Res Chem Intermed (2012) 38:195–205
DOI 10.1007/s11164-011-0336-5

Organocatalysis with cysteine derivatives: recoverable and cheap chiral catalyst for direct aldol reactions

Shi Li · Xiangkai Fu · Chuanlong Wu

Received: 10 May 2011 / Accepted: 30 May 2011 / Published online: 15 June 2011

Abstract Highly enantioselective, recoverable and cheap cysteine derivatives have been developed with improved solubility properties in common, nonpolar organic solvents. The reactions were catalyzed using 5 mol% **1e**, and the aldol products could be obtained with up to 99:1 *syn*/*anti* ratio and >99% *ee*. The catalyst could be easily recovered and reused, with only a slight decrease of enantioselectivity observed for five cycles. Catalyst **1e** can be efficiently used in large-scale reactions with enantioselectivity being maintained at the same level, which offers great possibility for application in industry.

Keywords Cysteine derivatives · Aldol reactions · Recoverable catalyst · Large-scale reactions

Introduction

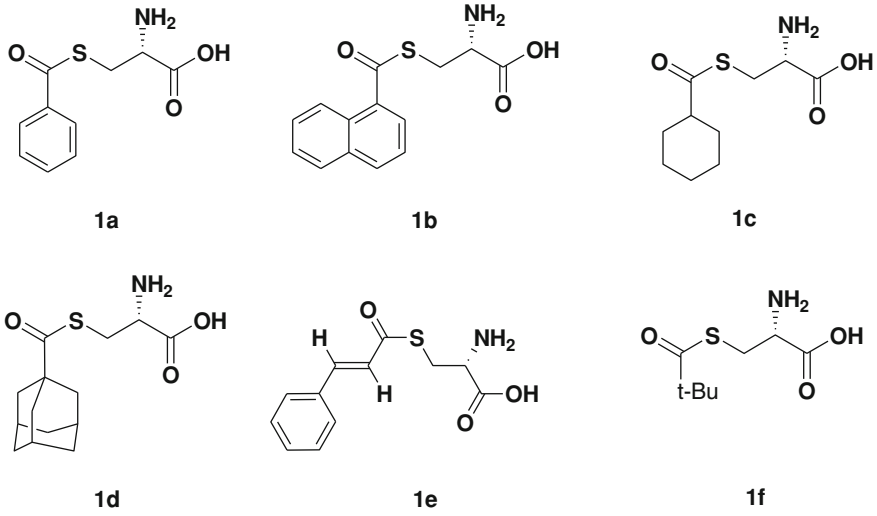
Recently, the development of new, inexpensive, simple and efficient organic molecules that catalyze enantioselective reactions has proved to be one of the successful strategies for preparation of chiral building blocks [1]. The aldol reaction is recognized as one of the most important carbon–carbon bond-forming reactions in

Electronic supplementary material The online version of this article (doi: 10.1007/s11164-011-0336-5) contains supplementary material, which is available to authorized users.

S. Li · X. Fu (✉) · C. Wu
College of Chemistry and Chemical Engineering, Southwest University, Institute of Applied Chemistry Southwest University, The Key Laboratory of Applied Chemistry of Chongqing Municipality, Chongqing 400715, People's Republic of China
e-mail: fxk@swu.edu.cn

S. Li · X. Fu · C. Wu
The Key Laboratory of Ecoenvironments in Three Gorges Reservoir Region Ministry of Education Chongqing, Chongqing 400715, People's Republic of China

