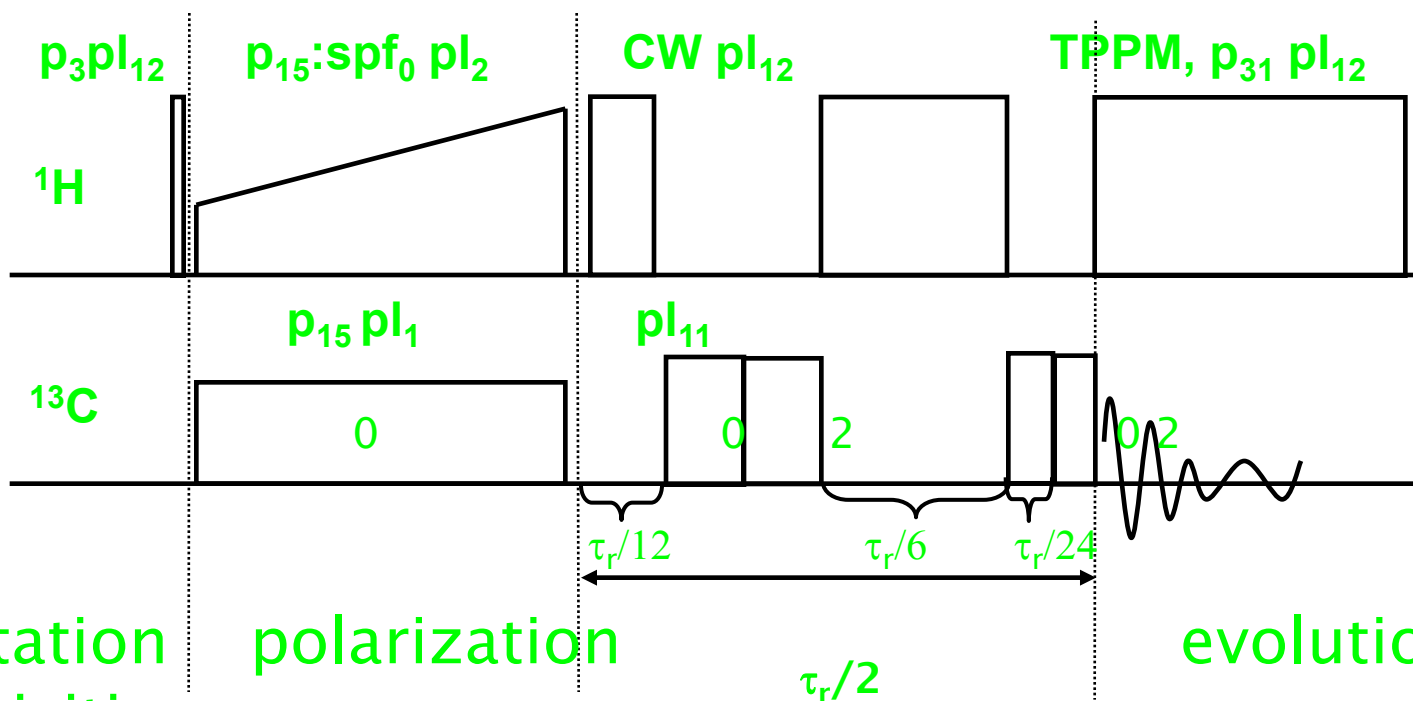
CP experiment



Advanced CP Experiments



- Seltics



Excitation acquisition

polarization transfer (PT)

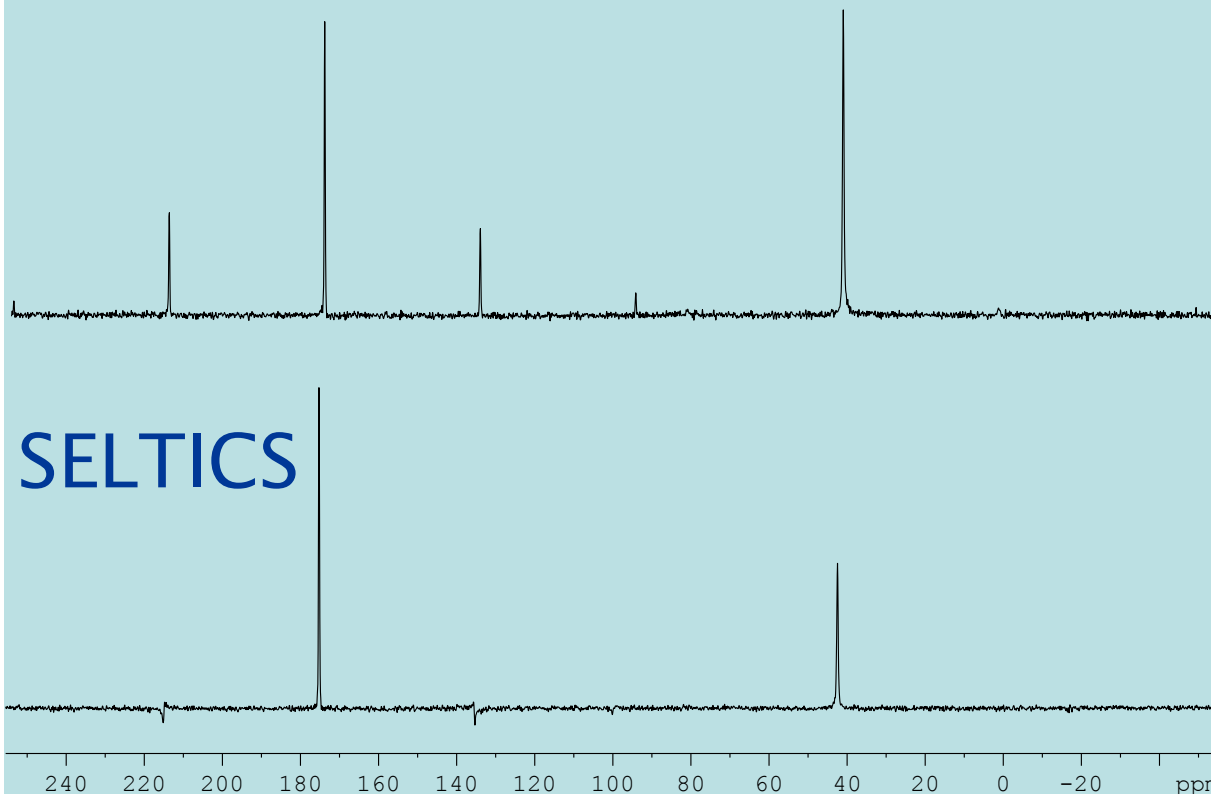
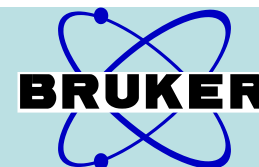
evolution,

decoupling

- Glycine CP

Class June 2001

Sample: Glycine
Rotation rate: 5kHz
SELTICS



Current Data Parameters
NAME class
EXPNO 300
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010604
Time 11.49
INSTRUM spect
PROBHD 4 mm MAS 1H/BB
PULPROG cp
TD 2176
SOLVENT chcl3
NS 5
DS 0
SWH 39062.500 Hz
FIDRES 17.951517 Hz
AQ 0.0279156 sec
RG 512
DW 12.800 usec
DE 6.00 usec
TE 373.0 K
D1 10.00000000 sec

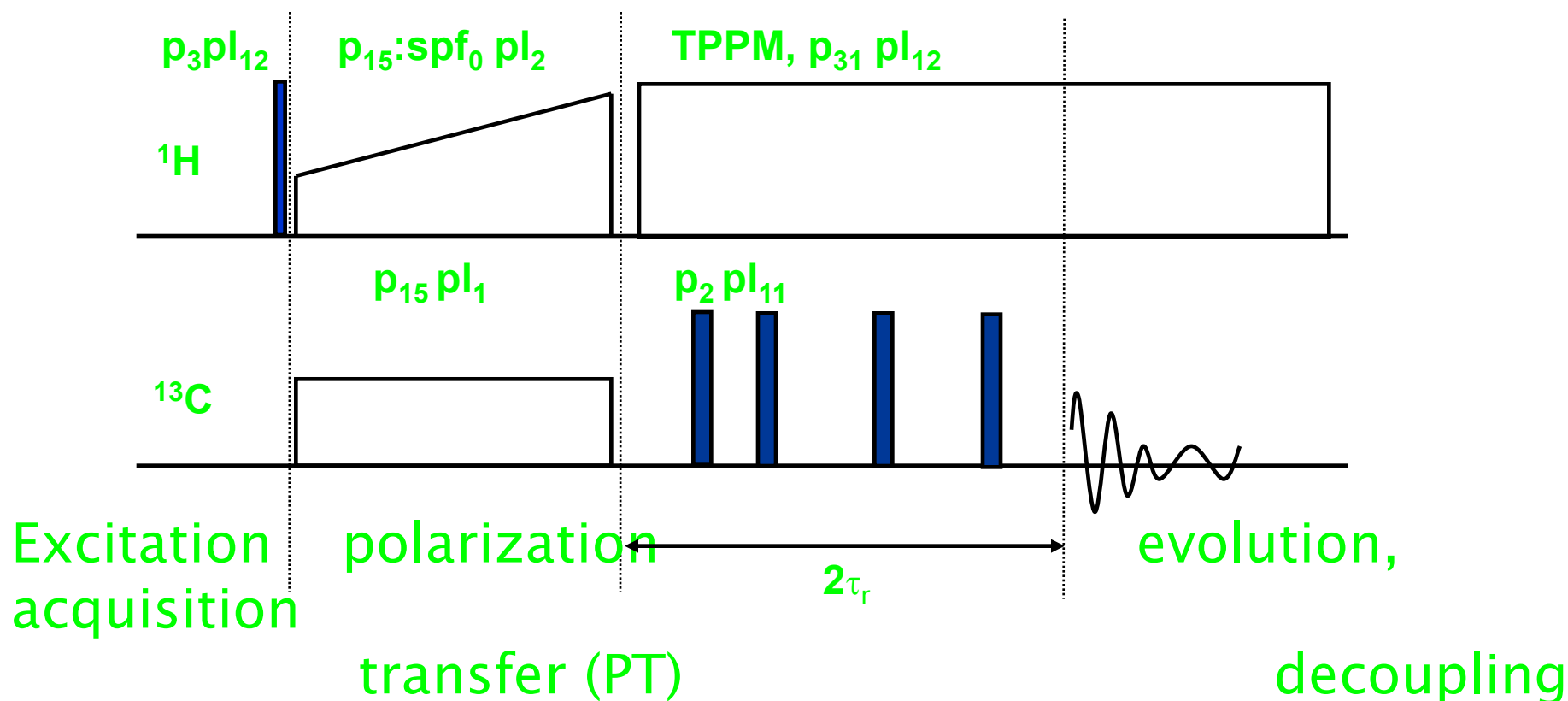
===== CHANNEL f1 =====
NUC1 13C
P15 1000.00 usec
PL1 12.10 dB
SFO1 125.6118849 MHz

===== CHANNEL f2 =====
CPDPRG2 tppm15
FQ1LIST freqlist
NUC2 1H
P3 3.00 usec
P31 6.00 usec
PL2 120.00 dB
PL12 4.00 dB
SFO2 499.5012500 MHz
SP0 -1.00 dB
SPNAM0 ramp.64
SPOFF0 0.00 Hz

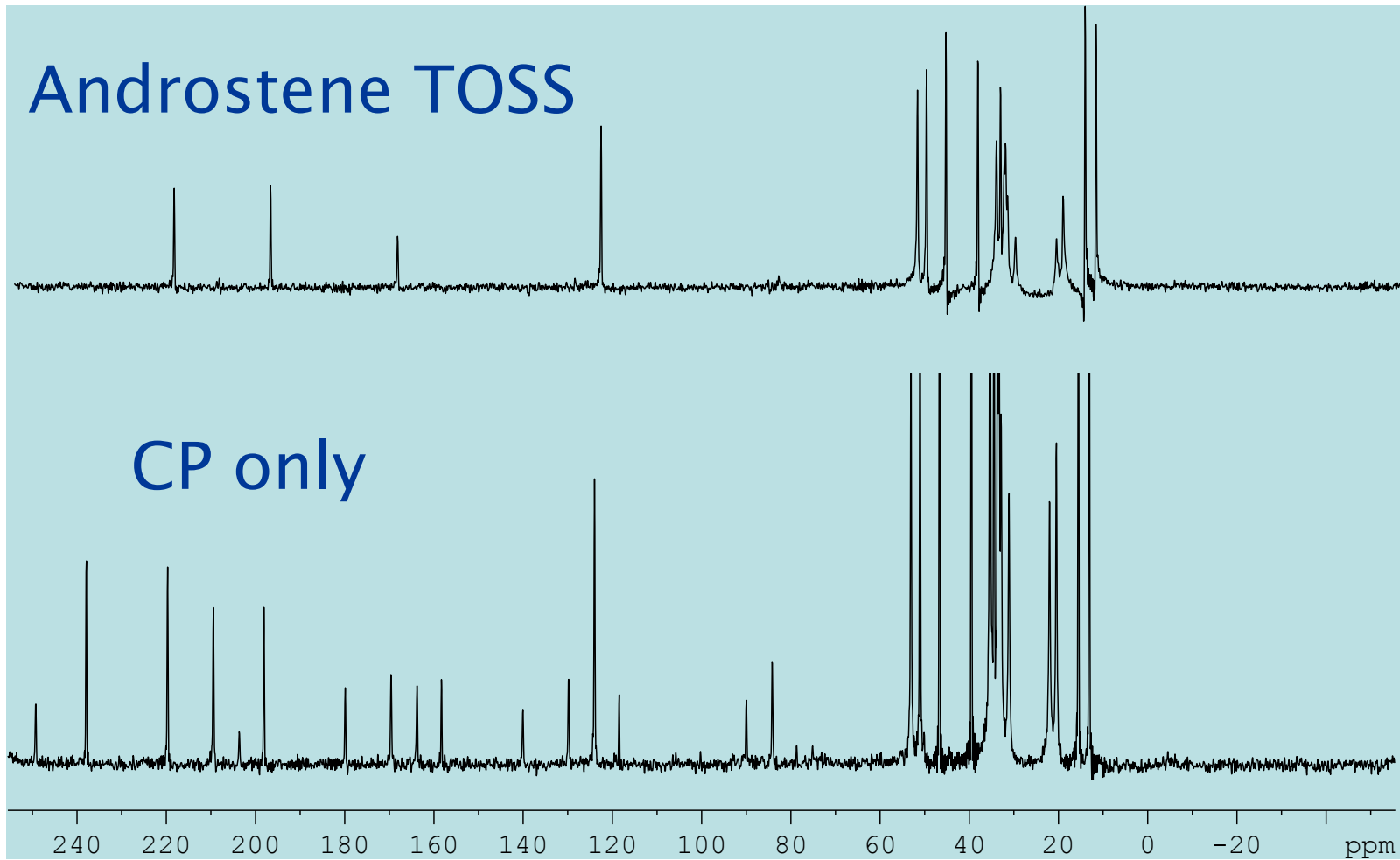
F2 - Processing parameters
SI 4096
SF 125.5993250 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

Advanced CP Experiments

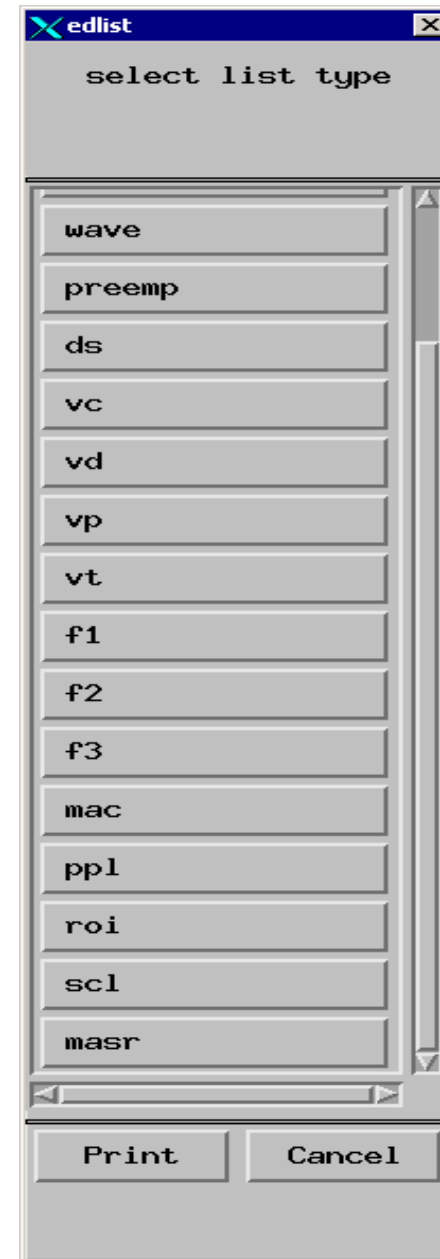
• TOSS



- Androstene TOSS



- Relaxation- and other pseudo 2D experiments
 - Using POPT
 - Using 2D pulse program 2D parameter set and
 - Variable delay or variable pulse list



- Lists are in the 'lists' directory, where also pp etc resides
 - Lists are textfiles,
 - delay lists (vdlist) units is seconds
 - Variable pulse lists (vplist) unit is us

Variable delay list

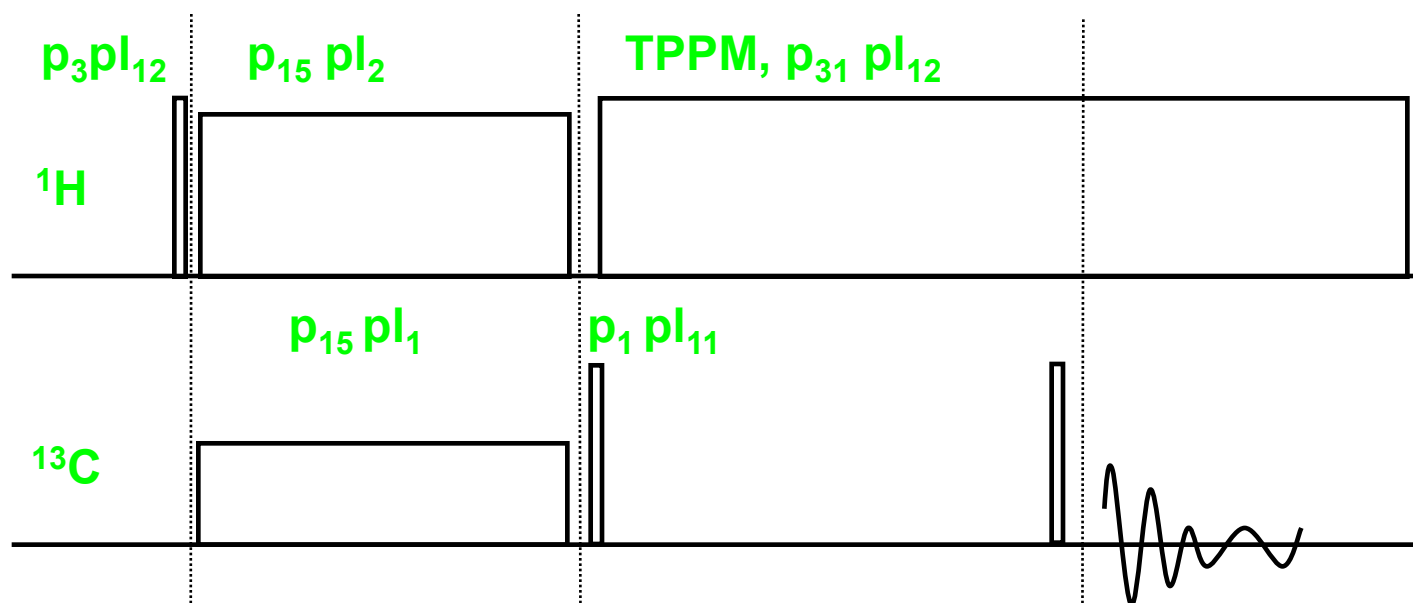
4m
16m
10m
6m
4m
10m
17m
11m
18m
12m

Variable pulse list

400u
1600u
1m
3m
5m
10m
15m
18m
30m

Relaxation Experiments

- T_1 relaxation experiment ^{13}C :



Excitation
acquisition

polarization
transfer (PT)

relaxation delay

evolution,
decoupling

Relaxation Experiments

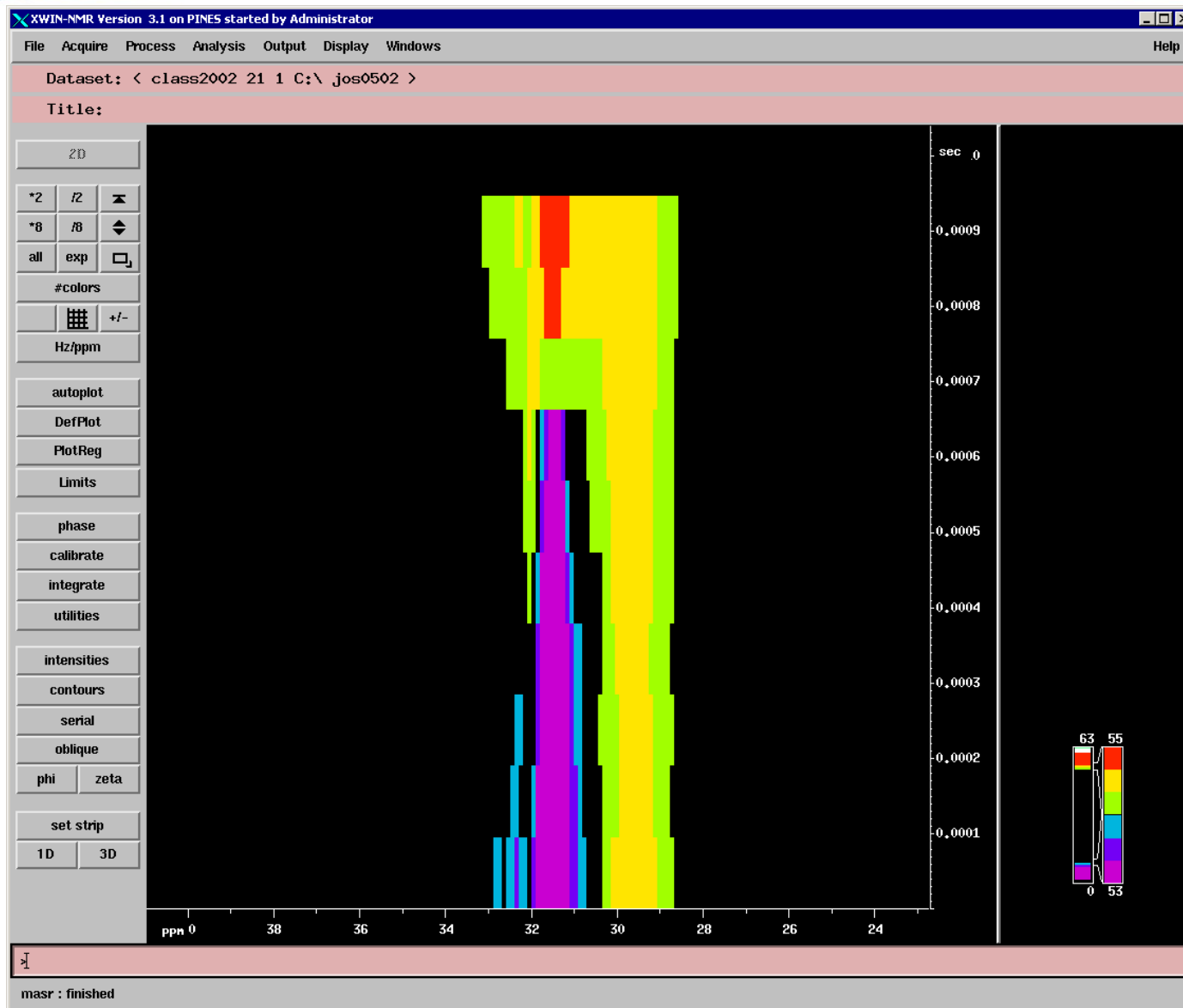
edpar

Acquisition Parameters F2 F1

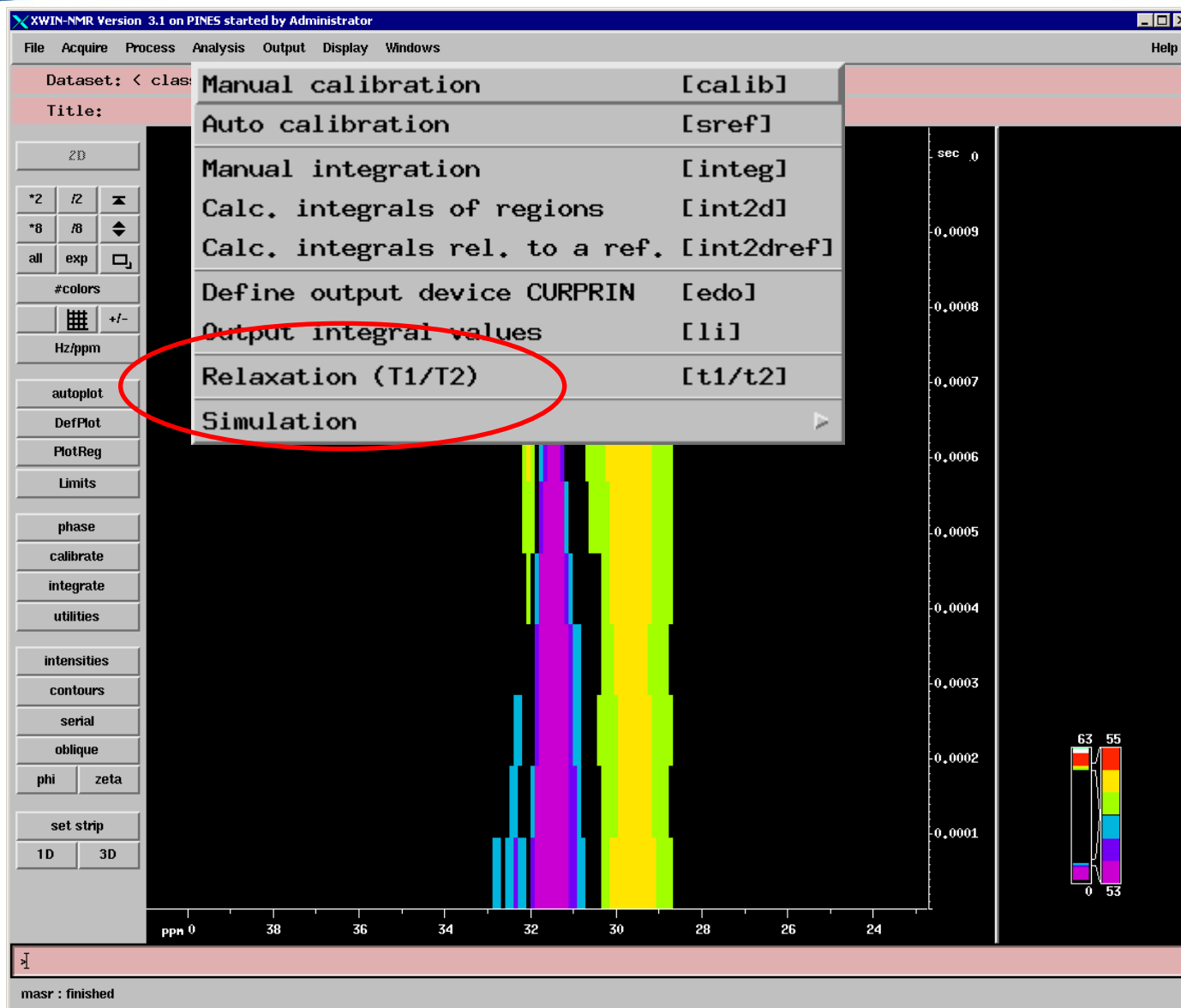
PULPROG	cpxt1.av	
AQ_mod	qsim	
FrMODE		undefined
TD	1024	10
PARMODE	2D	
NS	4	
DS	0	
TDO	1	
D	** Array **	sec
P	** Array **	usec
NDO		3
INO		0.00006300 sec
SW	199.5381	42.1247 ppm
SWH	25062.656	5291.005 Hz
FIDRES	24.475250	529.100525 Hz

