Catalytic asymmetric synthesis of α- and β-amino phosphonic acid derivatives

Jun-An Ma*

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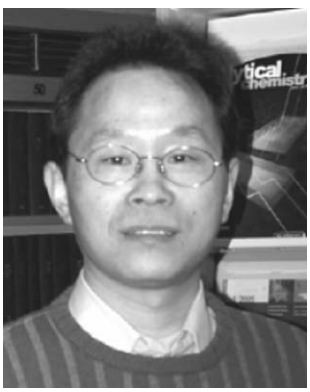
Catalytic asymmetric reactions provide one of the most powerful and economical synthetic approaches to a variety of enantiomerically enriched compounds. As being analogues of the corresponding α- and β-amino acids, optically active α- and β-amino phosphonic acid derivatives have found widespread use in medicinal chemistry and the pharmaceutical sciences. Using catalytic amounts of chiral materials, asymmetric synthesis of enantiomerically enriched α- and β-amino phosphonates has been a subject of growing interest. This *tutorial review* contains a compilation of the catalytic asymmetric synthetic methods developed to date and highlights their utility for obtaining these target compounds.

1. Introduction

Optically active α- and β-amino phosphonic acids serve as isosteric or bio-isosteric analogues of the corresponding amino acids, in which the planar and less bulky carboxylic acid group is replaced by a tetrahedral phosphonic acid functionality. These structural features cause diverse and interesting biological and biochemical properties giving rise to antibacterial and antifungal agents, a wide range of proteolytic enzyme inhibitors, and haptens for catalytic antibodies.[1–4] Therefore, this class of compounds has received considerable attention and resulted in intense efforts directed towards the development of suitable synthetic methodologies for their preparation.

Department of Chemistry, Tianjin University, Tianjin, 300072, China. E-mail: majun_an68@tju.edu.cn; Fax: (+86) 22 27403475



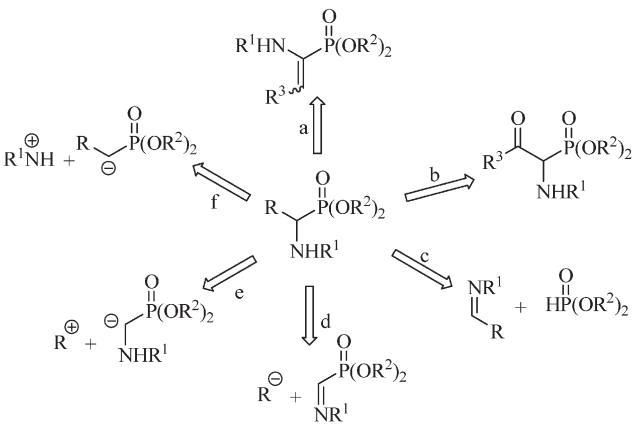
Jun-An Ma

Jun-An Ma was born in He'nan Province, China. He received his BS degree from He'nan University in 1991 and his MS degree from Nankai University in 1994. He then joined Guangzhou Baihua Flavor & Fragrance Co. as a Senior Research Fellow. From 1996 to 1999, he completed his PhD under the supervision of Professor Run-Qiu Huang at Nankai University, where he stayed co-working with Professor Qi-Lin Zhou and was appointed Associate Professor in December 2001. He took up postdoctoral fellowships with Dr D. Cahard (France) in 2003 and from 2004 to June of 2005 with Professor Dr M. T. Reetz (Germany). He was appointed to his present position at Tianjin University in July 2005. His research interests focus on asymmetric synthesis and catalysis, organofluorine chemistry, and the synthesis of biologically active compounds.

There have been numerous reports of resolution and chiral auxiliary-based approaches.[5–9] Compared to these classical processes, catalytic asymmetric routes are competitive and even superior synthetic methods.[10] In the past few years some advances have been made in the development of catalytic asymmetric procedures, providing straightforward and efficient access to enantiomerically enriched α- and β-amino phosphonic acid derivatives.

2. Catalytic asymmetric synthesis of α-amino phosphonic acid derivatives

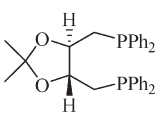
Several protocols for efficient catalytic asymmetric synthesis of α-amino phosphonic acid derivatives have emerged in the recent years. These catalytic asymmetric reactions involve different bond-forming processes, namely carbon–hydrogen bond (path a and b), carbon–phosphorus bond (path c), carbon–carbon bond (path d and e), and carbon–nitrogen bond formation (path f) (Scheme 1). Depending on the type of bond formed in the reactions, some recent examples and related strategies for the preparation of these derivatives will be illustrated.



