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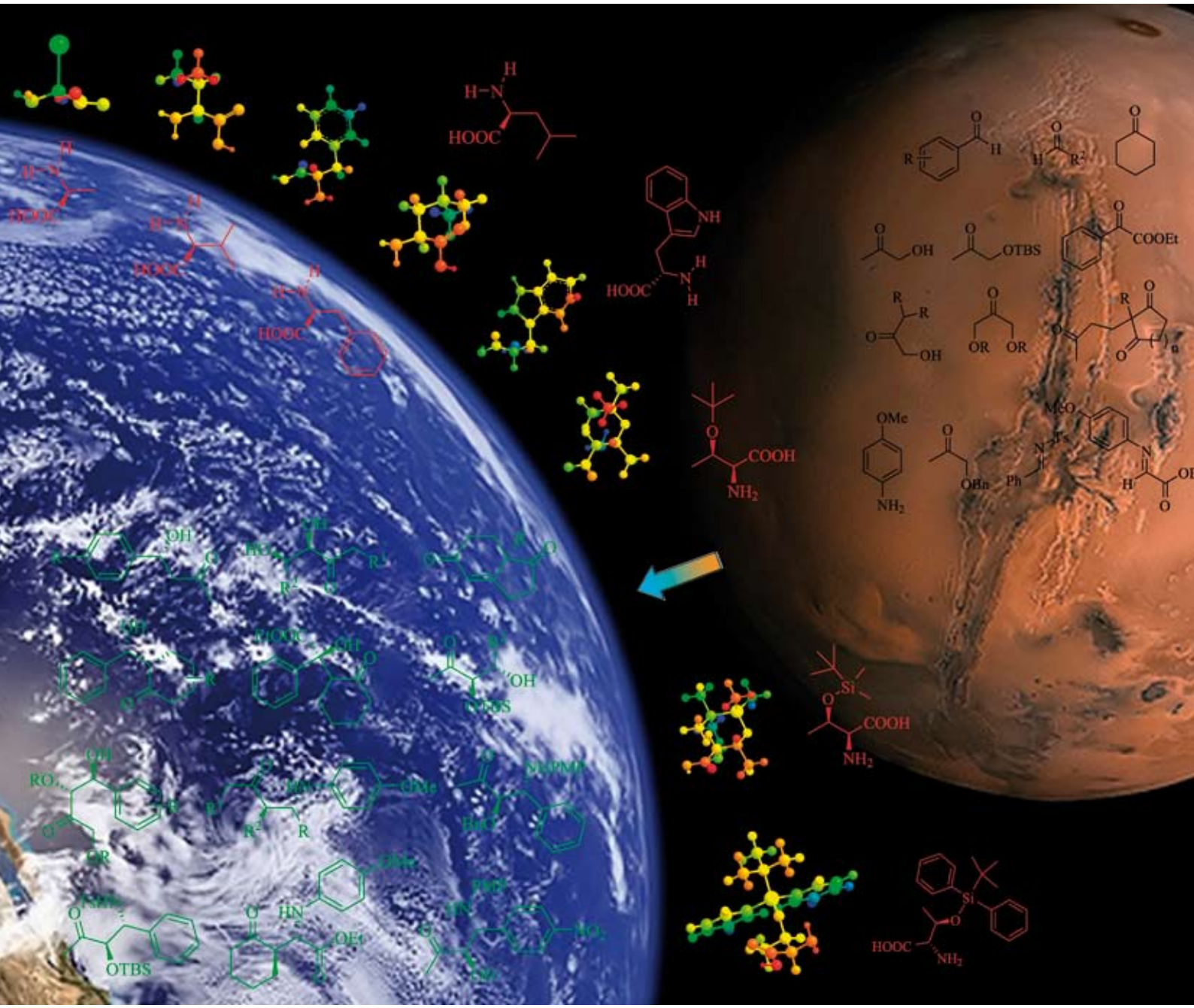

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Primary amino acids: privileged catalysts in enantioselective organocatalysis

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Despite the recent spectacular advances in asymmetric organocatalysis, proline and its analogues have been predominantly employed as organocatalysts in reactions utilizing enamine intermediates. Recent studies of enantioselective organocatalytic reactions promoted by primary amino acids and their derivatives are described in this account. The primary amino functions, rather than the secondary pyrrolidine moiety, have been shown to provide unique reactivity and stereoselectivity in asymmetric aldol and Mannich reactions.

