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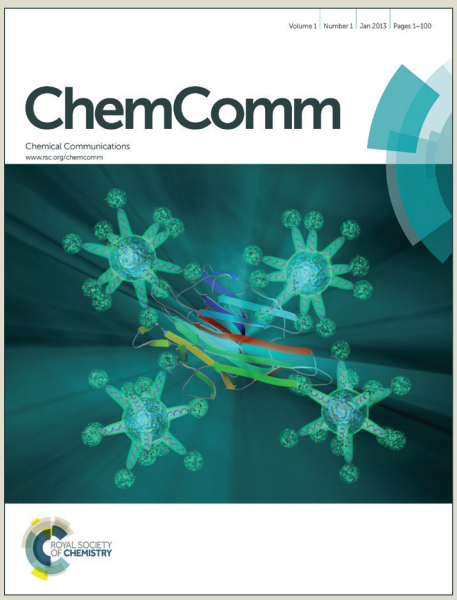

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Catalytic, Highly Enantioselective, Direct Amination of Enecarbamates

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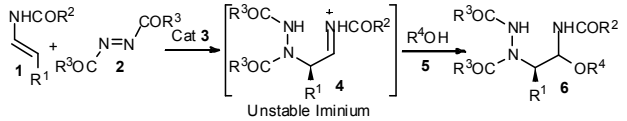
Amination of enecarbamates with dibenzylazodicarboxylate and oxygenated nucleophiles in the presence of a catalytic amount of chiral phosphoric acid afforded optically active stable precursors of α-hydrazinoimines, which were reduced or oxidized respectively to vicinal diamines or α-amino acid precursors with excellent yield and enantioselectivity.

Electrophilic amination reactions are powerful methods to prepare chiral amines,[1] which are important building blocks in organic synthesis. Although many catalytic asymmetric α-amination of carbonyl derivatives[2] and related compounds[2] have been developed, only limited examples using enamides has been reported. For instance, Kobayashi *et al*. presented the first enantioselective amination reaction of (*E*)-enecarbamates derived from acetophenones catalyzed by chiral copper(II)–diamines complexes.[3] Few years later, Feng *et al.* developed a complementary enantioselective α-amination of (*Z*)-α-arylenamides using chiral copper(II) complexes as catalysts.[4] In 2011, we reported chiral Lewis acid calcium bis(phosphate) complexes as efficient catalysts for the enantioselective amination of (*E*)-α-arylenamides.[5] However, in spite of the significant progress, enantioselective electrophilic amination of α-unsubstituted enecarbamates has hardly been described.[3] This fact is probably because of the formation of *N*-acyliminium ion intermediate **4** that easily undergoes hydrolyses, isomerises or polymerises, renders electrophilic amination more challenging (Scheme 1).[6] Developing an efficient amination of α-unsubstituted enecarbamates is highly desirable.

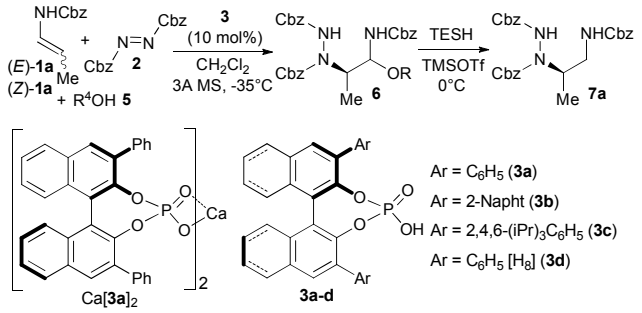


Scheme 1 Rational design for a three-component amination reaction of enamides, azodicarboxylates and alcohols.

