Progress in Asymmetric Biomimetic Transamination of Carbonyl Compounds

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TUTORIAL REVIEW

Progress in Asymmetric Biomimetic Transamination of Carbonyl Compounds

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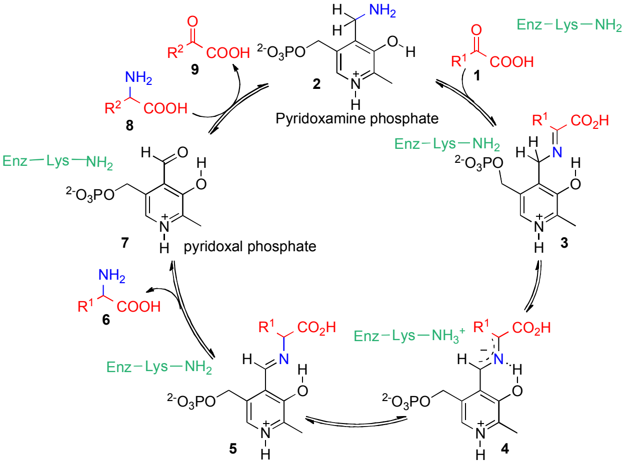
Transamination of α-keto acids with transaminases and pyridoxamine phosphate is an important process to form optically active α-amino acids in biological systems. Various biomimetic transamination systems have been developed for carbonyl compounds including α-keto acid derivatives, fluoroalkyl ketones, and unactivated ketones with chiral vitamin B_6 analogues, artificial transaminase mimics, chiral nitrogen sources, and chiral catalysts. This review describes a brief summary in this area.

Key learning points

(1) Introduction of biological transamination of α-keto acids.
(2) Design of chiral pyridoxamine analogues and artificial transaminase mimics.
(3) Development of catalytic asymmetric transamination of carbonyl compounds.

1. Introduction

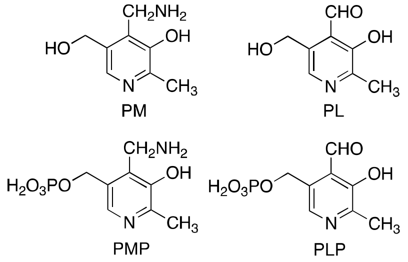
Optically active amino acids and their derivatives play a very important role in biological systems and chemical synthesis. Transamination of α-keto acids is an important biological process to generate α-amino acids (Scheme 1).[1,2] In this process, α-keto acid **1** reacts with pyridoxamine phosphate (**2**) to form ketimine **3**, which is converted into aldimine **5** via asymmetric [1,3]-hydrogen shift mediated by a transaminase. Aldimine **5** is hydrolyzed to α-amino acid **6** and pyridoxal phosphate (**7**). Pyridoxamine phosphate **2** could be regenerated from pyridoxal phosphate (**7**) and another α-amino acid (**8**) via a reverse process. Great efforts have been made in developing asymmetric biomimetic transamination processes to generate optically active amino acids and related compounds via various strategies including chiral pyridoxamine derivatives, artificial transaminase mimics, chiral nitrogen sources, chiral catalysts etc.[3-7] This review will briefly highlight the development in this area.



Scheme 1. Biological transamination of α-keto acids

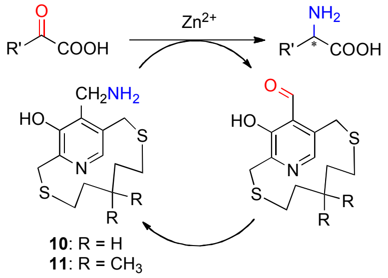
2. Vitamin B_6 Analogues

Pyridoxamine 5'-phosphate (PMP) and pyridoxal 5'-phosphate (PLP) belong to the vitamin B_6 family (Scheme 2) and function as co-enzymes for the transamination in biological systems. A variety of chiral pyridoxamine analogues have been synthesized and investigated for the asymmetric biomimetic transamination.



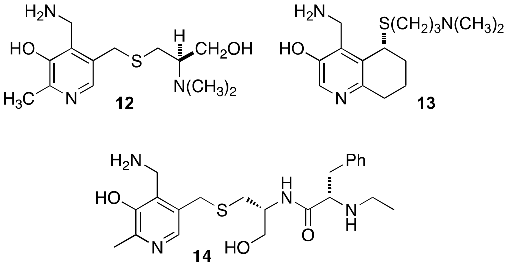
Scheme 2. Members of the vitamin B_6 family

For example, in 1978, Kuzuhara and coworkers reported their studies on transamination of α-keto acids with chiral “ansa chain” based pyridoxamine analogue **10** (Scheme 3).[8] Phenylalanine was obtained in 55-83% yield and 6-26% ee when the sodium salt of phenylpyruvic acid was treated with **10** in the presence of Zn^{2+} at room temperature.[8] Further studies showed that higher ee was obtained with **11** than **10**. The molar ratio of Zn^{2+}/**10** or **11** was important for the enantioselectivity. A number of amino acids were obtained in 60-96% ee when the reactions were carried out with sodium salts of α-keto acids (2 equiv), pyridoxamine analogue **11** (1 equiv), and $Zn(ClO_4)_2\cdot 6H_2O$ (0.5 equiv) in MeOH at room temperature. In all cases, the corresponding aldehyde of **11** can be isolated in 75-85% yield.[9-11] With chiral pyridoxamine analogue **11**, several non-natural fluorophenylalanines were obtained in 33-66% ee from the corresponding α-keto acids.[12]

