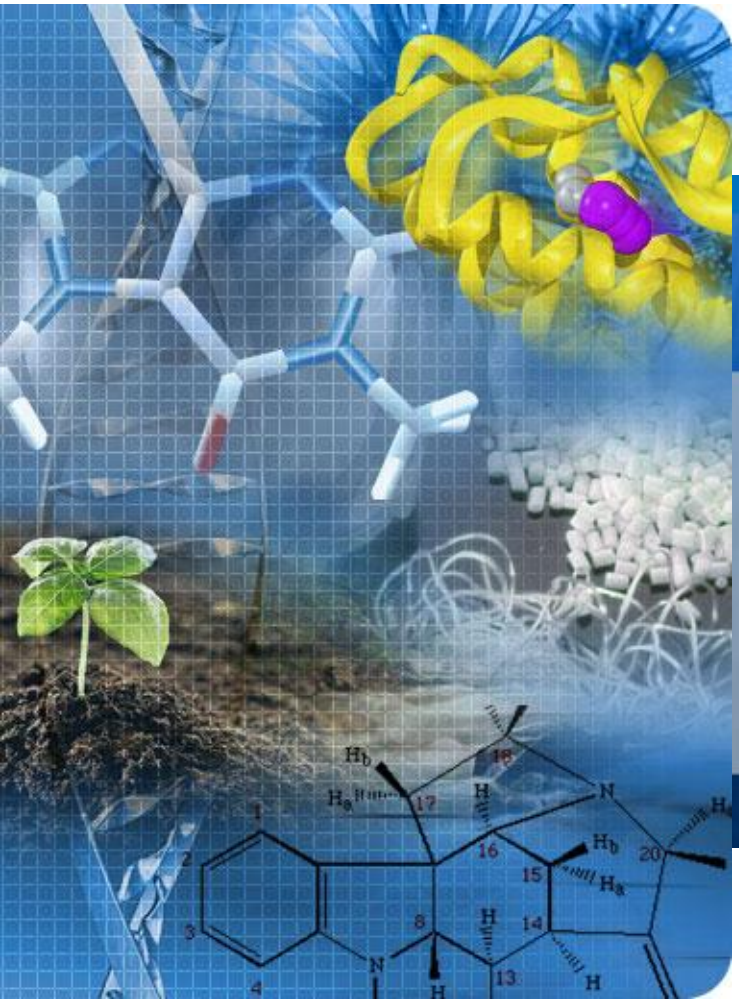


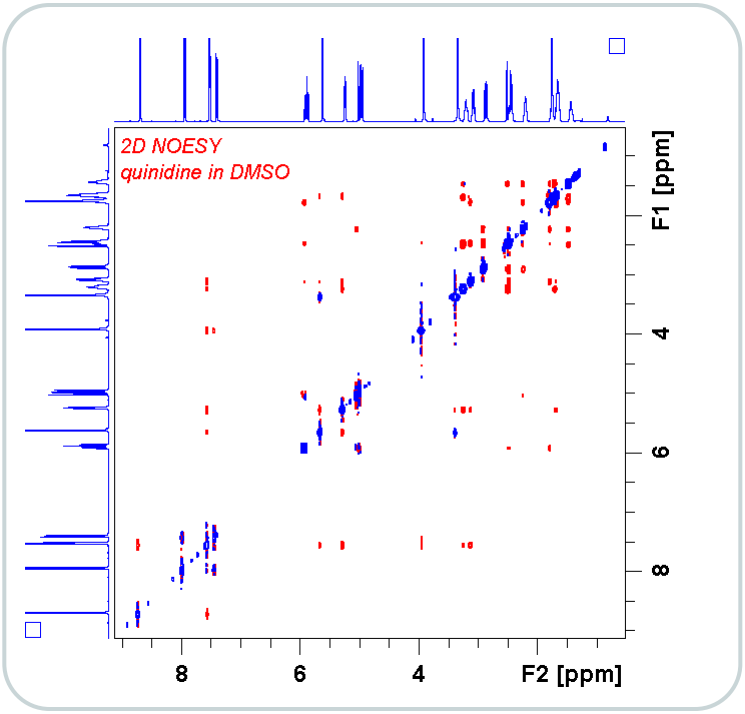
New tools for 1D and 2D selective experiments

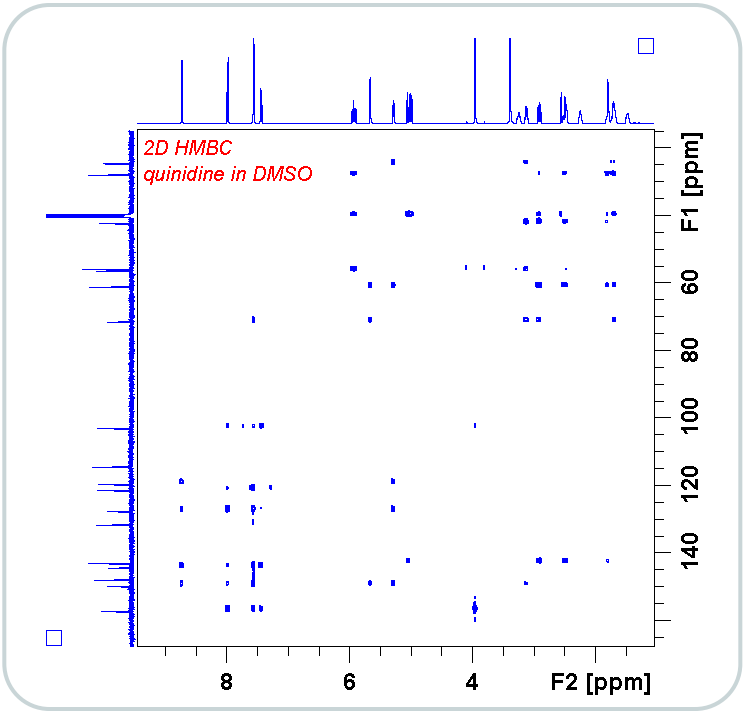
Eric Johnson

Symposium on Frontiers in Biomolecular NMR
Vanderbilt University
May 4, 2012

Why use selective experiments?

- 2D homonuclear and 2D heteronuclear experiments are easy to set up and are loaded with information

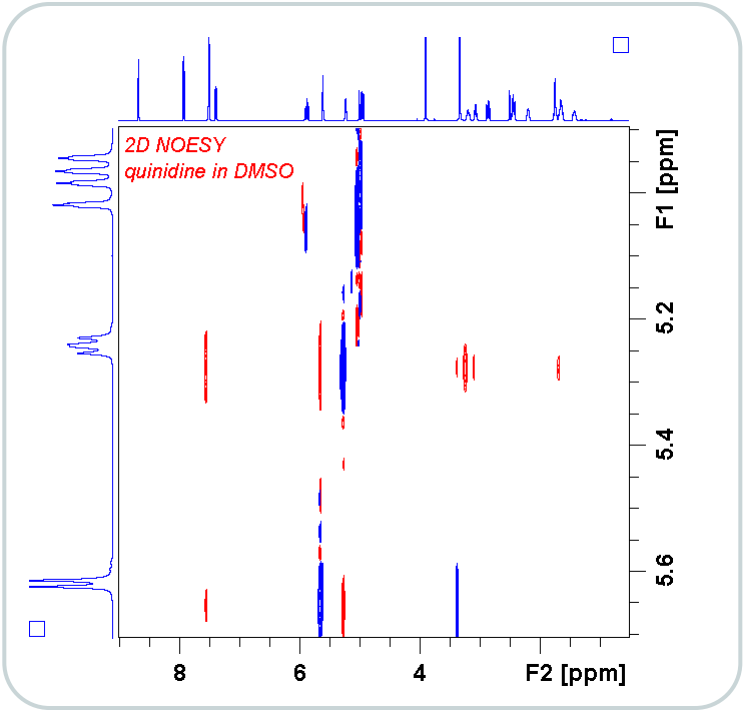




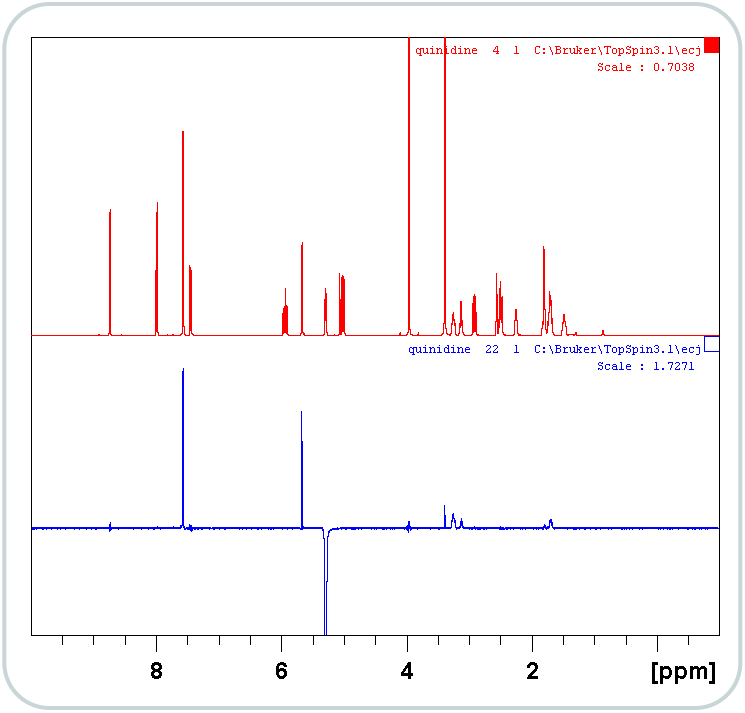
Individual experiments give correlations throughout the molecule

Why use selective experiments?

- When we're looking for a specific correlation



expt: 46 min

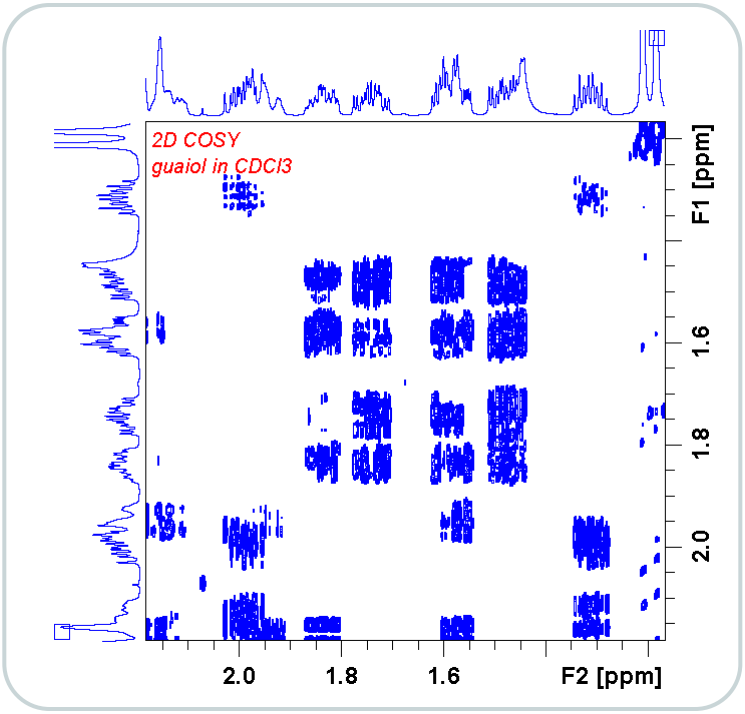


expt: 2 min 16 sec

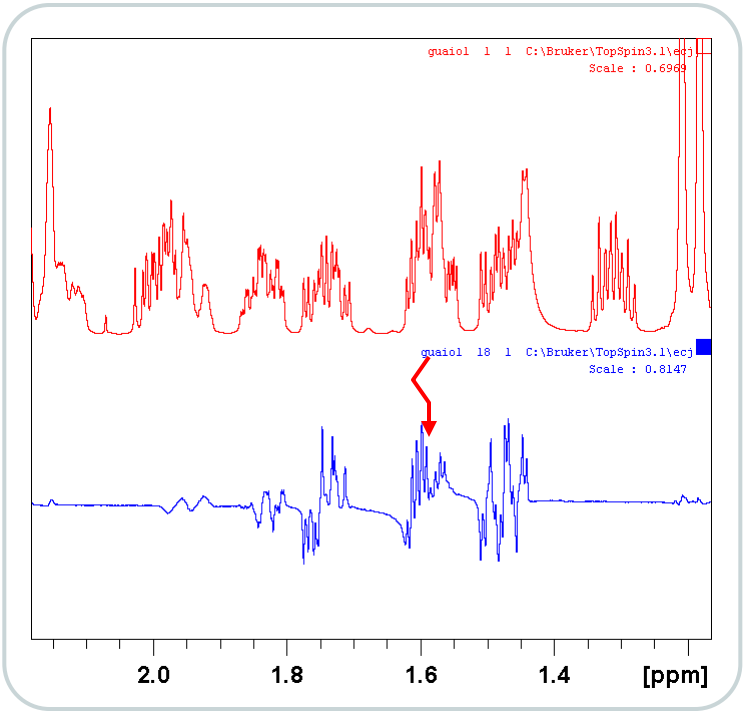
- Shorter acquisition time

Why use selective experiments?

- When we're looking for a specific correlation



expt: 7 min

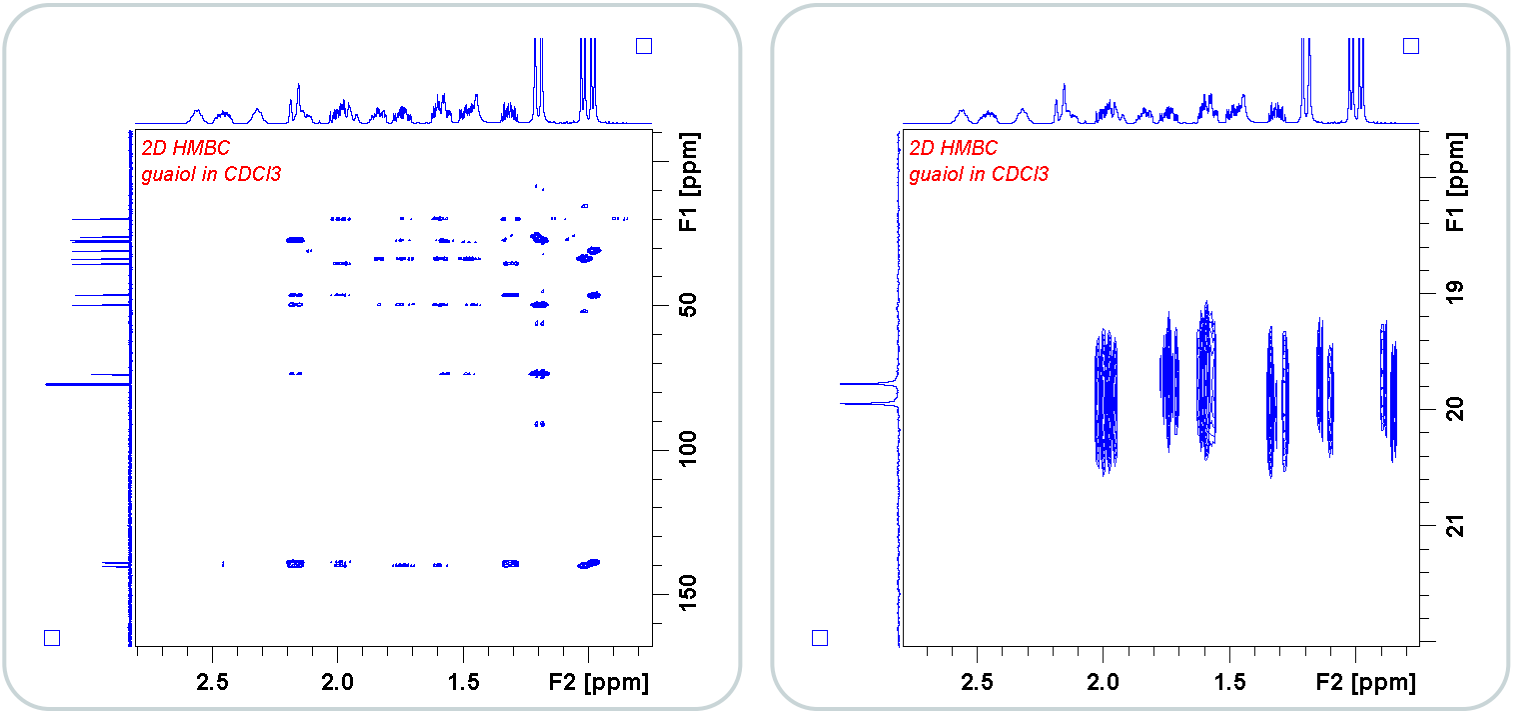


expt: 55 sec

- Selective 1D's have usually have higher resolution than 2D spectrum

Why use selective experiments?

