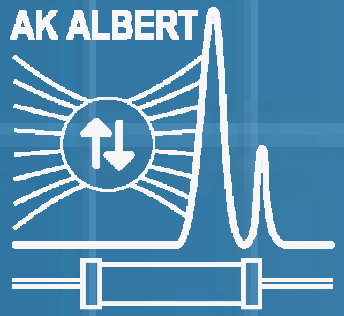
About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

About OMICS Group Conferences

OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Pharma scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bangalore and Mumbai.



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UNIVERSITÄT
TÜBINGEN



Improving the Understanding of the Properties and Retention Behavior of Chemically Bonded Phases Employing NMR Spectroscopy

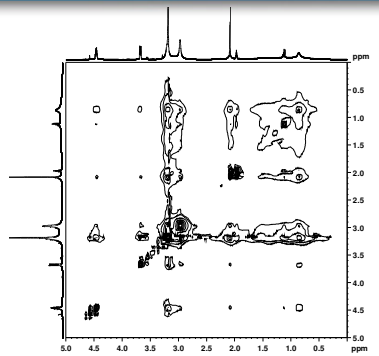
Klaus Albert, Volker Friebolin, Silvia Marten, and Helen Yeman

University of Tübingen, Institute of Organic Chemistry,
Auf der Morgenstelle 18, D-72076 Tübingen
Germany

Research Areas of the Group of Prof. Klaus Albert, University of Tübingen

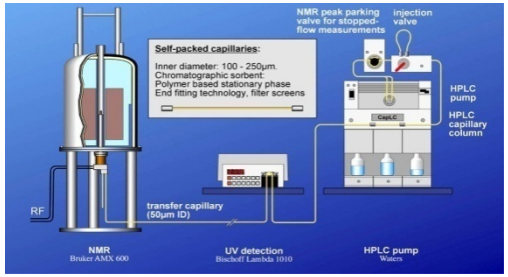
NMR Spectroscopy

Liquid-state
Solid-state
Suspended-state

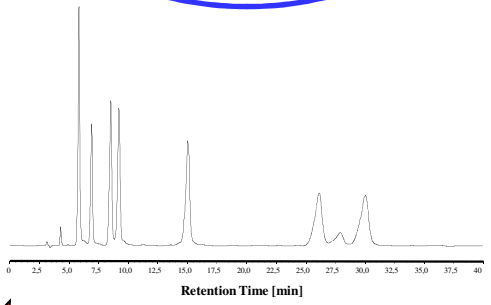


Chromatography

Synthesis and characterization of new materials for extraction, enrichment and separation of complex mixtures of bioactive compounds

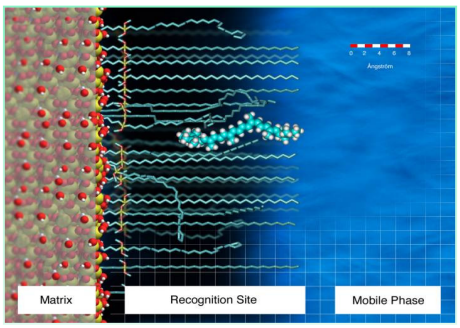


PHYSICAL ORGANIC CHEMISTRY



Hyphenated Techniques

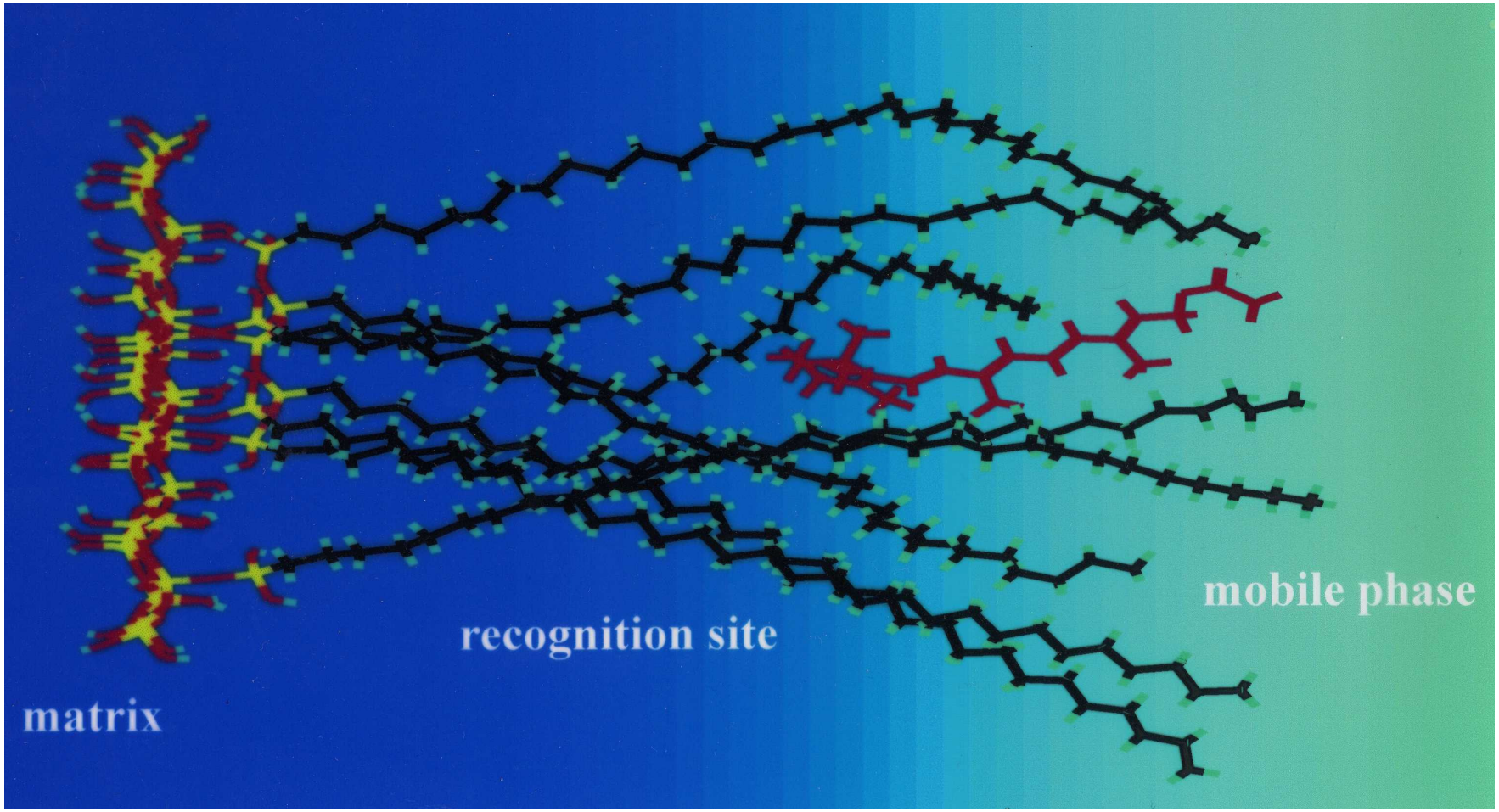
LC-NMR
LC-MS
GC-NMR
GC-MS



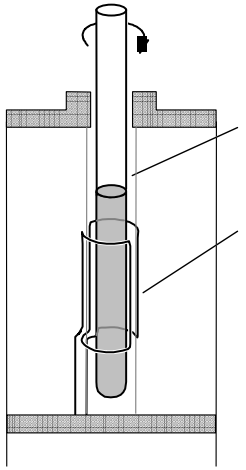
Molecular Recognition

Towards an understanding of the chromatographic separation process

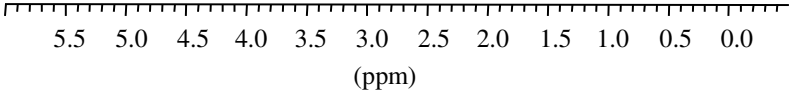
Molecular Recognition NMR Studies

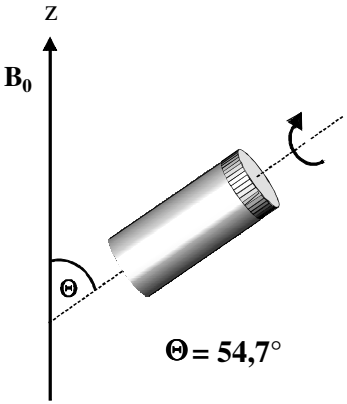


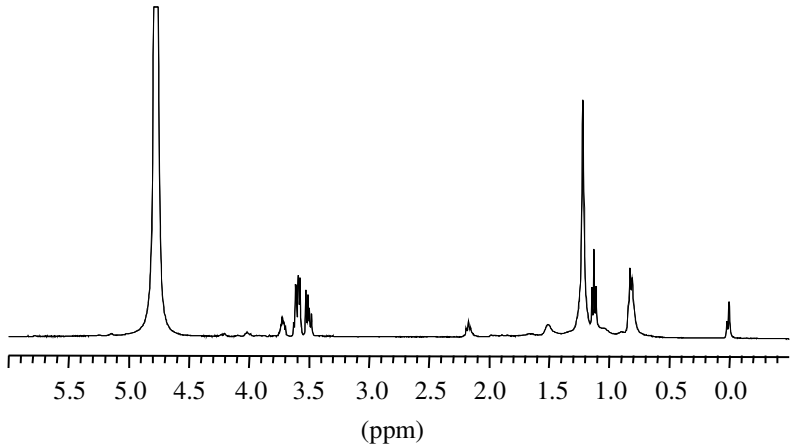
Comparison of ^{1}H HR-MAS and ^{1}H HR-NMR Spectroscopy







