Journal of Molecular Catalysis B: Enzymatic 60 (2009) 191–194

Contents lists available at ScienceDirect

Journal of Molecular Catalysis B: Enzymatic

journal homepage: www.elsevier.com/locate/molcatb

Synthesis of 4-phenylpyrrolidin-2-one via dynamic kinetic resolution catalyzed by ω-transaminases

Dominik Koszelewski, Dorina Clay, Kurt Faber, Wolfgang Kroutil*

Department of Chemistry, Organic and Bioorganic Chemistry, Research Centre Applied Biocatalysis, University of Graz, Heinrichstrasse 28, A-8010 Graz, Austria

ARTICLE INFO

Article history:
Received 25 February 2009
Received in revised form 8 May 2009
Accepted 20 May 2009
Available online 28 May 2009

Keywords:
Transamination
Dynamic kinetic resolution
Asymmetric synthesis
ω-Transaminases
Co-solvent

ABSTRACT

Enantiomerically enriched 4-phenylpyrrolidin-2-one was prepared within only three steps starting from a commercial compound employing dynamic kinetic resolution (DKR) as the key asymmetric step. To the best of our knowledge, for the first time a DKR was performed involving an enzymatic enantioselective amination reaction catalyzed by ω-transaminases. Careful optimization of co-solvent and pH conditions allowed enhancing the enantioselectivity. The general method allows access to 4-arylpyrrolidin-2-ones derivatives, the cyclic analogues of γ-aminobutyric acid (GABA) derivatives.

1. Introduction

3-ArylGABA (γ-aminobutyric acid) derivatives [1–10] play an important role in several nervous system functions [11,12]. The malfunctioning of the central GABA system is responsible for the development and outbreak of epilepsy, Huntington's and Parkinson's diseases [13], and other psychiatric disorders, such as anxiety and pain.

The biological activity of 3-arylGABA derivatives is known to be connected to the (*R*)-enantiomer [8,10,13,14], while the (*S*)-antipode exhibits lower affinity to the same receptor site. Due to the increasing demand of enantiomerically pure drugs for the pharmaceutical industry, an efficient asymmetric synthesis for compounds such as 3-phenylGABA and 4-phenylpyrrolidin-2-one (**4**) is highly desired [15].

A number of enantioselective [16–23] and chemoenzymatic [24–27] syntheses of both enantiomers of 3-phenylGABA and 4-phenylpyrrolidin-2-one (**4**) [28] have been reported in the literature.

Recently, α- and ω-transaminases have received increasing interest due to their great potential for the production of natural and unnatural amino acids as well as chiral amines, as demanded by the pharmaceutical industry [29–31]. The ω-transaminases are employed for the kinetic resolution of amines [32–37], as well as for the asymmetric transamination of prochiral ketones [38–40].

The strategy presented here for the synthesis of enantiomerically enriched 4-phenylpyrrolidin-2-one (**4**) is based on deracemization [41–47] of 4-oxo-3-phenylbutyric acid ethyl ester (**3**) catalyzed by a ω-transaminase (ATA) (Scheme 1). To the best of our knowledge, dynamic kinetic resolution involving ω-transaminases has not been reported yet. Overall, this strategy would provide a novel, flexible synthesis to 4-arylpyrrolidin-2-ones and their acyclic GABA analogs.

