

Fast Data Acquisition Methods

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2008

Fast Methods



FDM (Filter Diagonalisation Method)⁺

(Mandelstam & Shaka)

Hadamard⁺

(Kupce & Freeman)

Red. Dimensionality:
GFT* / MWD⁻ / APSY⁺

(Szyperski, Wüthrich, Brutscher,
Gronenborn, Billeter,
Markley, Zhou...)

Projection Reconstruction⁺

(Kupce & Freeman)

Non-Linear Sampling⁻

(Wagner, Hoch, Orekhov...
Marion, Kozminski)

Ultrafast 2D^{*}

(Frydman, Pelupessy)

Covariance NMR⁺

(Brüschweiler,...)

Spectrum Folding

(Sidebottom, Berger,...)

Sharc NMR⁺

(Sakhaii)

Rapid Pulsing

(Ross, Pervushin, Brutscher,...)

Simultaneous data acquisition

(Soerensen, Griesinger, Parella,...)

Bruker BioSpin



FDM

FDM

Filter Diagonalisation Method

harmonic inversion problem (harminv)



xf2

solve harminv (on column)

=> number of frequencies

frequency, amplitude, phase, decay

reconstruct interferogram

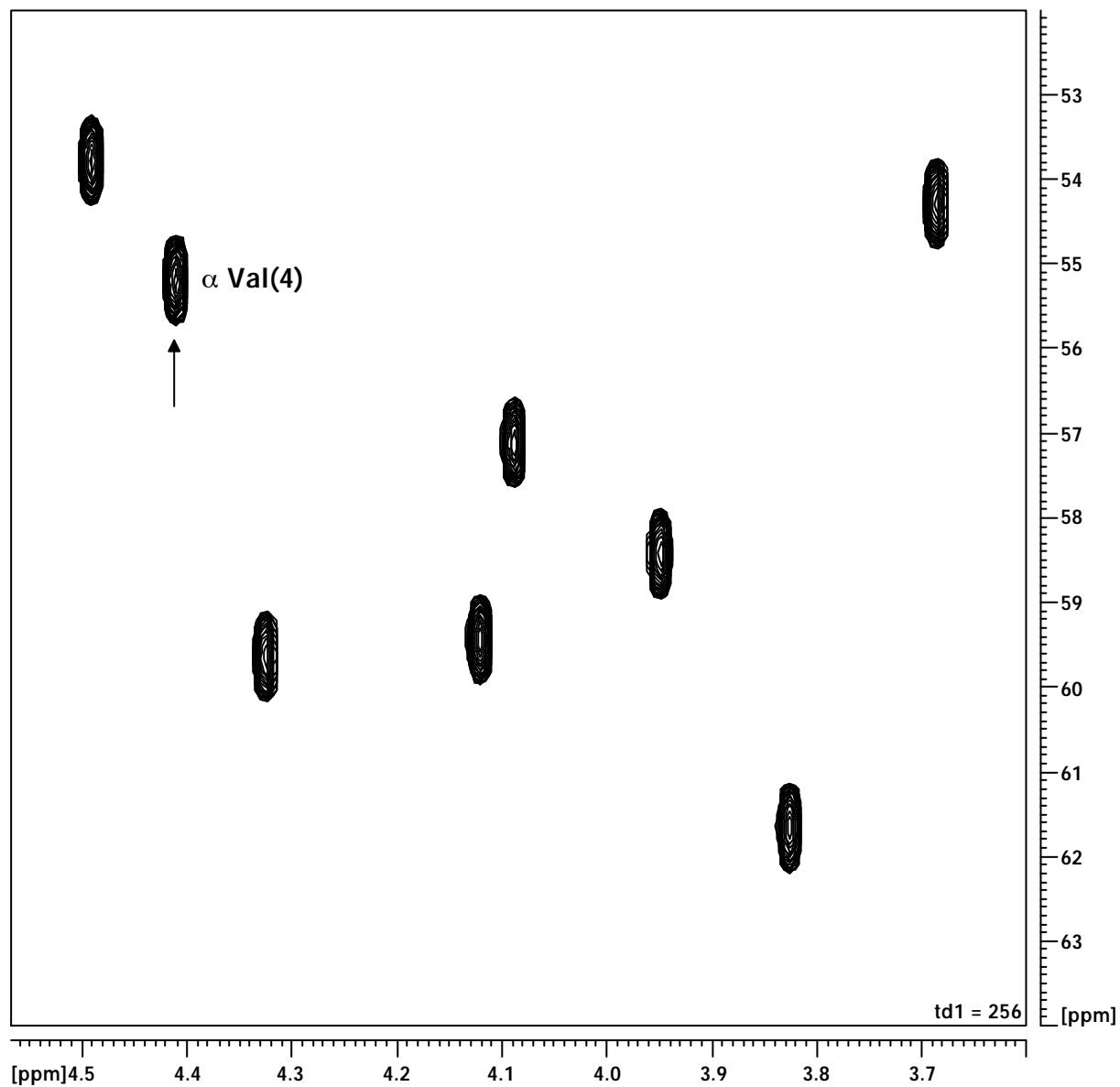
xf1

GNU: harminv-1.3.1.tar.gz Steven G. Johnson, MIT

requires: BLAS, LAPACK, (part of Red Hat Enterprise Linux WS 4)

Bruker BioSpin

HSQC

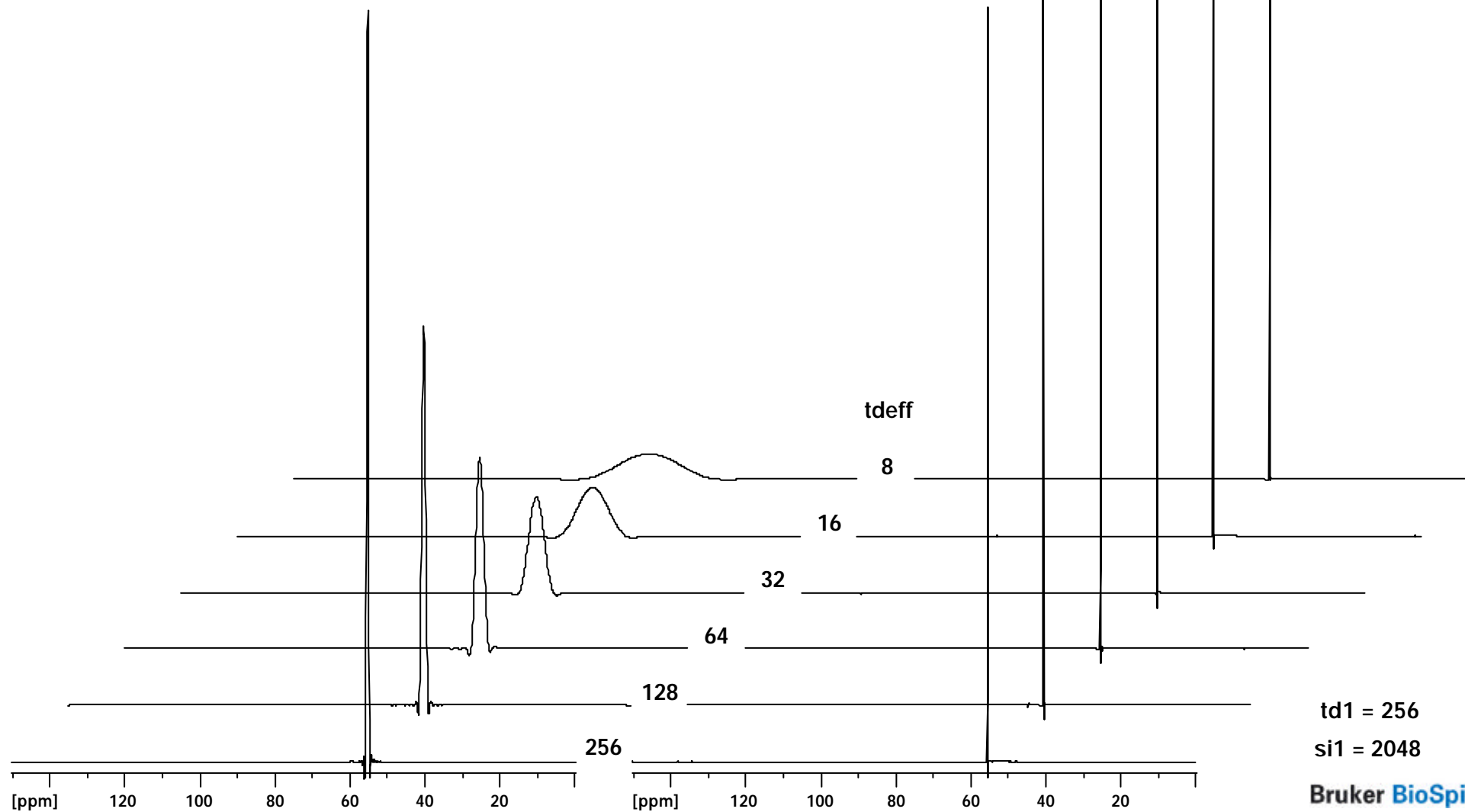


FDM



HSQC: Val Ca

Hymenistatin (simulated)



FDM



Hymenistatin
(simulated)

HSQC: Val Ca

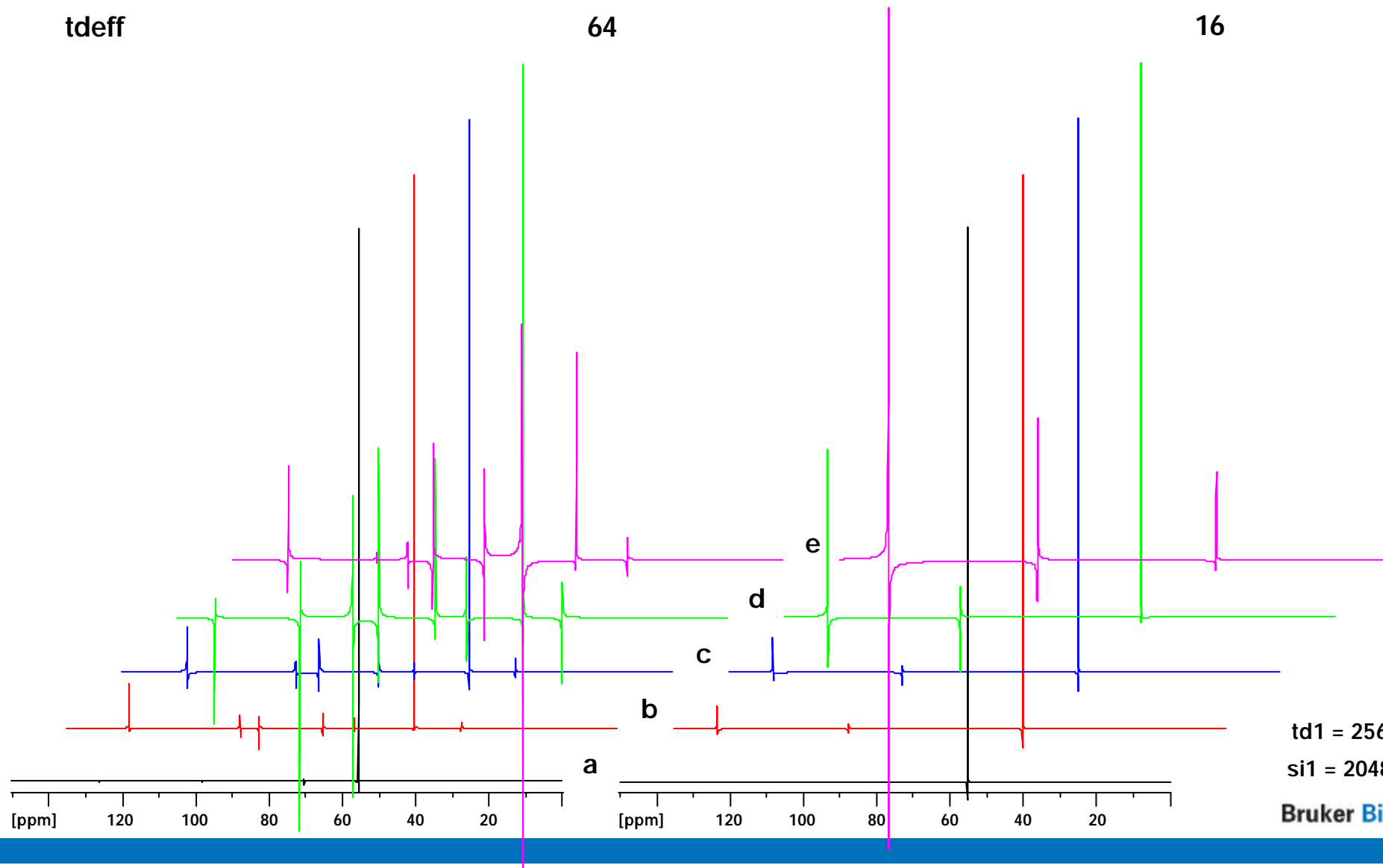
tdeff	number of frequencies	frequency	figure of merit
256	19	-2983.37	1.356
128	4	-2983.46	1.356
64	4	-2983.08	1.356
32	3	-2983.11	1.356
16	3	-2983.75	1.356
8	1	-2980.43	1.355
4	-	-	-

FDM



Hymenistatin (simulated)

HSQC: Val Ca



FDM



Hymenistatin
(simulated)

HSQC: Val Ca, + added noise

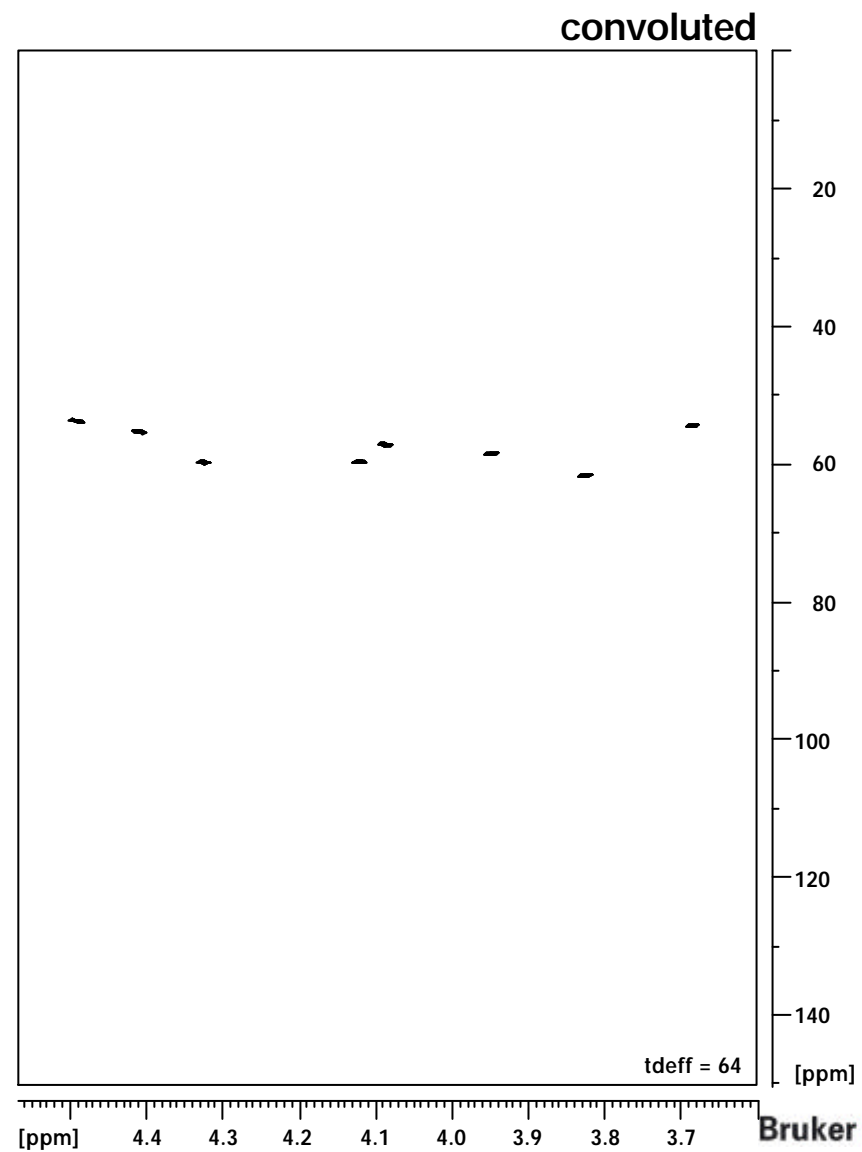
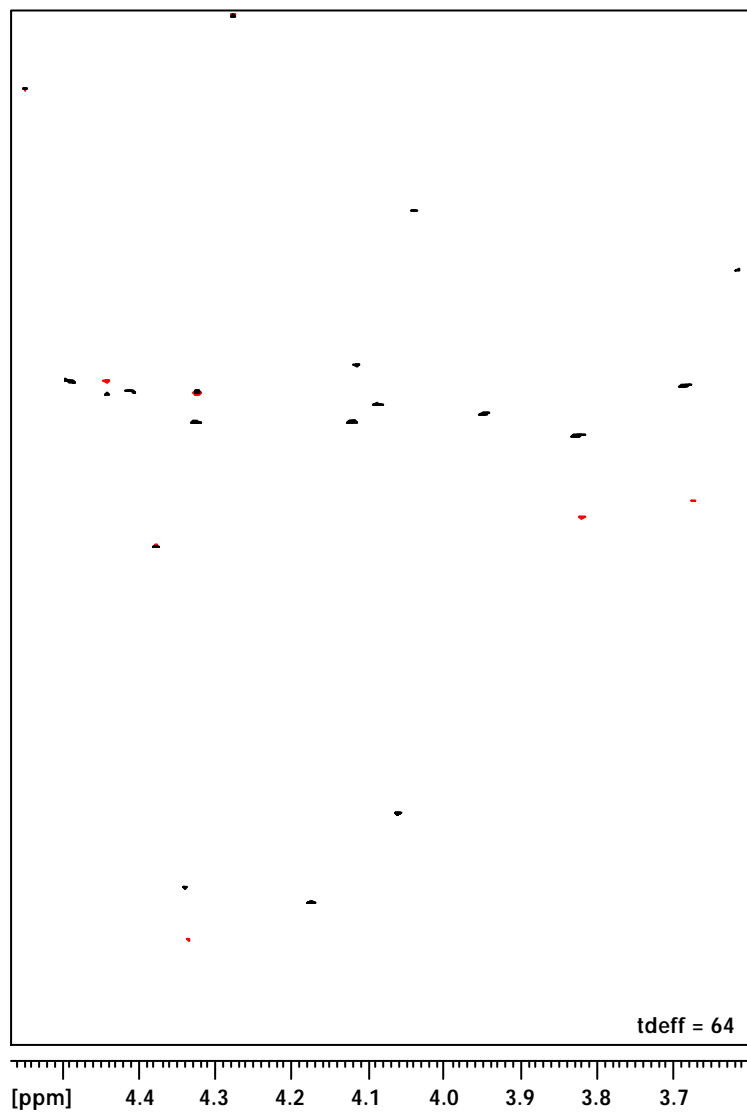
	tdeff 0	64		16	
	S/N	S/N	number of frequencies	S/N	number of frequencies
a	2076.5	1012.1	6	536.3	3
b	206.7	100.9	7	55.8	3
c	103	50.5	7	27.8	3
d	19.8	10.0	8	5.1	3
e	2.8	1.6	9	1.1	3
	ok	ok after convolution		not ok	

FDM



Hymenistatin
(simulated)

HSQC + added noise (S/N 50.5)



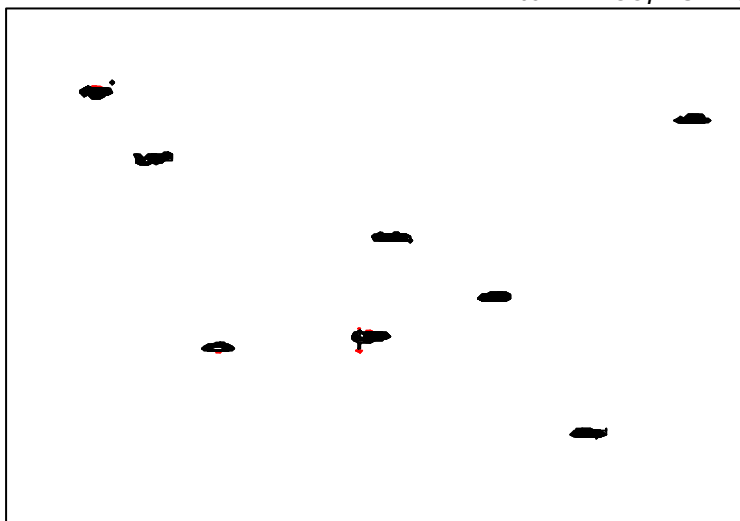
FDM



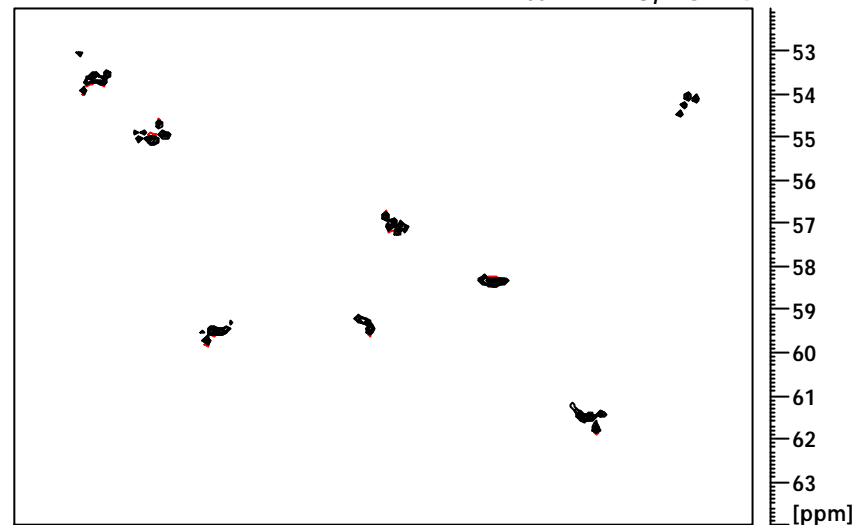
Hymenistatin

HSQC (convoluted)

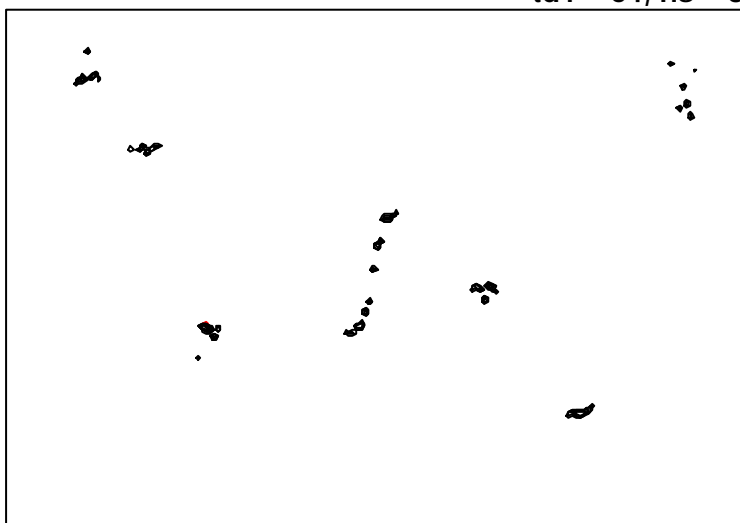
td1 = 256, ns = 4



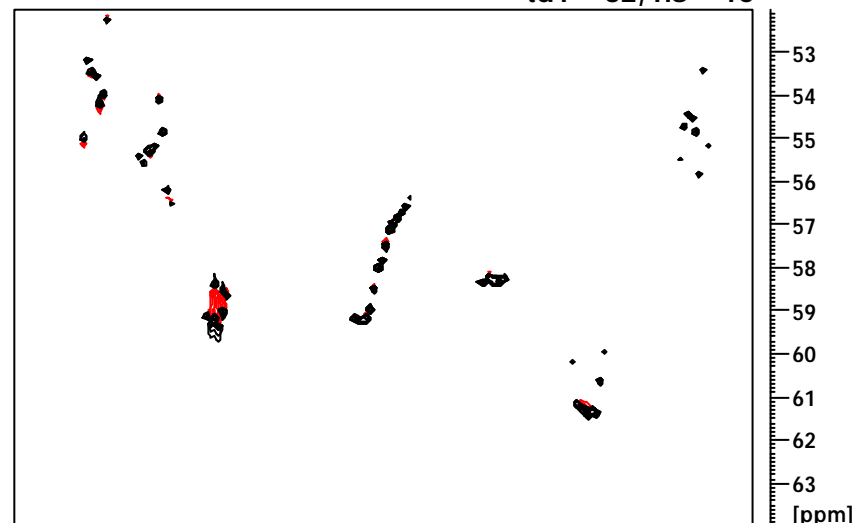
td1 = 128, ns = 4



td1 = 64, ns = 8



td1 = 32, ns = 16



[ppm] 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7

[ppm] 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7

S/N ca. 100

Bruker BioSpin

si1 = 2048

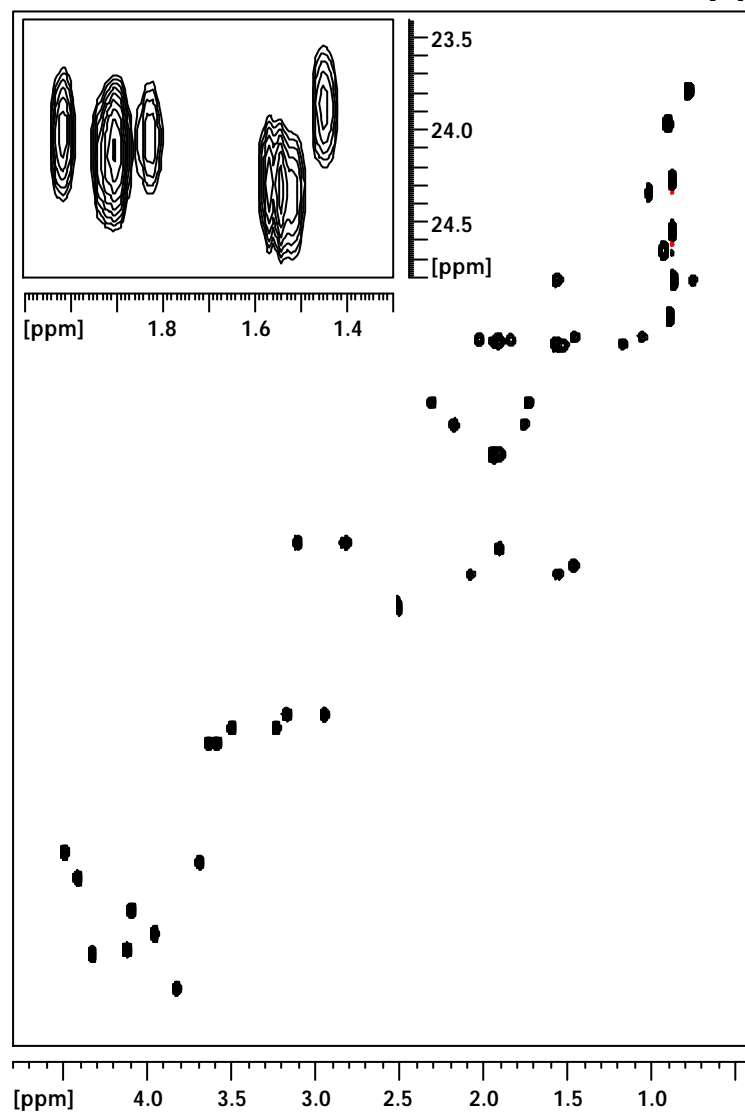
FDM



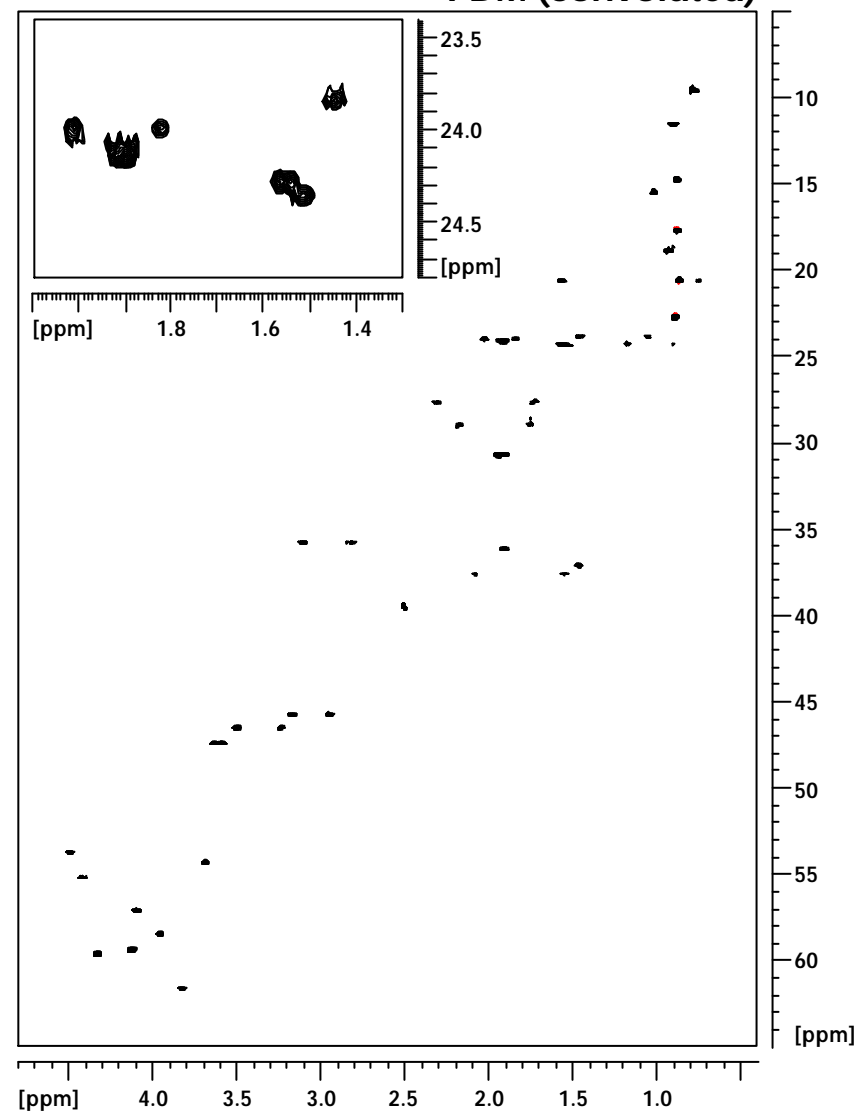
Hymenistatin

HSQC

FT



FDM (convoluted)



Bruker BioSpin

FDM



Hymenistatin
(simulated)