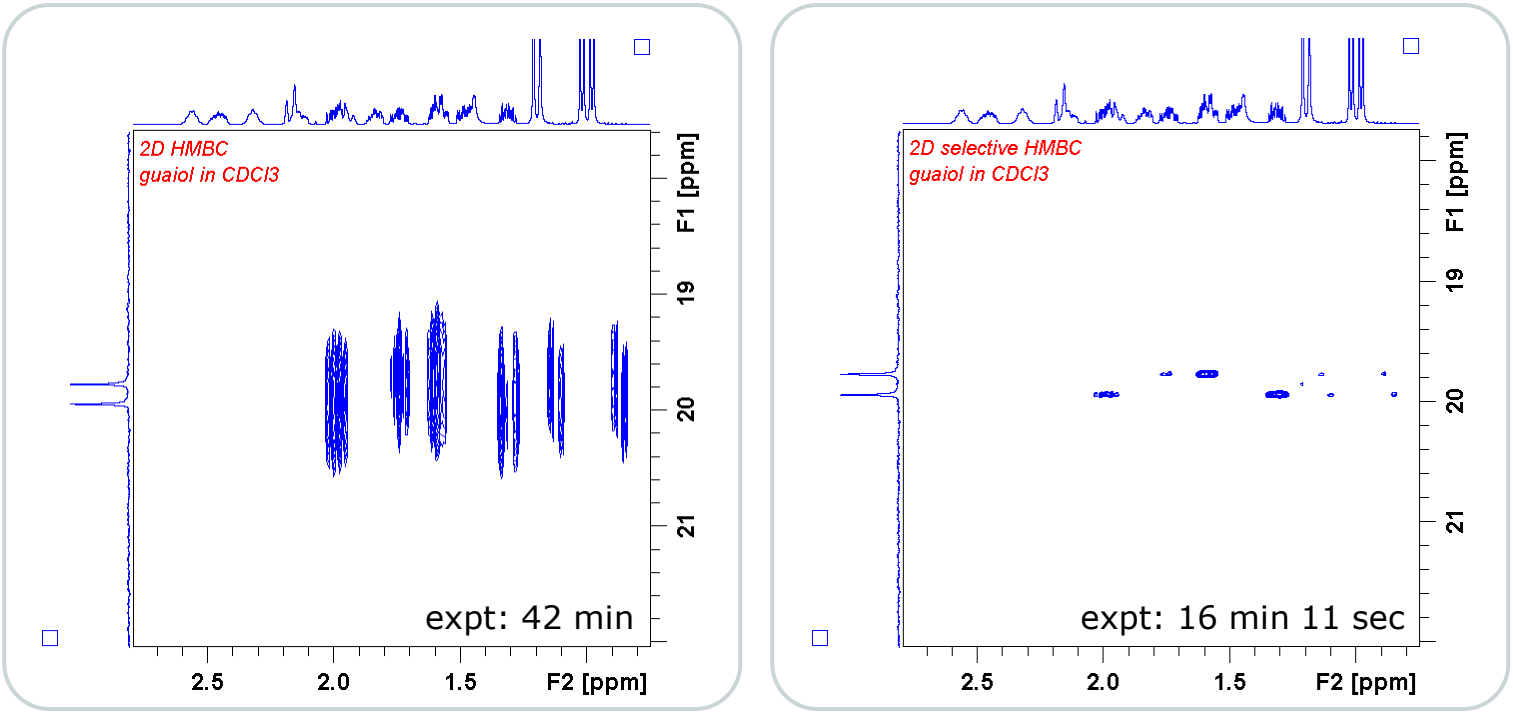
- When we need higher resolution for a specific region of the HMBC



- Increase TD(F1) ⟶ increase experiment time
- Decrease SW(F1) ⟶ aliasing/folding of peaks

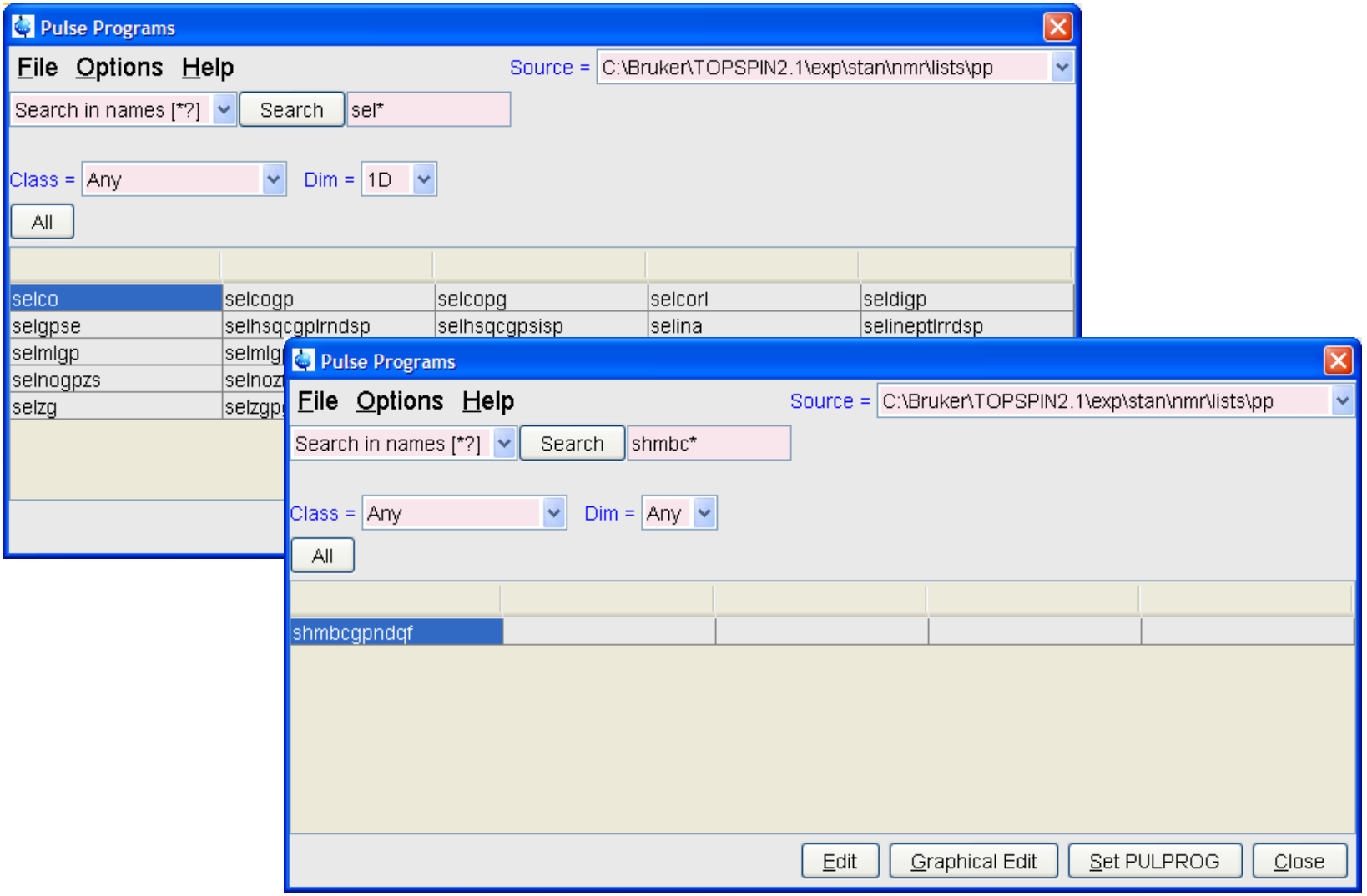
Why use selective experiments?

- 2D selective HMBC:

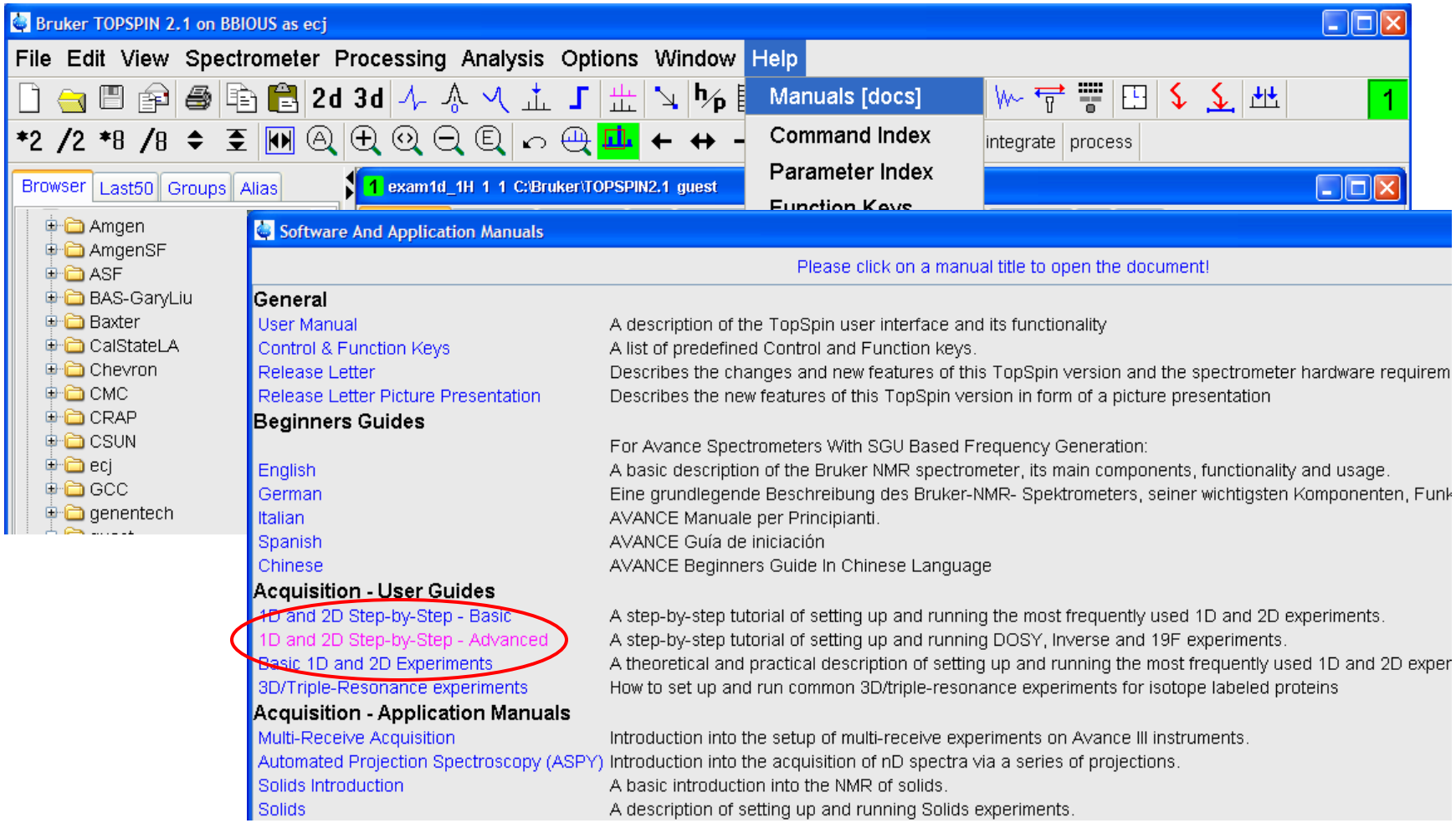


- Decrease SW(F1)
- Use ^{13}C selective pulse to prevent aliasing/folding

1D and 2D selective experiments aren't new



1D and 2D selective experiments aren’t new



1D and 2D selective experiments aren't new

1D and 2D Experiments
Step-by-Step Tutorial

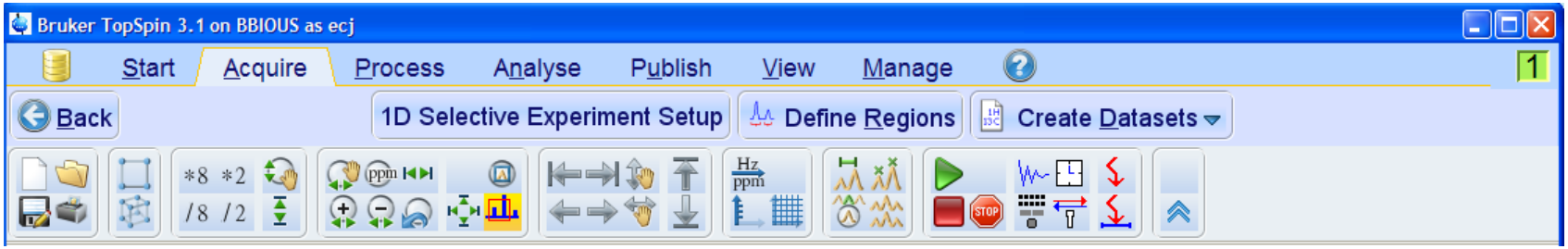
Advanced Experiments
User Guide

Setting up selective experiments in TopSpin2.1

- Easiest method for 1D sel. expts:
  - Selective excitation at center of spectrum (set O1)
  - Use shaped pulse from prosol
- Setting excitation frequency away from O1 requires manual calculation of offset
- Adjusting selectivity requires using ShapeTool
- Setting up 2D selective HMBC requires ShapeTool to calculate shape pulse parameters