SAVE Parameter Next CANCEL

T₁ Relaxation Experiment on PE



T₁ Relaxation Experiment on PE



T₁ Relaxation Experiment on PE



T₁ Relaxation Experiment on PE



XWIN-NMR Version 3.1 on PINES started by Administrator point 1028, 3970.23 Hz, 31.610 ppm

File Acquire Process Analysis Output Display windows Help

Dataset: Setup t1 parameters [edt1]

Title: Multi-component fit [simfit]

0.72

*2 /2 ▲

*8 /8 ▼

◀ ▶ ▶▶

↑ ↓ ↕

← →

#

return

Multi-component fit (all peaks)	[simfit all]
Fit data from ASCII file t1ascii	[simfit asc]
Fit all peaks read from ASCII file	[simfit asc all]
Calculate the t1 value	[ct1]
Calculate the t2 value	[ct2]
Calculate t1 for all peaks	[dat1]
Calculate t2 for all peaks	[dat2]
Eliminate a point from the fit	[elim]
Display the next peak	[nxtp]
List data for the current peak	[lstp]
List data for all peaks	[lsta]
Peak pick a series of spectra	[pd]
Pick intensities exactly at point	[pd0]
Pick points from a serial file	[pf]
Pick points from a t2 fid	[pft2]
Print the x,y pairs	[prxy]
Include all eliminated points	[rstp]
Read SER slice for point selection	[rfid]
Read SMX slice for peak selection	[rspc]

700 800 900 sec

>

masr : finished



T₁ Relaxation Experiment on PE



edt1

T1 Parameters

NUMPTS	10	Number of data points used for fit
FITTYPE	intensity	Use peak areas or intensities for fit
LISTTYP	vdlist	Name of list file with x-coordinates
LISTINC	0.001	Increment used if LISTTYP=auto
CURSOR	1	Position of current peak in spectra
DRIFT	5	Allowed peak drift for peak picking
START	1	First slice to peak pick from
INC	1	Increment for the next slice
X_START	1	Start of x axis
X_END	1000	End of x axis
Y_START	-3.76998e+08	Start of y axis
Y_END	1.50822e+08	End of y axis
FCTTYPE	t1/t2	Type of fitting function
NUMTERM	3	Number of terms to vary in fit function
COMPNO	1	Number of components
EDGUESS	ed	Setup guesses for fit parameters

SAVE 2-COL Parameter Next CANCEL



T₁ Relaxation Experiment on PE



XWIN-NMR Version 3.1 on PINES started by Administrator point 1028, 3970.23 Hz, 31.610 ppm

File Acquire Process Analysis Output Display Windows Help

Dataset: Setup t1 parameters [edt1]

Title: Multi-component fit [simfit]

 Multi-component fit (all peaks) [simfit all]

 Fit data from ASCII file t1ascii [simfit asc]

 Fit all peaks read from ASCII file [simfit asc all]

 Calculate the t1 value [ct1]

 Calculate the t2 value [ct2]

 Calculate t1 for all peaks [dat1]

 Calculate t2 for all peaks [dat2]

 Eliminate a point from the fit [elim]

 Display the next peak [nxtp]

 List data for the current peak [lstp]

 List data for all peaks [lsta]

 Peak pick a series of spectra [pd]

 Pick intensities exactly at point [pd0]

 Pick points from a serial file [pf]

 Pick points from a t2 fid [pft2]

 Print the x,y pairs [prxy]

 Include all eliminated points [rstp]

 Read SER slice for point selection [rfid]

 Read SMX slice for peak selection [rspc]