modern organic synthesis (for reviews on direct aldol reactions, see [2–4]), creating the β-hydroxy carbonyl structural unit found in many natural products and drugs, and has received much attention in recent years. A wide range of small organic molecules, including proline and various other chiral pyrrolidine derivatives, have been shown to be efficient catalysts for asymmetric aldol reactions (for reviews on direct aldol reactions, see [5–13]; for selected examples of anti-aldol reactions, see [14–22]). Barbas [23–26], Hayashi [27–30], Gong [31–35] and Xiao et al. [36, 37] reported intermolecular aldol reactions of ketone–aldehyde type and aldehyde–aldehyde type catalyzed by L-proline or its derivatives and analogues. Synthesis a series of widely used industrial catalyst requires the following conditions: it should be easy to synthesize, and the initial material should be cheap and easy to obtain. Currently, aldol reaction catalysts are always complicated, and although a relatively small amount of catalyst (1–5 mol%) is added, the cost is high. On the other hand, the catalyst should be recyclable. In large-scale processes, it should maintain high enantioselectivity. However, their shortcomings have also been realized. One of the major limitations of organocatalyzed reactions is the high catalyst loading (10–30 mol%) generally required to complete the transformations in large equivalents of ketone within reasonable timescales. This raises cost concerns when large amounts of chiral materials are used for large-scale synthesis in industrial applications. Our group carried out a series of reactions using threonine- and serine-based organocatalysts for aldol and Mannich reactions [38–41]. These catalysts achieved high efficiency, but we did not carry out in-depth and careful studies on cysteine. Based on these points, we wish to synthesize sample, cheap and recyclable cysteine derivative catalysts **1a–f** (Scheme 1) that promote asymmetric direct aldol reactions.



Scheme 1 Cysteine-based organocatalysts

Experimental

General information

All reagents were commercial products. Reactions were monitored by thin-layer chromatography (TLC). Column and preparative TLC purification were carried out using silica gel. Flash column chromatography was performed on silica gel (200–300 mesh). Nuclear magnetic resonance (NMR) spectra were recorded on a 300-MHz instrument. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS) as internal reference, and coupling constants (J) in Hz. Infrared (IR) spectra were recorded on a spectrometer. Melting points were measured on a digital melting point apparatus. Mass spectra (MS) were measured with a spectrometer. Analytical high-performance liquid chromatography (HPLC) was carried out on Agilent 1200 instrument using Chiralpak AD (4.6 mm × 250 mm), Chiralcel OD-H (4.6 mm × 250 mm) or Chiralcel OJ-H (4.6 mm × 250 mm) columns. Optical rotations were measured on a JASCO P-1010 polarimeter at $\lambda = 589$ nm.

General procedure for preparation of catalysts **1a**–**1f** [42, 43]

Catalysts **1a**–**1f** (Scheme 1) were prepared in excellent yields from L-cysteine and acyl chloride. The white solids were washed by four portions of Et_2O, and then dried them in the oven at 70 °C for 24 h in a ventilated hood to give *S*-acyl-L-cysteine hydrochloride, after that dissolved the hydrochloride products in water and added an equivalent amount of Et_3N. The white suspensions were stirred at room temperature for 10 min and filtered by vacuum. The white crystals were washed with two portions of H_2O and dried to give *S*-acylated cysteine-based organocatalysts. This essentially pure material was used for the next step without further purification.

*(S)-S-(n-benzoyl)-L-cysteine (**1a**)*

White solid; Yield: 89%; $[\alpha]_D^{20} = -33.1$ (c = 1, MeOH); ^{1}H NMR [300 MHz, dimethyl sulphoxide (DMSO)]: $\delta = 3.23$–3.48 (d, $J = 5.5$ Hz, 2H), 4.17 (br. s, 1H), 7.45 (d, $J = 4.5$ Hz, 2H), 7.58 (br. s, 1H), 7.97 (d, $J = 6$ Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 33.2$, 54.0, 128.1, 128.1, 129.0, 129.0, 134.2, 134.7, 174.9, 191.5 ppm; MS [electrospray ionisation (ESI)] *m/z* calcd. for $C_{10}H_{11}NO_3S$ 225.05 found 225.74.

*(S)-S-(1-naphthoyl)-L-cysteine (**1b**)*

White solid; Yield: 89%; $[\alpha]_D^{20} = -28.9$ (c = 1, MeOH); ^{1}H NMR (300 MHz, DMSO): $\delta = 3.13$–3.39 (d, $J = 5.8$ Hz, 2H), 4.25 (br. s, 1H), 7.42–7.88 (m, 6H), 8.72 (br. s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 33.2$, 54.0, 120.3,127.3, 127.4, 129.8, 130.1, 131.4, 132.8, 134.2, 195.6 ppm; MS (ESI) *m/z* calcd. for $C_{14}H_{13}NO_3S$ 275.06 found 275.69.