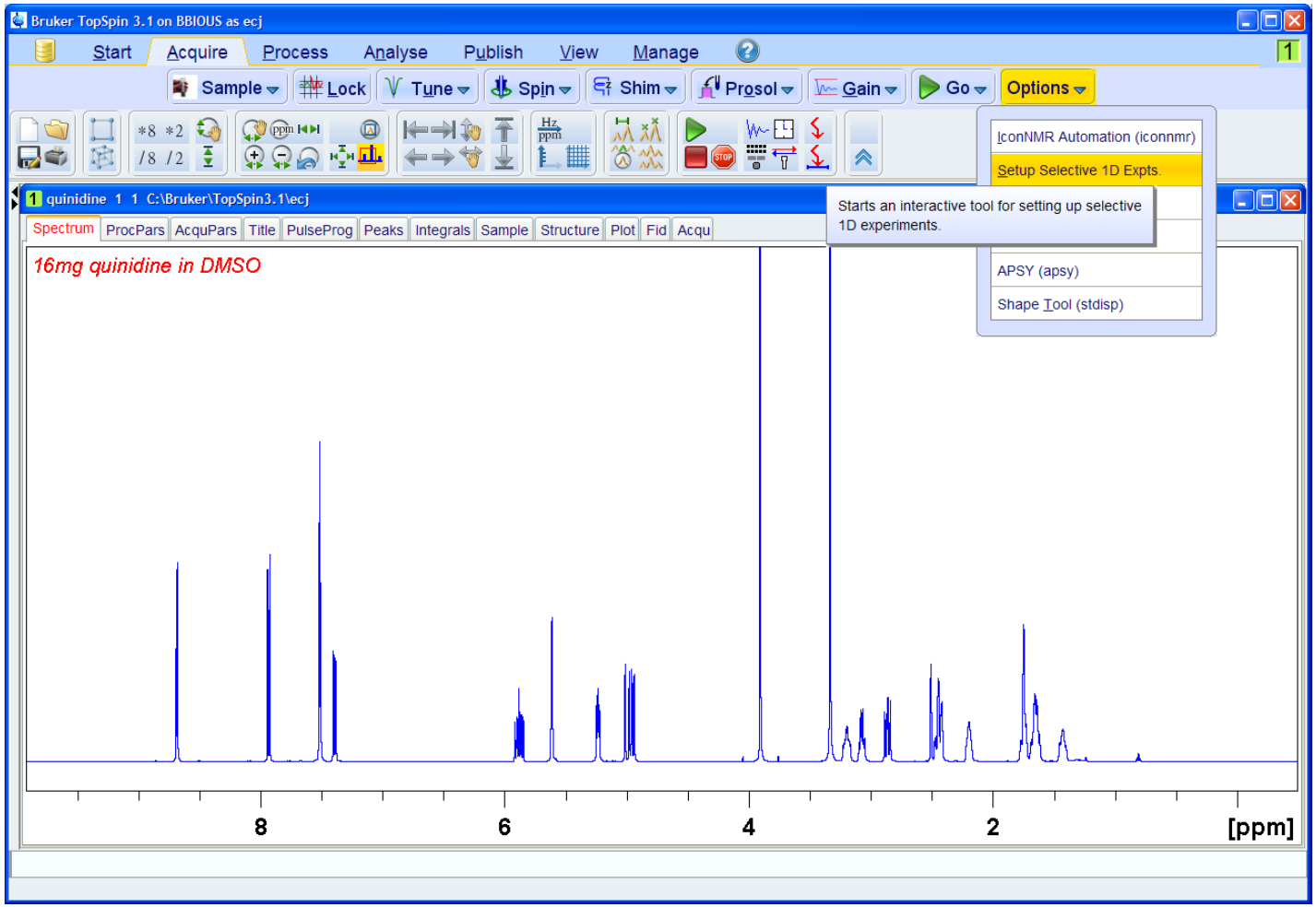
New in TopSpin3.1

- Flow interface to facilitate setting up selective experiments



- All calculations are performed automatically

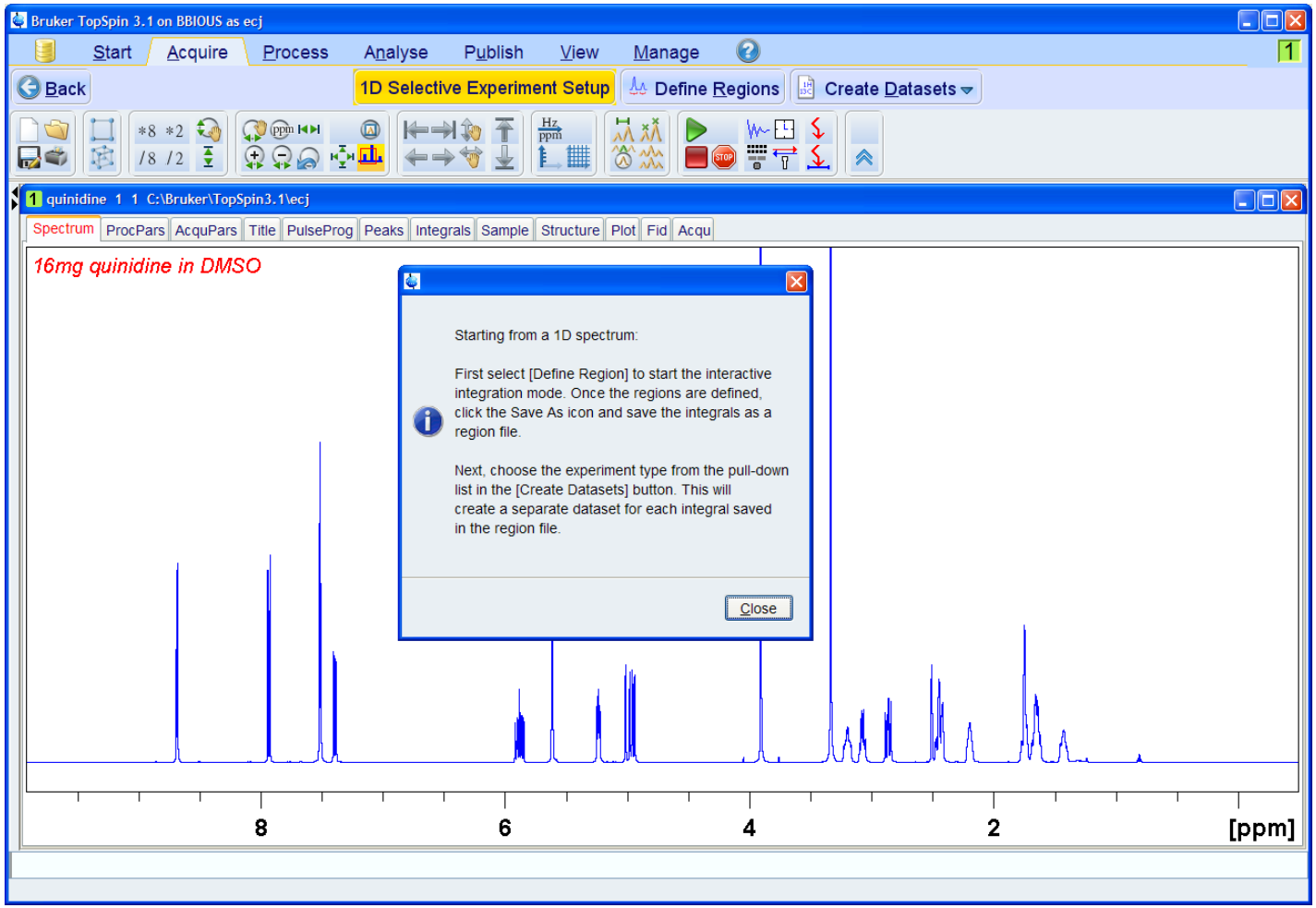
1D selective experiments



Step 1: Acquire and process a 1D PROTON

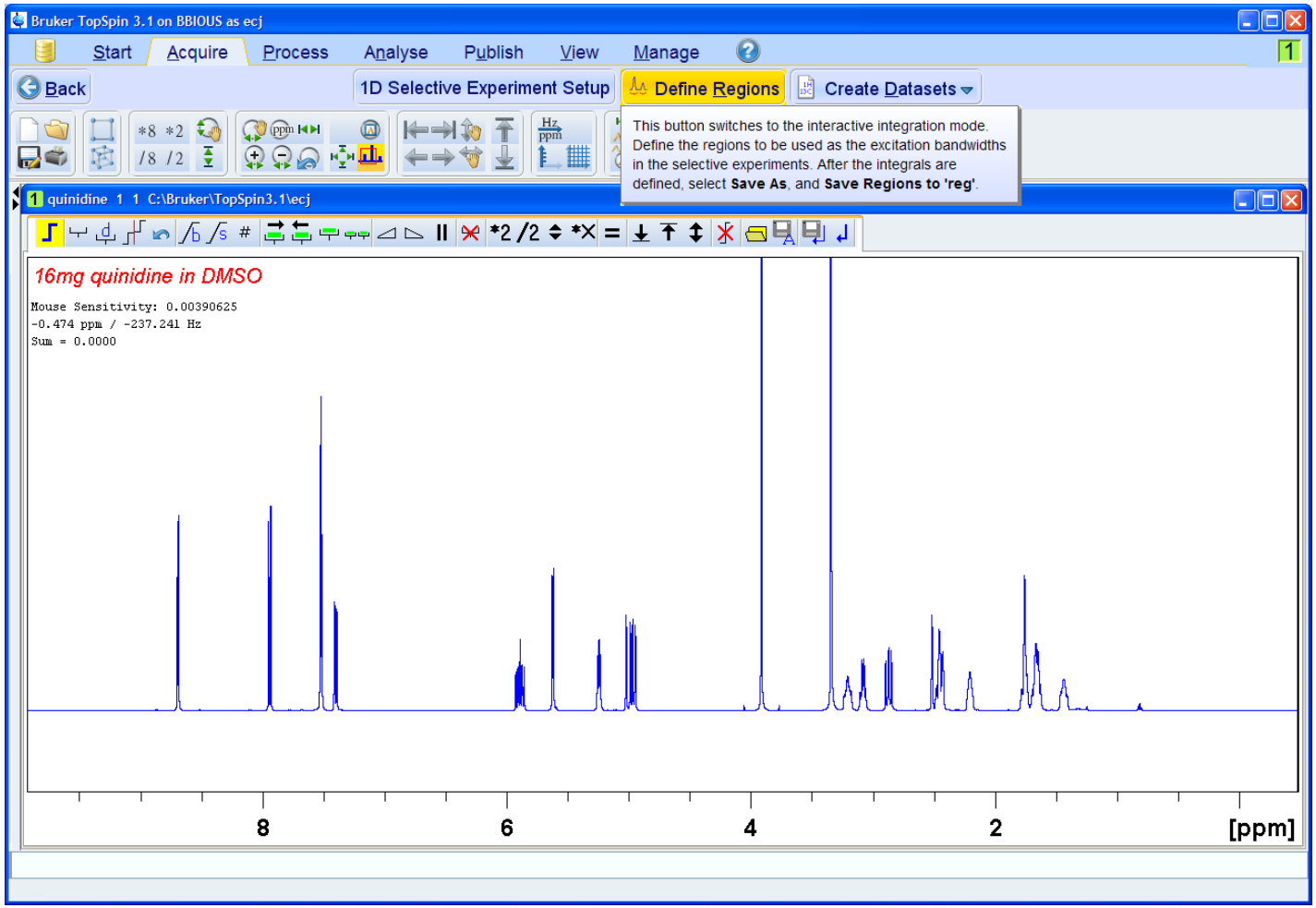
Step 2: Select Setup Selective 1D Expts. from Acquire → Options

1D selective experiments



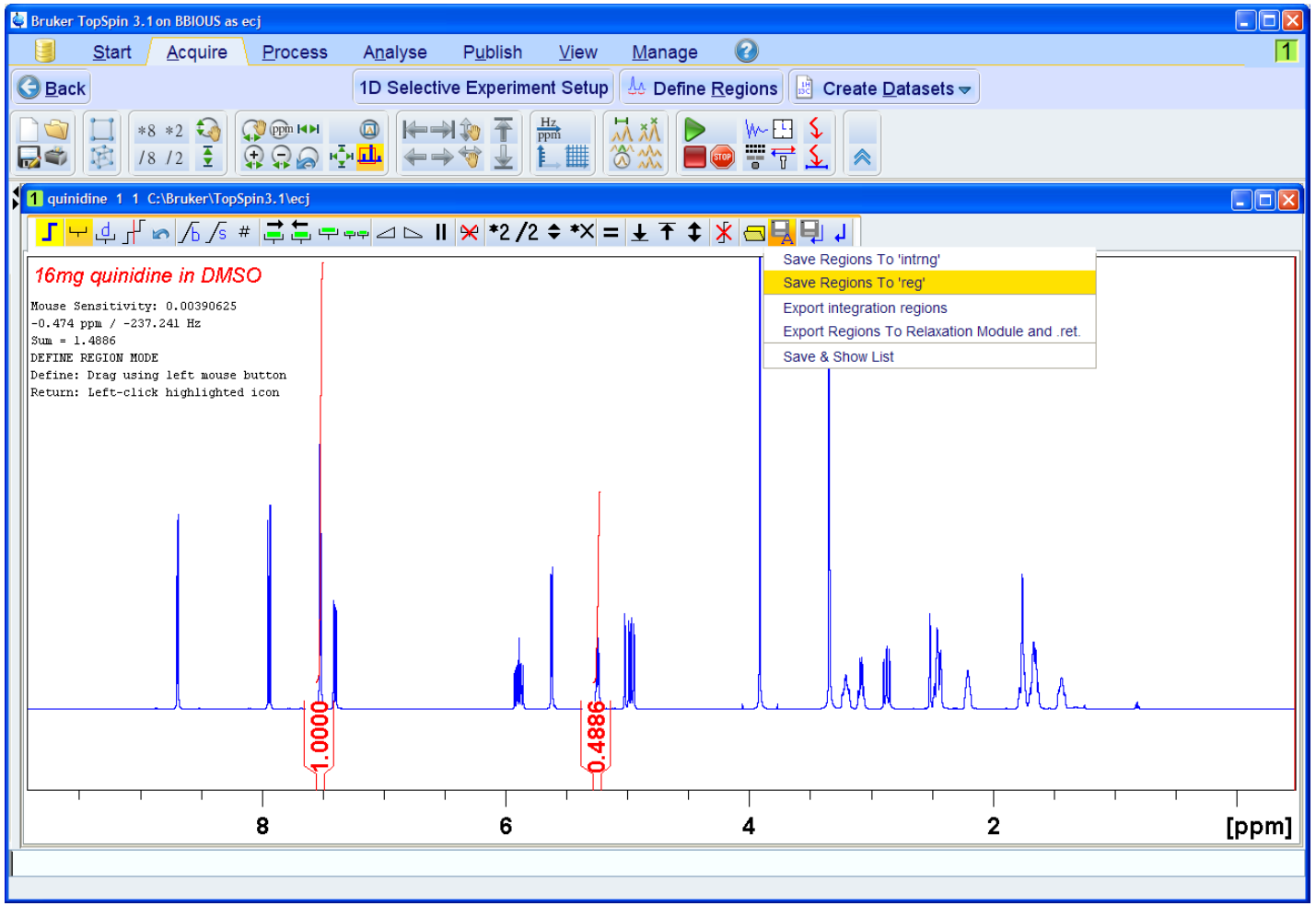
1st button gives instructions (but has no other functions)

1D selective experiments



Step 3: Click Define Regions button to start the interactive integration mode

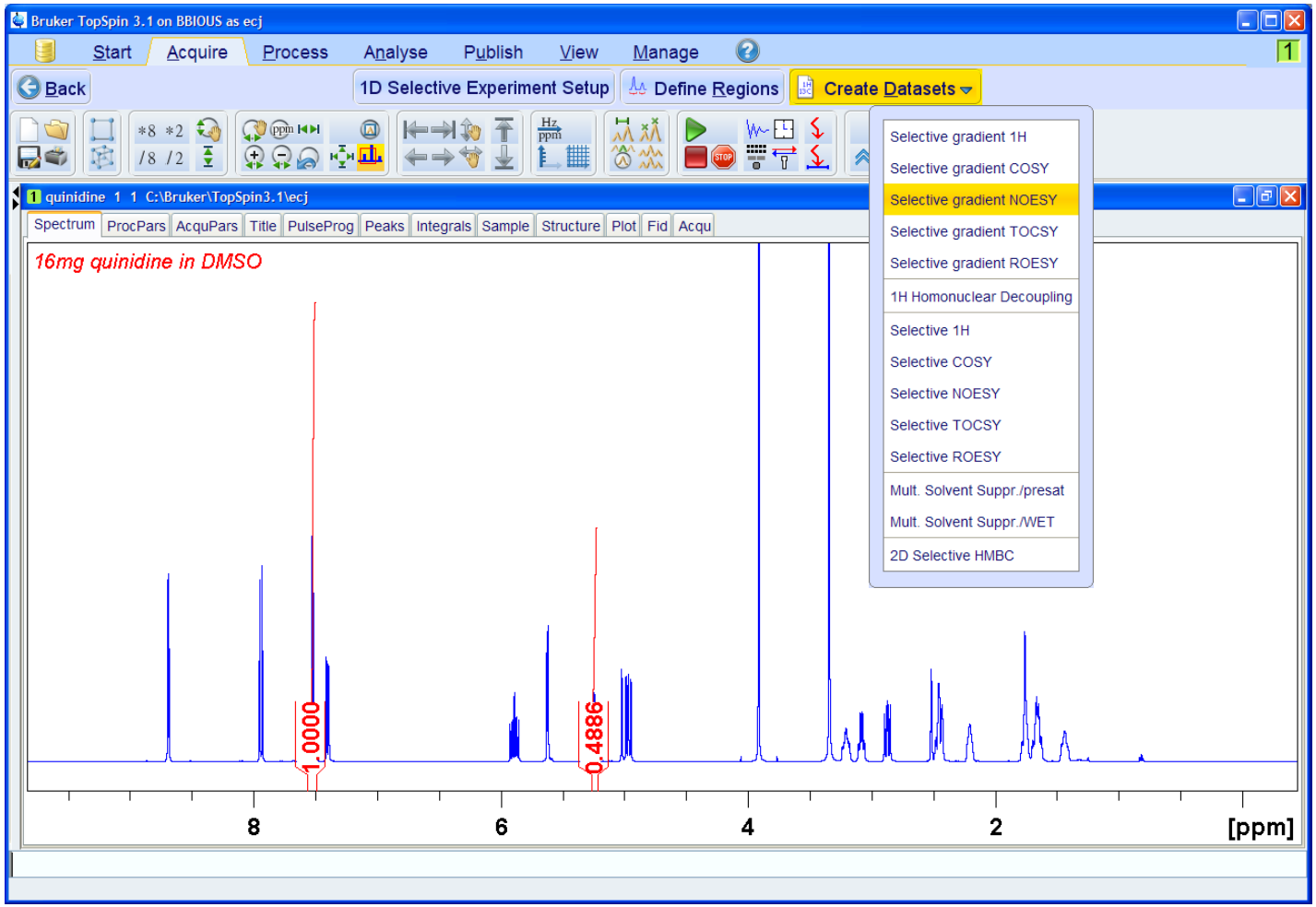
1D selective experiments



Step 4: Integrate peaks of interest and select  → Save Regions To 'reg'

