Electronic Supplementary Information (ESI)

Zero-quantum filtered pure shift TOCSY

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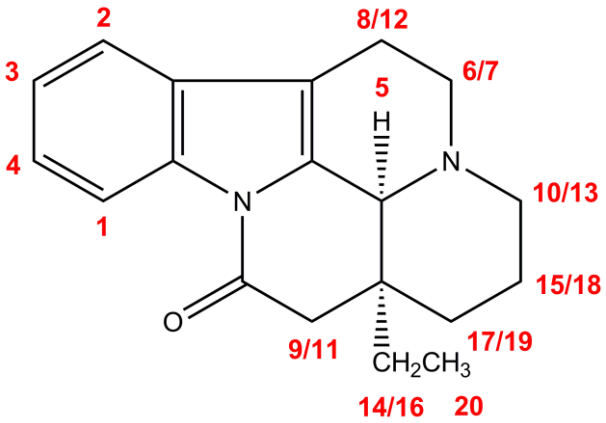
Experimental

All TOCSY experiments were performed in $CDCl_3$ at 25 °C on a Bruker Avance DPX400 spectrometer equipped with a 5 mm BBFO probehead. A 20 ms DIPSI-2 sequence was used for the isotropic mixing. The conventional phase sensitive ZQF TOCSY spectrum of (−)-eburnamonine was recorded using a spectral width of 3491.62 Hz in both dimensions, 2 k data points, 256 t_1 increments, and 8 transients. The experimental time was 1 h 23 min. The data was zero-filled to a 2 k × 2 k matrix before Fourier transformation. The phase sensitive pure shift TOCSY spectra of (−)-eburnamonine were recorded using 2 k data points, 32 t_2 increments and 128 t_1 increments, and 4 transients. The experimental times were 11 h 34 min (non-ZQF version) and 11 h 59 min (ZQF version). Spectral widths were 3491.62, 99.761, and 3491.62 Hz in *F*3, *F*2, and *F*1 dimensions, respectively. The pure shift spectra were recorded with the same receiver gain setting. The Bruker AU program "pshift" (modified to cope with the aqseq 321 data) was used to generate a 2D data set in which the *F*2 dimension was decoupled. The data was zero-filled to a 2 k × 2 k matrix before covariance processing (the Bruker AU program "covariance"). All data processing was made using TopSpin 3.0 software.

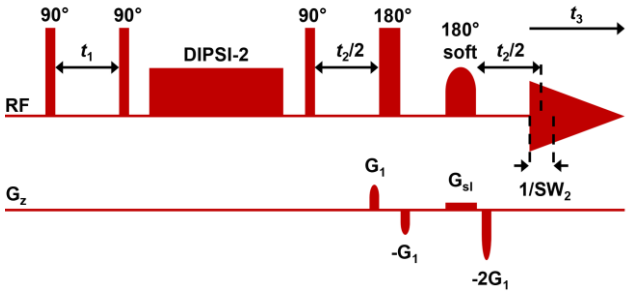
Molecular structure of (−)-eburnamonine



Scheme S1 Molecular structure of the indole alkaloid (−)-eburnamonine. Proton assignments are shown in red. The assigned ^{1}H spectrum is shown in Fig. S2 (*F*2 projection).

Pulse sequence timing diagrams for the non-ZQF pure shift TOCSY and conventional ZQF TOCSY experiments

(a)



(b)

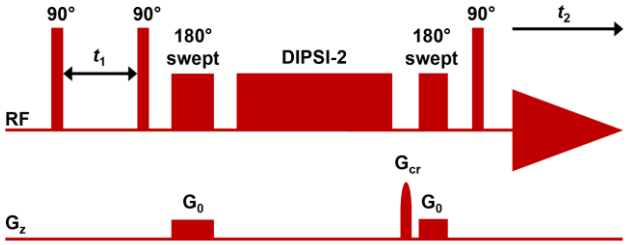


Fig. S1 Pulse sequences for the pure shift TOCSY experiment without zero-quantum filtering (a) and for the conventional ZQF TOCSY experiment (b).

