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Organocatalytic asymmetric Michael addition of ethyl nitroacetate to enones using natural amino acids-derived C_1-symmetric chiral primary–secondary diamines

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ABSTRACT

A highly organocatalytic asymmetric Michael addition of ethyl nitroacetate to enones by using C_1-symmetric chiral primary–secondary diamines has been developed. In assistance of o-nitrobenzoic acid, chiral amine **1f** which was derived from L-tryptophane and D-camphor can effectively promote the transformation in high yields (up to 96%) and enantioselectivities (up to 95%) under mild conditions.

Asymmetric Michael addition of nitro compounds to α,β-unsaturated ketones as an efficient atom-economical carbon–carbon bond formation strategy in organic synthesis chemistry delivers versatile chiral γ-nitro ketone adducts which can be transformed into various useful enantiopure building blocks, such as mutisubstituted pyrrolines, pyrrolidines, lactones, and unnatural amino acids.[1] As a consequence, the enantioselective catalytic variants have attracted great interest, and steady progress has been achieved by development of various catalytic systems including both traditional transition metal-catalysis[2] and newly rising organocatalysis.[3] Among them, secondary amine,[4] primary amine,[5] thiourea,[6] and quaternary ammonium salt[7] are the four kinds of most widely used common organocatalysts. Jøgensen developed two types of novel secondary amine from phenylalanine, and obtained up to 92% ee value.[8] zhao and wang, respectively, synthesized several new kinds of chiral primary–secondary diamines based on phenylalanine or tryptophane, which proved to be efficient catalysts to facilitate several conjugate additions of enones with excellent yields and enantioselectivities.[9] Apart from common nitroalkanes such as nitromethane and 2-nitropropoane, α-nitro esters are another commercially available functional group enriched nitro source. Nevertheless, there are few reported examples concerning the conjugated additions using α-nitro esters as Michael donors.[10] Lu[10b] and Kim,[10c] respectively, reported cinchona alkaloid-based primary amine catalyzed asymmetric Michael addition of nitro ester to enones, and high to 99% enantioselectivities were achieved. Compared with the well-established pyrrolidine-based chiral secondary amine organocatalyst systems, chiral primary amine can efficiently activate the carbonyl group of enone via iminium activation.[11] Despite the above advancements, it should be noted that the existent primary amine catalysts are still limited to expensive chiral sources, tedious classes, and bureaucratic procedures. Therefore, it is still necessary to explore a simple and easily available chiral catalyst to enrich the catalyst library to tolerate broad substrate scope.

Very recently, our group designed and prepared a group of novel chiral diamines from commercially available inexpensive natural amino acids and camphor (Fig. 1), and successfully applied them in the asymmetric catalytic Henry reaction and Michael addition.[12] As part of our ongoing work, we envisioned that ethyl nitroacetate as a practically useful stabilized carbanion precursor may also serve as a proper nucleophilic partner in the primary amine activated reaction of the enone. Herein, we report a successful example of amino acid and camphor-derived C_1-symmetric chiral primary–secondary diamine catalyzed asymmetric Michael addition of ethyl nitroacetate to enones.

At the beginning, the model reaction between ethyl nitro acetate (**2**) and *trans*-4-methoxyphenyl-3-buten-2-one (**3a**) was chosen to optimize the reaction parameters. On the basis of Lu's work,[10b] L-camphorsulfonic acid (L-CSA) was used as acid additive to screen the chiral diamines as organocatalyst to facilitate the conjugate addition, and the results are summarized in Table 1. As listed in entries 1–4, different combinations of L- or D-phenylala-

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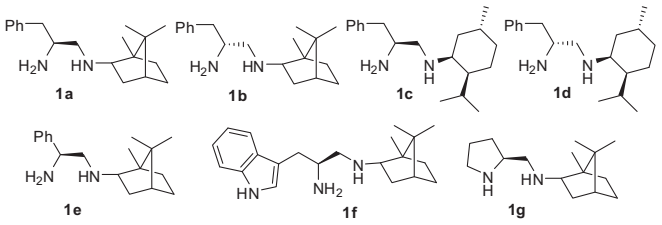


Figure 1. Structures of chiral diamine organocatalysts.

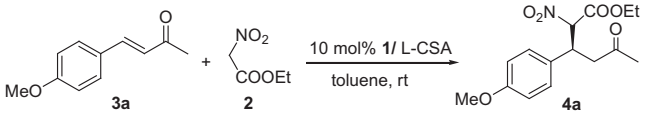
nine with exo-(−)-bornylamine or (+)-(1*S*,2*S*,5*R*)-menthylamine were firstly built to promote the transformation. It is evident to note that the stereochemical outcome of the process was mainly controlled by the amino acid part and the camphor framework owed better chiral induction than the menthone skeleton. At the same time, the combination of L-type amino acid and exo-(−)-bornylamine proved to be the most "matched" one providing the highest ee value. These results are well in agreement with our previous observations.[12] Then, some other amino acids with the amino group (L-phenylglycine and L-tryptophane) and imino group (L-proline) were selected to combine with exo-(−)-bornylamine. Among them, **1f** turned out to be the potential catalyst affording the highest enantioselectivity albeit with modest diastereoselectivity (entry 6). Secondary diamine **1g** gave inferior results of much lower yield of the expected adduct in almost racemic form even after a prolonged reaction time (entry 7). This phenomenon indicates that the amino group was pivotal for the high efficiency of iminium activation of the enone substrate.

