

## Supporting Information

**Table S I. Detailed list of the enzymes used in this study.**

| ser. no.  | trade name                               | source of hydrolase                      |
|---|--|--|
| Roche Molecular Biochemicals (Mannheim, Germany): |  |  |
| 1   | Chirazyme <sup>®</sup> L-1               | <i>Pseudomonas cepacia</i>               |
| 2   | Chirazyme <sup>®</sup> L-2               | <i>Candida antarctica</i> (lipase B)     |
| 3   | Chirazyme <sup>®</sup> L-5               | <i>Candida antarctica</i> (lipase A)     |
| 4   | Chirazyme <sup>®</sup> L-6               | <i>Pseudomonas sp.</i>                   |
| 5   | Chirazyme <sup>®</sup> L-7               | porcine pancreas                         |
| 6   | Chirazyme <sup>®</sup> L-8               | <i>Humicola sp.</i>                      |
| 7   | Chirazyme <sup>®</sup> L-9               | <i>Rhizomucor miehei</i>                 |
| 8   | Chirazyme <sup>®</sup> L-10              | <i>Alcaligines sp.</i>                   |
| 9   | Chirazyme <sup>®</sup> E-1               | pig liver (esterase)                     |
| 10  | Chirazyme <sup>®</sup> E-2               | hog liver (esterase)                     |
| 11  | lipase                                   | <i>Rhizopus arrhizus</i>                 |
| 12  | lipase                                   | pig pancreas                             |
| Amano Pharmaceutical Co, Ltd. (Nagoya, Japan):    |  |  |
| 13  | lipase PS                                | <i>Pseudomonas cepacia</i>               |
| 14  | ACS                                      | <sup>a</sup>                             |
| 15  | lipase R                                 | <i>Penicillium roqueforti</i>            |
| 16  | lipase F                                 | <i>Rhizopus javanicus</i>                |
| 17  | lipase A                                 | <i>Aspergillus niger</i>                 |
| 18  | lipase D                                 | <i>Rhizopus delemar</i>                  |
| 19  | lipase AH                                | <i>Pseudomonas cepacia</i>               |
| 20  | lipase M                                 | <i>Rhizomucor javanicus</i>              |
| 21  | lipase AK                                | <i>Pseudomonas fluorescens</i>           |
| 22  | lipase G                                 | <i>Penicillium cyclopium</i>             |
| 23  | lipase AY                                | <i>Candida rugosa</i>                    |
| 24  | amano S                                  | Seaprose                                 |
| 25  | Papain W                                 | <i>Carica papaya L.</i>                  |
| Novo Nordisk                                      |  |  |
| 26  | SP 382                                   | <i>Candida antarctica</i> (lipase A + B) |
| 27  | SP 435                                   | <i>Candida antarctica</i> (lipase B)     |
| 28  | SP 523                                   | <i>Mucor miehei</i>                      |
| 29  | SP 525                                   | <i>Candida antarctica</i> (lipase B)     |
| Fluka Chemie AG (Buchs, Switzerland):             |  |  |
| 30  | lipase from <i>Rhizopus arrhizus</i>     | <i>Rhizopus arrhizus</i>                 |
| 31  | lipase from <i>Rhizopus niveus</i>       | <i>Rhizopus niveus</i>                   |
| 32  | lipase from <i>Candida lipolytica</i>    | <i>Candida lipolytica</i>                |
| 33  | esterase from hog liver                  | hog liver                                |
| 34  | protease from <i>Bacillus subtilis</i>   | <i>Bacillus subtilis</i>                 |
| 35  | protease from <i>B. subtilis var. A.</i> | <i>Bacillus subtilis</i> (var. A.)       |
| 36  | protease N from <i>B. subtilis</i>       | <i>Bacillus subtilis</i>                 |
| 37  | protease 2A from <i>Asp. oryzae</i>      | <i>Aspergillus oryzae</i>                |
| 38  | protease 6 from <i>Asp. niger</i>        | <i>Aspergillus niger</i>                 |

