



Supporting Information

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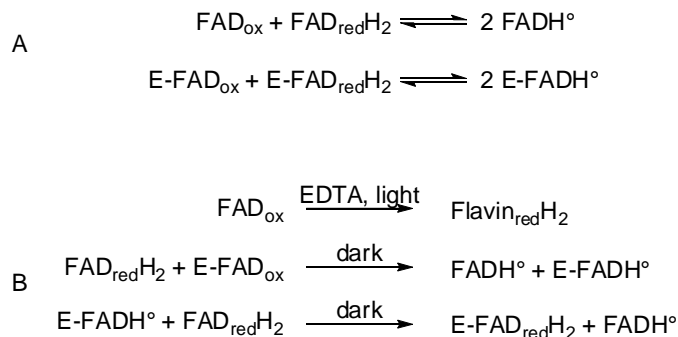
69451 Weinheim, Germany

## A light-driven stereoselective biocatalytic oxidation

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### Electron-transfer reactions during the reduction of enzyme-bound FAD: [Ref. 5b]



A) The equilibrium of the synproportionation reaction of free FAD lies on the left side, whereas the equilibrium of the enzyme bound FAD lies on the right side.

B) The reduced free flavin subsequently serves as electron donor for the reduction of the enzyme bound FAD.

### Preparation of PAMO:

PAMO-P3 was expressed in *E. coli* TOP10 and purified as described elsewhere [Ref. 7a]

**Reagents were obtained from the following suppliers used as received:** EDTA (Applichem), Tris (Applichem), NADP<sup>+</sup> (Julich Chiral Solutions), FAD (Sigma) and substrate (Sigma or Fluka).

**100 mM stock solutions of substrates in acetonitrile were used.**

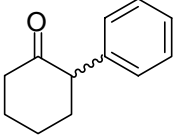
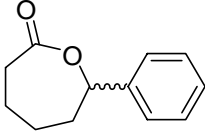
**Product standards for GC analysis were prepared by *m*CPBA-oxidation.**

## GC-method for 2-phenyl cyclohexanone

### Achiral method:

Instrument : AT 6890N; 528  
Column : 15m ZB-1 0.25/0.5df; G/495a  
Detector : FID  
Temperature : 220/ 80 8/min 195 20/min 340,5min iso/350  
Gas : 0.6 bar H2 split ca. 20  
Sample size : 1µl/Auto  
Recorder : Kipp&Zonen, 1mV

### Retention times

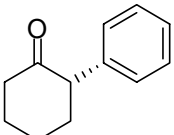
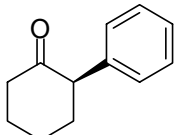
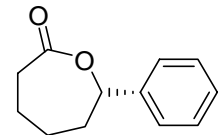
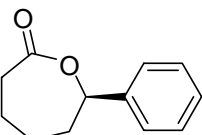
compound	<b>1a</b> 	<i>n</i> C16 internal GC- standard	<b>2a</b> 
r.t. / min	7.96	9.55	10.85

GC-factor correction was performed vs. *n*-C16-standard: correction factor = 1.15.

### Chiral method:

Optimized for separation of product enantiomers  
Instrument : 525, 6890N Agilent Technologies  
Column : 30m BGB-176 /BGB-15 0.25id 0.1df; G/494  
Detector : FID  
Temperature : 220/10.5min iso 150 50/min 160, 16min iso/350  
Gas : 0.6 bar H2  
Sample size : 1µl/Auto  
Recorder : Kipp&Zonen, 1mV

### Retention times

compound	<b>(S)-1a</b> 	<b>(R)-1a</b> 	<b>(S)-2a</b> 	<b>(R)-2a</b> 
r.t. / min	9.56	9.77	21.20	21.51

