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Review

Catalytic asymmetric formation of carbon–carbon bond in the presence of water

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Contents

Abstract

This review gives a brief introduction of the catalytic asymmetric carbon–carbon bond formation reactions, such as aldol, Mannich, Diels–Alder, and Michael reactions, which were carried out in aqueous media or positively influenced by water addition. Many examples are given here to demonstrate that water has a potency to accelerate the reaction and/or enhance the selectivity. The induction of some catalyst structures to the chirality of the corresponding products is also discussed.

Keywords: Water; Asymmetric catalytic reaction; C–C bond formation; Enantioselectivity

1. Introduction

Water has long been deemed a detrimental contaminant in organic synthesis, especially in the Lewis-acid catalyzed asymmetric reactions. Sometimes, even the presence of trace amounts of water damages the reaction, complicates the product composition and/or reduces the stereoselectivity. Therefore, organic chemists are willing to undertake tedious anhydrous manipulation to enhance the possibility of success. However, the discovery that water raises the rate and selectivity of Diels–Alder reaction has had an impact on the traditional prejudice against water and triggered widespread interest to the use of water in organic reactions [1]. More and more researchers documented that water, as a solvent or an additive, can positively affect many important types of organic reactions, such as Claisen-rearrangements, aldol reactions, allylation reactions, oxidations, hydrogenations and ring-opening reactions. The brilliant contributions in this area have been excellently reviewed by some organic chemists such as Li [2], Lindstrom [3], Ribe and Wipf [4] and Manabe and Kobayashi [5]. Herein this review focuses on the fundamental catalytic asymmetric carbon–carbon bond formation reactions in organic chemistry. These reactions was

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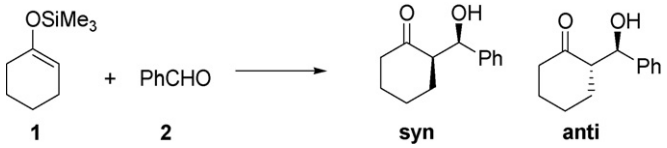
carried out in aqueous media or in organic solvent but was positively influenced by water as an additive. The content is categorized by the reaction type, such as aldol reaction, Mannich reaction, Diels–Alder reaction and so on.

2. Mukaiyama-aldol and direct aldol reaction

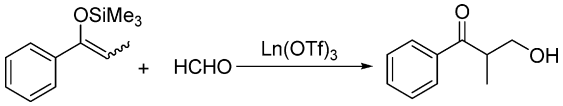
Kobayashi's group found that water molecules not only accelerated the reaction but also played an important role in the good enantioselectivity. Initially, they screened group 1–15 metal chlorides, perchlorates and triflates in the Mukaiyama-aldol reaction, and established the criteria for water-compatible Lewis acids [6]. These results were briefly reviewed by the authors themselves [5,7] In terms of their research work, water alone could promote the Mukaiyama-aldol reaction between the trimethylsilyl enol ether **1** and benzaldehyde **2** (Scheme 1, 23% yield, ***syn*/*anti*** = 85:15, 20 °C, 5 days) [8]. Toluene, oxolane, CH_2Cl_2, CH_3CN, in the absence of catalyst, could not do this even after 15 days under atmospheric pressure. Water promoting-ability may be related to its large cohesive energy *E*, high interfacial energy and hydrophobic interactions. The stereoselectivity in water (***syn*** preference) was the reverse of that catalyzed by the Lewis acid in organic solvent (***anti*** preference) [9], but identical to that under high pressure [10]. Addition of equal amount of oxolane to water increased the yield but decreased the selectivity at the same time (45% yield, ***syn*/*anti*** = 74:26, 20 °C, 5 days).

In 1991, lanthanide triflates were successfully applied to the Mukaiyama-aldol reaction between trimethylsilyl enol ether and formaldehyde [11a], and then extended to other aldehydes by Hachiya and Kobayashi [11b]. These triflates show strong Lewis-acidity and resistance toward hydrolysis, which make them unique for aqueous catalysis. Developing water-compatible Lewis acids has important practical value. Some important reagents, such as formaldehyde, are commercially available as aqueous solution. Tedious manipulation was required to make them anhydrous. Compatibility of water normally means the compatibility of the proton-containing substituents, such as hydroxy, amino, and carboxylic groups. Because of this compatibility, organic chemists can avoid the protecting and deprotecting steps of these proton-containing substituents in their organic synthesis. At the same time, it is generally much easier to recycle water-compatible Lewis acids than those water-labile ones. Several lanthanide triflates ($Ln(OTf)_3$, Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Yb) are effective catalysts in this aqueous medium when THF is employed as a cosolvent (Table 1). They are more soluble in water than in organic solvents, and can be quantitatively recovered and reused without obvious loss of activity.



Scheme 1. Condensation of silyl enol ethers with aldehydes.

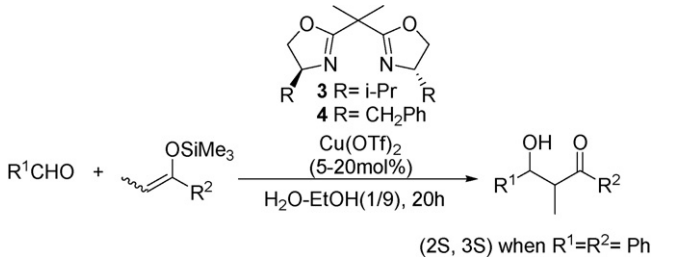
Table 1
Effect of lanthanide triflates



$Ln(OTf)_3$	Yield (%)		
	100 mol%		20 mol% 36 h
	24 h	1 h	
$La(OTf)_3$	90	23	88
$Pr(OTf)_3$	92	40	80
$Nd(OTf)_3$	74	6	89
$Sm(OTf)_3$	92	51	91
$Eu(OTf)_3$	92	28	93
$Gd(OTf)_3$	92	20	79
$Dy(OTf)_3$	89	20	85
$Ho(OTf)_3$	91	38	86
$Er(OTf)_3$	90	44	83
$Yb(OTf)_3$	94	5	94

Interestingly, conversion is low in pure THF or pure water. The best yields were obtained when the ratios of water were 10–20%. Other solvents with different polarity, Et_2O, ROH, DMF and DMSO, were also tested as an additive in THF, but none were effective. Besides, the stereoselectivity gradually shifted from ***anti*** preference (in pure THF) to ***syn*** preference with increasing amount of water. The authors postulated that the change of the coordination environment by the addition of water caused this preference shift. To avoid the involvement of organic cosolvents and overcome the solubility problem of organic compounds in water, the authors resorted to surfactants, such as sodium dodecylsulfate (SDS), to create micellar systems [12]. This strategy was quite successful. Even the highly water-labile ketene silyl acetals can be employed as the substrates in this case. This means that the surfactants formed hydrophobic reaction field including micelles in water. However, the triflates, such as $Sc(OTf)_3$, are water soluble. Therefore, it is reasonable to conclude that their concentration in the hydrophobic reaction field is low. To solve this problem, Kobayashi and co-workers developed Lewis-acid surfactant combined catalyst (LASC) [13]. The aldol reaction catalyzed by LASC in water was 5000 times faster than that in dichloromethane. Besides, carrying out the reaction in solvent free conditions also resulted in a great decrease in yield [14a]. Combination of LASC with Brønsted acid, especially HCl, dramatically accelerated the reaction [14b].

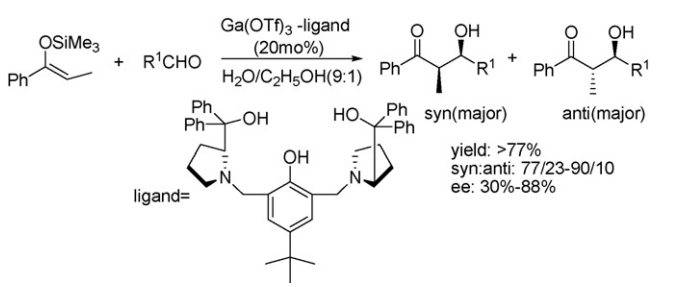
Previously, asymmetric Mukaiyama-aldol reactions were usually carried out in anhydrous aprotic environments at −78 °C. This conventional method was altered by Kobayashi et al. (Scheme 2) [15]. The reaction was performed in ethanol–water (9:1) at −15 to 0 °C, and catalyzed by chiral copper(II)–*bis*(oxazoline) complex (**3** or **4**). Moderate to excellent yields were obtained. Ligands **3** and **4** exhibited the same levels of diastereo- and enantioselectivities. The diastereoselective ratios (***syn*/*anti***) ranged from 1.6/1 to 5.7/1, and ee values from 42% to 85%. The aldehyde part included aromatic, α,β-unsaturated, heterocyclic and even aliphatic aldehydes. As for the enolates, the *Z*-isomers were superior to the *E*-isomers