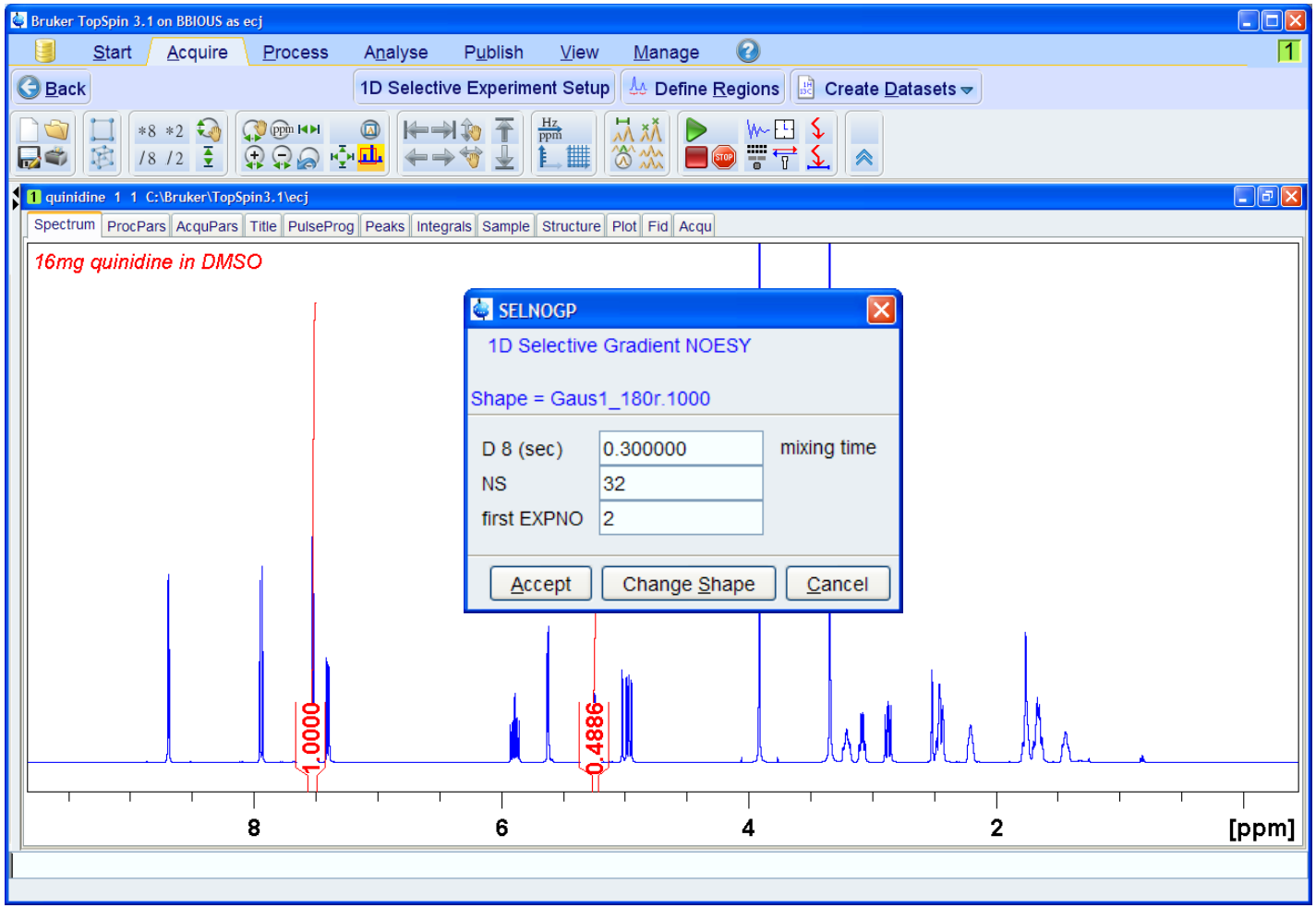
Step 5: Return from integration mode

1D selective experiments



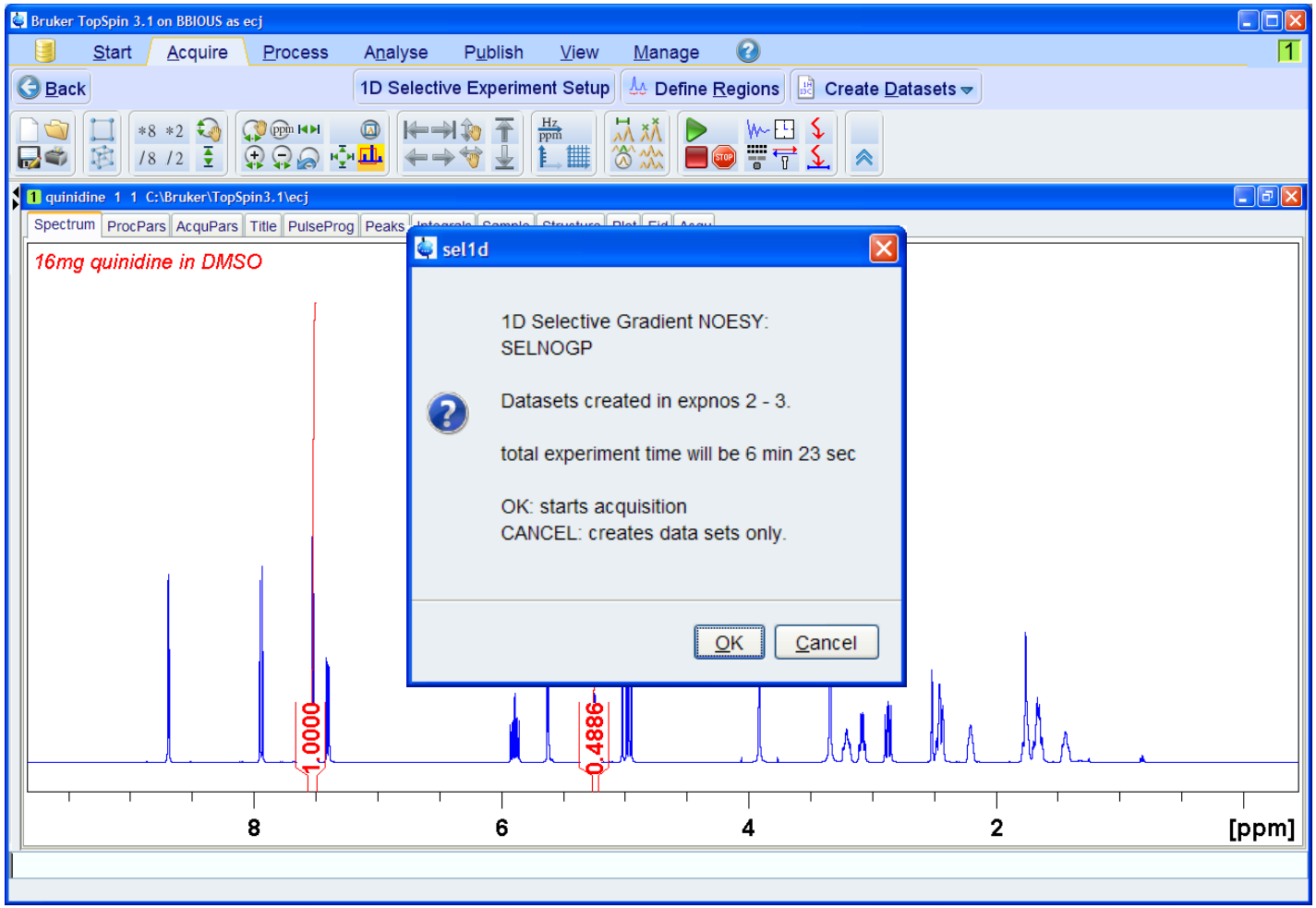
Step 6: Choose selective experiment from list under Create Datasets button

1D selective experiments



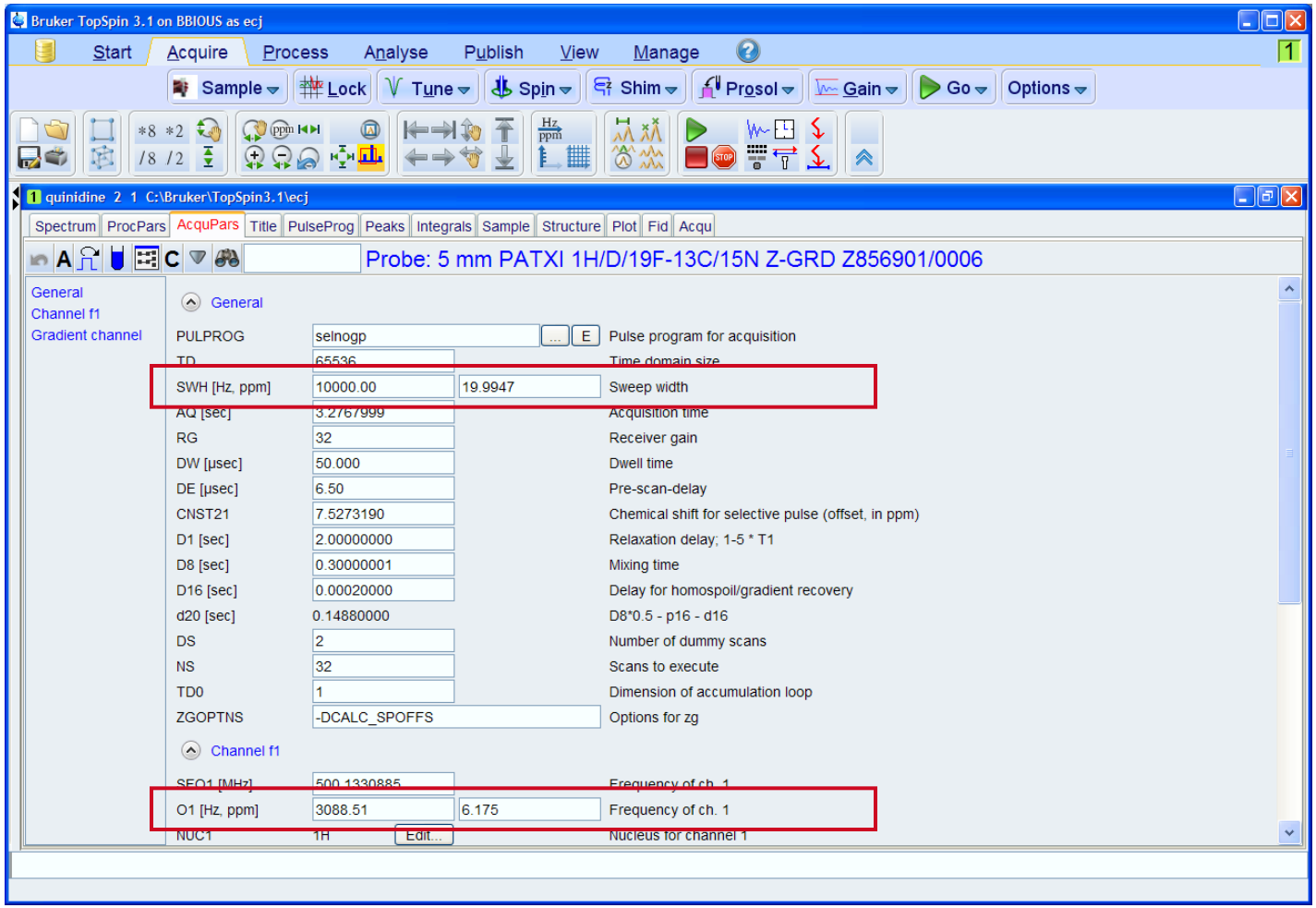
Default parameters are taken from standard parameter sets (i.e. SELNOGP)

1D selective experiments



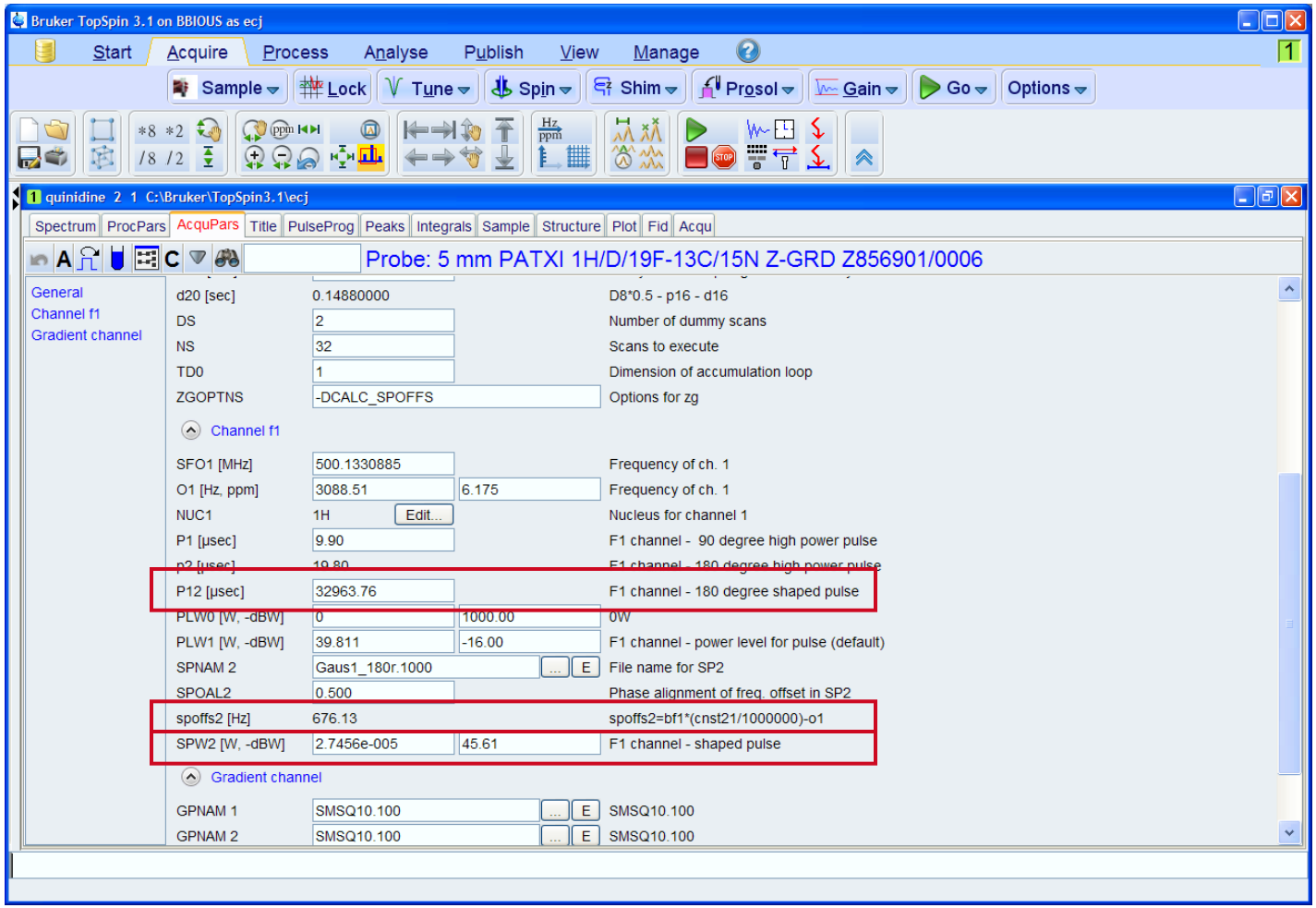
New datasets are created and all parameters are automatically set

1D selective experiments



SW and O1 are taken from starting 1D PROTON experiment

1D selective experiments



Power, duration and offset of shaped pulse are automatically calculated from integrals

1D selective experiments

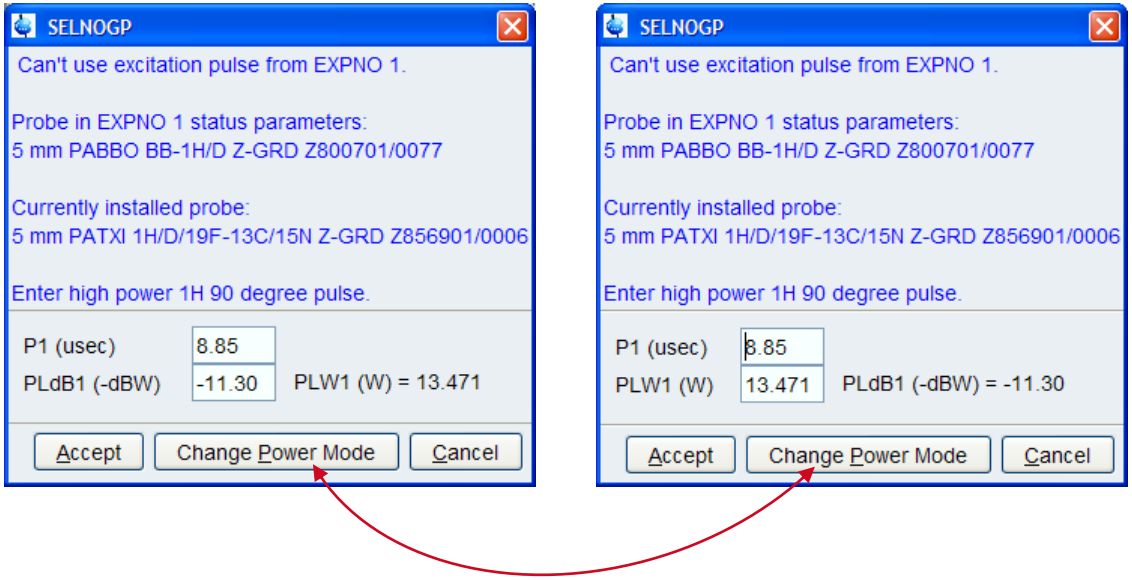
New modifications:

Compare currently installed probe with the probe used for starting EXPNO

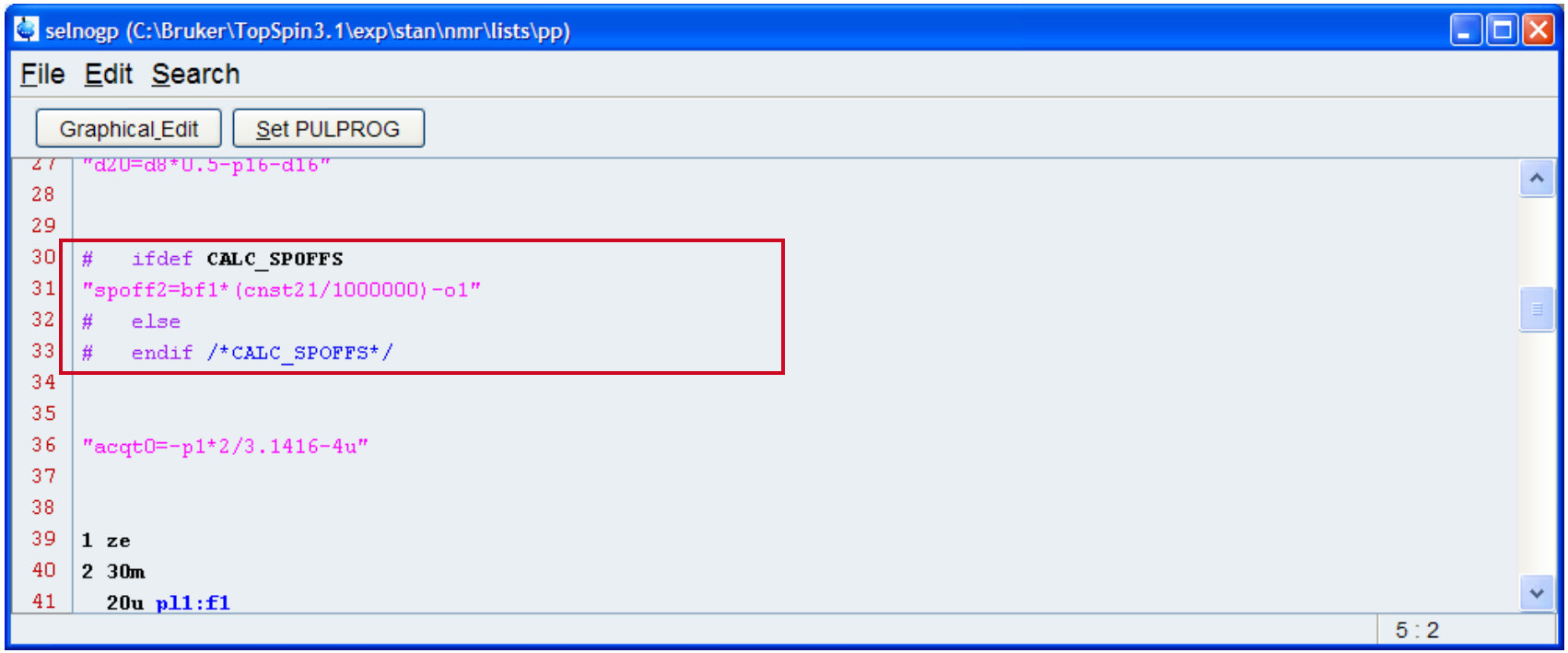
- If same probe: getprosol 1H <P1> <PLdB1>