### Assignment of compound peaks according to sample from:

F. Schulz, F. Leca, F. Hollmann, M. T. Reetz

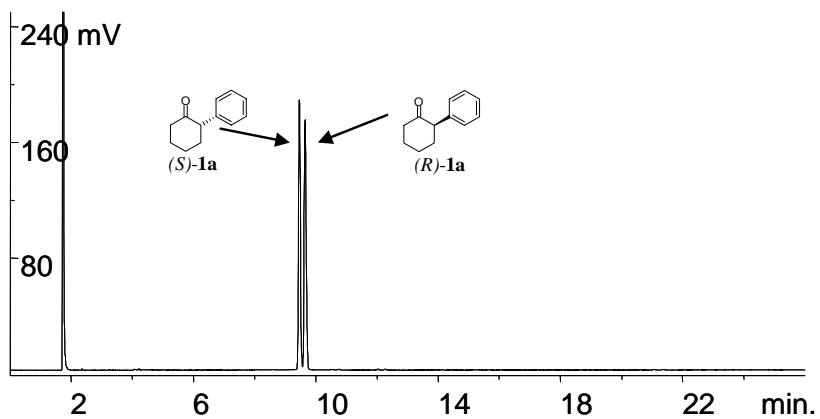
Towards Practical Biocatalytic Baeyer-Villiger Reactions: Applying a Thermostable Enzyme in the Gram-Scale Synthesis of Optically-Active Lactones in a Two-Liquid-Phase System.

*Beilstein J. Org. Chem.* **2005**, *1*:10.

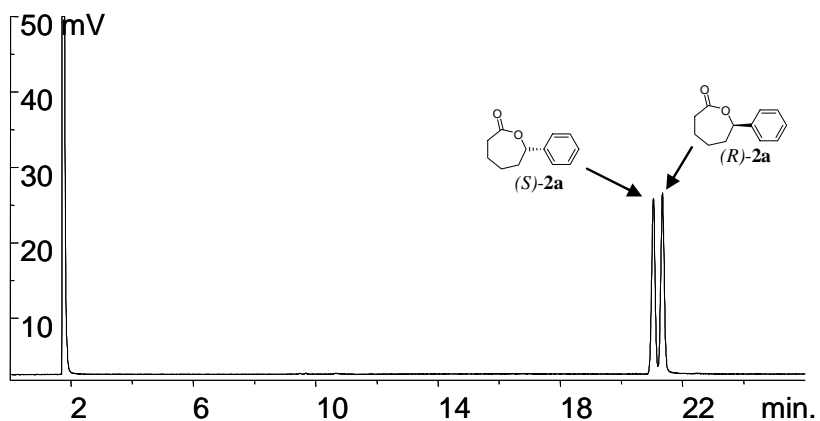
**Peak assignment was in accordance with GC-MS analysis** (Ionisation: GC-EI, Instrument: Finnigan SSQ7000)

