ORGANIC LETTERS

2012
Vol. 14, No. 20
5270–5273

An Efficient Asymmetric Biomimetic Transamination of α-Keto Esters to Chiral α-Amino Esters

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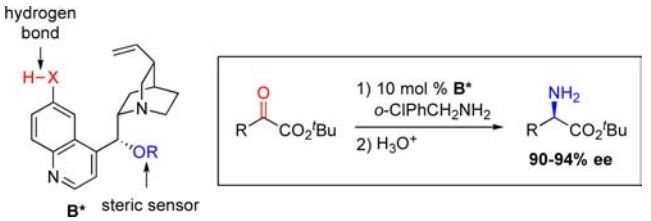
Received September 1, 2012

ABSTRACT



An efficient asymmetric biomimetic transamination of α-keto esters with quinine derivatives as chiral bases was described. A wide variety of α-amino esters containing various functional groups can be synthesized in high yield and enantioselectivity.

Optically active α-amino acids and their derivatives play crucial roles in biological systems and are important for drug and food development as well as organic synthesis.[1−5] In biological systems, transamination of α-keto acids (**1**) with pyridoxamine (**2**)[6,7] as an amine donor catalyzed by transaminase is an important process to generate α-amino acids (Scheme 1).[8] An analogous

Scheme 1. Biological Transamination

biomimetic transamination with simple chiral catalysts provides an attractive approach to synthesize optically active α-amino acids and their derivatives, which has been challenging and underdeveloped. Earlier, Berg et al.[9] reported chiral guanidine catalyzed transamination of isolated α-ketimine esters with up to 45% ee. Chiral Lewis acid catalyzed transamination with in situ formation of

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(1) For a recent book, see: *Amino Acids, Peptides and Proteins in Organic Chemistry*; Hughes, A. B., Ed.; Wiley-VCH: Weinheim, Germany, 2009.

(2) For leading reviews on enzymatic synthesis of α-amino acids, see: (a) Li, T.; Kootstra, A. B.; Fotheringham, I. G. *Org. Process Res. Dev.* **2002**, *6*, 533. (b) De Wildeman, S. M. A.; Sonke, T.; Schoemaker, H. E.; May, O. *Acc. Chem. Res.* **2007**, *40*, 1260. (c) Zhu, D.; Hua, L. *Biotechnol. J.* **2009**, *4*, 1420. (d) Ward, J.; Wohlgemuth, R. *Curr. Org. Chem.* **2010**, *14*, 1914. (e) Mathew, S.; Yun, H. *ACS Catal.* **2012**, *2*, 993.

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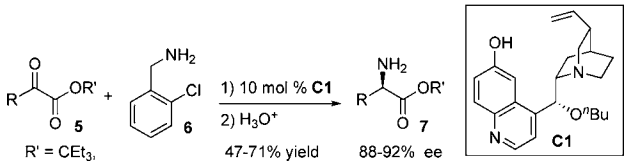
10.1021/ol302427d
Published on Web 10/01/2012

α-ketimine esters was described by Jørgensen et al.,[10] and up to 46% ee was obtained.[11−13] Recently, we reported a highly enantioselective biomimetic transamination of α-keto esters **5** with readily available quinine-derived compound **C1** as the catalyst and *o*-ClPhCH$_2$NH$_2$ (**6**) as the amine donor, giving a wide variety of α-amino esters **7** in 47−71% yield and 88−92% ee (Scheme 2).[14] Studies show that the 6′-OH group and the ether group at the 9 position of catalyst **C1** are very important for the reactivity and enantioselectivity of the transamination process (Figure 1). It is likely that the OH group forms a H-bond with the imine to activate the substrate and influence the stereodifferentiation (Figure 2).[14] In efforts to further understand the effect of the catalyst structure on the transamination and develop more effective processes, we examined a series of quinine derivatives[15] with different H-bond donors at the 6′-position for the transamination (Figure 3). Herein we wish to report our preliminary results on this subject.

