Organic LETTERS

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N-Heterocyclic Carbene-Catalyzed Activation of Esters of *N*-Hydroxyphthalimide: A Highly Enantioselective Route to Chiral Dihydropyridinones Bearing an All Carbon Quaternary Stereogenic Center

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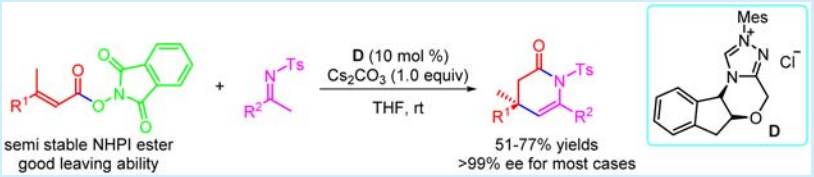
Supporting Information



ABSTRACT: An N-heterocyclic carbene-catalyzed highly enantioselective [3 + 3] annulation reaction of *N*-hydroxyphthalimide (NHPI) 3,3-disubstituted acrylates and N-Ts ketimines was developed. In most cases, the desired chiral dihydropyridinone products bearing an all carbon quaternary stereogenic center could be obtained in good yields with excellent enantioselectivities (>99% ee's), which demonstrated the NHPI acrylates as a kind of excellent substrate in NHC-catalysis.

With the rapid development of organocatalysis, N-heterocyclic carbenes (NHCs) have become one of the most important kinds of catalysts for organic synthesis and received intense attention in the past decade.[1] In (oxidative[2]) NHC-catalysis, reactions of enals,[3] ynals,[4] enones,[5] α-hydroxyenones,[6] and α-bromoenals[7] or α,β-unsaturated acyl fluorides[8] with imines, active carbonyl compounds, electron-deficient carbon−carbon or carbon-hetereo double bonds have been extensively studied, leading to various transformations through the catalytical generation of enolate and homoenolate equivalent intermediates (Figure 1). However, these kinds of different substrates are usually expensive and unstable, and they are often hard to prepare and handle.

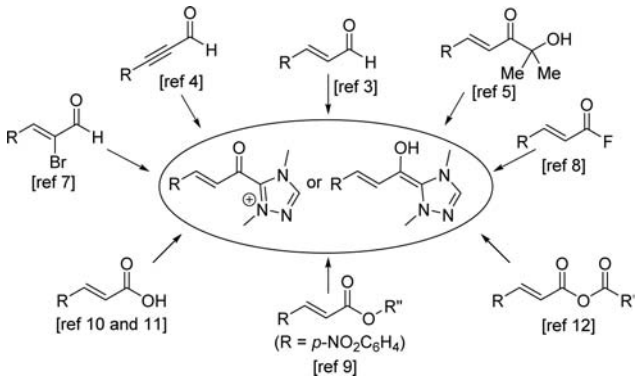


Figure 1. Formation of homoenolate or α,β-unsaturated acyl azolium intermediate with NHC catalysts.

Recently, the use of *para*-nitro phenyl esters instead of the compounds mentioned above for the generation of enolate and homoenolate equivalent intermediates in NHC-catalyzed reactions reported by the Chi group solved this problem well.[9] Alternately, the Scheidt[10] and Ye[11] groups reported the formation of an α,β-unsaturated acyl azolium intermediate from α,β-unsaturated carboxylic acid via *in situ* generation of cross anhydride, while a similar strategy developed by the Chi group through the use of anhydrides derived from the acids was also reported.[12] Although several examples of carboxylic acid and their derivatives employed as substrates have been achieved, the development of more successful examples in NHC-catalysis is still sought-after.