Asahi Chemical

39 lipase from *Chrom. visc.* *Chromobacter viscosum*

Gist Brocades

40 Lipase Puur *Pseudomonas alcaligenes*

Diversa Corporation (USA, San Diego): all enzymes are from thermophilic microorganisms

41 BD019  
42 BD021  
43 BD022  
44 BD027  
45 BD036  
46 BD045  
47 BD048  
48 BD051  
49 BD064  
50 BD073  
51 BD078  
52 BD094  
53 BD099  
54 BD100  
55 BD102  
56 BD104  
57 BD105  
58 BD120  
59 BD133  
60 BD135  
61 BD137  
62 BD138  
63 BD151  
64 BD196  
65 BD197  
66 BD202  
67 BD213  
68 BD214  
69 BD236  
70 BD240  
71 BD245  
72 BD265  
73 BD266  
74 BD273  
75 BD277  
76 BD400  
77 BD402  
78 BD405  
79 BD421  
80 BD423  
81 BD429  
82 BD433  
83 BD434

- 84 BD468
- 85 BD473
- 86 BD519
- 87 BD544
- 88 BD551
- 89 BD553
- 90 BD556

ThermoGen (USA, Chicago, IL): all enzymes are from thermophilic microorganisms

- 91 E001
- 92 E002
- 93 E003
- 94 E004
- 95 E005
- 96 E006
- 97 E007
- 98 E008
- 99 E009
- 100 E010
- 101 E011
- 102 E012
- 103 E013
- 104 E014
- 105 E015
- 106 E016
- 107 E017b
- 108 E018b
- 109 E019
- 110 E020

self-produced recombinant esterases:

- 111 *Pseudomonas fluorescens* I
  - 112 *Pseudomonas fluorescens* II
  - 113 *Bacillus stearothermophilus*
  - 114 *Streptomyces diastatochromogenes*
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**Table S II. Detailed list of the GC-columns used in this study.**

| ser. no. | specification of the GC-column  | supplier   |
|----------|---|--|
| I        | Heptakis-(2,3)-di-O-acetyl-6-O-TBDMS- $\beta$ -cyclodextrin<br>25 m; 0.25 mm ID   | Prof. W. A. König (University<br>of Hamburg; Germany)    |
| II       | Heptakis-(2,3,6-tri-O-methyl)- $\beta$ -cyclodextrin / Polysiloxan<br>50 m; 0.25 mm ID<br>FS-Cyclodex beta-I/P                      | CS Chromatographie Service<br>GmbH (Langerwehe; Germany) |
| III      | Heptakis-(2,6-di-O-methyl-3-O-pentyl)- $\beta$ -cyclodextrin<br>diluted with OV 1701; 25 m; 0.25 mm ID<br>Hydrodex <sup>®</sup> -3P | Macherey-Nagel GmbH & Co.<br>KG (Düren, Germany)         |
| IV       | Heptakis-(6-TBDMS-2,3-methyl)- $\beta$ -cyclodextrin<br>diluted with 50 % OV 1701; 25 m; 0.25 mm ID                                 | Prof. W. A. König (University<br>of Hamburg; Germany)    |

**Table S III. Survey about the GC-analysis (columns; temperature programs; retention times) for the determination of the enantiomeric excesses of the compounds investigated.**

