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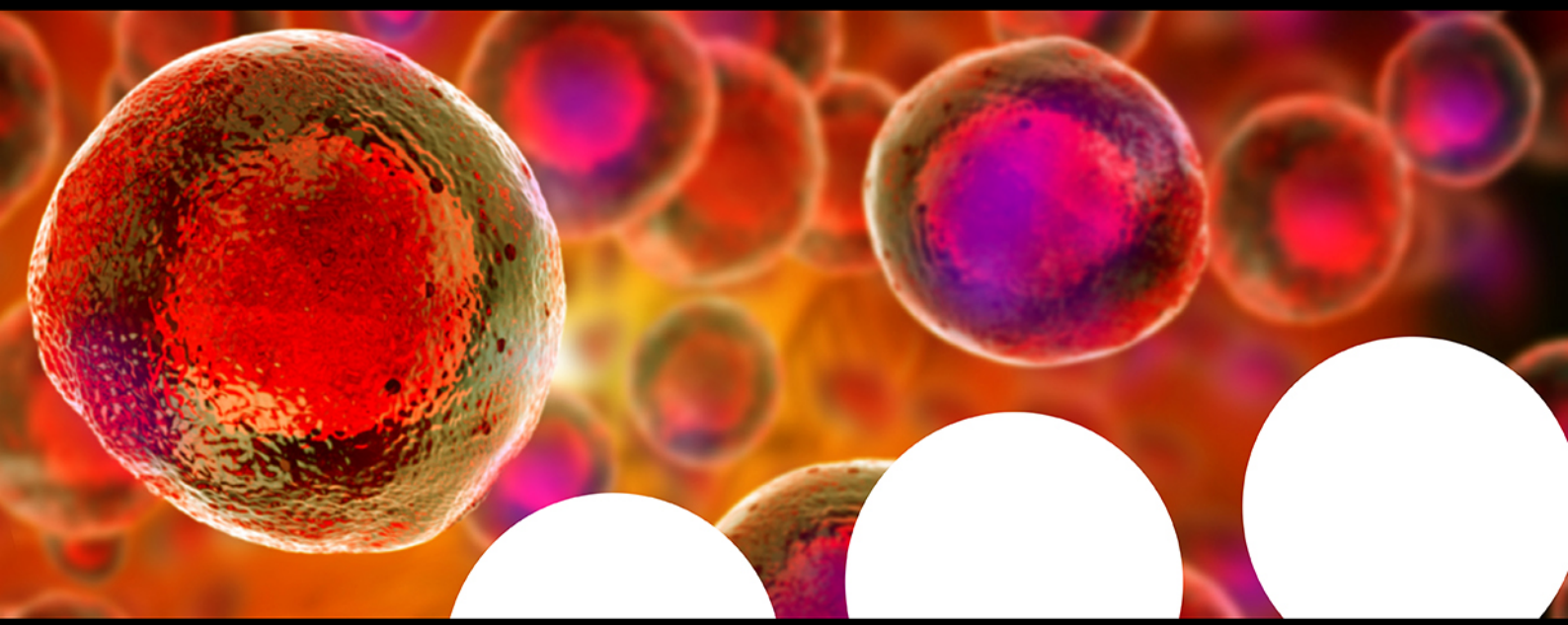

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Enantioselective Dual Catalysis of *N*-Heterocyclic Carbene and Hydrogen-Bond Donor Organocatalysts

Hongling Wang,[a] Yonggui Robin Chi,*[b] and Xuan Huang*[a]

N-heterocyclic carbene (NHC) catalysis has become a versatile catalysis strategy for building molecules via unique reaction modes. Dual catalytic processes using NHCs in combination with additional modulating agents such as another organocatalyst or transition-metal catalyst have also been studied. The clear selection of cocatalysts has led to enhanced reactivity, increased yields, and/or improved stereoselectivity. This minireview is to provide readers with a brief overview of the development and applications of NHC and hydrogen-bond donor for dual catalytic reactions.

1. Introduction

The development and discovery of fruitful catalytic methods for the transformation of sophisticated molecules is a continuing challenge. *N*-Heterocyclic carbene (abbreviated as NHC or carbene) catalysis has emerged as a powerful strategy in this regard, which allows for access to catalytically converted acyl enolate, homoenolate, acyl anion, azolium dienolate, acylazolium and α,β-unsaturated acylazolium, and radical intermediate.[1] Besides, NHCs can be used to activate aldehydes, esters, imines, activated ketones, and alkenes for both normal polarity and polarity-inversion reactions via either electron-pair-transfer or single-electron-transfer processes.[1c] However, cooperative catalysis with NHCs has remarkably increased reaction efficiency and selectivity and expanded beyond a single-catalyst manifold. A number of new activation and reaction modes were developed, with rich synthetic transformations and new mechanistic understanding established (Figure 1).[2]

Transition metal catalysts are widely explored to accomplish unique activations and chemical transformations for the synthesis of functional molecules.[3] It has been envisioned that merging transition metal catalysts with NHCs should provide an effective strategy for chemical transformation.[4] Extensive investigations have been carried out in the development of cooperative catalytic reactions with transition metals and NHC organic catalysts during the past decade.[5] Compared with the strong binding interactions between NHCs and transition metals, the interactions between NHCs/Lewis acids[2e,6] and NHCs/Brønsted acids[7] are much weaker. As a result, it would be much easier for the NHC organic catalysts to be compatible with cocatalysts. Several previous reviews covering multicatalysts systems have already tried to simplify the classification,[8] but with the growing complexity and diversity of multicatalysis, clear systematization is tough. The goal of this minireview, we will supply a comprehensive review of the enantioselective cooperative catalysis of *N*-heterocyclic carbene and hydrogen-bond donor in a single-flask reaction.

