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Camphor containing organocatalysts in asymmetric aldol reaction on water

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ABSTRACT

A new class of bifunctional organocatalysts were synthesized and proved to be effective in catalyzing aldol reaction on water with high to excellent diastereo- and enantioselectivities.

Recently, the use of water as a reaction medium for chemical transformations has been the subject of organic synthesis due to cost, safety and environmental concerns.[1] The development of metal free small organic molecules, which catalyze enantioselective reactions has received much attention in recent years.[2] Since the successful demonstration of L-proline on the intermolecular aldol reaction in 2000, spectacular advances have been made by using this remarkable efficient, operationally simple and environmentally benign methodology.[3] The design and synthesis of structural versatility of chiral organocatalysts has emerged as a viable strategy for preparation of chiral building blocks. Various enantioselective transformations, such as conjugate reaction,[4] aldol reaction,[5] Mannich reaction,[6] aza-Diels–Alder reaction,[7] Friedel–Crafts reaction,[8] Strecker reaction,[9] aza-Morita–Baylis–Hillman reaction,[10] carbon–heteroatom bond formation,[11] and others have been reported.[12] The aldol reaction is one of the key reactions for carbon–carbon bond formation and of the reported examples on direct aldol condensation, *only a few organocatalytical reactions proceed in the presence of a large amount of water*.[13] Limited examples with satisfactory results with respect to material yields, stereoselectivities, and amount of catalyst loading, have been reported of the organocatalysis on water.[14] The design and synthesis of efficient organocatalysts to catalyze organic reactions in pure water remains a challenging objective.

We envision that the assembly of a structurally well-defined camphor scaffold with a thiourea motif[15] and amine functionalities could constitute a new class of bifunctional organocatalysts.[16] The synergistically activation of both the nucleophilic and electrophilic substrate via the enamine-iminium formation process and hydrogen bond activation can be anticipated. The rigid bicyclic camphor structure can serve dual roles as an efficient stereocontrolling element and assemble with hydrophobic substrates on water. Herein, we describe the preliminary results of the aldol reaction, utilizing thiourea–amine moiety bearing a camphor scaffold for catalyzing cyclohexanone (2.0 equiv) and various arylaldehydes on water. High to excellent levels of chemical yield (>90%) and stereoselectivities (up to >99:1 dr and >99% ee) were obtained (Fig. 1).

The synthesis of organocatalysts **1**–**5** began with the reaction of *o*-phenyldiamine with the in situ prepared ketopinic acid derived isothiocyanate ($SOCl_2$ and NH_4SCN) in acetone (Scheme 1). The corresponding 2-aminophenyl thiourea derivative was condensed with Boc-protected L-proline followed by TFA treatment to give **1** with 55% overall yield (5 steps). A similar synthetic route was employed to prepare the analogous *trans*-4-hydroxy-L-proline organocatalyst **2** (52% overall yield) which was subsequently protected as its *t*-butyldiphenylsilyl ether **3** without incident. Attempts to protect the 4-hydroxyl group of the pyrrolidine ring as its benzyl ether failed, which of note, resulted in the formation of an unexpected benzylisothiourea **4** in reasonable chemical yield (61% yield). Similar reaction affords (naphthalen-1-yl)methylisothiourea **5** when 1-(bromomethyl)naphthalene was used. The structures of these organocatalysts **1**–**5** were fully characterized by ^1H, ^{13}C NMR, HRMS, IR analyses and compound **4** was further confirmed by single crystal X-ray analysis.

As a model investigation, we explored the aldol reaction using cyclohexanone and *p*-nitrobenzaldehyde in the presence of organocatalysts (**1**–**5**), water was employed as the reaction medium. Rea-