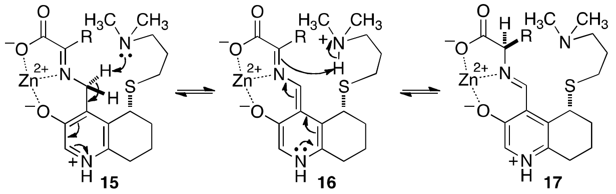


Scheme 3. Transamination of α-keto acids

Breslow and coworkers investigated a series of chiral pyridoxamine analogues containing basic side chains such as **12**[13], **13**[14,15], and **14**[16] for the transamination of α-keto acids (Scheme 4). Up to 92% ee was obtained for α-amino acids when the reaction was carried out with α-keto acids and bicyclic compound **13** in the presence of $Zn(OAc)_2$ in MeOH (pH = 4.0) at 30 °C.[14,15] The high enantioselectivity obtained with **13** can be attributed to the rigidity of the basic side arm, which allows the proton transfer to occur predominately from one face (Scheme 5).[14] Significant rate acceleration was also observed for the transamination as compared to pyridoxamine analogue without the basic group in the side chain.[13-15]



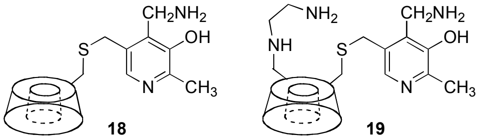
Scheme 4. Chiral pyridoxamine analogues with basic side chains



Scheme 5. Enantioselective deprotonation and protonation

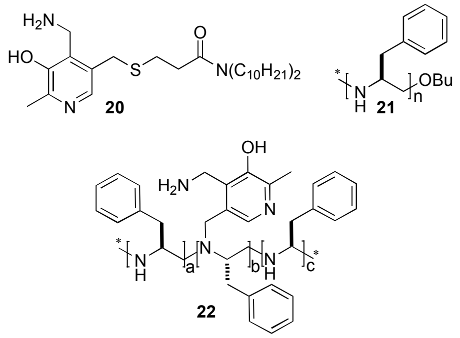
3. Artificial Transaminase Mimics

Transamination with a pyridoxamine linked to β-cyclodextrin (**18**) was reported by Breslow and coworkers in 1980 (Scheme 6).[17] A 200-fold rate acceleration was observed with **18** as compared to pyridoxamine itself for the conversion of indolepyruvic acid to tryptophan. A 5:1 ratio of L-Phe to D-Phe was obtained for the transamination of phenylpyruvic acid with **18**.[18,15] In 1985, Tabushi and coworkers showed that β-cyclodextrin-pyridoxamine-ethylenediamine **19** was highly effective for the transamination, giving L-phenylalanine, L-tryptophan, and L-phenylglycine in 90-96% ee (Scheme 6).[19,20]



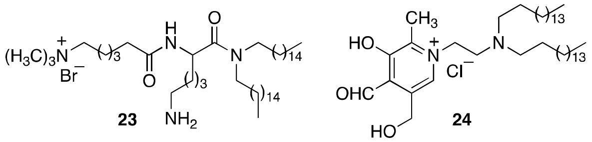
Scheme 6. β-Cyclodextrin-pyridoxamines

Bresolw and coworkers also investigated the asymmetric transamination with pyridoxamine analogues bound to chiral dendrimers[21,22] and polymers[23] (Scheme 7). For example, up to 66% ee was obtained for L-Val at the initial stage of the reaction with pyridoxamine **20** bound to chiral PEI **21** via hydrophobic interactions in 40% aqueous methanol at pH 7.3-7.8.[23] Racemization of the amino acid was observed under the reaction conditions. With covalently bound chiral polymer-pyridoxamine **22**, L-phenylalanine was obtained in 58% ee from phenylpyruvic acid.[23] Little racemization of the amino acid occurred with this system. In 2004, Nicholls and coworkers reported that a transition state analogue-imprinted polymer could act as a transaminase mimic, giving phenylalanine in 32% ee.[24]

