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*N*-Heterocyclic Carbenes | *Very Important Paper*

VIP

# An Enantioselective Assembly of Dihydropyranones through an NHC/LiCl-Mediated in situ Activation of α,β-Unsaturated Carboxylic Acids

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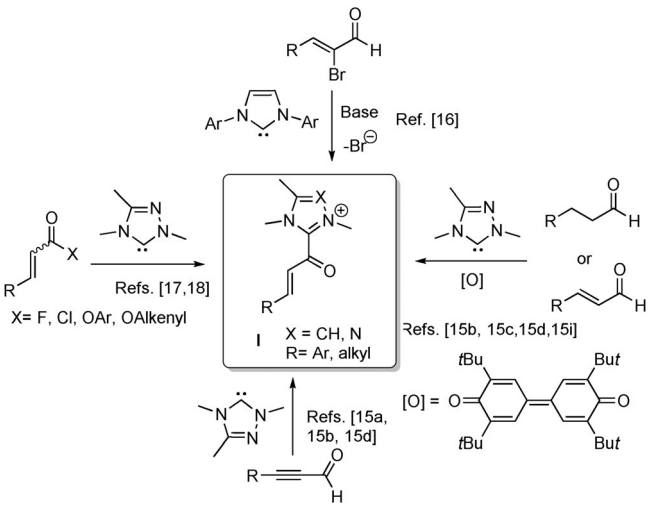
*Dedicated to Professor Huazheng Yang at Nankai University, China, on the occasion of her 80th birthday*

**Abstract:** A straightforward *N*-heterocyclic carbene (NHC)/LiCl-mediated synthesis of dihydropyranones from α,β-unsaturated carboxylic acids and 1,3-dicarbonyl compounds was realized through the in situ activation strategy. The key advantages of this protocol include ready availability and high stability of starting materials, good yields, and excellent enantioselectivity.

The dihydropyranone scaffold is widely found in numerous natural products and therapeutically significant compounds.[1] Their derivatives were also commonly utilized in the synthesis of substituted benzenoids, γ-lactones, pyridones, and so forth.[2] Thus, the efficient modification and assembly of dihydropyranone scaffolds has aroused great interest in organic synthesis.[3] So far, several strategies including lactonization of substituted δ-hydroxy acid derivatives,[4] oxidation of substituted dihydropyranone derivatives,[5] ring-closing metathesis,[6] and other miscellaneous methods[7] have been developed for the effective construction of dihydropyranone skeletons. Besides, enantioselective syntheses of dihydropyranones could be achieved successfully through the hydrogen-bonding catalyzed cyclization and metal-mediated multistep transformations.[8,9] Furthermore, a convenient enantioselective method to dihydropyranones from readily available material is still desirable.

In recent years, the substrate scope of *N*-heterocyclic carbene (NHC)-catalyzed reactions has been extended from aldehydes[10] to Michael acceptors,[11] ketenes,[12] and carboxylic acid derivatives.[13–14] Therefore, much effort has been devoted to the exploration of the facile formation and reactivity of NHC-bounded intermediates, for example, α,β-unsaturated acyl azolium generated easily from enals,[15b,c,d,i] ynals,[15a,b,d] α-bromoenals,[16] α,β-unsaturated acyl compounds,[17] α,β-unsaturated esters[14i,18] (**I**; Scheme 1), for it could serve as an important 1,3-bi-




**Scheme 1.** Generation of α,β-unsaturated acyl azoliums from aldehydes and carboxylate derivatives.

selectrophilic synthon to react with binucleophiles including 1,3-dicarbonyl compounds and β-enaminones to furnish six-membered cyclic compounds.[14h,15,21] The carboxylic acids are more readily available and stable compared with enals and the functionalized aldehydes including α-aryloxy acetal aldehydes and halogenated aldehydes employed previously in NHC-catalyzed reactions. Besides, they are less liable to generate an enolate than ketones and activated esters, and this might avoid some side reactions such as Aldol condensation, Claisen condensation, and Michael reaction. These two notable advantages make the carboxylic acids an ideal feedstock in organic synthesis.[19] Scheidt and co-workers reported that carboxylic acids could be transformed into NHC-bounded enolates via the in situ activation strategy in the presence of carbonyldiimi-