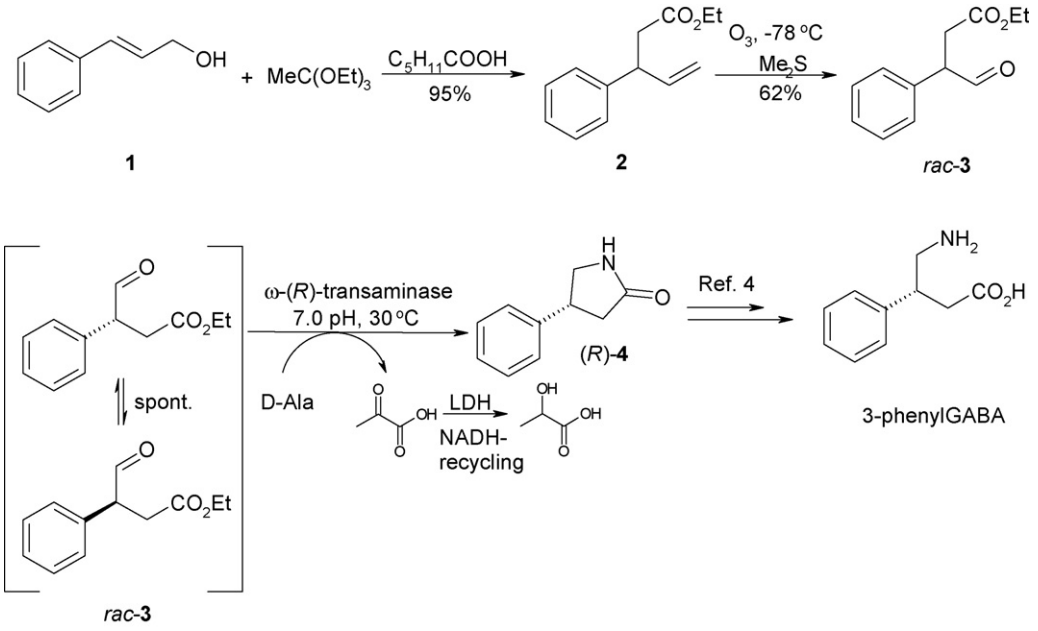
2. Experimental

2.1. General methods

Cinnamyl alcohol, triethyl orthoacetate as well as solvents were purchased from Sigma–Aldrich (Vienna, Austria), BASF (Ludwigshafen, Germany) and were used as received unless otherwise stated. ω-Transaminases ATA-113, 114, 117 and ATA from *Vibrio fluvialis* (ω-ATVf) (transaminase ATA-113, 102907WW, 0.46 U/mg; transaminase ATA-117, 102907WW, 1.9 U/mg; transaminase ATA-114, 1091108MW, 2.7 U/mg; transaminase from *V. fluvialis*, 020207KVP, 7.3 U/mg) as well as amine transaminase screening kit (no. ATA-17000A, 4121207MY) and lactate dehydrogenase mix (LDH, PRM-102, 101807KVP, mixture of lactate dehydrogenase, glucose dehydrogenase, glucose, NAD^+) were obtained from Codexis Inc. One unit of ω-transaminase was defined as the amount of enzyme that catalyzes the formation of 1 μmol acetophenone from α-methylbenzylamine at pH 9.0 at 22 °C. All chemicals used were of analytical grade. Optical rotations were measured on a Perkin Elmer Polarimeter 341 in a 1 mL cuvette of 10 cm length. ^1H and

* Corresponding author. Fax: +43 316 380 9840.
E-mail address: wolfgang.kroutil@uni-graz.at (W. Kroutil).

1381-1177/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcatb.2009.05.006



Scheme 1. Synthesis of enantiomerically enriched (*R*)-4-phenylpyrrolidin-2-one (**4**).

^{13}C NMR were recorded on a Bruker 360 MHz spectrometer at 360 and 90 MHz, respectively, using TMS as internal standard. Chemical shifts are reported in ppm and coupling constants (*J*) are given in Hertz (Hz). The conversion of amines was measured by gas chromatography using a Varian GC 3900 that was equipped with a coating DB-1701 DF 0.25 column (Ø0.25 mm × 30 m). All e.e. values were analyzed by using a Shimadzu HPLC apparatus that was equipped with a Chiralcel OJ column (Ø4.6 mm × 250 mm, from Diacel Chemical Ind., Ltd.). All reactions were monitored by TLC on Merck silica gel Plates 60 F254.

