

Highly Efficient Direct Asymmetric Aldol Reactions Catalyzed by a Prolinethioamide Derivative in Aqueous Media

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L-Prolinethioamide derivative **1c**, prepared from the readily available natural amino acids L-proline and L-valine, was studied for the direct asymmetric aldol reaction of acetone with various aromatic aldehydes at 0 °C or room tempera-

ture. A loading of only 0.1–0.2 mol-% of derivative **1c** was employed in this catalytic system, and excellent enantioselectivities and yields (up to 98 % yield, >99 % ee) could be achieved in aqueous media.

Introduction

The direct asymmetric aldol reaction is an important method to form carbon–carbon bonds, which provides straightforward access to the optically active β -hydroxycarbonyl structural unit found in many natural products and drugs.^[1] Since List and Barbas reported the direct aldol reaction catalyzed by L-proline in 2000, recent years have witnessed an explosive growth in the field of related asymmetric reactions catalyzed by organocatalysts,^[2] especially with L-proline^[3] and its derivatives,^[4] including prolineamides,^[5] prolinethioamides,^[6] sulfonamides,^[7] chiral amines,^[8] and so on.

The mechanism of proline and its derivatives as organocatalysts has been proposed to proceed via an enamine intermediate, which is considered to be similar to enzymes catalysis.^[9] Chiral amines of low molecular weight based on enamine catalysts have become versatile organocatalysts for asymmetric reactions, and the application of a catalytic amount of a chiral catalyst for control of the asymmetric reactions is undoubtedly a big achievement of modern organic chemistry. However, typical asymmetric aldol reactions employ high loadings of organocatalyst (10–20 mol-%) to obtain the products in good yields and stereoselectivities. To the best of our knowledge, reports on the use of low catalytic loadings (<1 mol-%) in asymmetric reactions occurring by enamine catalysis are still very few up to date.^[10] Hence, better insight into the catalytic mechanism of enamine catalysis may in particular be useful to solve

this major challenge. Very recently, Wennemers's group found that the loading of the organocatalyst could be reduced to as little as 0.1 mol-% for a broad range of substrates based on kinetic studies of the enamine mechanism.^[11] This is the lowest catalyst loading achieved in enamine catalysis so far, successfully suggesting the potential of organocatalytic reactions. On the other hand, water acts as the best solvent for enzymes to facilitate optimization of the performance of the enzyme. Moreover, compared to the reactions in organic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), the use of water as a reaction medium has been regarded as a goal in modern organic chemistry due to its cost, safety, and environmentally benign character.^[12] The pioneer work of the organocatalyzed direct aldol reaction in water has been independently reported by Hayashi^[13] and Barbas.^[14] Since then, many efforts have been devoted to asymmetric organocatalytic reactions performed in aqueous media.^[15] For example, Singh and co-workers reported L-prolineamide organocatalyst **1a** for the direct asymmetric aldol reaction of ketone with an aldehyde acceptor in excellent enantioselectivity and with low catalyst loading (0.5–1 mol-%) in aqueous media.^[16] Gryko employed 2.5–10 mol-% of L-prolinethioamide to effectively catalyze the aldol reaction of cyclohexanone and aromatic aldehydes in the presence of water.^[17] Nevertheless, there are fewer reports on the direct asymmetric aldol reaction carried out in water for acyclic acetone than for cyclic ketones. Consequently, it still remains a challenge to develop highly efficient organocatalysts for the direct asymmetric aldol reactions of acetone and aromatic aldehydes in water with the amount of organocatalysts as low as possible.^[18]

Recently, our group reported a successful asymmetric aldol reaction catalyzed by the new prolinethioamide organocatalyst **1b** where the terminal hydroxy group is a primary alcohol, which is different from previously reported prerequisite secondary or tertiary alcohols of prolineamides.^[19]

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As a continuation of our work, we further modified catalyst **1b** to synthesize organocatalyst **1c** based on previous studies^[20] and applied it in direct asymmetric aldol reactions in aqueous media (Figure 1).