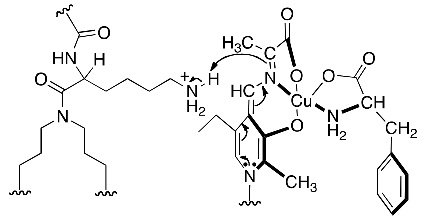


Scheme 7. Chiral polymer-pyridoxamines

Murakami and coworkers reported the asymmetric transamination with supramolecular bilayer membrane based artificial aminotransferase.[25-27] For example, up to 92% ee was obtained for D-alanine when the reaction was carried out with pyruvate (5 equiv), L-Phe (5 equiv), peptide lipid **23** (1 equiv), hydrophobic pyridoxal analogue **24** (0.05 equiv), and $Cu(ClO_4)_2$ (0.05 equiv) in aqueous 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) buffer (pH 7.0) at 30 °C (Scheme 8).[27] L-Phenylalanine not only acted as the nitrogen source for the conversion of pyruvate to D-alanine, but also played an important role in the enantioselectivity as a chiral ligand for the Cu(II) complex (Scheme 9).[27] Distefano and coworkers illustrated that high enantioselectivity (up to 94% ee) can be achieved for the transamination with protein-pyridoxamine conjugates linked via disulfide bond.[28]



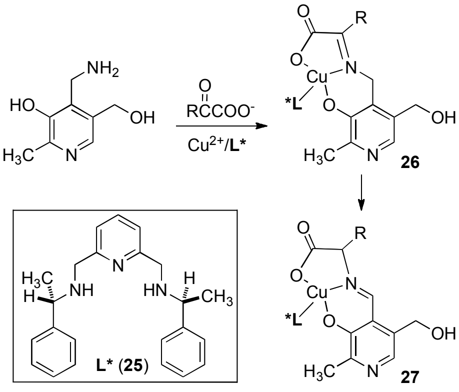
Scheme 8. Compounds for supramolecular bilayer membrane



Scheme 9. Stereoselective protonation of the ketimine complex

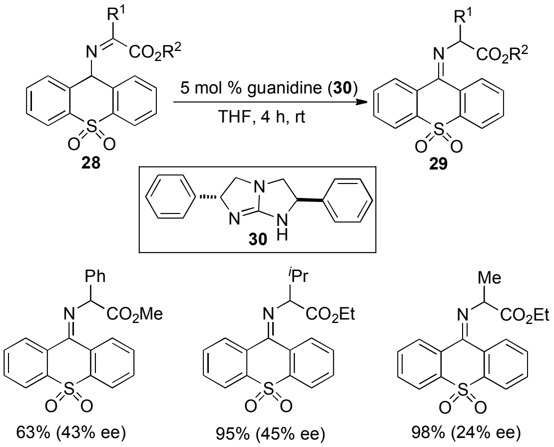
4. Catalytic Asymmetric Transamination

In 1983, Bernauer and coworkers reported that optically active phenylalanine was formed from phenylpyruvic acid with pyridoxamine and a chiral Cu(II) catalyst (Scheme 10).[29,30] The Cu(II) catalyst promoted the ketimine-aldimine isomerization and induced the chirality for the reaction. It was found that the enantioselectivity decreased as the reaction proceeded likely due to in situ racemization of aldimine complex **27**. The ee was estimated to be 80% ee at the beginning of the reaction.



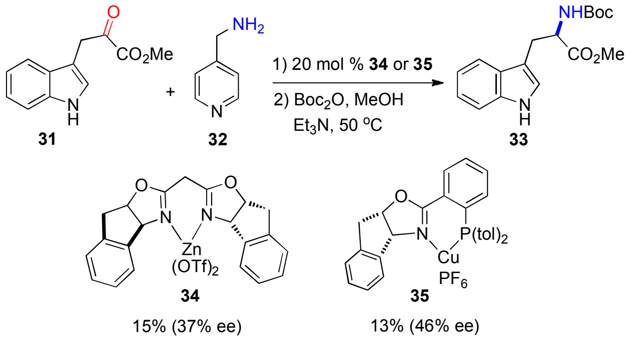
Scheme 10. Cu(II)-catalyzed asymmetric proton transfer

In 2002, Berg and coworkers showed that ketimines **28**, derived from α-keto esters and 9-aminothioxanthene 10,10-dioxide, were efficiently isomerized to ketimines **29** in up to 45% ee with 5 mol% chiral guanidine catalyst **30** (Scheme 11).[31] Studies suggest that the reaction may proceed via a stepwise, bifunctional mechanism, which provides valuable insight for the development of more effective systems.



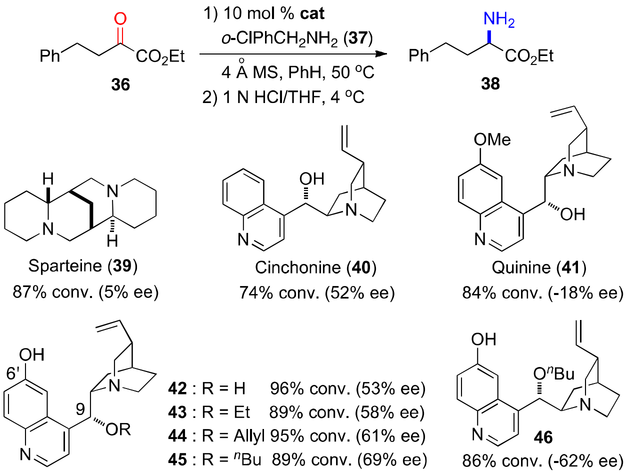
Scheme 11. Chiral guanidine-catalyzed ketimine-aldimine isomerization

In 2003, Jørgensen and coworkers reported that asymmetric transamination was realized with chiral Lewis acids via in situ formation of the ketimine. Methyl-3-indole pyruvate (**31**) was converted into amino ester **33** in 37% and 46% ee, respectively, with catalysts **34** and **35** using 4-picolylamine (**32**) as amine donor (Scheme 12).[32,33] The pyridine of **32** was found to be important for the reactivity as benzylamine was shown to be ineffective for the reaction. The solvent had significant impact on the enantioselectivity, with $MeNO_2$ being the best.