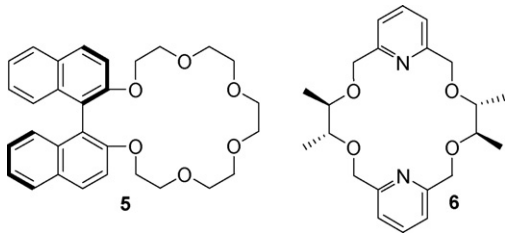
Scheme 2. Catalytic asymmetric aldol reaction catalyzed by copper-*bis*(oxazoline).

in yields, diastereoselectivities and enantioselectivities. The authors also demonstrated that water accelerated the desired chiral reaction and suppressed the undesired achiral side reaction to afford the adduct with a high yield and good selectivity while the pure ethanol or dichloromethane favored the achiral side reaction to give rise to the corresponding product with a reduced yield and diastereo- and enantioselectivities. It was assumed that the dissociated copper(II) coordinated by bis(oxazoline) **3** or **4** was the active catalyst, and the presence of water assisted in its dissociation. Cu-based LASC such as copper bis(dodecyl sulfate) and ligand **3**, plus the catalytic amount of lauric acid, can catalyze the reaction in water at ambient temperature to produce the corresponding adducts with moderate yields and selectivities [16]. Similar results were also reported by Wang and co-workers in 2002 (Scheme 3) [17]. Wang employed the $Ga(OTf)_3$ and Trost semi-crown ligand to catalyze the Mukaiyama-aldol reaction in water/ethanol (1:9). In fact, without the ligand, the $Ga(OTf)_3$ alone cannot catalyze the reaction, and leads to the undesired hydrolysis of the silyl enol ether. Diastereo- and stereoselectivites remained high as the amount of water was increased in the mixture solvent and reactions proceeded even better with only water as solvent, but Diastereo- and stereoselectivities decreased noticeably in pure ethanol, which means water is essential in this system.

The Mukaiyama-aldol reaction catalyzed by $Pb(OTf)_2$-**5** complex in water/2-propanol (1:4.5) led to high diastereoselectivities (***syn/anti*** > 82:18), as shown in Scheme 4 [18]. Even the aliphatic aldehydes worked well in this system. The matching between the metal diameter and the hole size of the crown ether is one of the key factors determining the catalytic efficiency, which is also true in the lanthanide (Ln)-**6** and rare earth metal (RE)-**6** catalytic system [19,20]. A preliminary kinetic study revealed that $Pb(OTf)_2$-**5** and $Pb(OTf)_2$ showed comparable catalytic activities, which means that the ligand did not reduce the



Scheme 3. Aldol reaction in the presence of semi-crown ligand.

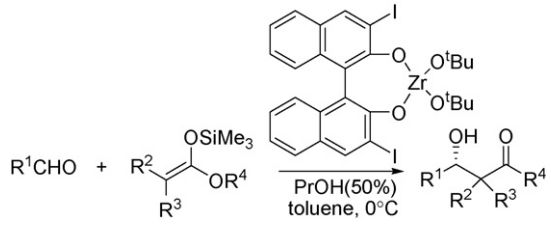


Scheme 4. Chiral crown ethers.

Lewis-acidity of the metal cation although the ligand **6** strongly bound to certain RE cations and reduced the activities. Water played a critical role in producing the adol product with high yields and selectivities in these cosolvents while solely utilizing the organic solvent led to much worse results.

An X-ray crystal structure of the Pr cation and **6** was obtained for $[Pr(NO_3)_2 \cdot \mathbf{6}][Pr(NO_3)_6]$, in which Pr cation complexed with **6** is located almost in the plane of the crown ring while the methyl groups of **6** are all axial. On the basis of this X-ray structure, a transition state model was proposed to explain the absolute configuration of the favored enantiomer, as shown in Fig. 1. When an aldehyde coordinates with $[Pr(NO_3)_2 \cdot \mathbf{6}]^+$, the *si* face of the coordinated aldehyde carbonyl is shielded by the methyl group in the axial position in $[Pr(NO_3)_2 \cdot \mathbf{6}]^+$, allowing nucleophilic attack of the silyl enol ether predominately from the *re* face. In this way, the stereoselectivity of the product was controlled by steric hindrance in the nucleophilic attack.

On the other hand, the role of water may be attributed to two aspects: (1) suppressing significant loss of the Lewis-acidity of $RE(OTf)_3$ by the coordination of **6**, and (2) creating an effective chiral environment of the RE^{3+}-**6** complex [20]. ***Anti***-selectivity was also achieved by utilizing the chiral zirconium complex (Scheme 5) [21a], and the addition of propanol could accelerate the regeneration of the chiral ligand. This system worked efficiently for aromatic and α,β-unsaturated aldehydes. When aliphatic aldehydes were employed as the reaction substrates, the reactions suffered low yields and poor reproducibility [21b]. Fortunately, addition of 5–20 mol% of water could improve the yields and selectivities, but too much water (40 mol%) stopped the reaction. It was assumed that the role of water in this catalyst system was to put the catalyst structure in order. Namely, the desired structure was formed from the oligomeric structure by adding water. After the formation of the catalyst, the presence or absence of water in the system made no difference. Therefore, it is reasonable to conclude that water affected the formation of catalyst, but had no influence on the aldol reaction itself.



Scheme 5. Catalytic asymmetric aldol reaction using (naphthalenediolato)-dialkoxyzirconium.

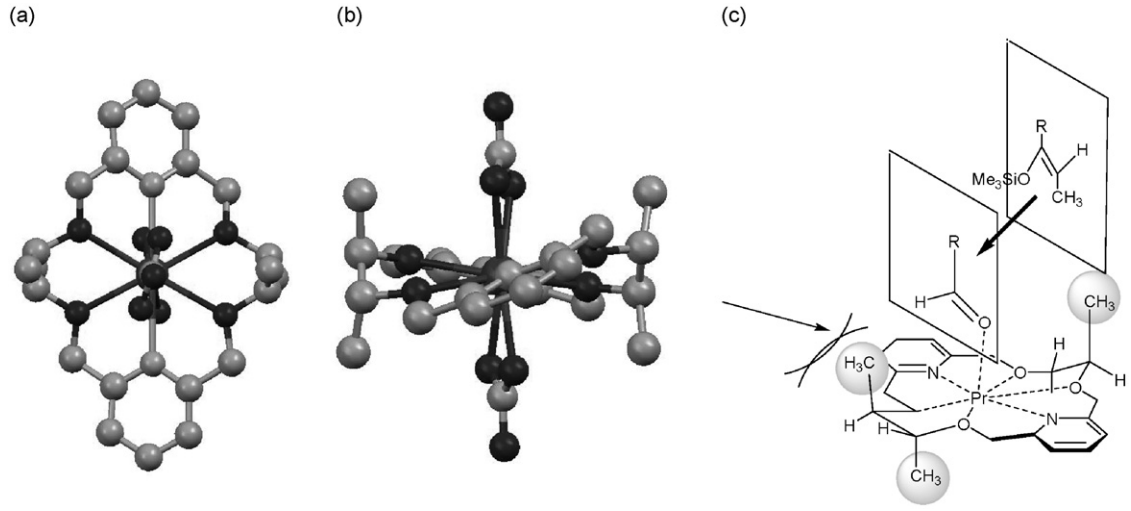
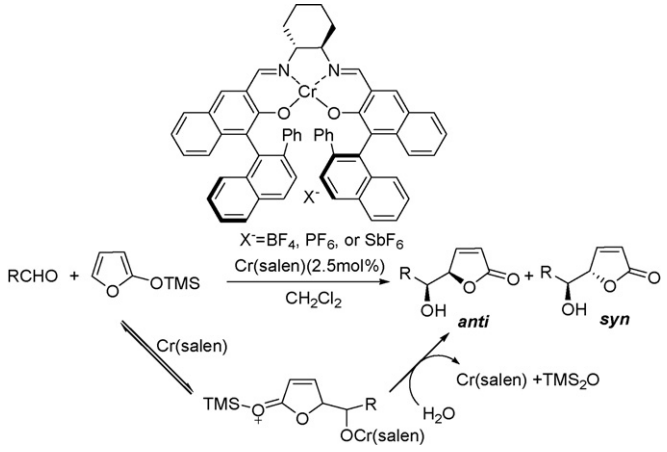


Fig. 1. $[Pr(NO_3)_2{\cdot}\mathbf{6}]^+$ moiety in the X-ray structure of $[Pr(NO_3)_2{\cdot}\mathbf{6}]_3[Pr(NO)_3]_6$. Hydrogen atoms are omitted for clarity. (a) Top view. (b) Side view. (c) assumed transition state model in the asymmetric adol reaction using Pr^{3+} -**6**.

Similar observations were also made in the Pd(II)-BINAP and chiral Pt(II) complex catalytic systems by Shibasaki and co-workers [22] and Fujimura [23]. The zirconium catalyst showed ***anti***-selectivity independent of enolate geometry. The *E*- and *Z*-isomers produced similar results, which indicated the involvement of acyclic transition states. Coupled with *in situ* cyclization reaction (Hetero Diels–Alder reaction), this system can also be extended to the asymmetric synthesis of chiral pyran derivatives, such as (+)-prelactone [24]. Katsuki and co-workers reported the asymmetric Mukaiyama-aldol reaction between 2-trimethylsilyloxyfuran and aldehydes catalyzed by Cr(salen) in 2003 (Scheme 6) [25a].

