

PSYCHE pure shift NMR: spectral simplification and its applications

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NMR Methodology group

The University of Manchester

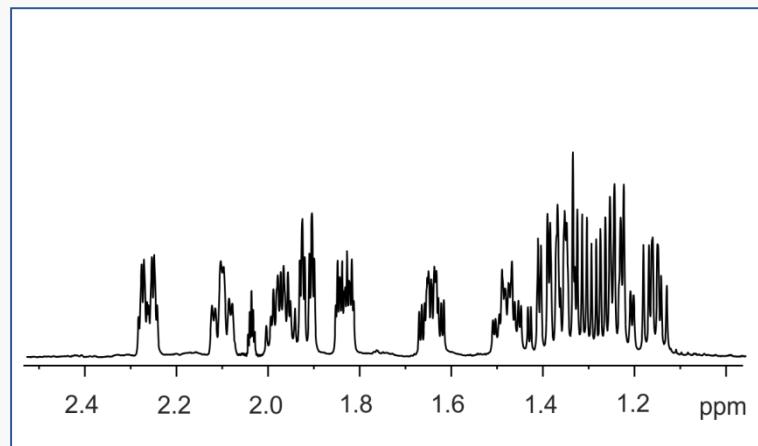
Small Molecule NMR Conference

September 11th-14th, 2016

La Jolla, California, USA.

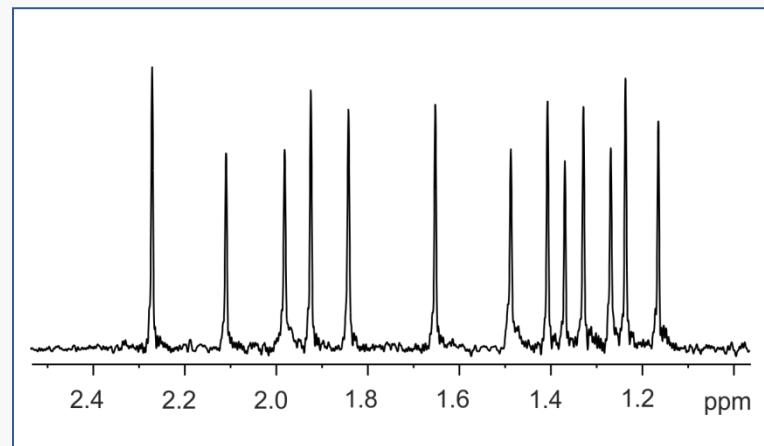
PROBLEM

Signal overlap &
poor spectral resolution



SOLUTION

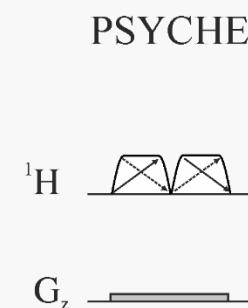
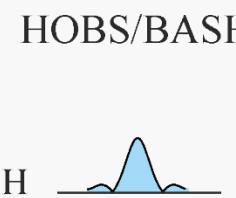
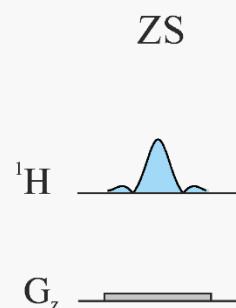
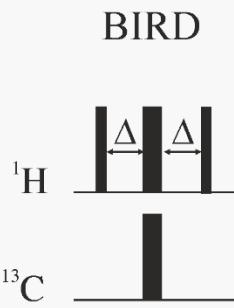
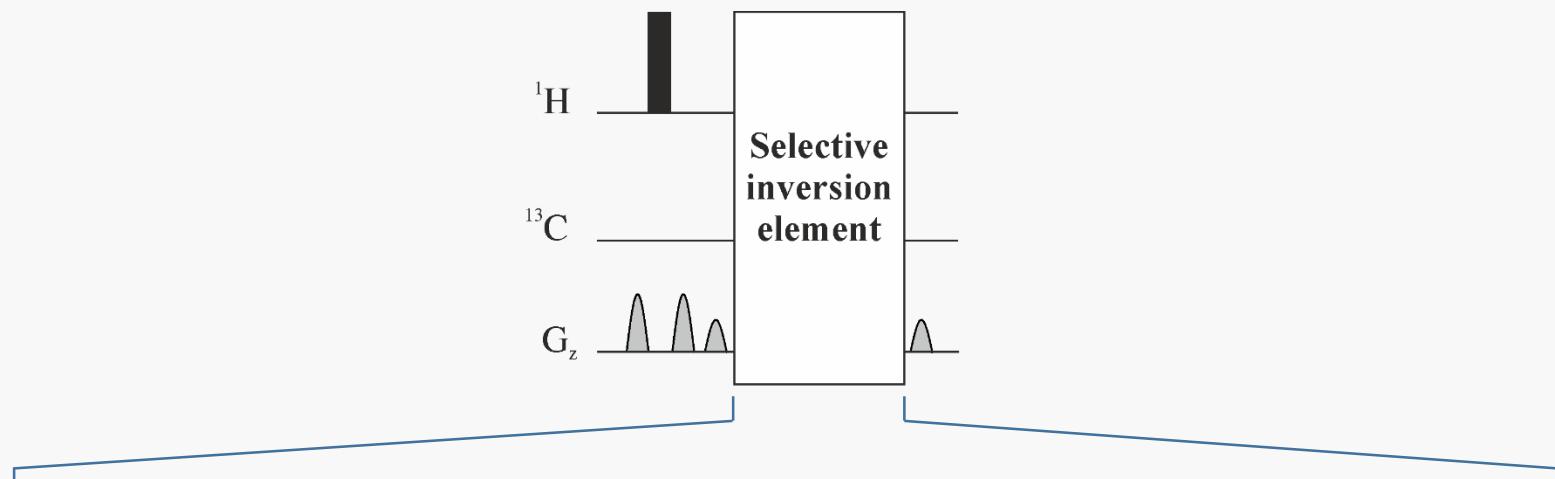
^1H Broadband homodecoupled
spectrum