As a continuation of our research program,[5,7] we assumed that fast trapping of the iminium ion with an appropriate nucleophile might overcome problems associated with instability of **4**. This approach would provide a direct synthetic route to chiral vicinal diamines **7**, which are ubiquitous motifs in various natural products, pharmacologically active compounds, and ligands.[8] However this is not exempt of risk, since the second nucleophile, which would be present in the mixture, would have time to react with electrophile **2**. To circumvent this, we envisioned to interrupt the process with a temporary nucleophile providing a stable precursor of enantiomerically enriched α-hydrazinoimines **6**[9] which could subsequently be employed in further transformations (Scheme 1). Alcohols and water were evaluated as temporary nucleophiles, since their addition to an iminium intermediate is reversible. Herein we report a highly enantioselective three-component electrophilic amination of enecarbamates catalysed by chiral phosphoric acids.[10] In this process, amination was successfully coupled to a subsequent reduction or oxidation leading to 1,2-diamines and α-hydrazinoimides, respectively, with high yields and excellent enantioselectivities.

On the basis of our previous work,[5] we examined the reaction of benzylprop-1-enylcarbamate ((*E*)-**1a**) with dibenzyl azodicarboxylate (**2**) and one equivalent of ethanol in the presence of chiral calcium phosphate catalyst Ca[**3a**]$_2$ (10 mol%)[11] and 3 Å molecular sieves in dichloromethane at −35°C (Table 1). We were delighted to find that desired *N*-carbamoylaminoether product **6a** (R = Et) was exclusively formed in 62% yield albeit diastereo- and enantioselectivity were moderate (entry 1).[12] This can be due to the instability of the calcium complex in the presence of ethanol.[12j] Pleasingly, metal-free chiral phosphoric acid (**3a**)[10] gave much better enantioselectivity than calcium phosphate salt Ca[**3a**]$_2$ (entry 2 vs. 1). Increasing the amount of ethanol (from 1 to 3 equivalents) led to a decrease in enantioselectivity (entry 3), indicating that the alcohol might disturb the interaction of substrates with the phosphoric acid catalyst. A rapid screening of chiral phosphoric acids (Table 1, entries 4–6) designated **3d** as the best catalyst for both yield and enantioselectivity. Diastereoselectivity of **6a** was low, but this was not a problem since the new stereogenic center is to be lost in further

Table 1 Survey of reaction conditions for the three-component electrophilic amination of enecarbamate **1a**



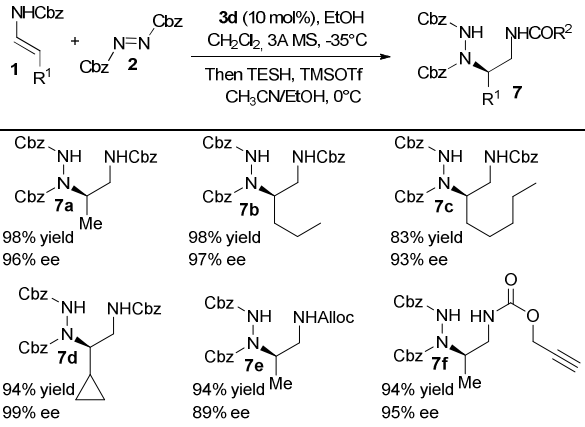
entry	3	R	1a	6 Yield (%)[a,b]	6 ee_{dias1}/ ee_{dias2} (%)[c]	7a Yield (%)[d]	7a ee (%)[c]
1	$Ca[\mathbf{3a}]_2$	Et	*E*	62	41/36[e]		
2	**3a**	Et	*E*	91	95/94[e]		
3	**3a**	Et	*E*	91	88/86[e,f]		
4	**3b**	Et	*E*	99	79/78[e]		
5	**3c**	Et	*E*	53	32/20[e]		
6	**3d**[g]	Et	*E*	99	97/95[e]	99[h]	96
7	**3d**[g]	Et	*E*	-		30[b]	94
8	**3d**[g]	Me	*E*	-		80[b]	92
9	**3d**[g]	*i*Pr	*E*	-		49[b]	89
10	**3d**[g]	*t*Bu	*E*	-		35[b]	75
11	**3d**[g]	H	*E*	-		45[b]	99
12	**3d**[g]	H	*E*	-		76[b,i]	98
13	**3d**[g]	Et	*Z*	-		<5[b]	ND