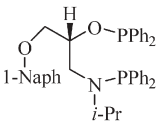
Scheme 1 Processes for the synthesis of α-amino phosphonic acid derivatives.

2.1 Catalytic asymmetric hydrogenation and reduction

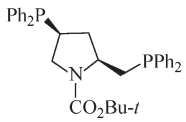
Catalytic asymmetric hydrogenation of dehydroamino acids is a mature area of organic chemistry, and a considerable number of catalytic systems are known to provide α-amino acids with enantioselectivities exceeding 95%.[11] By comparison, there are only a few catalytic hydrogenation methods available to access optically active α-amino phosphonic acid derivatives. The first asymmetric synthesis of α-amino phosphonates **2** was the hydrogenation of enamido phosphonates **1** catalyzed by $[Rh^{I}(NBD)Cl]_2$ (NBD = norbornadiene) and biphosphine ligand (+)-DIOP which was developed by Schöllkopf in 1985.[12] A similar approach was used by Talley in 1992.[13] For instance, from the parent compound (formamido)ethenyl-phosphonate **1** (R = R^1 = H, R^2 = Me), L-(1-aminoethyl)phosphonic acids were obtained with 76% ee(enantiomeric excess). A single crystallization from water/methanol increased the optical purity of the desired product to 93% (Scheme 2).



(+)-DIOP



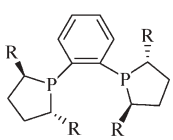
(*S*)-PROPRAPHOS



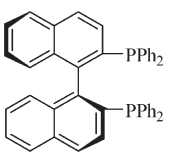
(*S, S*)-BPPM

In 1996, Oehme and coworkers tested various frequently used chiral Rh^{I}-complexes for catalytic activity in the asymmetric hydrogenation of (*E*)-phenyl-substituted enamido phosphonates **1** (R = Ph, R^1 = Ph) and found that PROPRAPHOS and BPPM were the best ligands due to their high reaction rates and relatively high stereoselectivities. So BPPM can provide ee up to 96%.[14] Since PROPRAPHOS is available in both configurations, (*R*) and (*S*) α-amino phosphonic acid derivatives could be obtained in a very efficient way as wanted.

Three years later, Burk's group developed Rh^{I}-complexes of DuPhos ligands as effective catalysts for the asymmetric hydrogenation of *N*-acyl and *N*-Cbz (Cbz = benzyloxycarbonyl) enamido phosphonates (R = H).[15] The Et-DuPhos-Rh^{I} catalyst provided optimum enantioselectivities for both substrates (95% and 94% ee, respectively). Interestingly, aryl-substituted enamido phosphonates give lower enantioselectivities compared to their alkyl counterparts (R = *i*-Pr, 95% ee). Reduction of (*E*)-phenyl-substituted *N*-Cbz enamido phosphonate with Me-DuPhos-Rh^{I} yielded α-amino phosphonate in 76% ee.

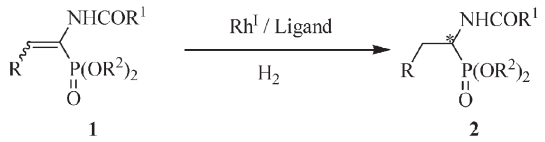


(*S, S*)-Me-DuPhos, R = Me
(*S, S*)-Et-DuPhos, R = Et



(*S*)-BINAP

Noyori and colleagues disclosed that Ru^{II}-BINAP complexes catalyze the enantio-selective hydrogenation of 1-(formamido)alkenylphosphonates in methanol under low pressure hydrogen and at 30 °C to give the corresponding α-formamido phosphonates in quantitative yields with >97% ee.[16] Use of a (*S*)-BINAP-Ru^{II} catalyst affords predominantly the (*R*)-products, while the (*R*)-BINAP complexes form the (*S*)-enriched compounds. This method allows the synthesis of phosphoalanine, phosphoethylglycine, and phosphophenylalanine with high enantiomeric purity. The dependence of the reactivity on substrate geometry is observed. The (*E*)-configurated substrates are more reactive than the (*Z*)-isomers by a factor of 100.



