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Utilization of biocatalytic promiscuity for direct Mannich reaction

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ABSTRACT

A lipase-catalyzed direct Mannich reaction of arylamines with aromatic aldehydes and ketones including cyclohexanone, butanone and 1-hydroxy-2-propanone was developed under EtOH/H_2O system in a "one-pot" strategy. A series of experiments on the promiscuous activity of lipases were performed to optimize the biocatalytic process, and a wide scope of substrates was expanded with good yields.

1. Introduction

Nowadays, the usefulness of various biocatalysts (such as enzymes and whole sells) for organic synthesis has become more and more recognized [1–4]. Among them, the enzymatic promiscuity has been regarded as one of the most outstanding concepts in biocatalysis [5–6]. This concept involves the abilities of a certain enzyme to catalyze different synthetic reactions, which maybe more or less far from their natural role [3,7–10]. The importance of the promiscuity concept in biocatalysis is noteworthy, since it not only highlights the existing catalysts, but may provide novel and practical synthetic pathways which are not currently available [11–17,31]. Within biocatalysis, the use of hydrolases has been extensively documented and some excellent examples of the enzymatic promiscuity were presented. For example, Gotor group found that lipase B from *Candida antarctica* (Lipase CAL-B) are able to promiscuously catalyze Michael-type addition of secondary amines to acrylonitrile [18]. Berglund and co-workers found that CAL-B not only can catalyze the aldol reaction between adipic aldehydes, but can catalyze direct epoxidation reaction of α,β-unsaturated aldehydes [19,20]. Wu et al. reported that Penicillin G acylase, which is widely used in biosynthesis of β-lactam antibiotics, is also capable of Markovnikov addition of allopurinol to vinyl ester [16]. Although the catalytic activities were quite low in some experiments, these cases and other relevant reports indeed provide novel synthesis pathways for organic synthesis [3]. Lipases are the most used and well-known hydrolases, which have high stability and activity, and can be used for different kinds of transformations with low cost. Therefore, to find new promiscuous reaction of lipase is more attractive and might provide novel process for industrialization.

On the other hand, in organic synthesis, the development of efficient and environmentally friendly chemical processes for the preparation of biologically active molecules remains a major challenge for chemists and biologists. Among them, Mannich reaction is one of the most important C–C bond formations in organic synthesis. They provide β-amino carbonyl compounds, which are important intermediates for various pharmaceuticals and natural products [21,22]. The preferable process is the use of a "one-pot" three-component strategy that allows for a wide range of structural variations. However, most reaction methodology (referred to as the indirect Mannich reaction) relies on the two-component system using preformed electrophiles, such as imines, and stable nucleophiles, such as enolates, enol ethers, and enamines [23–30]. Compared to direct Mannich reaction (carries out the reaction with unmodified ketone donors), these methods need to firstly prepare and isolate the intermediates, which is complicated and not atom economic. Hence, to realize the direct Mannich reaction in "one pot" strategy is currently concerned (Scheme 1), which is also the trend for green chemistry.

Recently, we reported the lipase-catalyzed direct Mannich reaction of aromatic aldehydes with arylamines and acetone in the presence of water [32]. Although high yield was achieved in acetone and water system (v/v = 1:1), the solvent was not environment friendly because of the excessive acetone. Meanwhile this reaction medium could hardly extend to other ketones due to the competing reaction between of acetone and other ketones with aldehydes and aniline. Therefore, to assess the generality of promiscuous lipase-catalyzed Mannich reaction, herein we present a more

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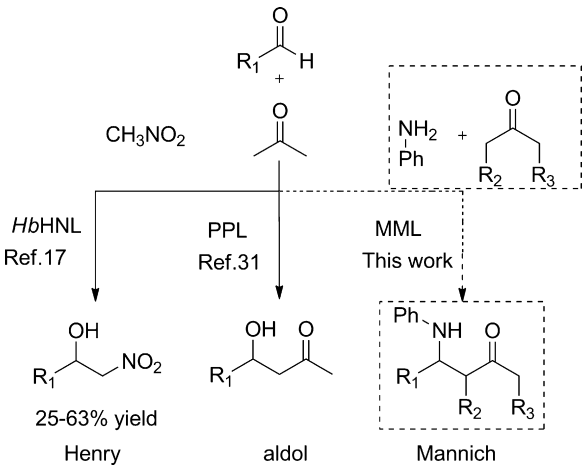


Scheme 1. Lipase-catalyzed reactions utilizing of biocatalytic promiscuity

benign reaction system (ethanol/water) for the direct Mannich reaction. Meanwhile, more substrates were tested including cyclohexanone, butanone and 1-hydroxy-2-propanone, which indicated the wide application of the lipase-catalyzed biocatalytic promiscuity in organic synthesis.