[a]General conditions: **1a** (0.10 mmol), dibenzylazodicarboxylate (**2**) (0.15 mmol), **5** (0.10 mmol), **3** (0.01 mmol) at -35°C for 16 h; [b]Yields refer to chromatographically pure product calculated from **1a**. [c]*ee* determined by HPLC analysis on chiral stationary phases. [d]Reduction conditions: Et_3SiH (0.50 mmol) and TMSOTf (0.10 mmol) in CH_3CN/EtOH (1.9/0.1 ml) at 0 °C overnight. [e]2:1 ratio of separable diastereomers. [f] With 3 equiv. of EtOH. [g]Derived from octahydro-(*R*)-BINOL. [h]Yields refer to chromatographically pure product calculated from **6a** (R = Et). [i]Reaction performed with 5 equiv of H_2O **5e.** ND not determined

transformations of the corresponding intermediates. Therefore, at this stage, we turned our attention to investigating reduction of these derivatives. After several trials, the best conditions were obtained with an excess of triethylsilane, affording vicinal diamine **7a** without enantioselectivity loss (entry 6, see supporting information). Next, we tried to combine the two reactions and operate in a one-pot fashion. Unfortunately, desired product **7a** was formed with lower yield (entry 7). A subsequent screening of alcohols such as MeOH, *i*PrOH, and *t*BuOH (entries 8–10) was conducted, but no improvement in enantioselectivity was noticed. We also observed a relatively lower yield when water was used as temporary nucleophile **5e** (entry 11). Interestingly, a much better yield (76%) was achieved for diamine **7a** when 5 equivalents of water were used (entry 12).[14] Nevertheless, ethanol was retained as a partner in the reaction, although enantioselectivity was slightly lower, yield being much higher than when using water instead. Finally, the influence of geometry of enecarbamate **1a** was investigated and it was observed that changing the double bond configuration to *Z* resulted in a dramatic loss in reactivity and selectivity (entry 13).

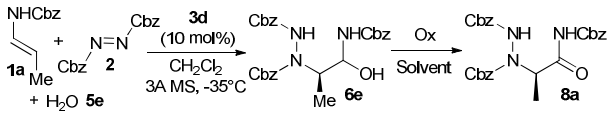
Under the optimal conditions established, the scope of this asymmetric α-amination, iminium reduction sequence was then explored. As shown in Table 2, the reaction of various β-substituted enecarbamates bearing linear alkyl group cleanly afforded the corresponding (*R*)-diamines **7b-7c** in good yields and with excellent enantioselectivities. Use of vinylcarbamates substituted by cyclopropyl group at the β-position altered neither yield nor *ee*, demonstrating compatibility of the process with substrates having a branched, hindered nucleophilic position (**7d**). A variety of protecting groups attached to the nitrogen atom of **1**, including allyl (**7e**) and propargyl (**7f**) carbamates was well tolerated.

Table 2 Substrate scope of the enantioselective phosphoric acid-catalysed sequential synthesis of vicinal diamines[a,b,c]



[a] Reaction conditions: **1a** (0.10 mmol), dibenzylazodicarboxylate (**2**) (0.15 mmol), **5a** (0.10 mmol), **3d** (0.01 mmol) at -35 °C for 16 h, followed by reduction of **7** with Et_3SiH (0.5 mmol) and TMSOTf (0.10 mmol) in CH_3CN/EtOH (1.9/0.1 ml) at 0°C overnight. [b]Yields refer to chromatographically pure product calculated from **1**. [c]*ee* determined by HPLC analysis on chiral stationary phases.