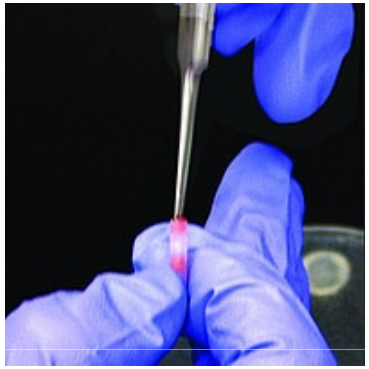




Practical Set-up



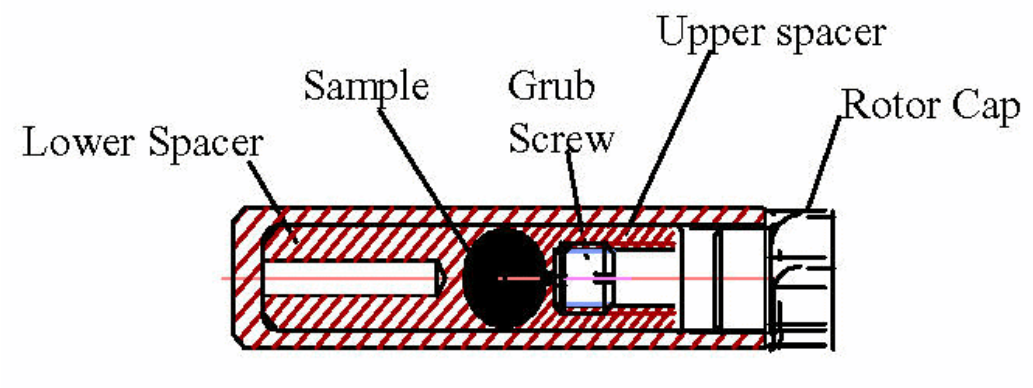
4mm HR-MAS Rotor (ZrO_2)



Rotor filling

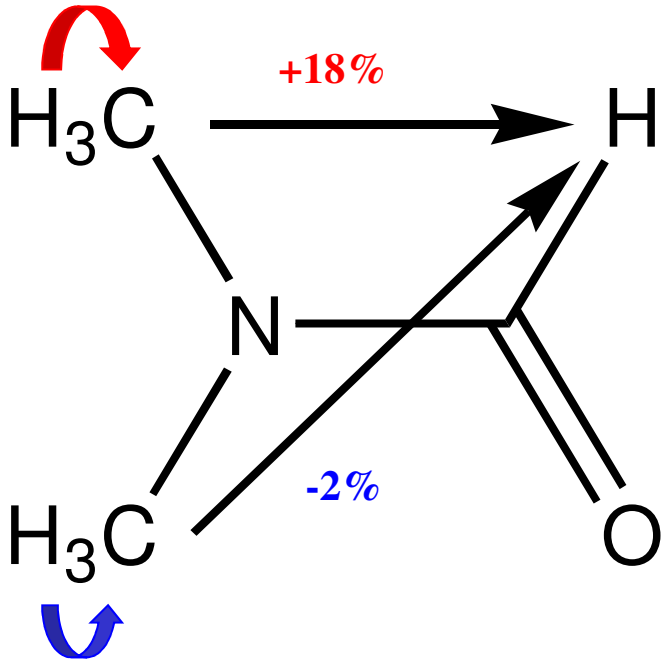


Upper Probe head chamber with MAS Stator in Magic Angle Position (54.74°)



http://www.bruker-biospin.com; http://nmr.magnet.fsu.edu

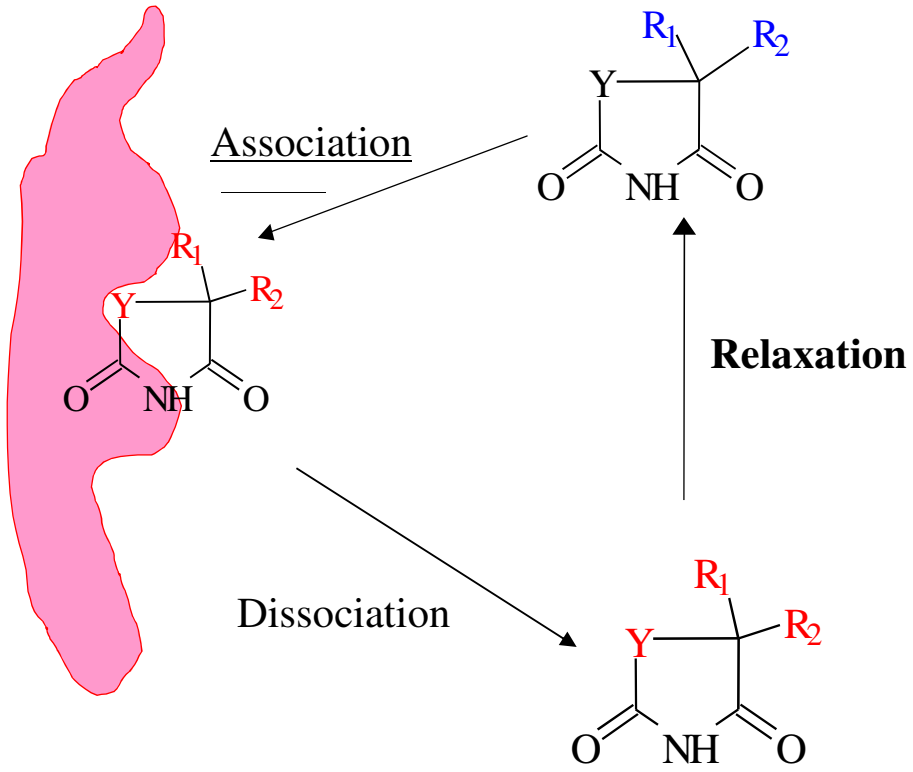
Transferred - Nuclear-Overhauser-Effect



Basic idea of the transferred-NOE:

To use the chemical exchange between the bound and unbound nuclei to obtain information by cross relaxation processes between the free and bound state respectively.

Transferred NOE (trNOE)