2. Experimental

2.1. General

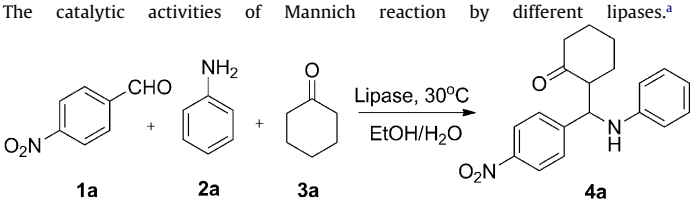
Lipase from *C. antarctica* (CAL-B, 10,000 u/g), lipase from porcine pancreas (PPL,100,000–400,000 u/g), lipase from *Candida cylindracea* (CCL, 7290 u/g), lipase from *Candida rugosa* (CRL, 700 u/mg) and lipase from *Mucor javanicus* (MJL, 10,000 u/g) were purchased from Sigma (St. Louis, USA). Lipase from *Mucor miehei* (MML, 86.8 u/g) was purchased from Fluka (Buchs, Switzerland). Lipase from *Pseudomonas fluorescens* (PFL, 10.2 u/g) and lipase from *Burkholderia cepacia* (BCL, 23,000 u/g) were a gift from Amano (Nagoya, Japan). For CRL, MML, MJL and PPL, one unit of enzyme activity is defined as the amount of enzyme that hydrolyzes 1.0 microequivalent of fatty acid from a triglyceride in 1 h at pH 7.7 at 37 °C; while for CCL, PFL and CAL-B, one unit corresponds to the amount of enzyme which liberates 1 mol oleic acid per minute at pH 8.0 and 40 °C. All other chemicals and reagents were obtained commercially and used as received.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 400. Chemical shifts are given in δ relative to tetramethylsilane (TMS). HPLC was carried out using a Shimadzu organizer consisting of a LC-2010A HT integrator, a UV/VIS detector. AD-H column was used in the HPLC experiments with *n*-hexane/*iso*-propanol = 85:15 (v/v), 0.8 ml/min and UV = 254 nm, Rt (**4a**) = 14.5 min, 18.4 min, 21.7 min, 25.2 min. Electrospray ionization (ESI) mass spectrometry experiments were performed on Bruker Daltonics Bio TOF mass spectrometer.

2.2. Substrate expansion

Reaction conditions: 100 mg CRL was added to a mixture of aldehyde (1 mmol), amine (1.1 mmol) and ketone (3 mmol) in 10 ml ethanol/water medium. The mixture was maintained at 30 °C and shaken at 200 rpm for 24 or 48 h. The residue was filtered off and the solvent was evaporated. A single product was prepared by silica gel chromatography with an eluent consisting of petroleum ether/ethyl acetate (4:1, v/v).

Table 1
The catalytic activities of Mannich reaction by different lipases.[a]



Entry	Catalyst	Conversion (%)[b]
1	No enzyme	–
2	Lipase from *Candida rugosa* (CRL)	52.0
3	Lipase from *Candida cylindracea* (CCL)	43.6
4	Lipase from *Pseudomonas fluorescens* (PFL)	41.3
5	Lipase from *Mucor miehei* (MML)	27.4
6	Lipase from porcine pancreas, type II (PPL)	25.1
7	Lipase from *Burkholderia cepacia* (BCL)	27.8
8	Lipase from *Candida antarctica* (CAL-B)	23.8
9	Lipase from *Mucor javanicus* (MJL)	5.6
10	Bovine Serum Albumin (BSA)	–
11	Denatured CRL[c]	<5

[a] *Reaction conditions*: a solution of 4-nitrobenzaldehyde (**1a**, 0.1 mmol), aniline (**2**, 0.11 mmol), cyclohexanone (**3a**, 0.2 ml), 2 ml solvent (the water content is 10% in volume) and 10 mg enzyme was shaken at 200 rpm at 30 °C for 24 h.
[b] Conversion was calculated based on **1a** detected by HPLC.
[c] Denatured CRL was treated by urea at 100 °C for 24 h.

