Publications

Available Online

J. Sci. Res. **15** (1), 285-300 (2023)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Review Article

Recent Developments on Brønsted Acid Catalyzed Asymmetric Aldol Reactions and the Fate of the Catalysts

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Received 9 May 2022, accepted in final revised form 29 September 2022

Abstract

Since the innovative work of Terada and Akiyama, asymmetric reaction using chiral Brønsted acid has attracted great attention. Asymmetric aldol reactions are extensively studied in different organocatalysis. Brønsted acid-catalyzed aldol reaction may be carried out directly without modification of the substrates or Mukaiyama type aldol reaction using silyl enol ether as nucleophiles. The reaction may proceed through the formation of enol intermediate followed by the attack to the electrophile while Mukaiyama type aldol reactions may follow two mechanistic pathways- Brønsted acidic pathways where Brønsted acid directly activates the substrate or Lewis acid pathways where Brønsted acid acts as pre-catalyst. Here, the recent advancement of asymmetric aldol reactions using chiral Brønsted acid as a catalyst and the fate of the catalysts in the reaction has been discussed in this review. It is observed that some kinds of aldol reactions have rarely been studied and need more attention.

Keywords: Asymmetric; Aldol; Brønsted acid; Organocatalysis.

doi: http://dx.doi.org/10.3329/jsr.v15i1.59614 J. Sci. Res. **15** (1), 285-300 (2023)

1. Introduction

Aldol reaction is predominantly used in chemical transformations in synthetic organic chemistry. It has immense application in the preparation of many important biologically active compounds, e.g., antibiotics, antitumor compounds, antiproliferative, antifungal, and heart diseases drugs, etc. [1-3]. The reaction is important in many aspects, such as it can generate a new carbon-carbon bond with the generation of one or more stereogenic centers. Generally, an aldol reaction can be carried out in the presence of acid or base to form β-hydroxy ketone or aldehyde, but the concept of catalysis is needed to develop the environmentally benign process. In the catalytic process, a reaction can be accomplished under milder conditions by using a very small quantity of catalyst. So, extensive research is undergoing to develop a new catalytic process and control the chiral centers' absolute

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stereochemistry over 50 years [4,5]. Among the various asymmetric approaches, the most favored one is asymmetric catalysis, where a sub-stoichiometric amount of asymmetric catalysts are used [6-10].

The first asymmetric catalytic aldol type reaction was developed by Mukaiyama *et al*. in1973 with silyl enol ethers using a metal catalyst [11-13]. Since then, enormous studies have been carried out to improve the metal-catalyzed enantioselective aldol reactions [14-18] and were used in several valuable syntheses [19]. However, the drawback of metal catalysis is that synthesizing these catalysts requires stoichiometric amounts of chiral sources, instability under aerobic conditions, and moisture sensitivity; some of them are toxic, and there are also several other limitations in synthetic applications [20,21]. So, a complementary catalytic approach, coined organocatalysis, was developed [22]. Asymmetric organocatalysisis performed in the presence of a small amount of pure chiral organic compound to induce enantioselectivity and is completely devoid of metals**.** The uses of the organocatalysts are superior as their limitations are very less than metal catalysts, and they are environmentally friendly. Over the last two decades, asymmetric organocatalysis has witnessed tremendous growth with newer concepts [23,24]. The latest addition was the asymmetric Brønsted acid catalysis developed independently by Akiyama and Tereda with their discovery of *pseudo*–C_2-symmetric chiral phosphoric acids [25,26]. Since then, the asymmetric Brønsted acid catalyst has been extensively studied. Chiral Brønsted acids have emerged as efficient enantioselective catalysts for the activation of a variety of functional groups such as imines, vinyl ethers, carbonyl groups, alkenes, and many more [27-29].

2. Aim of This Review

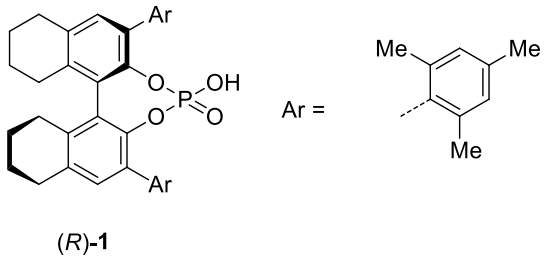
The objective of this review is mainly to focus on the recent development of catalytic asymmetric aldol reactions in the presence of chiral Brønsted acids. In the case of direct aldol reaction, the activation of the substrate can occur via hydrogen bonding or protonation, but it is often difficult to distinguish between these modes of activation [30]. In the case of Mukaiyama type aldol reaction, activation may occur either through direct protonation of the carbonyl compound by the Brønsted acid. Brønsted acid may first be silylated with silylenol ether, and the silylated Brønsted acid then activates the carbonyl compounds acting as pre-catalysts. This review will not discuss weak hydrogen bond donor catalysts such as chiral thioureas, chiral TADDOLs, etc. catalyzed aldol reactions [31-34]. The discussion on Chiral Brønsted acid catalyzed asymmetric Mannich type reaction [27-29], asymmetric acetylation [24], enantioselective aza-Friedel-Crafts reaction [35,36], asymmetric nitro-aldol, enantioselective aza-Darzens reaction, and many more[27-29] are not discussed in this review.

