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## COMMUNICATION

Highly enantioselective aldol reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters promoted by simple chiral primary–tertiary diamine catalystsLin Peng,<sup>a,b</sup> Liang-Liang Wang,<sup>a,b</sup> Jian-Fei Bai,<sup>a,b</sup> Li-Na Jia,<sup>a,b</sup> Yun-Long Guo,<sup>a,b</sup> Xi-Ya Luo,<sup>a,b</sup> Fei-Ying Wang,<sup>a</sup> Xiao-Ying Xu<sup>\*a</sup> and Li-Xin Wang<sup>\*a</sup>

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A series of primary–tertiary diamine catalysts were successfully applied to promote the enantioselective aldol reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters in excellent yields (up to 99%) and enantioselectivities (up to 96% ee).

The chiral tertiary alcohol framework occurs prevalently in a variety of natural products and biologically active compounds, as well as being a class of useful synthetic building blocks in organic synthesis.<sup>1</sup> Tremendous efforts have been devoted to the synthesis of these attractive subunits, with methods including asymmetric oxidation,<sup>2</sup> enantioselective desymmetrization,<sup>3</sup> stereospecific insertion of carbene into secondary alcohols<sup>4</sup> and nucleophilic addition.<sup>5</sup> Among them, the aldol reaction of carbonyl compounds (ketones and aldehydes) with  $\alpha$ -keto esters, especially organocatalytic versions, is a straightforward way to access chiral tertiary alcohols.<sup>6</sup> Up till now, the functional reactants of this transformation included mainly the aromatic  $\alpha$ -keto esters (or  $\alpha$ -keto acids) and  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters. The reaction of cyclohexanone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto ester has been well-documented and excellent results have been obtained.<sup>7</sup> However, the highly efficient reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto ester has been less exploited. Tang<sup>7a</sup> and Zhao<sup>7b</sup> reported the reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters catalyzed by L-proline derivatives individually and only poor enantioselectivities (up to 45% ee) were achieved. Very recently, Chan and Kwong<sup>8</sup> revealed a *Cinchona* alkaloid derivative primary amine promoted the enantioselective aldol reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters in excellent enantioselectivities (up to 94% ee), the only and the highest enantioselective example up to the present. For further and deeper understanding and expanding of this useful and asymmetric transformation, it is still highly desirable to develop more and efficient organocatalytic protocols for the syntheses of optically active chiral tertiary alcohols.

Over the past decades, chiral aminocatalysis has emerged as a powerful synthetic strategy in organic synthesis.<sup>9</sup> Chiral 1,2-diphenylethane-1,2-diamine and cyclohexane-1,2-diamine, sim-

ple and commercially available, are widely used in asymmetric transformation,<sup>10</sup> and can be easily transformed to tunable primary–tertiary diamine bifunctional catalysts.<sup>11</sup> As a part of our continuing interest in asymmetric synthesis based on chiral primary amine catalysis,<sup>12</sup> herein we wish to report a highly enantioselective (up to 96% ee) aldol reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters catalyzed by simple chiral primary–tertiary diamines to construct types of chiral tertiary alcohols.

The reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto ester **2a** was chosen as a model reaction to optimize the reaction conditions. A series of catalysts (Fig. 1) and acid additives<sup>13</sup> were examined and the results are summarized in Table 1, and moderate yield and enantioselectivity (46% yield and 40% ee, Table 1, entry 1) was observed in the presence of 20 mol% **1a** in  $\text{CH}_2\text{Cl}_2$  at room temperature. A remarkable improvement was achieved when 4-nitrobenzoic acid was added as an acid additive (Table 1, entry 2). In the presence of the same additive, a variety of primary–tertiary diamine catalysts **1b–1f** were further evaluated, and all the cases afforded the adducts with better enantioselectivities than their counterparts without additive (Table 1, entries 3–7). Particularly, primary–tertiary diamine **1a** gave better results (64% yield and 73% ee; Table 1, entry 2), and was selected for further screening of acid additives. All the additives afforded moderate to good yields and enantioselectivities except acetic acid, trifluoroacetic acid and *p*-toluenesulfonic acid (Table 1, entries 8–21). 3,5-Dinitrobenzoic acid gave the best yield and enantioselectivity (70% yield and 81% ee; Table 1, entry 16), and was selected for other optimizations.

