Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 49 (2008) 2681–2684
Tetrahedron Letters

(*S*)-Pyrrolidine sulfonamide catalyzed asymmetric direct aldol reactions of aryl methyl ketones with aryl aldehydes

Kui Mei [a], Shilei Zhang [a,*], Songtao He [b], Ping Li [a], Mei Jin [a], Fei Xue [a], Guangshun Luo [a], Haoyi Zhang [a], Lirong Song [a], Wenhu Duan [a,b,*], Wei Wang [a,c,*]

[a] *Department of Pharmaceutical Sciences, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, People's Republic of China*
[b] *Shanghai Institute of Materia Medica, Shanghai Institutes of Biological Sciences, Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Shanghai 201203, People's Republic of China*
[c] *Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131-0001, USA*

Received 9 January 2008; revised 17 February 2008; accepted 29 February 2008
Available online 5 March 2008

Abstract

A (*S*)-pyrrolidine sulfonamide catalyzed asymmetric direct aldol reaction of aryl methyl ketones with aromatic aldehydes has been developed with moderate to good enantioselectivities. The study considerably broadens the substrate scope of chiral amines promoted aldol processes.

Keywords: Aldol reaction; Aryl alkyl ketones; Pyrrolidine sulfonamide

The seminal work by List et al. using L-proline catalyzed direct intermolecular aldol reactions has triggered a broad interest in organocatalysis.[1] Subsequently, a number of research groups have developed proline analogues for the aldol process aimed at improving reactivity, broadening substrate scope and enhancing stereoselectivity.[2,3] Despite the fact that in many cases, these proline analogues displayed high catalytic activity and enantio- and diastereoselectivity, they suffered from a narrow substrate scope. For example, it was found that when ketones were used as donors, they were restricted to ones with alkyl groups at both ends. In contrast, the use of less reactive aryl alkyl ketones has created a formidable challenge and the survey of the literature reveals that only single study was reported by Saito and Yamamoto.[3g] The process was catalyzed by proline-derived tetrazole in low to high yields (35–93%) and with moderate to high ees (67–97%), but only worked out for highly active trichloro- and trifluoroacetaldehydes as aldol acceptor. Therefore, the general methods mainly rely on the indirect chiral Lewis acid catalyzed asymmetric Mukaiyama aldol reaction of preformed silyl enol ethers.[4]

As a result of this deficiency, we have recently initiated an investigation aimed at broadening the scope of chiral amines catalyzed direct cross aldol reactions. In this Letter, we report the results of a study which has led to the development of a (*S*)-pyrrolidine sulfonamide promoted a direct aldol reaction of aromatic methyl ketones with aromatic aldehydes in high efficiency.[5,6]

To identify active promoters for the activation of less reactive aryl methyl ketones, our investigation began with the design of new bifunctional amines and screening of them including some known organocatalysts (Fig. 1). Our strategy in the design of more active bifunctional amine catalysts is the incorporation of acidic groups, which can effectively activate aldol acceptors. In the recent past, thioureas with the ability of affording two H-bond donors have been widely used as general acid for effective activation of

* Corresponding authors. Tel.: +86 21 6425 1973 (S.Z.); tel.: +86 21 5080 6032 (W.D.); tel.: +1 505 277 0756; fax: +1 505 277 2609 (W.W.).
E-mail addresses: zhangshilei@ecust.edu.cn (S. Zhang), wduan@mail.shcnc.ac.cn (W. Duan), wwang@unm.edu (W. Wang).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.02.164

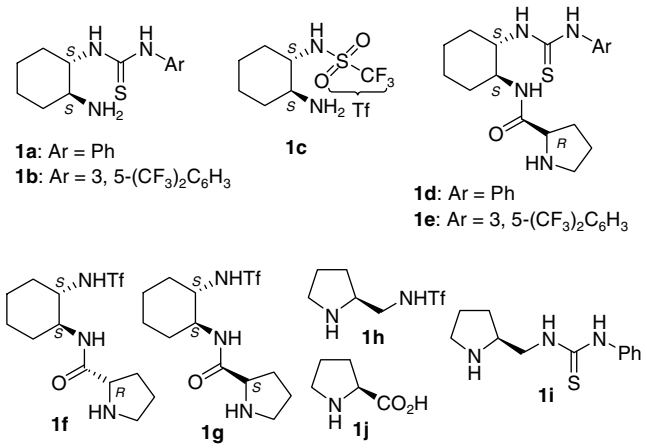


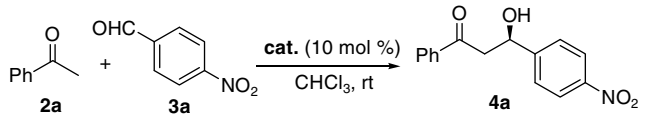
Fig. 1. Organocatalysts evaluated in the direct cross aldol reaction.

