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Highly stereoselective anti-aldol reactions catalyzed by simple chiral diamines and their unique application in configuration switch of aldol products

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ABSTRACT

Chiral derivatives of *trans*-1,2-diaminocyclohexane with different *N*,*N*-dialkyl groups in well-defined orientations have been synthesized, and applied as catalysts for the asymmetric aldol reaction between a variety of aldehydes and ketones. Enantiomeric catalyst **1j** catalyzed the reaction in ethanol and provided excellent diastereoselectivity and enantioselectivity. Significantly, simple replacement of organic solvents with water switched the products of the aldol reactions from *anti* to *syn* configuration. Such catalytic reactions led to the products with *anti* to *syn* diastereoselectivity up to 99:1 in ethanol, while in water gave the products with *syn* to *anti* diastereoselectivity up to 99:1.

The aldol reaction is one of the most fundamental tools for the construction of carbon–carbon bonds, it can produce β-hydroxyl carbonyl compounds, which are key intermediates or synthetic building blocks for many natural products and drugs.[1]

Asymmetric aldol reactions of ketones with aldehydes usually offer chiral compounds with one or multiple stereocenters, and such highly enantio- and diastereo-selective reactions generating two stereocenters in one step are valuable for asymmetric synthesis. Generally, four products with different mirror images derived from the reaction of symmetric ketone and aromatic aldehyde can be obtained as shown in Scheme 1. According to the previous reports, chiral catalysts would generate the relevant products for each pair of ketones and aldehydes, either *syn*[2] or *anti* enantiomers.[3] So far, in the reaction between cyclohexanone and aldehydes, almost all of the organocatalyts are known to provide *anti*-aldol adducts predominantly, albeit with a few limited exceptions which afford *syn*-products. Thus, employing one single chiral catalyst to control the relative stereochemical configuration of aldol products in such reactions is still challenging.

Since List and Barbas reported the direct aldol reaction of acetone with aryl aldehydes catalyzed by L-proline[4], many kinds of proline-derivated catalysts have been developed for asymmetric aldol reactions.[3a,3b,3d,5] Recently, the application of chiral *trans*-1,2-diaminocyclohexane (abbreviated as DACH) derivatives, which are stable and easy to obtain and modify, has received rapidly growing attention. However, most successful DACH based catalysts are involved with the modification of the monoamines, for example lactamization, sulfonamidization, and thioureation,[6] mimicking enzymatic activities.[1h,6a,6b,7]

Chiral *N*,*N*-dialkyl diamines have been successfully applied by Cheng[2b,8] to catalyze a series of asymmetric aldol reactions. In their reactions of cyclohexanone with aldehydes,[8c] the results with main products in *anti*-configuration were fairly good (up to 95% yield, 10:1 *anti*/*syn*, 98% ee). However, no compounds in *syn* configuration as major products were mentioned. To our knowledge, only Gao and his co-workers[9] recently reported a configuration switch in asymmetric aldol reactions. In their experiments, a chiral diamine combined with succinic acid could catalyze the *syn*-aldol reaction of both cyclohexanone and cycloheptanone with five aromatic aldehydes (up to 94% yield, 1.8:1–5:1 *syn*/*anti*, 53–88% *ee*), either by increasing the size of the additive acids or by introducing a hydrogen-bond donor into the additive acids.

Herein reported is a series of modified diamine catalysts derived from DACH that exhibit excellent diastereoselectivity and enantioselectivity in aldol reactions in ethanol, and their application in the challenging *syn*-aldol reaction.