*(S)-S-(n-cyclohexoyl)-L-cysteine (**1c**)*

White solid; Yield: 92%; $[\alpha]_D^{20} = -30.0$ (c = 1, MeOH); ^{1}H NMR (300 MHz, DMSO): $\delta = 1.46–1.93$ (m, 10H), 2.37 (m, 1H), 3.42–3.49 (d, $J = 5.7$ Hz, 2H), 4.09 (br. s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 25.3, 25.3, 28.0, 29.9, 29.9, 33.7, 50.9, 54.1, 180.9, 211.7$ ppm; MS (ESI) *m/z* calcd. for $C_{10}H_{17}NO_3S$ 231.09 found 231.81.

*(S)-S-(n-adamantanoyl)-L-cysteine (**1d**)*

White solid; Yield: 93%; $[\alpha]_D^{20} = -27.2$ (c = 1, MeOH); ^{1}H NMR (300 MHz, DMSO): $\delta = 1.17–1.83$ (m, 13H), 3.38–3.44 (d, $J = 5.3$ Hz, 2H), 4.24 (br. s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 28.5, 30.5, 30.5, 34.2, 37.8, 37.8, 37.8, 39.6, 39,6, 39.6, 45.7, 54.8, 180.1, 207.4$ ppm; MS (ESI) *m/z* calcd. for $C_{14}H_{21}NO_3S$ 283.12 found 283.47.

*(S)-S-(n-cinnamoyl)-L-cysteine (**1e**)*

White solid; Yield: 86%; $[\alpha]_D^{20} = -23.0$ (c = 1, MeOH); ^{1}H NMR (300 MHz, DMSO): $\delta = 3.46–3.48$ (d, $J = 5.8$ Hz, 2H), 4.17 (br. s, 1H), 7.01 (d, $J = 3$ Hz, 1H), 7.17–7.43 (m, 5H), 7.64 (d, $J = 3$ Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 33.7, 54.9, 126.7, 127.4, 129.3, 129.7, 129.9, 136.3, 177.2, 189.1$ ppm; MS (ESI) *m/z* calcd. for $C_{12}H_{13}NO_3S$ 251.06 found 251.67.

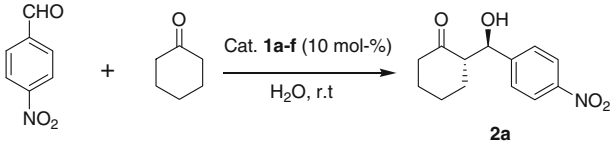
*(S)-S-(t-butoyl)-L-cysteine (**1f**)*

White solid; Yield: 83%; $[\alpha]_D^{20} = -13.1$ (c = 1, MeOH); ^{1}H NMR (300 MHz, DMSO): $\delta = 1.19$ (br. s, 9H), 3.36–3.38 (d, $J = 5.4$ Hz, 2H), 4.06 (d, $J = 5.1$ Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): $\delta = 27.2, 28.2, 46.5, 51.9, 169.4, 204.6$ ppm; MS (ESI) *m/z* calcd. for $C_8H_{15}NO_3S$ 205.08 found 205.89.

Results and discussion

The organocatalyzed aldol reaction was carried out using cyclohexanone with 4-nitrobenzaldehyde as a model reaction to investigate different parameters, such as the catalysts, solvents and loading of the catalysts. In our initial investigation, cysteine and its derivatives **1a–f** were screened as catalysts. As can be seen from the results summarized in Table 1, although natural cysteine was not an efficient organocatalyst in water (Table 1, entry 1), all the catalysts could catalyze the asymmetric direct intermolecular aldol reaction of 4-nitrobenzaldehyde and cyclohexanone to give the product in good yields (80–93%) with different *ee* values (75–90% *ee* for *anti*) in water at room temperature (Table 1, entries 2–7). Among the six derivatives, the catalyst containing the cinnamyl group gave a good yield (88%) and enantioselectivity (90% *ee* for *anti*). The cysteine-based organocatalyst **1e** turned out to be the most efficient catalyst (Table 1, entry 6).