carbonyl groups with a great success.[7] Furthermore, we have found that acidic sulfonamides are also strong activators for electrophiles.[5] On the other hand, recently, chiral primary amines have gained a great deal of interest in organocatalysis.[8] They have been shown to serve as effective activators for facilitating the forming enamines from ketones and aldehydes. In particular, Jacobsen and co-workers have demonstrated that primary amine thioureas can efficiently catalyze aromatic alkyl ketones to produce enamines for a highly enantioselective conjugate nitroalkene addition process.[8d] With these considerations in mind, we designed and synthesized chiral bifunctional *trans*-cyclohexanediamine-based organic catalysts **1a**–**g**, which consist of these functional groups.[9]

To explore their catalytic ability of these organocatalysts for aldol process, a model reaction between phenyl methyl ketone **2a** and *p*-nitrobenzaldehyde **3a** was performed in chloroform at room temperature in the presence of 10 mol % an organocatalyst (Table 1). As revealed in Table 1, their catalytic activities varied significantly. Disappointingly, these new organocatalysts **1a**–**g** exhibited poor catalyst activity for the aldol reaction (entries 1–7). Poor reaction yields (8–19%) and low enantioselectivities (5–16% ee) were obtained with long reaction times (5 d). A similar trend was observed for catalyst (*S*)-pyrrolidine thiourea **1i** (entry 9). No desired product was formed when (*S*)-proline was used and only a by-product bicyclic 1,3-oxazolidine[10] resulted from the reaction of the catalyst with *p*-nitrobenzaldehyde isolated in 58% yield based on (*S*)-proline (entry 10). Among the organocatalysts probed, it was found that (*S*)-pyrrolidine sulfonamide **1h**[5] displayed high catalytic activity for the aldol reaction in a good yield (76%), but the enantioselectivity was low (21% ee, Table 1, entry 8). Subsequently, catalyst **1h** was selected for further condition optimizations mainly aimed at improving enantioselectivity of the aldol process.

We first investigated the solvent effect on the cross aldol reaction. As shown in Table 2, the reaction yields and enantioselectivities were highly solvent dependent. Lower enantioselectivity was observed when less polar aprotic solvents were used (entries 1–5), while more polar ones afforded aldol adduct **4a** with significant improved ees (entries 8 and 9). Notably, a high level of enantioselectivity (82% ee, entry 9) was achieved with DMSO (analytic

Table 1
Asymmetric direct aldol reaction of phenyl methyl ketone with *p*-nitrobenzaldehyde catalyzed by organocatalysts **1a**–**j**[a]

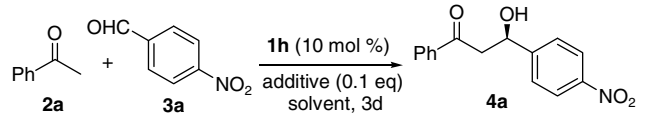


2a **3a** **4a**

Entry	Cat	*t* (d)	Yield[b] (%)	ee[c] (%)
1	**1a**	5	19	6
2	**1b**	5	16	5
3	**1c**	5	7	−7
4	**1d**	5	14	−12
5	**1e**	5	8	−11
6	**1f**	5	10	−7
7	**1g**	5	11	16
8	**1h**	**3**	**76**	**21**
9	**1i**	5	20	15
10	**1j**	5	—[d]	—

[a] The reaction was carried out with **3a** (0.2 mmol) and **2a** (1.0 mmol, 5 equiv) in the presence of 10 mol % an organocatalyst in 0.3 mL of $CHCl_3$ at rt.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis (Chirapak AD-H column).
[d] No desired product was obtained.