Collapsing of typical J_{HH} coupling multiplicity to singlets

- ✓ Simplified NMR spectra
- ✓ Enhanced signal resolution

J-refocusing element



Broadband



Sensitivity

1.1%



0.5-5%



100%

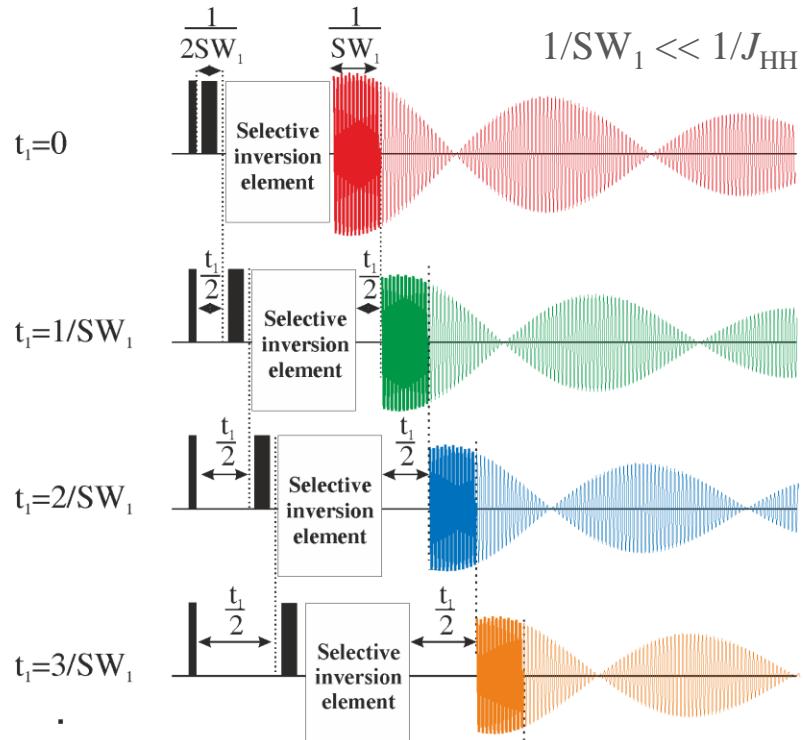


10-20%

Acquisition mode

Interferogram

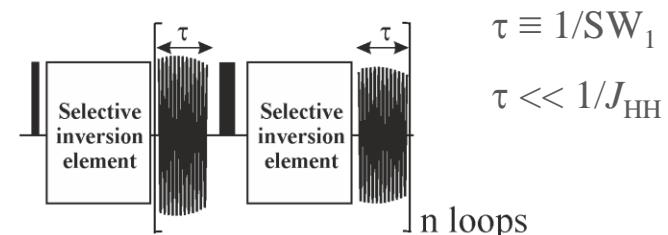
2D acquisition



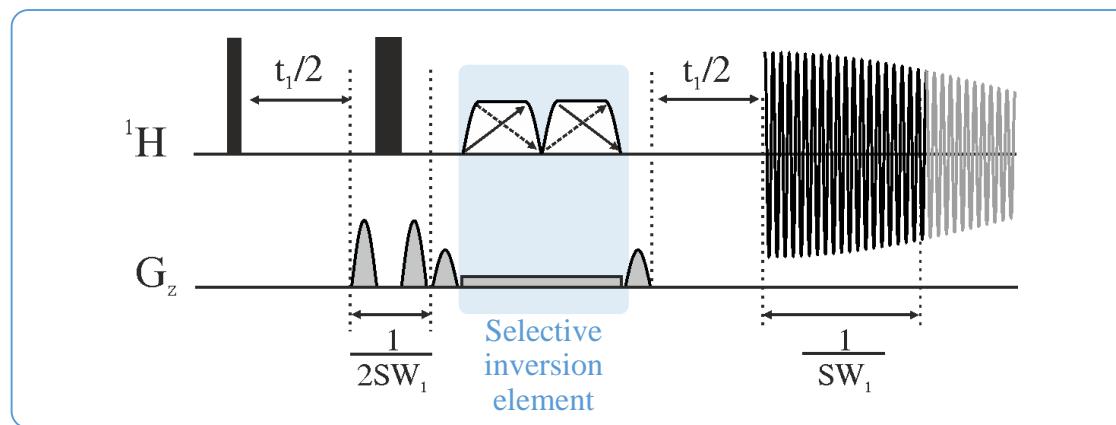
Real time

1D acquisition

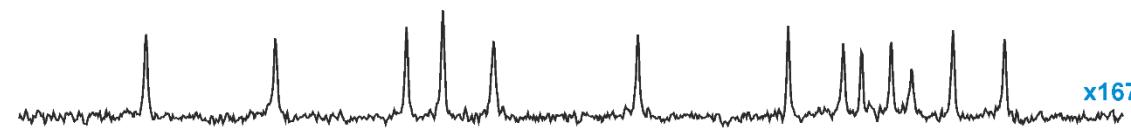
- ✗ Selective pulses > 20 ms
- ✗ PSYCHE



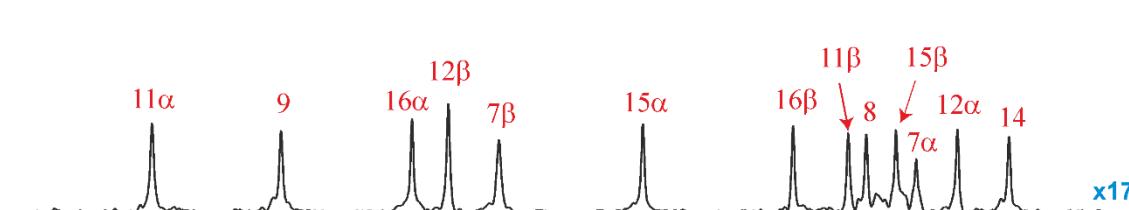
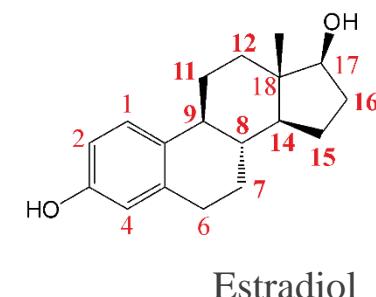
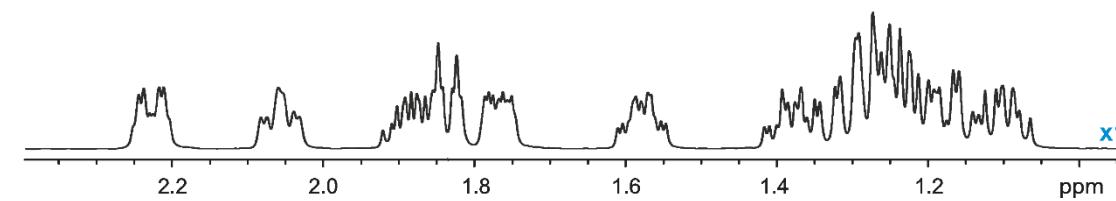
Pure Shift Yielded by CHirp Excitation (PSYCHE)



ZS

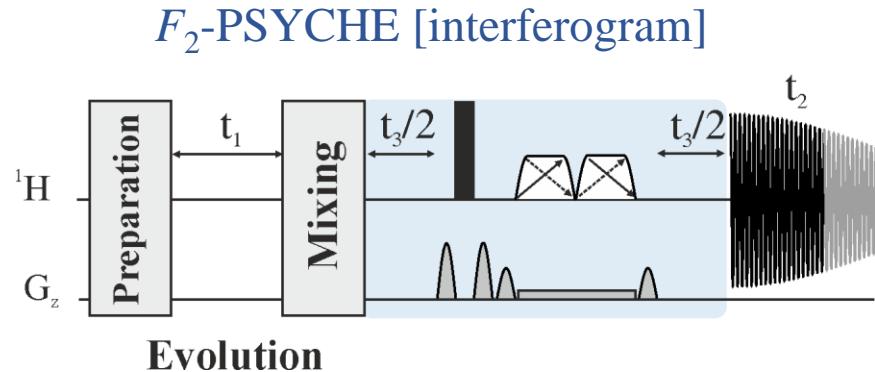
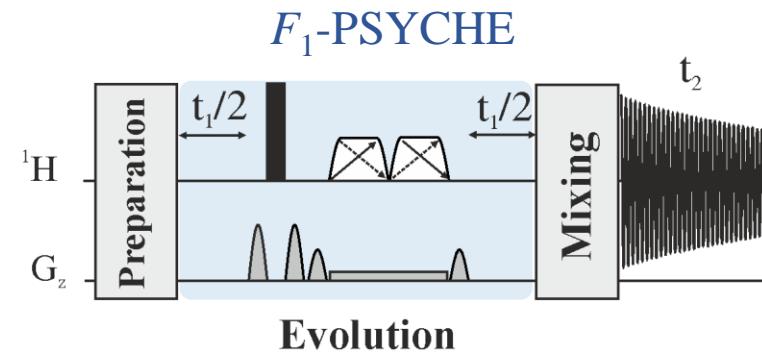
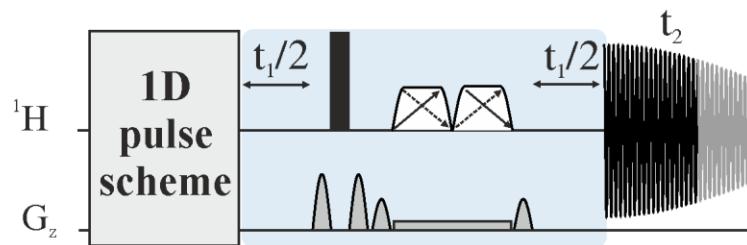