Full conventional and pure shift TOCSY spectra

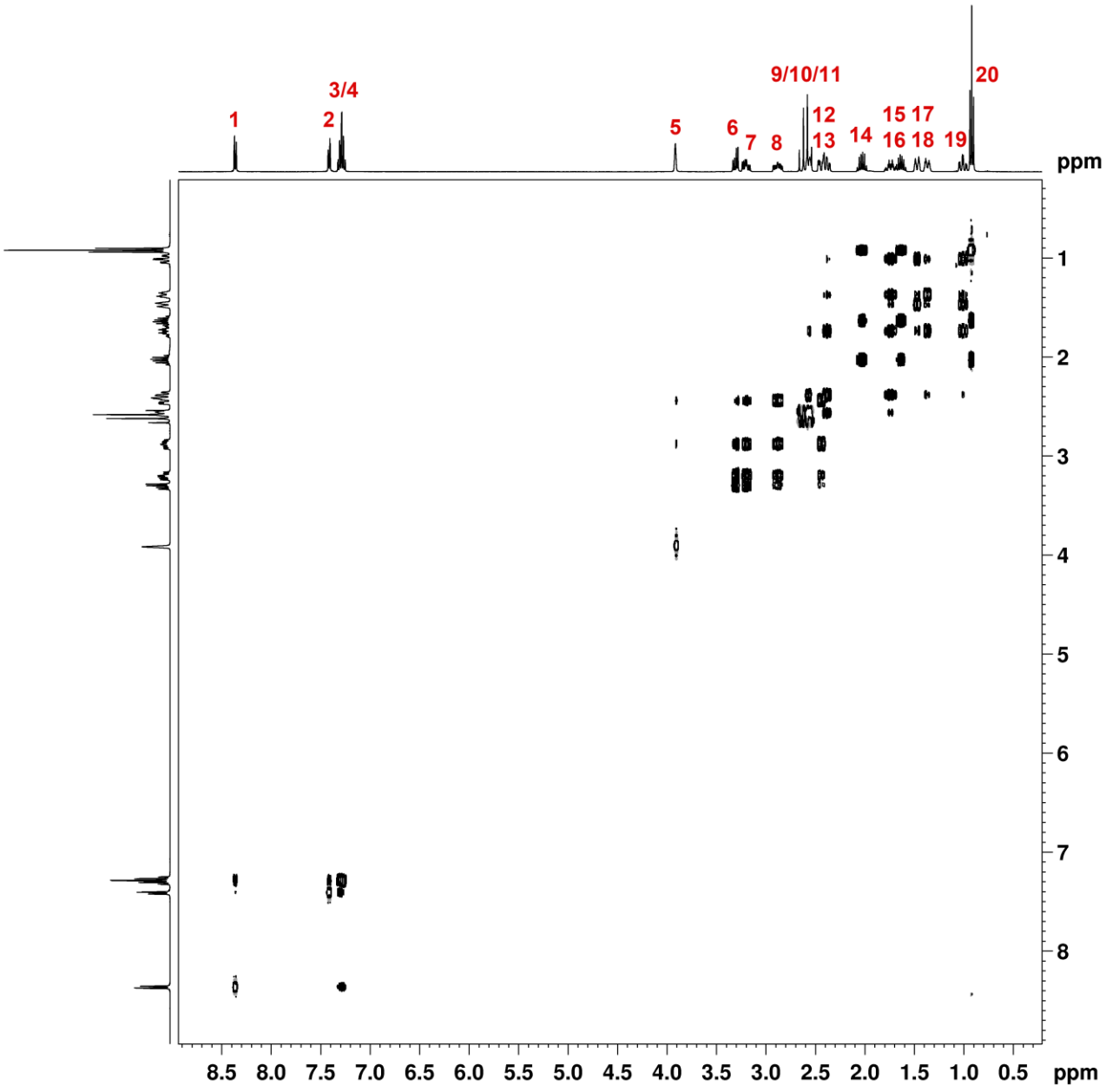


Fig. S2 Conventional ZQF TOCSY spectrum of (−)-eburnamonine. Projections: conventional ^{1}H spectra. Proton assignments are given in red (*F*2 projection).

