OPTIMIZATION AND PRACTICAL IMPLEMENTATION OF ULTRAFAST 2D NMR EXPERIMENTS

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Figure 1S. (a) Graphical representation of continuous spatial encoding, in which a chirp pulse is applied concomitantly to a gradient pulse ($G_e$) along $z$ axis. (b) The scheme proposed by Pelupessy comprises the application of a 90º hard pulse followed by two π chirp pulses applied together with a bipolar pair of gradients.

Figure 2S. (a) Representation of the ultrafast dimension acquisition by the application of a gradient pulse, in order to remove the dephasing created during the spatial encoding step. As result, the echo peaks are formed as the dephasing is being refocused. (b) Representation of the conventional dimension acquisition by the use of a bipolar pair of gradient pulses, which results in the monitoring of conventional parameters evolution as a series of sub-spectra are being collected.

Figure 3S. Image of the excitation profile obtained from the pulse sequence in Figure 1 (with the extra block) and after phase correction, allowing for the chirp pulse power calibration before performing ultrafast experiments. The acquisition and processing parameters are the same mentioned for the Figure 2b, unless the chirp pulse power that was 0.32 W.

Figure 4S. Ultrafast COSY pulse sequence based on the constant-time spatial encoding scheme proposed by Pelupessy. To perform this experiment, the coherence selection gradients strength was 45 G/cm during 1000 µs, and the purge gradient strength was -10 G/cm with 400 µs of duration. The acquisition times for direct and indirect dimensions were 65.59 and 0.12 ms, respectively. For the acquisition 35 and -35.008 G/cm (to compensate for shearing effects) gradients were applied for 236 µs each, with a gradient rise time of 20 µs (recovery delay in pulse sequence).

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Figure 5S. Ultrafast HSQC pulse sequence based on the constant-time spatial encoding scheme proposed by Pelupessy. An asymmetric phase cycle ($x,-x,x,x$) was used within each single shot acquisition on the decoupling pulse to avoid the formation of decoupling artifacts. It was also used a real phase cycle ($x,-x$), requiring several scans, on the last $13^C$ 90° pulse and the receiver. To perform this experiment, identical chirp pulses than those for UF-COSY were used, but applied in the presence of ± 20 G/cm encoding gradients to account for the larger $13^C$ frequency range. The acquisition times for direct and indirect dimensions were 65.59 and 0.02 ms, respectively. Acquisition gradients were identical to those employed for UF-COSY. The INEPT delay was set to 1.72 ms. Eight scans were recorded for sensitivity and phase-cycling purposes.

PULSE SEQUENCE FOR UF-COSY

```
;ufcosy
;avance-version

;CLASS=HighRes
;DIM=1D
;TYPE=
;SUBTYPE=
;COMMENT=
#include <Avance.incl>
#include <Grad.incl>
#include <De.incl>
1 ze
100u UNBLKGRAD
2 d1 p1:f1
  p1 ph1
  10u gron0
  p11:sp1:f1 ph2
  10u groff
  10u gron1
  p11:sp1:f1 ph4
  10u groff
  10u p11:f1
  10u p23:gp23
  10u
  p1 ph1
  10u
  p26:gp26
  10u gron25
  10u groff
  10u ACQ_START(ph30,ph31)
  1u DWELL_GEN:f1
  3 d20 gron2
  \rightarrow 90° pulse
  \rightarrow spatial encoding block
  \rightarrow 180° pulse
  \rightarrow coherence selection gradient
  \rightarrow mixing period
  \rightarrow coherence selection gradient
  \rightarrow purge gradient
  \rightarrow starting acquisition
  \rightarrow positive acquisition gradient
```

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**PULSE SEQUENCE FOR UF-HSQC**

```
;ufhsqc
;avance-version

;CLASS=HighRes
;DIM=2D
;TYPE=
;SUBTYPE=
;COMMENT=
#include <Avance.incl>
#include <Grad.incl>
#include <De.incl>

"p2=p1*2"
"p4=p3*2"
"d4=1s/(const2*4)"
"d6=d4-d15"
"d10=p20"
"d11=p21"
"p15=(td*dw)/(2*l3)-2*d17-p4"
1 ze
100u UNBLKGRAD
2 30m p2:f2
  d1 p1:f1
  p1 ph0
  d4
  (center (p2 ph1) (p4 ph4):f2 )
  d4
  p1 ph2
  (p3 ph3):f2
  d11
  10u gron0
  p7:sp1:f2 ph1
  10u groff
  d10
  10u
  p2 ph1
  10u
  10u gron1
  p7:sp1:f2 ph1
  10u groff
  d14 gron4 p2:f2
  10u groff
```

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Pulse sequence for UF-HSQC

1. **90° Pulse**: $90°$ pulse
2. **Spatial Encoding Block**: $100u$ UNBLKGRAD
3. **Coherence Selection Gradient**: $10u$ gron0, $10u$ gron1, $10u$ gron25
4. **Mixing Period**: $10u$ p1 ph1
5. **Starting Acquisition**: $ACQ\_START(ph30,ph31)$
6. **Positive Acquisition Gradient**: $1u$ DWELL\_GEN:f1
7. **Gradient Recovery Delay**: $d6$ groff
8. **Negative Acquisition Gradient**: $d20$ gron3
9. **Loop for Acquisition**: $rcyc=2$
10. **Inept Block**: $10u$ gron0, $p7:sp1:f2 ph1$, $d11$, $d10$, $10u$ groff
11. **Spatial Encoding Block**: $d6=d4-d15$
12. **180° Pulse**: $d4=1s/(const2*4)$
Optimization and practical implementation of ultrafast 2D NMR experiments

(p3 ph5):f2
(p1 ph1)
d4
(center (p2 ph1) (p4 ph4):f2 )
d6
d15 gron5 \rightarrow coherence selection and folding gradient
d15 gron7 \rightarrow purge gradient
ACQ_START(ph30,ph31)
l1 DWELL_GEN:f1
3 p15:gp15 \rightarrow positive acquisition gradient
(p4 ph6):f2 \rightarrow decoupling pulse
d17 \rightarrow recovery delay
p15:gp16 \rightarrow negative acquisition gradient
d17 \rightarrow recovery delay
(p4 ph6):f2 \rightarrow decoupling pulse
d17 ipp6 \rightarrow recovery delay / phase (ph6) increment

retro-INEPT block

lo to 3 times l3 \rightarrow loop for acquisition
rcyc=2
100u BLKGRAD
30m mc #0 to 2 F1QF(id2)
ext

ph0=0
ph1=0
ph2=1
ph3=0
ph4=0
ph5=0 2
ph6=0 2 0 0 \rightarrow asymmetric phase cycle on the
decoupling pulse to avoid the formation of
decoupling artifacts

ph7=1
ph8=3
ph30=0
ph31=0 2