The Mukaiyama-aldol is reversible in non-protonic solvent. Water can irreversibly hydrolyze the intermediate to the product. Gradual addition of water into the system steadily enhanced ee values of both ***syn*** and ***anti*** products, and the maxima were observed when water amounted to ten equivalents of the catalyst. Water exerted little influence on yield. Further study showed that alcohol was a much more efficient additive than water due to its easy interdiffusion with the solvent CH_2Cl_2 [25b].

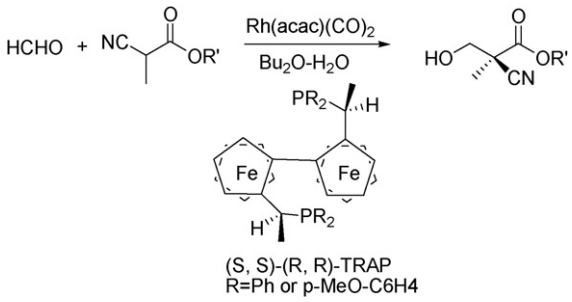


Scheme 6. Cr(salen)-mediated enantioselective addition of 2-(trimethylsilyloxy)furan to aldehyde.

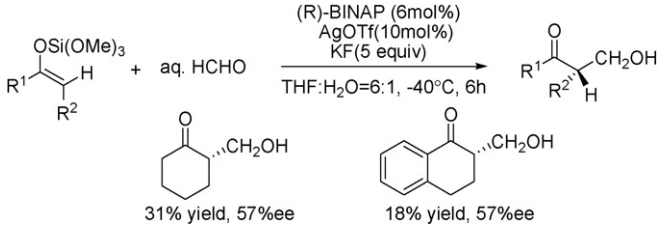
Formaldehyde is one of the most important C1 electrophiles in organic synthesis. Its aldol reaction was also known as hydroxymethylation reaction. In 1998, Ito and co-worker reported the reactions of 2-cyanopropionates and formaldehyde (10 w% in water) catalyzed by rhodium(I)–TRAP complex, with up to 93% ee (Scheme 7) [26].

(*R*)-BINAP-AgOTf complex was also applied to catalyze the aldol reaction between silyl enol ether and formalin. The KF was added as a mild activator. Two cyclic substrates were converted into the products in 57% ee (Scheme 8) [27].

Kobayashi also developed a system to promote the aldol reaction between the silyl enol ether and formalin by utilizing the $Pr(OTf)_3$-**6** complex in H_2O/THF. Not only several acyclic silyl enol ethers derived from aromatic ketones but also some derived from S-*tert*-butyl propanethioate can smoothly react



Scheme 7. Asymmetric aldol reaction with (*S*,*S*)-(*R*,*R*)-PhTRAP-Rh catalyst.



Scheme 8. Asymmetric aldol reaction of trimethoxylsilyl enol ethers with formalin aq solution activated by bifunctional system.

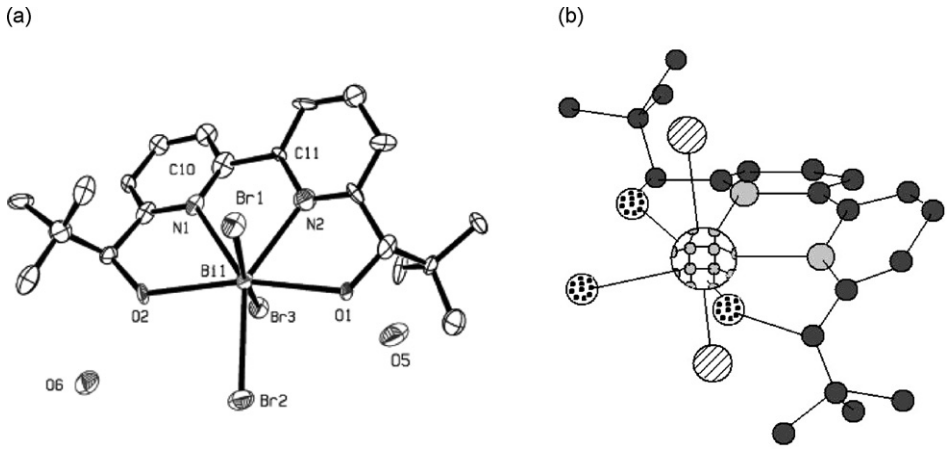


Fig. 2. (a) ORTEP drawing of the X-ray crystal structure of [$BiBr_3$·**7**]·H_2O·DMF. FMF is omitted for clarity. (b) ORTEP drawing of the X-ray crystal structure of [**7**·$ScBr_2$·H_2O]Br·H_2O. Hydrogen atoms are omitted for clarity.

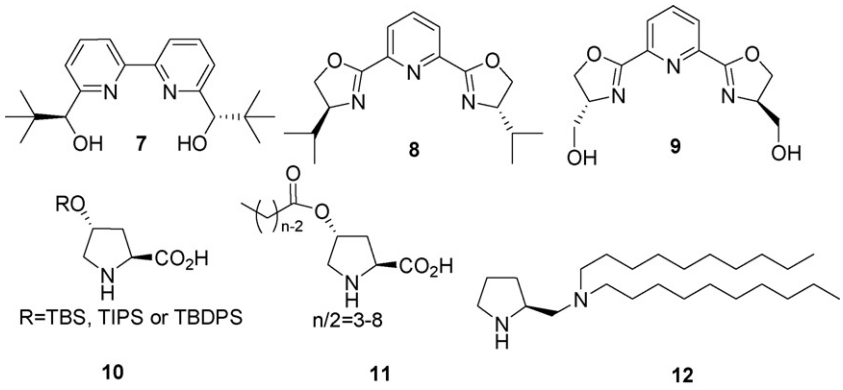
with formalin to generate the corresponding adducts with moderate ee values (23–54%) [28]. Much more successful results were obtained by $Sc(OTf)_3$-**7** [29a] and $Bi(OTf)_3$-**7** complexes [29b] in H_2O/DME(1:9). Pyboxes **8** and **9**, in combination with $Zn(OTf)_2$ or $FeCl_2$, were also reported to be able to catalyze the Mukaiyama-aldol reaction in aqueous media [30]. The direct aldol reaction between acetone and some aromatic aldehydes was catalyzed by Zn-(L)-amino acid complexes in water, giving the corresponding products in high yields and with moderate ee values [31].

X-ray crystal structure analyses were performed to obtain some information about the formation of chirality. The single crystal structures of $Sc(OTf)_3$-**7** and $Bi(OTf)_3$-**7** complexes are listed below.

[**7**·$ScBr_2$·H_2O] complex adopts a pentagonal bipyramidal structure in which the hydroxyl groups of **7** coordinate with Sc^{3+} in a tetradentate manner, as shown in Fig. 2. It was assumed that formaldehyde tends to react with the same face of the siliconenolatesin no reaction to the substituent. [$BiBr_3$·**7**] complex adopts a pentagonal bipyramidal structure in which the tetradentate ligand occupied four of the equational sites. The structure of the $BiBr_3$ complex of **7** is closely related to that of the corresponding $ScBr_3$ complex of **7**. The angle of O–Bi–O is 165°, while that of O–Sc–O is 151°. The torsional angle of two pyridines in the Bi complex is 27.0° and that in the Sc complex is 19.4°. Due to the difference of ion radius, the bond lengths of Bi–O and Bi–N are 2.49 and 2.51 Å while those of Sc–O and Sc–N are 2.17 and 2.30 Å, respectively, which indicates that [$BiBr_3$·**7**] has a better coordination environment and is easier to coordinate with the corresponding substrate than [**7**·$ScBr_2$·H_2O]. Perhaps this better coordination environment brings about a more efficient catalysis both in the yield and the ee value.

Recent research focused on the direct aldol reaction catalyzed by organocatalyst. Barbas and co-workers mentioned that less than 4 vol% of water in DMSO was tolerated in the proline-catalyzed aldol reaction, while too much water caused a dramatic decrease in enantioselectivities [32]. In 2004, Cordova and co-workers reported a highly enantioselective proline-catalyzed hydroxymethylation in DMSO by employing aqueous formaldehyde as a substrate [33]. Afterwards, many authors mentioned that water is a beneficial additive or cosolvent in the proline- [34], proline-derivatives- [35], other acyclic-amino-acids- or peptides-catalyzed [36] aldol reactions and can lead to higher yield, rate, and/or stereoselectivity. In these cases, water may play the role of: (1) hydrolyzing the unreactive oxazolidinone generated from the catalyst and aldehyde, ketone or aldol adduct to liberate the active catalyst; (2) facilitating proton transfer in the transition state, lowering the LUMO energy of the incoming electrophiles, and indirecting the enantioselectivity of the newly formed stereocentres; (3) increasing the solubility of the catalyst into the reaction mixture; (4) converting the aldehydes to their hydrate form, subsequently preventing the formation of iminium ions from aldeydes and catalysts, and others. However, too much water was always detrimental. In some systems, the results can be further improved by acidic additives [35f,37]. When hydroxyacetone and fluoroacetone were utilized as aldol donors, the addition of water can even alter the region selectivity to preferentially give 1,4-diol product [38]. The origin of stereoselectivity in primary amino acid catalyzed aldol reaction was discussed by Cordova and co-workers theoretically and experimentally [39].