3. Asymmetric Direct Aldol Reactions

One of the great challenging tasks in catalysis is to perform the aldol reaction in a direct catalytic diastereoselective and enantioselective way [37]. The earliest asymmetric direct

aldol reactions were reported by using enzymes as catalysts [38,39]. Bifunctional chiral metal complexes catalyzed by direct aldol reaction also enriched the field [40-43]. Since the seminal work of List, Lerner, and Barbas [44,45], organocatalyzed asymmetric direct aldol reactions have shown remarkable progress [46-48]. The organocatalytic enantioselective direct aldol reaction is mainly governed by aminocatalysis, where proline or other organocatalysts with primary or secondary amino groups catalyzed the aldol reaction via an enamine intermediate [49,50]. Other important organocatalysis that contributed to direct aldol reactions are asymmetric thioureas or weak hydrogen bond donor catalysis [51,52] and asymmetric cinchona alkaloids derived catalysis or basic catalysis [53-55].

Chiral Brønsted acid-catalyzed direct aldol reaction was a significant addition in this field and is still in the preliminary stage. Only a few examples are reported in this field from 2009-2011 [56-58]. This is because of the high activation energy required to activate the carbonyl group and the lack of proper acidic chiral Brønsted acid to catalyze carbonyl compounds. Blanchet *et al*. showed the potential of BINOL-derived chiral phosphoric acid (*R*)-**1** to catalyze direct aldol reaction with a variety of carbonyl nucleophiles like cyclic and aromatic ketones with limited scope to the electrophiles (Fig. 1) [57,58]. The development was a complementary approach to enamine catalysis as it solved the problem in enamine catalysis with hindered donors such as acetophenone and fused cyclic aromatic ketones. Besides, the α,β-unsaturated ketones are challenging substrates in amine catalysis due to the probable trap of amine catalysts through an irreversible 1,4-Micheal type addition are also found suitable. But the reaction was limited to only activated electrophile ethyl glyoxalate. Low yields and moderate enantioselectivities are other limitations in this catalysis. To date, there are no improved methods reported.



(*R*)-**1**

Fig. 1. Catalysts for direct aldol reactions [57,58].

5. Asymmetric Mukaiyama Aldol Reactions

The most commonly studied asymmetric aldol reaction is the Mukaiyama Type aldol reaction. Traditionally, the reaction is performed between an aldehyde or a ketone and a silyl enol ether to obtain an aldol adduct containing one or more chiral centers [11-13]. Many successful examples of enantioselective Mukaiyama type aldol reactions employed Lewis acid [59] or Lewis base [60] catalysts. Here, the recent development of the Brønsted acid-catalyzed asymmetric Mukaiyama type aldol reactions will be discussed.

6. Chiral Brønsted Acid Catalyzed Asymmetric MukaiyamaAldol Reactions

The asymmetric version of Mukaiyama type aldol reaction in the presence of chiral Brønsted acid may follow two pathways: (a) Brønsted acidic pathway assuming the direct protonation of carbonyl compound by Brønsted acid itself (Fig. 2) [61] and (b) Lewis acid pathway assuming Brønsted acid may first be silylated with silylenol ether. The silylated Brønsted acid then activates the carbonyl compounds following counter-anion directed catalysis (Fig. 2) and is also known as Asymmetric counter anion directed catalysis (ACDC) involving chiral catalyst [62].

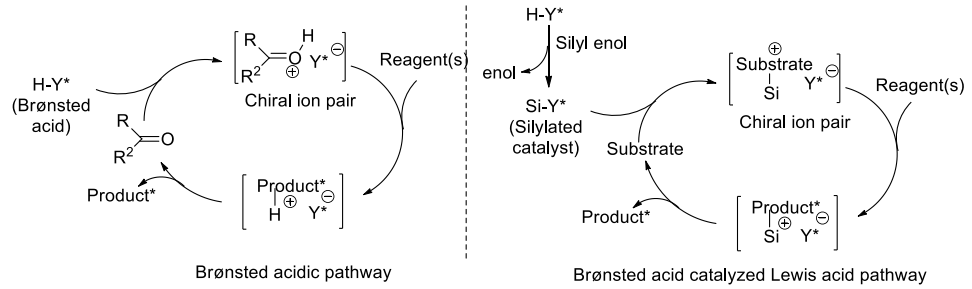


Fig. 2. General schematic diagram of chiral Brønsted acid catalyzed Mukaiyama aldol reaction.