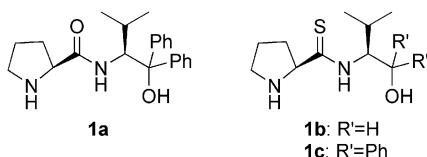
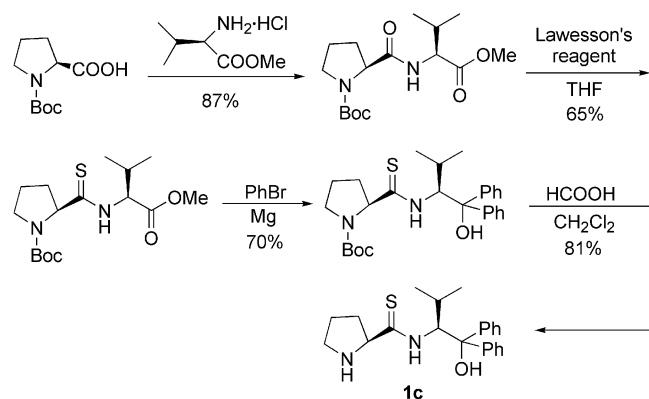


Figure 1. Different organocatalysts.

Results and Discussion

Organocatalyst **1c** was firstly synthesized in a short, good to high yielding reaction sequence, starting from commercially available N-Boc-L-proline and L-valinate hydrochloride through the general strategy shown in Scheme 1.



Scheme 1. Synthesis of organocatalyst **1c**.

In our initial studies, the efficacies of different organocatalysts **1** (Figure 1) were compared for the direct aldol reaction between acetone and 4-nitrobenzaldehyde as the model reaction by using PhCOOH as an additive in water. The results showed that high yields and excellent enantioselectivities could be obtained in the presence of catalyst **1a** or **1c**, whereas a poorer yield and a moderate *ee* value were obtained with **1b**, which possesses a primary alcohol group as the terminal hydroxy group (Table 1, Entries 1–3). The results are consistent with Singh's studies, where the hydrophobic groups of the organocatalyst play a significant role in obtaining high enantioselectivities in an aqueous medium.^[21] Moreover, we found that L-prolinethioamide **1c** displayed higher catalytic activity than L-prolineamide **1a**. A higher yield and a slightly increased enantioselectivity were obtained by catalyst **1c**. This may be due to the increasing NH acidity for prolinethioamide compared to prolineamide. To further improve the yield and enantioselectivity, the reaction was carried out in brine with organocatalyst **1c**. No improvement was observed. This demonstrated that the “salt effect” has no obvious influence in our highly efficient

catalytic system compared to catalyst **1a**. Next, we tested a lower loading of catalyst **1c** in water. To our delight, the decreased catalyst loading (from 2 to 1 mol-%) could still maintain the product yield and enantioselectivity. When further decreasing the amount of catalyst **1c** to 0.5 mol-%, up to 96% yield and 98% enantioselectivity were obtained by extending the reaction time. Even with 0.1 mol-% of catalyst **1c**, similar results were still obtained in this reaction at room temperature (Table 1, Entry 10). In comparison to organocatalyst **1c**, the yield and enantioselectivity decreased obviously when the loading of organocatalyst **1a** was reduced to 0.1 mol-%. Only 74% yield and 88% *ee* were obtained under the same conditions (Table 1, Entry 11). The above results indicate that the thioamide functional group is beneficial for higher catalytic activity. Then, the effect of additive of this reaction was investigated. In the absence of PhCOOH, the yield and enantioselectivity dramatically decreased (Table 1, Entry 12). It could be concluded that the combination of organocatalyst **1c** and PhCOOH is crucial for the reactivity of this catalytic system. For further details, the loading of the additive was also studied. The reaction afforded a good *ee* value but only a moderate yield when a larger amount of additive was used (20 mol-%; Table 1, Entry 13). However, a much higher yield was obtained when this reaction was carried out with 2–10 mol-% of PhCOOH (Table 1, Entries 7, 14, and 15). Thus, the most efficient catalytic system involved 0.1–0.2 mol-% of catalyst **1c** and 2 mol-% of PhCOOH in water.