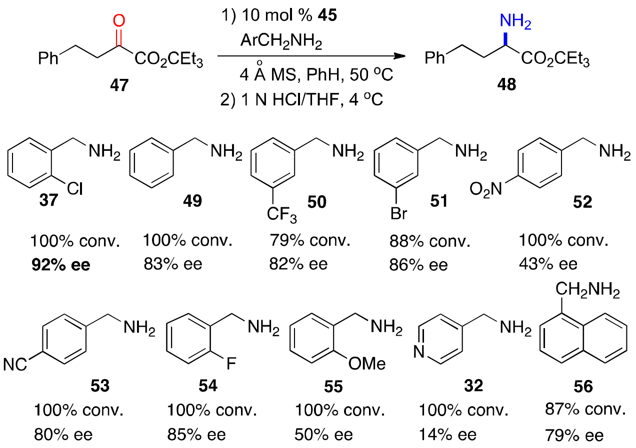


Scheme 12. Chiral Lewis acid-catalyzed transamination of α-keto ester

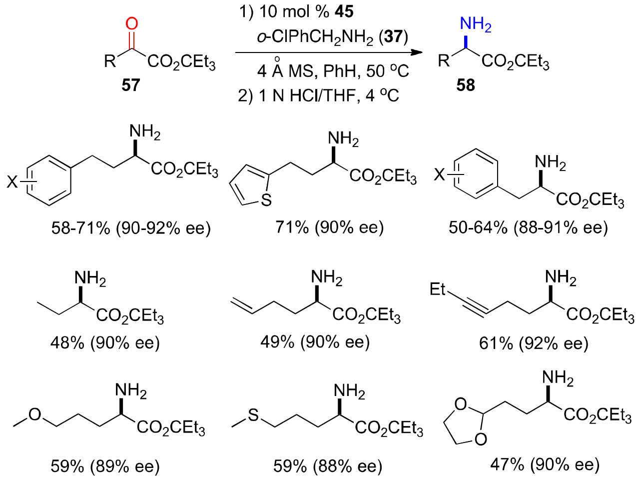
In 2011, Shi and coworkers reported an effective chiral base-catalyzed transamination of α-keto esters.[34] Various chiral bases were examined with ethyl 2-oxo-4-phenylbutanoate (**36**) as substrate and *o*-ClPhCH$_2$NH$_2$ (**37**) as nitrogen source (Scheme 13). Up to 69% ee was obtained with quinine derived catalyst **45**. Studies showed that the enantioselectivity was increased with a bigger ester group. For example, 92% ee was obtained with α-keto ester **47** using *o*-ClPhCH$_2$NH$_2$ (**37**) (Scheme 14). The enantioselectivity was found to be highly dependant on the structures of amine donors, with *o*-ClPhCH$_2$NH$_2$ (**37**) being the best in terms of both reactivity and enantioselectivity (Scheme 14). The transamination reaction with **45** and **37** was extended to a wide variety of α-keto esters, giving the corresponding α-amino esters in 88-92% ee (Scheme 15).