2.2. Synthesis of 3-phenyl-4-pentenoic ethyl ester (**2**)

A mixture of cinnamyl alcohol (33.7 g, 0.25 mol), triethyl orthoacetate (46.1 mL, 0.25 mol), and hexanoic acid (0.19 mL, 1.5 mmol) as catalyst was placed in a 250 mL, round-bottomed flask equipped with a thermometer, Claisen head, and condenser. The solution was heated in an oil bath with distillation of ethanol. After 3 h, distillation of ethanol slowed down and another 0.1 mL of hexanoic acid was added. Additional portions (0.1 mL) of the catalyst were added again at 3.5 and 4.5 h. After 6 h, a total of 27 mL of ethanol, out of a theoretical 29.2 mL, had been collected, and GC analysis indicated that no cinnamyl alcohol remained. Over this 6-h period, the internal temperature increased from 100 to 166 °C. The mixture was cooled to room temperature, and the crude product was purified by silica gel flash chromatography using hexane/ethyl acetate to afford product **2** with 95% yield as a colorless oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 3H), 2.70 (dd, J = 15.0, 7.5 Hz, 1H), 2.74 (dd, J = 15.0, 7.8 Hz, 1H), 3.86 (q, J = 7.2 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 5.04 (m, 1H), 5.09 (m, 1H), 5.98 (ddd, J = 17.4, 10.2, 7.2 Hz, 1H), 7.29 (m, 5H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.1, 40.3, 45.6, 60.3, 114.7, 126.7, 127.6, 128.5, 140.3, 142.5, 171.7; LRMS (EI) m/z calcd. for $C_{13}H_{16}O_2$ [M$^{\bullet+}$] 204.27, found 204.1 (M$^{\bullet+}$, 12%).

2.3. Synthesis of 4-oxo-3-phenylbutyric acid ethyl ester (**3**)

A solution of 3-phenyl-4-pentenoic ethyl ester (1.2 g, 5.87 mmol) in dichloromethane/methanol (1/1, 100 mL) was treated with ozone at −78 °C for 1 h. The ozonide was reduced to the aldehyde by addition of Me_2S (0.4 mL) at −78 °C and stirring while slowly warming to room temperature for 1 h. The solvent was evaporated and the resulting oil was purified by column chromatography (hexane/ethyl acetate). Product *rac*-**3** was obtained in 62% yield as a colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.21 (t, J = 7.1 Hz, 3H), 2.60 (dd, J = 7.0, 15.0 Hz, 1H), 3.18 (dd, J = 7.0, 15.0 Hz, 1H), 3.94–4.40 (m, 2H), 5.10 (dd, J = 7.0, 15.0 Hz, 1H), 7.10–7.58 (m, 5H), 9.60 (s, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.4, 34.9, 54.9, 61.1, 127.8, 128.3, 128.8, 129.0, 129.1, 129.5, 171.8, 198.8; LRMS m/z calcd. for $C_{12}H_{14}O_3$ [M$^{\bullet+}$] 206.2, found 206.1 (M$^{\bullet+}$, 8%). ^{1}H NMR data were in agreement with the literature [48].

2.4. Synthesis of *tert*-butyl-2-oxo-4-phenylpyrrolidine-1-carboxylate

tert-Butyl-2-oxo-4-phenylpyrrolidine-1-carboxylate was prepared according to the literature procedure with 89% yield after purification by flash chromatography (hexane/ethyl acetate) [22]. ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.53 (s, 9H), 2.70 (dd, J = 8.0 Hz, 1H), 2.90 (dd, J = 8.0 Hz, 1H), 3.49–3.60 (m, 1H), 3.62 (m, 1H), 4.12–4.20 (m, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 27.8, 28.0, 36.4, 40.3, 53.1, 83.0, 126.7, 127.4, 128.9, 140.0, 151.0, 174.0; HPLC-OJ (heptane/ethanol 95:5; at 254 nm; flow rate 0.8 mL/min), R_{tR} = 23.4 min, R_{tS} = 28.9 min.

2.5. Determination of enantiomeric excess

In order to measure the enantiomeric purity of 4-phenylpyrrolidin-2-ones (**4**), *tert*-butoxycarbonyl (*N*-BOC)-derivatives were prepared and subjected to HPLC analysis on a chiral stationary phase (Chiralcel OJ column, Ø4.6 mm × 250 mm, from Diacel Chemical Ind., Ltd., heptane/ethanol; 95/5; at 254 nm; flow rate 0.8 mL/min) [22].