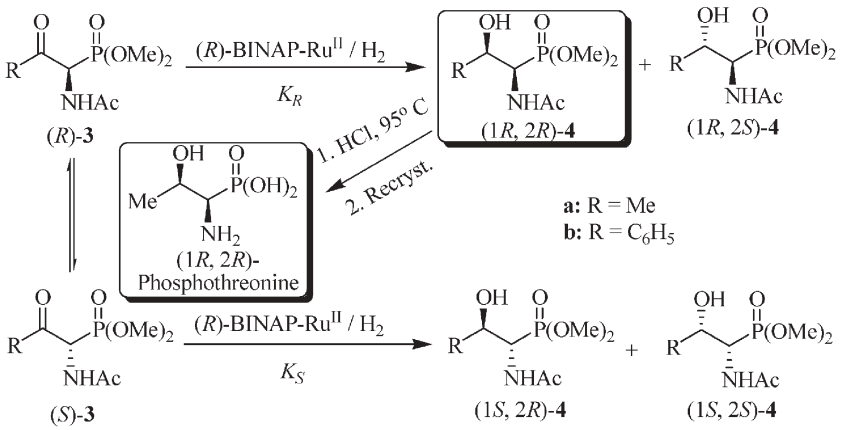
Scheme 2 Catalytic asymmetric hydrogenation of enamido phosphonates.

The extension of the Ru^{II}-BINAP-catalyzed hydrogenation[17,18] to an efficient method for the preparation of β-hydroxy α-amino phosphonates has also been impressively demonstrated by the same group.[19,20] Using a Ru^{II}-BINAP-catalyzed hydrogenation of racemic α-acetamido β-keto phosphonic esters **3** *via* dynamic kinetic resolution, the desired products **4** were prepared with high diastereoselectivities (*syn*/*anti* up to 98/2) and excellent enantioselectivities (95–98% ee). Furthermore, the product (1*R*, 2*R*)-**4a** (R = Me) was successfully converted to the enantiomerically pure (1*R*, 2*R*)-phosphothreonine in 92% yield (Scheme 3). In fact, the combination of the configurational lability of the α-substituted β-keto phosphonate, the electronegative nature of the α-amido group, and the chiral discriminating properties of (*R*)-BINAP as well as the appropriate reaction conditions leads to the predominant formation of (*R*, *R*)-α-amido β-hydroxy phosphonate with high diastereo- and enantiomeric purity in excellent yield among four possible stereoisomers.

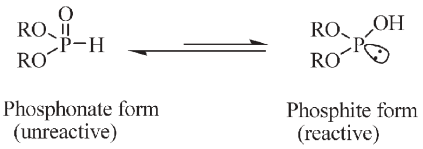
2.2 Catalytic asymmetric hydrophosphonylation of imines

The addition of phosphites to imines is probably the most general and direct approach to α-amino phosphonates. In most cases, phosphonates have been used as P-nucleophiles. It is known that a phosphonate–phosphite tautomerism exists with the phosphite form as the active nucleophilic species and the phosphonate tautomer as the almost exclusively favored but non-nucleophilic (resting) form[21,22] (Scheme 4).

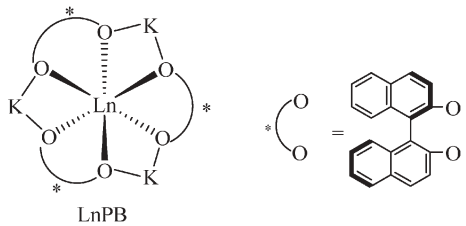
Shibasaki and coworkers demonstrated the first highly enantioselective hydrophosphonylation process has been demonstrated by using chiral heterobimetallic catalysts.[23,24] In the presence of 5–20 mol% lanthanoid-potassium-BINOL (BINOL = 1, 1′-binaphth-2, 2′-diol) bimetallic complexes (LnPB), the addition of a P-nucleophile to imines **5** produced optically active α-amino phosphonates **6** in good yields (25–87%) with modest to high enantioselectivities (38–96% ee). The phosphonate products were further converted into the corresponding α-amino phosphonic acids in up to quantitative yields (Scheme 5). It is noteworthy that this impressive enantioselective preparation strategy for the manufacture of α-amino phosphonic acids has found an industrial application.[25]



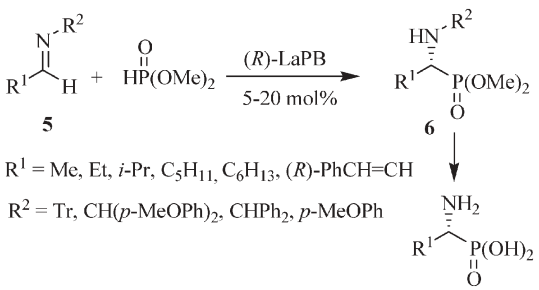
Scheme 3 Catalytic asymmetric hydrogenation of racemic α-acetamido β-keto phosphonate by dynamic kinetic resolution.