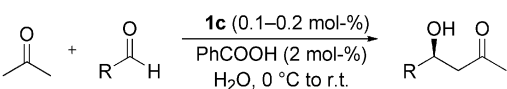
Table 1. Reaction parameter screening in the direct asymmetric aldol reaction of 4-nitrobenzaldehyde with acetone catalyzed by organocatalyst **1**.^[a]

Entry	Solvent	Catalyst	Cat. loading [mol-%]	PhCOOH [mol-%]	Time [h]	Yield [%] ^[b]	<i>ee</i> [%] ^[c]	
1	H ₂ O	1a	2	10	8	81	96	
2	H ₂ O	1b	2	10	24	20	60	
3	H ₂ O	1c	2	10	8	91	98	
4	brine	1c	2	10	8	91	96	
5	H ₂ O	1c	1	10	8	89	99	
6	H ₂ O	1c	0.5	10	12	96	98	
7	H ₂ O	1c	0.2	10	12	94	96	
8	H ₂ O	1a	0.2	10	12	78	93	
9	H ₂ O	1c	0.1	10	24	86	95	
10 ^[d]	H ₂ O	1c	0.1	10	24	90	95	
11 ^[d]	H ₂ O	1a	0.1	10	24	74	88	
12	H ₂ O	1c	0.2	–	24	40	70	
13	H ₂ O	1c	0.2	20	12	64	96	
14	H ₂ O	1c	0.2	5	12	91	95	
15	H ₂ O	1c	0.2	2	12	92	95	

[a] Unless stated otherwise, the reaction was carried out with acetone (0.2 mL, 2.5 mmol, 5 equiv.) and 4-nitrobenzaldehyde (0.5 mmol, 1 equiv.) at 0 °C in water or brine (1 mL) according to the general procedure. [b] Isolated yield. [c] Determined by chiral HPLC analysis by using a Chiralpak AS-H column, and the configuration was assigned as *R* by comparison of the optical rotation. [d] The reaction was carried out at room temperature.

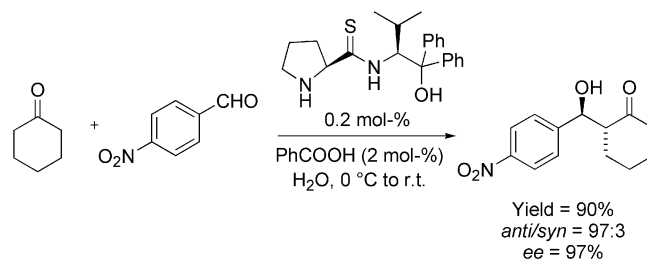
Then, the scope of the aldehyde substrates in the direct asymmetric aldol reactions of acetone was examined under the optimal conditions (Table 2). In most cases, excellent enantioselectivities were achieved, though the rate and yield of the aldol reaction strongly depended on the electrophilicity of the aldehyde substrate. From the results shown in Table 2, we found that aromatic aldehydes bearing an electron-withdrawing group gave excellent conversions due to the strong electrophilicity of the substrates. For example, *o*-, *m*-, and *p*-nitrobenzaldehydes or *o*- and *p*-trifluoromethylbenzaldehyde (Table 2, Entries 2–4, 8, 9) are the most reactive, yielding the aldol products in excellent yields after only 12 h at 0 °C with as little as 0.1 mol-% loading of organocatalyst **1c**. Weak electrophilic aldehydes, such as 4-methylbenzaldehyde, required a longer reaction time to give the corresponding aldol products in moderate yield (Table 2, Entry 12). Nevertheless, as for less-reactive aliphatic aldehydes such as isobutyraldehyde, only a trace amount of the aldol adduct could be obtained in this system (Table 2, Entry 15). This may be due to the fact that the formation of imidazolidinethiones between isobutyraldehyde and the organocatalyst occurs more quickly in this reaction system. Notably, good to high yields with excellent enantioselectivities up to >99% *ee* were obtained by using only 0.1–0.2 mol-% of organocatalyst **1c** in water with PhCOOH as an additive.