2.6. Racemization studies on 4-oxo-3-phenylbutyric acid ethyl ester (**3**)

All reactions were performed at 30 °C in sodium phosphate buffer (100 mM, pH 7) containing pyridoxal-5′-phosphate (1 mM) in a 2 mL eppendorf tube. The reaction buffer (850 μL) was mixed with ω-transaminase ATA-117 (2 mg), D-alanine (250 mM), lactate

dehydrogenase mix (40 mg, LDH is a mixture of lactate dehydrogenase, glucose dehydrogenase, glucose, NAD^+), and DMSO (150 μL). The reaction mixture contained 50 mM of the corresponding aldehyde **3**. During a 6 h observation period, a sample was analyzed every 30 min after extraction with ethyl acetate (600 μL, twice). The organic phase was dried using anhydrous Na_2SO_4. The enantiomeric excess of the remaining aldehyde **3** was analyzed by gas chromatography on a chiral phase using Hydrodex-β-6TBDM column (Ø0.25 mm × 25 m); GC program parameters; injector 250 °C; flow 14.5 psi; temperature program 100 °C/hold 2.00 min; 130 °C/rate 1 °C/min/hold 10 min; 150 °C/rate 10 °C/min/hold 5 min; 170 °C/rate 10 °C/min/hold 20 min; R_{t1} = 55.9 min, R_{t2} = 56.6 min.

2.7. Representative example for amination. Preparation of (*R*)-4-phenylpyrrolidin-2-one (**4**)

In a 50 mL screw cap tube 4-oxo ester **3** (100 mg, 0.45 mmol) was suspended in phosphate buffer (17 mL, 100 mM, pH 7.0, 15% (v/v) DMSO, 1 mM PLP). D-Alanine (2.25 mmol) and a crude preparation of lactate dehydrogenase mix (200 mg) were added. The reaction was started by addition of a crude preparation of ω-transaminase ATA-117 (30 mg) and shaken at 30 °C (120 rpm). After 24 h, the pH of the mixture was adjusted to pH 14 with NaOH (10 M), and the lactam (*R*)-**4** was extracted five times with dichloromethane (5× 10 mL). The solvent of the combined extracts was evaporated and (*R*)-**4** was obtained with 92% yield as a white solid. $[\alpha]_D^{20} + 22$ (*c* 0.5, MeOH); lit. −33.8 (*c* 0.89, MeOH) for (*S*)-enantiomer [22]; mp 98–98.5 °C [lit. 98–99 °C] [18]; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.48 (dd, *J* = 6.8, 16.8 Hz, 1H), 2.71 (dd, *J* = 8.8, 16.8 Hz, 1H), 3.38 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.65 (q, 1H), 3.75 (dd, *J* = 8.8, 8.4 Hz, 1H) 7.22 (m, 3H), 7.30 (m, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 38.0, 40.3, 49.6, 126.7, 127.1, 128.8, 142.1, 178.0; LRMS (*m*/*z*) calcd. for $C_{10}H_{11}NO$ ($M^{\bullet+}$) 161.2, found 161.1 ($M^{\bullet+}$, 18%). ^{1}H NMR data were in agreement with the literature [20].

3. Results and discussion

The deracemization of 4-oxo-3-phenylbutyric acid ethyl ester (**3**) was achieved via a dynamic kinetic resolution employing commercial ω-transaminases (ATA-113, ATA-114, ATA-117) and from *V. fluvialis* (ω-ATVf) in combination with L- or D-alanine as amino donor.

Compound *rac*-**3** was prepared within two steps as follows: the reaction of cinnamyl alcohol (**1**) with triethyl orthoacetate catalyzed by hexanoic acid proceeded smoothly within 10 h to give the racemic 3-phenyl-4-pentenoic ethyl ester (**2**) in 95% yield [49]. Subsequent ozonolysis of the double bond led to the corresponding aldehyde *rac*-**3** with 62% yield.

The transformation of racemic aldehyde **3** (24 mM) was tested with various ω-transaminases in buffered solution at various pH at 30 °C. To shift the equilibrium to the side of the product **4** the pyruvate formed was removed by reduction using lactate dehydrogenase (LDH) in a coupled reaction system [50,51]. By using fivefold excess of the amino donor (120 mM, D- or L-alanine), almost complete conversion was reached after 24 h. The excess of amino donor was required to achieve a reasonable fast reaction; using less amino donor resulted in longer reaction times. Under the conditions employed aldehyde *rac*-3 racemised spontaneously ensuring a dynamic kinetic resolution (see below).

We found that all tested ω-transaminases led to perfect conversion and excellent isolated yield for lactam **4** (Table 1).