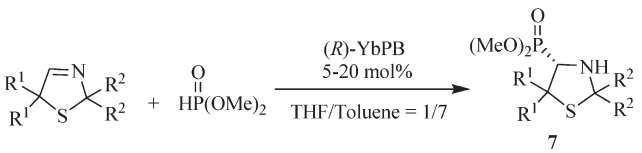
Scheme 4 Phosphonate–phosphite tautomerism.



Furthermore, by using heterobimetallic catalysts, the first catalytic asymmetric synthesis of cyclic α-amino phosphonates was realized by the same research group.[26] The pharmaceutically interesting 4-thiazolidinyl phosphonates of type **7** were synthesized with enantioselectivities of up to 98% ee and in yields of up to 98% when using (*R*)-YbPB (20 mol%) as a catalyst (Scheme 6). In contrast to the reaction with acyclic imines **5**, the use of (*R*)-LnPB catalysts, which include a (relatively) small lanthanoid^{III} center ion (*e.g.* ytterbium), produced the best results. Using other types of organometallic catalysts (titanium^{IV} complexes), the reaction proceeded with modest enantioselectivity.

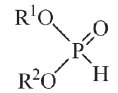


Scheme 5 Catalytic asymmetric hydrophosphonylation of acyclic imines; Tr = trityl.



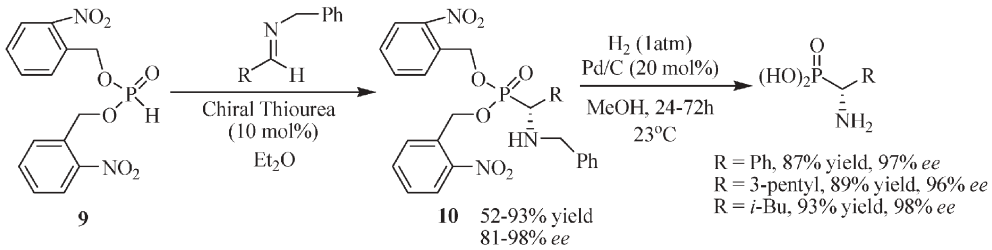
Scheme 6 Catalytic asymmetric hydrophosphonylation of cyclic imines.

Somewhat later, Shibasaki and coworkers found that it is also possible to replace dimethyl phosphite with different P-nucleophiles in the asymmetric addition reaction with several cyclic imines.[27,28] For examples, by utilization of the sterically rigid cyclic phosphites **8a–c**, the performance (enantioselectivity and yield) was significantly increased: various chiral thiazolidinyl phosphonates were synthesized in excellent optical purities up to 99% ee and high chemical yields of up to 99%. The required amount of catalyst was reduced (to 2.5 mol%) as well as the required surplus of phosphite. Steric and electronic reasons were found to be responsible for the amended activity shown within the catalytic cycle by these cyclic phosphites.

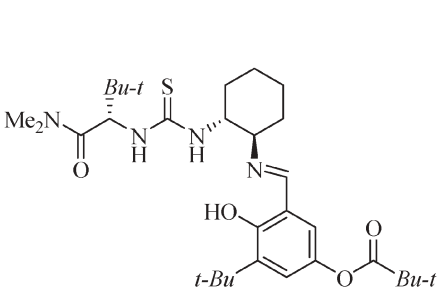


8a $R^1 / R^2 = -(CH_2)_3-$
b $R^1 / R^2 = -CH_2C(CH_3)_2CH_2-$
c $R^1 / R^2 = -CH_2CH=CHCH_2-$

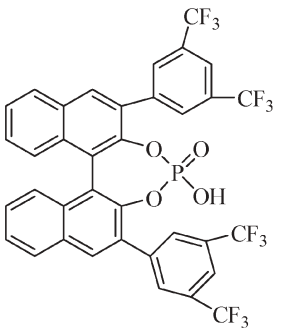
While significant advances have been made in the development of asymmetric hydrophosphonylation methodologies, the highest selectivities are generally restricted to cyclic imine substrates, and an excess of nucleophilic phosphite is required. Recently, Jacobsen and Joly described a highly enantioselective hydrophosphonylation of *N*-benzyl imines promoted by a chiral thiourea catalyst (Scheme 7).[29] The addition of di(*o*-nitrobenzyl) phosphite **9** to *N*-benzyl imines **10** catalyzed by the chiral thiourea proved to be remarkably general under optimized conditions (nonpolar ethereal solvents and low temperature 4 °C). High enantioselectivities (90–99% ee) were obtained for a wide range of both branched aliphatic and aromatic imines, except for two imines bearing an alkenyl side chain and pyrrole functionality (81% and 82% ee, respectively). Unbranched aliphatic imines are not useful substrates due to



