Biocatalytic Asymmetric Hydrogen Transfer employing *Rhodococcus ruber* DSM 44541

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Supporting Information

Contents

1. GC Analyses on achiral columns	S1
2. GC Analyses on chiral columns	S3
3. Optical rotation values	S5
4. Supporting References	S6

1. GC Analyses on achiral columns

Achiral columns were used for determination of activity.

The following achiral columns were used: column A: Hewlett Packard HP 1301 (30 m x 0.25 mm x 0.25 μ m, 1.0 bar N₂); column B: Hewlett Packard HP 1701 (30 m x 0.25 mm x 0.25 μ m, 1.0 bar N₂); column C: J&W Scientific Agilent Technologies HP-1 (30 m x 0.25 mm x 0.25 μ m, 1.0 bar N₂); column D: Hewlett Packard HP-INNOWax (30 m x 0.25 mm x 0.25 μ m, 1.0 bar N₂); column E: Chrompack Chirasil Dex (25 m x 0.32 mm x 0.25 μ m, 1.0 bar H₂);

Table S1. Determination of conversion.

Compound	Program ^a	Column	Retention time [min]	
			Ketone a	Alcohol b
1	100/9/30/240	A	10.4	10.6
2	90/9/30/240	A	8.8	8.9
3	80/5/10/105/0/30/240	A	7.0	7.3
4	80/5/10/105/0/30/240	A	4.8	5.1
5	50/5/4/90/0/12/150	E	7.4	11.7
6	55/7/5/80/0/10/160	A	6.8	7.1
7	100/5/12/160/10	E	2.1	5.5
8	100/5/12/160/10	E	7.8	8.8
9	100 isotherm	A	3.4	3.5
10	100/12/5/160/10	E	20.1	23.2
11	90/12/15/130/0/30/250	C	16.6	16.2
12	120/10/20/160	E	4.7	7.9
13	70/2/5/120/2/160	E	10.1	11.9
14	120/0/20/250	C	4.6	4.4
15	100/9/30/240	A	12.1	12.2
16	45 isotherm	A	7.3	8.5
17	45 isotherm	A	4.0	4.5
18	40 isotherm	A	2.4	2.5
19	80/5/10/105/0/30/240	A	7.8	8.4
20	55/7/5/80/0/10/160	A	6.7	6.8
21	50/5/10/250	D	10.1	12.1
22	50/5/10/250	D	8.0	10.2
23	80/3/30/250	B	9.7	7.6
24	80/3/30/250	B	9.5	8.8
25	100/5/12/160/10	E	3.8	6.0
26	100/5/12/160/10	E	5.5	8.8

27	100/5/12/160/10	E	3.5	9.9
28	100/5/12/160/10	E	3.6	6.7
29	100/5/12/160/10	E	3.2	7.3
30	100/5/12/160/10	E	2.7	8.7
31	100/5/12/160/10	E	3.4	8.8
32	100/5/12/160/10	E	2.9	8.6
33	100/5/12/160/10	E	8.0	9.0
34	100/5/12/160/10	E	6.1	8.7
35	70/7.5/10/160	E	10.2	12.9
36	100/11/30/240	A	13.0	13.1
37	80/17/12/160	E	19.7	22.2
38	80/17/12/160	E	21.6	23.1
39	70/7.5/10/160	E	10.2	11.9
40	100/13/10/160	E	5.2	10.9

a Program: initial temp. [°C]/time [min]/slope [°C/min]/ temp. [°C]/ time [min]/slope [°C/min]/ temp. [°C].

2. GC Analyses on chiral columns

Chiral columns used for determination of enantiomeric excess.

The following chiral columns were used: column E: Chrompack Chirasil Dex (25 m x 0.32 mm x 0.25 μ m, H₂); column F: Astec Chiraldex G-PN (30 m x 0.32 mm, 1.0 bar H₂).

The ee of **3b**, **5b**, **7b** was determined as previously described.ⁱ

Table S2. Determination of ee values

Compound	Program ^a	Column	Retention time [min]
1b^b	80/7/10/160	F	10.27 (<i>S</i>), 10.38 (<i>R</i>)
2b^b	60/7/4/80/10/160	F	13.52 (<i>S</i>), 13.69 (<i>R</i>)
3b^b	60/7/4/80/10/160	F	9.75 (<i>S</i>), 10.18 (<i>R</i>)
4b^b	60/7/4/80/10/160	F	8.48 (<i>S</i>), 9.08 (<i>R</i>)
5b	50/5/4/90/12/150	E	11.72 (<i>S</i>), 12.24 (<i>R</i>)
6b^b	55/7/5/80/10/160	F	10.35 (<i>S</i>), 10.58 (<i>R</i>)
7b	100/5/12/160/10	E	5.53 (<i>R</i>), 5.99 (<i>S</i>)
8b	100/5/12/160/10	E	8.85 (<i>R</i>), 9.01 (<i>S</i>)
9b^b	90 isotherm	E	5.93 (<i>S</i>), 8.19 (<i>R</i>)
10b	100/12/5/160/10	E	23.18 (<i>R</i>), 23.56 (<i>S</i>)
11b	100/12/5/160/10	E	9.75 (<i>S</i>), 9.99 (<i>R</i>)
12b	120/10/20/160	E	7.85 (<i>S</i>), 8.38 (<i>R</i>)
13b	70/2/5/120/0/12/160	E	11.9, 12.1
14b^b	80/6.5/10/160/10	E	13.31 (<i>S</i>), 13.47 (<i>R</i>)
15b^b	55/0/10/140/1.5	E	8.95, 9.18
16b^b	40 isotherm	F	7.29 (<i>S</i>), 8.53 (<i>R</i>)
17b^b	40 isotherm	F	3.00 (<i>S</i>), 3.24 (<i>R</i>)
18b^b	40 isotherm	F	2.07 (<i>S</i>), 2.34 (<i>R</i>)
24b	115/15/12/160/0	E	26.63 (<i>R</i>), 26.97 (<i>S</i>)
25b	100/5/12/160/10	E	6.00 (<i>R</i>), 6.57 (<i>S</i>)
26b	100/5/12/160/10	E	8.76 (<i>R</i>), 9.06 (<i>S</i>)
27b	100/5/12/160/10	E	9.88 (<i>R</i>), 10.10 (<i>S</i>)
28b	100/5/12/160/10	E	6.72 (<i>R</i>), 7.16 (<i>S</i>)
29b	100/5/12/160/10	E	7.28 (<i>R</i>), 7.49 (<i>S</i>)
31b	100/5/12/160/10	E	8.76 (<i>R</i>), 8.99 (<i>S</i>)
33b	100/5/12/160/10	E	9.03 (<i>R</i>), 9.18 (<i>S</i>)
35b	70/7.5/10/160	E	12.88 (<i>R</i>), 13.03 (<i>S</i>)