Table 1 Screening of organocatalysts



2a

Entry	Catalyst	Cat. loading (%)	Time (h)	Yield[a] (%)	*Anti*:*syn*[b]	*ee*[b] (%)
1	L-Cys	20	48	–	nd	nd
2	**1a**	10	24	83	68:32	80
3	**1b**	10	24	82	78:22	75
4	**1c**	10	24	80	82:18	77
5	**1d**	10	24	80	87:13	85
6	**1e**	10	24	88	90:10	90
7	**1f**	10	24	93	80:20	78

The reactions were performed with 4-nitrobenzaldehyde (1 mmol), cyclohexanone (2.5 mmol) and catalyst **1a–f** (0.1 mmol) in presence of water (2 mL) at room temperature

[a] Isolated yield

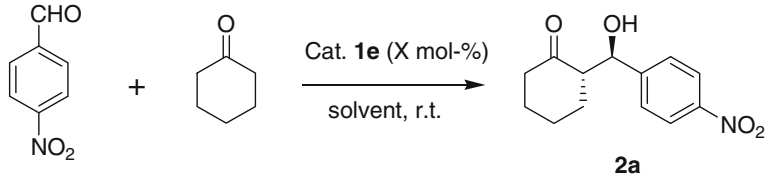
[b] Determined by chiral HPLC analysis (AD–H column)

Solvent screening was then performed at room temperature to identify the best reaction conditions (Table 2, entries 1–7). Among the organic solvents tested, when 10 mol% **1e** was used, 1,2-dichloroethane was slightly better in terms of both diastereoselectivity and enantioselectivity. Then, using 1,2-dichloroethane as reaction medium, we investigated the above reaction employing different amounts of catalyst **1e** (Table 2, entries 8–9). When the amount was decreased to 5 mol%, the *dr* and *ee* values were increased.

Using 1,2-dichloroethane as solvent and **1e** as catalyst, the effects of ketone loading on the reaction of 4-nitrobenzaldehyde and cyclohexanone were investigated (Table 3). When 5 mol% **1e** was used, the reaction could be obviously accelerated by increasing ketone from 1 to 8 equiv, and the aldol product could be obtained in high yield with good stereoselectivity even with only 4 equiv cyclohexanone.

To test the substrate generality of this organocatalyzed direct aldol reaction, the reactions of various aromatic aldehydes with cyclohexanone were studied under the optimized conditions. The results are summarized in Table 4. It can be seen that a wide range of aromatic aldehydes can effectively participate in the aldol reactions. From Table 4, we were able to access aldol adducts **2a–o** derived from their corresponding aromatic aldehydes and cyclohexanone. In general, the reactions between cyclohexanone and aromatic aldehydes bearing electron-withdrawing substituents furnished β-hydroxy carbonyl aldol products in good yields (80–92%) and enantioselectivities (91–99% *ee* for *anti*-isomer) within 20–40 h (Table 4, entries 1–9). In contrast, longer reaction times (48 h) were required for aromatic aldehydes containing an electron-donating group to give comparatively lower yields

Table 2 Effects of solvent and catalyst loading on the organocatalyzed direct aldol reaction



2a

Entry	Cat. loading (%)	Solvent	Yield[a] (%)	*Anti*:*syn*[b]	*ee*[b] (%)
1	10	H_2O	88	90:10	90
2	10	$ClCH_2CH_2Cl$	85	92:8	92
3	10	$CHCl_3$	90	93:7	91
4	10	THF	83	84:16	87
5	10	CH_3OH	82	82:18	89
6	10	DMSO	79	79:21	83
7	10	NMP	63	63:37	81
8	5	$ClCH_2CH_2Cl$	87	98:2	97
9	2	$ClCH_2CH_2Cl$	80	82:18	71

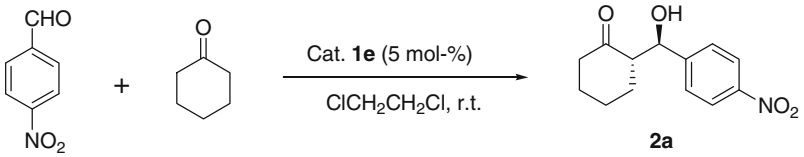
The reactions were performed with 4-nitrobenzaldehyde (1 mmol), cyclohexanone (2.5 mmol) and catalyst **1e** (see Table 2) in the specified solvent (2 mL, see Table 2) at room temperature

THF tetrahydrofuran; *NMP* N-methyl-2-pyrrolidone

[a] Isolated yield

[b] Determined by chiral HPLC analysis (AD–H column)

