

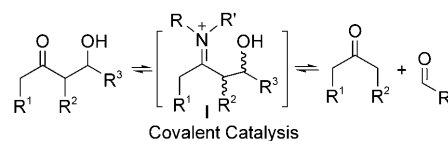
## Asymmetric Retro- and Transfer-Aldol Reactions Catalyzed by a Simple Chiral Primary Amine

Sanzhong Luo,<sup>\*,[a]</sup> Pengxin Zhou,<sup>[b]</sup> Jiuyuan Li,<sup>[a]</sup> and Jin-Pei Cheng<sup>\*,[b]</sup>

As one of the most versatile C–C bond forming reactions in organic synthesis, the aldol reaction is well known to be an intrinsically reversible process.<sup>[1]</sup> Over the years, it has been routine practice to prevent the undesired retro-aldol pathways to achieve catalytic stereoselective aldol reactions. Microscopically, the asymmetric retro-aldol reaction would address those challenging substrates that are normally sluggish under the typical asymmetric aldol conditions. Unfortunately, though principally conceivable, such asymmetric retro-aldol processes remain underdeveloped in asymmetric synthesis.<sup>[1,2]</sup> The situation becomes further aggravated by the fact that most of the asymmetric aldol catalysts developed may not promote the retro reactions in a stereoselective fashion, as would be expected. For example, L-proline and its derivatives, representing those of the most extensively explored asymmetric direct aldol catalysts,<sup>[2]</sup> have been shown to be totally nonselective in retro-aldol reactions due, at least partially, to the general base-catalyzed alternative reaction pathway.<sup>[2b]</sup> To date, only antibody aldolases<sup>[3]</sup> and transition-metal catalysts<sup>[4]</sup> have been reported to catalyze enantioselective retro-aldol reactions. Asymmetric organo-catalysts that stereoselectively promote retro-aldol reactions have not been reported so far.<sup>[5]</sup>

It is well known that aldolases, for example, type I aldolases,<sup>[6]</sup> stereoselectively and reversibly catalyze aldol processes. Similarly, antibody aldolases, such as 38C2,<sup>[2,3]</sup> have

also been shown to promote selectively a broad range of aldol and retro-aldol reactions with synthetic practicability. In both examples, the  $\epsilon$ -primary amine of lysine serves as the highly conserved catalytically active group. The inherent advantage of primary aminocatalysts over typical secondary aminocatalysts for retro-aldol reactions may be ascribed to the ease of primary amines to form the sterically demanding covalent intermediates **I** (Scheme 1). Despite these enzymatic examples, a simple chiral primary amine mimic for the stereoselective retro-aldol reaction remains unknown.



Scheme 1. Primary amine catalyzed reversible aldol reaction.

Previously, we have developed simple chiral primary amines, such as **1a**, that could promote a range of asymmetric aldol reactions in a way that functionally mimics type I aldolases (Scheme 1).<sup>[7,8]</sup> To explore the potential of chiral primary amine catalyzed retro-aldol reactions, we studied the retro-aldol reaction of the optically pure aldol product (1*R*,2*S*)-**2a** in the presence of chiral primary amine **1a**/TfOH. The reaction catalyzed by (*R,R*)-**1a**/TfOH was found to be 37-fold faster than that catalyzed by (*S,S*)-**1a**/TfOH (Scheme 2), suggesting a highly stereospecific retro-aldol process catalyzed by chiral primary amine **1a**/TfOH. Herein, we describe the first asymmetric retro-aldol reactions catalyzed by a simple chiral primary amine. This retro-aldol process enables the synthesis of optically pure aldol products that are difficult to make by direct asymmetric aldol reactions. Furthermore, an unprecedented asymmetric transfer-aldol reaction has also been realized for the first time by utilizing the above retro-aldol reactions, leading to the formation of two chiral aldol adducts with opposite chiral induction originating from a single chiral catalyst.