Example

R_1 = Methyl

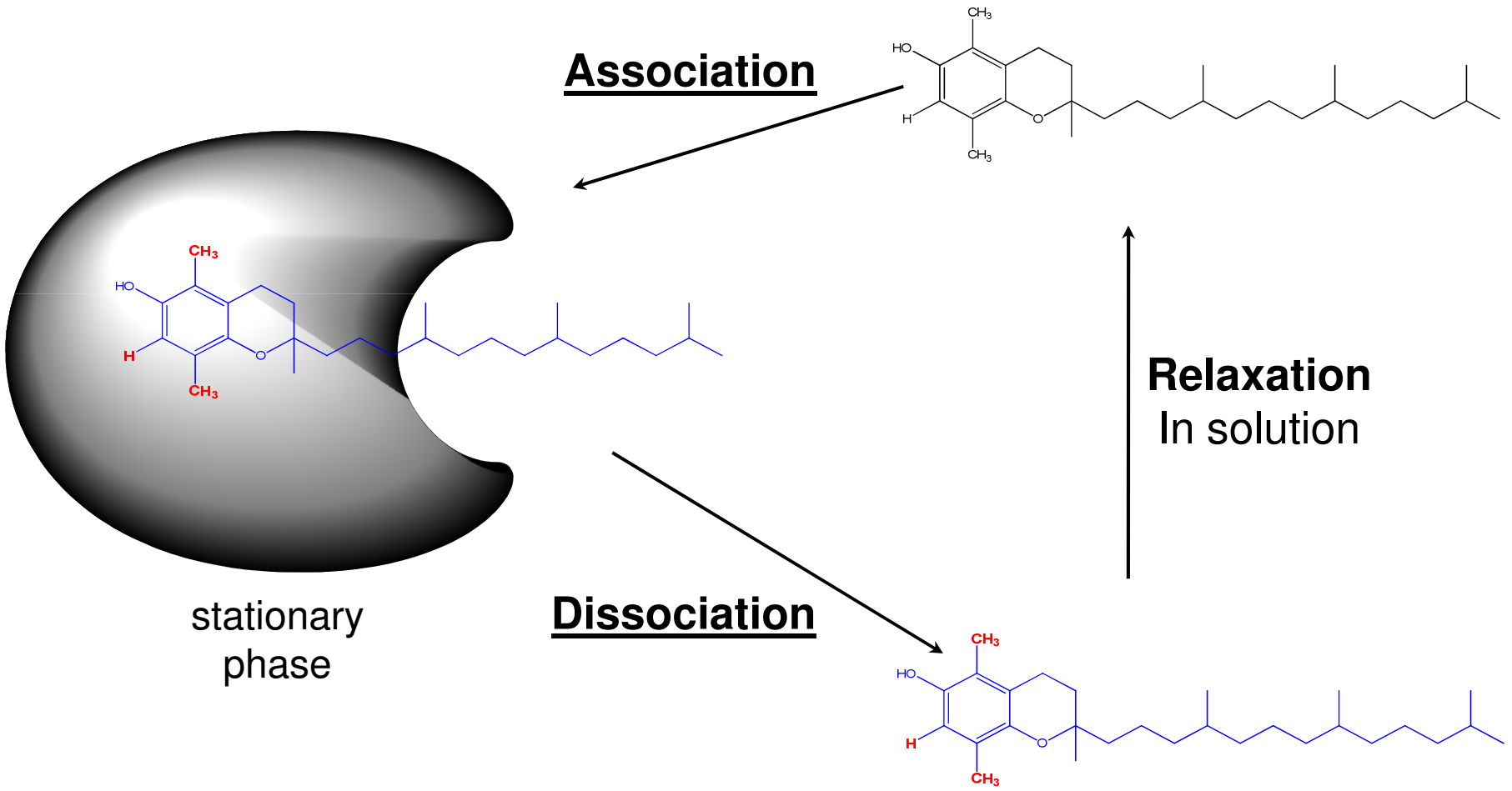
R_2 = Phenyl

Y = CH_2
Methylphenylsuccinimide

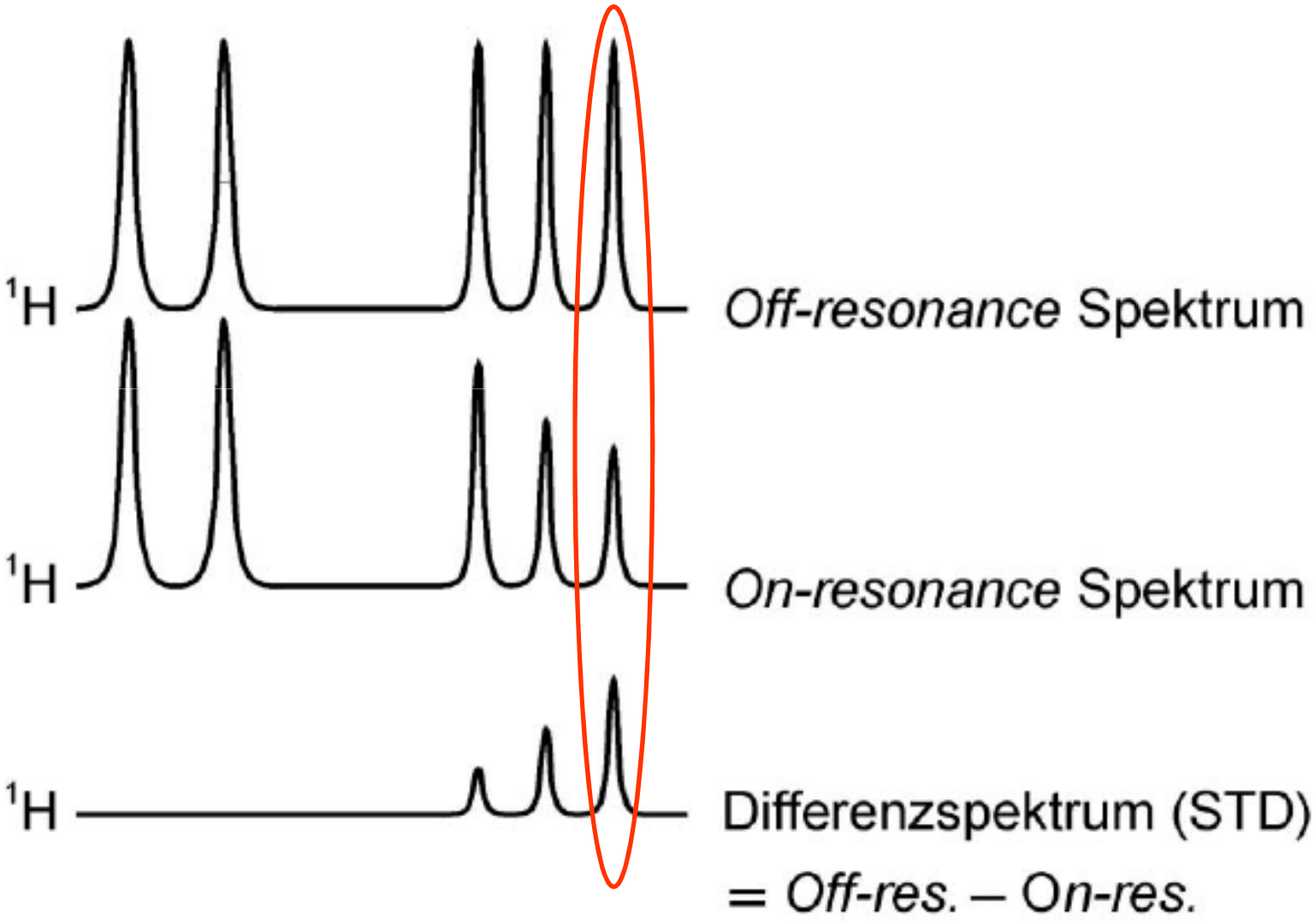
Y = NH
Methylphenylhydantoine

H. Händel, E. Gesele, K. Gottschall, K. Albert,
Angew. Chem. Int. Ed.. **2003**, 42, 438-442.

Molecular Recognition by NMR Spectroscopy



Saturation-Transfer-Difference-NMR-Spectroscopy (STD)



B. Mayer, T. Peters, *Angew. Chem.* **2003**, 115, 890-918.

Interaction Mechanism of Chromatography

Investigation of the Strength of Interaction between Analyte and Stationary Phase due to:

Structural Changes of the Stationary Phase

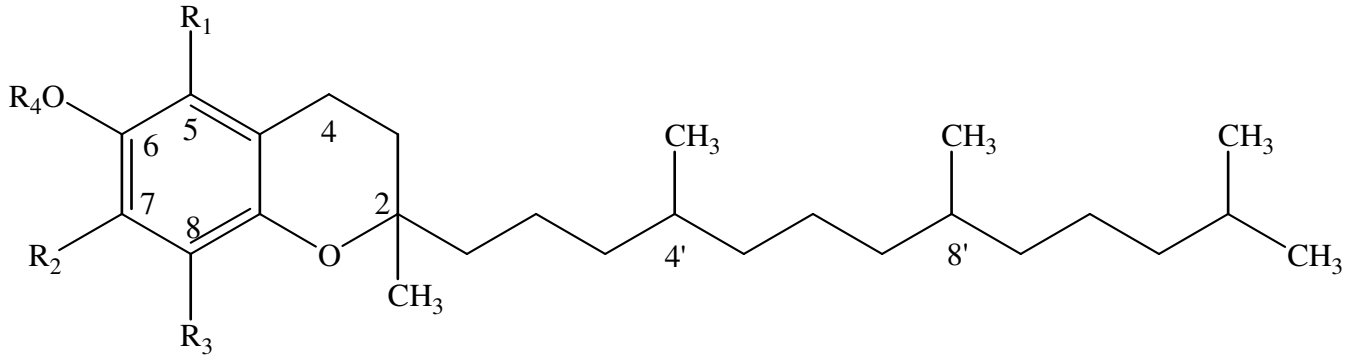
Structural Changes of the Analyte

Changes in the Solvent Composition

Separation of Tocopherol Homologues

S. Schauff, V. Friebolin, M.D. Grynbaum, C. Mayer, K. Albert, *Anal. Chem.* **2007**, 79, 8323-8326.

Tocopherol Homologues (Vitamin E)

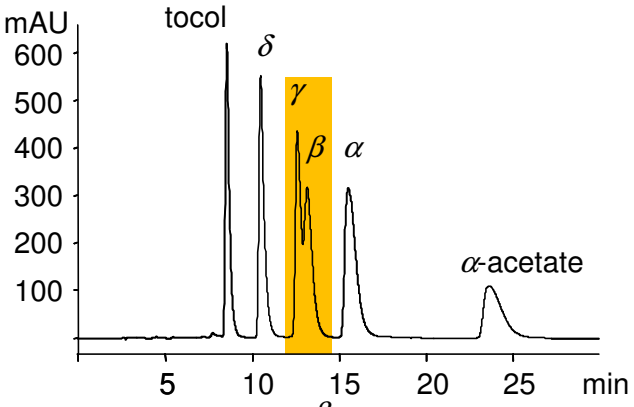


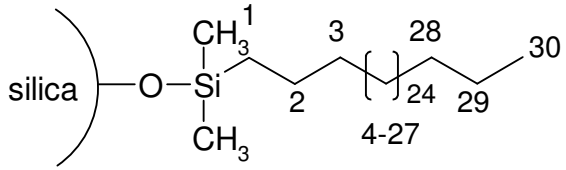
Homologue:	**R_1**	**R_2**	**R_3**	**R_4**
tocol	-H	-H	-H	-H
δ-tocopherol	-H	-H	$-CH_3$	-H
γ-tocopherol	-H	$-CH_3$	$-CH_3$	-H
β-tocopherol	$-CH_3$	-H	$-CH_3$	-H
α-tocopherol	$-CH_3$	$-CH_3$	$-CH_3$	-H
α-tocopherol acetate	$-CH_3$	$-CH_3$	$-CH_3$	$-COCH_3$

Vitamin E is a potent natural antioxidant that inhibits lipid oxidation and quenches reactive singlet oxygen.

