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Construction of chiral quaternary carbon center *via* catalytic asymmetric aza-Henry reaction with α-substituted nitroacetates†

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The catalytic enantioselective aza-Henry reaction of *N*-Boc aldimines **2** and 2-nitropropionic acid ethyl ester **3** in the mixed solvents of toluene–saturated brine (10 : 1) was catalyzed by *cinchona* quaternary ammonium salts to form a new quaternary carbon center. High yields (up to 90%), and excellent enantioselectivities (up to 99% ee) and diastereoselectivity ratio (up to 22 : 1) were successfully obtained with mild conditions.

Introduction

In organic chemistry, the efficient construction of a quaternary carbon center has always been a very important task for researchers.[1] In this area, the construction of a chiral quaternary carbon center is even more appealing, and it often involves not only enantioselectivity but also diastereoselectivity in some transformations,[2] which makes it one of the most challenging topics in modern organic chemistry.

Enantioselective catalytic aza-Henry reaction (or nitro-Mannich reaction) is a useful C–C bond-forming process, the nitro group of the product β-nitramine can easily be converted to the corresponding amino functional group, to further obtain biologically active compounds or chiral synthetic blocks.[3] As a result, considerable efforts have been directed towards the asymmetric aza-Henry reaction over the past several years. Both metal catalysis and organocatalysis have achieved some interesting results in this field.[4] However, the nitro-substrates of the aza-Henry reaction mostly focused on the straight-chain, unsubstituted nitroalkanes and simple products were reported.[5] In fact, α-substituted nitroacetates are very good nucleophiles to imines, in which adjacent quaternary and tertiary chiral centers could be constructed concurrently. This transformation is more challenging in organic synthesis, and good results were relatively less reported in the literature. In 2008, Li and Chen[6] demonstrated the aza-Henry reaction between α-substituted nitroacetates and *N*-Boc imines, which were catalyzed by bifunctional thiourea–secondary-amine with naphthalene, and 96% ee, 17 : 1 dr were obtained. Inspired by this, Puglisi and Benaglia[7] used thiourea catalysts derived from *N*,*N*-dimethyl amino for this transformation to get the corresponding products with yields range from 48–81%, the ee value 27–81%, but the diastereoselectivities have not been reported. Huang and Dong,[8] applied thiourea–guanidine to this transformation, resulting in moderate yield (up to 80%), dr (up to 7.6 : 1) and ee value (up to 88%). Meanwhile, some other groups tried different substrates to build the chiral quaternary carbon center *via* a similar procedure.[9] However, the majority of these reports focused on thiourea catalysts, some synthetic steps of the catalysts were complicated, and the substrate scope needed to be further broadened. In addition, only few high diastereoselectivities ratios and ee values were observed. Therefore, it's still an important issue to build up a practical high enantioselective and diastereoselective method in this challenging area.

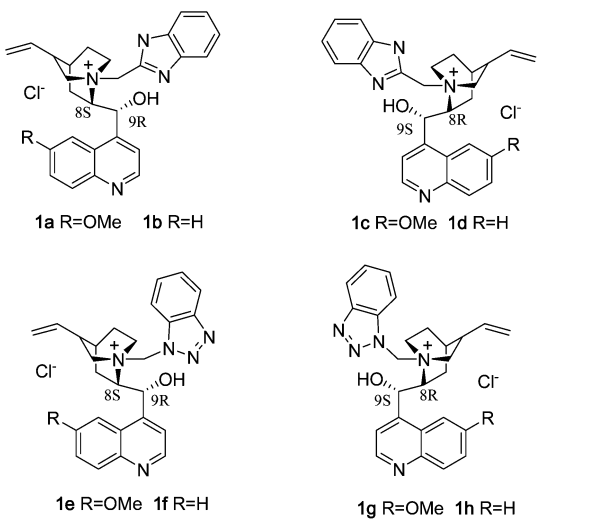

Fig. 1 Structure of the quaternary ammonium salts.

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Recently, we have developed a series of novel quaternary ammonium salts **1a–1h** (Fig. 1), which have showed excellent chiral induction in the enantioselective alkylations of *N*-(diphenylmethylene) glycine *tert*-butyl ester and the aza-Henry reaction between simple nitroalkane and α-amido sulfones.[10] Considering the benefits of the quaternary ammonium salts in organic catalysis, such as low cost, mild conditions, environmental benign and high enantioselectivities, we attempt to use these chiral quaternary ammonium salts to catalyze the aza-Henry reaction between α-substituted nitroacetates and *N*-Boc imines in this work, and expect to investigate the versatility of these organocatalysts.

