

Accelerated acquisition in pure-shift spectra based on prior knowledge from ^1H NMR

Electronic Supplementary Information

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Fig.1, top panel, presents a burst sampling schedule example: ones denote acquiring measurement points, and zeros denote their omission. Unlike conventional non-uniform sampling in NMR, not separate measurement points, but their chunks are either acquired or omitted. Fig.1, bottom panel, is the sampling schedule Fourier transform, or the point-spread function. When the sampling schedule is applied in an experiment, the spectrum is convolved with the point-spread function as a result of the undersampling. In Fig.2, two simulated spectra are presented. Fully “measured” ones are plotted with a red line, and the undersampled ones are plotted with a blue line. One of the spectra (top panel) yields then a strong artefact, while the other (bottom panel) does not. Thus, a “good” or a “bad” schedule is spectrum-specific.

We measured ^1H and full pure-shift spectra of the following samples: α -asarone, (R)-(+)-limonene, L-menthol, α -pinene, quinine in CDCl_3 ; D-glucose and sucrose in D_2O ; β -estradiol in CD_3OD ; all 50mM solutions; and a mixture of 0.5M (R)-(+)-limonene and 50mM α -pinene in CDCl_3 . We introduced the mixture sample to have an example with a large difference in peak heights.

We acquired the spectra with the standard PSYCHE pulse sequence on Varian 700MHz spectrometer equipped with HCN room-temperature probe. We set the “tau delay” parameter corresponding to the length of the chunk to 4 ms (the standard one is 8 ms) to ensure better decoupling. It also required a change of several other parameters for the sequence to function properly: rof1, rof2, gstab and gt1.

The raw data along with the “procar” files with the acquisition parameters can be downloaded from <http://nmr.cent.uw.edu.pl/downloads/>, section “Pure Shift” – > “Pseudo-2D pure shift sampling optimizer”.

For each ^1H spectrum, we performed automated multiplet analysis and automated peak picking with MestreNova software (11.0 version). The results are in “multiplets1.txt” and “peaks1.txt” files in the corresponding folders. The peak-picking procedure was carried out to have peak widths at our disposal.

We used the following python script to find the best and the worst samplings according to two different criteria: the maximum criterion (corresponding to the

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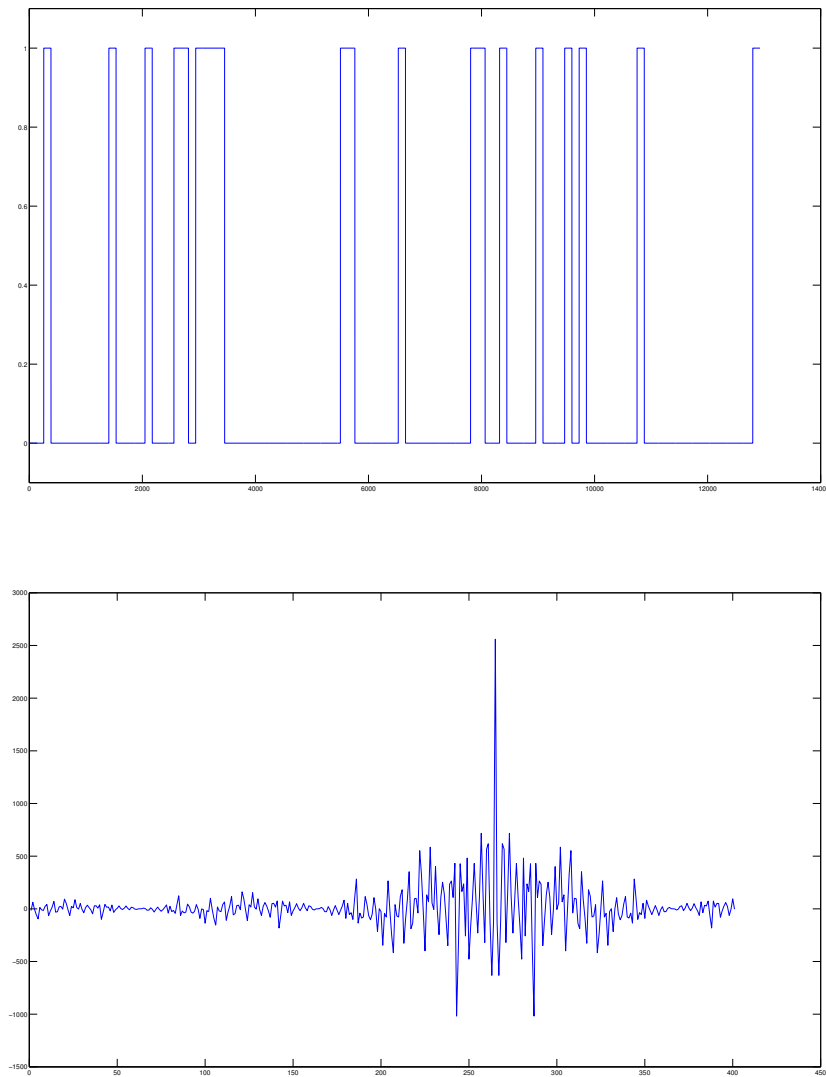


Figure 1 A simulated burst sampling schedule (top panel) and its point-spread function (bottom panel).

l_∞ norm of the reconstruction procedure input, that is why the name “Linf” is used) and the sum criterion (“L1”, as corresponding to the l_1 norm). The same script then artificially undersamples the pure-shift data according to the “best” and “worst” samplings of both criteria and then performs the reconstruction. In practical applications, the user will only need the sampling schedules. It is stated in the script which part of it should be omitted in this case.

```
#!/usr/bin/python

import numpy as np
import matplotlib.pyplot as plt
import nmrglue as ng
import math
import os
import itertools
import scipy
import time
```

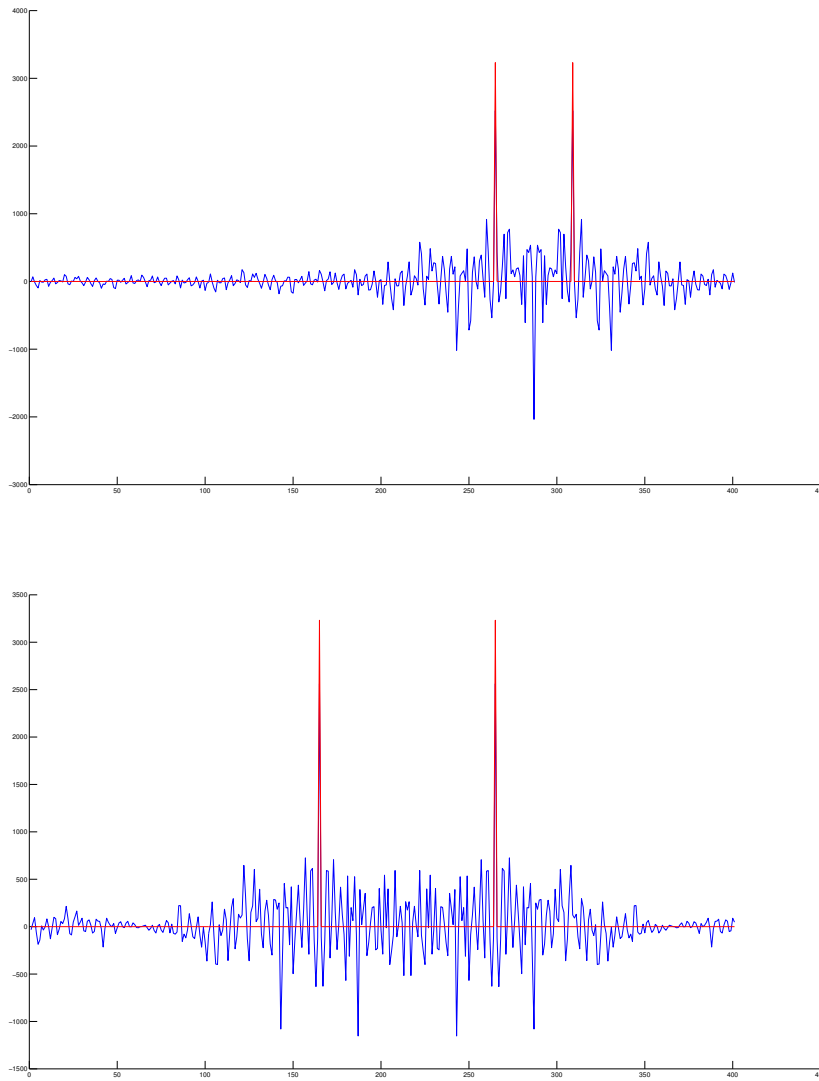


Figure 2 Two simulated spectra (red lines, divided by 4) and the results of their undersampling (blue lines, original scale) with the sampling schedule given in Fig.1. Both spectra are undersampled with the same schedule, but the one in the top panel yields a strong artefact, while the one in the bottom panel does not.

```
import struct

##### General parameters and Mnova data import
factor = 0.2 # proportion of chunks measured
samp_limit = int(1e4)

multiplets = np.loadtxt('multiplets1.txt')
shift_ppm = multiplets[:, 0]
a = multiplets[:, 1]

peakwidths = np.loadtxt('peaks1.txt')
fwhm_Hz = np.mean(peakwidths)*math.pi

##### PSYCHE parameters
dirs = os.listdir(os.getcwd())
for i in range(len(dirs)):
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if "PSYCHE" in dirs[i]:
    psyche_dir = os.getcwd() + '/' + dirs[i]
    break

dic, data = ng.varian.read(dir=psyche_dir, fid_file='fid',
    procpa_file='procpa')
dic1 = ng.varian.read_procpa(psyche_dir+'/procpa')
npo = int(dic1['np']['values'][0])/2
at = float(dic1['at']['values'][0])
reffrq = float(dic1['reffrq']['values'][0])
sfrq = float(dic1['sfrq']['values'][0])
sw = float(dic1['sw']['values'][0])
sw1 = float(dic1['sw1']['values'][0])
rp = float(dic1['rp']['values'][0])
lp = float(dic1['lp']['values'][0])

D = len(data)
data = data*np.exp(-1j*rp*math.pi/180) # p0 phasing
data = np.flipud(np.fft.fftshift(np.fft.fft(data)))
data = data*np.exp(-1j*np.arange(D)*lp*math.pi/(D*180)) # p1 phasing
data = np.fft.ifft(np.flipud(np.fft.fftshift(data)))

#####
chunk = int(math.floor(sw/sw1 + 0.5))
print '\nChunk = ', chunk, 'points'
t = np.linspace(0, at, npo)
shift_Hz = (sfrq - (shift_ppm*1e-6*reffrq + reffrq))*1e6
shift = np.round(shift_Hz*npo/sw + npo/2)
fwhm_t = fwhm_Hz*npo/sw
fwhm = fwhm_t*at/npo

##### Simulating singlet spectrum
fid = np.zeros((npo,), dtype=complex)
n = np.linspace(0, npo-1, npo);
for i in range(len(a)):
    fid = fid + a[i]*np.exp((2*math.pi*1j*shift[i]/npo - fwhm)*n)
s = np.fft.fft(fid)
peak_for_normalization = np.argmax(np.abs(s))
s = s/np.abs(s[peak_for_normalization])

##### Generating samplings
full_number_of_chunks = int(math.floor(npo/chunk))
number_of_measured_chunks = int(math.floor(full_number_of_chunks*factor))
print 'Full number of chunks -', full_number_of_chunks, ', number of
    measured chunks -', number_of_measured_chunks
number_of_samplings =
    int(math.floor(scipy.misc.comb(full_number_of_chunks-1,
        number_of_measured_chunks-1)))
print 'Number of all samplings: ', number_of_samplings

print '\nGenerating sampling schedules...'
start = time.time()
np.random.seed(1)
if number_of_samplings > samp_limit:

```

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print 'Using randomly selected samplings!'
Chunks_measured = np.ones((samp_limit+2, number_of_measured_chunks))
for i in range(samp_limit):
    Chunks_measured[i, 1:] = np.sort(np.random.permutation(np.arange(2,
        full_number_of_chunks)) \
        [:number_of_measured_chunks - 1])
Chunks_measured[samp_limit, :] = np.linspace(1,
    number_of_measured_chunks, number_of_measured_chunks) # truncation
Chunks_measured[samp_limit+1, :] = Chunks_measured[samp_limit,
    :]*math.floor(1/factor) - \
    (math.floor(1/factor) - 1) # uniform distribution
else:
    print 'Using all samplings!'
    C = np.array(list(itertools.combinations(np.linspace(2,
        full_number_of_chunks, full_number_of_chunks-1), \
        number_of_measured_chunks-1)))
    Chunks_measured = np.hstack((np.ones((np.shape(C)[0], 1)), C))
    Chunks_measured = Chunks_measured.astype(int)
    print '\nSamplings: ', Chunks_measured, np.shape(Chunks_measured)

##### Comparing samplings
s_nus = np.zeros((np.shape(Chunks_measured)[0], len(s)), dtype=complex)
max_artefact = np.zeros((np.shape(Chunks_measured)[0],))
L1 = np.zeros((np.shape(Chunks_measured)[0],))
L2 = np.zeros((np.shape(Chunks_measured)[0],))

if os.path.isfile('s_nus.npy'):
    s_nus = np.load('s_nus.npy')
    for j in range(np.shape(Chunks_measured)[0]):
        max_artefact[j] = np.max(np.abs(s_nus[j, :]-s))
        L1[j] = np.sum(np.abs(s_nus[j, :]-s))
else:
    for j in range(np.shape(Chunks_measured)[0]):
        a = Chunks_measured[j, :]
        fid_nus = np.zeros(np.shape(fid), dtype=complex)
        for k in range(np.shape(Chunks_measured)[1]):
            fid_nus[(a[k]-1)*chunk:a[k]*chunk] = fid[(a[k]-1)*chunk:a[k]*chunk]
        s_nus[j, :] = np.fft.fft(fid_nus)
        s_nus[j, :] = s_nus[j, :]/np.abs(s_nus[j, peak_for_normalization])

        max_artefact[j] = np.max(np.abs(s_nus[j, :]-s))
        L1[j] = np.sum(np.abs(s_nus[j, :]-s))

end = time.time()
print 'done!'
print 'Time: ', end - start, 's'

criterion = {}
criterion['Linf'] = max_artefact
criterion['L1'] = L1

main_folder = os.getcwd()

```

```

def best_and_worst_samplings(c, bw):
    global s
    os.chdir(main_folder)
    if bw == 'best':
        C = np.argmin(criterion[c])
    if bw == 'worst':
        C = np.argmax(criterion[c])
    selected_spectrum = s_nus[C, :]
    selected_fid = np.fft.ifft(s_nus[C, :])*np.abs(s_nus[C,
        peak_for_normalization])
    selected_sampling = Chunks_measured[C, :]
    print selected_sampling

    print 'Saving figures of simulated FIDs...'
    plt.figure()
    plt.plot(t, np.real(selected_fid))
    plt.title(bw + ' sampling sampling - ' + c + ' criterion (simulated FID)')
    plt.savefig(bw + '_' + c + '_FID.eps')

    plt.figure()
    plt.plot(np.abs(selected_spectrum))
    plt.plot(np.abs(s))
    plt.title(bw + ' sampling - ' + c + ' criterion \n(simulated spectrum
        with artefacts)')
    plt.savefig(bw + '_' + c + '_spec0.eps')
    print 'done!'

    ### From this point forward, the script performs the artificial
    undersampling of the fully measured data and the subsequent
    reconstruction. In practical applications, the following section of
    the function should be commented out for the script to yield only the
    sampling schedules ###

    print 'Preparing files for reconstruction...'
    folder_r = main_folder + '/' + c
    if not os.path.exists(folder_r):
        os.makedirs(folder_r)
    os.chdir(folder_r)

    folder_r_bw = folder_r + '/' + c + '_' + bw
    if not os.path.exists(folder_r_bw):
        os.makedirs(folder_r_bw)
    os.chdir(folder_r_bw)

    np.savetxt(bw + '_sampling.txt', selected_sampling, fmt='%d')

    folder_r_bw0 = folder_r_bw + '/0th_iteration_' + c + '_' + bw
    if not os.path.exists(folder_r_bw0):
        os.makedirs(folder_r_bw0)
    ng.fileio.varian.write(folder_r_bw0, dic, selected_fid, overwrite=True)

    I = len(selected_sampling)*chunk
    ind = np.zeros(I,)
    for k in range(len(selected_sampling)):

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    ind[chunk*k:chunk*(k+1)] = np.arange((selected_sampling[k] - 1)*chunk,
        selected_sampling[k]*chunk, 1)
ind = ind.astype(int)

k = 0
ind_alternated = np.zeros(2*I)
for i in range(I):
    ind_alternated[k] = 2*ind[i]
    ind_alternated[k + 1] = ind_alternated[k] + 1
    k = k + 2
ind_alternated = ind_alternated.astype(int)

regions = 1
dimensions = 2
line1 = str(dimensions) + ' 1 ' + str(regions*2*I) + '\n'
line2 = str(regions) + ' ' + str(2*D)
s1 = ''
for i in range(2*I):
    s1 = s1 + '\n' + str(0) + ' ' + str(ind_alternated[i])

folder = folder_r_bw + '/MDD'
if not os.path.exists(folder):
    os.makedirs(folder)
os.chdir(folder)

fid_alternated = np.empty(2*I)
fid_alternated[0::2] = np.real(data[ind])
fid_alternated[1::2] = np.imag(data[ind])
f = ''
for j in range(2*I):
    f = f + '\n' + str(fid_alternated[j])
contents = 'mdd asc sparse f180.0 \n ./MDD/region01.mdd \n MDD sparse\n $
    \n' + line1 + line2 + s1 + f # contains the data to be written to .mdd
    file

name = str(1)
file = open(name + '.mdd', 'w')
file.write(contents)
file.close()

command = 'cssolver ' + name + ' CS_alg=IST CS_niter=300 CS_VE=n
    MDD_NOISE=1 > ./' + name + '.log'
command = "tcsh -c '" + command + "'"
os.system(command) # executes .mdd file
print 'done!'

print 'Reading reconstruction results...'
file = open(name + '.cs', 'rb')
cs = np.empty(2*D)
for j in range(2*D):
    cs[j] = float(struct.unpack('f', file.read(4))[0])
file.close()
fid_rec = cs[0::2].astype(np.float32) + 1j*cs[1::2].astype(np.float32)
print 'done!'

```

```
print 'Writing reconstructed FIDs...'
ng.fileio.varian.write(folder_r_bw, dic, fid_rec, overwrite=True)
print 'done!'

return None

bw = ['best', 'worst']
c = ['Linf', 'L1']
for i in c:
    for j in bw:
        print '\n', j, 'sampling for', i, 'criterion'
        best_and_worst_samplings(i, j)