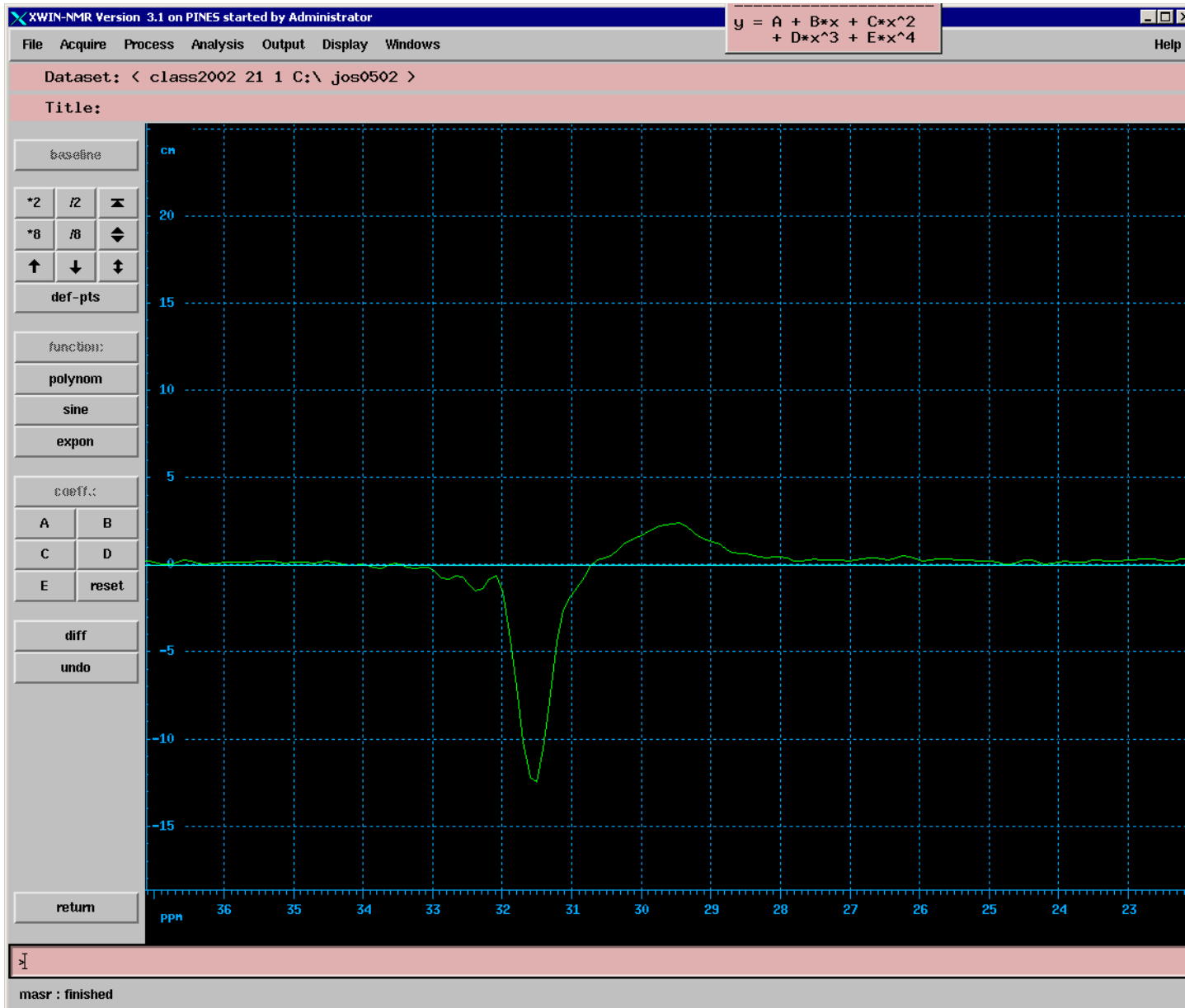
return

>

masr : finished



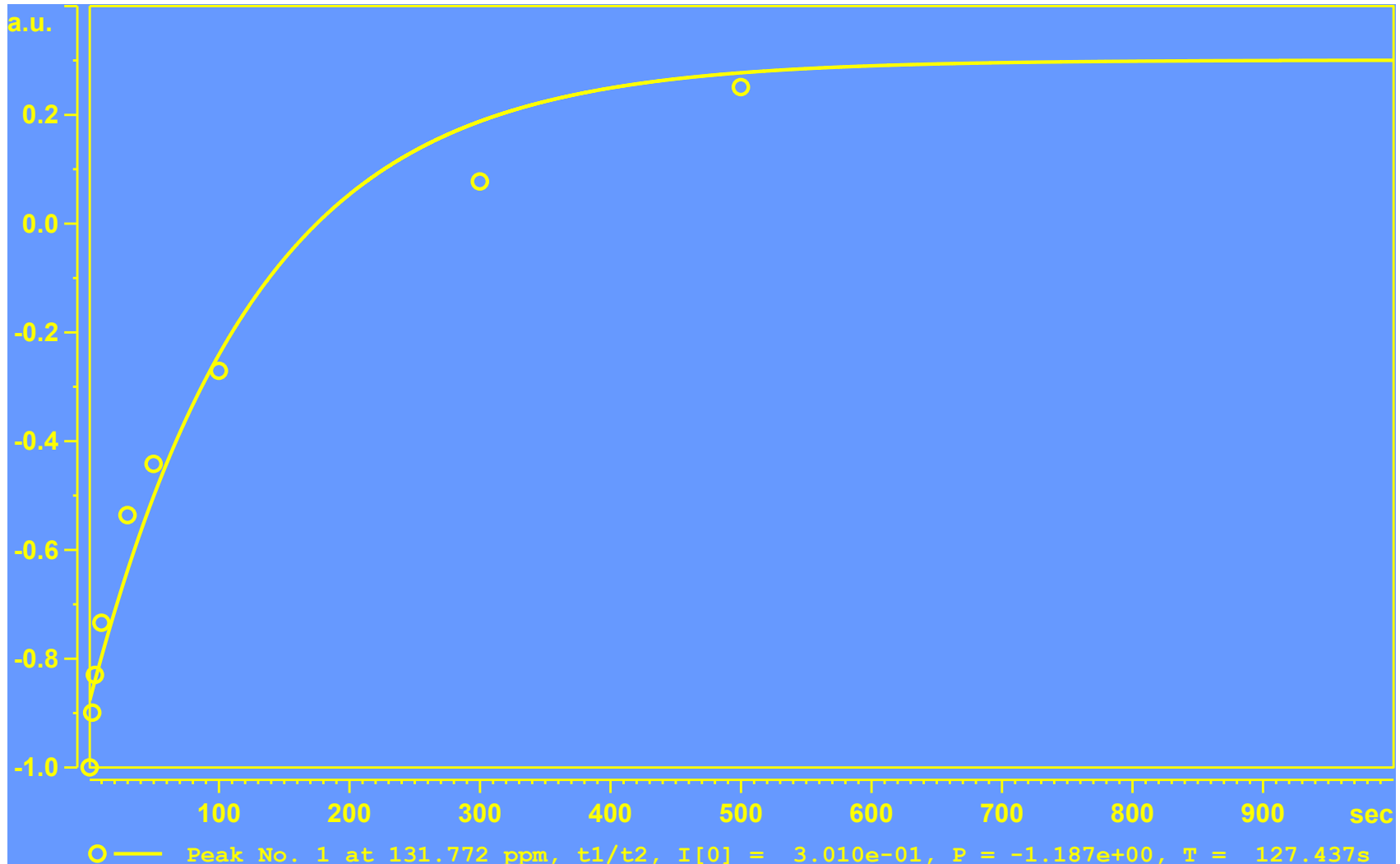
T₁ Relaxation Experiment on PE



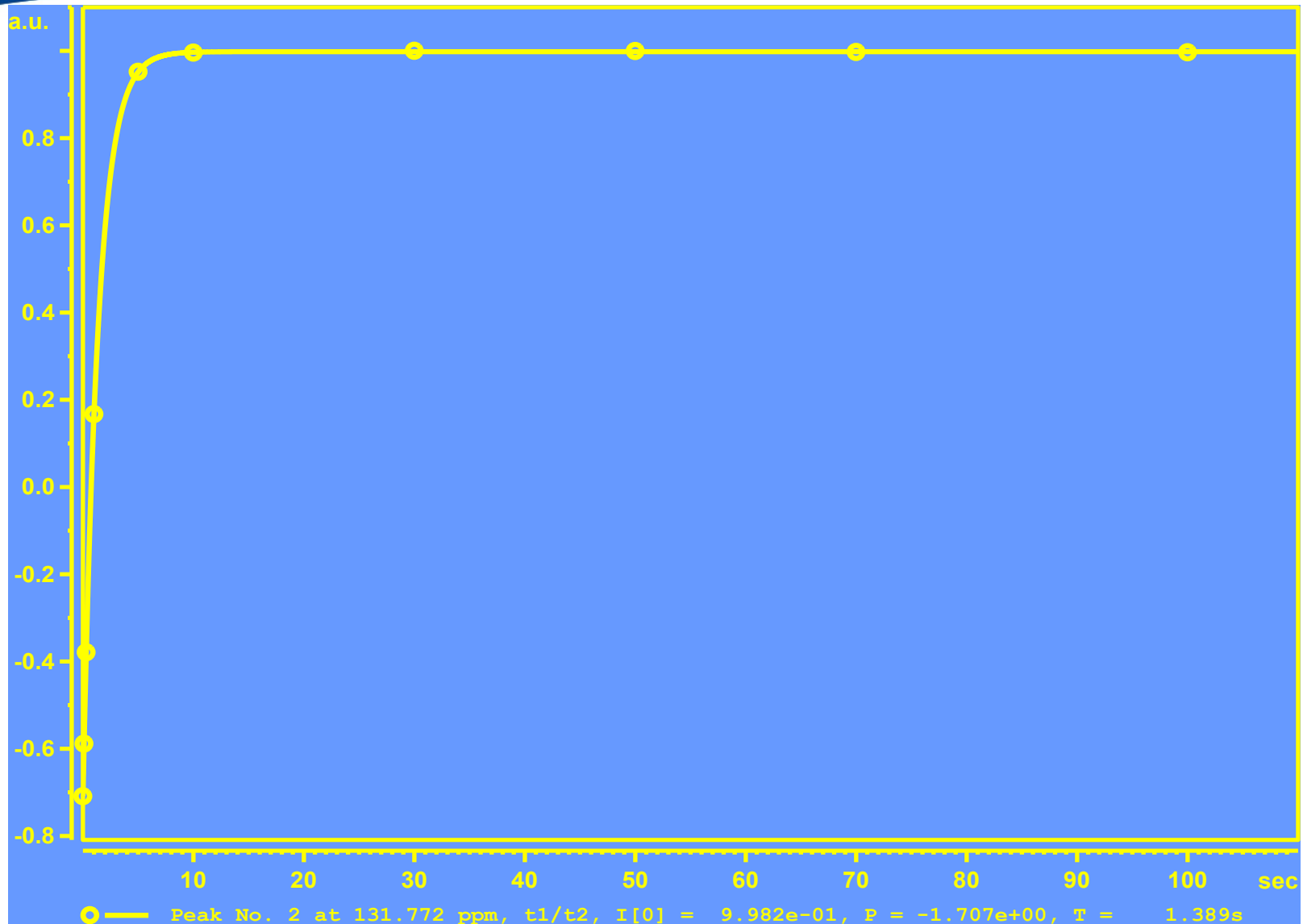
T₁ Relaxation Experiment on PE



- PE ¹³C T₁ experiment T1/T2 module

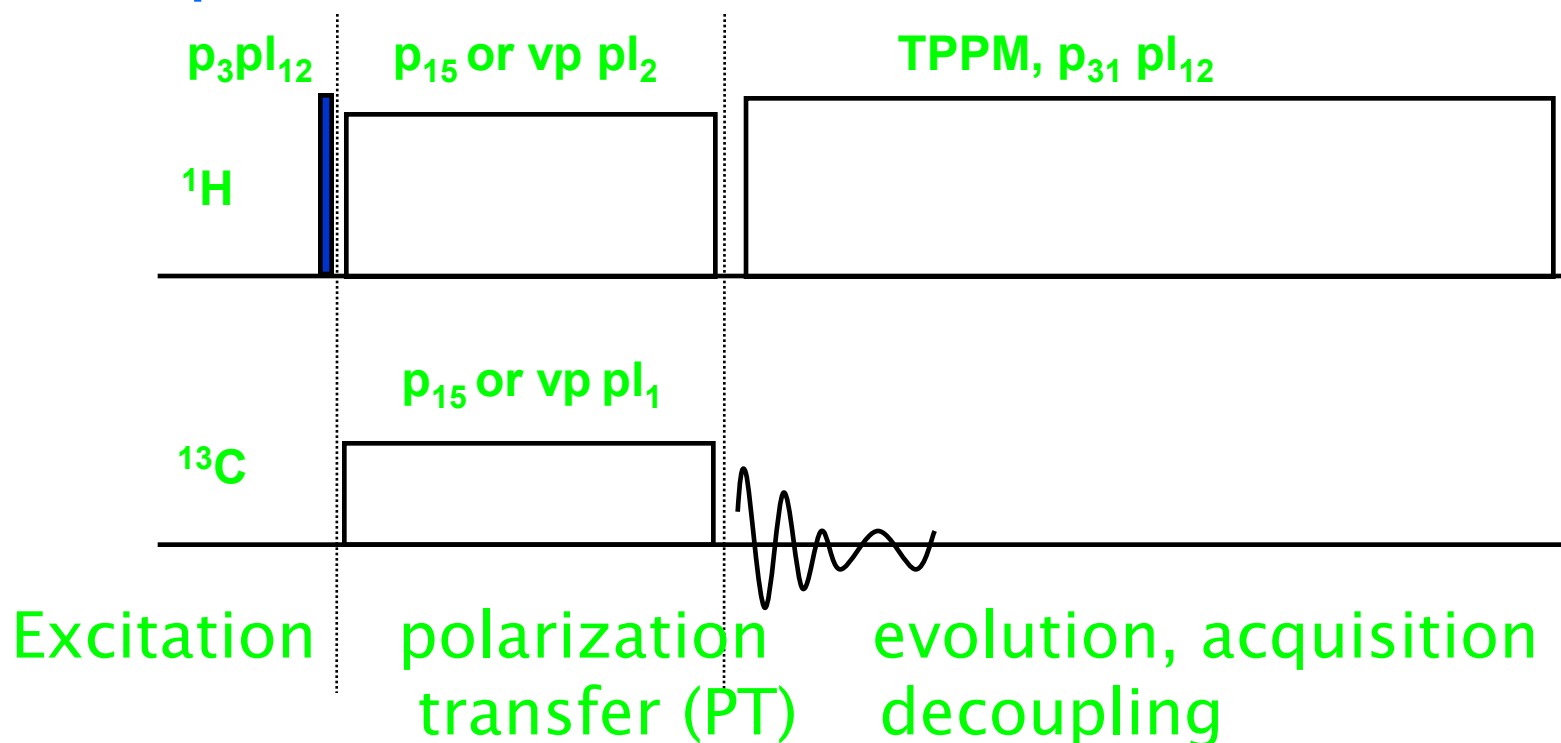


T_1 Relaxation Experiment on Adamantane



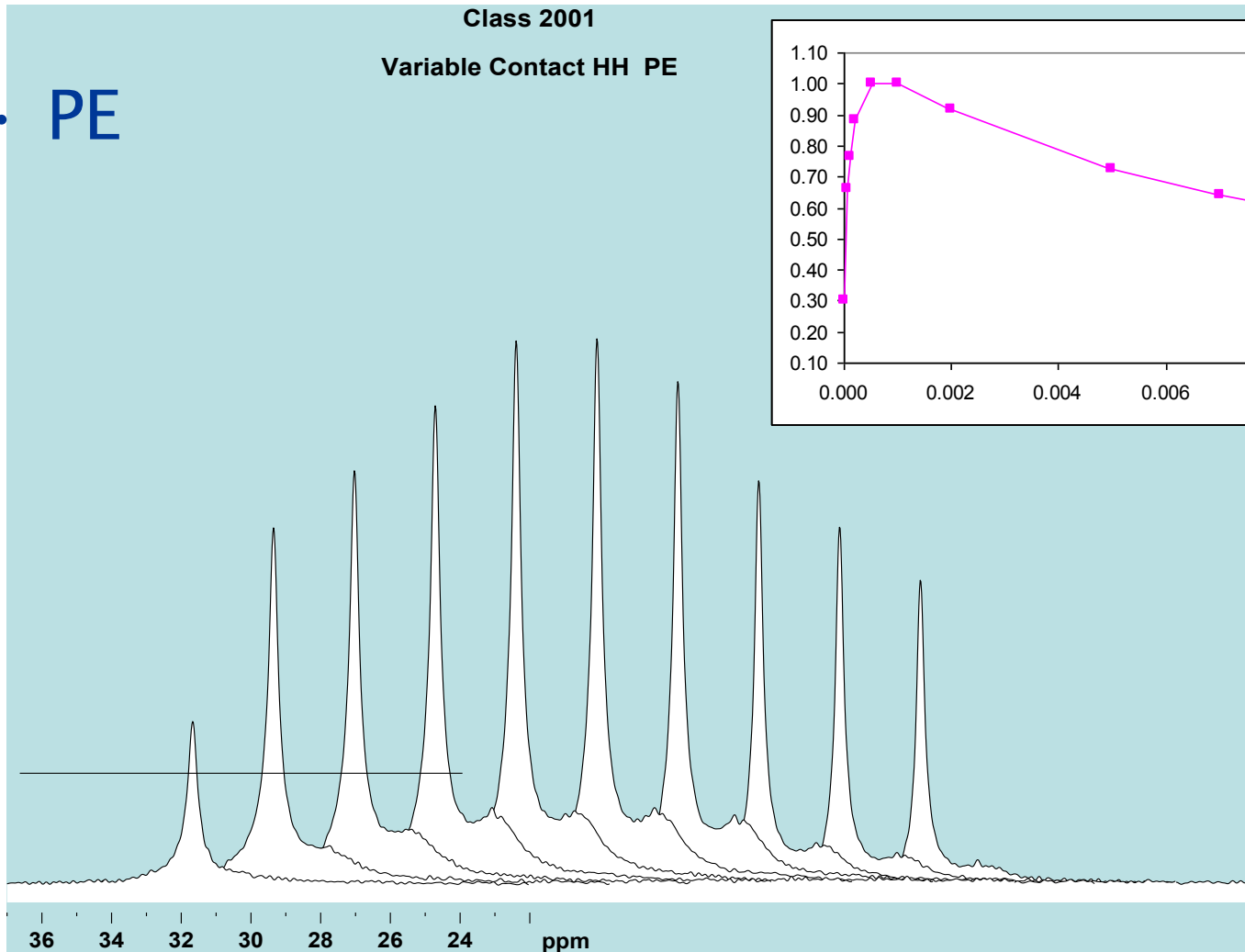
Variable Contact Experiment

- Variable contact, increment $p15$ or use vp -list

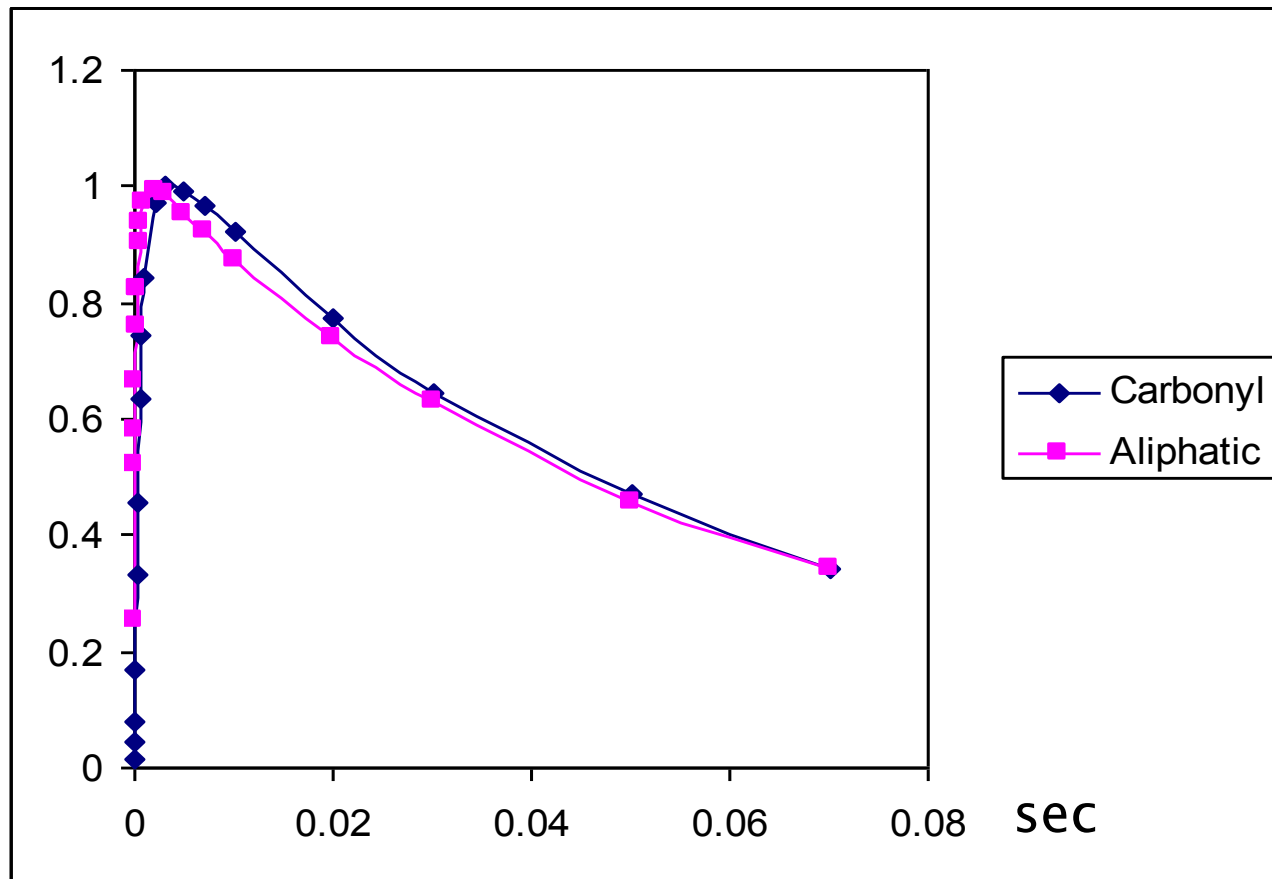


Variable Contact Experiment

• PE

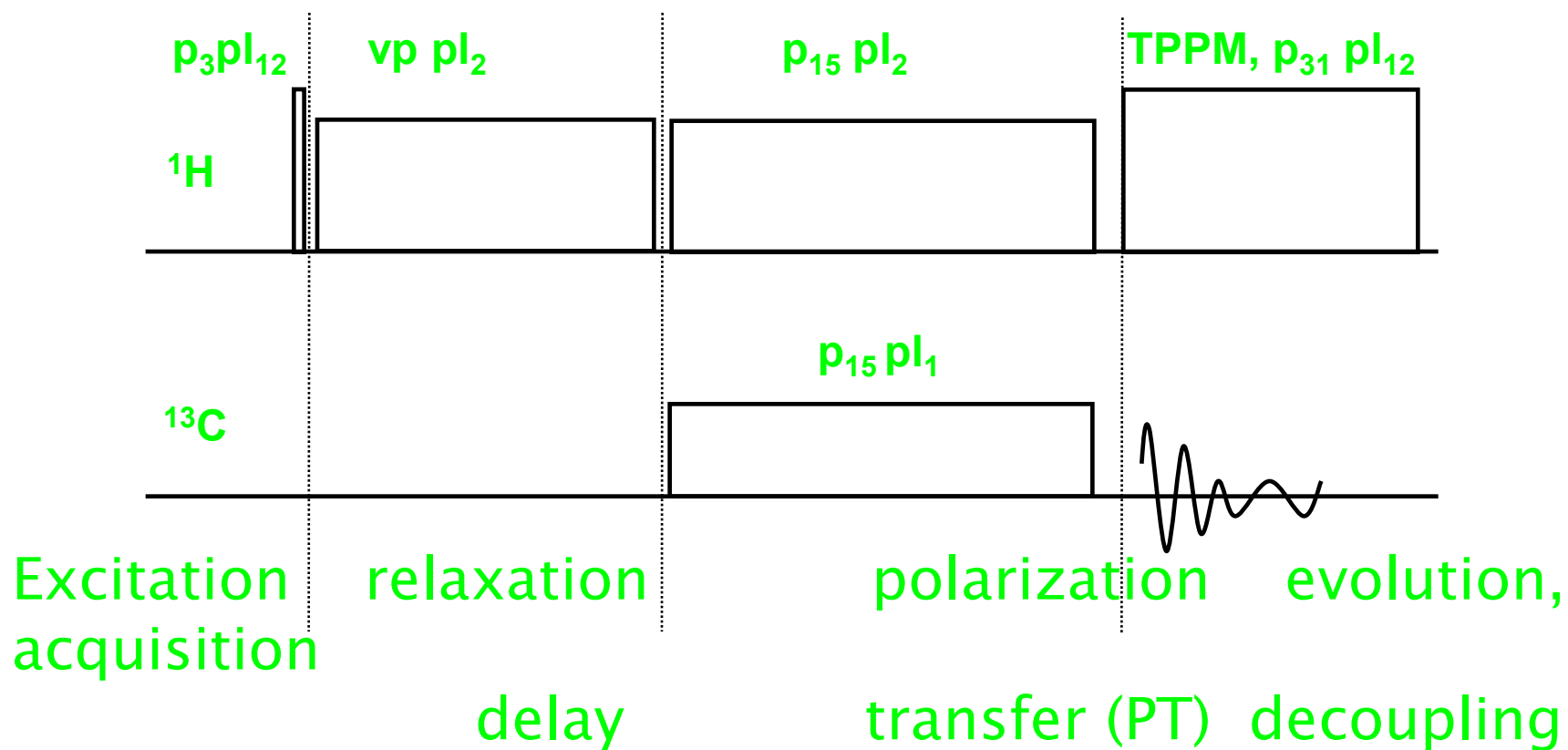


- Glycine variable contact



Cross Polarization Experiments

- $T_{1\rho}$ relaxation experiment ^1H

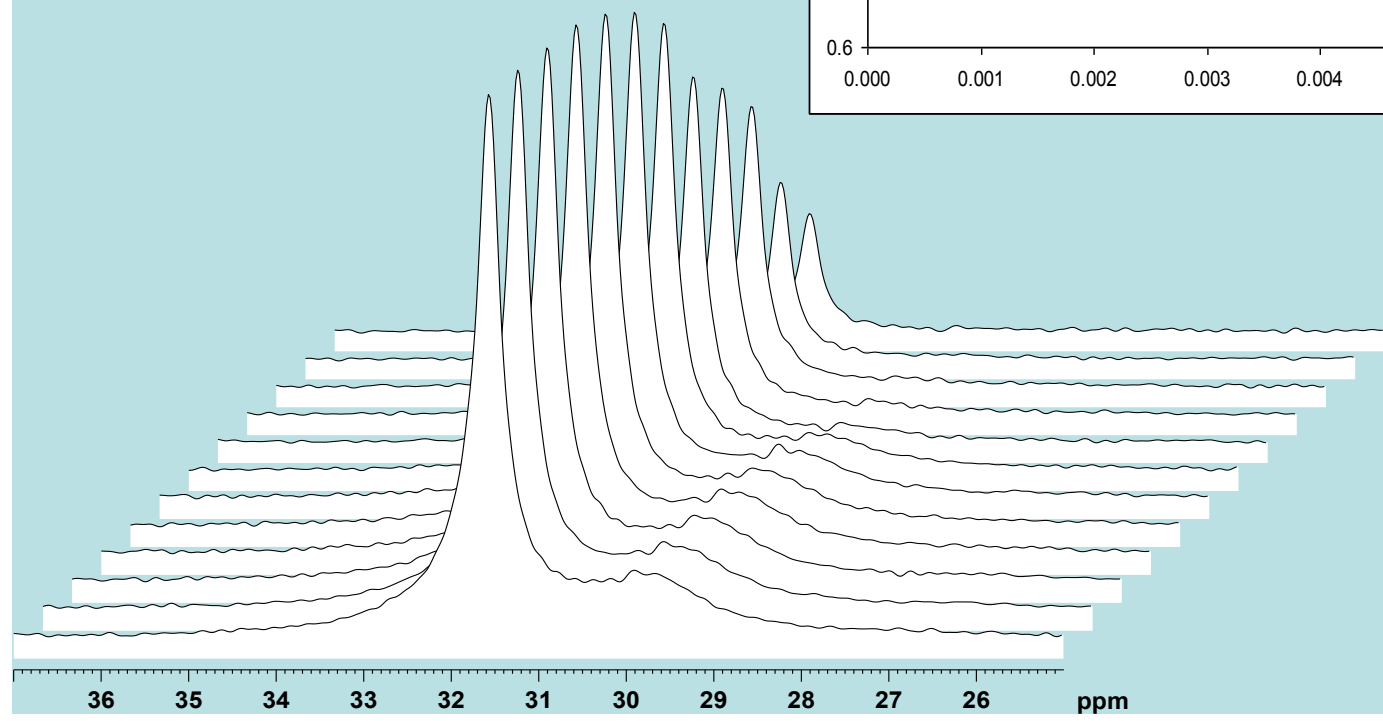
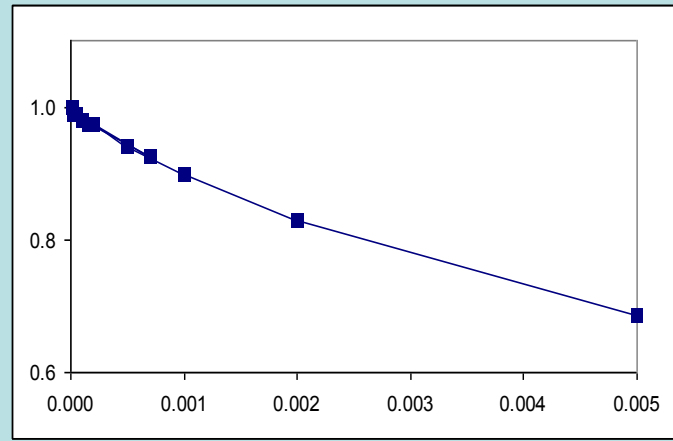


Cross Polarization Experiments



- PE
 ^1H $T_{1\rho}$ experiment

Class June 2001
Sample: PE
Rotation rate: 5kHz
T1_rho 1H through 13C detect



Triple Resonance Experiments

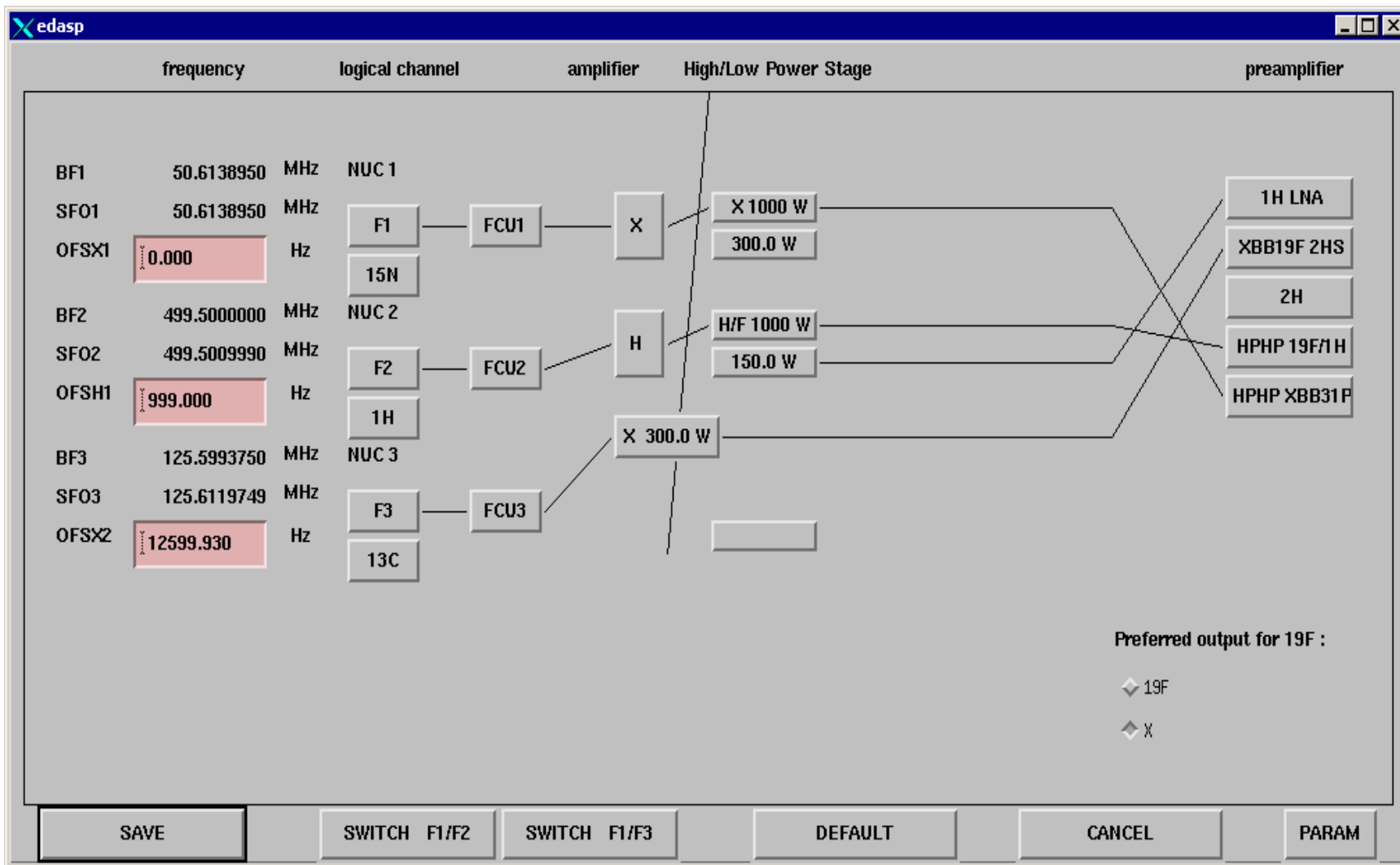


- Setup:
 - Adjust ^{15}N parameters
 - Get ^{13}C parameters
 - Load triple resonance experiment
 - some fine adjustments



Triple Resonance Experiments

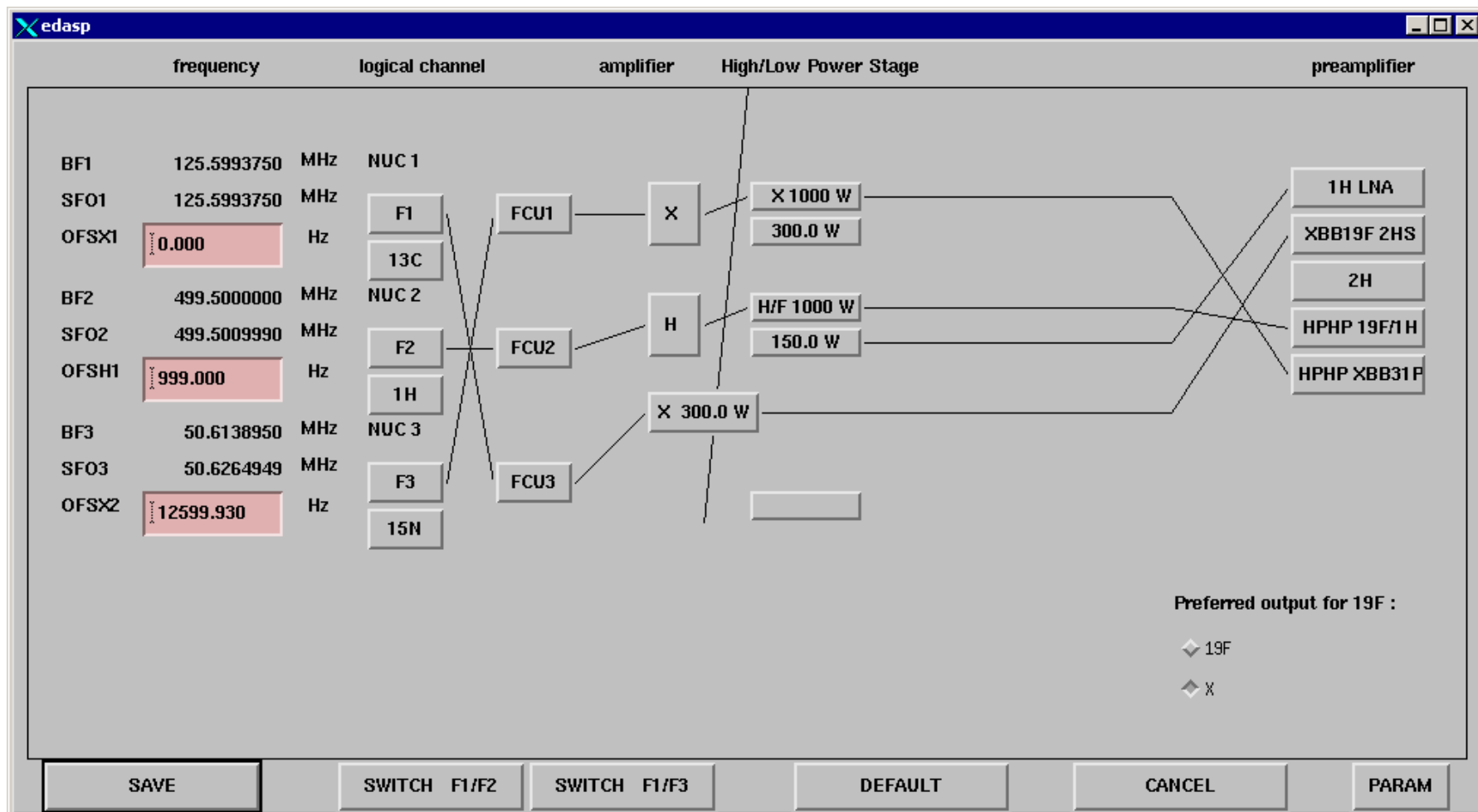
• ^{15}N setup



Triple Resonance Experiments

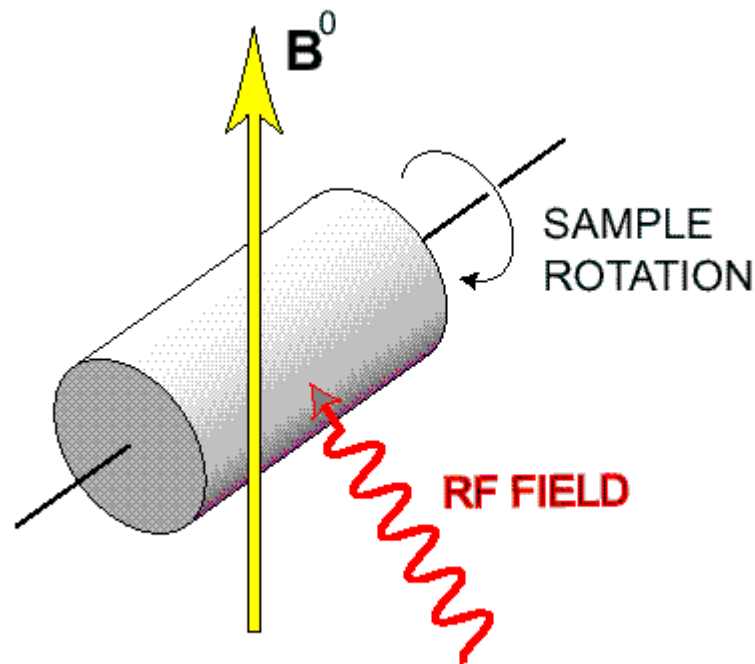


• ^{13}C setup

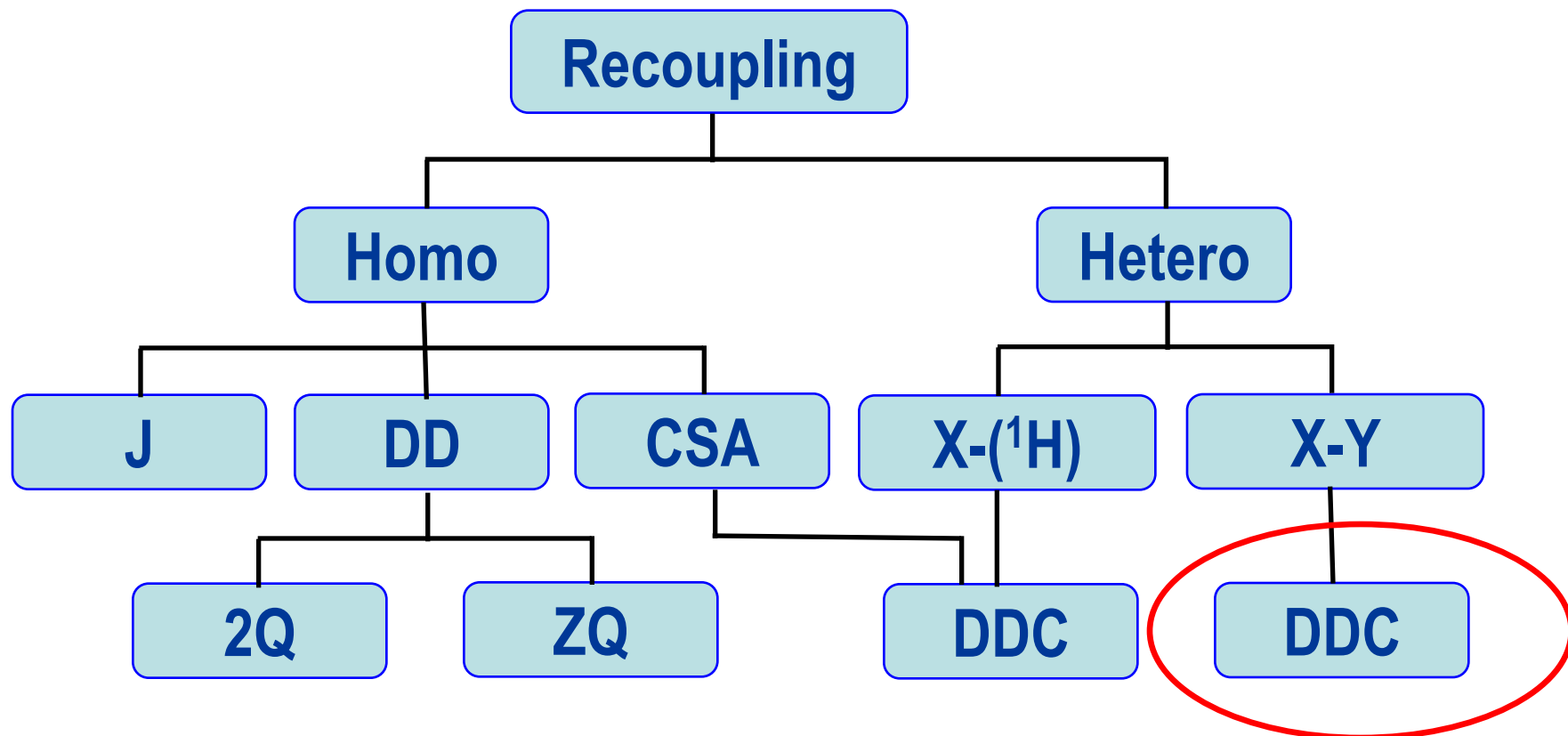


NMR in solid systems:

- Average by MAS
- Problem now: Lost information through averaging
- Solution: MAS + Radio Frequency (RF) field → Recoupling
- Create heteronuclear Dipole Dipole Correlation (DDC)

