Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

CLIP-HSQMBC: Easy measurement of small proton-carbon coupling constants in organic molecules

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Supporting information

1. Pulse sequence code (Bruker) for the CLIP-HSQMBC experiment
2. Pulse sequence code (Bruker) for the CLIP-HSQMBC-TOCSY experiment

```
;CLIP-HSQMBC
;2D proton-selective CLIP-HSQMBC experiment
;for an easy measurement of long-range
;proton-carbon coupling constants

#include <Avance.incl>
#include <Grad.incl>
#include <Delay.incl>


"p2=p1*2"
"d4=1s/(cnst2*4)"
"d11=30m"
"d0=3u"
"in0=inf1/2"
"DELTA1=50u+p16+d16"
"DELTA2=d4-larger(p12,p14)/2-50u-p16-d16"
"DELTA=p16+d16+50u+p2+d0*2+50u"


1 ze
  d11 pl12:f2
2 d1 pl1:f1
3 (p1 ph1)
  50u UNBLKGRAD
  p16:gp3
  d16
  DELTA2 pl0:f2 pl0:f1
  4u
  (center (p12:sp2 ph1) (p14:sp3 ph6):f2 )
  4u
  DELTA2 pl2:f2 pl1:f1
  50u
  p16:gp3
  d16
  (center (p1 ph2):f1 (p3 ph3):f2 )
  d0
  (p2 ph5)
  d0
  50u
  p16:gp1*EA
  d16 pl0:f2
  d12
  (p24:sp7 ph4):f2
   DELTA pl2:f2
  (p3 ph4):f2
  50u
  p16:gp4
  d16
```

```
  (p1 ph2):f1
  50u
  p16:gp5
  d16
  DELTA2 pl0:f2 pl0:f1
  (center (p12:sp2 ph1) (p14:sp3 ph1):f2 )
  DELTA2 pl2:f2 pl1:f1
  50u
  p16:gp5
  4u
  p16:gp2
  d16 BLKGRAD
  (p3 ph1):f2
  go=2 ph31
  d1 mc #0 to 2
    F1EA(igrad EA, id0 & ip3*2 & ip6*2 & ip31*2)
exit

ph1=0
ph2=1
ph3=0 2
ph4=0
ph5=0
ph6=0
ph14=0
ph31=0 2


;pl0 : 120dB
;pl1 : f1 channel - power level for pulse (default)
;pl2 : f2 channel - power level for pulse (default)
;pl3 : f3 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;sp3: f2 channel - shaped pulse 180 degree for inversion
;sp7: f2 channel - shaped pulse 180 degree for refocussing
;p1 : f1 channel -  90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;p3 : f2 channel -  90 degree high power pulse
;p14: f2 channel - 180 degree shaped pulse for inversion
;p16: homospoil/gradient pulse
;p22: f3 channel - 180 degree high power pulse
;p24: f2 channel - 180 degree shaped pulse for refocussing
;d0 : incremented delay (2D)                    [3 usec]
;d1 : relaxation delay; 1-5 * T1
;d4 : 1/(4J)XH
;d11: delay for disk I/O                        [30 msec]
;d16: delay for homospoil/gradient recovery
;cnst2: = J(XH)
;inf1: 1/SW(X) = 2 * DW(X)
```

;in0: 1/(2 * SW(X)) = DW(X)
;nd0: 2
;NS: 1 * n
;DS: >= 16
;td1: number of experiments
;FnMODE: echo-antiecho

;use gradient ratio:
;gpz1: 80%
;gpz2: 20.1% for C-13
;gpz3: 33%
;gpz4: 50%
;gpz5: 17%