plt.show()
```

The script yields:

- the best and worst samplings for both criteria (text files and figures)
- the reconstruction results for the best and worst samplings for both criteria (raw spectrometer output format).

The comparisons for the best and worst samplings for each criterion (the reconstruction results), as well the comparisons of the different criteria best results, are shown below for each sample. The corresponding samplings are presented as well in the form of the convolution with the simulated spectrum of singlets (step 3 of the workflow described in the main text).

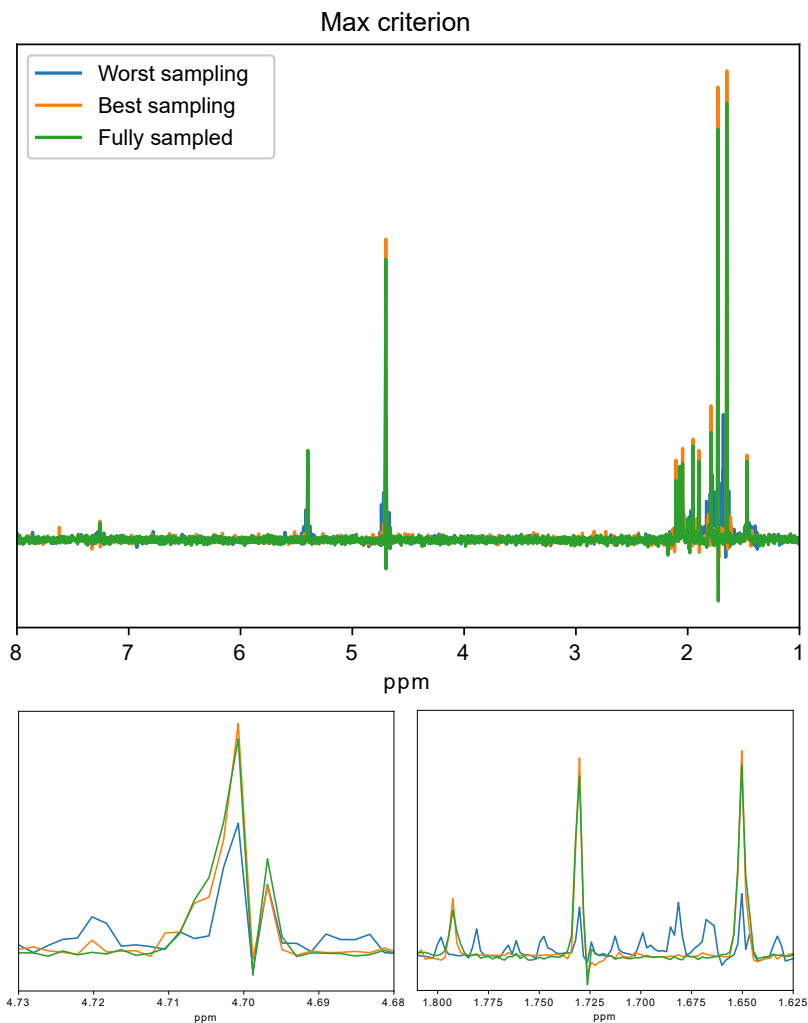


Figure 3 (R)-(+)-limonene, 50mM in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

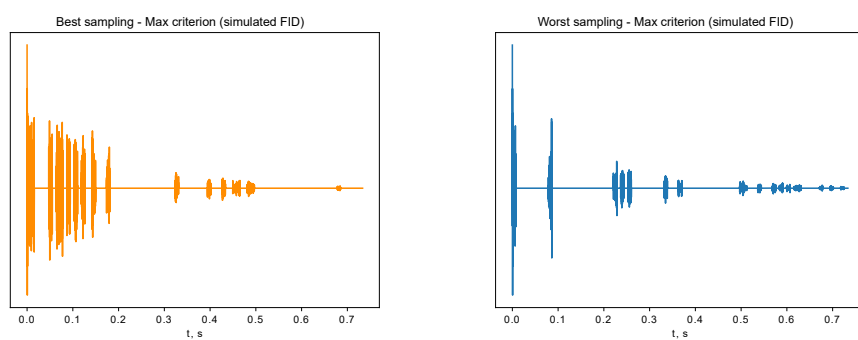


Figure 4 Maximum criterion for (R)-(+)-limonene: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

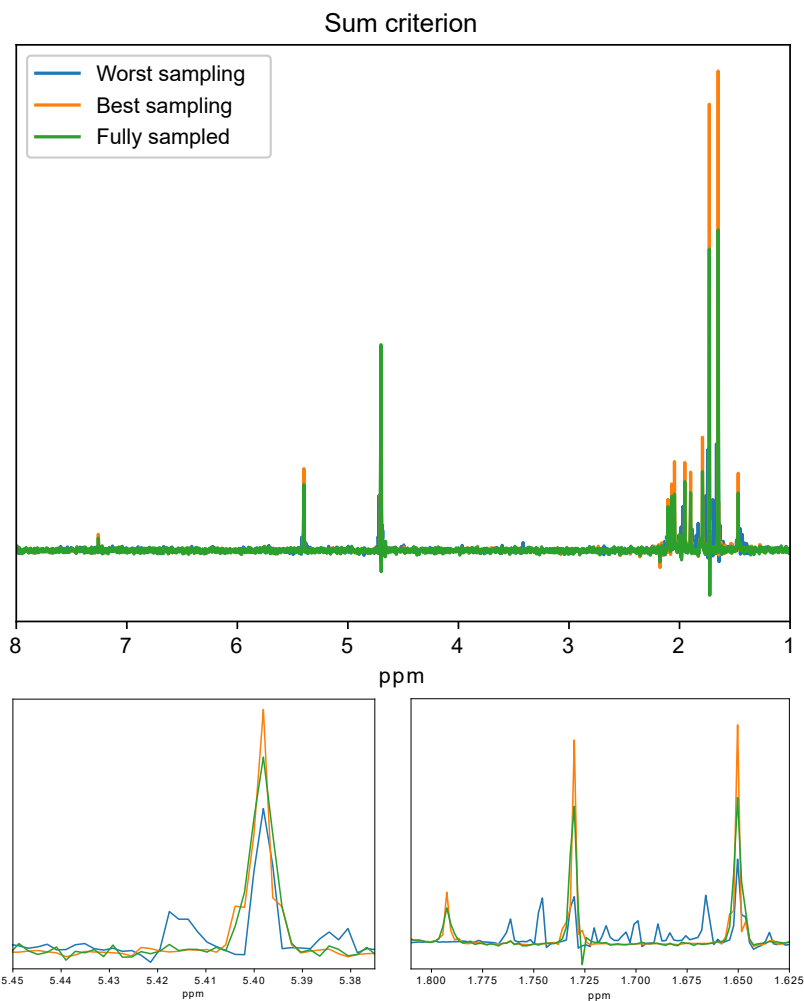


Figure 5 (R)-(+)-limonene, 50mM in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

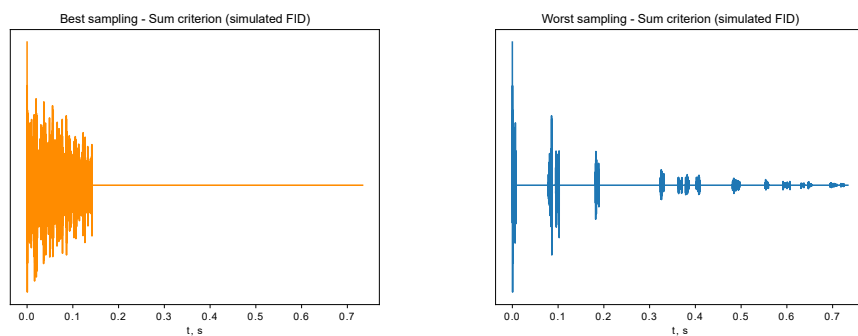


Figure 6 Sum criterion for (R)-(+)-limonene: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

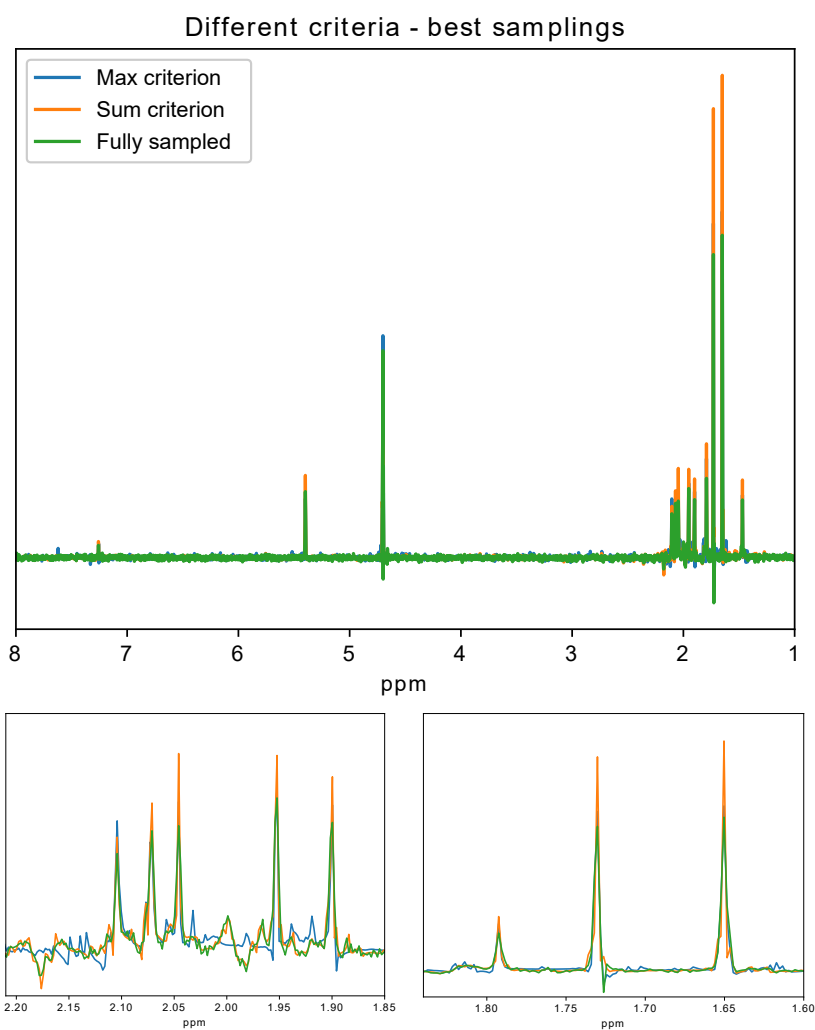


Figure 7 (R)-(+)-limonene, 50mM in CDCl₃. Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum.

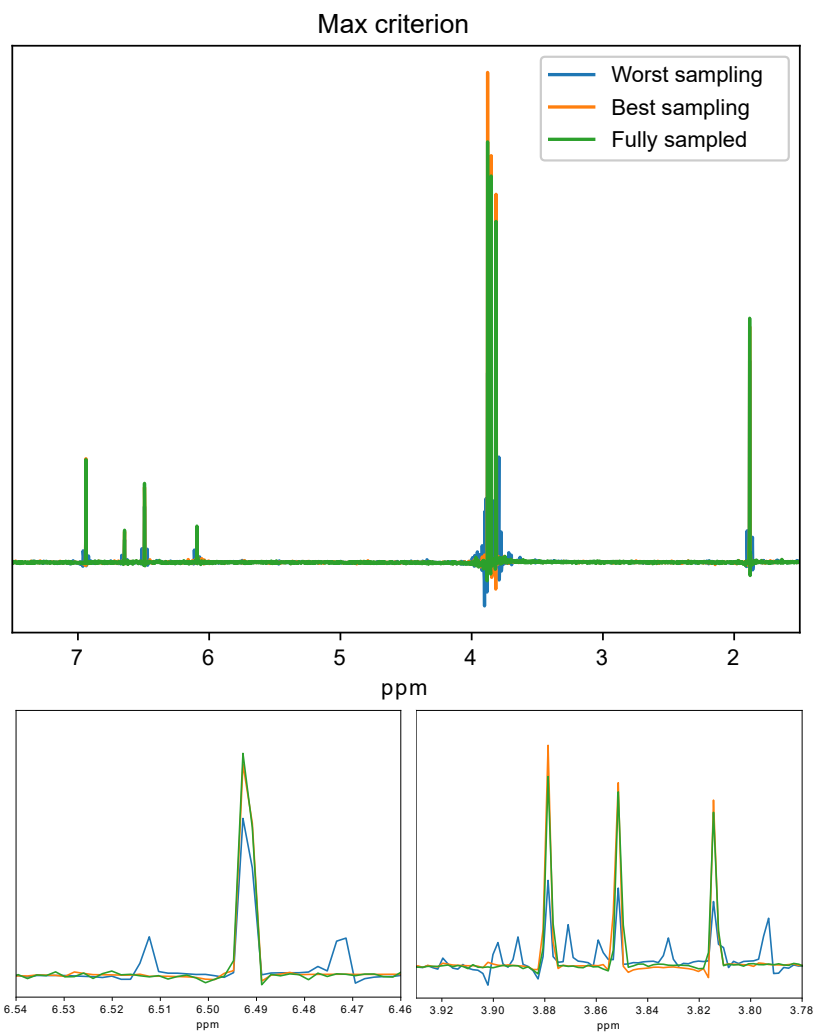


Figure 8 α -asarone, 50mM in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

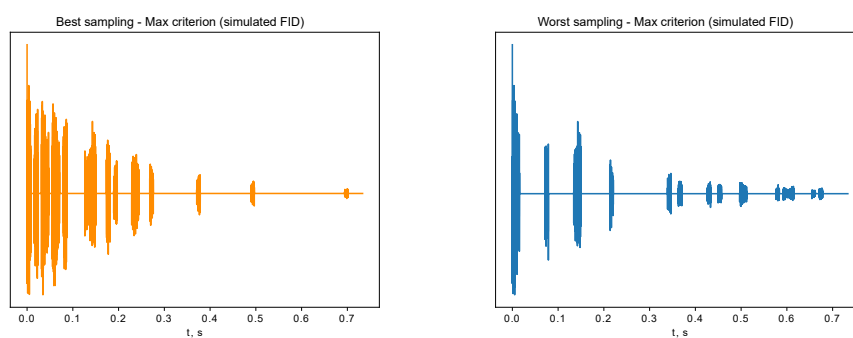


Figure 9 Maximum criterion for α -asarone: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

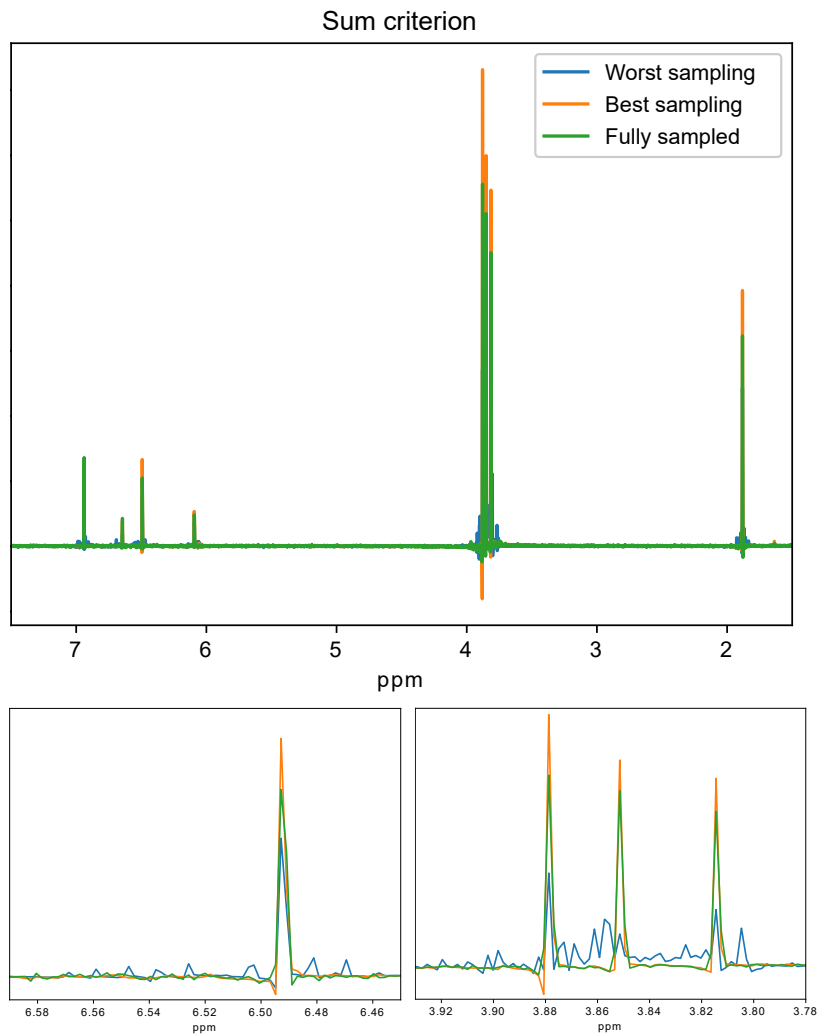


Figure 10 α -asarone, 50mM in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

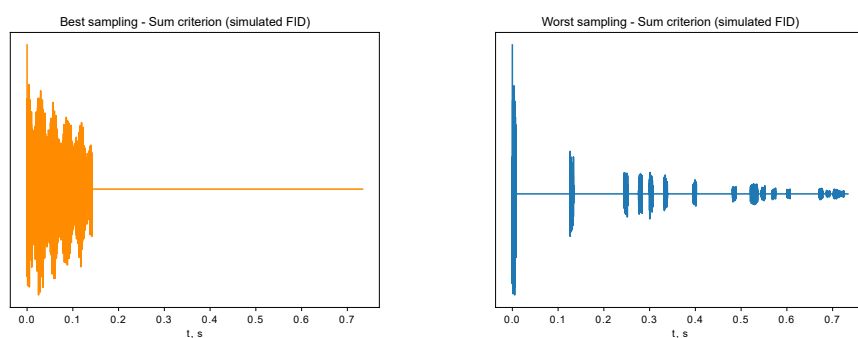


Figure 11 Sum criterion for α -asarone: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

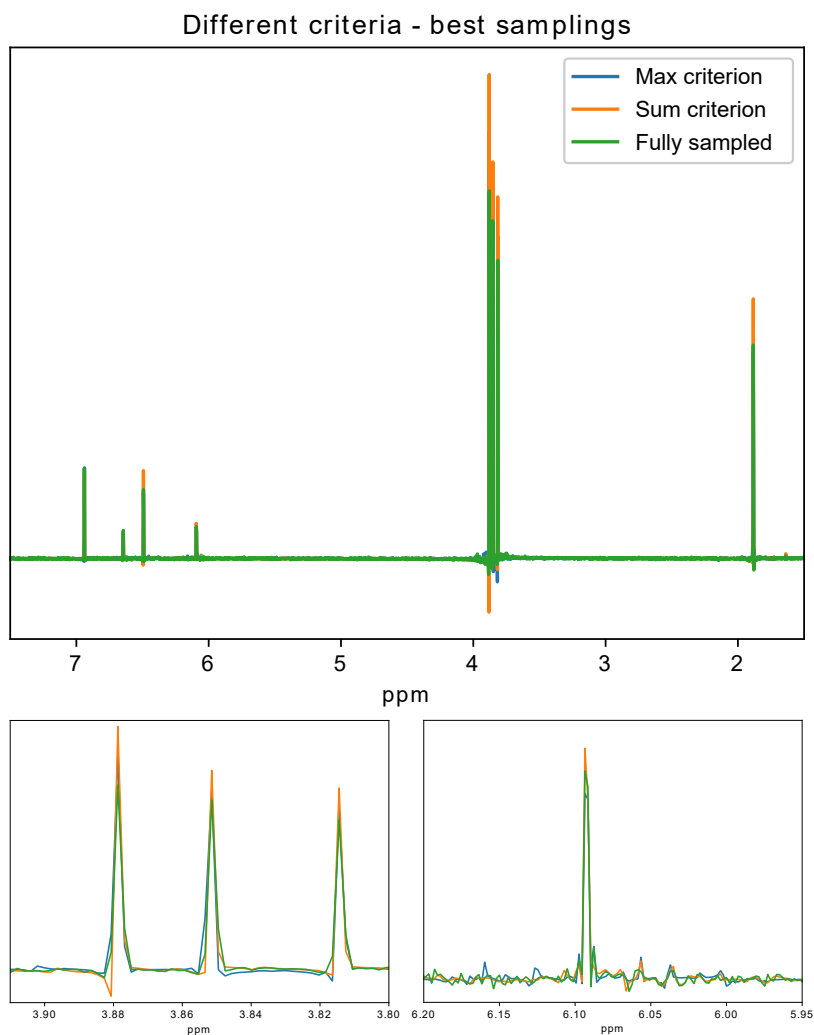


Figure 12 α -asarone, 50mM in CDCl_3 . Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum.