From starting EXPNO

- If probes differ:



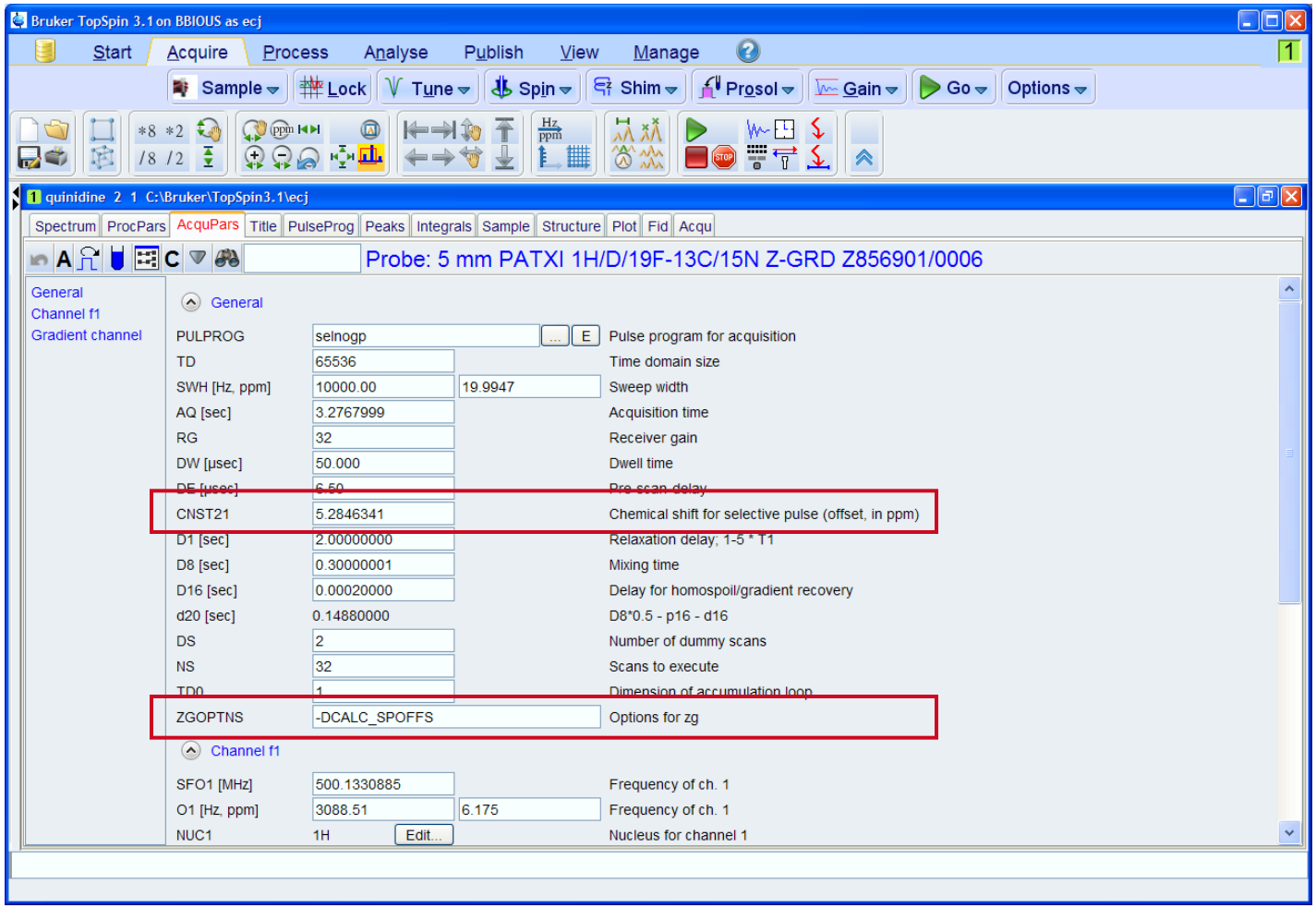
1D selective experiments



New modification to pulse programs calculates SPOFFS from CNST21

- Excitation frequency can be set by simply entering value into CNST21
- After selective experiment is set up, the spectral limits can be changed without affecting the selective excitation frequency.

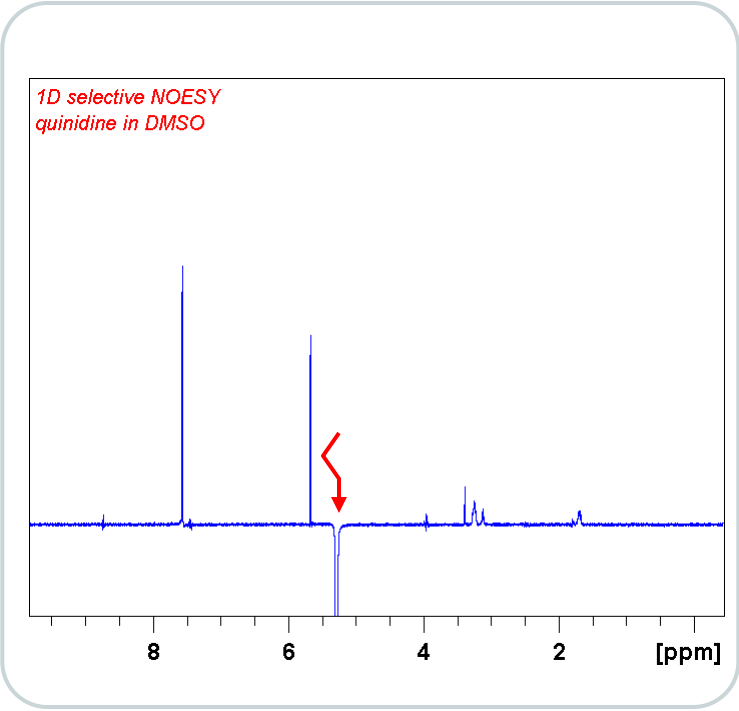
1D selective experiments

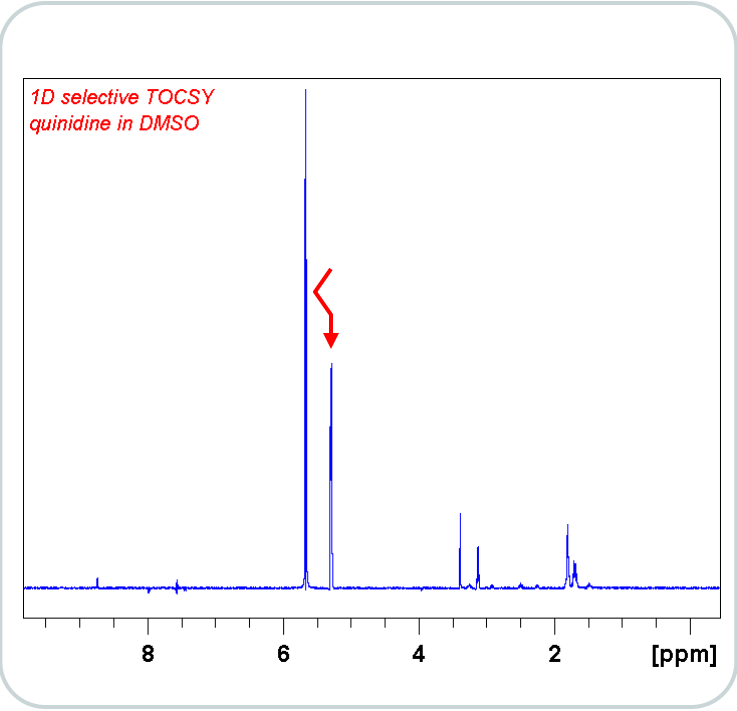


Chemical shift of excitation pulse is stored in parameter CNST21

1D selective experiments

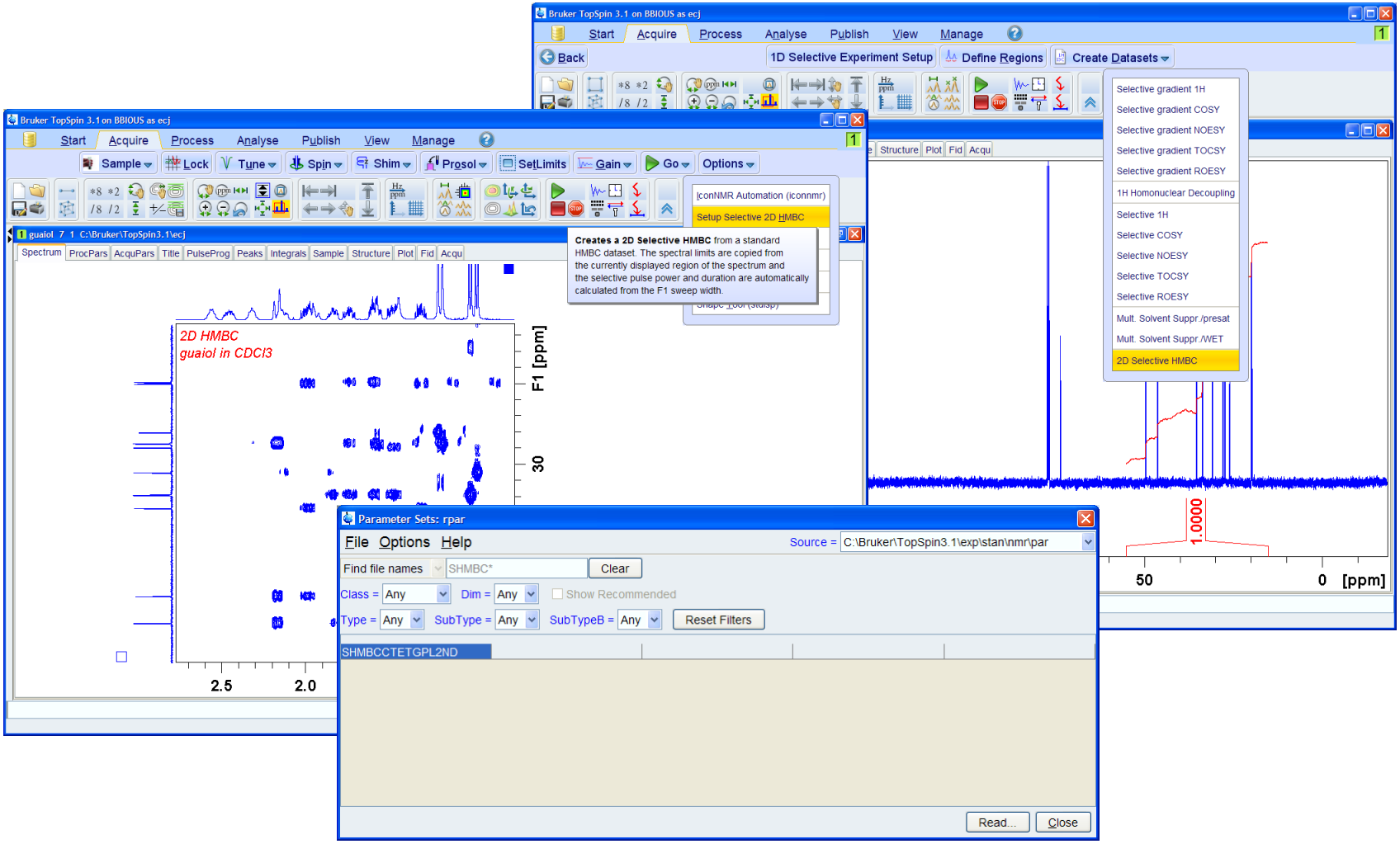
Excitation frequency is not always obvious in 1D selective experiments