Having achieved these hopeful preliminary results, we continued to optimize the reaction parameters systematically. Considering the probably existed synergistic effects between the chiral organocatalyst and acid additive, a group of chiral and achiral acids were firstly screened and the results are illustrated in Table 2. D-CSA made the reaction become sluggish resulting comparable dr and ee values (entry 2). As a result of our previously work, a series of N-protected amino acids were used for the following optimization, but none of them gave better results (entries 3–7). Then, the most widely used common benzoic acid analogies were investigated. A large number of benzoic acids with various electronic property substitutes on different positions were utilized in this model reaction (entries 8–15). 2-Nitrobenzoic acid was found as the best acid additive generating the highest enantioselectivity (entry 10). At last, in case of much stronger acids such as toluenesulfonic acid (TsOH) or trifluoromethylsulfonic acid (TfOH), only a trace mount of product was observed, probably due to their strong interaction with the amine organocatalyst which made the amino motifs totally protonated and resulted in the deactivation of the catalyst (entry 16).

Next, the solvent effects were further assessed. All the results were disclosed in Table 3. Aromatic solvents including toluene, o-xylene, and m-xylene all furnished similar good results, while hexane and ether delivered little decreasing enantiomeric excess (entries 1–5). Protic solvent methanol generated much lower ee value, while aprotic polar solvent DMF just provided racemic product with moderate yield (entries 6 and 7). Halogenated solvents also yielded satisfied results as aromatic solvents, and dichloromethane proved to be the most suitable medium in terms of yield and enantioselectivity (entry 8).

As soon as the optimized reaction conditions were established, the substrate scope and limitations were explored and the results are presented in Table 4. A variety of enones (**3**) were treated with 2 equiv of ethyl nitroacetate (**2**) in the presence of 10 mol % catalyst **1f** with the assistance of 2-nitrobenzoic acid in dichloromethane at room temperature for specified time. In general, the positions and electronic nature of the substituent on the aromatic ring do not exert any big influences on this asymmetric catalytic transformation (entries 1–11). In most cases, enones with certain structural variations could undergo the asymmetric Michael addition smoothly to afford the desired products with high yields and enantioselectivities under the identical reaction conditions. It is noteworthy that the diastereoselectivities were not satisfying due to the acidity of the α-H of nitro group that was strong and might epimerize by basic amine catalyst. Additionally, in case of a slightly more sterically hindered enones **3l** bearing the ethyl group on the R^2 position, the reactivity decreased a little albeit with no erosion in the enantioselectivity (entry 12). Moreover, chalcone **3m** can also be tolerated in this catalytic system, but

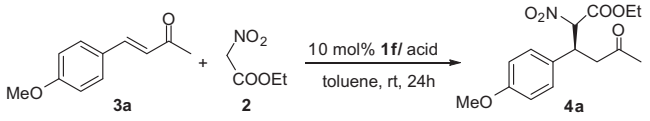
Table 1
Catalyst screening[a]



Entry	Catalyst	*t* (h)	Yield[b] (%)	dr[c]	ee[d] (%)
1	**1a**	24	89	1:1	85/84
2	**1b**	24	75	1:1	−65/−70
3	**1c**	24	70	1:2	85/32
4	**1d**	24	77	1:1	−45/−33
5	**1e**	24	90	1:3	77/74
6	**1f**	24	86	1:1.2	89/88
7	**1g**	48	20	1:2	6/1

[a] Reactions were performed with **3a** (0.2 mmol) and **2** (44 μL, 0.4 mmol, 2 equiv) in the presence of catalyst **1a**–**1g** (0.02 mmol) and acid additive L-CSA (0.02 mmol) in the solvent toluene (0.5 mL) at room temperature.
[b] Isolated yield.
[c] Determined by ^{1}H NMR spectroscopy analysis.
[d] Determined by chiral HPLC analysis using Chiralcel AD-H as a column.

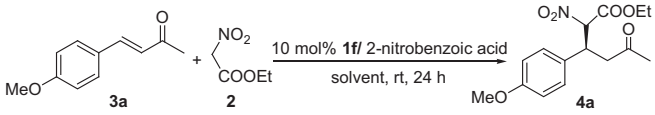
Table 2
Acid additive screening[a]