Table 2. Scope of direct asymmetric aldol reactions of acetone with various aldehydes catalyzed by organocatalyst **1c**.^[a]

					
Entry	R	Product	Time [h]	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1	Ph	2a	16	92	97
2	4-NO ₂ C ₆ H ₄	2b	12	92	95
3 ^[d]	3-NO ₂ C ₆ H ₄	2c	12	88	>99
4 ^[d]	2-NO ₂ C ₆ H ₄	2d	12	98	99
5	4-BrC ₆ H ₄	2e	16	76	96
6	3-BrC ₆ H ₄	2f	16	91	>99
7	2-BrC ₆ H ₄	2g	16	90	98
8 ^[d]	4-CF ₃ C ₆ H ₄	2h	10	91	98
9 ^[d]	2-CF ₃ C ₆ H ₄	2i	10	96	99
10	4-FC ₆ H ₄	2j	16	89	98
11	4-ClC ₆ H ₄	2k	16	90	98
12	4-MeC ₆ H ₄	2l	24	72	98
13	β-naphthyl	2m	12	77	96
14	2-furyl	2n	12	67	84
15	<i>i</i> Pr	2o	36	<10	–

[a] Unless stated otherwise, the reaction was carried out with acetone (0.2 mL, 2.5 mmol, 5 equiv.) and various aldehydes (0.5 mmol, 1 equiv.) under optimal reaction conditions in the presence of organocatalyst **1c** (0.2 mol-%). [b] Isolated yield. [c] Determined by chiral HPLC analysis by using a Chiralpak AD-H, AS-H, or OJ-H column, and the configuration was assigned as *R* by comparison of the optical rotation. [d] The reaction was carried out in the presence of 0.1 mol-% of organocatalyst **1c**.

Finally, to further examine the generality of this catalytic system, cyclohexanone was used as the aldol donor. Up to 90% yield and excellent diastereoselectivity and enantioselectivity were obtained under the optimal reaction conditions summarized as follows: cyclohexanone (1 mmol), *p*-nitrobenzaldehyde (0.5 mmol), and **1c** (0.2 mol-%) at 0 °C to room temperature with PhCOOH as an additive (Scheme 2).



Scheme 2. Direct aldol reaction of cyclohexanone with 4-nitrobenzaldehyde catalyzed by organocatalyst **1c**.

Conclusions

In summary, L-prolinethioamide **1c** is a very highly efficient chiral organocatalyst for the asymmetric aldol reactions of various aldehydes with acetone or cyclohexanone in water. Moreover, it is worthwhile to highlight that the reactions could achieve high enantioselectivity ranging from 84 to 99% *ee* and up to 98% yield by employing only 0.1–0.2 mol-% of organocatalyst **1c**. The advantages of this catalytic system are clear, and it is to some extent a green and atom economical approach. Further application of these L-prolinethioamide organocatalysts to other important asymmetric reactions is underway.