Table 3 Effect of amount of cyclohexanone on the aldol reaction between cyclohexanone and 4-nitrobenzaldehydes catalyzed by **1e**



2a

Entry	Cyclohexanone (equiv)	Yield[a] (%)	*Anti*:*syn*[b]	*ee*[b] (%)
1	1	81	81:19	84
2	2.5	87	98:2	97
3	4	90	>99	99
4	8	91	92:8	88

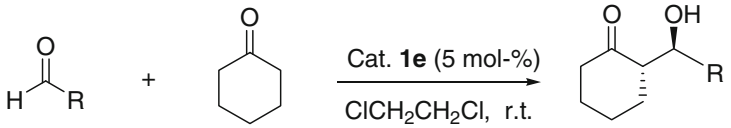
The reactions were performed with 4-nitrobenzaldehyde (1 mmol), cyclohexanone (see Table 3) and catalyst **1e** (0.05 mmol) in 1,2-dichloroethane (2 mL) at room temperature

[a] Isolated yield

[b] Determined by chiral HPLC analysis (AD–H)

(65–77%), but without decrease of enantioselectivities, especially for *p*-tolualdehyde (Table 4, entry 10, >99 *anti*/*syn* ratio and 97% *ee*) (Table 4, entries 10–12). This can be explained in that electron-withdrawing groups enhance the

Table 4 Organocatalyst **1e**-catalyzed direct aldol reactions



2a-o

Entry	Product	Time (h)	Yield (%)[a]	*Anti*:*syn*[b]	*ee* (%)[b]
1	**2a** (R = *p*–NO_2–C_6H_4)	23	85	>99	>99
2	**2b** (R = *o*–NO_2–C_6H_4)	24	89	90:10	93
3	**2c** (R = *m*–NO_2–C_6H_4)	26	83	95:5	91
4	**2d** (R = 2,4-dinitrophenyl)	20	80	97:3	92
5	**2e** (R = *p*–CN–C_6H_4)	24	88	95:5	95
6	**2f** (R = *p*–CF_3–C_6H_4)	24	88	97:3	98
7	**2g** (R = *p*–Br–C_6H_4)	36	90	97:3	94
8	**2h** (R = *p*–Cl–C_6H_4)	40	92	93:7	96
9	**2i** (R = *o*–Cl–C_6H_4)	40	86	90:10	97
10	**2j** (R = *p*–CH_3–C_6H_4)	44	70	>99	97
11	**2k** (R = *p*–OMe–C_6H_4)	48	77	95:5	95
12	**2l** (R = *m*–OMe–C_6H_4)	48	65	91:9	96
13	**2m** (R = 2-naphthyl)	30	76	98:2	94
14	**2n** (R = 1-naphthyl)	36	74	>99	90
15	**2o** (R = C_6H_5)	31	77	96:4	91

The reactions were performed with *p*-nitrobenzaldehyde (1.0 mmol), ketone (4.0 mmol) and catalyst (0.05 mmol) in solvent (2 mL) at room temperature

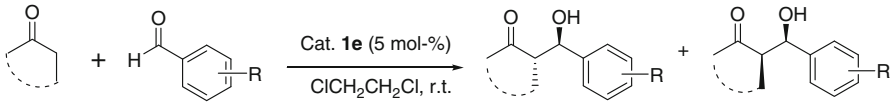
[a] Isolated yield

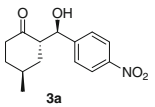
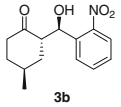
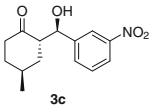
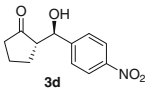
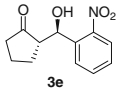
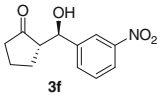
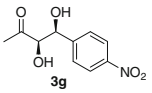
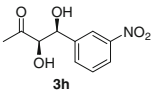
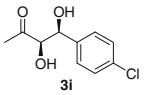
[b] Determined by chiral HPLC analysis (AD–H)

electrophilicity of carbonyl carbons in aldehydes, which facilitates the reaction, while electron-donating groups lessen the electrophilicity. Moreover, the direct aldol reactions of neutral aldehydes catalyzed by the cysteine-based organocatalyst **1e** also afforded the aldol products with high enantioselectivities and diastereoselectivities, especially the 2-naphthyl aldehyde (Table 4, entry 13, 98/2 *anti*/*syn* ratio and 94% *ee*) (Table 4, entries 13–15).