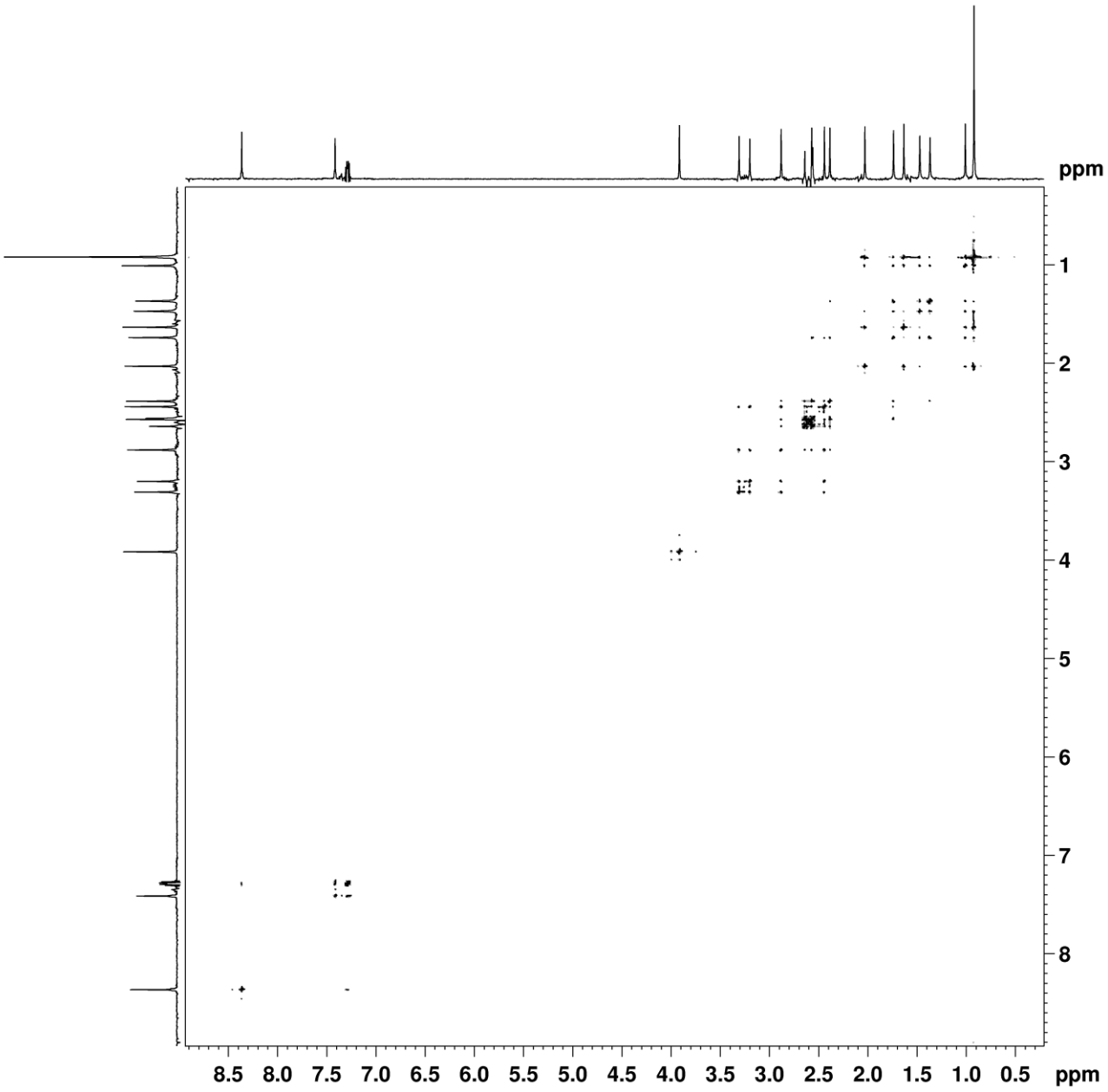


Fig. S3 Non-ZQF pure shift TOCSY spectrum of (−)-eburnamonine. Projections: 1D ^{1}H pure shift spectra.[1]