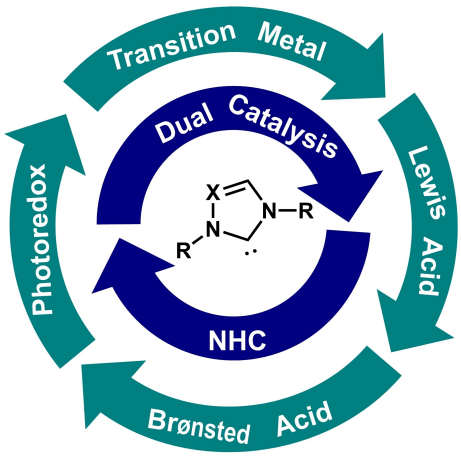

Figure 1. Cooperative catalysis with NHCs.

2. Bifunctional *N*-Heterocyclic Carbenes

2.1. Structures of Bifunctional *N*-Heterocyclic Carbenes

As nucleophilic carbenes in transition metal catalysis and organocatalysis, there are many different classes of carbene precursors with various substitution patterns, ring sizes, and degrees of heteroatom stabilizations, and many different types of carbenes have been reported.[1b] Typical subclasses of bifunctional chiral azolium precursors are presented in Figure 2.

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2.2. Synthesis of Bifunctional *N*-Heterocyclic Carbene Precursors and their Applications

With a majority of *N*-heterocyclic carbene catalysts reported, several methods have been described in some journals.[9] This section will focus on the synthesis of bifunctional carbene precursors and their application.

The bifunctional NHC catalysis is initiated by thiazolylalanine-derived catalysts, although the concept is simple. The peptide-based thiazolium catalyst **A** found to function as an enantioselective catalyst for an intramolecular Stetter reaction[10] and aldehyde-imine cross-coupling[11] by Miller and coworkers in 2005 (Scheme 1).

In 2013, Coquerel and Rodriguez has been prepared a series of original imidazolinium salts functionalized with urea-type hydrogen-bond donor moieties.[12] In the transition metal catalysis, the hydroxy-imidazolium salts **9** were selected as enantioselective copper ligands and first prepared by Mauduit and coworkers.[13] Actually, the urea-type derivatives imidazolinium salts **B** would be obtained from the corresponding amino-imidazolinium salts **11** derived from hydroxy-imidazolium salts **9**. This approach is the use of commercial and abundant natural chiral amino acids as the starting material. Besides, the synthetic procedure isn't difficult and the pure desired products, the 1,3-imidazolinium salts **B**, are obtained in excellent yields (Scheme 2).

The corresponding 1,3-imidazolinium carbenes **B** are proved competent as organocatalysts in an enantioselective reaction involving homoenolate intermediate from enals (Scheme 3).

Until now, *N*-heterocyclic carbene catalysis using stable carbenes is dominated not by thiazolium or imidazolium salts but triazolium salts. The first triazolium scaffolds for catalysis were introduced by Enders and Teles in 1995[14] and these catalysts have been revealed in many different transformations afterward. At the same time, the vast majority of bifunctional NHCs are derived from triazolium precursors (see triazolium salts **C** from Figure 2). In 2008, Ye and Enders' coworkers independently developed the *L*-pyroglutamic acid-derived carbene precursor **C14**–**C16** bearing a trialkylsilyloxy group.[15] Based on the carbene precursor **C14**–**C16**, Ye and coworkers reported the silyl group could be removed under acid to obtain a free hydroxy group[16] and thus resulting in bifunctional carbene precursor **C6**–**C13** (Scheme 4). These bifunctional NHCs showed marvelous effects due to additional activation via H-bonding. The type of *L*-pyroglutamic acid-derived bifunctional NHCs bearing a free hydroxyl group, which the field contributions are acknowledged, has been comprehensively and exhaustively reviewed with the most recent by the Ye group.[17] Therefore, we will not fully discuss the application of *L*-pyroglutamic acid-derived bifunctional NHCs in this section.

Ye and coworkers successfully got the benzoin products in good to high yields with up to 99% ee using the bifunctional

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Xuan Huang received his bachelor's degree in applied chemistry from Sichuan University in 2009. In 2014, he completed his Ph.D. under the supervision of Prof. Bo Liu from Sichuan University. Following that, he carried out two years of postdoctoral training at the School of Physical and Mathematical Sciences at Nanyang Technological University Singapore. He then joined the international joint research center for molecular science and the college of chemistry and environmental engineering, Shenzhen University as a research associate. His research interests include NHC catalyst for the total synthesis of natural products, green chemistry, and industrial application.