Amino-acid- or peptide-catalyzed asymmetric aldol in water has some special significance in explaining the terrestrial evolution of homochirality, because it is closely related to the prebiotic formation of D-sugars. Pizzarello and Weber reported the synthesis of *threose* and *erythrose* via glycoaldehyde self-condensation in an aqueous triethylammonium acetate buffer (prebiotic conditions) by the alanine and a probiotic amino acid, isovaline (L-2-amino-2-methylbutyric acid) [40a]. The largest ee (12%) was obtained for D-*threose* with L-isovaline catalyst. On the contrary, under the same conditions but with dipeptides as catalysts, *erythrose* was the main recipient of asymmetric effect, and *threose* was affected only partially or not at all [40b]. Up to 80% ee was reached for D-*erythrose* when L-Val-L-Val was used. Proline alone cannot catalyze the reaction in the conditions, but can catalyze the reaction between acetone and 4-nitrobenzaldehyde in aqueous media, especially with D-camphorsulfonic acid as a co-organocatalyst [41]. Cordova and co-workers also applied some small peptides to catalyze the aldol in water [42]. Good



Scheme 9. Chiral bipyridine, pyboxes and proline derivatives.

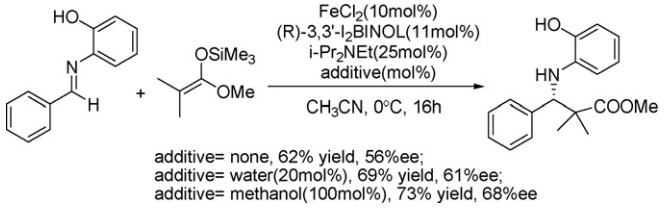
selectivity was obtained with the aid of surfactant (SDS), organic cosolvents or alpha-cyclodextrin. And dihydroxyacetone (DHA) can be directly utilized as donor here. Proline-based amide salts were also tested to promote the aldol reaction between acetone and aromatic aldehydes in water, thus achieving moderate selectivities [43]. Barbas and co-workers and Hayashi and co-workers have also designed some proline derivatives (**10**, **11**, and **12** in Scheme 9) to catalyze the aldol reaction in water [44]. Interestingly, with the cyclic ketone as donor, tryptophan alone can act as an efficient catalyst in pure water (heterogeneous system) [45].

Immobilized organocatalysts were also prepared to catalyze the aldol reaction in water. Besides their high efficiency, they can be easily separated from the reaction mixture and reused for several times without loss of activity [46].

3. Mannich-type reaction

Mannich reaction is closely related to aldol reaction in mechanism, and some successful catalysts in aldol reaction are also applicable in Mannich reaction [34c,d,36d]. Similarly, water can also positively affect this reaction. In the $FeCl_2$ and (*R*)-3,3′-I_2BINOL (BINOL = 1,1′-binaphthalen-2,2′-diol) catalyzed Mannich-type reaction, it was found that the addition of 20 mol% of water slightly raised the chemical and optical yield. The best additive was methanol (Scheme 10) [47].

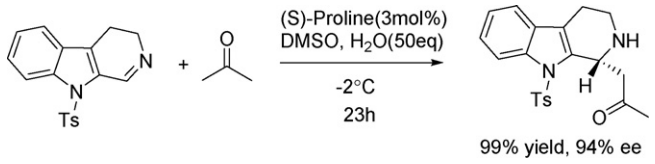
The enantioselectivity of the proline-catalyzed coupling reaction between cyclic imine and acetone was also improved by the participation of water (Scheme 11) [48], but water reduced the reaction rate, probably due to hydrolysis of an intermediary enamine obtained from acetone and proline. The optimal amount of water is about 50–100 equiv. with respect to the substrate. In the optimized conditions, the reaction generated the corresponding product in 99% yield and with 94% ee. On the other hand, Cordova and co-workers found that water (2–5 equiv.) accelerated the three-component Mannich reaction catalyzed by proline or serine [34c,d].



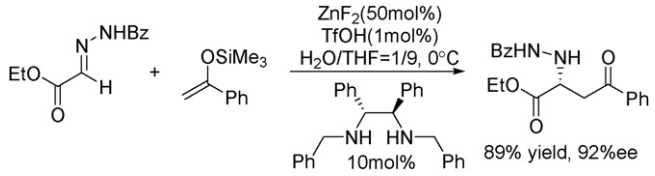
Scheme 10. Catalytic asymmetric Mannich-type reaction using the chiral Fe catalyst.

The first catalytic asymmetric Mannich-type reaction between hydrazono ester and silyl enol ether in aqueous media ($THF/H_2O = 9:1$) was reported by Kobayashi et al. (Scheme 12) [49a]. The combination of chiral diamine with ZnF_2 catalyst generated the corresponding product with a high enantioselectivity but with a low yield. Acidic additive TfOH (1 mol%) greatly improved the yield without negative effect on the enantioselectivity. The absence of the chiral diamine ligand or water in the system gave a much worse result. The reaction was postulated to proceed with double activation where Zn^{2+} acted as a Lewis acid to activate the hydrozono ester and fluoride ion acted as a Lewis base to attack the silicon atom.

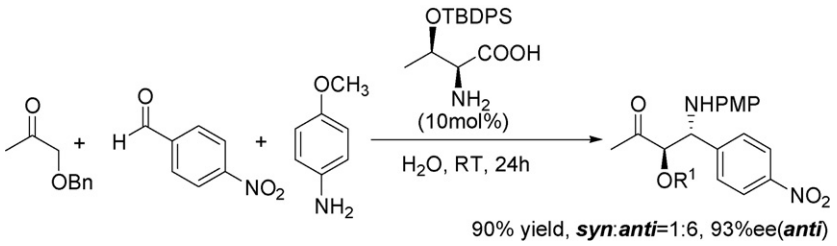
By modification of the chiral ligand, the reaction can be carried out in pure water with high yields and enantioselectivities [49b]. When the silyl ethers derived from alpha-monosubstituted carbonyl compounds were used, cetyltrimethylammonium bromide (CTAB) had to be added in some cases, and the configuration of silyl enol ethers ((*E*) or (*Z*)) determined the



Scheme 11. Reaction of 9-tosyl-3,4-dihydro-β-carboline with acetone in the presence of (*S*)-proline.



Scheme 12. Catalytic asymmetric Mannich-type reaction.



Scheme 13. Direct three-component Mannich reactions with aliphatic aldehydes promoted by the threonine-derived organocatalyst.

configurations of the major products (***anti*** or ***syn***). Therefore, either isomer can be selectively synthesized by choice of the starting material. Under neat conditions, the reaction produced a much lower yield, which indicated the importance of water. Further investigation revealed that the TfOH did not act as a protic acid, but as a triflate anion source, for the replacement of it with TfONa could bring about a better result. The amount of ZnF_2 can be reduced to 20% when suitable diamine was selected to catalyze the reaction [49c].

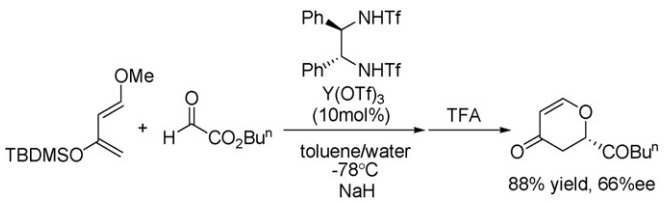
Quite recently, Lu and co-workers reported the first highly enantioselective, direct three-component ***anti***-selective Mannich reactions in pure water promoted by organocatalysts derived from threonine (Scheme 13) [50]. Performing the reaction in neat conditions decreased the stereoselectivity. Both the aromatic and aliphatic aldehydes can be used as suitable substrates in this system.

4. Diels–Alder recation

In 1995, Mikami et al. reported that water, as an additive, was beneficial to the chemical and the optical yield of the hetero Diels–Alder reaction between Danishefsky's diene and butyl glyoxylate (Scheme 14) [51]. In the Ag-catalyzed asymmetric cycloadditions between arylimines and Danishefsky diene, water can also be used as a beneficial cosolvent [52]. On the other hand, the reaction perhaps proceeded via a cascade of Mukaiyama-aldol (Mannich) and cyclization reaction [24].

Interestingly, Desimoni at al. demonstrated that, with the same ligand and metallic cation, the presence or absence of water in the reaction system led to opposite enantioselectivity. Water changed the coordination around Mg(II) from tetrahedral to octahedral, and altered the enantiopreference (Scheme 15) [53].