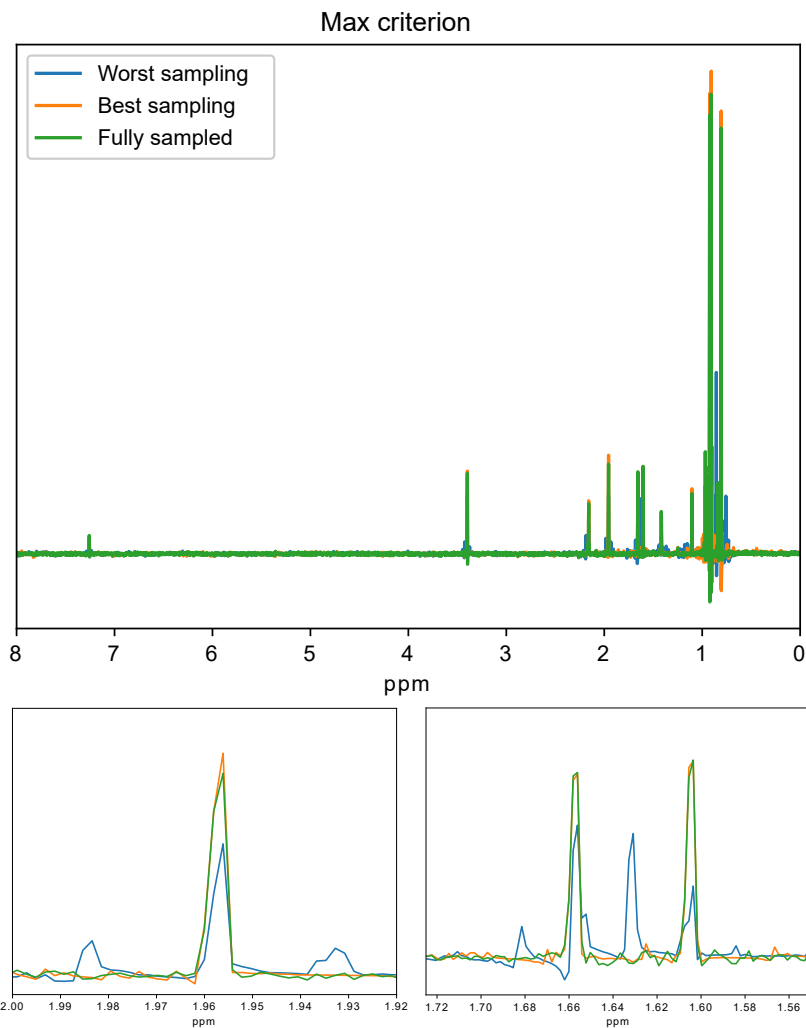


Figure 13 L-menthol, 50mM in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

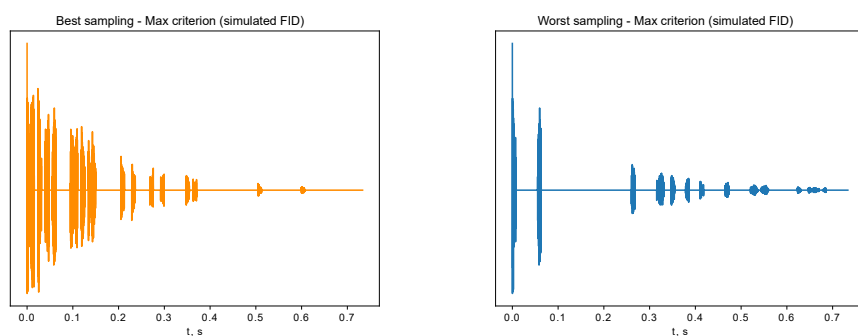


Figure 14 Maximum criterion for L-menthol: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

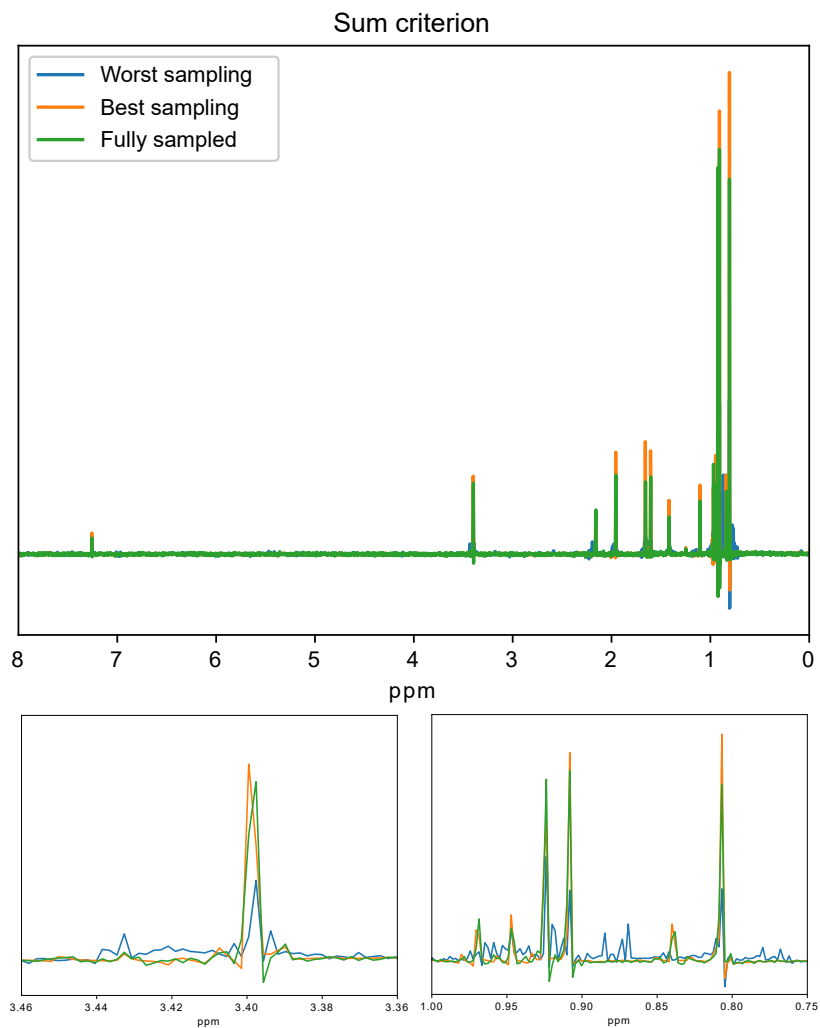


Figure 15 L-menthol, 50mM in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

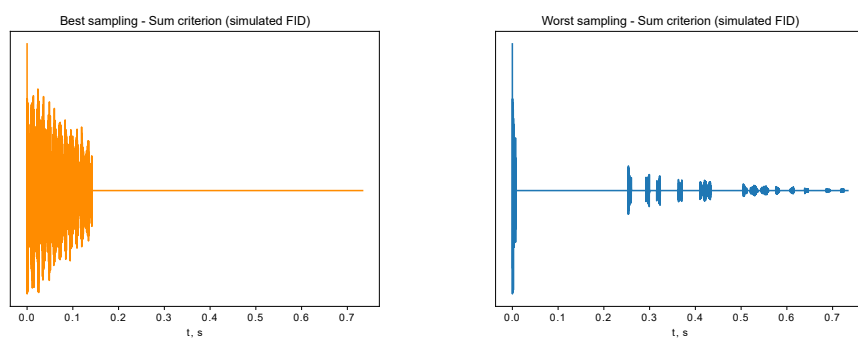


Figure 16 Sum criterion for L-menthol: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

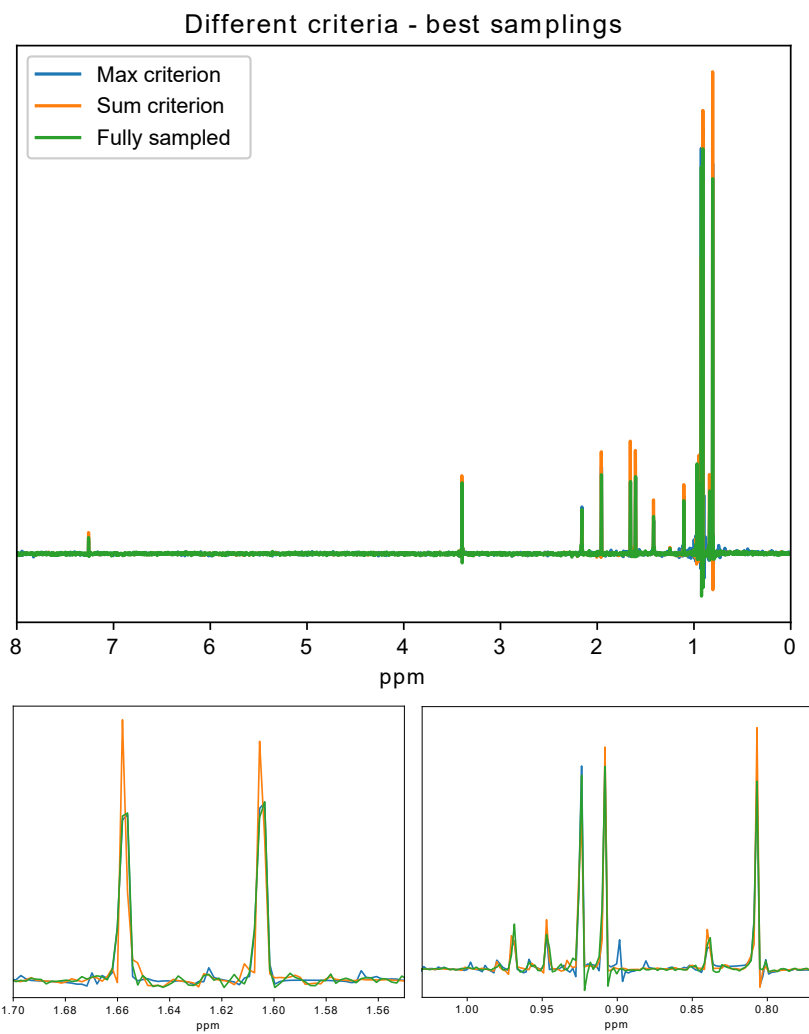


Figure 17 L-menthol, 50mM in CDCl_3 . Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum.

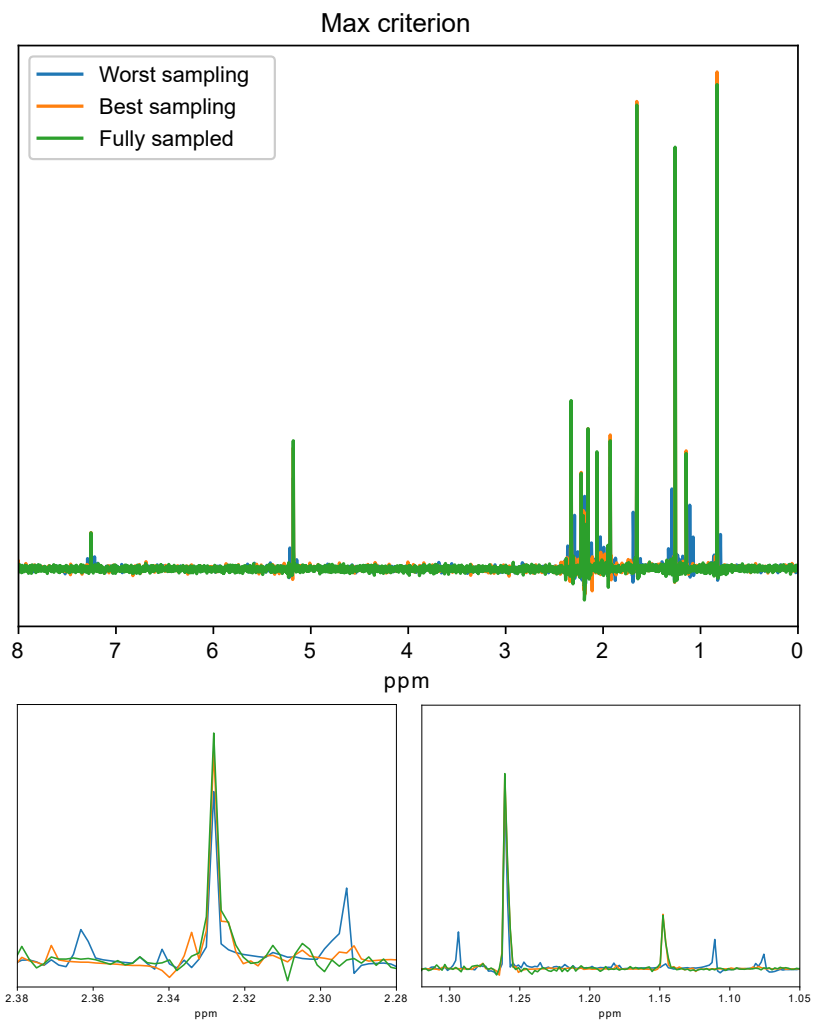


Figure 18 α -pinene, 50mM in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

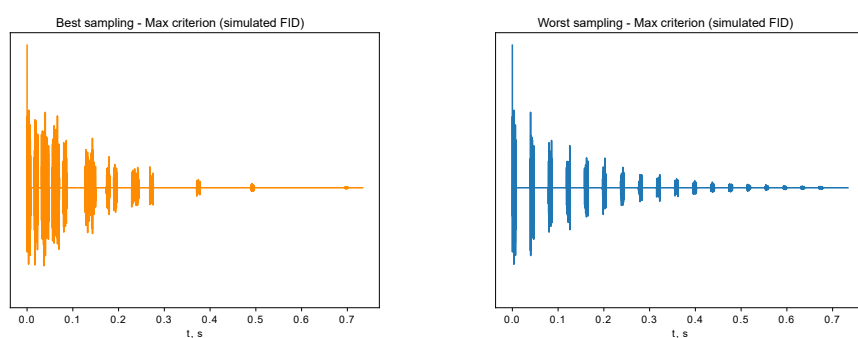


Figure 19 Maximum criterion for α -pinene: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

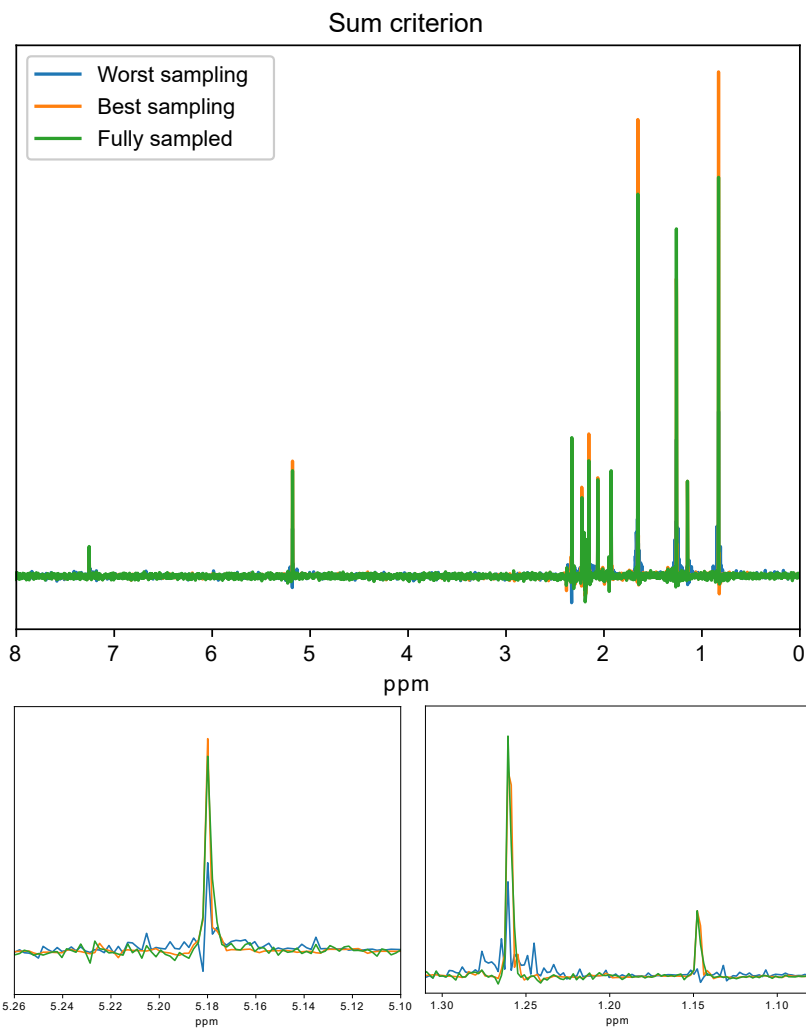


Figure 20 α -pinene, 50mM in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

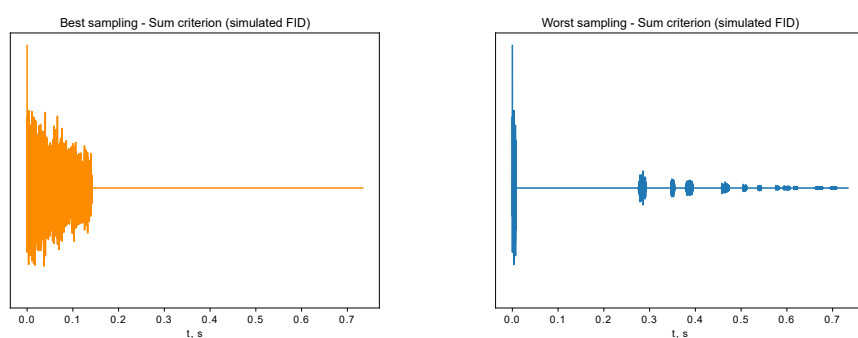


Figure 21 Sum criterion for α -pinene: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

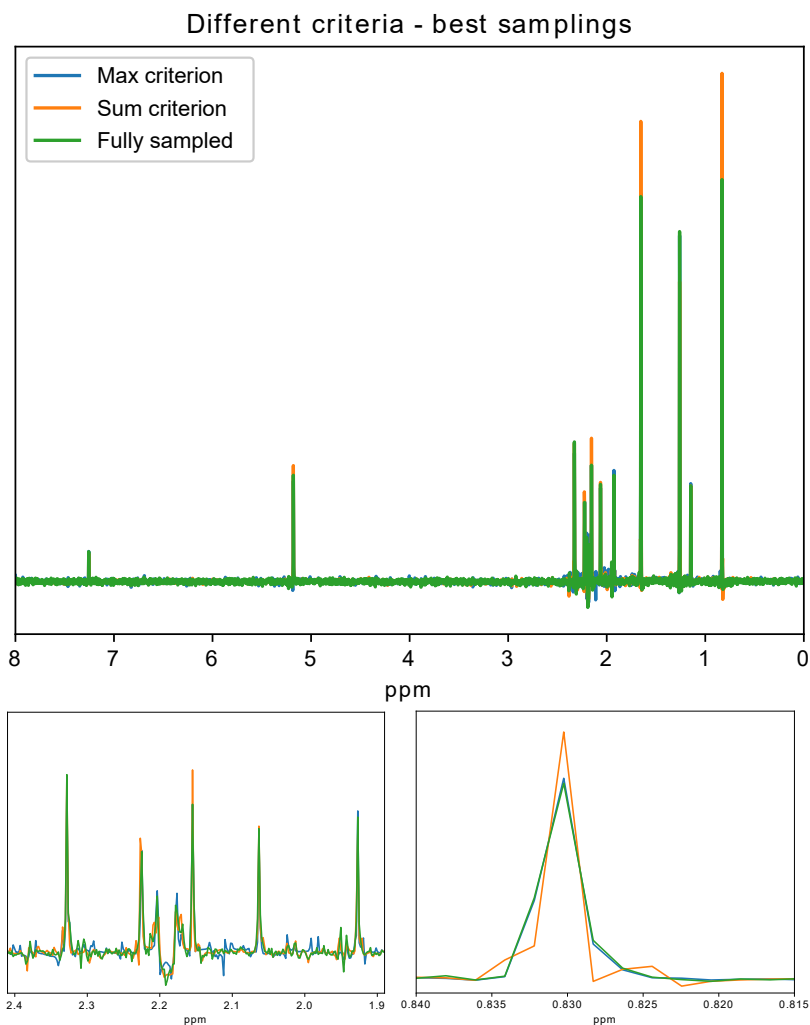


Figure 22 α -pinene, 50mM in CDCl_3 . Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum. In the bottom zoomed panel on the right, the results of the maximum criterion follow the fully sampled spectrum.

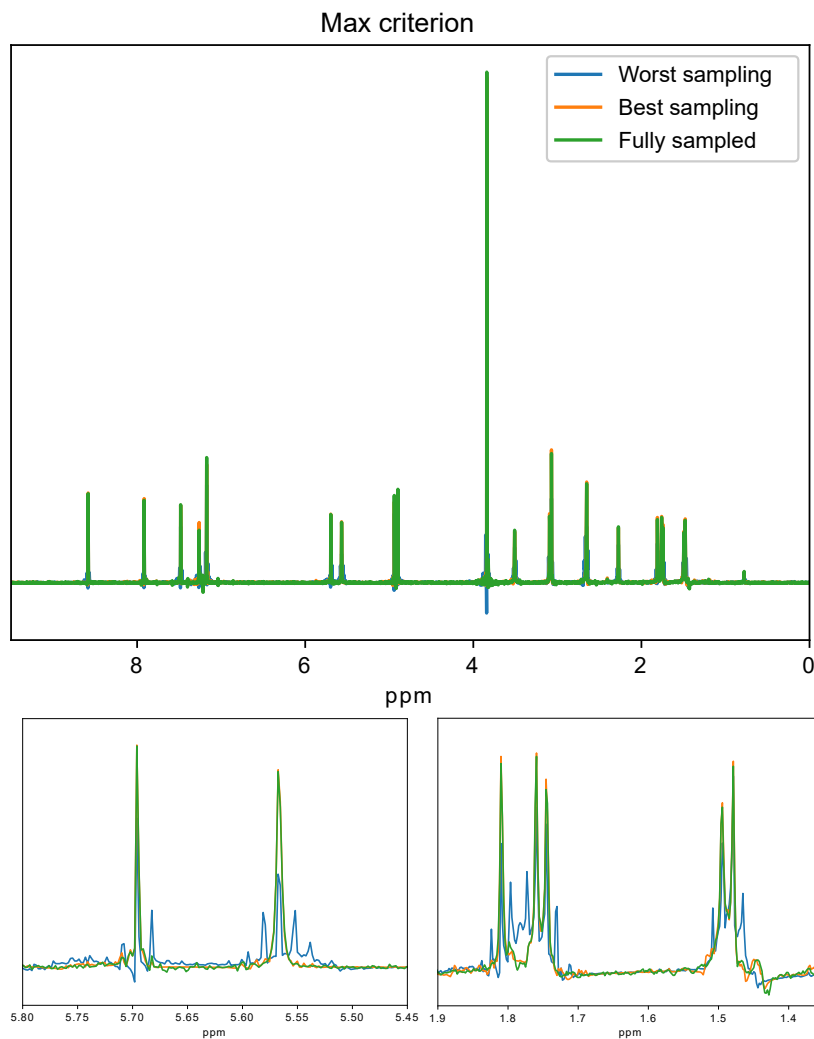


Figure 23 Quinine, 50mM in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

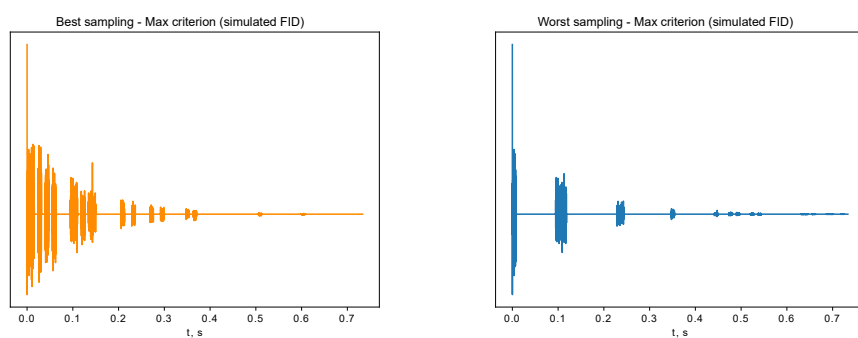


Figure 24 Maximum criterion for quinine: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

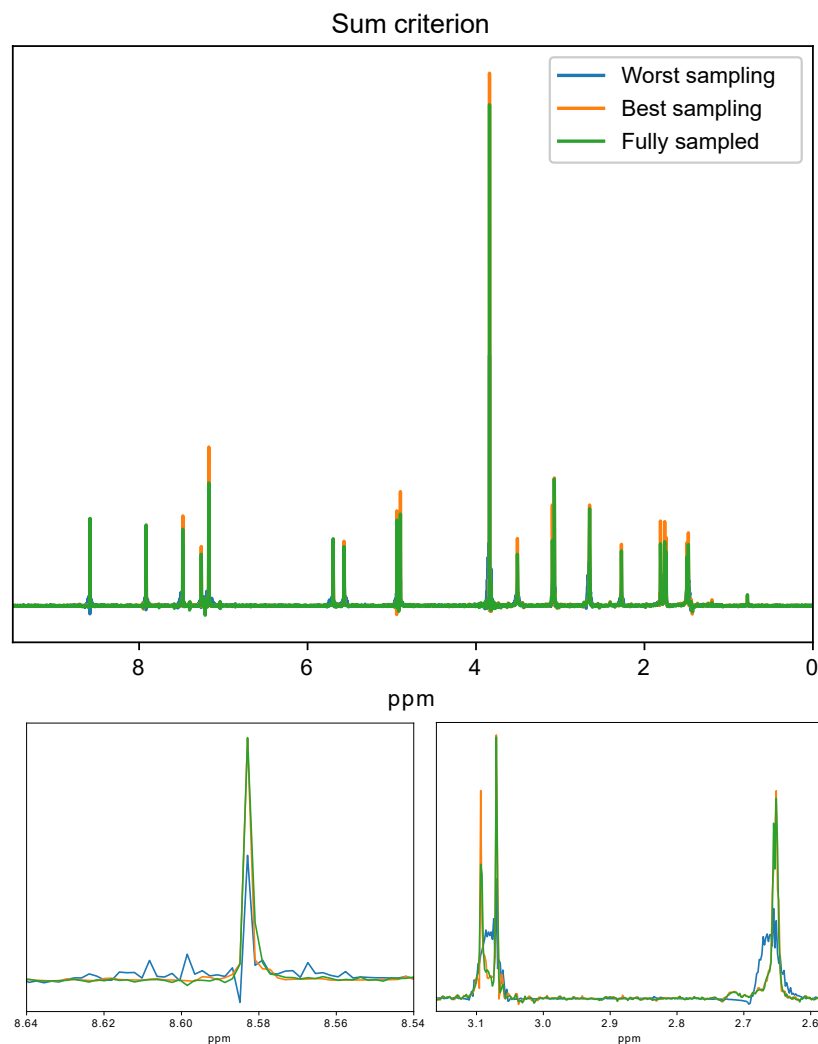


Figure 25 Quinine, 50mM in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

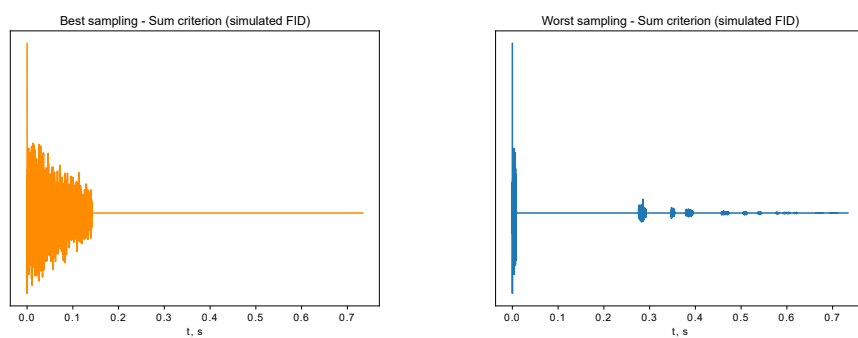


Figure 26 Sum criterion for quinine: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

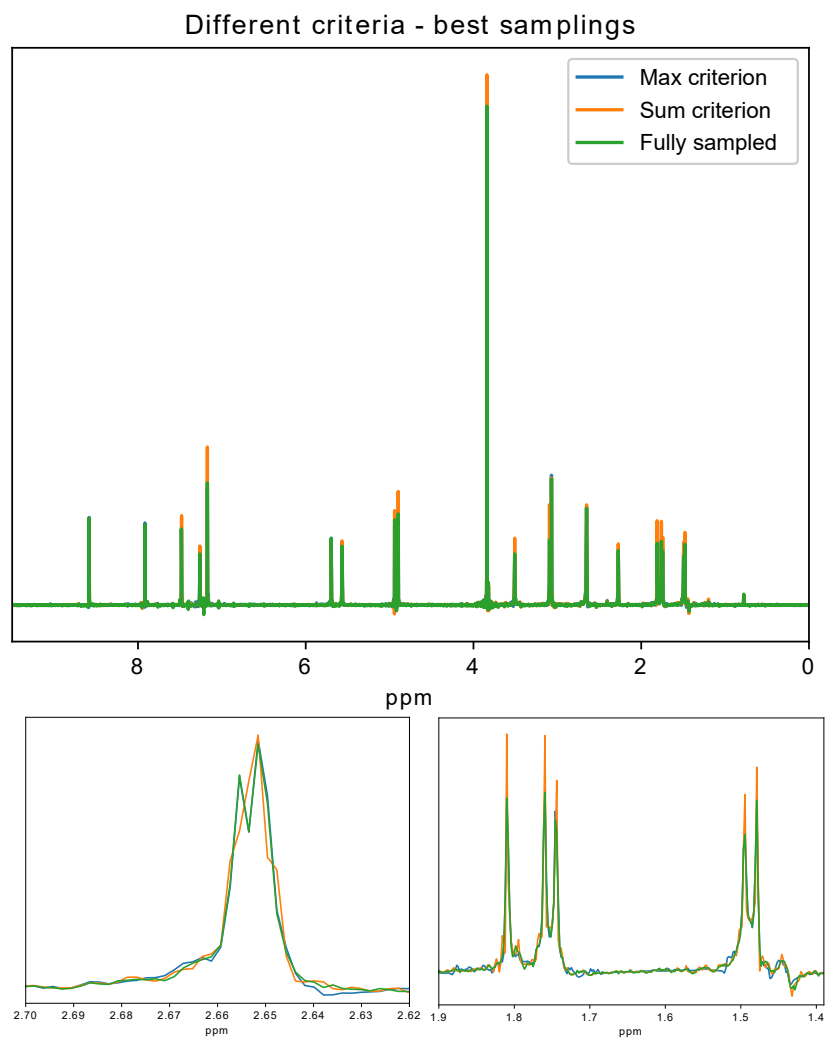