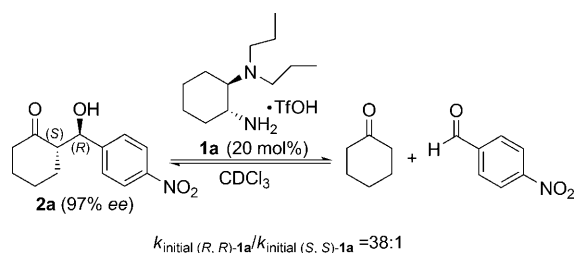
[a] Prof. Dr. S. Luo, J. Li

Beijing National Laboratory for Molecular Sciences (BNLMS)  
CAS Key Laboratory of Molecular Recognition and Function  
Institute of Chemistry, Chinese Academy of Sciences  
Beijing, 100190 (P.R. China)  
Fax: (+86) 10-6255-4449  
E-mail: luosz@iccas.ac.cn

[b] P. Zhou, Prof. Dr. J.-P. Cheng

Department of Chemistry and State-key Laboratory of  
Elemento-organic Chemistry, Nankai University  
Tianjin, 300071 (P.R. China)  
E-mail: chengjp@most.cn

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Scheme 2.

The racemic aldol adduct **2b** was chosen as a model substrate. A quick survey of our chiral primary–tertiary diamine catalysts indicated that the use of the diethylamino catalyst **1b**/TfOH gave the optimal results in terms of both activity and stereoselectivity in the retro reaction. The kinetic resolution of *rac*-**2b** catalyzed by **1b**/TfOH was then monitored by <sup>1</sup>H NMR spectroscopy and HPLC and the changes over time in conversion, diastereomeric excess (*de*), and enantiomeric excess (*ee*) were recorded. As shown in Figure 1, the diastereoselectivity remained essentially unchanged during the whole process and the reaction reached a plateau over 50% conversion. At this stage, the reaction barely proceeded further and an enantioselectivity of >95% *ee* was achieved, indicating a nearly ideal kinetic resolution process. Optimal conditions were then determined and the reaction can be conveniently conducted in dichloromethane at a 0.25 M concentration of the substrate. Under these conditions, the resolution of **2b** in the presence of **1b**/TfOH (20 mol%) gave the optically pure aldol product (98:2 *anti*/

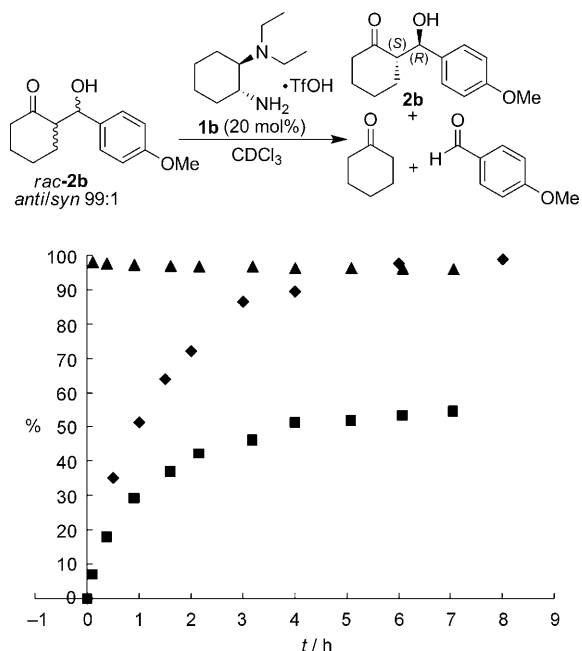


Figure 1. Retro-aldol reaction of racemic *anti*-**2a** catalyzed by **1b** monitored by <sup>1</sup>H NMR spectroscopy and HPLC. ■ = conversion, ▲ = *de*, ◆ = *ee*.