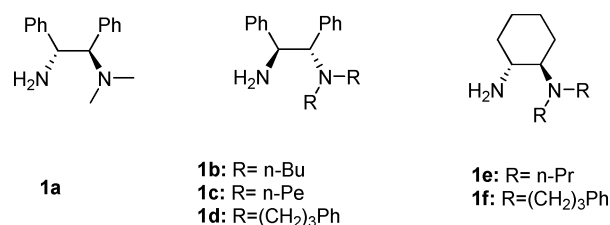
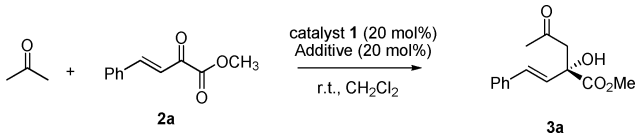


Fig. 1 Chiral catalysts evaluated.

The effects of solvents, the amount of acetone, catalyst loading, reaction temperature and reactant concentration were then studied and the results are summarized in Table 2, and solvents exerted a significant effect on the yields and enantioselectivities. Polar

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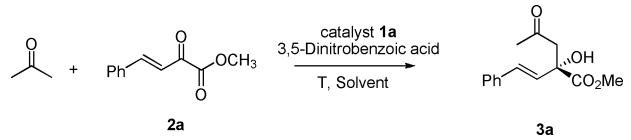
**Table 1** The effects of additives<sup>a</sup>


Entry	Catalyst	Additive	Time/h	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>1a</b>	—	112	46	40
2	<b>1a</b>	4-NO <sub>2</sub> PhCOOH	112	64	73
3	<b>1b</b>	4-NO <sub>2</sub> PhCOOH	112	44	48
4	<b>1c</b>	4-NO <sub>2</sub> PhCOOH	112	46	48
5	<b>1d</b>	4-NO <sub>2</sub> PhCOOH	112	61	44
6	<b>1e</b>	4-NO <sub>2</sub> PhCOOH	112	56	61
7	<b>1f</b>	4-NO <sub>2</sub> PhCOOH	112	66	65
8	<b>1a</b>	AcOH	112	20	49
9	<b>1a</b>	CF <sub>3</sub> COOH	72	79	34
10	<b>1a</b>	<i>p</i> -TsOH	72	78	43
11	<b>1a</b>	2-OHPhCOOH	112	64	72
12	<b>1a</b>	2-NO <sub>2</sub> PhCOOH	112	61	66
13	<b>1a</b>	4-COOHPhCOOH	112	71	53
14	<b>1a</b>	2,6-di-FPhCOOH	112	50	65
15	<b>1a</b>	2,3-di-OHPhCOOH	112	81	77
16	<b>1a</b>	3,5-di-NO <sub>2</sub> PhCOOH	112	70	81
17	<b>1a</b>	2-NO <sub>2</sub> -4-ClPhCOOH	112	55	71
18	<b>1a</b>	2-CH <sub>3</sub> -3-NO <sub>2</sub> PhCOOH	112	51	68
19	<b>1a</b>	3-OH-4-NO <sub>2</sub> PhCOOH	112	68	77
20	<b>1a</b>	D-camphor-10-sulfonic acid	112	71	66
21	<b>1a</b>	L-camphor-10-sulfonic acid	112	72	55

<sup>a</sup> Unless otherwise specified, all reactions were carried out with acetone (2.0 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**, 0.20 mmol), additive (0.04 mmol, 20 mol%), the catalyst **1** (0.04 mmol, 20 mol%) in 1 mL CH<sub>2</sub>Cl<sub>2</sub> at room temperature. <sup>b</sup> Isolated yield after silica gel column chromatography. <sup>c</sup> The ee values were determined by HPLC using Chiral OD-H column.

solvents such as methanol, CH<sub>3</sub>CN, DMF and DMSO gave excellent yields (80–90%) and poor enantioselectivities (10–44% ee, Table 2, entries 14–17), while nonpolar or low polarity solvents such as alkylhalides, toluene, alkanes and ethers gave good enantioselectivities (74–84% ee, Table 2, entries 1–10), and the best results (94% yield and 84% ee) were obtained in cyclohexane (Table 2, entry 6). When 20 equivalents of acetone in cyclohexane were used, 85% ee and 96% yield were obtained (Table 2, entry 19). When the catalyst loading was lowered to 10 mol%, the enantioselectivity was slightly decreased to 84% ee without loss of reactivity (Table 2, entry 21). Still, excellent yields were obtained without any observable effects of the substrate concentration (98%–99% yield, Table 2, entries 23–25). In general, the reaction temperature has significant effects on the enantioselectivities. Lowering the reaction temperature to –20 °C, the best enantioselectivity was obtained (94% ee, Table 2, entry 28). When it was further lowered to –25 °C, the yield and enantioselectivity were slightly decreased, and a longer reaction time was required (93% and 93% ee, Table 2, entry 29). Through these screenings, the optimized reaction conditions were found to be a combination of 20 mol% of **1a** with 20 mol% of 3,5-dinitrobenzoic acid, 20 eq. acetone, in cyclohexane (0.6 mL) at –20 °C.