N-Hydroxysuccinimide (NHSI)[13] and *N*-hydroxyphthalimide (NHPI)[14] are widely seen in the preparation of amine-reactive esters of carboxylate groups for chemical labeling, cross-linking, and solid-phase immobilization applications. In these cases, carboxylic acids (−COOH) react to NHSI or NHPI in the presence of a carbodiimide such as DCC or EDC, resulting in a semistable NHSI or NHPI ester, which then reacts with primary amines to form amide cross-links, thus enhancing the coupling efficiency greatly (Figure 2). Since either the NHSI or NHPI unit acts as a good leaving group in such reactions, we envisioned that this type of semistable ester units might be applicable in the NHC-catalyzed activation of carbonyl functionalities, where the α,β-unsaturated acyl azolium intermediates could be easily generated. Herein, we report a

Received: September 2, 2015
Published: October 6, 2015

DOI: 10.1021/acs.orglett.5b02527
Org. Lett. 2015, 17, 5052−5055

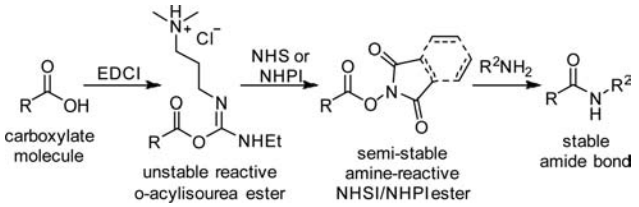


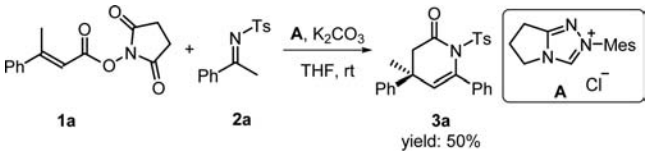
Figure 2. Formation of amide cross-links through NHSI or NHPI esters.

highly enantioselective [3 + 3] annulation reaction of 3,3-disubstituted acrylates and N-Ts ketimines via the NHC-catalyzed activation of the NHPI acrylates.

Considering the wide application of the chiral dihydropyridinone[9a,15] scaffold in organic synthesis, we are very interested in the formation of dihydropyridinone derivatives via the reaction of N-Ts ketimines and the *in situ* generated *β*-disubstituted *α,β*-unsaturated acyl azolium intermediate with NHCs, affording the products with an all carbon quaternary sterogenic center. In this approach, the NHSI and NHPI esters used are readily available, cheap, and easy to handle, and a series of optically pure dihydropyridinone derivatives were conveniently obtained in good yields and excellent enantioselectivities under mild conditions. Thus, we hope that this kind of esters could be generally employed as an alternative strategy to form activated Michael acceptors in NHC catalysis.

At the very onset, NHSI 3,3-disubstituted acrylates **1a** and the N-Ts ketimine **2a** were tested as the electro- and nucleophile precursors, respectively (Scheme 1). To our

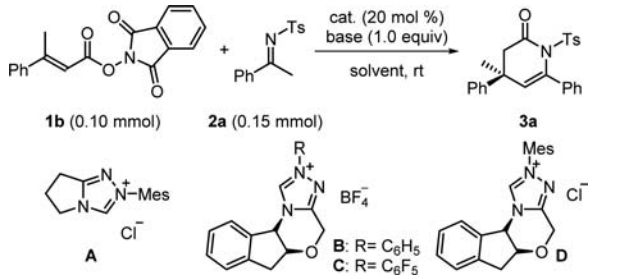
Scheme 1. Investigation of NHSI and NHPI Esters in the Cyclization Reaction



delight, the reaction proceeded smoothly in the presence of the achiral NHC catalyst **A** and provided the desired product **3a** in 50% yield, which encouraged us in further investigation with chiral NHC catalysts. When the reaction was catalyzed by the Rovis triazolium catalyst **D** which is widely used in enantioselective NHC catalysis, the product **3a** was obtained in 45% yield, surprisingly, the enantiomeric excess (ee) was excellent (99% ee). We next tried to use NHPI acrylate **1b** instead of **1a** in the reaction, and it was found that the yield of **3a** was improved to 67% with an even better ee value (>99% ee) (Table 1, entry 4). Thus, the NHPI ester was selected in the subsequent reaction condition optimization.

The screening of different chiral triazolium catalysts was carried out, and when catalyst **B** was used the product **3a** was given in only 30% yield with 98% ee (Table 1, entry 2). Catalyst **C** with a pentafluorophenyl group could not promote the reaction efficiently; only a trace amount of product was detected (Table 1, entry 3). Subsequent screening of bases indicated that $CsCO_3$ was the best due to the highest yield and enantioselectivity. Other bases, such as K_2CO_3, DBU, and C_2H_5ONa, provided lower yields, but ee values were still excellent (Table 1, entries 4–7).