Results and discussion

The reaction between *N*-Boc benzaldimine **2a** and 2-nitropropionic acid ethyl ester **3** was selected as the model reaction to screen the catalysts **1a–1h** (Fig. 1). The results were shown in Table 1. Our initial studies with the diversely structured catalysts **1a–1h** for the analogous reaction failed to give significant chiral induction (Table 1, entries 1–8). Nevertheless, a relatively high ee value was obtained by **1h** (entry 8). Hence **1h** has been chosen to further screen the additives.

Then the additives and reaction temperature were screened. It was observed that a basic additive is needed to promote the reaction when it was carried out at a low temperature. As it was shown in Table 2, both organic bases and inorganic bases can improve the ee value of limited. All of which, K_2CO_3 was observed to induce moderate ee value (entry 7). The reaction temperature was then screened, because in several asymmetric reactions, a lower temperature is beneficial to improve the ee value. Strangely, when the temperature was decreased to −10 °C, the ee value did not improve (entry 12 *vs.* 7). The temperature was also increased to 0 °C, the ee value maintained at the same level (entry 13 *vs.* 7). So, −5 °C was chosen to further screen the conditions.

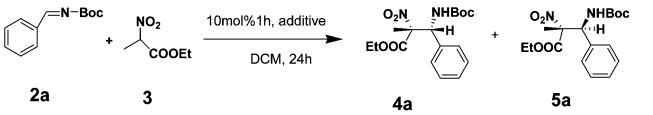
Table 1 Screening of organocatalysts in the aza-Henry reaction of *N*-Boc benzaldimine **2a** and 2-nitropropionic acid ethyl ester **3**[a]

2a **3** **4a** **5a**

Entry	Catalyst	Yield[b]	dr[c]	ee[d]
1	**1a**	45/37	1 : 1	21
2	**1b**	38/41	1 : 1	18
3	**1c**	42/39	1 : 1	8
4	**1d**	39/41	1 : 1	21
5	**1e**	40/38	1 : 1	23
6	**1f**	38/36	1 : 1	15
7	**1g**	33/35	1 : 1	18
8	**1h**	45/40	1 : 1	33

[a] All the reactions were carried out with 0.15 mmol of 2-nitropropionic acid ethyl ester **3** and 0.2 mmol of *N*-Boc benzaldimine **2a** in DCM (1 mL) in the presence of 10 mol% of catalyst at ambient temperature for 24 h. [b] Isolated yield of pure **4a** and **5a**. [c] Calculated from the isomers **4a** and **5a**. [d] ee of **4a** was determined by chiral HPLC analysis using Chiralpak AD-H column; low ee (<10%) was observed for **5a** in the tested reactions.

Table 2 Screening of additives in the aza-Henry reaction of *N*-Boc benzaldimine **2a** and 2-nitropropionic acid ethyl ester **3**[a]



2a **3** **4a** **5a**

Entry	Additives (1eq)	Yield[b]	dr[c]	ee[d]
1	Et_3N	40/39	1 : 1	37
2	Et_2NH	35/33	1 : 1	47
3	Pyridine	38/36	1 : 1	45
4	2,2-Bipyridine	33/34	1 : 1	3
5	DIAD[e]	35/30	1 : 1	39
6	DBU[f]	36/38	1 : 1	3
7	K_2CO_3	45/30	1.5 : 1	50
8	Na_2CO_3	40/39	1 : 1	45
9	NaOH	42/40	1 : 1	40
10	NaOAC	40/39	1 : 1	41
11	KOH	39/40	1 : 1	31
12[g]	K_2CO_3	40/30	1 : 1	47
13[h]	K_2CO_3	47/40	1 : 1	43

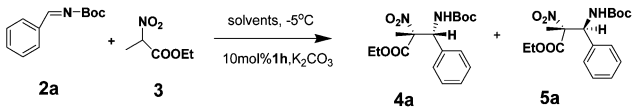
[a] All the reactions were carried out with 0.15 mmol of 2-nitropropionic acid ethyl ester **3** and 0.2 mmol of *N*-Boc benzaldimine **2a** in DCM (1 mL) in the presence of 10 mol% **1h** at −5 °C for 24 h. [b] Isolated yield of pure **4a** and **5a**. [c] Calculated from the isomers **4a** and **5a**. [d] ee of **4a** was determined by chiral HPLC analysis using Chiralpak AD-H column; low ee (<10%) was observed for **5a** in the tested reactions. [e] Diisopropyl azodiformate. [f] 1,8-Diazabicyclo[5,4,0] undec-7-ene. [g] At −10 °C. [h] At 0 °C.