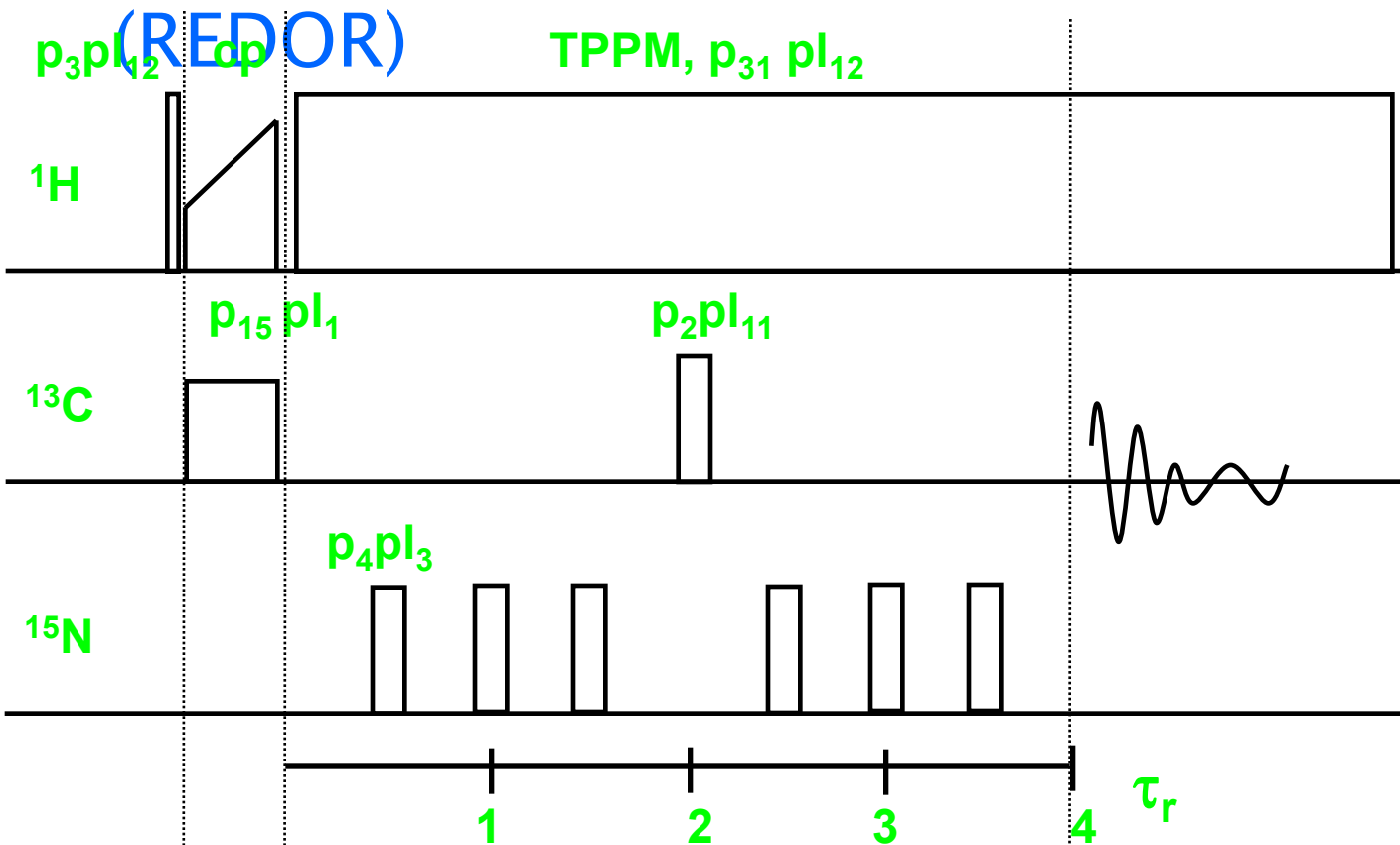


- Types of Recoupling



Triple Resonance Experiments

• Rotational Echo Double Resonance (REDOR)



Excitation acquisition

PT

rotor synchronized heteronuclear dipolar recoupling

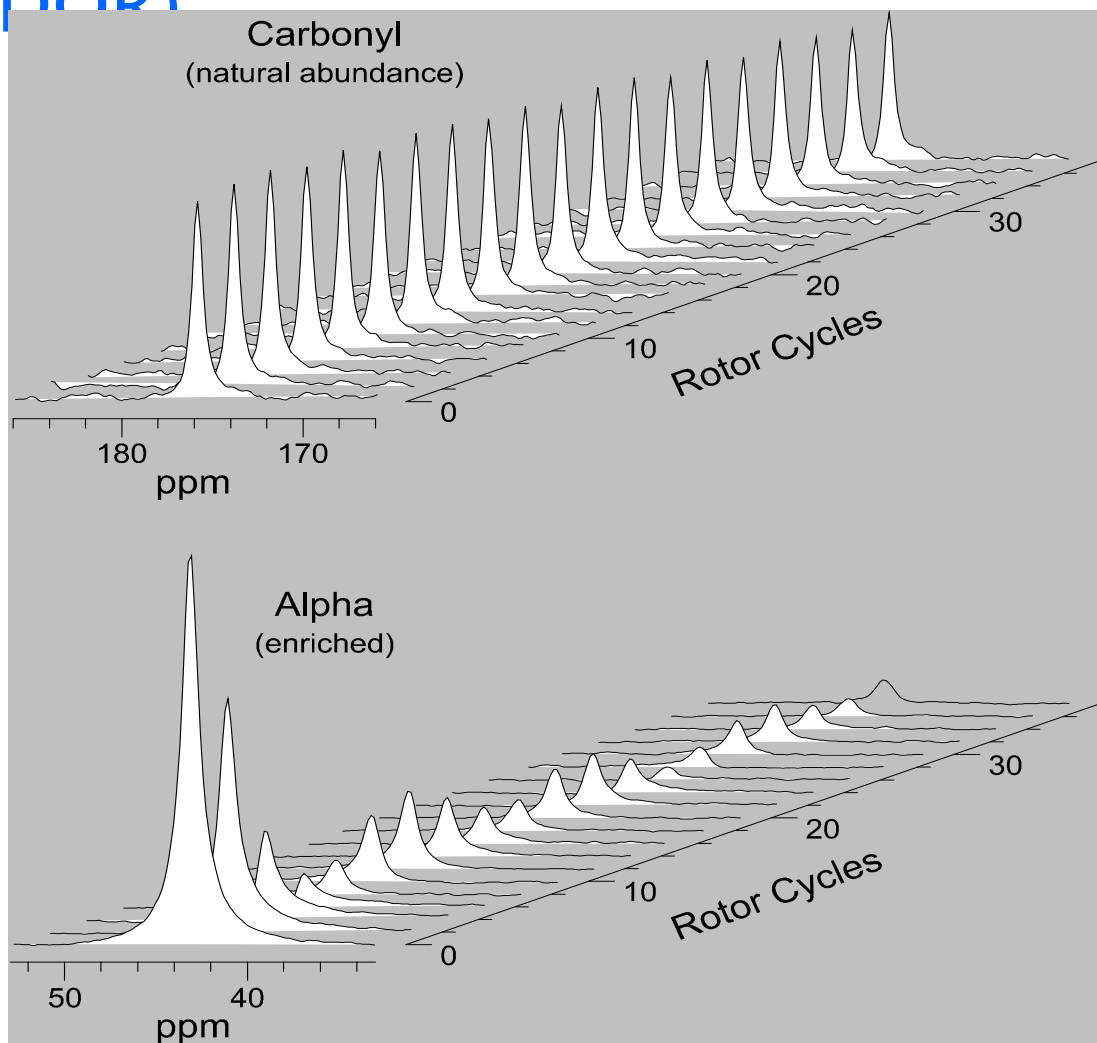
evolution, decoupling

heteronuclear dipolar recoupling

BRUKER BIOSPIN

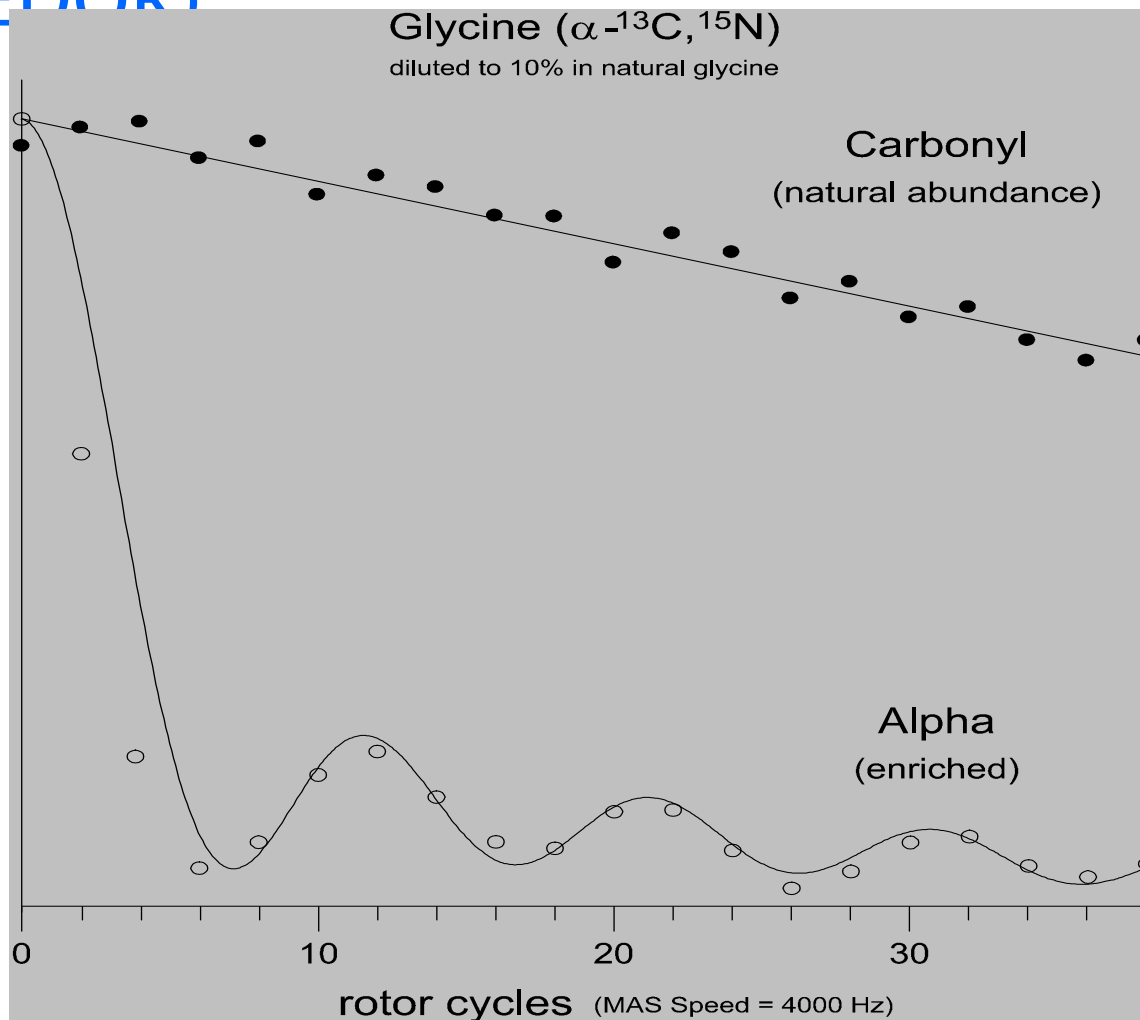
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)



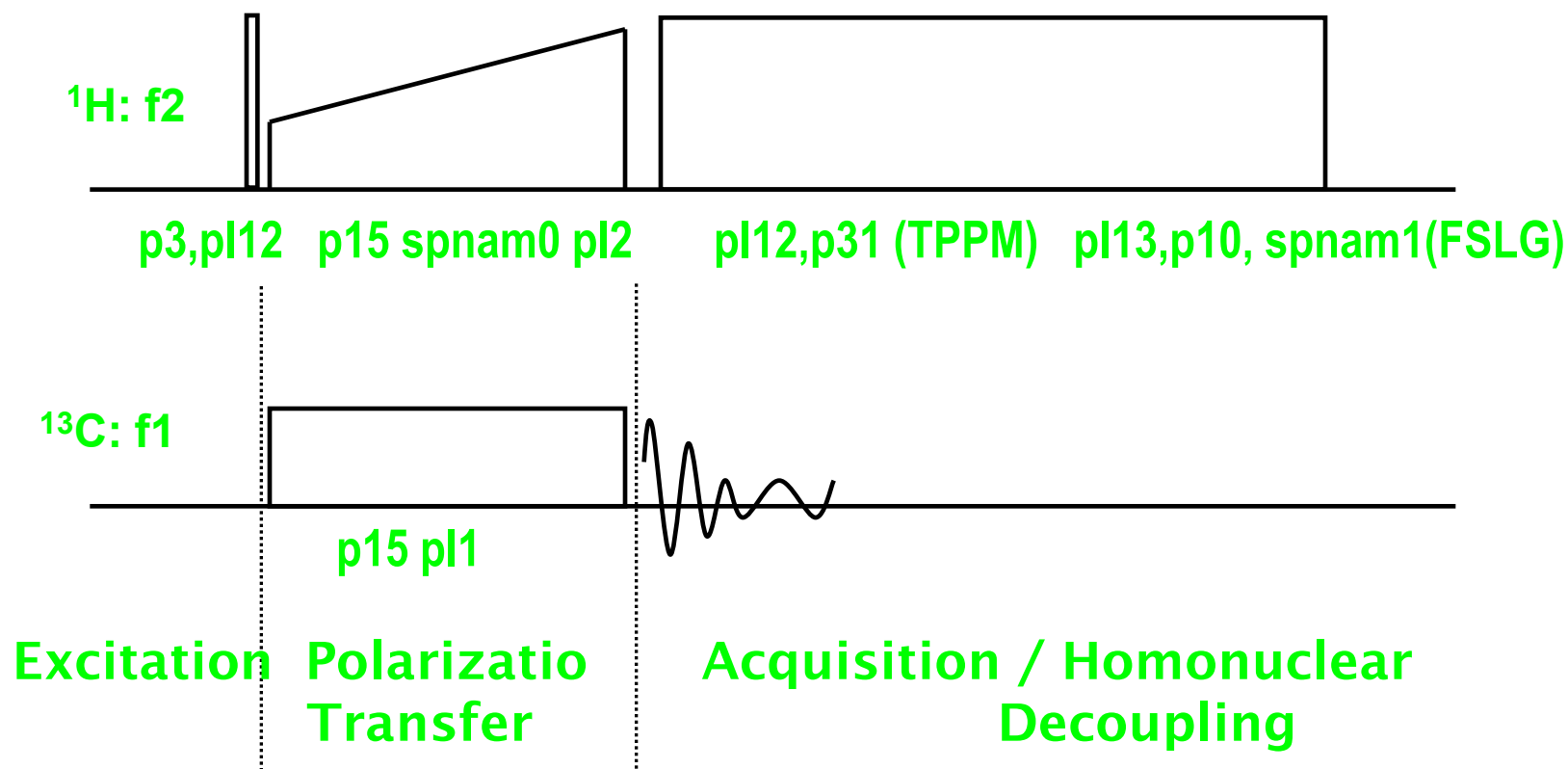
Triple Resonance Experiments

- Rotational Echo Double Resonance (REDOR)

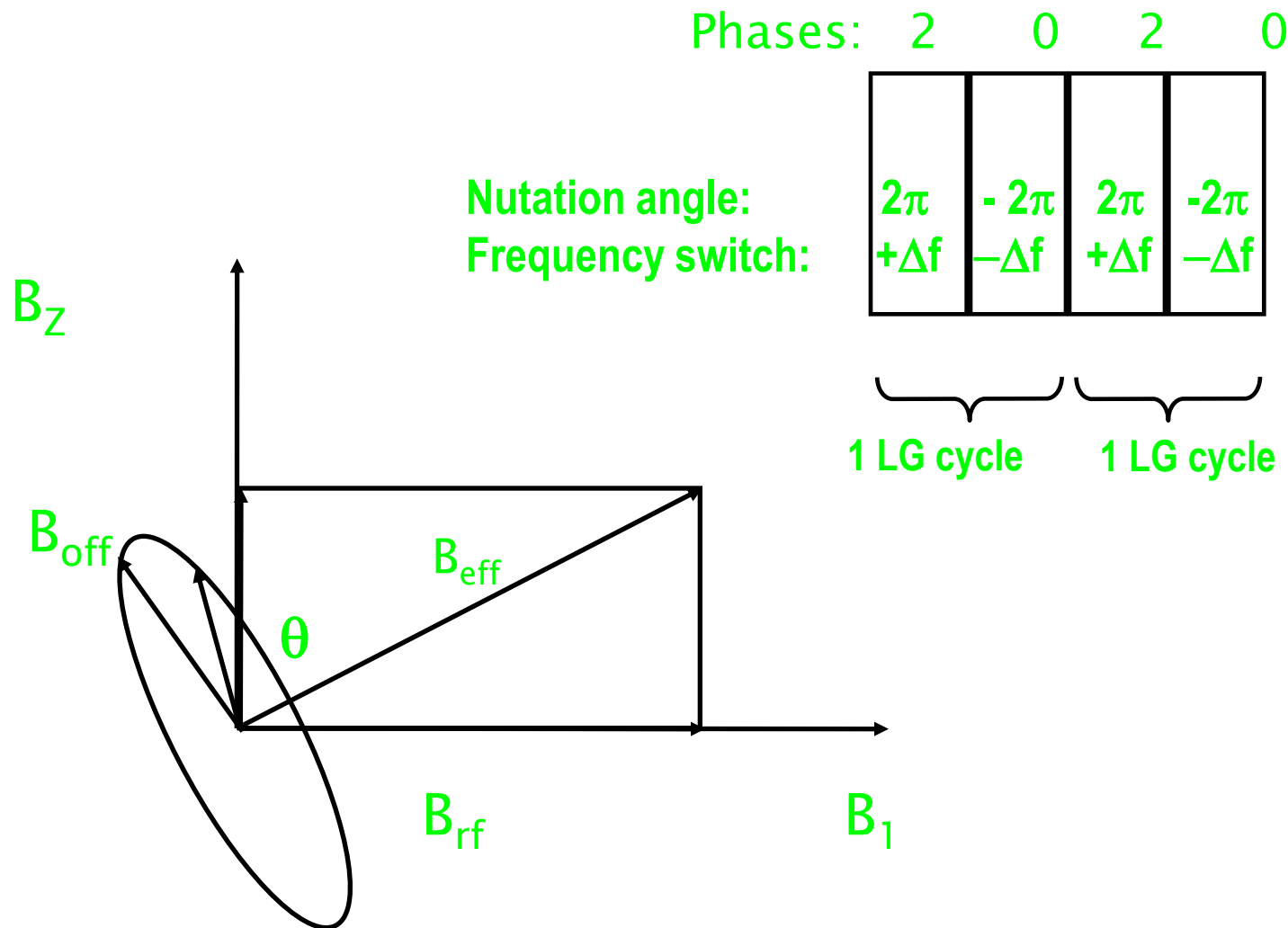


FSLG Experiments Setup

Basic experimental scheme: Measures J coupling



FSLG Experiments



- Conventions:

- Use include file: lgcalc.incl

- Uses **cnst20** for B1 field in Hz and calculates

- **p5** 294 degree pulse

- **cnst21=0** for on resonance

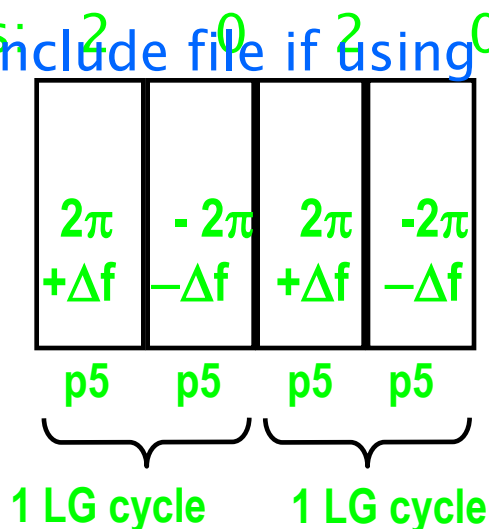
- **cnst22** and **cnst23** for \pm LGfrequency offset, **$+\Delta f$** - **Δf**

- **cnst24** for offset of center of \pm LGfrequency offsets

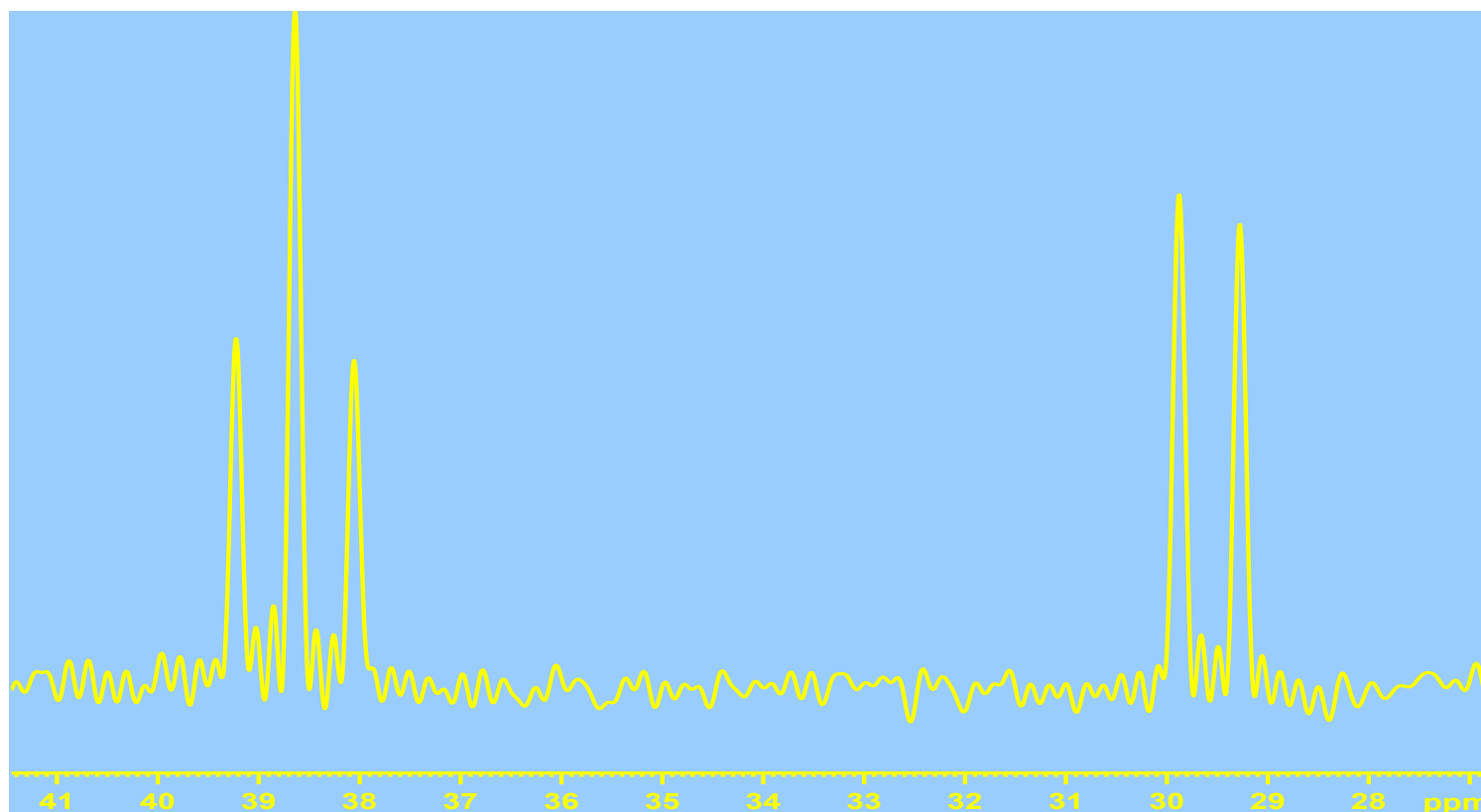
- Use same include file if using PMLG shape as well - convenient

Nutation angle:

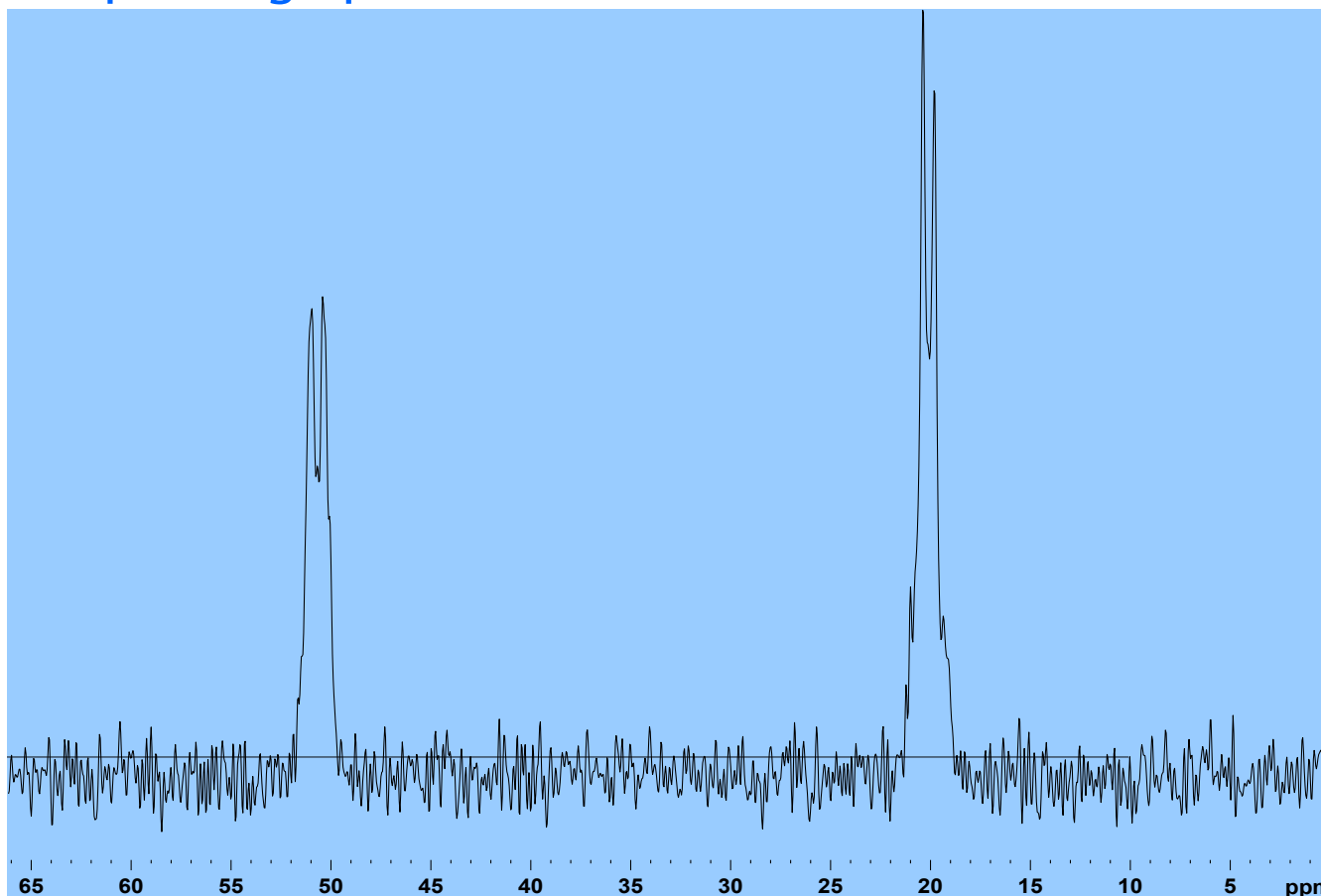
Frequency switch:



- Homonuclear decoupling during acquisition:
 - J-coupling resolved on adamantane
 - Optimized for best splitting, width and depth
 - Spinning speed 7 kHz

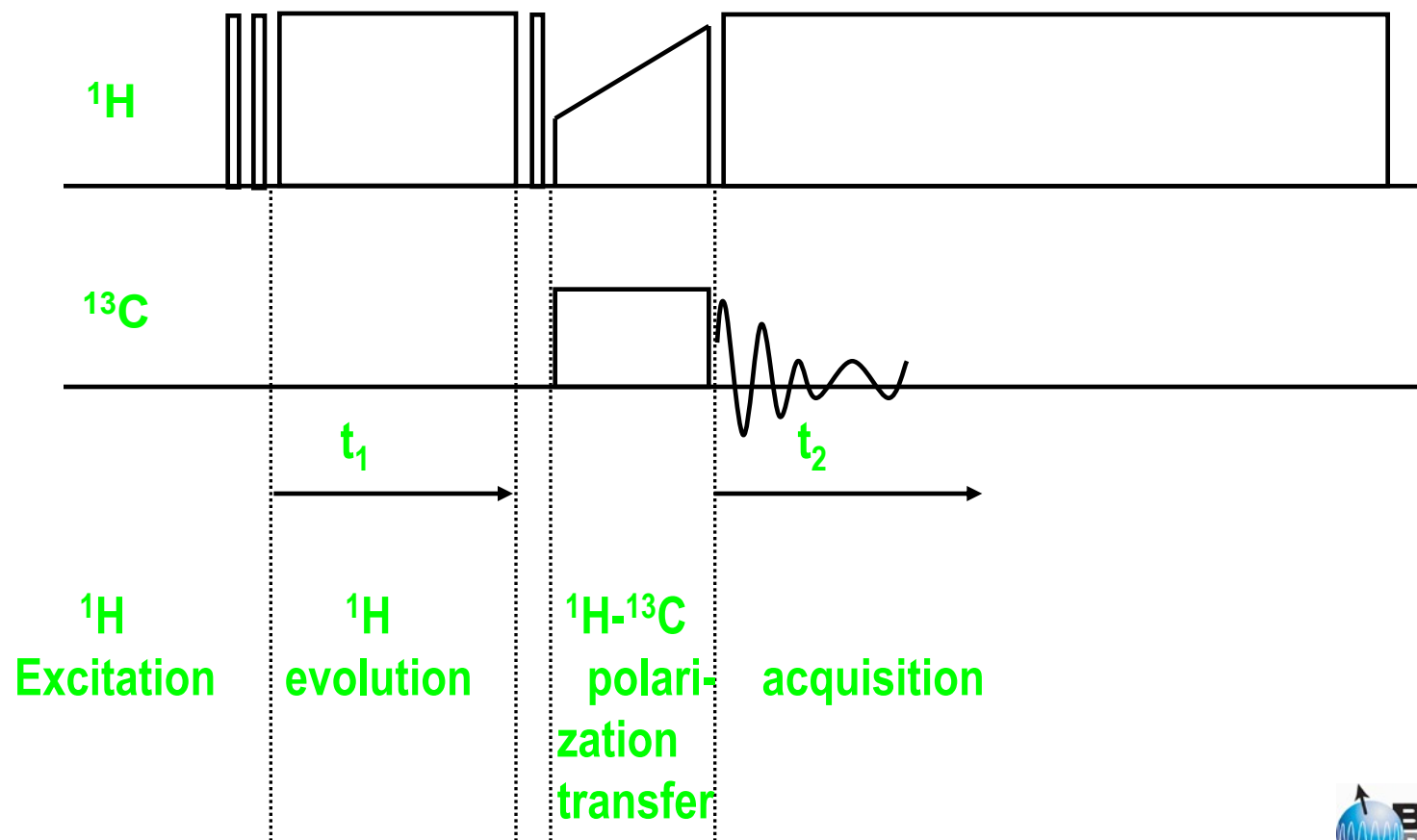


- Homonuclear decoupling during acquisition:
 - J-coupling resolved on alanine
 - Optimized for best splitting, width and depth
 - Spinning speed 12.5 kHz



- **Application: Heteronuclear correlation spectroscopy**

- B.-J. van Rossum et al. JMR124 (1997)
- Pulse program: IghettCP.av **TPPM decoupling**



- Tips for pulse programming
 - set parameters simultaneously

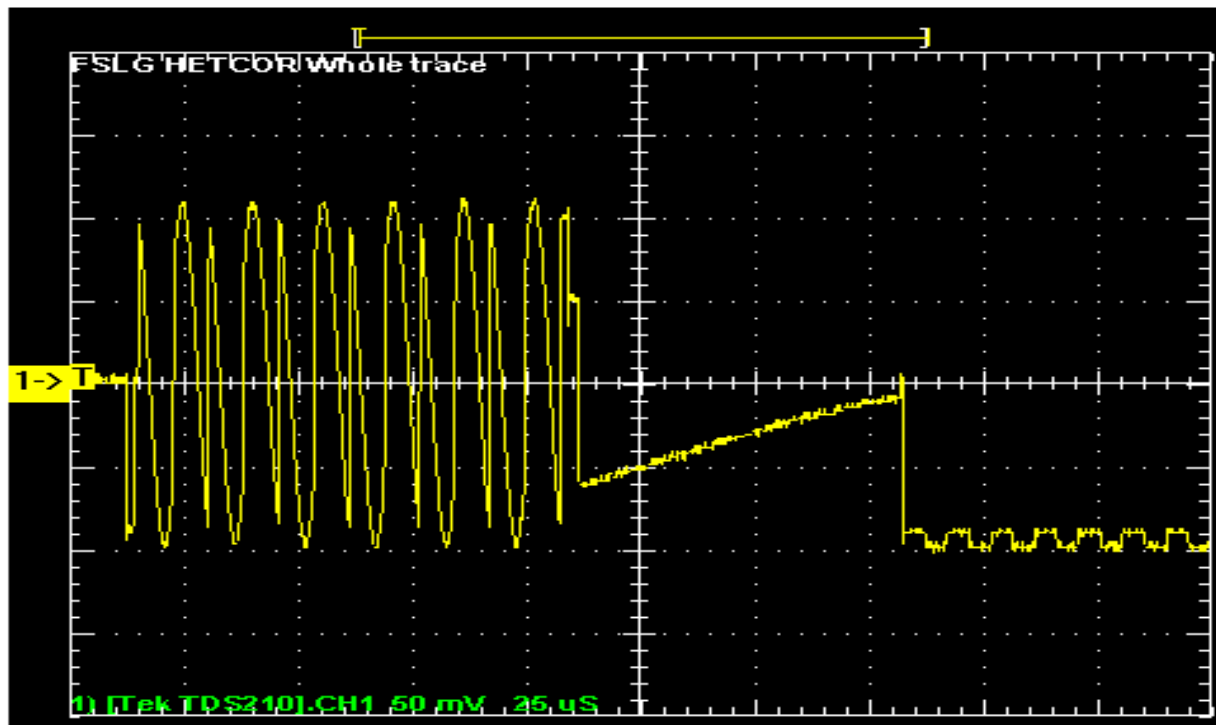
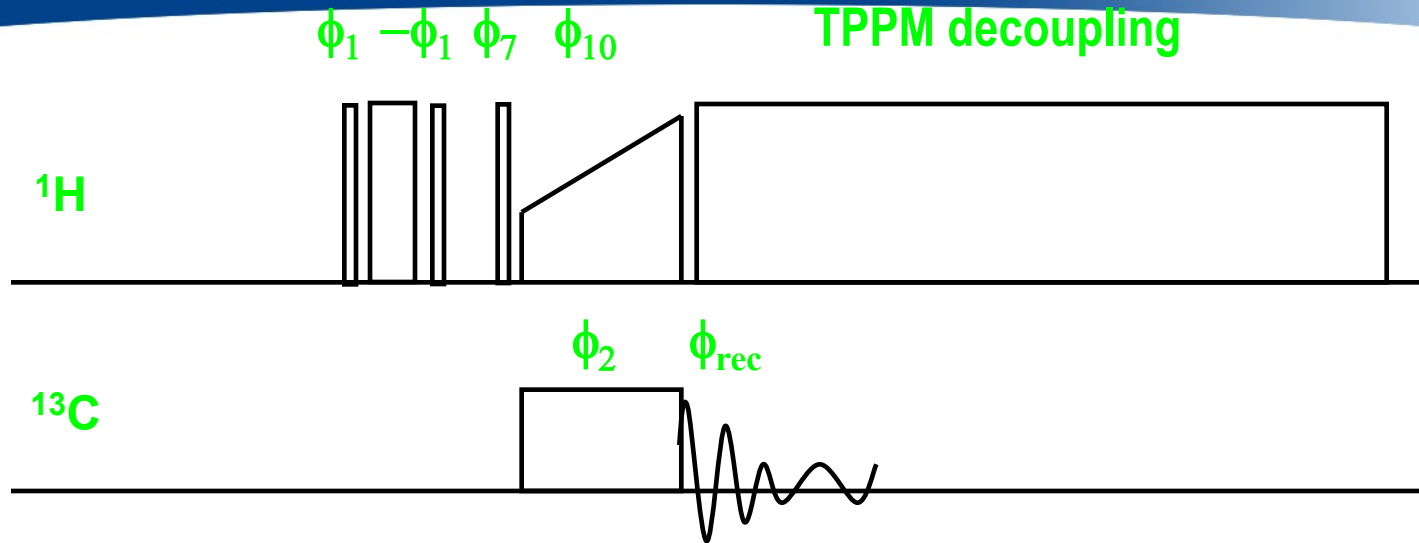
e.g. instead of

```
1u fq=cnst21:f2
1u p113:f2
(p23 ph7):f2
```

FSLG Sequence in AV Pulse Program:

```
3 (p5 ph3 fq=cnst22 p113):f2 ;+LG frequency
  p5:f2 ph4 fq=cnst23:f2 ;-LG frequency
  p5:f2 ph3 fq=cnst22:f2 ;+LG frequency
  p5:f2 ph4 fq=cnst23:f2 ;-LG frequency
lo to 3 times l1 ;l1 increment of t1 in F1 dimension
```

FSLG Experiments



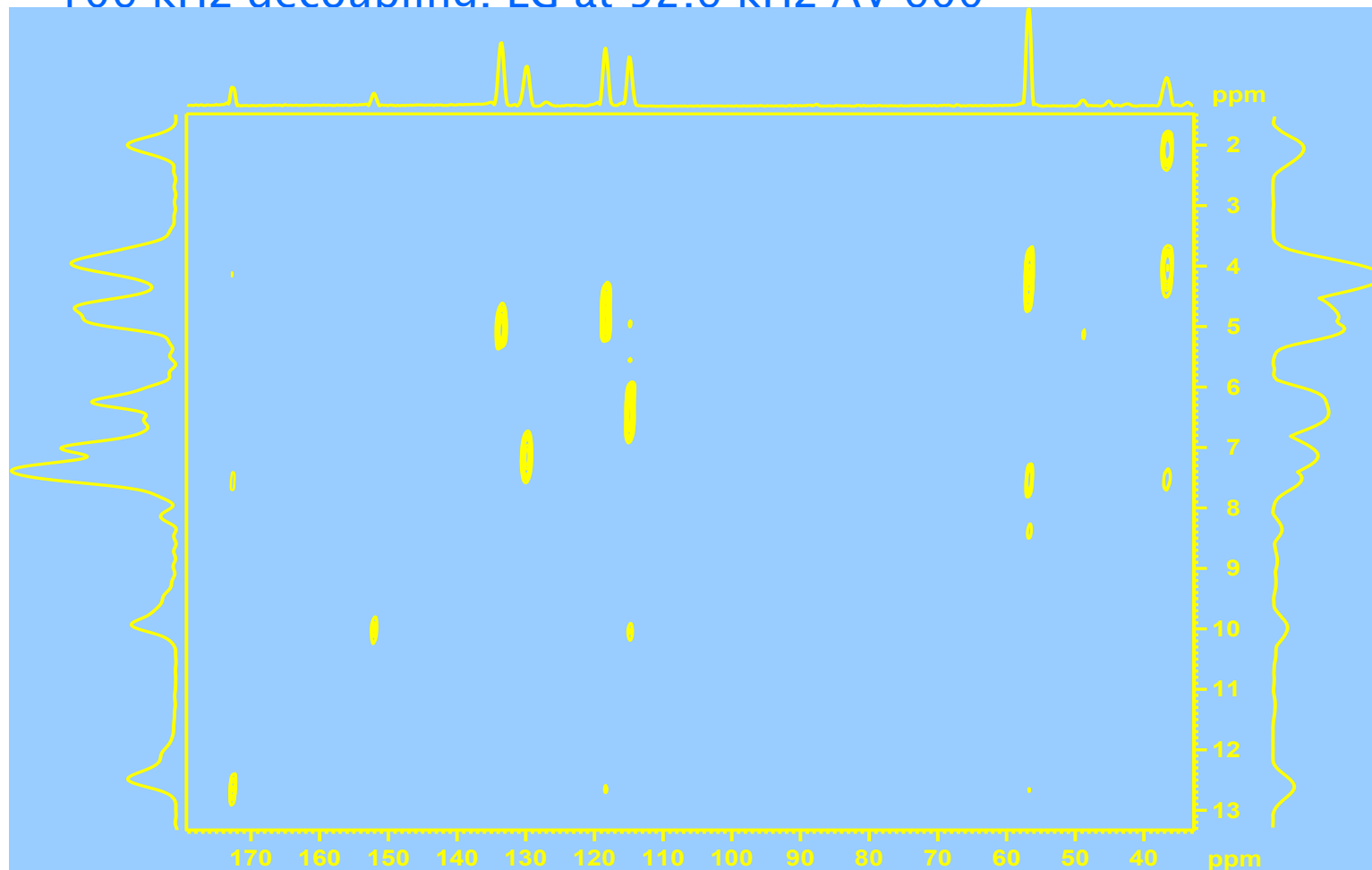
FSLG Experiments

FSLG/HETCOR tyrosine HCl

right trace: projection

left trace: BR-24 CRAMPS on the same 4mm CP/MAS probe

106 kHz decoupling, LG at 92.6 kHz AV 600



- Frequency switch through phase ramps:

$$2\pi f = \partial\theta / \partial\tau$$

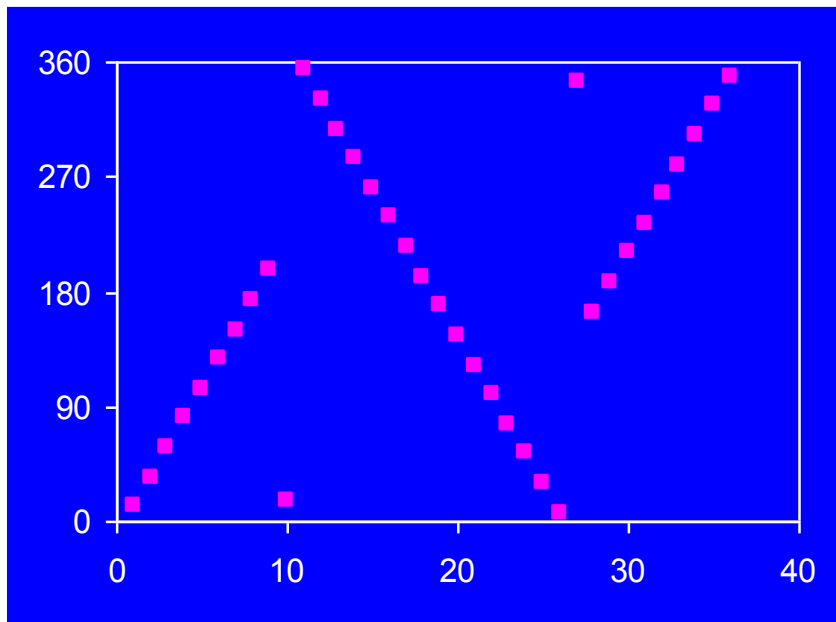
- Create phase ramp use: AU program pmlg_vega
- Au program uses Vinogradovs results to calculate shape
 - Choices in au program:
 - number of slices per 294 degree pulse
 - number of fslg-cycles per block (x,x_bar)
 - Time reversed blocks (x_bar,x)

$$(x\bar{x})_n (\bar{x}x)_n$$

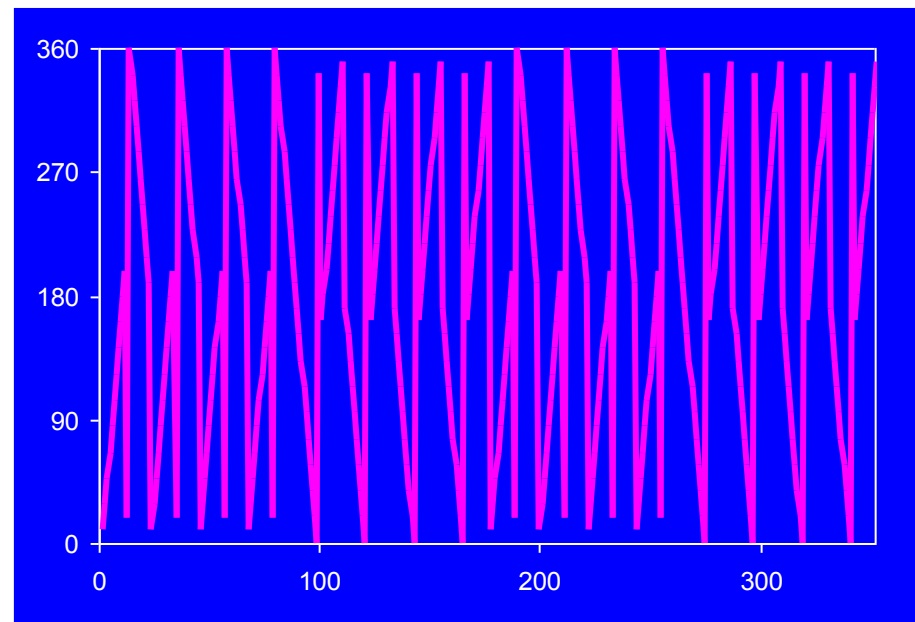
E. Vinogradov, P.K. Madhu, and S. Vega, Chem. Phys. Lett. 314, 443-450 (1999)

- Typical PMLG shapes

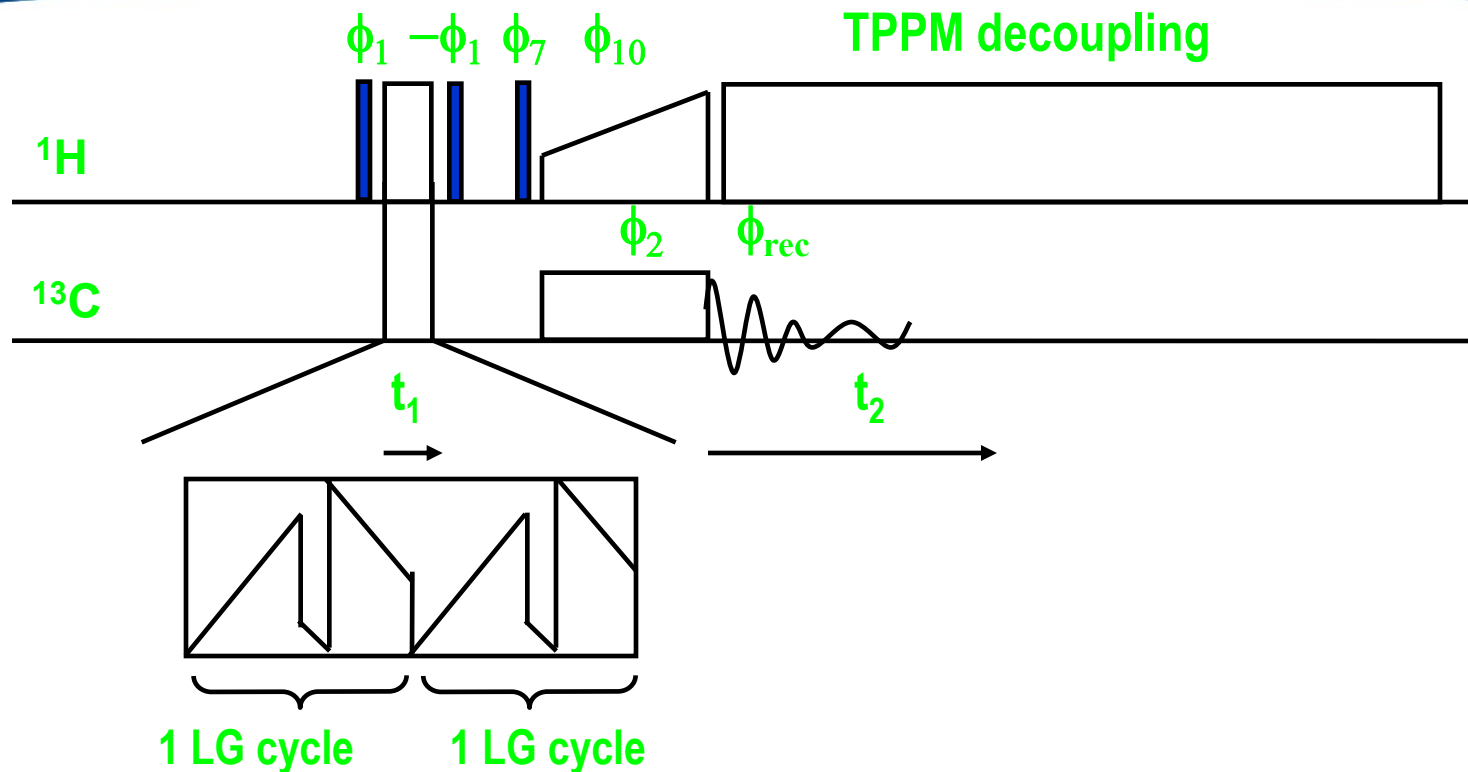
$$(x\bar{x})(\bar{x}x)$$



$$(x\bar{x})_4(\bar{x}x)_4(x\bar{x})_4(\bar{x}x)_4$$



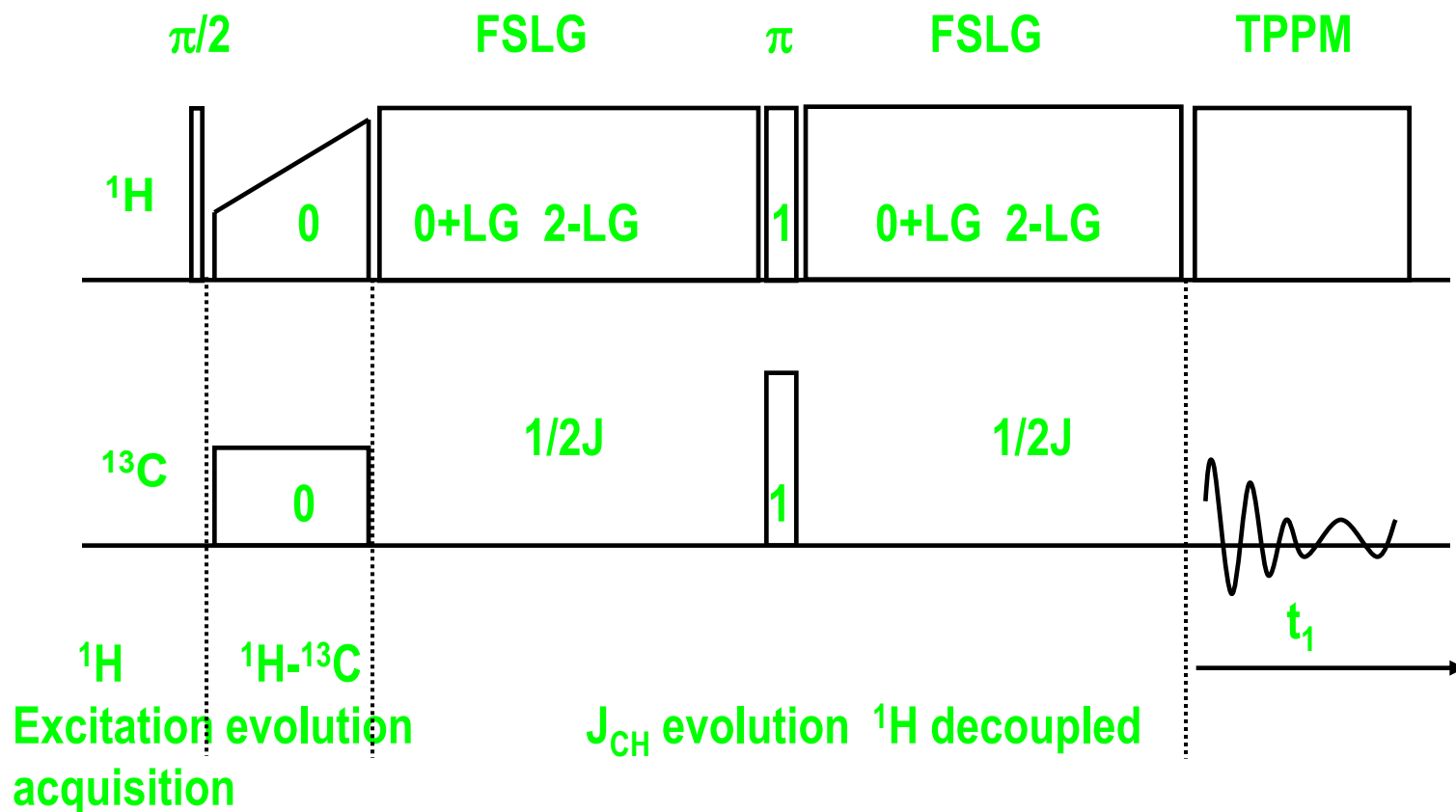
PMLG Experiments



Pulse Program using normal shape: [lghetshape.av](#)