Scheme 7 Enantioselective hydrophosphonylation of imines catalyzed by chiral thiourea.



Jacobsen chiral Thiourea



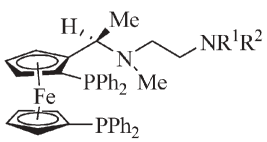
Akiyama chiral Brønsted acid

their rapid decomposition under the reaction conditions. In general, the best reaction rates were realized with branched aliphatic imines, whereas electron-poor aromatic substrates required longer reaction time, and, in certain cases, elevated temperature. A mild procedure (with 20 mol% Pd/C under an atmosphere of hydrogen) for the global deprotection of the hydrophosphonylation products was also demonstrated, providing straightforward access to enantiomerically enriched α-amino phosphonic acids.

As a chiral Brønsted acid, BINOL-derived cyclic phosphoric acid (such as Akiyama chiral Brønsted acid) was also shown to be an efficient catalyst for the hydrophosphonylation of aldimines at room temperature.[30] Among the dialkyl phosphates examined, diisopropyl phosphate gave the optimum results. α-amino phosphonates were obtained in high yields (72–97%) with good enantio-selectivities (52–77% ee). Interestingly, imines derived from cinnamaldehydes exhibited relatively high enantioselectivitives (81–90% ee).

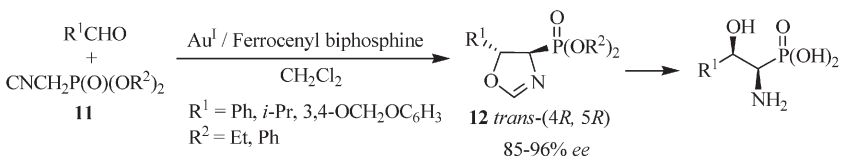
2.3 Catalytic asymmetric carbon–carbon bond-forming reactions

The addition of phosphonate derived α-phosphonate carbanions to different electrophilic substrates, through a carbon–carbon bond-forming process, constitutes an important entry to α-amino phosphonate synthesis. Building on previous work by Ito and Hayashi,[31] both the Togni and Hayashi groups, independently, reported asymmetric synthesis of α-amino phosphonic acids *via* an aldol reaction of α-isocyanomethylphosphonates catalyzed by chiral ferrocenyl phosphine-Au^{I} complexes.[32,33] Reaction of aldehydes with α-isocyano-methylphosphonates **11** in the presence of 1 mol% catalyst gave high yields of *trans*-5-alkyl-2-oxazoline-4-phosphonates **12** with enantioselectivities ranging between 85–96% ee. These products were readily converted to the phosphonic acid analogues of optically active phenylalanine and β-alkylserines upon hydrolysis (Scheme 8).

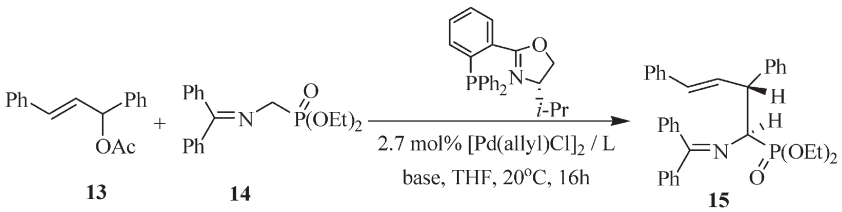


Ferrocenyl Biphosphine Ligands
Togni ligand: $R^1 = R^2 = Me$
Hayashi ligand: $R^1/R^2 = -(CH_2)_5-$