Scheme 2. Chiral Base-Catalyzed Biomimetic Transamination



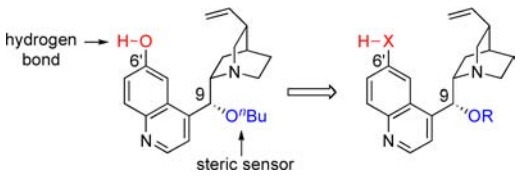


Figure 1. Quinine derivatives with different H-bond donors.

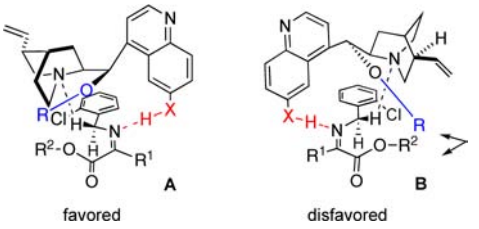


Figure 2. Possible transition states for transamination.

To evaluate the effect of the H-bond donor of the catalyst on the transamination, several quinine derivatives containing various nitrogen groups at the 6′-position were

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(12) For leading references on other asymmetric 1,3-proton shift of imines, see: (a) Soloshonok, V. A.; Kirilenko, A. G.; Galushko, S. V.; Kukhar, V. P. *Tetrahedron Lett.* **1994**, *35*, 5063. (b) Willems, J. G.; Vries, J. G.; Nolte, R. J.; Zwanenburg, B. *Tetrahedron Lett.* **1995**, *36*, 3917. (c) Soloshonok, V. A.; Yasumoto, M. *J. Fluorine Chem.* **2007**, *128*, 170. (d) Michaut, V.; Metz, F.; Paris, J.; Plaquevent, J. *J. Fluorine Chem.* **2007**, *128*, 500. (e) Han, J.; Sorochinsky, A. E.; Ono, T.; Soloshonok, V. A. *Curr. Org. Synth.* **2011**, *8*, 281.

(13) For leading references on asymmetric 1,3-proton shift with chiral benzyl imine, see: (a) Soloshonok, V. A.; Ono, T. *J. Org. Chem.* **1997**, *62*, 3030. (b) Soloshonok, V. A.; Ono, T.; Soloshonok, I. V. *J. Org. Chem.* **1997**, *62*, 7538. (c) Xiao, J.; Zhang, X.; Yuan, C. *Heteroat. Chem.* **2000**, *11*, 536. (d) Soloshonok, V. A.; Ohkura, H.; Yasumoto, M. *J. Fluorine Chem.* **2006**, *127*, 924. (e) Soloshonok, V. A.; Ohkura, H.; Yasumoto, M. *J. Fluorine Chem.* **2006**, *127*, 930.

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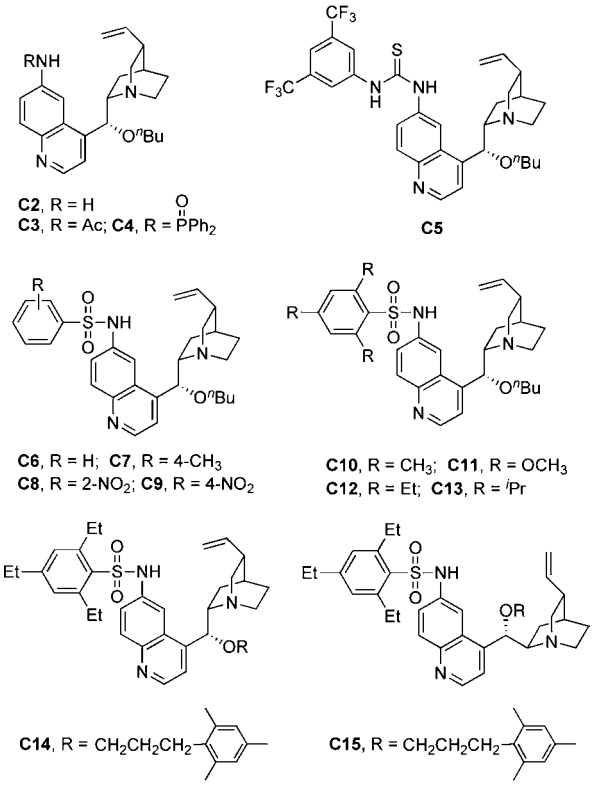
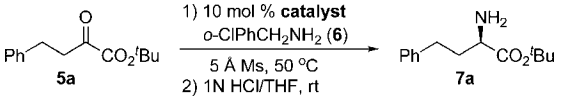