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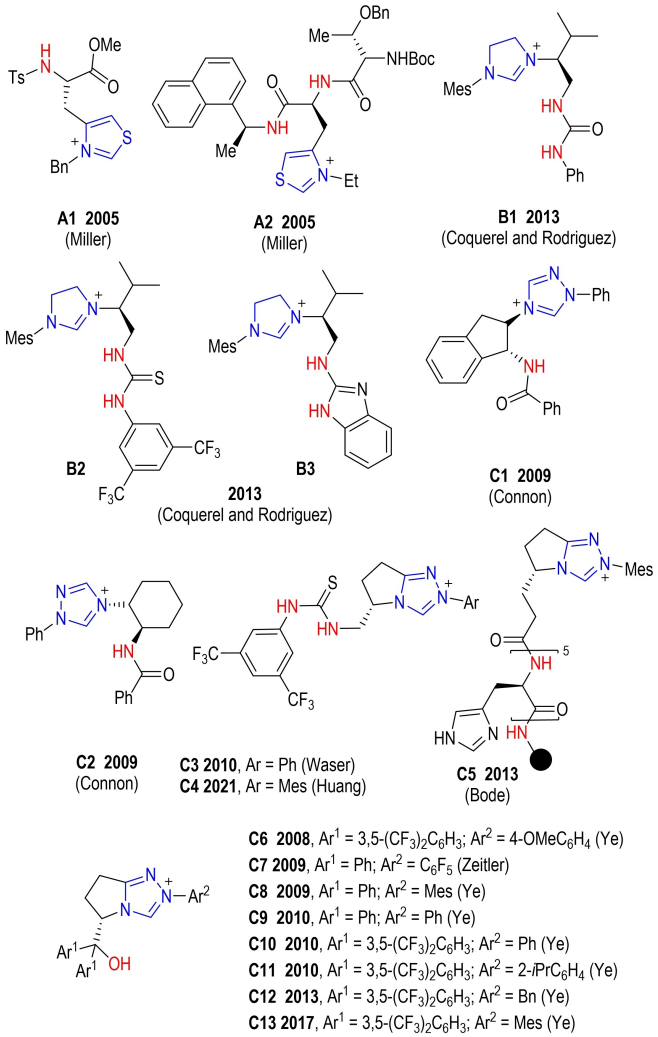
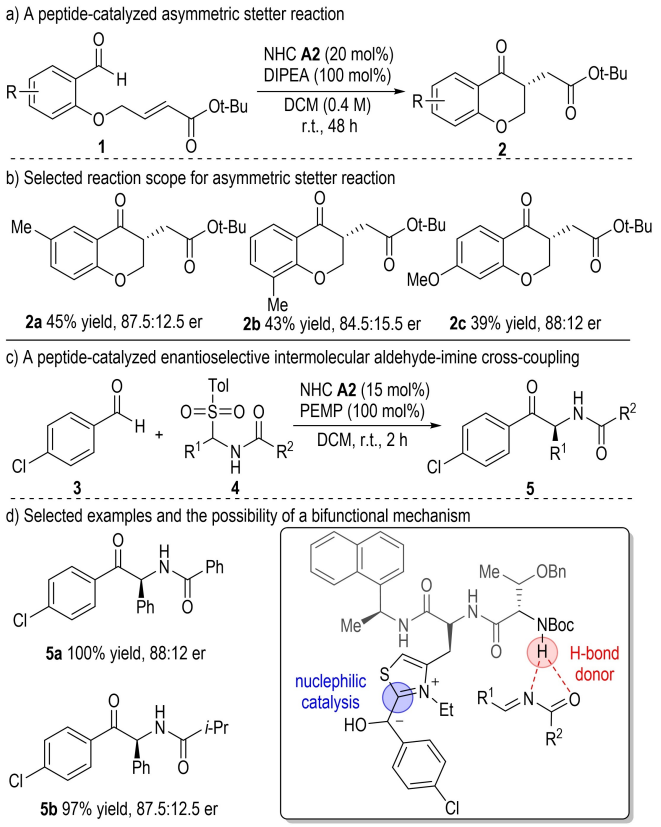


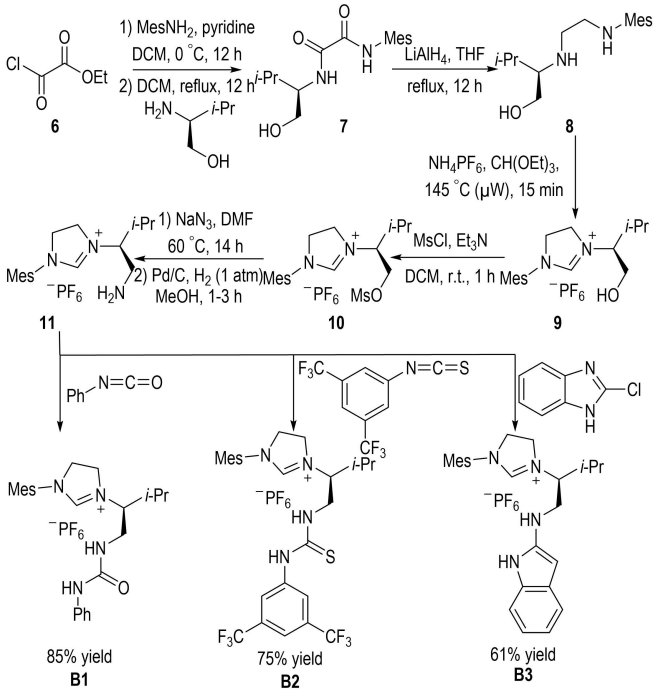
Figure 2. Selected bifunctional NHC precursors.

carbenes strategy.[18] In 2013, the same group developed an aza-benzoin reaction of enals with activated ketimines with excellent yield and ee value (Scheme 5a).[19] Interestingly, this reaction did not carry out using normal precatalyst **C14**. It was possible competing for reaction through the homoenolate or enolate intermediates, which were totally suppressed by the bifunctional NHCs with a free hydroxyl group and a sterically appropriate substituent. Besides, the L-pyroglutamic acid-derived bifunctional NHCs were efficiently used as catalysts for the [2 + 4] cycloaddition of ketenes **26** and 3-aroylcoumarins **27** (Scheme 5b).[20] It is worth noting that the normal precatalyst **C15** provided the desired product with worse levels of diastero- and enantiocontrol than bifunctional NHCs **C9**. The free hydroxyl group of the carbene has dramatically affected the transition state. The author speculated the hydrogen bonding between the hydroxyl group of the azolium enolate and 3-aroylcoumarins directed the facial selectivity (**TS F**).