Figure 27 Quinine, 50mM in CDCl₃. Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum. In the bottom zoomed panels, the results of the maximum criterion follow the fully sampled spectrum.

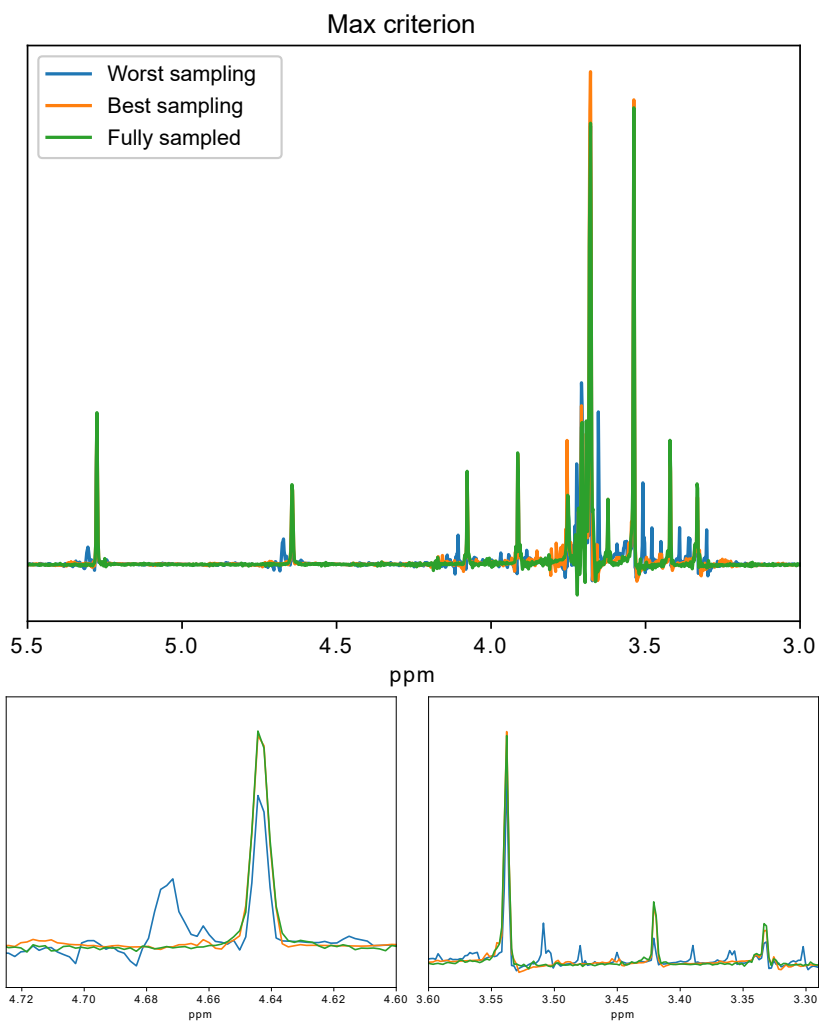


Figure 28 Sucrose, 50mM in D₂O. Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

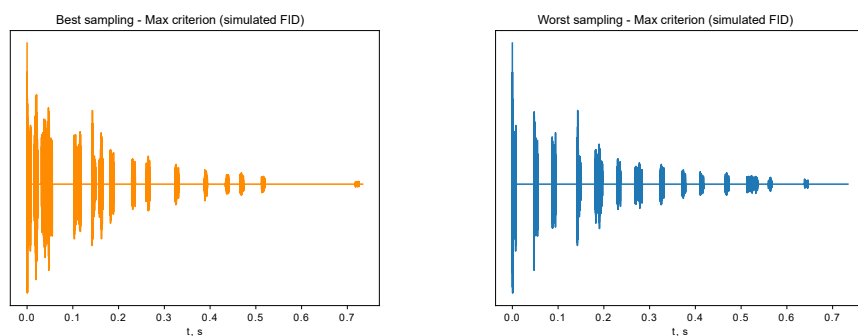


Figure 29 Maximum criterion for sucrose: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

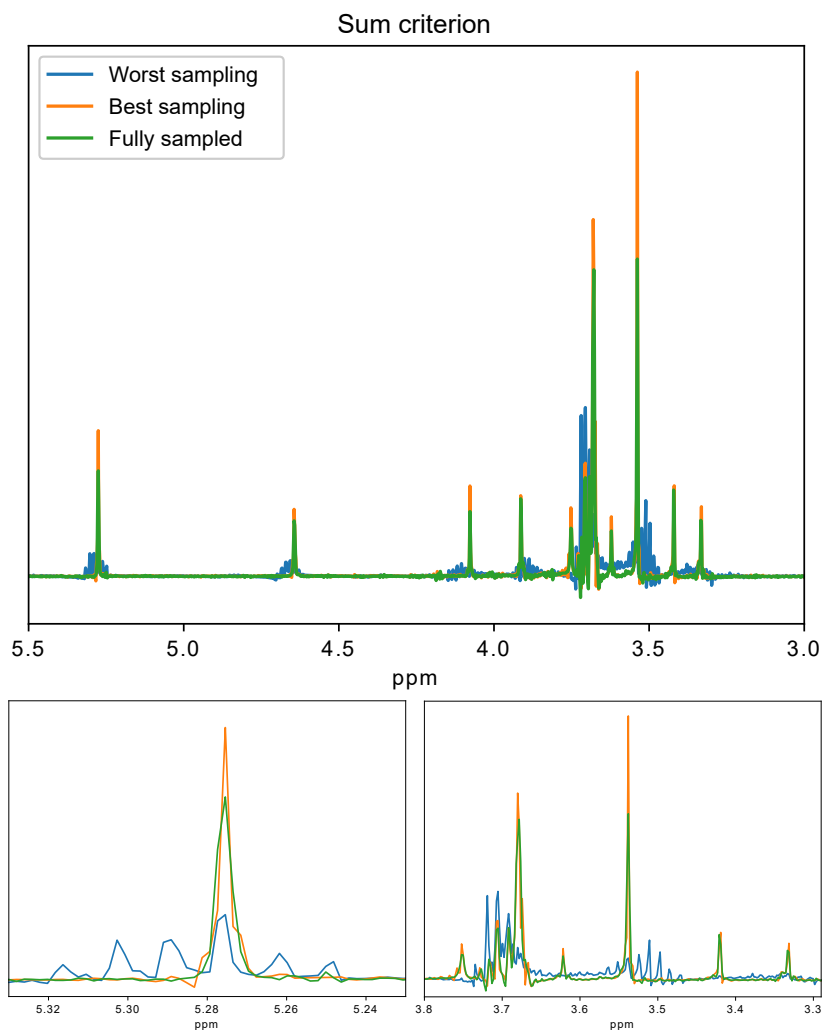


Figure 30 Sucrose, 50mM in D₂O. Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

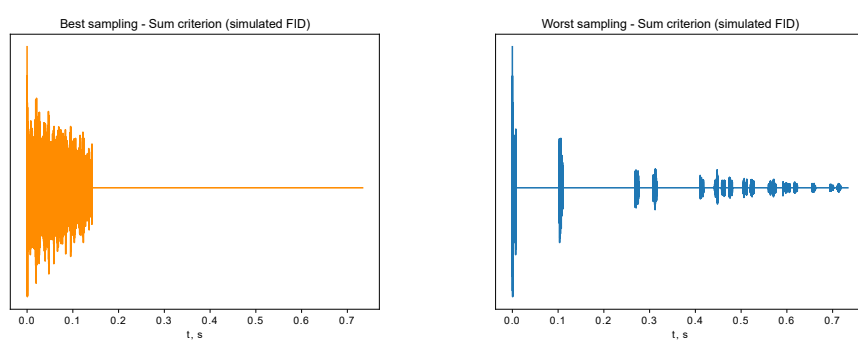


Figure 31 Sum criterion for sucrose: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

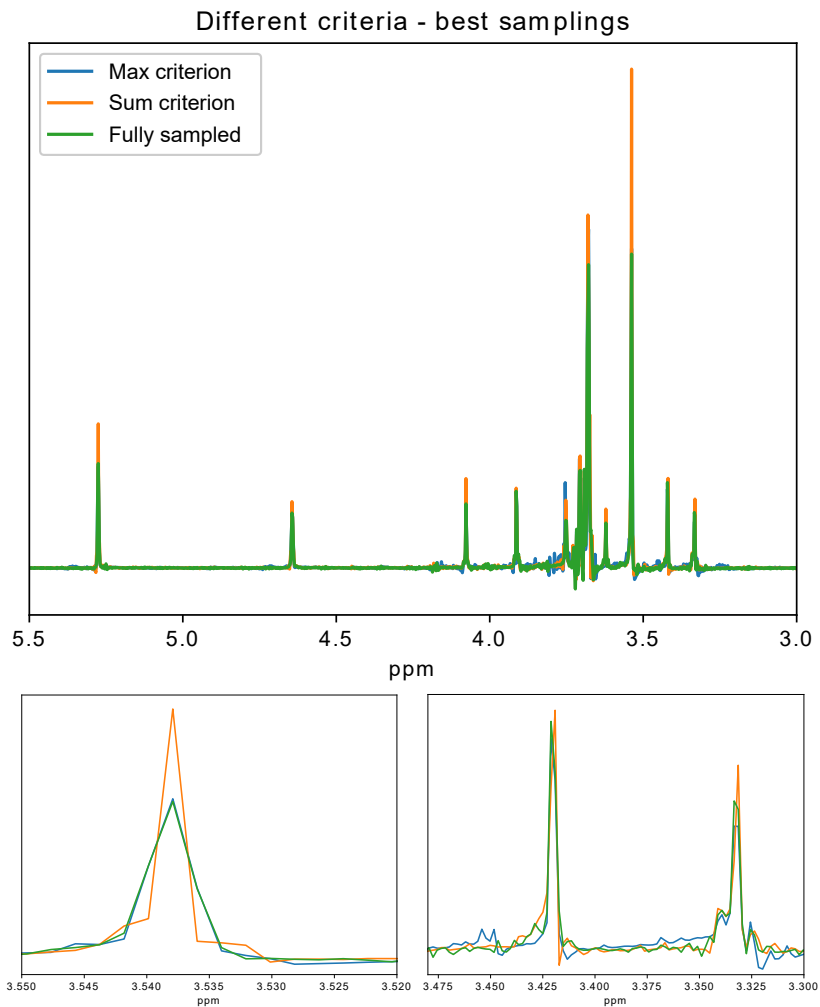


Figure 32 Sucrose, 50mM in D₂O. Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum. In the bottom zoomed panel on the left, the results of the maximum criterion follow the fully sampled spectrum.

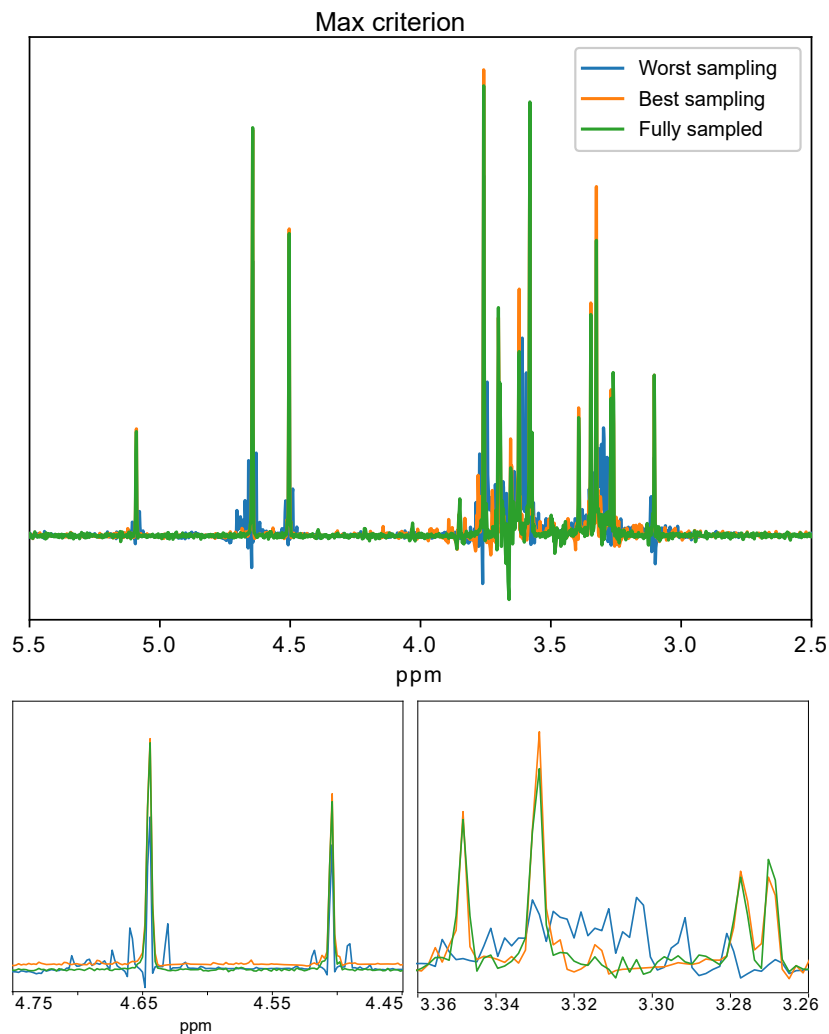


Figure 33 D-glucose, 50mM in D₂O. Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

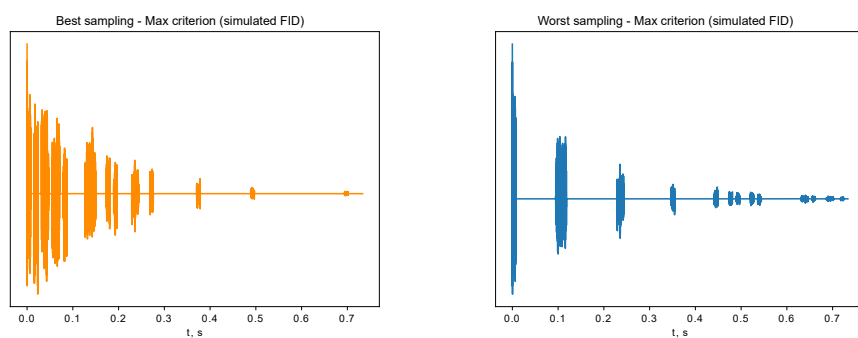


Figure 34 Maximum criterion for d-glucose: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

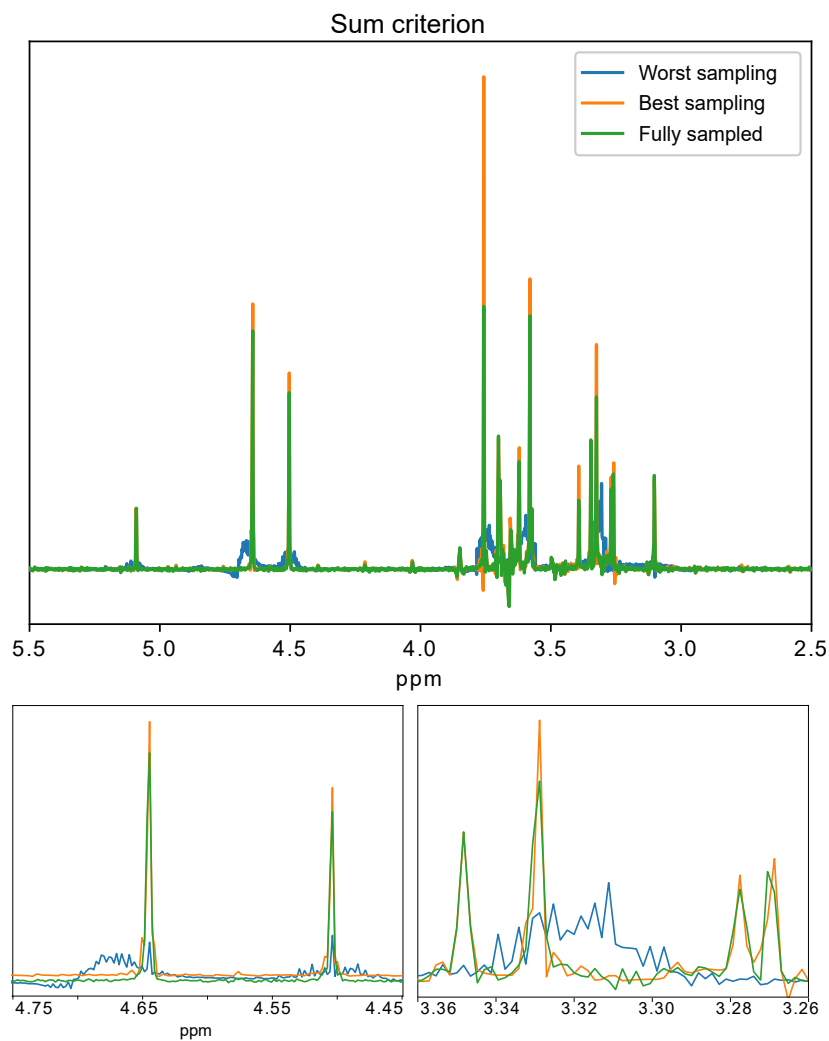


Figure 35 D-glucose, 50mM in D_2O . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

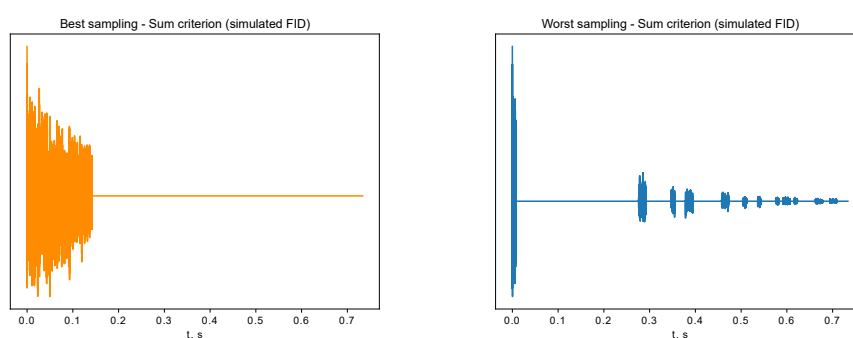


Figure 36 Sum criterion for D-glucose: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

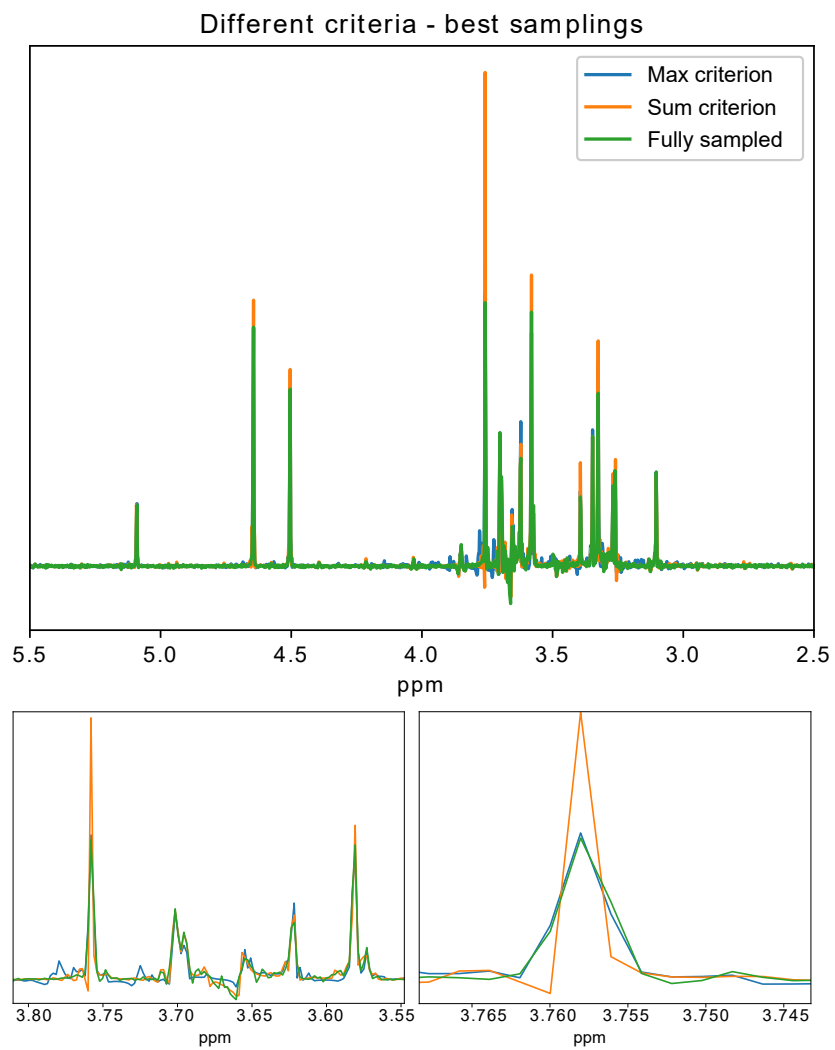


Figure 37 D-glucose, 50mM in D₂O. Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum.

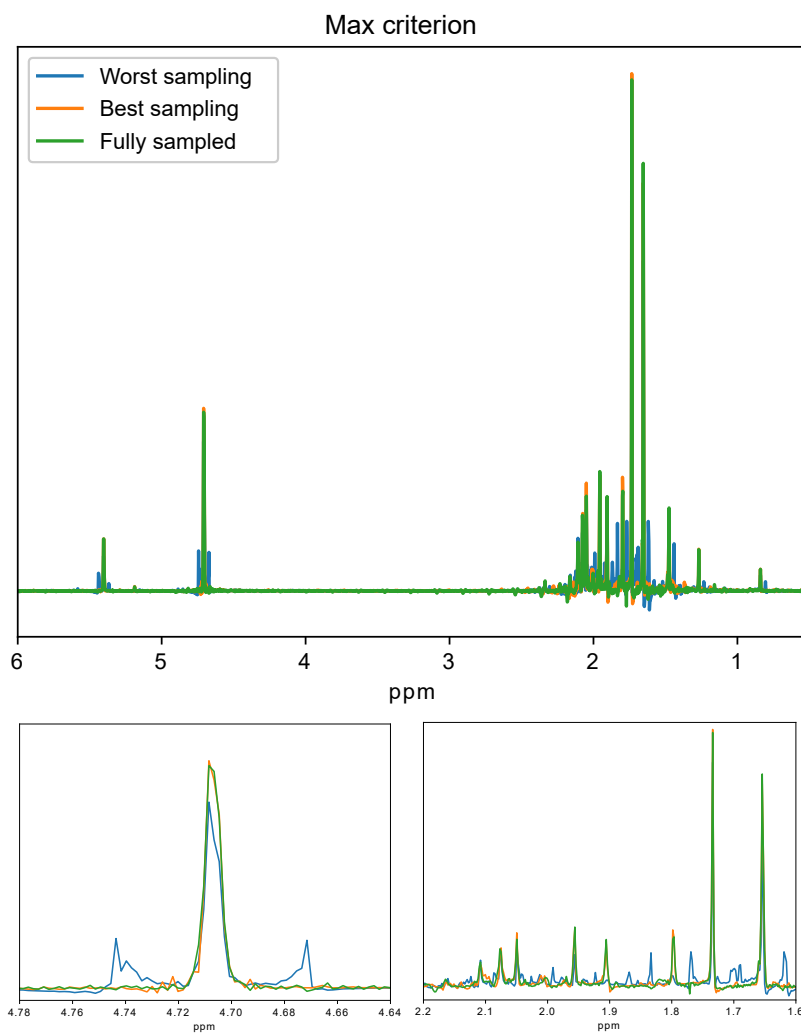


Figure 38 Mixture of 0.5M (R)-(+)-limonene and 50mM α -pinene in CDCl_3 . Maximum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

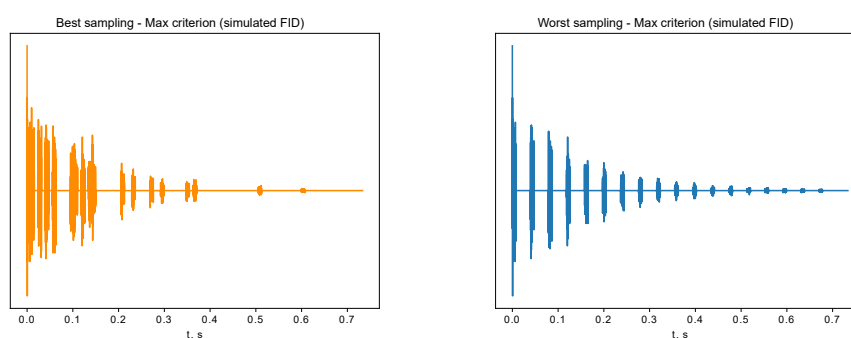


Figure 39 Maximum criterion for the mixture: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