Figure 3. Selected examples of catalyst examined.

initially synthesized (Figure 3) and tested for the transamination with α-keto ester **5a** as the substrate and *o*-ClPhCH$_2$NH$_2$ (**6**) as the amine donor (Table 1). As shown in Table 1, catalysts with amine (**C2**), acetylamine (**C3**), phosphorylamine (**C4**), and thiourea (**C5**)[16] gave lower ee's than the catalyst with the OH group (**C1**)[14,17] (entries 1−5). However, comparable enantioselectivity was obtained with catalyst containing benzenesulfonamide (**C6**) (Table 1, entry 6). Further studies showed that substituents on the phenyl group of benzenesulfonamide have a significant effect on the enantioselectivity (Table 1, entries 7−13), and up to 92% ee was obtained with 2,4,6-triethylbenzenesulfonamide substituted quinine derivative **C12** (Table 1, entry 12). A slightly higher ee was obtained

Table 1. Studies on Catalysts and Solvents[a]



entry	cat.	solvent	time (h)	conv. (%)[b]	ee (%)[c]
1	**C1**	benzene	36	60	83
2	**C2**		36	19	68
3	**C3**		36	45	54
4	**C4**		36	12	66
5	**C5**		36	76	59
6	**C6**		36	40	85
7	**C7**		36	43	88
8	**C8**		36	23	85
9	**C9**		36	47	82
10	**C10**		36	25	91
11	**C11**		36	8	86
12	**C12**		36	30	92
13	**C13**		36	32	91
14	**C14**		36	40	93
15[d]	**C14**		60	85	94
16[d]	**C14**	toluene	60	81	92
17[d]	**C14**	*n*-hexane	60	86	85
18[d]	**C14**	$CHCl_3$	60	52	84
19[d]	**C14**	THF	60	59	41
20[d]	**C14**	EtOAc	60	51	70
21[d]	**C14**	MeOH	60	57	8
22[d]	**C14**	CH_3CN	60	68	54
23[d]	**C15**	benzene	60	80	−91

[a] All reactions were carried out with α-keto ester **5a** (0.20 mmol), *o*-ClPhCH$_2$NH$_2$ (**6**) (0.20 mmol), catalyst (0.020 mmol), and 5 Å molecular sieves (0.020 g) in solvent (4.0 mL) at 50 °C unless otherwise noted. [b] The conversion was determined by ^{1}H NMR of the crude reaction mixture based on α-keto ester and corresponding α-keto imine. [c] The ee's were determined by chiral HPLC (Chiralcel OD-H column) after the amino esters were converted into their *N*-benzoyl derivatives. [d] *o*-ClPhCH$_2$NH$_2$ (**6**) (0.60 mmol) and 5 Å molecular sieves (0.10 g) were used.

by increasing the size of the ether group (Table 1, entries 14 and 15). The reaction conversion increased to 85% by increasing the amount of *o*-ClPhCH$_2$NH$_2$ (**6**) and molecular sieves with a longer reaction time (Table 1, entry 15). Among various solvents examined, benzene and toluene gave the highest ee (Table 1, entries 15 and 16). The quinidine-derived catalyst (**C15**) gave amino ester product **7a** in 80% conversion and 91% ee with the opposite configuration (Table 1, entry 23).