In 2009, Connon and coworkers designed a new class of 2-aminocyclopentan-1-ol derived triazolium salt precursors incorporating hydrogen bond-donating substituents.[21] The synthesis



Scheme 1. Miller's bifunctional peptide-based thiazolium NHCs.



Scheme 2. Synthesis of hydrogen-bond-donor functionalized imidazolium salts.

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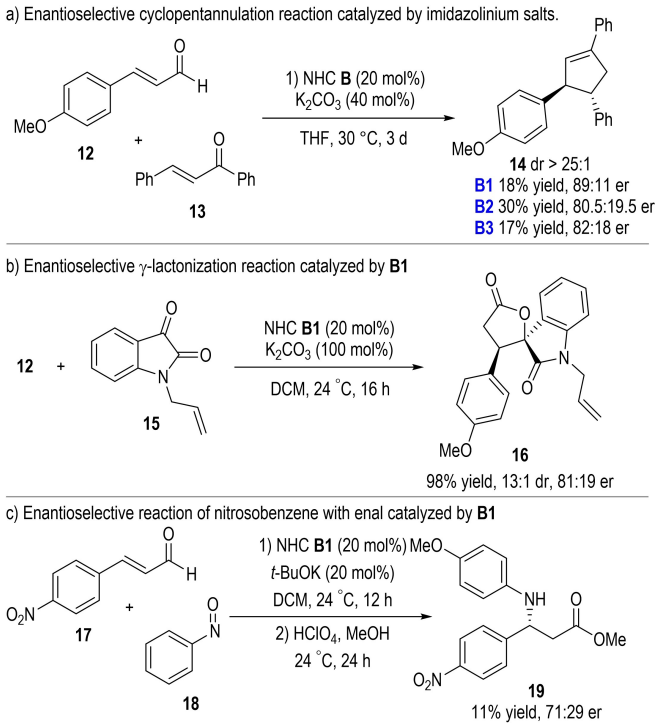
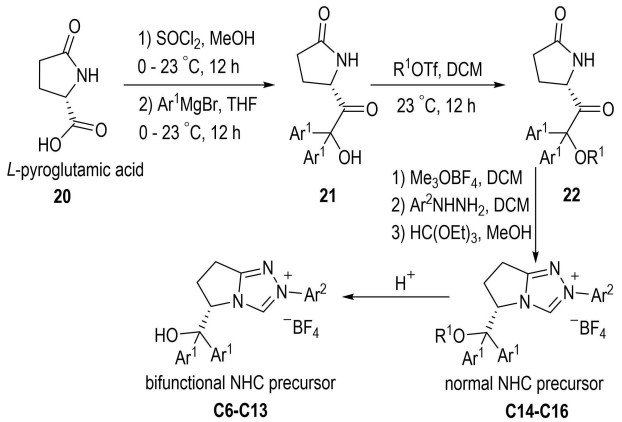
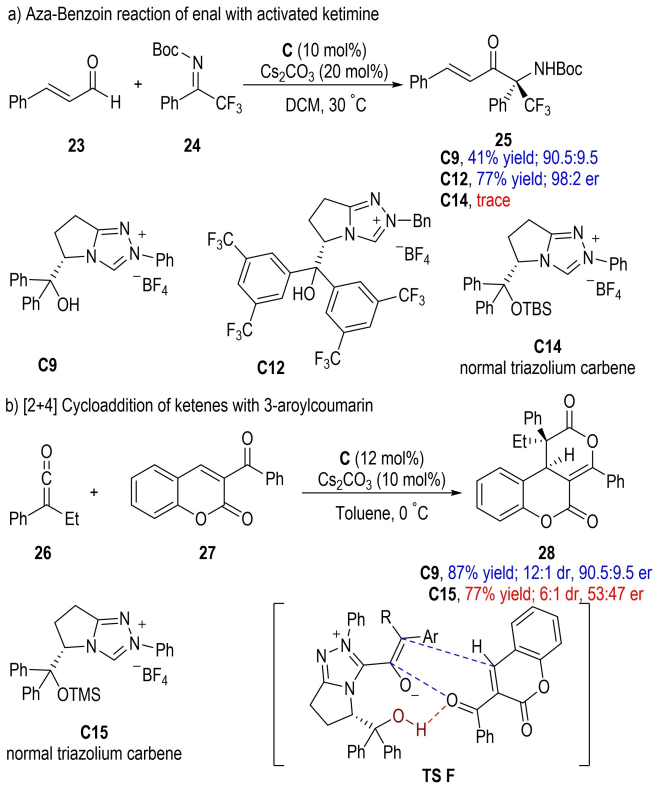


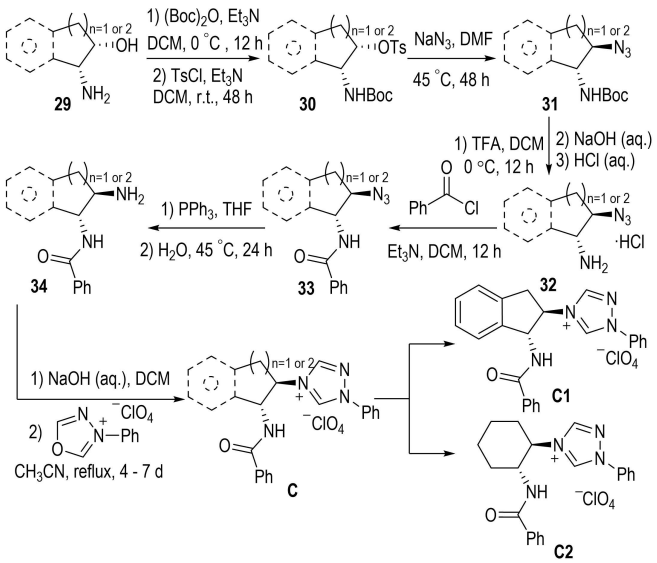
Scheme 3. Enantioselective reactions involving homoenolate intermediates catalyzed by imidazolinium salts **B**.