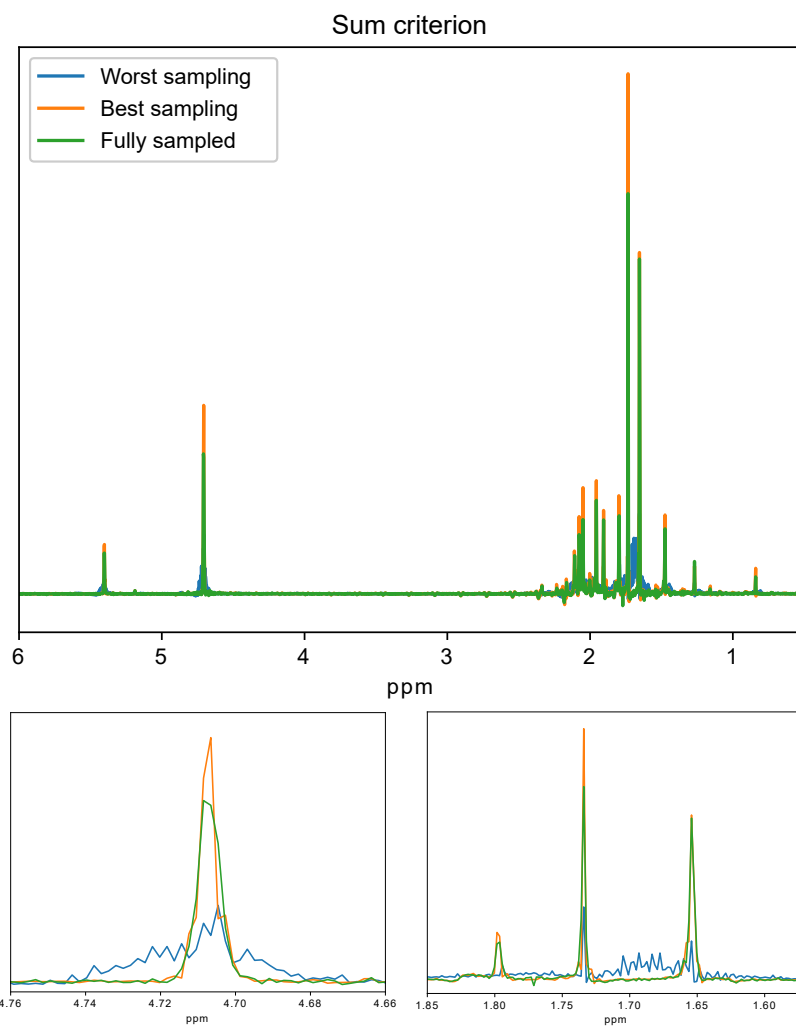


Figure 40 Mixture of 0.5M (R)-(+)-limonene and 50mM α -pinene in CDCl_3 . Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

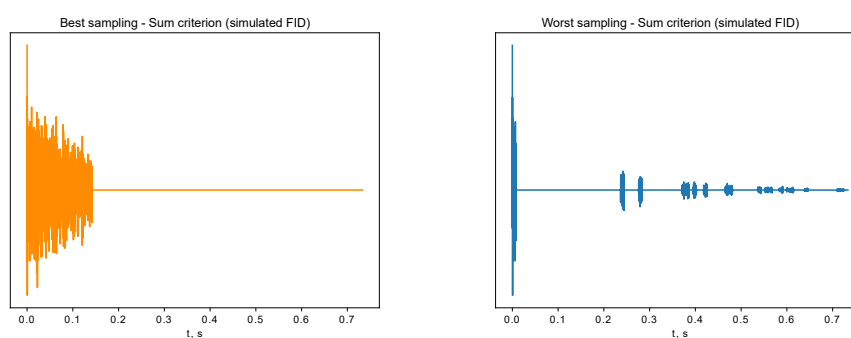


Figure 41 Sum criterion for the mixture: best and worst samplings applied to simulated FID of singlets (point 3 of the workflow).

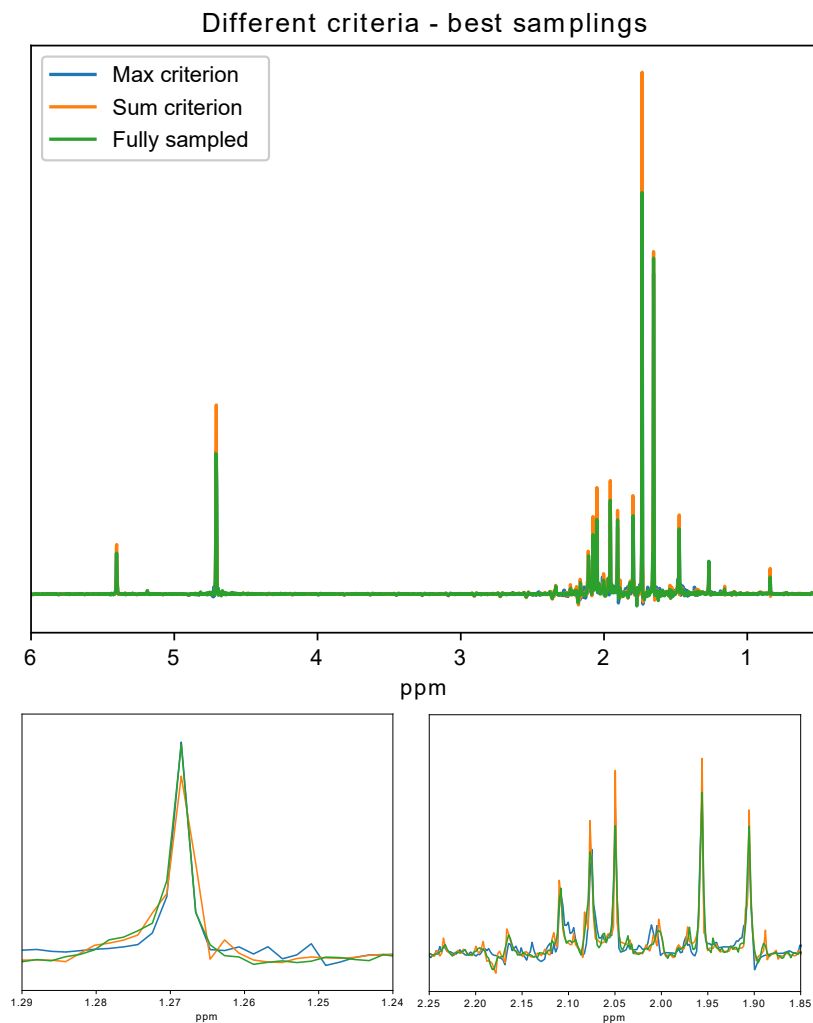


Figure 42 Mixture of 0.5M (R)-(+)-limonene and 50mM α -pinene in CDCl_3 . Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum.

The results for the β -estradiol sample (50mM in CD_3OD), maximum criterion, are given in the main text, Fig.1. Here, we present the results for the sum criterion of the same sample:

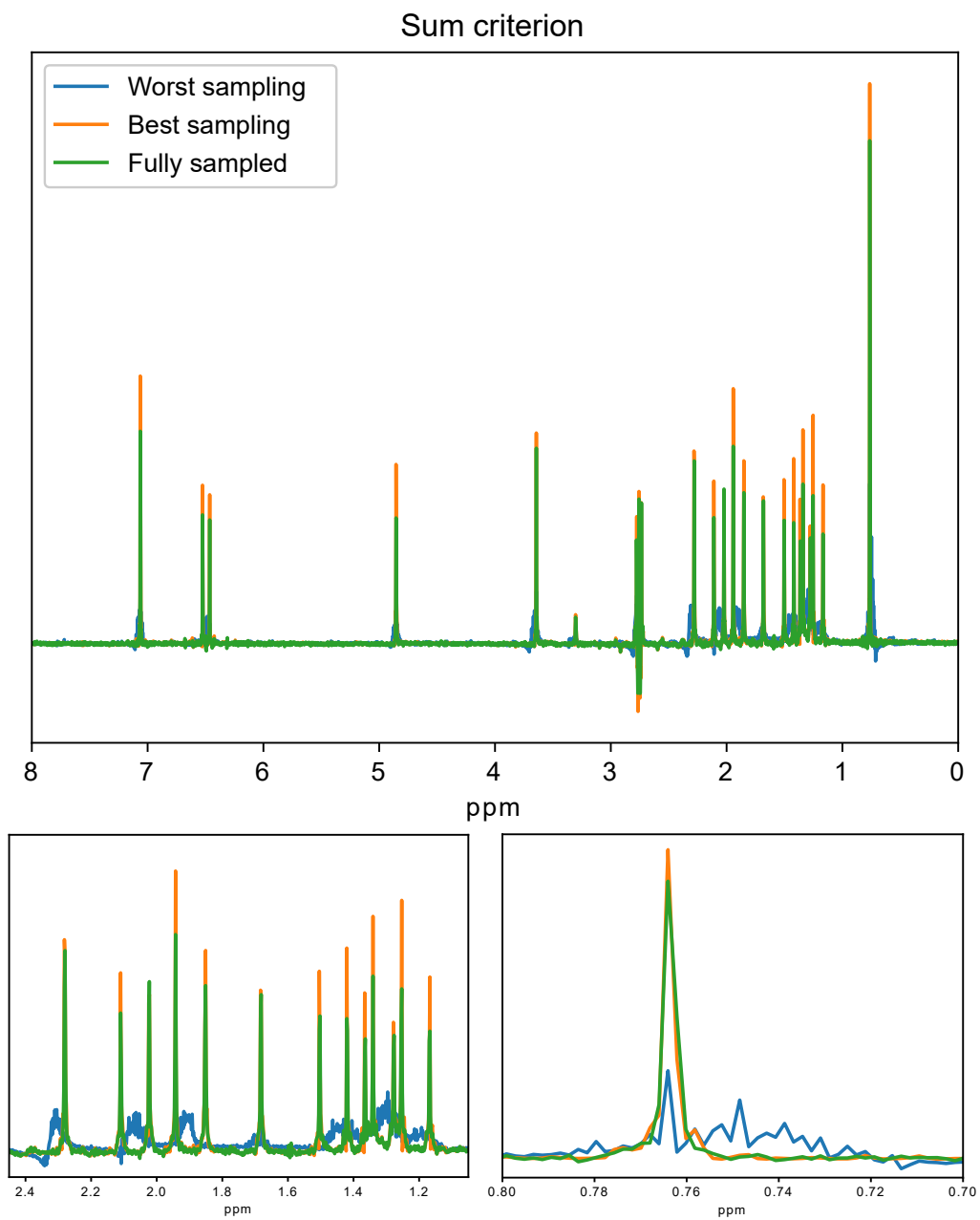


Figure 43 Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum. β -estradiol, 50mM in CD_3OD .

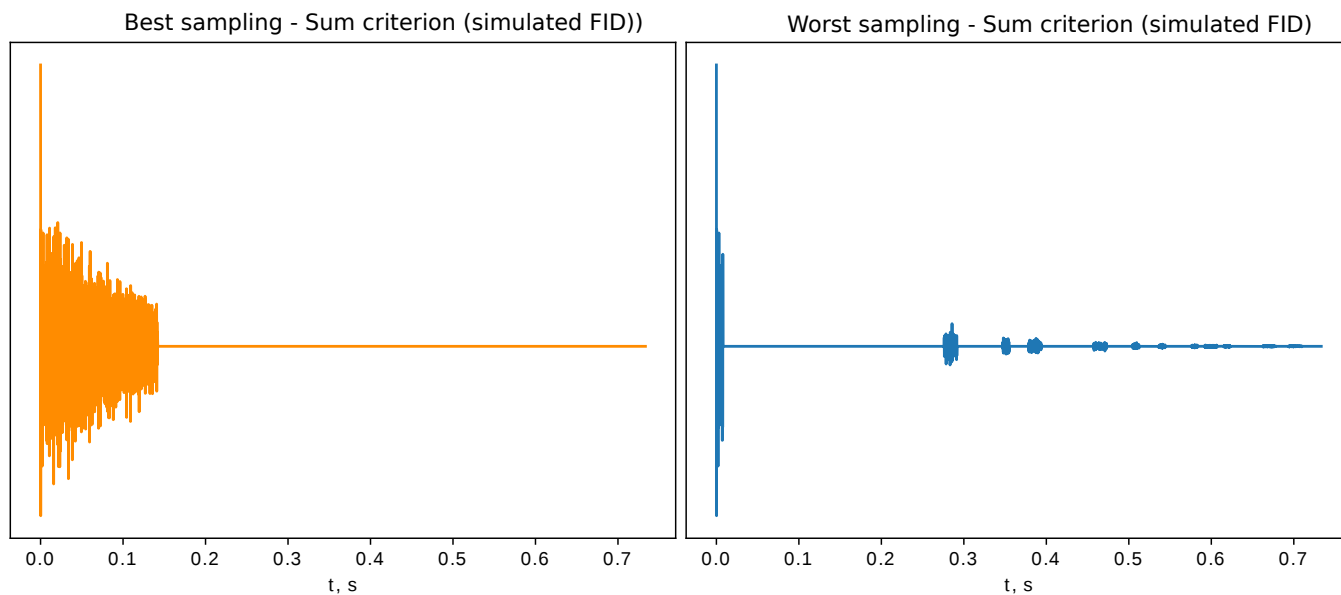


Figure 44 Sum criterion: best and worst samplings applied to simulated FID of singlets (step 3 of the work-flow).

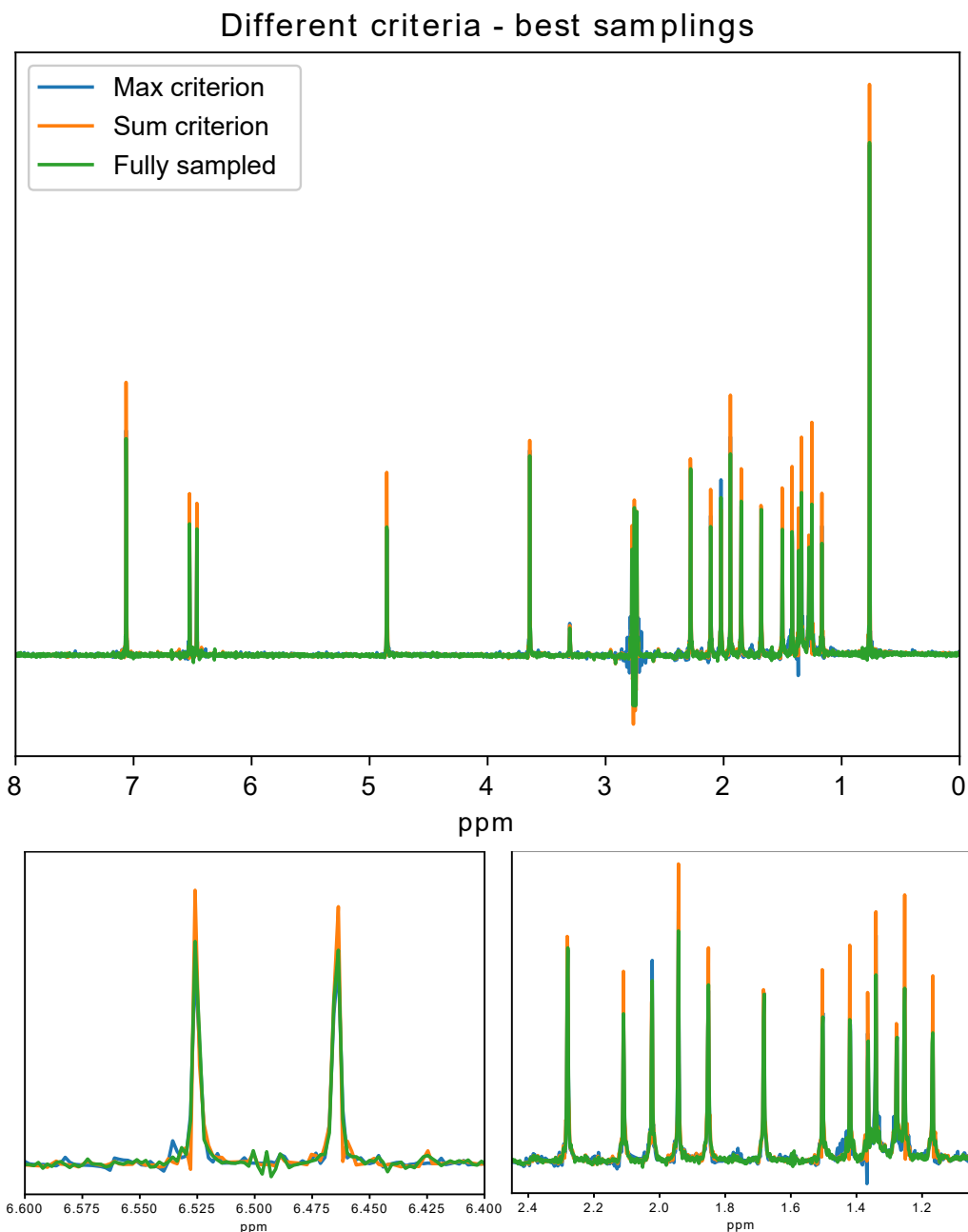


Figure 45 Maximum and sum criterion comparison and the original fully sampled pure-shift spectrum. β -estradiol, 50mM in CD_3OD . See the results for other samples in ESI†.

The sum criterion often yields FID truncation as the best sampling. We also explored if it is worth to reconstruct this truncated FID with linear prediction instead of compressed sensing, as we normally do. It turns out that linear prediction does not cope with the task, as is illustrated in Figs.46.

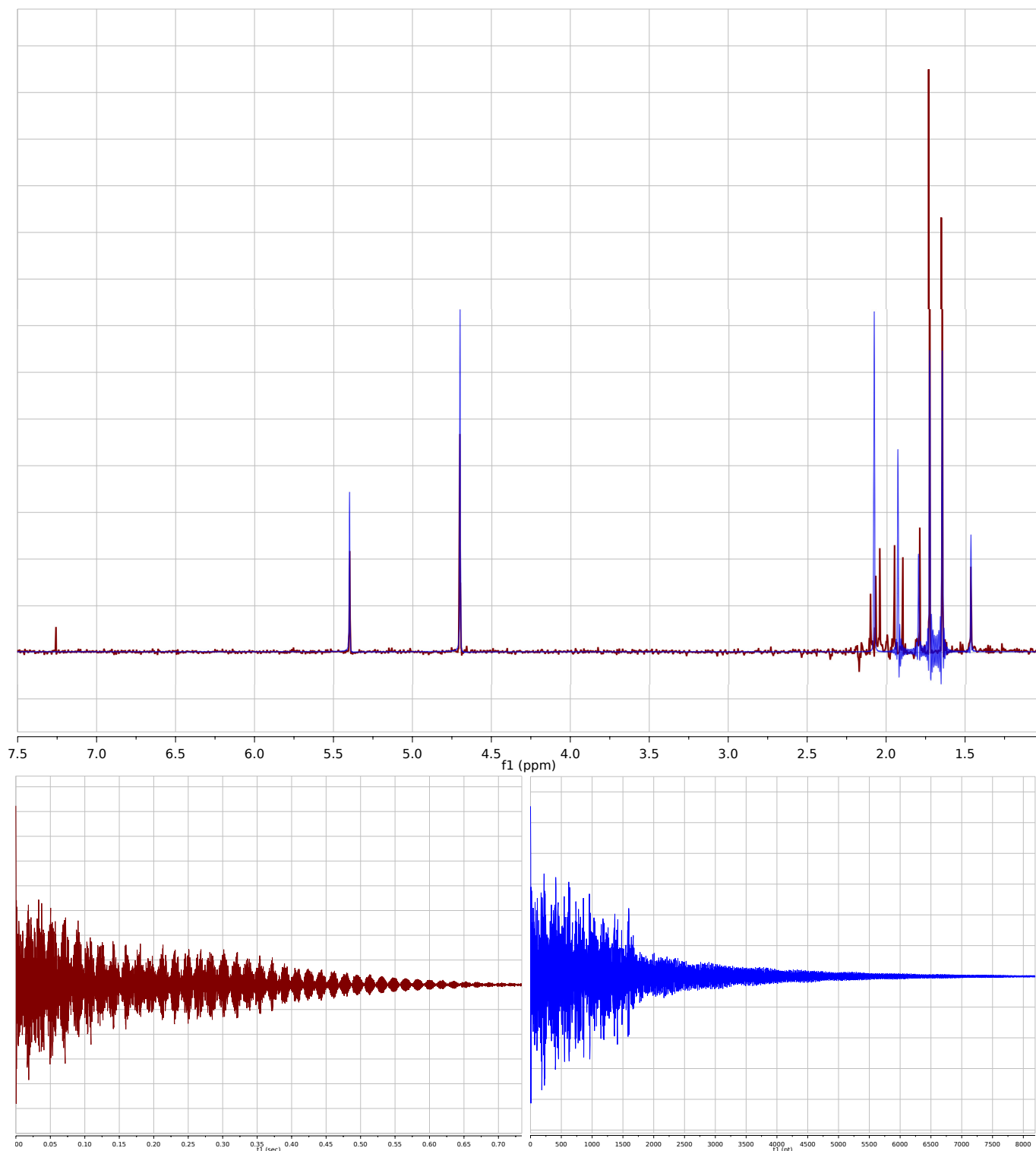


Figure 46 (R)-(+)-limonene: reconstruction of the truncated FID (best sampling according to the sum criterion) with iterative soft thresholding algorithm belonging to the compressed sensing family (red) and with linear prediction (blue). Top panel: reconstructed spectra. Bottom panels: reconstructed FIDs. The linear prediction reconstruction is carried out in MestreNova 11.0 software with standard parameters. The compressed sensing reconstruction is carried out with mddnmr software with standard parameters.