Table 1. Condition Optimization of the Cyclization Reaction



entry	cat.	base	solvent	time [h]	yield [%][a]	ee [%][b]
1	**A**	K_2CO_3	THF	20	62	–
2	**B**	K_2CO_3	THF	48	30	98
3	**C**	K_2CO_3	THF	48	trace	n.d.
4	**D**	K_2CO_3	THF	24	67	>99
5	**D**	Cs_2CO_3	THF	12	77	>99
6	**D**	DBU	THF	5	55	>99
7	**D**	C_2H_5ONa	THF	1	36	>99
8	**D**	Cs_2CO_3	CH_3CN	48	13	98
9	**D**	Cs_2CO_3	EA	48	18	>99
10[c]	**D**	**Cs_2CO_3**	**THF**	**24**	**78**	**>99**
11[d]	**D**	Cs_2CO_3	THF	24	53	>99

[a]Yield of the isolated product. [b]Determined by chiral HPLC (see the Supporting Information). [c]10 mol % catalyst was used. [d]5 mol % catalyst was used.

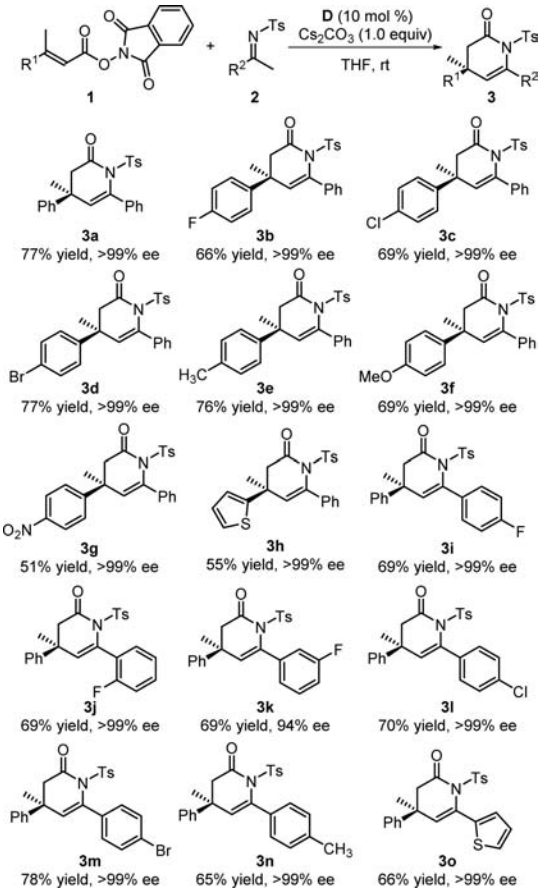
Solvent screening revealed that solvents significantly influenced the reaction yields; however, the enantioselectivities were all excellent. Dramatically decreases in yields were observed when polar solvents such as CH_3CN and EtOAc were used (Table 1, entries 8 and 9). And THF showed the best result in yield. A comparable result (78% yield and >99% ee) was achieved when half the amount of catalyst was used with an extension of the reaction time to 24 h (Table 1, entry 10); further decreasing the catalyst loading to 5 mol % led to a lower yield (53%, Table 1, entry 11). Thus, the best reaction conditions were established when the reaction was performed in the presence of 10 mol % of **D** and 1.0 equiv of $CsCO_3$ in THF at room temperature.

Having established the optimized reaction conditions, we turned our attention to the exploration of the reaction scope through variation of different NHPI acrylates and imines; the results are listed in Scheme 2. From the scheme we observed that the esters **1** with electron-donating and -withdrawing groups on R^1 were all well tolerated in the reaction. The desired dihydropyridinone derivatives were isolated in moderate to good yields (51–77%), and the enantioselectivities were all excellent (more than 99% ee's) (**3a**-**3h**). The hetereoaryl acrylates **3o** also reacted well providing the desired product (**3h**) in 55% yield with >99% ee.