Scheme 4. Synthesis of *L*-pyroglutamic acid derived bifunctional NHCs.



Scheme 5. Synthesis of *L*-pyroglutamic acid derived bifunctional NHCs.



Scheme 6. Synthesis of precursors **C1** and **C2**.

of catalysts **C1** and **C2** were prepared via hydrochloride salts **32** and comprehensive steps are shown in Scheme 6. And the bifunctional triazolium precatalyst **C1** and **C2** promote the asymmetric benzoin condensation with excellent efficiency and unprecedented enantioselectivity.

The first bifunctional carbenes bearing a (thio)urea moiety as an H-bond donor group is reported by Waser in 2010,[22] which have been highly successful as H-bond donors in catalysis. Different analogs could be accessed in several steps from pyroglutamic acid in good overall yields (Scheme 7a). The synthesized carbenes were active enantioselective benzoin condensation of a range of aromatic aldehydes.

Very recently, Huang and Chen reported a bifunctional NHC bearing a (thio)urea moiety with an embedded H-bonding that shows remarkable tolerance of various Michael acceptors in an enantioselective aza-conjugate addition reaction (Scheme 7b).[23] The synergy between the hydrogen-bond acceptor (NHC) and the hydrogen-bond donor (thiourea) was essential to both the catalytic activity and enantiomeric control.

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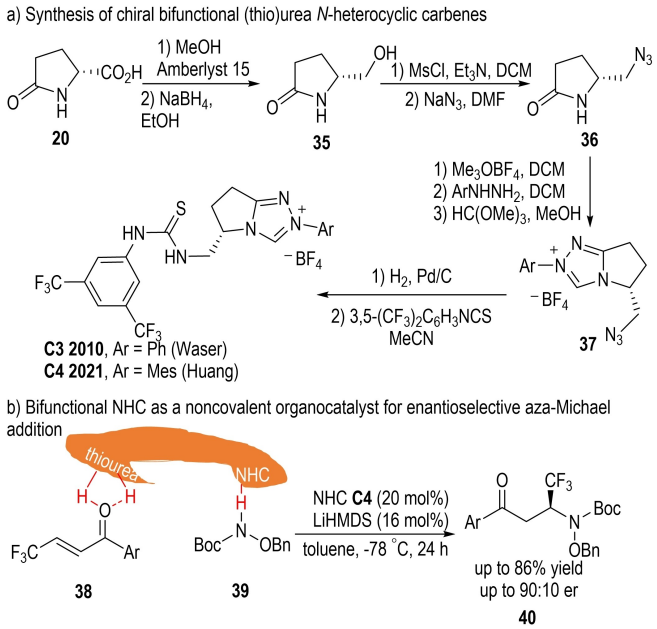
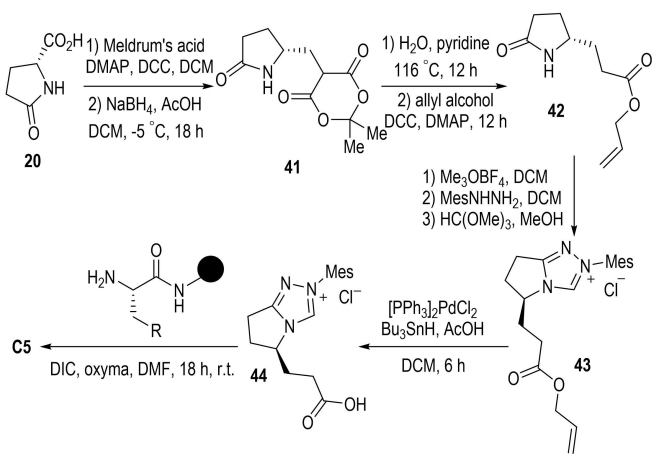


Scheme 7. Synthesis of chiral bifunctional (thio)urea carbenes and aza-Michael addition reaction.

More interestingly, the synthesis of polymer-supported peptide-carbenes **C5** multifunctional catalyst is prepared a solid-phase peptide (Scheme 8). Bode and coworkers have demonstrated that the bifunctional catalyst cooperatively facilitates the redox amidation reaction of aldehydes and amines with a high yield. Unfortunately, their work didn't evaluate enantioselective redox amidations.[24]

In general, the bifunctional carbene catalyst evaluation studies strongly support the involvement of hydrogen bond donation by the catalyst in the stereocenter forming step of the catalytic cycle.



Scheme 8. Synthesis of chiral carboxylic acid functionalized triazolium salt **C5**.

