**Supplementary data**

**Enzymatic dynamic reductive kinetic resolution towards 12% w/v *(S)*-2-phenylpropanol**

Christian Rappa, Simone Pivala,c, Erika Tassanob, Bernd Nidetzkya,c, Regina Kratzera\*

aInstitute of Biotechnology and Biochemical Engineering, Graz University of Technology, NAWI Graz, 8010 Graz, Austria. bDepartment of Chemistry, University of Graz, Heinrichstrasse 28, NAWI Graz, 8010 Graz, Austria. cAustrian Centre of Industrial Biotechnology (acib), 8010 Graz, Austria.

\*Corresponding author phone +43 316 873 8412, e-mail: regina.kratzer@tugraz.at

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*Figure S1*. Time course of the reduction of 0.5mM substrate with 240 U/mL isolated D51A *Ct*XR. Blue dots (*S*)-2-phenylpropanal, orange dots (*R*)-2-phenylpropanol.

**2 Biotransformation of 100mM racemic 2-phenylpropanal**

*Table S1*. Data for Figure 1.

**3 Reversed phase, chiral HPLC**

*Figure S2*. Overlay of HPLC traces for rac-2-phenylpropanal (1), acetophenone (2), 1-phenylethanol (3), (*R,S*)-2-phenylpropanol (4), reaction buffer with NAD+ (5), reaction buffer (6), bioreduction sample 1M 2-phenylpropanal reacted with 40gCDW/L and 6mM NAD+ (7).

*Table S2 (data to Figure S1)*. Retention times for main products and by-products obtained from reversed phase, chiral HPLC.

**4 Chiral GC-FID**

*Figure S3*. Selected GC traces for bioreduction replicates (N=6) of 1M 2-phenylpropanal reacted with 40gCDW/L and 6mM NAD+.

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**5 1H-NMR**

*Figure S4*. 1H-spectra in MeOD. Graph shows a spectrum of isolated product of a reaction with 78 % analytical yield (HPLC). Spectra were recorded immediately after work-up. Ethyl acetate related signals at 1.75, and 3.9ppm; acetophenone related signal at 2.45ppm.

**1 Reduction of racemic 2-phenylpropanal by isolated D51A *Ct*XR Time course**

*Figure S1*. Time course of the reduction of 0.5mM substrate with 240 U/mL isolated D51A *Ct*XR. Blue dots (*S*)-2-phenylpropanal, orange dots (*R*)-2-phenylpropanol.

**2 Biotransformation of 100mM racemic 2-phenylpropanal**

*Table S1 (data for Figure 1)*. Conversions and product e.e.-values of 100mM racemic 2-phenylpropanal reduction by lyophilized whole-cell catalyst and cell-free catalyst. Effects of catalyst form and loadinga.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Whole-cell catalyst(gCDW/L) | Cell-free catalyst(gCDW/L) | Conversion(%) | e.e. (%)  | Ratio(gsubstrate/gCDW) |
| 4 | 0 | 41.3 | 95.3 | 3.4 |
| 10 | 0 | 66.5 | 61.3 | 1.4 |
| 20 | 0 | 69.4 | 49.0 | 0.7 |
| 40 | 0 | 72.4 | 45.8 | 0.3 |
| 0 | 4 | 29.1 | 95.7 | 3.4 |
| 0 | 10 | 72.7 | 58.1 | 1.4 |
| 0 | 20 | 69.6 | 41.7 | 0.7 |
| 0 | 40 | 76.9 | 27.5 | 0.3 |

aNAD+ concentration 6mM, reaction time 24h. Data are based on HPLC analysis.

**3 Reversed phase, chiral HPLC**

Separation of main products and by-products on HPLC (stationary phase Chiralpak® AD-RH column from Daicel, mobile phase 25 % acetonitrile in ddH2O, 40°C).



*Figure S2*. Overlay of HPLC traces for rac-2-phenylpropanal (1), acetophenone (2), rac. 1-phenylethanol (3), (*R,S*)-2-phenylpropanol (4), reaction buffer with NAD+ (5), reaction buffer (6), bioreduction sample 1M 2-phenylpropanal reacted with 40gCDW/L and 6mM NAD+ (7).

*Table S2 (data corresponding to Figure S1)*. Retention times for main products and by-products on reversed phase, chiral HPLC.

|  |  |
| --- | --- |
| Analyte | Retention time (min) |
| rac-2-Phenylpropanal | broad peak, not applicable |
| (*R*)-2-Phenylpropanol | 15.8 |
| (*S*)-2-Phenylpropanol | 14.5 |
| Acetophenone | 18.6 |
| rac.- 1-Phenylethanol | 9.9 (no separation) |

**4Chiral GC-FID**

*(S)-*2-phenylpropanol

|  |
| --- |
| *(R)-*2-phenylpropanol*rac*-2-phenylpropanalAcetophenone |

*Figure S3*. GC traces for bioreduction replicates (N=6) of 1M 2-phenylpropanal reacted with 40gCDW/L and 6mM NAD+.

*Table S3 (data corresponding to Figure S2)*. Retention times for main products and by-products on chiral GC.

|  |  |
| --- | --- |
| Analyte | Retention time (min) |
| (*R*)-2-Phenylpropanal | 8.2 |
| (*S*)-2-Phenylpropanal | 8.8 |
| (*R*)-2-Phenylpropanol | 14.8 |
| (*S*)-2-Phenylpropanol | 15.4 |
| Acetophenone | 6.9 |

**5 1H-NMR**

**Bioreduction analysis**

The isolate (extraction with ethylacetate) of a bioreduction mixture from 1M 2-phenylpropanal reacted with 40gCDW/L and 6mM NAD+ was analyzed by 1H-NMR.

*Figure S4*. 1H-spectra in MeOD. Graph shows a spectrum of isolated product of a reaction with 78 % analytical yield (HPLC). Spectra were recorded immediately after work-up. Ethyl acetate related signals at 1.75, and 3.9ppm; acetophenone related signal at 2.45ppm.