Modified diamine catalysts were synthesized starting from the commercial chiral diamine **2**. All catalysts except **1a** and **1k** were easily prepared from **2** in a 4-step sequence as shown in Scheme 2, whereas **1a** was obtained by omitting step (c) and **1k** was prepared

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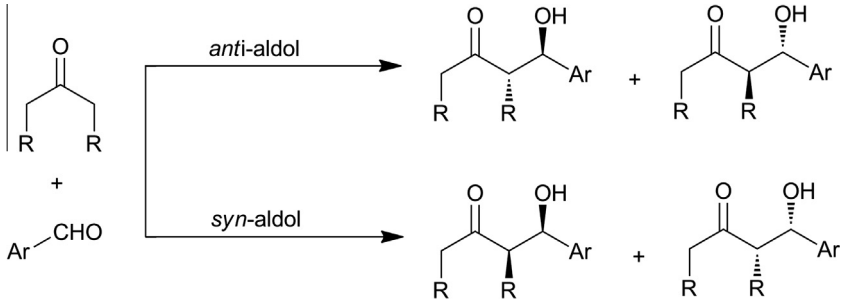
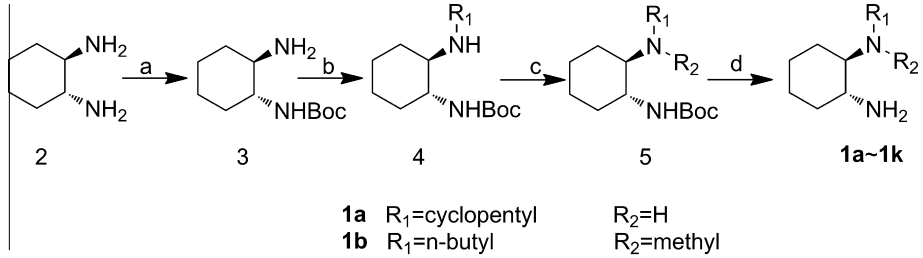


Scheme 1. Four stereoisomeric products of asymmetric aldol reactions between symmetric alkanone and aryl aldehyde.



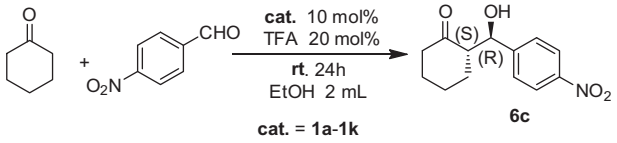
1a R_1=cyclopentyl R_2=H
1b R_1=n-butyl R_2=methyl
1c R_1=i-butyl R_2=methyl
1d R_1=t-pentyl R_2=methyl
1e R_1=cyclohexyl R_2=methyl
1f R_1=cyclopentyl R_2=methyl
1g R_1=cyclopentyl R_2=ethyl
1h R_1=cyclopentyl R_2=n-propyl
1i R_1=cyclopenyl R_2=n-butyl
1j R_1=cyclopentyl R_2=n-pentyl
1k R_1=cyclopentyl R_2=cyclopentyl

Scheme 2. Synthesis of catalysts. Reagents and conditions: (a) Boc_2O, CH_3OH; (b) alkyl aldehyde or ketone, $NaBH_4$, CH_3OH; (c) alkyl aldehyde or ketone, $NaBH_3CN$, CH_3OH; (d) HCl, H_2O.

by a literature method.[10] To probe the activity of different catalysts, asymmetric aldol reaction between cyclohexanone and *p*-nitrobenzaldehyde was firstly carried out as a model experiment (shown in Table 1). The poor catalytic performances observed for **1a** and **1k** (entries 1 and 11) highlighted the importance of the *N*, *N*-dialkylated DACH structure. Among catalysts **1b**–**1f** (entries 2–6), which have different R_1 but the same R_2 group, **1f** had the best effect (R_1 = cyclopentyl). This result confirmed that spatial hindrances would create specific interactions between the organocatalyst and their substrates.[8a,11] Catalyst **1g** with the same R_1 as **1f** and a little long alkyl group (R_2 = ethyl) afforded better diastereoselectivity than **1f** (entry 6 vs 7). This result inspired us looking for the longer alkyl carbon chain of R_2 (entries 6–10). And finally, in consideration of the catalytic effect and the difficulty of synthesis, **1j** gave the optimal results. This result may be due to the two dialkyl substituents on the monoamine, since the cyclopentyl group is one of the most stable rigid aliphatic rings, and meanwhile the pedant-armed group increases the hindrance additionally.