DIPSI2: Val

tdeff number of frequencies

0 212

512 121

256 58

128 30

64 15

32 7

16 2

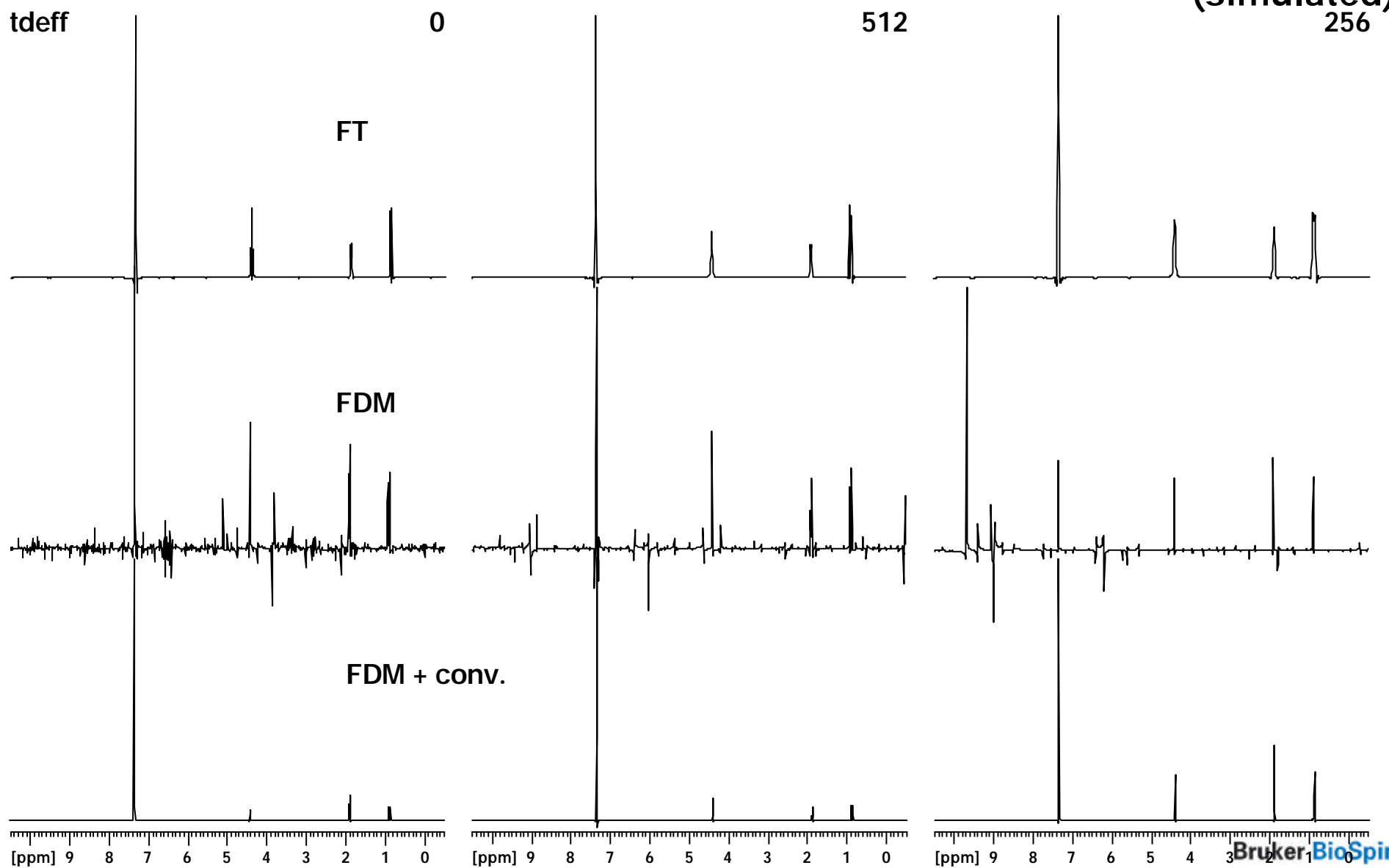
8 1

FDM



Hymenistatin
(simulated)
256

DIPSI2: Val

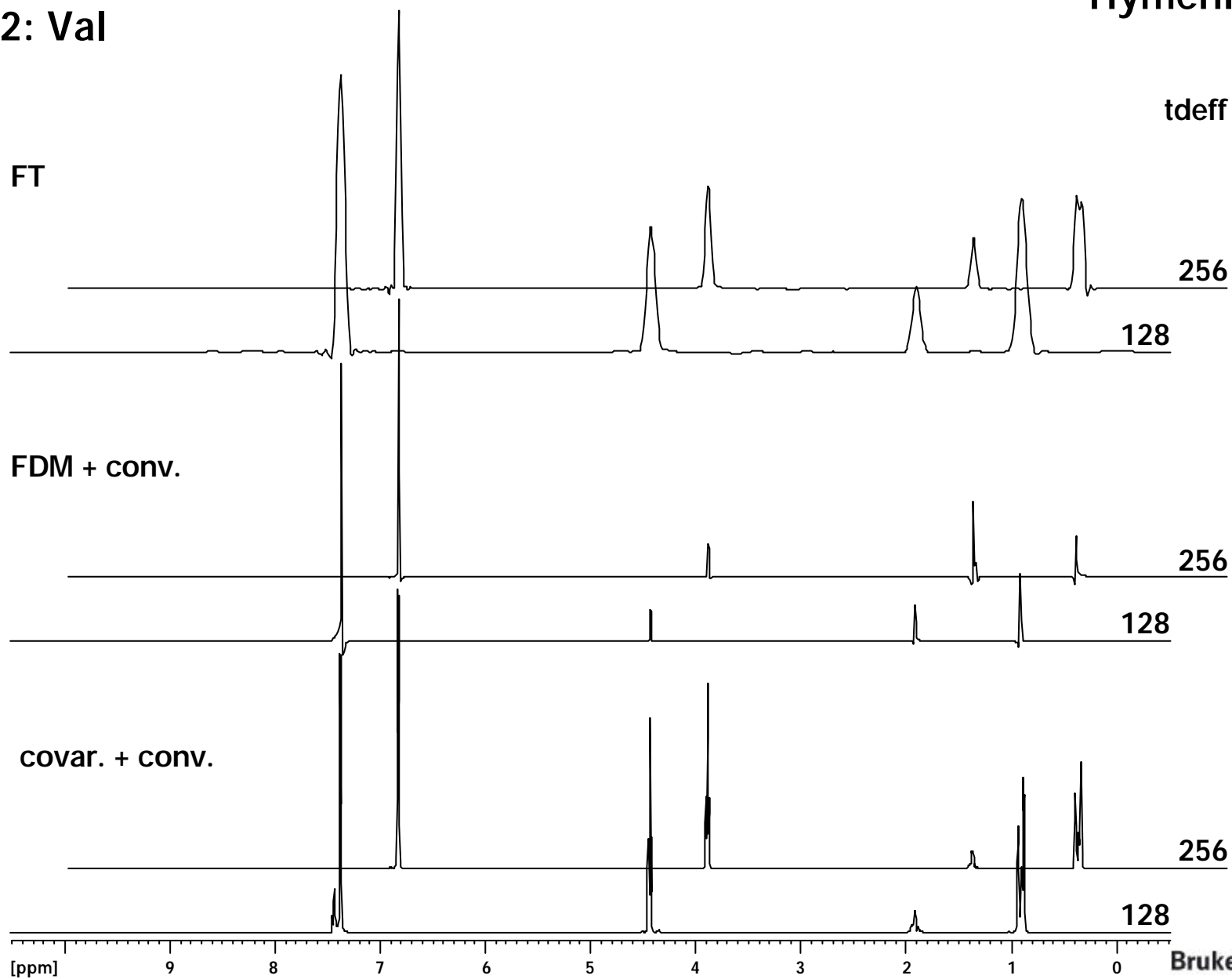


FDM



Hymenistatin

DIPSI2: Val





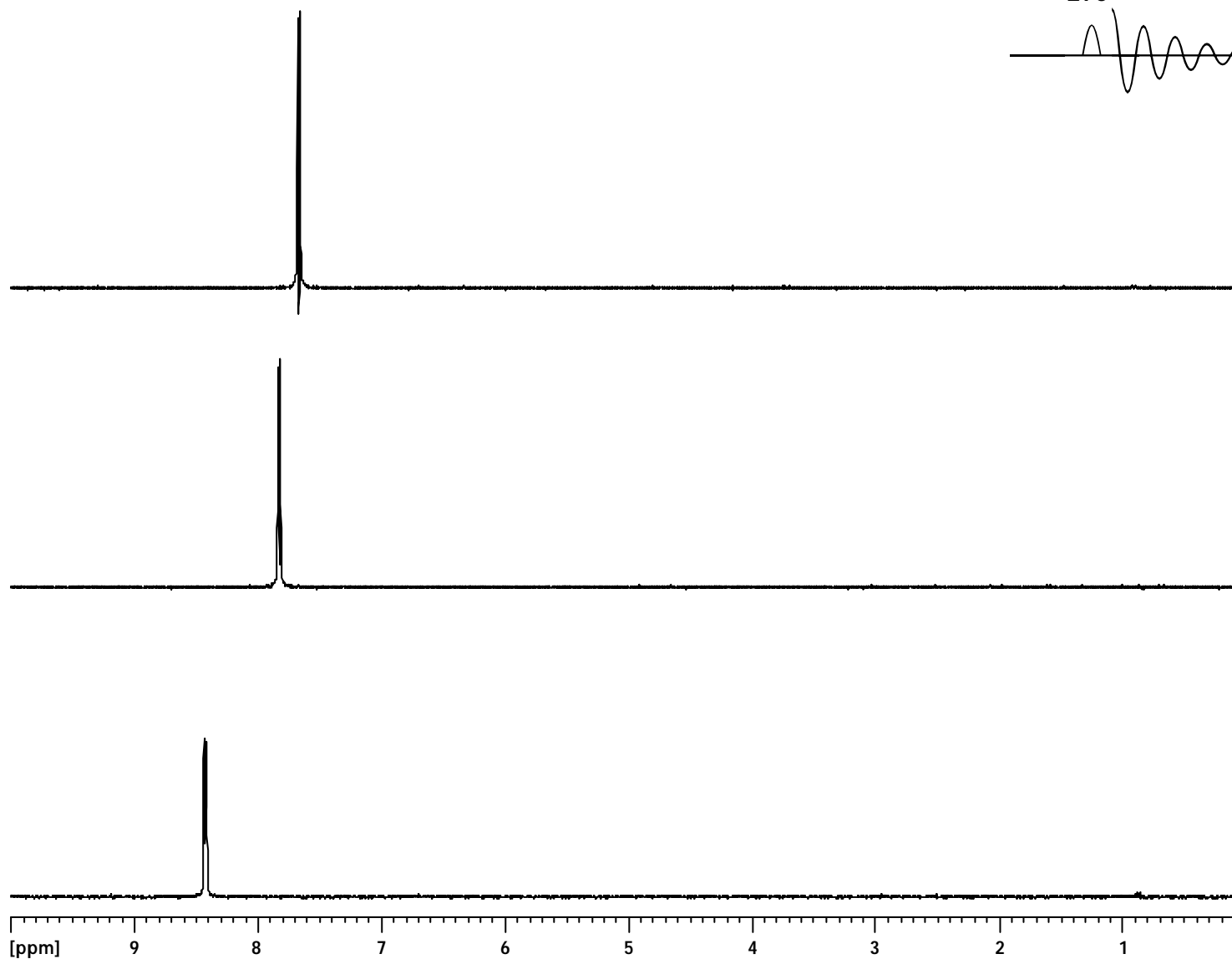
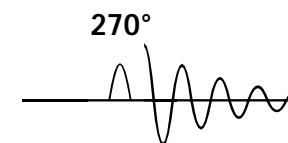
Hadamard

Hadamard 2D



Hymenistatin

selective excitation



Bruker BioSpin

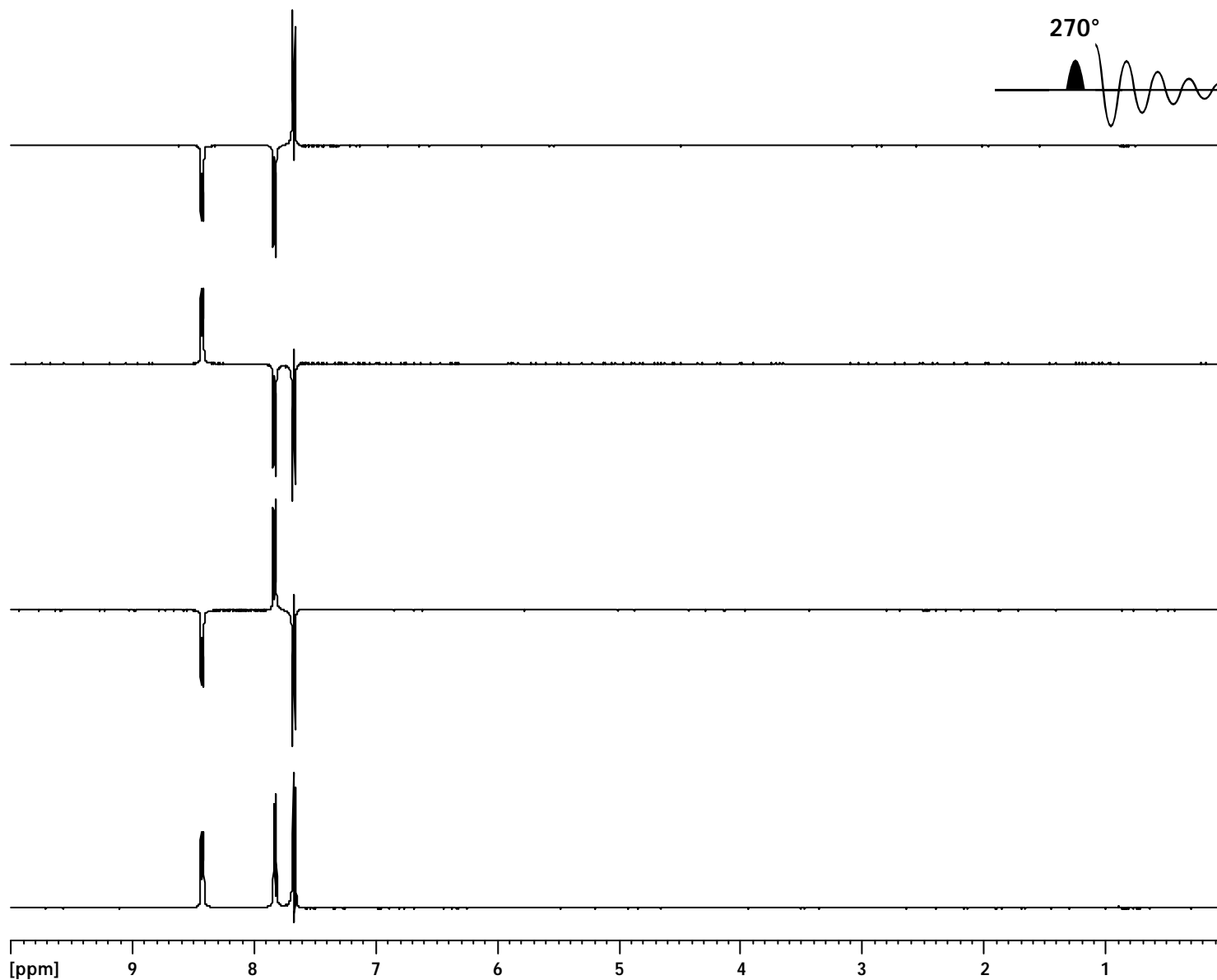
100ms Gaus1_270.1000

Hadamard 2D



Hymenistatin

selective excitation



Bruker BioSpin

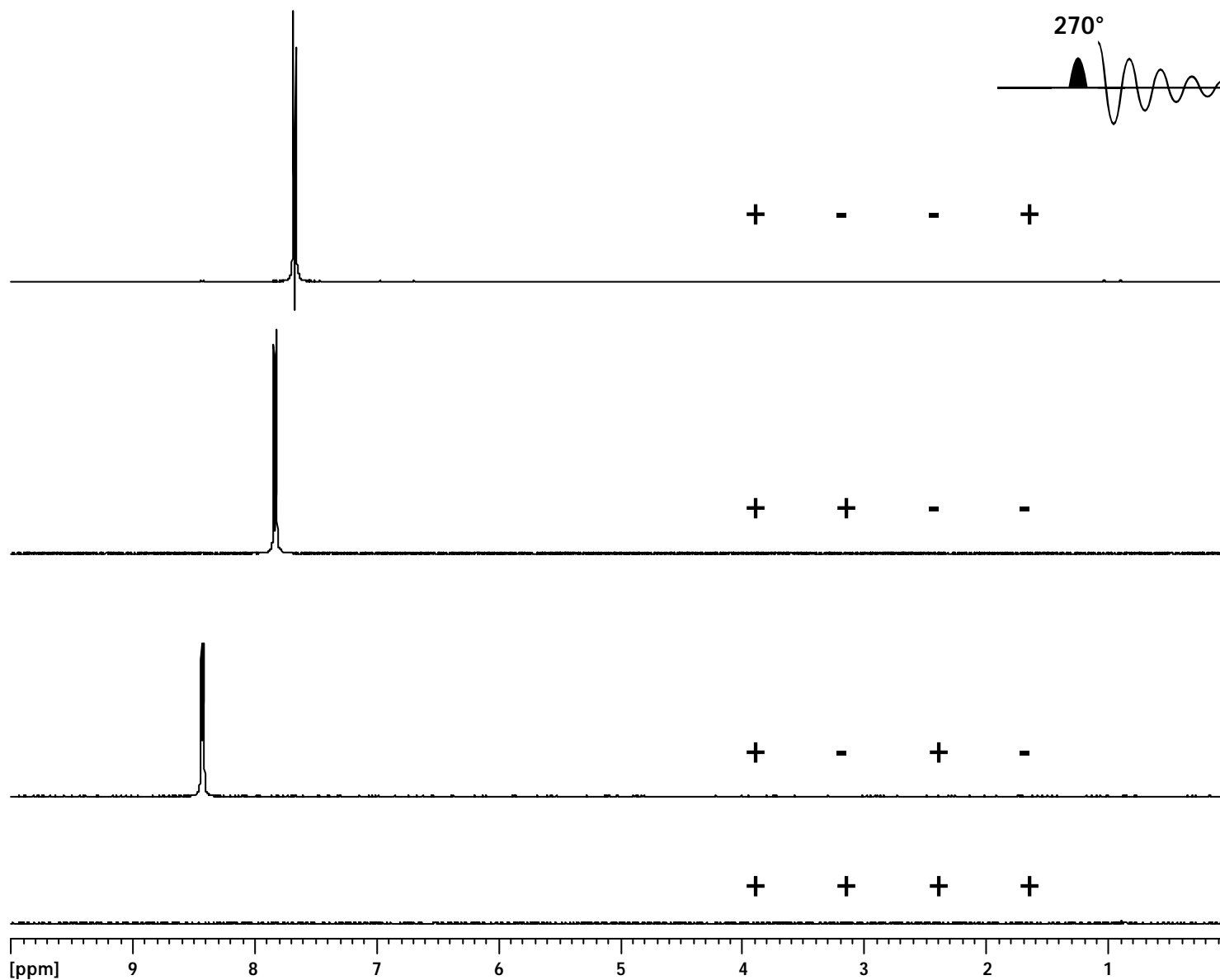
100ms Gaus1_270.1000

Hadamard 2D



Hymenistatin

selective excitation + hadamard matrix



Bruker BioSpin

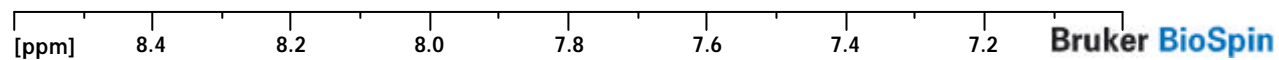
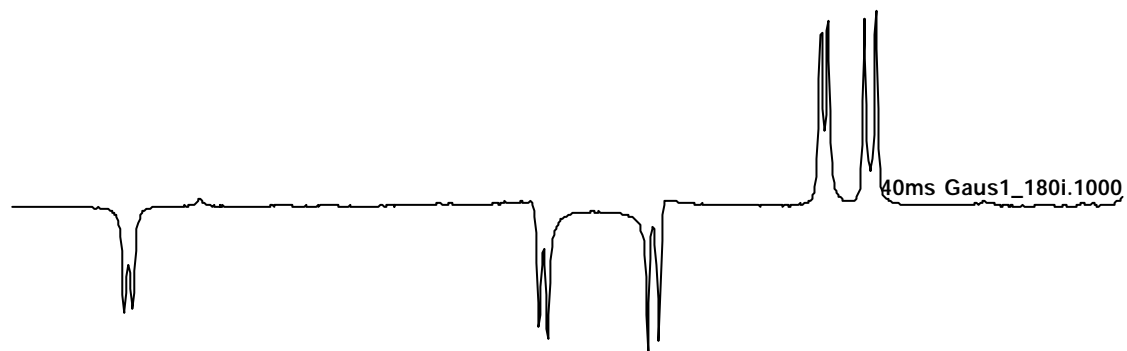
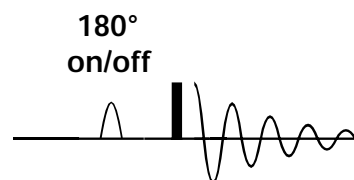
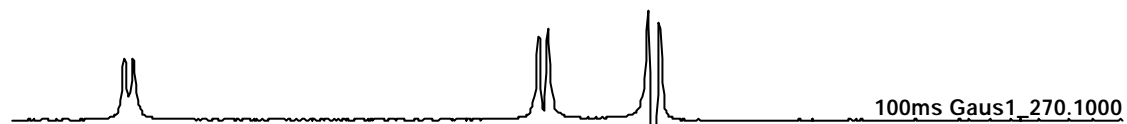
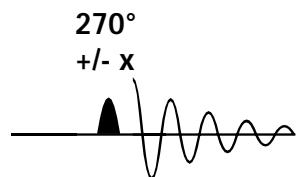
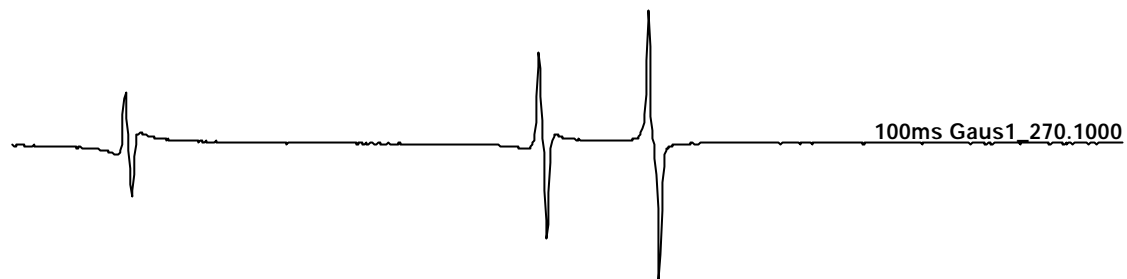
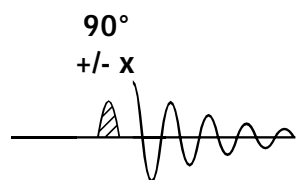
100ms Gaus1_270.1000

Hadamard 2D



Hymenistatin

selective excitation



Hadamard 2D



Hymenistatin

hadamard matrix: 2^n

$n = 1$

+	+
+	-

$n = 2$

+	+
+	-

=

+	+	+	+
+	-	+	-
+	+	-	-
+	-	-	+

$n = 3$

+	+
+	-

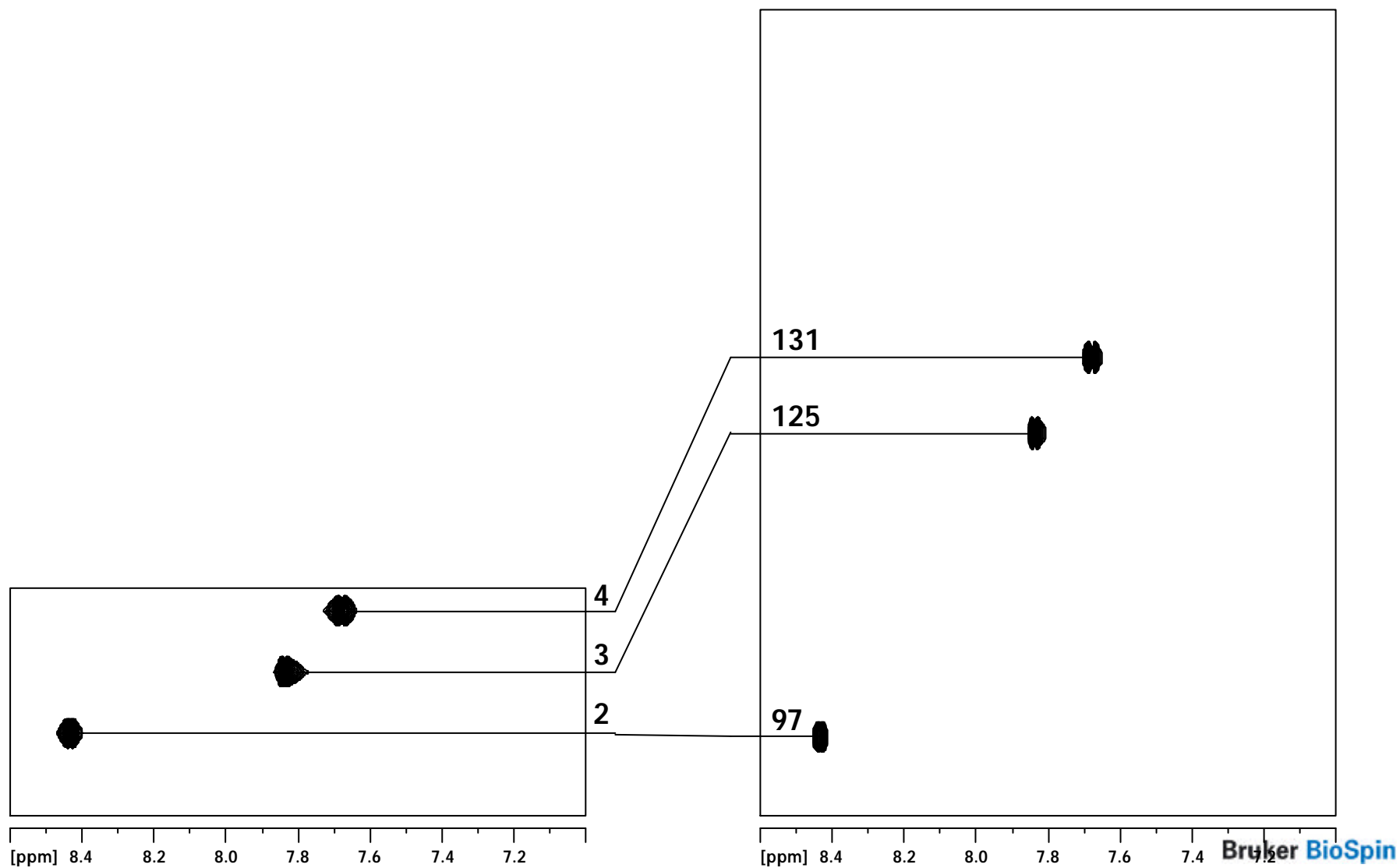
= ...

Hadamard 2D

pseudo 2D



Hymenistatin



Bruker BioSpin

100ms Gaus1_270.1000

Hadamard 2D



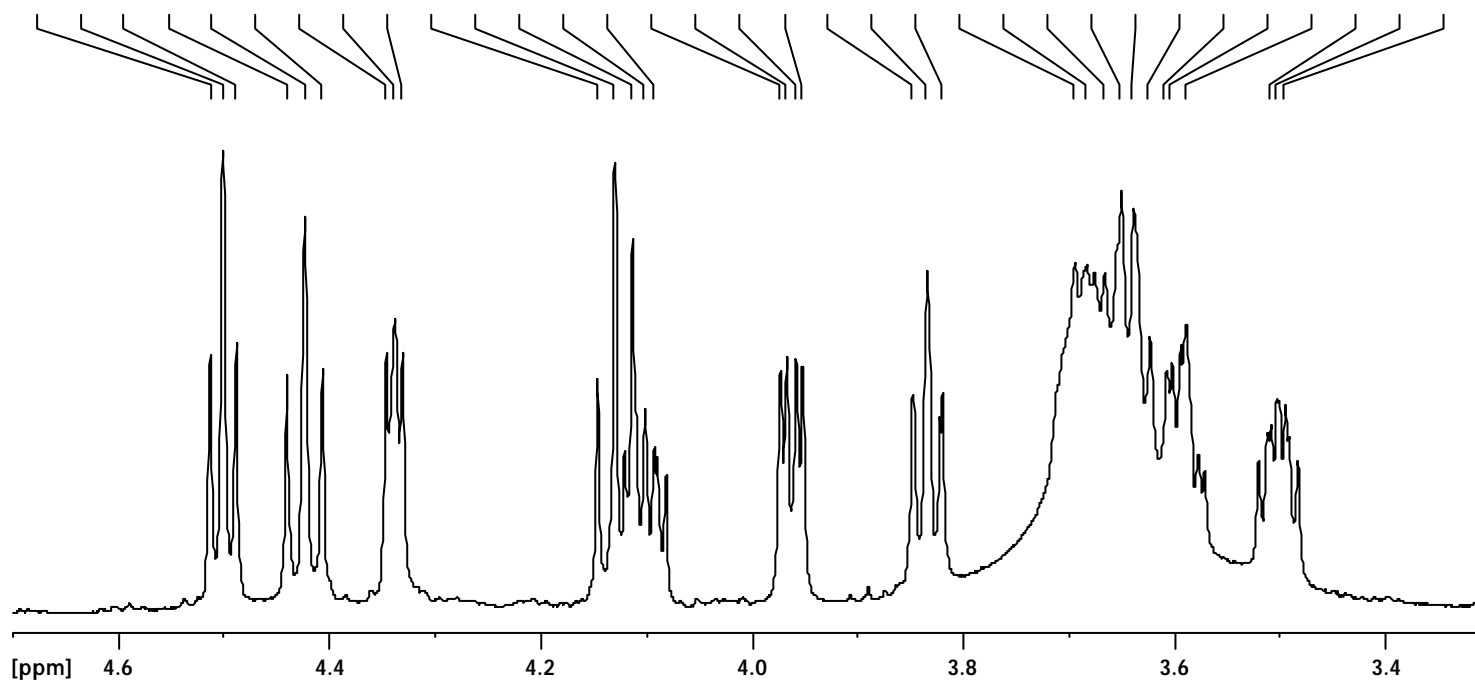
Hymenistatin

peak picking: no LB

bandwidth filter (18.4 Hz)



11 peaks



Bruker BioSpin

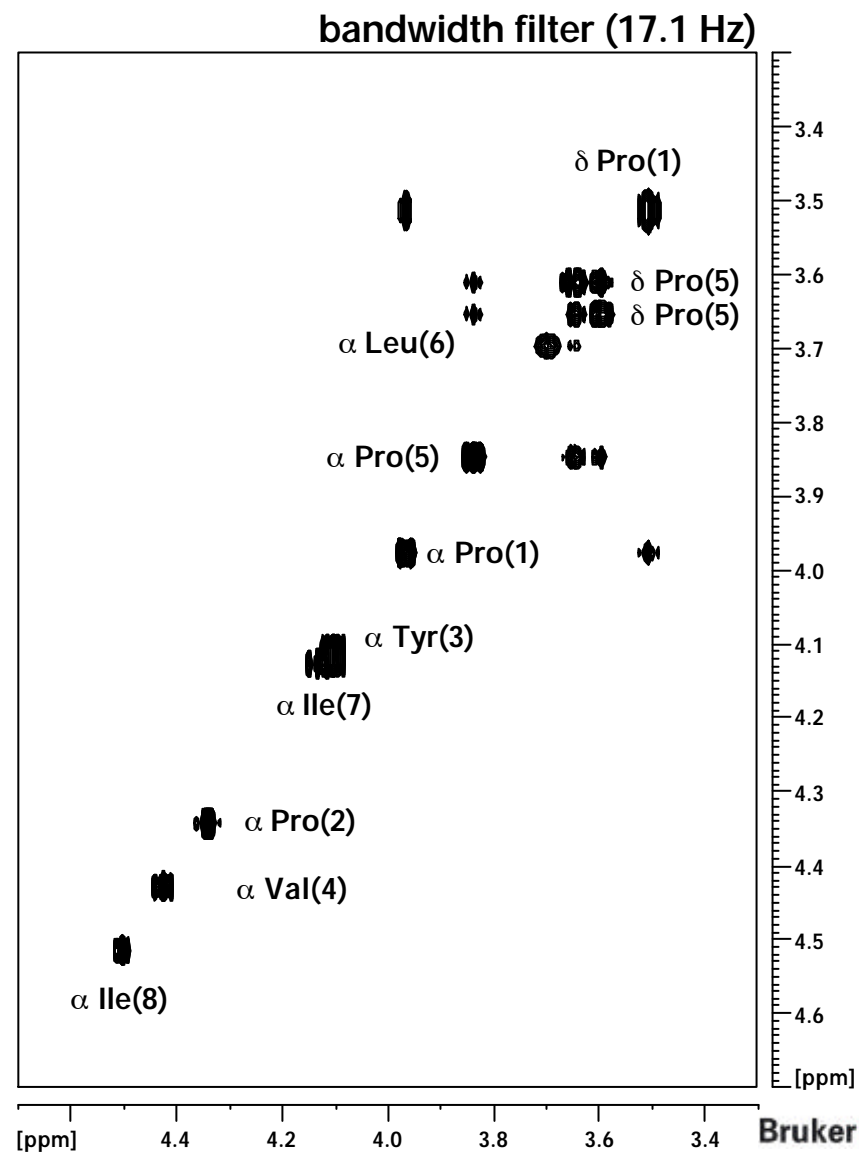
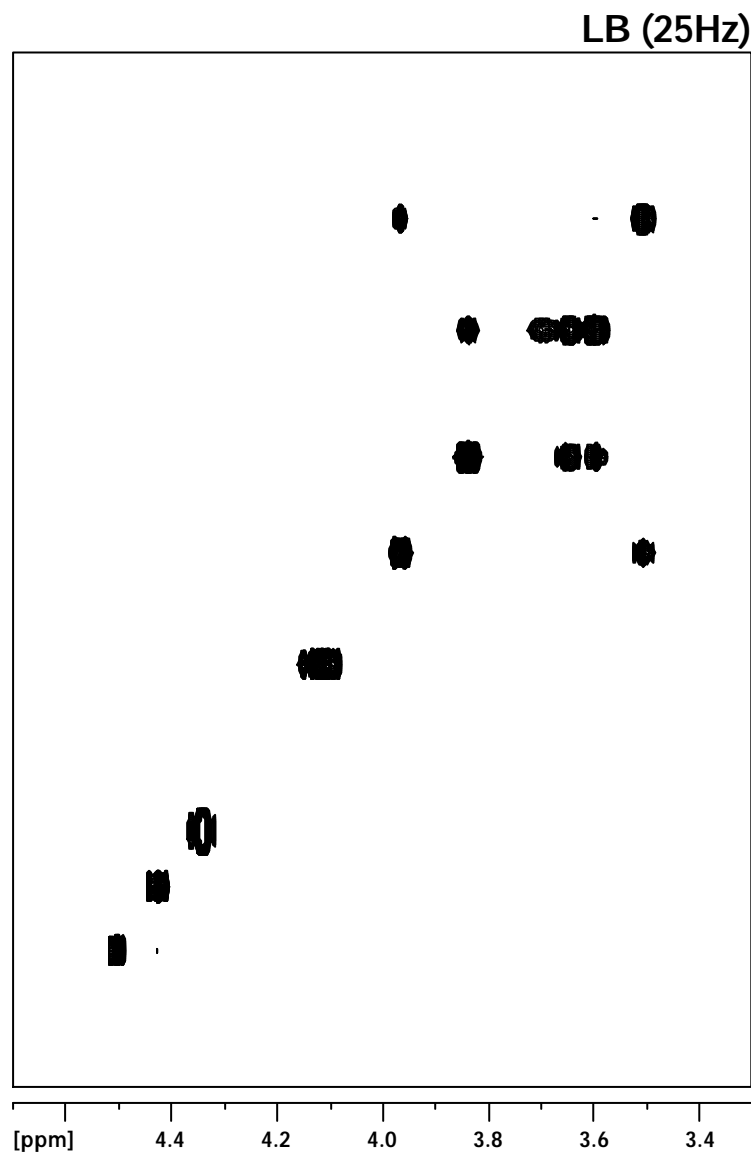
40ms Gaus1_180i.1000

Hadamard 2D: had. DIPSI2 (9.6kHz, 60ms)