We also explored the issue of decreasing the number of measured chunks on the example of D-glucose and β -estradiol. In the main text, as well as in all the other examples here, the number of measured chunks was 18 out of 93. For these two examples, we performed the same sampling optimization and reconstruction

procedure for 17, 16, ... etc. chunks. The results for the maximum criterion and the sum criterion are shown in Figs.47, 49, 51, 53. Figs.48, 50, 52, 54 present the corresponding best samplings.

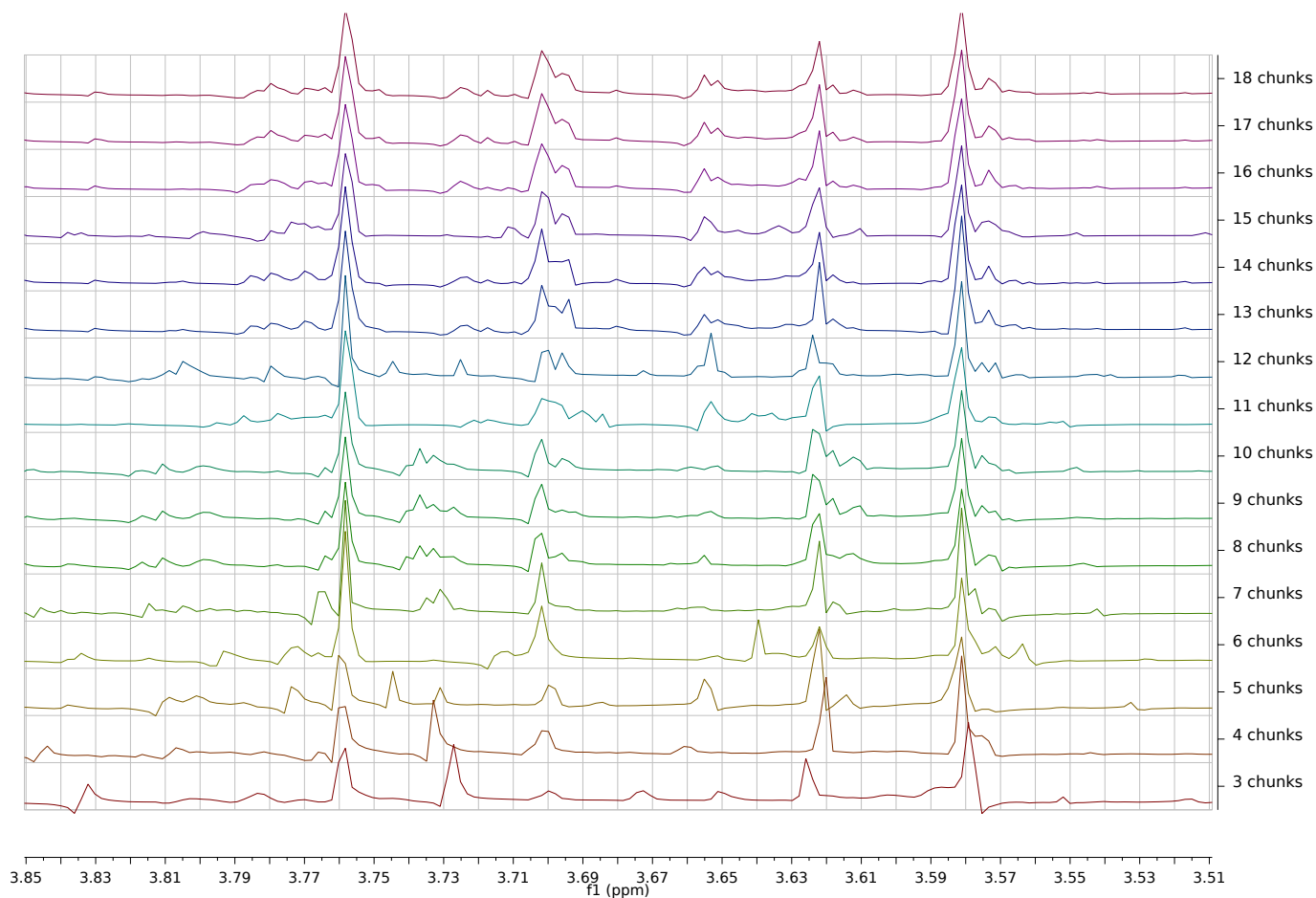


Figure 47 Decreasing the number of measured chunks: sampling optimization with the maximum criterion and reconstruction of the best sampling results. 50 mM glucose.

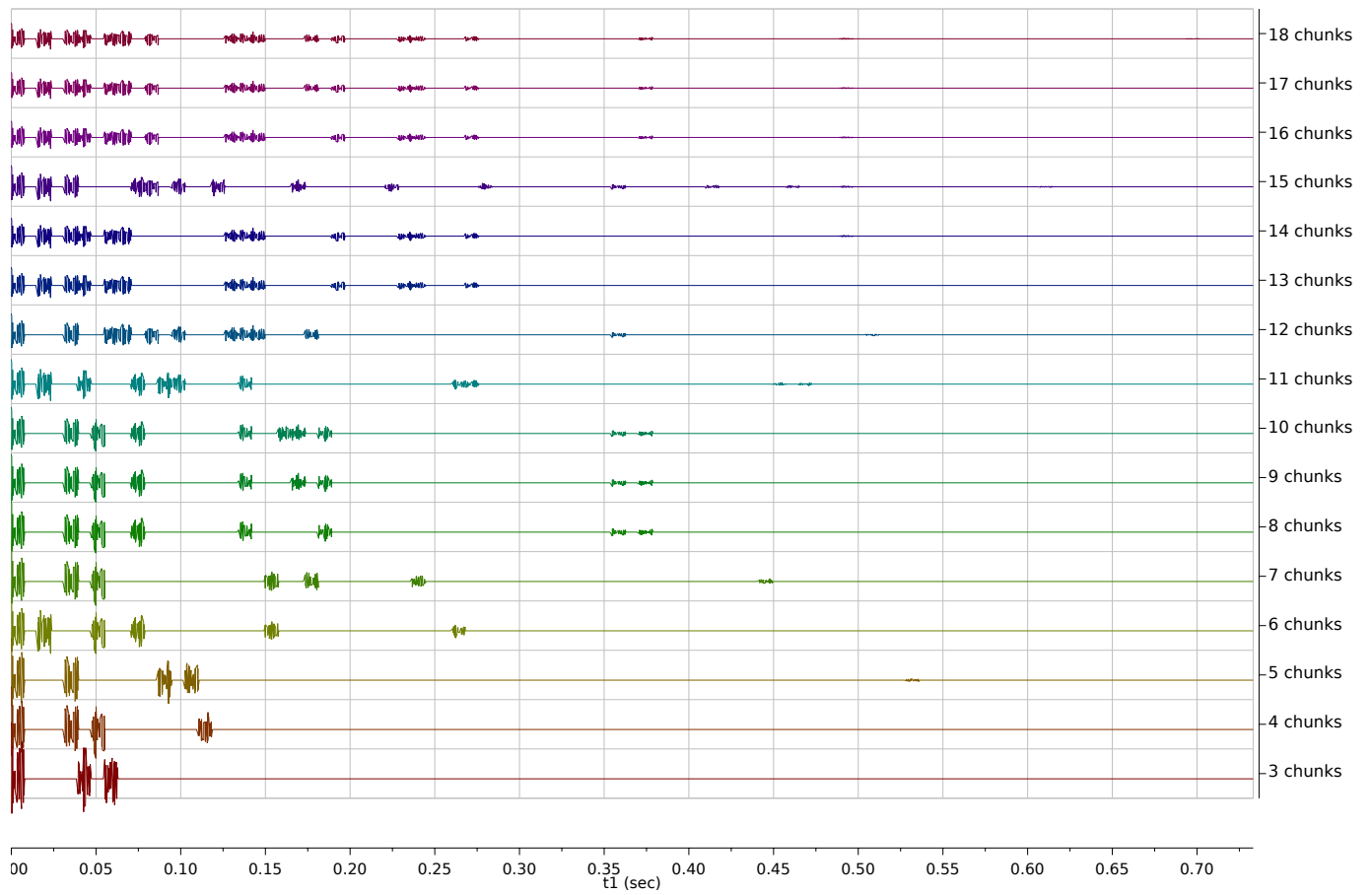


Figure 48 Decreasing the number of measured chunks: best samplings according to the maximum criterion.

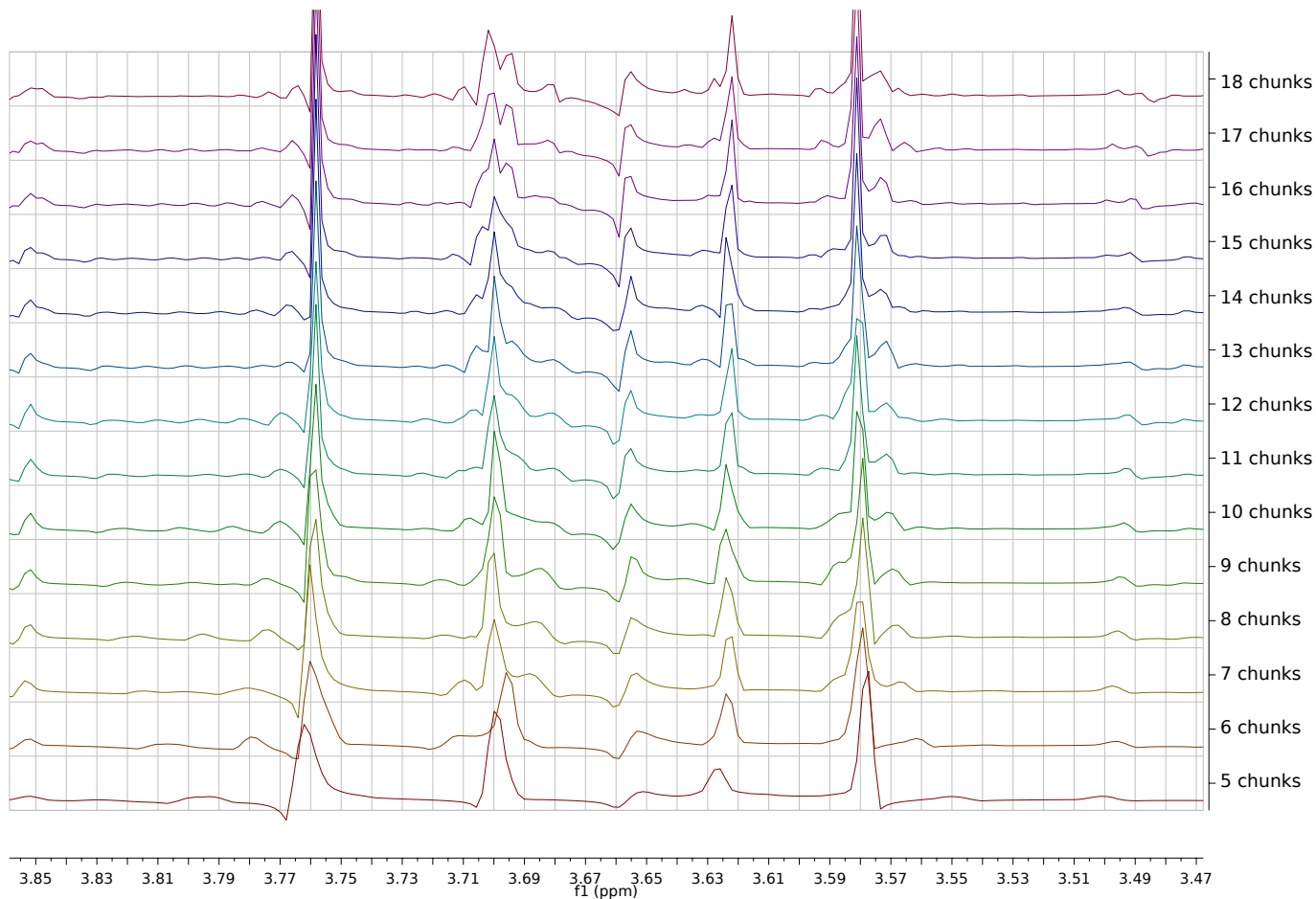


Figure 49 Decreasing the number of measured chunks: sampling optimization with the sum criterion and reconstruction of the best sampling results. 50 mM glucose.

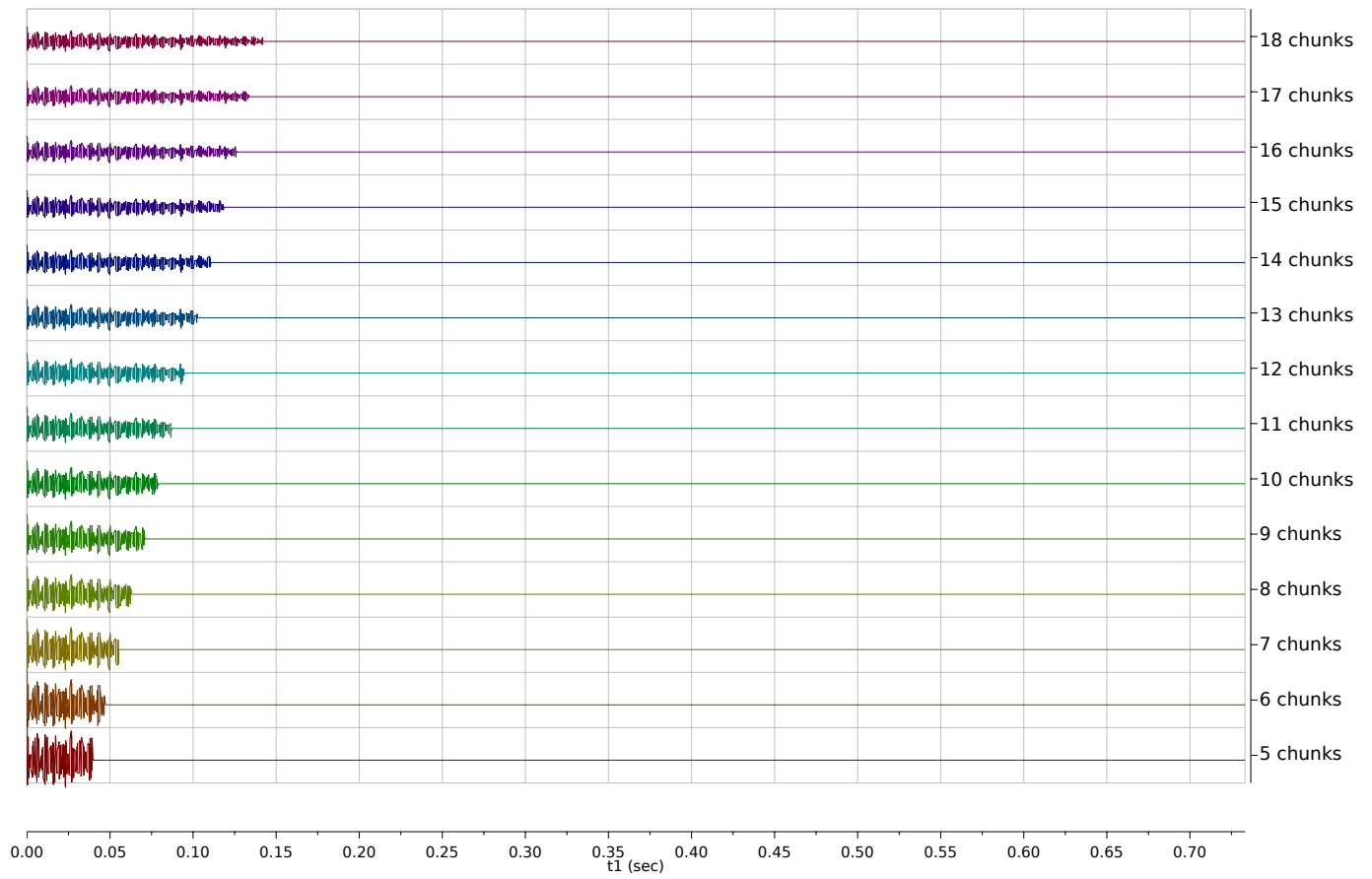


Figure 50 Decreasing the number of measured chunks: best samplings according to the sum criterion.

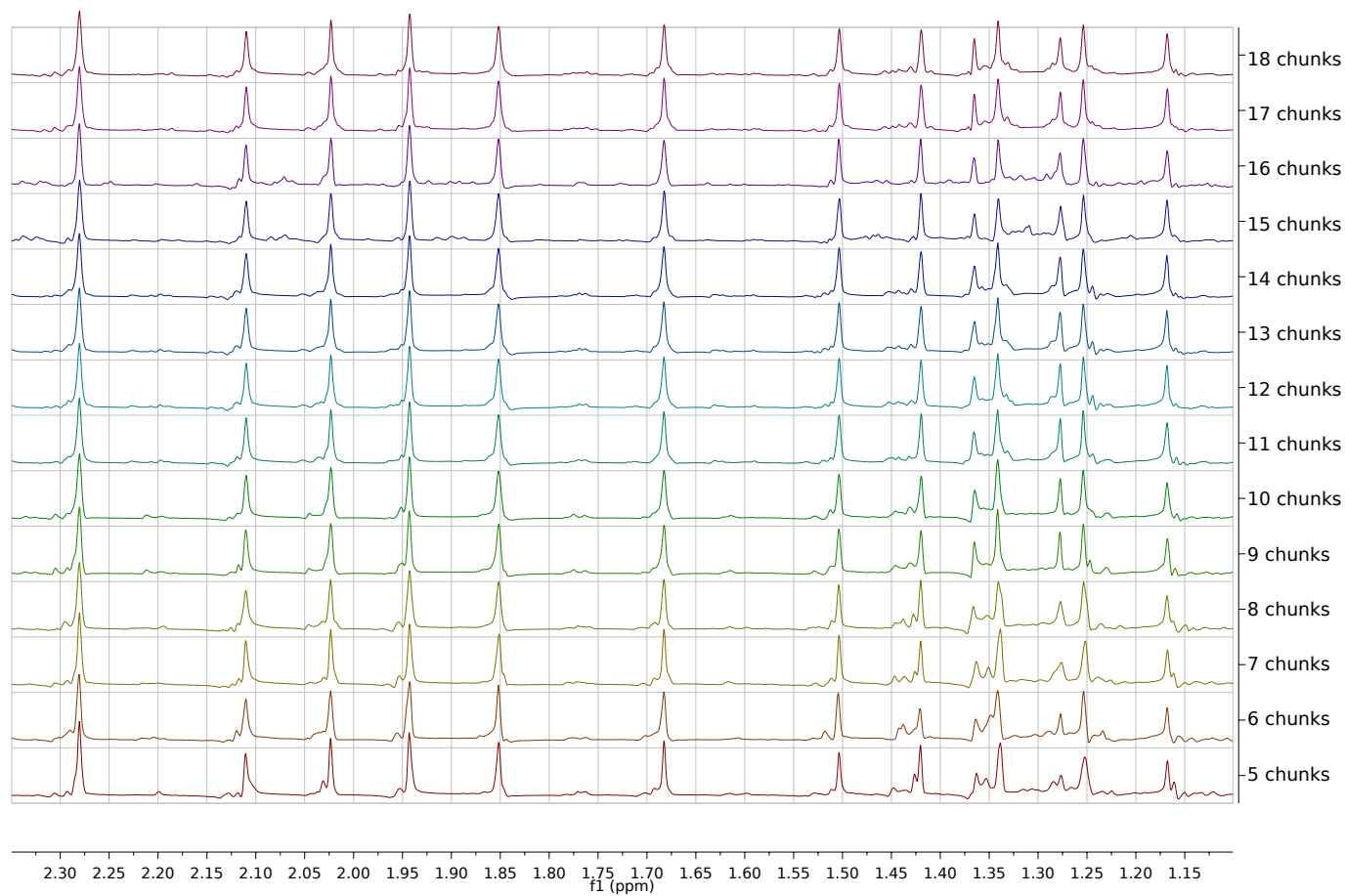


Figure 51 Decreasing the number of measured chunks: sampling optimization with the maximum criterion and reconstruction of the best sampling results. 50 mM β -estradiol.

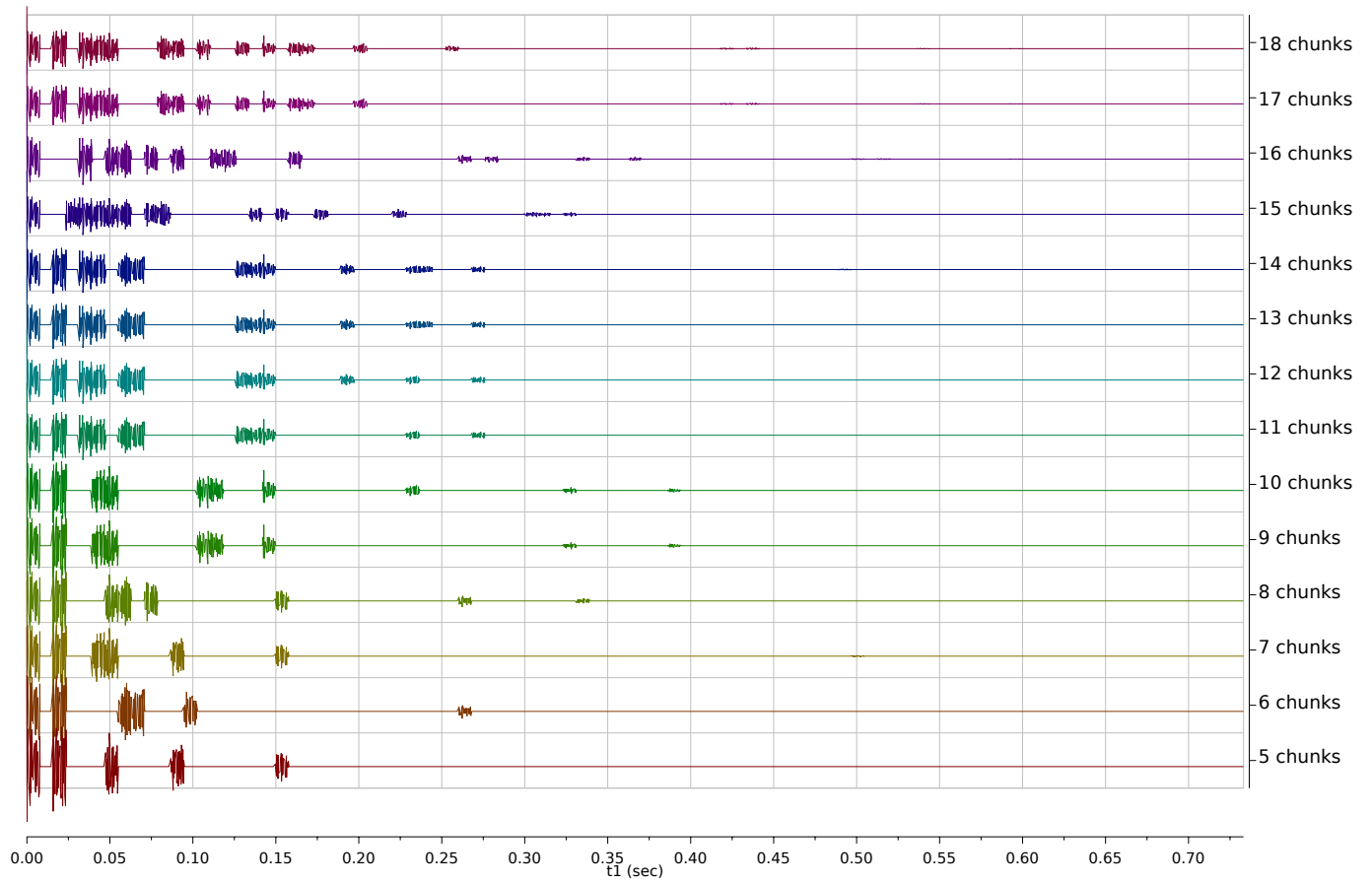


Figure 52 Decreasing the number of measured chunks: best samplings according to the maximum criterion.

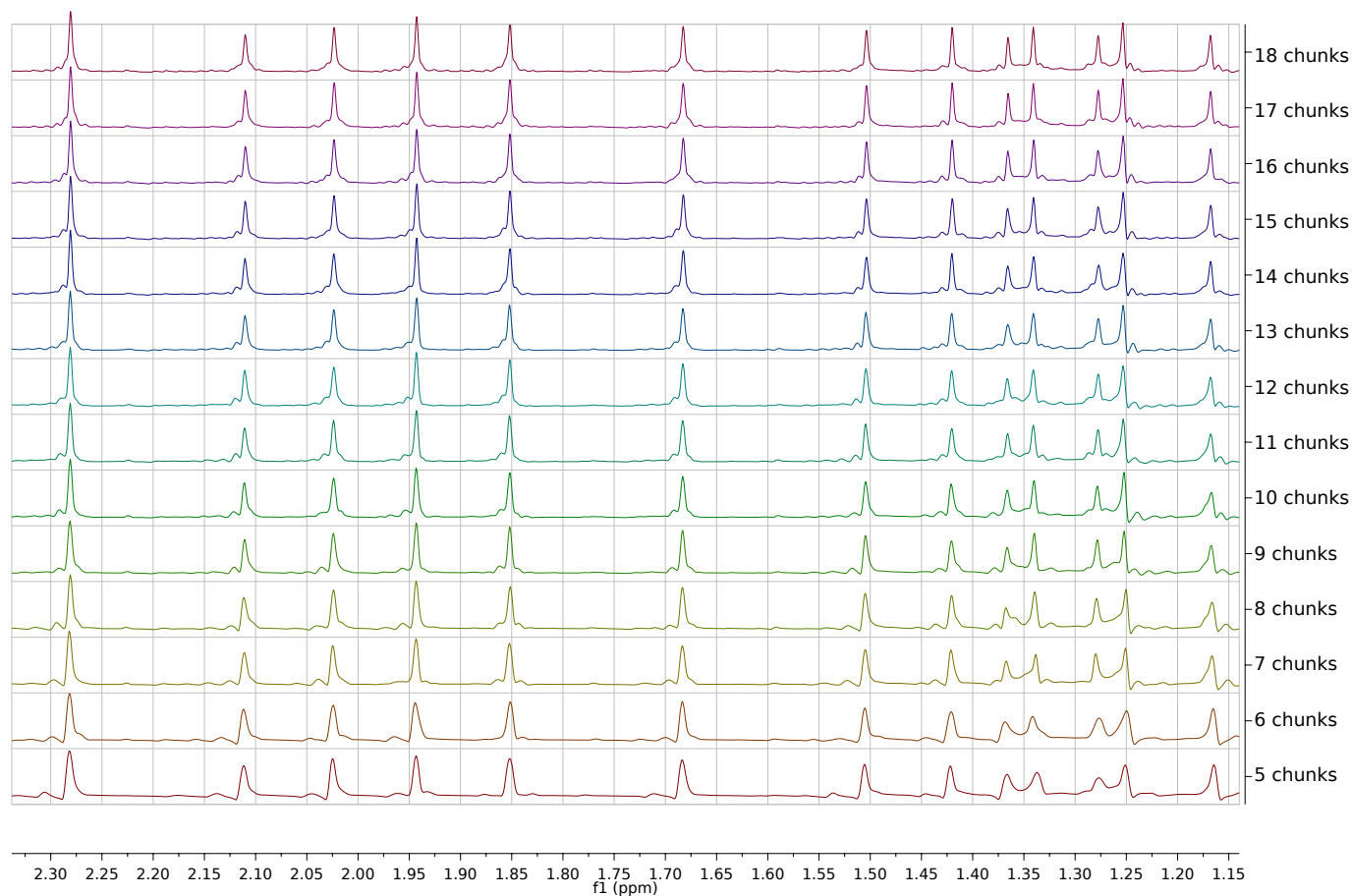


Figure 53 Decreasing the number of measured chunks: sampling optimization with the sum criterion and reconstruction of the best sampling results. 50 mM β -estradiol.

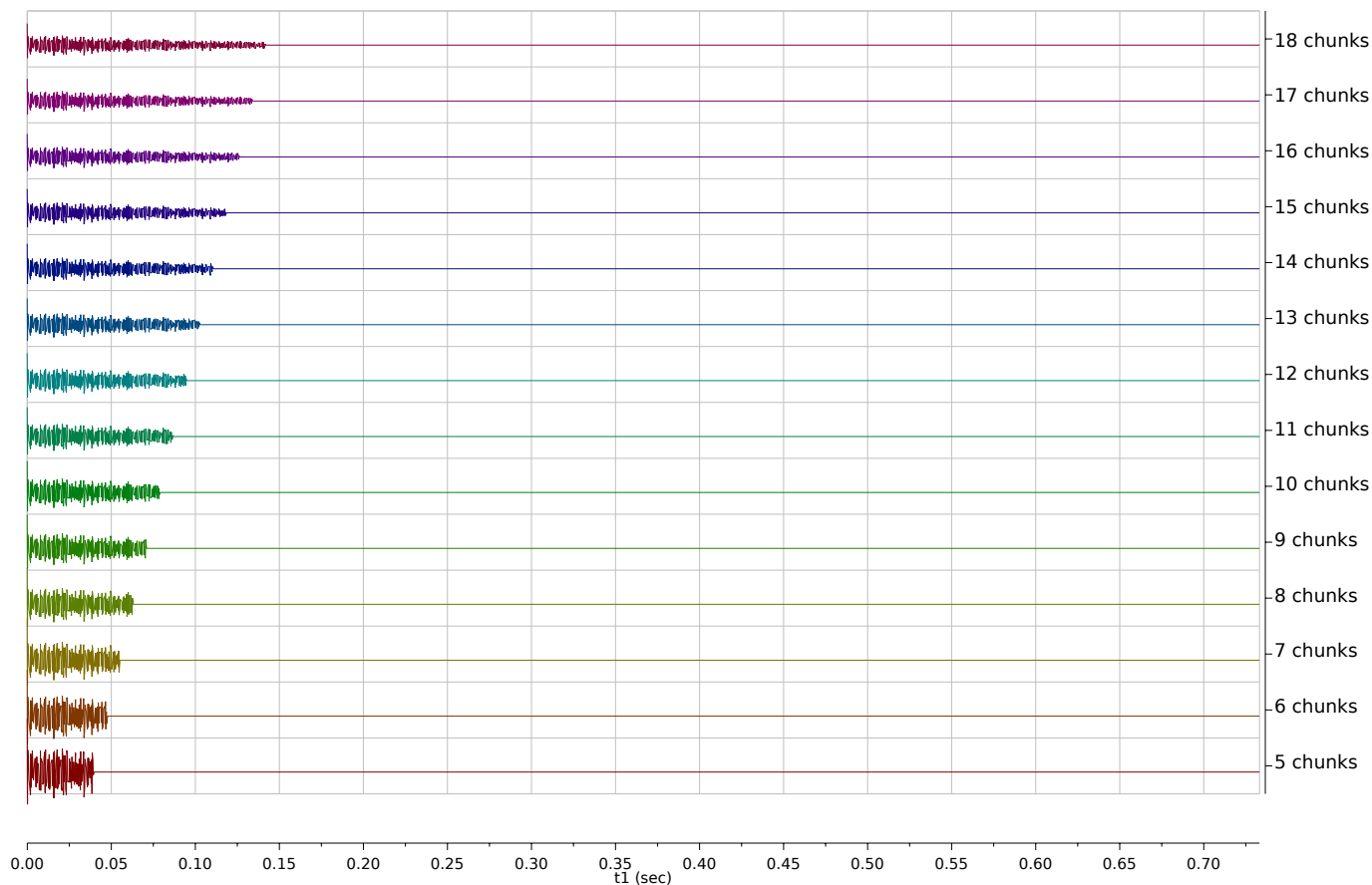


Figure 54 Decreasing the number of measured chunks: best samplings according to the sum criterion.