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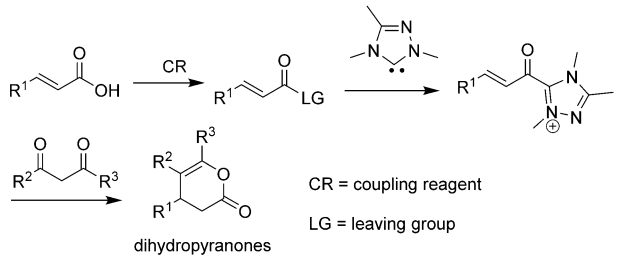
dazole (CDI).[20] In addition, Ye and co-workers demonstrated an elegant access to α,β-unsaturated acyl azlolium through mixed anhydride generated in situ from an α,β-unsaturated acid and acyl chloride.[21] Recently, our group described NHC-catalyzed β-activation of saturated carboxylic acid to assemble spirocyclic oxindolo-γ-butyrolactones in the presence of peptide coupling reagents through the in situ activation approach.[22] Since these activation reagents could promote the formation of homoenolates and amides successfully through the generation of esters or anhydrides, we envisioned that the in situ conversion of these activators and α,β-unsaturated acids into α,β-unsaturated acyl azloliums and the following reaction with 1,3-dicarbonyl compounds may pave a new avenue to dihydropyranones (Scheme 2).[14h,i,15,18,21] Additionally, Nair et al also reported an NHC-catalyzed effectual transformation of enal into dihydropyranone.[25]




**Scheme 2.** An NHC-catalyzed α,β-unsaturated acyl azoliums formation through the in situ activation of acids.

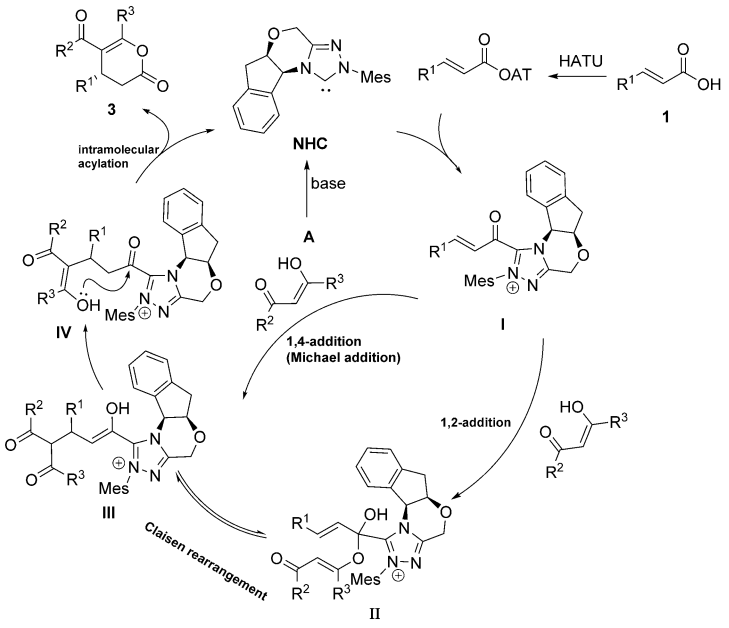
Initially, several coupling reagents including 2-(7-aza-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU), CDI, and 1,3-dicyclohexylcarbodiimide (DCC)/1-Hydroxybenzotriazole (HOBt) were screened to find a suitable activation reagent in the presence of chiral catalyst **A**. To our pleasure, we found that HATU was more effective to generate α,β-unsaturated acyl azlolium treated with 1,3-dicarbonyl compound **2a** in 36% yield with 81% *ee* compared with CDI and DCC.

Thus, we used α,β-unsaturated acid **1a** and 1,3-dicarbonyl compound **2a** as model substrates to optimize the reaction conditions in the presence of HATU and the results are shown in Table 1. Under the basic reaction conditions, no formation of desired product **3a** was observed in the absence of an NHC (Table 1, entry 1). Next, the influence of chiral catalysts was examined and chiral catalyst **A** showed good catalytic reactivity with 81% *ee* during the preliminary screening (Table 1, entries 2–5). Subsequently, the screening of organic and inorganic bases proved 1,4-diazabicyclo[2.2.2]octane (DABCO) to be the best among $Cs_2CO_3$, $K_2CO_3$, DABCO, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and *t*BuOK (Table 1, entries 6–9). The optimization of solvents identified toluene to be superior to THF and $CH_2Cl_2$ (Table 1, entries 10 and 11). Then LiCl, 4 Å MS, $La(OTf)_3$, $Y(OTf)_3$, and $Sc(OTf)_3$ were introduced into the reaction system to enhance the enantioselectivity. We found that the product *ee* value was improved up to 88% when the LiCl was added (Table 1, entries 12–16). After the optimization of the reaction temperature and the amount of LiCl, the *ee* increased to 91% with 62% yield when the reaction was carried out with DABCO as the base, toluene as solvent in the presence of 200 mol% of LiCl at 0 °C (Table 1, entry 19).