Hymenistatin

peak picking



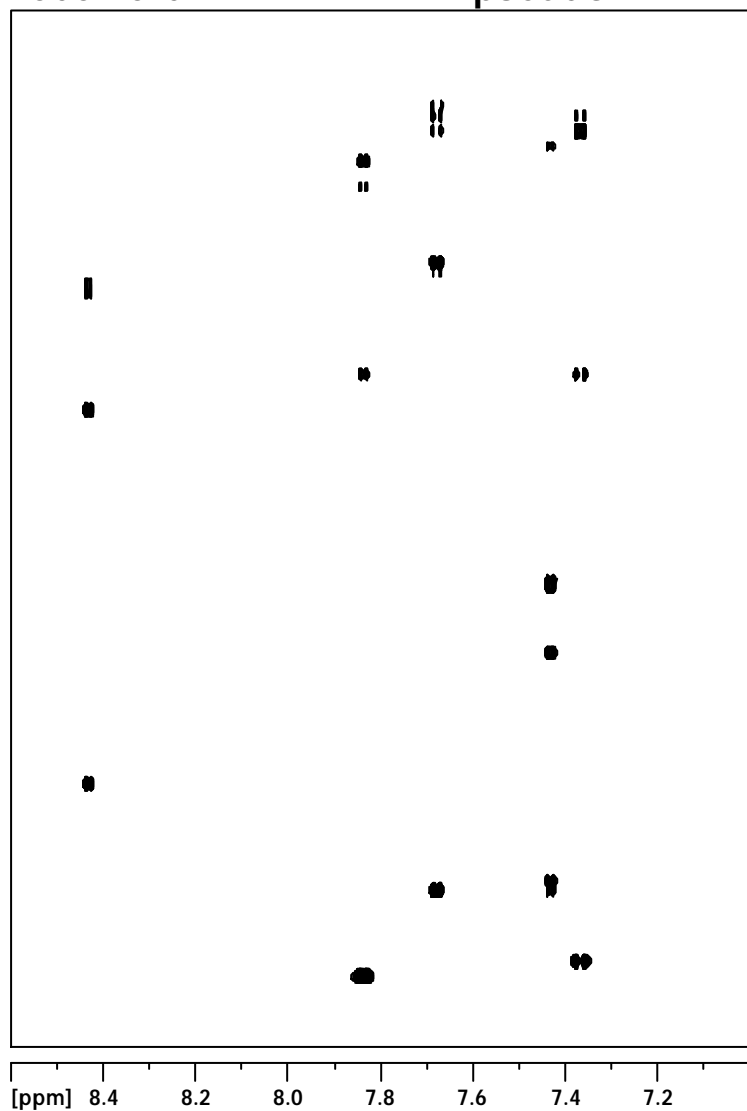
Hadamard 2D



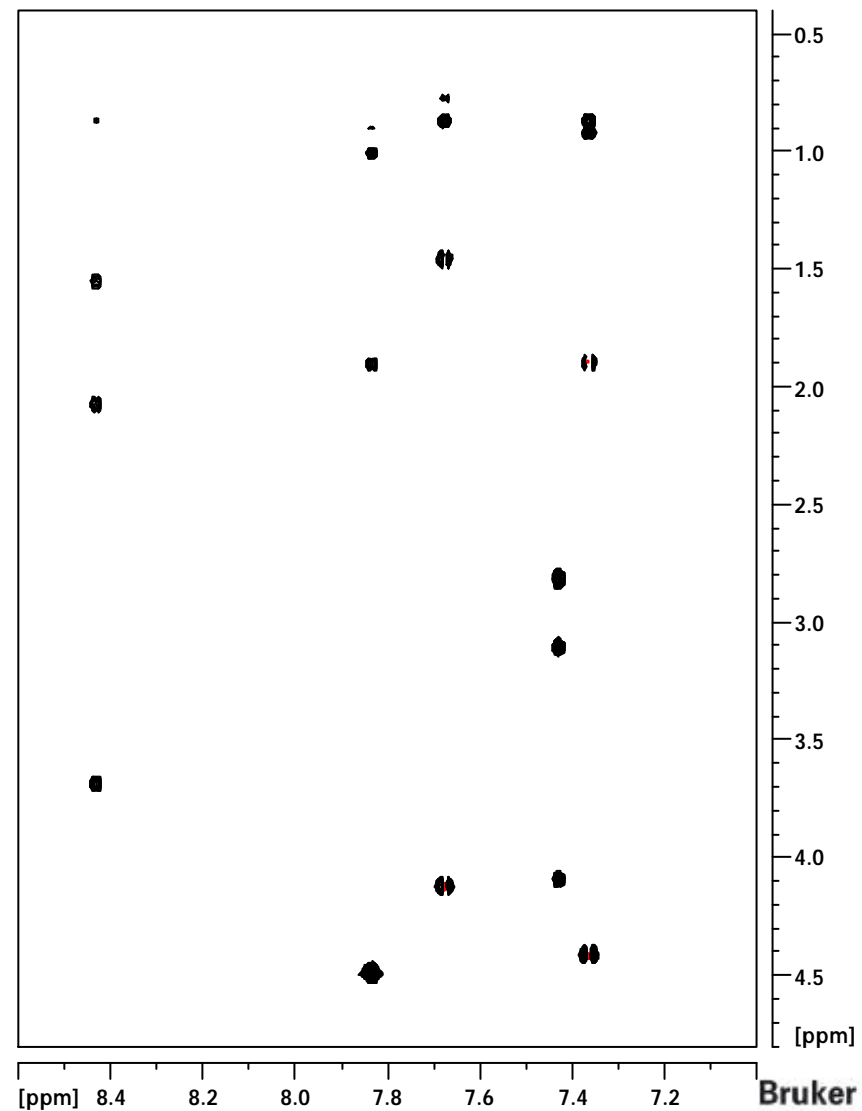
Hymenistatin

DIPSII2 (9.6kHz, 60ms)

hadamard pseudo LB = 12



2D



Bruker BioSpin

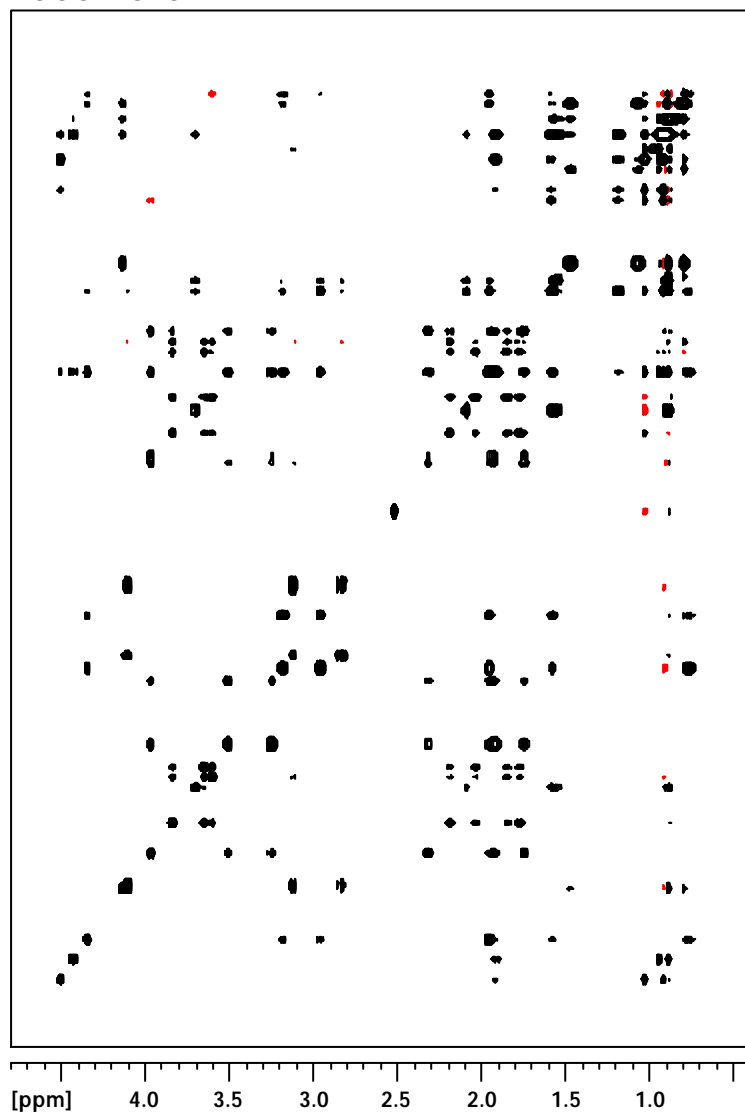
Hadamard 2D



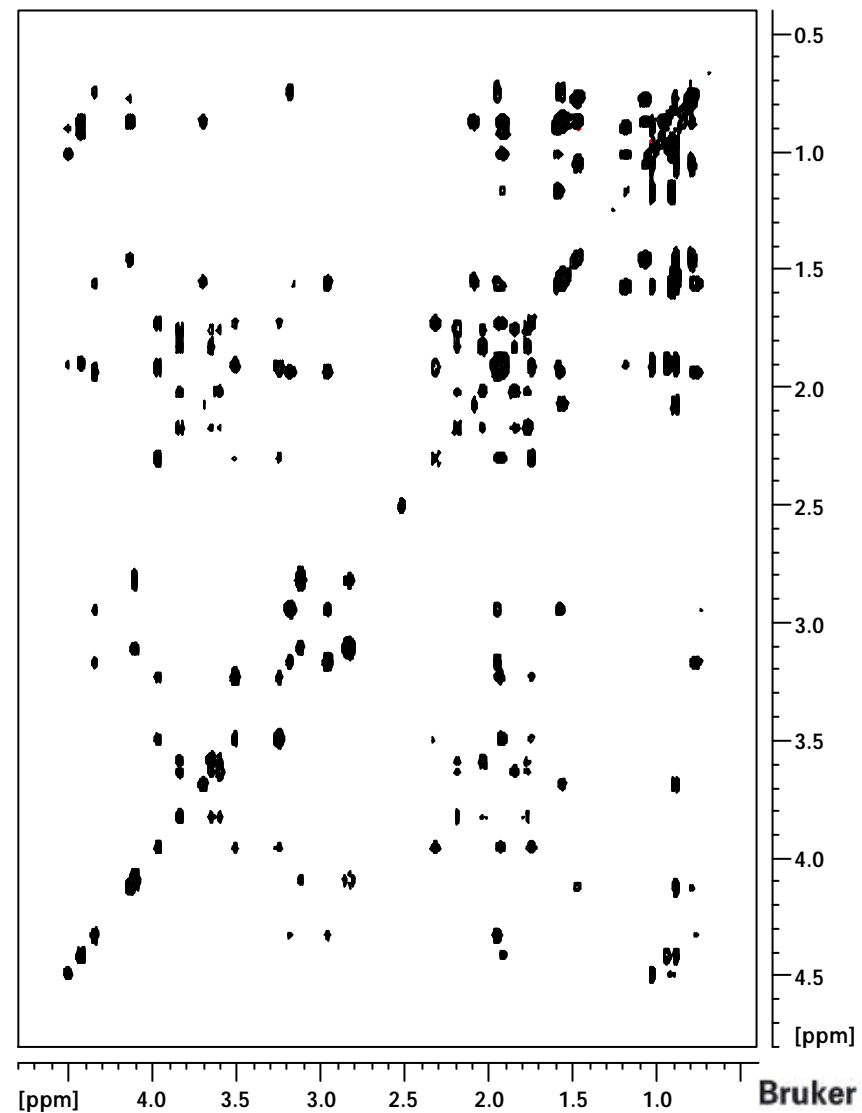
Hymenistatin

DIPSII2 (9.6kHz, 60ms)

hadamard



2D

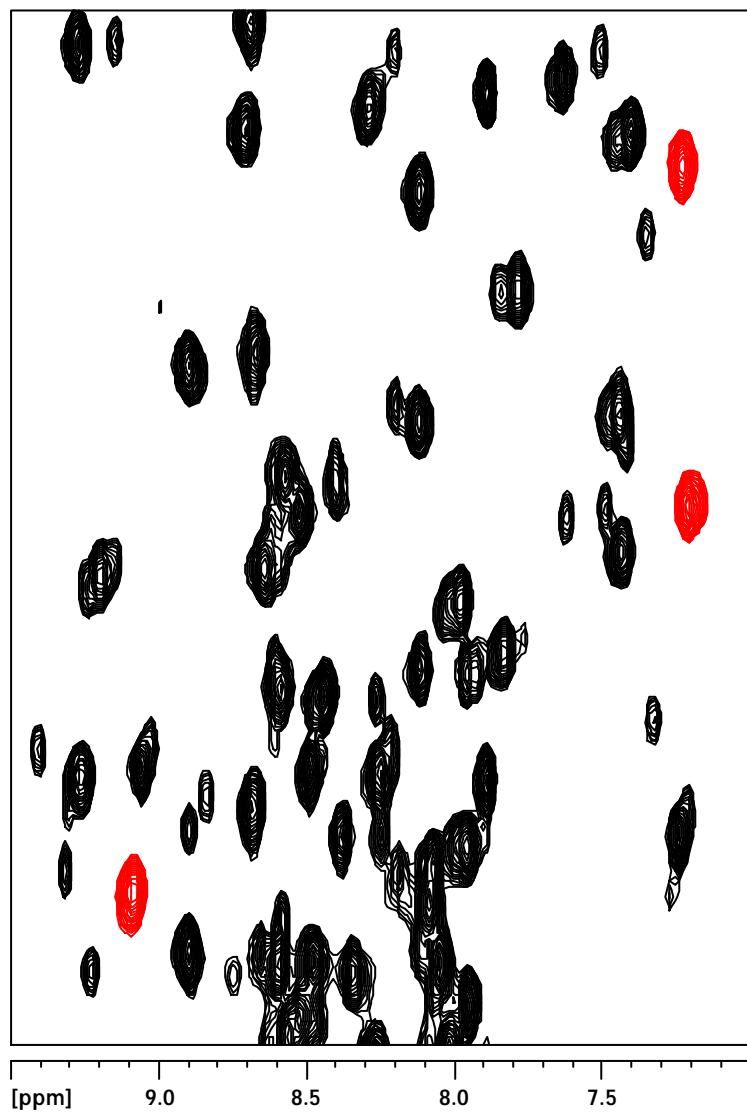


Bruker BioSpin

Hadamard 2D

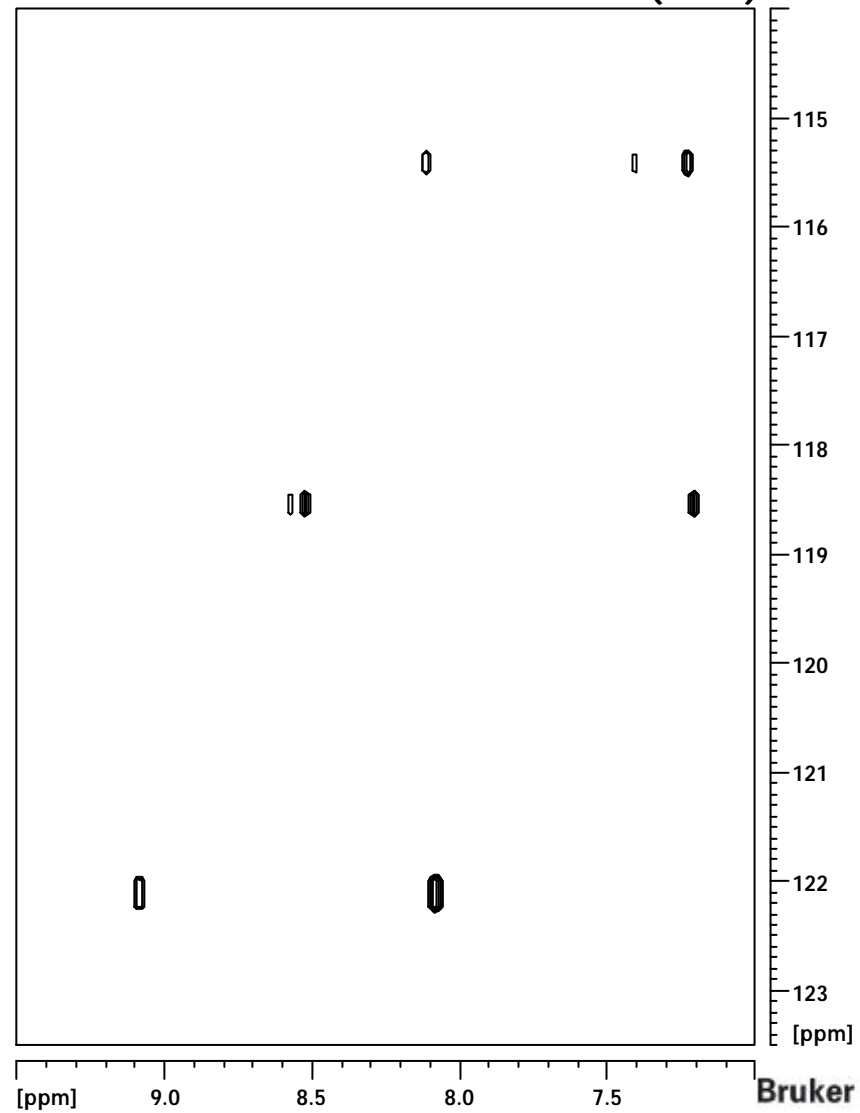
^{15}N fHSQC

2D



Hadamard

LB 9.9 (=BW)

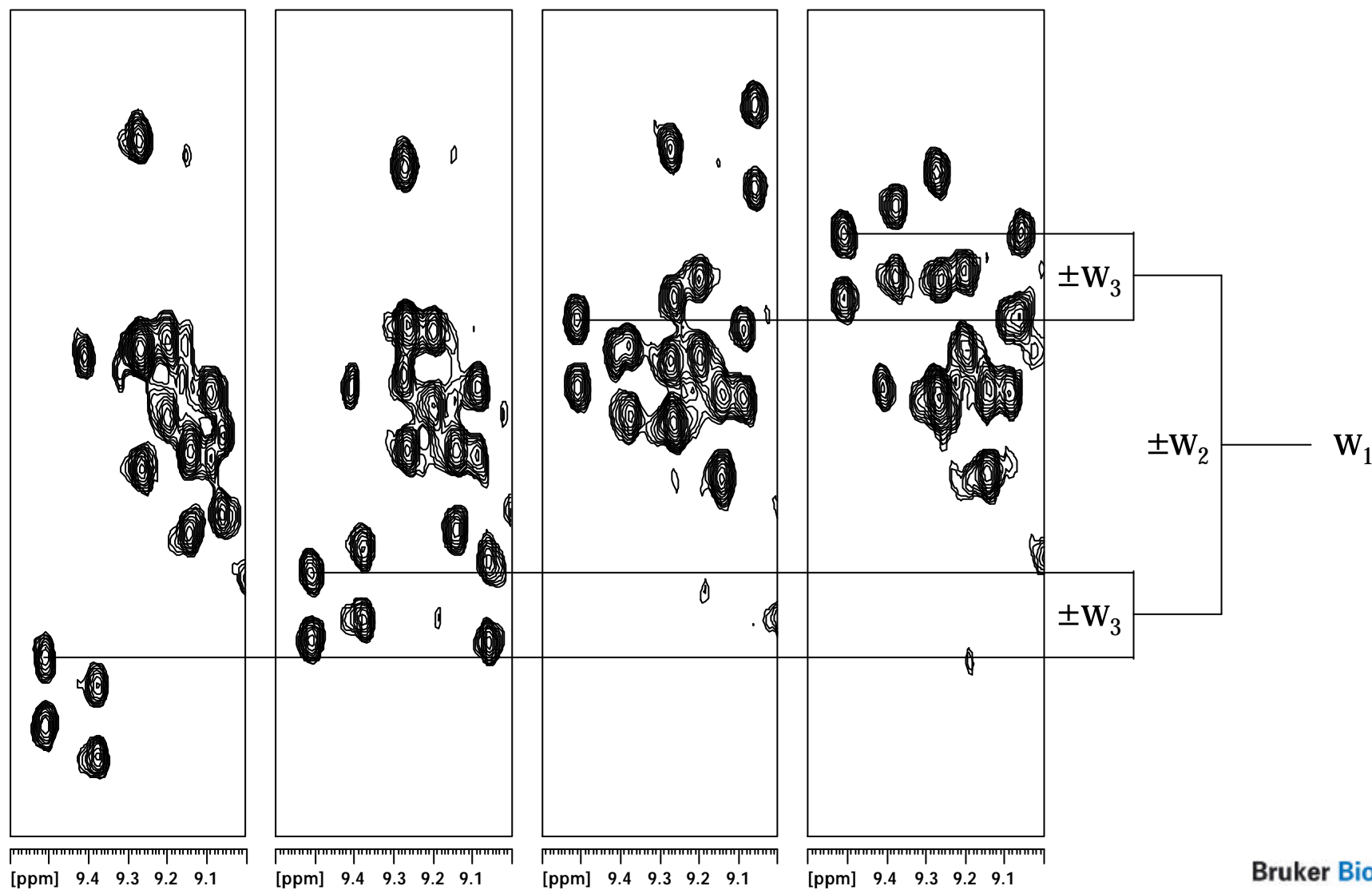




Reduced Dimensionality

Reduced Dimensionality / GFT

4,2 CbCaCONH (after splitting)