Transaminases ω-ATVf, ATA-113, ATA-114 showed (*S*)-preference (entries 1–3, Table 1), while ATA-117 displayed (*R*)-preference (entries 4–12, Table 1); furthermore, ATA-117 showed promising stereoselectivity (e.e. 61%; entry 4, Table 1). Since, the (*R*)-enantiomer of the desired product **4** exhibits higher biological activity [8,10,14] we devoted our studies to improve the reaction conditions for the reaction catalyzed by ATA-117 leading to the desired (*R*)-enantiomer.

Table 1
Dynamic kinetic resolution of aldehyde 3 catalyzed by various commercially available ω-transaminases.

Entry	ATA[a]	pH	Co-solvent (% v/v)	*c*[b] (%)	Yield[c] (%)	e.e.[d] (%)
1	ω-ATVf	7.0	DMSO (10)	98	90	6 (*S*)
2	114	7.0	DMSO (10)	99	80	45 (*S*)
3	113	7.0	DMSO (15)	>99	91	14 (*S*)
4	117	7.0	–	98	93	61 (*R*)
5	117	7.0	DMSO (5)	95	91	65 (*R*)
6	117	7.0	DMSO (10)	>99	95	65 (*R*)
7	117	7.0	DMSO (15)	>99	80	53 (*R*)
8	117	7.0	*i*Pr$_2$O (10)	68	60	58 (*R*)
9	117	7.0	MeOH (10)	93	74	51 (*R*)
10	117	6.5	DMSO (15)	95	92	68 (*R*)
11	117	8.0	DMSO (15)	>99	93	32 (*R*)
12	117	9.0[e]	DMSO (15)	>99	91	42 (*R*)

[a] ATA = ω-transaminase; reagents and conditions: aldehyde *rac*-**3** (100 mg, 24 mM), ATA (30 mg), LDH mix (200 mg, 1 mM NAD^+, glucose, glucose dehydrogenase), pH 7.0, 1 mM PLP, 30 °C, 24 h.
[b] Determined by GC.
[c] Isolated yield of **4**.
[d] Determined by chiral HPLC analysis.
[e] Carbonate buffer (100 mM).

The effect of organic solvents on activity and stereoselectivity of ω-transaminases has been scarcely studied. Two water-miscible organic solvents (methanol, DMSO) were tested to improve the solubility of the substrate in buffer (entries 5–7 and 9, Table 1). In case of ω-transaminase ATA-117, 10% (v/v) of DMSO influenced the conversion (entries 4–7, Table 1). At 15% (v/v) the enantioselectivity decreased leading to 53% instead of 65% e.e. at 10% (v/v) of DMSO (entry 7, Table 1). Since, biphasic system (organic solvent – buffer) can enhance the enantioselectivity of enzymes, 10% (v/v) of *iso*-propyl ether [50] was applied to the reaction (entry 8, Table 1). However, no beneficial amplification of stereoselectivity was observed. Further optimization of the reaction conditions (entries 10–12, Table 1) with respect to pH and co-solvent concentration for ATA-117 led to a slight enhancement of stereoselectivity (68% e.e.) (entry 10, Table 1). Employing this strategy, optical enriched lactam **4** could be obtained from 100 mg racemic aldehyde **3** in 92% isolated yield.

Chiral analysis of the aldehyde **3** during the reaction course proved that the aldehyde is always available in its racemic form, thus it is very quickly racemised. Therefore, the moderate optical purity of the obtained lactam **4** results exclusively from the stereorecognition of the ω-transaminases for the stereogenic center in α-position of the employed aldehyde **3** and not from kinetic effects due to depletion of the preferred substrate enantiomer [52].

In summary, we have developed a concept for the asymmetric synthesis of 4-phenylpyrrolidin-2-one via dynamic kinetic resolution by stereoselective amination utilizing commercially available ω-transaminase ATA-117 under very mild conditions. Further tests to identify more stereoselective ω-transaminases are ongoing work. The reported general synthetic strategy allows obtaining optical enriched 4-arylpyrrolidin-2-one within only three synthetic steps starting from commercial substrates with 54% overall yield, which represents a significant improvement compared to other approaches since less steps are required and since the cumbersome synthesis of racemic amine-derivatives is avoided.