*syn*, >99% *ee*) with an excellent recovered yield in 8 h (48% recovered yield, Table 1, entry 1). In addition, the *p*-anisaldehyde that was generated could be quantitatively recovered. The selectivity (*s*) factor is as high as 115 in this resolution.

Table 1. Substrate scope of the **1b**-catalyzed retro-aldol reaction.<sup>[a]</sup>

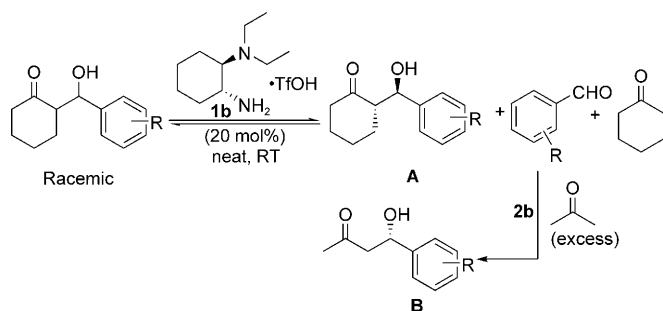
Entry	Product	<i>t</i> [h]	Yield [%] <sup>[b]</sup>	<i>anti/syn</i> <sup>[c]</sup>	<i>ee</i> [%] <sup>[d]</sup>	<i>s</i> <sup>[e]</sup>
1		8	48	98:2	99	115
2		12	46	98:2	95	35
3		12	43	94:6	96	24
4		9	41	98:2	98	23
5		6	40	99:1	>99	24
6		24	47	95:5	97	55
7		12	45	95:5	93	25
8 <sup>[f]</sup>		22	33	99:1	98	12
9		36	46	–	91	24
10		36	35 <sup>[g]</sup>	98:2	50	44
11		36	16 <sup>[g]</sup>	95:5	18	42

[a] All reactions were carried out at 0.25 M in CH<sub>2</sub>Cl<sub>2</sub> with catalyst (20 mol%) at RT. [b] Yield of the isolated product. [c] Determined by <sup>1</sup>H NMR spectroscopy of the crude product. [d] Determined by HPLC on a chiral phase. [e] Calculated according to the equation developed by Kagan and Fiaud.<sup>[9a]</sup> [f] The racemic *syn*-aldol adduct was used. [g] Conversion calculated based on the recovered product.

The applicability of this retro-aldol reaction was next examined and the results were summarized in Table 1. Due to their easy accessibility through NaOH mediated aldol reactions, racemic aldol products of cyclohexanone were selected as our target substrates. To our delight, aldol products of highly electron-donating aromatic aldehydes, which are gen-

erally difficult to make by the asymmetric aldol reaction, were indeed quite good substrates for retro-aldol reactions. In all these cases, the resolution reactions proceeded smoothly affording the optically pure aldol adducts in excellent *ee* (95–99% *ee*) with 40–48% yield (Table 1, entries 1–5). The reactions worked well with racemic aldol adducts derived from less electron-donating aromatic aldehydes, such as *p*-*tert*-butylbenzaldehyde and *trans*-cinnamaldehyde, with *s* factors over 20 (Table 1, entries 6 and 7). In all these cases, good *anti* diastereoselectivities were maintained for the isolated products. Notably, the resolution could be equally applied to *syn*-aldol products derived from electron-donating aldehydes, such as **2i**, and in this case the optically pure product was recovered in 33% yield, 99:1 *syn/anti* and 98% *ee* (Table 1, entry 8). The aldol product derived from acetone was also applicable in the current protocol with an *s* factor of 24 (Table 1, entry 9).