3. Results and discussion

3.1. The catalytic activities of different lipases for the Mannich reaction

Initially, we chose the reaction of 4-nitrobenzaldehyde (**1a**), aniline (**2**) and cyclohexanone (**3a**) with the formation of **4a** as a model transformation, which is a common process of Mannich reaction (Table 1). Despite the diverse synthetic routes so far developed for the Mannich reaction, only a few one-pot procedures using unmodified aldehydes or ketones in water have been reported in the literature [33–39]. Based on the previous results, we believe that the water could accelerate the protonation of ketones and make it easier to react with the Schiff base formed by arylamines and aromatic aldehydes. In our previous work, acetone/water system was chosen as the reaction medium, in which acetone is one of reactants of the reaction as well as the solvent to dissolve other reactants. To test the generality of promiscuous lipase-catalyzed Mannich reaction, we initially process our reaction using 4-nitrobenzaldehyde, aniline and cyclohexanone in acetone/water 9:1 (v/v) medium, and the result indicated that the major product was the Schiff base transformed from aldehydes and aniline and further reaction could not proceed to form Mannich product at 30 °C in 48 h, which indicated that this reaction medium is only suitable for acetone and could not extend to other ketones. Therefore, to develop a universal biocatalytic process for the synthesis of β-amino-ketone compounds under benign conditions, we primarily chose ethanol/water 9:1 (v/v) as the reaction medium.

The effect of various enzymes on model reaction was investigated and the results are shown in Table 1. Lipase from *C. rugosa* (CRL, Table 1, entry 2) was identified to be the best catalyst for this direct Mannich reaction, CCL and PFL presented moderate activities (Table 1, entries 3 and 4); while other tested lipases (Table 1, entries 5–8) resulted in low conversion and no product was detected in the absence of enzymes. Therefore, CRL was chose as the catalyst in the following experiments. Additionally, although Catalytic promiscuity in enzymes is more common than generally appreciated [40,7], to prove this direct Mannich reaction is not catalyzed by impurities in enzymes, Bovine Serum Albumin (BSA) and denatured CRL were investigated and the results indicated that denatured CRL showed

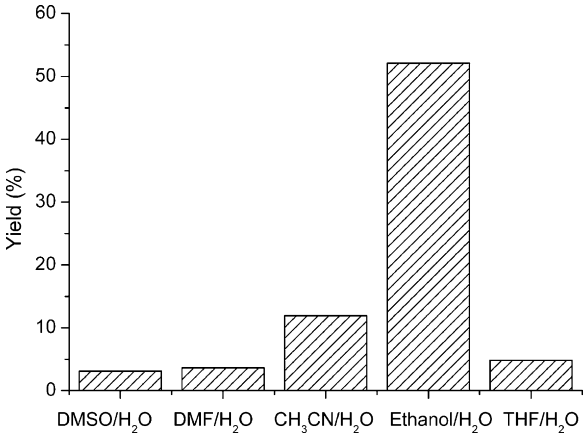


Fig. 1. The influence of solvents on the direct Mannich reaction. *Reaction conditions*: a solution of 4-nitrobenzaldehyde (**1a**, 0.1 mmol), aniline (**2,** 0.11 mmol), cyclohexanone (**3a**, 0.2 ml), 2 ml solvent (the water content is 10% in volume) and 10 mg CRL was shaken at 200 rpm at 30 °C for 24 h.

poor activity (less than 5%, Table 1, entry 11), while BSA could not catalyze this reaction which indicated that the protein could not exhibit the catalytic activity. These results proved that the specific structure of lipase is important to this reaction, and make us tend to believe that the Mannich reaction is catalyzed by lipase rather than impurities.

3.2. The influence of solvents on the direct Mannich reaction

Several other protic solvents in the presence of water were also investigated (Fig. 1
). The results indicated that ethanol/water system is the best reaction medium for the model Mannich reaction, and poor yields were observed in other medium. Therefore, ethanol/water system was applied in the following process.

3.3. The effect of the amount of ketone

We next surveyed the effect of the amount of the cyclohexanone (Fig. 2). The yield can be improved by increasing the amount of the cyclohexanone, and it got to the highest point at 30 equivalent. Further increasing of ketone/aldehyde ratio failed to improve the yield. Therefore, 30 equivalent cyclohexanone was used in the following reaction.