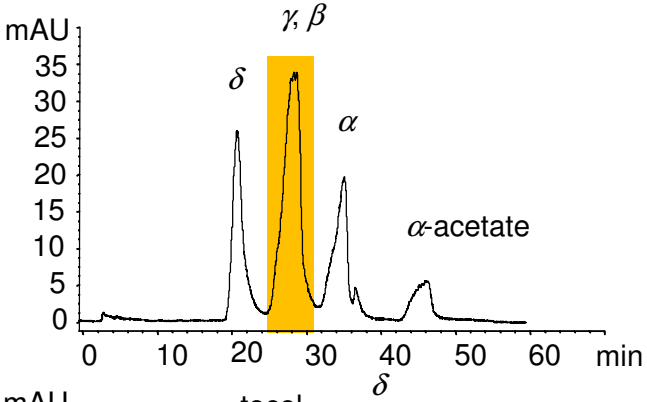
HPLC chromatograms of tocopherol homologues on (a) C_{30} phase (b) PEAA phase and (c) C_{18} phase.

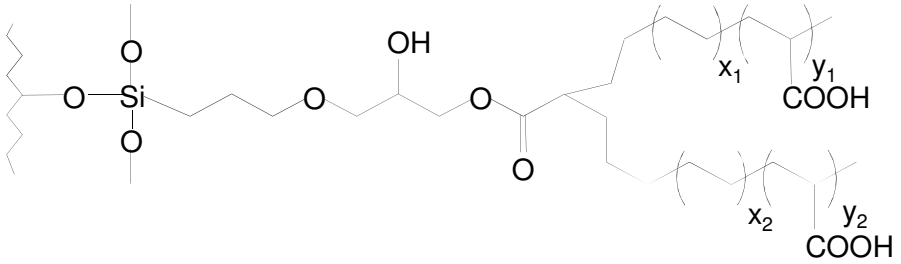
a)



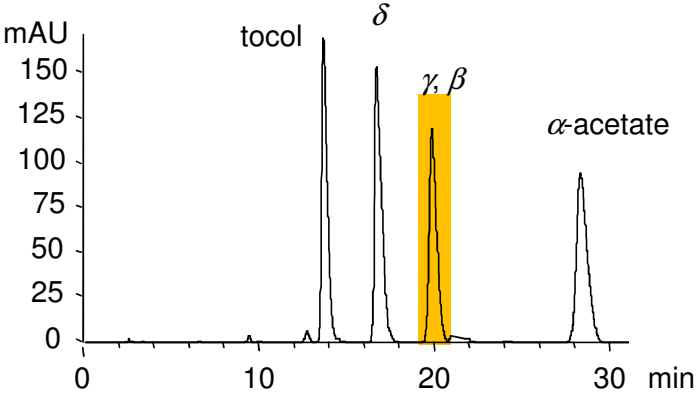


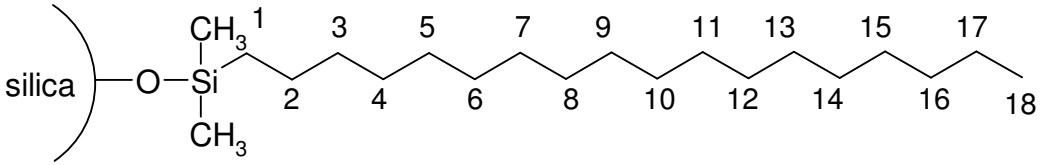
b)



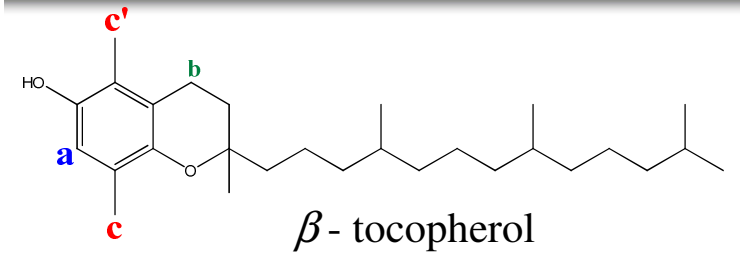


c)

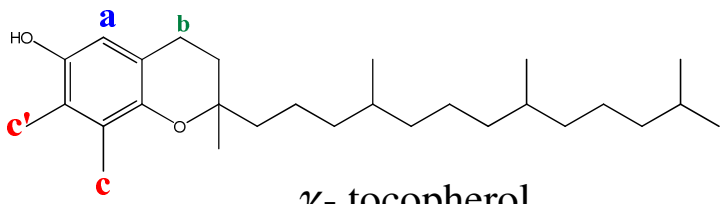




^{1}H HR/MAS-NMR spectra of β– and γ- tocopherol

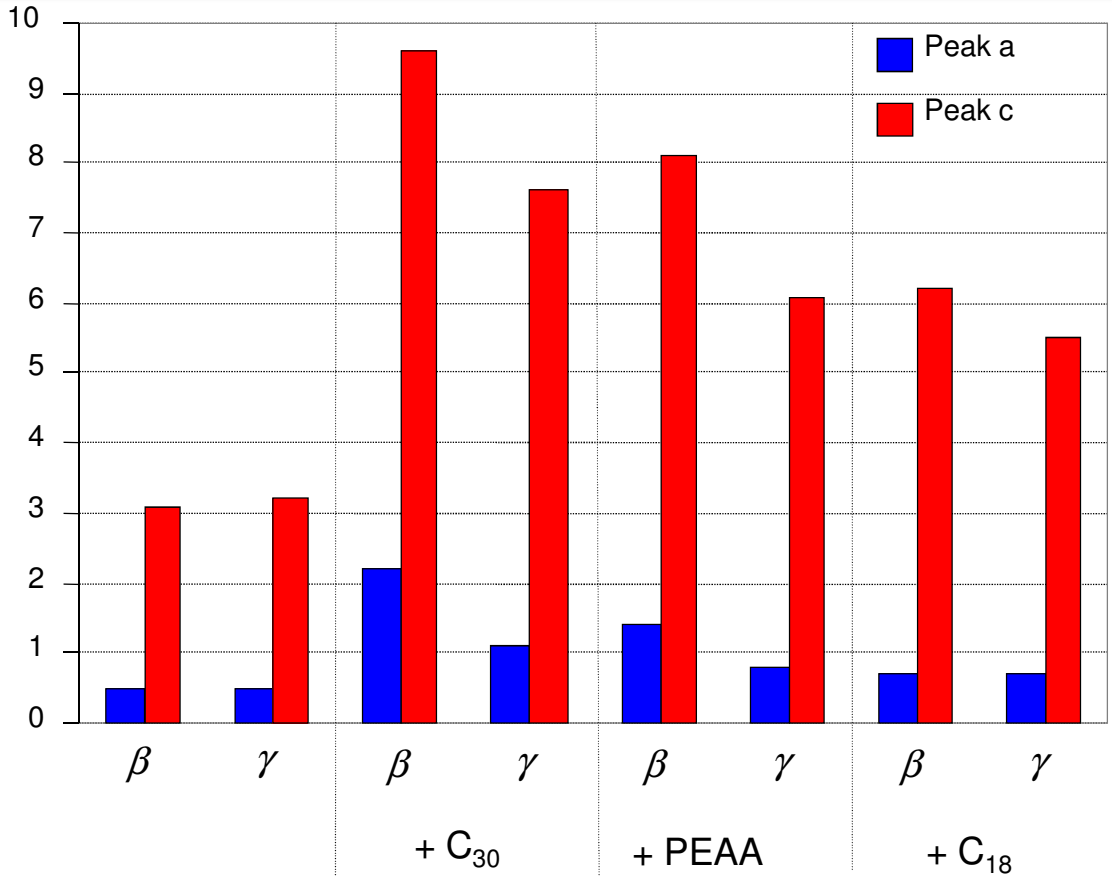


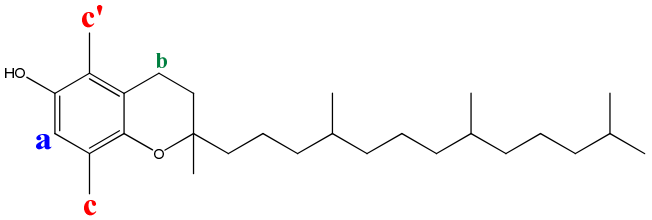
β- tocopherol



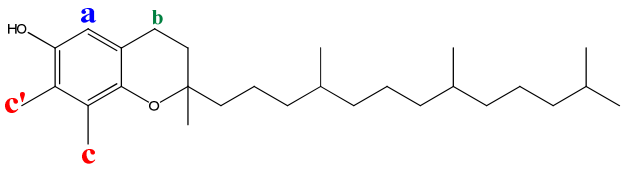
γ- tocopherol

Bar diagram reflecting the measured peak integrals of peak a and c from ^{1}H suspended-state STD HR/MAS NMR spectra