1D PSYCHE

 ^1H NMR

Estradiol

Implementing PSYCHE in 1D & 2D experiments



Oneshot-PSYCHE DOSY

Practical applications

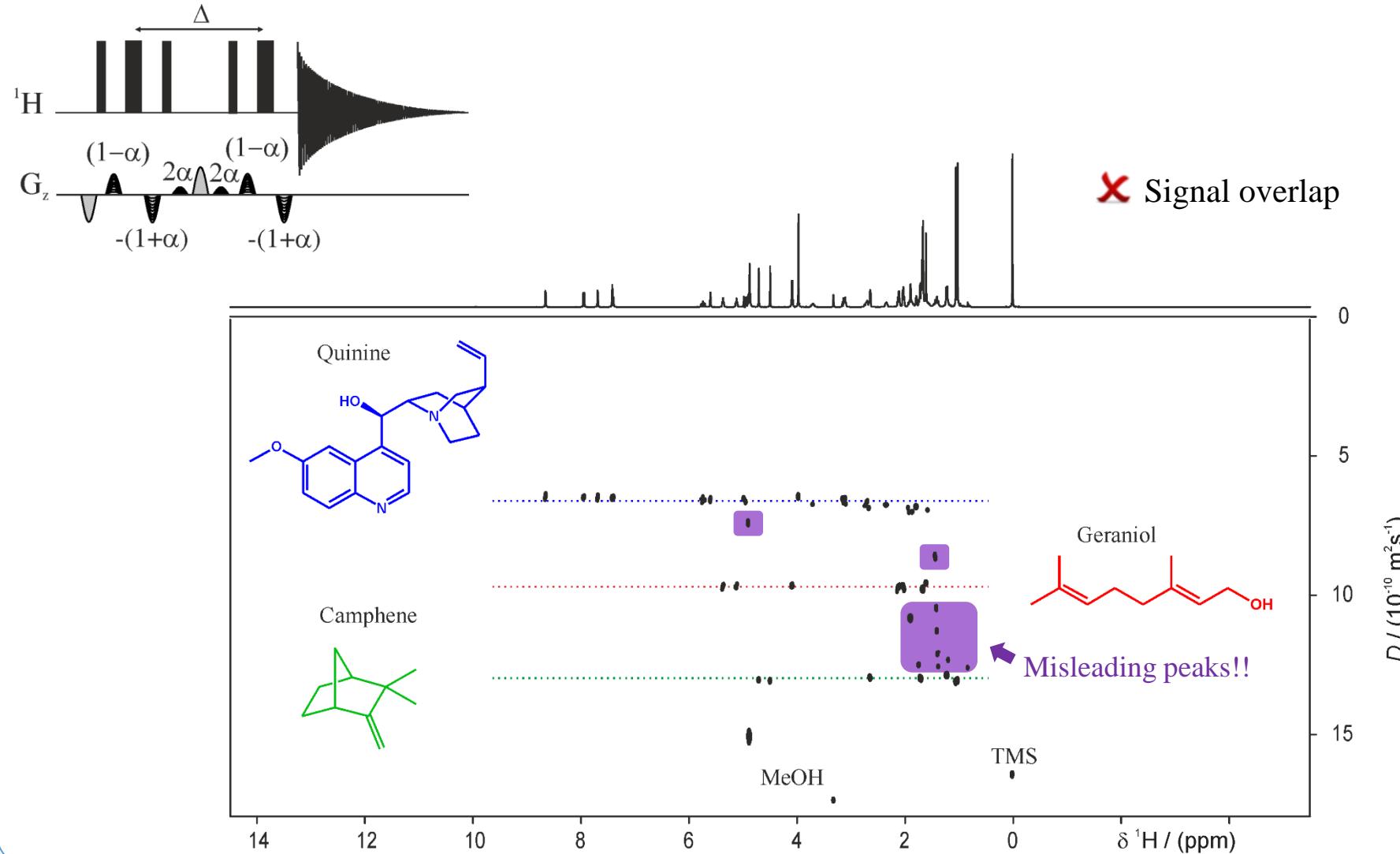
Selective 1D TOCSY-PSYCHE

Spectral simplification
Higher signal resolution

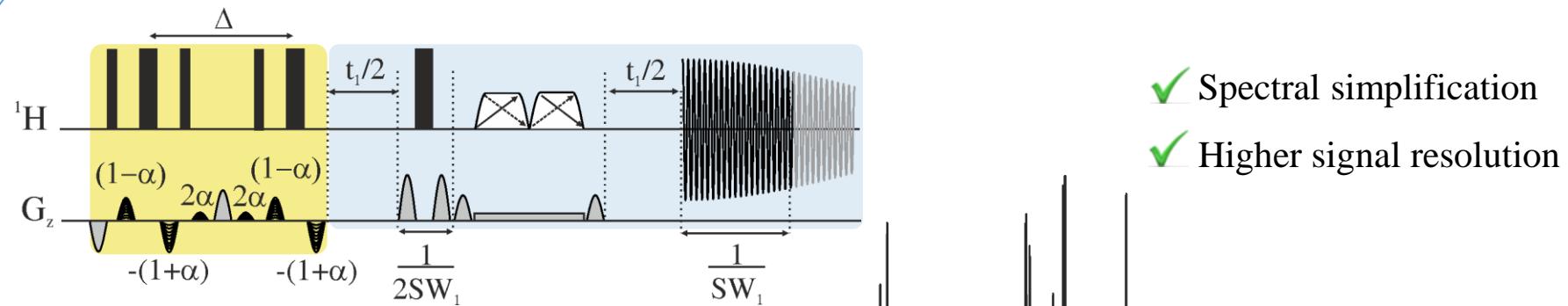
F_1 -PSYCHE-CLIP-COSY

- Analysis of mixtures