Additionally, auxiliary acids were evaluated by catalyzing the reaction between cyclohexanone and *o*-nitrobenzaldehyde in alcohol (shown in Table 2). It was observed that the ratio of *syn*-product had a slight increase with *anti*/*syn* of the product reaching 35:1 from 48:1 (Table 2, entry 6 vs Table 1, entry 10), but the reaction time was extended to 3 days when the temperature was decreased to 0 °C. This result demonstrated that the formation of *syn*-product could be controlled by the temperature. Five different acids were tested, but only TFA gave the best result (entries 1–5). It is significantly noted that the increase of the size of the additive acid was not an effective way to improve the *syn*/*anti* ratio. This fact was also confirmed in Gao's work[9], though they attributed the increased ratio of *syn*-/*anti*- aldol products to the increasing size of the acids. The amount of auxiliary acid seemed to be an important factor (entries 5–9) in the reaction. The highest amount of *anti*-product was observed by increasing the TFA amount to

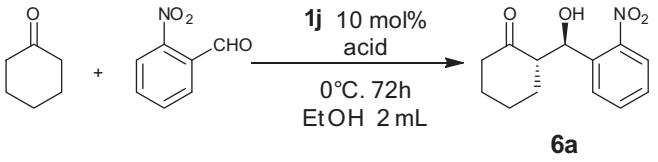
Table 1
Screening of catalysts



Entry[a]	Cat.	Yield[b] (%)	Anti/syn[c]	*ee*[d] (%)
1	1a	5	3:1	23
2	1b	37	5:1	96
3	1c	34	14:1	97
4	1d	67	7:1	94
5	1e	58	14:1	96
6	1f	82	27:1	>99
7	1g	74	34:1	>99
8	1h	73	43:1	>99
9	1i	78	48:1	>99
10	1j	95	49:1	>99
11	1k	Trace	—	—

[a] The reaction of *p*-nitrobenzaldehyde (0.5 mmol) with cyclohexanone (1.5 mmol) in ethanol (2 mL) was carried out in the presence of cat. (0.05 mmol) and TFA (0.1 mmol) at room temperature.
[b] Isolated yields.
[c] Determined by HPLC using chiral column.
[d] Determined by HPLC analysis of the *anti* product.

Table 2
Screening of auxiliary acid in the aldol reaction



6a

Entry[a]	Acid	Cat.:acid	Yield[b] (%)	*Anti*/*syn*[c]	*ee*[d] (%)
1	AcOH	1:1	65	5:1	19
2	PhCOOH	1:1	82	7:1	64
3	HDA	1:1	66	5:1	2
4	TfOH	1:1	67	14:1	92
5	TFA	1:1	75	15:1	96
6	TFA	1:2	93	35:1	99
7	TFA	1:3	86	24:1	97
8	TFA	1:4	91	7:1	98
9	TFA	1:5	87	7:1	98

[a] Reaction of *o*-nitrobenzaldehyde (0.5 mmol) with cyclohexanone (1.5 mmol) in ethanol (2 mL) was carried out in the presence of **1j** (0.05 mmol) at 0 °C.
[b] Isolated yields.
[c] Determined by HPLC using chiral column.
[d] Determined by HPLC analysis of the *anti* product.

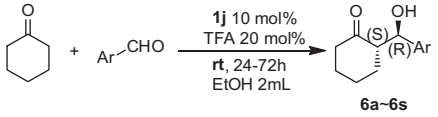
20 mol % (entry 6 vs 5 and 7), and further addition of TFA may lead to the increase of *syn*-product. However, the amount of acid was found to be a predominated factor to promote the ratio of the *syn*-aldol product, but the *anti*-product was still the major product.

