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## Digest paper Recent topics in dual hydrogen bonding catalysis

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Dual hydrogen bonding donors have received much attention in

the area of organocatalysis after the discovery of chiral thiourea

derivatives that function as asymmetric catalysts.<sup>1</sup> The rigid inter-

action between dual hydrogen bonding donors and Lewis basic

functionalities can be effective for electrophilic activation as well

as transition-state organization. Many thiourea derivatives bearing

various chiral scaffolds have been developed to enable a variety of

asymmetric transformations. As significant advances have been

made in this field and introduced by a number of excellent reviews

and books, this digest focuses on the most recent topics (since 2013) to complement the previous contributions.<sup>2</sup> First, recent

progress on enhanced hydrogen bonding donor catalysis will be addressed. Although research into this topic has continued since the early days of this field, new active catalysts have still been

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#### Contents

Introduction

#### ABSTRACT

Dual hydrogen bonding donors have received much attention in the area of organocatalysis after the discovery of chiral thiourea derivatives that act as asymmetric catalysts. This digest focuses on recent advances in this area categorized in the following three topics: 1) enhanced hydrogen bonding donor catalysis; new scaffolds with improved reactivity and selectivity are introduced and compared with established catalysts; 2) anion binding catalysis; recent advances in terms of catalysts and their applications is addressed; 3) multiple catalysis involving dual hydrogen bonding catalysts; a relatively new field of dual hydrogen bonding donor catalysis combined with other catalysis is introduced.

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emerging. Second, the new discovery of anion binding catalysis and its development will be discussed. Once the concept of this catalysis was broadly accepted and various compounds have been recognized as anion binding agents, more attention has been drawn to such catalysts for innovative processes. As the result of the advances described above, multiple catalysis involving dual hydrogen bonding donor catalysis has turned out to be possible in a number of asymmetric reactions. In particular, multiple catalysis driven not by a multi-functional single catalyst, but by multicatalysts with different functions, will be covered in the last part of this review.

#### Enhanced hydrogen bonding donor catalysis

In the early stage of the development of thiourea catalysis, it was found that the acidity of the hydrogen bonding donors influenced the catalytic performance. One successful example was introduction of the 3,5-bis(trifluoromethyl)phenyl group as an

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Scheme 1. Relative reaction rates in the presence of catalyst A or B.

electron-withdrawing group in a thiourea, which provided enhanced acidity with high catalytic performance not only in the reaction rate but also in the stereoselectivity.<sup>3,4</sup> Ongoing research to increase the acidity of hydrogen bonding catalysts led to the new reactive thiourea **B** bearing a 3-pyridinium group (Scheme 1).<sup>5</sup> The enhanced reactivity of pyridinium thiourea **B** over Schreiner's thiourea **A** was observed in Friedel-Crafts alkylation of *N*-methylindole **1** with *trans*- $\beta$ -nitrostyrene **2** in the presence of these catalysts. This result indicates that the two charged centers in **B** are more effective than the four CF<sub>3</sub> groups in **A**, resulting in a highly active catalyst that is 400 times more reactive.

Similar approaches to expand the potential of hydrogen bonding catalysis have centered around ionic hydrogen bonding donors such as guanidinium, aminopyridinium, (amino)quinolinium, and aminophosphonium.<sup>6</sup> We also focused on pyridinium phosphoramide **C** as a highly acidic dual hydrogen bonding catalyst (Scheme 2).<sup>7</sup> In the structure of **C**, the pyridinium ring can be expected to function as an electron-withdrawing group (EWG) which activates the adjacent amide proton, generating an acidic imide proton. We envisioned a strong dual proton donor could arise from the imide-like proton cooperating with the pyridinium proton in **C**. Catalyst screening employing **C-E** in the Diels-Alder reaction between amidediene **4** and maleimide **5** revealed that the simultaneous presence of both protons in **C** is necessary for good reactivity and enantioselectivity. The best catalyst in our study was **F** having a methoxy group on the pyridine ring, implying



Scheme 2. Pyridinium phosphoramide as a dual H-bonding donor catalyst.



Scheme 3. Bisthiosuqaramide as a highly soluble and acidic dual H-bonding donor catalyst.

a balance of the stability and acidity of the pyridinium phosphoramide is crucial.

Neutral hydrogen bonding catalysts have also been developed by modifying the established scaffolds. Rawal and co-workers have developed dithiosquaramide to override the inherent drawbacks of the original squaramides, such as their low solubility in nonpolar solvents which limit their use in some reactions (Scheme 3).<sup>8</sup> Thiosquaramides feature not only a higher solubility in a range of solvents but also increased acidity than those of their oxo-counterparts. The performance of new catalyst I was demonstrated in the previously unreported enantioselective conjugate addition of barbituric acid derivative 7 to nitroalkene 2, showing superior results to those of the corresponding thiourea G and squaramide **H**. The reaction with I proceeded within 10 h even at a catalyst loading of 0.05 mol% with full conversion and 96% ee, indicating an outstanding catalytic ability of the thiosquaramide.

Another possibility for a different scaffold from conventional hydrogen bonding donors has been investigated. Pittelkow and co-workers have been examined the ability of croconamides as anion receptors. Tetrahydropyranylation of phenol **10** with dihydropyran **9** was chosen to compare the catalytic performance of croconamide **J** with Schreiner's thiourea **A** (Scheme 4).<sup>9</sup> Although thiourea **A** was reported to catalyze the present reaction under neat conditions, the reaction under dilute conditions applied in this study led to no conversion. On the other hand, the reaction proceeded in the presence of catalyst **J**. Furthermore, the authors investigated the anion binding affinity of croconamides, thioureas and squaramides by a computational method. The results showed that the favorable affinity is estimated as the order squaramide > croconamide > thiourea. This estimation was in accordance with the experimental result shown in Scheme **4**.



Scheme 4. Croconamides as a new scaffold for dual hydrogen bonding donors.

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