Scheme 13. Chiral base-catalyzed transamination

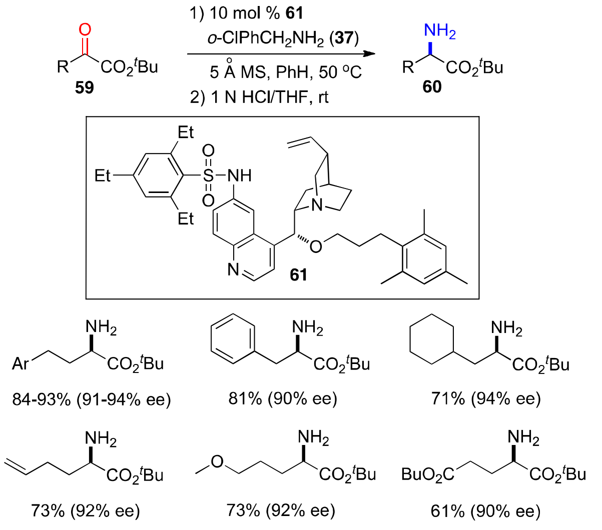


Scheme 14. The effect of benzylamine on transamination

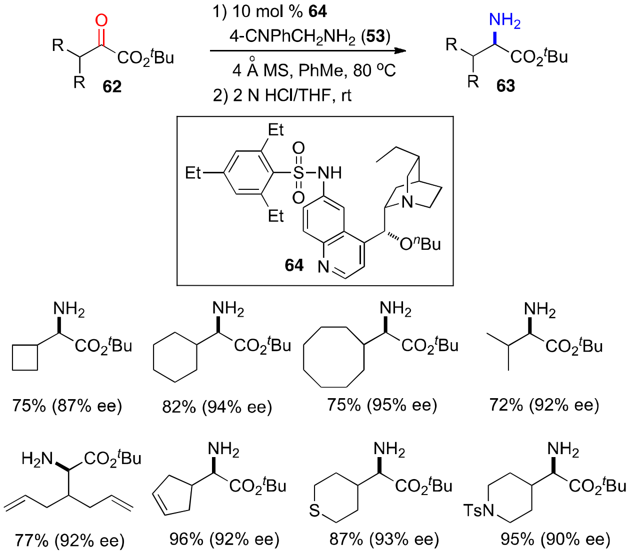


Scheme 15. Asymmetric transamination of α-keto esters

The 6'-OH in catalyst **45** played a very important role in the transamination for both reactivity and enantioselectivity, likely via a H-bond with the imine to facilitate the reaction and influence the enantioselectivity. To further understand the effect of the H-bonding, catalysts with different H-bond donors at the 6' position were investigated for the transamination.[35] A quinine derivative containing 2,4,6-triethylbenzenesulfonamide (**61**) was found to be a highly effective catalyst (Scheme 16). A wide variety of α-amino esters were obtained from more readily available *t*-Bu keto esters in 61-93% yield and 90-94% ee with **61** and **37** in benzene at 50 °C. The transamination was amenable to gram scale. With a related catalyst **64**, various β-branched α-keto esters were transaminated to the corresponding amino esters in 50-96% yield and 87-95% ee with 4-CNPhCH$_2$NH$_2$ (**53**) as nitrogen source (Scheme 17).[36] The 4-CN group of the benzylamine likely enhanced the acidity of the ketimine and facilitated the proton transfer.

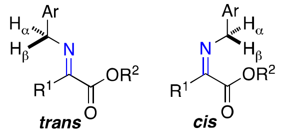


Scheme 16. Asymmetric transamination of α-keto esters

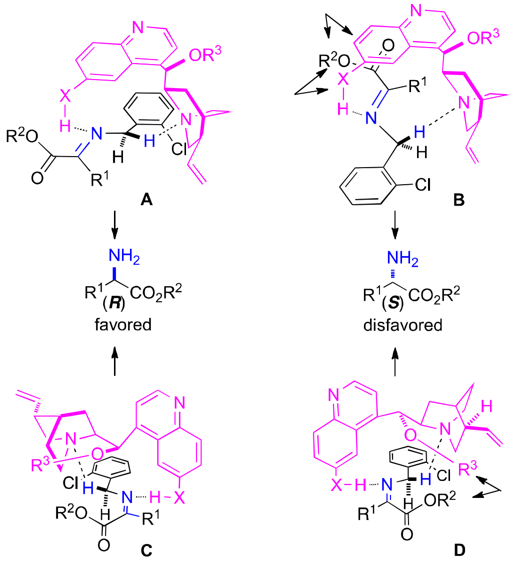


Scheme 17. Asymmetric transamination of β-branched α-keto esters

The ketimine can adopt two possible (*trans* and *cis*) configurations for the base catalyzed proton shift (Scheme 18). The relative content of the *trans* and *cis* configurations is likely dependant on the relative size of the side chain and the ester group of the keto ester. Two possible transition states for each configuration are outlined in Scheme 19. The (*R*)-amino ester is formed predominately via transition state **A** and/or **C**. The (*S*)-enantiomer is disfavored likely due to the steric interaction between the ester group of the substrate and the catalyst in transition state **B** and **D**. The enantioselectivity appears to be more influenced by the size of the ester group than the side chain, thus providing a broad scope for the keto ester substrate (Schemes 15-17).