We also checked the aldol reactions of other ketones (4-methylcyclohexanone, cycloheptanone and hydroxyacetone) with aromatic aldehydes using catalyst **1e** (5 mol%) (Table 5). 4-Methylcyclohexanone gave high stereoselectivities and good yield (Table 5, entries 1–3). When cyclopentanone was used as an aldol donor, good yield (84–90%) and good *ee* (84–90%) for the anti-isomer were achieved; however, the diastereomeric ratio obtained was only (60/40–63/38) *anti*/*syn* (Table 5, entries 4–6). Moreover, we examined the feasibility of using hydroxyacetone as aldol donor. Although longer reaction times were required in comparison with cyclic ketones, satisfactory results were obtained. The hydroxyacetone reacted smoothly

Table 5 Direct asymmetric aldol reactions between ketones and aromatic aldehydes catalyzed by **1e**



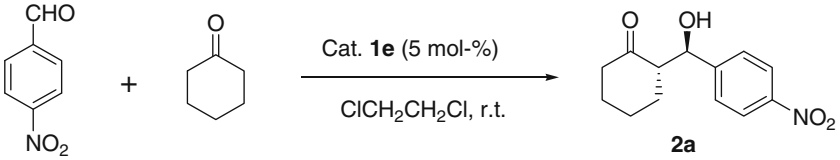
Entry	Product	Time (h)	Yield (%)[a]	*Anti*:*syn*[b]	*ee* (%)[b]
1	 **3a**	24	90	95:5	93
2	 **3b**	27	91	83:17	89
3	 **3c**	25	87	88:12	91
4	 **3d**	25	84	60:40	87
5	 **3e**	24	90	91:9	91
6	 **3f**	27	88	62:38	89
7	 **3g**	40	90	20:80	88
8	 **3h**	46	81	15:85	91
9	 **3i**	48	77	10:90	90

The reactions were performed with *p*-nitrobenzaldehyde (1.0 mmol), ketone (4.0 mmol) and catalyst (0.05 mmol) in solvent (2 mL) at room temperature

[a] Isolated yield

[b] Determined by chiral HPLC analysis (AD–H)

Table 6 Recycling and reuse of catalyst **1e**



Run	Time (h)	Yield[a] (%)	*Anti*:*syn*[b]	*ee*[b] (%)
1	23	90	99:1	99
2	24	85	94:6	94
3	26	85	90:10	94
4	26	82	89:11	90
5	30	80	85:15	88
6	48	75	79:21	85

The reactions were performed with *p*-nitrobenzaldehyde (1.0 mmol), ketone (4.0 mmol) and catalyst (0.05 mmol) in solvent (2 mL) at room temperature

[a] Isolated yield

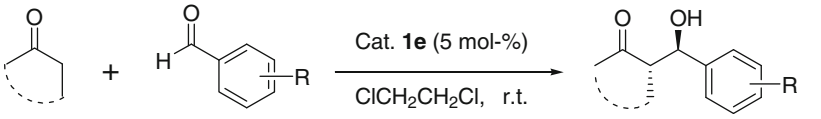
[b] Determined by chiral HPLC analysis (AD–H)

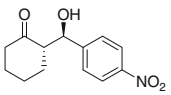
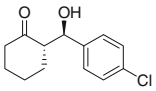
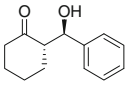
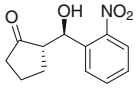
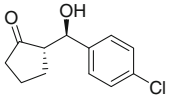
with nitrobenzaldehyde and 4-chlorobenzaldehyde under optimal conditions to give the corresponding *syn*-aldol products in good yields of 77–90% (Table 5, entries 7–9).