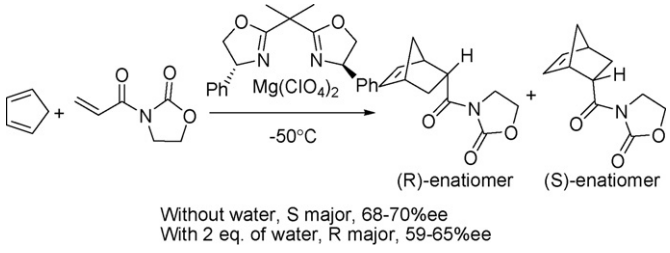
Engberts and co-workers reported the first asymmetric Diels–Alder reaction between 3-phenyl-1-(2-pyridyl)-2-propen-1-one and cyclopentadiene in water (Scheme 16) [54].



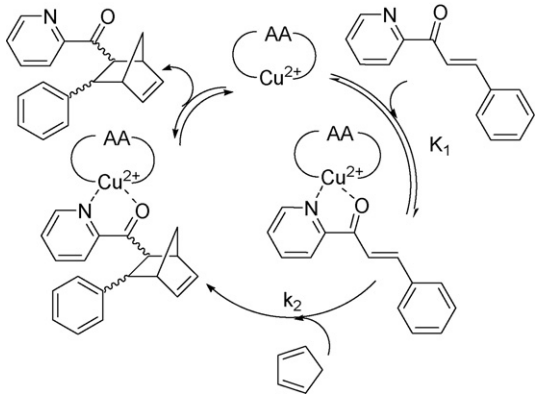
Scheme 14. Asymmetric hetero Diels–Alder reaction of Danishefsky's diene.

Amino acids, glycine, valine, leucine, phenylalanie, tyrosine, tryptophan, and abrine, were used as chiral ligands. Significant enantioselectivities were observed exclusively for the α-amino acids containing aromatic side groups. The best result (74% ee) was obtained when abrine was used. This suggests that arene–arene interactions are important in discriminating between the two pathways leading to the enantiomeric Diels–Alder adducts. Aliphatic amino acids reduced the equilibrium constant (K_1) for binding the dienophile to the copper–ligand complex, but the aromatic amino acids raised it. The highest ee value corresponded to the highest K_1. These amino acids, both aliphatic and aromatic, exerted little influence on the second-order rate constants k_2 for the reaction of the complex with cyclopentadiene. Poorer results were obtained when organic solvents were used instead of water, due to the weakened arene–arene interaction.

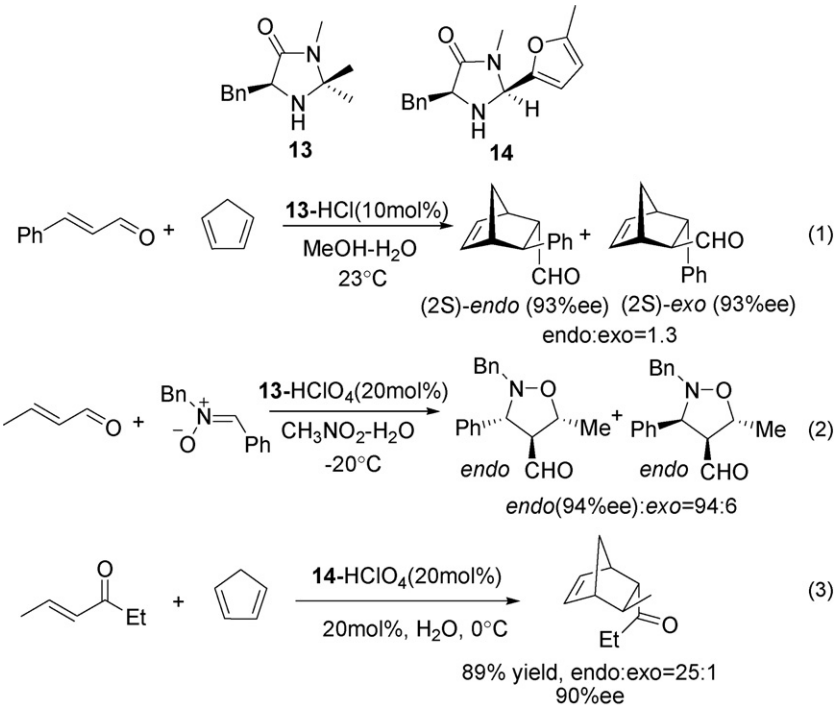
MacMillan and co-workers achieved a highly selective organocatalyzed [4 + 2] cycloaddition between α,β-unsaturated aldehydes and conjugate dienes (cyclic or acyclic) in



Scheme 15. *bis*(Oxazolines)-catalyzed DA reaction.



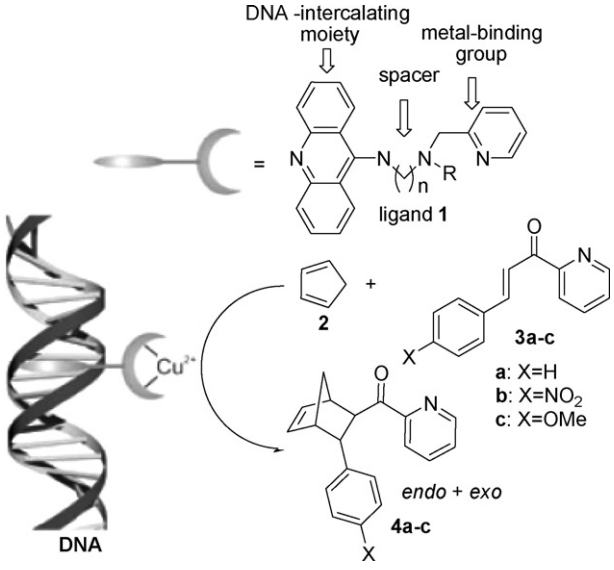
Scheme 16. α-amino-catalyzed Diels–Alder reaction.



Scheme 17. Organocatalyzed cycloadditions.

MeOH/water (Eq. (1), Scheme 17) [55a] and [3 + 2] cycloaddition between α,β-unsaturated aldehydes and nitrone in nitromethane/water (Eq. (2), Scheme 17) [55b] by virtue of the LUMO-lowering activation strategy. Excellent yields and enantioselectivities were observed when a reasonable wide scope of substrates were tested, and with a minor adjustment in the catalyst, this strategy can be extended to the Diels–Alder reaction of α,β-unsaturated ketones and dienes, where Lewis acid showed low enantio-differentiation (Eq. (3), Scheme 17) [55c] Immobilized versions were also reported by Cozzi and co-workers [56a] and Pihko and co-workers [56b]. Catalyst **13** was also employed by Kim and co-workers to catalyze the Diels–Alder reaction in ionic liquids with 5% (v/v) of water [57]. The product can be extracted by organic solvents, and the remaining system can be recycled for several times. Water played an important role in the catalyst regeneration by hydrolyzing the iminium ion, for increasing the water content from 5% to 20% greatly improved the yield and ee value.

The DNA-based asymmetric Diels–Alder reaction in water was reported by Roelfes and Feringa (Scheme 18) [58a]. An achiral ligand was employed, containing three key structural features: a DNA-intercalating moiety, a spacer component and a metal-binding group, which intimately anchored the metal-complexes to DNA (from salmon testes and calf thymus) to use its chiral information. The substituent *R* and the spacer length *n* of the ligand are crucial for both the observed enantioselectivity and the enantiopreference. However, neither the catalyst/substrate ratio nor the source of DNA used had a significant effect on the result. Removing the spacer and integrating the metal-binding site and DNA anchor into one moiety brought about much closer enantio-communication, which resulted in a

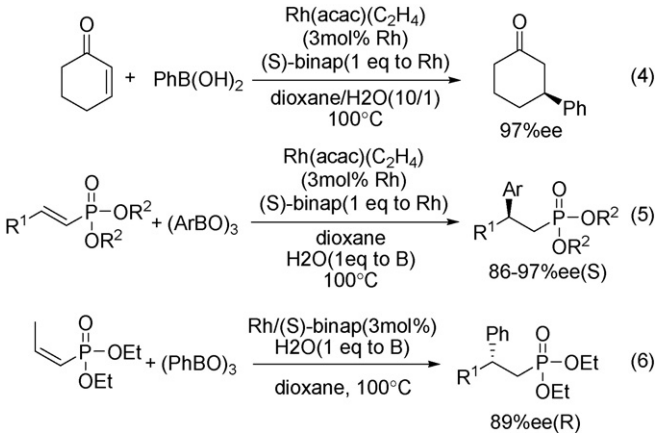


Scheme 18. Asymmetric Diel–Alder reaction of cyclopentadiene with azachalcone catalyzed by copper complexes of ligand **1** in the presence of DNA.

dramatic increase in the enantioselectivity [58b]. Combination of amphiphilic phthalocyanine–copper complex with various serum albumins was also successfully applied to asymmetrically catalyze this reaction in water [59].