Acknowledgments

We thank the FFG and the Province of Styria for their financial support. Codexis is acknowledged for providing various enzymes.

References

[1] A.L.L. Garcia, M.J.S.A. Carpes, C.B.M. de Oca, M.A.G. dos Santos, C.C. Santana, C.R.D. Correia, J. Org. Chem. 70 (2005) 1050–1053.
[2] O. Belda, S. Lundgren, C. Moberg, Org. Lett. 5 (2003) 2275–2278.
[3] A.A. Abdel-Hafez, B.A. Abdel-Wahab, Bioorg. Med. Chem. 16 (2008) 7983–7991.
[4] J. Colonge, J.-M. Pouchol, Bull. Soc. Chim. Fr. (1962) 598–603.
[5] S.A.A. Ebrik, B. Rigo, C. Vaccher, M.-P. Vaccher, N. Flouquet, M. Debaert, P.J. Berthelot, Heterocycl. Chem. 35 (1998) 579–583.
[6] N.G. Bowery, D.R. Hill, A.L. Hudson, A. Doble, N.D. Middemiss, J. Shaw, M. Turnbull, Nature 283 (1980) 92–94.
[7] R.B. Silverman, M.A. Levy, J. Biol. Chem. 256 (1981) 11565–11568.
[8] R.D. Allan, M.C. Bates, C.A. Drew, R.K. Duke, T.W. Hambley, G.A.R. Johnston, K.N. Mewett, I. Spence, Tetrahedron 46 (1990) 2511–2524.
[9] N.E. Bowery, Trends Pharm. Sci. 31 (1982) 400–403.
[10] H.R. Olpe, H. Demieville, V. Baltzer, W.L. Bencze, W.P. Koella, P. Wolf, H.L. Haas, Eur. J. Pharmacol. 52 (1978) 133–136.
[11] J.G. Hardman, L.E. Limbird, A. Goodman Gilman, Goodman and Gilman's The Pharmacological Basis of Therapeutics, 10th ed., McGraw-Hill, New York, 2001 (Section III).
[12] P.L. McGeer, E.G. McGeer, in: G.J. Siegel, B. Agranoff, R.W. Albens, P. Molinoff (Eds.), Basic Neurochemistry: Molecular, Cellular and Medical Aspects, 4th ed., Raven, New York, 1989.
[13] P. Krogsgaard-Larsen, J. Scheel-Krueger, H. Kofod, GABA-Neurotransmitters. Pharmacochemical, Biochemical and Pharmacological Aspects, Munksgaard, Copenhagen, 1979.
[14] J. Ong, D.I.S. Kerr, D.J. Doolette, R.K. Duke, K.N. Mewett, R.D. Allen, G.A.R. Johnston, Eur. J. Pharmacol. 233 (1993) 169–172.
[15] C. Desiderio, D.V. Rossetti, F. Perri, B. Giardina, I. Messana, M. Castagnola, J. Chromatogr. B 875 (2008) 280–287.
[16] E.J. Corey, F.Y. Zhang, Org. Lett. 2 (2000) 4257–4259.
[17] J. Vesely, G.-L. Zhao, A. Bartoszewicz, A. Cordova, Tetrahedron Lett. 49 (2008) 4209–4212.
[18] N. Langlois, N. Dahuron, H.-S. Wang, Tetrahedron 52 (1996) 15117–15126.
[19] C.C. Tseng, S. Terashima, S. Yamada, Chem. Pharm. Bull. 25 (1977) 166–170.
[20] A.S. Paraskar, A. Sudalai, Tetrahedron 62 (2006) 4907–4916.
[21] V.V. Thakur, M.D. Nikalje, A. Sudalai, Tetrahedron: Asym. 14 (2003) 581–586.
[22] A.I. Meyers, L. Snyder, J. Org. Chem. 58 (1993) 36–42.
[23] J. Ji, D.M. Barnes, J. Zhang, S.A. King, S.J. Wittenberger, H.E. Morton, J. Am. Chem. Soc. 121 (1999) 10215–10216.
[24] M.-X. Wang, S.-M. Zhao, Tetrahedron Lett. 43 (2002) 6617–6620.
