DOI: 10.1002/adsc.201300184

Stereoselective Lewis Base-Catalyzed Asymmetric Hydrosilylation of α-Acetamido-β-enamino Esters: Straightforward Approach for the Construction of α,β-Diamino Acid Derivatives

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Received: February 28, 2013; Revised: April 23, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300184.

Abstract: The Lewis base-organocatalyzed asymmetric hydrosilylation of α-acetamido-β-enamino esters was investigated. Among various chiral Lewis base catalysts, a novel catalyst derived from L-serine was found to be the most efficient one which can promote the reaction to afford a series of α,β-diamino acid derivatives with high yields (up to 99%), excellent enantioselectivities (up to 98% *ee*) and moderate diastereoselectivities (up to 80:20 *dr*). The absolute configuration of one of the products was determined by the X-ray crystallographic analysis. In addition, the mechanism and the transition state of the reaction were proposed.

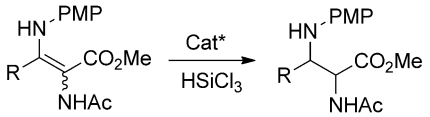
Keywords: amino acids; asymmetric catalysis; hydrosilylation; Lewis bases

Optically active α,β-diamino acids are important structural components present in many natural products, synthetic peptides and therapeutically useful compounds.[1] Consequently, considerable research efforts have been devoted to the asymmetric synthesis of chiral α,β-diamino acids.[2] Up to now, the syntheses of chiral α,β-diamino acids mainly focus on asymmetric aza-Mannich reactions,[3] aza-Henry reactions,[4] asymmetric diamination,[5] ring opening of chiral aziridines[6] and other transformations.[7]

Among various synthetic approaches, the direct catalytic asymmetric hydrogenation of α-amido-β-enamino esters is an elegant and efficient strategy to construct chiral α,β-diamino acids. However, to the best of our knowledge, there are only a few examples dealing with this method. In 2001, Robinson and co-workers reported the Rh-catalyzed asymmetric hydrogenation of α,β-diamidopropenoate and α,β-diamidobutenoate through which they obtained chiral α,β-diaminopropanoic acid derivatives and α,β-diaminobutanoic acid derivatives in good *ee* values (> 95%).[8] However, the generality of the reaction has not been examined. In addition, the organocatalytic reduction of α-amido-β-enamino ester has not been reported yet.

Over the past decade, the chiral Lewis base-catalyzed asymmetric hydrosilylation of C=N bonds has become an efficient method to obtain chiral amines and amino acids.[9,10] Our group has been actively engaged in research on chiral Lewis base-organocatalyzed hydrosilylation of a wide range of C=N double bond compounds.[10n–s] Recently, we demonstrated a highly diastereoselective and enantioselective hydrosilylation of α-acetoxy-β-enamino esters through which various valuable α-hydroxy-β-amino esters were prepared efficiently.[10q] Inspired by our success on the hydrosilylation of α-heteroatom substituted β-enamino esters, we attempted to extend this methodology to the transformation of α-amido-β-enamino esters to α,β-diamino acid derivatives. Thus α-acetamido-β-enamino esters (**1**) were designed, synthesized and subjected to the Lewis base-catalyzed asymmetric hydrosilylation. The reactions proceeded smoothly to give the chiral α,β-diamino acid derivatives (**2**) with high yields (up to 99%), excellent enantioselectivities (up to 98% *ee*) and moderate diastereoselectivities (up to 80:20 *dr*) (Scheme 1).

During our ongoing research on the Lewis base-catalyzed hydrosilylation of C=N double bond compounds, we have developed several kinds of highly



Scheme 1. Asymmetric hydrosilylation of α-acetamido-β-enamino esters (**1**).

active and selective chiral picolinamide Lewis base catalysts **3**–**5** (Figure 1). Moreover, we designed and synthesized a kind of novel catalyst **6** analogous to **5** which delivered good results in the hydrosilylation of α-acetoxy-β-enamino esters.[10q] Catalysts **6a**–**6c** were prepared from L-serine *via* facile steps.[10s] Compared to **5**, **6** contains one more aryl group at C-2 of the ring, which makes it bulkier so that it might be more stereoselective in hydrosilylation.