Table 3 Survey of reaction conditions for the two-step reaction sequence: amination/oxidation of **1a**



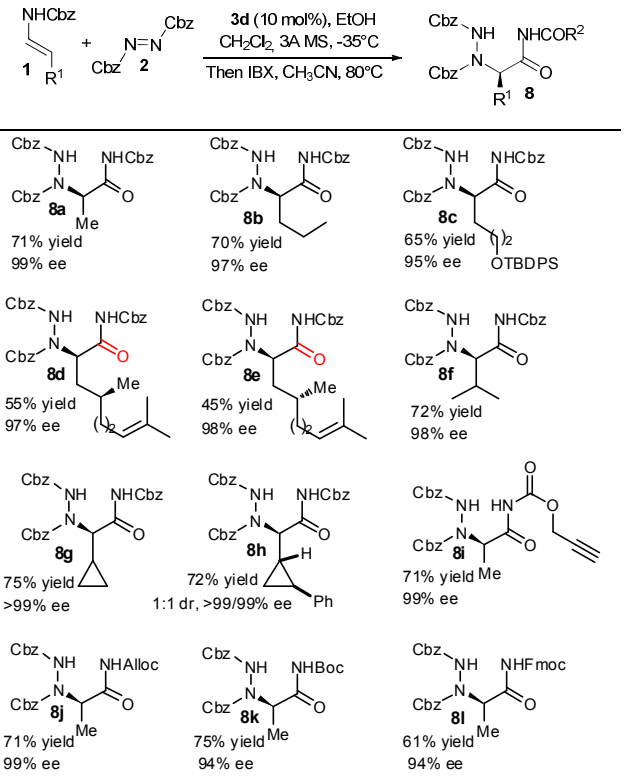
entry	Ox	Ox equiv	T°C	Solvent	8 Yield (%)[a,b]	8 ee (%)[c]
1[d]	$FeCl_3$/TEMPO /$NaNO_2$/O_2	0.3	60	Toluene	52	95
2[e]	IBX	3	80	CH_3CN	71	99
3[f]	IBX	1.2	80	CH_3CN	71	99
4[g]	IBX	1.2	80	CH_3CN	54	94

[a]General conditions: **1a** (0.10 mmol), dibenzylazodicarboxylate (**2**) (0.15 mmol), **5e** (0.50 mmol), **3d** (0.01 mmol) at -35°C for 16 h. [b]Yields refer to chromatographically pure product calculated from **1**. [c]*ee* determined by HPLC analysis on chiral stationary phases. [d]Oxidation conditions: $FeCl_3$ (0.03 mmol), TEMPO (0.03 mmol), $NaNO_2$ (0.03 mmol) and O_2 balloon at 60°C overnight. [e]Oxidation conditions: IBX at 80°C for 1 h. [f]For 3 h. [g]Sequential one-pot 4CR/oxidation process.

We next turned our attention to application of this method to the preparation of non-proteinogenic amino acids. These important motifs are constituents of new drug structures,[14] which make them attractive targets. In light of our recent success in iron-catalyzed aerobic oxidative amidation,[15] we reasoned that enantioenriched hemiaminal **6e** (R = H) could be oxidized for the synthesis of amino acid precursors **8**. We initially attempted to perform the oxidation of **6a** using a catalytic amount of a $FeCl_3$/$NaNO_2$/TEMPO mixture

under an oxygen atmosphere (Table 3, entry 1); however, desired α-hydrazinoamide **8a** was only obtained in moderate yield. After several discouraging results, we were pleased to find that the use of an excess of IBX as an oxidizer gave desired amide **8a** with good yield and excellent enantioselectivity (99% *ee*, entry 2). Decreasing the amount of IBX to 1 equivalent resulted in a similar yield, although the reaction time was slightly increased (entry 2 vs. 3). Finally, the one-pot amination reaction/oxidation was investigated and was found to be less efficient than the two-step procedure (entry 4).