6.1. *Brønsted acid catalyzed asymmetric Mukaiyama aldol reactions following Brønsted acidic pathways*

The pioneering works on Brønsted acid catalyzed asymmetric Mukaiyama Aldol reaction was reported by Zhuang and co-workers in 2005 employing chiral bis-sulfonamide Brønsted acid catalysts **19** (Fig. 3). This was the first instance of asymmetric Mukaiyama aldol reaction following Brønsted acidic pathways [63]. In 2010, Cheon and Yamamoto developed chiral triflylthiophophoramide **3** catalyzed Mukaiyama type aldol reactions of aldehydes with silyl enol ether of ketones**,** where they observed that at low temperature, the reaction follows Brønsted acid catalyzed pathway (Fig. 3)[61].

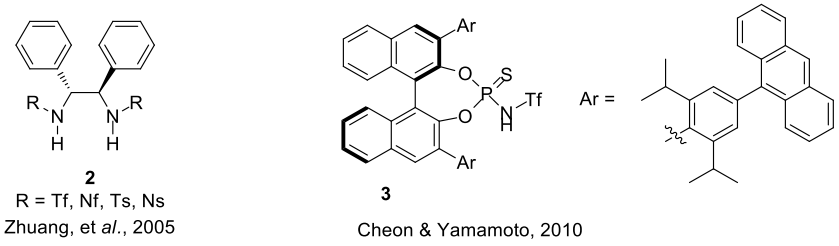


Fig. 3. Catalysts that follow Brønsted acidic pathway in Mukaiyama Aldol reactions [61,63].

Later, in 2015, Sai and Yamamoto expanded the scope of Brønsted acid catalyzed Mukaiyama aldol reactions with newer thiophosphoramide catalysts **4** introducing a

perfluoroalkyl group on the sulfonamide and *tert*-butyldiphenylsilyl (TBDPS) groups on the 3,3′-positions of the aromatic groups (Fig. 4) [64].

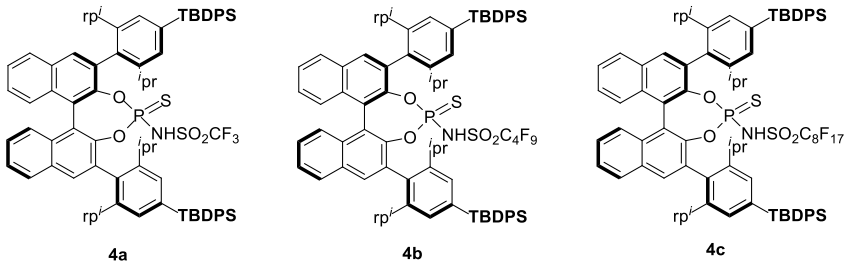


Fig. 4. New thiophosphoramide catalysts **4** [64].

At the optimized conditions, the authors found that the new chiral *N*-(perfluorooctanesulfonyl)thiophosphoramide catalyst **4c** was more reactive compared to other thiophosphoramide catalysts and delivered higher diastereo- and enantioselectivities for the Mukaiyama type aldol reactions of aldehydes **6** with various silyl enol ethers **5** (up to 98 % ee and 99:1 d.r.) (Fig. 5). But, the catalyst **4c** was ineffective to produce the desired aldol product from aliphatic aldehydes.

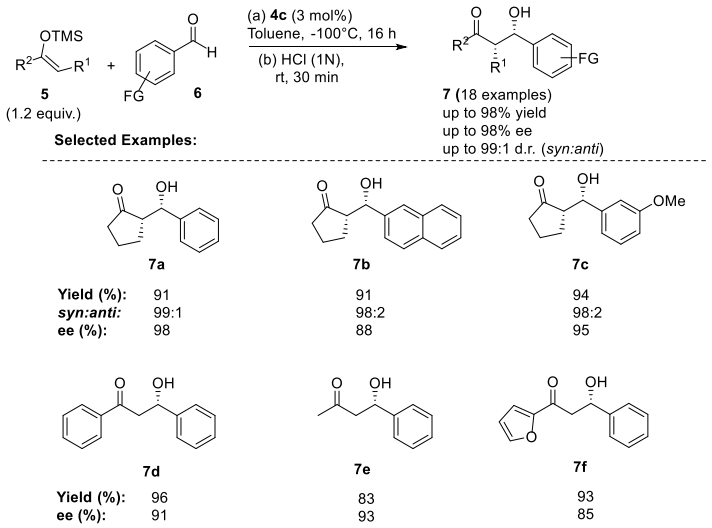


Fig. 5. Chiral **4c** catalyzed asymmetric Mukaiyama aldol reactions [64].