Meanwhile, to verify that the cysteine derivative organocatalyst **1e** could be recovered and reused, we performed a recycling study of **1e** using the aldol reaction between cyclohexanone and 4-nitrobenzaldehyde (Table 6). Catalyst **1e** could be easily recovered from the reaction mixture after completion of the reaction by acid treatment. The aldol product was extracted with Et_2O, with evaporation of the organic solution to obtain the aldol product. Catalyst **1e** exists in the acidic aqueous layer, and, on adding an equivalent amount of Et_3N, the resulting white suspension was filtered by vacuum and the white crystals used directly in subsequent aldol reaction without adding any new catalyst. In each reuse, the same amounts of substrates were used, and the recovered **1e**, without further purification, retained essentially its catalytic activity without any decrease of enantioselectivity for six cycles (Table 6).

Furthermore, a large-scale test was performed. With 25 mmol aromatic aldehydes and 4 equiv ketones, the same catalyst loading of 5 mol% as for the experimental scale was used. The experiments could be facilely carried out using the same procedure as for the experimental-scale reactions. As can be seen from the results summarized in Table 7, pleasingly, the enantioselectivities were maintained at the same level in the large-scale reactions.

Table 7 Large-scale asymmetric aldol reactions



Entry	Product	Time (h)	Yield[b] (%)	*Anti*:*syn*[b]	*ee*[b] (%)
1		30	89	98:2	99
2		52	85	90:10	91
3		35	90	88:12	90
4		33	89	62:38	87
5		50	83	60:40	89

The reactions were performed with aromatic aldehydes (25 mmol), ketones (100 mmol) and catalyst (1.25 mmol) in solvent (50 mL) at room temperature

[a] Isolated yield

[b] Determined by chiral HPLC analysis (AD–H)

Conclusions

We have designed and synthesized a new series of cysteine-based organocatalysts in one step. A wide range of aromatic aldehydes with cyclic ketones and unprotected hydroxyacetone can effectively participate in the aldol reactions. Catalyst **1e** can be readily recovered and reused without significant loss of catalytic activity or stereoselectivity. Notably, these organocatalyzed asymmetric direct aldol reactions can be performed on a large scale with enantioselectivities maintained at the same level, which offers great possibility for applications in industry.

Acknowledgments Authors are grateful to Southwest University of China for financial support.

References

1. P.I. Dalko, L. Moisan, Angew. Chem. Int. Ed. **116**, 5248–5286 (2004)
2. R. Mahrwald (ed.), Modern Aldol Additions (Wiley-VCH, Weinheim, 2004)