β- tocopherol

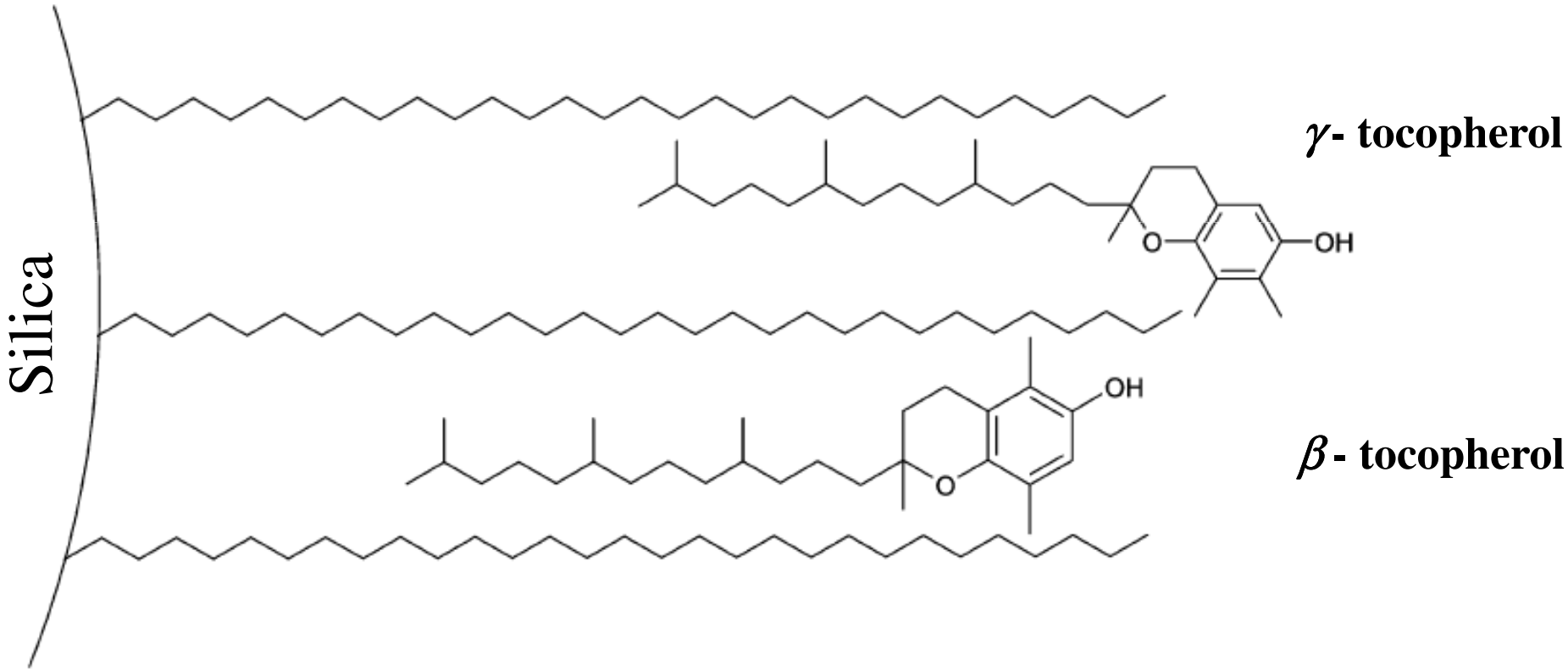


γ- tocopherol

BLUE represents intensity of signal a

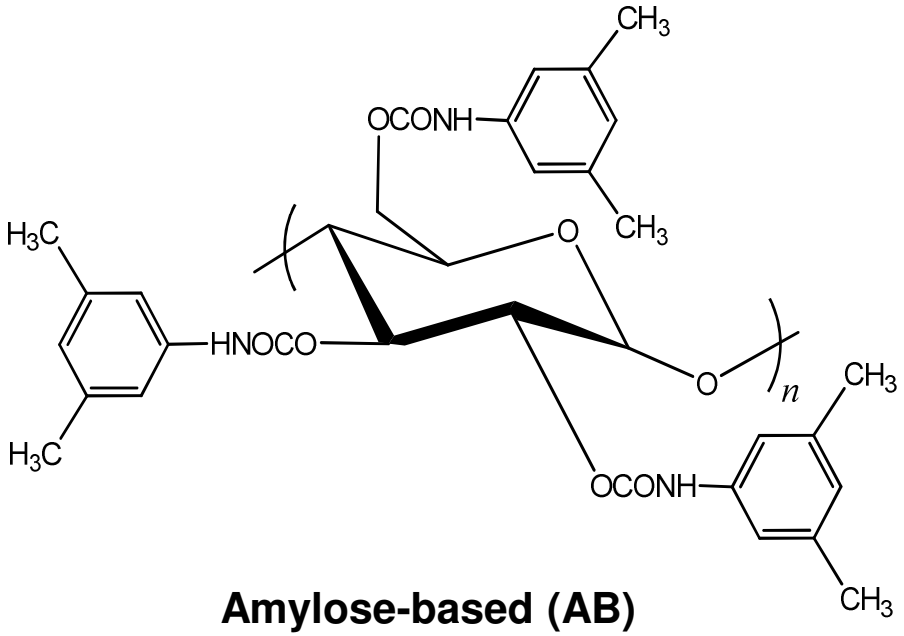
RED represents intensity of signal c,c'

Schematic picture of (a) γ-tocopherol and (b) β-tocopherol penetrating between the C_{30} alkyl chains

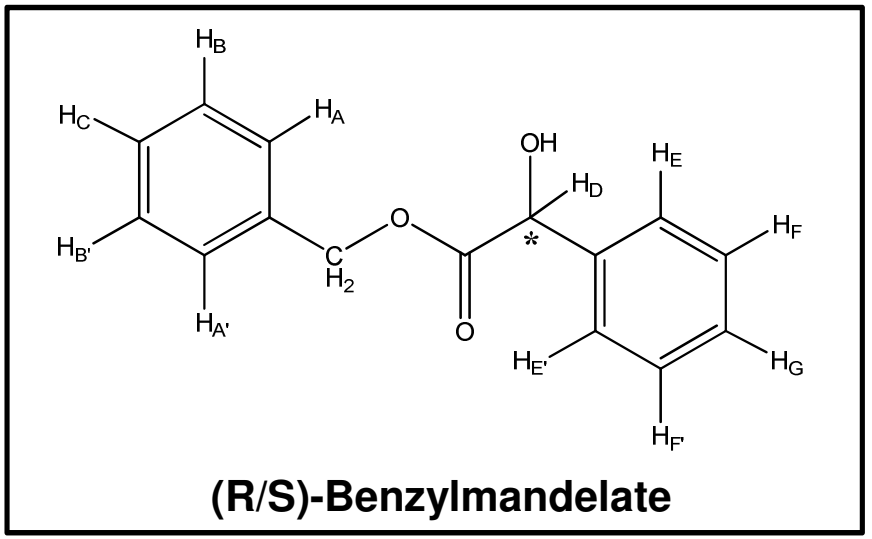


Chiral Recognition

Investigated System

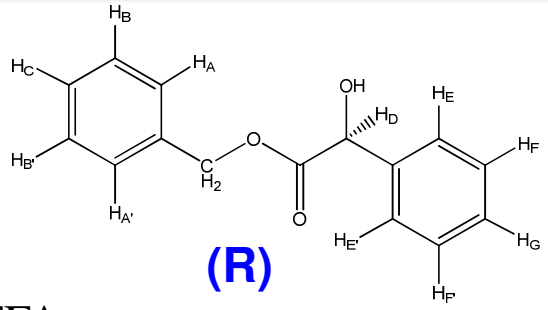


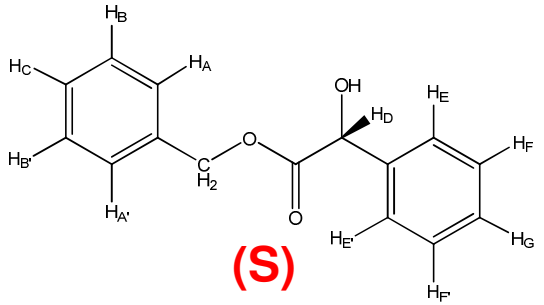
Amylose-based (AB)
Chiral Stationary Phase