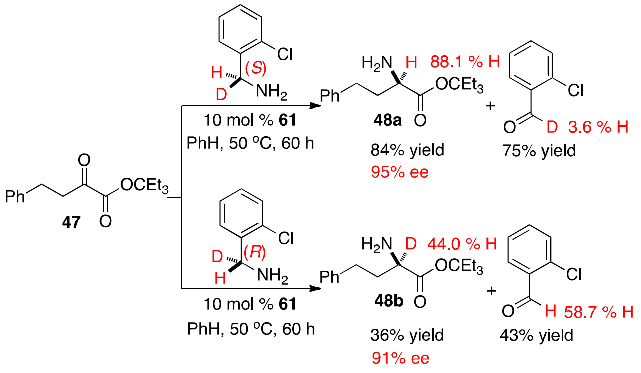


Scheme 18. The *trans* and *cis* configurations of the ketimine



Scheme 19. Proposed transition state model for transamination

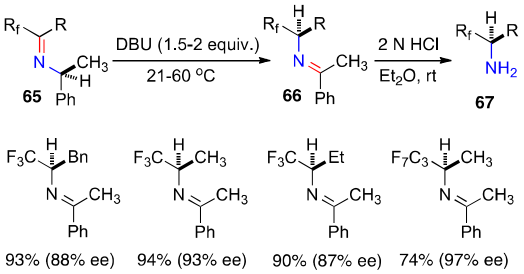
The extent of the involvement for each transition state likely depends on the structure of the keto ester. To further probe this issue, the transamination of keto ester **47** was carried out with catalyst **61** and optically active deuterated *o*-chlorobenzylamine[37] (Scheme 20). It appears that the proton shift from the ketimine to the aldimine predominately proceeded via transition state **A** in this case, based on the yield and ee of the amino ester (**48a** & **48b**) as well as the deuterium content of the amino ester and *o*-chlorobenzaldehyde.[38]



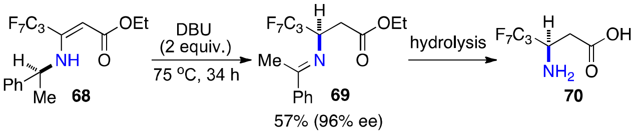
Scheme 20. Transamination with optically active deuterated benzylamines

5. Transamination of Fluoroalkyl Ketones

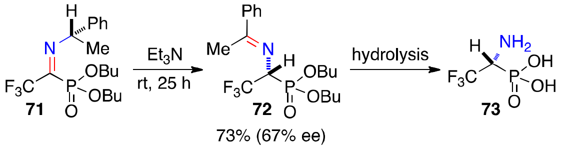
Optically active fluoroalkyl amines are very important functional moieties in various biologically and medicinally important molecules. Efforts have been made in the synthesis of fluoroalkyl amines from fluoroalkyl ketones via transamination using either chiral amine sources or chiral catalysts. In 1997, Soloshonok and coworkers showed that ketimines **65**, prepared by the direct condensation of the corresponding fluoroalkyl ketones and (*S*)-α-phenylethylamine, were stereoselectively isomerized to ketimines **66** in up to 97% ee with DBU (Scheme 21).[39] The use of DBU as both base and solvent was found to be crucial for the reaction. The isomerization process was used for the synthesis of optically active β-fluoroalkyl-β-amino acids.[40] For example, 96% ee was obtained for aldimine **69** from the isomerization of **68** with DBU (Scheme 22). Yuan and coworkers reported that 1-amino-2,2,2-trifluoroethanephosphonic acid was synthesized from ketimine **71** via a base-catalyzed transamination and subsequent hydrolysis (Scheme 23).[41]



Scheme 21. Isomerization of fluoroalkyl ketimines

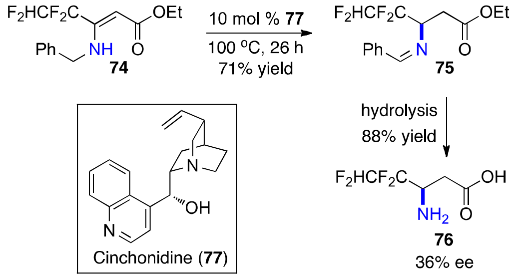


Scheme 22. Isomerization of fluoroalkyl enamines

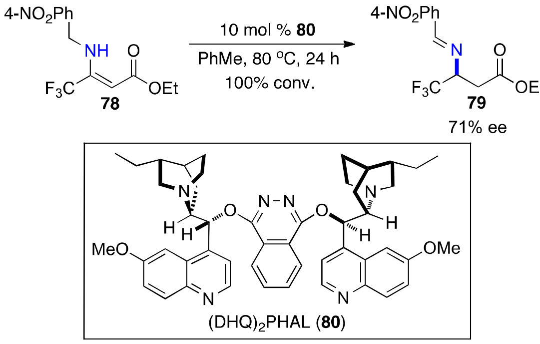


Scheme 23. Isomerization of 1-imino-2,2,2-trifluoroethanephosphonate

In 1994, Soloshonok and coworkers reported that β-fluoroalkyl-β-amino acids were obtained with up to 36% ee via chiral base-catalyzed isomerization of enamines under solvent-free conditions (Scheme 24).[42] In 2007, Plaquevent and coworkers showed that trifluoromethyl enamines such as **78** were isomerized to the corresponding aldimines in up to 71% ee with dimeric cinchona alkaloid $(DHQ)_2$PHAL (Scheme 25).[43]