All of these chiral Lewis bases were evaluated in the hydrosilylation of α-acetamido-β-enamino ester **1a** in 1,2-dichloroethane at 0 °C. The results are summarized in Table 1. Catalyst **3**[10n] delivered very poor diastereoselectivity as well as enantioselectivity (Table 1, entry 1). Although good diastereoselectivity was observed for catalyst **4**,[10p] the *ee* value of the major diastereomer was very poor (Table 1, entry 2). When **5a** was employed, the *syn*-diastereomer was obtained with a good *ee* value of 90%, however, almost the same yield of the *anti*-diastereomer was generated in very low enantioselectivity (Table 1, entry 3). Catalysts **5b**–**5d** resulted in higher *dr* values but very poor *ee* values for the major diastereomer (Table 1, entries 4–6). Catalysts **6a**–**6c** exhibited better enantioselectivities (Table 1, entries 7–9) whereby **6a** gave the major diastereomer with up to 95% *ee* (Table 1, entry 7). The acetonide function of the catalysts **6a** is

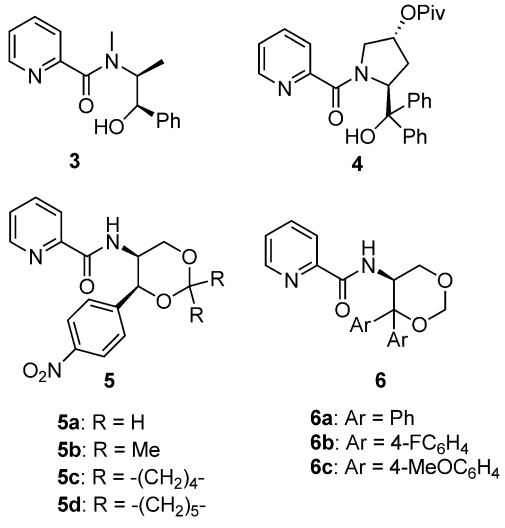
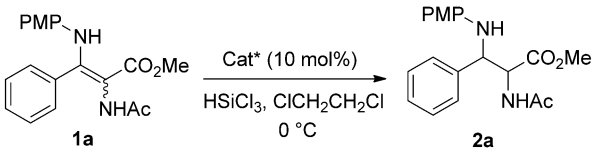


Figure 1. Chiral Lewis base organocatalysts **3**–**6** evaluated in this study.

Table 1. Screening of chiral Lewis base catalysts in the asymmetric hydrosilylation of α-acetamido-β-enamino ester **1a**.[a]



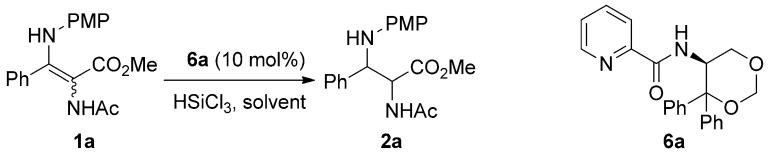
Entry	Cat*	Yield [%][b]	*syn*:*anti*[c]	*ee* [%][d] *syn, anti*
1	**3**	98	20:80	21, 57
2	**4**	96	4:96	40, 6
3	**5a**	96	51:49	90, 20
4	**5b**	89	20:80	49, 8
5	**5c**	85	17:83	62, 5
6	**5d**	92	33:67	82, 3
7	**6a**	98	53:47	95, 31
8	**6b**	96	54:46	92, 25
9	**6c**	90	35:65	93, 37

[a] Unless otherwise specified, the reactions were carried out on a 0.15-mmol scale with 2.0 equiv. of $HSiCl_3$ in 1.5 mL of $ClCH_2CH_2Cl$.
[b] Isolated yield based on **1a**.
[c] The relative comfiguration of **2a** was determined by comparison of the vicinal coupling constants (see the Supporting Information). The *dr* value of **2a** was determined by chiral HPLC analysis.
[d] The *ee* values were determined by chiral HPLC.

stable under the reaction conditions and we can recover the catalyst after the reaction. Although the diastereoselectivity is not satisfactory yet, **6a** was determined as the optimal catalyst and employed in further investigations.