(R/S)-Benzylmandelate

HPLC chromatogram of (R)- and (S)-Benzylmandelate on the amylose-based chiral stationary phase

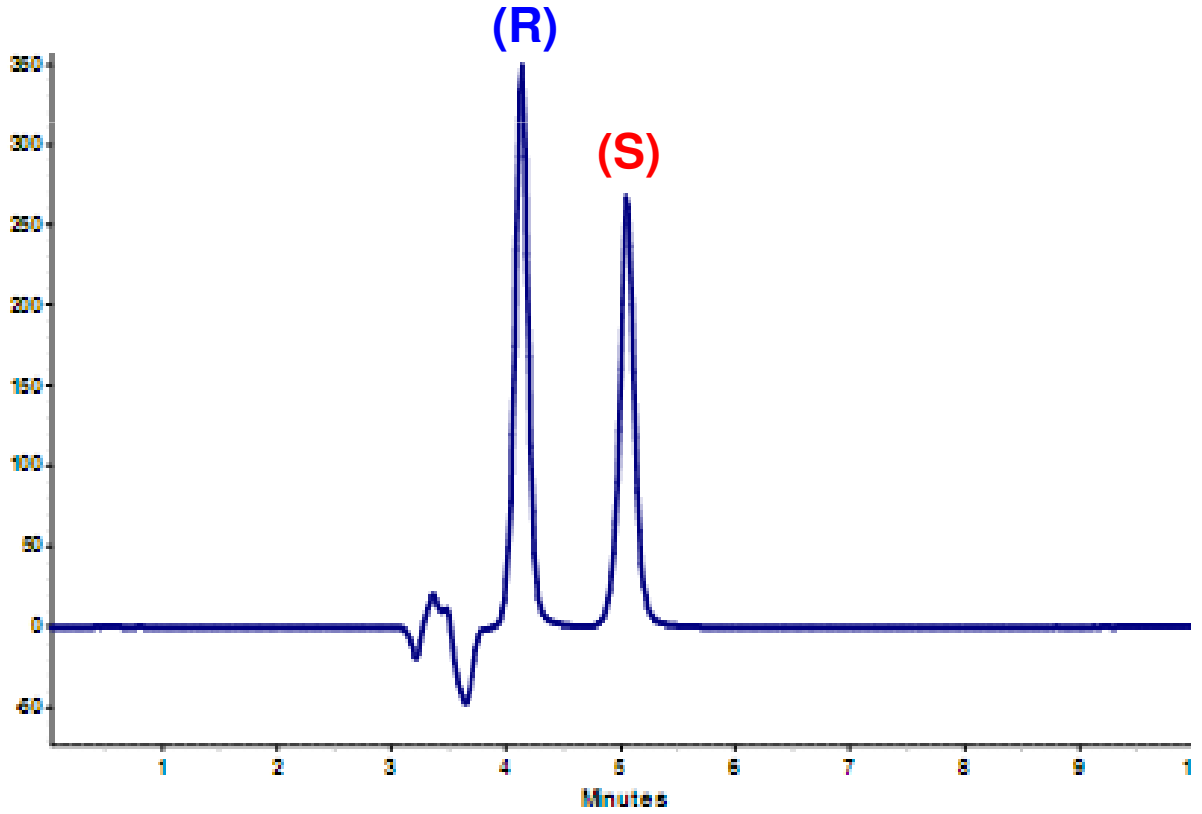




Eluent: Methanol + 0.1 % TFA
Flow rate: 1.0 ml/min (isocratic)
Temperature: 25 °C
10 µl injection

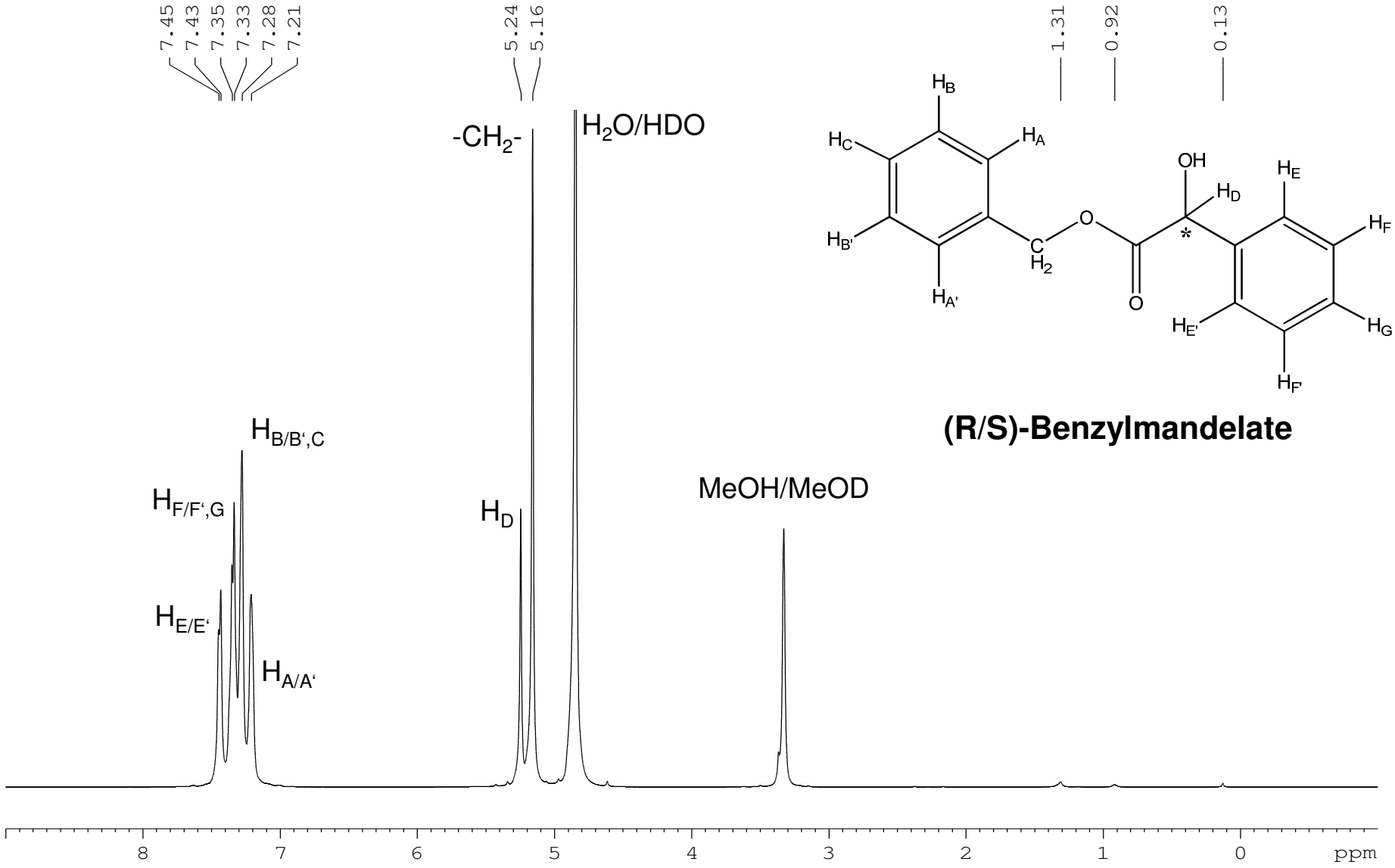
k´ (R) = 0.28
k´ (S) = 0.42
} α = 1.50

UV-Detection at λ=210 nm



^{1}H HR/MAS-NMR spectrum of (R/S)-Benzylmandelate together with the chiral stationary phase material

(Methanol-d4 acidified with 0.1% dTFA)



Spin-Lattice (T_1) Relaxation Time Measurements

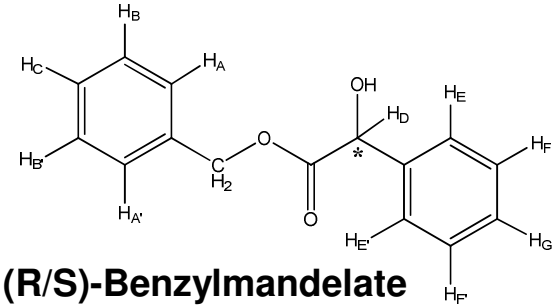
Signal assignment	Chemical Shift [ppm]	R (free molecule) T_1 [s]	R & CSP T_1 [s]	S & CSP T_1 [s]
$H_{E/E'}$	7.44	**3.15**	**3.00**	**2.52**
$H_{F/F',G}$	7.34	**2.99**	**2.99**	**2.47**
$H_{B/B',C}$	7.28	**3.60**	**3.10**	**2.69**
$H_{A,A'}$	7.21	**3.49**	**3.30**	**2.63**
H_D	5.24	**3.62**	**3.30**	**2.71**
$-CH_2-$	5.16	**2.00**	**2.08**	**1.80**