Introduction

Enantioselective organocatalysis has received much attention in recent years and has become increasingly important in the production of chiral molecules.[1] Even though initial reports on the Hajos–Parrish–Eder–Sauer–Wiechert reaction were disclosed in the early 1970s,[2] the use of small molecules to catalyze organic reactions remained largely unexplored for several decades. The year 2000 saw a renaissance of organocatalysis, and thereafter proline emerged as one of the most prominent catalysts in a wide range of asymmetric reactions.[3] It has been regarded as the simplest enzyme.[4] To date, a large number of proline analogues were prepared and were used more or less successfully in a huge number of organocatalytic reactions.

Nature is an absolute master of performing asymmetric synthesis, and enzymes are highly efficient biocatalysts in living systems. While the catalytic efficiencies of enzymes are astonishing, the interaction forces that enzymes utilize to engage substrates at their active sites are quite trivial, such as hydrogen bonding, Van der Waals forces, and electrostatic, hydrophobic and dipole–dipole interactions. Small molecule catalysts also make use of the above interactions in catalysis. Developing small organic catalysts into enzyme mimics represents a very interesting and intriguing, yet extremely formidable task.

Similar to aldol reactions catalyzed by proline, natural class I aldolases catalyze aldol reactions in water *via* the enamine mechanism, in which the enamine is formed at the lysine residue in the enzyme active site.[5] In this context, it is quite surprising that only proline and its structural analogues have been intensively investigated in organocatalytic reactions in the past few years, while the potential of other amino acids as organocatalysts was virtually neglected. In this review, we will present a number of recent studies in which primary amino acids and their derivatives have been shown to act as efficient organocatalysts in enantioselective aldol and Mannich reactions.

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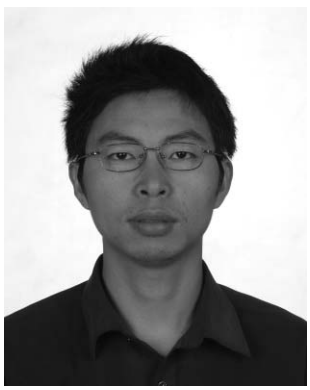
Primary amino acids as organocatalysts in intramolecular aldol reactions

Although not well appreciated by the scientific community, primary amino acids were investigated as potential catalysts



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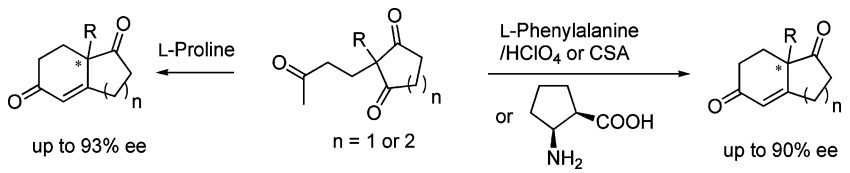
for intramolecular Hajos–Parrish–Eder–Sauer–Wiechert reactions some time ago, as described in a number of early reports.[2] Eder, Sauer and Wiechert showed that phenylalanine was a quite good catalyst, only slightly inferior to proline.[2a] In the initial report by Hajos and Parrish,[2b] phenylalanine was tested as an alternative catalyst in intramolecular aldol reactions, albeit the chemical and optical yields of the desired product were rather poor. Subsequently, Buchschacher *et al.*[6] reported that primary β-amino acids, such as β^3-homophenylalanine, as well as γ-amino acids, were effective catalysts in intramolecular asymmetric aldol condensations. Danishefsky and co-workers[7] found that employing a slight excess of phenylalanine, in combination with $HClO_4$, yielded the intramolecular condensation product with high optical purity, whereas proline only led to disappointing results for the same reaction. Tsuji,[8a] Hagiwara[8b] and Corey[8c] later employed phenylalanine with either $HClO_4$ or camphorsulfonic acid to effect key intramolecular aldol reactions in steroid synthesis. In addition, there were a number of reports on applications of amino acid-catalyzed Hajos–Parrish–Eder–Sauer–Wiechert reactions in total syntheses.[9] Recently, Davies and Smith reported[10] that the β-amino acid (1*R*,2*S*)-cispentacin promoted the Hajos–Parrish–Eder–Sauer–Wiechert reaction with a level of enantioselectivity comparable to that observed with the proline-catalyzed reaction. This represents the best enantioselectivity obtained for this particular reaction using an amino acid catalyst containing a primary amino functionality (Scheme 1).