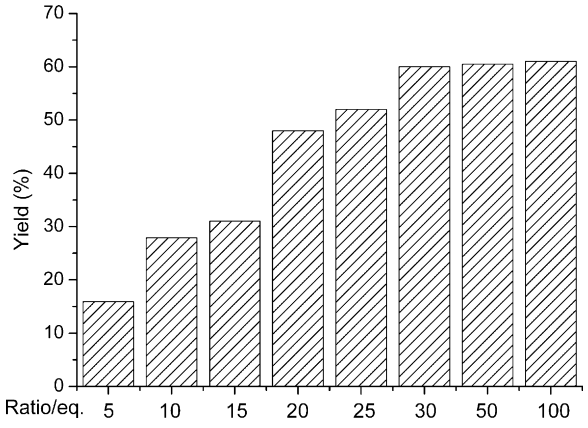


Fig. 2. Influence of molar equivalents of cyclohexanone on the direct Mannich reaction. *Reaction conditions*: a solution of 4-nitrobenzaldehyde (**1a**, 0.1 mmol), aniline (**2**, 0.11 mmol), 2 ml solvent (the water content is 10% in volume) and 10 mg CRL was shaken at 200 rpm at 30 °C for 24 h. Conversion was calculated based on **1a** detected by HPLC.

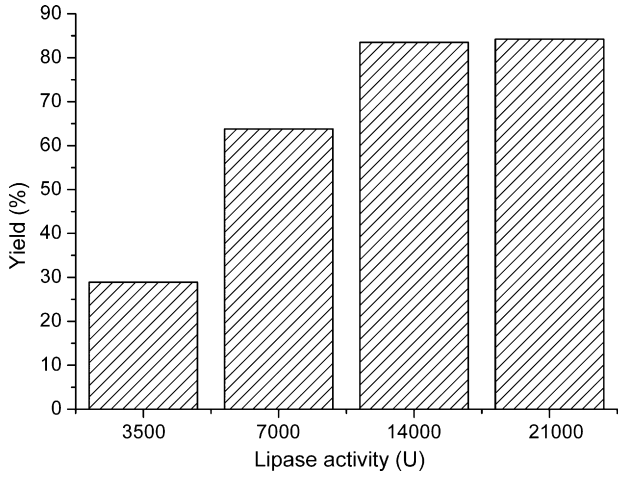


Fig. 3. The effect of lipase activity. *Reaction conditions*: a solution of 4-nitrobenzaldehyde (**1a**, 0.1 mmol), aniline (**2**, 0.11 mmol), cyclohexanone (**3a**, 0.2 ml), 2 ml solvent (the water content is 10% in volume) was shaken at 200 rpm at 30 °C for 24 h. 2.5 mg/ml of CRL correspond to 1750 U activity in 1 ml solution. Conversion was calculated based on **1a** detected by HPLC.

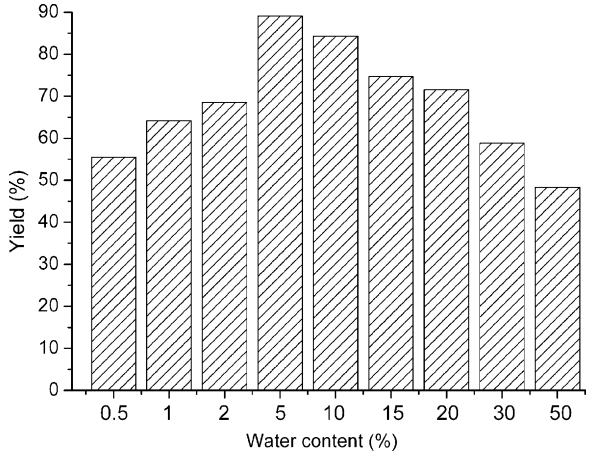


Fig. 4. The influence of water content on the CRL catalyzed Mannich reaction. *Reaction conditions*: a solution of 4-nitrobenzaldehyde (**1a**, 0.1 mmol), aniline (**2**, 0.11 mmol), cyclohexanone (**3a**, 0.3 ml), 2 ml solvent (the water content is from 0–60% in volume) and 20 mg CRL was shaken at 200 rpm at 30 °C for 24 h. Conversion was calculated based on **1a** detected by HPLC.