Estimated error: ± 0.1 s

NOESY vs. trNOESY
(R/S)-Benzylmandelate & Chiral Stationary Phase

NOESY

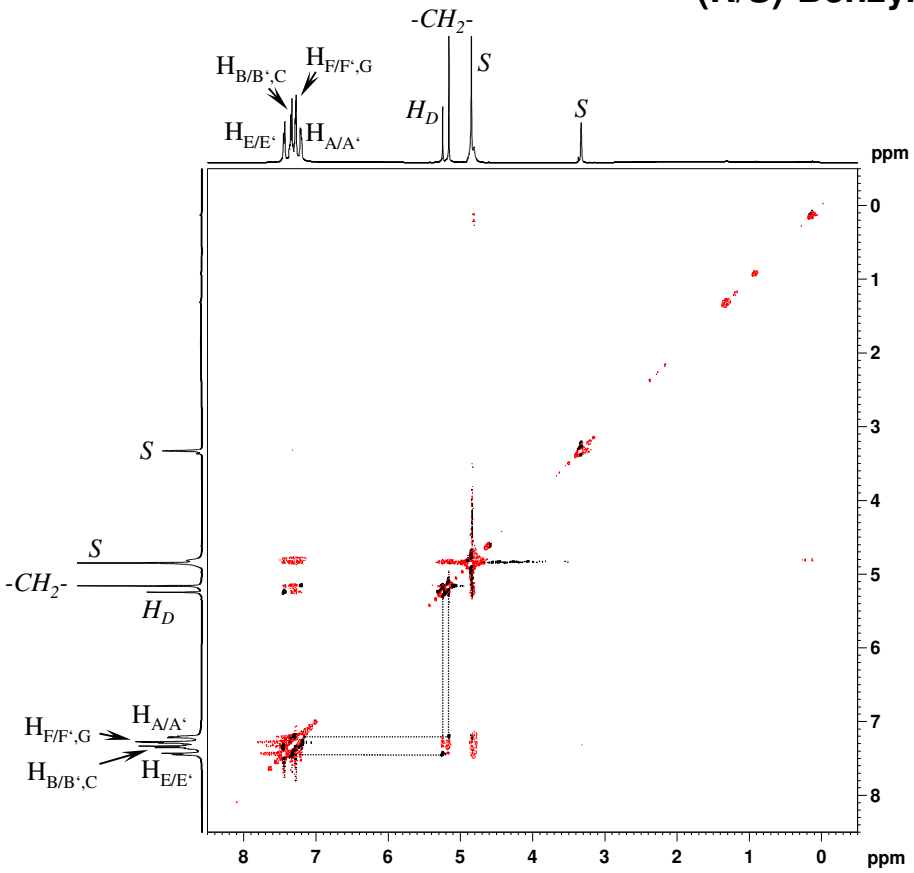
τ_m: 2 s

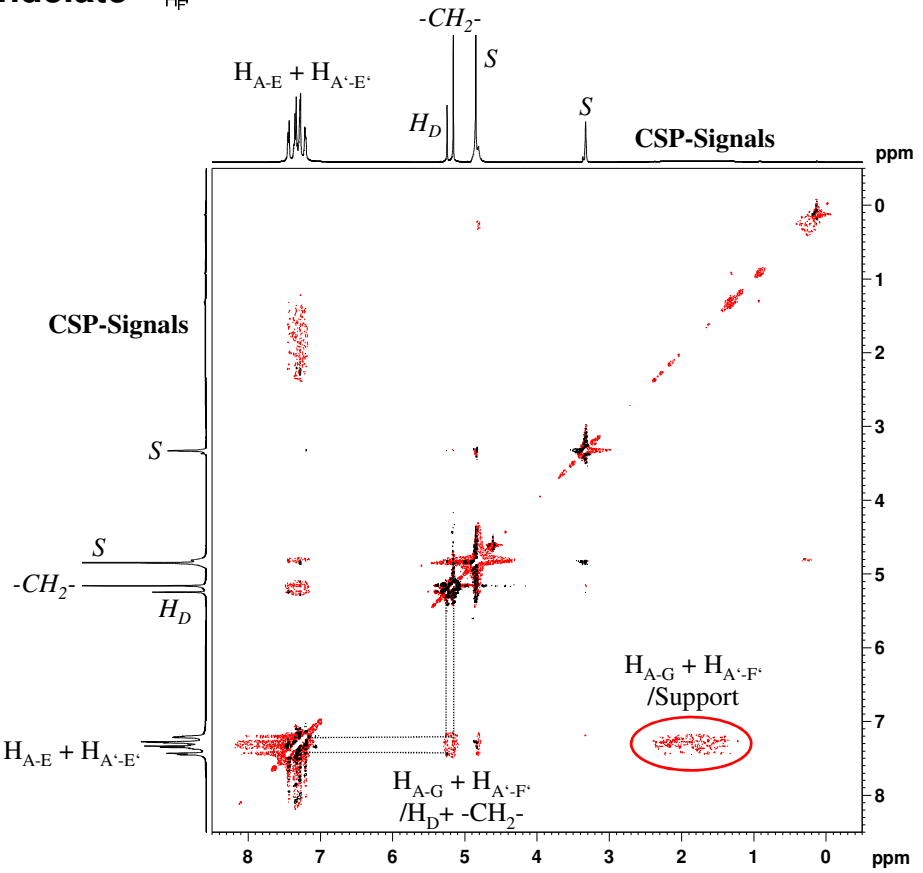


(R/S)-Benzylmandelate

trNOESY

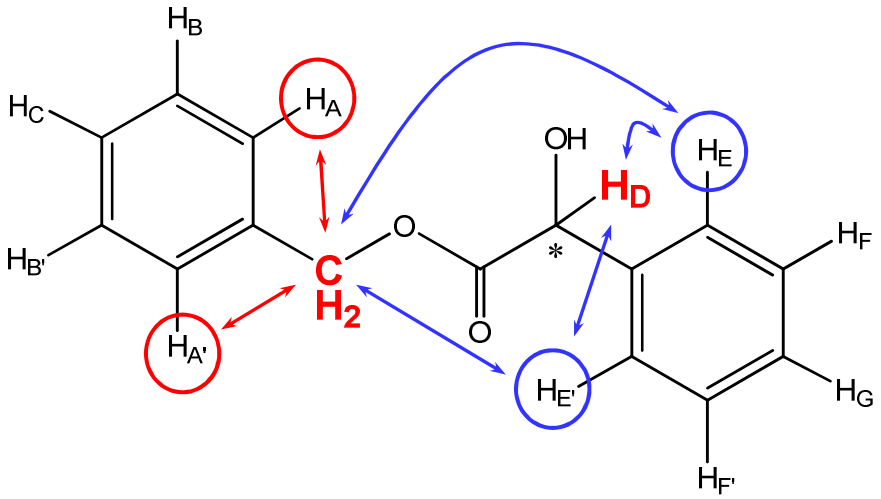
τ_m: 200 ms





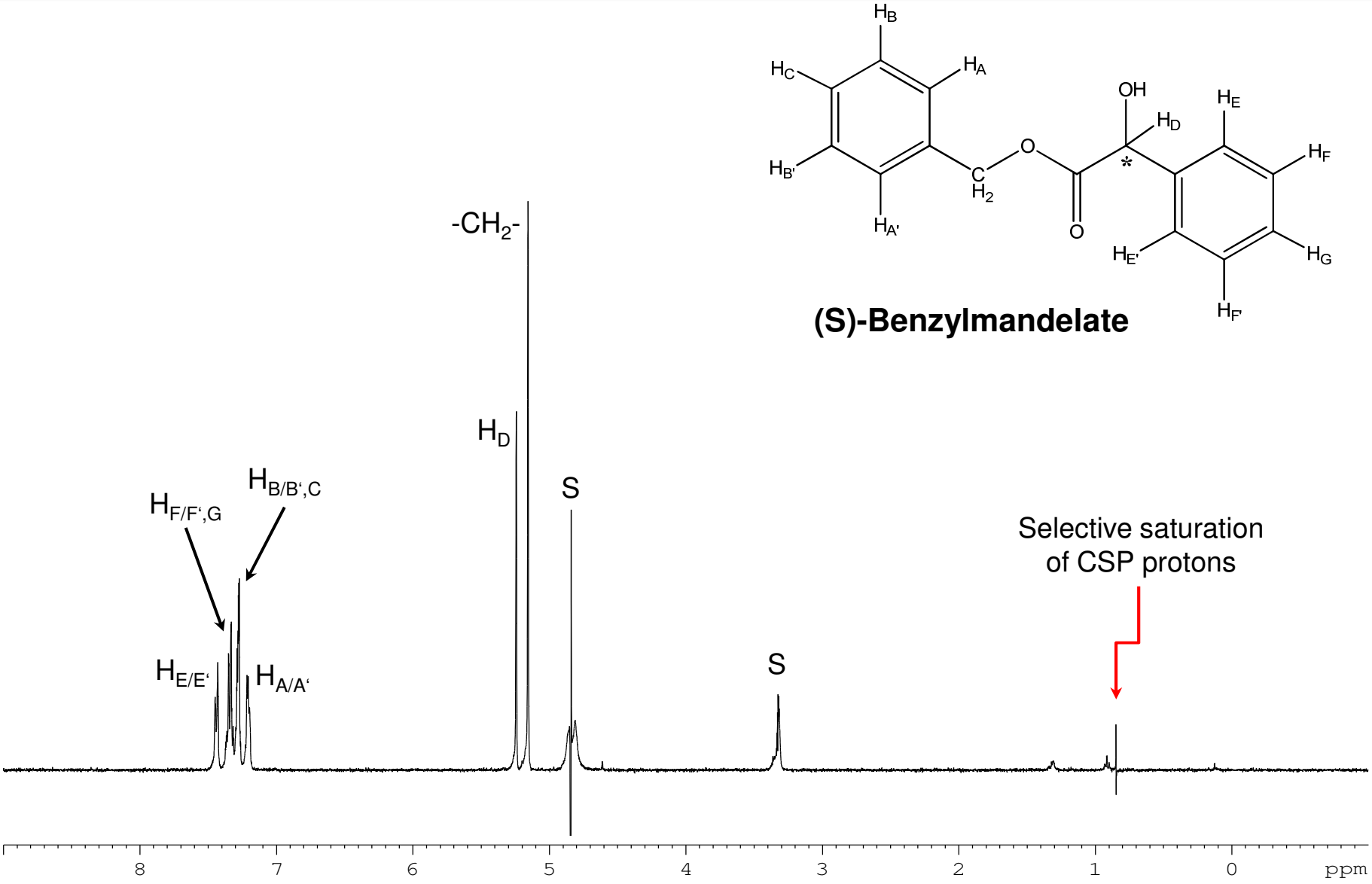
NOESY / trNOESY

(R/S)-Benzylmandelate & Chiral Stationary Phase

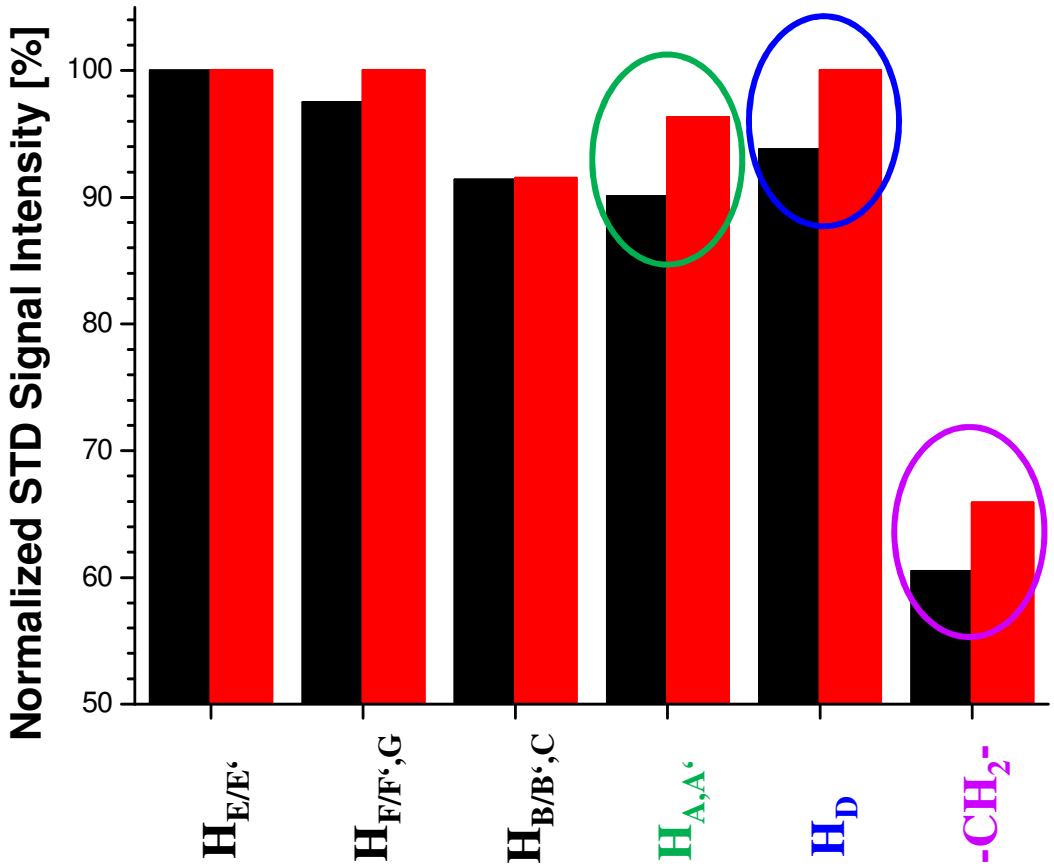


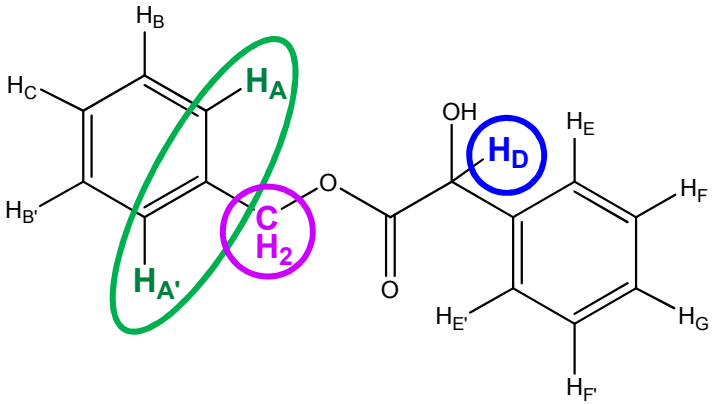
	NOESY [Integral x 10^{-2}]				trNOESY [Integral x 10^{-2}]			
Cross-Peaks	**R/S**	**R/S & Silica**	**R & CSP**	**S & CSP**	**R/S**	**R/S & Silica**	**R & CSP**	**S & CSP**
$H_{E/E'}$ - H_D	-0.06	+2.5	-0.8	-1.0	-0.3	+0.3	-3.1	-2.8
$H_{A/A'}$ – CH_2	+2.2	+ 2.0	-2.4	-2.3	+0.2	-0.02	-2.6	-2.6
Phenyl-Support	-	-	-	-	-	-	**-7.7**	**-15.4**

Representative STD ^{1}H HR/MAS NMR spectrum of (S)-Benzylmandelate and the amylose-based chiral stationary phase