According to their Mechanistic studies, the reaction followed the Brønsted acidic activation pathway in the presence of Chiral *N*-(perfluorooctanesulfonyl)thiophosphoramide **4c** at low temperature rather than the Lewis acidic pathway as described before [61,65].

6.2. *Brønsted acid catalyzed asymmetric Mukaiyama aldol reactions following Lewis acid pathways:*

Strong achiral Brønsted acid and Triflimide have shown tremendous potential in counter-anion-directed Mukaiyama type aldol reaction [66,67]. Several chiral Brønsted acid-catalyzed ACDC types were reported in 2009 by List and co-workers using bis-sulfonimide catalyst [65,68-71]. In this review, the main focus will be given to the reported findings catalyzed by chiral Brønsted acid from 2015 onwards.

In 2016, List and co-workers synthesized new chiral disulfonimide **8** (Fig. 6) and successfully employed it in the asymmetric counter anion directed [65, 72-74] alkynylogous Mukaiyama aldol reaction of aldehydes **6** with silyl alkynyl ketene acetals **9** (Fig. 7) [75].

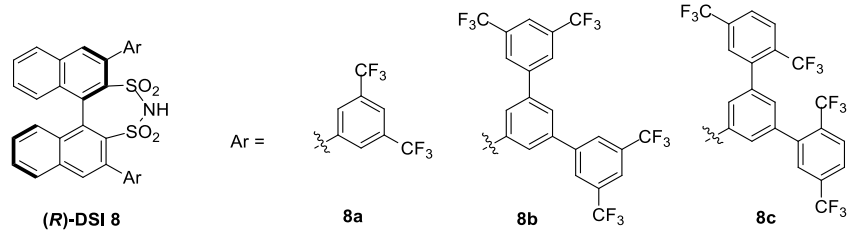


Fig. 6. New bis-sulfonimide catalysts developed for asymmetric Mukaiyama aldol reactions [75].

The authors discovered that all the newly designed DSI catalysts DSI-**8** (Fig. 6) were efficient in providing tetra-substituted allene **10a,** although **8c** was the most effective one in providing high regioselectivities, diastereoselectivities, and enantioselectivities. The catalyst **DSI 8c** afforded the carbinol allenoates **10** in high yields, diastereoselectivities, and enantioselectivities (Fig. 7). Unfortunately, aliphatic aldehydes remained challenging in Mukaiyama type aldol reaction with the catalysts disulfonimide **8**.

Mechanistic studies revealed that the reaction follows counter-anion-directed catalysis of strong chiral Brønsted acid (ACDC) (Fig. 2) [65,72-74]. Noticeably, the aldol products are conveniently transformed into highly substituted enantiomerically enriched various building blocks, e.g., γ-lactones **11**, δ-lactones **12**, dihydrofurans, and *E*-olefins (Fig. 8).

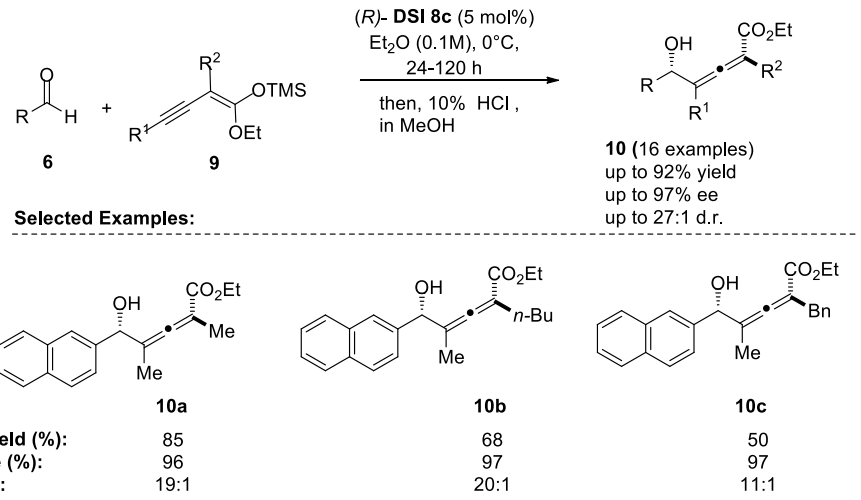


Fig. 7. Asymmetric alkynylogous Mukaiyama aldol reaction catalyzed by DSI-**8c** [75].