Experimental Section

Typical Procedure for the Direct Asymmetric Aldol Reaction: To a mixture of catalyst **1c** and benzoic acid in water (1 mL) was added acetone (0.2 mL, 2.5 mmol, 5 equiv.). Then, the aldehyde (0.5 mmol, 1 equiv.) was added at 0 °C. After TLC analysis indicated complete consumption of the starting material, the reaction mixture was quenched with saturated NH₄Cl aqueous solution, extracted with EtOAc, and dried with anhydrous Na₂SO₄. The crude product was purified by flash silica gel chromatography (hexane/EtOAc) to afford pure aldol products. All aldol products are known compounds, and their spectroscopic data are identical to those reported in the literature. The *ee* values were determined by chiral HPLC analysis.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures, characterization data for all new compounds, and HPLC data.

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- [1] a) G. Casiraghi, F. Zanardi, G. Appendino, G. Rassu, *Chem. Rev.* **2000**, *100*, 1929–1972; b) T. D. Machajewski, C. H. Wong, *Angew. Chem. Int. Ed.* **2000**, *39*, 1352–1374.

- [2] a) S. Mukherjee, J. W. Yang, S. Hoffmann, B. List, *Chem. Rev.* **2007**, *107*, 5471–5569; b) J. Seayad, B. List, *Org. Biomol. Chem.* **2005**, *3*, 719–724; c) H. Pellissier, *Tetrahedron* **2007**, *63*, 9267–9331; d) K. Sakthivel, W. Notz, T. Bui, C. F. Barbas III, *J. Am. Chem. Soc.* **2001**, *123*, 5260–5267; e) W. Notz, F. Tanaka, C. F. Barbas III, *Acc. Chem. Res.* **2004**, *37*, 580–591; f) P. Dziedzic, W. B. Zou, J. Hafren, A. Cordova, *Org. Biomol. Chem.* **2006**, *4*, 38–40; g) S. Adachi, T. Harada, *Eur. J. Org. Chem.* **2009**, 3661–3671.
- [3] B. List, R. A. Lerner, C. F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2395–2396.
- [4] a) B. M. Trost, C. S. Brindle, *Chem. Soc. Rev.* **2010**, *39*, 1600–1632; b) C. Aprile, F. Giacalone, M. Gruttadauria, A. M. Marculescu, R. Noto, J. D. Revell, H. Wennemers, *Green Chem.* **2007**, *9*, 1328–1334; c) J. D. Revell, H. Wennemers, *Adv. Synth. Catal.* **2008**, *350*, 1046–1052; d) Y. Qian, X. Zheng, Y. Wang, *Eur. J. Org. Chem.* **2010**, 3672–3677.
- [5] a) Z. Tang, F. Jiang, L. T. Yu, X. Cui, L. Z. Gong, A. Q. Mi, Y. Z. Jiang, Y. D. Wu, *J. Am. Chem. Soc.* **2003**, *125*, 5262–5263; b) Z. Tang, L. Z. Gong, A. Q. Mi, Y. Z. Jiang, *Catal. Fine Chem. Synth.* **2004**, *3*, 208–210; c) Z. Tang, F. Jiang, X. Cui, L. Z. Gong, A. Q. Mi, Y.-Z. Jiang, Y. D. Wu, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5755–5760; d) F. B. Chen, S. Huang, H. Zhang, F. Y. Liu, Y. G. Peng, *Tetrahedron* **2008**, *64*, 9585–9591; e) Y. Q. Fu, Z. C. Li, L. N. Ding, J. C. Tao, S. H. Zhang, M. S. Tang, *Tetrahedron: Asymmetry* **2006**, *17*, 3351–3357; f) Z. Xu, P. Daka, I. Budik, H. Wang, F. Q. Bai, H. X. Zhang, *Eur. J. Org. Chem.* **2009**, 4581–4585.