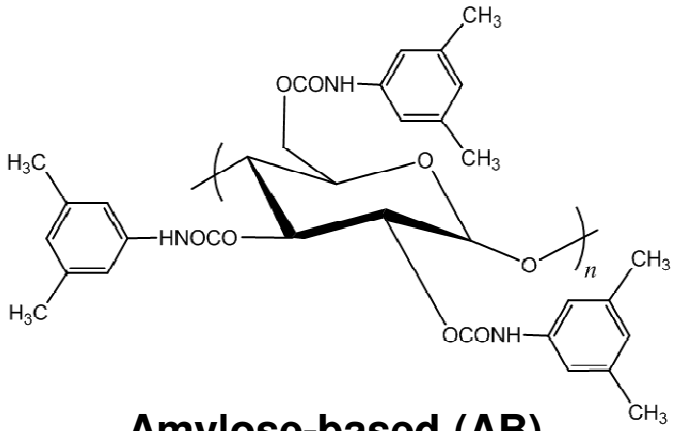


Saturation transfer of single protons in relation to the OFF-Resonance ^{1}H HR/MAS NMR spectrum





(R/S) Benzylmandelate



Amylose-based (AB)
Chiral Stationary Phase



Conclusion

NMR spectroscopy with its different measurement techniques is an extreme versatile tool in physical organic chemistry deriving structural and dynamic information of organic molecules.

Acknowledgements

EBERHARD KARLS
UNIVERSITÄT
TÜBINGEN



Coworkers

Dr. Manuela Gradl, Dr. Simon Green, Dr. Marc David Grynbaum, Dr. Heidi Händel, Berthold Maier, Dr. Christoph Meyer, Phong Thu Nguyen, Dr. Tim Nicholson, Dr. Siri Schauff, Brigitte Schindler, Paul Schuler, Dr. Urban Skogsberg, Dr. Lisa Steinhauser, Dr. Norbert Welsch

Cooperations

Prof. Dr. Maria Matyska-Pesek and Prof. Dr. Joseph J. Pesek
Department of Chemistry, San Jose State University, CA 95192, USA

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Tübingen