Under the optimal reaction conditions, the scopes and limitations of the reaction of acetone and  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters **2** were further investigated. As shown in Table 3, the steric hindrances of the ester groups slightly affected the yields and enantioselectivities and good results were obtained

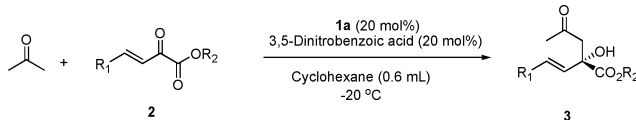
**Table 2** Optimization of reaction conditions<sup>a</sup>


Entry	Solvent	Acetone/ equiv.	Catalyst/ mol (%)	Time/h	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	CH <sub>2</sub> Cl <sub>2</sub>	10	20	112	70	81
2	ClCH <sub>2</sub> CH <sub>2</sub> Cl	10	20	112	84	79
3	CHCl <sub>3</sub>	10	20	112	73	77
4	PhCH <sub>3</sub>	10	20	112	80	79
5	<i>p</i> -xylene	10	20	112	90	78
6	cyclohexane	10	20	112	94	84
7	hexane	10	20	112	92	84
8	Et <sub>2</sub> O	10	20	112	99	82
9	1,4-dioxane	10	20	72	82	74
10	MTBE	10	20	112	83	82
11	EtOAc	10	20	112	89	82
12	(CH <sub>3</sub> ) <sub>2</sub> CO	10	20	48	85	72
13	THF	10	20	112	47	64
14	CH <sub>3</sub> OH	10	20	48	90	10
15	CH <sub>3</sub> CN	10	20	112	80	44
16	DMF	10	20	48	84	38
17	DMSO	10	20	48	86	37
18	cyclohexane	5	20	112	83	75
19	cyclohexane	20	20	72	96	85
20	cyclohexane	40	20	96	99	66
21	cyclohexane	20	10	72	98	84
22	cyclohexane	20	30	72	99	85
23 <sup>d</sup>	cyclohexane	20	20	48	98	83
24 <sup>e</sup>	cyclohexane	20	20	48	99	86
25 <sup>f</sup>	cyclohexane	20	20	48	99	85
26 <sup>g,h</sup>	cyclohexane	20	20	48	99	91
27 <sup>e,h</sup>	cyclohexane	20	20	48	99	92
28 <sup>e,i</sup>	cyclohexane	20	20	72	95	94
29 <sup>e,j</sup>	cyclohexane	20	20	96	93	93

<sup>a</sup> Unless otherwise specified, all reactions were carried out with acetone (4.0 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**, 0.20 mmol), 3,5-dinitrobenzoic acid (0.04 mmol, 20 mol%), the catalyst **1a** (0.04 mmol, 20 mol%) in 1 mL solvent at room temperature. <sup>b</sup> Isolated yield after silica gel column chromatography. <sup>c</sup> The ee values were determined by HPLC using Chiral OD-H column. <sup>d</sup> Cyclohexane: 0.4 mL. <sup>e</sup> Cyclohexane: 0.6 mL. <sup>f</sup> Cyclohexane: 0.8 mL. <sup>g</sup> Temperature: 0 °C. <sup>h</sup> Temperature: –10 °C. <sup>i</sup> Temperature: –20 °C. <sup>j</sup> Temperature: –25 °C.

(up to 95% yield and 94% ee, Table 3, entries 1–4). Almost in each case, moderate to excellent yields (up to 99%) and excellent enantioselectivities (up to 96% ee) were achieved with various  $\beta,\gamma$ -unsaturated  $\alpha$ -keto ester derivatives bearing either electro-donating or electron-withdrawing substituents at *para*- (Table 3, entries 5–8), *meta*- (Table 3, entries 9–14) or *ortho*-positions (Table 3, entries 15, 16) in aromatic rings. Further broadening the substrates to heteroaromatic  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters, the reaction also gave excellent enantioselectivity with only moderate yield (40% yield and 90% ee, Table 3, entry 18). To understand the potential applications of our catalyst system, the present procedure was scaled up to 1 mmol of the starting  $\alpha$ -keto ester and the corresponding product was also smoothly obtained in moderate yield (68%) without deleterious loss of the enantioselectivity (92% ee vs. 94% ee, Table 3, entry 19 vs. entry 1).