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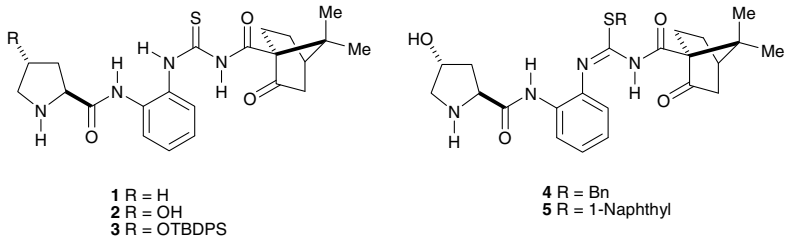
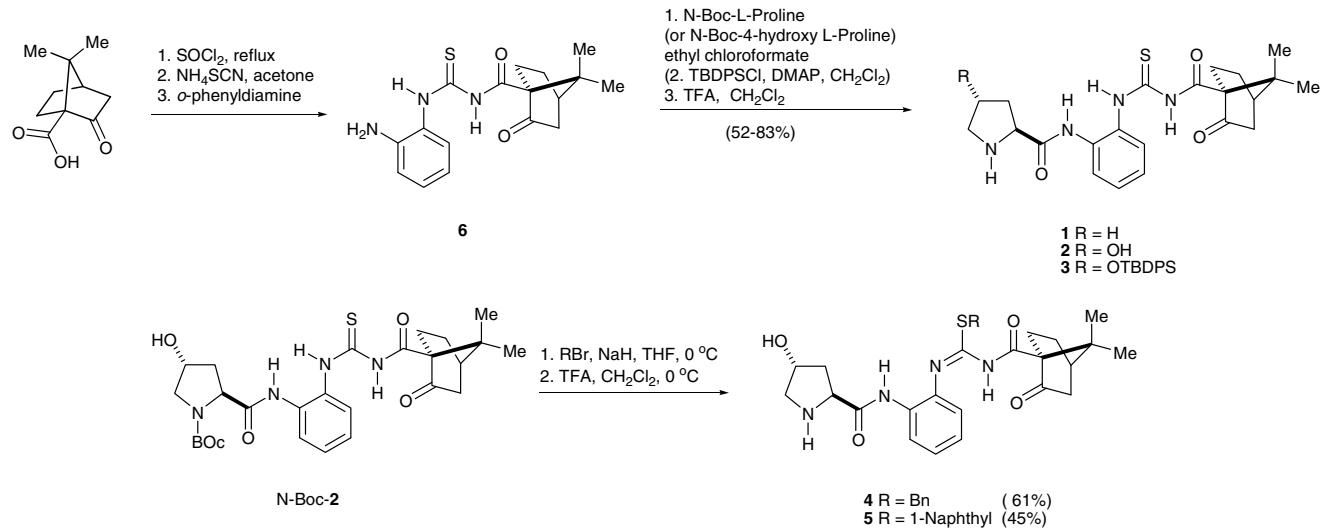


Figure 1. Structures of camphor containing thiourea–amine catalysts **1**–**5**.

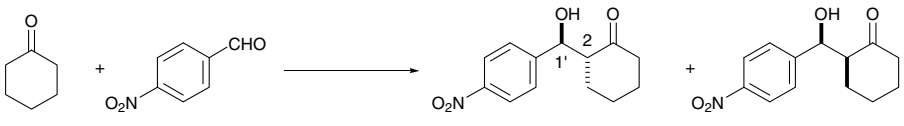


Scheme 1. Synthesis of camphor containing thiourea–amine catalysts **1**–**5**.

sonable chemical yields (65%) and stereoselectivities (*anti*/*syn* = 68/32; 73% ee for *anti* product) were obtained under neat conditions in 4 days. To our satisfaction, treatment of the probe substrate with a catalytic amount of **1** (20 mol %) gave the desired product with a 92% yield on water in 24 h. The products were obtained with a reasonable diastereomeric ratios (*anti*/*syn* = 76/24) and enantiomeric excess (*anti*, 77% ee) (Table 1, entry 1). Comparable results were achieved when brine was used as the reaction medium (Table 1, entry 2). Slight improvements in selectivity were obtained when 4-hydroxyproline derived catalyst **2** and siloxyproline derivative **3** were used (Table 1, entries 3 and 4). The selectivities were further improved when benzylisothiourea and (naphthalen-1-yl)methylisothiourea **4** and **5** were used under the same conditions, suggesting that increasing the sterical demand of the catalyst increases the selectivities (Table 1, entries 5 and 6). From all organocatalysts screened under these conditions, the *anti* aldol products dominated with the newly generated stereochemistry to be (1′*S*,2*R*).[14a,17]

Encouraged by the preliminary data, we continued to modify the catalysis conditions. We hypothesized that the presence of an additional proton may help the rapid formation of enamine species and subsequently accelerates the reaction to proceed. To test this,

Table 1
Diastereo- and enantioselective aldol reaction of cyclohexanone and *p*-nitrobenzaldehyde catalyzed by organocatalysts **1**–**5**[a]