Table 2
Effects of solvents and additives on the asymmetric direct aldol reaction of phenyl methyl ketone and *p*-nitrobenzaldehyde catalyzed by **1h**[a]



2a **3a** **4a**

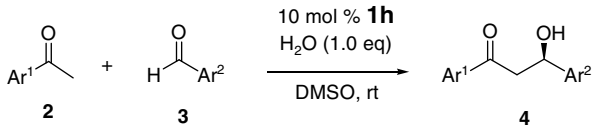
Entry	Solvent	Additive	Yield[b] (%)	ee[c] (%)
1	$CHCl_3$	None	76	21
2	Toluene	None	30	25
3	Dioxane	None	46	30
4	THF	None	38	47
5	MeCN	None	72	51
6	*i*-PrOH	None	46	11
7	H_2O	None	67	50
8	DMF	None	71	70
9	DMSO	None	74	82
10	DMSO	AcOH	37	81
11	DMSO	$PhCO_2H$	41	82
12	DMSO	CF_3CO_2H	<5	nd[e]
13	DMSO	H_2O (0.5 equiv)	81	82
14	DMSO	H_2O (1.0 equiv)	86	82
15	DMSO	H_2O (5.0 equiv)	72	81
16[d]	DMSO	H_2O (1.0 equiv)	45	90

[a] Unless stated otherwise, the reaction was carried out with 1.0 mmol (0.12 mL, 5 equiv) **2a** and 0.2 mmol **3a** in the presence of 10 mol % catalyst in 0.3 mL of solvent and stirred at rt for 3 d.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] 0 °C, 2.0 mmol (0.24 mL, 10 equiv) **2a** was used, 5 d.
[e] Not determined.

grade). Protic solvents such as *i*-PrOH and water tested seemed to have an adverse influence on enantioselectivity (entries 6 and 7). A possible reason for the aprotic polar solvent DMSO afford the best results was due to its ability of stabilizing the charged transition state, while protic solvents disrupted the transition state. The effect of additives in DMSO on enantioselectivity was also probed. Acid additives such as AcOH, $PhCO_2H$ and CF_3CO_2H retarded the process and the reaction yields dropped dramatically but without affecting ee values (entries 10–12); it was found that water could increase the yield slightly, but it did not deteriorate the enantioselectivity either (Table 2, entry 13–15). Scrutinizing the amount of water implied that the use of 1.0 equiv was optimal in terms of reaction yield and enantioselectivity (entry 14). Finally, lowering the temperature to 0 °C increased the ee of the product from 82% to 90% but the yield decreased significantly from 86% to 45% (Table 2, entry 14 vs entry 16).

Having established optimized conditions for the model reaction, we next probed the generality of this asymmetric direct aldol reaction with a wide range of aromatic ketones and aryl aldehydes (Table 3). Aromatic methyl ketones bearing various substituents were first investigated as aldol donors with *p*-nitrobenzaldehyde (Table 3, entries 1–7). The neutral (entry 1), electron-withdrawing (entries 2–4), -donating (entries 5–6), and heterocyclic (entry 7) groups could be tolerated in the **1h**-promoted aldol processes.

Table 3
Scope of catalyst **1h** catalyzed asymmetric aldol reactions of aryl methyl ketones with aryl aldehydes[a]



2 **3** **4**

Entry	Ar^1	Ar^2	*t* (d)	Yield[b] (%)	ee[c] (%)
1	Ph	*p*-$NO_2C_6H_4$	3	**4a**, 74	82
2	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	2	**4b**, 91	70
3	*p*-ClC_6H_4	*p*-$NO_2C_6H_4$	3	**4c**, 74	76
4	2,4-$Cl_2C_6H_3$	*p*-$NO_2C_6H_4$	3	**4d**, 47	80
5	*p*-$MeOC_6H_4$	*p*-$NO_2C_6H_4$	3	**4e**, 65	79
6	*p*-MeC_6H_4	*p*-$NO_2C_6H_4$	3	**4f**, 77	87
7	*o*-Thienyl	*p*-$NO_2C_6H_4$	5	**4g**, 51	62
8	Ph	*o*-$NO_2C_6H_4$	3	**4h**, 68	87
9	Ph	*m*-$NO_2C_6H_4$	3	**4i**, 45	81
10	Ph	*p*-FC_6H_4	5	**4j**, 32	73
11	Ph	*p*-BrC_6H_4	5	**4k**, 26	80
12	Ph	*o*-BrC_6H_4	5	**4l**, 31	76
13	Ph	Ph	5	**4m**, 18	80
14	*p*-$NO_2C_6H_4$	*m*-$NO_2C_6H_4$	2	**4n**, 87	71
15	*p*-$NO_2C_6H_4$	*o*-$NO_2C_6H_4$	2	**4o**, 83	80
16	*p*-$MeOC_6H_4$	*m*-$NO_2C_6H_4$	4	**4p**, 51	80
17	*p*-$MeOC_6H_4$	*o*-$NO_2C_6H_4$	3	**4q**, 57	91