As expected, the retro reaction of aldol products, either *anti* or *syn* adducts, derived from activated aromatic aldehydes showed very sluggish reaction rates, but high *s* factors were still maintained in these cases (Table 1, entries 10 and 11). The generally high *s* factors in these resolutions suggest that high enantioselectivity would be achieved if the equilibrium could be displaced in favor of the retro-aldol reactions. Bearing in mind that the same primary amine catalyst could promote both the aldol and retro-aldol reactions, it is thus conceived that the consumption of the in situ generated aldehyde by an aldol reaction catalyzed by the same catalyst (e.g., **1b**/TfOH, Scheme 3) would drive the equilibrium of the retro-aldol reaction to achieve optimal resolution (Scheme 3). The net outcome would be a transfer-aldol process between a racemic aldol product and an active aldol donor (e.g., acetone, Scheme 3). In principle, such a transfer-aldol reaction would lead to two aldol products **A** and **B** with opposite chiral induction by taking advantage of both the retro-aldol and aldol catalytic properties of **1b**/TfOH. Our subsequent experiments proved that the hypothetical transfer-aldol reaction was indeed possible in the presence of an excess of active aldol donors, such as acetone. When conducted in neat acetone, the resolution reaction of racemic **2a** in the presence of **1b**/TfOH (20 mol%) proceeded smoothly and the expected two enantioenriched aldol adducts were isolated in approximately theoretical yield with good enantioselectivity (98 and 78% *ee* for **2a** and **3b**, re-



Scheme 3. Primary amine catalyzed transfer-aldol reaction.

spectively, Table 2, entry 1). To the best of our knowledge, this represents the first asymmetric transfer-aldol reaction that generates two optically pure aldol adducts with opposite configurations.<sup>[10]</sup>

Table 2. Asymmetric transfer-aldol reaction.<sup>[a]</sup>

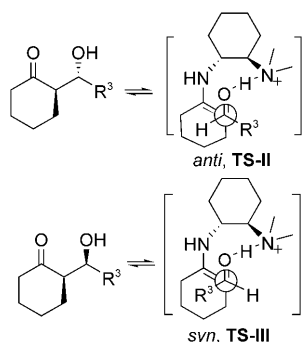
Entry	R	Yield [%] <sup>[b]</sup>	A		B	
			<i>anti/syn</i> <sup>[b]</sup>	<i>ee</i> [%] <sup>[c]</sup>	Yield [%] <sup>[b]</sup>	<i>ee</i> [%] <sup>[c]</sup>
1	4-NO <sub>2</sub>	<b>2a</b> /50	98:2	98	<b>3b</b> /50	78
2	2-NO <sub>2</sub>	<b>2k</b> /48	98:2	98	<b>3c</b> /50	83
3	H	<b>2l</b> /50	97:3	97	<b>3d</b> /36	84
4		<b>2b</b> /48	98:2	99	<b>3e</b> /24	90
5 <sup>[d]</sup>	4-MeO	<b>2b</b> /46	99:1	98	<b>3e</b> /11	80
6	2-Cl	<b>2m</b> /40	98:2	98	<b>3f</b> /42	86
7	4-Cl	<b>2n</b> /44	98:2	98	<b>3g</b> /49	80
8	2,4-Cl <sub>2</sub>	<b>2o</b> /45	98:2	98	<b>3h</b> /47	70
9	4-Ph	<b>2p</b> /45	98:2	91	<b>3i</b> /30	84
10	1-naphthyl	<b>2q</b> /42	98:2	98	<b>3j</b> /40	81
11 <sup>[e]</sup>	4-NO <sub>2</sub>	<b>2j</b> /46	89:11	94	<b>3b</b> /50	11

[a] Unless otherwise specified, all reactions were carried out with racemic *anti*-aldol products at 0.25 M in acetone with catalyst (20 mol%) at 25°C for 36 h. [b] Yield of the isolated product based on the racemic substrate. [c] Determined by HPLC on a chiral phase. [d] 4.25 mmol scale (0.5 M) in the presence of catalyst (10 mol%). [e] The reaction was carried out with the *syn*-aldol adduct at 50°C, the starting *syn/anti* ratio was 99:1.