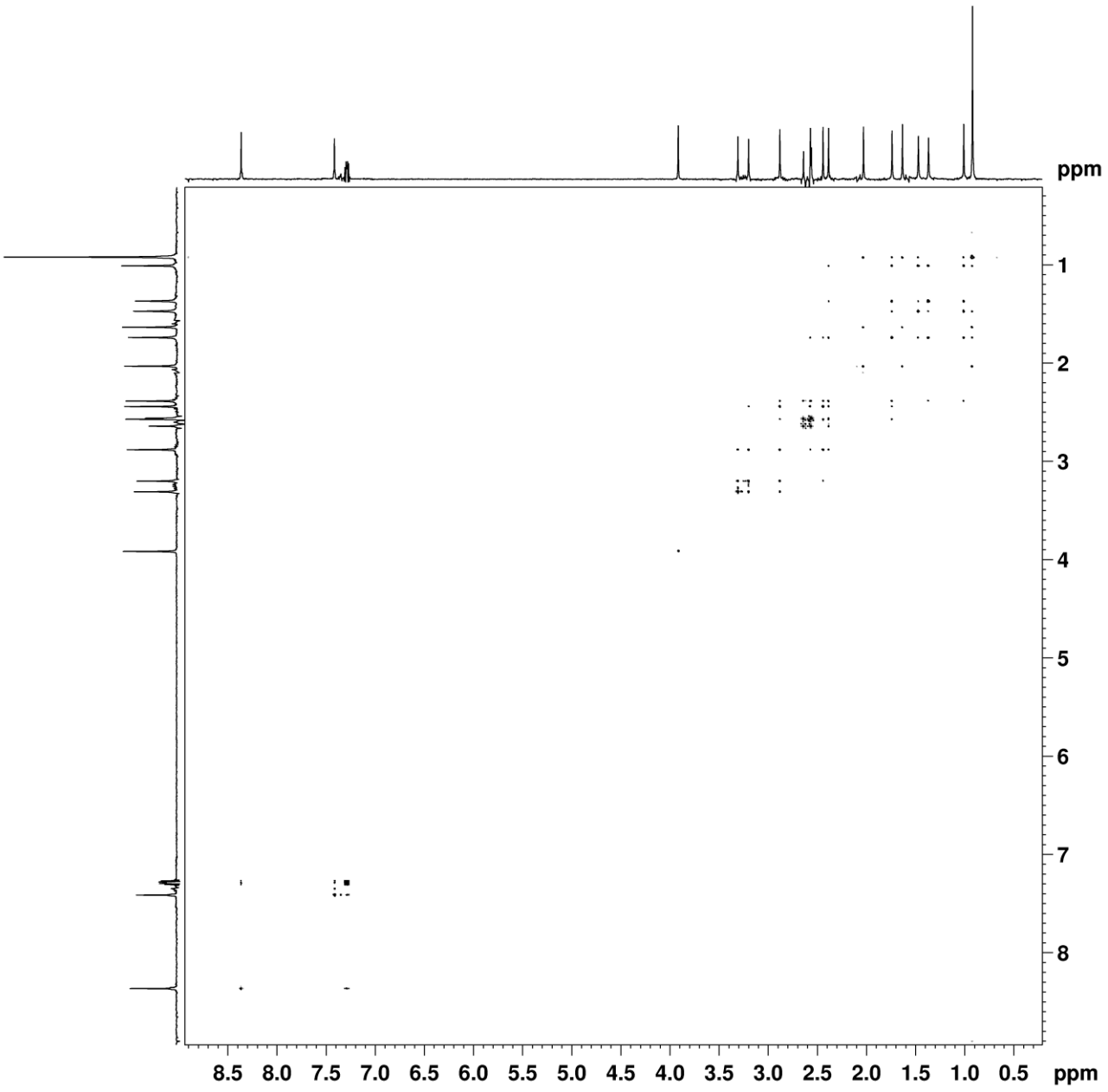


Fig. S4 ZQF pure shift TOCSY spectrum of (−)-eburnamonine. Projections: 1D ^{1}H pure shift spectra.[1]