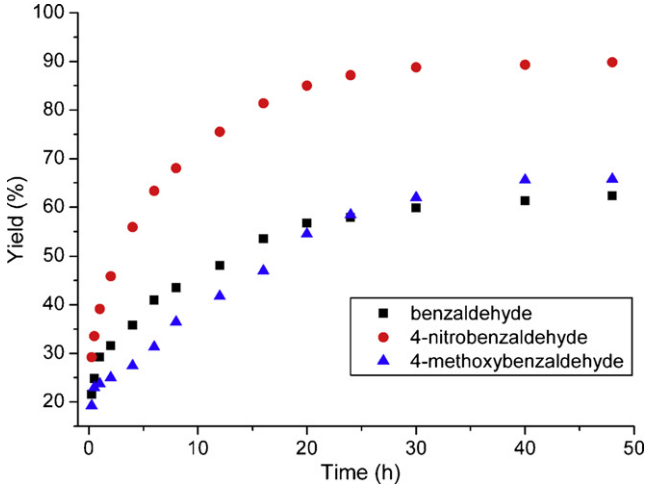
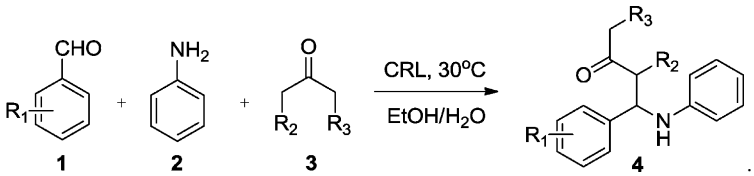


Fig. 5. Time course of the lipase-catalyzed Mannich reaction. *Reaction conditions*: a solution of aromatic aldehyde (**1**, 0.25 mmol), aniline (**2**, 0.28 mmol), cyclohexanone (**3a**, 0.75 ml), 5 ml solvent (the water content is 5% in volume) and 50 mg CRL was shaken at 200 rpm at 30 °C. Conversion was calculated based on **1** detected by HPLC.

Table 2

Direct Mannich reaction of various aryl aldehydes and ketones with aniline.[a]



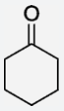
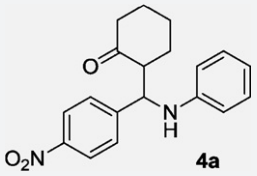
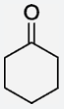
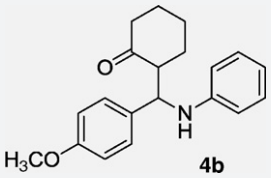
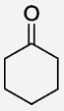
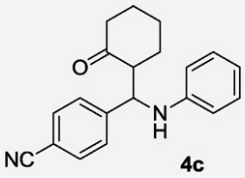
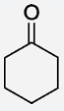
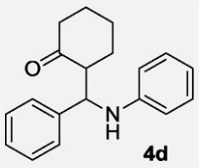
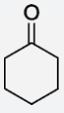
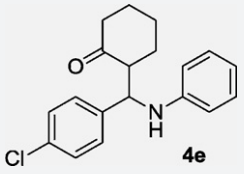
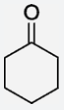
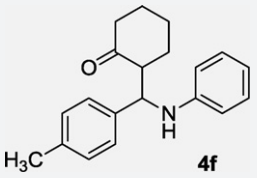
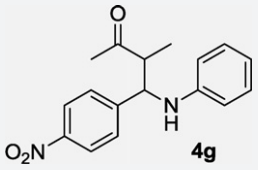
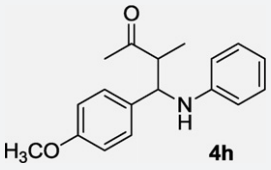
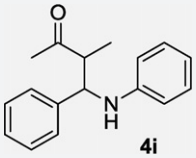
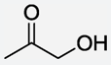
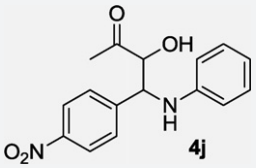
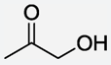
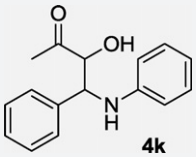
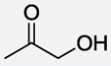
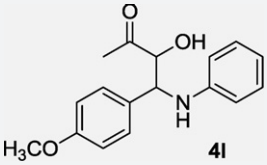
Entry	R_1	Ketone	Product	Yield (%)[b]	Dr.[c]
1	$-NO_2$		 **4a**	91	2:1
2	$-OCH_3$		 **4b**	74	1.6:1
3	$-CN$		 **4c**	62	2.4:1
4	$-H$		 **4d**	82	1.7:1
5	$-Cl$		 **4e**	94	1:1
6	$-CH_3$		 **4f**	90	1.4:1
7	$-NO_2$		 **4g**	20	n.d.
8	$-OCH_3$		 **4h**	21	n.d.