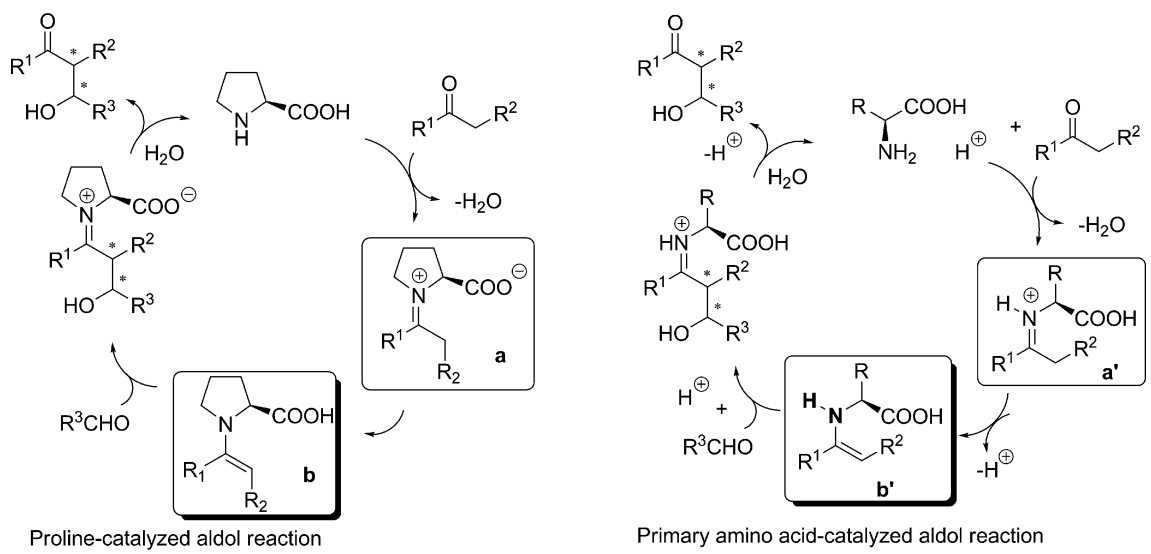
The above intramolecular aldol reactions catalyzed by primary amino acids amply demonstrated the power and potential of primary amino group-mediated organic catalysis, thus paving the way for the further exploration of such catalysts in a broader scope of organic transformations.

Primary *versus* secondary amino acids in intermolecular condensations: mechanistic considerations

Aminocatalysis *via* the enamine mechanism has become one of the most important activation methods in asymmetric organocatalysis. The key of such activation is the transformation of the carbonyl group into an enamine intermediate, which would increase the HOMO of the nucleophiles. In this context, proline and its structural analogues have been demonstrated to be powerful catalysts for a large variety of reactions, including aldol reactions, Mannich reactions, Michael reactions and α-functionalizations of carbonyl compounds, among others. However, primary amino acid-promoted enamine catalysis is rather limited. In fact, in the initial report by List and Barbas on proline-catalyzed direct intermolecular asymmetric aldol reactions,[3a,b] it was shown that primary amino acids, such as valine and phenylalanine, were poor catalysts for aldol reactions under the reaction conditions investigated. The catalytic cycles of enamine catalysis by proline and primary amino acids are compared in Scheme 2. It has long been thought that a secondary enamine is better stabilized by hyperconjugation, whereas a primary amine gives the predominant imine form. For primary amino acids to serve as efficient catalysts in enamine catalysis, effective tautomerization of their imine



Scheme 1 L-Proline and primary amino acid-promoted Hajos–Parrish–Eder–Sauer–Wiechert reactions.