To explore the versatility of the organocatalyst **1j**, a variety of aromatic aldehydes bearing diversified substituents were employed as aldol acceptors in the presence of 10 mol % catalyst at room temperature. As shown in Table 3, by using cyclohexanone as a donor, the reaction worked well with aromatic aldehydes bearing both electron-donating and electron-withdrawing groups to afford aldol adducts **6a**–**6n** in low to high yields with excellent diastereomeric ratios and enantioselectivities for *anti*-products. And the rate of the reaction was found to be dependent on the electronic nature of the substituents on the aromatic nucleus. Moreover, polycyclic aromatic aldehydes, heterocyclic aldehydes and even aliphatic cyclohexanecarboxaldehyde appeared to be good candidates for an electrophilic partner (entries 15–19) as well. It is notable that all of the reactions afforded *anti*-aldol products with 2*S*, 1′*R* configuration.

Other ketones were also evaluated under the same conditions (Table 4). Along with *p*-nitrobenzaldehyde, ketones such as acetone, cyclopentanone, cycloheptanone, 4-methylcyclohexanone, and 3-pentanone, also proved to be good donors and the aldol products were obtained in good yields with excellent diastereoselectivities and enantioselectivities. Among them, **6t** was of *S*-configuration, **6u**–**6w** were *anti*-aldol products of 2*R*, 1′*S* configuration, whereas **6x** was found with interest to be a *syn*-aldol product of (2*S*, 1′*S*) configuration.

Following the aldol reaction between cyclohexanone and *o*-nitrobenzaldehyde in the presence of ligand **1j** 10 mol % and TFA 40 mol % (Table 2, entry 8), we tentatively started to gain a *syn*-aldol product in different solvents, whose results are shown in Table 2. The results clearly revealed that the formation of *syn*- or *anti*-aldol products could be controlled by the solvent used. Highly polar solvents like water or brine mainly gave the *syn*-product, but the *anti*-product was mainly obtained when organic solvents were involved (Table 5, entries 1–6). Compared with organic solvents, water is a unique green solvent, possessing extraordinary properties such as high polarity and hydrogen bonding capabilities.[12] It may destroy the hydrogen bonding between aldehyde and the diamine, and lead to the increase of kinetics control products. Notably, the yield was not satisfactory, this is partly due to the heterogeneous phase of the solution, which was enhanced by the amount of acid that trapped the catalyst in salt form and reduced the concentration of the free diamine in the reaction.

Table 3
Asymmetric aldol reactions between cyclohexanone and various aldehydes catalyzed by organocatalyst **1j**

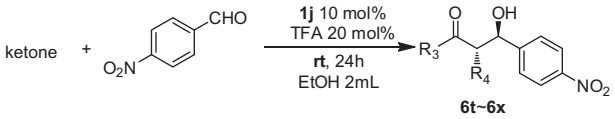


6a~6s

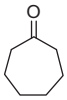
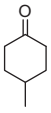
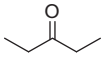
Entry[a]	Ar	Time (h)	Yield[b] (%)	*anti*/*syn*[c]	*ee*[d] (%)
1	2-NO_2Ph	24	**6a**/93	>99:1	>99
2	3-NO_2Ph	24	**6b**/87	>99:1	>99
3	4-NO_2Ph	24	**6c**/95	49:1	>99
4	4-CF_3Ph	24	**6d**/80	>99:1	>99
5	4-CNPh	24	**6e**/88	>99:1	99
6	2-FPh	40	**6f**/48	>99:1	>99
7	3-FPh	40	**6g**/64	46:1	97
8	4-FPh	40	**6h**/75	>99:1	>99
9	2-ClPh	48	**6i**/83	99:1	>99
10	3-ClPh	48	**6j**/54	36:1	98
11	4-ClPh	48	**6k**/40	>99:1	99
12	Ph	48	**6l**/73	>99:1	>99
13	4-CH_3Ph	72	**6m**/38	>99:1	>99
14	4-OMePh	72	**6n**/36	>99:1	>99
15	1-Naphthyl	24	**6o**/43	>99:1	>99
16	2-Naphthyl	24	**6p**/50	>99:1	99
17	2-Furanyl	24	**6q**/73	50:1	96
18	4-Pyridinyl	24	**6r**/82	35:1	>99
19	Cyclohexyl	48	**6s**/79	>99:1	>99