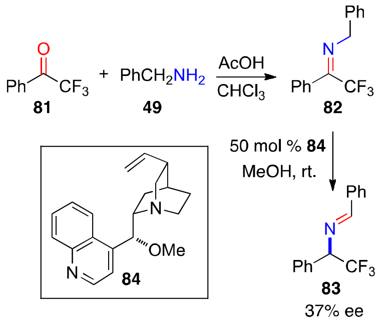


Scheme 24. Chiral base-catalyzed isomerization of enamines



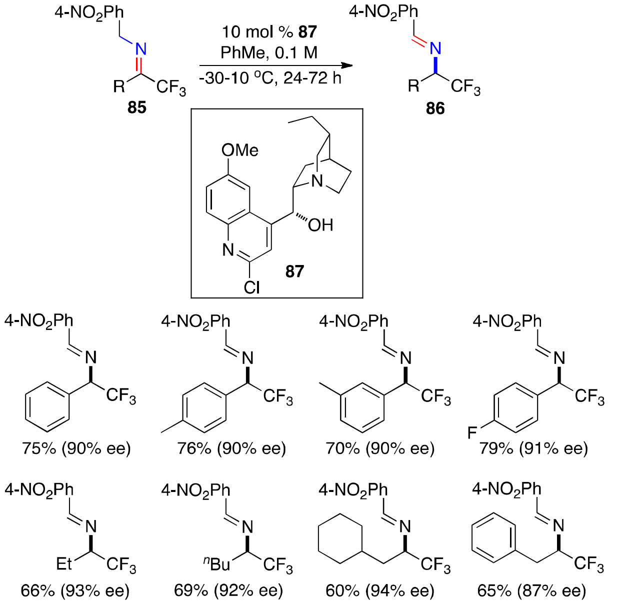
Scheme 25. Chiral base-catalyzed isomerization of trifluoromethyl enamines

In 2007, Soloshonok and coworkers reported their studies on the chiral base-catalyzed isomerization of a trifluoromethyl ketimine (**82**).[44] Aldimine **83** was obtained in 37% ee with cinchonidine-derived catalyst **84** in MeOH over an extended period of time (Scheme 26).



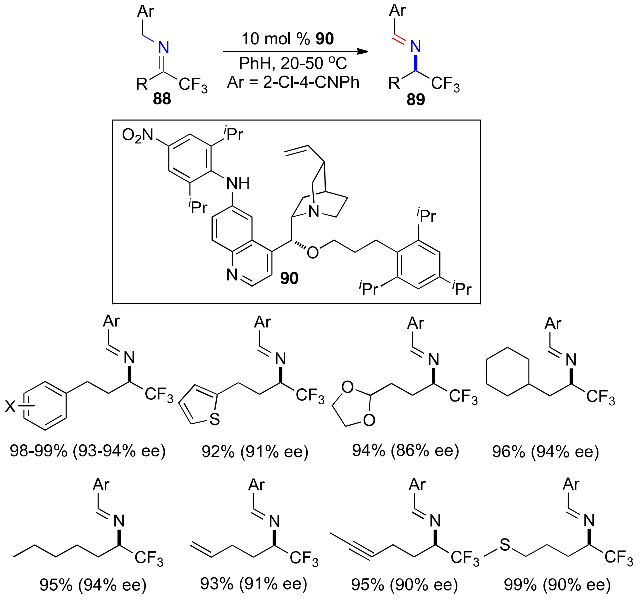
Scheme 26. Chiral base-catalyzed isomerization of trifluoromethyl ketimine

In 2012, Deng and coworkers reported the asymmetric isomerization of trifluoromethyl ketimines (**85**) derived from trifluoromethyl ketone and $4\text{-}NO_2PhCH_2NH_2$ (Scheme 27).[45] The corresponding trifluoromethyl aldimines containing aryl or alkyl groups were obtained in up to 94% ee with cinchona alkaloid derivative **87** as catalyst, and they were hydrolyzed to trifluoromethyl amines in high yields.

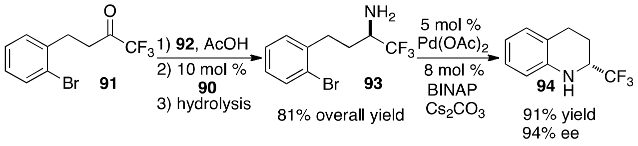


Scheme 27. Chiral base-catalyzed isomerization of trifluoromethyl ketimines

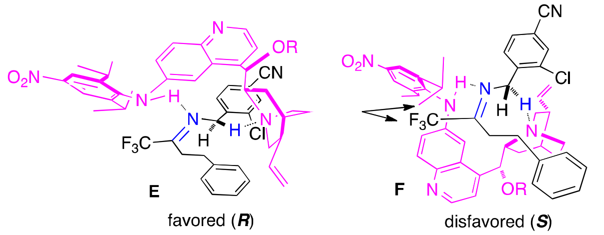
In their studies, Shi and coworkers showed that trifluoromethyl ketimines **88** were readily converted to aldimines **89** with catalyst **90** in up to 99% yield and up to 94% ee (Scheme 28).[46] As illustrated in Scheme 29, trifluoromethyl amine **93** was prepared from the corresponding ketone (**91**) in 81% overall yield via condensation of **91** with 2-Cl-4-CNPhCH$_2$NH$_2$ (**92**), asymmetric proton shift, and subsequent hydrolysis. The Pd-catalyzed cyclization of amine **93** gave optically active tetrahydroquinoline **94** in 91% yield. The asymmetric isomerization of ketimine **88** to aldimine **89** was proposed to predominately proceeded via transition state **E**, favoring the (*R*)-enantiomer (Scheme 30).