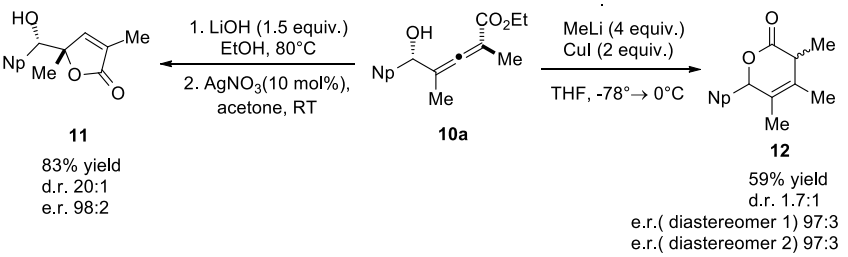


Fig. 8. Derivatization of the enantiomerically enriched carbinol allenoate **10a** [75].

Tsujihara and co-workers synthesized helically chiral [6]-helicene-based disulfonimide **(*P*)-15** and evaluated those in the Mukaiyama type aldol reaction of 2-naphthaldehyde with silyl ketene acetal **13** and found all the catalysts **15** are effective to provide aldol products **(*R*)-14** in good yields albeit with very low enantioselectivities (up to 24 %) (Fig. 9) [76].

List and co-workers designed various new types of confined Brønsted acid catalysts for asymmetric catalysis [77]. Some of them were found to be extremely active in ACDC type Mukaiyama type aldol reactions [78,79].

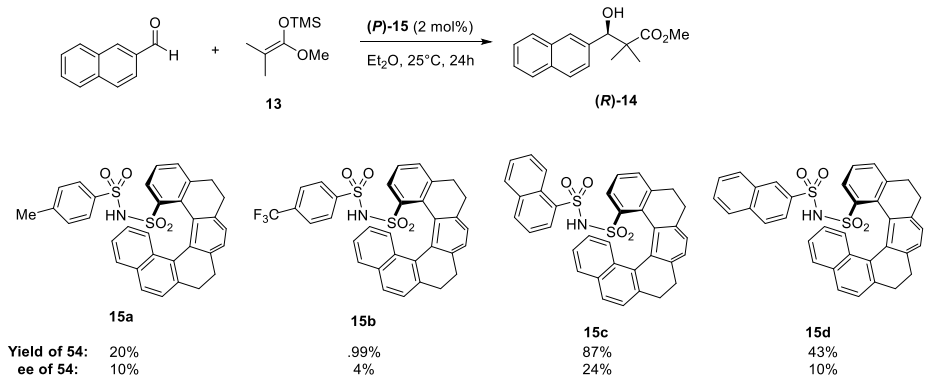


Fig. 9. Chiral [6]helicene-based (*P*)-**15** catalyzed Mukaiyama aldol reactions [76].

In 2018, they explored confined imidodiphosphorimidate (IDPi) **16** in a highly challenging C-C bond-forming reaction in a Mukaiyama-type aldol reaction (Fig. 10). [80] The catalysts were found extremely active in the addition reaction of simple silylenolate of acetaldehyde **17** to various aromatic and aliphatic acceptor aldehydes **6** (Fig. 11).

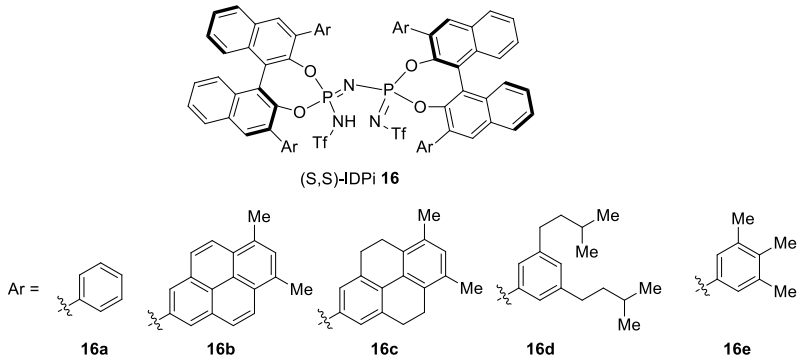


Fig. 10. IDPi **16** for Mukaiyama Aldol reaction using silylenolate of acetaldehyde as a donor [80].

The reaction was accomplished in the presence of 0.5 to 1.5 mol % of catalyst IDPi catalyst **16a-e**. The resulting aldol products **18** were obtained from moderate to high enantioselectivities (up to 98 %). These examples showed the efficiency of IDPi catalyst **16** compared to the disulfonimides **8** described before, where the latter failed to catalyze aliphatic aldehydes in the Mukaiyama type aldol reaction.