Entry	Acid additive	Yield[b] (%)	dr[c]	ee[d] (%)
1	L-CSA	86	1:1.2	89/88
2[e]	D-CSA	25	1:2.4	85/84
3	N-Boc-L-phenylalanine	93	1:1	77/73
4	N-Cbz-L-phenylalanine	91	1:1	66/65
5	N-Boc-L-phenylglycine	92	1:1	80/79
6	N-Boc-L-tryptophane	80	1:1.3	67/65
7	N-Cbz-L-tryptophane	85	1:1	76/75
8	2-BrC_6H_4COOH	87	1:1.3	86/81
9	2-IC_6H_4COOH	84	1:1.3	82/75
10	2-$NO_2C_6H_4$COOH	89	1:1.2	91/91
11	3-FC_6H_4COOH	88	1:1.2	79/73
12	4-FC_6H_4COOH	75	1:1.6	81/73
13	4-ClC_6H_4COOH	80	1:1.4	82/76
14	4-$NO_2C_6H_4$COOH	83	1:1	75/73
15	3,5-di$NO_2C_6H_4$COOH	82	1:1	80/80
16[e]	TsOH or TfOH	trace	nd[f]	nd[f]

[a] Reactions were performed with **3a** (0.2 mmol) and **2** (44 μL, 0.4 mmol, 2 equiv) in the presence of catalyst **1f** (0.02 mmol) and acid additive (0.02 mmol) in the solvent toluene (0.5 mL) at room temperature for 24 h.
[b] Isolated yield.
[c] Determined by ^{1}H NMR spectroscopy analysis.
[d] Determined by chiral HPLC analysis.
[e] Reaction time is 48 h.
[f] Not determined.

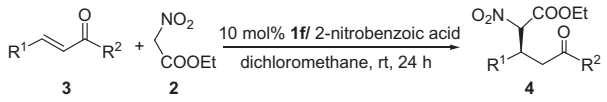
Table 3
Solvent screening[a]



Entry	Solvent	Yield[b] (%)	dr[c]	ee[d] (%)
1	Toluene	89	1:1.2	91/91
2	*o*-Xylene	93	1:1.5	93/91
3	*m*-Xylene	92	1:1.5	93/93
4	Hexane	90	1:1.8	85/80
5	Ether	91	1:1.2	85/82
6	Methanol	88	1:1.2	69/68
7	DMF	65	1:1.3	3/3
8	Dichloromethane	91	1:1.2	94/93
9	Chloroform	86	1:1.2	93/93

[a] Reactions were performed with **3a** (0.2 mmol) and **2** (44 μL, 0.4 mmol, 2 equiv) in the presence of catalyst **1f** (0.02 mmol) and acid additive 2-nitrobenzoic acid (0.02 mmol) in the solvent (0.5 mL) at room temperature for 24 h.
[b] Isolated yield.
[c] Determined by ^{1}H NMR spectroscopy analysis.
[d] Determined by chiral HPLC analysis.

Table 4
Substrate scope exploration[a]



Entry	R^1	R^2	Yield[b] (%)	dr[c]	ee[d] (%)
1	4-MeOC_6H_4	Me	91 (**4a**)	1:1.2	94/93
2	4-MeSC_6H_4	Me	95 (**4b**)	1.8:1	84/85
3	4-MeC_6H_4	Me	89 (**4c**)	1.3:1	86/85
4	4-ClC_6H_4	Me	87 (**4d**)	1.3:1	93/93
5	4-$NO_2C_6H_4$	Me	93 (**4e**)	1.3:1	90/90
6	2-ClC_6H_4	Me	85 (**4f**)	1.1:1	93/92
7	2-BrC_6H_4	Me	86 (**4g**)	1.1:1	95/94
8	3-MeOC_6H_4	Me	93 (**4h**)	1.3:1	89/88
9	2,4-diClC_6H_3	Me	87 (**4i**)	1.1:1	95/93
10	3,4-di$MeOC_6H_3$	Me	89 (**4j**)	1.3:1	91/92
11	Ph	Me	96 (**4k**)	1.2:1	95/92
12[e]	Ph	Et	76 (**4l**)	1.1:1	95/94
13[e]	Ph	Ph	70 (**4m**)	1.2:1	75/75

[a] Reactions were performed with enone **3** (0.2 mmol) and **2** (44 μL, 0.4 mmol, 2 equiv) in the presence of catalyst **1f** (0.02 mmol) and acid additive 2-nitro benzoic acid (0.02 mmol) in dichloromethane (0.5 mL) at room temperature for 24 h.
[b] Isolated yield.
[c] Diastereomeric ratios (*anti*/*syn*) were determined by ^{1}H NMR spectroscopy analysis.
[d] Determined by chiral HPLC analysis.
[e] The reaction time was prolonged to 40 h.

prolonged reaction time was required to complete the process. Simultaneously, a sharp decrease in the enantioselectivity was observed (entry 13).

In conclusion, L-tryptophane and D-camphor derived chiral primary–secondary diamine **1f** as organocatalyst in combination with proper acid additive 2-nitrobenzoic acid had shown high efficiency for the asymmetric Michael addition of nitro ester to a broad range of enones with high yields (up to 96%) and excellent enantioselectivities (up to 95%) under mild conditions. These simple and easily available chiral amine catalysts had enriched the catalyst library for asymmetric Michael addition reactions. However, the diastereoselctivities were not satisfying, and further efforts will be devoted in this area to improve the results.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04.005.

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