5. Michael-type reaction

In 1997, Miyaura and co-workers developed a rhodium-catalyzed conjugate addition of aryl- or 1-alkenylboronic acid to enones in aqueous media [60]. Water was found to be beneficial



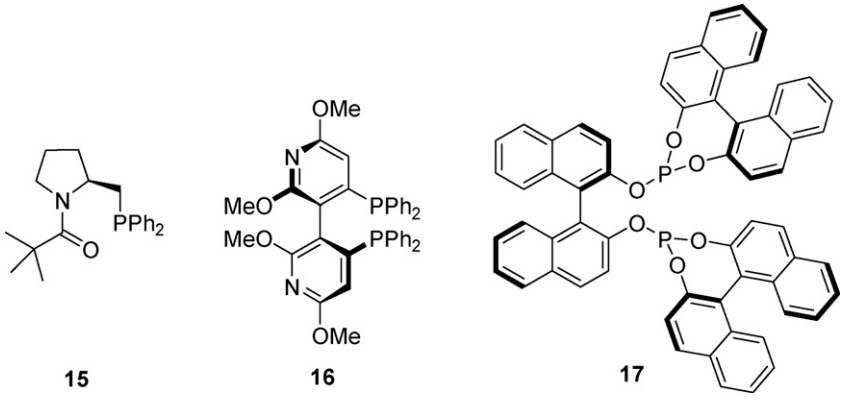
Scheme 19. Asymmetric 1,4-addtion of boronic acides to enones catalyzed by (*S*)-binap.

to the reaction. Hayashi and co-workers reported an asymmetric version in the next year, as shown in Eq. (4) of Scheme 19 [61a]. This system was highly suitable for a wide range of substrates, cyclic and acyclic enones and aryl- and alkenyl boronic acids. Interestingly, raising the reaction temperature from 40 to 120 °C greatly increased the yield, but showed no influence on the enantioselectivity.

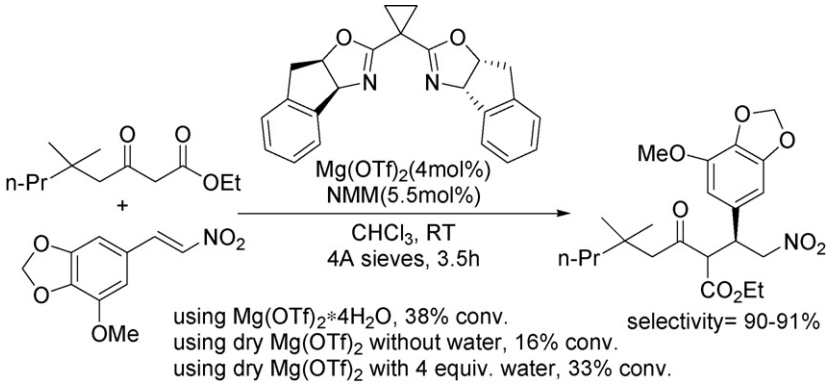
By reducing the amount of water to 1 equiv. relative to triboroxane, the system was also effective in catalyzing the asymmetric addition of α,β-unsaturated phosphonates by triarylcyclotriboroxanes (Eq. (5), Scheme 19) [61b] The *E*- and *Z*-isomers gave opposite enantiomers under the same conditions (Eqs. (5) and (6), Scheme 19). Similar conditions were also applicable to the reaction between nitroalkenes and organoboronic acids [61c] and some others [61d]. Ligands **15** [62], **16** [63] and **17** [64] (Scheme 20) were also successfully applied to similar reactions. Supported 2,2′-*bis*(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand permitted to carry out the reaction in water without any organic cosolvent [65].

Barnes et al. recorded that water played a dual role on the Michael reaction (Scheme 21) [66]. Addition of molecular sieves raised reaction rate and selectivity, and these sieves served only to remove the water taken into the system by the $Mg(OTf)_2$ tetrahydrate. However, employing a dry $Mg(OTf)_2$ (containing only 20 mol% water) caused a dramatic drop in the reaction rate, but the selectivity remained invariant. The reactivity of the catalyst could be restored by addition of water. Thus, while water is an inhibitor of the catalyst, it is nonetheless necessary for water to be present during the complexation step to generate the fully active catalyst.

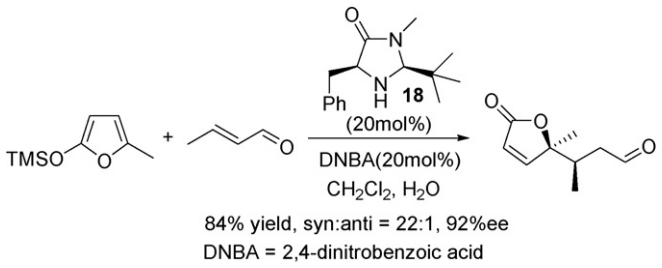
Many highly efficient organocatalysts have been developed to promote the Michael reactions in aqueous media or in water. MacMillan and co-workers developed a unique asymmetric Mukaiyama–Michael reaction catalyzed by imidazolidinone



Scheme 20. Asymmetric catalysts: amidomonophosphine, (*S*)-P-Phos and binol derived diphosphite.



Scheme 21. Conjugate addition catalyzed by the complex of *bis*(oxazoline) with $Mg(OTf)_2$.

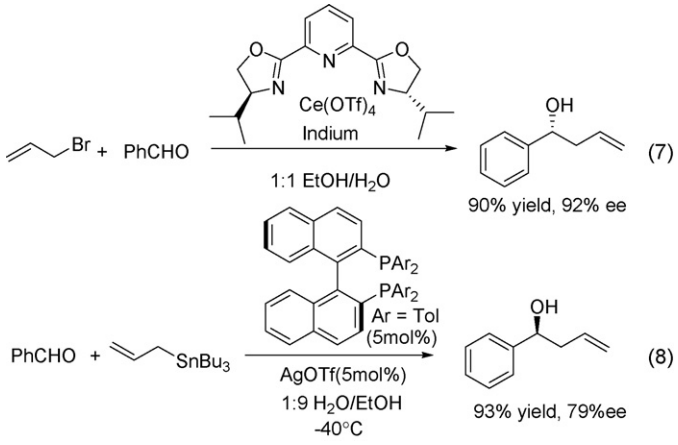


Scheme 22. Asymmetric Mukaiyama–Michael reaction catalyzed by imidazolidinone.

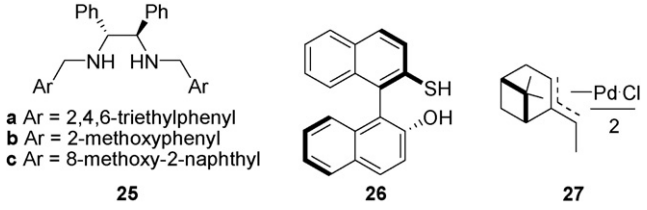
18 (Scheme 22) [67]. Water was involved here to help the turnover of catalyst. Dipeptide (*S*)-ala-(*S*)-ala catalyzed the addition of cyclohexanone to nitrostyrene in DMSO/NMP (1:1) with the addition of 10 equiv. water (69% yield, 22:1dr, 91% ee) [36d]. Proline was not a good catalyst [34d], but some of its derivatives were quite efficient. Barbas and co-workers have demonstrated that the chiral diamine **12** was also suitable to catalyze the Michael reaction in brine or sea water [68]. Cheng and co-workers designed a series of surfactant-type asymmetric organocatalysts (STAO), as shown in Scheme 23, to catalyze Michael addition to nitrostyrenes in water [69]. Those STAOs were synthesized by a simple anion metathesis of chiral imidazolium bromides with surfactant sodium salts or by the neutralization of chiral imidazolium hydroxides with surfactant Brønsted acid. Wang and co-workers introduced a fluorous tag into the catalyst (**20**) to easily recycle the catalyst [70]. By using simple fluorous silica gel based solid–liquid extraction, the catalyst retained its activity and high levels of enantio- and diastereo-selectivity even after 6 cycles. Some other water-tolerant proline-derived catalysts (**21** [71], **22** [72], **23** [73], and **24** [74]) were also reported recently.

6. Allylation reaction

The first catalytic asymmetric allylation reaction in aqueous media was reported by Loh and Zhou (Eq. (7), Scheme 24) [75a]. In the reaction between allyl bromide and benzaldehyde, a 92% ee value was reached under optimized conditions. Only

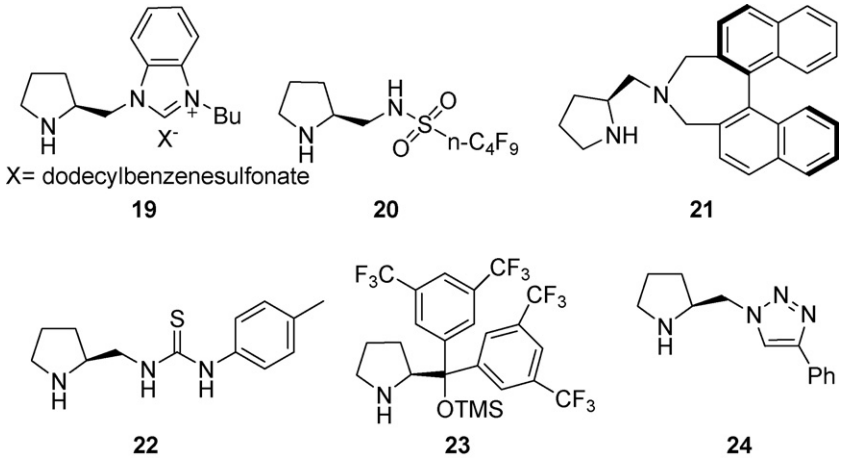


Scheme 24. Enantioselective allylation reactions of aldehydes in an aqueous medium.