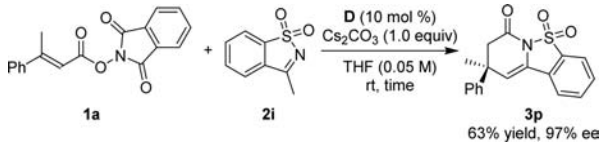
The influence of functionalities and substitutions on the N-Ts ketimines **2** was also investigated. Both electron-withdrawing and electron-rich substituents on the phenyl group of the imine were also well tolerated, affording the desired products **3i**–**3o** in good yields with excellent enantioselectivities. The product from 3-fluorophenyl N-Ts ketimine **3k** was obtained in slightly lower ee; however, a noticeable electronic effect of the imine substituents was not observed in the reaction. Furthermore, the cyclic sulfonic imine **3i** was also tested and the desired tricyclic product was achieved in 63% yield with 97% ee (Scheme 3). Unfortunately, only a trace

DOI: 10.1021/acs.orglett.5b02527
Org. Lett. 2015, 17, 5052–5055

Scheme 2. Substrate Scope



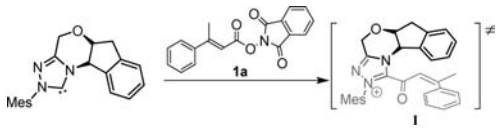
Scheme 3. Cyclization Reaction of 2i with NHPI Ester



amount of the desired product was observed when the aliphatic disubstituted acrylates were used. The absolute configuration of the cyclization products was confirmed to be *S* by comparison with the optical rotation data reported in the literature.[9a]

We thought that the reaction follows a similar reaction pathway to the literatures.[17] Due to the high leaving ability of the NHPI group on the semi stable ester **1a**, the key α,β-unsaturated acyl azolium intermediate **I** could be easily generated through the addition of the NHC catalyst to the ester (Scheme 4), which would greatly benefit the following steps of the reaction and the stereoselectivity, as proposed by Bode[18] and related literature.[7h] Then, a 1,2-addition of the enamine isomerized from imine **2** under basic conditions would occur, after further Claisen rearrangement, tautomerization, and

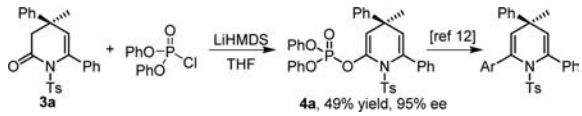
Scheme 4. Proposed Transition State



lactam formation transformation sequences, and the desired product would be obtained with regeneration of the catalyst.

Because the six-membered lactams and derivatives are important building blocks and scaffolds in organic synthesis and pharmaceuticals, the derivation of cyclization products with simple protocols was carried out. The optically enriched product **3a** was transformed to the phosphoric ester **4a** with a little erosion of the ee value in moderate yield (49% yield and 95% ee in Scheme 5), which could be a useful intermediate for

Scheme 5. Derivation of the Dihydropyridine



the synthesis of chiral trisubstituted dihydropyridines bearing an all carbon quaternary center. Some other transformations could also be achieved by reduction, hydrogenation, and deprotection, and different chiral intermediates could be obtained conveniently.[9a,16]

In conclusion, an NHC-catalyzed highly enantioselective [3 + 3] cyclization reaction of NHPI acrylates with N-Ts ketimines was developed. In most cases, the desired products were obtained in good yields with >99% ee values, which illustrate that the NHPI esters could be another type of excellent substrate in NHC catalysis. Given the advantages of the NHPI esters, we expect it could be widely applied in more organic reactions and methodologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02527.

Experimental procedures and analytical data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Science Foundation of China (No. 21373073), the Young National Natural Science Foundation of China (Nos. 21302033 and 21302032), the PCSIRT (IRT 1231), and Hangzhou Normal University for financial support. X.-F. acknowledges a Xihu Scholar award from Hangzhou City, and G.Z. appreciated a Qianjiang Scholarship from Zhejiang Province in China.

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DOI: 10.1021/acs.orglett.5b02527
Org. Lett. 2015, 17, 5052−5055