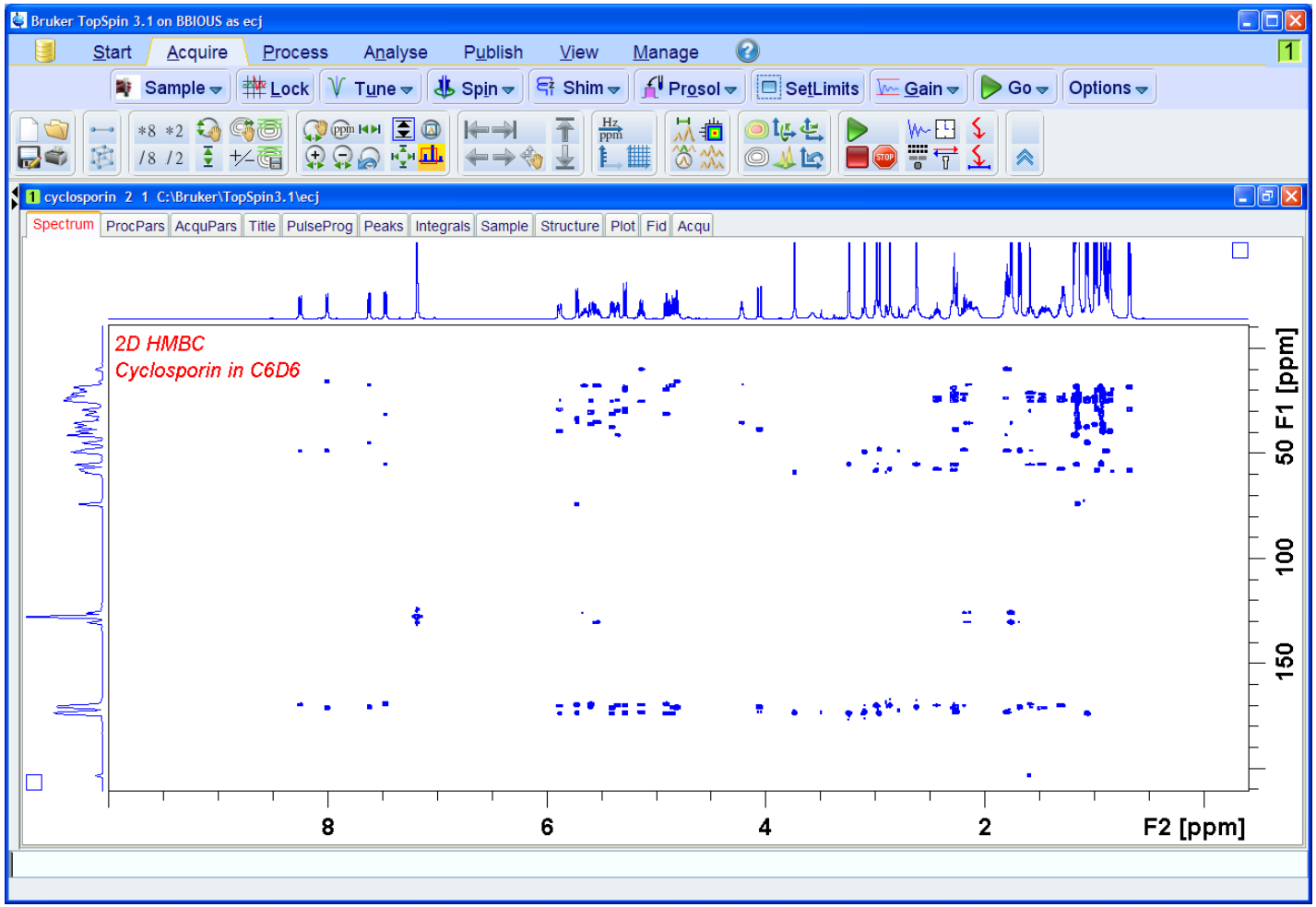


CNST21 = 5.28 in both spectra

2D selective HMBC

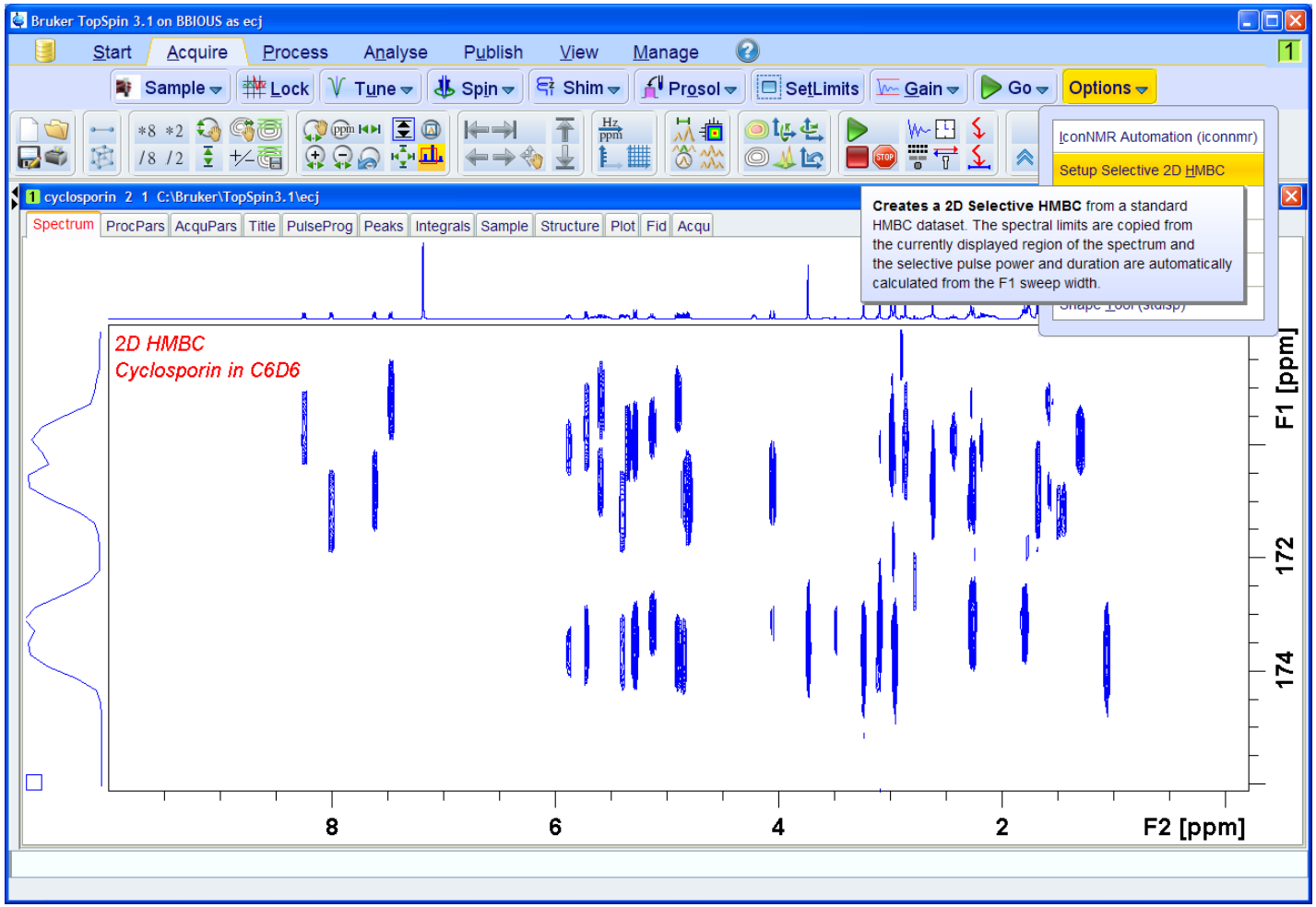


2D selHMBC



Method 1: Start by acquiring a standard 2D HMBC

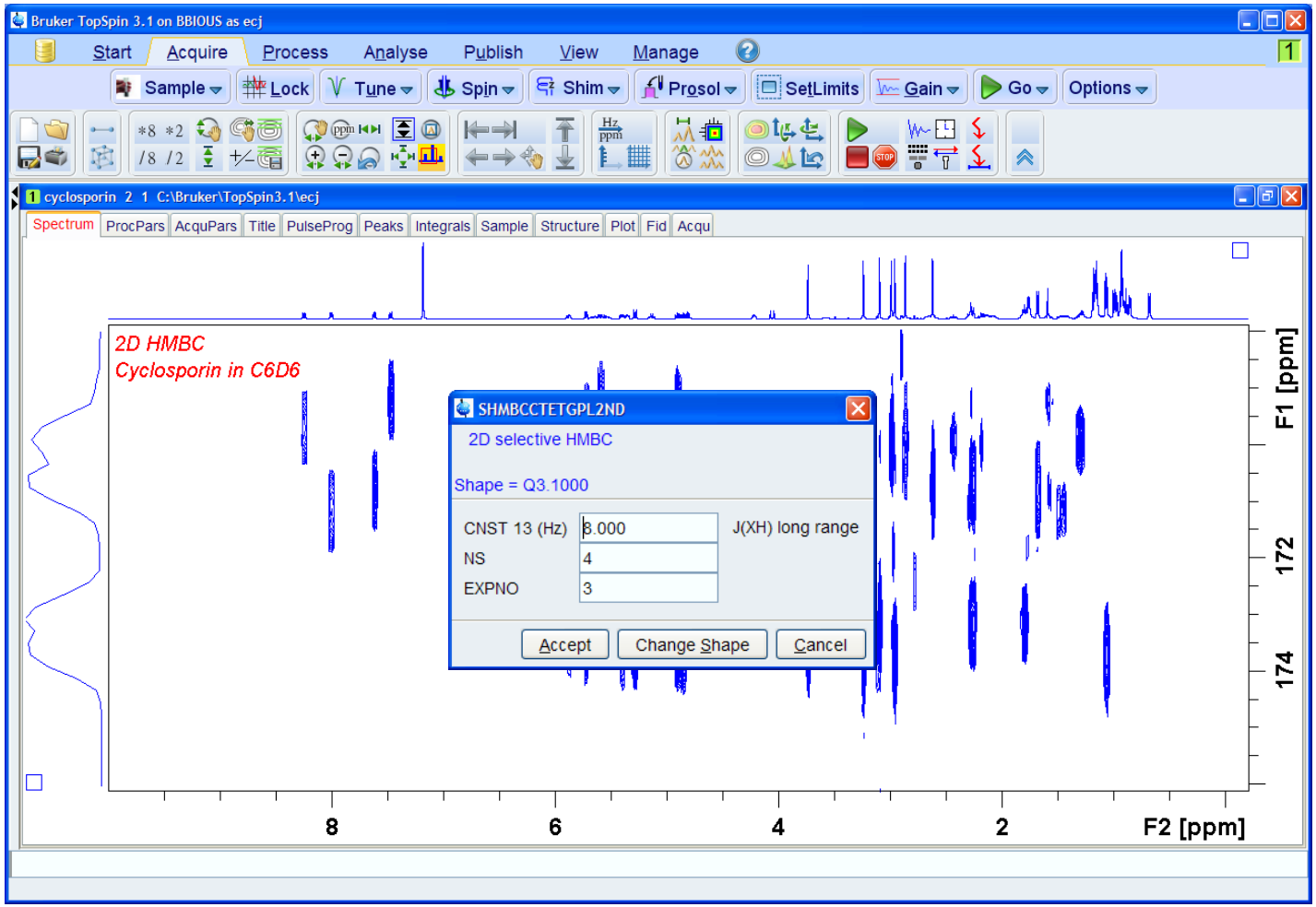
2D selHMBC



Step 2: Zoom into region of interest

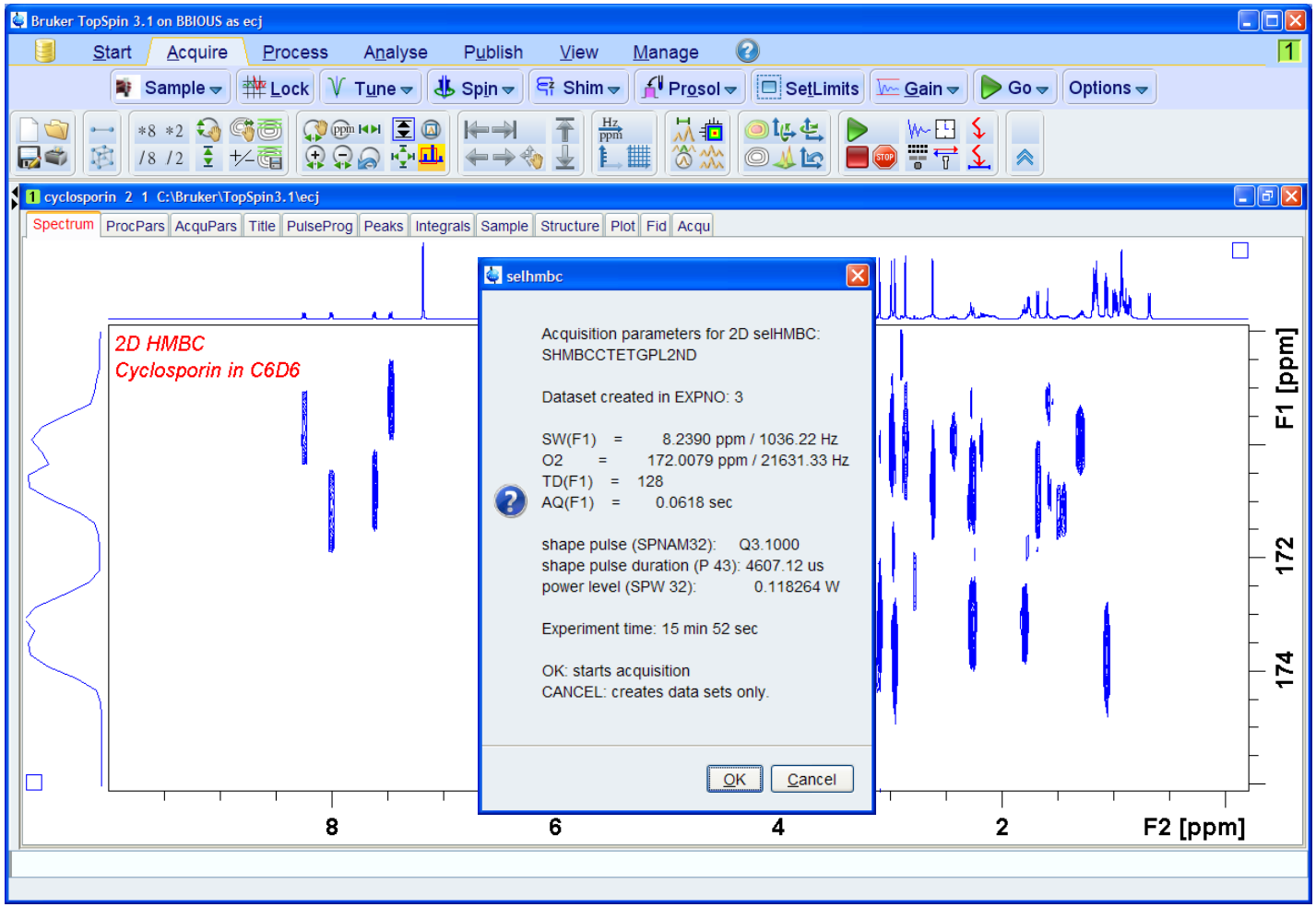
Step 3: Select Setup Selective 2D HMBC from Acquire → Options

2D selHMBC



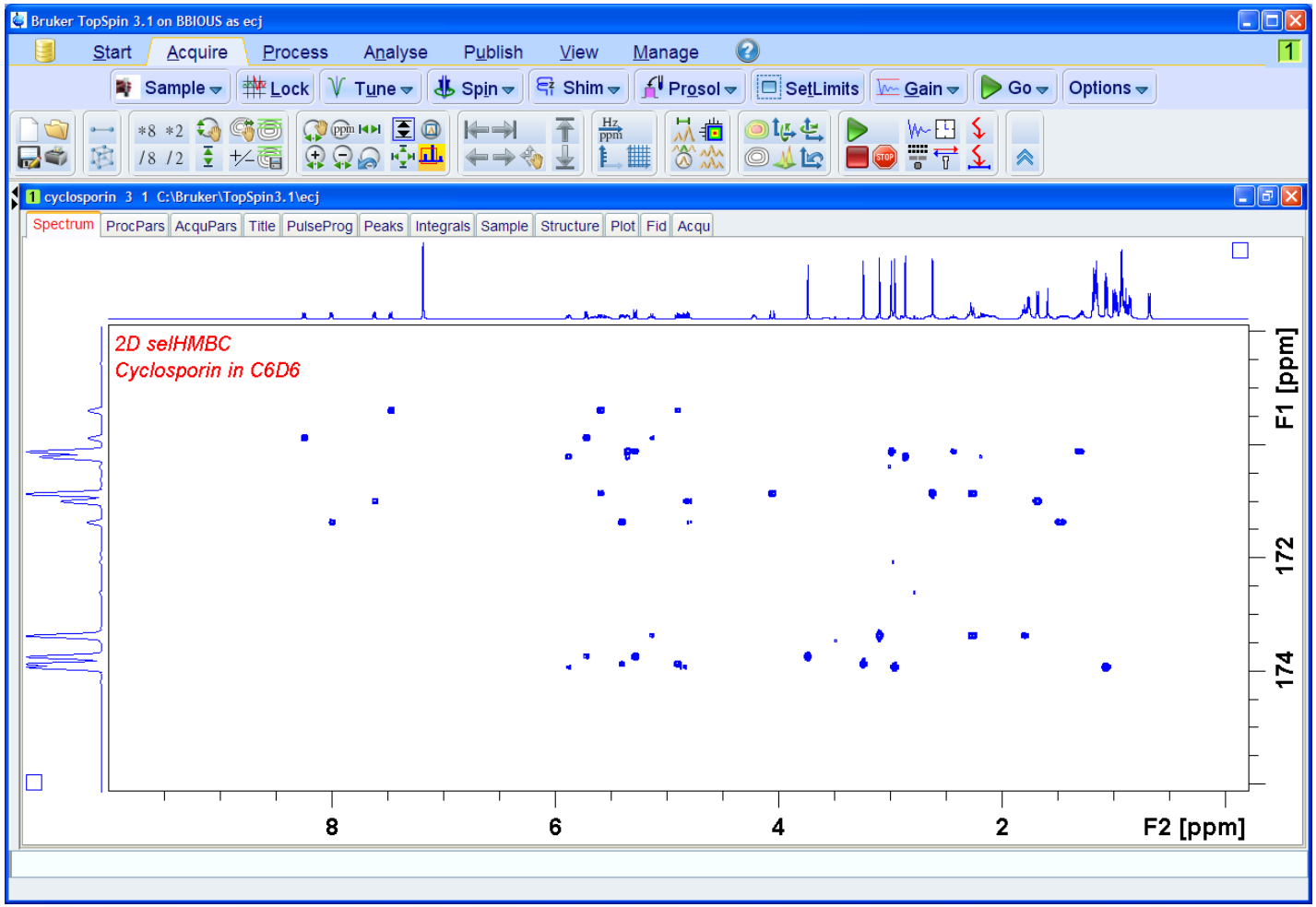
Default parameters are taken from standard parameter set (SHMBCCTETGPL2ND)

2D selHMBC



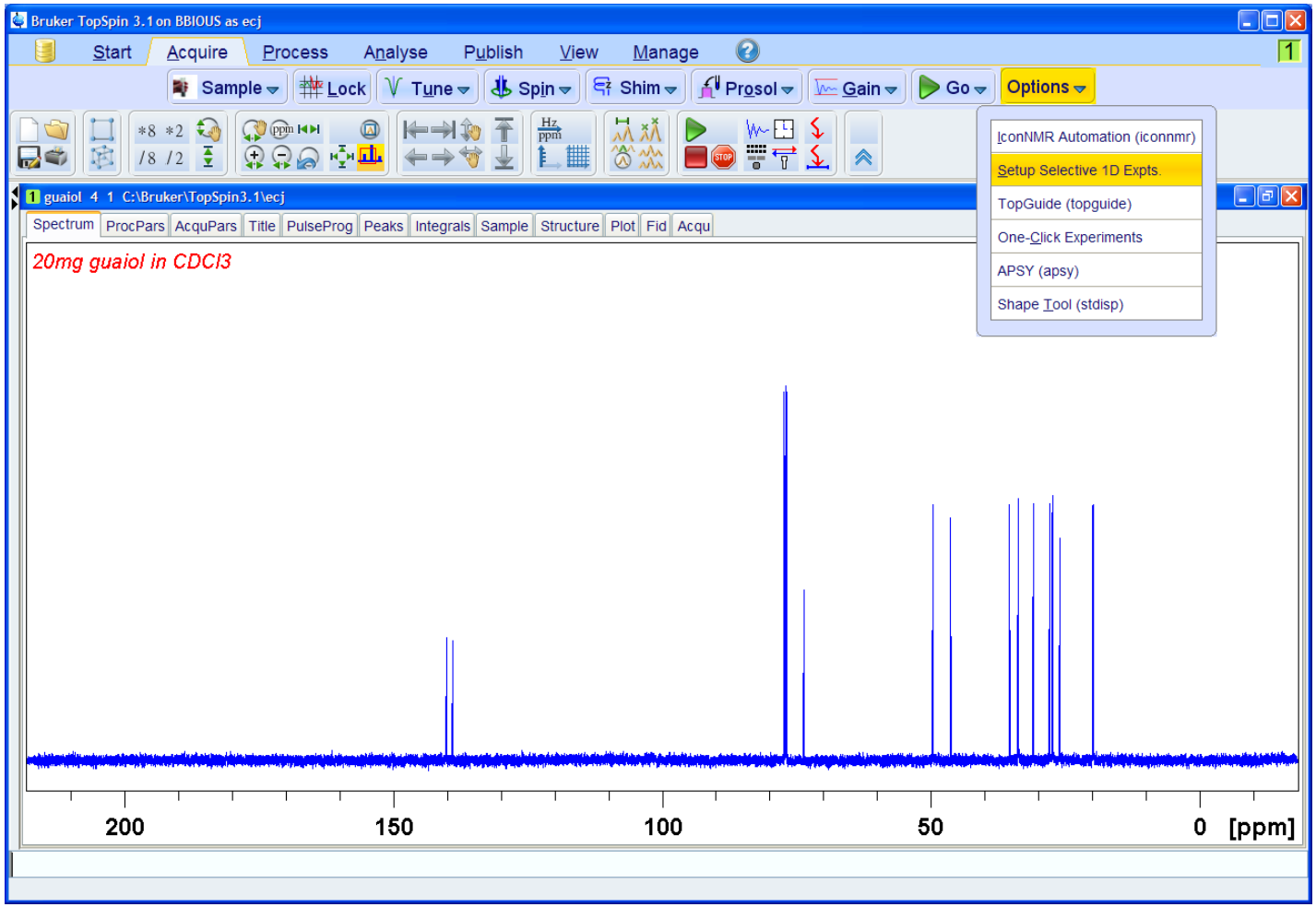
All parameters are automatically calculated and stored in new dataset