Scheme 28. Chiral base-catalyzed isomerization of trifluoromethyl ketimines



Scheme 29. Asymmetric transamination of trifluoromethyl ketone and cyclization

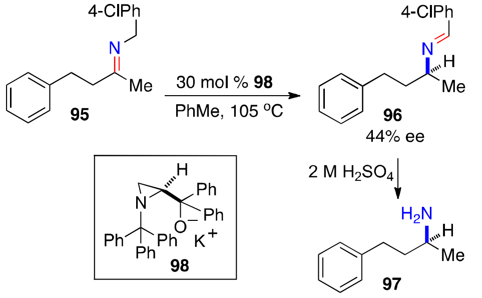


Scheme 30. The proposed transition state model for transamination

6. Transamination of Unactivated Ketones

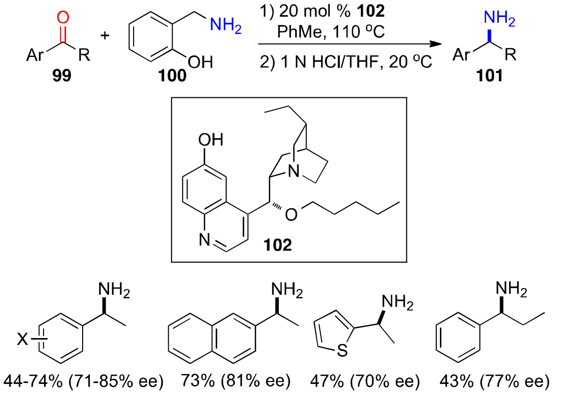
Significant progress has been made for the asymmetric transamination of α-keto esters and fluoroalkyl ketones. In these ketones, the electron-withdrawing ester and fluoroalkyl groups greatly facilitate the reactions. The transamination for ketones without these electron-withdrawing groups still remains challenging. Efforts have also been made in this area.

In 1995, Zwanenburg and coworkers reported the chiral base-catalyzed isomerization of ketimines to the corresponding aldimines.[47] With aminoalcohol derived chiral base **98**, aldimine **96** was obtained from ketimine **95** in up to 44% ee (Scheme 31).

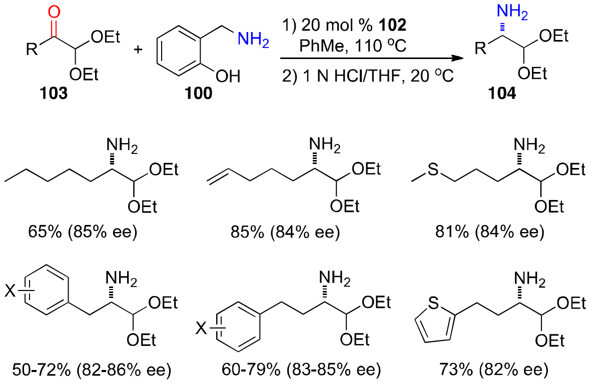


Scheme 31. Chiral base-catalyzed isomerization of ketimine

In 2012, Shi and coworkers showed that aromatic ketones **99** can be transaminated to the corresponding amines (**101**) in 70-85% ee with quinine-derived base **102** as catalyst and *o*-HOPhCH$_2$NH$_2$ (**100**) as nitrogen source in toluene at 110 °C (Scheme 32).[48] Under similar reaction conditions, α-amino acetals were obtained from α-keto acetals in 82-86% ee (Scheme 33).[49] *o*-HOPhCH$_2$NH$_2$ was found to be crucial for the reaction. The *o*-OH group of the benzylamine likely formed a H-bond with the imine and facilitated the transamination.[48,50]



Scheme 32. Chiral base-catalyzed transamination of aromatic ketones



Scheme 33. Chiral base-catalyzed transamination of α-keto acetals

Conclusions

Optically active α-amino acids can be efficiently generated from α-keto acids via transamination with vitamin B_6 dependant transaminases in biological systems. Biomimetic asymmetric transamination of carbonyl compounds provides an attractive approach to optically active amine derivatives and has received considerable attention. Great progress has been made in the last few decades. Earlier studies focused on the development of chiral vitamin B_6 analogues and artificial transaminase mimics. High enantioselectivity has been achieved in some cases. In recent years, highly enantioselective transamination processes have been developed for α-keto acid derivatives and fluoroalkyl ketones with chiral catalysts particularly chiral bases. Some mechanistic understanding of the enantioselectivity has also been gained. Asymmetric transamination for ketones without electron-withdrawing ester or fluoroalkyl groups has also been shown to be feasible. It can be expected that more effective transamination systems will emerge with further understanding of the reaction mechanism and development of new catalysts. It would be particularly useful if a simple ketone can be efficiently transaminated to an optically active amine under mild conditions. We hope that this review would stimulate new ideas in this area.

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