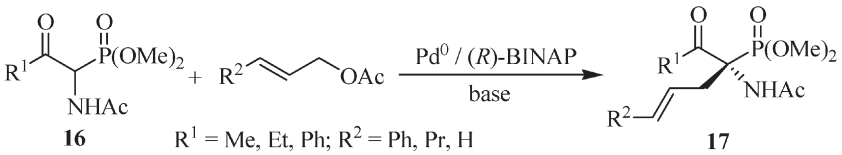
Among the transition-metal-catalyzed reactions known to form carbon–carbon bonds, the palladium-catalyzed allylic substitution stands out as one of the most valuable synthetic tools available. Williams and coworkers presented the Pd^0-catalyzed reaction between allyl acetates and Schiff base derivatives **14** of α-amino phosphonates[34] (Scheme 9). In this procedure, a chiral Pd^0-complex with a phosphorus-containing oxazoline ligand was used as the catalyst. With a suitable substrate **13**, good diastereo- and high enantioselectivity was observed [diastereomeric ratio (dr) up to 87/13, ee up to 96%]. When propenyl acetate was reacted with the nucleophile **14**, the substitution product was obtained with low levels of enantioselectivity (<20% ee).



Scheme 8 Catalytic asymmetric synthesis of *trans*-5-alkyl-2-oxazoline-4-phosphonates.



Scheme 9 Pd^0-catalyzed allylic substitution of α-imino phosphonate.



Scheme 10 Pd^0-catalyzed asymmetric allylation of α-amino phosphonates.

Enantioselective construction of quaternary α-carbon centers from α-amino phosphonates *via* catalytic asymmetric allylation was developed by Ito's group[35,36] (Scheme 10). The reaction of α-acetamido β-keto phosphonates **16** was promoted in the presence of potassium *tert*-butoxide as a base, with a palladium catalyst derived from [Pd(π-allyl)(COD)]BF_4 (COD = 1, 5-cyclooctadiene) and (*R*)-BINAP. α-Alkyl α-amino phosphonates **17** were obtained with good enantioselectivities (65–88% ee). Diastereoselective reduction of the carbonyl group in the product afforded β-hydroxy α-amino phosphonic acid derivatives with *syn*-selectivity.

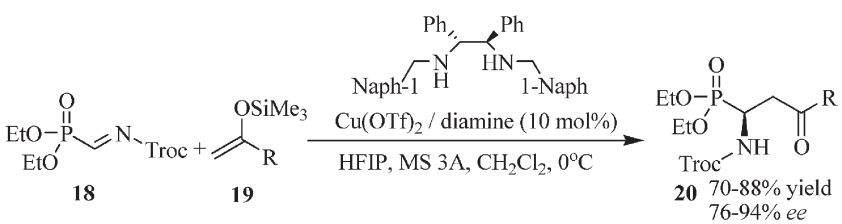
The addition of nucleophiles to cationic phosphonoglycine equivalents is an alternative approach to α-amino phosphonates *via* enantioselective carbon–carbon bond-forming reactions. Kobayashi and coworkers developed an asymmetric reaction of *N*-acyl-α-imino phosphonate **18** with silicon enolate **19** in the presence of a copper(II) complex derived from $Cu(OTf)_2$ and a chiral diamine (Scheme 11).[37] Silicon enolates derived from various aromatic and aliphatic ketones worked well to produce the corresponding adducts **20** in high yields (70–88%) with high enantioselectivities (76–94% ee). It was found that some additives [hexafluoroisopropyl alcohol (HFIP) and molecular sieves (MS) 3A] were important for high levels of yield and enantioselection. In addition, considering the background reaction, the slow addition of the substrates to the catalyst is preferable for the asymmetric induction. It is noteworthy that this reaction opens a new pathway to several kinds of biologically interesting, nonracemic α-amino phosphonate derivatives.

Based on Mannich-type reactions, Risch's group recently provided an efficient procedure for the synthesis of novel α-amino phosphonates.[38] The aminoalkylation of enamines with a phosphonate-substituted iminium salt was carried out under mild conditions to yield the functionalized α-amino phosphonates in good yields. Even though the products are racemic, this straightforward and efficient methodology is impressive.