Table 2 (*Continued*)

Entry	R_1	Ketone	Product	Yield (%)[b]	Dr.[c]
9	–H		 **4i**	32	n.d.
10	$–NO_2$		 **4j**	81[d]	1.5:1
11	–H		 **4k**	90[d]	2:1
12	$–OCH_3$		 **4l**	76[d]	3:1

[a] *Reaction conditions*: a solution of aromatic aldehyde (**1**, 1.0 mmol), aniline (**2**, 1.1 mmol), ketone (**3**, 30 mmol), 10 ml ethanol/water medium (the water content is 5% in volume) and 100 mg CRL was shaken at 200 rpm at 30 °C for 24 h or 48 h (entry 7–9).
[b] Isolated yield.
[c] Determined by HPLC (etntry 1 and entry 4) or ^{1}H NMR spectroscopy of the crude products.
[d] 1-Hydroxy-2-propanone (**3c**, 5 mmol).

3.4. The effect of the enzyme concentration on Mannich reaction

The effect of the enzyme concentration on Mannich reaction was also investigated. As shown in Fig. 3, the yields were improved with the increase of enzyme concentration within the range of 2.5–10 mg/ml (3500–21,000 U). However, continuing to increase the amount of enzyme loading, the yield increased only a little. Thus, the subsequent experiments were performed with an enzyme concentration of 10 mg/ml (14,000 U).

3.5. The influence of water concentration on the Mannich reaction

Based on previous results, water plays an important role in the reaction process, it is necessary to confirm the optical percentage of water in ethanol/water system. Therefore, experiments were performed to ascertain the catalytic activity of CRL with different amounts of water in the reaction system (Fig. 4). Interestingly, 5% water content in ethanol shows the best catalytic activity, which is different from the MML-catalyzed reaction in acetone/water system [32].

3.6. Time course of the reaction

The effects of time and substituent group of aldehydes on the yield of Mannich reaction by CRL were assessed by using three different aromatic aldehydes with electron-withdrawing and electron-donating groups at the same reaction conditions. The results are shown in Fig. 5. In general, the substituent group showed significant influences on the initial rate of the reaction and the reaction achieved equilibrium after 30 h. From this comparison, the conclusion can be drawn that the reaction with 4-nitrobenzaldehyde showed a higher activity for the experimental conditions applied.

3.7. The generality of the lipase promiscuous catalyzed Mannich reaction on other substrates

Based on the above results obtained we extend the reaction with a series of aldehydes bearing electron-withdrawing and electron-donating groups and ketones including cyclohexanone, butanone and 1-hydroxy-2-propanone in order to ascertain the generality and scope of this one-pot Mannich reaction. It was found that a wide range of aromatic aldehydes could effectively participate in CRL catalyzed Mannich reaction to give the corresponding β-amino carbonyl compounds. The reaction was favored by electron-withdrawing substituents of aldehyde. The regioselectivity of this lipase catalyzed Mannich reaction was investigated, but poor regioselectivity was found. Both C1 and C3 site product of butanone were observed, while only C3 site product was found for the 1-hydroxy-2-propanone, because C3-H exhibits much higher reactivity than C1-H. The highest diastereomeric ratio (Dr.) for 1-hydroxy-2-propanone is 3:1, which we believe this is due to the promiscuity of lipase for the Mannich reaction and hard to improve through traditional methods. Meanwhile, several aliphatic aldehydes were also tested, but no products were detected under the same conditions (Table 2).

4. Conclusion

In summary, we have demonstrated the scope and utility of lipase-catalyzed direct Mannich reaction utilization of biocatalytic promiscuity under ethanol/water medium in a “one-pot” strategy. Lipase from *C. rugosa* (CRL) was identified as best catalyst for this

direct Mannich reaction among the tested lipases. A wide scope of substrates was expanded to assess the generality of the promiscuity. This lipase-catalyzed C–C bond formation would not only largely expand the application of hydrolases in biocatalysis, but be a potential method as a practical strategy for green organic synthesis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcatb.2010.08.004.

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