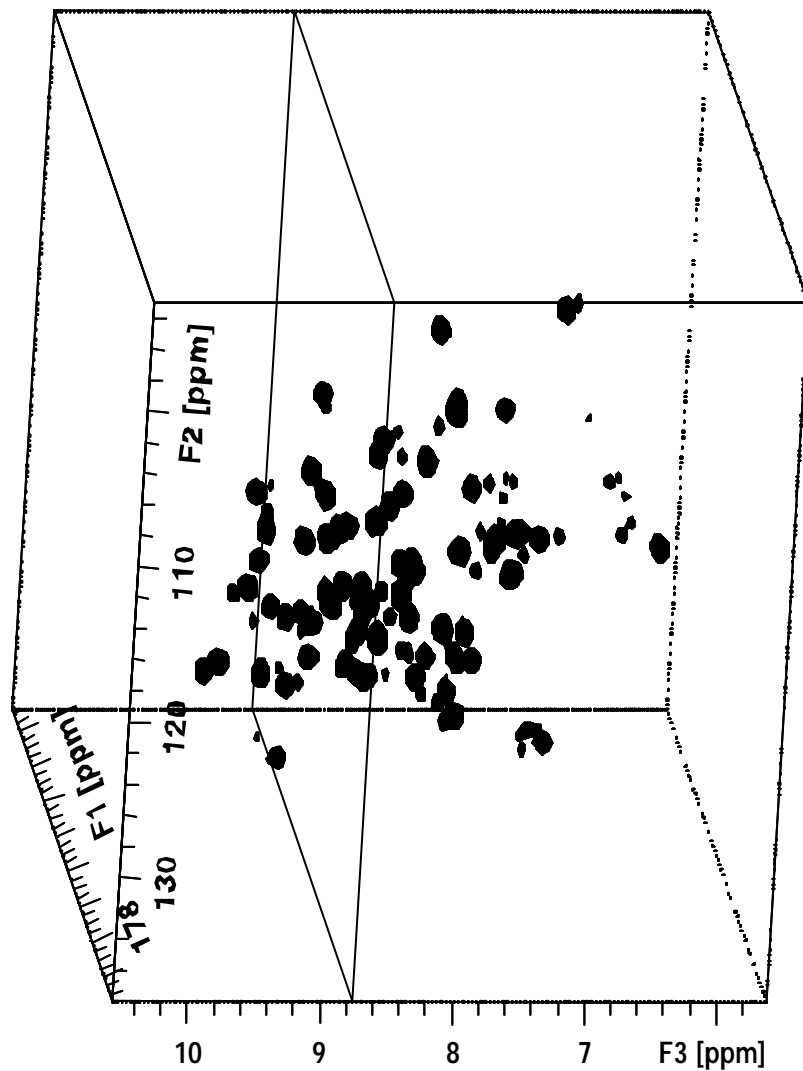




Projection Reconstruction

Projection Reconstruction

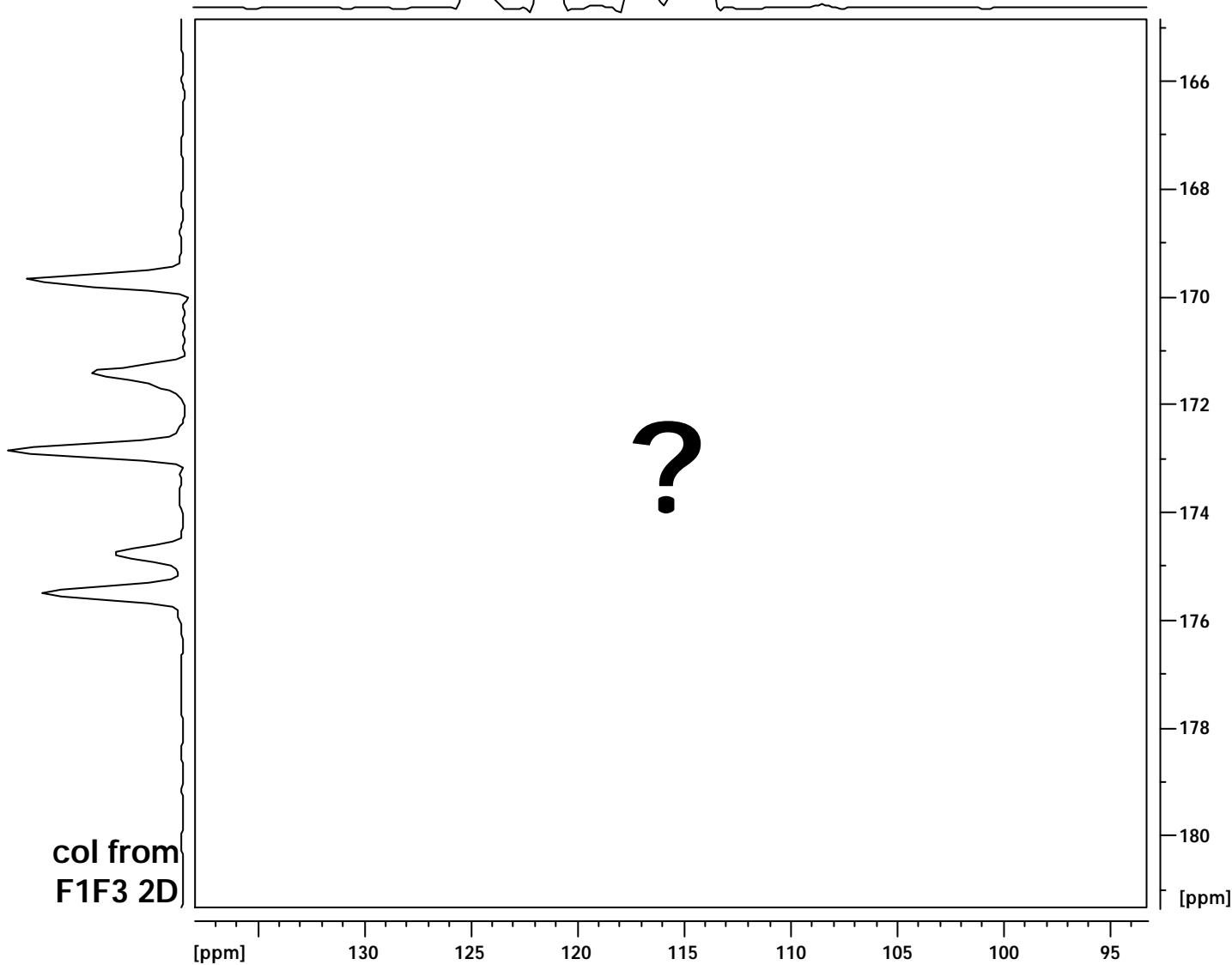
3D HNCO



Projection Reconstruction

PR HNCO

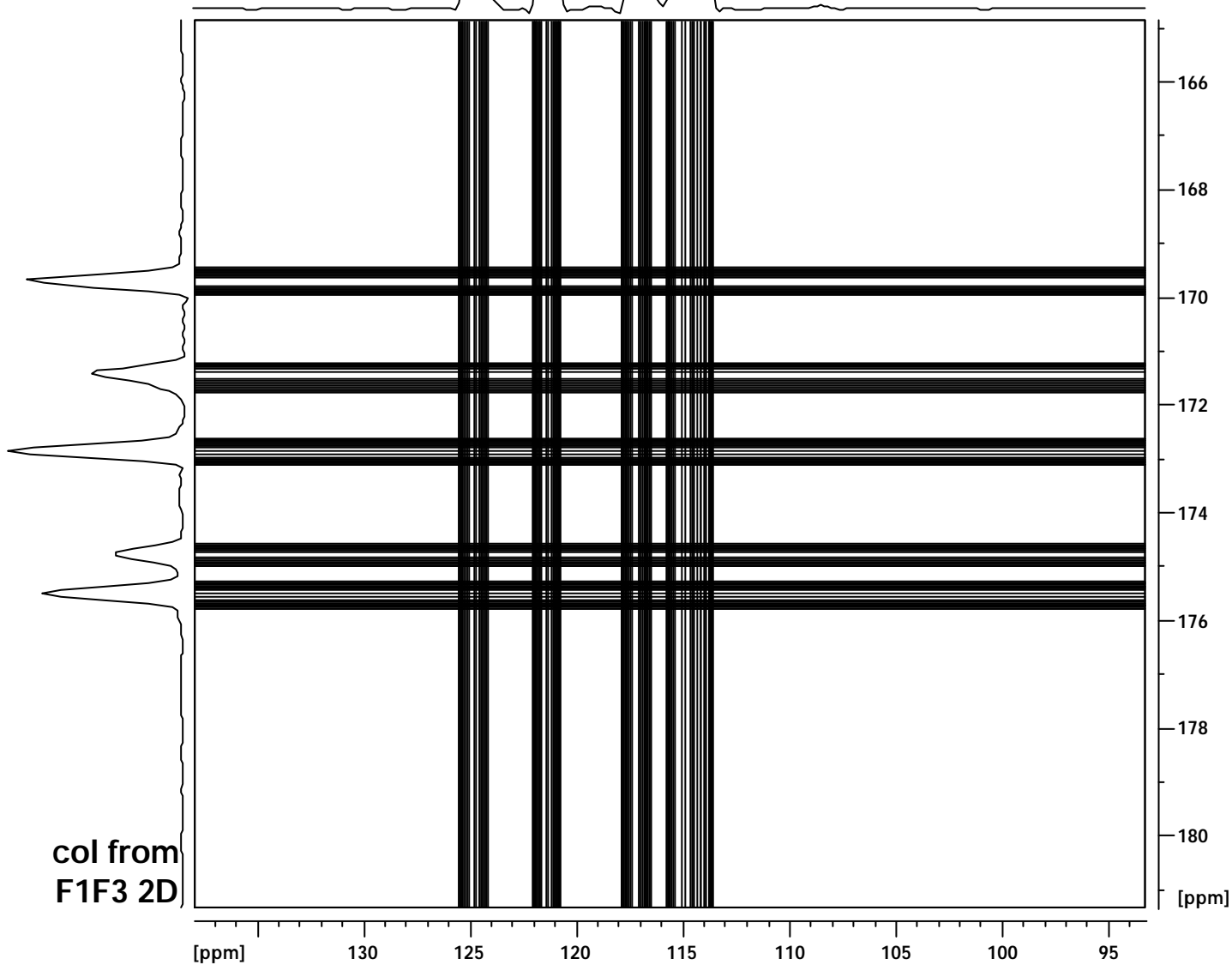
col from
F2F3 2D



Projection Reconstruction

PR HNCO

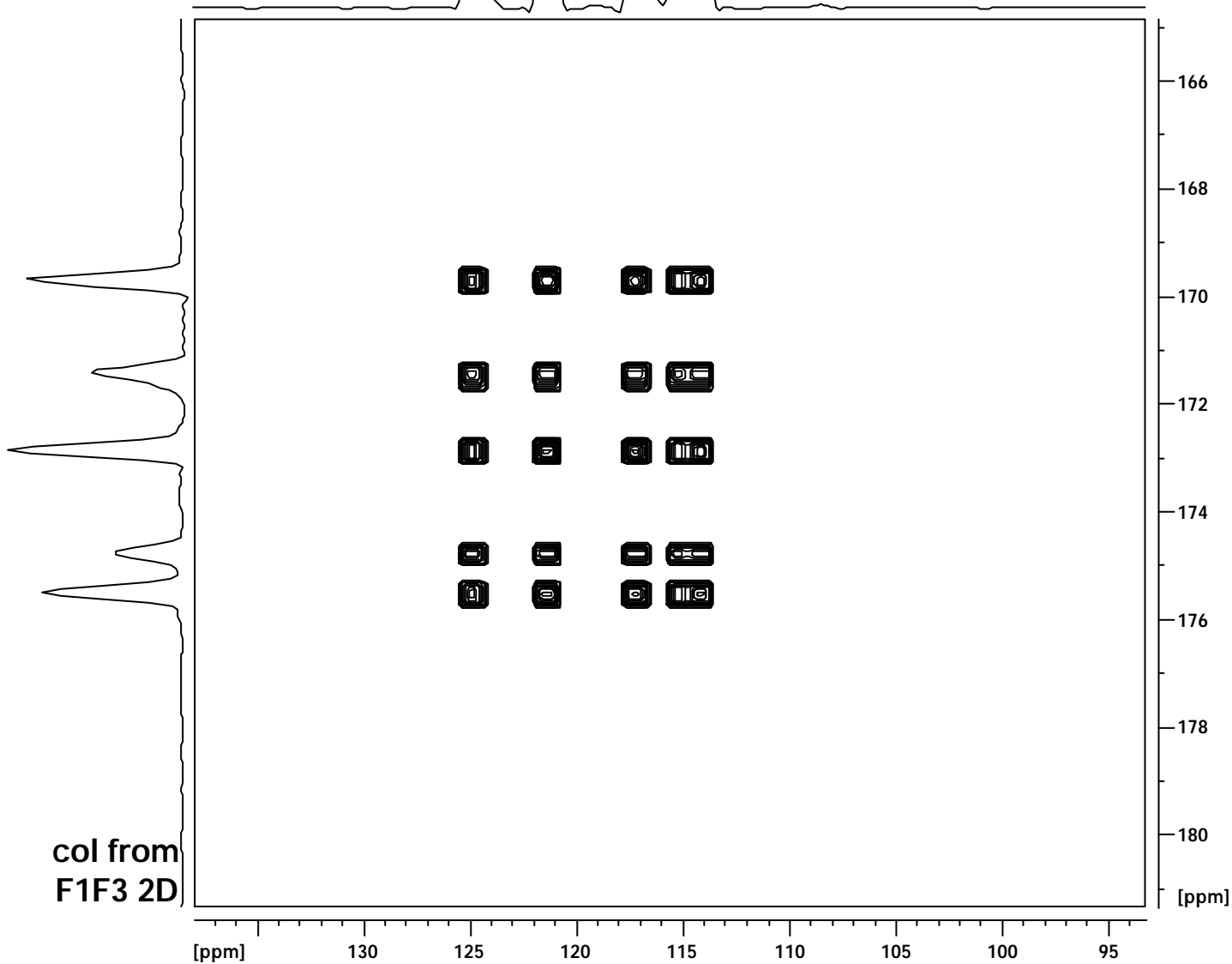
col from
F2F3 2D



Projection Reconstruction

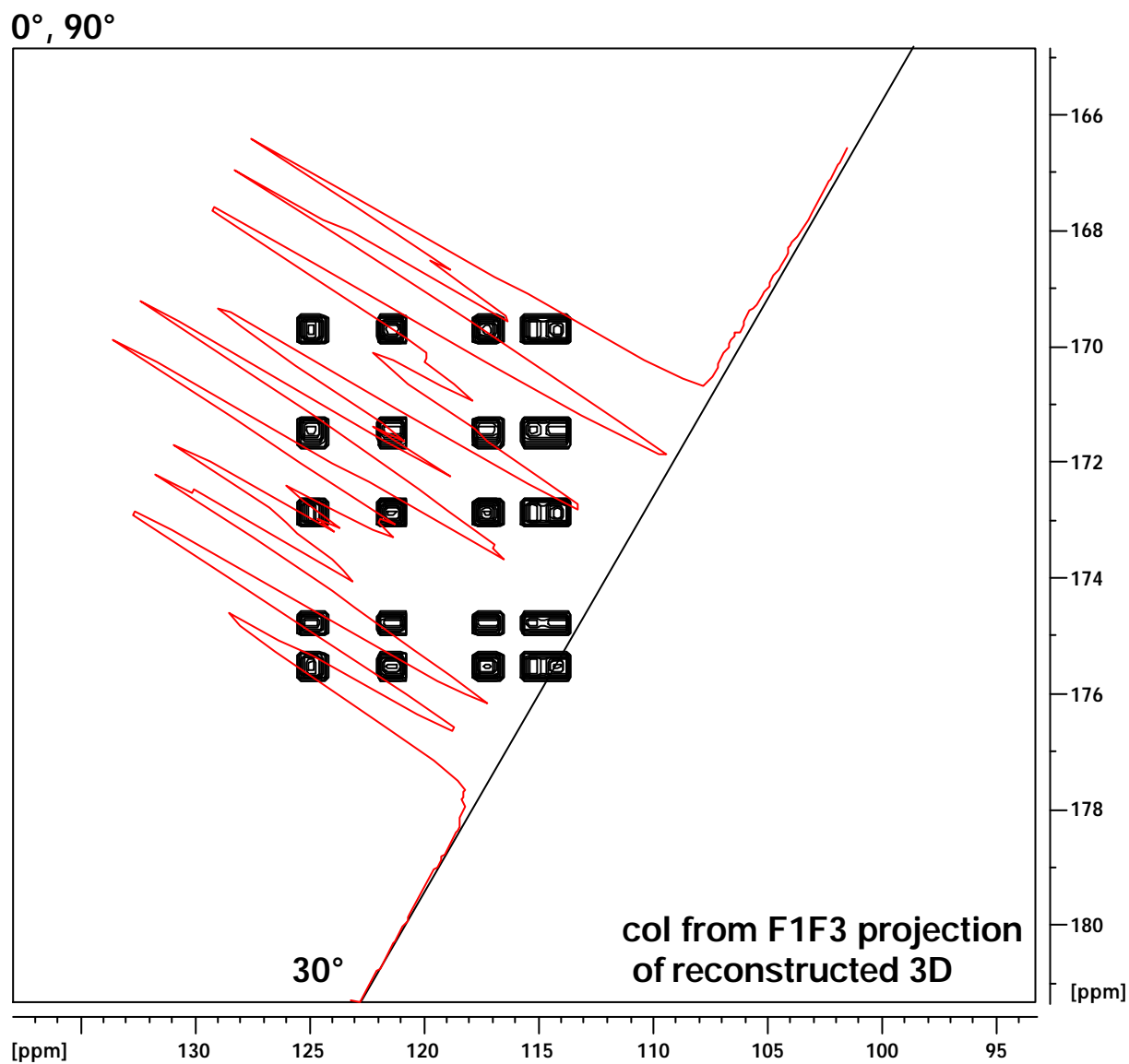
PR HNCO

col from
F2F3 2D



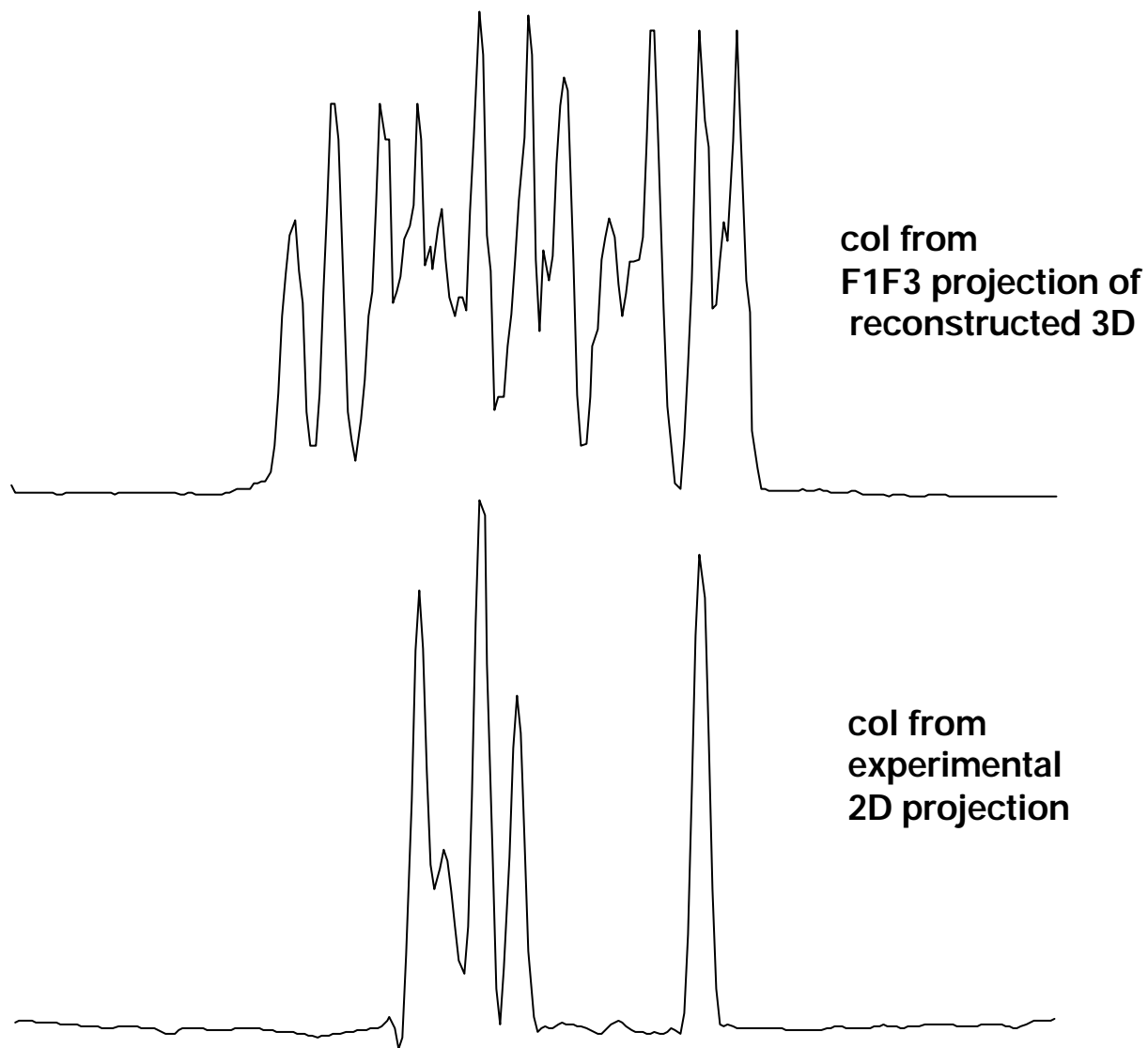
Projection Reconstruction

PR HNC0



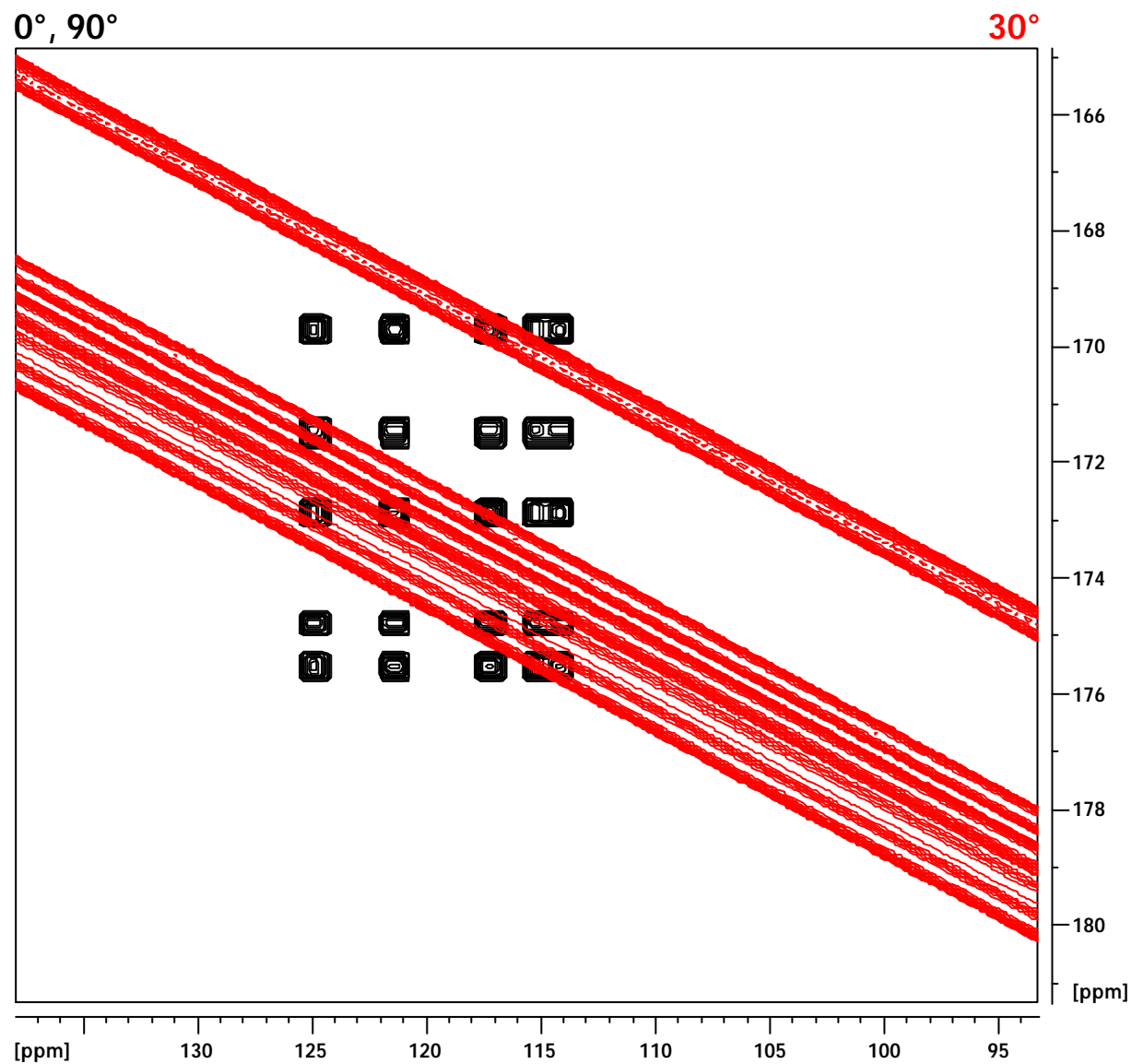
Projection Reconstruction

PR HNCO



Projection Reconstruction

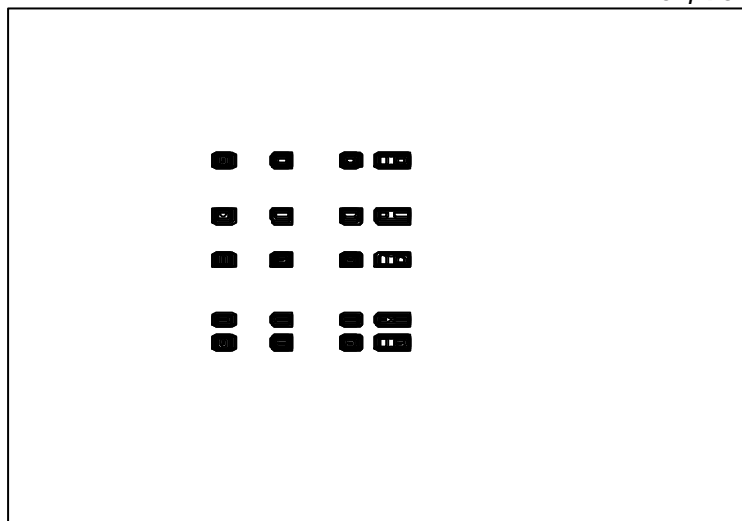
PR HNC0



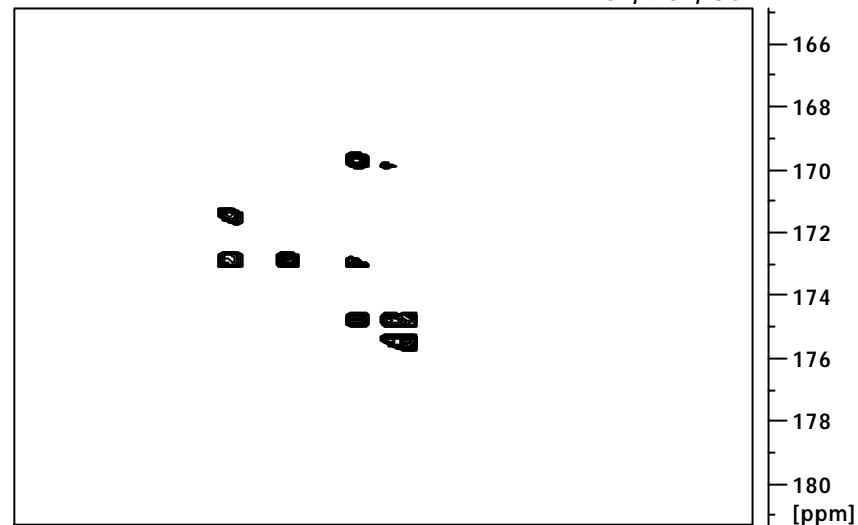
Projection Reconstruction

PR HNC0

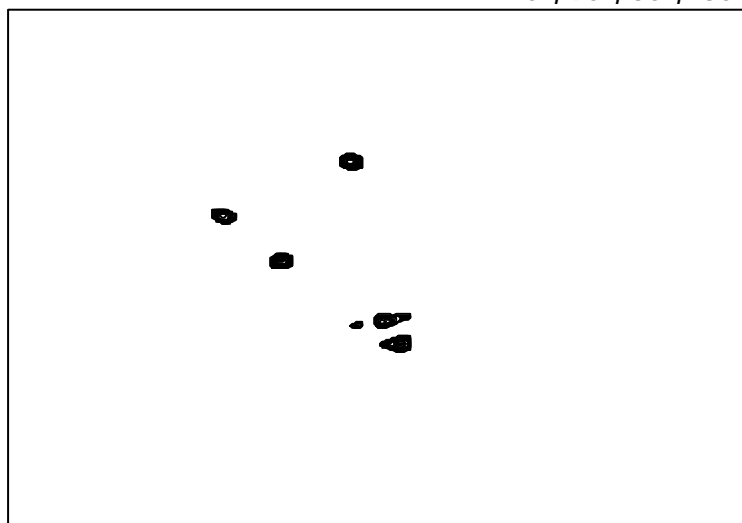
0°, 90°



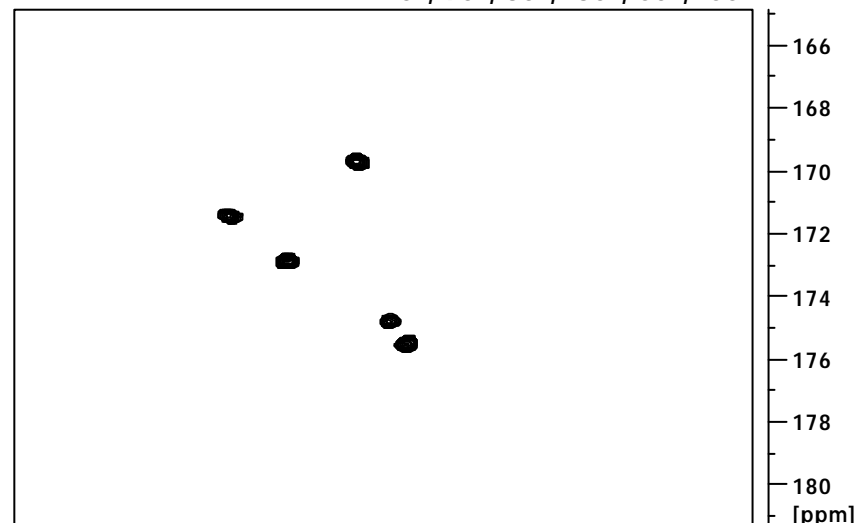
0°, 90°, 30°



0°, 90°, 30°, -30°



0°, 90°, 30°, -30°, 60°, -60°

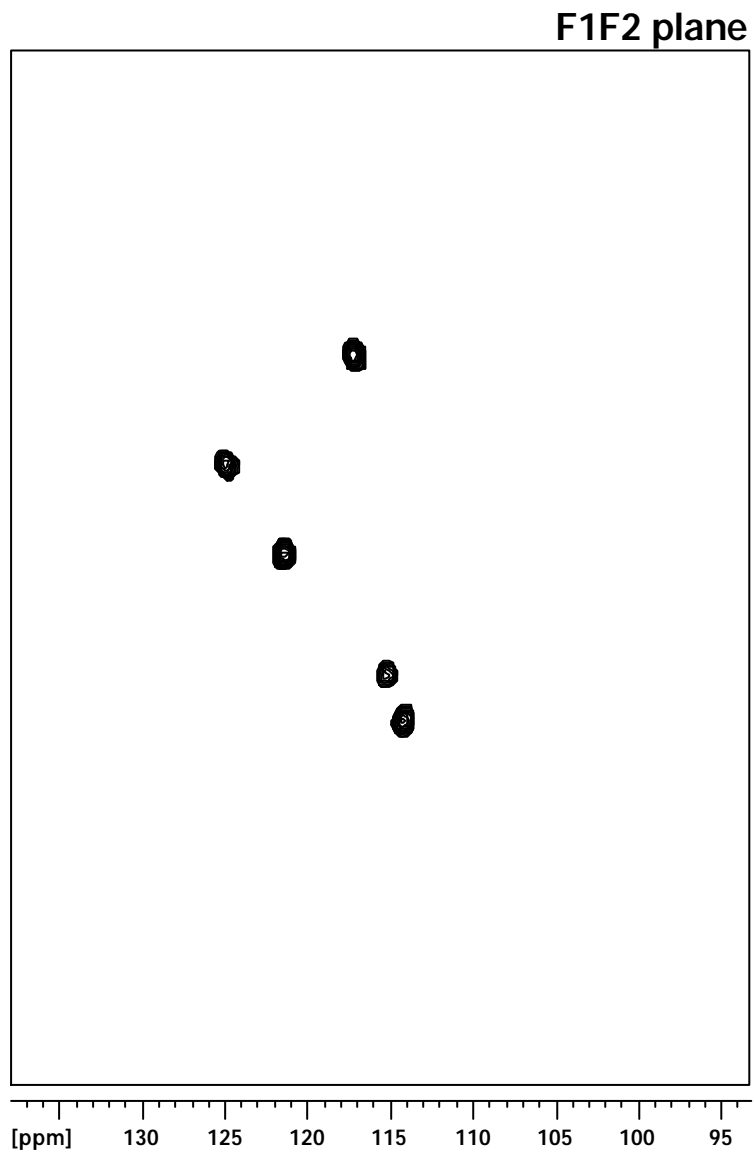


[ppm] 130 125 120 115 110 105 100 95

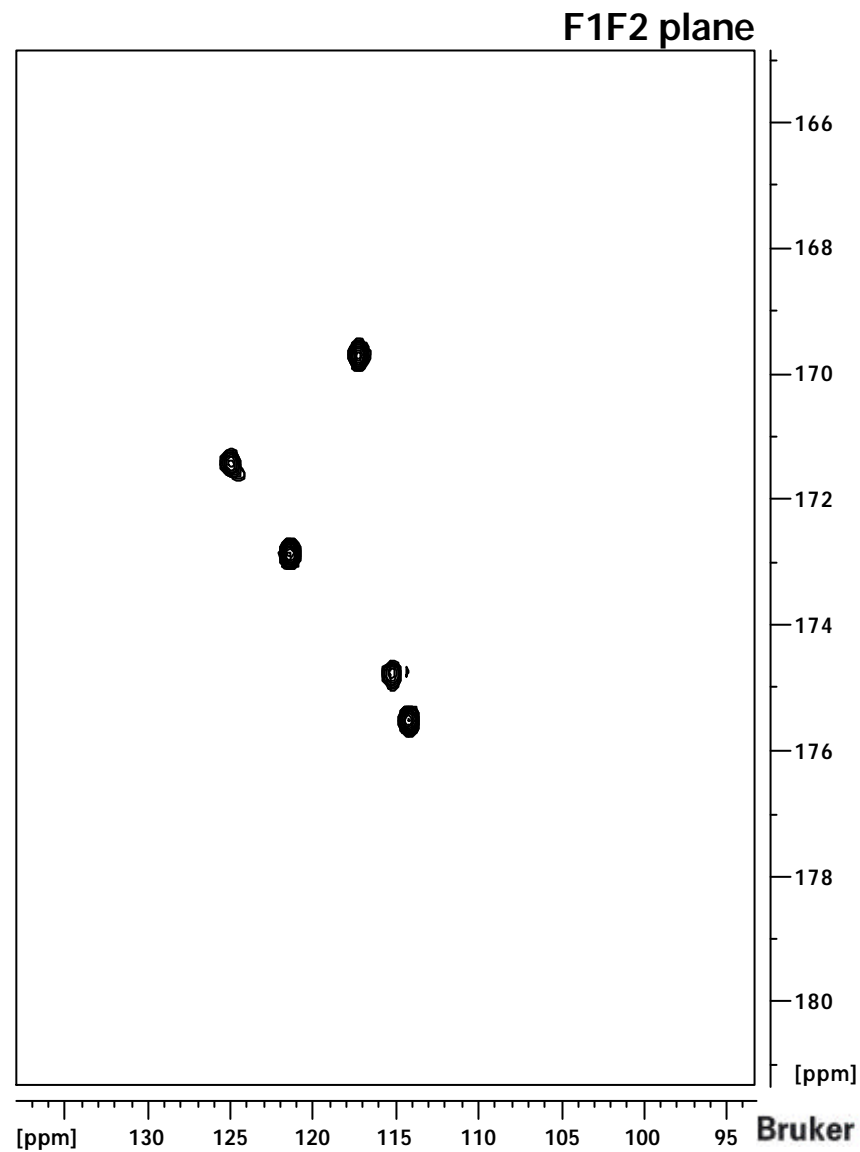
[ppm] 130 125 120 115 110 105 100 95

Projection Reconstruction

PR HNCO



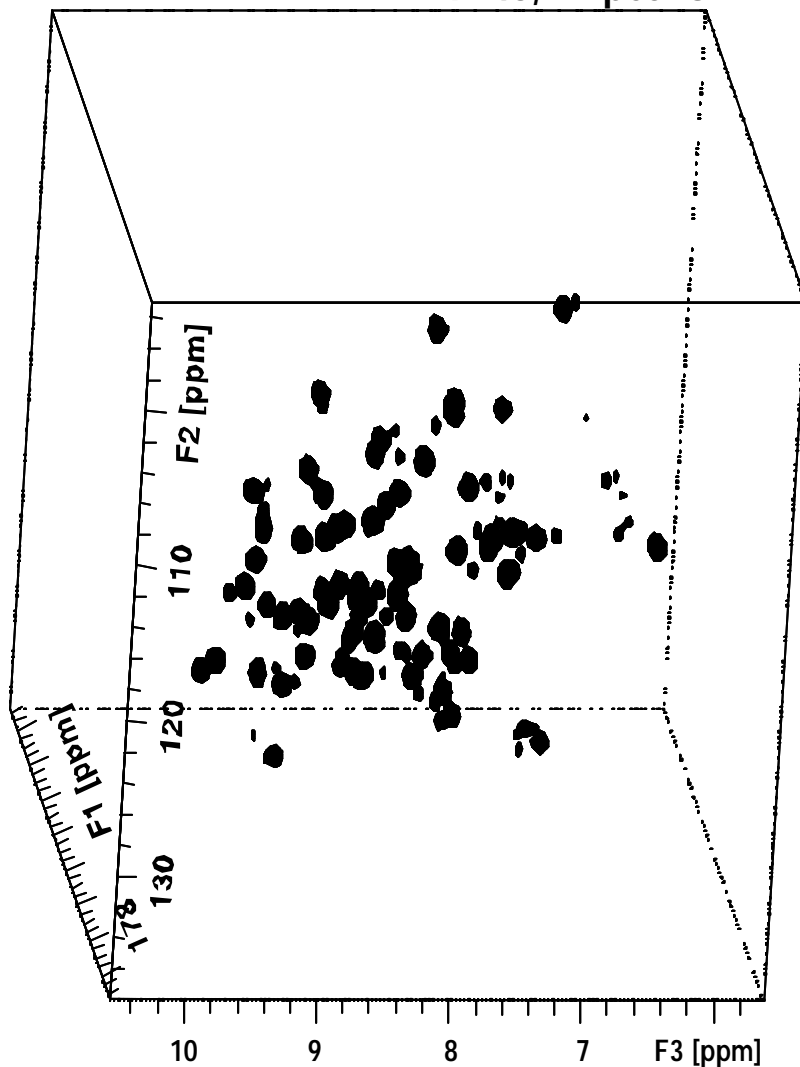
3D HNCO



Projection Reconstruction

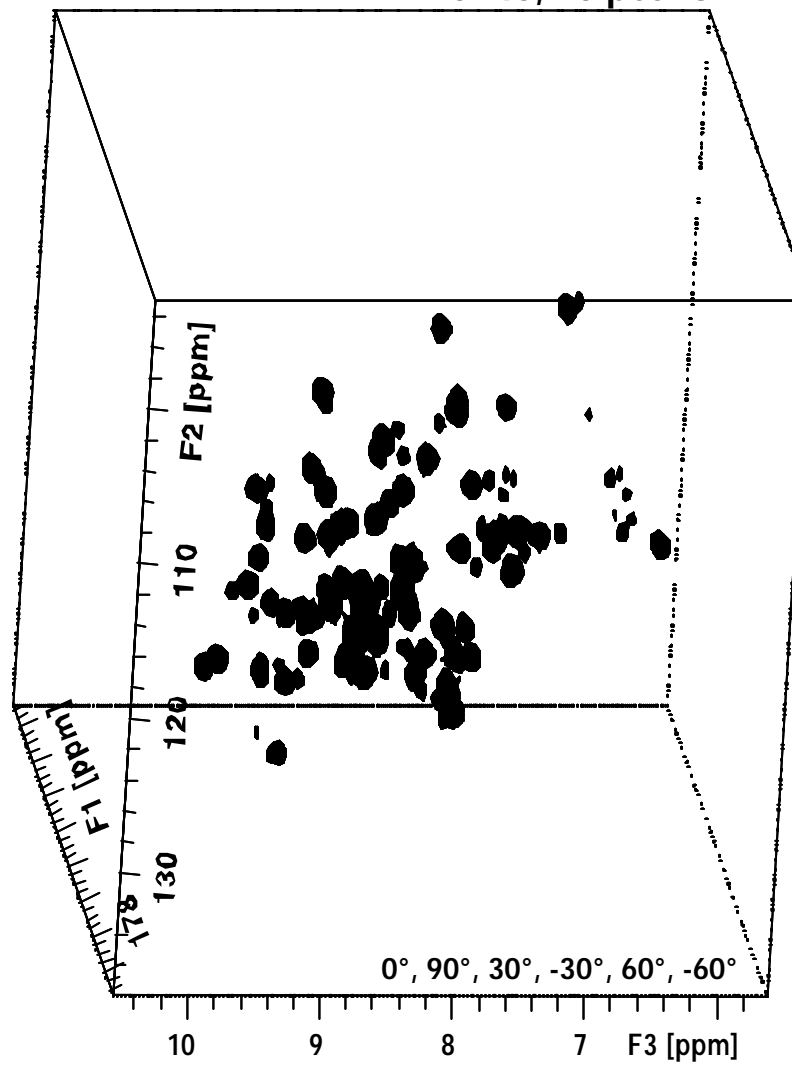
3D HNCO

9h45, 71 peaks



PR HNCO

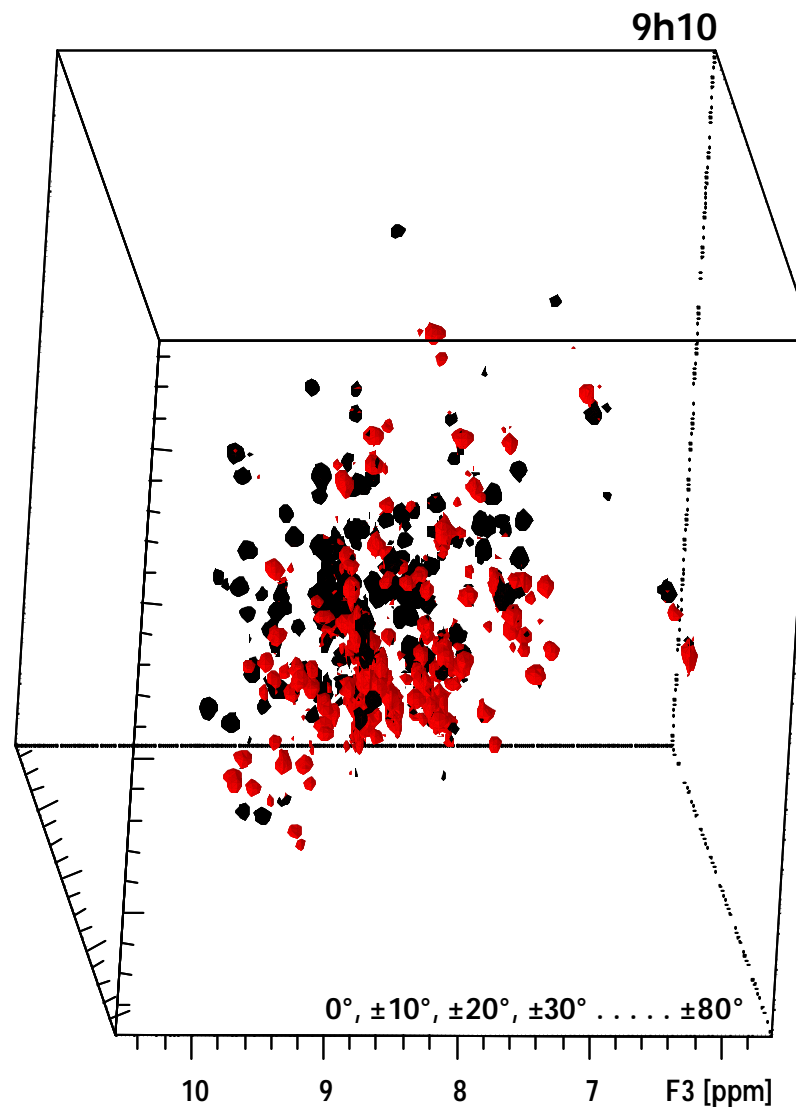
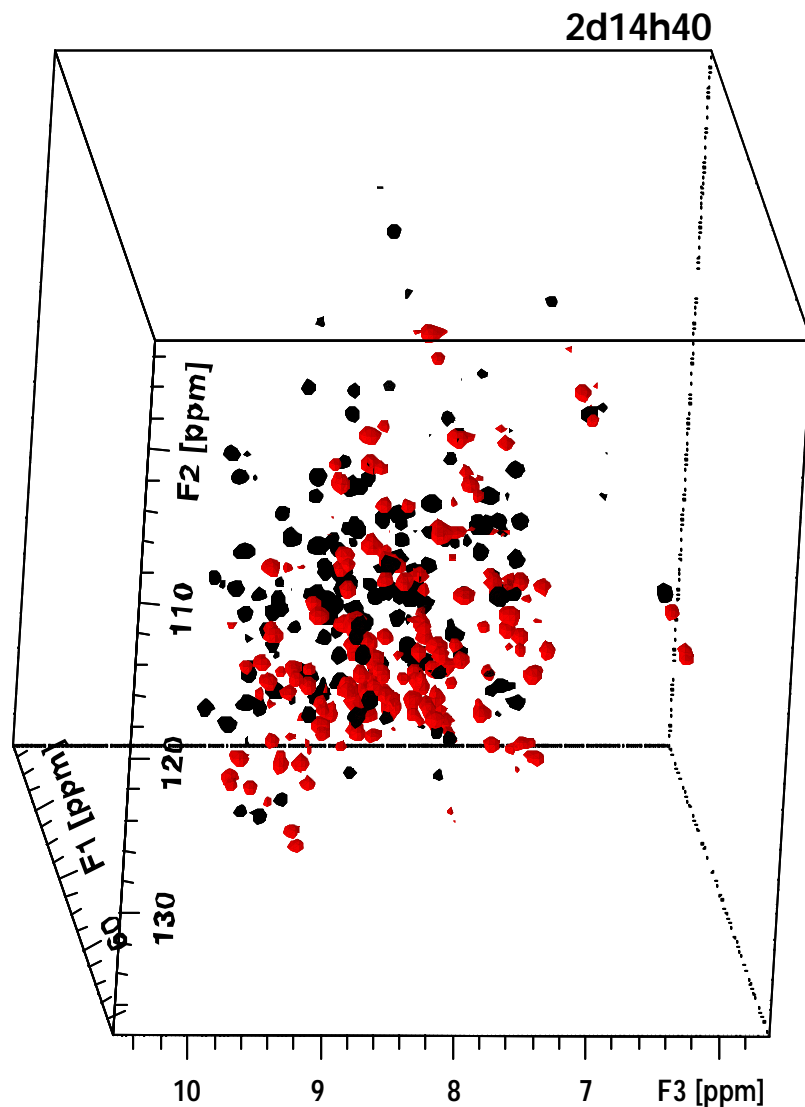
0h45, 70 peaks