- Structure determination of complex molecules

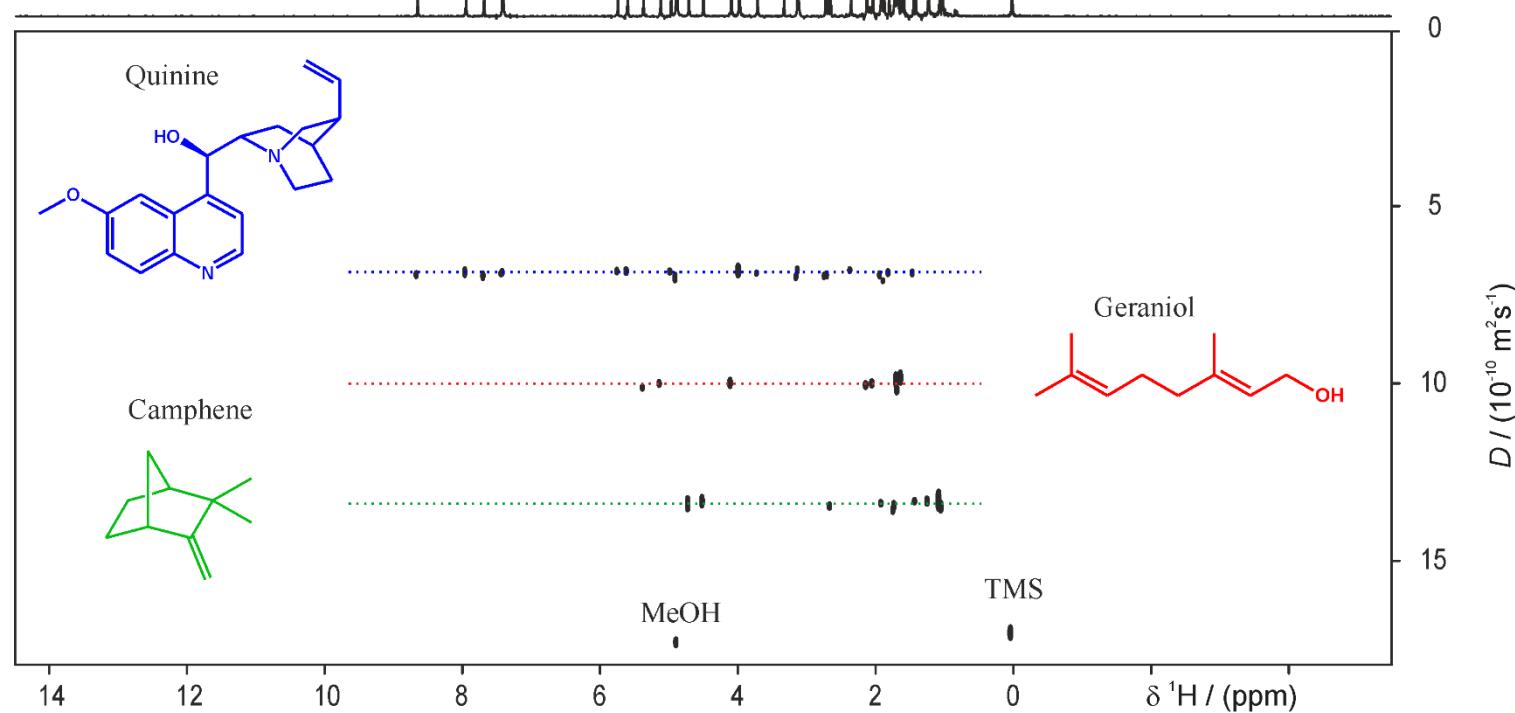
Mixture analysis: Oneshot DOSY



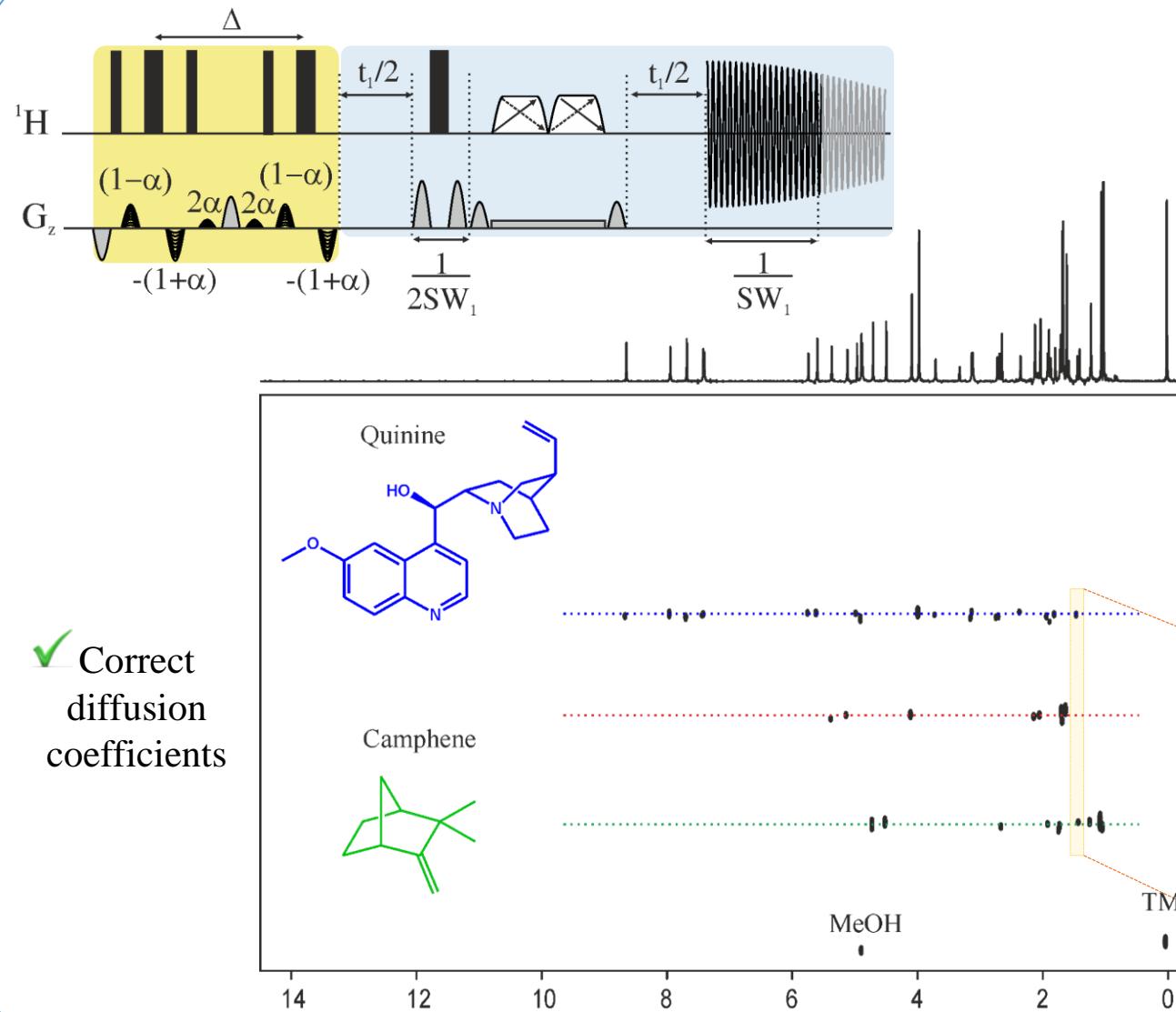
Mixture analysis: Oneshot-PSYCHE DOSY



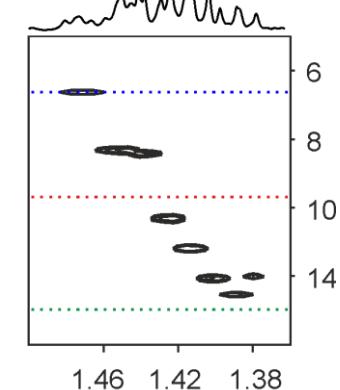
- ✓ Spectral simplification
- ✓ Higher signal resolution