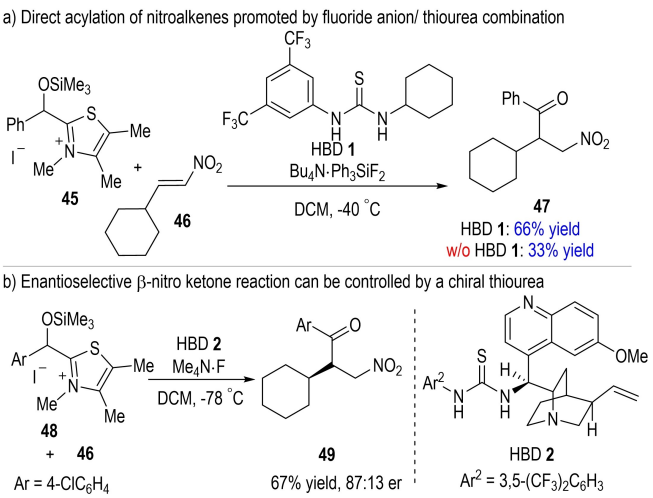
3. Cocatalyzed Reaction Involving NHC and Hydrogen-Bond Donor

3.1. Cocatalyzed Reaction Involving NHCs and (Thio)urea

In 2006, Scheidt and coworkers reported the direct nucleophilic acylation of nitroalkene to get β-nitro ketones by the combination of a fluoride source with silyl-protected thiazolium carbinols **45**[25] (Scheme 9a). Surprisingly, this transformation further improved yield by 33% to 66% with the addition of thiourea additive (HBD **1**). Besides, the β-nitro ketone **49** formed stereocenter in this reaction can be controlled by chiral thiourea in 67% yield and 87:13 er (Scheme 9b). Although the reaction is simple, this is the first report of carbonyl anion, which could undergo a 1,2-hydrogen shift from thiazolium carbinol **45**, with thiourea promoted reaction.

After the seminal report, Chi and coworkers reported the first organocatalytic enantioselective sulfonation **51** of α,β-unsaturated ketones **13** by cooperative carbene/thiourea/tertiary-amine multicatalysis in 2013 (Scheme 10).[26] In this reaction, they described a highly enantioselective cascade reaction that consisted of an NHC **C17** catalyzed N–S bond cleavage obtained toluenesulfonate ion and the stereoselective Michael addition that was induced by a thiourea-tertial amine (HBD **3**) based multifunctional cocatalyst. This protocol did not proceed with enantioselective sulfonation without HBD **3**, but good yields and excellent enantioselectivities were achieved in the presence of a thiourea-tertial amine (HBD **3**).

The further elegant transformation has been developed via a new model for NHC catalyzed azolium-bound orthoquinone methides intermediate (*o*-QMs) with urea by the Chi group (Scheme 11).[27] Additionally, the article described a urea/NHC cooperative catalytic process, in which an achiral urea cocatalyst significantly and consistently improved the enantioselectivity of the reaction. They found that using achiral thiourea (HBD **4**) as a cocatalyst could improve the desired product **54** er values of



Scheme 9. Direct nucleophilic acylation of nitroalkenes promoted by thiourea/fluoride combination.

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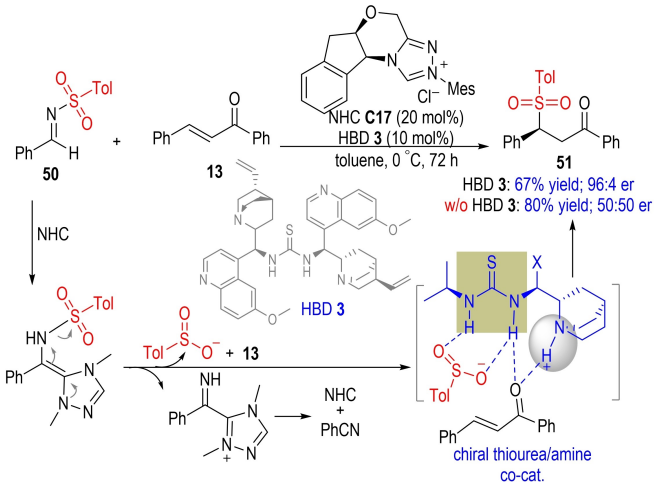
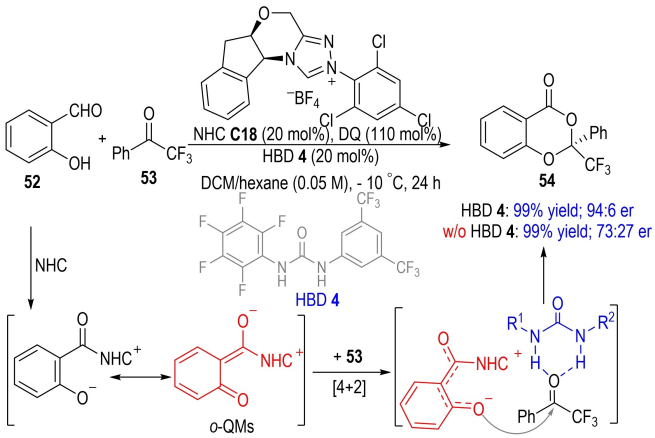


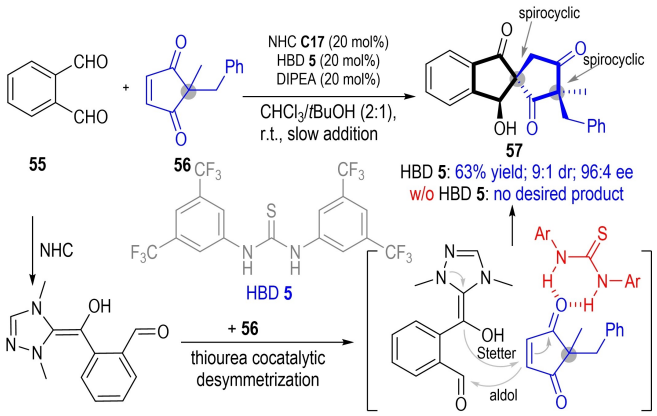
Scheme 10. Enantioselective catalytic sulfonation of enones.