[a] Unless stated otherwise, the reaction was carried out with 0.2 mmol **3** and 1.0 mmol (5 equiv) **2** in the presence of 10 mol % organocatalyst **1h** and water (1 equiv) in 0.3 mL of DMSO at rt.
[b] Isolated yield after chromatographic purification.
[c] Determined by chiral HPLC analysis (Chirapak AD, AS or OD-H column).

Moderate to good yields (47–91%) and moderate to high ees (62–87%) were observed. The study in a variation of aldol donors revealed that the reaction yields varied significantly, but the enantioselectivity was not affected much with achieving moderate to high levels of enantioselectivity (71–87% ee, entries 8–17). Low reaction yields were attained when phenyl methyl ketone was used as aldol donor (entries 8–13). Similar observation was noticed with *p*-MeO-benzaldehyde (entries 16–17). However, *p*-NO_2-benzaldehyde afforded aldol adducts with higher yields (83–87%, entries 14 and 15).

The absolute configuration of aldol products was determined to be *R* by comparison of the optical rotation value and sign of **4m** with those of the literature reported.[11]

In conclusion, we have developed a (*S*) pyrrolidine sulfonamide **1h** catalyzed asymmetric aldol reaction of aromatic methyl ketones with aromatic aldehydes. Moderate to good enantioselectivities were obtained under the optimized reaction conditions. The study considerably widens the substrate scope of chiral amine promoted direct aldol processes by allowing the use of difficult aromatic methyl ketones for aldol reaction with aromatic aldehydes. A full scope of investigation of the strategy is underway in our laboratory.

Acknowledgments

This work was supported by Shanghai Basic Research Project from the Shanghai Science and Technology Commission (Grants 06JC14080) and start-up funding from School of Pharmacy, East China University of Science and Technology.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.164.

References and notes

1. List, B.; Lerner, R. A.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2000**, *122*, 2395.
2. Recent reviews of chiral secondary amine catalyzed enamine chemistry, see: (a) List, B. *Acc. Chem. Res.* **2004**, *37*, 548; (b) Notz, W.; Tanaka, F.; Barbas, C. F., III. *Acc. Chem. Res.* **2004**, *37*, 580; (c) Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471.
3. Selected examples of proline analogues catalyzed aldol reactions, see: (a) Sakthivel, K.; Notz, W.; Bui, T.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2001**, *123*, 5260; (b) Saito, S.; Nakadai, M.; Yamamoto, H. *Synlett* **2001**, 1245; (c) Tang, Z.; Jiang, F.; Yu, L.-T.; Cui, X.; Gong, L.-Z.; Mi, A.-Q.; Jiang, Y.-Z.; Wu, Y.-D. *J. Am. Chem. Soc.* **2003**, *125*, 5262; (d) Krattiger, P.; McCarthy, C.; Pfaltz, A.; Wennemers, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1722; (e) Kofoed, J.; Nielsen, J.; Reymond, J.-L. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 2445; (f) Cobb, A. J. A.; Shaw, D. M.; Ley, S. V. *Synlett* **2004**, 558; (g) Torii, H.; Nakadai, M.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1983; (h) Lacoste, E.; Landais, Y.; Schenk, K.; Verlhac, J.-B.; Vincent, J.-M. *Tetrahedron Lett.* **2004**, *45*, 8035; (i)