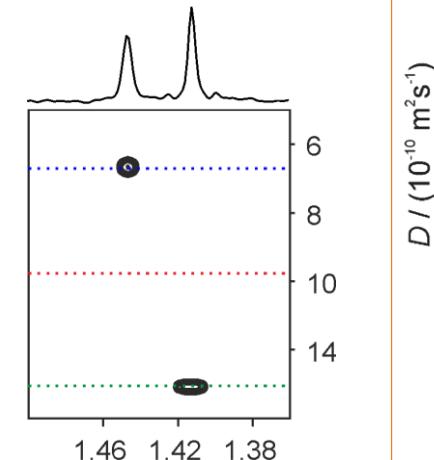
Mixture analysis: Oneshot-PSYCHE DOSY



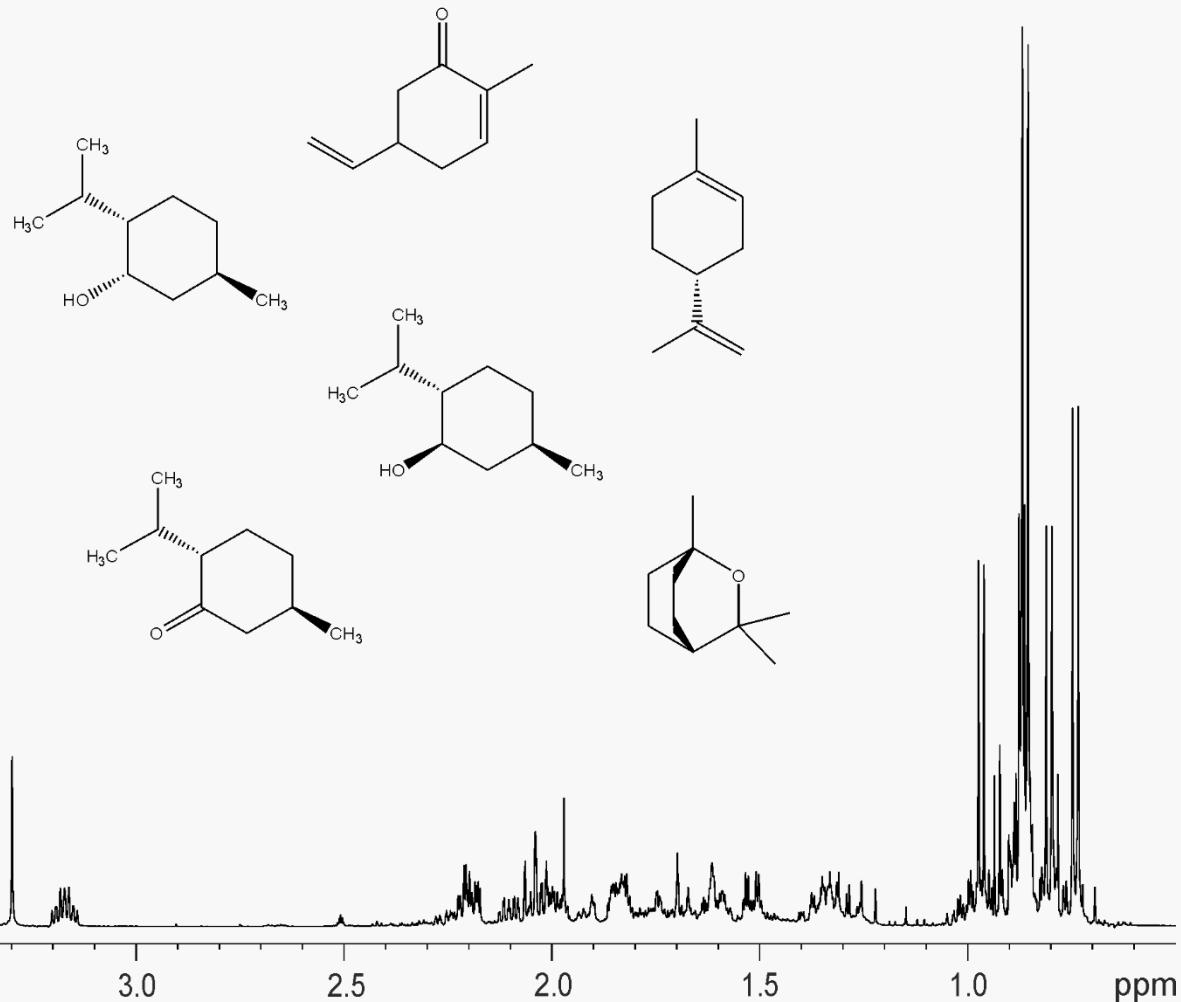
Conventional



Pure shift

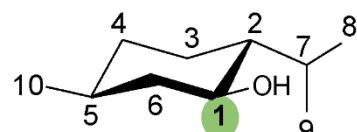


Mixture analysis: peppermint oil

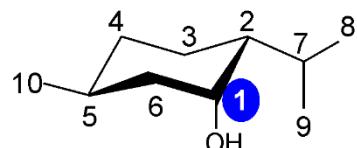


Mixture analysis: selective 1D TOCSY

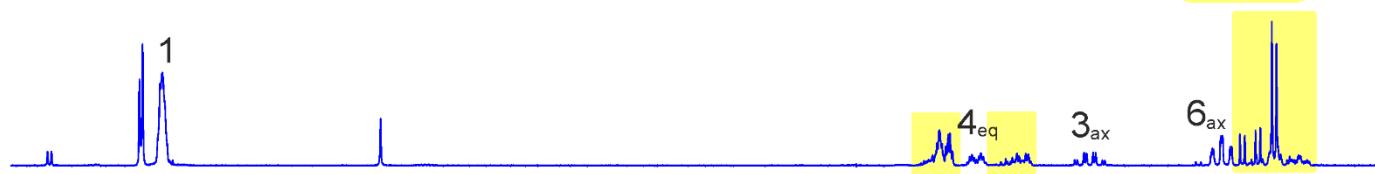
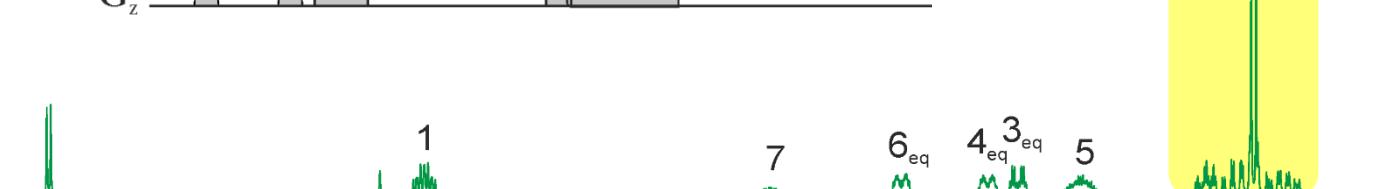
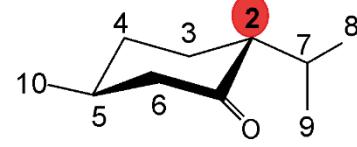
Menthol



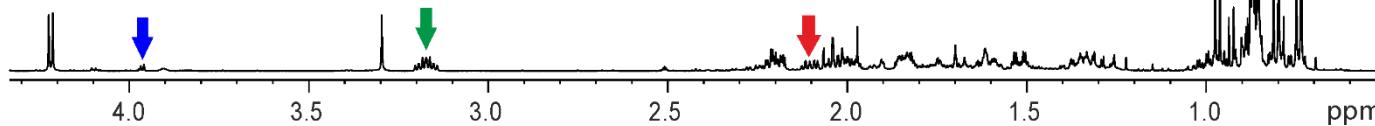
Neomenthol



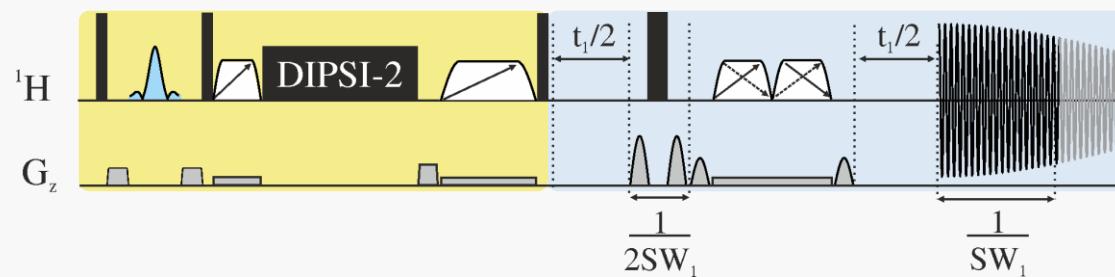
Menthone



Selective excitation

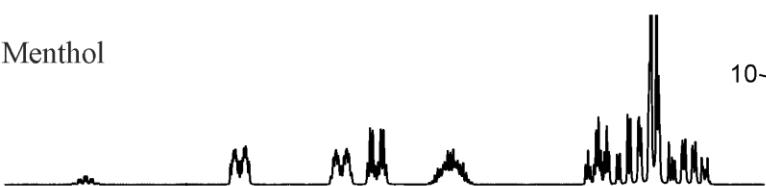


Mixture analysis: selective 1D TOCSY-PSYCHE



Conventional

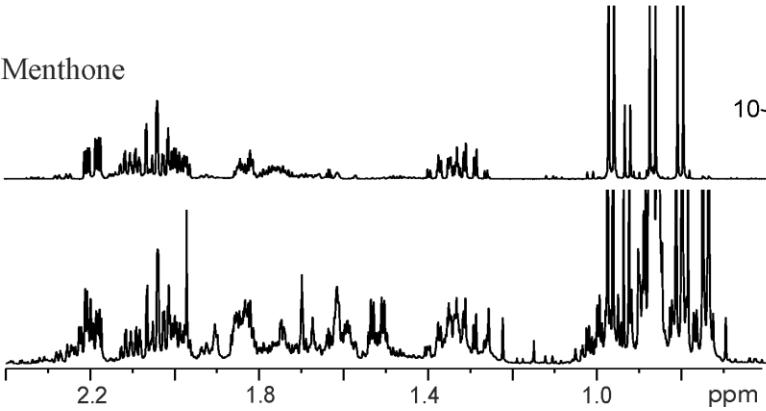
Menthol



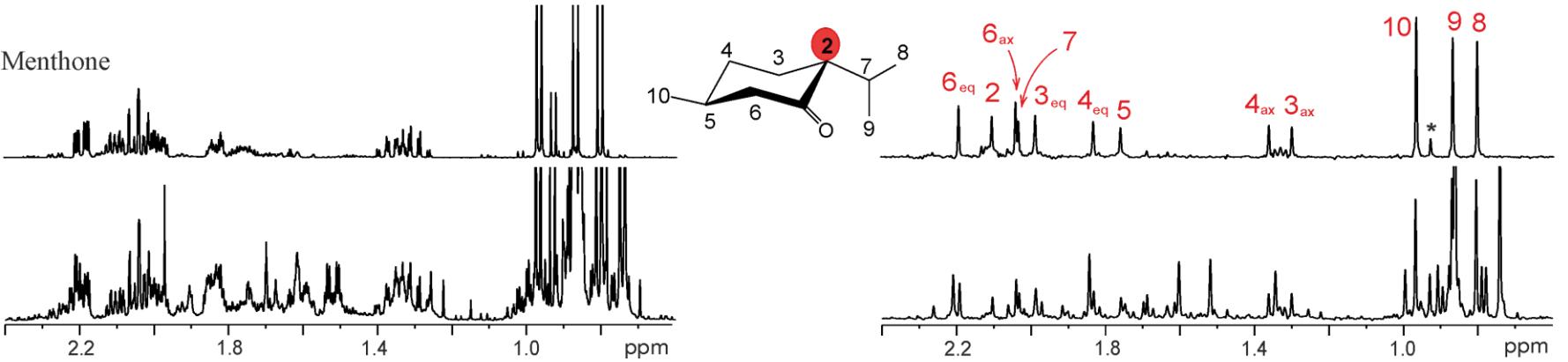
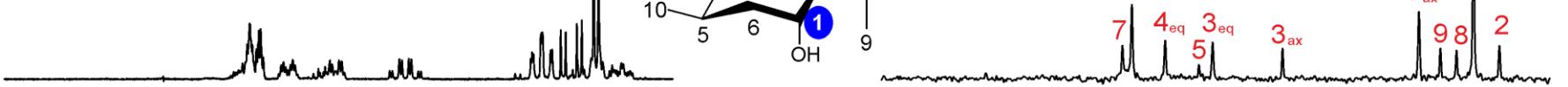
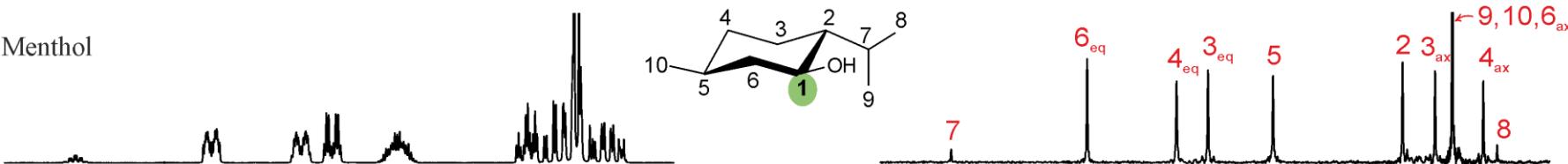
Neomenthol