The generality of the transamination was subsequently examined with catalyst **C14**. Substituted 2-oxo-4-phenylbutanoates were found to be highly effective substrates, giving various homophenylalanine derivatives in 84−91% yield and 93−96% ee (Table 2, entries 1−6). High yields and ee's were also obtained for substrates containing other aromatics such as naphthalene and thiophene (Table 2, entries 7−9). When 2-oxo-3-phenylpropanoate was used as substrate, phenylalanine ester was formed in 81% yield and 90% ee (Table 2, entry 10). The transamination can be extended to nonaromatic keto esters, giving amino esters in 61−82% yield and 90−95% ee (Table 2, entries 11−18). The side chains of amino esters can be saturated (Table 2, entries 11−13) or unsaturated aliphatic groups (Table 2,

(16) For leading references related to thiourea catalyst **C5**, see: (a) Marcelli, T.; van der Haas, R. N. S.; van Maarseveen, J. H.; Hiemstra, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 929. (b) Biddle, M. M.; Lin, M.; Scheidt, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 3830. (c) Liu, Y.; Sun, B.; Wang, B.; Wakem, M.; Deng, L. *J. Am. Chem. Soc.* **2009**, *131*, 418. (d) Dickmeiss, G.; Sio, V. D.; Udmark, J.; Poulsen, T. B.; Marcos, V.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 6650. (e) Xie, H.; Zhang, Y.; Zhang, S.; Chen, X.; Wang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 11773. (f) Rana, N. K.; Singh, V. K. *Org. Lett.* **2011**, *13*, 6520.

(17) For leading references related to the 6′ OH cinchona alkaloid derivatives, see: (a) Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906. (b) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732. (c) Bandini, M.; Sinisi, R.; Umani-Ronchi, A. *Chem. Commun.* **2008**, 4360. (d) Wang, H.-F.; Cui, H.-F.; Chai, Z.; Li, P.; Zheng, C.-W.; Yang, Y.-Q.; Zhao, G. *Chem.—Eur. J.* **2009**, *15*, 13299. (e) Bui, T.; Candeias, N. R.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2010**, *132*, 5574.

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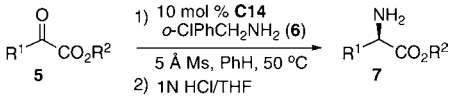
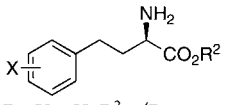
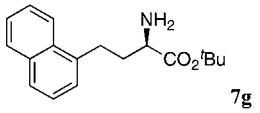
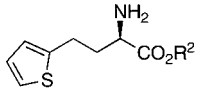
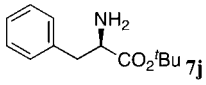
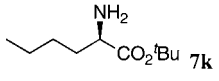
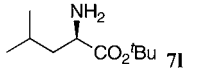
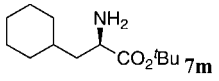
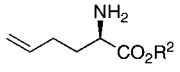
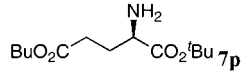
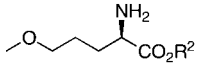
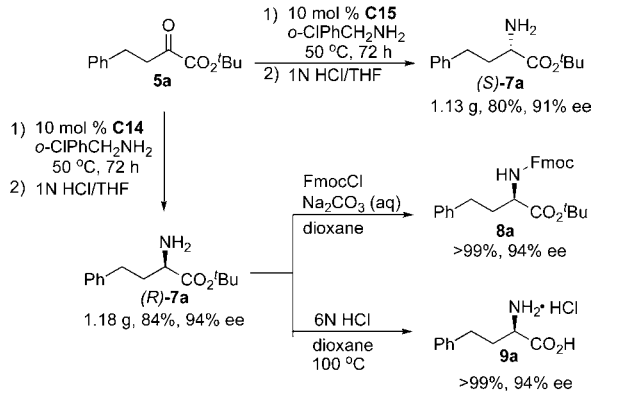
Table 2. Catalytic Asymmetric Transamination of α-Keto Esters[a]