It was found that solvents have a great effect on the asymmetric reactions. So, different solvents were screened in the presence of **1h** (Table 3). High yields and low ee values could be obtained in non-polar solvents (entry 1 and 2). Good yields and moderate ee value were observed in ether (entry 3). Ethyl acetate, isopropanol, and acetone were found to show a poor chiral induction (entries 4–6). Comparing entry 8 to entry 7, it could be concluded that dried dichloromethane was inferior to the untreated dichloromethane, which indicated that a bit of water was benefit for this reaction (entry 8 *vs.* 7). When toluene was used as the solvent, the ee value could be improved dramatically (entry 10). Not surprisingly, the best result (90% isolated yield, >99% ee of **4a**, 22 : 1 dr) was obtained using the mixed solvent toluene–saturated brine (10 : 1) (entry 11). However, when the ratio of saturated brine in mixed solvent was increased, both the ee value and dr ratio decreased significantly (entry 12).

To summarize, the optimal condition was: 10 mol% of **1h** as the catalyst, 1 equivalent of K_2CO_3, at −5 °C in the mixture of toluene–saturated brine (10 : 1). Then, the reaction scope for *N*-Boc imine was investigated, and the products were summarized in Fig. 2.

The *N*-Boc aldimines were derived from different kinds of substituted aldehyde. From Fig. 2, we can see that the optimal condition has good substrates applicability. Both the electron-

Table 3 Screening of solvents in the aza-Henry reaction of *N*-Boc benzaldimine **2a** and 2-nitropropionic acid ethyl ester **3**[a]



Entry	Solvent	Yield[b]	dr[c]	ee[d]
1	Hexane	47/34	2 : 1	21
2	Pentane	41/40	1 : 1	11
3	Ether	78/9	8 : 1	40
4	Ethyl acetate	44/40	1 : 1	20
5	Isopropanol	40/36	1 : 1	7
6	Acetone	43/40	1 : 1	3
7	Dried dichloromethane	45/40	1 : 1	17
8	Dichloromethane	45/30	1.5 : 1	50
9	*m*-Xylene	78/5	16 : 1	61
10	Toluene	82/5	17 : 1	82
11[e]	Toluene–saturated brine	86/4	22 : 1	>99
12[f]	Toluene–saturated brine	80/4	20 : 1	77

[a] All the reactions were carried out with 0.15 mmol of 2-nitropropionic acid ethyl ester **3** and 0.2 mmol of *N*-Boc benzaldimine **2a** in solvents (1 mL) in the presence of 10 mol% of **1h** and 0.15 mmol K_2CO_3 at −5 °C for 15 h. [b] Isolated yield of pure **4a** and **5a**. [c] Calculated from the isomers **4a** and **5a**. [d] ee of **4a** was determined by chiral HPLC analysis using Chiralpak AD-H column; low ee (<10%) was observed for **5a** in the tested reactions. [e] Reaction for 12 h, 1.1 mL toluene–saturated brine (10 : 1). [f] Reaction for 12 h, 1 mL toluene–saturated brine (1 : 1).

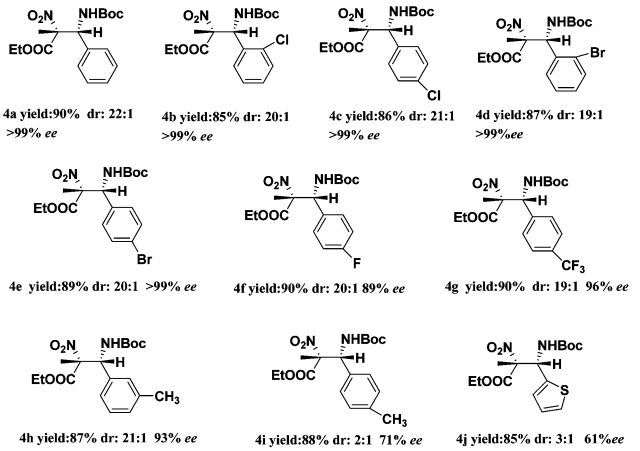


Fig. 2 Scope of stereoselective aza-Henry reaction of *N*-Boc aldimines **2** and 2-nitropropionic acid ethyl ester **3**.

withdraw group and the electron-donating group that connected to the benzene ring can give good yields, and the majority of corresponding products can be obtained with excellent ee values and diastereoselectivities. The *o*,*m*,*p*-substituted substrates gave different results. Where *ortho*, *para*-substituted chlorine, bromine gave excellent results, *para*-substituted fluorine and trifluoromethyl can give high yield and ee value. When methyl is connected to the benzene ring, *meta*-substituted can get better result than *para*-substituted. In general, when substituting the aldehyde with the electron-withdraw group, the ee value was higher than electron-donating group. Moderate results were obtained for thiophene-substituted imine. The aliphatic substrates were also tested, but the result was not satisfactory.[11] It should be emphasized that the optical rotation of the enantiomer products **4** obtained by this methodology were just opposite to the literature,[6] and to the best of our knowledge, they were not reported by others so far.