Under the optimized reaction conditions, the scope of the substrates was scrutinized (Table 2). Firstly, a variety of α,β-unsaturated acids were employed to investigate the influence of the nature of their substituents on this reaction. The electron-withdrawing groups (4-Br and 4-F) were well tolerated and gave the desired dihydropyranones **3b** and **3c**, respectively, in good yields with high enantioselectivities. Cinnamic acids with a *meta*-substituent (3-$FC_6H_4$, 3-$BrC_6H_4$) were compatible with the reaction conditions (**3e** and **3f**). The challenging conversion of cinnamic acid with an *ortho*-substituted (2-$MeC_6H_4$) was also successful (**3d**). Interestingly, the reaction involving disubstituted cinnamic acids (3,5-$Cl_2C_6H_3$) gave the desired product **3h** in good yield and excellent enantioselectivity. Notably, the heterocyclic and polycyclic α,β-unsaturated acids were well tolerated (**3g**, **3i**). Unfortunately, alkyl-substituted carboxylic acids (e.g., Me) were not successful. The scope of 1,3-dicarbonyl compounds was also probed and the results showed that methyl 3-oxobutanoate, ethyl 3-oxobutanoate, isopropyl 3-oxobutanoate, ethyl 3-oxopentanoate, and 1-phenylbutane-1,3-dione were applicable to this annulation, thus giving the desired products with good enantioselectivities (**3j**–**3n**).

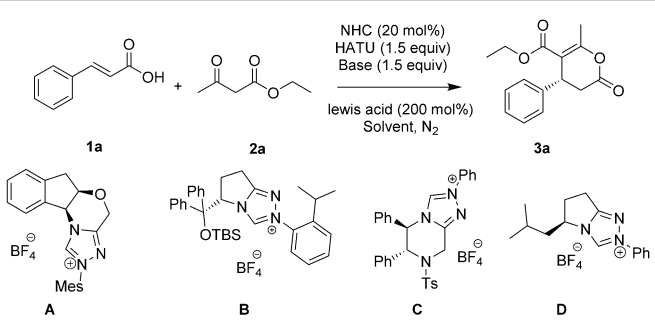
The optical rotation and HPLC analysis data of dihydropyranone **3j** were in good agreement with the reported results.[15g] Thus, the absolute configuration could be determined by comparison.

A possible catalytic cycle of this NHC-catalyzed reaction through the in situ activation strategy is shown in Scheme 3.




**Scheme 3.** Possible catalytic cycle.

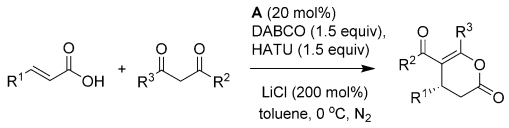
**Table 1.** Optimization of the Reaction Conditions.




| Entry | Catalystt | Lewis acid | *T* [°C] | Solvent | Base | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|---|---|---|---|
| 1 | – | – | rt | toluene | $Cs_2CO_3$ | – | – |
| 2 | **A** | – | rt | toluene | $Cs_2CO_3$ | 36 | 81 |
| 3 | **B** | – | rt | toluene | $Cs_2CO_3$ | – | – |
| 4 | **C** | – | rt | toluene | $Cs_2CO_3$ | – | – |
| 5 | **D** | – | rt | toluene | $Cs_2CO_3$ | – | – |
| 6 | **A** | – | rt | toluene | $K_2CO_3$ | trace | – |
| 7 | **A** | – | rt | toluene | DABCO | 58 | 84 |
| 8 | **A** | – | rt | toluene | DBU | trace | – |
| 9 | **A** | – | rt | toluene | *t*BuOK | trace | – |
| 10 | **A** | – | rt | THF | DABCO | 40 | 57 |
| 11 | **A** | – | rt | $CH_2Cl_2$ | DABCO | trace | – |
| 12 | **A** | LiCl | rt | toluene | DABCO | 61 | 88 |
| 13 | **A** | 4 Å MS | rt | toluene | DABCO | 58 | 77 |
| 14 | **A** | $Sc(OTf)_3$ | rt | toluene | DABCO | 54 | 69 |
| 15 | **A** | $La(OTf)_3$ | rt | toluene | DABCO | trace | – |
| 16 | **A** | $Y(OTf)_3$ | rt | toluene | DABCO | trace | – |
| 17 | **A** | LiCl | 40 | toluene | DABCO | 63 | 85 |
| 18 | **A** | LiCl | 10 | toluene | DABCO | 60 | 91 |
| 19 | **A** | LiCl | 0 | toluene | DABCO | 62 | 91 |
| 20 | **A** | LiCl | −10 | toluene | DABCO | 58 | 82 |
| 21[c] | **A** | LiCl | 0 | toluene | DABCO | 63 | 90 |
| 22[d] | **A** | LiCl | 0 | toluene | DABCO | 60 | 91 |