Scheme 11. Simple aryl aldehyde activation and O–H bond functionalization.

from 73:27 to 94:6. This result illustrated that a hydrogen-bond donating (urea or thiourea) interaction was likely to play an important role in controlling and enhancement of the reaction enantioselectivity.

In 2019, Chi and coworkers studied a carbene- and thiourea-cocatalyzed desymmetrization process with the simultaneous installation of a spirocyclic core.[28] The spirocyclic core **57** was obtained from the phthalaldehyde **55** and was slowly added to the reaction mixture with cyclic enone **56** at room temperature (Scheme 12). It is interesting to note that the use of a thiourea cocatalyst is critical to turn on this reaction, as no product was formed in the absence of thiourea (HBD **5**). The authors proposed that the thiourea cocatalyst probably activates the 1,3-cyclopentenedione **56** substrate through hydrogen bonding. Based on this work, Biju's group developed the desymmetrization of prochiral maleimides via an NHC-catalyzed asymmetric Stetter/aldol/oxidation sequential reaction also with thiourea cocatalyst in 2021.[29]

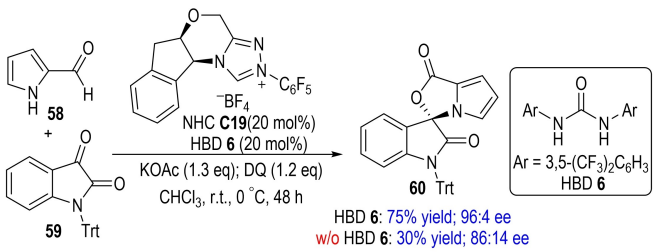


Scheme 12. Carbene- and thiourea-catalyzed quick access to sophisticated spirocyclic molecules.

Shortly after these studies, Jin and coworkers demonstrated the aromatic nitrogen atoms of heteroaryl aldehyde was activated by NHC catalysts to react with ketones (Scheme 13).[30] However, the aza-[3+2] reaction between pyrrole aldehyde **58** and N-Trtisatin **59** proceeded poorly yield and enantioselectivity just using NHC **C19**, when the scope of ketones. The yield and enantioselectivity of the corresponding desired product **55** could be dramatically improved by the addition of a urea molecule (HBD **6**) that could successfully enhance the reaction er from 86:14 to 96:4.

The thiourea was also found to be efficient catalysts for the [3+3] annulation of 2-substituted 1,4-naphthoquinones **61** with α,β-unsaturated aldehydes **23**.[31] Interestingly, the synthesis of functionalized dihydrocoumarins **62** by performing the reaction using 20 mol% thiourea and 4 Å MS as additives was formed in 84% isolated yield (Scheme 14a). Furthermore, preliminary studies on the enantioselective version of the reaction were also carried out (Scheme 14b).

The carbene catalyzed oxidative reaction of functionalized aldimines as 1,4-dipole precursors and the asymmetric reaction was independently developed by Chi and Fu et. al.[32] More importantly, Fu and coworkers demonstrated the use of carbene catalysts with the same absolute configuration, leading to both (R)- and (S)- enantiomers of six-membered heterocycles **66** (Scheme 15). Interestingly, the enantioselectivity could be fully switched by achiral thiourea (HBD **5**). In this case, the



Scheme 13. Carbene-catalyzed enantioselective aromatic N-nucleophilic addition of heteroarenes to ketones.

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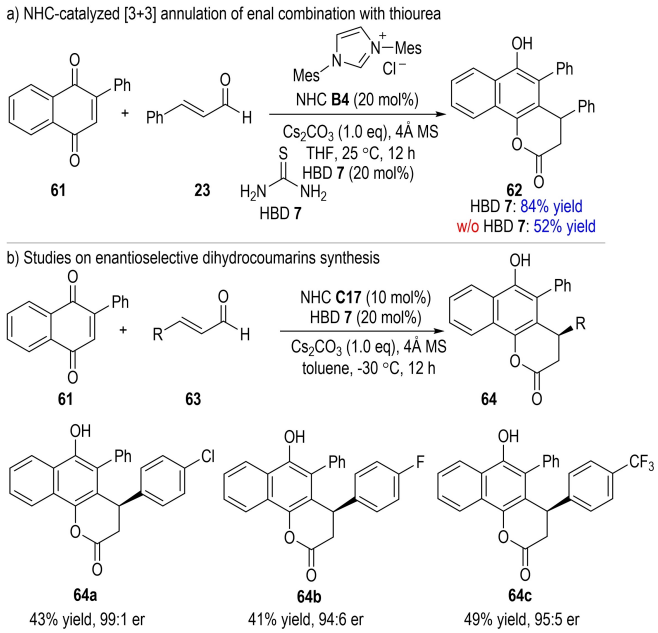
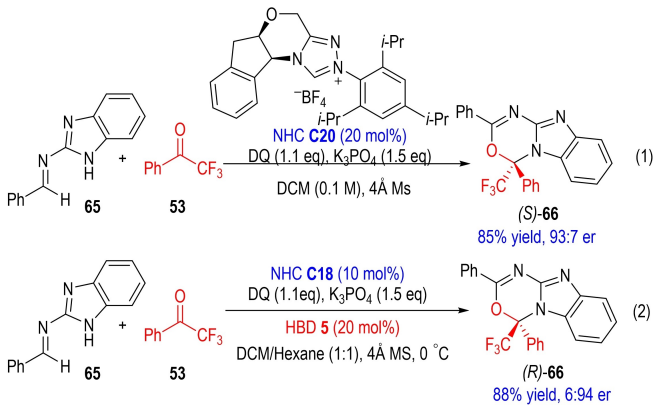


Scheme 14. NHC-catalyzed [3 + 3] annulation by Biju.