In order to improve the results, the other conditions were modified. First, several solvents were tested. The reaction in dichloromethane did not give the product with a better *dr* value (Table 2, entry 2). Surprisingly, it was found that the reaction in chloroform gave only a trace of the product (Table 2, entry 3). The reason has not been found out yet. To our delight, the reaction in THF resulted in an evidently higher *dr* value and the *ee* value of the major diastereomer was not affected (Table 2, entry 4). Perhaps the hydrogen bonding of THF with the the α-acetamide group in the substrate can diminish the intramolecular hydrogen bonding of the substrate (see Scheme 3 below), and thus reduce the probability of generation of the *anti*-product. Therefore, THF was selected as the optimal solvent for the reaction. Afterwards, when the reaction was conducted at −10 °C, a higher *dr* value and a slightly higher *ee* value were obtained (Table 2, entry 5). Further decreasing the temperature to −20 °C did not improve the result any more (Table 2, entry 6). Therefore, −10 °C was determined as the optimal temperature of the reaction. When the reaction was conducted in diluted solution, the *dr* value increased obviously, however, the *ee* value of the major

Table 2. Modification of the conditions for the asymmetric hydrosilylation of **1a**.[a]



Entry	Solvent	Temperature [°C]	Yield [%][b]	*syn*:*anti*[c]	*ee* [%][d] *syn, anti*
1	$ClCH_2CH_2Cl$	0	98	53:47	95, 31
2	CH_2Cl_2	0	97	47:53	95, 33
3	$CHCl_3$	0	trace	–	–
4	THF	0	94	66:34	94, 34
5	THF	−10	98	73:27	96, 26
6	THF	−20	99	73:27	96, 16
7[e]	THF	−10	77	82:18	48, 31
8[f]	THF	−10	77	70:30	64, 16

[a] Unless otherwise specified, the reactions were carried out on a 0.15-mmol scale with 2.0 equiv. of $HSiCl_3$ and 10 mol% of **6a** in 1.5 mL of the solvent.
[b] Isolated yield based on **1a**.
[c] The relative comfiguration of **2a** was determined by comparison of the vicinal coupling constants (see the Supporting Information). The *dr* value of **2a** was determined by chiral HPLC analysis.
[d] The *ee* values were determined by using chiral HPLC analysis.
[e] 3 mL of THF were used.
[f] 5 mol% of **6a** were used.

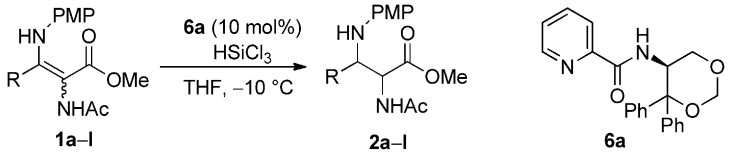
diastereomer dropped sharply (Table 2, entry 7). Decreasing the catalyst loading to 5 mol% also caused a dramatic reduction in the *ee* value of the major diastereomer (Table 2, entry 8).

Having established the optimal conditions, the scope of the reaction was investigated. In the presence of 10 mol% of catalyst **6a**, various α-acetamido-β-enamino esters were hydrosilylated in THF at −10 °C. The results are summarized in Table 3. Generally, moderate *dr* values were obtained for all of the reactions. Good enantioselectivities for the major isomers were observed with β-phenyl and β-*para*- or β-*meta*-substituted-phenyl substrates (Table 3, entries 1–8). The electronic property of the substituents exhibited little effect on the results. However, we failed to synthesize the β-*ortho*-substituted-phenyl substrates to test the effect of *ortho*-substitution. β-2-Naphthyl substrate **1i** also delivered good enantioselectivity for the major diastereomer (Table 3, entry 9). The β-2-furyl substrate **1j** gave a slightly lower *ee* value for the major diastereomer (Table 3, entry 10). As for β-alkyl substrates, the *ee* values decreased obviously. β-Methyl substrate **1k** generated the major diastereomer in only moderate *ee* value (Table 3, entry 11) and β-benzyl substrate **1l** afforded even lower enantioselection for the major diastereomer (Table 3, entry 12). This suggested that the β-aryl ring might have an arene-arene interaction with the catalyst so that good enantioselections could be obtained. In contrast there is no arene-arene interaction between β-alkyl substrate and the catalyst, therefore, poor enantioselectivities were observed. In addition, comparing the *E*/*Z* ratios of the substrates and the results, it can be concluded that the *E*/*Z* ratios do not correlate with the stereoselectivities.

Afterwards, the major isomer of product **2g** was subjected to cyclization with thiophosgene to generate the cyclic product **7** (Scheme 2). The absolute configuration of **7** was unambiguously confirmed as (4*R*,5*S*) by the X-ray crystallographic analysis.[11] Thus the absolute configuration of **2g** was determined as (2*R*,3*S*) accordingly.