Entry	Cat.	Solvent	*t* (h)	Yield[b] (%)	*anti*:*syn*[c]	% ee (*anti*)[c]
1	**1**	H_2O	24	92	76:24	77
2	**1**	Brine	24	90	76:24	79
3	**2**	H_2O	48	89	88:12	81
4	**3**	H_2O	48	79	86:14	76
5	**4**	H_2O	72	99	91:9	85
6	**5**	H_2O	72	99	89:11	81

[a] Unless otherwise specified, all reactions were carried out using *p*-nitrobenzaldehyde (75.6 mg, 0.50 mmol), cyclohexanone (103.6 μL, 1.0 mmol, 2.0 equiv) and catalyst (20 mol %) under the solvent indicated (1.0 mL) at ambient temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis (Chiralpak AD-H).

Table 2
Optimization of enantioselective aldol reaction of cyclohexanone and *p*-nitrobenzaldehyde catalyzed by organocatalysts **1**–**3** on water[a]

Entry	Cat.	Additive	*t* (h)	Yield[b] (%)	*anti*:*syn*[c]	% ee (*anti*)[c]
1	**1**	HCl	40	91	86:14	90
2	**1**	Citric acid	24	96	80:20	80
3	**1**	CH_3CO_2H	24	91	84:16	80
4	**1**	TFA	24	93	93:7	93
5	**1**	(+)-CSA[d]	40	57	90:10	90
6	**1**	NH_4Cl	40	94	91:9	94
7	**2**	NH_4Cl	10	94	94:6	89
8	**3**	NH_4Cl	36	99	86:14	83
9	**1**	DBSA[e]	21	97	93:7	92
10	**2**	DBSA[e]	36	99	95:5	94
11	**3**	DBSA[e]	36	95	96:4	>99

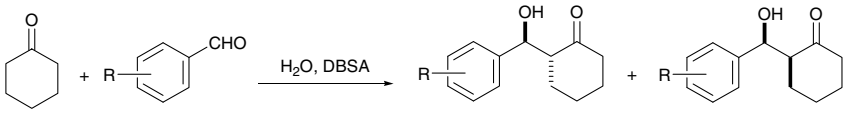
[a] Unless otherwise specified, all reactions were carried out using *p*-nitrobenzaldehyde (75.6 mg, 0.50 mmol), cyclohexanone (103.6 μL, 2.0 equiv), acid additive (20 mol %) and catalyst (20 mol %) on water (1.0 mL) at ambient temperature.
[b] Total isolated yield.
[c] Determined by chiral HPLC analysis (Chiralpak AD-H).
[d] D-(+)-10-Camphorsulfonic acid.
[e] The reaction was carried out at 0 °C. DBSA: Dodecylbenzenesulfonic acid.

we then studied the additive effects of the aldol reaction with organocatalysts **1**–**3** on water. Excellent chemical yields and good to high stereoselectivities were obtained when 20 mol % of HCl (0.033 M, 1.0 mL) and citric acid (0.033 M, 1.0 mL) were added when **1** was used (Table 2, entries 1 and 2). Comparable results were obtained when acetic acid was added as the acidic additive and the stereoselectivities were further improved when TFA was used (Table 2, entries 3 and 4). The stereoselectivity increased at the expense of decreasing reactivity when camphorsulfonic acid was added (Table 1, entry 1 vs Table 2, entry 5). Both the chemical yields and selectivities were improved when a mild acidic additive, such as NH_4Cl (0.033 M, 1.0 mL) was added (Table 2, entries 6–8). The study of a Brønsted acid-surfactant combined catalyst, such as dodecylbenzenesulfonic acid (DBSA), to form colloidal dispersion with organic materials in water, and subsequently accelerate the reaction rate have been reported.[18] We envision that the presence of DBSA may be beneficial for the improvement of both the reactivities and selectivities, and is the focus of the present study. To this end, DBSA (20 mol %) was employed with organocatalyst **1** on water to promote aldol condensation in 97%, 93/7 *anti*/*syn* ratio, and 92% ee for the *anti* enantiomer (Table 2, entry 9). Further improvement was observed when organocatalyst **2** and **3** were used (Table 2, entries 10 and 11). It is worth noting that only 2.0 equiv of the donor cyclohexanone to the acceptor aldehyde was used under the catalytical process which represented a significant improvement over the conventional aldol condensation in organic solvents. *These data are comparable to the best results reported on the same aldol reaction carried out on water.*