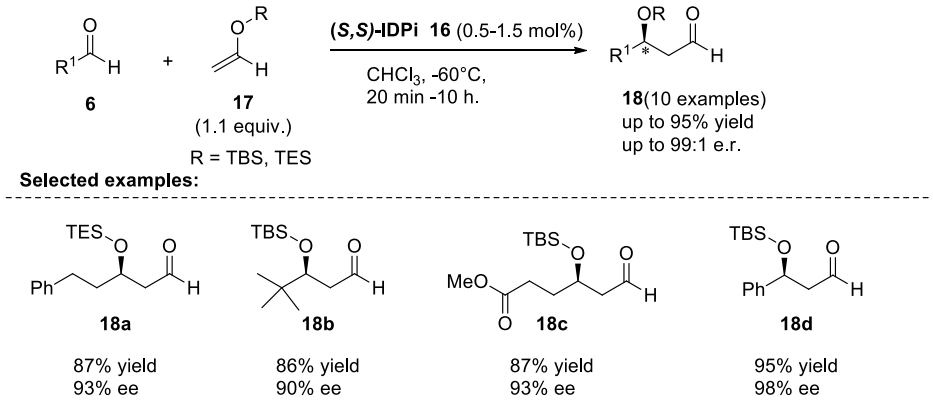


Fig. 11. IDPi-catalyzed Mukaiyama aldol reaction using enolsilanes of acetaldehyde as a donor [80].

Their Mechanistic studies followed an asymmetric counter-anion-directed Lewis acidic pathway (Fig. 2) where the strong Brønsted acid IDPi acts as a pre-catalyst [72-74, 80].

Remarkably, the aldol products were used to prepare biologically active molecules, e.g., the formal synthesis of (*S*)-duloxetine **21** (antidepressant) (Fig. 12) [81].

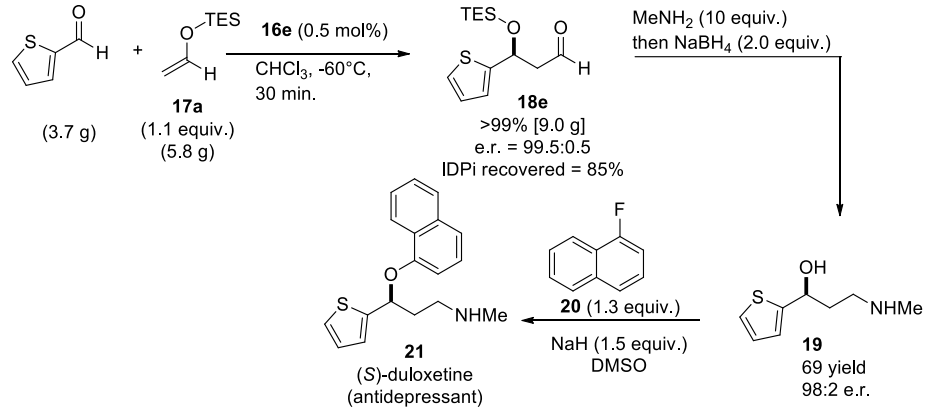


Fig. 12. Application of aldol reaction in the synthesis of (*S*)-duloxetine [80].

In the same year, they also reported another application of modified extremely active catalyst confined imidodiphosphorimidate (IDPi**) 22** (Fig. 13) in a Mukaiyama type aldol reaction of silyl ketene acetal **24** (Fig. 14) [82]. The authors observed that the Mukaiyama aldol reaction of silyl ketene acetal **24** with 2-acetonaphthone afforded the aldol product **25** in the presence of **22a** (0.1 mol %) within 3 min. At the same time, the DSI-**8** failed to promote the reaction even after 24 h. Observing this tremendous potential, the authors optimized several IDPi catalysts **22a-e** (Fig. 13) and observed that all the imidodiphosphorimidate (IDPi) **22** catalysts were affording aldol adducts **25** in

quantitative yields within a very short time with good to excellent enantioselectivities while the IDPi catalysts **22b, 22d** and **22e** were exceptionally efficient to provide quantitative yield with excellent selectivities using 50-500 ppm of catalyst loading[82].

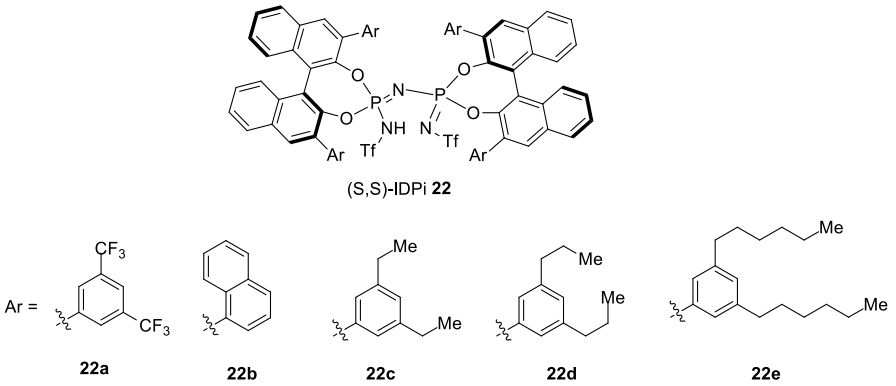


Fig. 13. IDPi **22** for asymmetric aldol reaction of silyl ketene acetals.