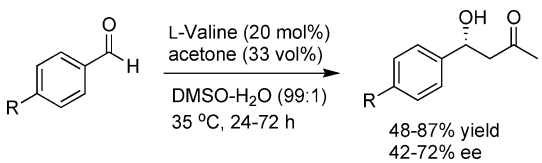
Scheme 2 L-Proline and primary amino acid-promoted intermolecular aldol reactions *via* the enamine mechanism.

form (**a′**) to the enamine form (**b′**) is absolutely essential. In a recent report,[11] Wong and co-workers found that water molecules participated in a proton relay *via* a hydrogen-bonding network to effect the conversion of an imine formed between a lysine residue and acetaldehyde to the enamine form. Amedjkouh[12] subsequently demonstrated that the presence of water was crucial for the primary amino acid-mediated aldol reactions to take place. Tanaka and Barbas also showed that organic solvent (*e.g.* DMSO) with a small amount of water as the additive facilitated enamine-based reactions involving primary amines.[13] Taken together, these results suggest that it is certainly feasible to employ primary amino acids as potential catalysts in reactions involving enamine intermediates, provided that the corresponding enamines can be generated effectively. In addition, the presence of an extra N–H in the enamine (**b′**) intermediate derived from the primary amino group may facilitate the control of the enamine structure, and direct the reaction to occur with specific reactivity and selectivity, which may not be attainable *via* proline catalysis. Moreover, the ready availability of natural amino acids offers great flexibility in structural variation for the design of chiral organocatalysts. All these factors combined make primary amino acids interesting and promising catalysts in organocatalysis.

Intermolecular aldol reactions catalyzed by primary amino acids and their derivatives

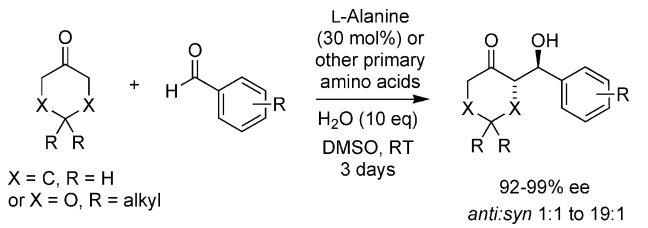
In an effort to establish the potential role that amino acids might have played in the origin of homochirality, Pizzarello and Weber[14] showed that alanine and isovaline could catalyze aldol condensations of glycoaldehyde in water to produce tetroses. Although the enantioselectivity was very low (*ca.* 10% ee for threose, 5.4% ee for erythrose), the results of this study indicate that it has prebiotic plausibility.

The most exciting developments in this field are all very recent. In 2005, Amedjkouh[12] found that L-valine was an effective catalyst in asymmetric direct aldol reactions between acetone and a variety of aromatic aldehydes, affording products in 48–83% yields and with moderate enantiomeric excesses (42–72%) (Scheme 3). The best results were obtained using either DMSO or DMF as solvent in the presence of one molar equivalence of water.



Scheme 3 L-Valine-catalyzed intermolecular aldol reactions.

In the same year, Córdova and co-workers[15] reported that a number of primary amino acids could serve as excellent catalysts for direct asymmetric aldol reactions of cyclic ketones. For example, alanine, valine, leucine, isoleucine, serine, phenylalanine and threonine were all found to be excellent catalysts, furnishing the corresponding *anti*-selective β-hydroxy ketones in high yields and with up to >99% ee (Scheme 4). Moreover, phenylglyoxylate was also shown to be a suitable acceptor for the above aldol reactions. Notably, the best results were obtained when the reactions were performed in wet polar solvents, *i.e.* with the addition of a small amount of water. The authors mentioned that the beneficial effect



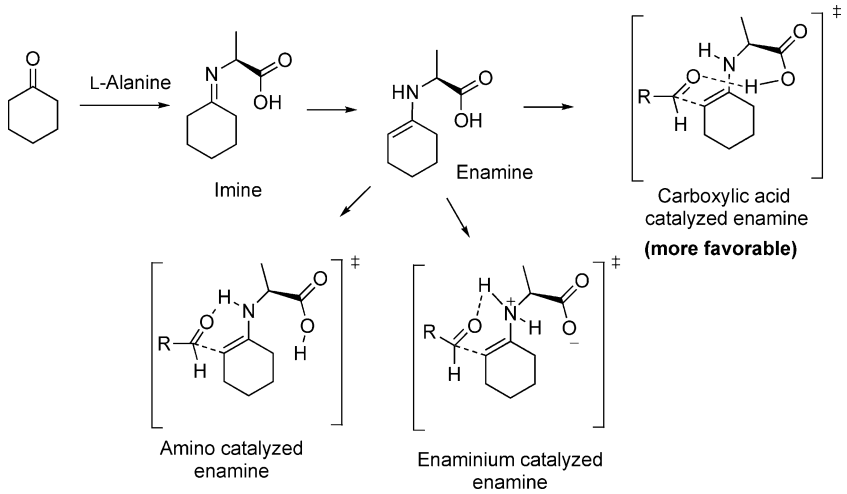
Scheme 4 L-Alanine-catalyzed intermolecular aldol reactions.