The substrate generality of this aldol reaction using cyclohexanone catalyzed by **1**–**5** with a series of arylaldehyde was then examined under optimum reaction conditions. In most of the cases, *anti* aldol products were obtained in high to excellent diastereo- and enantioselectivities and the reaction rate depends upon the nature of the substituent of the arylaldehydes. Excellent selectivities were observed when *o*-nitrobenzaldehyde was employed as the acceptor while the use of *m*-nitrobenzaldehyde resulted in a decrease in both the reactivities and selectivities (Table 3, entries 1 and 2). Excellent enantioselectivity was observed with diminished reactivity when *p*-cyanobenzylaldehyde was used and the chemical yield was further decreased to 55% when benzaldehyde was used (Table 3, entries 3 and 4). Although high enantioselectivities of the *anti* product was observed, for electron-donating substituent acceptor aldehydes the reactivity decreases dramatically as expected (Table 3, entries 5–7). Excellent diastereo- and enantioselectivity were obtained when *p*-fluorobenzaldehyde was catalyzed by isothiourea catalysts **4** and **5** with only 29% chemical yield (Table 3, entries 9 and 10).

Althought the reaction mechanism is not clear at this moment, it is obvious that substrates and catalyst were 'pushed' into close contact by water molecules. The presence of a camphor skeleton and bulky groups (siloxy, benzylisothiourea, and (naphthalen-1-yl)methylisothiourea) increase the hydrophobic characteristic of the catalysts and forms a hydrophobic microenvironment in the presence of Brønsted acid-surfactant DBSA from which the reaction take places.[18a] The hydrophobic aggregation may play a decisive role in affecting the stereochemical outcome of the aldol reaction. Presumably the reaction was facilitated by hydrogen bonds between organocatalyst and acceptor in the transition state which is followed by the addition of enamine to the *si* face of the aldehyde carbonyl group.[19] It is believed that the thiourea moiety coordinates strongly with the nitro group to give the aldol product with high diastereo- and enantioselectivities (Tables 2 and 3, entries 1 and 2). While, in contrast, the weak hydrogen bonds formed between the catalyst and the carbonyl group of the arylaldehydes

Table 3
Enantioselective aldol reaction of cyclohexanone and various arylaldehydes catalyzed by organocatalysts **3**–**5** under the optimum conditions[a]



Entry	Cat.	R	*t* (d)	Yield[b] (%)	*anti*:*syn*	% ee (*anti*)
1	**3**	*o*-NO2	2	87	99:1	98[c]
2	**3**	*m*-NO2	2	83	81:19	80[d]
3	**3**	*p*-CN	2	75	88:12	94[d]
4	**3**	H	7	55	97:3	94[c]
5	**3**	*p*-Me	7	42	91:9	85[c]
6	**3**	*p*-OMe	7	26	85:15	80[d]
7	**3**	1-Naphthyl	7	35	90:10	89[e]
8	**3**	*p*-F	7	32	89:11	73[d]
9	**4**	*p*-F	7	29	98:2	98[d]
10	**5**	*p*-F	7	29	93:7	>99[d]

[a] Unless otherwise specified, all reactions were carried out using arylaldehyde (0.50 mmol), cyclohexanone (2.0 equiv), DBSA (20 mol %) and catalyst (20 mol %) on H_2O (1.0 mL) at ambient temperature. The stereoselectivity was determined by chiral HPLC analysis of the crude products.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis (Chiralpak OD-H).
[d] Determined by chiral HPLC analysis (Chiralpak AD-H).
[e] Determined by chiral HPLC analysis (Chiralpak OJ-H).

led to a decrease in both the reactivity and stereoselectivity (Table 3, entries 4–10).

In conclusion, we have demonstrated a practical method for organocatalytic direct aldol reaction to afford the *anti* products with excellent chemical yield and diastereo- and enantioselectivity on water. The bifunctional thiourea–amine organocatalysts bear a hydrophobic camphor scaffolding, which can be readily synthesized with good overall chemical yields. Further study of these newly developed camphor containing bifunctional organocatalysts (**1**–**5**) in asymmetric reactions is being under investigated.

Acknowledgments

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