3. C. Palomo, M. Oiarbide, J.M. Garcia, Chem. Eur. J. **8**, 36–44 (2002)
4. T.D. Machajewski, C.H. Wong, Angew. Chem. Int. Ed. **39**, 1352–1374 (2000)
5. W. Notz, F. Tanaka, C.F. Barbas III, Acc. Chem. Res. **37**, 580–591 (2004)
6. S. Mukherjee, J.W. Yang, S. Hoffman, B. List, Chem. Rev. **107**, 5471–5569 (2007)
7. X.H. Liu, L.L. Lin, X.M. Feng, Chem. Commun. **41**, 6145–6158 (2009)
8. M. Raj, V.K. Singh, Chem. Commun. **42**, 6687–6703 (2009)
9. L.W. Xu, J. Luo, Y.X. Lu, Chem. Commun. **14**, 1807–1821 (2009)
10. L.W. Xu, Y.X. Lu, Org. Biomol. Chem. **6**, 2047–2053 (2008)
11. F.Z. Peng, Z.H. Shao, J. Mol. Catal. A. **285**, 1–13 (2008)
12. Y.C. Chen, Synlett **13**, 1919–1930 (2008)
13. G. Bartoli, P. Melchiorre, Synlett **12**, 1759–1771 (2008)
14. J. Casas, M. Engqvist, I. Ibrahem, B. Kaynak, A. Córdova, Angew. Chem. Int. Ed. **44**, 1343–1345 (2005)
15. A. Córdova, W. Zou, I. Ibrahem, E. Reyes, M. Engqvist, W.W. Liao, Chem. Commun. **28**, 3586–3588 (2005)
16. I. Ibrahem, A. Córdova, Tetrahedron Lett. **46**, 3359–3363 (2005)
17. H. Torii, M. Nakadai, K. Ishihara, S. Saito, H. Yamamoto, Angew. Chem. Int. Ed. **43**, 1983–1986 (2004)
18. N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C.F. Barbas III, J. Am. Chem. Soc. **128**, 734–735 (2006)
19. Y. Hayashi, T. Sumiya, J. Takahashi, H. otoh, T. Urshima, M. Shoji, Angew. Chem. Int. Ed. **45**, 958–961 (2006)
20. S. Samanta, J. Liu, R. Dodda, C.G. Zhao, Org. Lett. **7**, 5321–5323 (2005)
21. A. Córdova, W. Zou, P. Dziedzic, I. Ibrahem, E. Reyes, Y. Xu, Chem. Eur. J. **12**, 5383–5397 (2006)
22. Y. Hayashi, T. Itoh, N. Nagae, M. Ohkubo, H. Ishikawa, Synlett **10**, 1565–1570 (2008)
23. N. Mase, F. Tanaka, C.F. Barbas III, Org. Lett. **5**, 4369 (2003)
24. R. Thayumanavan, F. Tanaka, C.F. Barbas III, Org. Lett. **6**, 3541 (2004)
25. N. Utsumi, M. Imai, F. Tanaka, S.S.V. Ramasastry, C.F. Barbas III, Org. Lett. **9**, 3445 (2007)
26. G.F. Zhong, J.H. Fan, C.F. Barbas III, Tetrahedron Lett. **45**, 5681 (2004)
27. S. Aratake, T. Itoh, T. Okano, N. Nagae, T. Sumiya, M. Shoji, Y. Hayashi, Chem. Eur. J. **13**, 10246 (2007)
28. S. Aratake, T. Itoh, T. Okano, T. Usui, M. Shoji, Y. Hayashi, Chem. Commun. **24**, 2524 (2007)
29. Y. Hayashi, S. Aratake, T. Itoh, T. Okano, T. Sumiya, M. Shoji, Chem. Commun. **9**, 957 (2007)
30. Y. Hayashi, S. Aratake, T. Okano, J. Takahashi, T. Sumiya, M. Shoji, Angew. Chem. Int. Ed. **45**, 5527 (2006)
31. Z. Tang, F. Jiang, L.T. Yu, X. Cui, L.Z. Gong, A. Qiao, Y.Z. Jiang, Y.D. Wu, J. Am. Chem. Soc. **125**, 5262 (2003)
32. Z. Tang, F. Jiang, L.T. Yu, X. Cui, L.Z. Gong, A.Q. Mi, Y.Z. Jiang, Y.D. Wu, Proc. Natl. Acad. Sci. USA **101**, 5775 (2004)
33. Z. Tang, Z.H. Yang, L.F. Cun, L.Z. Gong, A.Q. Mi, Y.Z. Jiang, Org. Lett. **6**, 2285 (2004)
34. Z. Tang, Z.H. Yang, X.H. Chen, L.F. Cun, A.Q. Mi, Y.Z. Jiang, L.Z. Gong, Am. Chem. Soc. J. **127**, 9285 (2005)
35. L. He, Z. Tang, L.F. Cun, A.Q. Mi, Y.Z. Jiang, L.Z. Gong, Tetrahedron **62**, 346 (2005)
36. J.R. Chen, H.H. Lu, X.Y. Li, L. Cheng, J. Wan, W.J. Xiao, Org. Lett. **7**, 4543 (2005)
37. J.R. Chen, X.Y. Li, X.N. Xing, W.J. Xiao, J. Org. Chem. **71**, 8198 (2006)
38. C.L. Wu, X.K. Fu, X.B. Ma, S. Li, C. Li, Tetrahedron Lett. **51**, 5775–5777 (2010)
39. C.L. Wu, X.K. Fu, X.B. Ma, S. Li, Tetrahedron Asymmetry **21**, 2465–2470 (2010)
40. C.L. Wu, X.K. Fu, S. Li, Eur. J. Org. Chem. **7**, 1291–1299 (2011)
41. C.L. Wu, X.K. Fu, S. Li, Tetrahedron **67**, 4283–4290 (2011)
42. E. Yousefi-Salakdeh, J. Johansson, R. Stromberg, Biochem. J. **343**, 557–562 (1999)
43. A. Makriyannis, W.H.H. Gunther, H.G. Mautner, J. Am. Chem. Soc. **95**, 8403–8412 (1973)