entry	amino ester (**5**)[b]	yield (%)[c]	ee (%)[d]
1	 **7a**, X = H, R^2 = ^{t}Bu	87	94
2	**7b**, X = H, R^2 = CEt_3	91	96
3	**7c**, X = *o*-F, R^2 = ^{t}Bu	91	93
4	**7d**, X = *m*-Cl, R^2 = ^{t}Bu	84	93
5	**7e**, X = *p*-Cl, R^2 = ^{t}Bu	85	93
6	**7f**, X = *p*-OCH_3, R^2 = ^{t}Bu	88	94
7	 **7g**	93	93
8	 **7h**, R^2 = ^{t}Bu	88	91
9	**7i**, R^2 = CEt_3	90	94
10	 **7j**	81	90
11	 **7k**	70	93
12[e]	 **7l**	61	92
13	 **7m**	71	94
14	 **7n**, R^2 = ^{t}Bu	73	92
15	**7o**, R^2 = CEt_3	82	94
16[e]	 **7p**	61	90
17	 **7q**, R^2 = ^{t}Bu	73	92
18	**7r**, R^2 = CEt_3	77	95

[a] The reactions were carried out with α-keto esters **5** (0.50 mmol), *o*-$ClPhCH_2NH_2$ (**6**) (1.50 mmol), catalyst **C14** (0.050 mmol), and 5 Å molecular sieves (0.25 g) in dry benzene (10.0 mL for entries 1−7 and 16, 5.0 mL for entries 8−15 and 17−18) at 50 °C for 60 h. [b] For entries 1 and 2, the absolute configurations (*R*) were determined by comparing the optical rotations with reported ones of α-aminio acids after hydrolysis (ref 18). The absolute configurations of remaining amino esters were tentatively proposed by analogy. [c] Isolated yield based on α-keto esters **5**. [d] The ee's were determined by chiral HPLC (Chiralcel OD-H column) after the amino esters were converted into their *N*-benzoyl derivatives. [e] The reaction time was 72 h.

Scheme 3



entries 14 and 15). Other functional groups such as ester (Table 2, entry 16) and ethers (Table 2, entries 17 and 18) are also tolerated under the transamination conditions. Overall the substrate scope for this transamination is quite broad. It is worth mentioning that high ee's can be obtained for *t*-Bu keto esters under the current conditions while the previously reported transamination with compound **C1** as the catalyst requires a sterically larger CEt_3 group to obtain a high ee.[14] The *t*-Bu group has some practical advantages over the CEt_3 group. The transamination was also carried out on gram scale. Both (*R*)- and (*S*)-**7a** were synthesized in 84% and 80% yield with 94% and 91% ee, respectively, using catalysts **C14** and **C15** (Scheme 3). (*R*)-**7a** was further converted into *N*-Fmoc derivative **8a** and amino acid hydrochloride **9a** quantitatively without loss of ee's (Scheme 3).

In summary, we have found that the H-bond donors at the 6′-position of quinine have a large effect on the reactivity and enantioselectivity of transamination and discovered that certain substituted benzenesulfonamide quinine derivatives are highly effective catalysts for transamination of α-keto esters. A wide variety of α-amino esters have been obtained in 61−93% yield and 90−96% ee with 2,4,6-triethylbenzenesulfonamide substituted quinine derivative **C14** as the catalyst and *o*-$ClPhCH_2NH_2$ (**6**) as the amine donor. Optically active α-amino acid derivatives can also be obtained in gram scale via this transamination. These studies provide a better understanding of the structural effect of the catalyst on transamination and new insights for the development of more effective catalytic systems for α-keto esters and other carbonyl compounds.

Acknowledgment. We gratefully acknowledge the National Basic Research Program of China (973 program, 2010CB833300) and the Chinese Academy of Sciences for financial support.

Supporting Information Available. Experimental procedures, characterization data, data for determination of enantiomeric excess, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.