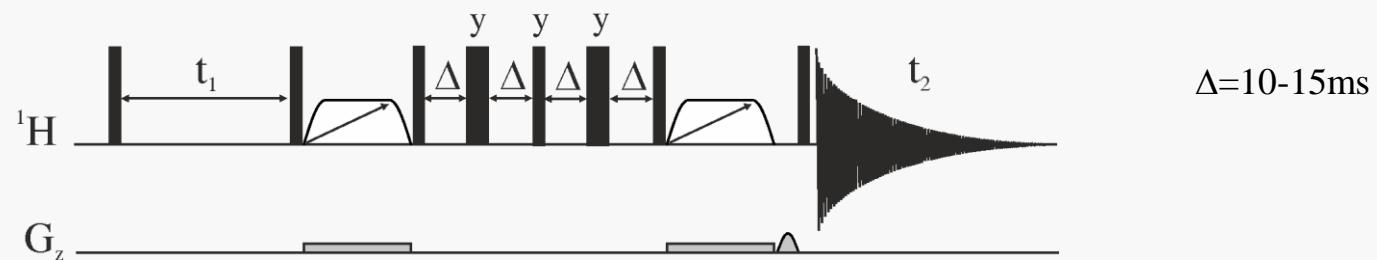
Menthone



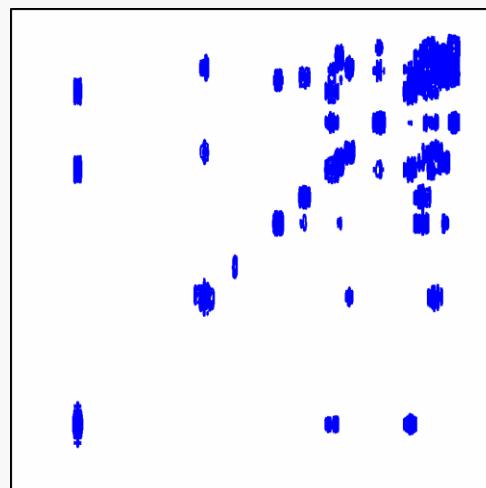
Pure shift



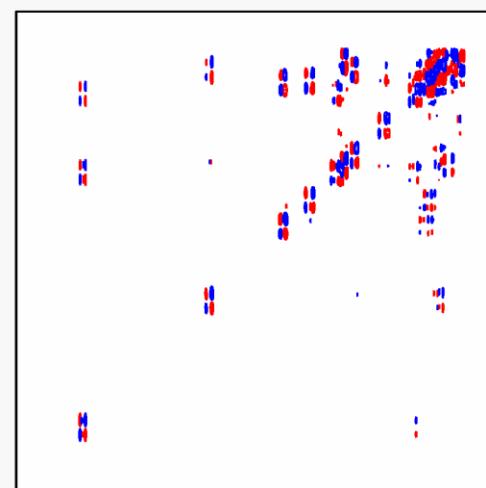
CLean In-Phase COSY

 $\Delta=10-15\text{ms}$

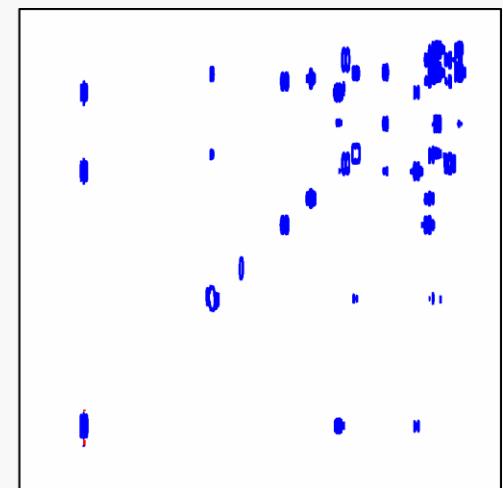
COSY (mc)



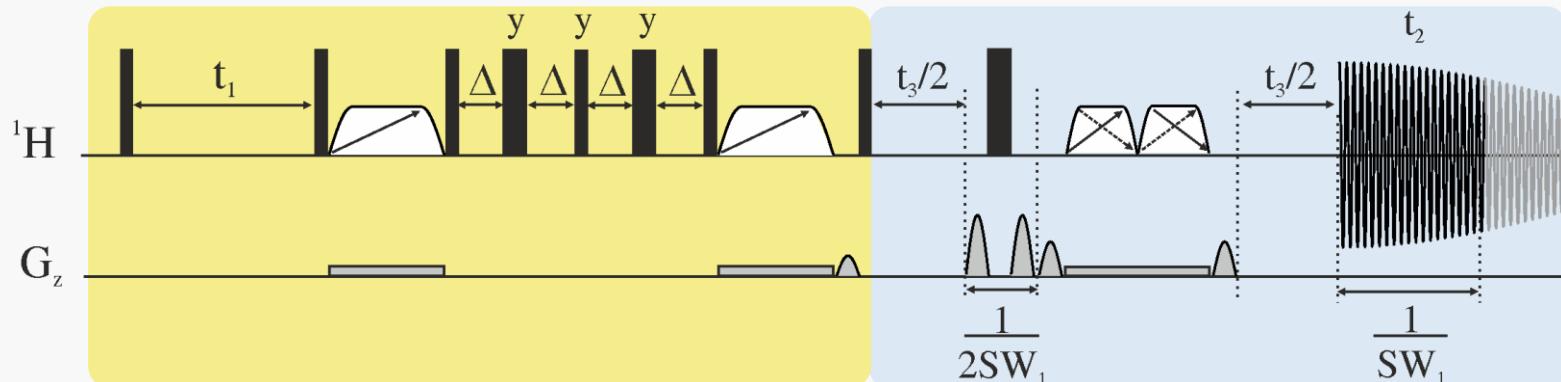
DQF-COSY (ph)



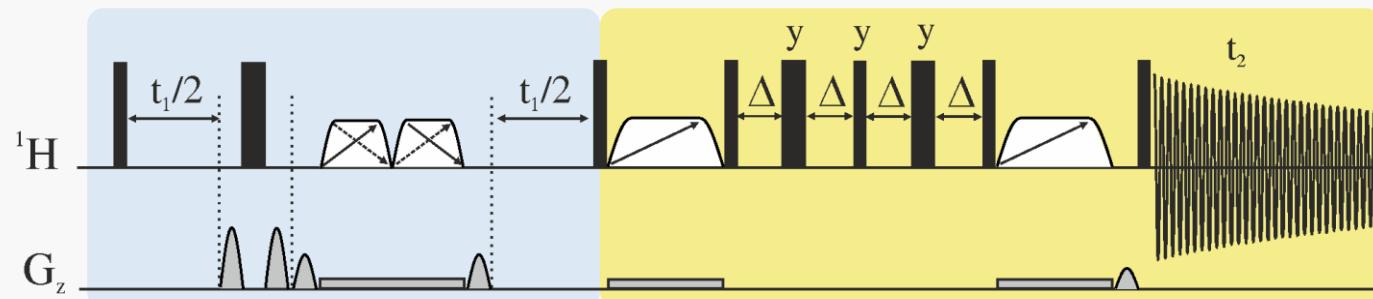
CLIP-COSY (ph)



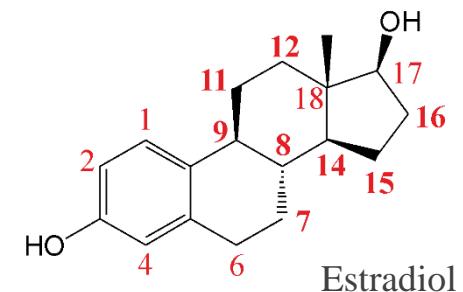
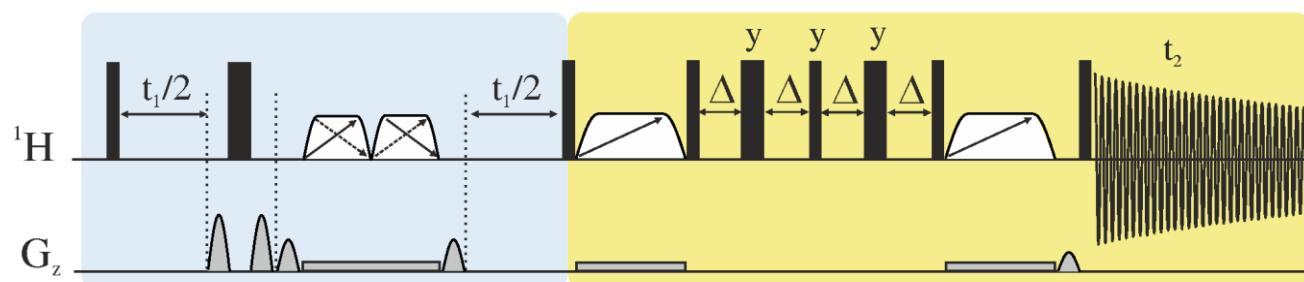
PSYCHE-CLIP-COSY