2D selHMBC



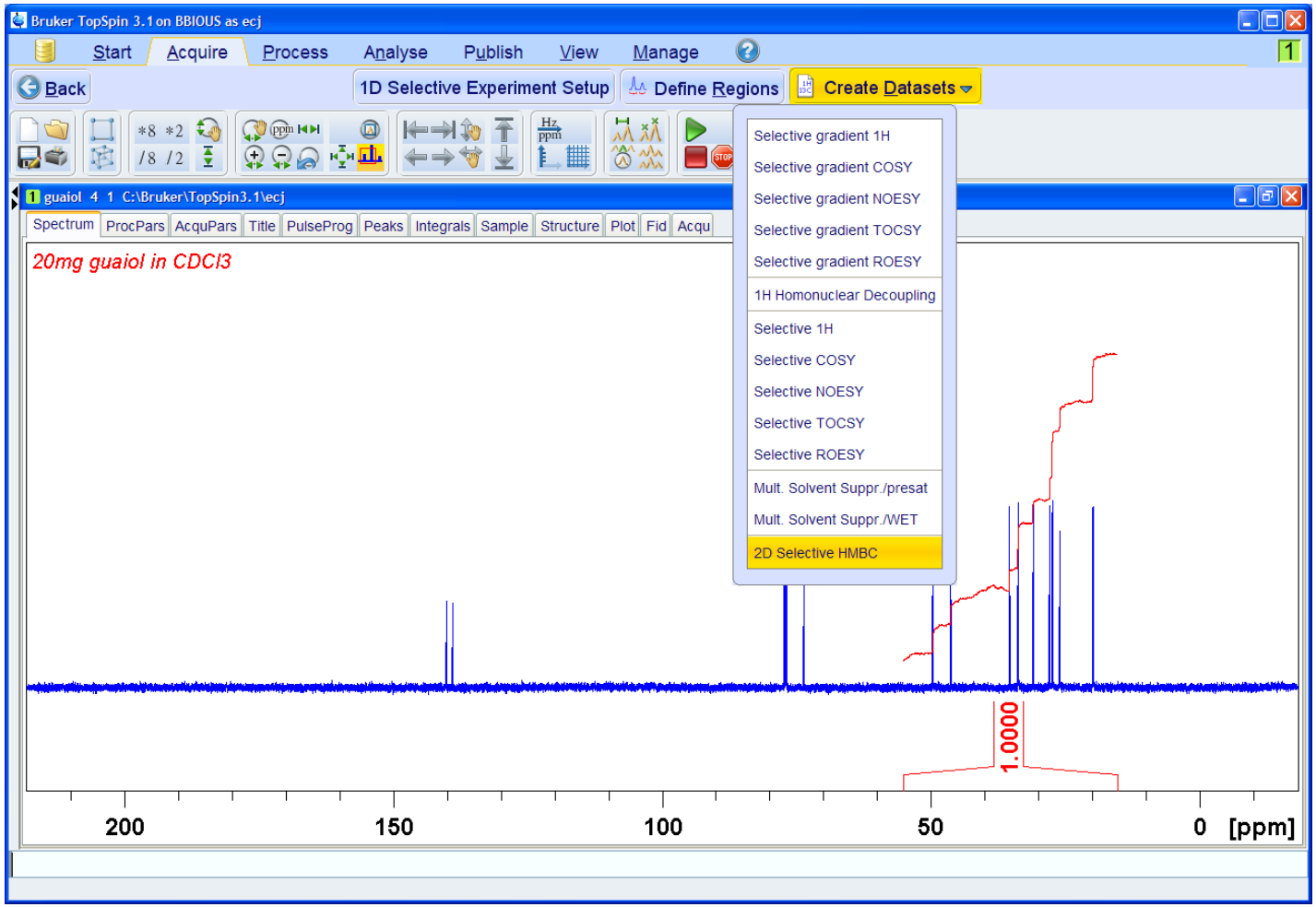
Significantly higher ^{13}C resolution compared to standard HMBC

2D selHMBC



Alternate method: start from a 1D ^{13}C spectrum

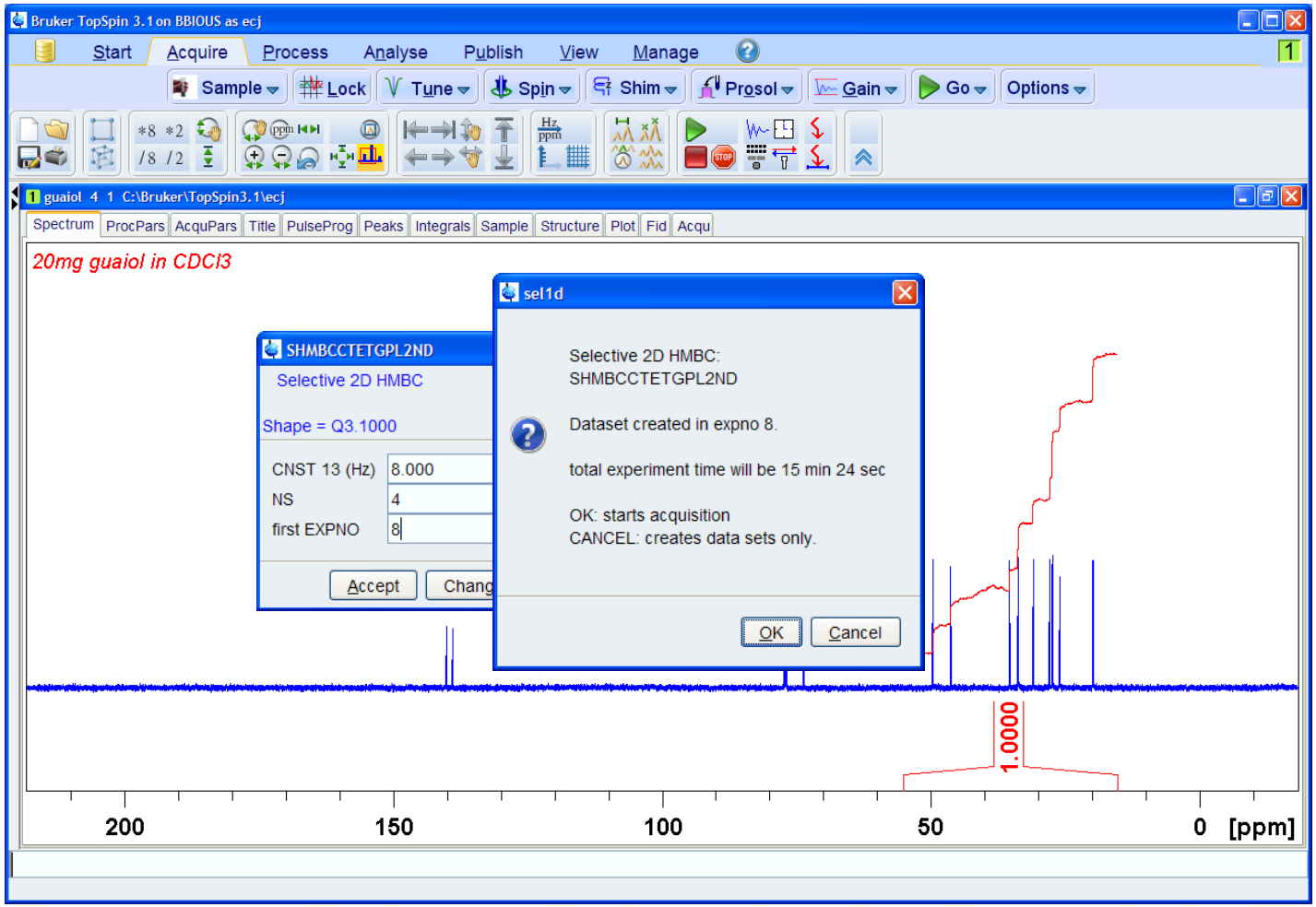
2D selHMBC



Follow same flow as 1D selective experiments:

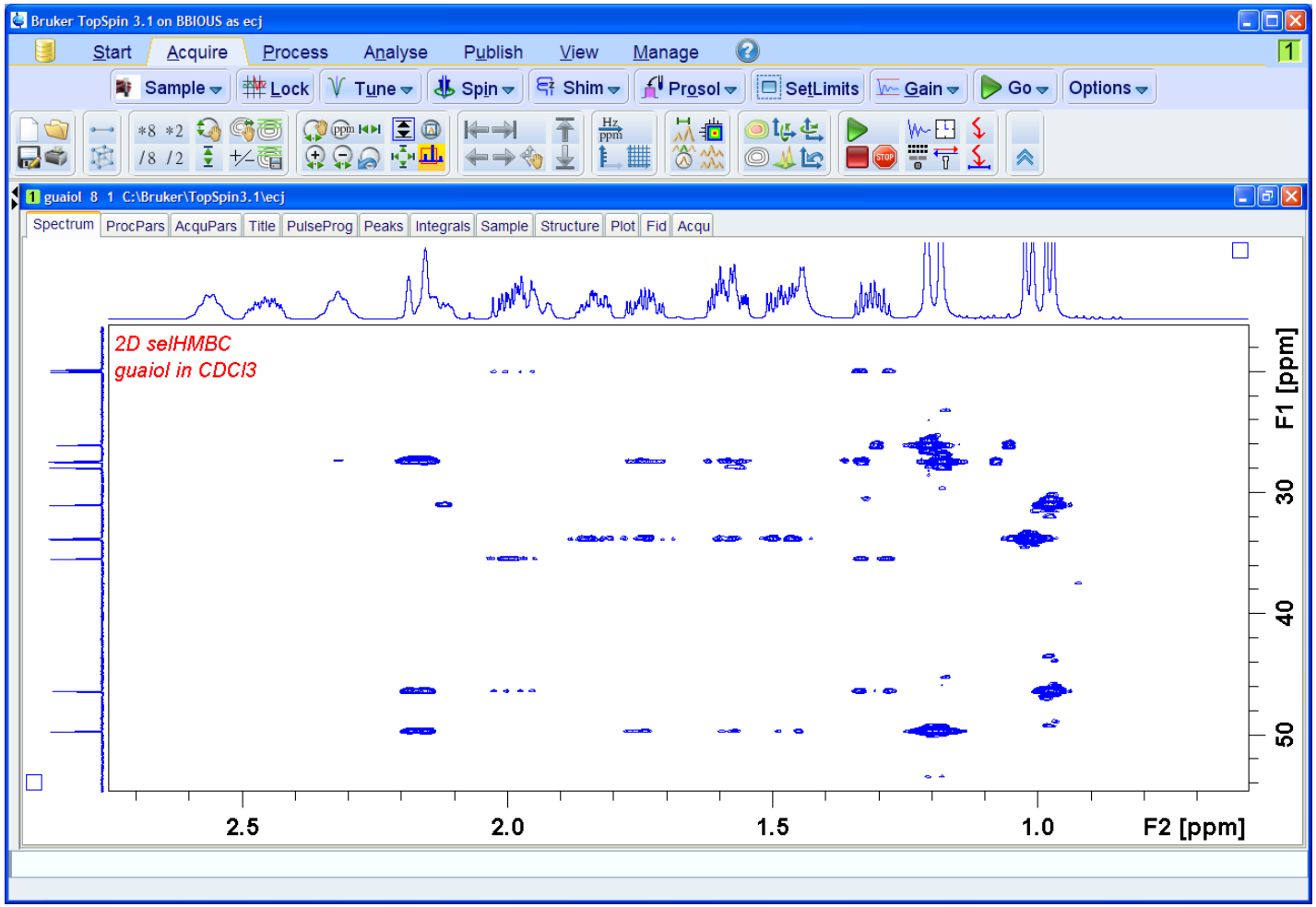
- Save integral to region file…

2D selHMBC

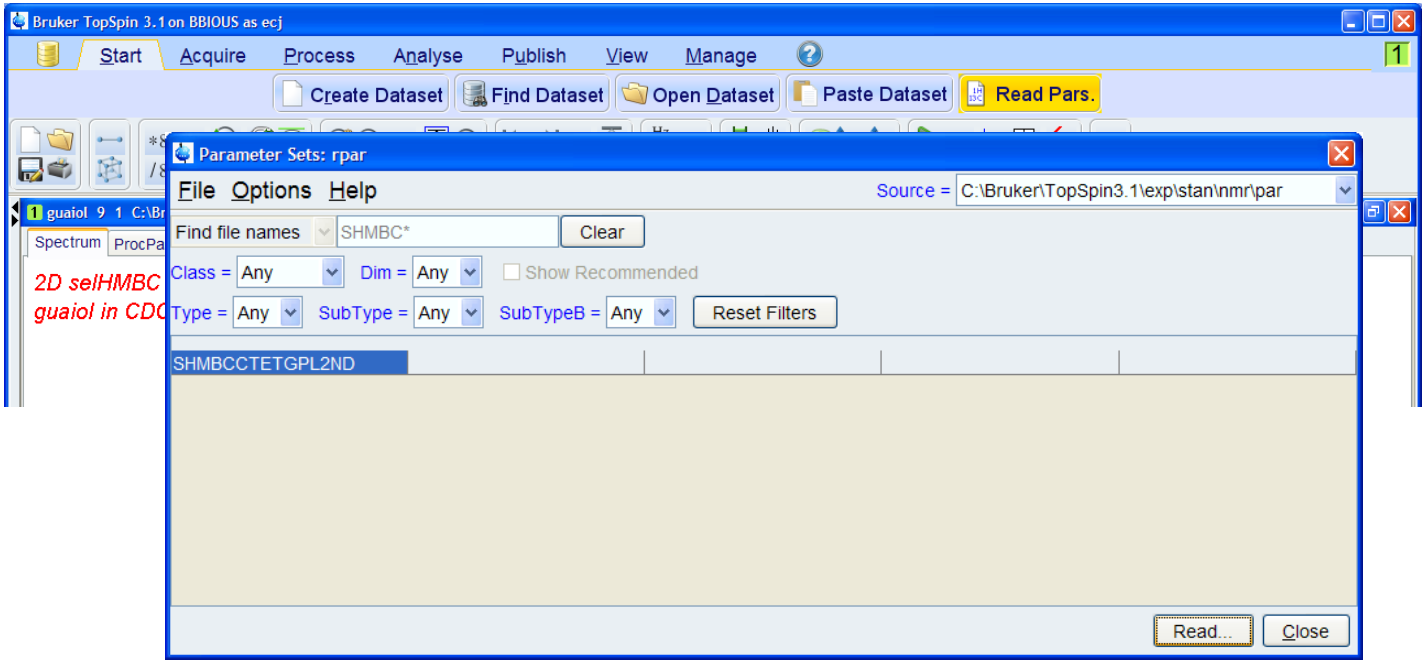


Datasets are automatically created

2D selHMBC


Bruker TopSpin 3.1 on BBIOUS as ecj
Start
Acquire
Process
Analyse
Publish
View
Manage
Sample
Lock
Tune
Spin
Shim
Prosol
SetLimits
Gain
Go
Options
guaiol 8 1 C:\Bruker\TopSpin3.1\ecj
Spectrum
ProcPars
AcquPars
Title
PulseProg
Peaks
Integrals
Sample
Structure
Plot
Fid
Acqu
2D selHMBC
guaiol in CDCl3
F1 [ppm]
30
40
50
2.5
2.0
1.5
1.0
F2 [ppm]