- [6] a) D. Almasi, D. A. Alonso, C. Najera, *Adv. Synth. Catal.* **2008**, *350*, 2467–2472; b) D. Almasi, D. A. Alonso, A. N. Balaguer, C. Najera, *Adv. Synth. Catal.* **2009**, *351*, 1123–1131; c) D. Gryko, R. Lipinski, *Adv. Synth. Catal.* **2005**, *347*, 1948–1952.
- [7] a) E. Tsandi, C. G. Kokotos, S. Kousidou, V. Ragoussis, G. Kokotos, *Tetrahedron* **2009**, *65*, 1444–1449; b) S. P. Zhang, X. K. Fu, S. D. Fu, J. F. Pan, *Catal. Commun.* **2009**, *10*, 401–405; c) J. Wang, H. Li, Y. J. Mei, B. S. Lou, D. G. Xu, D. Q. Xie, H. Guo, W. Wang, *J. Org. Chem.* **2005**, *70*, 5678–5687; d) K. Mei, S. Zhang, S. He, P. Li, M. Jin, F. Xue, G. Luo, H. Zhang, L. Song, W. Duan, W. Wang, *Tetrahedron Lett.* **2008**, *49*, 2681–2684.
- [8] a) X. H. Yua, W. Wang, *Org. Biomol. Chem.* **2008**, *6*, 2037–2046; b) S. Z. Luo, H. Xu, J. Y. Li, L. Zhang, J. P. Cheng, *J. Am. Chem. Soc.* **2007**, *129*, 3074; c) S. Z. Luo, H. Xu, L. Zhang, J. Y. Li, J. P. Cheng, *Org. Lett.* **2008**, *10*, 653–656; d) L. Li, L. W. Xu, Y. D. Ju, G. Q. Lai, *Synth. Commun.* **2009**, *39*, 764–774; e) J. Y. Li, S. Z. Luo, J. P. Cheng, *J. Org. Chem.* **2009**, *74*, 1747–1750; f) C. S. Da, L. P. Che, Q. P. Guo, F. C. Wu, X. Ma, Y. N. Jia, *J. Org. Chem.* **2009**, *74*, 2541–2546; g) B. L. Zheng, Q. Z. Liu, C. S. Guo, X. L. Wang, L. He, *Org. Biomol. Chem.* **2007**, *5*, 2913–2915.
- [9] a) M. Mohammad, N. J. Eric, *Science* **2002**, *298*, 1904–1905; b) S. Bahmanyar, K. N. Houk, *J. Am. Chem. Soc.* **2001**, *123*, 11273–11283.
- [10] a) P. Krattiger, R. Kovasy, J. D. Revell, S. Ivan, H. Wennemers, *Org. Lett.* **2005**, *7*, 1101–1103; b) G. Pousse, F. L. Cavelier, L. Humphreys, J. Rouden, J. Blanchet, *Org. Lett.* **2010**, *12*, 3582–3585; c) T. Kano, Y. Yamaguchi, O. Tokuda, K. Maruoka, *J. Am. Chem. Soc.* **2005**, *127*, 16408–16409; d) M. Wiesner, J. D. Revell, S. Tonazzi, H. Wennemers, *J. Am. Chem. Soc.* **2008**, *130*, 5061–5062; e) S. L. Zhu, S. Y. Yu, D. W. Ma, *Angew. Chem. Int. Ed.* **2008**, *47*, 545–548; f) T. Kano, Y. Yamaguchi, K. Maruoka, *Angew. Chem. Int. Ed.* **2009**, *48*, 1838–1840; g) M. Wiesner, M. Neuburger, H. Wennemers, *Angew. Chem. Int. Ed.* **2008**, *47*, 1871–1874; h) M. Wiesner, J. D. Revell, H. Wennemers, *Chem. Eur. J.* **2009**, *15*, 10103–10109.
- [11] M. Wiesner, G. Upert, G. Angelici, H. Wennemers, *J. Am. Chem. Soc.* **2010**, *132*, 6–7.