[25] F. Felluga, V. Gombac, G. Pitacco, E. Valentin, Tetrahedron: Asym. 16 (2005) 1341–1345.
[26] M.-X. Wang, C.-S. Liu, J.-S. Li, O. Meth-Cohn, Tetrahedron Lett. 41 (2000) 8549–8552.
[27] M.-X. Wang, C.-S. Liu, J.-S. Li, Tetrahedron: Asym. 12 (2001) 3367–3373.
[28] S.J.P. Yoon-Miller, S.M. Opalka, E.T. Pelkey, Tetrahedron Lett. 48 (2007) 827–830.
[29] P. Christen, D.E. Metzler, Transaminases, 1st ed., John Wiley & Sons, New York, 1985.
[30] P.P. Taylor, D.P. Pantaleone, R.F. Senkpeil, G. Fotheringham, Trends Biotechnol. 16 (1998) 412–418.
[31] D. Koszelewski, I. Lavandera, D. Clay, G.M. Guebitz, D. Rozzell, W. Kroutil, Angew. Chem. Int. Ed. 120 (2008) 9477–9480.
[32] B.-Y. Hwang, B.-K. Cho, H. Yun, K. Koteshwar, B.-G. Kim, J. Mol. Catal. B: Enzym. 37 (2005) 47–55.
[33] C.U. Ingram, M. Bommer, M.E.B. Smith, P.A. Dalby, J.M. Ward, H.C. Hailes, G.J. Lye, Biotechnol. Bioeng. 96 (2006) 559–569.
[34] R.L. Hanson, B.L. Davis, Y. Chen, S.L. Goldberg, W.L. Parker, T.P. Tully, M.A. Montana, R.N. Patel, Adv. Synth. Catal. 350 (2008) 1367–1375.
[35] B.-K. Cho, H.-Y. Park, J.-H. Seo, J. Kim, T.-J. Kang, B.-S. Lee, B.-G. Kim, Biotechnol. Bioeng. 99 (2008) 275–284.
[36] J.-S. Shin, B.-G. Kim, D.-H. Shin, Enzyme Microbiol. Technol. 29 (2001) 232–239.
[37] M. Höhne, K. Robins, U.T. Bornscheuer, Adv. Synth. Catal. 350 (2008) 807–812.
[38] M. Höhne, S. Kühl, K. Robins, U.T. Bornscheuer, Chem. Biochem. 9 (2008) 363–365.
[39] J.S. Shin, B.G. Kim, Biotechnol. Bioeng. 65 (1999) 206–211.
[40] M.D. Truppo, J.D. Rozzell, J.C. Moore, N.J. Turner, Org. Biomol. Chem. 7 (2009) 395–398.
[41] Y. Ahn, S.-B. Ko, M.-J. Kim, J. Par, Coord. Chem. Rev. 252 (2008) 647–658.
[42] R. Carr, M. Alexeeva, A. Enright, T.S.C. Eve, M.J. Dawson, N.J. Turner, Angew. Chem. Int. Ed. 42 (2003) 4807–4810.
[43] J. Paetzold, J.E. Bäckvall, J. Am. Chem. Soc. 127 (2005) 17620–17621.
[44] A.J. Blacker, M.J. Stirling, M.I. Page, Org. Process Res. Dev. 11 (2007) 642–648.
[45] M.-J. Kim, W.-H. Kim, K. Han, Y.K. Choi, J. Park, Org. Lett. 9 (2007) 1157–1159.
[46] S. Gastaldi, S. Escoubet, N. Vanthuyne, G. Gil, M.P. Bertrand, Org. Lett. 9 (2007) 837–839.
[47] B.M. Matute, J.-E. Backvall, Curr. Opin., Chem. Biol. 11 (2007) 226–232.
[48] L. Carman, L.D. Kwart, T. Hudlicky, Synth. Comm. 16 (1986) 169–182.
[49] F.B. Gonzalez, P.A. Bartlett, Org. Synth. 64 (1986) 175–181.
[50] D. Koszelewski, I. Lavandera, D. Clay, D. Rozzell, W. Kroutil, Adv. Synth. Catal. 350 (2008) 2761–2766.
[51] J.-S. Shin, B.-G. Kim, Biotechnol. Bioeng. 77 (2002) 832–837.
[52] M. Kitamura, M. Tokunaga, R. Noyori, J. Am. Chem. Soc. 115 (1993) 144–152.