 F_2 -CLIP-COSY-PSYCHE

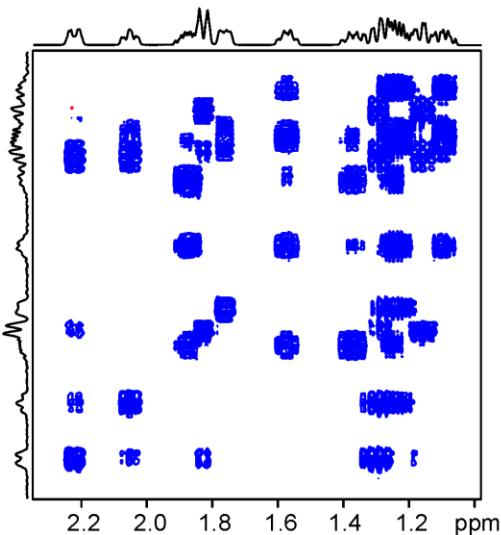
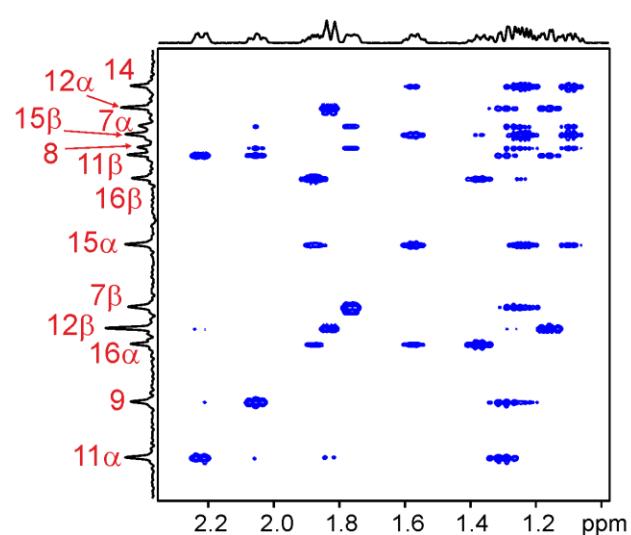
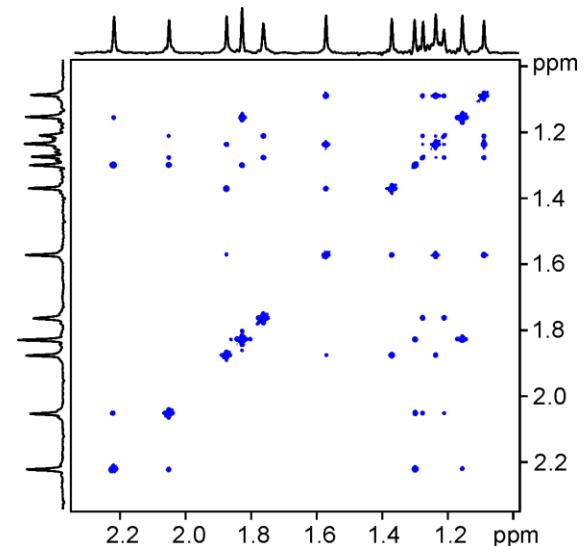
M. R. M. Koos, G. Kummerlöwe, L. Kaltschnee, C. M. Thiele, B. Luy, *Angew. Chem. Int. Ed.* **2016**, 55, 765.

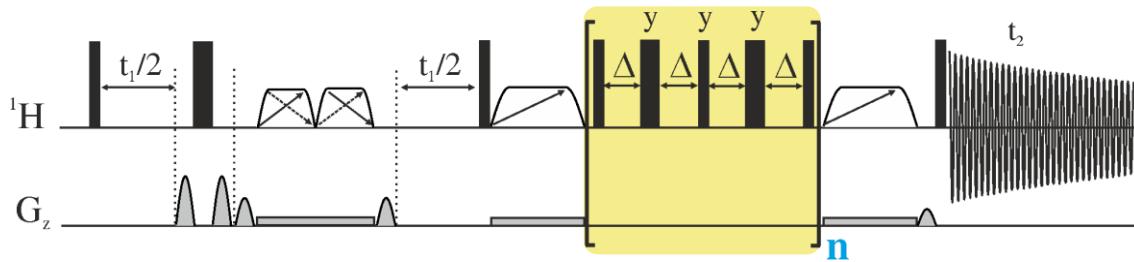
 F_1 -PSYCHE-CLIP-COSY

Unpublished

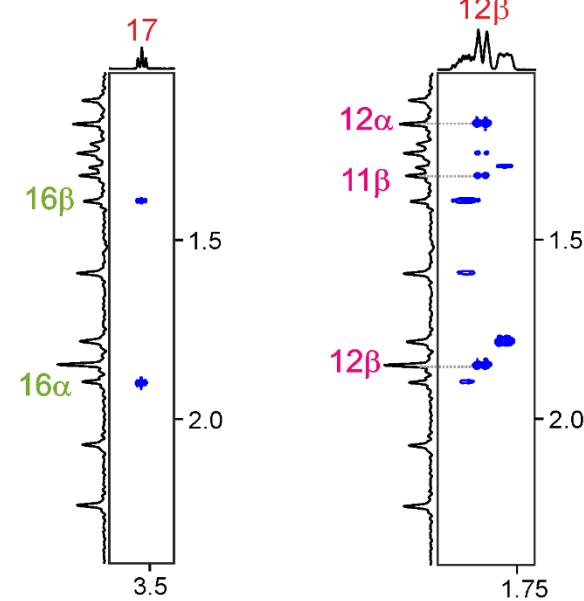
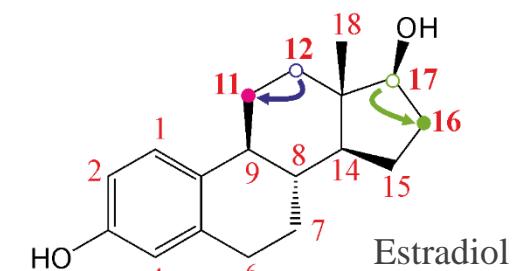
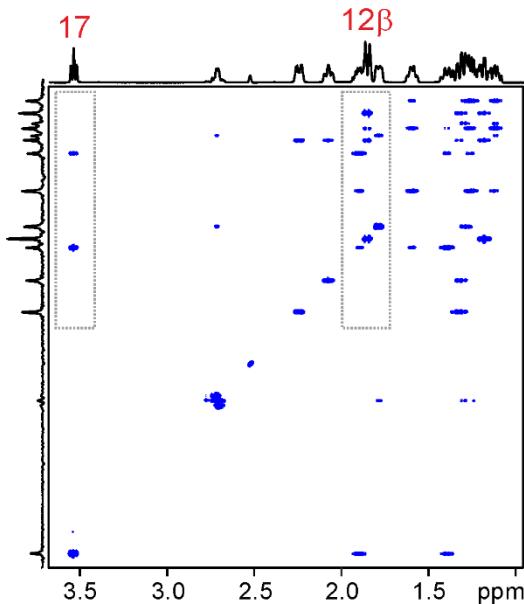
F_1 -PSYCHE-CLIP-COSY