[a] The reaction of aldehyde (0.5 mmol) with ketone (1.5 mmol) in ethanol (2 mL) was carried out in the presence of **1j** (0.05 mmol) and TFA (0.1 mmol) at room temperature.
[b] Isolated yields.
[c] Determined by HPLC using chiral column.
[d] Determined by HPLC analysis of the *anti* product.

Table 4
Reaction of ketones with *p*-nitrobenzaldehyde catalyzed by **1j**

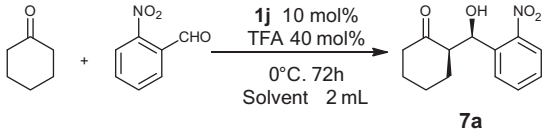


6t~6x

Entry[a]	Ketone	R_3	R_4	Yield[b] (%)	*anti*/*syn*[c]	*ee*[d] (%)
1		CH_3	H	**6t**/95	—	96
2		$CH_2CH_2CH_2$		**6u**/66	3.8:1	98
3		$CH_2CH_2CH_2CH_2CH_2$		**6v**/71	60:1	99
4		$CH_2CH_2CH(CH_3)CH_2$		**6w**/77	82:1	98
5		CH_2CH_3	CH_3	**6x**/68	1:99	93

[a] The reaction of *p*-nitrobenzaldehyde (0.5 mmol) with ketone (1.5 mmol) in ethanol (2 mL) was carried out in the presence of **1j** (0.05 mmol) and TFA (0.1 mmol) at room temperature.
[b] Isolated yields.
[c] Determined by HPLC using chiral column
[d] Determined by HPLC analysis of the major product.

Table 5
Screening solvents for a *syn*-aldol product



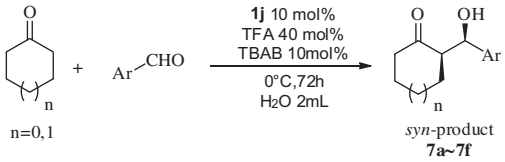
Entry[a]	Solvent	Yield[b] (%)	*anti*/*syn*[c]	*ee*[d] (%)
1	MeOH	86	5:1	91
2	EtOH	91	7:1	98
3	MeCN	35	2:1	99
4	Glycol	32	3.9:1	96
5	H_2O	61	1:2.7	98
6	Brine	64	1:2.1	99
7[e]	H_2O	63	1:2.8	92
8[f]	H_2O	84	1:4.1	99

[a] Reaction of *o*-nitrobenzaldehyde (0.5 mmol) with cyclohexanone (1.5 mmol) in solvent (2 mL) was carried out in the presence of **1** (0.05 mmol) and TFA (0.2 mmol) at 0 °C.
[b] Isolated yields.
[c] Determined by HPLC using chiral column.
[d] Determined by HPLC analysis of the major product.
[e] 0.05 mmol benzyltriethylammonium chloride (BTEAC) was added.
[f] 0.05 mmol tetrabutyl ammonium bromide (TBAB) was added.

When a phase transfer catalyst (PTC) was used to increase the reaction yield and improve the polarity of the solution, TBAB gave the better result (Table 5, entries 7 and 8). Thus, the optimum reaction conditions were achieved by performing the reaction of 3 equiv of cycloketone with 1 equiv of aryl aldehyde and 10 mol % catalyst loading in water, adding 40 mol % TFA and 10 mol % TBAB.