Scheme 15. Activation of aldimines under carbene organocatalysis.

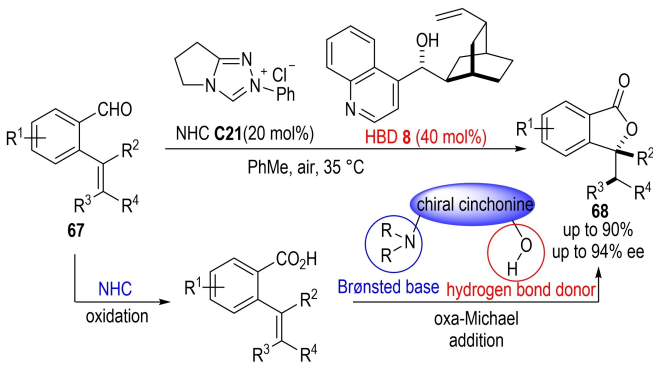
hydrogen-bonding donors play a unique role in the controlling of stereocenter in organic synthesis. To gain more insight into the key factors for determining the enantioselectivity, the DFT calculation indicated the enantioselectivity could be switched by weakening the C–H···F hydrogen bond interactions.

3.2. Cocatalyzed Reaction Involving NHCs and Other Hydrogen-Bond Donors

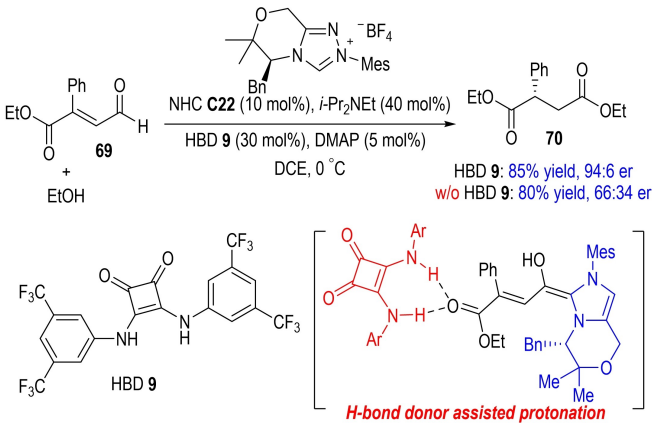
The utilization of (thio)urea as hydrogen bonding donors have been well combined with carbene organocatalysis. This strategy was then successfully expanded to the other type of hydrogen-bond donors. In 2014, Youn reported an NHC/cinchonine dual catalyzed asymmetric synthesis of 3-substituted phthalides **68**.[33] The cinchonine (HBD **8**) is used as bifunctional catalysts containing amine and H-bond donor moieties could significantly improve the efficiency of these asymmetric domino cocatalysts (Scheme 16).

Except for the improvement of stereoselectivity for the reaction, multicatalysis is also useful to develop new transformations because of their additional interaction via hydrogen bonding. In 2015, Scheidt and coworkers disclosed the cooperative NHC/H-bond donor (HBD **9**) catalyzed the enantioselective β-protonation reaction of enals **69** (Scheme 17).[34] The authors envisioned that the HBD **9** to induce hydrogen bonding interactions with enal **69** would be able to dramatically improve the enantioselectivity of β-protonation. This novel cooperative process is a new, metal-free protocol for succinic esters and the strategy expands the concepts and utility of carbene.

In an analogous multicatalysis, the enantioselective lactonization **72** generated from the simple enanls **23** and α-ketoesters **71**, which has been discovered using a new ternary cooperative catalytic system (Scheme 18).[35] The highly selective annulation was achieved by using a combination of a chiral NHC, a hydrogen bond donor, and a metal salt, facilitating the self-assembly of the reactive partners. This dual catalytic system could improve both reaction yield and enantioselectivity.



Scheme 16. Youn's NHC/cinchonine catalyzed lactonization.



Scheme 17. Enantioselective β-protonation by a cooperative catalysis strategy.

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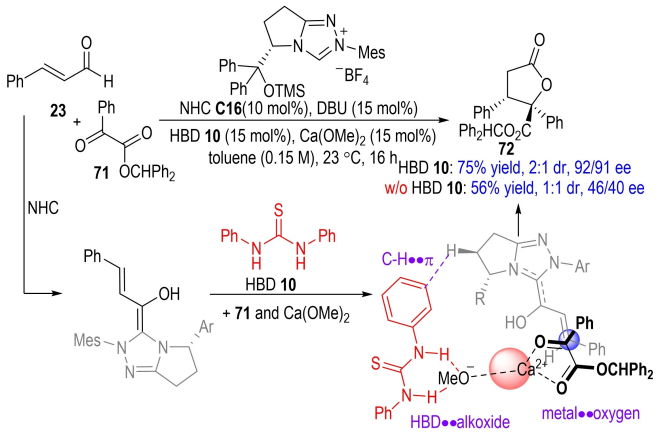

Scheme 18. A Cooperative ternary catalysis system for asymmetric lactonizations of α-ketoesters.

4. Summary and Outlook

In summary, dual catalysis involving NHC and hydrogen-bond donor organic catalysts has received considerable attention. Main advances include bifunctional molecules where NHC and the hydrogen-bond donor moieties are incorporated in the same molecules and combined use of two individual molecules of NHC and hydrogen-bond donor catalysts. Examples of hydrogen-bond donor catalysts include thioureas, ureas, and cinchonine et. al. These dual catalysis methods have provided synthetic solutions that are difficult to achieve with only one of the two catalysts.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Enantioselective · Dual catalysis · *N*-heterocyclic carbene · Hydrogen-bond donor · Organocatalysis

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