In all the cases presented above, the sum criterion yielded a simple truncation of the FID as the best sampling. However, this is not always the case: when the FID does not fully decay during the acquisition time, the sum criterion will yield another type of sampling, as is illustrated in Figs.56 (samplings) and 57 (results). This may occur in practice when one does not need a long FID, as all peaks are already resolved earlier. Among our examples, quinine demonstrated such a behaviour. Fig 55 shows that a short acquisition of 0.1835 s (16 chunks of 128 points) is enough in this case.

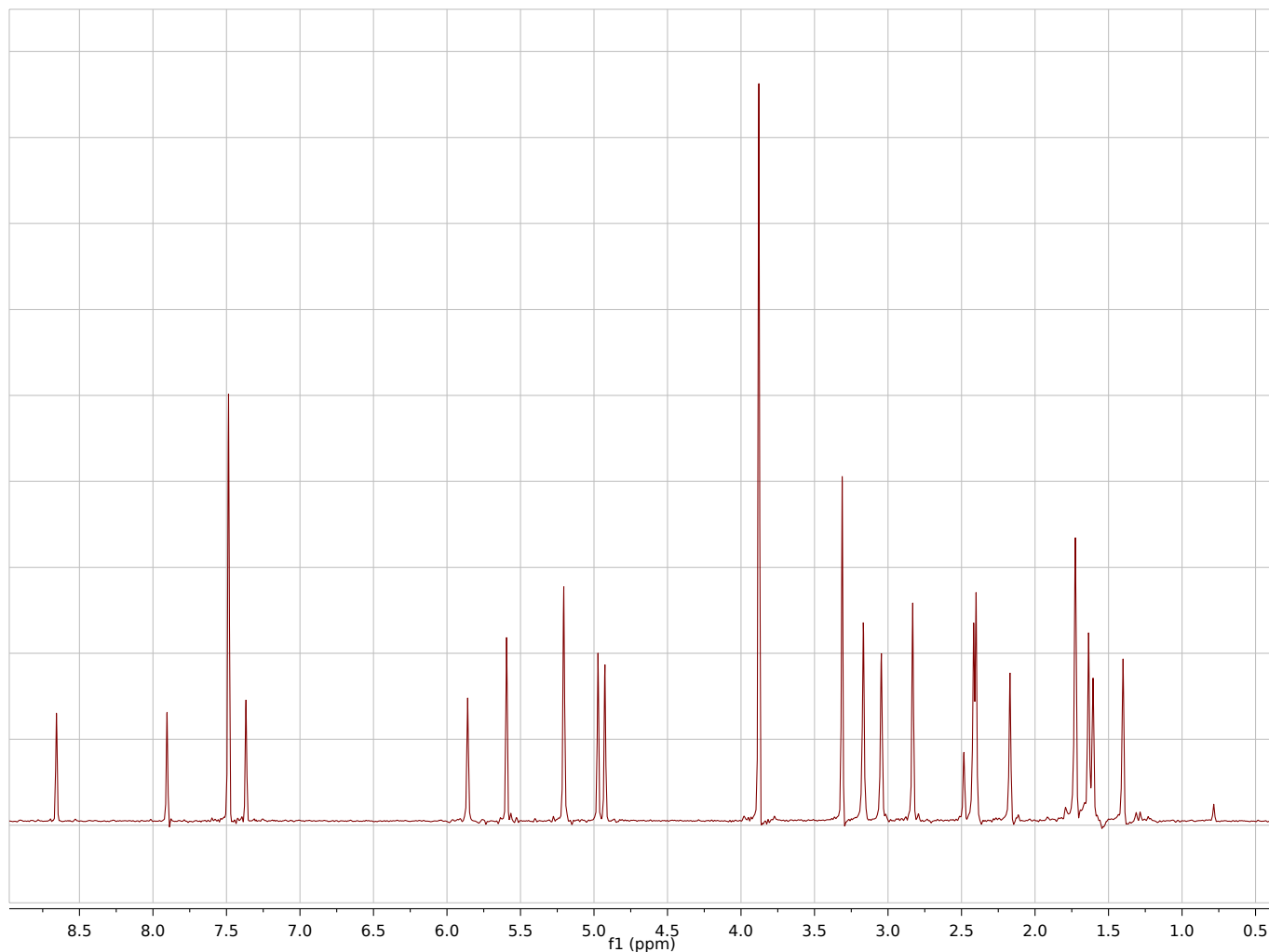


Figure 55 Quinine, 50mM in CDCl_3 , PSYCHE shorter acquisition: 0.1835 s (16 chunks of 128 points). All peaks are resolved.

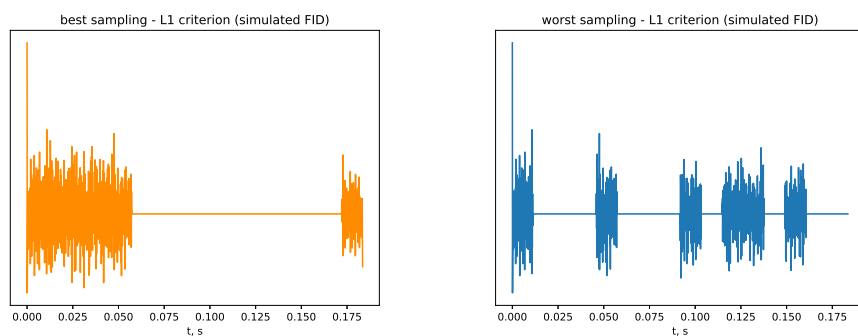


Figure 56 Sum criterion for quinine, shorter acquisition: 0.1835 s (16 chunks of 128 points): best and worst samplings applied to simulated FID of singlets (point 3 of the workflow). 6 measured chunks out of 16. The best sampling is not a truncated one.

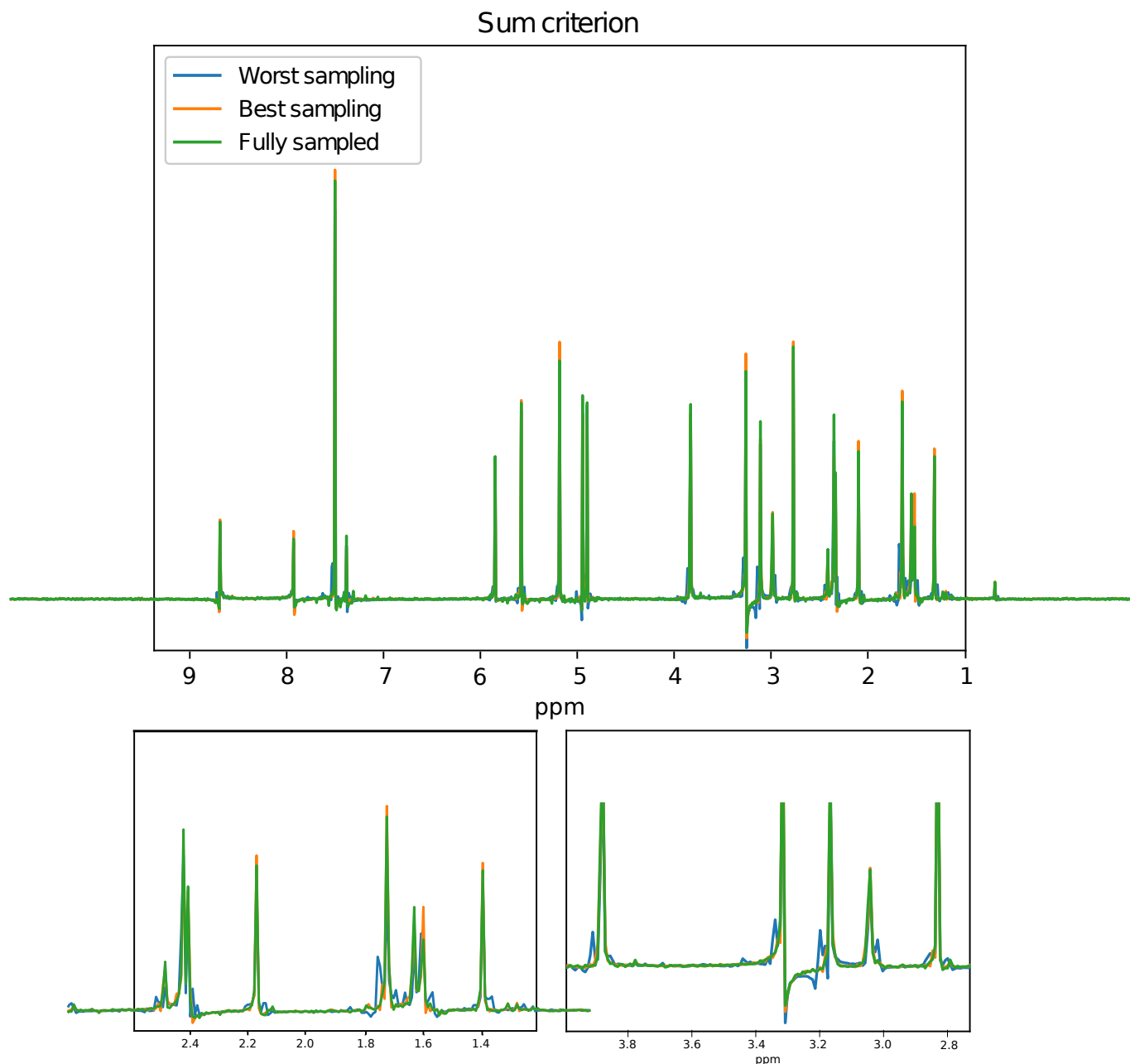


Figure 57 Quinine, 50mM in CDCl_3 , shorter acquisition: 0.1835 s. 6 measured chunks out of 16. Sum criterion: reconstructions for the best sampling, the worst sampling and the original fully sampled pure-shift spectrum.

To demonstrate how the results of the proposed optimization procedure depend on the multiplet analysis quality, we artificially removed some multiplets from the list and performed the whole procedure otherwise normally. We chose the sample of sucrose for this aim, as it has a dense region at about 3.7 ppm. This region is highly sensitive to such changes, as is illustrated in Figs.59, 61, 63 (best sampling reconstruction results, maximum criterion, superimposed with the full PSYCHE spectrum). Figs.58, 60, 62 present the spectra simulated on the basis of the corresponding multiplet lists superimposed with the sucrose proton spectrum. Figs.59 and 58 present the results for the full list of multiplets. Figs.61 and 60 illustrate the removal of two multiplets in the region of interest. This results in a worse