Berkessel, A.; Koch, B.; Lex, J. *Adv. Synth. Catal.* **2004**, *346*, 1141; (j) Mangion, I. K.; Northrup, A. B.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6722; (k) Shi, L.-X.; Sun, Q.; Ge, Z.-M.; Zhu, Y.-Q.; Cheng, T.-M.; Li, R.-T. *Synlett* **2004**, 2215; (l) Cobb, A. J. A.; Shaw, D. M.; Longbottom, D. A.; Ley, S. V. *Org. Biomol. Chem.* **2005**, *3*, 84; (m) Chimni, S. S.; Mahajan, D.; Babu, V. V. S. *Tetrahedron Lett.* **2005**, *46*, 5617; (n) Bellis, E.; Kokotos, G. *Tetrahedron* **2005**, *61*, 8669; (o) Chen, J.-R.; Lu, H.-H.; Li, X.-Y.; Cheng, L.; Wan, J.; Xiao, W.-J. *Org. Lett.* **2005**, *7*, 4543; (p) Samanta, S.; Liu, J.; Dodda, R.; Zhao, C.-G. *Org. Lett.* **2005**, *7*, 5321; (q) Gryko, D.; Lipinski, R. *Adv. Synth. Catal.* **2005**, *347*, 1948; (r) Jiang, M.; Zhu, S.-F.; Yang, Y.; Gong, L.-Z.; Zhou, X.-G.; Zhou, Q.-L. *Tetrahedron: Asymmetry* **2006**, *17*, 384; (s) Silva, F.; Sawicki, M.; Gouverneur, V. *Org. Lett.* **2006**, *8*, 5417; (t) Guillena, G.; Hita, M. C.; Njera, C. *Tetrahedron: Asymmetry* **2006**, *17*, 729; (u) Raj, M.; Vishnumaya, S. K.; Ginotra, S. K.; Singh, V. K. *Org. Lett.* **2006**, *8*, 4097; (v) Gryko, D.; Kowlaczyk, B.; Zawadzki, L. *Synlett* **2006**, 1059; (w) Cheng, C.; Sun, J.; Wang, C.; Zhang, Y.; Wei, S.; Jiang, F.; Wu, Y. *Chem. Commun.* **2006**, 215; (x) Gu, L.; Yu, M.; Wu, X.; Zhang, Y.; Zhao, G. *Adv. Synth. Catal.* **2006**, *348*, 2223; (y) Mase, N.; Nakai, Y.; Ohara, N.; Yoda, H.; Takabe, K.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2006**, *128*, 734; (z) Hayashi, Y.; Sumiya, T.; Takahashi, J.; Gotoh, H.; Urushima, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 958; Kano, T.; Yamaguchi, Y.; Tanaka, Y.; Maruoka, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1738.

