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Primary and secondary amine-(thio)ureas and squaramides and their applications in asymmetric organocatalysis

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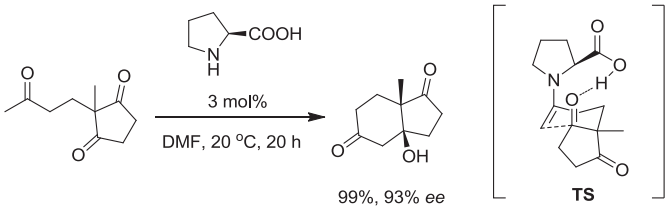
1. Introduction and background

Asymmetric aminocatalysis is by definition the use of small chiral primary and secondary amines to catalyze asymmetric organic transformations.[1] Ever since the rebirth of organocatalysis in 2000,[2] this powerful methodology has been systematically employed in the functionalization of carbonyl compounds via enamine[3] and iminium ion[4] intermediates, complementing the classical organometallic-based approach and offering a powerful synthetic way for the production of useful chiral molecules from achiral starting materials. Among the various classes of aminocatalysts, chiral cyclic secondary amines claim the lion's share, in particular (*S*)-proline[5] and its derivatives,[6] as well as, MacMillan's imidazolidinones.[4a,7] However, in the last few years, researchers have also recognized the potential of chiral primary amines[8] to effectively activate carbonyl compounds; a chemistry exploited by enzymes, such as type I aldolases,[9] which contain catalytic lysine residues.

The deciphering of the, for decades evasive, mechanism of the proline catalyzed Hajos–Parrish–Eder–Sauer–Wiechert reaction,[10,11] highlighted the significance of hydrogen bonding in proline catalysis and, the notion of bifunctional organocatalysts. In this milestone reaction, proline activates the nucleophile through enamine formation, while simultaneously the carboxylic acid group serves to activate the electrophile through hydrogen bonding interaction (LUMO activation), and control the selectivity of the C–C bond formation by orienting the electrophile in a highly organized transition state (Scheme 1).



Scheme 1. The proline catalyzed Hajos–Wiechert reaction and the transition state model (**TS**) proposed by Houk and co-workers.[11d,e]

Ureas and thioureas were known to be capable of activating electrophilic reaction components by forming two hydrogen bonds.[12,13] In a seminal study, Sigman and Jacobsen introduced the activating properties of the (thio)urea functionality on a chiral α-amino acid-derived scaffold to promote the highly enantioselective Strecker reaction of *N*-allyl aldimines.[14] In 2003, Takemoto and coworkers developed this idea further with the design of the first chiral bifunctional organocatalyst, consisting of a tertiary amino group and a thiourea functionality as the hydrogen bond donor, for the Michael addition of malonates to nitroolefins.[15] The authors invoked a dual activation protocol, in which the basic tertiary amine deprotonates the pronucleophile, while simultaneously the electrophile is activated by LUMO lowering hydrogen bond interactions with the thiourea moiety. Following these reports, a plethora of bifunctional catalysts combining the (thio)urea and Bronsted or Lewis base functionalities in the same chiral scaffold have been reported. In this review, we will focus on (thio)urea catalysts bearing a primary or secondary amino group (Fig. 1), since tertiary amine-thioureas have been the subject of several excellent reviews[16] and we will provide a comprehensive overview of the methodologies developed in this field.[17]

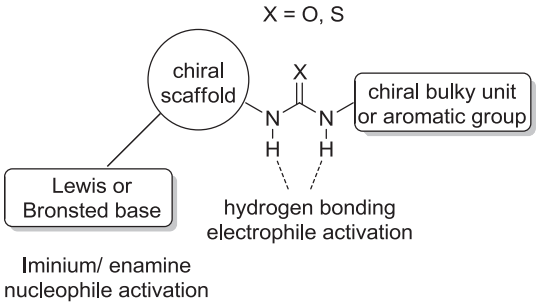


Fig. 1. General dual activation mode of bifunctional catalysts bearing ureas or thioureas.

2. Asymmetric 1,4-conjugate addition reactions

The vast majority of primary and secondary amine-thiourea mediated reactions revolve around the asymmetric Michael addition. This reaction constitutes one of the most powerful methods for the formation of new C–C and C–X bonds in organic synthesis. Especially after the development of organocatalysis, the aforesaid transformation has experienced exponential growth, with a large number of new catalysts exhibiting impressive results in terms of efficiency and selectivity.[18] Herein, we will categorize the reactions according to the Michael acceptor, with nitro compounds being the most popular as the nitro group is well recognized by the thiourea moiety forming strong hydrogen bonds.

2.1. Nitroalkenes as acceptors

2.1.1. Primary amine-(thio)urea-mediated reactions. The first paradigms of primary amine-derived chiral thioureas as effective bifunctional organocatalysts were reported in 2006 within just a few months apart, for the asymmetric Michael addition of ketones or aldehydes to nitroalkenes. Tsogoeva and Wei[19] utilized as catalyst a thiourea based on (1*S*,2*S*)-diphenylethylene-1,2-diamine and a chiral arylethyl moiety (**2**), in the Michael reaction between aliphatic ketones and aromatic nitroolefins (Scheme 2). When acetone **1a** was employed as the Michael donor, the products were obtained in high yields (84–99%) and enantioselectivities (90–91% ee), in the presence of 15 mol % of catalyst **2**. When the nonsymmetrical methyl ethyl ketone **1b** was employed, the Michael adduct *anti*-**3** was delivered in high yield and diastereoselectivity and in excellent enantiocontrol (>99% ee). Cyclic ketones (**4**), like cyclohexanone or tetrahydrothiopyran-4-one, also reacted with *trans*-β-nitrostyrene **5** under the same conditions, to afford the

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