of water is due to improved catalytic turnover *via* rapid hydrolysis of the intermediates in the enamine catalytic cycle, as well as to suppression of catalyst inhibition.

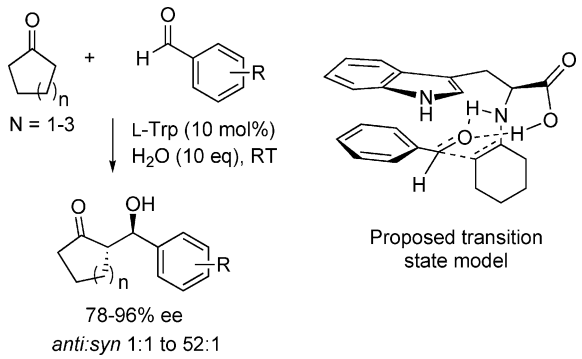
Córdova and Himo next carried out computational studies to understand the origin of the observed stereoselectivity.[15c] DFT calculations on the alanine-catalyzed aldol reaction were performed to provide a key understanding of the reaction mechanism. The carboxylic acid catalyzed enamine mechanism is a more reasonable pathway, as it requires the lowest activation energy. The amino catalyzed enamine mechanism, and the enaminium catalyzed mechanism are less likely, as much higher activation energies are required (Scheme 5). On the basis of the proposed mechanism, the proper stereochemistry of the reaction could be accurately predicted.

Our group[16] investigated the feasibility of hydrophobic primary amino acid-promoted aldol reactions in aqueous media. We reasoned that a hydrophobic catalyst should associate strongly with hydrophobic substrates in water.[17] As a result of optimizing hydrophobic interactions, the transition state may be better defined and high enantioselectivity might be achieved. We demonstrated for the first time that the hydrophobic amino acid tryptophan could be used as an efficient catalyst for the intermolecular direct aldol reaction in aqueous media in the absence of any organic solvent. The aldol reactions of various aromatic aldehydes with cyclic ketones were highly enantioselective, environmentally benign and operationally simple. In the proposed transition state, it was hypothesized that the indole moiety of tryptophan facilitated the formation of a hydrophobic core with other hydrophobic substrates in water, and the reactions may involve π–π stacking (Scheme 6). Very recently, Amedjkouh[18] reported similar results for aldol reactions in water mediated by L-tryptophan and other primary amino acids, whereby organic bases, such as DBU and TMG, were used as co-catalysts. It is believed that an organic base would facilitate enamine formation and thus accelerate the reaction.

We subsequently discovered that serine and threonine derivatives are highly efficient organocatalysts for asymmetric aldol reactions in water.[19] Although these amino acids were not efficient organocatalysts in direct aldol reactions between cyclohexanone and benzaldehyde, their hydrophobic derivatives (*e.g.* *O*-TBS-threonine) proved to be very efficient catalysts. The desired aldol products were obtained in excellent yields (up to 99%), and with nearly perfect enantiomeric control (up to 99% ee) (Scheme 7, equation 1). The substrates were extended to include hydroxyacetone as a donor. The *O*-TBS-threonine-catalyzed direct aldol reaction between hydroxyacetone and *para*-nitrobenzaldehyde in water was ineffective, presumably due to the hydrophilicity of hydroxyacetone. Protection of the free hydroxy function with the TBS group gave a hydrophobic substrate, which then efficiently



Scheme 5 Possible mechanisms of L-alanine-catalyzed aldol reactions.