Projection Reconstruction

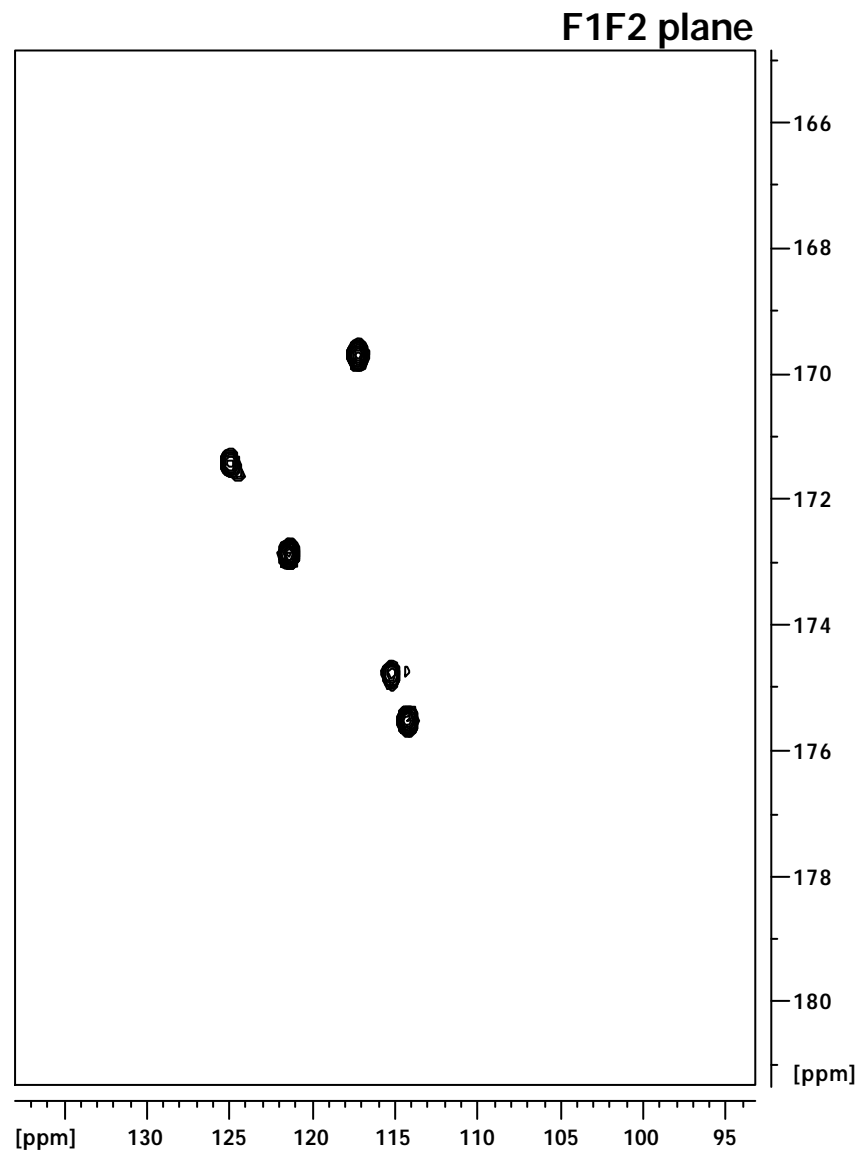
3D HNCaCb

PR HNCaCb

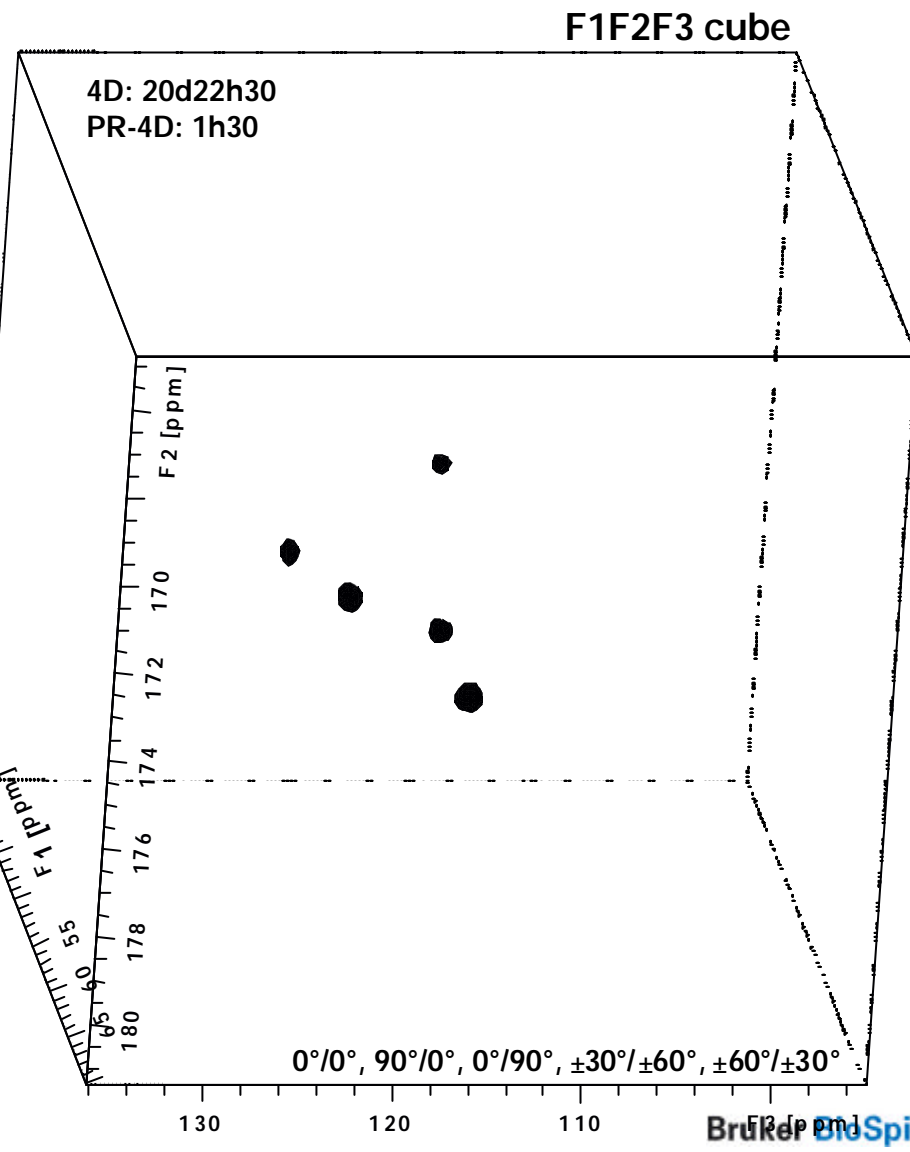


Projection Reconstruction

3D HNCO

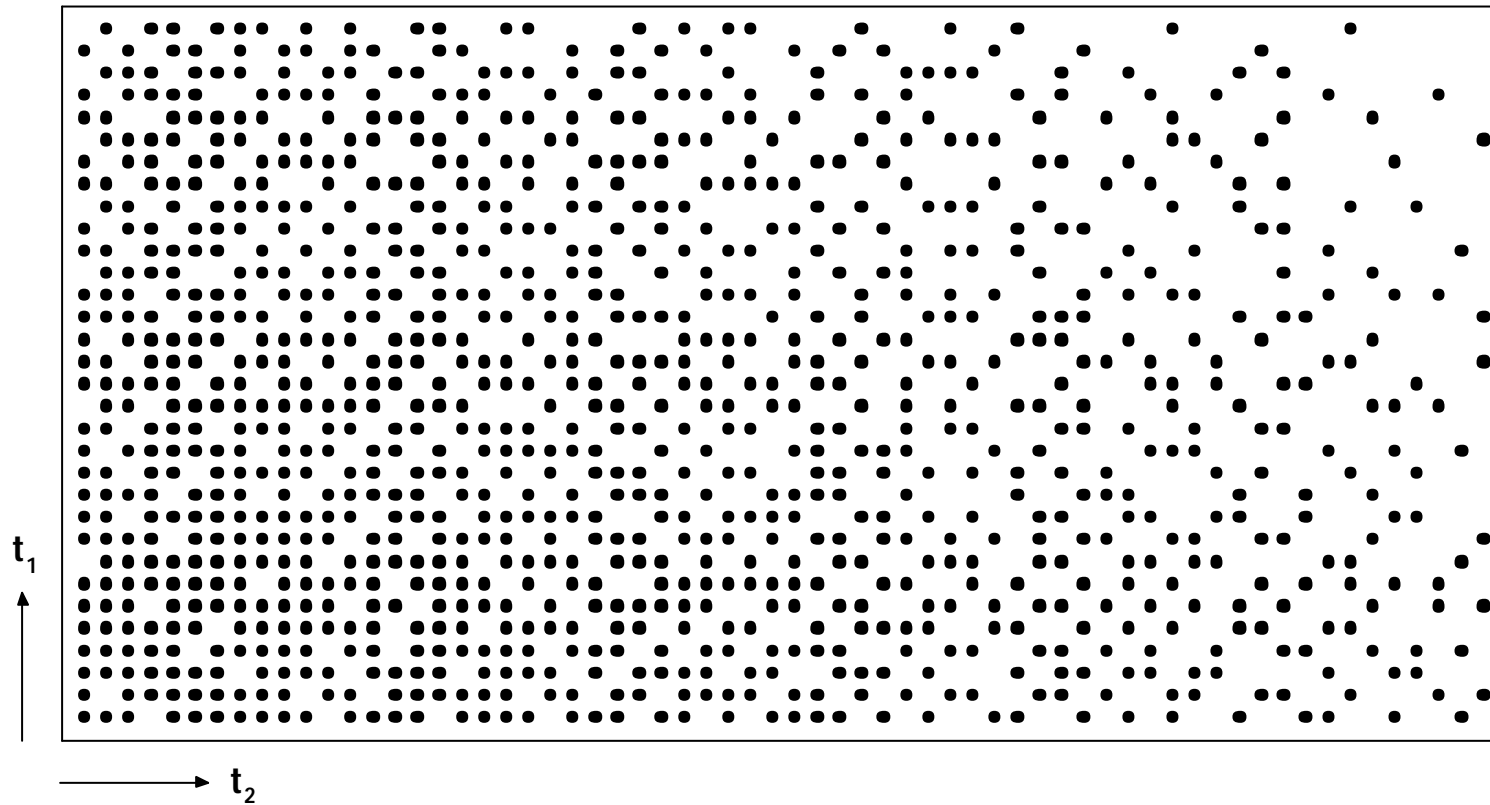


4D HNCOCa



Non-linear Sampling

Non-Linear Sampling





Covariance NMR

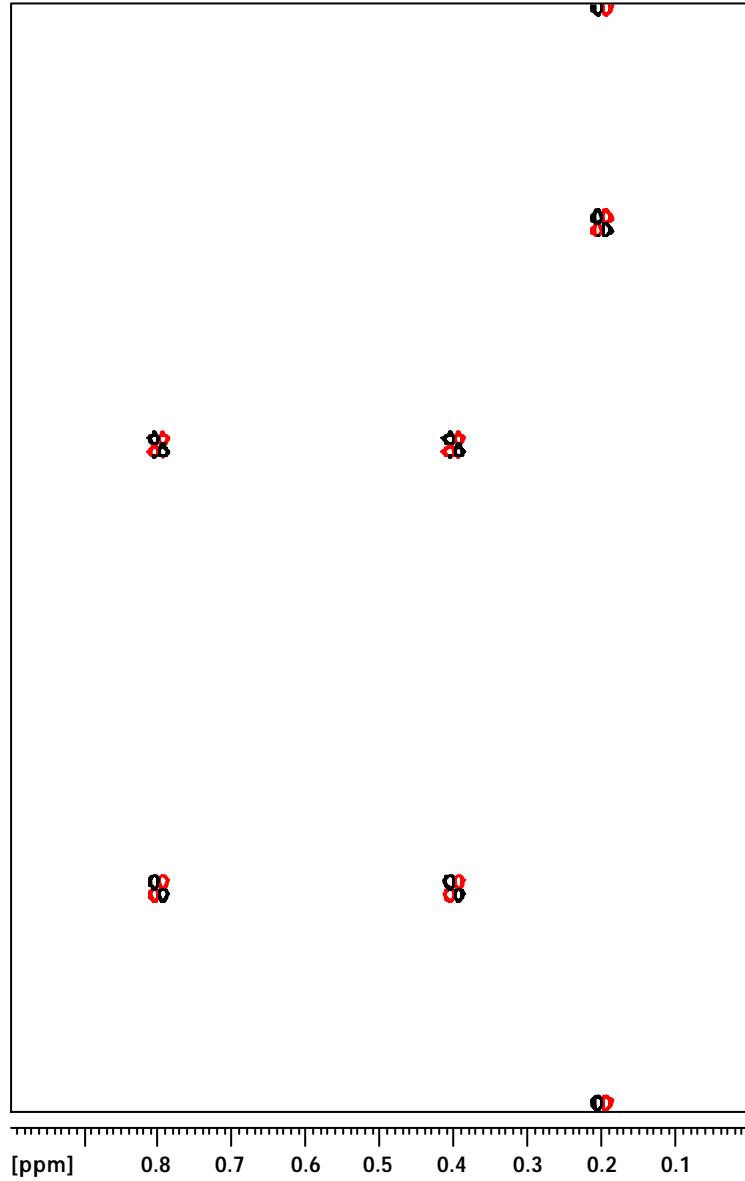
covariance NMR



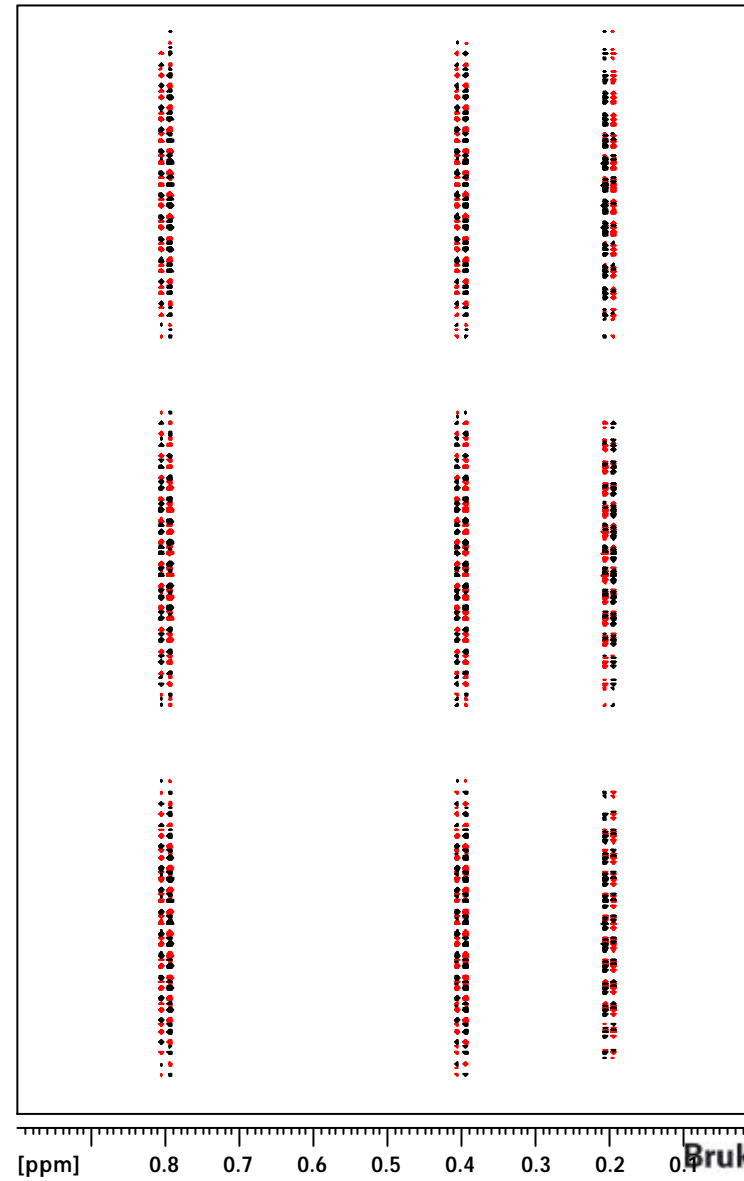
simulation

DQF COSY

xfb: td1=512 / si1=256



xf2: td1=512 / si1=256



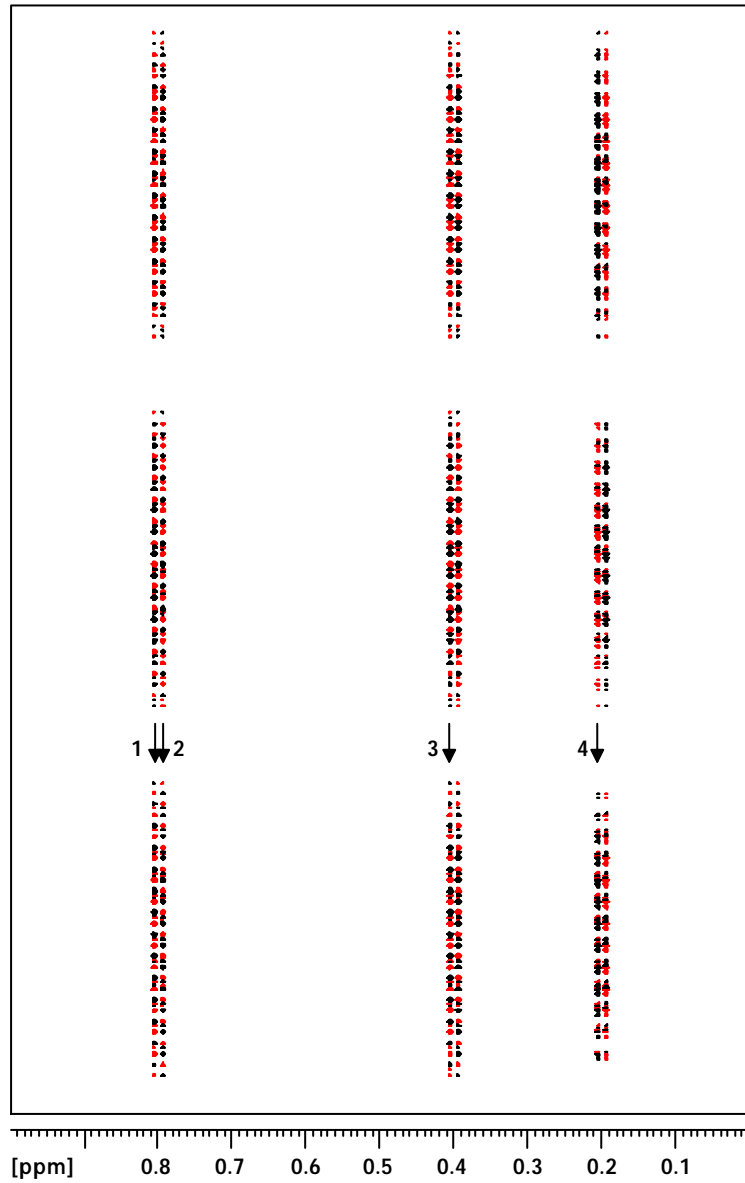
covariance NMR



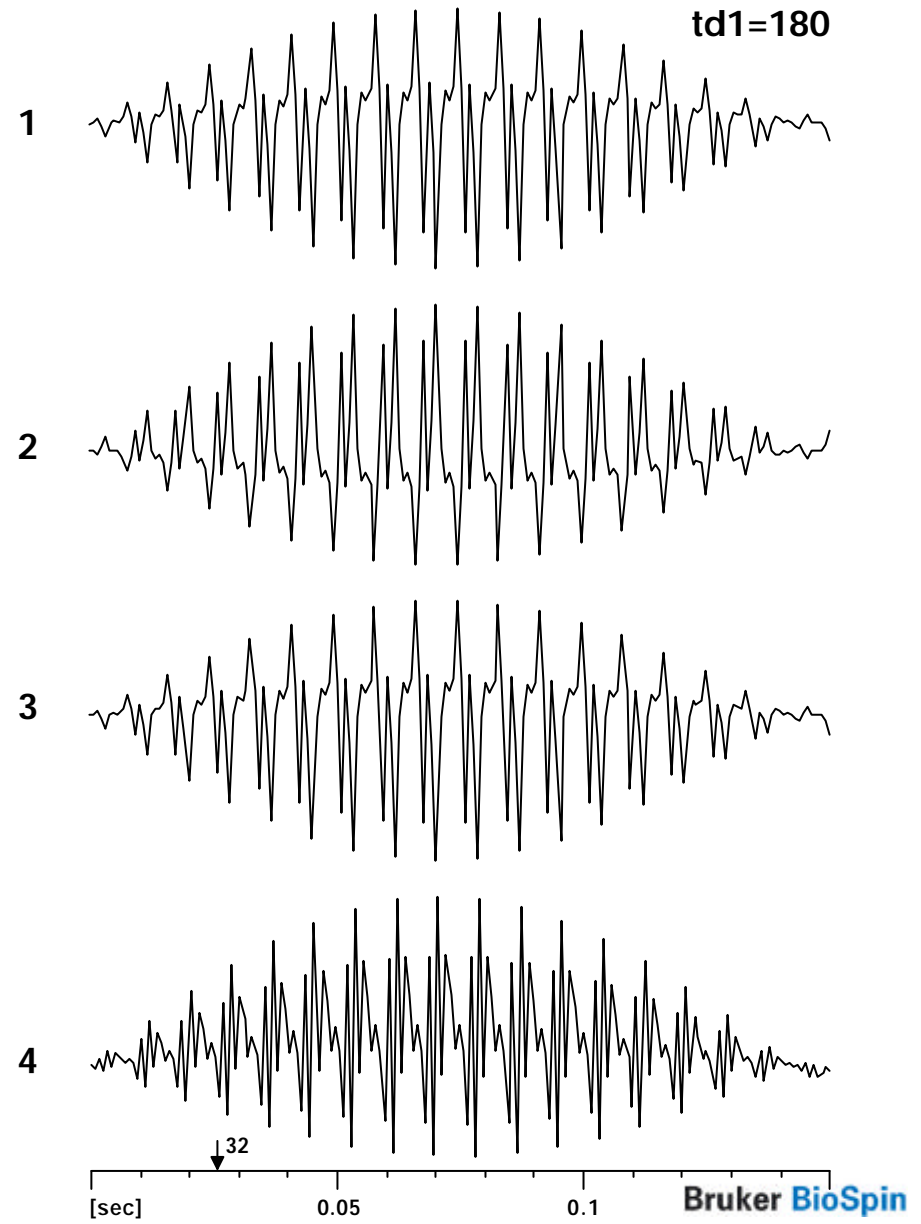
simulation

DQF COSY

xf2: td1=512 / si1=256



td1=180



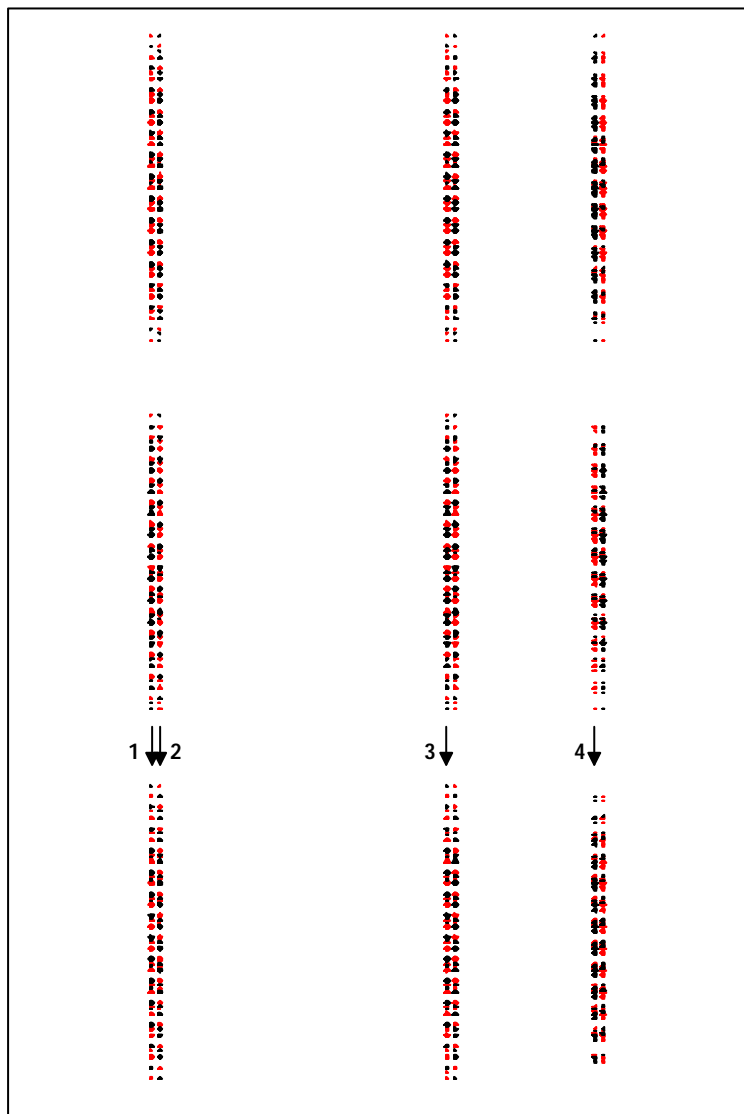
covariance NMR



simulation

DQF COSY

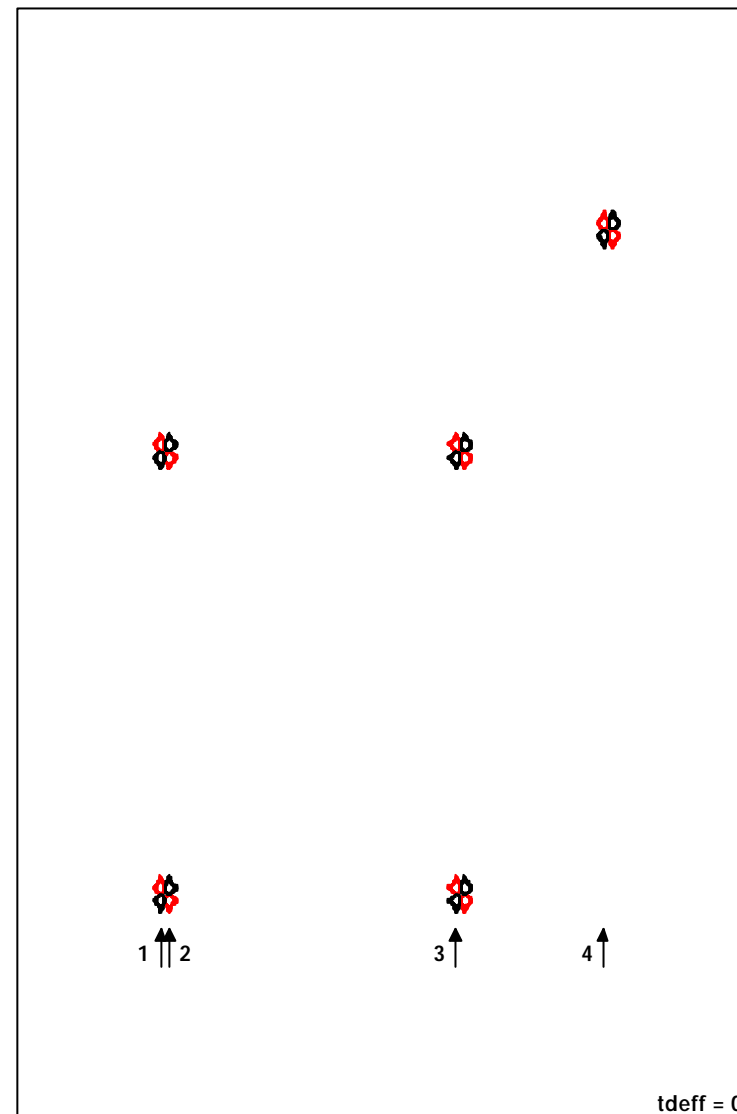
xf2: td1=512 / si1=256



[ppm] 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1

DQF COSY

xf2 + covariance



[ppm] 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1

Brucker BioSpin

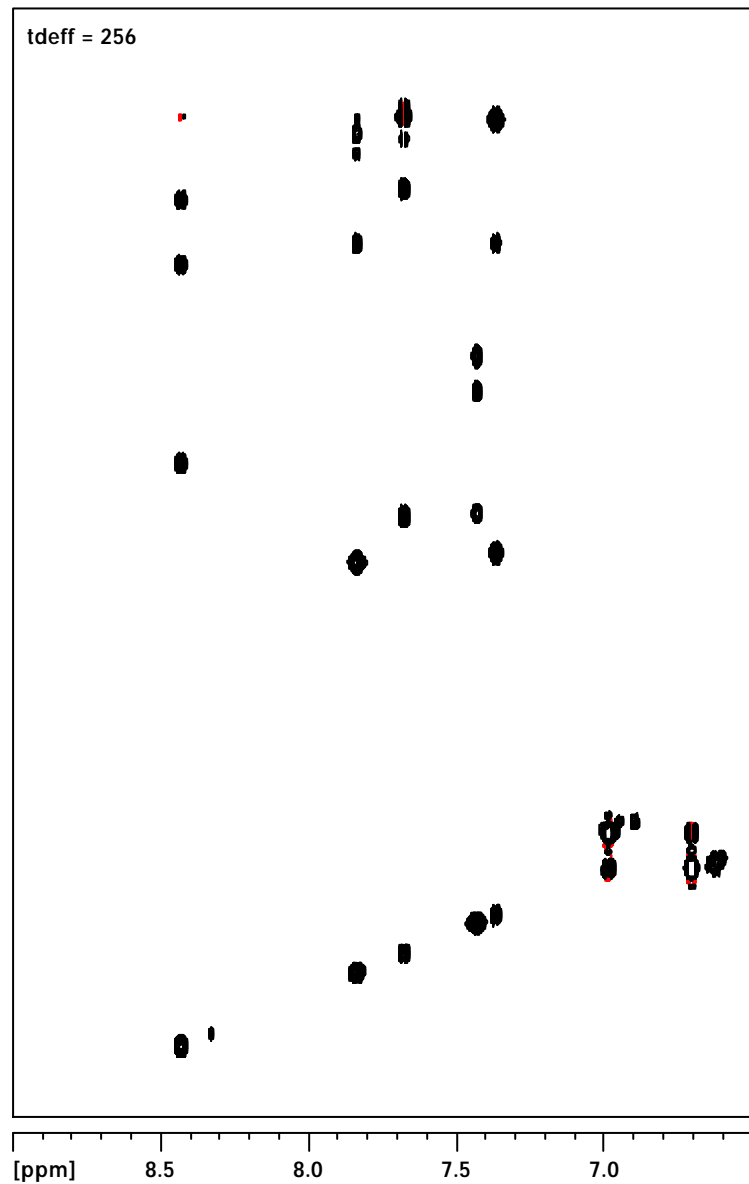
covariance NMR



20mM Hymenistatin

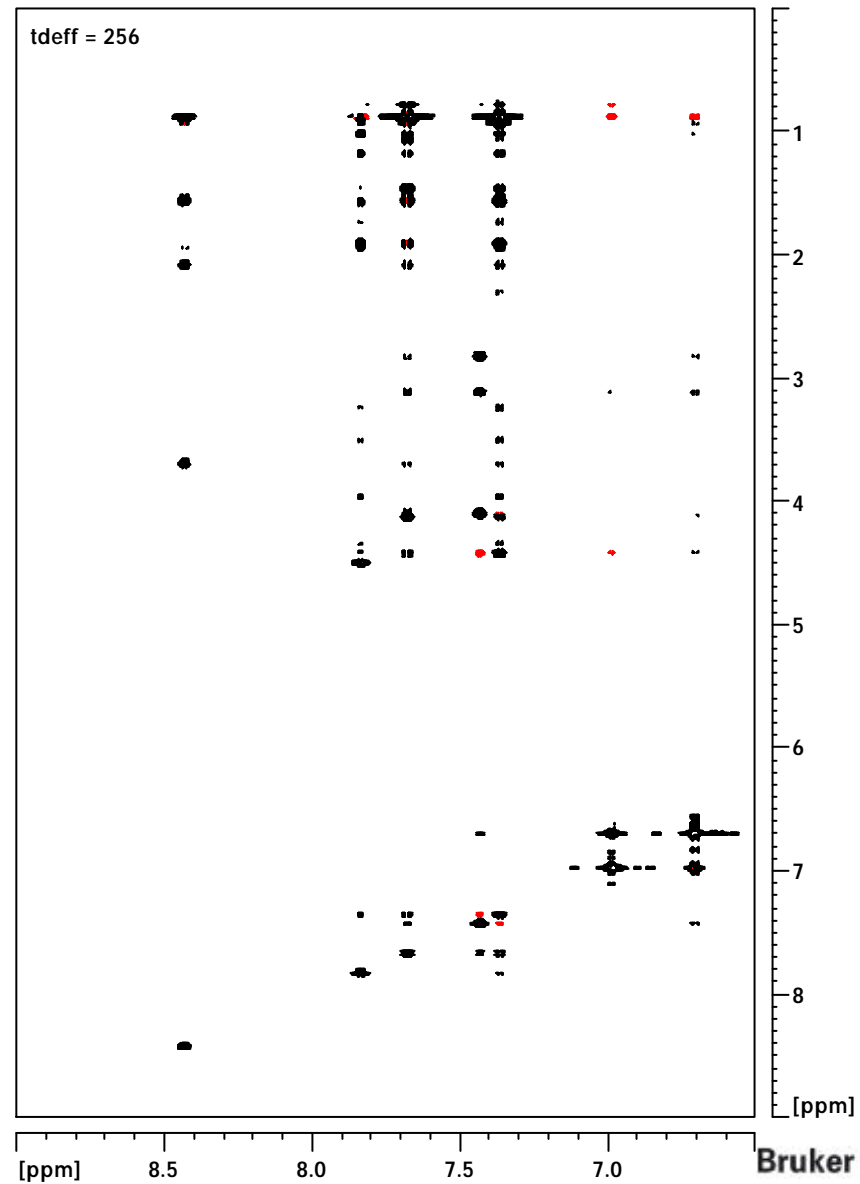
DIPS12

xfb



DIPS12

xf2 + covariance



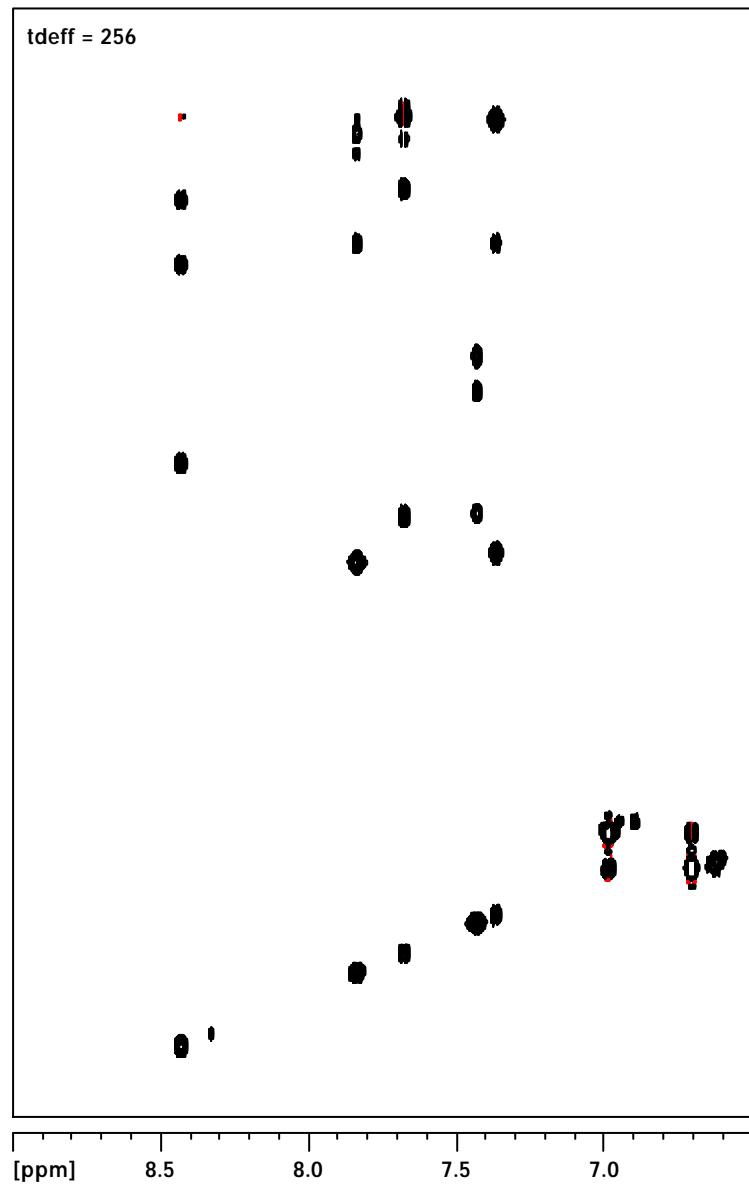
covariance NMR



20mM Hymenistatin

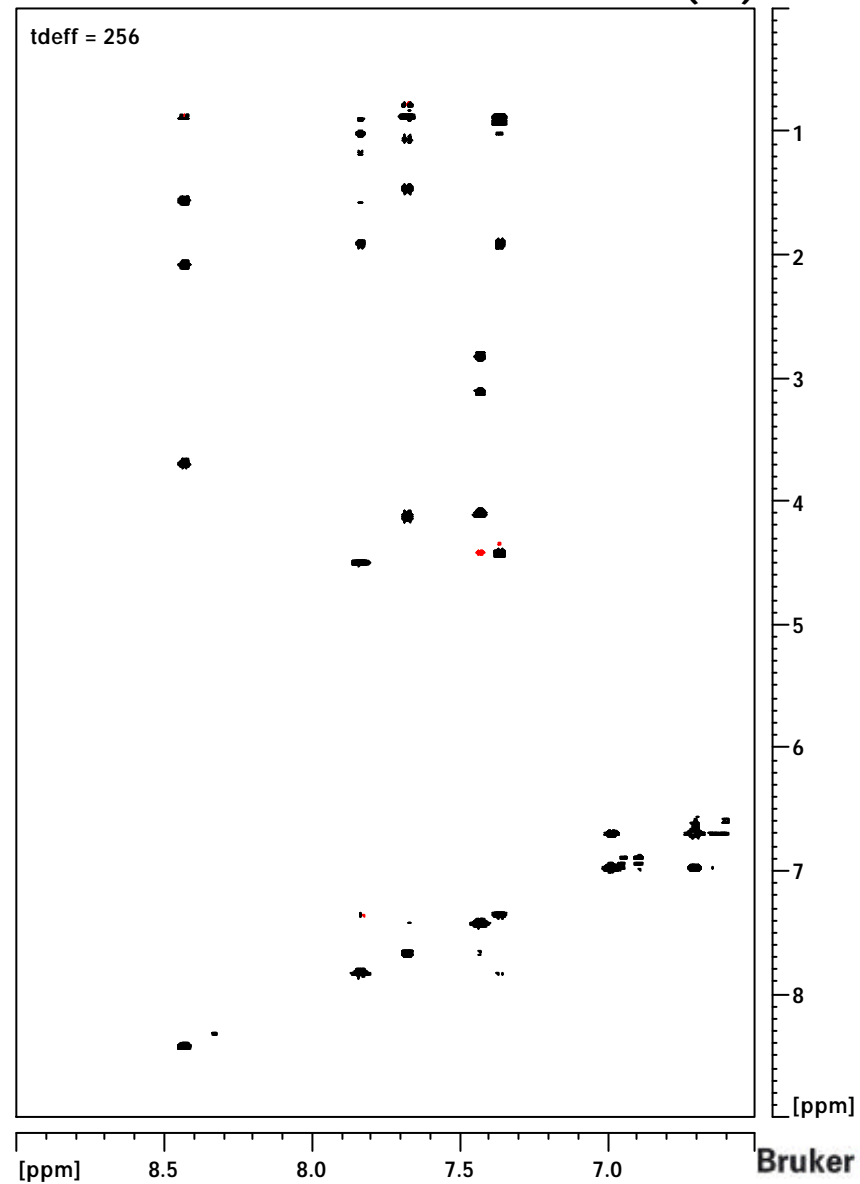
DIPS12

xfb



DIPS12

xf2 + covariance ($\ddot{O}C$)