Scheme 25. Chiral organocatalysts used in the asymmetric allylation reactions.

moderate selectivity can be obtained when other aldehydes were used. When a large amount of initial chiral ligand (2.6 equiv.), indium (10 equiv.) and allyl bromide (10 equiv.) was employed, they failed to recover the chiral ligand after the reaction. Therefore, this reaction is not atom-economical. Loh and Zhou also employed the (*S*)-BINAP-$AgNO_3$ combination (10 mol%) to catalyze the reaction between aldehydes and allyltributyltin (1 equiv.) in ethanol/water (9:1) at low temperature (Eq. (8), Scheme 24) [75b]. The counterions of silvers salt exhibited no influence. The employment of $AgClO_4$, $AgNO_3$ and AgOTf led to similar results, which was probably due to complete ionic dissociation in aqueous media.



Scheme 23. Surfactant-type asymmetric organocatalysts.

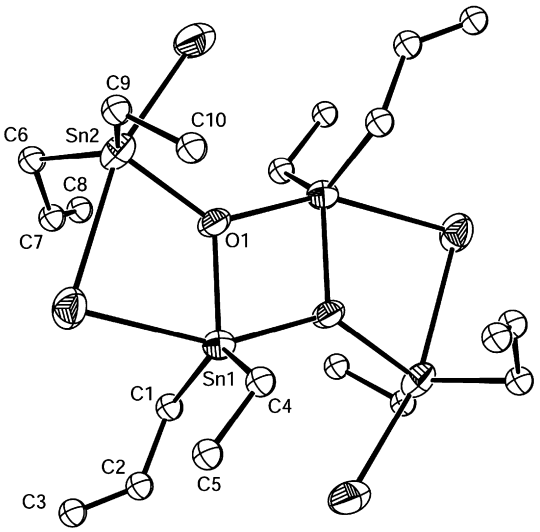
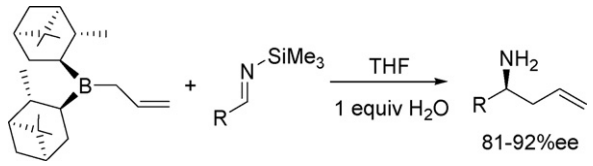


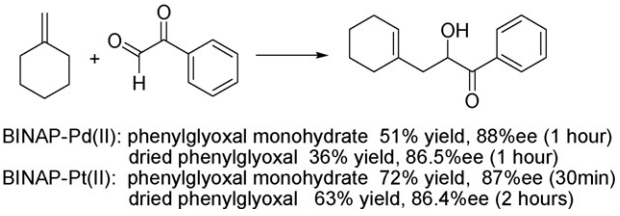
Fig. 3. View showing molecular structure of $Sn_4(\mu_3\text{-}O)_2(\mu_2\text{-}Cl)_2Cl_2Et_4(CH_2CH=CH_2)_4$. Minor disorder components and hydrogen atom excluded for clarity.

Kobayashi et al. discovered that the reaction of allyltributyltin and carbonyl compounds in aqueous media was dramatically accelerated by ligands such as *N*,*N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine [76a], and they developed a **25a**-$CdBr_2$ (Scheme 25) catalytic system in EtOH/H_2O (9:1) [76b]. Ligand acceleration also proceeded in this system, because adding excess $CdBr_2$ to the ligand **25a** did not significantly reduce the enantioselectivity. In the same year, they also reported an asymmetric allylation of hydrozono esters with allyltrimethoxysilane catalyzed by **25b**(**c**)-ZnF_2 in THF/H_2O (9:1) [76c]. Woodward and Cunningham developed a ketone allylation reaction with mixtures of allylstannanes ($Sn(CH_2CH=CH_2)_4$ contaminated by 15–30% $EtSn(CH_2CH=CH_2)_3$) and this reaction was promoted by ligand **26** (Scheme 25) [77]. Interestingly, the mixture produced a higher ee than either of the pure components. The mixture with 70 mol% $Sn(CH_2CH=CH_2)_4$ and 30 mol% $RSn(CH_2CH=CH_2)_3$ (R = Et or Bu) was the most efficient catalyst. Careful studies have revealed that the origin of the highly active and selective catalysts for the allylation of aryl/methyl ketones are formed from ligand **26**, and impure tetraallytin containing $EtSn(CH_2CH=CH_2)_3$, $ClSn(CH_2CH=CH_2)_3$ and especially $ClSn(CH_2CH=CH_2)_3$. The last compound appears to lead to formation of the optimal catalyst through hydrolysis to a distannoxne, whose structure is shown in Fig. 3.

In this structure, the bridging Sn–Cl bond distance [2.7537(13)] is significantly longer than the non-bridging bond distance [2.4720(14)]. This tetraorgano-distannoxne leads to the formation of a rather selective catalyst with **26** at low mol fractions of tin. This derived species appears to be responsible for the selective catalysis. In the allylation of aromatic ketone. In addition, they found that the ee dropped as the conversion increased under the anhydrous conditions, which might be due to the autocatalysis of some achiral compounds generated in the reaction. Addition of a small amount of water inhibited those undesired background reactions, and made the ee value independent of the reaction conversion. In the asymmetric allylation of imines by catalyst **27** (Scheme 25), Yamamoto and co-workers found that adding 1 equiv. of water increased the yield and enantioselectivity, and, what is more important, ensured the reproducibility of the results [78]. Water might coordinate with the tetravalent stannane to facilitate the C–Sn bond cleavage, and thereby accelerate the reaction.



Scheme 26. Asymmetric allylboration of N-silylimine.



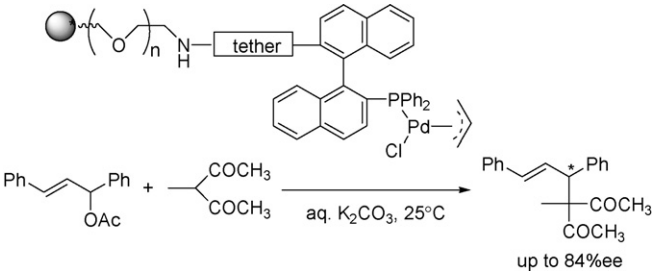
Scheme 27. Enantioselective carbonyl-ene reaction catalyzed by BINAP-Pd(II) and BINAP-Pt(II).

Ramachandran and Burghardt found that in the reagent controlled asymmetric allylation reaction between chiral allylborane and imine (Scheme 26), the reaction did not proceed in the absence of water, and the reaction took place quickly during the aqueous workup process [79]. Based on this discovery, the authors improved the reaction by addition of 1 equiv. water in the course of the reaction at low temperature.

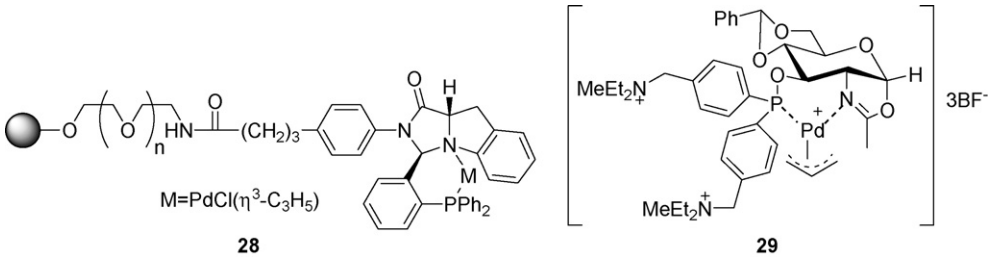
Another method to prepare the allylic alcohol was the carbonyl-ene reaction. Luo et al. have developed a water-tolerant BINAP-Pd(II) and BINAP-Pt(II) to catalyze the reaction (Scheme 27) [80]. In these catalytic systems, the phenylglyoxal monohydrate worked as equally well as, and, in some cases, even better than its anhydrous form, which greatly simplified the experimental operation.

7. Allylic substitution reaction

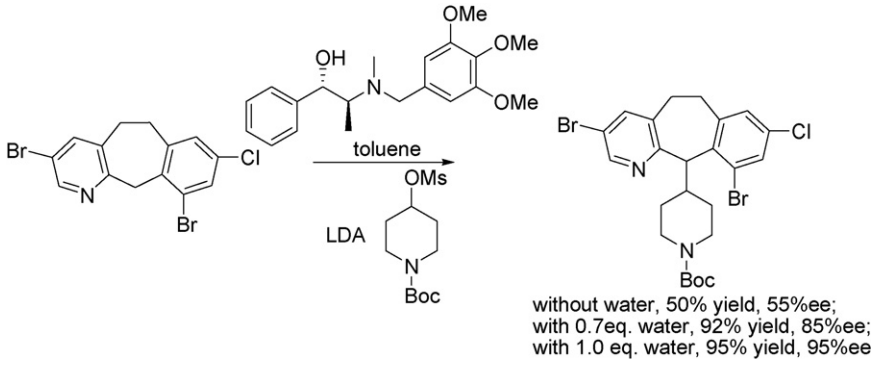
Uozumi et al. reported the aqueous allylic substitution catalyzed by amphiphilic palladium–phosphine complexes bound to PEG-PS resin in 1997 [81a], and extended this system to



Scheme 28. Asymmetric allylic substitution catalyzed by amphiphilic palladium–phosphine complexes bound to PEG-PS resin.