In this study, the diastereocontrol is somewhat lower than those of α-aryl, α-alkyl, and α-OAc substrates reported previously.[10g,q] We reasoned that the hydrogen of the α-acetamide group in the substrate might be in charge of this result. As can be seen in Scheme 3, the enamine tautomer isomerizes to generate an *E*-imine tautomer and a *Z*-imine tautomer. Generally, formation of the *E*-imine is much easier. However, in this case, the *Z*-imine can be stabilized by hydrogen bonding between the hydrogen of the α-acetamide group and the nitrogen atom of the imine so that considerable amount of *Z*-imine can be generated. For the *E*-imine tautomer, as described by Malkov and Kočovsky et al.,[10g] the ester carbonyl and the imine group are held together either by hydrogen bonding (in the protonated form, the proton might be generated from the reaction of trichlorosilane and traces of water in the solvent) or by chelation to silicon, thus it undergoes the hydrosilylation to provide a *syn*-product. While, for the *Z*-imine tautomer, the acetamide group and the imine group are held together by intramolecular hydrogen bonding

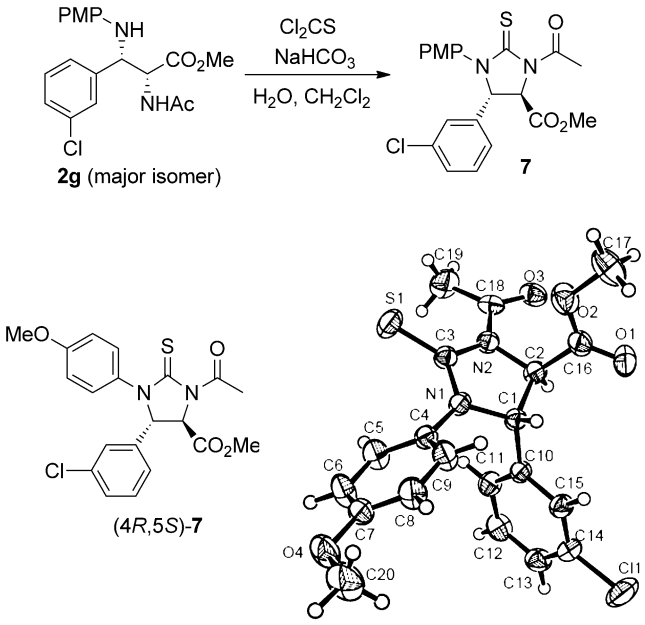
Table 3. Asymmetric hydrosilylation of α-acetamido-β-enamino esters **1a–l** under the optimal conditions.[a]



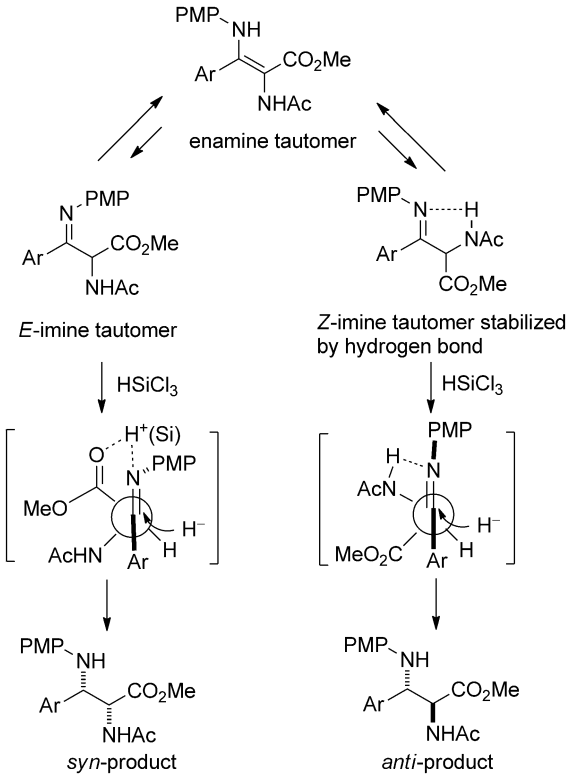
Entry	1	R	*E*/*Z*[b]	Yield [%][c]	*syn*:*anti*[d]	*ee* [%][e] *syn, anti*
1	**1a**	Ph	4.6/1	98	73:27	96, 26
2[e]	**1b**	4-MeC_6H_4	3.5/1	99	71:29	96, 25
3	**1c**	4-MeOC_6H_4	3.3/1	98	71:29	96, 25
4	**1d**	4-BnOC_6H_4	4.3/1	93	66:34	96, 17
5	**1e**	4-FC_6H_4	5.2/1	98	75:25	95, 30
6[e]	**1f**	4-BrC_6H_4	6.1/1	88	80:20	98, 34
7[e]	**1g**	3-ClC_6H_4	5.7/1	89	67:33	95, 50
8	**1h**	3,4-$(MeO)_2C_6H_3$	4.8/1	98	70:30	96, 26
9	**1i**	2-naphthyl	4.6/1	97	67:33	94, –[g]
10	**1j**	2-furanyl	2.3/1	97	65:35[h]	90, 59
11[f]	**1k**	Me	2.8/1	98	71:29[h]	80, 35
12[f]	**1l**	Bn	3.0/1	98	72:28[h]	62, 25