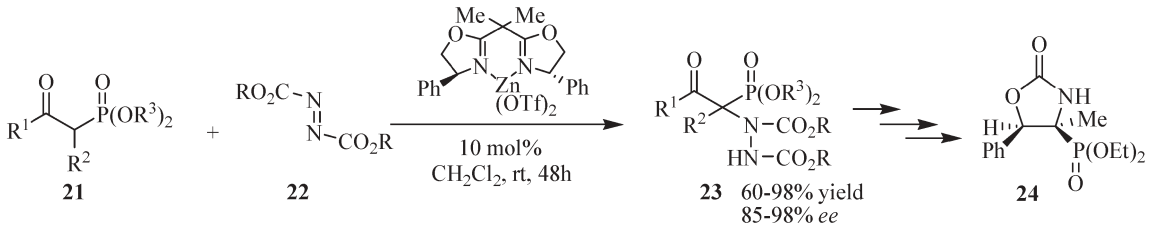
2.4 Catalytic asymmetric amination of β-keto phosphonates

The electrophilic amination of a α-phosphonate carbanion is another attractive solution to the amination of α-phosphonate carbanions. Following this strategy, the first catalytic asymmetric direct amination of β-keto phosphonates was reported.[39] The enantioselective α-amination was shown to be a general reaction for both acyclic and cyclic β-keto phosphonates **21** using diethyl and dibenzyl azodicarboxylate **22** as the nitrogen sources and (*S*)-Ph-BOX-$Zn^{II}(OTf)_2$ (BOX = bisoxazoline) as the catalyst. The aminated products **23** were obtained in high yields and with excellent enantioselectivities. Further transformations (reduction, deprotection and N–N bond cleavage) of the aminated product (R^1 = Ph, R^2 = Me, R^3 = Et) afforded the oxazolidinyl-phosphonic acid derivative **24** in a 60% overall yield and with a diastereomeric ratio of >10 : 1 (Scheme 12). The formation of **24** represents an alternative process to the Ru^{II}-BINAP procedure developed by Noyori.[19]

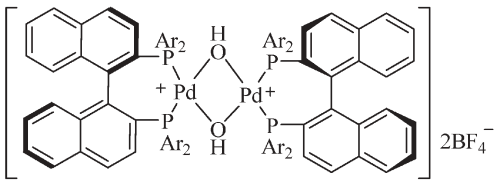
Almost simultaneously, palladium(II)-BINAP complexes were utilized in a similar enantioselective amination reaction of β-keto phosphonates with diethyl azodicarboxylate. In the presence of 2.5 mol% catalyst **25**, the reaction proceeded to produce α-aminated products with up to 96% ee.[40]



Scheme 11 Cu^{II}-catalyzed reaction of *N*-Troc- α-imino phosphonate with silicon enolate (Troc = 2,2,2-trichloroethoxycarbonyl, 1-Naph = 1-naphthyl).



Scheme 12 Catalytic enantioselective α-amination of β-keto phosphonate esters.



25 Ar = 3, 5-dimethylphenyl

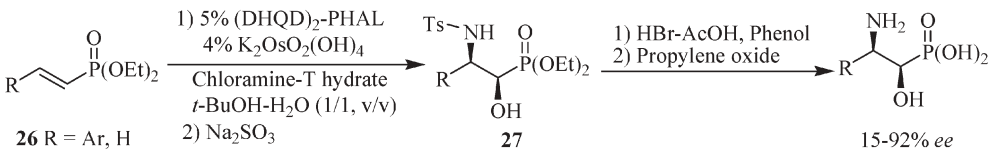
3. Catalytic asymmetric synthesis of β-amino phosphonic acid derivatives

It is known that β-amino phosphonic acids, which function as β-amino acid surrogates, are biologically important molecules. Several traditional diastereoselective methodologies have been applied as effective tools for the construction of these compounds.[9] However, catalytic asymmetric synthesis has not been thoroughly studied. The first truly catalytic synthesis of β-amino phosphonates was accomplished through the asymmetric aminohydroxylation (AA) of α,β-unsaturated phosphonates which was developed by Sisti and coworkers in 1998.[41] Diethyl-substituted α,β-unsaturated phosphonates **26** were successfully oxyaminated using potassium osmium(VI) dihydrate and the cinchona alkaloid ligand $(DHQD)_2$-PHAL (dihydroquinidine 1,4-phthalazinediyl diether) as the asymmetric inductor and reaction accelerator. The reaction required 2–24 h to reach over 95% conversion and gave the β-amino-α-hydroxy derivatives **27** with no detectable amounts of the other regioisomers. As in the case of α,β-unsaturated carbonyl esters, $(DHQD)_2$-PHAL directs the addition to the β-face of **26** (*re, si* approach), giving rise to a (1*R*, 2*R*)-*syn*-configuration. Purification with enantioselective enrichment was found possible by recrystallization. β-Amino-α-hydroxy phosphonates **27** (R = Ar) can be hydrolyzed in excellent yields to the corresponding β-amino-α-hydroxy phosphonic acids in moderate to high enantioselectivities (15–92% ee) (Scheme 13).