| Sub.      | column | temperature program <sup>a</sup> |       |          |      |       |          |      |       | carrier<br>[psi] | retention time |                   |      |   |
|-----------|--------|----------------------------------|-------|----------|------|-------|----------|------|-------|------------------|----------------|-------------------|------|---|
|           |        | T 1                              | Iso 1 | Ramp 1   | T 2  | Iso 2 | Ramp 2   | T 3  | Iso 3 |                  | enantiomers    |                   |      |   |
|           |        | [°C]                             | [min] | [°C/min] | [°C] | [min] | [°C/min] | [°C] | [min] |                  | [min]          | [min]             |      |   |
| <b>1a</b> | I      | 130                              | 10    | 4        | 170  | 5     |          |      |       | 9                | 20.9           | R                 | 21.9 | S |
|           | II     | 150                              | 10    | 5        | 190  | 5     |          |      |       | 15               | 7.5            | ?                 | 7.7  | ? |
|           | III    | 130                              | 15    | 10       | 170  | 5     |          |      |       | 4                | 12.2           | S                 | 12.7 | R |
|           | IV     | 130                              | 10    | 4        | 170  | 5     |          |      |       | 9                | 15.3           | R                 | 15.8 | S |
| <b>1b</b> | I      | 130                              | 10    | 4        | 170  | 5     |          |      |       | 9                | 7.9            | R                 | 10.9 | S |
|           | II     | 150                              | 10    | 5        | 190  | 5     |          |      |       | 15               | 10.3           | n.r. <sup>b</sup> |      |   |
|           | III    | 130                              | 15    | 10       | 170  | 5     |          |      |       | 4                | 13.4           | ?                 | 13.8 | ? |
|           | IV     | 130                              | 10    | 4        | 170  | 5     |          |      |       | 9                | 4.5            | R                 | 5.1  | S |
| <b>2a</b> | I      | 32                               |       |          |      |       |          |      |       | 3                | 30.8           | ?                 | 33.9 | ? |
|           | II     | 50                               | 15    | 5        | 90   | 10    | 10       | 180  | 5     | 8                | 12.1           | R                 | 12.3 | S |
| <b>2b</b> | I      | 32                               |       |          |      |       |          |      |       | 3                | 47.8           | ?                 | 50.8 | ? |
|           | II     | 50                               | 15    | 5        | 90   | 10    | 10       | 180  | 5     | 8                | 24.9           | S                 | 25.9 | R |
| <b>3a</b> | I      | 50                               | 30    | 10       | 170  | 5     |          |      |       | 4                | 10.2           | S                 | 11.6 | R |
|           | II     | 60                               | 12    | 10       | 180  | 5     |          |      |       | 12               | 6.6            | R                 | 6.9  | S |
| <b>3b</b> | I      | 50                               | 30    | 10       | 170  | 5     |          |      |       | 4                | 5.5            | R                 | 6.9  | S |
|           | II     | 60                               | 12    | 10       | 180  | 5     |          |      |       | 12               | 8.8            | R                 | 9.4  | S |
|           | IV     | 50                               | 30    | 10       | 170  | 5     |          |      |       | 4                | 6.7            | R                 | 9.7  | S |
| <b>3c</b> | I      | 50                               | 30    | 10       | 170  | 5     |          |      |       | 4                | 14.7           | R                 | 17.2 | S |
|           | II     | 60                               | 12    | 10       | 180  | 5     |          |      |       | 12               | 17.5           | R                 | 17.7 | S |
| <b>4a</b> | I      | 80                               | 10    | 10       | 110  | 10    | 10       | 170  | 5     | 8                | 17.7           | ?                 | 18.7 | ? |
|           | II     | 60                               | 12    | 10       | 180  | 5     |          |      |       | 12               | 20.2           | n.r.              |      |   |
|           | III    | 60                               | 10    | 5        | 170  | 5     |          |      |       | 10               | 13.8           | n.r.              |      |   |
|           | IV     | 110                              | 15    | 10       | 170  | 5     |          |      |       | 5                | 11.3           | S                 | 12.4 | R |
| <b>4b</b> | I      | 80                               | 10    | 10       | 110  | 10    | 10       | 170  | 5     | 8                | 7.0            | ?                 | 8.1  | ? |
|           | II     | 60                               | 12    | 10       | 180  | 5     |          |      |       | 12               | 20.8           | R                 | 21.0 | S |
|           | III    | 60                               | 10    | 5        | 170  | 5     |          |      |       | 10               | 14.6           | R                 | 15.3 | S |
|           | IV     | 110                              | 15    | 10       | 170  | 5     |          |      |       | 5                |                | n.r.              |      |   |

<sup>a</sup> The temperatures of the injector and detector (FID) are dependent of the GC-device: 200°C, 230 or 250°C, respectively. <sup>b</sup> n.r. = not resolved