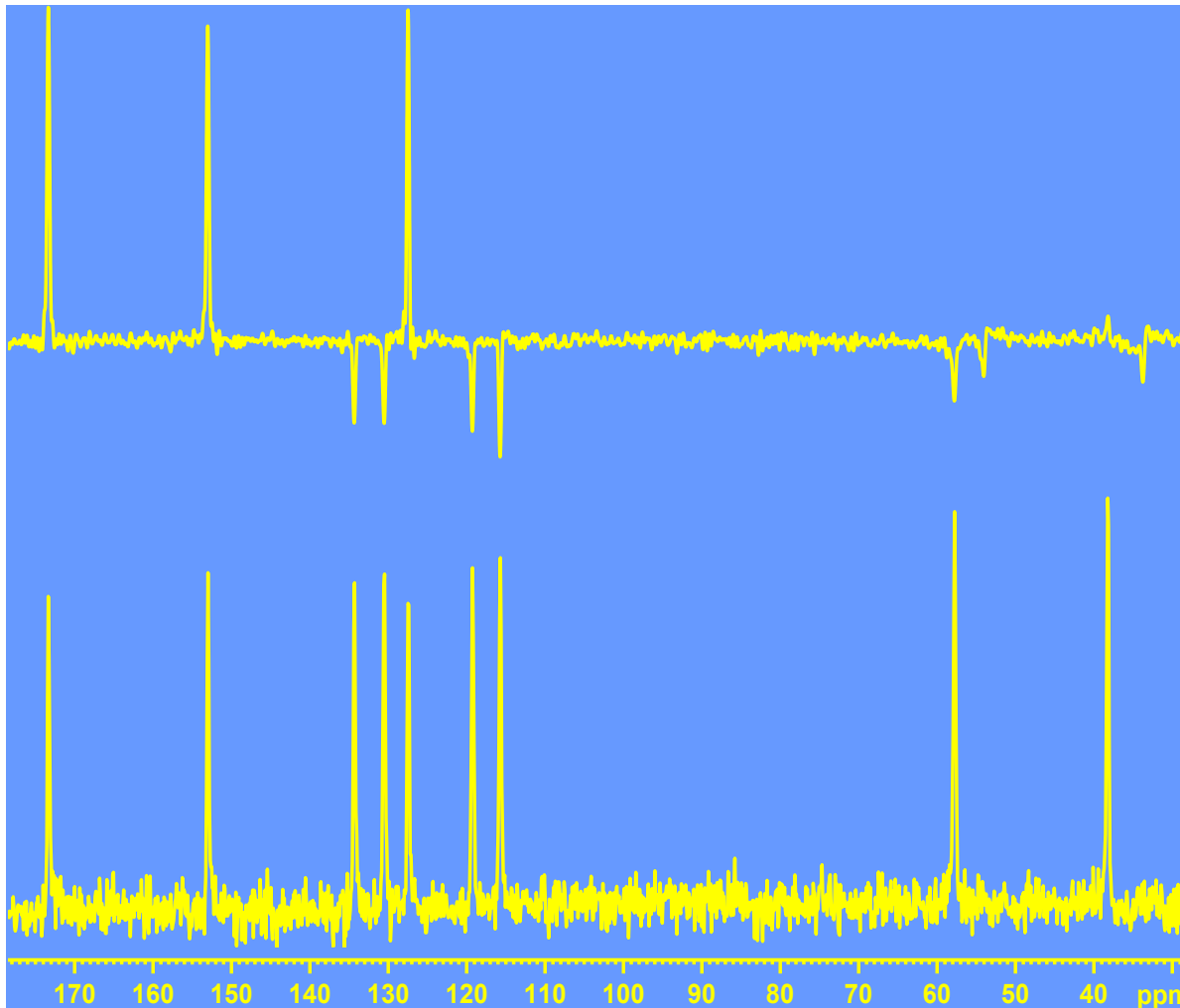
Pulse Program using fast shape: [lghetloop.av](#)

- Attached Proton Test in Solid State NMR



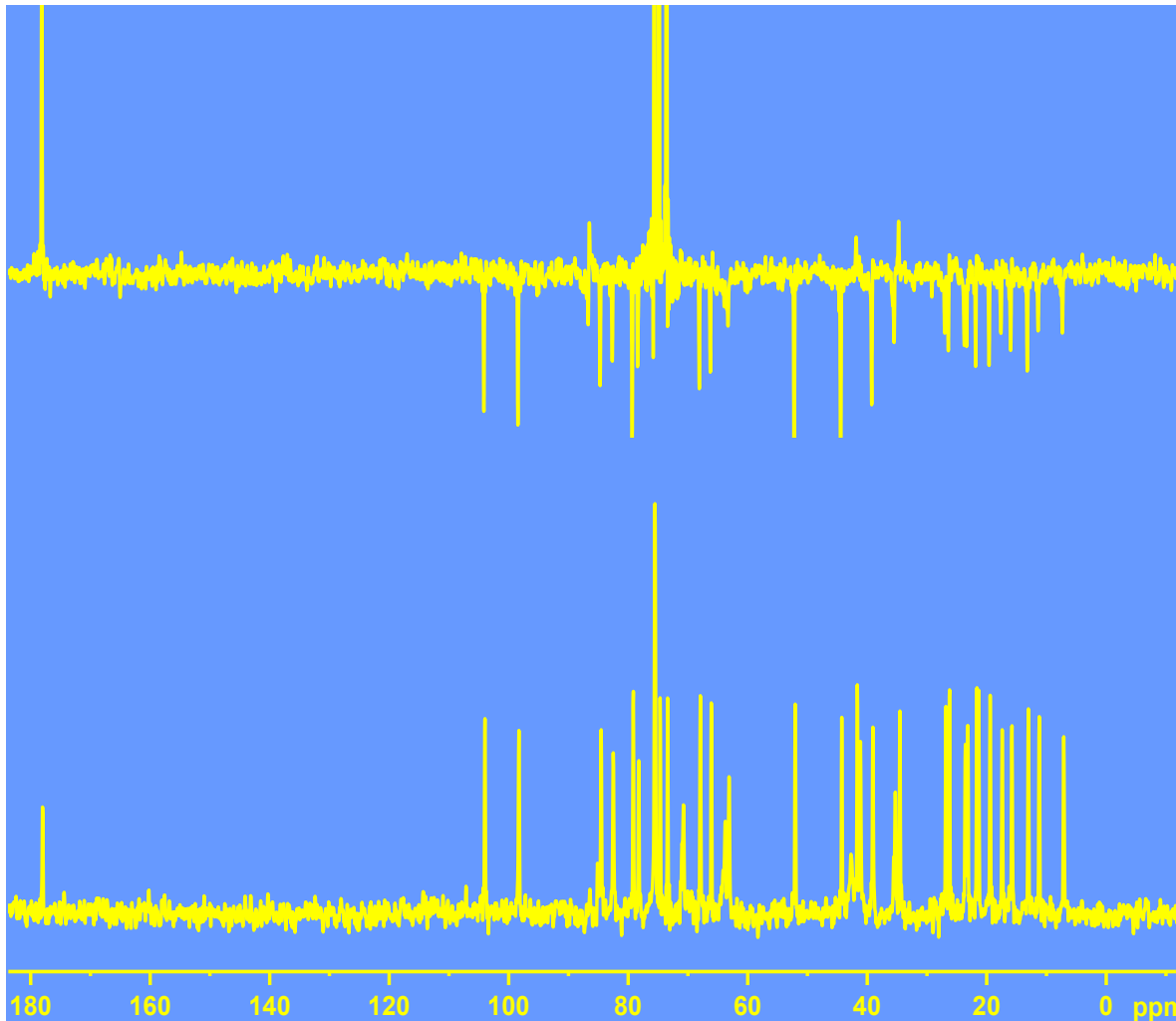
A. Lesage, S. Steuernagel, L. Emsley, J. Am. Chem. Soc. 1998, 120, 7095-7100

Attached Proton Test



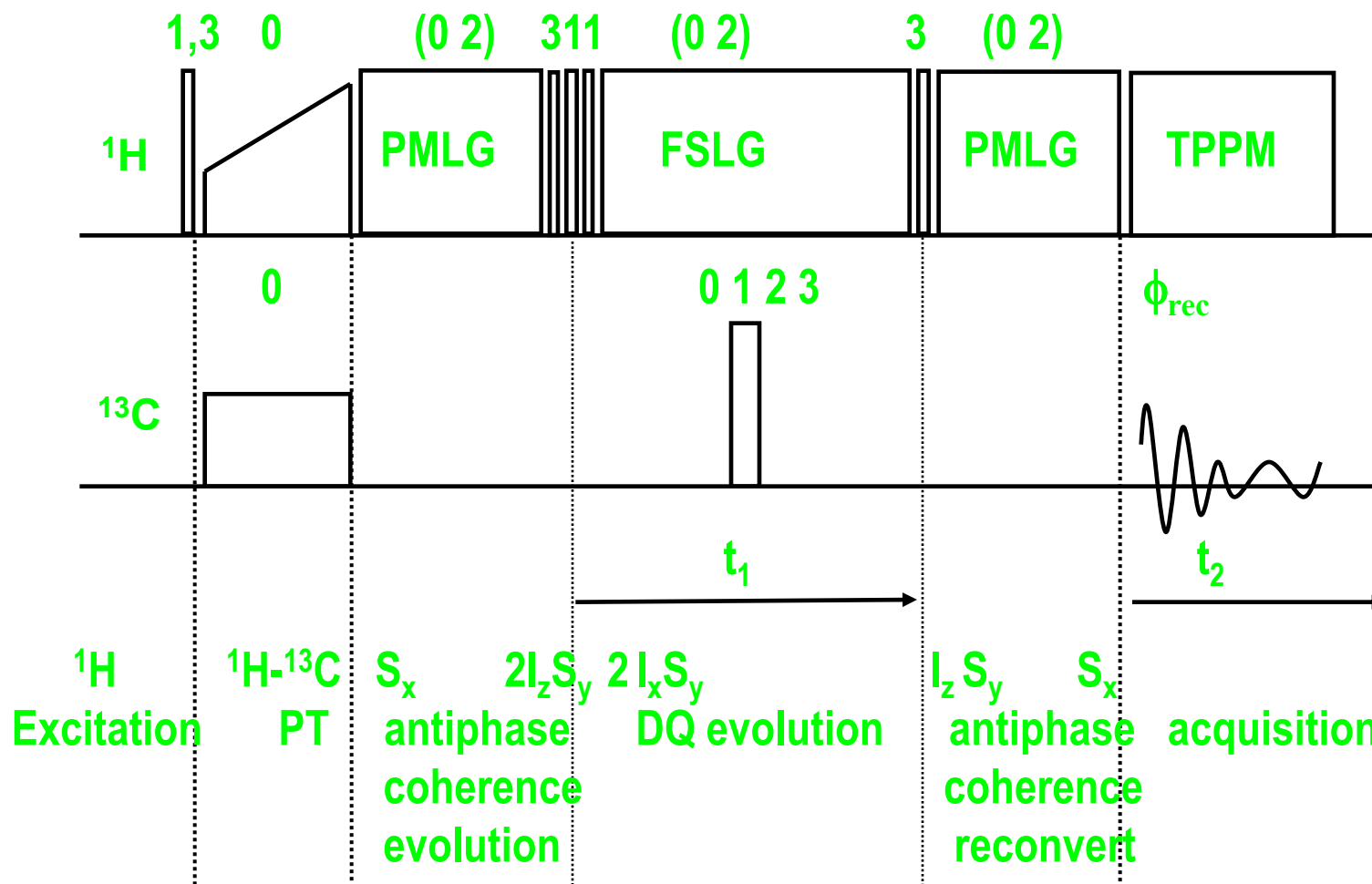
- Avance 500 WB
- Tyrosine HCl
- 4 mm DVT probe
- $^1\text{H}/^{13}\text{C}$, 1 ms contact
- ± 80.6 kHz frequency switch
- ^{13}C rf field: 67 kHz
- ^1H rf field:
 - 67 kHz contact
 - 114 kHz TPPM and FSLG
- $\tau = 5.5$ ms
- 256 scans
- 2.5 s recycle delay

Attached Proton Test

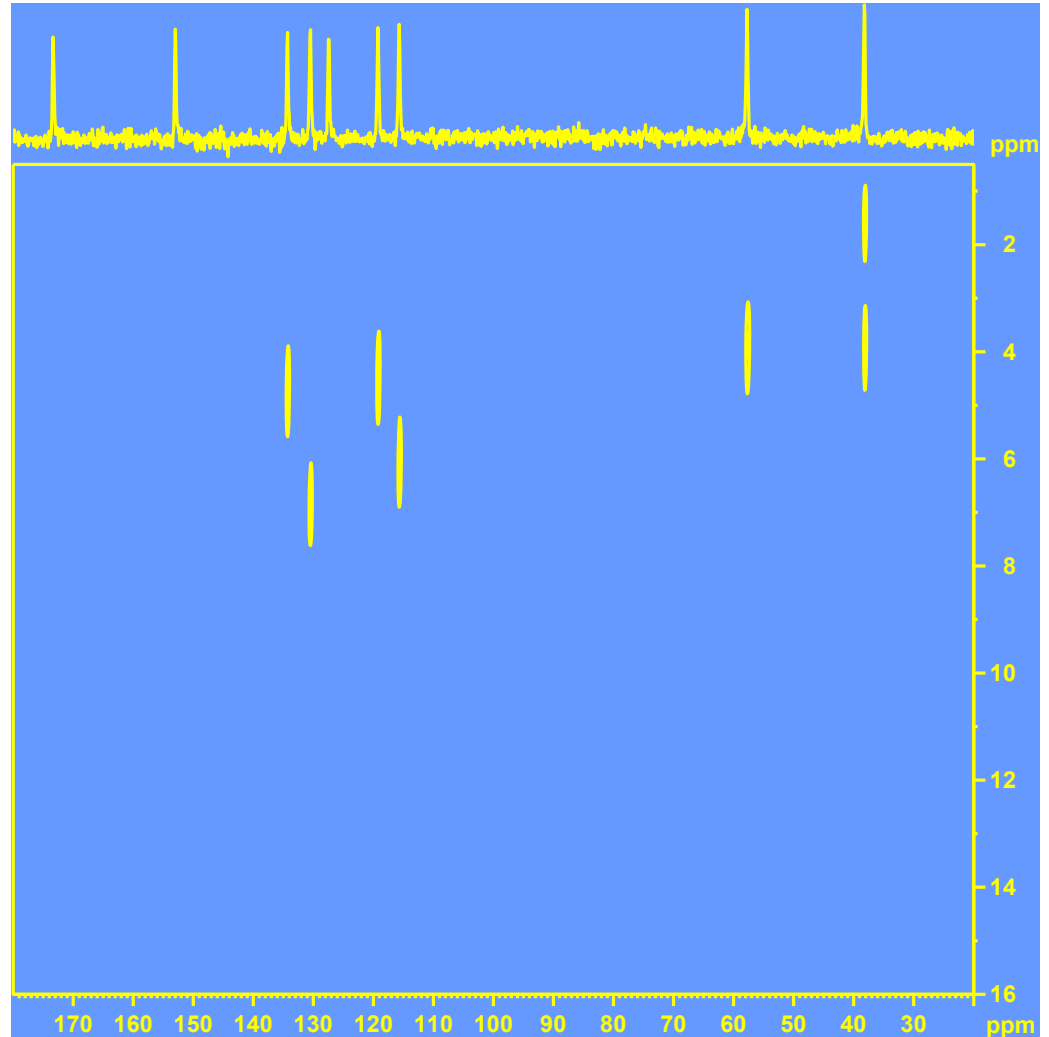


- Avance 500 WB
- 4 mm DVT probe
 - $^1\text{H}/^{13}\text{C}$, 1 ms contact
 - ± 80.6 kHz frequency switch
 - ^{13}C rf field: 67 kHz
 - ^1H rf field:
 - 67 kHz contact
 - 114 kHz TPPM and FSLG
 - $\tau = 5.5$ ms
 - 256 scans
 - 2.5 s recycle delay

MAS-J- HMQC

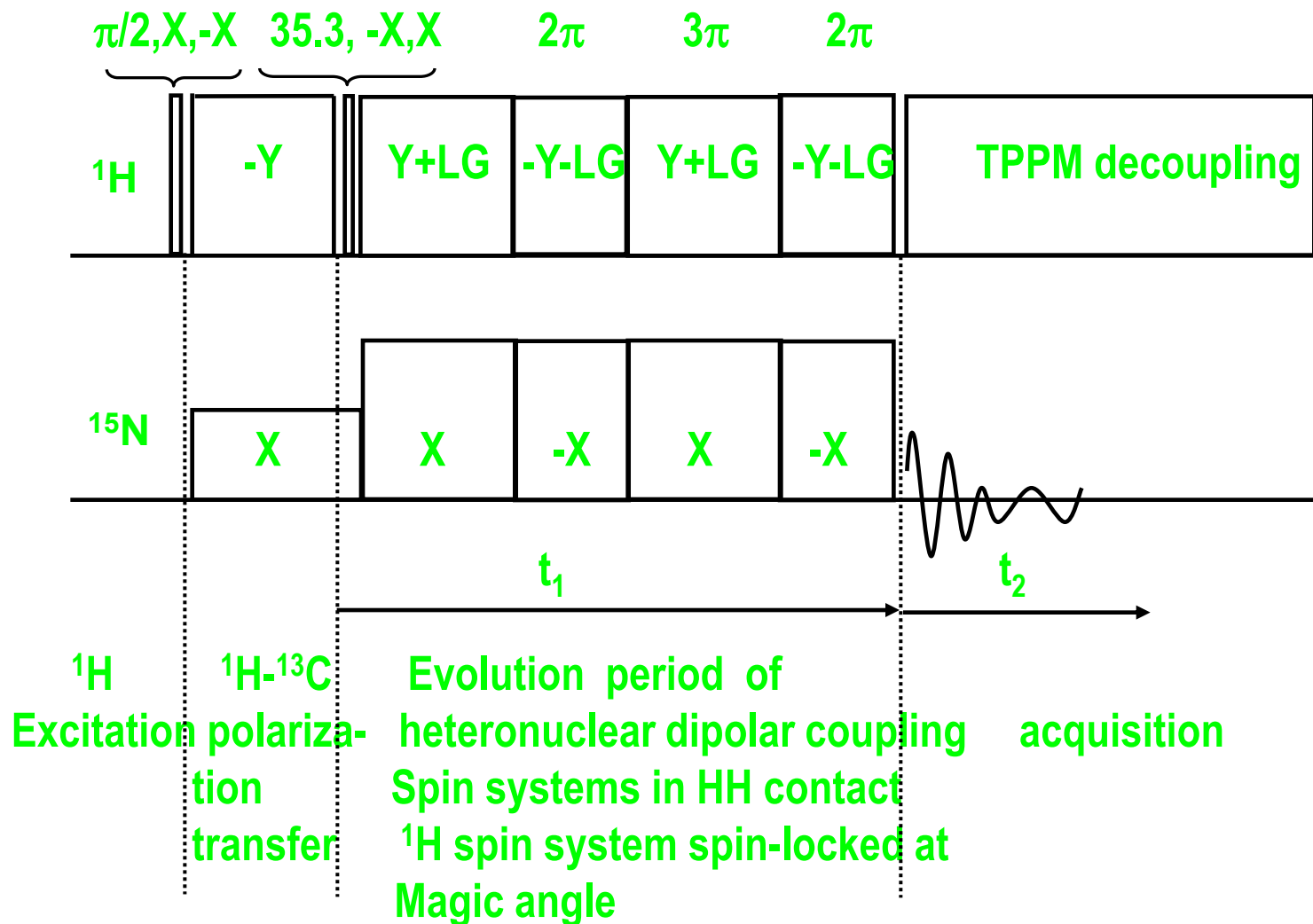


- Avance 500 WB
- 4 mm DVT probe
 - $^1\text{H}/^{13}\text{C}$, 1 ms contact
 - ± 80.6 kHz frequency switch
 - ^{13}C rf field: 67 kHz
 - ^1H rf field:
 - 67 kHz contact
 - 114 kHz TPPM and FSLG
 - 96 scans
 - 2.5 s recycle delay



Experiments using FSLG or PMLG

• PISEMA



- PISEMA setup

- Determine all pulses and power levels using ^{15}N labeled Glycine with 1D CP experiments:
 - ^1H pulses and power levels
 - Calculate LG frequency
 - ^{15}N pulses and power levels
 - Set LG frequency and calculate required power level for ^{15}N
 - optimize HH contact by variation of power level for ^{15}N

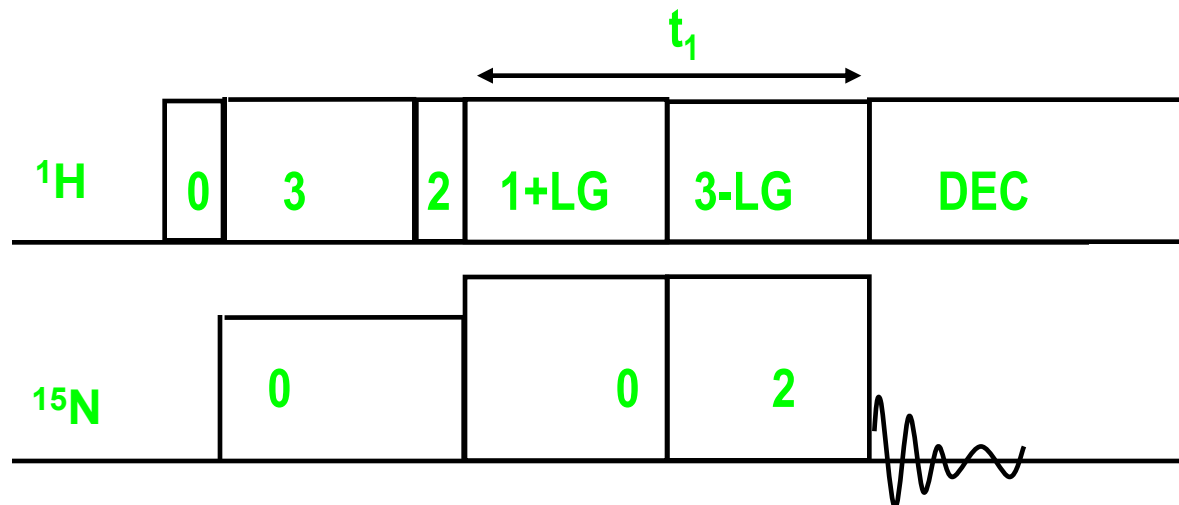
Alternatively:

- Measure ^1H pulses and power levels
- Calculate LG frequency assuming ^1H B_1 field is effective field. Calculate required power level range for ^1H
- Set LG frequency and calculated power level for ^1H
- optimize HH contact by variation of power level for ^1H

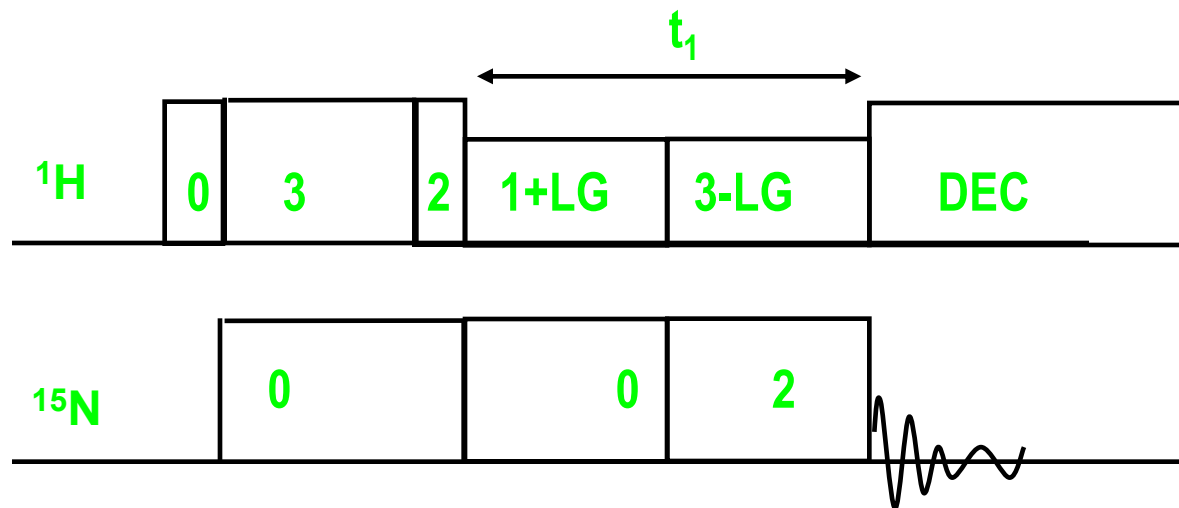
Experiments using FSLG or PMLG



- Version 1



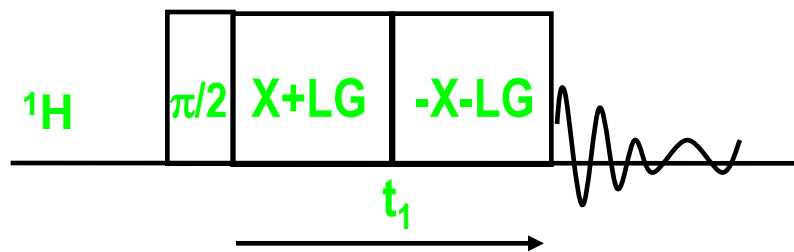
- Version 2



- PISEMA setup additional experiments

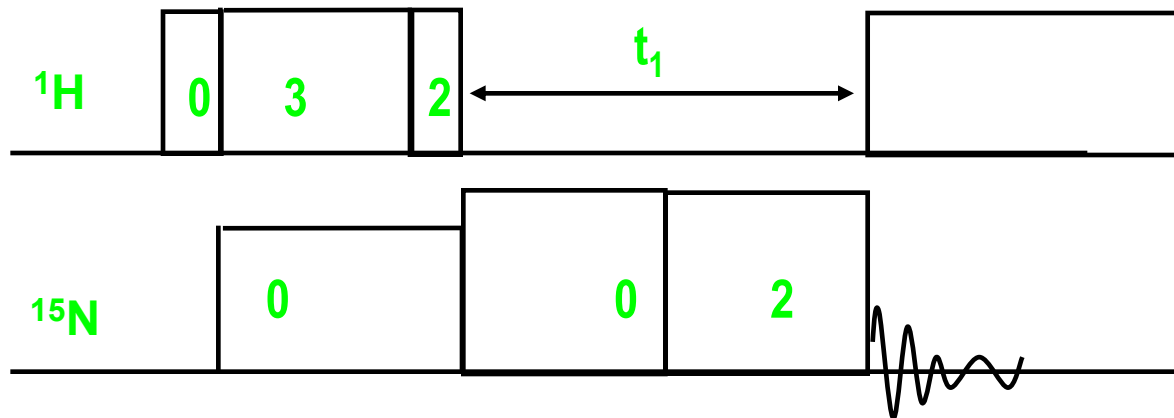
- Optimize LG decoupling using water sample

- Check resonance
 - measure scaling factor
 - (Measure reflected power using directional coupler)

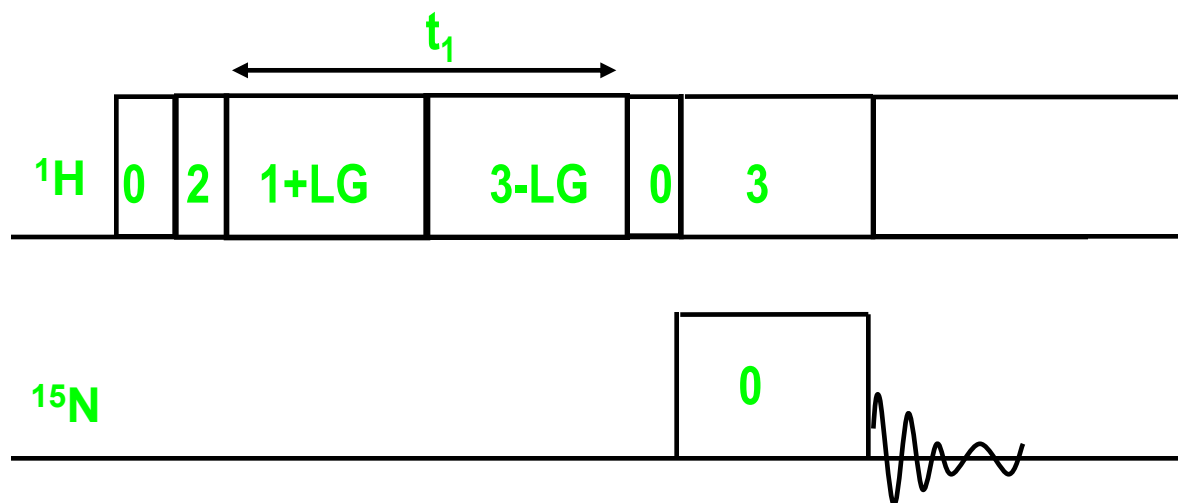


- Test spin lock ^{15}N -

- no oscillation of ^{15}N magnetization during spin lock



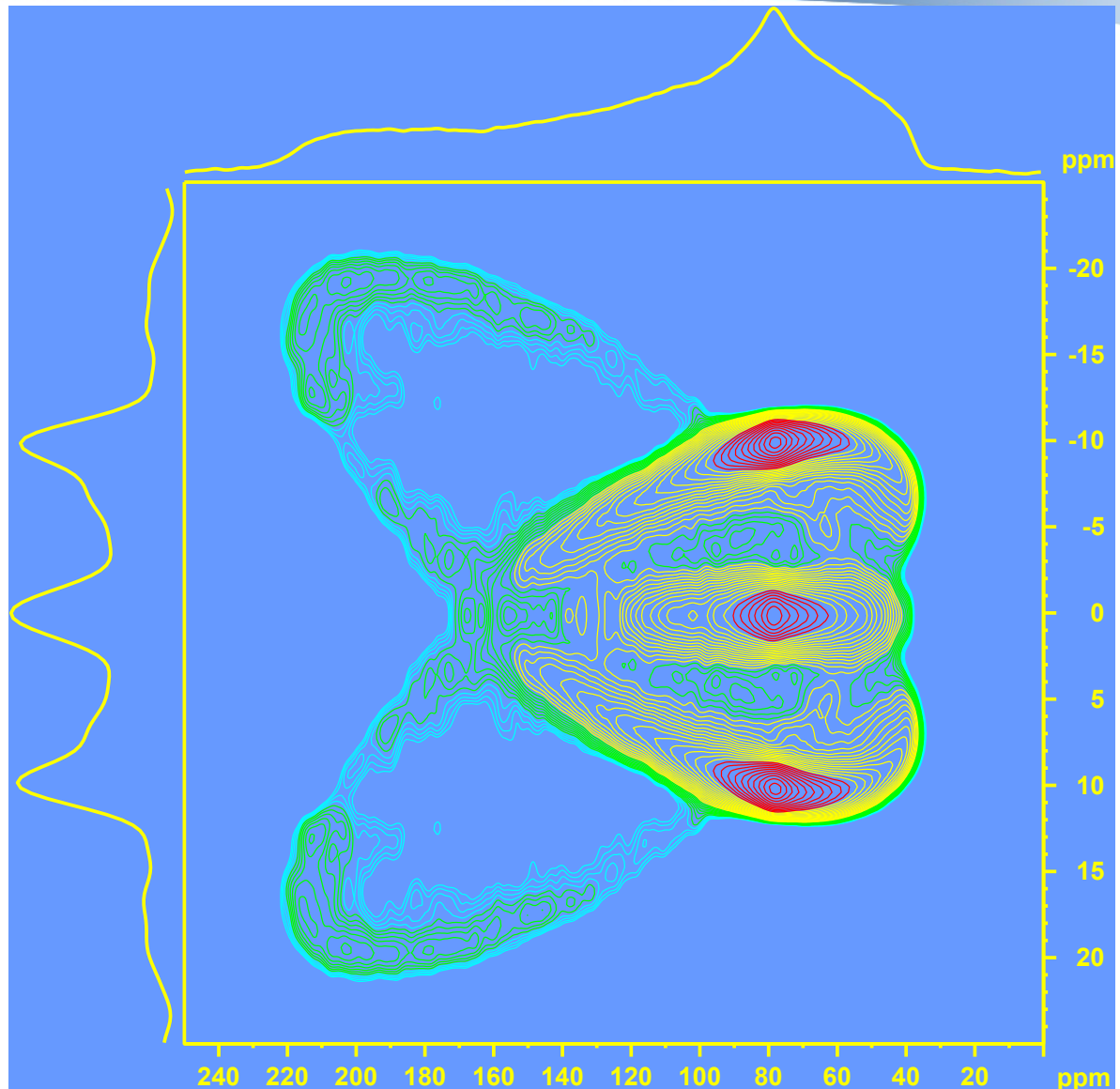
- PISEMA setup
 - Test spin lock ^1H



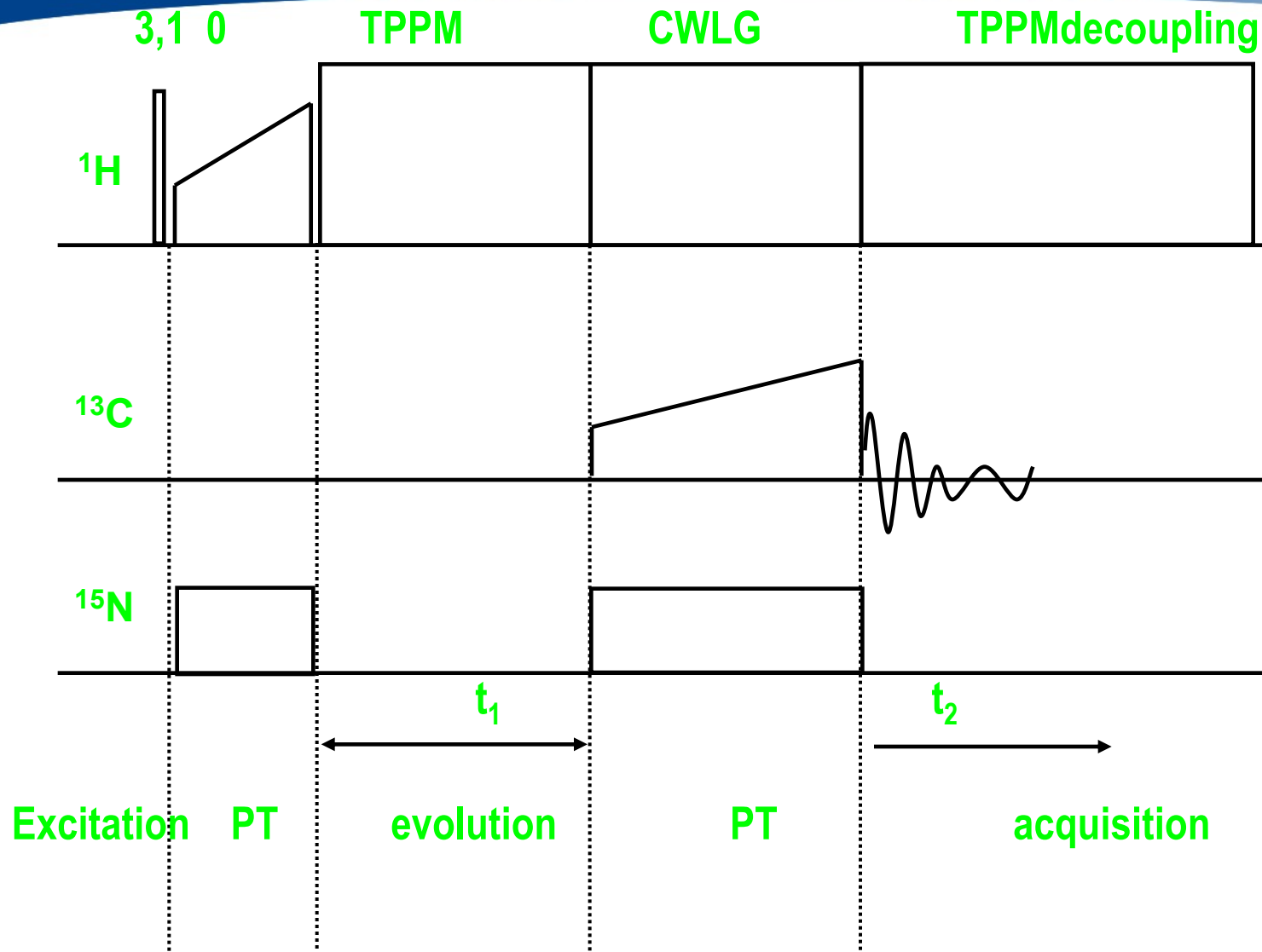
A. Ramamoorthy, C.H. Wu, and S.J. Opella, *Experimental aspects of multidimensional Solid State NMR Correlation Spectroscopy*,

J. Magn. Reson. 140, 131-140 (1999)

- Avance 500 WB
- 4 mm DVT probe
 - $^1\text{H}/^{15}\text{N}$, 5 ms contact
 - ± 46600 Hz frequency switch
 - ^{15}N rf field: 80.5 kHz
 - ^1H rf field:
 - 65.8 kHz (FSLG)
 - 80.5 kHz TPPM and HH contact
 - 32 scans
 - 30 s recycle delay
 - 8 h experiment time

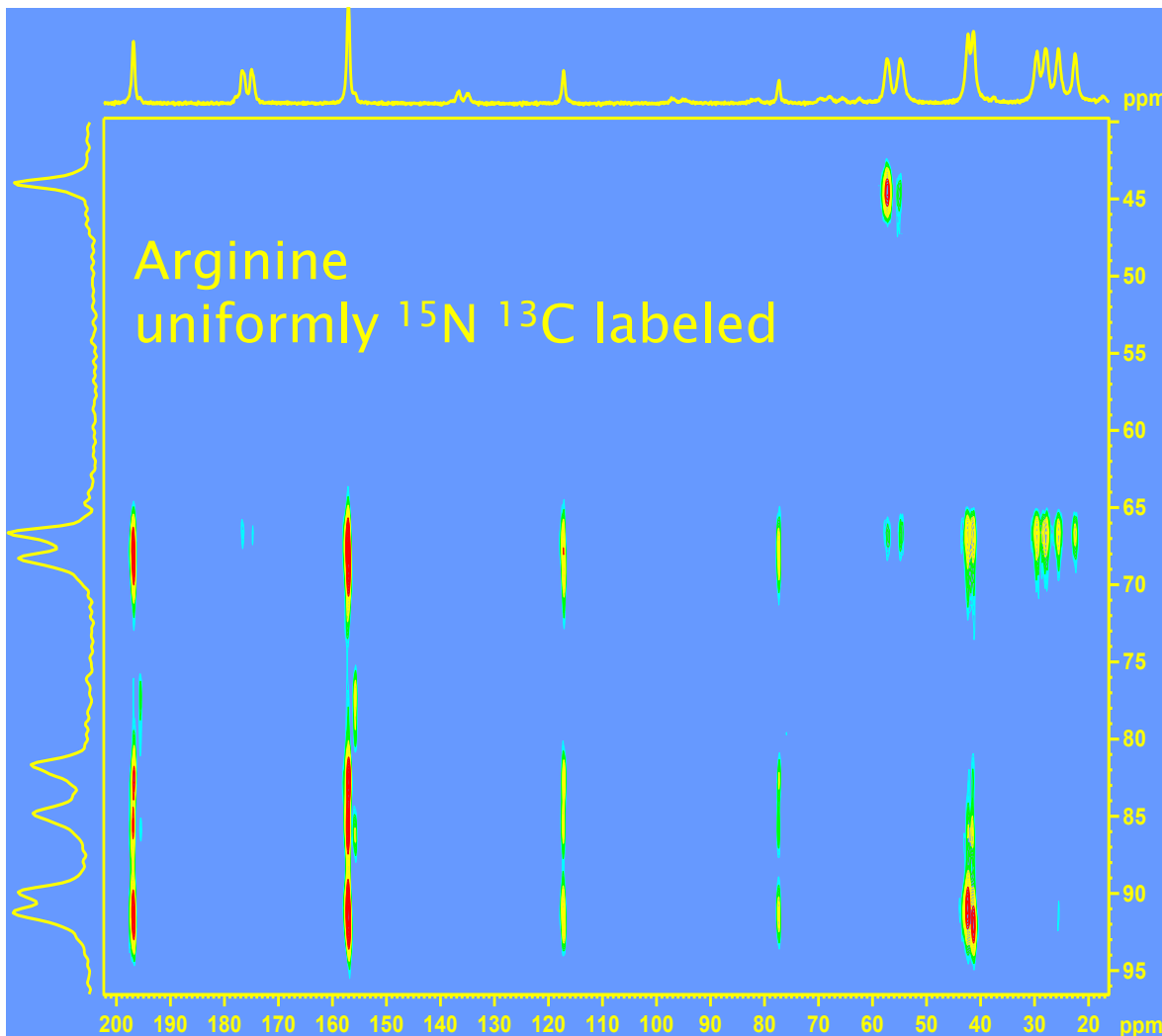


Double Cross Polarization



- DCP setup
 - Setup routing as in the DCP experiments
 - Use normal CP experiments to optimize HH for ^{15}N
 - Use normal CP experiment to optimize HH for ^{13}C without changing parameters on ^1H channel
 - Load DCP pulse program and all parameters as determined except the power level for HH contact between ^{15}N and ^{13}C . Subtract 3dB in power level for ^{13}C if ramp is used.
 - Calculate LG frequency offset for cw-LG decoupling during the second polarization transfer step
 - Run experiment as 1D and optimize ^{13}C contact
 - Load real sample setup 2D experiment.

Double Cross Polarization



• Avance 500 WB
4 mm probe

– $^1\text{H}/^{15}\text{N}$, 1 ms
contact

– $^{15}\text{N}/^{13}\text{C}$, 5 ms
contact

– variable amplitude
(50% ramp)

– ^{15}N rf field: 35 kHz

– ^{13}C rf field 35 kHz

– ^1H rf field: 72 kHz

Double Cross Polarization

Avance 600 WB

2.5 mm probe

$^1\text{H}/^{15}\text{N}$, 2 ms contact

$^{15}\text{N}/^{13}\text{C}$, 1 ms contact

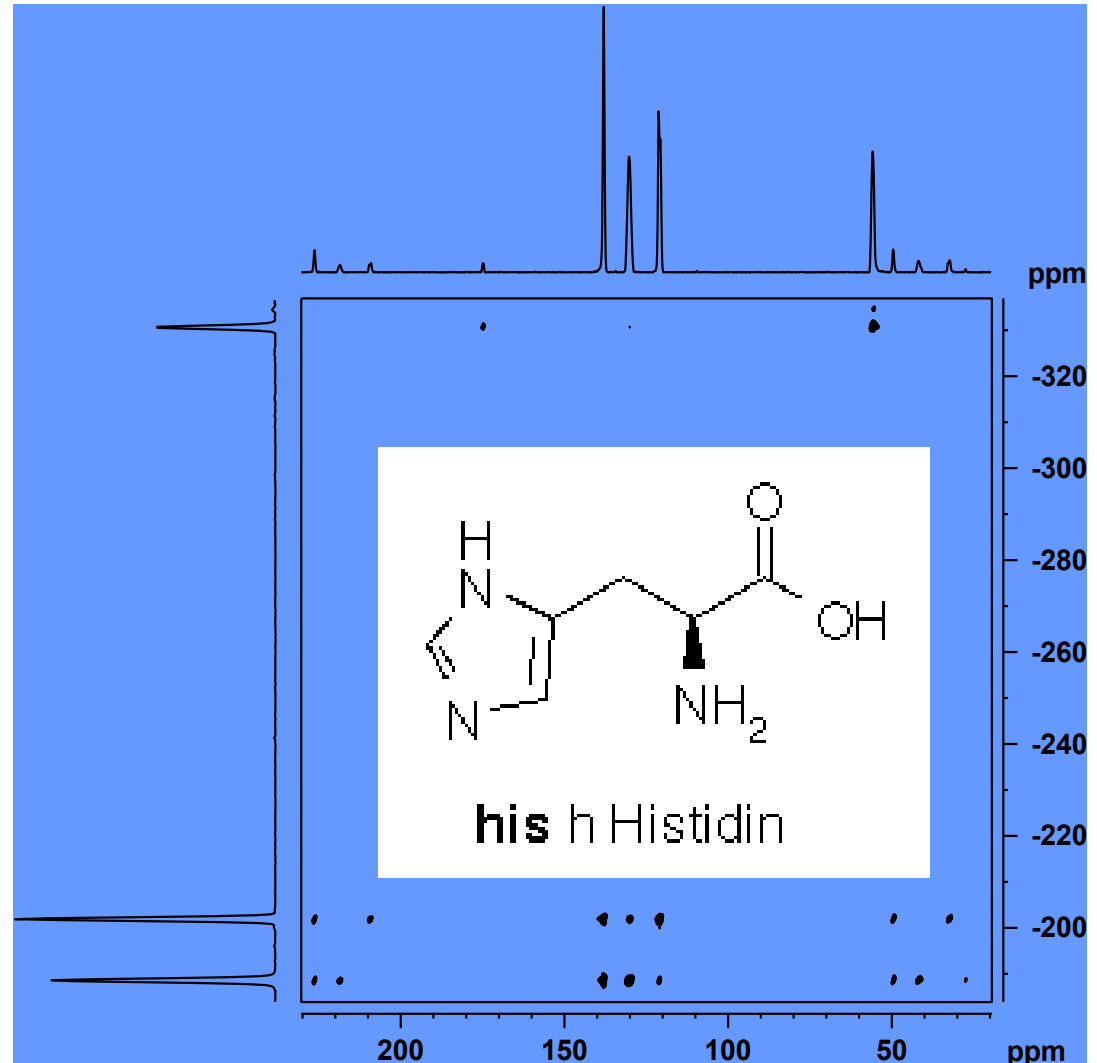
variable amplitude

(50 % ramp)