reconstruction, though still fairly acceptable. Figs.63 and 62 present the removal of two other multiplets, which are outside the dense region. Such a removal, in its turn, does not lead to a considerable contamination of the reconstruction results.

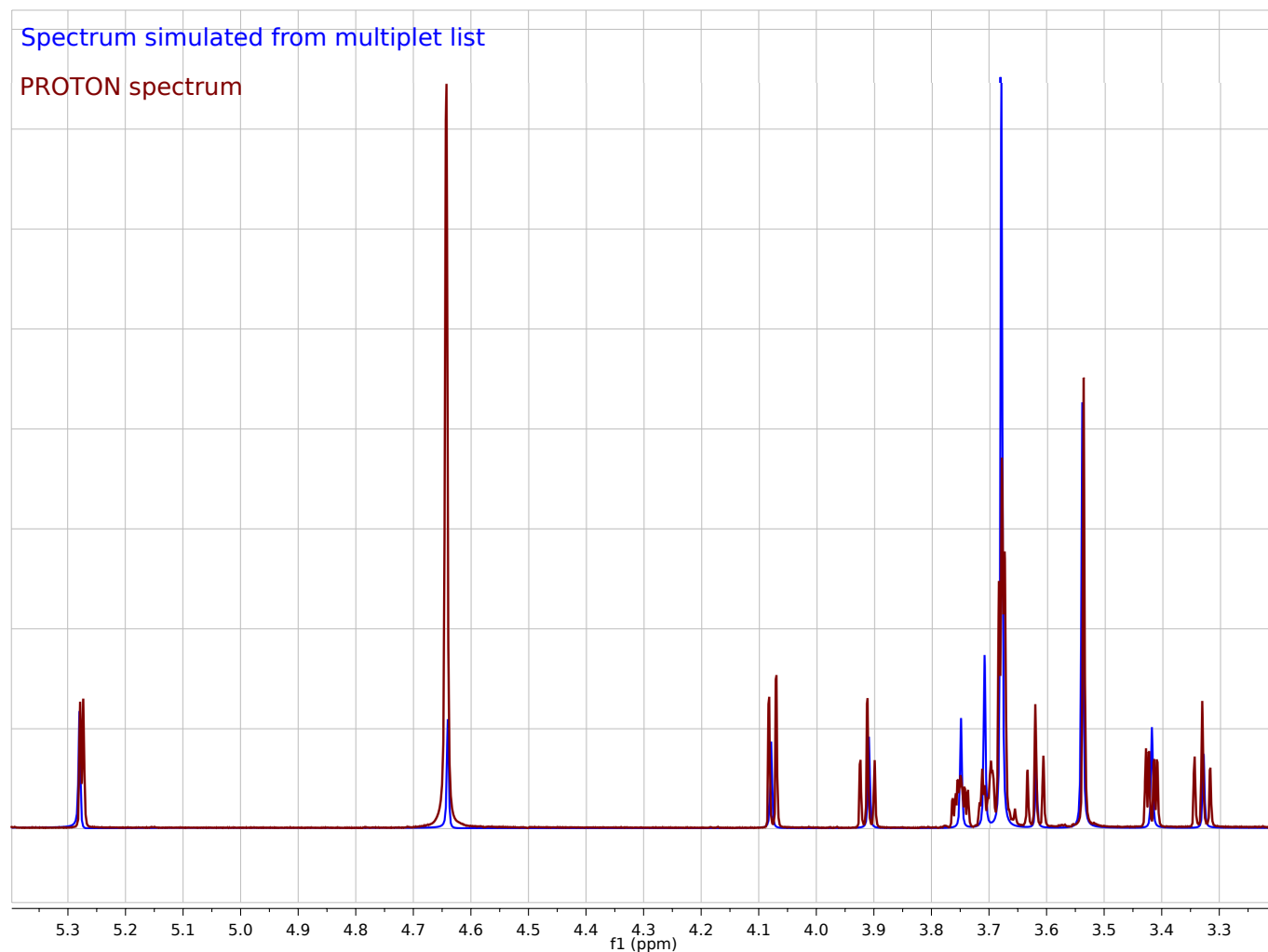


Figure 58 ^1H spectrum of β -estradiol, 50mM in CD_3OD , red line, and spectrum simulated from full multiplet list, blue line.

Full PSYCHE

Best sampling (maximum criterion)
reconstruction results

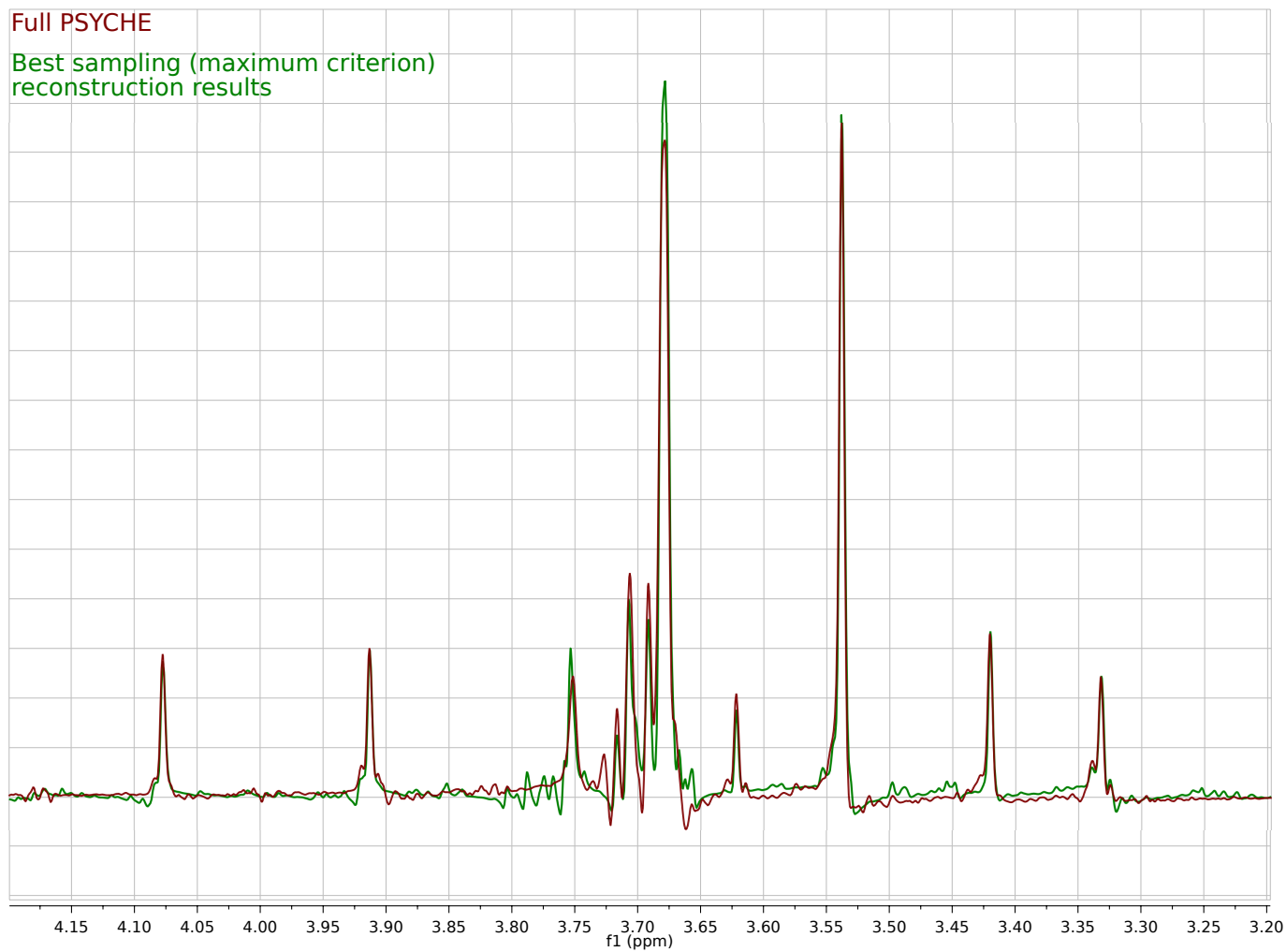


Figure 59 Full PSYCHE spectrum of β -estradiol, 50mM in CD₃OD, red line, and reconstruction from the best sampling scheme (maximum criterion) simulated from correct full multiplet list, green line.

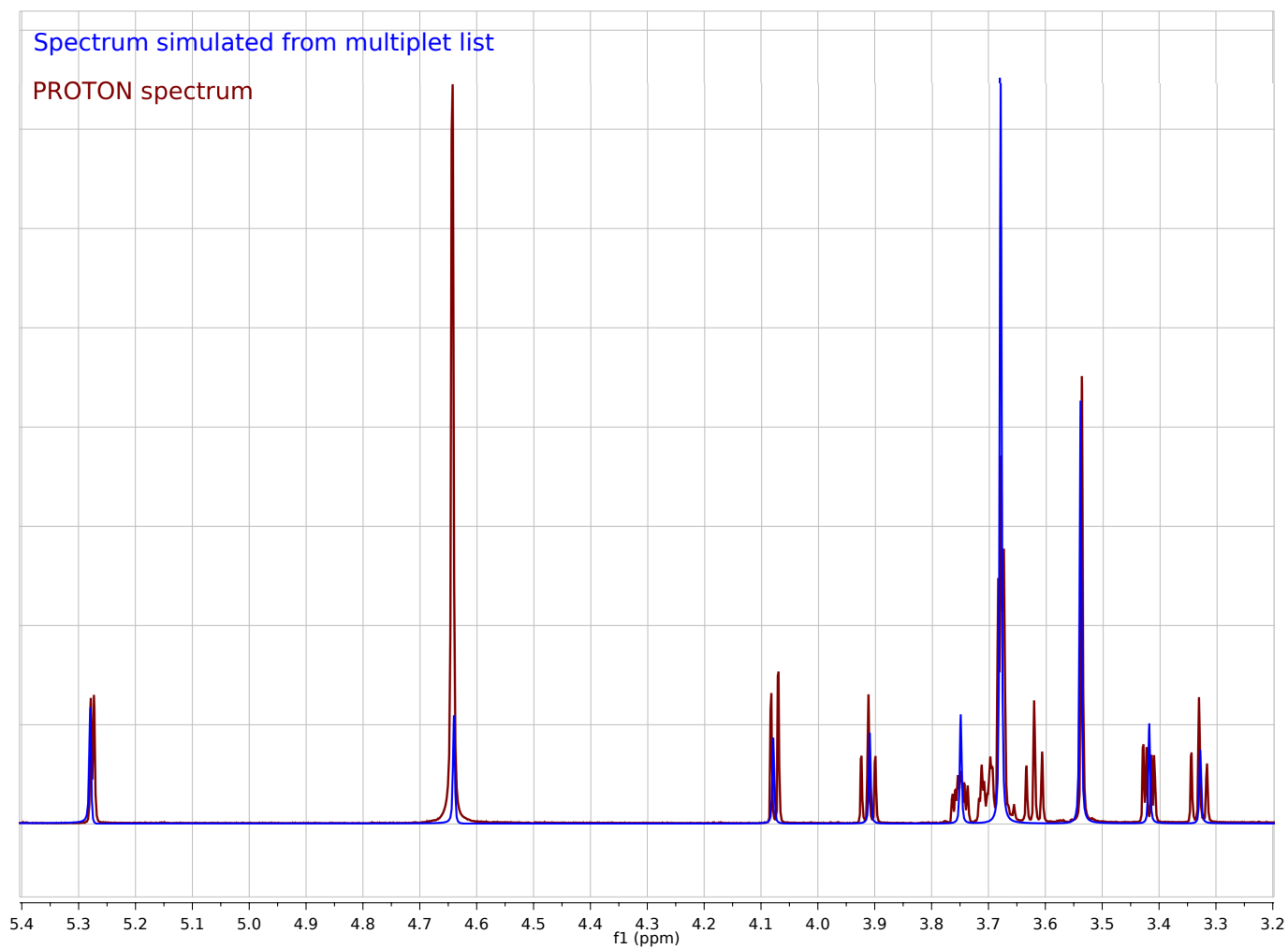


Figure 60 ^1H spectrum of β -estradiol, 50mM in CD_3OD , red line, and spectrum simulated from corrupted multiplet list, blue line, with multiplets removed in the region of interest.

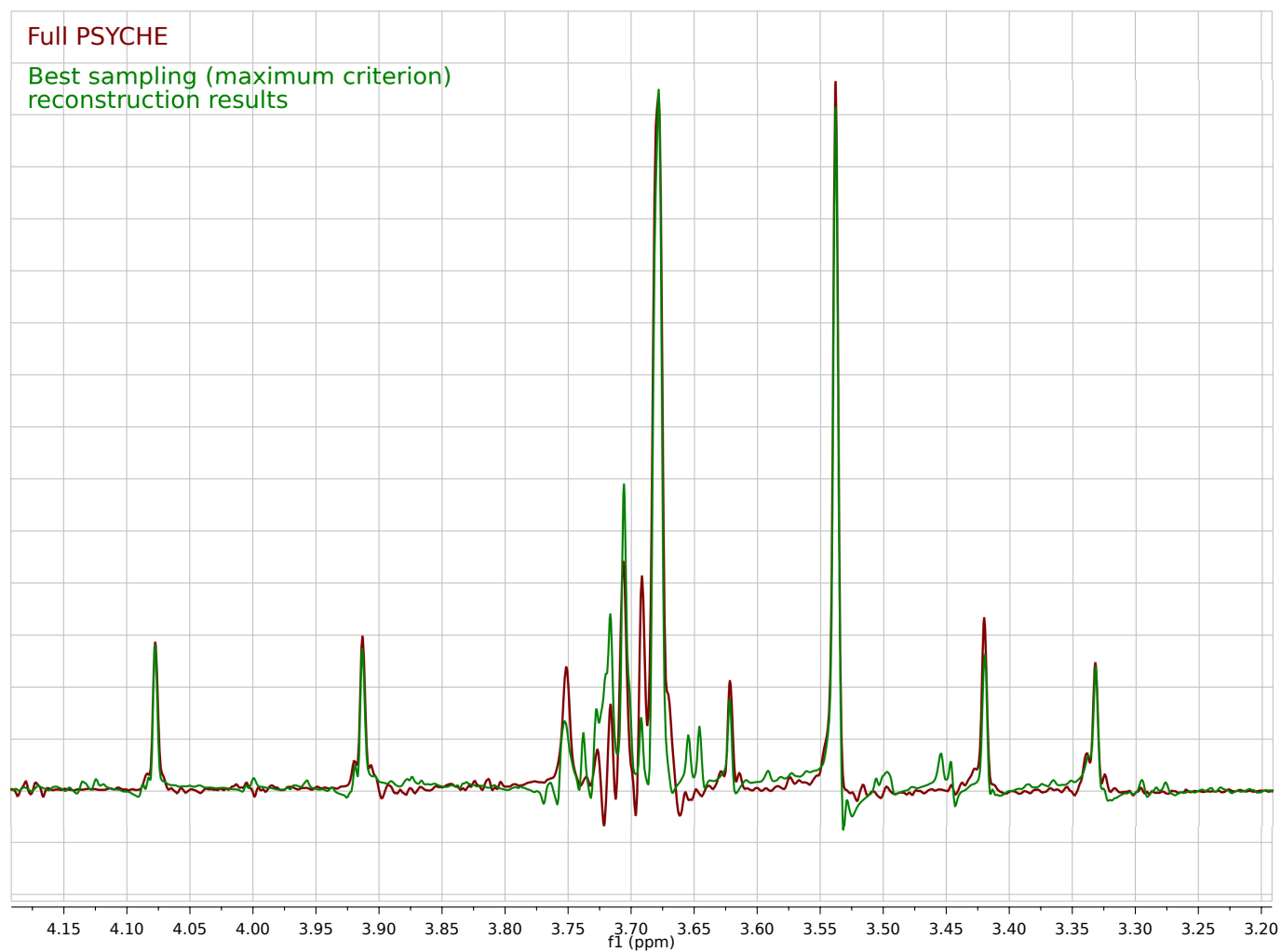


Figure 61 Full PSYCHE spectrum of β -estradiol, 50mM in CD_3OD , red line, and reconstruction from the best sampling scheme (maximum criterion) simulated from corrupted multiplet list (multiplets removed in the region of interest), green line.

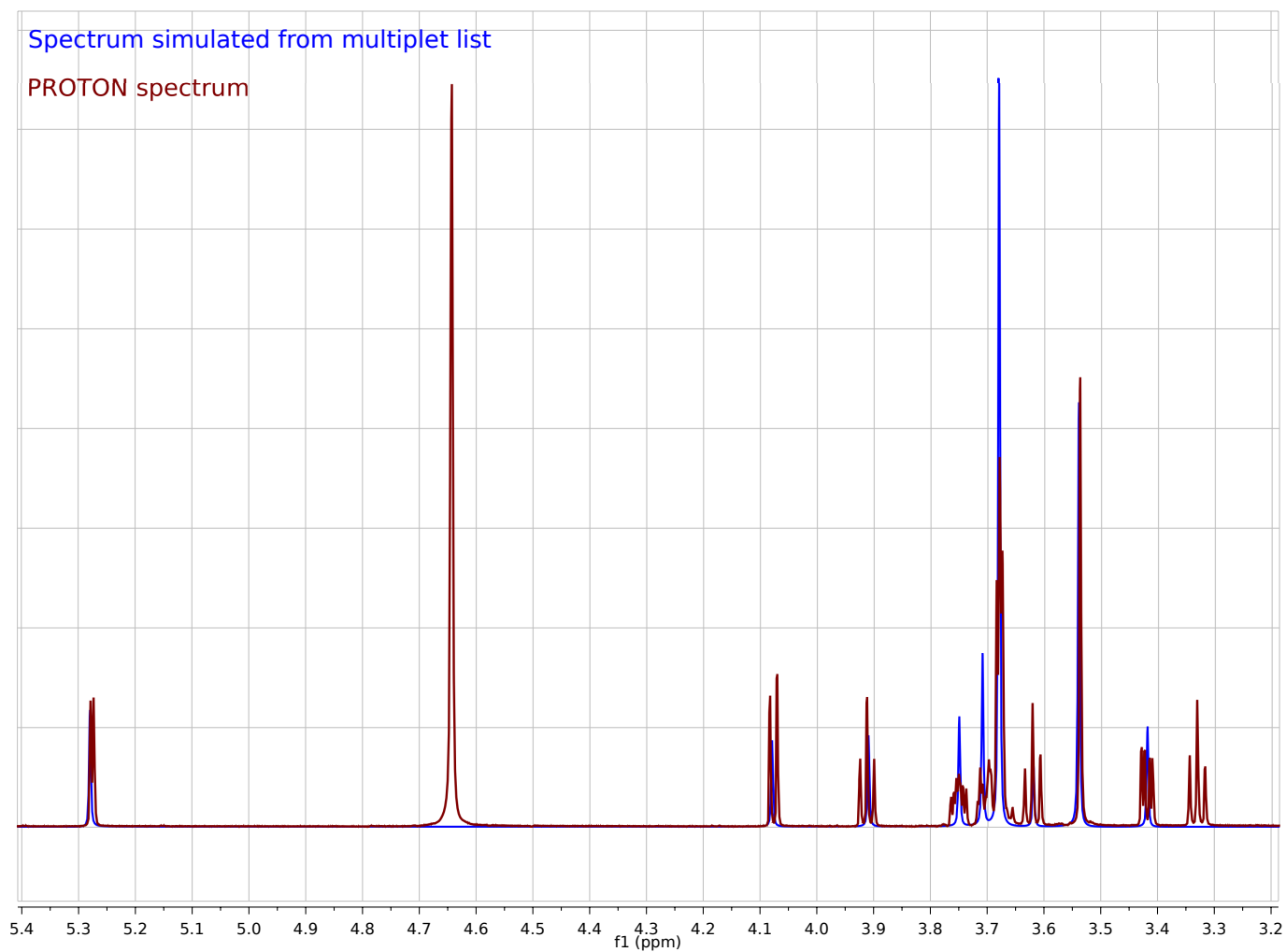


Figure 62 ^1H spectrum of β -estradiol, 50mM in CD_3OD , red line, and spectrum simulated from corrupted multiplet list, blue line, with multiplets removed outside the region of interest.

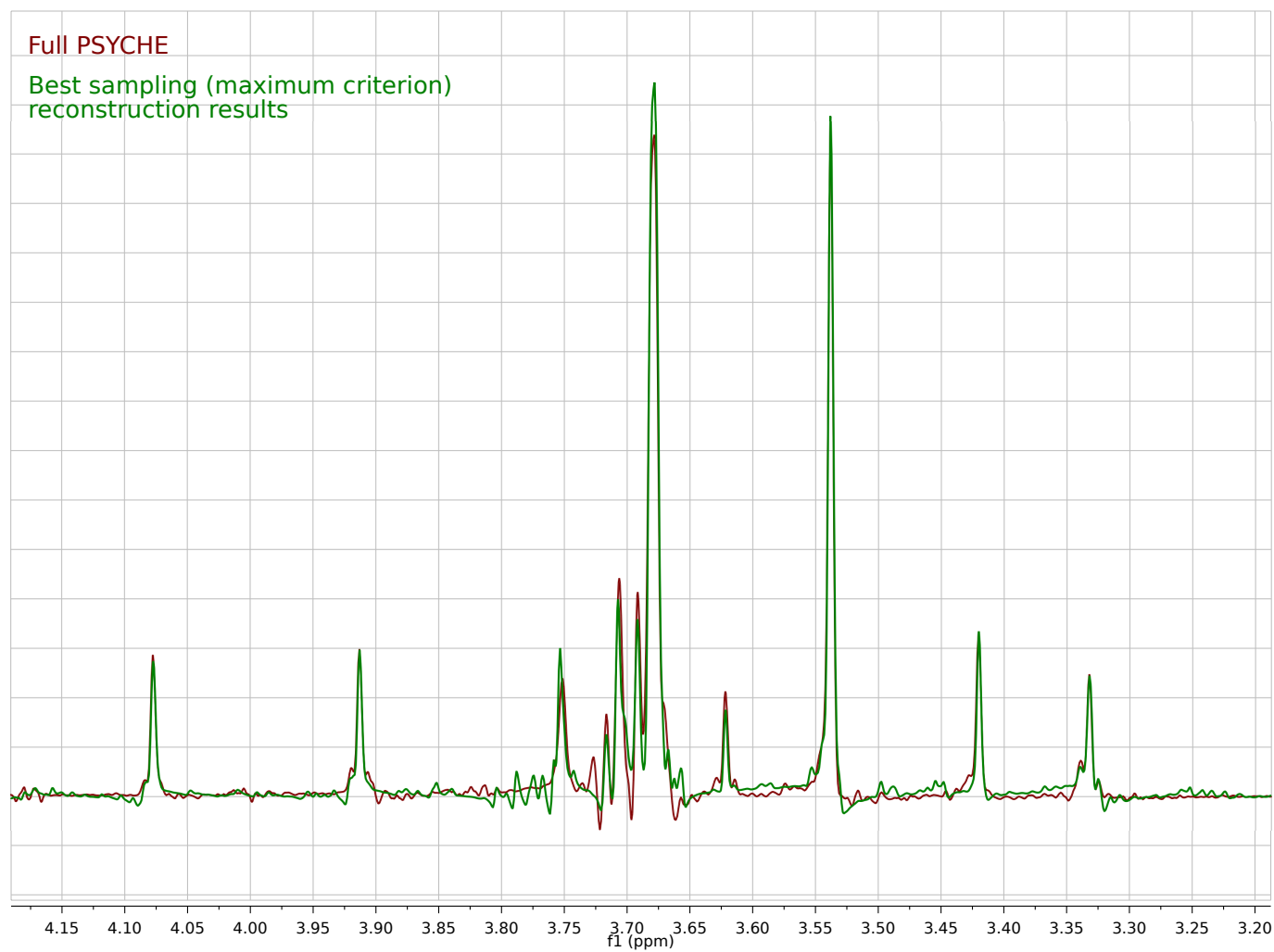


Figure 63 Full PSYCHE spectrum of β -estradiol, 50mM in CD_3OD , red line, and reconstruction from the best sampling scheme (maximum criterion) simulated from corrupted multiplet list (multiplets removed outside the region of interest), green line.