The scope of the asymmetric transfer-aldol reaction was explored next. As shown in Table 2, racemic aldol adducts derived from either electron-withdrawing or electron-donating aromatic aldehydes can be applied in the present transfer-aldol protocol. The reactions normally reached equilibrium in 36 h, affording two enantioenriched aldol adducts in high (recovery) yields with good to excellent enantioselectivities (Table 2, entries 1–10). Importantly, the transfer-aldol reaction also enabled the kinetic resolution of *syn*-aldol adducts of cyclic ketones, such as *rac*-**2j** (Table 2, entry 11). The desired enantioenriched *syn*-aldol product (*S,S*)-**2j** was isolated in 46% yield and 94% *ee*. High temperature was applied in this case to facilitate the reaction with, unfortunately, a sacrifice of the enantioselectivity of the aldol adduct **3b** (11% *ee*, Table 2, entry 11). A decrease of the *syn* diastereoselectivity from 99:1 to 89:11 was observed in this case. A large scale (4.25 mmol) transfer reaction has also been examined in the presence of **1b**/TfOH (10 mol%) (Table 2, entry 5), which gave consistently excellent resolution, illustrating the synthetic applicability of this reaction.

Based on the microscopic principle, an enamine catalytic cycle and the same transition state (**TS-II** and **TS-III** for *anti* and *syn* products, respectively) as that in the aldol reaction may be proposed for the retro, as well as for the transfer-

aldol reactions (Scheme 4). In the retro reactions, aldol adducts with configurations as shown in Scheme 4 are kinetically favored and the other enantiomers are therefore enantioenriched in these processes.



Scheme 4. Proposed transition state for the retro reaction.

The putative imine/enamine intermediate **I** can be trapped by in situ reduction with sodium borohydride. Upon mixing catalyst **1b**/TfOH and *rac*-**2a**, the mixture was stirred for 30 mins. An aliquot of the mixture was diluted with methanol and treated with NaBH<sub>4</sub> at room temperature for 10 mins. ESI/MS analysis of the mixture showed the signals *m/z* 171, 306, and 404, corresponding to catalyst **1b**-H<sup>+</sup>, the reductive amination product of **1b** with *p*-nitrobenzaldehyde, and the reduced intermediate **I**, respectively (see the Supporting Information).

In summary, we have developed a highly enantioselective retro-aldol reaction catalyzed by a simple primary-tertiary diamine catalyst, such as **1b**. This retro-aldol protocol enables an ideal catalytic kinetic resolution of racemic aldol products that are usually difficult to obtain through forward processes as illustrated by the resolutions of cyclohexanone aldol adducts. An intriguing feature of this process is that one chiral primary amine (e.g., **1b**) could catalyze stereoselectively the resolution of both *anti*- and *syn*-aldol adducts, whereas the forward reactions with the same catalyst yield selectively *anti*-aldol products. In addition, the catalytic power of **1b**/TfOH on both aldol and retro-aldol reactions has also made possible an unprecedented asymmetric transfer-aldol reaction that can generate two enantioenriched aldol adducts with opposite chiral induction from a single chiral catalyst. Overall, the current retro and transfer protocols provide an efficient synthesis of three diastereoisomers of cyclohexanone aldol products with excellent enantioselectivities (91–99% *ee*) and diastereoselectivities (>95:5) by using one common chiral primary amine catalyst **1b**/TfOH. Further explorations on the retro- and transfer-aldol reactions, as well as detailed mechanistic studies are underway in our laboratory.

## Experimental Section

**Typical experimental procedure for the retro-aldol reaction:** Catalyst **1b**/TfOH (6.4 mg, 0.02 mmol) was added to a solution of racemic aldol product **2a** (24.9 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL). The resulting reaction solution was stirred at RT for the given time. The reaction mixture was then directly subjected to flash chromatography to give enantioenriched aldol products. The conversion is calculated from the recovery of the pure product.

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**Keywords:** aldol reaction • enantioselectivity • kinetic resolution • organocatalysis • retro reactions

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