37b	80/17/12/160	E	22.20 (<i>S</i>), 22.29 (<i>R</i>)
39b	70/7.5/10/160	E	11.88 (<i>S</i>), 11.99 (<i>R</i>)
40b	100/13/10/160	E	10.89 (<i>S</i>), 11.34 (<i>R</i>)

a Program: initial temp. [°C]/time [min]/slope [°C/min]/ temp. [°C]/ time [min]/slope [°C/min]/ temp. [°C].

b Enantiomeric excess determined as the corresponding acetate derivative.

3. Optical rotation values

(*S*)-2-Decanol **1b**: $[\alpha]_{\text{D}}^{20} +6.97$ (c 1.00, EtOH) 58.3% ee, lit.ⁱⁱ +10.3 (c 0.80, EtOH) 99% ee.

(*S*)-Sulcatol **5b**: $[\alpha]_{\text{D}}^{20} +9.55$ (c 2.4, CHCl₃) 99% ee, lit.ⁱⁱ +12.0 (c 2.93, CHCl₃) 99% ee.

(*S*)-3-Octanol **6b**: $[\alpha]_{\text{D}}^{22} 9.15$ (c 4.33, CHCl₃) 97% ee, lit.ⁱⁱⁱ 8.8 (c 0.49 CHCl₃).

(*R*)-1-Cyclohexyl ethanol **9b**: $[\alpha]_{\text{D}}^{20} 8.87$ (c 1.01, Et₂O) 99% ee, lit.^{iv} -7.79 (c 3.10, Et₂O) 96 % ee.

(*S*)-β-Tetralol **14b**: $[\alpha]_{\text{D}}^{20} -29.6$ (c 0.50, CHCl₃) 85% ee, lit.^v -73.9 (c 1.52, CHCl₃).

(*S*)-1-(4-Hydroxyphenyl) ethanol **24b**: $[\alpha]_{\text{D}}^{20} -29.61$ (c 0.89, EtOH), 98% ee, lit.^{vi} -47.5 (c 4.98, EtOH).

(*S*)-1-(4-Fluorophenyl) ethanol **25b**: $[\alpha]_{\text{D}}^{20} -33.1$ (c 1.00, MeOH abs), 98% ee, lit.ⁱⁱ -37.7 (c 0.931, MeOH) 99% ee.

(*R*)-1-(4-Chlorophenyl) ethanol **26b**: $[\alpha]_{\text{D}}^{20} 36.73$ (c 1.00, CHCl₃), 88% ee, lit.^{vii} -48.8 (c 3.13, CHCl₃) for (*S*)-enantiomer.

(*R*)-1-(4-Bromophenyl) ethanol **27b**: $[\alpha]_{\text{D}}^{20} 27.64$ (c 1.00, CHCl₃), 89.4% ee, lit.ⁱⁱ -37.9 (c 1.13, CHCl₃) 99% ee (*S*).

(*R*)-1-(4-Methylphenyl) ethanol **28b**: $[\alpha]_{\text{D}}^{20} 27.54$ (c 1.00, MeOH), 87% ee, lit.ⁱⁱ -43.5 (c 0.994, MeOH) 99% ee (*S*).

(*R*)-1-(3-Methylphenyl) ethanol **29b**: $[\alpha]_{\text{D}}^{20}$ 30.59 (c 1.00, EtOH), 96% ee, lit.ⁱⁱ -39.8 (c 0.944, EtOH) 99% ee (*S*).

(*R*)-1-(3-Chlorophenyl) ethanol **31b**: $[\alpha]_{\text{D}}^{20}$ 27.73 (c 3.5, CHCl₃), 87% ee, lit.ⁱⁱ -43.5 (c 1.08, CHCl₃) 99% ee (*S*).

(*S*)-1-(3-Methoxyphenyl) ethanol **33b**: $[\alpha]_{\text{D}}^{20}$ -28.80 (c 3.00, MeOH), 98% ee, lit.ⁱⁱ -34.9 (c 0.85, MeOH abs) 99% ee (*S*).

(*R*)-4-Phenyl-2-butanol **40b**: $[\alpha]_{\text{D}}^{20}$ -15.2 (c 1.21 CHCl₃), 94% ee, lit.^{viii} 17.4 (c 1.80, CHCl₃) for the (*S*)-enantiomer.

Supporting References

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