4. For recent review of Mukaiyama-aldol reactions, see: (a) Shiina, I. In *Modern Aldol Reactions*; Mahrwald, R., Ed.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 105–166; Selected examples, see: (b) Shibasaki, M. *Tetrahedron: Asymmetry* **1995**, *6*, 71; (c) Li, H.-J.; Tian, H.-Y.; Chen, Y.-J.; Wang, D.; Li, C.-J. *Chem. Commun.* **2002**, 2994; (d) Mlynarski, J.; Jankowska, J. *Adv. Synth. Catal.* **2005**, *347*, 521; (e) Li, H.-J.; Tian, H.-Y.; Wu, Y.-C.; Chen, Y.-J.; Liu, L.; Wang, D.; Li, C.-J. *Adv. Synth. Catal.* **2005**, *347*, 1247; (f) Itsuno, S.; Arima, S.; Haraguchi, N. *Tetrahedron* **2005**, *61*, 12074; (g) Jankowska, J.; Paradowska, J.; Mlynarski, J. *Tetrahedron Lett.* **2006**, *47*, 5281; (h) Jankowska, J.; Paradowska, J.; Rakiel, B.; Mlynarski, J. *J. Org. Chem.* **2007**, *72*, 2228.
5. For examples of (*S*)-pyrrolidine sulfonamides promoted reactions, see: (a) Wang, W.; Wang, J.; Li, H. *Tetrahedron Lett.* **2004**, *45*, 7235; (b) Wang, W.; Wang, J.; Li, H. *Tetrahedron Lett.* **2004**, *45*, 7243; (c) Wang, W.; Li, H.; Wang, J. *Tetrahedron Lett.* **2004**, *45*, 8229; (d) Wang, W.; Wang, J.; Li, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369; (e) Wang, W.; Li, H.; Wang, J. *Tetrahedron Lett.* **2005**, *46*, 5077; (f) Wang, J.; Li, H.; Mei, Y.; Lou, B.; Xu, D.; Xie, D.; Guo, H.; Wang, W. *J. Org. Chem.* **2005**, *70*, 5678; (g) Wang, J.; Li, H.; Lou, B.; Zu, L.-S.; Guo, H.; Wang, W. *Eur. Chem. J.* **2006**, *12*, 4321; (h) Wang, J.; Li, H.; Zu, L.-S.; Wang, W. *Adv. Synth. Catal.* **2006**, *348*, 425; (i) Zu, L.-S.; Wang, J.; Li, H.; Yu, X-H.; Wang, W. *Org. Lett.* **2006**, *8*, 3077; (j) Cao, C.-L.; Sun, X.-L.; Zhou, J.-L.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 4073; (k) Cao, C.-L.; Sun, X.-L.; Kang, Y.-B.; Tang, Y. *Org. Lett.* **2007**, *9*, 4151.
6. The aromatic β-hydroxyketones are versatile building blocks in organic synthesis and drug discovery. They can be conveniently converted into diols and amine alcohols: as chiral ligands in catalysis: (a) Dubrovina, N. V.; Tararov, I.; Monsees, A.; Spannenberg, A.; Kostas, I. D.; Boerner, A. *Tetrahedron: Asymmetry* **2005**, *16*, 3640; (b) Ohtsuka, Y.; Kubota, T.; Ikeno, T.; Nagata, T.; Yamada, T. *Synlett* **2000**, 535; (c) Roos, G. H. P.; Donovan, A. R. *Tetrahedron: Asymmetry* **1999**, *10*, 991; Synthesis of isoxazolines: (d) Jaeger, V.; Buss, V.; Schwab, W. *Tetrahedron Lett.* **1978**, *19*, 3133; (e) As intermediates for preparation of nucleoside derivatives as antiviral, antitumor, and antidiabetic prodrug agents: Reddy, R. K.; Erion, M. D. Patent WO 2006033709.
7. Reviews regarding thioureas catalysis: see: (a) Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289; (b) Takemoto, Y. *Org. Biomol. Chem.* **2005**, *3*, 4299; (c) Akiyama, T.; Itoh, J.; Fuchibe, K. *Adv. Synth. Catal.* **2006**, *348*, 999; (d) Taylor, M. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1520; (e) Connon, S. J. *Chem. Eur. J.* **2006**, *12*, 5419; (f) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713.
8. Selected examples of chiral primary amines catalyzed reactions, see: (a) Davies, S. G.; Sheppard, R. L.; Smith, A. D.; Thomson, J. E. *Chem. Commun.* **2005**, 3802; (b) Tsogoeva, S. B.; Wei, S. *Tetrahedron: Asymmetry* **2005**, *16*, 1947; (c) Dziedzic, P.; Zou, W.; Hfren, J.; Córdova, A. *Org. Biomol. Chem.* **2006**, *4*, 38; (d) Huang, H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2006**, *128*, 7170; (e) Lalonde, M. P.; Chen, Y.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 6366; (f) Ramasastry, S. S. V.; Zhang, H.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2007**, *129*, 288; (g) Chen, W.; Du, W.; Duan, Y.-Z.; Wu, Y.; Yang, S.-Y.; Chen, Y.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 7667; (h) Xie, J.-W.; Chen, W.; Li, R.; Zeng, M.; Du, W.; Yue, L.; Chen, Y.-C.; Wu, Y.; Zhu, J.; Deng, J.-G. *Angew. Chem., Int. Ed.* **2007**, *46*, 389.
9. See Supplementary data for the preparation of these organocatalysts and some of them have been recently disclosed by other group during our investigation: **1a**,**b** reported in: (a) Tsogoeva, S. B.; Wei, S. W. *Chem. Commun.* **2006**, 1451; **1i** reported in: (b) Shen, Z.-X.; Zhang, Y.-Q.; Jiao, C.-J.; Li, B.; Ding, J.; Zhang, Y.-W. *Chirality* **2007**, *19*, 307; (c) Cao, C.-L.; Ye, M.-C.; Sun, X.-L.; Yang, Y. *Org. Lett.* **2006**, *8*, 2901.
10. Kano, T.; Takai, J.; Tokuda, O.; Maruoka, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3055.
11. $[\alpha]_D^{25}$ +85.4 (*c* 0.85, $CHCl_3$) for **1m**, lit.: $[\alpha]_D^{20}$ −85.3 (*c* 1.3, $CHCl_3$) for (*S*) enantiomer in: Mandal, S. K.; Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. *J. Org. Chem.* **2003**, *68*, 4600.