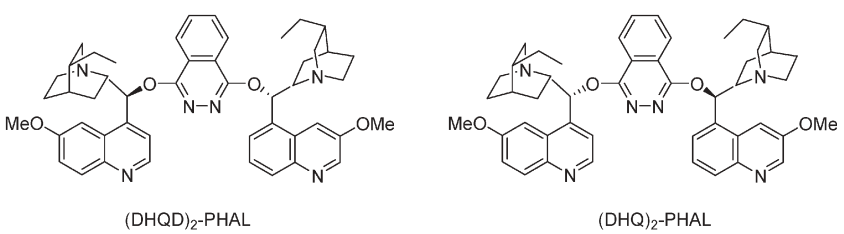
One year later, Sharpless reported a similar approach using the *pseudo*-enantiomeric ligand $(DHQ)_2$-PHAL (dihydroquinine 1,4-phthalazinediyl diether) as the asymmetric inductor for the synthesis of β-amino-α-hydroxy phosphonates.[42] Several aryl-substituted unsaturated phosphonates **26** were examined to afford *ent*-**27**. The corresponding alkyl-substituted substrates failed to react even upon prolonged heating. Despite the subsequent low yields of AA products (20–53%), in almost all cases purity was high after recrystallization or preparative thin layer chromatography (90–99% ee). Interestingly, a γ-amino-β-hydroxyphosphonate containing an α-methylene moiety was similarly prepared, albeit with lower enantioselectivities (42–77% ee).

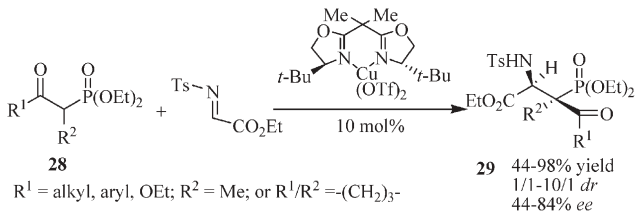
An enantioselective addition of compounds with acidic/enolizable C–H bonds to imine and azodicarboxylate esters constitutes a versatile method for preparation of amino acids.[43,44] This strategy has been applied for the formation of β-amino phosphonate analogues. In the presence of a chiral Lewis catalyst [$Cu^{II}(OTf)_2$-*t*-Bu-BOX], the reaction proceeds in high yields (up to 98%) and with moderate diastereoselectivities (dr: 1/1–10/1) and moderate to good enantioselectivities (43–84% ee). The reaction produced functionalized β-amino phosphonates **29** from various β-keto phosphonates **28** (Scheme 14).[45] A bidentate coordination of the substrate to a copper(II) center of the chiral catalyst leads to shielding of the *Si*-face of the β-enol phosphonate and leaves the *Re*-face open for the approach of the activated imino ester.

Catalytic asymmetric hydrogenation of β-aminoacrylic acid derivatives is one of the simplest and most straightforward ways to enantiomerically enriched β-amino acids. Several



Scheme 13 Catalytic asymmetric aminohydroxylation of α,β-unsaturated phosphonates; Ts = *p*-toluenesulfonyl.





Scheme 14 Catalytic asymmetric addition of β-keto phosphonates to α-imino ester.

successful examples have been published on the formation of these compounds using this strategy.[44,46] Strangely, to date there have been no reports of useful extensions of this methodology to the synthesis of β-amino phosphonate analogues. Although diastereoselective syntheses of β-amino phosphonate compounds have been accomplished by the reduction of chiral and achiral β-enamino phosphonate esters with hydrides,[9] direct catalytic asymmetric hydrogenation of β-enamino phosphonate esters is still an attractive and potentially practical process for the preparation of optically active desired products.

4. Outlook

In summary, the stereoselective formation of optically active α- and β-amino phosphonic acid derivatives is an appealing target for organic chemists because of the interesting and important biological properties of these compounds. It is clear that the exploitation of catalytic asymmetric reactions for the construction of these derivatives has just begun. Several different methodologies have been applied as powerful tools for the synthesis of optically active α-amino phosphonates, whereas for β-amino phosphonic acids, effective catalyzed enantioselective approaches are rare; there is still a great demand for new processes and more investigations. It is almost certain that the growing importance of these compounds in the study of biochemical processes will stimulate many more achievements in the years to come. In the area of catalytic asymmetric synthesis of α- and β-amino phosphonic acid derivatives, further advances are on the horizon.

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