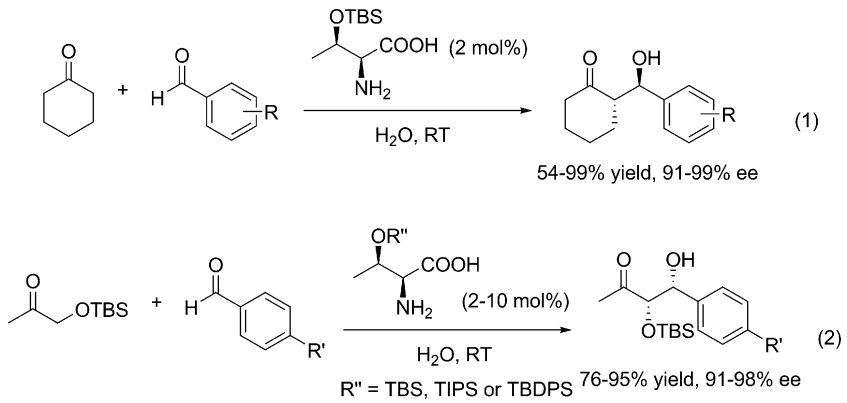


Scheme 6 L-Tryptophan-catalyzed intermolecular aldol reactions.

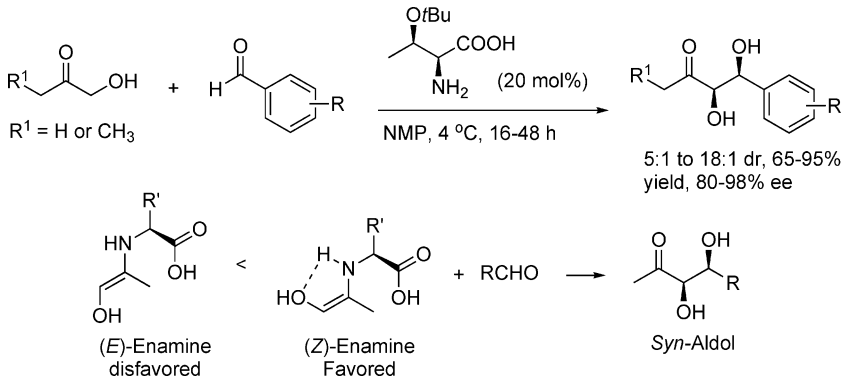
reacted with aldehydes to yield *syn*-diols (equation 2). The reactions reported in this paper may be very suitable for large scale production.

Barbas and co-workers[20] independently reported that primary amino acid catalysts, such as L-tryptophan, L-threonine and *O*-*t*Bu-L-threonine could catalyze direct aldol reactions between β-hydroxy-ketone and various aromatic aldehydes. The aldol reactions proceeded effectively at 4 °C in NMP to afford *syn*-diols with high diastereoselectivity and excellent enantioselectivity (Scheme 8). It was observed that both diastereoselectivity and enantioselectivity increased with the addition of water in many cases. The generation of the *syn*-aldol product was attributed to predominant (*Z*)-enamine formation, resulting from hydrogen bonding between the NH group of the primary amino acid-derived enamine and the hydroxy group. It is interesting to note that *O*-*t*Bu-L-threonine mediated the desired *syn*-aldol product formation with good diastereoselectivity (up to 15 : 1 dr) and excellent enantioselectivity (up to 98% ee). These results are consistent with our findings[19] that sterically hindered hydrophobic *O*-siloxy-L-threonines are excellent catalysts for aldol reactions of hydroxyacetone and aromatic aldehydes.

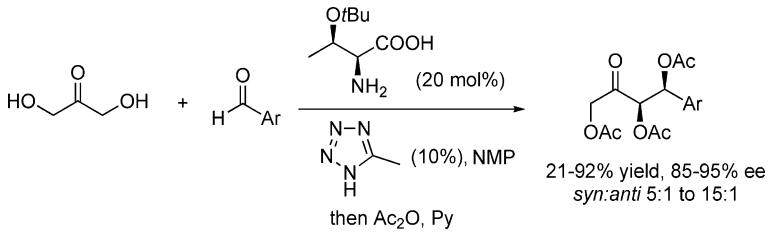
The Barbas group recently extended organocatalytic enantioselective *syn*-aldol reactions to the synthesis of carbohydrates involving the use of unprotected dihydroxyacetone (Scheme 9).[21] In the optimized *O*-*t*Bu-L-threonine catalysis with 5-methyl-1*H*-tetrazole as an additive, the desired *syn*-aldol products were obtained with good diastereoselectivity (up to 15 : 1 dr) and excellent enantioselectivity (up to 99% ee), which typically exceeded the ee values of these same reactions promoted by proline.