## 2-phenyl cyclohexanone

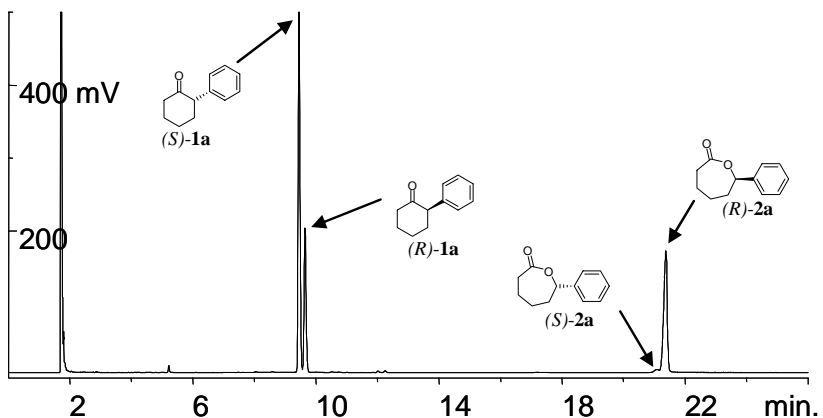
racemic substrate



racemic product

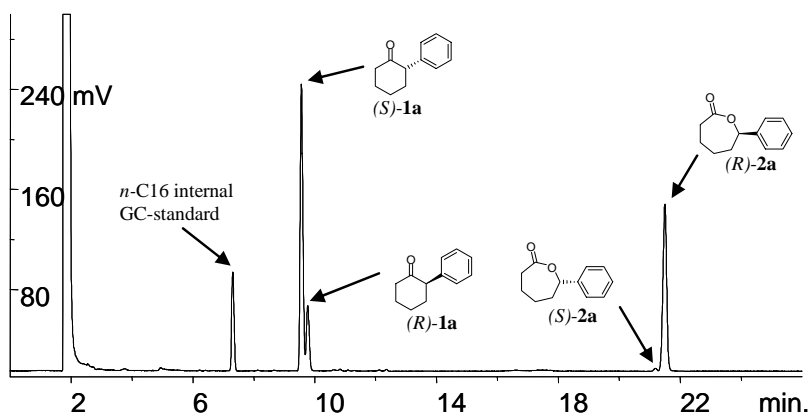


native reductant



light-driven reaction

(note: this sample contains internal standard)



## GC-method for 2-benzyl-cyclohexanone

### Achiral method:

Instrument : AT 6890N; 528  
Column : 15m ZB-1 0.25/0.5df; G/495a  
Detector : FID  
Temperature : 220/80 8/min 320,1min iso/350  
Gas : 0.5 bar H<sub>2</sub> tf. ca. 45  
Sample size : 1µl/Auto  
Recorder : Kipp&Zonen, 1mV

### Retention times

compound	<b>1b</b>	<b>2b</b>
r.t. / min	9.59	12.46

### Chiral method:

Instrument : 525, 6890N Agilent Technologies  
Column : 30m BGB-176 /BGB-15 0.25id 0.1df; G/494  
Detector : FID  
Temperature : 220/12.5min iso 150 100/min 200, 5min iso/350  
Gas : 0.6 bar H<sub>2</sub>  
Sample size : 1µl/Auto  
Recorder : Kipp&Zonen, 1mV

### Retention times

compound	<b>(R)-1b</b>	<b>(S)-1b</b>	<b>(R)-2b</b>	<b>(S)-2b</b>
r.t. / min	11.72	11.97	16.86	17.12

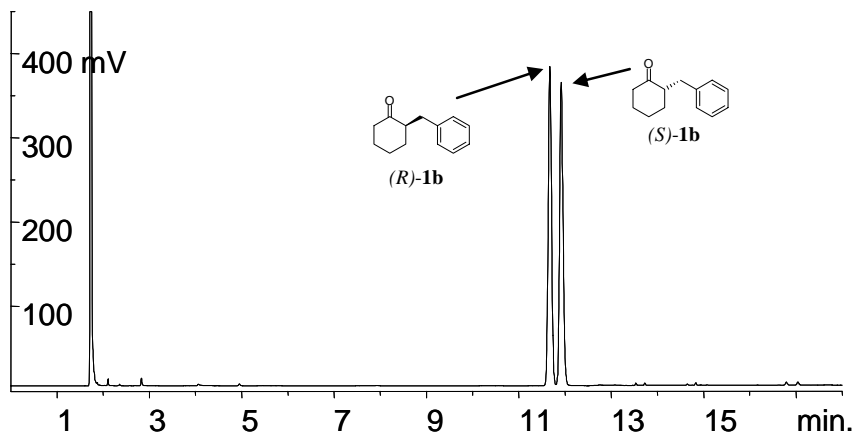
### Assignment of GC-peaks according to reference sample from:

M. Bocla, F. Schulz, F. Leca, A. Vogel, M. W. Fraaije, M. T. Reetz  
Converting Phenylacetone Monooxygenase into Phenylcyclohexanone Monooxygenase by  
Rational Design: Towards Practical Baeyer-Villiger Monooxygenases.  
*Adv. Synth. Catal.* **2005**, *347*, 979-986.