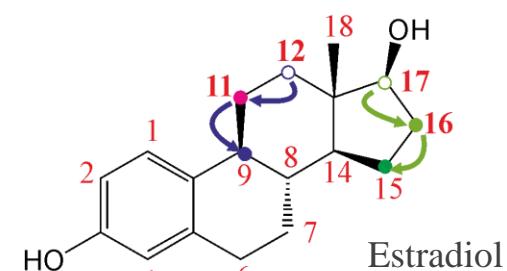
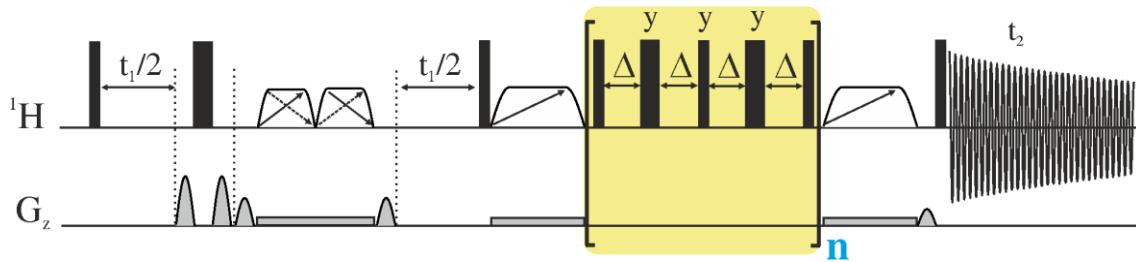
CLIP-COSY

 F_1 -PSYCHE-CLIP-COSY F_1 -PSYCHE-CLIP-COSY
+ Covariance

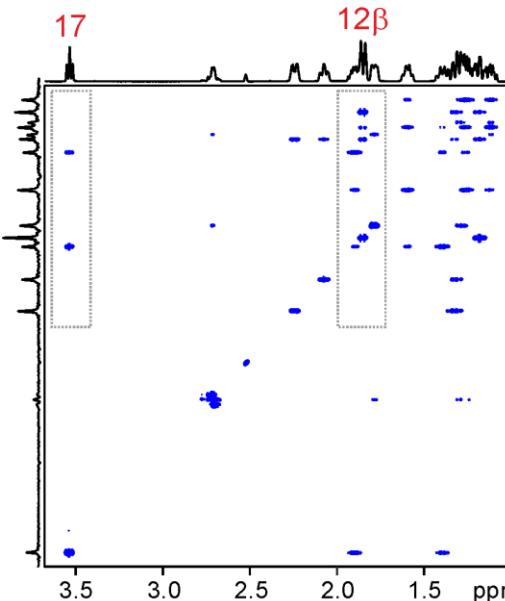
F_1 -PSYCHE-CLIP-COSY & RELAY F_1 -PSYCHE-CLIP-COSY

[n=1]

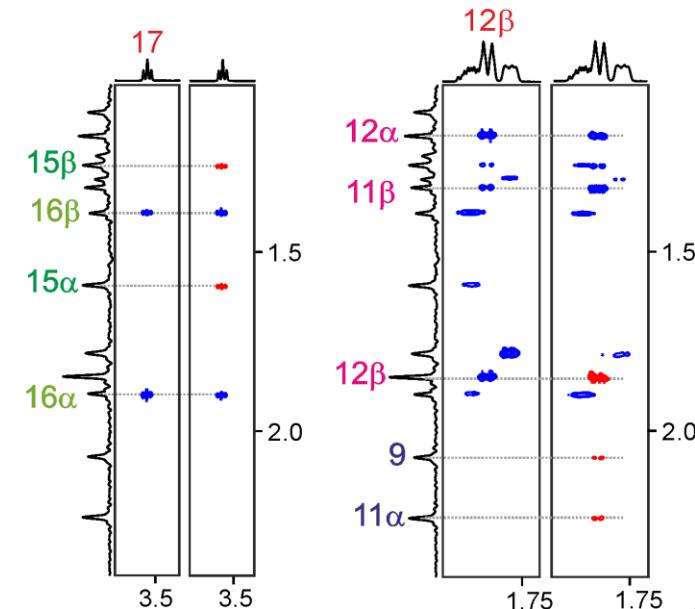
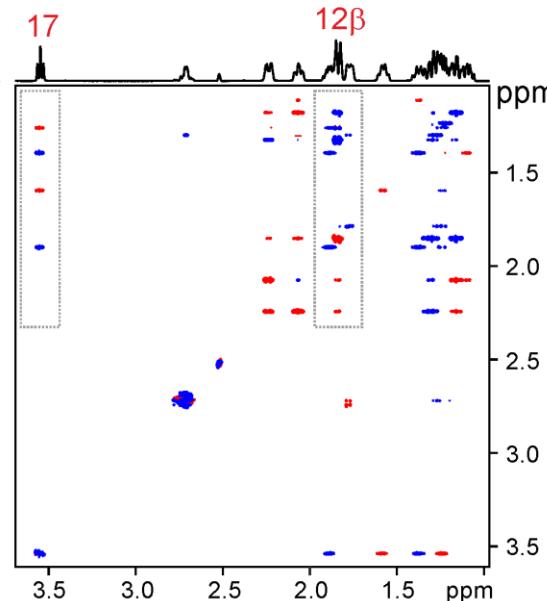


F_1 -PSYCHE-CLIP-COSY & RELAY

F_1 -PSYCHE-CLIP-COSY
[n=1]



F_1 -PSYCHE-RELAY
[n=2]



Summary & Conclusions

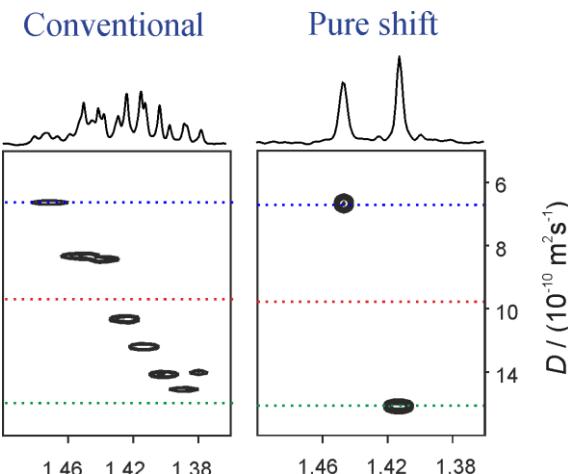
PSYCHE pure shift NMR



Spectral simplification
Higher signal resolution
Reduced signal overlap

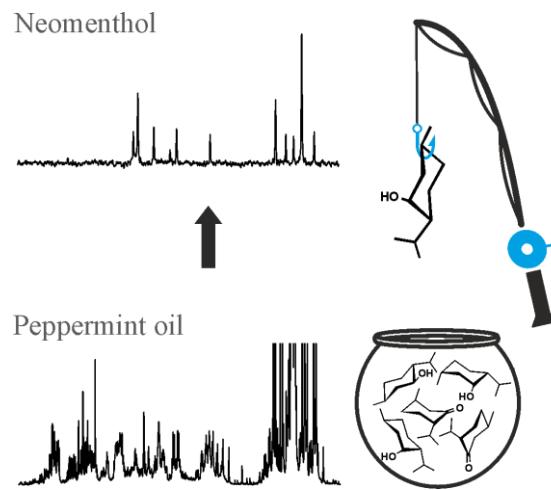
Mixture analysis
Structure determination

Oneshot-PSYCHE DOSY



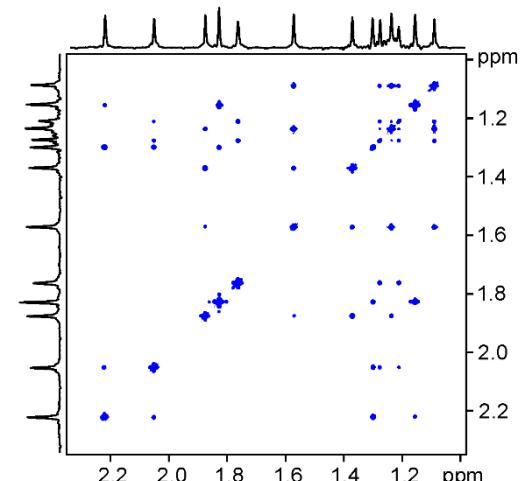
Minimises misleading peaks
Correct diffusion coefficients

Selective 1D PSYCHE-TOCSY



Pure shift spectra of individual components
in intact complex mixtures

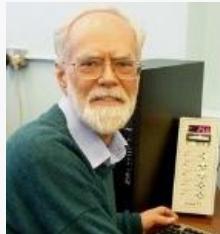
F_1 -PSYCHE-CLIP-COSY & RELAY



Combination with covariance processing
Ultra-high resolution phase-sensitive COSY

Acknowledgments

Prof. Gareth A. Morris



Dr. Mathias Nilsson



Dr. Mohammadali Foroozandeh



Guilherme Dal Poggetto



Dr. Ralph W. Adams



Dr. Peter Kiraly



Pinelopi Moutzouri



Aaron Hernandez-Cid



**Thank you very much
for your attention**