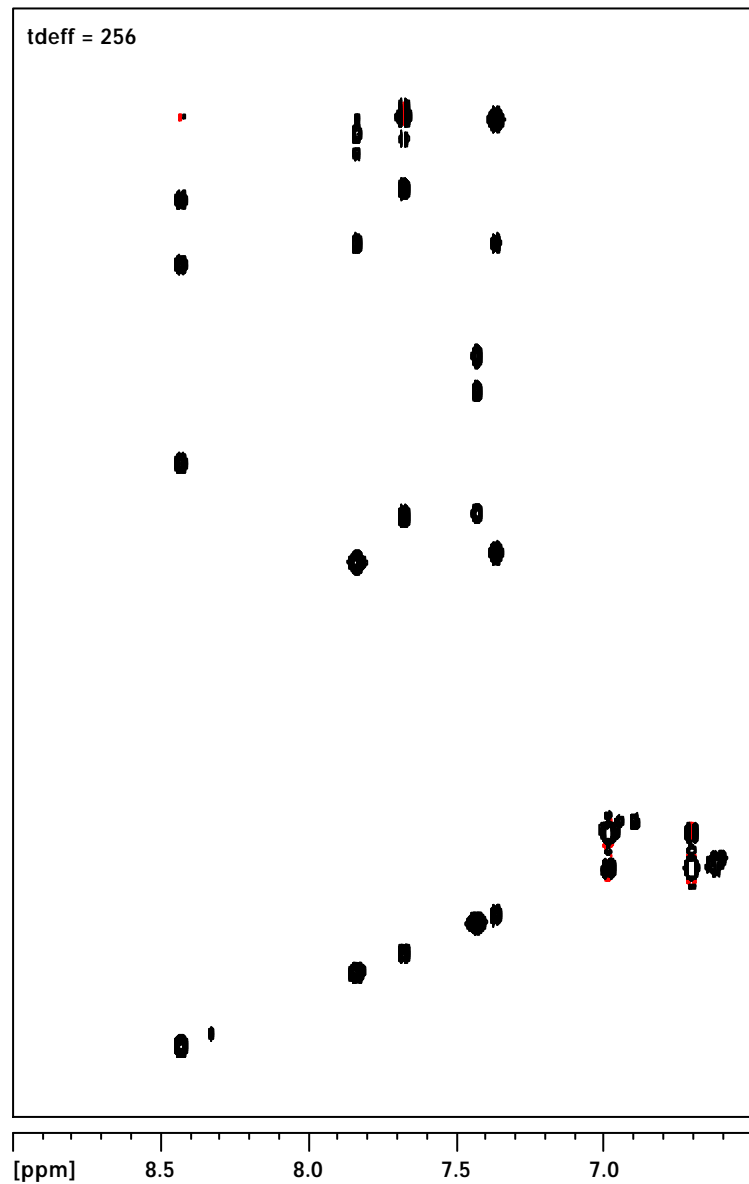
covariance NMR



20mM Hymenistatin

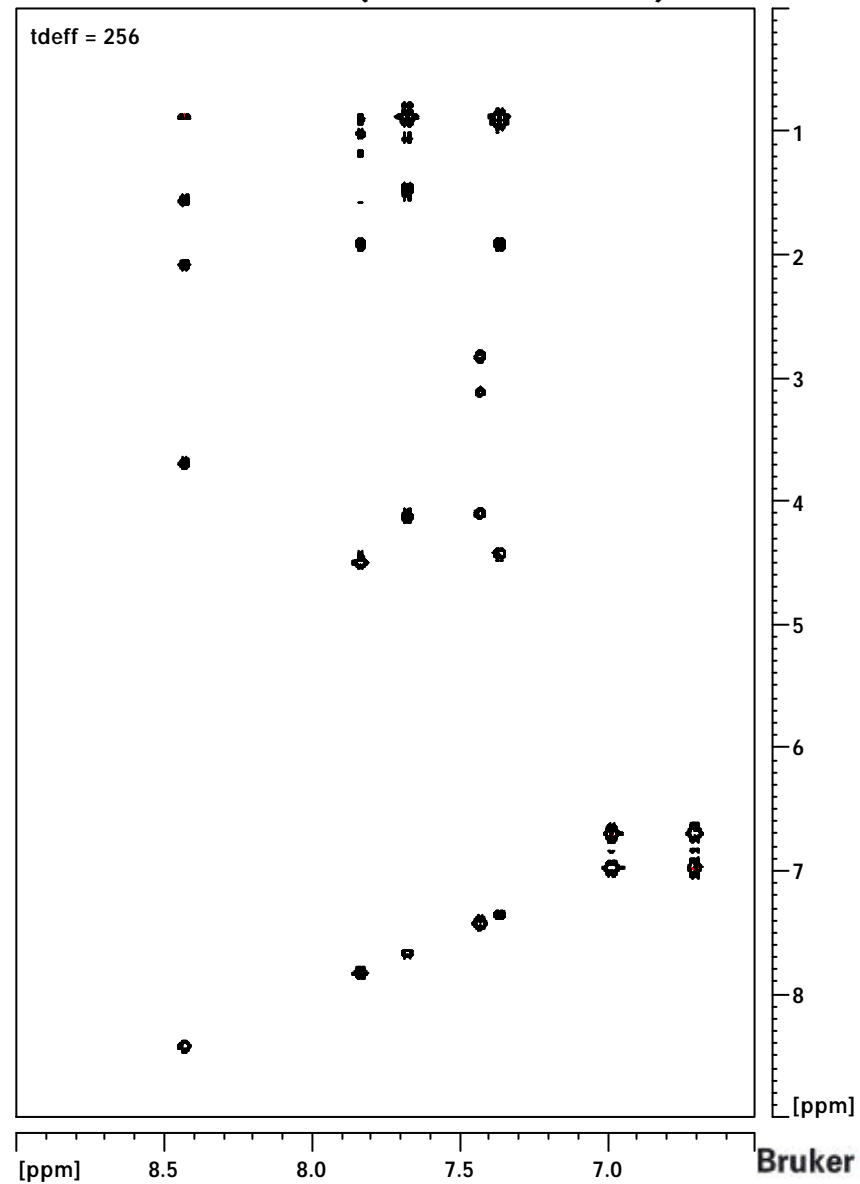
DIPS12

xfb



DIPS12

(xf2 + covariance) x 2D



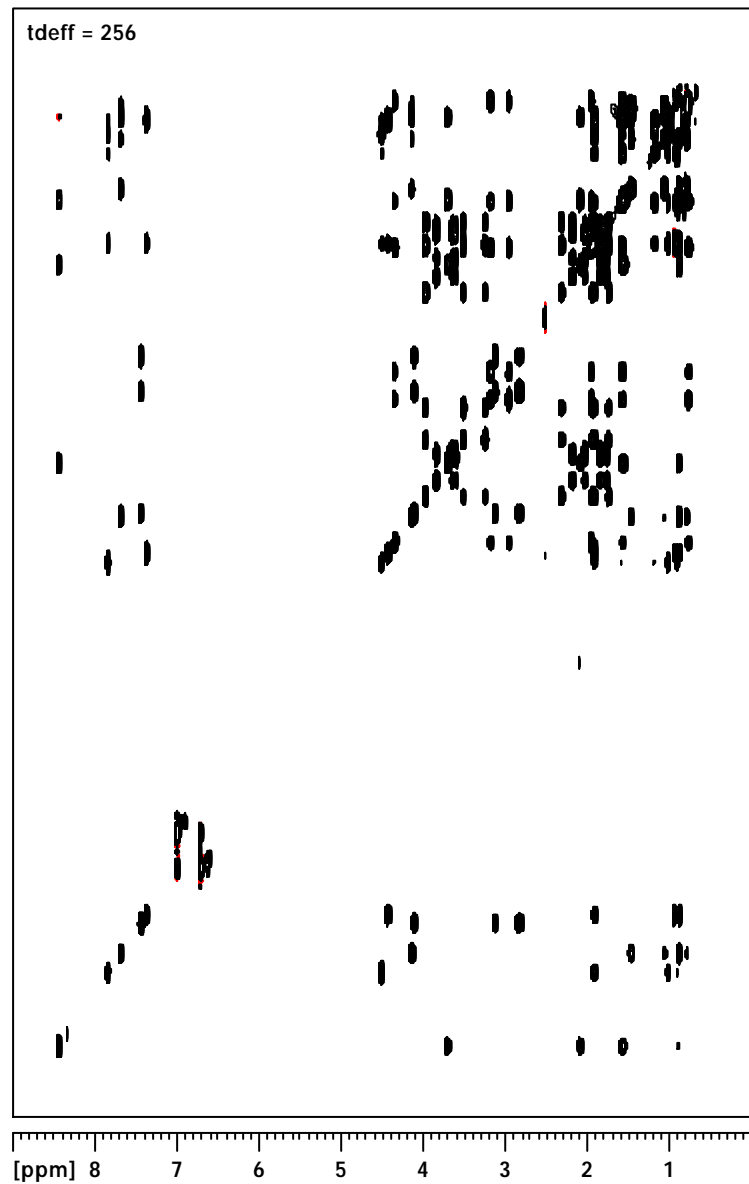
covariance NMR



20mM Hymenistatin

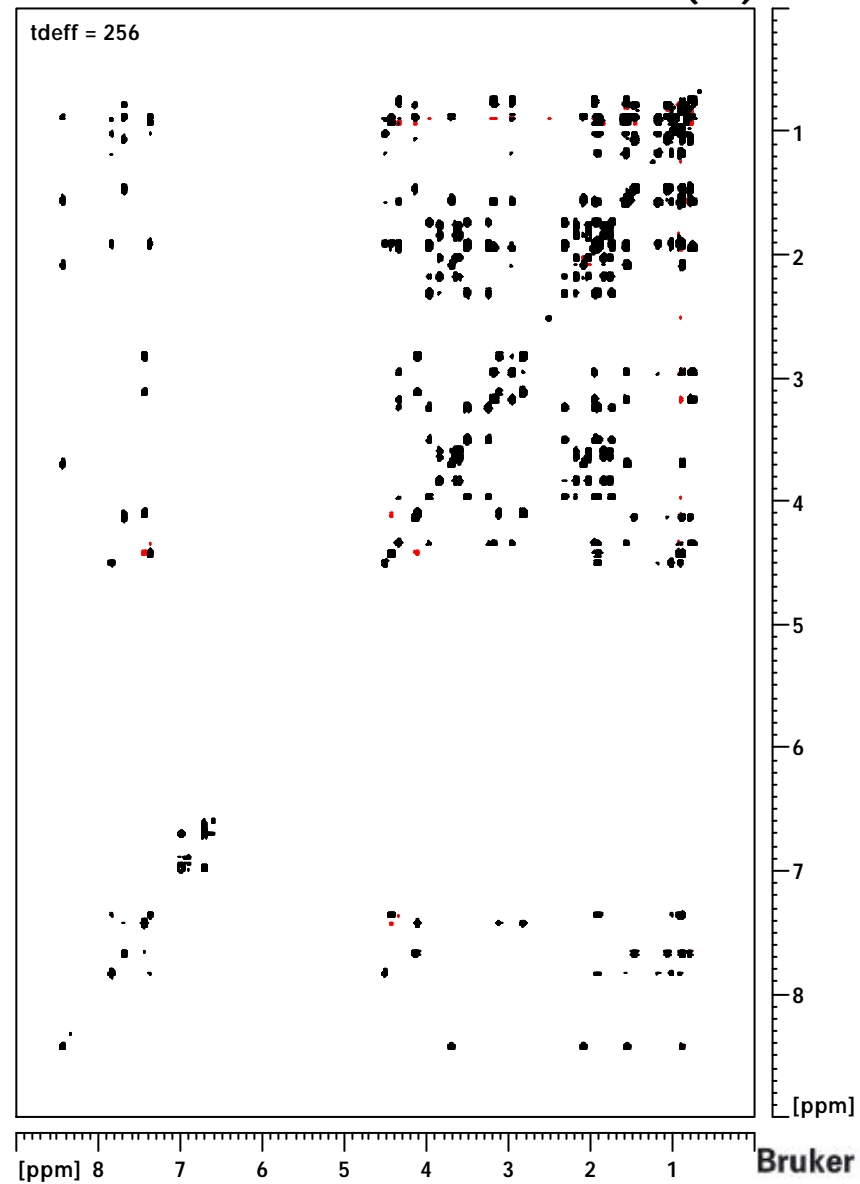
DIPS12

xfb



DIPS12

xf2 + covariance ($\ddot{O}C$)



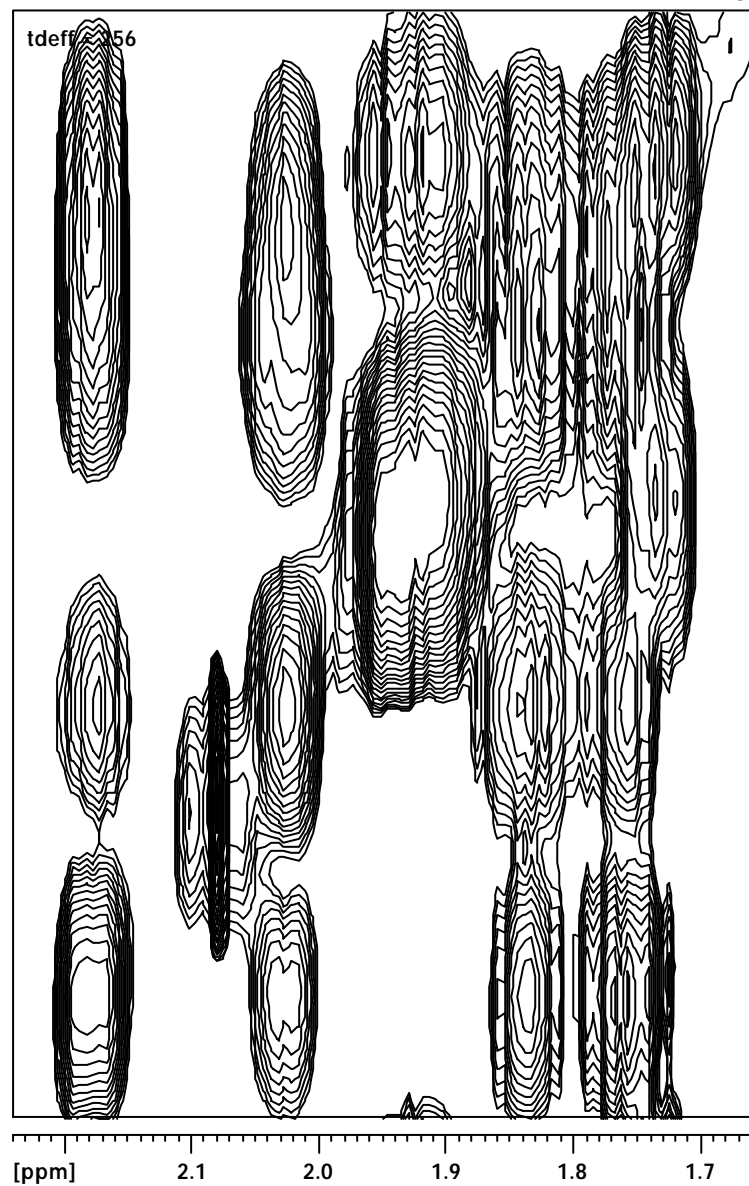
covariance NMR



20mM Hymenistatin

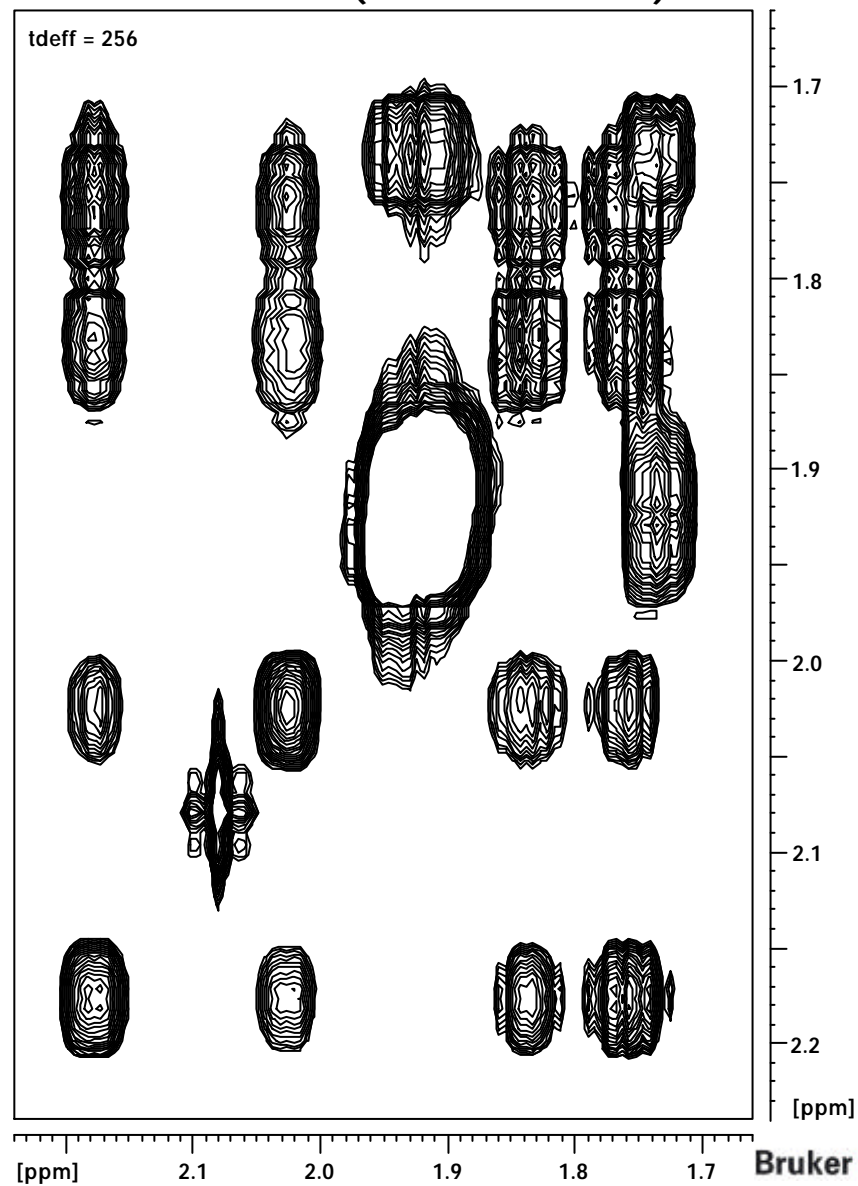
DIPSI2

xfb



DIPSI2

(xf2 + covariance) x 2D



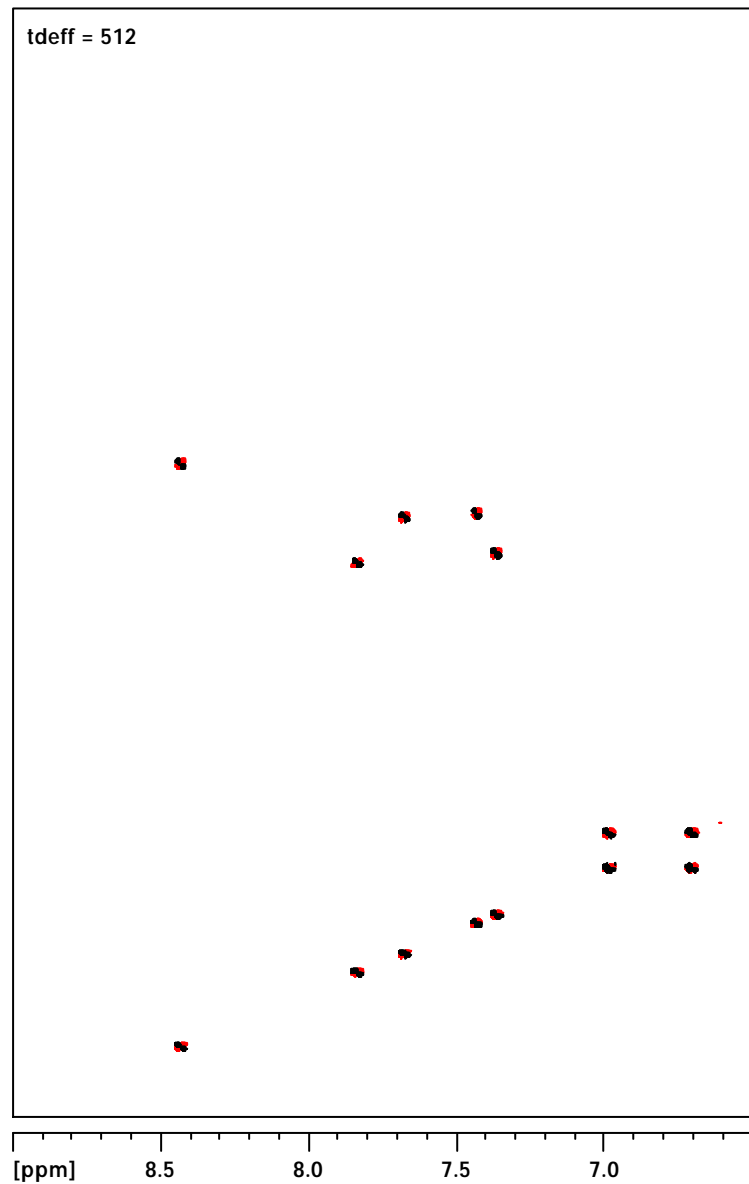
covariance NMR



20mM Hymenistatin

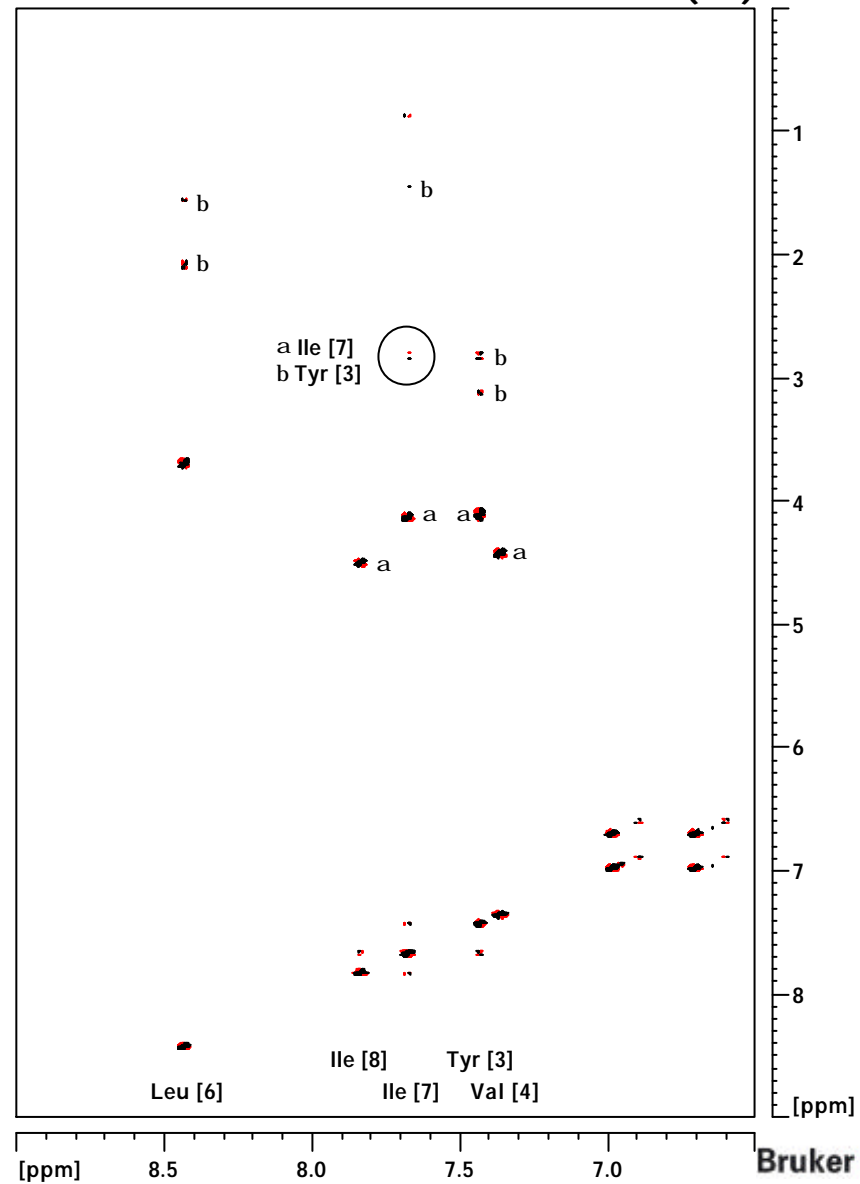
DQF COSY

xfb



DQF COSY

xf2 + covariance (°C)



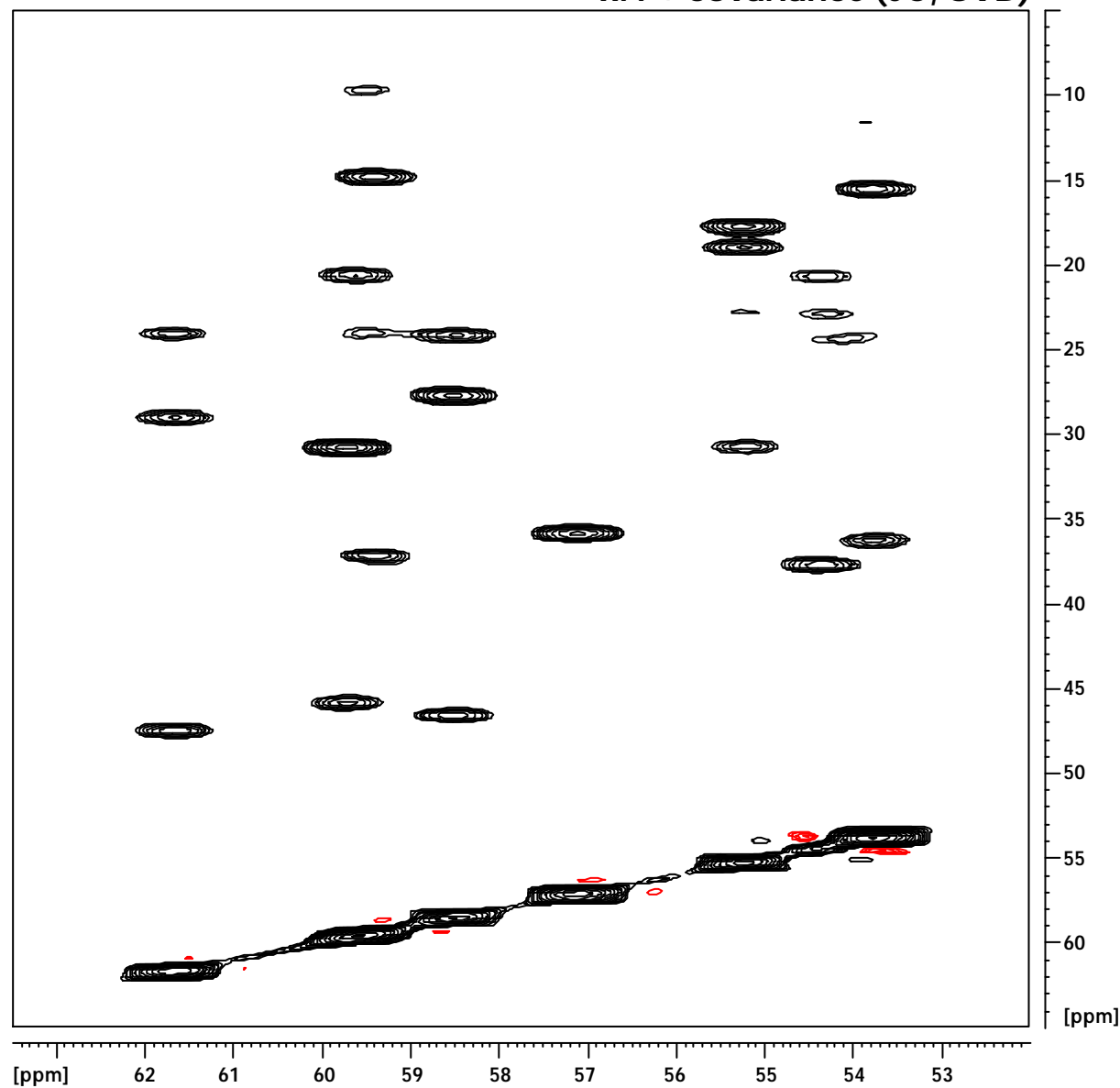
covariance NMR



20mM Hymenistatin

HSQC-TOCSY

xf1 + covariance ($^1\text{O}C$, SVD)



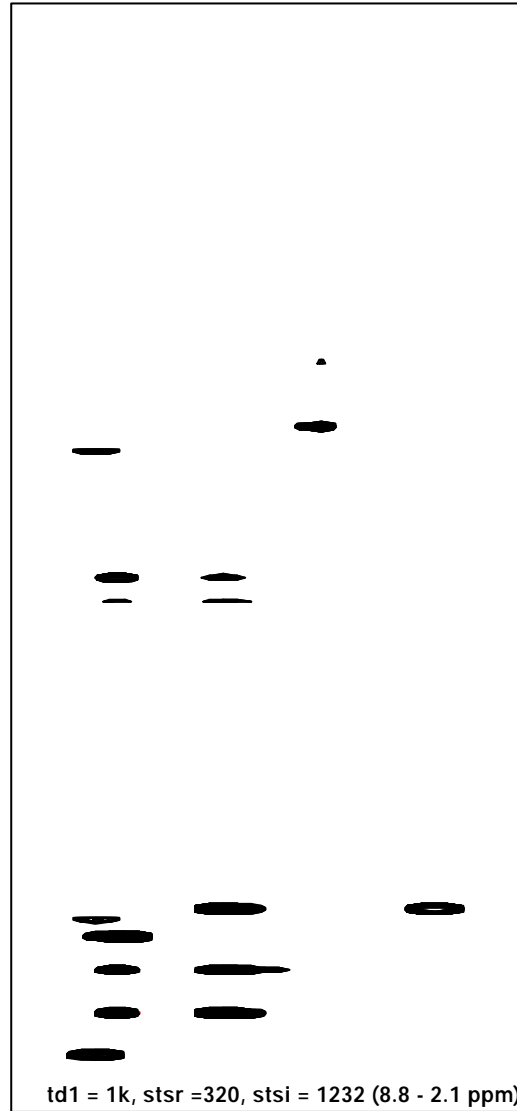
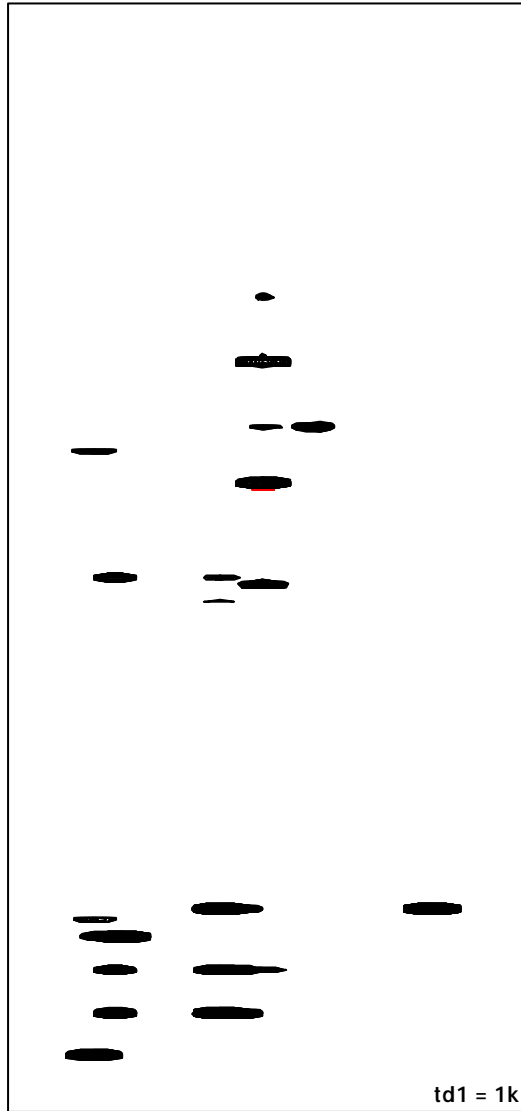
covariance NMR