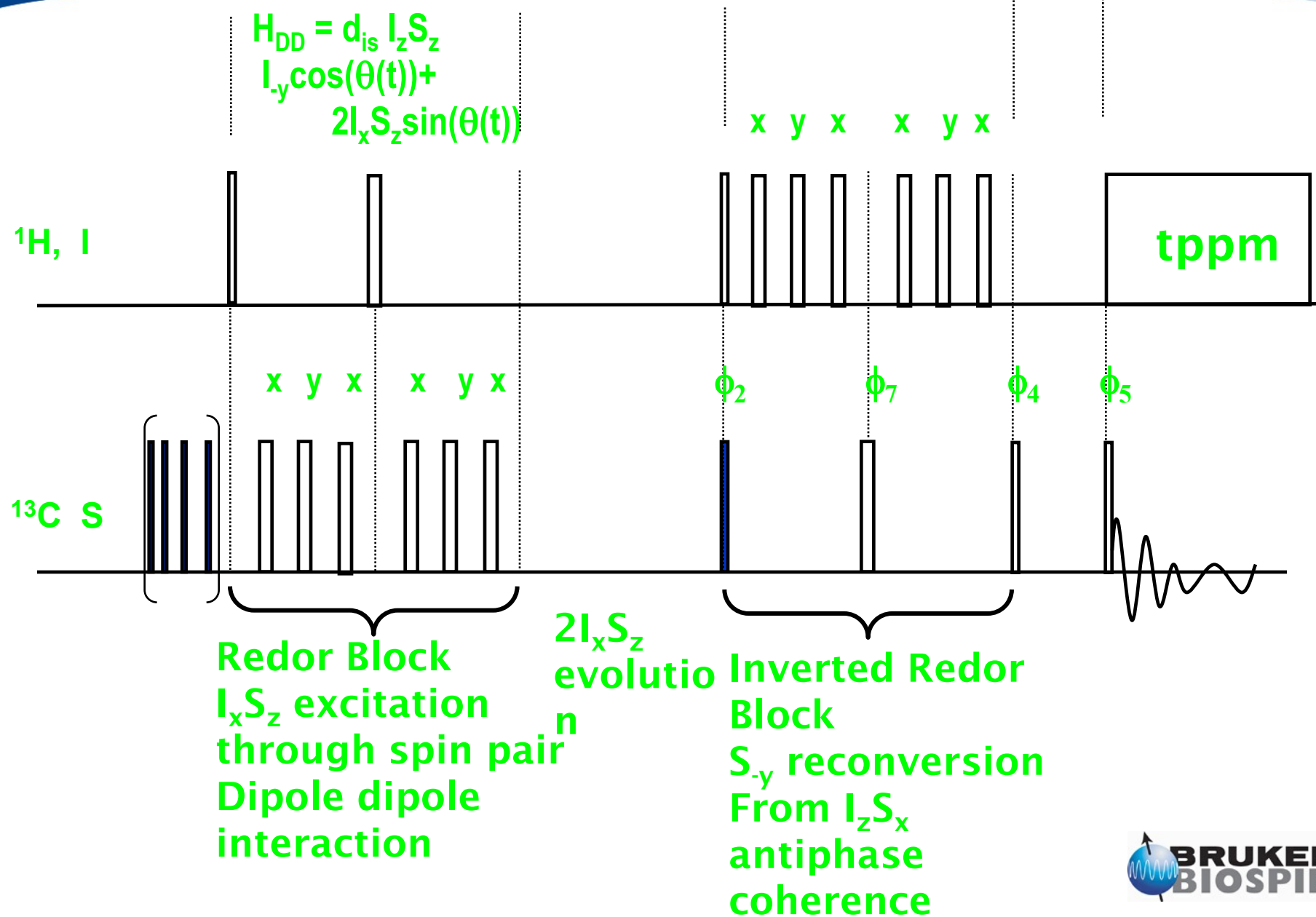
^{15}N RF field: 60 kHz

^{13}C RF field: 60 kHz

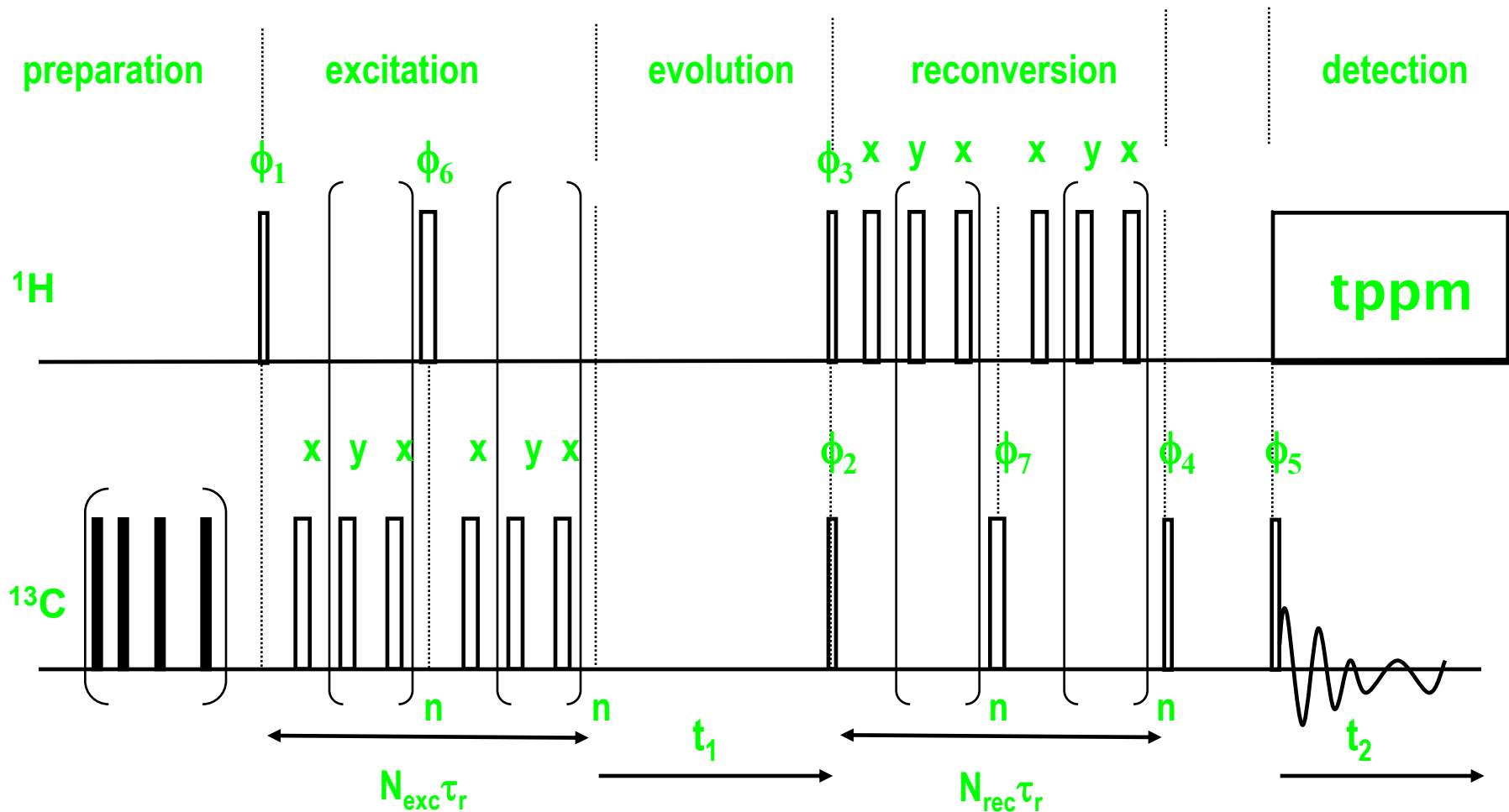
^1H RF field: 100 kHz



Recoupled Polarization Transfer HSQC



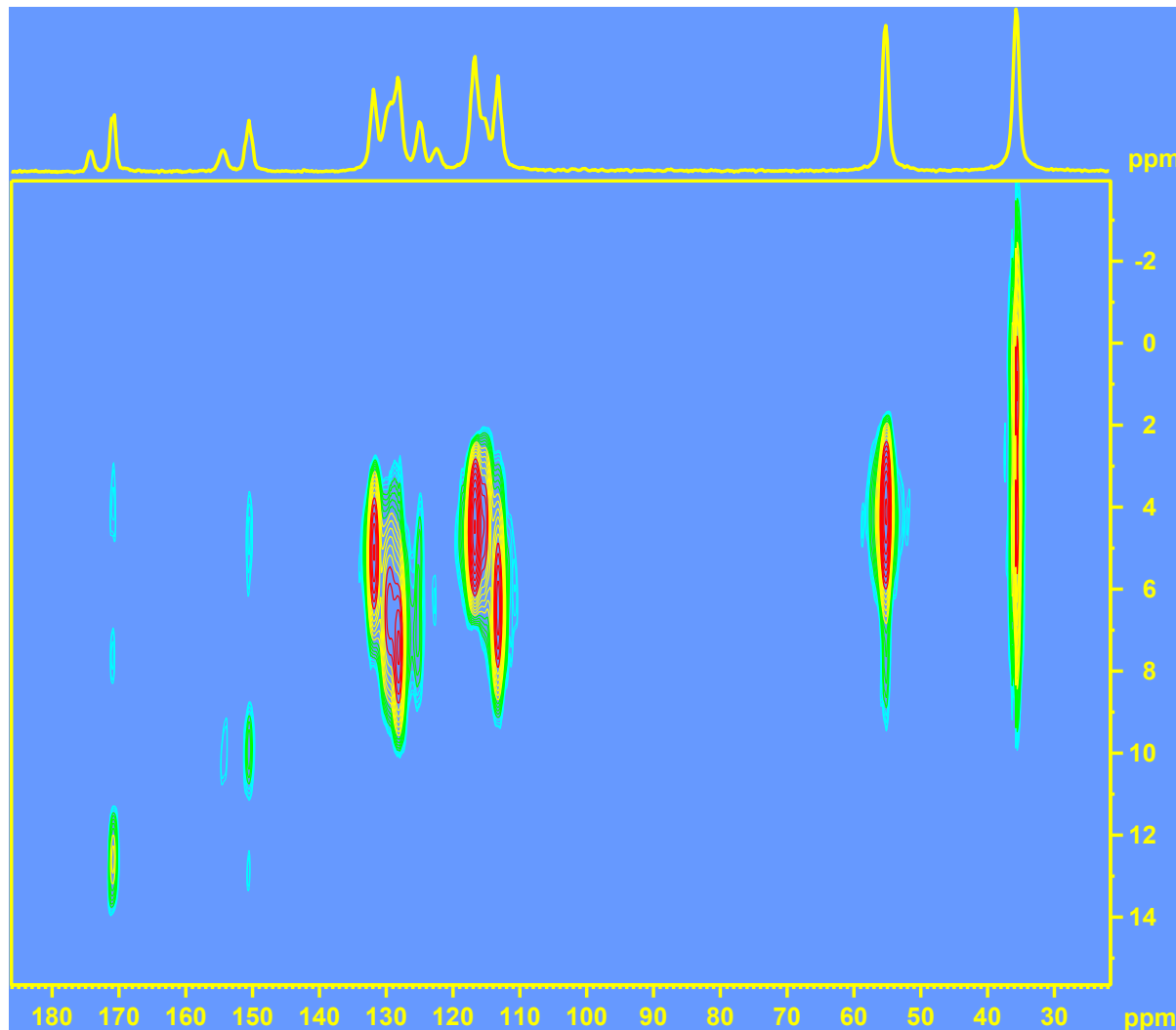
Recoupled Polarization Transfer HSQC



Recoupled Polarization Transfer HSQC



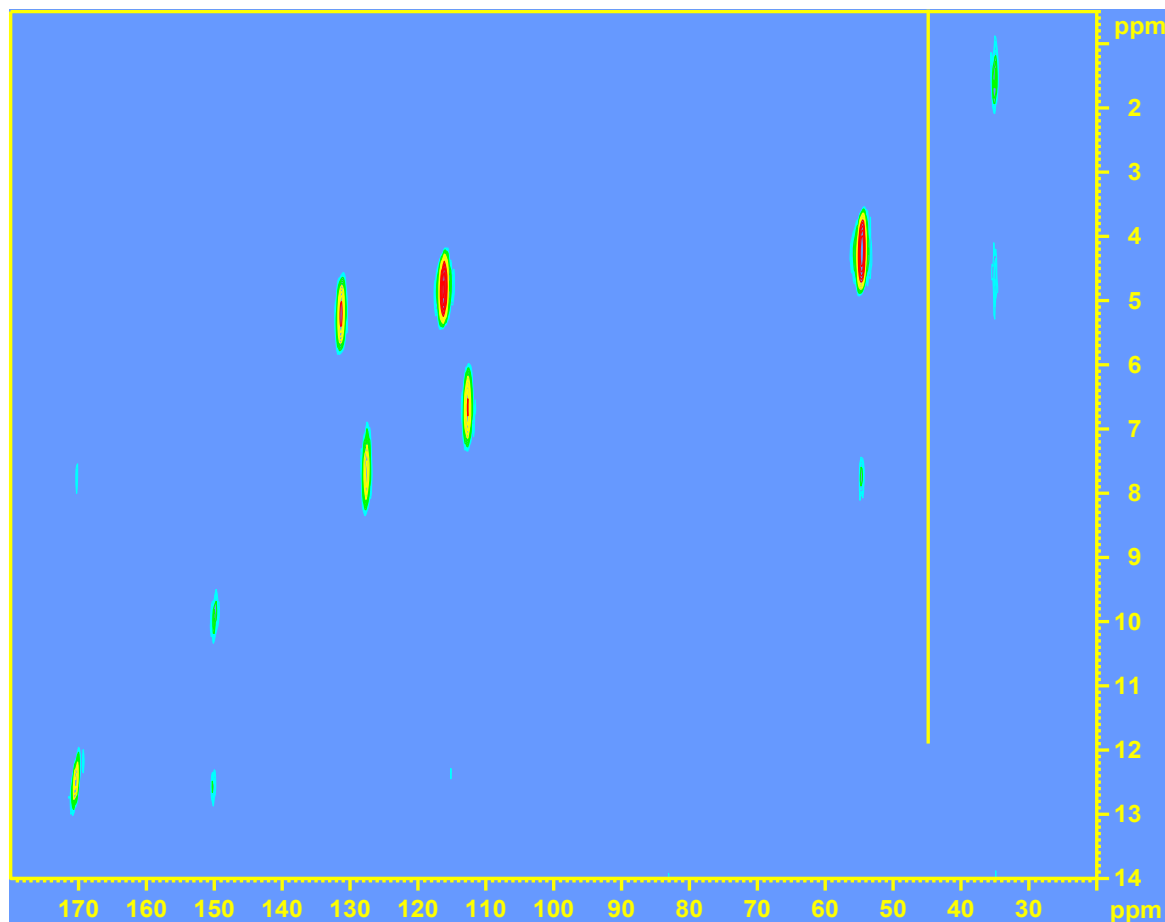
- Avance 500 WB
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
 - 33 kHz sample rotation
 - 16 scans
 - ^{13}C $\pi/2 = 2.3$ us
 - ^1H $\pi/2 = 1.3$ us
 - 38 min experiment



Recoupled Polarization Transfer HSQC



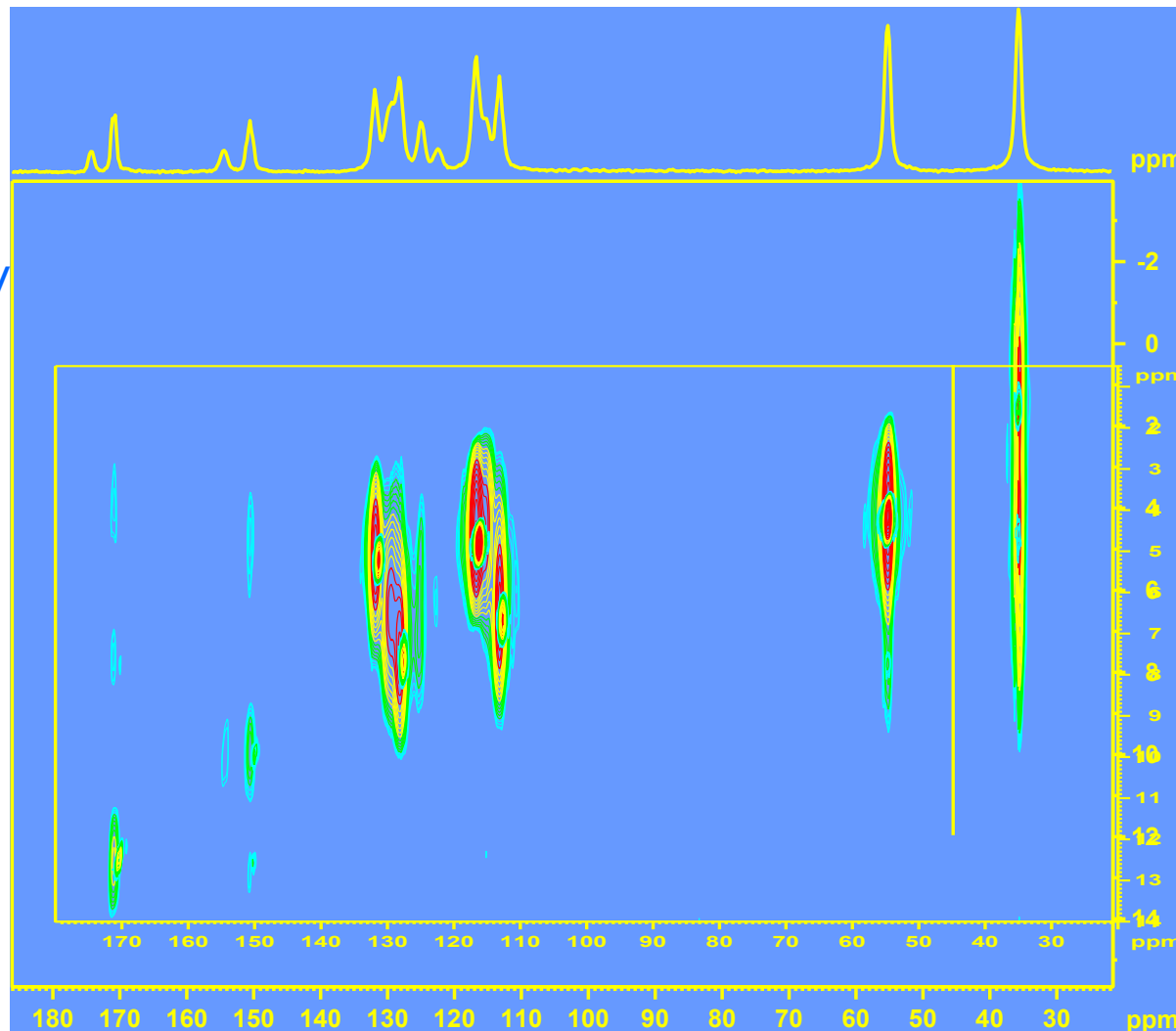
- Avance 700 SB
 - Courtesy of Graf et al.
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
 - 33 kHz sample rotation
 - 37 min experiment



Recoupled Polarization Transfer HSQC

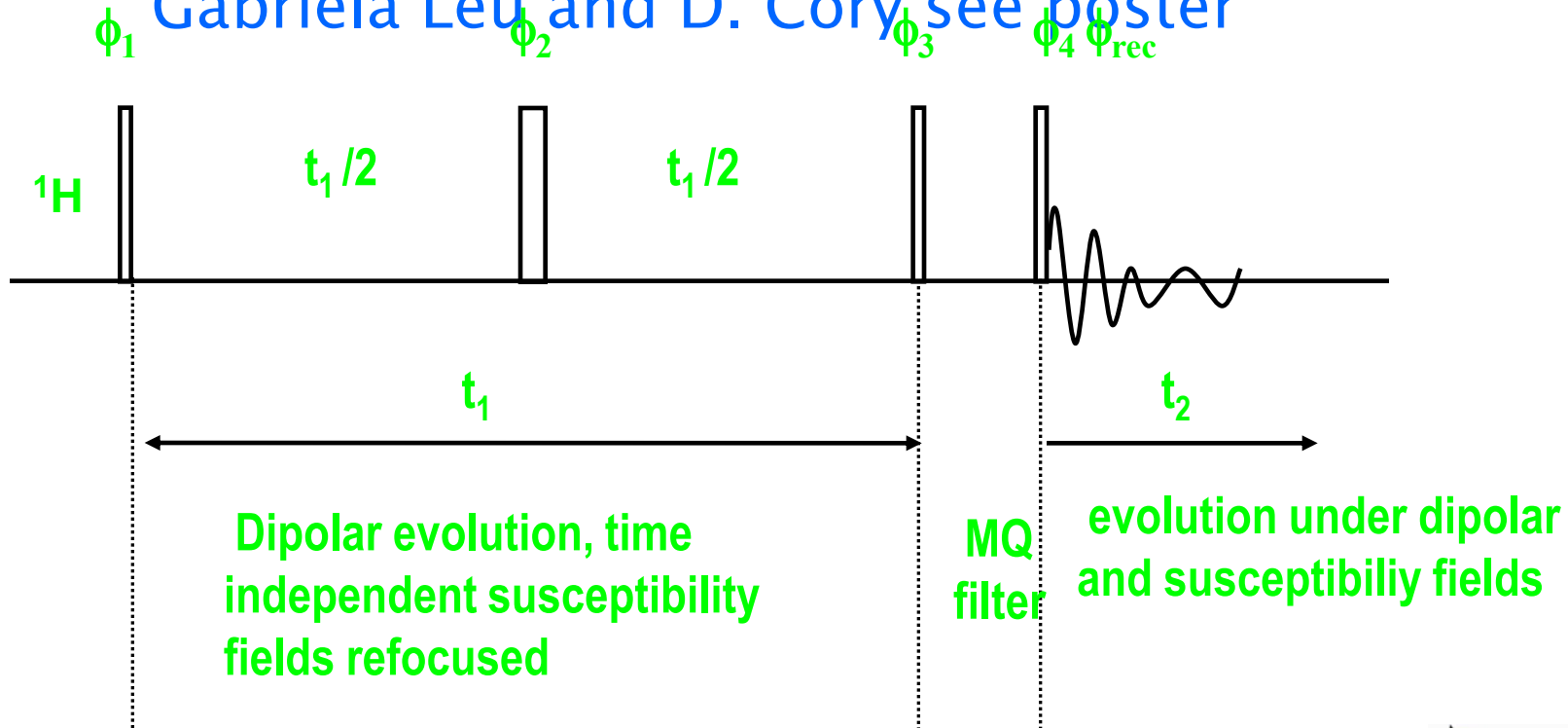


- Avance 700 SB
 - Courtesy of Graf et al.
- Tyrosine HCl uniformly labeled
- 2.5 mm probe
 - 33 kHz sample rotation
 -

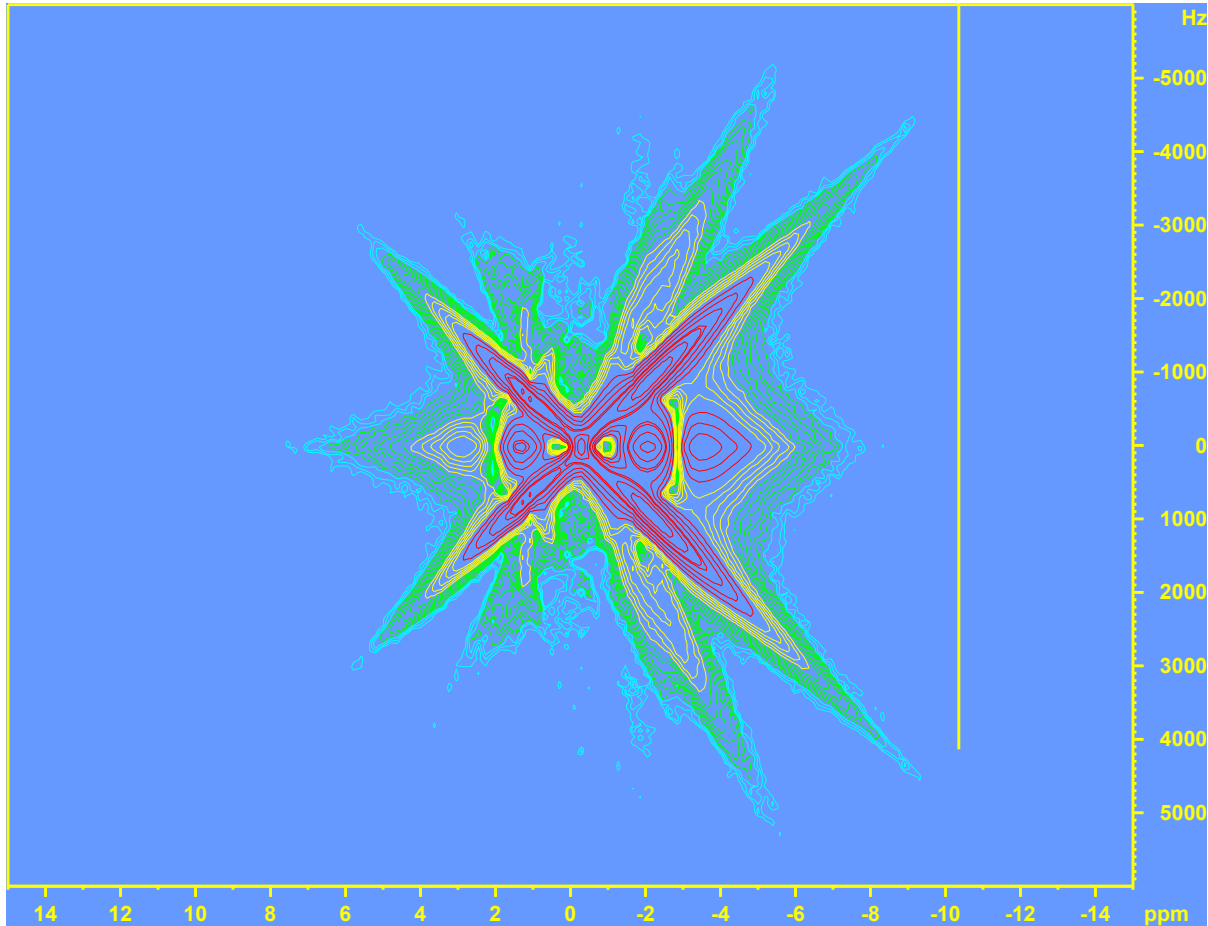


- Separated Local Field Spectroscopy
 - Experiment correlates susceptibility+dipole dipole interaction with dipole dipole interaction in f1.

Gabriela Leu and D. Cory see poster



Separated local field spectroscopy



Separated local field spectroscopy