The authors also investigated the performance of the catalyst **22e** on the Deca-gram scale using 25 ppm catalyst loading and extremely low catalyst loading reaction <1 ppm and obtained the aldol products in high yields with excellent yields enantioselectivities (>90 % ee). They also performed repeated addition experiments of materials after consumption of the initial reaction mixture and found extremely good turnover (TON ~ 911,000) using the sub-ppm level of catalyst loading (< 1 ppm) [82].

Accordingly, this was the first instance of sub-ppm level loading of an organocatalyst in a challenging carbon-carbon bond forming reaction with high enantioselectivity.

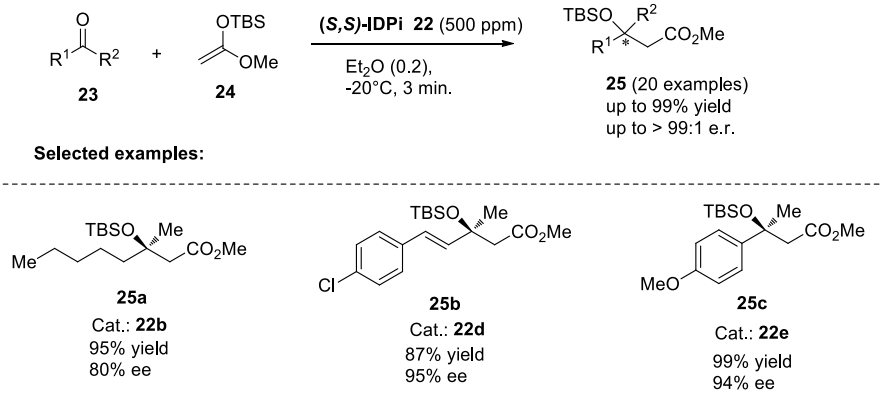


Fig. 14. Imidodiphosphorimidate (IDPi) **22** catalyzed asymmetric Mukaiyama Aldol reactions [82].

To know the mechanistic pathway, the authors performed a real-time analytical investigation using in-situ Fourier transform infrared (FT-IR) spectroscopy. The analysis confirmed that IDPi catalyst acts as a strong Brønsted acid pre-catalyst, and the reaction

proceeded through the formation of a silylated ion pair **27**. Counter-anion-directed Lewis acidic asymmetric control determined the selectivity of the aldol product (Fig. 15) [82].

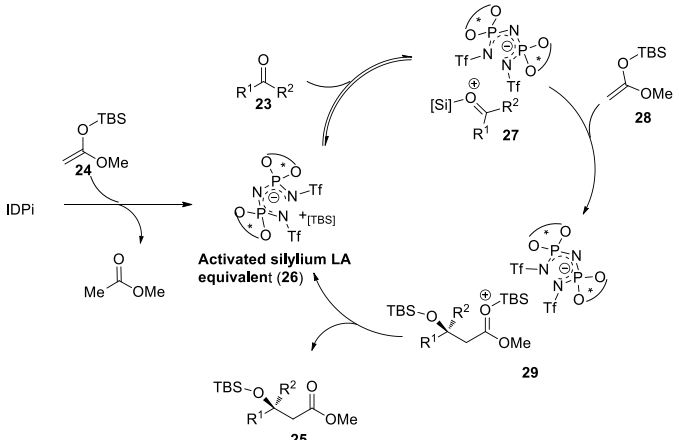


Fig. 15. Proposed reaction ACDC mechanism using the IDPi-catalysts in Mukaiyama Aldol reaction [82].

The remarkable difference in catalytic activity between two catalysts **DSI-8 (8** did not catalyze the reaction) and IDPi **22a** (reaction completed within 3 min), was explained by counter-anion basicities. The authors measured p*Ka* values of several different chiral Brønsted acid catalysts, including D**SI 8** (p*Ka*=8.4) and IDPi-**22a** (p*Ka* = 4.5) catalyst, with reference to some achiral acids in acetonitrile and concluded that the **DSI 8** anion is sufficiently basic to deprotonate oxocarbenium ion to produce the corresponding enol silane. So, the reaction did not proceed. In contrast, the IDPi **22** anion is too weak a base to deprotonate the oxocarbenium ion and facilitates only the Mukaiyama aldol pathway [82].

Recently, another interesting application of newly designed IDPi **30** catalysts (Fig. 16) was reported from the same group where propionaldehyde enolsilanes, a very challenging substrate in enantioselective Mukaiyama aldol reactions, were successfully used for single aldolization and obtained protected aldols **32** (*anti*) and **33** (*syn*) in excellent yields and selectivities with various aromatic aldehydes (Fig. 17) [83]. Noticeably, IDPi catalysts delivered all the four possible stereoisomers (Fig. 17), while triflimide, a well-established catalyst for Mukaiyama aldol reactions, failed to produce a single aldolization product due to complete oligomerization of enolsilane. The enzyme-like activity of the IDPi catalysts is thought to be responsible for the exclusive aldolization.