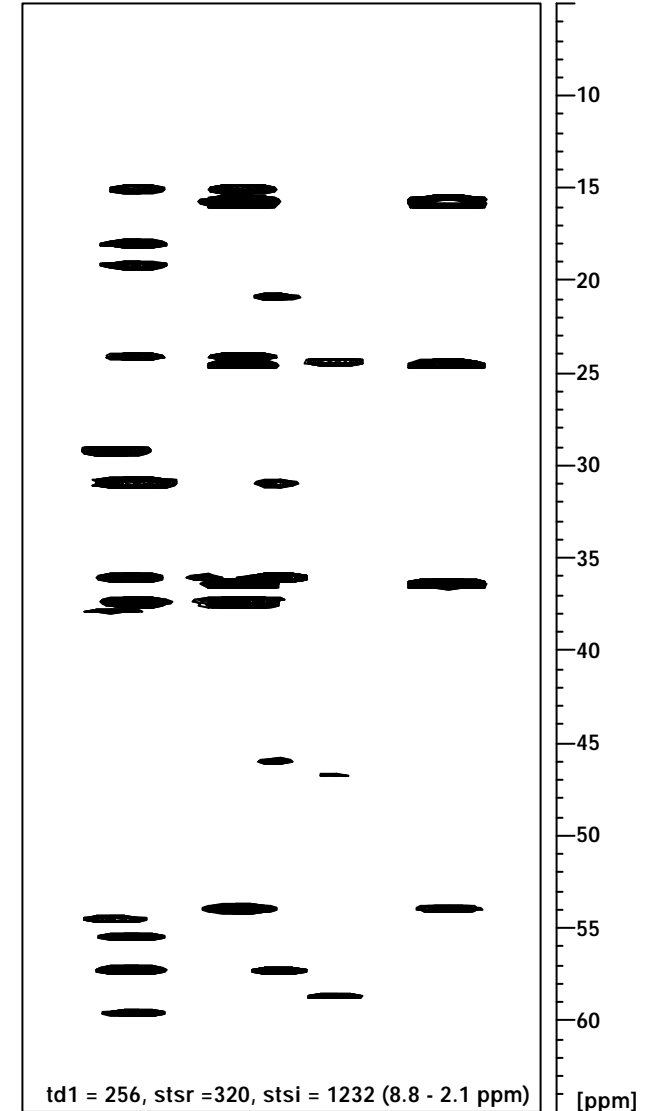
covariance in F2 (freq/freq, k=7)

20mM Hymenistatin

HMBC/HSQC



HMBC



[ppm] 171 170 169

[ppm] 171 170 169

[ppm] 171 170 169

Bruker BioSpin

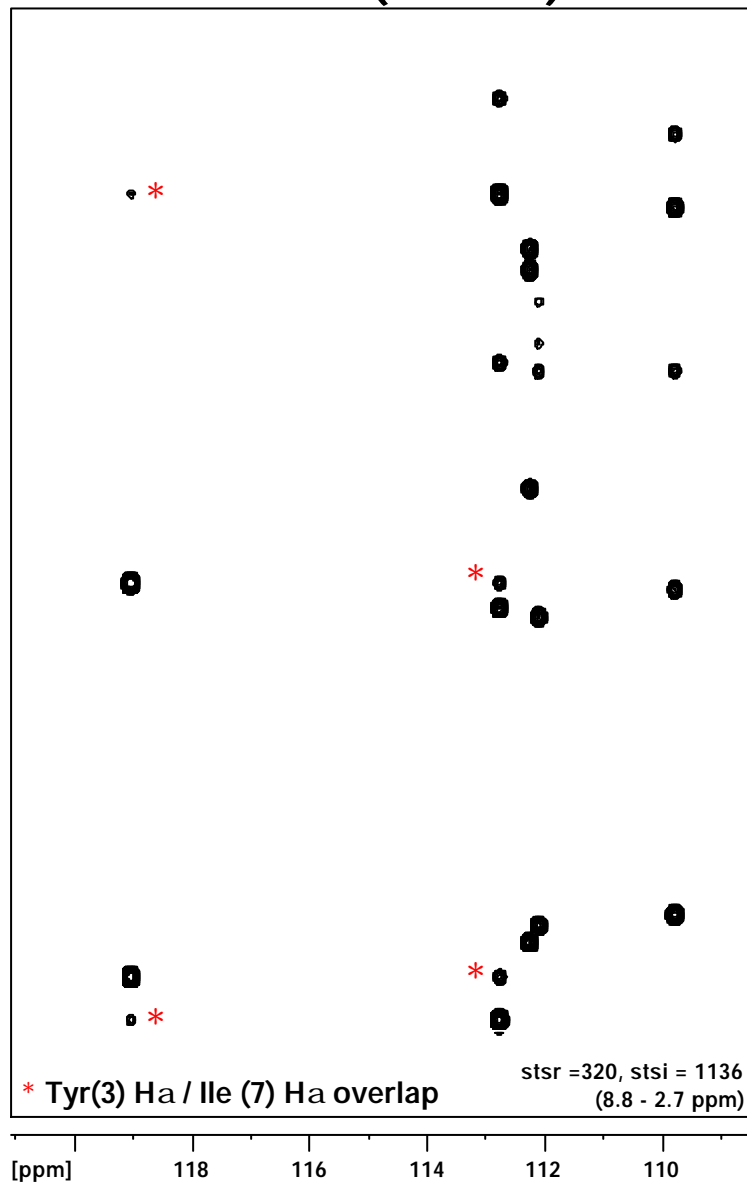
covariance NMR



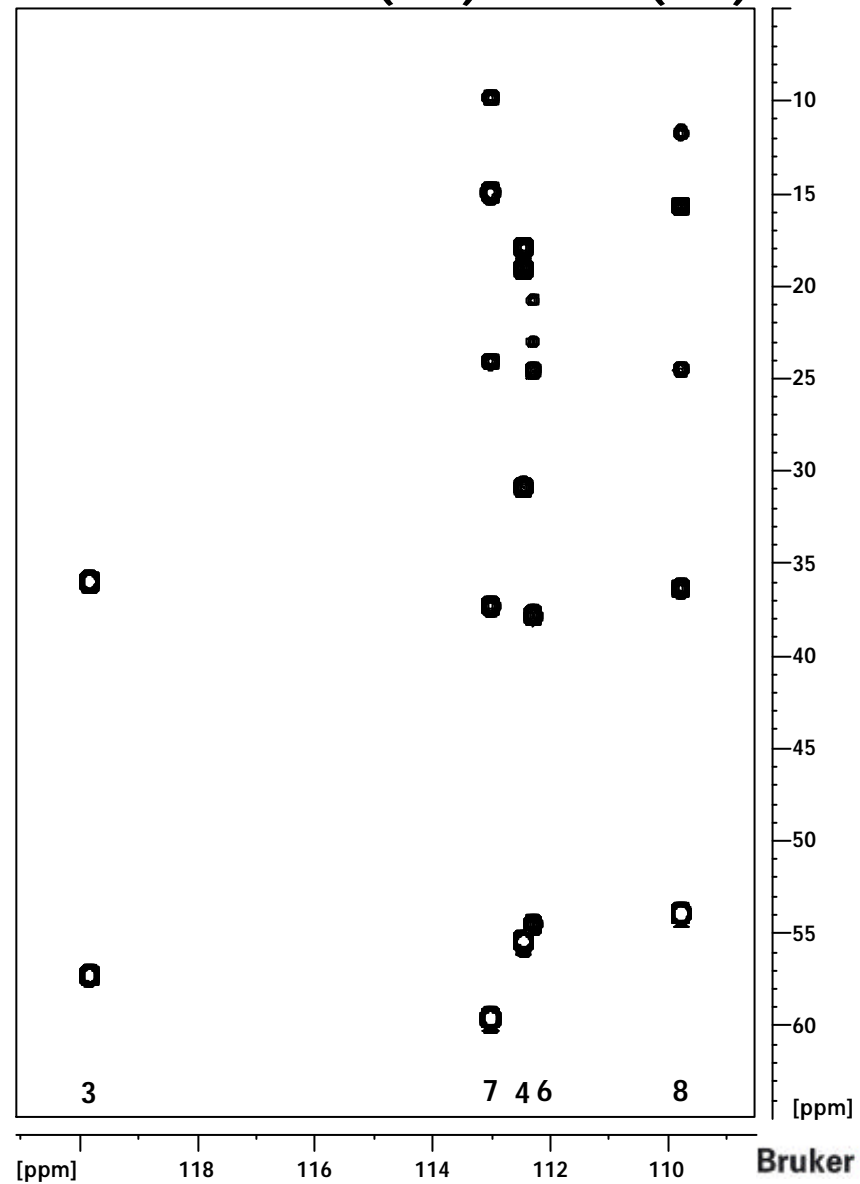
covariance in F2 (freq/freq, k=5)

20mM Hymenistatin

HSQC-TOCSY ($^{13}\text{C}/^{15}\text{N}$)



HSQC-TOCSY (^{13}C)/HSQC(^{15}N)





Ultrafast 2D

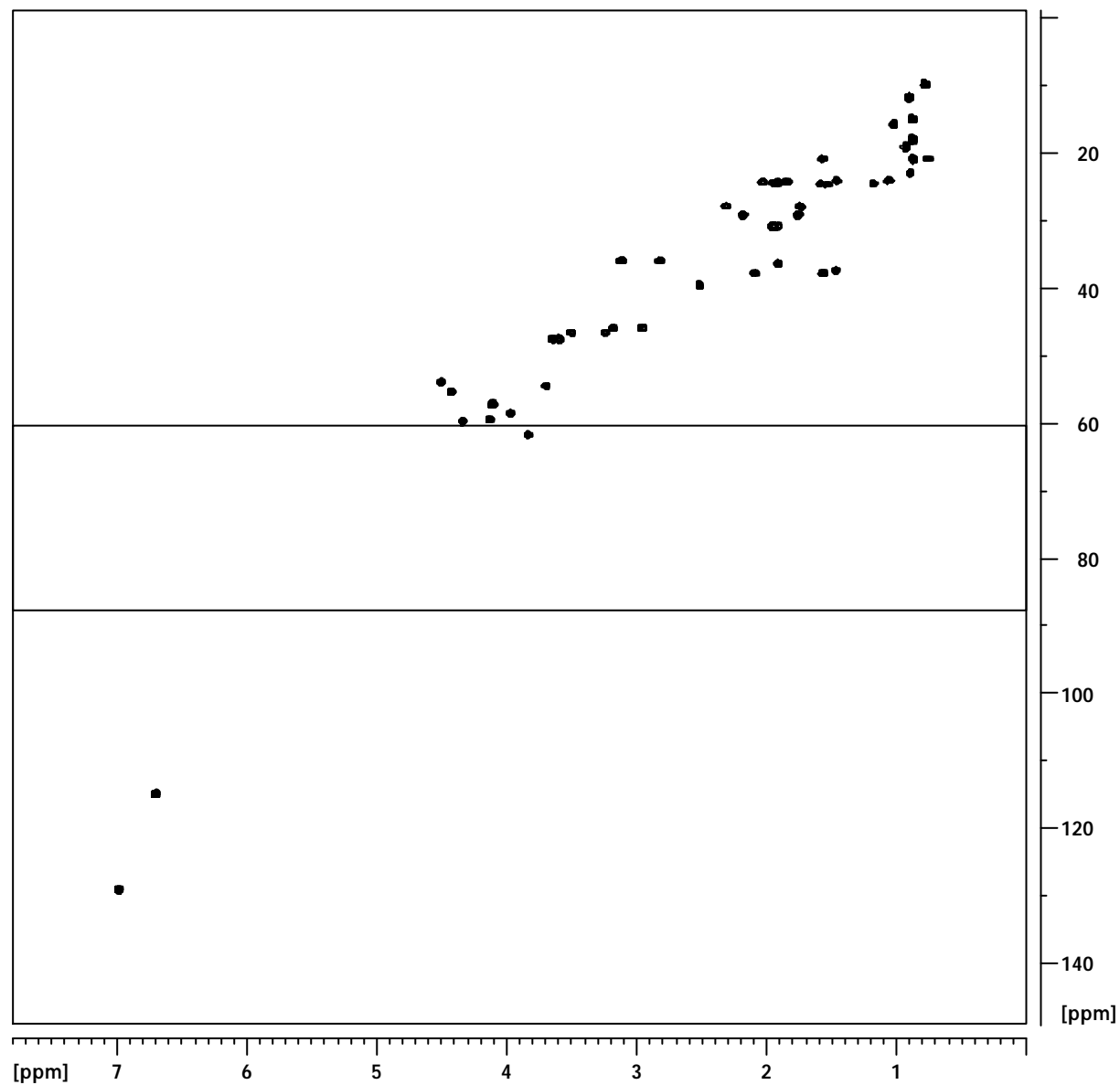
Folding

Folding

HSQC



Hymenistatin

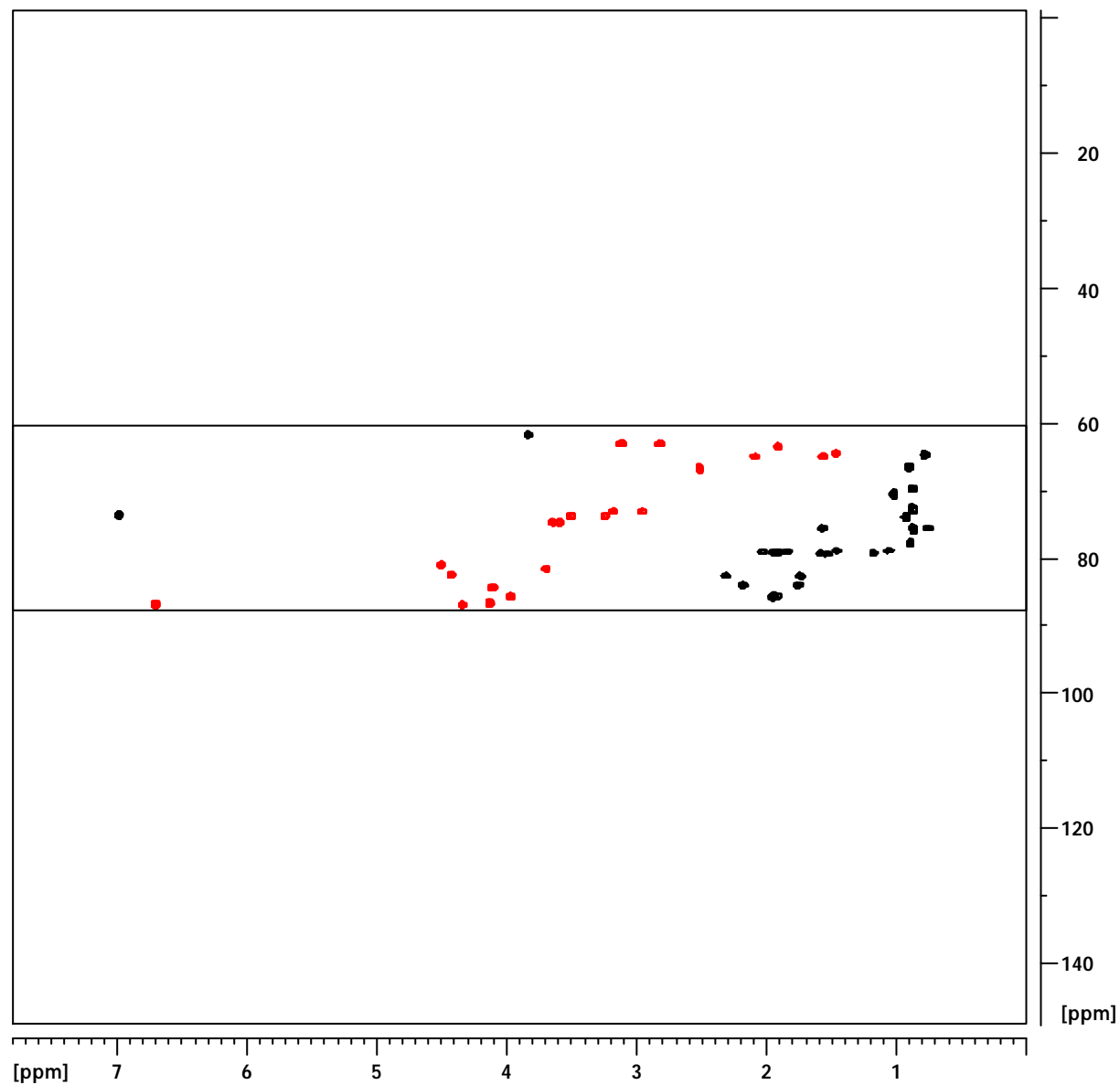


Folding

HSQC



Hymenistatin

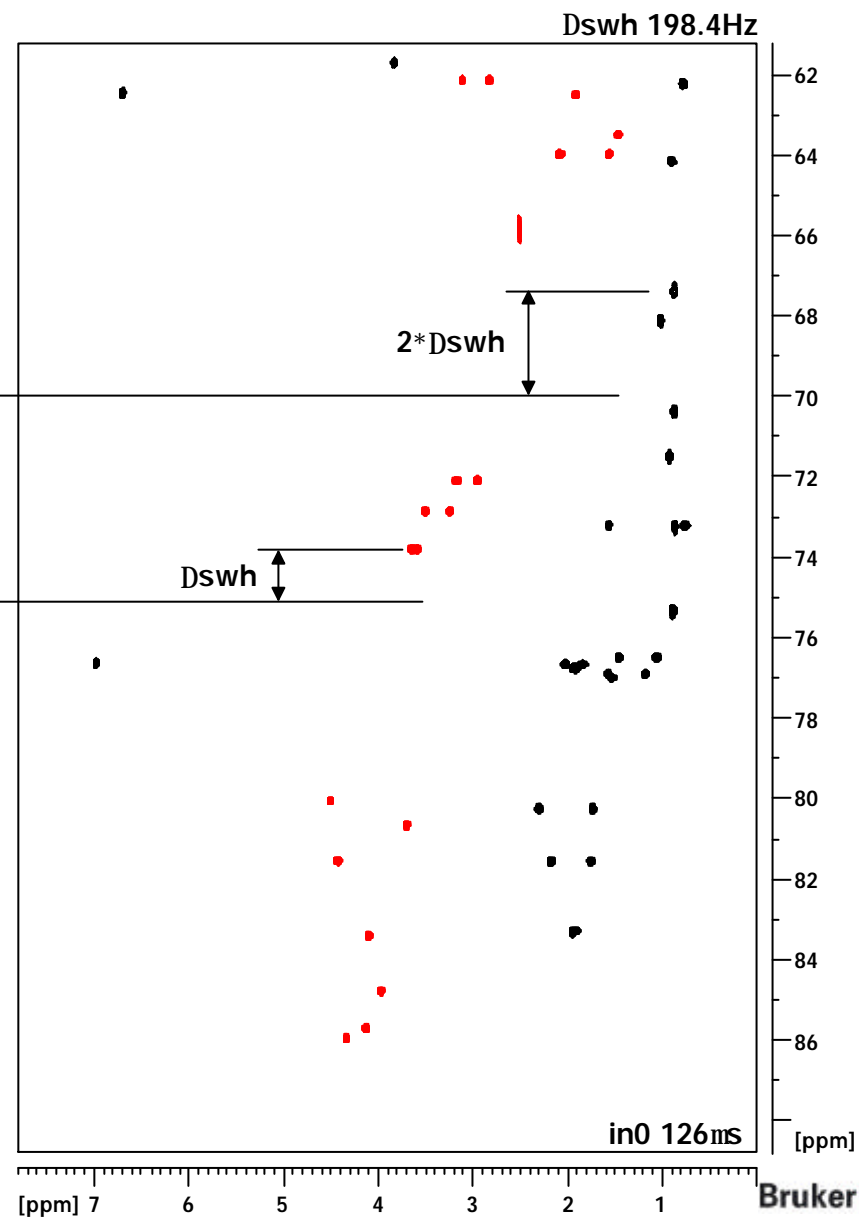
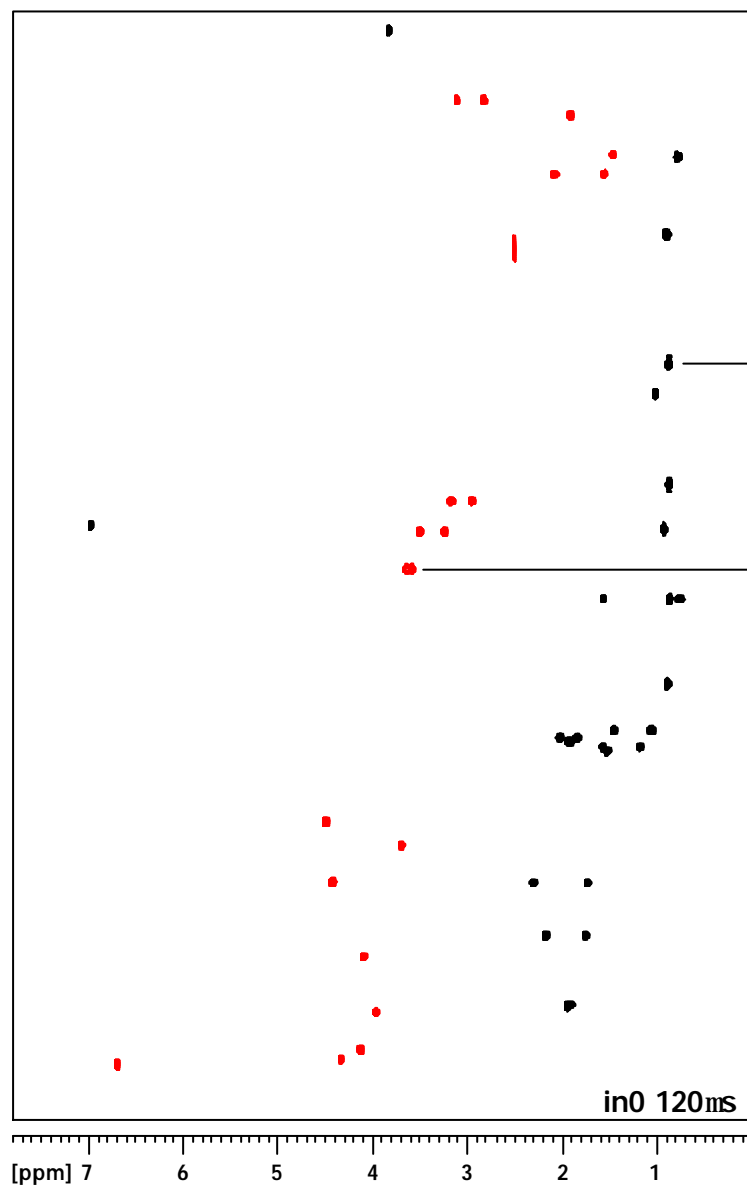


Folding



Hymenistatin

HSQC



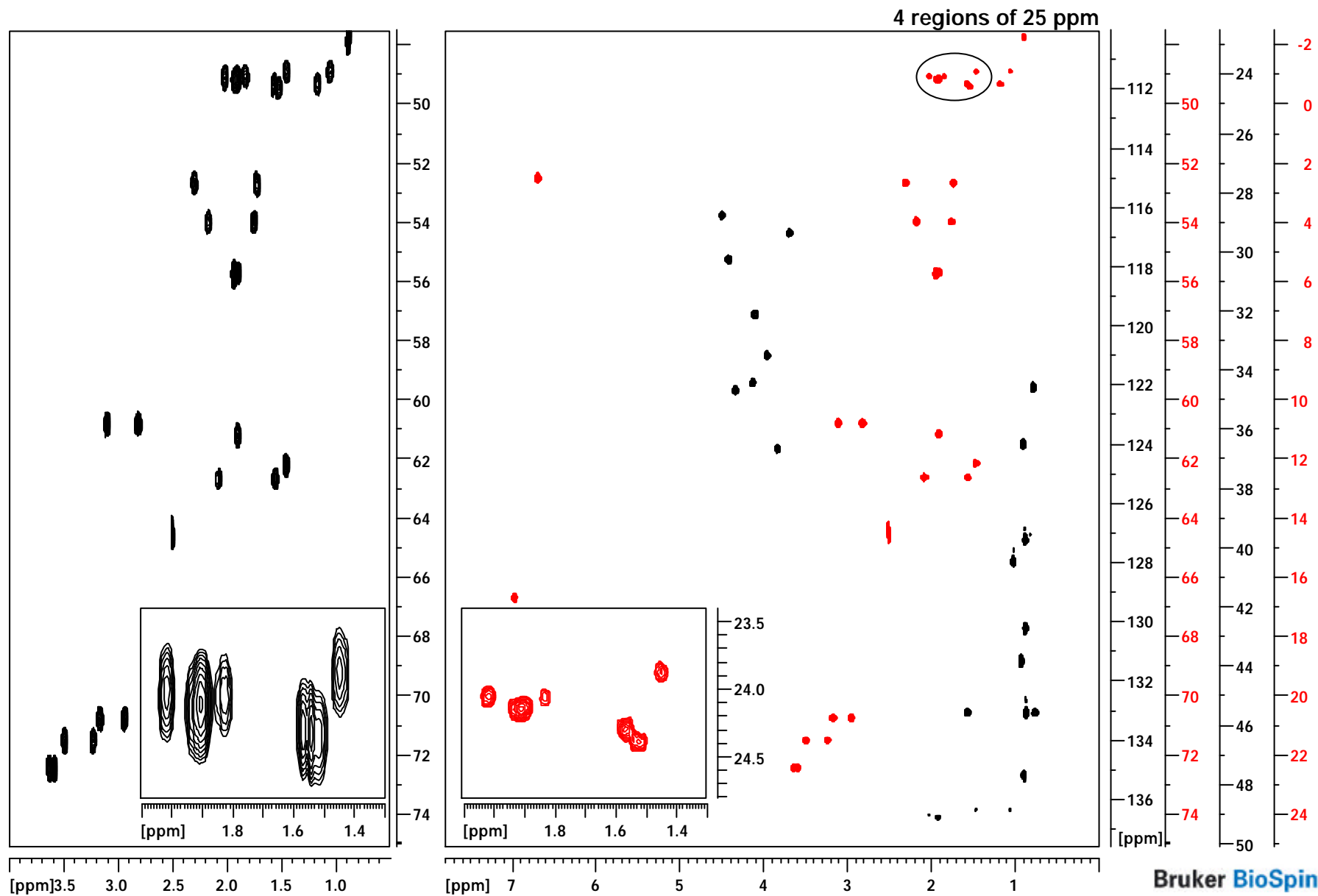


SHARC NMR

Sharc HSQC



Hymenistatin

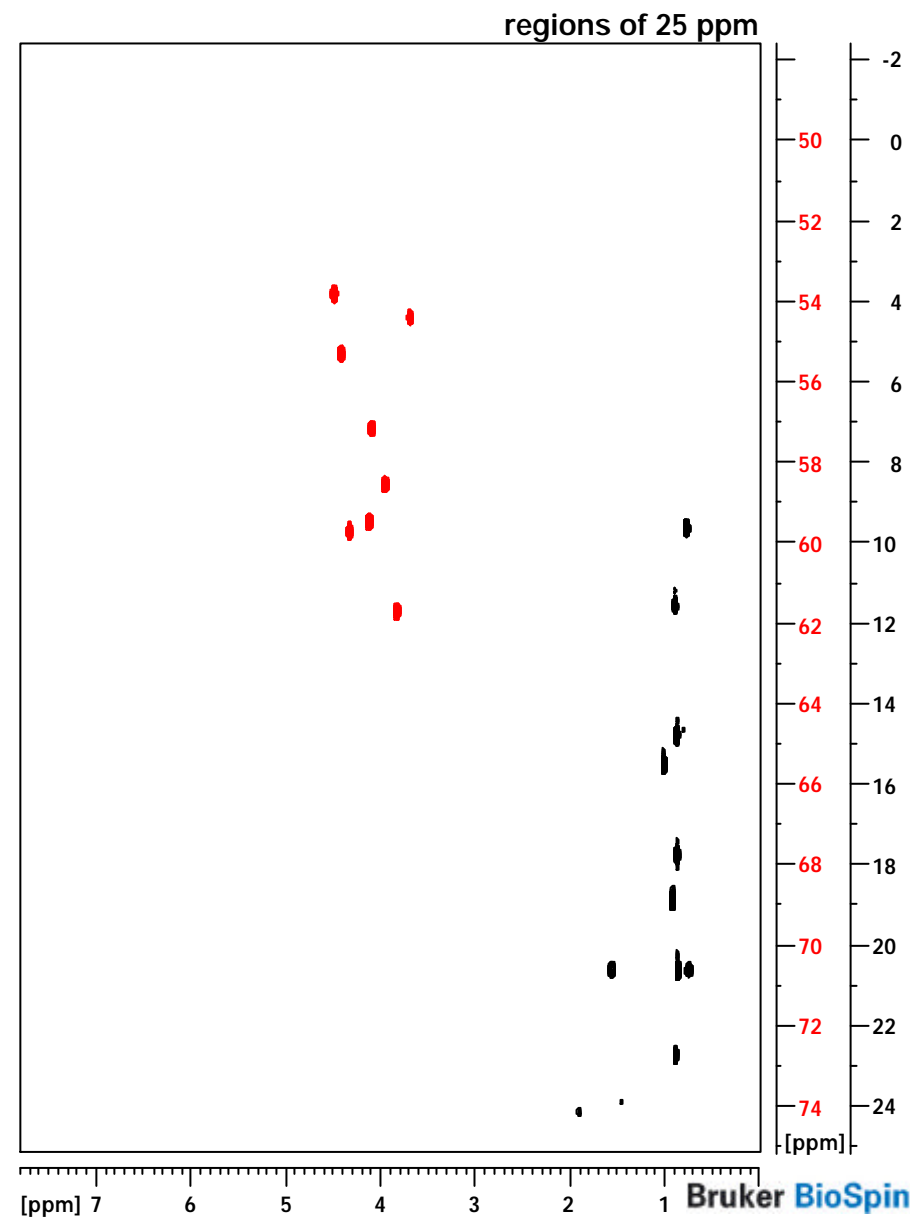
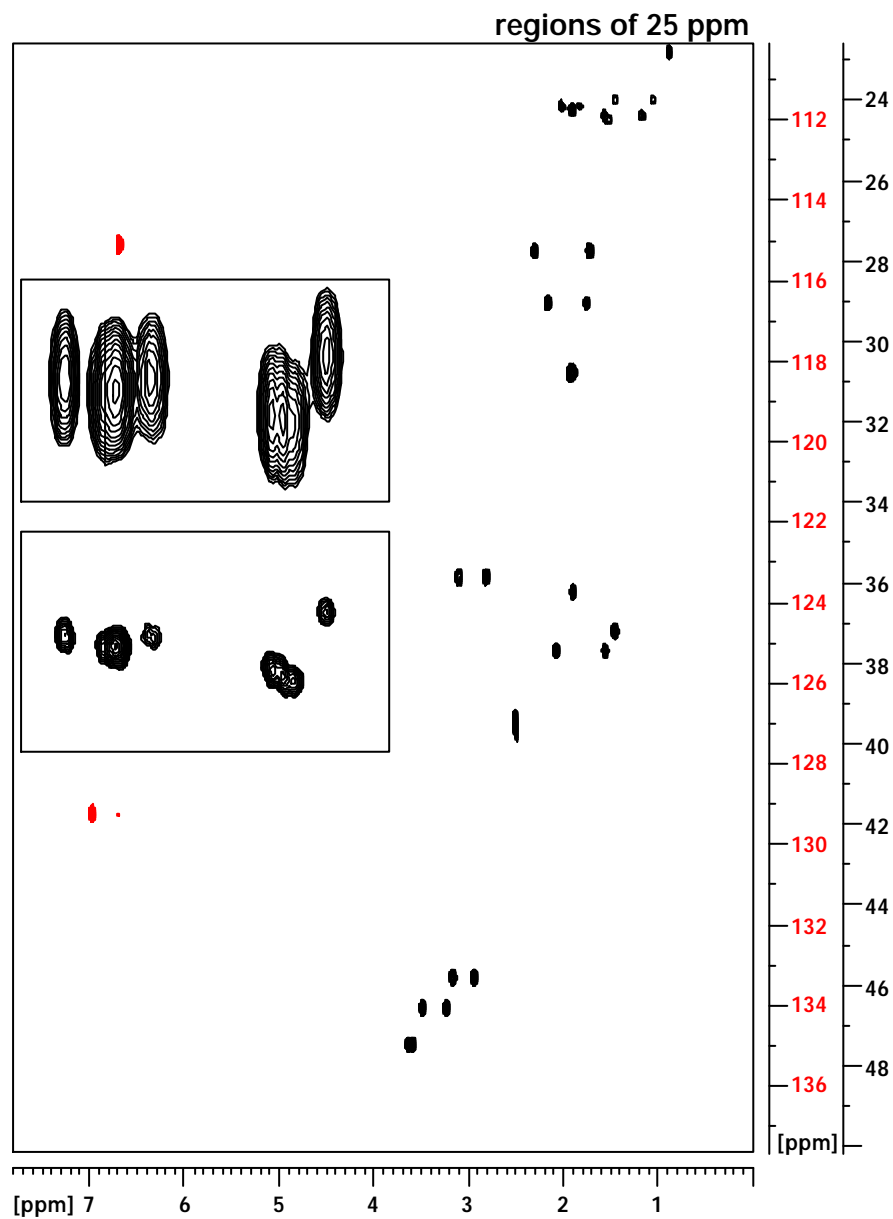