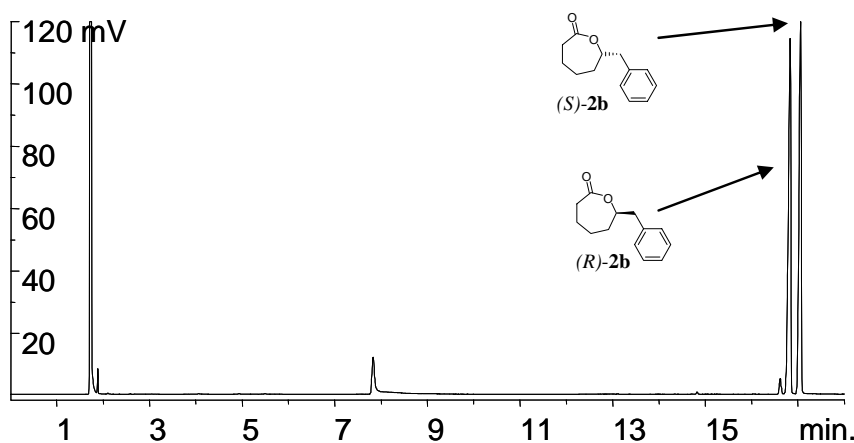
**Peak assignment was in accordance with GC-MS analysis** (Ionisation: GC-EI, Instrument: Finnigan SSQ7000)

## 2-benzyl cyclohexanone

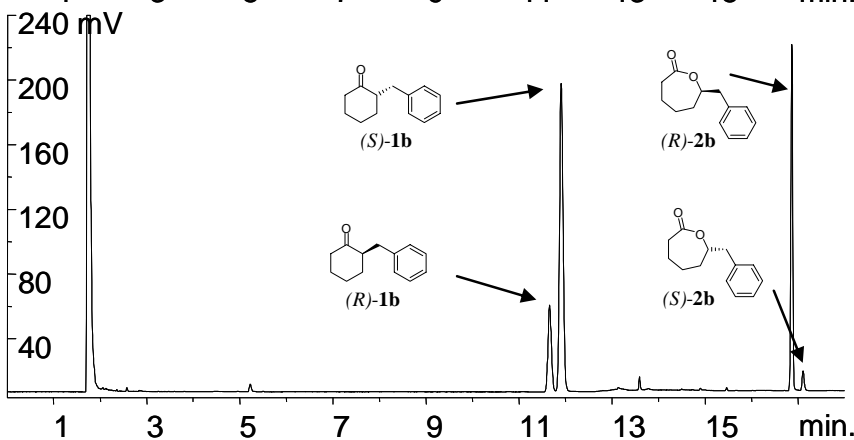
racemic substrate



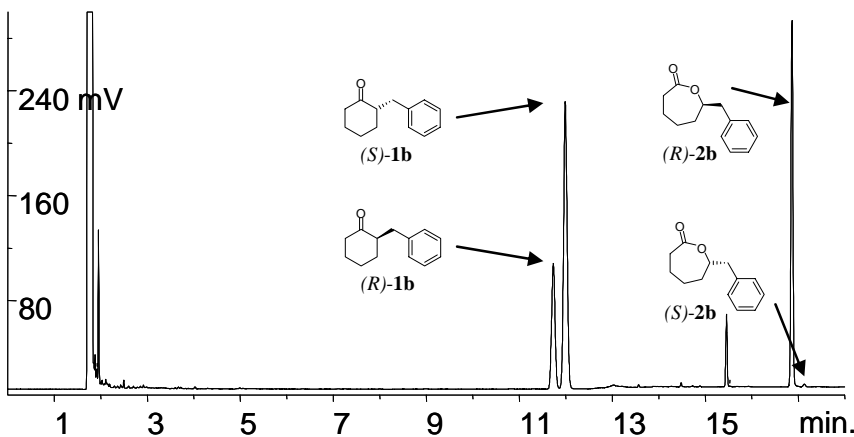
racemic product



native reductant



Light-driven reaction

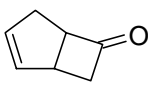
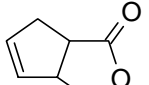
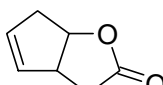


## GC-method for bicyclo[3.2.0]hept-2-en-6-one:

### Achiral method

Instrument : AT 6890N; 527  
Column : 30m RTX-5 0.25/0.25df; G/121  
Detector : FID  
Temperature : 220/60 6/min 330,10 min iso/350  
Gas : 0.6 bar H<sub>2</sub> tf. ca. 55  
Sample size : 1ul/Auto  
Recorder : Kipp & Zonen 1mV