1 J. A. Aguilar, S. Faulkner, M. Nilsson and G. A. Morris, *Angew. Chem., Int. Ed.*, 2010, **49**, 3901-3903.

Pulse sequence for the ZQF pure shift TOCSY experiment (Bruker spectrometers)

```
;push2dzs_zqf_tocsy
;
;Zangger-Sterk pure shift sequence
;2D homonuclear Hartman-Hahn transfer using DIPSI-2 sequence for mixing
;with gradient/rf spoil pulses (ZQ-filter)
;phase sensitive
;
;Jari J. Koivisto, Aalto University (12th September 2012)
;
;Morris, G. A.; Aguilar, J. A.; Evans, R.; Haiber, S.; Nilsson, M. J. Am. Chem. Soc. 2010, 132, 12770-12772.
;Aguilar, J. A.; Faulkner, S.; Nilsson, M.; Morris, G. A. Angew. Chem., Int. Ed. 2010, 49, 3901-3903.
;Thrippleton, M. J.; Keeler, J. Angew. Chem., Int. Ed. 2003, 42, 3938-3941.

;Data can be reconstructed using the 'pshift' macro (mod. by JJK to cope with the aqseq 321 data).

;$CLASS=HighRes
;$DIM=3D
;$TYPE=
;$SUBTYPE=
;$COMMENT=

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

define delay tauA
define delay tauB
define delay tauC

;TOCSY:
"d12=20u"
"in0=inf1"
"d0=in0/2-p1*4/3.1416"
"FACTOR1=(d9/(p6*115.112))/2"
"l1=FACTOR1*2"
;ZS:
"in10=inf2/2"
"p2=p1*2"
"tauA=in10/2-p16-d16"
"tauB=in10-p16-d16-300u"
"tauC=in10/2-p16-d16-350u-(dw*2)-(dw*2*cnst4)-de"

aqseq 321

1       ze
2       d1
3       d12 pl1:f1
        50u UNBLKGRAD
        p1 ph1
        d0
        p1 ph2
        10u gron0                       ;start ZQF 1
        (p32:sp29 ph7):f1               ;SmoothedChirp
        d16 groff                       ;end ZQF 1
        d12 pl10:f1                     ;power level for DIPSI-2
4       p6*3.556 ph23                   ;start TOCSY spinlock (DIPSI-2)
        p6*4.556 ph25
        p6*3.222 ph23
        p6*3.167 ph25
        p6*0.333 ph23
        p6*2.722 ph25
        p6*4.167 ph23
        p6*2.944 ph25
        p6*4.111 ph23
        p6*3.556 ph25
        p6*4.556 ph23
```

```
        p6*3.222 ph25
        p6*3.167 ph23
        p6*0.333 ph25
        p6*2.722 ph23
        p6*4.167 ph25
        p6*2.944 ph23
        p6*4.111 ph25
        p6*3.556 ph25
        p6*4.556 ph23
        p6*3.222 ph25
        p6*3.167 ph23
        p6*0.333 ph25
        p6*2.722 ph23
        p6*4.167 ph25
        p6*2.944 ph23
        p6*4.111 ph25
        p6*3.556 ph23
        p6*4.556 ph25
        p6*3.222 ph23
        p6*3.167 ph25
        p6*0.333 ph23
        p6*2.722 ph25
        p6*4.167 ph23
        p6*2.944 ph25
        p6*4.111 ph23
        lo to 4 times l1                ;end TOCSY spinlock (DIPSI-2)
        p31:gp1                         ;crusher gradient
        10u gron0                       ;start ZQF 2
        (p34:sp30 ph7):f1               ;SmoothedChirp
        20u groff                       ;end ZQF 2
        d31                             ;recovery delay
        d12 pl1:f1
        p1 ph3                          ;end TOCSY
        d10                             ;start ZS, incremented delay
        tauA
        p16:gp1*0.5                     ;gradient +0.5
        d16
        p2 ph8                          ;hard 180
        tauB
        p16:gp1*-0.5                    ;gradient -0.5
        d16
        300u gron2                      ;slice selection gradient on
        p12:sp2:f1 ph9:r                ;soft 180 (Rsnob.1000)
        100u groff                      ;slice selection gradient off
        200u
        p16:gp1*-1.0                    ;gradient -1
        d16
        50u BLKGRAD
        tauC
        d10                             ;incremented delay
5       go=2 ph31
        30u
        d1 mc #0 to 2
                F1PH(rd10 & ip1, id0)
                F2QF(id10)
exit

;TOCSY
ph1=0 2                                 ;1st hard 90
ph2=0 0 0 0 2 2 2 2                     ;2nd hard 90
ph3=0 0 0 0 2 2 2 2                     ;3rd hard 90
ph7=0                                   ;ZQF 1 + 2
ph23=3                                  ;DIPSI-2
ph25=1                                  ;DIPSI-2
;ZS:
ph8= 0 0 0 0 0 0 0 0                    ;hard 180
ph9= 0 0 1 1 0 0 1 1                    ;soft 180
ph31=0 2 2 0 1 3 3 1                    ;receiver

;Processing
;PHC0(F1): 90
;PHC1(F1): -180
;FCOR(F1): 1
```