2D selHMBC

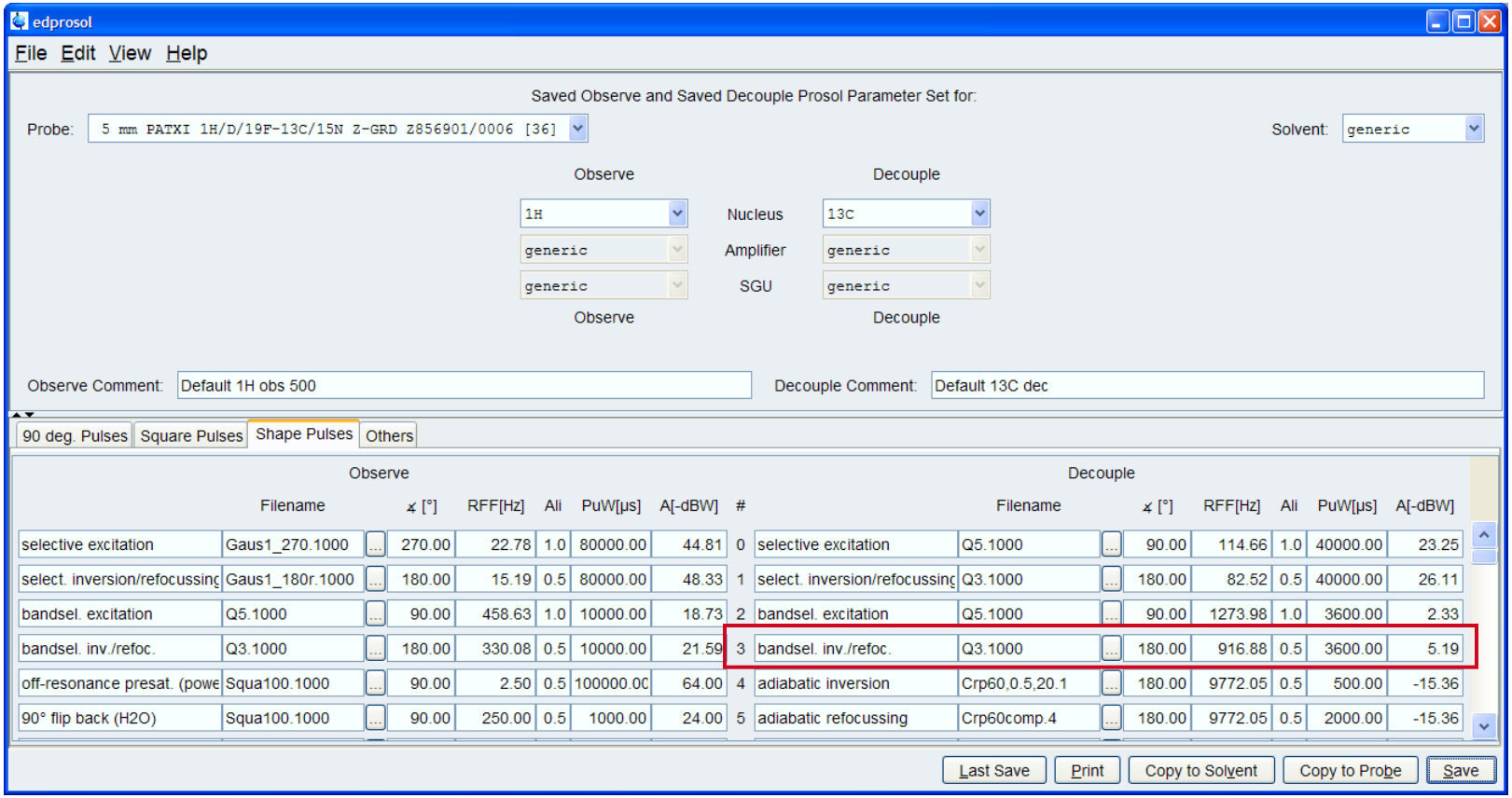


Next alternate method: start from standard parameter set: SHMBCCTETGPL2ND

- Default SW(F1) is 10.6 ppm

Read Pars. → Set O2P → Prosol → Gain → Go

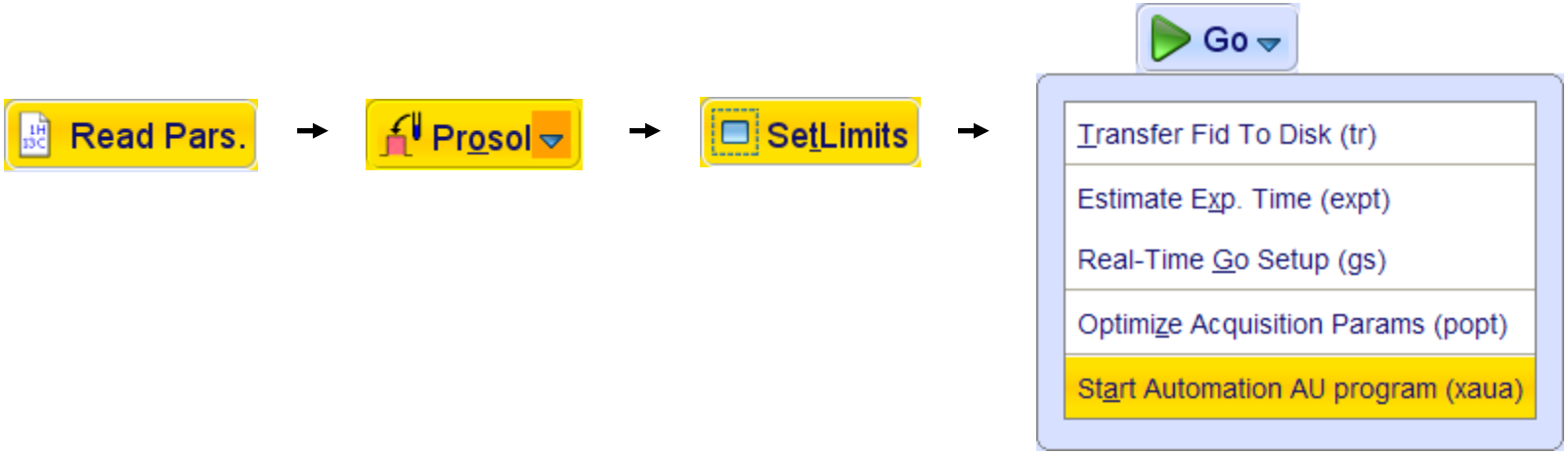
2D selHMBC



SHMBCCTETGPL2ND uses Q3.1000 pulse in prosol

2D selHMBC

Starting from parameter set SHMBCCTETGPL2ND, but manually setting SW(F1)…

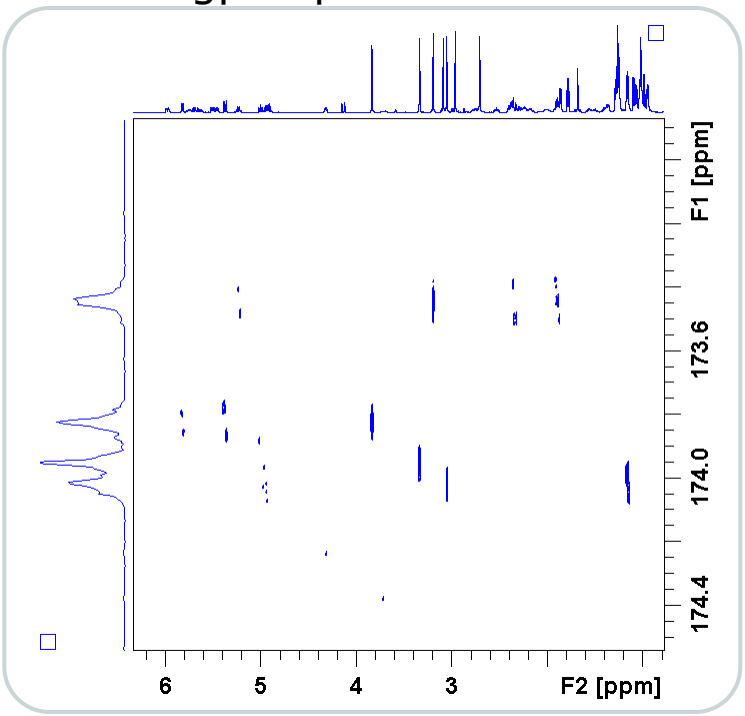


Automation AU program ***au_selhmbc*** will calculate shape pulse parameters based on SW(F1) and starts acquisition

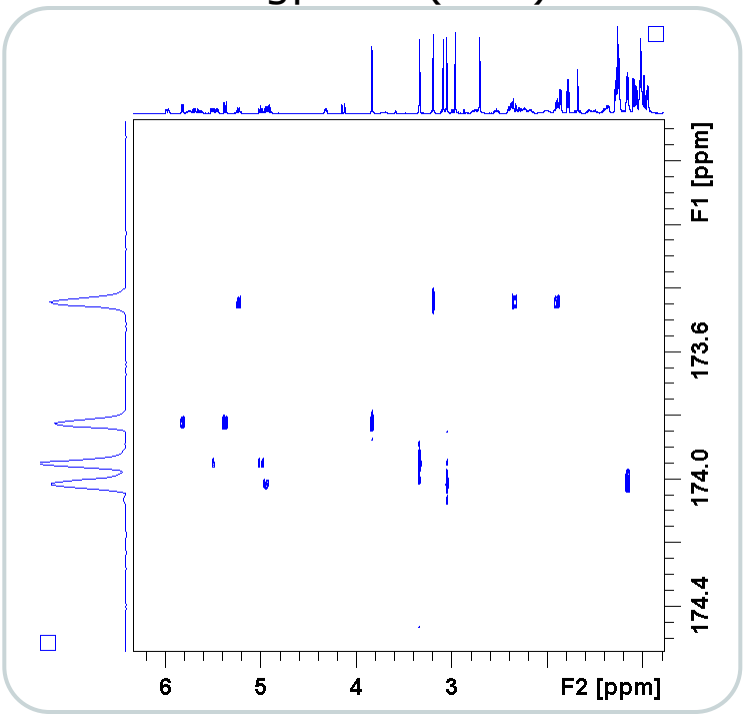
2D selHMBC: pulse sequence

Use constant time version to remove J_{HH} couplings

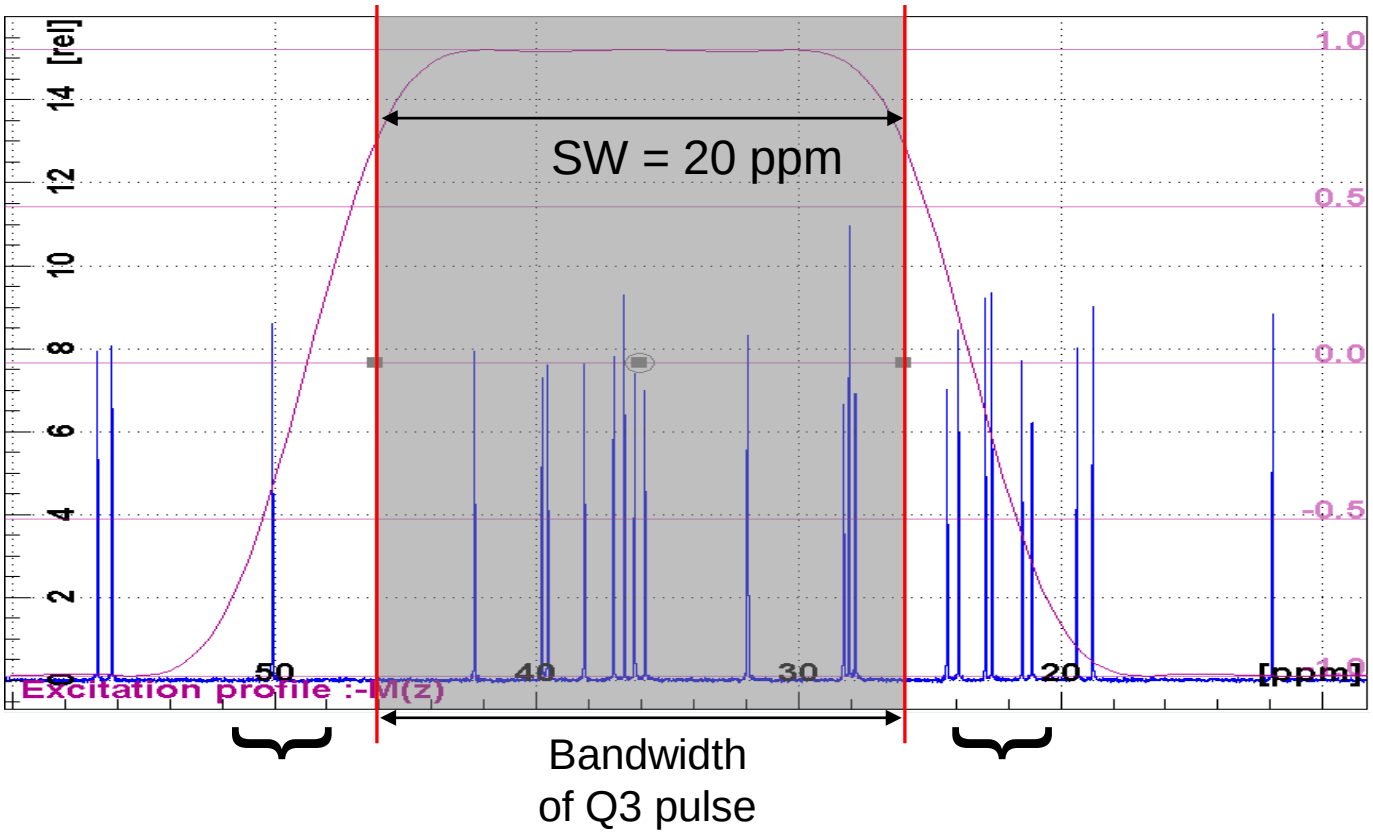
shmbcgpndqf



shmbcctetgpl2nd (new)



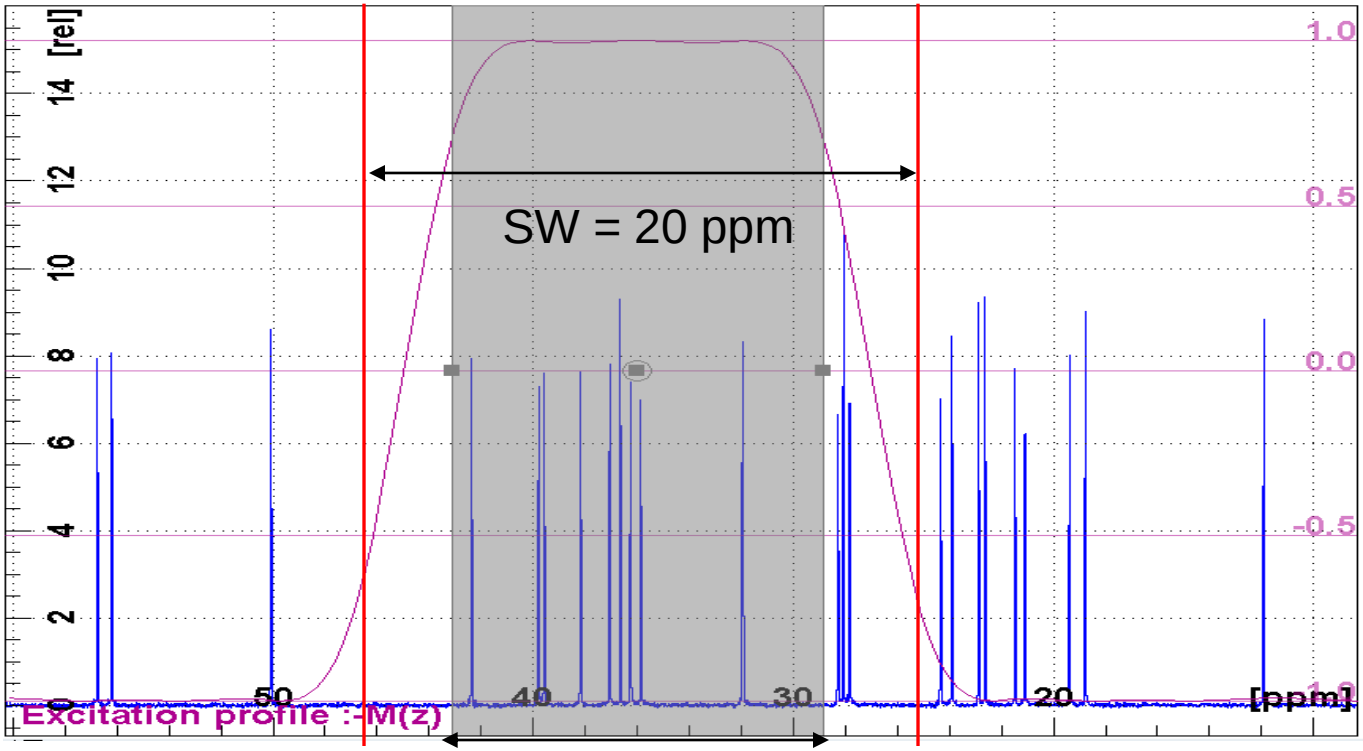
2D selHMBC: excitation profile



If SW matches the bandwidth of excitation of selective pulse:

- Peaks outside SW can alias into spectrum

2D selHMBC: excitation profile



Bandwidth of
Q3 pulse

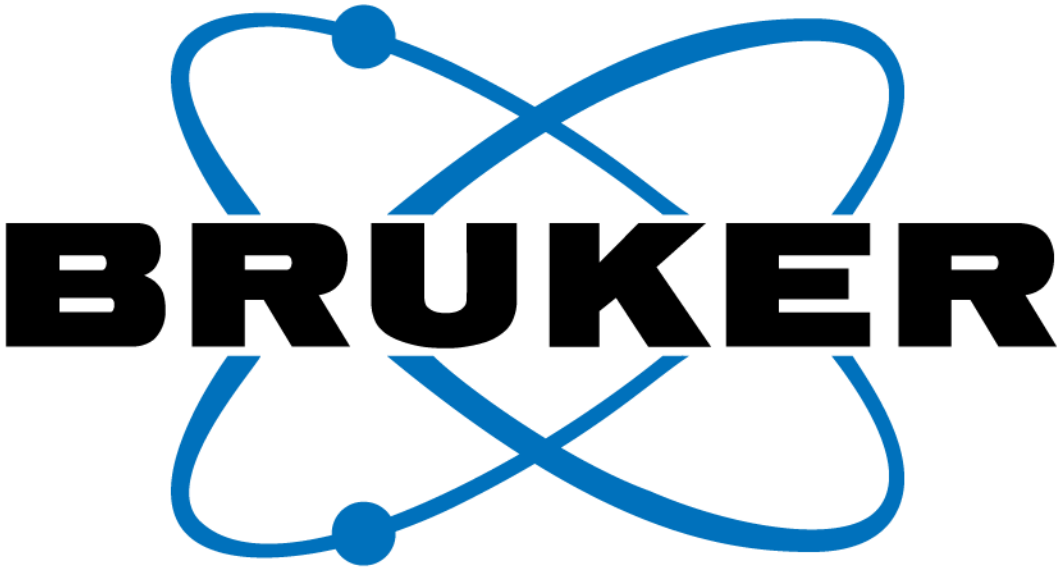
Compromise: Reduce bandwidth of selective pulse by a factor of 1.4

- Less aliasing of peaks outside SW.
- Some attenuation of peaks near edges of spectrum.

Availability

- Everything is included in Topspin 3.1

- Topspin 3.0: I can provide the AU programs and the modifications to the Flowbar



www.bruker-biospin.com