[a] Unless otherwise specified, the reactions were carried out on a 0.15-mmol scale with 2.0 equiv. of $HSiCl_3$ and 10 mol% of **6a** in 1.5 mL of THF.
[b] The *E*/*Z* ratios were determined by ^1H NMR spectroscopy.
[c] Isolated yield based on **1**.
[d] The relative comfigurations of **2a–2i** were determined by X-ray crystallographic analysis and comparison of the vicinal coupling constants (see the Supporting Information). The *dr* values were determined by chiral HPLC analysis.
[e] The *ee* values were determined by chiral HPLC.
[f] 4.0 equiv. of $HSiCl_3$ were used.
[g] The *ee* value of the *anti*-diastereomer was not determined.
[h] The relative configurations cannot be determined.

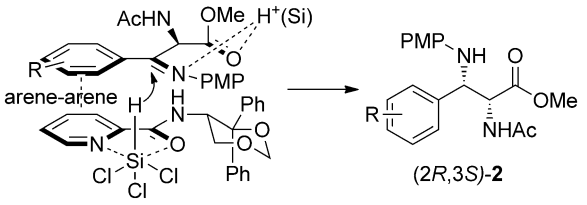
and the reaction gives an *anti*-product. Hence, it is not surprising that the reaction cannot result in good



Scheme 2. Cyclization of **2g** with thiophosgene and the crystal determination of its absolute configuration.



Scheme 3. Proposed mechanism of the generation of *syn*- and *anti*-products.



Scheme 4. Proposed transition state for the asymmetric hydrosilylation of α-acetamido-β-enamino esters.

diastereoselectivity. We tried to improve the diastereoselectivity by replacing the acetamide group by an *N*,*N*-disubstituted group. However, we failed to prepare such a substrate.

Finally, a plausible transition state for the reaction has been proposed. As can be seen in Scheme 4, Cl_3SiH coordinates to the catalyst at the place remote from the diphenyl groups. From the transition state, it is easy to understand that the (*R*)-*E*-imine undergoes the reaction preferentially. The (*R*)-*E*-imine is activated by a proton. The imine group and the ester carbonyl are held together by hydrogen bonding or by chelation to silicon. Meanwhile an arene-arene interaction between the β-aryl group of the substrate and the pyridine ring of the catalyst fixes the transition state. Hence, the hydride attacks the imine from the *Si* face to generate the (2*R*,3*S*)-product.

In summary, we have developed a stereoselective hydrosilylation of α-acetamido-β-enamino esters catalyzed by a novel Lewis base derived from L-serine. This transformation enables us to prepare various enantioenriched α-acetamido-β-amino esters in good yields, good enantioselectivities and moderate diastereoselectivities. Afterwards, one of the products was cyclized with thiophosgene and the absolute configuration of the resulted cyclic compound was determined by the X-ray crystallographic analysis. Accordingly the absolute configuration of the product was determined. The mechanism and the transition state of the reaction have been proposed. Further work is ongoing to explore new applications of this methodology.

Experimental Section

General Procedure for Enantioselective Hydrosilylation of α-Acetamido-β-enamino Esters 1a–1l

A solution of trichlorosilane (31 μL, 0.3 mmol, 2.0 equiv.) in 120 μL of THF was added to a stirred solution of the corresponding α-acetamido-β-enamino ester (0.15 mmol) and the catalyst (0.015 mmol) in THF (1.5 mL) at −10 °C. The mixture was stirred at the same temperature until the reaction was completed. Then the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and the solvents were evaporated. Purification by column chromatography (silica gel, hexane/EtOAc = 1:1) afforded the diastereomers. The *dr* values and the *ee* values were determined using established HPLC techniques with chiral stationary phases.

Acknowledgements

We are grateful for the financial support from National Sciences Foundation of China (20972155, 21172217) and National Basic Research Program of China (973 Program) (2010CB833300).

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[11] CCDC 926418 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

COMMUNICATIONS