Scheme 29. Supported P,N-chelating palladium complex and D-glucosamine derived chiral complex used in the allylic alkylation.



Scheme 30. Asymmetric benzylic alkylation catalyzed by trimethoxybenzyl-norephedrine ligand.

asymmetric catalysis the next year (Scheme 28) [81b]. The work was further polished by a combinational approach in 2006 [81c].

They also designed a supported P,N-chelating palladium complex catalyst **28** (Scheme 29) to promote the allylic substitution in water [82a]. For both cyclic and acyclic substrates, good yields and excellent enantioselectivities were obtained. The catalyst can be reused three times without significant loss of reactivity. Amines [82b], phenol [82c] and nitromethane [82d] were also suitable nucleophiles in this catalytic system. This catalyst worked more efficiently in water than in dichloromethane. A chiral complex **29** prepared from D-glucosamine can also promote the allylic alkylation in aqueous media, and can be recycled by pH-controlled extraction [83].

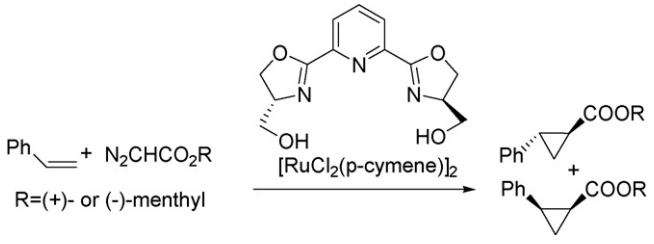
Surfactants, especially cetyltrimethylammonium hydrogen sulfate, were beneficial additives when palladium complex was prepared *in situ* from $[Pd(C_3H_5)Cl]_2$ and BINAP was used to catalyze the allylic substituton in water [84].

8. Alkylation reaction

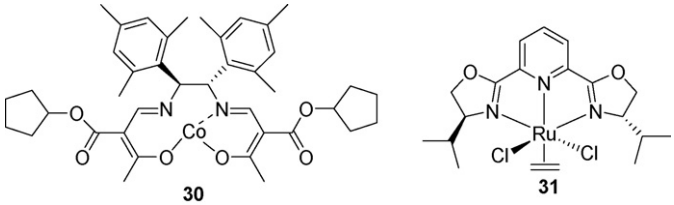
Asymmetric alkylation of glycine-imine by chiral phase-transfer catalyst (PTC) was a convenient method to prepare α-amino acid. Recently contributions in this area were reviewed by Maruoka and Ooi [85], Lygo and Andrews [86], and O'Donnell [87]. An asymmetric benzylic alkylation, a key step to achieve the asymmetric synthesis of Lonafarnib, was counter-intuitively influenced by water (Scheme 30) [88]. In the anhydrous conditions, the ee value of the product fluctuated from run to run. A lower range of ee values was observed when moisture was vigorously excluded from the system. After water was added, both the chemical and optical yield increased and reached maximum when 1 equiv. of water was used.

9. Cyclopropanation reaction

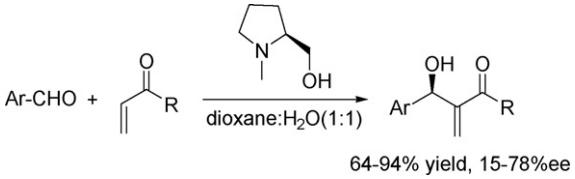
Nishiyama and co-workers employed the pybox–Ru complex to catalyze the reaction between styrene and chiral diazoacetates (Scheme 31) [89]. They found that addition of water enhanced the yield, diastereo- and enantio-selectivities of the reaction, and attributed the enhancement to the increased solubility of the catalyst in water. Water, as an additive, also accelerated the β-ketoiminato cobalt complex **30**-catalyzed cyclopropanation reaction (Scheme 32) [90].



Scheme 31. Asymmetric cyclopropanation conducted by chiral bis(hydroxymethyl-dihydrooxazolyl)pyridine-ruthenium catalyst.



Scheme 32. Catalysts for asymmetric cyclopropanation.



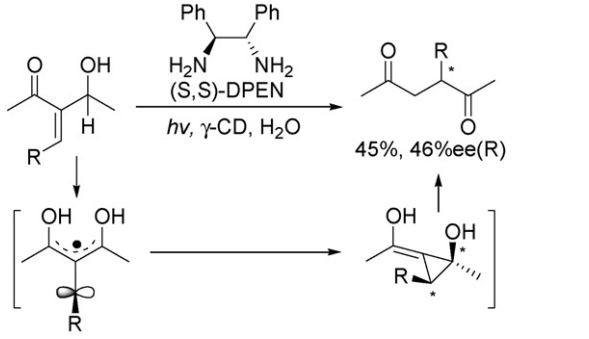
Scheme 33. Proline-derived amino alcohol catalyzed Baylis–Hillman.

Charette and Wurz reported **31**-catalyzed (Scheme 32) cyclopropanation reaction in water [91]. Considering the explosive nature of diazoacetate, it is desirable to carry out a large-scale cyclopropanation reaction in water, because aqueous system permits to generate the diazoacetate *in situ* from corresponding amine. Another asymmetric catalytic system in water was reported by Ubeda and co-workers recently [92].

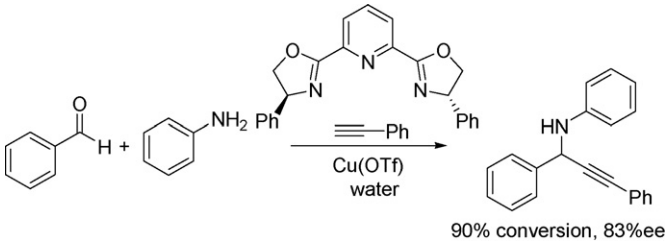
10. Other reactions

Krishna et al. reported the proline-derived amino alcohol catalyzed Baylis–Hillman in dioxane/water (Scheme 33) [93]. The Baylis–Hillman adducts can undergo a photochemical carbon skeletal reorganization to afford the 1,4-dicarbonyl compounds [94a]. In the presence of C_2-symmetric chiral controller, (*S*,*S*)-DPEN, and γ-CD in water, the corresponding 1,4-dicarbonyl compound was obtained in 45% yield and with 46% ee (Scheme 34) [94b]. The recovered substrate also showed 20% ee (*R*). The chirality of the substrate and the controller also affected the enantiopurity of the product. In a matched case ((*R*)-substrate and (*S*,*S*)-DPEN), 80% ee was reached.

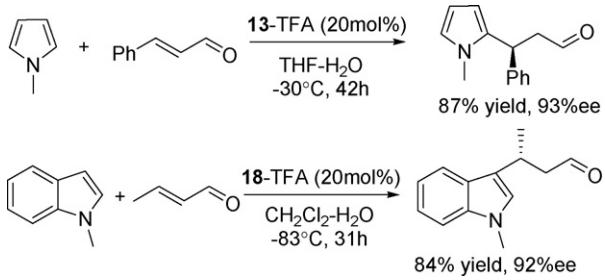
The pybox-Cu(I) catalyzed three-component reaction can also proceed in water (Scheme 35) [95]. Much better results were obtained when some organic solvents were used.



Scheme 34. (*S*,*S*)-DPEN catalyzed carbon skeletal rearrangement of Morita–Baylis–Hillman products.



Scheme 35. Pybox-Cu(I) catalyzed three-component reaction.



Scheme 36. Enantioselective organocatalytic Friedel–Crafts alkylation.

As for the asymmetric Henry reaction, water was a beneficial additive in the Shibasaki's bimetallic catalytic system [96]. The organo-catalyzed Friedel–Crafts reaction can also proceed in the presence of water (Scheme 36) [97].

11. Conclusion

Water is an essential substance for natural life, and how it affects the organic reactions remains an elusive puzzle. Recently Sharpless indicated that the acceleration of water on the organic reactions can be attributed to its "on water" conditions [98]. Marcus indicated that the reaction on water occurred at an oil–water boundary, in which approximately one in every four interfacial water molecules has a dangling OH group that protrudes into the organic phase [99]. These OH's can form strong hydrogen bonds with the reaction transition state and reduce the energy of the transition state, resulting in the acceleration in the reaction. One supposes that these hydrogen bonds can also affect the attack direction of a reaction reagent to a reaction substrate, which has an influence on the stereoselectivity of a product. Somehow, water has a great influence on the stereoselectivities of the products. We believe that chemists will solve this puzzle in the future.

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