Based on the previous mechanism studies[7,9a] of the aza-Henry reaction and the experiment results, a potential transition state to reveal the possible mechanism of this asymmetric catalytic aza-Henry reaction was proposed. As shown in Fig. 3, the hydrogen-bound may be formed between the carbonyl group of *N*-Boc benzaldehyde imine and 9-hydroxy group of cinchonine. Meanwhile, an ion pair may be formed between the carbon anion generated from 2-nitropropionic acid ethyl ester with the help of base and ammonium cation of **1h**. Subsequently, the Si-face attack of the imine affords the desired adducts **4a** with (*R*, *R*) configuration. The scaffold of the bifunctional catalyst plays a significant role in stereocontrolling of the aza-Henry reaction. The hydrogen bonding and ion pair interactions between the catalyst and the two reactants may be synergistically responsible for the excellent stereoselectivity. Nevertheless, the real transition state model still needs further investigation.

Moreover, four new compounds were prepared with high yields, dr ratio and excellent ee value. Our work is a good complement to the previous report.

Experimental

General

All the starting materials and reagents were purchased from commercial suppliers and used without further purification. Solvents were purified by standard procedures. NMR spectra were recorded on a Bruker AV-400 spectrometer with $CDCl_3$ as solvent. High-Resolution Mass Spectroscopy (HRMS) was carried out on a BRUKER APEX-II. High performance liquid chromatography (HPLC) was performed by an Agilent 1260 interfaced to an HP 71 series computer workstation with Daicel Chiralpak AD-H chiral column. The yields are of materials isolated by column chromatography gel plates.

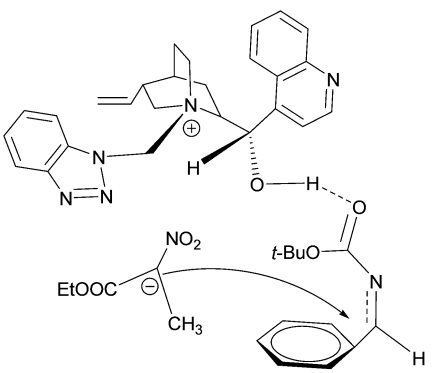


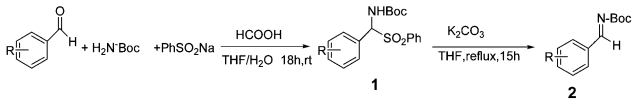
Fig. 3 Proposed transition state for the reaction.

Procedure for the synthesis of organocatalysts

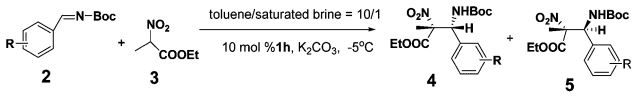
The quaternary ammonium salts **1a–1h** were synthesized by condensation of four natural *cinchona* alkaloids with 2-chloromethyl benzimidazole or 1-chloromethyl benzotriazole respectively, following our previously reported procedure.[10]

Procedure for the synthesis of *N*-Boc benzaldimine 2a

N-Boc benzaldimine **2a** was prepared with high yields, following the reported procedure with minor improvements.[12]



Representative procedure for the organocatalytic asymmetric aza-Henry reaction



Into a solution of 0.2 mmol of *N*-Boc benzaldimine **2a** in 1.1 mL toluene–saturated brine (10 : 1), 10 mol% of catalyst **1h**, 0.15 mmol of 2-nitropanoinate **3**, 0.15 mmol K_2CO_3 was added, and the mixture was stirred for 12 h at −5 °C. The reaction mixture was then concentrated and purified by flash chromatography on silica gel (hexane–EtAc, 50/1). Among all the aza–Henry reaction adducts, **4d**, **4e**, **4g**, **4h** are new compounds.