;use gradient files:
;gpnam1: SINE.100
;gpnam2: SINE.100
;gpnam3: SINE.100
;gpnam4: SINE.100
;gpnam5: SINE.100

```
;CLIP-HSQMBC-TOCSY
;2D proton-selective CLIP-HSQMBC experiment
;for an esay measurement of long-range
;proton-carbon coupling constants

#include <Avance.incl>
#include <Grad.incl>
#include <Delay.incl>


"p2=p1*2"
"d4=1s/(cnst2*4)"
"d11=30m"
"d0=3u"
"in0=inf1/2"
"DELTA1=50u+p16+d16"
"DELTA2=d4-larger(p12,p14)/2-50u-p16-d16"
"DELTA=p16+d16+50u+p2+d0*2+50u"


1 ze
  d11 pl12:f2
2 d1 pl1:f1
3 (p1 ph1)
  50u UNBLKGRAD
  p16:gp3
  d16
  DELTA2 pl0:f2 pl0:f1
  4u
  (center (p12:sp2 ph1) (p14:sp3 ph6):f2 )
  4u
  DELTA2 pl2:f2 pl1:f1
  50u
  p16:gp3
  d16
  (center (p1 ph2):f1 (p3 ph3):f2 )
  d0
  (p2 ph5)
  d0
  50u
  p16:gp1*EA
  d16 pl0:f2
  d12
  (p24:sp7 ph4):f2
   DELTA pl2:f2
  (p3 ph4):f2
  50u
  p16:gp4
  d16
```

```
  (p1 ph2):f1
  50u
  p16:gp5
  d16
  DELTA2 pl0:f2 pl0:f1
  (center (p12:sp2 ph1) (p14:sp3 ph1):f2 )
  DELTA2 pl2:f2 pl1:f1
  50u
  p16:gp5

  (p1 ph1):f1

;starts tocsy

  d12 pl10:f1

4 p6*3.556 ph22
  p6*4.556 ph24
  p6*3.222 ph22
  p6*3.167 ph24
  p6*0.333 ph22
  p6*2.722 ph24
  p6*4.167 ph22
  p6*2.944 ph24
  p6*4.111 ph22

  p6*3.556 ph24
  p6*4.556 ph22
  p6*3.222 ph24
  p6*3.167 ph22
  p6*0.333 ph24
  p6*2.722 ph22
  p6*4.167 ph24
  p6*2.944 ph22
  p6*4.111 ph24

  p6*3.556 ph24
  p6*4.556 ph22
  p6*3.222 ph24
  p6*3.167 ph22
  p6*0.333 ph24
  p6*2.722 ph22
  p6*4.167 ph24
  p6*2.944 ph22
  p6*4.111 ph24

  p6*3.556 ph22
  p6*4.556 ph24
  p6*3.222 ph22
```

```
  p6*3.167 ph24
  p6*0.333 ph22
  p6*2.722 ph24
  p6*4.167 ph22
  p6*2.944 ph24
  p6*4.111 ph22
  lo to 4 times l1

  5u pl0:f1
  300u gron6
  p13:sp4:f1 ph7
  100u groff
  d16

;end tocsy

  4u pl1:f1
  p1 ph1
  DELTA1
  (p2 ph1):f1
  50u
  p16:gp2
  d16 BLKGRAD

  (p3 ph1):f2


 go=2 ph31
 d1 mc #0 to 2
    F1EA(igrad EA, id0 & ip3*2 & ip6*2 & ip31*2)



ph1=0
ph2=1
ph3=0 2
ph4=0
ph5=0
ph6=0
ph7=0
ph14=0
ph22=3
ph24=1
ph31=0 2


;pl0 : 120dB
;pl1 : f1 channel - power level for pulse (default)
;pl2 : f2 channel - power level for pulse (default)
```

```
;pl3 : f3 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;sp3: f2 channel - shaped pulse 180 degree for inversion
;sp7: f2 channel - shaped pulse 180 degree for refocussing
;p1 : f1 channel -  90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;p3 : f2 channel -  90 degree high power pulse
;p14: f2 channel - 180 degree shaped pulse for inversion
;p16: homospoil/gradient pulse
;p22: f3 channel - 180 degree high power pulse
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;d0 : incremented delay (2D)                    [3 usec]
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;cnst2: = J(XH)
;inf1: 1/SW(X) = 2 * DW(X)
;in0: 1/(2 * SW(X)) = DW(X)
;nd0: 2
;NS: 1 * n
;DS: >= 16
;td1: number of experiments
;FnMODE: echo-antiecho

;use gradient ratio:
;gpz1: 80%
;gpz2: 20.1% for C-13
;gpz3: 33%
;gpz4: 50%
;gpz5: 17%
;gpz6: ca. 3%

;use gradient files:
;gpnam1: SINE.100
;gpnam2: SINE.100
;gpnam3: SINE.100
;gpnam4: SINE.100
;gpnam5: SINE.100
```