[a] Yield of the isolated product. [b] Determined by HPLC. [c] LiCl (150 mol%). [d] LiCl (220 mol%).

**Table 2.** Enantioselective Synthesis of Dihydropyranones




| Entry | $R^1$ | $R^2$ | $R^3$ | Product | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|---|---|---|
| 1 | Ph | OEt | Me | **3a** | 62 | 91 |
| 2 | 4-$BrC_6H_4$ | OEt | Me | **3b** | 78 | 91 |
| 3 | 4-$FC_6H_4$ | OEt | Me | **3c** | 85 | 90 |
| 4 | 2-$CH_3C_6H_4$ | OEt | Me | **3d** | 93 | 92 |
| 5 | 3-$FC_6H_4$ | OEt | Me | **3e** | 88 | 91 |
| 6 | 3-$BrC_6H_4$ | OEt | Me | **3f** | 83 | 91 |
| 7 | 2-Naphthyl | OEt | Me | **3g** | 90 | 91 |
| 8 | 3,5-$Cl_2C_6H_3$ | OEt | Me | **3h** | 84 | 91 |
| 9 | Thienyl | OEt | Me | **3i** | 73 | 94 |
| 10 | Ph | OMe | Me | **3j** | 65 | 90 |
| 11 | Ph | O*i*Pr | Me | **3k** | 80 | 90 |
| 12 | 4-$CH_3C_6H_4$ | O*i*Pr | Me | **3l** | 76 | 91 |
| 13 | Ph | OEt | Et | **3m** | 69 | 90 |
| 14 | Ph | Ph | Me | **3n** | 83 | 85 |
| 15 | Me | OEt | Me | **3o** | – | – |

[a] Yield of the isolated product. [b] Determined by HPLC.

The addition of NHC to the α,β-unsaturated ester, which was formed in situ from the α,β-unsaturated acid and HATU, gave the corresponding α,β-unsaturated acyl azolium intermediate **I**. From this point onwards, two approaches could be viable. One could be that **I** reacted with 1,3-dicarbonyl compounds through an 1,4-addition and intramolecular acylation to deliver the final dihydropyranone and regenerated the NHC catalyst.[18,23] The other feasible approach was that the 1,2-addition of intermediate **I** and the dinucleophile, followed by a Claisen rearrangement and intramolecular acylation, could also liberate the NHC catalyst and furnish the ultimate product.[15a,24]

In summary, we have discovered an NHC/LiCl-mediated enantioselective [3+3] cyclocondensation of α,β-unsaturated carboxylic acids with 1,3-dicarbonyl compounds to afford the dihydropyranones through in situ activation. The mild conditions, easily available materials, and high enantioselectivities make this approach attractive in organocatalysis. Other NHC-catalyzed reactions involving carboxylic acids through in situ activation are underway in our laboratory.

## Experimental Section

### General Procedure

**1** (0.3 mmol), **2** (0.2 mmol), DABCO (33.6 mg, 0.3 mmol), HATU (114 mg, 0.3 mmol), LiCl (16.8 mg, 0.4 mmol), and chiral catalyst **A** (17 mg, 0.04 mmol) were added to a Schlenk tube (10 mL) equipped with a magnetic stir bar. The tube was closed with a septum, evacuated, and refilled with nitrogen. Freshly distilled toluene (4 mL) was added and the mixture was stirred for 12 h at 0 °C. After the completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure to afford the residue. The residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10, v/v).

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**Keywords:** asymmetric synthesis · carbenes · carboxylic acids · dihydropyranones · enantioselectivity

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