Scheme 7 Intermolecular aldol reactions mediated by threonine derivatives.



Scheme 8 The synthesis of *syn*-1,2-diols *via* *O*-*t*Bu-thr-catalyzed aldol reactions.



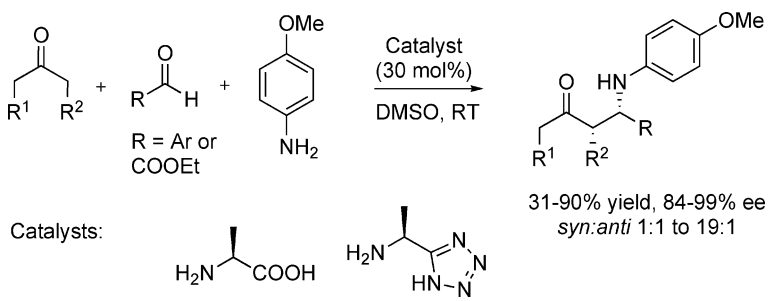
Scheme 9 Carbohydrate synthesis using dihydroxyacetone.

These reactions mimic the reactions catalyzed by aldolases. The utilization of protected dihydroxyacetone and hydroxyacetone as donors in the preparation of carbohydrates and polyol derivatives was also explored.[21b] The observed *syn*-selectivity indicates that this method complements the proline-based synthetic methods, which give *anti*-products.

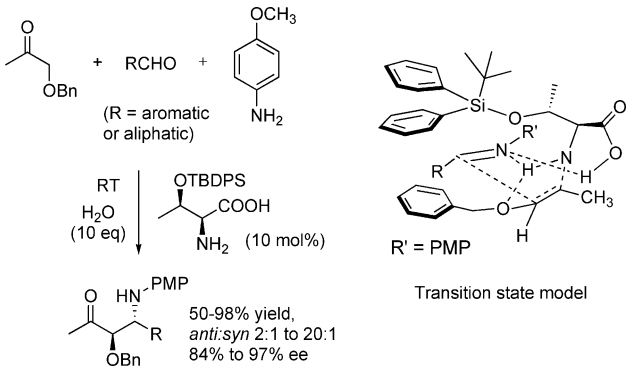
Mannich reactions promoted by primary amino acids and their analogues

The asymmetric Mannich reaction has enormous importance for the construction of chiral β-amino carbonyl compounds, and many primary amino acid-promoted Mannich reactions have been reported recently. The first direct three-component asymmetric Mannich reactions mediated by primary amino acids were reported by Córdova *et al.*[22] Simple primary amino acids, such as alanine, valine, and serine, catalyzed the three-component asymmetric Mannich reactions between unmodified ketones, *p*-anisidine, and aldehydes with high chemo- and stereoselectivity, furnishing the corresponding Mannich products with up to 99% ee and in up to 90% yield (Scheme 10).

To extend the applications of *O*-siloxy threonine organocatalysts, our group[23] next examined them in direct three-component Mannich reactions. We found that the reactions of *O*-benzyl hydroxyacetone, *p*-anisidine and aromatic or aliphatic aldehydes in the presence of *O*-TBDPS-L-threonine afforded the *anti*-1,2-amino alcohols in good-to-excellent yields and with enantioselectivities of up to 97% (Scheme 11). Water was the sole solvent used for this reaction, and in the absence of water, the observed enantioselectivity was lower. This study is the first demonstration that direct three-component Mannich reactions can be promoted by a primary amino acid in a pure aqueous system. The *anti*-Mannich product results from the (*Z*)-enamine intermediate, which is believed to be more favorable due to hydrogen bonding and a π–π stacking interaction.

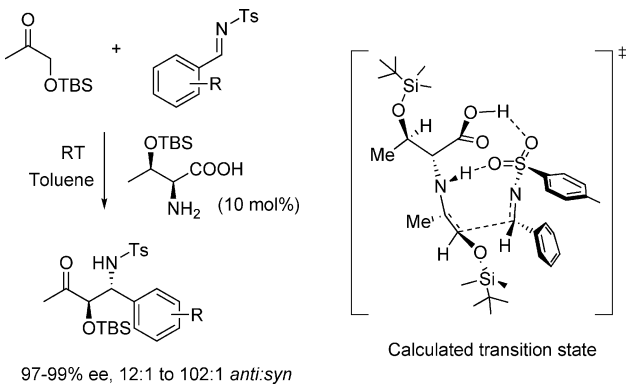


Scheme 10 Three-component direct Mannich reactions catalyzed by primary amino acids and their derivatives.