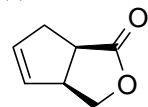
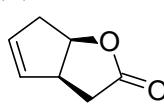
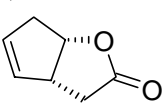
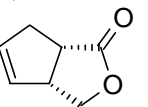
### Retention times

compound	<b>3</b> 	<b>4</b> 	<b>5</b> 
r.t. / min	4.60	9.79	9.91

### Chiral method

Instrument : 524; 6890 plus Agilent  
Column : 30 m BGB-178/ OV-1701 0.25/0.25df; G/455  
Detector : FID  
Temperature : 220/ 14.5min iso, 125 10/min 230, 5min iso/ 350  
Gas : 0.7 bar H<sub>2</sub> gas saver 80, 1min, tf: ca. 10  
Sample size : 1µl/Auto  
Recorder : Kipp & Zonen 1mV

### Retention times

compound	<b>(-)-4</b> 	<b>(+)-5</b> 	<b>(-)-5</b> 	<b>(+)-4</b> 
r.t. / min	10.61 major	11.30	11.98 major	12.50

### Assignment of compound peaks according to reference sample from:

F. Schulz, F. Leca, F. Hollmann, M. T. Reetz

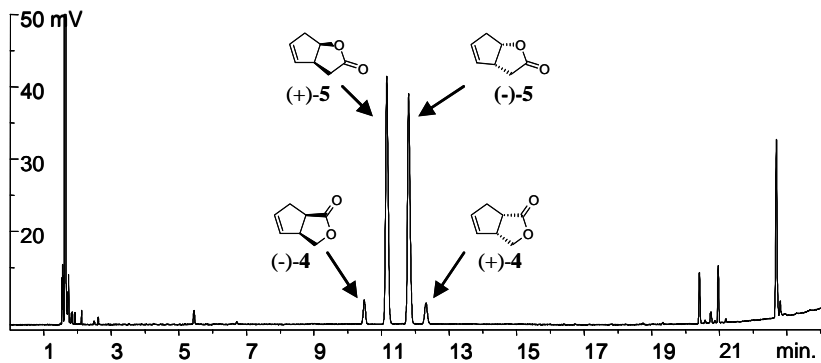
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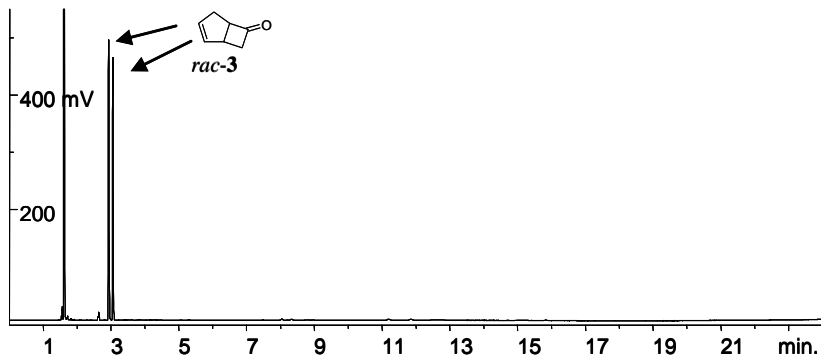
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**bicyclo[3.2.0]hept-2-en-6-one**

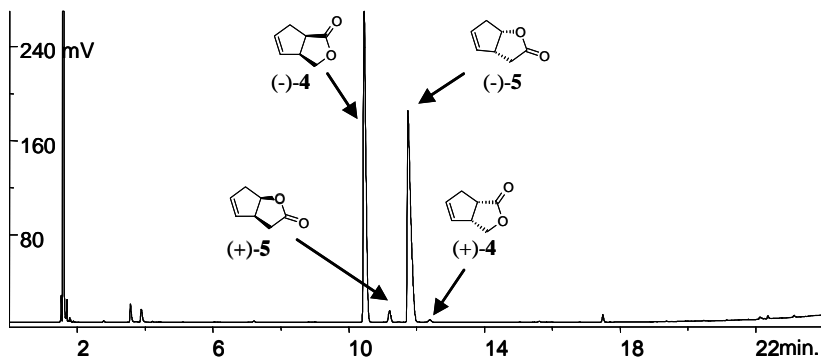
racemic products



racemic substrate



native reductant



light-driven reaction