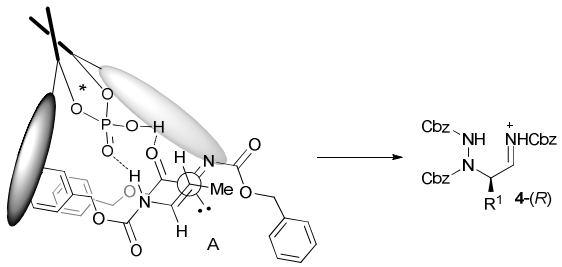
Table 4 Substrate scope of the enantioselective phosphoric acid-catalysed sequential synthesis of α-hydrazinoamides[a,b,c]



[a] Reaction conditions: **1** (0.10 mmol), dibenzylazodicarboxylate (**2**) (0.15 mmol), **5e** (0.50 mmol), **3d** (0.01 mmol) for 16 h, followed by oxidation of **7** with IBX (0.12 mmol) in CH_3CN (0.7 ml) at 80°C for 1.5 h. [b] Yields refer to chromatographically pure products calculated from **1**. [c] *ee* determined by HPLC analysis on chiral stationary phases.[d] Absolute configuration (*R*) was determined by X-ray crystal-structure analysis of a derivative of **8i** (see supporting information).[17]

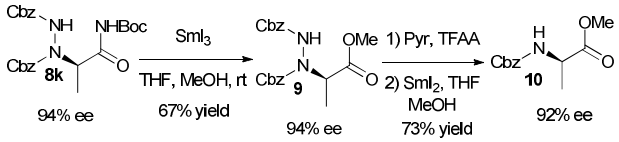
With the optimized conditions in hand, we next explored the substrate scope of this asymmetric α-amination, oxidation sequence. As shown in Table 4, the other β-substituted linear enecarbamates were converted into corresponding α-hydrazinoamides **8b** and **8c** in good yields with excellent enantioselectivities. Even enecarbamates bearing branched cyclopropyl groups could be utilised, leading to aminoacid precursors **8g-8h**, which are found in various biologically active compounds.[17] Noteworthy is that the racemic enecarbamate formed a 1:1 mixture of diastereomers **8h** with 99% and >99% ee, respectively. As for functional group tolerance, silyl ether (**8c**) and triple bond (**8i**) were well tolerated. The nature of carbamate had no influence on the process, apart from the use of Fmoc group (**8l**), which resulted in a decrease of the yield. In addition, these reactions are enantiocontrolled by the sole catalyst, no matched and mismatched effects being observed. Indeed, chiral enecarbamate derived from (*R*) and (*S*)-citronellol afforded respectively **8d** and **8e** in a similar *ee* in favour of (*R*)-diamines.

To help rationalize chiral induction mechanism of our electrophilic amination process, a plausible transition state **A** is proposed in scheme 2. In this assembly, the chiral phosphoric acid may act as a bifunctional catalyst[10a-e] to activate both enecarbamate **1** and azodicarboxylate **2** by hydrogen bonding.[18] The phenyl group on the 3,3' position of **3d** may shield the Re face of **2**, and the enecarbamate **1** would only attack the Si face of **2**. Accordingly, from transition state **A**, the (*R*)-**4** adduct would be formed through a pseudo-intramolecular Si-face attack of **1** to **2**.



Scheme 2 Proposed transition state (TS) for the amidation reaction.

Finally, we have demonstrated that hydrazides **8** are practical precursors to enantiomerically pure α-amino acid derivatives. Methanolyse of **8k** with 10 mol % of SmI_3 in the presence of MeOH afforded the ester **9**. Then, the trifluoroactelylization followed by SmI_2-mediated reductive N-N bond cleavage to provide the *N*-Boc α-amino ester **10** in 73% yield with almost no erosion in enantiomeric purity (Scheme 3).[19]



Scheme 3 Reductive cleavage of hydrazine group in 8k.

Conclusions

In conclusion, we have successfully developed the first enantioselective three-component electrophilic amination of α-unsubstituted enecarbamates using chiral phosphoric acid catalysis. Subsequent reduction or oxidation of the resulting α-hydrazinoimines provides a simple and efficient route to vicinal diamines or α-amino acid precursors, respectively. For all cases, excellent yields and enantioselectivities were achieved. The mild reaction conditions can tolerate a range of functional groups. Further work will be devoted to synthetic applications of the developed strategy.

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Notes and references

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