Sharc



HSQC : separated

Hymenistatin

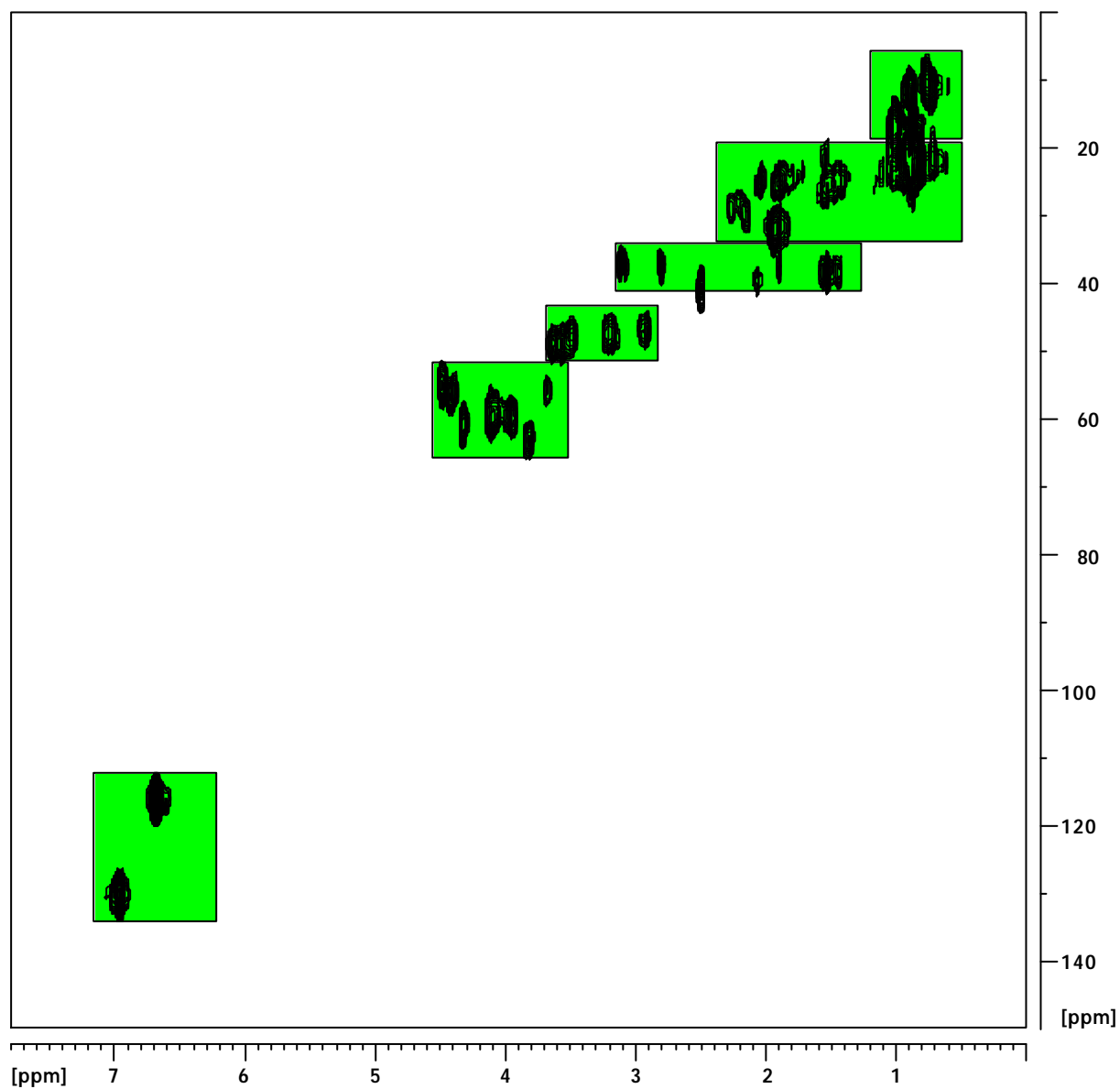


Sharc

HMQC



Hymenistatin



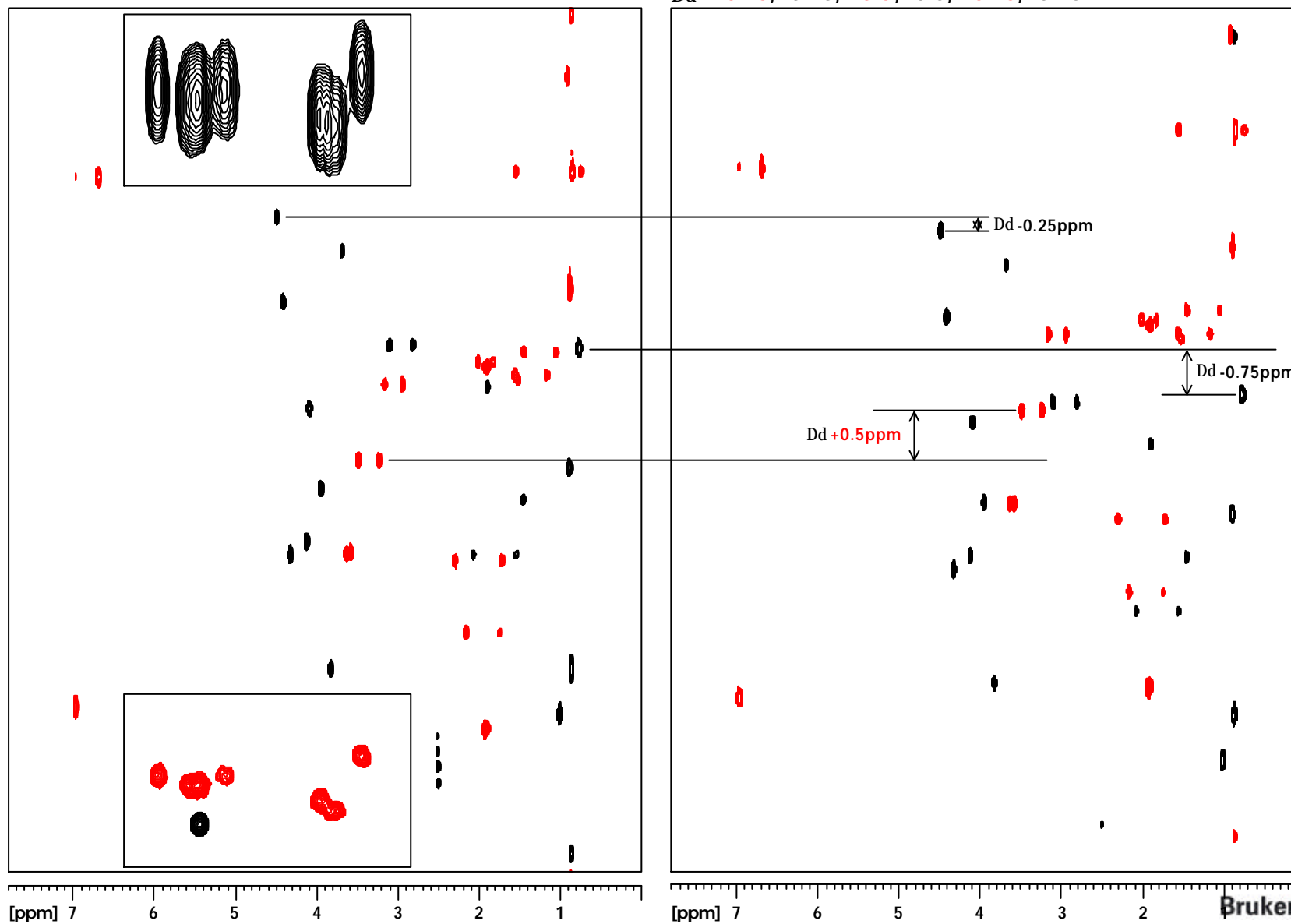
Sharc



Hymenistatin

HSQC 6 regions of different width

Dd: +0.25, -0.25, +0.5, -0.5, +0.75, -0.75





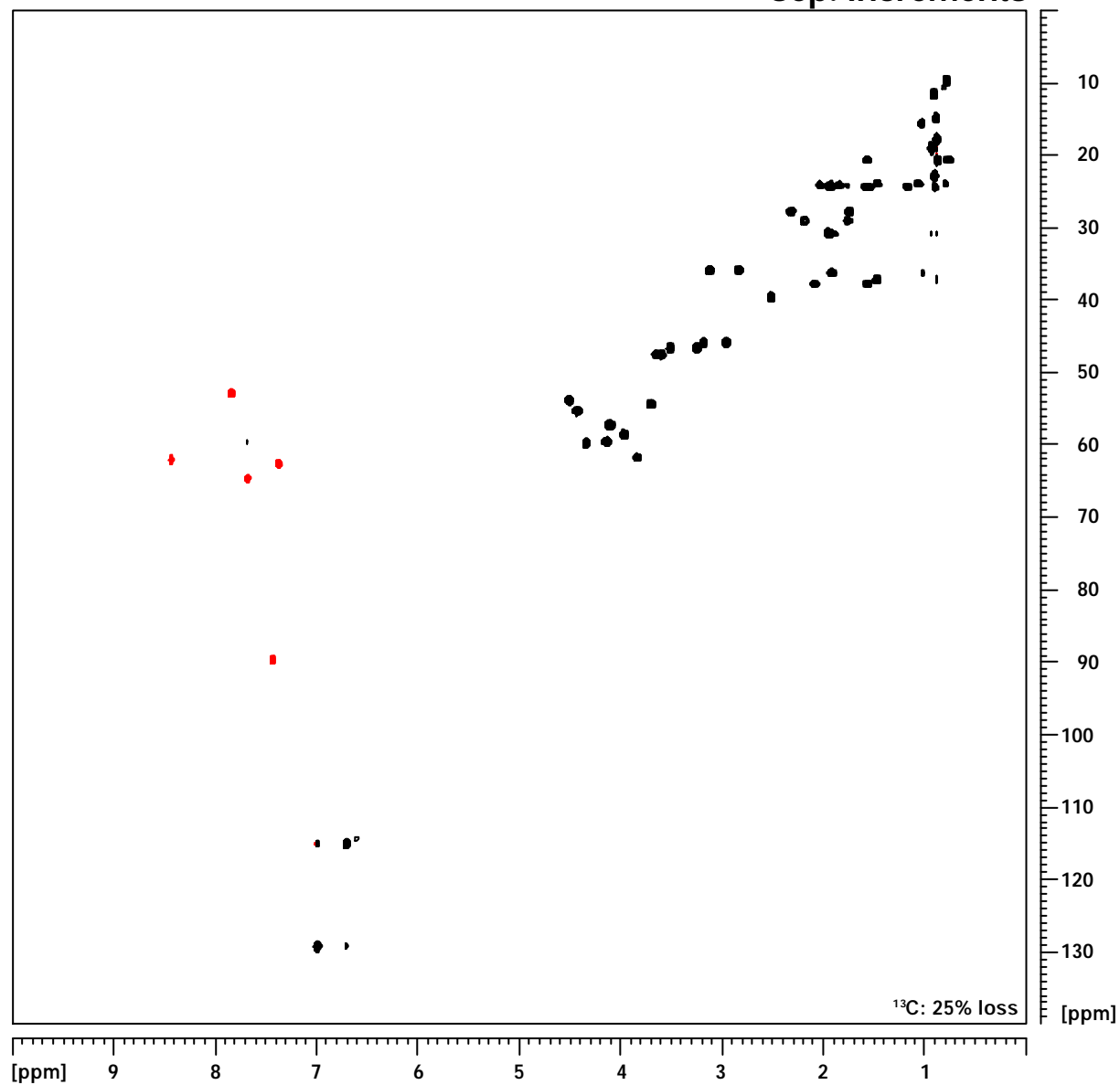
simultaneous data acquisition

Hymenistatin



sm. si-HSQC

sep. increments



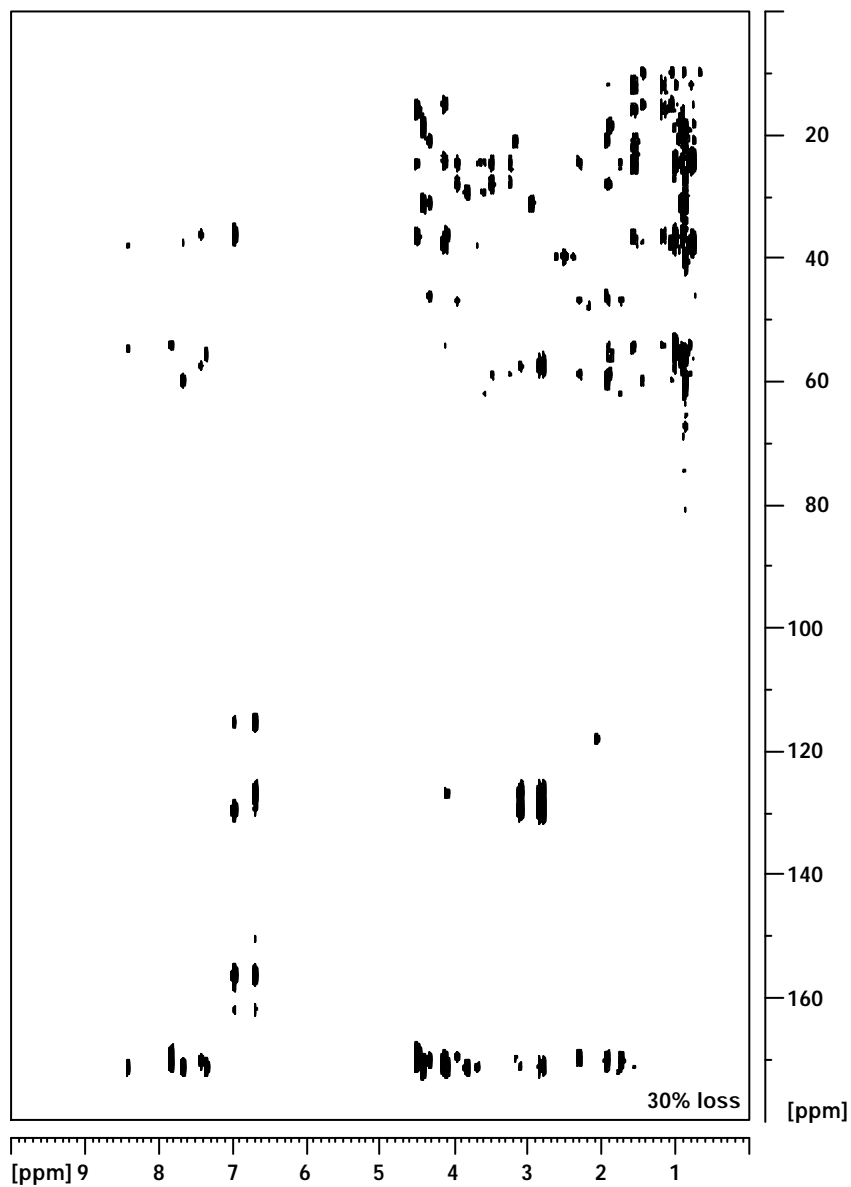
SW(C) 22727 Hz
SW(N) 2500 Hz

Bruker BioSpin

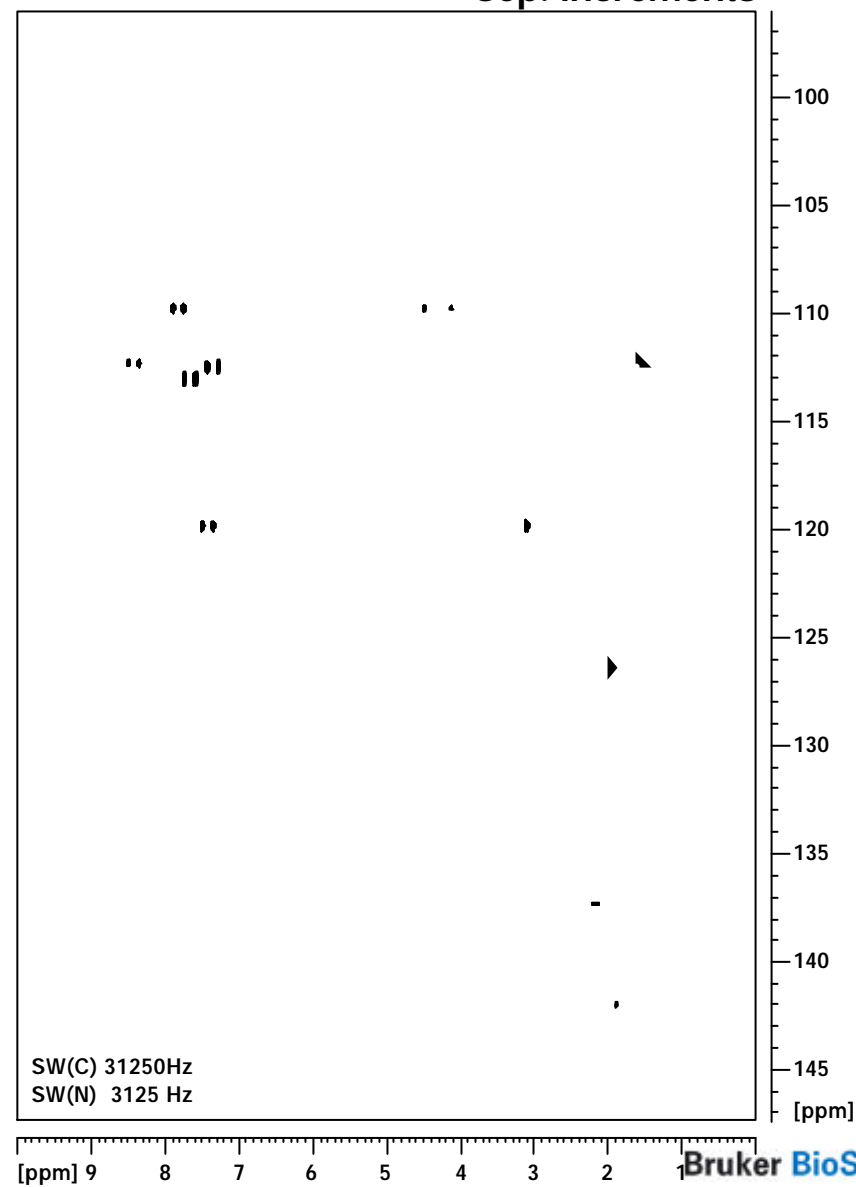
Hymenistatin



sm. HMBC - separated



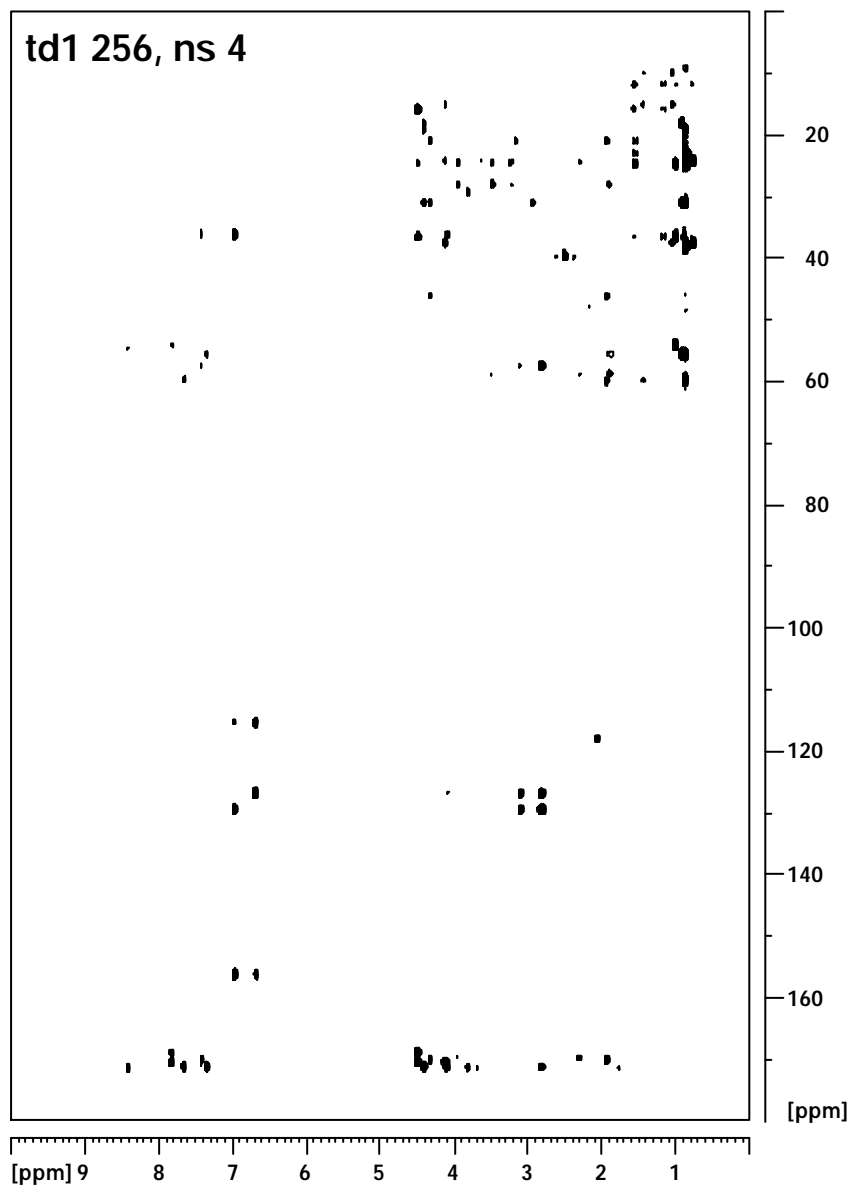
sep. increments



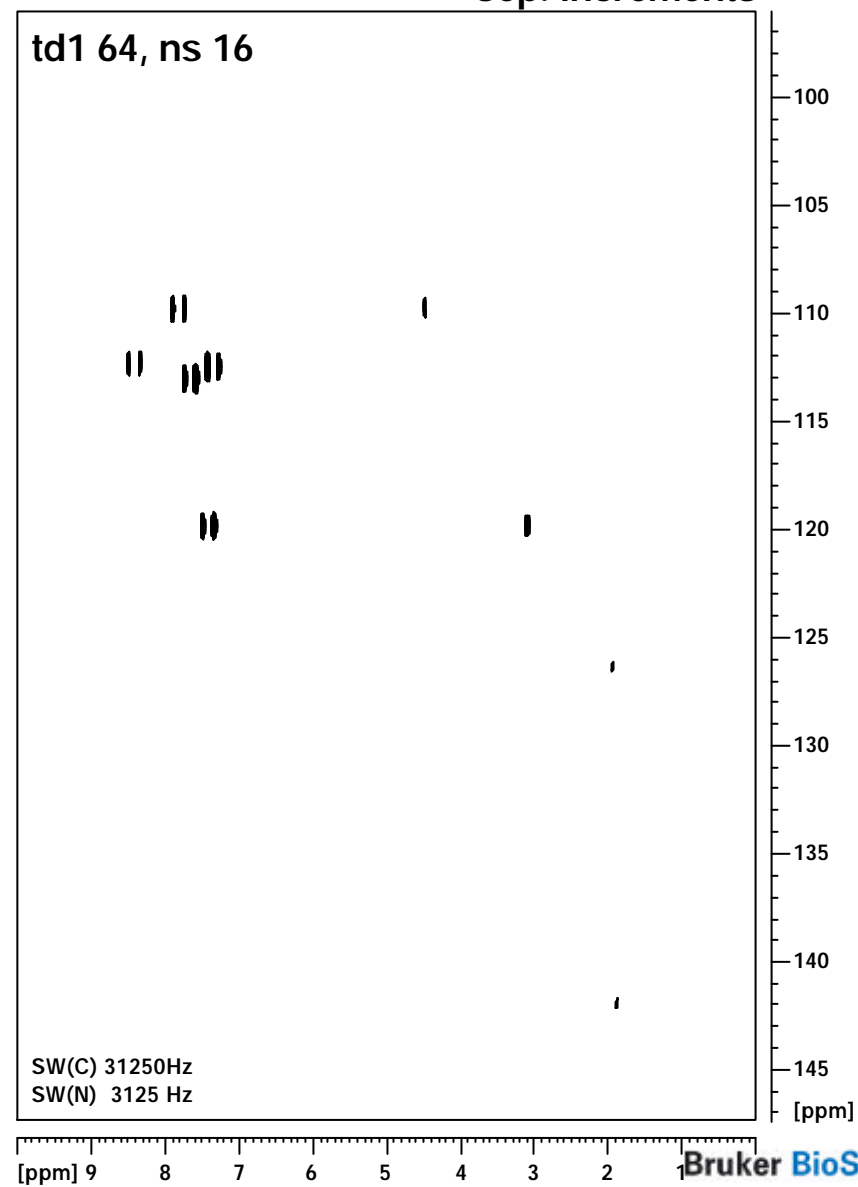
Hymenistatin



sm. HMBC - separated



sep. increments



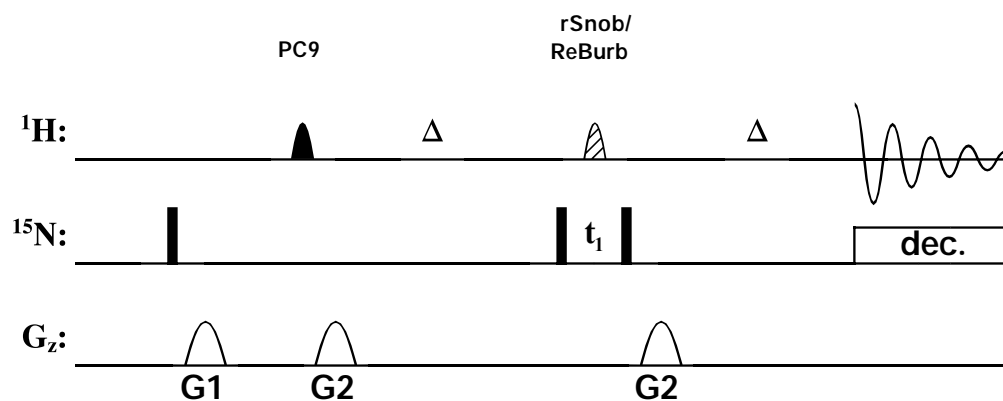


Rapid Pulsing

Rapid Pulsing

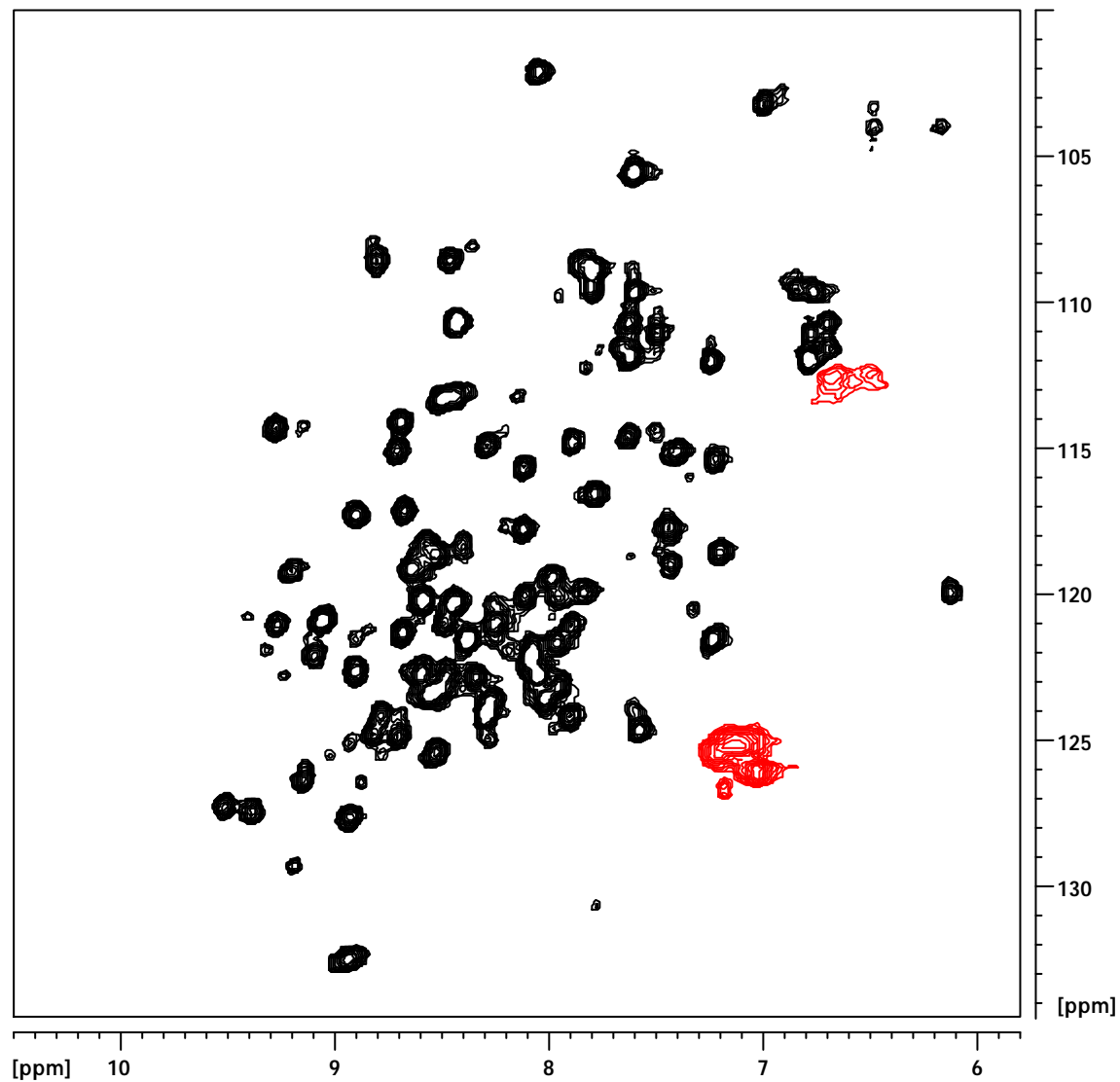


SoFast HMQC



Rapid Pulsing

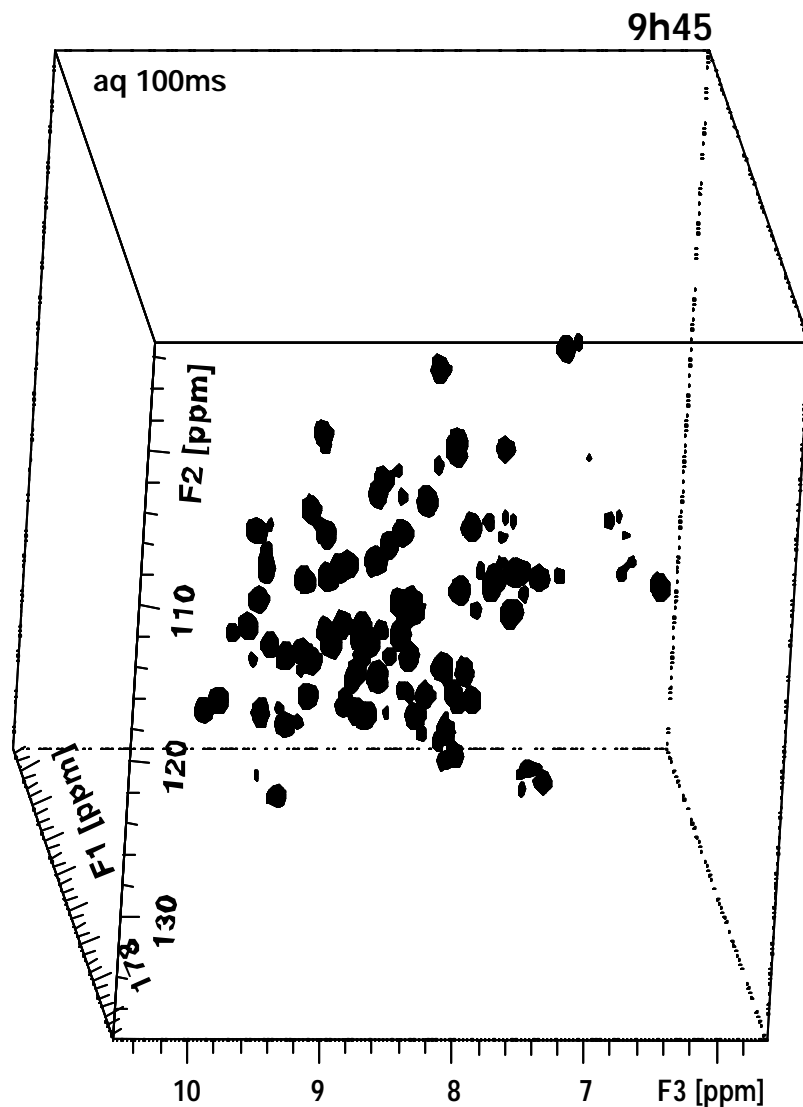
^{15}N SoFast HMQC



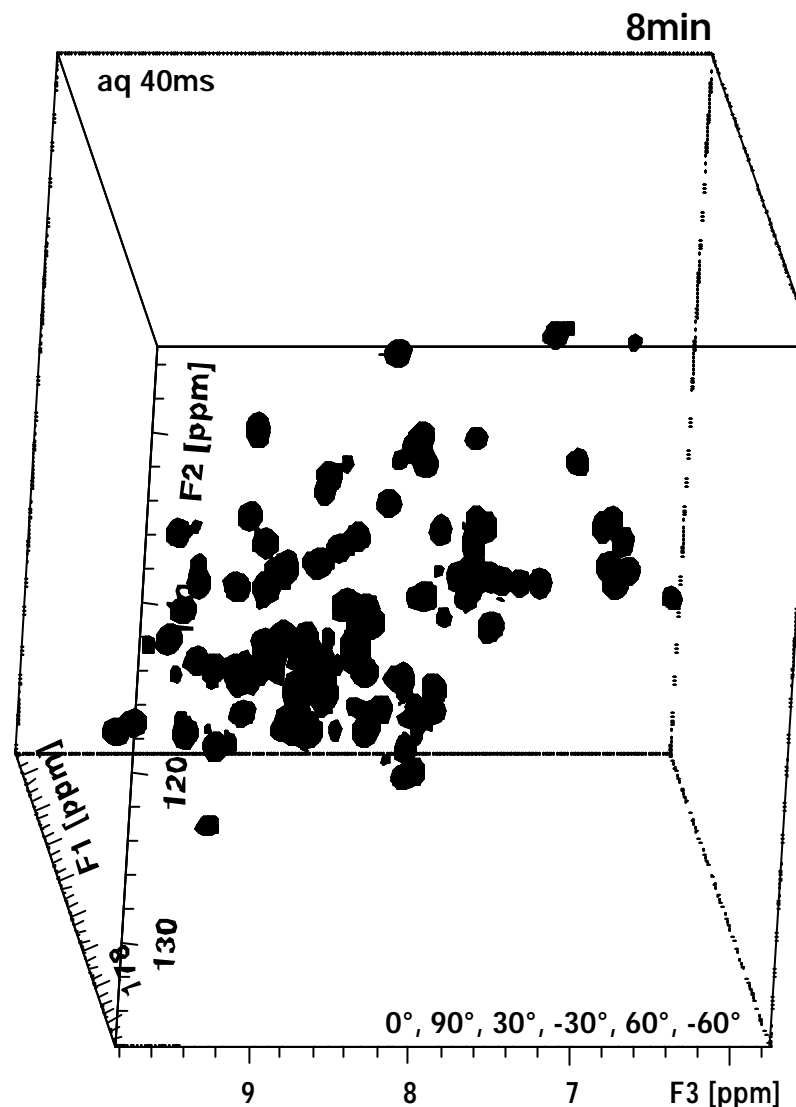
d1	10 ms
aq	40 ms
td1	256
ns	2
expt	57 s

Projection Reconstruction

3D HNCO



PR best-HNCO





Werner Maußhardt

Covariance

**Rafael Brüsweiler
Hartmut Schäfer (SVD)**

SHARC NMR

Peyman Sakhaii

**Sim. Data Acquisition
Teo Parella**



**Thank
You**