Scheme 11 *O*-TBDPS-Thr-promoted direct three-component Mannich reactions.

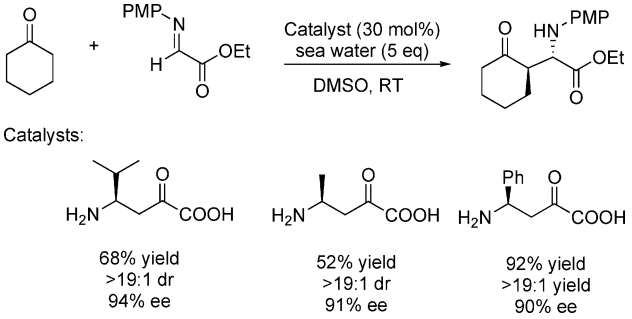
With the same siloxy-threonine as catalyst, we discovered[24] that the use of *N*-tosylimines resulted in remarkably efficient enantioselective *anti*-Mannich reactions (Scheme 12). The catalyst was applicable to virtually any aromatic aldehyde, regardless of the electronic nature of the aryl aldehydes, and very high *anti*-selectivity (up to 102 : 1 dr) and nearly perfect enantioselectivity (97–99% ee) were attainable. Preliminary computational studies revealed the involvement of both oxygen atoms of the sulfone in a hydrogen bonding network in the transition state, which may have implications for the design of novel organocatalytic systems.



Scheme 12 The highly enantioselective *anti*-Mannich reaction using *N*-tosylimines.

Barbas and co-workers[20] also reported a simple and efficient route to highly enantiomerically enriched *anti*-1,2-amino alcohols. L-Tryptophan and *O*-*t*Bu-L-threonine were shown to catalyze direct Mannich reactions of hydroxyacetone, *p*-anisidine and aromatic aldehydes to afford 1,2-amino alcohols with good *anti*-selectivity (up to 19 : 1 dr) and excellent enantioselectivity (up to 98% ee) (Scheme 13).

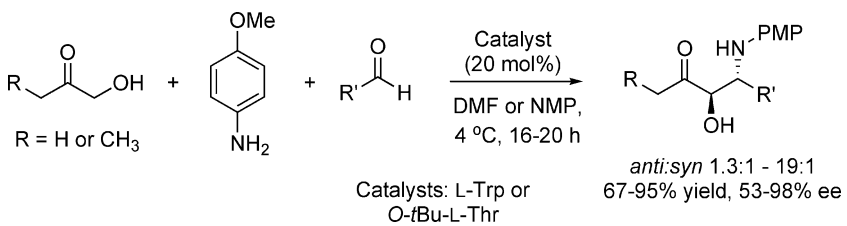
Although β-amino acids were less effective than proline and primary amino acids in intermolecular aldol reactions, Córdova *et al.* recently reported that primary β-amino acids could catalyze direct Mannich-type reactions in "sea water" with high chemo-, diastereo-, and enantio-selectivity (Scheme 14).[25]



Scheme 14 β-Amino acid-catalyzed Mannich reactions.

Summary and outlook

The recent studies on aldol and Mannich reactions catalyzed by primary amino acids and their derivatives led to the exciting discoveries of several highly diastereo- and enantioselective organocatalytic reactions, which clearly demonstrate the great potential of primary amino acid-based amino catalysis. It is noteworthy that many reactions described in this review gave better results than the corresponding reactions catalyzed by proline and its analogues, and many primary amino acid-catalyzed reactions complemented existing proline-based methods. To further advance this emerging field, it is essential to expand the scope of reactions that can be promoted by primary amino acids. It is expected that more comprehensive and intensive research in this area is to come in the near future, which undoubtedly will establish primary amino acids and their derivatives as privileged organocatalysts.



Scheme 13 L-Tryptophan- or *O*-*t*Bu-L-Thr-catalyzed Mannich reactions.

Acknowledgements

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