- [12] a) M. Benaglia, M. Cinquini, F. Cozzi, G. Celentano, *Org. Biomol. Chem.* **2004**, *2*, 3401–3407; b) R. Mestres, *Green Chem.* **2004**, *6*, 583–603.
- [13] a) Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima, M. Shoji, *Angew. Chem. Int. Ed.* **2006**, *45*, 958–961; b) S. Aratake, T. Itoh, T. Okano, T. Usui, M. Shoji, Y. Hayashi, *Chem. Commun.* **2007**, 2524–2526; c) S. Aratake, T. Itoh, T. Okano, N. Nagae, T. Sumiya, M. Shoji, Y. Hayashi, *Chem. Eur. J.* **2007**, *13*, 10246–10256.
- [14] a) A. Cordova, W. Notz, C. F. Barbas III, *Chem. Commun.* **2002**, 3024–3025; b) N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc.* **2006**, *128*, 734–735; c) S. S. V. Ramasastry, H. Zhang, F. Tanaka, C. Barbas III, *J. Am. Chem. Soc.* **2007**, *129*, 288–289.
- [15] a) Y. Watanabe, K. Sawada, M. Hayashi, *Green Chem.* **2010**, *12*, 384–386; b) S. S. V. Ramasastry, K. Albertshofer, N. Utsumi, C. F. Barbas III, *Org. Lett.* **2008**, *10*, 1621–1624; c) S. Guizzetti, M. Benaglia, L. Raimondi, G. Celentano, *Org. Lett.* **2007**, *9*, 1247–1250; d) M. Lei, L. X. Shi, G. Li, S. Chen, W. H. Fang, Z. M. Ge, T. M. Cheng, R. T. Li, *Tetrahedron* **2007**, *63*, 7892–7898; e) J. F. Zhao, L. He, J. Jiang, Z. Tang, L. F. Cun, L. Z. Gong, *Tetrahedron Lett.* **2008**, *49*, 3372–3375; f) S. S. Chimni, S. Singh, D. Mahajan, *Tetrahedron: Asymmetry* **2008**, *19*, 2276–2284; g) Z. Jiang, H. Yang, X. Han, J. Luo, M. W. Wong, Y. Lu, *Org. Biomol. Chem.* **2010**, *8*, 1368–1377; h) M. Gruttadauria, *Eur. J. Org. Chem.* **2009**, 5437–5444.
- [16] a) M. Raj, G. Parashari, V. Singh, *Adv. Synth. Catal.* **2009**, *351*, 1284–1288; b) V. Maya, M. Raj, V. K. Singh, *Org. Lett.* **2007**, *9*, 2593–2595; c) M. Raj, Vishnumaya, S. K. Ginotra, V. K. Singh, *Org. Lett.* **2006**, *8*, 4097–4099.
- [17] a) D. Gryko, M. Zimmnicka, R. Lipinski, *J. Org. Chem.* **2007**, *72*, 964–970; b) D. Gryko, W. J. Saletta, *Org. Biomol. Chem.* **2007**, *5*, 2148–2153.
- [18] a) Y. N. Jia, F. C. Wu, X. Ma, G. J. Zhu, C. S. Da, *Tetrahedron Lett.* **2009**, *50*, 3059–3062; b) M. Jiang, S. F. Zhu, Y. Yang, L. Z. Gong, X. G. Zhou, Q. L. Zhou, *Tetrahedron: Asymmetry* **2006**, *17*, 384–387.
- [19] B. Wang, G. H. Chen, L. Y. Liu, W. X. Chang, J. Li, *Adv. Synth. Catal.* **2009**, *351*, 2441–2448.
- [20] a) X. L. Geng, J. Wang, G. X. Li, P. Chen, S. F. Tian, J. Qu, *J. Org. Chem.* **2008**, *73*, 8558–8562; b) R. S. Schwab, F. Z. Galotto, J. B. Azeredo, A. L. Braga, D. S. Ludtke, M. W. Paixao, *Tetrahedron Lett.* **2008**, *49*, 5094–5097.
- [21] M. R. Vishnumaya, V. K. Singh, *J. Org. Chem.* **2009**, *74*, 4289–4297.

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