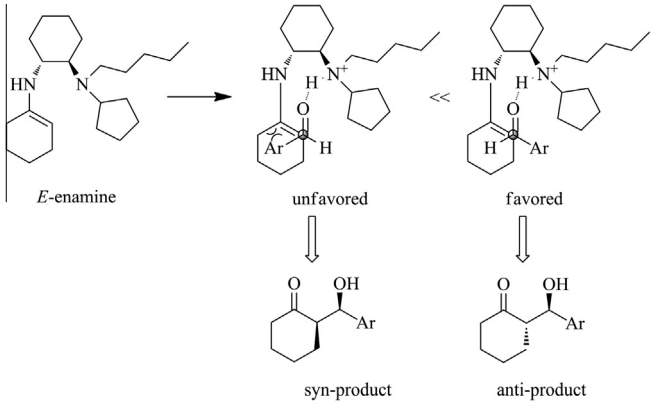
Next, we focused our attention on the intermolecular cross–aldol reaction of cycloketones and aryl aldehydes with different substituents (shown in Table 6). By using cyclohexanone as a substrate, *syn*-aldol products (7a–7e) were gained with the diastereomeric ratios 1.7:1–8.3:1 under the selected condition (entries 1–5). When coming to *p*-nitrobenzaldehyde, a purified *syn*- product was afforded with the diastereomeric ratio up to 99:1. Enantioselective aldol reactions were also extended to cyclopentanone, when *p*-nitrobenzaldehyde as an acceptor. It is also gratifying to see a remarkable switch of configuration in water (34:1 *syn*/*anti*, 99% *ee* in Table 6, entry 6). Meanwhile, we have made many efforts to supplement the research process about the electron-donating or

Table 6
Syn-aldol reactions between cycloketones and various aryl aldehydes



Entry[a]	n	Ar	Yield[b] (%)	*syn*/*anti*[c]	*ee*[d] (%)	
					syn	anti
1	1	2-NO_2Ph	**7a**/84	4.1:1	>99	>99
2	1	4-NO_2Ph	**7b**/86	>99:1	>99	—
3	1	4-CF_3Ph	**7c**/84	8.3:1	98	86
4	1	4-ClPh	**7d**/72	2.8:1	94	98
5	1	1-Naphthyl	**7e**/34	1.7:1	78	87
6	0	4-NO_2Ph	**7f**/67	34:1	>99	97

[a] The reaction of aldehyde (0.5 mmol) with ketone (1.5 mmol) in water (2 mL) was carried out in the presence of **1j** (0.05 mmol), TFA (0.2 mmol) and TBAB (0.05 mmol) at 0 °C.
[b] Isolated yields.
[c] Determined by HPLC using chiral column.
[d] Determined by HPLC analysis of the *anti* or *syn* product.



Scheme 3. Possible transition state model.

m-substituted aromatic aldehydes, but the results were disappointing. For electron-donating aldehydes, the reaction, as can be seen from Table 4, was very slow due to the passivation of the phenyl ring, and this effect was more significant in lower temperature (from room temperature to 0 °C). Only a trace amount of product (<5%) was afforded, which made the separation and detection impossible. And *m*-substituted aromatic aldehydes were found not to be switched, this may be due to the electron effect compared with *o*- or *p*-substituted substrates.

From previous studies[3b,9,13], it is anticipated that cyclic ketone may give the *anti*-aldol product through the *E*-enamine intermediate (shown in Scheme 3), because of its stabilization by hydrogen bonding with the hydrogen of the primary amino group, which is not possible in the reactions catalyzed by secondary amine-based catalysts. However, the formation of *syn*-configured aldol adducts through PTC is incredible. It is assumed that thermodynamically driven retro-aldol processes are possibly responsible for this stereochemical outcome.[14]

In summary, we have developed a new catalyst system for direct aldol reactions in an environmentally friendly solvent EtOH or H_2O combined with TFA. This system demonstrates up to 99% enantioselectivity and 99% diastereoselectivity and near quantitative yields for stoichiometric direct aldol reactions of several aryl aldehydes and ketones. More interesting is that the *syn*-aldol product can be mainly gained only by changing the solvent from organic solvents to water, namely, aqueous solvent induced configuration switch.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.09.053.

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