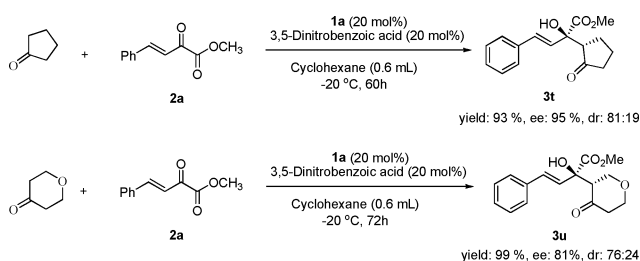
Cyclic ketones, such as cyclopentanone and dihydro-2*H*-pyran-4(3*H*)-one were also investigated under the optimized reaction conditions. As shown in Scheme 1, the corresponding products

**Table 3** Aldol reaction between acetone and **2**<sup>a</sup>


Entry	R <sub>1</sub>	R <sub>2</sub>	Time/h	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	Ph	Me	72	95 ( <b>3a</b> )	94
2	Ph	Et	72	91 ( <b>3b</b> )	92
3	Ph	<i>i</i> -Pr	72	90 ( <b>3c</b> )	91
4	Ph	<i>n</i> -Bu	72	84 ( <b>3d</b> )	93
5	4-FC <sub>6</sub> H <sub>4</sub>	Me	60	96 ( <b>3e</b> )	91
6	4-ClC <sub>6</sub> H <sub>4</sub>	Me	72	64 ( <b>3f</b> )	93
7	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Me	72	85 ( <b>3g</b> )	95
8	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Me	72	90 ( <b>3h</b> )	92
9	3-FC <sub>6</sub> H <sub>4</sub>	Me	60	99 ( <b>3i</b> )	92
10	3-ClC <sub>6</sub> H <sub>4</sub>	Me	60	95 ( <b>3j</b> )	93
11	3-BrC <sub>6</sub> H <sub>4</sub>	Me	60	54 ( <b>3k</b> )	93
12	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Et	60	98 ( <b>3l</b> )	93
13	3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Me	60	98 ( <b>3m</b> )	93
14	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Me	60	98 ( <b>3n</b> )	90
15	2-ClC <sub>6</sub> H <sub>4</sub>	Me	36	91 ( <b>3o</b> )	91
16	2-BrC <sub>6</sub> H <sub>4</sub>	Me	36	98 ( <b>3p</b> )	91
17	1-naphthyl	Me	72	93 ( <b>3q</b> )	96
18	2-thienyl	Et	72	40 ( <b>3r</b> )	90
19 <sup>d</sup>	Ph	Me	72	68 ( <b>3s</b> )	92

<sup>a</sup> Unless otherwise specified, all reactions were carried out with acetone (4.0 mmol), **2** (0.20 mmol), 3,5-dinitrobenzoic acid (0.04 mmol, 20 mol%), the catalyst **1a** (0.04 mmol, 20 mol%) in 0.6 mL cyclohexane at -20 °C.

<sup>b</sup> Isolated yield after silica gel column chromatography. <sup>c</sup> The ee values were determined by HPLC using Chiral OD-H, chiralpak AD-H and chiralpak AS-H column; the absolute configurations were determined to be *S*-configuration by comparison with literature data.<sup>7,8</sup> <sup>d</sup> In 1.0 mmol scale: acetone (20.0 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**, 1.0 mmol), 3,5-dinitrobenzoic acid (0.20 mmol, 20 mol%), the catalyst **1a** (0.20 mmol, 20 mol%) in 3.0 mL cyclohexane at -20 °C.

**Scheme 1** Reaction of cyclopentanone and dihydro-2*H*-pyran-4(3*H*)-one with **2a**.

were obtained in excellent yields (93%–99%) and satisfactory enantioselectivities (81%–95% ee).

In summary, we have developed a highly enantioselective aldol reaction of acetone with  $\beta,\gamma$ -unsaturated  $\alpha$ -keto esters catalyzed by simple chiral primary–tertiary diamines in excellent yields (up to 99%) and enantioselectivities (up to 96% ee). This highly enantioselective protocol presents a chiral quaternary carbon center together with four functional groups (hydroxy, carbon–carbon double bond, ester, and carbonyl functional groups), which may be further transformed to types of potential chiral intermediates and functional materials. The protocol is practical and efficient. Further investigations on the applications in pharmaceutical preparations and in other asymmetric catalysis are in progress.

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