(2*R*,3*R*)-Ethyl 3-(2-bromophenyl)-3-(*tert*-butoxycarbonyl amino)-2-methyl-2-nitropropanoate 4d. Enantiomeric excess was determined to be 99% by HPLC on Chiralpak AD-H column (10% 2-propanol–*n*-hexane, 1 mL min^{-1}), UV 220 nm, t_{major} = 9.40 min, t_{minor} = 7.03 min. $[\alpha]_D^{20}$ +11.3 (in EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.0, 1H), 7.31 (t, 1H), 7.2 (t, 2H), 6.58 (d, J = 9.6, 1H), 6.23 (d, J = 9.2, 1H), 4.43–4.31 (m, 2H), 1.80 (s, 3H), 1.42 (s, 9H), 1.37 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR δ = 166.4, 154.4, 135.6, 133.4, 130.2, 128.6, 128.4, 125.5, 96.8, 80.4, 63.6, 56.3, 28.2, 20.7, 13.9 ppm; HRMS: calcd for $C_{17}H_{23}BrN_2O_6$ + Na 453.0632, found 453.0635.

(2*R*,3*R*)-Ethyl 3-(4-bromophenyl)-3-(*tert*-butoxycarbonyl amino)-2-methyl-2-nitropropanoate 4e. Enantiomeric excess was determined to be 99% by HPLC on Chiralpak AD-H column (10% 2-propanol–*n*-hexane, 1 mL min^{-1}), UV 220 nm, t_{major} = 16.06 min, t_{minor} = 7.94 min. $[\alpha]_D^{20}$ −24.5 (in EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.49 (d, J = 8.4, 2H), 7.25 (d, J = 8.4, 2H), 6.41–6.39 (m, 1H), 5.48–5.46 (m, 1H), 4.36–4.24 (m, 2H), 1.75 (s, 3H), 1.40 (s, 9H), 1.30 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR δ = 165.5, 154.6, 135.0, 131.8, 131.5, 130.3, 127.9, 122.9, 94.4, 80.6, 63.3, 59.4, 28.2, 22.4, 13.6 ppm; HRMS: calcd for $C_{17}H_{23}BrN_2O_6$ + Na 453.0632, found 453.0634.

(2*R*,3*R*)-Ethyl 3-(*tert*-butoxycarbonylamino)-2-methyl-2-nitro-3-(4-(trifluoromethyl)phenyl)propanoate 4g. Enantiomeric excess was determined to be 96% by HPLC on Chiralpak AD-H column (10% 2-propanol–*n*-hexane, 1 mL min^{-1}), UV 220 nm, t_{major} = 11.95 min, t_{minor} = 8.89 min. $[\alpha]_D^{20}$ −12.3 (in EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4, 2H), 7.52 (d, J = 8, 2H), 6.46–6.43 (m, 1H), 5.59–5.56 (m, 1H), 4.34–4.27 (m, 2H), 1.77 (s, 3H), 1.41 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR δ = 165.5, 154.6, 140.0, 131.1, 130.7, 129.1, 125.6, 125.5, 94.3, 80.7, 63.4, 59.5, 28.2, 22.3, 13.6 ppm; HRMS: calcd for $C_{18}H_{23}F_3N_2O_6$ + Na 443.1400, found 443.1406.

(2*R*,3*R*)-Ethyl 3-(*tert*-butoxycarbonylamino)-2-methyl-2-nitro-3-*m*-tolylpropanoate 4h. Enantiomeric excess was determined to be 93% by HPLC on Chiralpak AD-H column (10% 2-propanol–*n*-hexane, 1 mL min^{-1}), UV 220 nm, t_{major} = 9.10 min, t_{minor} = 5.89 min. $[\alpha]_D^{20}$ −9.6 (in EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 1H), 7.15–7.13 (m, 3H), 6.41 (d, J = 8.8, 1H), 5.49 (d, J = 9.6, 1H), 4.33–4.28 (m, 2H), 2.36 (s, 3H), 1.74 (s, 3H), 1.41 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR δ = 165.7, 154.7, 138.3, 135.7, 129.4, 129.3, 128.5, 125.5, 94.7, 80.2, 65.8, 63.1, 59.8, 28.2, 22.5, 21.5, 15.2, 13.6 ppm; HRMS: calcd for $C_{18}H_{25}N_2O_6$ + Na 389.1683, found 389.1683.

Conclusions

In summary, a series of readily available *cinchona* quaternary ammonium salts were successfully applied in the asymmetric aza-Henry reaction between esters of α-substituted nitro-acetic and *N*-Boc aldimines with excellent enantioselectivities, yields and diastereoselectivities. Series of new high enantioselective nitro–amino esters containing chiral quaternary carbon centers were successfully synthesized. Cheap catalysts, mild reaction conditions and good results make this methodology very practical. Use of this protocol to synthesize biologically active molecules is ongoing in our laboratory.

Acknowledgements

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