The facial selectivity change in the case of **30d** was explained through the possible intramolecular hydrogen bonding leading to a smaller pocket size of the confined IDPi catalyst. The aldol products can easily be used in the syntheses of diverse, complex polyketide motifs. They explained their results through computational (DFT) and analytical mechanistic studies [83].

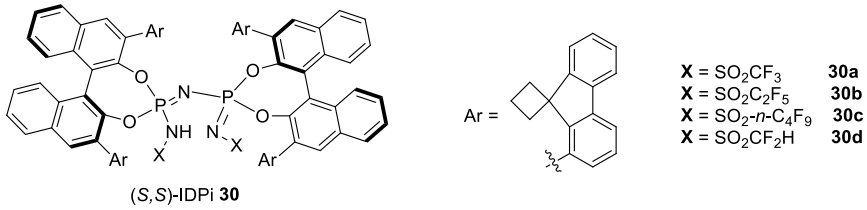


Fig. 16. New IDPi catalysts for ACDC type Mukaiyama aldol reactions [83].

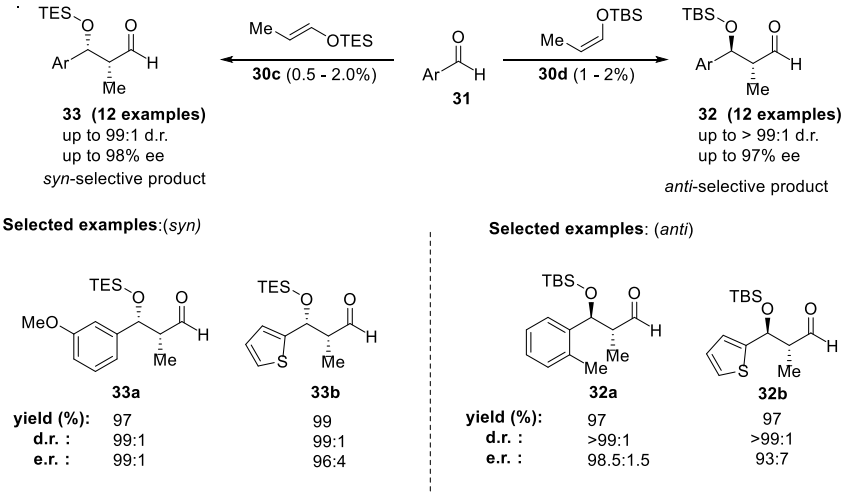


Fig. 17. (*S,S*)-IDPi **30** catalyzed Mukaiyama aldol reaction of propionaldehyde enolsilanes [83].

7. Conclusion

In this review article, the recent development of chiral Brønsted acids catalyzed asymmetric aldol reactions, and the fate of the catalysts have been summed up. Chiral Brønsted acid catalyzed Asymmetric direct aldol reaction using carbonyl pronucleophiles was given a promising beginning, but it did not progress at all in the last ten years. Many limitations remain in Brønsted acid-catalyzed direct aldol reactions, and much more attention is required to improve the environmental issues in asymmetric aldol reactions like the use of water in place of organic solvents; decrease in catalysts loading, and improving selectivities. Moreover, a remedy for more challenging substrates such as weakly acidic groups, amides, and non-activated esters should find an interest in developing more diverse direct aldol reactions like vinylogous direct aldol reactions should be given. Furthermore, detailed mechanistic studies of Brønsted acid-catalyzed direct aldol reactions are required to know the function of the catalysts.

On the contrary, chiral Brønsted acid catalyzed asymmetric Mukaiyama type aldol reactions using silyl enol ethers are highly enriched with asymmetric counter-anion directed catalytic pathway where the Brønsted acid acted as a pre-catalyst. While very rare examples are found where Mukaiyama type aldol reaction was controlled by the Brønsted acidic pathway, although the exact mechanistic studies were not performed. Since any kind of pathway has its own limitation regarding substrate scope or selectivities, improvement is always an essential part of the research. In this regard, Brønsted acidic pathway may overcome its limitations with extensive theoretical and experimental studies to determine the actual interactions involved during the reactions. It is expected that the pioneering results of Brønsted acid-catalyzed aldol reactions reviewed here will encourage numerous research groups around the world, and the field of Brønsted acid-catalyzed aldol reactions will witness tremendous growth.

Acknowledgments

I am thankful to Sreegopal Banerjee College, Bagati, for providing computer facilities, software, and internet facilities.

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